Oxalates as Activating Groups for Alcohols in Visible Light Photoredox Catalysis: Formation of Quaternary Centers by Redox-Neutral Fragment Coupling

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Supporting Information – Table of Contents

Materials and Methods:

Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen or argon using anhydrous solvents (either freshly distilled or passed through activated alumina columns). All commercially obtained reagents were used as received. Methyl vinyl ketone, acrolein, methacrylonitrile, methyl methacrylate and cyclopentenone were distilled prior to use. $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$[1] was prepared according to literature procedures. All alcohols whose synthesis is not described were either obtained from commercial suppliers or prepared using the referenced literature procedures. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 50 F_{254} pre-coated plates (0.25 mm) or Analtech Uniplate (0.25 mm), and visualized by exposure to UV light (254 nm) and potassium permanganate staining. EMD silica gel 60 (particle size 0.040−0.063 mm) or Fluka (200−400 mesh) was used for flash column chromatography. ^1H NMR spectra were recorded at 500 or 600 MHz. Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded at 126 MHz. Data for ^{13}C NMR spectra are reported in terms of chemical shift. NMR spectra are internally referenced to residual proton solvent signals (note: $CDCl_3$ referenced at 7.26 for ^1H NMR and 77.16 ppm for ^{13}C NMR). IR spectra of oils and solids were recorded on a FT-IR and ATR-FTIR spectrometers, respectively, and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained from the Princeton University and UC Irvine Mass Spectrometry Facilities. Optical rotations were measured with a polarimeter. Kessil KSH150B LED Grow Light 150, Blue was purchased from http://www.amazon.com.

Pictures of Photoredox-Catalyzed Reaction Experimental Setup:

Figure S1. Side view. Box length: 6 inches. Two 34 W Kessil KSH150B Blue LED Grow Light 150 are positioned on both sides.

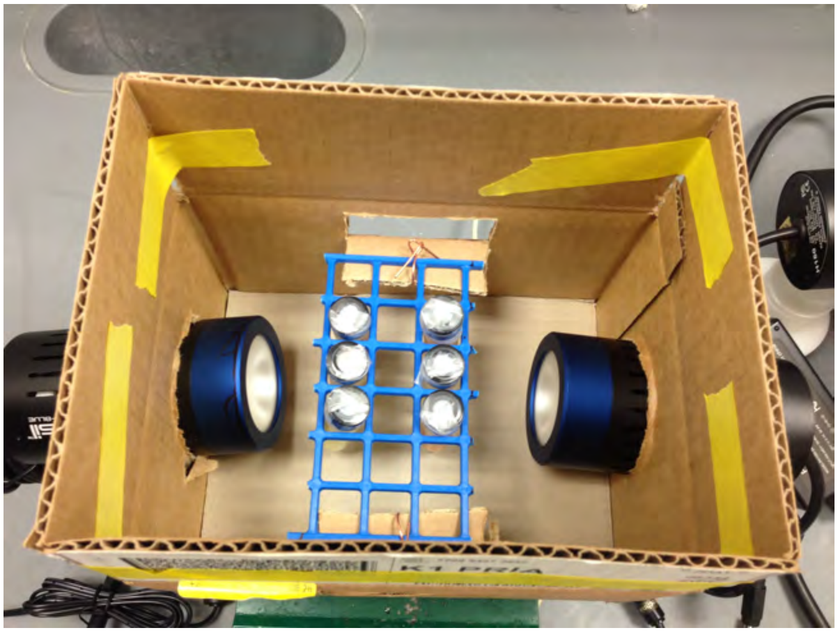
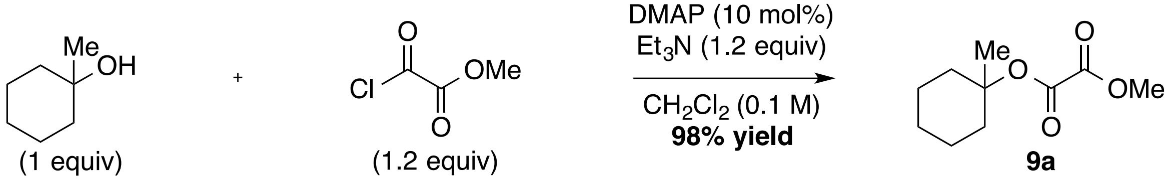
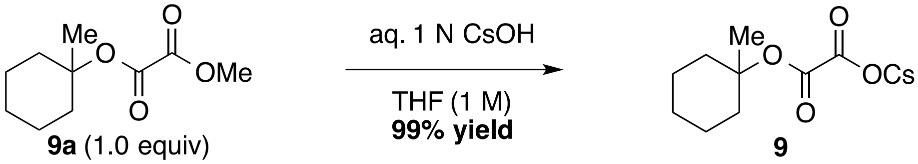


Figure S2. Top view. Note: a lid is placed on top of the box after LED lamps are turned on.

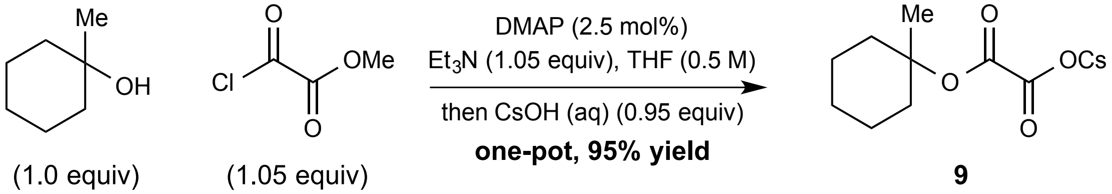
Experimental Procedures:



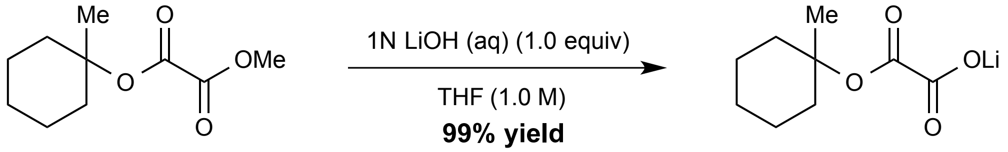
Methyl (1-methylcyclohexyl) oxalate (9a): A round-bottom flask was charged with 1-methylcyclohexan-1-ol (2.3 g, 20 mmol, 1.0 equiv) and CH_2Cl_2 (DCM) (200 mL, 0.1M). Triethylamine (3.4 mL, 24 mmol, 1.2 equiv) and DMAP (250 mg, 2 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (2.2 mL, 24 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 ºC, then quenched with sat. NH_4Cl (aq) (100 mL). The aqueous phase was extracted with DCM (100 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (85:15 hexanes:Et_2O) to give **9a** as colorless oil (576 mg, 94% yield). R*f* 0.45 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.88 (s, 3H), 2.23−2.21 (m, 2H), 1.60−1.49 (m, 10H), 1.32−1.28 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.3, 156.9, 87.0, 53.5, 36.5, 25.3, 25.2, 22.1; IR (thin film): 2936, 1736, 1734, 1200, 1138 cm^{-1}; HRMS-ESI (*m*/*z*) $[M + Na]^+$ calculated for $C_{10}H_{16}O_4Na$, 223.0946; found, 223.0943.



Cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (9): A round-bottom flask was charged with methyl (1-methylcyclohexyl) oxalate **9a** (3.9 g, 19.5 mmol, 1.0 equiv) followed by the addition of THF (19.5 mL, 1 M). To this solution, 1 N aq. CsOH (19.5 mL, 19.5 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **9** as a colorless solid (6.2 g, 99% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 2.01 (app d, *J*=15.6, 2H), 1.52−1.44 (m, 3H), 1.36−1.33 (m, 7H), 1.26−1.20 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 168.0, 164.0, 79.8, 36.7, 25.8, 25.5, 21.9; IR (thin film): 3441, 2932, 1713, 1635, 1202 cm^{-1}; HRMS-ESI (*m/z*) [M − Cs]$^-$ calculated for $C_9H_{13}O_4$, 185.0814; found, 185.0816.

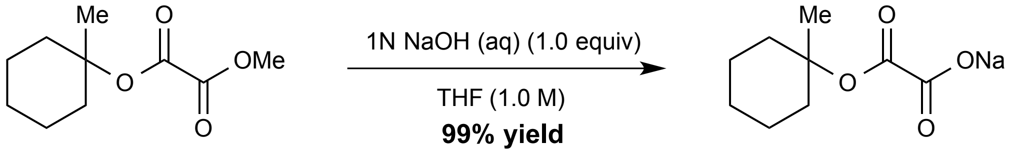


One-Pot Procedure for cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (9): 1-methylcyclohexan-1-ol (2.28 g, 20 mmol, 1.0 equiv) was dissolved in THF (40 mL, 0.5 M). Triethylamine (2.9 mL, 21 mmol, 1.05 equiv) and DMAP (61 mg, 0.5 mmol, 0.025 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (1.9 mL, 21 mmol, 1.05 equiv). The reaction was stirred for 1 hour at room temperature, then quenched with sat. brine (50 mL). The layers were separated and the organic extracts washed again with 50% sat. brine (50 mL). The organic extracts were then treated with 1 M CsOH (aq) (19 mL, 19 mmol, 0.95 equiv), and the mixture was shaken until the intermediate methyl oxalate was consumed as judged by TLC (<5min). Hexanes (75 mL) were added, and the aqueous phase was collected. The organic extracts were washed with a second portion of water (10 mL), and the combined aqueous phases were concentrated under reduced pressure to give **9** as a colorless solid (6.07 g, 95% yield). Spectral data were consistent with reported data from the 2-step procedure for preparing **9**, and the material prepared in this way performed as well in the photoredox coupling reaction.



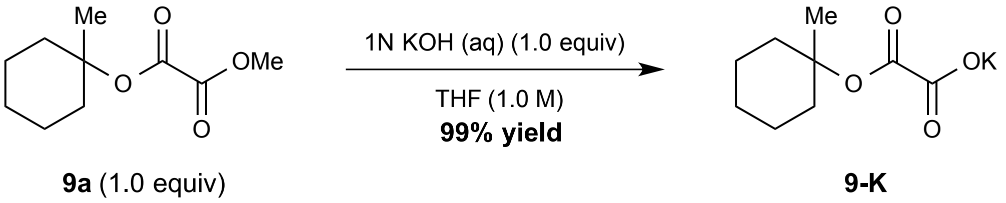
9a (1.0 equiv) **9-Li**

Lithium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (9-Li): A round-bottom flask was charged with 1-methylcyclohexyl methyl oxalate **9a** (200 mg, 1.0 mmol, 1 equiv) followed by the addition of THF (1.0 mL, 1 M). To this solution, 1 N LiOH (aq) (1.0 mL, 1.0 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **9-Li** as a colorless solid (190 mg, 99% yield): IR (thin film, cm^{-1}) 2931, 2862, 1705, 1655, 1409, 1268, 1240, 1107. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 2.02 (app d, *J* = 13.0 Hz, 2H), 1.54 – 1.32 (m, 10H), 1.27-1.16 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 167.3, 163.4, 79.6, 36.2, 25.3, 25.0, 21.5. HRMS (ESI–TOF) *m/z* calculated for $C_9H_{13}O_4Li$ ([M–Li]$^-$) 185.0814; found 185.0816.

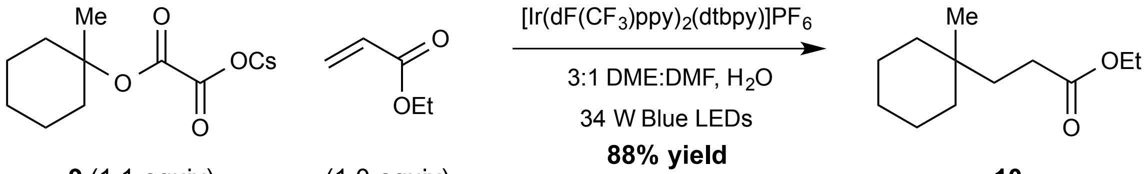


9a (1.0 equiv) **9-Na**

Sodium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (9-Na): A round-bottom flask was charged with 1-methylcyclohexyl methyl oxalate **9a** (200 mg, 1.0 mmol, 1 equiv) followed by the addition of THF (1.0 mL, 1 M). To this solution, 1 N NaOH (aq) (1.0 mL, 1.0 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **9-Na** as a colorless solid (206 mg, 99% yield): IR (thin film, cm^{-1}) 2930, 2861, 1733, 1709, 1659, 1659, 1405, 1265, 1218. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 2.02 (app d, *J* = 13.0 Hz, 2H), 1.54 – 1.32 (m, 10H), 1.28 – 1.17 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 167.3, 163.7, 79.6, 36.2, 25.3, 25.0, 21.5. HRMS (ESI–TOF) *m/z* calculated for $C_9H_{13}O_4Na$ ([M–Na]$^-$) 185.0814; found 185.0807.

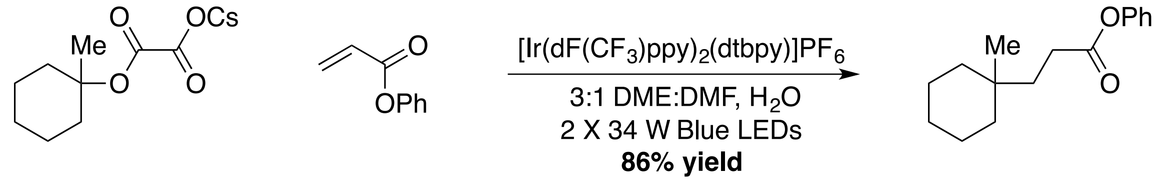


Potassium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (9-K): A round-bottom flask was charged with 1-methylcyclohexyl methyl oxalate **9a** (200 mg, 1.0 mmol, 1 equiv) followed by the addition of THF (1.0 mL, 1 M). To this solution, 1 N KOH (aq) (1.0 mL, 1.0 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **9-K** as a colorless solid (221 mg, 99% yield): IR (thin film, cm^{-1}) 2933, 2863, 1720, 1710, 1642, 1413, 1201, 1145. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 2.02 (app d, *J* = 13.2 Hz, 2H), 1.54 – 1.31 (m, 10H), 1.27 – 1.16 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 167.5, 163.6, 79.3, 36.2, 25.3, 25.0, 21.5. HRMS (ESI–TOF) *m/z* calculated for $C_9H_{13}O_4K$ ([M–K]$^-$) 185.0814; found 185.0807.



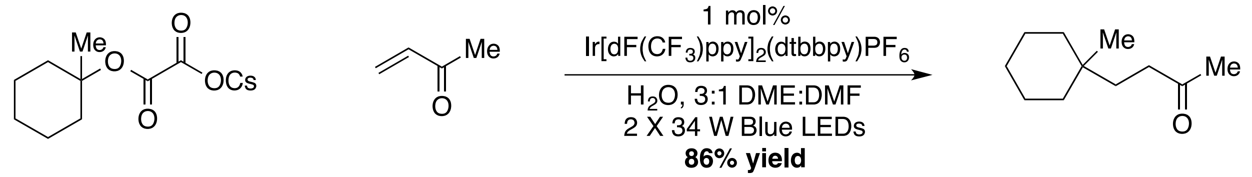
9 (1.1 equiv) (1.0 equiv) **10**

Ethyl 3-(1-methylcyclohexyl)propanoate (10): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **9** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and ethyl acrylate (50 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (98:2 hexanes:EtOAc) to give **10** as a yellow oil (87 mg, 88% yield): Rf = 0.30 (95:5 hexanes:ethyl acetate, stained with KMnO4); IR (KBr disk, cm^{-1}) 2927, 2859, 1738, 1452, 1375, 1302, 1176, 1039. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.12 (q, J = 7.1 Hz, 2H), 2.27 – 2.21 (m, 2H), 1.59 – 1.54 (m, 2H), 1.49 – 1.20 (m, 13H), 0.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 60.4, 37.6, 36.8, 32.4, 29.2, 26.6, 24.6, 22.1, 14.4. HRMS (ESI–TOF) *m*/*z* calculated for $C_{12}H_{22}O_2$ ([M+Na]$^+$) 221.1517; found 221.1523.



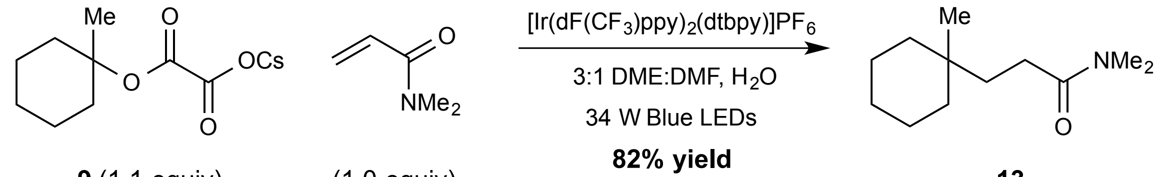
9 (1.5 equiv) (1.0 equiv) **11**

Phenyl 3-(1-methylcyclohexyl)propanoate (11): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **9** (238 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and phenyl acrylate (69 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:EtOAc) to give **11** as a pale yellow oil (106 mg, 86%): $R_f = 0.57$ (9:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 2970, 2924, 2854, 1752, 1370, 1229, 1216, 1196, 1161, 1120 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.24 – 7.21 (m, 1H), 7.09 – 7.07 (m, 2H), 2.53 – 2.50 (m, 2H), 1.73 – 1.70 (m, 2H), 1.51 – 1.44 (m, 5H), 1.35 – 1.26 (m, 5H), 0.92 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.24, 150.92, 129.52, 125.83, 121.70, 37.65, 32.57, 29.31, 26.54, 22.11; HRMS (ESI–TOF) *m/z* calculated for $C_{16}H_{23}O_2^+$ ($[M+H]^+$) 247.1693; found 247.1692.



9 **12**

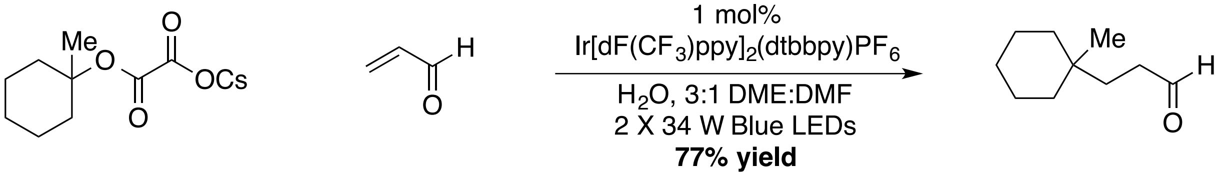
4-(1-methylcyclohexyl)butan-2-one (12): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate **(9)** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and methyl vinyl ketone (42 μL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. Li Cl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et_2O) to give **12** as a yellow oil (72 mg, 86% yield). R*f* 0.3 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 2.36 (t, *J*=8.2, 2H), 2.15 (s, 3H), 1.50 (t, *J*=8.3, 2H), 1.46−1.39 (m, 5H), 1.32−1.29 (m, 1H), 1.25−1.20 (m, 4H), 0.84 (s, 3H). Spectral data match those previously reported.[2]



9 (1.1 equiv) (1.0 equiv) **13**

***N*,*N*-dimethyl-3-(1-methylcyclohexyl)propanamide (13):** An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **9** (175 mg, 0.55

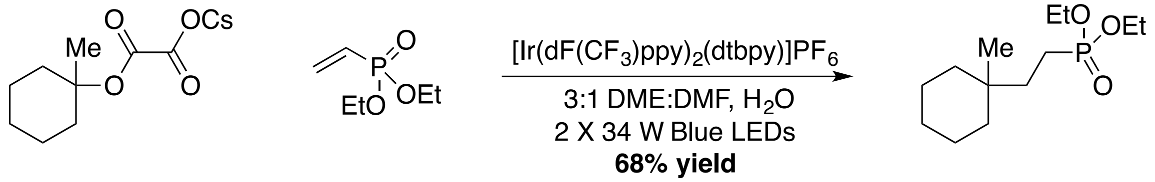
mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and *N*,*N*-dimethylacrylamide (50 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (50:50 hexanes:EtOAc) to give **13** as a yellow oil (81 mg, 82% yield). Spectral data were consistent with previously reported data.[2]



9

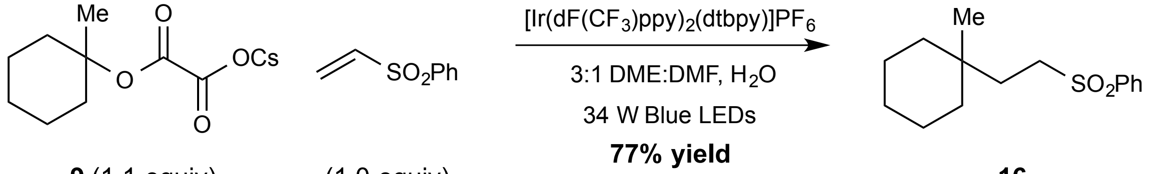
14

3-(1-methylcyclohexyl)propanal (14): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate **(9)** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and acrolein (34 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et_2O) to give **14** as a yellow oil (59 mg, 77% yield). R*f* 0.4 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.79 (t, *J*=2.4, 1H), 2.39 (t, *J*=1.8, 2H), 1.57 (t, *J*=3.6, 2H), 1.48−1.41 (m, 5H), 1.33−1.30 (m, 1H), 1.29−1.21 (m, 4H), 0.86 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 203.6, 38.9, 37.7, 33.9, 32.4, 30.5, 26.6, 24.7, 22.1; IR (thin film): 2923, 2713, 1730, 1454, 1378 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calculated for $C_{10}H_{18}ONa$, 177.1255; found, 177.1257.



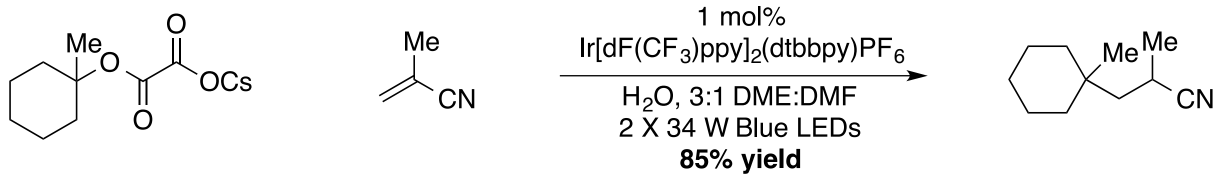
9 (1.1 equiv) (1.0 equiv) **15**

Diethyl (2-(1-methylcyclohexyl)ethyl)phosphonate (15): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate **(9)** (175 mg, 0.55 mmol, 1.1 equiv) and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and diethyl vinyl phosphonate (77 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (1:1 hexanes:acetone) to give **15** as a yellow oil (89 mg, 68% yield). R*f* 0.3 (7:3 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.14−4.04 (m, 4H), 1.71−1.63 (m, 2H), 1.56−1.39 (m, 7H), 1.33 (app t, *J*=7.0, 7H), 1.25−1.19 (m, 4H), 0.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 61.6 (d, J_{C-P}=6.4), 37.4, 34.0, 26.6, 24.4, 22.1, 20.7, 19.6, 16.7 (d, J_{C-P}=6.0); IR (thin film): 2925, 1456, 1231, 1080, 957 cm^{-1}; HRMS-ESI (*m/z*) [M + Na]$^+$ calculated for $C_{13}H_{27}O_3PNa$, 285.1595; found, 285.1596.



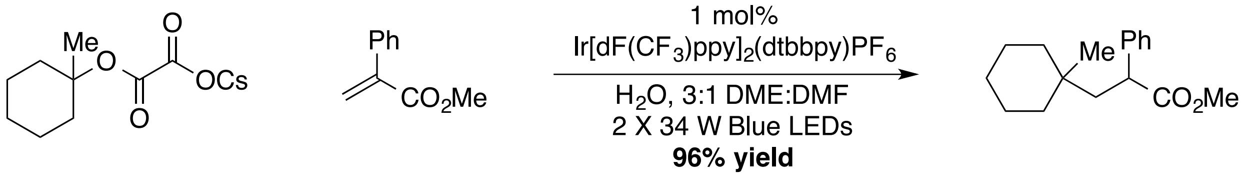
9 (1.1 equiv) (1.0 equiv) **16**

((2-(1-methylcyclohexyl)ethyl)sulfonyl)benzene (16): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **9** (175 mg, 0.55 mmol, 1.1 equiv) and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (95:5 hexanes:EtOAc) to give **16** as a yellow oil (102 mg, 77% yield). Spectral data were consistent with previously reported data.[2]



9 **17**

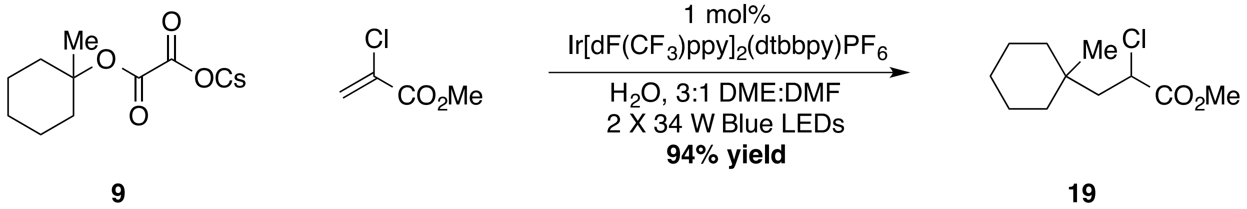
2-methyl-3-(1-methylcyclohexyl)propanenitrile (17): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate **(9)** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and methacrylonitrile (34 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et$_2$O) to give **17** as a yellow oil (70 mg, 85% yield). R*f* 0.45 (9:1 hexanes:acetone); visualized with KMnO$_4$. ^{1}H NMR (600 MHz, CDCl$_3$): δ 2.63−2.60 (m, 1H), 1.79 (dd, *J*=13.8, 9.6, 1H), 1.57−1.44 (m, 6H), 1.38−1.25 (m, 10H), 0.99 (s, 3H). Spectral data match those previously reported.[3]



9 **18**

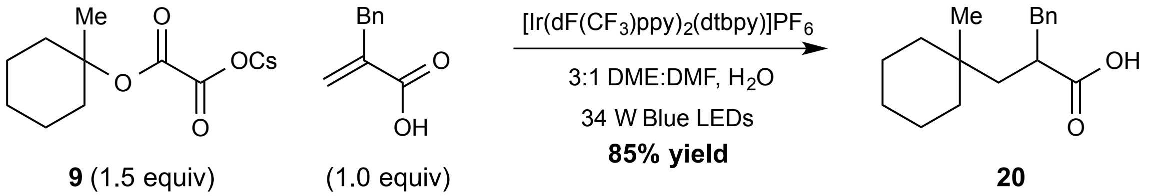
Methyl 3-(1-methylcylohexyl)-2-phenylpropanoate (18): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-

methylcyclohexyl)oxy)-2-oxoacetate **(9)** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and methyl 2-phenylacrylate[4] (81 mg, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:EtOAc) to give **18** as a yellow oil (125 mg, 96% yield). R*f* 0.4 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.26 (m, 5H), 3.72 (dd, *J*=9.0, 3.5, 1H), 3.67 (s, 3H), 2.34 (dd, *J*=14.0, 9.0, 1H), 1.65 (dd, *J*=14.0, 4.0, 1H), 1.50−1.42 (m, 5H), 1.34−1.24 (m, 5H), 0.91 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 175.6, 141.4, 128.8, 128.0, 127.2, 52.2, 47.2, 46.4, 38.0, 37.9, 33.6, 26.5, 24.5, 22.2, 22.1; IR (thin film): 2933, 1735, 1453, 1152, 670 cm^{-1}; HRMS-CI (*m/z*) $[M + NH_4]^+$ calculated for $C_{17}H_{28}NO_2$, 278.2120; found, 278.2122.

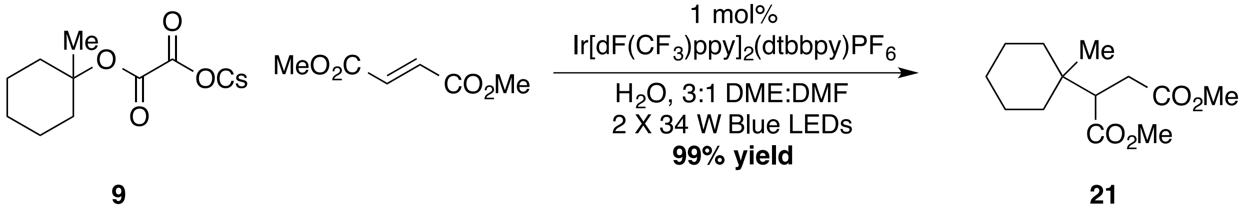


Methyl 2-chloro-3-(1-methylcyclohexyl)propanoate (19): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate **(9)** (175 mg, 0.55 mmol, 1.1 equiv) and

Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and α-chloro methacrylate (51 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et_2O) to give **19** as a yellow oil (102 mg, 94% yield). R*f* 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.36−4.34 (m, 1H), 3.78 (s, 3H), 2.18 (dd, *J*=14.4, 7.8, 1H), 1.90 (dd, *J*=12.7, 5.4, 1H) 1.47−1.44 (m, 6H), 1.29 (t, *J*=5.4, 2H), 1.27−1.24 (m, 2H), 0.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.4, 53.7, 53.1, 47.3, 38.0, 37.9, 33.6, 26.3, 24.7, 22.0, 21.0; IR (thin film): 2926, 1742, 1437, 1161, 687 cm^{-1}; HRMS-CI (*m/z*) $[M + NH_4]^+$ calculated for $C_{11}H_{23}ClNO_2$, 236.1417; found, 236.1415.

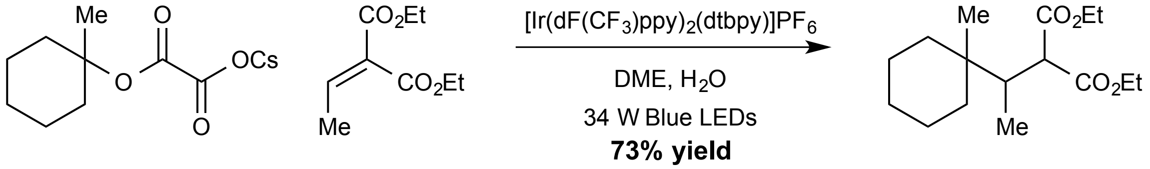


2-Benzyl-3-(1-methylcyclohexyl)propanoic acid (20): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **9** (239 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and 2-benzylacrylic acid (81 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and 1 N HCl (aq) (2 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (94:5:1 hexanes:THF:AcOH) to give **20** as a yellow oil (110 mg, 85% yield): Rf = 0.45 (75:25 hexanes:ethyl acetate, stained with KMnO4); IR (KBr disk, cm^{-1}) 2928, 2860, 2671, 1705, 1453, 1419, 1291. ^1H NMR (600 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.23 – 7.16 (m, 3H), 2.96 (dd, *J* = 12.7, 7.0 Hz, 1H), 2.75 – 2.65 (m, 2H), 1.83 (dd, *J* = 14.3, 9.2 Hz, 1H), 1.44 – 1.13 (m, 11H), 0.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.9, 139.0, 129.1, 128.5, 126.6, 43.8, 43.1, 40.9, 37.9, 37.8, 33.2, 26.4, 24.5, 22.02, 21.97. HRMS (ESI–TOF) *m/z* calculated for $C_{17}H_{24}O_2$ ($[M–H]^-$) 259.1698; found 259.1690.



9 **21**

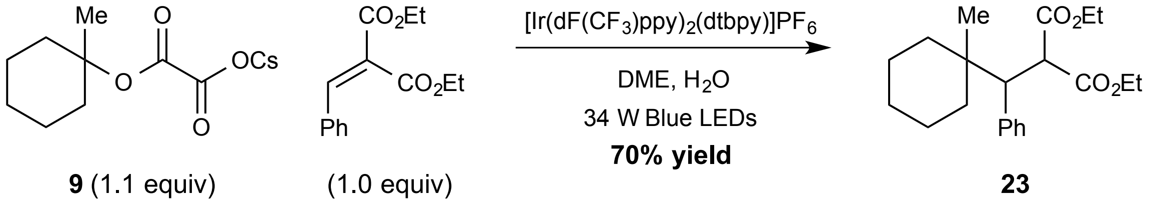
Dimethyl 2-(1-methylcyclohexyl)succinate (21): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate **(9)** (175 mg, 0.55 mmol, 1.1 equiv) and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and dimethyl fumarate (72 mg, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et_2O) to give **21** as a yellow oil (120 mg, 99% yield). R*f* 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 3.69 (s, 3H), 3.66 (s, 3H), 2.83−2.76 (m, 2H), 2.47 (d, *J*=14.1, 1H), 1.62−1.57 (m, 1H), 1.52−1.37 (m, 6H), 1.31−1.22 (m, 3H), 0.92 (s, 3H). Spectral data match those previously reported.[2]



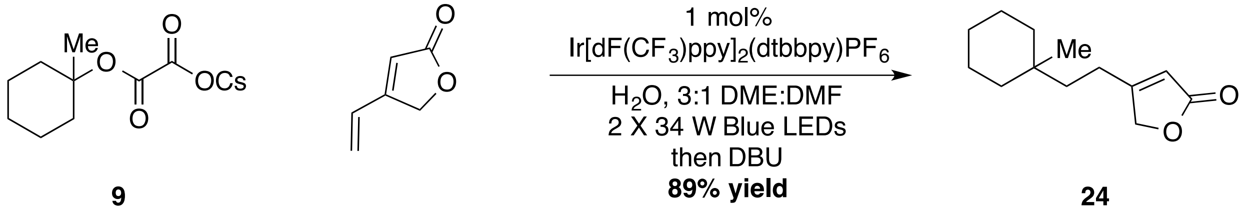
9 (1.1 equiv) (1.0 equiv) **22**

Diethyl 2-(1-(1-methylcyclohexyl)ethyl)malonate (22): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **9** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). DME (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and diethyl ethylidenemalonate (93 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 48 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (97:3 hexanes:EtOAc) to give **22** as a yellow oil (104 mg, 73% yield): Rf = 0.20 (95:5

hexanes:ethyl acetate, stained with KMnO4); IR (KBr disk, cm^{-1}) 2982, 2931, 2858, 1747, 1725, 1463, 1371, 1301, 1151. ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.22 – 4.12 (m, 4H), 3.55 (d, *J* = 4.7 Hz, 1H), 2.36 – 2.28 (m, 1H), 1.55 – 1.16 (m, 16H), 0.99 (d, *J* = 7.3 Hz, 3H), 0.81 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 170.5, 169.9, 61.5, 61.0, 52.4, 42.1, 36.3, 35.94, 35.92, 26.3, 22.02, 21.96, 19.5, 14.2, 11.1. HRMS (ESI–TOF) *m/z* calculated for $C_{16}H_{28}O_4$ ([M+Na]$^+$) 307.1885; found 307.1894.



Diethyl 2-((1-methylcyclohexyl)(phenyl)methyl)malonate (23): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **9** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). DME (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and diethyl benzylidenemalonate (124 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 48 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (95:5 hexanes:EtOAc) to give **23** as a yellow oil (121 mg, 70% yield): Rf = 0.20 (95:5 hexanes:ethyl acetate, stained with KMnO4); IR (thin film, cm^{-1}) 2929, 2860, 1759, 1728, 1464, 1299, 1149, 1033, 910. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.24 – 7.12 (m, 5H), 4.27 – 4.14 (m, 2H), 4.00 (d, J = 10.6 Hz, 1H), 3.74 – 3.64 (m, 2H), 3.50 (d, J = 10.6 Hz, 1H), 1.56 – 1.01 (m, 13H), 0.95 (s, 3H), 0.79 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 168.5, 139.7, 127.4, 126.6, 61.8, 61.3, 56.0, 54.6, 37.2, 36.9, 35.9, 26.1, 22.1, 22.0, 19.2, 14.1, 13.5. HRMS (ESI–TOF) *m*/*z* calculated for $C_{21}H_{30}O_4$ ([M+Na]$^+$) 369.2042; found 369.2048.

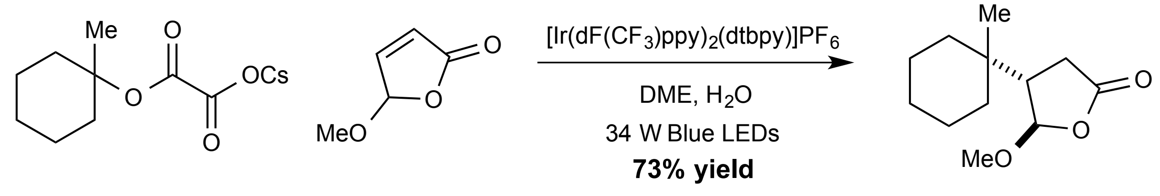


9

24

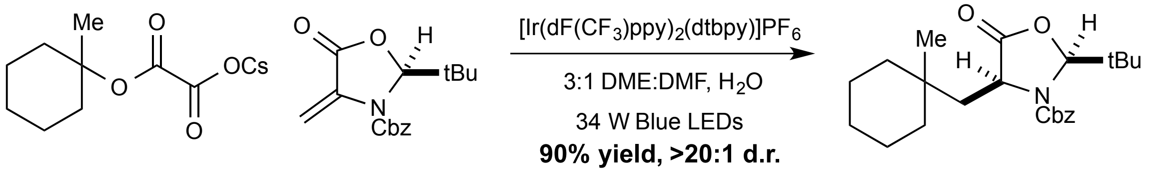
4-(2-(1-methylcyclohexyl)ethyl)furan-2(5*H*)-one (24). An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate **(9)** (124 mg, 0.38 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (4.0 mg, 0.0035 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (7 mL, 0.05 M) was added, followed by water (63 μL, 3.5 mmol, 10 equiv) and vinyl butenolide[5] (39 mg, 0.35 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h. Air was blown over the reaction vessel to maintain the temperate at 23 °C. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The residue was redissolved in DCM (9 mL, 0.04 M) and DBU (63 μL, 0.42 mmol, 1.2 equiv) was added. The mixture was maintained at 23 °C for 10 min. The reaction was diluted with DCM (10 mL), washed with 2 N aq. HCl (3 x 10 mL). Combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by flash chromatography (4:1 hexanes:EtOAc) to yield **24** (64 mg, 88%) as a yellow oil. R*f* 0.3 (4:1 hexanes:EtOAc);

visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 5.89 (s, 1H), 4.80 (s, 2H), 2.40 (t, *J*=7.8, 2H), 1.57−1.50 (m, 7H), 1.41−1.28 (m, 5H), 0.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.4, 171.7, 115.1, 73.3, 39.6, 37.7, 32.7, 26.5, 24.6, 23.1, 22.1; IR (thin film): 2923, 1778, 1744, 1636, 884 cm^{-1}; HRMS-CI (*m*/*z*) $[M + NH_4]^+$ calculated for $C_{13}H_{24}NO_2$, 226.1807; found, 226.1803.



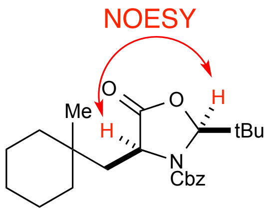
9 (1.1 equiv) (1.0 equiv) **25**

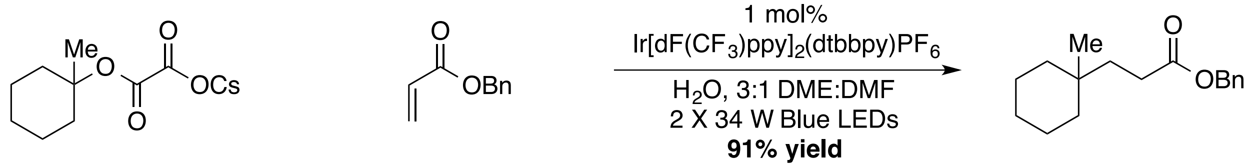
***trans*-5-Methoxy-4-(1-methylcyclohexyl)dihydrofuran-2(3*H*)-one (25):** An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **9** (175 mg, 0.55 mmol, 1.1 equiv) and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). DME (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and γ-methoxy butenolide[6] (57 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 36 h maintaining ambient temperature via cooling with a flow of air from a fan. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (90:10 hexanes:EtOAc) to give **25** as a yellow oil which was a single diastereomer (77 mg, 73% yield). Spectral data were consistent with previously reported data.[2]



9 (1.1 equiv) (1.0 equiv) **26**

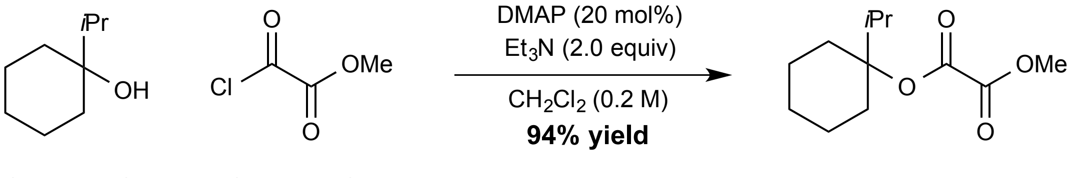
Benzyl (2*S*,4*S*)-2-(*tert*-butyl)-4-((1-methylcyclohexyl)methyl)-5-oxooxazolidine-3-carboxylate (26): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **9** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[7] (145 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (95:5 hexanes:EtOAc) to give **26** as a yellow oil which was a single diastereomer (175 mg, 90% yield): Rf = 0.30 (90:10 hexanes:ethyl acetate, stained with KMnO4); $[\alpha]^{23.4}_{D}$ +36.2º, $[\alpha]^{23.4}_{577}$ +37.9º, $[\alpha]^{23.4}_{546}$ +43.3º, $[\alpha]^{23.4}_{435}$ +77.5º, $[\alpha]^{23.4}_{405}$ +98.1º (*c* = 1.0, $CHCl_3$). IR (KBr disk, cm^{-1}) 2930, 2863, 1791, 1711, 1455, 1396, 1318, 1192. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 5H), 5.55 (s, 1H), 5.19 (d, *J* = 11.8 Hz, 1H), 5.13 (d, *J* = 11.9 Hz, 1H), 4.41 (d, *J* = 6.3 Hz, 1H), 1.90 (dd, *J* = 14.3, 8.2 Hz, 1H), 1.67 (dd, *J* = 14.3, 2.8 Hz, 1H), 1.50 – 1.15 (m, 10H), 0.96 (app s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 155.9, 135.3, 129.1, 128.85, 128.80, 96.2, 68.5, 53.7, 47.8, 38.1, 37.8, 37.0, 33.4, 26.4, 25.1, 24.3, 22.05, 22.04. HRMS (ESI–TOF) *m*/*z* calculated for $C_{23}H_{33}NO_4$ ($[M+Na]^+$) 410.2307; found 410.2315. Product stereochemistry was confirmed by a NOESY correlation:





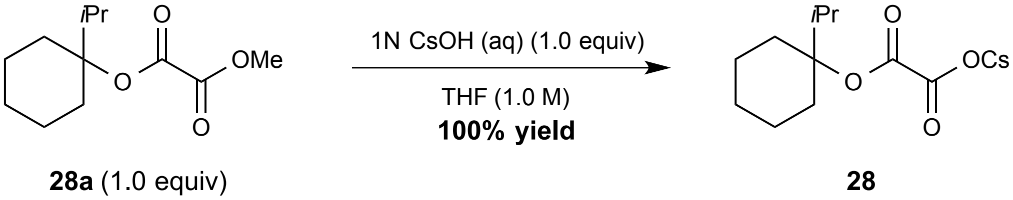
9 **27**

Benzyl 3-(1-methylcyclohexyl)propanoate (27): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate **(9)** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 μL, 0.50 mmol, 1.0 equiv) The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et_2O) to give **27** as a yellow oil (118 mg, 91% yield). R*f* 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39−7.32 (m, 5H), 5.12, (s, 2H), 2.34 (t, *J*=6.0, 2H), 1.61 (t, *J*=6.0, 2H), 1.48−1.40 (m, 5H), 1.34−1.30 (m, 1H), 1.27−1.22 (m, 4H), 0.86 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.6, 136.2, 128.7, 128.4, 128.3, 66.3, 37.6, 36.8, 32.4, 29.1, 26.5, 24.6, 22.1; IR (thin film): 2923, 2850, 1730, 1157, 696 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calculated for $C_{17}H_{24}O_2Na$, 283.1674; found, 283.16748.

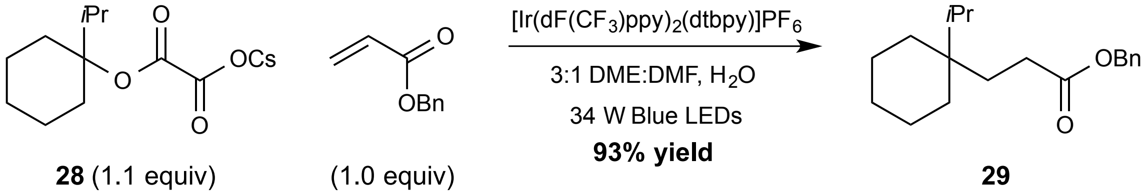


(1.0 equiv) (1.8 equiv) **28a**

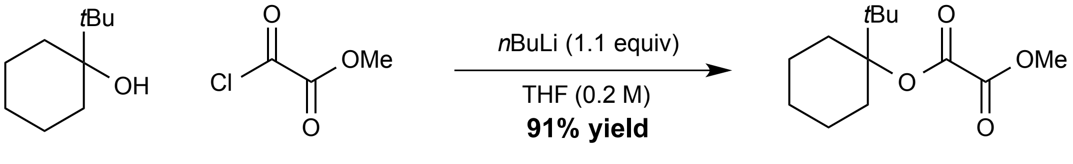
1-Isopropylcyclohexyl methyl oxalate (28a): 1-isopropylcyclohexan-1-ol (380 mg, 2.68 mmol, 1.0 equiv) was dissolved in DCM (13 mL, 0.2 M). Triethylamine (750 µL, 5.4 mmol, 2.0 equiv) and DMAP (66 mg, 0.54 mmol, 0.2 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (440 µL, 4.83 mmol, 1.8 equiv). The reaction was stirred for 8 hours at 35 ºC, then quenched with sat. NH_4Cl (aq) (20 mL). The aqueous phase was extracted with DCM (40 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (90:10 hexanes:EtOAc) to give **28a** as a colorless oil (576 mg, 94% yield): Rf = 0.40 (90:10 hexanes:ethyl acetate, stained with KMnO4); IR (thin film, cm^{-1}) 2938, 2866, 1763, 1733, 1449, 1323, 1200, 1136. ^1H NMR (500 MHz, $CDCl_3$) δ 3.87 (s, 3H), 2.65 (hept, *J* = 6.9 Hz, 1H), 2.26 (app d, *J* = 11.5 Hz, 2H), 1.72-1.57 (m, 3H), 1.54 – 1.39 (m, 4H), 1.26 – 1.13 (m, 1H), 0.91 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 156.8, 93.4, 53.3, 33.3, 30.0, 25.6, 21.6, 17.4. HRMS (ESI–TOF) *m/z* calculated for $C_{12}H_{20}O_4$ ($[M+Na]^+$) 251.1259; found 251.1251.



Cesium 2-((1-isopropylcyclohexyl)oxy)-2-oxoacetate (28): A round-bottom flask was charged with 1-isopropylcyclohexyl methyl oxalate **28a** (563 mg, 2.47 mmol, 1 equiv) followed by the addition of THF (2.5 mL, 1 M). To this solution, 1 N CsOH (aq) (2.5 mL, 2.5 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **28** as a colorless solid (855 mg, 100% yield): IR (thin film, cm^{-1}) 2967, 2934, 1707, 1698, 1654, 1368, 1193, 1141, 946. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 2.56 (hept, *J* = 7.0 Hz, 1H), 2.06 (app d, *J* = 12.8 Hz, 2H), 1.56 (app d, *J* = 12.7 Hz, 1H), 1.53 – 1.39 (m, 4H), 1.29 (td, *J* = 12.9, 4.7 Hz, 2H), 1.17-1.06 (m, 1H), 0.83 (d, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 167.6, 163.7, 84.9, 32.9, 29.7, 25.4, 21.0, 17.1. HRMS (ESI–TOF) *m/z* calculated for $C_{11}H_{17}O_4Cs$ ([M–Cs]$^-$) 213.1127; found 213.1129.

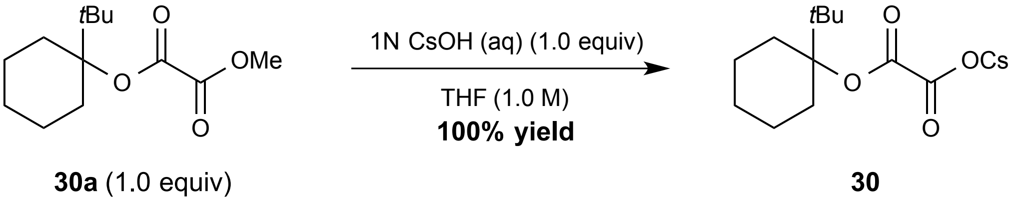


Benzyl 3-(1-isopropylcyclohexyl)propanoate (29): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **28** (190 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (98:2 hexanes:EtOAc) to give **29** as a yellow oil (134 mg, 93% yield): Rf = 0.35 (95:5 hexanes:ethyl acetate, stained with KMnO4); IR (KBr disk, cm^{-1}) 2933, 2866, 1729, 1456, 1388, 1216, 1163. ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 5.12 (s, 2H), 2.29 – 2.23 (m, 2H), 1.74 – 1.69 (m, 2H), 1.65 (hept, *J* = 6.9 Hz, 1H), 1.52 – 1.15 (m, 10H), 0.82 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 136.3, 128.7, 128.32, 128.29, 66.3, 36.6, 31.8, 31.2, 28.8, 27.6, 26.5, 21.5, 16.8. HRMS (ESI–TOF) *m/z* calculated for $C_{19}H_{28}O_2$ ($[M+Na]^+$) 311.1987; found 311.1982.

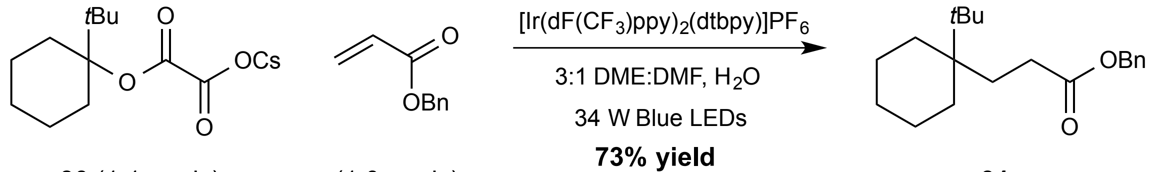


30a

1-(*tert*-Butyl)cyclohexyl methyl oxalate (30a): A round-bottom flask was charged with 1-(*tert*-butyl)cyclohexan-1-ol (234 mg, 1.5 mmol, 1.0 equiv) and THF (7.5 mL, 0.2 M) under an atmosphere of argon. The solution was stirred and cooled to –78 ºC before a 2.5M solution of *n*-BuLi in hexanes (660 μL, 1.65 mmol, 1.1 equiv) was added drop-wise. The solution was stirred for 5 min, then methyl chlorooxoacetate (160 μL, 1.8 mmol, 1.2 equiv) was added drop-wise. The reaction was stirred for 1 hour, then warmed to room temperature and quenched with sat. $NaHCO_3$(aq) (20 mL). The aqueous phase was extracted with EtOAc (40 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (97:3 hexanes:EtOAc) to give **30a** as a colorless oil (331 mg, 91% yield): Rf = 0.45 (90:10 hexanes:ethyl acetate, stained with KMnO4); IR (thin film, cm^{-1}) 2941, 2870, 1764, 1735, 1450, 1324, 1216, 1122. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (s, 3H), 2.59 – 2.49 (m, 2H), 1.72-1.62 (m, 3H), 1.44 – 1.32 (m, 4H), 1.21-1.09 (m, 1H), 1.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 157.6, 97.0, 53.3, 39.5, 30.1, 26.5, 25.1, 22.4. HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{22}O_4$ ($[M+Na]^+$) 265.1416; found 265.1420.

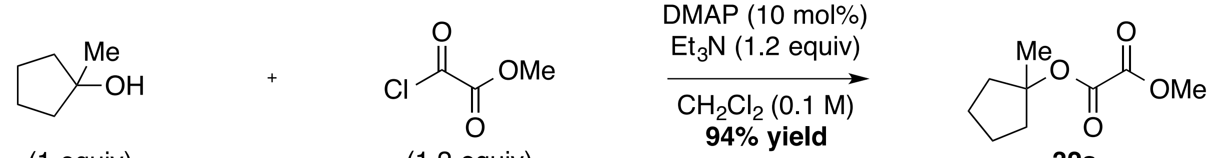


Cesium 2-((1-(*tert*-butyl)cyclohexyl)oxy)-2-oxoacetate (30): A round-bottom flask was charged with 1-(*tert*-butyl)cyclohexyl methyl oxalate **30a** (311 mg, 1.29 mmol, 1 equiv) followed by the addition of THF (1.3 mL, 1 M). To this solution, 1 N CsOH (aq) (1.3 mL, 1.3 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **30** as a colorless solid (467 mg, 100% yield): IR (thin film, cm^{-1}) 2940, 2872, 1709, 1623, 1612, 1397. 1196, 1127. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.34 (app d, J = 12.3 Hz, 2H), 1.57-1.36 (m, 5H), 1.24 (td, J = 13.0, 4.3 Hz, 2H), 1.14-1.04 (m, 1H), 0.91 (s, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.1, 164.1, 88.3, 38.8, 29.8, 26.3, 25.0, 21.8. HRMS (ESI–TOF) *m/z* calculated for $C_{12}H_{19}O_4Cs$ ($[M–Cs]^-$) 227.1283; found 227.1273.



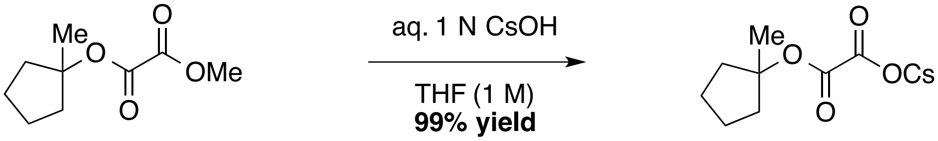
30 (1.1 equiv) (1.0 equiv) **31**

Benzyl 3-(1-(*tert*-butyl)cyclohexyl)propanoate (31): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **30** (198 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (98:2 hexanes:EtOAc) to give **31** as a yellow oil (110 mg, 73% yield): Rf = 0.40 (95:5 hexanes:ethyl acetate, stained with KMnO4); IR (thin film, cm^{-1}) 2934, 2868, 1734, 1455, 1370, 1294, 1135, 1079. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 – 7.29 (m, 5H), 5.12 (s, 2H), 2.46 – 2.39 (m, 2H), 1.86 – 1.80 (m, 2H), 1.63 (app d, *J* = 13.0 Hz, 1H), 1.53 (app d, *J* = 13.3 Hz, 2H), 1.43 – 1.24 (m, 6H), 1.09 – 0.99 (m, 1H), 0.86 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 174.6, 136.3, 128.7, 128.32, 128.31, 66.3, 38.9, 37.3, 31.2, 29.7, 26.7, 26.1, 25.7, 22.5. HRMS (ESI–TOF) *m/z* calculated for C$_{20}$H$_{30}$O$_2$ ([M+Na]$^+$) 325.2144; found 325.2133.



32a

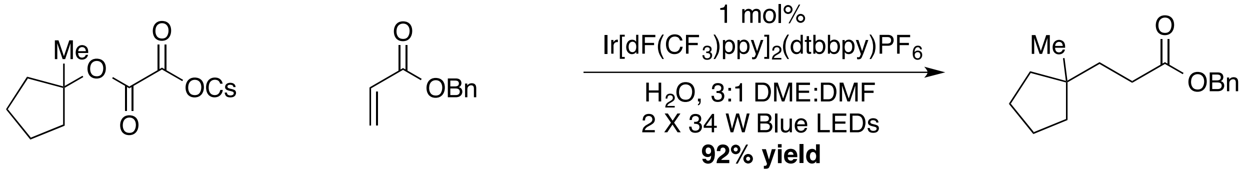
Methyl (1-methylcyclopentyl) oxalate (32a): A round-bottom flask was charged with 1-methylcyclopentan-1-ol (620 mg, 6.2 mmol, 1.0 equiv) and DCM (62 mL, 0.1M). Triethylamine (1.0 mL, 7.5 mmol, 1.2 equiv) and DMAP (76 mg, 0.62 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.7 mL, 7.5 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 ºC, then quenched with sat. NH_4Cl (aq) (100 mL). The aqueous phase was extracted with DCM (100 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (9:1 hexanes:EtOAc) to give **32a** as colorless oil (1.1 g, 94% yield). R*f* 0.5 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.87 (s, 3H), 2.22−2.20 (m, 2H), 1.78−1.75 (m, 4H), 1.69−1.64 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.2, 157.2, 94.5, 53.5, 39.0, 24.1, 23.9; IR (thin film): 2958, 1762, 1735, 1151, 789 cm^{-1}; HRMS-CI (*m/z*) $[M + NH_4]^+$ calculated for $C_9H_{18}NO_4$, 204.1236; found, 204.1233.



32a **32**

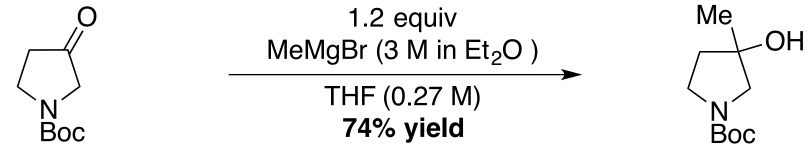
Cesium 2-((1-methylcyclopentyl)oxy)-2-oxoacetate (32): A round-bottom flask was charged with methyl (1-methylcyclopentyl) oxalate (**32a**) (1.0 g, 5.4 mmol, 1.0 equiv) followed by the addition of THF (5.4 mL, 1 M). To this solution, 1 N aq. CsOH (5.4 mL, 5.4 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **32** as a colorless solid (1.6 g, 99% yield). ^{1}H NMR

(600 MHz, DMSO-d$_6$): δ 1.98−1.95 (m, 2H), 1.63−1.54 (m, 6H), 1.46 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.6, 163.6, 87.2, 38.6, 24.3, 23.3; IR (thin film): 3430, 2957, 1723, 1637, 1173 cm^{-1}; HRMS-ESI (*m*/*z*) [M − Cs]$^-$ calculated for $C_8H_{11}O_4$, 171.0657; found, 171.0661.



32 **33**

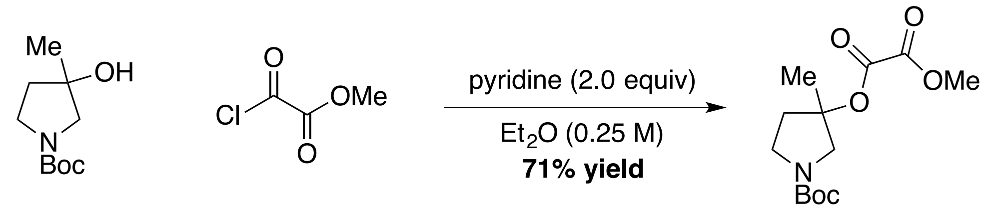
Benzyl 3-(1-methylcyclopentyl)propanoate (33): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclopentyl)oxy)-2-oxoacetate **(32)** (170 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 μL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et$_2$O) to give **33** as a yellow oil (113 mg, 92% yield). R*f* 0.5 (9:1 hexanes:acetone); visualized with KMnO$_4$. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.39−7.32 (m, 5H), 5.12, (s, 2H), 2.37 (t, *J*=4.2, 2H), 1.70−1.59 (m, 6H), 1.40−1.32 (m, 4H), 0.90 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 174.5, 136.3, 128.8, 128.5, 128.4, 66.4, 41.8, 39.3, 37.1, 31.1, 25.7, 24.6; IR (thin film): 2951, 1733, 1455, 1159, 696 cm^{-1}; HRMS-CI (*m*/*z*) [M + NH$_4$]$^+$ calculated for $C_{16}H_{26}NO_2$, 264.1964; found, 264.1967.



(1.0 equiv)

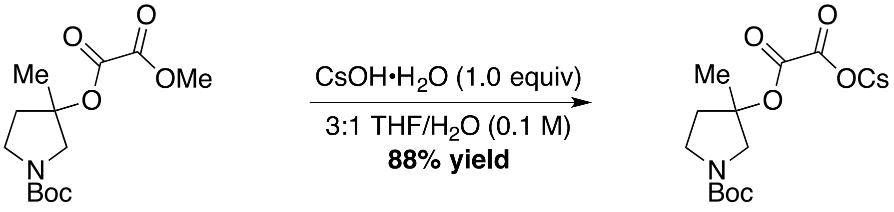
34a

***tert*-Butyl 3-hydroxy-3-methylpyrrolidine-1-carboxylate (34a):** A solution of methyl magnesium bromide (3 M in Et_2O; 10.8 mL, 32.39 mmol, 1.2 equiv) was added dropwise to *tert*-butyl 3-oxopyrrolidine-1-carboxylate (5.0 g, 26.99 mmol, 1.0 equiv) in THF (100 mL) at 0 ºC over 5 min. The resulting solution was warmed to room temperature overnight quenched with saturated aqueous NH_4Cl solution (50 mL) and diluted with Et_2O (100 mL). The layers were separated and the aqueous phase was extracted with Et_2O (3 x 50 mL). The combined ethereal extracts were washed with brine (50 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (3:7 – 1:1 EtOAc:hexanes) to give **34a**[8] as a beige solid (4.02 g, 74%): R_f = 0.17 (2:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 3384, 2970, 2908, 1716, 1656, 1417, 1367, 1156, 1144, 1105 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 3:1 mixture of rotamers (major given) δ 3.53 – 3.44 (m, 2H), 3.41 – 3.33 (m, 1H), 3.27 – 3.20 (m, 1H), 1.92 – 1.81 (m, 2H), 1.68 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) mixture of rotamers (both given) δ 154.80, 79.45, 59.13, 58.79, 45.13, 44.65, 39.62, 39.13, 28.67, 25.54; HRMS (ESI–TOF) *m/z* calculated for $C_{10}H_{20}NO_3^+$ ($[M+H]^+$) 202.1438; found 202.1436.



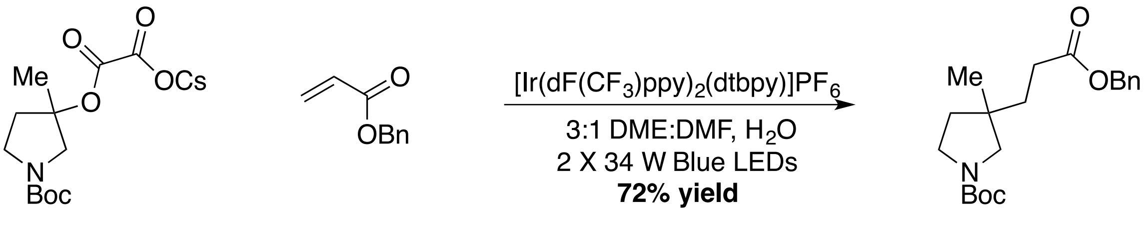
34a (1.0 equiv) (2.0 equiv) **34b**

1-(*tert*-Butoxycarbonyl)-3-methylpyrrolidin-3-yl methyl oxalate (34b): Methyl chlorooxoacetate (920 μL, 9.94 mmol, 2.0 equiv) was added to a solution of *tert*-butyl 3-hydroxy-3-methylpyrrolidine-1-carboxylate **34a** (1.0 g, 4.97 mmol, 1.0 equiv) and pyridine (760 μL, 9.94 mmol, 2.0 equiv) in Et_2O (20 mL) and the resulting yellow solution was stirred at room temperature for 4 hours. The organic phase was washed with water (2 x 20 mL) and saturated aqueous $NaHCO_3$ solution (20 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on a short column of silica gel (1:9 – 1:4) EtOAc:hexanes) to give **34b** as a colorless oil (1.03 g, 71%): R_f = 0.32 (2:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 2974, 2907, 2848, 1740, 1715, 1692, 1635, 1397, 1207, 1160, 1125, 1102 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.91 – 3.83 (m, 1H), 3.88 (s, 3H), 3.50 – 3.41 (m, 3H), 2.49 – 2.46 (m, 1H), 2.04 – 1.99 (m, 1H), 1.69 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) mixture of rotamers δ 158.25, 156.79, 156.73, 154.27, 89.48, 88.75, 79.81, 79.66, 55.98, 53.54, 44.24, 43.72, 37.03, 36.59, 28.47, 21.28. HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{22}NO_6^+$ ($[M+H]^+$) 288.1442, found 288.1439.



34b (1.0 equiv) **34**

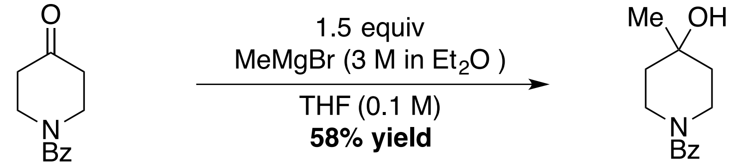
Cesium 2-((1-(*tert*-butoxycarbonyl)-3-methylpyrrolidin-3-yl)oxy)-2-oxoacetate (34): CsOH•H_2O (175 mg, 1.04 mmol, 1.0 equiv) in water (5 mL) was added to mixed oxalate **34b** (300 mg, 1.04 mmol, 1.0 equiv) in THF (10 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then concentrated under reduced pressure. The resulting colorless solid was triturated with toluene (3 x 5 mL) and dried *in vacuo* to give **34** as a colorless solid that was used without further purification (370 mg, 88%): IR (ATR) ν_{max} 2975, 2908, 2848, 1716, 1685, 1628, 1403, 1205, 1175, 1102 cm^{-1}; ^{1}H NMR (500 MHz, D_2O) δ 3.81 – 3.71 (m, 1H), 3.40 – 3.32 (m, 3H), 2.38 (dt, *J* = 12.3, 5.8 Hz, 1H), 1.99 (dt, *J* = 14.2, 8.9 Hz, 1H), 1.55 (s, 3H), 1.35 (s, 9H); Mixture of 2 rotamers: ^{13}C NMR (126 MHz, D_2O) δ 164.31, 163.72, 156.32, 55.75, 55.22, 44.26, 43.65, 36.26, 35.77, 27.64, 20.06. HRMS (ESI–TOF) *m/z* calculated for $C_{12}H_{18}NO_6^-$ ([M–Cs]$^-$) 272.1140; found 272.1137.



34 (1.1 equiv) (1.0 equiv) **35**

***tert*-Butyl 3-(3-(benzyloxy)-3-oxopropyl)-3-methylpyrrolidine-1-carboxylate (35):** An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **34** (304 mg, 0.75 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbpy)PF_6 (5.6 mg, 0.005

mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 μL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 – 9:1 hexanes:EtOAc) to give **35** as a colorless film (126 mg, 72%): R_f= 0.29 (19:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 2968, 2874, 1736, 1690, 1397, 1364, 1154, 1100 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 5.11 (s, 2H), 3.46 – 3.30 (m, 2H), 3.14 – 3.08 (m, 1H), 3.07 – 3.02 (m, 1H), 2.39 – 2.35 (m, 2H), 1.77 – 1.73 (m, 2H), 1.68 – 1.57 (m, 2H), 1.45 (s, 9H), 1.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) mixture of rotamers δ 173.46, 173.42, 154.75, 154.69, 135.85, 135.82, 128.61, 128.34, 128.31, 79.17, 66.45, 66.41, 57.58, 56.96, 44.81, 44.48, 41.08, 40.21, 37.52, 36.68, 34.29, 34.17, 30.35, 30.30, 28.55, 22.90; HRMS (ESI–TOF) *m/z* calculated for $C_{20}H_{29}NaNO_4^+$ ($[M+Na]^+$) 370.1989; found 370.1992.

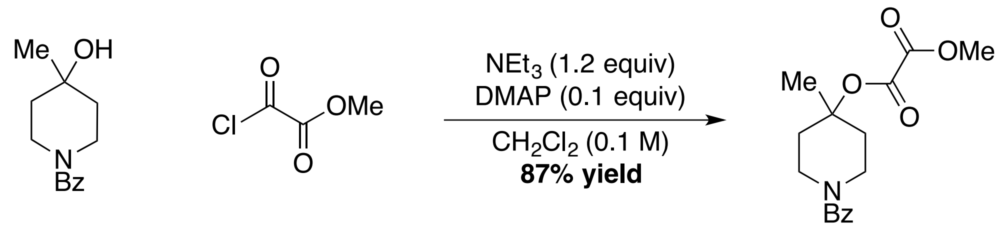


(1.0 equiv)

36a

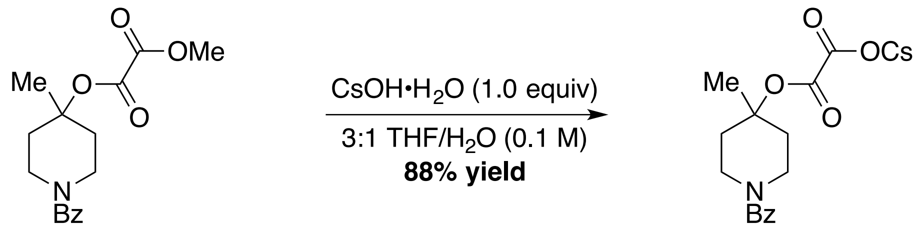
(4-Hydroxy-4-methylpiperidin-1-yl)(phenyl)methanone (36a): A solution of methyl magnesium bromide (3 M in Et_2O; 4.92 mL, 14.76 mmol, 1.5 equiv) was added dropwise to 1-

benzoyl-4-piperidone (2.0 g, 9.84 mmol, 1.0 equiv) in THF (100 mL) at 0 ºC over 5 min. The resulting solution was warmed to room temperature over 1 h, stirred for a further 1 hour and then quenched with 1 M hydrochloric acid (50 mL). The resulting aqueous mixture was extracted with Et_2O (4 x 50 mL) and the combined ethereal extracts were washed with brine (50 mL), dried $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (4:1 – 1:0 EtOAc:hexanes) to give **36a** as a viscous, colorless oil (1.24 g, 58%): R_f= 0.47 (neat EtOAc, stained with $KMnO_4$); IR (film) ν_{max} 3323, 2964, 2901, 1601, 1575, 1447, 1257, 1109 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 5H), 4.33 – 4.31 (m, 1H), 3.46 – 3.33 (m, 3H), 1.67 – 1.55 (m, 4H), 1.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) mixture of rotamers δ 170.43, 136.34, 129.62, 128.56, 126.93, 68.18, 44.23, 39.22, 38.64, 38.44, 30.47; HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{18}NO_2^+$ ($[M+H]^+$) 220.1332; found 220.1331.



36a (1.0 equiv) (1.2 equiv) **36b**

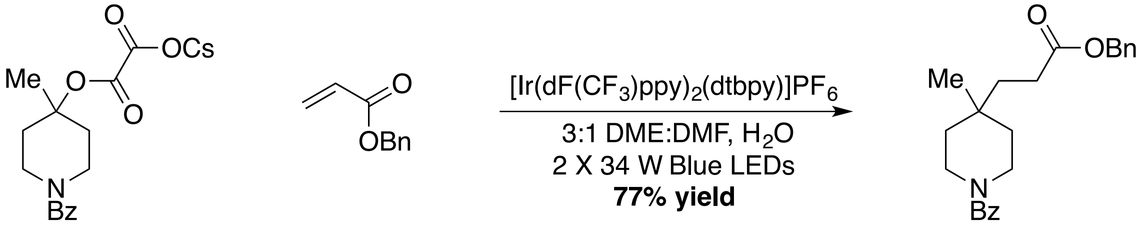
1-Benzoyl-4-methylpiperidin-4-yl methyl oxalate (36b): Methyl chlorooxoacetate (373 μL, 4.05 mmol, 1.2 equiv) was added to a solution of (4-hydroxy-4-methylpiperidin-1-yl)(phenyl)methanone **36a** (740 mg, 3.37 mmol, 1.0 equiv), triethylamine (564 μL, 4.05 mmol, 1.2 equiv) and DMAP (42 mg, 0.34 mmol, 0.1 equiv) in CH_2Cl_2 (30 mL) and the resulting yellow solution was stirred at room temperature for 6 hours. Water (50 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic extracts were washed with water (50 mL) and saturated aqueous $NaHCO_3$ solution (50 ml), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (1:1 EtOAc:hexanes) to give **36b** as a sticky white foam (894 mg, 87%): R_f = 0.42 (1:4 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 3003, 2981, 2940, 2913, 1761, 1628, 1438, 1325, 1261, 1209, 1166, 1139 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 5H), 4.44 (broad s, 1H), 3.91 (s, 3H), 3.59 (broad s, 1H), 3.34 (broad s, 1H), 3.24 (broad s, 1H), 2.41 (broad s, 1H), 2.28 (broad s, 1H), 1.77 (broad s, 1H), 1.66 (s, 3H), 1.63 (broad s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) mixture of rotamers δ 170.45, 158.53, 156.55, 135.75, 129.78, 128.54, 126.88, 83.81, 53.50, 43.56, 37.96, 36.26, 35.44, 24.77; HRMS (ESI–TOF) *m/z* calculated for $C_{16}H_{20}NO_5^+$ ([M+H]$^+$) 306.1336; found 306.1335.



36b (1.0 equiv) **36**

Cesium 2-((1-benzoyl-4-methylpiperidin-4-yl)oxy)-2-oxoacetate (36): $CsOH \cdot H_2O$ (407 mg, 2.42 mmol, 1.0 equiv) in water (5 mL) was added to mixed oxalate **36b** (740 mg, 2.42 mmol, 1.0 equiv) in THF (15 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then concentrated under reduced pressure. The resulting colorless solid was triturated with toluene (3 x 5 mL) and dried *in vacuo* to give **36** as a colorless solid that was used without further purification (952 mg, 93%): IR (ATR) ν_{max} 2934, 2910, 1714, 1616, 1575, 1438, 1203, 1171, 1138, 966 cm^{-1}; ^{1}H NMR (500 MHz, D_2O) δ 7.53 – 7.46 (m, 3H), 7.40 – 7.38

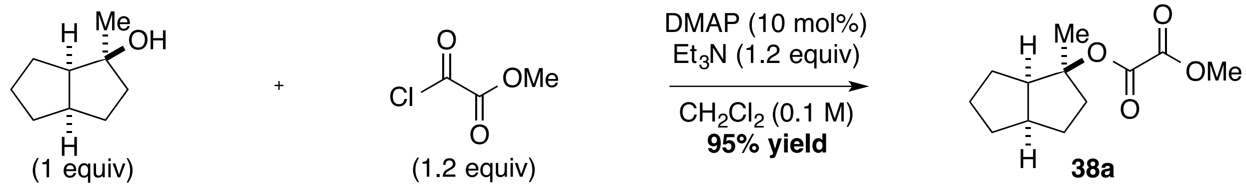
(m, 2H), 4.22 – 4.19 (m, 2H), 3.52 – 3.49 (m, 1H), 3.37 – 3.26 (m, 2H), 2.39 – 2.34 (m, 1H), 2.19 – 2.16 (m, 1H), 1.82 – 1.76 (m, 1H), 1.72 – 1.65 (m, 1H), 1.57 (s, 3H); ^{13}C NMR (126 MHz, D_2O) mixture of rotamers δ 172.25, 164.81, 163.91, 134.49, 130.25, 128.73, 126.36, 82.23, 60.91, 44.05, 38.56, 35.39, 34.82, 23.76. HRMS (ESI–TOF) *m/z* calculated for $C_{15}H_{16}NO_5^-$ ([M–Cs]$^-$) 290.1034; found 290.1037.



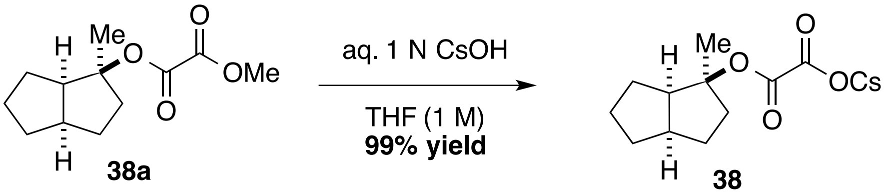
36 (1.1 equiv) (1.0 equiv) **37**

Benzyl 3-(1-benzoyl-4-methylpiperidin-4-yl)propanoate (37): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **36** (232 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs.. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 – 9:1 hexanes:EtOAc) to give **37** as a colorless film (141 mg, 77%): R_f = 0.30 (2:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 3027, 2935, 2872, 1735, 1627, 1434, 1370, 1229, 1230, 1216 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42

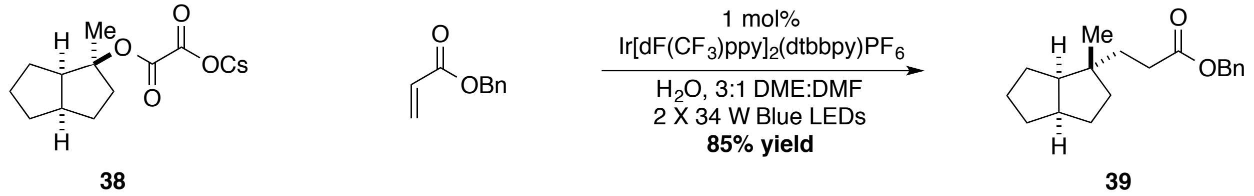
– 7.29 (m, 10H), 5.14 (s, 2H), 4.02 (broad s, 1H), 3.44 (broad s, 2H), 3.27 (broad s, 1H), 2.38 – 2.35 (m, 2H), 1.73 – 1.70 (m, 2H), 1.49 (broad s, 2H), 1.35 – 1.28 (m, 2H), 2.99 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) mixture of rotamers δ 173.71, 170.30, 136.29, 135.85, 129.47, 128.60, 128.44, 128.34, 128.33, 126.82, 66.42, 43.98, 40.00, 38.30, 37.32, 36.28, 31.53, 28.76, 23.04; HRMS (ESI–TOF) *m/z* calculated for $C_{23}H_{28}NO_3^+$ ($[M+H]^+$) 366.2064; found 366.2066.



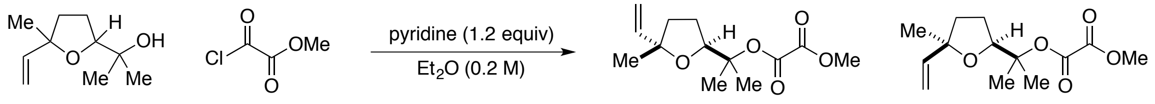
Methyl ((1*S*, 3*R*, 6*R*)-1-methyloctahydropentaien-1-yl) oxalate (38a): A round-bottom flask was charged with (1*S*,3*R*,6*R*)-1-methyloctahydropentalen-1-ol[9] (280 mg, 2.0 mmol, 1.0 equiv) and DCM (20 mL, 0.1M). Triethylamine (0.35 mL, 2.4 mmol, 1.2 equiv) and DMAP (25 mg, 0.2 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.22 mL, 2.4 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 ºC, then quenched with sat. NH_4Cl (aq) (100 mL). The aqueous phase was extracted with DCM (100 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (85:15 hexanes:Et_2O) to give **38a** as colorless oil (430 mg, 95% yield). R*f* 0.4 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.85 (s, 3H), 2.58−2.54 (m, 1H), 2.51−2.48 (m, 1H), 2.12−2.08 (m, 1H), 1.89−1.84 (m, 2H), 1.81−1.75 (m, 1H), 1.70−1.61 (m, 2H), 1.56 (s, 3H), 1.53−1.49 (m, 1H), 1.47−1.40 (m, 1H), 1.34−1.24 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.2, 156.9, 93.6, 53.5, 53.3, 41.6, 36.5, 35.5, 29.0, 28.7, 27.2, 24.0; IR (thin film): 2952, 1766, 1738, 1160, 732 cm^{-1}; HRMS-CI (*m*/*z*) $[M + NH_4]^+$ calculated for $C_{12}H_{22}NO_4$, 244.1549; found, 244.1544.



Cesium 2-(((1*S*,3*R*,6*R*)-1-methyloctahydropentalen-1-yl)oxy)-2-oxoacetate (38): A round-bottom flask was charged with methyl ((1*S*, 3*R*, 6*R*)-1-methyloctahydropentaien-1-yl) oxalate (**38a**) (390 mg, 1.7 mmol, 1.0 equiv) followed by the addition of THF (1.7 mL, 1 M). To this solution, 1 N aq. CsOH (1.7 mL, 1.7 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **38** as a colorless solid (590 mg, 99% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 2.47−2.37 (m, 2H), 1.88−1.74 (m, 2H), 1.72−1.64 (m, 2H), 1.58−1.51 (m, 1H), 1.50−1.40 (m, 2H), 1.38 (s, 3H), 1.36−1.28 (m, 1H), 1.25−1.16 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.0, 163.4, 86.9, 52.7, 40.7, 36.4, 35.2, 28.3, 28.1, 26.6, 24.2; IR (thin film): 2947, 1722, 1635, 1210, 1121 cm^{-1}; HRMS-ESI (*m/z*) [M − Cs]$^-$ calculated for $C_{11}H_{15}O_4$, 211.0970; found, 211.0970.

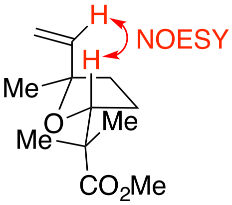


Benzyl 3-((1*S*,3*R*,6*R*)-1-methyloctahydropentalen-1-yl)propanoate (39): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-(((1*S*,3*R*,6*R*)-1-methyloctahydropentalen-1-yl)oxy)-2-oxoacetate **(38)** (190 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et_2O) to give **39** as a yellow oil (122 mg, 85% yield). R*f* 0.4 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.34 (m, 5H), 5.12, (s, 2H), 2.49−2.46 (m, 1H), 2.34 (t, *J*=8.0, 2H), 1.96 (q, *J*=8.5, 1H), 1.87−1.79 (m, 2H), 1.65−1.59 (m, 3H), 1.58−1.51 (m, 1H), 1.41−1.32 (m, 3H), 1.28−1.22 (m, 2H), 1.16−1.11 (m, 1H), 0.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.6, 136.3, 128.8, 128.4, 128.3, 66.4, 53.6, 43.7, 42.9, 38.0, 36.7, 35.2, 31.6, 30.5, 29.4, 28.1, 21.3; IR (thin film): 2944, 2861, 1732, 1653, 1154 cm^{-1}; HRMS-CI (*m*/*z*) [M + NH_4]$^+$ calculated for $C_{19}H_{30}NO_2$, 304.2277; found, 204.2266.

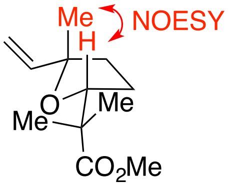


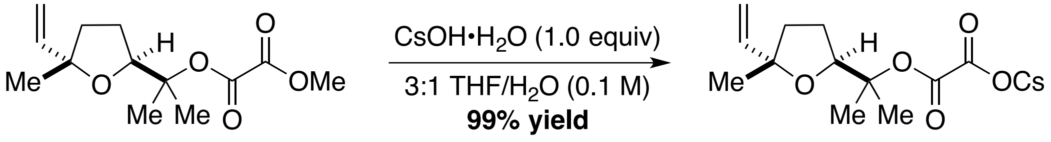
(1.0 equiv) (1.2 equiv) **40a (30% yield)** **40b (32% yield)**

Linalool oxide-derived mixed oxalate (40a): Methyl chlorooxoacetate (1.30 mL, 14.10 mmol, 1.2 equiv) was added to a solution of linalool oxide (purchased from Aldrich as a mixture of isomers; 2.0 g, 11.75 mmol, 1.0 equiv) and pyridine (1.41 mL, 14.10 mmol, 1.2 equiv) in Et_2O (50 mL) and the resulting white suspension was stirred at room temperature for 16 hours. The reaction mixture was quenched with water (50 mL) and the organic phase was washed with water (2 x 50 mL) and saturated aqueous $NaHCO_3$ solution (50 ml), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (1:19 – 1:9 EtOAc:hexanes) to give two diastereomers as colorless oils. Eluted first was the desired *trans* isomer **40a** (973 mg, 30%): R_f = 0.24 (19:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 2979, 2881, 1765, 1740, 1327, 1203, 1174, 1147, 1128 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.85 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.18 (dd, *J* = 17.3, 1.5 Hz, 1H), 4.99 (dd, *J* = 10.7, 1.5 Hz, 1H), 4.06 (dd, *J* = 7.4, 6.2 Hz, 1H), 3.85 (s, 3H), 2.04 – 1.76 (m, 4H), 1.58 (s, 3H), 1.55 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.87, 156.71, 143.62, 111.58, 87.49, 83.92, 83.89, 53.40, 37.02, 26.60, 26.56, 22.37, 21.47. HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{21}O_5^+$ ($[M+H]^+$) 257.1384, found 257.1386 The *trans* stereochemistry was confirmed by an observed NOESY correlation between the vinyl group and the methane:



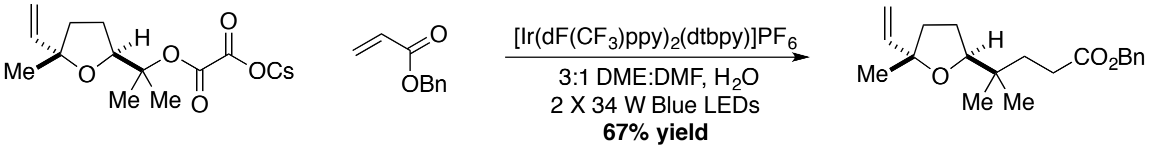
Eluted second was a fraction containing predominantly the ***cis* isomer (40b)** (1.04 g, 32% yield): R_f = 0.21 (19:1 hexanes:EtOAc, stained with $KMnO_4$) ^1H NMR (500 MHz, $CDCl_3$) δ 5.99 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.19 (dd, *J* = 17.3, 1.5 Hz, 1H), 4.97 (dd, *J* = 10.8, 1.5 Hz, 1H), 4.11 (t, *J* = 6.8 Hz, 1H), 3.84 (s, 3H), 2.01 – 1.72 (m, 4H), 1.57 (s, 3H), 1.54 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.85, 156.76, 144.03, 111.67, 87.42, 83.79, 83.56, 53.37, 37.69, 26.83, 25.73, 22.48, 21.60; HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{21}O_5^+$ ($[M+H]^+$) 257.1384, found 257.1382. The *cis* stereochemistry was confirmed by an observed NOESY correlation between the methyl and methine groups:





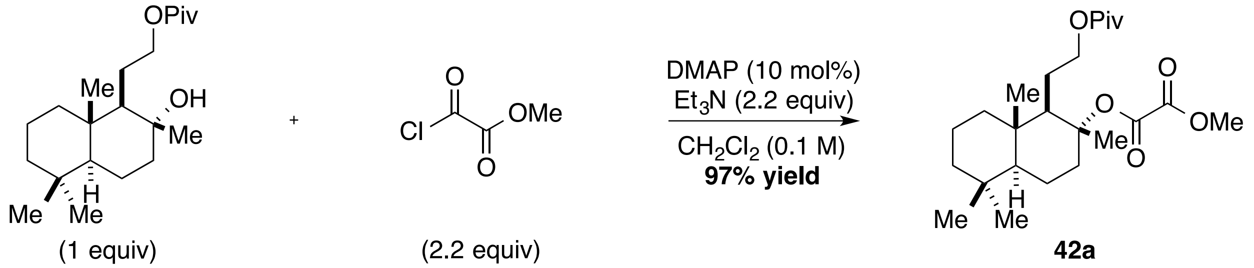
40a (1.0 equiv) **40**

***trans*-Linalool oxide-derived oxalate cesium salt (40):** CsOH•H$_2$O (328 mg, 1.95 mmol, 1.0 equiv) in water (5 mL) was added to linalool oxide-derived mixed oxalate **40a** (500 mg, 1.95 mmol, 1.0 equiv) in THF (15 mL) dropwise over 5 min. The resulting solution was stirred for a further 5 min after addition had complete then concentrated to give the **40** as a colorless semi-solid that was not purified further (729 mg, 99%): IR (ATR) ν_{max} 2977, 1719, 1627, 1385, 1371, 1213, 1121, 1096, 1027 cm^{-1}; ^{1}H NMR (500 MHz, D$_2$O) δ 5.93 (dd, *J* = 17.4, 10.4 Hz, 1H), 5.19 (d, *J* = 17.4 Hz, 1H), 5.07 (d, *J* = 10.4 Hz, 1H), 4.29 (t, *J* = 6.8 Hz, 1H), 2.11 – 1.79 (4H, m), 1.51 (s, 3H), 1.49 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (126 MHz, D$_2$O) δ 165.27, 164.12, 143.16, 142.77, 111.94, 107.80, 86.62, 84.62, 83.91, 67.74, 36.35, 26.08, 25.01, 21.35, 20.00. HRMS (ESI–TOF) *m/z* calculated for $C_{12}H_{17}O_5^-$ ([M–Cs]$^-$) 241.1082; found 241.1079.



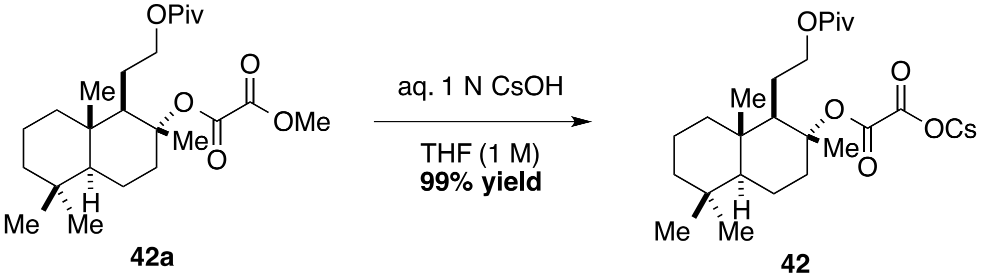
40 (1.1 equiv) (1.0 equiv) **41**

***trans*- Linalool oxide-derived Michael adduct (41):** An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **40** (281 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:EtOAc) to give **41** as a pale yellow oil (105 mg, 67%): R_f = 0.51 (24:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 2966, 2872, 1734, 1366, 1295, 1150, 1025 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 5.85 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.16 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.11 (s, 2H), 4.96 (dd, *J* = 10.6, 1.6 Hz, 1H), 3.68 (t, *J* = 7.2 Hz, 1H), 2.45 – 2.35 (m, 2H), 1.87 – 1.60 (m, 6H), 1.27 (s, 3H), 0.87 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.47, 144.28, 136.24, 128.67, 128.35, 128.29, 111.07, 85.74, 82.43, 66.29, 37.40, 35.89, 34.21, 29.71, 26.96, 26.43, 22.95, 22.33. HRMS (ESI–TOF) *m/z* calculated for $C_{20}H_{29}O_3^+$ ($[M+H]^+$) 317.2111; found 317.2111.



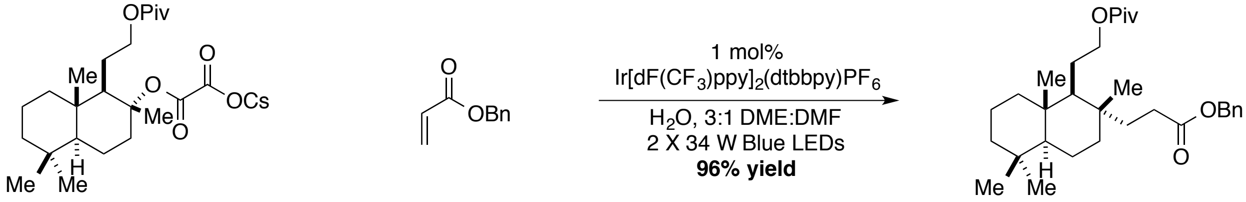
Methyl ((1*R*,2*R*,4*S*,8*S*)-2,5,5,8a-tetramethyl-1-(2-(pivaloyloxy)ethyl)decahydronaphthalen-2-yl) oxalate (42a): A round-bottom flask was charged with 2-((1*R*,2*R*,4*S*,8*S*)-2-hydroxy-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)ethyl pivalate[2] (340 mg, 1.0 mmol, 1.0 equiv) and DCM (10 mL, 0.1M). Triethylamine (0.17 mL, 1.2 mmol, 1.2 equiv) and DMAP (12 mg, 0.1 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.11

mL, 1.2 mmol, 1.2 equiv). The homogeneous reaction mixture was maintained at 23 °C for 1 h. Additional triethylamine (140 µL, 1.0 mmol, 1.0 equiv) and methyl chlorooxalate (90 µL, 1.0 mmol 1.0 equiv) were added. The reaction was warmed to 35 °C and maintained at that temperature for 4 h. The reaction was quenched by slow addition of saturated aq. NH_4Cl (10 mL). The aqueous phase was extracted with DCM (10 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (9:1 hexanes:Et_2O) to give **42a** as colorless solid (410 mg, 97% yield). R_f 0.4 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. *c* = 1.00 (MeOH), $[\alpha]^{D}_{22.5}$ −2.83, $[\alpha]^{577}_{22.5}$ −3.12, $[\alpha]^{546}_{22.5}$ −3.78, $[\alpha]^{435}_{22.5}$ −6.30, $[\alpha]^{405}_{22.5}$ −7.96; ^1H NMR (600 MHz, $CDCl_3$): δ 4.22 (qd, *J*=8.0, 1.9, 1H), 4.11 (qd, *J*=8.0, 1.9, 1H), 3.86 (s, 3H), 2.83−2.81 (m, 1H), 1.62 (s, 3H), 1.59 (br s, 2H), 1.49−1.46 (m, 1H), 1.40 (app d, *J*=13.3, 1H), 1.29 (qd, *J*=12.5, 3.1, 1H), 1.21 (s, 9H), 1.18 (td, *J*=13.5, 4.1, 1H), 1.01 (dd, *J*=14.1, 1.5, 1H), 0.96 (dd, *J*=11.4, 3.6, 1H), 0.89 (s, 3H), 0.86 (s, 3H), 0.80 (S, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.8, 159.1, 156.2, 92.4, 65.8, 55.8, 55.5, 53.5, 42.0, 39.6, 39.3, 38.9, 33.5, 33.4, 27.5, 25.1, 21.6, 20.1, 18.5, 15.8; IR (thin film): 2935, 1762, 1733, 1721, 1164, 1127 cm^{-1}; HRMS-ESI (*m*/*z*) $[M + Na]^+$ calculated for $C_{24}H_{40}O_6Na$, 447.2722; found, 447.2708.



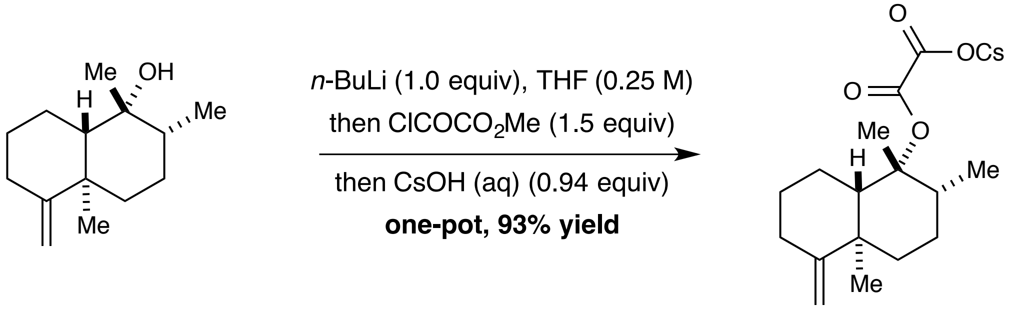
Cesium 2-oxo-2-(((1*R*,2*R*,4*S*,8*S*)-2,5,5,8a-tetramethyl-1-(2-(pivaloyloxy) ethyl) decahydronaphthalen-2-yl)oxy)acetate (42): A round-bottom flask was charged with methyl

((1*R*,2*R*,4*S*,8*S*)-2,5,5,8a-tetramethyl-1-(2-(pivaloyloxy)ethyl)decahydronaphthalen-2-yl) oxalate (**42a**) (420 mg, 1.0 mmol, 1.0 equiv) followed by the addition of THF (1.0 mL, 1 M). To this solution, 1 N aq. CsOH (1.0 mL, 1.0 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **42** as a colorless solid (540 mg, 99% yield). *c* = 1.00 (MeOH), $[\alpha]^{D}_{22.7}$ −2.48, $[\alpha]^{577}_{22.7}$ −2.75, $[\alpha]^{546}_{22.7}$ −3.09, $[\alpha]^{435}_{22.7}$ −5.15, $[\alpha]^{405}_{22.7}$ −6.17; ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 4.05−4.03 (m, 2H), 2.55−2.52 (m, 1H), 1.70−1.55 (m, 5H), 1.52−1.46 (m, 2H), 1.41 (s, 3H), 1.39−1.32 (m, 2H), 1.30−1.24 (m, 2H), 1.13 (s, 9H), 1.00−0.91 (m, 2H), 0.86 (app s, 4H), 0.76 (app d, *J*=5.1, 5H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 177.4, 167.0, 163.1, 84.9, 65.6, 55.1, 54.3, 41.4, 38.4, 38.3, 38.1, 33.2, 32.8, 27.0, 24.6, 21.3, 20.3, 19.4, 17.9, 15.2; IR (thin film): 2956, 1762, 1718, 1635, 1161, cm^{-1}; HRMS-ESI (*m/z*) [M − Cs]$^-$ calculated for $C_{23}H_{37}O_6$, 409.2590; found, 409.2599.



42 **43**

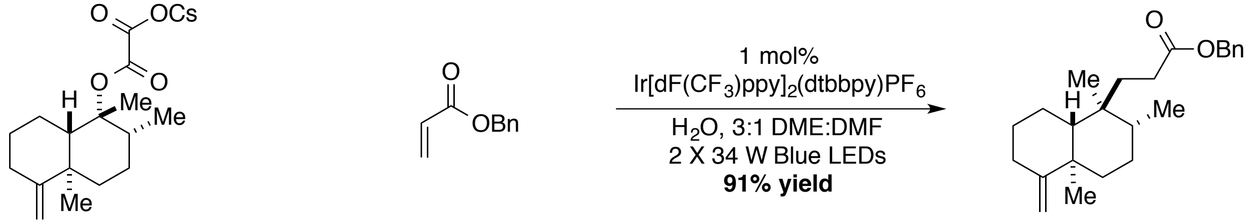
2-((1*S*,2*S*,4*S*,8*S*)-2-(3-(benzyloxy)-3-oxopropyl)-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)ethyl pivalate (43): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-oxo-2-(((1*R*,2*R*,4*S*,8*S*)-2,5,5,8a-tetramethyl-1-(2-(pivaloyloxy) ethyl) decahydro-naphthalen-2-yl)oxy)acetate **(42)** (209 mg, 0.39 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (3.9 mg, 0.0035 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (3.5 mL, 0.1M) was added, followed by water (54 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (54 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et_2O) to give **43** as a yellow oil (162 mg, 96% yield). R*f* 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$. *c* = 1.00 (MeOH), $[\alpha]^{D}_{22.7}$ +1.16, $[\alpha]^{577}_{22.7}$ +1.67, $[\alpha]^{546}_{22.7}$ +1.82, $[\alpha]^{435}_{22.7}$ +3.45, $[\alpha]^{405}_{22.7}$ +4.02; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37−7.33 (m, 5H), 5.11 (s, 2H), 4.07−4.02 (m, 1H), 3.93−3.88 (m, 1H), 2.32 (t, *J*=7.7, 2H), 1.81−1.75 (m, 1H), 1.68 (app d, *J*=12.6, 1H), 1.60−1.55 (m, 2H), 1.53−1.50 (m, 2H), 1.43−1.38 (m, 3H), 1.33−1.26 (m, 3H), 1.20 (s, 9H), 1.14 (td, *J*=12.9, 3.3, 2H), 0.90−0.88 (m, 1H), 0.87 (s, 3H), 0.85 (S, 3H), 0.83 (s, 3H), 0.80 (s, 3H), 0.72 (t, *J*=3.5, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.8, 174.5, 136.3, 128.8, 128.5, 128.4, 66.5, 66.4, 56.5, 56.1, 42.2, 40.2, 39.3, 39.1, 38.8, 37.4, 33.5, 29.0, 27.5, 25.4, 22.6, 21.8, 19.3, 18.7, 18.5, 16.3, 14.3; IR (thin film): 2921, 1734, 1720, 1252, 1166 cm^{-1}; HRMS-CI (*m*/*z*) $[M + NH_4]^+$ calculated for $C_{31}H_{52}NO_4$, 502.3896; found, 502.3884.



69 (1.0 equiv)

44

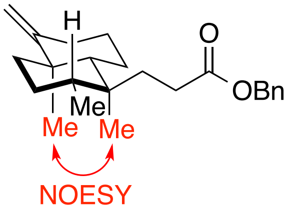
Cesium 2-oxo-2-(((1*R*,2*R*,4*R*,8*S*)-1,2,4a-trimethyl-5-methylenedecahydronaphthalen-1-yl) oxy)acetate (44): A round-bottom flask was charged with 3º alcohol **69**[10] (233 mg, 1.12 mmol, 1.0 equiv) and THF (4.5 mL, 0.25 M) under an atmosphere of argon. The solution was stirred and cooled to –78 ºC before a 2.5 M solution of *n*-BuLi in hexanes (450 µL, 1.12 mmol, 1.0 equiv) was added drop-wise. The solution was stirred for 15 min, then methyl chlorooxoacetate (160 µL, 1.68 mmol, 1.5 equiv) was added drop-wise. The reaction was stirred for 1 hour at -78 ºC, then at cryogenic temperature as the dry ice bath slowly warmed to room temperature (2-3 h). The reaction was diluted with 5 mL of THF, and the organic extracts were washed (2X) with sat. $NaHCO_3$ (aq) (5 mL), then 1X with 50% sat. brine (5 mL). The organic extracts were then treated with 0.5 M CsOH (aq) (2.1 mL, 1.05 mmol, 0.94 equiv), and the mixture was shaken until the intermediate methyl oxalate was consumed as judged by TLC (<5 min). Hexanes (10 mL) were added, and the aqueous phase was collected. The organic extracts were washed with a second portion of water (5 mL), and the combined aqueous phases were concentrated under reduced pressure to give **44** as a colorless solid (427 mg, 93% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 4.52 (d, *J*=10.0, 2H), 2.30 (td, *J*=16.2, 5.8, 1H), 2.05 (app d, *J*=14.9, 1H), 1.93−1.86 (m, 2H), 1.65 (qd, *J*=15.7, 3.4, 1H), 1.60−1.49 (m, 6H), 1.39−1.31 (m, 2H), 1.19 (qt, *J*=15.9, 4.8, 1H), 1.10 (s, 3H), 1.04 (dd, *J*=14.9, 2.9, 1H), 0.88 (d, *J*=7.9, 3H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.6, 163.7, 158.8, 103.6, 83.9, 54.0, 43.2, 39.0, 36.7, 32.3, 27.9, 26.6, 22.8, 22.7, 20.2, 16.5; IR (thin film): 2394, 1670, 1608, 1214, 1160 cm^{-1}; HRMS-ESI (*m*/*z*) [M − Cs]$^-$ calculated for $C_{16}H_{23}O_4$, 279.1596; found, 279.1590.

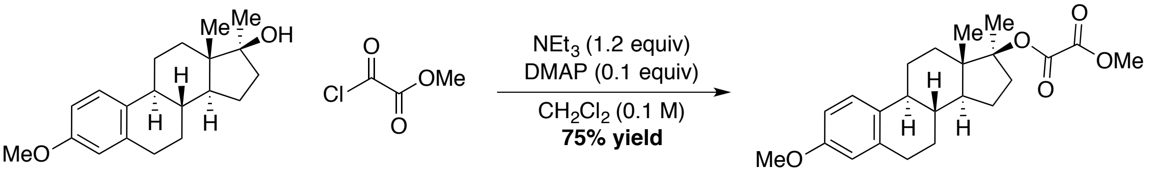


44 **45**

2-((1*S*,2*S*,4*S*,8*S*)-2-(3-(benzyloxy)-3-oxopropyl)-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)ethyl pivalate (45): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-oxo-2-(((1*R*,2*R*,4*R*,8*S*)-1,2,4a-trimethyl-5-methylenedecahydronaphthalen-1-yl)oxy)acetate **(44)** (137 mg, 0.39 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (3.9 mg, 0.0035 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (3.5 mL, 0.1M) was added, followed by water (63 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (54 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et$_2$O) to give **45** as a yellow oil (113 mg, 91% yield). R*f* 0.5 (9:1 hexanes:acetone); visualized with KMnO$_4$. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.38−7.33 (m, 5H), 5.11 (s, 2H), 4.50 (s, 2H), 2.31−2.21 (m, 2H), 2.16−2.09 (m, 2H), 1.88−1.85 (m, 1H), 1.74−1.64 (m, 2H), 1.63−1.55 (m, 2H), 1.51−1.47 (m, 1H), 1.46−1.42 (m, 1H), 1.37−1.31 (m, 1H), 1.29−1.24 (m, 1H), 1.05 (s, 3H), 0.96 (dd, *J*=14.8, 2.7, 1H), 0.88−0.83 (m, 2H), 0.81 (d, *J*=6.8, 3H), 0.77 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 174.4, 160.6, 136.3, 128.8, 128.5, 128.4, 102.8, 66.4, 49.0, 40.2, 39.2, 37.4, 37.0, 33.2, 32.9, 28.8, 28.5, 27.6, 21.8, 21.0, 18.1, 16.2; IR (thin film): 2924, 1734, 1456, 1158, 889 cm^{-1}; HRMS-

CI (m/z) $[M + NH_4]^+$ calculated for $C_{24}H_{38}NO_2$, 372.2903; found, 372.2893. Product stereochemistry was confirmed by a NOESY correlation:

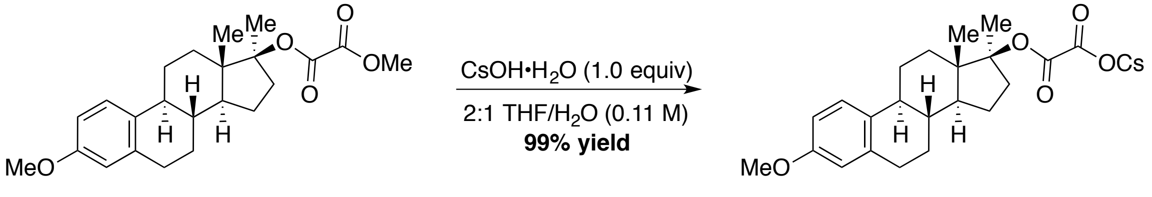




(1.0 equiv) (1.2 equiv) **46a**

Estrone-derived mixed oxalate (46a): Methyl chlorooxoacetate (514 µL, 4.19 mmol, 1.2 equiv) was added to a solution of the known sterol[2] (1.05 g, 3.50 mmol, 1.0 equiv), triethylamine (424 µL, 4.19 mmol, 1.2 equiv) and DMAP (43 mg, 0.35 mmol, 0.1 equiv) in CH_2Cl_2 (35 mL) and the resulting yellow solution was stirred at room temperature for 5 hours. Water (50 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic extracts were washed with water (50 mL) and saturated aqueous $NaHCO_3$ solution (50 ml), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (1:9 – 1:4 EtOAc:hexanes) to give **46a** as a sticky white foam (1.01 g, 75%): R_f= 0.49 (9:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 2989, 2942, 2877, 2841, 2808, 1757, 1738, 1323, 1205, 1171, 1144, 1037 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, J = 8.6 Hz, 1H), 6.72 (dd, J = 8.6, 2.7 Hz, 1H), 6.63 (d, J = 2.7 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 2.92 – 2.81 (m, 2H), 2.37 – 2.31 (m, 1H), 2.25 – 1.16 (m, 3H), 1.92 – 1.88 (s, 2H), 1.79 – 1.71 (m, 1H), 1.62 (dt, J = 12.7, 3.8 Hz, 1H), 1.56 (3H, s), 1.54 – 1.47 (m, 2H), 1.45 – 1.37 (m, 3H); ^{13}C NMR

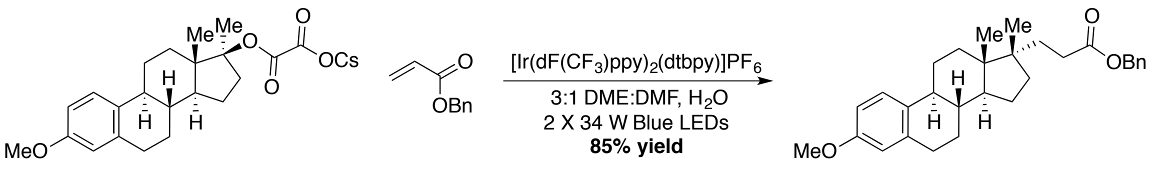
(126 MHz, $CDCl_3$) δ 159.07, 157.50, 157.04, 137.87, 132.34, 126.33, 113.81, 111.51, 95.04, 55.23, 53.28, 48.24, 47.07, 43.69, 39.26, 36.28, 32.02, 29.81, 27.48, 26.17, 23.27, 21.21, 14.33; HRMS (ESI–TOF) *m/z* calculated for $C_{23}H_{31}O_5^+$ ($[M+H]^+$) 387.2166, found 387.2164.



46a (1.0 equiv)

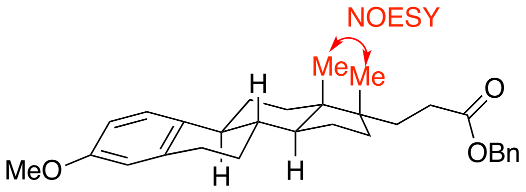
46

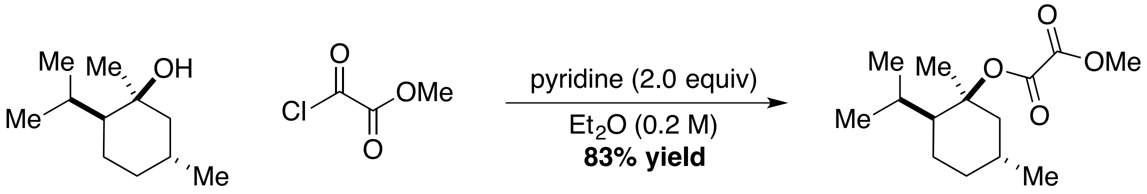
Estrone-derived oxalate cesium salt (46): $CsOH{\bullet}H_2O$ (367 mg, 2.24 mmol, 1.0 equiv) in water (5 mL) was added to estrone-derived mixed oxalate **46a** (867 mg, 2.24 mmol, 1.0 equiv) in THF (15 mL) dropwise over 5 min. The resulting solution was stirred for a further 5 min after addition had completed then concentrated to give **46** as an off-white solid that was dried *in vacuo* but not purified further (1.13 g, 99%): IR (ATR) ν_{max} 2977, 2939, 2867, 1705, 1610, 1227, 1209, 1148, 1039 cm^{-1}; ^1H NMR (500 MHz, DMSO-*d6*) δ 7.18 (d, *J* = 8.6 Hz, 1H), 6.68 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.61 (d, *J* = 2.7Hz, 1H), 3.69 (s, 3H), 2.84 – 2.74 (m, 2H), 2.32 – 2.29 (m, 1H), 2.15 – 2.12 (m, 1H), 2.01 (t, *J* = 7.7Hz, 2H), 1.83 – 1.80 (m, 1H), 1.74 (dt, *J* = 12.1, 2.9 Hz, 1H), 1.64 (dq, *J* = 13.6, 6.0 Hz, 1H), 1.55 (td, *J* = 12.8, 3.8 Hz, 1H), 1.40 (s, 3H), 1.39 – 1.27 (m, 5H), 0.81 (s, 3H); ^{13}C NMR (126 MHz, DMSO-*d6*) δ 167.43, 163.59, 157.03, 137.39, 132.05, 126.18, 113.42, 111.48, 88.77, 54.86, 47.72, 46.41, 43.14, 39.78, 39.00, 36.60, 31.88, 29.31, 27.04, 26.00, 22.94, 21.40, 14.01; HRMS (ESI–TOF) *m/z* calculated for $C_{22}H_{27}O_5^-$ ($[M{-}Cs]^-$) 371.1864; found 371.1863.



46 (1.5 equiv) (1.0 equiv) **47**

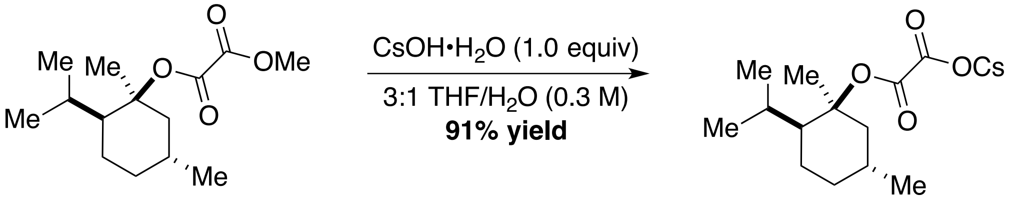
Estrone-derived Michael adduct (47): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **46** (378 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 μL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et$_2$O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over MgSO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 – 9:1 hexanes:EtOAc) to give **47** as an off-white solid (190 mg, 85%): R$_f$ = 0.45 (12:1 hexanes:EtOAc, stained with KMnO$_4$); IR (ATR) ν_{max} 2933, 2869, 1733, 1608, 1298, 1279, 1254, 1235, 1154, 1037 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.27 – 7.20 (m, 5H), 7.10 (d, *J* = 8.6 Hz, 1H), 6.60 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.52 (d, *J* = 2.6 Hz, 1H), 5.02 (s, 2H), 3.66 (s, 3H), 2.80 – 2.70 (m, 2H), 2.33 – 2.22 (m, 2H), 2.20 – 2.16 (m, 1H), 2.09 – 2.04 (m, 1H), 1.79 – 1.75 (m, 1H), 1.64 – 1.33(m, 9H), 1.31 – 1.21 (m, 2H), 1.18 – 1.09 (m, 1H), 0.77 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 174.54, 157.28, 137.98, 135.98, 132.85, 128.47, 128.17, 128.12, 126.16, 113.66, 111.27, 66.16, 55.09, 49.26, 45.82, 45.33, 43.63, 39.41, 33.17, 31.68, 31.60, 30.52, 29.86, 28.06, 26.24, 24.56, 20.38, 16.07; HRMS (ESI–TOF) *m/z* calculated for $C_{30}H_{39}O_3^+$ ([M+H]$^+$) 447.2894; found 447.2895. The configuration at the newly formed stereocenter was determined by NOESY experiments where a strong interaction between the two methyl groups was observed:[11]





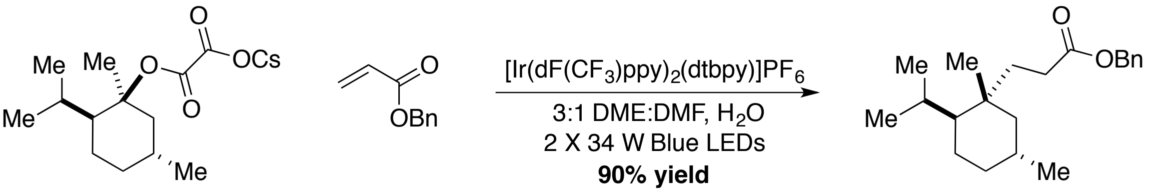
(1.0 equiv) (2.0 equiv) **48a**

Menthone-derived mixed oxalate (48a): Methyl chlorooxoacetate (1.08 mL, 11.74 mmol, 2 equiv) was added to a solution of the known alcohol[12] (4:1 mixture of diastereomers; major shown; 1.00 g, 5.87 mmol, 1.0 equiv) and pyridine (0.95 mL, 11.74 mmol, 2 equiv) in Et_2O (50 mL) and the resulting yellow solution was stirred at room temperature for 2 hours. The organic phase was washed with water (2 x 50 mL) and saturated aqueous $NaHCO_3$ solution (50 mL), dried $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (1:24 EtOAc:hexanes) to give **48a** as a colorless oil (4:1 mixture of diastereomers; 1.23 g, 83%): R_f= 0.51 (19:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 2954, 2871, 1765, 1738, 1201, 1172, 1101 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.88 (s, 3H), 2.76 (dt, *J* = 14.4, 2.9 Hz, 1H), 2.25 – 2.18 (m, 1H), 1.83 – 1.77 (m, 1H), 1.63 (s, 3H), 1.60 – 1.45 (m, 4H), 1.08 (ddd, *J* = 11.7, 4.3, 1.8 Hz, 1H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.92 (dd, *J* = 12.5, 4.7 Hz, 1H) 0.86 (d, *J* = 6.6 Hz, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.97, 156.47, 89.24, 53.24, 52.55, 43.82, 34.82, 28.03, 26.09, 24.22, 23.82, 21.99, 17.57. HRMS (ESI–TOF) *m/z* calculated for $C_{14}H_{25}O_4^+$ ($[M+H]^+$) 257.1747; found 257.1746.



48a (1.0 equiv) **48**

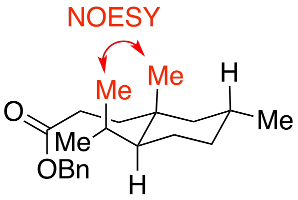
Menthone-derived cesium oxalate (48): CsOH•H_2O (1.05 g, 6.24 mmol, 1.0 equiv) in water (5 mL) was added to mixed oxalate **48a** (1.60 g, 6.24 mmol, 1.0 equiv) in THF (15 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then concentrated under reduced pressure. The resulting colorless solid was triturated with toluene (3 x 10 mL) and dried *in vacuo* to give **48** as a colorless solid that was used without further purification (1.56 g, 91%): IR (film) ν_{max} 2952, 2868, 1711, 1629, 1153, 1190, 1153 cm^{-1}; ^1H NMR (500 MHz, D_2O) δ 2.56 – 2.56 (m, 1H), 2.22 – 2.14 (m, 1H), 1.76 – 1.73 (m, 1H), 1.56 (s, 3H), 1.53 – 1.37 (m, 4H), 1.14 – 1.11 (m, 1H), 1.04 (t, *J* = 12.4 Hz, 1H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.86 (d, *J* = 6.9 Hz), 0.82 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, D_2O) δ 166.71, 165.60, 88.47, 88.46, 51.79, 43.84, 39.96, 34.31, 30.41, 27.67, 25.93, 25.54, 23.77, 22.90, 21.36, 20.19, 17.08. HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{21}O_4^-$ ($[M–Cs]^-$) 241.1445; found 241.1446.

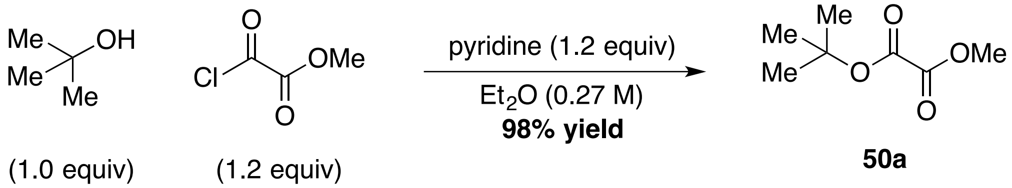


48 (1.1 equiv) (1.0 equiv) **49**

Menthone-derived Michael adduct (49): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **48** (206 mg, 0.55 mmol, 1.1

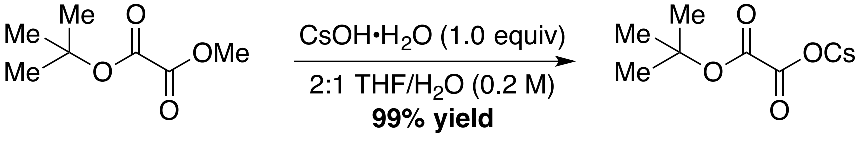
equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et$_2$O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over MgSO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:EtOAc) to give **49** as a pale yellow oil (142 mg, 90%): R$_f$ = 0.59 (19:1 hexanes:EtOAc, stained with KMnO$_4$); IR (ATR) ν_{max} 2951, 2923, 2866, 1735, 1455, 1157 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39 – 7.31 (m, 5H), 5.12 (s, 2H), 2.33 – 2.26 (m, 2H), 1.95 – 1.87 (m, 1H), 1.79 – 1.59 (m, 3H), 1.53 – 1.43 (m, 2H), 1.31 – 1.21 (m, 2H), 1.11 – 0.92 (m, 2H), 0.90 – 0.87 (7H, m), 0.81 (d, *J* = 6.4 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 174.66, 136.24, 128.68, 128.36, 128.31, 66.32, 48.88, 48.01, 37.40, 35.91, 28.91, 28.25, 25.32, 24.90, 23.11, 21.90, 20.58, 18.64. HRMS (ESI–TOF) *m/z* calculated for C$_{21}$H$_{33}$O$_2^+$ ([M+H]$^+$) 317.2475; found 317.2475. Product stereochemistry was confirmed by a NOESY correlation:





50a

***tert*-Butyl methyl oxalate (50a):** Methyl chlorooxoacetate (2.98 mL, 32.38 mmol, 1.2 equiv) was added to a solution of *tert*-butanol (2.56 mL, 26.98 mmol, 1.0 equiv) and pyridine (3.24 mL, 32.38 mmol, 1.2 equiv) in Et$_2$O (100 mL) and the resulting yellow solution was stirred at room temperature for 4 hours. The organic phase was washed with water (2 x 50 mL) and saturated aqueous NaHCO$_3$ solution (50 mL), dried over MgSO$_4$ and concentrated. The crude material was purified by flash column chromatography on a short column of silica gel (1:19 – 1:9 Et$_2$O:hexanes) to give **50a** as a colorless oil (4.26 g, 98%): R$_f$ = 0.41 (10:1 hexanes:EtOAc, stained with KMnO$_4$); IR (ATR) ν_{max} 1981, 1760, 1737, 1371, 1327, 1211, 1137 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.85 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 159.14, 156.88, 85.15, 53.40, 27.84. Data match those previously reported.[13]

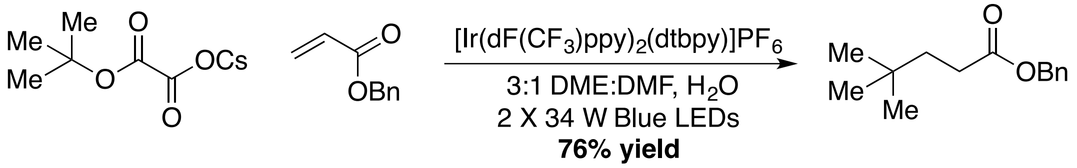


50a (1.0 equiv)

50

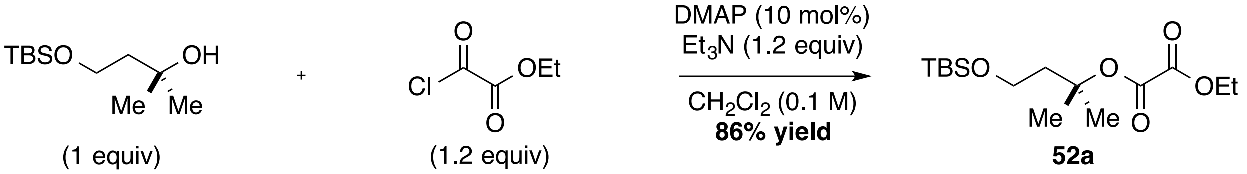
Cesium 2-(*tert*-butoxy)-2-oxoacetate (50): CsOH•H$_2$O (1.05 g, 6.24 mmol, 1.0 equiv) in water (10 mL) was added to *tert*-butyl methyl oxalate **50a** (1.00 g, 6.24 mmol, 1.0 equiv) in THF (20 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then concentrated under reduced pressure. The resulting colorless solid was dried *in vacuo* to give **50** that was used without further purification (1.73 g, 99%): IR (ATR) ν_{max} 2975, 1721, 1634, 1364, 1222, 1148, 1033 cm^{-1}; ^{1}H NMR (500 MHz, D$_2$O) δ 1.50 (s, 9H); ^{13}C NMR

(126 MHz, D_2O) δ 165.39, 164.12, 84.23, 27.04. HRMS (ESI–TOF) *m/z* calculated for $C_6H_9O_4^-$ ([M–Cs]$^-$) 145.0506; found 145.0506.

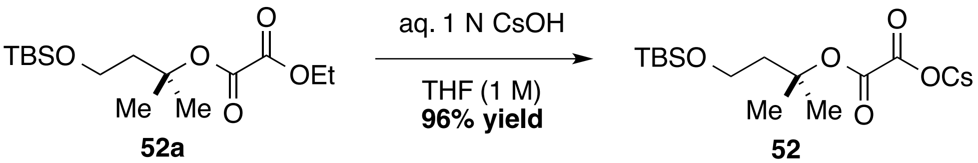


50 (1.1 equiv) (1.0 equiv) **51**

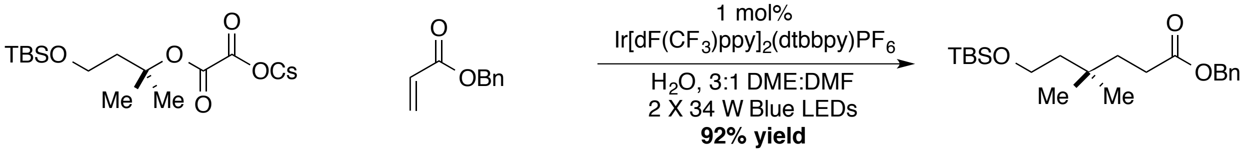
Benzyl 4,4-dimethylpentanoate (51): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with *tert*-butyl cesium oxalate **50** (153 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 μL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:EtOAc) to give **51** as a pale yellow oil (84 mg, 76%): R_f= 0.48 (19:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 3035, 2955, 2867, 1734, 1138 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 5H), 5.03 (s, 2H), 2.26 (t, *J* = 8.5 Hz, 2H), 1.50 (t, *J* = 8.5 Hz, 2H), 0.81 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.29, 136.08, 128.57, 128.25, 128.20, 66.21, 38.53, 30.14, 29.03; HRMS (ESI–TOF) *m/z* calculated for $C_{14}H_{20}NaO_2^+$ ($[M+Na]^+$) 243.1356; found 243.1355. Data match those previously reported in the literature.[14]



4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl ethyl oxalate (52a): A round-bottom flask was charged with 4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-ol (2.4 g, 11 mmol, 1.0 equiv) and DCM (110 mL, 0.1M). Triethylamine (0.35 mL, 2.4 mmol, 1.2 equiv) and DMAP (25 mg, 0.62 mmol, 0.1 equiv) were added followed by drop-wise addition of ethyl chlorooxoacetate (1.5 mL, 13 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 ºC, then quenched with sat. NH_4Cl (aq) (100 mL). The aqueous phase was extracted with DCM (100 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (9:1 hexanes:EtOAc) to give **52a** as colorless oil (3.0 g, 86% yield). R_f 0.55 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 4.32 (q, *J*=7.2, 2H), 3.76 (t, *J*=6.6, 2H), 2.11 (t, *J*=6.6, 2H), 1.58 (s, 6H), 1.36 (t, *J*=7.2, 3H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.7, 157.2, 86.5, 63.0, 59.1, 43.1, 26.4, 26.1, 18.4, 14.1; IR (thin film): 2930, 1764, 1739, 1186, 834 cm^{-1}; HRMS-ESI (*m*/*z*) $[M + H]^+$ calculated for $C_{15}H_{31}O_5Si$, 319.1941; found, 319.1933.



Cesium 2-((4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate (52): A round-bottom flask was charged with 4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl ethyl oxalate (**52a**) (1.6 g, 5.0 mmol, 1.0 equiv) followed by the addition of THF (5.0 mL, 1 M). To this solution, 1 N aq. CsOH (5.0 mL, 5.0 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **52** as a colorless solid (2.1 g, 96% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 3.65 (t, *J*=7.2, 2H), 1.94 (t, *J*=6.6, 2H), 1.37 (s, 6H), 0.86 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.4, 163.4, 79.4, 58.7, 42.6, 26.5, 25.8, 17.8, −5.3; IR (thin film): 2930, 1722, 1633, 1207, 770 cm^{-1}; HRMS-ESI (*m*/*z*) [M − Cs]$^-$ calculated for $C_{13}H_{25}O_5Si$, 289.1471; found, 289.1464.

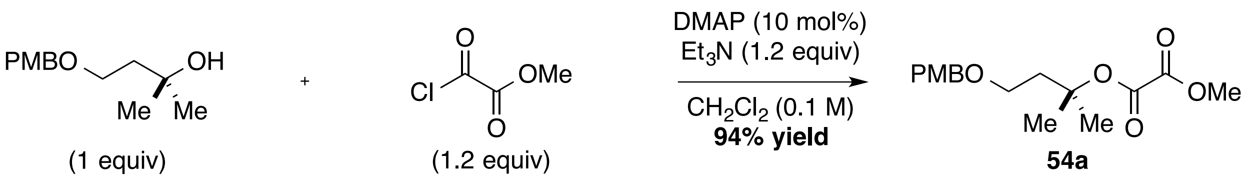


52

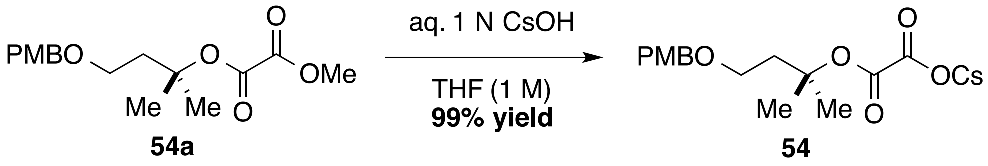
53

Benzyl 6-((*tert*-butyldimethylsilyl)oxy)-4,4-dimethylhexanoate (53): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate **(52)** (233 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et$_2$O) to give **53** as a yellow oil (167 mg,915% yield). R*f* 0.5 (9:1 hexanes:acetone); visualized with

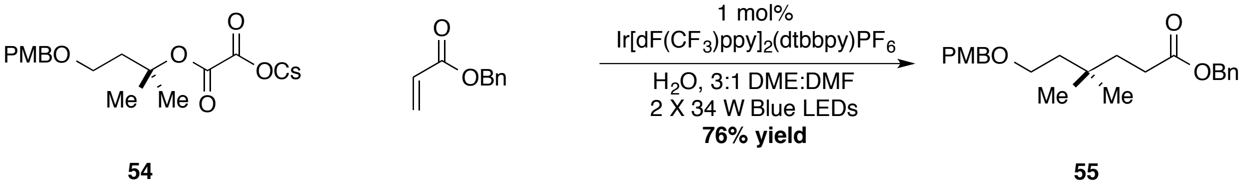
$KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.35 (m, 5H), 5.12 (s, 2H), 3.66 (t, *J*=7.5, 2H), 2.35 (t, *J*=8.5, 2H), 1.60 (t, *J*=6.0, 2H), 1.47 (t, *J*=7.0, 2H), 0.89 (s, 15H), 0.05 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.4, 136.3, 128.8, 128.5, 128.4, 66.4, 60.1, 44.1, 37.1, 32.1, 29.8, 27.3, 26.2, 18.5, −5.1; IR (thin film): 2955, 2928, 1737, 1091, 834 cm^{-1}; HRMS-CI (*m*/*z*) [M + H]$^+$ calculated for $C_{21}H_{37}O_3Si$, 365.2512; found, 365.2515.



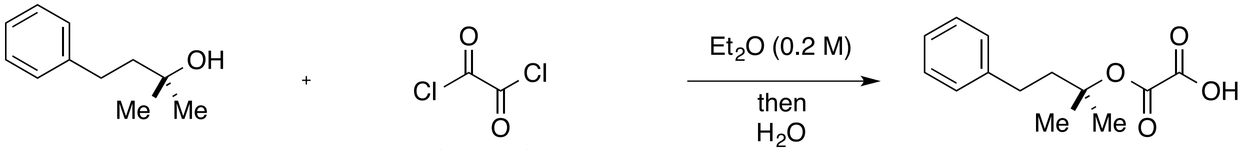
4-((4-methoxybenzyl)oxy)-2-methylbutan-2-yl methyl oxalate (54a): A round-bottom flask was charged with 4-((4-methoxybenzyl)oxy)-2-methylbutan-2-ol (1.9 g, 8.3 mmol, 1.0 equiv) and DCM (83 mL, 0.1M). Triethylamine (1.4 mL, 9.9 mmol, 1.2 equiv) and DMAP (100 mg, 0.83 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.9 mL, 9.9 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 ºC, then quenched with sat. NH_4Cl (aq) (100 mL). The aqueous phase was extracted with DCM (100 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (4:1 hexanes:Et_2O) to give **54a** as colorless oil (2.4 g, 95% yield). R$_f$ 0.4 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 (d, *J*=10.2, 2H), 6.88 (d, *J*=10.2, 2H), 4.42 (s, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 3.58 (t, *J*=7.8, 2H), 2.19 (t, *J*=7.8, 2H), 1.58 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.3, 159.1, 156.9, 130.5, 129.4, 114.0, 86.4, 72.9, 66.0, 55.5, 53.5, 39.9, 26.4; IR (thin film): 1762, 1738, 1512, 1203, 1131 cm^{-1}; HRMS-ESI (*m*/*z*) [M + Na]$^+$ calculated for $C_{16}H_{22}O_6Na$, 333.1314; found, 333.1326.



Cesium 2-((4-((4-methoxybenzyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate (54): A round-bottom flask was charged with methyl 4-((4-methoxybenzyl)oxy)-2-methylbutan-2-yl methyl oxalate (**54a**) (2.3 g, 7.4 mmol, 1.0 equiv) followed by the addition of THF (7.4 mL, 1 M). To this solution, 1 N aq. CsOH (7.4 mL, 7.4 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **54** as a colorless solid (2.7 g, 99% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.23 (d, *J*=10.2, 2H), 6.89 (d, *J*=10.2, 2H), 4.35 (s, 2H), 3.73 (s, 3H), 3.48 (t, *J*=8.4, 2H), 2.01 (t, *J*=8.4, 2H), 1.38 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.4, 163.4, 158.6, 130.5, 129.1, 113.6, 79.4, 71.6, 65.6, 55.0, 39.6, 26.4; IR (thin film): 1720, 1634, 1513, 1243, 1139 cm^{-1}; HRMS-ESI (*m*/*z*) [M − Cs]$^-$ calculated for $C_{15}H_{19}O_6$, 295.1182; found, 295.1183.

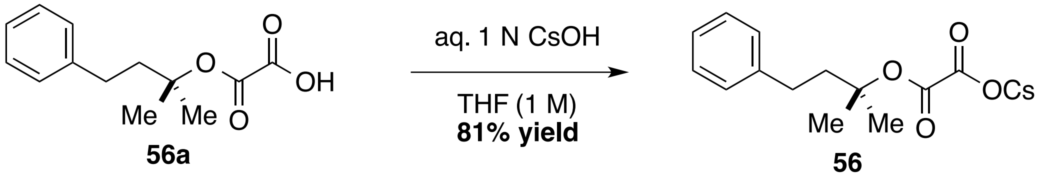


Benzyl 6-((4-methoxybenzyl)oxy)-4,4-dimethylhexanoate (55): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((4-((4-methoxybenzyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate **(54)** (236 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et_2O) to give **55** as a yellow oil (140 mg, 76% yield). R*f* 0.4 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37−7.34 (m, 5H), 7.26 (d, *J*=8.4, 2H), 6.88 (d, *J*=7.8, 2H), 5.12, (s, 2H), 4.42 (s, 2H), 3.81 (s, 3H), 3.51 (t, *J*=6.6, 2H), 2.35 (t, *J*=7.8, 2H), 1.61 (t, *J*=8.4, 2H), 1.58−1.56 (m, 2H), 0.91 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.3, 159.3, 136.2, 130.8, 129.4, 128.8, 128.4, 114.0, 72.9, 67.1, 66.4, 55.5, 40.9, 37.1, 32.1, 29.8, 27.3; IR (thin film): 2955, 1733, 1512, 1245, 1033 cm^{-1}; HRMS-CI (*m*/*z*) $[M + NH_4]^+$ calculated for $C_{23}H_{34}NO_4$, 388.2488; found, 388.2482.

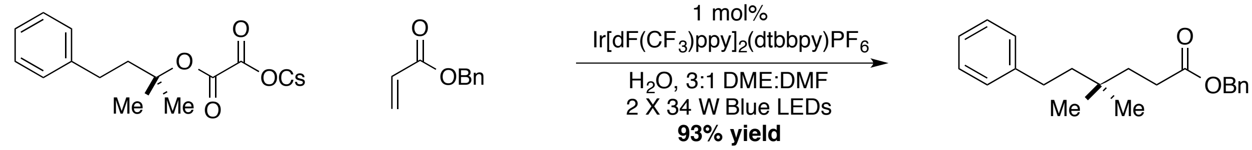


(1 equiv) (2 equiv) **99% yield** **56a**

2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid (56a): A round-bottom flask was charged with 2-methyl-4-phenylbutan-2-ol (10.4 g, 63.4 mmol 1.0 equiv) followed by the addition of Et_2O (320 mL, 0.2 M). The solution was cooled to 0 °C. Next, oxalyl chloride (11 mL, 127 mmol, 2 equiv) was added dropwise. The homogeneous reaction mixture was warmed to 23 °C and maintained at that temperature for 18 h. The reaction was cooled to 0 °C and quenched by slow addition of H_2O (200 mL). The resulting mixture was transferred to a separatory funnel with Et_2O (100 mL). The resulting biphasic mixture was extracted with Et_2O (3 x 100 mL) and the organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure to yield **56a** (14.8 g, 99%) as a brown solid. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.32−7.29 (m, 2H), 7.23−7.20 (m, 3H), 2.17 (t, *J*=5.4, 2H), 2.17 (t, *J*=4.8, 2H), 1.65 (s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 157.5, 157.1, 141.4, 128.7, 128.5, 126.3, 88.7, 42.3, 30.4, 25.9; IR (thin film): 3215, 2983, 1766, 1722, 1195 cm^{-1}; HRMS-ESI (*m*/*z*) [M - H]$^-$ calculated for $C_{13}H_{15}O_4$, 235.0970; found, 235.0962.

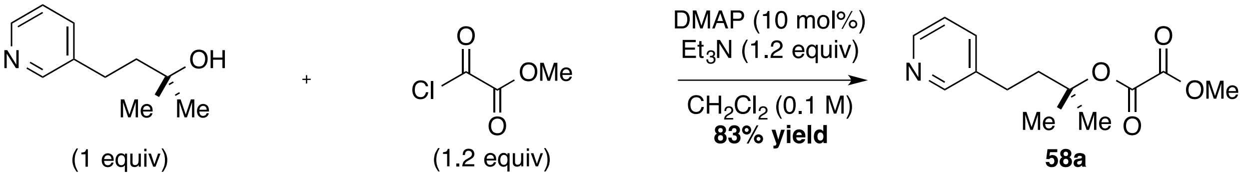


Cesium 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetate (56): A round-bottom flask was charged with 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid (**56a**) (1.8 g, 7.5 mmol, 1.0 equiv) followed by the addition of THF (7.5 mL, 1 M). To this solution, 1 N aq. CsOH (7.5 mL, 7.5 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **56** as a colorless solid (2.7 g, 99% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.28−7.25 (m, 2H), 7.19−7.15 (m, 3H), 2.58 (t, *J*=8.4, 2H), 1.99 (t, *J*=8.4, 2H), 1.41 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.5, 163.5, 142.2, 128.3, 128.2, 125.6, 79.9, 42.1, 29.5, 26.1; IR (thin film): 1717, 1635, 1369, 1198, 1120 cm^{-1}; HRMS-ESI (*m*/*z*) [M − Cs]$^-$ calculated for $C_{13}H_{15}O_4$, 235.0970; found, 235.0979.

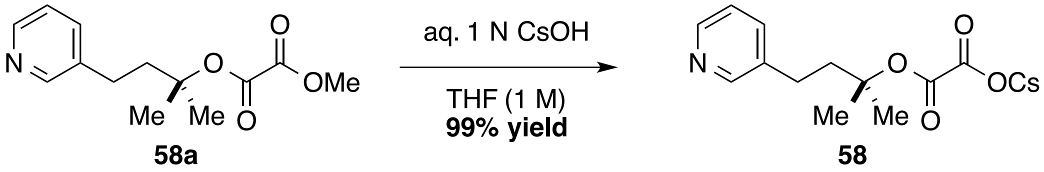


56 **57**

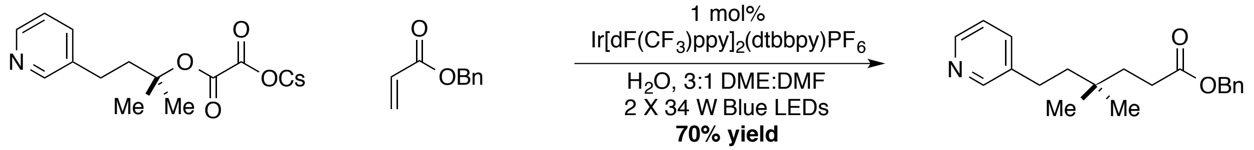
Benzyl 4,4-dimethyl-6-phenylhexanoate (57): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetate **(56)** (167 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 μL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et_2O) to give **57** as a yellow oil (113 mg, 93% yield). R*f* 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.34 (m, 5H), 7.30−7.27 (m, 2H), 7.19−7.17 (m, 3H), 5.13 (s, 2H), 2.57 (t, *J*=5.0, 2H), 2.37 (t, *J*=8.0, 2H), 1.67 (t, *J*=8.5, 2H), 1.51 (t, *J*=5.0, 2H), 0.96 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.4, 143.3, 136.2, 128.8, 128.6, 128.5, 128.46, 128.4, 125.8, 66.5, 44.2, 36.5, 32.9, 32.9, 30.8, 29.8, 26.9; IR (thin film): 2955, 1733, 1258, 1151, 656 cm^{-1}; HRMS-CI (*m*/*z*) [M + Na]$^+$ calculated for $C_{21}H_{26}O_2Na$, 333.1830; found, 333.1838.



Methyl (2-methyl-4-(pyridin-3-yl)butan-2-yl) oxalate (58a): A round-bottom flask was charged with 2-methyl-4-(pyridin-3-yl)butan-2-ol(120 mg, 0.73 mmol, 1.0 equiv) and DCM (7.5 mL, 0.1M). Triethylamine (0.12 mL, 0.88 mmol, 1.2 equiv) and DMAP (9 mg, 0.073 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.08 mL, 0.88 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 ºC, then quenched with sat. NH_4Cl (aq) (20 mL). The aqueous phase was extracted with DCM (20 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 CH_2Cl_2:MeOH) to give **58a** as colorless oil (150 mg, 83% yield). R_f 0.3 (19:1 CH_2Cl_2:MeOH); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 8.45 (s, 2H), 7.49 (br s, *J*=6.6, 1H), 7.20 (d, *J*=4.8, 1H), 3.86 (s, 3H), 2.70−2.67 (m, 2H), 2.15−2.12 (m, 2H), 1.60 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.2, 157.1, 150.3, 148.0, 137.1, 136.2, 123.8, 86.7, 53.7, 42.4, 27.7, 26.1; IR (thin film): 3406, 2954, 1764, 1740, 1201 cm^{-1}; HRMS-ESI (*m*/*z*) $[M + Na]^+$ calculated for $C_{13}H_{17}NO_4Na$, 274.1055; found, 274.1048.

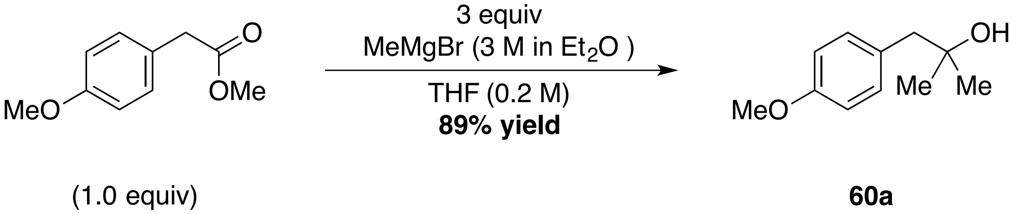


Cesium 2-((2-methyl-4-(pyridin-3-yl)butan-2-yl)oxy)-2-oxoacetate (58): A round-bottom flask was charged with methyl (2-methyl-4-(pyridin-3-yl)butan-2-yl) oxalate (**58a**) (190 mg, 0.74 mmol, 1.0 equiv) followed by the addition of THF (0.75 mL, 1 M). To this solution, 1 N aq. CsOH (0.75 mL, 0.75 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **58** as a beige solid (270 mg, 99% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 8.41 (d, *J*=1.8, 1H), 8.38 (dd, *J*=4.8, 1.2, 1H), 7.60 (d, *J*=7.8, 1H), 7.29 (dd, *J*=7.8, 4.8, 1H), 2.50 (t, *J*=1.8, 2H), 2.00 (t, *J*=4.8, 2H), 1.42 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.6, 163.4, 149.5, 147.1, 137.6, 135.6, 123.5, 79.7, 41.6, 26.6, 26.1; IR (thin film): 3430, 2974, 1739, 1721, 1189 cm^{-1}; HRMS-ESI (*m/z*) [M − Cs]$^-$ calculated for $C_{12}H_{14}NO_4$, 236.0923; found, 236.0922.

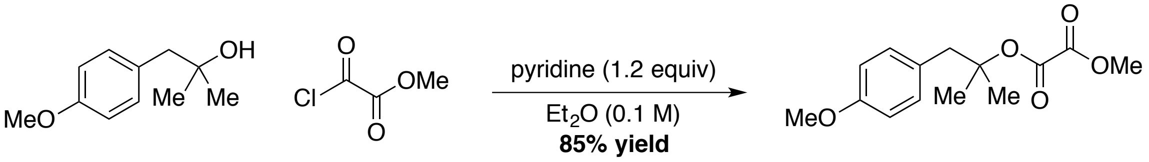


58 **59**

Benzyl 4,4-dimethyl-6-(pyridin-3-yl)hexanoate (59): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((2-methyl-4-(pyridin-3-yl)butan-2-yl)oxy)-2-oxoacetate **(58)** (120 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 μL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (1:1 hexanes:Et_2O) to give **59** as a yellow oil (76 mg, 70% yield). R*f* 0.4 (1:1 hexanes:EtOAc); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (d, *J*=5.5, 2H), 7.55 (d, *J*=7.5, 1H), 7.45−7.28 (m, 5H), 7.27 (dd, *J*=8.0, 5.0, 1H), 5.20 (s, 2H), 2.63 (t, *J*=5, 2H), 2.43 (t, *J*=8.5, 2H), 1.75 (t, *J*=6.0, 2H), 1.56 (t, *J*=8.5, 2H), 1.03, (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.2, 150.0, 147.4, 138.4, 136.1, 135.9, 128.8, 128.5, 128.4, 123.5, 66.5, 43.9, 36.4, 32.9, 29.8, 28.0, 26.8; IR (thin film): 3430, 2960, 1739, 1569, 1233, 1090 cm^{-1}; HRMS-CI (*m/z*) [M + H]$^+$ calculated for $C_{20}H_{26}NO_2$, 312.1964; found, 312.1953.

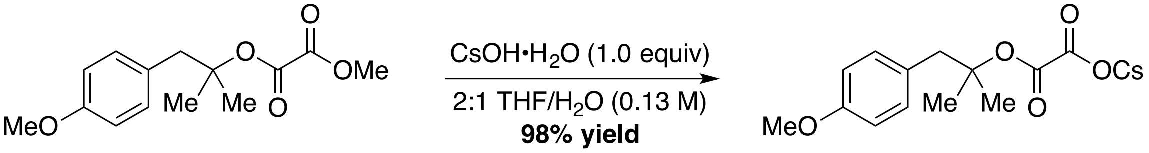


1-(4-methoxyphenyl)-2-methylpropan-2-ol (60a): A solution of methyl phenylacetate (1.75 mL, 11.09 mmol, 1.0 equiv) in THF (50 mL) was added dropwise to a 0 ºC solution of methyl magnesium bromide (3 M in Et_2O; 11.0 mL, 33.29 mmol, 3 equiv) over 20 min. After addition had completed, the resulting yellow solution was warmed to rt, stirred for 6 hours, quenched with saturated aqueous NH_4Cl solution (50 mL) and diluted with Et_2O (50 mL). The layers were separated and the aqueous phase was extracted with Et_2O (3 x 50 mL). The combined ethereal extracts were washed with brine (50 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (3:7 EtOAc:hexanes) to give **60a** as a colorless oil (1.78 g, 89%): $R_f = 0.21$ (4:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 3351, 2970, 2908, 2847, 1715, 1632, 1211, 1181, 1051 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 2.73 (s, 2H), 1.23 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.32, 131.40, 129.80, 113.62, 70.76, 55.24, 48.82, 29.08; HRMS (ESI–TOF) *m/z* calculated for $C_{11}H_{17}O_2^+$ ($[M+H]^+$) 181.1223; found 181.1224.



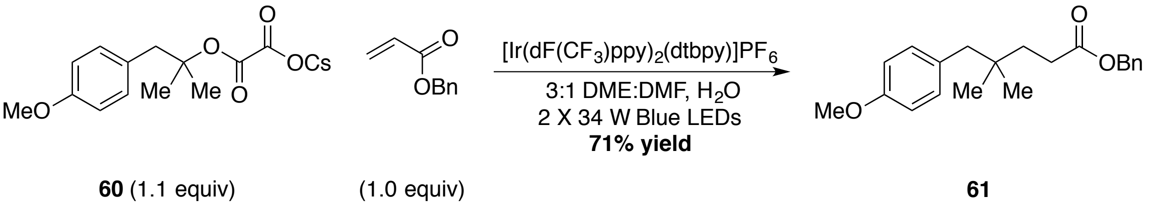
60a (1.0 equiv) (1.2 equiv) **60b**

1-(4-Methoxyphenyl)-2-methylpropan-2-yl methyl oxalate (60b): Methyl chlorooxoacetate (1.02 mL, 11.05 mmol, 1.2 equiv) was added to a solution of 1-(4-methoxyphenyl)-2-methylpropan-2-ol **60a** (1.77 g, 9.21 mmol, 1.0 equiv) and pyridine (1.11 mL, 11.05 mmol, 1.2 equiv) in Et_2O (100 mL) and the resulting yellow solution was stirred at room temperature for 4 hours. The organic phase was washed with water (2 x 50 mL) and saturated aqueous $NaHCO_3$ solution (50 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on a short column of silica gel (1:9 EtOAc:hexanes) to give **60b** as a colorless oil (2.08 g, 85%): $R_f = 0.34$ (9:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 2907, 2847, 1716, 1632, 1210, 1199, 1051 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 3.79 (s, 3H), 3.04 (s, 2H), 1.52 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.85, 158.49, 156.73, 313.58, 128.33, 113.51, 55.21, 53.33, 45.79, 25.28; HRMS (ESI–TOF) *m/z* calculated for $C_{11}H_{17}O_2^+$ ($[M+H]^+$) 267.1227, found 267.1230.

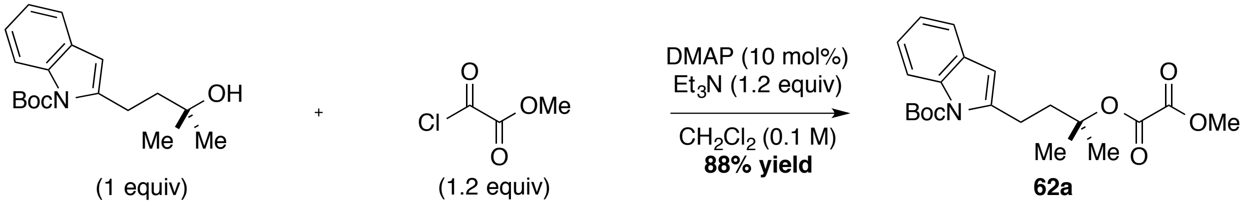


60b (1.0 equiv) **60**

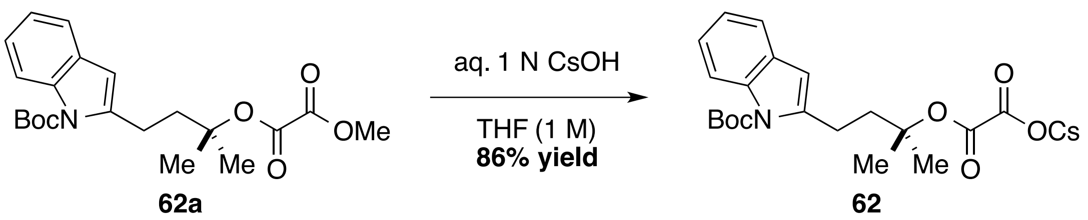
Cesium 2-((1-(4-methoxyphenyl)-2-methylpropan-2-yl)oxy)-2-oxoacetate (60): CsOH•H_2O (315 mg, 1.88 mmol, 1.0 equiv) in water (5 mL) was added to mixed oxalate **60b** (500 mg, 1.88 mmol, 1.0 equiv) in THF (10 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then concentrated under reduced pressure to give **60** as a colorless solid that was used without further purification (522 mg, 98%): IR (ATR) ν_{max} 2907, 2847, 1715, 1632, 1210, 1188, 1051 cm^{-1}; ^{1}H NMR (500 MHz, D_2O) δ 7.21 – 7.19 (m, 2H), 6.94 – 6.92 (m, 2H), 3.79 (s, 3H), 3.08 (s, 2H), 1.45 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.14, 164.27, 157.51, 131.72, 129.72, 113.59, 85.78, 55.26, 43.88, 25.10. HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{15}O_5^-$ ([M–Cs]$^-$) 251.0925; found 251.0925.



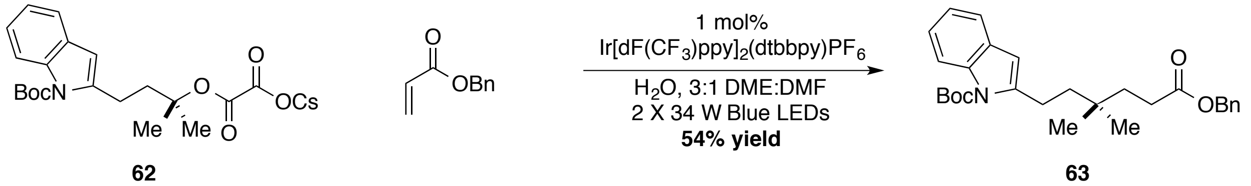
Benzyl 5-(4-methoxyphenyl)-4,4-dimethylpentanoate (61): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **60** (211 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 – 9:1 hexanes:EtOAc) to give **61** as a colorless film (116 mg, 71%): R_f = 0.67 (19:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 3005, 2970, 2954, 1736, 1510, 1368, 1230, 1216 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 5H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 5.12 (s, 2H), 3.79 (s, 3.79), 2.45 (s, 2H), 2.39 (t, *J* = 8.4 Hz, 2H), 1.60 (t, *J* = 8.4 Hz, 2H), 0.84 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.15, 157.90, 136.05, 131.43, 130.79, 128.58, 128.22, 113.16, 66.25, 55.22, 47.38, 36.50, 33.88, 29.81, 26.27; HRMS (ESI–TOF) *m/z* calculated for $C_{21}H_{27}O_3^+$ ($[M+H]^+$) 327.1955, found 327.1956.



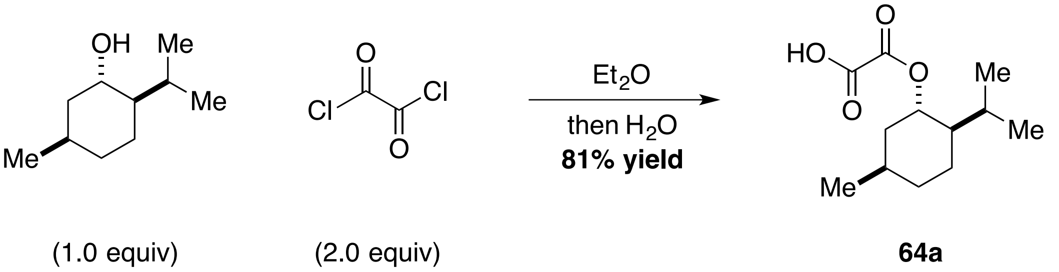
4-(1-(*tert*-butoxycarbonyl)-1*H*-indol-2-yl)-2-methylbutan-2-yl methyl oxalate (62a): A round-bottom flask was charged with *tert*-butyl 2-(3-hydroxy-3-methylbutyl)-1*H*-indole-1-carboxylate[2] (930 mg, 3.1 mmol, 1.0 equiv) and DCM (31 mL, 0.1M). Triethylamine (0.51 mL, 3.7 mmol, 1.2 equiv) and DMAP (37 mg, 0.31 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.34 mL, 3.7 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 ºC, then quenched with sat. NH_4Cl (aq) (100 mL). The aqueous phase was extracted with DCM (100 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (85:15 hexanes:Et_2O) to give **62a** as colorless oil (2.4 g, 95% yield). R_f 0.3 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (br s, 1H), 7.54 (d, *J*=7.5, 1H), 7.38 (br s, 1H), 7.32 (t, *J*=7.5, 1H), 7.25 (d, *J*=7.5, 1H), 3.89 (s, 3H), 2.28 (t, *J*=8.5, 2H), 2.25 (t, *J*=8.5, 2H), 1.68−1.66 (app d, 15H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.1, 156.9, 150.0, 135.8, 130.6, 124.6, 122.6, 122.4, 120.4, 119.1, 115.5, 86.9, 83.6, 53.5, 40.4, 28.4, 25.8, 19.5; IR (thin film): 1754, 1733, 1721, 1451, 1117 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calculated for $C_{21}H_{27}NO_6Na$, 412.1736; found, 412.1748.



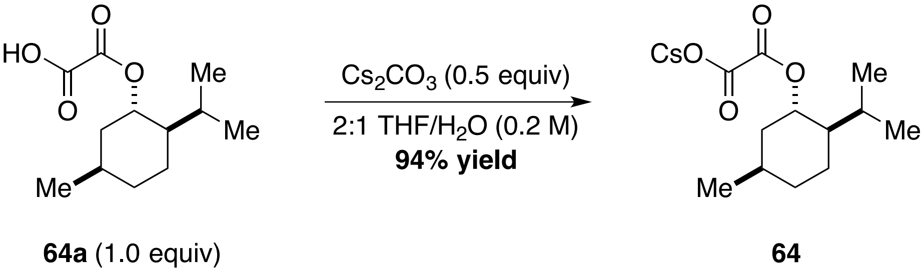
Cesium 2-((4-(1-(*tert*-butoxycarbonyl)-1*H*-indol-2-yl)-2-methylbutan-2-yl)oxy)-2-oxoacetate (62): A round-bottom flask was charged with 4-(1-(*tert*-butoxycarbonyl)-1*H*-indol-2-yl)-2-methylbutan-2-yl methyl oxalate (**62a**) (1.0 g, 2.6 mmol, 1.0 equiv) followed by the addition of THF (2.6 mL, 1 M). To this solution, 1 N aq. CsOH (2.6 mL, 2.6 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **62** as a colorless solid (1.1 g, 86% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 8.04 (d, *J*=9.6, 1H), 7.60 (d, *J*=9.0, 1H), 7.41 (s, 1H), 7.31 (t, *J*=9.0, 1H), 7.24 (t, *J*=9.0, 1H), 2.67 (t, *J*=10.2, 2H), 2.09 (t, *J*=10.8, 2H), 1.61 (s, 9H), 1.45 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.7, 163.5, 149.1, 134.9, 130.2, 124.3, 122.4, 122.0, 120.9, 119.4, 114.7, 83.4, 79.8, 39.4, 27.7, 26.1, 18.7; IR (thin film): 2986, 1754, 1722, 1206, 1152, 748 cm^{-1}; HRMS-ESI (*m*/*z*) [M − Cs]$^-$ calculated for $C_{20}H_{24}NO_6$, 374.1604; found, 374.1608.



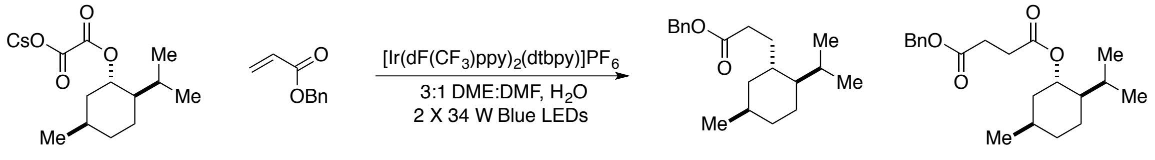
***tert*-butyl 2-(6-(benzyloxy)-3,3-dimethyl-6-oxohexyl)-1*H*-indole-1-carboxylate (63):** An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((4-(1-(*tert*-butoxycarbonyl)-1*H*-indol-2-yl)-2-methylbutan-2-yl)oxy)-2-oxoacetate **(62)** (195 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et_2O) to give **62** as a yellow oil (85 mg, 54% yield). R*f* 0.2 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (br s, 1H), 7.50 (d, *J*=8.0, 1H), 7.38−7.30 (m, 7H), 7.25−7.23 (m, 1H), 5.13, (s, 2H), 2.64 (t, *J*=8.5, 2H), 2.38 (t, *J*=8.0, 2H), 1.71 (t, *J*=8.5, 2H), 1.68 (s, 9H), 1.61 (t, *J*=9.0, 2H), 1.00 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.3, 150.0, 136.2, 130.8, 128.8, 128.6, 128.5, 128.4, 124.4, 122.5, 122.1, 121.8, 119.0, 115.5, 83.4, 66.5, 41.4, 36.5, 32.8, 29.8, 28.5, 26.8, 19.7; IR (thin film): 2955, 1727, 1452, 1368, 1153 cm^{-1}; HRMS-CI (*m*/*z*) $[M - Boc + H]^+$ calculated for $C_{23}H_{28}NO_2$, 350.2120; found, 350.2129.



Isomenthol-derived alkyl hydrogen oxalate (64a): (+)-Isomenthol (2.0 g, 12.80 mmol, 1.0 equiv) in Et_2O (100 mL) was added dropwise over 20 min. to a 0 ºC solution of oxalyl chloride (2.17 mL, 25.60 mmol, 2.0 equiv) in Et_2O. The resulting pale yellow solution was stirred at 0 ºC for 2 hours then concentrated under reduced pressure. Unreacted oxalyl chloride was removed *in* *vacuo* and the resulting yellow oil was redissolved in Et_2O (50 mL) and carefully treated with water (50 mL). The biphasic reaction mixture was stirred vigorously for 1 hour and the layers were separated. The aqueous phase was extracted with $E_{t2}O$ (3 x 50 mL) and the combined ethereal extracts were washed with water (2 x 100 mL) and brine (100 mL), dried over $MgSO_4$ and concentrated to give **64a** as a colorless oil that was used without further purification (2.36 g, 81%): IR (ATR) ν_{max} 2956, 2872, 1751, 1732, 1185, 1138 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (br. s, 1H), 5.23 – 5.19 (m, 1H), 1.99 – 1.93 (m, 1H), 1.80 – 1.71 (m, 2H), 1.68 – 1.62 (m, 1H), 1.60 – 1.45 (m, 4H), 1.30 – 1.21 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.99, 157.77, 77.25, 45.43, 35.34, 29.65, 27.44, 26.24, 20.78, 20.57, 20.31, 18.86; HRMS (ESI–TOF) *m/z* calculated for $C_{12}H_{21}O_4^+$ ($[M+H]^+$) 229.1434; found 229.1435.

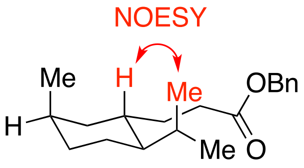


Isomenthol-derived cesium oxalate (64): Cs_2CO_3 (928 mg, 2.85 mmol, 0.5 equiv) in water (5 mL) was added dropwise to acid **64a** (1.30 g, 5.69 mmol, 1 equiv) in THF (10 mL). The resulting solution was stirred for 10 min then concentrated under reduced pressure to give **64** as a white powder that was washed with toluene (2 x 5 mL) and dried *in vacuo* (1.93 g, 94%): IR (ATR) ν_{max} 2958, 2932, 2869, 1716, 1223, 1644, 1368, 1383, 1198 cm^{-1}; ^1H NMR (500 MHz, D_2O) δ 7.55 – 7.51 (m, 1H), 4.42 (br. s, 1H), 4.23 (dp, *J* = 13.4, 6.8 Hz, 1H), 4.15 – 1.03 (m, 3H), 3.98 – 3.89 (m, 3H), 3.82 – 3.76 (m, 1H), 3.41 (d, *J* = 6.8 Hz, 3H), 3.38 (d, *J* = 6.8 Hz, 3H), 3.29 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, D_2O) δ 164.60, 74.89, 45.72, 35.47, 29.46, 27.32, 25.92, 19.99, 19.78, 19.01, 17.67. HRMS (ESI–TOF) *m/z* calculated for $C_{12}H_{19}O_4^-$ ([M–Cs]$^-$) 227.1289; found 227.1291.

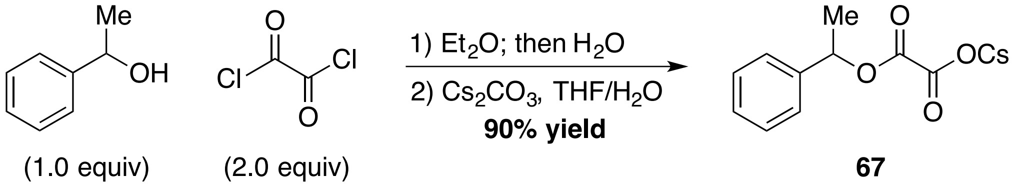


64 (1.1 equiv) (1.0 equiv) **65 (51% yield)** **66 (29% yield)**

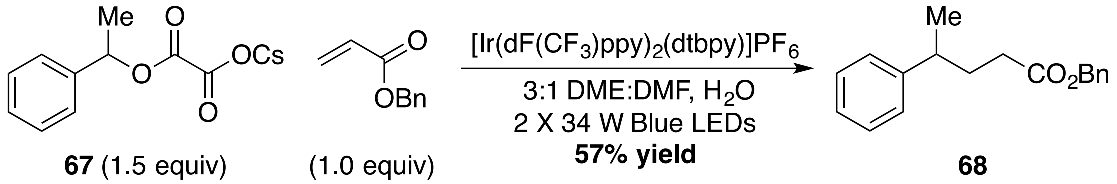
Isomenthol-derived Michael adduct (65): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **64** (270 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:EtOAc) to give **65** and **66**, both obtained as pale yellow oils. Eluted first was **65** (79 mg, 51%): R_f = 0.35 (24:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 2953, 2925, 2869, 1735, 1455, 1161 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 5.12 (s, 2H), 2.40 – 2.28 (m, 2H), 1.90 – 1.78 (m, 2H), 1.75 – 1.70 (m, 1H), 1.66 – 1.61 (m, 2H), 1.44 – 1.40 (m, 3H), 1.35 – 1.19 (m, 3H), 0.95 – 0.90 (m, 1H), 0.86 (d, *J* = 6.8 Hz, 6H), 0.82 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.14, 136.22, 128.66, 128.36, 128.29, 66.23, 45.52, 35.74, 33.68, 32.32, 30.91, 28.35, 27.14, 26.62, 21.67, 20.95, 20.75, 18.78; HRMS (ESI–TOF) *m/z* calculated for $C_{21}H_{33}O_2^+$ ($[M+H]^+$) 317.2475; found 317.2475. Product stereochemistry was confirmed by NOESY correlation:



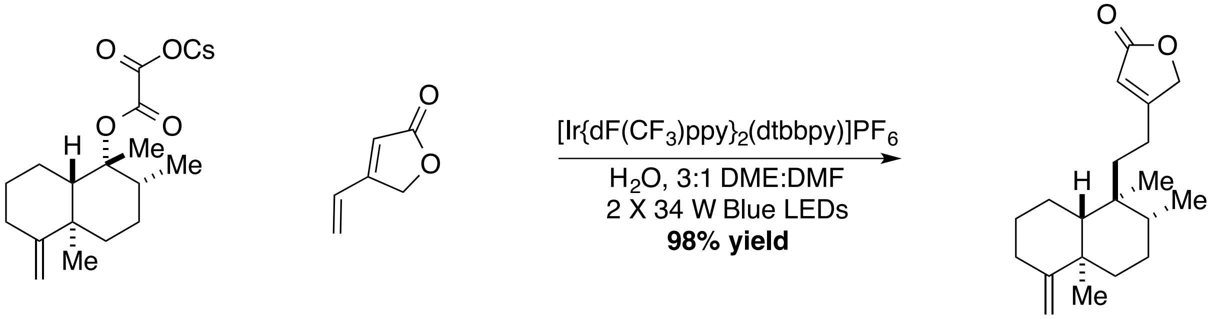
Eluted second was the **isomenthol alkoxylcarbonyl radical adduct (66)** (50 mg, 29%): R_f = 0.30 (24:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 2955, 2927, 2871, 1730, 1212, 1154, 1140 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 5H), 5.15 (s, 2H), 5.09 – 5.06 (m, 1H), 2.72 – 2.69 (m, 2H), 2.68 – 2.65 (m, 2H), 1.91 – 1.85 (m, 1H), 1.78 – 1.71 (m, 1H), 1.61 – 1.55 (m, 2H), 1.52 – 1.56 (m, 3H), 1.35 – 1.26 (m, 2H), 0.94 (app. t, *J* = 7.4 Hz, 6H), 0.86 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.20, 171.56, 135.79, 128.57, 128.27, 128.22, 72.23, 66.52, 45.59, 35.67, 29.89, 29.58, 29.33, 27.52, 26.25, 20.90, 20.82, 20.56, 19.08. HRMS (ESI–TOF) *m/z* calculated for $C_{21}H_{31}O_4^+$ ($[M+H]_+$) 347.2217; found 347.2213.



Cesium 2-oxo-2-(1-phenylethoxy)acetate (67): 1-phenylethanol (7.9 mL, 65.5 mmol, 1.0 equiv) in Et_2O (100 mL) was added dropwise over 20 min to a 0 ºC solution of oxalyl chloride (11.08 mL, 131 mmol, 2.0 equiv) in Et_2O (300 mL). The resulting pale yellow solution was stirred at 0 ºC for 2 hours then concentrated under reduced pressure. Unreacted oxalyl chloride was removed *in vacuo* and the resulting yellow oil was redissolved in Et_2O (100 mL) and carefully treated with water (100 mL). The biphasic reaction mixture was stirred vigorously for 1 hour and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 100 mL) and the combined ethereal extracts were washed with water (2 x 100 mL) and brine (100 mL), dried over $MgSO_4$ and concentrated to give the crude acid as a colorless oil that was redissolved in THF (200 mL). Cs_2CO_3 (10.67 g, 32.75 mmol, 0.5 equiv) in water (50 mL) was added dropwise and the resulting solution was stirred for 10 min then concentrated under reduced pressure. The resulting white solid was triturated with toluene (3 x 50 mL) to give **67** as a white powder that was dried *in vacuo* but not purified further (19.36 g, 90%): IR (ATR) ν_{max} 3035, 2992, 1719, 1634, 1602, 1371, 1192, 1050 cm^{-1}; ^{1}H NMR (500 MHz, D_2O) δ 1.47 – 1.37 (m, 5H), 5.90 – 5.86 (m, 1 H), 1.60 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, D_2O) δ 173.47, 163.85, 141.07, 128.84, 128.33, 125.89, 75.11, 21.33. HRMS (ESI–TOF) *m/z* calculated for $C_{10}H_9O_4^-$ ([M–Cs]$^-$) 193.0506; found 193.0506.



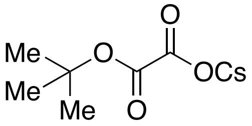
Benzyl 4-phenylpentanoate (68): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **67** (244 mg, 0.75 mmol, 1.5 equiv) and $Ir[dF(CF_3)ppy)]_2(dtbpy)PF_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 μL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:EtOAc) to give **68** as a pale yellow oil (89 mg, 57%): R_f = 0.61 (24:1 hexanes:EtOAc, stained with $KMnO_4$); IR (ATR) ν_{max} 3029, 2960, 1735, 1454, 1157 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 7H), 7.20 – 7.14 (m, 3H), 5.09 (d, *J* = 12.4, 1H), 5.05 (d, *J* = 12.4 Hz, 1H), 2.75 – 2.67 (1H, m), 2.30 – 2.19 (m, 2H), 2.00 – 1.87 (m, 2H), 1.26 (d, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.49, 146.18, 136.02, 128.55, 128.46, 128.22, 128.20, 127.03, 126.21, 66.14, 39.41, 33.17, 32.55, 22.17; HRMS (ESI–TOF) *m/z* calculated for $C_{18}H_{21}O_2^+$ ($[M+H]^+$) 269.1536; found 269.1537.



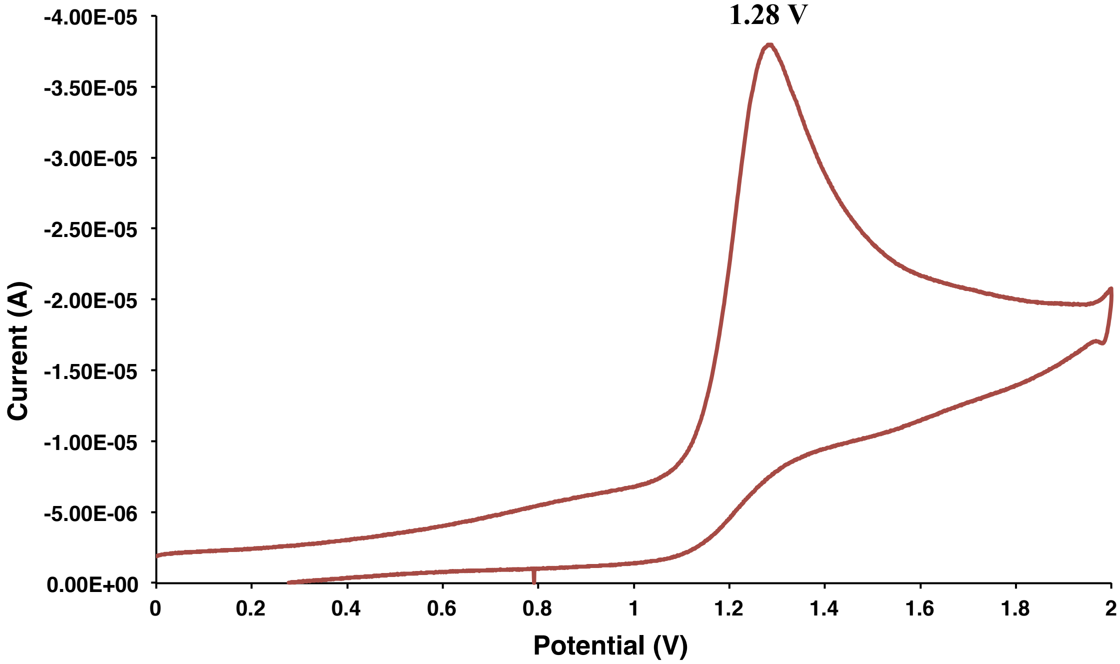
44 **70**

4-(2-((1*S*,2*R*,4*R*,8*R*)-1,2,4a-trimethyl-5-methylenedecahydronaphthalen-1-yl)ethyl)furan-2(5*H*)-one (70): An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-oxo-2-(((1*R*,2*R*,4*R*,8*S*)-1,2,4a-trimethyl-5-methylenedecahydronaphthalen-1-yl)oxy)acetate **(44)** (159 mg, 0.45 mmol, 1.5 equiv) and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (3.4 mg, 0.003 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (6.0 mL, 0.05 M) was added, followed by water (54 μL, 3.0 mmol, 10 equiv) and vinyl butenolide[5] (33 mg, 0.30 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et_2O) to give **70** as a yellow oil (89 mg, 98% yield). R*f* 0.3 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. R*f* 0.3 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.83 (s, 1H), 4.73 (s, 2H), 4.53 (s, 2H), 2.28 (qd, *J*=16.8, 7.2, 2H), 2.16−2.10 (m, 2H), 1.95−1.89 (m, 1H), 1.65−1.58 (m, 2H), 1.55−1.48 (m, 5H), 1.45−1.39 (m, 1H), 1.31−1.20 (m, 3H), 1.07 (s, 3H), 0.83 (d, *J*=7.8, 3H), 0.80 (s, 3H). Spectral data match those previously reported.[10]

Cyclic Voltammetry Data for *tert*-Butyl Cesium Oxalate:



50



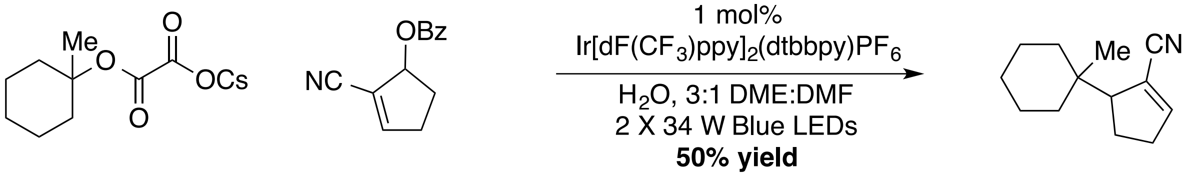
Instrument Model	CHI600E
Init E (V)	0
High E (V)	2
Low E (V)	0
Final E (V)	0
Init P/N	P
Scan Rate (V/s)	0.1
Segment	2
Sample Interval (V)	0.001
Quiet Time (sec)	2
Sensitivity (A/V)	0.001 A/V
Ep	1.282 V
Eh	1.202 V
ip	$-2.789e^{-5}$ A
Ah	$-2.398e^{-5}$ C

Effects of Counterions on the Efficiency of Coupling of Methyl Cyclohexyl Oxalate Salts with Benzyl Acrylate:

Counterion	Trial 1	Trial 2
Li	93% yield	92% yield
Na	86% yield	88% yield
K	90% yield	95% yield
Cs	97% yield	92% yield

Yield based on 1H NMR analysis of crude reaction mixture with 1,2-dibromo-4,5-(methylenedioxy)benzene as internal standard

Experimental Evidence for the Radical−Polar Crossover Mechanism:



9

5-(1-methylcyclohexyl)cyclopent-1-ene-1-carbonitrile: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate **(9)** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv) and 2-cyanocyclopent-2-en-1-yl benzoate[15] (107 mg, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 40 ºC because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et_2O) to give 5-(1-methylcyclohexyl)cyclopent-1-ene-1-carbonitrile as a yellow oil (47 mg, 50% yield). R*f* 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$. Spectral data match those previously reported.[15]

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11. Utilizing DFT calculations, the distance between hydrogen atoms on the 17*α*-methyl and the angular 18-methyl (steroid numbering) was found to be 4.3 Å. As a result, no NOE signal would be observed. In contrast, the distance between hydrogen atoms on the 17*β*-methyl and the angular 18-methyl was found to be 1.7 Å, leading to the observed NOE signal.

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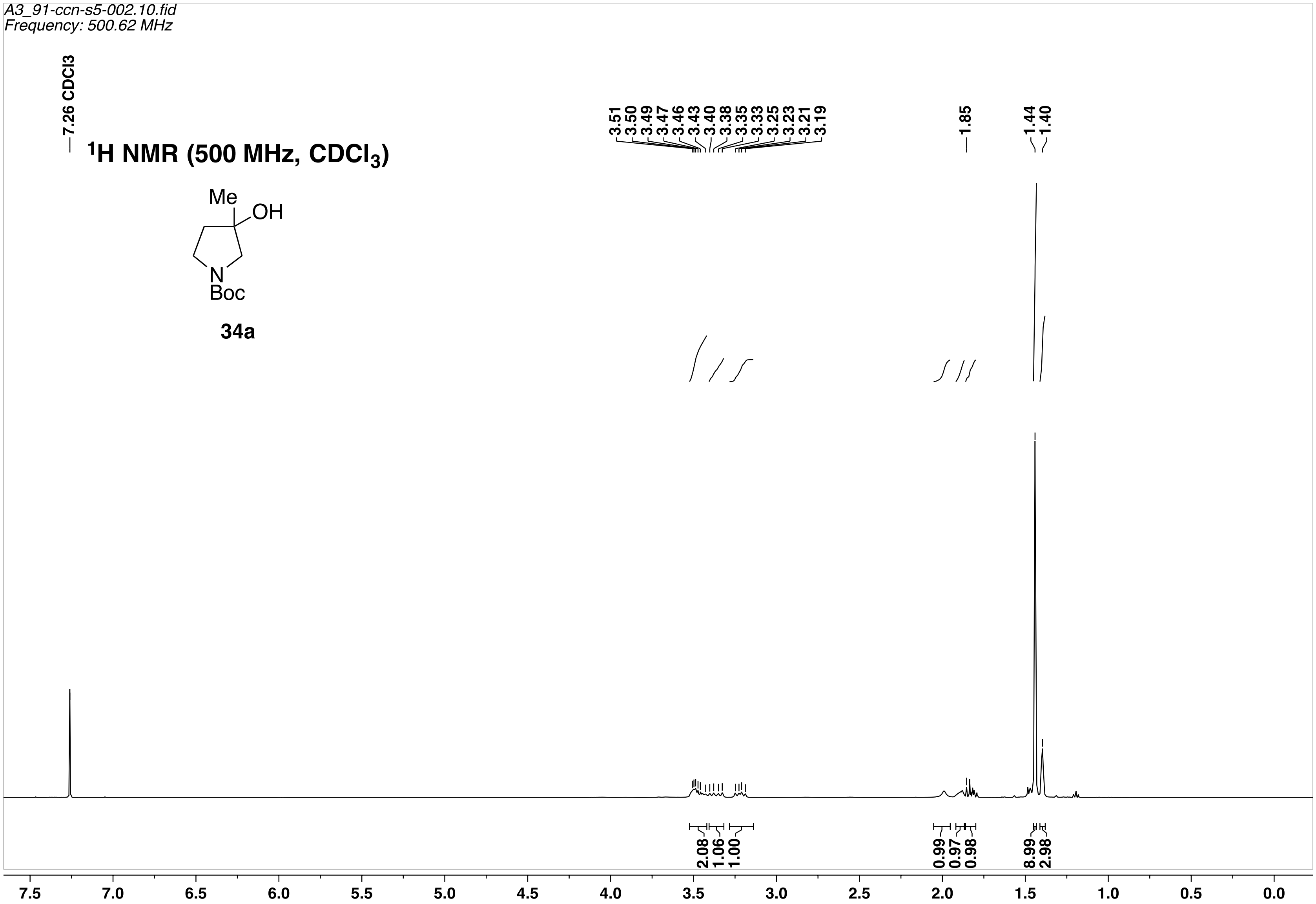
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¹H NMR (500 MHz, CDCl₃)
Me
OH
N
Boc
34a
3.51
3.50
3.49
3.47
3.46
3.43
3.40
3.38
3.35
3.33
3.25
3.23
3.21
3.19
1.85
1.44
1.40
2.08
1.06
1.00
0.99
0.97
0.98
8.99
2.98
7.5
7.0
6.5
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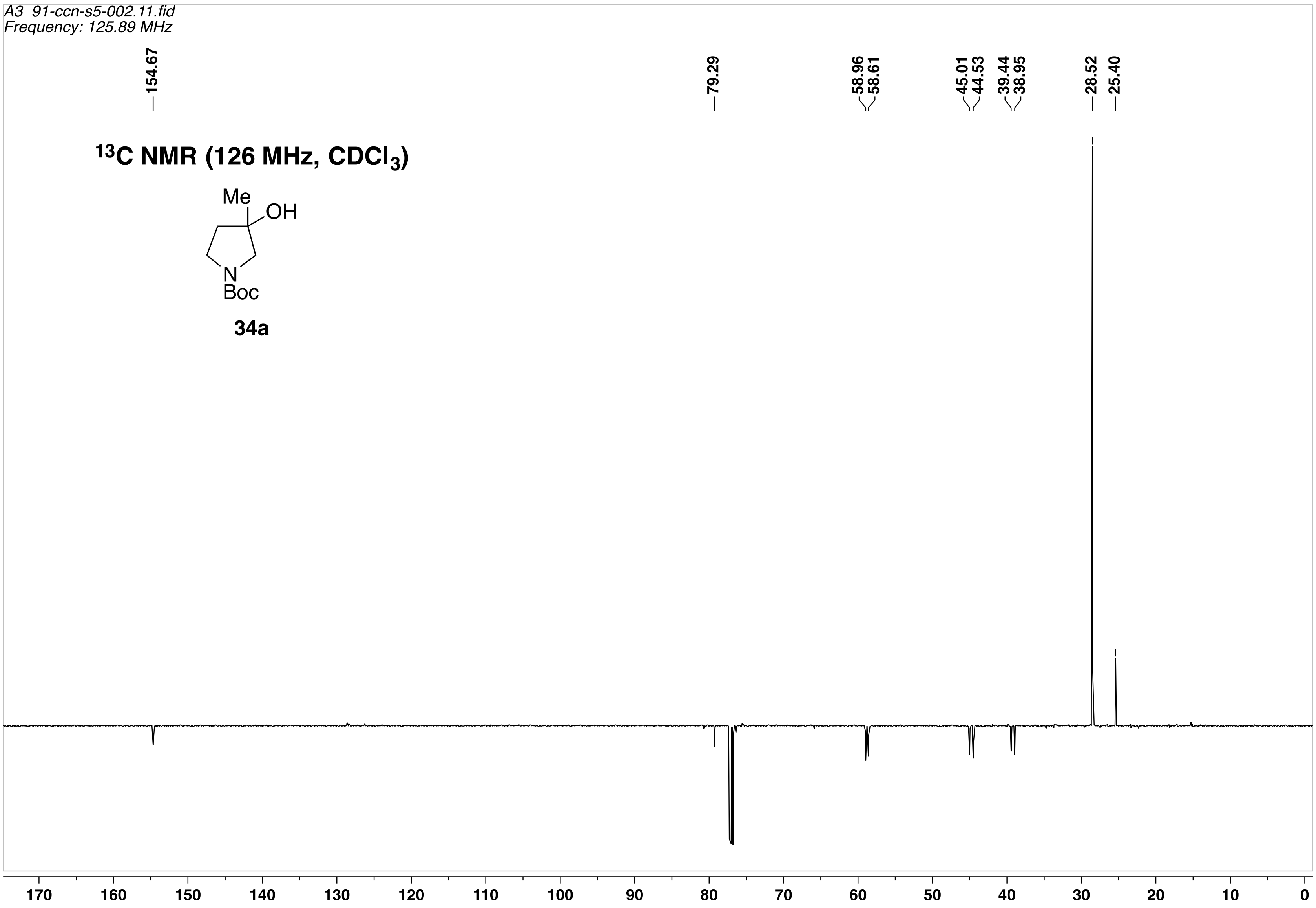
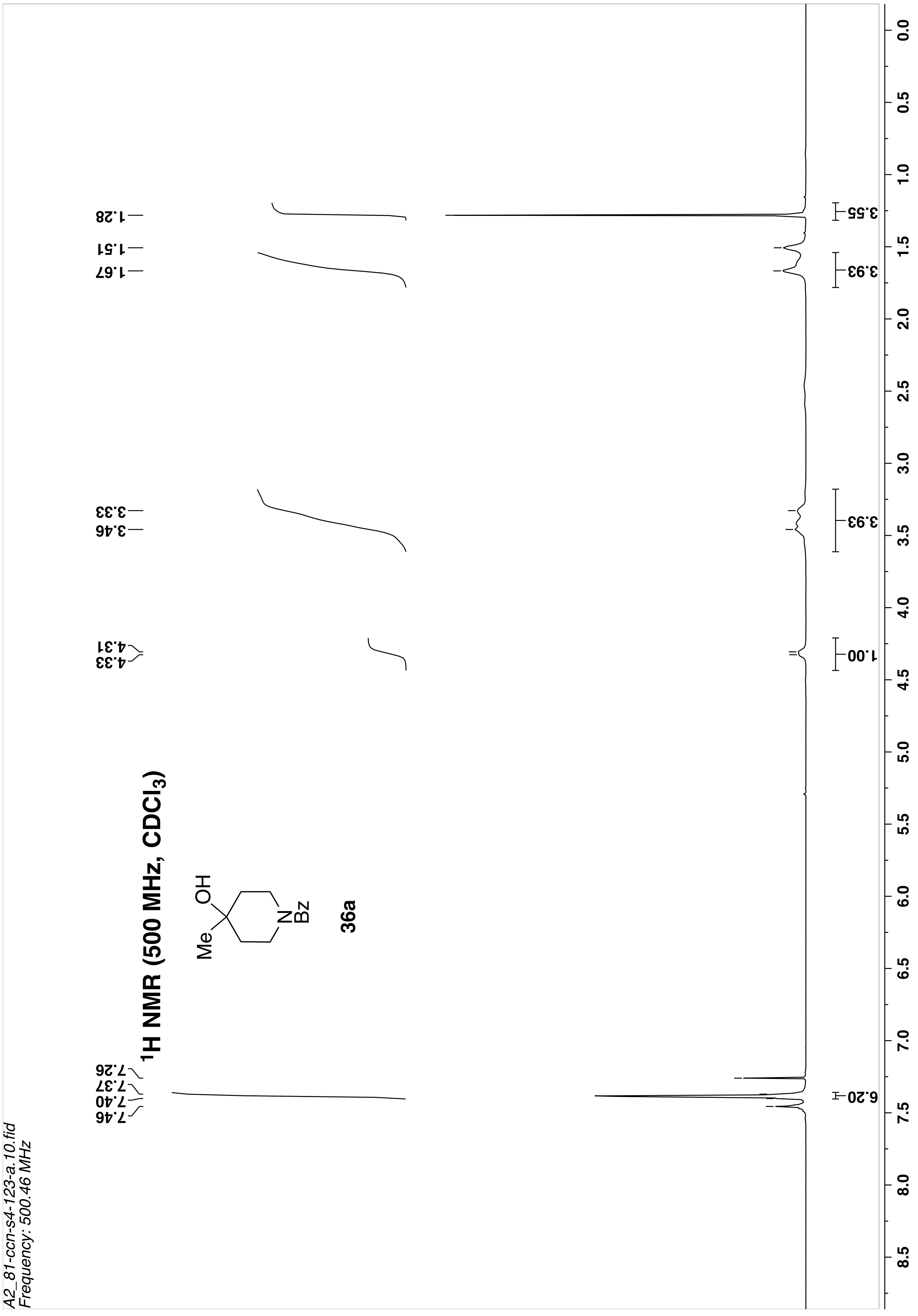
0.0



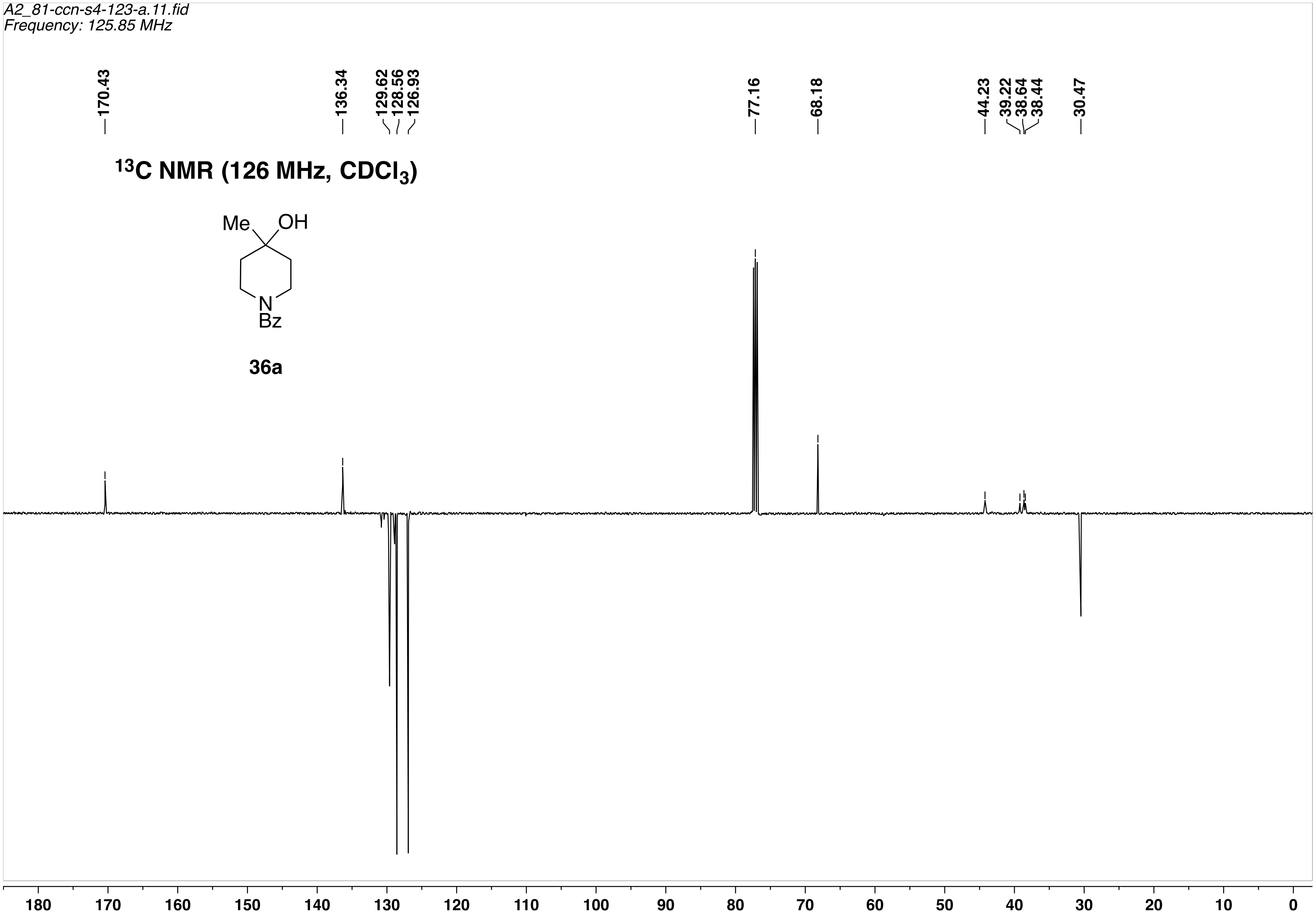
^{13}C NMR (126 MHz, $CDCl_3$)

34a



^{1}H NMR (500 MHz, $CDCl_3$)

36a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68.18
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38.44
30.47
13C NMR (126 MHz, CDCl3)
Me
OH
N
Bz
36a
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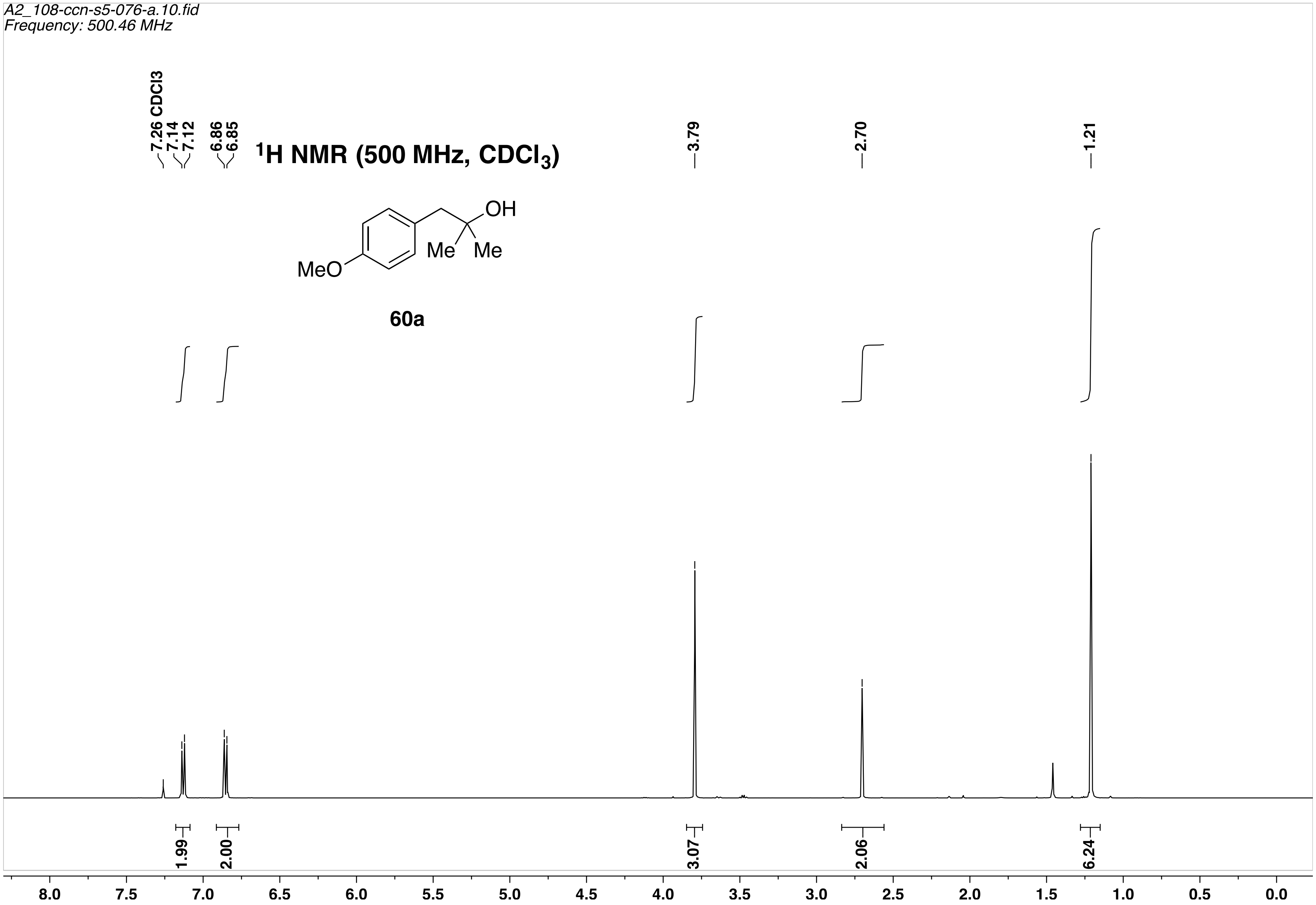
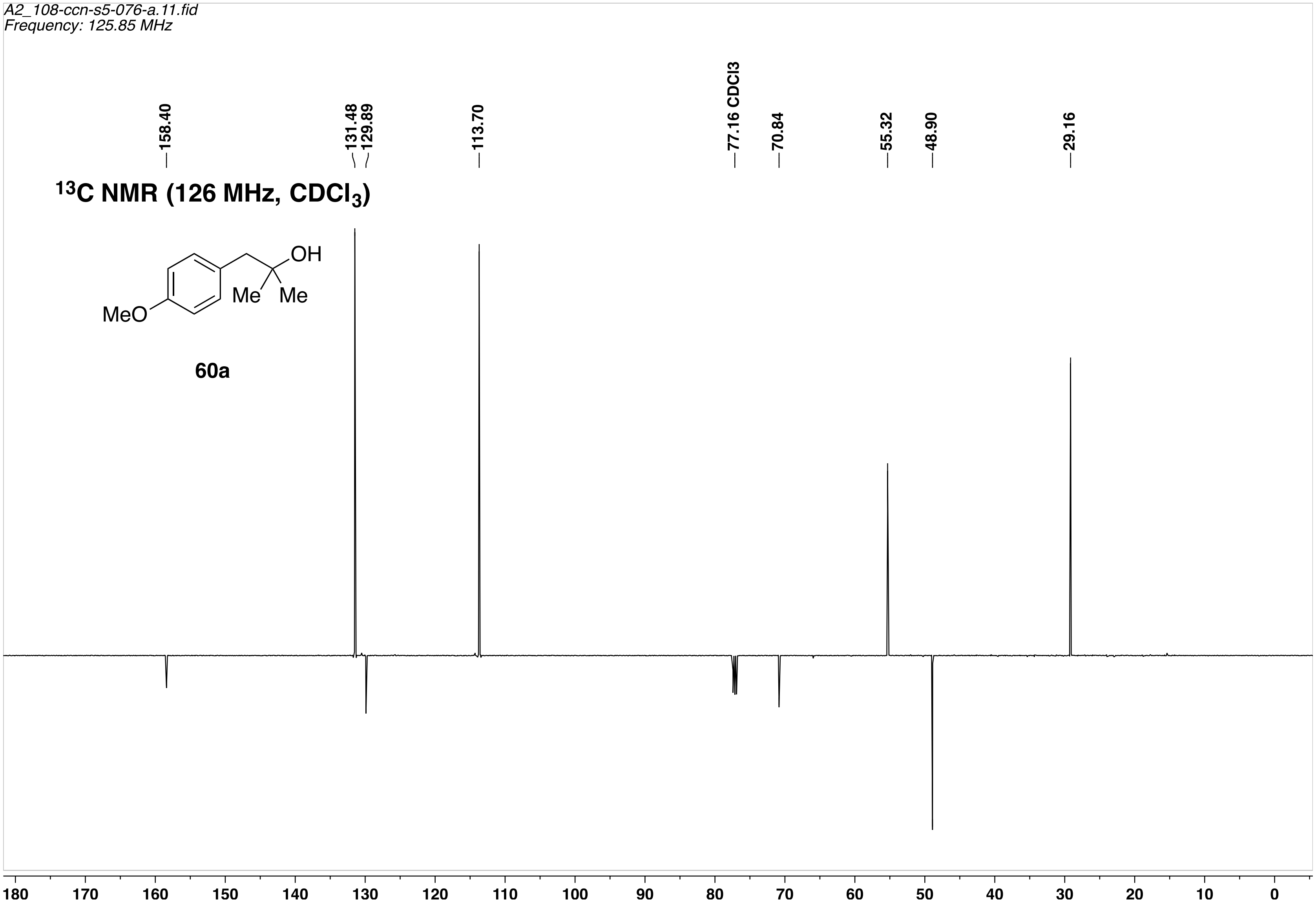
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



^{1}H NMR (500 MHz, CDCl$_3$)

60a


A2_108-ccn-s5-076-a.11.fid
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MeO
OH
Me
Me
60a
158.40
131.48
129.89
113.70
77.16 CDCl3
70.84
55.32
48.90
29.16
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40
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20
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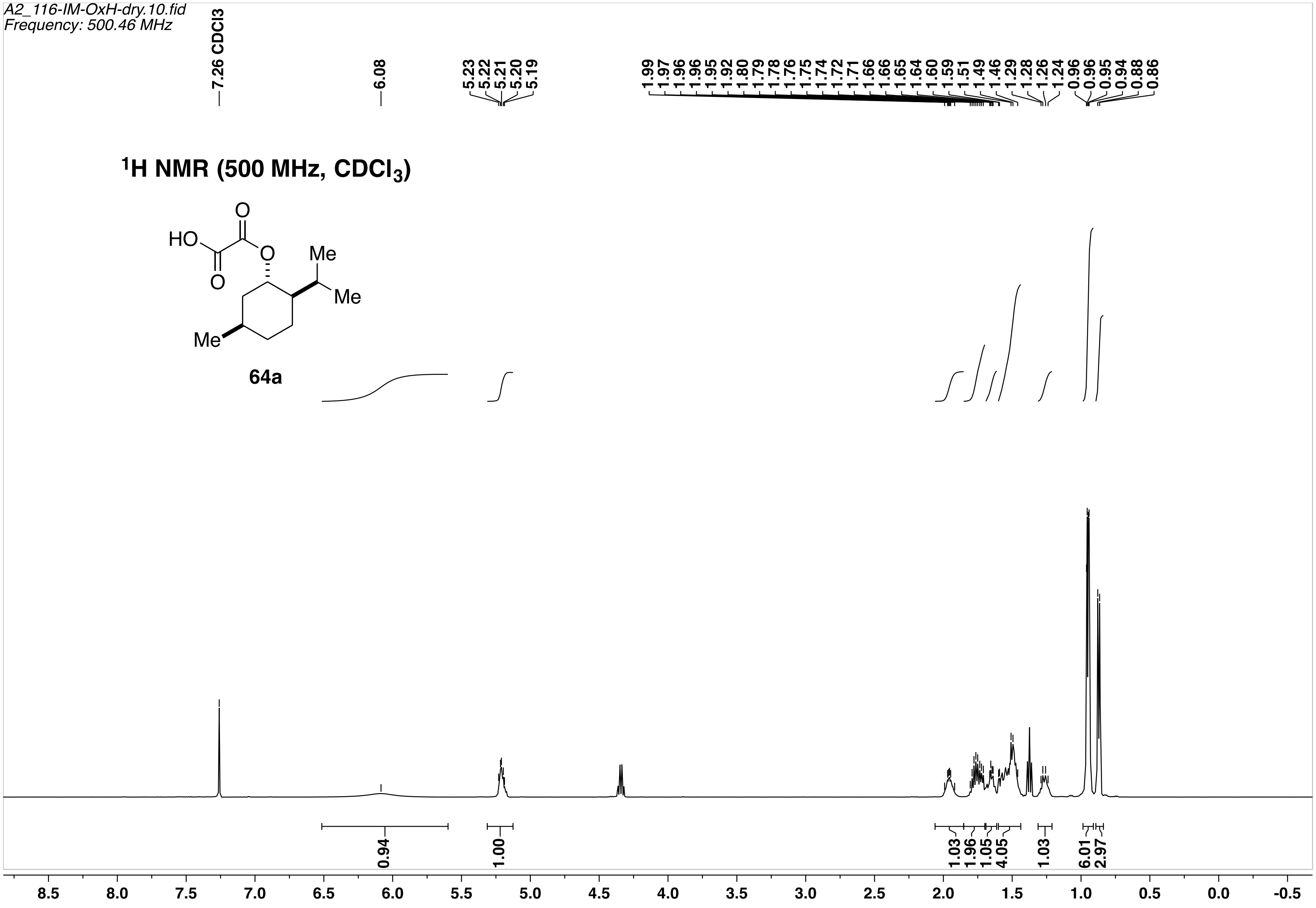
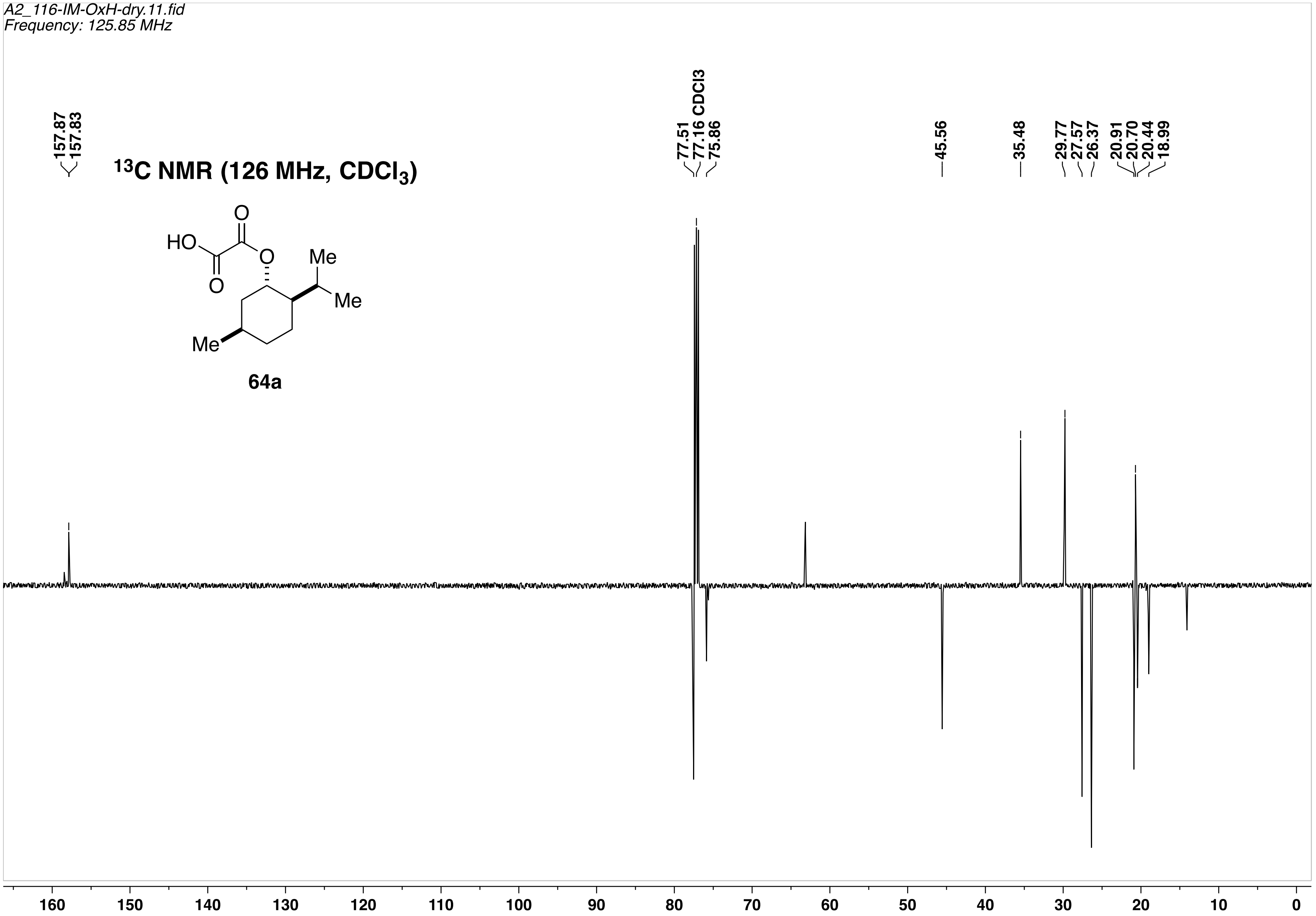


^{1}H NMR (500 MHz, CDCl$_3$)

64a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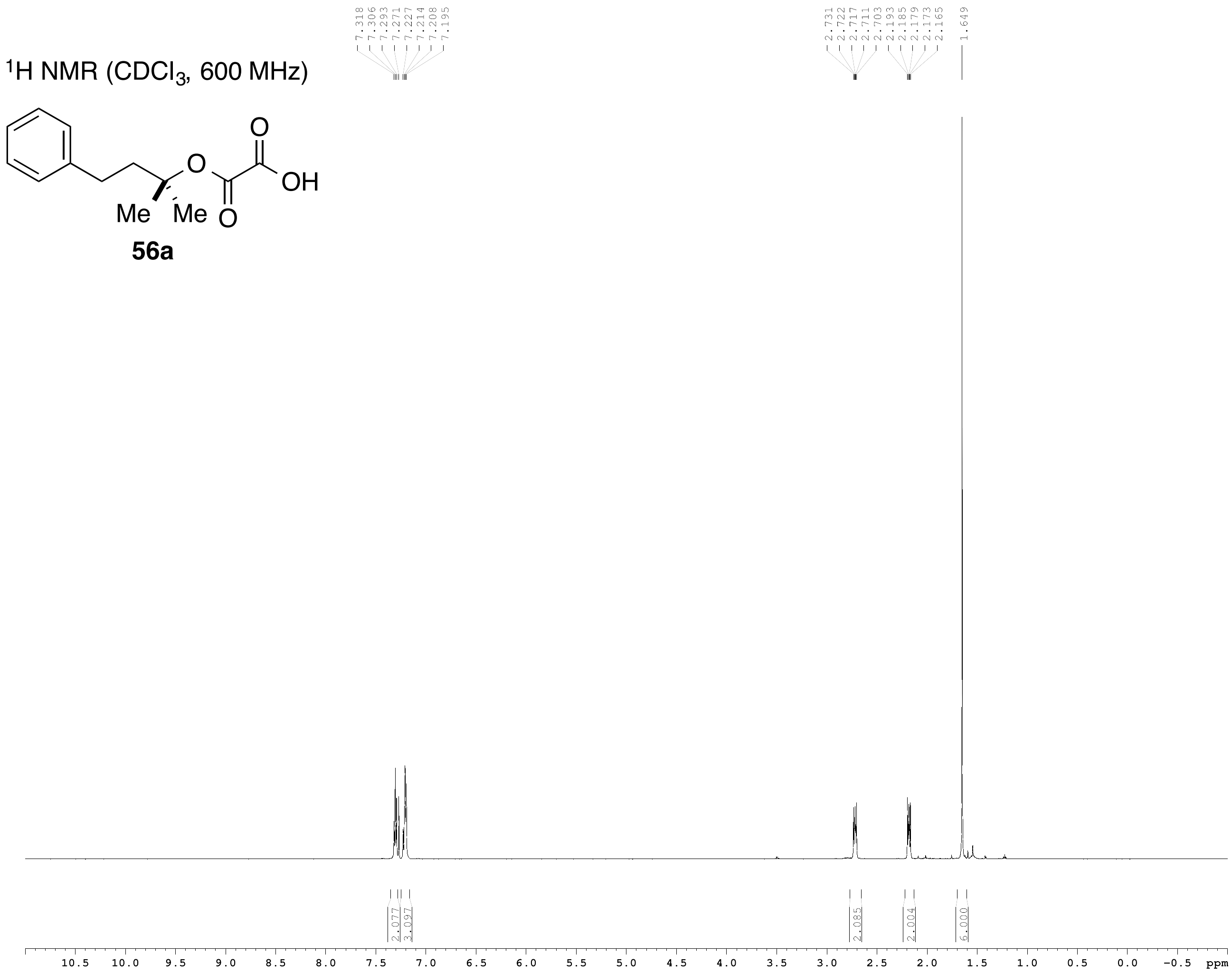
O
O
O
Me
Me
Me
64a
77.51
77.16 CDCl3
75.86
45.56
35.48
29.77
27.57
26.37
20.91
20.70
20.44
18.99
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

YS-II-149

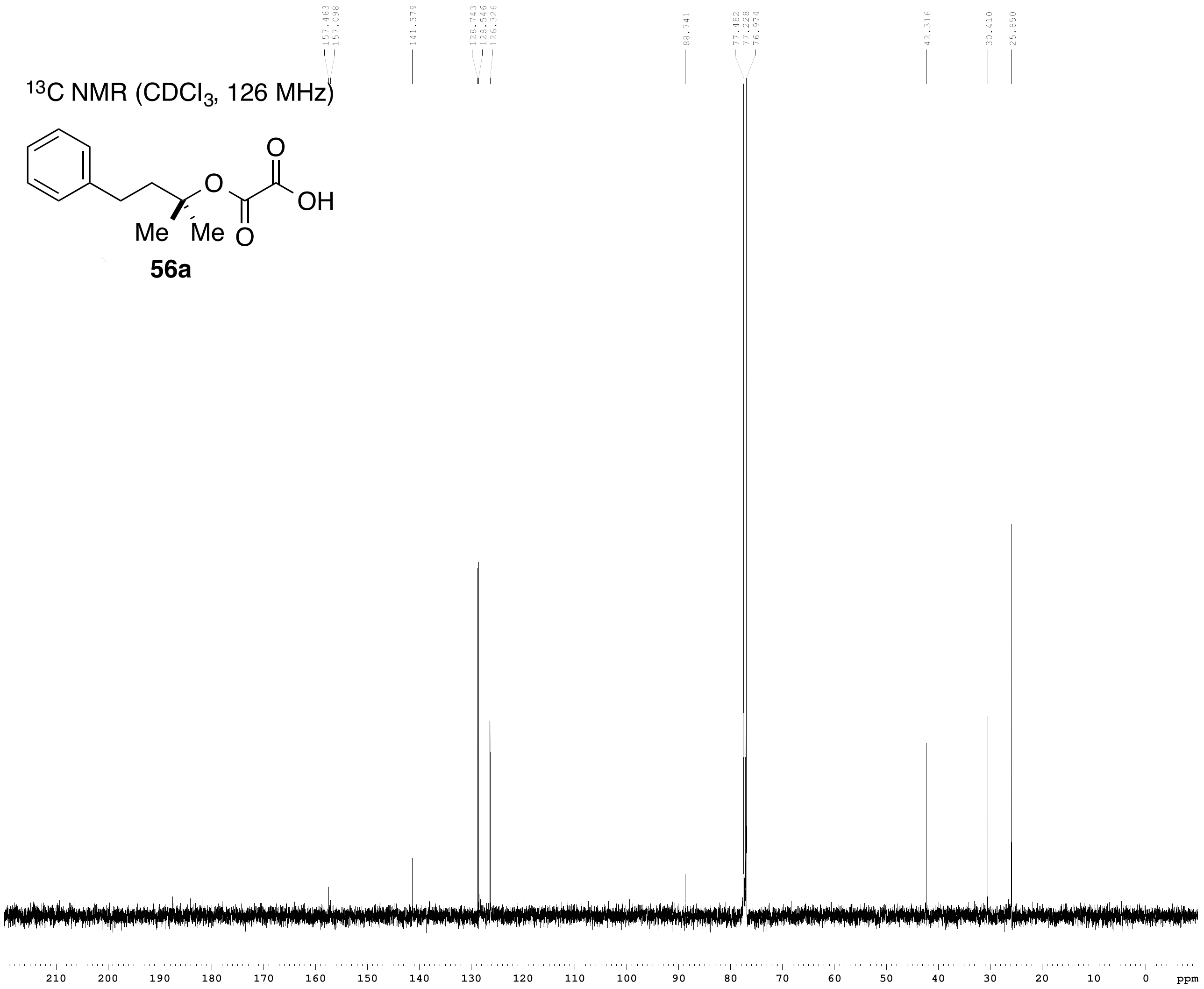
^{1}H NMR ($CDCl_3$, 600 MHz)

56a



```
Current Data Parameters
NAME          YS-II-149
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20141212
Time               8.59
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                19228
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.500072 Hz
AQ            0.9998560 sec
RG                  724
DW               52.000 usec
DE                14.54 usec
TE                298.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

F2 - Processing parameters
SI                65536
SF          600.1300278 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

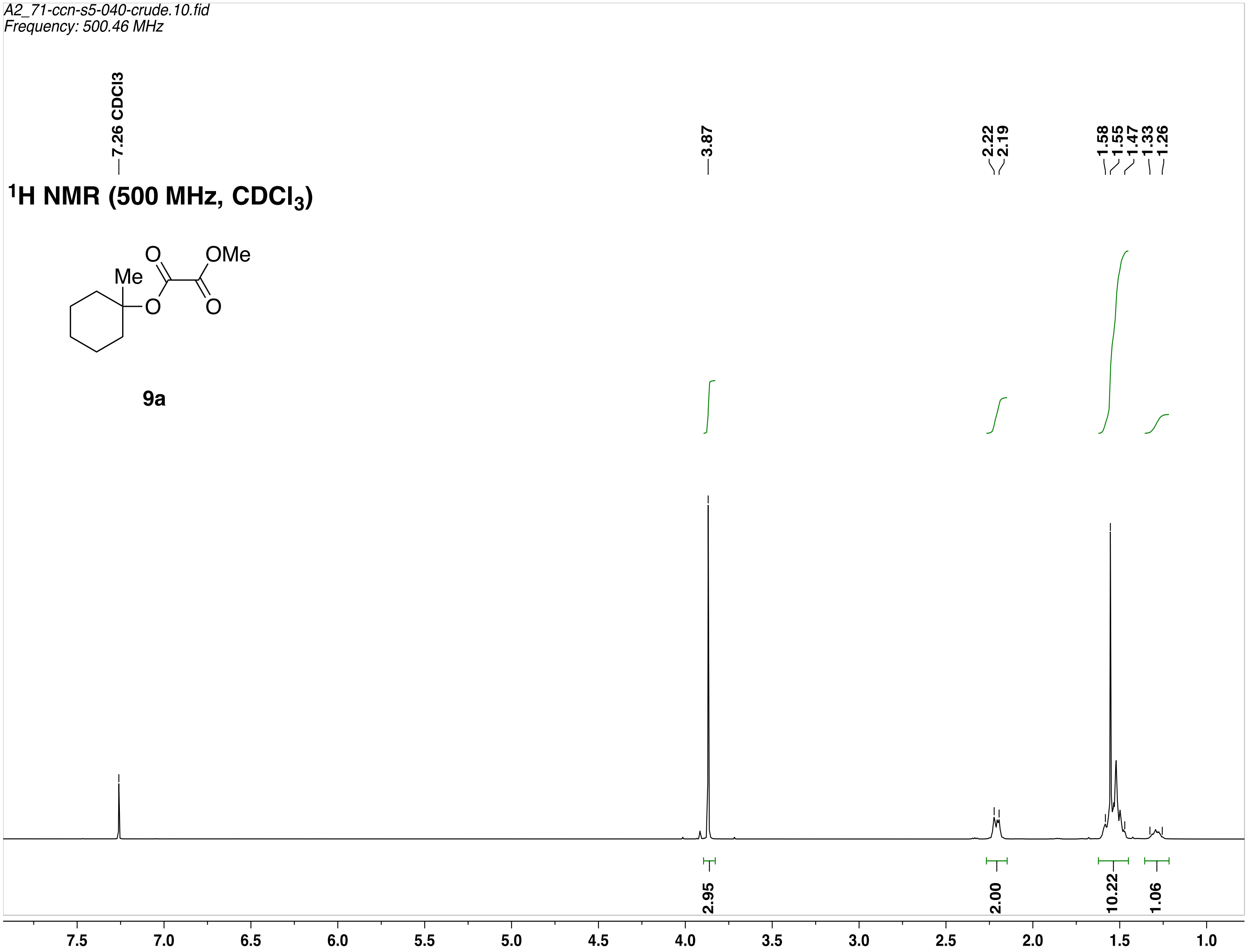
YS-II-152



^{13}C NMR ($CDCl_3$, 126 MHz)

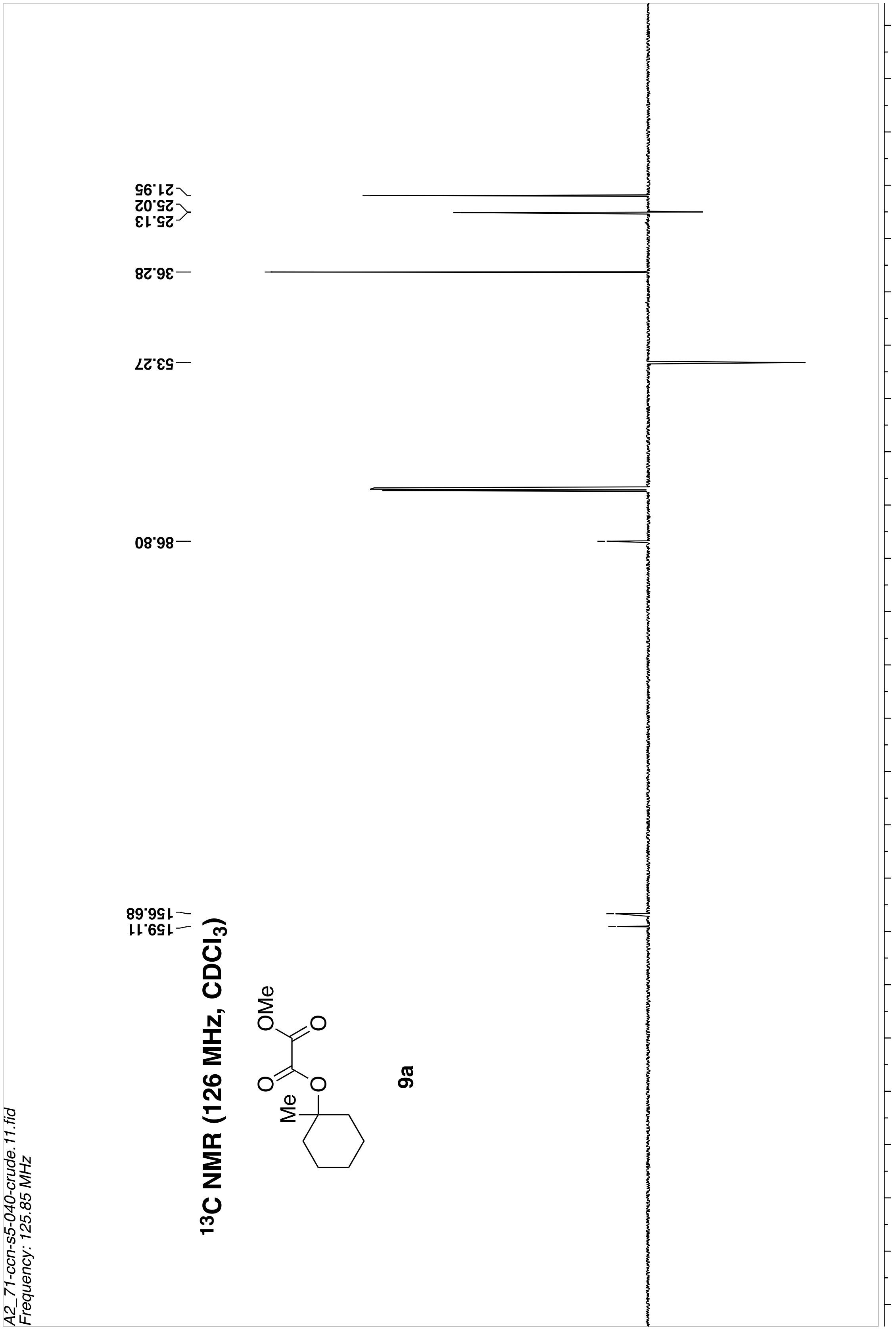
56a

```
Current Data Parameters
NAME          YS-II-152
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20141212
Time              14.14
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  552
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG              14596.5
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.75000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804002 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```


A2_71-ccn-s5-040-crude.10.fid
Frequency: 500.46 MHz

^{1}H NMR (500 MHz, CDCl$_3$)

9a



^{13}C NMR (126 MHz, CDCl$_3$)

9a

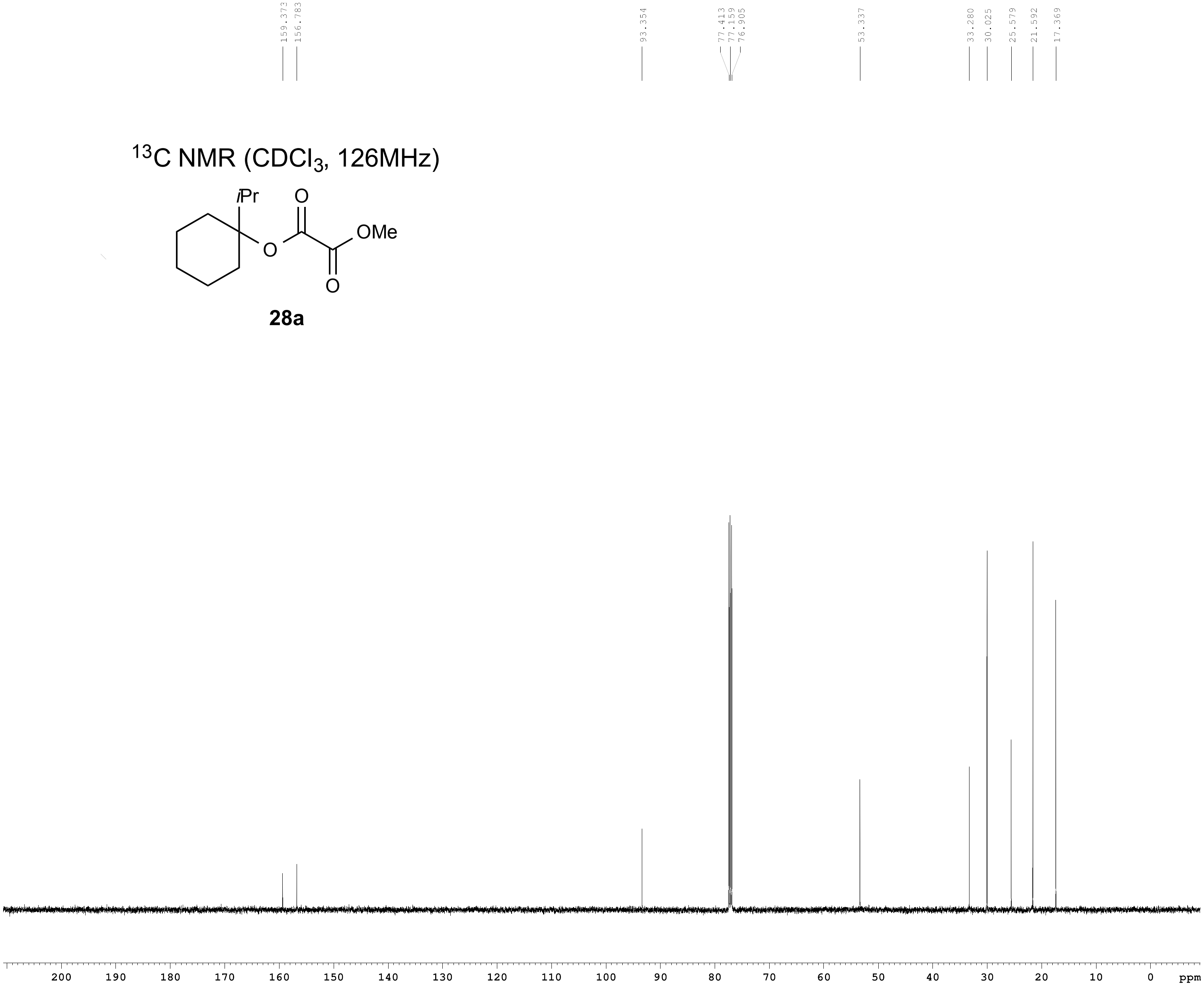
1H spectrum

^{1}H NMR (CDCl$_3$, 500MHz)

28a

```
Current Data Parameters
NAME      CRJ1-093-pure
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150223
Time               8.02
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998176 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200319 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling

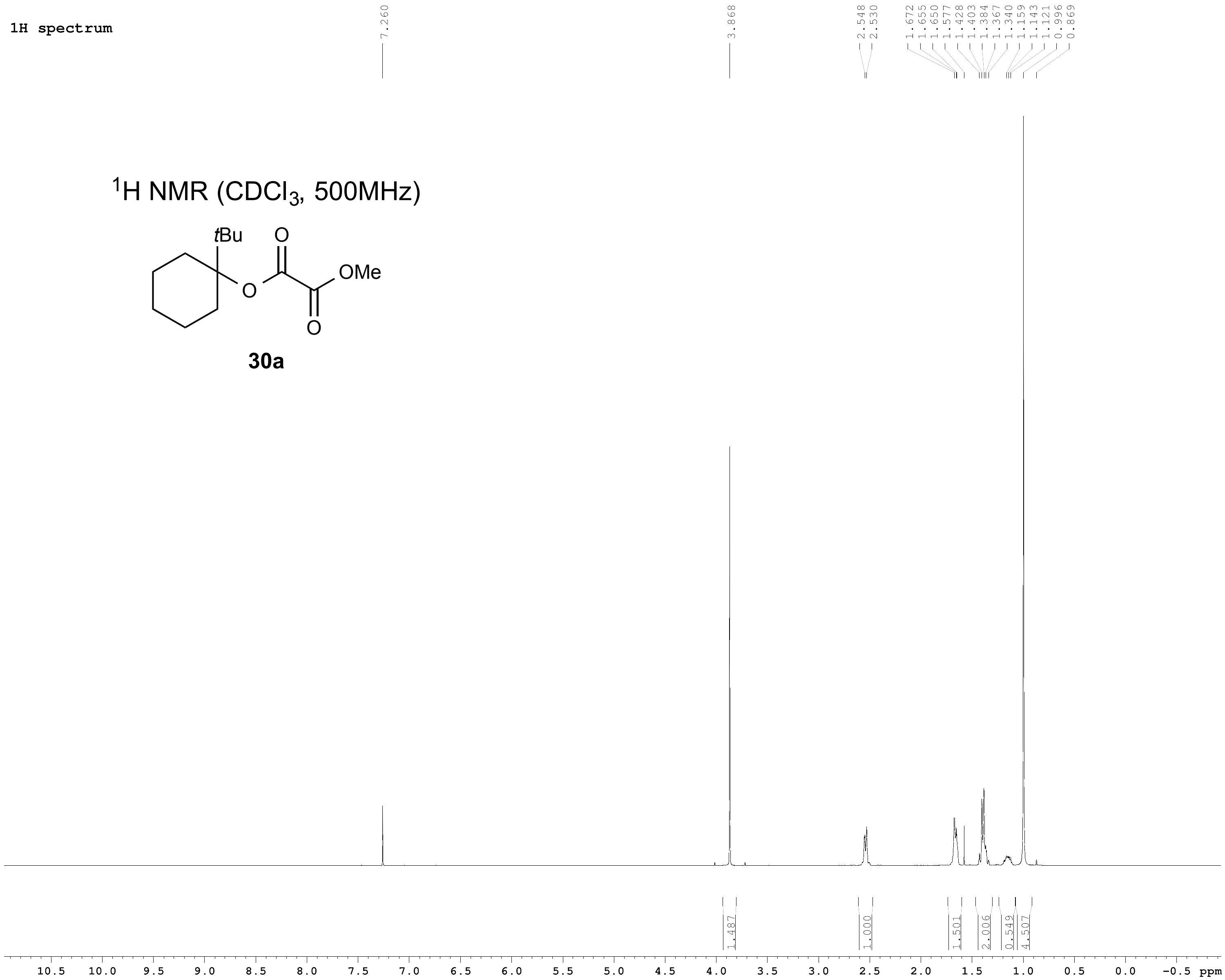


^{13}C NMR ($CDCl_3$, 126MHz)

28a

```
Current Data Parameters
NAME       CRJ1-093-pure
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150223
Time                8.05
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT             DMSO
NS                    96
DS                     4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                5792.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST    0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1    0 Hz
SPOFF2    0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804082 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```

1H spectrum



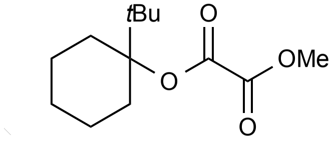
^{1}H NMR (CDCl$_3$, 500MHz)

30a

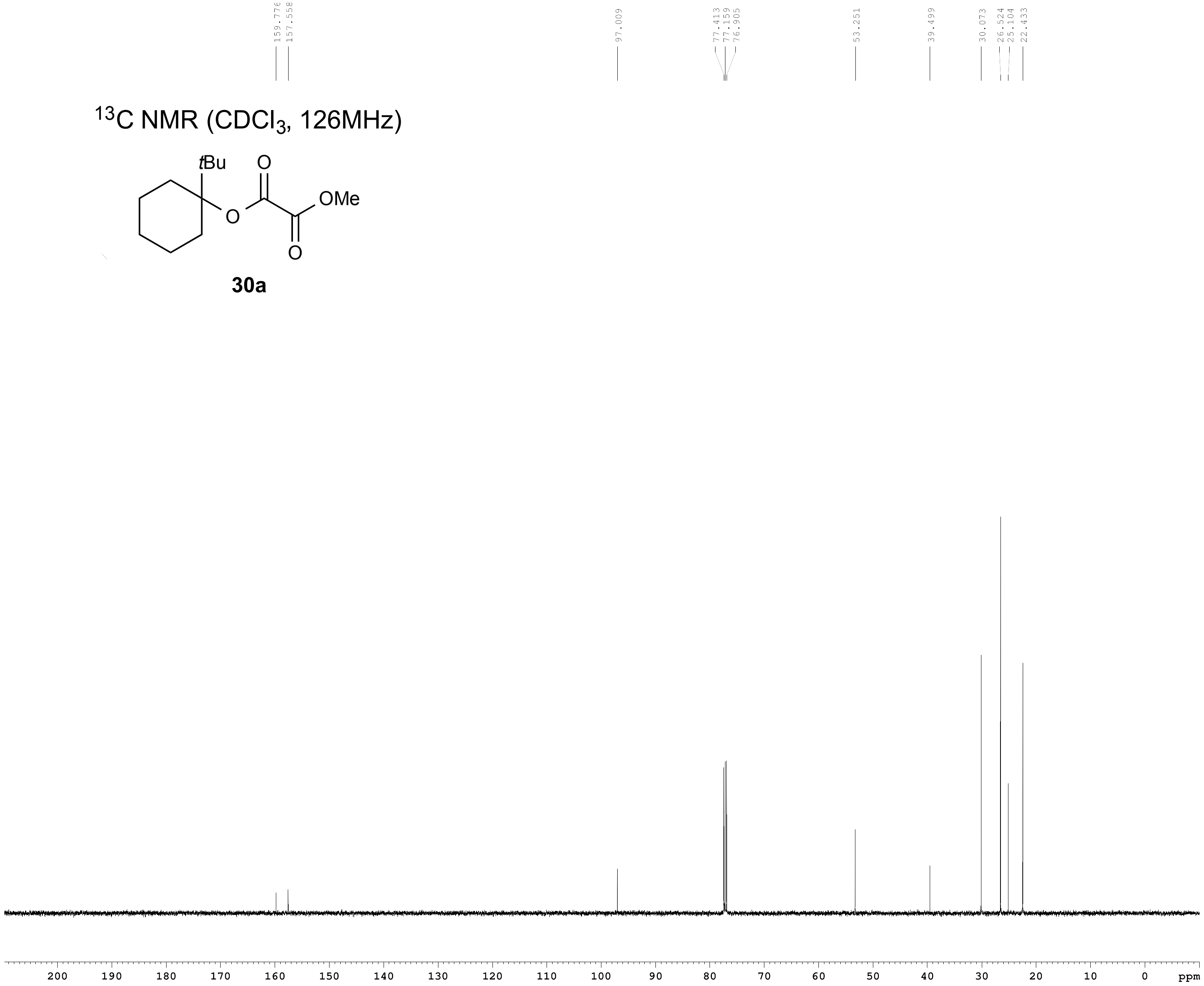
```
Current Data Parameters
NAME       CRJ1-137-pure
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150310
Time               13.32
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998176 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200311 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling

^{13}C NMR (CDCl$_3$, 126MHz)



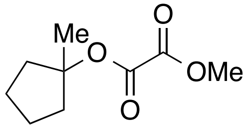
30a



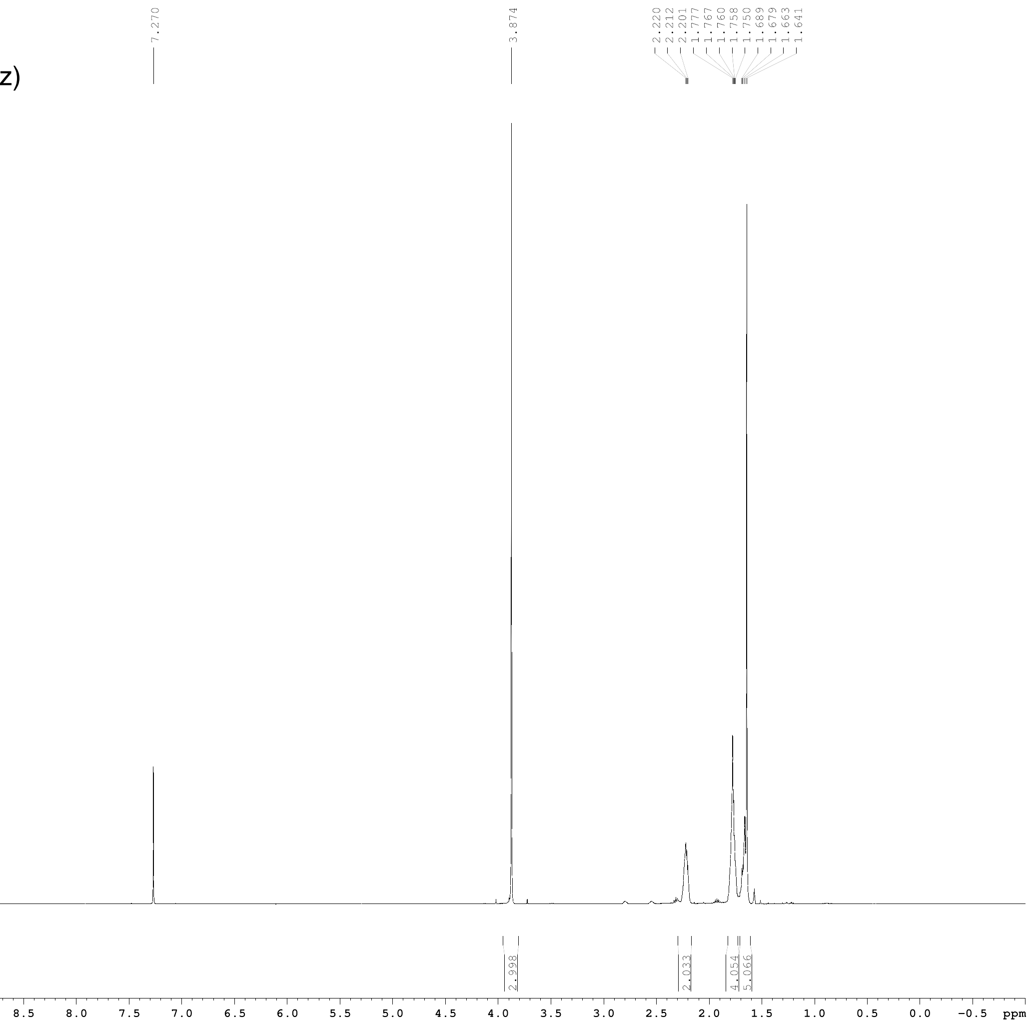
```
Current Data Parameters
NAME      CRJ1-137-pure
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150310
Time              13.34
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDC13
NS                   72
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               5160.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804081 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-240

^{1}H NMR (CDCl$_3$, 500 MHz)

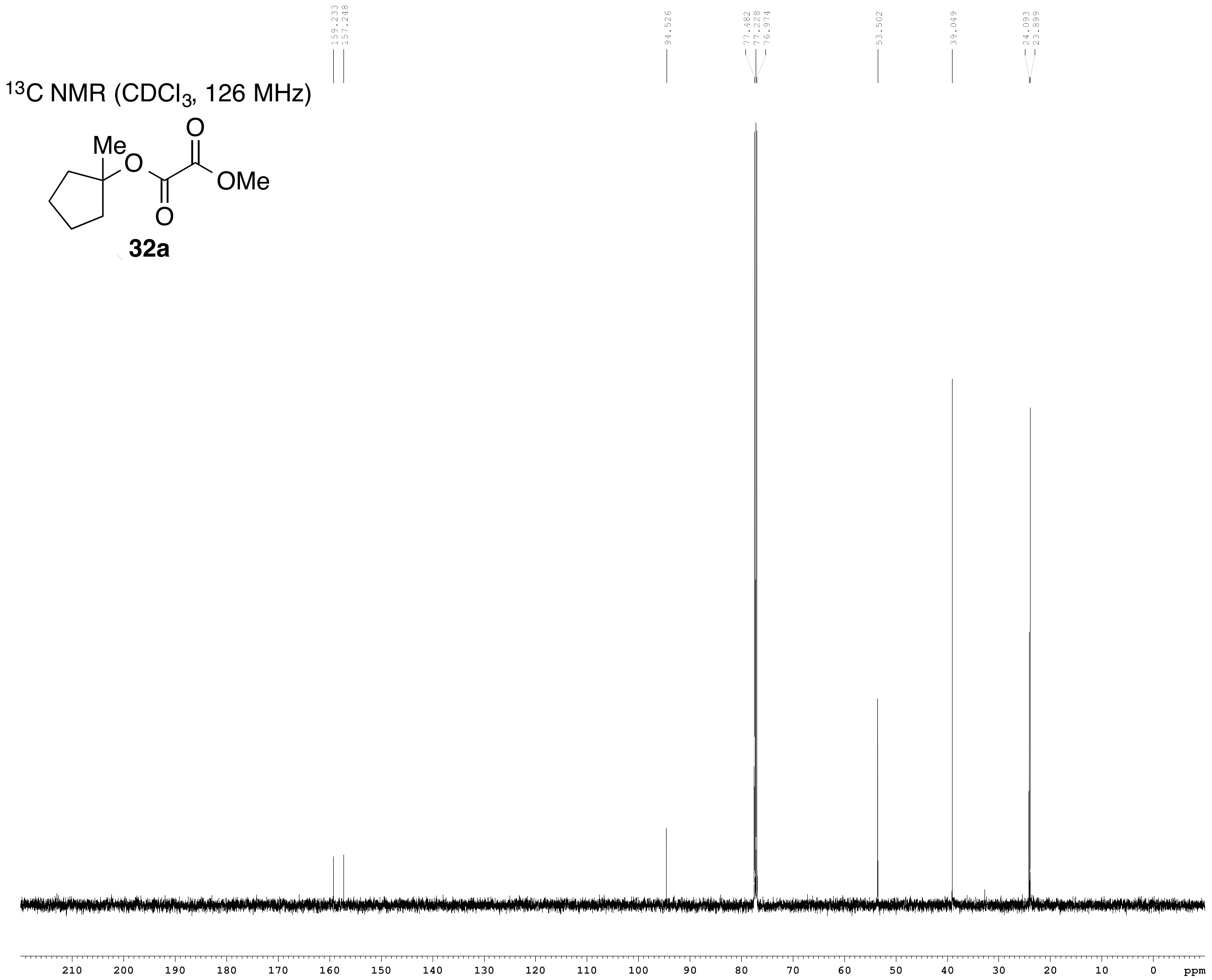


32a



```
Current Data Parameters
NAME          YS-II-240
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150212
Time              10.09
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200258 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

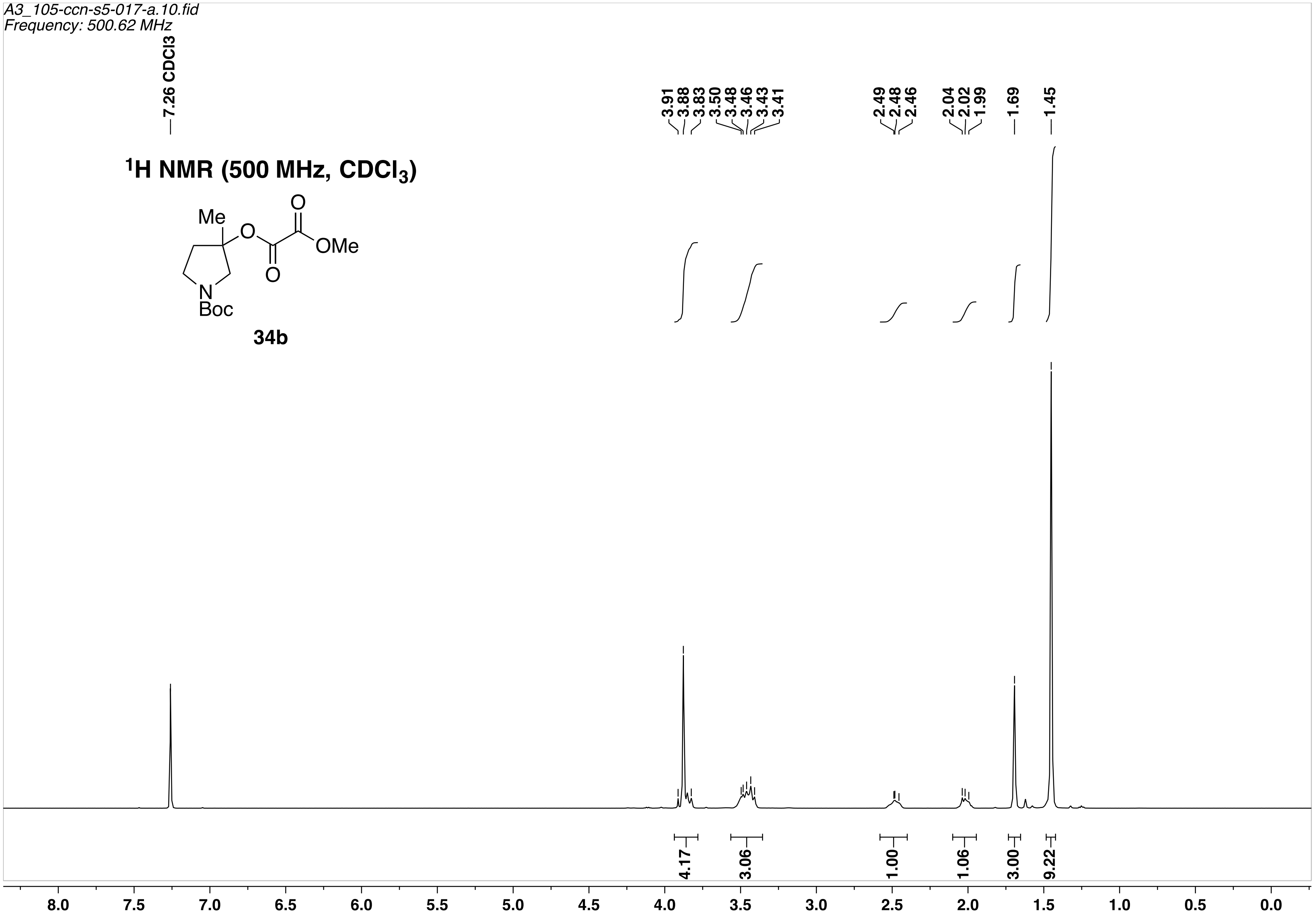
YS-II-240

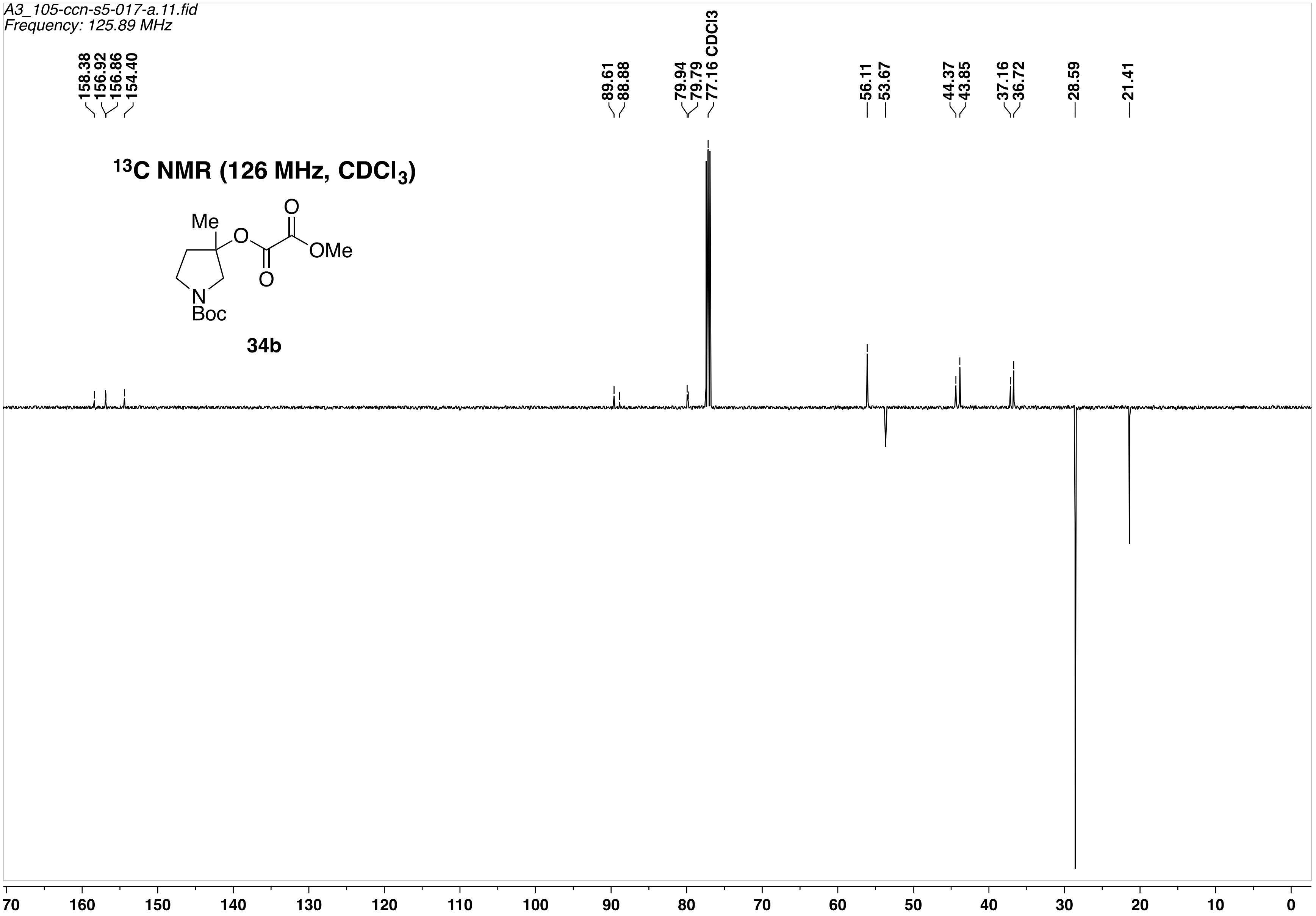


^{13}C NMR ($CDCl_3$, 126 MHz)

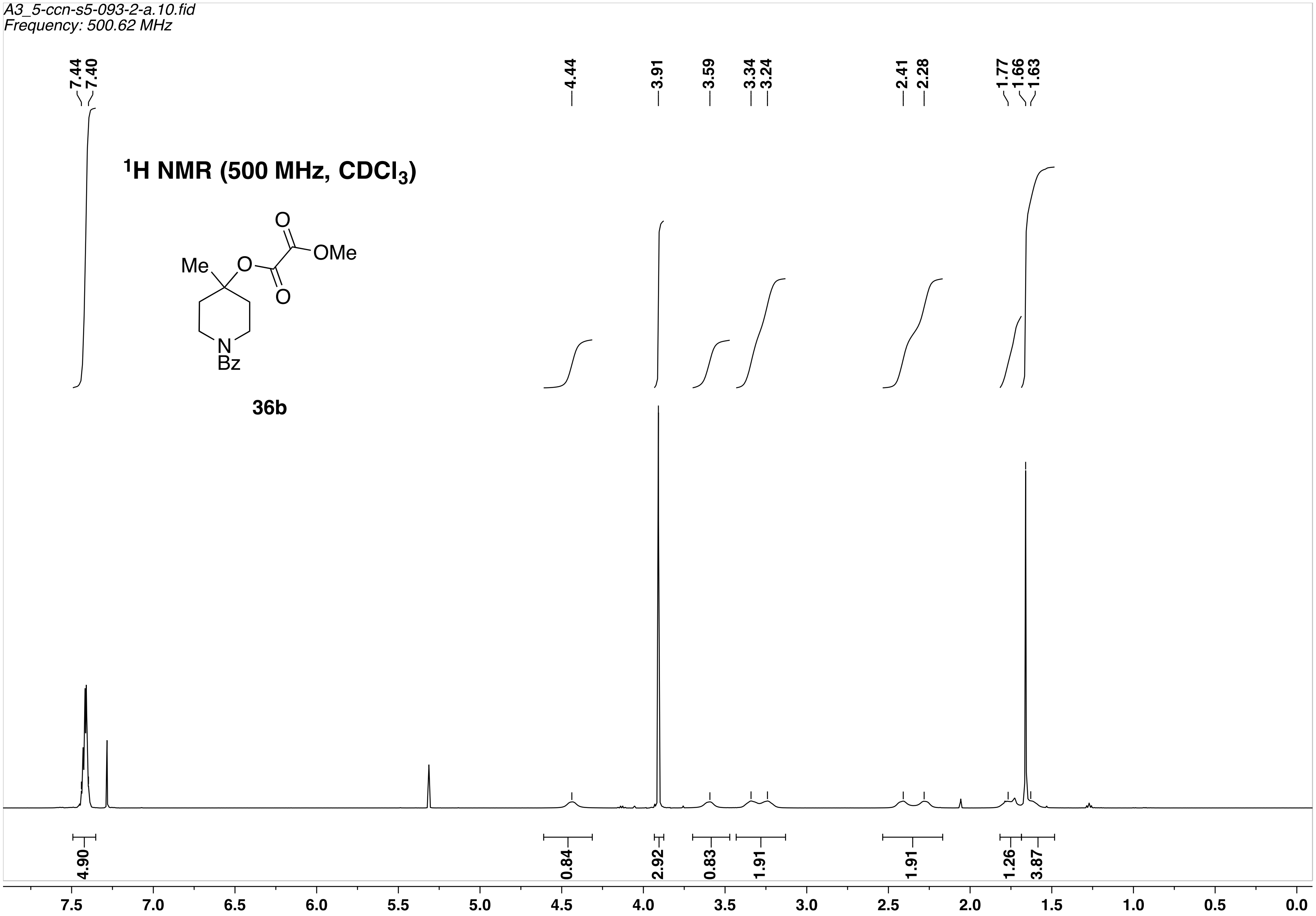
32a

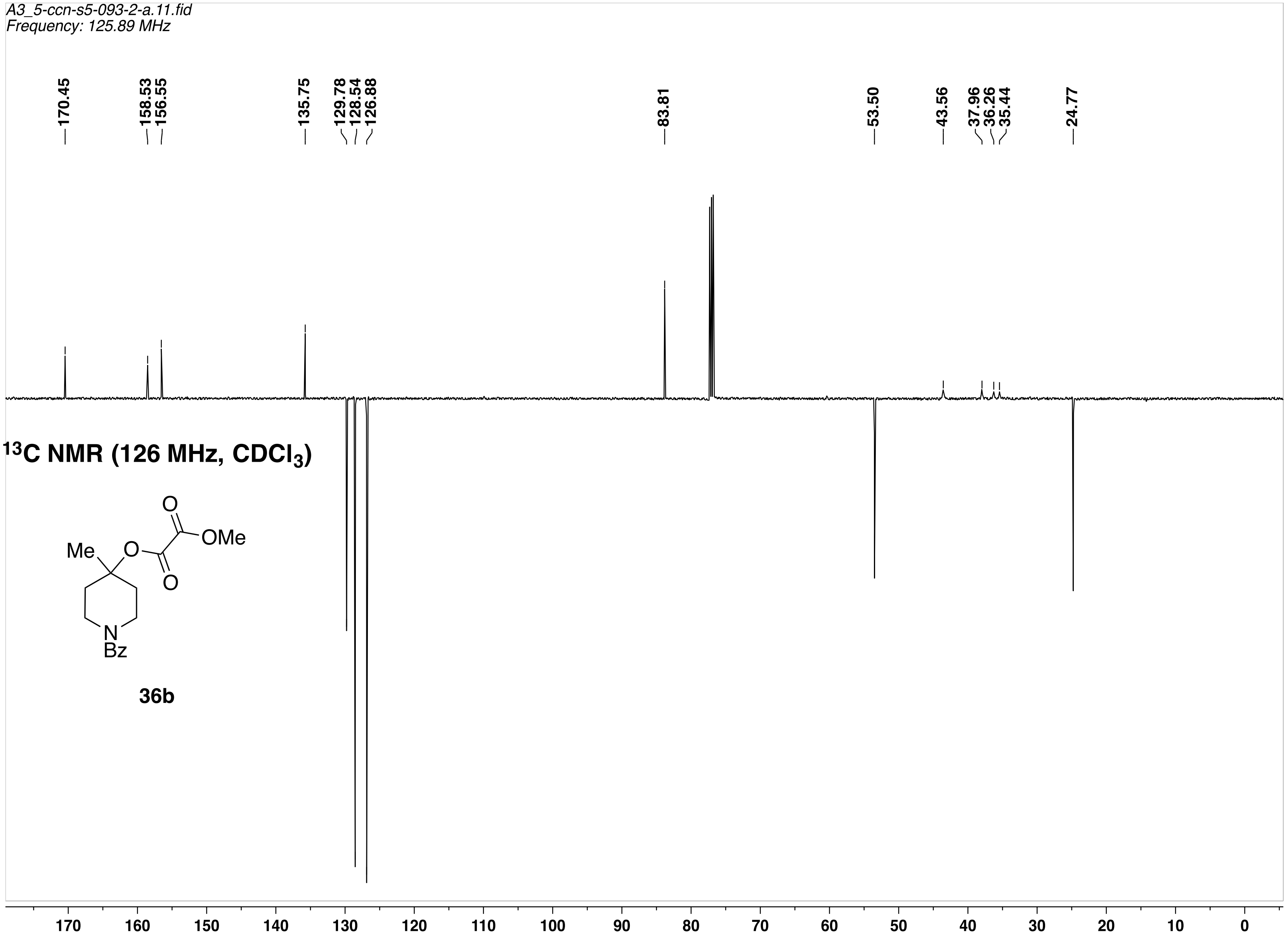
```
Current Data Parameters
NAME          YS-II-240
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20150212
Time              10.13
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  312
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803987 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```


A3_105-ccn-s5-017-a.10.fid
Frequency: 500.62 MHz
7.26 CDCl3
^{1}H NMR (500 MHz, CDCl$_3$)
Me
O
O
OMe
O
N
Boc
34b
3.91
3.88
3.83
3.50
3.48
3.46
3.43
3.41
2.49
2.48
2.46
2.04
2.02
1.99
1.69
1.45
4.17
3.06
1.00
1.06
3.00
9.22
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


A3_105-ccn-s5-017-a.11.fid
Frequency: 125.89 MHz
158.38
156.92
156.86
154.40
89.61
88.88
79.94
79.79
77.16 CDCl3
56.11
53.67
44.37
43.85
37.16
36.72
28.59
21.41
13C NMR (126 MHz, CDCl3)
Me
O
O
OMe
O
N
Boc
34b
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

A3_5-ccn-s5-093-2-a.10.fid
Frequency: 500.62 MHz

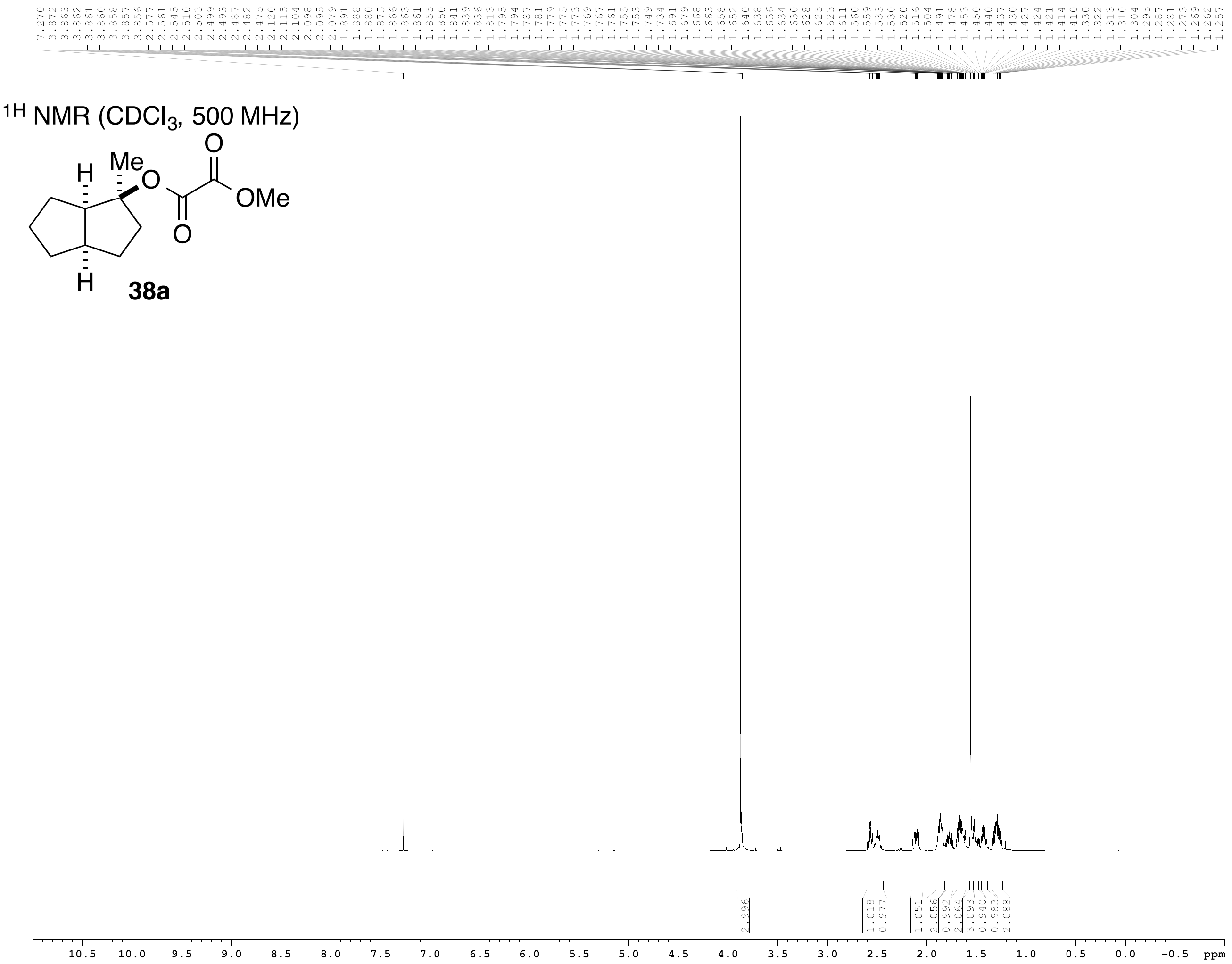




^{13}C NMR (126 MHz, CDCl$_3$)

36b

YS-II-286



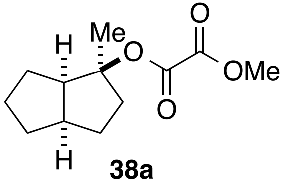
^{1H} NMR ($CDCl_3$, 500 MHz)

38a

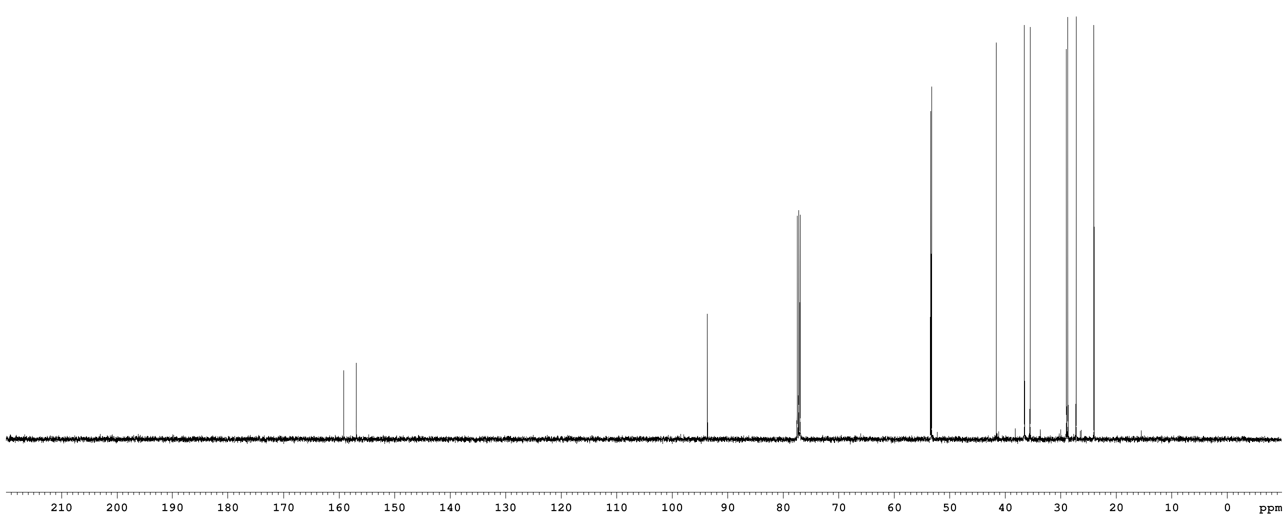
```
Current Data Parameters
NAME            YS-II-286
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150306
Time                17.55
INSTRUM             gn500
PROBHD   5 mm broadband
PULPROG              zg30
TD                  32048
SOLVENT            CDCl3T
NS                      8
DS                      2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9997952 sec
RG                  101.6
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                 -5.80 dB
SFO1          499.1834943 MHz

F2 - Processing parameters
SI                  65536
SF            499.1800217 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-II-286

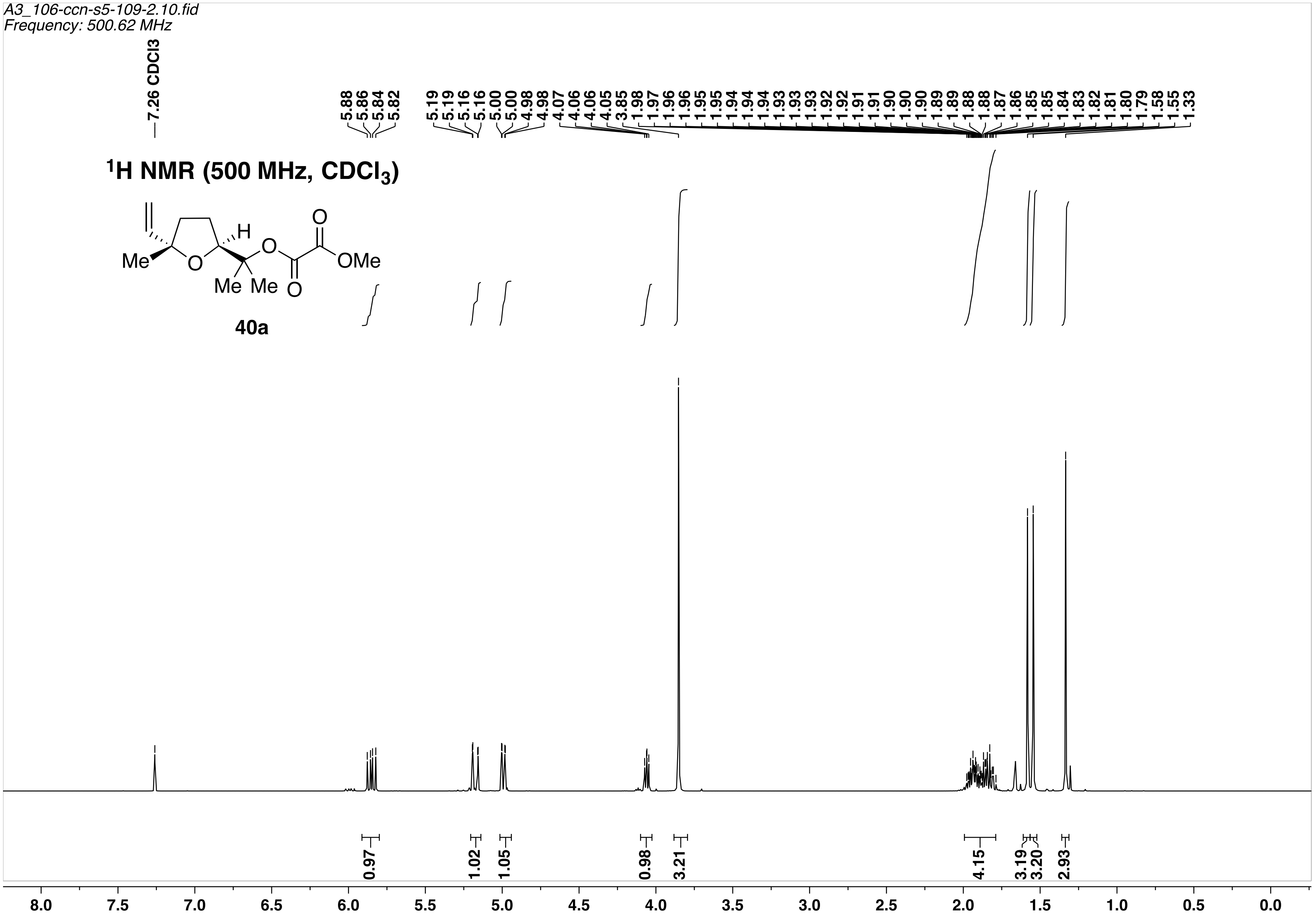
^{13}C NMR (CDCl$_3$, 126 MHz)



38a

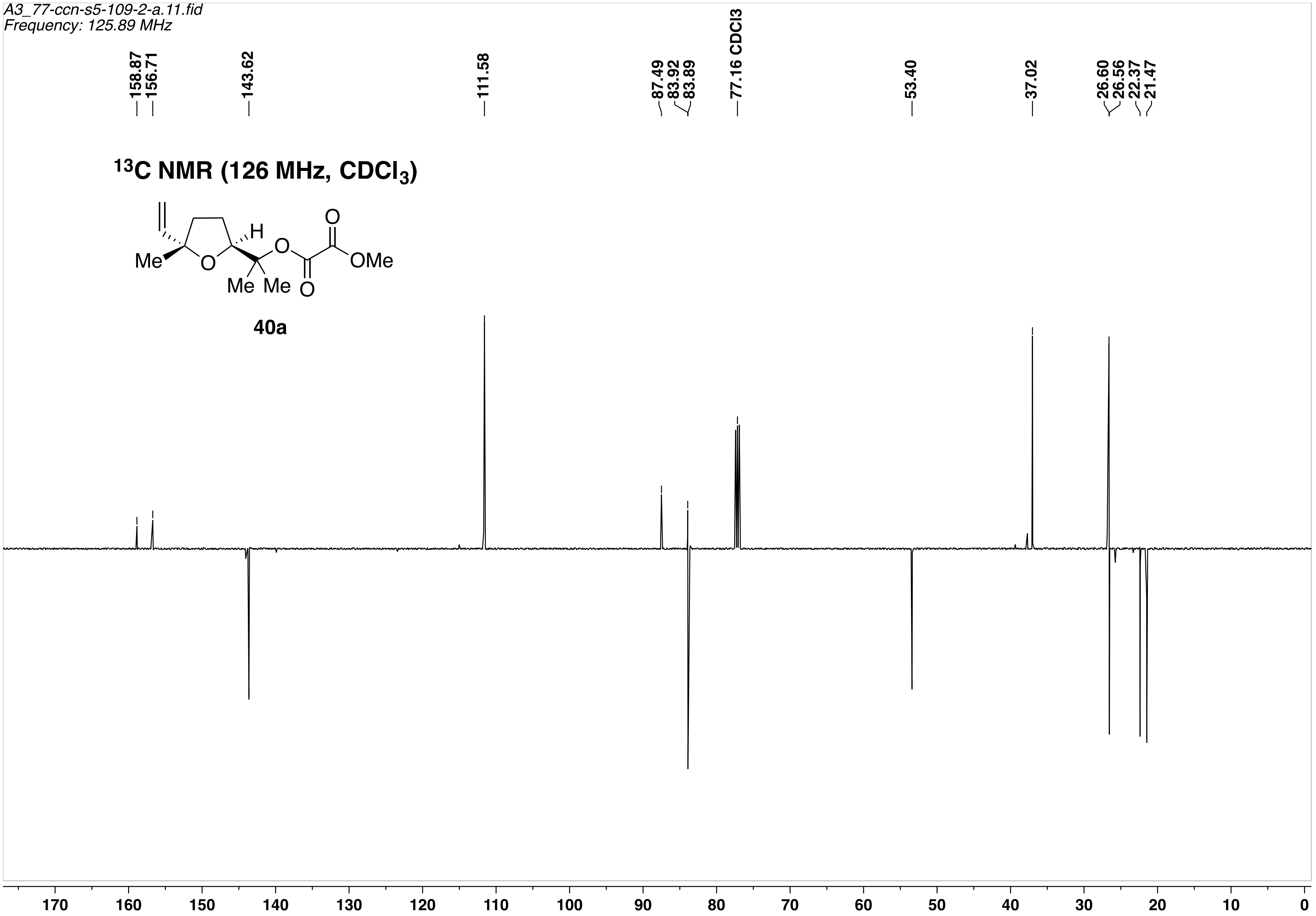


```
Current Data Parameters
NAME          YS-II-286
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20150309
Time              10.51
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  144
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803334 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



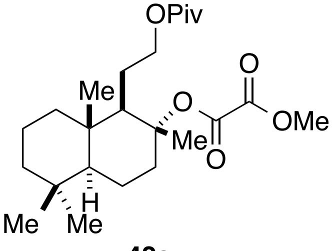
^{1}H NMR (500 MHz, CDCl$_3$)

40a

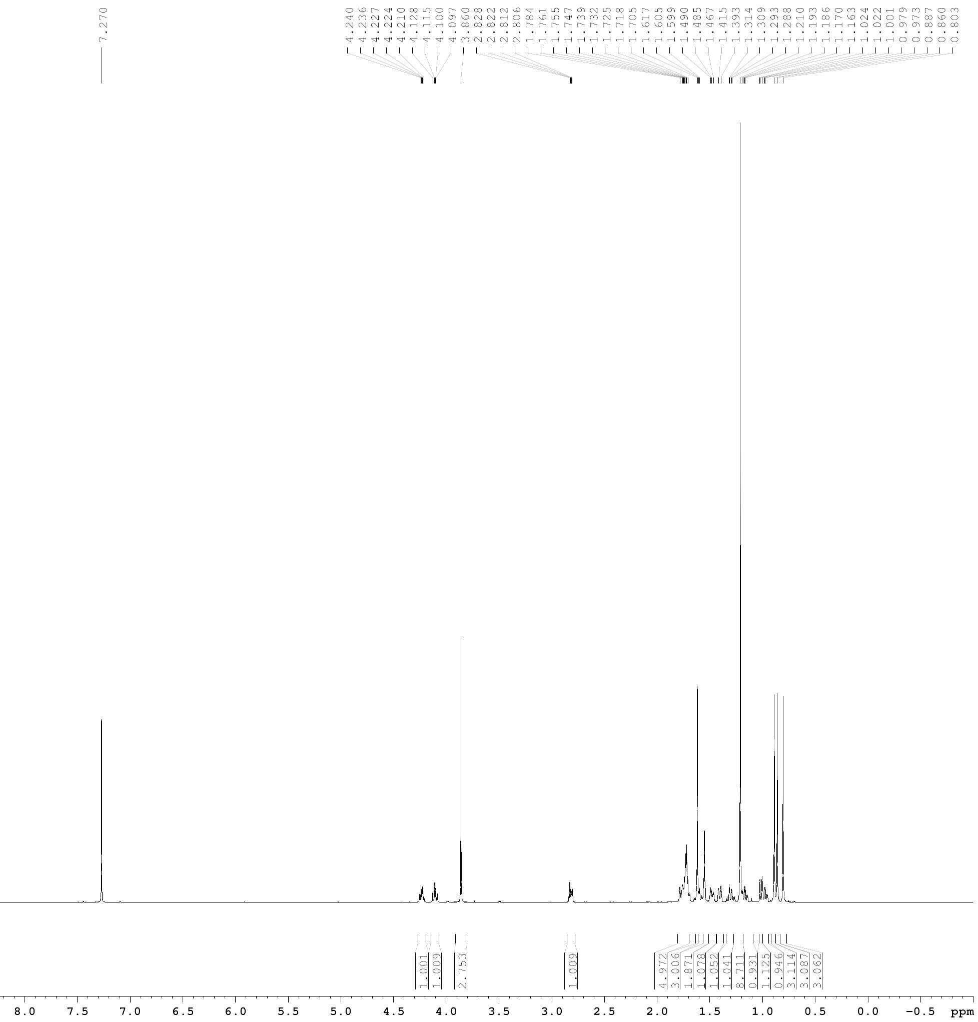

A3_77-ccn-s5-109-2-a.11.fid
Frequency: 125.89 MHz
158.87
156.71
143.62
111.58
87.49
83.92
83.89
77.16 CDCl3
53.40
37.02
26.60
26.56
22.37
21.47
^{13}C NMR (126 MHz, CDCl$_3$)
Me
O
H
O
O
OMe
Me
Me
O
40a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

YS-II-169

¹H NMR (CDCl$_3$, 600 MHz)



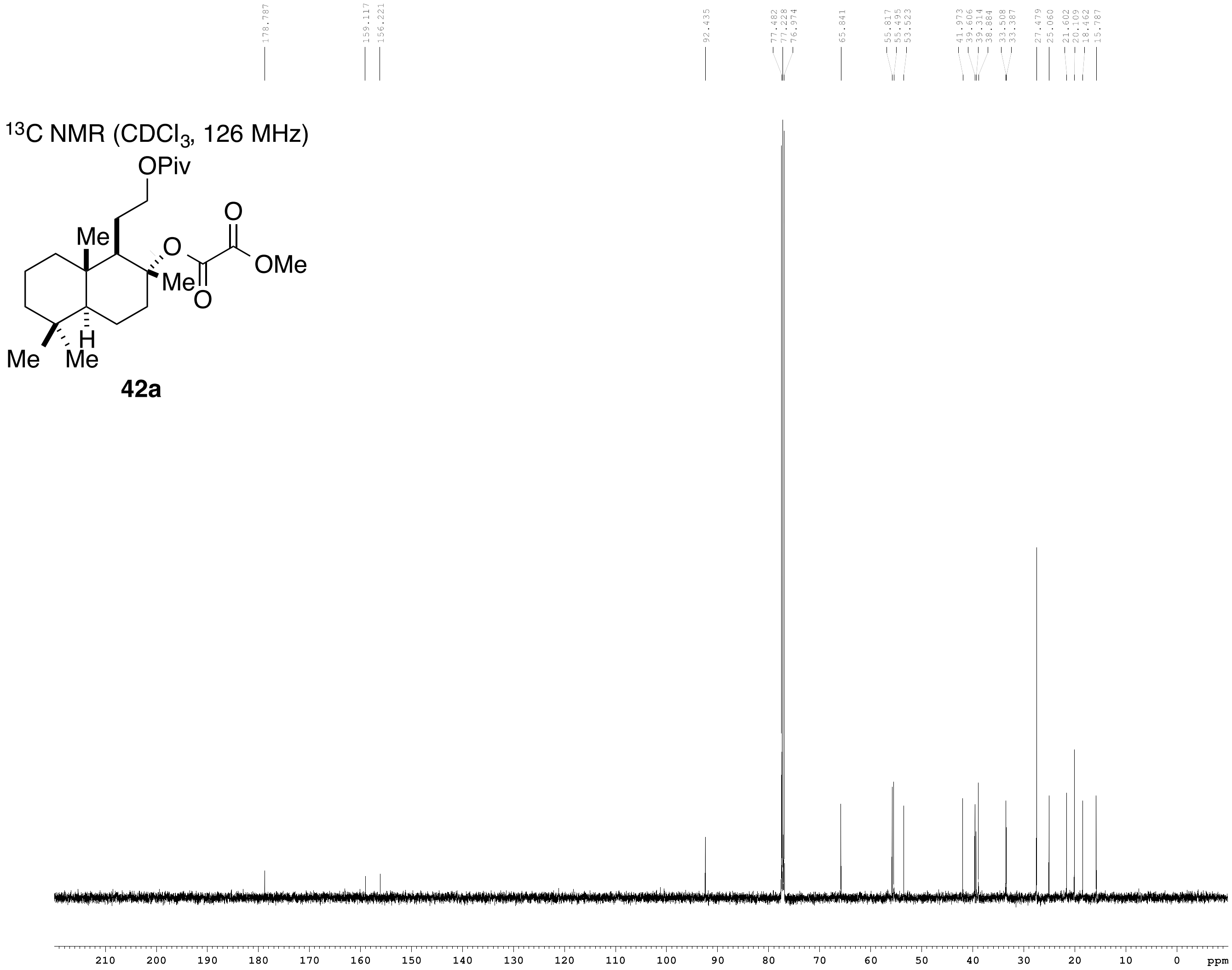
42a



```
Current Data Parameters
NAME          YS-II-169
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150110
Time               8.47
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                19228
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.500072 Hz
AQ            0.9998560 sec
RG                  362
DW               52.000 usec
DE                14.54 usec
TE                298.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

F2 - Processing parameters
SI                65536
SF          600.1300297 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

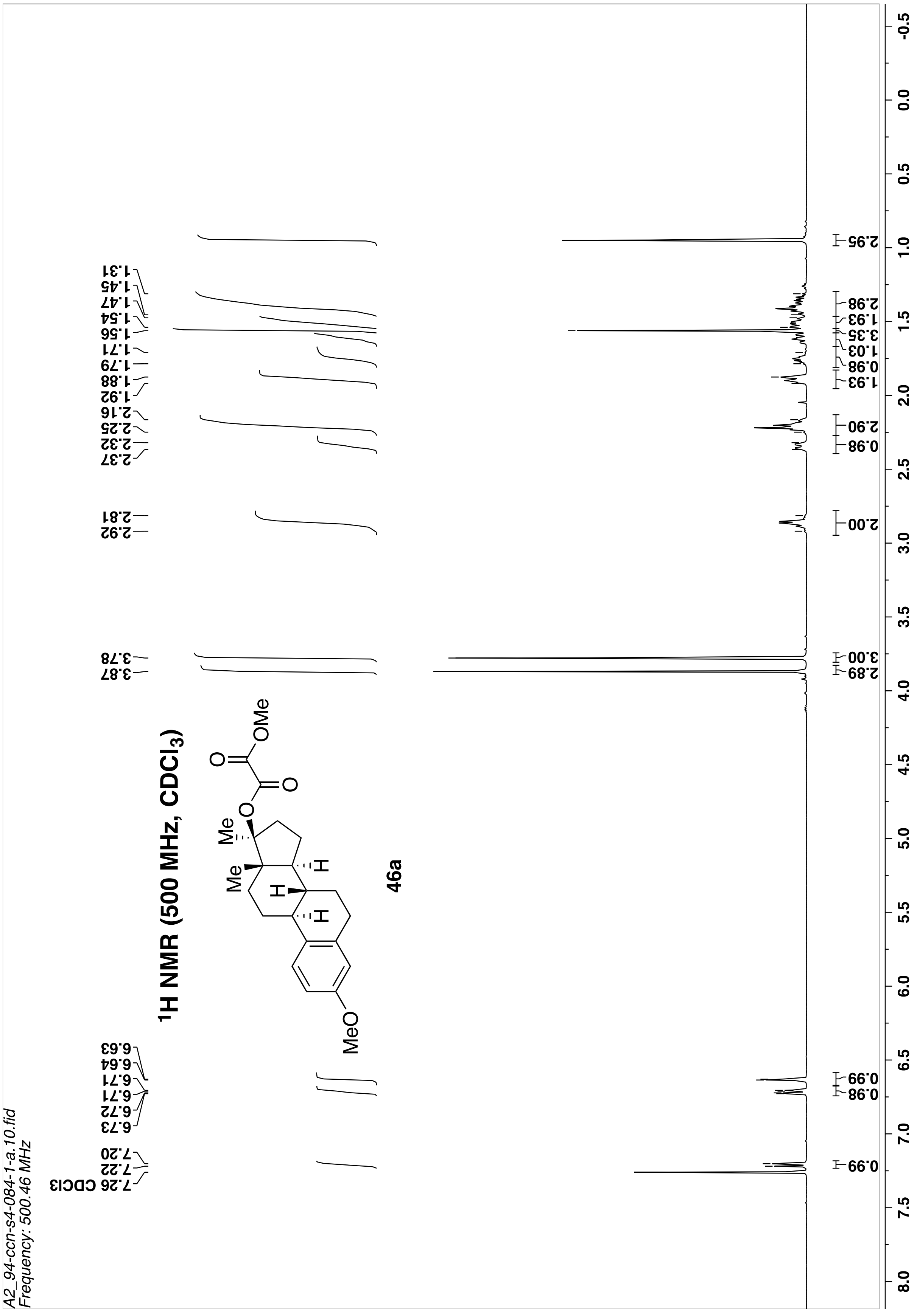
YS-II-169

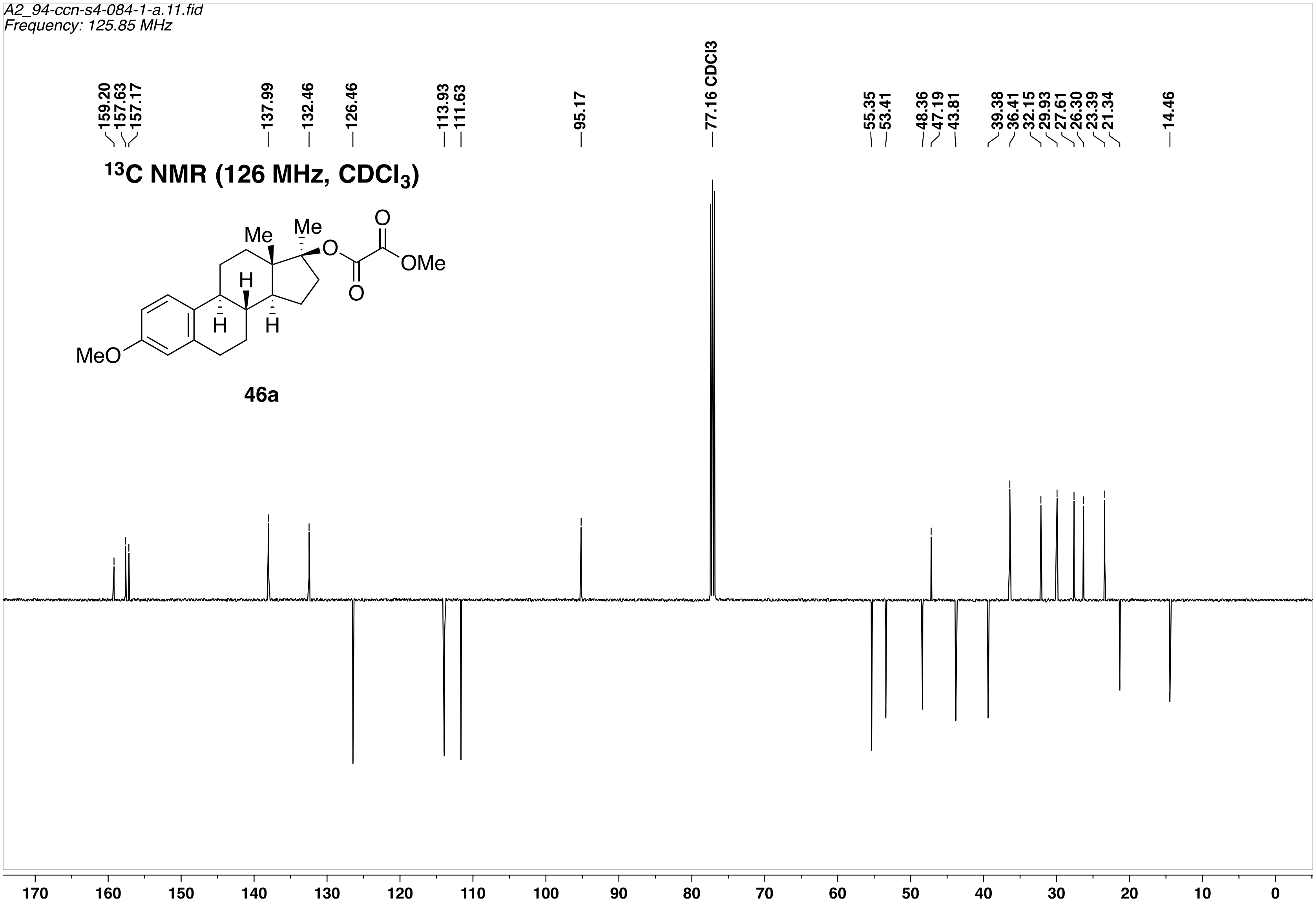
^{13}C NMR (CDCl$_3$, 126 MHz)



42a

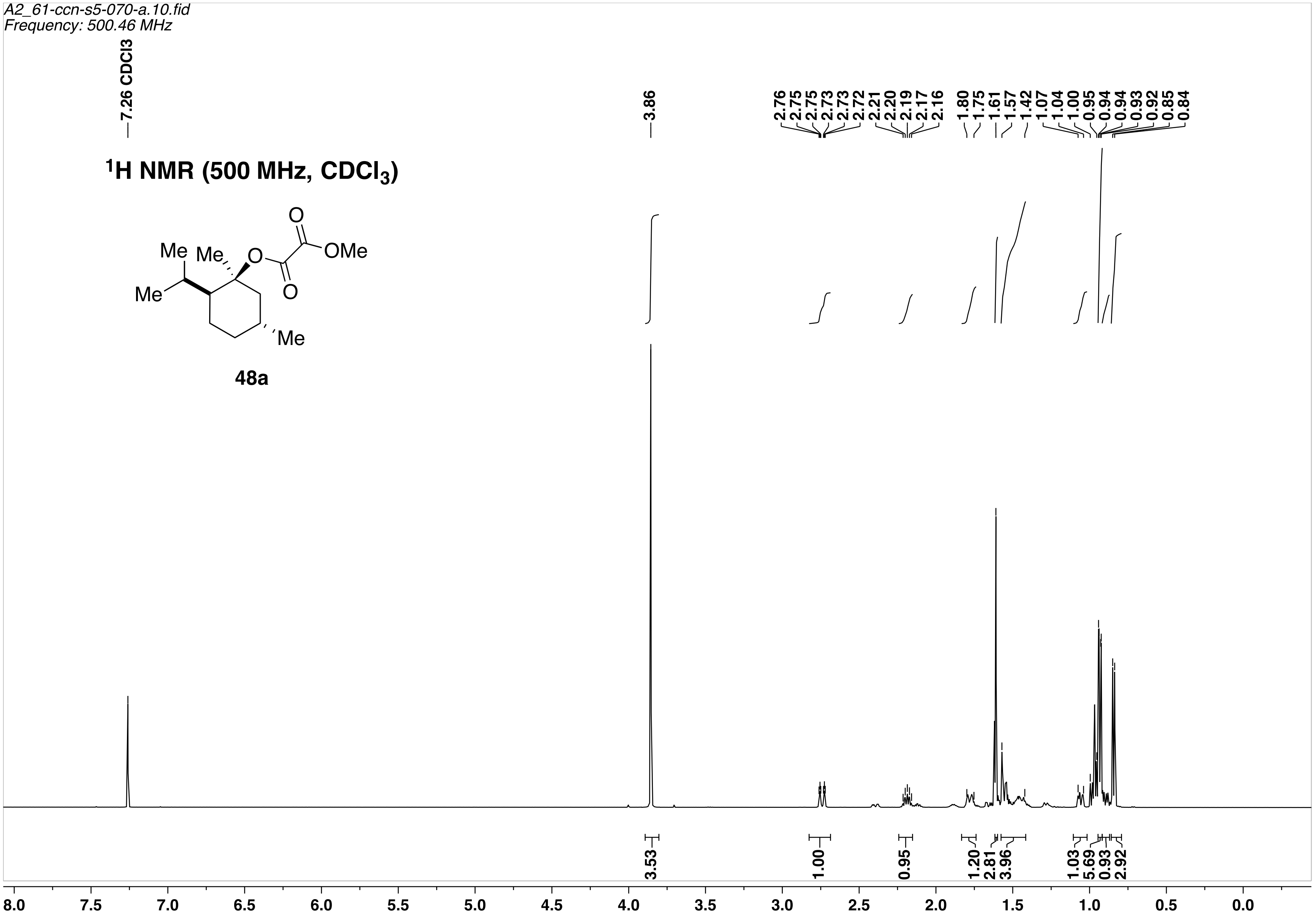
```
Current Data Parameters
NAME          YS-II-169
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150110
Time               9.06
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803825 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```


A2_94-ccn-s4-084-1-a.10.fid
Frequency: 500.46 MHz
^{1}H NMR (500 MHz, CDCl$_3$)
46a
MeO
Me
Me
H
H
H
O
O
O
OMe
7.26 CDCl3
7.22
7.20
6.73
6.72
6.71
6.71
6.64
6.63
3.87
3.78
2.92
2.81
2.37
2.32
2.25
2.16
1.92
1.88
1.79
1.71
1.56
1.54
1.47
1.45
1.31
0.99
0.98
0.99
2.89
3.00
2.00
0.98
2.90
1.93
0.98
1.03
3.35
1.93
2.98
2.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



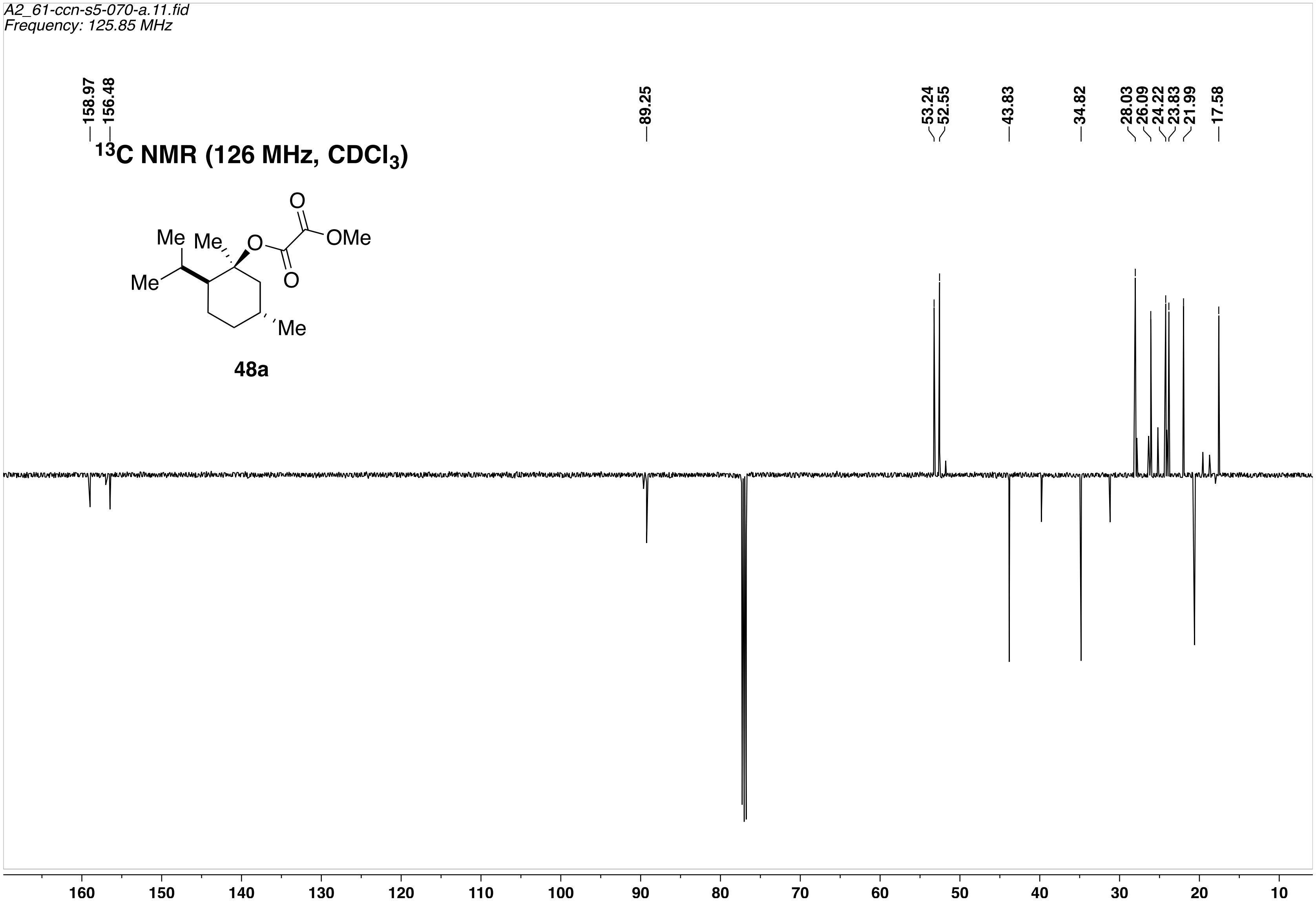
^{13}C NMR (126 MHz, CDCl$_3$)

46a



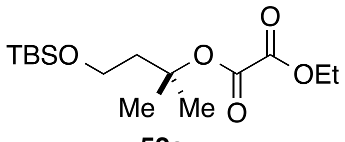
^{1}H NMR (500 MHz, CDCl$_3$)

48a

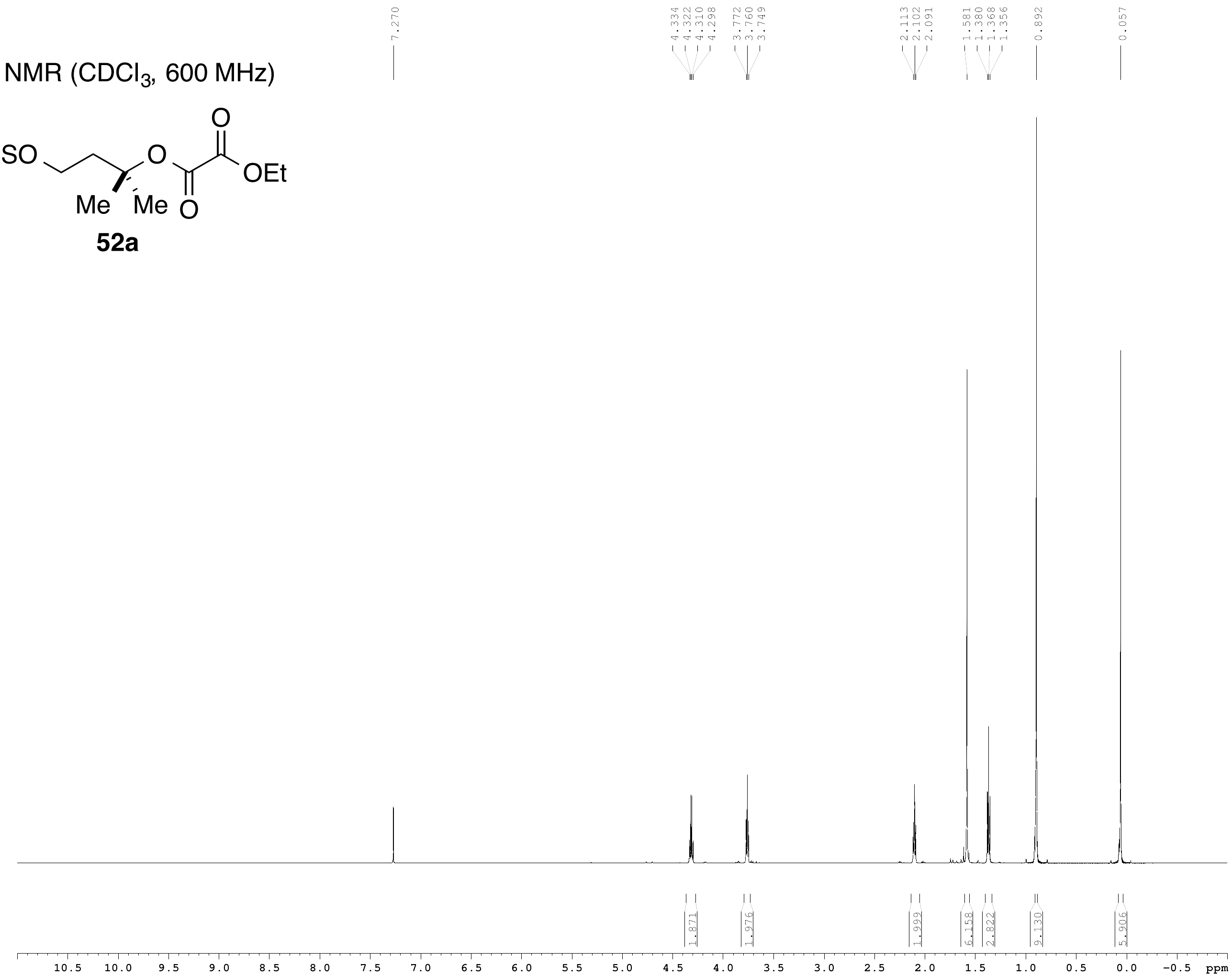

A2_61-ccn-s5-070-a.11.fid
Frequency: 125.85 MHz
158.97
156.48
89.25
53.24
52.55
43.83
34.82
28.03
26.09
24.22
23.83
21.99
17.58
^{13}C NMR (126 MHz, CDCl$_3$)
Me
Me
Me
O
O
OMe
O
Me
48a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

YS-II-199

¹H NMR (CDCl$_3$, 600 MHz)



52a

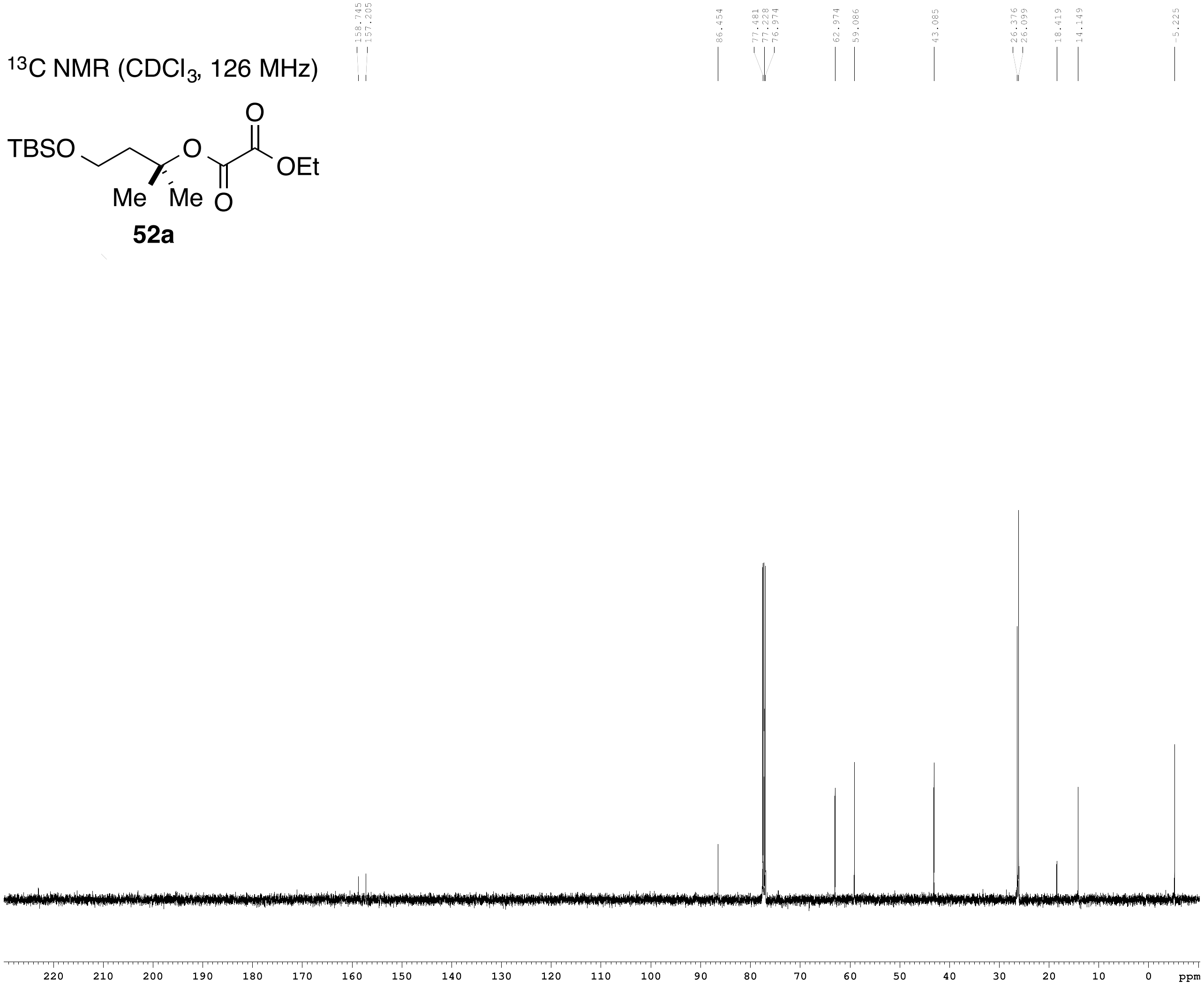


```
Current Data Parameters
NAME          YS-II-199
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150123
Time              17.08
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                19228
SOLVENT           CDCl3
NS                    8
DS                    2
SWH           9615.385 Hz
FIDRES        0.500072 Hz
AQ           0.9998560 sec
RG                  181
DW               52.000 usec
DE                14.54 usec
TE                298.2 K
D1          0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

F2 - Processing parameters
SI                65536
SF          600.1300296 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-II-199

^{13}C NMR (CDCl$_3$, 126 MHz)

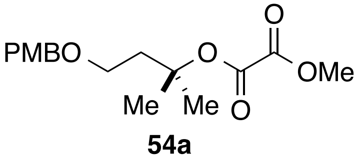
52a



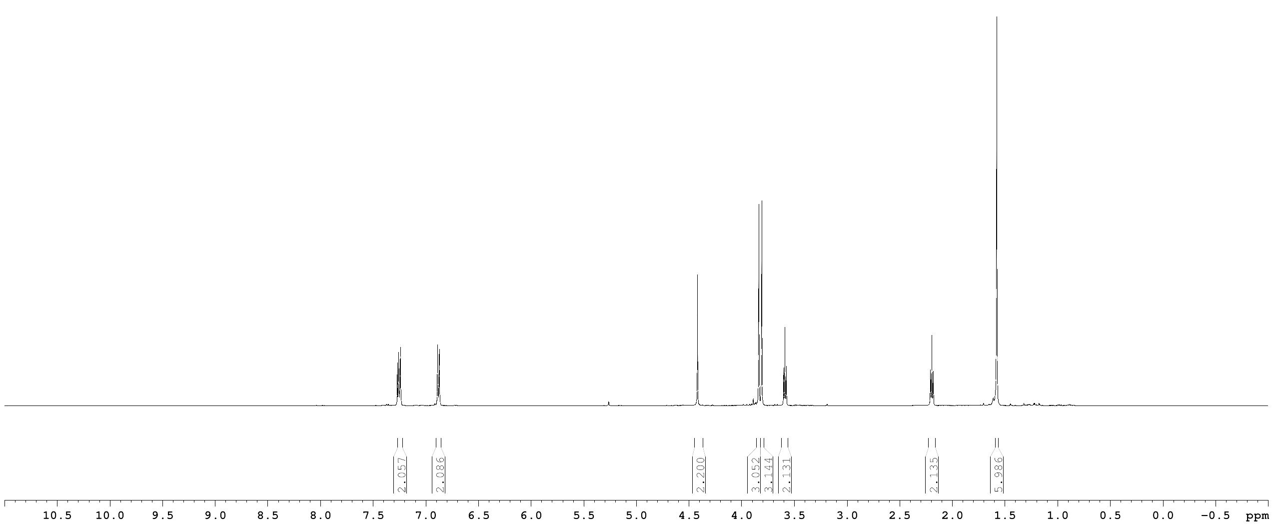
```
Current Data Parameters
NAME          YS-II-199
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20150425
Time               9.36
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  248
DS                   16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813440 sec
RG                13004
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST   0 sec
MCWRK       0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1               16.55 usec
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             24.50 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803988 MHz
WDW                  EM
SSB      0
LB                1.00 Hz
GB       0
PC                 2.00
```

YS-II-259

^{1}H NMR ($CDCl_3$, 500 MHz)



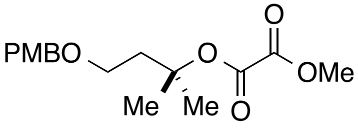
54a



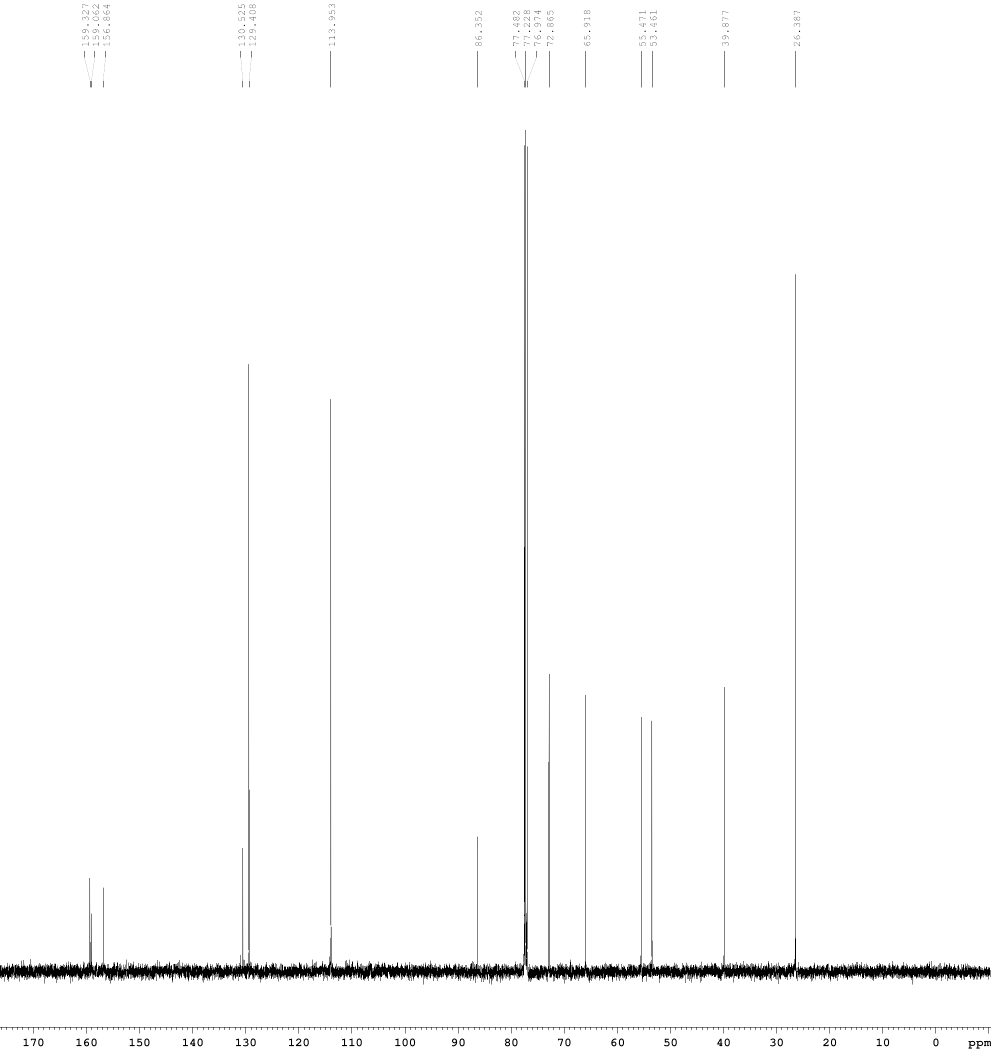
```
Current Data Parameters
NAME          YS-II-259
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150220
Time               8.52
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200271 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-259

^{13}C NMR (CDCl$_3$, 126 MHz)



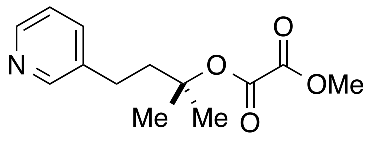
54a



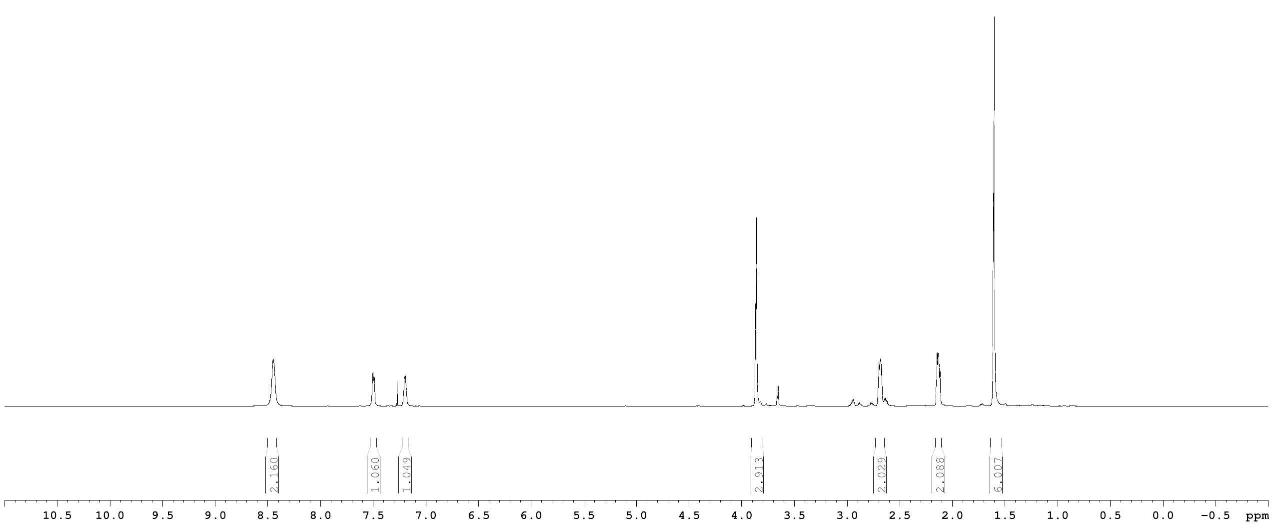
```
Current Data Parameters
NAME          YS-II-259
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150220
Time               8.55
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  256
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG              10321.3
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804006 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-III-54

^{1}H NMR (CDCl$_3$, 600 MHz)



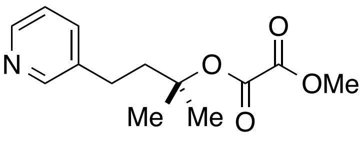
58a



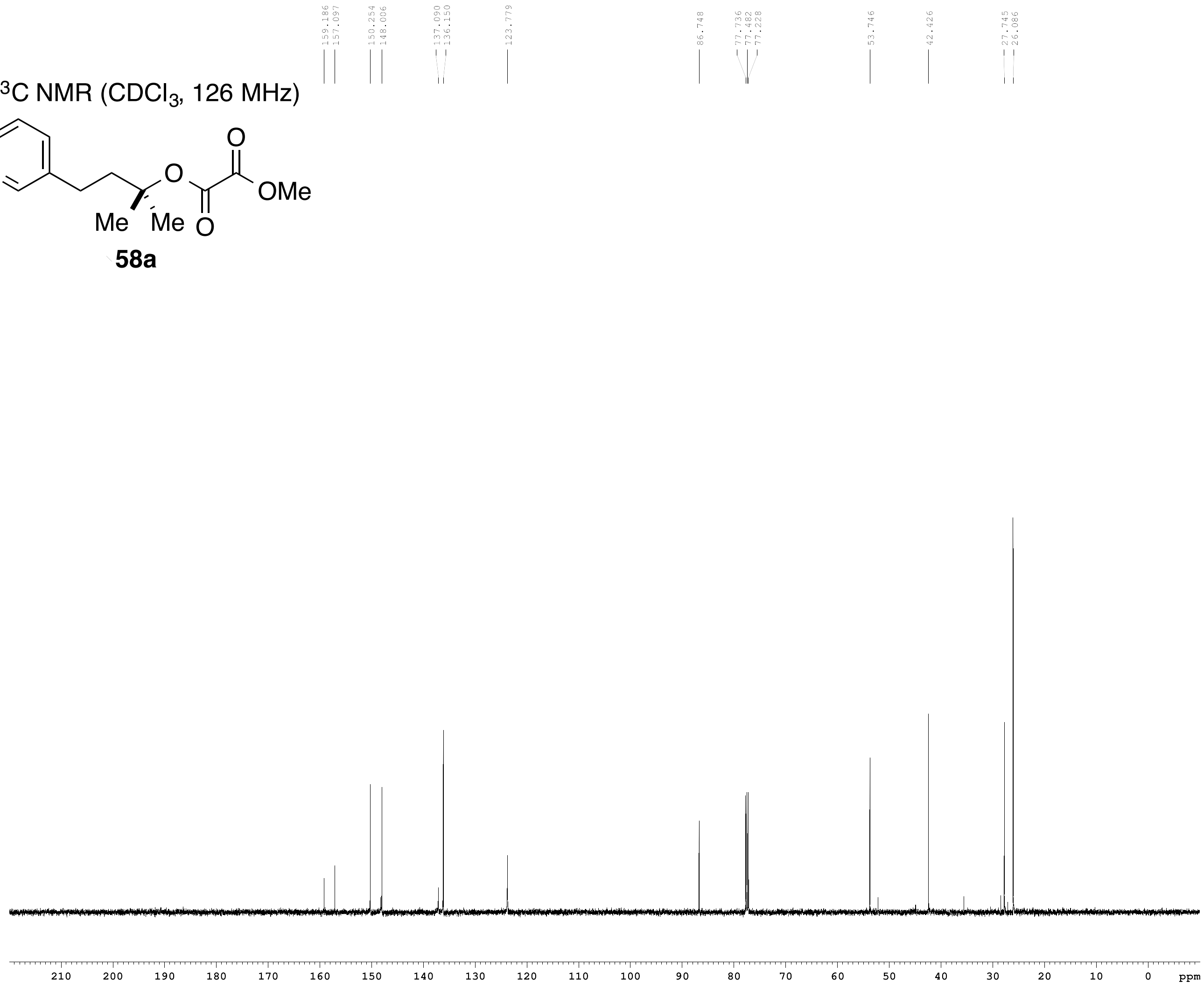
```
Current Data Parameters
NAME          YS-III-54
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150429
Time               8.29
INSTRUM           av600
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                38460
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                  161
DW               52.000 usec
DE                14.33 usec
TE                298.4 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 9.00 usec
PLW1        60.25600052 W

F2 - Processing parameters
SI                65536
SF          600.1300273 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-III-54

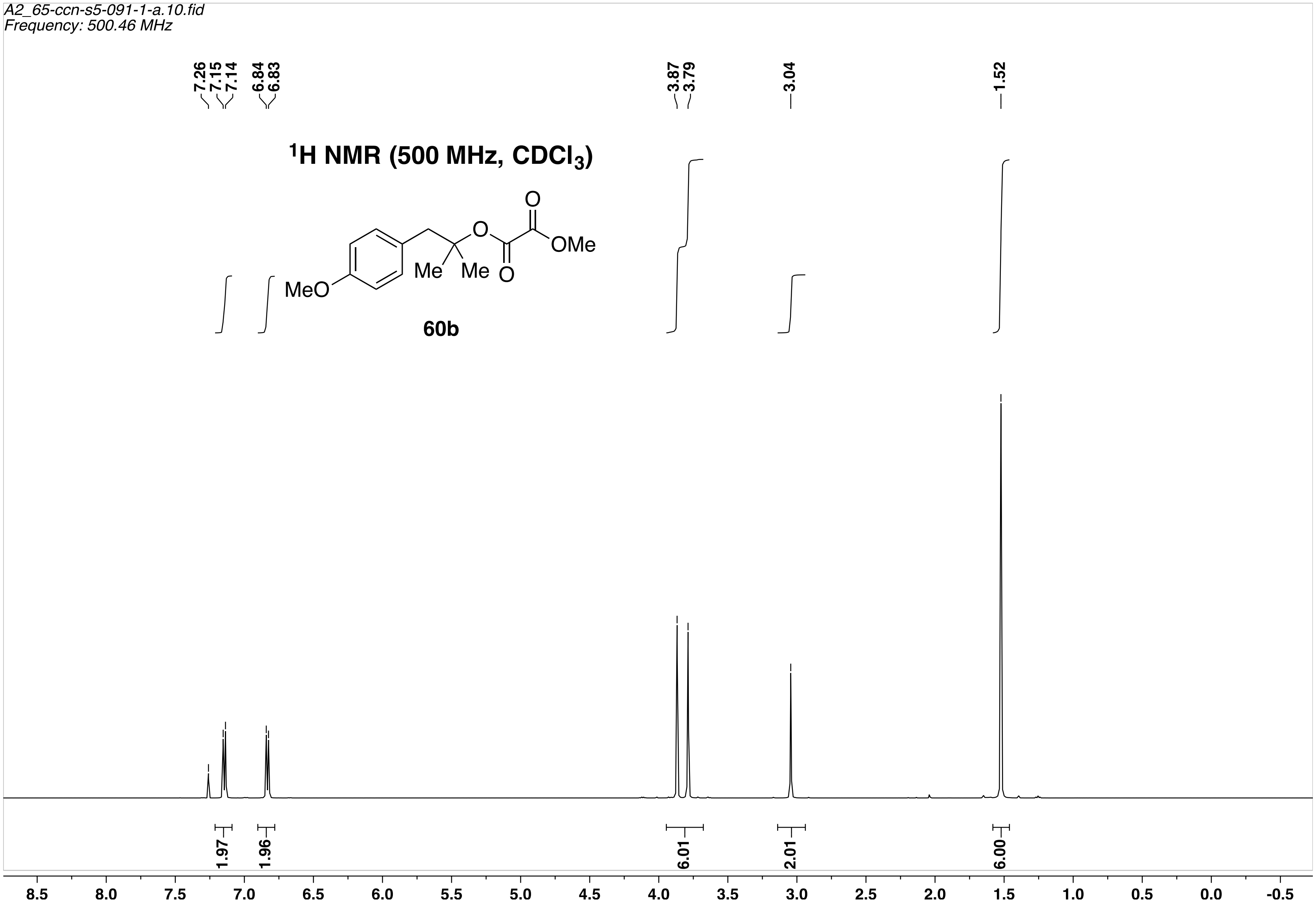
^{13}C NMR (CDCl$_3$, 126 MHz)

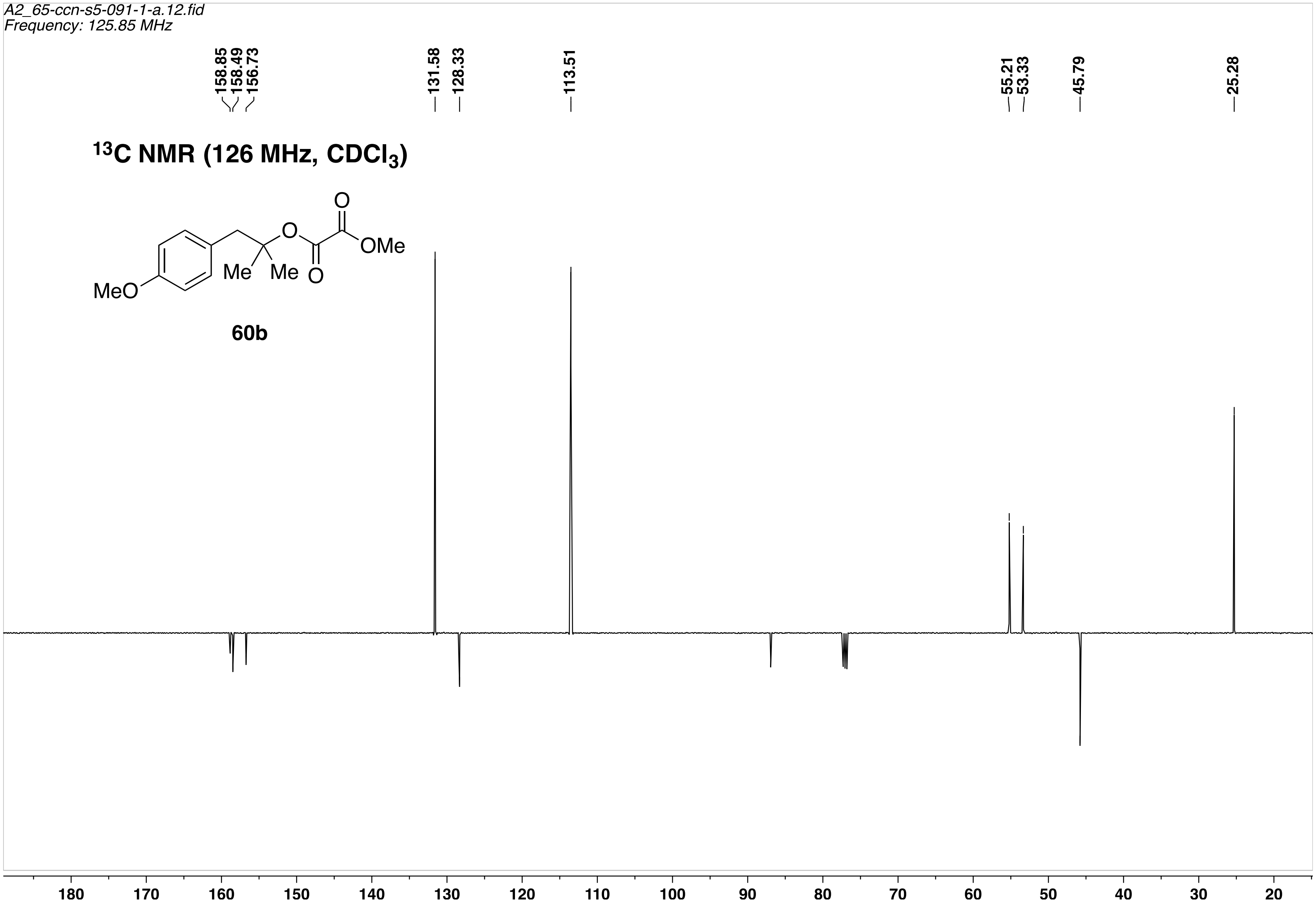


58a



```
Current Data Parameters
NAME          YS-III-54
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20150429
Time               8.22
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   56
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 4096
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803737 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```


A2_65-ccn-s5-091-1-a.10.fid
Frequency: 500.46 MHz
7.26
7.15
7.14
6.84
6.83
3.87
3.79
3.04
1.52
^{1}H NMR (500 MHz, CDCl$_3$)
MeO
Me
Me
O
O
O
OMe
60b
1.97
1.96
6.01
2.01
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

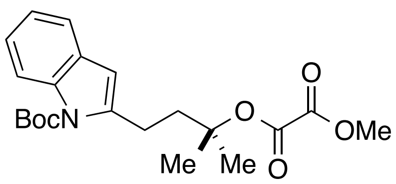


^{13}C NMR (126 MHz, $CDCl_3$)

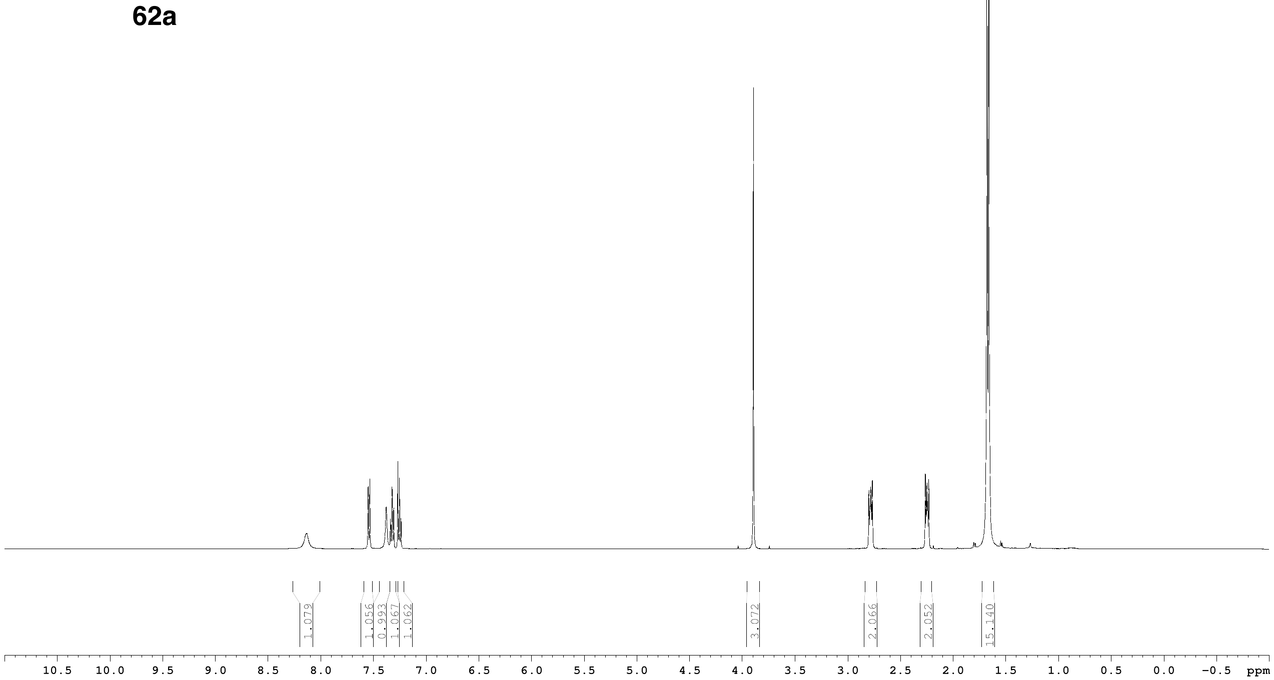
60b

YS-II-247

^{1}H NMR ($CDCl_3$, 500 MHz)



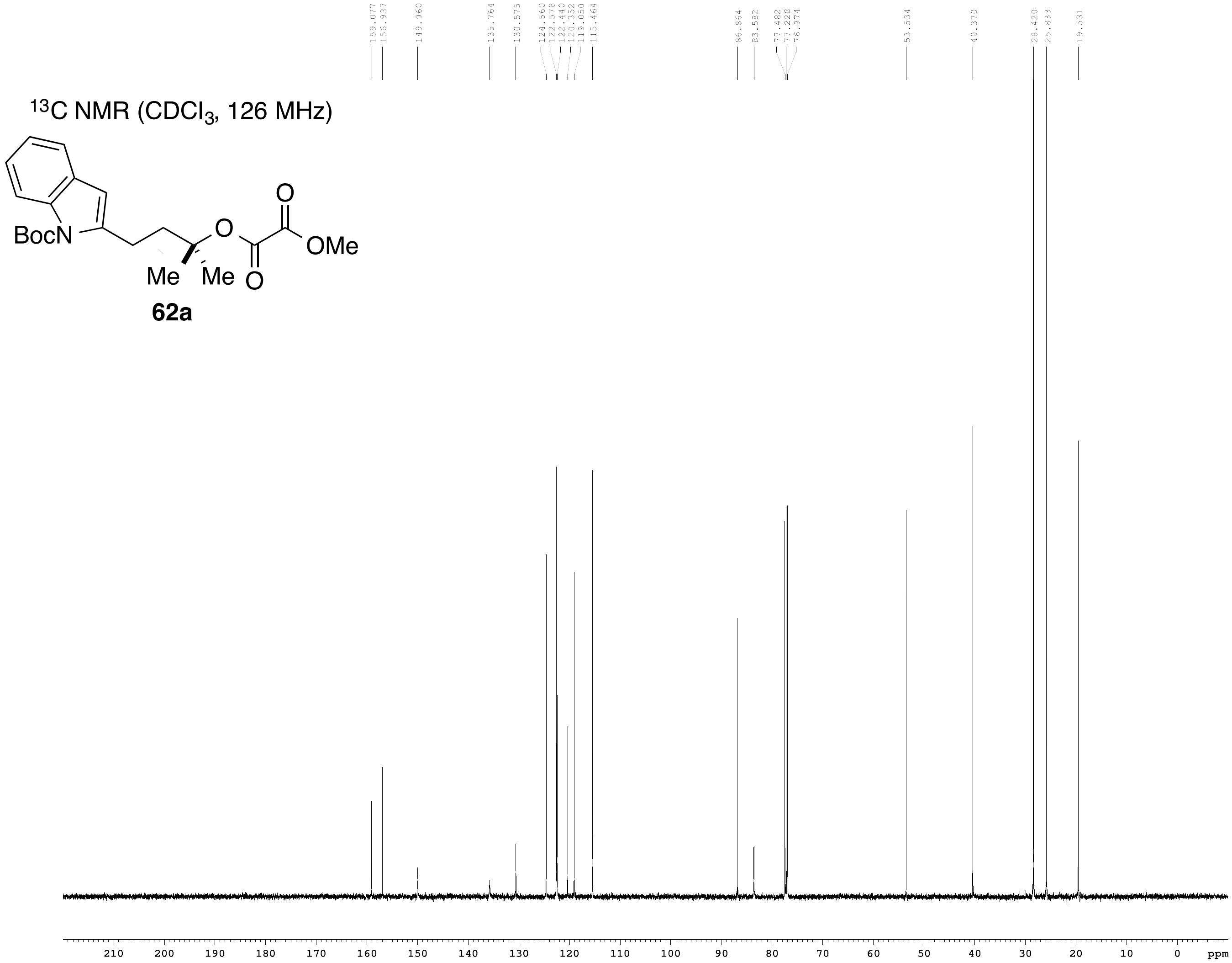
62a



```
Current Data Parameters
NAME           YS-II-247
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20150216
Time              13.21
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                  4.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200265 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-247

^{13}C NMR (CDCl$_3$, 126 MHz)

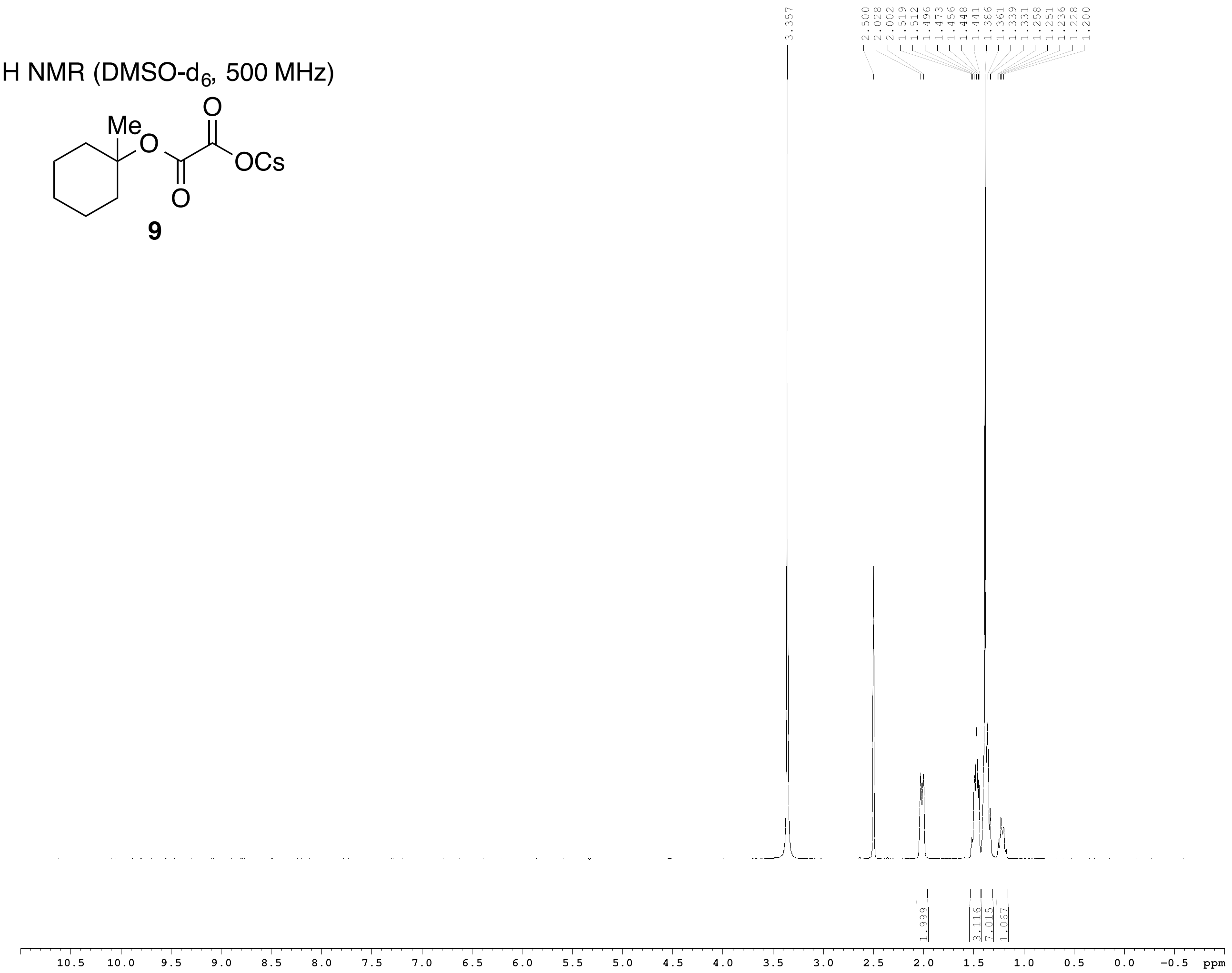


62a

```
Current Data Parameters
NAME          YS-II-247
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150216
Time              13.24
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  584
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 3251
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]      SINE.100
GPNAM[2]      SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804026 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-192

^{1}H NMR (DMSO-d$_6$, 500 MHz)

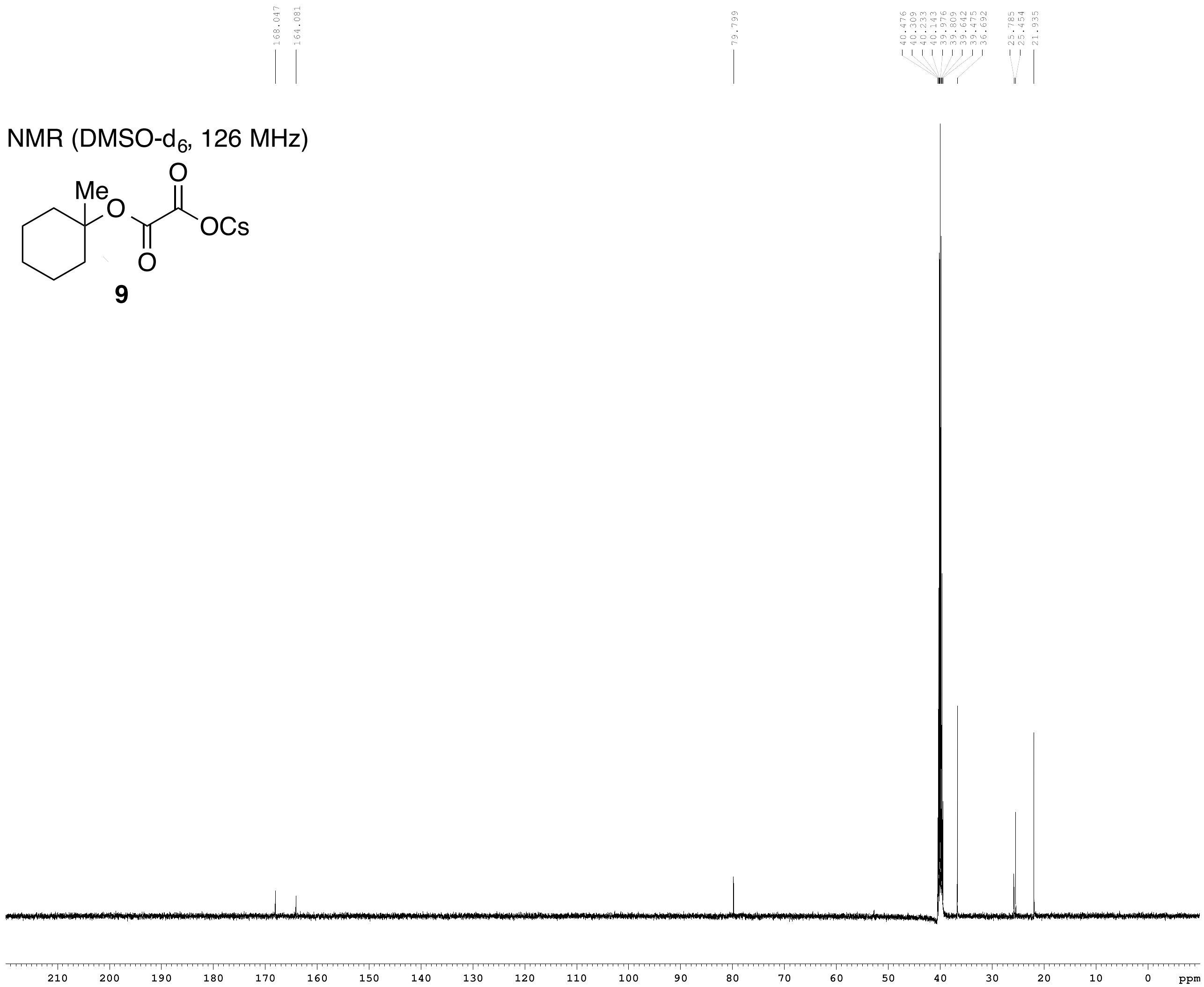


9

```
Current Data Parameters
NAME          YS-II-192
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150120
Time              14.17
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                16022
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.500114 Hz
AQ            0.9997728 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                297.8 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200134 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-192

^{13}C NMR (DMSO-d_6, 126 MHz)

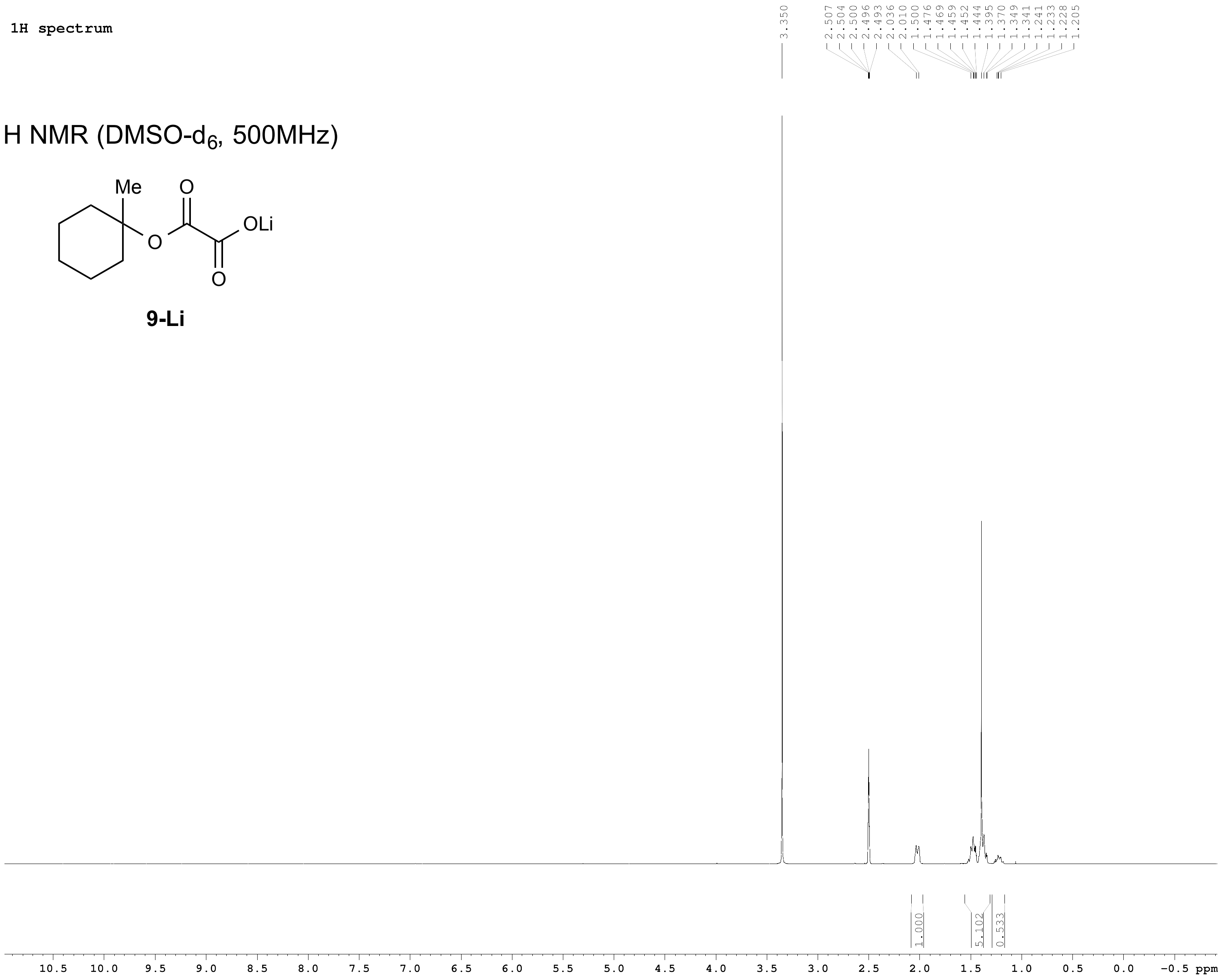


9

```
Current Data Parameters
NAME          YS-II-192
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150120
Time              14.19
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  232
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                297.9 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804190 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

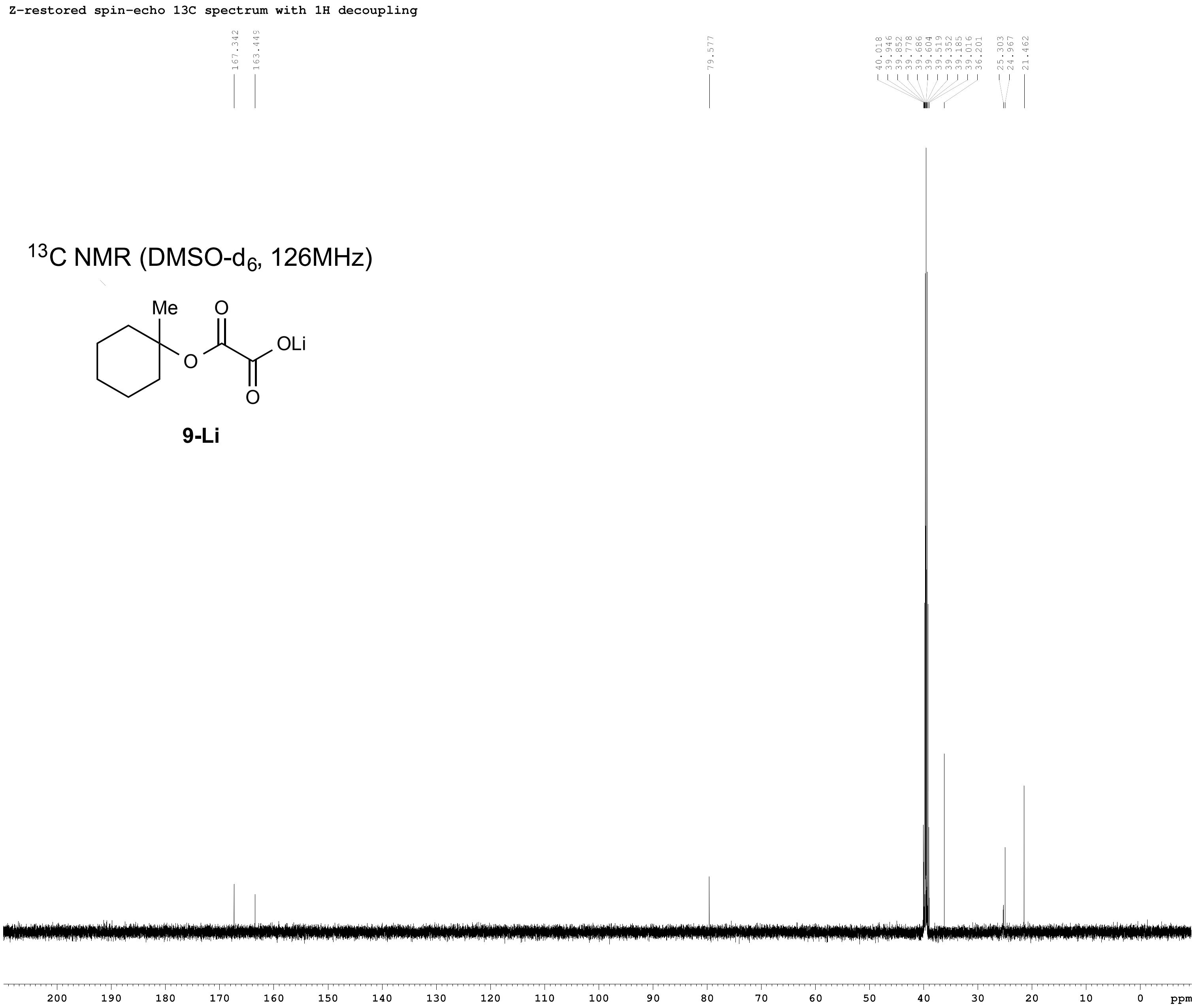
1H spectrum

^{1}H NMR (DMSO-d$_6$, 500MHz)



9-Li

```
Current Data Parameters
NAME         CRJ1-177-Li
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20150401
Time              14.03
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998176 sec
RG                 14.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200122 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```

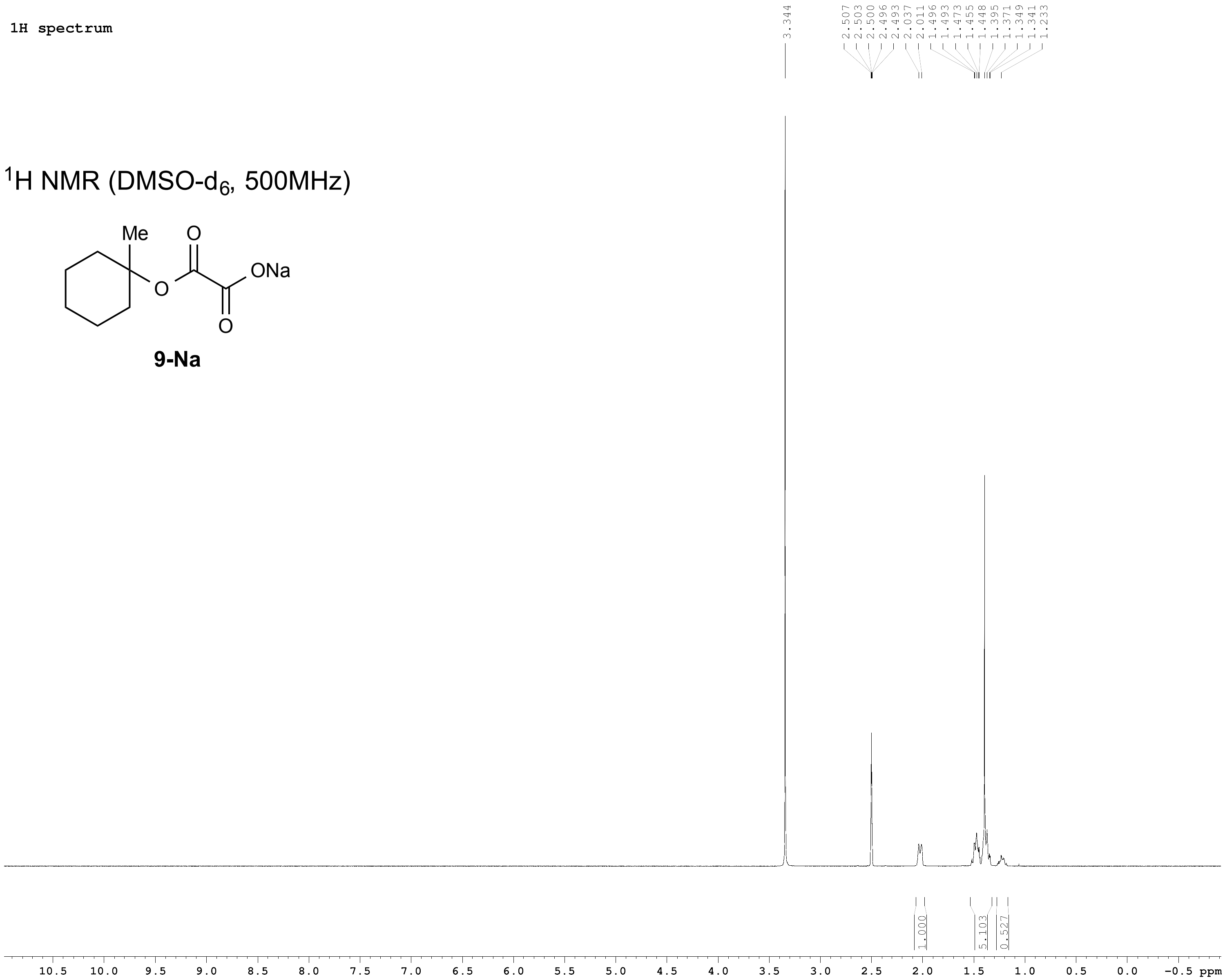


```
Current Data Parameters
NAME        CRJ1-177-Li
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150401
Time              14.06
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   64
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               2580.3
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804773 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 2.00
```

1H spectrum

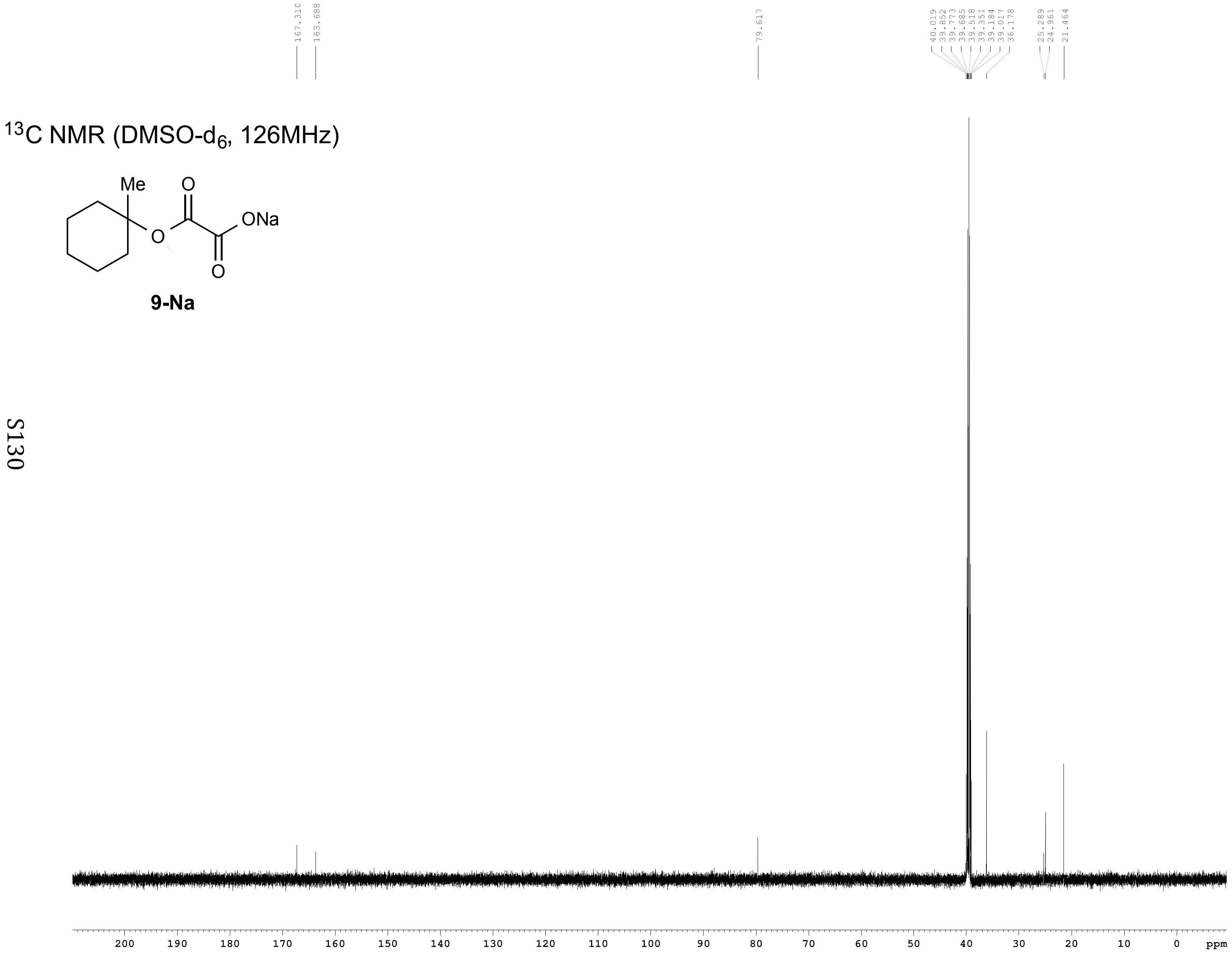
^{1}H NMR (DMSO-d$_6$, 500MHz)

9-Na



```
Current Data Parameters
NAME        CRJ1-177-Na
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150401
Time              14.11
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                   18
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200122 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling



^{13}C NMR (DMSO-d$_6$, 126MHz)

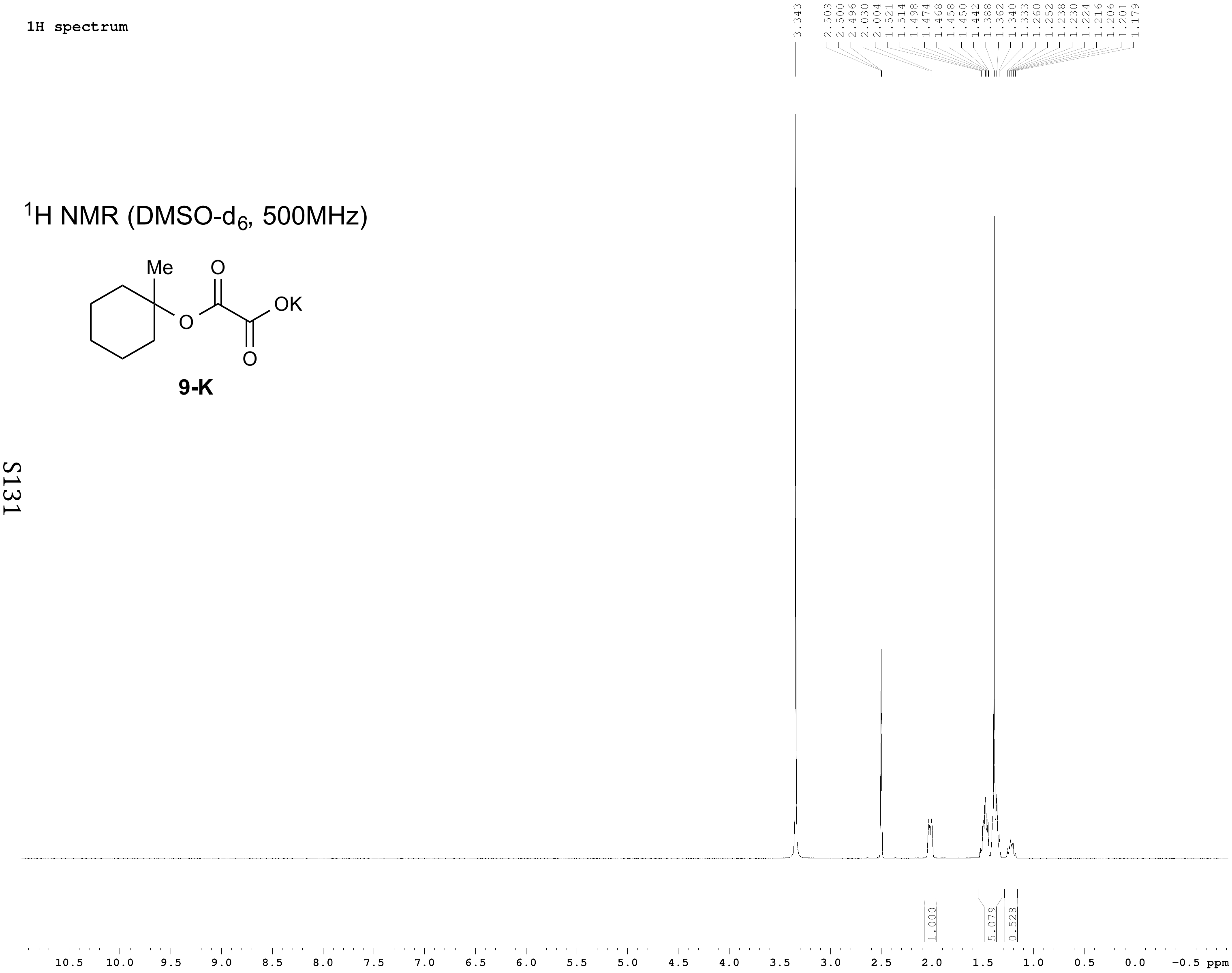
9-Na

```
Current Data Parameters
NAME        CRJ1-177-Na
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150401
Time              14.12
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDC13
NS                   64
DS                    2
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 8192
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804777 MHz
WDW                  no
SSB       0
LB        0 Hz
GB        0
PC                 2.00
```

1H spectrum

^{1}H NMR (DMSO-d_6, 500MHz)

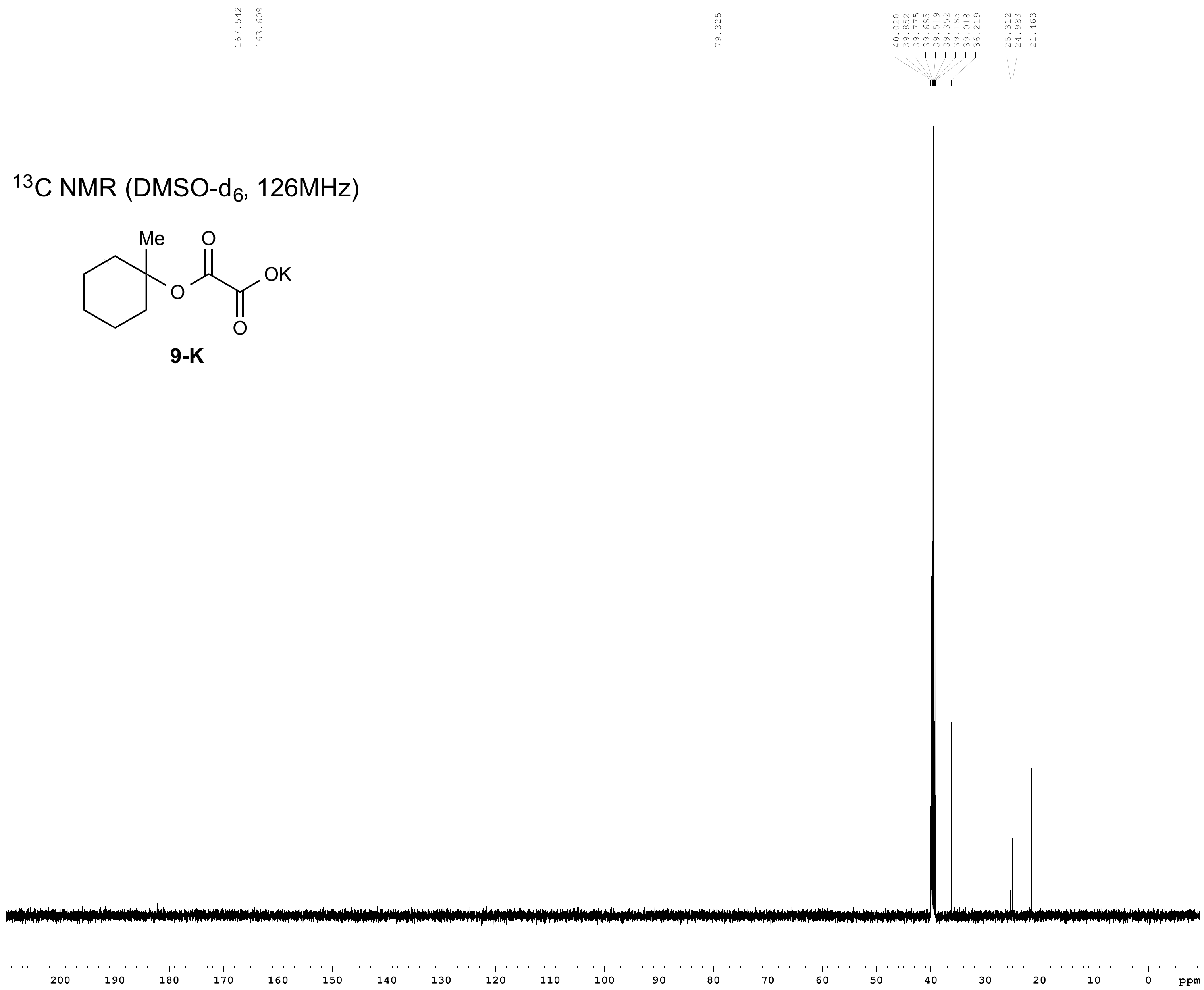
9-K



```
Current Data Parameters
NAME          CRJ1-177-K
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150401
Time               14.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9997952 sec
RG                  20.2
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200121 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling

^{13}C NMR (DMSO-d_6, 126MHz)

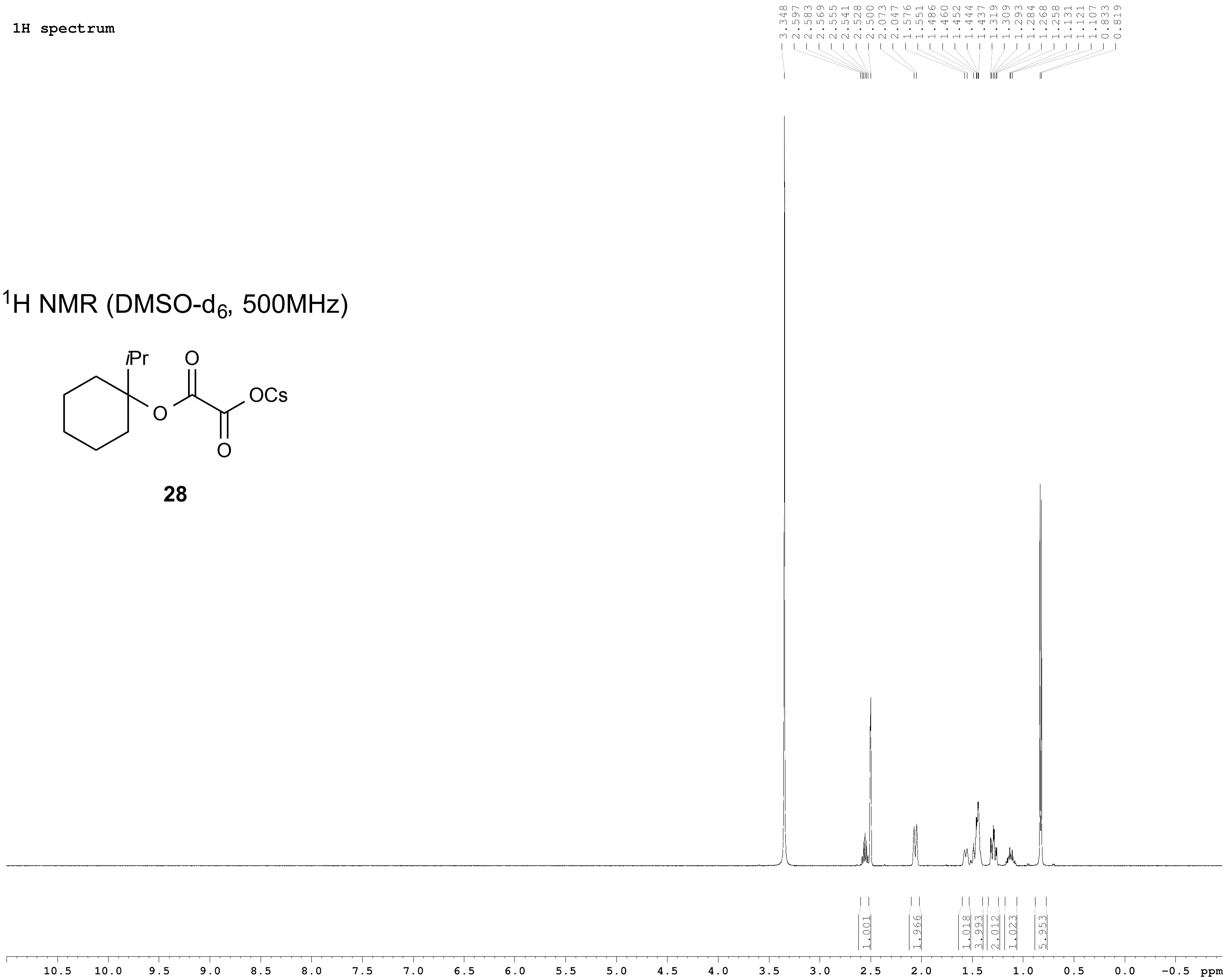


9-K

```
Current Data Parameters
NAME          CRJ1-177-K
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150401
Time               14.18
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                    80
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804779 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  2.00
```

1H spectrum

^{1}H NMR (DMSO-d_6, 500MHz)



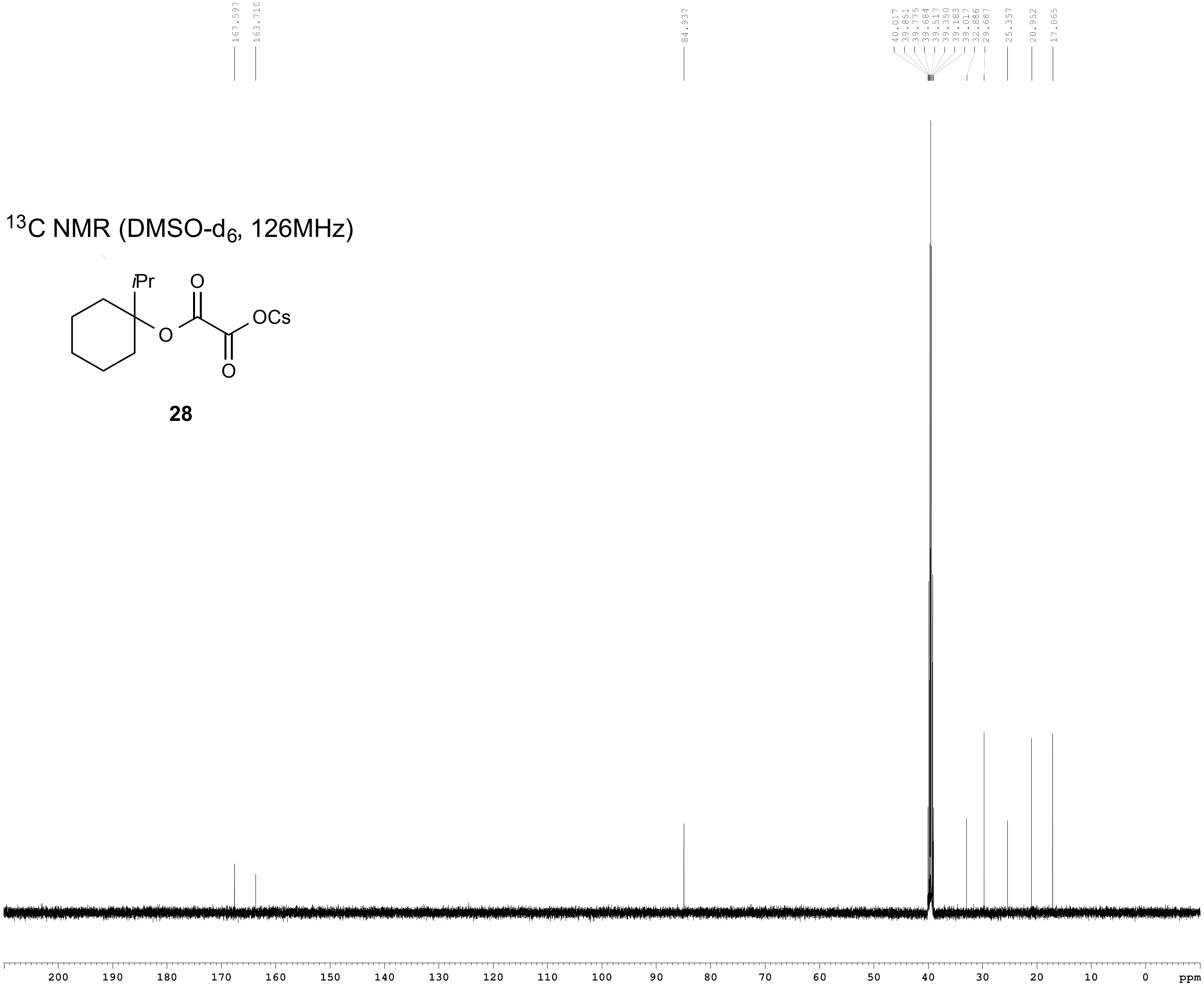
28

```
Current Data Parameters
NAME          CRJ1-094-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150223
Time               13.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                  10.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1           3.00000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200136 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling

^{13}C NMR (DMSO-d$_6$, 126MHz)

28

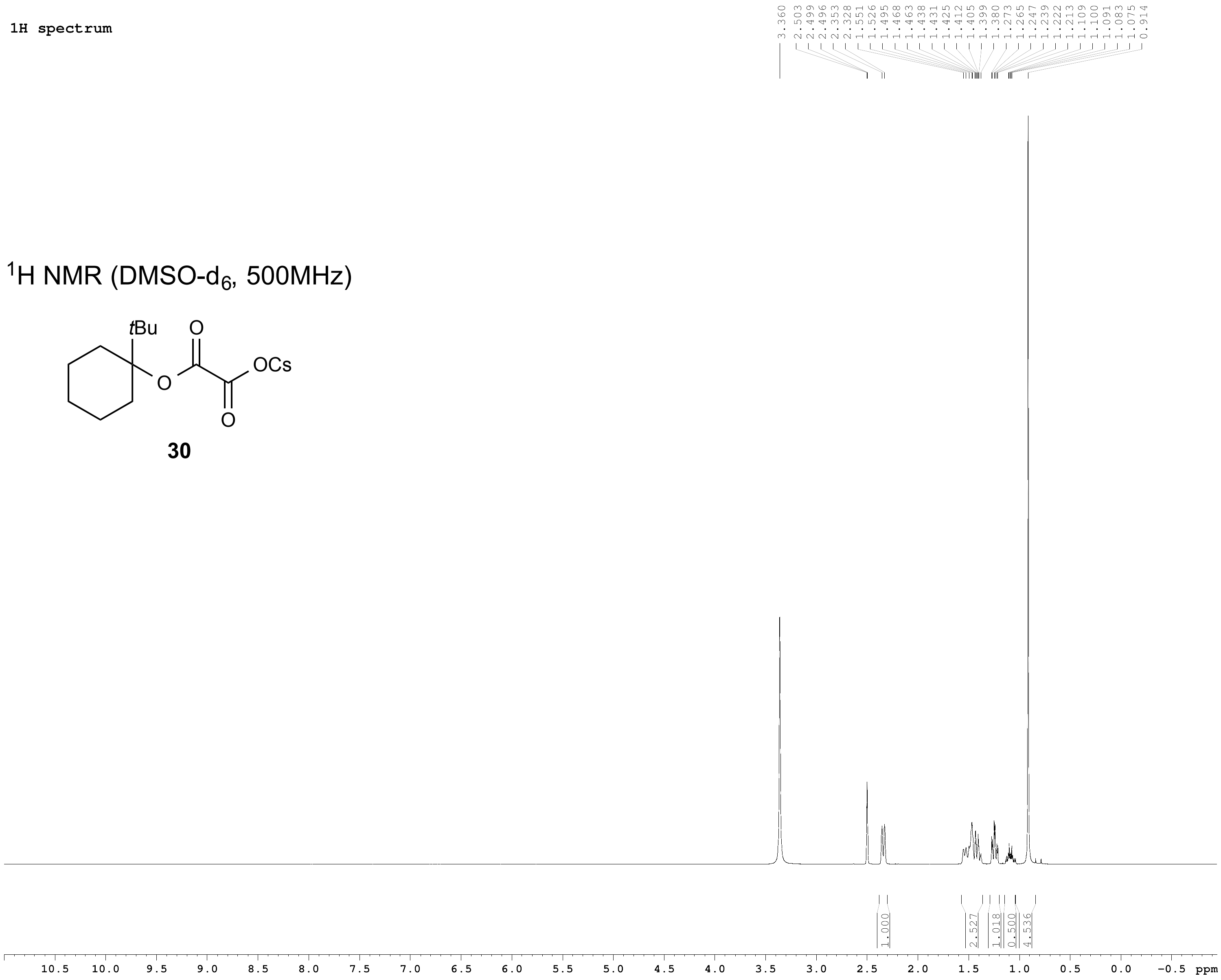


```
Current Data Parameters
NAME          CRJ1-094-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150223
Time               13.21
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDC13
NS                   128
DS                     4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF          125.7804783 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                  2.00
```

1H spectrum

^{1}H NMR (DMSO-d_6, 500MHz)

30

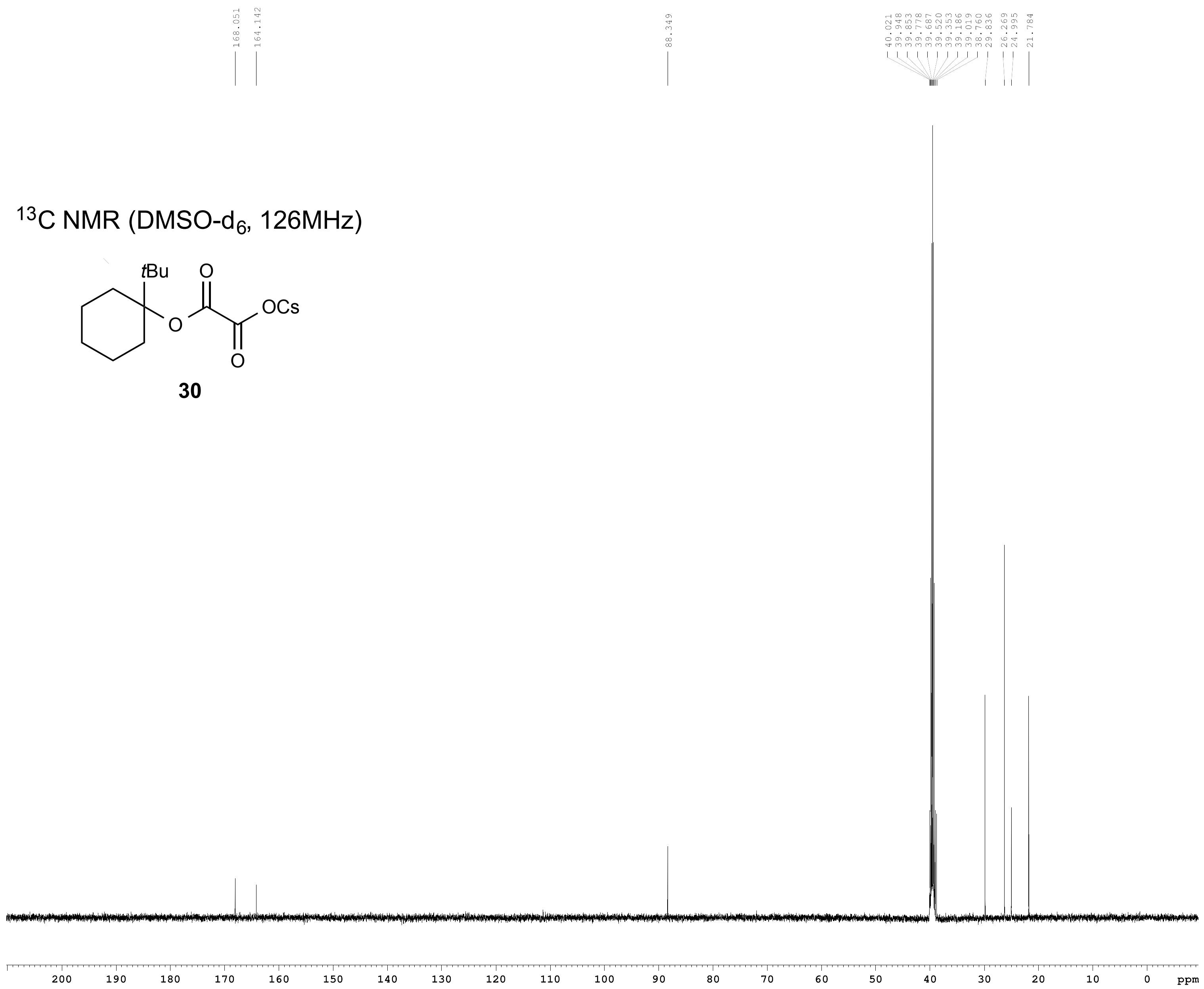


```
Current Data Parameters
NAME       CRJ1-127-pure
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20150311
Time              11.16
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998176 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200127 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling

^{13}C NMR (DMSO-d_6, 126MHz)

30

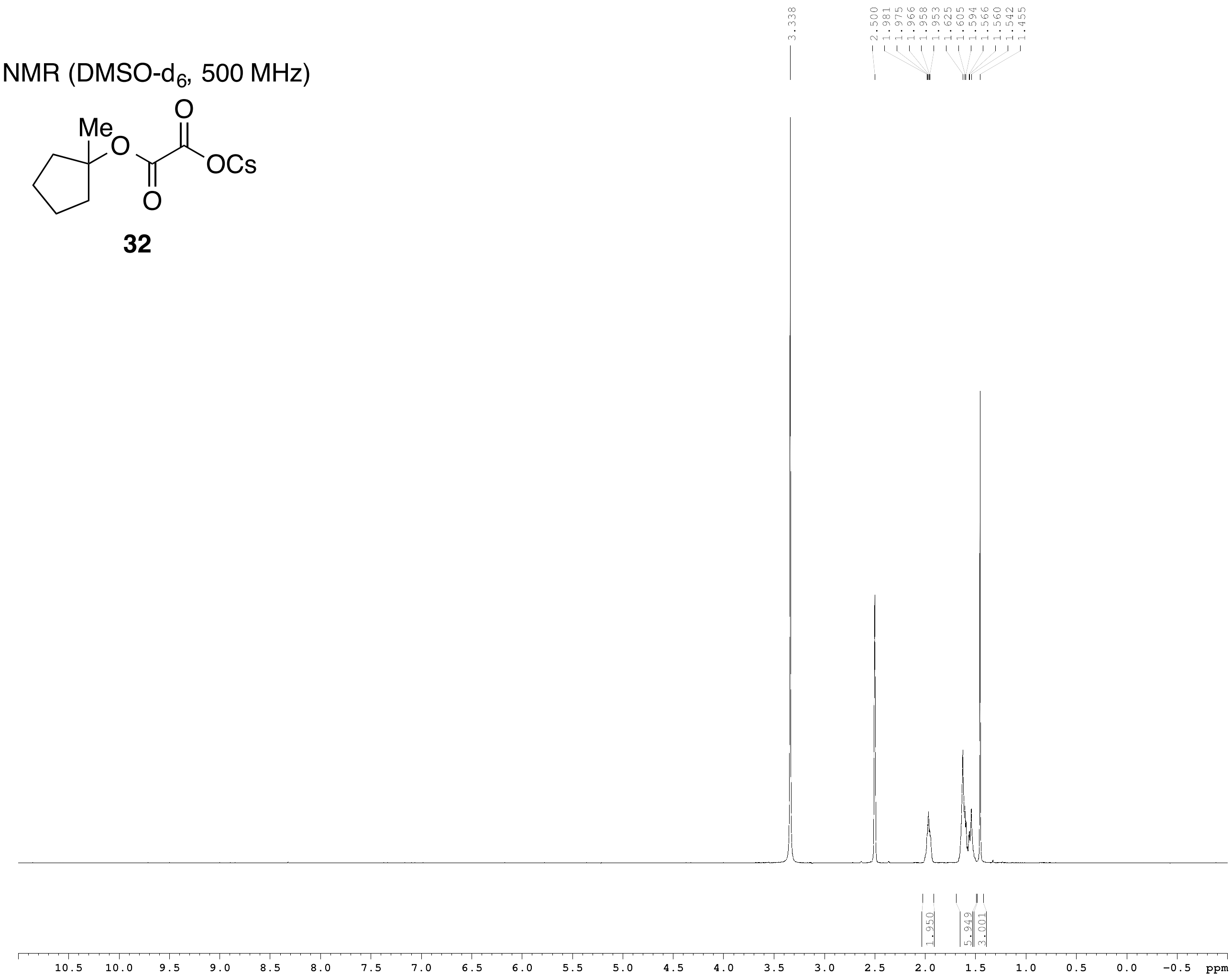


```
Current Data Parameters
NAME      CRJ1-127-pure
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150311
Time              11.18
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 3251
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804769 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-243

^{1}H NMR (DMSO-d_6, 500 MHz)

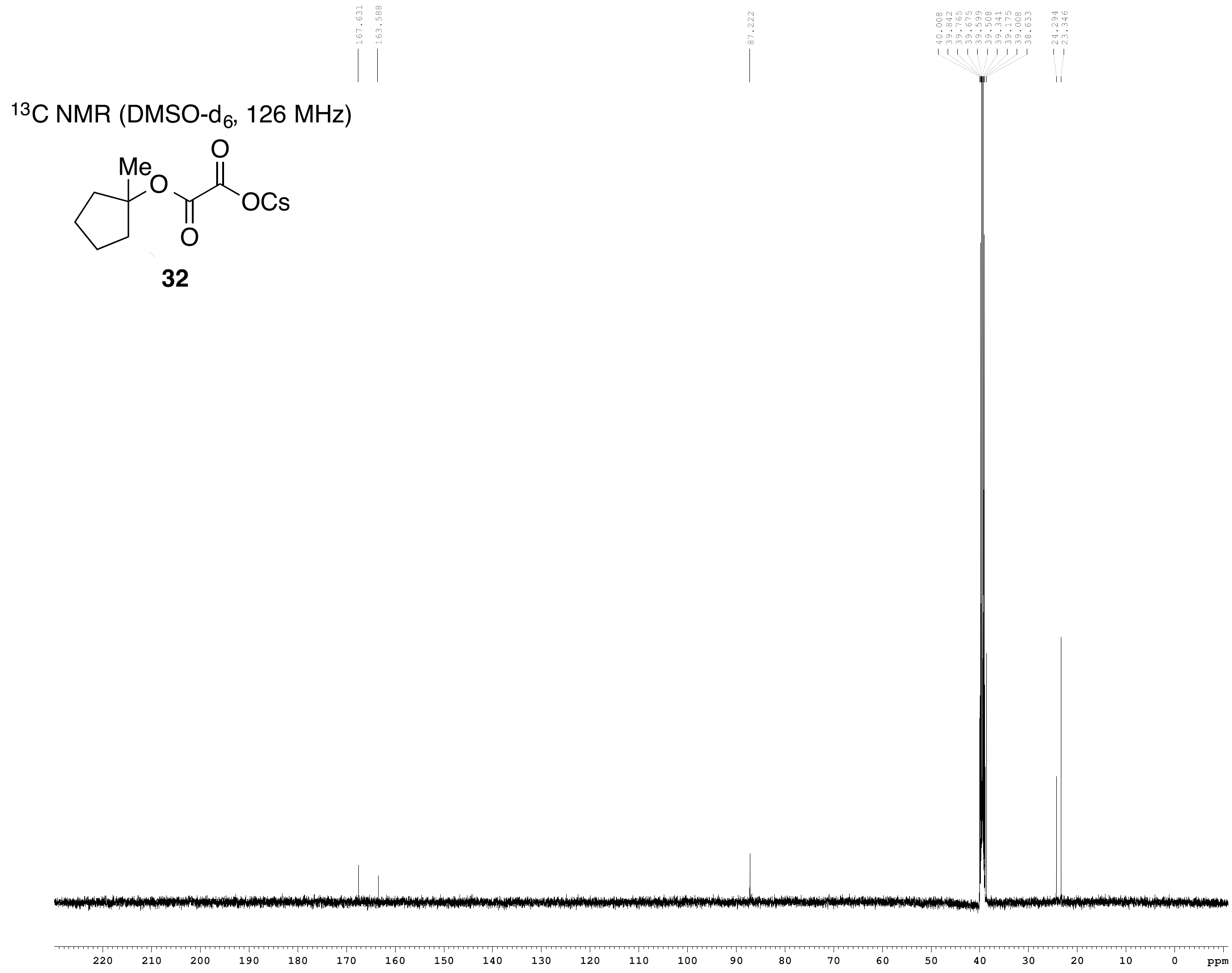
32



```
Current Data Parameters
NAME          YS-II-243
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150213
Time               8.59
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                 10.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1       500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200119 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

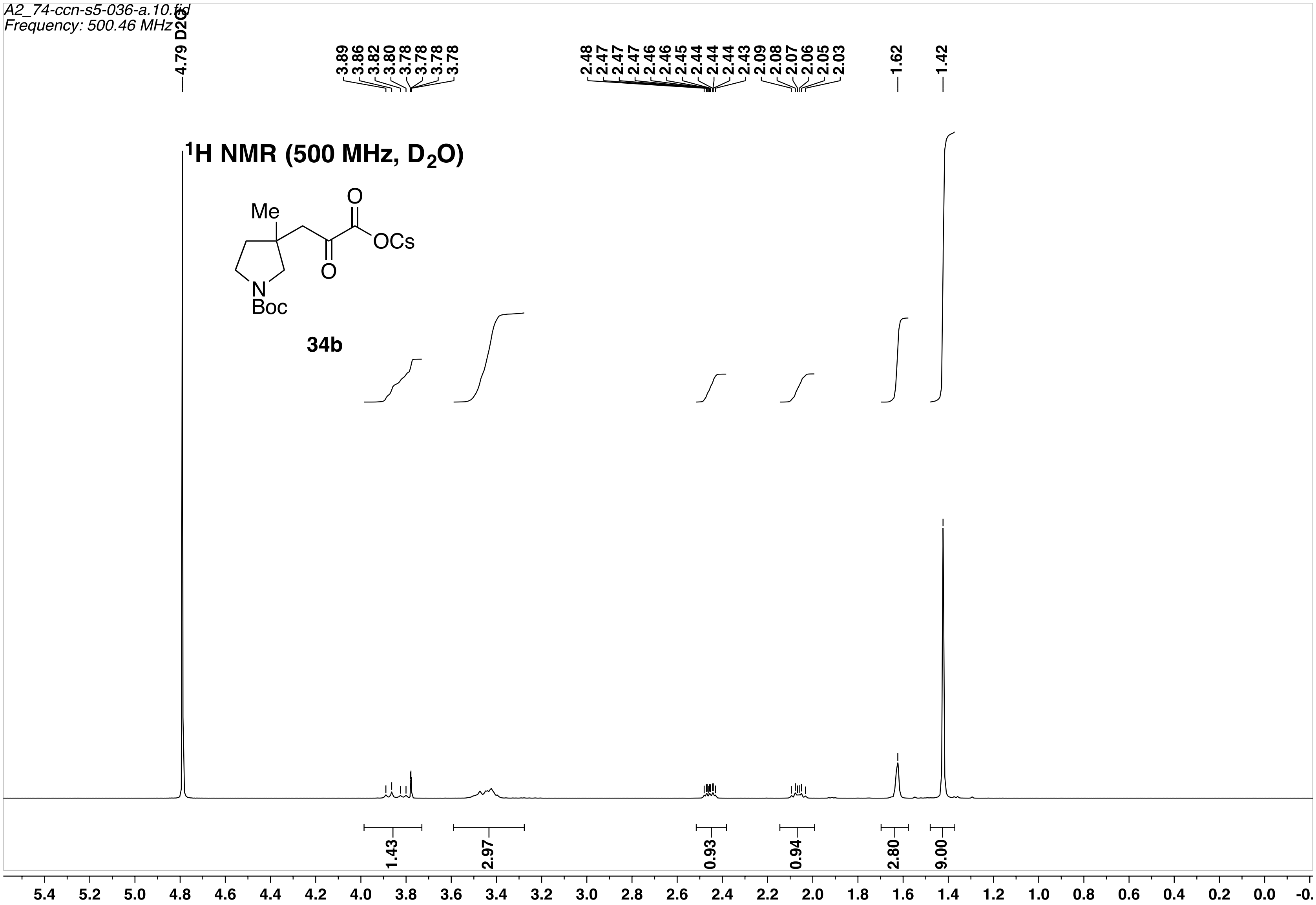
YS-II-243

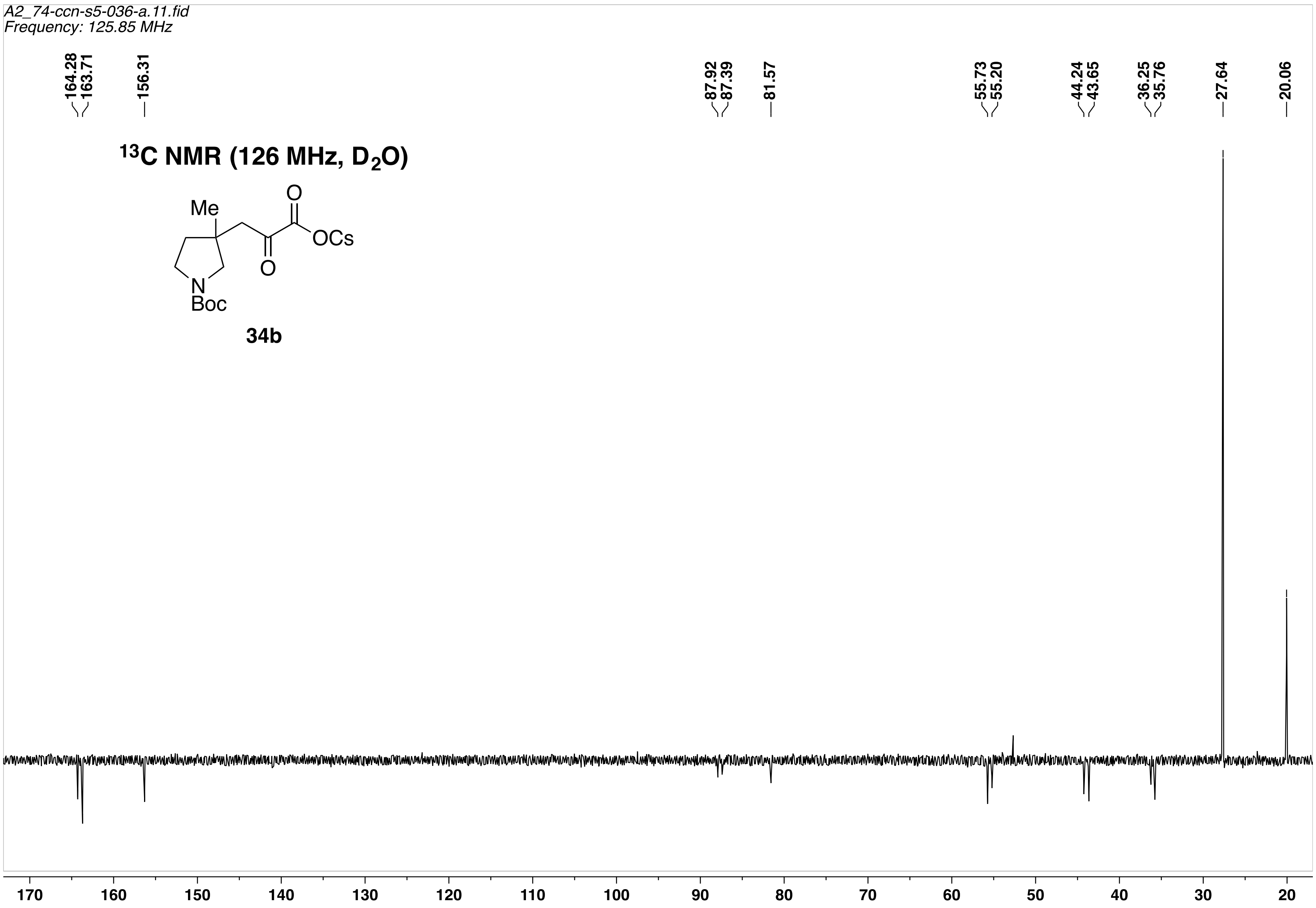
13C NMR (DMSO-d_6, 126 MHz)



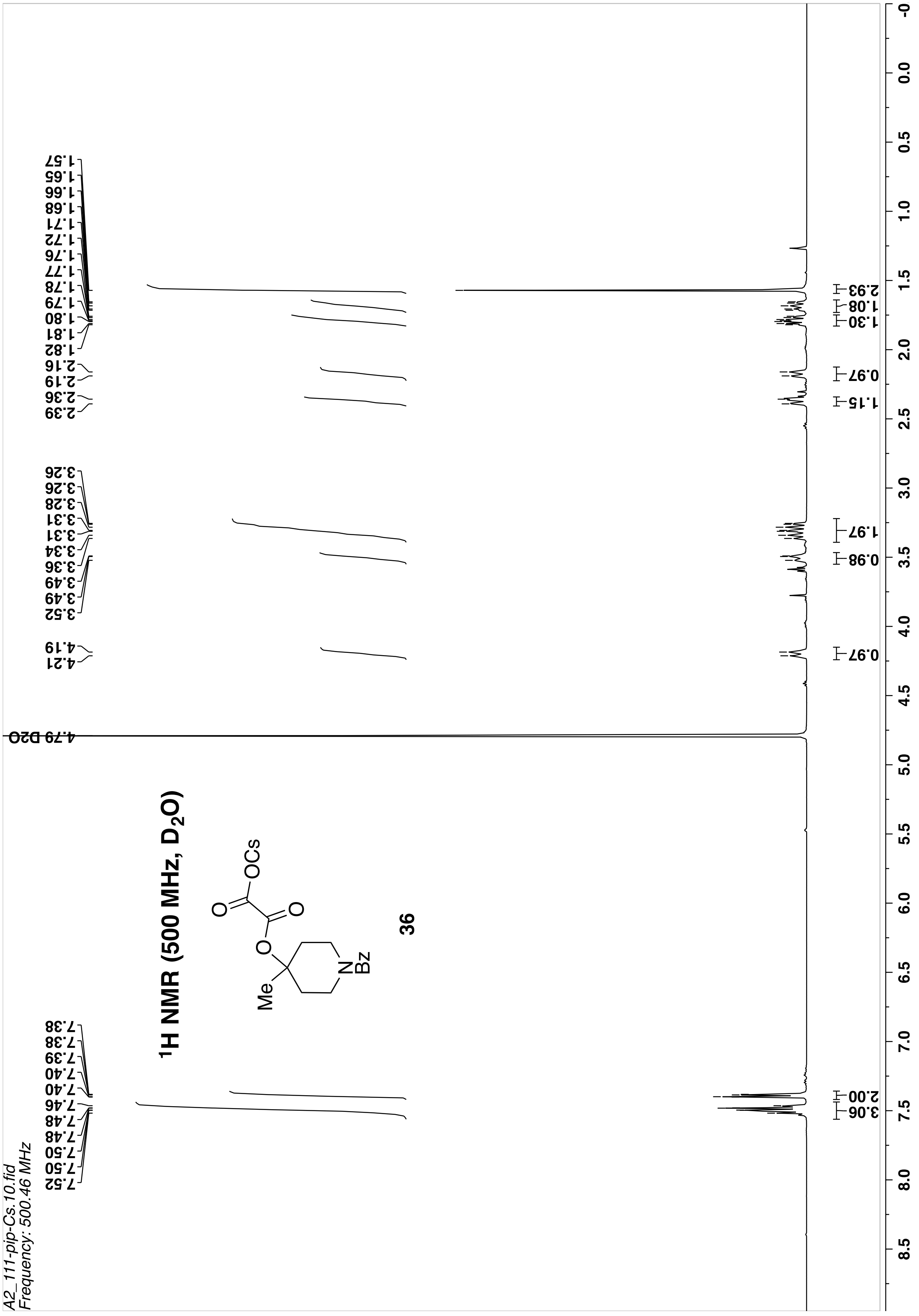
32

```
Current Data Parameters
NAME          YS-II-243
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150213
Time               9.02
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                  400
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               5792.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804792 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

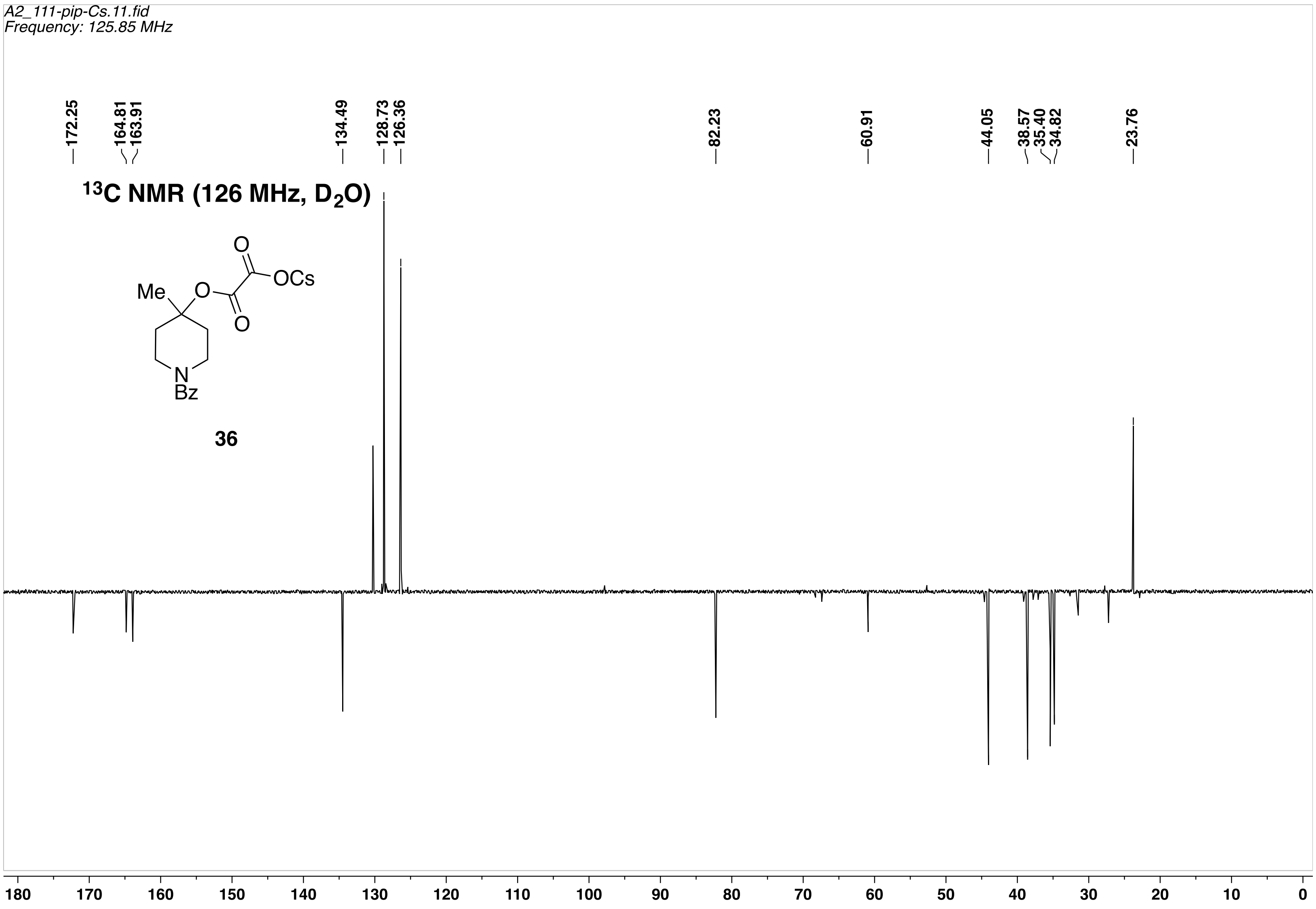

A2_74-ccn-s5-036-a.10.fid
Frequency: 500.46 MHz
4.79 D2O
3.89
3.86
3.82
3.80
3.78
3.78
3.78
3.78
2.48
2.47
2.47
2.46
2.46
2.45
2.44
2.44
2.44
2.43
2.09
2.08
2.07
2.06
2.05
2.03
1.62
1.42
1H NMR (500 MHz, D2O)
Me
O
OCs
O
N
Boc
34b
1.43
2.97
0.93
0.94
2.80
9.00
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.


^{13}C NMR (126 MHz, D_2O)

34b

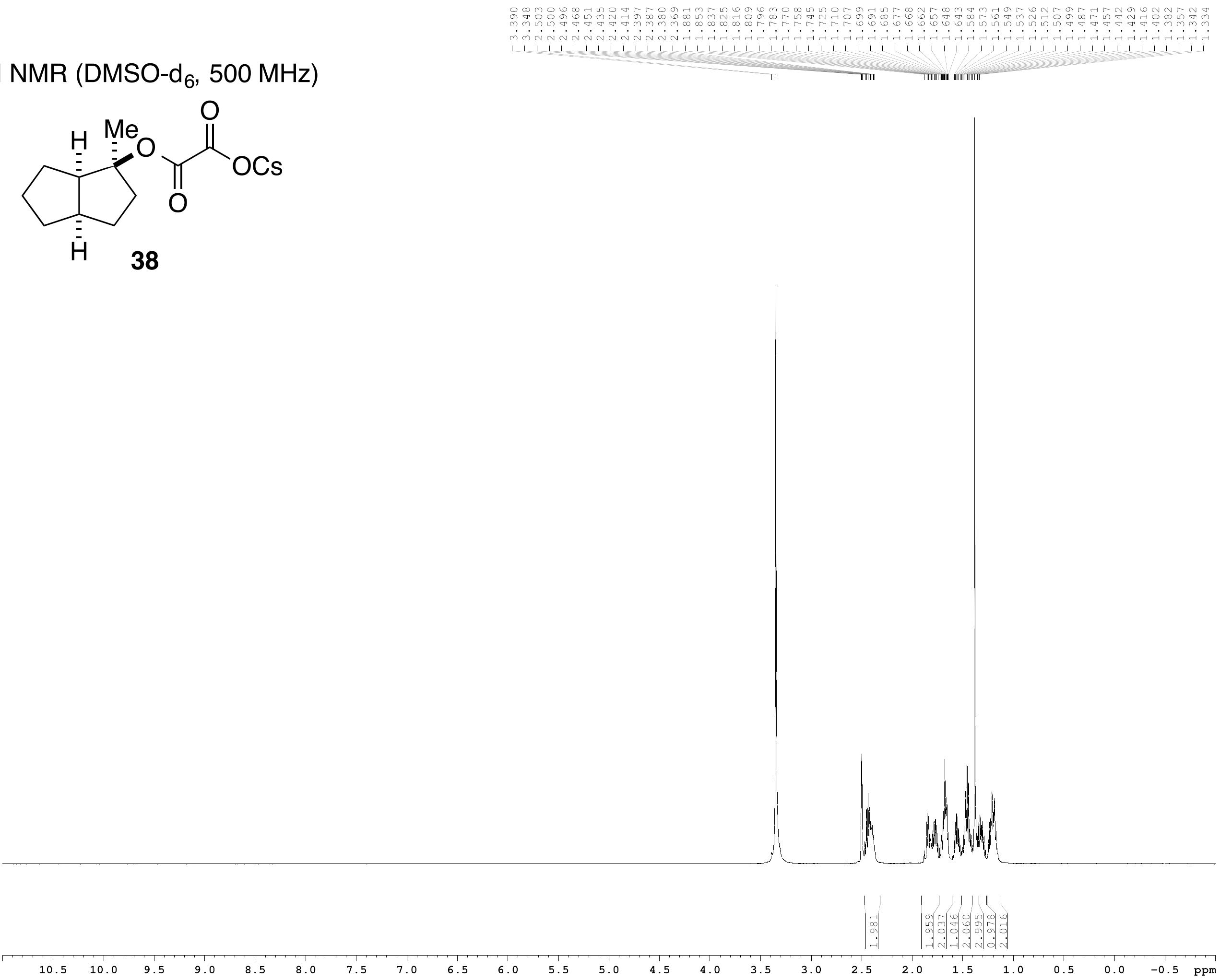

A2_111-pip-Cs.10.fid
Frequency: 500.46 MHz
1H NMR (500 MHz, D2O)
OCs
O
O
O
Me
N
Bz
7.52
7.50
7.50
7.48
7.48
7.46
7.40
7.40
7.39
7.38
7.38
4.79 D2O
4.21
4.19
3.52
3.49
3.49
3.36
3.34
3.31
3.31
3.28
3.26
3.26
2.39
2.36
2.19
2.16
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.72
1.71
1.68
1.66
1.65
1.57
3.06
2.00
0.97
0.98
1.97
1.15
0.97
1.30
1.08
2.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

36


A2_111-pip-Cs.11.fid
Frequency: 125.85 MHz
172.25
164.81
163.91
134.49
128.73
126.36
82.23
60.91
44.05
38.57
35.40
34.82
23.76
^{13}C NMR (126 MHz, D$_2$O)
Me
O
O
O
OCs
N
Bz
36
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

YS-II-288

^{1}H NMR (DMSO-d$_6$, 500 MHz)

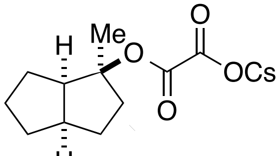


38

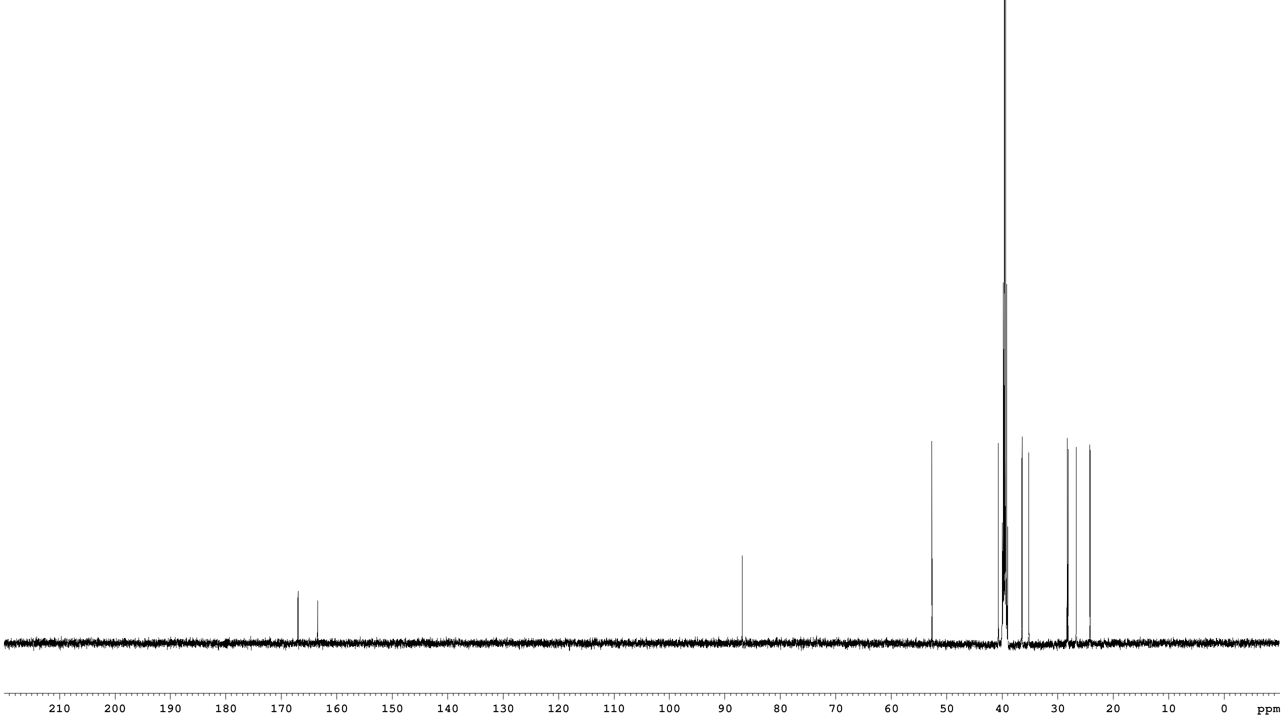
```
Current Data Parameters
NAME          YS-II-288
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150306
Time              18.00
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG            zg30
TD                32048
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                574.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -5.80 dB
SFO1        499.1834943 MHz

F2 - Processing parameters
SI                65536
SF          499.1800085 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-II-288

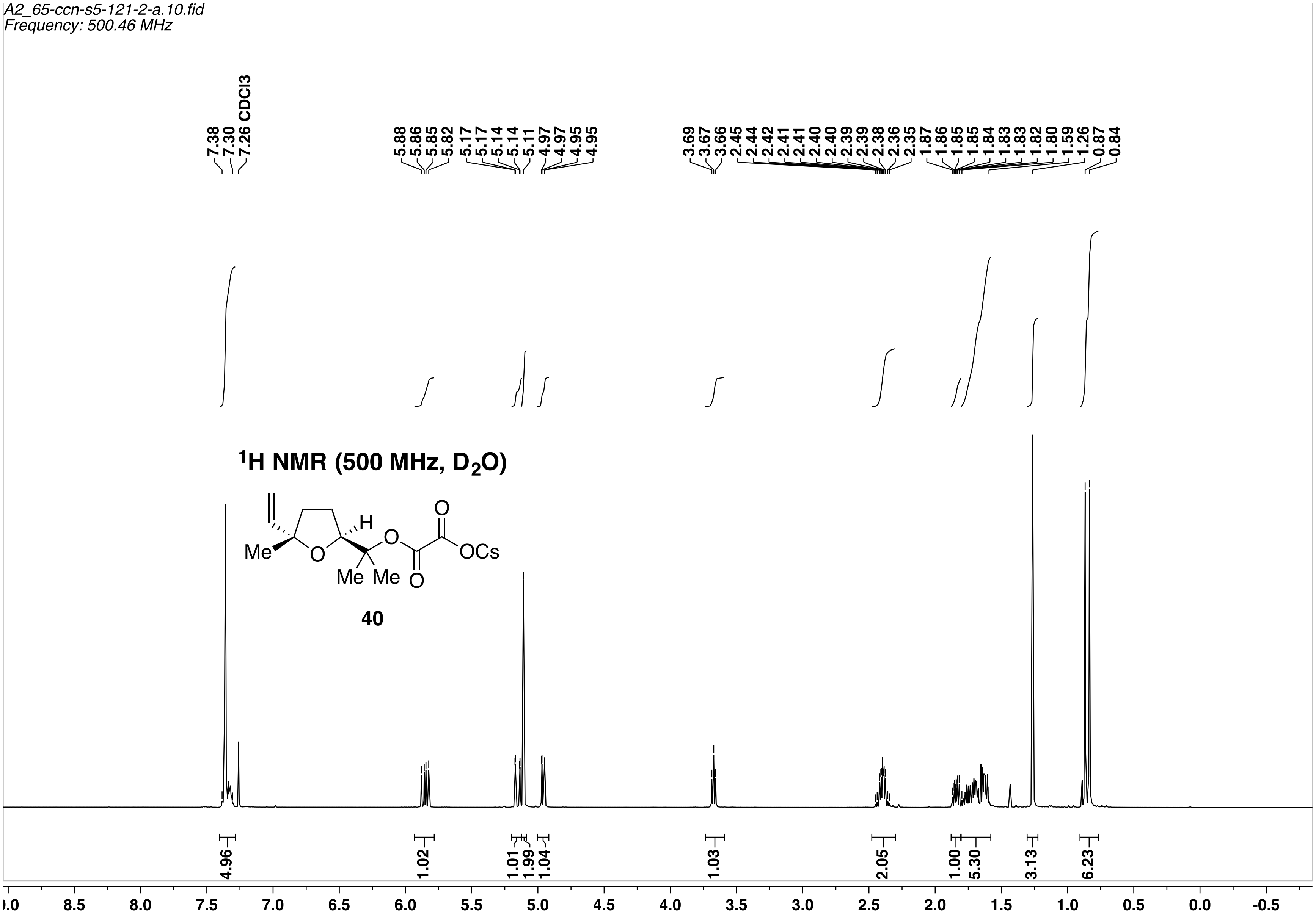
^{13}C NMR (DMSO-d_6, 126 MHz)



38

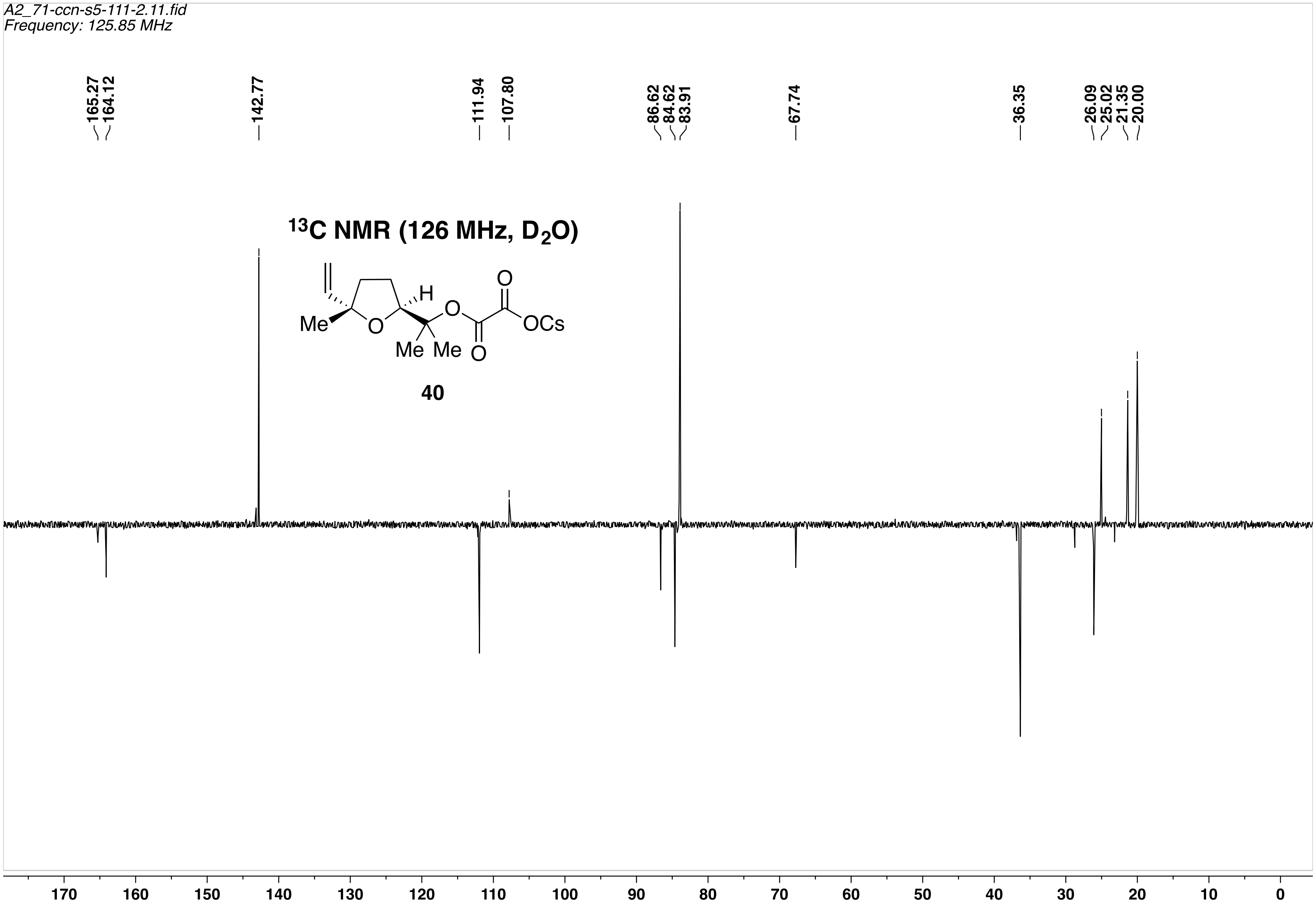


```
Current Data Parameters
NAME            YS-II-288
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150309
Time                10.56
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT              DMSO
NS                    248
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                10321.3
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1       0 %
GPX2       0 %
GPY1       0 %
GPY2       0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804793 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```



^{1}H NMR (500 MHz, D_2O)

40



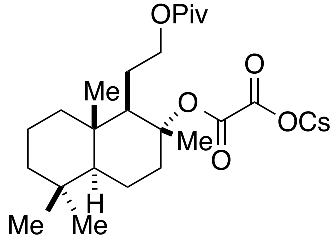
A2_71-ccn-s5-111-2.11.fid
Frequency: 125.85 MHz

^{13}C NMR (126 MHz, D_2O)

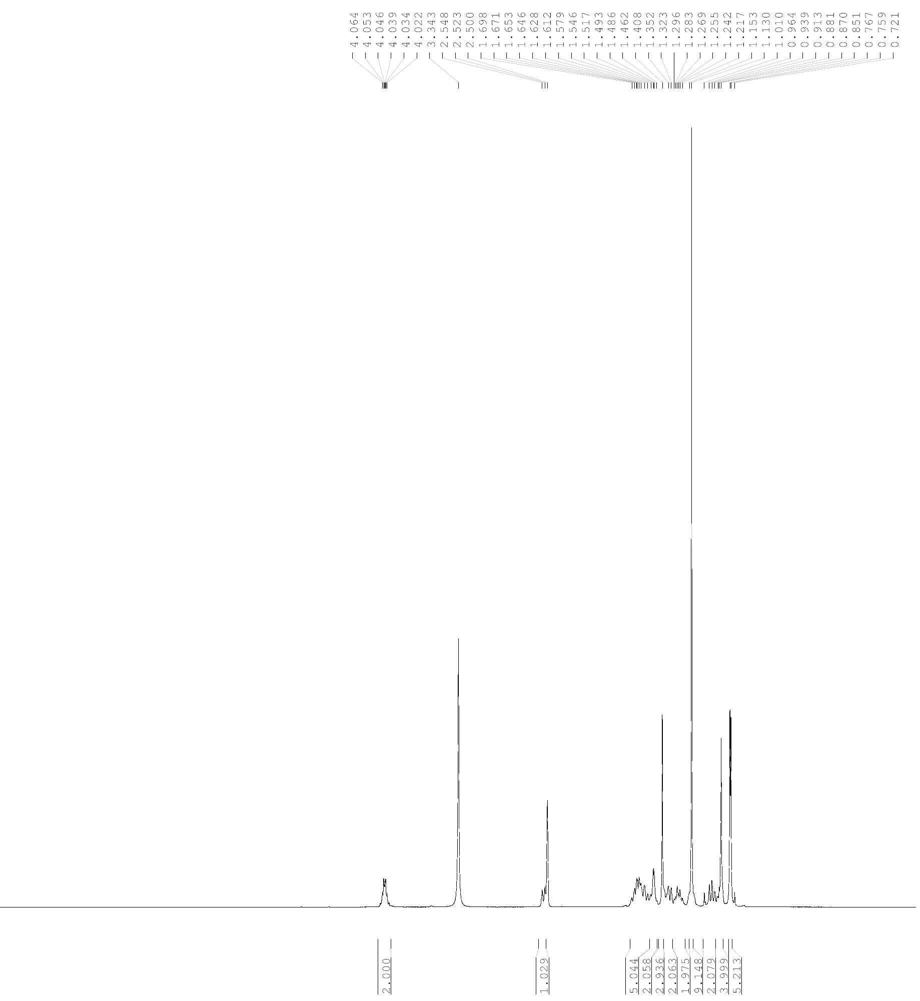
40

YS-II-268

^{1}H NMR (DMSO-d_6, 500 MHz)



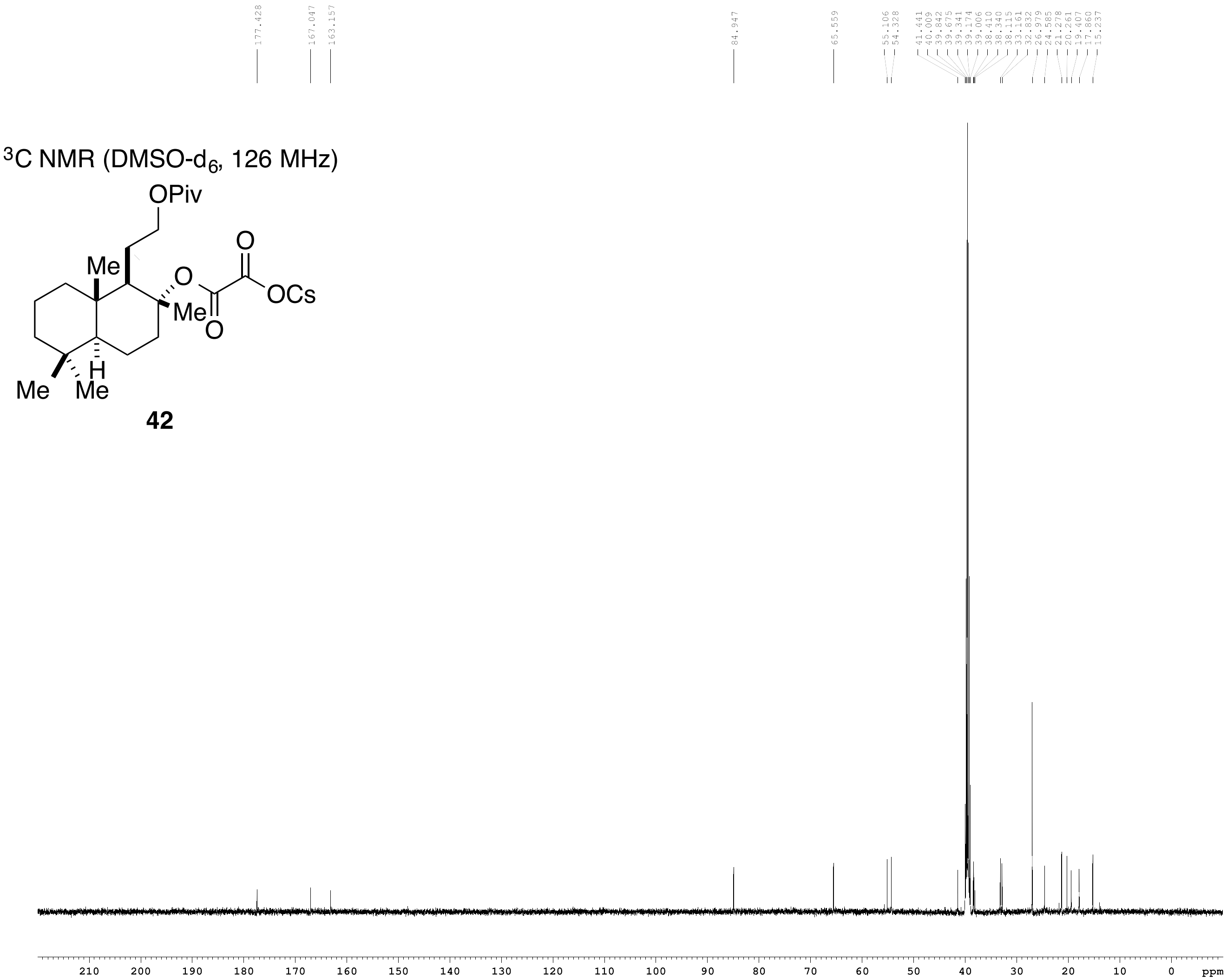
42



```
Current Data Parameters
NAME          YS-II-268
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150225
Time               9.44
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                  7.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200128 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-268

^{13}C NMR (DMSO-d$_6$, 126 MHz)



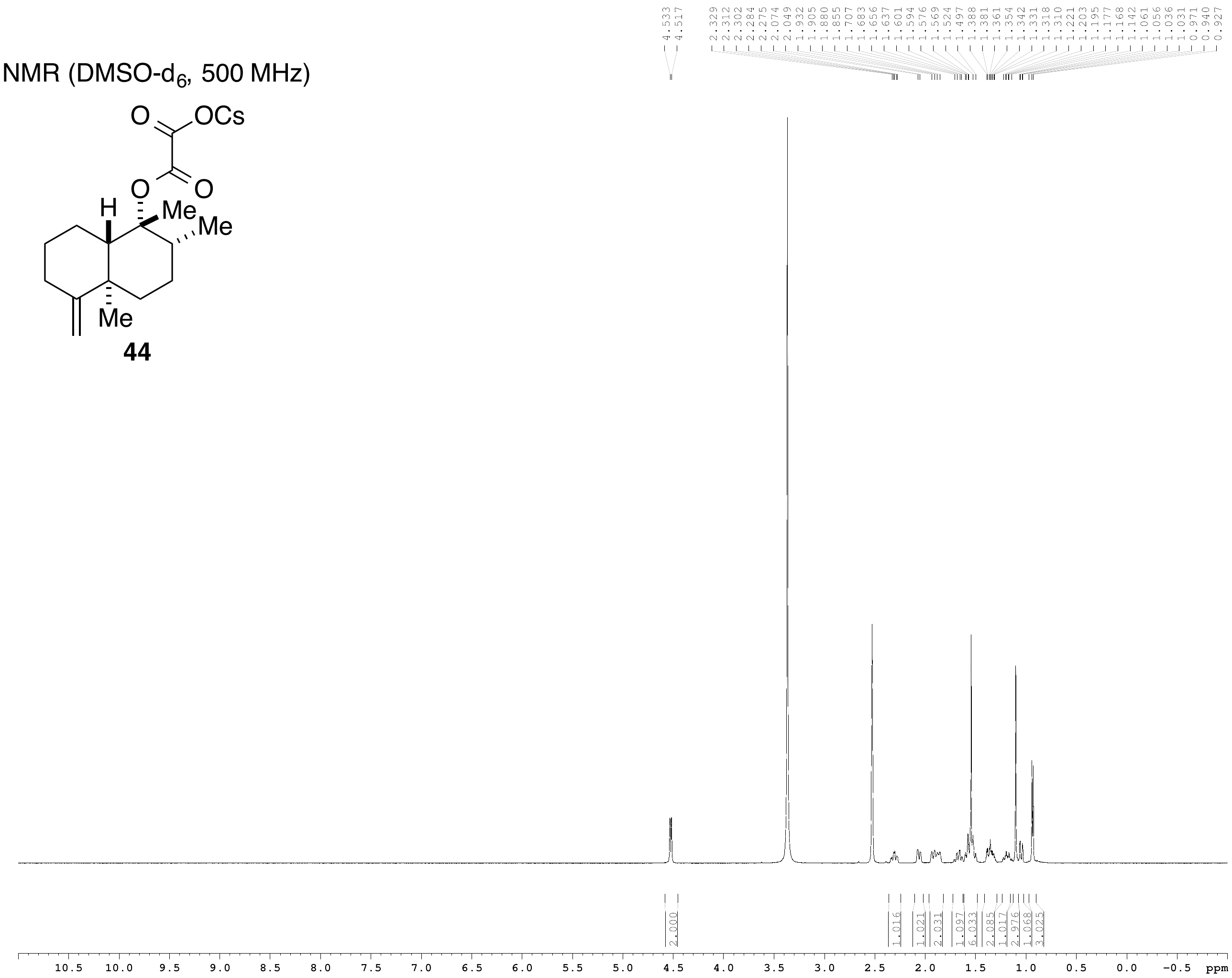
42

```
Current Data Parameters
NAME            YS-II-268
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150225
Time                 9.46
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT              DMSO
NS                    352
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 7298.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]      Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804795 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

YS-II-284

^{1}H NMR (DMSO-d$_6$, 500 MHz)

44

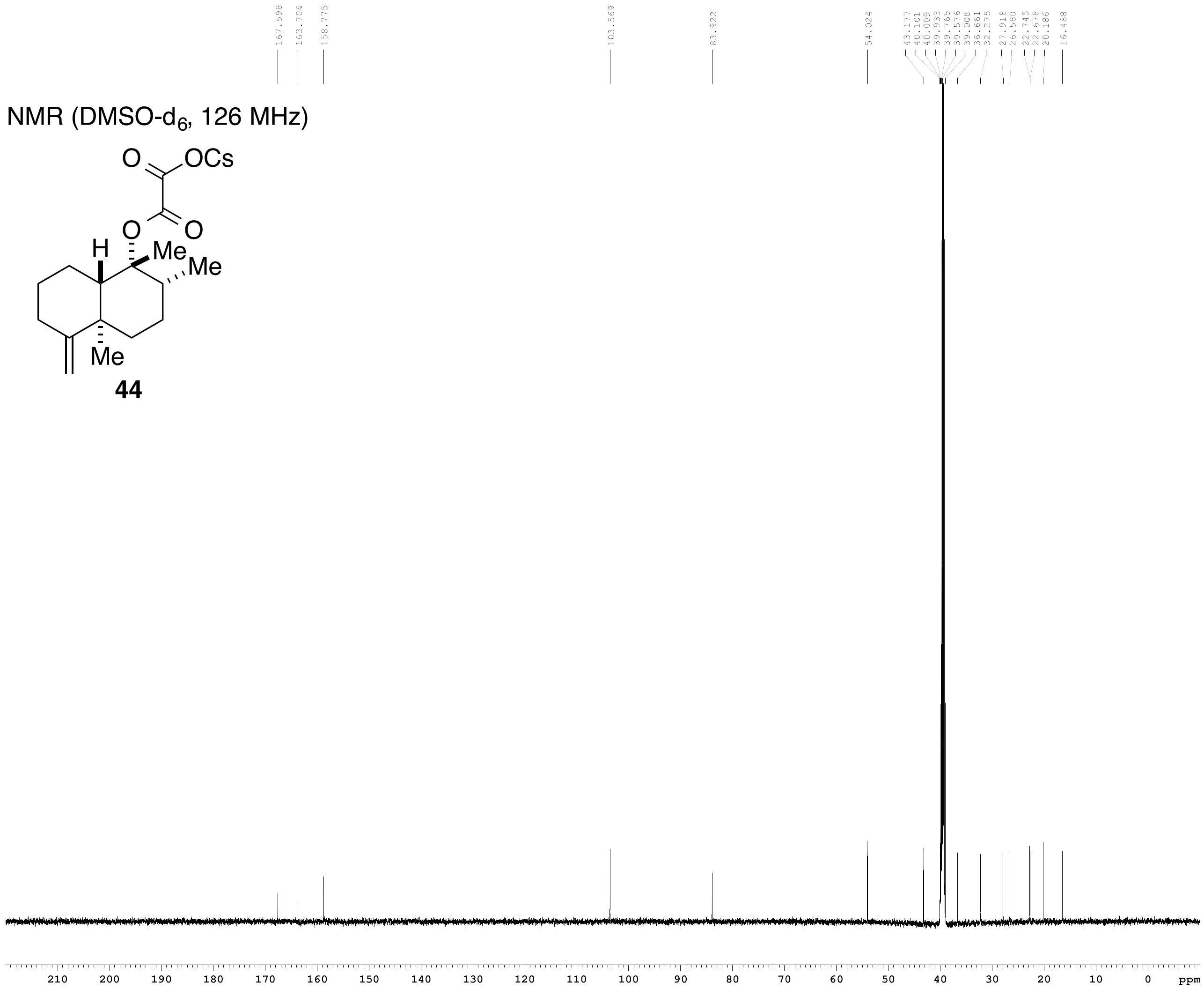


```
Current Data Parameters
NAME          YS-II-284
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150306
Time               8.44
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

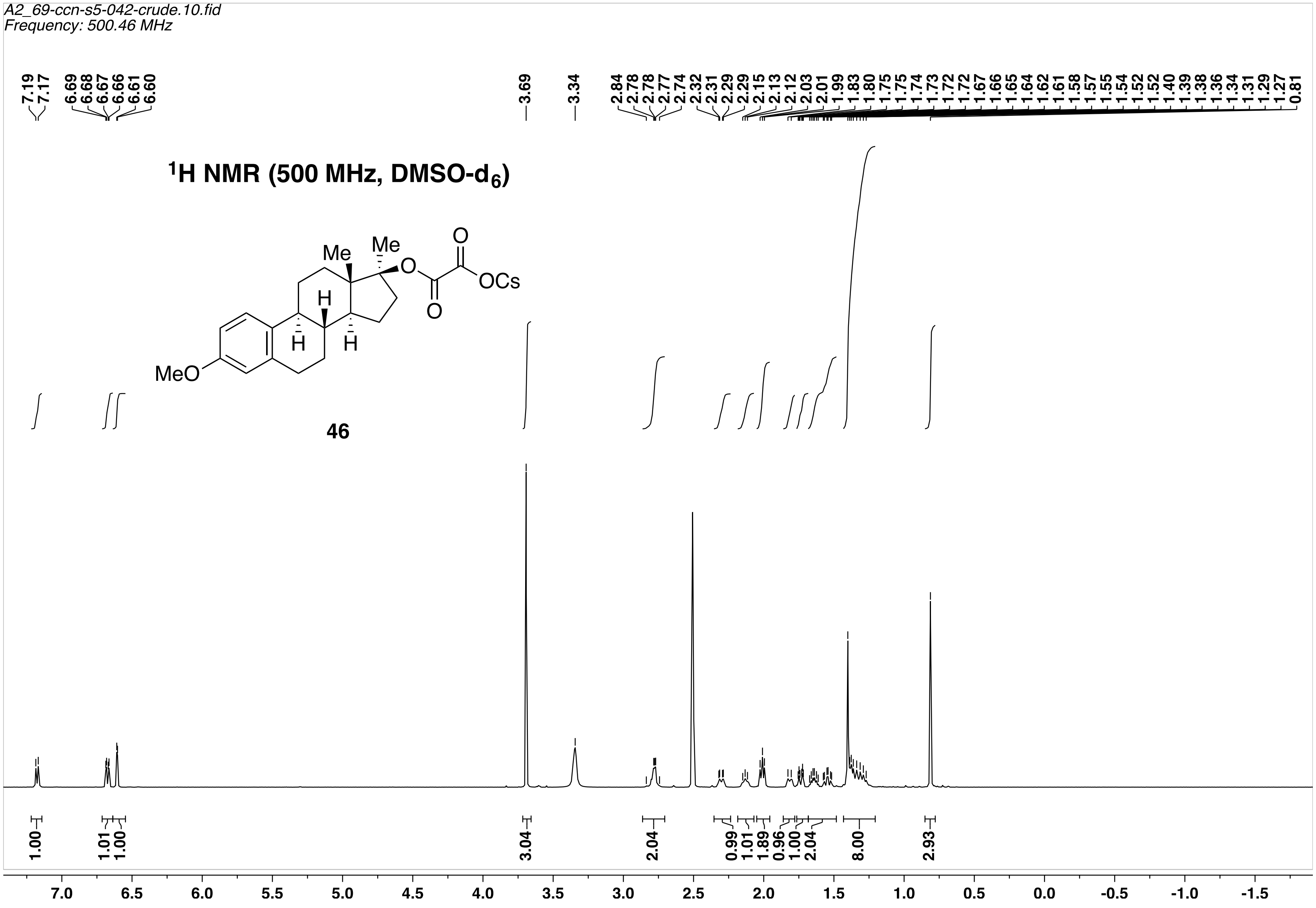
YS-II-284

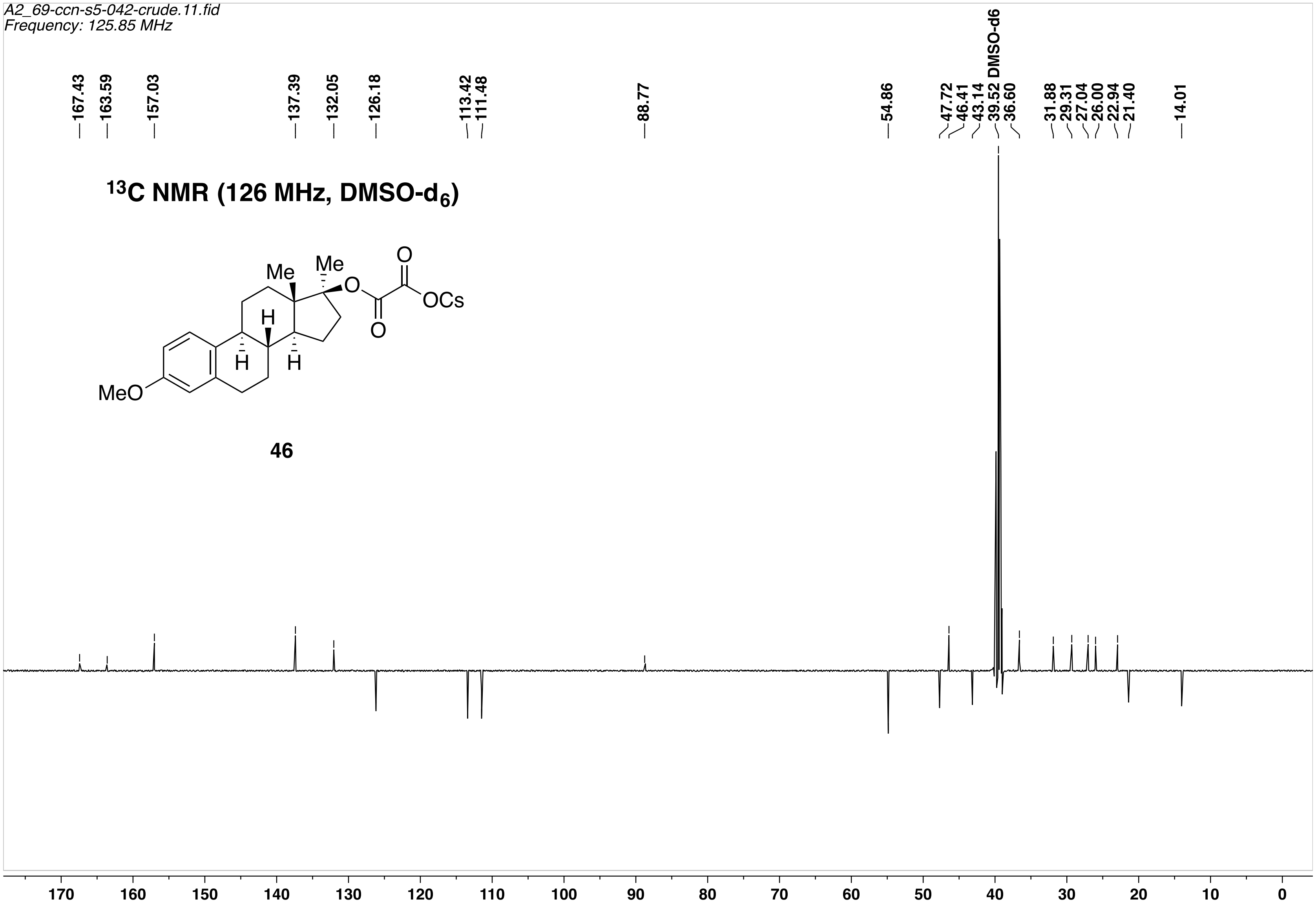
^{13}C NMR (DMSO-d_6, 126 MHz)

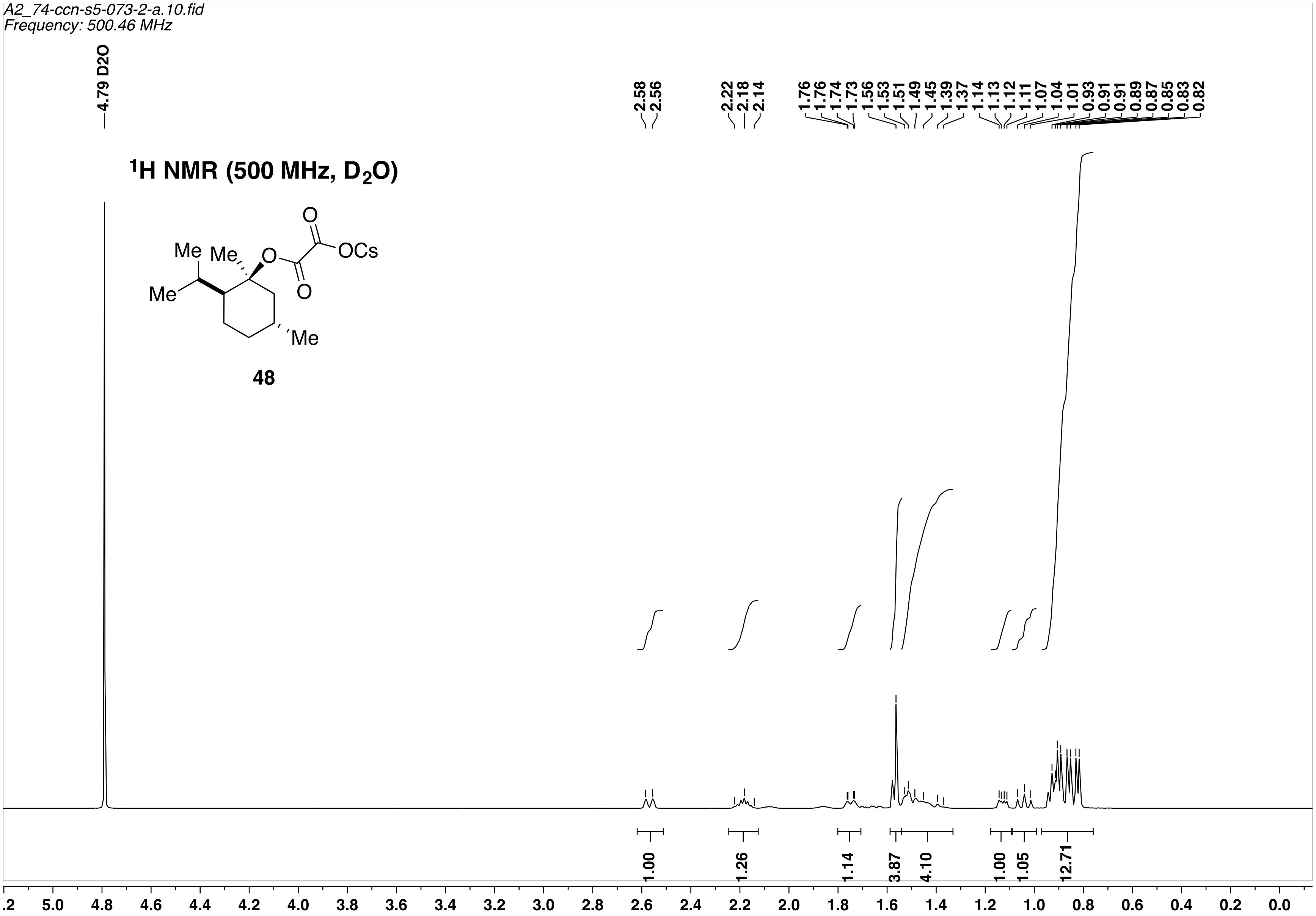
44



```
Current Data Parameters
NAME            YS-II-284
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150306
Time                 8.48
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT              DMSO
NS                   1024
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 5160.6
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804793 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

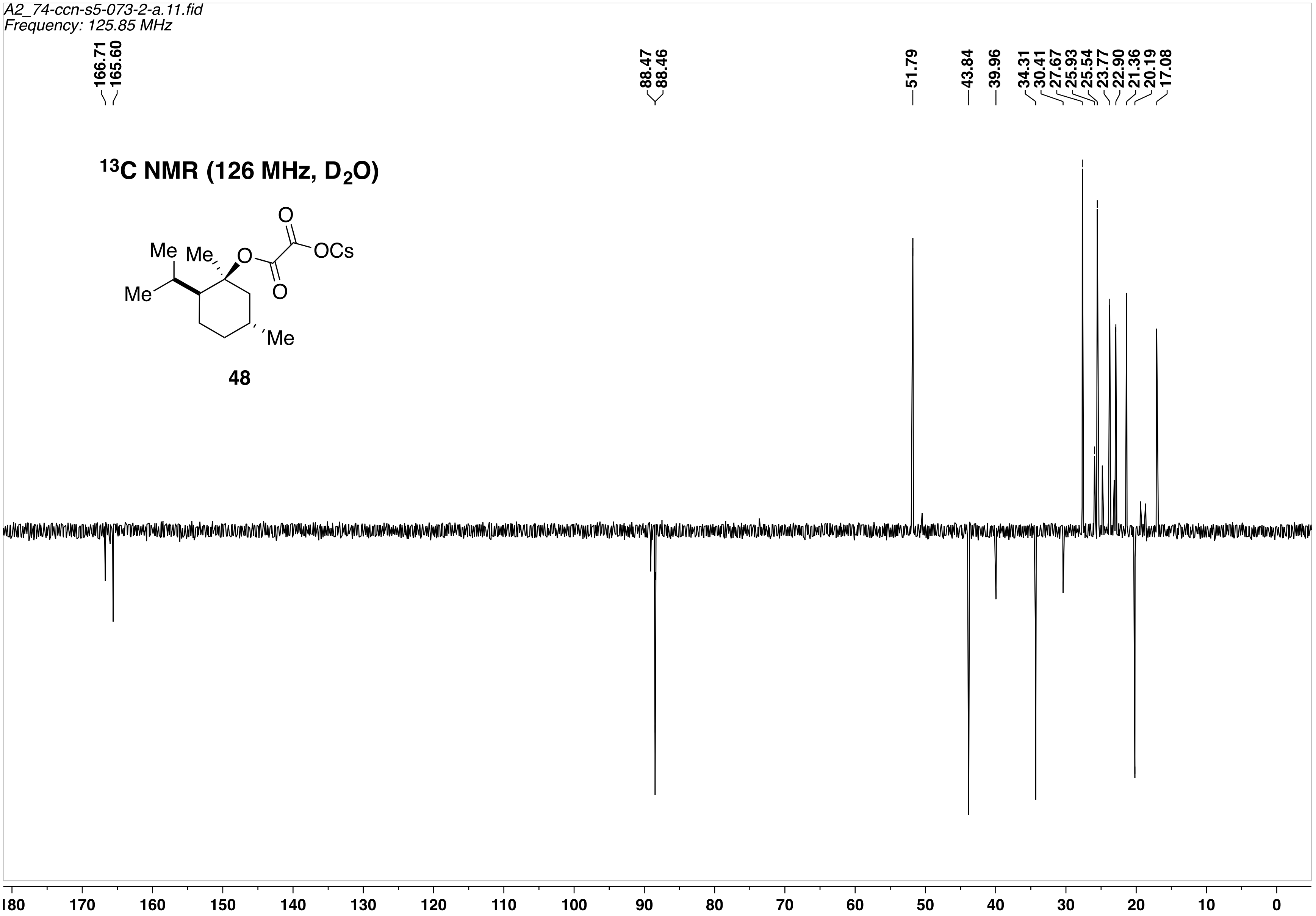

A2_69-ccn-s5-042-crude.10.fid
Frequency: 500.46 MHz
^{1}H NMR (500 MHz, DMSO-d$_6$)
Me
Me
O
O
OCs
O
H
H
H
MeO
46
7.19
7.17
6.69
6.68
6.67
6.66
6.61
6.60
3.69
3.34
2.84
2.78
2.78
2.77
2.74
2.32
2.31
2.29
2.29
2.15
2.13
2.12
2.03
2.01
1.99
1.83
1.80
1.75
1.75
1.74
1.73
1.72
1.72
1.67
1.66
1.65
1.64
1.62
1.61
1.58
1.57
1.55
1.54
1.52
1.52
1.40
1.39
1.38
1.36
1.34
1.31
1.29
1.27
0.81
1.00
1.01
1.00
3.04
2.04
0.99
1.01
1.89
0.96
1.00
2.04
8.00
2.93
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

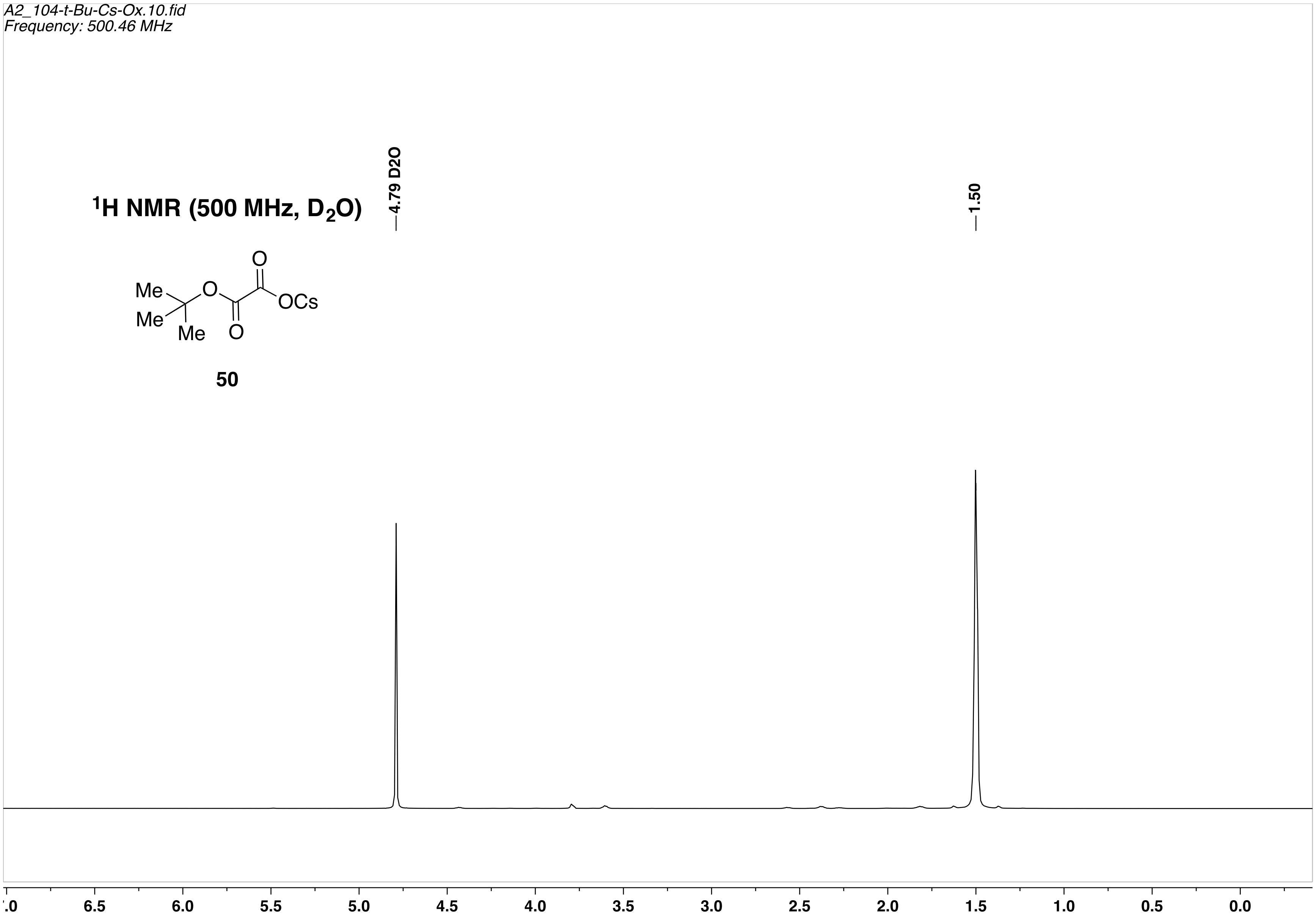

A2_69-ccn-s5-042-crude.11.fid
Frequency: 125.85 MHz
^{13}C NMR (126 MHz, DMSO-d$_6$)
Me
Me
O
O
OCs
O
H
H
H
MeO
46
167.43
163.59
157.03
137.39
132.05
126.18
113.42
111.48
88.77
54.86
47.72
46.41
43.14
39.52 DMSO-d6
36.60
31.88
29.31
27.04
26.00
22.94
21.40
14.01
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

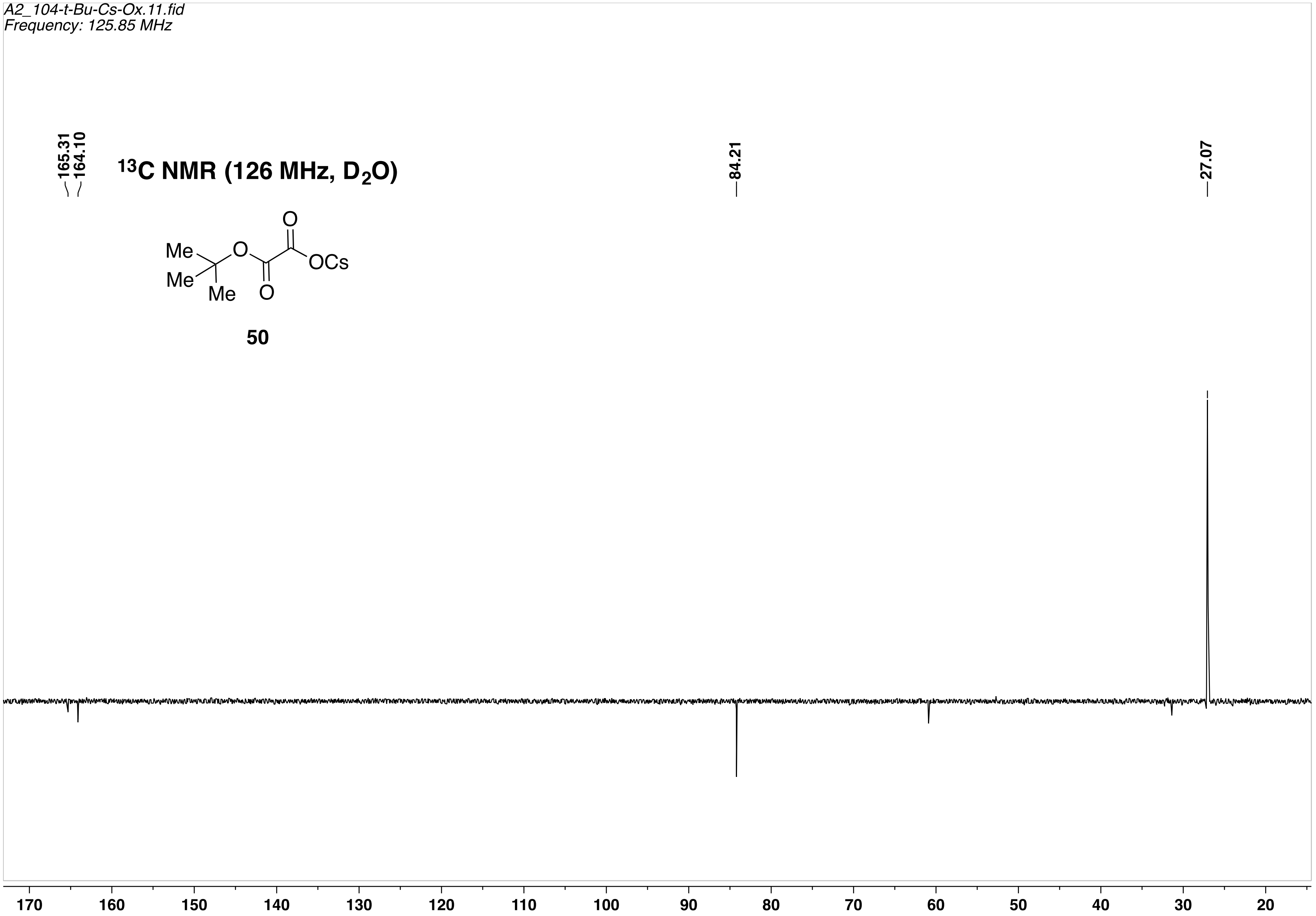


^{1}H NMR (500 MHz, D_2O)

48

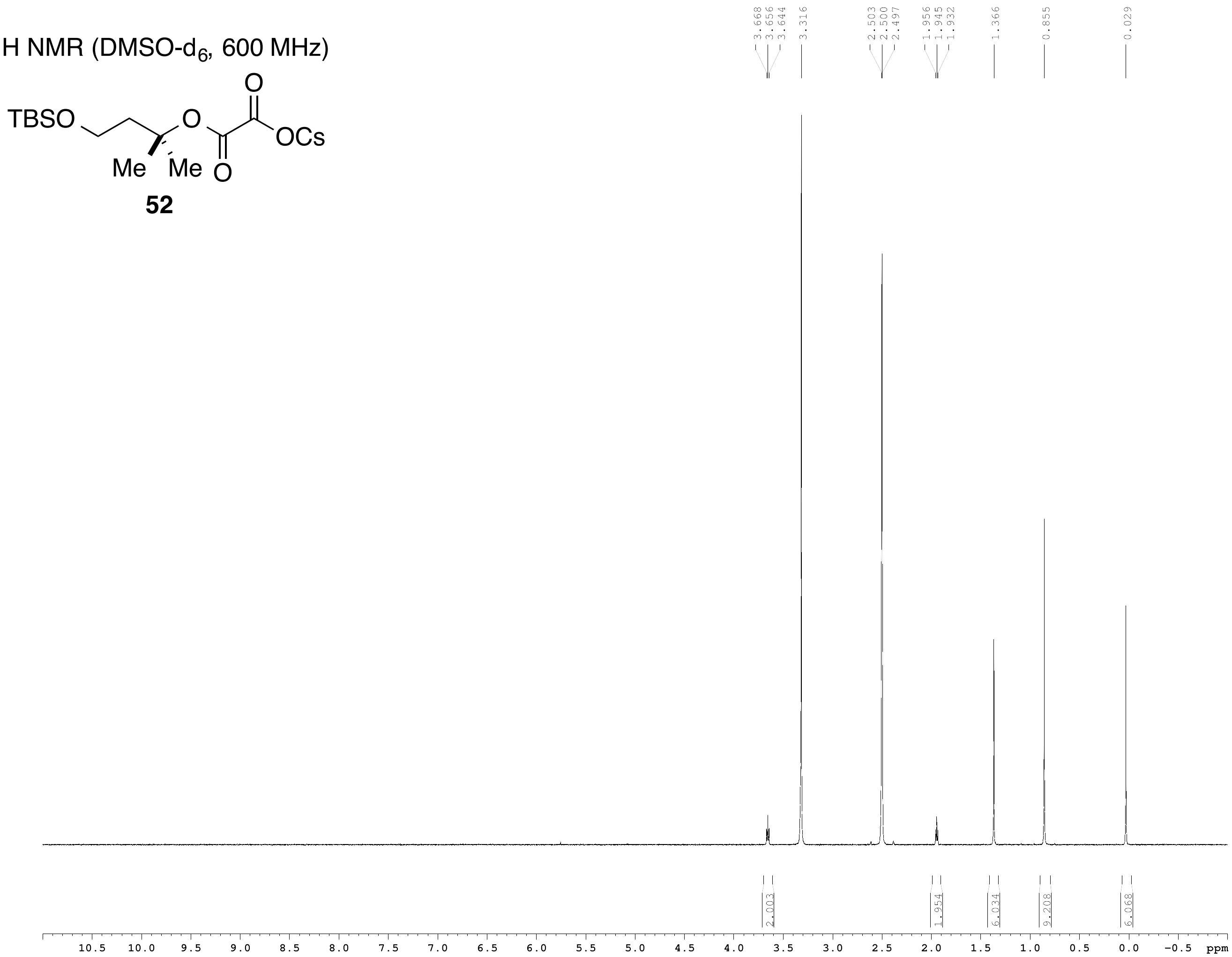

A2_74-ccn-s5-073-2-a.11.fid
Frequency: 125.85 MHz
166.71
165.60
88.47
88.46
51.79
43.84
39.96
34.31
30.41
27.67
25.93
25.54
23.77
22.90
21.36
20.19
17.08
^{13}C NMR (126 MHz, D$_2$O)
Me
Me
Me
O
O
O
OCs
Me
48
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


A2_104-t-Bu-Cs-Ox.10.fid
Frequency: 500.46 MHz
^{1}H NMR (500 MHz, D_2O)
Me
Me
Me
O
O
O
OCs
50
4.79 D2O
1.50
.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


A2_104-t-Bu-Cs-Ox.11.fid
Frequency: 125.85 MHz
^{13}C NMR (126 MHz, D$_2$O)
165.31
164.10
84.21
27.07
Me
Me
Me
O
O
O
OCs
50
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

YS-II-202

^{1}H NMR (DMSO-d$_6$, 600 MHz)

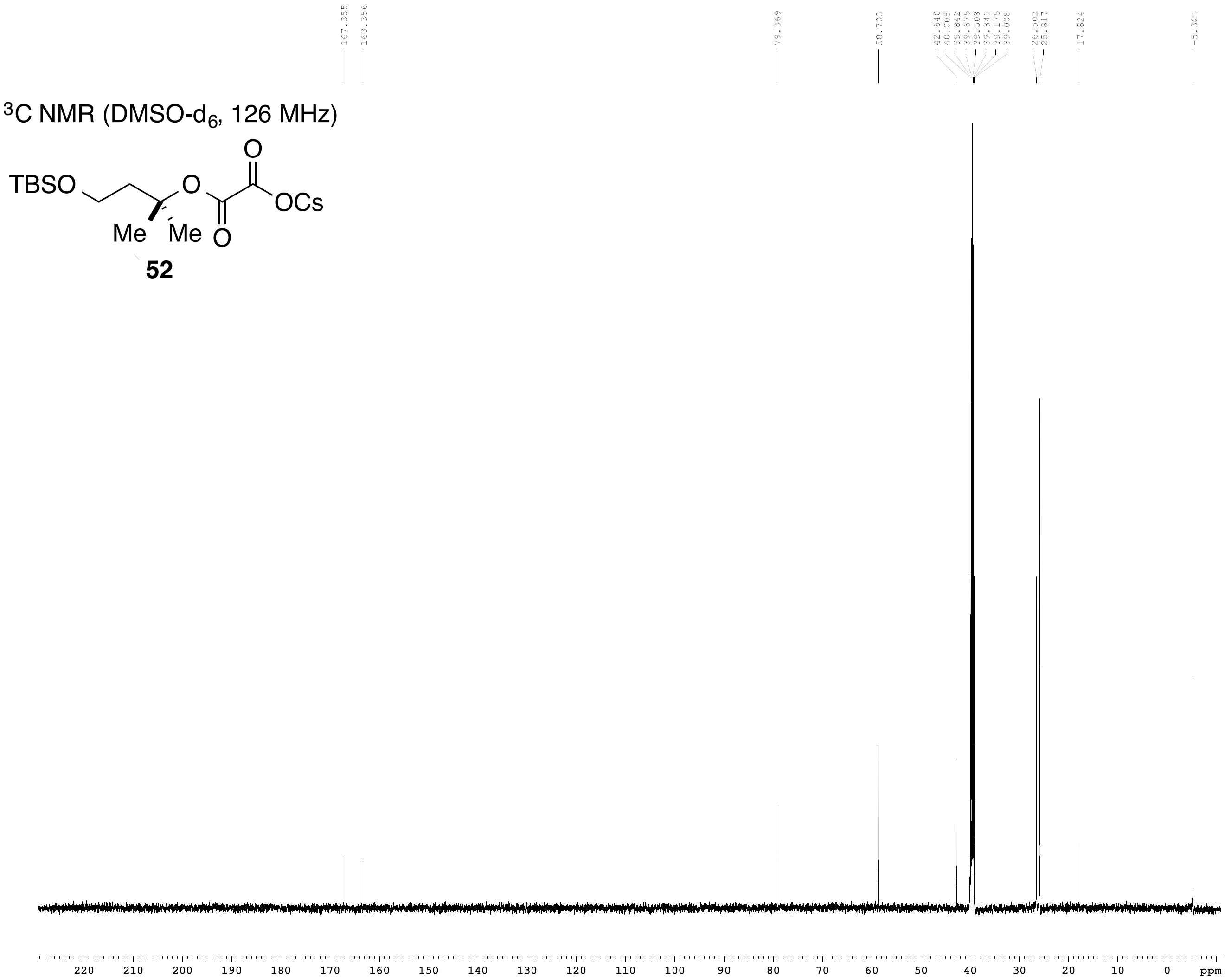


52

```
Current Data Parameters
NAME          YS-II-202
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20150127
Time               8.49
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                98074
SOLVENT            DMSO
NS                    8
DS                    2
SWH           9615.385 Hz
FIDRES        0.098042 Hz
AQ           5.0998478 sec
RG                 2050
DW               52.000 usec
DE                14.54 usec
TE                298.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

F2 - Processing parameters
SI                65536
SF          600.1300134 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-II-202

13C NMR (DMSO-d_6, 126 MHz)

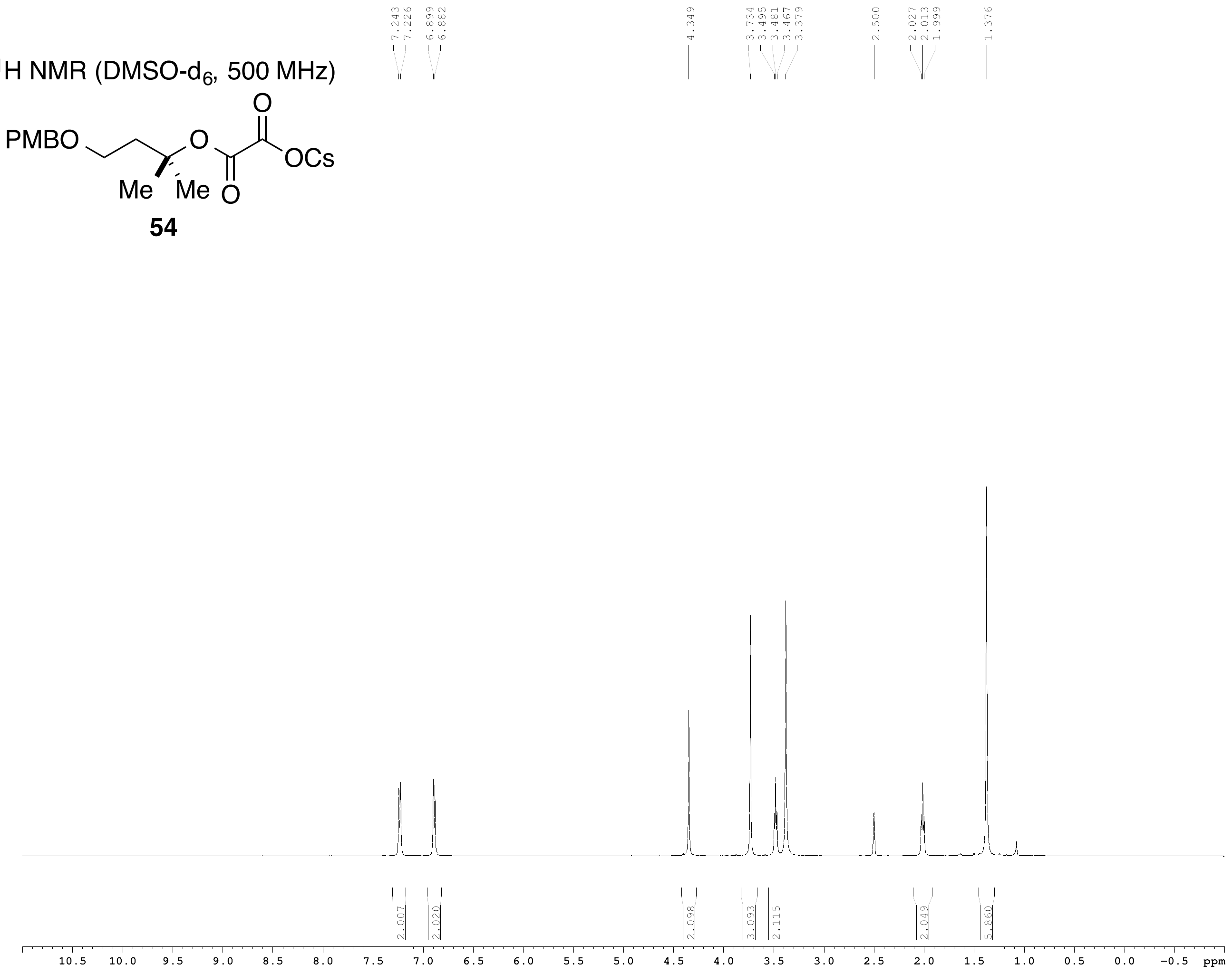


52

```
Current Data Parameters
NAME          YS-II-202
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20150425
Time               9.34
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                  144
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG              11585.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7805484 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-260

¹H NMR (DMSO-d₆, 500 MHz)



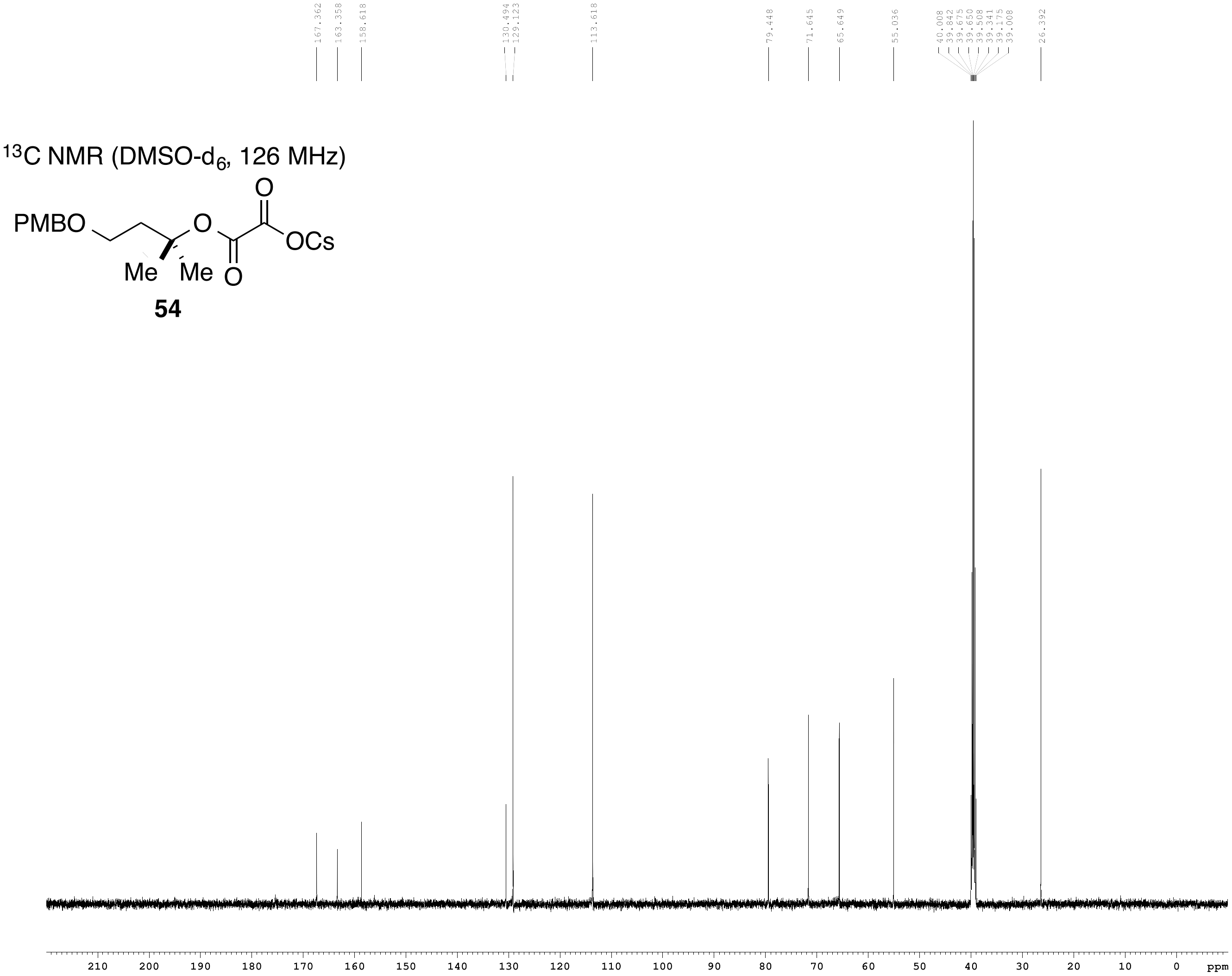
54

```
Current Data Parameters
NAME          YS-II-260
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150220
Time              13.25
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200138 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-260

^{13}C NMR (DMSO-d_6, 126 MHz)

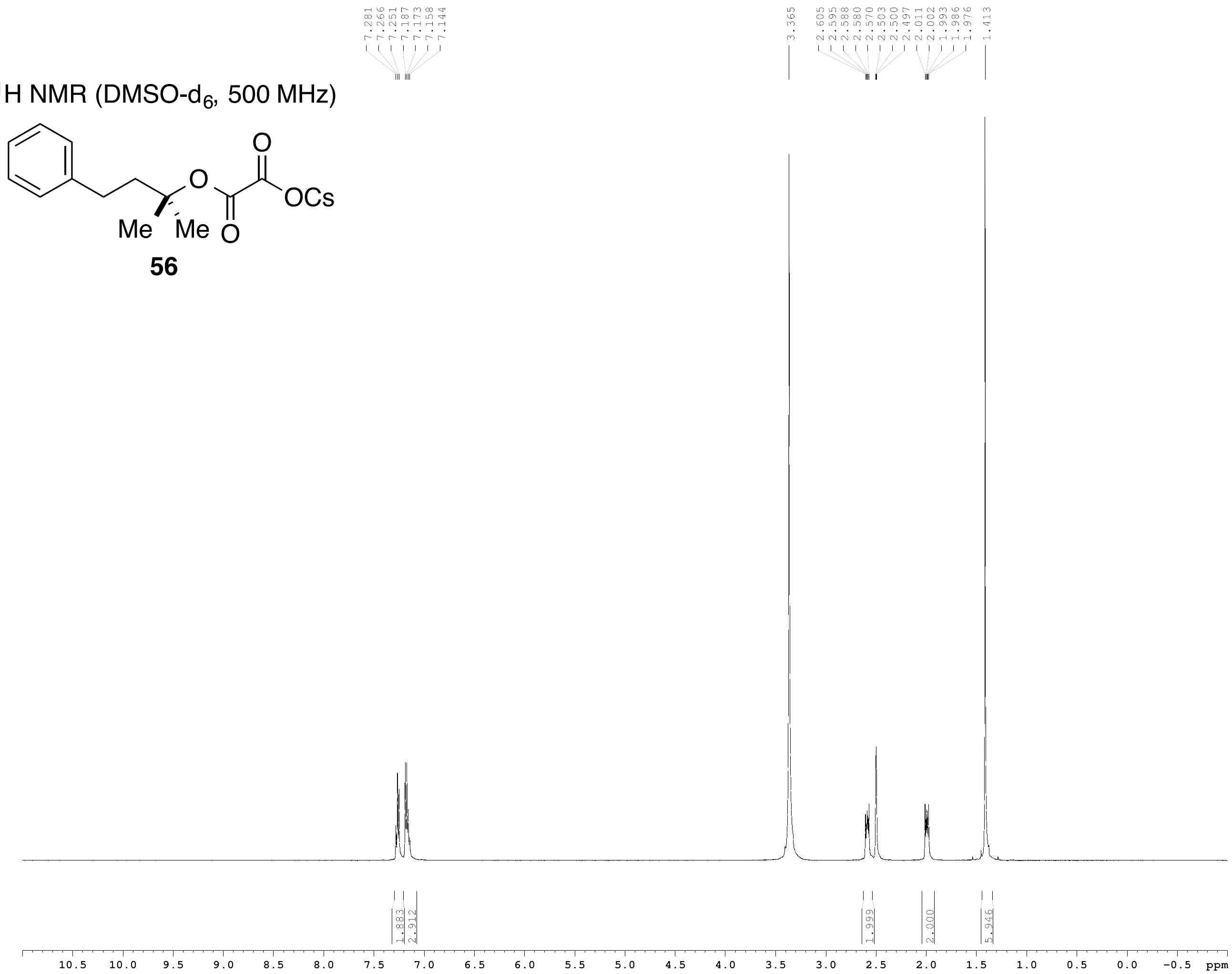
54



```
Current Data Parameters
NAME            YS-II-260
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150220
Time                13.29
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT              DMSO
NS                    128
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 7298.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804781 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

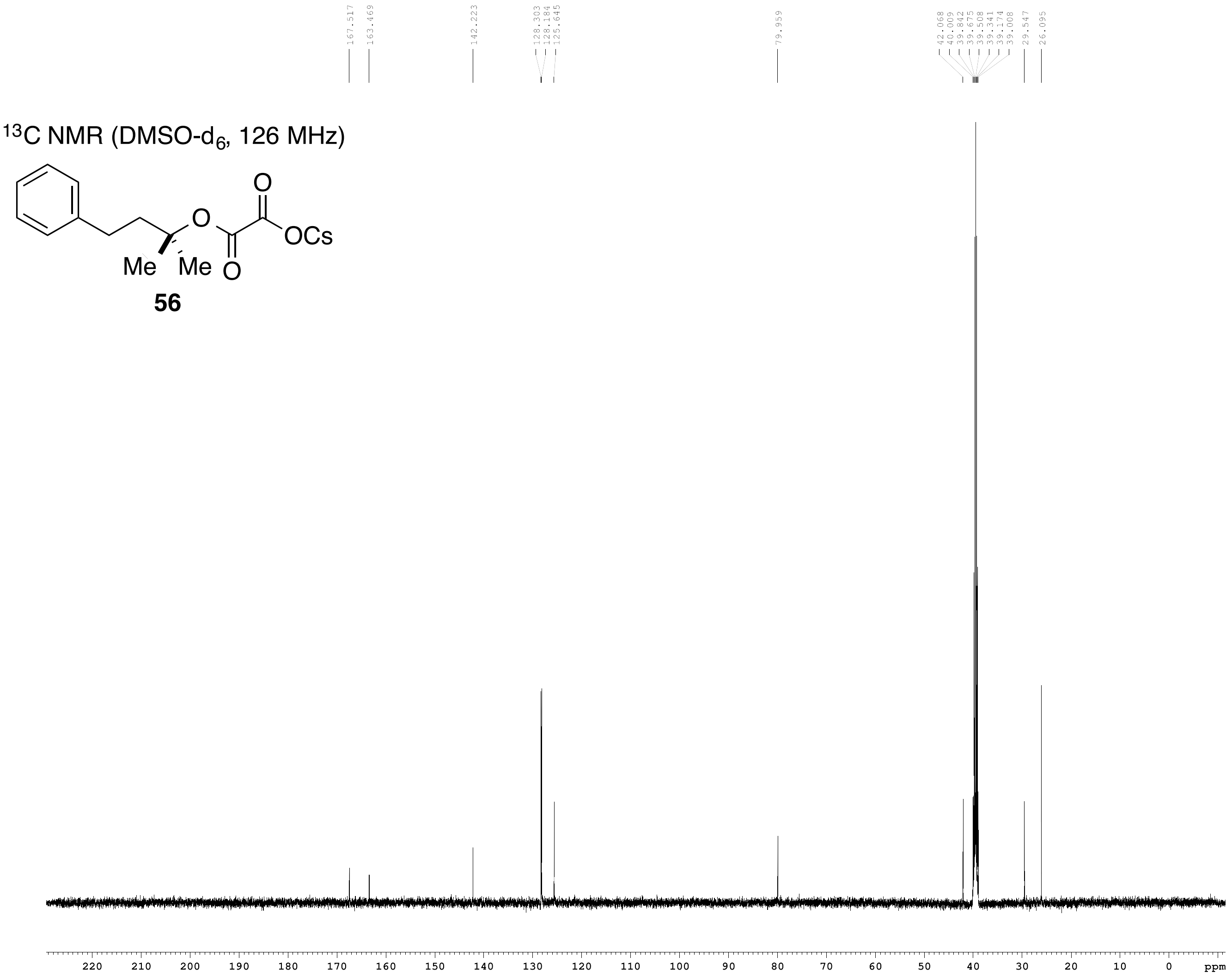
YS-II-195

^1H NMR (DMSO-d_6, 500 MHz)


56

```
Current Data Parameters
NAME          YS-II-195
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150502
Time              14.16
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG            zg30
TD                32048
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                912.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -5.80 dB
SFO1        499.1834943 MHz

F2 - Processing parameters
SI                65536
SF          499.1800087 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-II-195



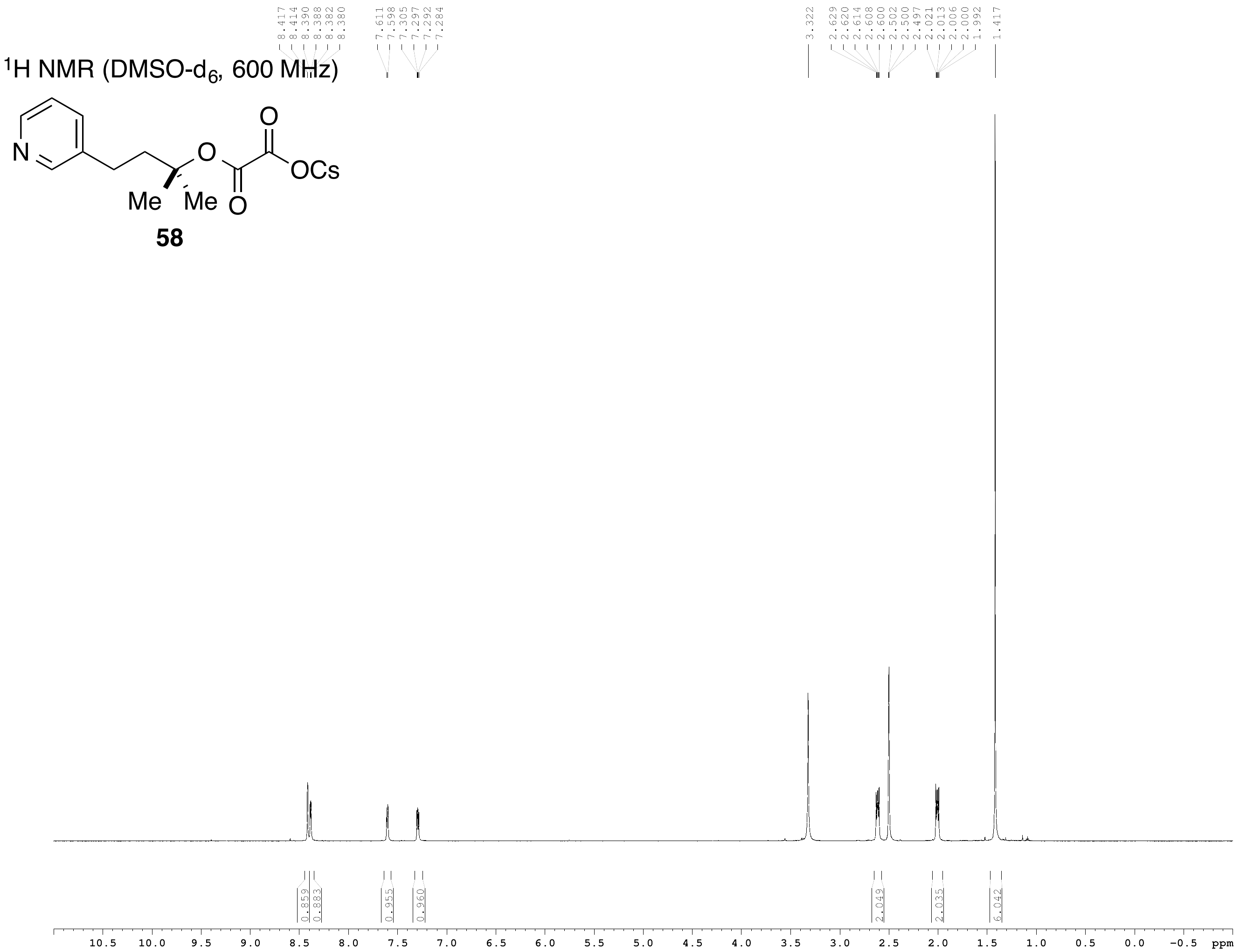
^{13}C NMR (DMSO-d$_6$, 126 MHz)

56

```
Current Data Parameters
NAME          YS-II-195
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150425
Time               9.26
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                  160
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7805494 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-III-41

^{1}H NMR (DMSO-d$_6$, 600 MHz)

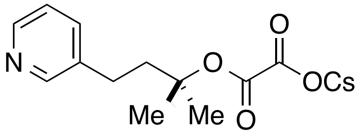


58

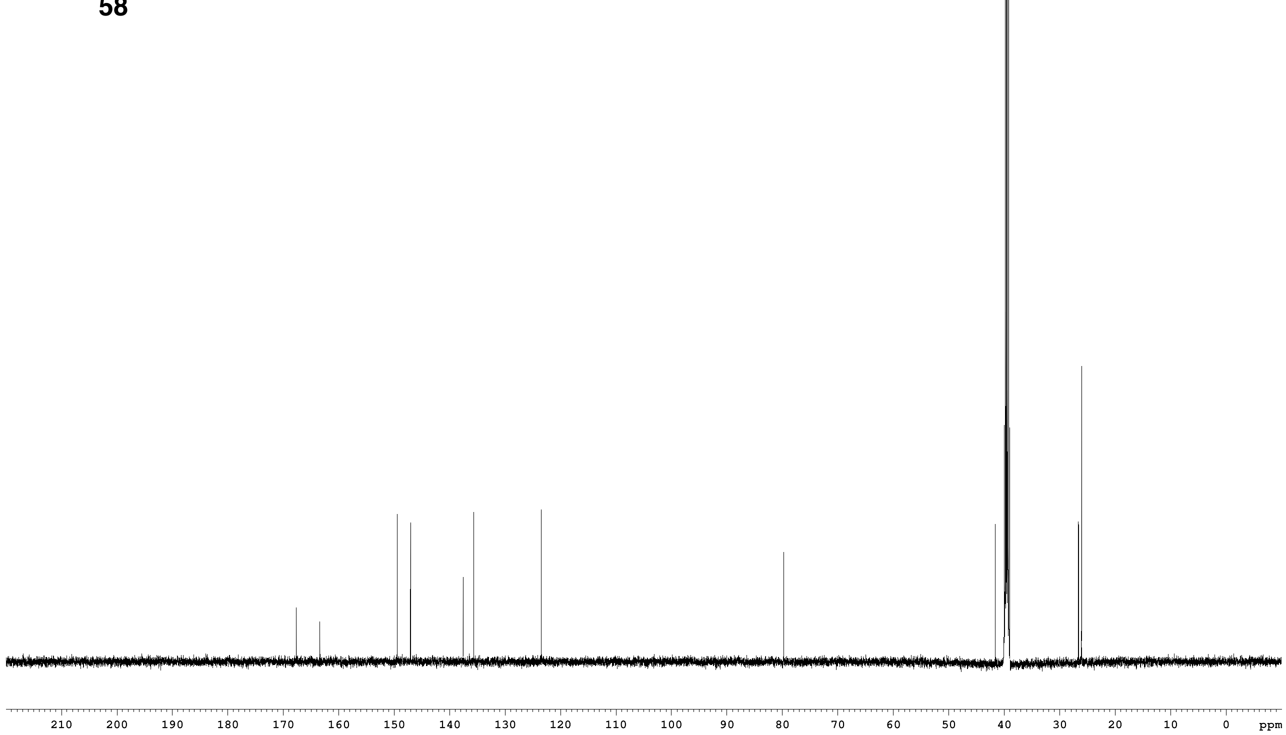
```
Current Data Parameters
NAME          YS-III-41
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150404
Time              14.53
INSTRUM           av600
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                38460
SOLVENT            DMSO
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                  512
DW               52.000 usec
DE                14.33 usec
TE                298.1 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 9.00 usec
PLW1        60.25600052 W

F2 - Processing parameters
SI                65536
SF          600.1300122 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-III-41

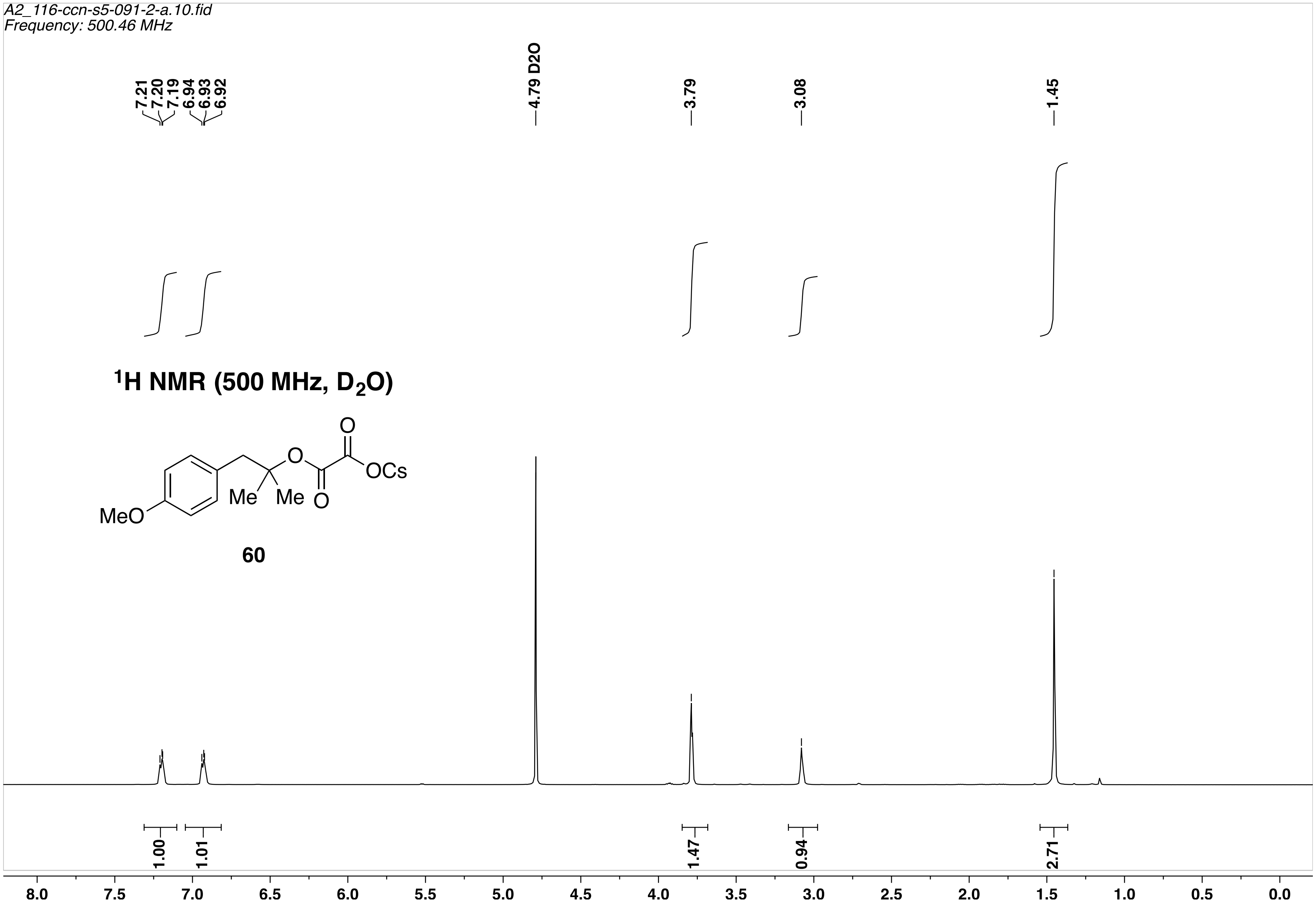
^{13}C NMR (DMSO-d_6, 126 MHz)



58

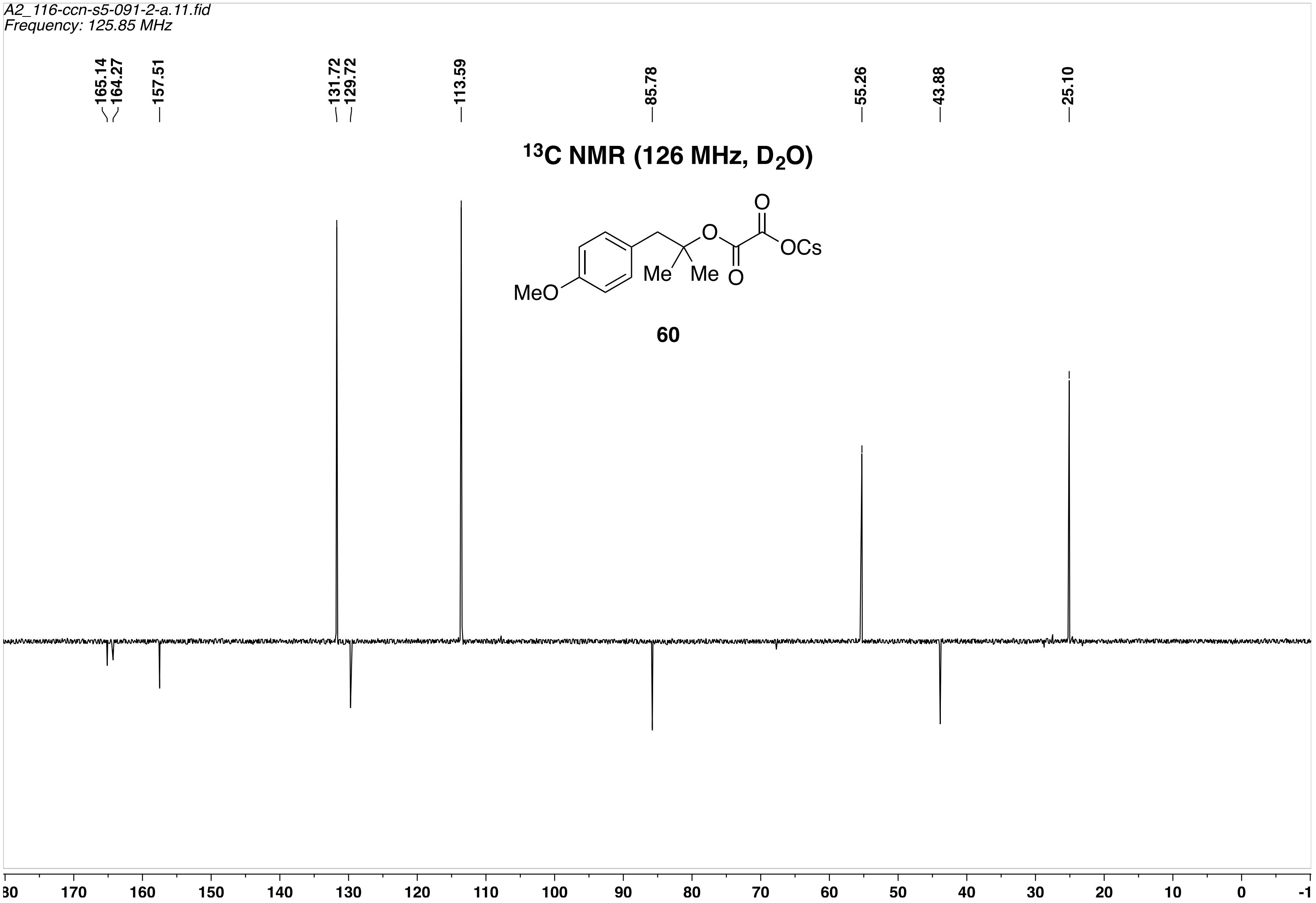


```
Current Data Parameters
NAME          YS-III-41
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150404
Time              15.23
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                  416
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7805417 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



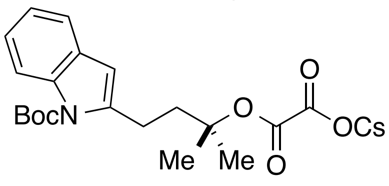
^{1}H NMR (500 MHz, D_2O)

60

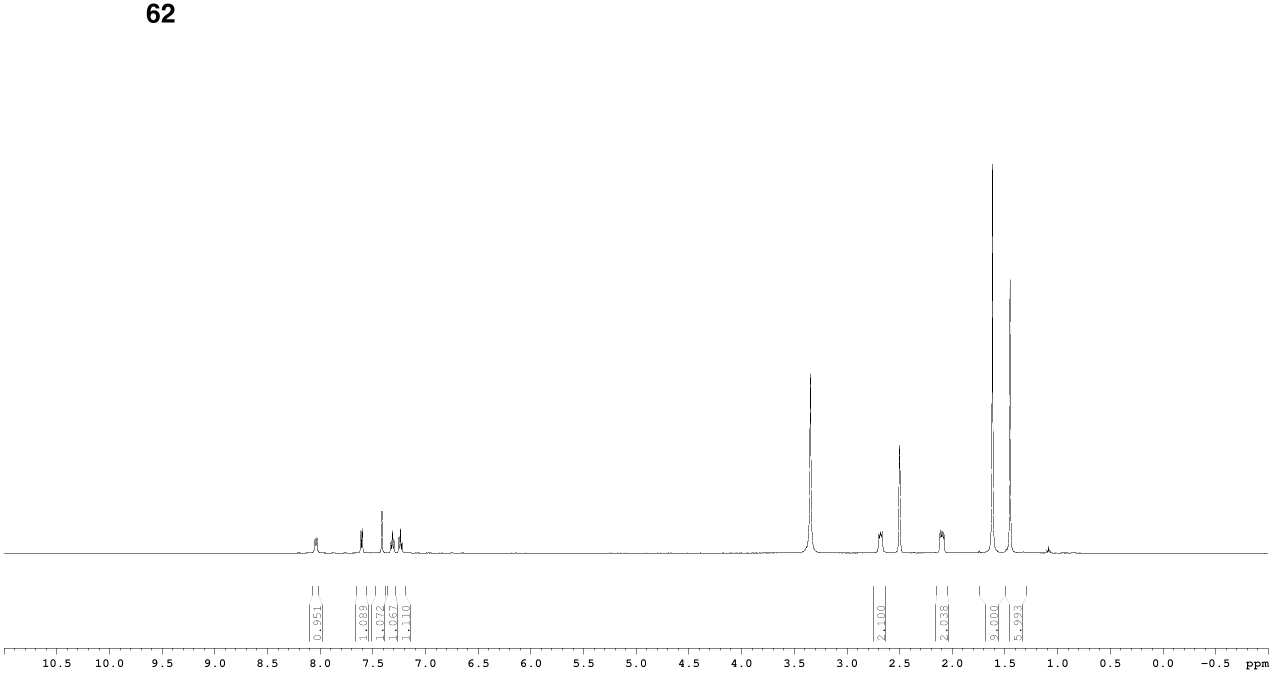

A2_116-ccn-s5-091-2-a.11.fid
Frequency: 125.85 MHz
165.14
164.27
157.51
131.72
129.72
113.59
85.78
55.26
43.88
25.10
^{13}C NMR (126 MHz, D_2O)
MeO
Me
Me
O
O
O
OCs
60
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

YS-II-251

^{1}H NMR (DMSO-d$_6$, 500 MHz)

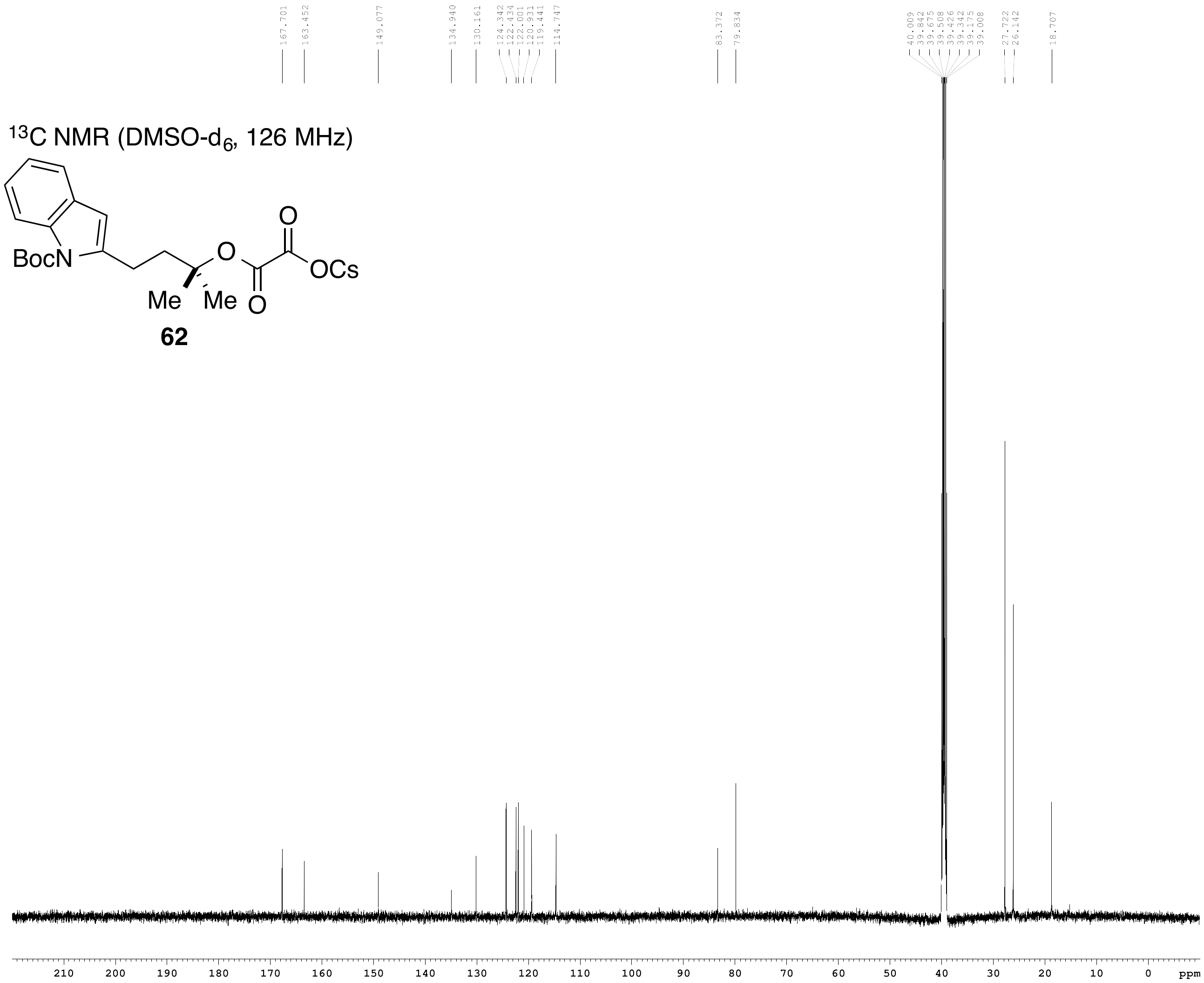


62



```
Current Data Parameters
NAME          YS-II-251
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150216
Time              13.38
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200118 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

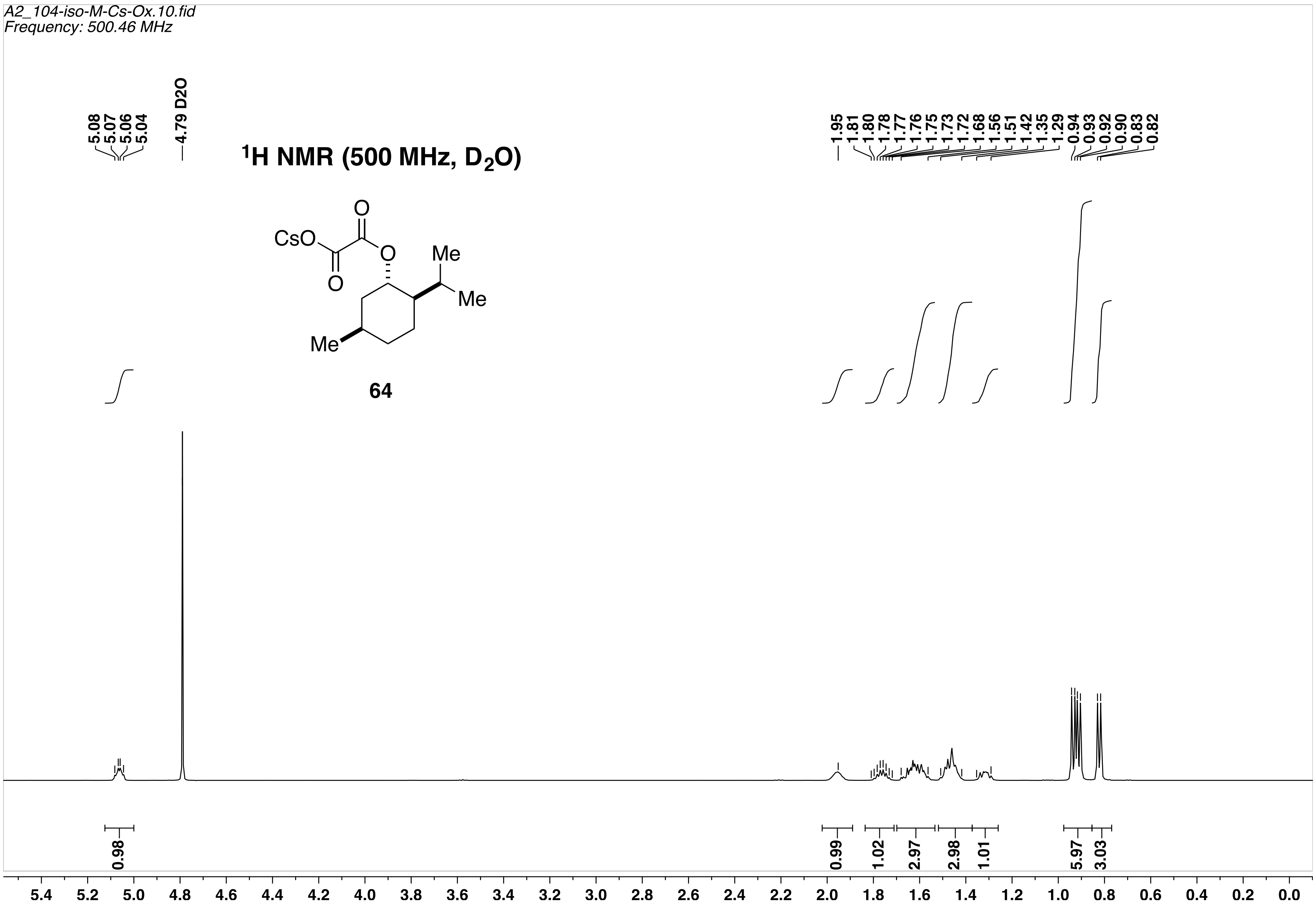
YS-II-251



^{13}C NMR (DMSO-d$_6$, 126 MHz)

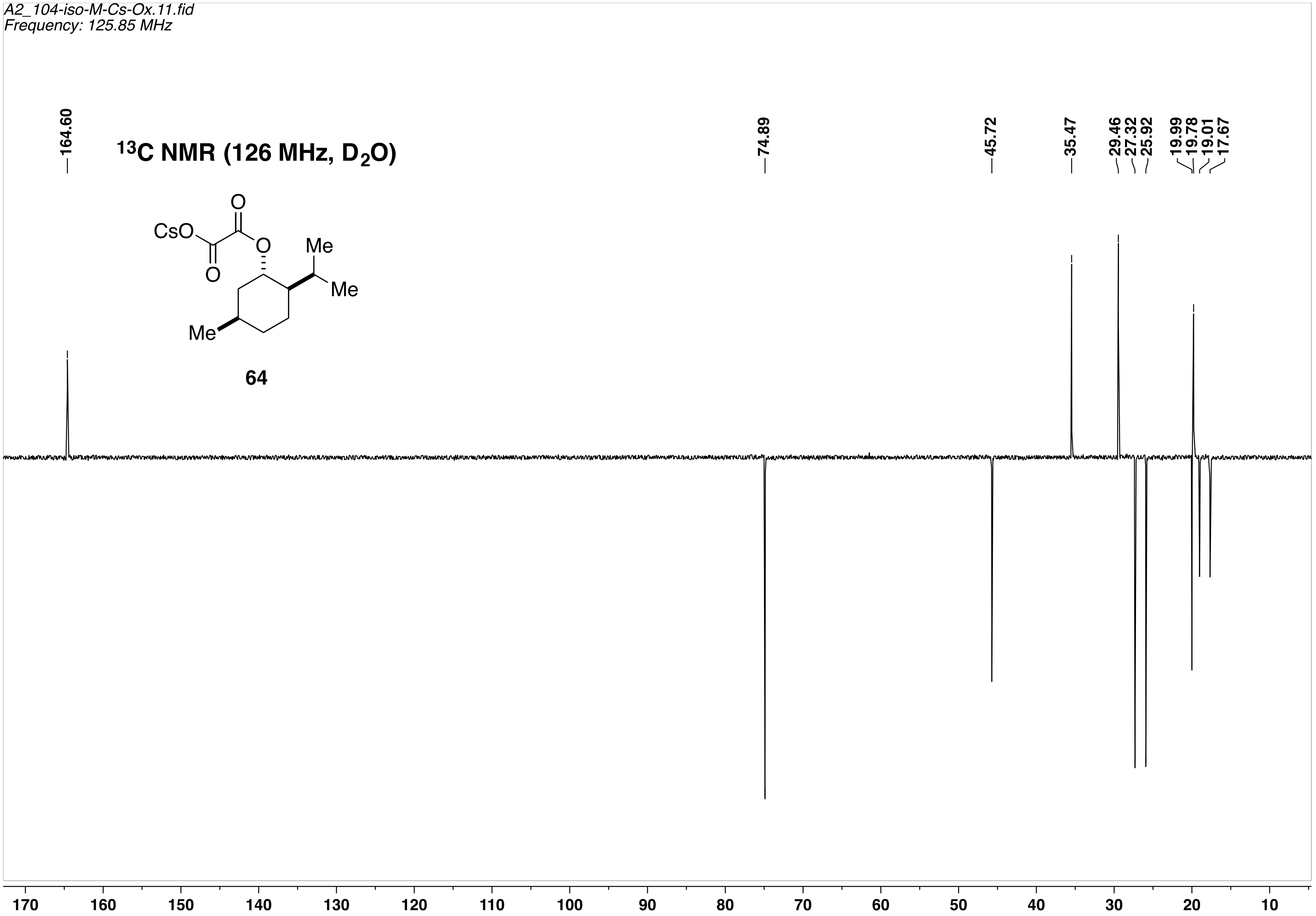
62

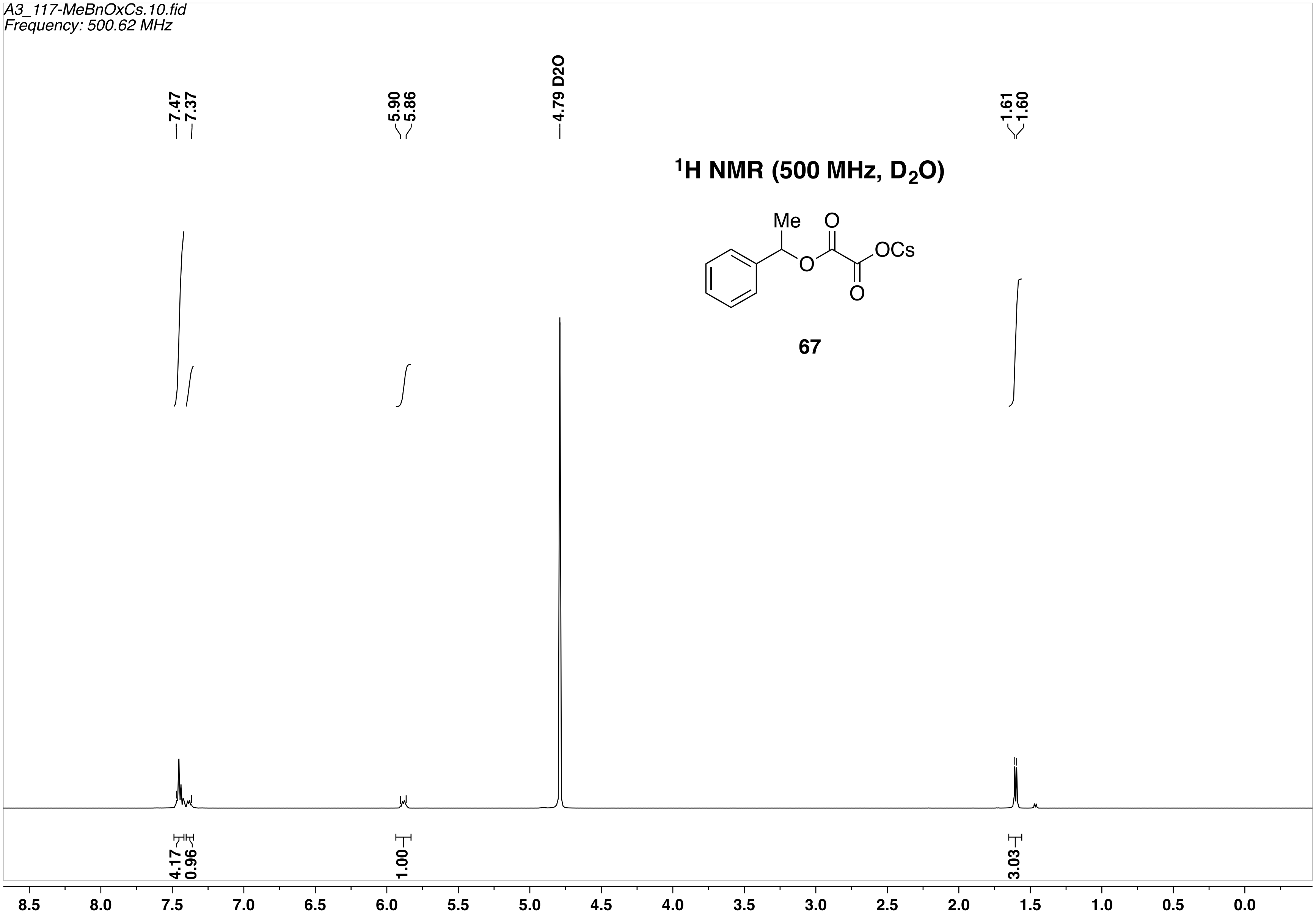
```
Current Data Parameters
NAME          YS-II-251
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150216
Time              13.41
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                  584
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.75000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804792 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



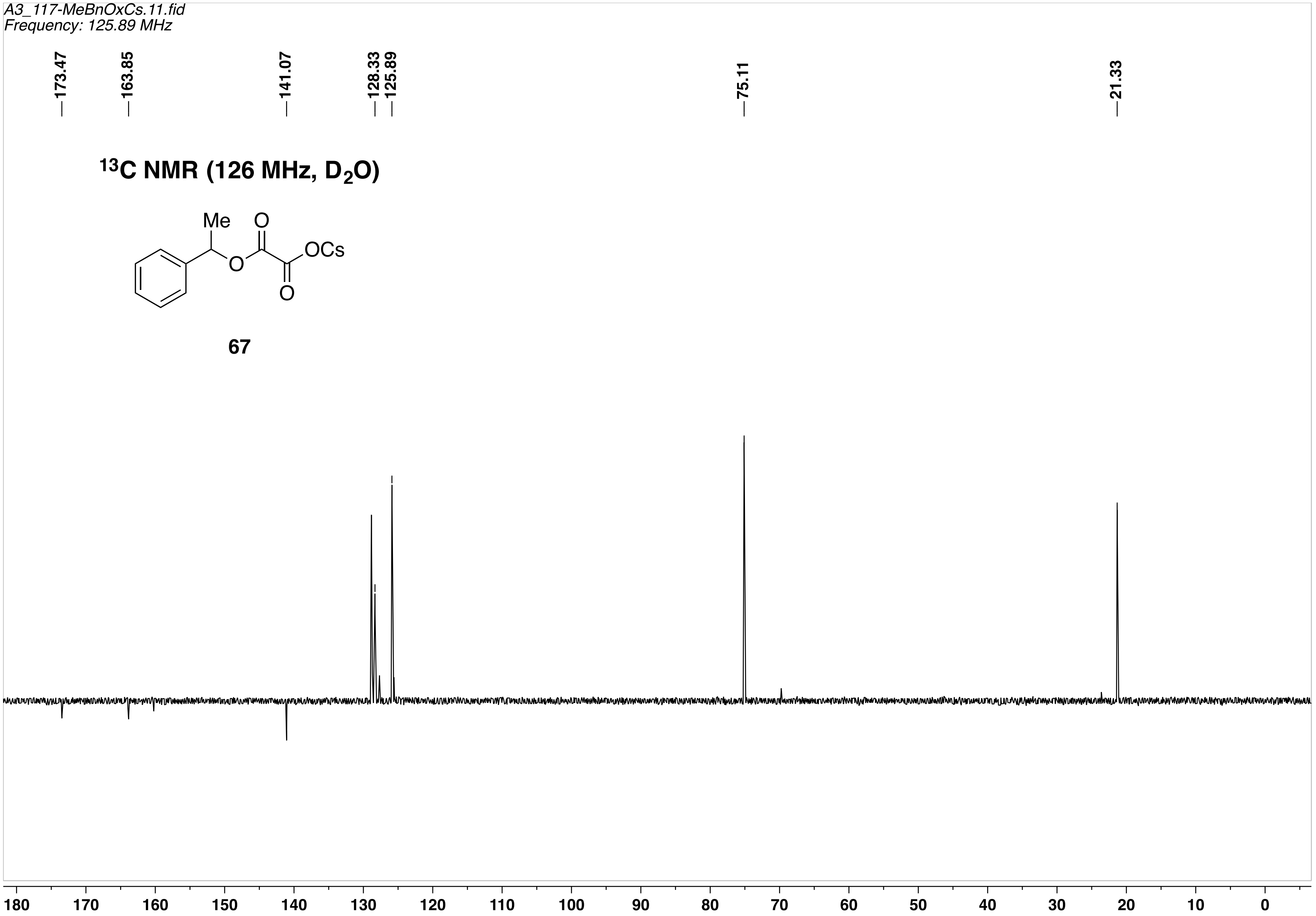
^{1}H NMR (500 MHz, D_2O)

64


A2_104-iso-M-Cs-Ox.11.fid
Frequency: 125.85 MHz
164.60
13C NMR (126 MHz, D2O)
CsO
O
O
O
Me
Me
Me
64
74.89
45.72
35.47
29.46
27.32
25.92
19.99
19.78
19.01
17.67
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


A3_117-MeBnOxCs.10.fid
Frequency: 500.62 MHz
7.47
7.37
5.90
5.86
4.79 D2O
1.61
1.60
¹H NMR (500 MHz, D₂O)
Me
O
OCs
O
O
4.17
0.96
1.00
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

67

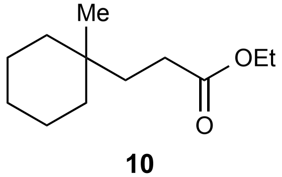


^{13}C NMR (126 MHz, D_2O)

67

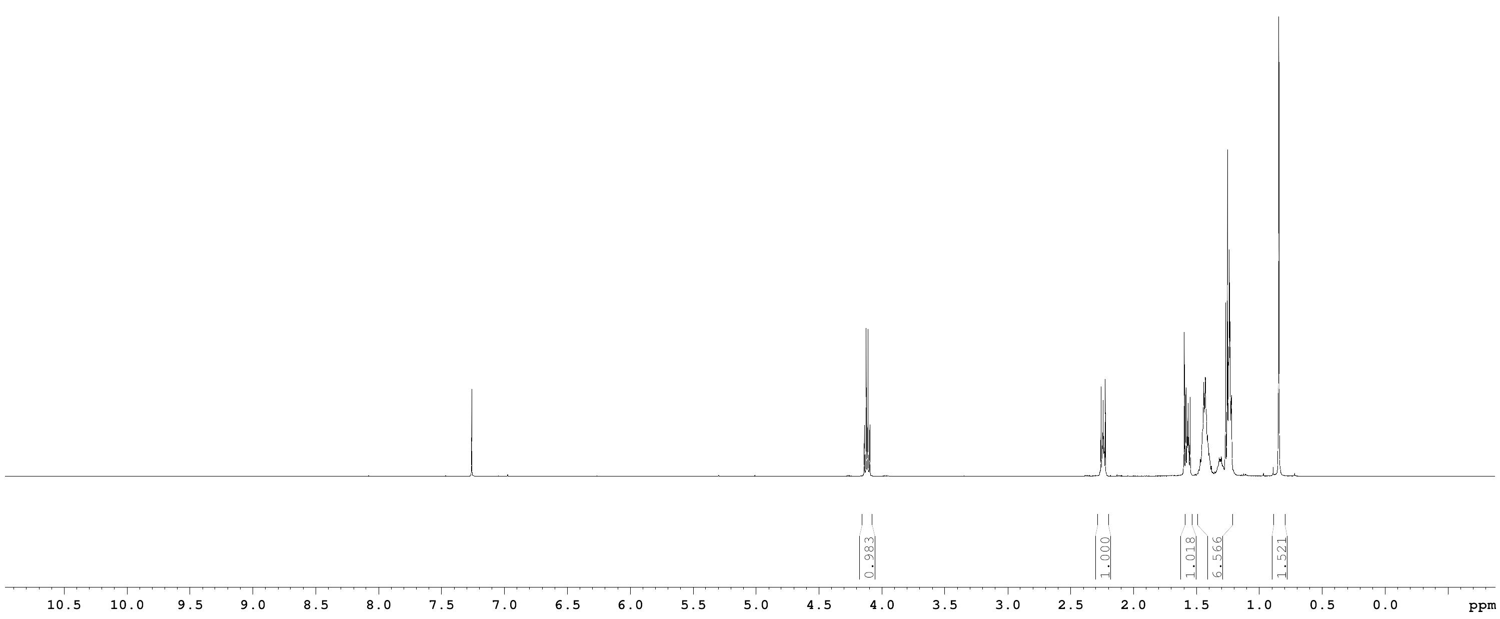
1H spectrum

^{1}H NMR ($CDCl_3$, 500MHz)



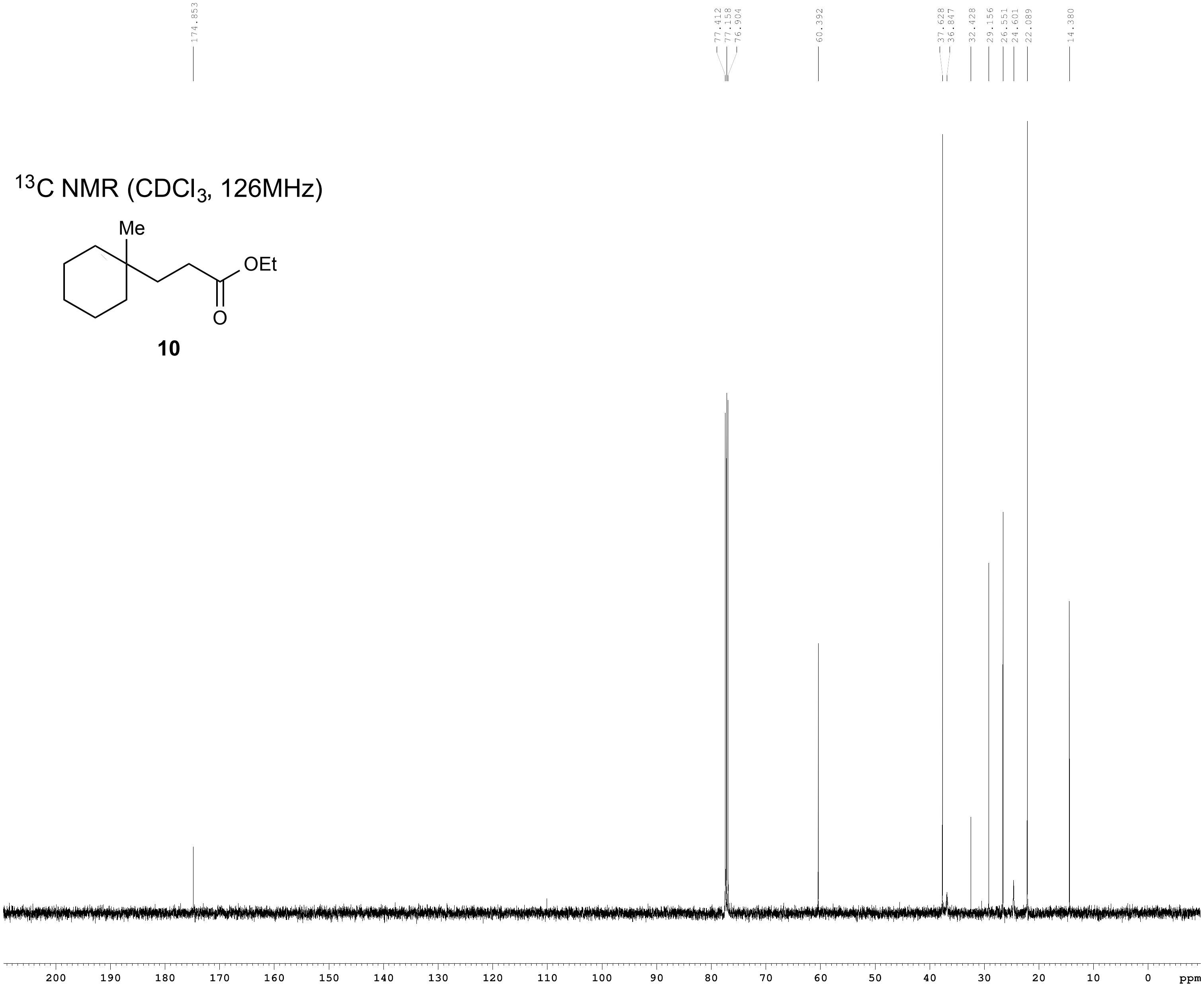
10

```
Current Data Parameters
NAME       CRJ1-249-pure
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150523
Time               17.33
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 80126
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.100003 Hz
AQ             4.9998622 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST    0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200315 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```



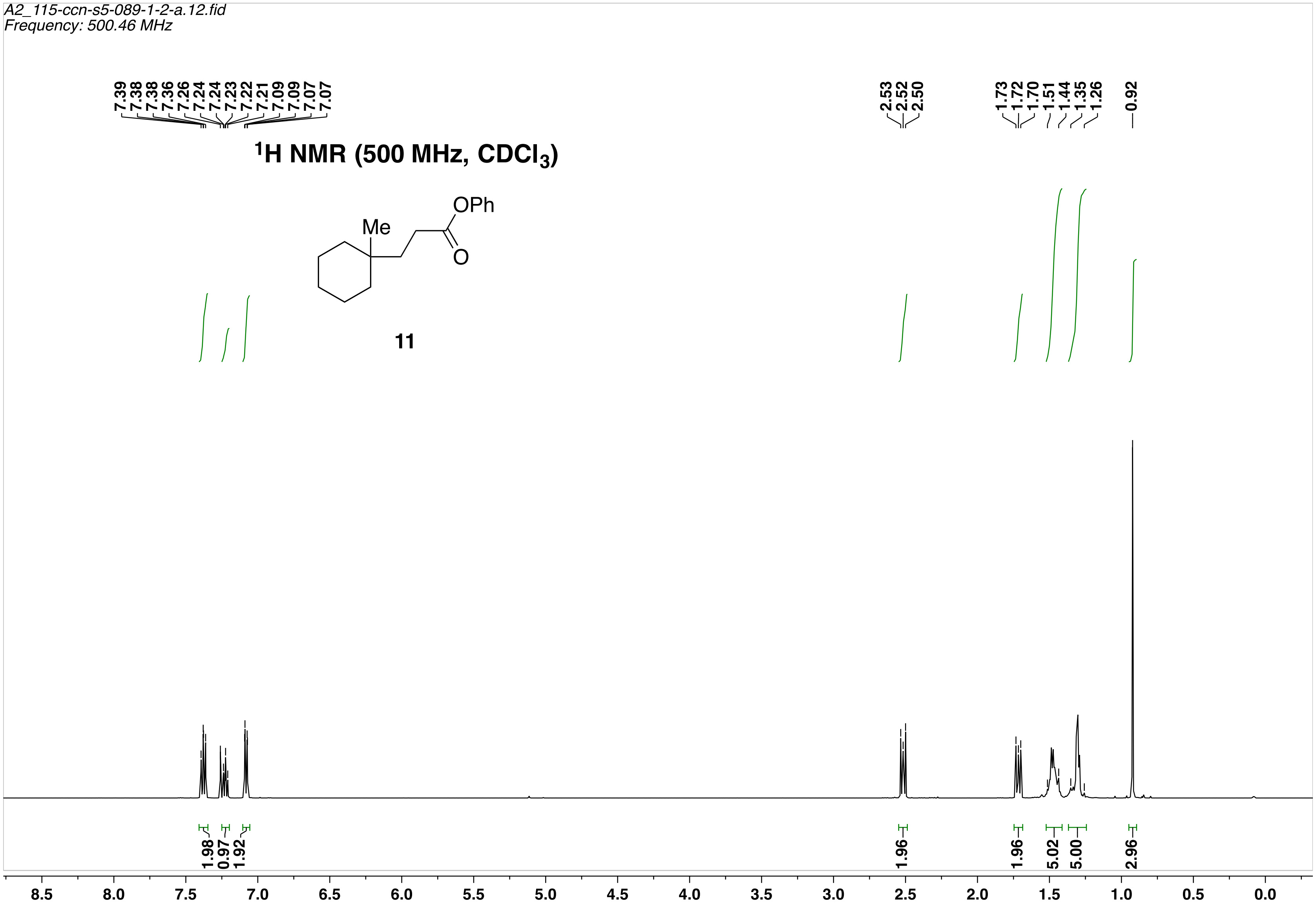
Z-restored spin-echo 13C spectrum with 1H decoupling

^{13}C NMR ($CDCl_3$, 126MHz)



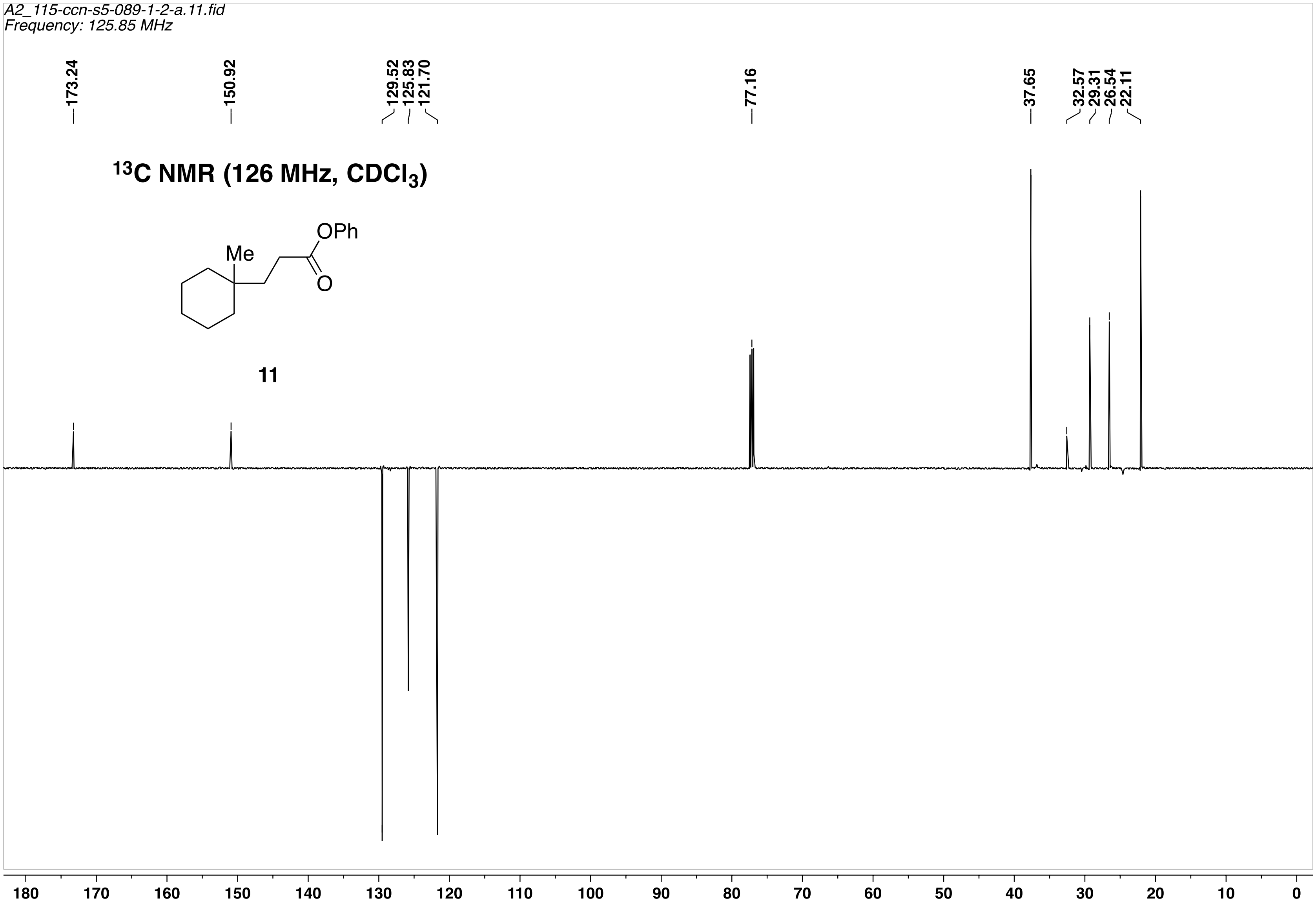
10

```
Current Data Parameters
NAME      CRJ1-249-pure
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150523
Time              17.40
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  160
DS                    8
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG              11585.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804080 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



^{1}H NMR (500 MHz, CDCl$_3$)

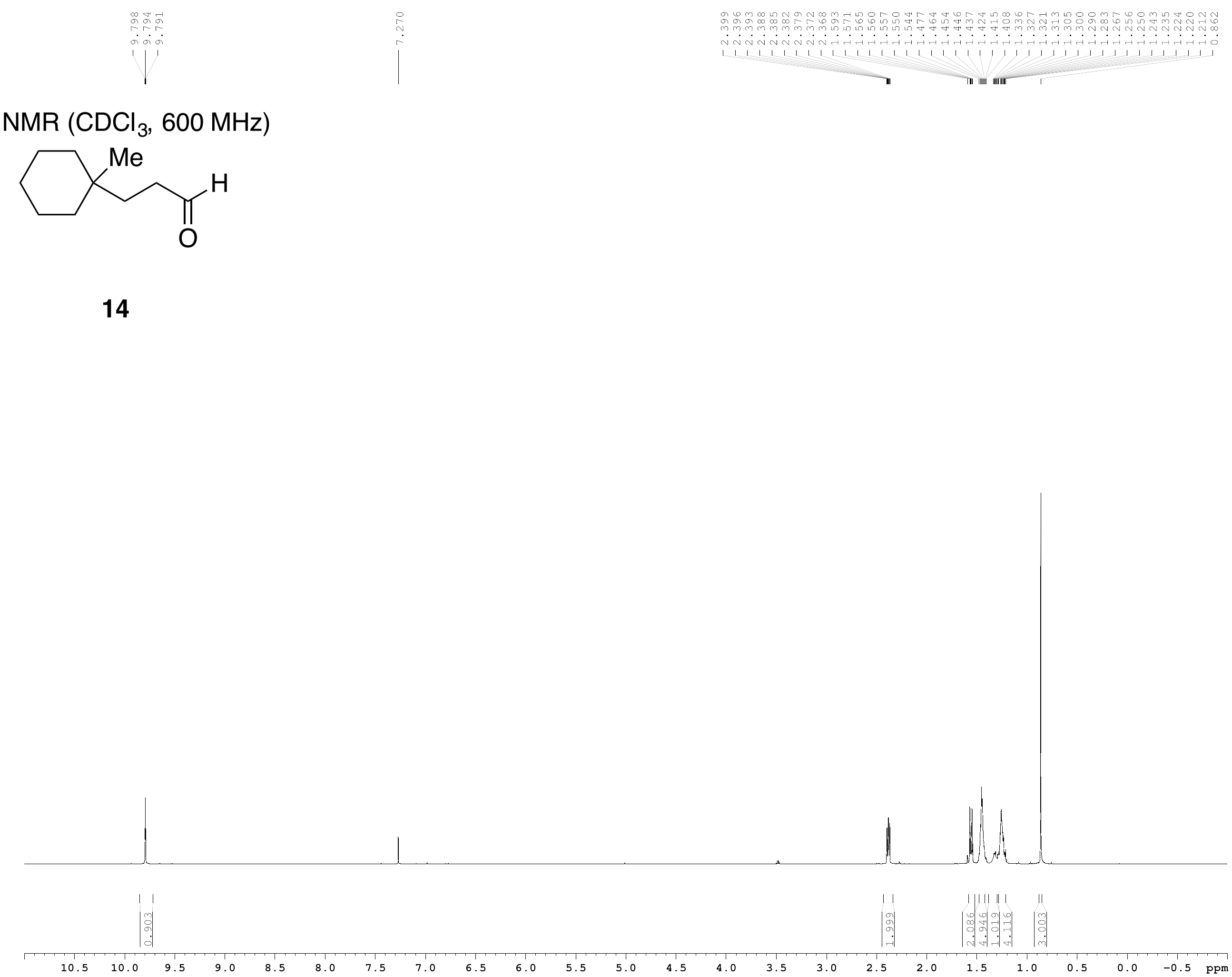
11



^{13}C NMR (126 MHz, CDCl$_3$)

11

YS-III-29A

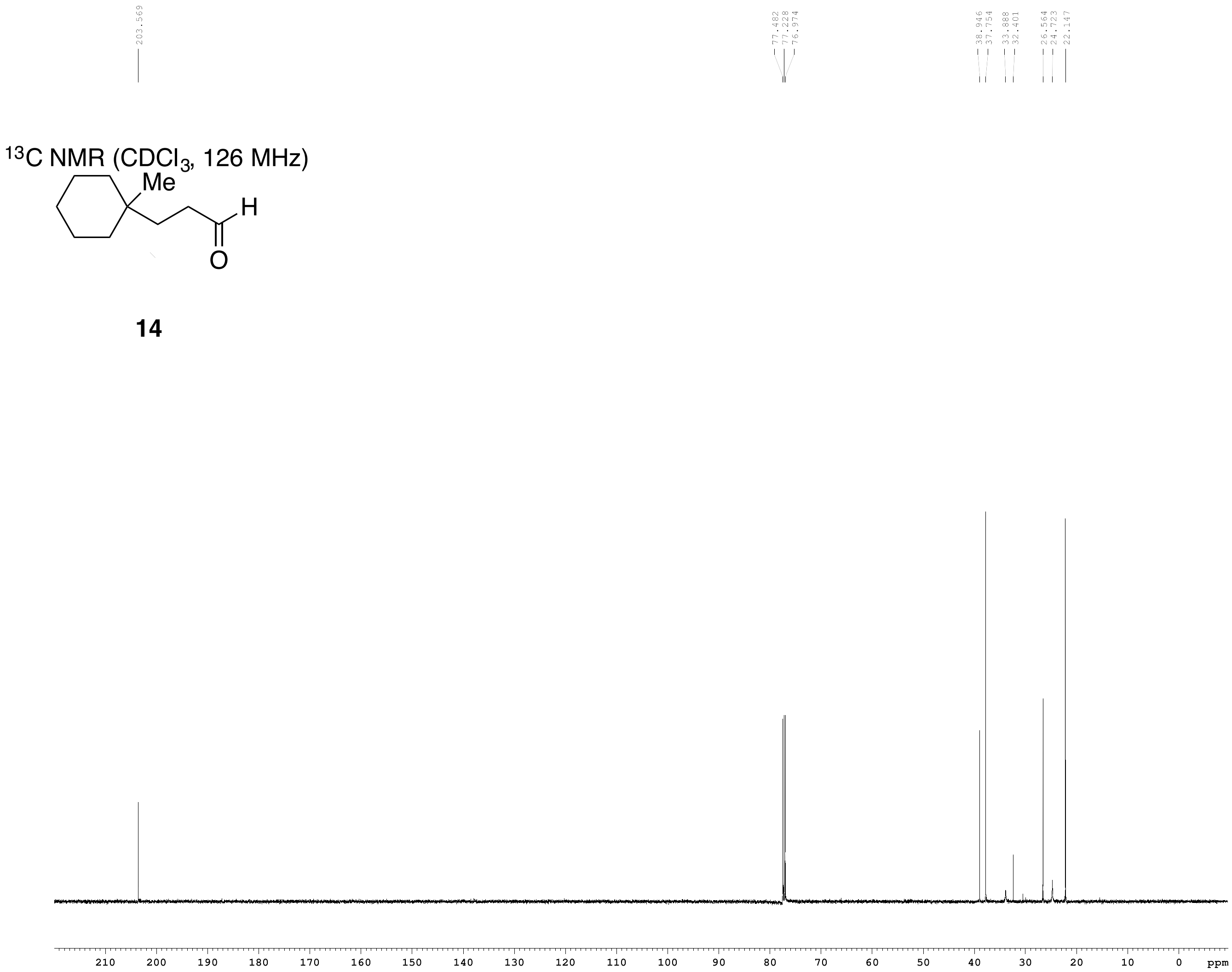


^{1}H NMR (CDCl$_3$, 600 MHz)

14

```
Current Data Parameters
NAME          YS-III-29A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150331
Time               16.08
INSTRUM            av600
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                   228
DW                52.000 usec
DE                 14.33 usec
TE                 298.3 K
D1          0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                  1H
P1                  9.00 usec
PLW1         60.25600052 W

F2 - Processing parameters
SI                 65536
SF          600.1300281 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

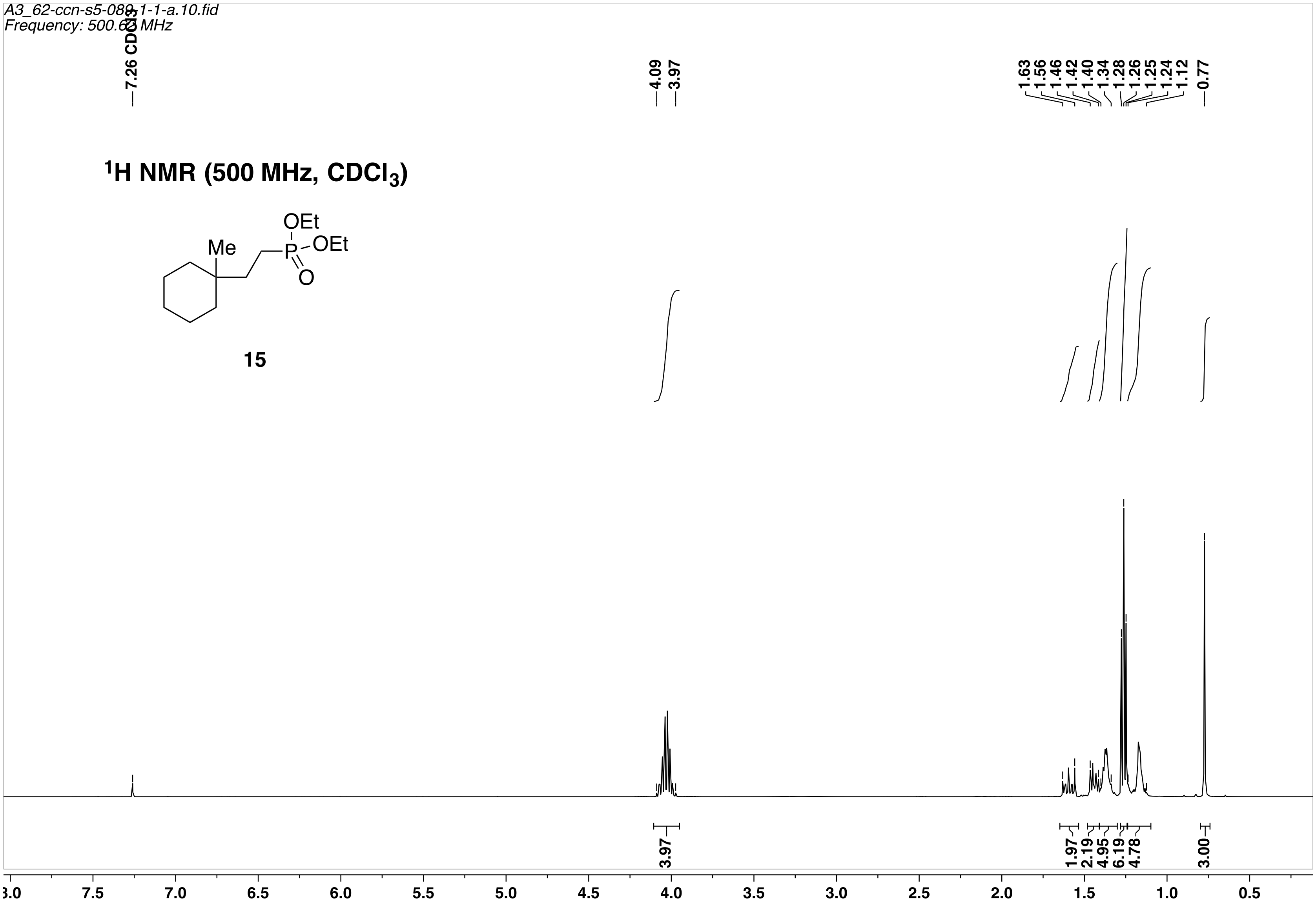
YS-III-29A



^{13}C NMR ($CDCl_3$, 126 MHz)

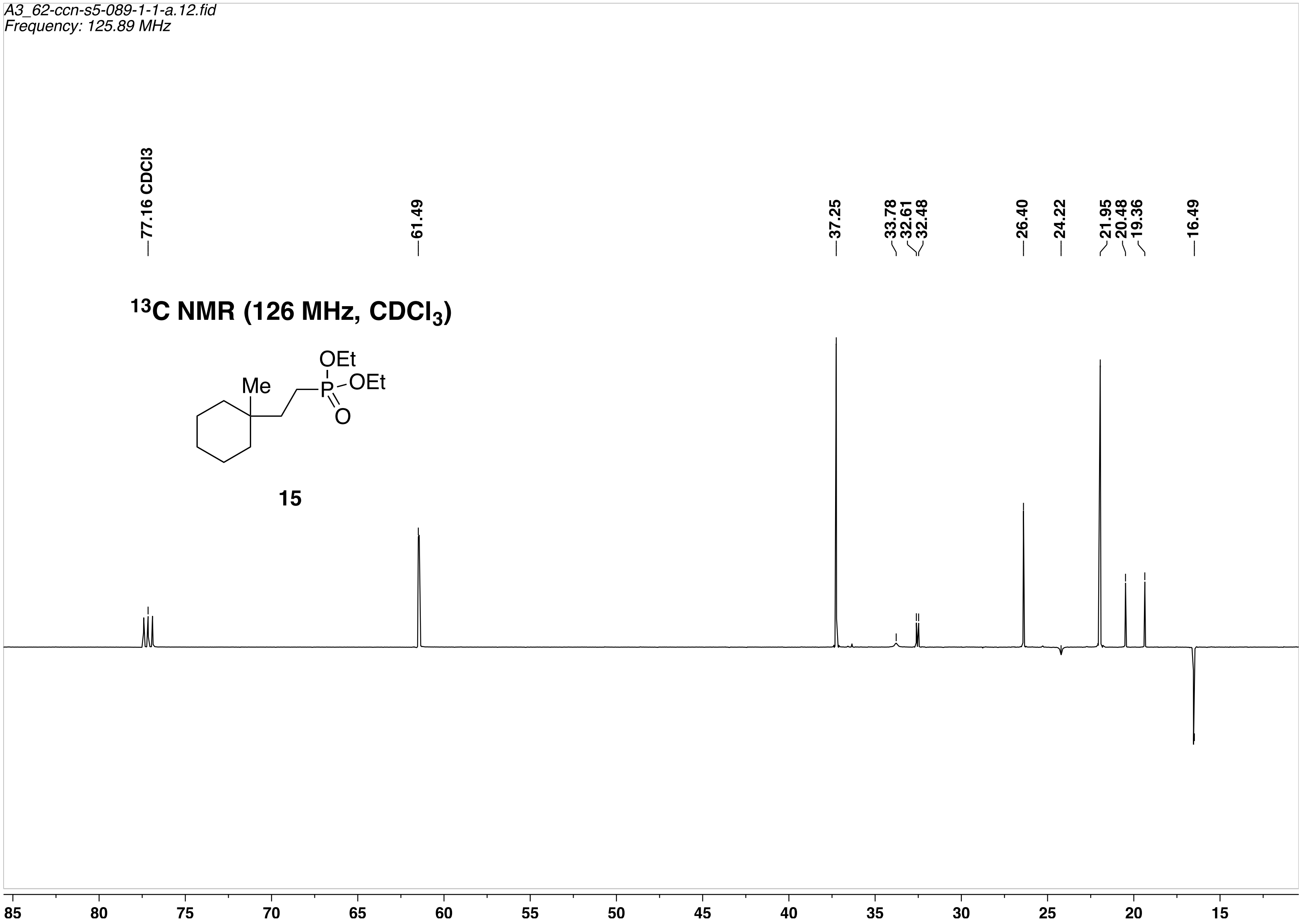
14

```
Current Data Parameters
NAME          YS-III-29A
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150401
Time               12.42
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCL3
NS                   288
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803131 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```



¹H NMR (500 MHz, $CDCl_3$)

15

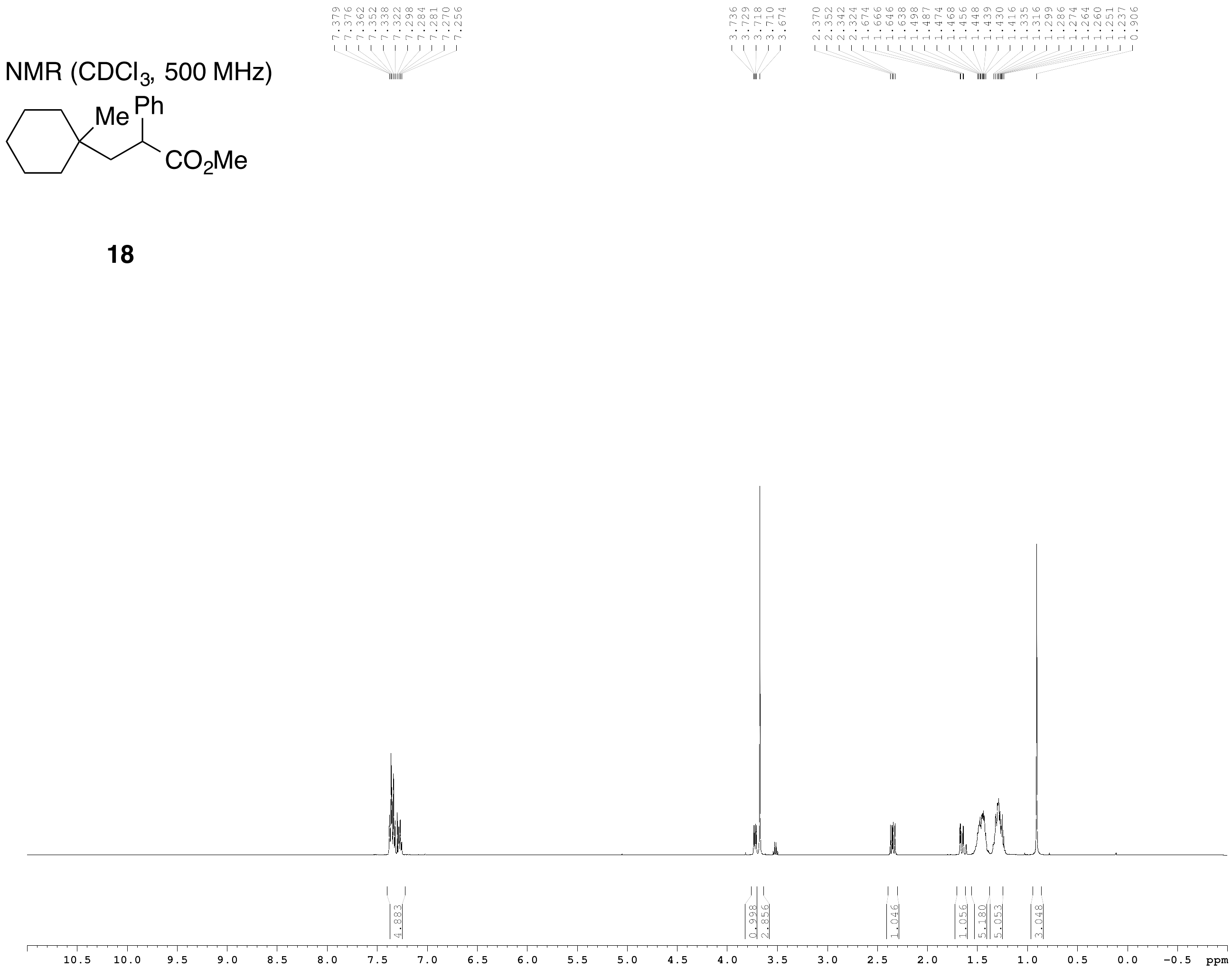


^{13}C NMR (126 MHz, CDCl$_3$)

15

YS-III-24B

^{1}H NMR (CDCl$_3$, 500 MHz)



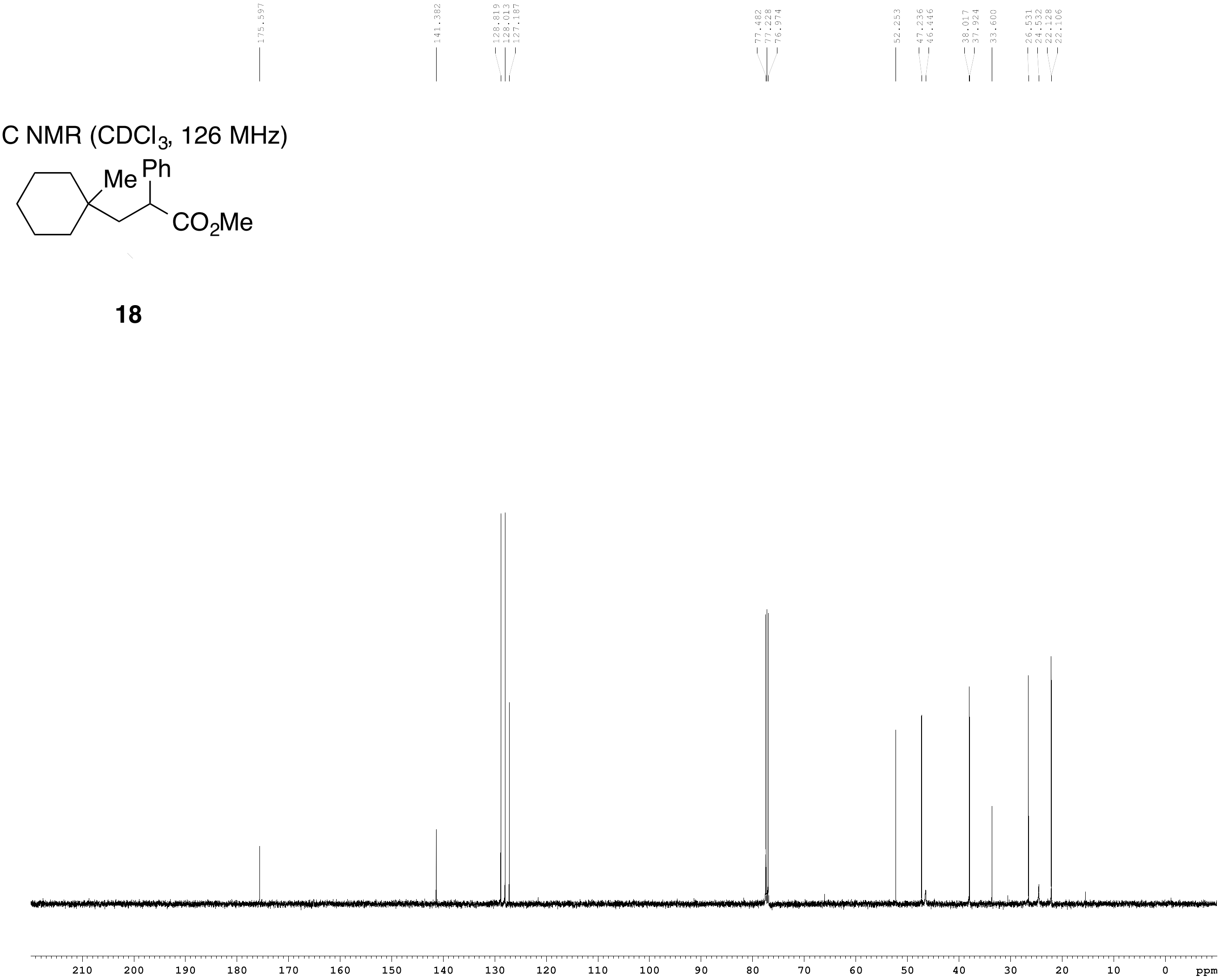
18

```
Current Data Parameters
NAME          YS-III-24B
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150326
Time               10.25
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9997952 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200117 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

YS-III-24B

^{13}C NMR (CDCl$_3$, 126 MHz)

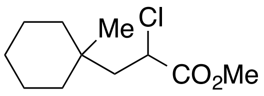
18



```
Current Data Parameters
NAME          YS-III-24B
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150326
Time               10.29
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   136
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803997 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

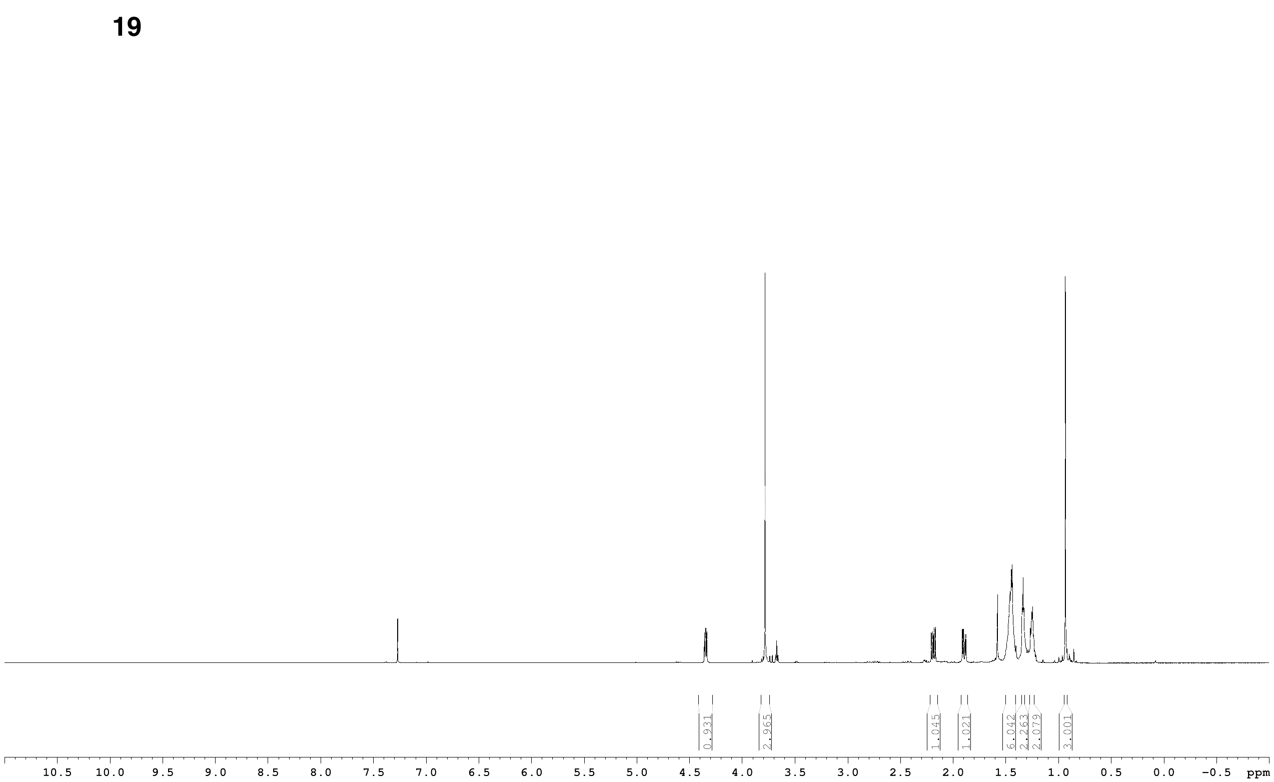
YS-III-47A

^{1}H NMR (CDCl$_3$, 600 MHz)



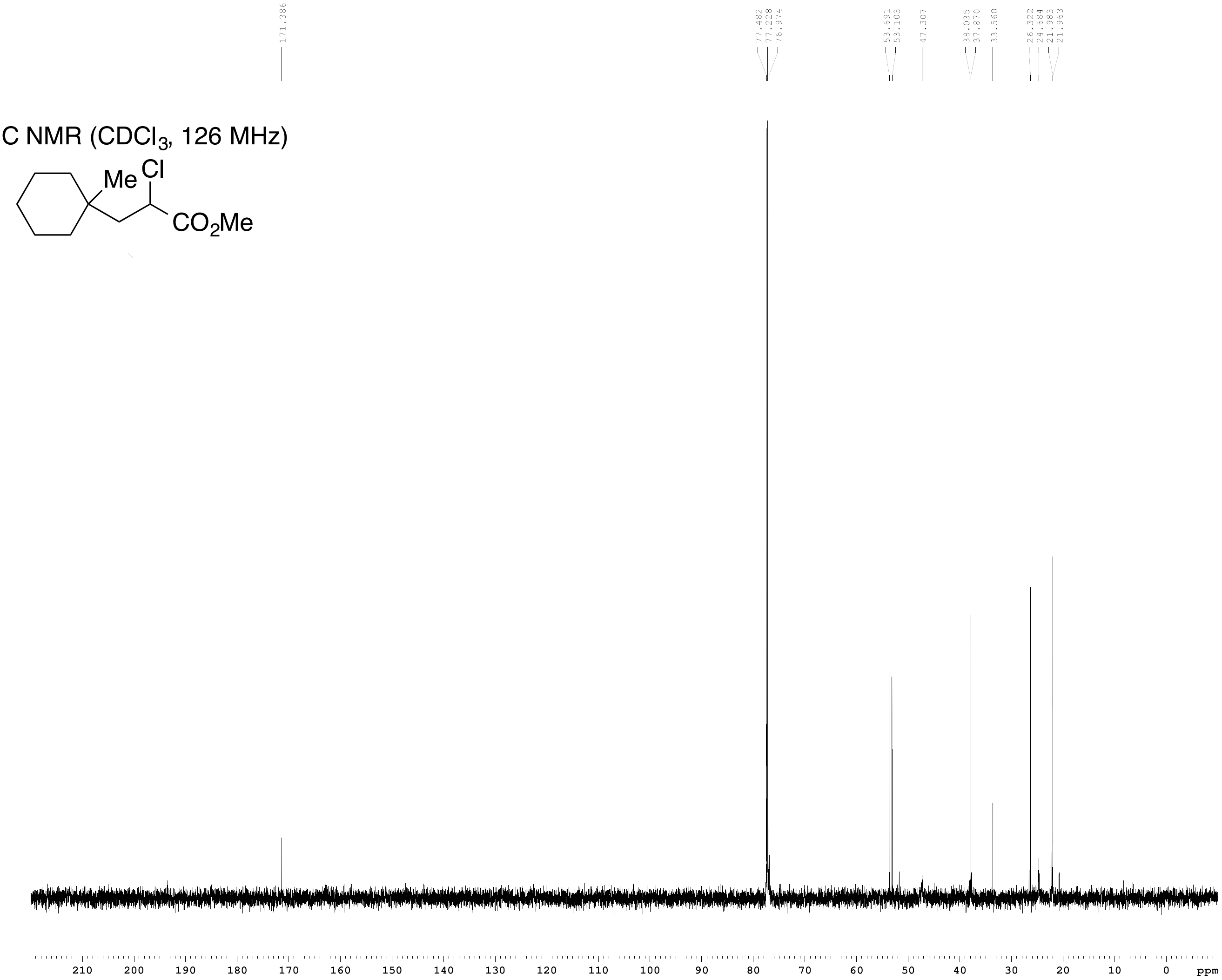
19

```
Current Data Parameters
NAME          YS-III-47A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150410
Time               16.32
INSTRUM            av600
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                   287
DW                52.000 usec
DE                 14.33 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  9.00 usec
PLW1         60.25600052 W

F2 - Processing parameters
SI                 65536
SF           600.1300283 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



YS-III-47A

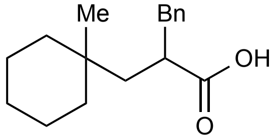
^{13}C NMR (CDCl$_3$, 126 MHz)



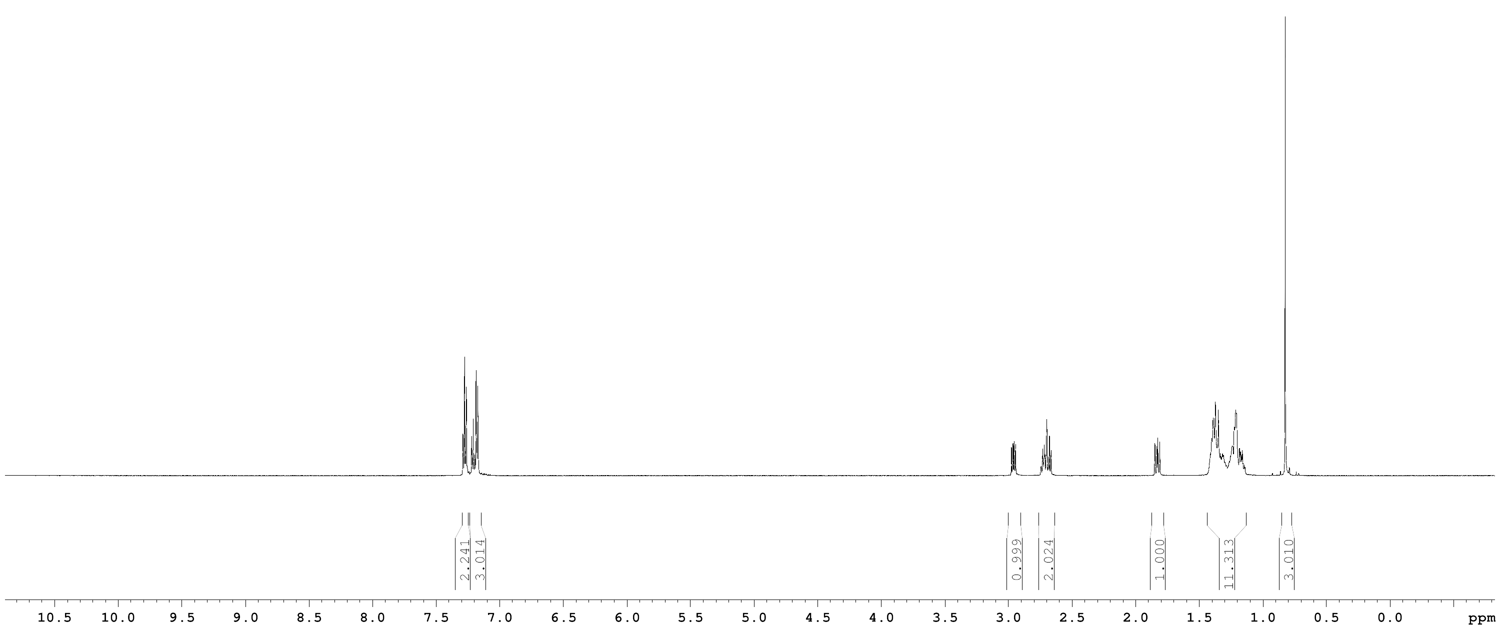
```
Current Data Parameters
NAME          YS-III-47A
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150427
Time                8.43
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   136
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803898 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum

^{1}H NMR ($CDCl_3$, 600MHz)



20

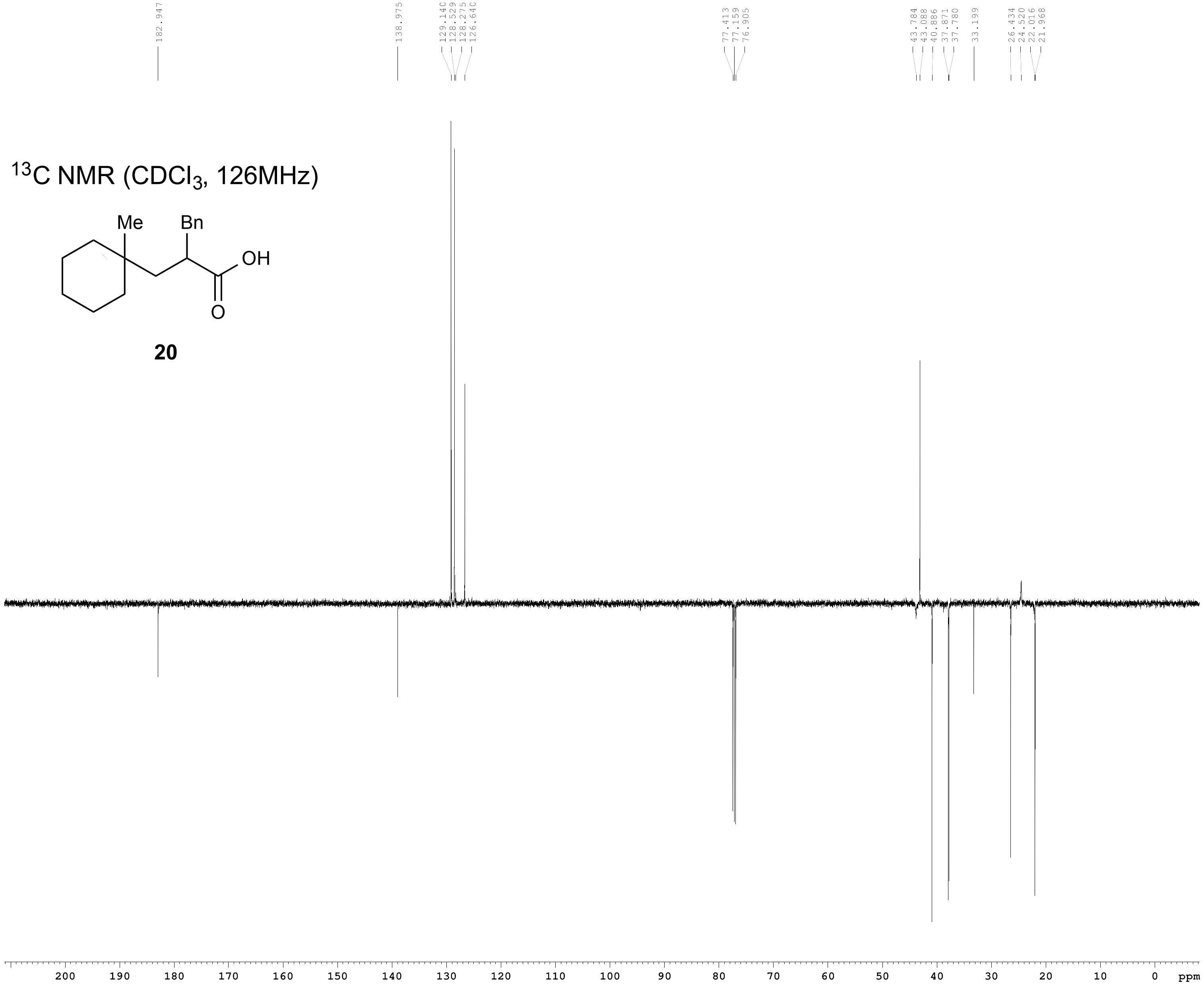


```
Current Data Parameters
NAME        CRJ1-156-pure
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150408
Time                18.01
INSTRUM             av600
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  76922
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             9615.385 Hz
FIDRES          0.125002 Hz
AQ             3.9999440 sec
RG                    256
DW                 52.000 usec
DE                  14.33 usec
TE                  298.2 K
D1            0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                   1H
P1                   9.00 usec
PLW1          60.25600052 W

F2 - Processing parameters
SI                  65536
SF           600.1300344 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```

deptq 13C spectrum with 1H decoupling (CH & CH3 one way up; C, CH2 and solvent the other)

^{13}C NMR (CDCl$_3$, 126MHz)

20

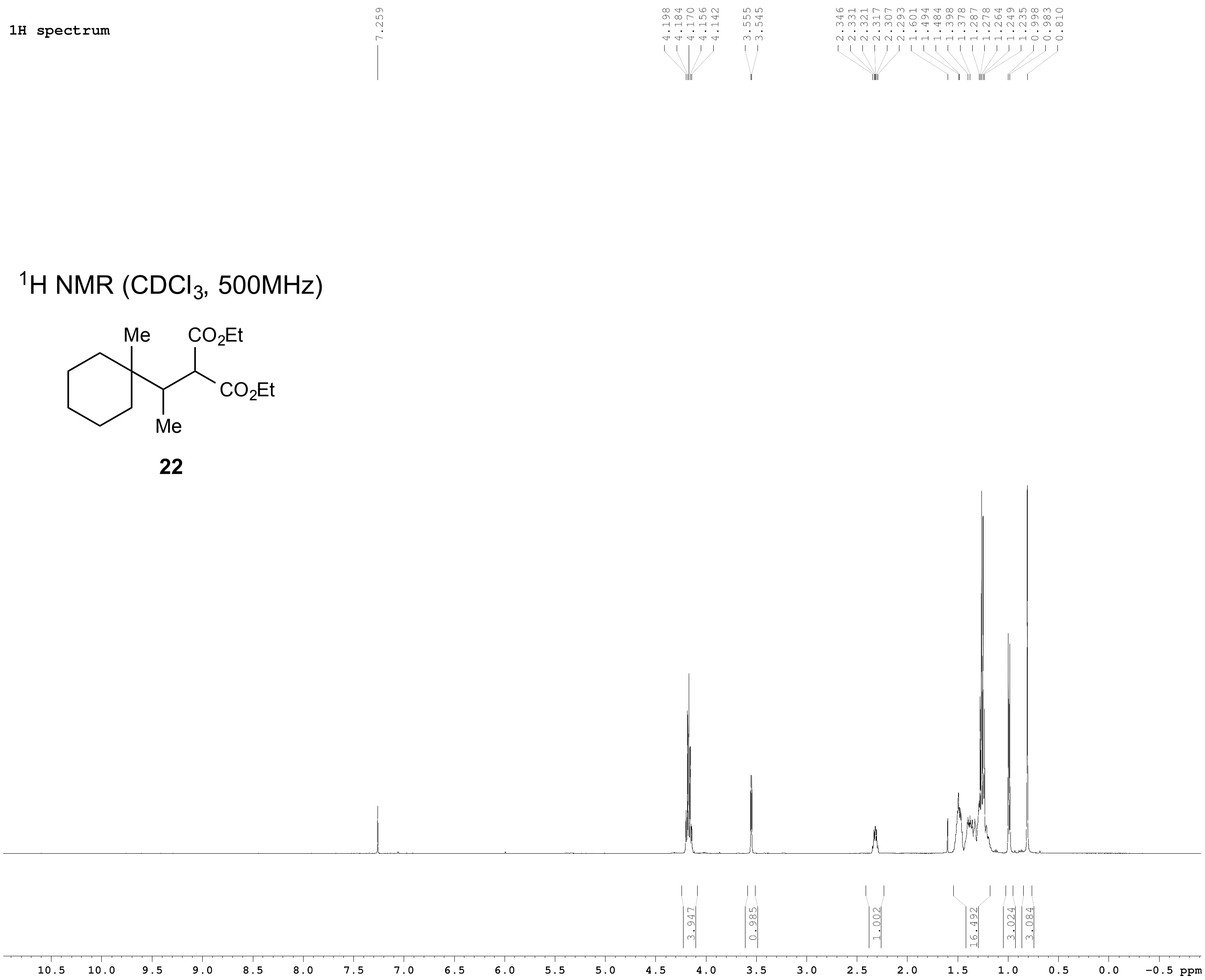


```
Current Data Parameters
NAME       CRJ1-156-pure
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150327
Time               15.15
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG        deptqgpsp
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                     8
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  2048
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
CNST2       145.0000000
CNST12        1.5000000
D1           1.00000000 sec
d2           0.00344828 sec
d12          0.00002000 sec
D16          0.00020000 sec
DELTA        0.00001707 sec
DELTA1       0.00228023 sec
DELTA2       0.00226483 sec
DELTA3       0.00224828 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SPNAM[2]    Crp60comp.4
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
p0                 11.55 usec
P3                  7.70 usec
p4                 15.40 usec
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPNAM[3]        SINE.100
GPX1       0 %
GPX2       0 %
GPX3       0 %
GPY1       0 %
GPY2       0 %
GPY3       0 %
GPZ1               31.00 %
GPZ2               31.00 %
GPZ3               31.00 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804079 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```

1H spectrum

^{1}H NMR (CDCl$_3$, 500MHz)

22

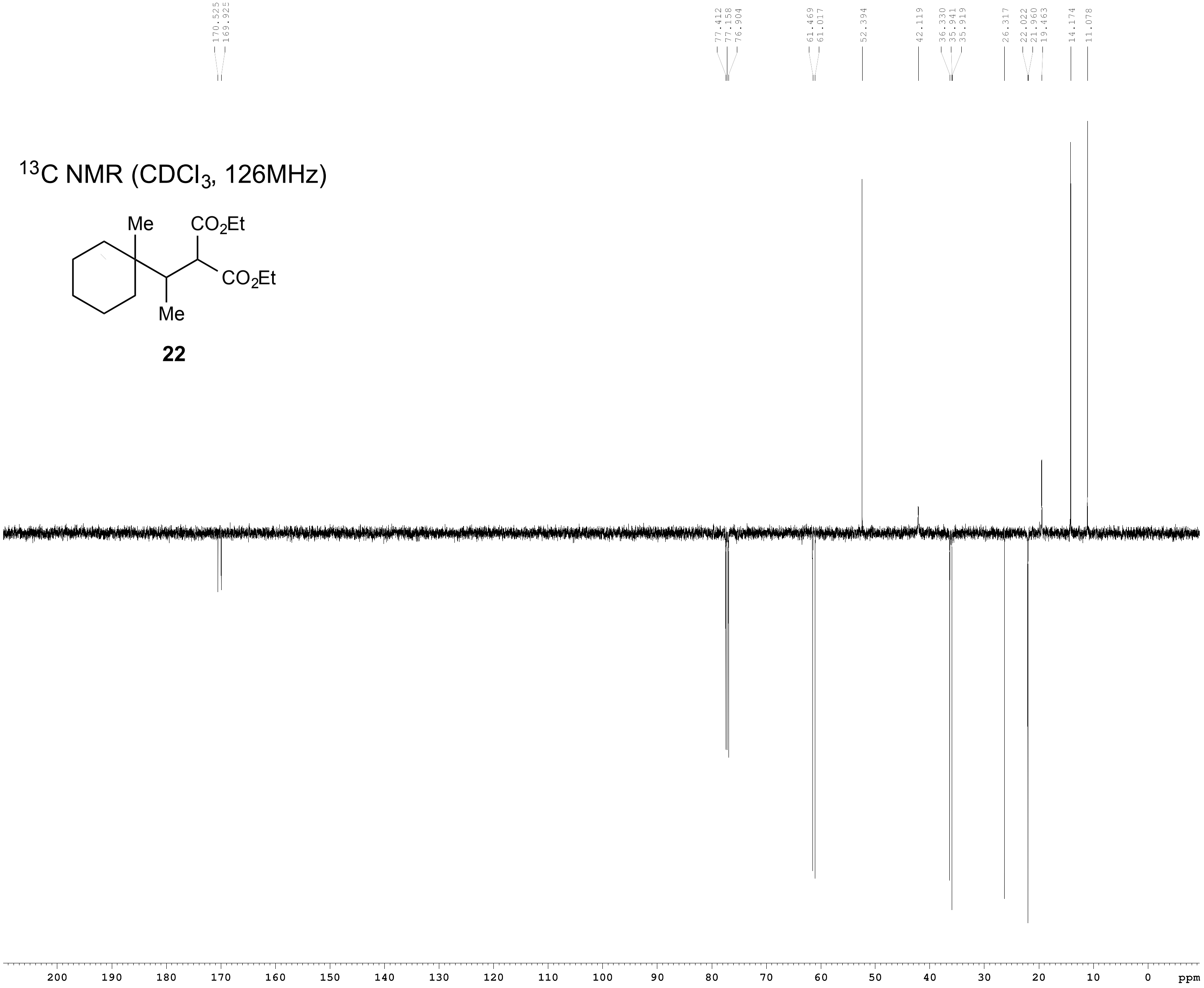


```
Current Data Parameters
NAME          CRJ1-084-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150211
Time               17.53
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998176 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200311 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

deptq 13C spectrum with 1H decoupling (CH & CH3 one way up; C, CH2 and solvent the other)

^{13}C NMR ($CDCl_3$, 126MHz)

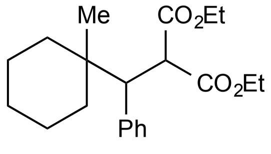
22



```
Current Data Parameters
NAME          CRJ1-084-1
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150211
Time               17.54
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG       deptqgpsp
TD                 65536
SOLVENT            CDCl3
NS                    48
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG               14596.5
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
CNST2        145.0000000
CNST12         1.5000000
D1            1.50000000 sec
d2            0.00344828 sec
d12           0.00002000 sec
D16           0.00020000 sec
DELTA         0.00001707 sec
DELTA1        0.00228023 sec
DELTA2        0.00226483 sec
DELTA3        0.00224828 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SPNAM[2]    Crp60comp.4
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
p0                 11.55 usec
P3                  7.70 usec
p4                 15.40 usec
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPNAM[3]        SINE.100
GPX1     0 %
GPX2     0 %
GPX3     0 %
GPY1     0 %
GPY2     0 %
GPY3     0 %
GPZ1               31.00 %
GPZ2               31.00 %
GPZ3               31.00 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804082 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

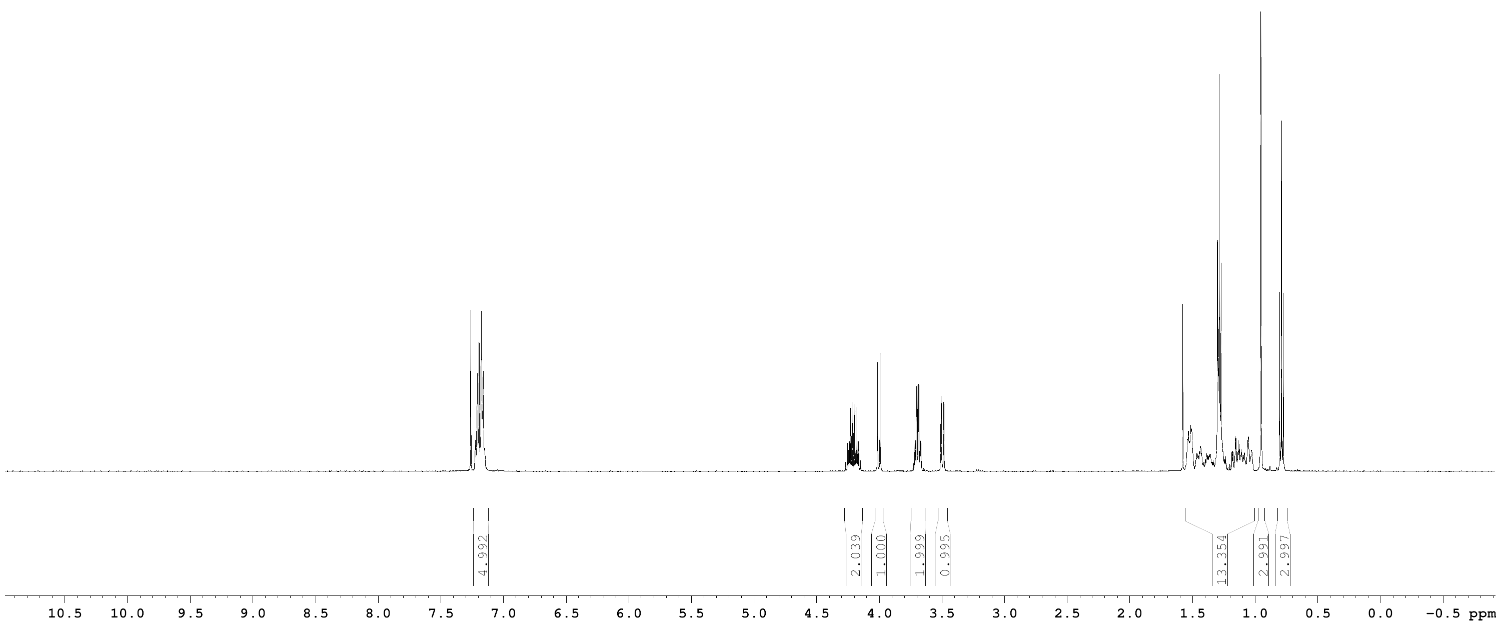
1H spectrum

^{1}H NMR ($CDCl_3$, 500MHz)

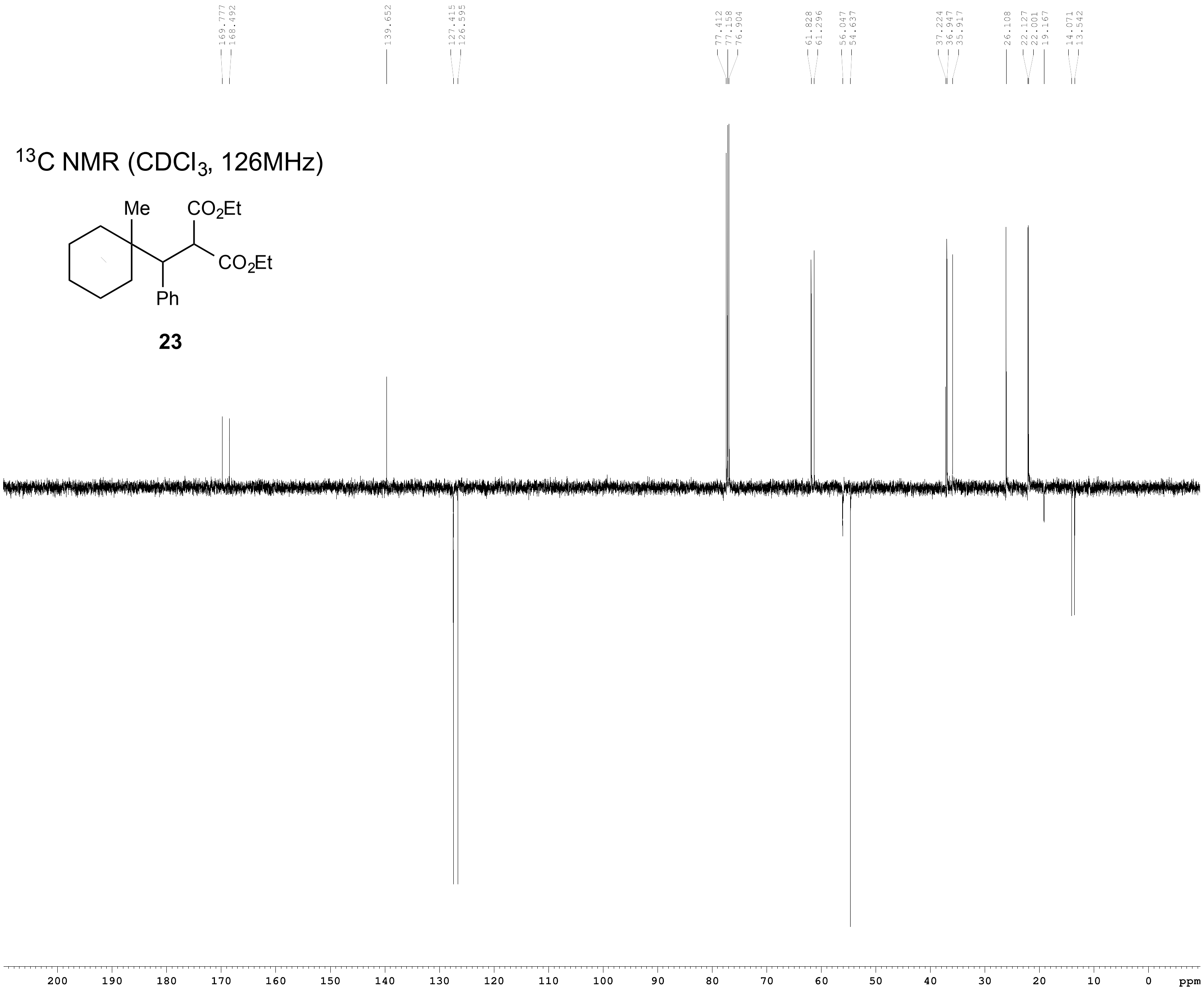


23

```
Current Data Parameters
NAME      CRJ1-205-pure
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150417
Time              13.05
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                64100
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.125005 Hz
AQ            3.9998400 sec
RG                  4.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200308 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```



deptq 13C spectrum with 1H decoupling (CH & CH3 one way up; C, CH2 and solvent the other)



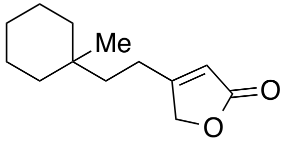
^{13}C NMR ($CDCl_3$, 126MHz)

23

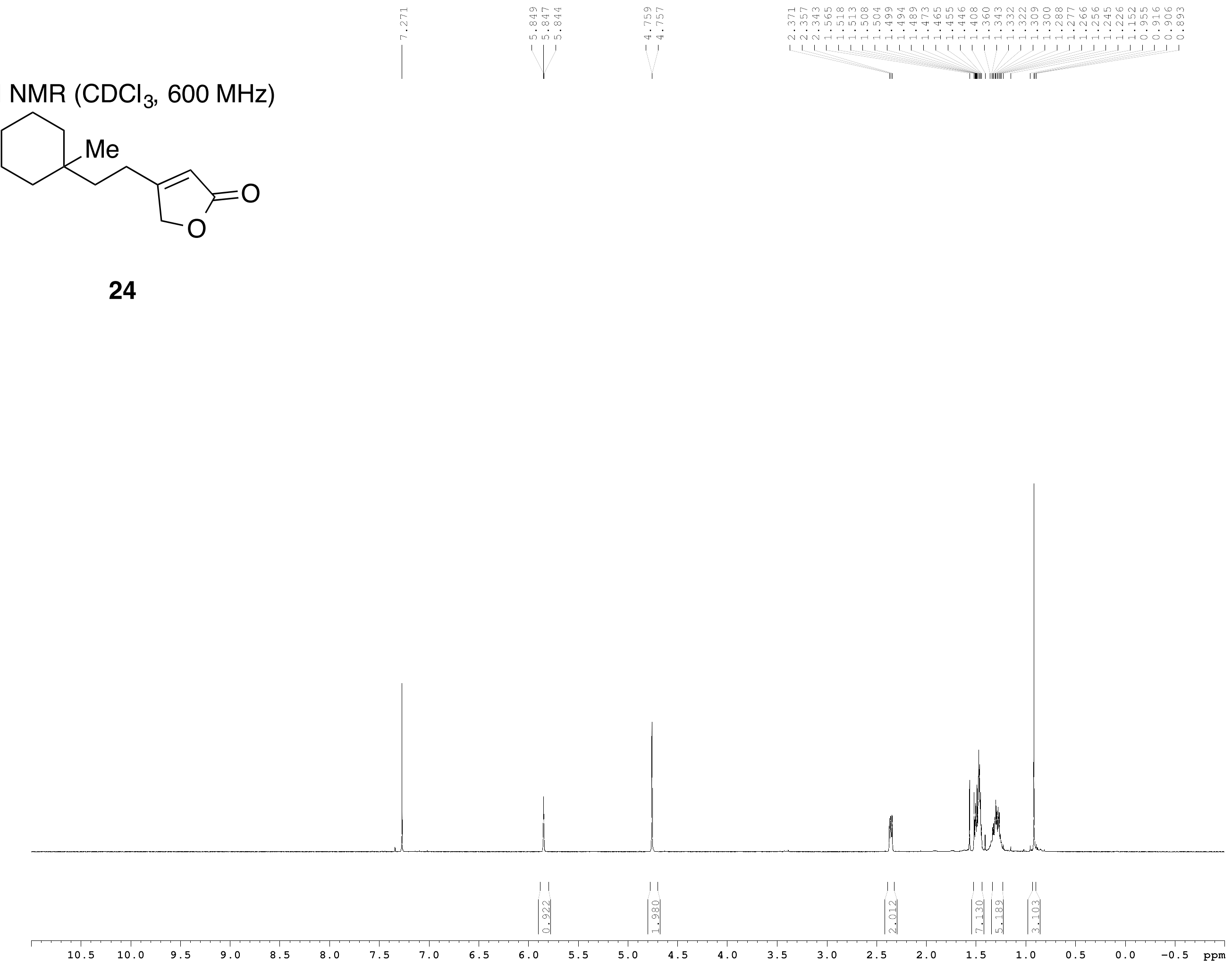
```
Current Data Parameters
NAME      CRJ1-205-pure
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150417
Time              13.08
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG       deptqgpsp
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               5160.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
CNST2       145.0000000
CNST12        1.5000000
D1           1.00000000 sec
d2           0.00344828 sec
d12          0.00002000 sec
D16          0.00020000 sec
DELTA        0.00001707 sec
DELTA1       0.00228023 sec
DELTA2       0.00226483 sec
DELTA3       0.00224828 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SPNAM[2]    Crp60comp.4
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
p0                11.55 usec
P3                 7.70 usec
p4                15.40 usec
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPNAM[3]       SINE.100
GPX1     0 %
GPX2     0 %
GPX3     0 %
GPY1     0 %
GPY2     0 %
GPY3     0 %
GPZ1              31.00 %
GPZ2              31.00 %
GPZ3              31.00 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804080 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-225B

^{1}H NMR (CDCl$_3$, 600 MHz)



24

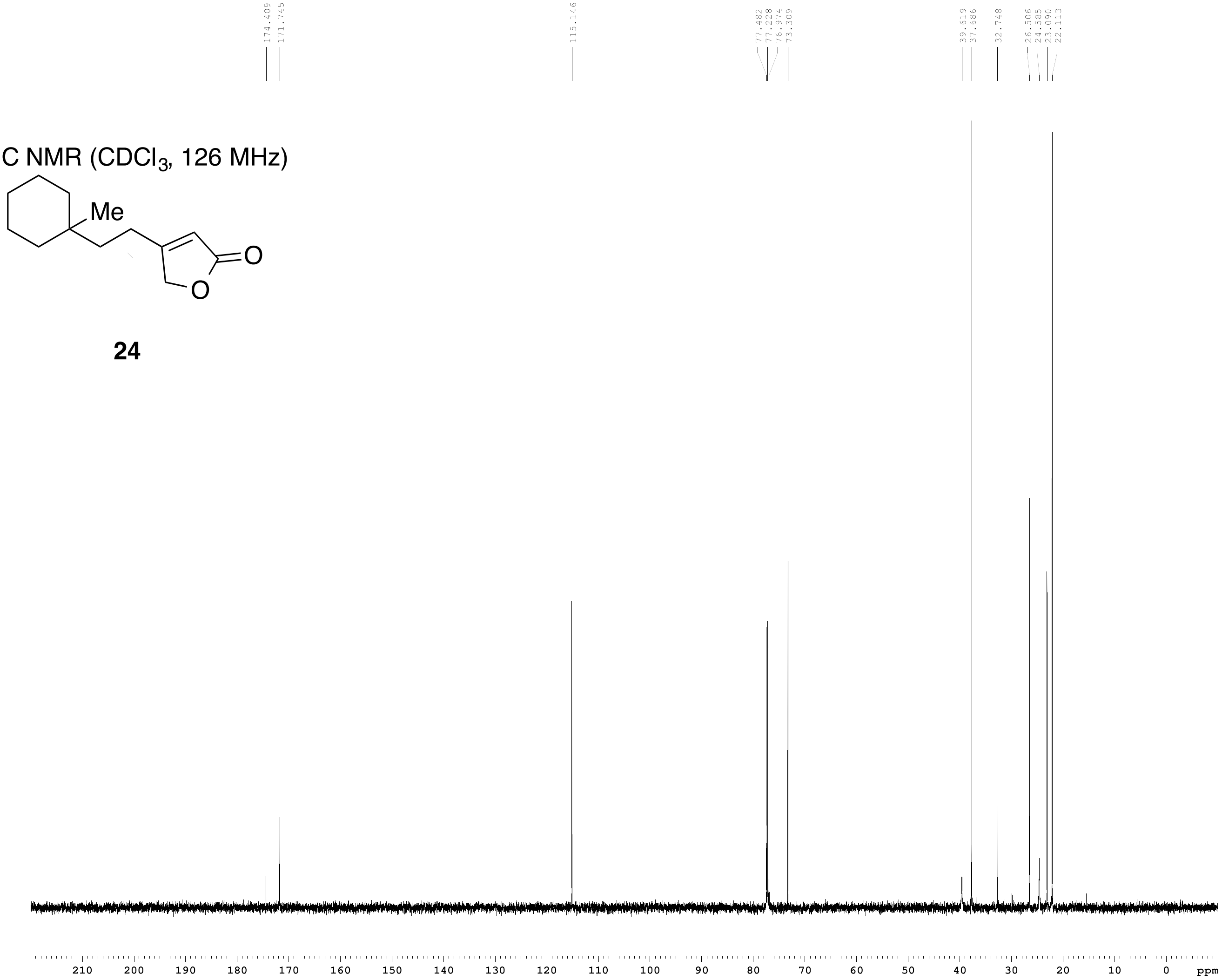


```
Current Data Parameters
NAME          YS-II-225B
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150210
Time               12.40
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                   512
DW                52.000 usec
DE                 14.54 usec
TE                 298.2 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         23.01441956 W

F2 - Processing parameters
SI                 65536
SF           600.1300291 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-II-225B

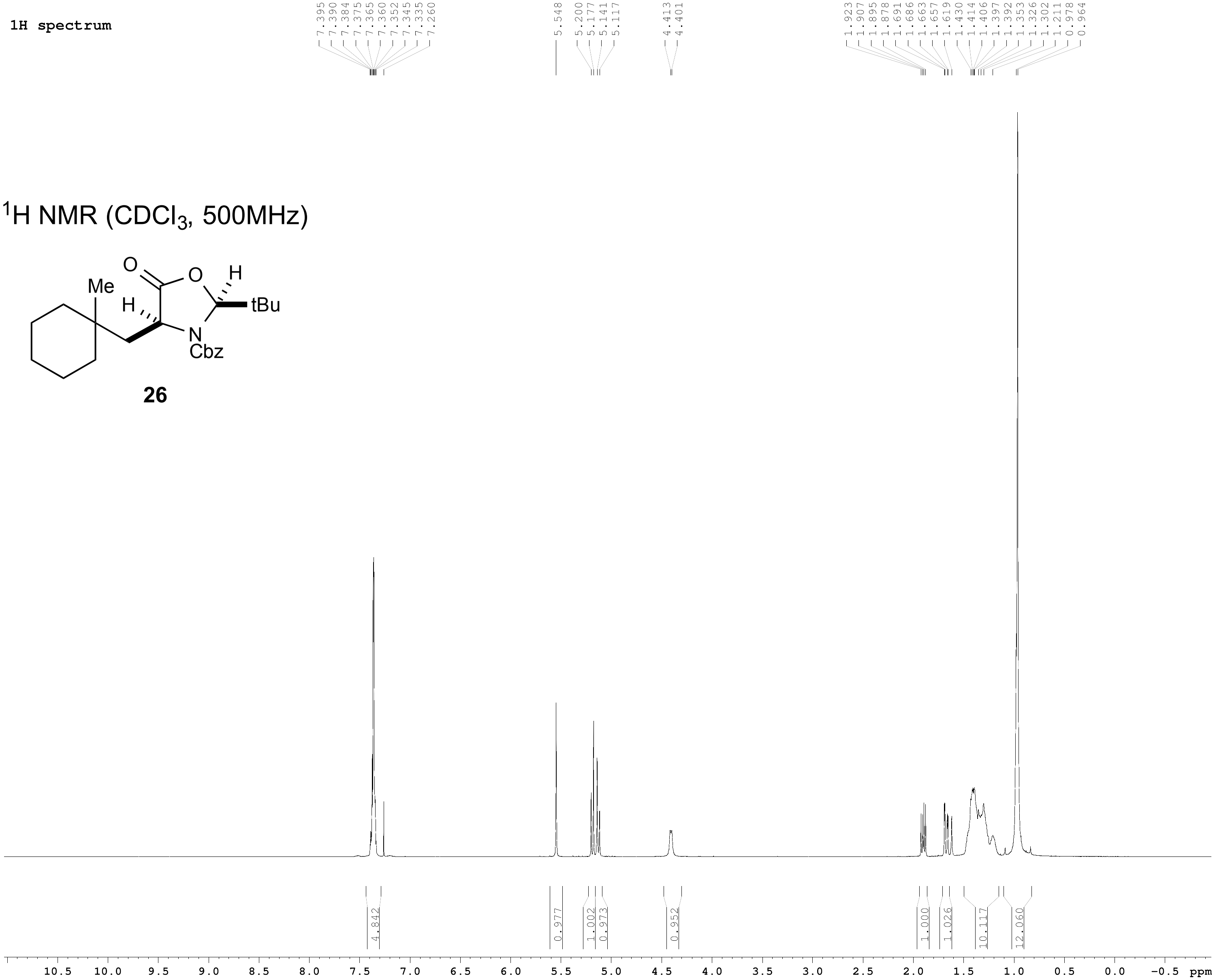
^{13}C NMR (CDCl$_3$, 126 MHz)

24



```
Current Data Parameters
NAME          YS-II-225B
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150427
Time                8.32
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   136
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1       0 %
GPX2       0 %
GPY1       0 %
GPY2       0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803954 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum



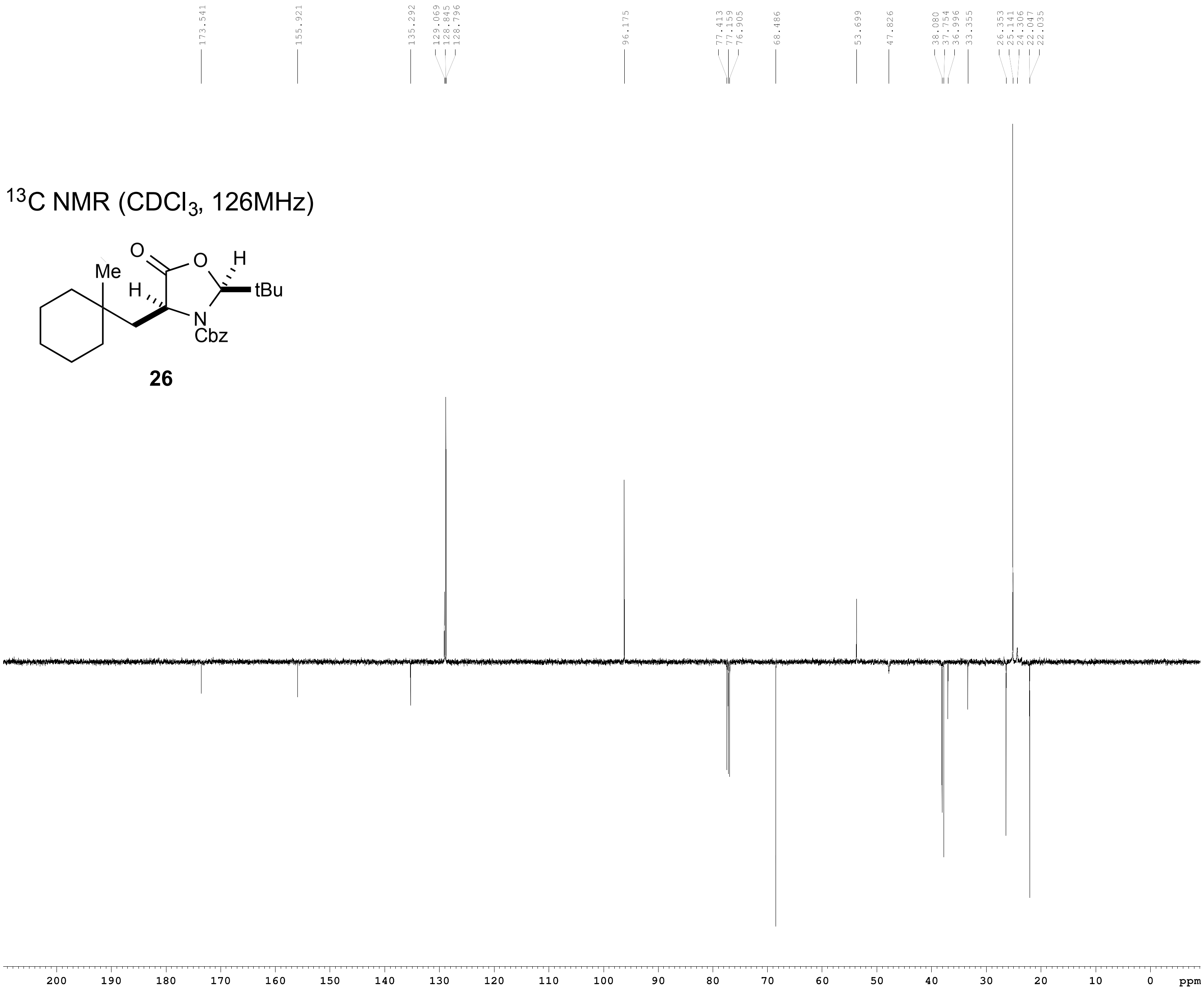
^{1}H NMR ($CDCl_3$, 500MHz)

26

```
Current Data Parameters
NAME        CRJ1-155-NOE
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150425
Time               14.46
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   3.2
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200308 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

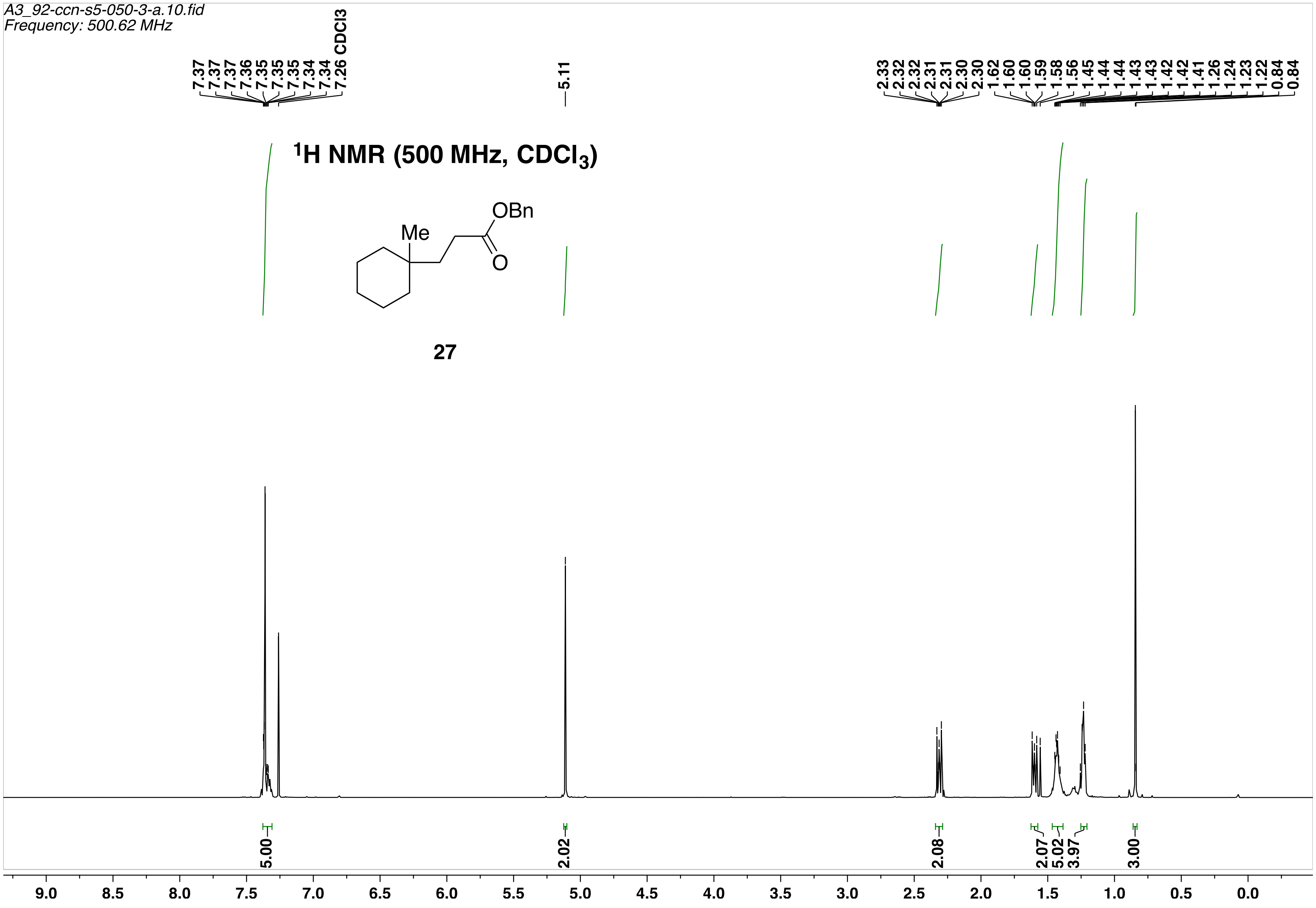
deptq 13C spectrum with 1H decoupling (CH & CH3 one way up; C, CH2 and solvent the other)

^{13}C NMR (CDCl$_3$, 126MHz)



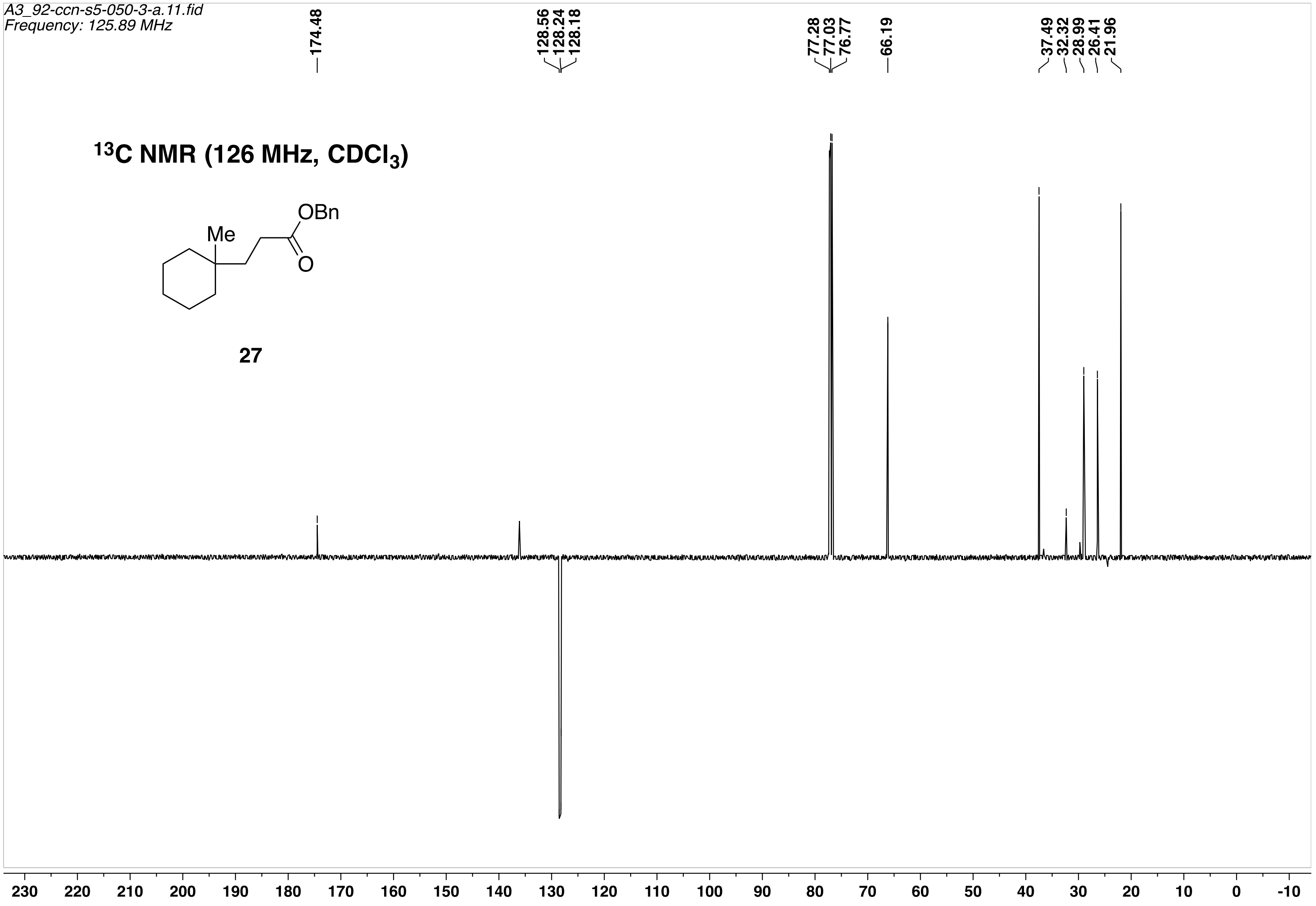
26

```
Current Data Parameters
NAME          CRJ1-082-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150211
Time               17.46
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG        deptqgpsp
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  2048
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
CNST2        145.0000000
CNST12         1.5000000
D1            1.50000000 sec
d2            0.00344828 sec
d12           0.00002000 sec
D16           0.00020000 sec
DELTA         0.00001707 sec
DELTA1        0.00228023 sec
DELTA2        0.00226483 sec
DELTA3        0.00224828 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SPNAM[2]    Crp60comp.4
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
p0                 11.55 usec
P3                  7.70 usec
p4                 15.40 usec
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPNAM[3]        SINE.100
GPX1      0 %
GPX2      0 %
GPX3      0 %
GPY1      0 %
GPY2      0 %
GPY3      0 %
GPZ1               31.00 %
GPZ2               31.00 %
GPZ3               31.00 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804094 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```



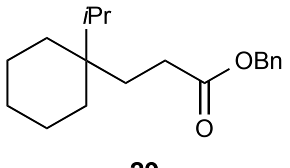
^{1}H NMR (500 MHz, CDCl$_3$)

27


A3_92-ccn-s5-050-3-a.11.fid
Frequency: 125.89 MHz
13C NMR (126 MHz, CDCl3)
Me
OBn
O
27
174.48
128.56
128.24
128.18
77.28
77.03
76.77
66.19
37.49
32.32
28.99
26.41
21.96
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

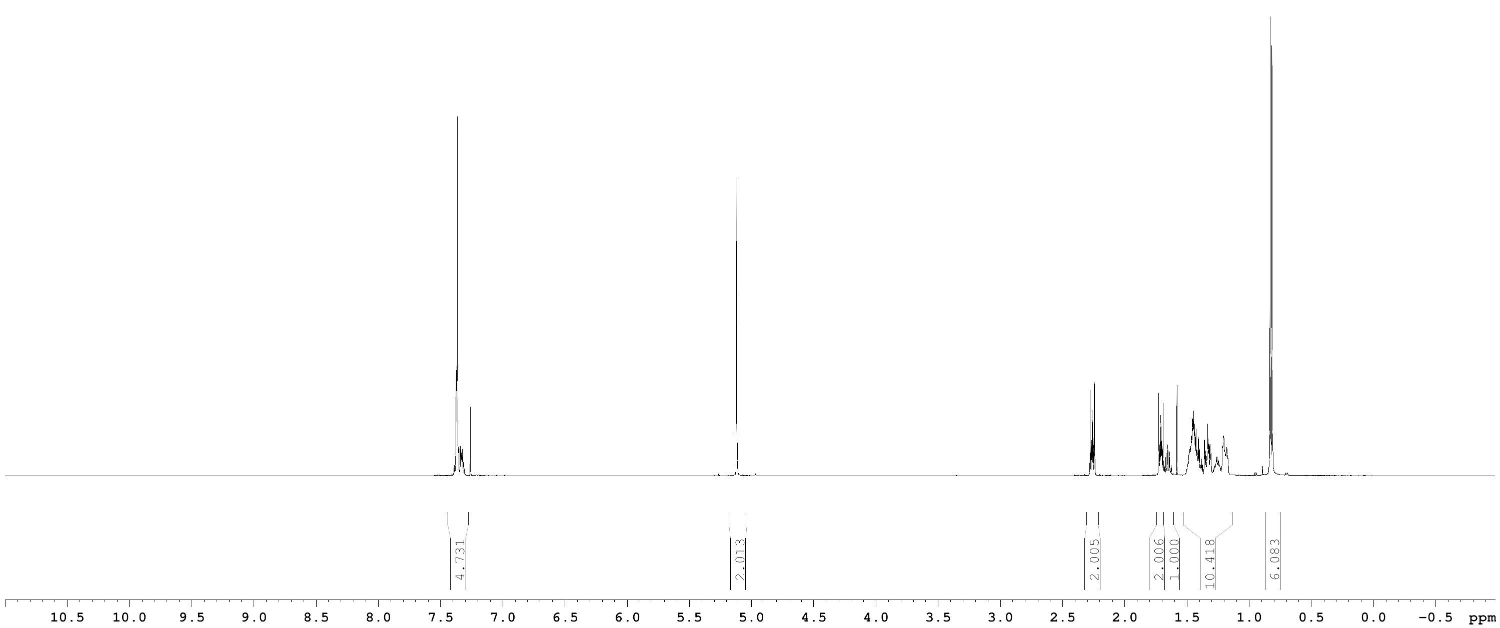
1H spectrum

^{1}H NMR ($CDCl_3$, 500MHz)



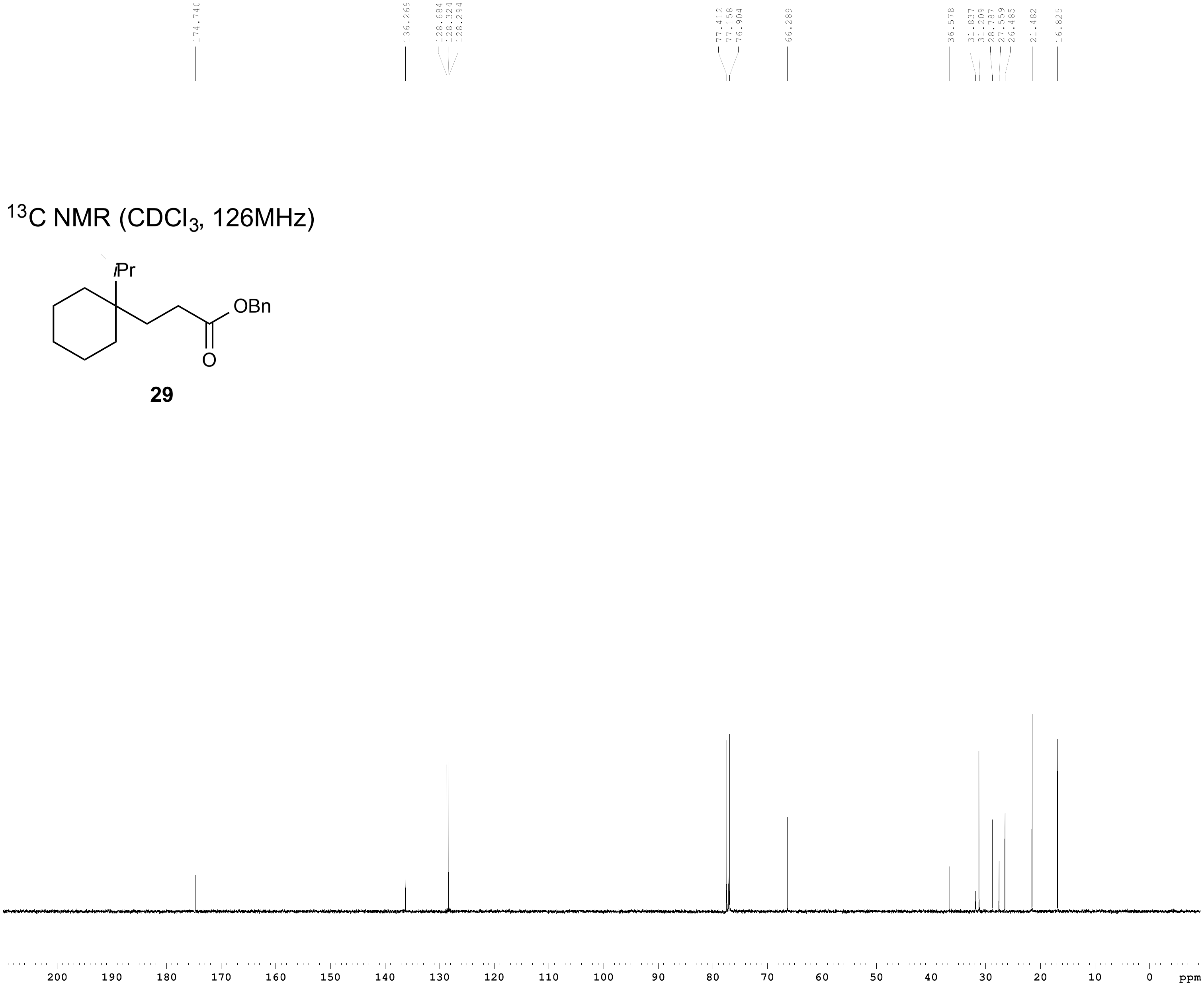
29

```
Current Data Parameters
NAME       CRJ1-152-pure
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20150317
Time              14.06
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998176 sec
RG                    4
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200311 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```



Z-restored spin-echo 13C spectrum with 1H decoupling

^{13}C NMR (CDCl$_3$, 126MHz)



29

```
Current Data Parameters
NAME       CRJ1-152-pure
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20150317
Time              14.08
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804091 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

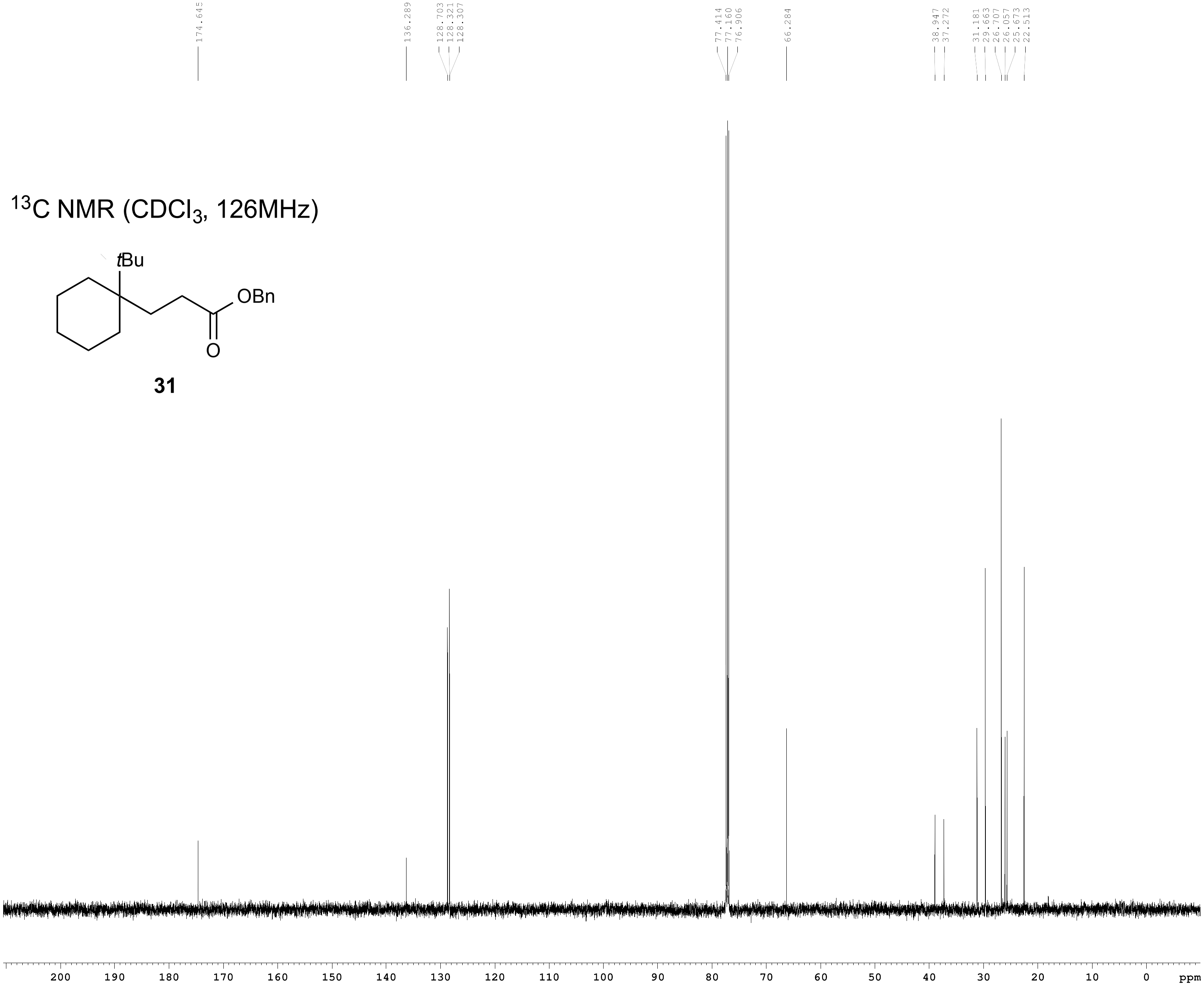
1H spectrum

^{1}H NMR ($CDCl_3$, 500MHz)

31

```
Current Data Parameters
NAME      CRJ1-153-pure
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150317
Time              14.14
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998176 sec
RG                    5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200309 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```

Z-restored spin-echo 13C spectrum with 1H decoupling



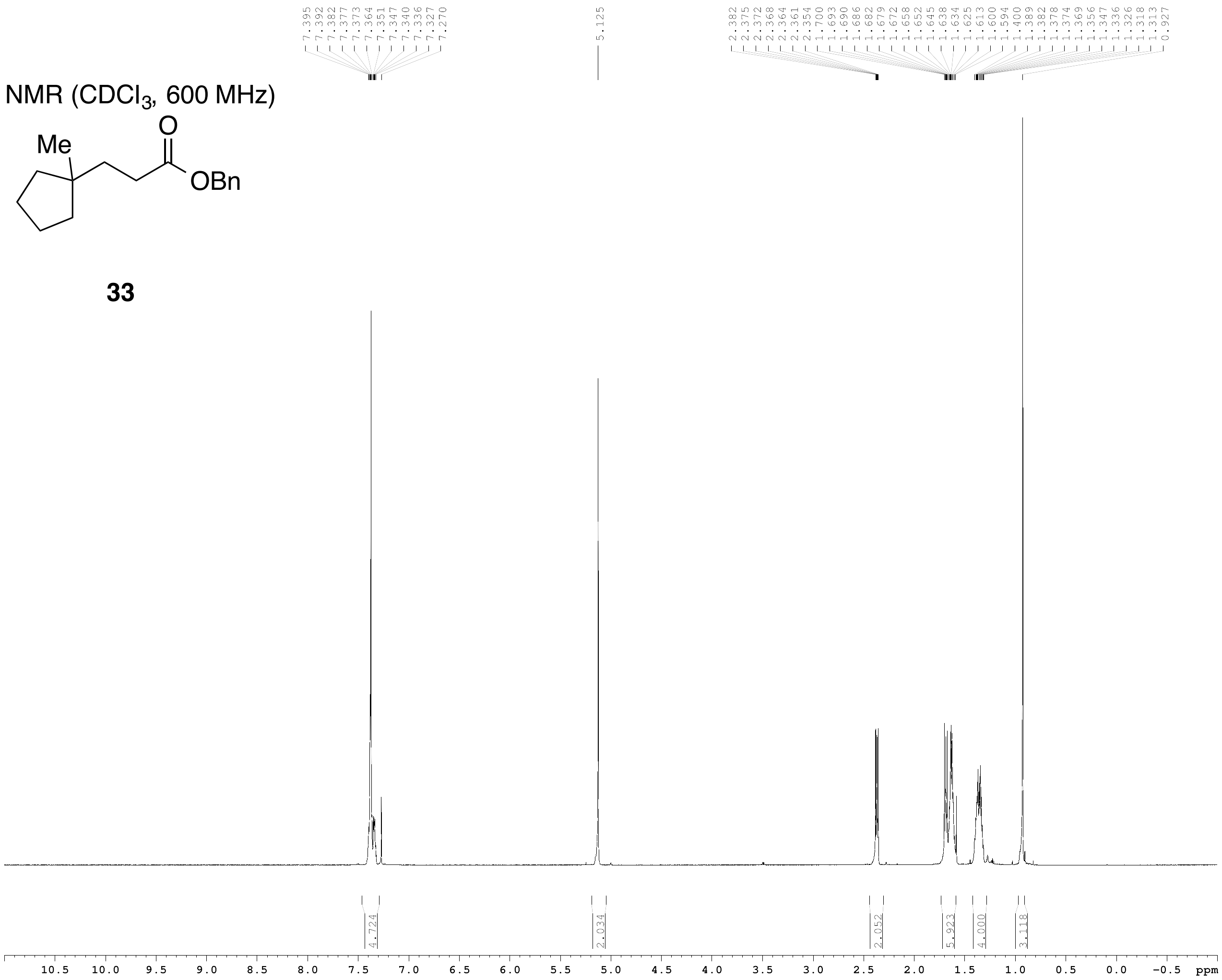
^{13}C NMR (CDCl$_3$, 126MHz)

31

```
Current Data Parameters
NAME       CRJ1-153-pure
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150317
Time               14.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804077 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-II-254A

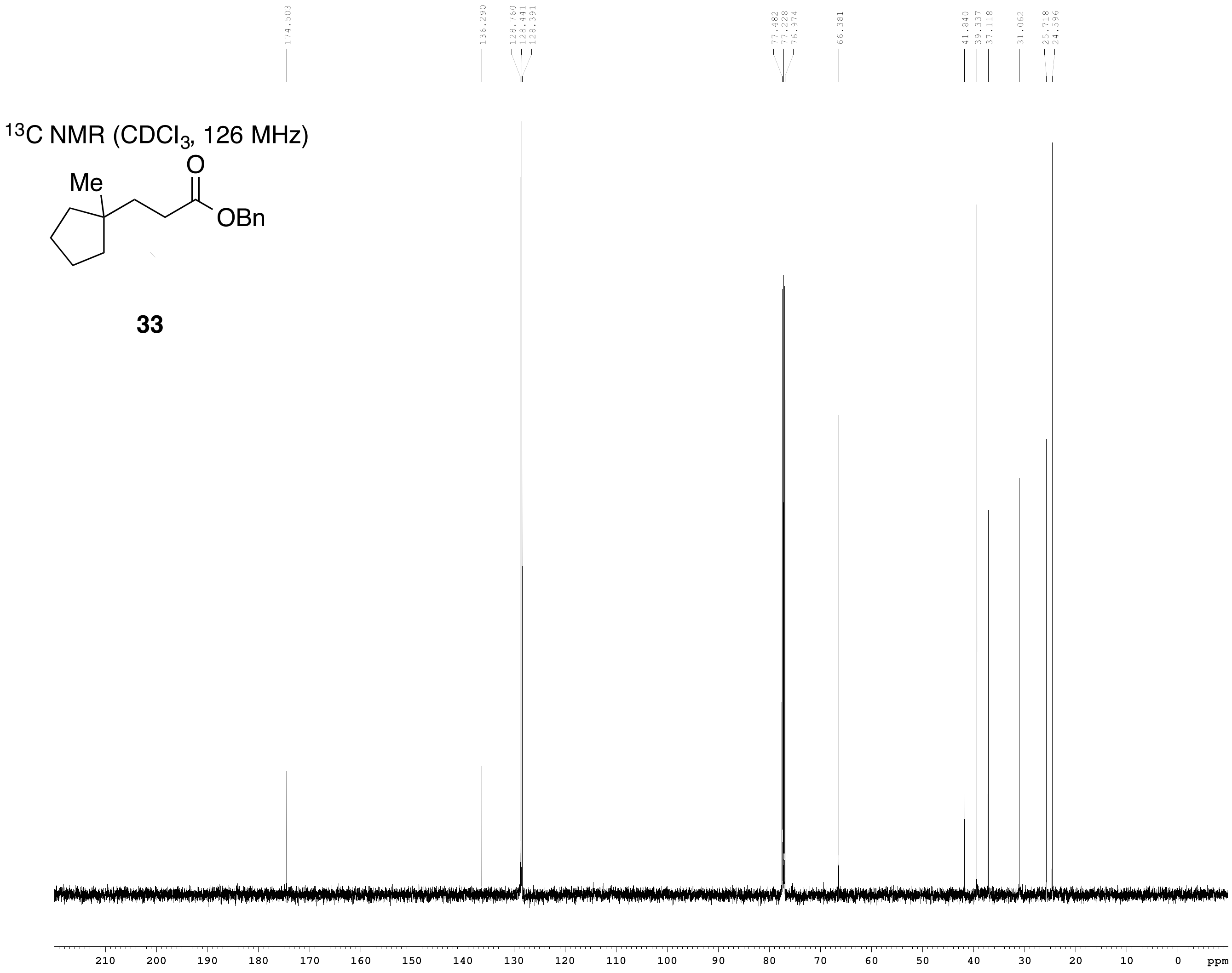
^{1}H NMR (CDCl$_3$, 600 MHz)



33

```
Current Data Parameters
NAME          YS-II-254A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150219
Time               14.59
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.250010 Hz
AQ             1.9999200 sec
RG                   161
DW                52.000 usec
DE                 14.54 usec
TE                 298.1 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         23.01441956 W

F2 - Processing parameters
SI                 65536
SF           600.1300300 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

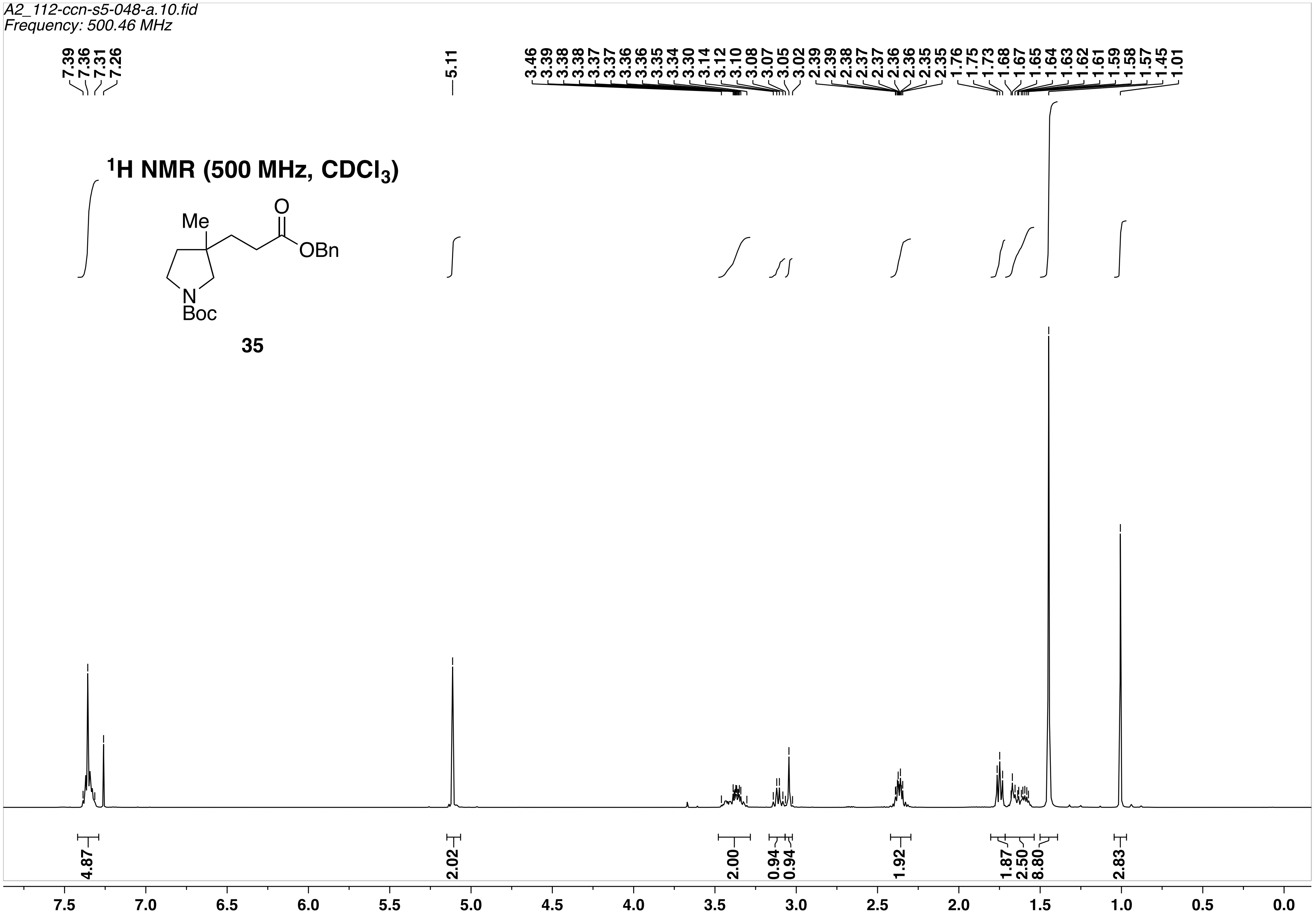
YS-II-254A

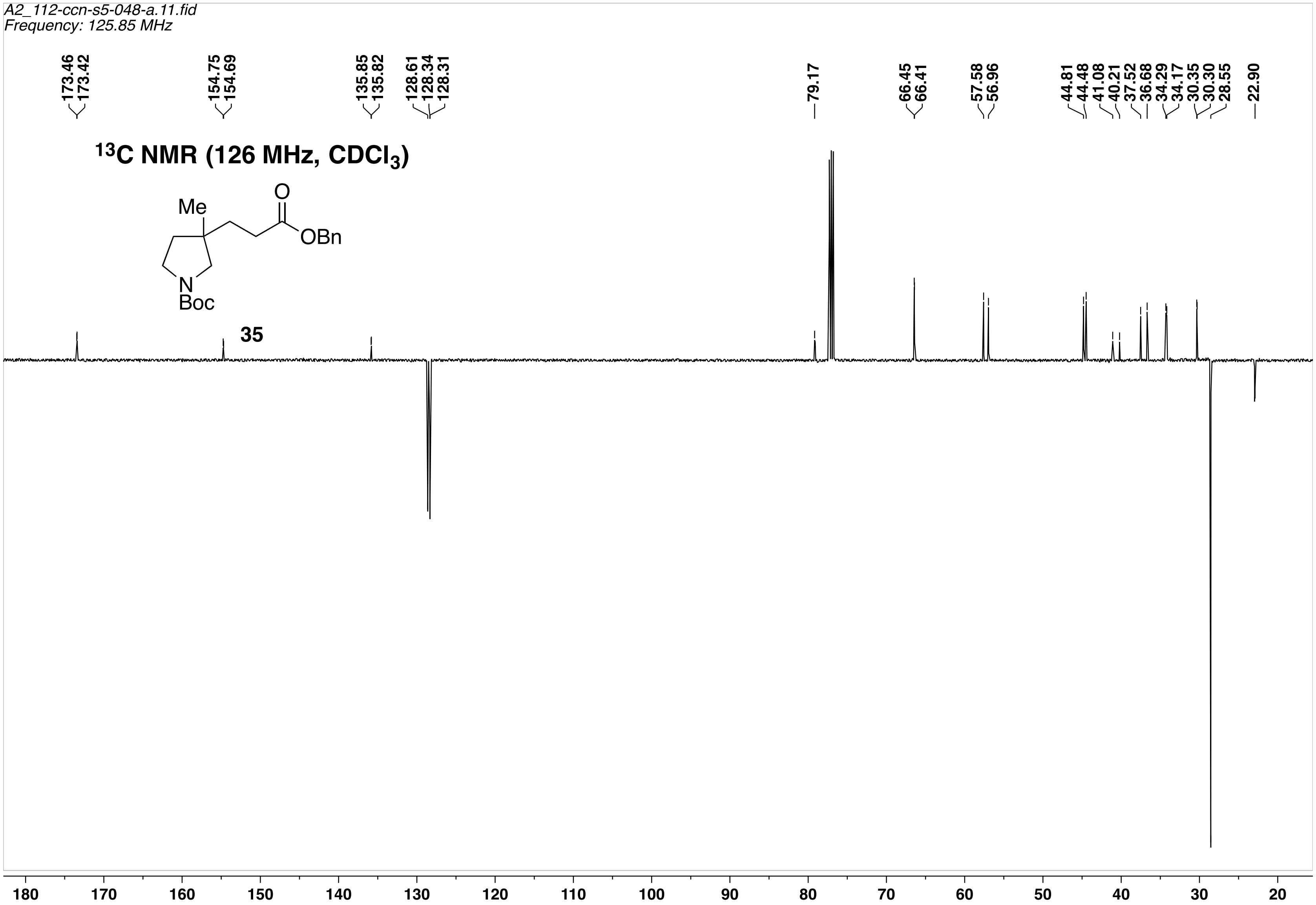


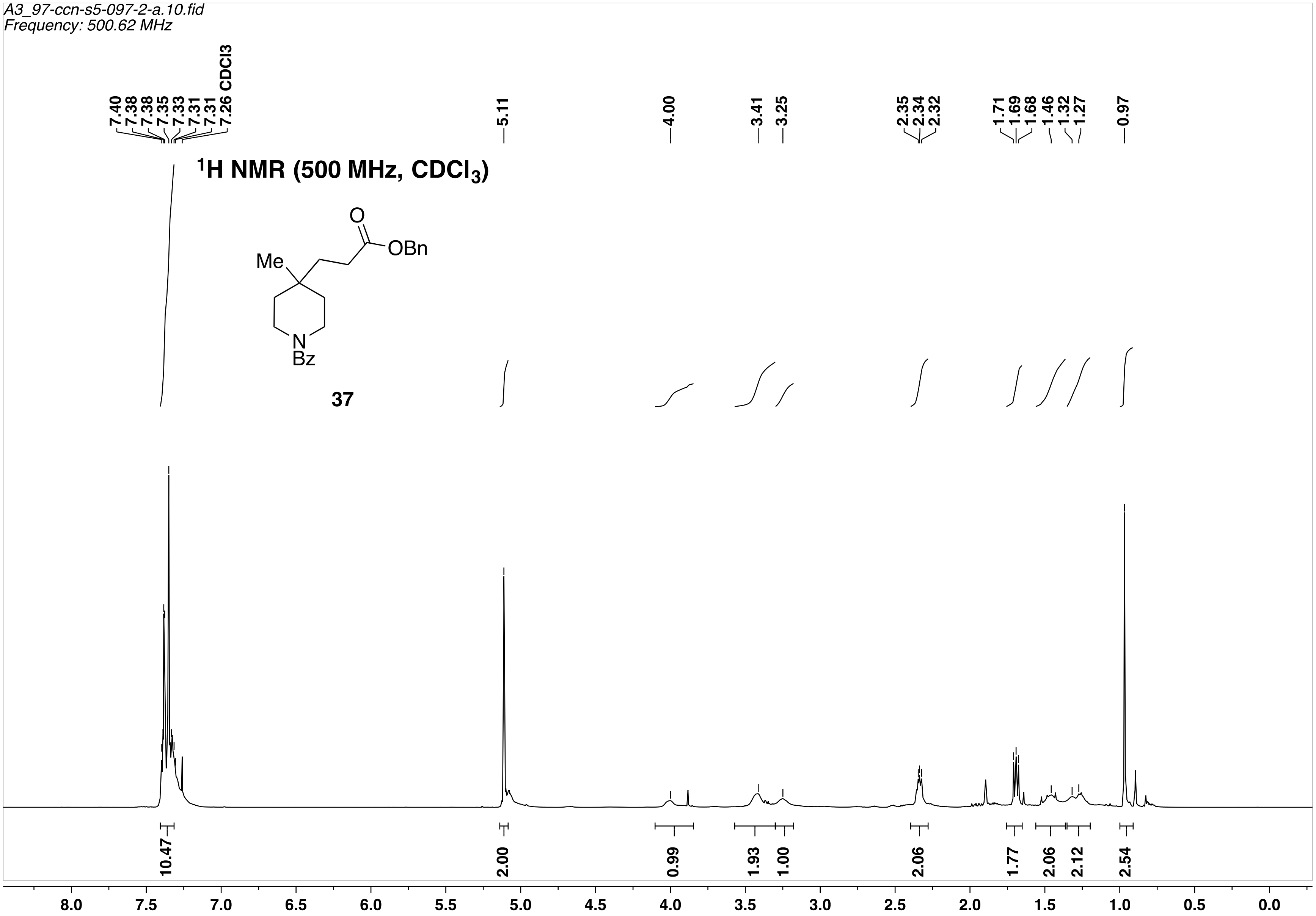
^{13}C NMR ($CDCl_3$, 126 MHz)

33

```
Current Data Parameters
NAME          YS-II-254A
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150219
Time               15.29
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   184
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  6502
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803362 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

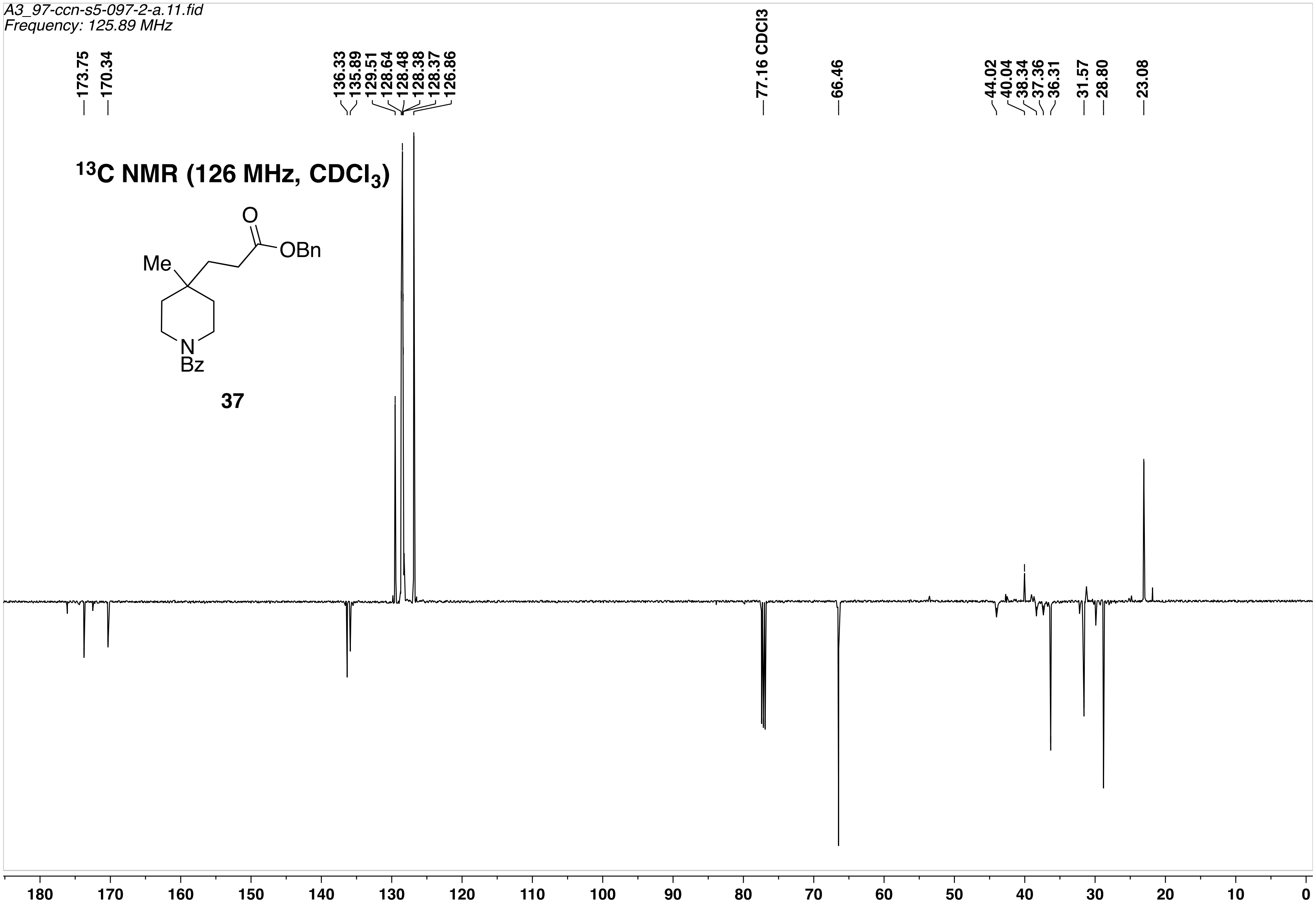

A2_112-ccn-s5-048-a.10.fid
Frequency: 500.46 MHz
7.39
7.36
7.31
7.26
5.11
3.46
3.39
3.38
3.38
3.37
3.37
3.36
3.36
3.35
3.34
3.30
3.14
3.12
3.10
3.08
3.07
3.05
3.02
2.39
2.39
2.38
2.37
2.37
2.36
2.36
2.35
2.35
1.76
1.75
1.73
1.68
1.67
1.65
1.64
1.63
1.62
1.61
1.59
1.58
1.57
1.45
1.01
¹H NMR (500 MHz, CDCl3)
Me
O
OBn
N
Boc
35
4.87
2.02
2.00
0.94
0.94
1.92
1.87
2.50
8.80
2.83
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


A2_112-ccn-s5-048-a.11.fid
Frequency: 125.85 MHz
173.46
173.42
154.75
154.69
135.85
135.82
128.61
128.34
128.31
79.17
66.45
66.41
57.58
56.96
44.81
44.48
41.08
40.21
37.52
36.68
34.29
34.17
30.35
30.30
28.55
22.90
13C NMR (126 MHz, CDCl3)
O
Me
OBn
N
Boc
35
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20



^{1}H NMR (500 MHz, CDCl$_3$)

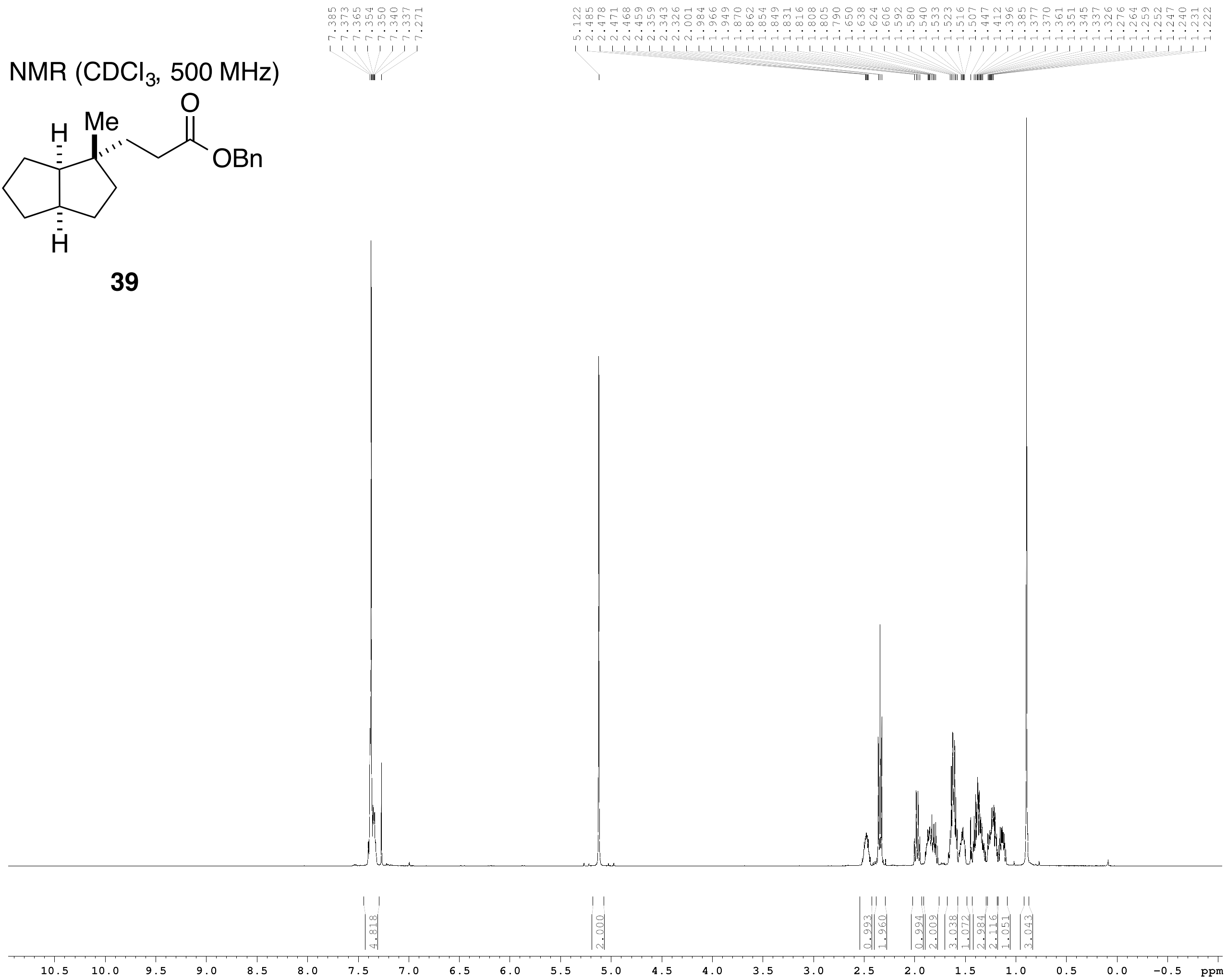
37


A3_97-ccn-s5-097-2-a.11.fid
Frequency: 125.89 MHz
173.75
170.34
136.33
135.89
129.51
128.64
128.48
128.38
128.37
126.86
77.16 CDCl3
66.46
44.02
40.04
38.34
37.36
36.31
31.57
28.80
23.08
^{13}C NMR (126 MHz, CDCl$_3$)
O
OBn
Me
N
Bz
37
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

YS-II-293

^{1}H NMR ($CDCl_3$, 500 MHz)

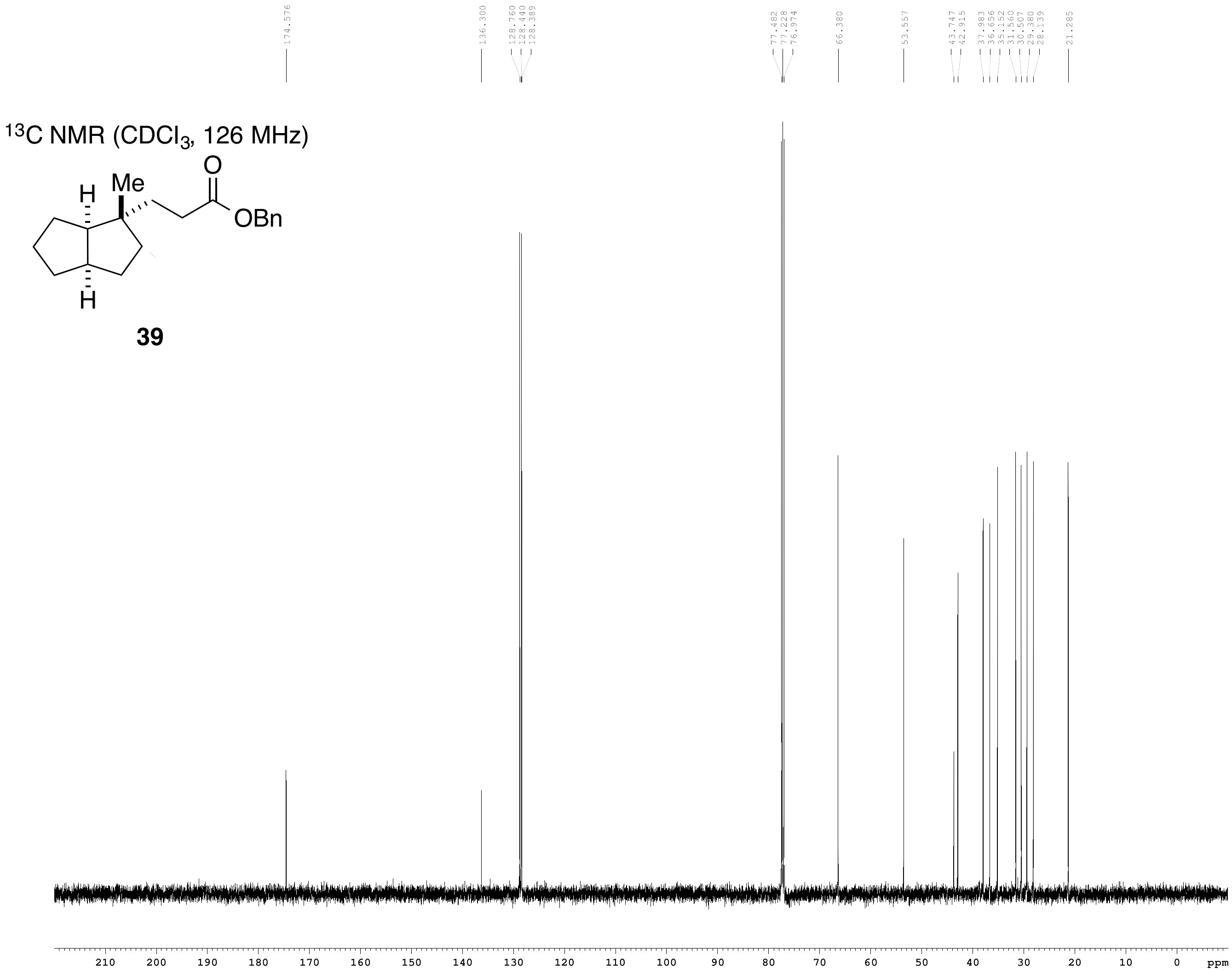
39



```
Current Data Parameters
NAME          YS-II-293
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150311
Time               8.48
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                    5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200254 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

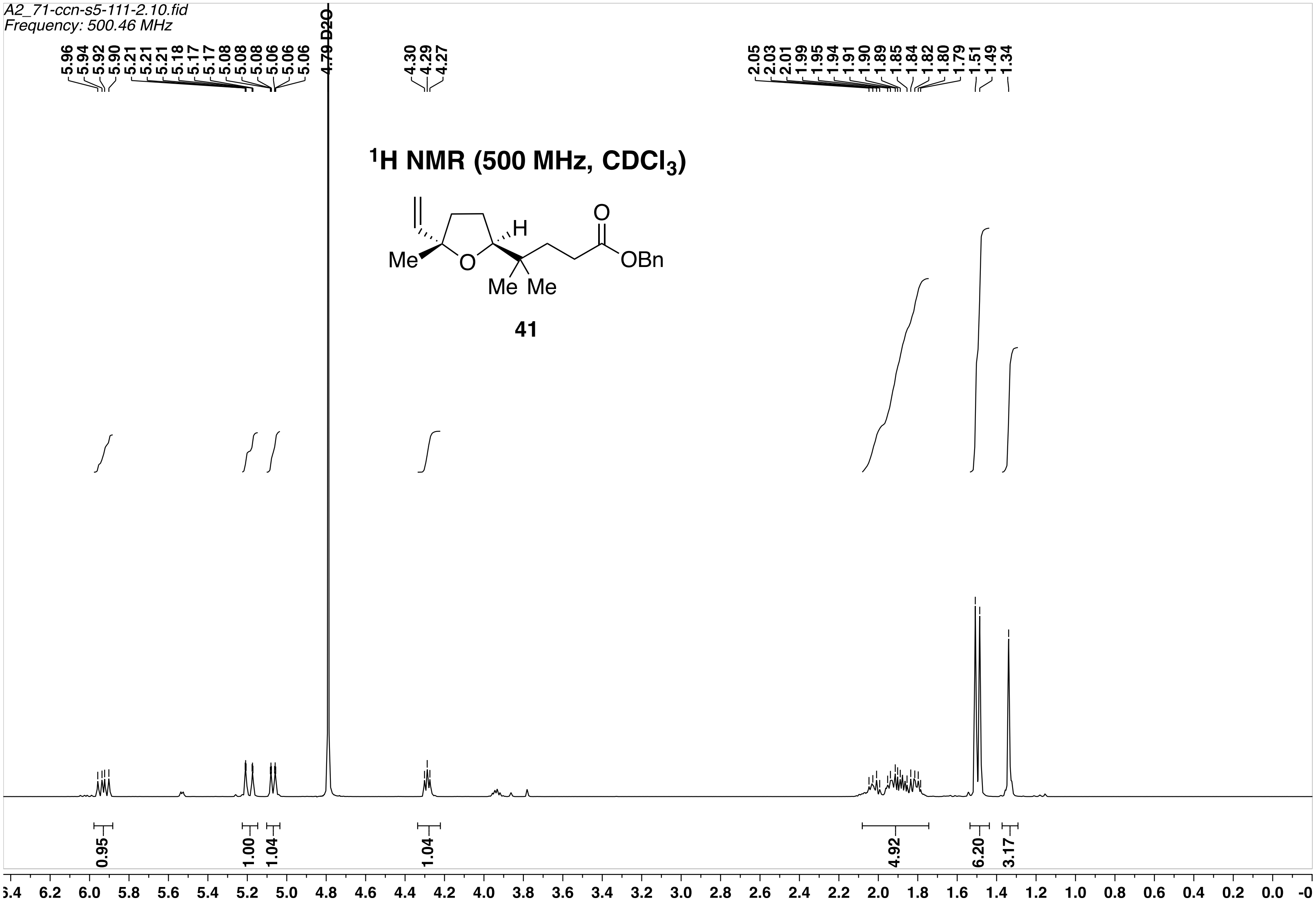
YS-II-293

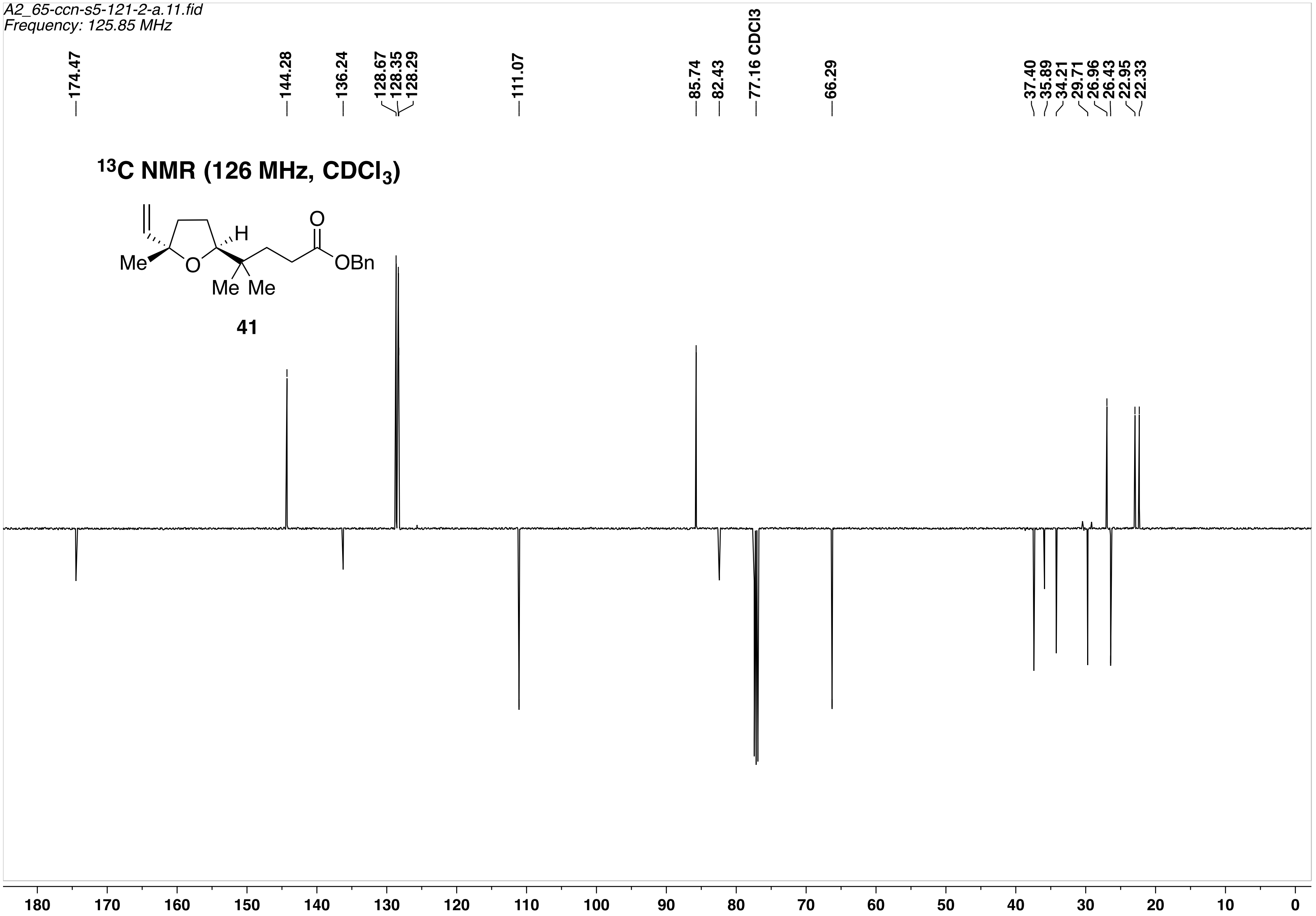
^{13}C NMR (CDCl$_3$, 126 MHz)



39

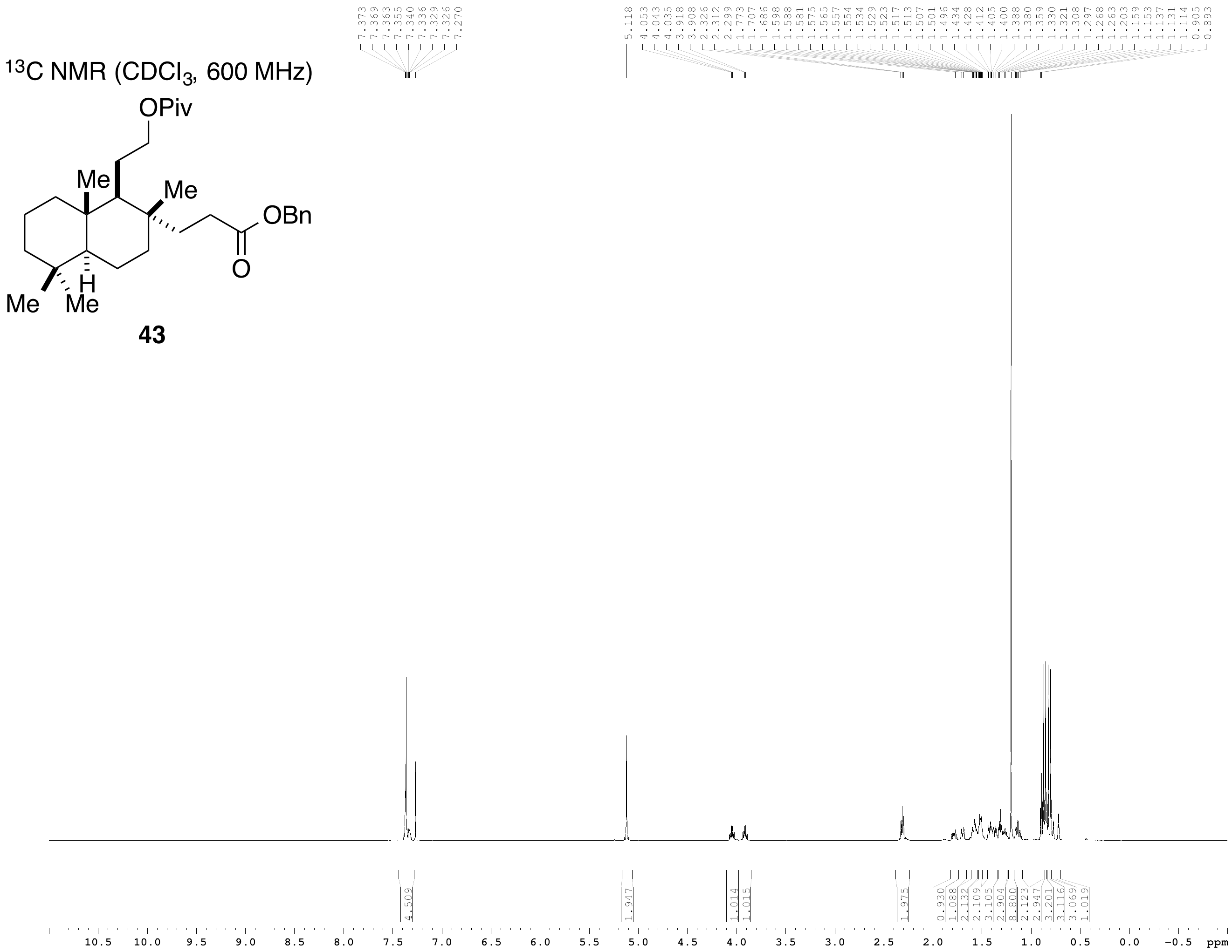
```
Current Data Parameters
NAME          YS-II-293
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150311
Time               8.50
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  224
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG              11585.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804001 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```


A2_71-ccn-s5-111-2.10.fid
Frequency: 500.46 MHz
5.96
5.94
5.92
5.90
5.21
5.21
5.21
5.18
5.17
5.17
5.08
5.08
5.08
5.06
5.06
5.06
4.79 D2O
4.30
4.29
4.27
2.05
2.03
2.01
1.99
1.95
1.94
1.91
1.90
1.89
1.85
1.84
1.82
1.80
1.79
1.51
1.49
1.34
1H NMR (500 MHz, CDCl3)
Me
H
O
OBn
Me Me
41
0.95
1.00
1.04
1.04
4.92
6.20
3.17
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0


A2_65-ccn-s5-121-2-a.11.fid
Frequency: 125.85 MHz
174.47
144.28
136.24
128.67
128.35
128.29
111.07
85.74
82.43
77.16 CDCl3
66.29
37.40
35.89
34.21
29.71
26.96
26.43
22.95
22.33
^{13}C NMR (126 MHz, CDCl$_3$)
H
O
Me
O
OBn
Me Me
41
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

YS-II-270A

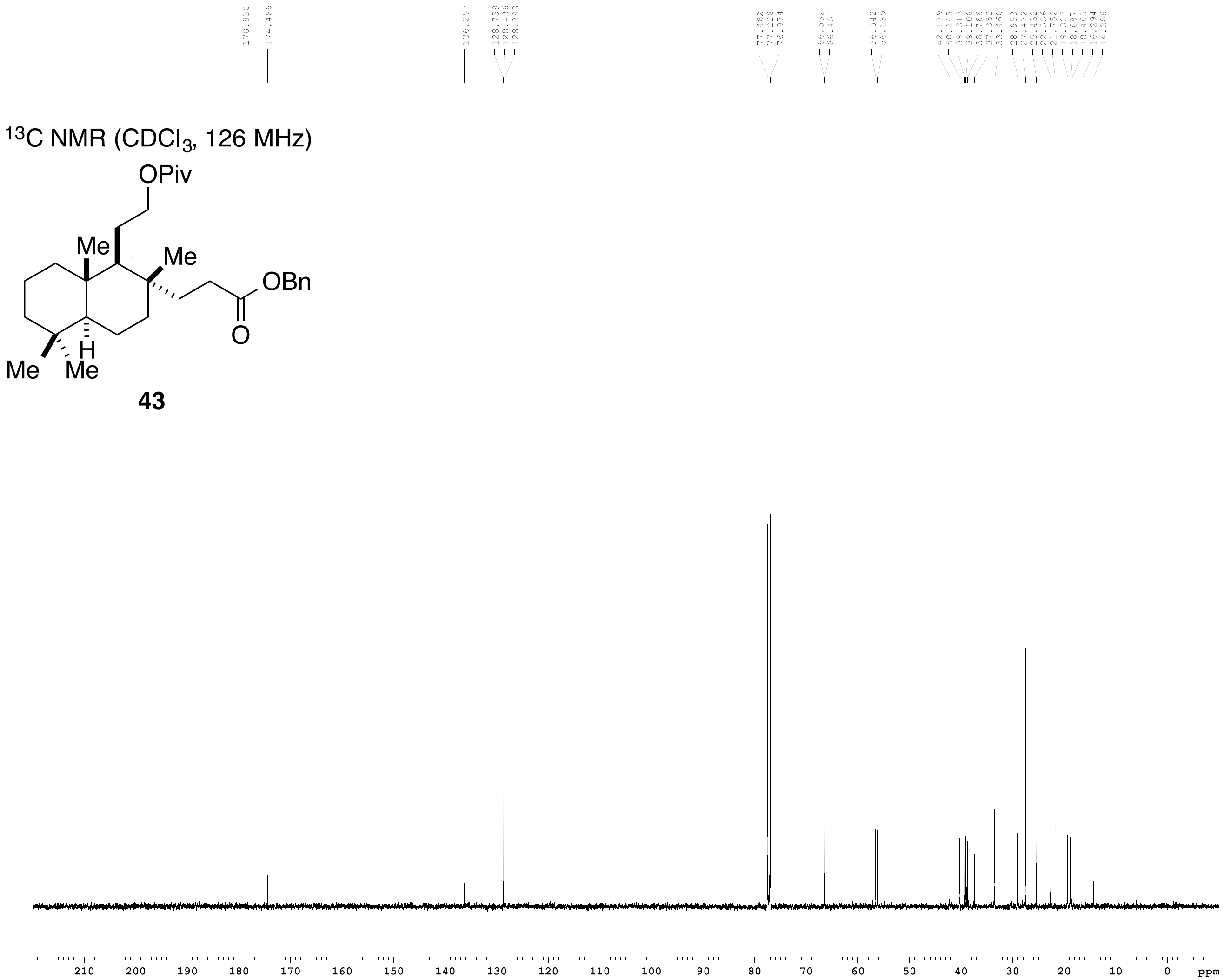
^{13}C NMR ($CDCl_3$, 600 MHz)



43

```
Current Data Parameters
NAME          YS-II-270A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150226
Time               14.06
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                   256
DW                52.000 usec
DE                 14.54 usec
TE                 298.1 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         23.01441956 W

F2 - Processing parameters
SI                 65536
SF           600.1300306 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-II-270A



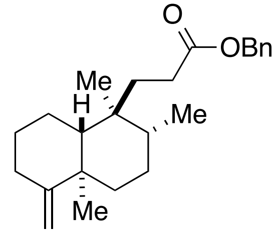
^{13}C NMR ($CDCl_3$, 126 MHz)

43

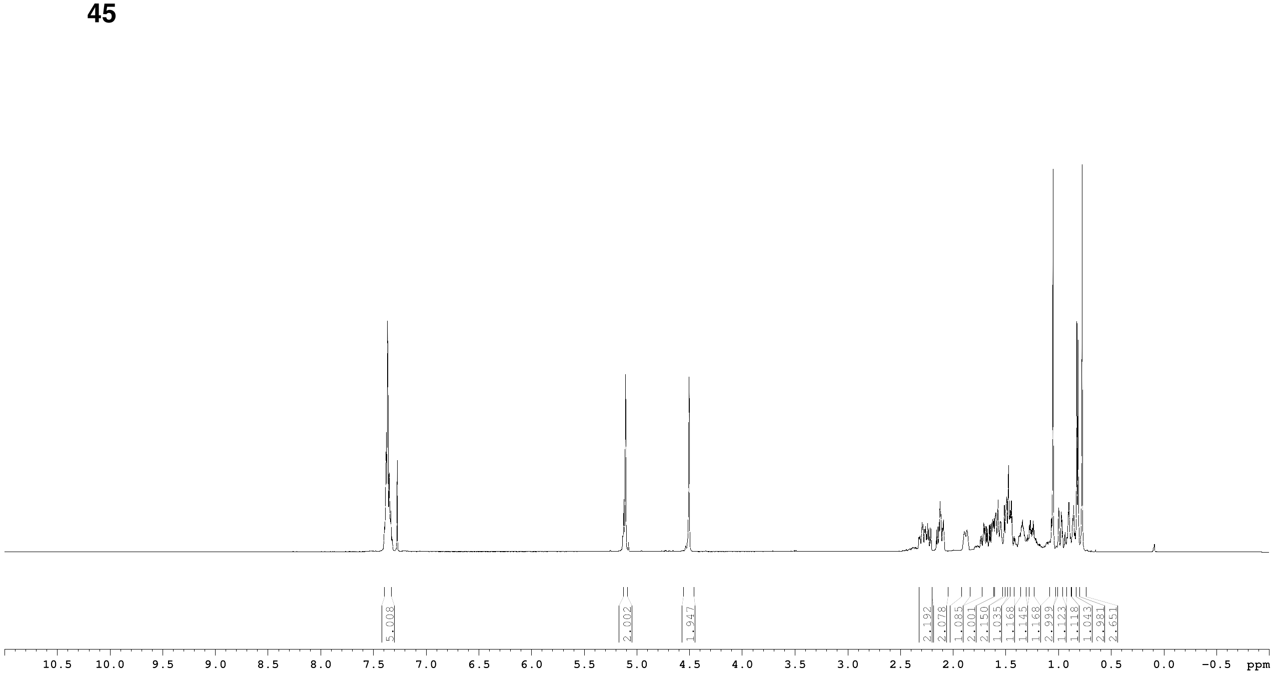
```
Current Data Parameters
NAME          YS-II-270A
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150226
Time               15.07
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   368
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                3649.1
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803988 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-II-270B

^{1}H NMR (CDCl$_3$, 500 MHz)



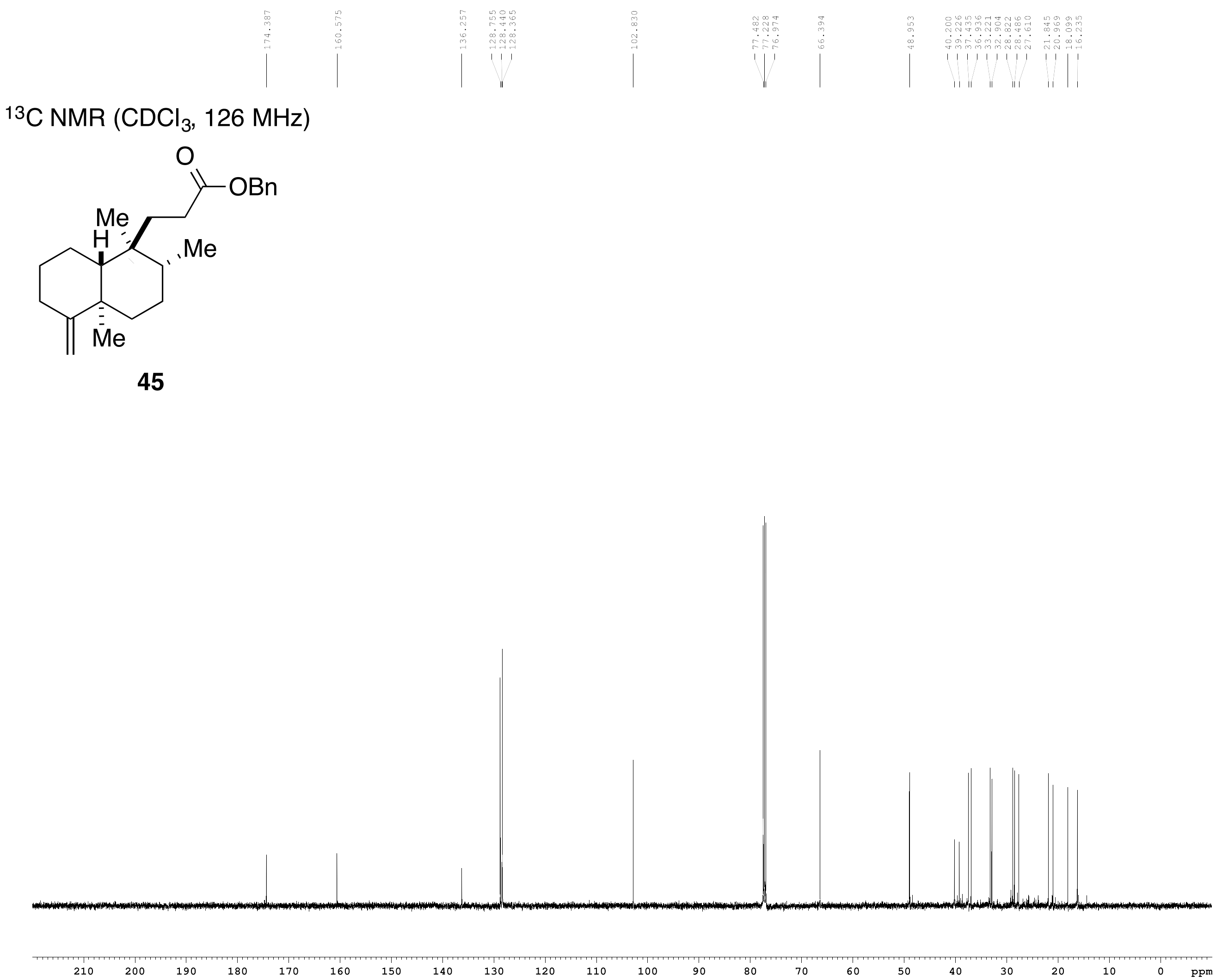
45



```
Current Data Parameters
NAME          YS-II-270B
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150228
Time               14.41
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 80126
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.100003 Hz
AQ             4.9998622 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200243 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

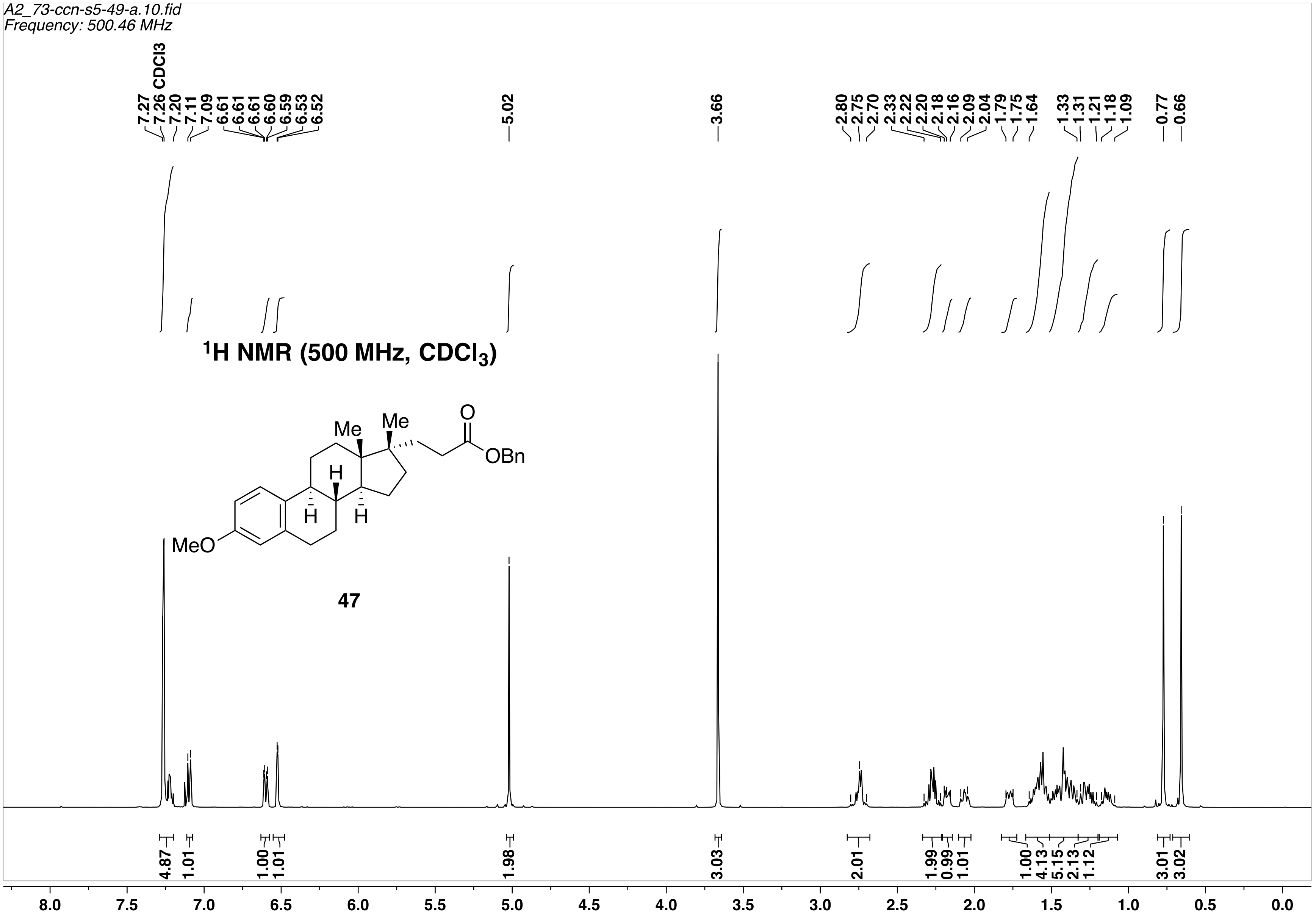
YS-II-270B

^{13}C NMR ($CDCl_3$, 126 MHz)



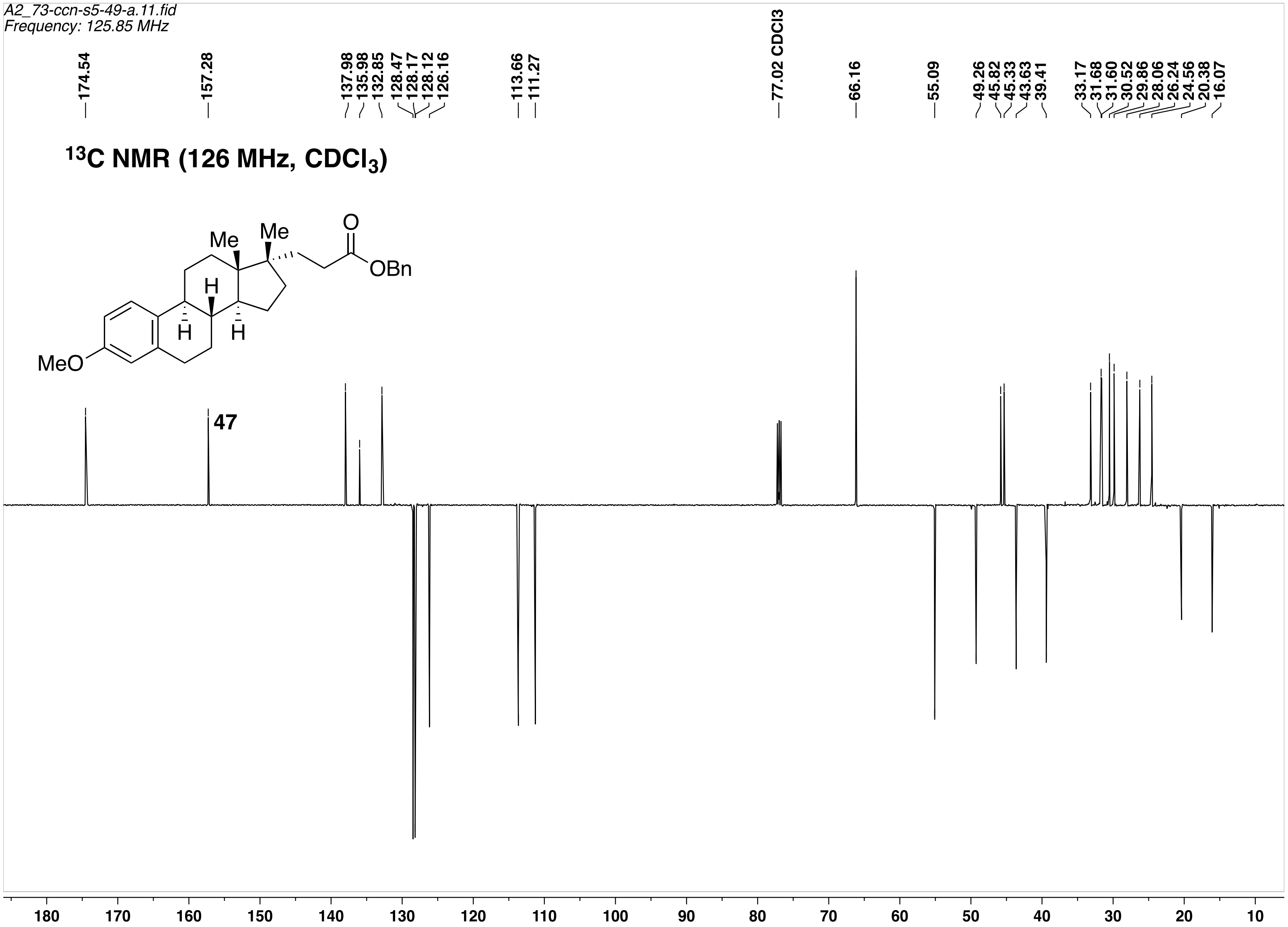
45

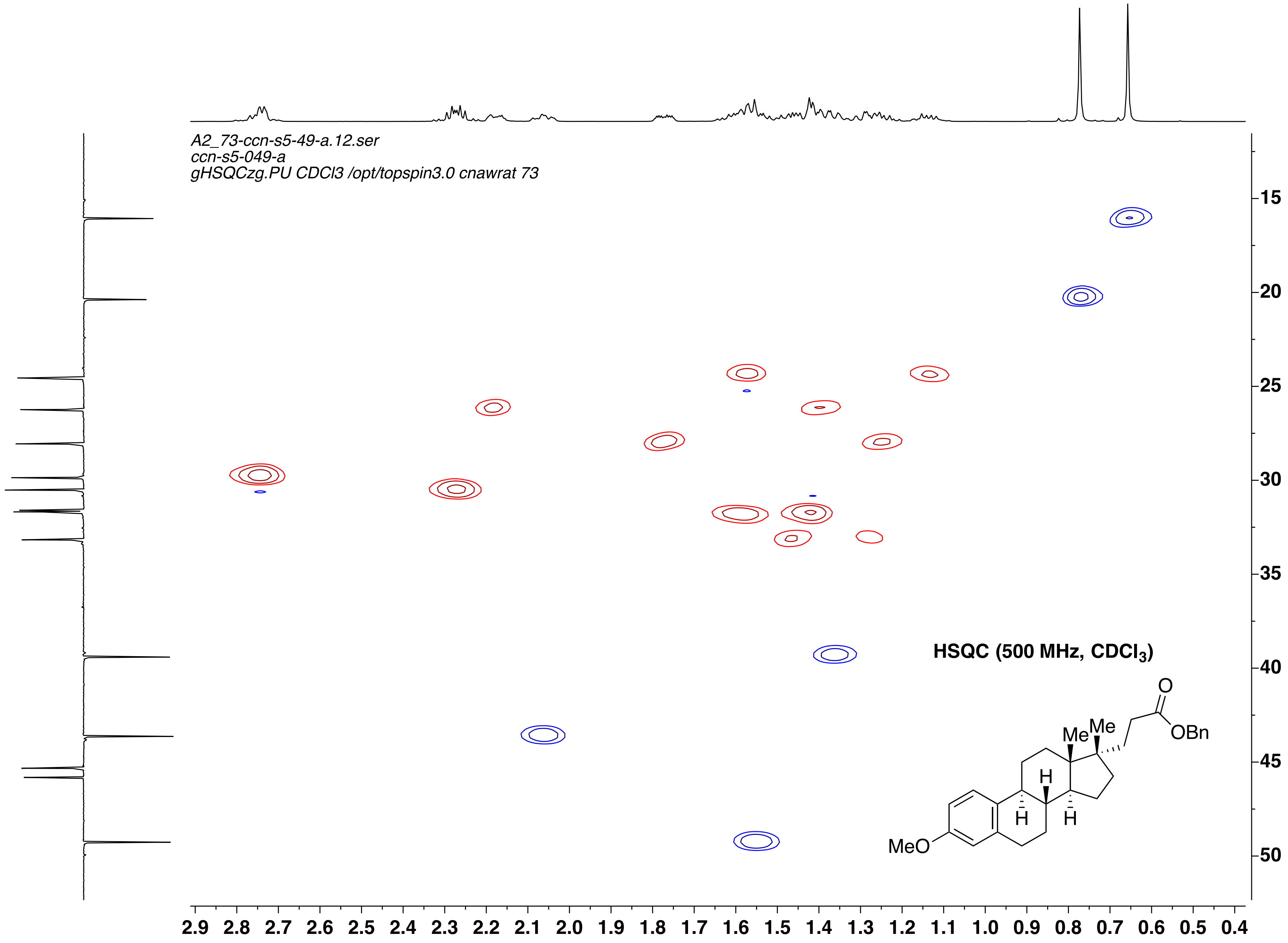
```
Current Data Parameters
NAME          YS-II-270B
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150228
Time               14.42
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   352
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                5792.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803996 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

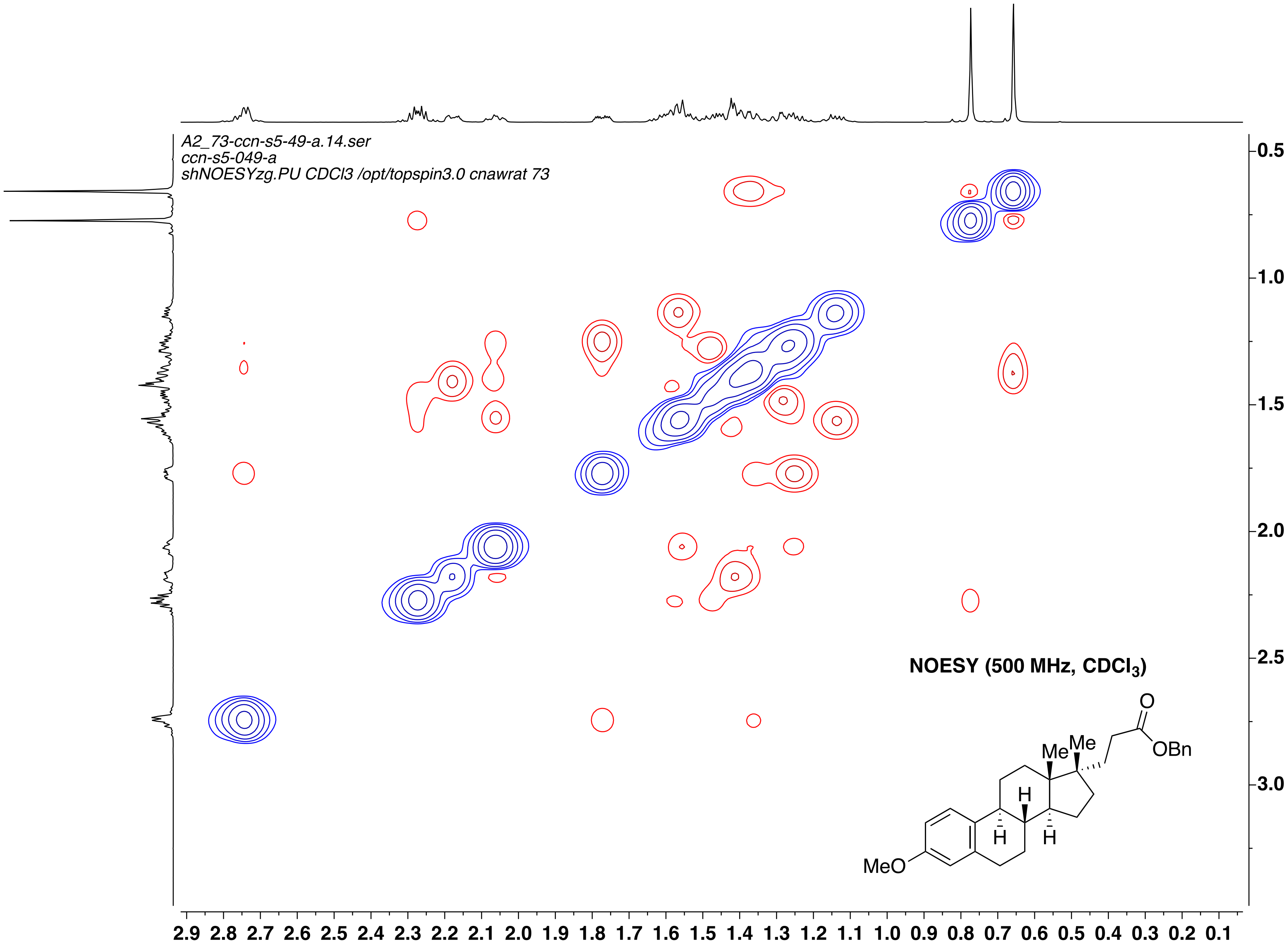


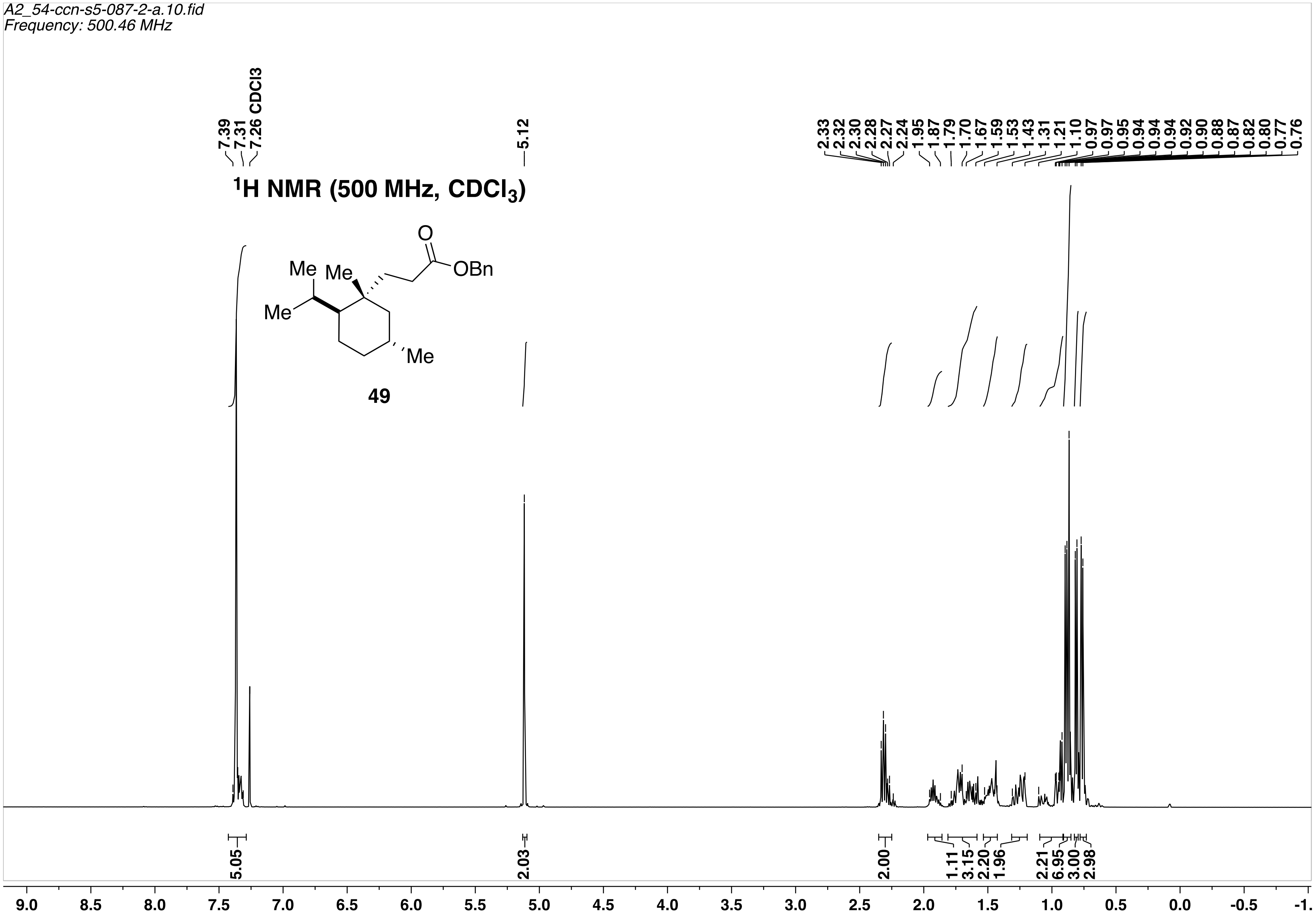
^{1}H NMR (500 MHz, $CDCl_3$)

47

A2_73-ccn-s5-49-a.11.fid
Frequency: 125.85 MHz
^{13}C NMR (126 MHz, CDCl$_3$)
Me
Me
O
OBn
H
H
H
MeO
47
174.54
157.28
137.98
135.98
132.85
128.47
128.17
128.12
126.16
113.66
111.27
77.02 CDCl3
66.16
55.09
49.26
45.82
45.33
43.63
39.41
33.17
31.68
31.60
30.52
29.86
28.06
26.24
24.56
20.38
16.07
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

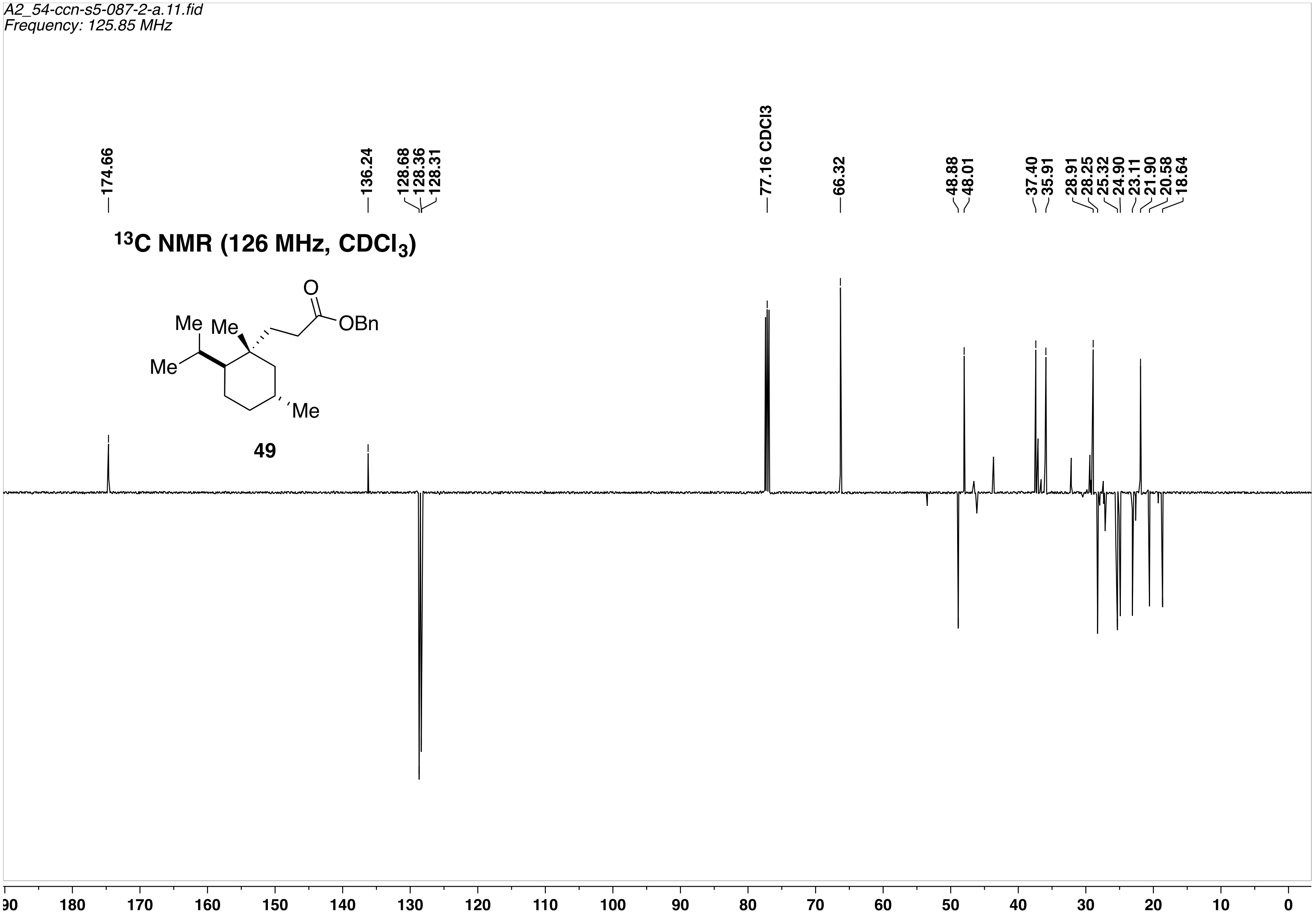

A2_73-ccn-s5-49-a.12.ser
ccn-s5-049-a
gHSQCzg.PU CDCl3 /opt/topspin3.0 cnawrat 73
HSQC (500 MHz, CDCl3)
O
OBn
Me
Me
H
H
H
MeO
15
20
25
30
35
40
45
50
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4


A2_73-ccn-s5-49-a.14.ser
ccn-s5-049-a
shNOESYzg.PU CDCl3 /opt/topspin3.0 cnawrat 73
NOESY (500 MHz, CDCl$_3$)
MeO
Me
Me
H
H
H
O
OBn
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1
0.5
1.0
1.5
2.0
2.5
3.0



^{1}H NMR (500 MHz, CDCl$_3$)

49



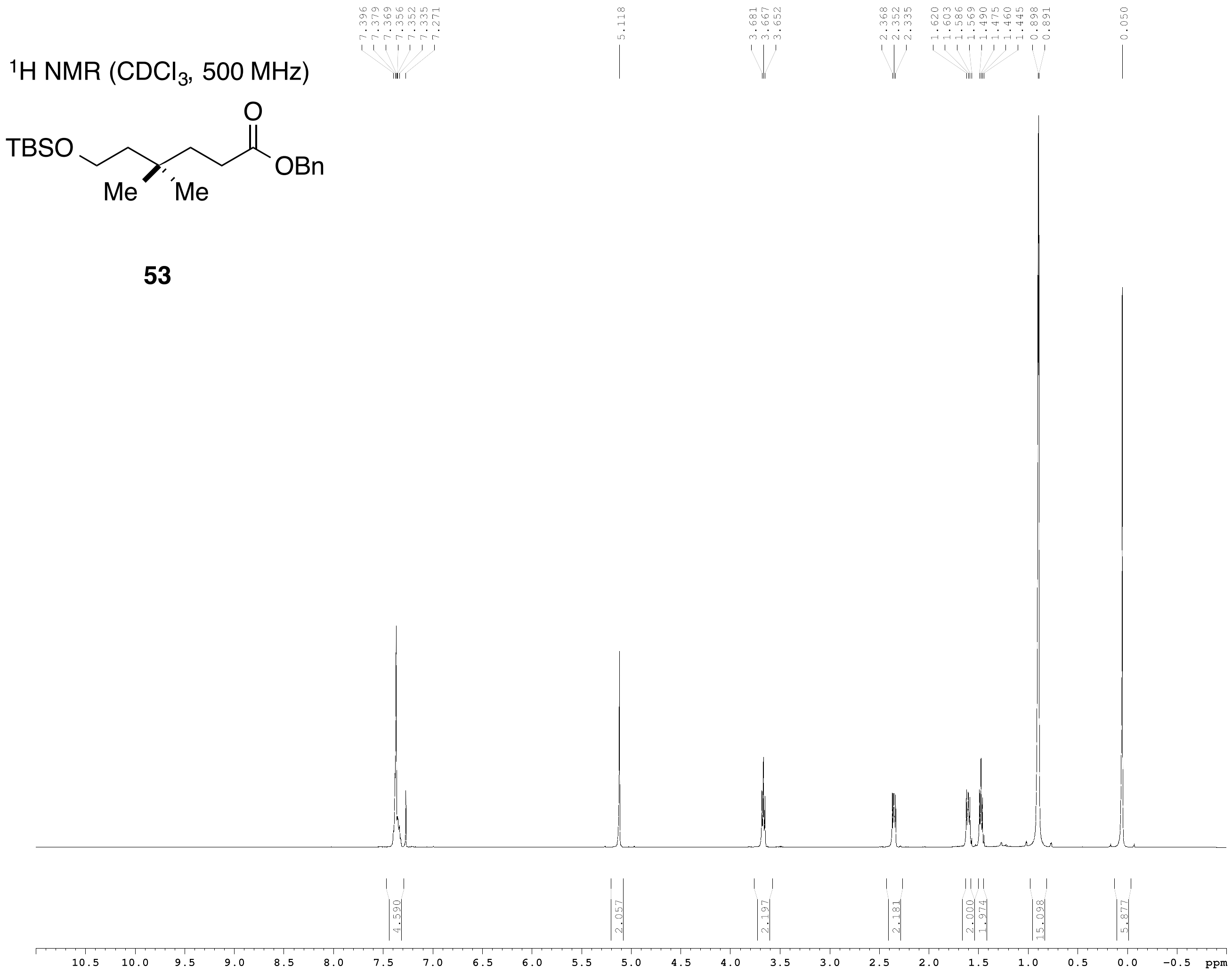
^{13}C NMR (126 MHz, CDCl$_3$)

49

YS-II-272A

^{1}H NMR ($CDCl_3$, 500 MHz)

53

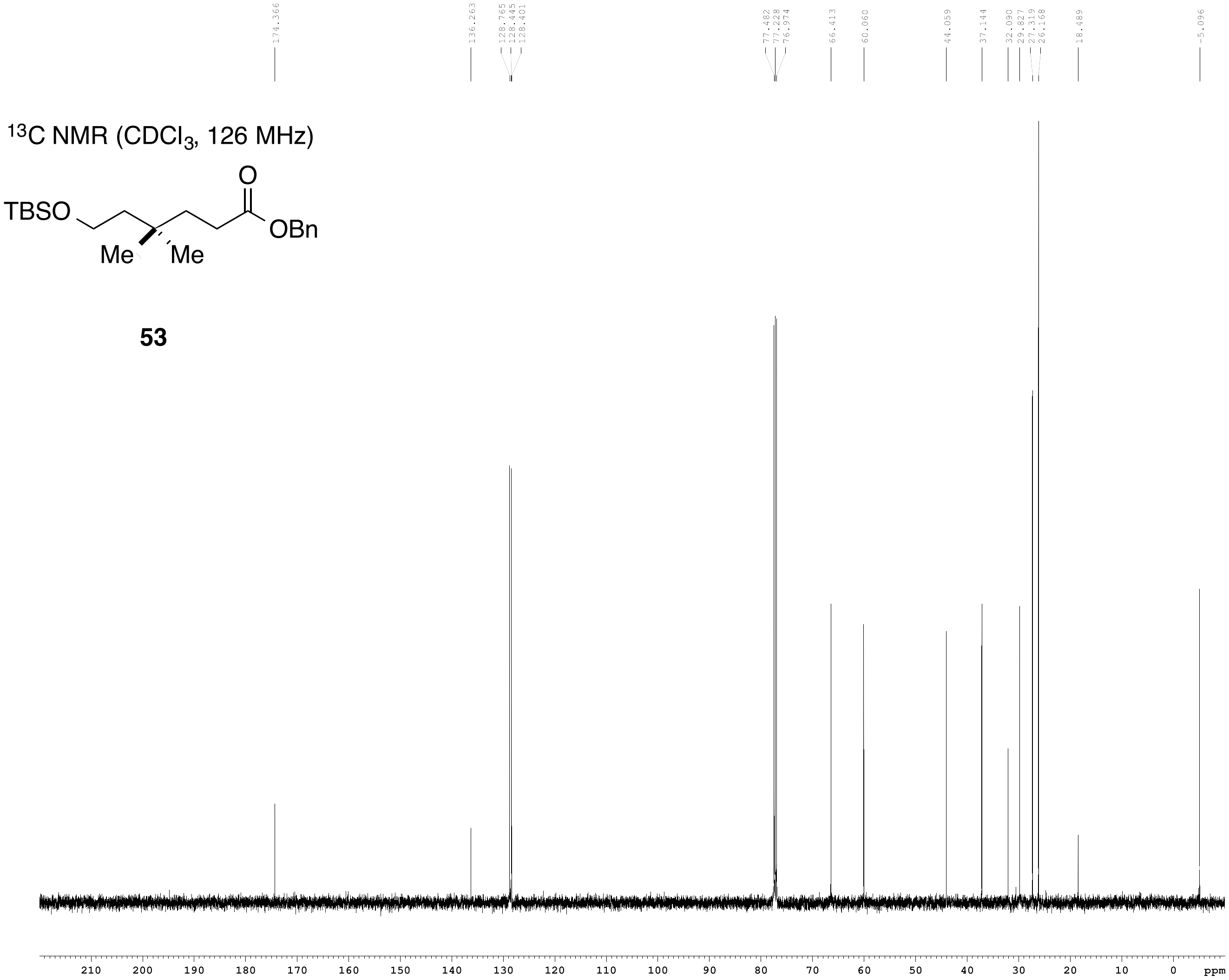


```
Current Data Parameters
NAME          YS-II-272A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150228
Time               14.33
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9997952 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200256 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-II-272A

^{13}C NMR (CDCl$_3$, 126 MHz)

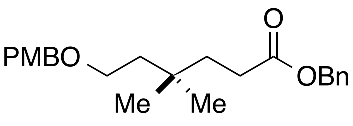
53



```
Current Data Parameters
NAME          YS-II-272A
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150228
Time               14.37
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   176
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  3251
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST    0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1    0 Hz
SPOFF2    0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803992 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```

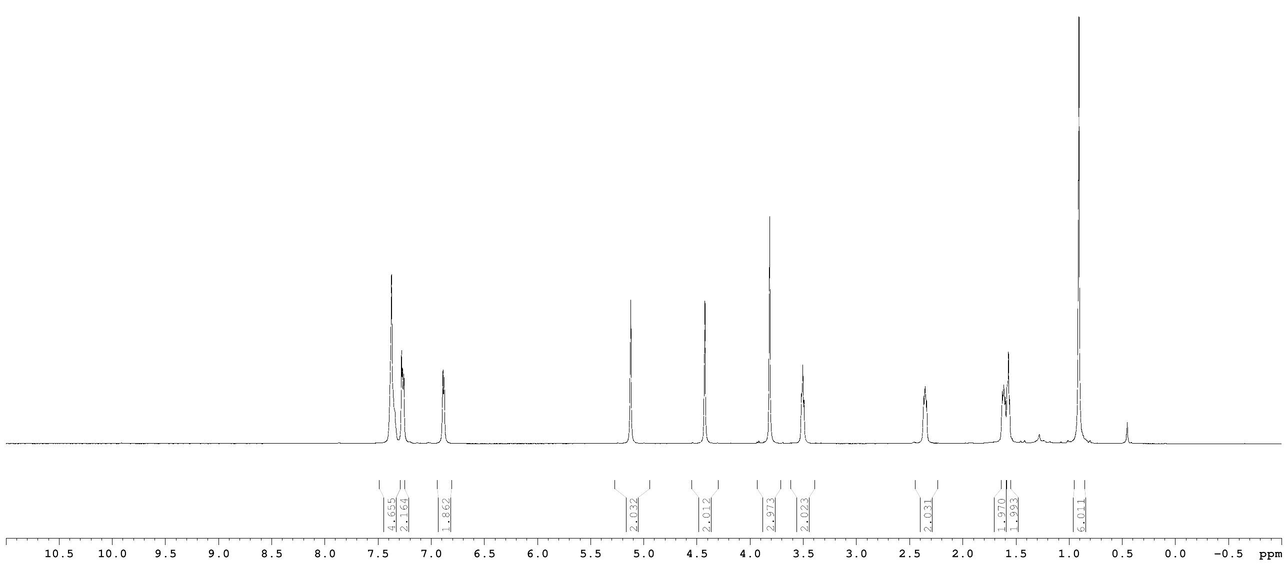
YS-II-272B

^{13}C NMR ($CDCl_3$, 600 MHz)

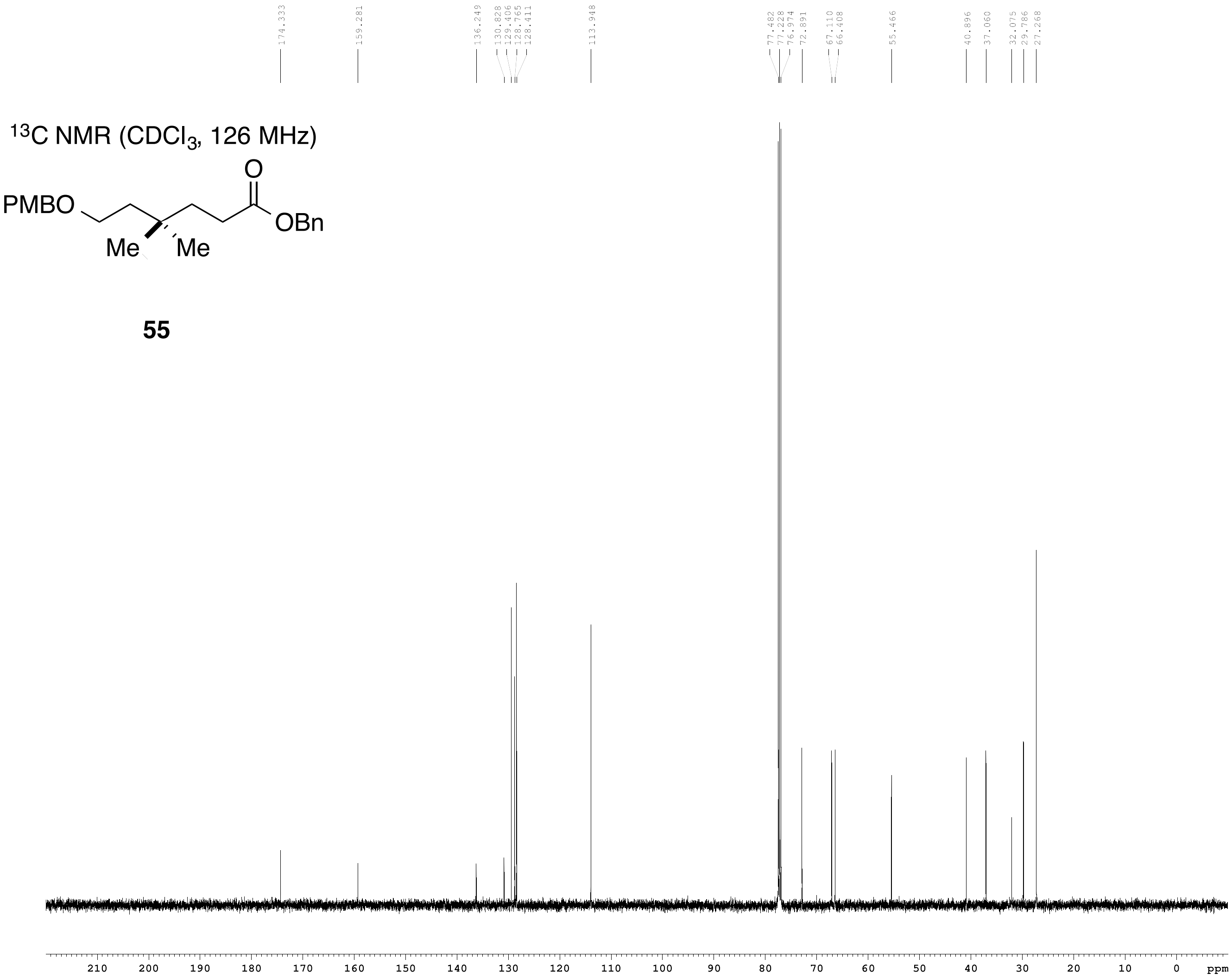


55

```
Current Data Parameters
NAME          YS-II-272B
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150228
Time               14.15
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.250010 Hz
AQ             1.9999200 sec
RG                   256
DW                52.000 usec
DE                 14.54 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         23.01441956 W

F2 - Processing parameters
SI                 65536
SF           600.1300268 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```



YS-II-272B



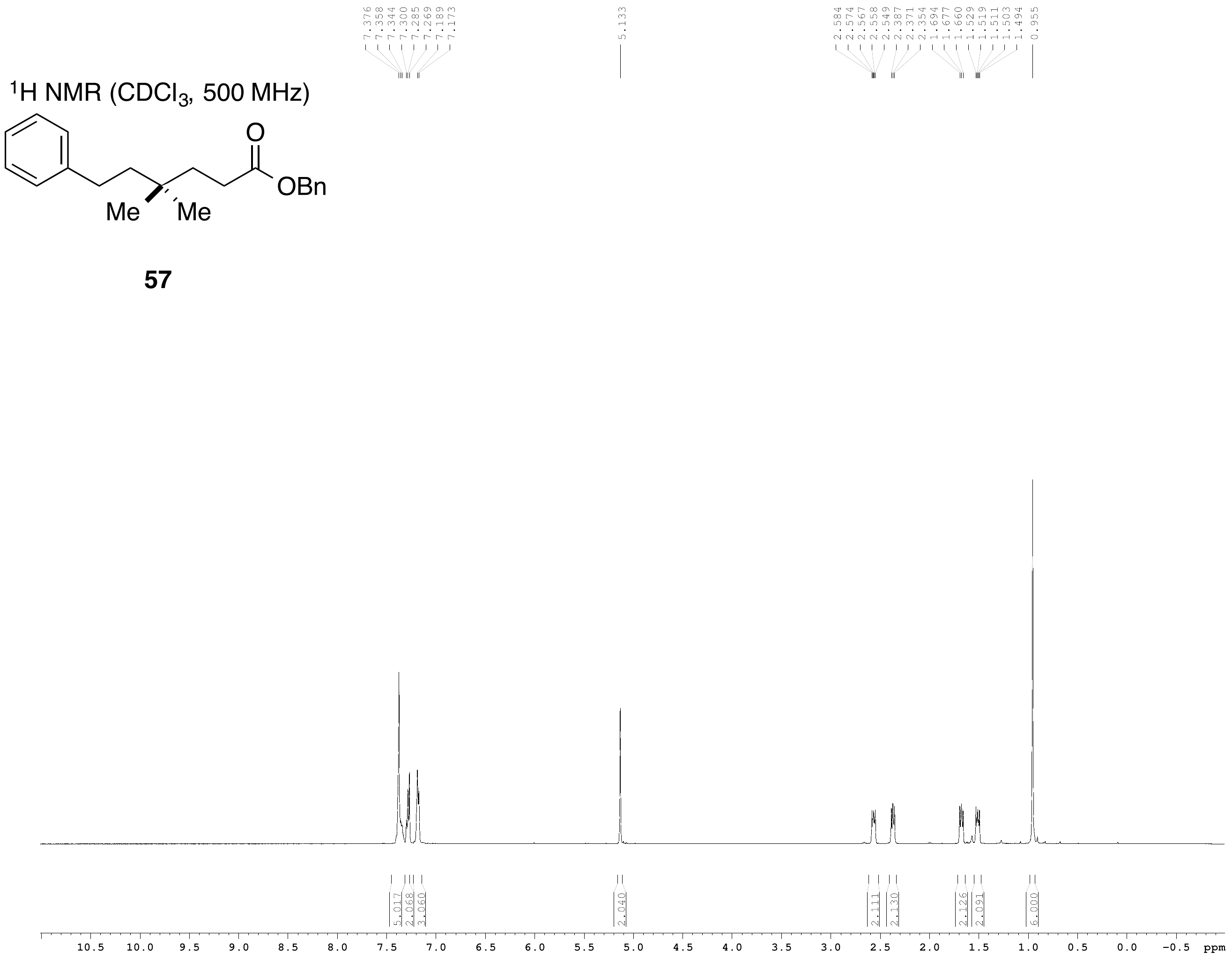
^{13}C NMR (CDCl$_3$, 126 MHz)

55

```
Current Data Parameters
NAME           YS-II-272B
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150228
Time                14.57
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    496
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 7298.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7803991 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

YS-II-141

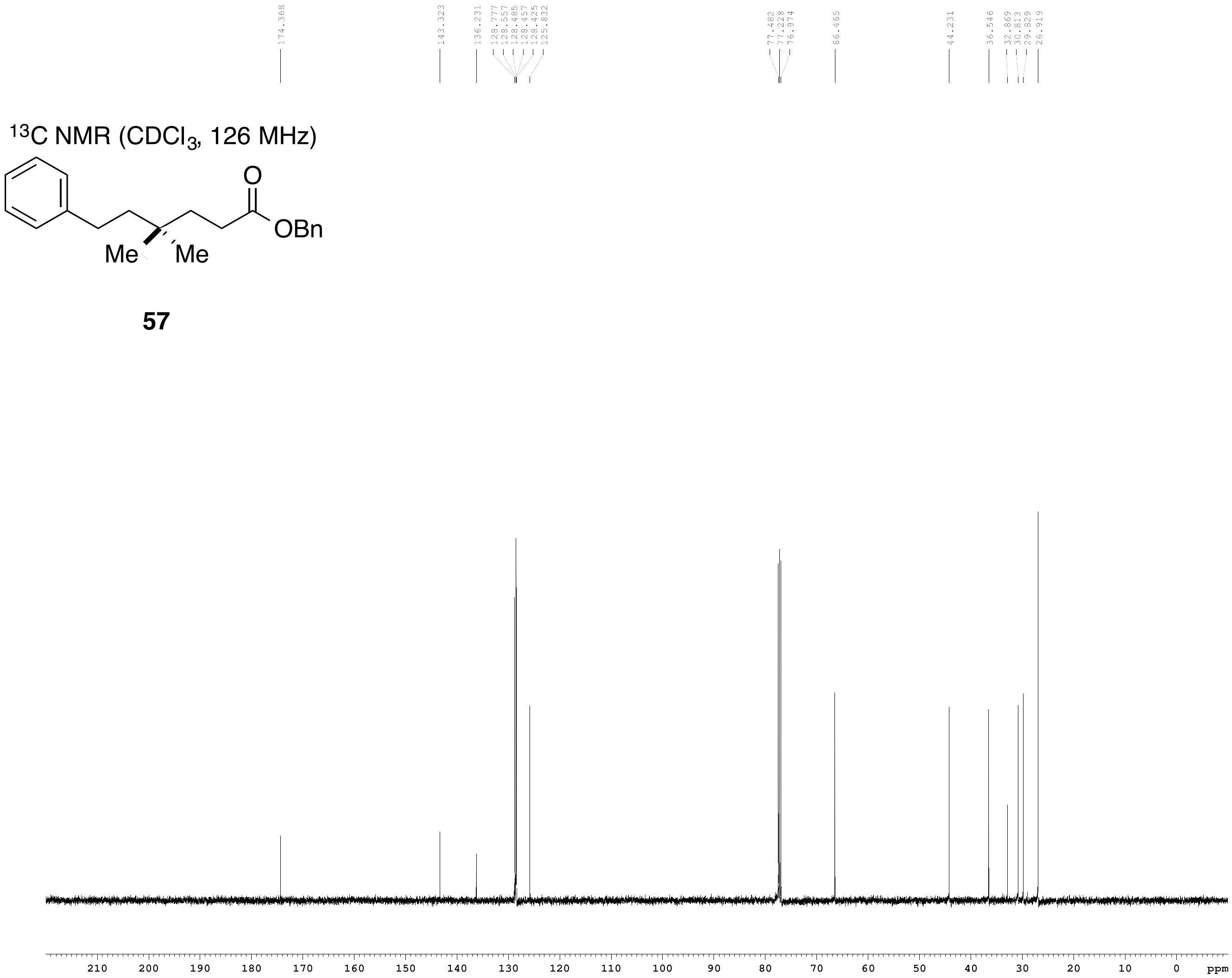
^{1}H NMR (CDCl$_3$, 500 MHz)



57

```
Current Data Parameters
NAME          YS-II-141
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20141125
Time              12.54
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                    5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200293 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-141



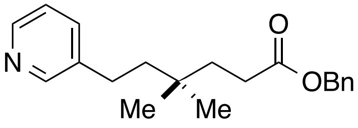
^{13}C NMR (CDCl$_3$, 126 MHz)

57

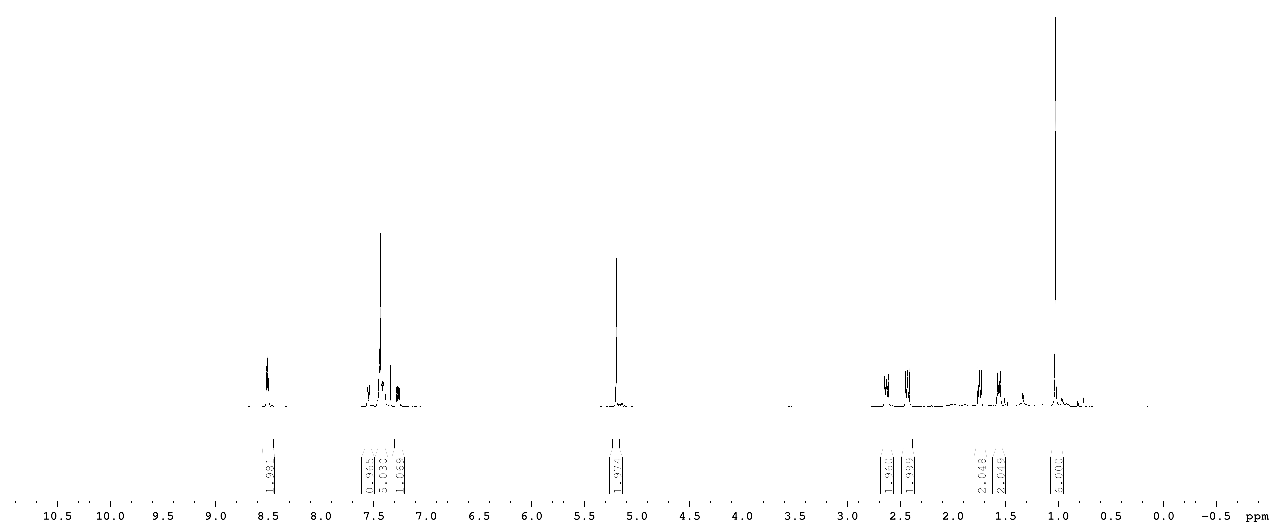
```
Current Data Parameters
NAME          YS-II-141
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20141125
Time              13.02
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  224
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.75000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804024 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-III-43

^{1}H NMR (CDCl$_3$, 500 MHz)

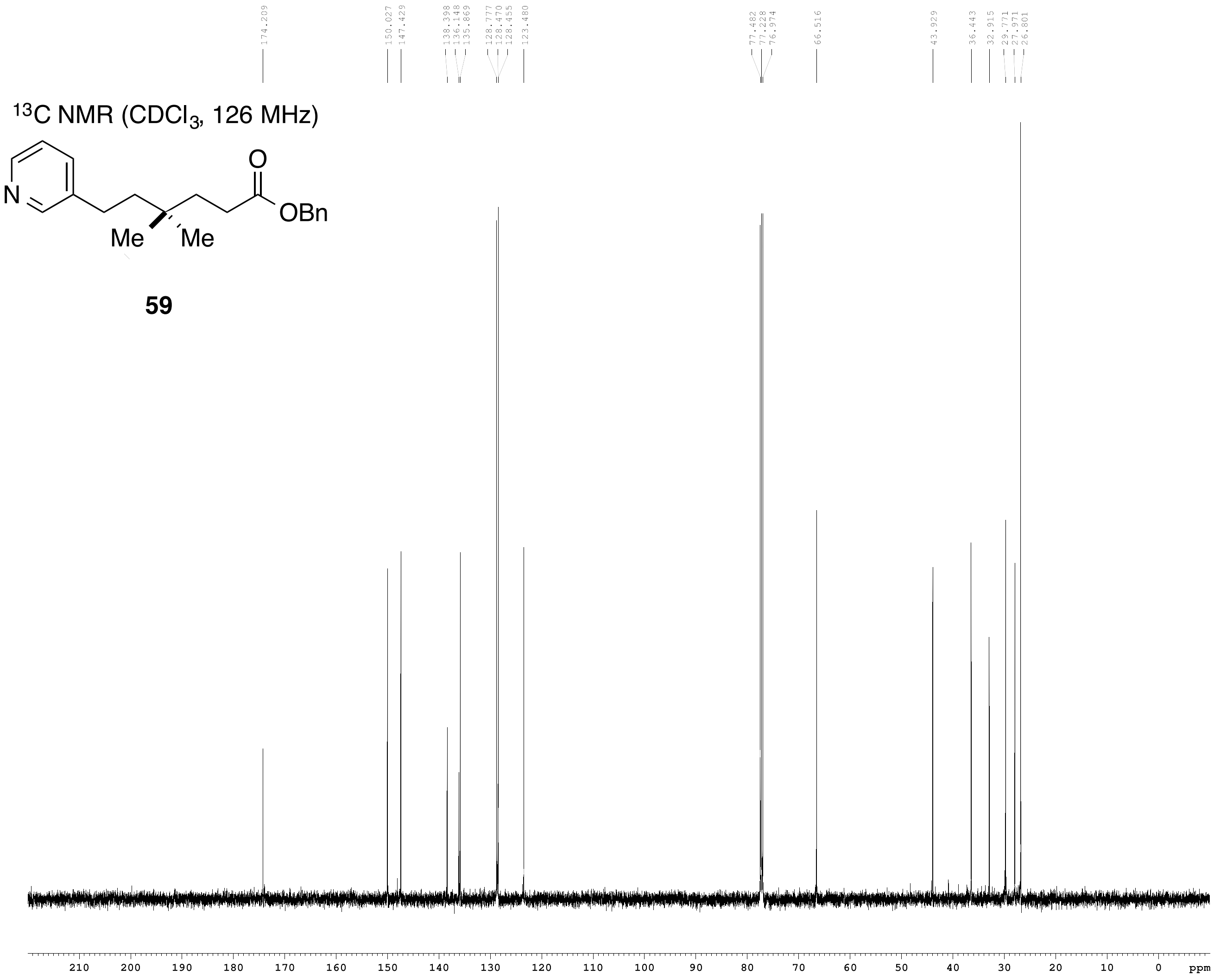


59



```
Current Data Parameters
NAME          YS-III-43
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150407
Time              17.51
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                  4.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2199908 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

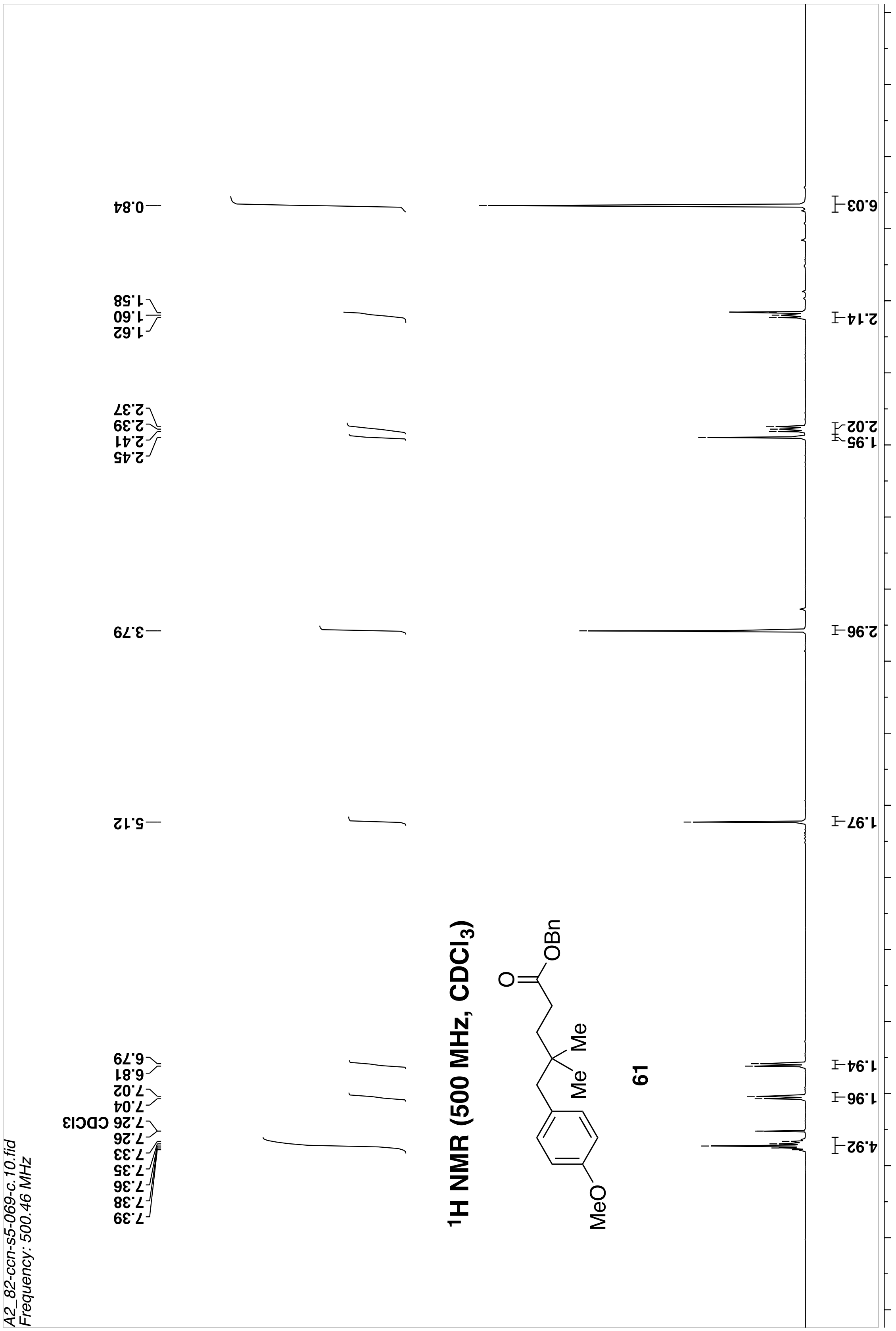
YS-III-43



^{13}C NMR ($CDCl_3$, 126 MHz)

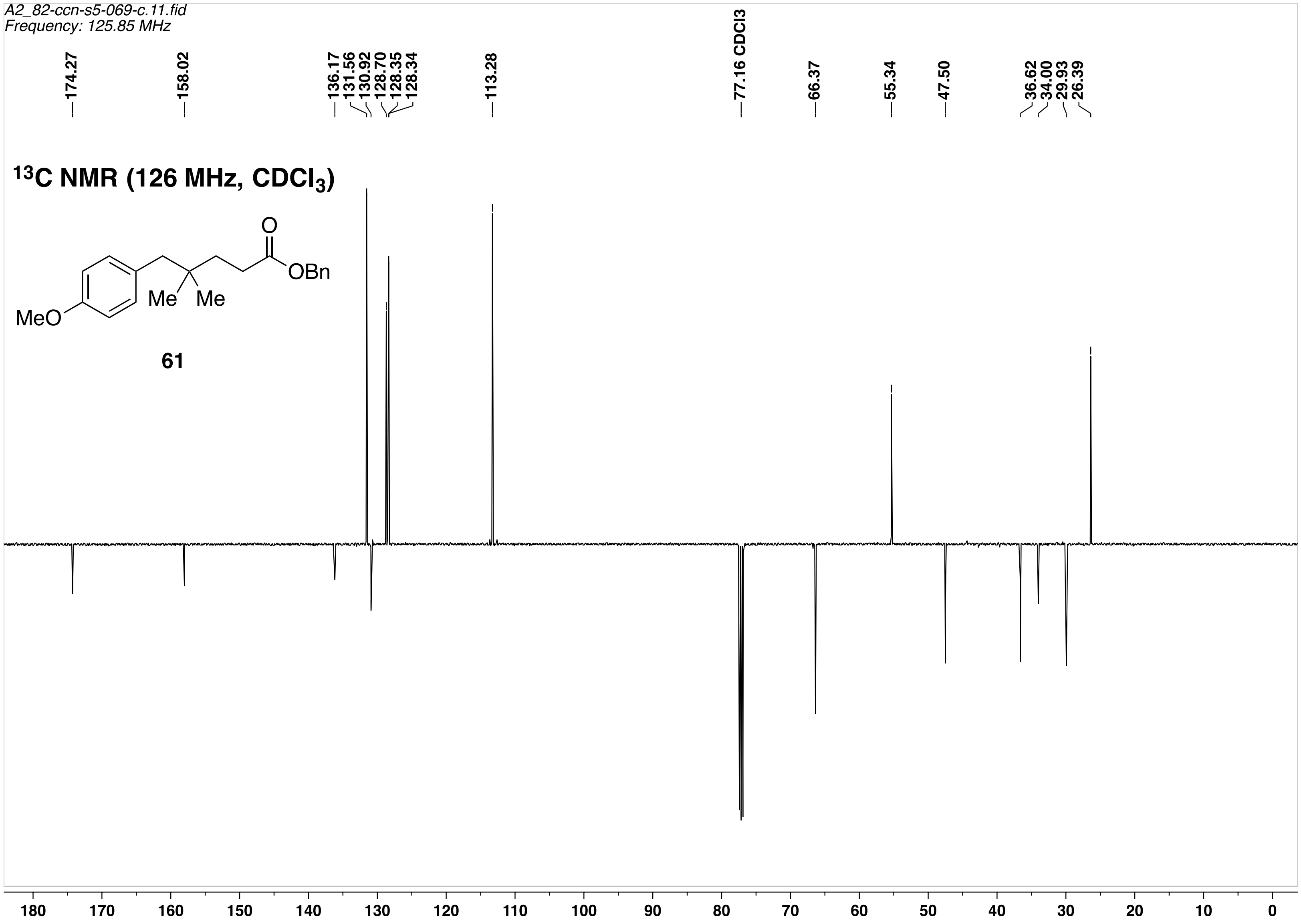
59

```
Current Data Parameters
NAME            YS-III-43
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150407
Time                17.54
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    208
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                  13004
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804012 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```



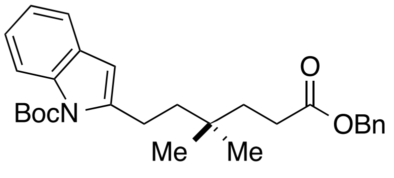
^{1}H NMR (500 MHz, CDCl$_3$)

61

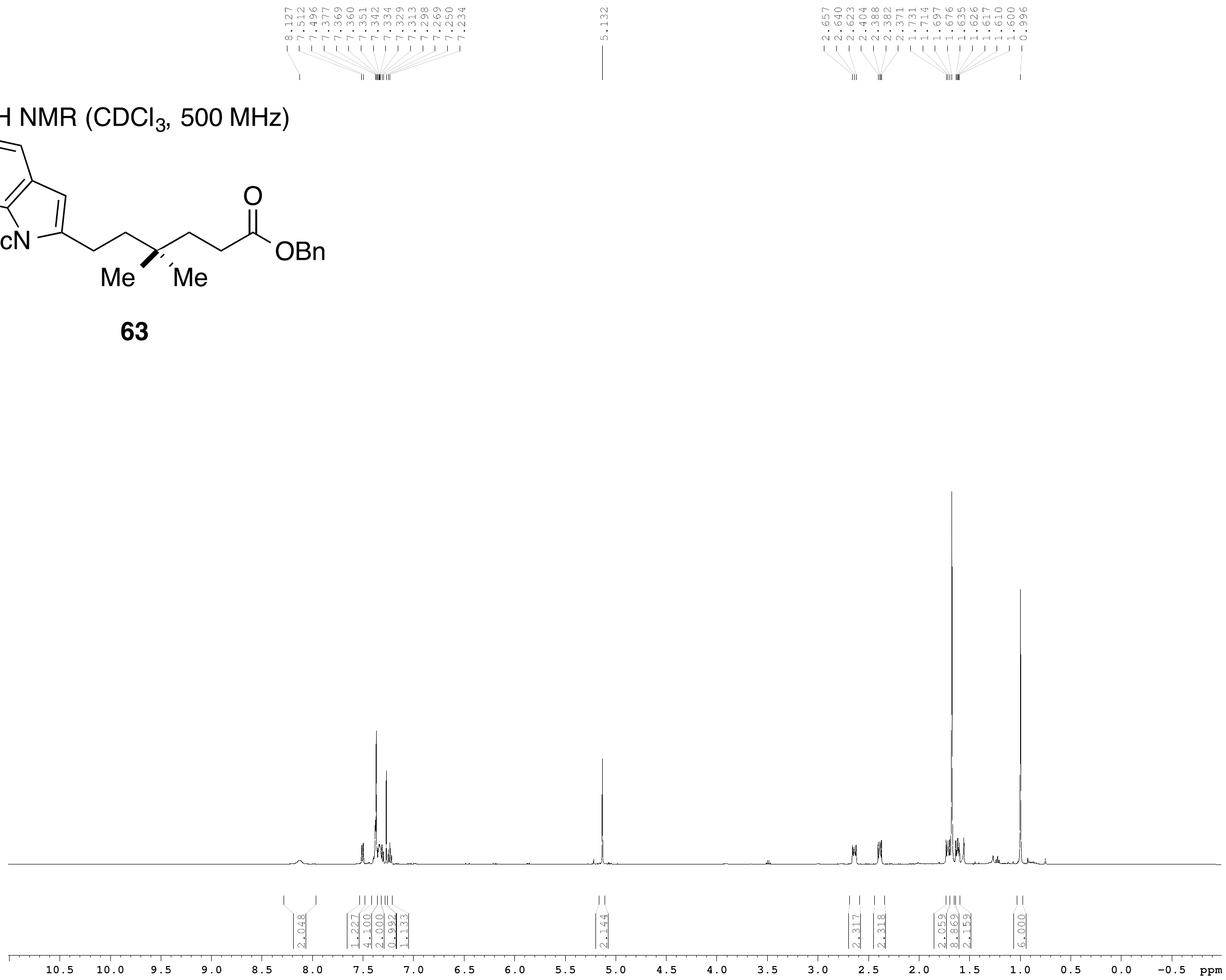

A2_82-ccn-s5-069-c.11.fid
Frequency: 125.85 MHz
174.27
158.02
136.17
131.56
130.92
128.70
128.35
128.34
113.28
77.16 CDCl3
66.37
55.34
47.50
36.62
34.00
29.93
26.39
^{13}C NMR (126 MHz, CDCl$_3$)
O
OBn
MeO
Me
Me
61
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

YS-II-279

^{1}H NMR (CDCl$_3$, 500 MHz)



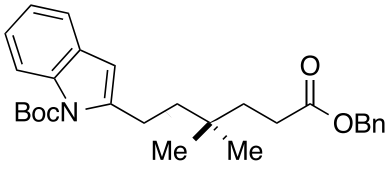
63



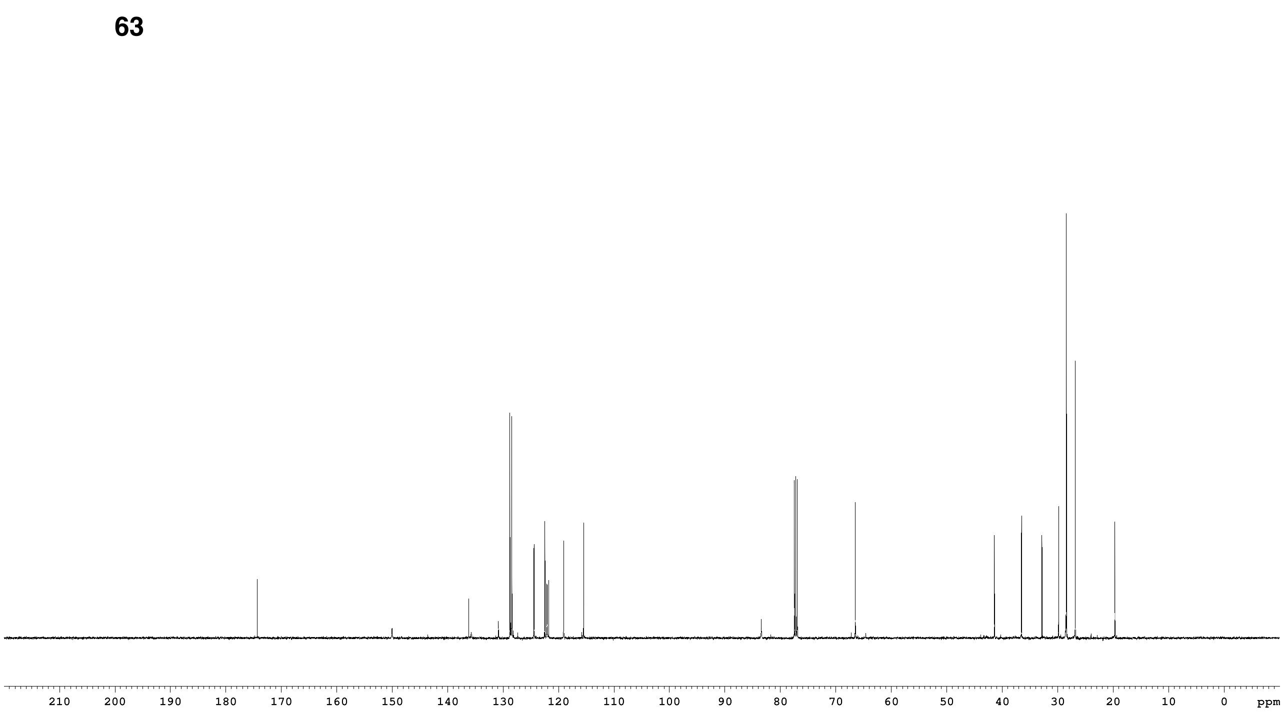
```
Current Data Parameters
NAME          YS-II-279
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150305
Time               8.57
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                  7.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST  0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200265 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 4.00
```

YS-II-279

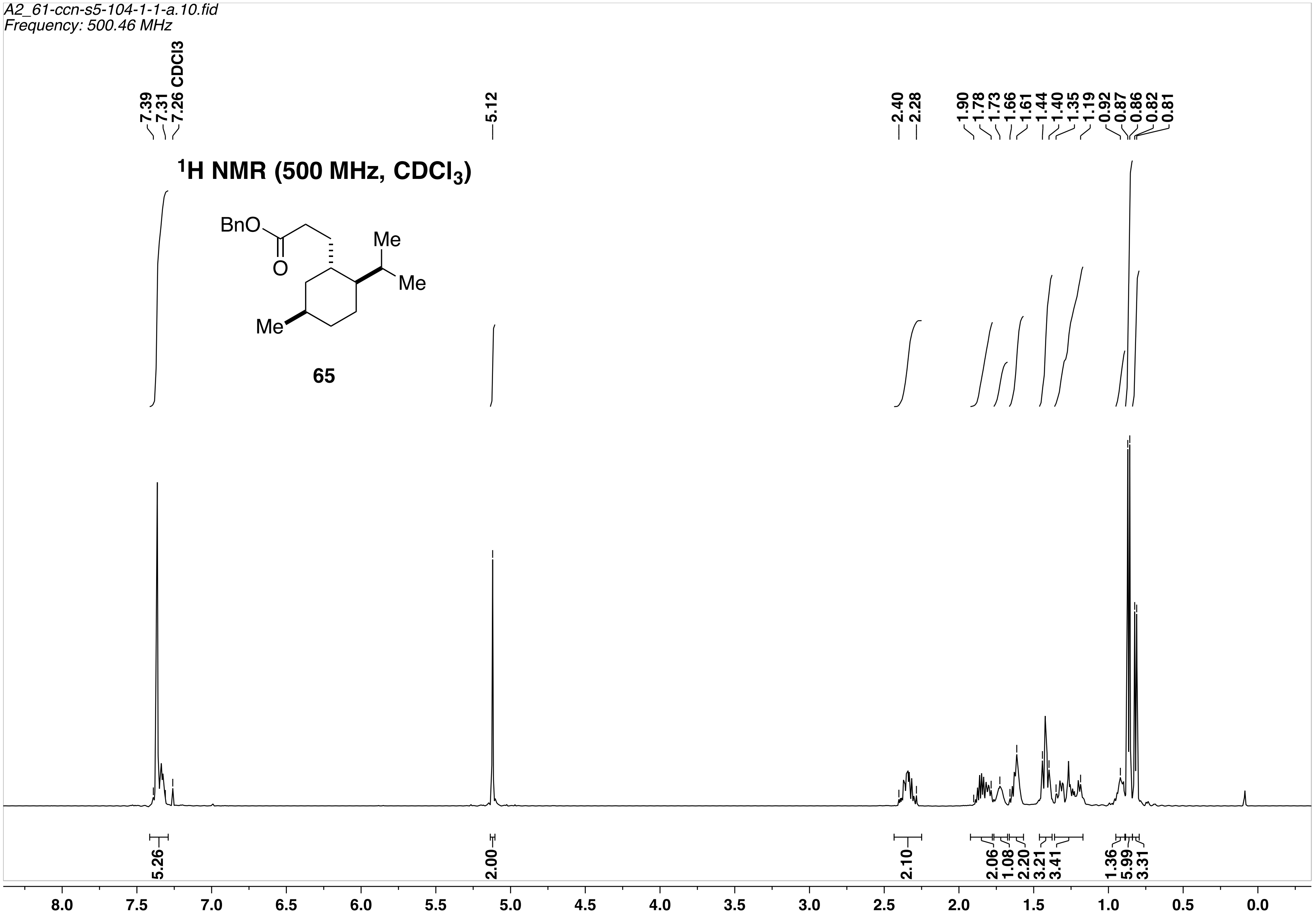
^{13}C NMR (CDCl$_3$, 126 MHz)

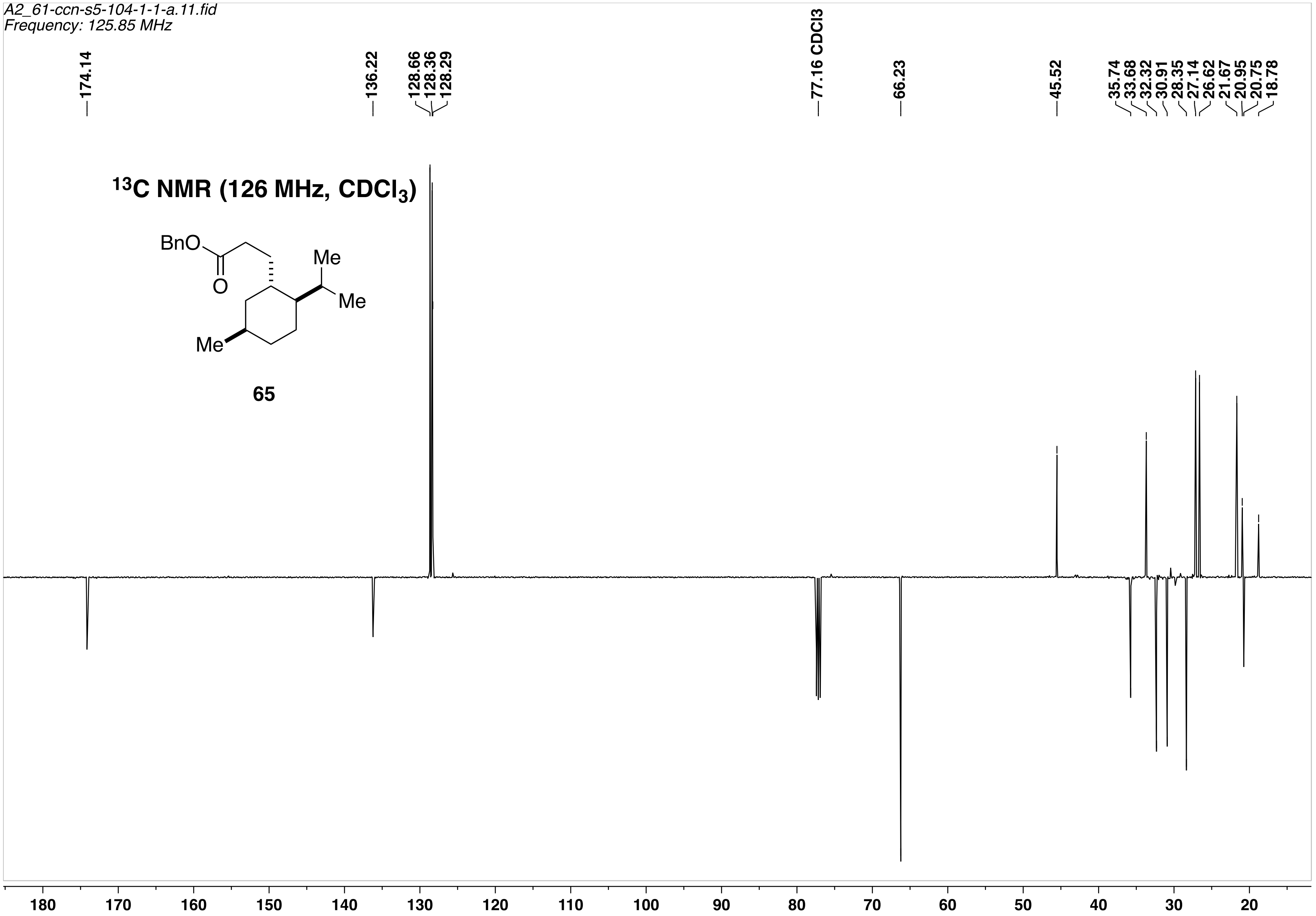


63

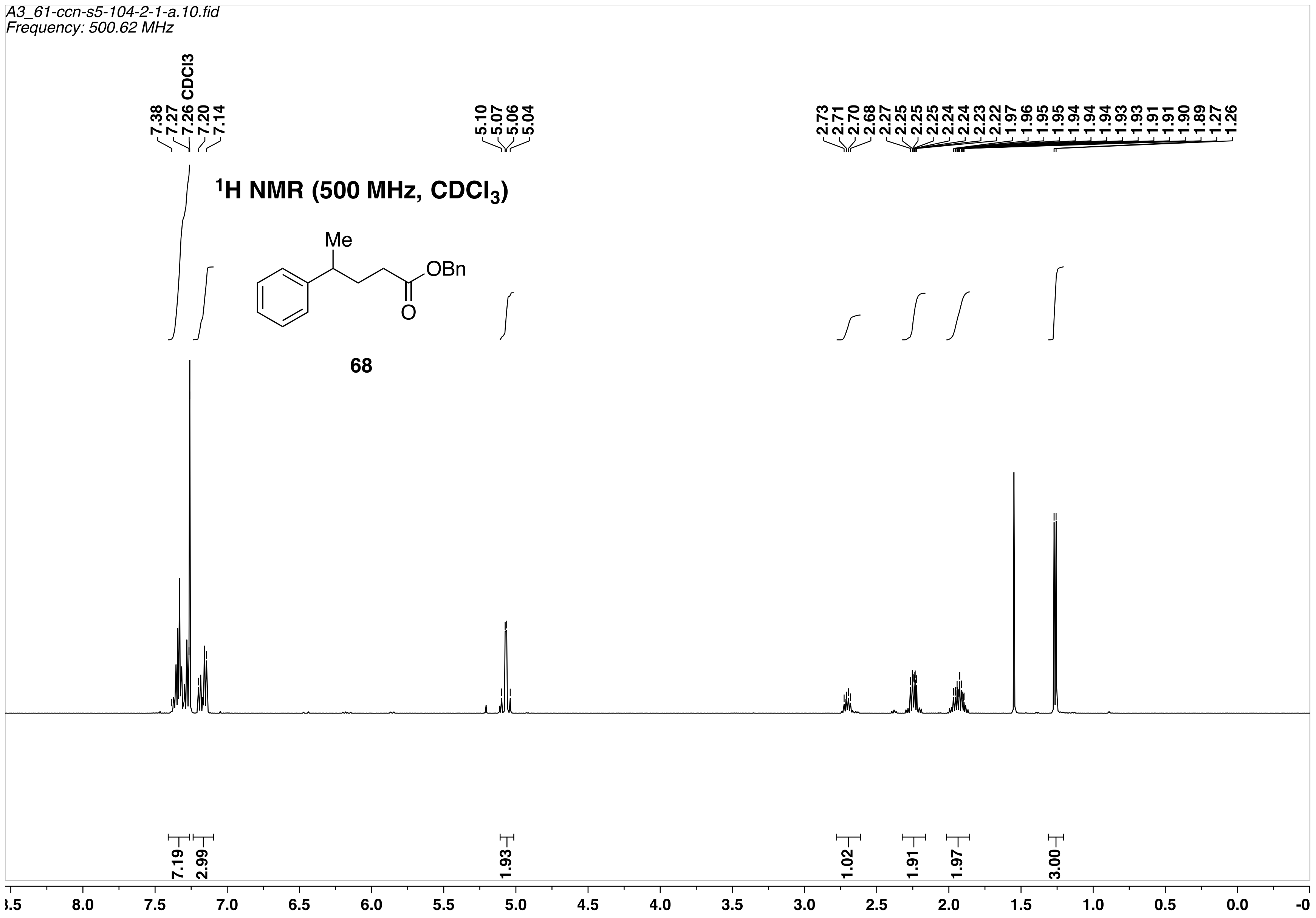


```
Current Data Parameters
NAME          YS-II-279
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20150309
Time              11.05
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  464
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               3649.1
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804019 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```


A2_61-ccn-s5-104-1-1-a.10.fid
Frequency: 500.46 MHz
7.39
7.31
7.26 CDCl3
5.12
2.40
2.28
1.90
1.78
1.73
1.66
1.61
1.44
1.40
1.35
1.19
0.92
0.87
0.86
0.82
0.81
¹H NMR (500 MHz, CDCl₃)
BnO
O
Me
Me
Me
65
5.26
2.00
2.10
2.06
1.08
2.20
3.21
3.41
1.36
5.99
3.31
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

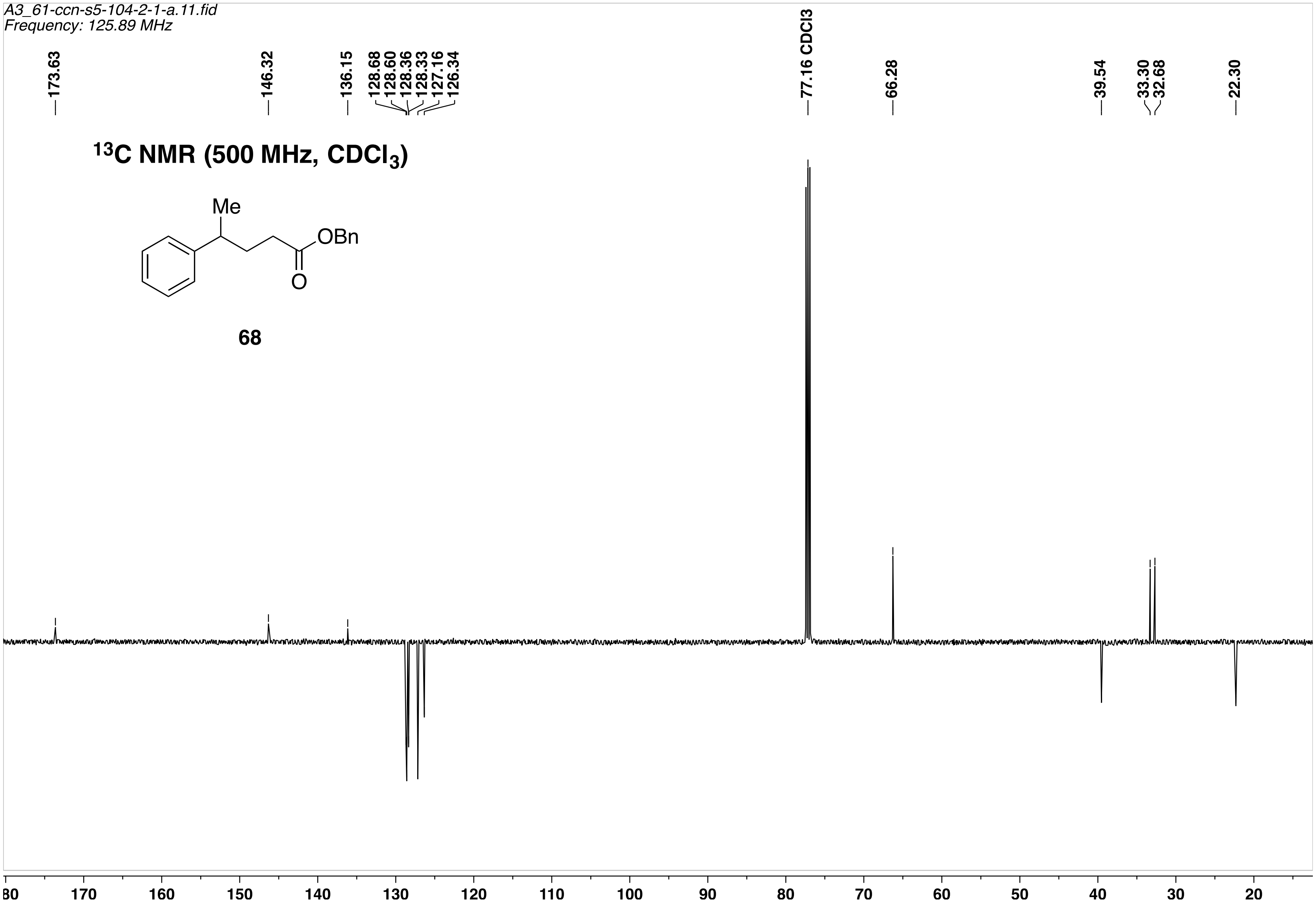

A2_61-ccn-s5-104-1-1-a.11.fid
Frequency: 125.85 MHz
174.14
136.22
128.66
128.36
128.29
77.16 CDCl3
66.23
45.52
35.74
33.68
32.32
30.91
28.35
27.14
26.62
21.67
20.95
20.75
18.78
^{13}C NMR (126 MHz, CDCl$_3$)
BnO
O
Me
Me
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

65



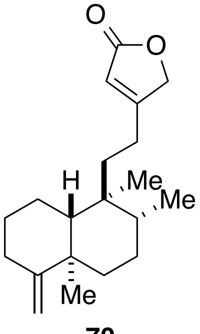
^{1}H NMR (500 MHz, $CDCl_3$)

68

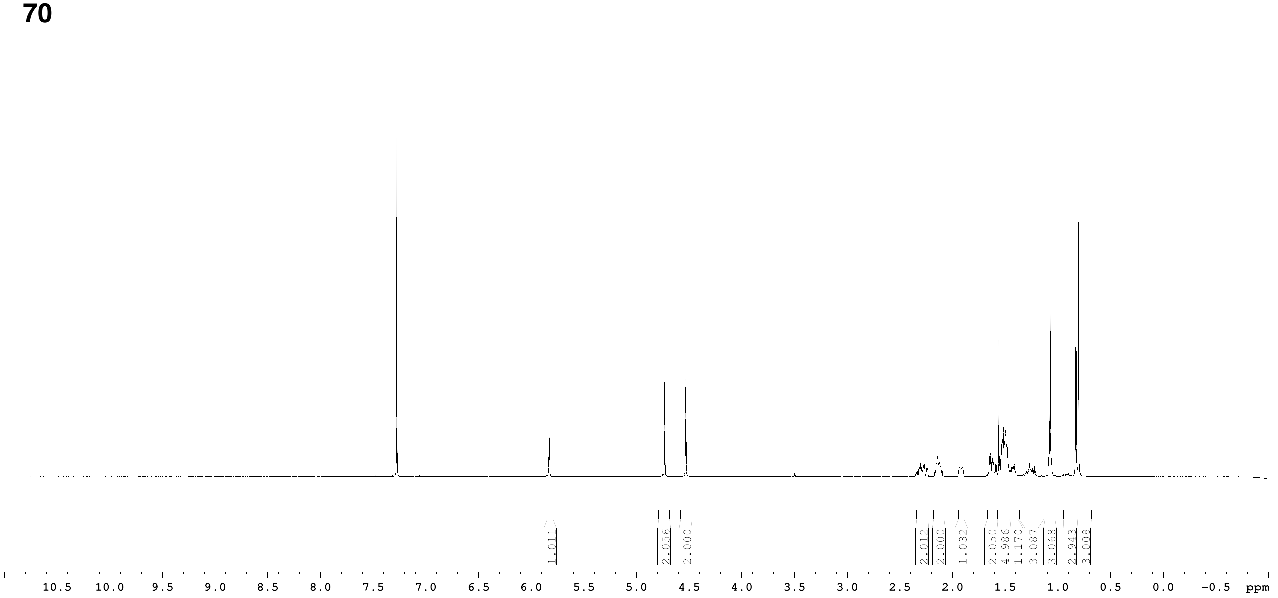

A3_61-ccn-s5-104-2-1-a.11.fid
Frequency: 125.89 MHz
173.63
146.32
136.15
128.68
128.60
128.36
128.33
127.16
126.34
77.16 CDCl3
66.28
39.54
33.30
32.68
22.30
^{13}C NMR (500 MHz, CDCl$_3$)
Me
OBn
O
68
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

YS-II-292

^1H NMR ($CDCl_3$, 500 MHz)



70



```
Current Data Parameters
NAME          YS-II-292
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150311
Time               8.45
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200241 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```