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Supplementary Materials for

Merging photoredox with nickel catalysis: Coupling of α-carboxyl sp^3-carbons with aryl halides

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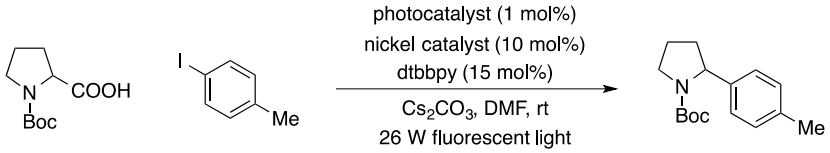
Materials and Methods

Commercial reagents were purchased from Sigma Aldrich and purified prior to use following the guidelines of Perrin and Armarego (*26*). All solvents were purified by passage through columns of activated alumina. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using an acetone-dry ice bath for volatile compounds. Chromatographic purification of products was accomplished by flash chromatography on silica gel (Fluka, 230-400 mesh). Thin layer chromatography (TLC) was performed on Analtech Uniplate 250 μm silica gel plates. Visualization of the developed chromatogram was performed by fluorescence quenching, *p*-anisaldehyde, potassium permanganate, or ceric ammonium molybdate stain. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 (500 and 125 MHz) instrument, and are internally referenced to residual protio solvent signals (note: $CDCl_3$ referenced at 7.26 and 77.0 ppm respectively). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. High resolution mass spectra were obtained at Princeton University mass spectrometry facilities. All amino acids were used from commercial suppliers. All aryl and heteroaryl halides were used from commercial suppliers or prepared using standard literature procedures.

Optimization Studies



Photocatalyst	Product %
$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	85%
$Ir(ppy)_2(dtbbpy)PF_6$	50%
$Ir(dFppy)_3$	0%
$Ir(ppy)_3$	trace

Using 0.1 equiv $NiCl_2$•glyme, 0.15 equiv dtbbpy, 3.0 equiv Boc-Pro-OH, 3.0 equiv Cs_2CO_3, 0.02 M, DMF at 23 °C (0.1 mmol scale).

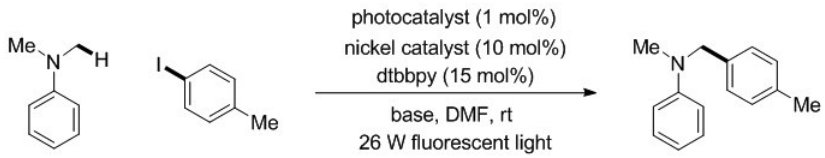
Nickel catalyst	Product %
$NiCl_2$•glyme	85%
$NiBr_2$•glyme	85%
$Ni(acac)_2$	0%
$Ni(COD)_2$	83%
$Ni(OTf)_2$	45%

Using 0.01 equiv $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, 0.15 equiv dtbbpy, 3.0 equiv Boc-Pro-OH, 3.0 equiv Cs_2CO_3, 0.02 M, DMF at 23 °C (0.1 mmol scale).

Control experiments	Product %
no light	0%
no photocatalyst	0%
no nickel catalyst	0%
no ligand	0%

Using 0.01 equiv $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, 0.1 equiv $NiCl_2$•glyme, 0.15 equiv dtbbpy, 3.0 equiv Boc-Pro-OH, 3.0 equiv Cs_2CO_3, 0.02 M, DMF at 23 °C (0.1 mmol scale).

Table S1. Optimization Studies for the Decarboxylative Arylation
* % Yields calculated by ^1H NMR using an internal standard.



Nickel catalyst	Product %
$NiCl_2$•glyme	25%
$Ni(OTf)_2$	4%
$NiBr_2$•glyme	15%

Using 0.01 equiv $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, 0.15 equiv dtbbpy, 3.0 equiv ITol, 3.0 equiv NaOAc, 0.05 M, DMF at 23 °C.

Photocatalyst	Product %
$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	48%
$Ir(ppy)_2(dtbbpy)PF_6$	48%
$Ru(bpy)_3(PF_6)_2$	46%
$Ru(bpy)_3Cl_2$•$6H_2O$	35%

Using 0.1 equiv $NiCl_2$•glyme, 0.15 equiv dtbbpy, 3.0 equiv ITol, 3.0 equiv NaOAc, 0.02 M, DMF at 23 °C.

Base	Product %
KOH	86%
Cs_2CO_3	53%
NaOH	57%
CsOH•H_2O	56%
NaOAc	48%

Using 0.01 equiv $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, 0.1 equiv $NiCl_2$•glyme, 0.15 equiv dtbbpy, 3.0 equiv ITol, 3.0 equiv base, 0.02 M, DMF at 23 °C.

Table S2. Optimization Studies for C-H Arylation.
* % Yields calculated by ^1H NMR using an internal standard.

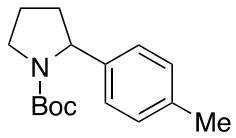
Supplementary Text

General Procedure A for the Decarboxylative Arylation (Arene Scope): An oven-dried 40 mL vial equipped with a Teflon septum and magnetic stir bar was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.00 μmol, 0.01 equiv), $NiCl_2$•glyme (0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.06 mmol, 0.15 equiv), the corresponding aromatic halides (0.40 mmol, 1.0 equiv), Boc-Pro-OH (0.60 mmol, 1.5 equiv), Cs_2CO_3 (0.60 mmol, 1.5 equiv), and 20 mL of DMF. The reaction mixture was degassed by bubbling argon stream for 20 min, then irradiated with two 26 W fluorescent lamps (at approximately 2 cm away from the light source). After 72h, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ solution, extracted with Et_2O (3 × 100 mL). The combined organic extracts were washed with water and brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

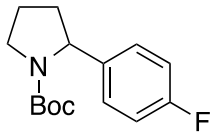
General Procedure B for the Decarboxylative Arylation (Amino Acid Scope) (*26*)**:** An oven-dried 40 mL vial equipped with a Teflon septum and magnetic stir bar was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.00 μmol, 0.01 equiv), $NiCl_2$•glyme (0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.06 mmol, 0.15 equiv), 4-bromoacetophenone (0.40 mmol, 1.0 equiv), the corresponding amino acids (1.20 mmol, 3.0 equiv), Cs_2CO_3 (1.20 mmol, 3.0 equiv), and 20 mL of DMF. The reaction mixture was degassed by bubbling argon stream for 20 min, then irradiated with a 34 W blue LED lamp (Fan was used to keep the reaction temperature below 28 ^oC). After 72h, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ solution, extracted with

Et_2O (3 × 100 mL). The combined organic extracts were washed with water and brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product. (Decarboxylative arylation of various amino acids with 4-bromoacetophenone could be performed on a 0.1 mmol scale using two 26 W fluorescent lamps with comparable efficiency.)

General Procedure C for the C–H Arylation: In the glovebox, an oven-dried 40 mL vial equipped with a Teflon septum and magnetic stir bar was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.00 μmol, 0.01 equiv), $NiCl_2$•glyme (0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.06 mmol, 0.15 equiv), the corresponding aromatic halide (0.40 mmol, 1.0 equiv), *N*,*N*-dimethylaniline (1.20 mmol, 3.0 equiv), KOH (1.20 mmol, 3.0 equiv), and 20 mL of DMF. The reaction mixture was then irradiated with a 26 W fluorescent lamp (at approximately 2 cm away from the light source). After 48 h, the reaction mixture was diluted with water (100 mL) and extracted with Et_2O (3 × 150 mL). The organic extracts were washed with brine (100 mL) and the combined aqueous layers were extracted once more with Et_2O (50 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

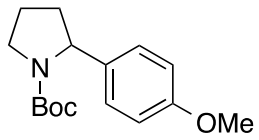


***tert*-Butyl 2-(*p*-tolyl)pyrrolidine-1-carboxylate** [known compound (*27*)]**:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-iodotoluene (89.0 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.60 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (15% ethyl acetate/hexane) as a pale yellow solid (81 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 7.10-7.03 (m, 4H), 4.92 and 4.74 (2 brs, 1H, rotamer), 3.60-3.47 (m, 2H), 2.32-2.20 (m, 4H), 1.91-1.79 (m, 3H), 1.46 (s, 3H), 1.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 154.65 (154.41), 142.07 (141.13), 135.92, (129.04) 128.75, 125.43 (125.28), 79.10 (78.88), 61.03 (60.45), (47.31) 47.01, 36.02 (34.90), (28.54) 28.20, (23.47) 23.11, 21.05; HRMS (ESI) m/z calcd for $C_{16}H_{23}NNaO_2$ $[(M+Na)^+]$ 284.1626, found 284.1630. IR (film) 2973, 1690, 1388, 1109, 812, 767 cm^{-1};



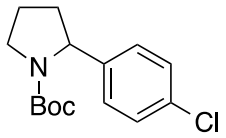
***tert*-Butyl 2-(4-fluorophenyl)pyrrolidine-1-carboxylate** [known compound (*28*)]**:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-fluoroiodobenzene (90.0 mg, 0.4 mmol,

1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (15% ethyl acetate/hexane) as a pale yellow oil (69 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 7.14-7.11 (m, 2H), 7.00-6.96 (m, 2H), 4.92 and 4.73 (2 brs, 1H, rotamer), 3.61-3.60 (m, 2H), 2.31-2.25 (m, 1H), 1.87-1.77 (m, 3H), 1.46 (s, 3H), 1.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 161.57 (d, J = 242.3 Hz), (154.71) 154.52, 140.89 (139.79), 126.96 (d, *J* = 7.1 Hz), (115.19) 114.89 (d, *J* = 21.3 Hz), 79.33 (78.89), 60.72 (60.11), (47.31) 47.07, 36.10 (34.90), (28.50) 28.17, (23.46) 23.17; HRMS (ESI) m/z calcd for $C_{15}H_{20}FNNaO_2$ $[(M+Na)^+]$ 288.1376, found 288.1375. IR (film) 2971, 1691, 1388, 1152, 829, 770 cm^{-1};

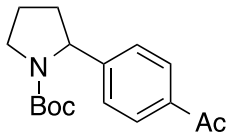


***tert*-Butyl 2-(4-methoxyphenyl)pyrrolidine-1-carboxylate** [known compound (*27*)]**:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-iodoanisole (96.0 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (15% ethyl acetate/hexane) as a yellow oil (82 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 7.08 (d, *J* = 7.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.90 and 4.72 (2 brs, 1H, rotamer), 3.79 (s, 3H), 3.61-3.51 (m, 2H), 2.28 (br, 1H), 1.92-1.78 (m, 3H), 1.46

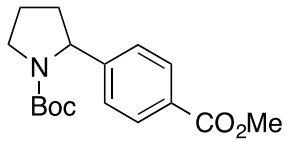
(s, 3H), 1.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 158.22, 154.67, 137.31 (136.28), 126.60, (113.77) 113.44, 79.13, 60.74 (60.12), 55.27, (47.27) 46.99, 36.05 (34.88), (28.54) 28.21, (23.47) 23.14; HRMS (ESI) m/z calcd for $C_{16}H_{23}NNaO_3$ [$(M+Na)^+$] 300.1576, found 300.1562. IR (film) 2972, 1688, 1387, 1158, 826, 768 cm^{-1};



***tert*-Butyl 2-(4-chlorophenyl)pyrrolidine-1-carboxylate** [known compound (*29*)]**:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 1-chloro-4-iodobenzene (96.0 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (15% ethyl acetate/hexane) as a pale yellow solid (87 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.90 and 4.73 (2 brs, 1H, rotamer), 3.62-3.49 (m, 2H), 2.33-2.28 (m, 1H), 1.92-1.82 (m, 2H), 1.80-1.74 (m, 1H), 1.45 (s, 3H), 1.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 154.51, 143.76 (142.73), (132.19) 132.10, (128.52) 128.30, 126.91 (126.84), 79.45, 60.80 (60.25), (47.39) 47.11, 36.03 (34.87), (28.53) 28.22, (23.55) 23.19; HRMS (ESI) m/z calcd for $C_{15}H_{20}NNaO_2Cl$ [$(M+Na)^+$] 304.1080, found 304.1078. IR (film) 2973, 1690, 1386, 1156, 1089, 821, 773 cm^{-1};

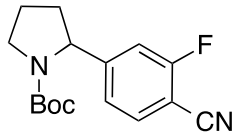


***tert*-Butyl 2-(4-acetylphenyl)pyrrolidine-1-carboxylate:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.80 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-bromoacetophenone (81.9 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (20% ethyl acetate/hexane) as a pale yellow solid (100 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.97 and 4.81 (2 brs, 1H, rotamer), 3.66-3.52 (m, 2H), 2.60-2.58 (m, 3H), 2.38-2.32 (m, 1H), 1.92-1.78 (m, 3H), 1.45 (s, 3H), 1.17 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 197.75, (154.43) 154.37, 150.79 (149.80), 135.66, (128.63) 128.41, 125.62 (125.54), (79.51) 79.45, 61.14 (60.65), (47.43) 47.11, 35.88 (34.76), (28.46) 28.12, 26.60, (23.63) 23.23; HRMS (ESI) m/z calcd for $C_{17}H_{23}NNaO_3$ [$(M+Na)^+$] 312.1576, found 312.1558. IR (film) 2974, 1682, 1389, 1266, 1159, 830 cm^{-1};



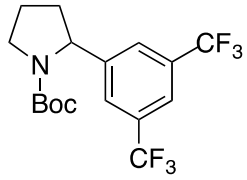
***tert*-Butyl 2-(4-(methoxycarbonyl)phenyl)pyrrolidine-1-carboxylate** [known compound (*28*)]**:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$

(4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), methyl-4-bromobenzoate (88.0 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a yellow oil (111 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 7.97 (d, *J* = 10.0 Hz, 2H), 7.24 (d, *J* = 5.0 Hz, 2H), 4.97 and 4.80 (2 brs, 1H, rotamer), 3.91 (s, 3H), 3.65-3.52 (m, 2H), 2.37-2.31 (m, 1H), 1.92-1.77 (m, 3H), 1.45 (s, 3H), 1.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 166.94, 154.37, 150.58 (149.54), (129.77) 129.58, 128.47, 125.45 (125.38), 79.44, 61.19 (60.63), 51.99 (51.66), (47.37) 47.12, 35.91 (34.74), (28.44) 28.10, (23.57) 23.25; HRMS (ESI) m/z calcd for $C_{17}H_{23}NNaO_4$ [$(M+Na)^+$] 328.1525, found 328.1517. IR (film) 2974, 1690, 1388, 1274, 1157, 1105, 704 cm^{-1};



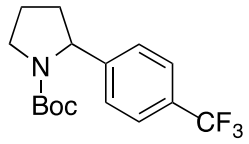
***tert*-Butyl 2-(4-cyano-3-fluorophenyl)pyrrolidine-1-carboxylate:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-bromo-2-fluorobenzonitrile (82.0 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (25% ethyl acetate/hexane) as a pale yellow oil (87 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$)

rotameric mixture: δ 7.56 (t, *J* = 7.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 9.5 Hz, 1H), 4.92 and 4.78 (2 brs, 1H, rotamer), 3.66-3.55 (m, 2H), 2.40-2.32 (m, 1H), 1.93-1.87 (m, 2H), 1.82-1.75 (m, 1H), 1.45 (s, 4H), 1.21 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ (163.40) 163.27 (d, *J* = 257.3 Hz), (154.50) 154.37, 154.40 (d, *J* = 6.5 Hz) (153.45), 134.38 (d, *J* = 8.9 Hz), (133.50) 133.36, 121.97 (d, *J* = 3.1 Hz), (114.11) 114.03, 113.42 (d, *J* = 19.9 Hz), (80.04) 79.95, 60.94 (60.50), (47.46) 47.16, 35.75 (34.63), (28.40) 28.13, (23.71) 23.27; HRMS (ESI) m/z calcd for $C_{16}H_{19}FN_2NaO_2$ [$(M+Na)^+$] 313.1328, found 313.1288. IR (film) 2977, 2235, 1689, 1388, 1365, 1161, 1105, 733 cm^{-1};

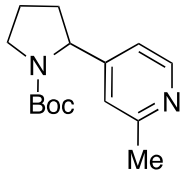


***tert*-Butyl 2-(3,5-bis(trifluoromethyl)phenyl)pyrrolidine-1-carboxylate:** According to the general procedure A, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 1,3-bis(trifluoromethyl)-5-bromobenzene (118.0 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a pale yellow oil (133 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 7.75-7.73 (m, 1H), 7.62-7.58 (m, 2H), 5.01 and 4.83 (2 brs, 1H, rotamer), 3.69-3.54 (m, 2H), 2.44-2.40 (m, 1H), 1.94-1.83 (m, 3H), 1.46 (s, 3H), 1.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture,

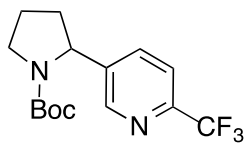
resonances for minor rotamer are enclosed in parenthesis (): δ (154.52) 154.18, 147.92 (146.82), 131.61 (q, *J* = 33.8 Hz), 125.85 (125.59), 123.34 (q, *J* = 271.3 Hz), (120.74) 120.56, (80.08) 80.00, 60.94 (60.32), (47.46) 47.28, 36.08 (34.81), (28.32) 27.98, (23.59) 23.47; HRMS (ESI) m/z calcd for $C_{17}H_{19}F_6NNaO_2$ [$(M+Na)^+$] 406.1218, found 406.1196. IR (film) 2978, 1694, 1378, 1275, 1125, 896, 681 cm^{-1};



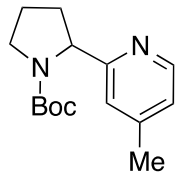
***tert*-Butyl 2-(4-(trifluoromethyl)phenyl)pyrrolidine-1-carboxylate:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-bromobenzotrifluoride (91.9 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a pale yellow oil (111 mg, 88%). ^1H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.97 and 4.81 (2 brs, 1H, rotamer), 3.66-3.55 (m, 2H), 2.38-2.32 (m, 1H), 1.91-1.86 (m, 2H), 1.82-1.77 (m, 1H), 1.46 (s, 3H), 1.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ (154.52) 154.44, 149.29 (148.26), 128.88 (q, *J* = 31.3 Hz), 125.79 (125.72), (125.41) 125.19, 124.25 (q, *J* = 270.0 Hz), 79.60, 61.06 (60.51), 47.44 (47.14), 39.97 (34.82), (28.49) 28.15, (23.57) 23.23; HRMS (ESI) m/z calcd for $C_{16}H_{20}F_3NNaO_2$ [$(M+Na)^+$] 338.1344, found 338.1324. IR (film) 2975, 1692, 1322, 1065, 832, 773 cm^{-1};



***tert*-Butyl 2-(2-methylpyridin-4-yl)pyrrolidine-1-carboxylate:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-bromo-2-methylpyridine (71.0 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (50% ethyl acetate/hexane) as a pale yellow oil (90 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 8.40 (d, *J* = 5.0 Hz, 1H), 6.95 (s, 1H), 6.90 (d, *J* = 5.0 Hz, 1H), 4.87-4.86 and 4.71-4.68 (2 m, 1H, rotamer), 3.63-3.49 (m, 2H), 2.53 (s, 3H), 2.36-2.29 (m, 1H), 1.90-1.85 (m, 2H), 1.81-1.76 (m, 1H), 1.46 (s, 3H), 1.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 158.23, 154.33 (154.21), 153.35, (149.06) 148.95, (120.15) 120.06, 117.89 (117.70), 79.58, 60.38 (59.91), (47.31) 47.02, 35.38 (34.28), (28.40) 28.07, (24.42) 24.37, (23.57) 23.16; HRMS (ESI) m/z calcd for $C_{15}H_{23}N_2O_2$ $[(M+H)^+]$ 263.1760, found 263.1758. IR (film) 2974, 1690, 1387, 1160, 1111, 828, 771 cm^{-1};

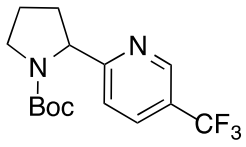


***tert*-Butyl 2-(6-(trifluoromethyl)pyridin-3-yl)pyrrolidine-1-carboxylate:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 5-bromo-2-(trifluoromethyl)pyridine (92.9 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (20% ethyl acetate/hexane) as a pale yellow solid (104 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 8.58 (s, 1H), 7.68-7.63 (m, 2H), 5.01 and 4.86 (2 brs, 1H, rotamer), 3.67-3.57 (m, 2H), 2.43-2.40 (m, 1H), 1.96-1.91 (m, 2H), 1.84-1.82 (m, 1H), 1.45 (s, 4H), 1.17 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ (154.47) 154.07, 148.01 (147.77), 146.61 (q, J = 35.0 Hz) [146.48 (q, J = 35.0 Hz)], 143.79 (142.80), (134.36) 134.20, 121.59 (q, J = 272.5 Hz), (120.16) 120.01, 79.97, 58.91 (58.58), (47.35) 47.13, 35.80 (34.55), (28.36) 28.08, (23.63) 23.28; HRMS (ESI) m/z calcd for $C_{15}H_{20}F_3N_2O_2$ $[(M+H)^+]$ 317.1477, found 317.1478. IR (film) 2976, 1690, 1387, 1337, 1130, 1084, 845, 736 cm^{-1};



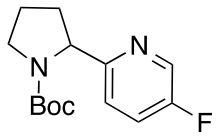
***tert*-Butyl 2-(4-methylpyridin-2-yl)pyrrolidine-1-carboxylate:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg,

0.06 mmol, 0.15 equiv), 2-bromo-4-methylpyridine (71.0 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.00 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (30% ethyl acetate/hexane) as a pale yellow oil (70 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 8.39-8.37 (m, 1H), 6.96-6.92 (m, 2H), 4.96-4.95 and 4.84-4.82 (2 m, 1H, rotamer), 3.67-3.50 (m, 2H), 2.38-2.26 (m, 4H), 2.01-1.96 (m, 1H), 1.91-1.84 (m, 2H), 1.46 (s, 3H), 1.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 163.47 (163.23), (154.63) 154.52, (149.06) 148.75, (147.32) 147.23, (122.63) 122.46, (120.88) 120.37, (79.27) 79.17, 62.72 (62.06), (47.41) 47.03, 34.17 (33.05), (28.47) 28.14, (23.75) 23.21, (21.21) 21.08; HRMS (ESI) m/z calcd for $C_{15}H_{23}N_2O_2$ [$(M+H)^+$] 263.1760, found 263.1754. IR (film) 2973, 1690, 1388, 1159, 1112, 822, 770 cm^{-1};



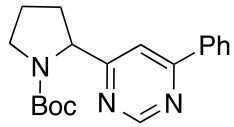
***tert*-Butyl 2-(5-(trifluoromethyl)pyridin-2-yl)pyrrolidine-1-carboxylate:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 2-bromo-5-(trifluoromethyl)pyridine (92.9 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (20% ethyl acetate/hexane) as a yellow oil (76 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 8.80 (s, 1H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 5.04-

5.02 and 4.94-4.91 (2 m, 1H, rotamer), 3.67-3.52 (m, 2H), 2.43-2.32 (m, 1H), 2.04-1.88 (m, 3H), 1.45 (s, 3H), 1.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 167.89 (166.77), (154.67) 154.28, [146.27 (q, *J* = 3.8 Hz)] 146.04 (q, *J* = 3.8 Hz), [133.62 (q, *J* = 3.8 Hz)] 133.37 (q, *J* = 3.8 Hz), 124.69 (q, *J* = 32.5 Hz), 123.61 (q, *J* = 270.0 Hz), (119.92) 119.46, (79.73) 79.67, 62.72 (62.16), (47.47) 47.12, 34.23 (32.99), (28.44) 28.15, (23.88) 23.25; HRMS (ESI) m/z calcd for $C_{15}H_{20}F_3N_2O_2$ [$(M+H)^+$] 317.1477, found 317.1474. IR (film) 2976, 1696, 1392, 1327, 1128, 1080, 1015, 773 cm^{-1}.

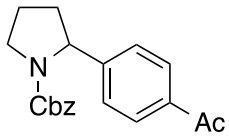


***tert*-Butyl 2-(5-fluoropyridin-2-yl)pyrrolidine-1-carboxylate:** According to the general procedure A, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 2-chloro-5-fluoropyridine (52.6 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a clear oil (68 mg, 64%). ^{1}H NMR (500 MHz, ($CDCl_3$) δ rotameric mixture: 8.38 (d, *J* = 2.9 Hz, 1H), 7.39-7.29 (m, 1H), 7.22-7.14 (m, 1H), 4.97 and 4.86 (2 brs, 1H), 3.66-3.46 (m, 2H), 2.43-2.20 (m, 1H), 2.08-1.80 (m, 3H), 1.44 (s, 3H), 1.21 (s, 6H); ^{13}C NMR (125 MHz, ($CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 159.69 (158.52), [158.26 (d, *J* = 253.9 Hz)] 158.20 (d, *J* = 253.8 Hz), (154.67) 154.41, [137.34 (d, *J* = 23.8 Hz)] 137.03 (d, *J* = 23.3 Hz), [123.01 (d,

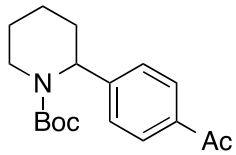
J = 18.1 Hz)] 122.94 (d, *J* = 18.2 Hz), [121.22 (d, *J* = 4.6 Hz)] 120.62 (d, *J* = 4.1 Hz), 79.48 (79.42), 62.20 (61.56), 47.38 (47.02), 34.28 (32.98), 28.47 (28.19), 23.82 (23.18); HRMS (ESI) m/z calcd for $C_{14}H_{19}FN_2NaO_2$ [$(M+Na)^+$] 289.1328, found 289.1323. IR (film) 2975, 2878, 1692, 1586, 1456, 1389, 1365, 1225, 1161, 1112, 1082 cm^{-1};



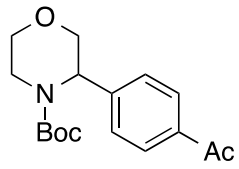
***tert*-Butyl 2-(6-phenylpyrimidin-4-yl)pyrrolidine-1-carboxylate:** According to the general procedure A, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-chloro-6-phenylpyrimidine (68.6 mg, 0.4 mmol, 1.0 equiv), Boc-Pro-OH (129.0 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (195.6 mg, 0.6 mmol, 1.5 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (20% ethyl acetate/hexane) as a clear oil (85 mg, 65%). ^{1}H NMR (500 MHz, ($CDCl_3$) rotameric mixture: δ 9.17 (s, 1H), 8.09-8.02 (m, 2H), 7.57 (s, 1H), 7.52-7.47 (m, 3H), 4.97 and 4.85 (2 brs, 1H, rotamer), 3.75-3.53 (m, 2H), 2.48-2.32 (m, 1H), 2.09-1.89 (m, 3H), 1.48 (s, 3H), 1.22 (s, 6H); ^{13}C NMR (125 MHz, ($CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 172.88 (171.70), (164.30) 164.16, (158.80) 158.71, (154.69) 154.30, (137.06) 136.67, 131.04 (130.77), 129.06 (128.90), (127.23) 127.09, (113.42) 112.47, 79.86, 62.45 (61.84), (47.51) 47.20, 33.94 (32.67), (28.46) 28.21, (24.00) 23.37; HRMS (ESI) m/z calcd for $C_{19}H_{24}N_3O_2$ [$(M+H)^+$] 326.1869, found 326.1862. IR (film) 2974, 2931, 1691, 1588, 1477, 1444, 1387, 1365, 1251, 1114, 1082 cm^{-1};



Benzyl 2-(4-acetylphenyl)pyrrolidine-1-carboxylate: According to the general procedure B, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.10 mg, 0.06 mmol, 0.15 equiv), 4-bromoacetophenone (82.0 mg, 0.4 mmol, 1.0 equiv), Cbz-Pro-OH (305.0 mg, 1.2 mmol, 3.0 equiv), Cs_2CO_3 (391.2 mg, 1.2 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (20% ethyl acetate/hexane) as a pale yellow oil (120 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 7.92-7.87 (m, 2H), 7.37-7.13 (m, 6H), 6.89 (d, *J* = 7.0 Hz, 1H), 5.17-4.92 (m, 3H), 3.71-3.62 (m, 2H), 2.60 and 2.58 (2s, 3H, rotamer), 2.40-2.33 (m, 1H), 1.93-1.89 (m, 2H), 1.87-1.82 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 197.64, 154.86, 149.90 (149.17), (136.85) 136.49, 135.86, (128.68) 128.62, (128.50) 128.17, (128.01) 127.93, (127.65) 127.41, 125.71, (66.87) 66.68, (61.27) 60.96, 47.73 (47.28), 35.78 (34.72), 26.65, (23.74) 23.06; HRMS (ESI) m/z calcd for $C_{20}H_{22}NO_3$ $[(M+H)^+]$ 324.1600, found 324.1586. IR (film) 2961, 1698, 1679, 1407, 1265, 1106, 731, 696 cm^{-1};

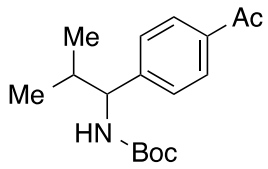


***tert*-Butyl 2-(4-acetylphenyl)piperidine-1-carboxylate** [known compound (*30*)]**:** According to the general procedure B, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-bromoacetophenone (82.0 mg, 0.4 mmol, 1.0 equiv), Boc-Pip-OH (276 mg, 1.2 mmol, 3.0 equiv), Cs_2CO_3 (391.2 mg, 1.2 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a pale yellow oil (99 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.43 (s, 1H), 4.07 (d, *J* = 13.0 Hz, 1H), 2.76 (td, *J* = 13.0 Hz, *J* = 3.5 Hz, 1H), 2.60 (s, 3H), 2.32-2.29 (m, 1H), 1.96-1.89 (m, 1H), 1.65-1.52 (m, 3H), 1.46 (s, 9H), 1.39-1.33 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.71, 155.52, 146.46, 135.44, 128.65, 126.68, 79.82, 53.42, 40.33, 28.39, 28.26, 26.60, 25.24, 19.37; HRMS (ESI) m/z calcd for $C_{18}H_{25}NNaO_3$ $[(M+Na)^+]$ 326.1732, found 326.1719. IR (film) 2936, 1680, 1266, 1154, 1031, 828, 734 cm^{-1};

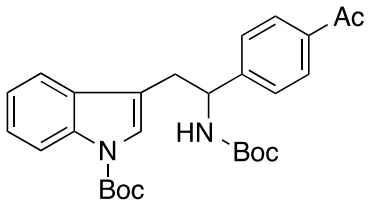


***tert*-butyl 3-(4-acetylphenyl)morpholine-4-carboxylate:** According to the general procedure B, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-bromoacetophenone (82 mg, 0.4 mmol, 1.0 equiv), Boc-Morph-OH (277.2 mg, 1.2 mmol, 3.0 equiv), Cs_2CO_3 (391.2 mg, 1.2 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (17% ethyl acetate/hexane) as a pale yellow solid (74.0 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.5 Hz,

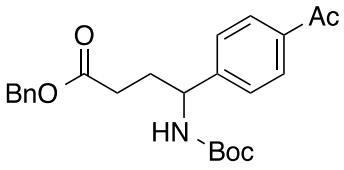
2H), 7.55 (d, *J* = 8.0 Hz, 2H), 5.11 (br, 1H), 4.35 (d, *J* = 7.0 Hz, 1H), 3.91-3.87 (m, 2H), 3.83-3.80 (m, 1H), 3.61 (td, *J* = 11.5 Hz, *J* = 2.5 Hz, 1H), 3.11 (td, *J* = 13.0 Hz, *J* = 3.5 Hz, 1H), 2.60 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.70, 154.76, 144.88, 136.01, 128.52, 127.77, 80.56, 68.91, 66.93, 53.26, 39.97, 28.35, 26.63; HRMS (ESI) m/z calcd for $C_{17}H_{23}NNaO_4$ [$(M+Na)^+$] 328.1525, found 328.1512. IR (film) 2975, 1681, 1266, 1163, 1109, 868, 733 cm^{-1};



***tert*-Butyl (1-(4-acetylphenyl)-2-methylpropyl)carbamate:** According to the general procedure B, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-bromoacetophenone (82.0 mg, 0.4 mmol, 1.0 equiv), Boc-Val-OH (260.7 mg, 1.2 mmol, 3.0 equiv), Cs_2CO_3 (391.2 mg, 1.2 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a pale yellow solid (83 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.12 (brs, 1H), 4.48 (s, 1H), 2.59 (s, 3H), 1.98 (br, 1H), 1.46 (s, 9H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.83, 154.41, 147.83, 135.90, 128.46, 126.97, 79.59, 60.35, 33.58, 28.35, 26.62, 19.67, 18.35; HRMS (ESI) m/z calcd for $C_{17}H_{25}NNaO_3$ [$(M+Na)^+$] 314.1732, found 314.1684. IR (film) 3348, 2970, 1679, 1364, 1166, 1007, 736 cm^{-1};

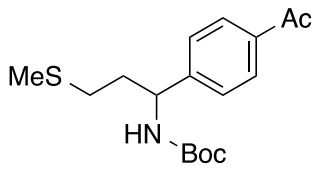


***tert*-Butyl 3-(2-(4-acetylphenyl)-2-((*tert*-butoxycarbonyl)amino)ethyl)-1*H*-indole-1-carboxylate:** According to the general procedure B, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-bromoacetophenone (82.0 mg, 0.4 mmol, 1.0 equiv), Boc-Trp(Boc)-OH (485.0 mg, 1.2 mmol, 3.0 equiv), Cs_2CO_3 (391.2 mg, 1.2 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (12% ethyl acetate/hexane) as a yellow solid (159 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (br, 1H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.36 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.26-7.22 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 5.11 (br, 1H), 4.98 (br, 1H), 3.14 (s, 2H), 2.59 (s, 3H), 1.64 (s, 9H), 1.39 (br, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.76, 155.18, 149.57, 148.03, 136.16, 135.37, 130.42, 128.70, 126.52, 124.52, 124.00, 122.57, 118.86, 115.87, 115.24, 83.65, 79.82, 54.27, 32.55, 28.32, 28.19, 26.65; HRMS (ESI) m/z calcd for $C_{28}H_{34}N_2NaO_5$ [$(M+Na)^+$] 501.2365, found 501.2342. IR (film) 3357, 2979, 1681, 1366, 1156, 1083, 733 cm^{-1};



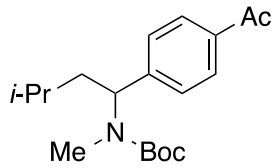
Benzyl 4-(4-acetylphenyl)-4-((*tert*-butoxycarbonyl)amino)butanoate: According to the general procedure B, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv),

$NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-bromoacetophenone (82.0 mg, 0.4 mmol, 1.0 equiv), Boc-Glu(OBzl)-OH (413.0 mg, 1.2 mmol, 3.0 equiv), Cs_2CO_3 (391.2 mg, 1.2 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (20% ethyl acetate/hexane) as a pale yellow solid (126 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.39-7.33 (m, 7H), 5.11 (s, 2H), 5.01 (br, 1H), 4.72 (br, 1H), 2.59 (s, 3H), 2.45-2.37 (m, 2H), 2.11-2.05 (m, 2H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.73, 172.88, 155.27, 147.91, 136.20, 135.71, 128.82, 128.60, 128.35, 128.29, 126.44, 79.73, 66.53, 54.29, 31.42, 31.09, 28.36, 26.64; HRMS (ESI) m/z calcd for $C_{24}H_{29}NNaO_5$ $[(M+Na)^+]$ 434.1943, found 434.1924. IR (film) 3380, 1680, 1511, 1250, 1162, 731 cm^{-1};

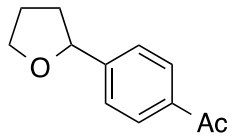


***tert*-Butyl (1-(4-acetylphenyl)-3-(methylthio)propyl)carbamate:** According to the general procedure B, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-bromoacetophenone (82.0 mg, 0.4 mmol, 1.0 equiv), Boc-Met-OH (300.0 mg, 1.2 mmol, 3.0 equiv), Cs_2CO_3 (391.2 mg, 1.2 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (20% ethyl acetate/hexane) as a pale yellow solid (107 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 5.00 (br, 1H), 4.82 (br, 1H), 2.59 (s, 3H), 2.49-2.43 (m, 2H), 2.10 (s, 3H), 2.06-2.01 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (125

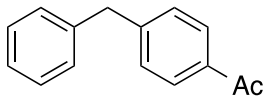
MHz, $CDCl_3$) δ 197.74, 155.18, 147.97, 136.12, 128.78, 126.49, 79.68, 53.96, 35.94, 30.63, 28.34, 26.63, 15.51; HRMS (ESI) m/z calcd for $C_{17}H_{25}NNaO_3S$ $[(M+Na)^+]$ 346.1453, found 346.1433. IR (film) 3342, 2976, 1678, 1363, 1266, 1163, 734 cm^{-1};



***tert*-Butyl (1-(4-acetylphenyl)-3-methylbutyl)(methyl)carbamate:** According to the general procedure B, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-bromoacetophenone (82.0 mg, 0.4 mmol, 1.0 equiv), Boc-*N*-Me-Leu-OH (296.0 mg, 1.2 mmol, 3.0 equiv), Cs_2CO_3 (391.2 mg, 1.20 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (9% ethyl acetate/hexane) as a pale yellow oil (117 mg, 91%). ^1H NMR (500 MHz, $CDCl_3$) rotameric mixture: δ 7.92 (d, J = 8.0 Hz, 2H), 7.38-7.37 (m, 2H), 5.54 and 5.33 (2 brs, 1H, rotamer), 2.60-2.57 (m, 6H), 1.86 (br, 1H), 1.68-1.64 (m, 2H), 1.49 (s, 9H), 1.00 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis (): δ 197.73, 155.90 (156.17), 146.62, 136.00, 128.46, (127.56) 127.44, 80.00 (79.61), 55.54 (54.46), 39.29 (39.01), 28.47, 26.64, 24.79, 23.49, 21.80; HRMS (ESI) m/z calcd for $C_{19}H_{29}NNaO_3$ $[(M+Na)^+]$ 342.2045, found 342.2048. IR (film) 2958, 1681, 1364, 1266, 1143, 829, 770 cm^{-1};

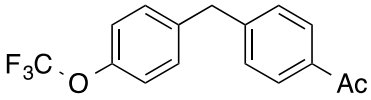


1-(4-(Tetrahydrofuran-2-yl)phenyl)ethan-1-one [known compound (*31*)]**:** According to the general procedure B, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-bromoacetophenone (82.0 mg, 0.4 mmol, 1.0 equiv), tetrahydro-2-furoic acid (139.0 mg, 1.2 mmol, 3.0 equiv), Cs_2CO_3 (391.2 mg, 1.2 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (15% ethyl acetate/hexane) as a pale yellow solid (63.0 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 4.95 (t, *J* = 7.5 Hz, 1H), 4.11 (q, *J* = 7.5 Hz, 1H), 3.97 (q, *J* = 7.0 Hz, 1H), 2.59 (s, 3H), 2.40-2.34 (m, 1H), 2.04-1.99 (m, 2H), 1.81-1.74 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.87, 149.21, 136.04, 128.48, 125.60, 80.14, 68.90, 34.73, 26.66, 25.98; HRMS (ESI) m/z calcd for $C_{12}H_{15}O_2$ $[(M+H)^+]$ 191.1072, found 191.1064. IR (film) 2965, 2896, 1680,1265, 1061, 831 cm^{-1};

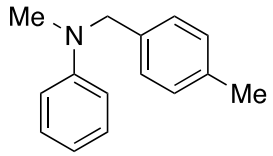


1-(4-Benzylphenyl)ethan-1-one [known compound (*32*)]**:** According to the general procedure B, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.2 mg, 1.0 μmol, 0.01 equiv), $NiCl_2$•glyme (2.2 mg, 0.01 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (4.0 mg, 0.015 mmol, 0.15 equiv), 4-bromoacetophenone (20.5 mg, 0.1 mmol, 1.0 equiv), phenylacetic acid (40.5 mg, 0.3 mmol, 3.0 equiv), Cs_2CO_3 (97.8 mg, 0.3 mmol, 3.0 equiv), and 5 mL of

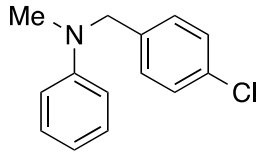
DMF were used. The product was isolated by flash chromatography (8% ethyl acetate/hexane) as a pale yellow solid (18 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93-7.90 (m, 2H), 7.35-7.25 (m, 5H), 7.22-7.19 (m, 2H), 4.06 (s, 2H), 2.60 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.83, 146.83, 140.05, 135.25, 129.13, 128.96, 128.66, 126.44, 41.93, 26.62; HRMS (ESI) m/z calcd for $C_{15}H_{15}O$ $[(M+H)^+]$ 211.1123, found 211.1114. IR (film) 3028, 1681, 1606, 1357, 1267, 728, 699 cm^{-1};



1-(4-(4-(Trifluoromethoxy)benzyl)phenyl)ethan-1-one: According to the general procedure B, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.2 mg, 1.0 μmol, 0.01 equiv), $NiCl_2$•glyme (2.2 mg, 0.01 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (4.0 mg, 0.015 mmol, 0.15 equiv), 4-bromoacetophenone (20.5 mg, 0.1 mmol, 1.0 equiv), 4-(trifluoromethoxy)phenylacetic acid (66.0 mg, 0.3 mmol, 3.0 equiv), Cs_2CO_3 (97.8 mg, 0.3 mmol, 3.0 equiv), and 5 mL of DMF were used. The product was isolated by flash chromatography (8% ethyl acetate/hexane) as a pale yellow solid (24 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91-7.89 (m, 2H), 7.28-7.26 (m, 2H), 7.20-7.18 (m, 2H), 7.15-7.13 (m, 2H), 4.04 (s, 2H), 2.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.72, 147.82, 146.01, 138.79, 135.48, 130.18, 129.10, 128.77, 121.20, 120.47 (q, J = 255 Hz), 41.14, 26.61; HRMS (ESI) m/z calcd for $C_{16}H_{14}F_3O_2$ $[(M+H)^+]$ 295.0946, found 295.0954. IR (film) 2924, 1682, 1508, 1258, 1162, 1018, 811 cm^{-1};

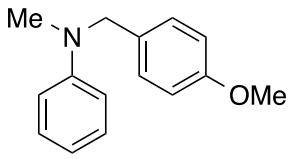


***N*-Methyl-*N*-(4-methylbenzyl)aniline** [(known compound (*33*)]**:** According to the general procedure C, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-iodotoluene (87.2 mg, 0.4 mmol, 1.0 equiv), *N*,*N*-dimethylaniline (152.1 μL, 1.2 mmol, 3.0 equiv), KOH (67.3 mg, 1.2 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (6% ethyl acetate/hexane) as a clear oil (71 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (td, *J* = 7.1, 2.1 Hz, 2H), 7.04 (s, 4H), 6.67 (d, *J* = 7.9 Hz, 2H), 6.62 (tt, *J* = 7.3, 1.1 Hz, 1H), 4.41 (s, 2H), 2.91 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.90, 136.54, 136.01, 129.35, 129.28, 126.83, 116.54, 112.45, 56.45, 38.53, 21.21.

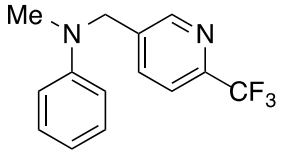


***N*-(4-Chlorobenzyl)-*N*-methylaniline** [known compound (*34*)]**:** According to the general procedure C, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 1-chloro-4-iodobenzene (95.4 mg, 0.4 mmol, 1.0 equiv), *N*,*N*-dimethylaniline (152.1 μL, 1.2 mmol, 3.0 equiv), KOH (67.3 mg, 1.2 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (8% ethyl acetate/hexane) as a clear oil (67 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d,

J = 8.4 Hz, 2H), 7.27 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.80-6.75 (m, 3H), 4.53 (s, 2H), 3.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.62, 137.65, 132.64, 129.35, 128.82, 128.22, 116.95, 112.54, 56.27, 38.69.

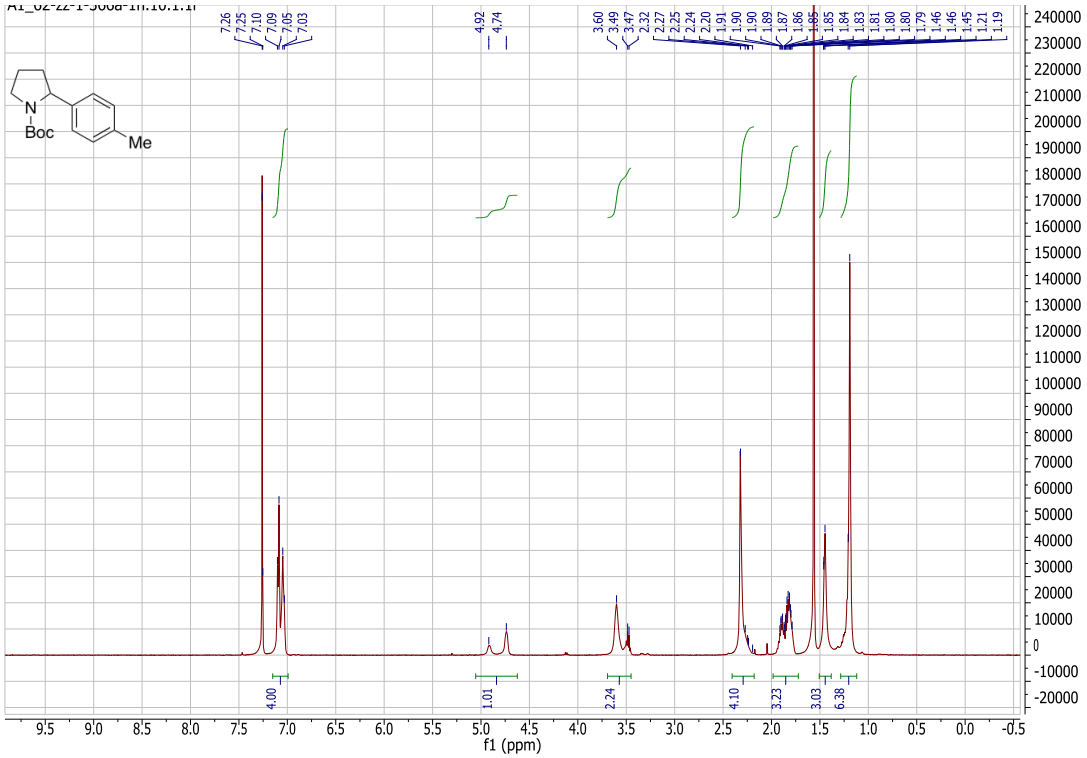


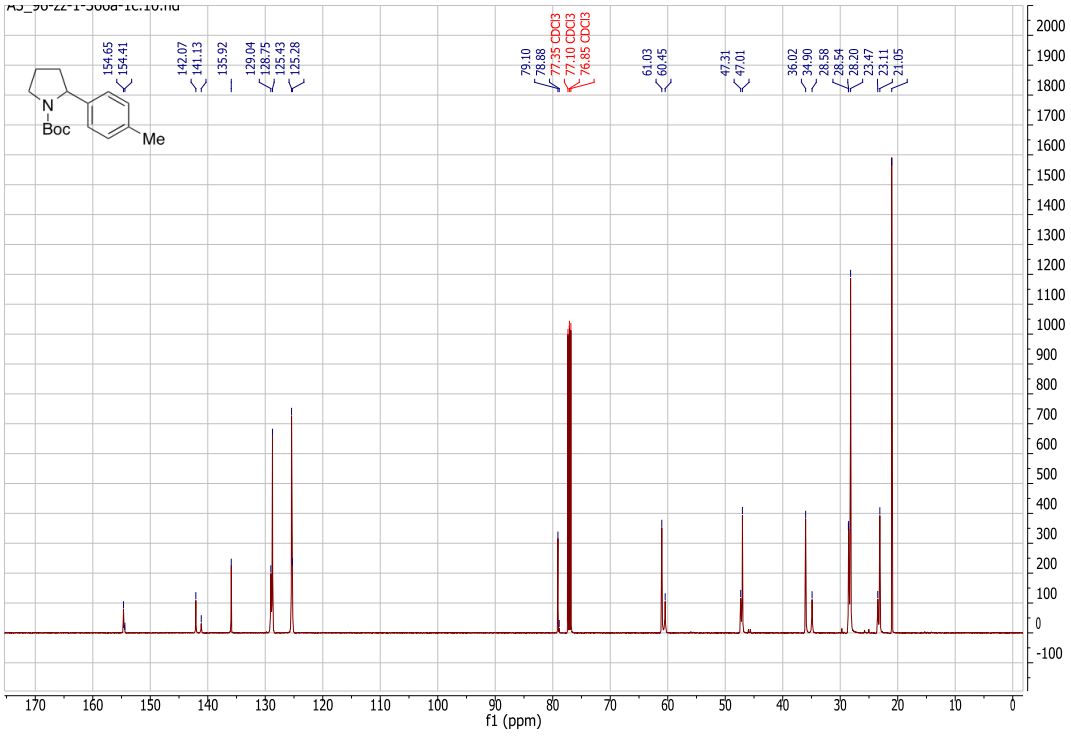
***N*-(4-Methoxybenzyl)-*N*-methylaniline** [known compound (*34*)]**:** According to the general procedure C, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv), $NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 4-iodoanisole (93.6 mg, 0.4 mmol, 1.0 equiv), *N*,*N*-dimethylaniline (152.1 μL, 1.2 mmol, 3.0 equiv), KOH (67.3 mg, 1.2 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (0-8% ethyl acetate/hexane) as a clear oil (85 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.81 (d, *J* = 8.2 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 4.51 (s, 2H), 3.83 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.68, 149.92, 131.00, 129.28, 128.06, 116.61, 114.05, 112.58, 56.14, 55.39, 38.43.



***N*-Methyl-*N*-((6-(trifluoromethyl)pyridin-3-yl)methyl)aniline:** According to the general procedure C, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.01 equiv),

$NiCl_2$•glyme (8.8 mg, 0.04 mmol, 0.1 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (16.1 mg, 0.06 mmol, 0.15 equiv), 5-bromo-2-(trifluoromethyl)pyridine (90.4 mg, 0.4 mmol, 1.0 equiv), *N*,*N*-dimethylaniline (152.1 μL, 1.2 mmol, 3.0 equiv), KOH (67.3 mg, 1.2 mmol, 3.0 equiv), and 20 mL of DMF were used. The product was isolated by flash chromatography (8% ethyl acetate/hexane) as a yellow oil (64 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 2H), 4.64 (s, 2H), 3.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.16, 149.07, 147.15 (q, *J* = 34.6 Hz), 138.19, 135.86, 129.53, 121.72 (q, *J* = 272.5 Hz), 120.49, 117.79, 112.86, 54.45, 38.97; HRMS (ESI) m/z calcd for $C_{14}H_{14}F_3N_2$ $[(M+H)^+]$ 267.1109, found 267.1104.


N
Boc
Me
f1 (ppm)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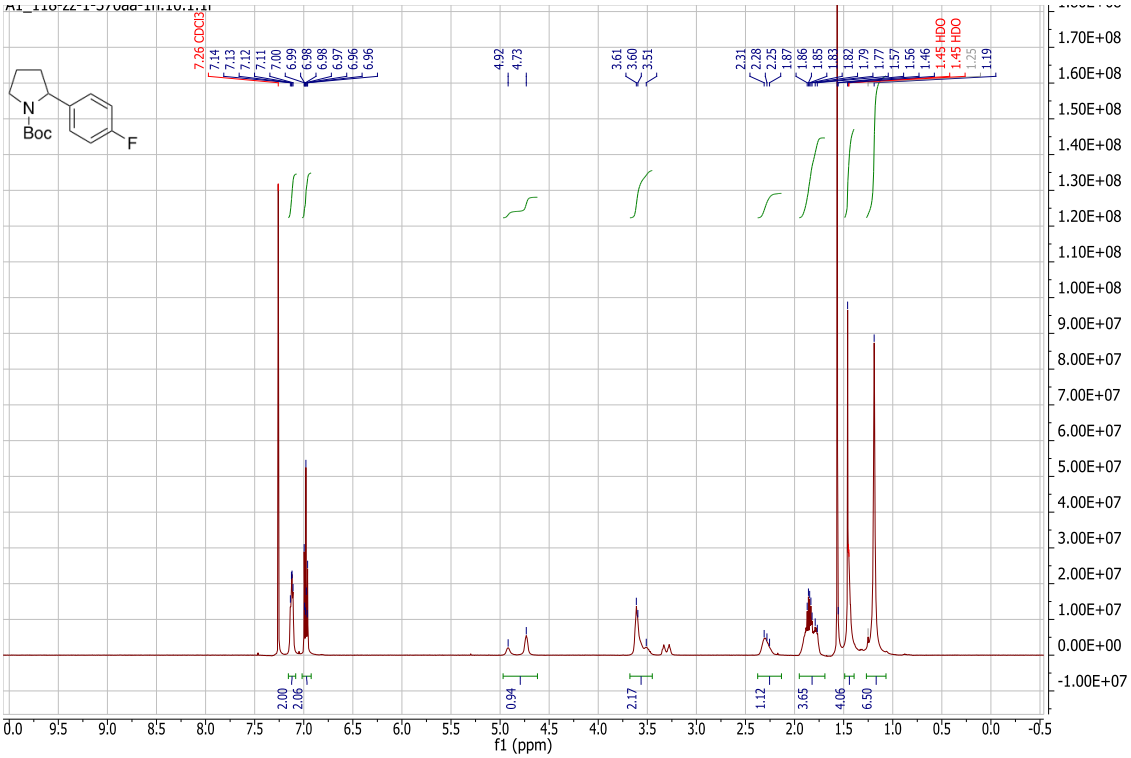
Boc
Me
f1 (ppm)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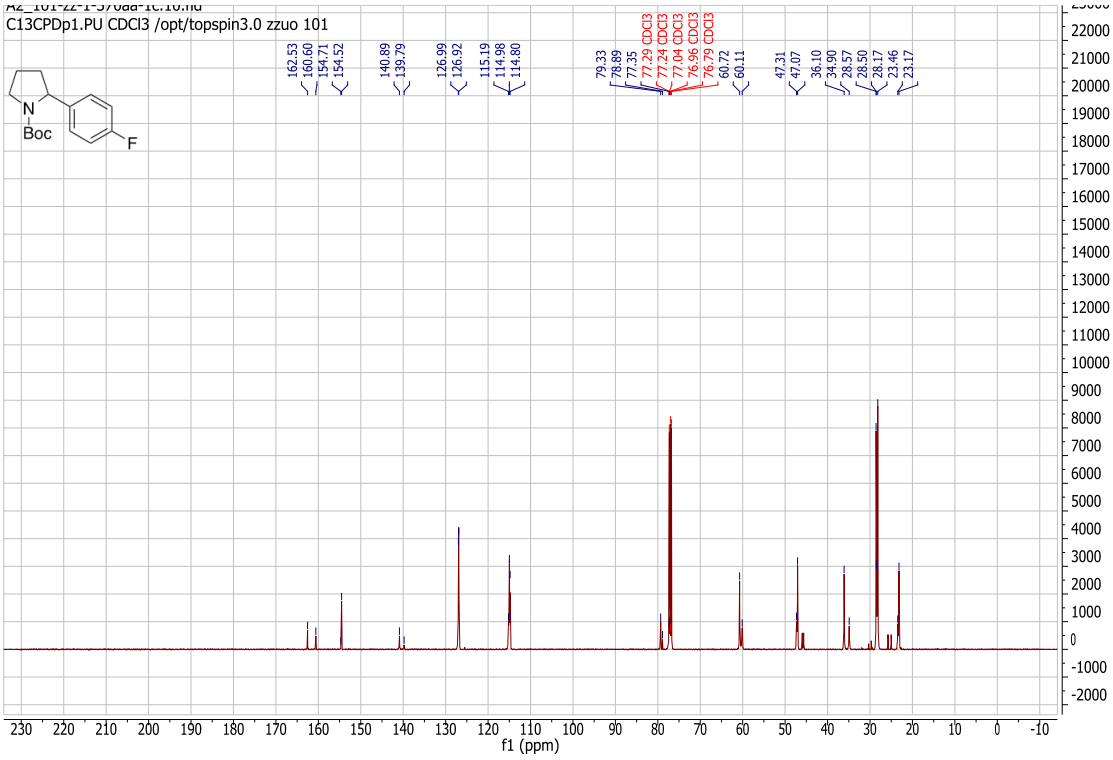
7.12
7.11
7.00
6.99
6.98
6.98
6.97
6.96
6.96
4.92
4.73
3.61
3.60
3.51
2.31
2.28
2.25
1.87
1.86
1.85
1.83
1.82
1.79
1.77
1.57
1.56
1.46
1.45 HDO
1.45 HDO
1.25
1.19
N
Boc
F
2.00
2.06
0.94
2.17
1.12
3.65
4.06
6.50
f1 (ppm)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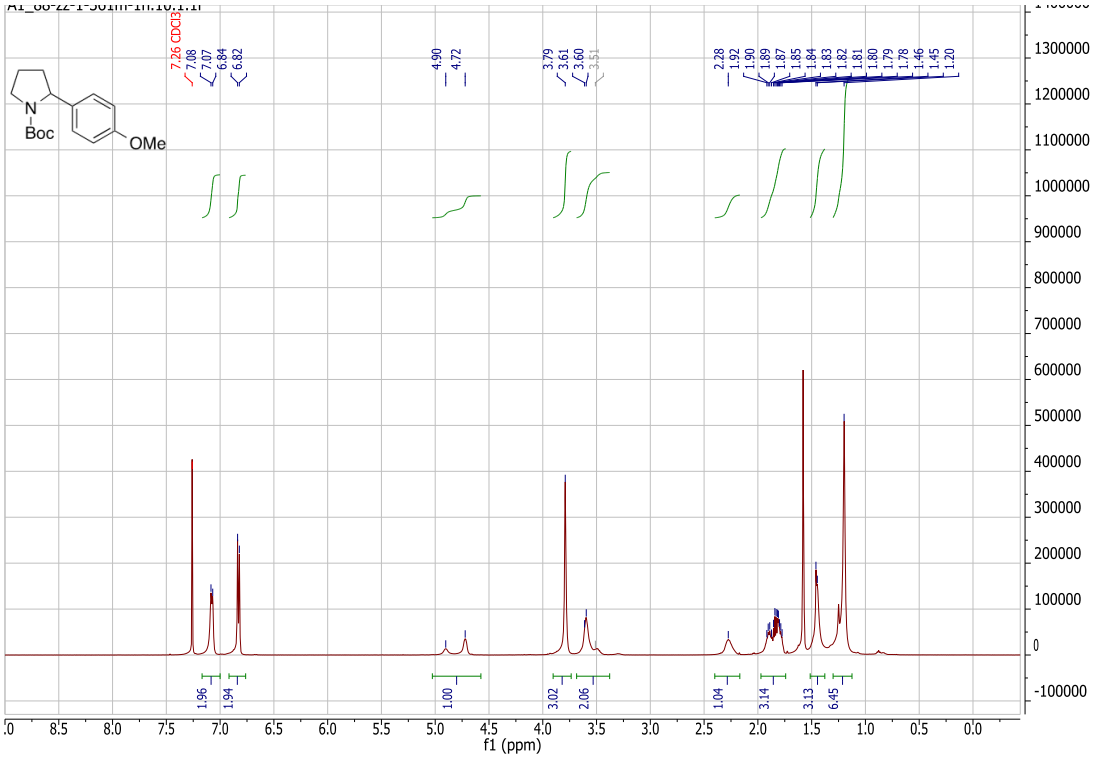
160.60
154.71
154.52
140.89
139.79
126.99
126.92
115.19
114.98
114.80
79.33
78.89
77.35
77.29 CDCl3
77.24 CDCl3
77.04 CDCl3
76.96 CDCl3
76.79 CDCl3
60.72
60.11
47.31
47.07
36.10
34.90
28.57
28.50
28.17
23.46
23.17
N
Boc
F
f1 (ppm)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7.07
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6.82
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4.72
3.79
3.61
3.60
3.51
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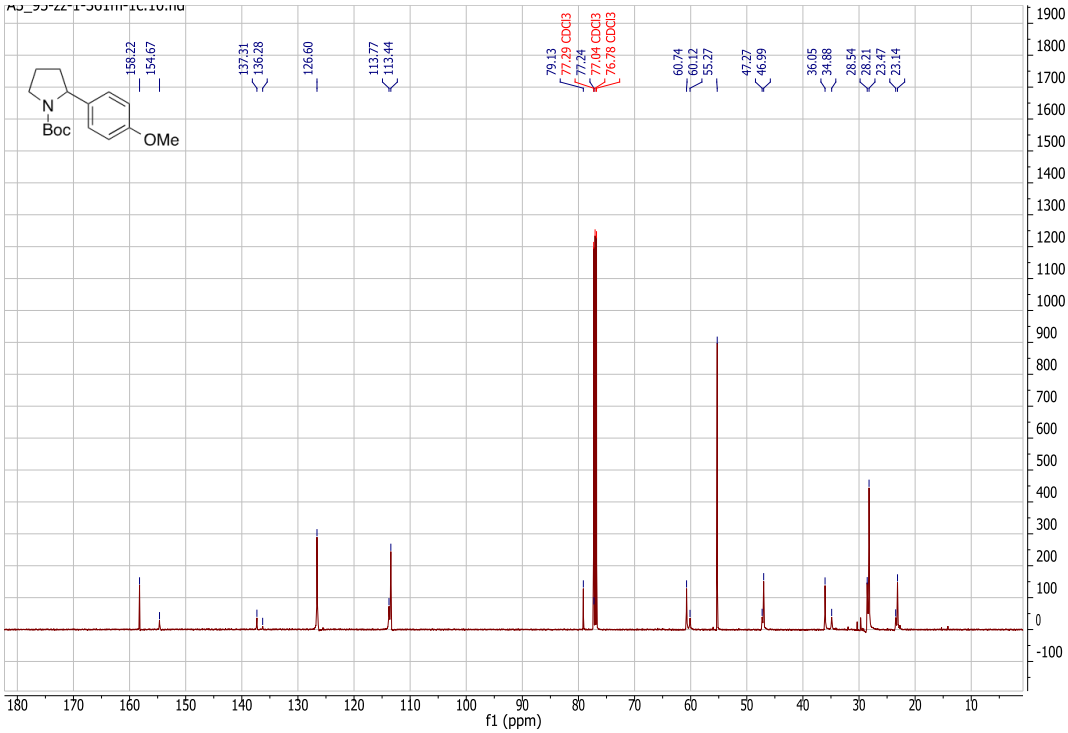
1.92
1.90
1.89
1.87
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.78
1.46
1.45
1.20
N
Boc
OMe
1.96
1.94
1.00
3.02
2.06
1.04
3.14
3.13
6.45
f1 (ppm)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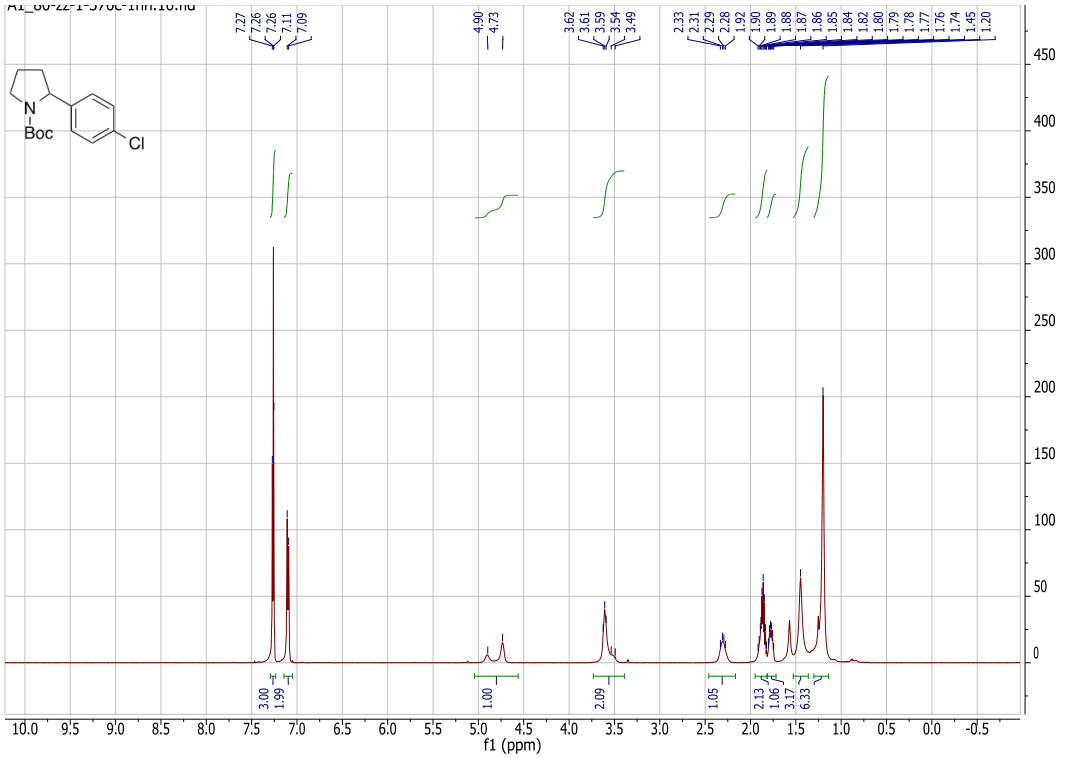
154.67
137.31
136.28
126.60
113.77
113.44
79.13
77.29 CDCl3
77.24
77.04 CDCl3
76.78 CDCl3
60.74
60.12
55.27
47.27
46.99
36.05
34.88
28.54
28.21
23.47
23.14
N
Boc
OMe
f1 (ppm)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7.26
7.26
7.11
7.09
4.90
4.73
3.62
3.61
3.59
3.54
3.49
2.33
2.31
2.29
2.28
1.92
1.90
1.89
1.88
1.87
1.86
1.85
1.84
1.82
1.80
1.79
1.78
1.77
1.76
1.74
1.45
1.20
N
Boc
Cl
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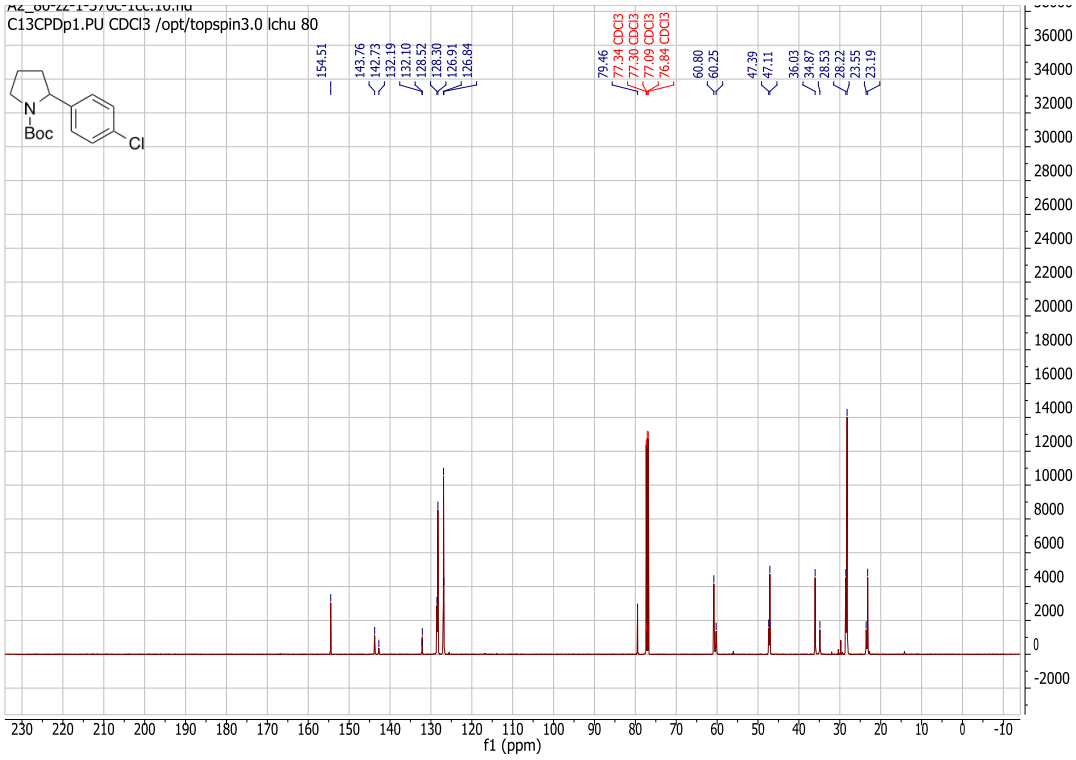
1.99
1.00
2.09
1.05
2.13
1.06
3.17
6.33
f1 (ppm)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143.76
142.73
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132.10
128.52
128.30
126.91
126.84
79.46
77.34 CDCl3
77.30 CDCl3
77.09 CDCl3
76.84 CDCl3
60.80
60.25
47.39
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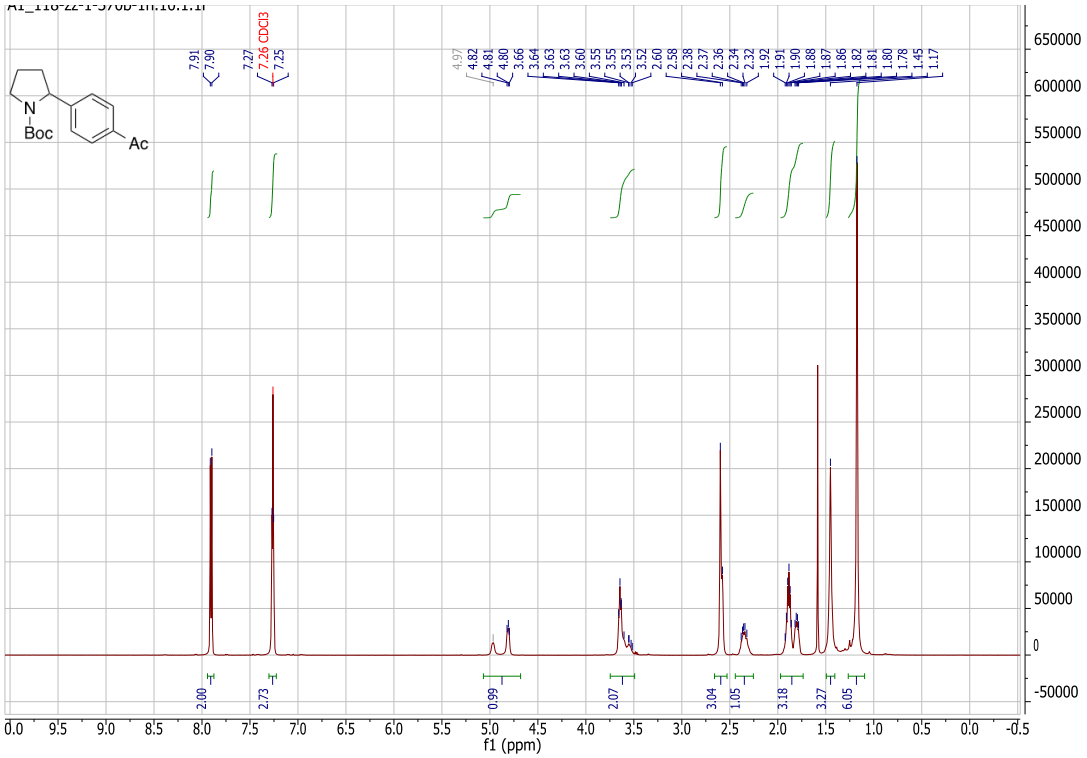
36.03
34.87
28.53
28.22
23.55
23.19
N
Boc
Cl
f1 (ppm)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7.90
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7.26 CDCl3
7.25
4.97
4.82
4.81
4.80
3.66
3.64
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3.63
3.60
3.55
3.55
3.53
3.52
2.60
2.58
2.38
2.37
2.36
2.34
2.32
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1.87
1.86
1.82
1.81
1.80
1.78
1.45
1.17
N
Boc
Ac
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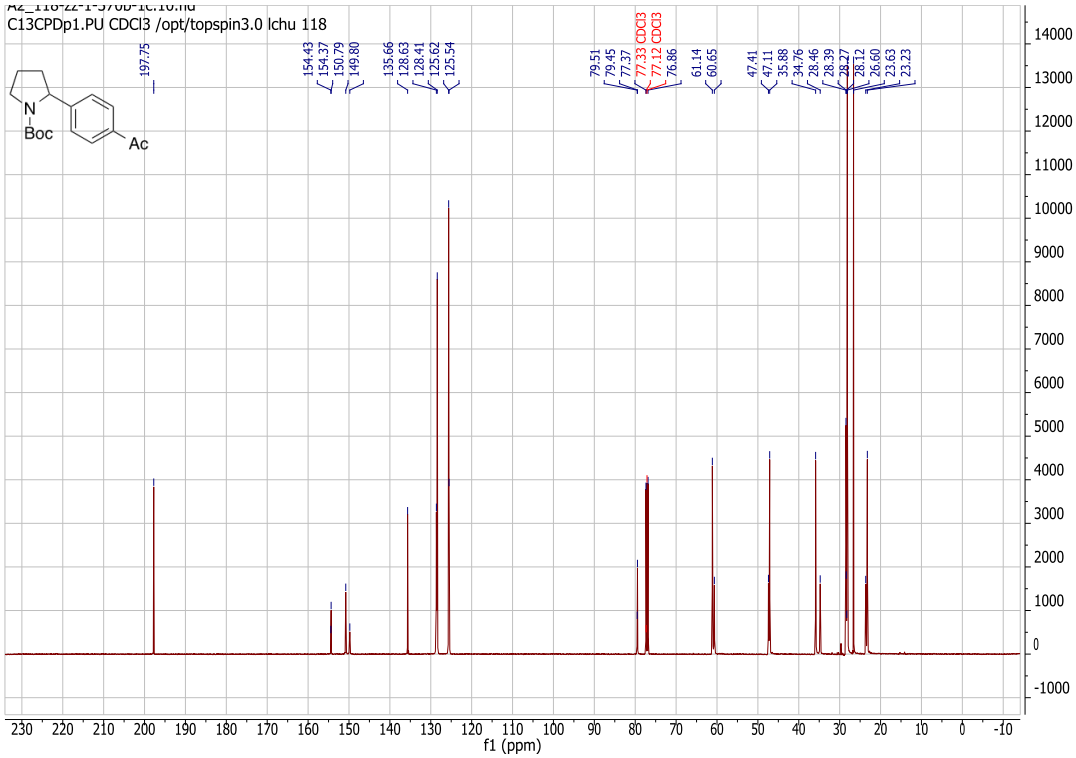
2.07
3.04
1.05
3.18
3.27
6.05
f1 (ppm)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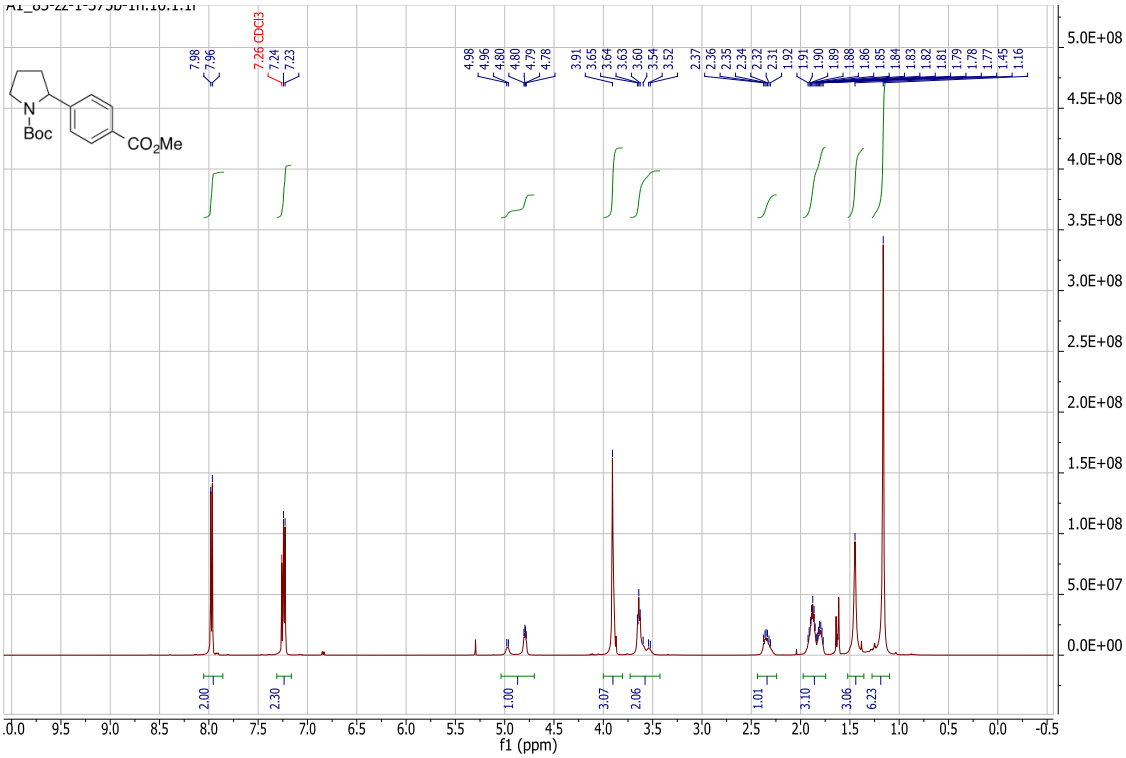
154.43
154.37
150.79
149.80
135.66
128.63
128.41
125.62
125.54
79.51
79.45
77.37
77.33 CDCl3
77.12 CDCl3
76.86
61.14
60.65
47.41
47.11
35.88
34.76
28.46
28.39
28.27
28.12
26.60
23.63
23.23
N
Boc
Ac
f1 (ppm)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7.96
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7.24
7.23
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4.79
4.78
3.91
3.65
3.64
3.63
3.60
3.54
3.52
2.37
2.36
2.35
2.34
2.32
2.31
1.92
1.91
1.90
1.89
1.88
1.86
1.85
1.84
1.83
1.82
1.81
1.79
1.78
1.77
1.45
1.16
Boc
CO2Me
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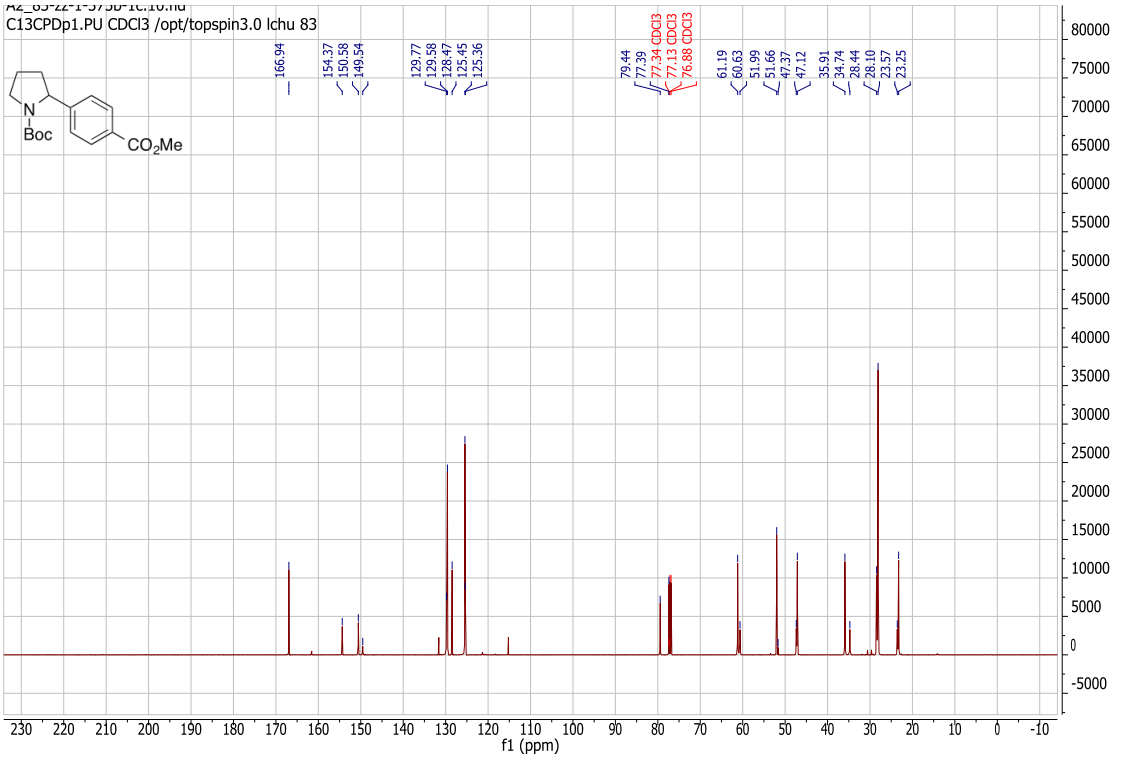
2.30
1.00
3.07
2.06
1.01
3.10
3.06
6.23
f1 (ppm)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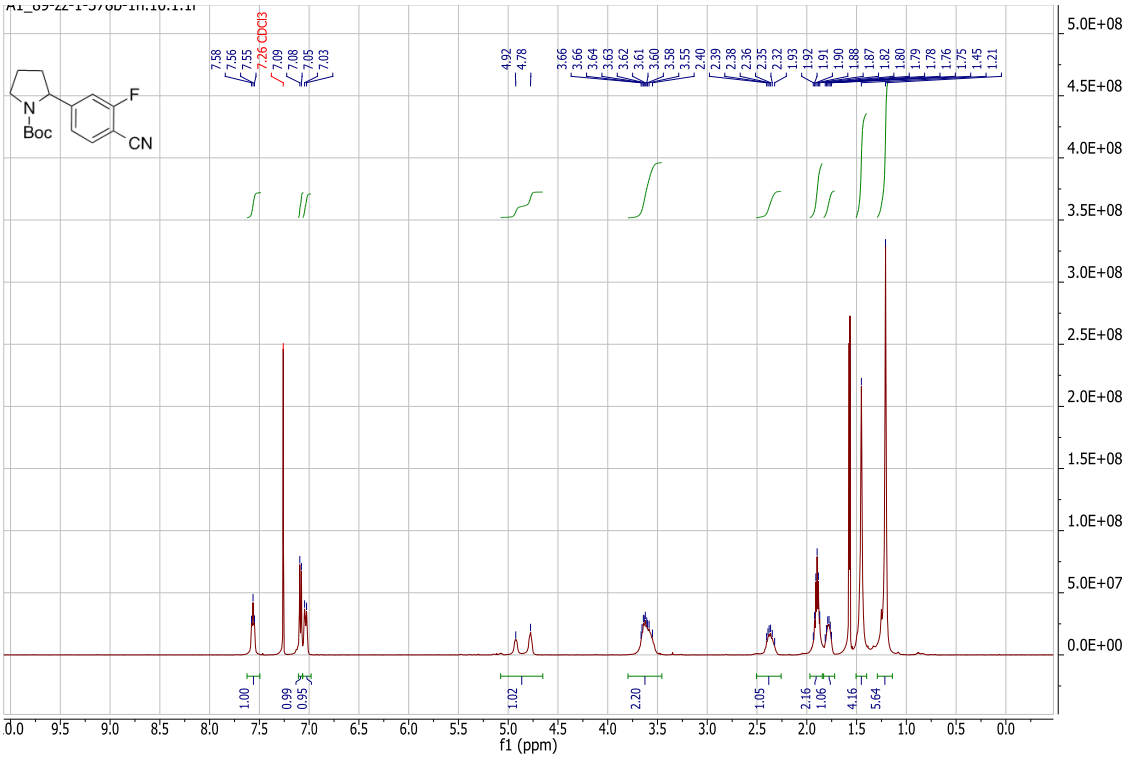
154.37
150.58
149.54
129.77
129.58
128.47
125.45
125.36
79.44
77.39
77.34 CDCl3
77.13 CDCl3
76.88 CDCl3
61.19
60.63
51.99
51.66
47.37
47.12
35.91
34.74
28.44
28.10
23.57
23.25
Boc
CO2Me
f1 (ppm)


7.58
7.56
7.55
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7.09
7.08
7.05
7.03
4.92
4.78
3.66
3.64
3.63
3.62
3.61
3.60
3.58
3.55
2.40
2.39
2.38
2.36
2.35
2.32
1.93
1.92
1.91
1.90
1.88
1.87
1.82
1.80
1.79
1.78
1.76
1.75
1.45
1.21
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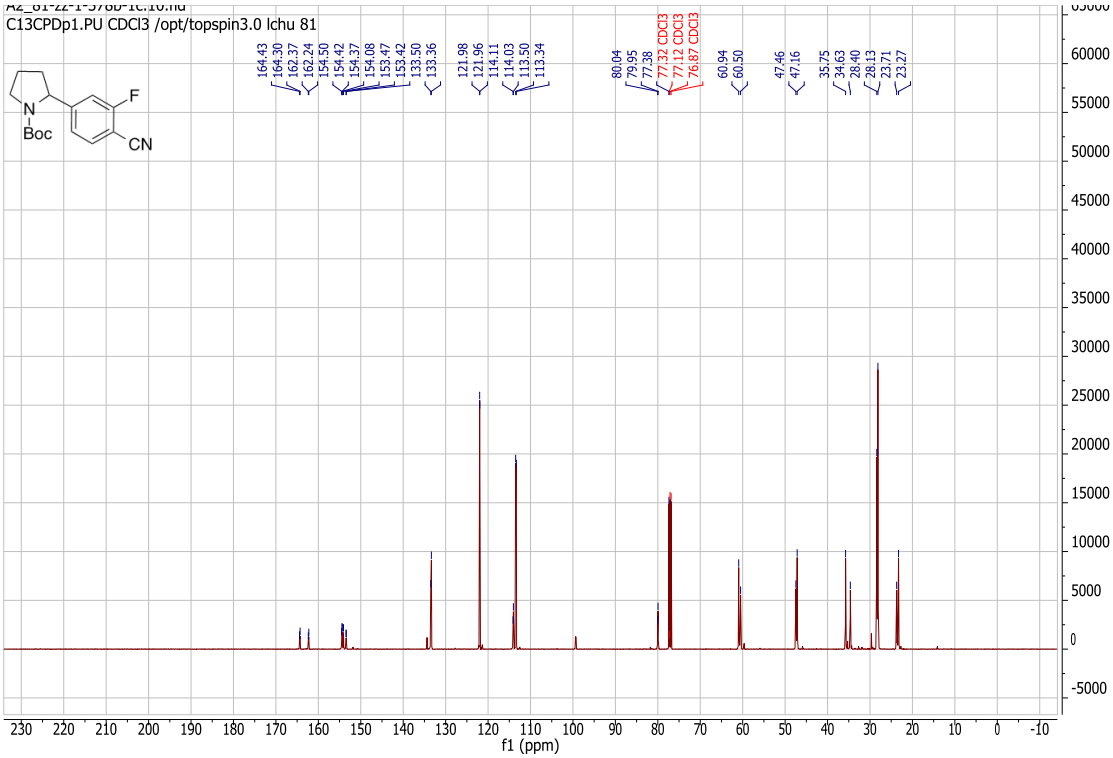
0.95
1.02
2.20
1.05
2.16
1.06
4.16
5.64
f1 (ppm)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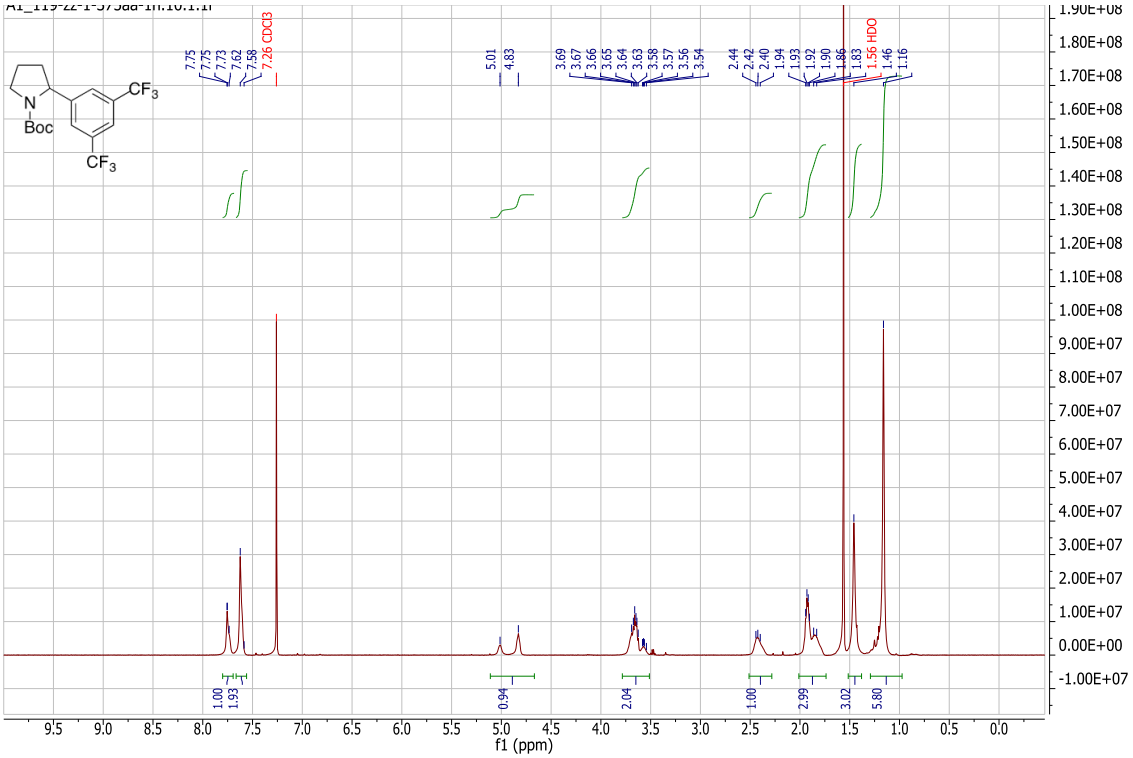
164.30
162.37
162.24
154.50
154.42
154.37
154.08
153.47
153.42
133.50
133.36
121.98
121.96
114.11
114.03
113.50
113.34
80.04
79.95
77.38
77.32 CDCl3
77.12 CDCl3
76.87 CDCl3
60.94
60.50
47.46
47.16
35.75
34.63
28.40
28.13
23.71
23.27
f1 (ppm)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3.67
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3.64
3.63
3.58
3.57
3.56
3.54
2.44
2.42
2.40
1.94
1.93
1.92
1.90
1.86
1.83
1.56 HDO
1.46
1.16
CF3
N
Boc
CF3
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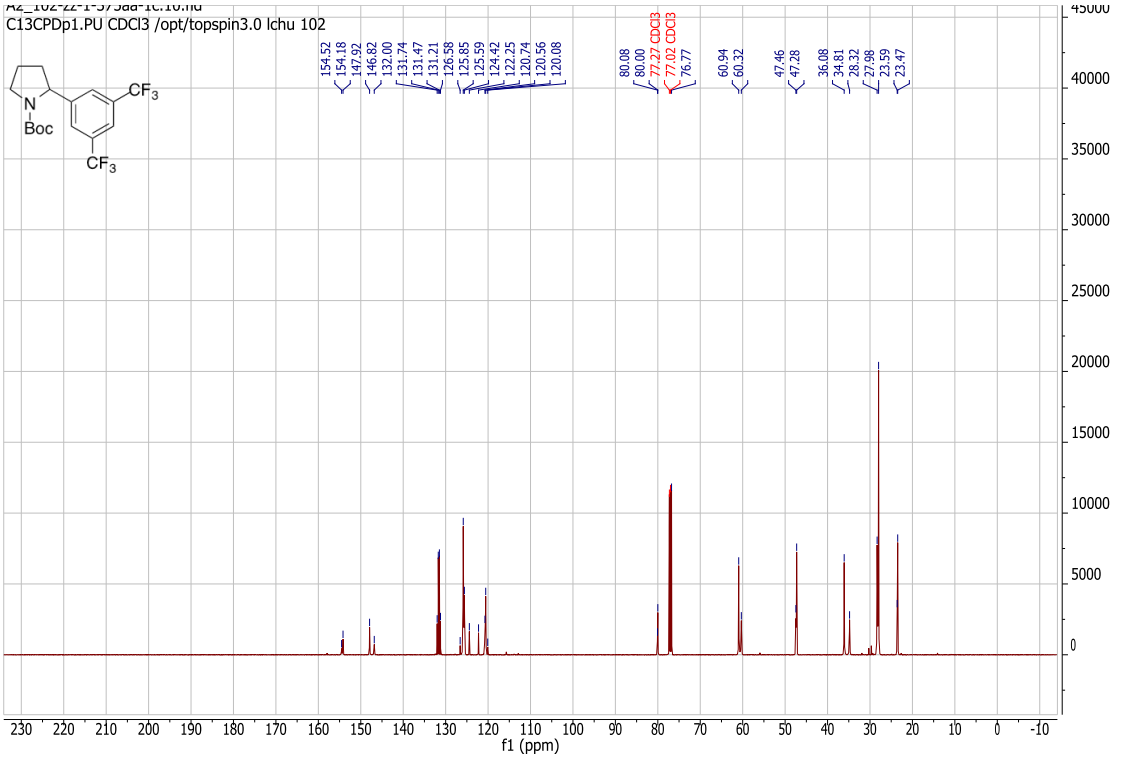
1.93
0.94
2.04
1.00
2.99
3.02
5.80
f1 (ppm)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131.21
126.58
125.85
125.59
124.42
122.25
120.74
120.56
120.08
80.08
80.00
77.27 CDCl3
77.02 CDCl3
76.77
60.94
60.32
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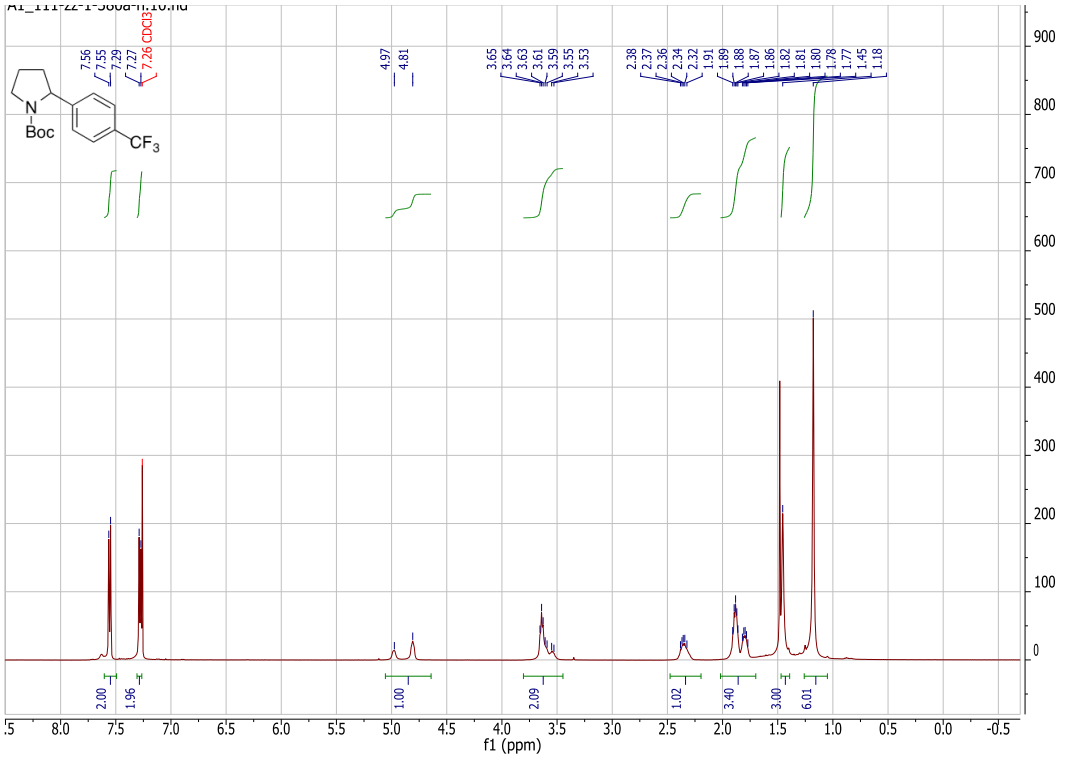
28.32
27.98
23.59
23.47
CF3
N
Boc
CF3
f1 (ppm)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3.63
3.61
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2.32
1.91
1.89
1.88
1.87
1.86
1.82
1.81
1.80
1.78
1.77
1.45
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Boc
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1.00
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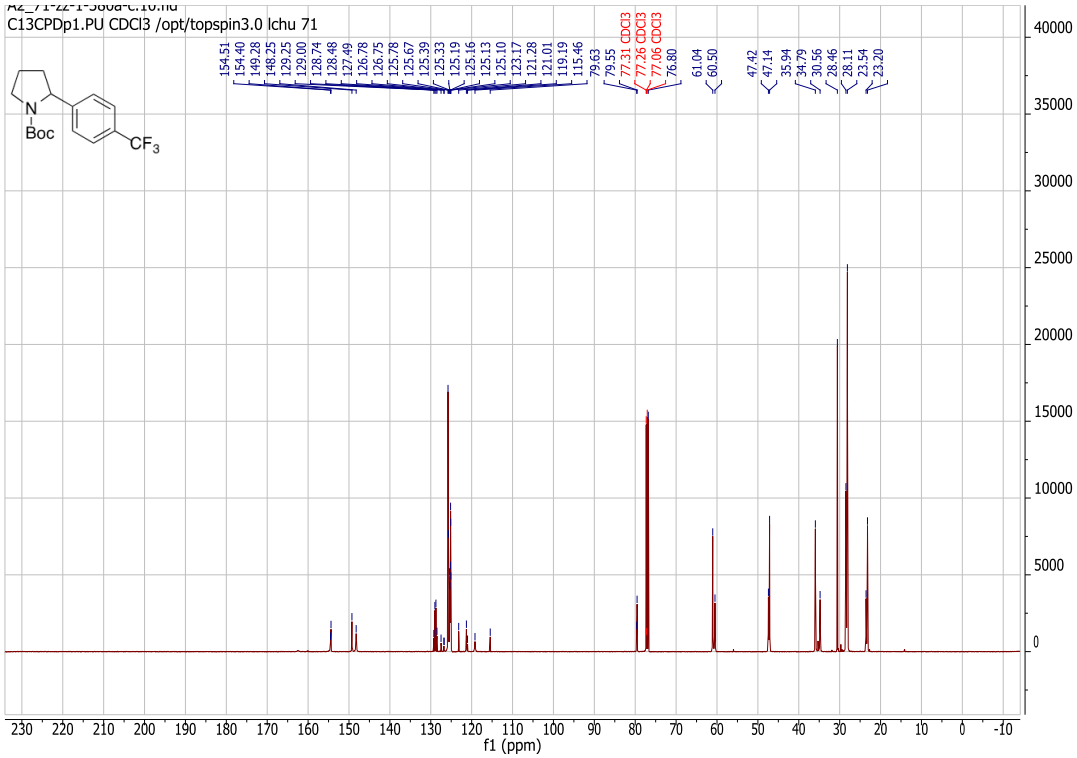
3.40
3.00
6.01
f1 (ppm)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149.28
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129.25
129.00
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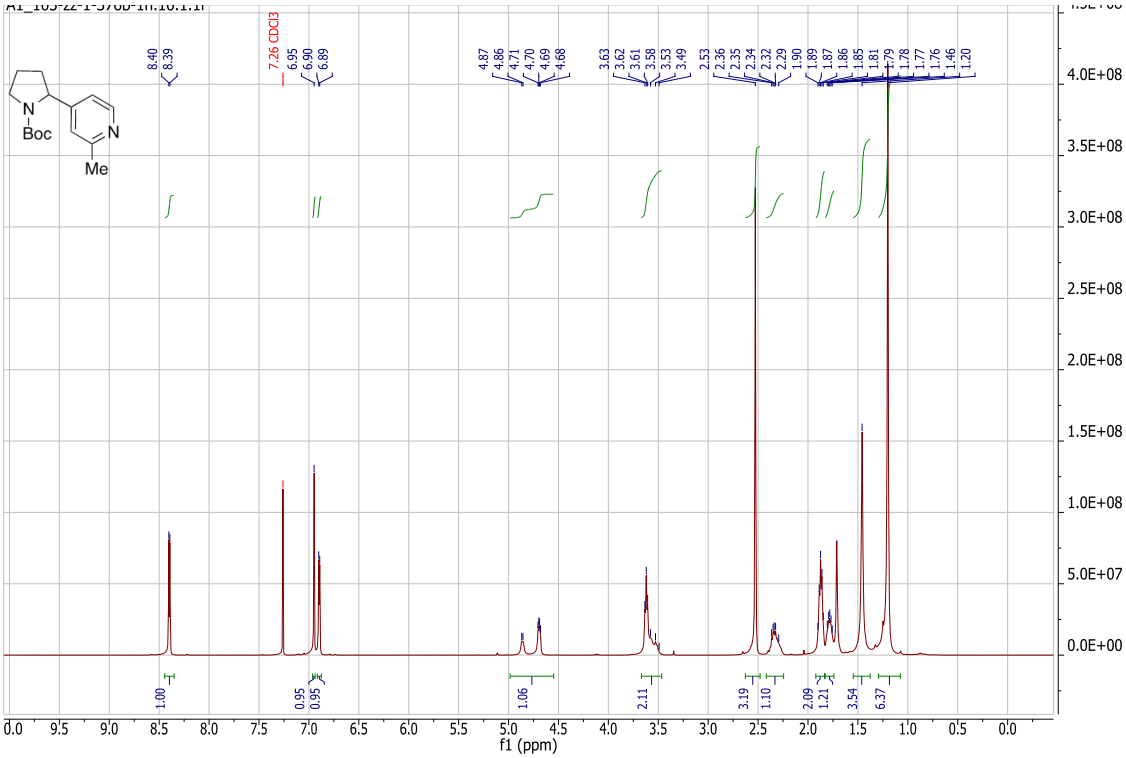
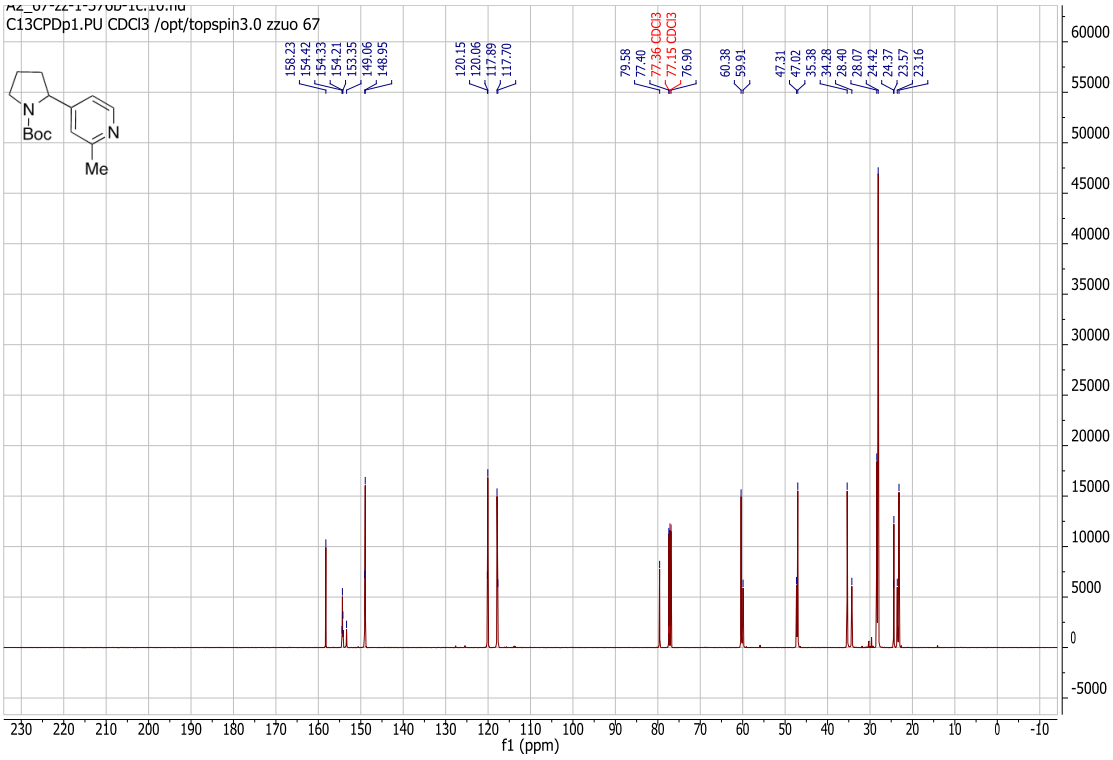
127.49
126.78
126.75
125.78
125.67
125.39
125.33
125.19
125.16
125.13
125.10
123.17
121.28
121.01
119.19
115.46
79.63
77.31 CDCl3
77.26 CDCl3
77.06 CDCl3
76.80
61.04
60.50
47.42
47.14
35.94
34.79
30.56
28.46
28.11
23.54
23.20
Boc
CF3
f1 (ppm)


7.26 CDCl3
f1 (ppm)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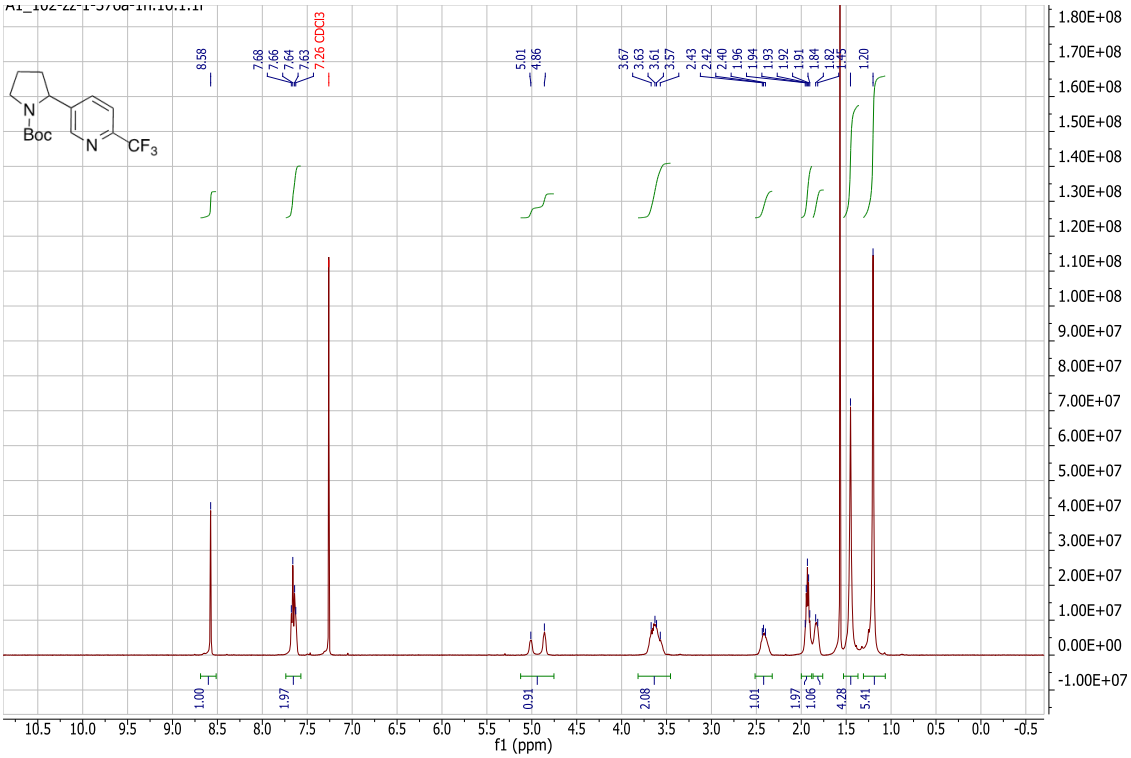
77.36 CDCl3
77.15 CDCl3
f1 (ppm)


8.58
7.68
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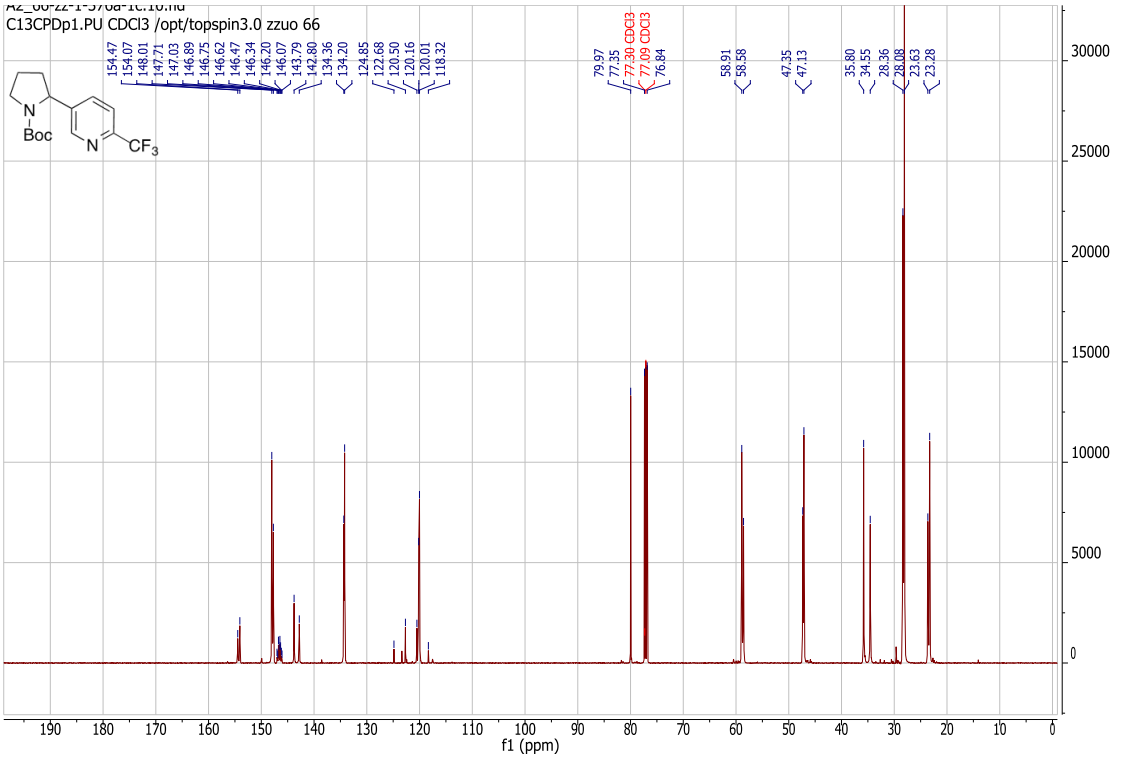
7.64
7.63
7.26 CDCl3
5.01
4.86
3.67
3.63
3.61
3.57
2.43
2.42
2.40
1.96
1.94
1.93
1.92
1.91
1.84
1.82
1.45
1.20
Boc
N
CF3
1.00
1.97
0.91
2.08
1.01
1.97
1.06
4.28
5.41
f1 (ppm)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146.47
146.34
146.20
146.07
143.79
142.80
134.36
134.20
124.85
122.68
120.50
120.16
120.01
118.32
79.97
77.35
77.30 CDCl3
77.09 CDCl3
76.84
58.91
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23.28
Boc
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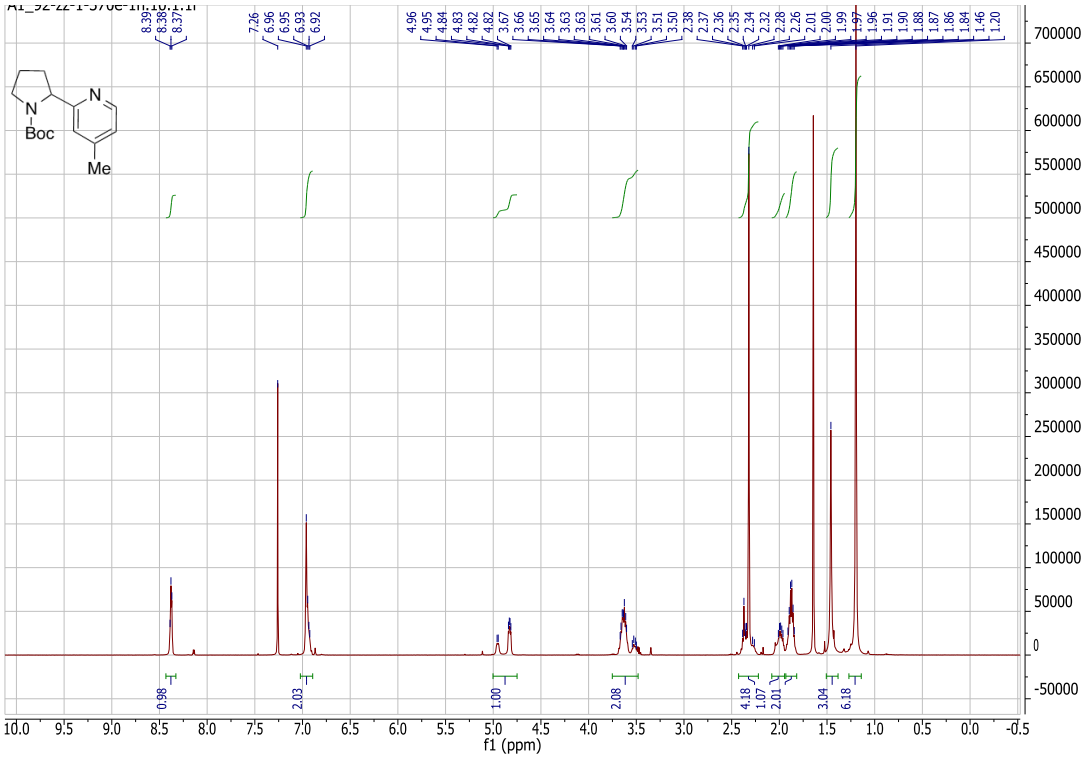
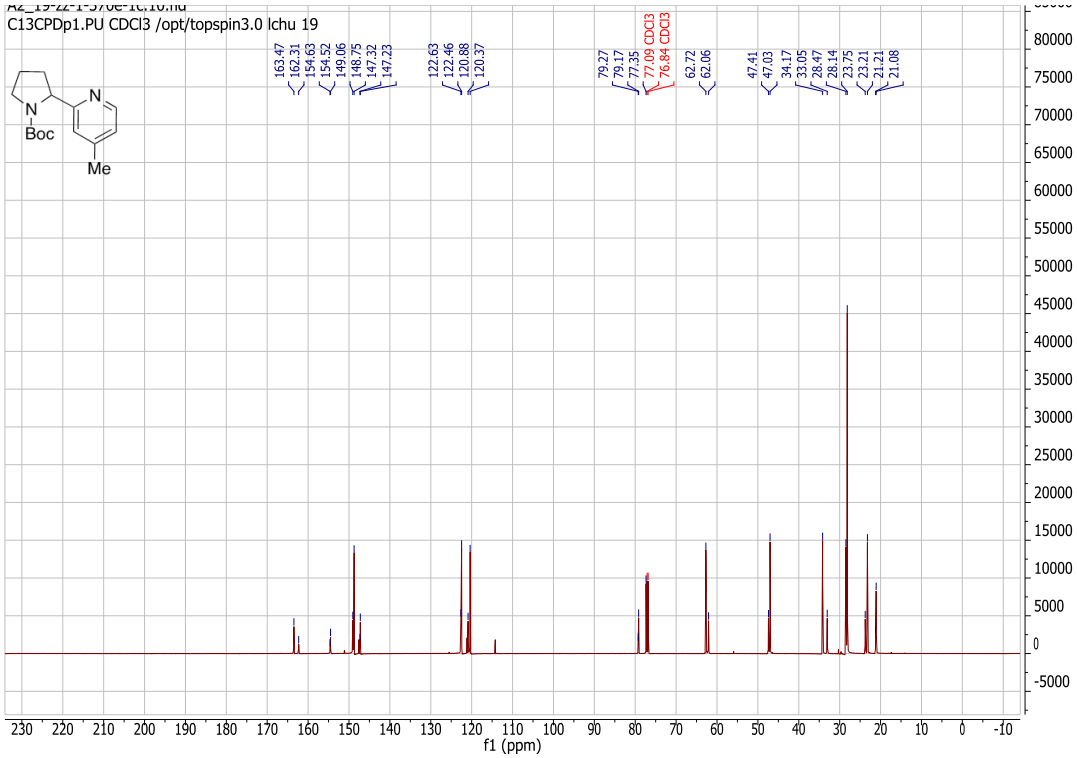
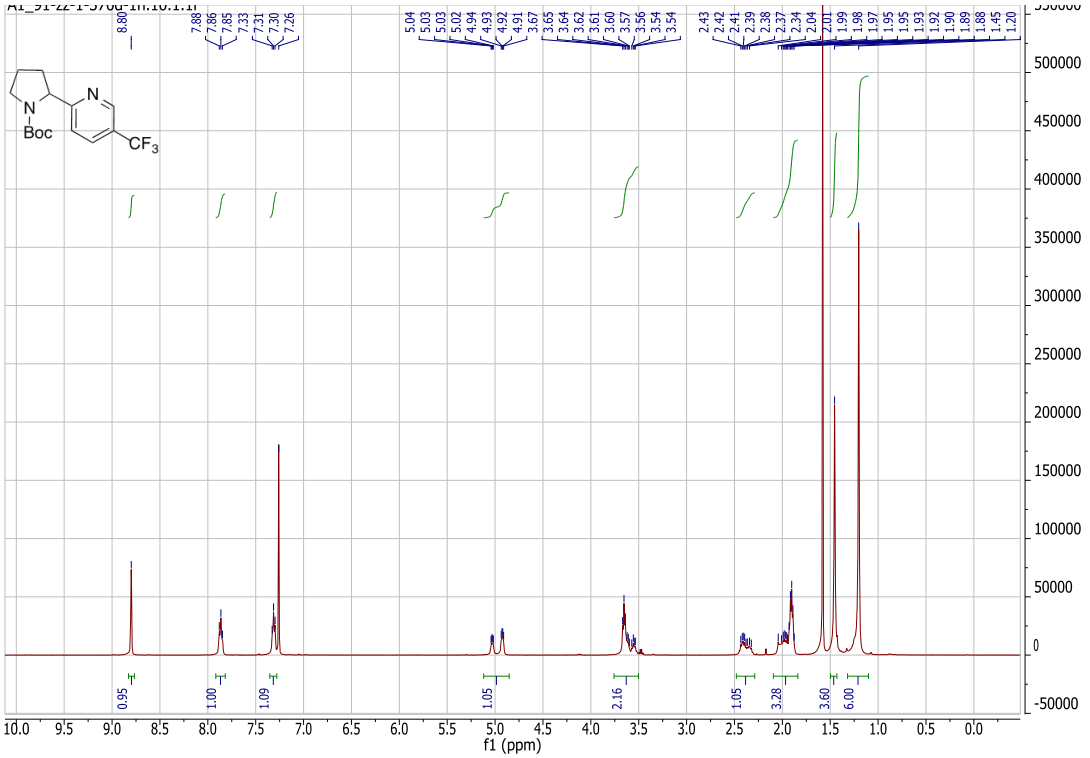
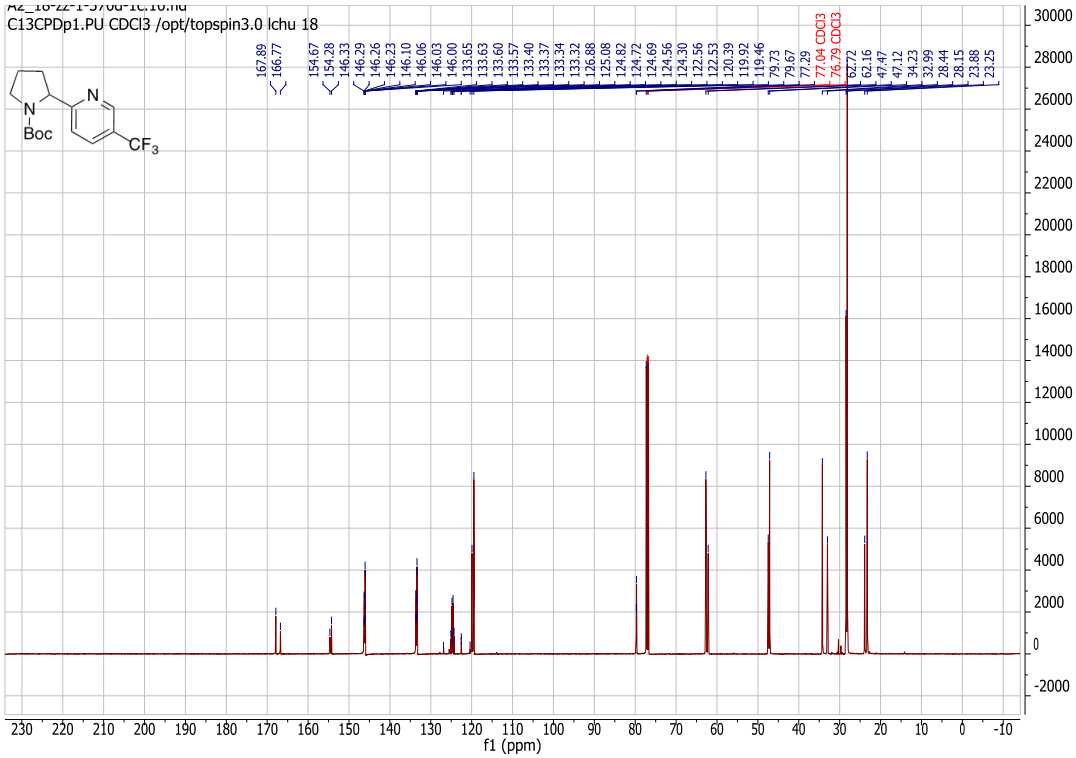
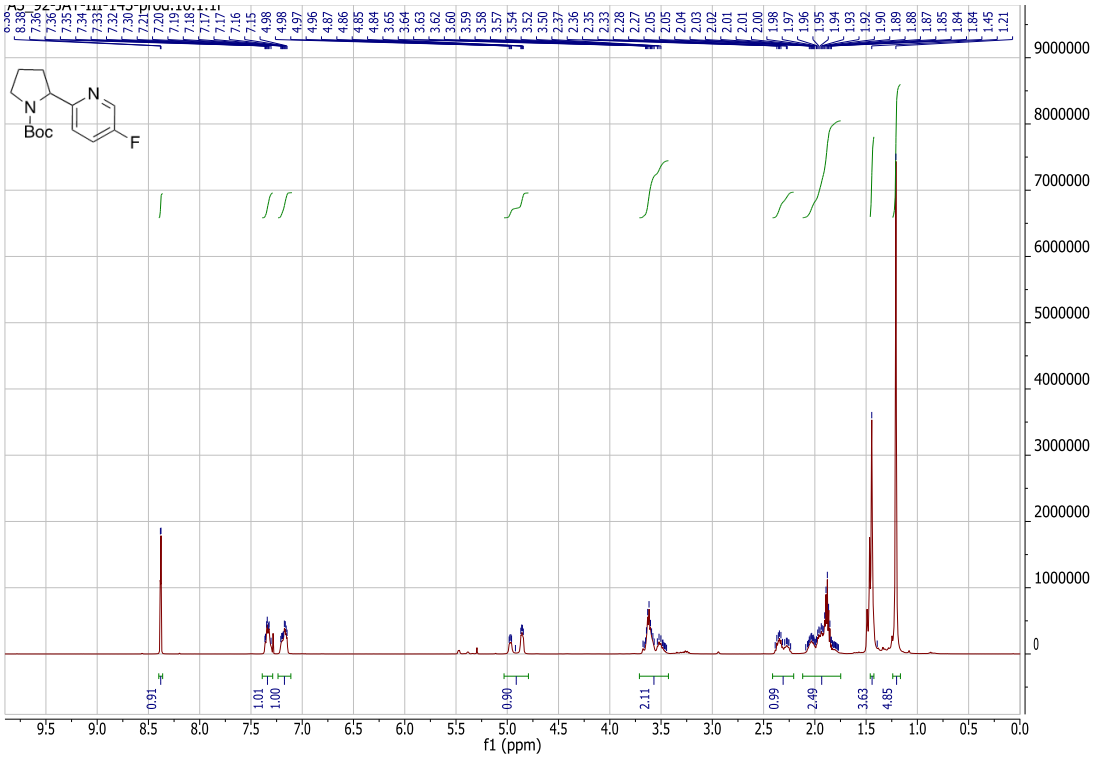
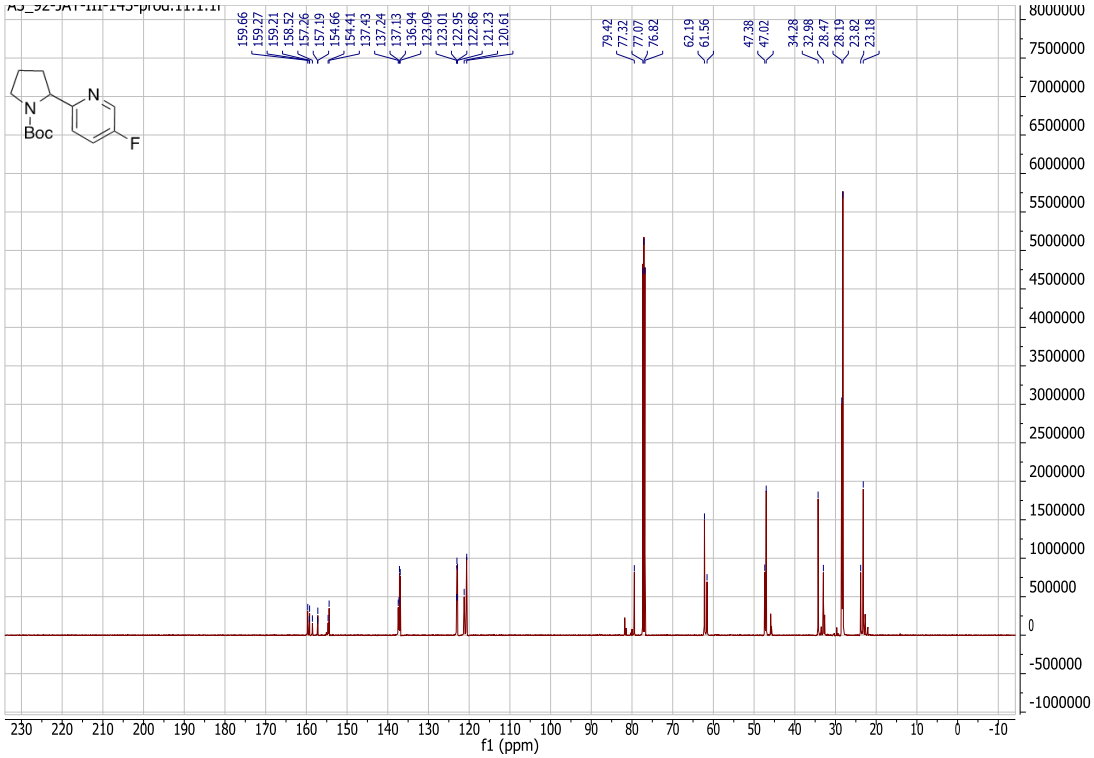

N
Boc
N
Me
f1 (ppm)

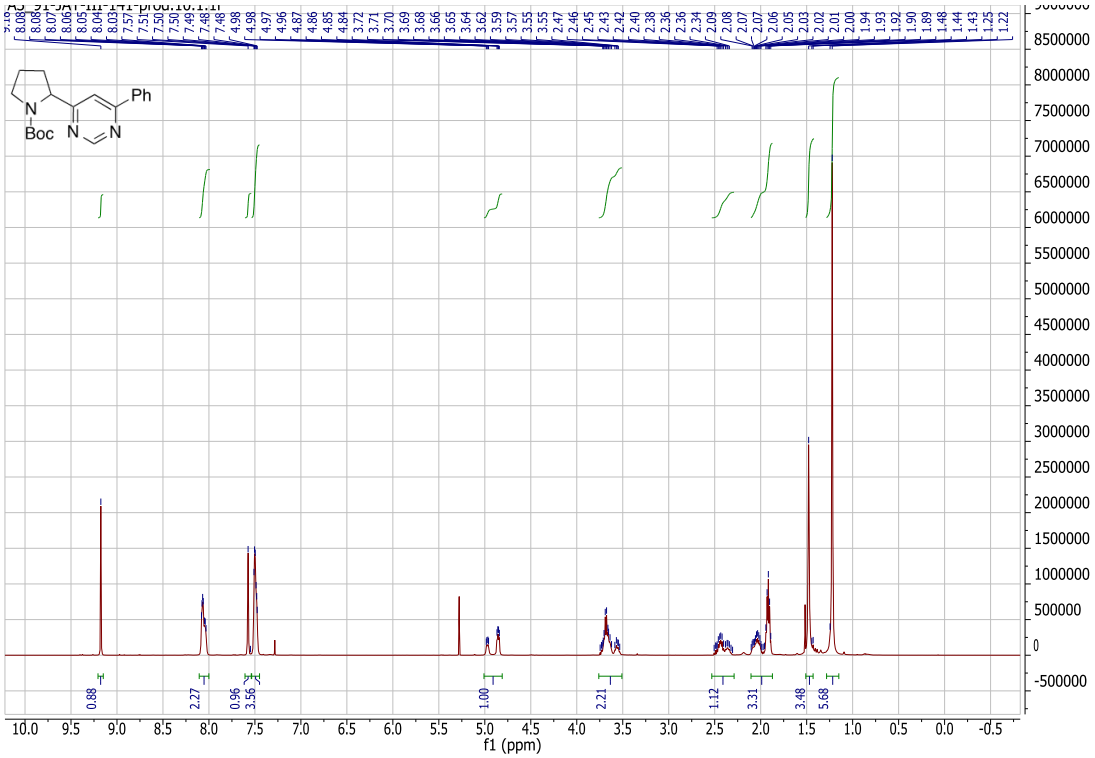

C13CPDp1.PU CDCl3 /opt/topspin3.0 lchu 19
N
Boc
N
Me
CDCl3
CDCl3
f1 (ppm)

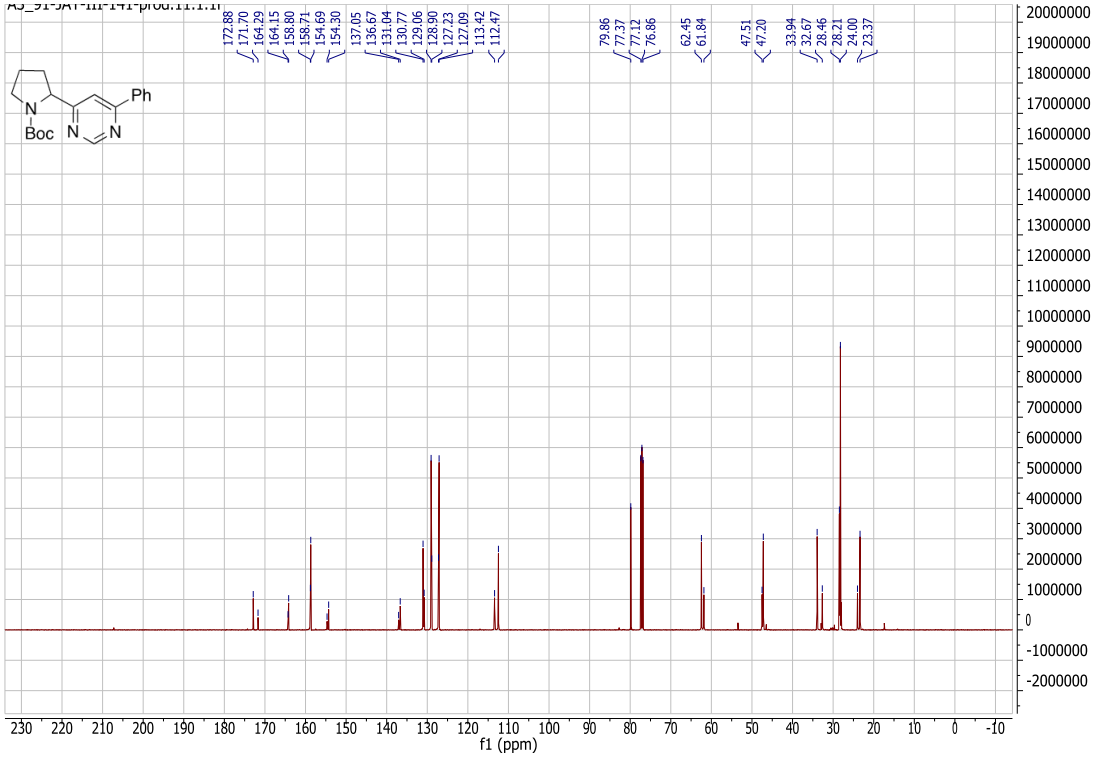

f1 (ppm)

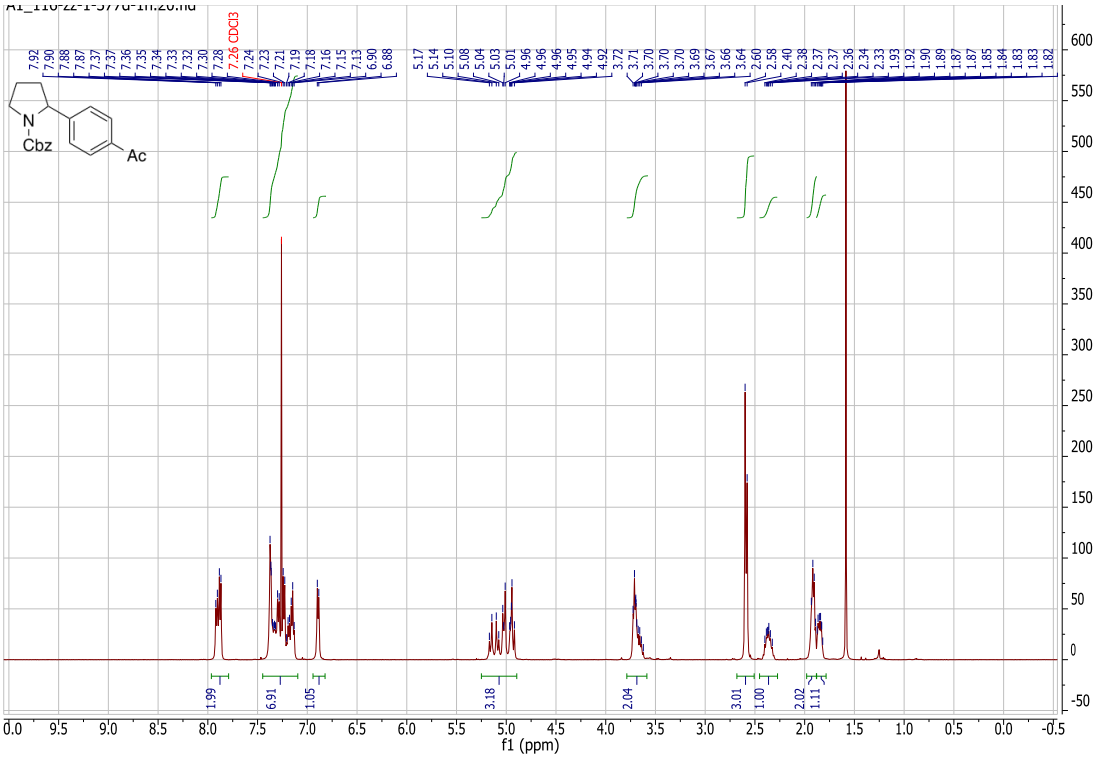

C13CPDp1.PU CDCl3 /opt/topspin3.0 lchu 18
f1 (ppm)

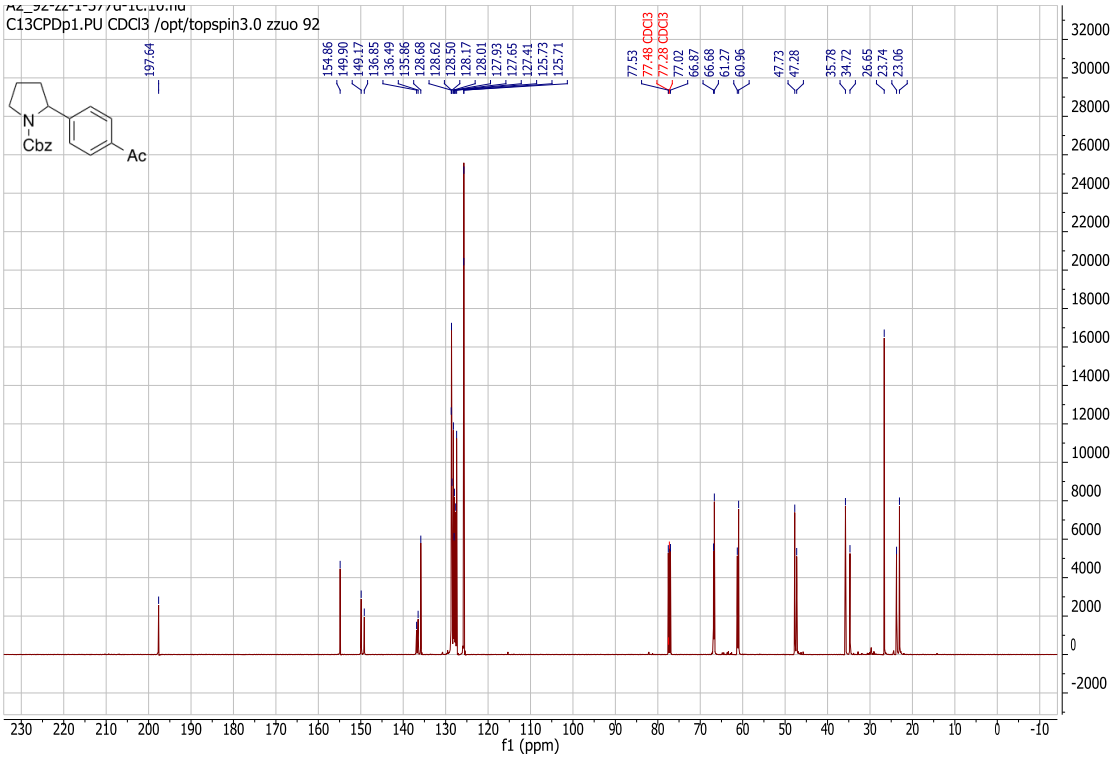

N
Boc
F
f1 (ppm)

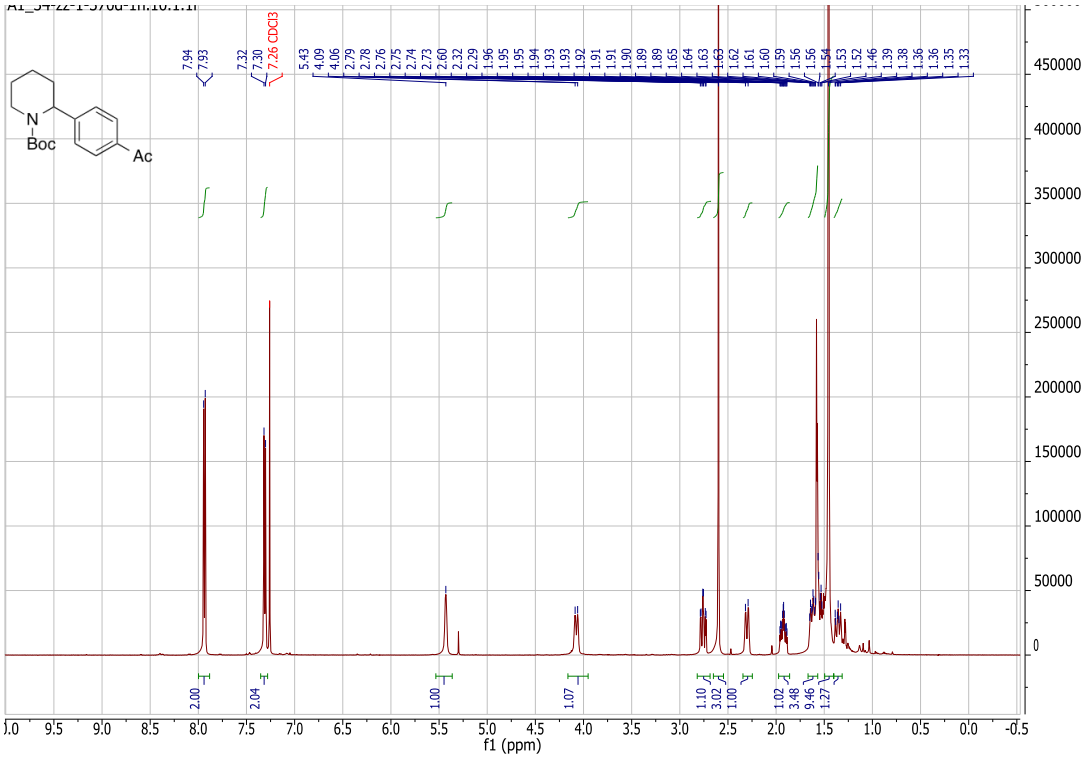

N
Boc
F
f1 (ppm)

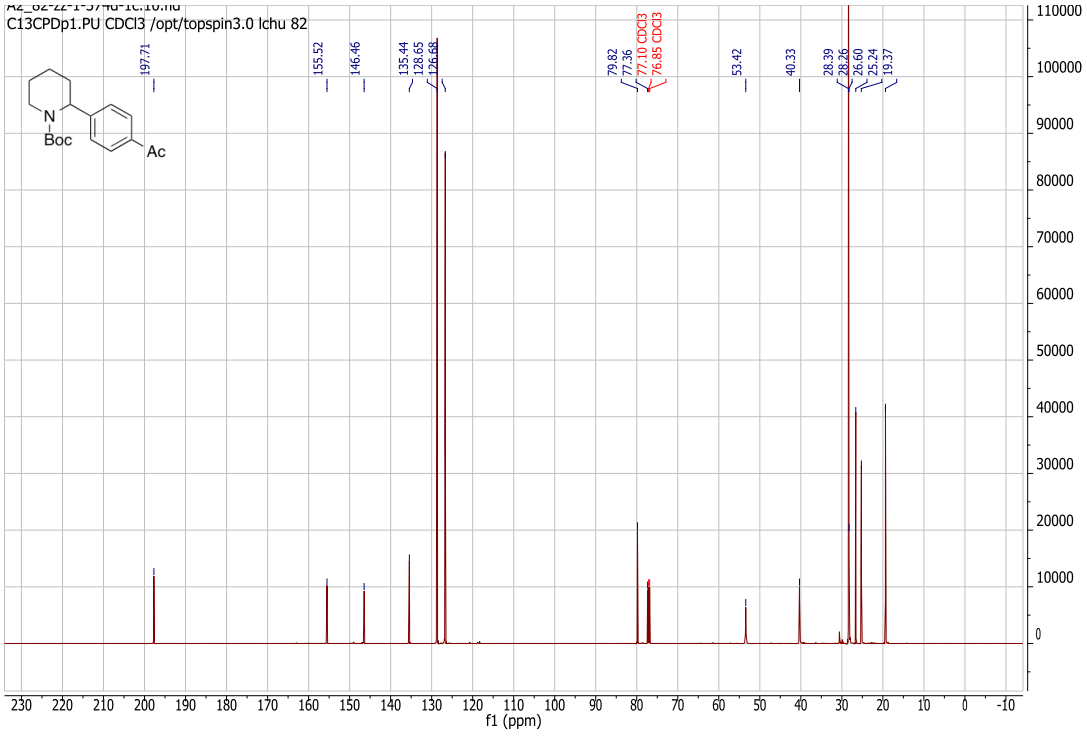

Ph
N
Boc
N
N
0.88
2.27
0.96
3.56
1.00
2.21
1.12
3.31
3.48
5.68
f1 (ppm)

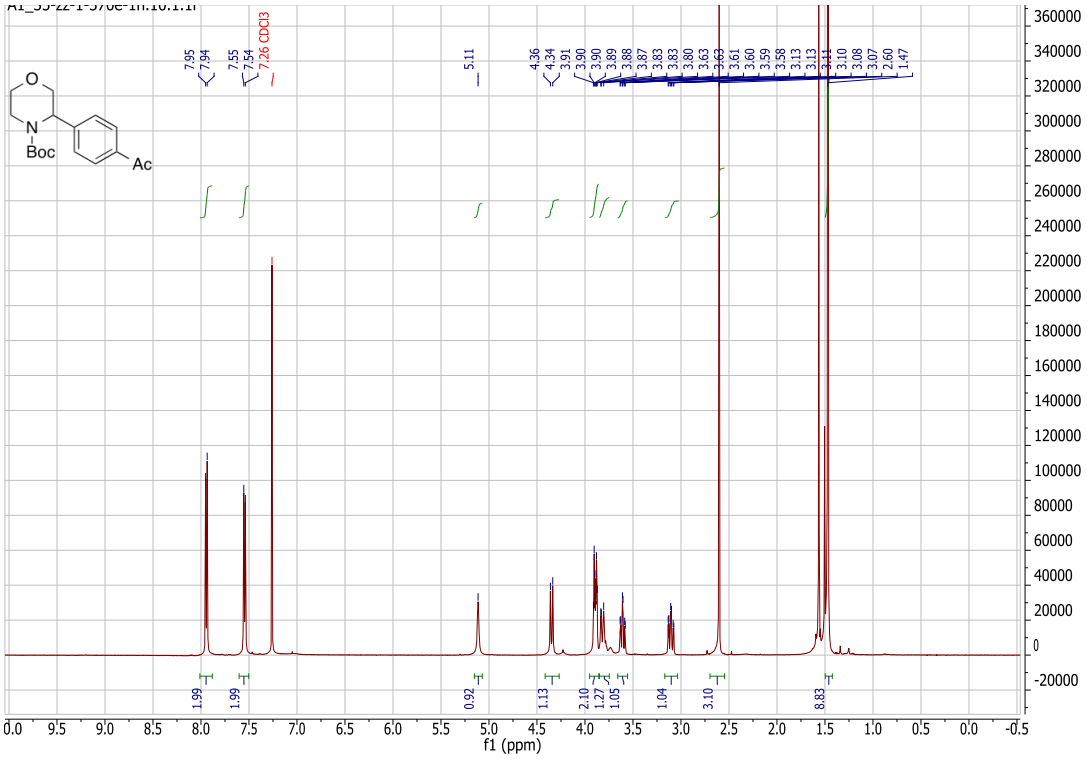

Ph
N
Boc
N
N
172.88
171.70
164.29
164.15
158.80
158.71
154.69
154.30
137.05
136.67
131.04
130.77
129.06
128.90
127.23
127.09
113.42
112.47
79.86
77.37
77.12
76.86
62.45
61.84
47.51
47.20
33.94
32.67
28.46
28.21
24.00
23.37
f1 (ppm)

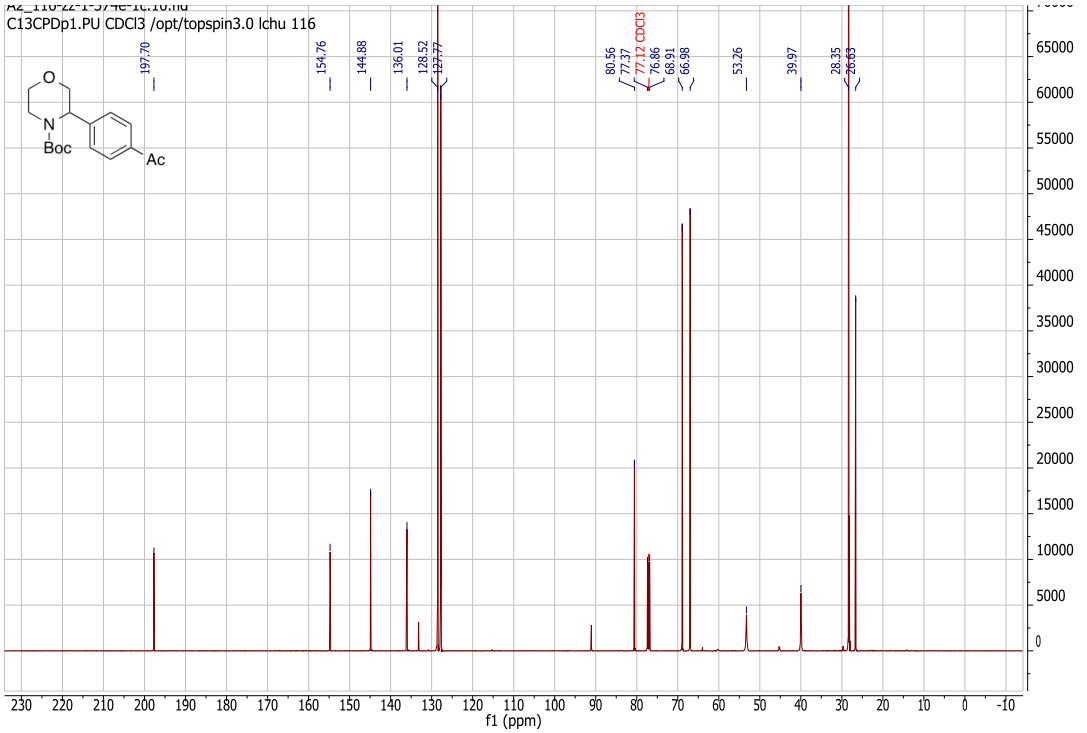

N
Cbz
Ac
f1 (ppm)

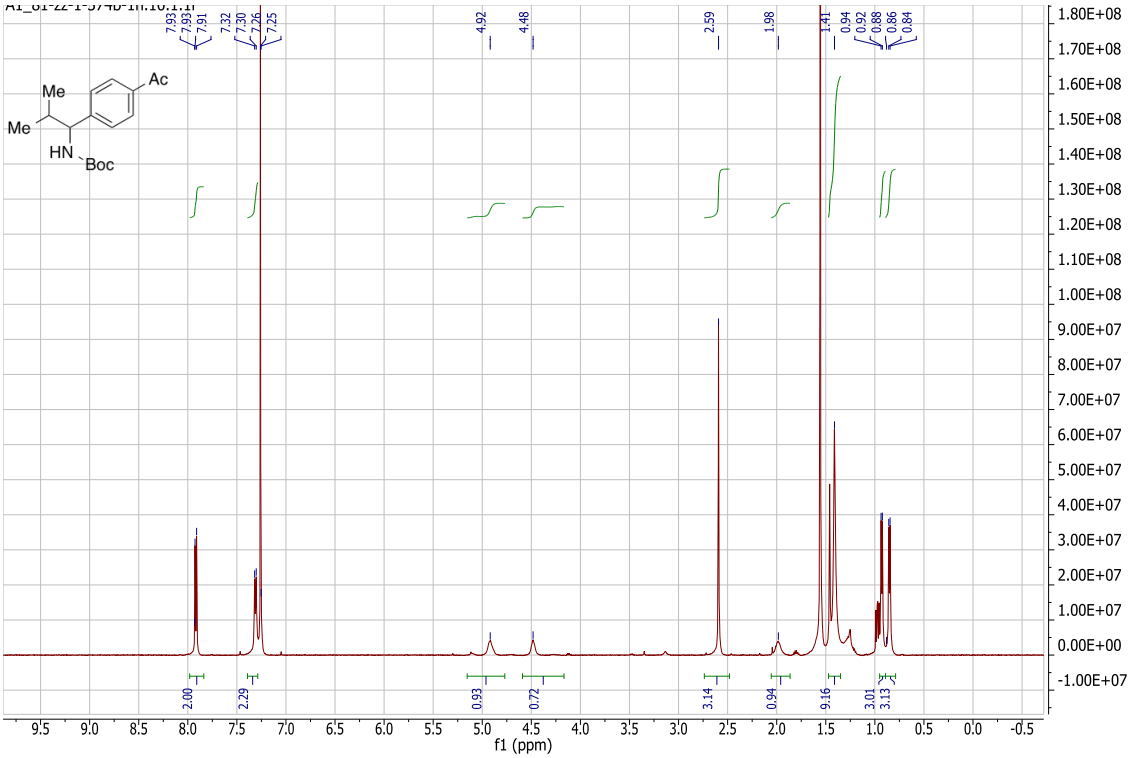

C13CPDp1.PU CDCl3 /opt/topspin3.0 zzuo 92
N
Cbz
Ac
f1 (ppm)

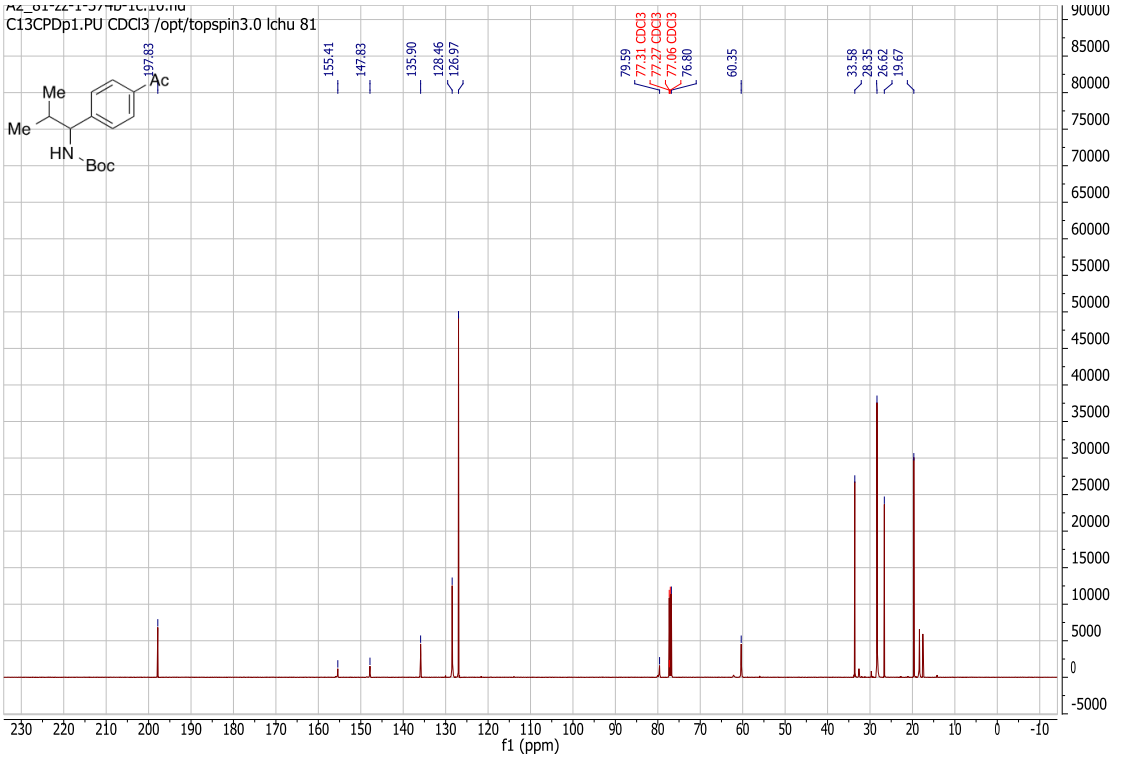

7.94
7.93
7.32
7.30
7.26 CDCl3
5.43
4.09
4.06
2.79
2.78
2.76
2.75
2.74
2.73
2.60
2.32
2.29
1.96
1.95
1.95
1.94
1.93
1.93
1.92
1.91
1.91
1.90
1.89
1.89
1.65
1.64
1.63
1.63
1.62
1.61
1.60
1.59
1.56
1.56
1.54
1.53
1.52
1.46
1.39
1.38
1.36
1.36
1.35
1.33
N
Boc
Ac
2.00
2.04
1.00
1.07
1.10
3.02
1.00
1.02
3.48
9.46
1.27
f1 (ppm)

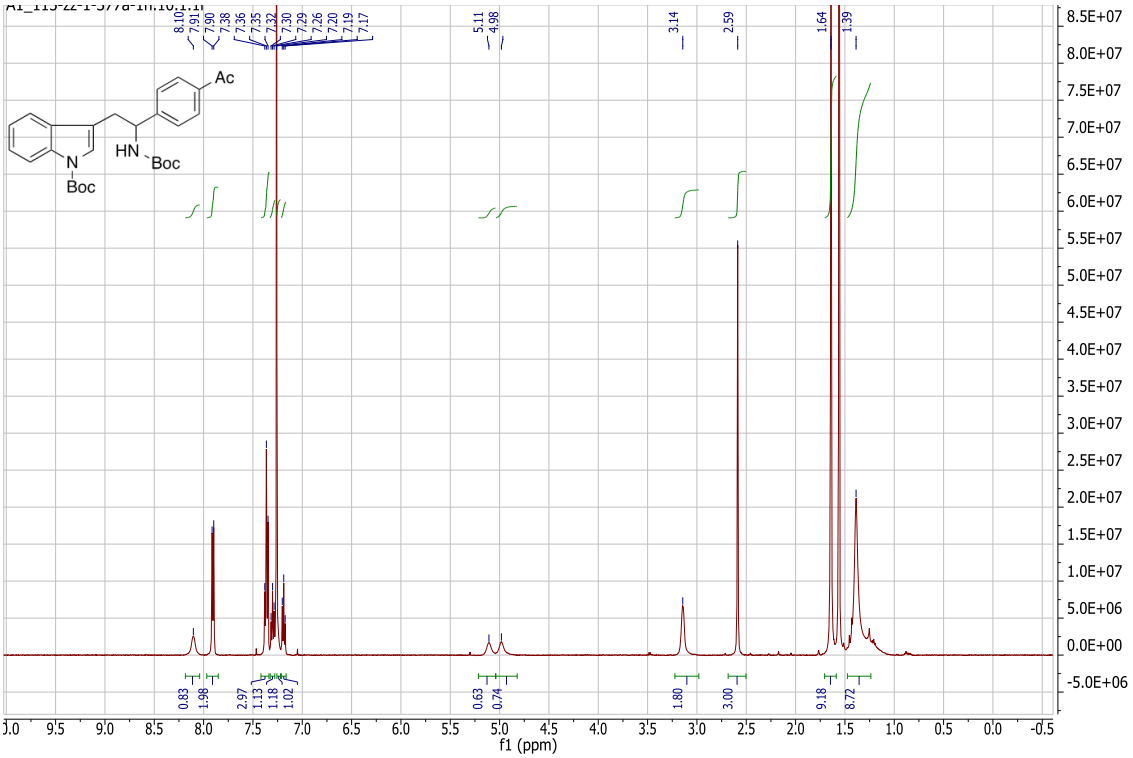

C13CPDp1.PU CDCl3 /opt/topspin3.0 lchu 82
197.71
155.52
146.46
135.44
128.65
126.68
79.82
77.36
77.10 CDCl3
76.85 CDCl3
53.42
40.33
28.39
28.26
26.60
25.24
19.37
N
Boc
Ac
f1 (ppm)

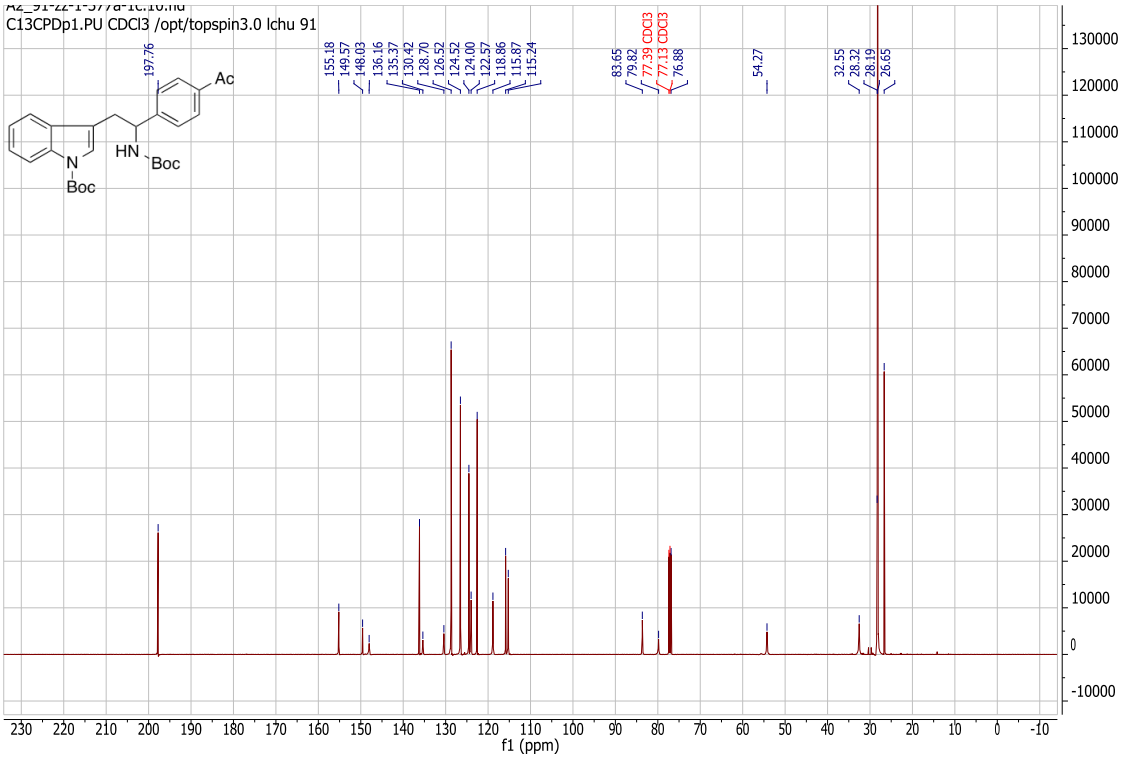

7.95
7.94
7.55
7.54
7.26 CDCl3
5.11
4.36
4.34
3.91
3.90
3.90
3.89
3.88
3.87
3.83
3.83
3.80
3.63
3.63
3.61
3.60
3.59
3.58
3.13
3.13
3.11
3.10
3.08
3.07
2.60
1.47
O
N
Boc
Ac
1.99
1.99
0.92
1.13
2.10
1.27
1.05
1.04
3.10
8.83
f1 (ppm)

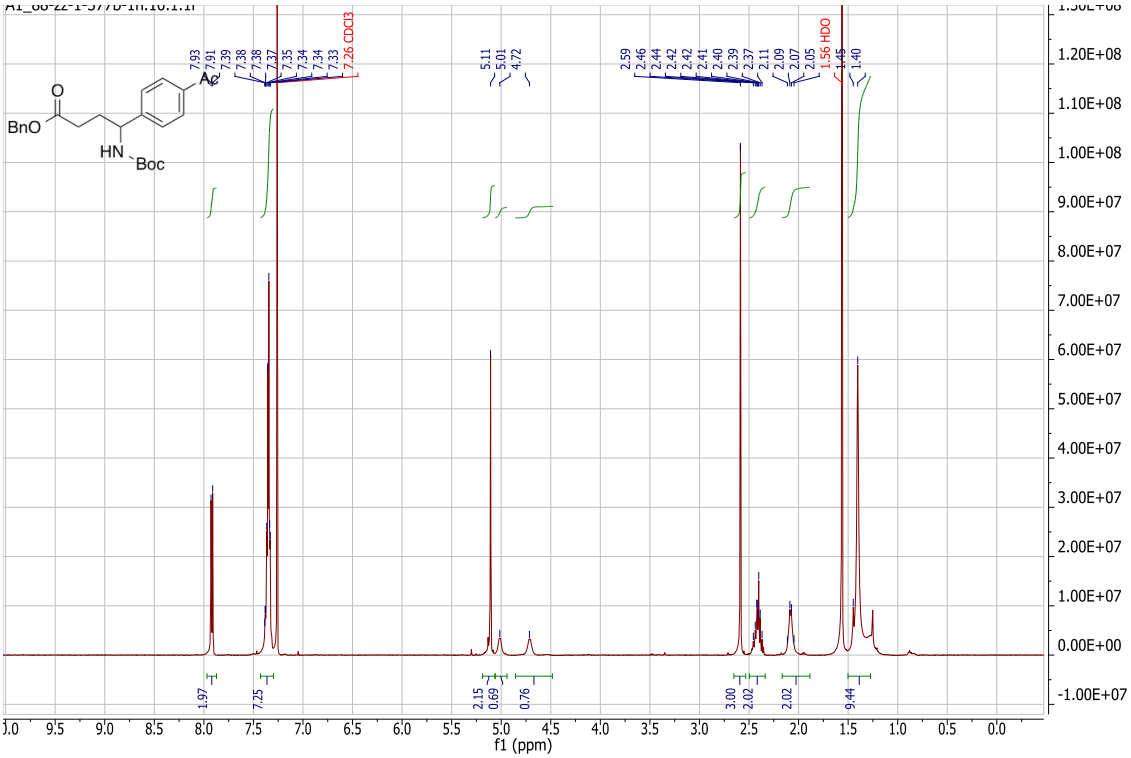

C13CPDp1.PU CDCl3 /opt/topspin3.0 lchu 116
197.70
154.76
144.88
136.01
128.52
127.77
80.56
77.37
77.12 CDCl3
76.86
68.91
66.98
53.26
39.97
28.35
26.63
O
N
Boc
Ac
f1 (ppm)

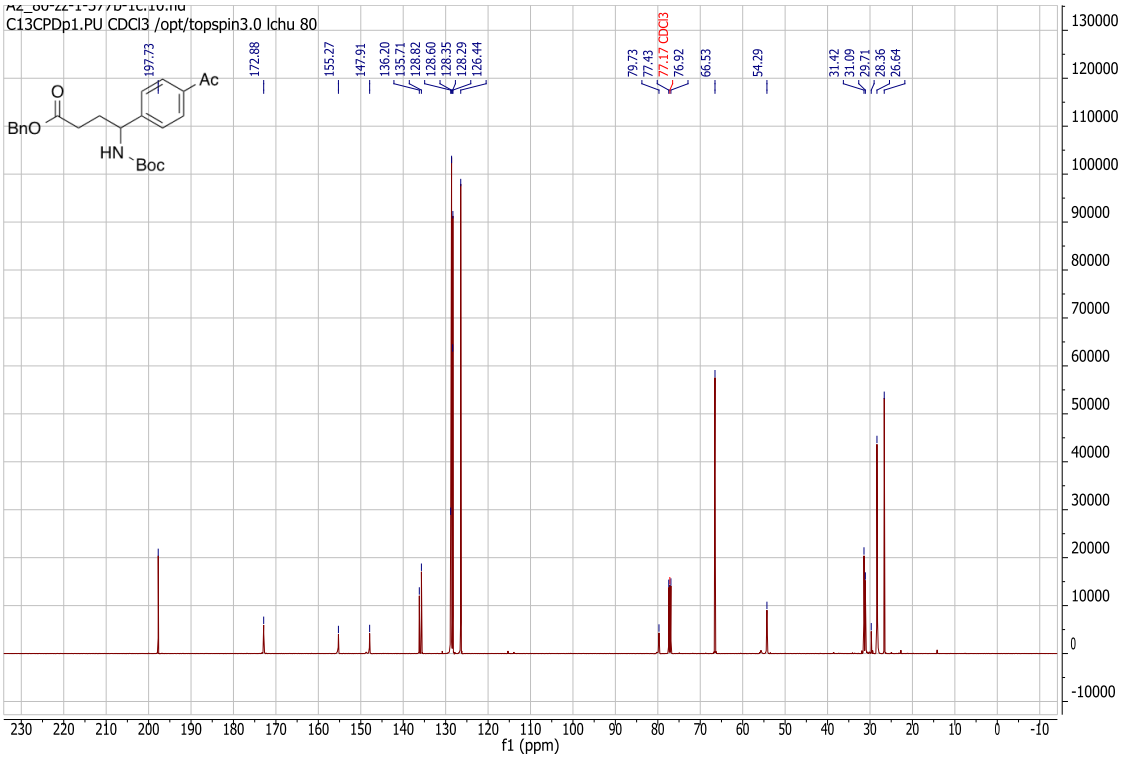

7.93
7.91
7.32
7.30
7.26
7.25
4.92
4.48
2.59
1.98
1.41
0.94
0.92
0.88
0.86
0.84
Me
Me
Ac
HN
Boc
2.00
2.29
0.93
0.72
3.14
0.94
9.16
3.01
3.13
f1 (ppm)

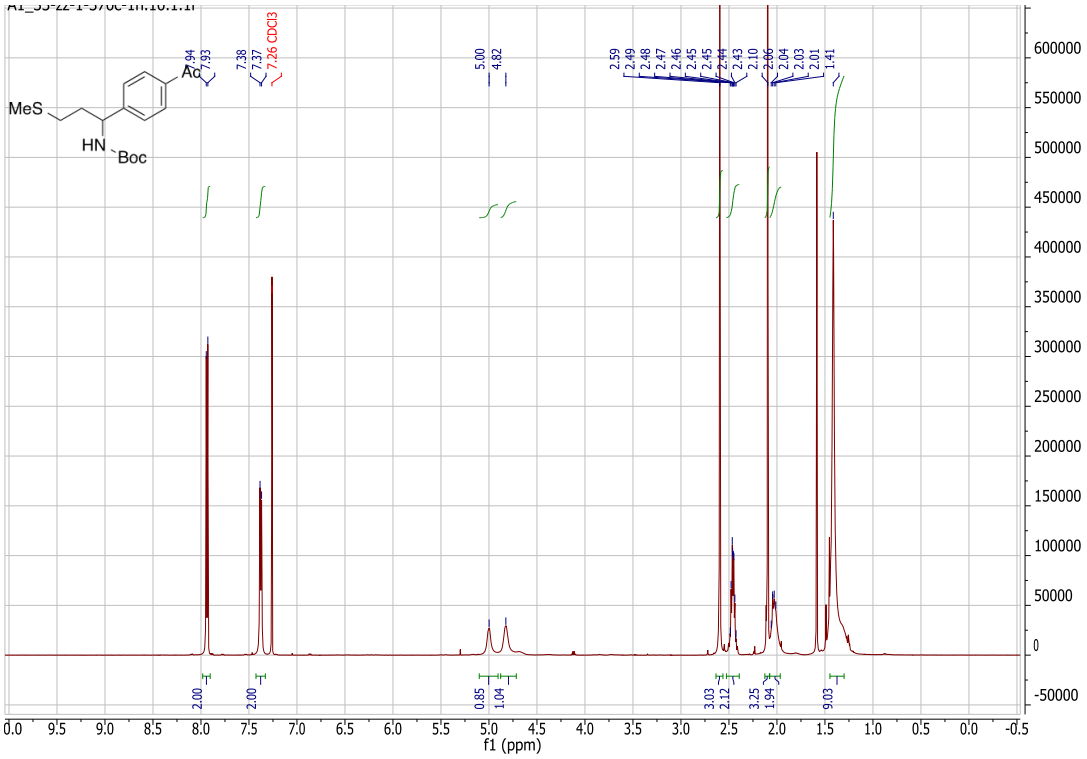

C13CPDp1.PU CDCl3 /opt/topspin3.0 lchu 81
197.83
155.41
147.83
135.90
128.46
126.97
79.59
77.31 CDCl3
77.27 CDCl3
77.06 CDCl3
76.80
60.35
33.58
28.35
26.62
19.67
Me
Me
Ac
HN
Boc
f1 (ppm)

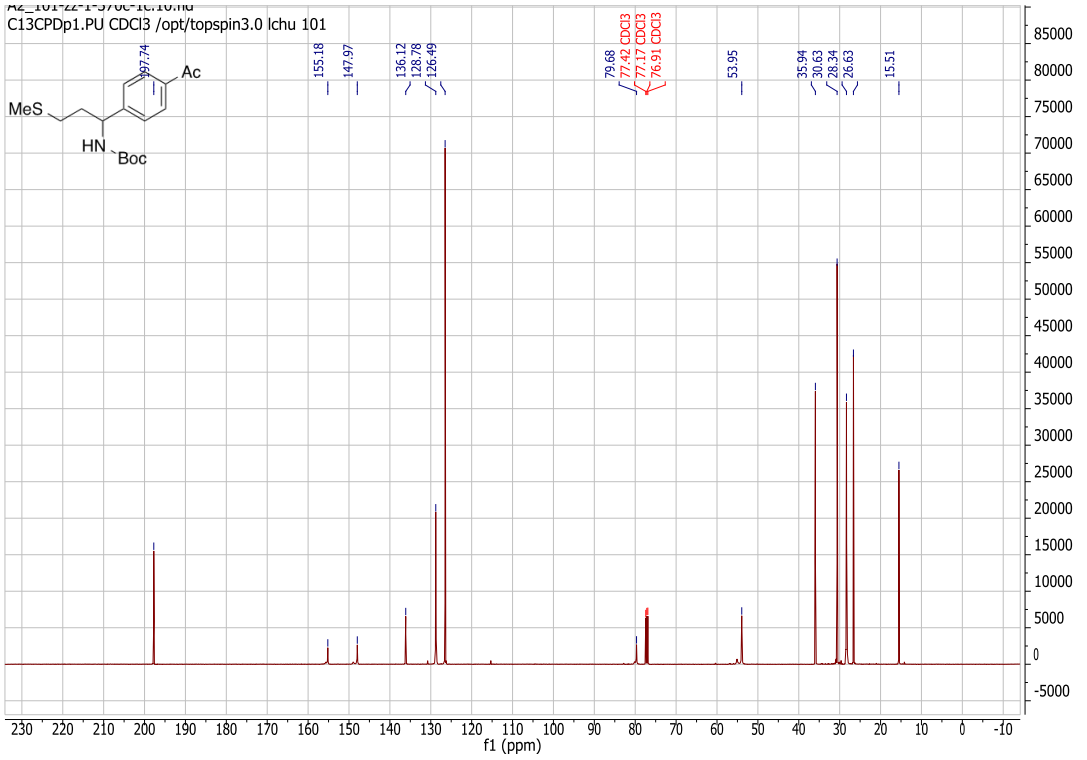

8.10
7.91
7.90
7.38
7.36
7.35
7.32
7.30
7.29
7.26
7.20
7.19
7.17
5.11
4.98
3.14
2.59
1.64
1.39
Ac
HN
Boc
N
Boc
0.83
1.98
2.97
1.13
1.18
1.02
0.63
0.74
1.80
3.00
9.18
8.72
f1 (ppm)

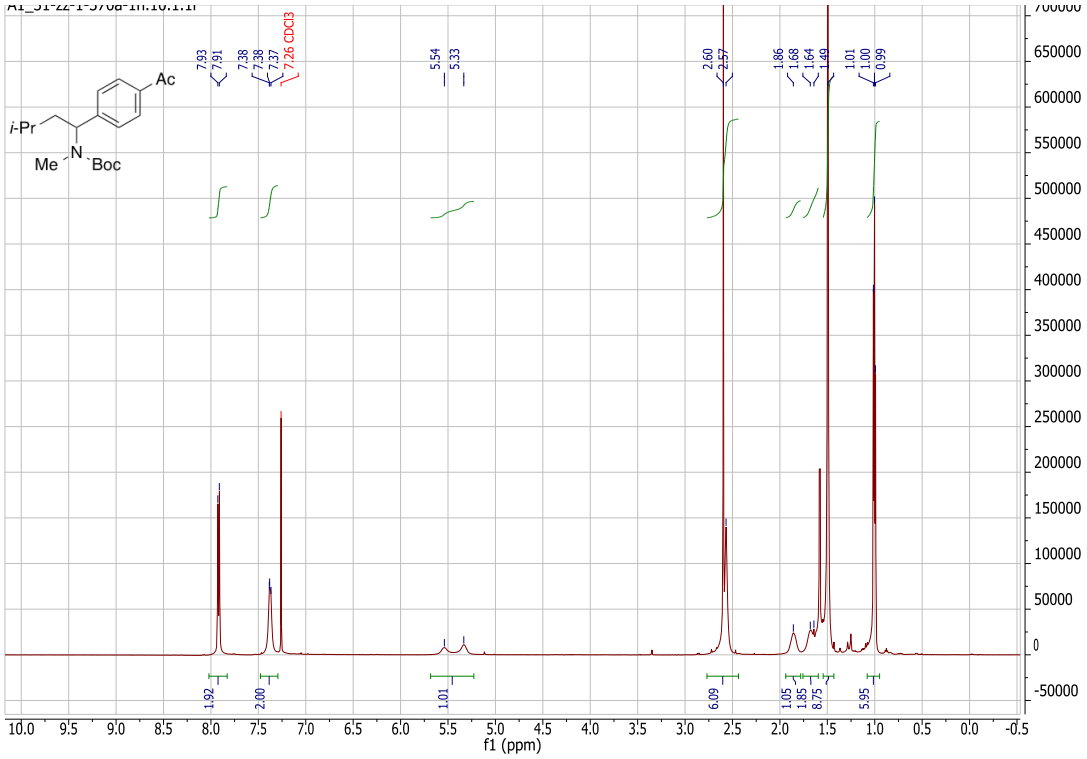

C13CPDp1.PU CDCl3 /opt/topspin3.0 lchu 91
197.76
155.18
149.57
148.03
136.16
135.37
130.42
128.70
126.52
124.52
124.00
122.57
118.86
115.87
115.24
83.65
79.82
77.39 CDCl3
77.13 CDCl3
76.88
54.27
32.55
28.32
28.19
26.65
Ac
HN
Boc
N
Boc
f1 (ppm)

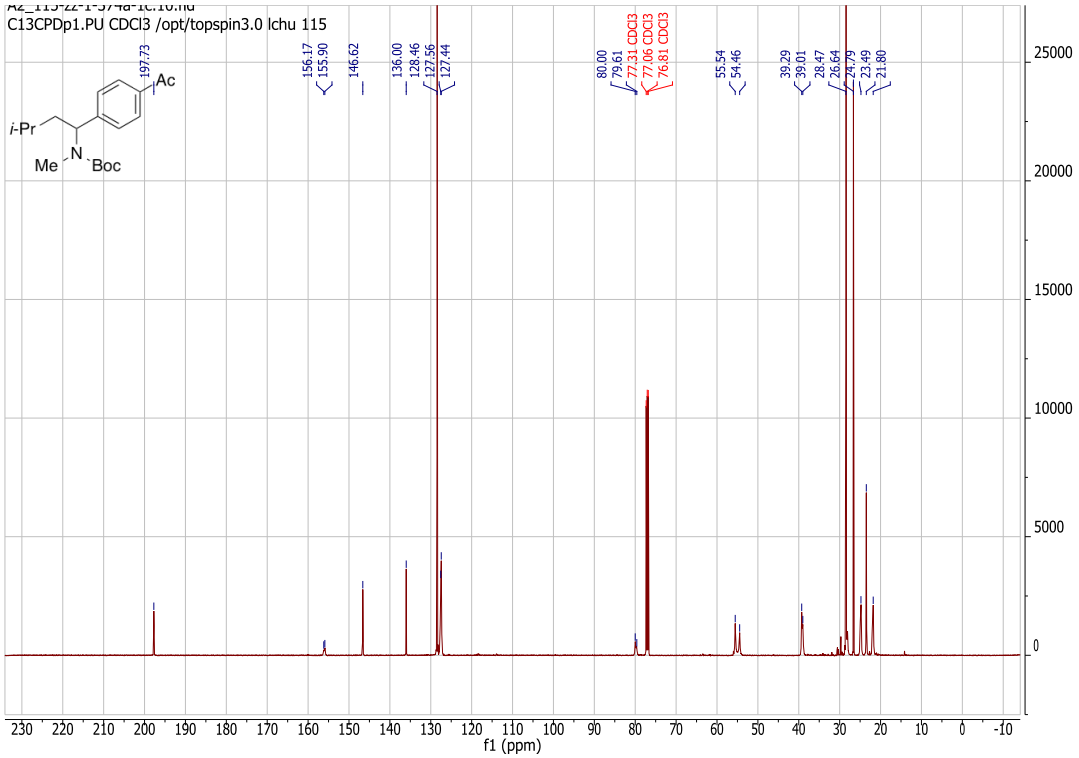

7.93
7.91
7.39
7.38
7.37
7.35
7.34
7.34
7.33
7.26 CDCl3
5.11
5.01
4.72
2.59
2.46
2.44
2.42
2.42
2.41
2.40
2.39
2.37
2.11
2.09
2.07
2.05
1.56 HDO
1.45
1.40
Ac
BnO
HN
Boc
1.97
7.25
2.15
0.69
0.76
3.00
2.02
2.02
9.44
f1 (ppm)

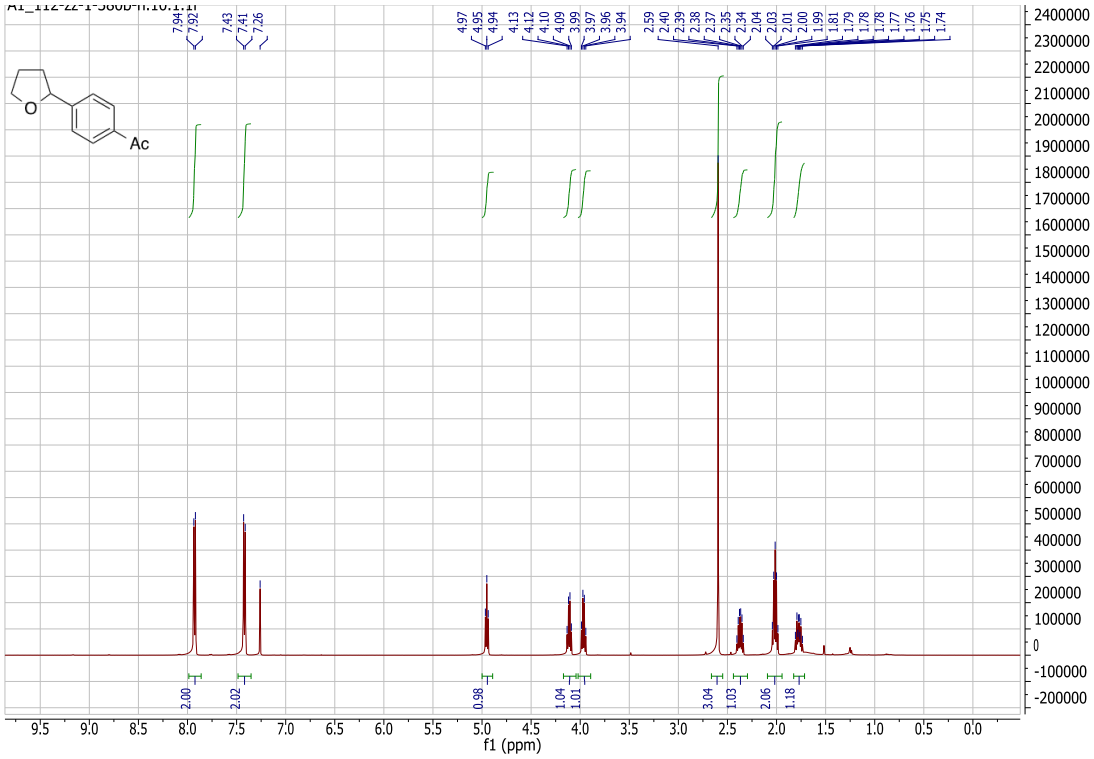

C13CPDp1.PU CDCl3 /opt/topspin3.0 lchu 80
197.73
172.88
155.27
147.91
136.20
135.71
128.82
128.60
128.35
128.29
126.44
79.73
77.43
77.17 CDCl3
76.92
66.53
54.29
31.42
31.09
29.71
28.36
26.64
Ac
BnO
HN
Boc
f1 (ppm)

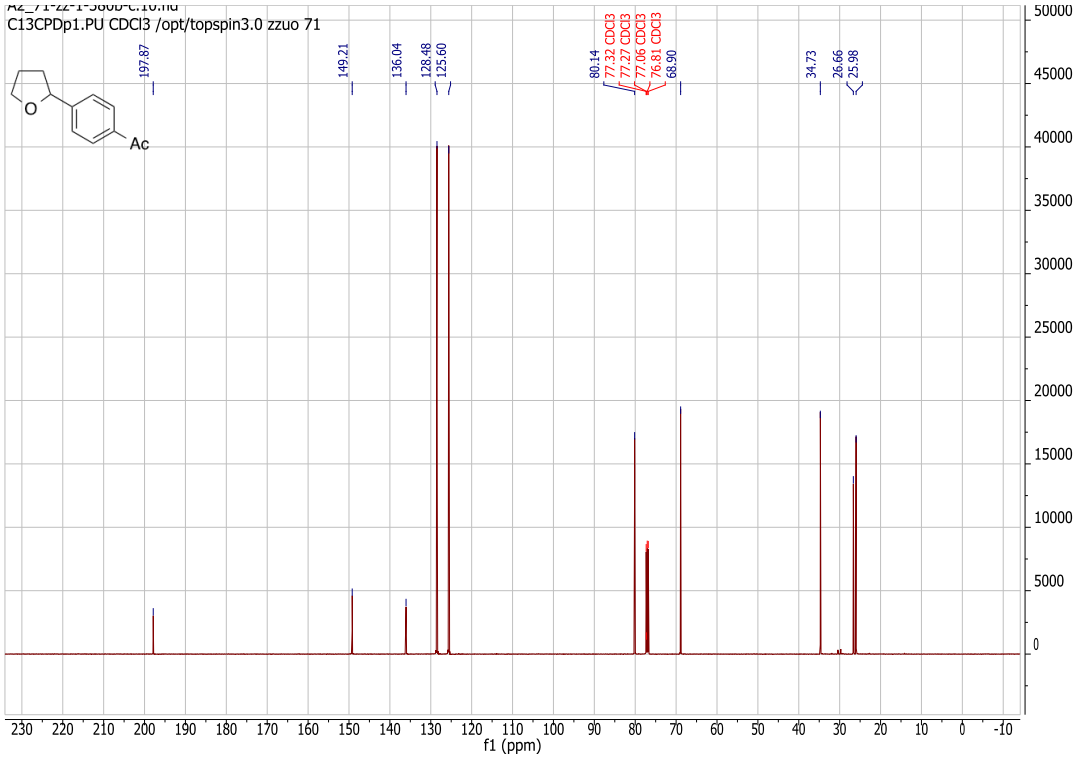

MeS
HN
Boc
Ac
7.94
7.93
7.38
7.37
7.26 CDCl3
5.00
4.82
2.59
2.49
2.48
2.47
2.46
2.45
2.45
2.44
2.43
2.10
2.06
2.04
2.03
2.01
1.41
2.00
2.00
0.85
1.04
3.03
2.12
3.25
1.94
9.03
f1 (ppm)

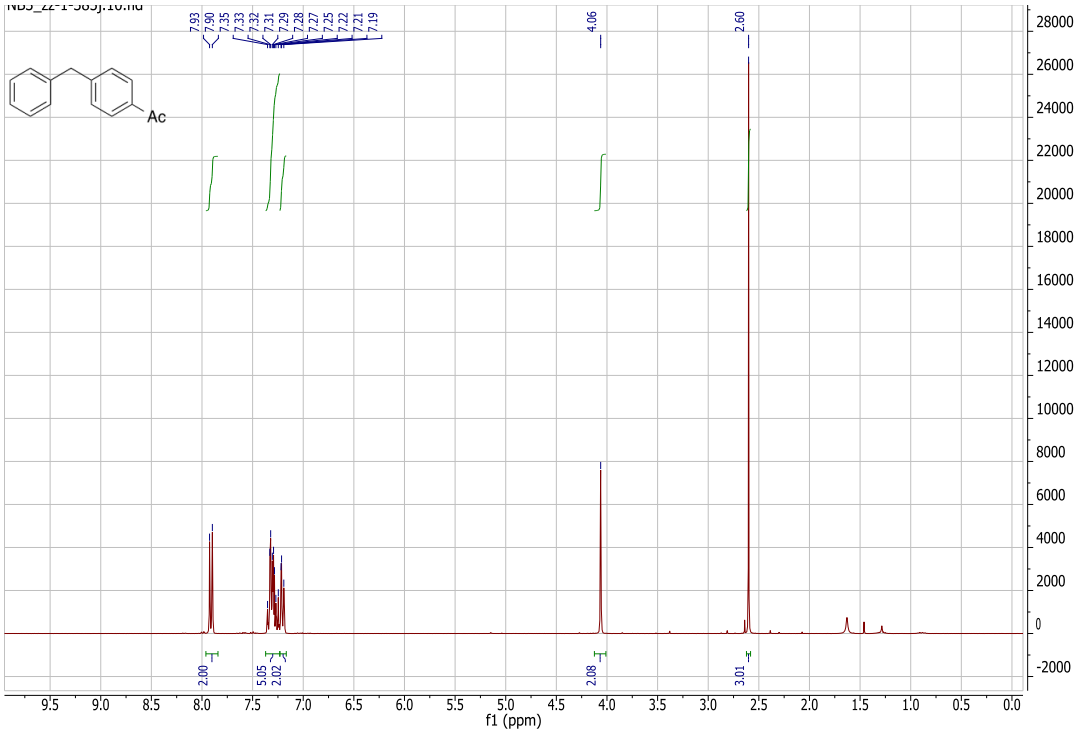

C13CPDp1.PU CDCl3 /opt/topspin3.0 lchu 101
MeS
HN
Boc
Ac
197.74
155.18
147.97
136.12
128.78
126.49
79.68
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
53.95
35.94
30.63
28.34
26.63
15.51
f1 (ppm)

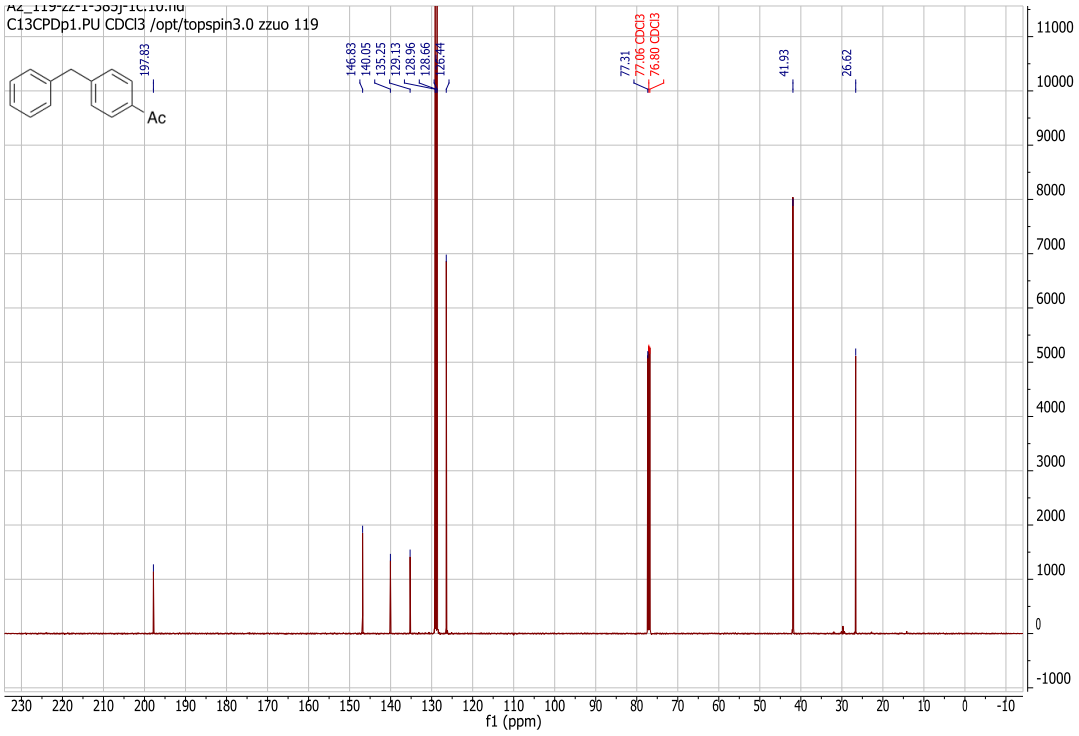

Ac
i-Pr
Me
N
Boc
7.93
7.91
7.38
7.38
7.37
7.26 CDCl3
5.54
5.33
2.60
2.57
1.86
1.68
1.64
1.49
1.01
1.00
0.99
1.92
2.00
1.01
6.09
1.05
1.85
8.75
5.95
f1 (ppm)

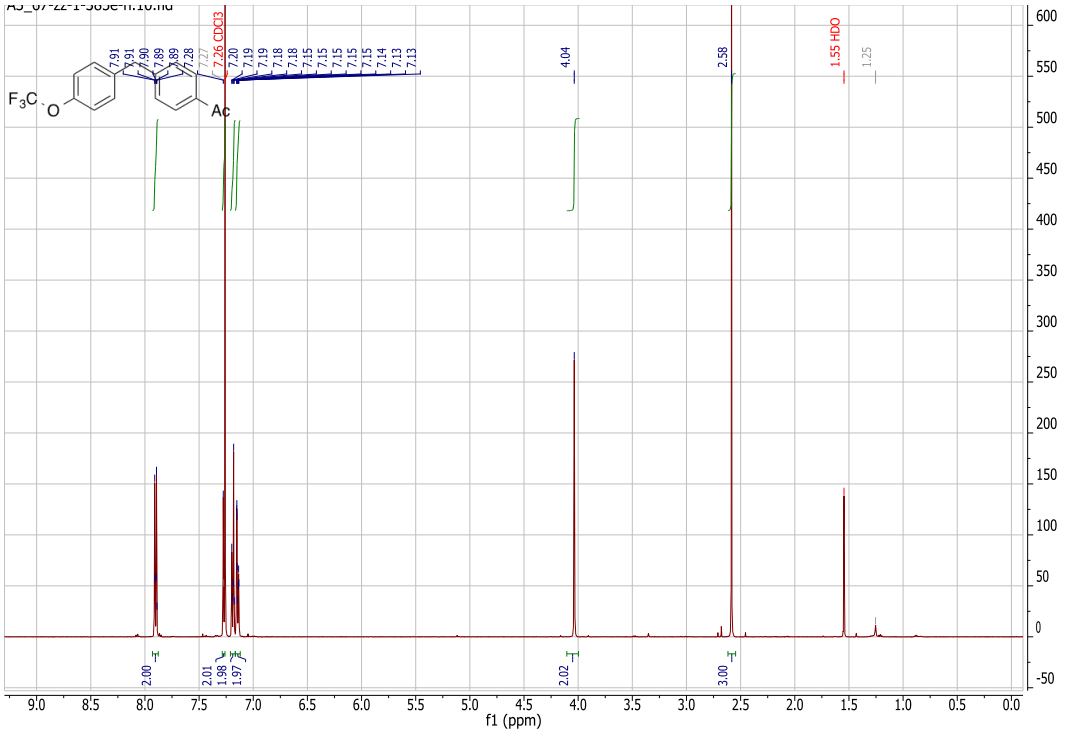

C13CPDp1.PU CDCl3 /opt/topspin3.0 lchu 115
Ac
i-Pr
Me
N
Boc
197.73
156.17
155.90
146.62
136.00
128.46
127.56
127.44
80.00
79.61
77.31 CDCl3
77.06 CDCl3
76.81 CDCl3
55.54
54.46
39.29
39.01
28.47
26.64
24.79
23.49
21.80
f1 (ppm)

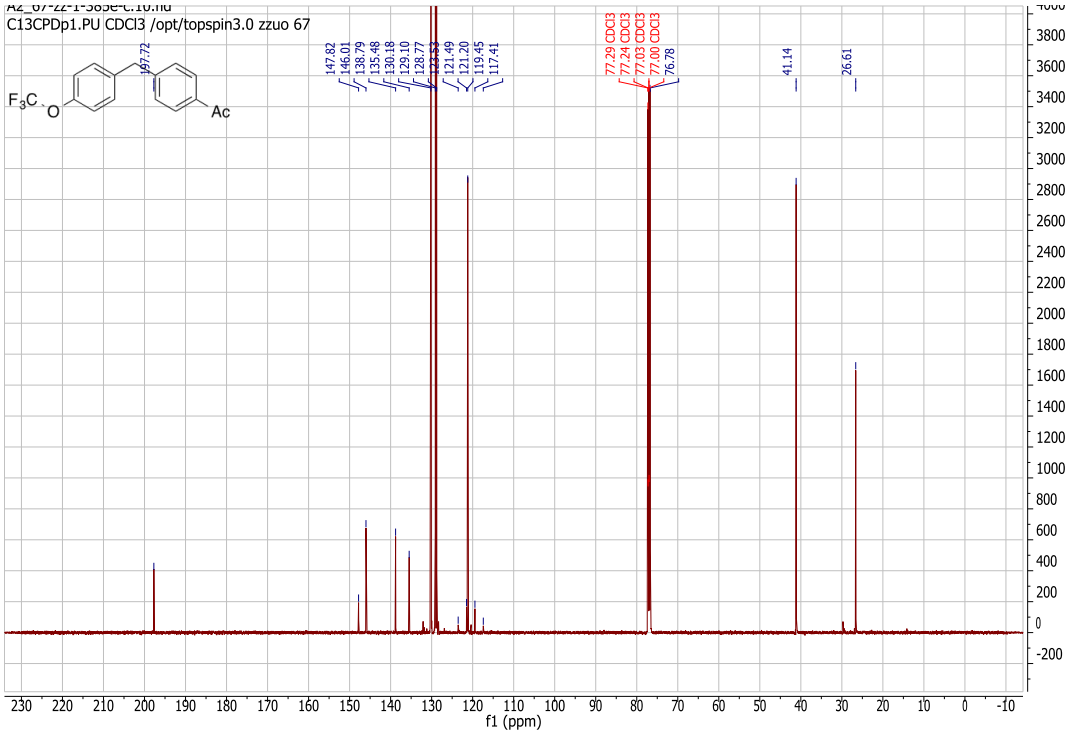

7.94
7.92
7.43
7.41
7.26
4.97
4.95
4.94
4.13
4.12
4.10
4.09
3.99
3.97
3.96
3.94
2.59
2.40
2.39
2.38
2.37
2.35
2.34
2.04
2.03
2.01
2.00
1.99
1.81
1.79
1.78
1.77
1.76
1.75
1.74
O
Ac
2.00
2.02
0.98
1.04
1.01
3.04
1.03
2.06
1.18
f1 (ppm)

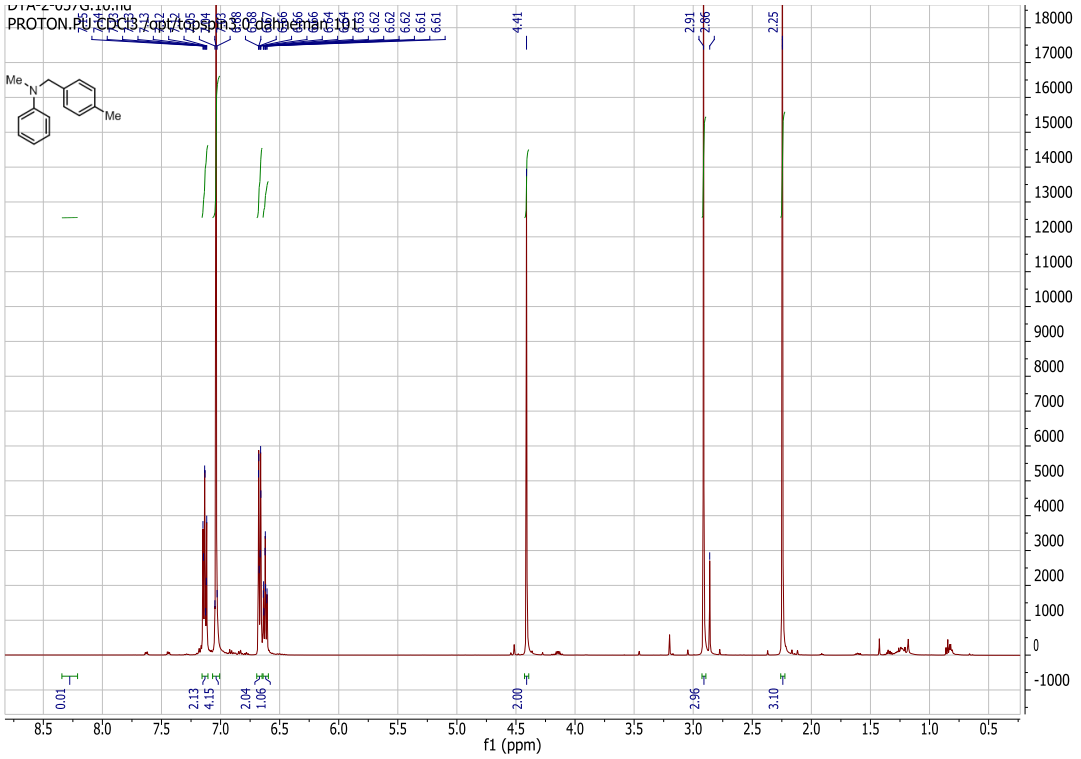

C13CPDp1.PU CDCl3 /opt/topspin3.0 zzuo 71
197.87
149.21
136.04
128.48
125.60
80.14
77.32 CDCl3
77.27 CDCl3
77.06 CDCl3
76.81 CDCl3
68.90
34.73
26.66
25.98
O
Ac
f1 (ppm)

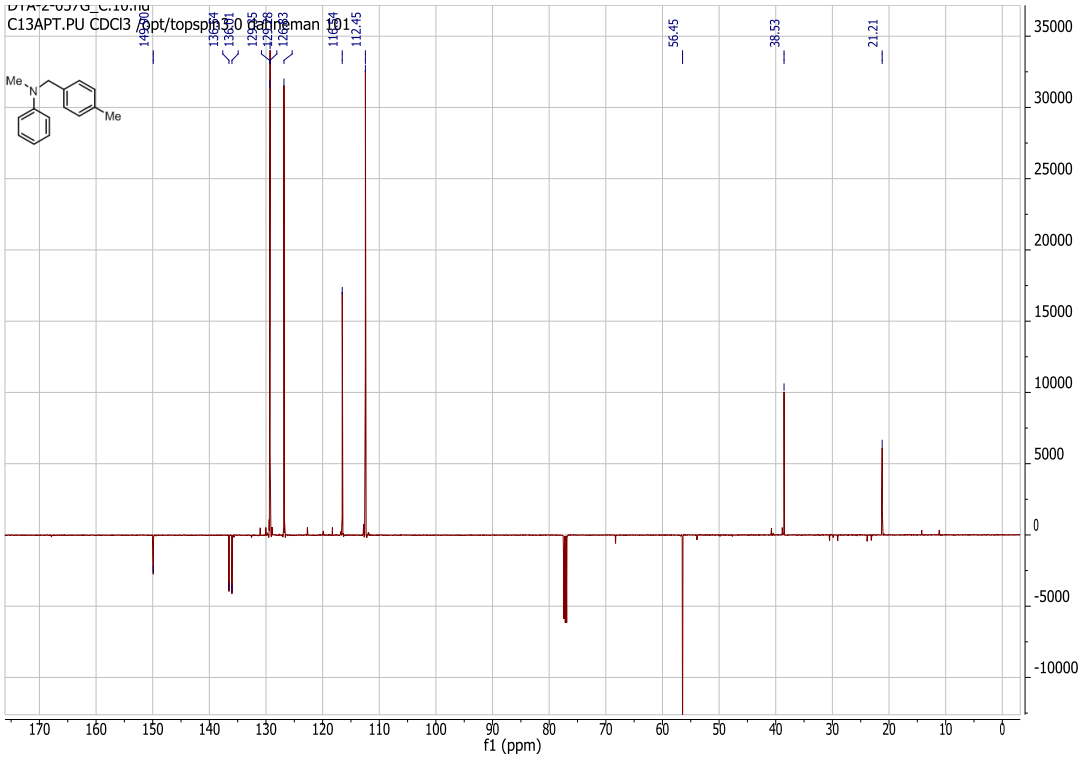

7.93
7.90
7.35
7.33
7.32
7.31
7.29
7.28
7.27
7.25
7.22
7.21
7.19
4.06
2.60
Ac
2.00
5.05
2.02
2.08
3.01
f1 (ppm)

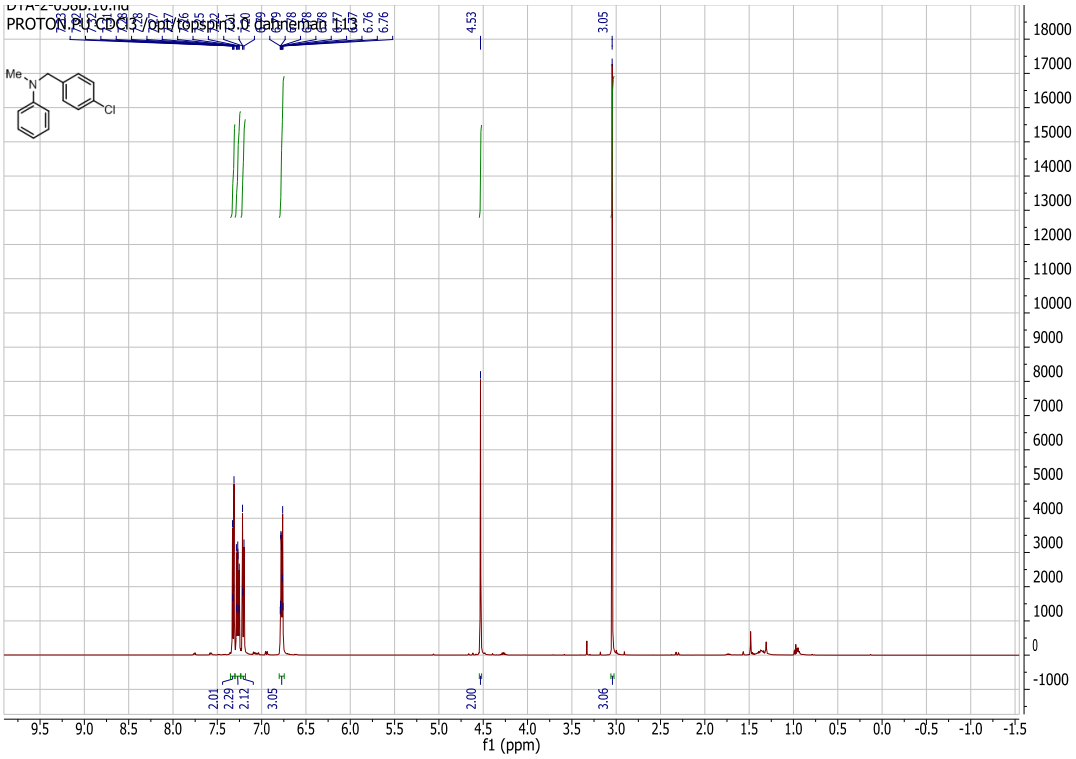

C13CPDp1.PU CDCl3 /opt/topspin3.0 zzuo 119
197.83
146.83
140.05
135.25
129.13
128.96
128.66
126.44
77.31
77.06 CDCl3
76.80 CDCl3
41.93
26.62
Ac
f1 (ppm)


7.91
7.91
7.90
7.89
7.89
7.28
7.27
7.26 CDCl3
7.20
7.19
7.19
7.18
7.18
7.15
7.15
7.15
7.15
7.14
7.13
7.13
4.04
2.58
1.55 H2O
1.25
F3C
O
Ac
2.00
2.01
1.98
1.97
2.02
3.00
f1 (ppm)


C13CPDp1.PU CDCl3 /opt/topspin3.0 zzuo 67
197.72
147.82
146.01
138.79
135.48
130.18
129.10
128.77
123.53
121.49
121.20
119.45
117.41
77.29 CDCl3
77.24 CDCl3
77.03 CDCl3
77.00 CDCl3
76.78
41.14
26.61
F3C
O
Ac
f1 (ppm)


PROTON.PU CDCl3 /opt/topspin3.0 dahmeman 101
Me
N
Me
4.41
2.91
2.86
2.25
0.01
2.13
4.15
2.04
1.06
2.00
2.96
3.10
f1 (ppm)


C13APT.PU CDCl3 /opt/topspin3.0 dahmeman 101
Me
N
Me
56.45
38.53
21.21
f1 (ppm)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Cl
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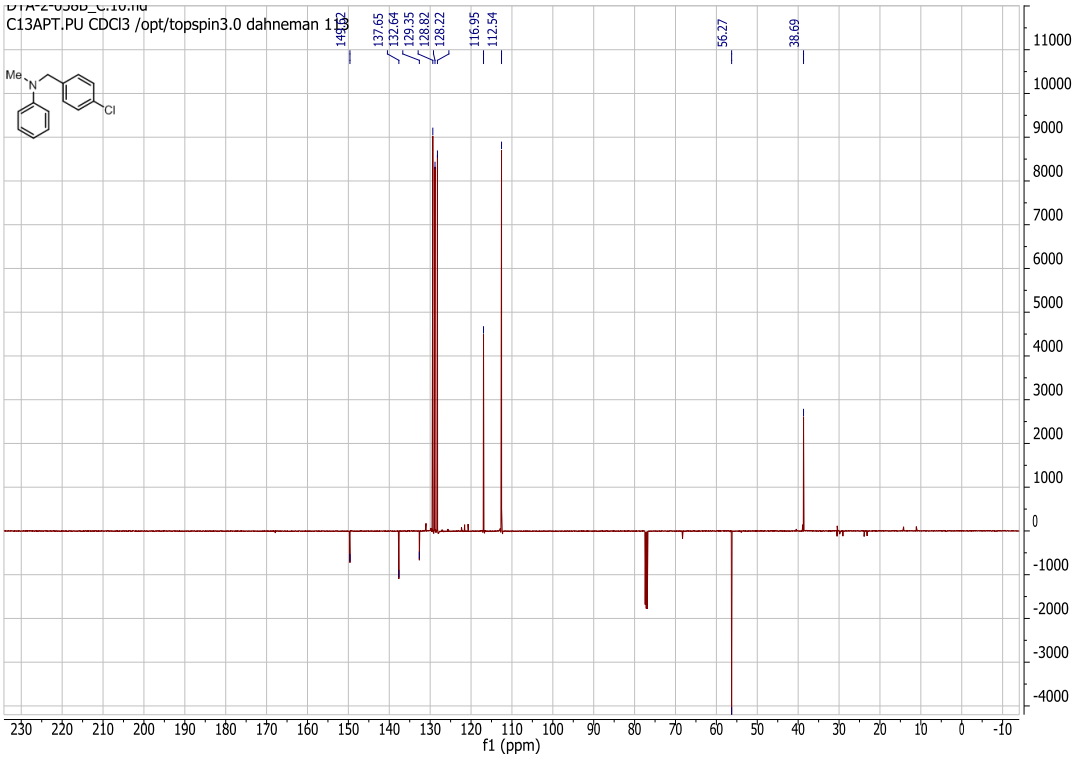
2.01
2.29
2.12
3.05
2.00
3.06
f1 (ppm)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Cl
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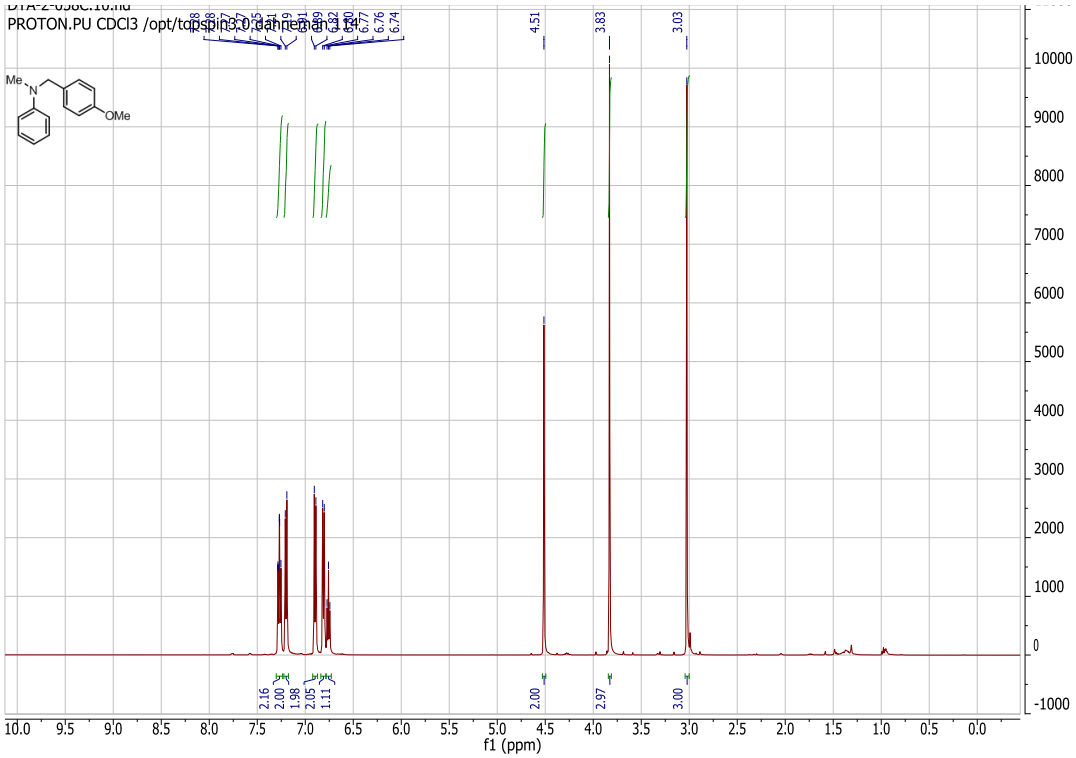
112.54
56.27
38.69
f1 (ppm)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OMe
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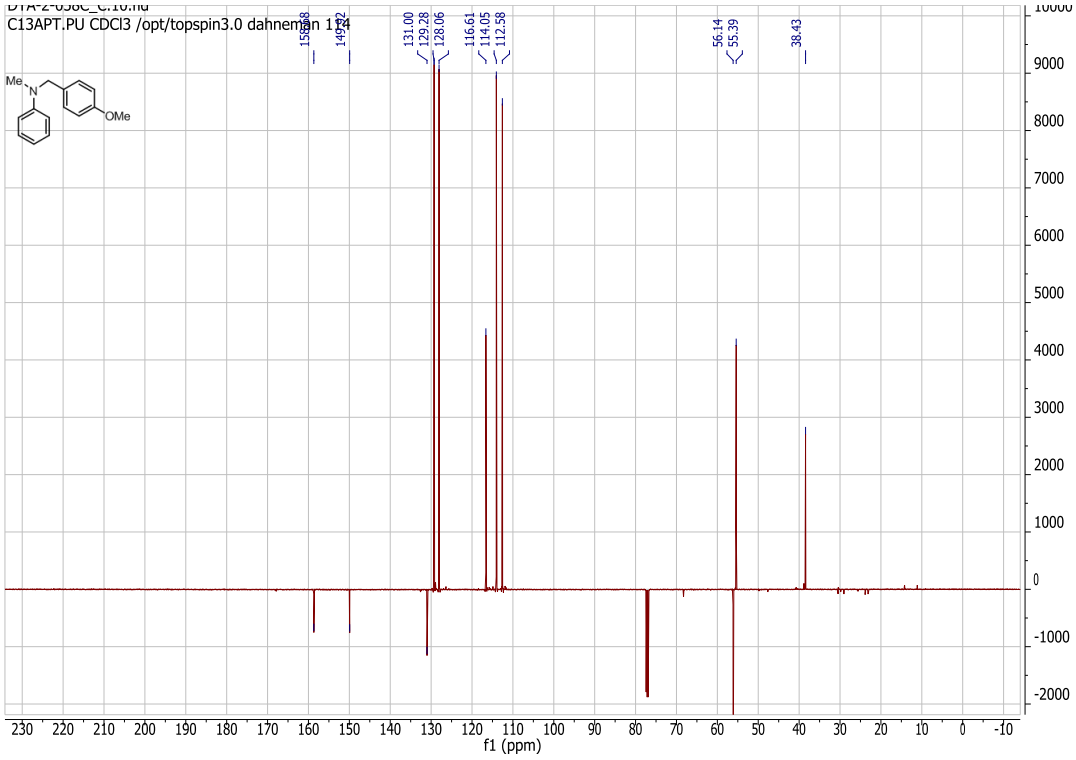
1.98
2.05
1.11
2.00
2.97
3.00
f1 (ppm)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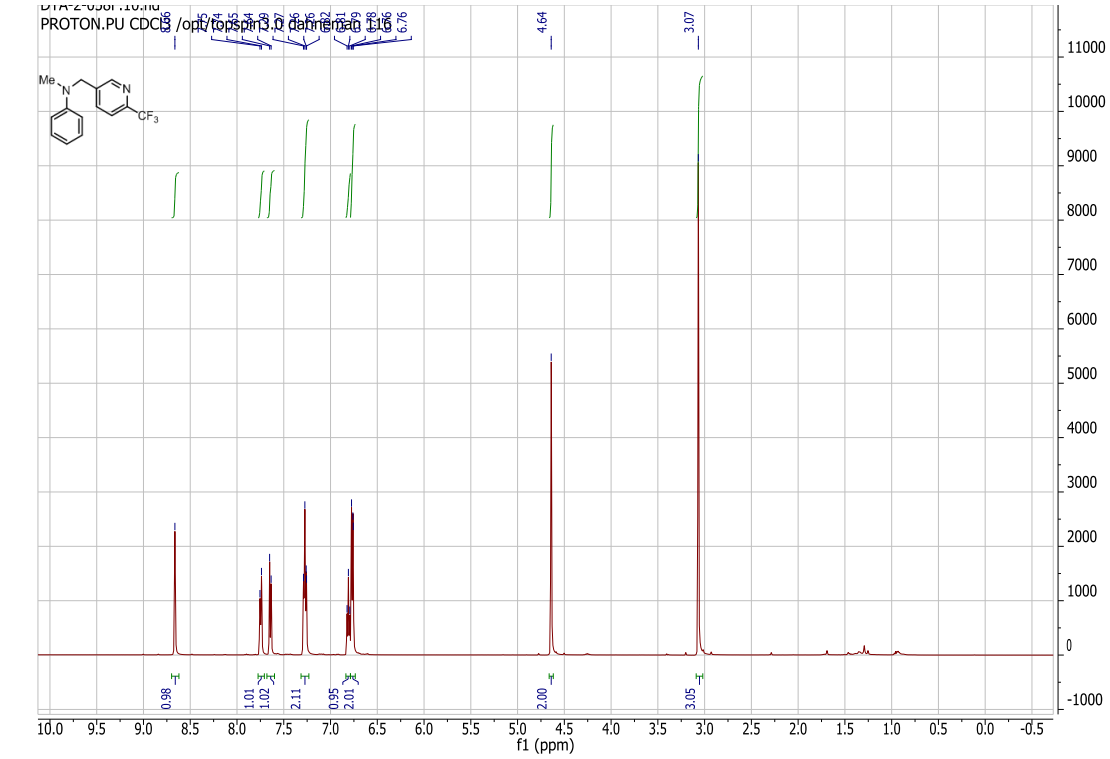
38.43
f1 (ppm)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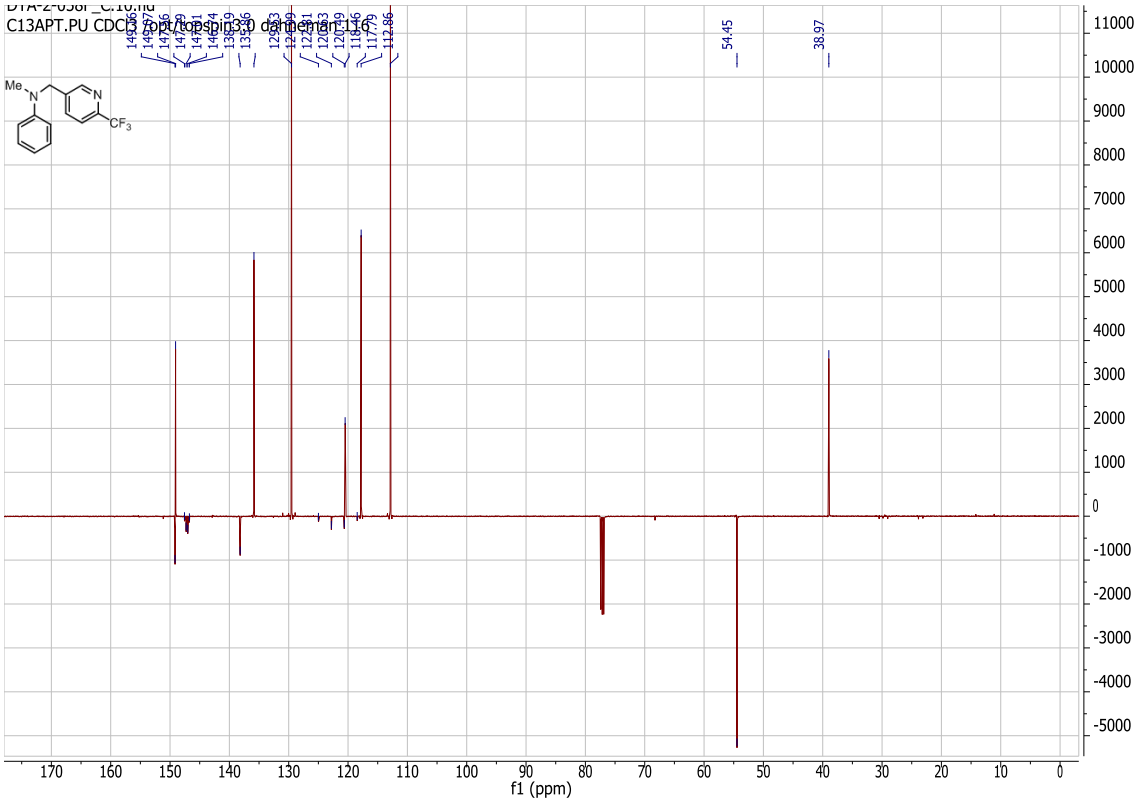
2.00
3.05
f1 (ppm)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38.97
f1 (ppm)

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