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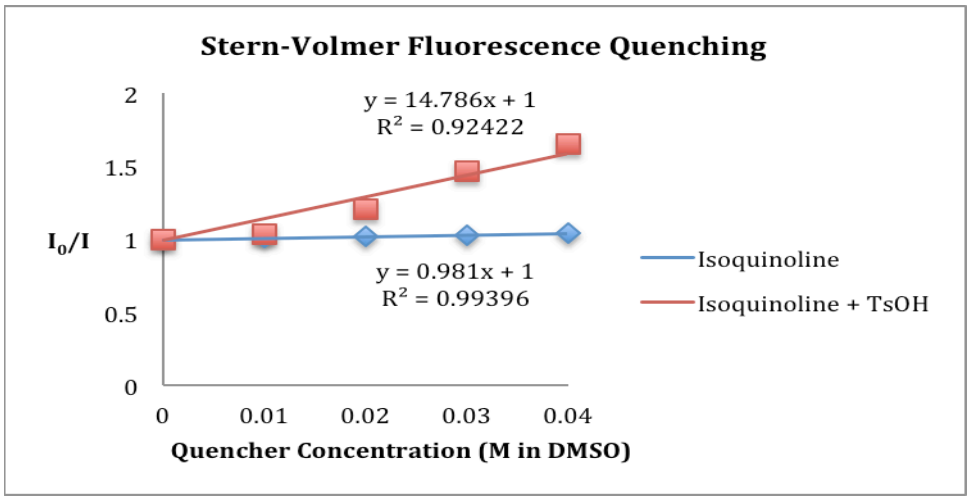
I. General Information

Commercial reagents, photocatalysts, thiol catalysts, *p*-toluenesulfonic acid monohydrate (TsOH), and dimethyl sulfoxide (DMSO) were purchased from Sigma–Aldrich and Acros Organics, and used directly without purification. All heteroarenes and alcohols were used directly from commercial suppliers. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using an isopropyl alcohol-dry ice bath. 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 0.25 mm 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 UltraShield Plus 500 MHz (125 MHz) instrument, and are internally referenced to residual protio solvent signals (note: $CDCl_3$ referenced at 7.26 and 77.0 ppm respectively; CD_3OD referenced at 3.31 and 49.0 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, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constant (Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in wavenumbers (cm^{-1}). High resolution mass spectra were obtained at Princeton University mass spectrometry facilities on Agilent Technologies 6220 Time-Of-Flight LC/MS with electrospray ionization method.

II. Mechanistic Studies



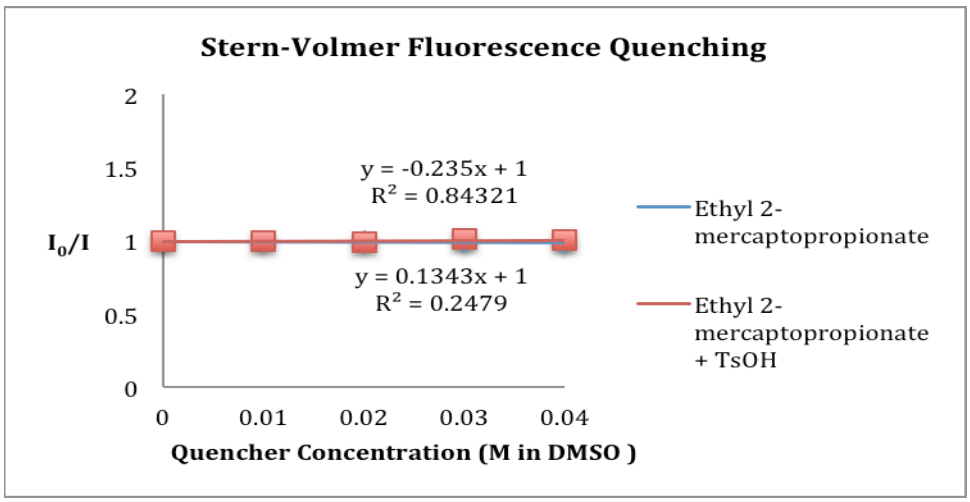
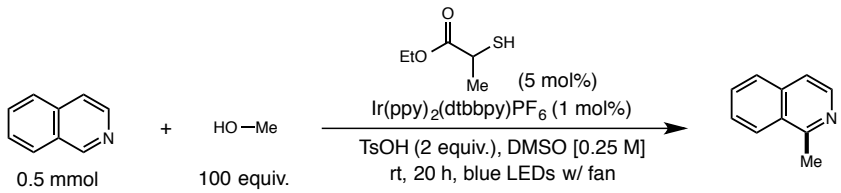


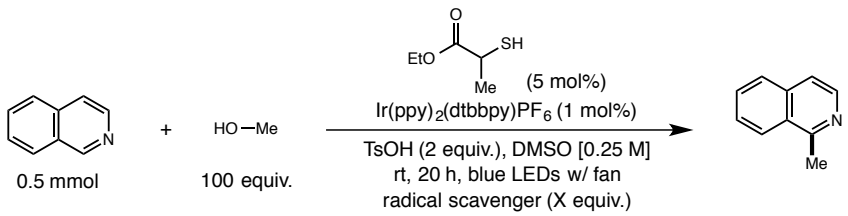
Fig. S1. Stern-Volmer quenching experiments of the heteroarene and thiol catalyst.



Entry	Control Conditions	Product
1	w/o photocatalyst	0%
2	w/o light	0%
3	w/o acid	0%
4	w/o thiol	3%
5	standard conditions, w/ all	98%

[1]H NMR yield using TsOH as the internal standard.

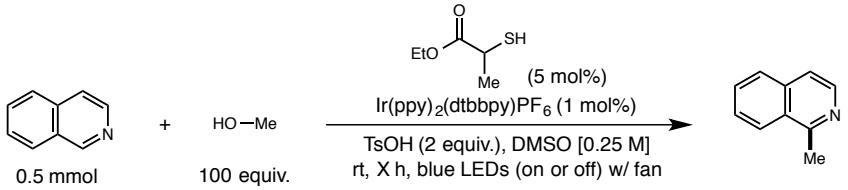
Fig. S2. Control experiments.



Entry	Radical Scavenger	Product
1	TEMPO (1.0 equiv.)	23%
2	TEMPO (2.0 equiv)	0%
3	1,1-diphenylethylene (1.0 equiv.)	0%

[1]H NMR yield using TsOH as the internal standard; TEMPO: 2,2,6,6-tetramethyl-1-piperidinyloxy.

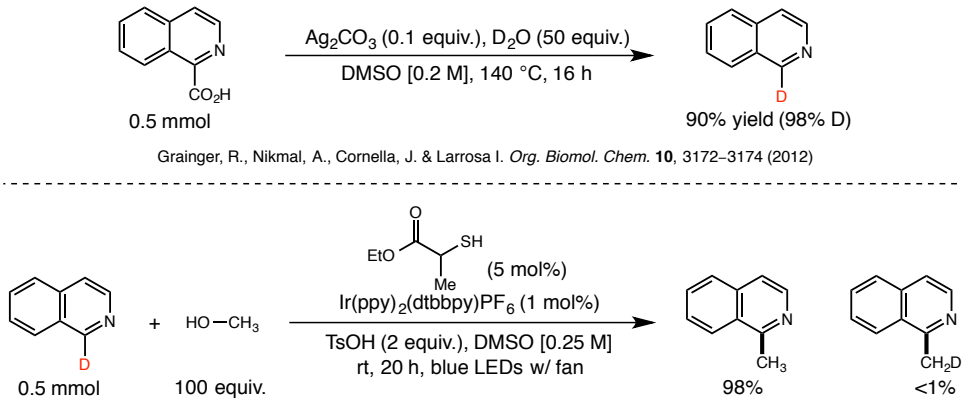
Fig. S3. Radical quenching experiments with TEMPO and 1,1-diphenylethylene.



Entry	Light On and Off Conditions	Product
1	on 4 h	28%
2	on 4 h, off 16 h	28%
3	on 20 h	98%

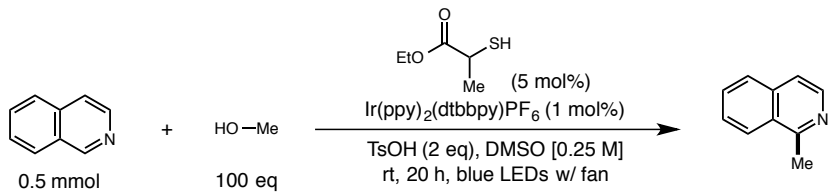
[1]H NMR yield using TsOH as the internal standard.

Fig. S4. Light on and off experiments.



[1]H NMR yield using TsOH as the internal standard, and checked with LC-MS.

Fig. S5. Deuterium-labeling experiments.



Entry	Degas Procedures	Product
1	none	56%
2	head space purging with N_2 for 15 min	98%
3	into solution sparging with N_2 for 15 min	99%
4	freeze-pump-thaw 3 times	98%

[1]H NMR yield using TsOH as the internal standard.

Fig. S6. Oxygen effect to the alkylation reaction.

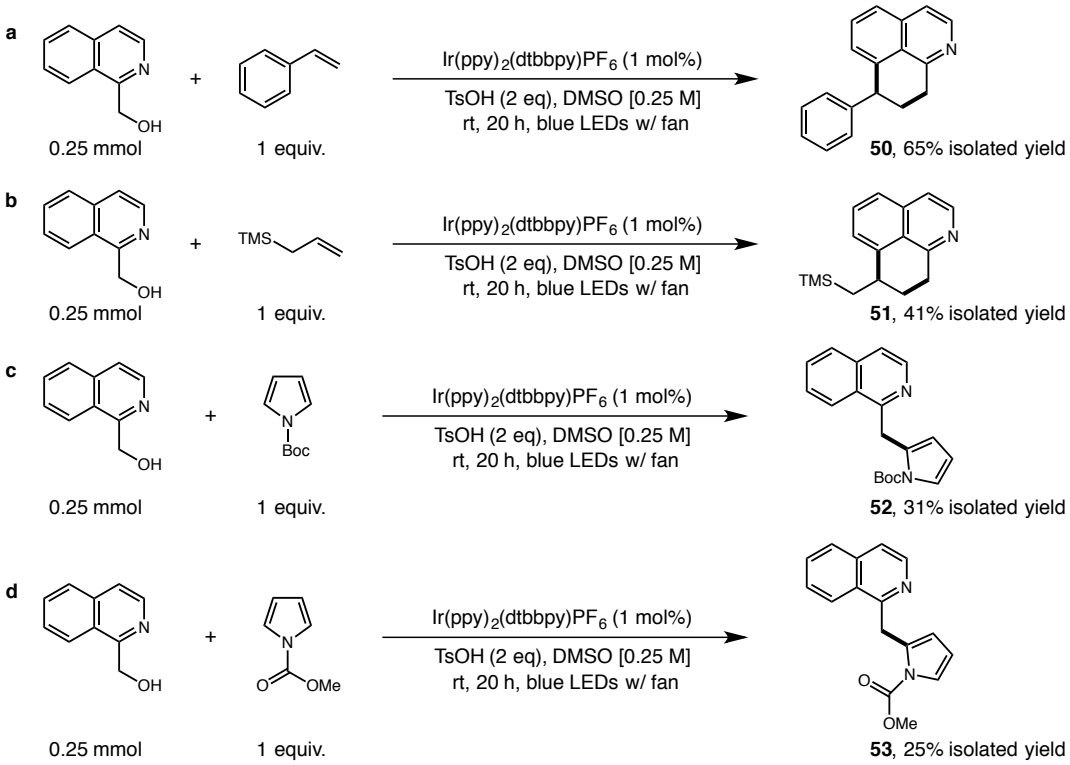


Fig. S7. Radical trapping experiments with olefins and arenes.

III. Reaction Setup

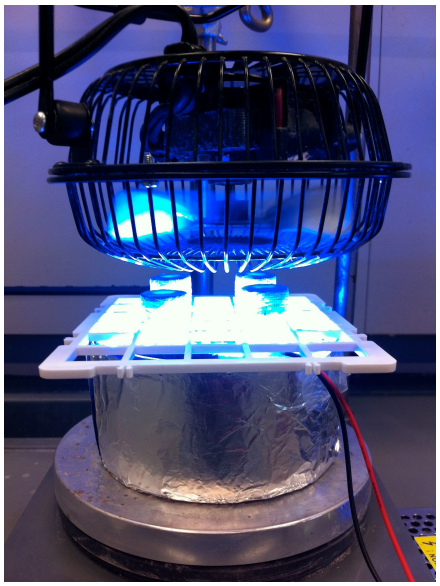
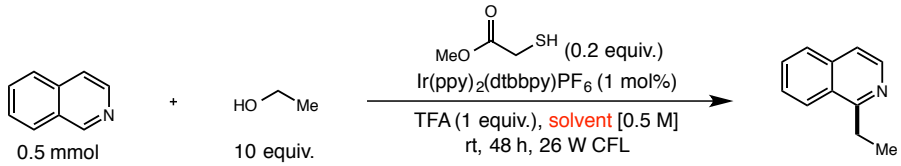


Fig. S8. Reaction setup with the magnetic stirrer, blue LED strip circled inside the glass dish (covered with aluminum foil outside), vial rack, and mini fan.

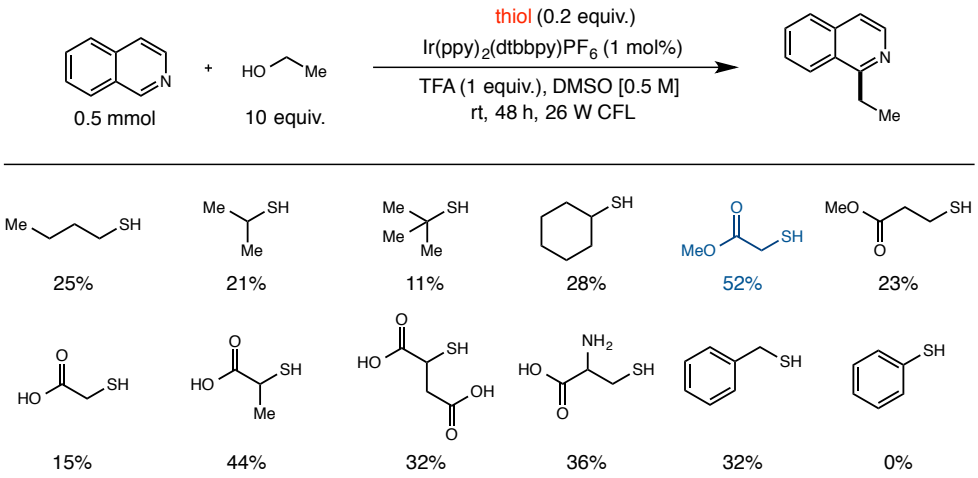
IV. Reaction optimization



Entry	Solvent	Product
1	acetonitrile	16%
2	propionitrile	22%
3	*N,N*-dimethylacetamide	31%
4	*N,N*-dimethylformamide	33%
5	dimethyl sulfoxide (DMSO)	56%
6	dichloromethane	20%
7	1,2-dichloroethane	21%
8	chloroform	29%
9	1,2-dimethoxyethane	19%
10	ethyl acetate	16%
11	toluene	10%
12	acetone	13%

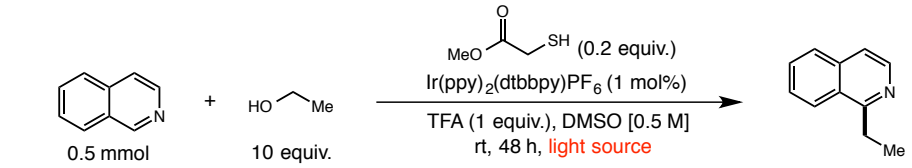
^{1}H NMR yield using 1,3-benzodioxole as the internal standard.

Fig. S9. Solvent evaluation.



[1]H NMR yield using 1,3-benzodioxole as the internal standard.

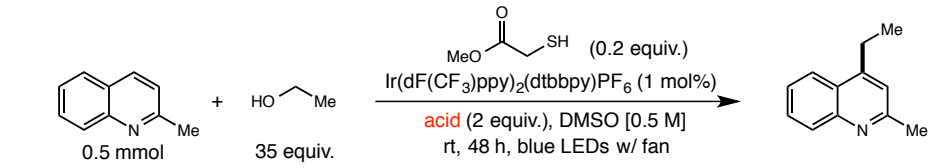
Fig. S10. Organocatalyst evaluation.



Entry	Light Source	Photocatalyst	Product
1	26 W CFL w/ fan, 23 °C	1 mol%	51%
2	26 W CFL w/o fan, 29 °C	1 mol%	62%
3	blue LEDs w/ fan, 23 °C	1 mol%	91%
4	blue LEDs w/o fan, 45 °C	1 mol%	83%
5	2 X 34 W LED w/ fan, 40 °C	1 mol%	79%

[1]H NMR yield using 1,3-benzodioxole as the internal standard.

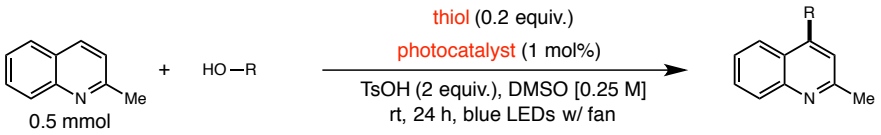
Fig. S11. Light source evaluation.

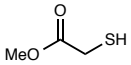
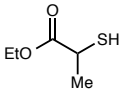
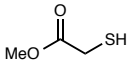
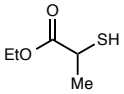


Entry	Acid	Product
1	TFA	8%
2	conc. HCl	9%
3	HBF_4 (48 wt.% in H_2O)	73%
4	$HClO_4$ (70%)	85%
5	conc. H_2SO_4	75%
6	TsOH	89%
7	TsOH (1 equiv.)	73%

[1]H NMR yield using 1,3-benzodioxole as the internal standard.

Fig. S12. Acid evaluation.



Entry	Alcohol	Thiol	Photocatalyst	Product	SM
1	MeOH 100 equiv.		$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	52%	47%
2			$Ir(ppy)_2(dtbbpy)PF_6$	75%	28%
3	MeOH 100 equiv.		$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	73%	22%
4			$Ir(ppy)_2(dtbbpy)PF_6$	95%	0%
5	EtOH 35 equiv.		$Ir(ppy)_2(dtbbpy)PF_6$	98%	0%
6	EtOH 35 equiv.		$Ir(ppy)_2(dtbbpy)PF_6$	24%	72%

^{1}H NMR yield using TsOH as the internal standard.

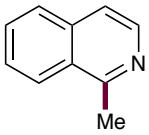
Fig. S13. Organocatalyst comparisons.

V. Experimental Procedures and Product Characterization

General Procedure A for the Alkylation (Heteroarene Scope): To an 8 mL vial equipped with a Teflon septum and a magnetic stir bar was charged $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), heteroarene (0.50 mmol, 1.0 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO. The reaction mixture was degassed by sparging with nitrogen for 10 min with an outlet needle, and added with ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), then irradiated with the blue LEDs (approximately 2 cm away from the light source) at room temperature under a mini fan. Upon reaction completion as judged by TLC and LCMS (20-48 hours), the reaction mixture was diluted with 1 M NaOH aqueous solution (2 mL) and CH_2Cl_2 (20 mL), washed with brine (3×10 mL), dried over Na_2SO_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.

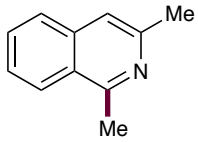
General Procedure B for the Alkylation (Alcohol Scope): To an 8 mL vial equipped with a Teflon septum and a magnetic stir bar was charged $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), alcohol (5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO. The reaction mixture was degassed by sparging with nitrogen for 10 min with an outlet needle, and added with methyl thioglycolate (2.5 μL, 25.0 μmol, 0.05 equiv.), then irradiated with the blue LEDs (approximately 2 cm away from the light source) at room temperature under a mini fan. Upon reaction completion as judged by TLC and LCMS (20-48 hours), the reaction mixture was diluted with 1 M NaOH aqueous solution (2 mL) and CH_2Cl_2 (20 mL), washed with brine (3×10 mL), dried over Na_2SO_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.



15

1-Methylisoquinoline (15): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 20 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and

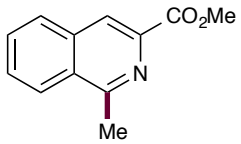
purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (65.6 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (d, J = 5.8 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.66 (dd, J = 8.1, 6.8 Hz, 1H), 7.58 (dd, J = 8.2, 6.8 Hz, 1H), 7.49 (d, J = 5.8 Hz, 1H), 2.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.5, 141.8, 135.8, 129.9, 127.4, 127.1, 127.0, 125.6, 119.2, 22.4; HRMS (ESI) m/z calculated for $C_{10}H_{10}N$ [$(M+H)^+$] 144.0808, found 144.0813. IR (film) 3051, 1622, 1562, 1390, 1357, 1241, 1020, 963 cm^{-1}. Spectra data are consistent with those reported in the literature: *Angew. Chem. Int. Ed.* **52**, 6983−6987 (2013).



16

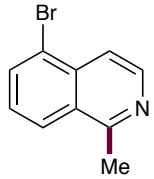
1,3-Dimethylisoquinoline (16): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 3-methylisoquinoline (73.1 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 20 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (71.5 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.60 (dd, J = 8.2, 6.7 Hz, 1H), 7.49 (dd, J = 8.2, 6.7 Hz, 1H), 7.32 (s, 1H), 2.93 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 150.2, 136.6, 129.8, 126.6, 126.0, 125.6, 125.5, 117.1, 24.2, 22.3; HRMS (ESI) m/z calculated for $C_{11}H_{12}N$ [$(M+H)^+$] 158.0964, found 158.0965. IR (film) 2919, 1625, 1591, 1567, 1441, 1391, 1361, 1182,

873 cm^{-1}. Spectra data are consistent with those reported in the literature: *Tetrahedron Lett.* **50**, 2305−2308 (2009).



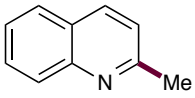
17

Methyl 1-Methylisoquinoline-3-carboxylate (17): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), methyl 3-isoquinolinecarboxylate (95.5 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 4.0 mL of MeOH and 4.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a white solid (98.5 mg, 98% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.15 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.72 (m, 2H), 4.02 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 159.3, 140.3, 135.4, 130.6, 129.3, 128.9, 128.6, 125.7, 122.9, 52.8, 22.6; HRMS (ESI) m/z calculated for $C_{12}H_{12}NO_2$ $[(M+H)^+]$ 202.0863, found 202.0866. IR (film) 2950, 1712, 1286, 1239, 1149, 1108, 1001, 902 cm^{-1}. Spectra data are consistent with those reported in the literature : *J. Org. Chem.* **79**, 7041−7050 (2014).

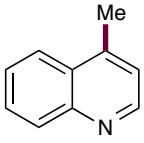


18

5-Bromo-1-methylisoquinoline (18): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 5-bromoisoquinoline (105.1 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 4.0 mL of MeOH and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (94.3 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (d, J = 6.0 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 7.5 Hz, 1H), 7.86 (d, J = 6.0 Hz, 1H), 7.43 (t, J = 7.9 Hz, 1H), 2.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 143.2, 135.1, 133.7, 128.5, 127.3, 125.3, 122.3, 118.1, 22.6; HRMS (ESI) m/z calculated for $C_{10}H_9BrN$ $[(M+H)^+]$ 221.9913, found 221.9912. IR (film) 3038, 1575, 1485, 1401, 1342, 1220, 1076, 829 cm^{-1}.



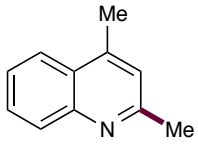
19a and



19b

2-Methylquinoline (19a) and 4-Methylquinoline (19b): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), quinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 4.0 mL of MeOH and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% ethyl acetate/hexanes) to provide the title compounds as colorless oils (30.8 mg, 43% yield for **19a**; 15.8 mg, 22% yield for **19b**). Compound **19a**: ^{1}H NMR (500 MHz,

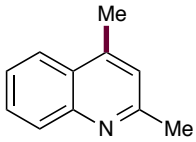
$CDCl_3$): δ 8.04 (d, *J* = 9.0 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 2.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 147.8, 136.1, 129.4, 128.6, 127.5, 126.4, 125.6, 122.0, 25.4; HRMS (ESI) m/z calculated for $C_{10}H_{10}N$ $[(M+H)^+]$ 144.0808, found 144.0813. IR (film) 3055, 1601, 1506, 1423, 1220, 1116, 1009, 819 cm^{-1}. Compound **19b**: ^1H NMR (500 MHz, $CDCl_3$): δ 8.78 (d, *J* = 4.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.71 (dd, *J* = 8.4, 6.6 Hz, 1H), 7.57 (dd, *J* = 8.2, 6.8 Hz, 1H), 7.24 (d, *J* = 4.3 Hz, 1H), 2.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.2, 148.0, 144.3, 130.0, 129.1, 128.3, 126.3, 123.8, 121.9, 18.7; HRMS (ESI) m/z calculated for $C_{10}H_{10}N$ $[(M+H)^+]$ 144.0808, found 144.0812. IR (film) 2925, 1595, 1508, 1454, 1391, 1305, 1138, 838 cm^{-1}. Spectra data are consistent with those reported in the literature: *J. Am. Chem. Soc.* **136**, 11910−11913 (2014).



20

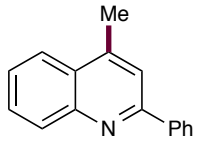
2,4-Dimethylquinoline (20): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 4-methylquinoline (67.0 μL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 20 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (74.6 mg, 95% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.66 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.49

(dd, J = 8.3, 6.8 Hz, 1H), 7.13 (s, 1H), 2.69 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6, 147.6, 144.1, 129.1, 129.0, 126.5, 125.3, 123.5, 122.6, 25.2, 18.5; HRMS (ESI) m/z calculated for $C_{11}H_{12}N$ [$(M+H)^+$] 158.0964, found 158.0967. IR (film) 2920, 1602, 1562, 1446, 1372, 1192, 1025, 858 cm^{-1}. Spectra data are consistent with those reported in the literature: *Org. Lett.* **10**, 173−175 (2008).



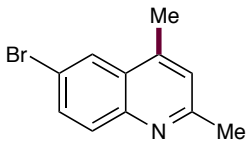
21

2,4-Dimethylquinoline (21): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 2-methylquinoline (66.0 μL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 20 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (73.1 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.66 (dd, J = 8.5, 6.8 Hz, 1H), 7.48 (dd, J = 8.3, 6.8 Hz, 1H), 7.11 (s, 1H), 2.68 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6, 147.7, 144.1, 129.1, 129.0, 126.5, 125.3, 123.5, 122.7, 25.2, 18.5; HRMS (ESI) m/z calculated for $C_{11}H_{12}N$ [$(M+H)^+$] 158.0964, found 158.0964. IR (film) 2919, 1602, 1562, 1445, 1372, 1192, 1035, 858 cm^{-1}. Spectra data are consistent with those reported in the literature: *Org. Lett.* **10**, 173−175 (2008).



22

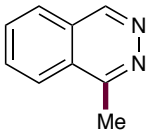
4-Methyl-2-phenylquinoline (22): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 2-phenylquinoline (103.7 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 4.0 mL of MeOH and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% ethyl acetate/hexanes) to provide the title compound as a white solid (99.9 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, J = 8.3 Hz, 1H), 8.17 (m, 2H), 7.99 (d, J = 8.3 Hz, 1H), 7.73 (t, J = 7.0 Hz, 1H), 7.71 (s, 1H), 7.55 (t, J = 7.0 Hz, 1H), 7.53 (m, 2H), 7.47 (m, 1H), 2.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.0, 148.1, 144.7, 139.8, 130.2, 129.3, 129.1, 128.7 (2C), 127.5 (2C), 127.2, 126.0, 123.6, 119.7, 19.0; HRMS (ESI) m/z calculated for $C_{16}H_{14}N$ [$(M+H)^+$] 220.1121, found 220.1121. IR (film) 3059, 1596, 1550, 1495, 1450, 1347, 1028, 861 cm^{-1}. Spectra data are consistent with those reported in the literature: *J. Am. Chem. Soc.* **136**, 11910−11913 (2014).



23

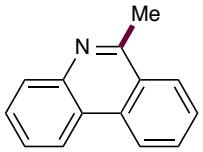
6-Bromo-2,4-dimethylquinoline (23): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 6-bromo-2-methylquinoline (115.0 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 4.0 mL of MeOH and 2.0 mL of

DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a white solid (105.0 mg, 89% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.85 (d, J = 8.9 Hz, 1H), 7.71 (dd, J = 8.9, 2.2 Hz, 1H), 7.12 (s, 1H), 2.66 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 146.3, 143.2, 132.4, 130.9, 127.8, 126.0, 123.4, 119.3, 25.2, 18.5; HRMS (ESI) m/z calculated for $C_{11}H_{11}BrN$ [$(M+H)^+$] 236.0069, found 236.0070. IR (film) 2915, 1600, 1496, 1370, 1337, 1216, 1071, 867 cm^{-1}.



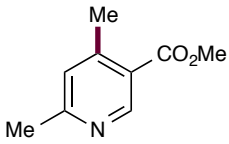
24

1-Methylphthalazine (24): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), phthalazine (66.5 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 4.0 mL of MeOH and 4.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (50% ethyl acetate/hexanes) to provide the title compound as a white solid (50.5 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.39 (s, 1H), 8.07 (d, J = 7.7 Hz, 1H), 7.87-7.93 (m, 3H), 3.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.3, 150.5, 132.4, 132.1, 126.7, 126.2, 126.1, 124.2, 19.8; HRMS (ESI) m/z calculated for $C_9H_9N_2$ [$(M+H)^+$] 145.0760, found 145.0765. IR (film) 3386, 1556, 1495, 1397, 1376, 1235, 952, 895 cm^{-1}.



25

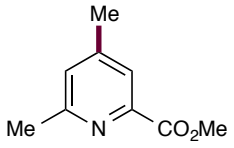
6-Methylphenanthridine (25): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), phenanthridine (91.5 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 2.0 mL of MeOH and 4.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a white solid (90.0 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.57 (d, J = 8.1 Hz, 1H), 8.50 (d, J = 8.1 Hz, 1H), 8.17 (d, J = 8.2 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.79 (t, J = 7.1 Hz, 1H), 7.70 (t, J = 7.1 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 3.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8, 143.6, 132.4, 130.4, 129.3, 128.5, 127.2, 126.4, 126.2, 125.8, 123.7, 122.2, 121.9, 23.4; HRMS (ESI) m/z calculated for $C_{14}H_{12}N$ $[(M+H)^+]$ 194.0964, found 194.0964. IR (film) 3066, 1611, 1585, 1485, 1373, 1138, 1035, 860 cm^{-1}. Spectra data are consistent with those reported in the literature: *Org. Lett.* **16**, 4642−4645 (2014).



26

Methyl 4,6-dimethylnicotinate (26): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), methyl 6-methylnicotinate (78.0 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-

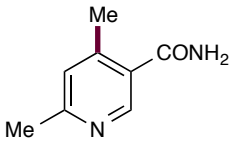
mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 20 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a white solid (67.7 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.96 (s, 1H), 7.03 (s, 1H), 3.90 (s, 3H), 2.57 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 161.8, 151.4, 149.6, 125.9, 122.9, 51.9, 24.4, 21.2; HRMS (ESI) m/z calculated for $C_9H_{12}NO_2$ $[(M+H)^+]$ 166.0863, found 166.0868. IR (film) 2953, 1720, 1600, 1439, 1281, 1169, 1089, 780 cm^{-1}. Spectra data are consistent with those reported in the literature: *J. Org. Chem.* **46**, 3040−3048 (1981).



27

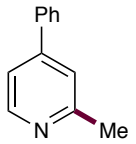
Methyl 4,6-dimethylpicolinate (27): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), methyl 6-methylpicolinate (78.0 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (66.5 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.15 (s, 1H), 3.97 (s, 3H), 2.59 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 158.7, 148.4, 147.3, 127.6,

123.5, 52.9, 24.4, 20.8; HRMS (ESI) m/z calculated for $C_9H_{12}NO_2$ $[(M+H)^+]$ 166.0863, found 166.0864. IR (film) 2953, 1718, 1607, 1438, 1332, 1237, 1196, 1017 cm^{-1}.

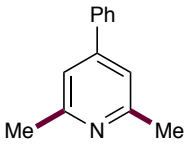


28

4,6-Dimethylnicotinamide (28): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 6-methylnicotinamide (69.5 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 4.0 mL of MeOH and 4.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% methanol/ethyl acetate, containing 0.1% triethylamine) to provide the title compound as a white solid (62.3 mg, 83% yield). ^1H NMR (500 MHz, CD_3OD): δ 8.43 (s, 1H), 7.22 (s, 1H), 4.88 (br s, 2H), 2.51 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD): δ 172.4, 160.7, 148.6, 147.7, 131.3, 126.9, 23.6, 19.6; HRMS (ESI) m/z calculated for $C_8H_{11}N_2O$ $[(M+H)^+]$ 151.0866, found 151.0867. IR (film) 3290, 3153, 1700, 1638, 1603, 1379, 1125, 860 cm^{-1}.



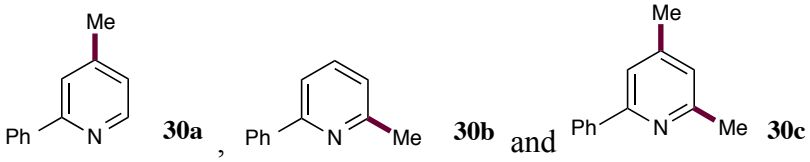
29a and



29b

2-Methyl-4-phenylpyridine (29a) and 2,6-Dimethyl-4-phenylpyridine (29b): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01

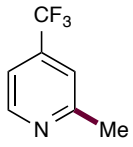
equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), (80.0 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% ethyl acetate/hexanes) to provide the title compounds as colorless oils (55.0 mg, 65% yield for **29a**; 10.8 mg, 12% yield for **29b**). Compound **29a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, J = 5.1 Hz, 1H), 7.61 (m, 2H), 7.45 (m, 2H), 7.42 (m, 1H), 7.36 (s, 1H), 7.30 (d, J = 4.9 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8, 149.5, 148.6, 138.4, 129.0 (2C), 128.8, 126.9 (2C), 121.2, 118.8, 24.5; HRMS (ESI) m/z calculated for $C_{12}H_{12}N$ [$(M+H)^+$] 170.0964, found 170.0967. IR (film) 3027, 1595, 1545, 1473, 1390, 1291, 1002, 838 cm^{-1}. Spectra data are consistent with those reported in the literature: *J. Am. Chem. Soc.* **135**, 3756−3759 (2013).



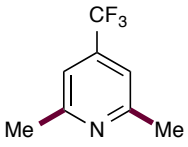
30a , **30b** and **30c**

4-Methyl-6-phenylpyridine (30a), 2-Methyl-6-phenylpyridine (30b) and 2,4-Dimethyl-6-phenylpyridine: According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 2-phenylpyridine (73.0 μL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 2.0 mL of MeOH and 2.0 mL of DMSO were used. After 20 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% ethyl acetate/hexanes) to provide the title compounds as colorless oils (51.6 mg, 61% yield for **30a**; 12.7 mg, 15% yield for

30b, 6.3 mg, 7% yield for **30c**). Compound **30a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (d, J = 5.0 Hz, 1H), 7.98 (d, J = 7.0 Hz, 2H), 7.55 (s, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 4.6 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.3, 149.4, 147.7, 139.5, 128.8, 128.6 (2C), 126.9 (2C), 123.1, 121.5, 21.2; HRMS (ESI) m/z calculated for $C_{12}H_{12}N$ [$(M+H)^+$] 170.0964, found 170.0962. IR (film) 3053, 1601, 1557, 1445, 1273, 1073, 1030, 866 cm^{-1}. Compound **30b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.7 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 2.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 157.0, 139.8, 136.8, 128.7 (3C), 127.0 (2C), 121.6, 117.6, 24.8; HRMS (ESI) m/z calculated for $C_{12}H_{12}N$ [$(M+H)^+$] 170.0964, found 170.0968, found 292.03339. IR (film) 3060, 1590, 1571, 1445, 1234, 1160, 1028, 805 cm^{-1}. Spectra data are consistent with those reported in the literature: *J. Am. Chem. Soc.* **134**, 1352−1356 (2012).



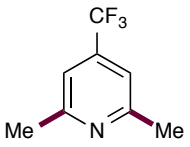
31a and



31b

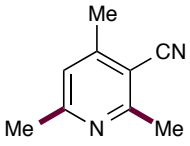
2-Methyl-4-(trifluoromethyl)pyridine (31a) and 2,6-Dimethyl-4-(trifluoromethyl)pyridine (31b): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 4-(trifluoromethyl)pyridine (60.0 μL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 4.0 mL of MeOH and 4.0 mL of DMSO were used. After 48 hours, the reaction mixture was checked by ^{1}H NMR using

TsOH as the internal standard (56% yield for **31a**; 25% yield for **31b**). The products are too volatile to isolated by routine procedure.



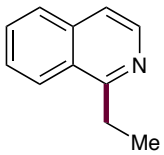
31b

2,6-Dimethyl-4-(trifluoromethyl)pyridine (31b): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 4-(trifluoromethyl)pyridine (60.0 μL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (14.0 μL, 0.1 mmol, 0.20 equiv.), 6.0 mL of MeOH and 6.0 mL of DMSO were used. (Caution: volatile product). After 48 hours, the reaction mixture was added with 3 mL of 2 M NaOH aqueous solution and heated at 50 °C for 3 hours (or stirred at room temperature for 24 hours) and then cooled down to room temperature, diluted with CH_2Cl_2 (20 mL), washed with brine (3×10 mL), dried over Na_2SO_4, and concentrated *in vacuo* with ice water bath carefully. The residue was purified by flash chromatography (dichloromethane) to provide the title compound as a colorless oil (71.0 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (s, 2H), 2.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2 (2C), 138.8 (q), 123.0 (q), 115.8 (q, 2C), 24.5 (2C); ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.9 (s); HRMS (ESI) m/z calculated for $C_8H_9F_3N$ $[(M+H)^+]$ 176.0682, found 176.0681. IR (film) 2929, 1582, 1388, 1350, 1235, 1129, 1107, 863 cm^{-1}.



32

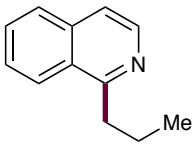
2,4,6-Trimethylnicotinonitrile (32): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), 4-methylnicotinonitrile (61.0 mg, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 μL, 25.0 μmol, 0.05 equiv.), 4.0 mL of MeOH and 4.0 mL of DMSO were used. (Caution: volatile product). After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% dichloromethane/hexanes) to provide the title compound as a white solid (66.5 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.95 (s, 1H), 2.71 (s, 3H), 2.53 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.3, 161.2, 151.2, 121.7, 116.6, 107.0, 24.7, 23.7, 20.3; HRMS (ESI) m/z calculated for $C_9H_{11}N_2$ $[(M+H)^+]$ 147.0917, found 147.0915. IR (film) 2926, 2219, 1606, 1556, 1449, 1374, 1320, 1028 cm^{-1}.



33

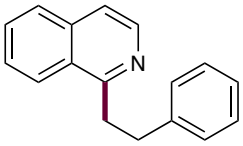
1-Ethylisoquinoline (33): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 μL, 25.0 μmol, 0.05 equiv.), ethanol (0.30 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 24 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (74.6 mg, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (d, J = 5.7 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.64 (dd, J =

7.8, 6.8 Hz, 1H), 7.56 (dd, J = 7.7, 6.8 Hz, 1H), 7.48 (d, J = 5.7 Hz, 1H), 3.32 (q, J = 7.6 Hz, 2H), 1.44 (t, J = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0, 141.8, 136.1, 129.7, 127.3, 126.9, 126.6, 125.1, 119.1, 28.4, 13.5; HRMS (ESI) m/z calculated for $C_{11}H_{12}N$ [$(M+H)^+$] 158.0964, found 158.0968. IR (film) 2971, 2934, 1621, 1561, 1501, 1385, 1006, 869 cm^{-1}.



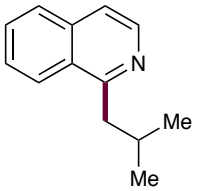
34

1-Propylisoquinoline (34): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 μL, 25.0 μmol, 0.05 equiv.), 1-propanol (0.38 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 24 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (82.2 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42 (d, J = 5.7 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.57 (dd, J = 7.7, 6.8 Hz, 1H), 7.48 (d, J = 5.8 Hz, 1H), 3.27 (t, J = 7.8 Hz, 2H), 1.90 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.1, 141.8, 136.2, 129.7, 127.3, 126.9, 126.8, 125.3, 119.1, 37.4, 23.0, 14.3; HRMS (ESI) m/z calculated for $C_{12}H_{14}N$ [$(M+H)^+$] 172.1121, found 172.1126. IR (film) 2959, 2870, 1622, 1561, 1501, 1386, 1009, 863 cm^{-1}.



35

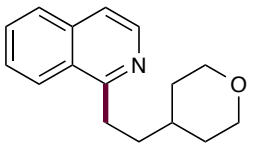
1-Phenethylisoquinoline (35): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 μL, 25.0 μmol, 0.05 equiv.), 2-phenylethanol (0.60 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% ethyl acetate/hexanes) to provide the title compound as a colorless oil (106.2 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (d, J = 5.6 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 7.55 (d, J = 5.7 Hz, 1H), 7.32 (m, 4H), 7.23 (m, 1H), 3.62 (t, J = 8.3 Hz, 2H), 3.21 (t, J = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.0, 141.8, 141.7, 136.2, 129.9, 128.5 (2C), 128.4 (2C), 127.4, 127.1, 126.9, 126.0, 125.0, 119.4, 37.2, 35.5; HRMS (ESI) m/z calculated for $C_{17}H_{16}N$ $[(M+H)^+]$ 234.1277, found 234.1277. IR (film) 3025, 1621, 1561, 1494, 1452, 1387, 1357, 821 cm^{-1}.



36

1-Isobutylisoquinoline (36): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 μL, 25.0 μmol, 0.05 equiv.),

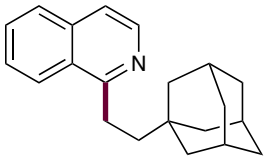
isobutanol (0.46 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (85.6 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (d, *J* = 5.7 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 5.7 Hz, 1H), 3.18 (d, *J* = 7.3 Hz, 2H), 2.29 (m, 1H), 1.00 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.6, 141.6, 136.3, 129.8, 127.4, 127.3, 126.9, 125.6, 119.2, 44.1, 29.6, 22.8 (2C); HRMS (ESI) m/z calculated for $C_{13}H_{16}N$ [$(M+H)^+$] 186.1277, found 186.1278. IR (film) 2955, 2867, 1623, 1585, 1561, 1463, 1383, 1165 cm^{-1}.



37

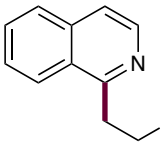
1-(2-(tetrahydro-2*H*-pyran-4-yl)ethyl)isoquinoline (37): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (5.0 μL, 50.0 μmol, 0.10 equiv.), 2-(tetrahydro-2*H*-pyran-4-yl)ethanol (0.65 g, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (108.6 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42 (d, *J* = 5.7 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 5.7 Hz, 1H), 3.98 (dd, *J* = 11.1, 4.0 Hz, 2H), 3.40 (td, *J* = 11.8, 2.0 Hz,

2H), 3.32 (m, 2H), 1.82 (m, 2H), 1.74 (d, J = 13.7 Hz, 2H), 1.67 (m, 1H), 1.40 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0, 141.7, 136.3, 129.9, 127.5, 127.1, 126.8, 125.1, 119.3, 68.1(2C), 36.6, 35.2, 33.0(2C), 32.3; HRMS (ESI) m/z calculated for $C_{16}H_{20}NO$ [$(M+H)^+$] 242.1539, found 242.1539. IR (film) 2918, 2840, 1622, 1562, 1443, 1386, 1233, 1135, 1016 cm^{-1}.



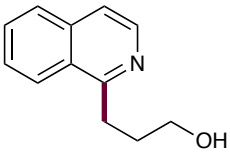
38

1-(2-(adamantan-1-yl)ethyl)isoquinoline (38): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 μL, 25.0 μmol, 0.05 equiv.), 1-adamantaneethanol (460.0 mg, 2.50 mmol, 5.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% ethyl acetate/hexanes) to provide the title compound as a white solid (134.0 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42 (d, J = 5.7 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.59 (, J = 7.6 Hz, 1H), 7.49 (d, J = 5.8 Hz, 1H), 3.27 (m, 2H), 2.02 (s, 3H), 1.72 (m, 6H), 1.66 (s, 6H), 1.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.3, 141.6, 136.3, 129.9, 127.4, 127.0, 126.8, 125.4, 119.2, 44.3, 42.3 (3C), 37.2 (3C), 32.7, 28.9, 28.7 (3C); HRMS (ESI) m/z calculated for $C_{21}H_{26}N$ [$(M+H)^+$] 292.2060, found 292.2060. IR (film) 2905, 2843, 1621, 1561, 1451, 1387, 1357, 820 cm^{-1}.



39

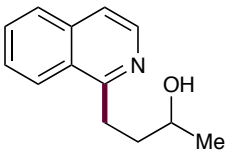
1-(3,3,3-trifluoropropyl)isoquinoline (39): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), 2,2,2-trifluoroethanethiol (2.5 μL, 25.0 μmol, 0.05 equiv., volatile, added after the reaction mixture was degassed), 3,3,3-trifluoropropanol (0.46 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (104.5 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (d, J = 5.7 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.56 (d, J = 5.7 Hz, 1H), 3.56 (m, 2H), 2.80 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.7, 141.6, 136.1, 130.1, 128.4, 127.5, 126.8, 126.3, 124.4, 119.9, 32.1 (q), 26.8 (q); ^{19}F NMR (376 MHz, $CDCl_3$): δ -66.5 (t, J = 10.9 Hz); HRMS (ESI) m/z calculated for $C_{12}H_{11}F_3N$ $[(M+H)^+]$ 226.0838, found 226.0838. IR (film) 3056, 1566, 1377, 1346, 1245, 1129, 1102, 977 cm^{-1}.



40

3-(Isoquinolin-1-yl)propan-1-ol (40): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 μL, 25.0 μmol, 0.05 equiv.), 1,3-propanediol (0.37 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of

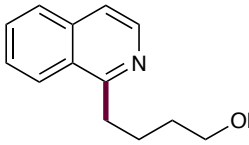
DMSO were used. After 24 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (80% ethyl acetate/hexanes) to provide the title compound as a colorless oil (82.3 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (d, J = 5.7 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.52 (d, J = 5.8 Hz, 1H), 4.48 (br s, 1H), 3.75 (t, J = 5.7 Hz, 2H), 3.50 (t, J = 6.9 Hz, 2H), 2.16 (p, J = 6.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.4, 140.9, 136.2, 130.2, 127.4, 127.3, 126.9, 125.2, 119.6, 62.2, 31.9, 30.9; HRMS (ESI) m/z calculated for $C_{12}H_{14}NO$ $[(M+H)^+]$ 188.1070, found 188.1068. IR (film) 3250, 2930, 1622, 1561, 1503, 1388, 1056, 1009 cm^{-1}.



41

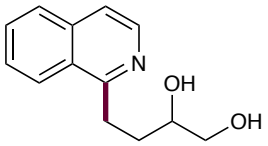
4-(Isoquinolin-1-yl)butan-2-ol (41): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (35.0 μL, 0.25 mmol, 0.50 equiv.), 1,3-butanediol (0.46 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 72 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (10% ethyl acetate/hexanes) to provide the title compound as a colorless oil (81.5 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, J = 5.7 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.53 (d, J = 5.7 Hz, 1H), 4.22 (br s, 1H), 3.86 (m, 1H), 3.51 (t, J = 7.0 Hz, 2H), 2.03 (m,

2H), 1.25 (d, J = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.6, 140.9, 136.3, 130.2, 127.4, 127.3, 126.9, 125.2, 119.6, 67.3, 37.2, 31.3, 23.5; HRMS (ESI) m/z calculated for $C_{13}H_{16}NO$ [$(M+H)^+$] 202.1226, found 202.1227. IR (film) 3301, 2964, 1623, 1562, 1503, 1388, 1127, 823 cm^{-1}.



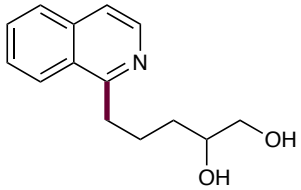
42

4-(Isoquinolin-1-yl)butan-1-ol (42): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), methyl thioglycolate (2.5 μL, 25.0 μmol, 0.05 equiv.), tetrahydrofuran (0.40 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 24 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (80% ethyl acetate/hexanes) to provide the title compound as a colorless oil (90.5 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (d, J = 5.7 Hz, 1H), 8.15 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.7 Hz, 1H), 7.49 (d, J = 5.6 Hz, 1H), 3.71 (t, J = 6.3 Hz, 2H), 3.58 (br s, 1H), 3.34 (t, J = 7.6 Hz, 2H), 1.98 (p, J = 7.4 Hz, 2H), 1.73 (p, J = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.8, 141.2, 136.2, 130.0, 127.3, 127.1, 126.9, 125.2, 119.4, 62.0, 34.2, 32.3, 25.3; HRMS (ESI) m/z calculated for $C_{13}H_{16}NO$ [$(M+H)^+$] 202.1226, found 202.1225. IR (film) 3265, 2931, 1622, 1561, 1503, 1388, 1059, 1013 cm^{-1}.



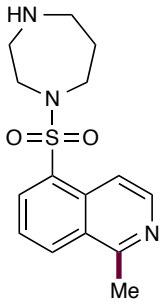
43

4-(Isoquinolin-1-yl)butane-1,2-diol (43): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (7.0 μL, 0.05 mmol, 0.10 equiv.), 3-hydroxytetrahydrofuran (0.42 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution (2 mL) and CH_2Cl_2 (20 mL), washed with brine (3×10 mL). The aqueous phase was extracted with CH_2Cl_2 (3×20 mL). The combined organic phase was then dried over Na_2SO_4, and concentrated *in vacuo*. and purified by flash chromatography (5% methanol/ethyl acetate) to provide the title compound as a white solid (78.3 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, J = 5.7 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.50 (d, J = 5.7 Hz, 1H), 5.51 (br s, 1H), 3.90-3.40 (br s, 1H), 3.81 (m, 1H), 3.66 (dd, J = 11.2, 3.6 Hz, 1H), 3.57 (dd, J = 11.1, 6.7 Hz, 1H), 3.51 (t, J = 6.9 Hz, 2H), 2.06 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.3, 140.7, 136.2, 130.3, 127.4, 127.3, 126.9, 125.2, 119.7, 71.7, 66.6, 31.4, 30.9; HRMS (ESI) m/z calculated for $C_{13}H_{16}NO_2$ $[(M+H)^+]$ 218.1176, found 218.1175. IR (film) 3325, 3091, 2849, 1559, 1388, 1100, 1038, 1015 cm^{-1}.



44

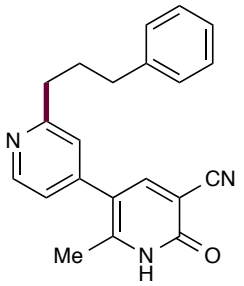
5-(Isoquinolin-1-yl)pentane-1,2-diol (44): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv.), TsOH (190.2 mg, 1.00 mmol, 2.0 equiv.), isoquinoline (61.0 μL, 0.50 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (7.0 μL, 0.05 mmol, 0.10 equiv.), tetrahydrofurfuryl alcohol (0.50 mL, 5.00 mmol, 10.0 equiv.) and 2.0 mL of DMSO were used. After 48 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution (2 mL) and CH_2Cl_2 (20 mL), washed with brine (3×10 mL). The aqueous phase was extracted with CH_2Cl_2 (3×20 mL). The combined organic phase was then dried over Na_2SO_4, and concentrated *in vacuo*. and purified by flash chromatography (5% methanol/ethyl acetate) to provide the title compound as a colorless oil (89.0 mg, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36 (d, J = 5.7 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 7.51 (d, J = 5.8 Hz, 1H), 3.90-3.40 (br s, 2H), 3.80 (m, 1H), 3.65 (dd, J = 11.2, 3.3 Hz, 1H), 3.51 (dd, J = 11.1, 7.2 Hz, 1H), 3.37 (m, 2H), 2.04 (m, 2H), 1.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.5, 140.9, 136.3, 130.2, 127.4, 127.3, 127.0, 125.2, 119.6, 71.5, 66.8, 33.9, 32.6, 24.6; HRMS (ESI) m/z calculated for $C_{14}H_{18}NO_2$ $[(M+H)^+]$ 232.1332, found 232.1333. IR (film) 3309, 2924, 1562, 1388, 1264, 1103, 1053, 822 cm^{-1}



45

1-Methylfasudil (45): According to the general procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 2.5 μmol, 0.01 equiv.), TsOH (95.1 mg, 0.50 mmol, 2.0 equiv.), fasudil

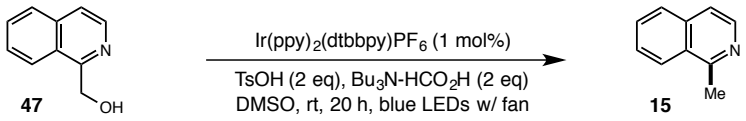
dihydrochloride (93.0 mg, 0.25 mmol, 1.0 equiv.), ethyl 2-mercaptopropionate (3.5 µL, 25.0 µmol, 0.10 equiv.), 4.0 mL of MeOH and 1.0 mL of DMSO were used. After 24 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5% methanol/ethyl acetate) to provide the title compound as a colorless oil (62.5 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.51 (d, J = 6.2 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H), 8.29 (d, J = 7.0 Hz, 1H), 7.64 (t, J = 7.9 Hz, 1H), 3.47 (t, J = 6.2 Hz, 2H), 3.42 (t, J = 5.4 Hz, 2H), 3.00 (s, 3H), 2.95 (t, J = 5.4 Hz, 2H), 2.92 (t, J = 6.2 Hz, 2H), 2.12 (br s, 1H), 1.81 (p, J = 6.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.4, 143.7, 135.0, 132.5, 131.8, 131.1, 128.1, 125.4, 116.0, 51.1, 50.2, 47.6, 47.3, 31.1, 23.1; HRMS (ESI) m/z calculated for $C_{15}H_{20}N_3O_2S$ [$(M+H)^+$] 306.1271, found 306.1270. IR (film) 2932, 1611, 1561, 1317, 1144, 1023, 978, 903 cm^{-1}.



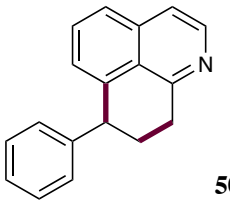
46

2-(3-Phenylpropyl)milrinone (46): According to the general procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 2.5 µmol, 0.01 equiv.), TsOH (95.1 mg, 0.50 mmol, 2.0 equiv.), milrinone (53.9 mg, 0.25 mmol, 1.0 equiv.), methyl thioglycolate (2.5 µL, 25.0 µmol, 0.10 equiv.), 3-phenyl-1-propanol (0.35 mL, 2.5 mmol, 10.0 equiv) and 1.0 mL of DMSO were used. After 72 hours, the reaction mixture was subjected to the workup procedure outlined in the general procedure and purified by flash chromatography (5%

methanol/ethyl acetate) to provide the title compound as a white solid (35.3 mg, 43% yield). ^{1}H NMR (500 MHz, CD_3OD): δ 8.49 (d, J = 5.1 Hz, 1H), 8.05 (s, 1H), 7.29 (s, 1H), 7.25 (d, J = 5.1 Hz, 1H), 7.24 (m, 2H), 7.19 (m, 2H), 7.13 (m, 1H), 2.86 (t, J = 7.8 Hz, 2H), 2.69 (t, J = 7.7 Hz, 2H), 2.36 (s, 3H), 2.06 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD): δ 163.7, 162.6, 152.5, 151.0, 150.0, 146.9, 143.2, 129.5(2C), 129.4(2C), 126.9, 125.0, 123.2, 118.8, 116.5, 102.7, 38.4, 36.6, 32.9, 18.6; HRMS (ESI) m/z calculated for $C_{21}H_{20}N_3O$ [$(M+H)^+$] 330.1601, found 330.1601. IR (film) 2925, 2225, 1656, 1599, 1567, 1483, 1173, 1030, 910 cm^{-1}.

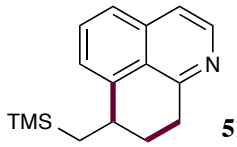


Reduction of 1-(Hydroxymethyl)isoquinoline via Photoredox Catalysis: To an 8 mL vial equipped with a Teflon septum and a magnetic stir bar was charged $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 2.5 μmol, 0.01 equiv.), TsOH (95.1 mg, 0.50 mmol, 2.0 equiv.), 1-(hydroxymethyl)isoquinoline (40.1 mg, 0.25 mmol, 1.0 equiv.), Bu_3N (120 μL, 0.50 mmol, 2.0 equiv.), HCO_2H (21 μL, 0.50 mmol, 2.0 equiv.) and 1.0 mL of DMSO. The reaction mixture was degassed by sparging with nitrogen for 10 min with an outlet needle, then irradiated with the blue LEDs (approximately 2 cm away from the light source) at room temperature under a mini fan. After 20 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution (1 mL) and CH_2Cl_2 (20 mL), washed with brine (3×10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel (20% ethyl acetate/hexanes) to provide 1-methylisoquinoline as a colorless oil (21.5 mg, 60% yield).



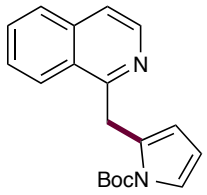
50

7-Phenyl-8,9-dihydro-7*H*-benzo[de]quinoline (50): To an 8 mL vial equipped with a Teflon septum and a magnetic stir bar was charged $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 2.5 μmol, 0.01 equiv.), TsOH (95.1 mg, 0.50 mmol, 2.0 equiv.), 1-(hydroxymethyl)isoquinoline (40.1 mg, 0.25 mmol, 1.0 equiv.), styrene (30 μL, 0.25 mmol, 1.0 equiv.) and 1.0 mL of DMSO. The reaction mixture was degassed by sparging with nitrogen for 10 min with an outlet needle, then irradiated with the blue LEDs (approximately 2 cm away from the light source) at room temperature under a mini fan. After 20 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution (1 mL) and CH_2Cl_2 (20 mL), washed with brine (3×10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (39.8 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (d, J = 5.8 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.58-7.53 (m, 2H), 7.32 (m, 2H), 7.27(m. 1H), 7.11 (m, 2H), 7.09 (d, J = 7.2 Hz, 1H), 4.44 (dd, J = 8.3, 4.5 Hz, 1H), 3.30 (t, J = 6.3 Hz, 2H), 2.49 (m, 1H), 2.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 144.3, 141.5, 140.9, 136.1, 130.3, 128.6(2C), 128.5(2C), 126.6, 126.4, 125.3, 125.0, 119.1, 46.0, 32.0, 31.5; HRMS (ESI) m/z calculated for $C_{18}H_{16}N$ [$(M+H)^+$] 246.1277, found 246.1277. IR (film) 3052, 2927, 1613, 1571, 1492, 1345, 1265, 1026, 838 cm^{-1}.



51

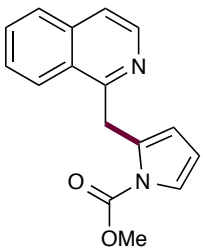
7-((Trimethylsilyl)methyl)-8,9-dihydro-7*H*-benzo[de]quinoline (51): Following the procedure for compound **50**, $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 2.5 μmol, 0.01 equiv.), TsOH (95.1 mg, 0.50 mmol, 2.0 equiv.), 1-(hydroxymethyl)isoquinoline (40.1 mg, 0.25 mmol, 1.0 equiv.), allyltrimethylsilane (41 μL, 0.25 mmol, 1.0 equiv.) and 1.0 mL of DMSO were used. After 20 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution (1 mL) and CH_2Cl_2 (20 mL), washed with brine (3×10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (26.2 mg, 41% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, J = 5.8 Hz, 1H), 7.63-7.56 (m, 2H), 7.47 (d, J = 5.7 Hz, 1H), 7.37 (d, J = 6.6 Hz, 1H), 3.40 (m, 1H), 3.30 (m, 1H), 3.19 (m, 1H), 2.25 (m, 1H), 2.05 (m, 1H), 1.03 (d, J = 7.5 Hz, 2H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.5, 145.1, 141.7, 136.2, 130.1, 124.3, 124.2, 124.0, 118.9, 35.3, 30.3, 29.6, 23.7, -0.6(3C); HRMS (ESI) m/z calculated for $C_{16}H_{22}NSi$ $[(M+H)^+]$ 256.1516, found 256.1517. IR (film) 3049, 2949, 1616, 1572, 1387, 1344, 1246, 1028, 856 cm^{-1}.



52

Tert-butyl 2-(isoquinolin-1-ylmethyl)-1*H*-pyrrole-1-carboxylate (52): Following the procedure for compound **50**, $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 2.5 μmol, 0.01 equiv.), TsOH

(95.1 mg, 0.50 mmol, 2.0 equiv.), 1-(hydroxymethyl)isoquinoline (40.1 mg, 0.25 mmol, 1.0 equiv.), *N*-Boc-pyrrole (43 μL, 0.25 mmol, 1.0 equiv.) and 1.0 mL of DMSO were used. After 20 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution (1 mL) and CH_2Cl_2 (20 mL), washed with brine (3×10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (24.0 mg, 31% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (d, J = 5.8 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.3 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.9 Hz, 1H), 7.56 (d, J = 6.2 Hz, 1H), 7.31 (m, 1H), 6.04 (t, J = 3.4 Hz, 1H), 5.54 (m, 1H), 4.90 (s, 2H), 1.46 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 149.7, 141.9, 136.2, 131.9, 130.0, 127.23, 127.20, 127.17, 125.5, 121.2, 119.7, 113.1, 110.1, 83.4, 35.5, 27.9(3C); HRMS (ESI) m/z calculated for $C_{19}H_{21}N_2O_2$ $[(M+H)^+]$ 309.1598, found 309.1598. IR (film) 3053, 2979, 1734, 1625, 1563, 1410, 1317, 1253, 1156, 1062 cm^{-1}.

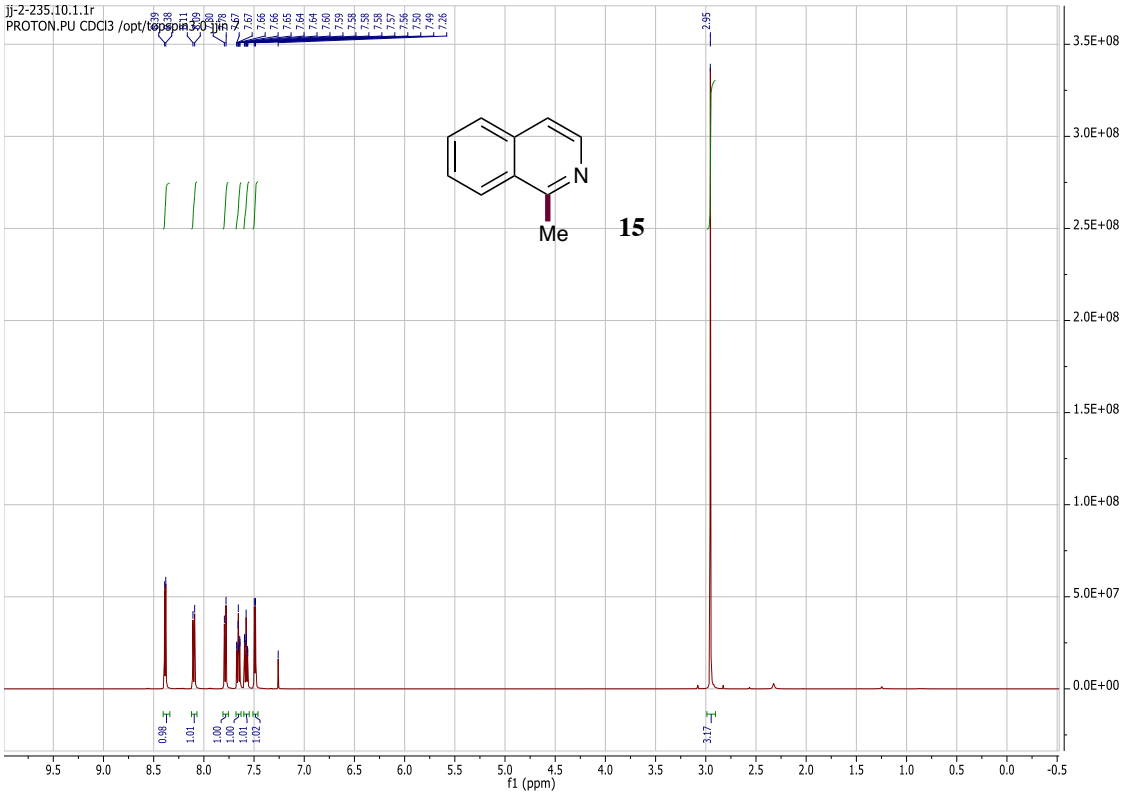


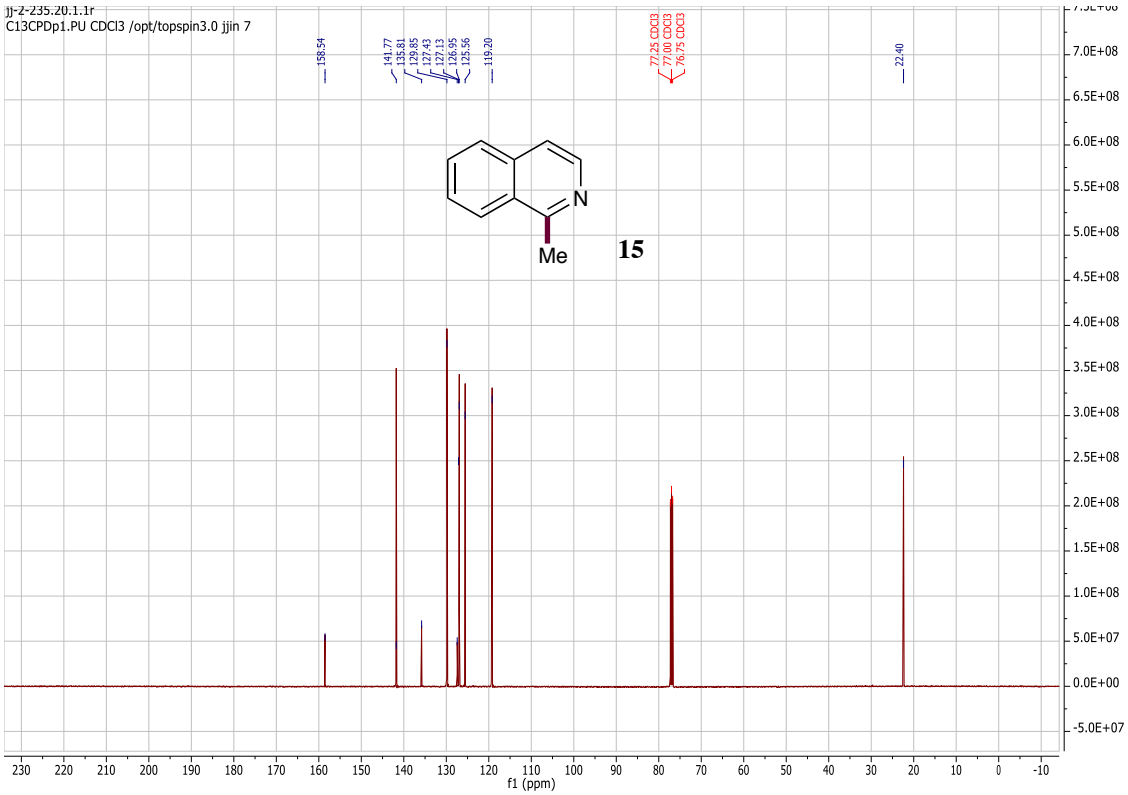
53

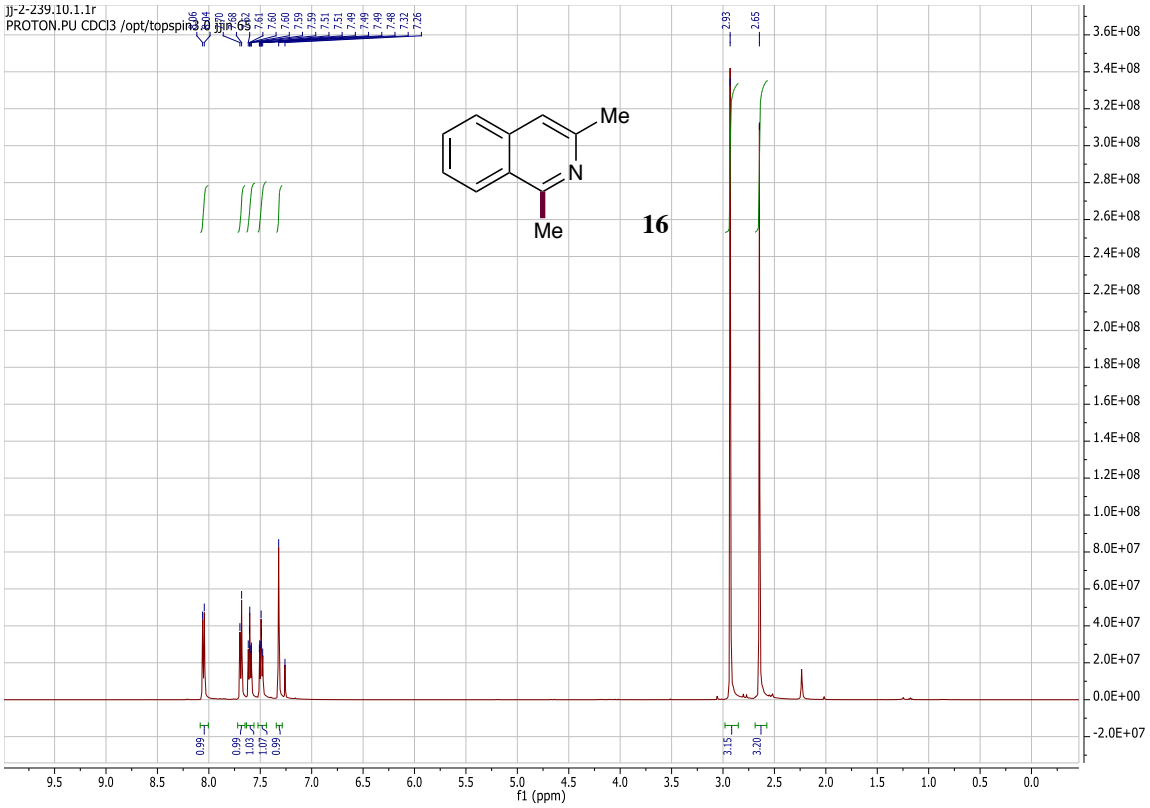
Methyl 2-(isoquinolin-1-ylmethyl)-1*H*-pyrrole-1-carboxylate (53): Following the procedure for compound **50**, $Ir(ppy)_2(dtbbpy)PF_6$ (2.3 mg, 2.5 μmol, 0.01 equiv.), TsOH (95.1 mg, 0.50 mmol, 2.0 equiv.), 1-(hydroxymethyl)isoquinoline (40.1 mg, 0.25 mmol, 1.0 equiv.), methyl 1-pyrrolecarboxylate (28 μL, 0.25 mmol, 1.0 equiv.) and 1.0 mL of DMSO were used. After 20 hours, the reaction mixture was diluted with 1 M NaOH aqueous solution (1 mL) and CH_2Cl_2 (20 mL), washed with brine (3×10 mL), dried over

Na_2SO_4, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel (20% ethyl acetate/hexanes) to provide the title compound as a colorless oil (16.7 mg, 25% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (d, J = 5.7 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.67 (m, 1H), 7.56 (m, 1H), 7.55 (d, J = 6.4 Hz, 1H), 7.30 (dd, J = 3.4, 1.7 Hz, 1H), 6.08 (t, J = 3.3 Hz, 1H), 5.61 (m, 1H), 4.92 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.9, 151.5, 142.1, 136.3, 132.8, 130.0, 127.32, 127.26, 127.25, 125.5, 121.0, 119.7, 113.6, 110.1, 53.7, 35.1; HRMS (ESI) m/z calculated for $C_{16}H_{15}N_2O_2$ $[(M+H)^+]$ 267.1128, found 267.1127. IR (film) 3053, 2955, 1741, 1624, 1562, 1440, 1317, 1228, 1121, 1065 cm^{-1}.

VI. NMR Spectra



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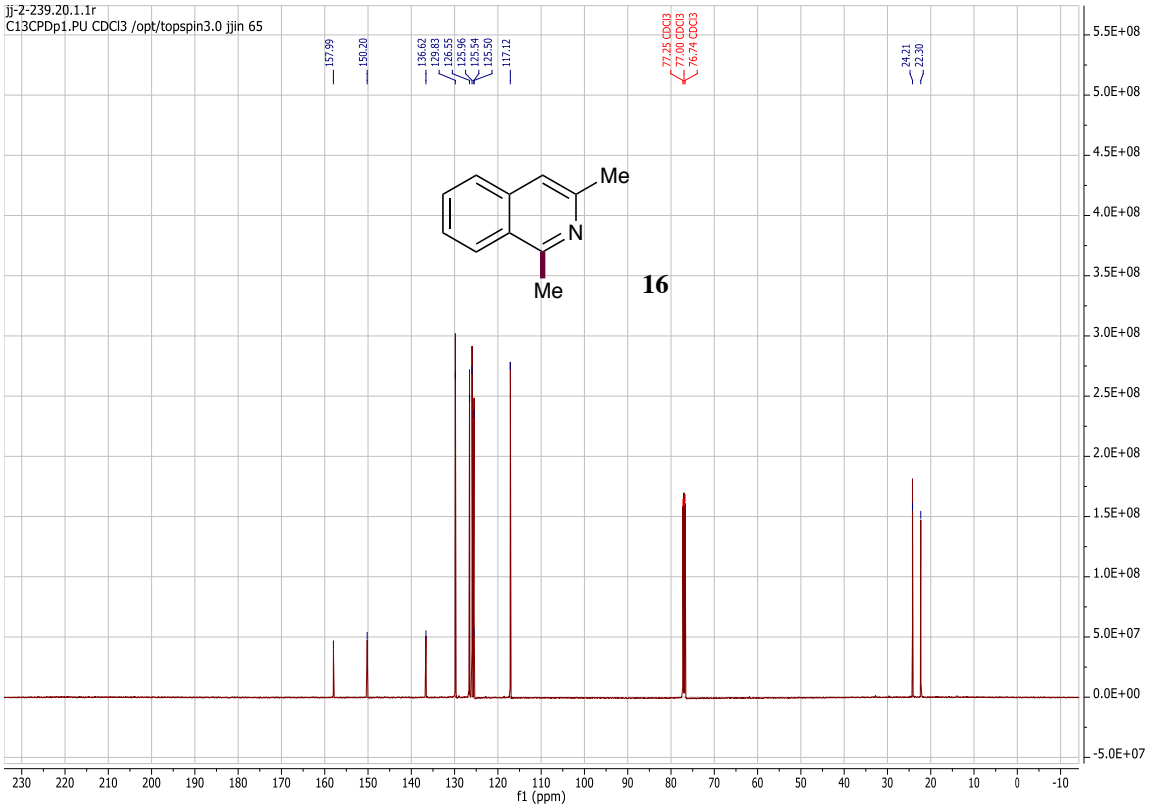
N
Me
16
f1 (ppm)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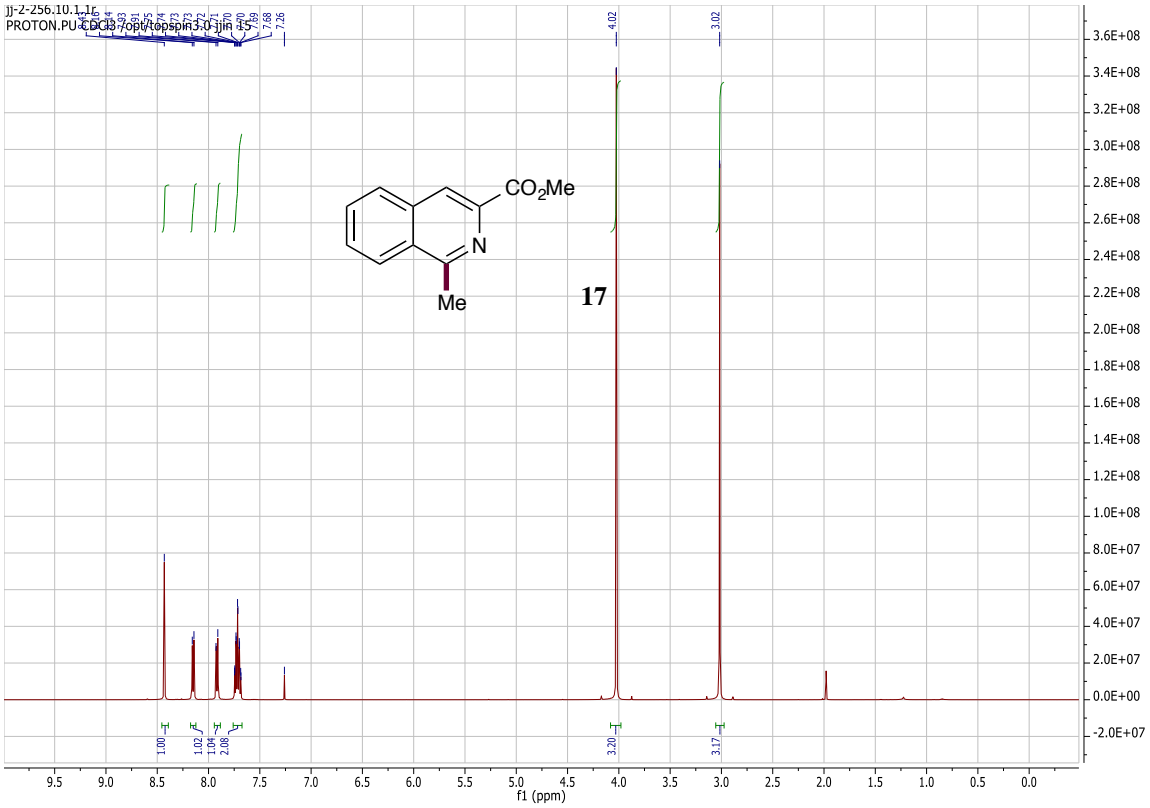
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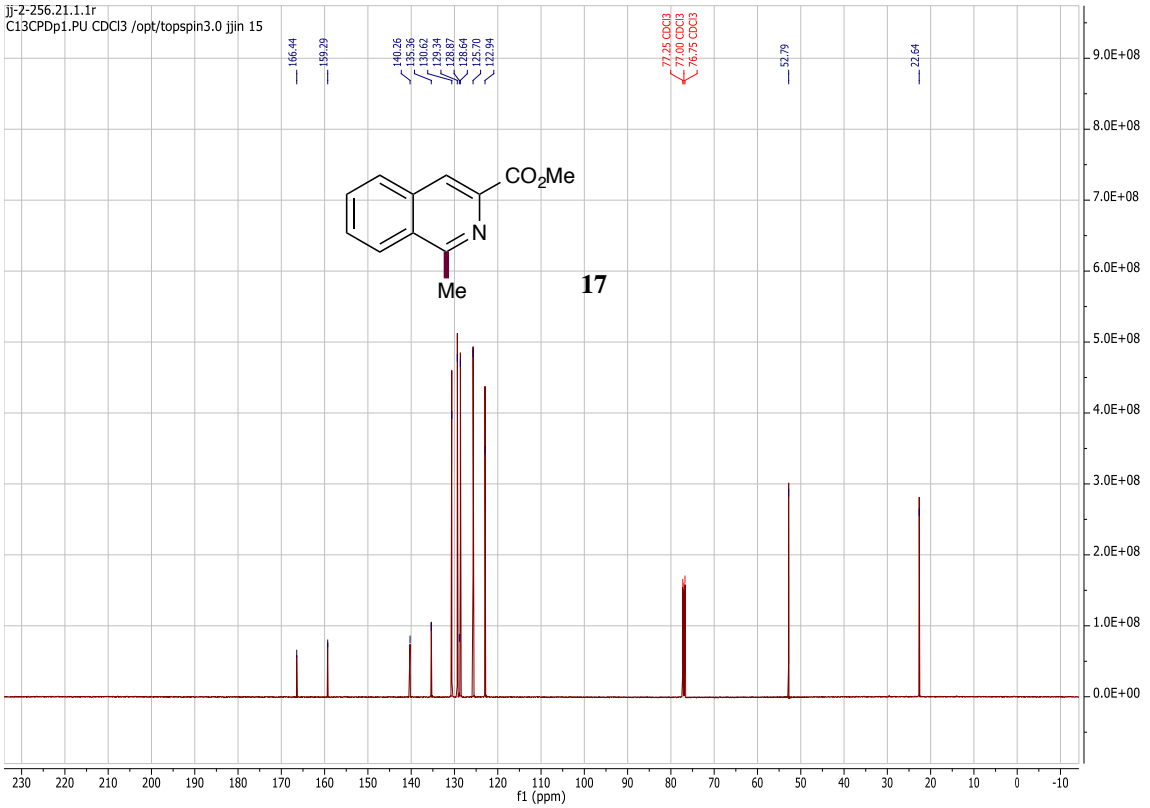
2.08
3.20
3.17
f1 (ppm)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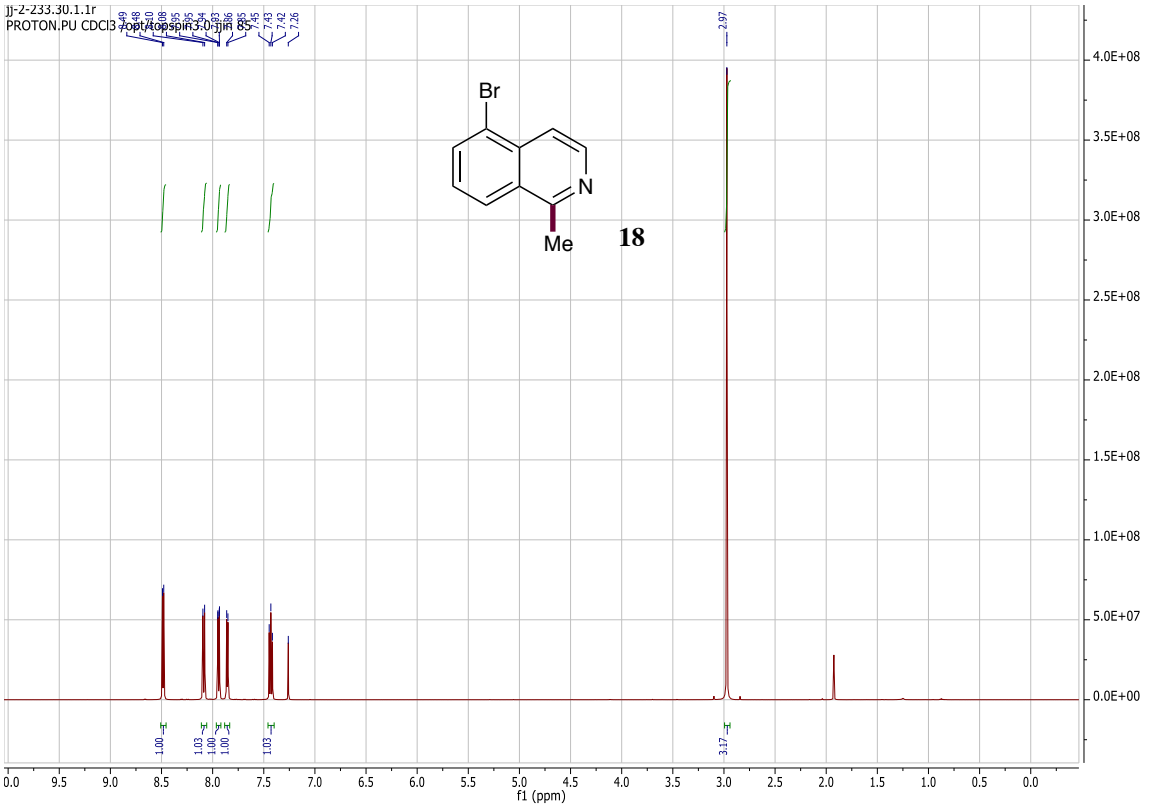
f1 (ppm)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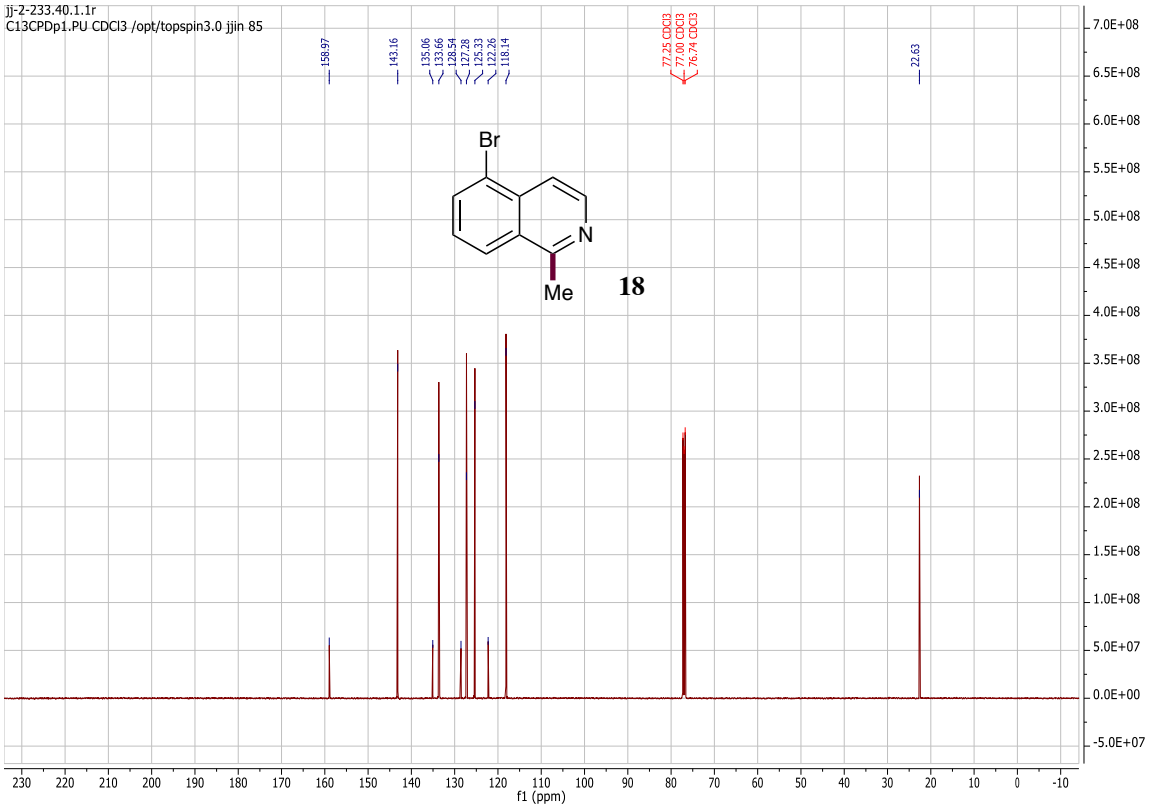
Me
18
f1 (ppm)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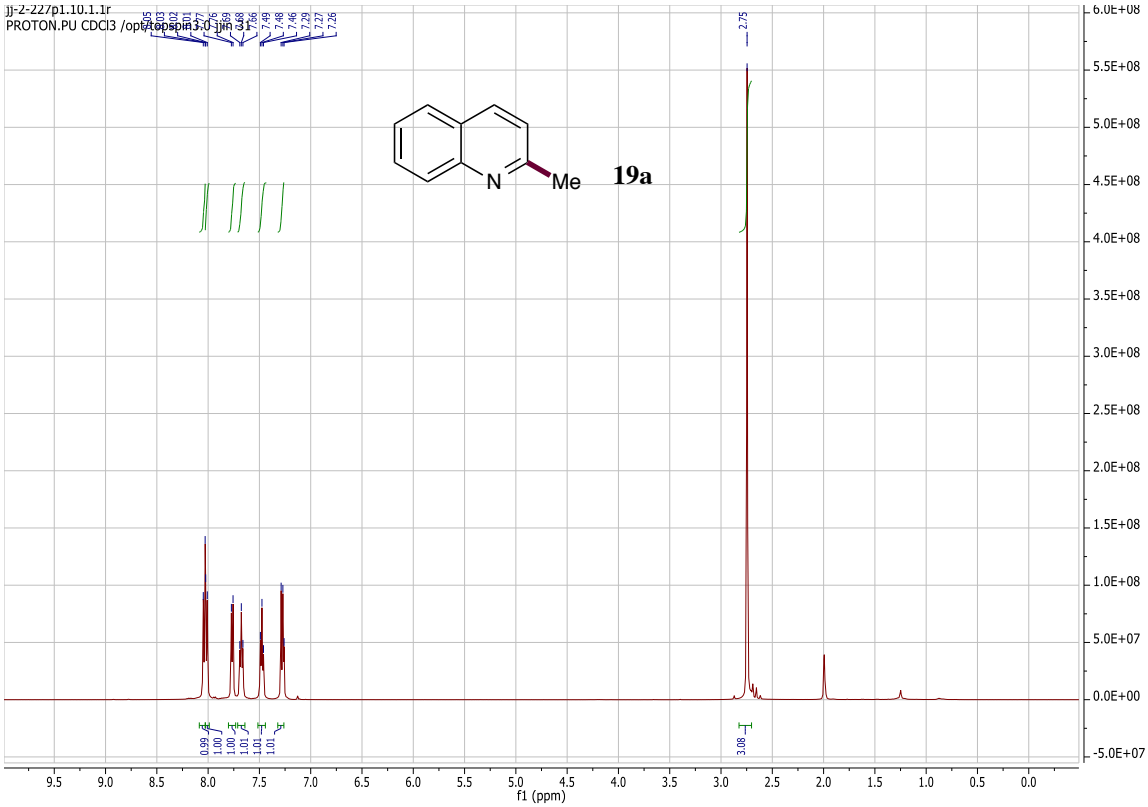
Me
18
f1 (ppm)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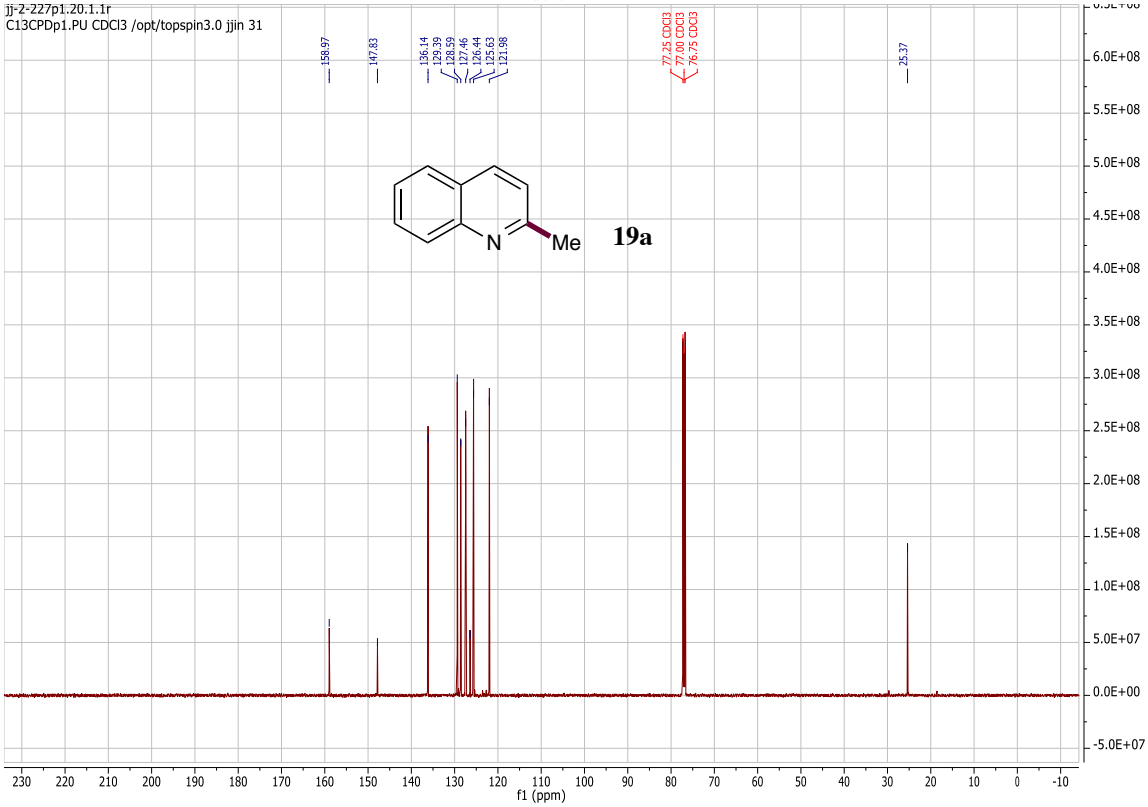
N
Me
19a
f1 (ppm)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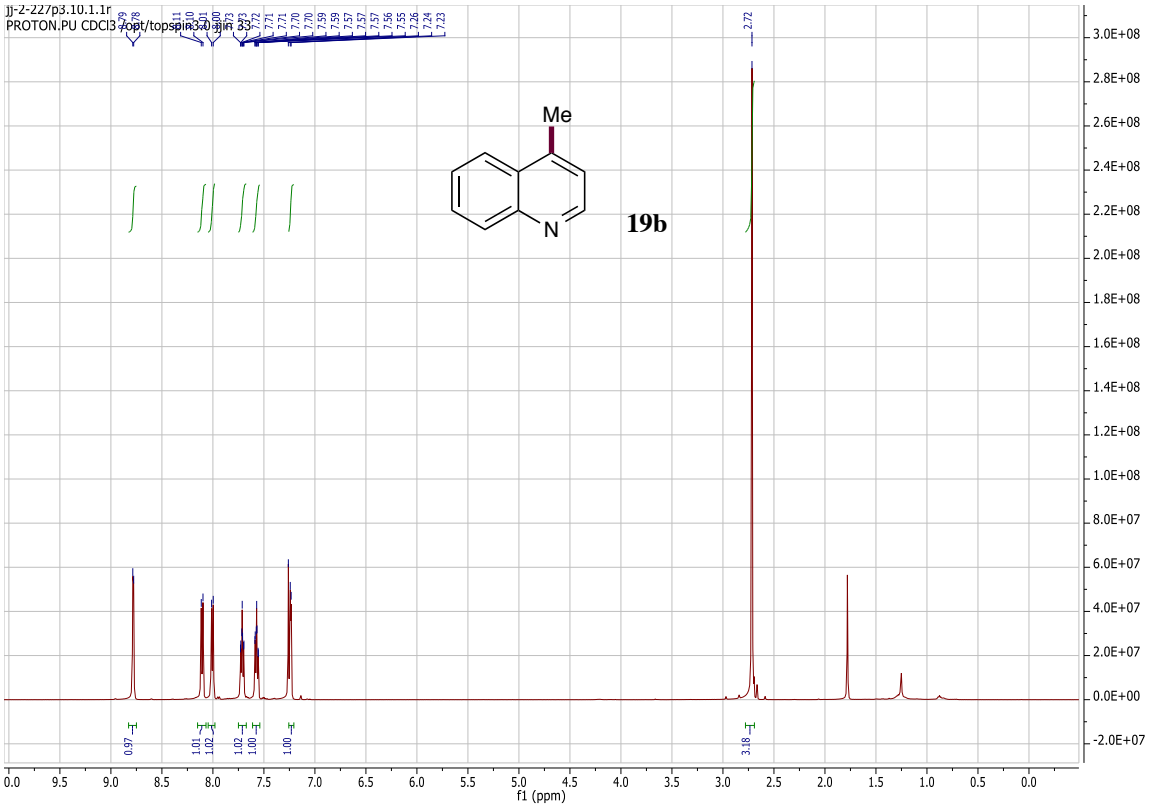
f1 (ppm)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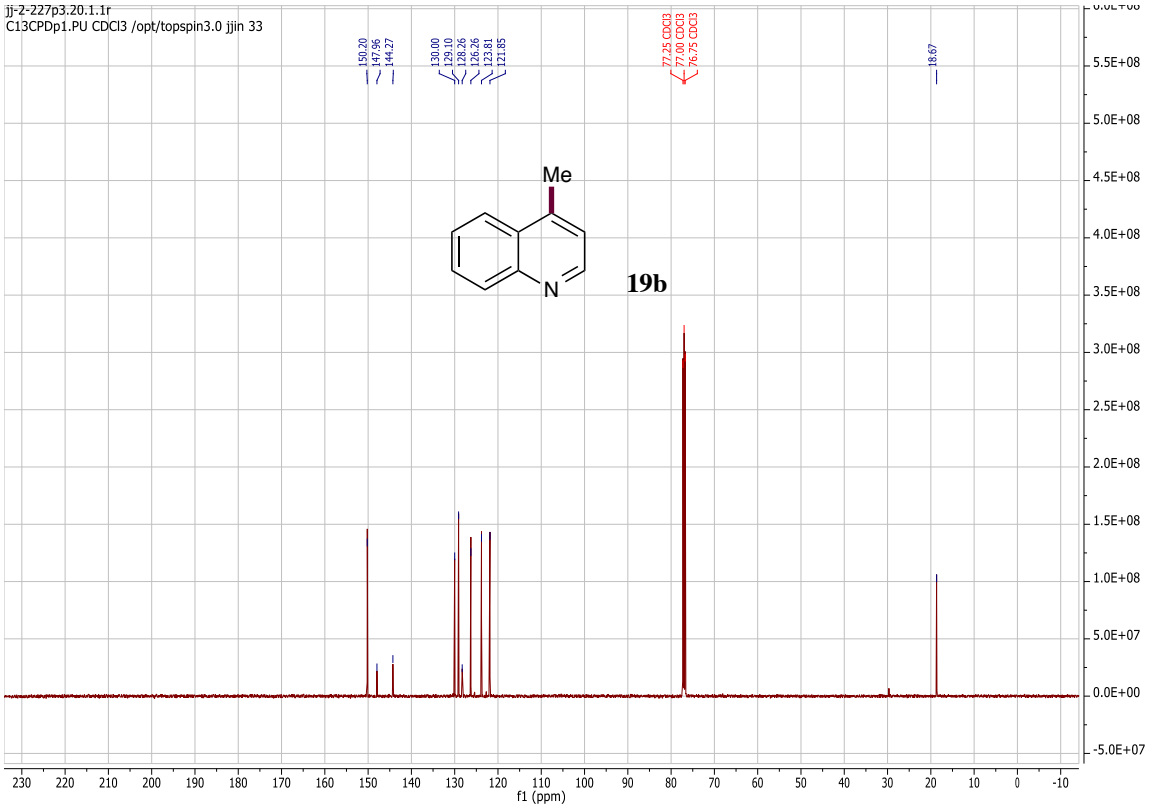
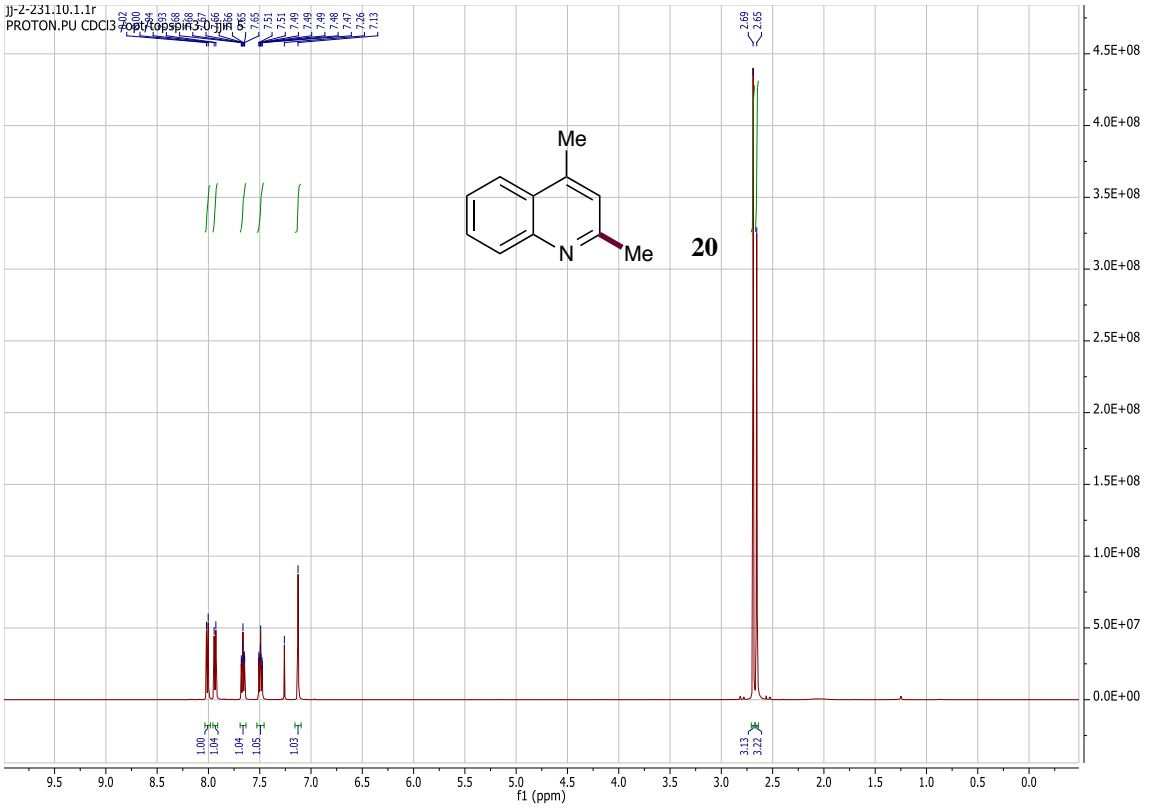
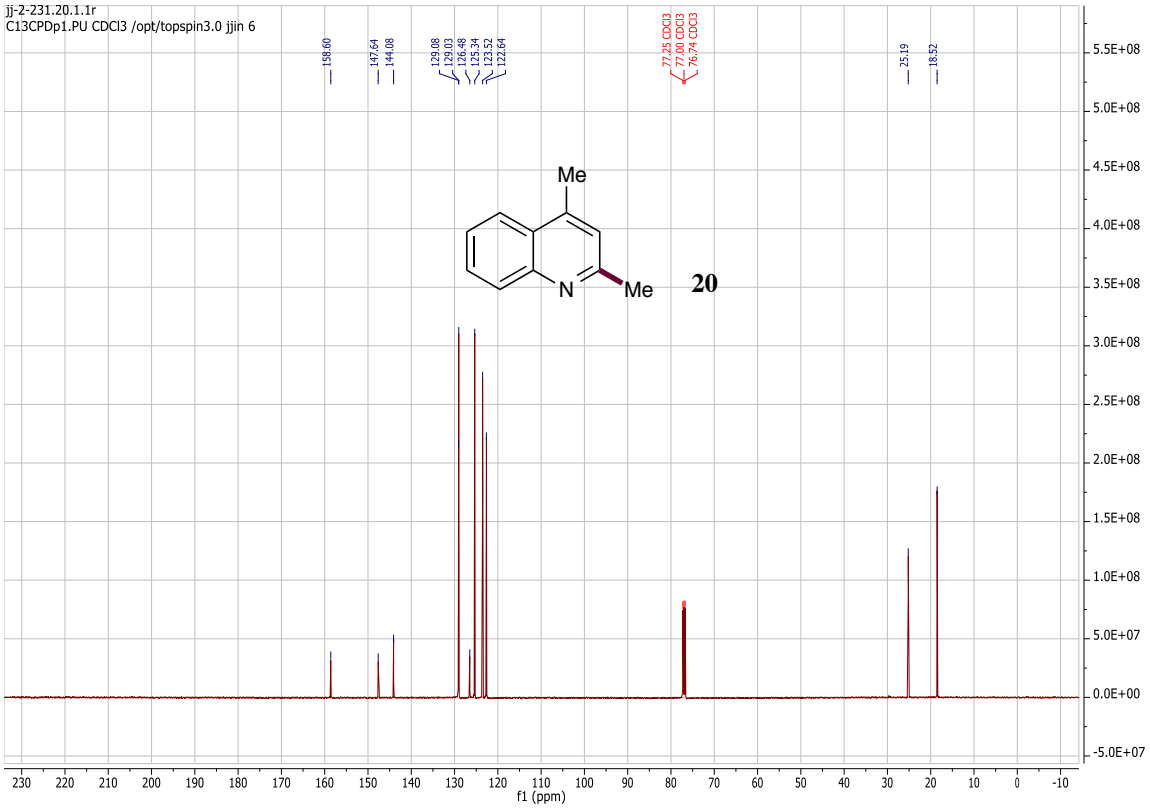
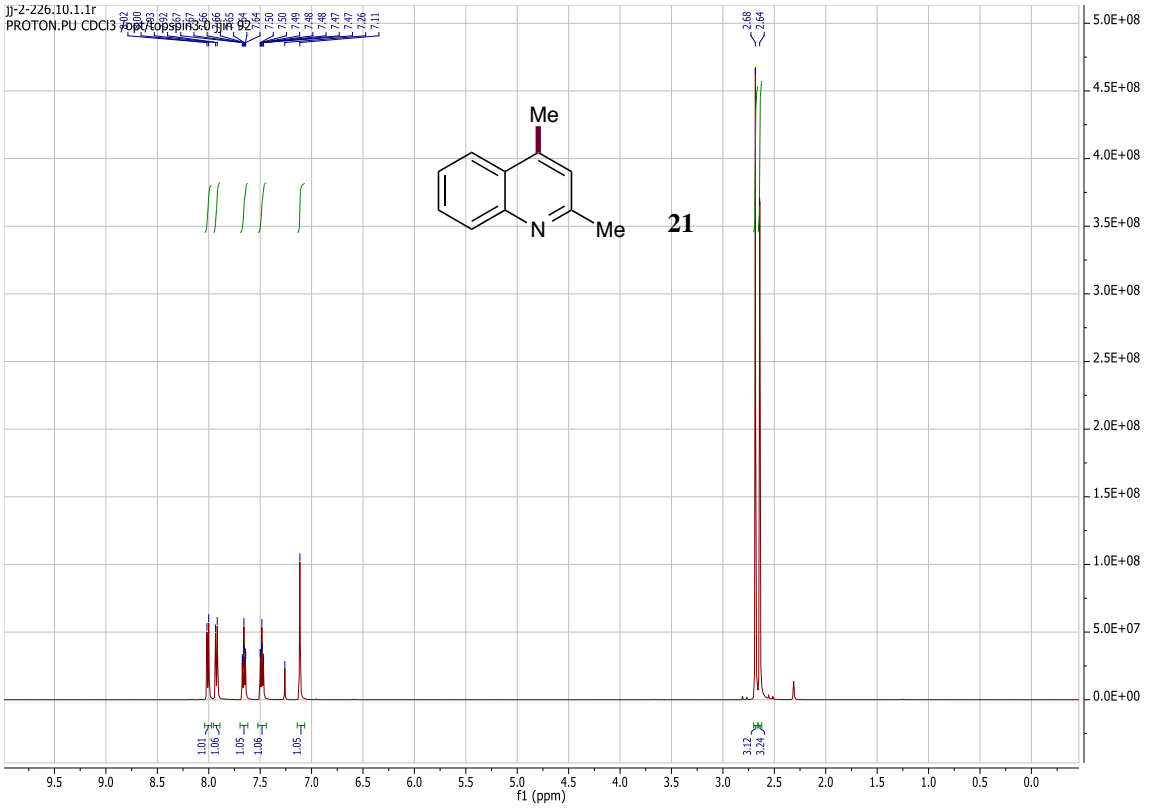
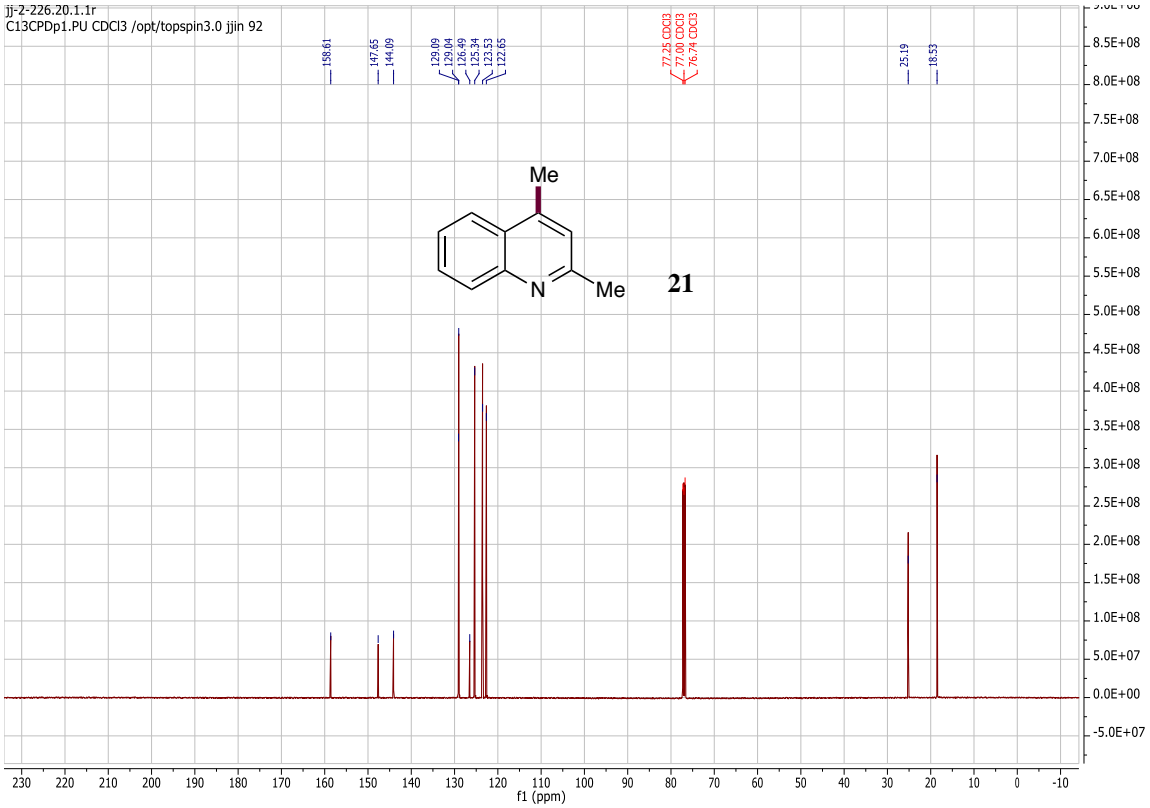
N
19b
f1 (ppm)

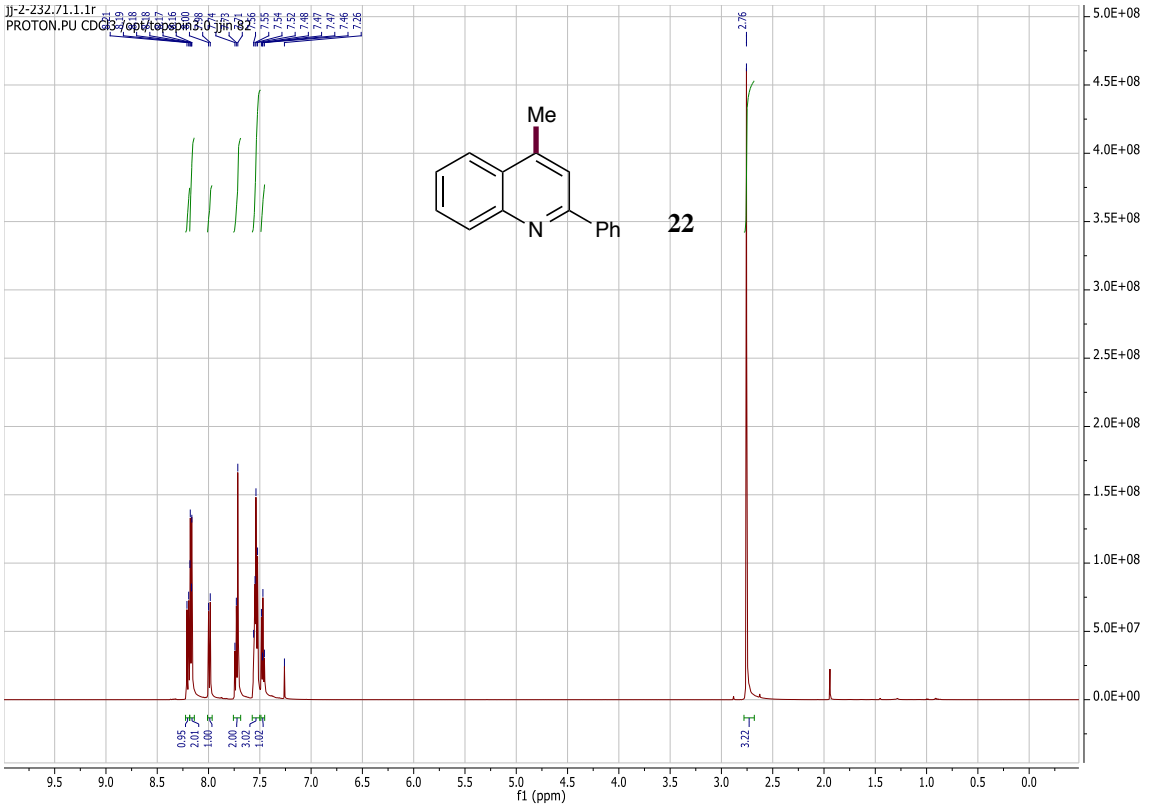

jj-2-227p3.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 33
Me
N
19b
f1 (ppm)

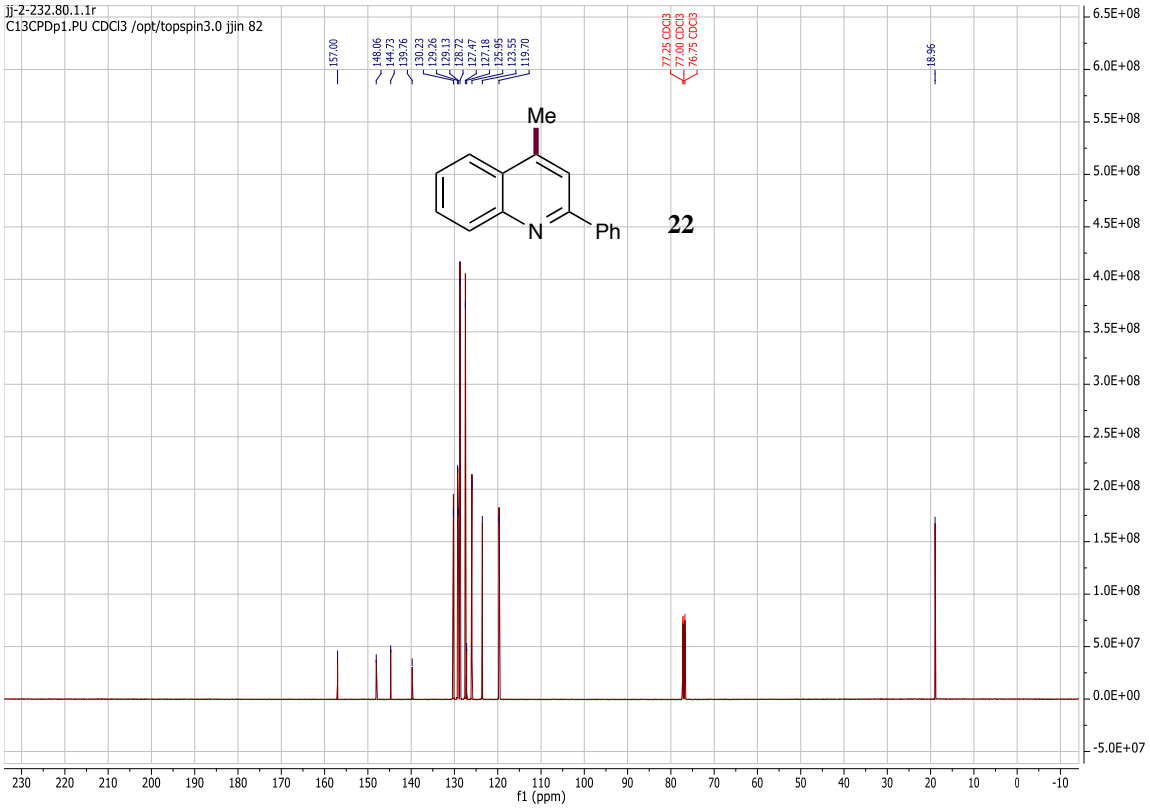

jj-2-231.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 5
Me
N
Me
20
f1 (ppm)

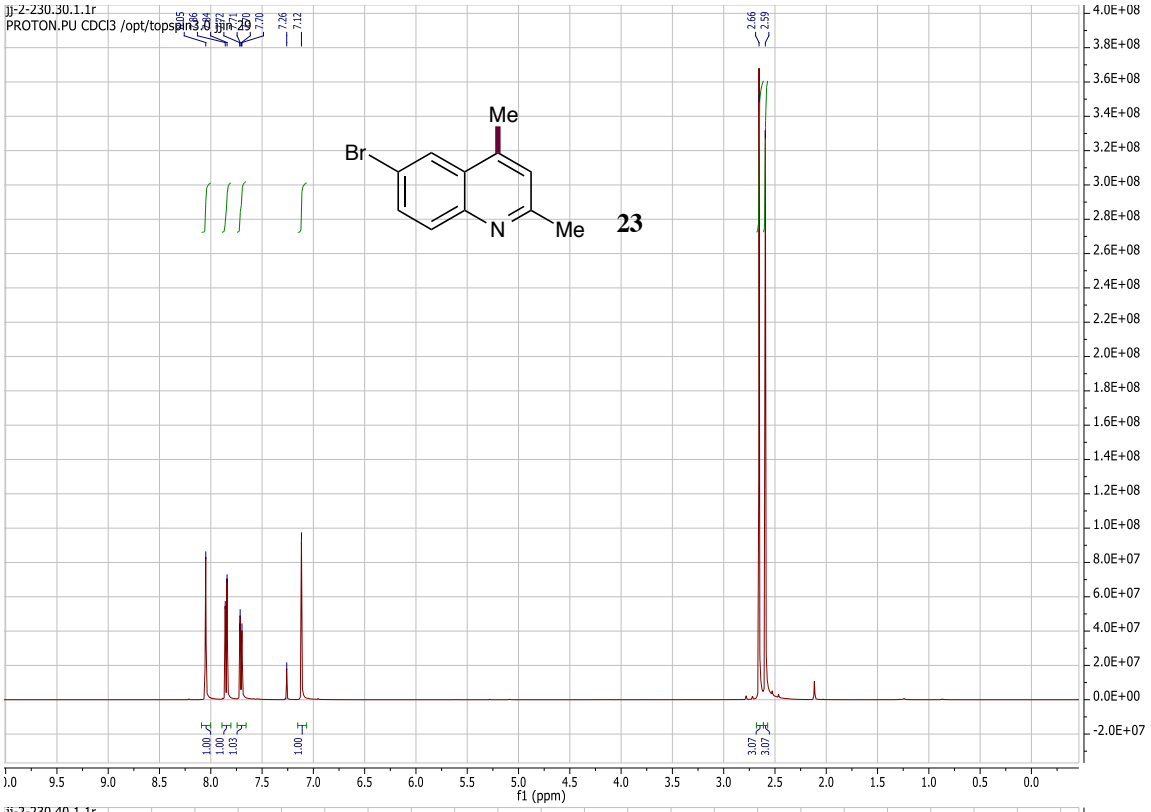

jj-2-231.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 6
Me
N
Me
20
f1 (ppm)

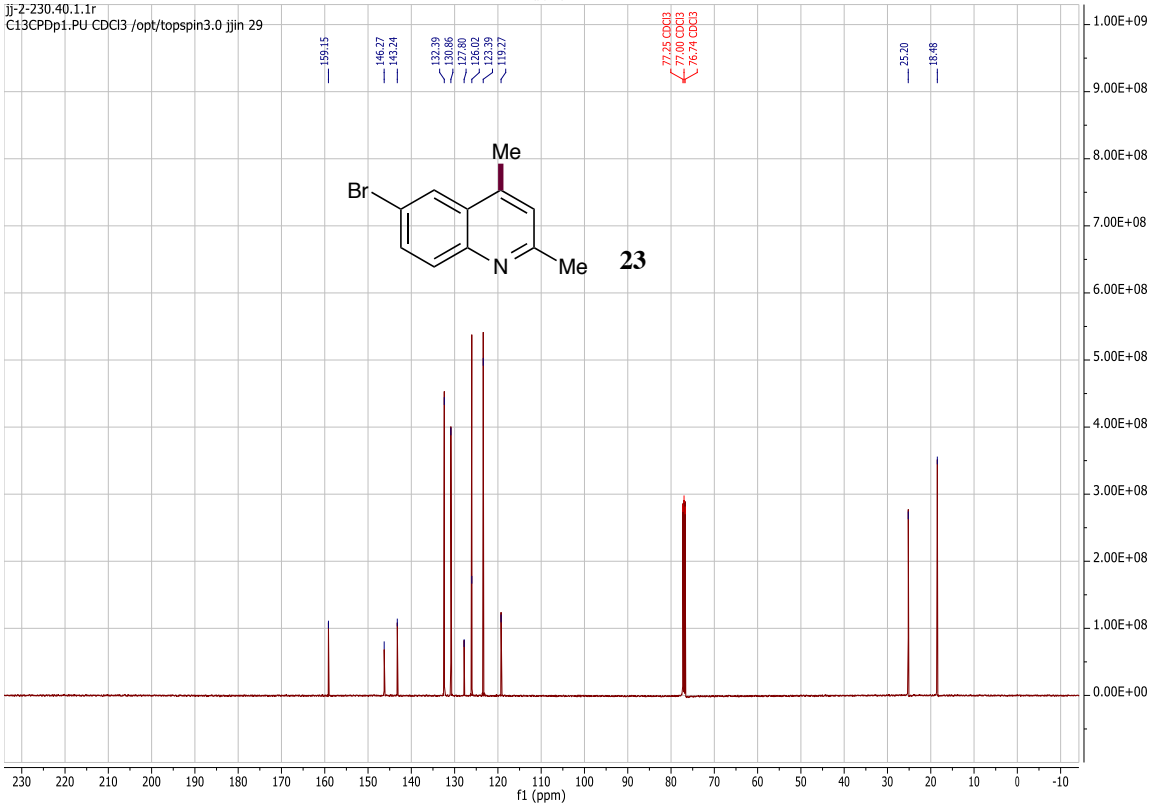

jj-2-226.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 92
Me
N
Me
21
f1 (ppm)

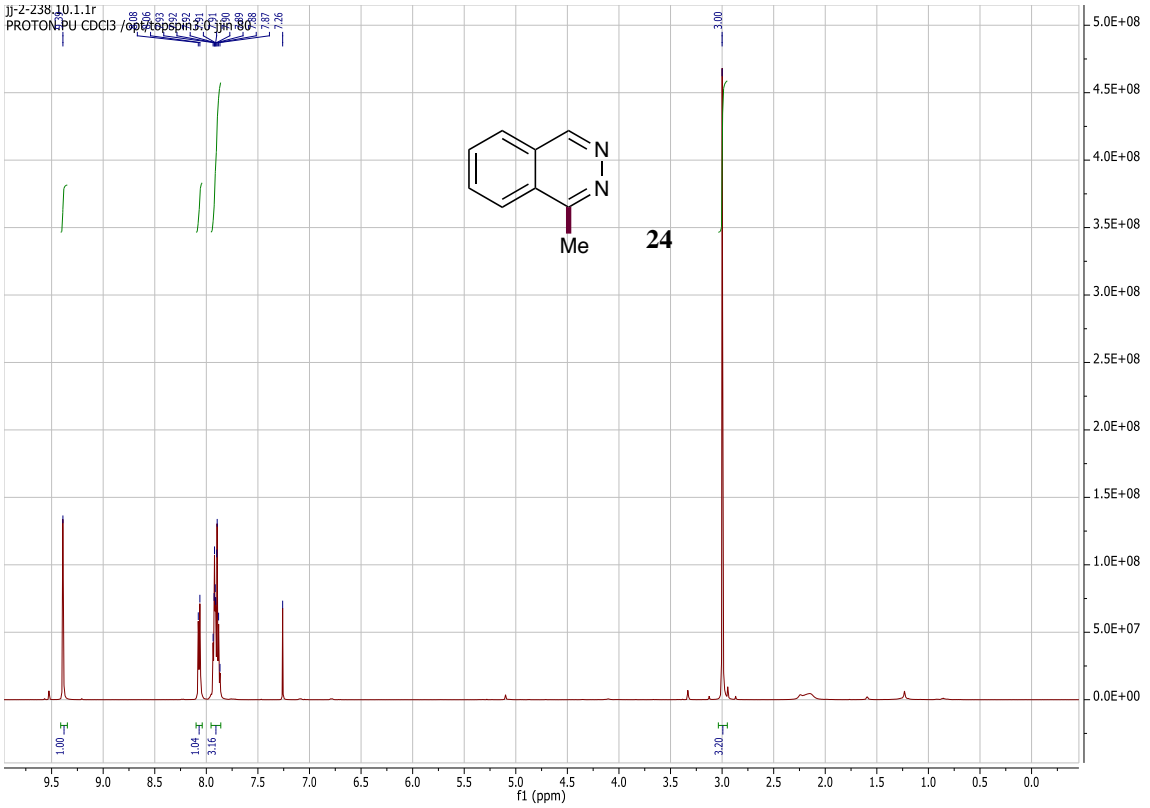

jj-2-226.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 92
Me
N
Me
21
f1 (ppm)

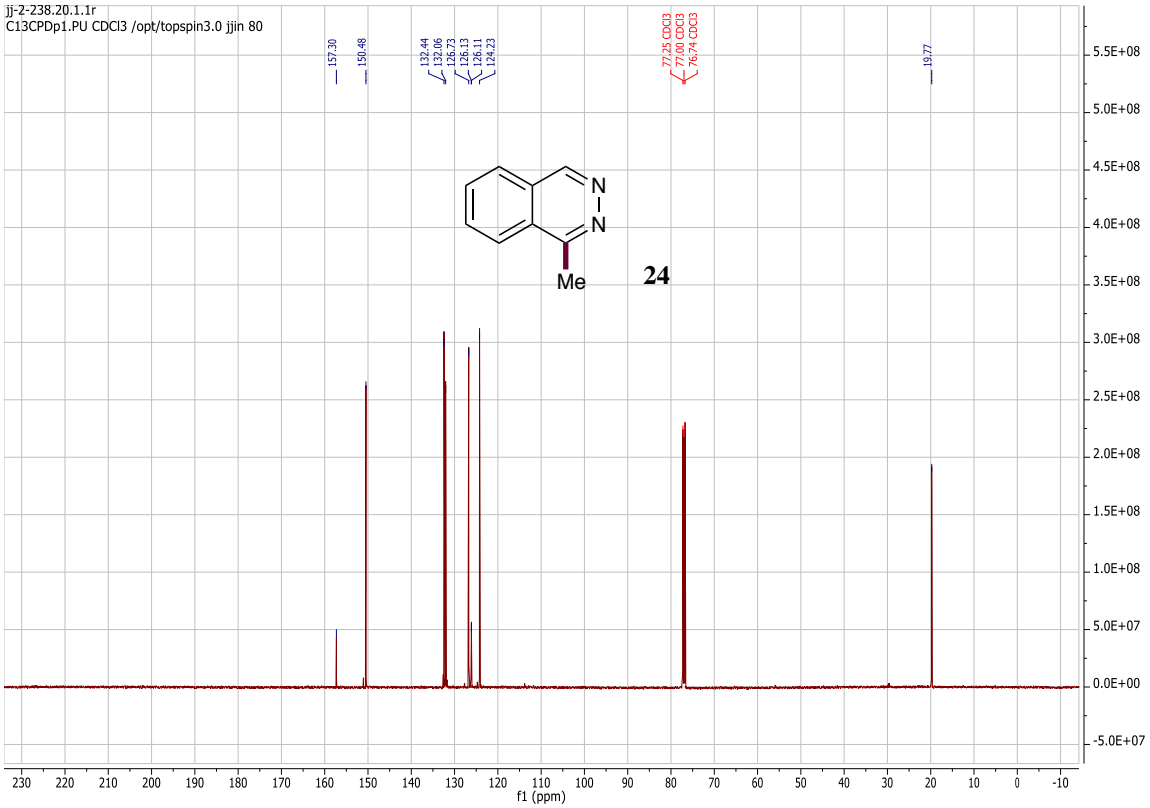

jj-2-232.71.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 82
Me
N
Ph
22
2.76
f1 (ppm)

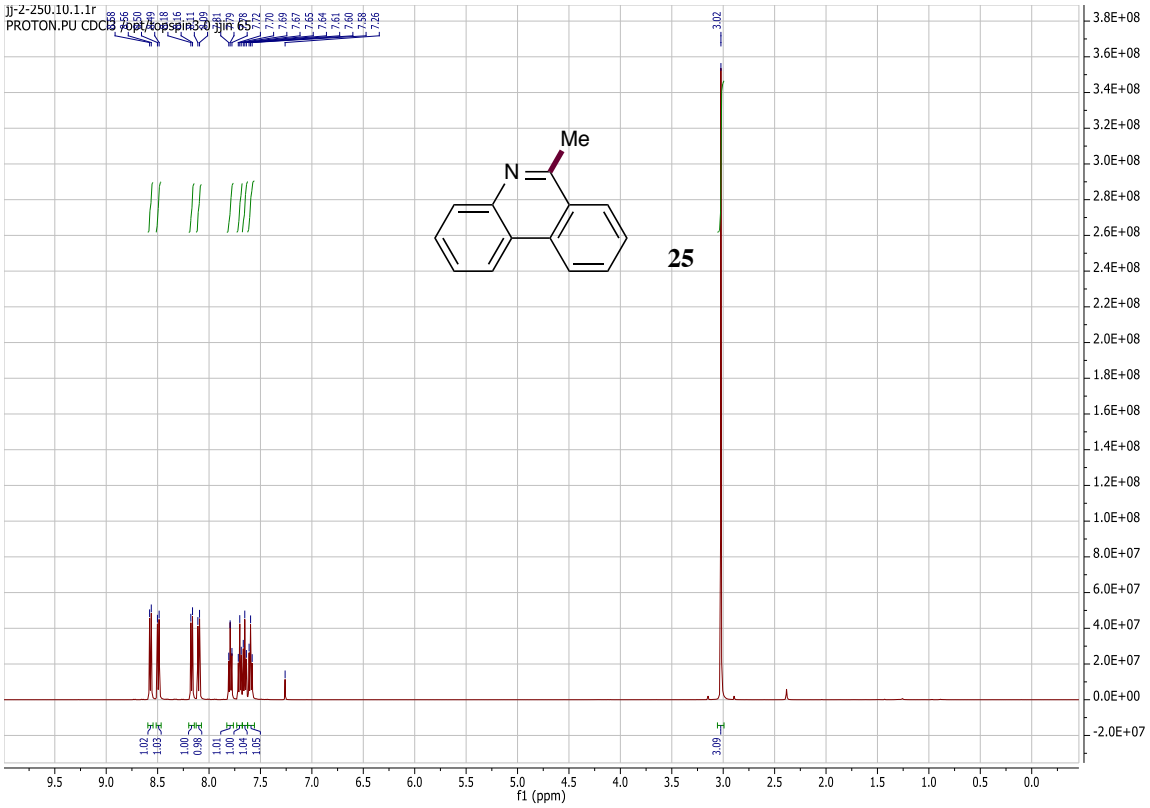

jj-2-232.80.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 82
157.00
148.06
144.73
139.76
130.23
129.26
129.13
128.72
127.47
127.18
125.95
123.55
119.70
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
18.96
Me
N
Ph
22
f1 (ppm)

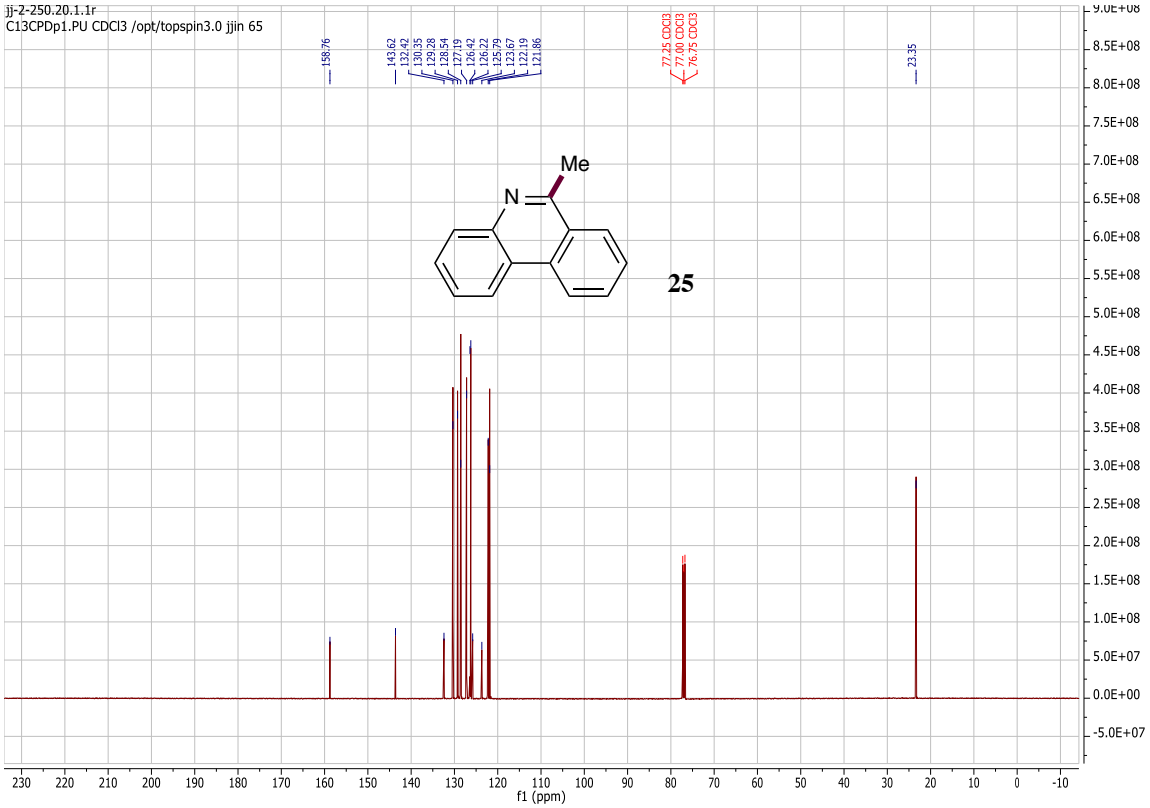

jj-2-230.30.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 29
8.05
7.86
7.84
7.72
7.71
7.70
7.26
7.12
2.66
2.59
Me
Br
N
Me
23
1.00
1.00
1.03
1.00
3.07
3.07
f1 (ppm)

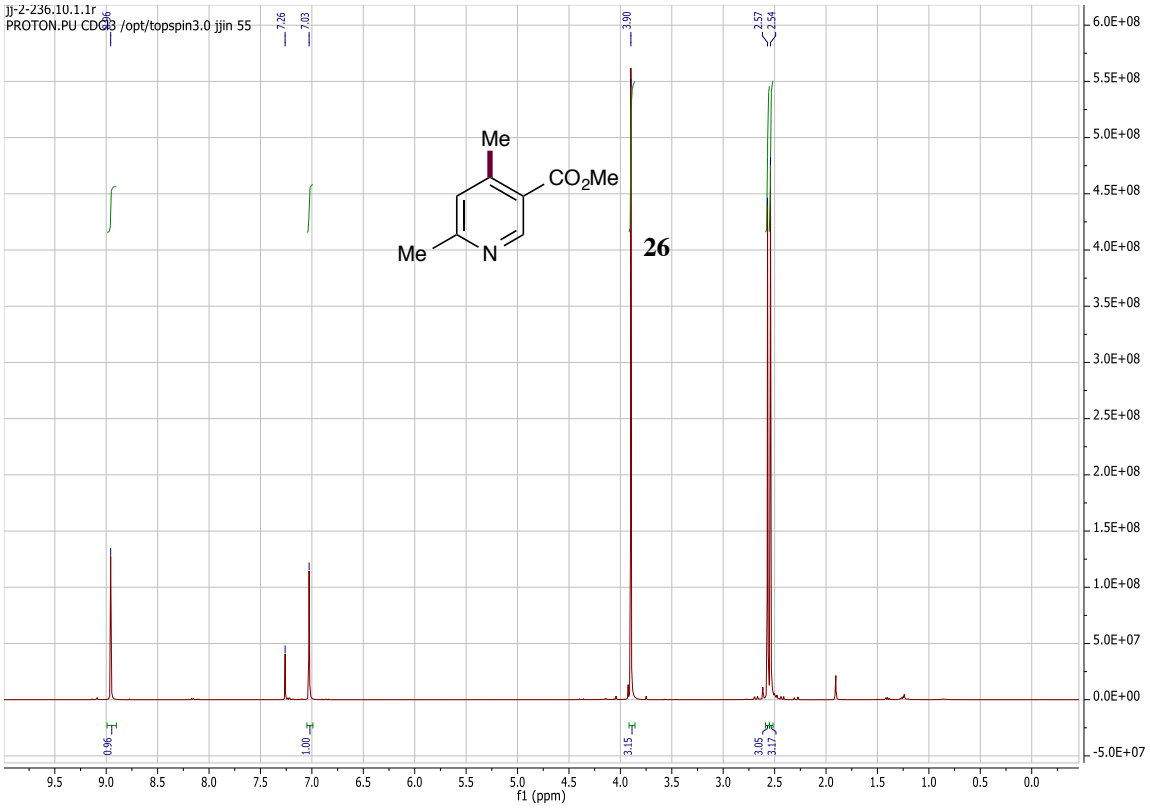

jj-2-230.40.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 29
159.15
146.27
143.24
132.39
130.86
127.80
126.02
123.39
119.27
77.25 CDCl3
77.00 CDCl3
76.74 CDCl3
25.20
18.46
Me
Br
N
Me
23
f1 (ppm)

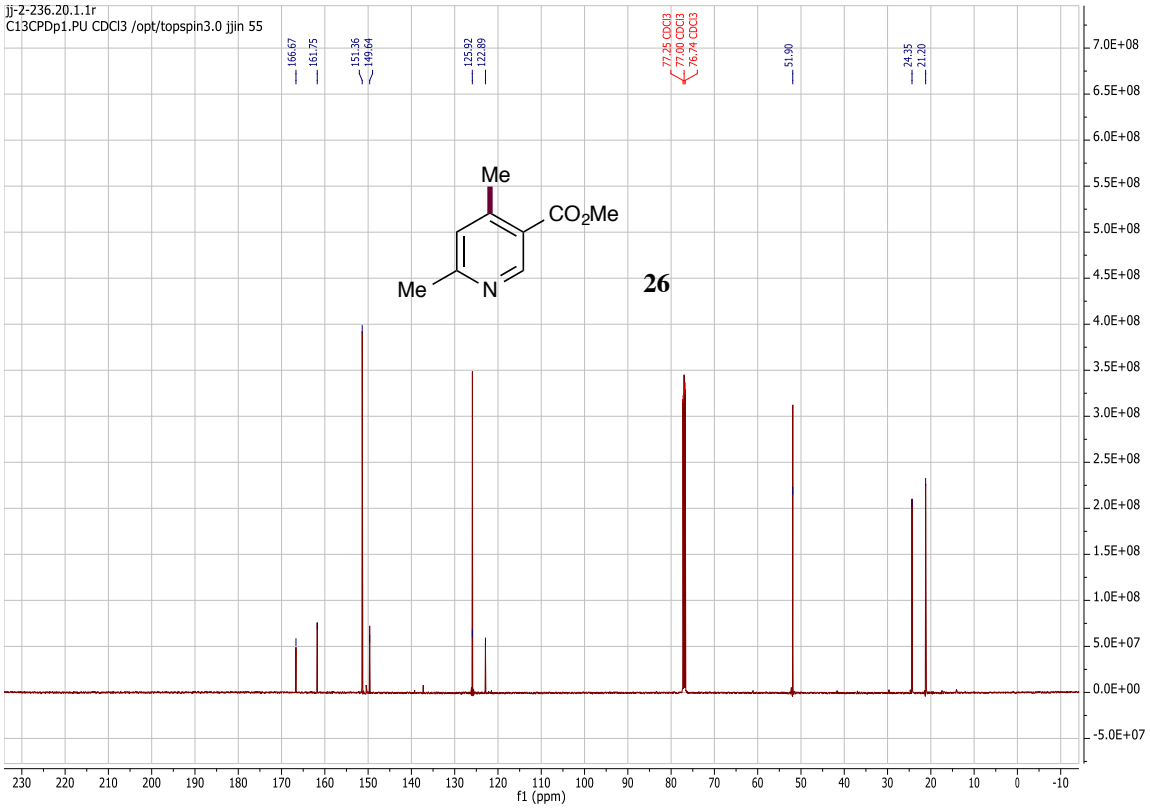

jj-2-238.10.1.1r
PROTON-PU CDCl3 /opt/topspin3.0 jjin 80
8.08
8.06
7.93
7.92
7.92
7.91
7.91
7.90
7.89
7.88
7.87
7.26
3.00
N
N
Me
24
1.00
1.04
3.16
3.20
f1 (ppm)

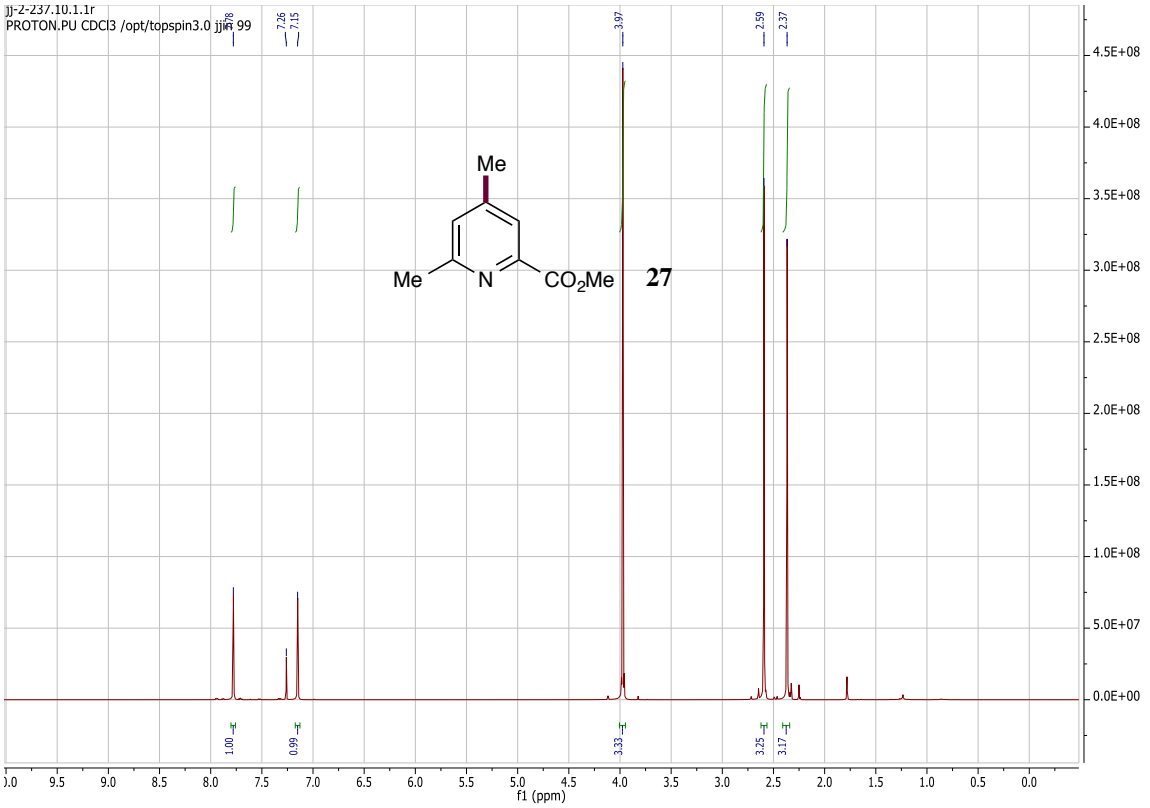

jj-2-238.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 80
157.30
150.48
132.44
132.06
128.73
126.13
125.11
124.23
77.25 CDCl3
77.00 CDCl3
76.74 CDCl3
19.77
N
N
Me
24
f1 (ppm)

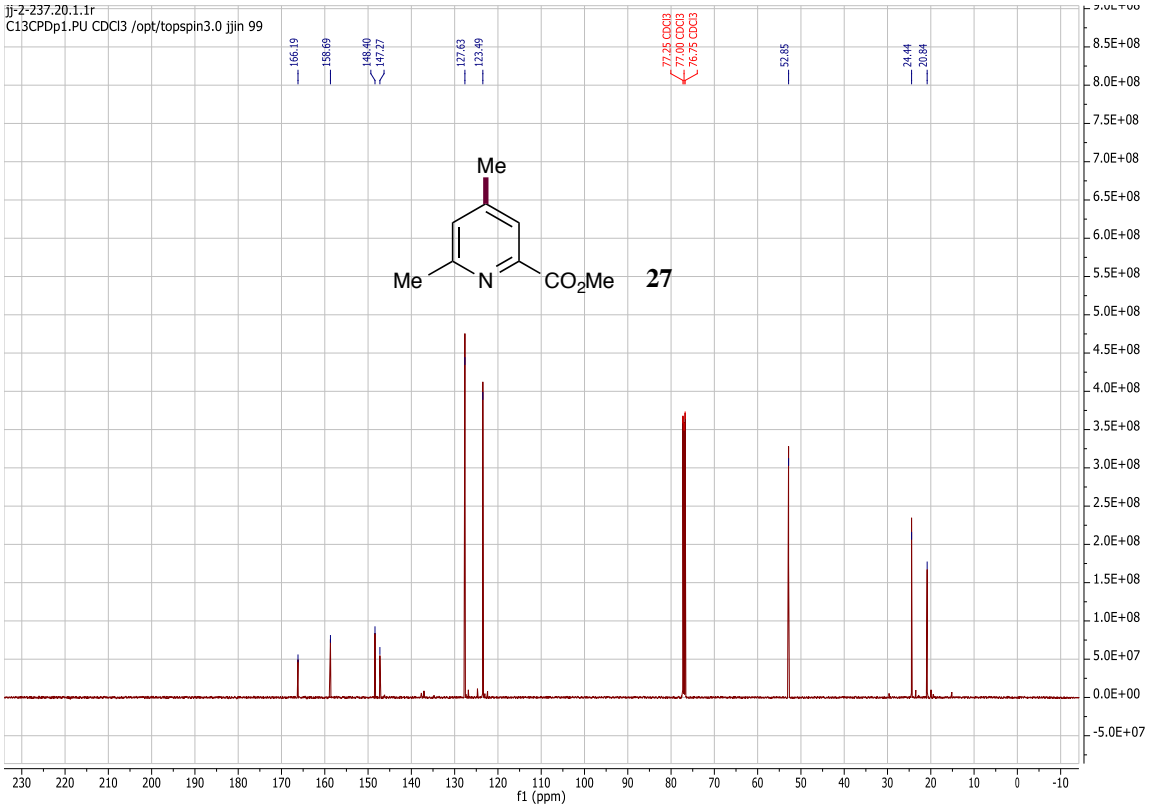

jj-2-250.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 65
Me
N
25
f1 (ppm)

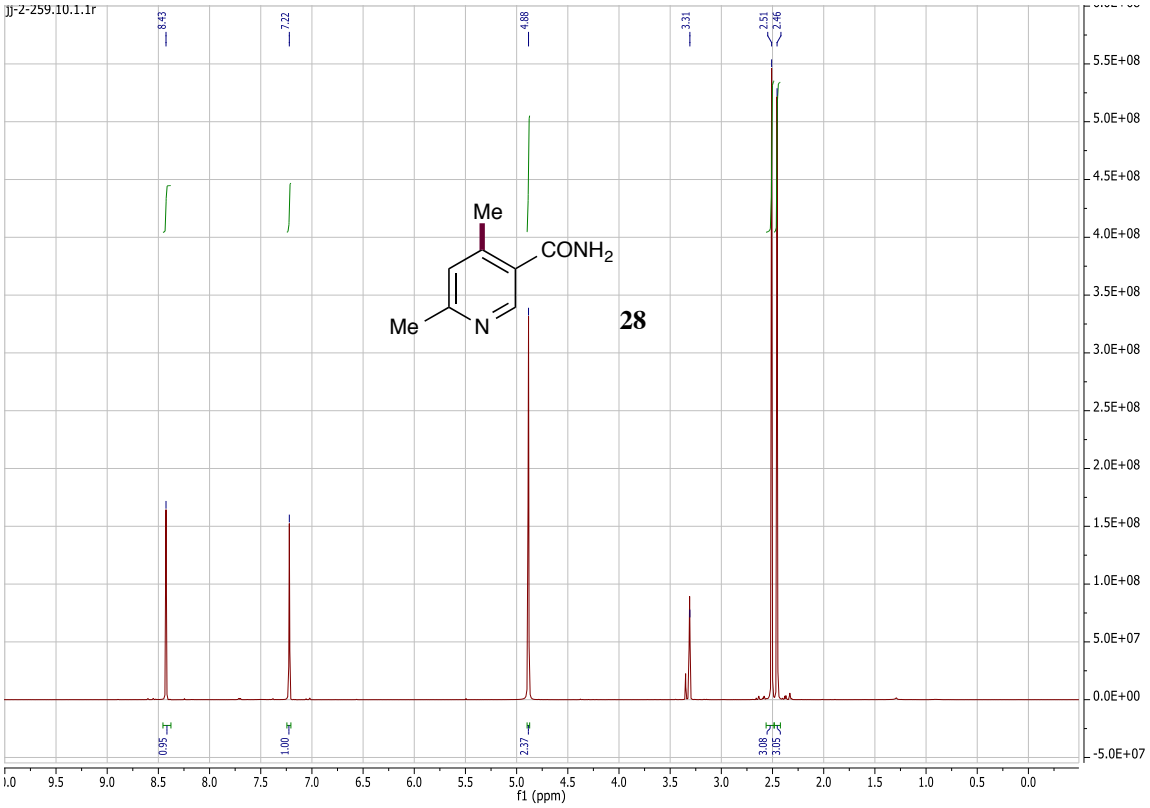

jj-2-250.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 65
Me
N
25
f1 (ppm)

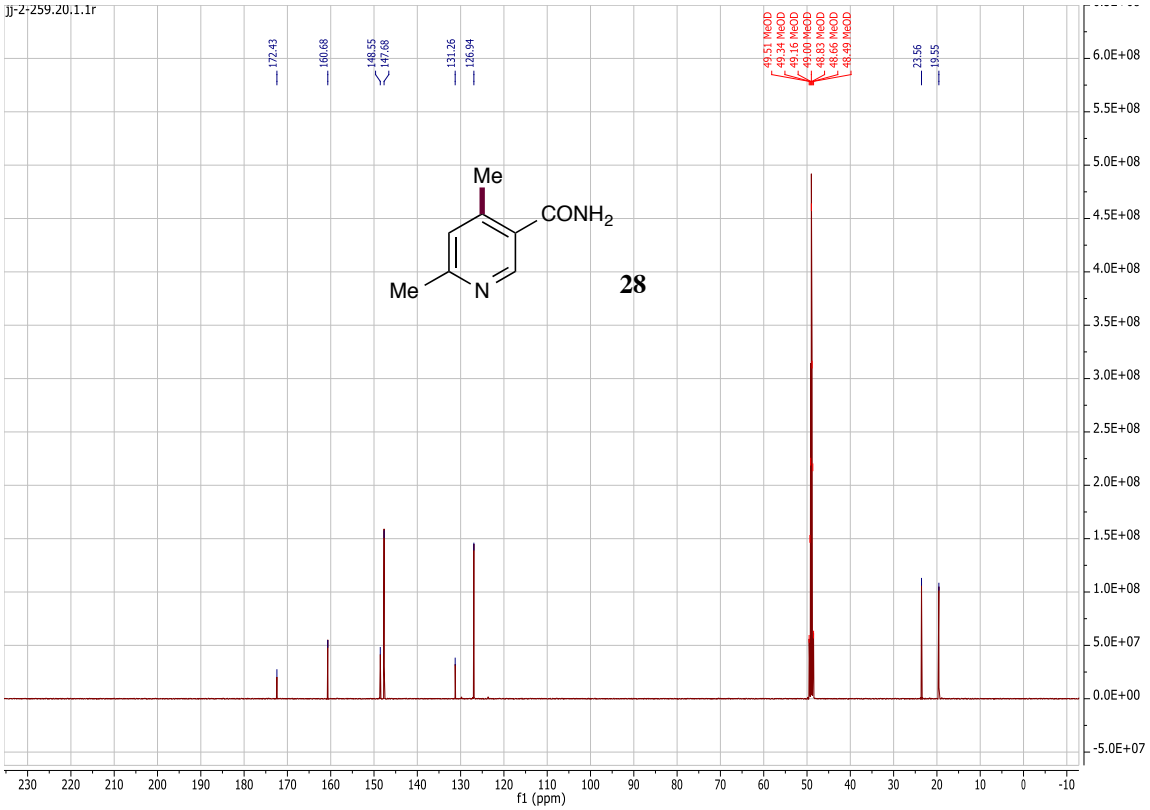

jj-2-236.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 55
Me
CO2Me
Me
N
26
f1 (ppm)

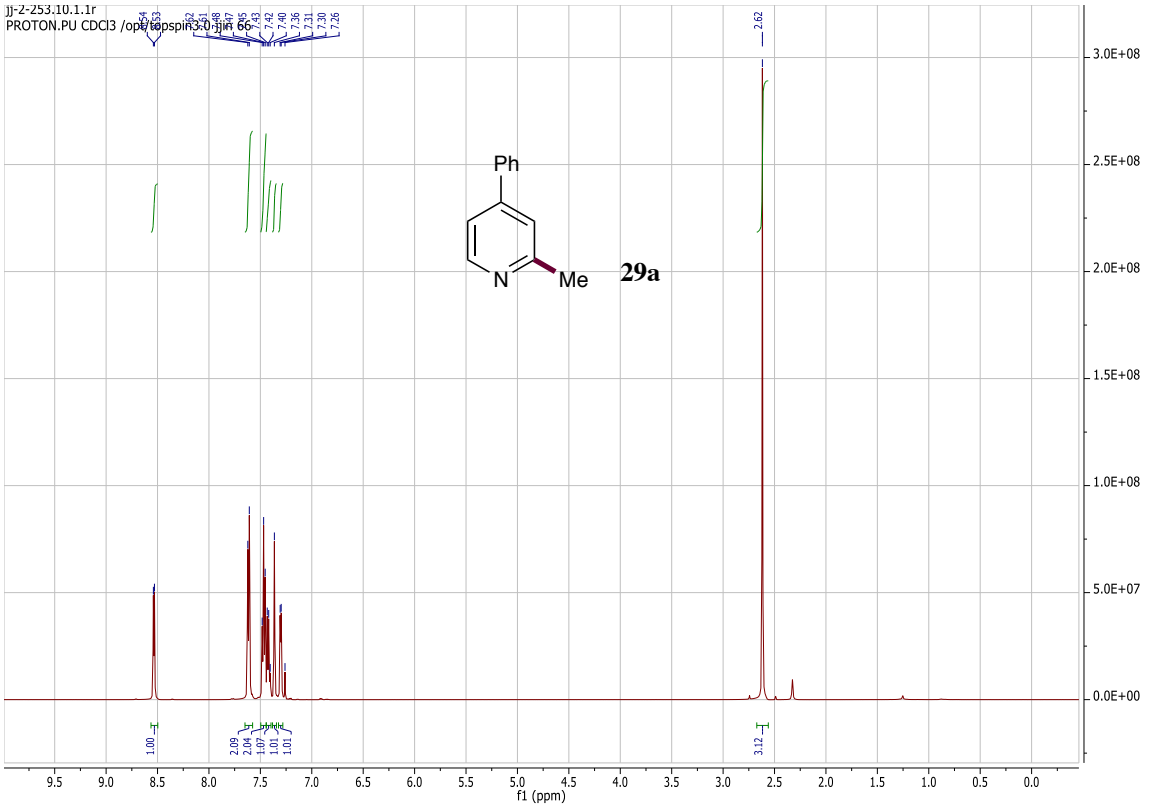

jj-2-236.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 55
Me
CO2Me
Me
N
26
f1 (ppm)

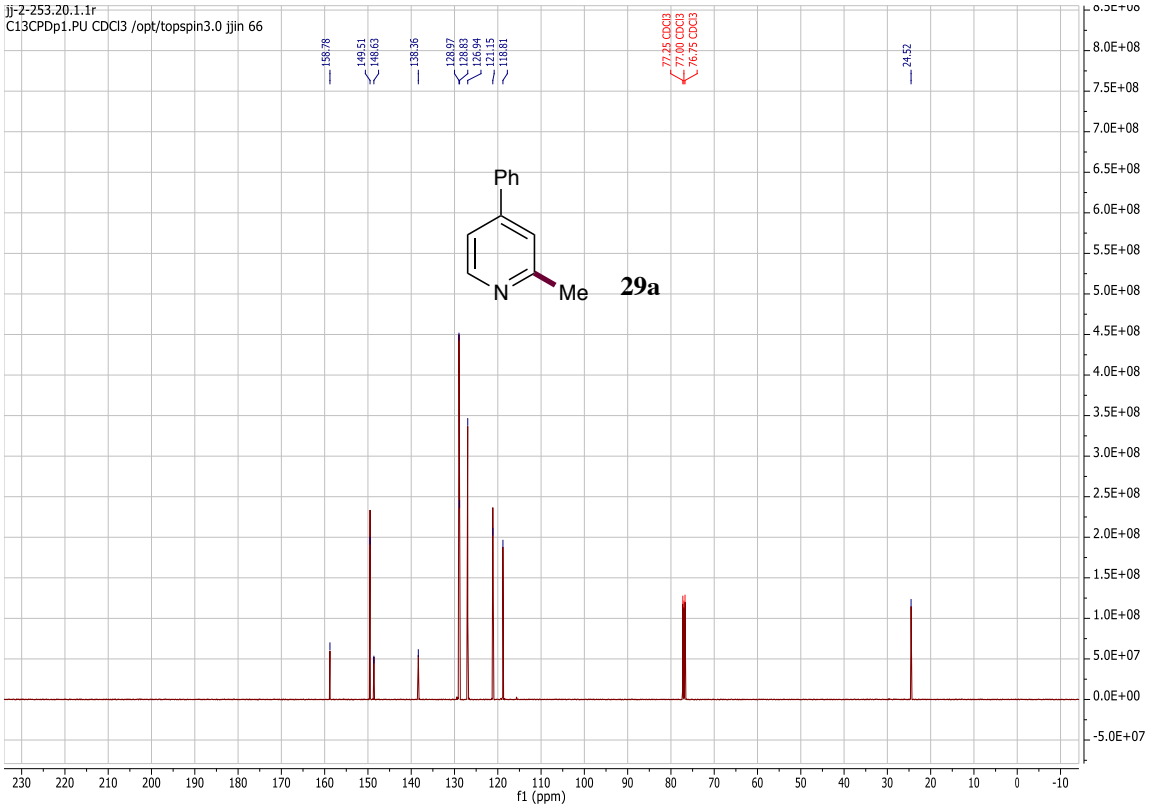

jj-2-237.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 99
7.78
7.26
7.15
3.97
2.59
2.37
Me
Me
N
CO2Me
27
1.00
0.99
3.33
3.25
3.17
f1 (ppm)

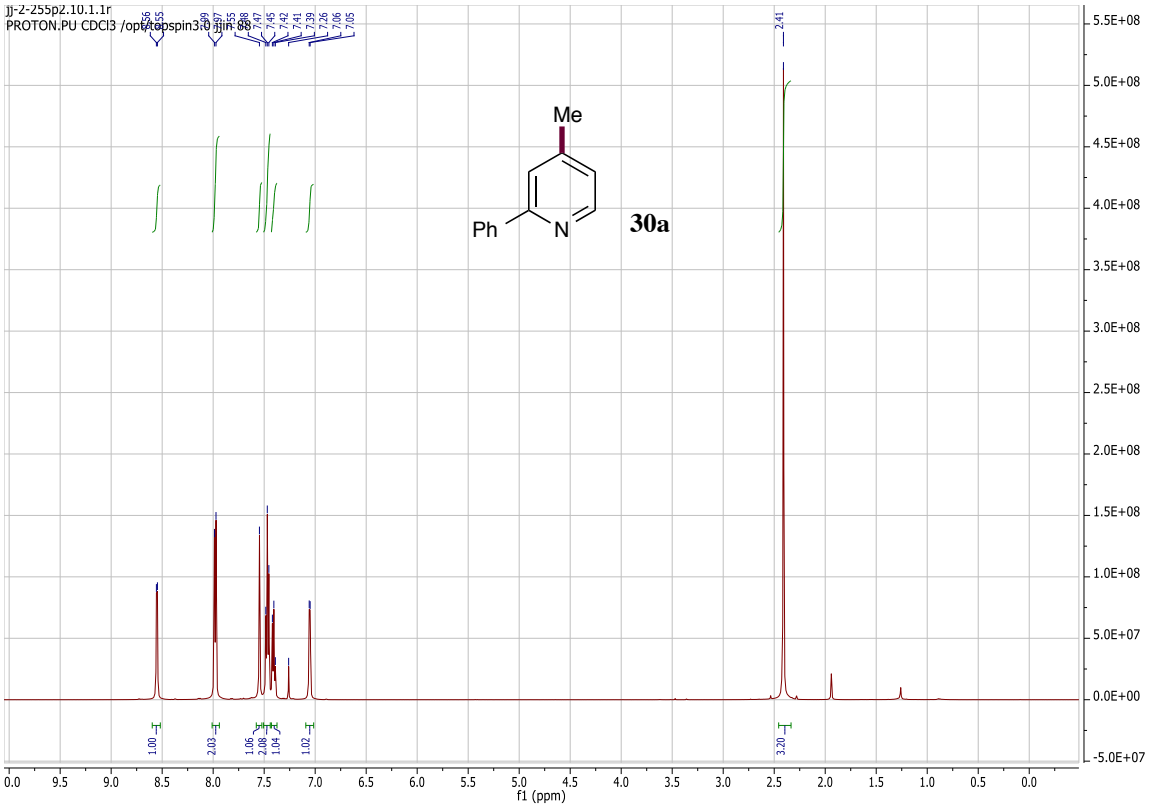

jj-2-237.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 99
166.19
158.69
149.40
147.27
127.63
123.49
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
52.85
24.44
20.84
Me
Me
N
CO2Me
27
f1 (ppm)

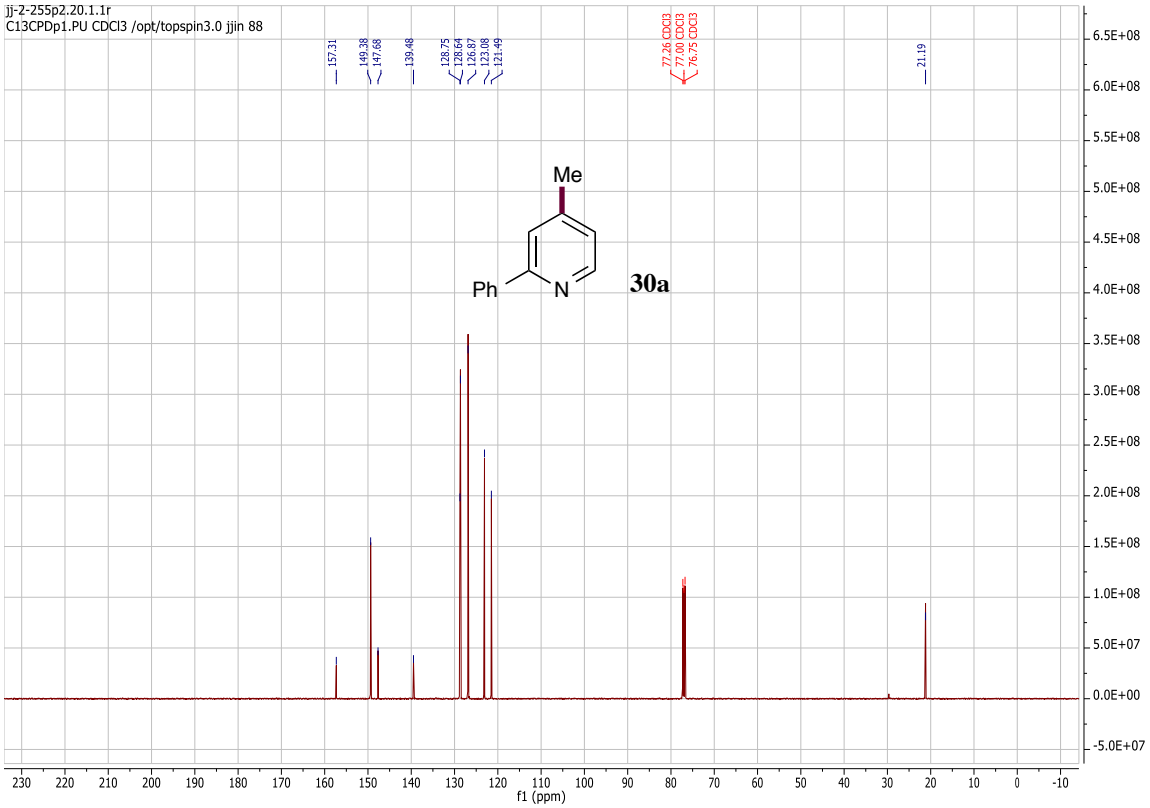

jj-2-259.10.1.1r
8.43
7.22
4.88
3.31
2.51
2.46
Me
CONH2
Me
N
28
0.95
1.00
2.37
3.08
3.05
f1 (ppm)

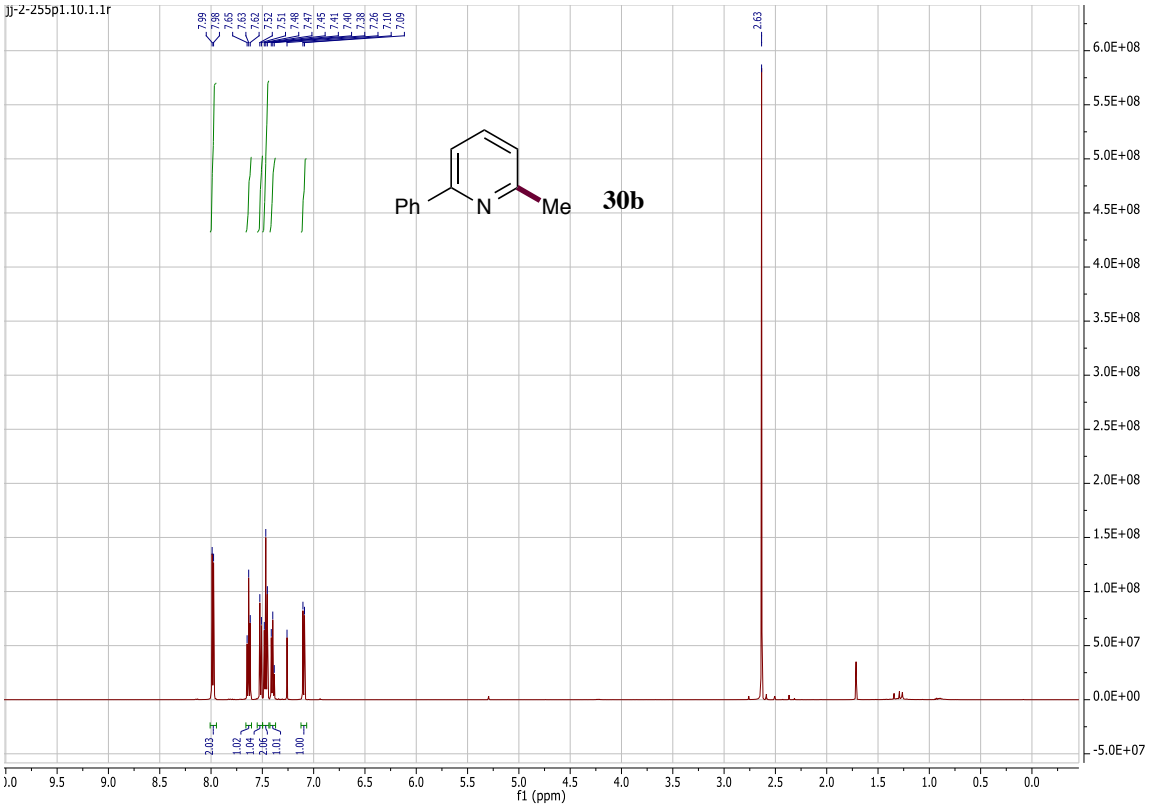

jj-2-259.20.1.1r
172.43
160.68
148.55
147.68
131.26
126.94
49.51 MeOD
49.34 MeOD
49.16 MeOD
49.00 MeOD
48.83 MeOD
48.66 MeOD
48.49 MeOD
23.56
19.55
Me
CONH2
Me
N
28
f1 (ppm)

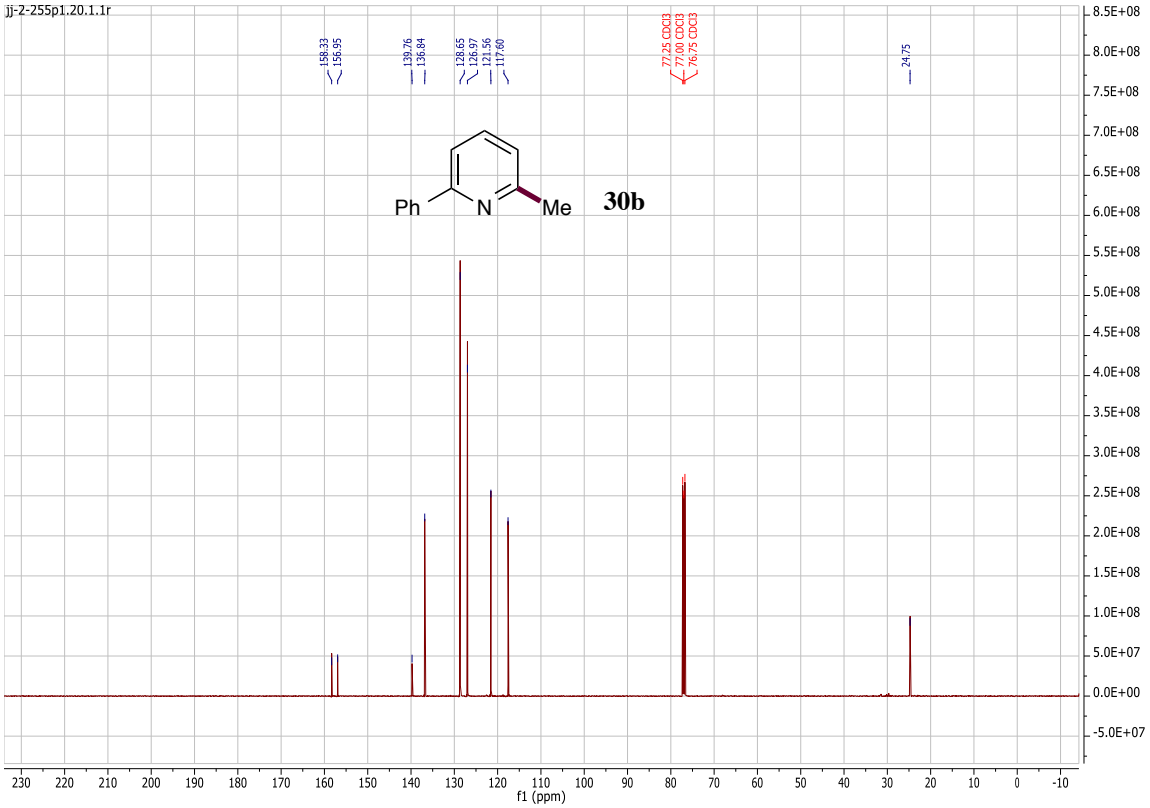

jj-2-253.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 66
Ph
N
Me
29a
f1 (ppm)

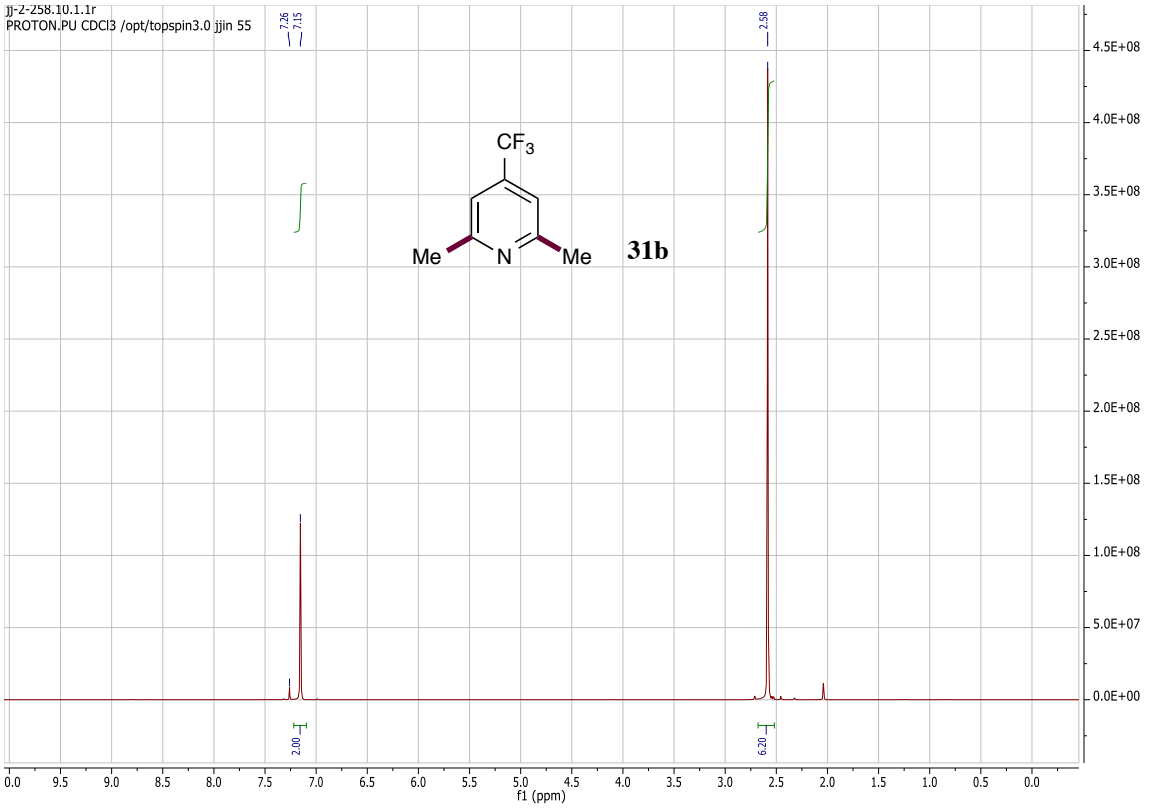

jj-2-253.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 66
Ph
N
Me
29a
f1 (ppm)

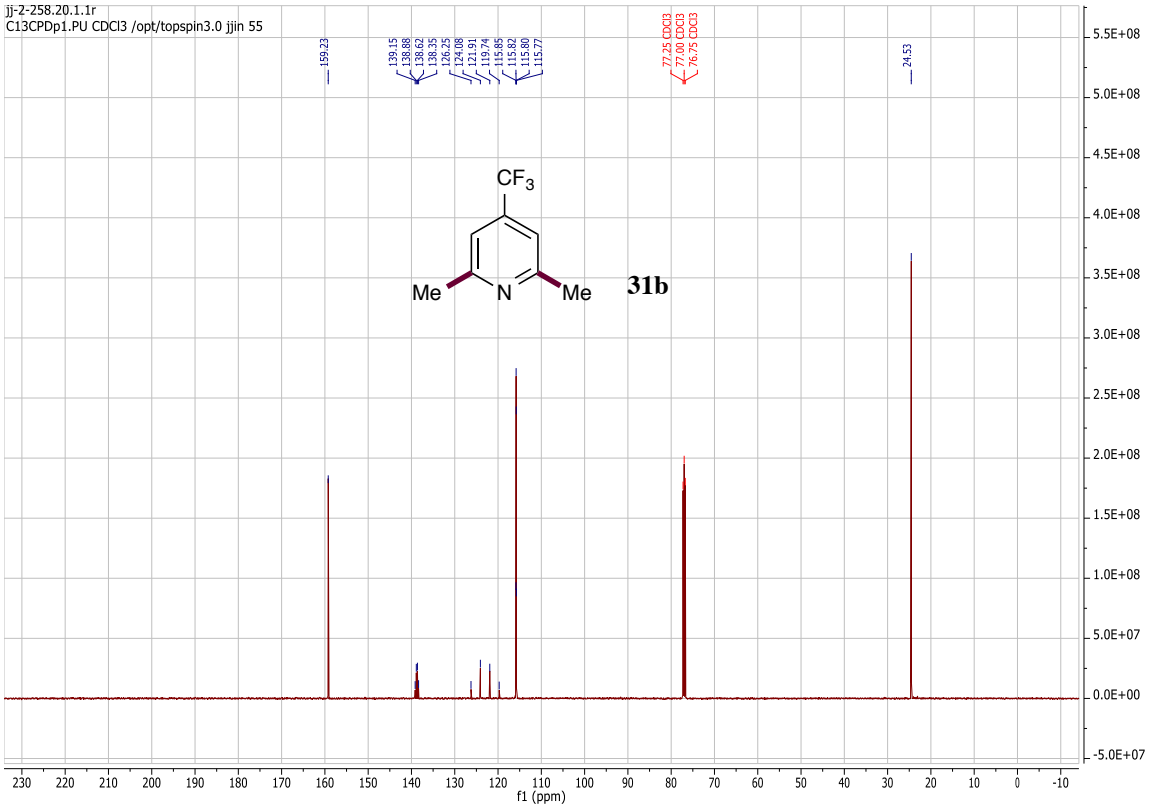

jj-2-255p2.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 88
8.56
8.55
7.99
7.97
7.55
7.48
7.47
7.45
7.42
7.41
7.39
7.26
7.06
7.05
2.41
Me
Ph
N
30a
1.00
2.03
1.06
2.08
1.04
1.02
3.20
f1 (ppm)

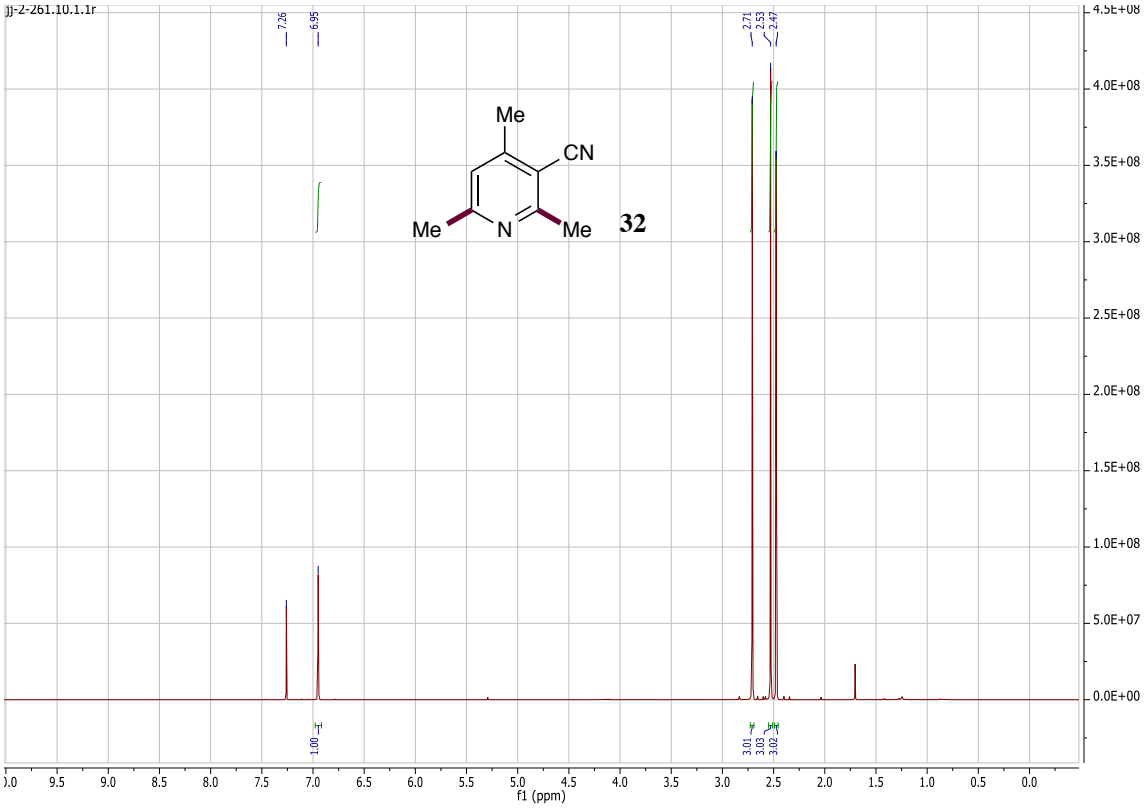

jj-2-255p2.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 88
157.31
149.38
147.68
139.48
128.75
128.64
126.87
123.08
121.49
77.26 CDCl3
77.00 CDCl3
76.75 CDCl3
21.19
Me
Ph
N
30a
f1 (ppm)

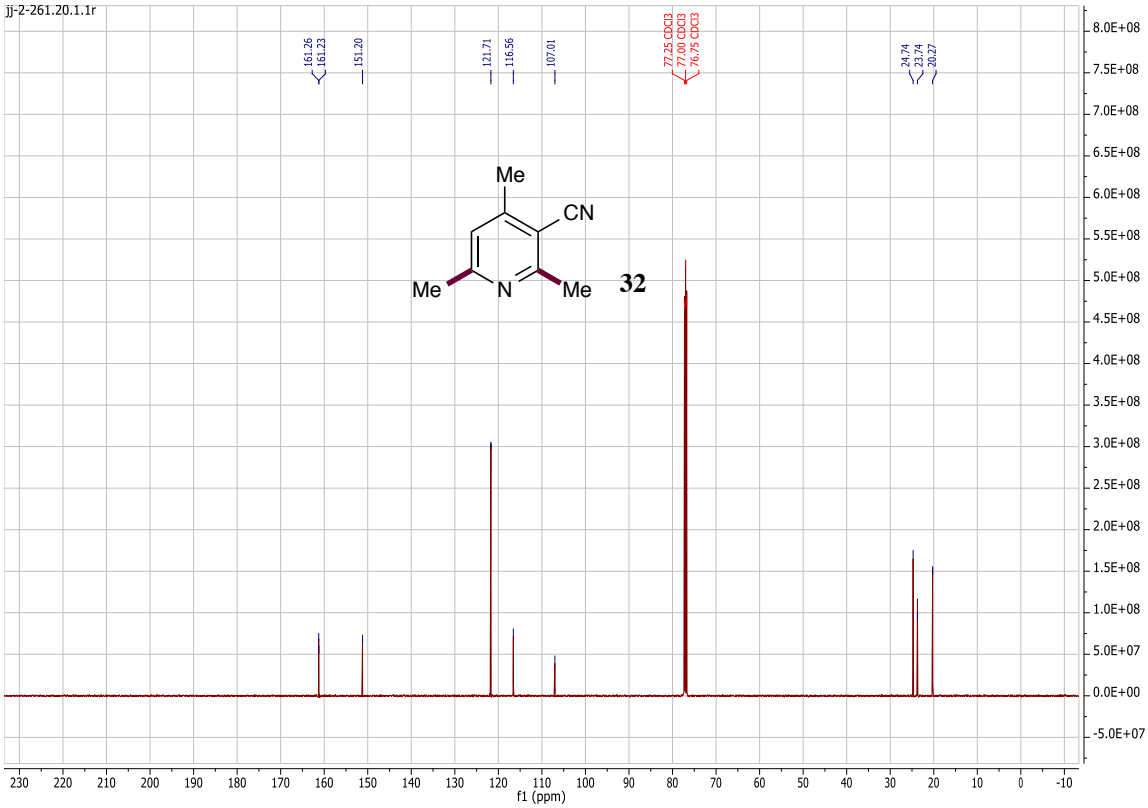

jj-2-255p1.10.1.1r
7.99
7.98
7.65
7.63
7.62
7.52
7.51
7.48
7.47
7.45
7.41
7.40
7.38
7.26
7.10
7.09
2.63
Ph
N
Me
30b
2.03
1.02
1.04
2.06
1.01
1.00
f1 (ppm)

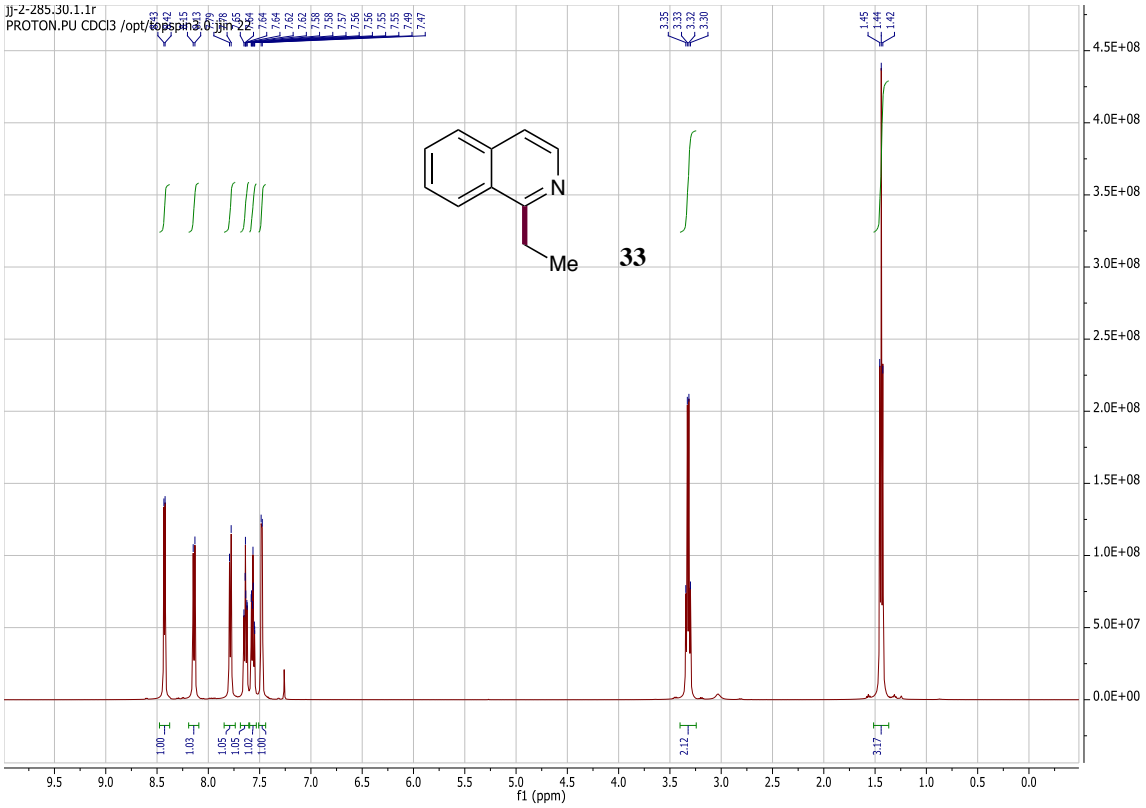

jj-2-255p1.20.1.1r
158.33
156.95
139.76
136.84
128.65
126.97
121.56
117.60
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
24.75
Ph
N
Me
30b
f1 (ppm)

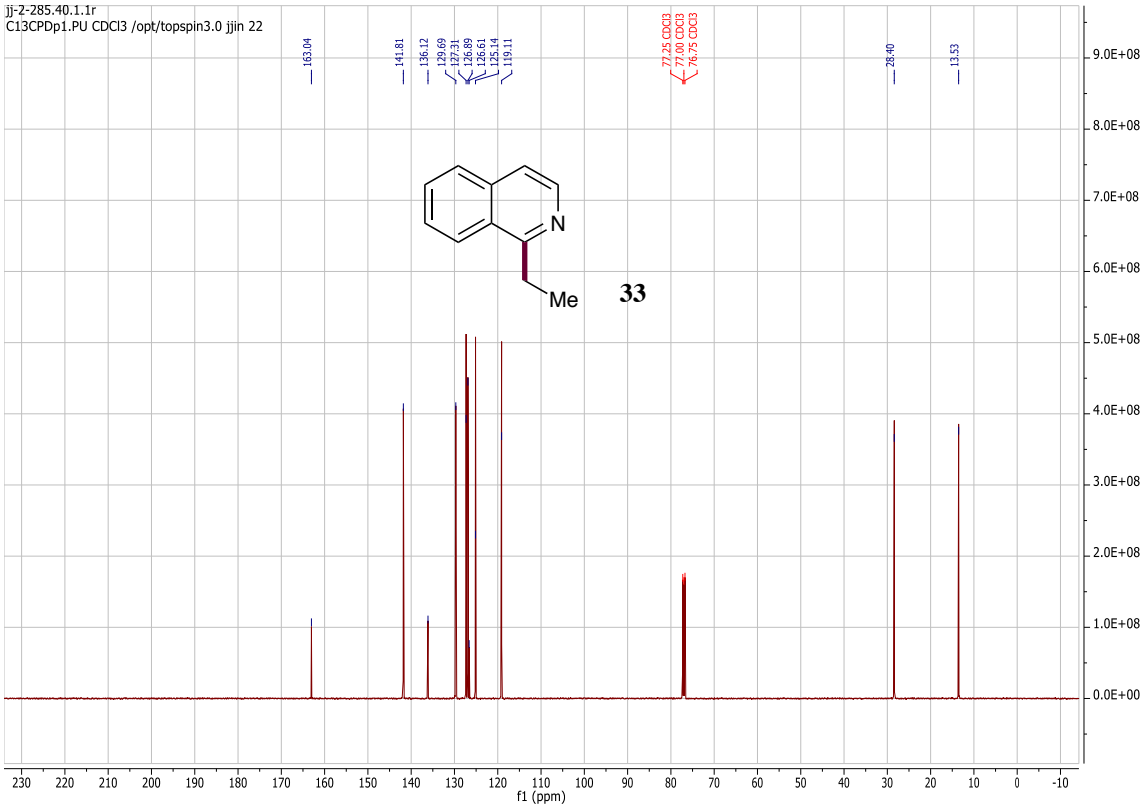

jj-2-258.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 55
7.26
7.15
2.58
CF3
Me
N
Me
31b
2.00
6.20
f1 (ppm)

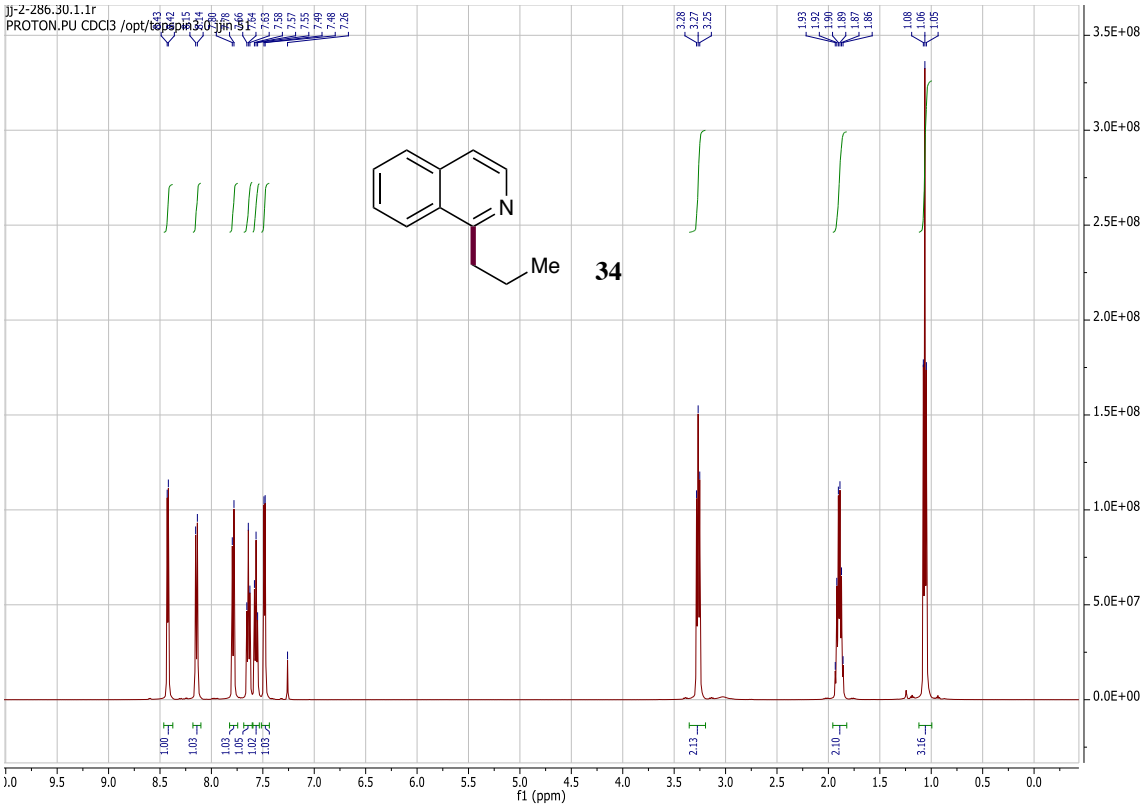

jj-2-258.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 55
159.23
139.15
138.88
138.62
138.35
126.25
124.08
121.91
119.74
115.85
115.82
115.80
115.77
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
24.53
CF3
Me
N
Me
31b
f1 (ppm)

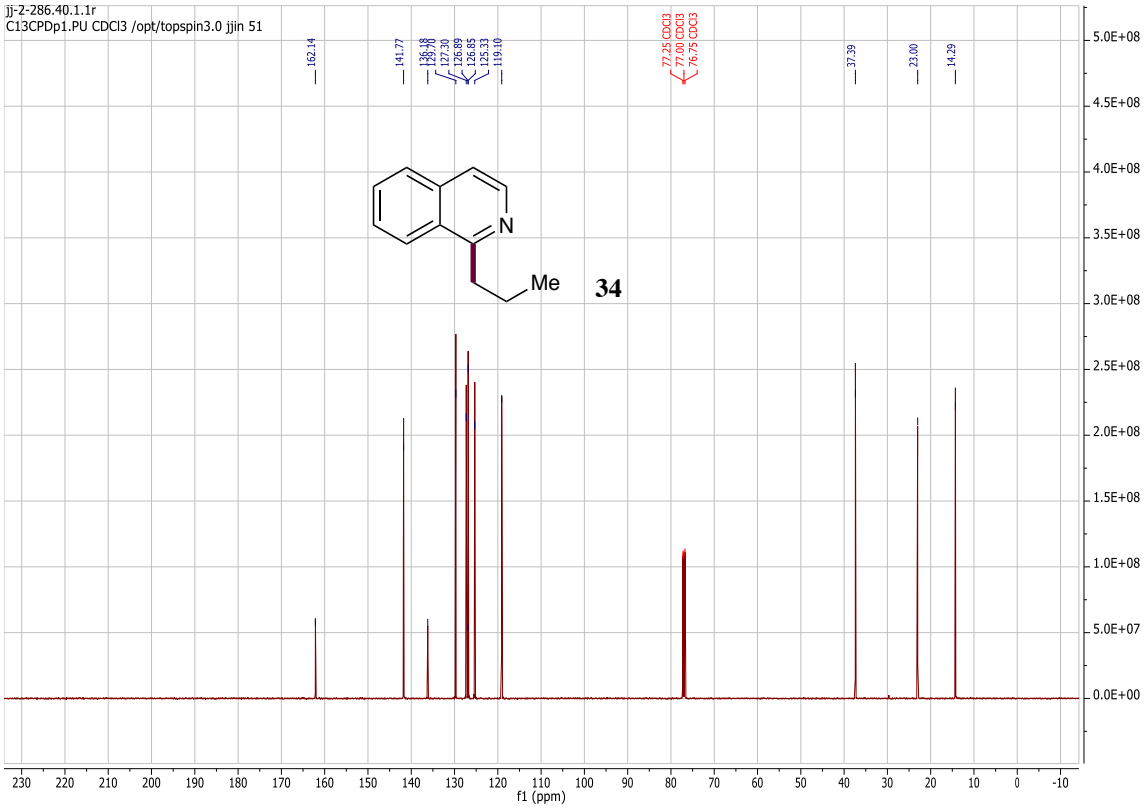

jj-2-261.10.1.1r
7.26
6.95
2.71
2.53
2.47
Me
CN
Me
N
Me
32
1.00
3.01
3.03
3.02
f1 (ppm)

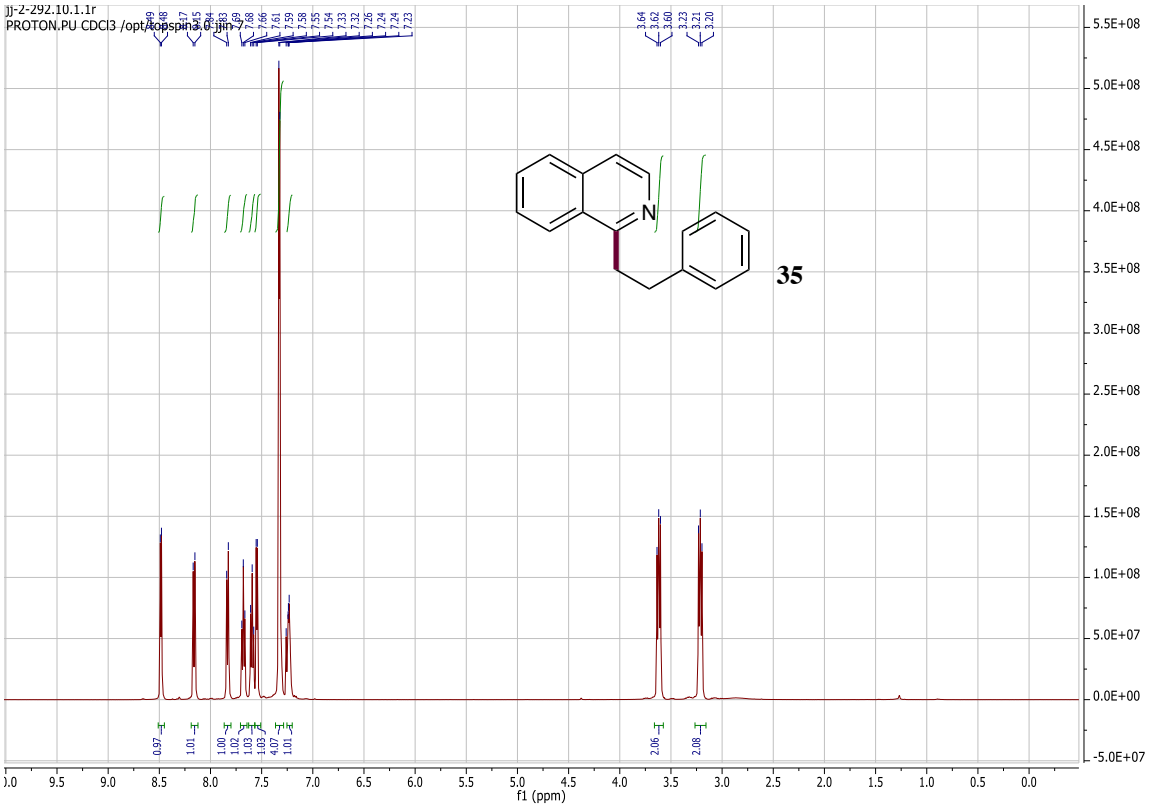

jj-2-261.20.1.1r
161.26
161.23
151.20
121.71
116.56
107.01
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
24.74
23.74
20.27
Me
CN
Me
N
Me
32
f1 (ppm)

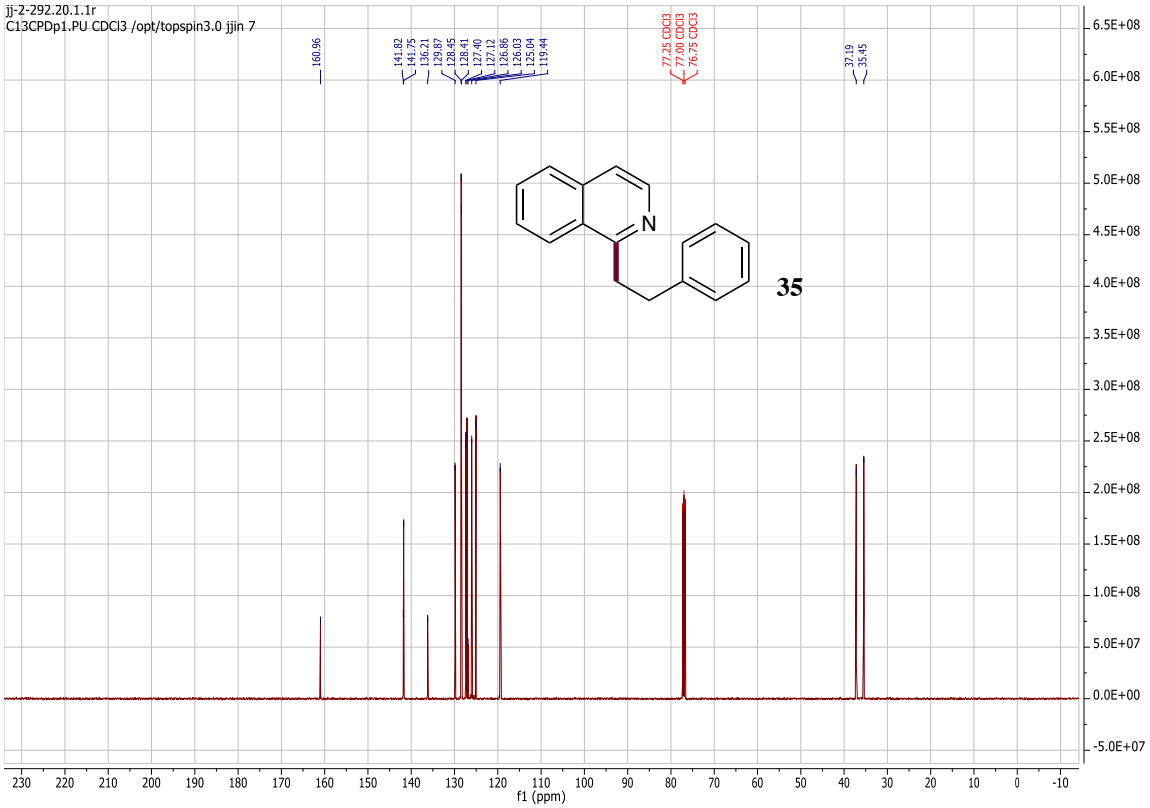

jj-2-285.30.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 22
N
Me
33
f1 (ppm)

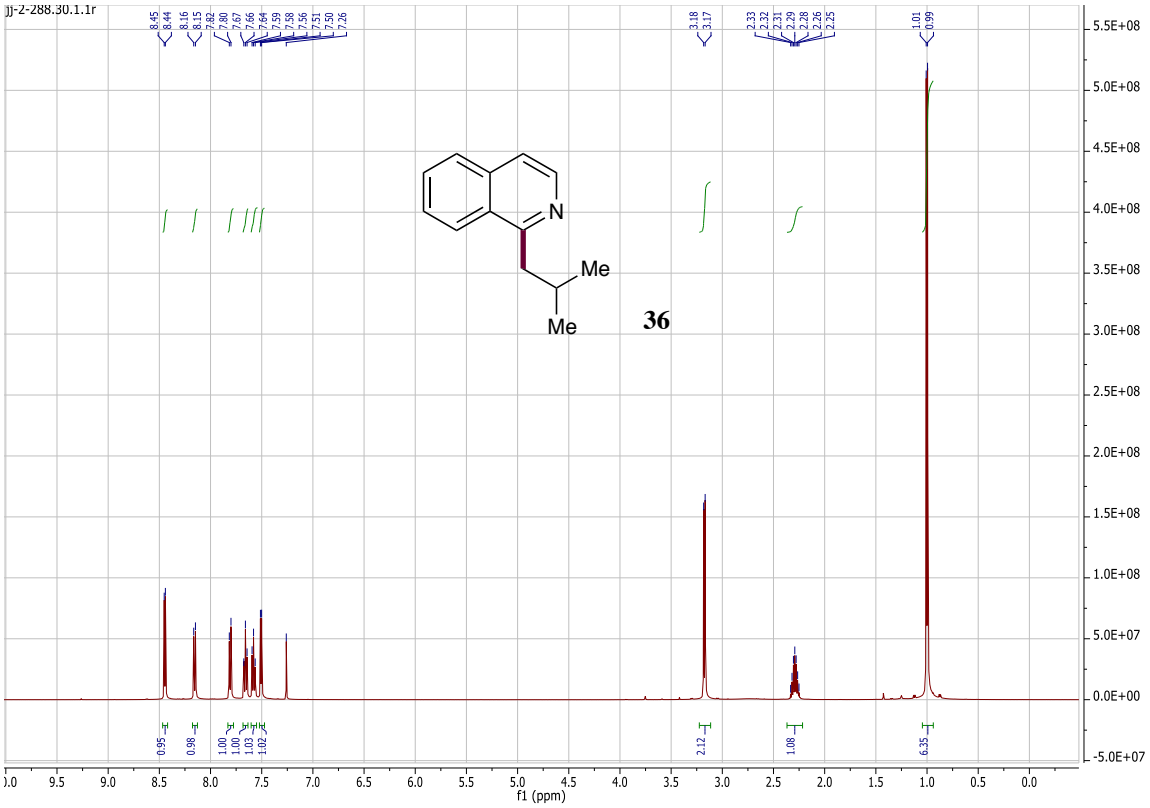

jj-2-285.40.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 22
163.04
141.81
136.12
129.69
127.31
126.89
126.61
125.14
119.11
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
28.40
13.53
N
Me
33
f1 (ppm)

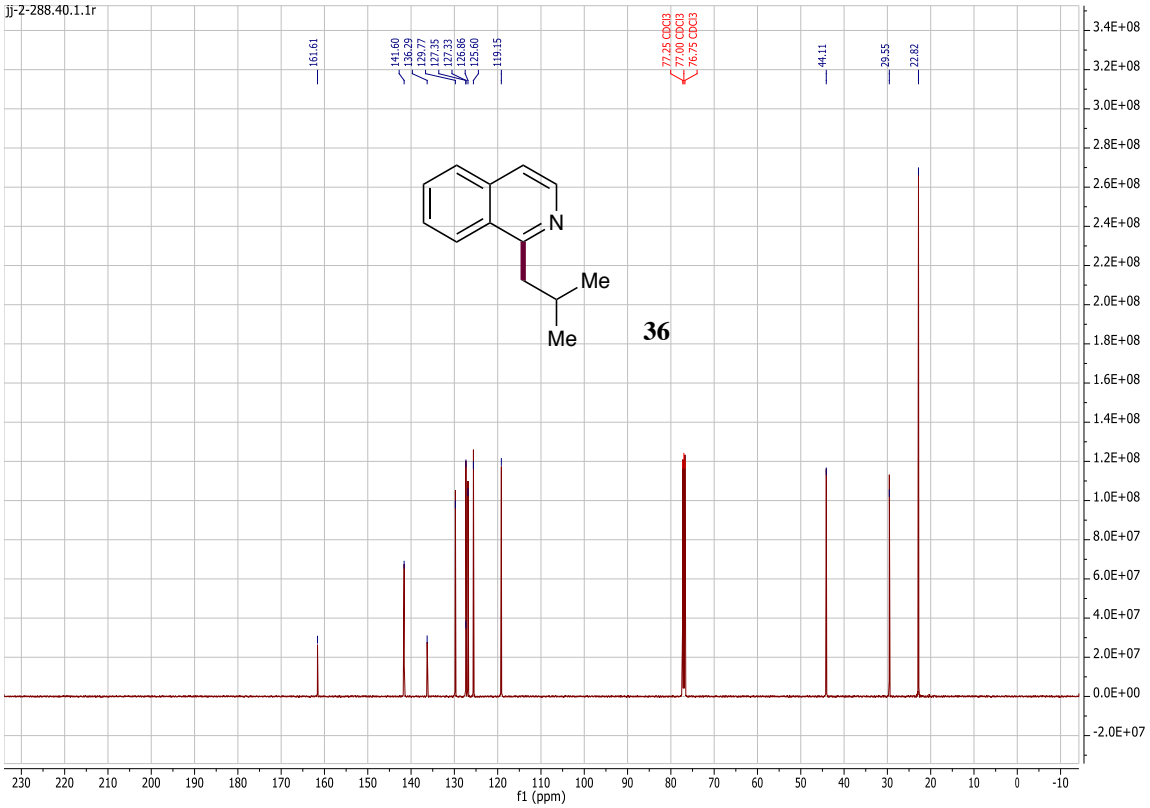

jj-2-286.30.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 51
Me
34
f1 (ppm)

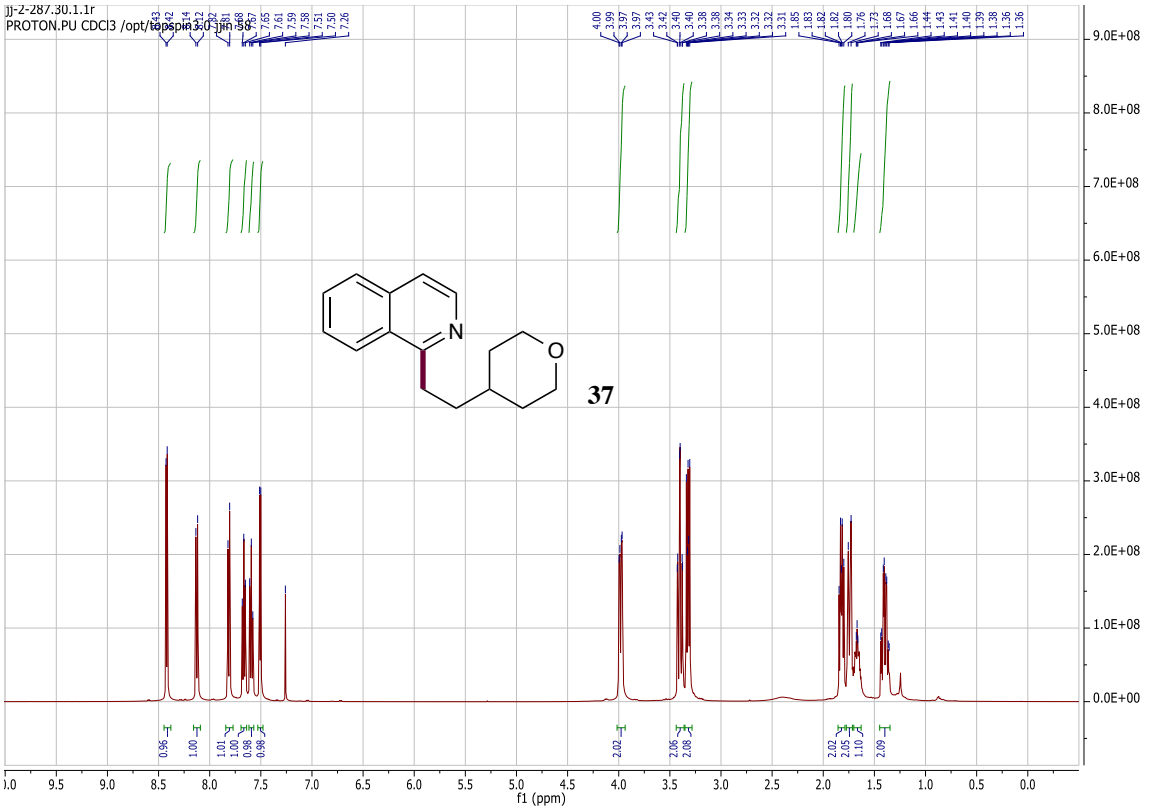

jj-2-286.40.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 51
Me
34
f1 (ppm)

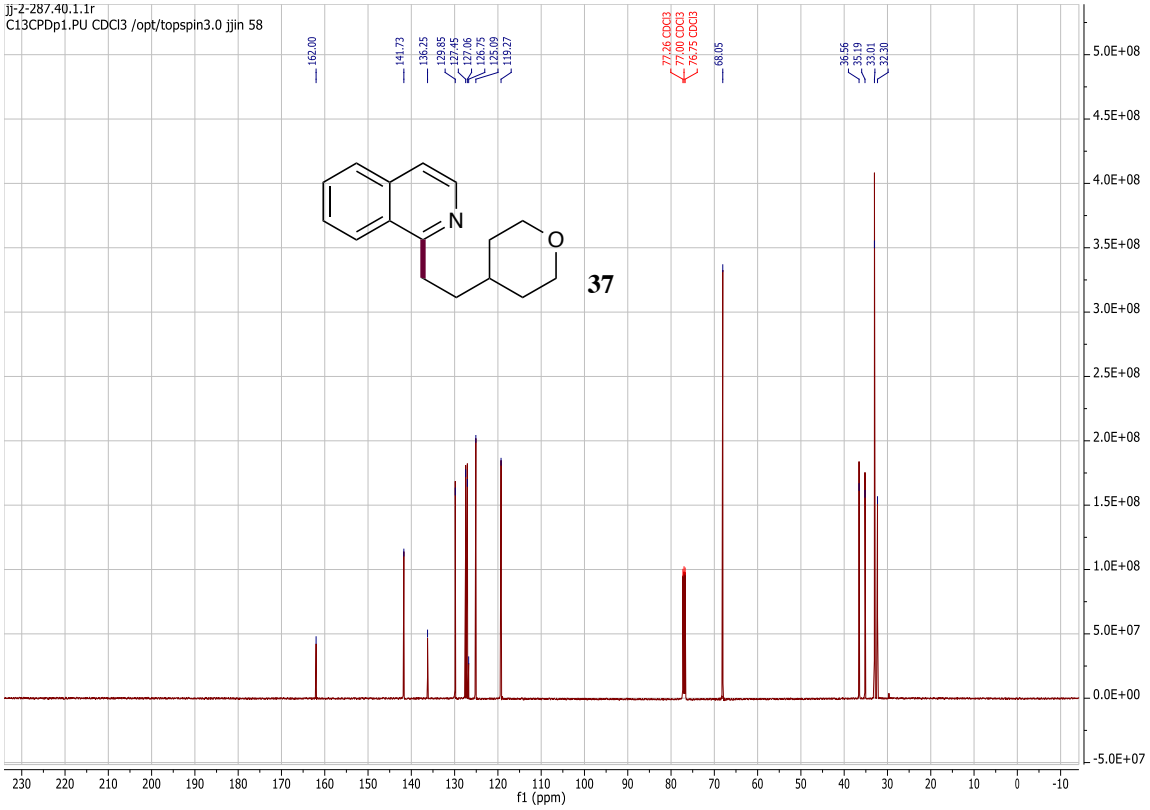

jj-2-292.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 7
35
f1 (ppm)

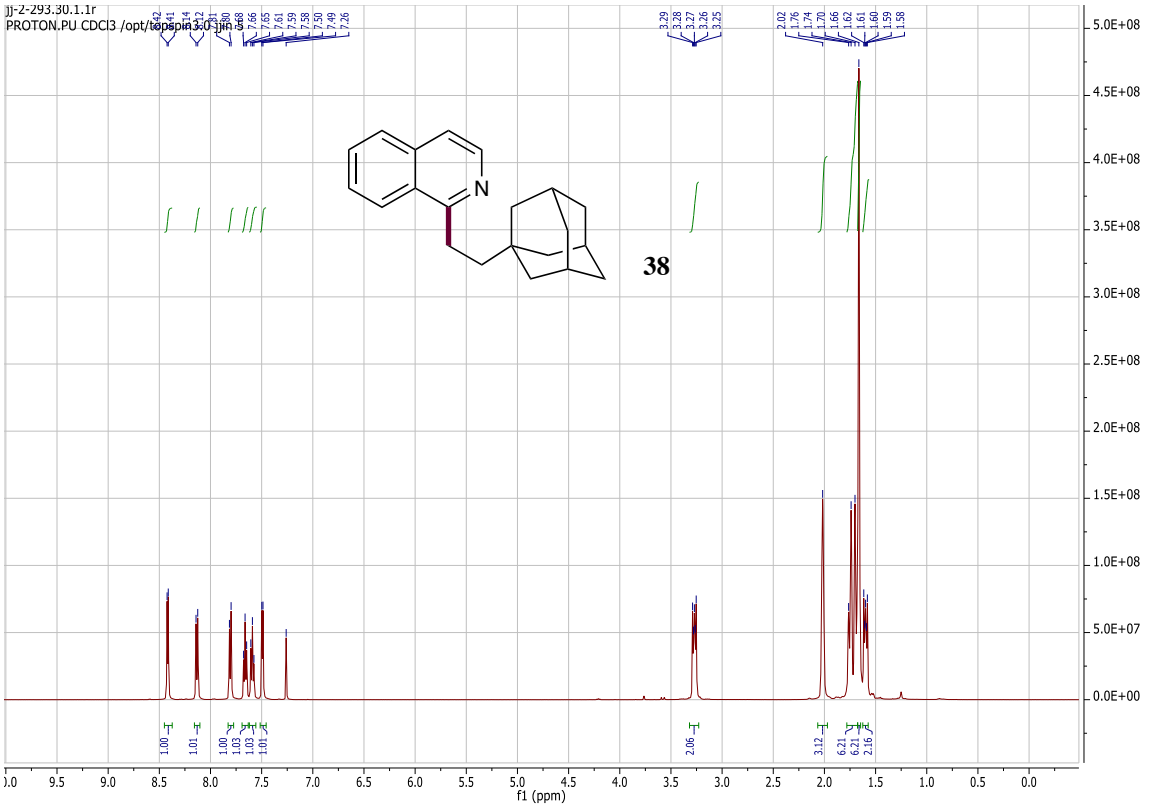

jj-2-292.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 7
35
f1 (ppm)

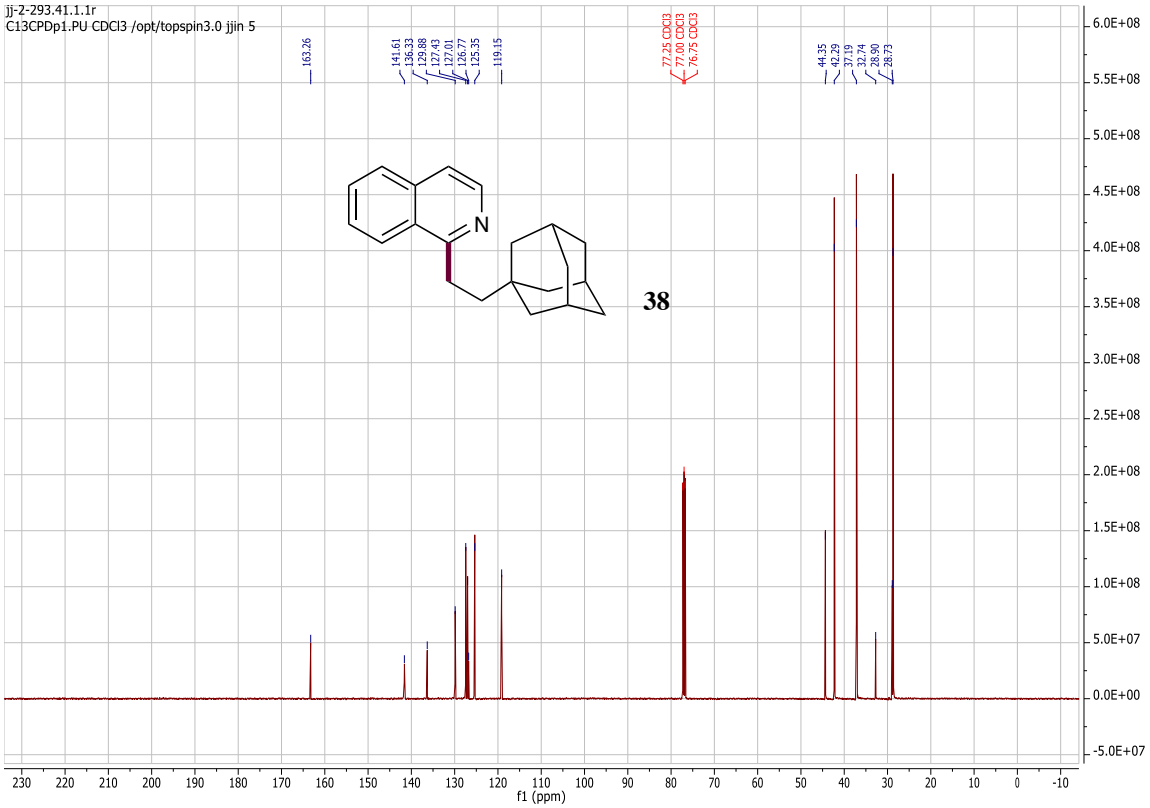

jj-2-288.30.1.1r
8.45
8.44
8.16
8.15
7.82
7.80
7.67
7.66
7.64
7.59
7.58
7.56
7.51
7.50
7.26
3.18
3.17
2.33
2.32
2.31
2.29
2.28
2.26
2.25
1.01
0.99
N
Me
Me
36
0.95
0.98
1.00
1.00
1.03
1.02
2.12
1.08
6.35
f1 (ppm)

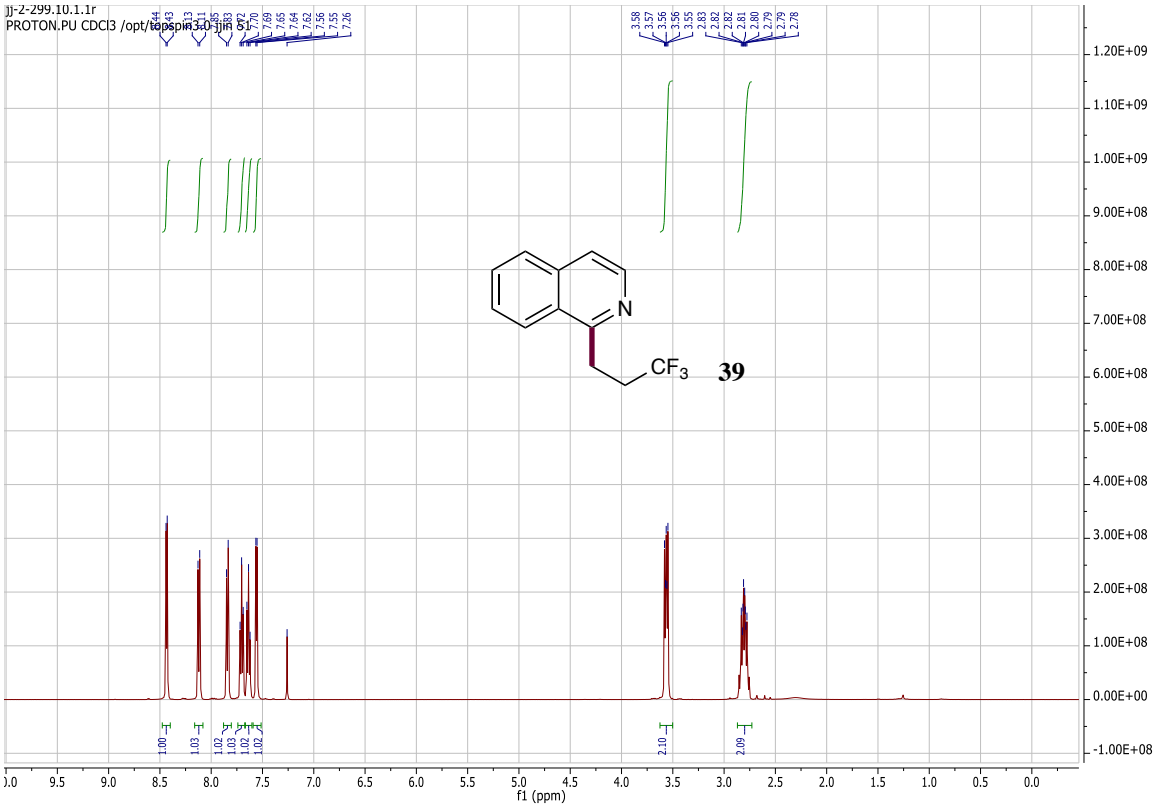

jj-2-288.40.1.1r
161.61
141.60
136.29
130.77
127.35
127.33
126.86
125.60
119.15
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
44.11
29.55
22.82
N
Me
Me
36
f1 (ppm)

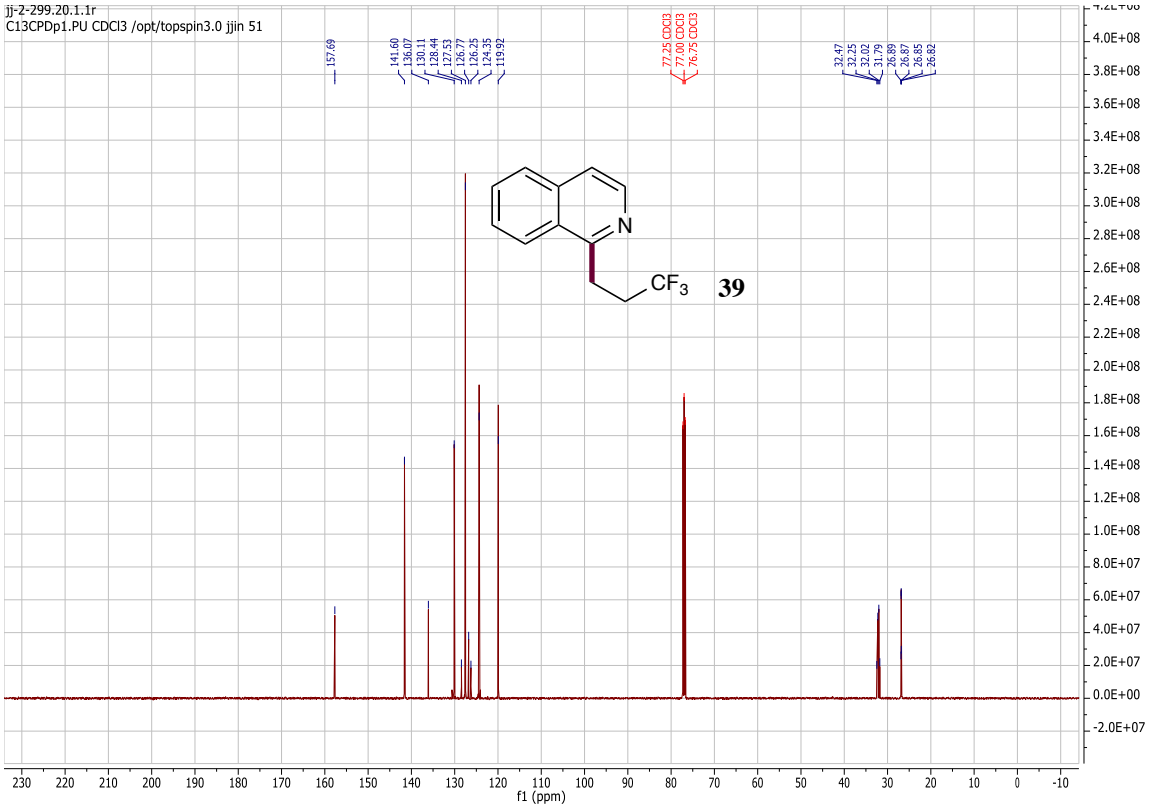

jj-2-287.30.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 58
37
f1 (ppm)

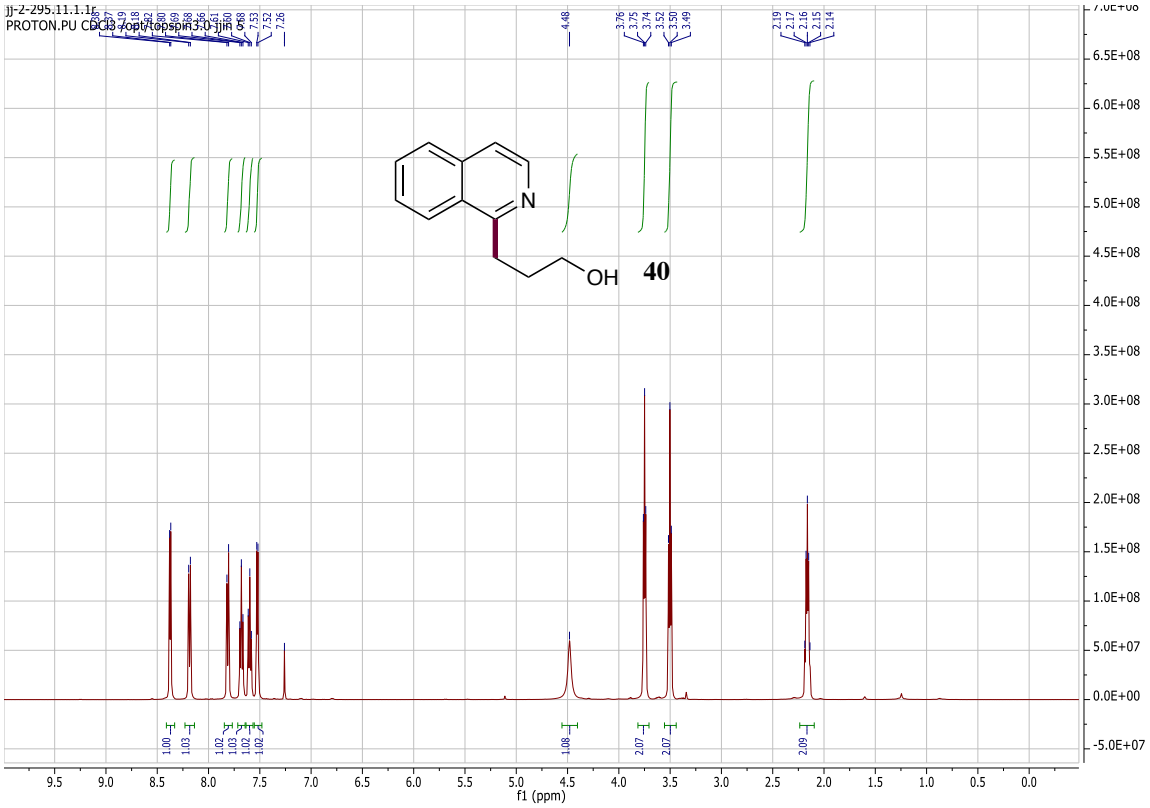

jj-2-287.40.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 58
37
f1 (ppm)

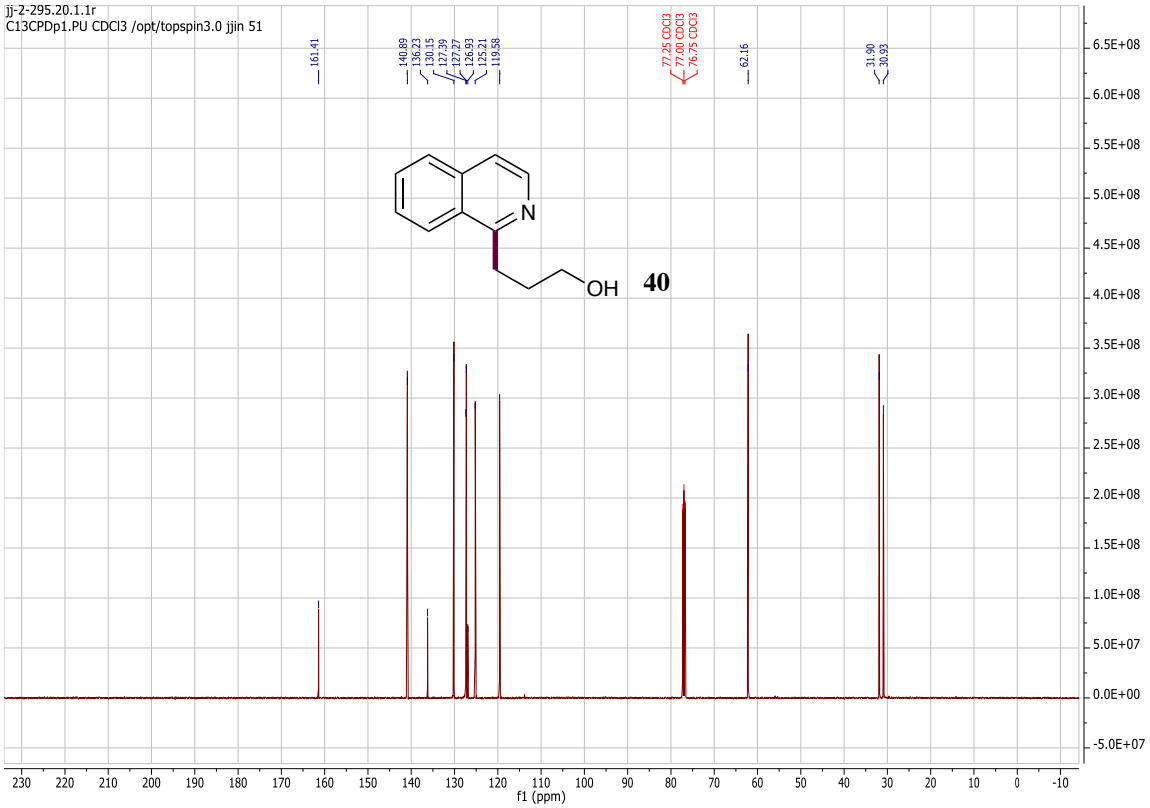

jj-2-293.30.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 5
38
f1 (ppm)

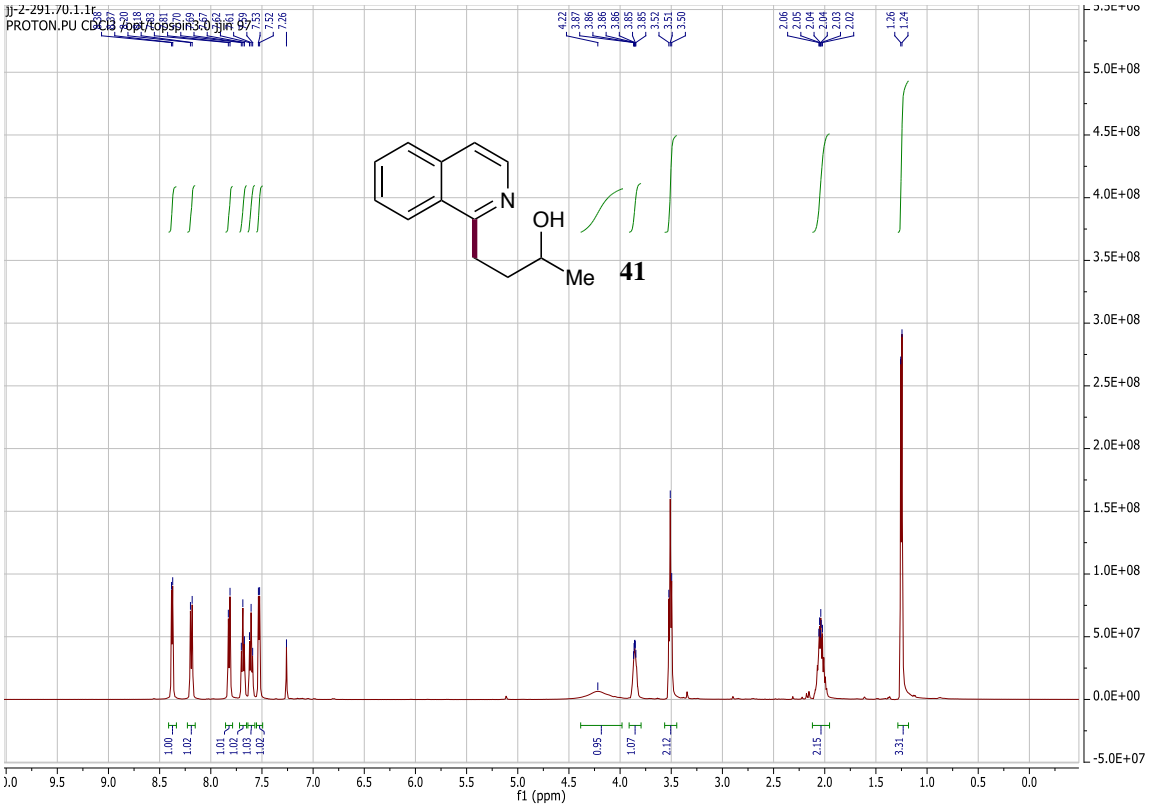

jj-2-293.41.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 5
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
38
f1 (ppm)

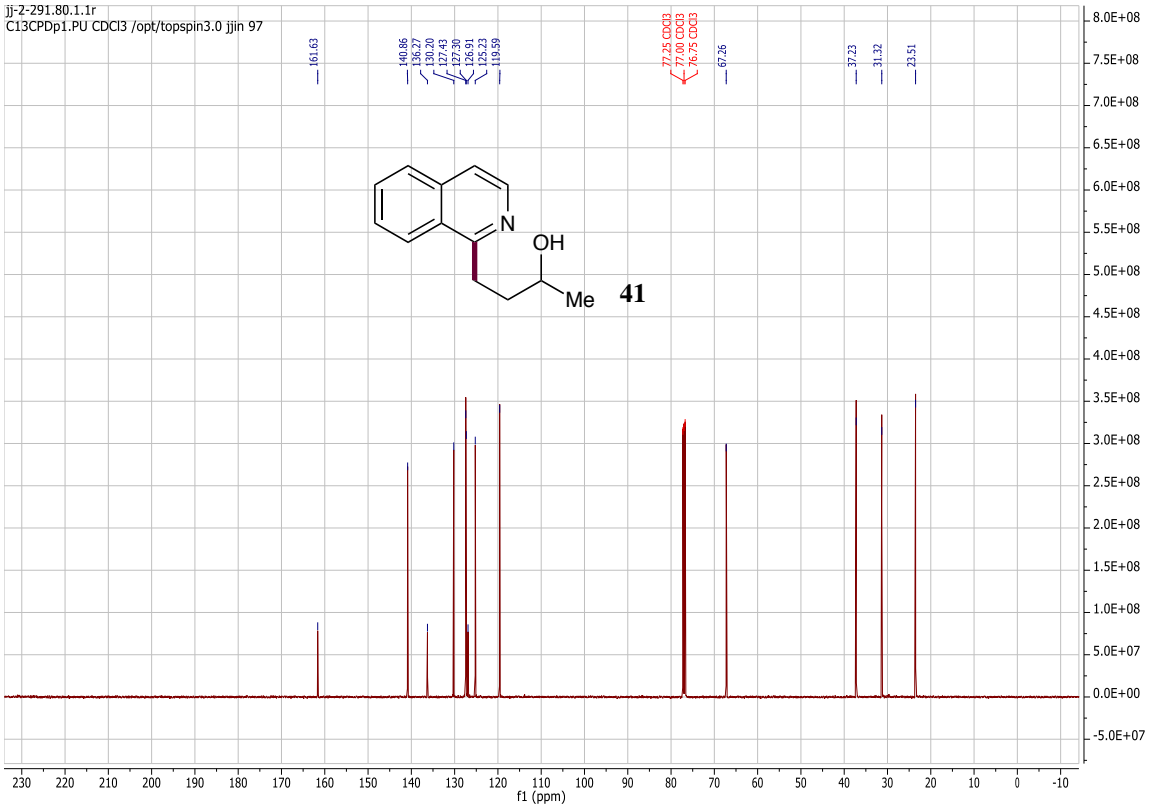

jj-2-299.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 51
7.44
7.43
7.13
7.11
7.85
7.83
7.72
7.70
7.69
7.65
7.64
7.62
7.56
7.55
7.26
3.58
3.57
3.56
3.56
3.55
2.83
2.82
2.82
2.81
2.80
2.79
2.79
2.78
1.00
1.03
1.02
1.03
1.02
1.02
2.10
2.09
N
CF3
39
f1 (ppm)

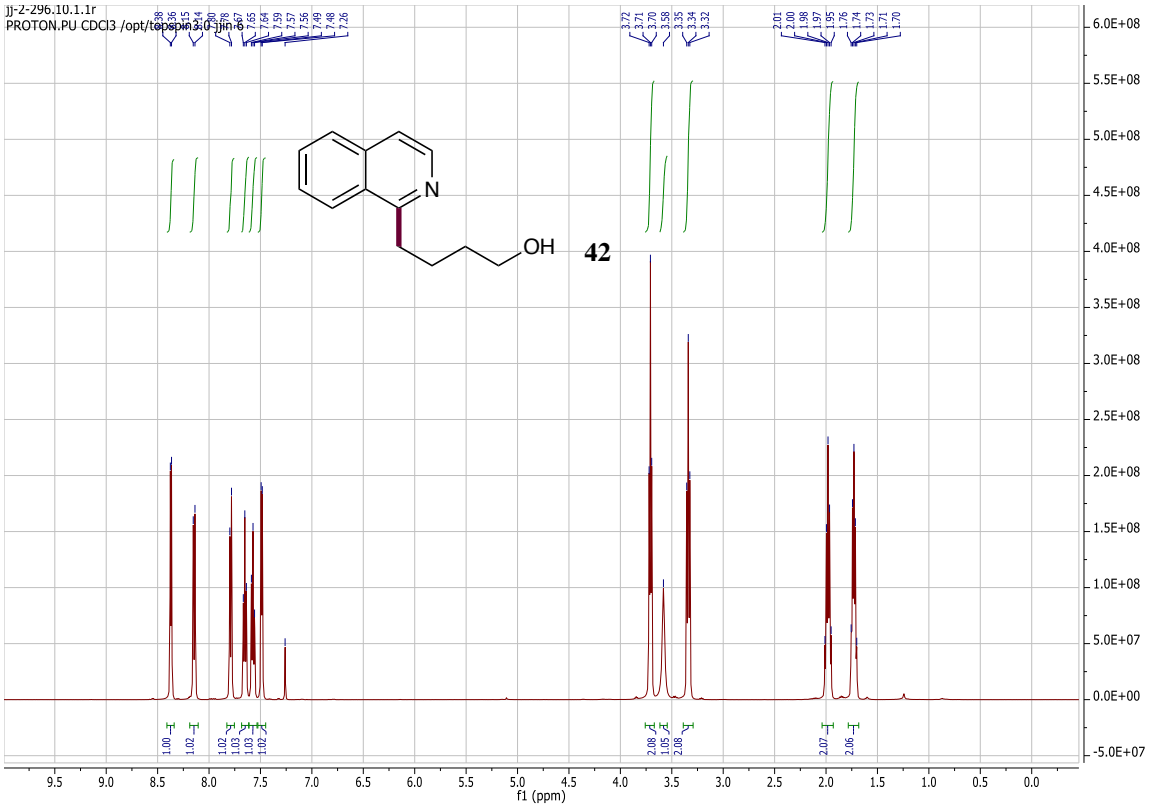

jj-2-299.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 51
157.69
141.60
136.07
130.11
128.44
127.53
126.77
126.25
124.35
119.92
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
32.47
32.25
32.02
31.79
26.89
26.87
26.85
26.82
N
CF3
39
f1 (ppm)

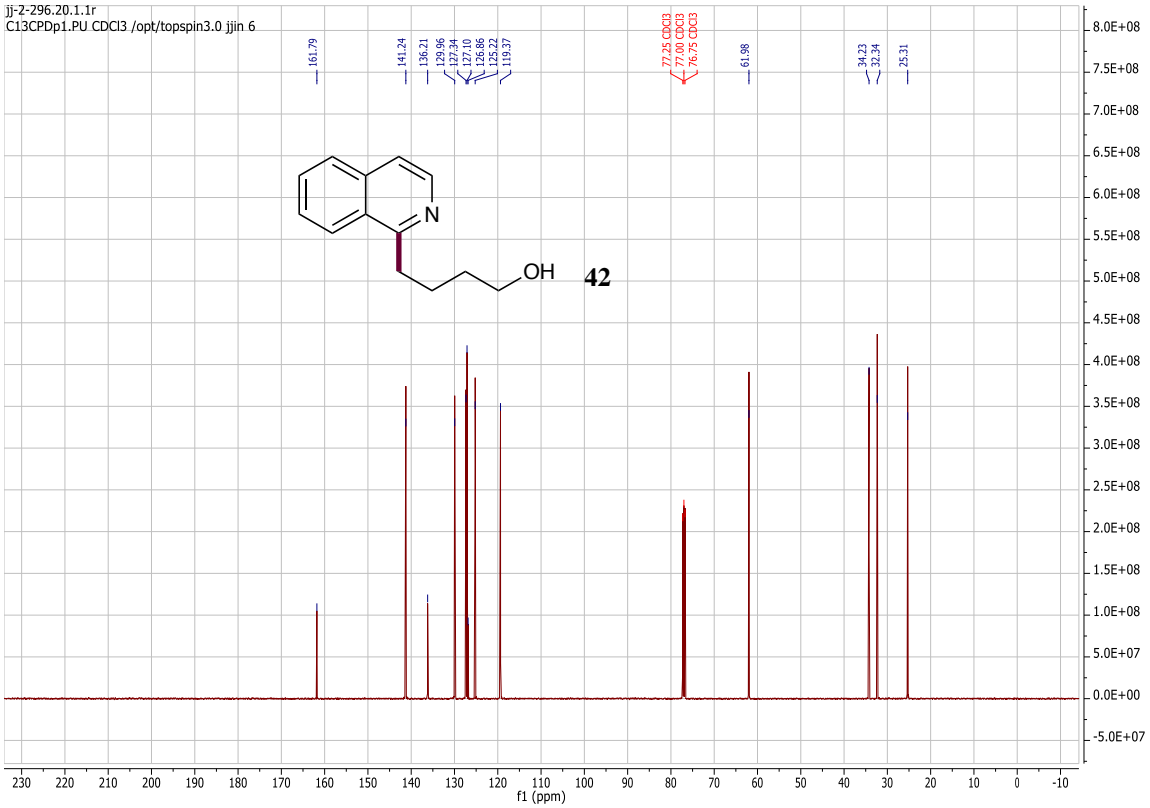

jj-2-295.11.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 6
7.27
7.19
7.18
7.02
7.00
6.99
6.88
6.86
6.61
6.60
6.58
6.56
7.53
7.51
7.26
4.48
3.76
3.75
3.74
3.52
3.50
3.49
2.19
2.17
2.16
2.15
2.14
N
OH
40
1.00
1.03
1.02
1.03
1.02
1.02
1.08
2.07
2.07
2.09
f1 (ppm)

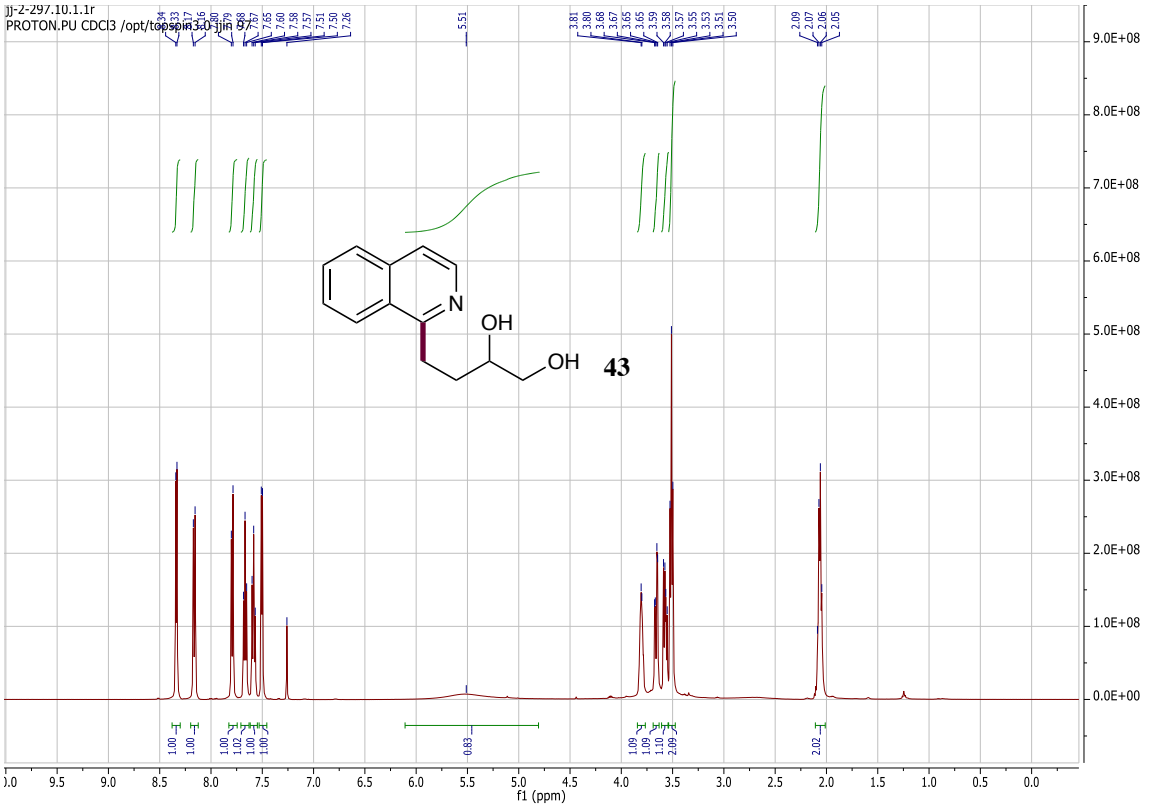

jj-2-295.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 51
161.41
140.89
136.23
130.15
127.39
127.27
126.93
125.21
119.58
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
62.16
31.90
30.93
N
OH
40
f1 (ppm)

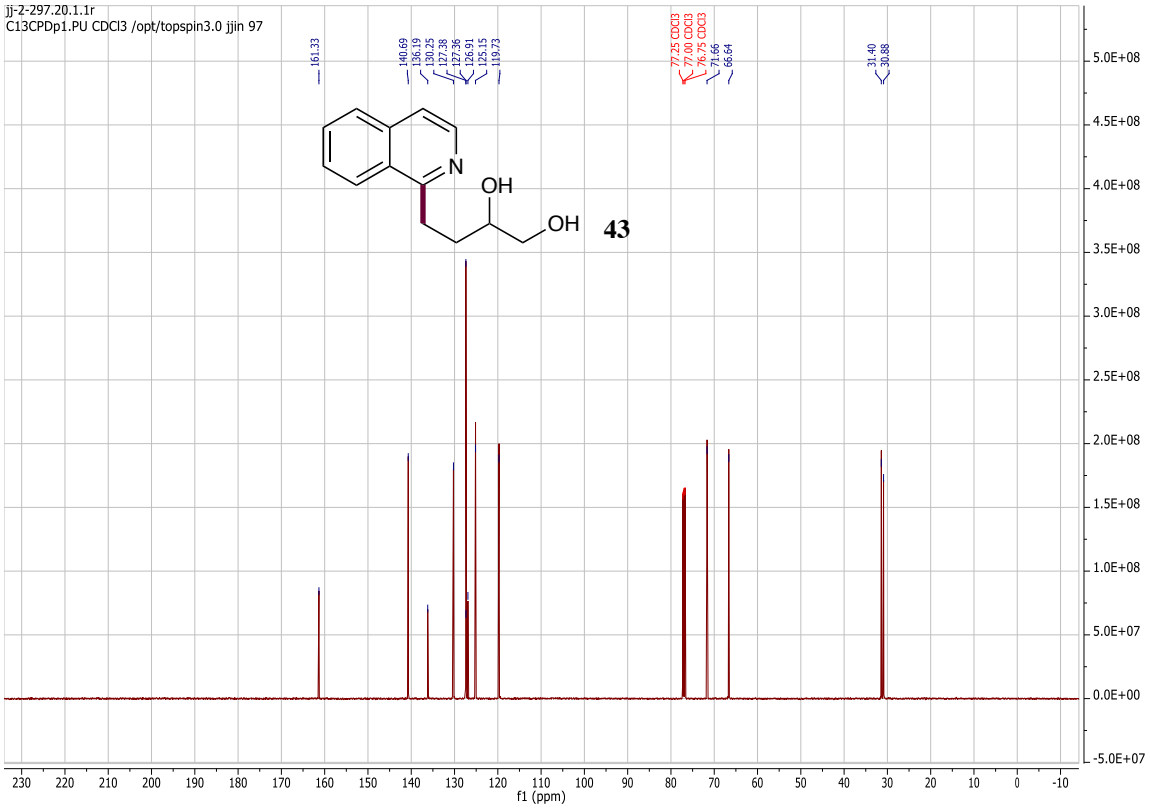

jj-2-291.70.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 97
OH
Me
41
f1 (ppm)

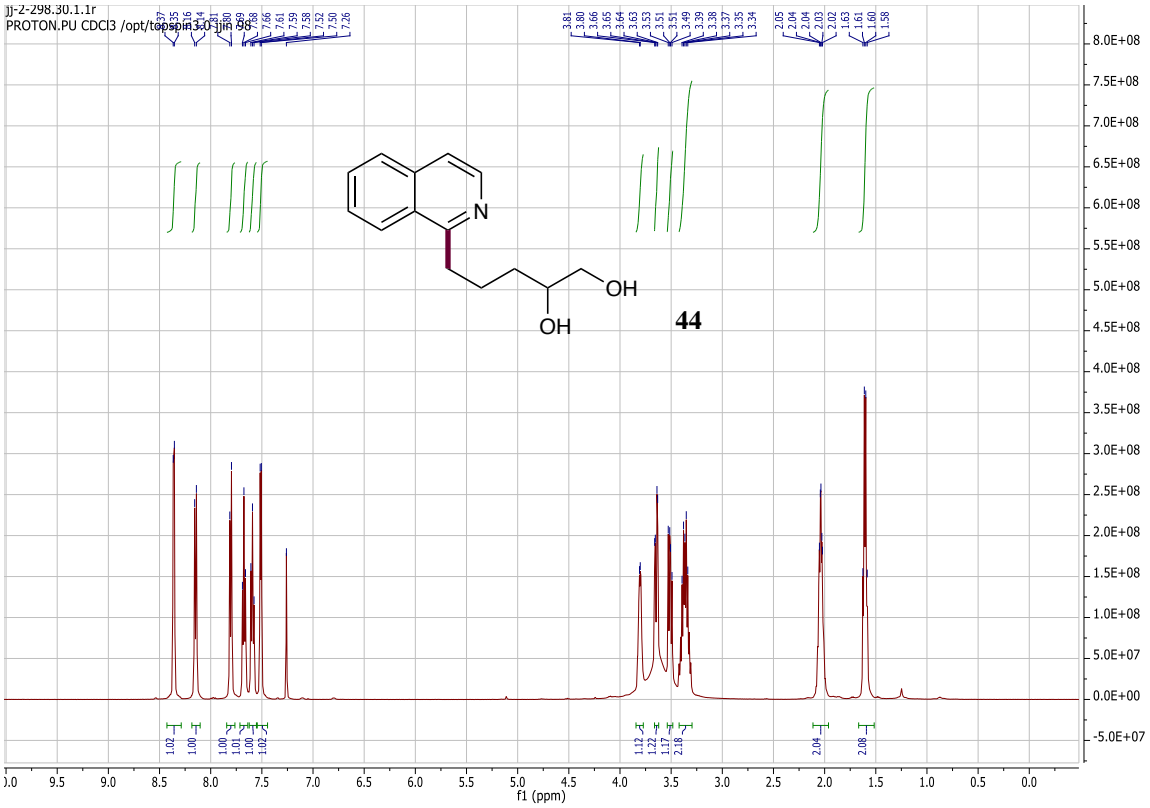

jj-2-291.80.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 97
OH
Me
41
f1 (ppm)

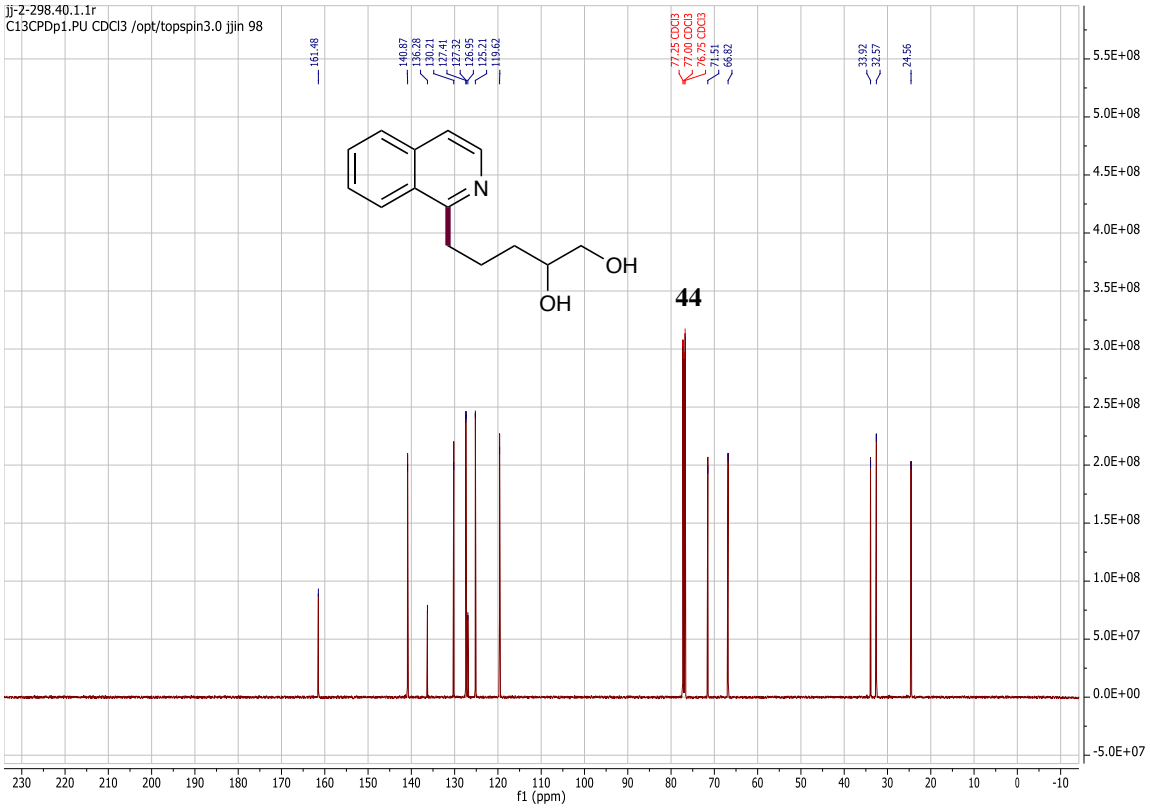

jj-2-296.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 6
N
OH
42
f1 (ppm)

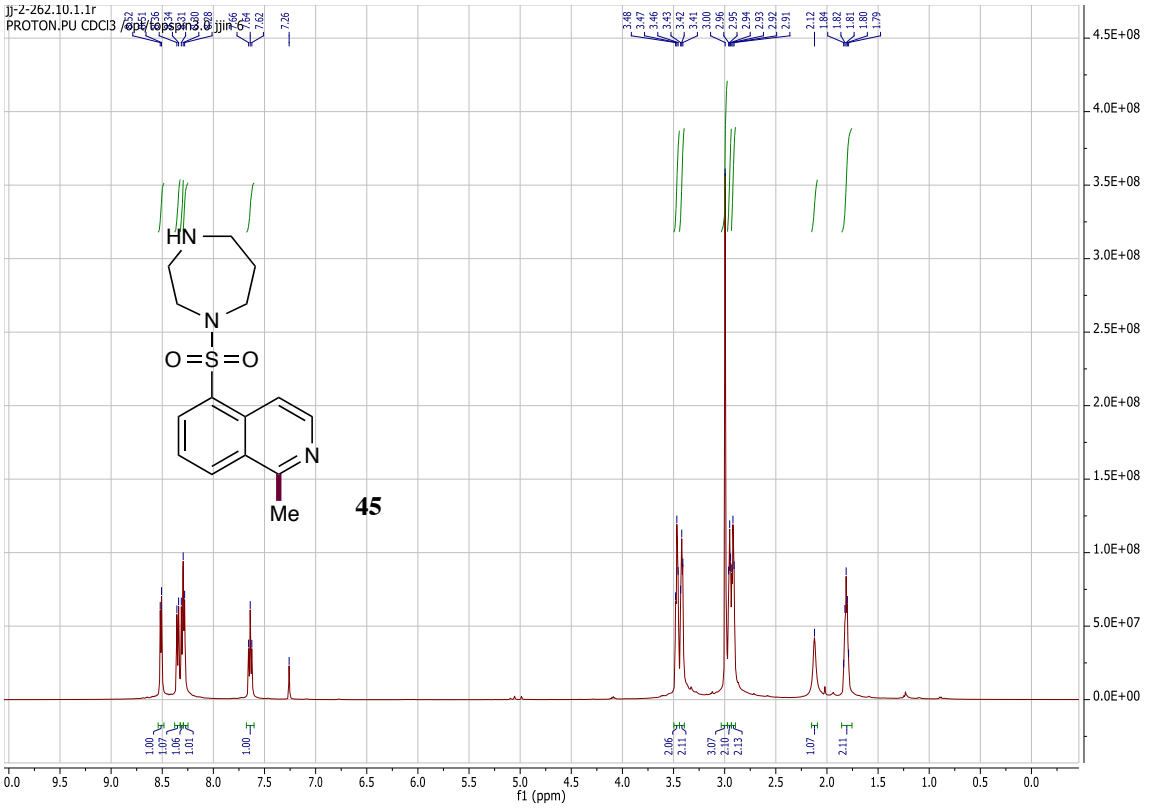

jj-2-296.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 6
N
OH
42
f1 (ppm)

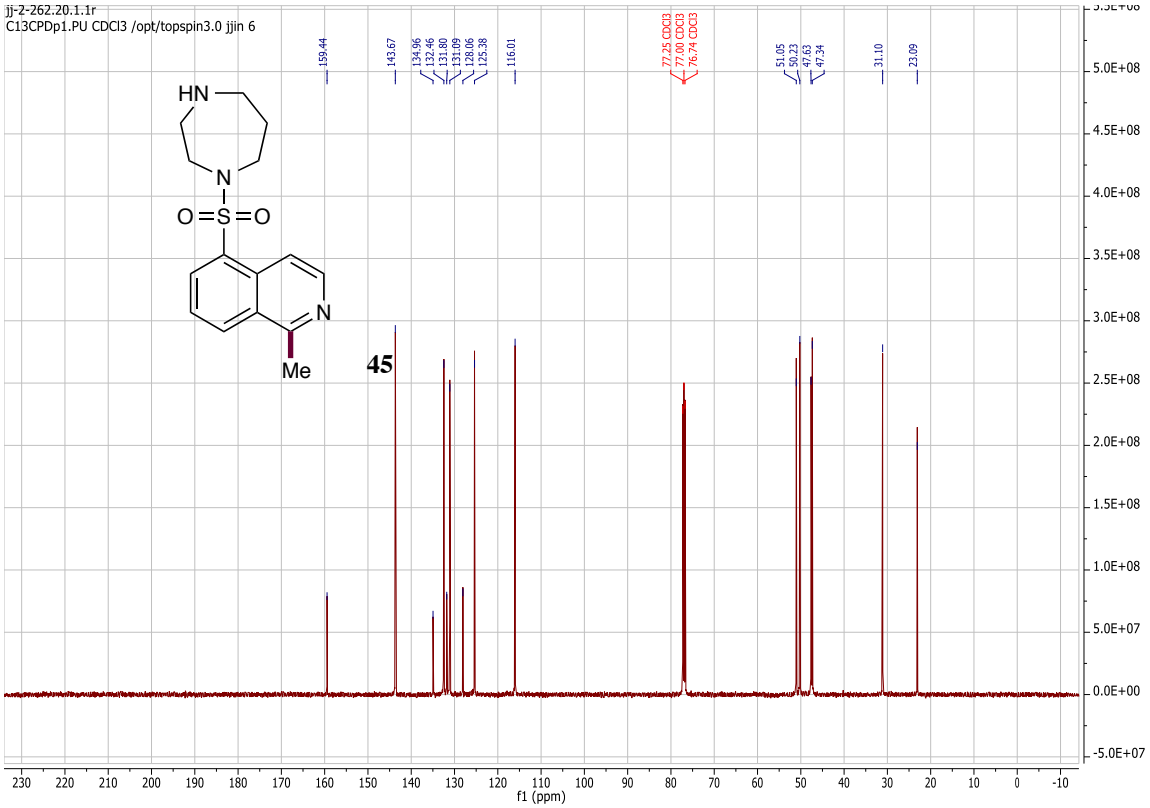

jj-2-297.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 97
N
OH
OH
43
f1 (ppm)

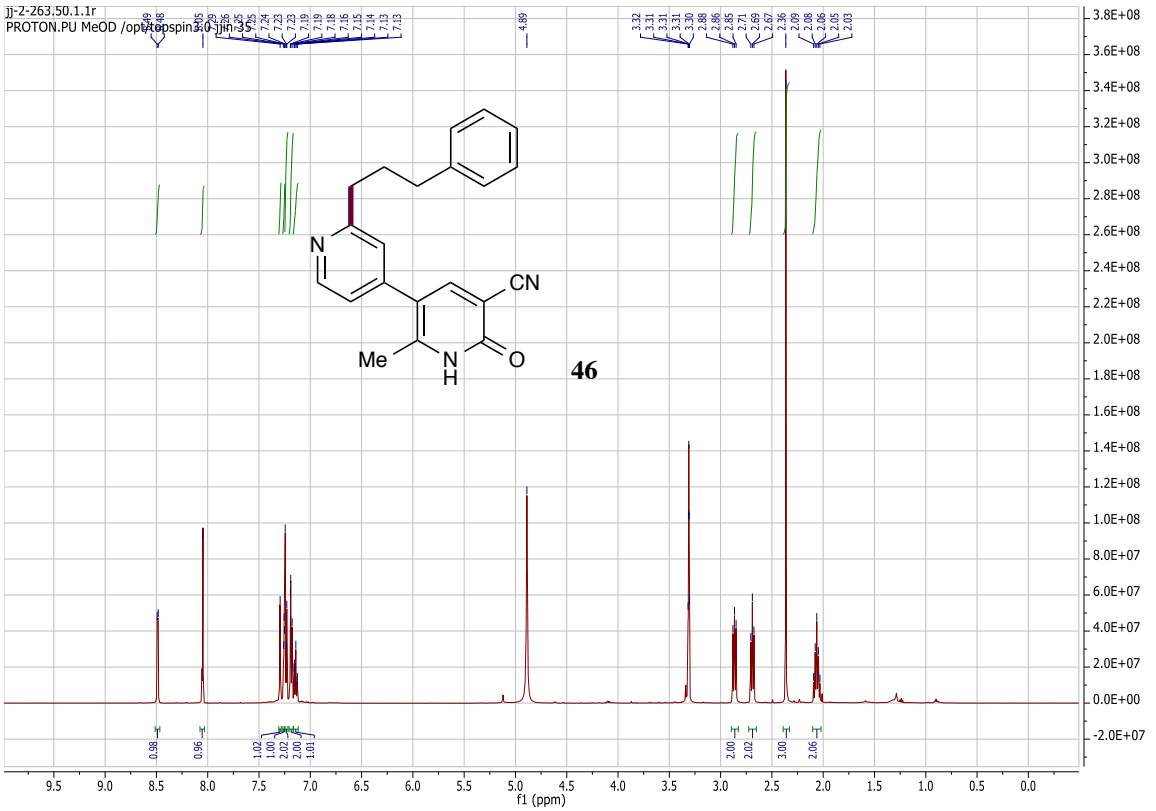

jj-2-297.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 97
N
OH
OH
43
f1 (ppm)

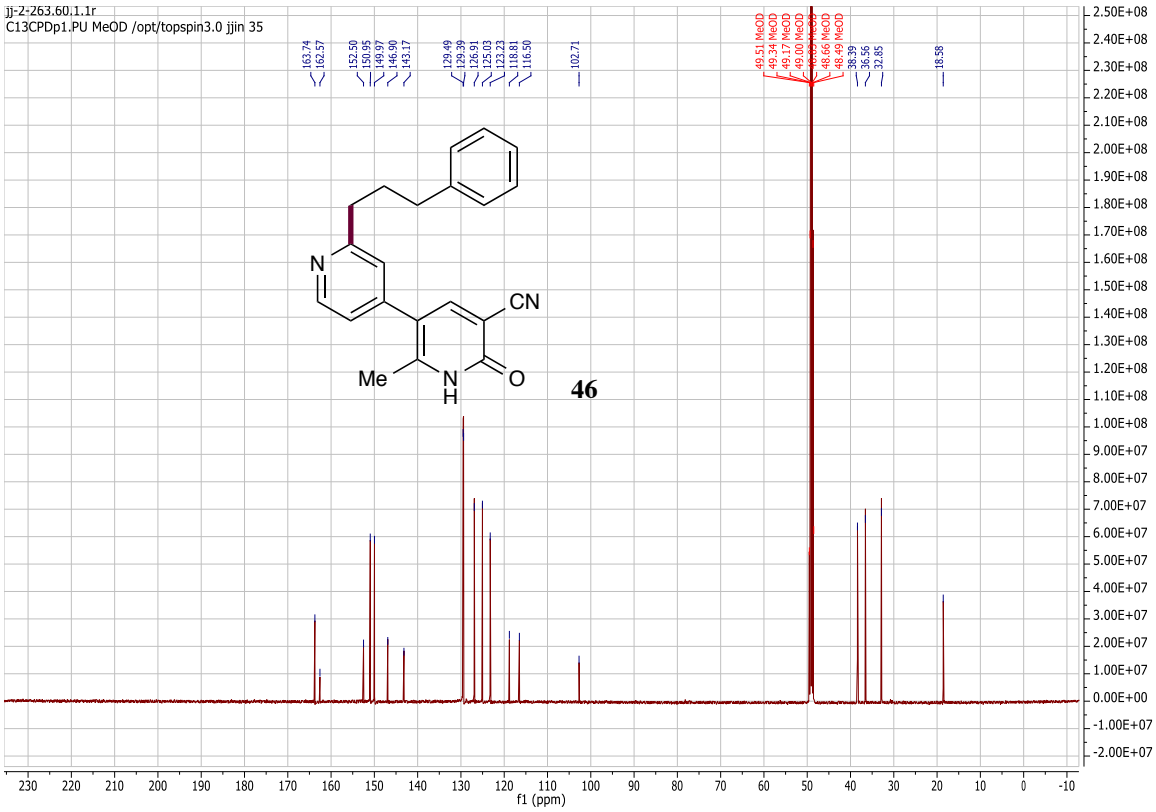

jj-2-298.30.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 98
N
OH
OH
44
f1 (ppm)

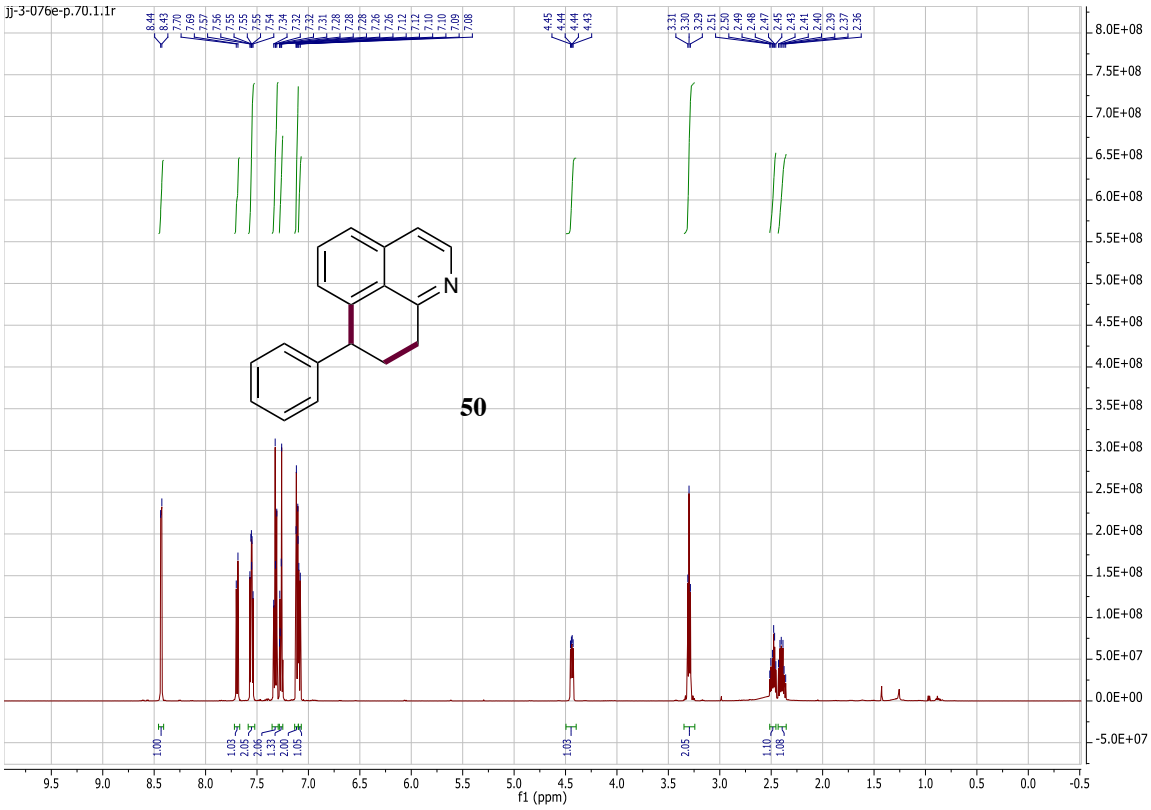

jj-2-298.40.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 98
N
OH
OH
44
f1 (ppm)

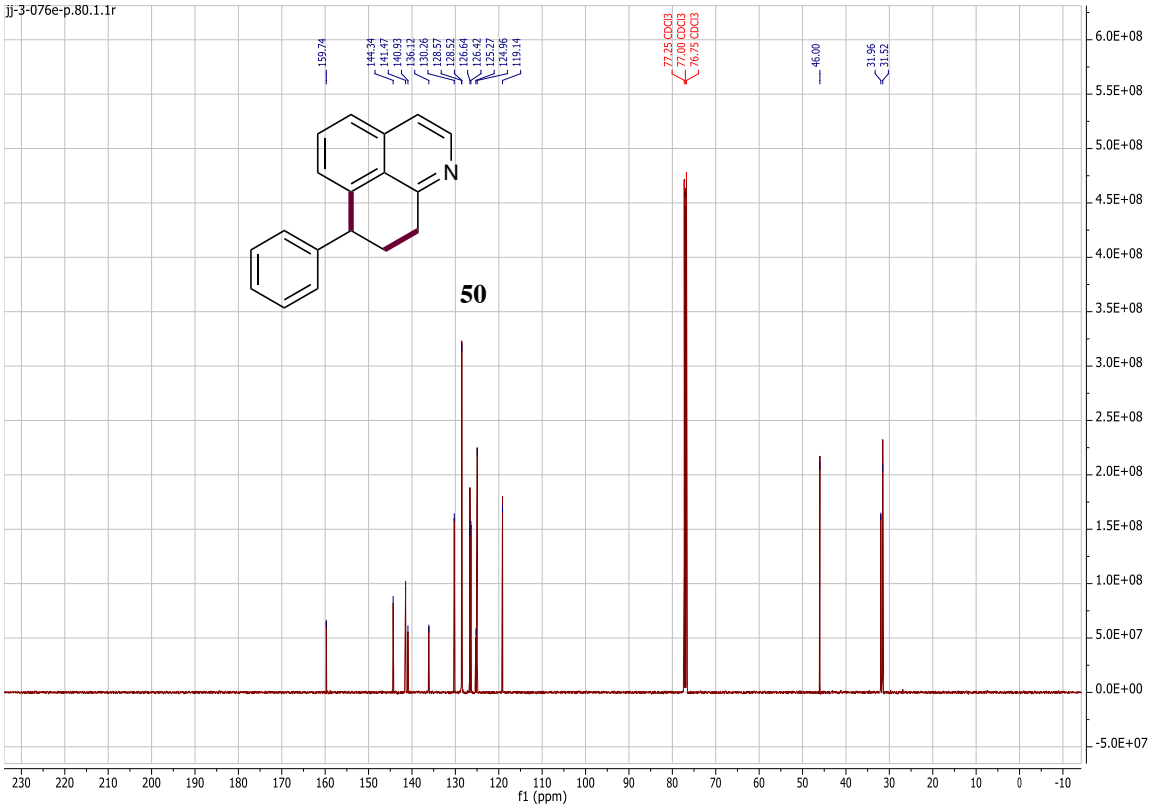

jj-2-262.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 5
HN
N
O=S=O
N
Me
45
f1 (ppm)

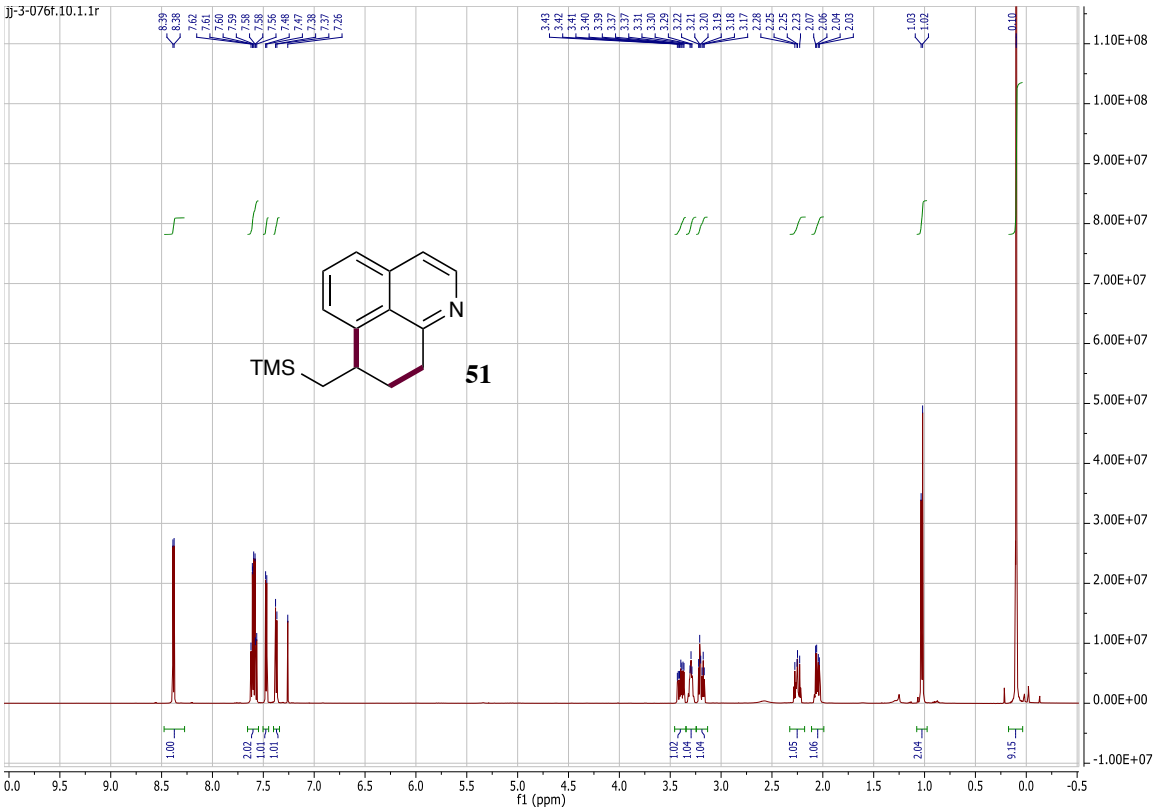

jj-2-262.20.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 6
HN
N
O=S=O
N
Me
45
f1 (ppm)

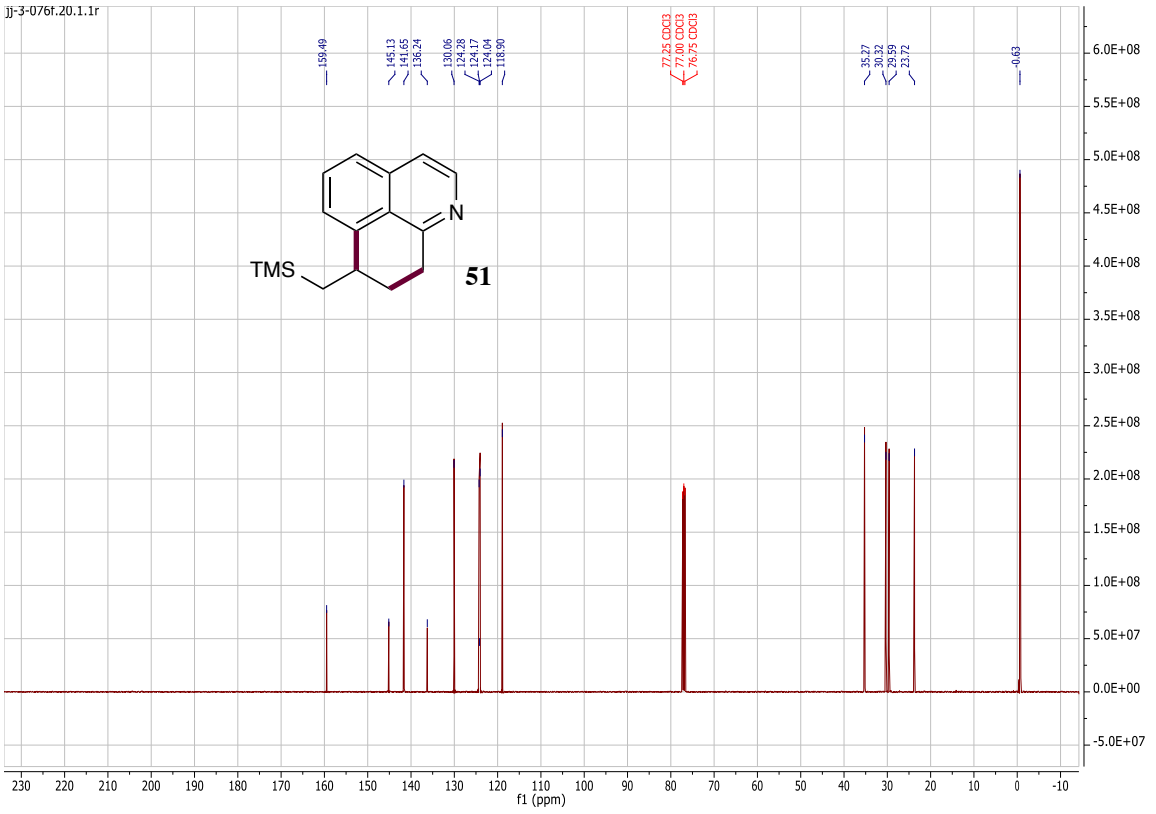

jj-2-263.50.1.1r
PROTON.PU MeOD /opt/topspin3.0 jjin 35
CN
Me
N
H
O
46
f1 (ppm)

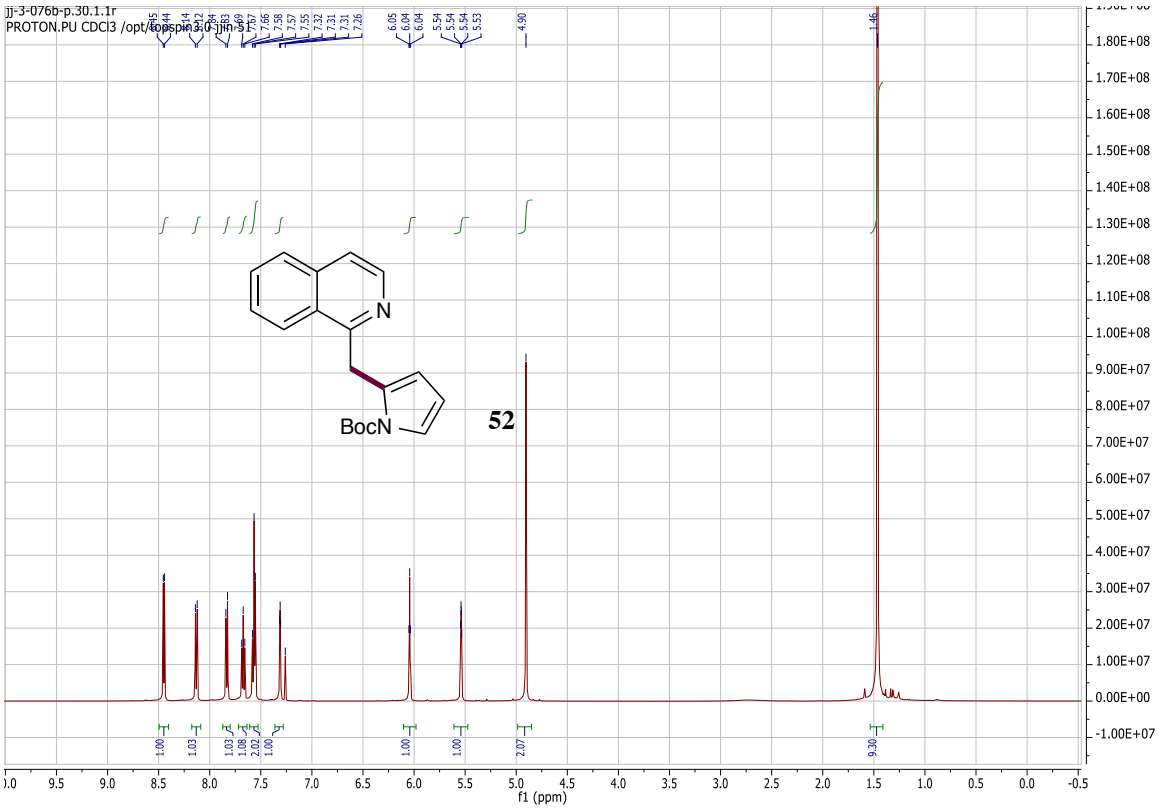

jj-2-263.60.1.1r
C13CPDp1.PU MeOD /opt/topspin3.0 jjin 35
CN
Me
N
H
O
46
f1 (ppm)

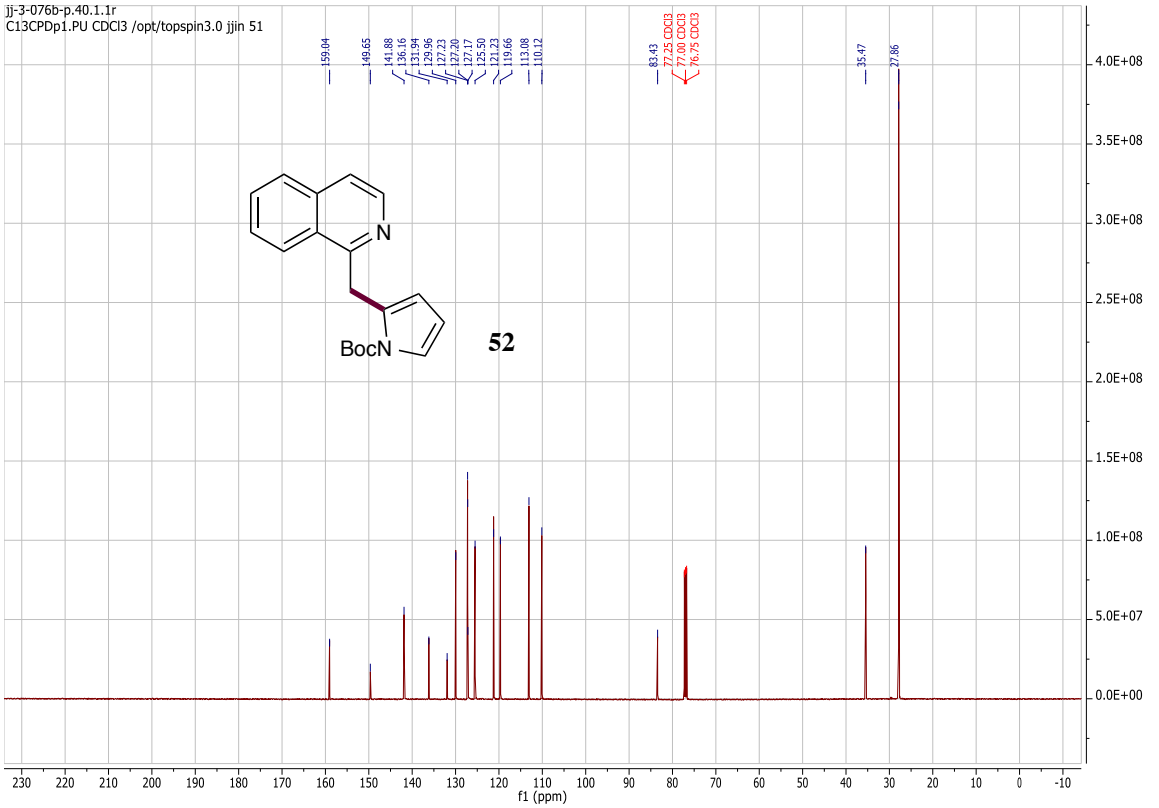

jj-3-076e-p.70.1.1r
8.44
8.43
7.70
7.69
7.57
7.56
7.55
7.55
7.55
7.54
7.34
7.32
7.31
7.28
7.28
7.28
7.26
7.26
7.12
7.10
7.10
7.09
7.08
4.45
4.44
4.44
4.43
3.31
3.30
3.29
2.51
2.50
2.49
2.48
2.47
2.45
2.43
2.41
2.40
2.39
2.37
2.36
N
50
1.00
1.03
2.05
2.06
1.33
2.00
1.05
1.03
2.05
1.10
1.08
f1 (ppm)

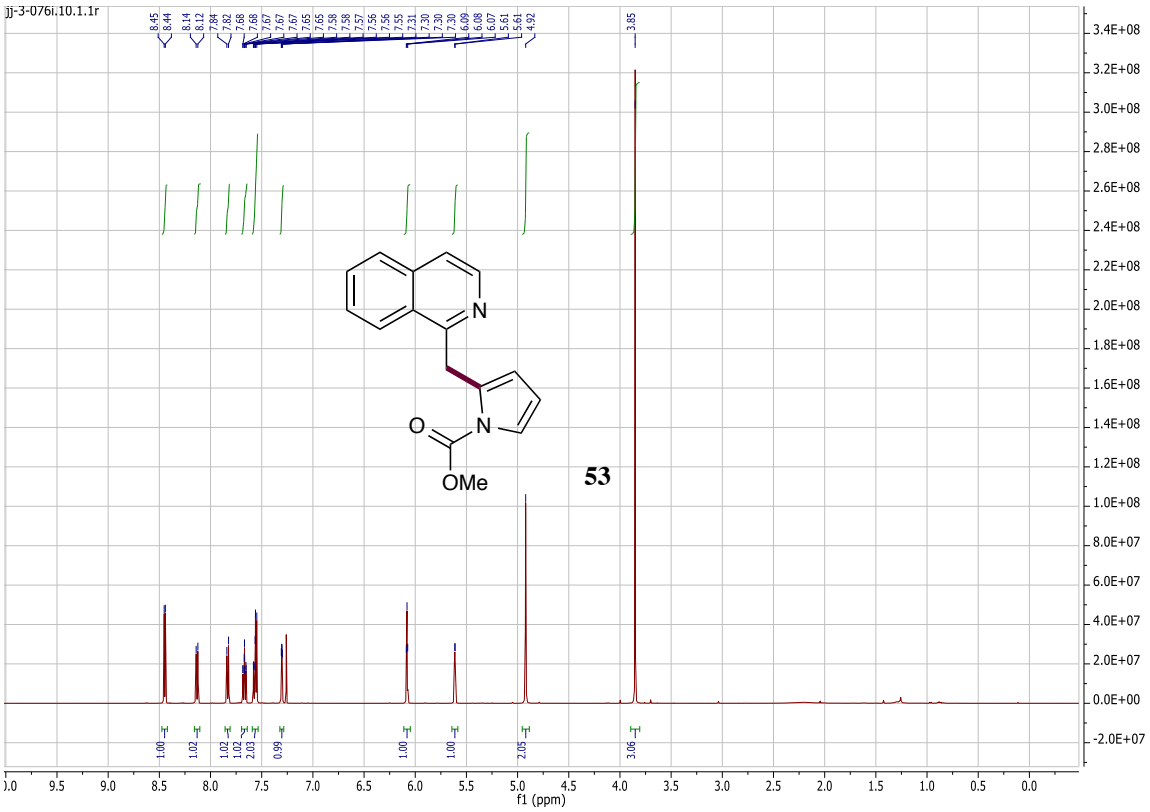

jj-3-076e-p.80.1.1r
159.74
144.34
141.47
140.93
136.12
130.26
128.57
128.52
126.64
126.42
125.27
124.96
119.14
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
46.00
31.96
31.52
N
50
f1 (ppm)

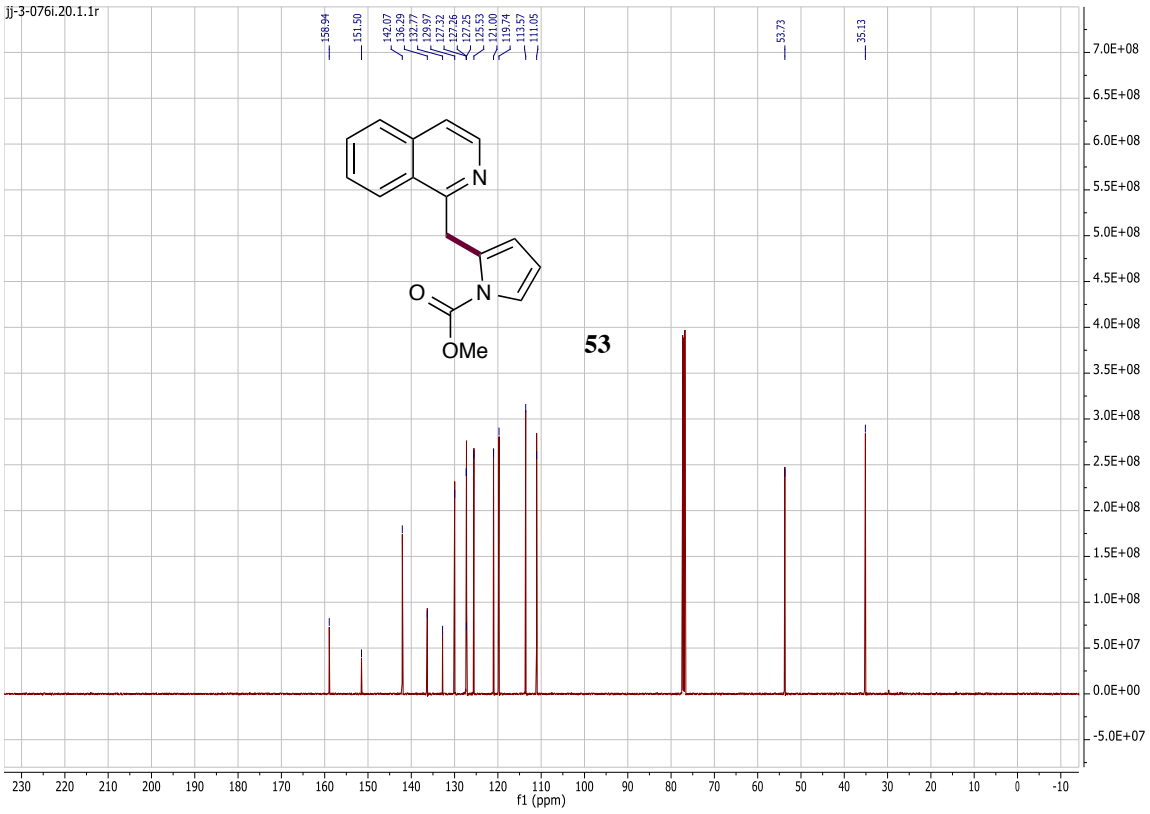

jj-3-076f.10.1.1r
TMS
N
51
f1 (ppm)


jj-3-076f.20.1.1r
TMS
N
51
f1 (ppm)


jj-3-076b-p.30.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jjin 51
N
BocN
52
f1 (ppm)


jj-3-076b-p.40.1.1r
C13CPDp1.PU CDCl3 /opt/topspin3.0 jjin 51
159.04
149.65
141.88
136.16
131.94
129.96
127.23
127.20
127.17
125.50
121.23
119.66
113.08
110.12
83.43
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
35.47
27.86
N
BocN
52
f1 (ppm)


jj-3-076i.10.1.1r
8.45
8.44
8.14
8.12
7.84
7.82
7.68
7.68
7.67
7.67
7.67
7.65
7.65
7.58
7.58
7.57
7.56
7.56
7.55
7.31
7.30
7.30
7.30
6.09
6.08
6.07
5.61
5.61
4.92
3.85
N
O
N
OMe
53
1.00
1.02
1.02
1.02
2.03
0.99
1.00
1.00
2.05
3.06
f1 (ppm)


jj-3-076i.20.1.1r
158.94
151.50
142.07
136.29
132.77
129.97
127.32
127.26
127.25
125.53
121.00
119.74
113.57
111.65
53.73
35.13
N
O
N
OMe
53
f1 (ppm)