Supporting Information

Rhodium(III)-Catalyzed Annulative Coupling between Arenes and Sulfoxonium Ylides via C-H Activation

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Contents

I. General consideration

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. Sulfoxonium ylides,[1] sulfoximines,[2] benzamidines,[3] oxime[4] and 2-phenylimidazo[1,2-a]pyridine[5] were prepared by following literature reports. All reactions were carried out using Schlenk techniques or in an N_2-filled glovebox. NMR Spectra were recorded on a 400 MHz NMR spectrometer in the solvent indicated. he chemical shifts (δ) are given in parts per million (ppm) relative to internal standard TMS (0 ppm for ^{1}H) and $CDCl_3$ (77.0 ppm for ^{13}C). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublet, dt = double of triplet, td = triple of doublet. HRMS data were obtained on a Thermo Scientific LTQ Orbitrap Discovery spectrometer (Germany). Column chromatography was performed on silica gel (300-400 mesh).

II. General procedures for annulative coupling between arenes and sulfoxonium ylides.

a) General procedures for the synthesis of 1,2-Benzothiazines and Isoquinolines.

Take synthesis of **3aa** as the example: $RhCp^*(CH_3CN)_3(SbF_6)_2$ (5 mol %), $Zn(OTf)_2$ (30 mol %), **1a** (0.2 mmol), **2a** (0.4 mmol) and DCE (2 mL) was added in to a screw-cap pressure tube under N_2 atmosphere in a glove-box. The tube was then sealed with a screw-cap and the reaction mixture was stirred at 100 ^{o}C for 36 h. After the reaction finished, the solvent was evaporated under vacuum. The residue was purified by column chromatography (petroleum ether/ethyl ether 20:1 (v/v)) to give the corresponding product **3aa** (54.5 mg, 86%).

b) General procedures for the synthesis of isoquinoline *N*-oxides.

Take synthesis of **5a** as the example: $[RhCp^*Cl_2]_2$ (4 mol %), $Zn(OTf)_2$ (50 mol %), HOAc (2.0 equiv), **4a** (0.2 mmol), **2a** (0.4 mmol), and TFE (2.0 mL) was added in to a screw-cap pressure tube under N_2 atmosphere in a glove-box. The tube was then sealed with a screw-cap and the reaction mixture was stirred at 100 ^{o}C for 12 h. After the reaction finished, the solvent was evaporated under vacuum. The residue was purified by column chromatography (PE/EtOAc/MeOH 5:1:1 (v/v)) to give the corresponding product **5a** (39.8 mg, 85%).

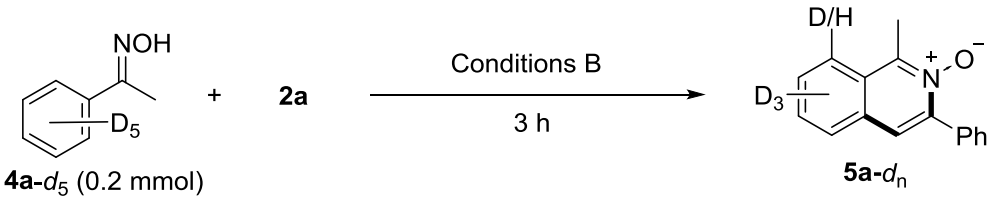
c) General procedures for C-H functionalization/carboannulation.

Take synthesis of **7a** as the example: $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), HOAc (1.0 equiv), **6a** (0.2 mmol), **2a** (0.3 mmol), and DCE (2.0 mL) was added in to a screw-cap pressure

tube under N_2 atmosphere in a glove-box. The tube was then sealed off with a screw-cap and the reaction mixture was stirred at 100 ^oC for 12 h. After the reaction finished, the solvent was evaporated under vacuum. The residue was purified by column chromatography (PE/EtOAc 5:1 (v/v)) to give the corresponding product **7a** (52.0 mg, 88%).

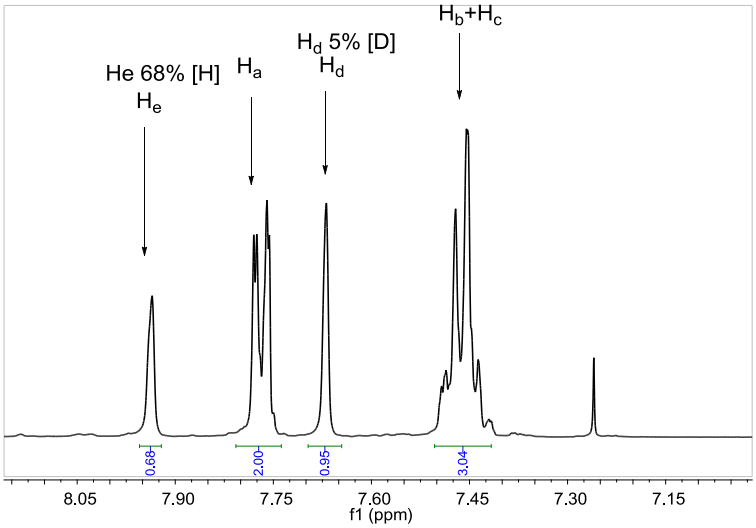
III. Mechanistic Studies

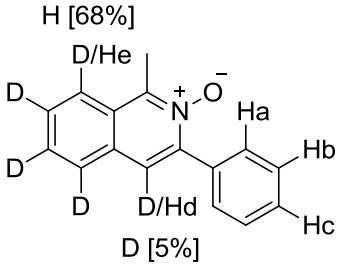
a) H/D exchange



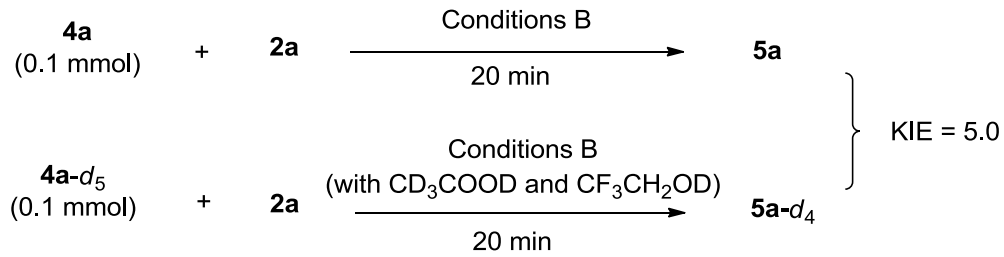
4a-d_5 (0.2 mmol) **5a-d_n**

$[RhCp^*Cl_2]_2$ (4 mol %), $Zn(OTf)_2$ (50 mol %), HOAc (2.0 equiv), d_5-**4a** (0.2 mmol), **2a** (0.4 mmol), and TFE (2.0 mL) was added in to a screw-cap pressure tube under N_2 atmosphere in a glove-box. The tube was then sealed with a screw-cap and the reaction mixture was stirred at 100 ^oC for 3 h. Then the solvent was evaporated under vacuum. The residue was purified by column chromatography (PE/EtOAc/MeOH 5:1:1 (v/v)) to give the corresponding product d_n-**5a**. H/D ratio was identified by ^1H NMR analysis (68% H).



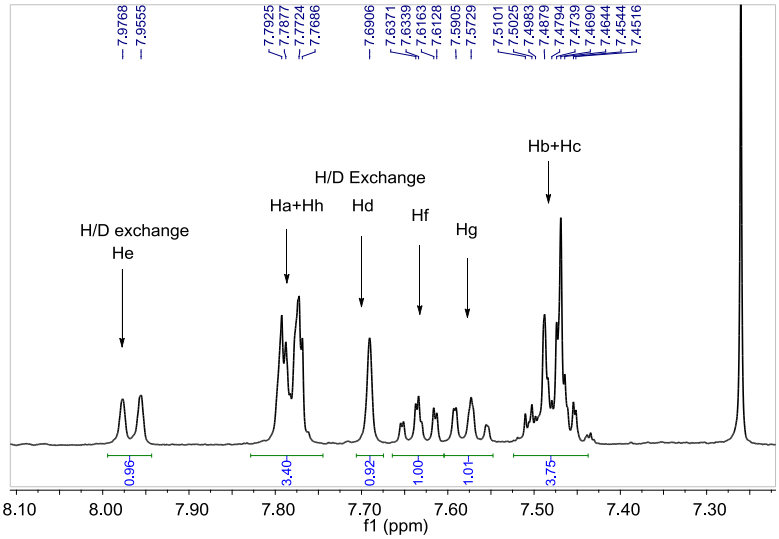


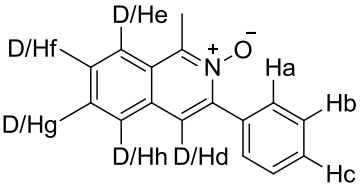
b) Independent KIE studies.



A mixture **4a** (0.1 mmol), sulfoxonium ylides **2a** (0.2 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), $Zn(OTf)_2$

(50 mol %), HOAc (2.0 equiv), and TFE (1.0 mL), were charged into a pressure tube under N_2. To another tube were added **4a**-d_5 (0.1 mmol), sulfoxonium ylides **2a** (0.2 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), $Zn(OTf)_2$ (50 mol %), d_4-HOAc (2.0 equiv), and d_4-TFE (1.0 mL). These two reaction mixtures were stirred side-by-side in the same oil bath at 100 ℃ for 20 min. The reactions tubes were quenched at 0 ^oC and these two mixtures were rapidly combined, and all the volatiles were rapidly removed under a reduced pressure. The residue was purified by silica gel chromatography using (PE/ EtOAc/MeOH 5:1:1 (v/v)) to afford the mixed product. KIE value (k_H/k_D = 5.0) was determined on the basis of ^1H NMR analysis. (During the H/D exchange experiment, no H/D exchange observed for H_a, H_h, H_f, H_g. $2([D_g]+[H_g])+[H_h]=3.40$, $[H_g]= [H_h] = 1$, $[D_g] = 0.2$, KIE = $[H_g]/[D_g] = 5.0$)





IV. Reference

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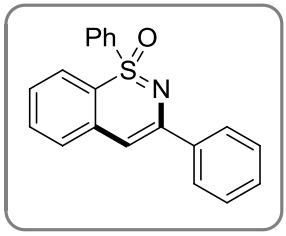
(3) (a). Y. Wang, H. Wang, J. Peng and Q. Zhu, *Org. Lett.* 2011, **13**, 4604. (b) Y. He, J. Huang, D. Liang, L. Liu and Q. Zhu, *Chem. Commun.* 2013, **49**, 7352.

(4) V. V. Angeles–Dunham, D. M. Nickerson, D. M. Ray and A. E. Mattson, *Angew. Chem., Int. Ed.* 2014**, 53**, 14538.

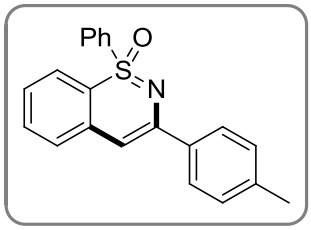
(5) (a) Z. Qi, S. Yu and X. Li, *J. Org. Chem.* 2015, **80**, 3471. (b) P. Li, X. Zhang and X. Fan, *J. Org. Chem.* 2015, **80**, 7508.

V. Characterization Data



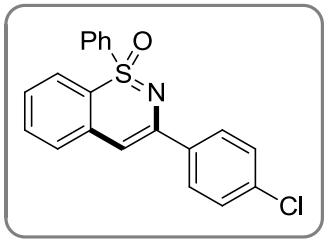
1,3-diphenylbenzo[*e*][1,2]thiazine 1-oxide 3aa

Yield: 86% (54.5 mg). Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 4H), 7.62 – 7.59 (m, 1H), 7.57 – 7.53 (m, 2H), 7.48 – 7.38 (m, 4H), 7.37 – 7.31 (m, 2H), 7.24 – 7.19 (m, 1H), 6.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 140.3, 138.7, 136.4, 133.3, 132.0, 129.3, 128.9, 128.7, 128.3, 126.8, 126.6, 126.2, 124.8, 119.5, 98.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{16}NOS^{+}$, ([M + H]$^{+}$), 318.0947, found 318.0963.



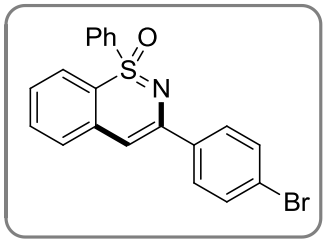
1-phenyl-3-(p-tolyl)benzo[*e*][1,2]thiazine 1-oxide 3ab

Yield: 84% (55.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.96 (m, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.59 – 7.52 (m, 2H), 7.48 – 7.40 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.16 (m, 3H), 6.78 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 140.5, 138.8, 136.6, 135.9, 133.3, 132.0, 129.2, 129.0, 128.9, 126.7, 126.5, 126.0, 124.9, 119.4, 97.5, 21.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{18}NOS^{+}$, ([M + H]$^{+}$), 332.1104, found 332.1116.



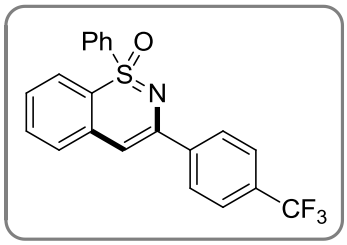
3-(4-chlorophenyl)-1-phenylbenzo[*e*][1,2]thiazine 1-oxide 3ac

Yield: 85% (60.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.22 (m, 1H), 6.79 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 140.1, 137.2, 136.2, 134.6, 133.5, 132.2, 129.0, 128.5, 127.9, 126.9, 126.5, 124.9, 119.7, 98.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{15}ClNOS^{+}$, ([M + H]$^{+}$), 352.0557, found 352.0555.



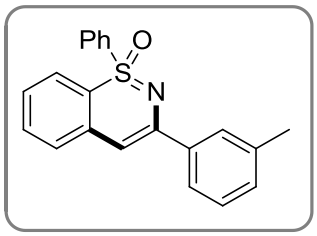
3-(4-bromophenyl)-1-phenylbenzo[*e*][1,2]thiazine 1-oxide 3ad

Yield: 78% (61.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.46 (m, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.21 (m, 1H), 6.79 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 140.1, 137.7, 136.2, 133.5, 132.2, 131.4, 129.3, 129.0, 128.1, 126.9, 126.5, 124.9, 122.9, 119.7, 98.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{15}BrNOS^{+}$, ([M + H]$^{+}$), 396.0052, found 396.0052.



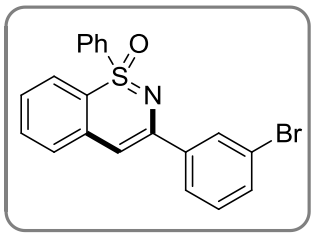
1-phenyl-3-(4-(trifluoromethyl)phenyl)benzo[*e*][1,2]thiazine 1-oxide 3ae

Yield: 76% (58.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 2H), 8.01 – 7.97 (m, 2H), 7.66 – 7.64 (m, 3H), 7.60 – 7.57 (m, 2H), 7.54 – 7.49 (m, 1H), 7.47 (d, J = 7.2 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.30 – 7.25 (m, 1H), 6.88 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 142.2, 140.0, 135.9, 133.6, 132.3, 130.3 (q, J = 32.3 Hz), 129.3, 129.1, 127.1, 1267.0, 126.8, 125.2 (q, J = 3.8 Hz), 124.9, 124.2 (q, J = 124.2 Hz), 120.1, 99.4. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{15}F_3NOS^+$, ([M + H]$^+$), 386.0821, found 386.0821.



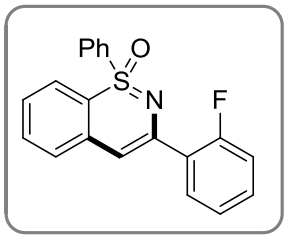
1-phenyl-3-(*m*-tolyl)benzo[*e*][1,2]thiazine 1-oxide 3af

Yield: 79% (52.2 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 2H), 7.76 (s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.51 – 7.46 (m, 2H), 7.41 – 7.34 (m, 2H), 7.25 – 7.20 (m, 2H), 7.16 – 7.10 (m, 2H), 6.72 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 140.4, 138.7, 137.9, 136.5, 133.3, 132.0, 129.6, 129.3, 128.9, 128.2, 127.4, 126.8, 126.2, 124.9, 123.7, 119.5, 98.1, 21.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{18}NOS^+$, ([M + H]$^+$), 332.1104, found 332.1109.



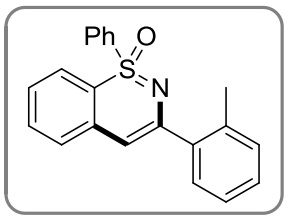
3-(3-bromophenyl)-1-phenylbenzo[*e*][1,2]thiazine 1-oxide 3ag

Yield: 79% (59.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (t, J = 1.6 Hz, 1H), 8.00 – 7.97 (m, 2H), 7.93 – 7.90 (m, 1H), 7.68 – 7.62 (m, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.53 – 7.42 (m, 3H), 7.32 (d, J = 8.0 Hz, 1H), 7.29 – 7.23 (m, 2H), 6.80 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 140.9, 140.0, 136.0, 133.5, 132.2, 131.5, 129.8, 129.6, 129.3, 129.0, 127.0, 126.7, 125.0, 124.9, 122.6, 119.9, 98.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{15}BrNOS^+$, ([M + H]$^+$), 396.0052, found 396.0054.



3-(2-fluorophenyl)-1-phenylbenzo[*e*][1,2]thiazine 1-oxide 3ah

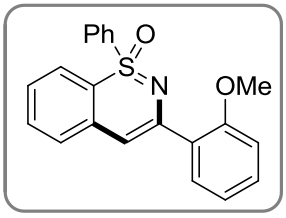
Yield: 79% (58.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 1H), 7.96 – 7.91 (m, 2H), 7.60 – 7.55 (m, 1H), 7.53 – 7.48 (m, 2H), 7.46 – 7.36 (m, 2H), 7.22 – 7.16 (m, 3H), 7.13 – 7.09 (m, 1H), 7.06 – 7.03 (m, 1H), 6.91 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (d, J = 249.5 Hz), 141.8 (d, J = 3.7 Hz), 140.2, 136.1, 133.4, 132.1, 130.8 (d, J = 2.5 Hz), 129.8 (d, J = 8.8 Hz), 129.4, 129.0, 127.2, 126.8 (d, J = 10.4 Hz), 124.8, 124.1 (d, J = 3.5 Hz), 119.8, 116.0 (d, J = 23.4 Hz), 103.3 (d, J = 12.6 Hz). Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{15}FNOS^+$, ([M + H]$^+$), 336.0853, found 336.0867.



1-phenyl-3-(o-tolyl)benzo[e][1,2]thiazine 1-oxide 3ai

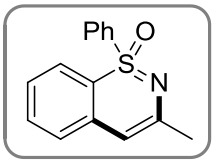
Yield: 64% (42.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.2 Hz, 2H), 7.72 – 7.43 (m, 5H), 7.39 (d, J = 8.0 Hz, 1H), 7.35 – 7.13 (m, 5H), 6.38 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7,

140.0, 139.9, 136.4, 136.2, 133.4, 132.0, 130.6, 129.4, 129.0, 128.9, 128.2, 126.5, 126.3, 125.6, 124.8, 118.8, 101.7, 20.4. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{18}NOS^+$, ($[M + H]^+$), 332.1104, found 332.1108.



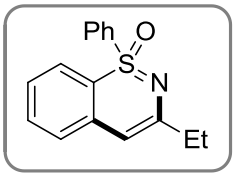
3-(2-methoxyphenyl)-1-phenylbenzo[*e*][1,2]thiazine 1-oxide 3aj

Yield: 67% (46.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.02 (m, 2H), 7.95 (dt, J = 7.7, 2.1 Hz, 1H), 7.64 – 7.55 (m, 3H), 7.49 – 7.41 (m, 2H), 7.35 – 7.28 (m, 2H), 7.25 – 7.19 (m, 1H), 7.04 – 6.98 (m, 3H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 144.5, 140.6, 136.4, 133.2, 131.8, 130.9, 129.44, 129.37, 128.9, 128.2, 127.1, 126.2, 124.8, 120.7, 119.4, 111.4, 103.0, 55.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{18}NO_2S^+$, ($[M + H]^+$), 348.1053, found 348.1058.



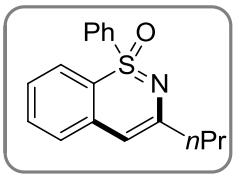
3-methyl-1-phenylbenzo[*e*][1,2]thiazine 1-oxide 3ak

Yield: 95% (48.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.61 – 7.59 (m, 1H), 7.58 – 7.52 (m, 2H), 7.45 – 7.40 (m, 1H), 7.28 – 7.22 (m, 2H), 7.17 – 7.12 (m, 1H), 6.11 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 140.2, 136.5, 133.3, 132.0, 129.0, 128.9, 125.6, 125.5, 124.8, 118.0, 99.1, 25.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{15}H_{14}NOS^+$, ($[M + H]^+$), 256.0791, found 256.0800.



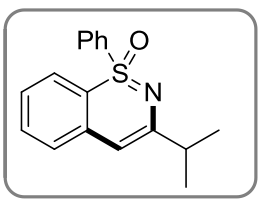
3-ethyl-1-phenylbenzo[*e*][1,2]thiazine 1-oxide 3al

Yield: 96% (51.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H), 7.67 – 7.59 (m, 1H), 7.59 – 7.53 (m, 2H), 7.45 – 7.41 (m, 1H), 7.27 (t, J = 7.5 Hz, 2H), 7.19 – 7.10 (m, 1H), 6.11 (s, 1H), 2.58 (q, J = 7.5 Hz, 2H), 1.30 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 140.5, 136.7, 133.3, 132.0, 129.2, 129.0, 125.9, 125.5, 124.9, 118.6, 97.6, 32.1, 12.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{16}NOS^+$, ($[M + H]^+$), 270.0947, found 270.0955.



1-phenyl-3-propylbenzo[*e*][1,2]thiazine 1-oxide 3am

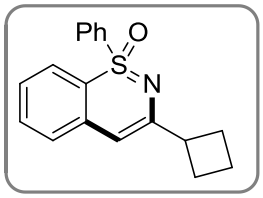
Yield: 93% (52.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 2H), 7.65 – 7.60 (m, 1H), 7.59 – 7.52 (m, 2H), 7.42 (ddd, J = 8.2, 7.1, 1.3 Hz, 1H), 7.26 (t, J = 8.0 Hz, 2H), 7.19 – 7.12 (m, 1H), 6.11 (s, 1H), 2.52 (td, J = 7.2, 1.8 Hz, 2H), 1.83 – 1.73 (m, 1H), 0.99 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ152.1, 140.5, 136.6, 133.3, 132.0, 129.2, 129.0, 125.9, 125.5, 124.9, 119.0, 98.8, 41.0, 21.6, 13.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{16}NOS^+$, ($[M + H]^+$), 284.1104, found 284.1115.



3-isopropyl-1-phenylbenzo[e][1,2]thiazine 1-oxide 3an

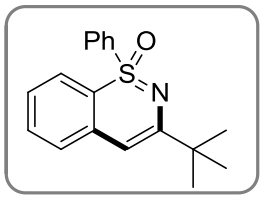
Yield: 92% (51.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.2, 1.6 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.58 – 7.53 (m, 2H), 7.44 – 7.39 (m, 1H), 7.30 – 7.25 (m, 2H), 7.17 – 7.12 (m, 1H), 6.11 (s, 1H), 2.79 – 2.72 (m, 1H), 1.31 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 140.7,

136.6, 133.1, 131.8, 129.1, 128.9, 126.1, 125.5, 124.8, 118.8, 96.1, 36.6, 21.4, 21.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{18}NOS^+$, ([M + H]$^+$), 284.1104, found 284.1106.



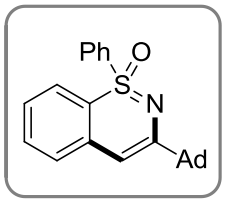
3-cyclobutyl-1-phenylbenzo[e][1,2]thiazine 1-oxide 3ao

Yield: 78% (45.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.07 (t, J = 7.6 Hz, 1H), 6.02 (s, 1H), 3.39 – 3.30 (m, 1H), 2.35 – 2.23 (m, 2H), 2.21 – 2.13 (m, 2H), 1.96 – 1.83 (m, 1H), 1.81 – 1.70 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 140.7, 136.5, 133.2, 131.9, 129.1, 128.9, 126.0, 125.5, 124.9, 118.7, 96.8, 42.6, 27.2, 27.1, 18.0. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{18}NOS^+$, ([M + H]$^+$), 296.1104, found 296.1110.



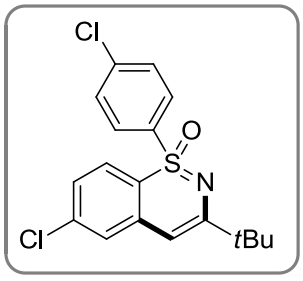
3-(*tert*-butyl)-1-phenylbenzo[e][1,2]thiazine 1-oxide 3ap

Yield: 91% (53.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 2H), 7.64 – 7.50 (m, 3H), 7.43 – 7.38 (m, 1H), 7.33 – 7.24 (m, 2H), 7.19 – 7.12 (m, 1H), 6.19 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 141.1, 136.7, 133.1, 131.8, 129.1, 128.9, 126.6, 125.7, 124.8, 118.7, 95.1, 37.6, 29.0. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{20}NOS^+$, ([M + H]$^+$), 298.1260, found 298.1268.



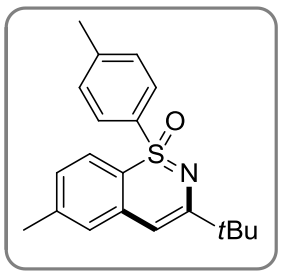
3-(adamantan-1-yl)-1-phenylbenzo[*e*][1,2]thiazine 1-oxide 3aq

Yield: 95% (71.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.63 – 7.52 (m, 3H), 7.42 – 7.36 (m, 1H), 7.30 – 7.25 (m, 2H), 7.14 (t, J = 7.6 Hz, 1H), 6.10 (s, 1H), 2.07 – 1.97 (m, 9H), 1.75 (bs, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 141.2, 136.7, 133.0, 131.6, 129.0, 128.8, 126.5, 125.5, 124.7, 118.8, 94.8, 40.7, 39.0, 36.9, 28.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{26}NOS^+$, ([M + H]$^+$), 376.1730, found 376.1734.



3-(*tert*-butyl)-6-chloro-1-(4-chlorophenyl)benzo[*e*][1,2]thiazine 1-oxide 3bp

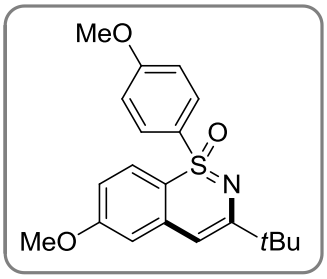
Yield: 75% (54.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 2H), 7.49 – 7.43 (m, 2H), 7.23 (d, J = 2.0 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 7.04 (dd, J = 8.4, 2.0 Hz, 1H), 6.05 (s, 1H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 140.2, 139.4, 138.22, 138.15, 130.3, 129.3, 126.3, 126.2, 125.7, 116.3, 94.6, 37.7, 28.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{18}Cl_2NOS^+$, ([M + H]$^+$), 366.0481, found 366.0476.



3-(*tert*-butyl)-6-methyl-1-(p-tolyl)benzo[e][1,2]thiazine 1-oxide 3cp

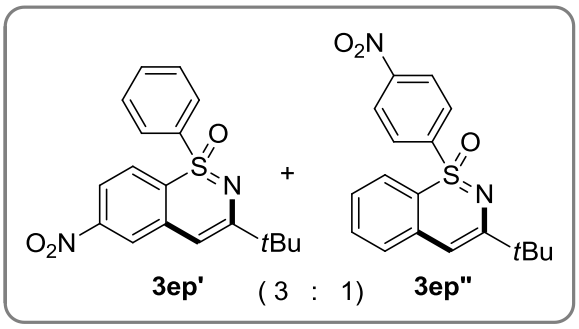
Yield: 98% (63.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 1H), 7.09 (s, 1H), 6.96 (dd, J = 8.0, 2.0 Hz, 1H), 6.11 (s, 1H), 2.42 (s, 3H), 2.34 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 143.8, 142.0,

138.5, 136.7, 129.4, 128.9, 127.0, 126.1, 124.6, 116.5, 94.6, 37.5, 29.0, 21.6, 21.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{24}NOS^+$, ([M + H]$^+$), 326.1573, found 326.1582.



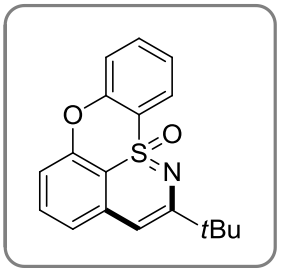
3-(*tert*-butyl)-6-methoxy-1-(4-methoxyphenyl)benzo[*e*][1,2]thiazine 1-oxide 3dp

Yield: 92% (65.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 2H), 7.21 (d, J = 8.4 Hz, 1H), 6.99 (d, J = 8.4 Hz, 2H), 6.73 (dd, J = 8.4, 2.0 Hz, 1H), 6.67 (d, J = 2.0 Hz, 1H), 6.10 (s, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 161.7, 160.4, 138.9, 133.3, 130.8, 126.6, 115.2, 114.0, 112.3, 106.9, 94.7, 55.6, 55.5, 37.5, 28.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{24}NOS^+$, ([M + H]$^+$), 358.1471, found 358.1480.



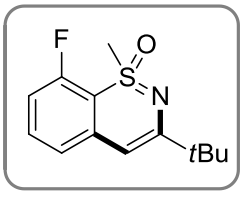
3ep, Yield: 91% (61.6 mg). The product can not be seperated by chlumn, so characterized by mixture. The ratio of isoer was determined by ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.9 Hz, 0.64H), 8.14 (d, J = 2.2 Hz, 1H), 7.99 (d, J = 8.9 Hz, 0.71H), 7.90 – 7.77 (m, 3H), 7.67 – 7.59 (m, 1H), 7.57 – 7.53 (m, 2H), 7.44 – 7.36 (m, 0.36H), 7.29 – 7.24 (m, 1.65H), 7.17 – 7.10 (m, 0.32H), 6.32 (s, 1H), 6.13 (s, 0.33H), 1.28 (s, 9H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 159.8, 150.3, 149.3, 147.3, 139.3, 137.4, 137.3, 134.0, 132.6, 129.9, 129.5, 129.3, 127.0, 126.5, 126.3, 124.8, 124.1, 122.1, 121.5, 119.2, 117.3, 95.0, 95.5, 38.0, 37.6, 28.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{19}N_2O_3S^+$, ([M + H]$^+$), 341.1111, found 343.1120.



2-(*tert*-butyl)phenoxathiino[1,10-*ef*][1,2]thiazine 12-oxide **3fp**

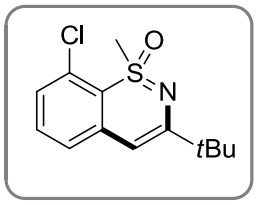
Yield: 98% (63.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.3, 1.6 Hz, 1H), 7.52 – 7.43 (m, 1H), 7.40 (t, J = 8.1 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.02 (dd, J = 8.1, 1.3 Hz, 2H), 6.23 (s, 1H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 151.9, 150.6, 135.9, 133.5, 132.7, 126.2, 124.9, 121.6, 120.2, 119.8, 112.2, 105.1, 97.2, 38.0, 29.0. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{18}NO_2S^+$, ([M + H]$^+$), 312.1053, found. 312 1049.



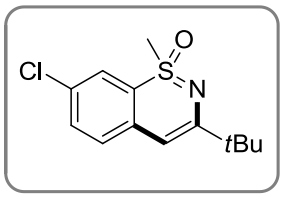
3-(*tert*-butyl)-8-fluoro-1-methylbenzo[e][1,2]thiazine 1-oxide 3gp

Yield: 94% (47.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 1H), 7.08 (d, J = 8.0 Hz, 1H), 7.00 – 6.95 (m, 1H), 6.13 (d, J = 4.0 Hz, 1H), 3.64 (d, J = 4.0 Hz, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4 (d, J = 0.7 Hz), 157.7 (d, J = 248.5 Hz), 139.2 (d, J = 1.7 Hz), 132.9 (d, J = 9.4 Hz), 122.5 (d, J = 3.2 Hz), 110.8 (d, J = 20.8 Hz), 107.0 (d, J = 18.0 Hz), 94.8 (d, J = 3.3 Hz), 47.4

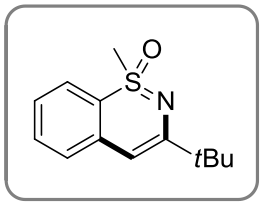
(d, J = 5.5 Hz), 37.3, 28.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{13}H_{17}FNOS^+$, ([M + H]$^+$), 254.1009, found 254.1008.



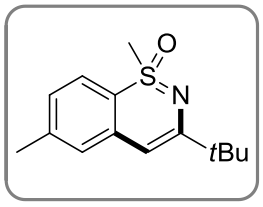
3-(*tert*-butyl)-8-chloro-1-methylbenzo[e][1,2]thiazine 1-oxide 3hp
Yield: 92% (49.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, J = 8.0 Hz, 1H), 7.30 (dd, J = 8.0, 4.0 Hz, 1H), 7.21 (dd, J = 8.0, 4.0 Hz, 1H), 6.05 (s, 1H), 3.72 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 139.8, 132.2, 123.0, 127.0, 126.2, 116.2, 95.0, 49.5, 37.1, 28.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{13}H_{17}ClNOS^+$, ([M + H]$^+$), 270.0714, found 270.0711.



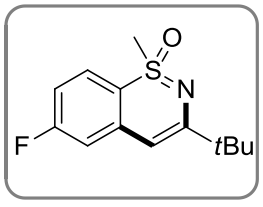
3-(*tert*-butyl)-7-chloro-1-methylbenzo[*e*][1,2]thiazine 1-oxide 3ip
Yield: 87% (47.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 1.9 Hz, 1H), 7.44 (dd, J = 8.6, 2.1 Hz, 1H), 7.24 (d, J = 8.6 Hz, 1H), 6.05 (s, 1H), 3.49 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 135.4, 132.7, 130.4, 128.4, 122.7, 118.2, 94.8, 45.0, 37.4, 28.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{13}H_{17}ClNOS^+$, ([M + H]$^+$), 270.0714, found 270.0708.



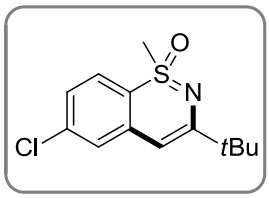
3-(*tert*-butyl)-1-methylbenzo[*e*][1,2]thiazine 1-oxide 3jp
Yield: 96% (45.2 mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.36 – 7.23 (m, 2H), 6.06 (s, 1H), 3.46 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 136.99, 132.2, 126.7, 125.6, 123.1, 117.6, 95.1, 44.9, 37.2, 28.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{13}H_{18}NOS^+$, ([M + H]$^+$), 236.1104, found 236.1113.



3-(*tert*-butyl)-1,6-dimethylbenzo[*e*][1,2]thiazine 1-oxide 3kp
Yield: 94% (46.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 1H), 7.15 – 7.12 (m, 1H), 7.07 (s, 1H), 5.98 (s, 1H), 3.43 (s, 3H), 2.39 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 142.9, 137.3, 127.1, 126.5, 123.2, 115.4, 94.9, 45.3, 37.3, 28.9, 21.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{14}H_{20}NOS^+$, ([M + H]$^+$), 250.1260, found 250.1267.

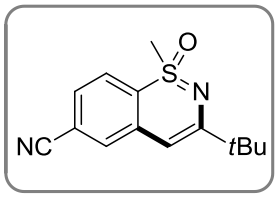


3-(*tert*-butyl)-6-fluoro-1-methylbenzo[e][1,2]thiazine 1-oxide 3lp
Yield: 89% (45.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 8.8, 5.4 Hz, 1H), 7.02 (td, J = 8.5, 2.5 Hz, 1H), 6.91 (dd, J = 10.0, 2.5 Hz, 1H), 5.99 (s, 1H), 3.44 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7 (d, J = 252.5 Hz), 161.4, 140.1 (d, J = 10.4 Hz), 126.4 (d, J = 10.3 Hz), 114.2 (d, J = 24.6 Hz), 113.9 (d, J = 2.1 Hz), 111.5 (d, J = 21.9 Hz), 95.0 (d, J = 2.6 Hz), 45.5, 37.4, 28.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{13}H_{17}FNOS^+$, ([M + H]$^+$), 254.1109, found 254.1015.



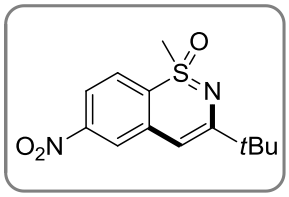
3-(*tert*-butyl)-6-chloro-1-methylbenzo[*e*][1,2]thiazine 1-oxide 3mp

Yield: 95% (56.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 5.99 (s, 1H), 3.46 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 138.6, 138.5, 126.0, 125.9, 124.9, 115.6, 94.6, 45.2, 37.5, 28.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{13}H_{17}ClNOS^{+}$, ([M + H]$^{+}$), 270.0714, found 270.0726.



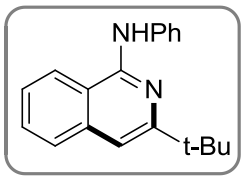
3-(*tert*-butyl)-1-methylbenzo[*e*][1,2]thiazine-6-carbonitrile 1-oxide 3np

Yield: 84% (43.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 1.3 Hz, 1H), 7.51 (dd, J = 8.2, 1.5 Hz, 1H), 6.12 (s, 1H), 3.53 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 137.1, 131.6, 127.2, 124.2, 119.3, 117.7, 115.9, 95.0, 44.7, 37.6, 28.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{14}H_{17}N_2OS^{+}$, ([M + H]$^{+}$), 261.1056, found 261.1061.



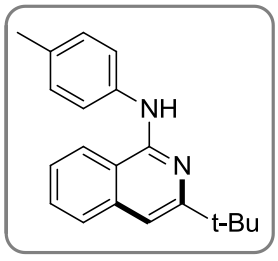
3-(*tert*-butyl)-1-methyl-6-nitrobenzo[*e*][1,2]thiazine 1-oxide 3op

Yield: 81% (45.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 2.2 Hz, 1H), 8.06 (dd, J = 8.7, 2.2 Hz, 1H), 7.86 (d, J = 8.7 Hz, 1H), 6.25 (s, 1H), 3.58 (s, 3H), 1.29 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 149.7, 137.9, 124.9, 122.3, 120.3, 119.2, 96.0, 44.8, 37.7, 28.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{13}H_{17}N_2O_3S^{+}$, ([M + H]$^{+}$), 281.0954, found 281.0947.



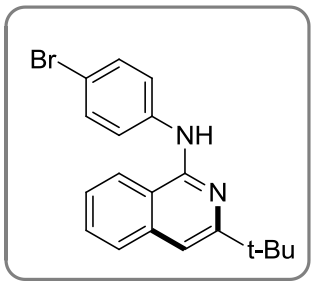
3-(*tert*-butyl)-N-phenylisoquinolin-1-amine 3pp

Yield: 78% (42.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, J = 8.4 Hz, 3H), 7.74 (d, J = 8.0 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.53 – 7.45 (m, 1H), 7.42 – 7.38 (m, 2H), 7.18 (s, 1H), 7.13 (s, 1H), 7.08 – 7.04 (m, 1H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 150.6, 140.9, 138.2, 129.5, 128.7, 127.6, 125.6, 121.7, 120.9, 119.3, 116.9, 107.0, 37.3, 30.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{21}N_2^{+}$, ([M + H]$^{+}$), 277.1699, found 277.1706.



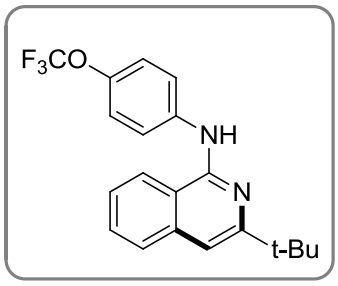
3-(*tert*-butyl)-N-(p-tolyl)isoquinolin-1-amine 3qp

Yield: 81% (47.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.1 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.16 (d, J = 8.3 Hz, 2H), 7.08 – 7.06 (m, 2H),, 2.34 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 150.8, 138.5, 138.3, 131.2, 129.4, 129.2, 127.6, 125.5, 121.0, 119.5, 116.9, 106.7, 37.3, 30.2, 20.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{23}N_2^{+}$, ([M + H]$^{+}$), 291.1856, found 291.1856.



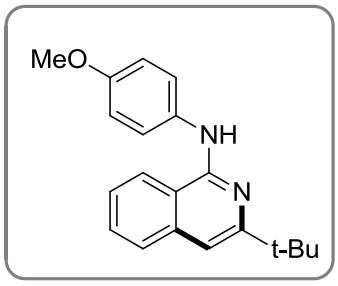
***N*-(4-bromophenyl)-3-(*tert*-butyl)isoquinolin-1-amine 3rp**

Yield: 71% (50.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.13 – 6.97 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 150.3, 140.0, 138.2, 131.6, 129.6, 127.7, 125.8, 121.0, 120.8, 116.9, 113.8, 107.4, 37.3, 30.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{20}N_2Br^+$, ([M + H]$^+$), 355.0804, found 355.0793.



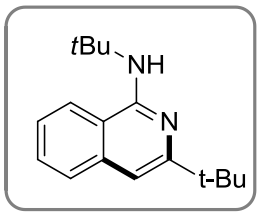
3-(*tert*-butyl)-*N*-(4-(trifluoromethoxy)phenyl)isoquinolin-1-amine 3sp

Yield: 64% (45.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.83 (m, 3H), 7.74 (d, J = 7.6 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.19 – 7.11 (m, 2H), 1.44 (S, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 150.3, 143.4, 139.7, 138.3, 129.7, 127.8, 125.8, 121.5, 120.8, 120.7 (q, J = 254.6 Hz), 120.0, 116.9, 107.5, 37.3, 30.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{20}F_3N_2O^+$, ([M + H]$^+$), 361.1522, found 361.1528.



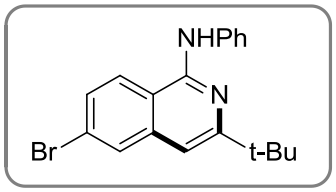
3-(*tert*-butyl)-*N*-(4-(methoxy)phenyl)isoquinolin-1-amine 3tp

Yield: 88% (54.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.15 – 7.04 (m, 2H), 6.94 (d, J = 8.4 Hz, 2H), 3.84 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 154.8, 151.0, 138.2, 134.4, 129.4, 127.6, 125.5, 121.2, 120.9, 116.8, 113.9, 106.4, 55.6, 37.3, 30.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{23}N_2O^+$, ([M + H]$^+$), 307.1805, found 307.1814.



***N*,3-di-*tert*-butylisoquinolin-1-amine 3up**

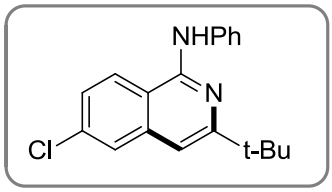
Yield: 84% (43.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, J = 8.6 Hz, 2H), 7.56 – 7.46 (m, 1H), 7.38 – 7.34 (m, 1H), 6.87 (s, 1H), 5.07 (s, 1H), 1.62 (s, 9H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 153.4, 137.9, 128.9, 127.4, 124.7, 121.1, 116.8, 103.6, 51.5, 37.2, 30.1, 29.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{25}N_2^+$, ([M + H]$^+$), 257.2012, found 257.2011.



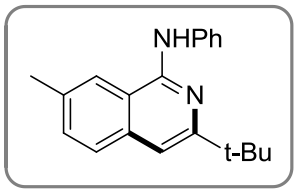
6-bromo-3-(*tert*-butyl)-*N*-phenylisoquinolin-1-amine 3vp

Yield: 73% (51.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.65 (m, 3H), 7.60 (d, J = 8.4 Hz, 1H), 7.44 (dd, J = 8.4, 4.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 2H), 7.03 (d, J = 7.2 Hz, 1H), 7.00 (s, 1H), 6.95 (s,

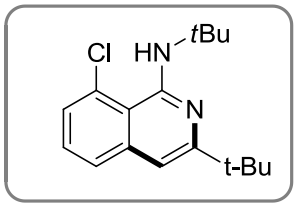
1H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 150.7, 140.5, 139.5, 129.6, 128.7, 128.6, 124.0, 122.7, 122.0, 119.4, 115.3, 106.1, 37.4, 30.0. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{20}BrN_2^+$, ([M + H]$^+$), 355.0804, found 355.0826.



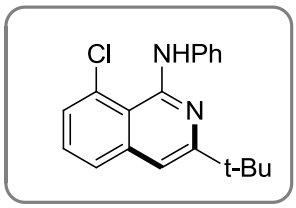
3-(*tert*-butyl)-6-chloro-*N*-phenylisoquinolin-1-amine 3wp
Yield: 76% (47.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.78 – 7.75 (m, 1H), 7.69 (d, J = 2.0 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.08 (t, J = 6.8 Hz, 2H), 7.02 (s, 1H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 150.6, 140.6, 139.3, 135.5, 128.7, 126.4, 126.1, 122.7, 122.0, 119.4, 115.1, 106.3, 37.4, 30.0. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{20}ClN_2^+$, ([M + H]$^+$), 311.1310, found 311.1319.



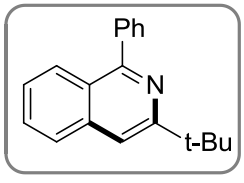
3-(*tert*-butyl)-7-methyl-*N*-phenylisoquinolin-1-amine 3xp
Yield: 80% (46.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.21 – 7.17 (m, 2H), 7.07 – 7.05 (m, 2H), 7.01 – 6.99(m, 1H), 6.86 (s, 1H), 2.27 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 138.8, 137.9, 129.7, 129.2, 128.9, 127.8, 127.5, 126.0, 125.7, 116.3, 31.8, 30.2, 21.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{23}N_2^+$, ([M + H]$^+$), 291.1856, found 291.1848.



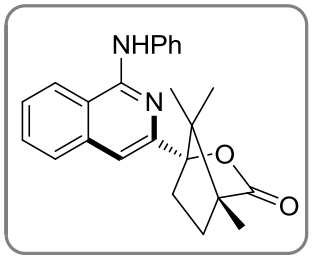
***N*,3-di-*tert*-butyl-8-chloroisoquinolin-1-amine 3yp**
Yield: 77% (44.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.0, 2.2 Hz, 1H), 7.30 – 7.19 (m, 3H), 6.74 (s, 1H), 1.58 (s, 9H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 153.1, 141.6, 129.4, 128.5, 127.3, 127.0, 114.2, 103.4, 52.0, 37.1, 29.9, 29.2. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{24}ClN_2^+$, ([M + H]$^+$), 291.1623, found 291.1628.



3-(*tert*-butyl)-8-chloro-*N*-phenylisoquinolin-1-amine 3y'p
Yield: 42% (26.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.87 (d, J = 7.8 Hz, 2H), 7.57 (dd, J = 7.8, 1.2 Hz, 1H), 7.43 – 7.33 (m, 4H), 7.05 (t, J = 7.4 Hz, 1H), 7.00 (s, 1H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 150.3, 141.6, 140.5, 129.0, 128.7, 128.6, 128.1, 127.3, 122.1, 120.2, 114.1, 106.7, 37.2, 29.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{20}ClN_2^+$, ([M + H]$^+$), 311.1310, found 311.1307.

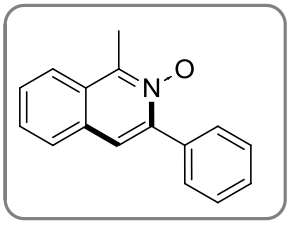


3-(*tert*-butyl)-1-phenylisoquinoline 3zp
Yield: 54% (28.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.68 – 7.66 (m, 2H), 7.54 – 7.48 (m, 2H), 7.46 – 7.31 (m, 4H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 158.9, 137.6, 130.2, 129.4, 128.2, 128.1, 127.2, 127.1, 126.1, 124.7, 113.4, 37.2, 30.2. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{20}N^+$, ([M + H]$^+$), 262.1590, found 262.1587.



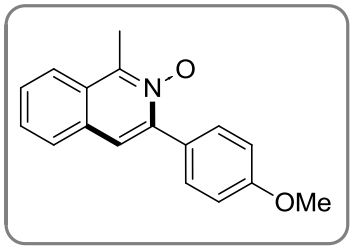
(1S,4R)-4,7,7-trimethyl-1-(1-(phenylamino)isoquinolin-3-yl)-2-oxabicyclo[2.2.1]heptan-3-one 3pr

Yield: 75% (56.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 1H), 7.80 – 7.72 (m, 3H), 7.70 – 7.61 (m, 1H), 7.58 – 7.54 (m, 1H), 7.43 (s, 1H), 7.37 – 7.73 (m, 2H), 7.23 (s, 1H), 7.07 (t, J = 7.2 Hz, 1H), 3.00 – 2.86 (m, 1H), 2.09 – 1.95 (m, 2H), 1.86 – 1.73 (m, 1H), 1.17 (s, 3H), 1.10 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 151.2, 146.6, 140.4, 137.6, 130.1, 128.7, 128.1, 126.7, 122.5, 121.1, 120.2, 117.8, 110.5, 95.6, 55.8, 54.2, 32.0, 29.6, 17.38, 16.8, 10.2. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{25}N_2O_2^+$, ([M + H]$^+$), 373.1911, found 373.1919.



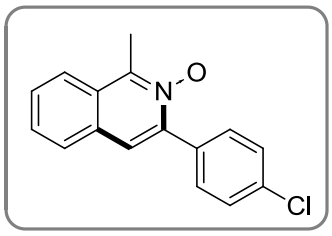
1-methyl-3-phenylisoquinoline 2-oxide 5a

Yield: 85% (39.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 1H), 7.77 (dd, J = 8.0, 2.0 Hz, 3H), 7.67 (s, 1H), 7.63– 7.59 (m, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.51 – 7.43 (m, 3H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 146.0, 133.7, 129.8, 129.0, 128.7, 128.6, 128.2, 128.1, 128.0, 127.3, 123.8, 122.5, 13.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{14}NO^+$, ([M + H]$^+$), 236.1070, found 236.1077.



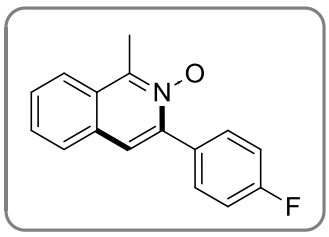
3-(4-methoxyphenyl)-1-methylisoquinoline 2-oxide 5b

Yield: 77% (40.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 1H), 7.81 – 7.71 (m, 3H), 7.65 (s, 1H), 7.62 – 7.50 (m, 2H), 7.05 – 6.94 (m, 2H), 3.86 (s, 3H), 2.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 146.4, 146.1, 131.2, 128.8, 128.3, 128.1, 128.0, 127.2, 126.0, 123.8, 122.1, 113.4, 55.3, 13.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{16}NO_2^+$, ([M + H]$^+$), 266.1176, found 266.1189.



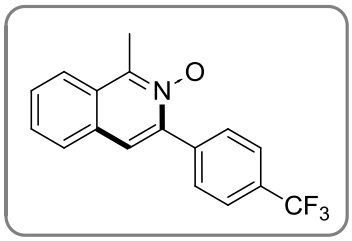
3-(4-chlorophenyl)-1-methylisoquinoline 2-oxide 5c

Yield: 76% (40.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 1H), 7.81 – 7.71 (m, 3H), 7.69 – 7.53 (m, 3H), 7.49 – 7.41 (m, 2H), 2.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 145.5, 135.2, 132.1, 131.2, 128.9, 128.6, 128.40, 128.36, 128.3, 127.4, 123.9, 122.6, 13.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}ClNO^+$, ([M + H]$^+$), 270.0680, found 270.0672



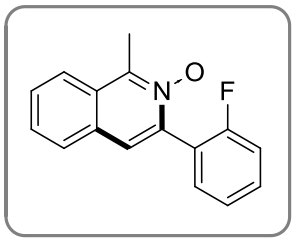
3-(4-fluorophenyl)-1-methylisoquinoline 2-oxide 5d

Yield: 86% (43.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.5 Hz, 1H), 7.82 – 7.72 (m, 3H), 7.67 (s, 1H), 7.66 – 7.61 (m, 1H), 7.60 – 7.54 (m, 1H), 7.18 – 7.11 (m, 2H), 2.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, J = 249.1 Hz), 146.3, 145.3, 131.9 (d, J = 8.4 Hz), 129.7 (d, J = 3.5 Hz), 128.8, 128.7, 128.4, 128.3, 127.4, 123.9, 122.5, 115.1 (d, J = 21.7 Hz, 2H), 13.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}FNO^+$, ([M + H]$^+$), 254.0976, found. 254.0979.



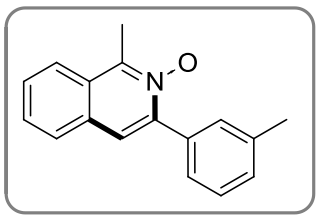
1-methyl-3-(4-(trifluoromethyl)phenyl)isoquinoline 2-oxide 5e

Yield: 75% (45.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 7.9 Hz, 1H), 7.75 – 7.68 (m, 3H), 7.68 – 7.62 (m, 1H), 7.58 (t, J = 7.5 Hz, 1H), 2.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 145.1, 137.2, 130.8 (q, J = 32.6 Hz), 130.2, 129.1, 128.5, 128.44, 128.40, 127.5, 124.9 (q, J = 3.8 Hz), 124.0 (q, J = 270.6 Hz), 123.9, 122.9, 13.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{13}F_3NO^+$, ([M + H]$^+$), 304.0944, found 304.0963.



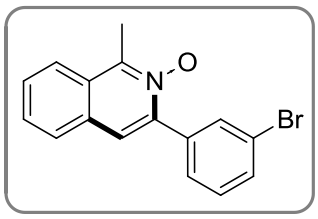
3-(2-fluorophenyl)-1-methylisoquinoline 2-oxide 5f

Yield: 87% (44.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.69 (s, 1H), 7.67 – 7.60 (m, 1H), 7.56 (td, J = 7.7, 1.3 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.31 – 7.16 (m, 2H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.52 (d, J = 249.5 Hz), 145.9, 142.3, 131.7 (d, J = 2.7 Hz), 131.1 (d, J = 8.4 Hz), 129.0, 128.7, 128.2, 127.5, 124.0 (d, J = 3.6 Hz), 123.9, 123.6, 122.0 (d, J = 15.0 Hz), 115.7 (d, J = 21.7 Hz), 13.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}FNO^+$, ([M + H]$^+$), 254.0976, found. 254.0990.



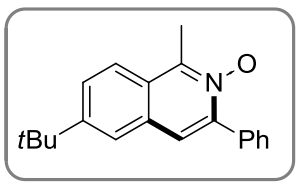
1-methyl-3-(m-tolyl)isoquinoline 2-oxide 5g

Yield: 71% (35.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.65 (s, 1H), 7.63 – 7.58 (m, 2H), 7.56 – 7.51 (m, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.28 – 7.24 (m, 1H), 2.93 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 146.0, 137.6, 133.7, 130.4, 129.9, 128.7, 128.6, 128.3, 128.1, 128.0, 127.4, 126.9, 123.8, 122.5, 21.5, 13.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{16}NO^+$, ([M + H]$^+$), 250.1226, found. 250.1217.



3-(3-bromophenyl)-1-methylisoquinoline 2-oxide 5h

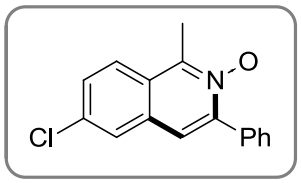
Yield: 79% (48.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.86 (m, 2H), 7.69 (d, J = 7.8 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.60 – 7.52 (m, 2H), 7.52 – 7.46 (m, 2H), 7.26 (t, J = 7.9 Hz, 1H), 2.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 145.2, 135.6, 132.7, 132.1, 129.6, 129.0, 128.5, 128.5, 128.4, 127.5, 123.9, 122.8, 122.0, 13.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}BrNO$, ([M + H]$^+$), 304.0944, found. 304.0961.



6-(*tert*-butyl)-1-methyl-3-phenylisoquinoline 2-oxide 5i

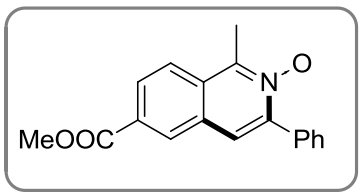
Yield: 75% (43.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.8 Hz, 1H), 7.77 (dd, J = 7.9, 1.6 Hz, 2H), 7.72 – 7.65 (m, 3H), 7.51 – 7.40 (m, 3H), 2.94 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 146.6, 146.0, 133.9, 129.9, 129.1, 129.0, 128.0, 127.6, 126.5,

123.9, 122.8, 122.6, 35.1, 31.0, 13.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{22}NO^+$, ([M + H]$^+$), 292.1696, found. 292.1709.



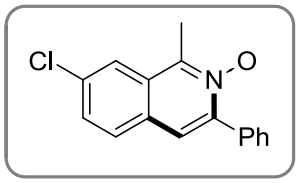
6-chloro-1-methyl-3-phenylisoquinoline 2-oxide 5j

Yield: 71% (41.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.8 Hz, 1H), 7.79 – 7.72 (m, 3H), 7.59 (s, 1H), 7.55 (dd, J = 8.8, 2.1 Hz, 1H), 7.51 – 7.44 (m, 3H), 2.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 146.6, 146.0, 133.9, 129.9, 129.1, 129.0, 128.0, 127.6, 126.5, 123.9, 122.8, 122.6, 35.1, 31.0, 13.6. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}ClNO^+$, ([M + H]$^+$), 270.0680, found. 270.0689.



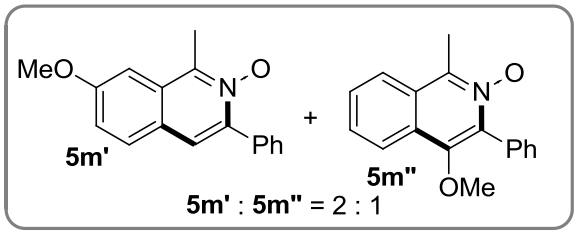
6-(methoxycarbonyl)-1-methyl-3-(o-tolyl)isoquinoline 2-oxide 5k

Yield: 72% (42.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 1.2 Hz, 1H), 8.18 (dd, J = 8.4, 1.6 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.80 – 7.74 (m, 3H), 7.54 – 7.46 (m, 3H), 4.00 (s, 3H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 147.7, 146.2, 133.2, 130.2, 129.9, 129.7, 129.4, 129.3, 128.1, 128.1, 127.7, 124.0, 123.3, 52.5, 13.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{16}NO_3^+$, ([M + H]$^+$), 294.1125, found. 294.1130.



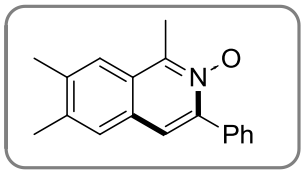
7-chloro-1-methyl-3-phenylisoquinoline 2-oxide 5l

Yield: 74% (42.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 1.6 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.70 (d, J = 8.7 Hz, 1H), 7.65 (s, 1H), 7.51 – 7.41 (m, 4H), 2.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 145.3, 134.7, 133.3, 129.7, 129.3, 129.1, 129.0, 128.9, 128.1, 126.8, 122.9, 122.2, 13.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{13}ClNO^+$, ([M + H]$^+$), 270.0680, found. 270.0668.



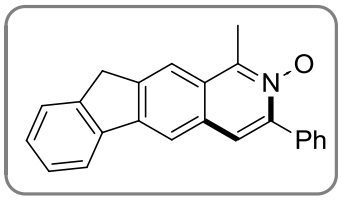
5m, Yield: 81% (42.7 mg). The product can not be seperated by chlumn, so characterized by mixture. The ratio of isoer was determined by ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.82 – 7.72 (m, 3H), 7.67 (d, J = 8.9 Hz, 0.54H), 7.60 (s, 0.53H), 7.54 – 7.40 (m, 6.53H), 7.21 (dd, J = 8.9, 2.4 Hz, 0.51H), 7.14 (d, J = 2.2 Hz, 0.5 H), 6.89 (dd, J = 6.8, 1.6 Hz, 1H), 3.98 (s, 3H), 3.97 (s, 1.5H), 2.91 (s, 3H), 2.90 (s, 1.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 155.2, 145.9, 145.7, 144.8, 144.6, 134.1, 133.9, 129.9, 129.8, 1297., 129.4, 129.2, 129.0, 128.90, 128.84, 128.01, 127.97, 124.2, 122.3, 120.9, 120.7, 117.3, 115.9, 106.3, 102.5, 55.8, 55.6, 13.9, 13.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{16}NO_2^+$, ([M + H]$^+$), 266.1176, found. 266.1189.



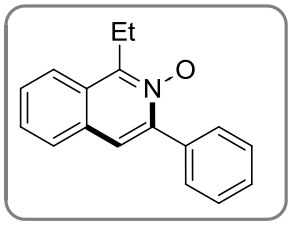
1,6,7-trimethyl-3-phenylisoquinoline 2-oxide 5n

Yield: 82% (43.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.0, 2.0 Hz, 2H), 7.68 (s, 1H), 7.55 (s, 1H), 7.50 (s, 1H), 7.48 – 7.41 (m, 3H), 2.91 (s, 3H), 2.47 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 145.3, 138.7, 138.6, 134.0, 129.8, 128.7, 127.9, 127.7, 127.0, 126.9, 123.5, 121.7, 20.6, 20.1, 13.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{18}NO^+$, ([M + H]$^+$), 264.1383, found. 264.1390.



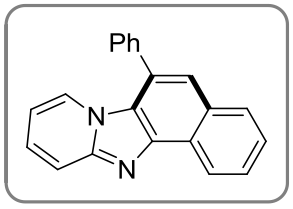
1-methyl-3-phenyl-10H-indeno[1,2-g]isoquinoline 2-oxide 5o

Yield: 71% (45.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 2H), 7.92 – 7.88 (m, 1H), 7.80 (dd, J = 8.0, 2.0 Hz, 2H), 7.74 (s, 1H), 7.60 (d, J = 6.8 Hz, 1H), 7.51 – 7.40 (m, 5H), 4.12 (s, 2H), 2.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 146.0, 144.2, 143.9, 143.0, 139.8, 133.9, 129.8, 129.0, 128.8, 128.7, 128.0, 127.4, 127.3, 125.4, 122.7, 121.1, 119.6, 117.1, 36.8, 13.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{18}NO^+$, ([M + H]$^+$), 324.1383, found. 324.1387.



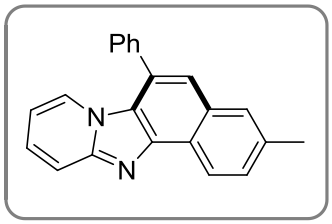
1-ethyl-3-phenylisoquinoline 2-oxide 5p

Yield: 84% (41.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.5 Hz, 1H), 7.80 – 7.76 (m, 3H), 7.67 (s, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.51 – 7.40 (m, 3H), 3.50 (q, J = 7.5 Hz, 2H), 1.39 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 146.8, 133.8, 129.9, 129.1, 128.9, 128.7, 128.0, 127.7, 127.5, 123.5, 122.7, 20.4, 10.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{14}NO^+$, ([M + H]$^+$), 250.1226, found. 250.1238.



6-phenylnaphtho[1',2':4,5]imidazo[1,2-a]pyridine 7a

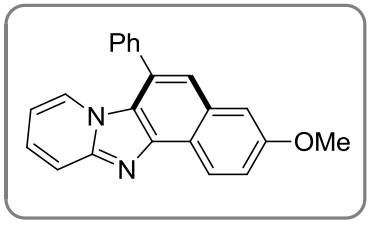
Yield: 88% (52.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.78 – 7.67 (m, 1H), 7.66 – 7.60 (m, 1H), 7.59 – 7.50 (m, 6H), 7.38 – 7.31 (m, 1H), 6.60 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 141.7, 138.2, 131.5, 129.4, 128.9, 128.3, 128.2, 127.3, 126.6, 126.43, 126.39, 126.1, 123.6, 123.0, 122.3, 118.0, 110.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{15}N_2^+$, ([M + H]$^+$), 295.1230, found. 295.1247.



3-methyl-6-phenylnaphtho[1',2':4,5]imidazo[1,2-a]pyridine 7b

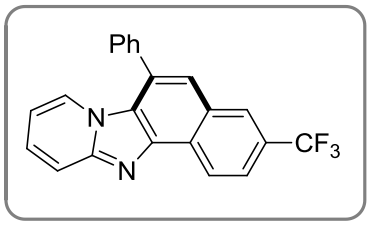
Yield: 91% (56.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 8.3 Hz, 1H), 7.89 – 7.80 (m, 2H), 7.75 (s, 1H), 7.61 – 7.51 (m, 6H), 7.47 (s, 1H), 7.31 (t, J = 7.6 Hz, 1H), 6.57 (t, J = 7.2 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 141.9, 138.4, 136.1,

131.8, 129.4, 128.9, 128.5, 128.3, 128.2, 127.5, 127.1, 126.5, 124.1, 123.2, 122.9, 121.9, 117.9, 110.5, 21.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{17}N_2^+$, ([M + H]$^+$), 309.1386, found. 309.1392.



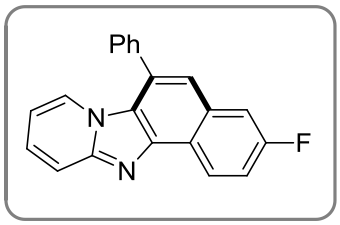
3-methoxy-6-phenylnaphtho[1',2':4,5]imidazo[1,2-a]pyridine 7c

Yield: 96% (61.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 8.8 Hz, 1H), 7.90 – 7.78 (m, 2H), 7.63 – 7.51 (m, 5H), 7.46 (s, 1H), 7.40 – 7.28 (m, 3H), 6.58 (t, J = 7.6, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 147.9, 142.0, 138.3, 132.9, 129.4, 128.9, 128.7, 128.3, 127.2, 126.5, 124.6, 122.8, 121.3, 120.8, 117.8, 117.7, 110.5, 107.6, 55.4. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{17}N_2O^+$, ([M + H]$^+$), 325.1335, found. 325.1330.



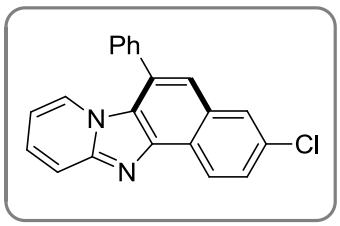
6-phenyl-3-(trifluoromethyl)naphtho[1',2':4,5]imidazo[1,2-a]pyridine 7d

Yield: 85% (61.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, J = 8.6 Hz, 1H), 8.26 (s, 1H), 7.91 – 7.79 (m, 3H), 7.63 – 7.54 (m, 6H), 7.37 (ddd, J = 9.1, 6.6, 1.1 Hz, 1H), 6.73 – 6.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 141.3, 137.6, 130.4, 129.7, 129.3, 129.1, 128.7, 128.1 (q, J = 32.0 Hz), 128.0, 126.7, 125.7 (q, J = 4.7 Hz), 124.6 (q, J = 270.5 Hz), 124.0, 123.7, 122.0 (q, J = 3.1 Hz), 118.1, 111.1. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{14}F_3N_2^+$, ([M + H]$^+$), 363.1104, found. 363.1114.



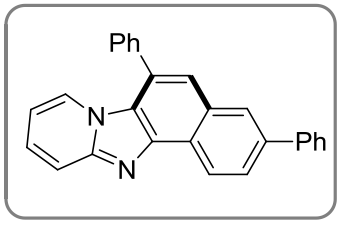
3-fluoro-6-phenylnaphtho[1',2':4,5]imidazo[1,2-a]pyridine 7e

Yield: 82% (51.2mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, J = 8.9, 5.7 Hz, 1H), 7.84 (dd, J = 5.5, 4.4 Hz, 2H), 7.63 – 7.53 (m, 6H), 7.48 – 7.43 (m, 2H), 7.41 – 7.31 (m, 1H), 6.62 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, J = 245.1 Hz), 148.0, 141.8, 137.9, 132.5 (d, J = 9.1 Hz), 129.5, 129.3, 129.0, 128.5, 127.6, 126.6, 125.4 (d, J = 9.1 Hz), 122.8, 122.6 (d, J = 4.3 Hz),121.8, 117.9, 115.9 (d, J = 24.5 Hz), 111.8 (d, J = 20.9 Hz).110.8. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{14}FN_2^+$, ([M + H]$^+$), 313.1136, found. 313.1347.



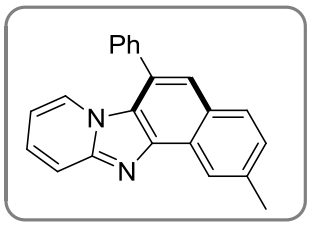
3-chloro-6-phenylnaphtho[1',2':4,5]imidazo[1,2-a]pyridine 7f

Yield: 87% (57.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 2.0 Hz, 1H), 7.85 (dd, J = 5.6, 4.4 Hz, 2H), 7.64 (dd, J = 8.7, 2.0 Hz, 1H), 7.63 – 7.50 (m, 5H), 7.45 (s, 1H), 7.39 – 7.34 (m, 1H), 6.63 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 141.5, 137.8, 132.3, 132.2, 129.5, 129.3, 129.0, 128.6, 127.8, 127.1, 127.0, 126.6, 124.7, 124.2, 122.5, 117.9, 111.0. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{14}ClN_2^+$, ([M + H]$^+$), 329.0840, found 329.0839.



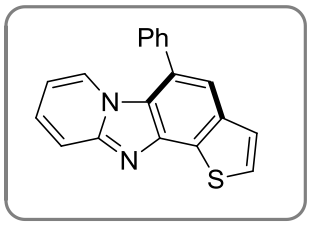
3,6-diphenylnaphtho[1',2':4,5]imidazo[1,2-a]pyridine 7g

Yield: 86% (63.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 8.5 Hz, 1H), 8.18 (d, J = 1.6 Hz, 1H), 7.98 (dd, J = 8.5, 1.8 Hz, 1H), 7.86 (dd, J = 8.4, 1.1 Hz, 2H), 7.81 – 7.74 (m, 2H), 7.62 – 7.54 (m, 6H), 7.50 (t, J = 8.0 Hz, 2H), 7.41 – 7.30 (m, 2H), 6.59 (td, J = 6.8, 1.2 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 141.7, 141.2, 139.1, 138.2, 131.8, 129.4, 129.0, 128.9, 128.6, 128.4, 127.5, 127.4, 126.6, 126.3, 126.0, 125.2, 123.9, 123.6, 122.4, 118.0, 110.7. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{19}N_2^+$, ([M + H]$^+$), 371.1543, found 371.1537.



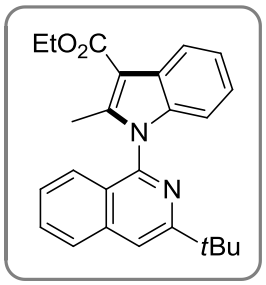
2-methyl-6-phenylnaphtho[1',2':4,5]imidazo[1,2-a]pyridine 7h

Yield: 75% (46.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.92 – 7.80 (m, 3H), 7.58– 7.51 (m, 6H), 7.45 (dd, J = 8.2, 1.5 Hz, 1H), 7.32 (ddd, J = 9.3, 6.6, 1.0 Hz, 1H), 6.63 – 6.53 (m, 1H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 141.4, 138.4, 136.5, 129.5, 129.5, 128.9, 128.4, 128. 2, 128.1, 127.2, 126.6, 126.1, 123.5, 122.4, 117.9, 110.6, 21.9. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{17}N_2$, ([M + H]$^+$), 309.1386, found. 309.1378.



5-phenylthieno[3'',2'':5',6']benzo[1',2':4,5]imidazo[1,2-a]pyridine 7i

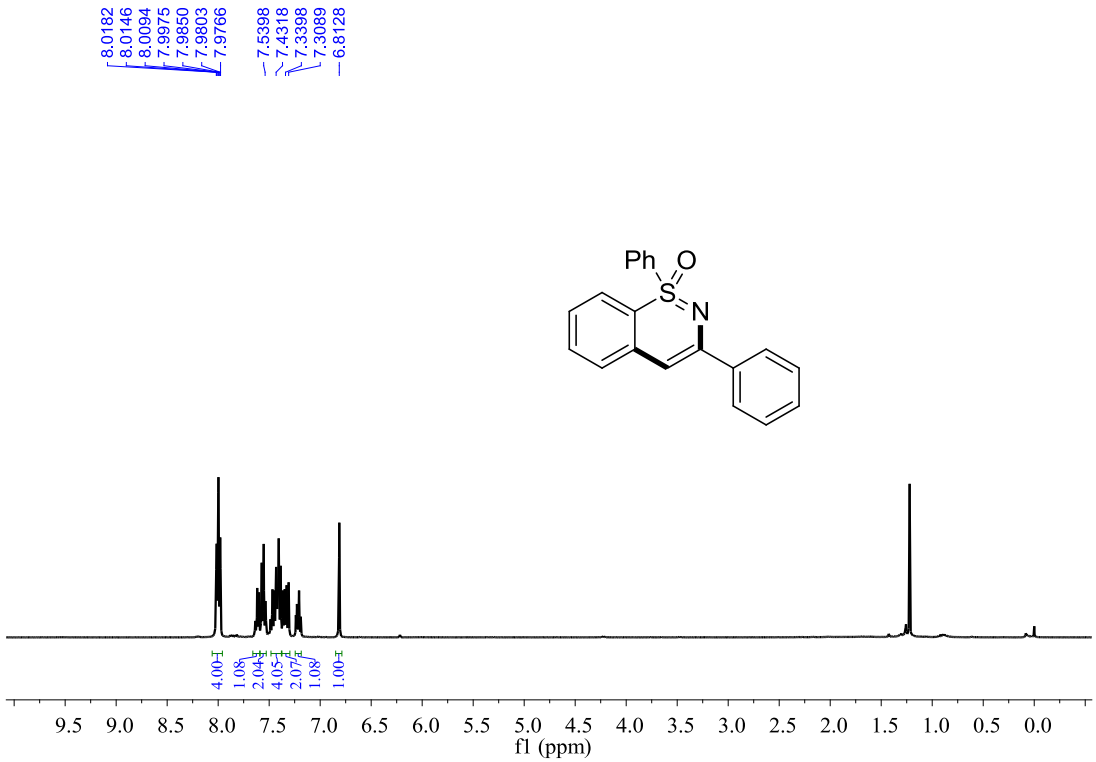
Yield:78% (46.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.68 – 7.46 (m, 8H), 7.35 (dd, J = 8.5, 7.3 Hz, 1H), 6.57 (t, J =7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 138.3, 137.7, 129.6, 129.2, 128.9, 128.3, 128.3, 127.1, 126.3, 126.2, 124.7, 122.4, 119.0, 117.8, 110.5. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{13}N_2S$, ([M + H]$^+$), 301.0794, found. 301.0790.



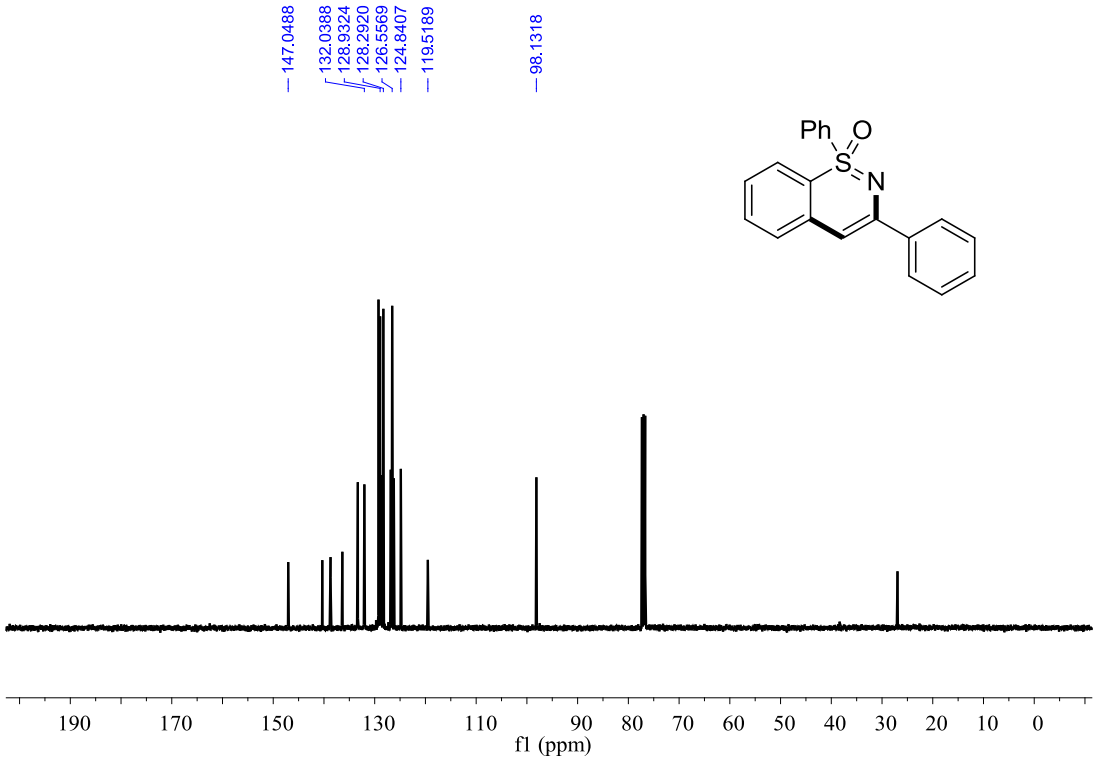
(S)-ethyl-1-(3-(*tert*-butyl)isoquinolin-1-yl)-2-methyl-1H-indole-3-carboxylate 8

Yield: 88% (68.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, J = 7.6 Hz, 2H), 7.45 – 7.34 (m, 2H), 7.24 – 7.17 (m, 2H), 7.10 (d, J = 7.8 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.73 (s, 1H), 4.40 (q, J = 7.1 Hz, 2H), 1.98 (s, 3H), 1.41 (t, J = 17.6 Hz, 3H), 1.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 162.5, 152.6, 142.9, 140.1, 139.4, 132.4, 131.3, 129.6, 129.5, 128.0, 119.3, 118.9, 113.5, 109.8, 105.8, 61.0, 36.8, 29.5, 19.7, 14.3. Mass Spectrometry: HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{27}N_2O_2^+$, ([M + H]$^+$), 387.2067, found. 387.2076.

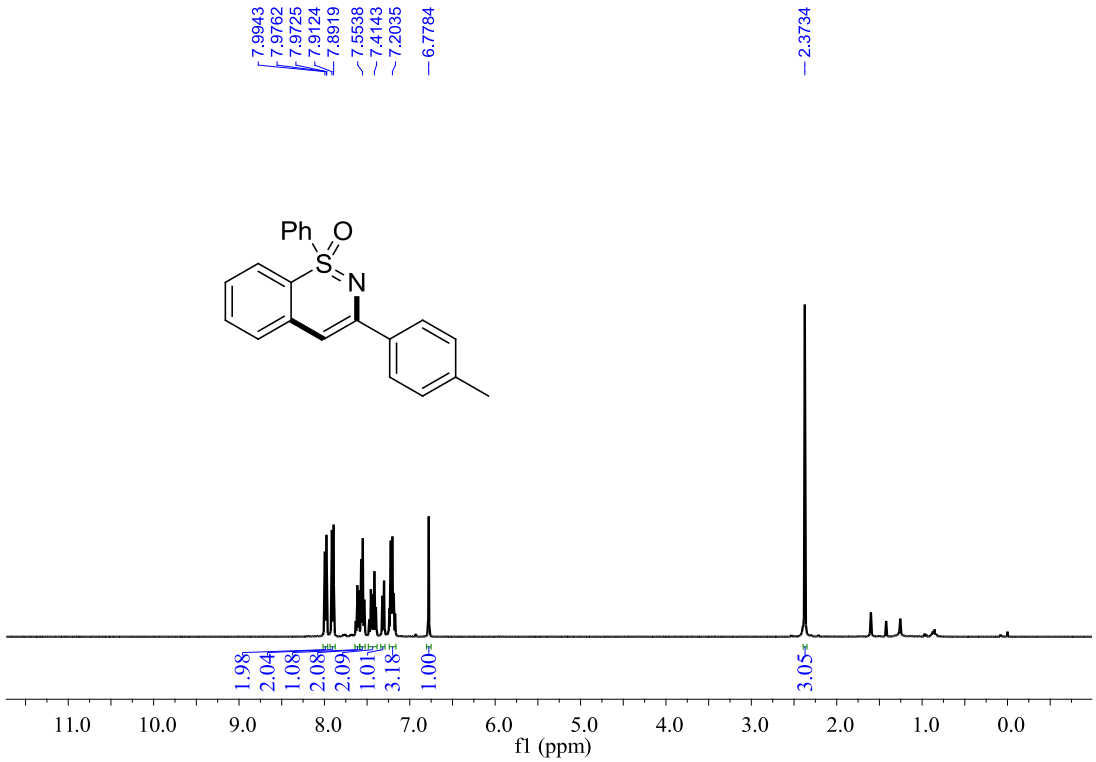
VI. NMR Spectra of Products



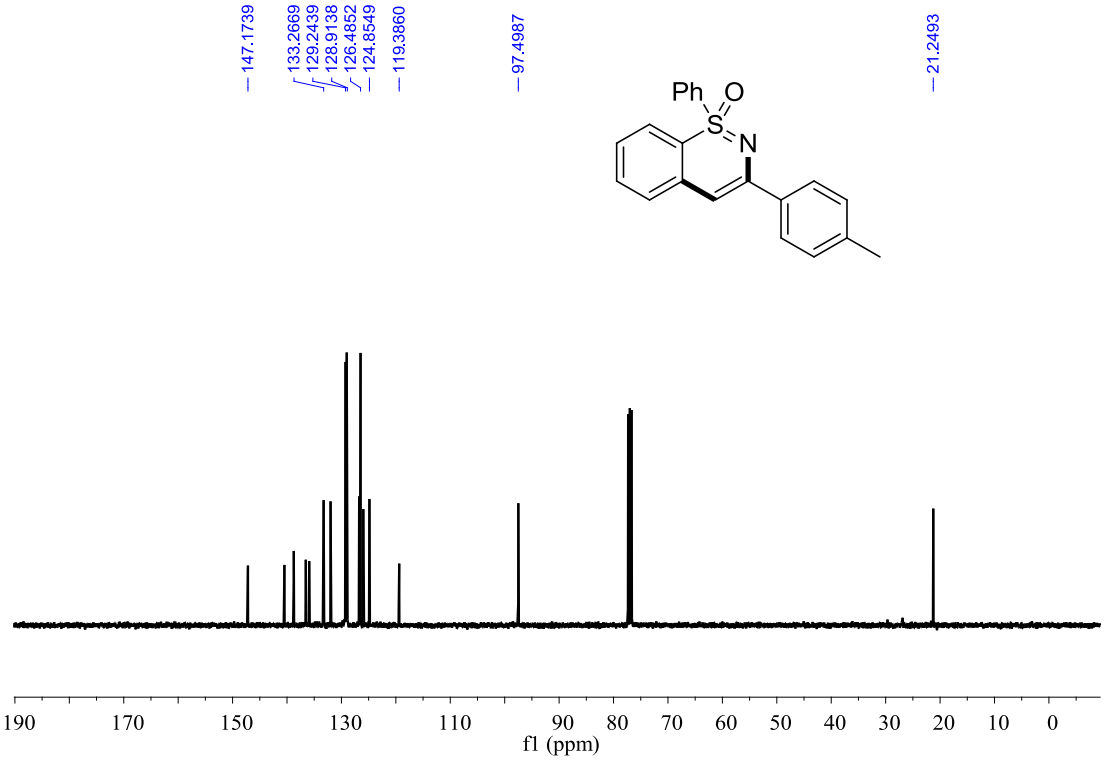
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3aa.



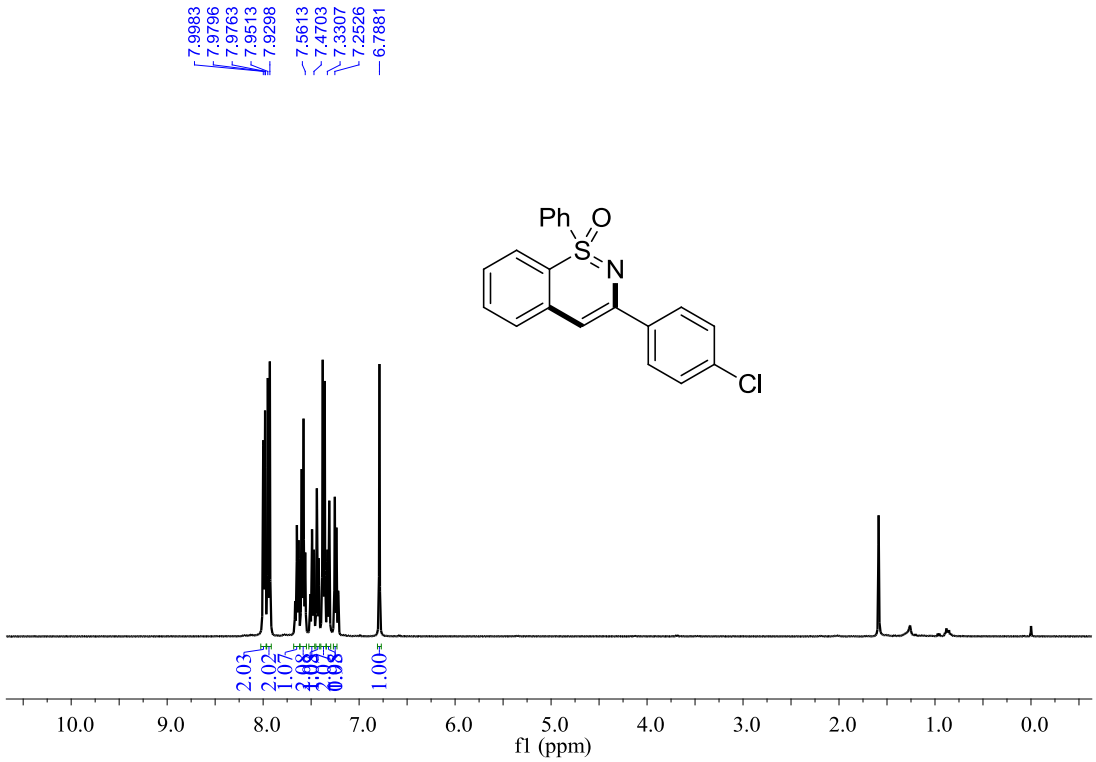
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3aa.



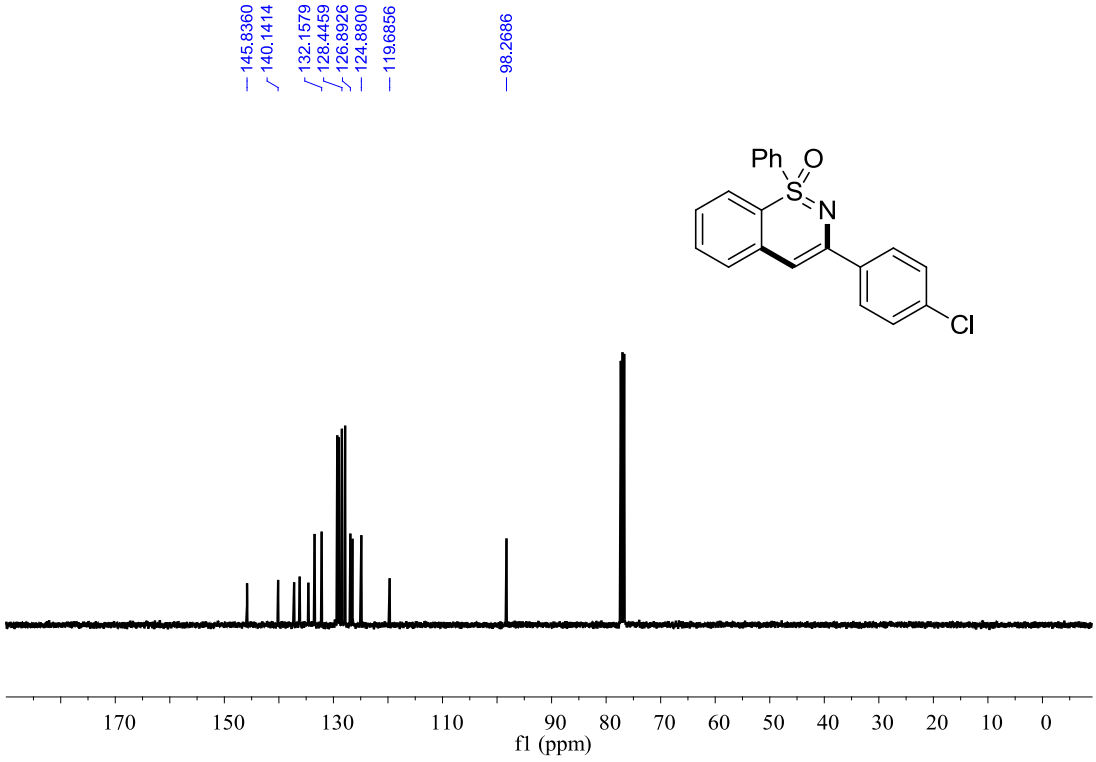
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3ab.



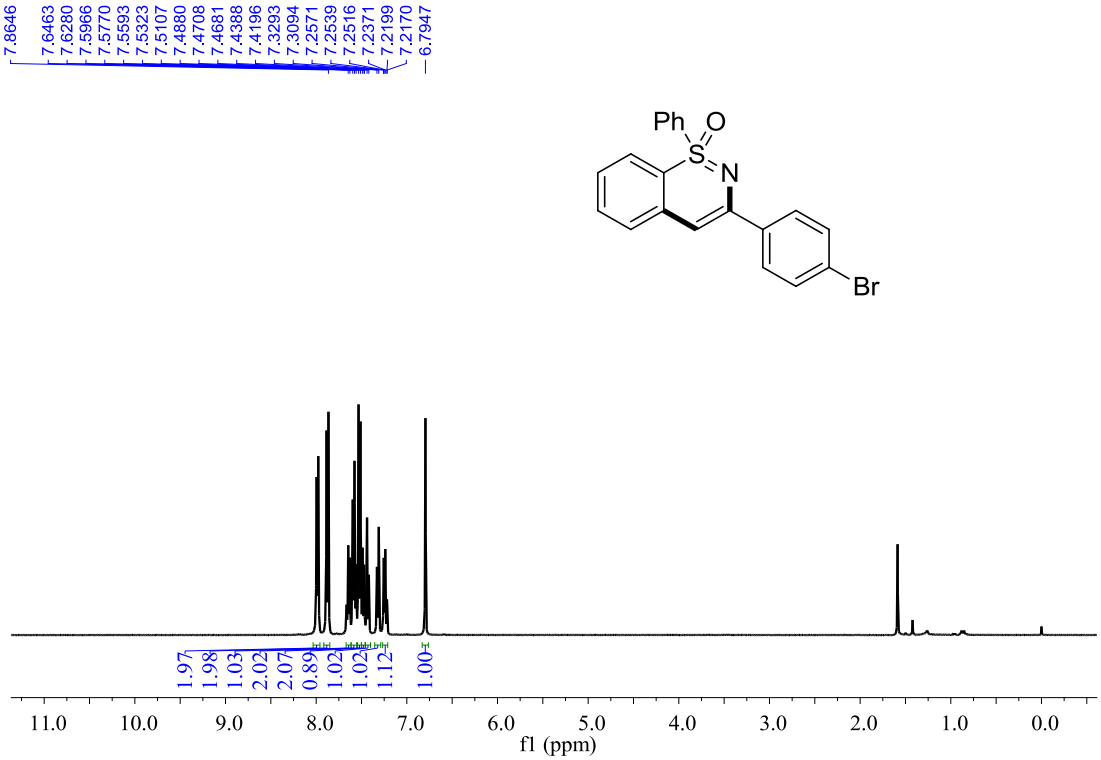
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3ab.



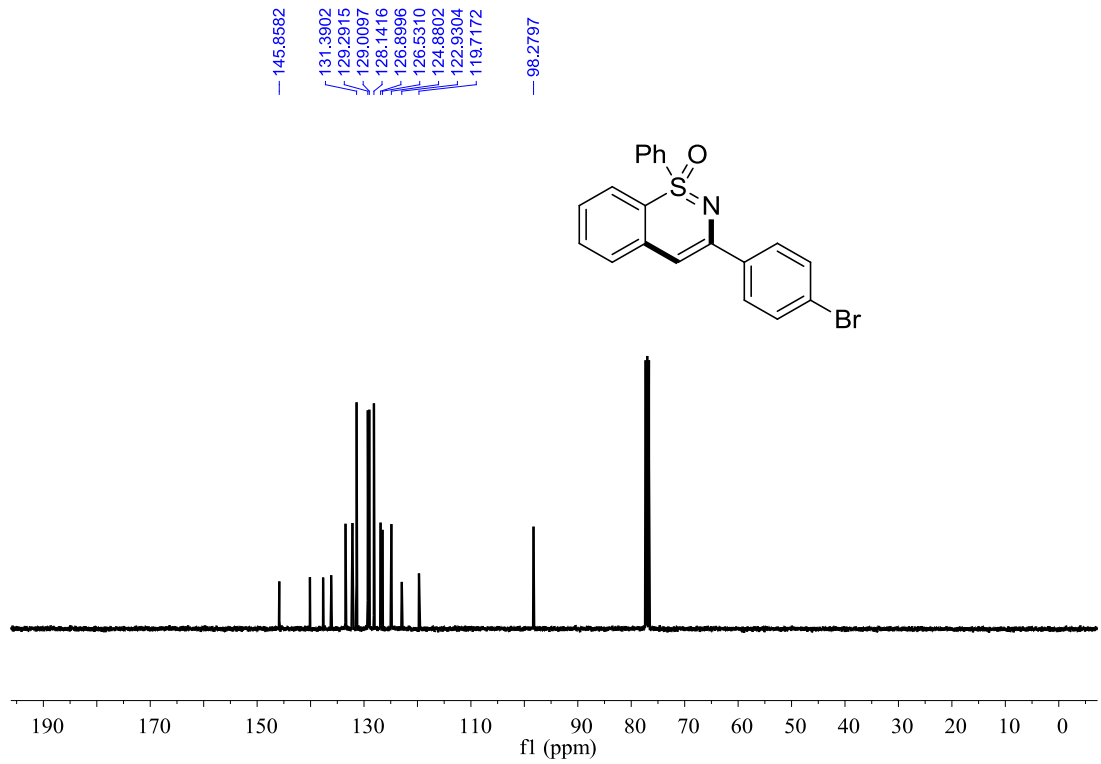
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3ac.



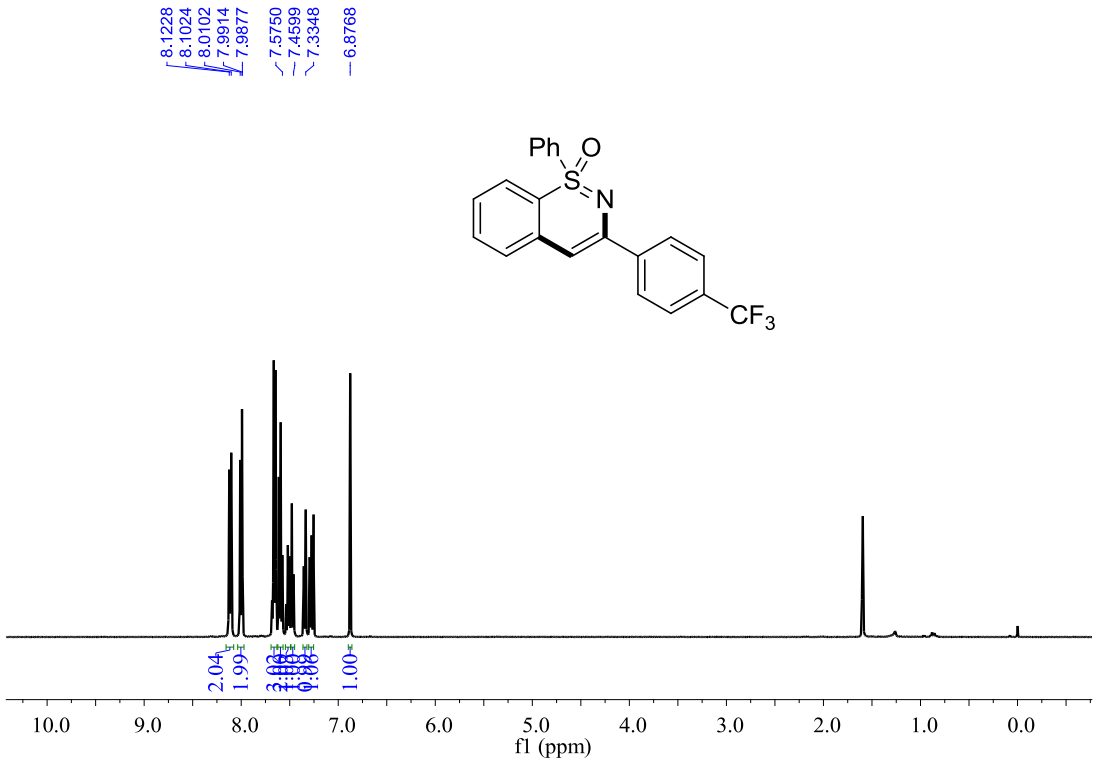
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3ac.



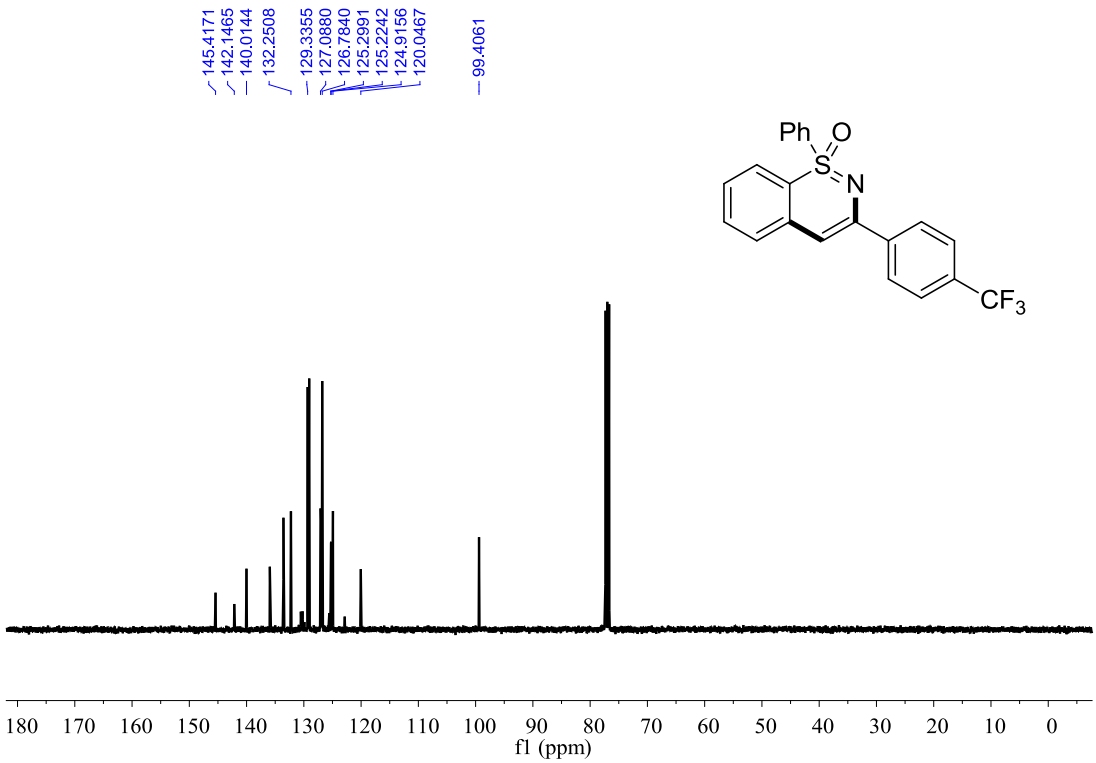
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3ad.



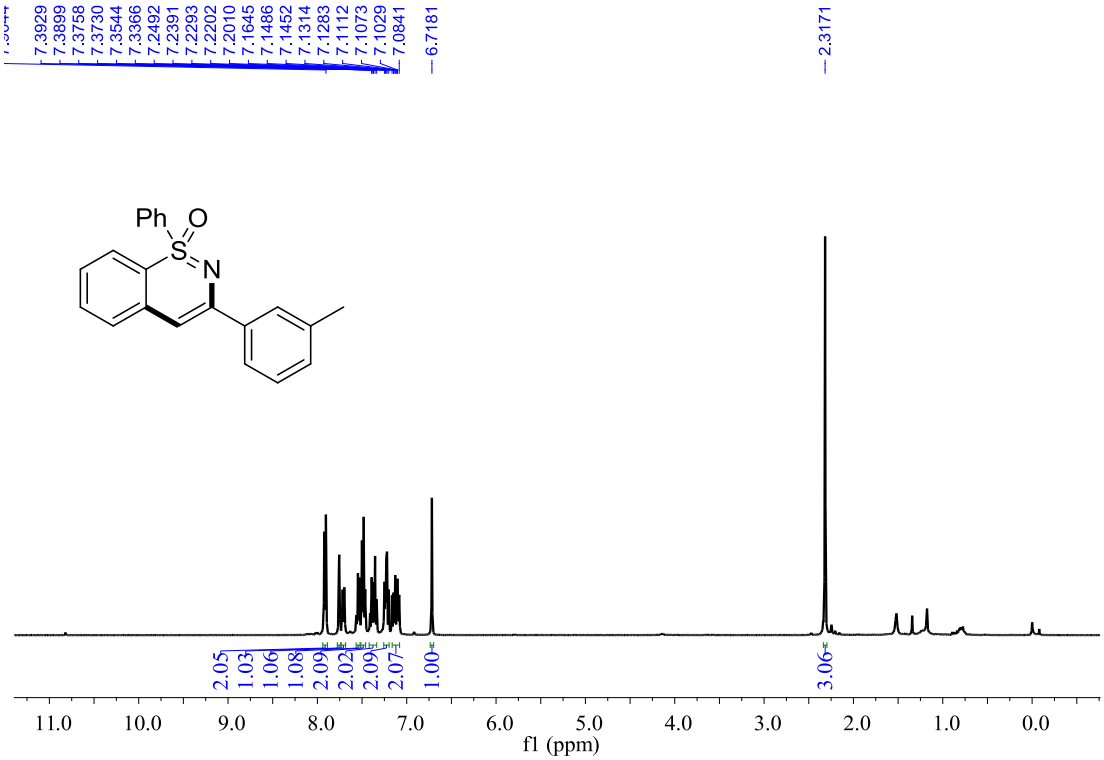
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3ad.



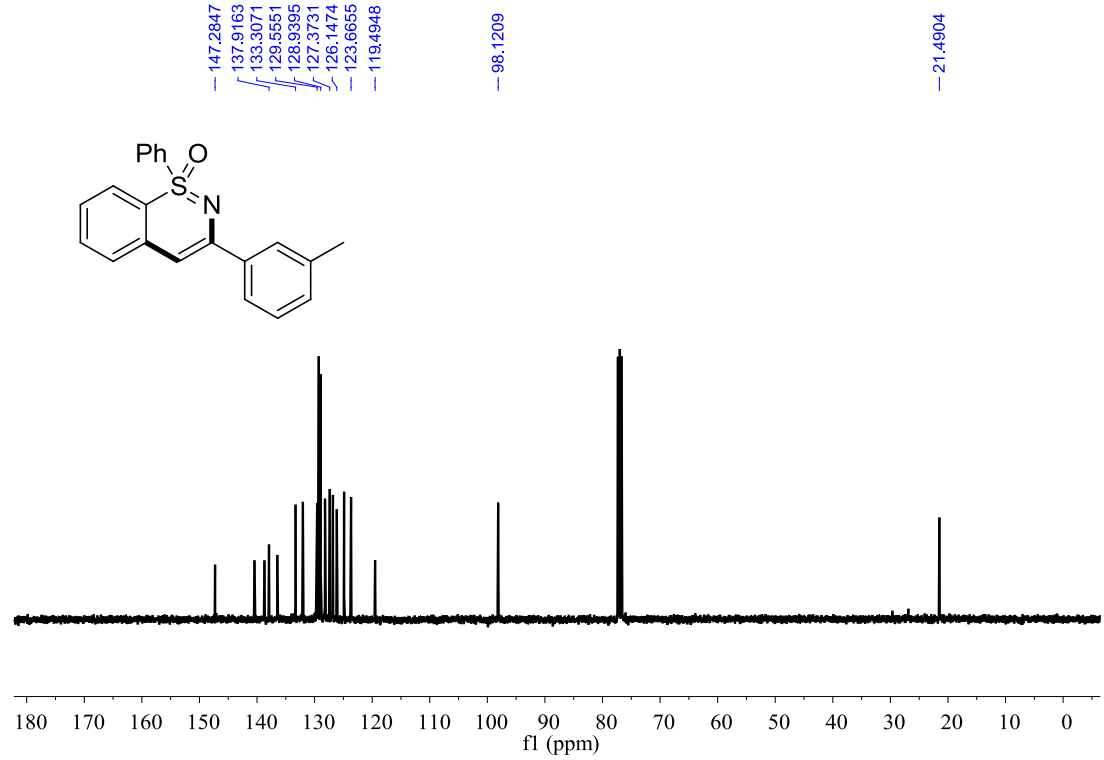
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3ae.



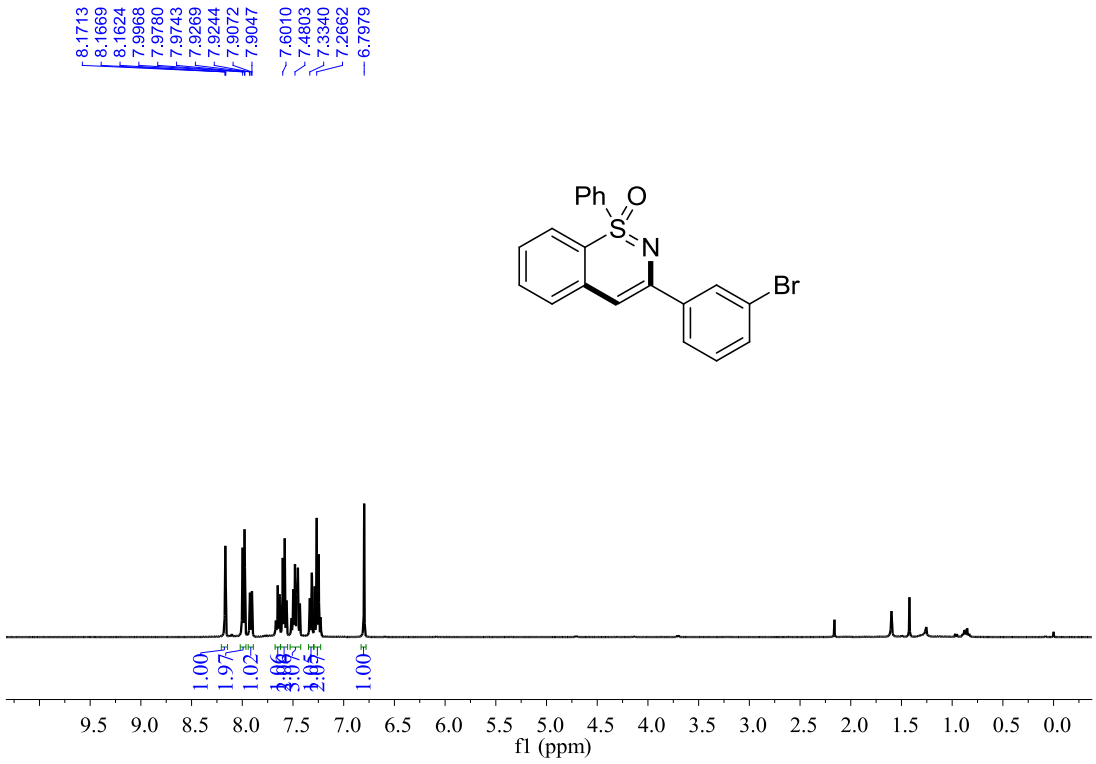
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3e.



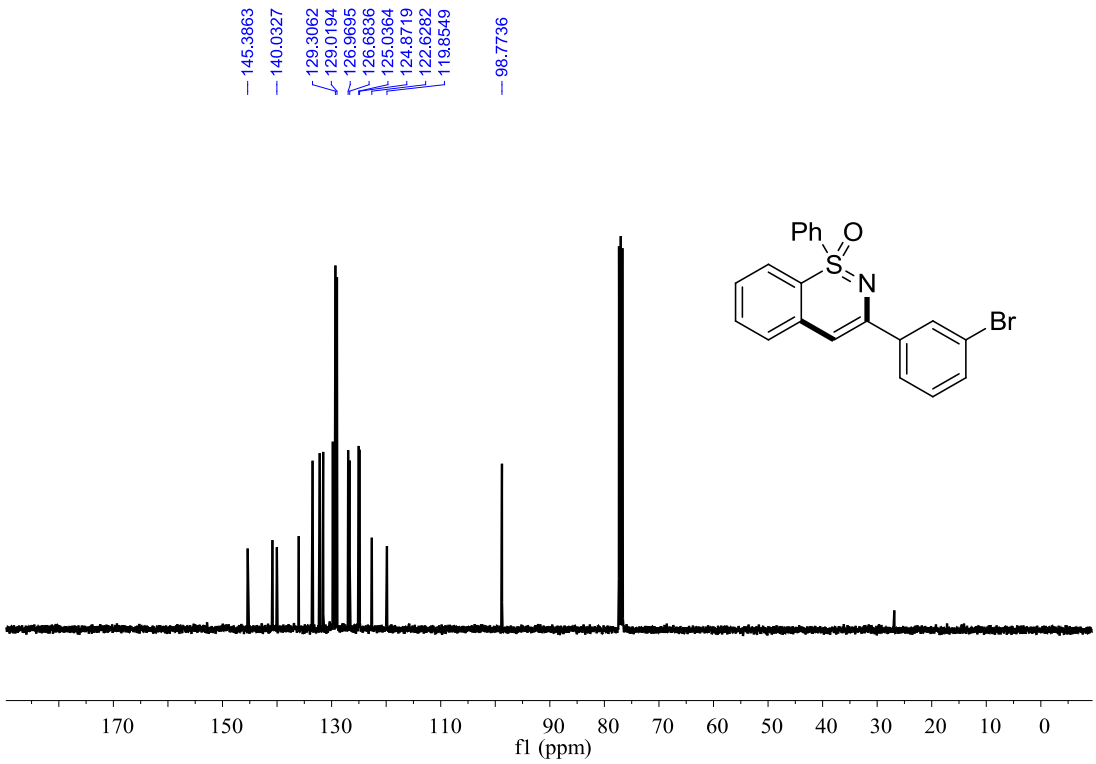
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3af.



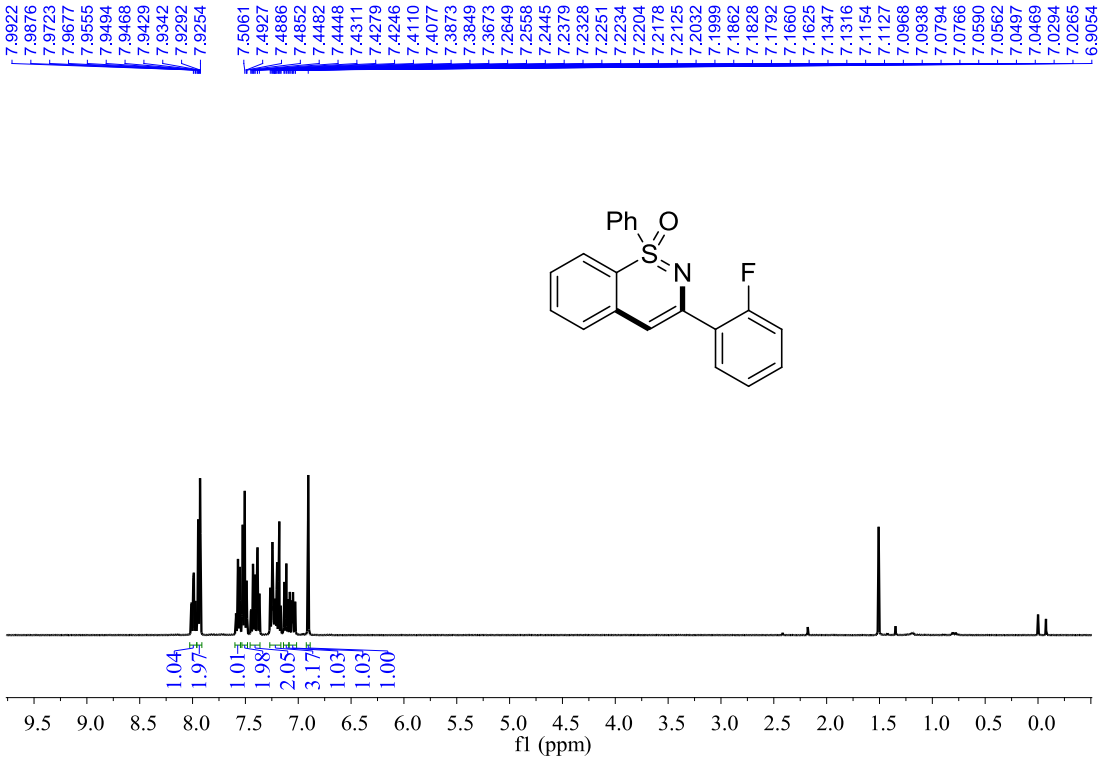
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3af.



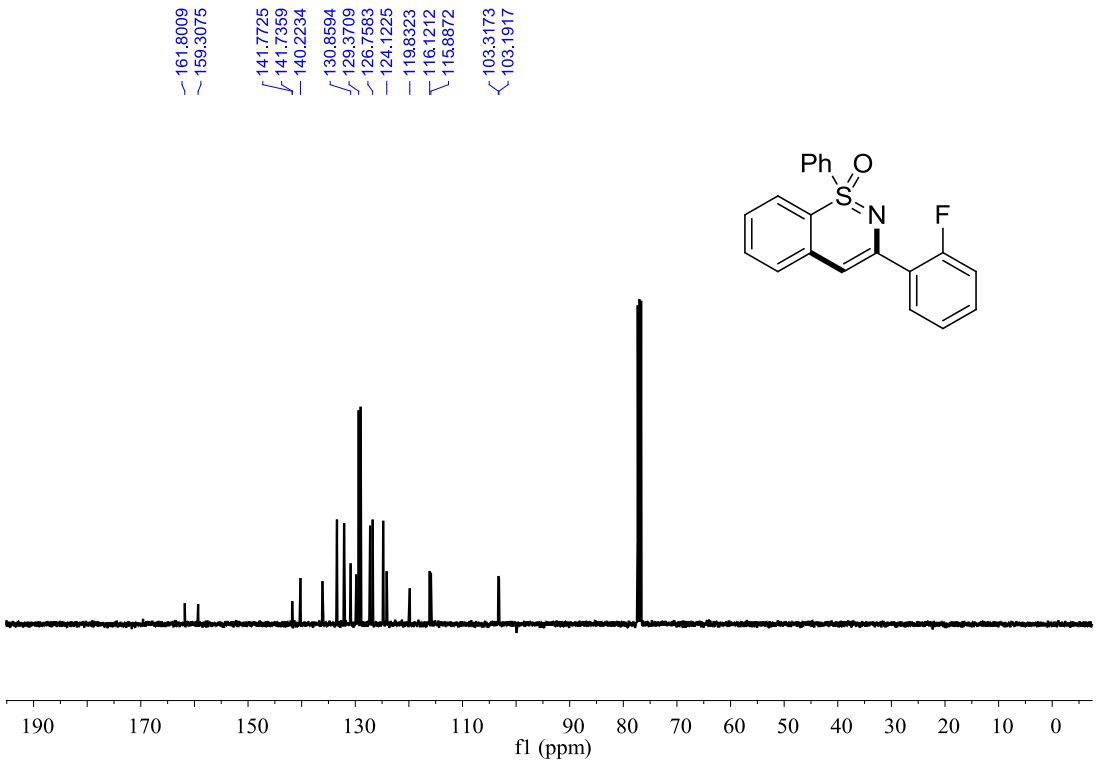
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3ag.



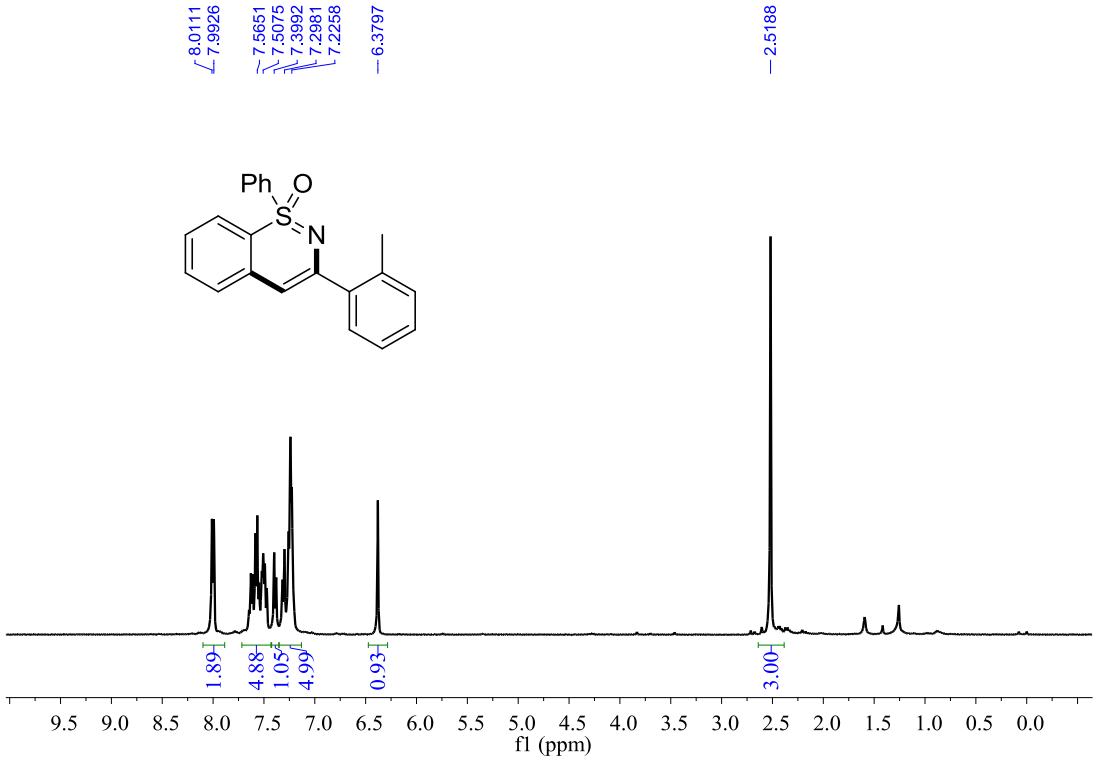
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3ag.



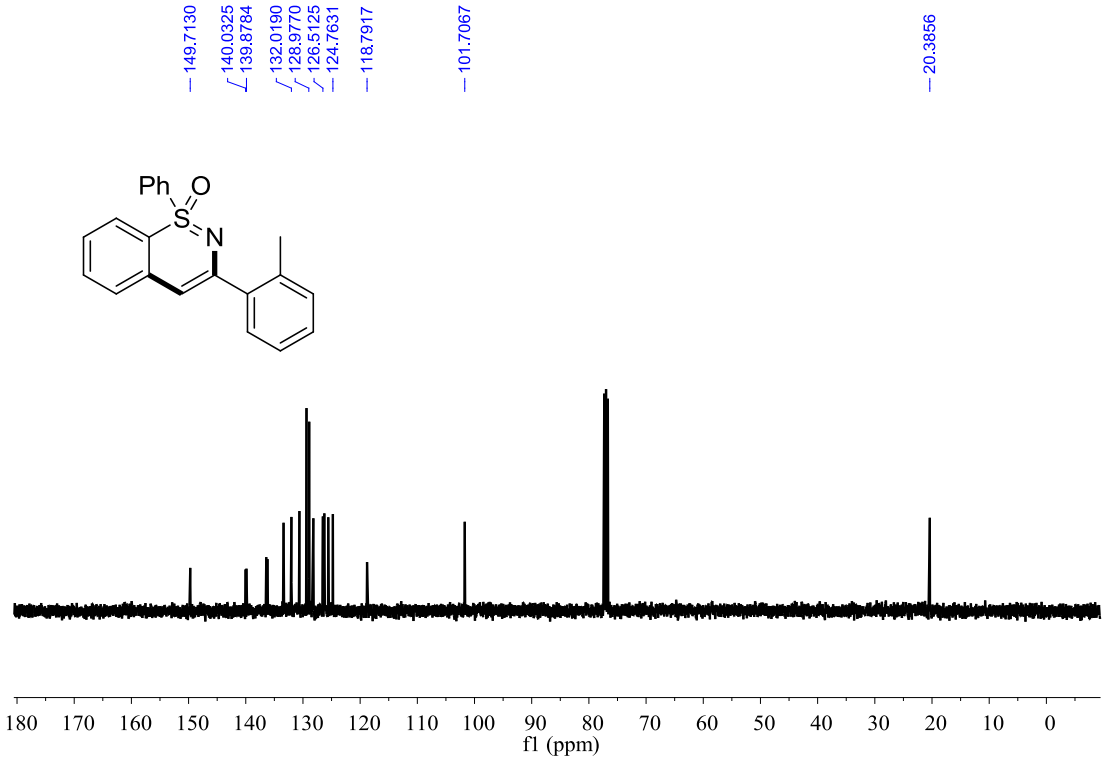
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3ah.



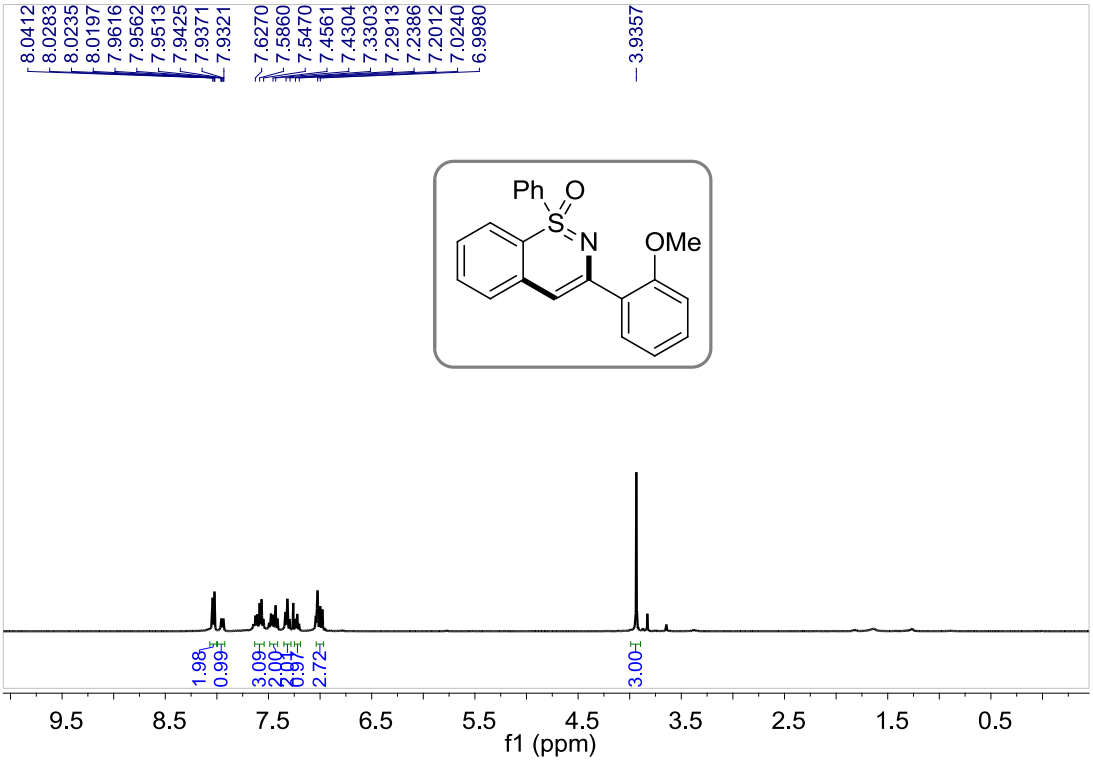
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3ah.



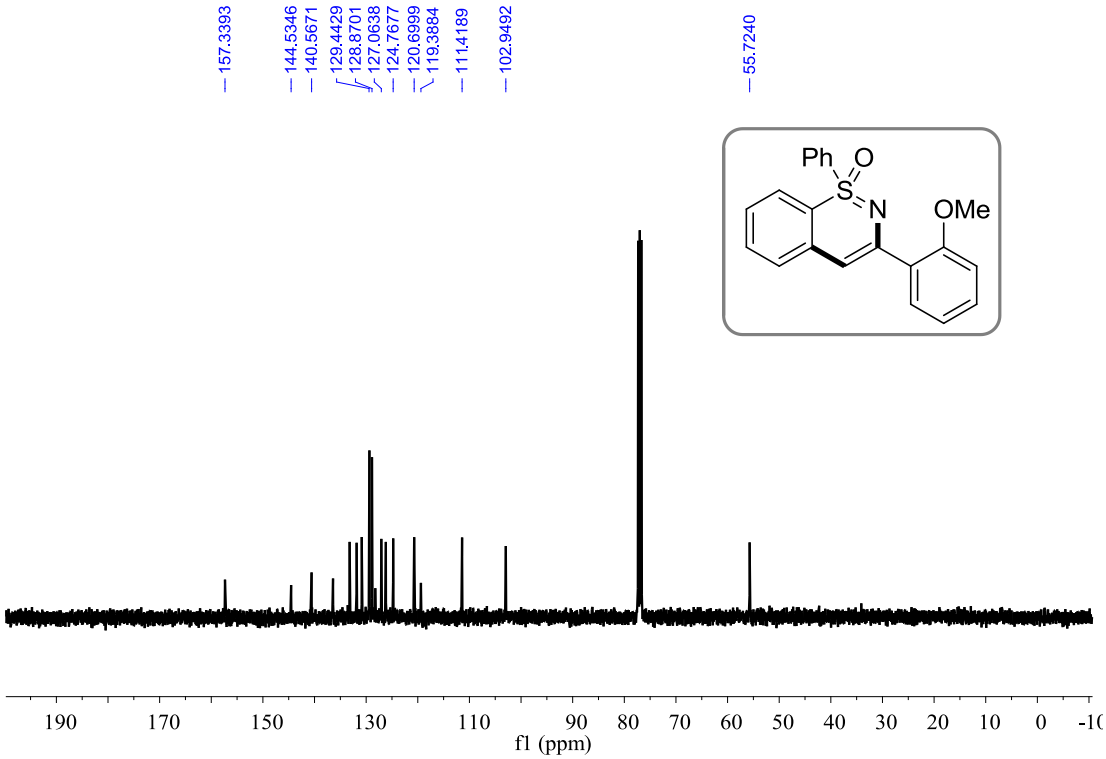
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3ai.



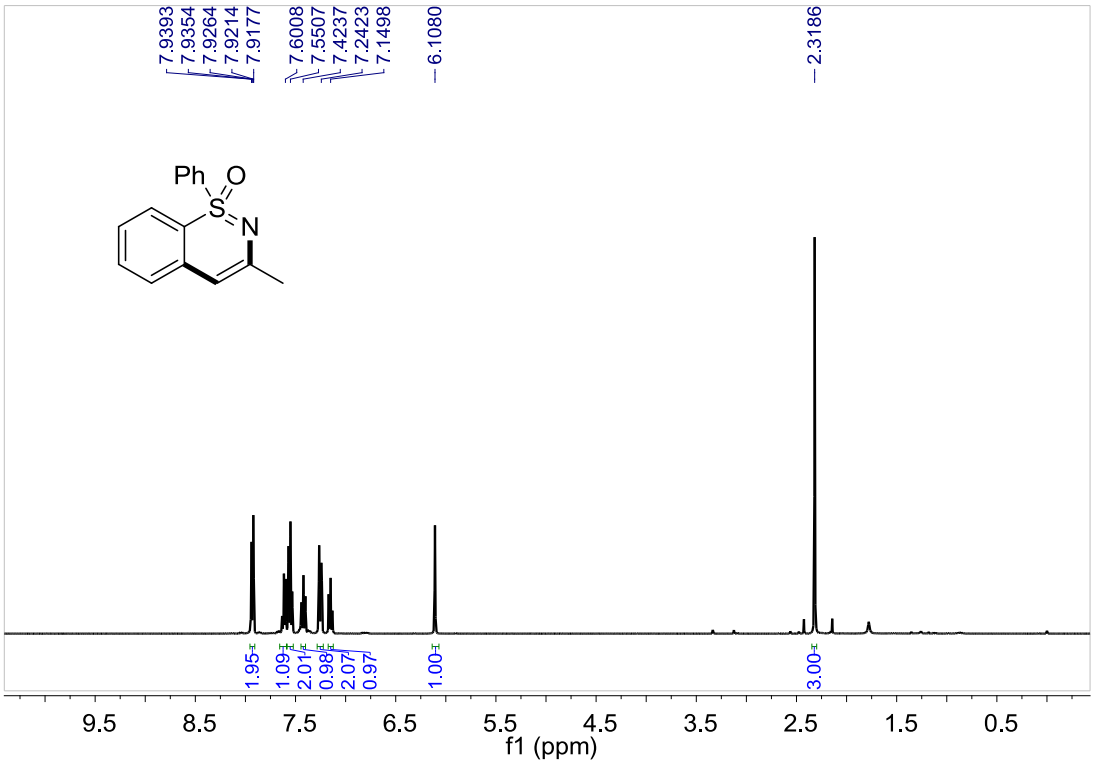
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3ai.



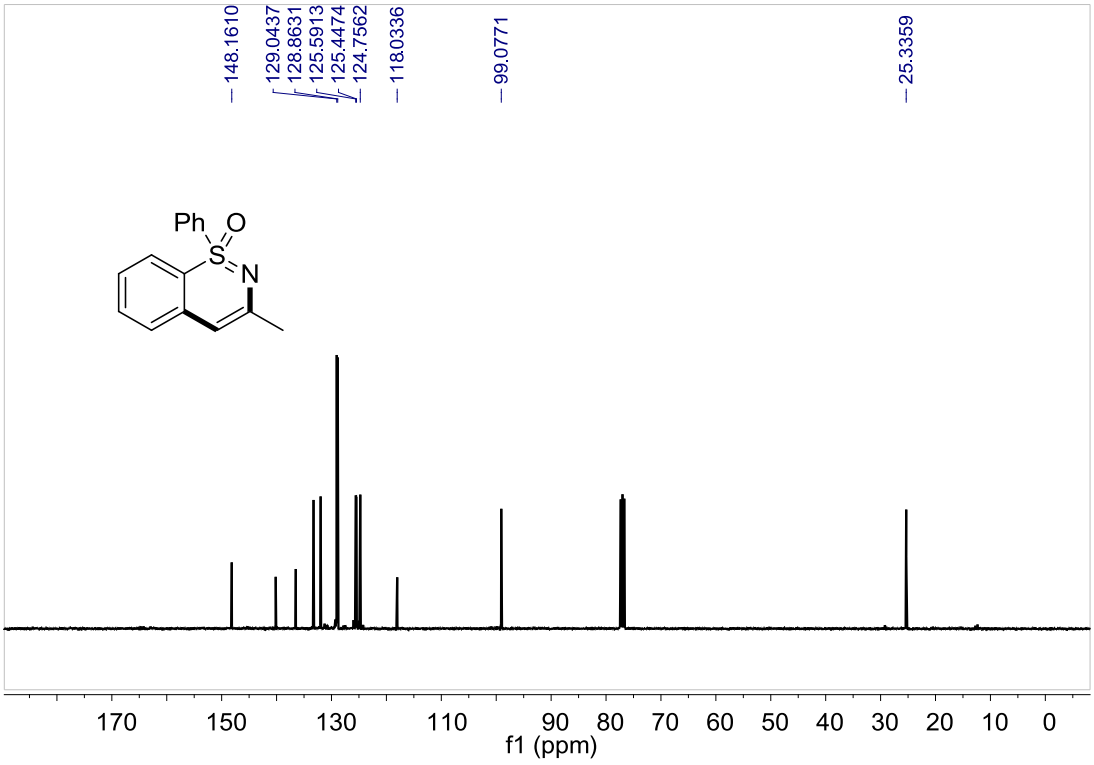
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3aj.



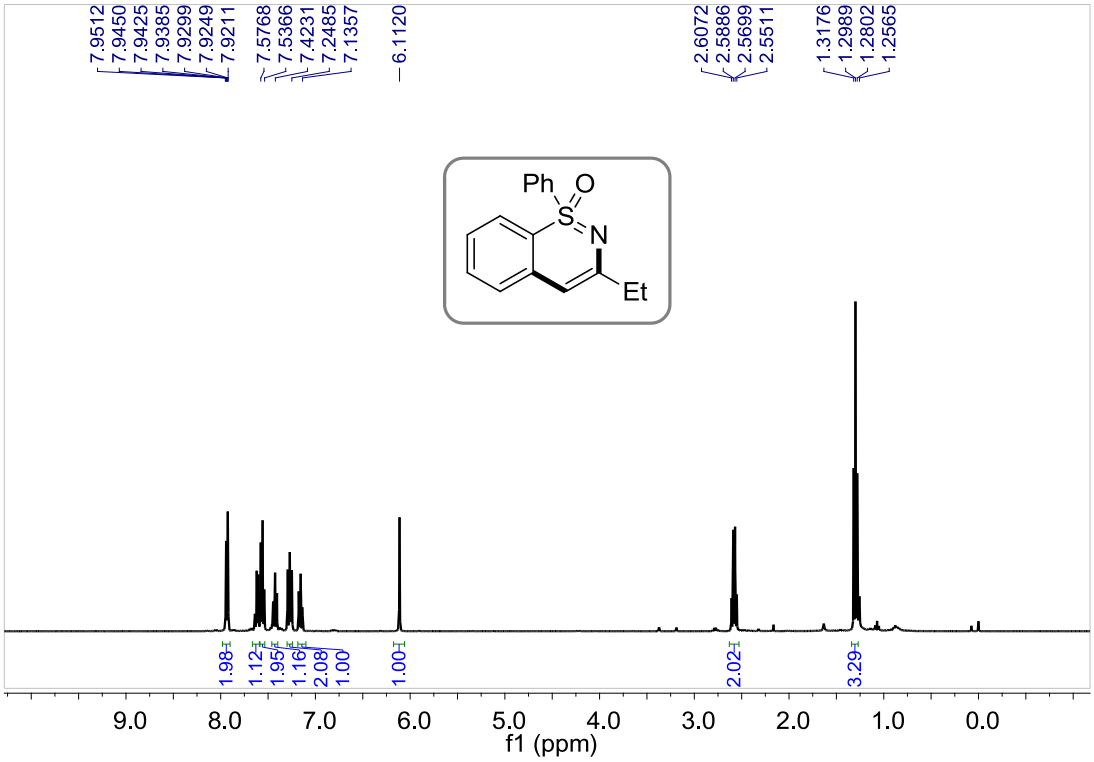
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3aj.



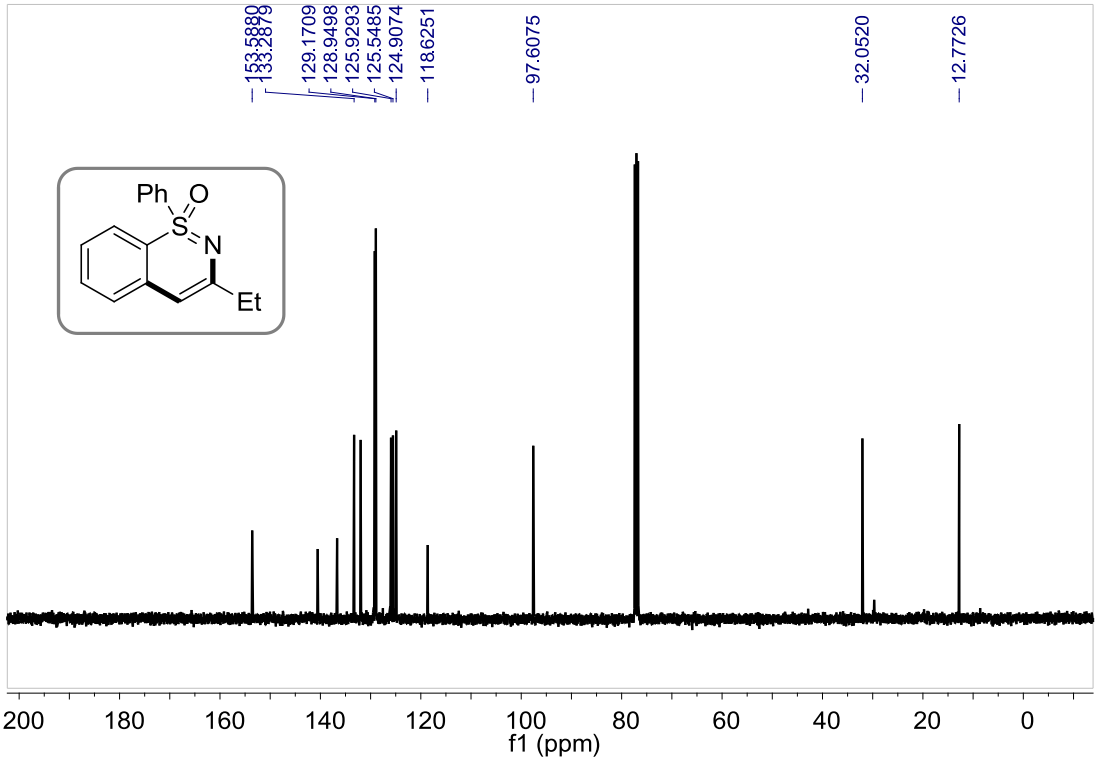
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3ak.



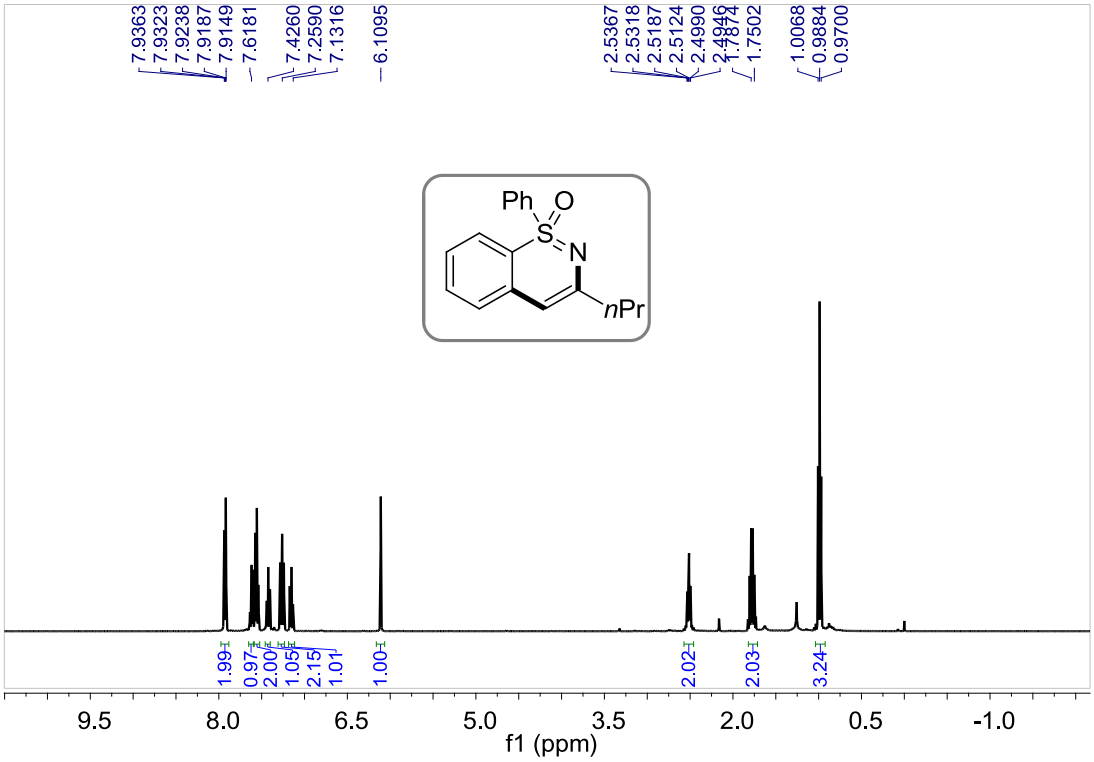
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3ak.



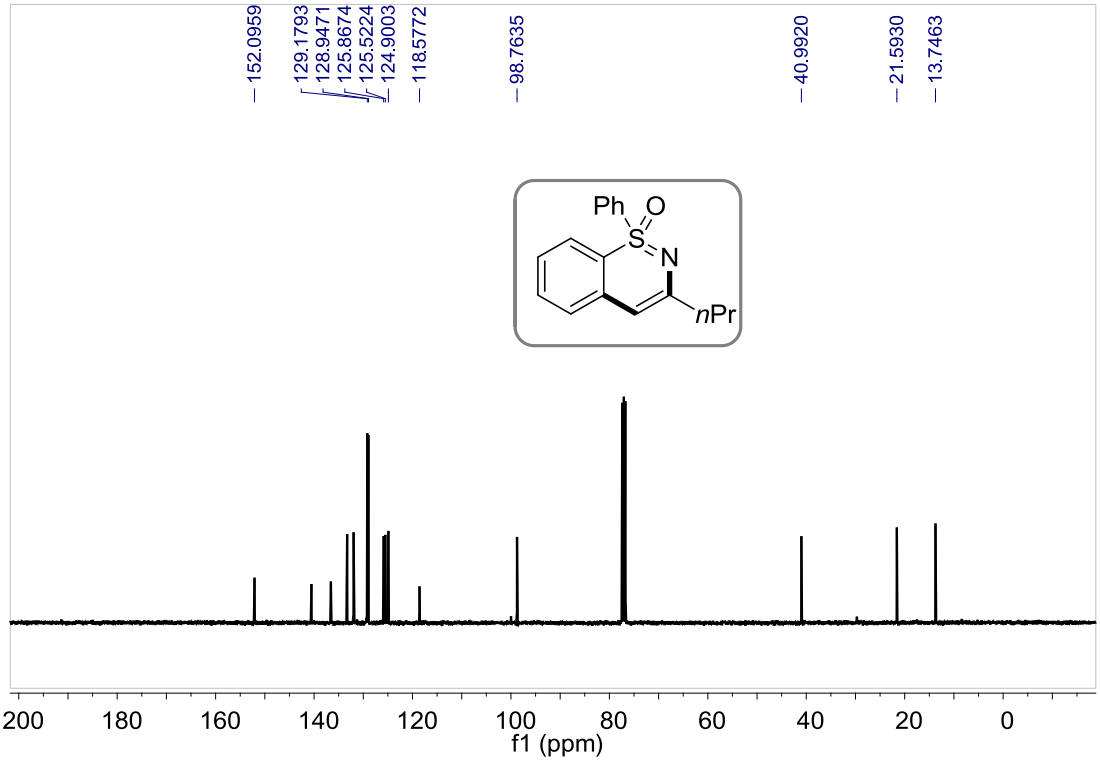
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3al.



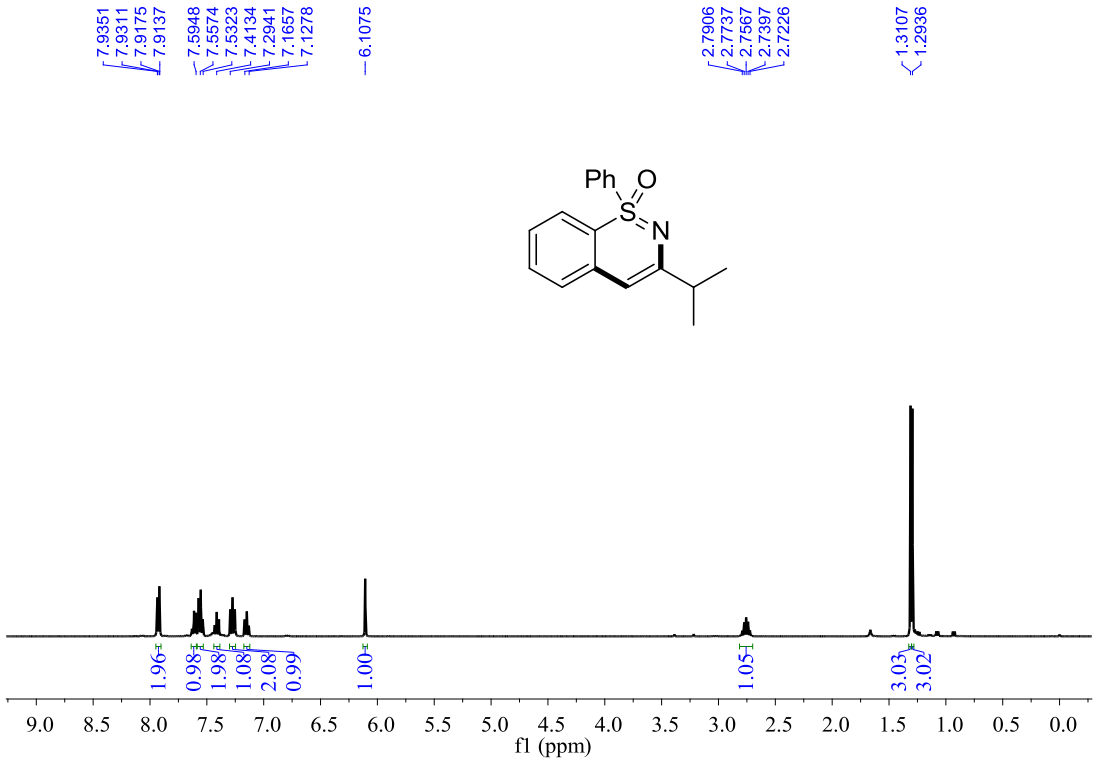
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3al.



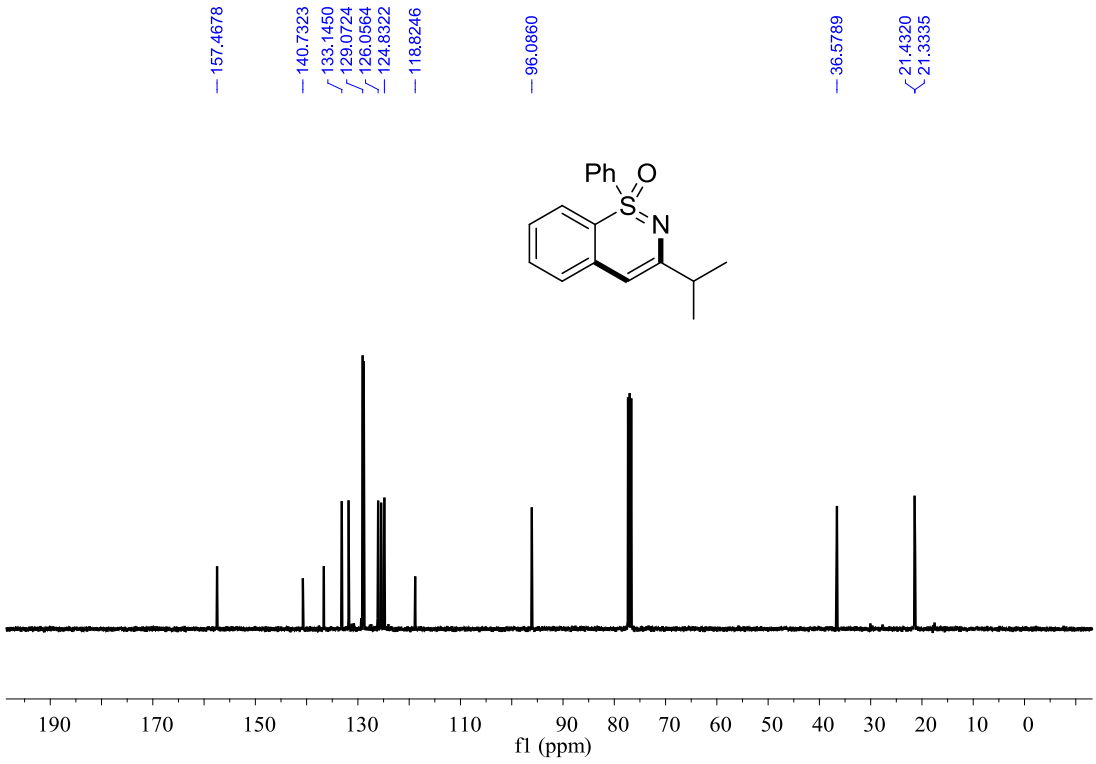
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3am.



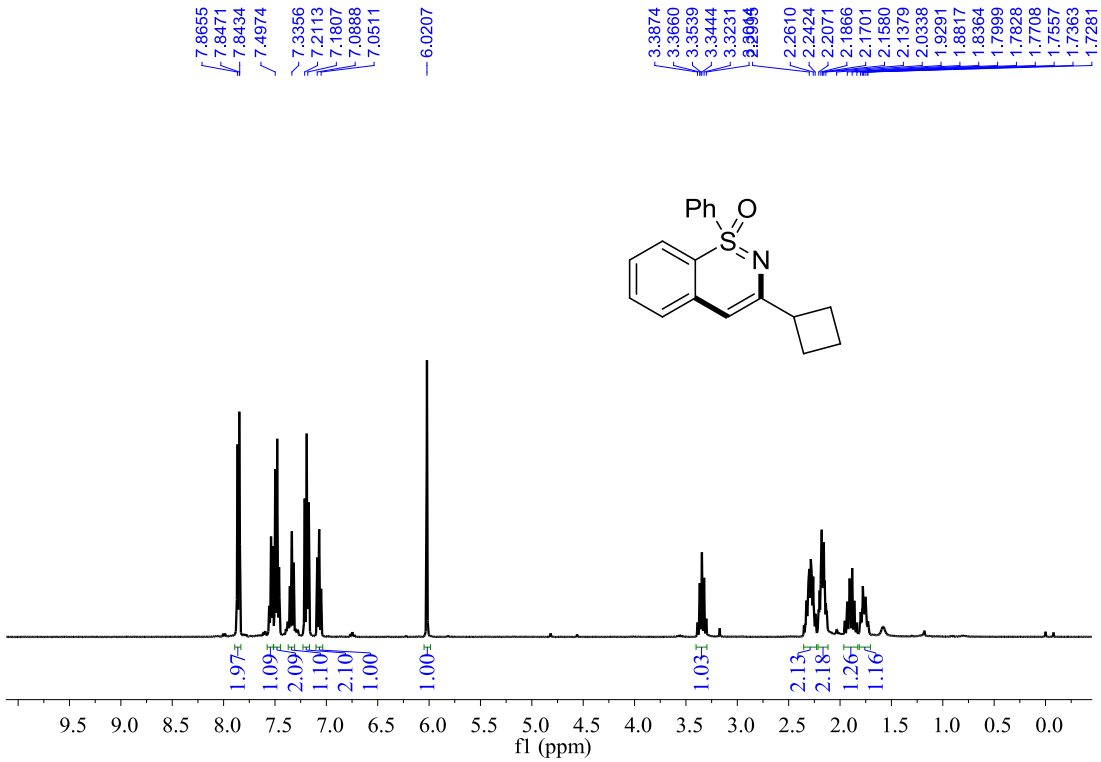
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3am.



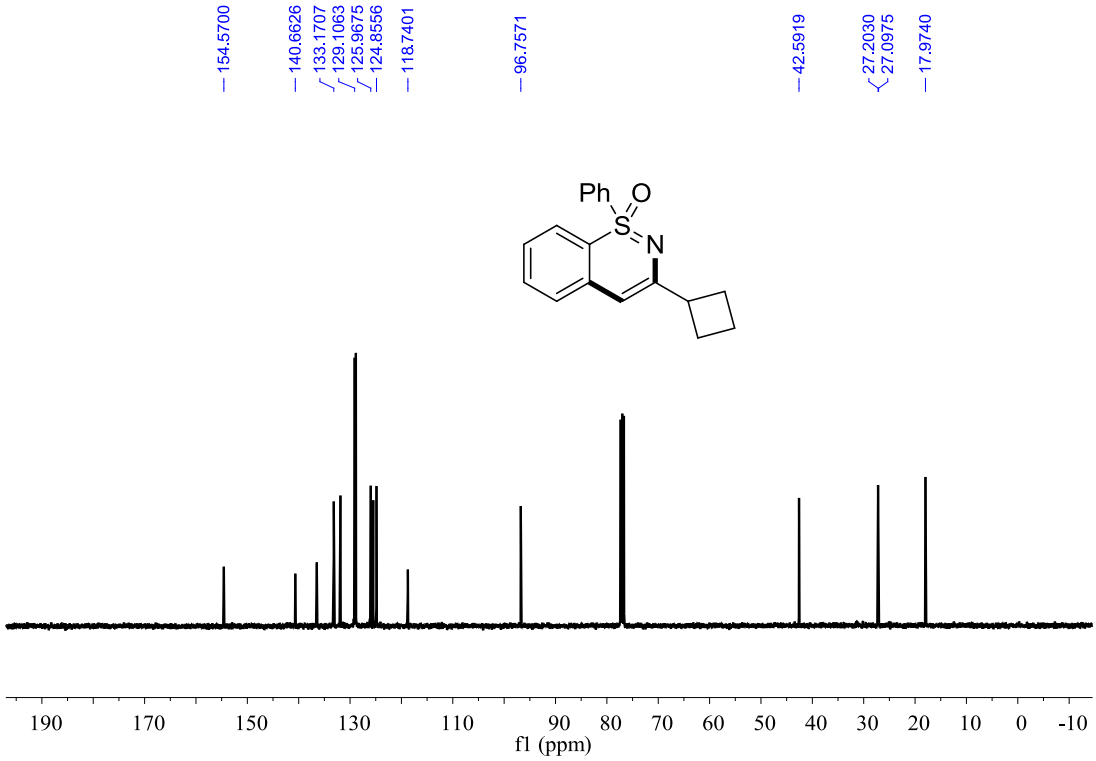
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3an.



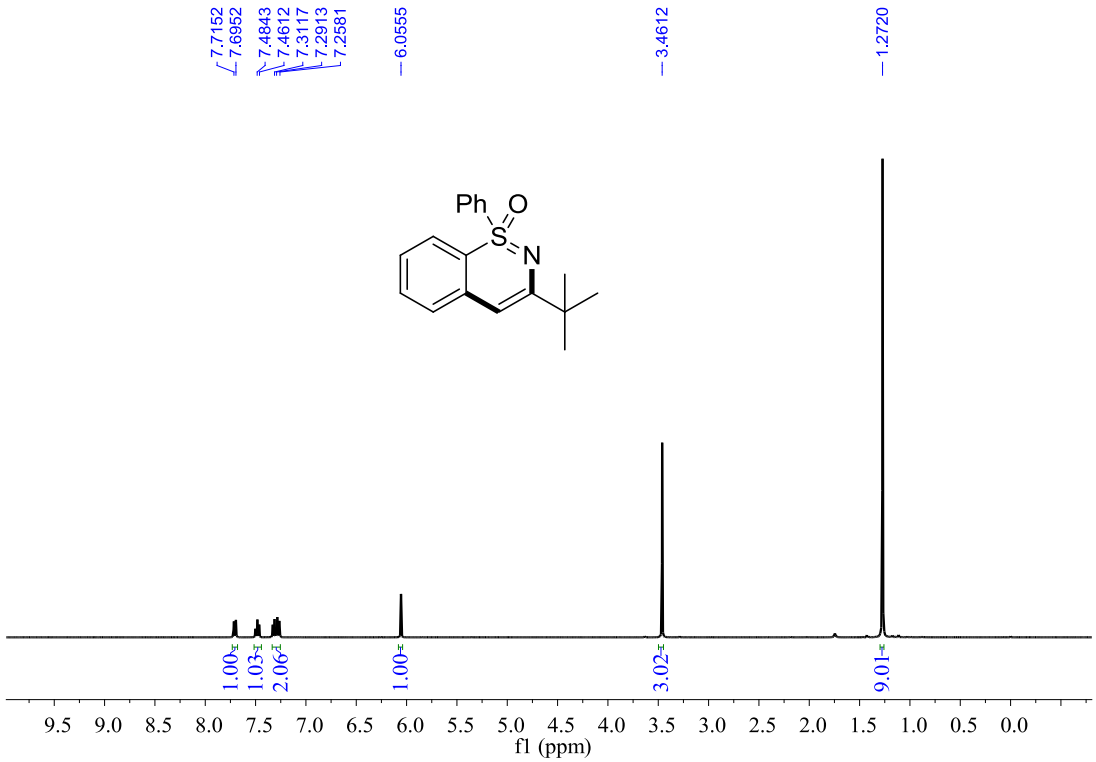
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3an.



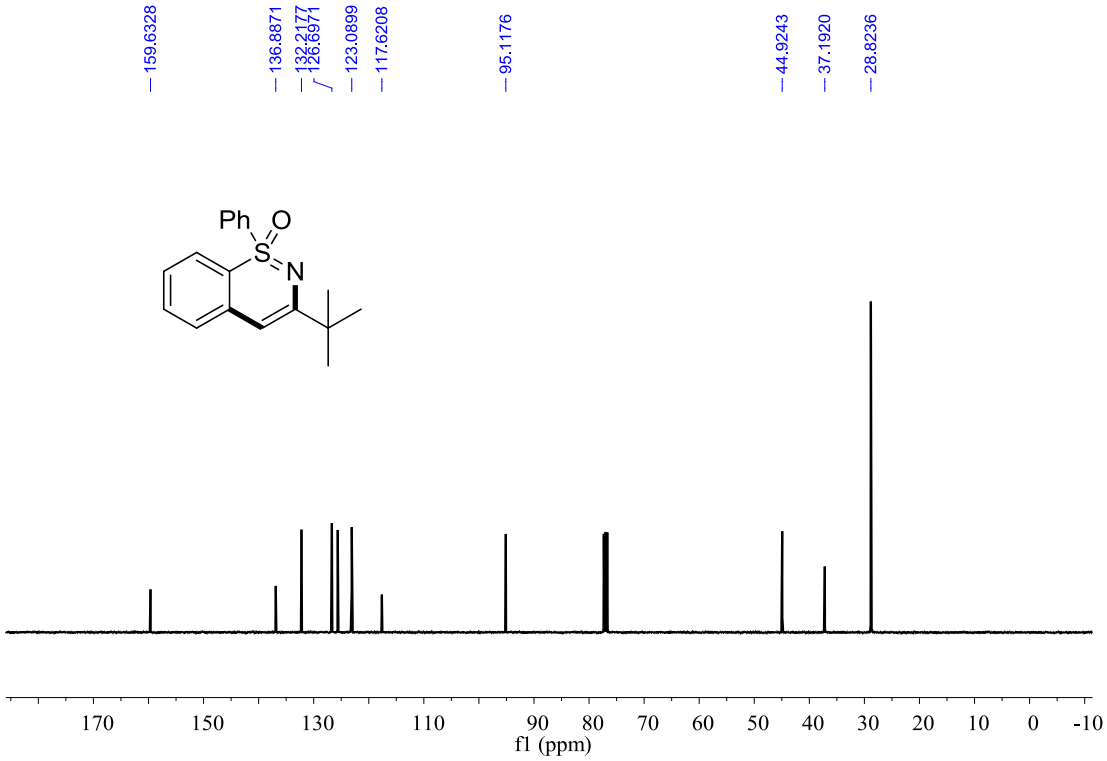
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3ao.



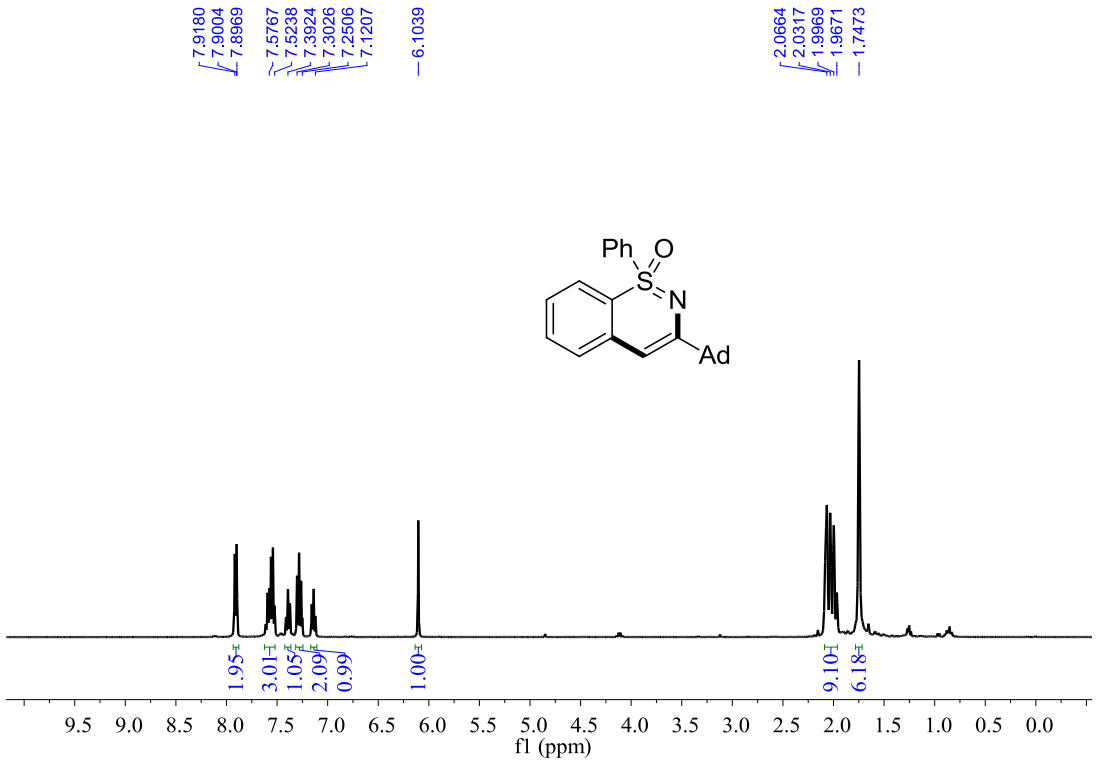
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3ao.



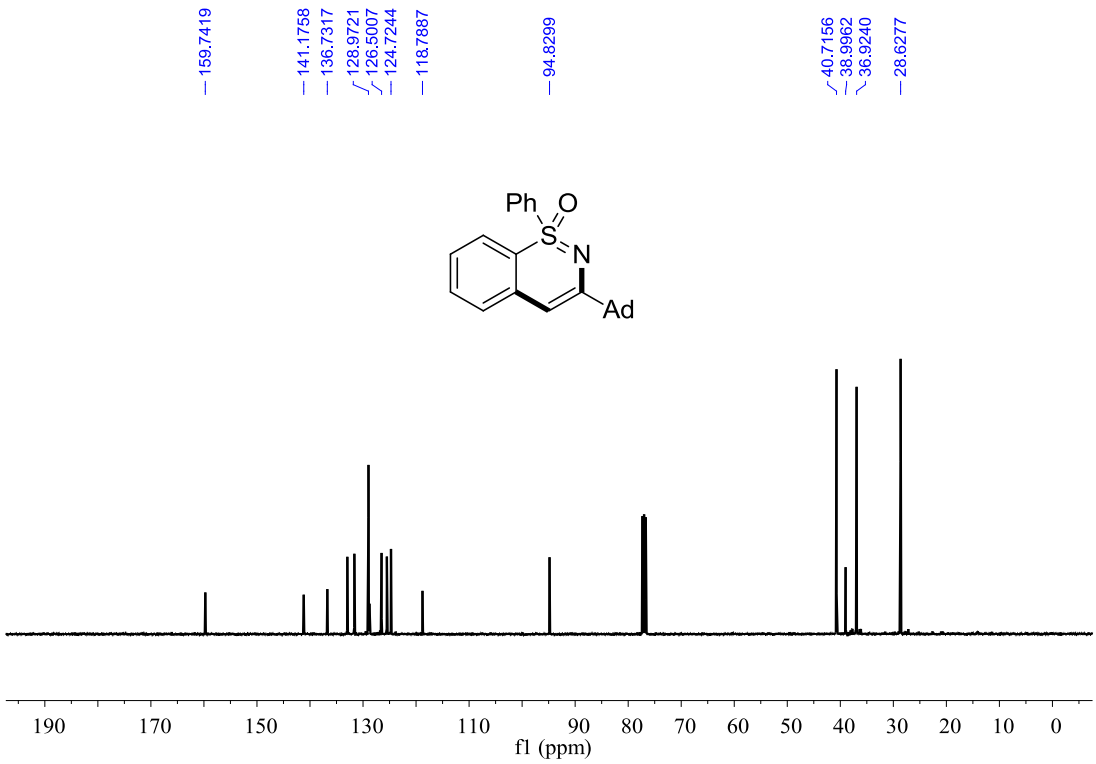
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3ap.



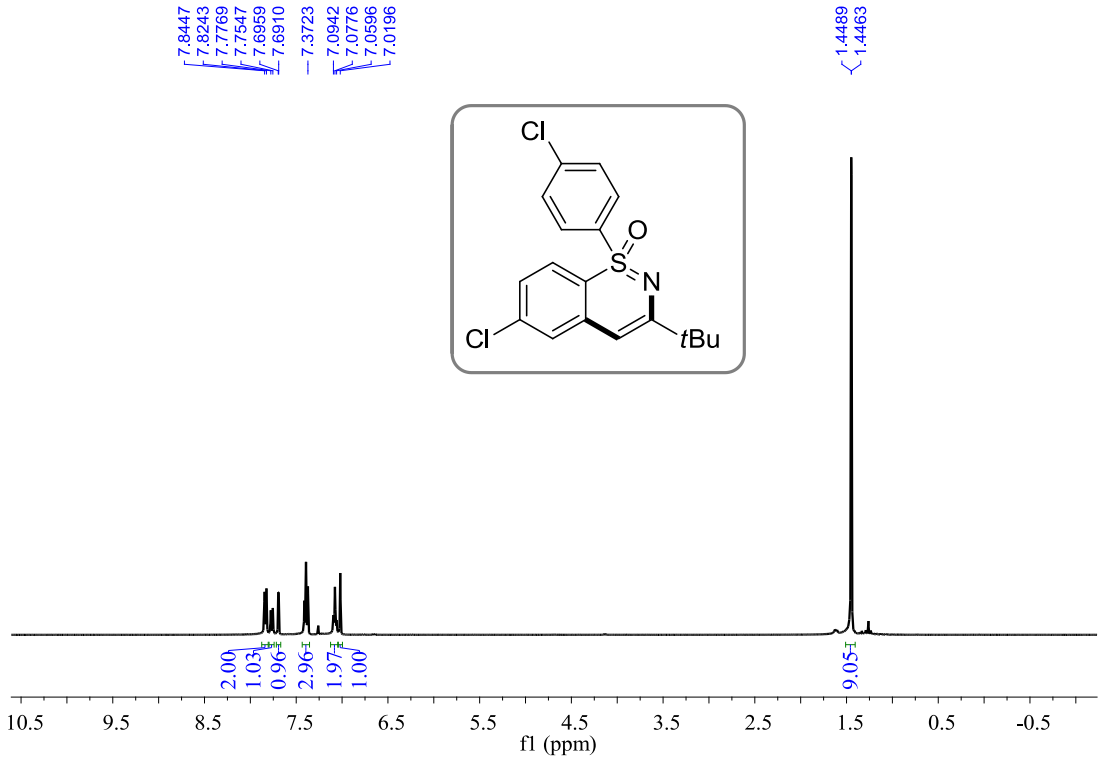
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3ap.



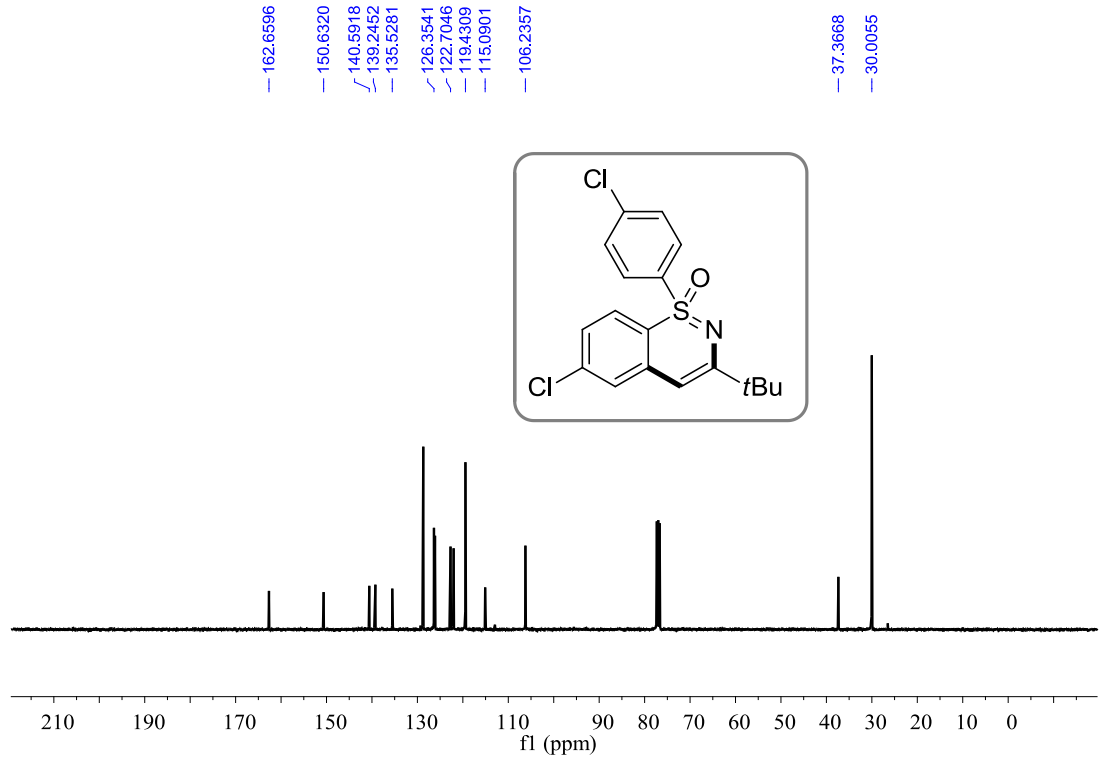
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3aq.



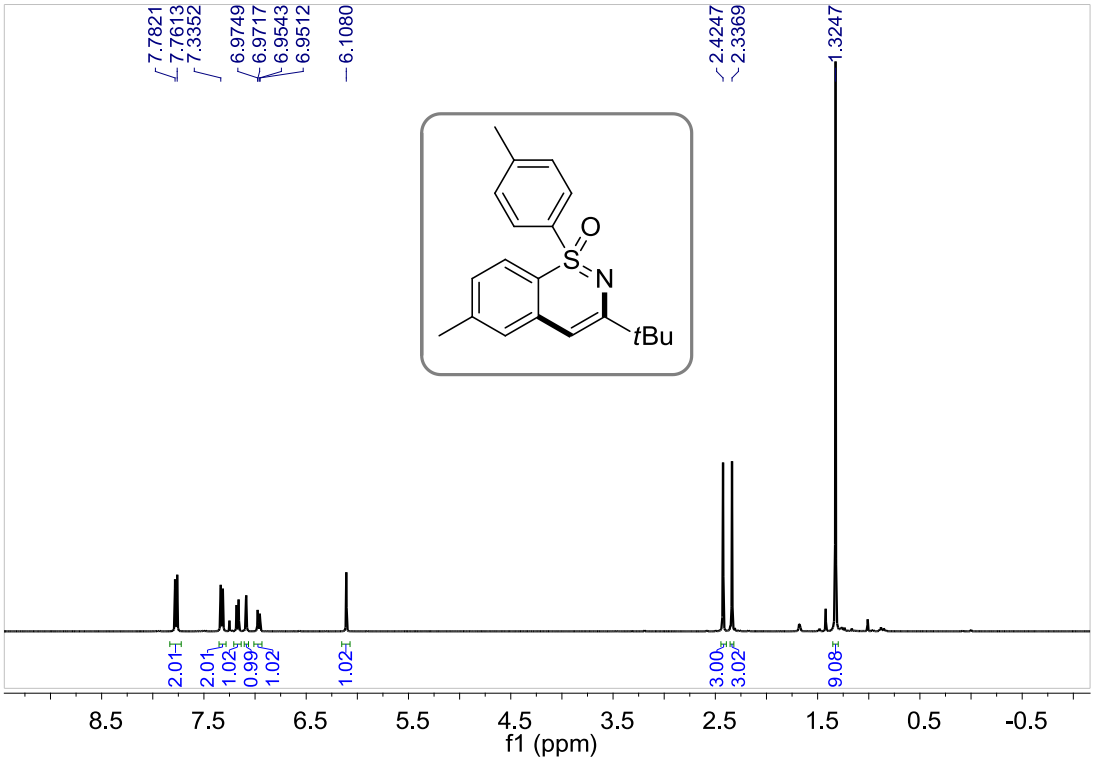
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3aq.



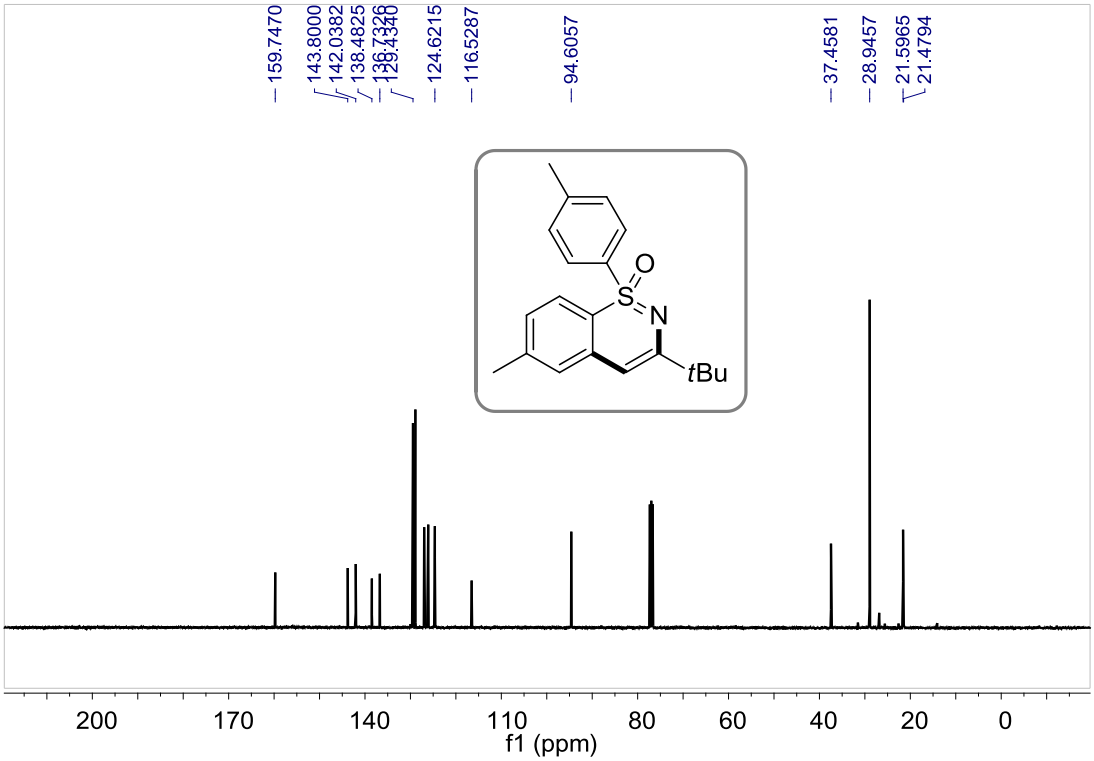
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3bp.



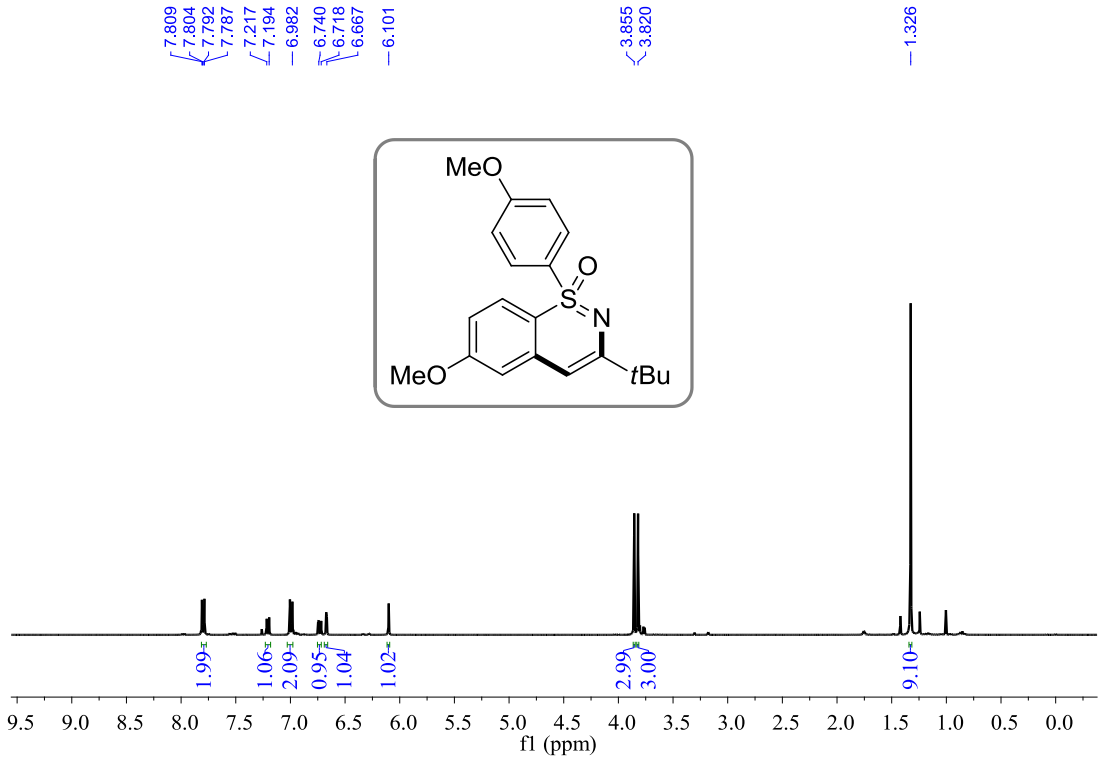
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3bp.



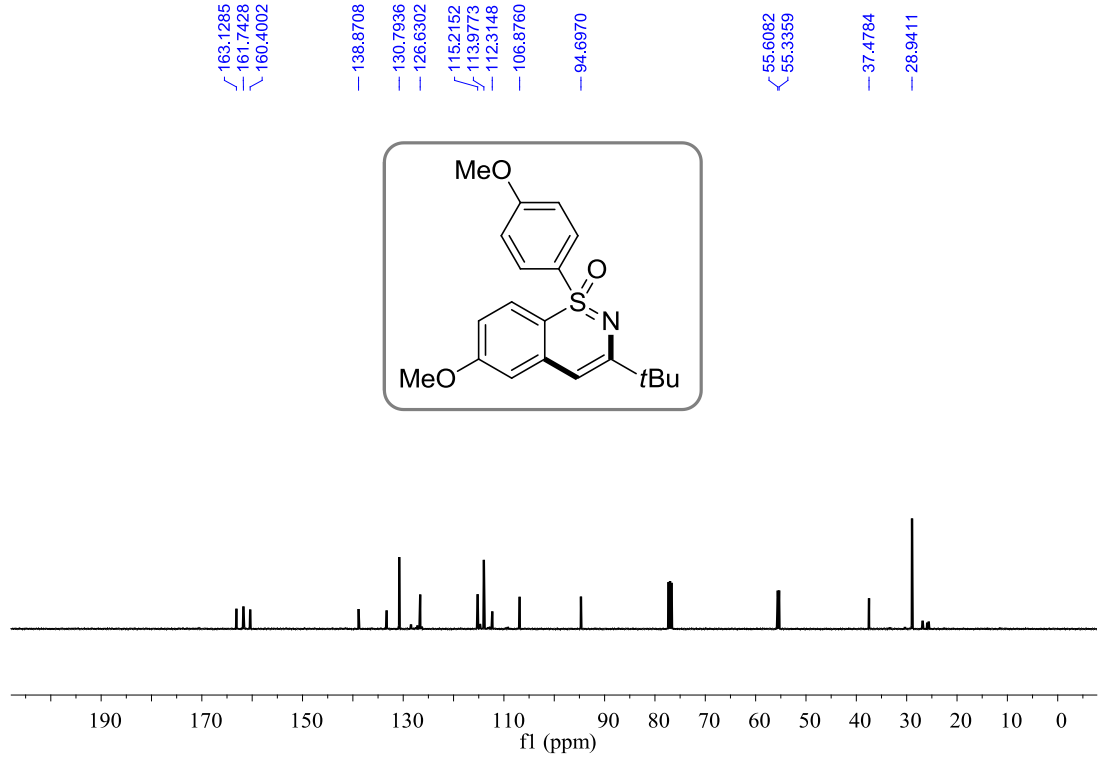
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3cp.



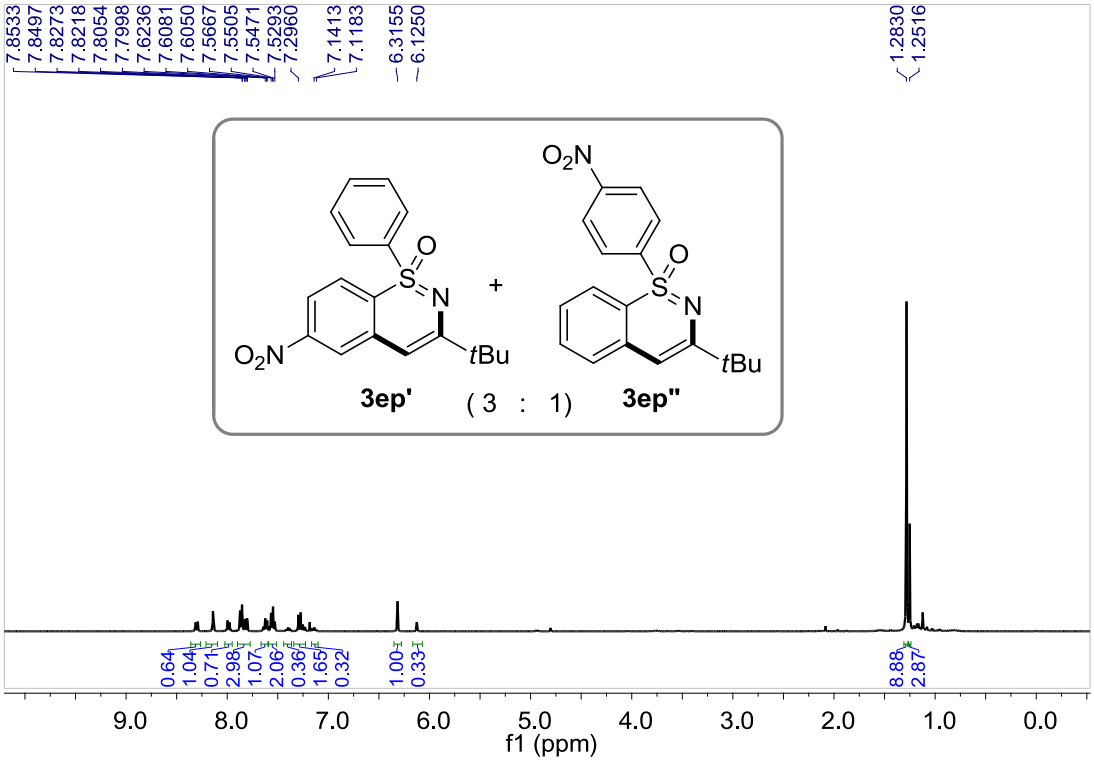
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3cp.



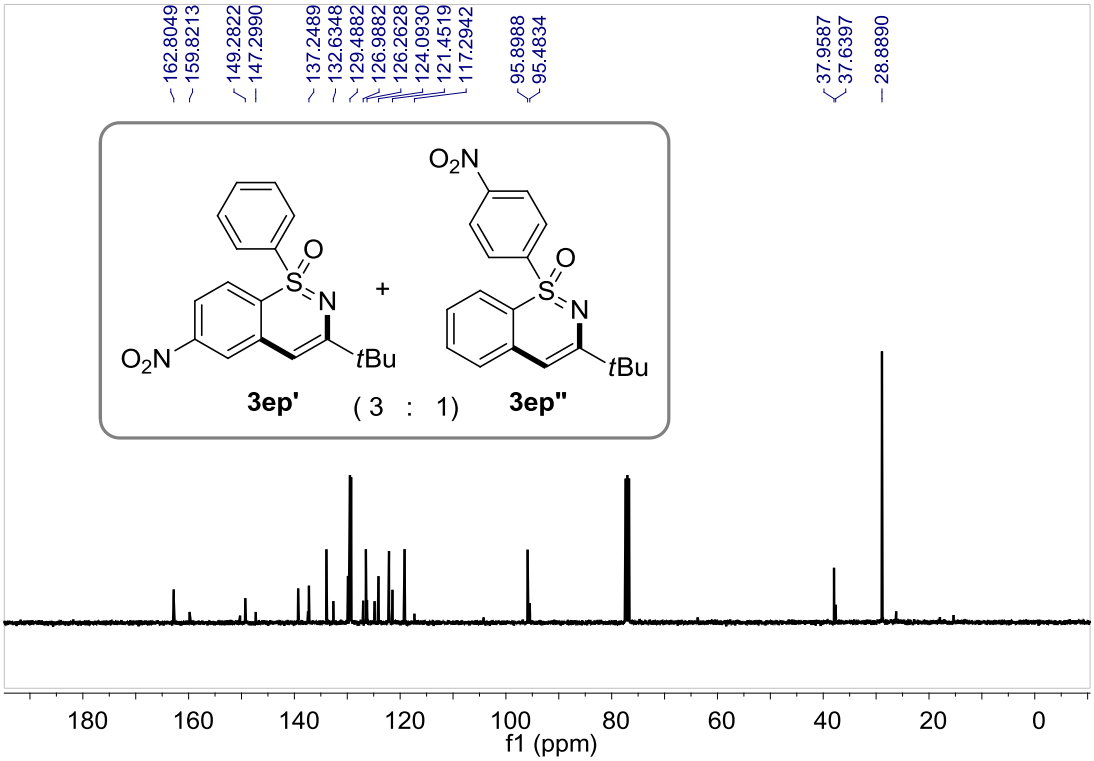
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3dp.



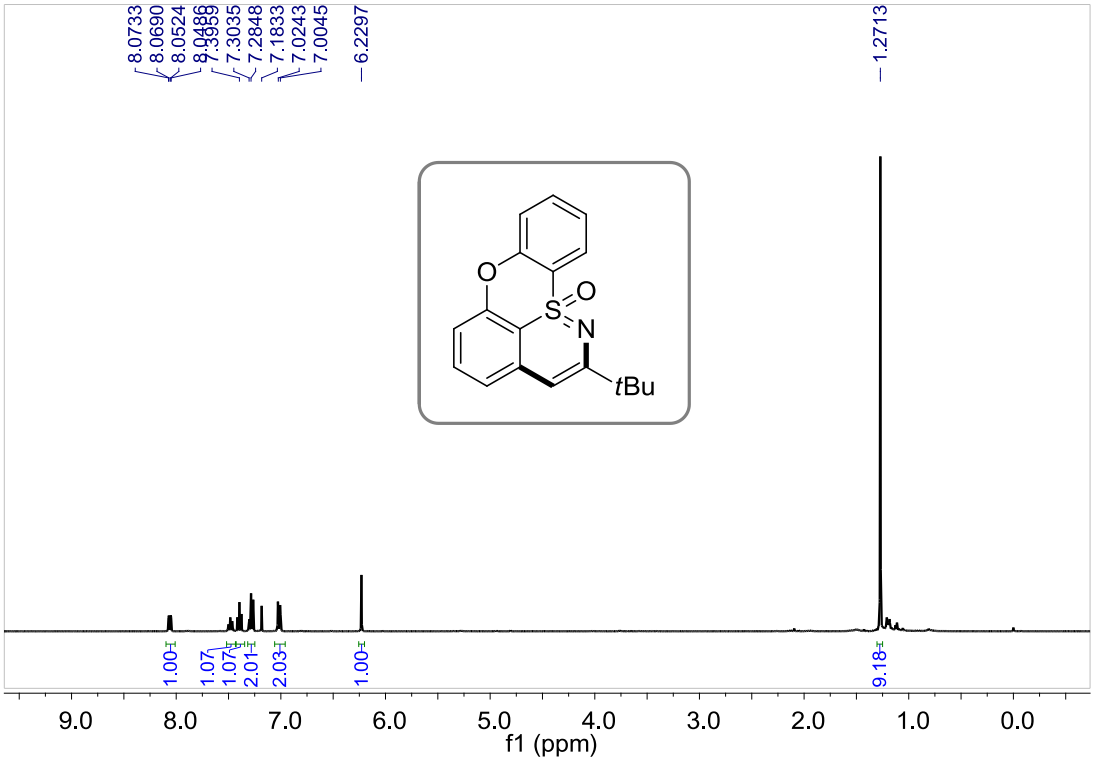
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3dp.



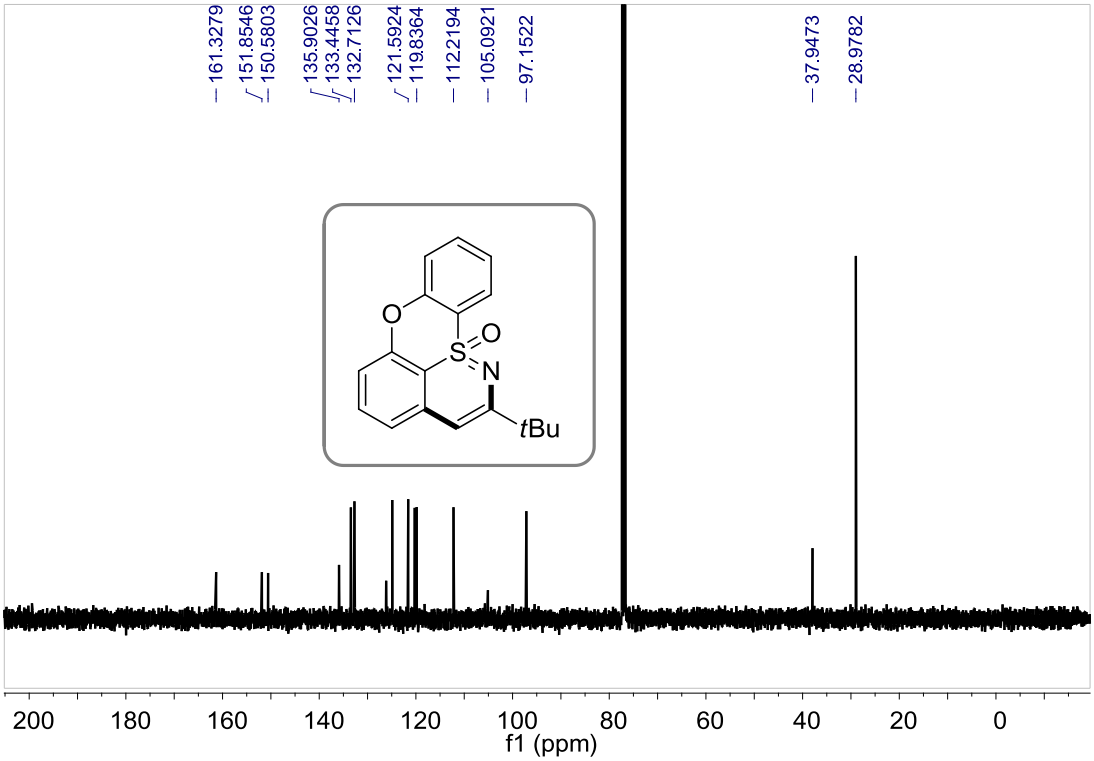
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3ep.



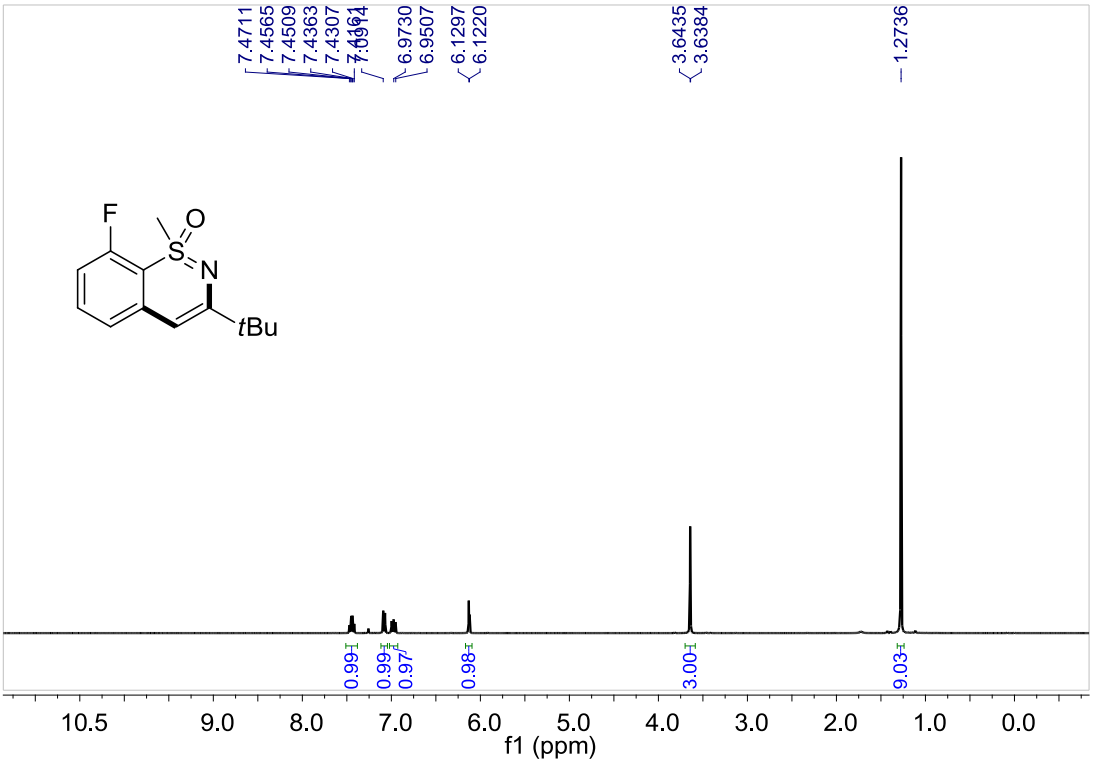
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3ep.



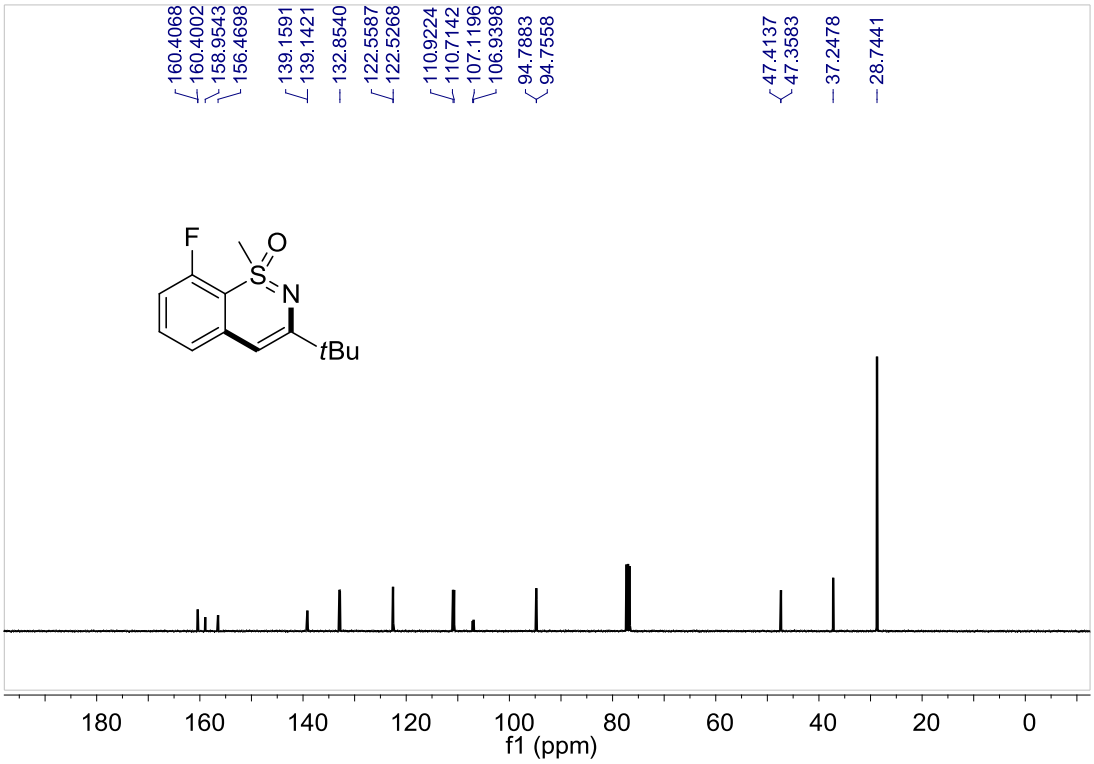
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3fp.



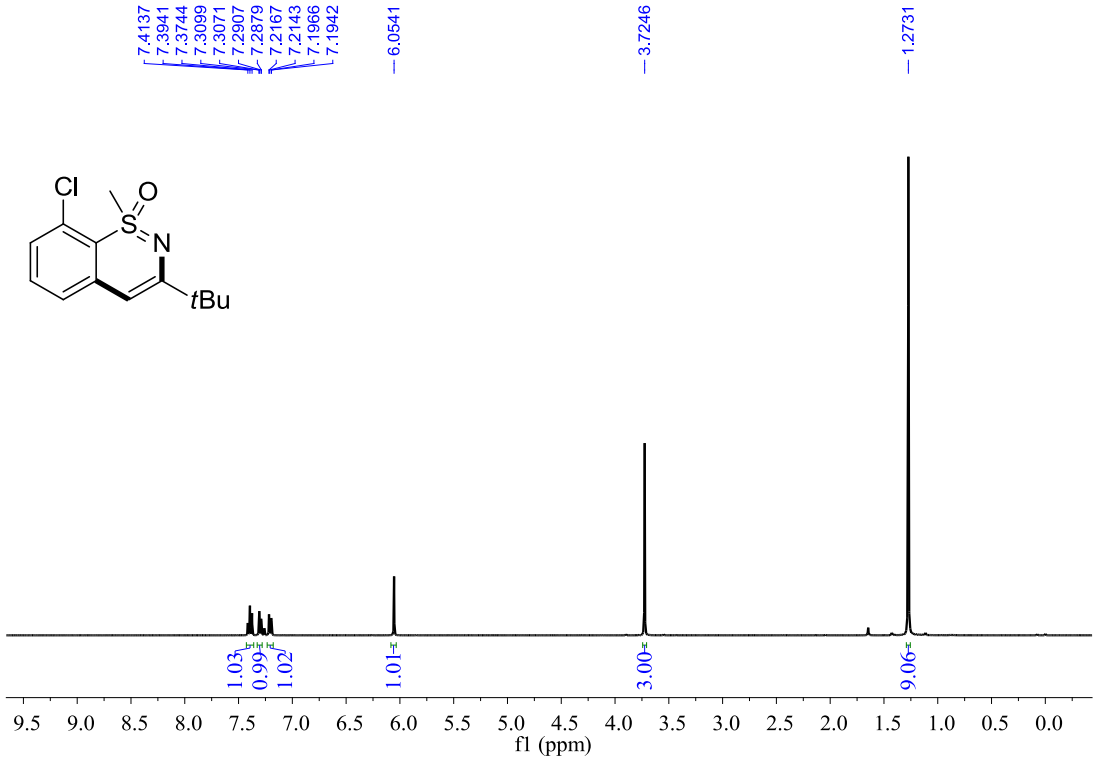
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3fp.



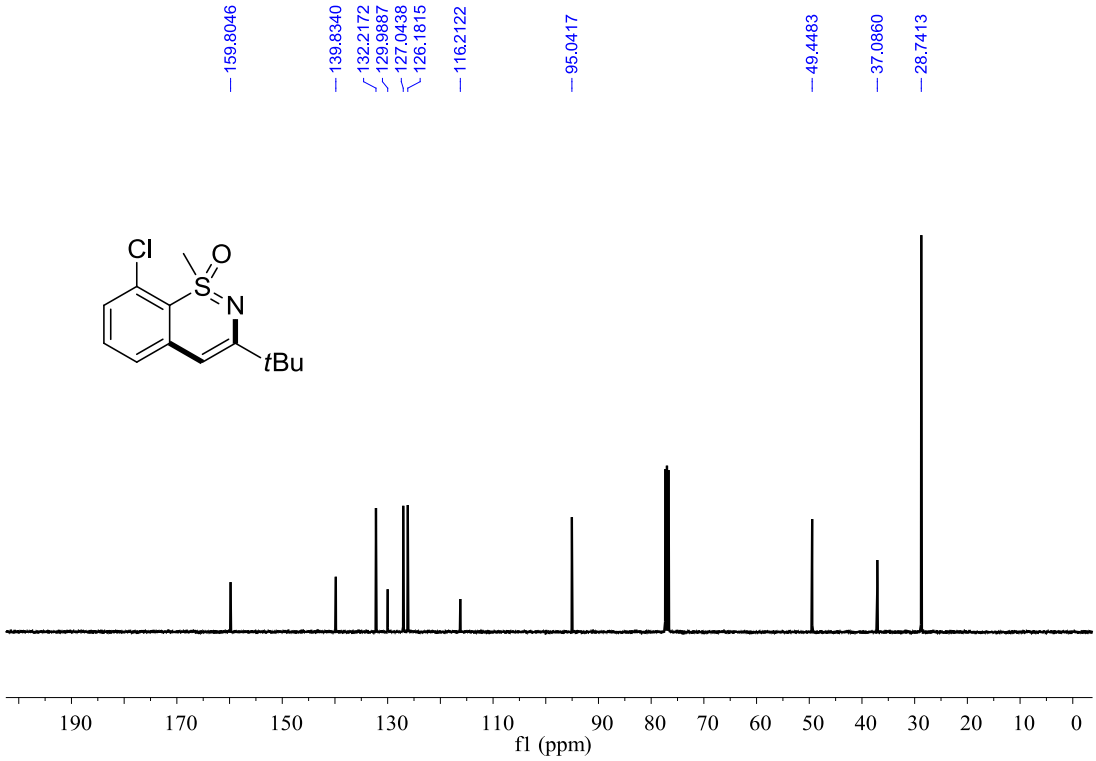
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3gp.



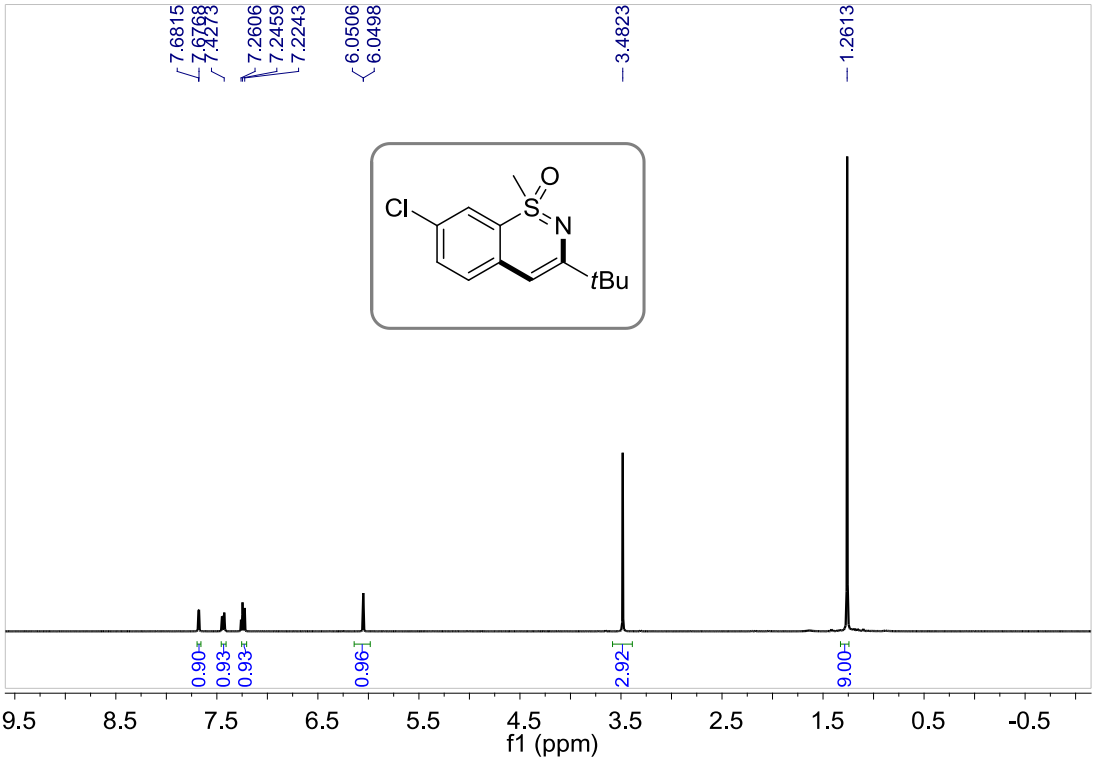
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3gp.



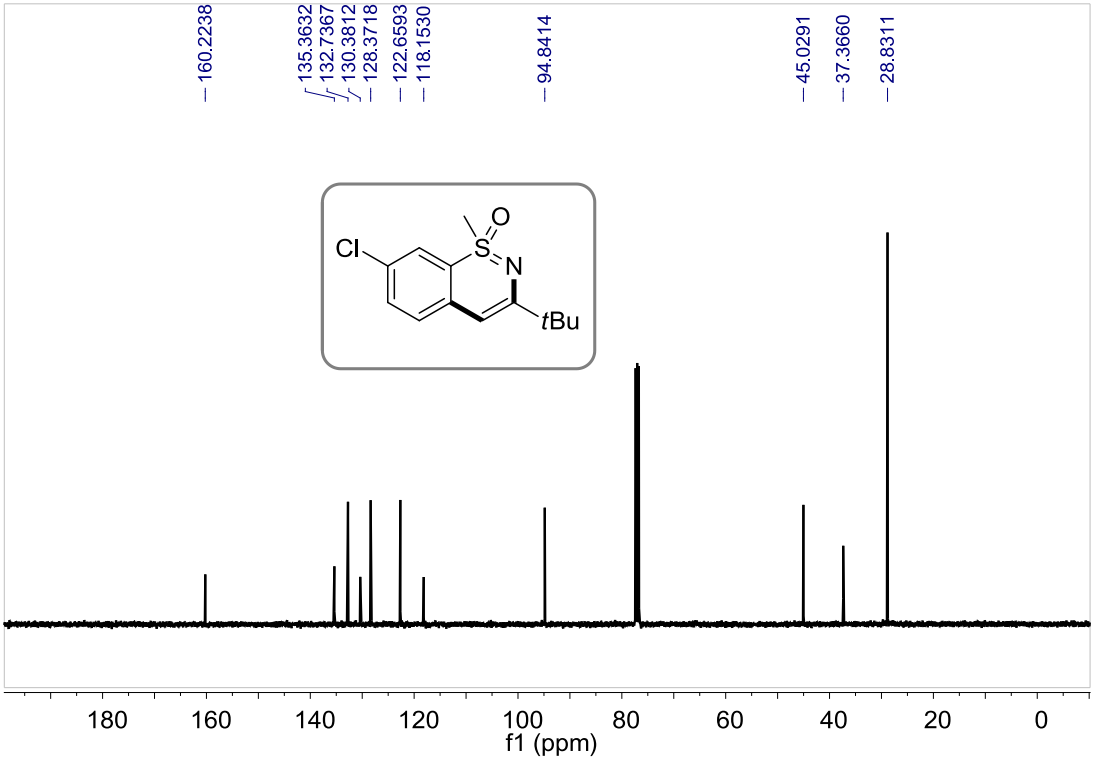
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3hp.



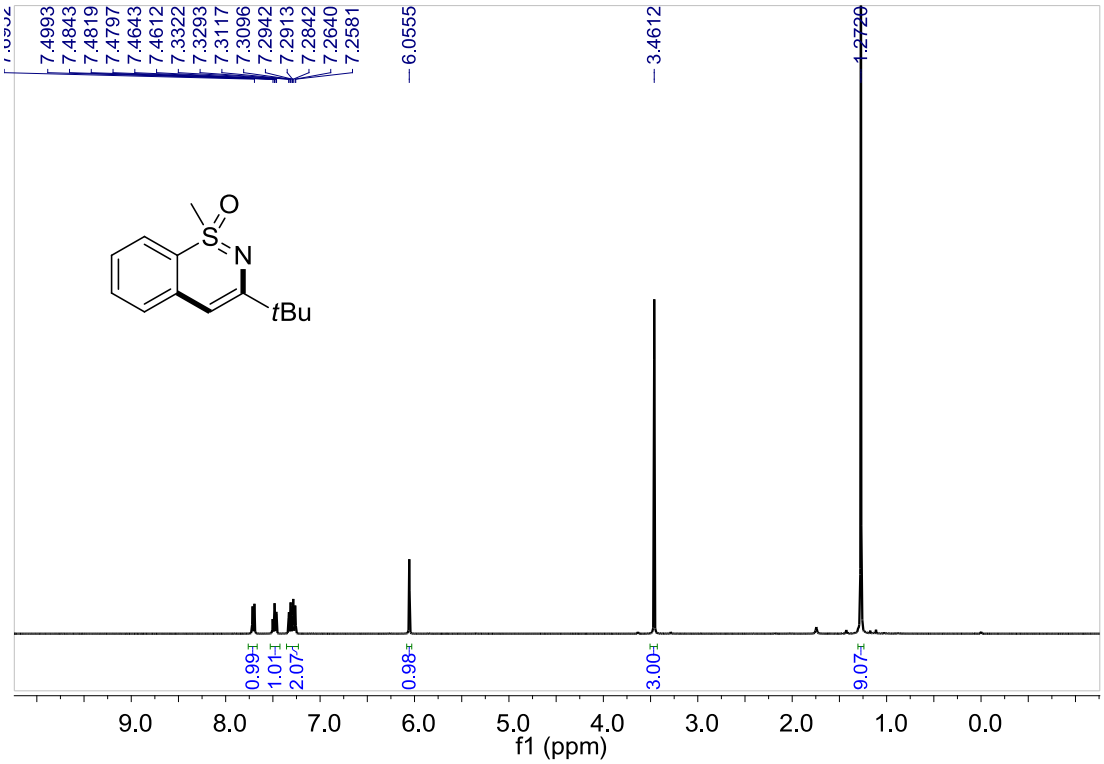
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3hp.



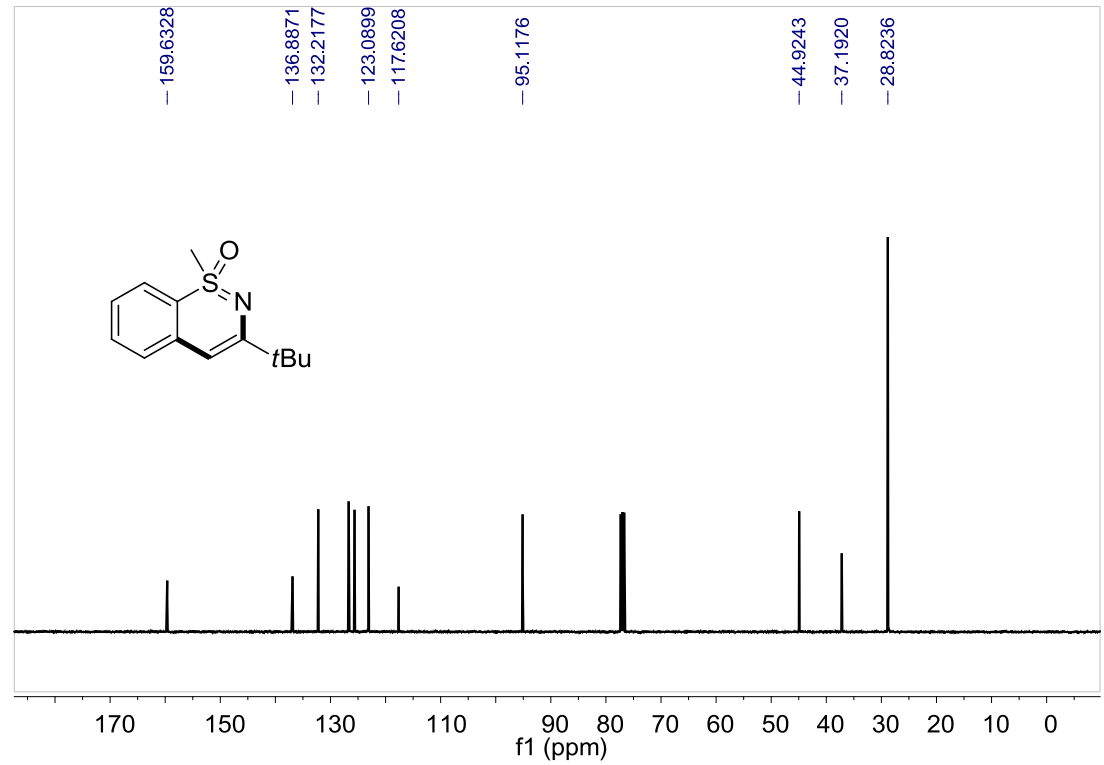
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3ip.



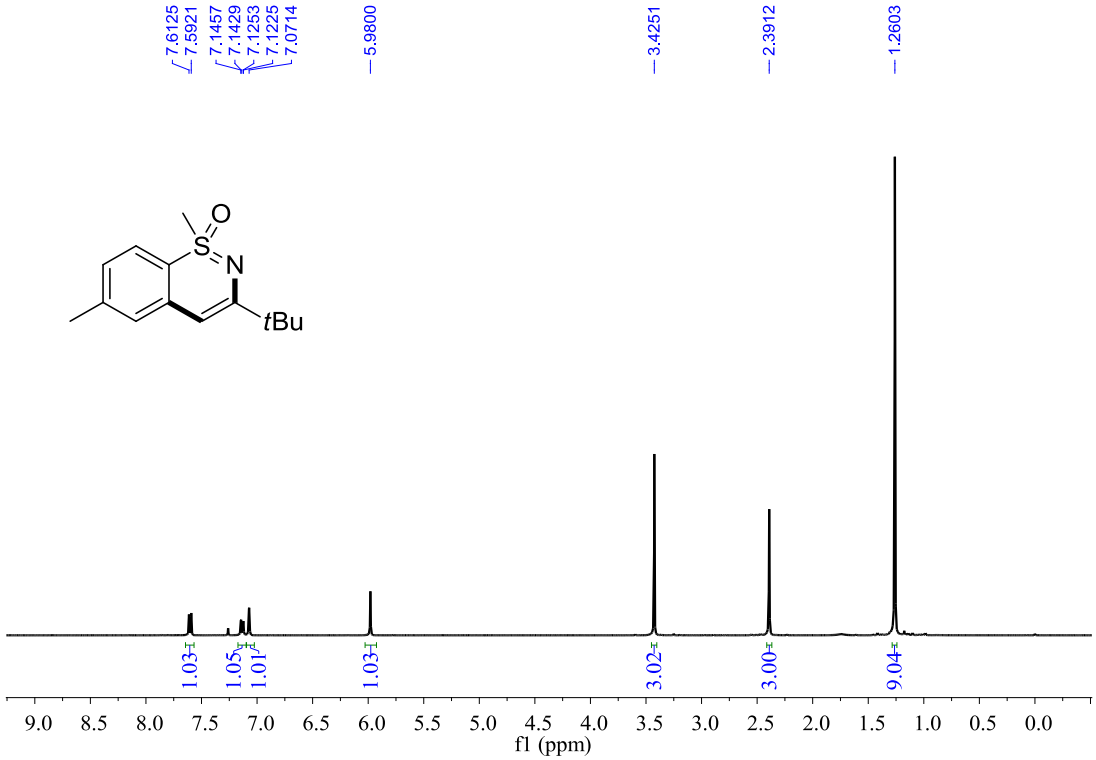
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3ip.



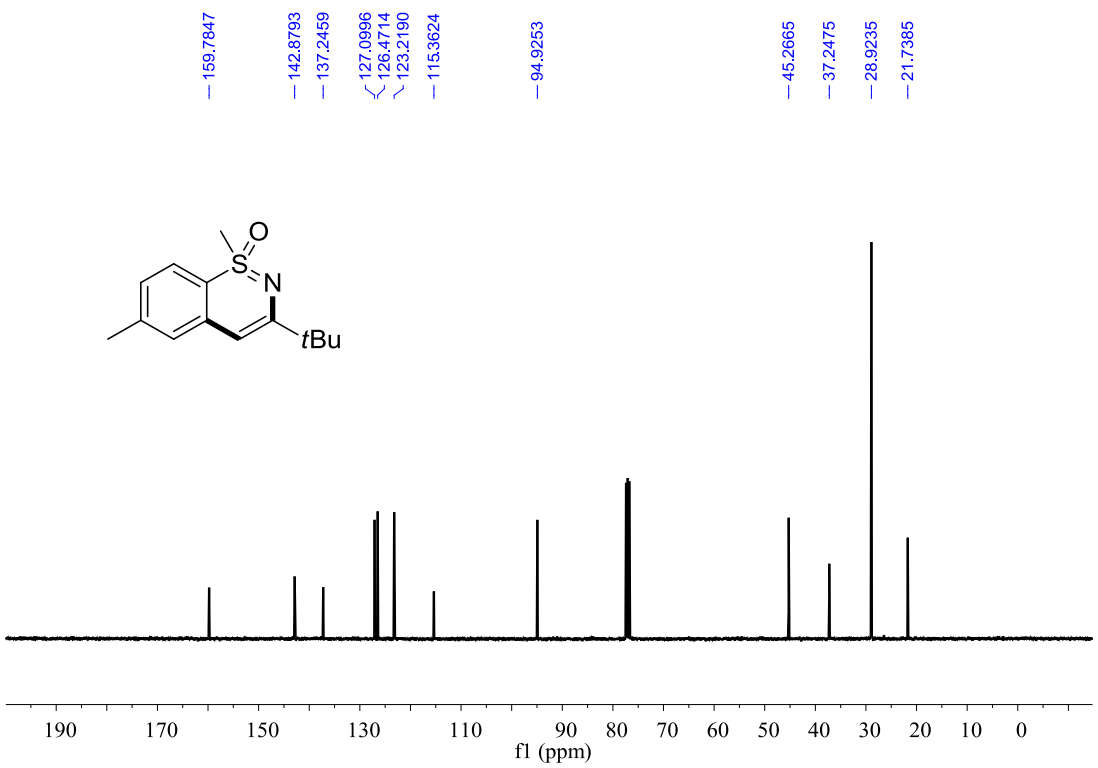
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3jp.



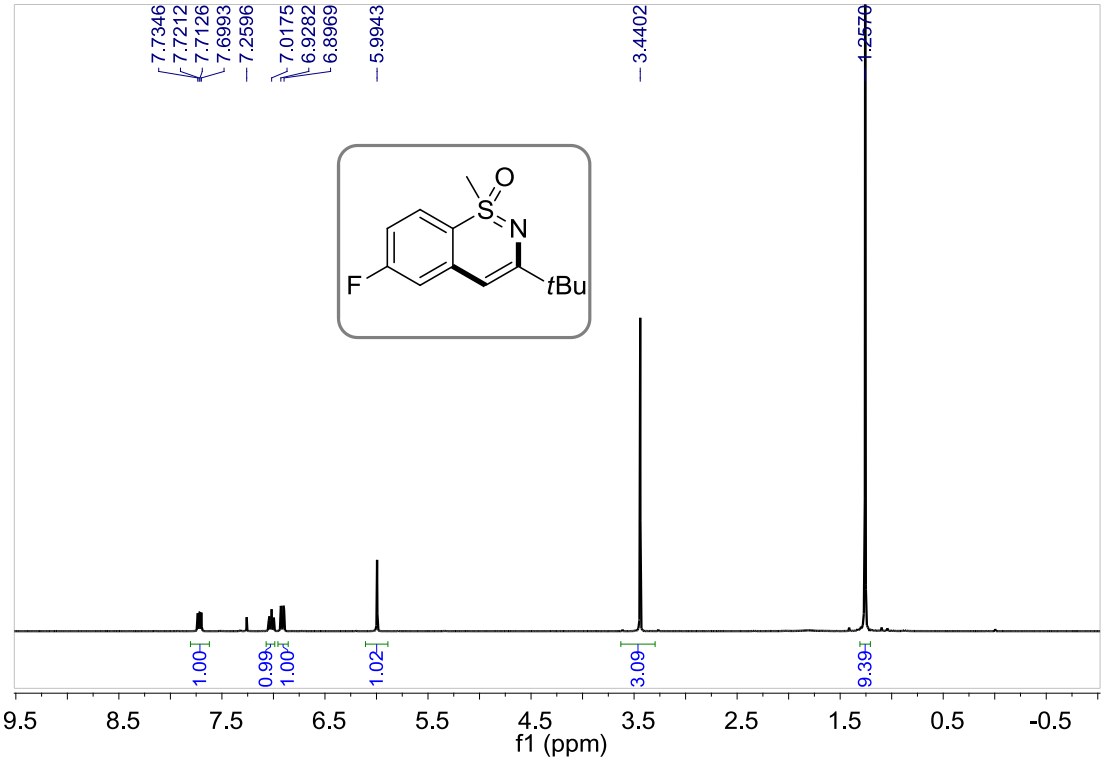
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3jp.



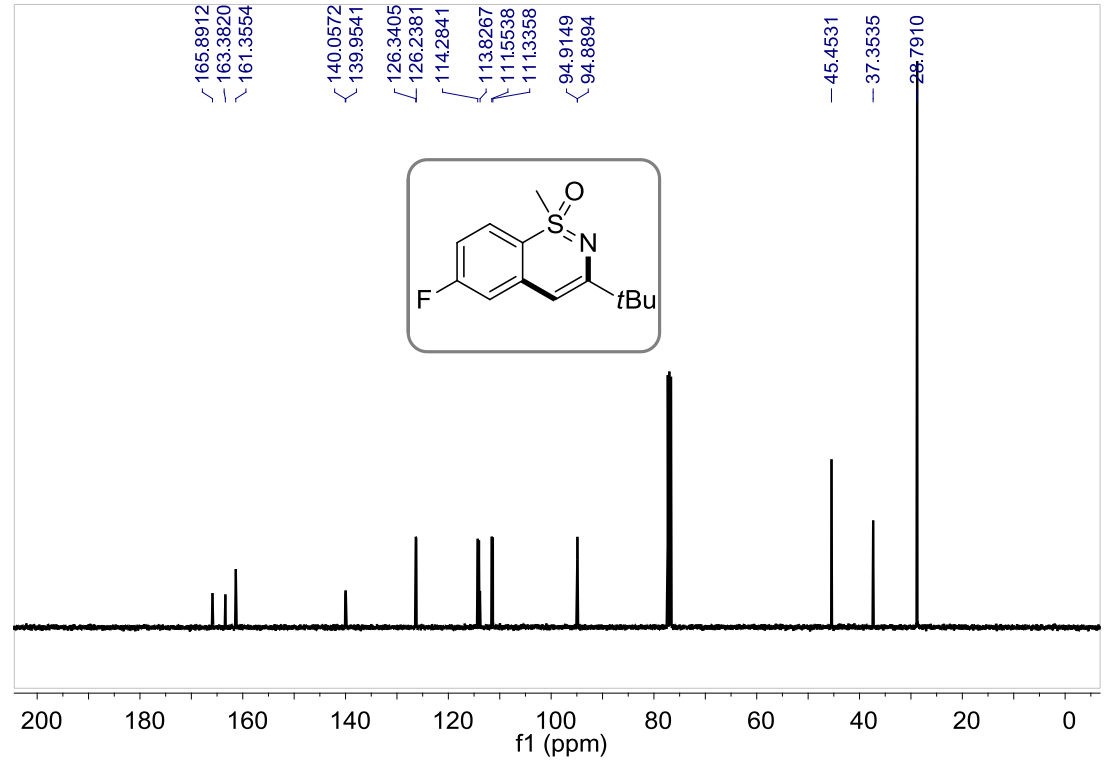
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3kp.



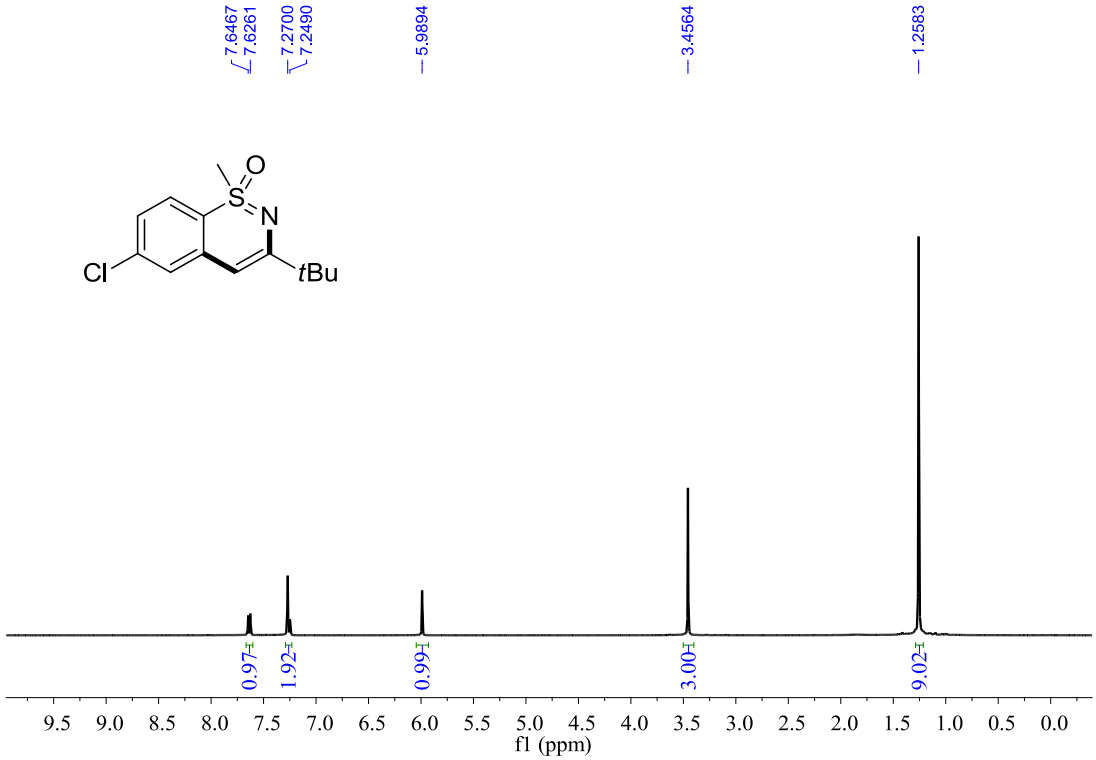
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3kp.



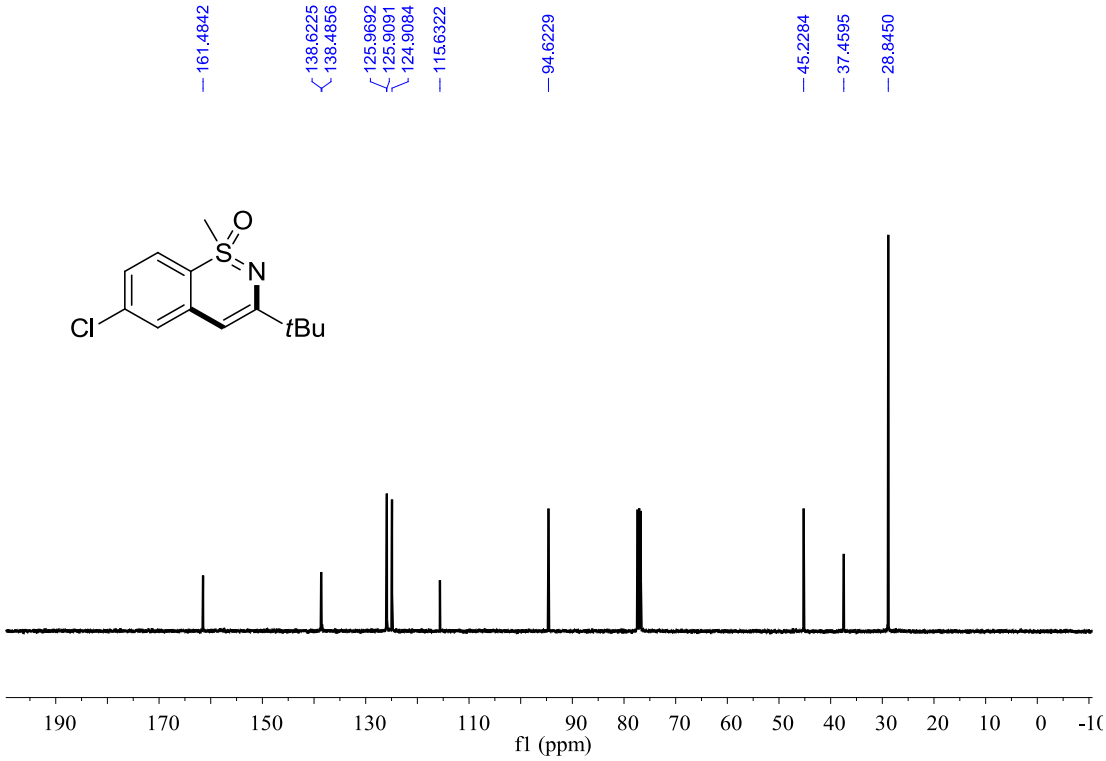
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3lp.



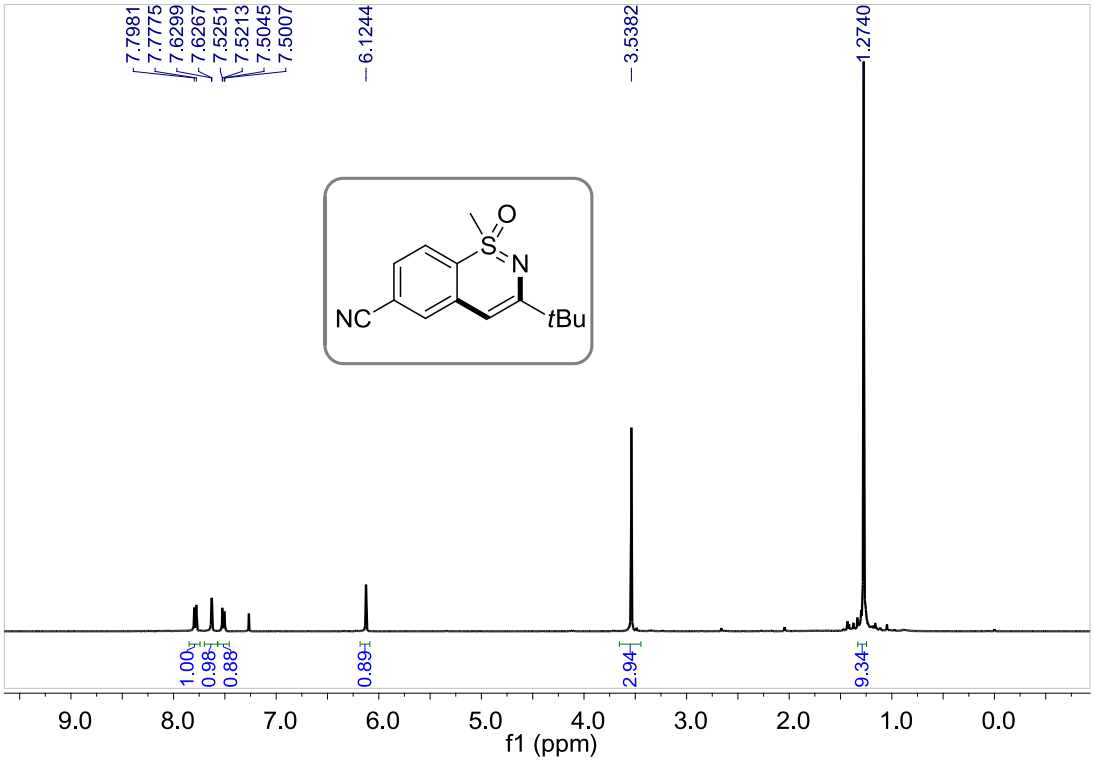
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3lp.



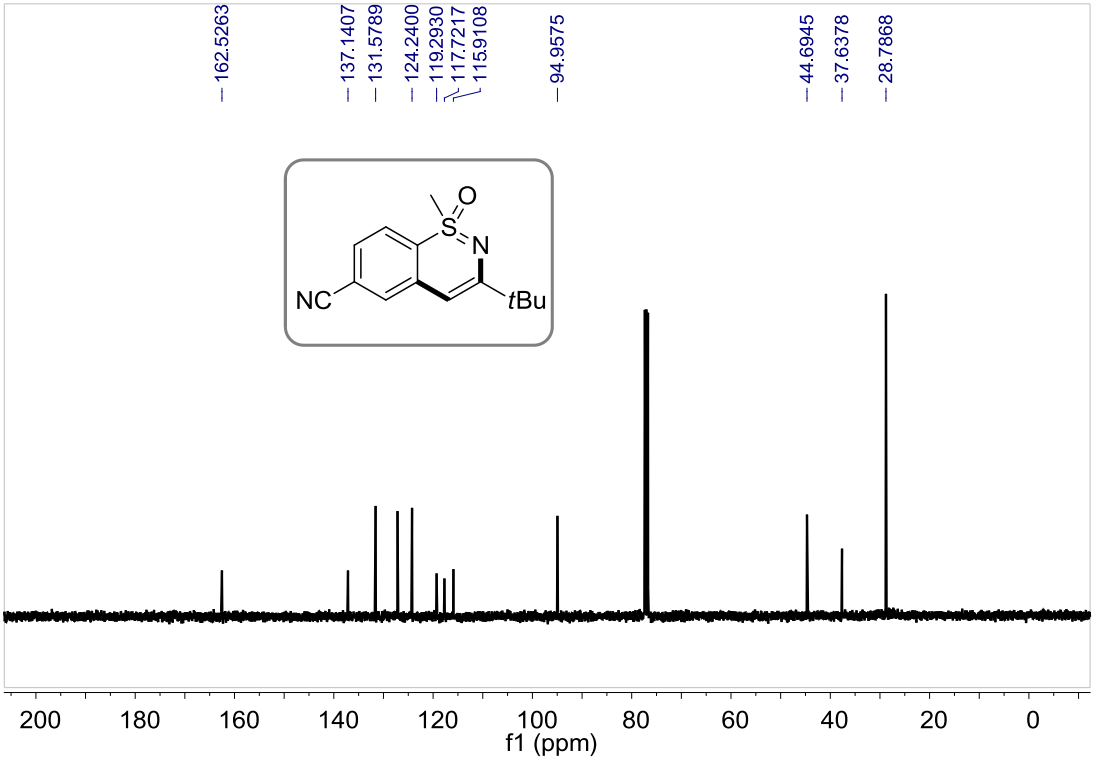
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3mp.



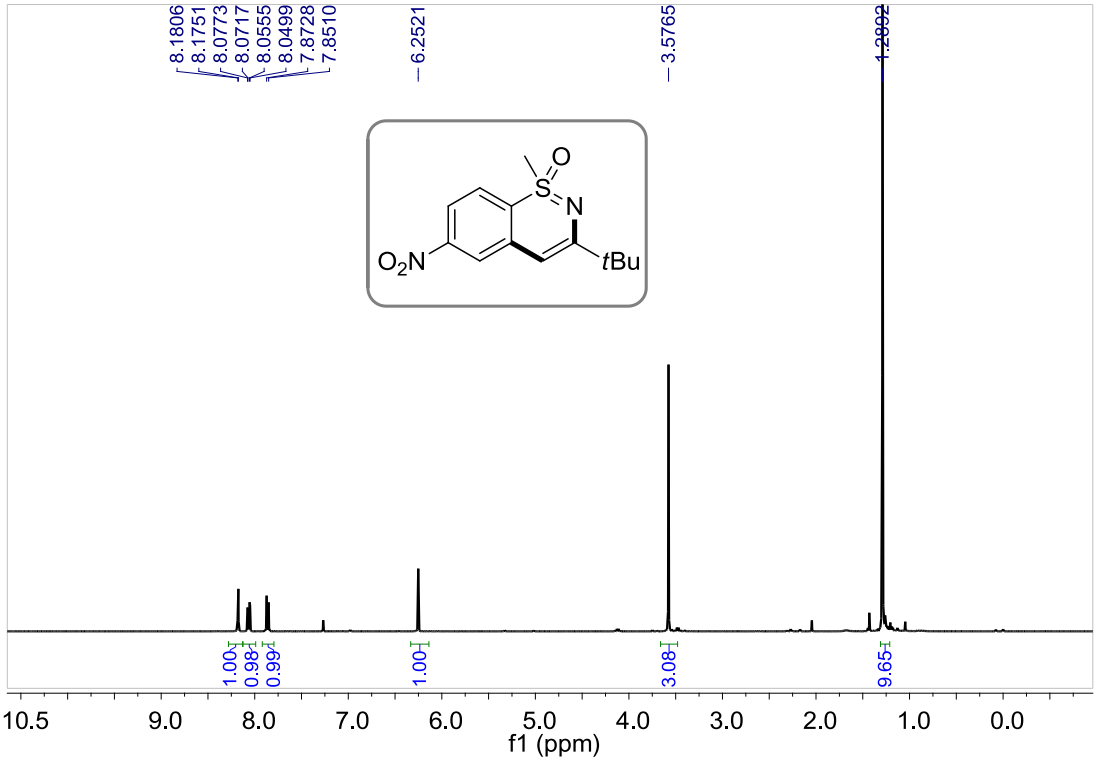
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3mp.



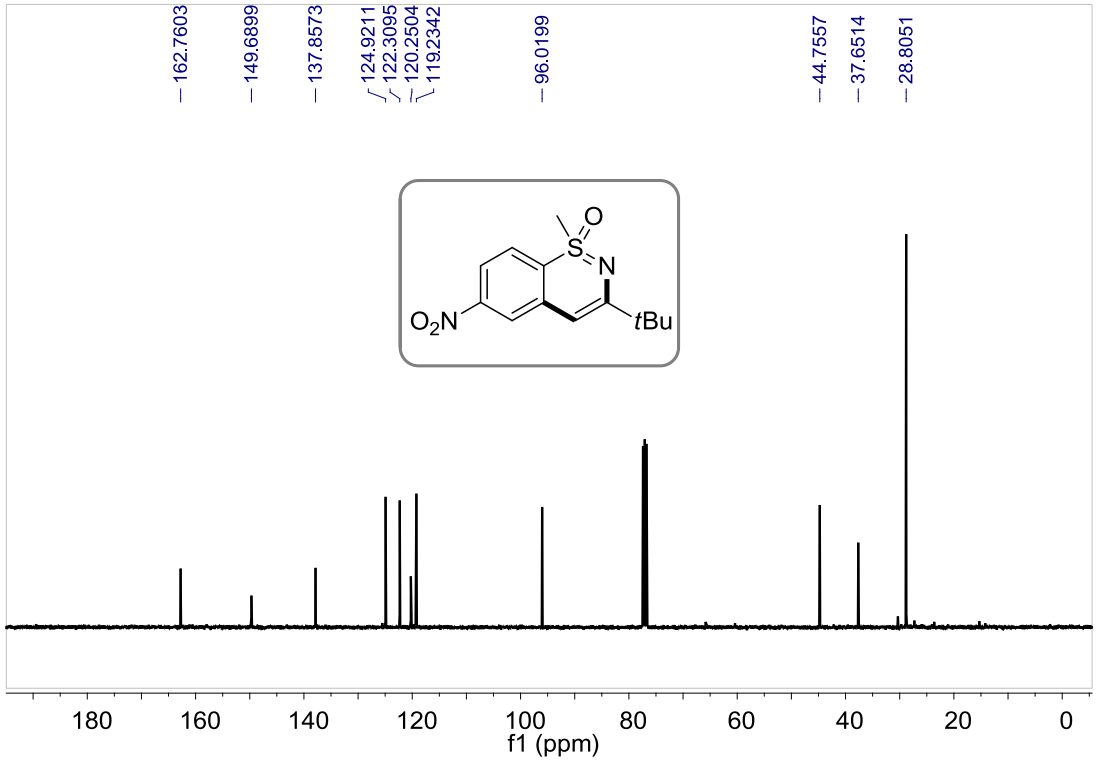
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3np.



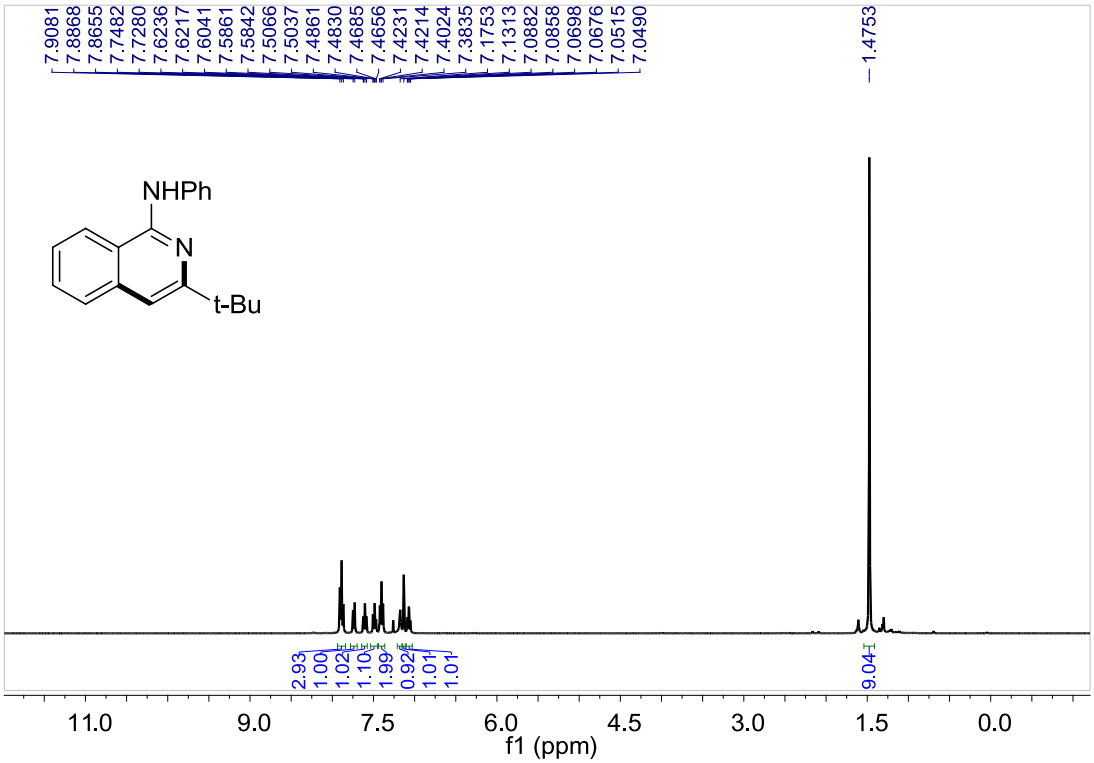
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3np.



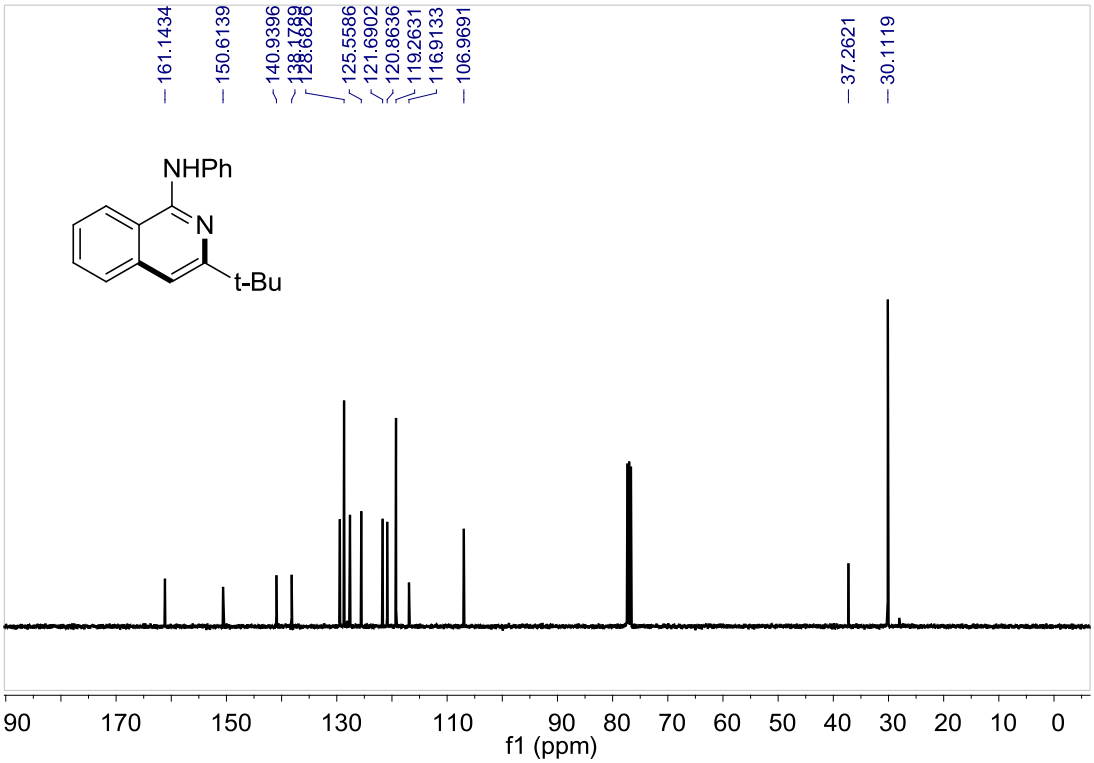
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3op.



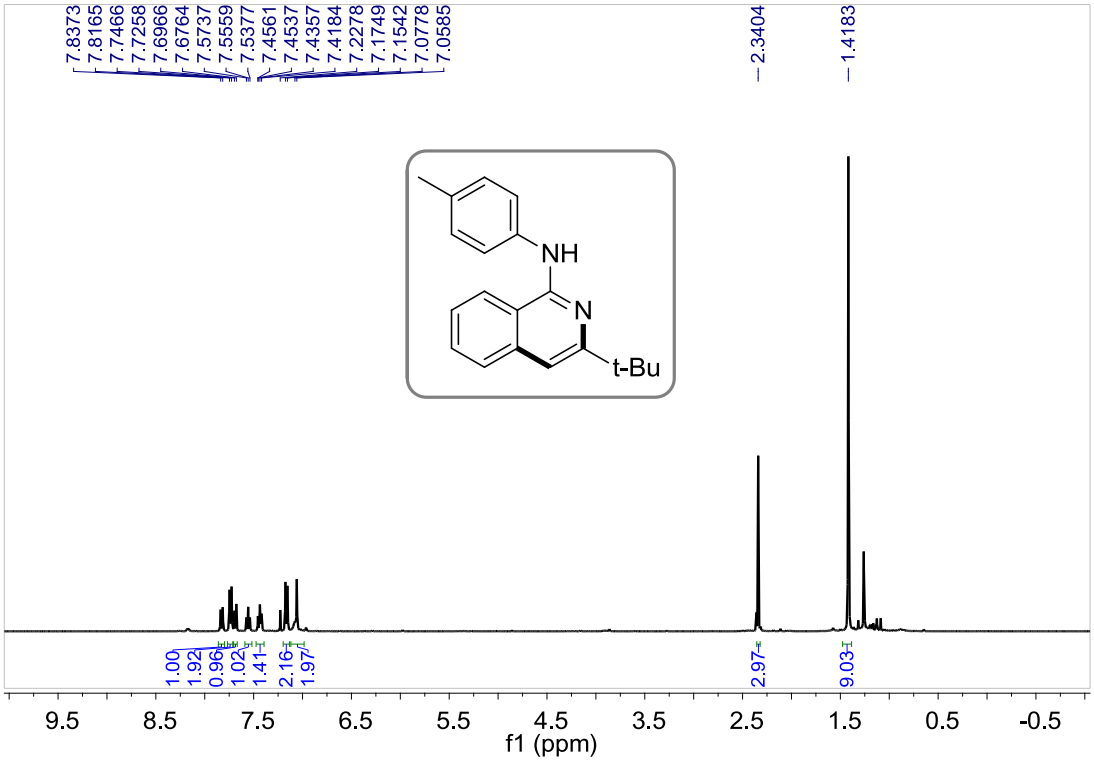
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3op.



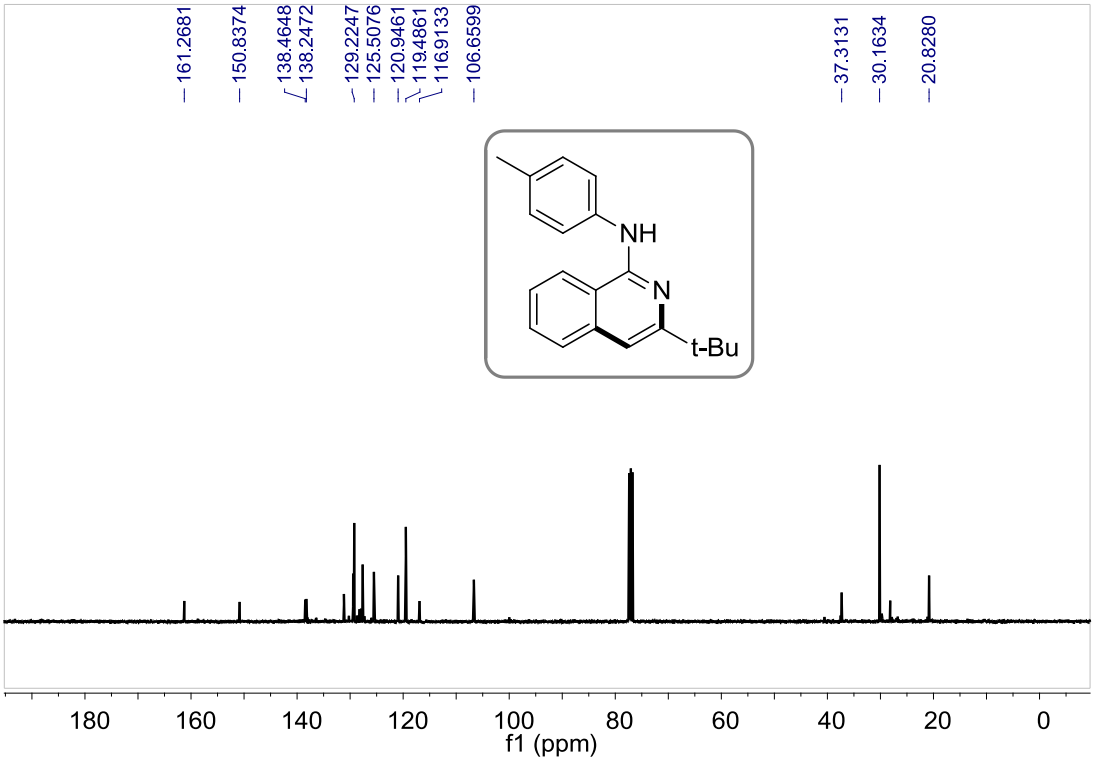
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3pp.



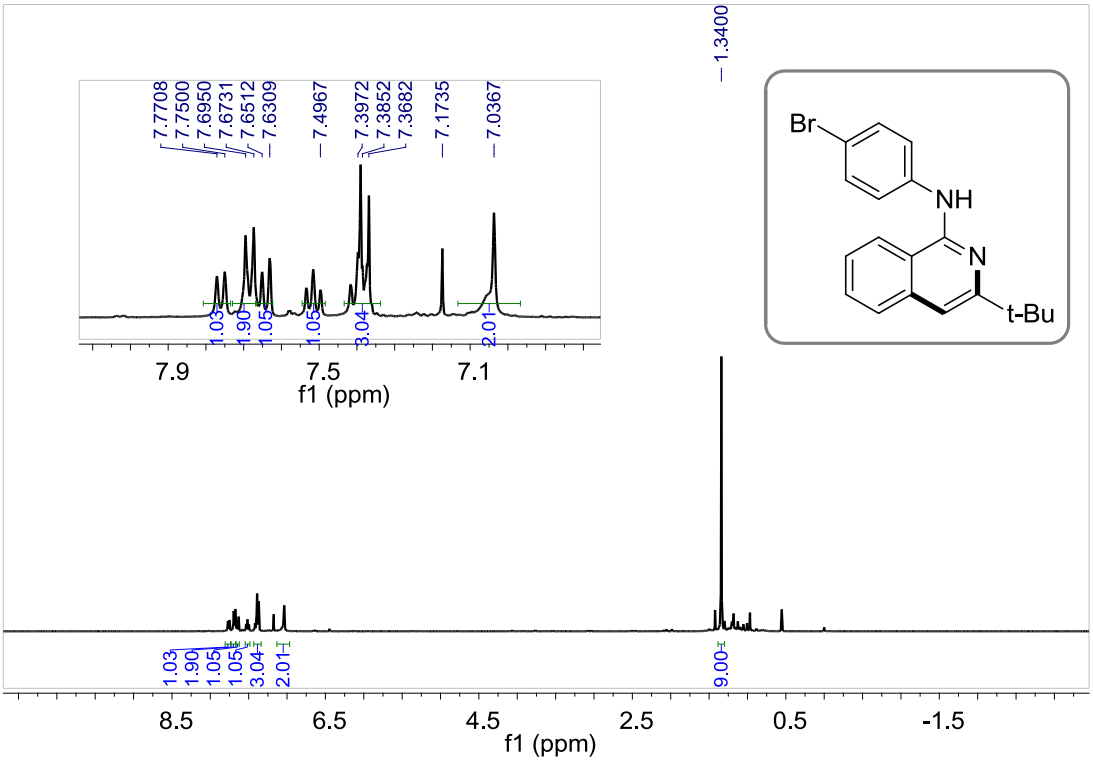
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3pp.



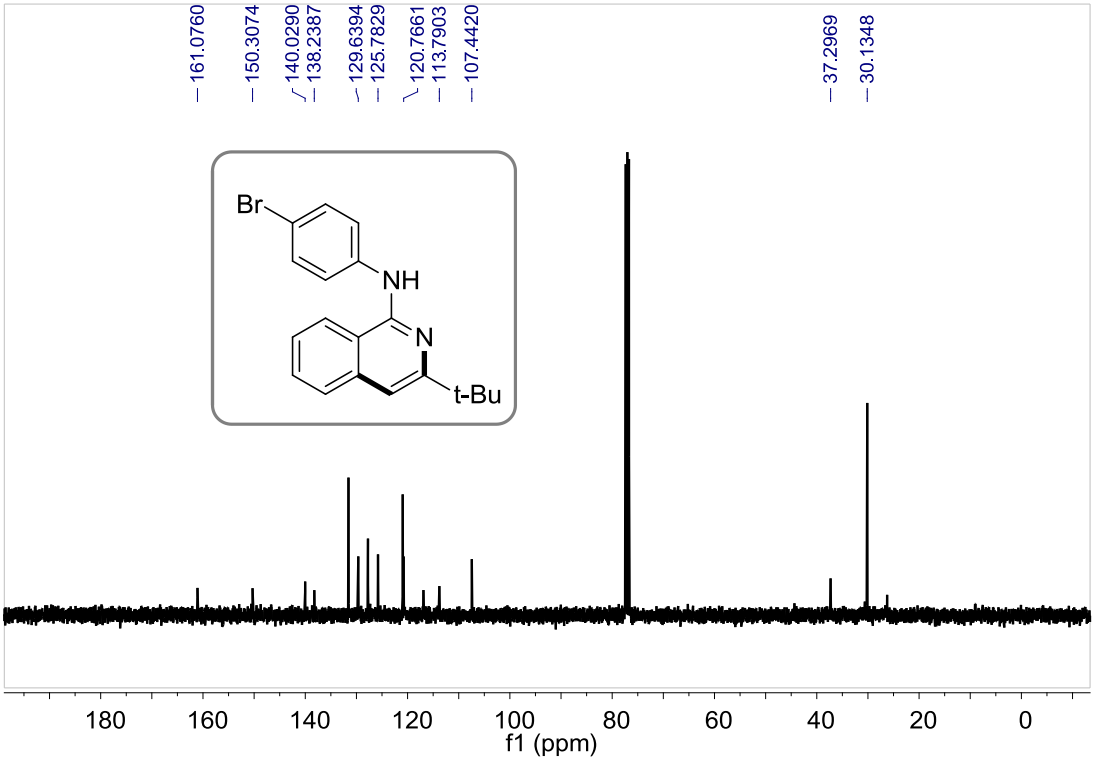
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3qp.



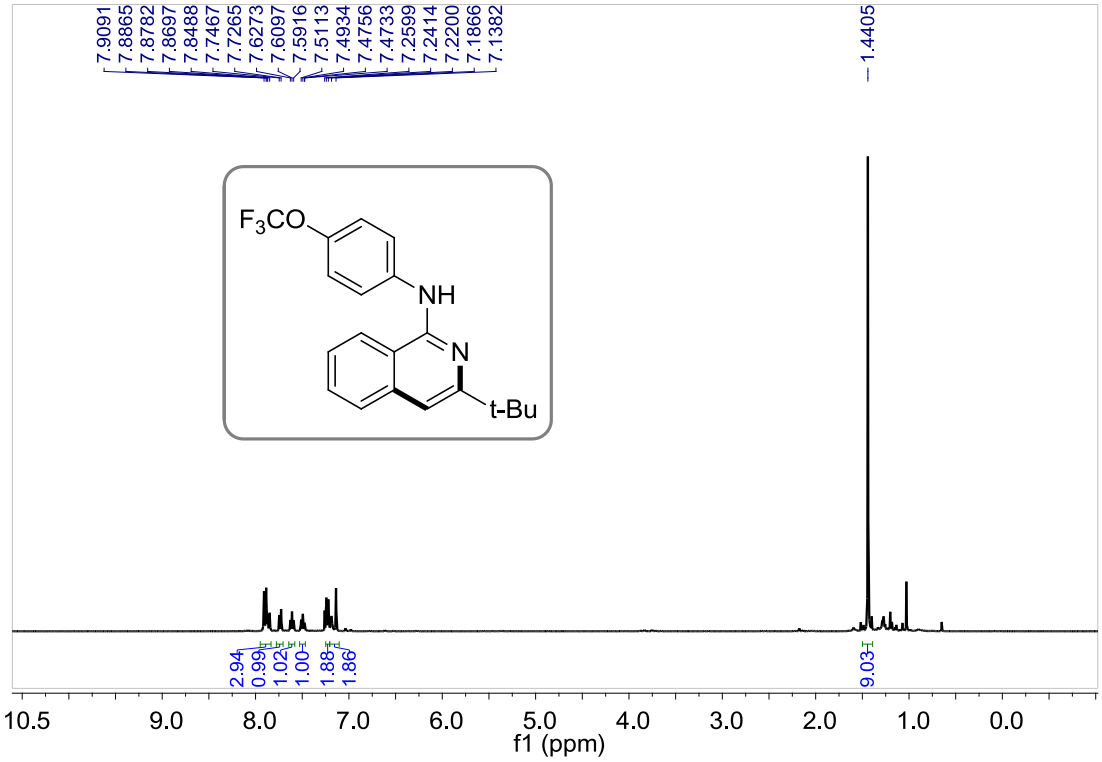
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3qp.



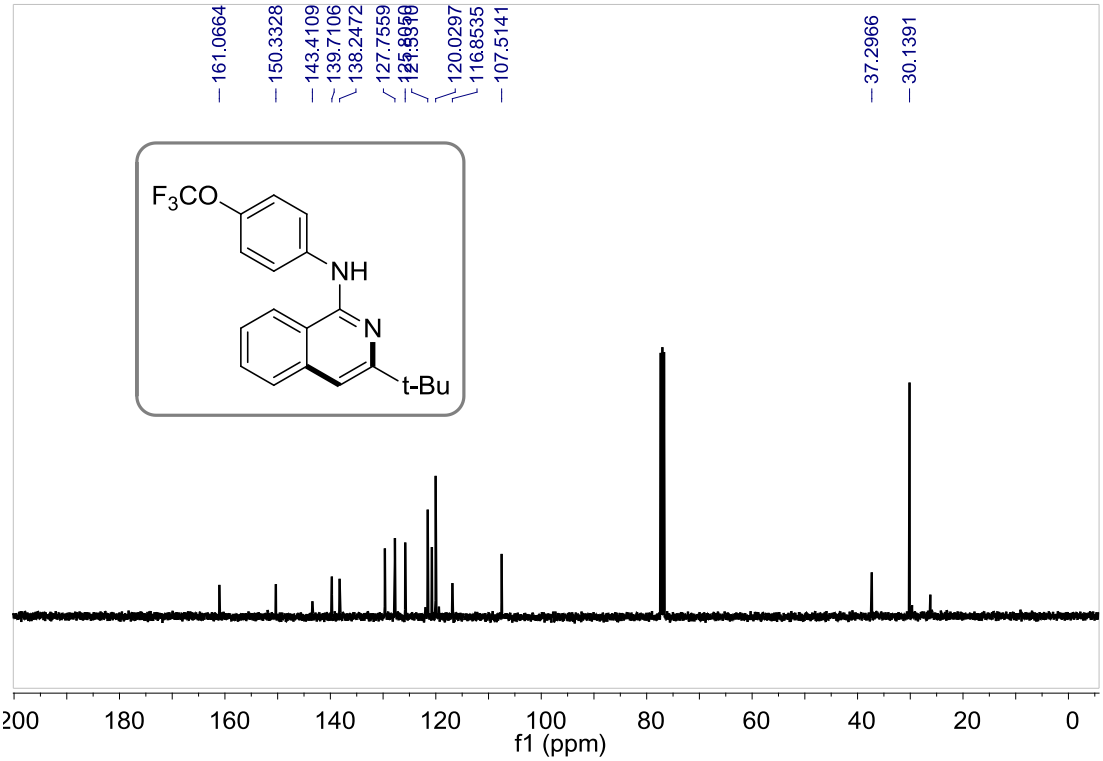
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3rp.



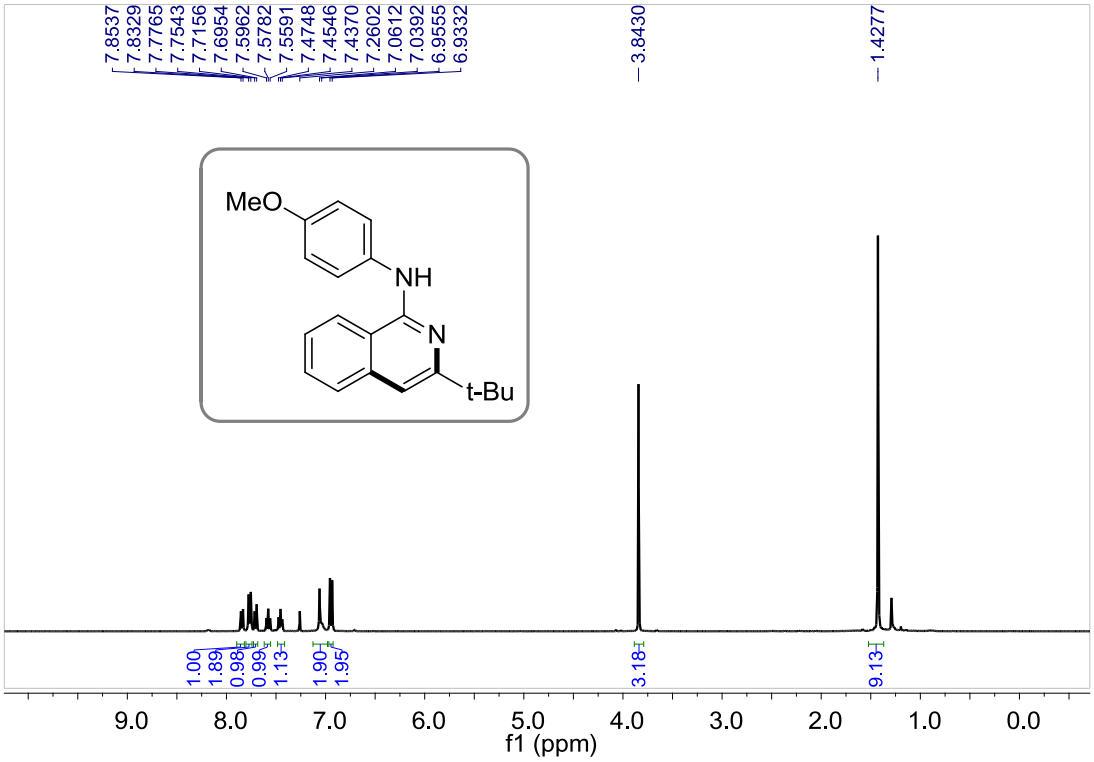
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3rp.



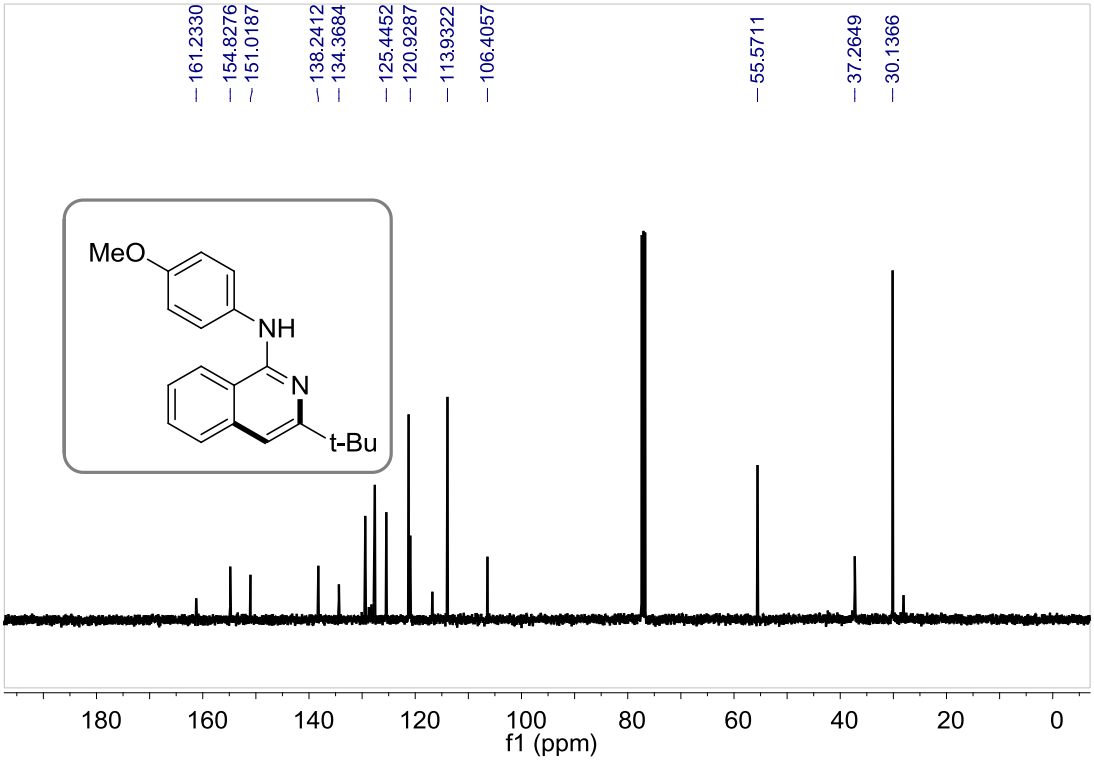
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3sp.



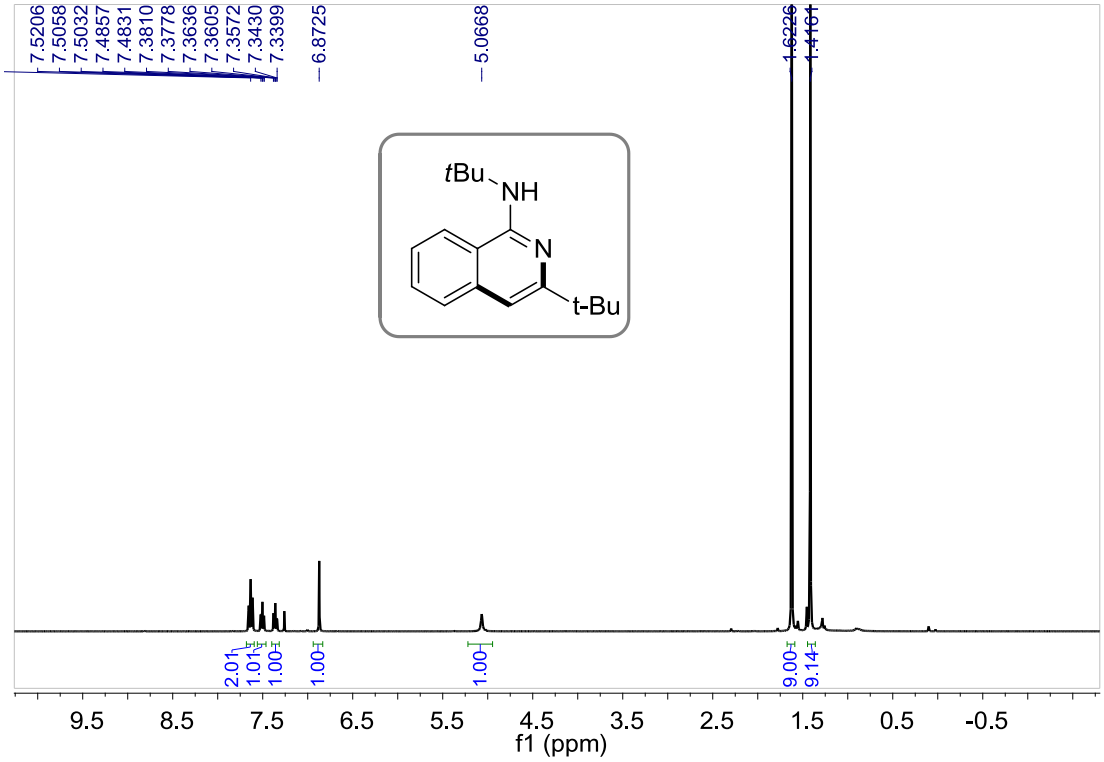
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3sp.



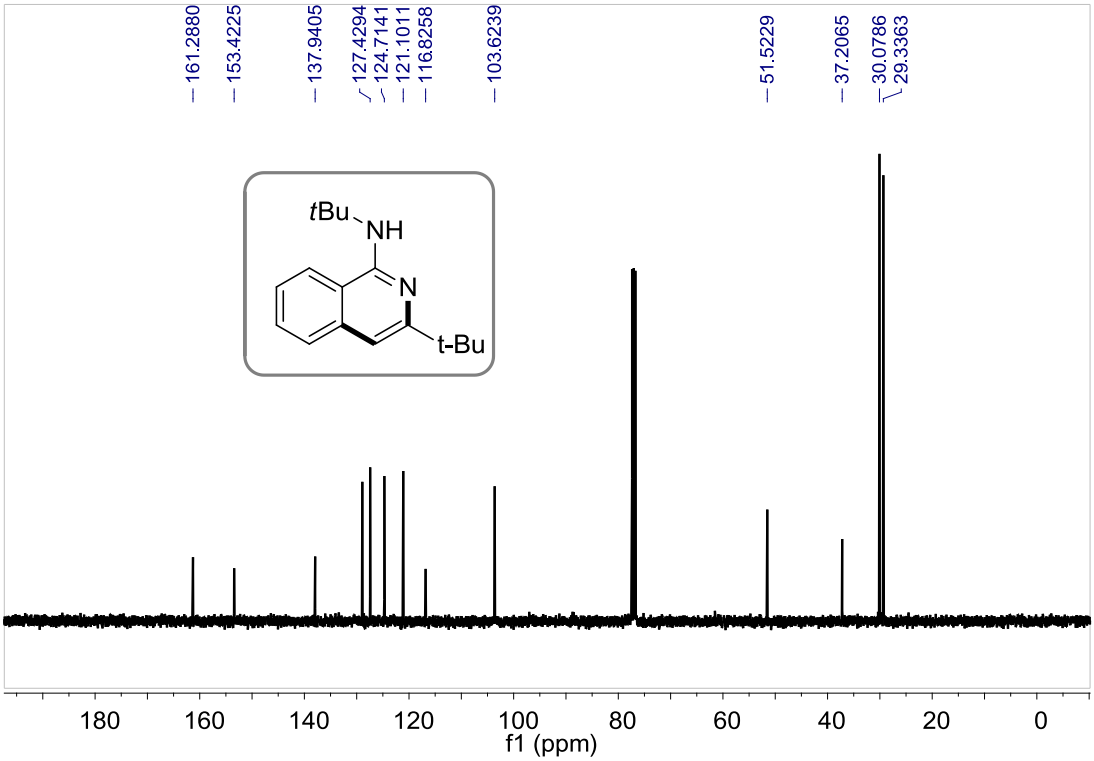
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3tp.



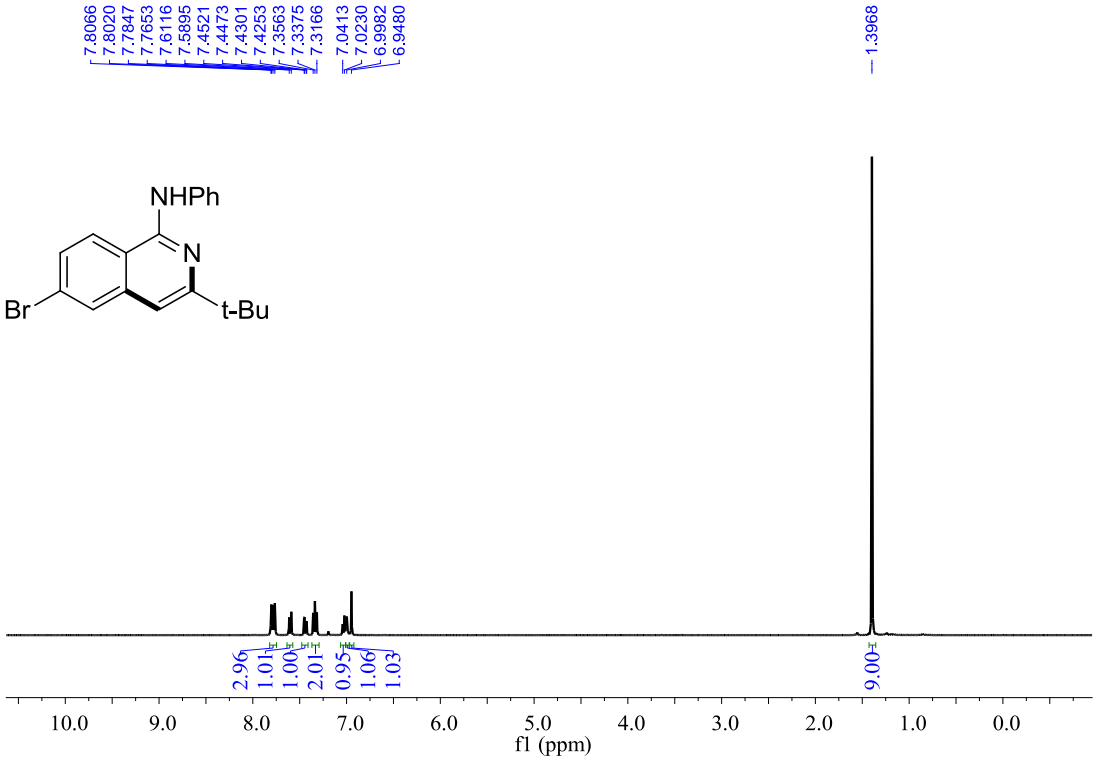
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3tp.



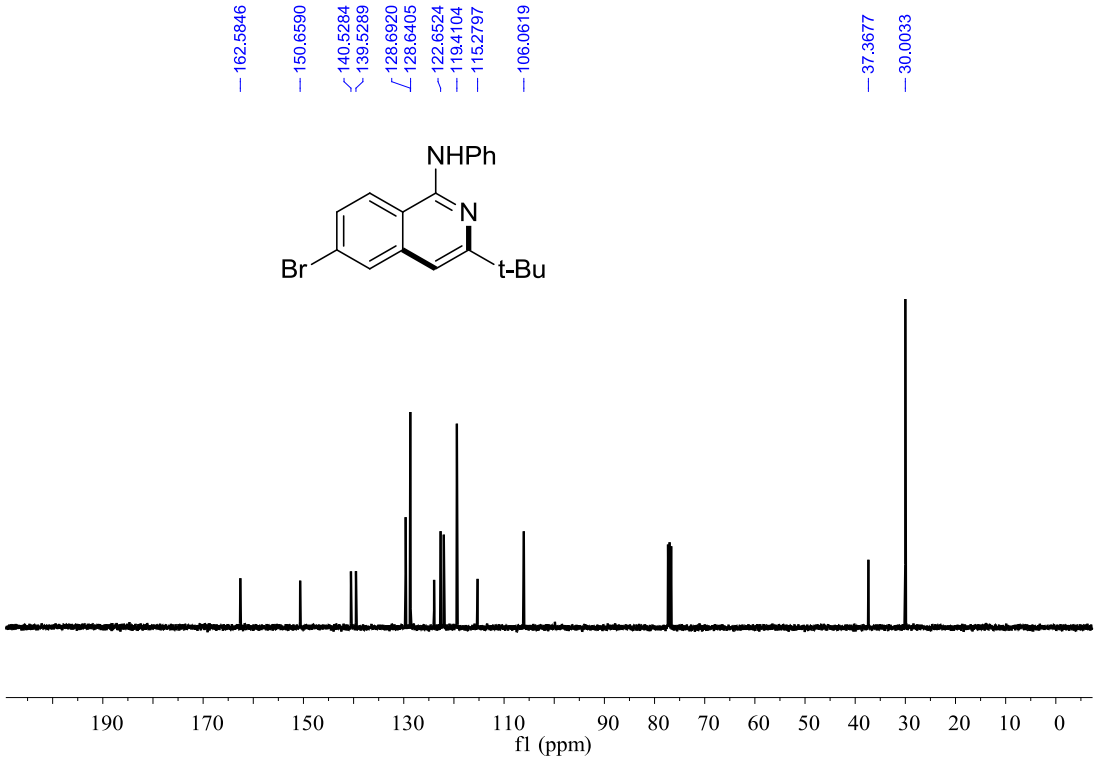
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3up.



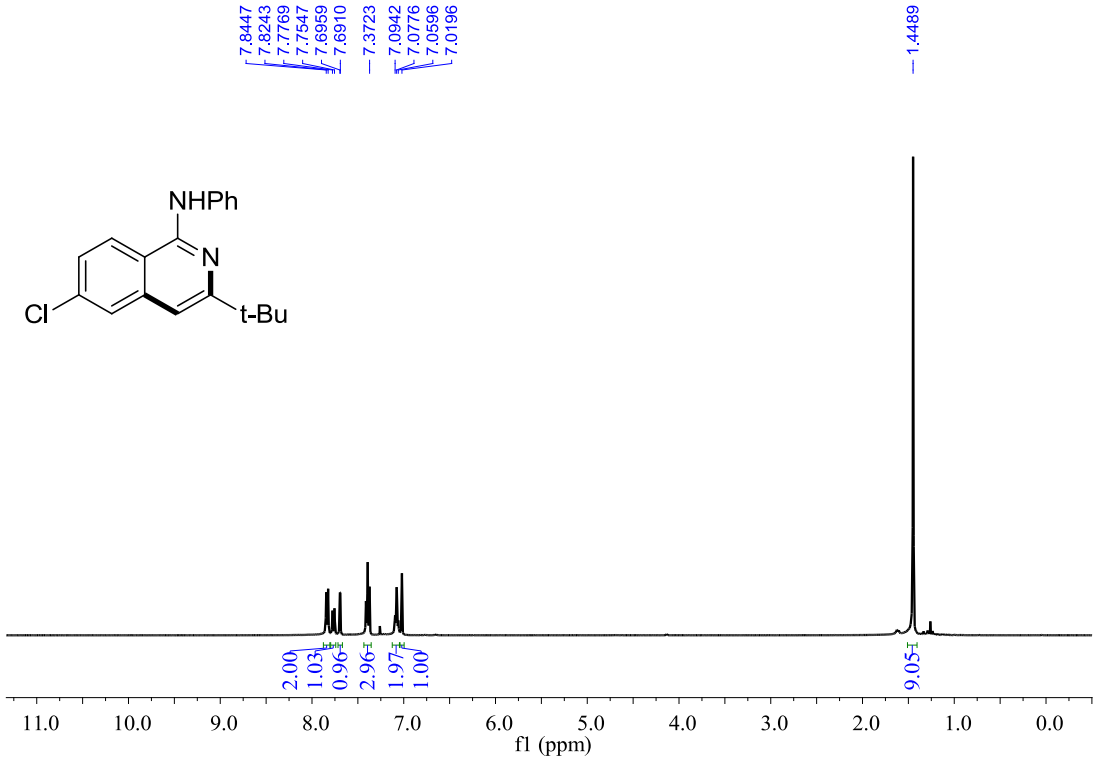
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3up.



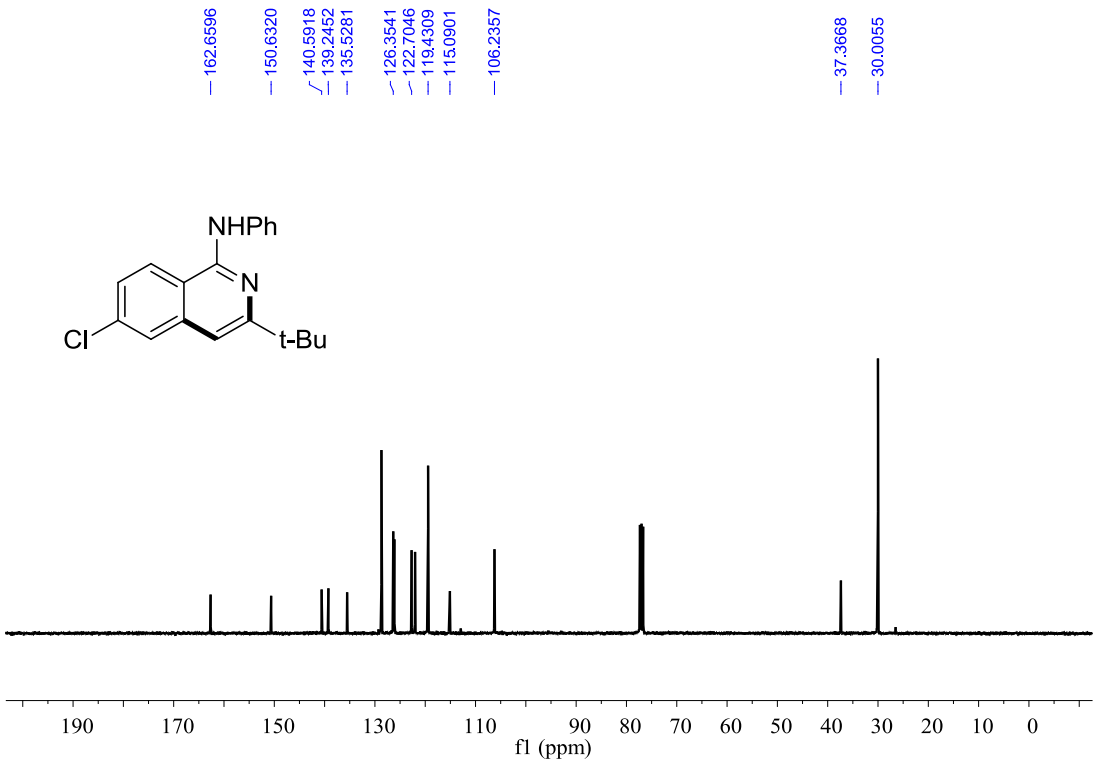
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3vp.



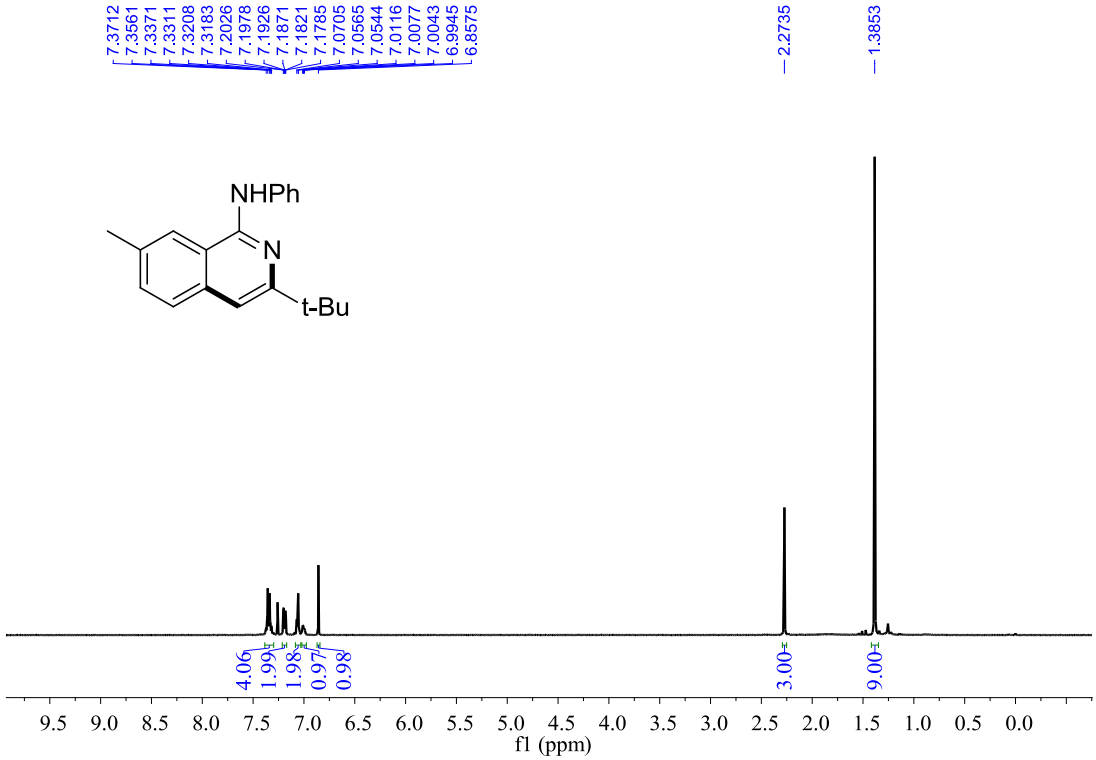
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3vp.



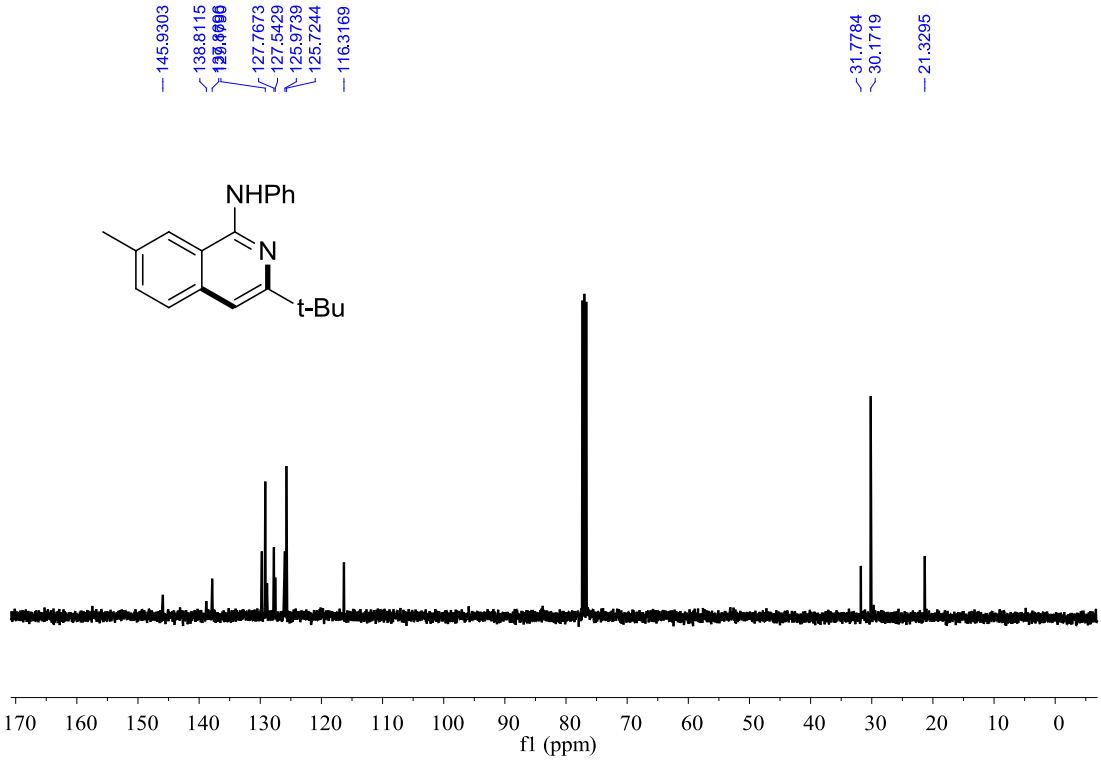
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3wp.



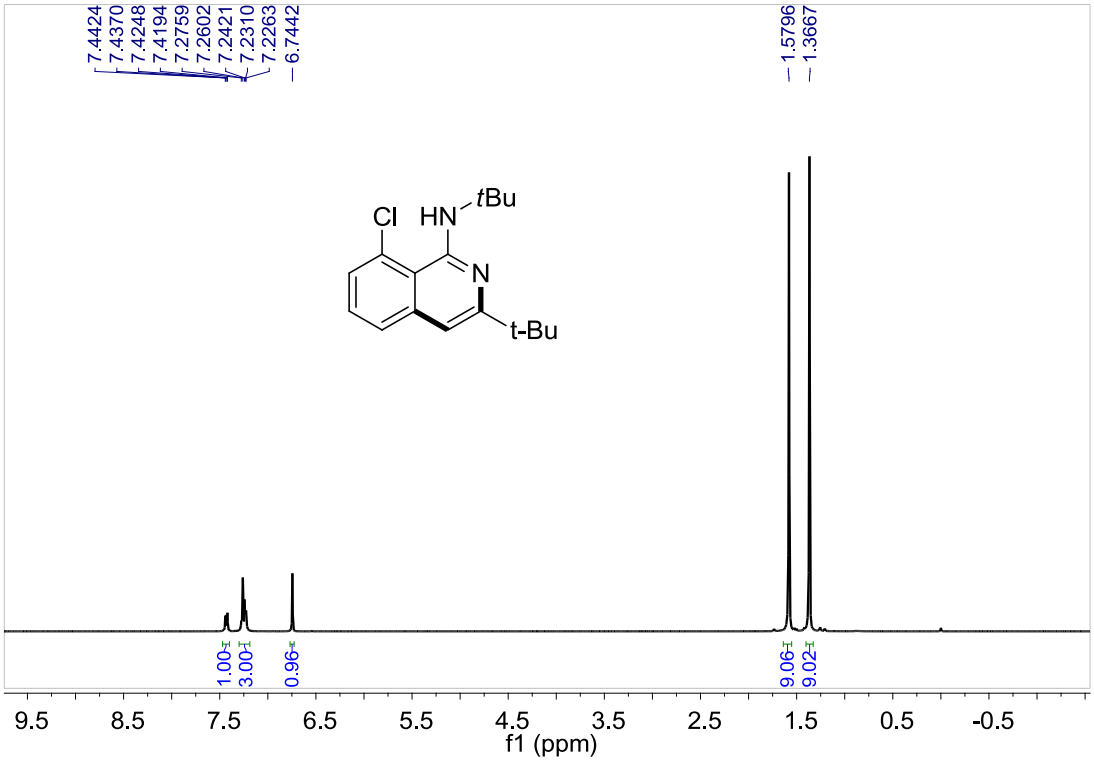
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3wp.



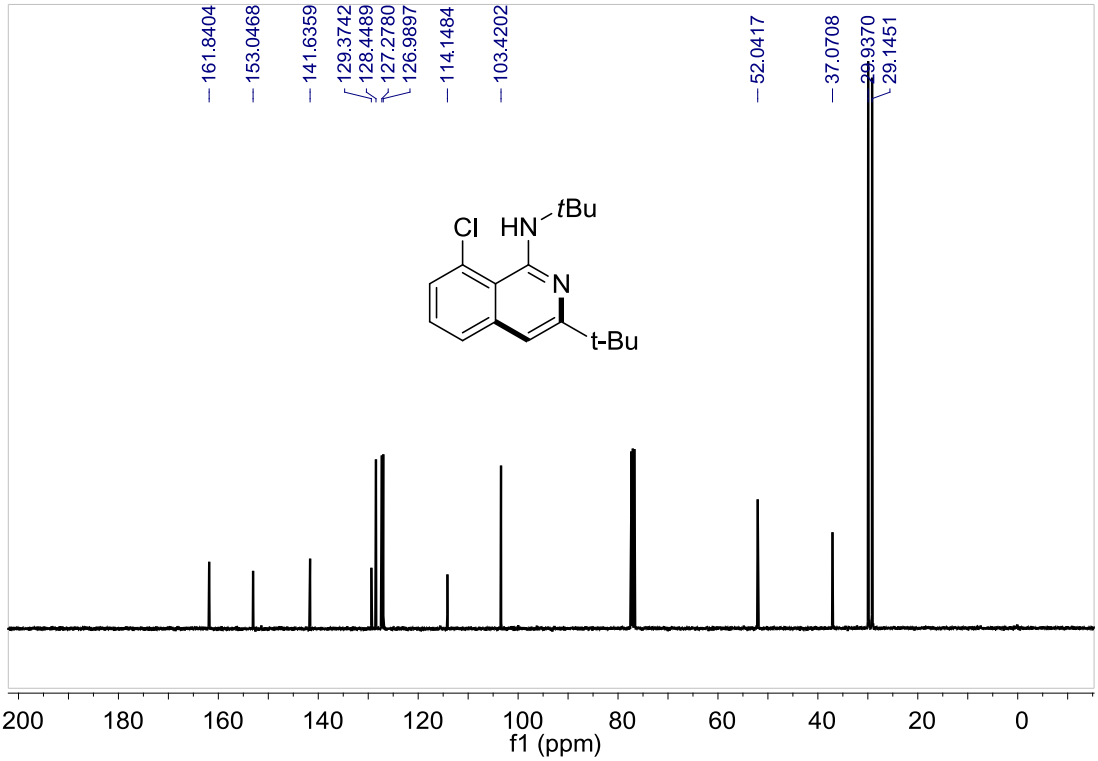
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3xp.



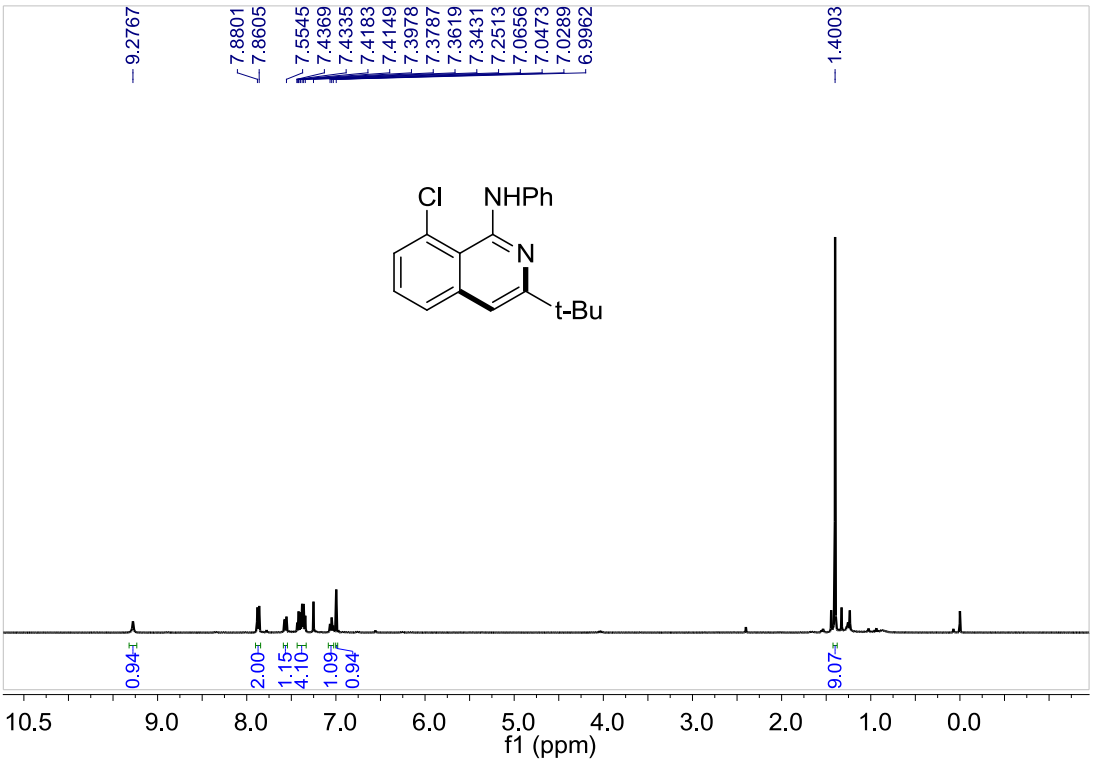
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3xp.



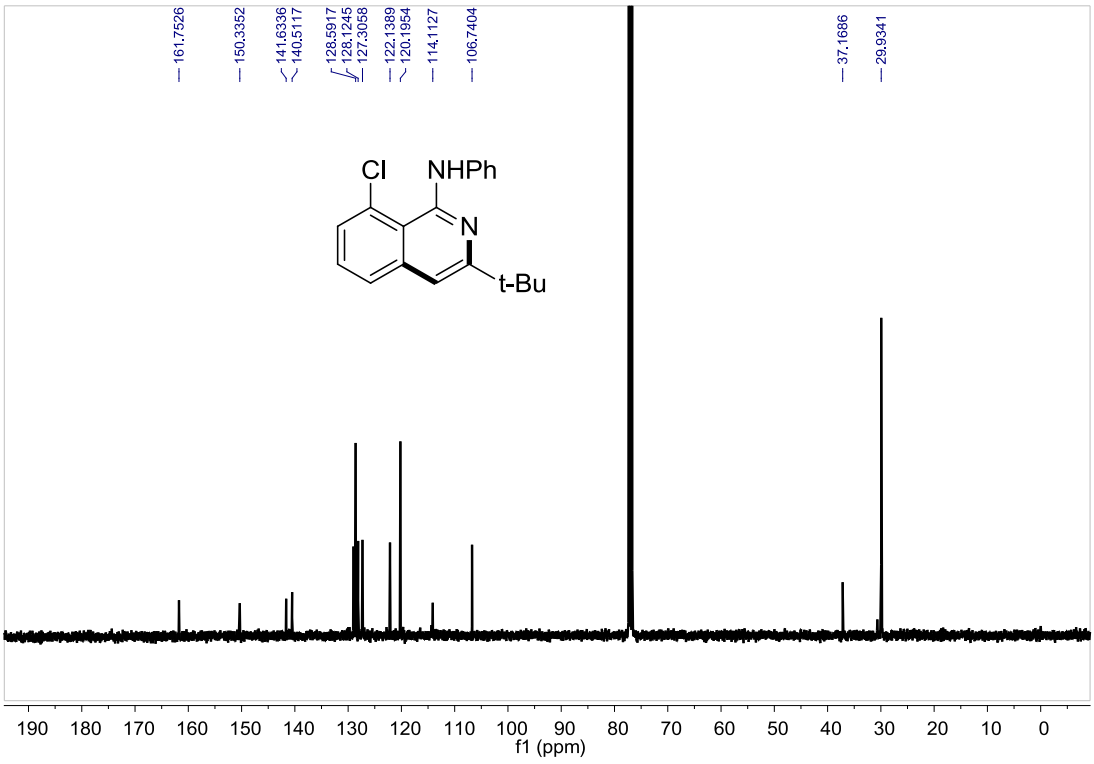
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3yp.



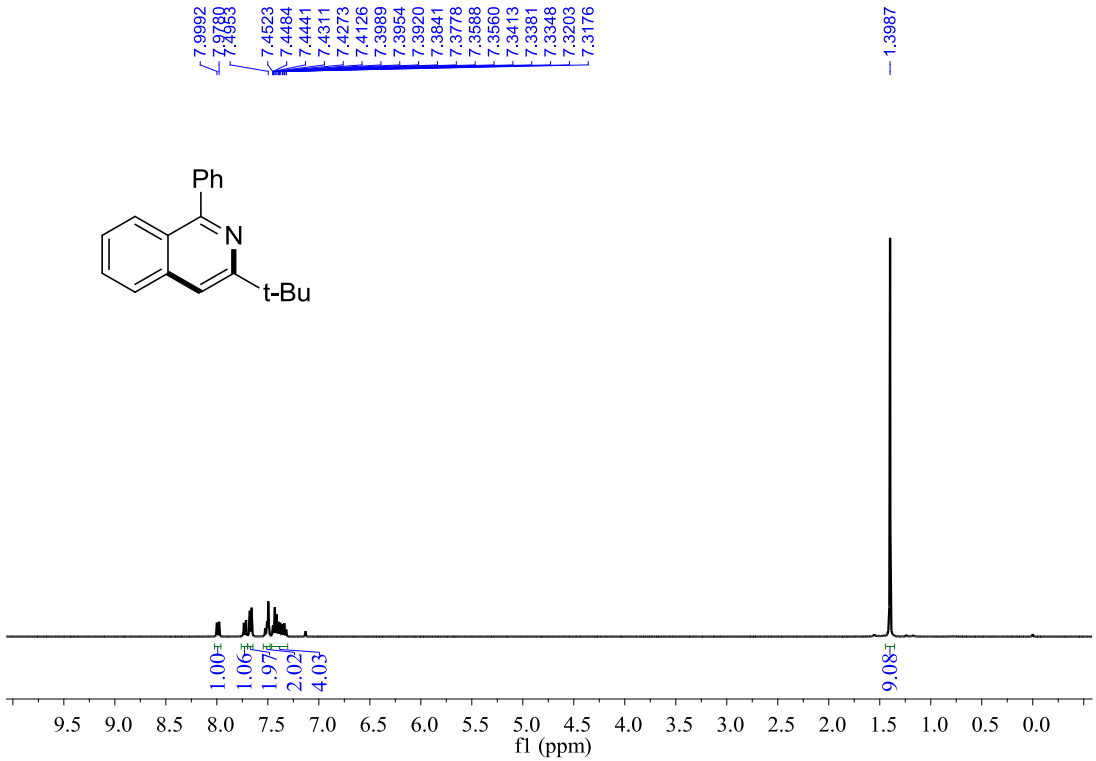
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3yp.



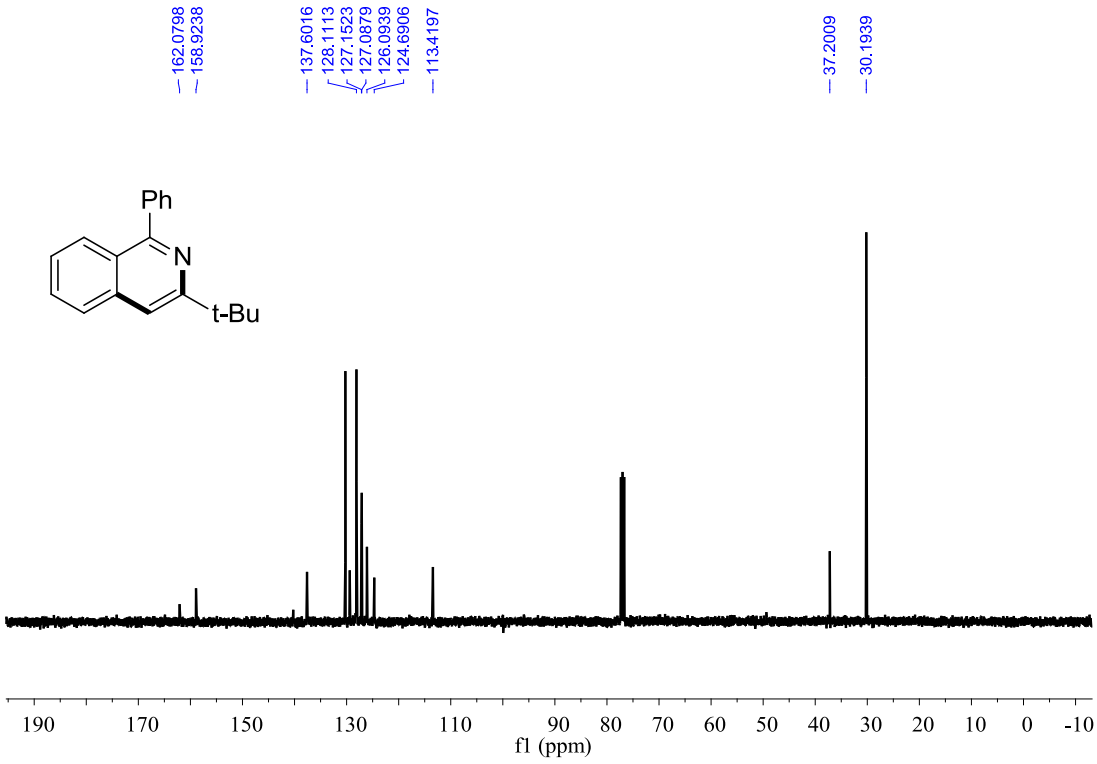
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3y'p.



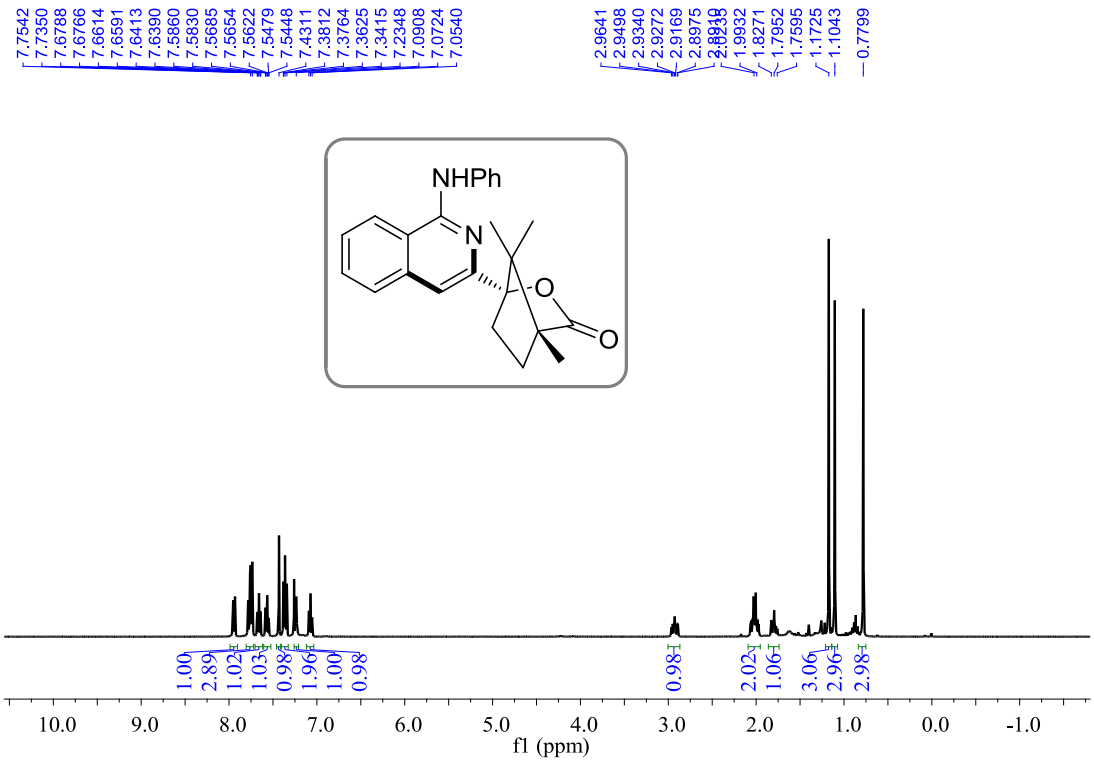
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3y'p.



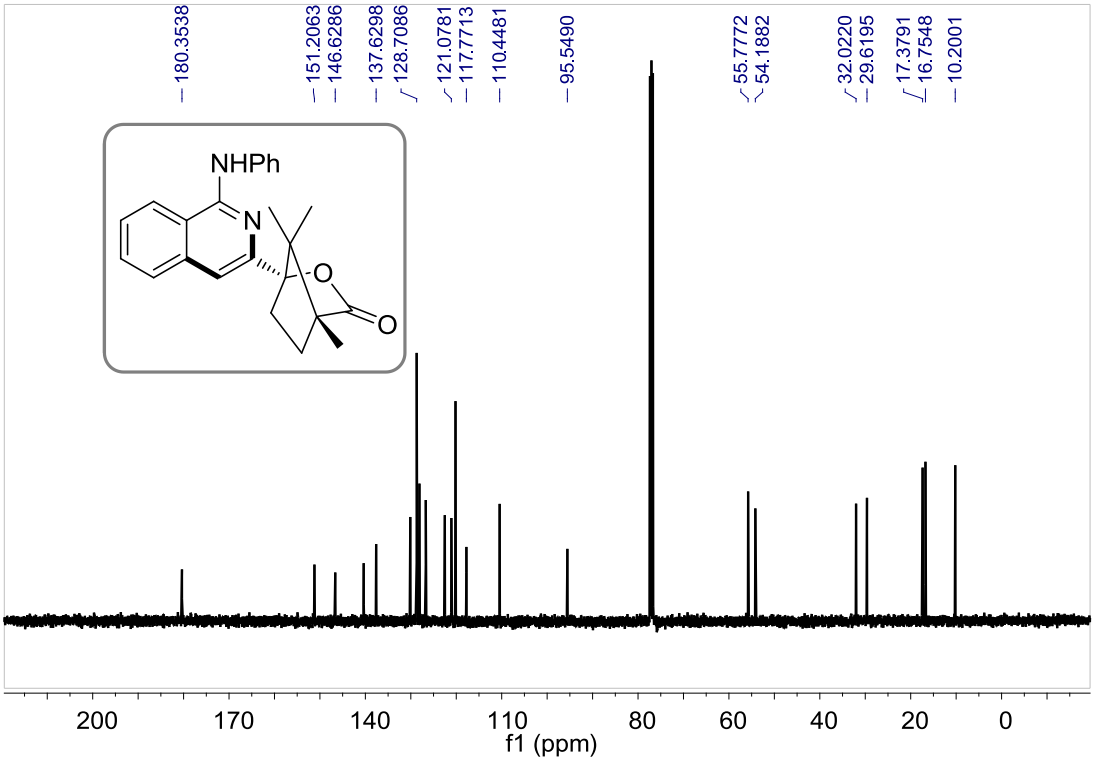
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3zp.



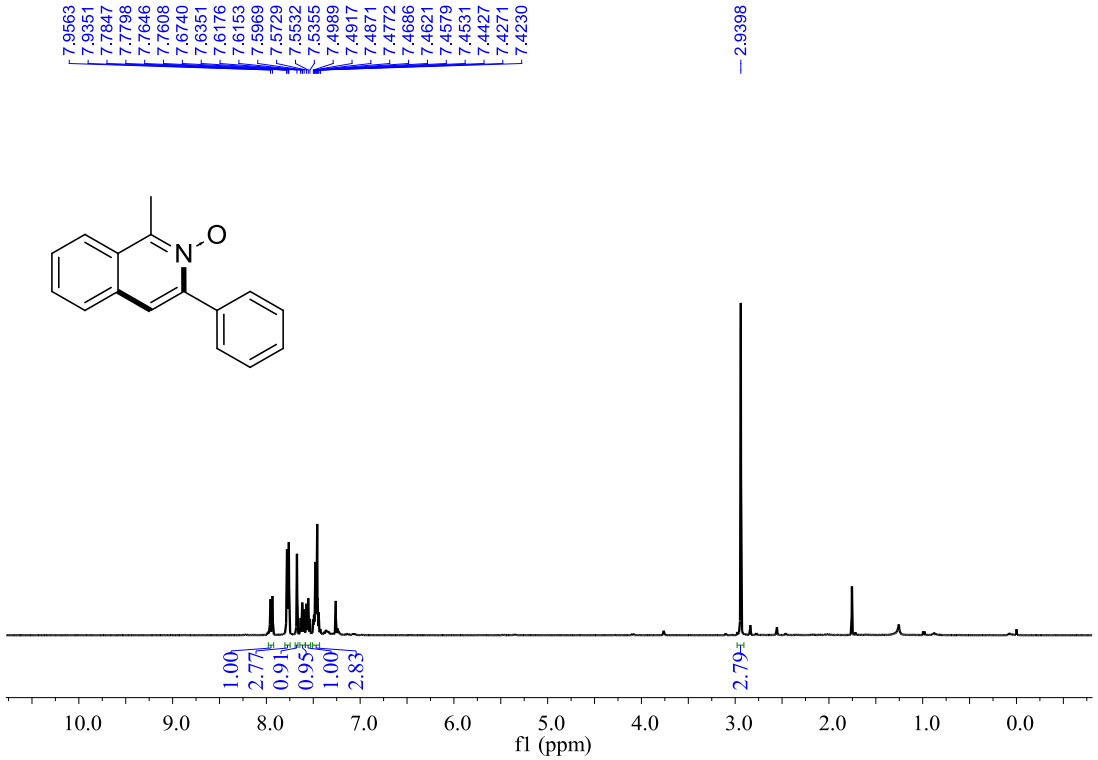
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3zp.



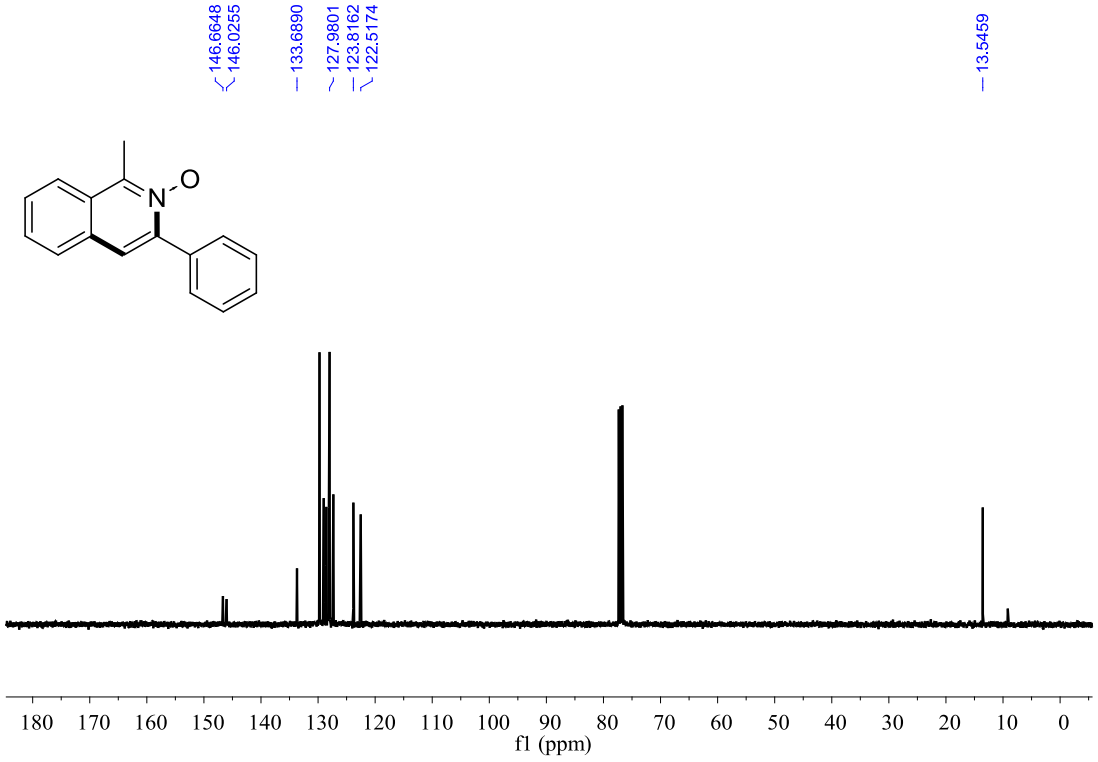
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 3pr.



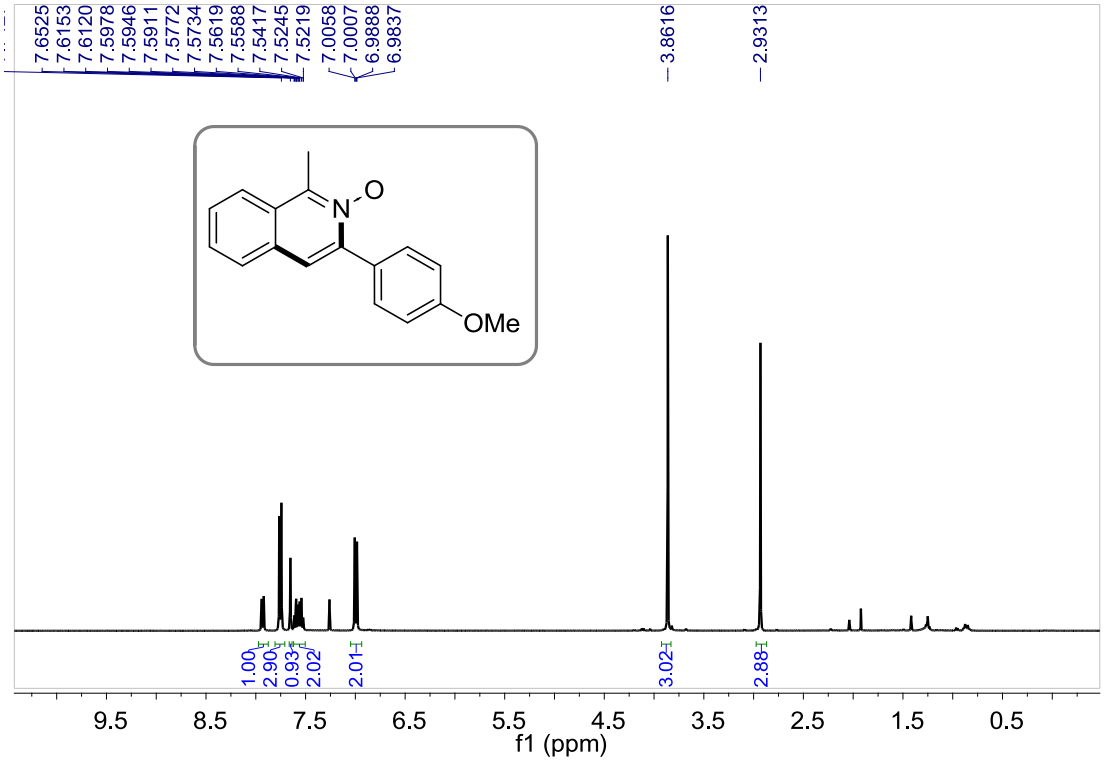
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 3pr.



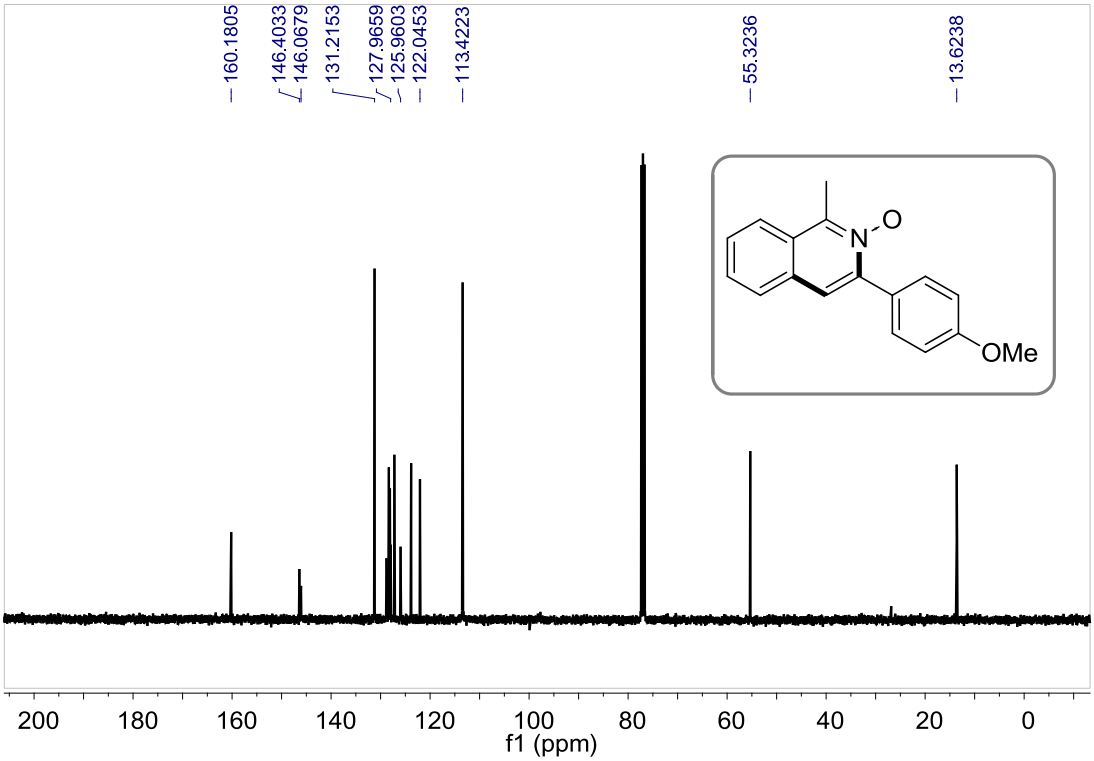
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5a.



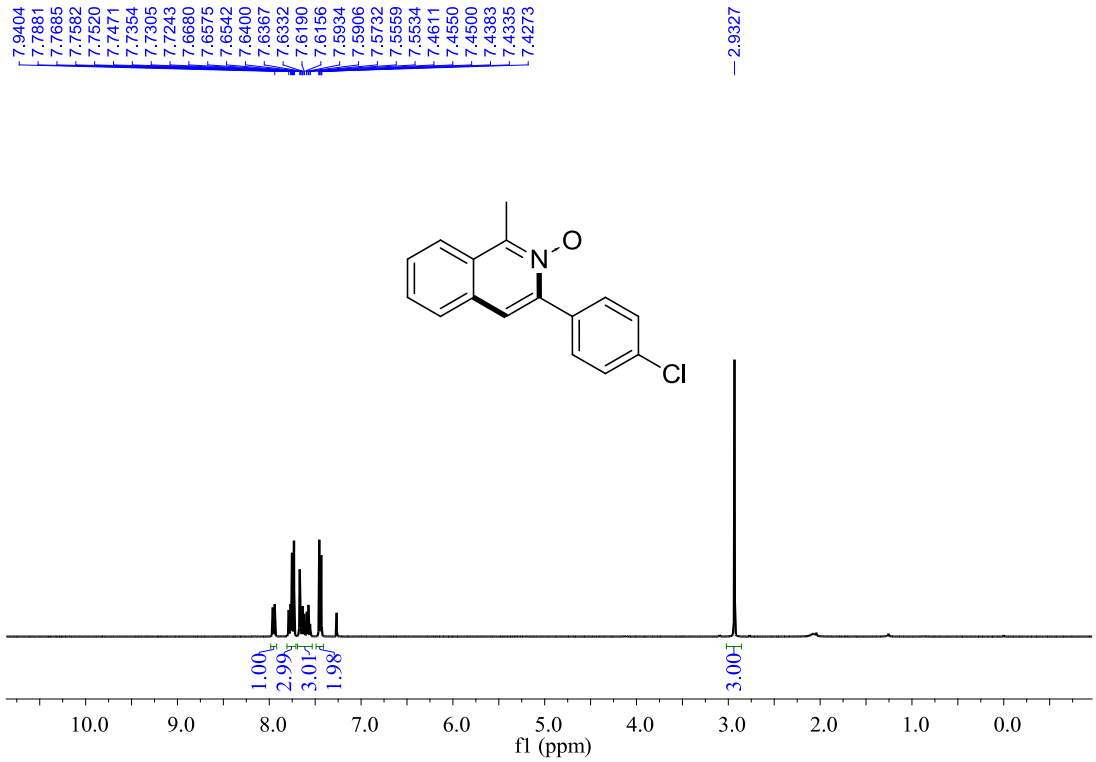
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5a.



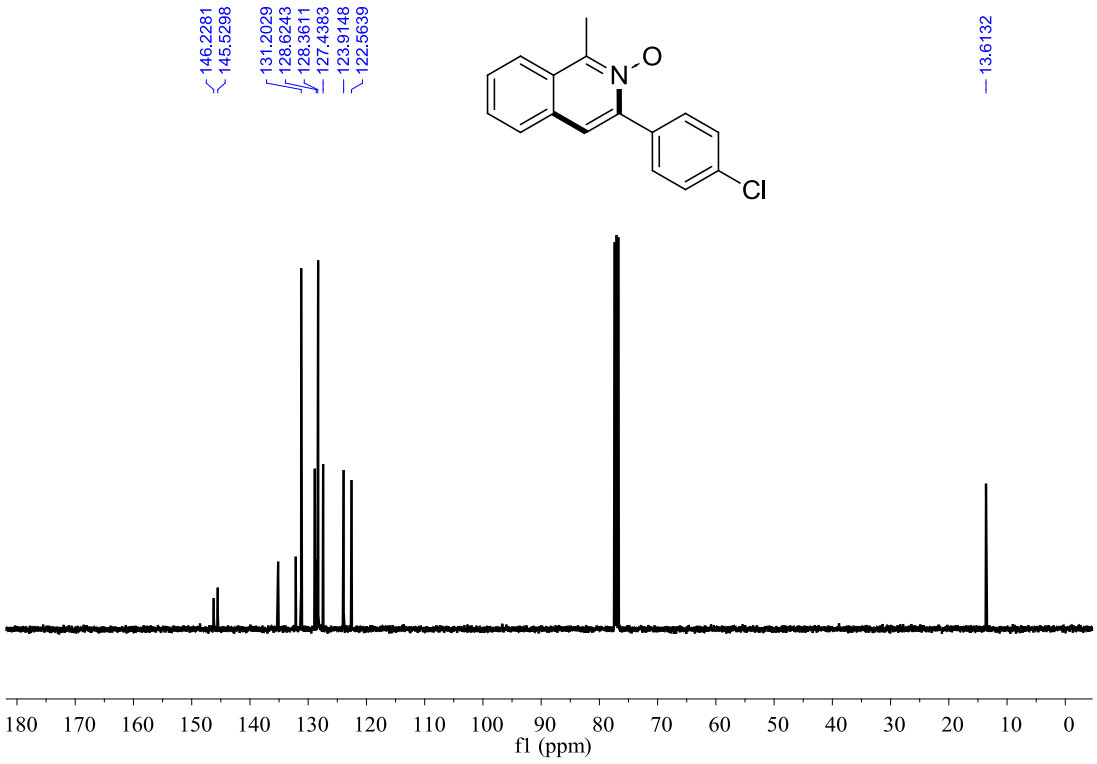
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5b.



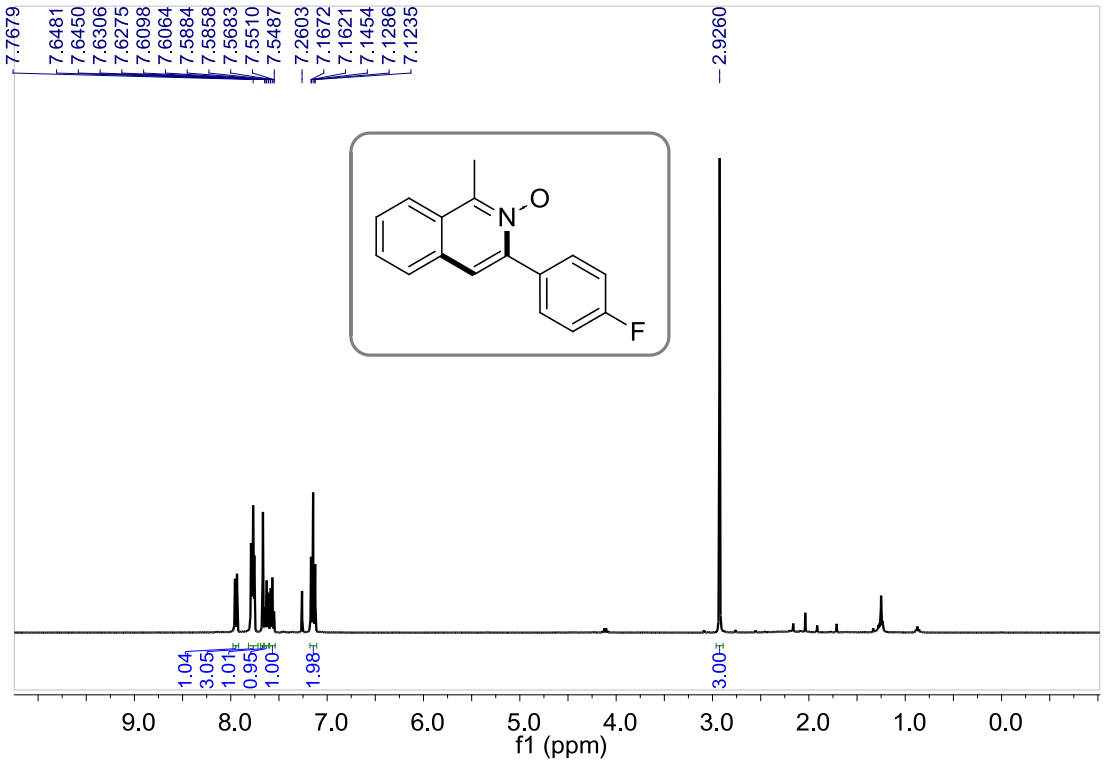
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5b.



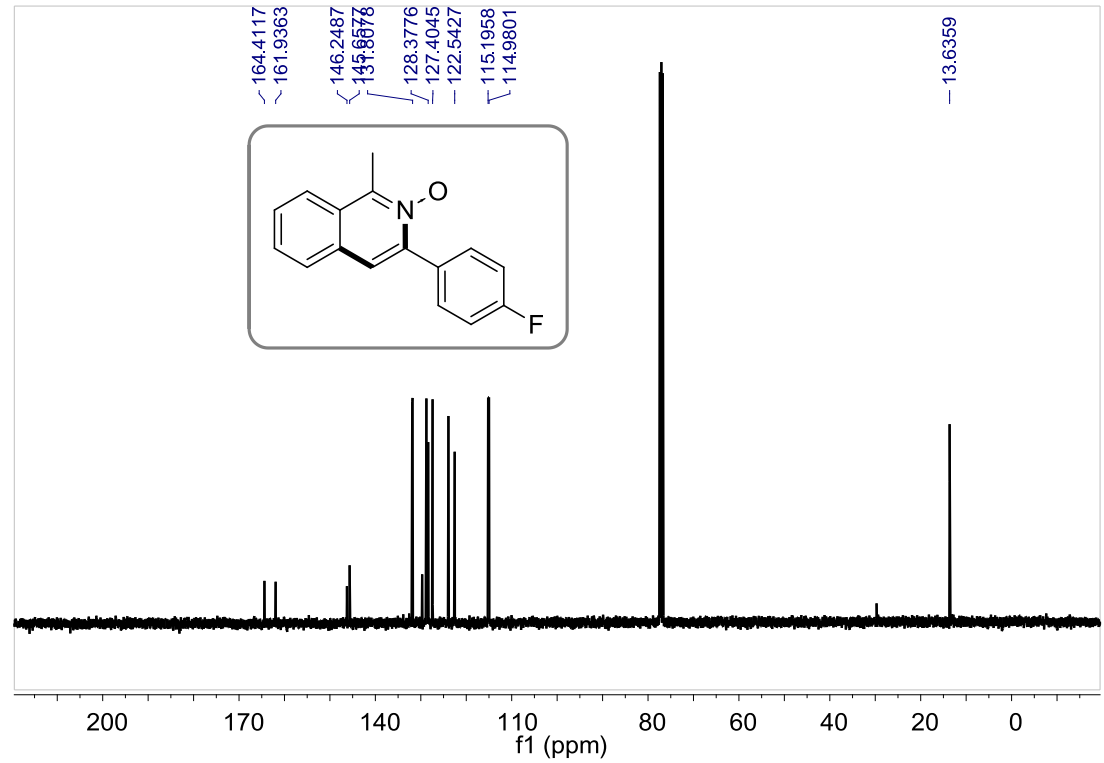
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5c.



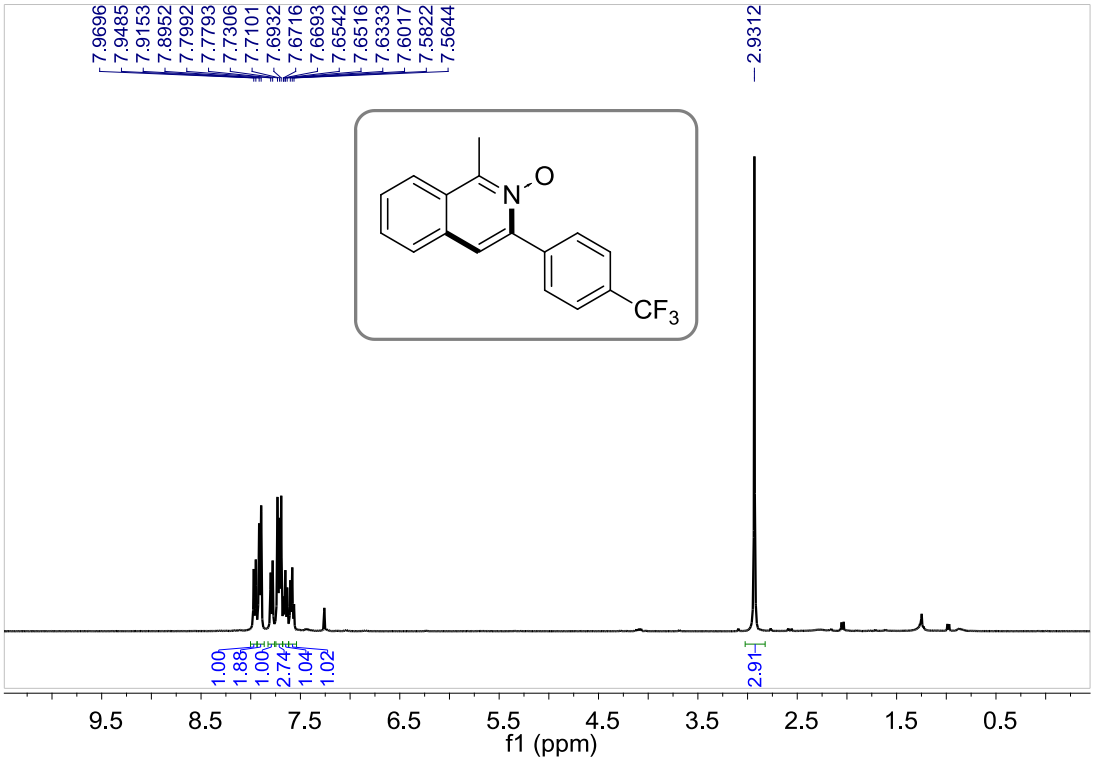
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5c.



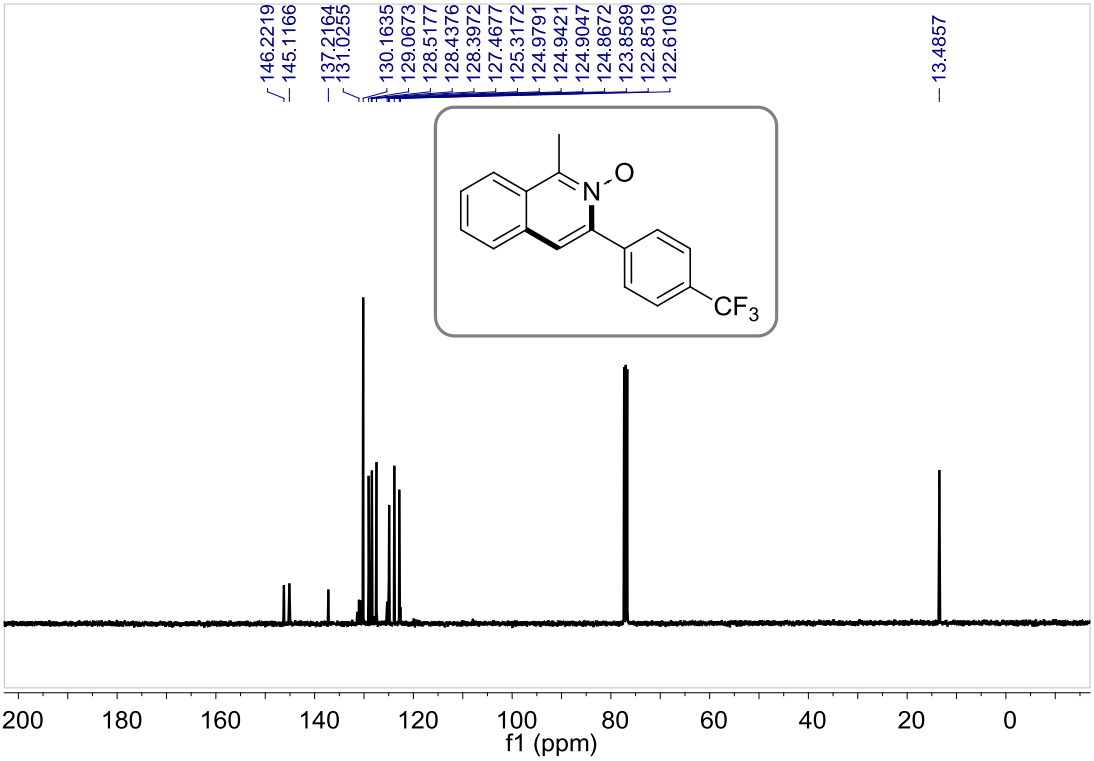
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5d.



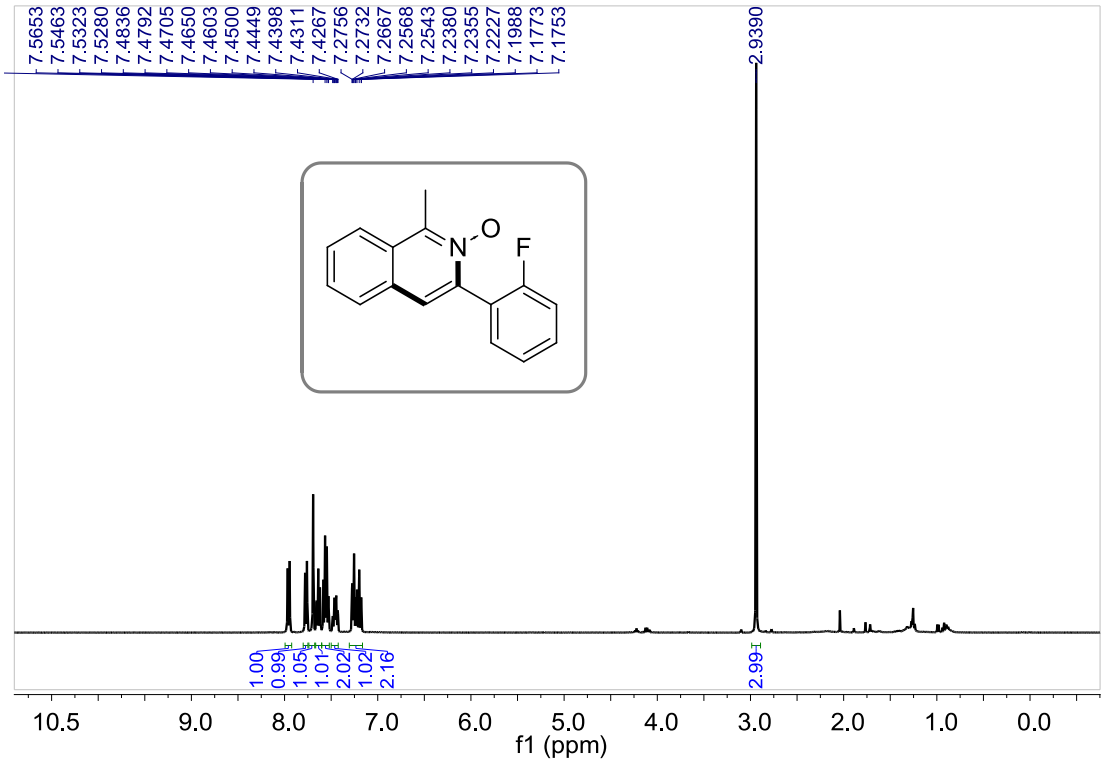
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5d.



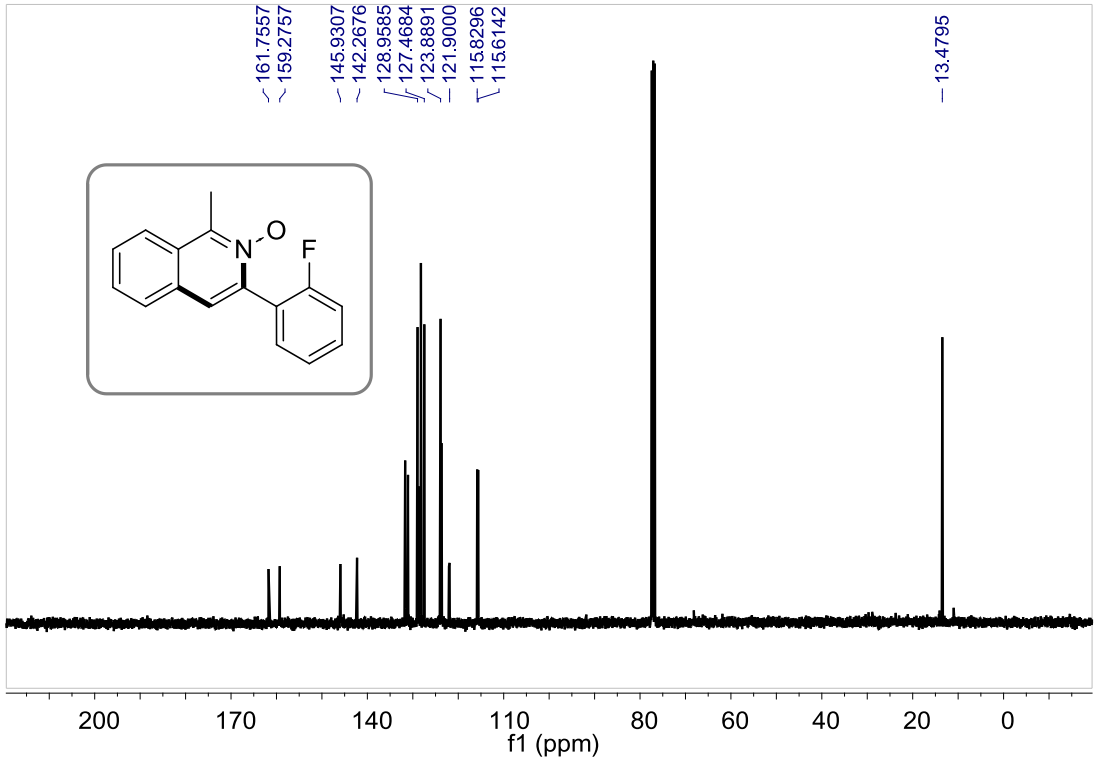
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5e.



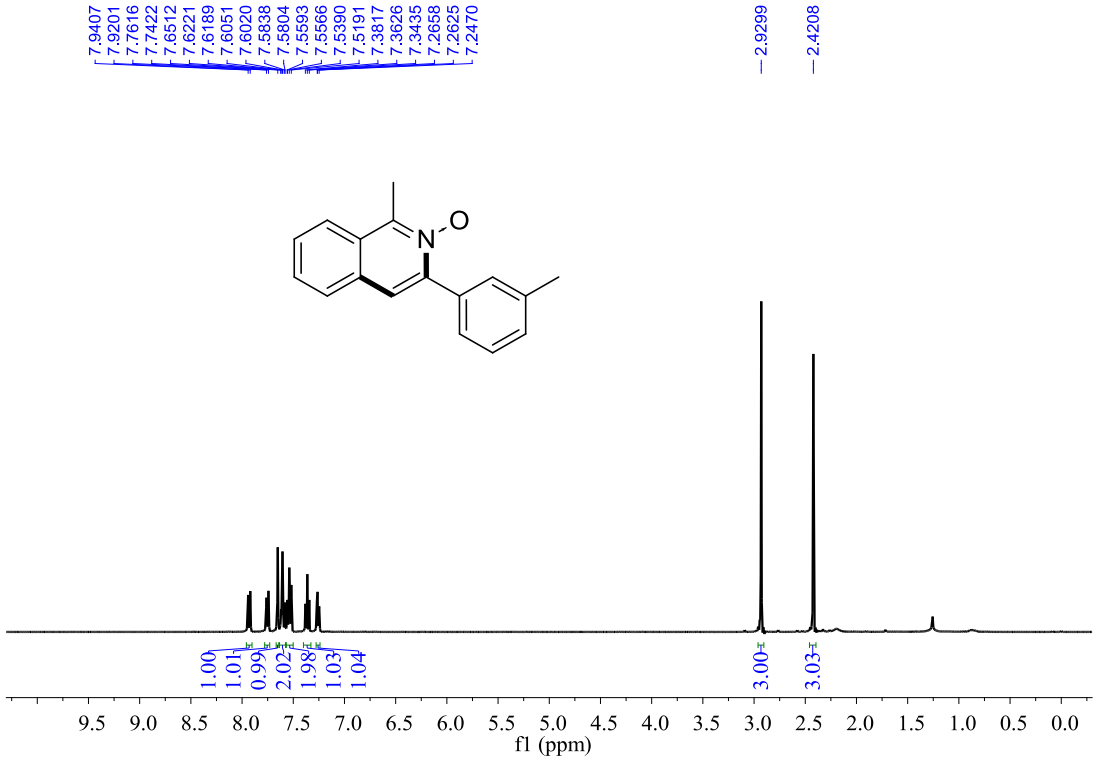
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5e.



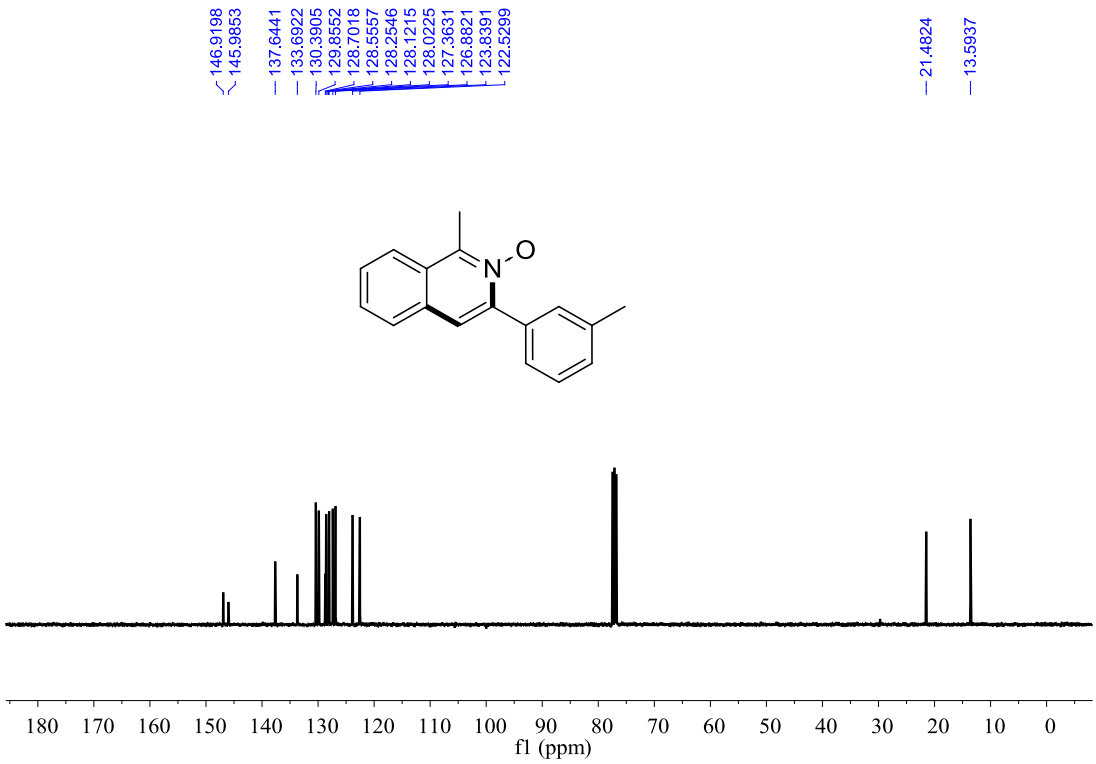
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5f.



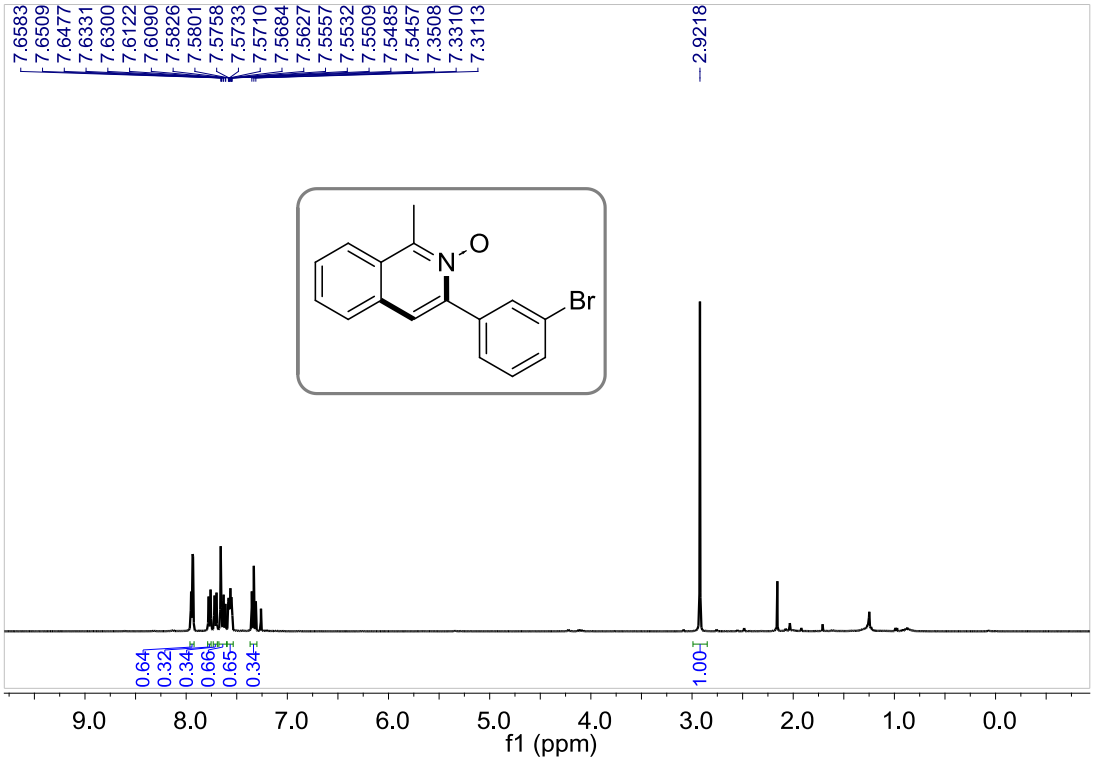
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5f.



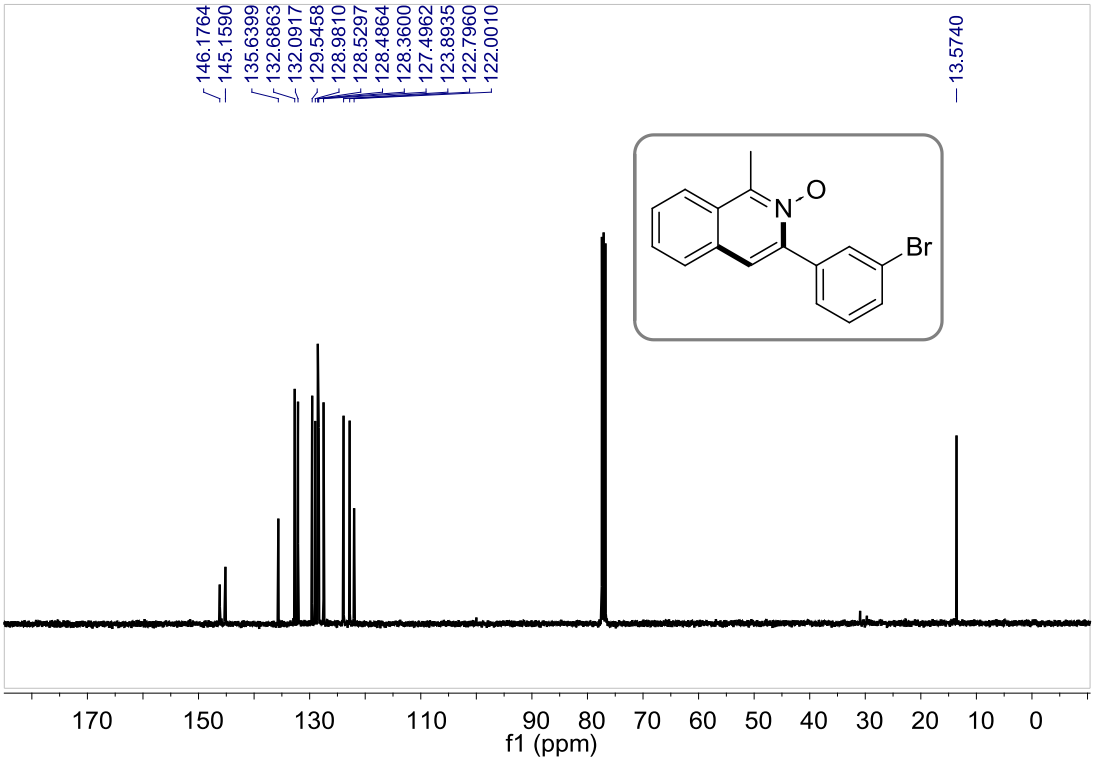
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5g.



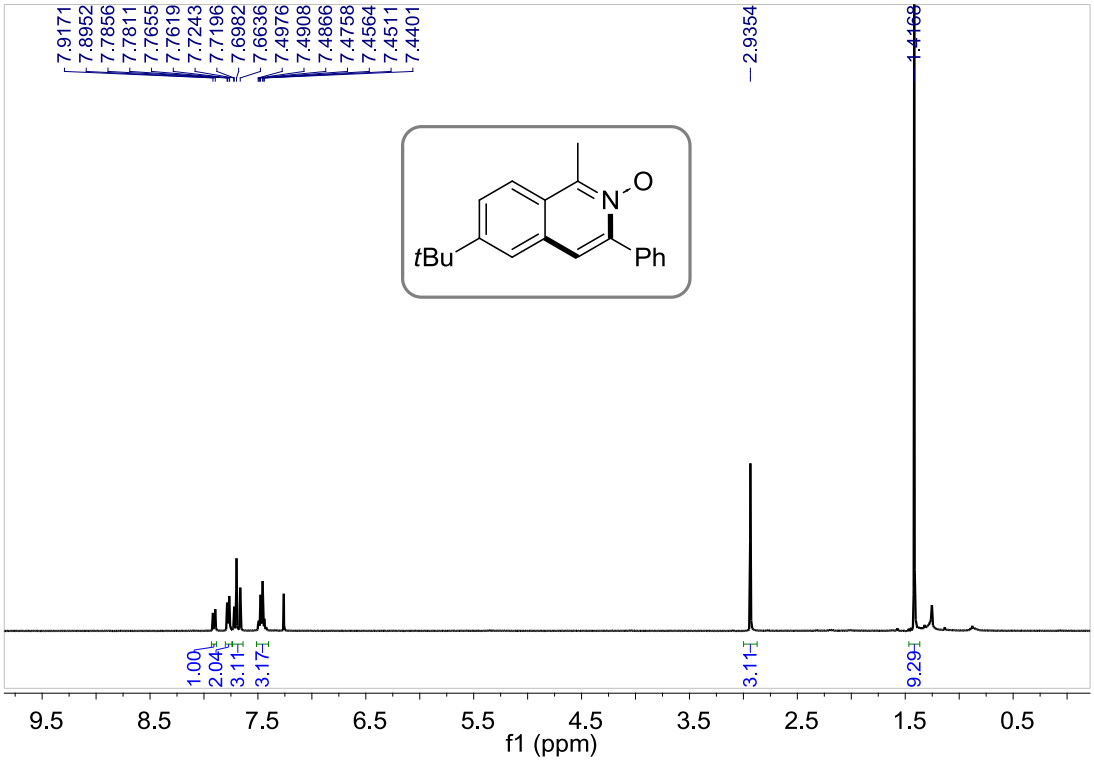
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5g.



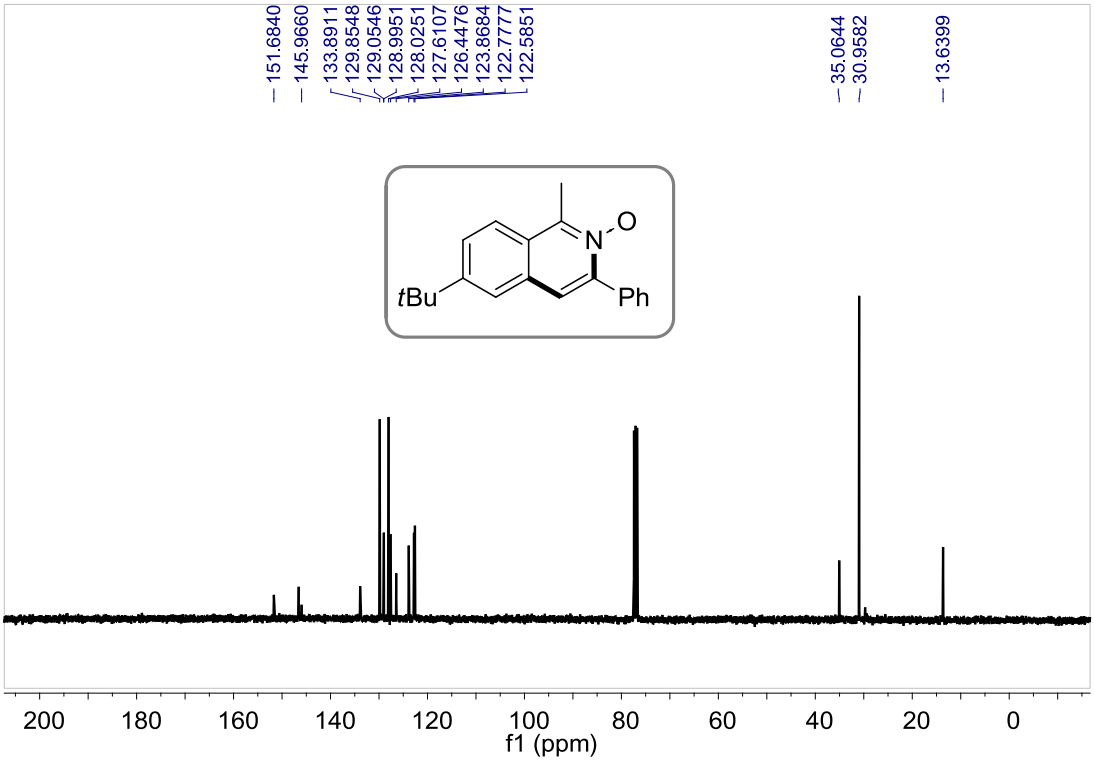
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5h.



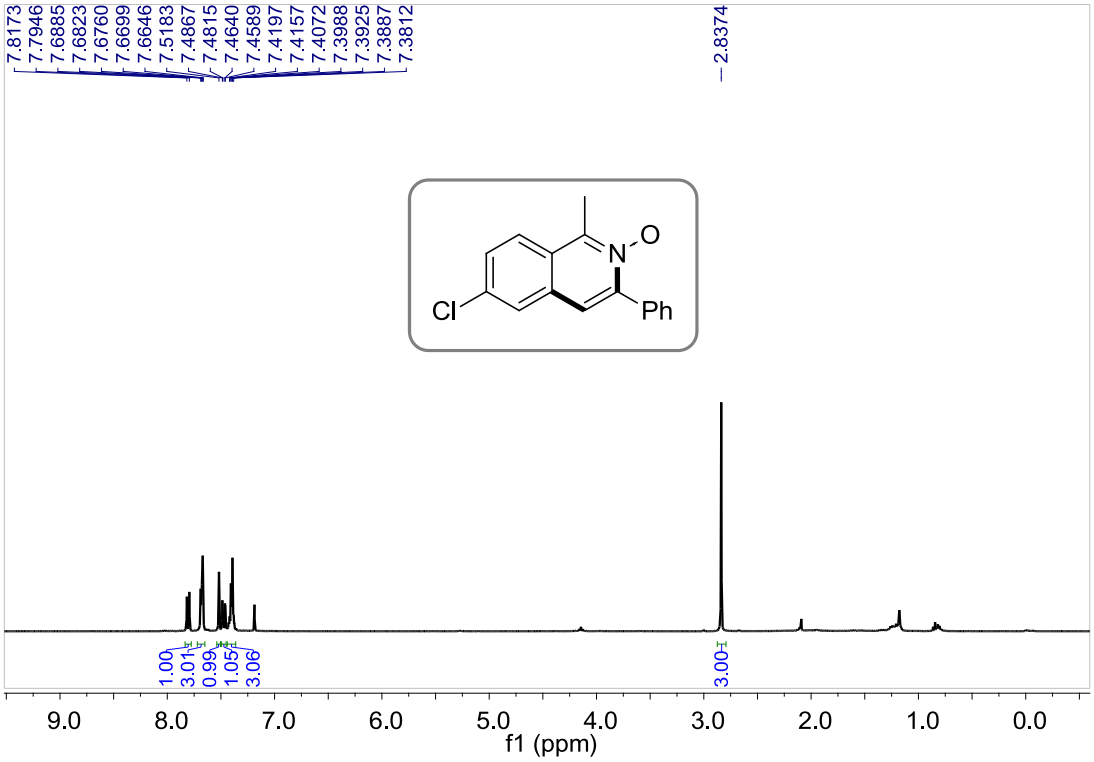
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5h.



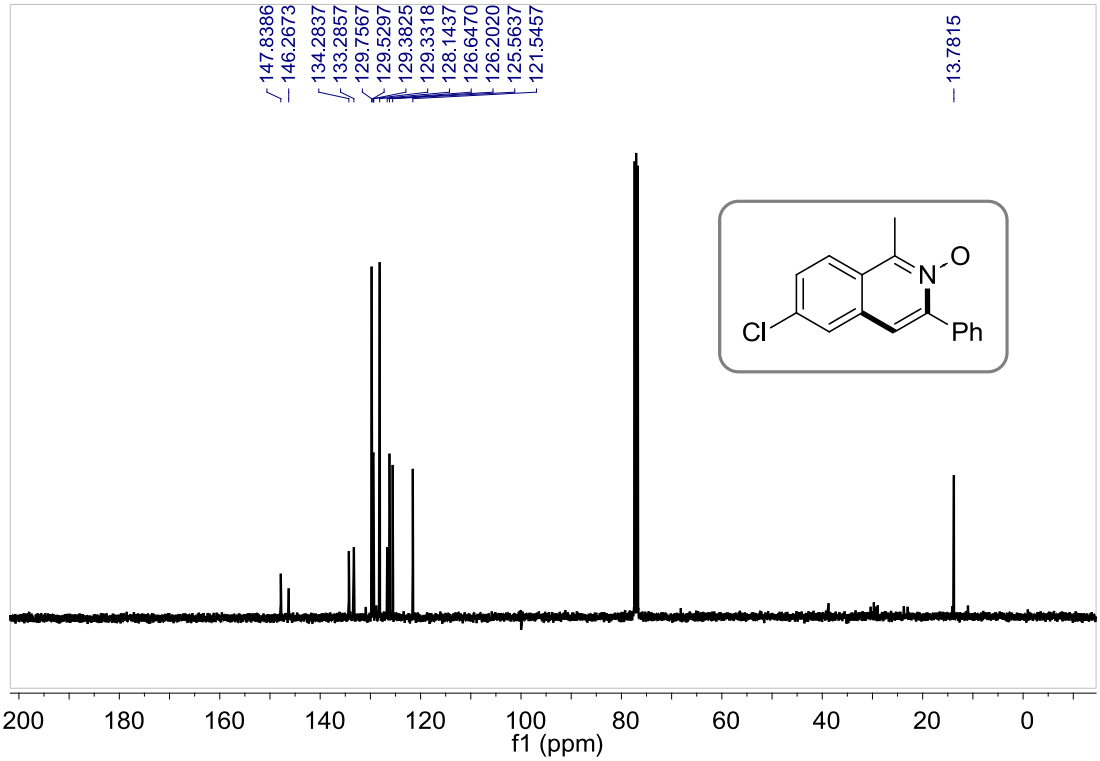
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5i.



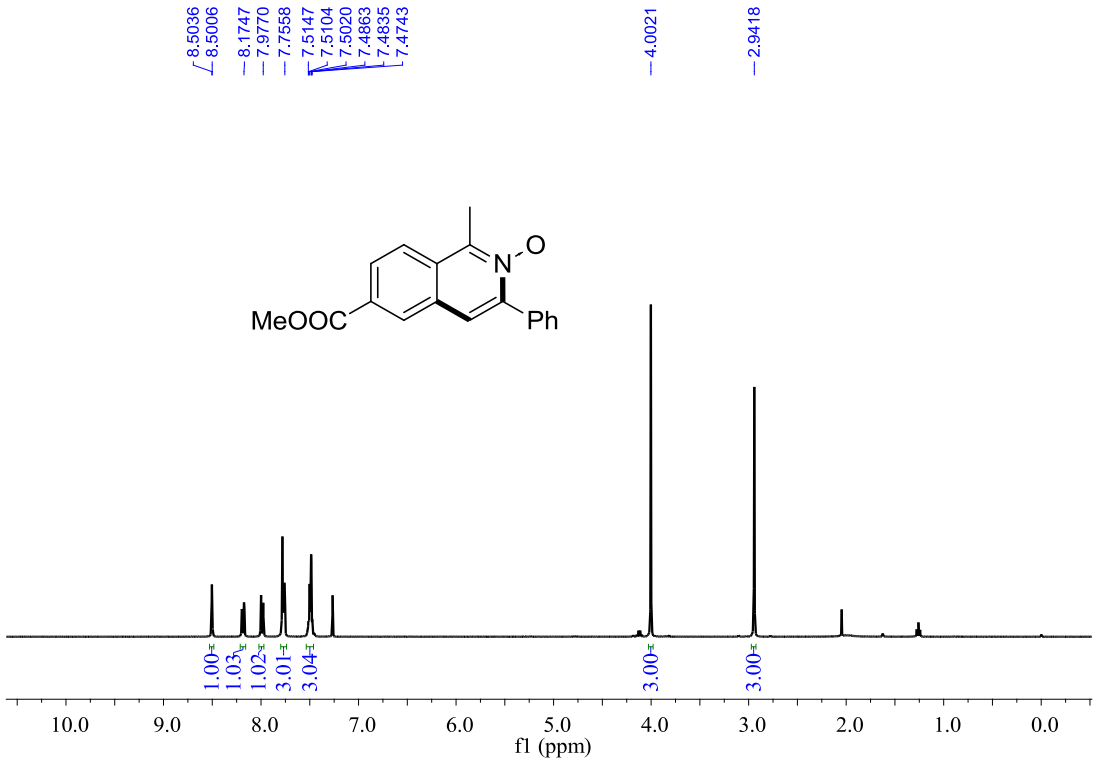
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5i.



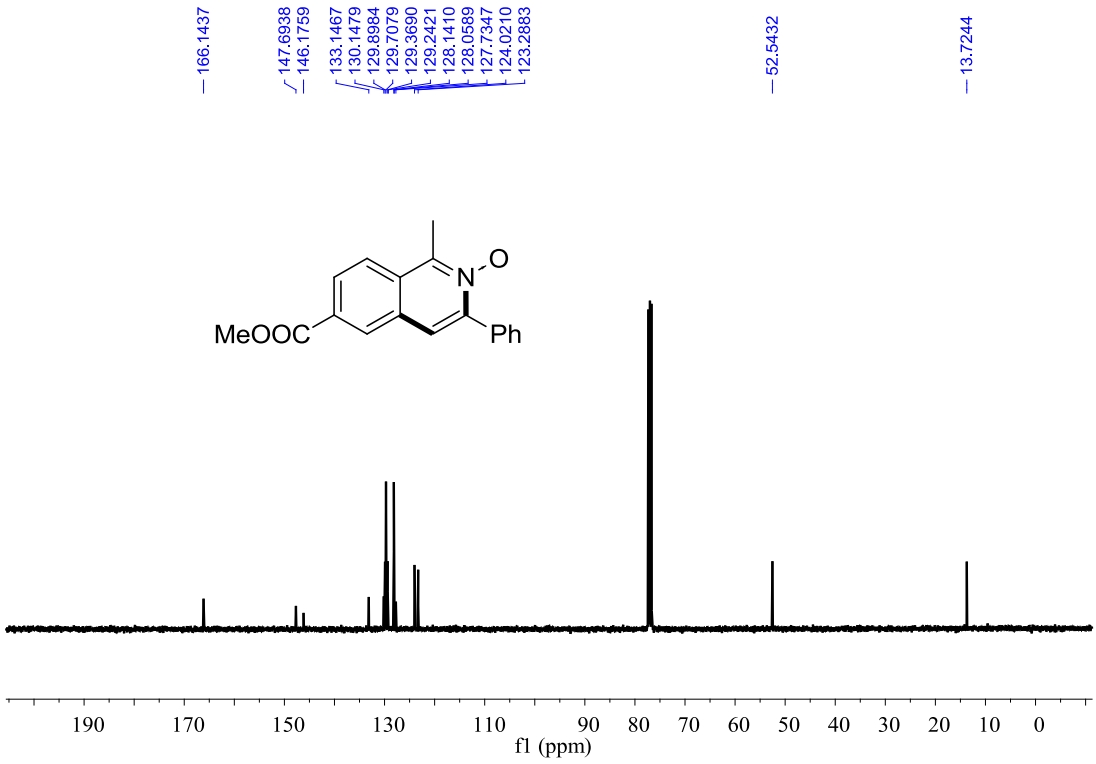
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5j.



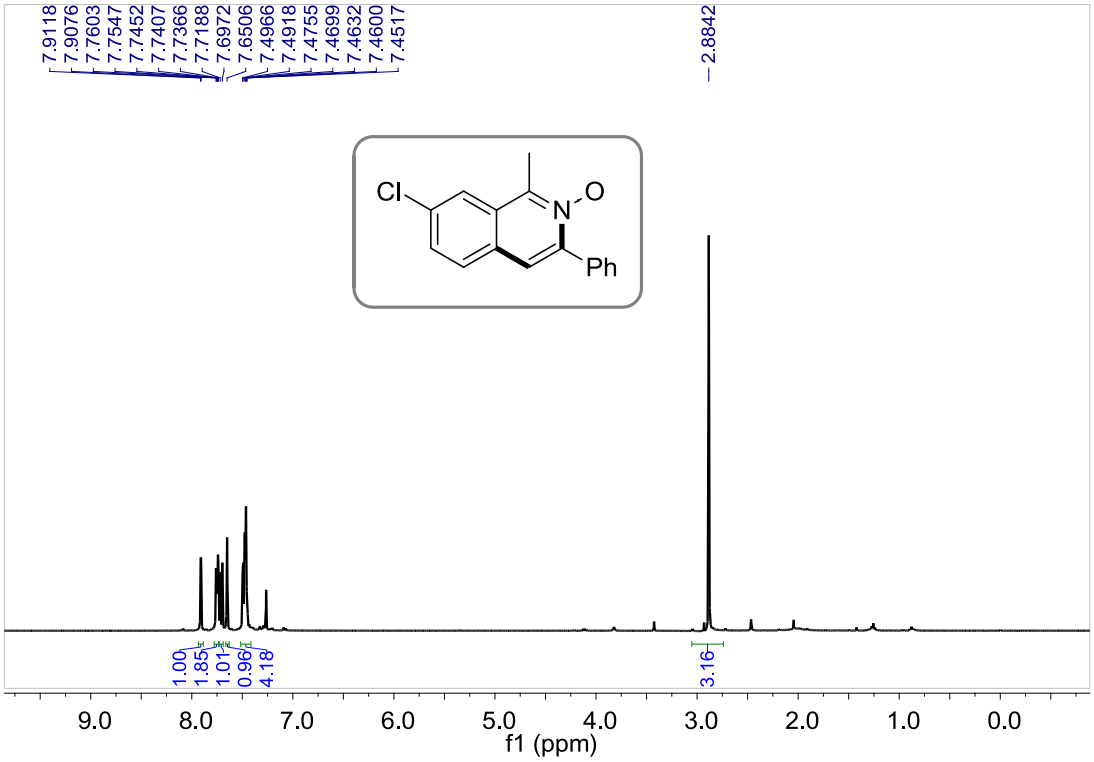
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5j



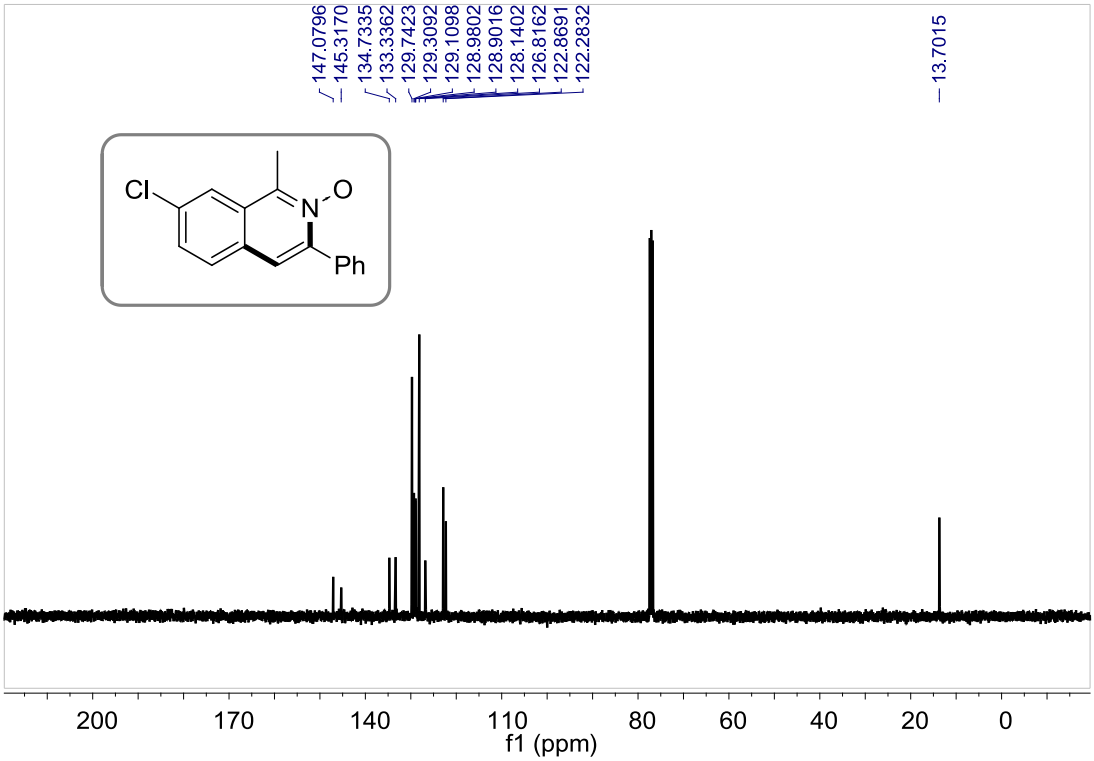
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5k.



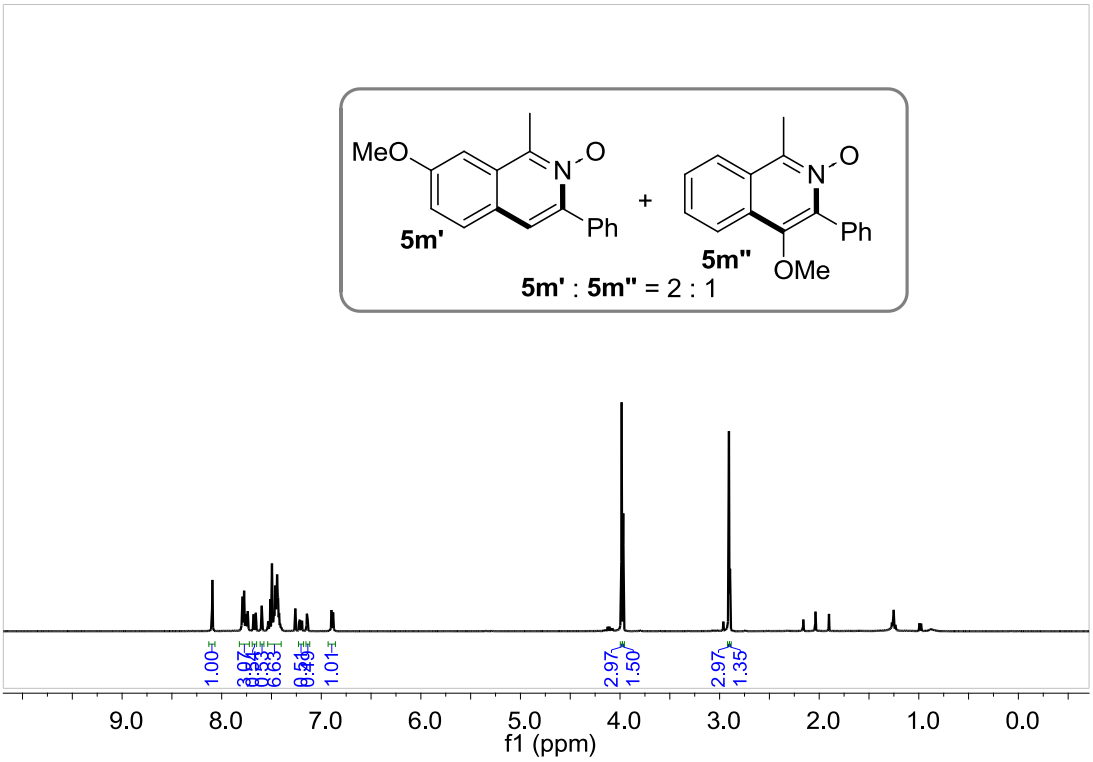
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5k.



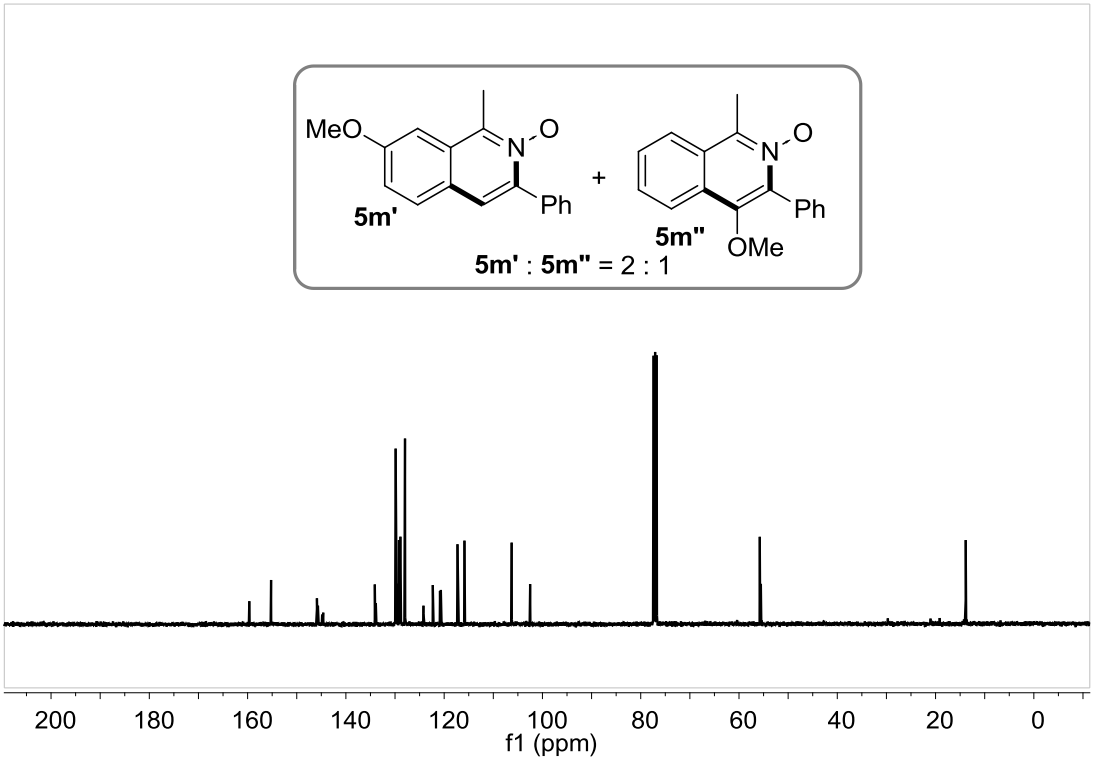
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5l.



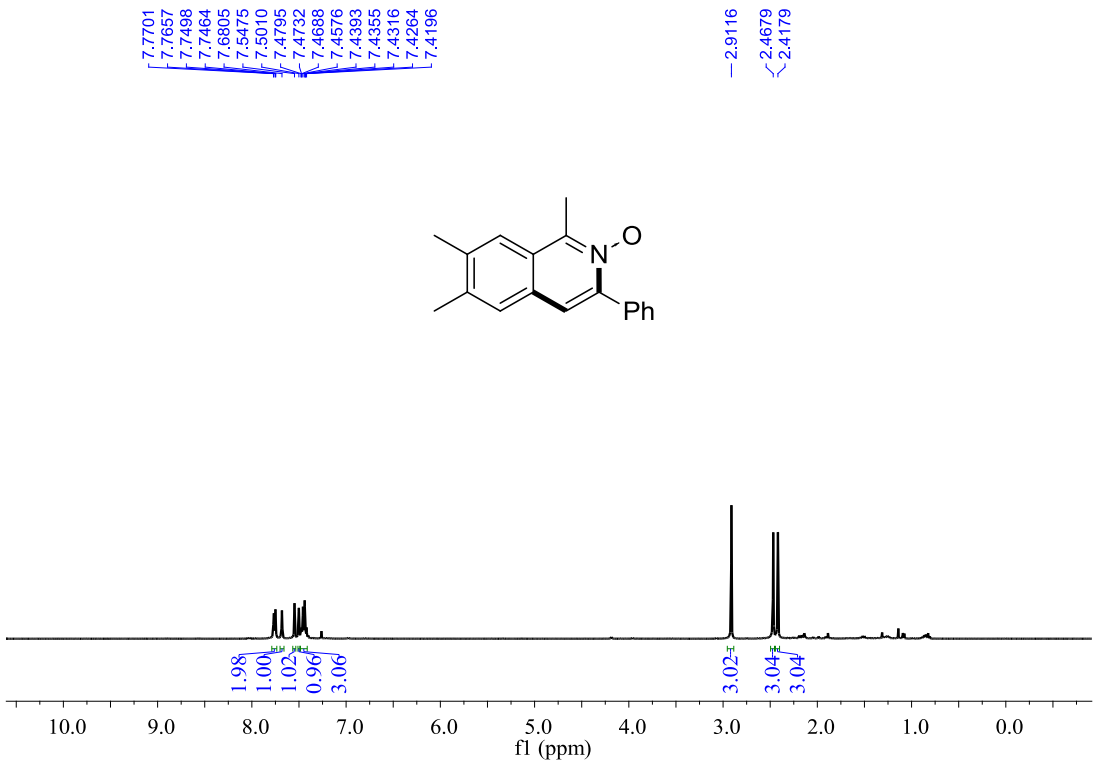
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5l.



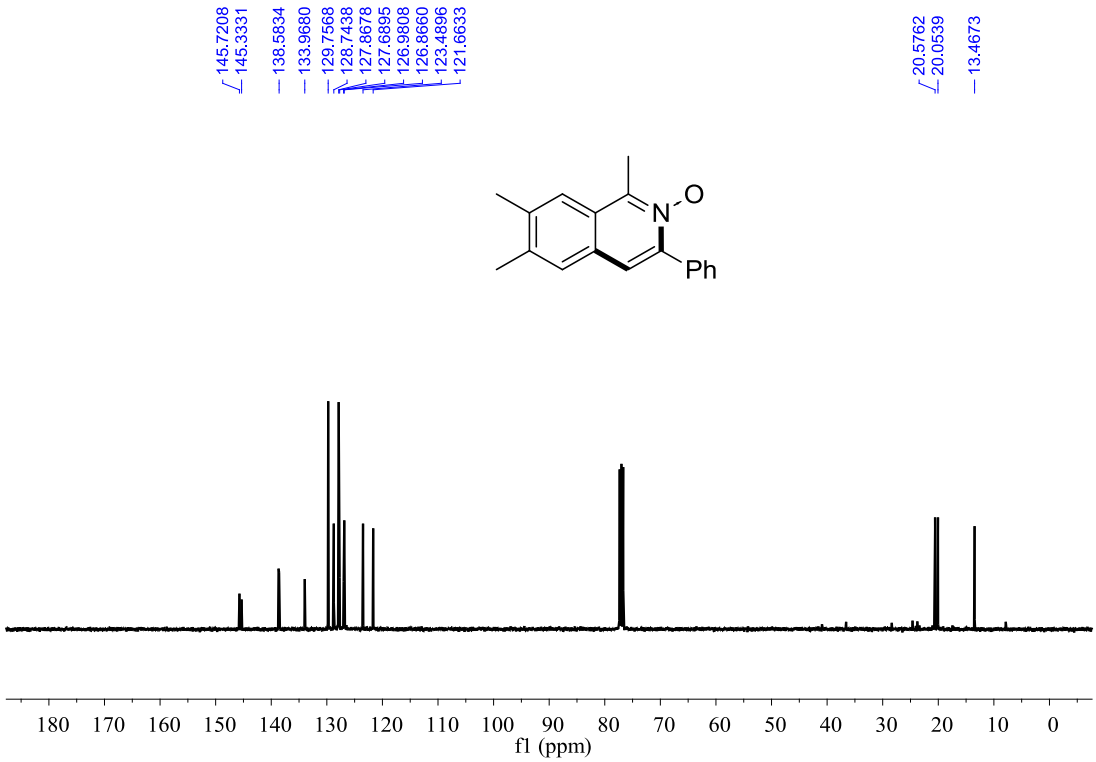
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5m.



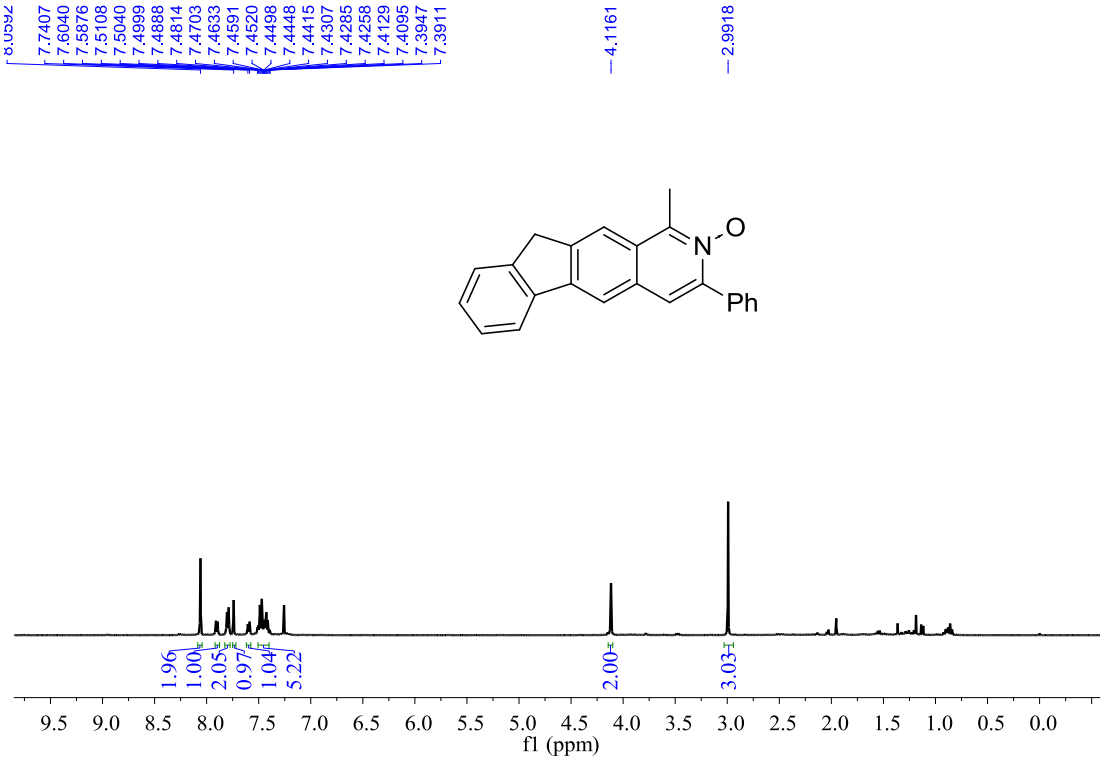
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5m.



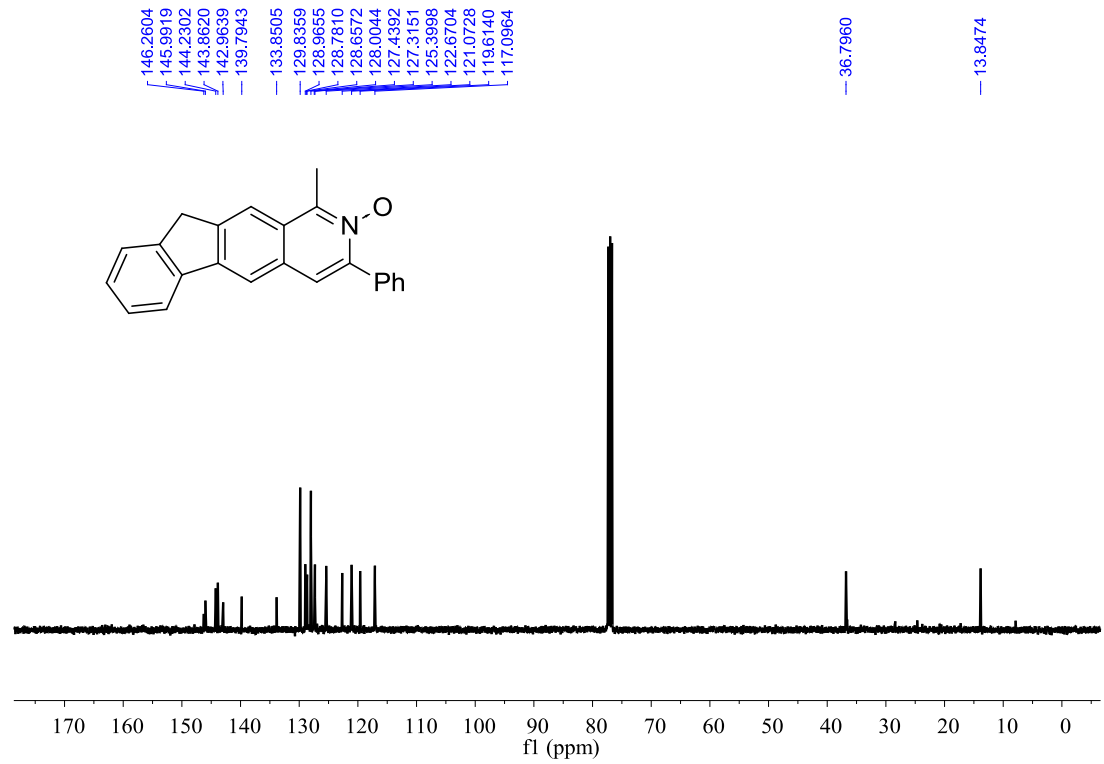
^{1}H NMR (400MHz, $CDCl_3$) spectrum for 5n.



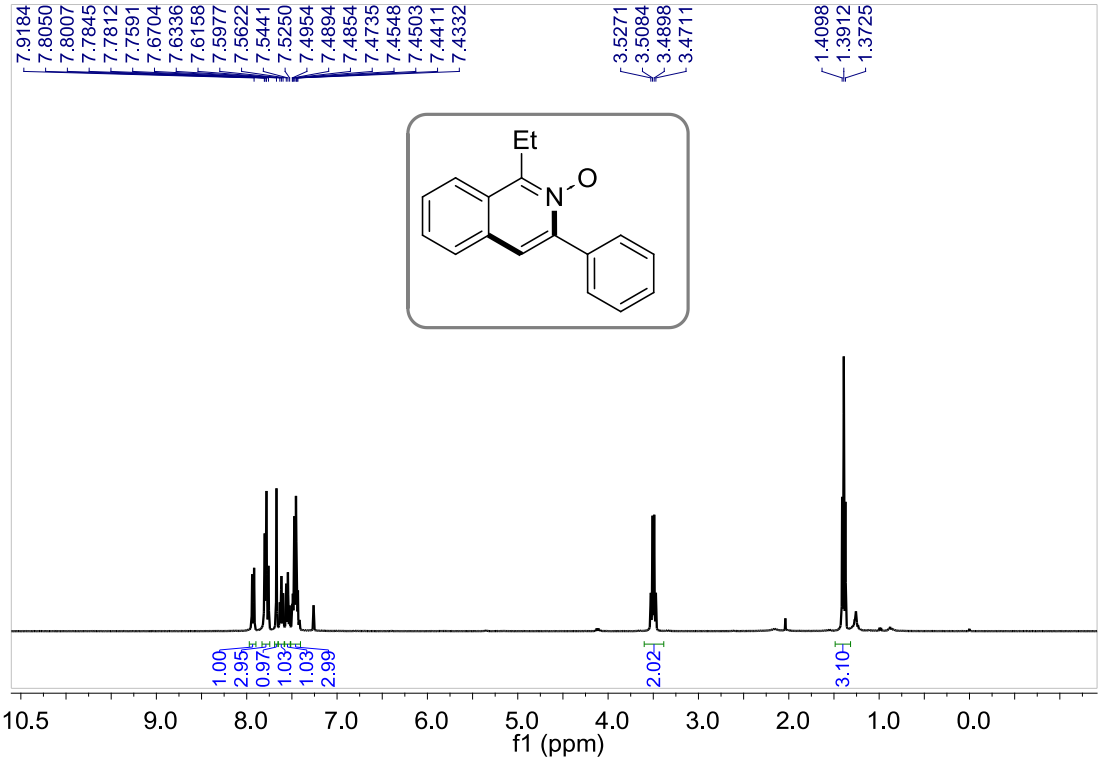
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5n.



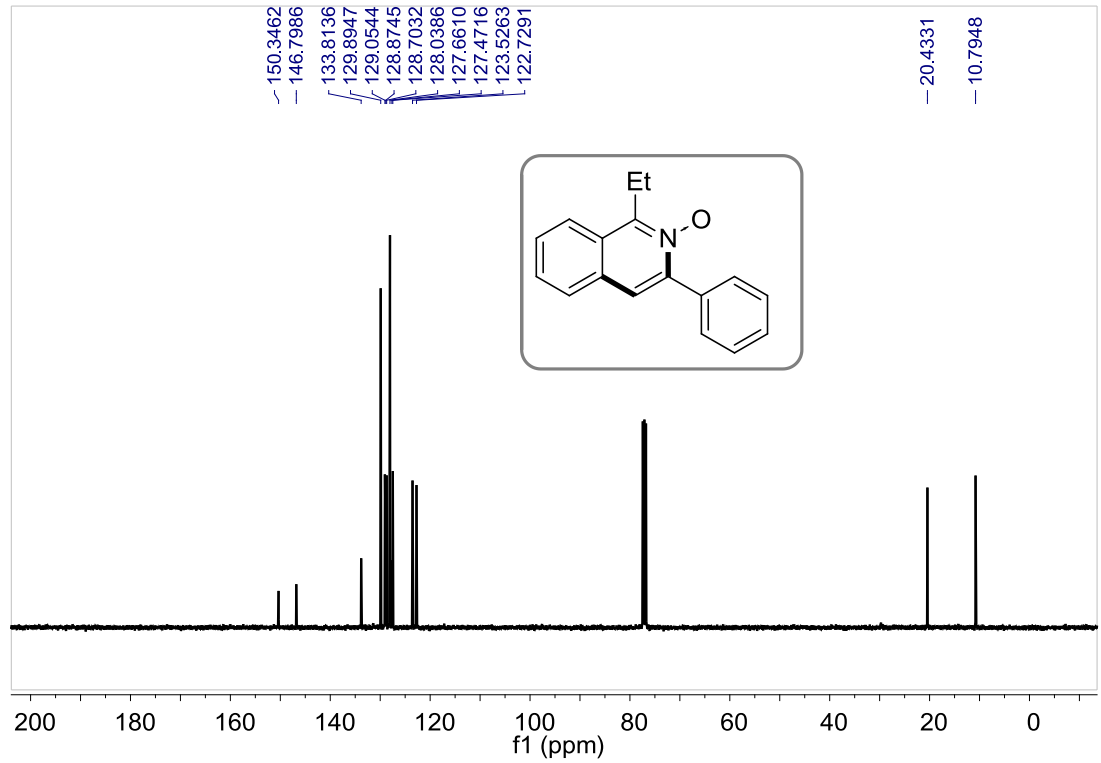
^{1}H NMR (400MHz, $CDCl_3$) spectrum for5o.



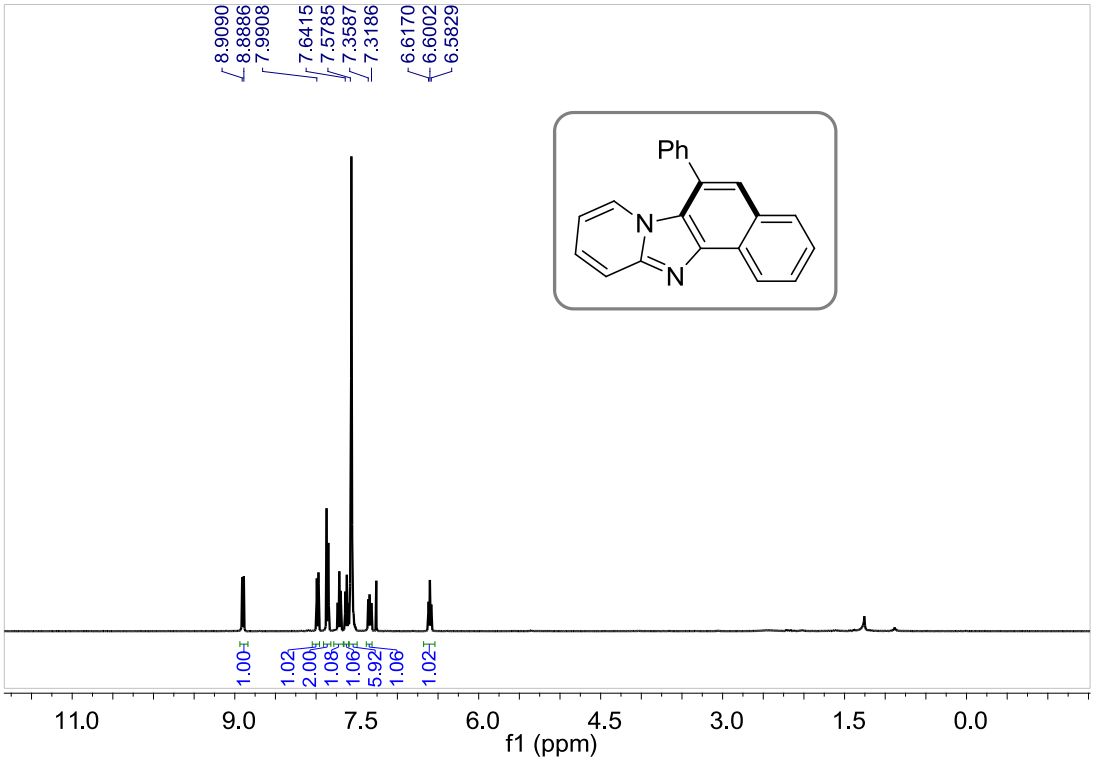
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5o.



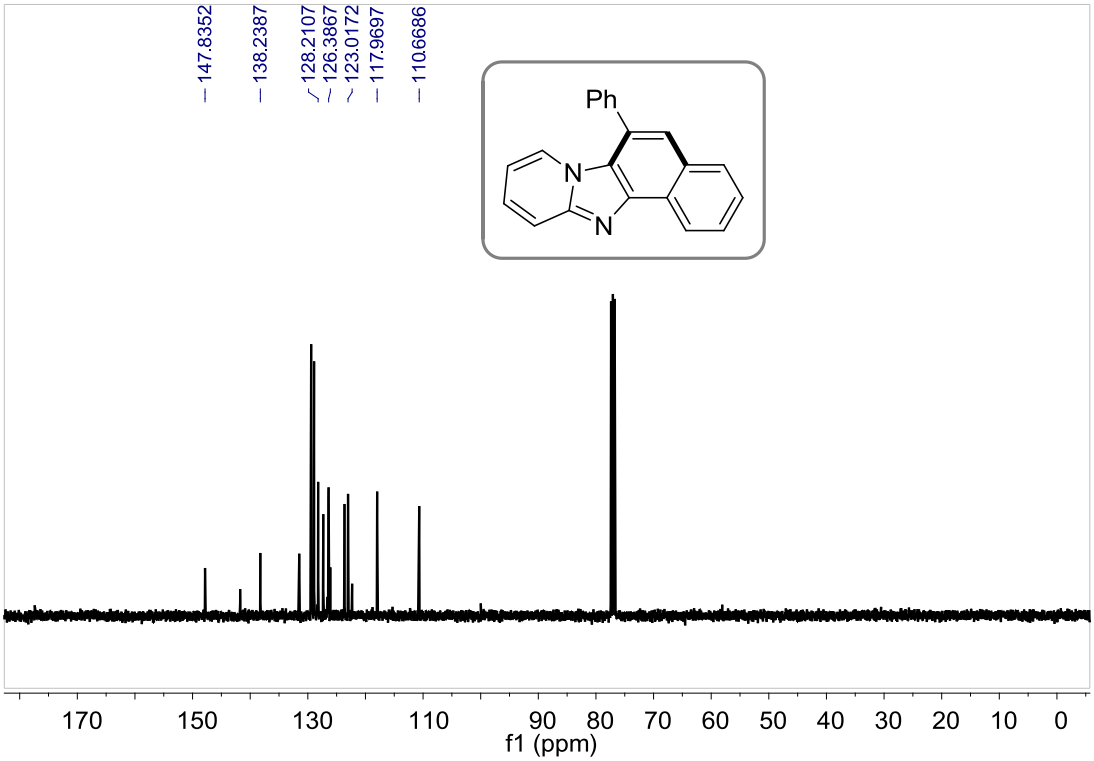
^{1}H NMR (400MHz, $CDCl_3$) spectrum for5p.



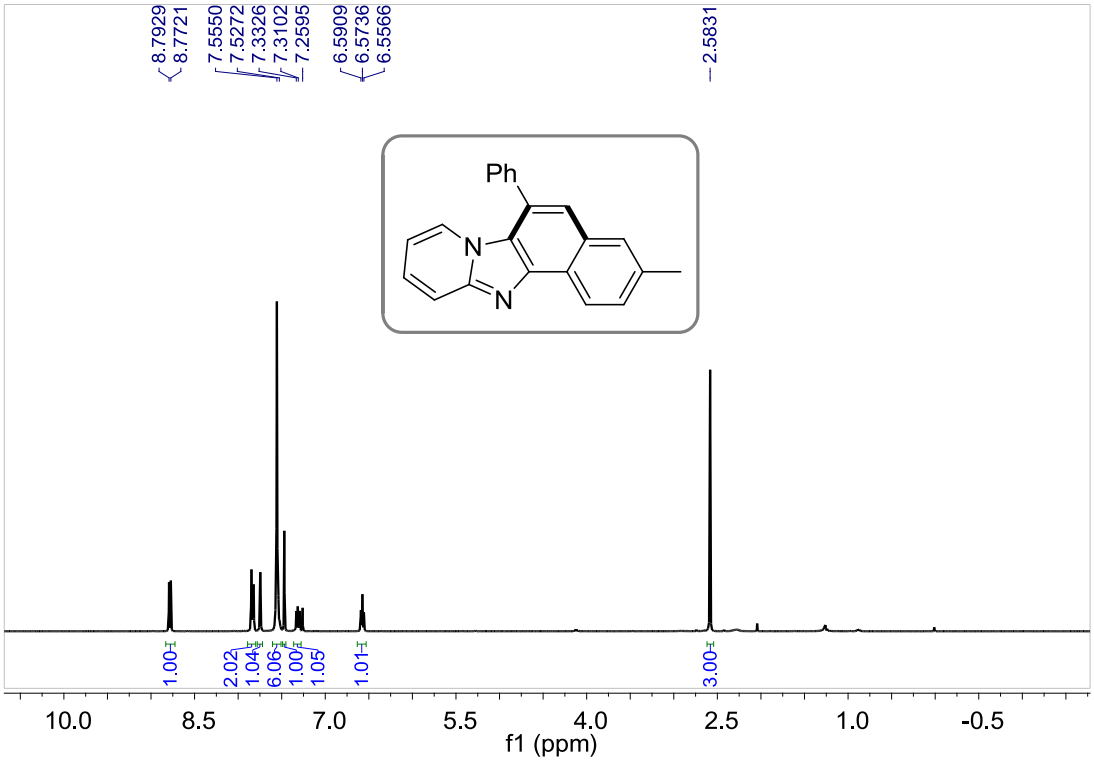
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 5p.



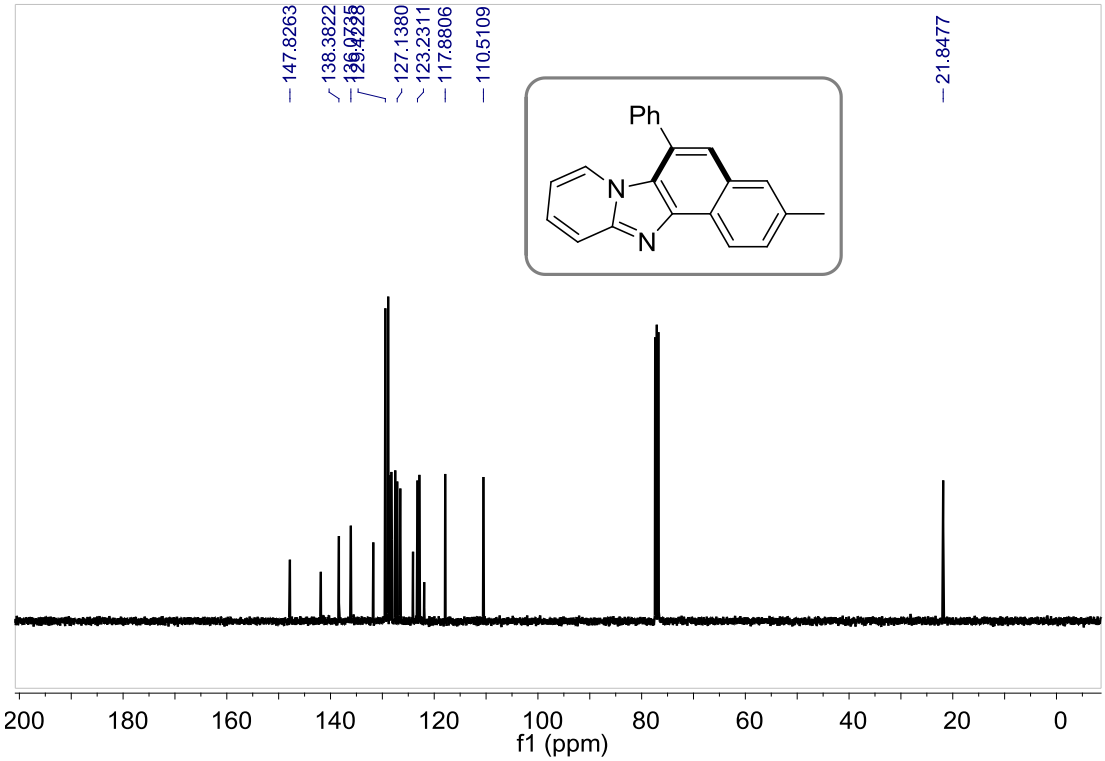
^{1}H NMR (400MHz, $CDCl_3$) spectrum for7a.



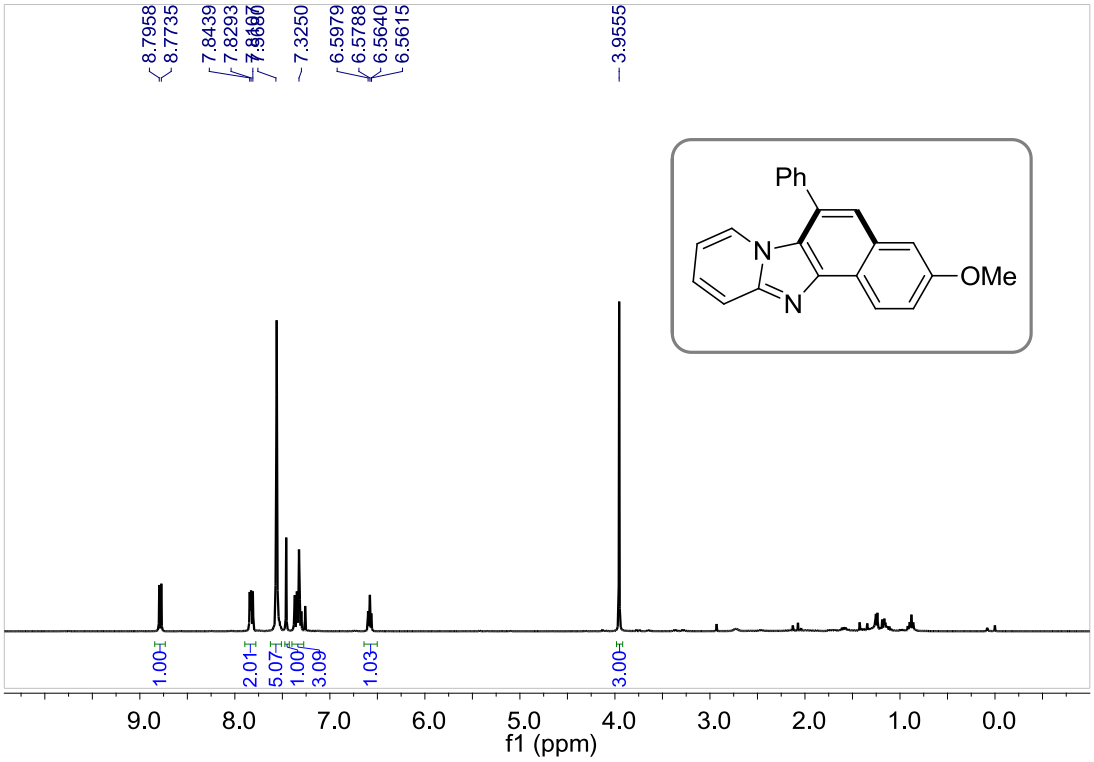
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 7a.



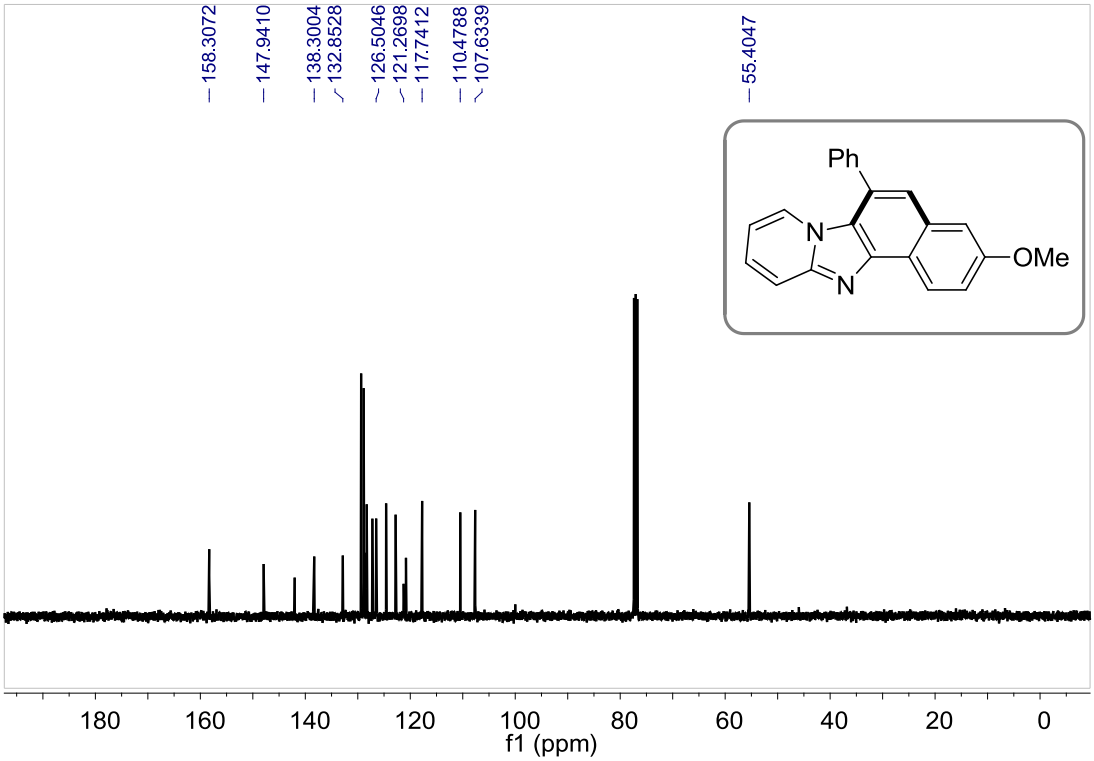
^{1}H NMR (400MHz, $CDCl_3$) spectrum for7b.



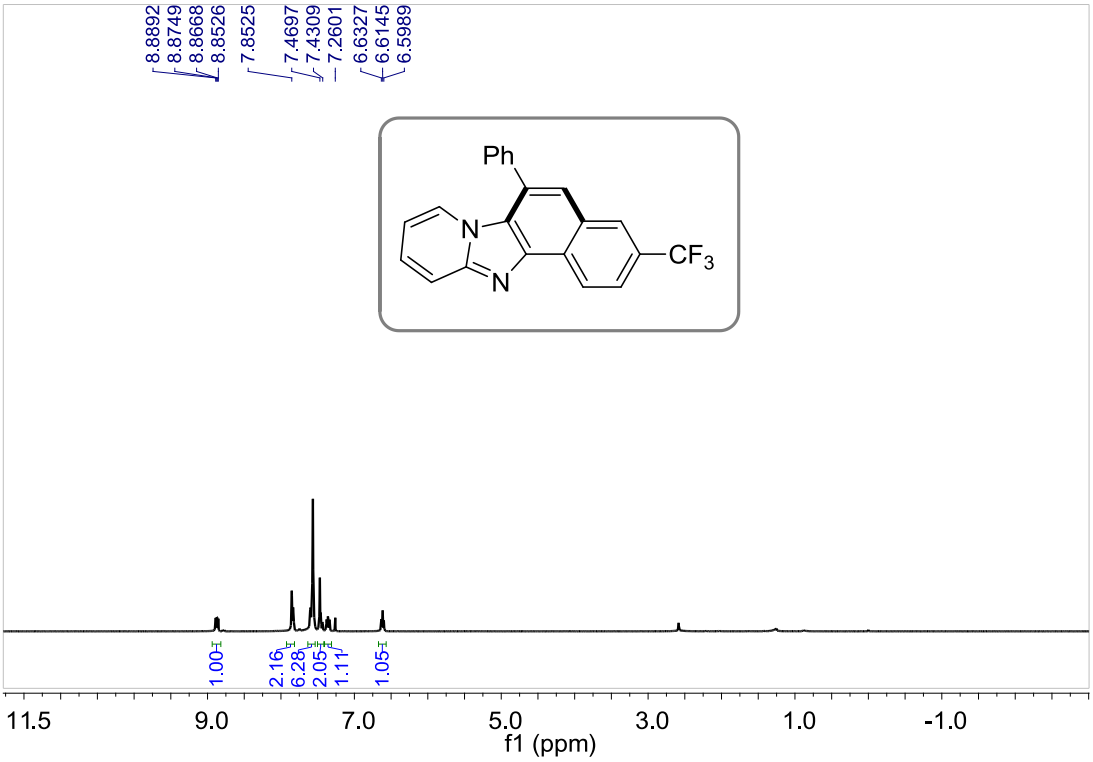
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 7b



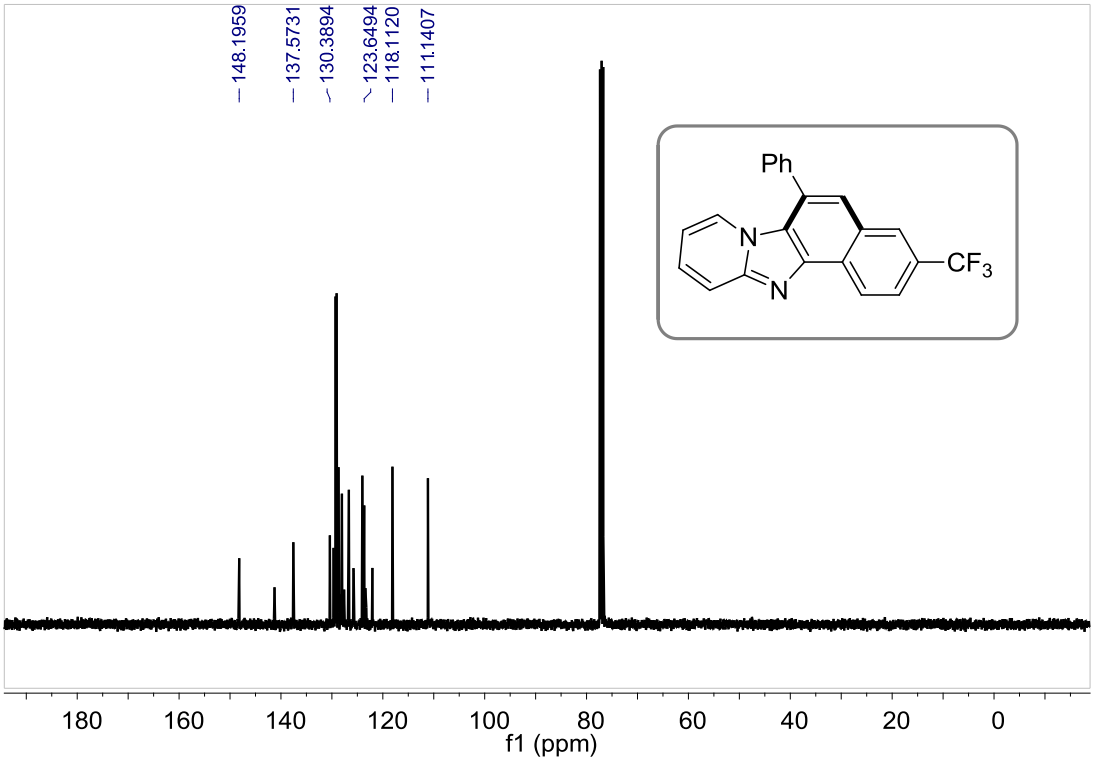
^{1}H NMR (400MHz, $CDCl_3$) spectrum for7c.



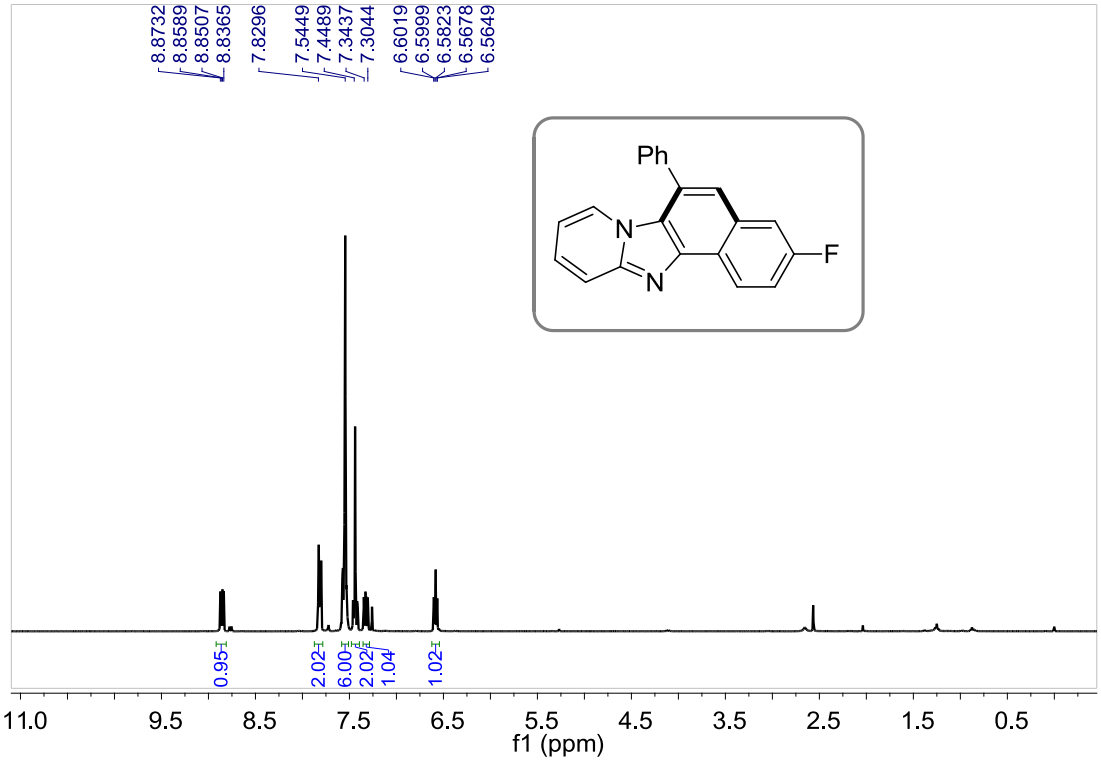
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 7c.



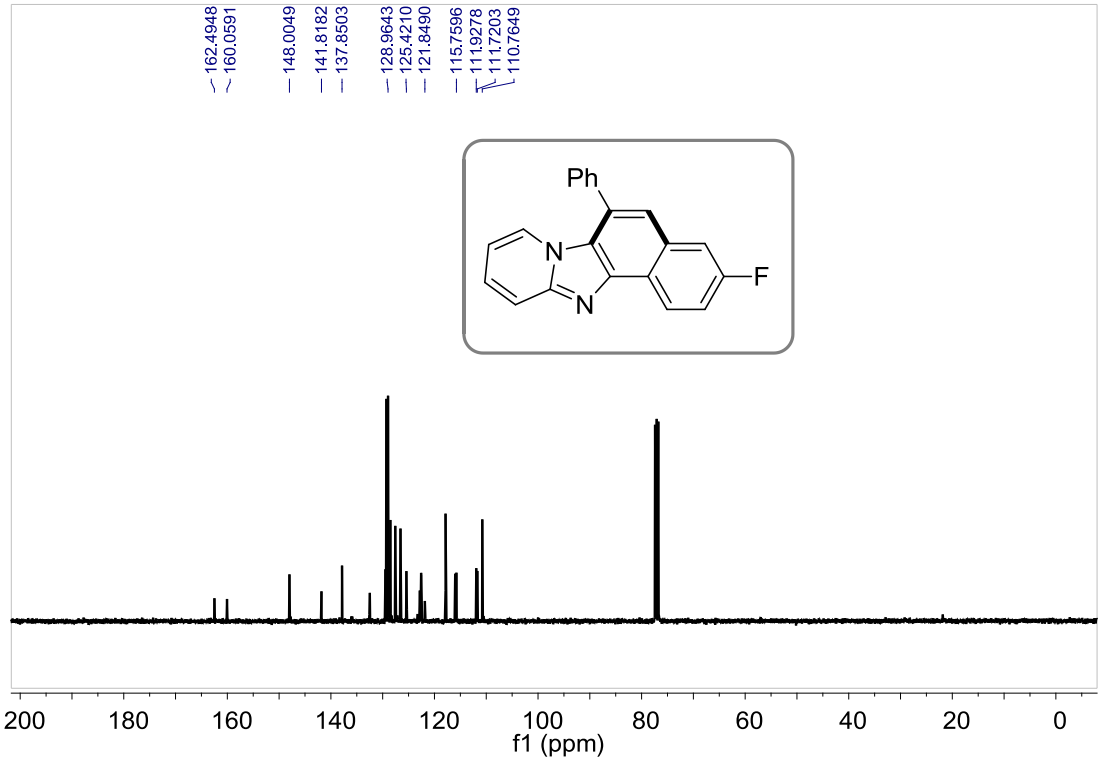
^{1}H NMR (400MHz, $CDCl_3$) spectrum for7d



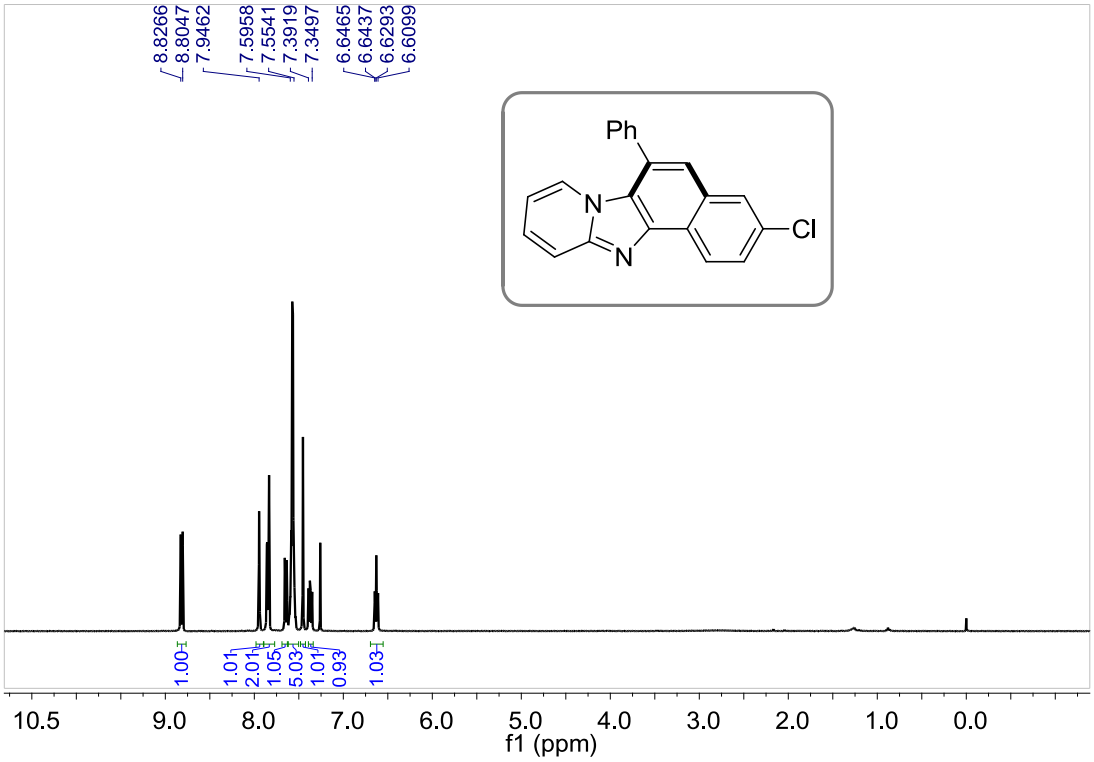
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 7d.



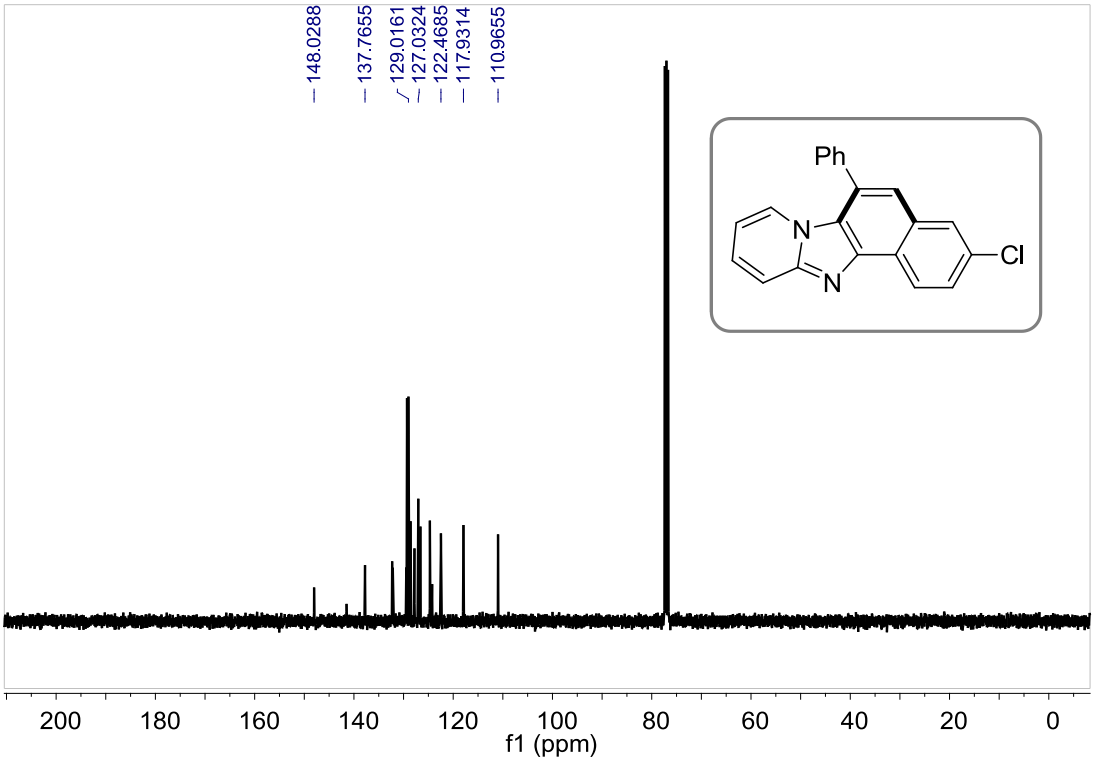
^{1}H NMR (400MHz, $CDCl_3$) spectrum for7e.



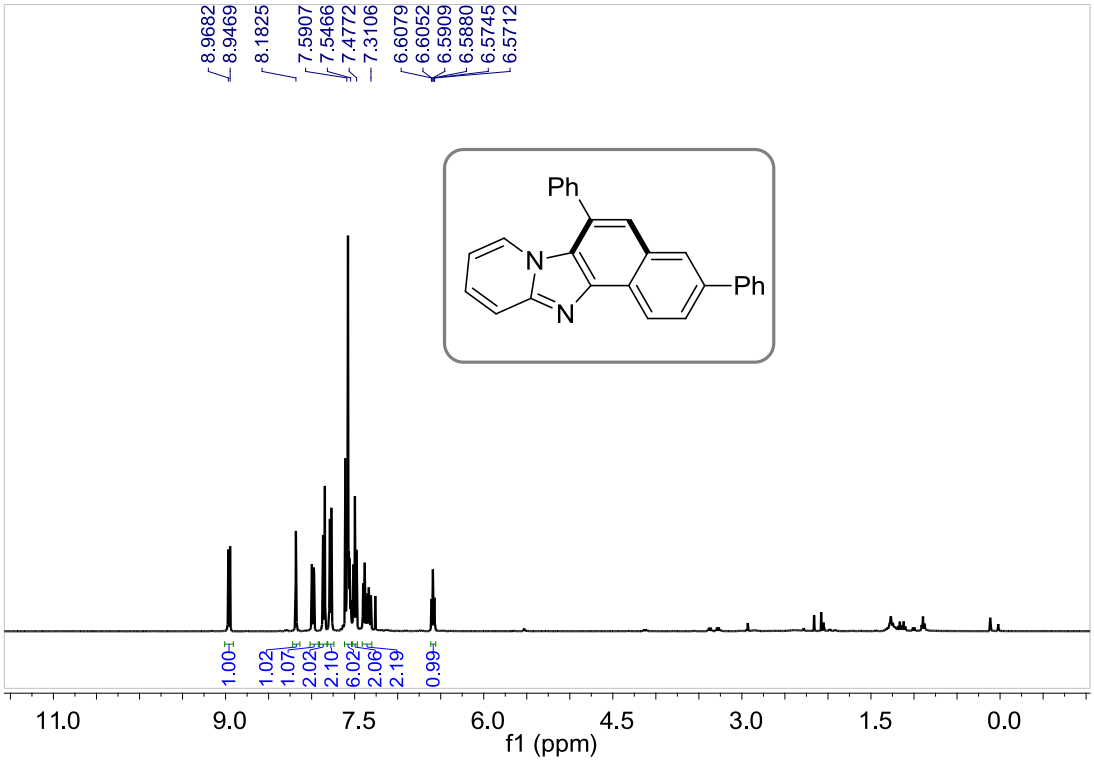
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 7e.



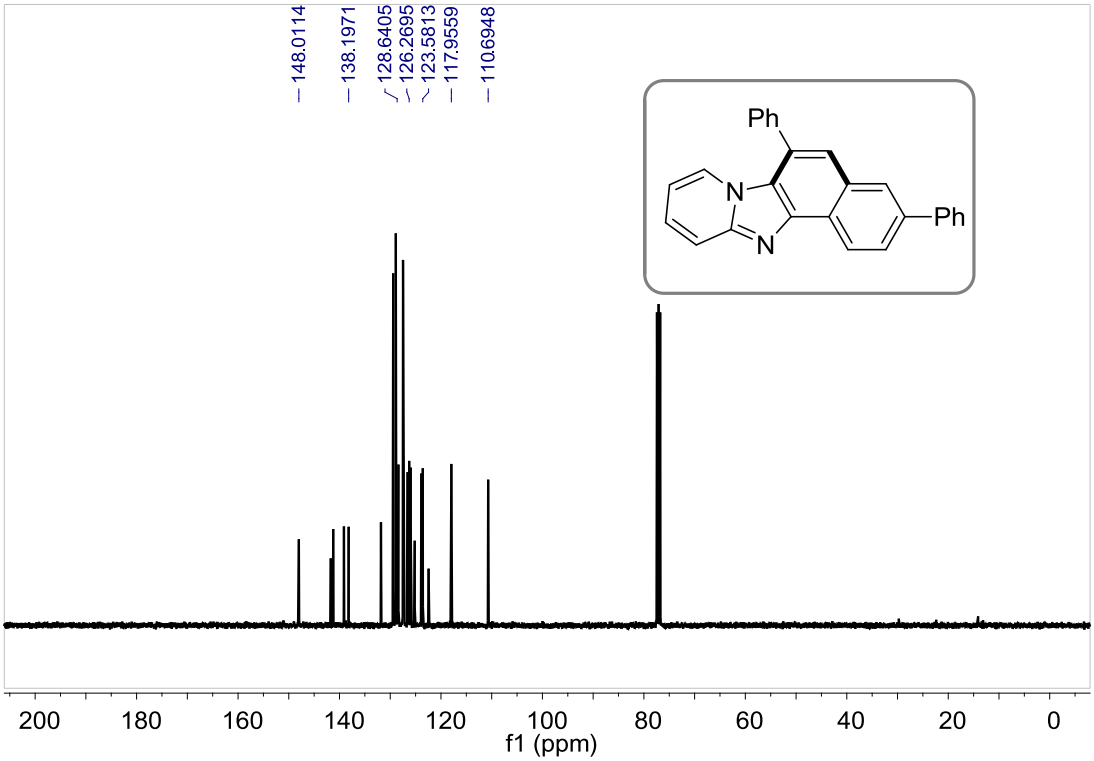
^{1}H NMR (400MHz, $CDCl_3$) spectrum for7f.



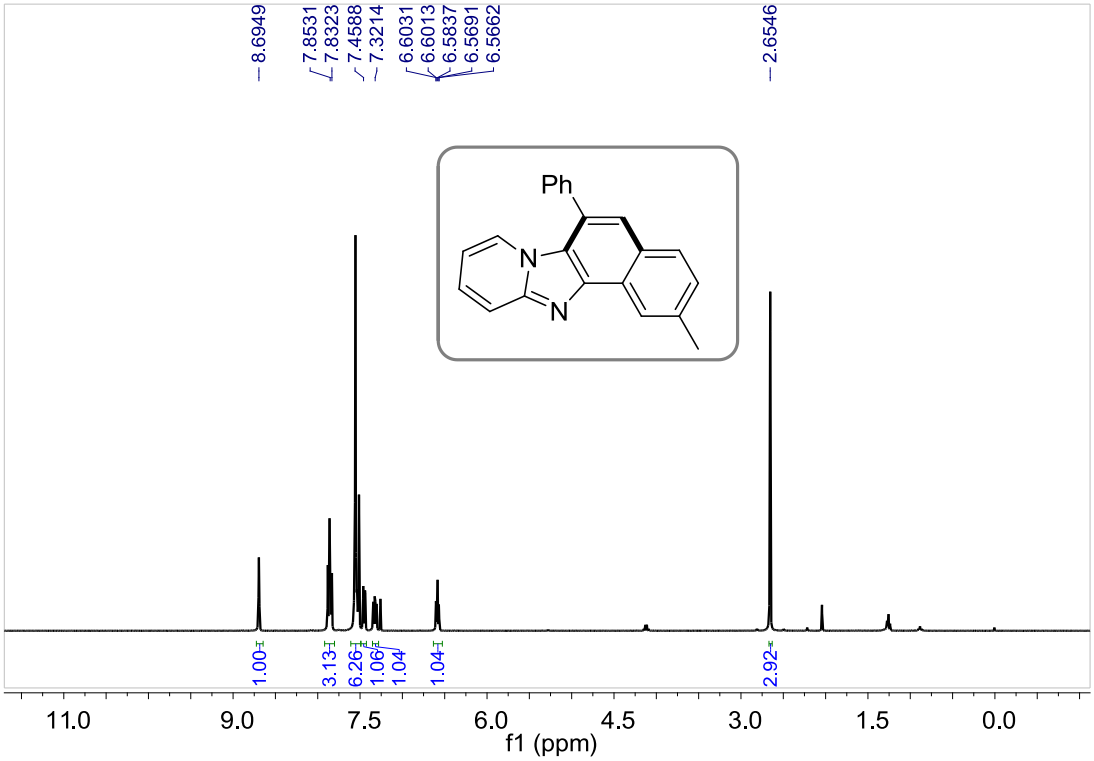
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 7f.



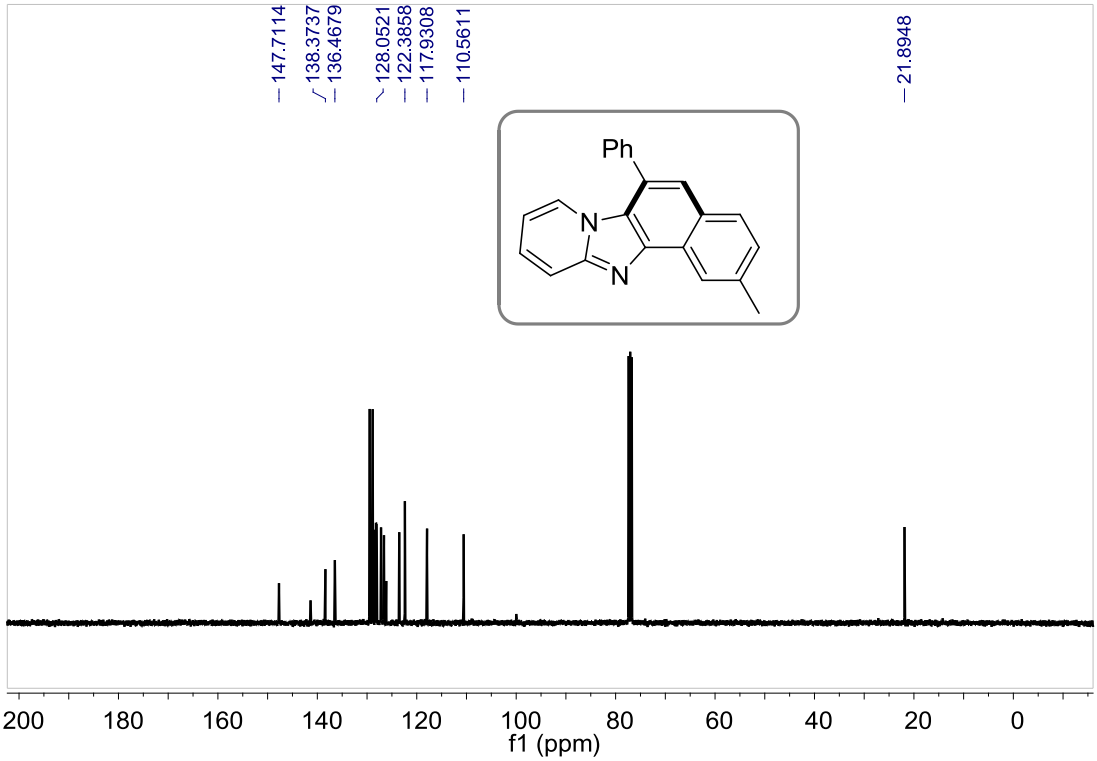
^{1}H NMR (400MHz, $CDCl_3$) spectrum for7g.



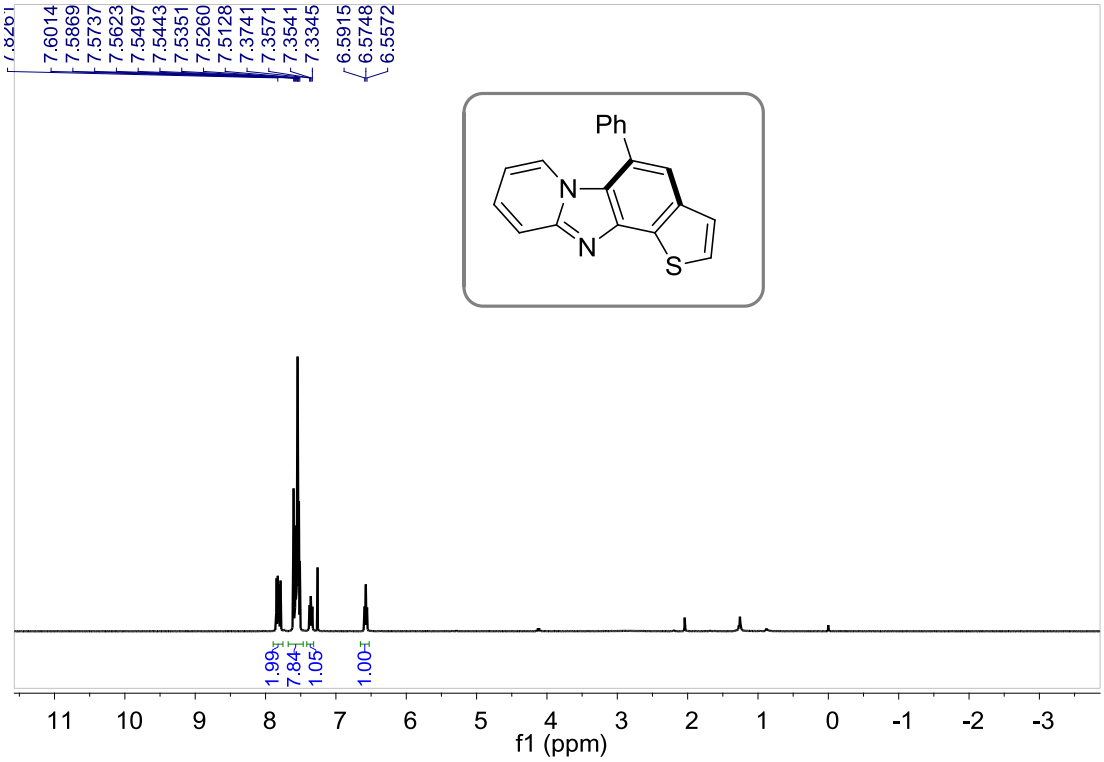
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 7g.



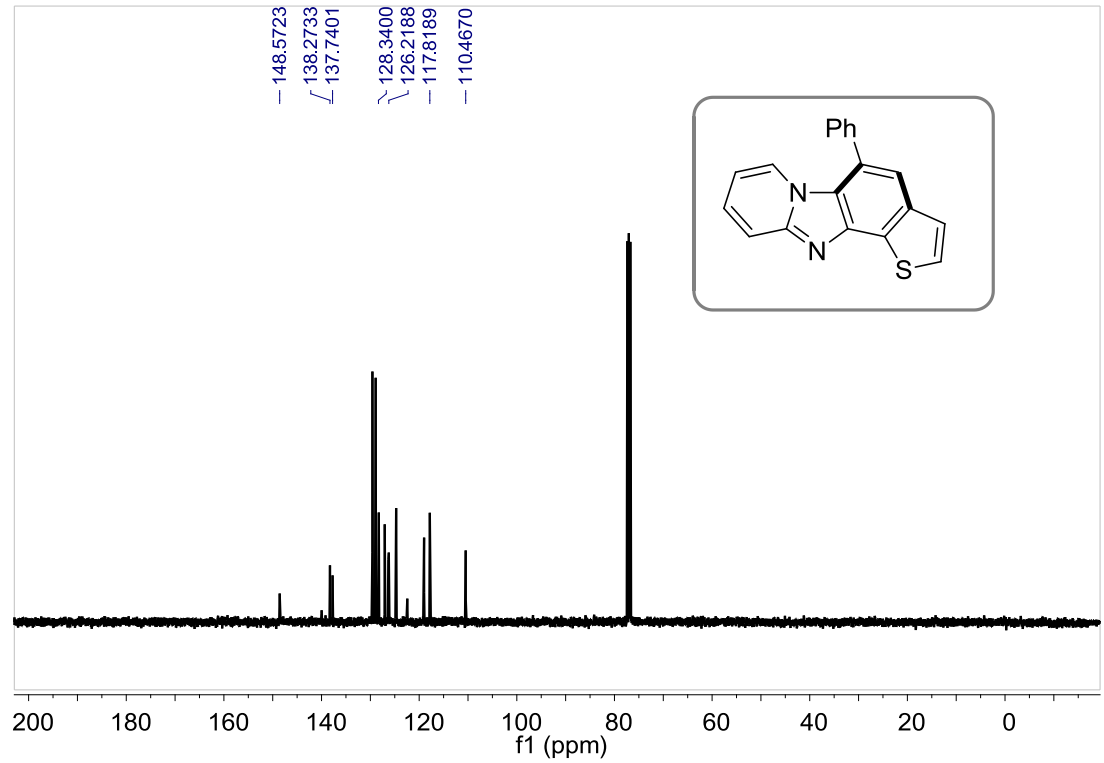
^{1}H NMR (400MHz, $CDCl_3$) spectrum for7h.



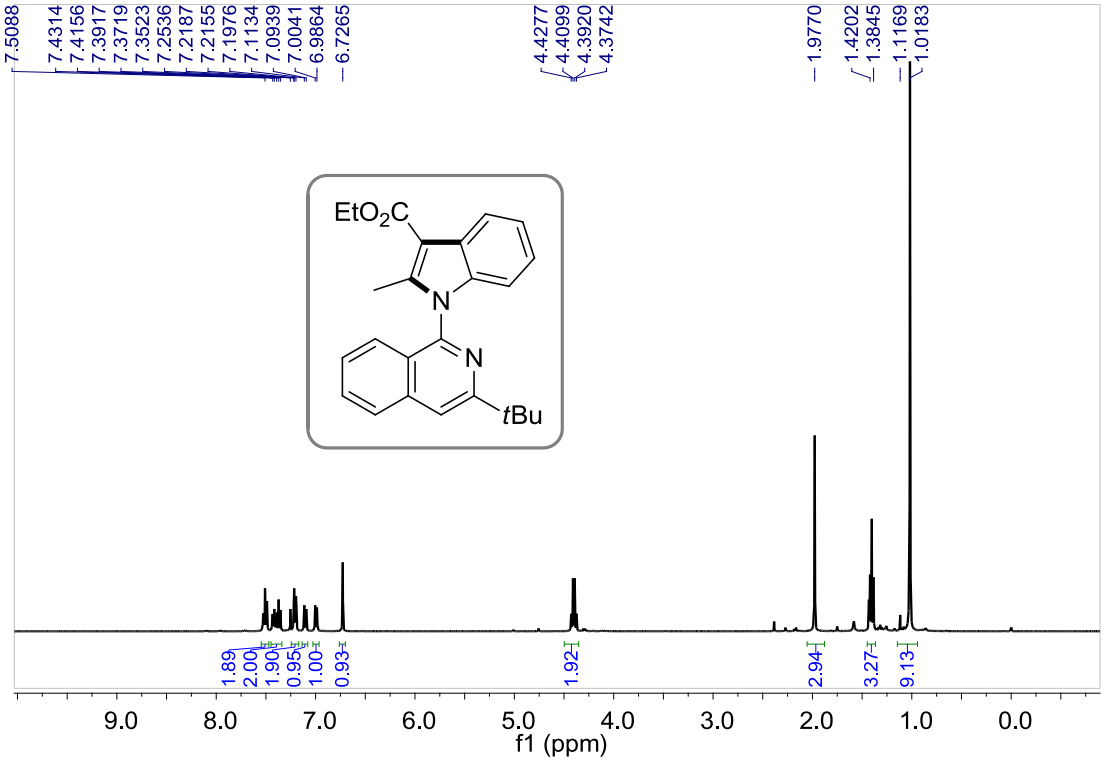
^{13}C NMR (100MHz, $CDCl_3$) spectrum for 7h.



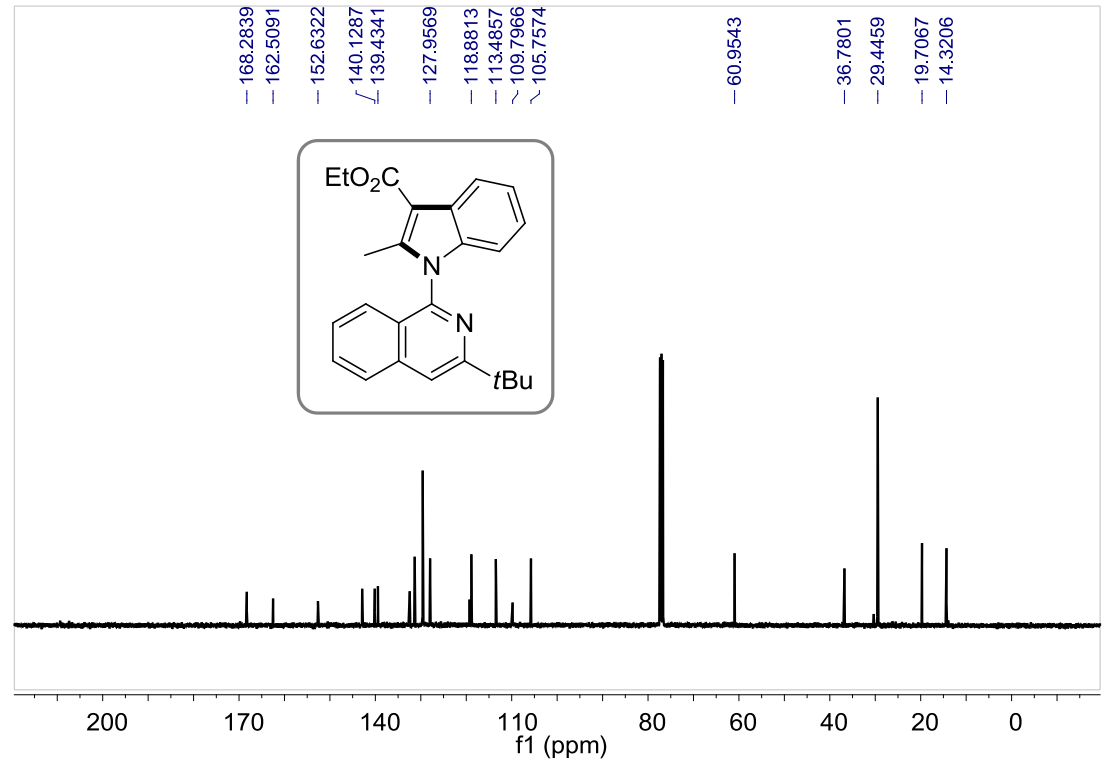
^{1}H NMR (400MHz, $CDCl_3$) spectrum for7i.



^{13}C NMR (100MHz, $CDCl_3$) spectrum for 7i.



^{1}H NMR (400MHz, $CDCl_3$) spectrum for8.



^{13}C NMR (100MHz, $CDCl_3$) spectrum for 8.