Supporting Information

Visible Light-Induced C(sp^3)-H Oxidative Arylation with Heteroarenes

Xing-An Liang‡, Linbin Niu‡, Shengchun Wang, Jiamei Liu and Aiwen Lei*

***corresponding author**

E-mail: aiwenlei@whu.edu.cn

Table of contents

1. **General information** S2

2. **Experiment procedure** S3

3. **Mechanistic studies** S3

4. **Characterization of products** S6

5. **References** S15

6. **NMR spectra of products** S16

1. General information

All manipulations were carried out by standard Schlenk techniques. Unless otherwise stated, analytical grade solvents and commercially available reagents were used to conduct the reactions. A 3W LED flashlight was purchased from LED wholesalers was used for the photoreaction (Figure S1). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether (bp. 60-80 ºC). Gradient flash chromatography was conducted and eluted with a continuous gradient from petroleum ether to the ethyl acetate. All the new compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. The known compounds were characterized by ^{1}H NMR and ^{13}C NMR. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for ^{1}H NMR), $CDCl_3$ (77.30 ppm for ^{13}C NMR). High resolution mass spectra (HRMS) were measured with a Bruker UltiMate 3000 & Compact and accurate masses were reported for the molecular ion + Hydrogen $(M+H)^+$.

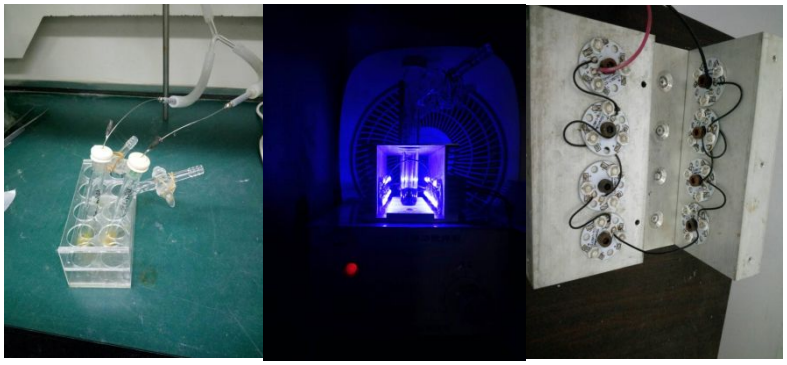


Fig. S1 The photochemical reactor (containing 24 small blue LEDs).

2. Experiment procedure

A solution of isoquinoline **1a** (0.3 mmol, 38.2 mg), cyclohexane **2a** (1.5 mL), selectfluor (0.6 mmol, 2 equiv., 213.4 mg), 2,2,2-trifluoroacetic acid (0.45 mmol, 1.5 equiv., 34.2 mg) in degassed dry CH_3CN (2.0 mL) were stirred under nitrogen atmosphere and irradiated by 3 W blue LEDs at 25 ˚C for 24 h. After completion of the reaction, the system was quenched by ethyl acetate and triethylamine. The conversion of reactants and the yield of product could be determined by GC with 1,4-dimethoxybenzene as the internal standard. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **3a** was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1).

3. Mechanistic studies

3.1 Procedure for the radical inhibition experiments

A solution of isoquinoline **1a** (0.3 mmol, 38.2 mg), cyclohexane **2a** (1.5 mL), selectfluor (0.6 mmol, 2 equiv., 213.4 mg), 2,2,2-trifluoroacetic acid (0.45 mmol, 1.5 equiv., 34.2 mg), TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy, 0.3 mmol, 1 equiv., 46.9 mg) or BHT (Butylated hydroxytoluene, 0.3 mmol, 1 equiv., 66.3 mg) in degassed dry CH_3CN were stirred under nitrogen atmosphere and irradiated by 3 W blue LEDs at 25 ˚C for 24 h. After completion of the reaction, the reaction results were monitored by TLC and GC-MS.

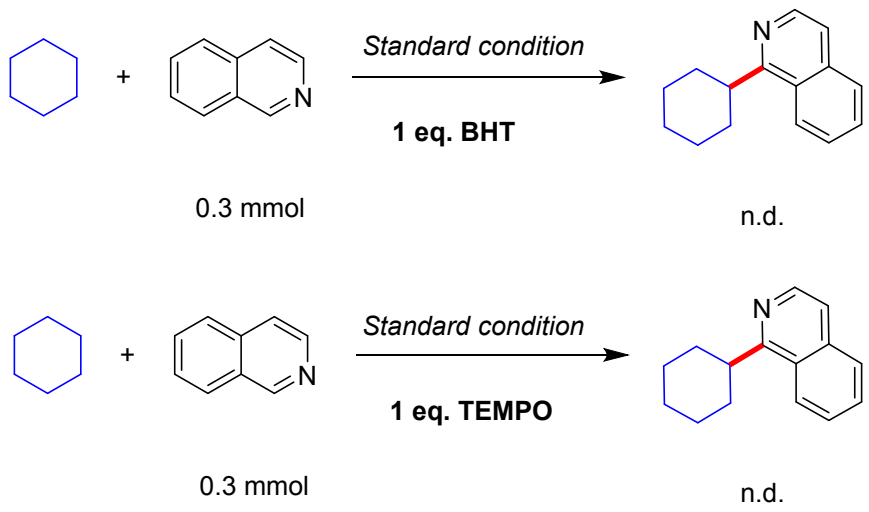


Fig. S2 The radical inhibition experiment.

3.2 Procedure for kinetic isotope effect (KIE) experiment

A solution of isoquinoline (0.3 mmol, 38.2 mg) and cyclohexane-d_{12} (0.75 mL), cyclohexane **2a** (0.75 mL), selectfluor (2 equiv., 213.4 mg) and 2,2,2-trifluoroacetic acid (0.45 mmol, 1.5 equiv., 34.2 mg) in degassed CH_3CN (2 mL) was stirred under nitrogen atmosphere and irradiation of 3W blue LEDs for 3.5h. After completion of the reaction, the system was quenched by ethyl acetate and triethylamine. The solvent was removed under reduced pressure by rotary evaporation, then the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate= 5:1) to afford 28% combined amination products. The ratio was K_H: K_D =3:1 determined by ^{1}H NMR spectrum.

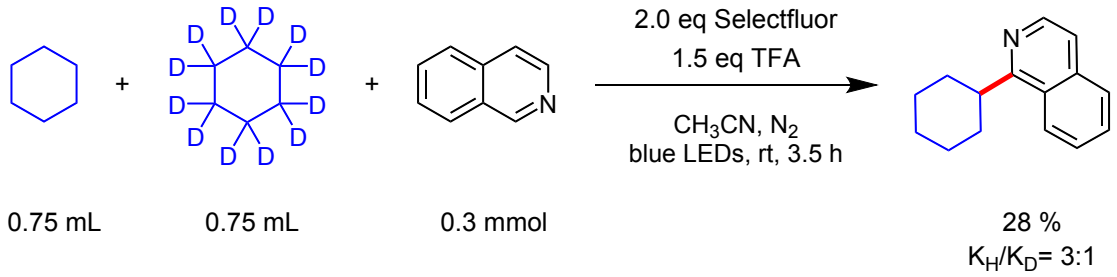


Fig. S3 The KIE experiment.

3.3 Procedure for EPR studies

A solution of selectfluor (0.6 mmol, 213.4 mg) in degassed dry CH_3CN (2.0 mL) were stirred under nitrogen atmosphere, which was irradiated by 3 W blue LEDs or under darkness at 25 ˚C for 2 h. After completion of the reaction, DMPO (30 μL) was added into the reaction system, which

was further irradiated by 3 W blue LEDs or under darkness at 25 ˚C for 10 mins. The solution sample was taken out into a small tube and analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.821452 GHz. Typical spectrometer parameters are shown as follows, scan range: 150 G; center field set: 3504.54 G; time constant: 163.84 ms; scan time: 30 s modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×104; microwave power: 21.59.

3.4. Procedure for light on/off experiments

A solution of selectfluor (0.6 mmol, 213.4 mg) in degassed dry CH_3CN (2.0 mL) were stirred under nitrogen atmosphere, which was irradiated by 3 W blue LEDs at 25 ˚C for 8 h. Then detected the yield by GC. A solution of selectfluor (0.6 mmol, 213.4 mg) in degassed dry CH_3CN (2.0 mL) were stirred under nitrogen atmosphere, which was irradiated by 3 W blue LEDs at 25 ˚C for 8 h. Then shaded the system for 4 hours, detected the yield by GC. A solution of selectfluor (0.6 mmol, 213.4 mg) in degassed dry CH_3CN (2.0 mL) were stirred under nitrogen atmosphere, which was irradiated by 3 W blue LEDs at 25 ˚C for 8 h. Then shaded the system for 4 hours, next continue irradiation for 4 hours detected the yield by GC. A solution of selectfluor (0.6 mmol, 213.4 mg) in degassed dry CH_3CN (2.0 mL) were stirred under nitrogen atmosphere, which was irradiated by 3 W blue LEDs at 25 ˚C for 8 h. Then shaded the system for 4 hours, continue irradiation for 4 hours and shaded the system for 4 hours finally detected the yield by GC. A solution of selectfluor (0.6 mmol, 213.4 mg) in degassed dry CH_3CN (2.0 mL) were stirred under nitrogen atmosphere, which was irradiated by 3 W blue LEDs at 25 ˚C for 8 h. Then shaded the system for 4 hours, continue irradiation for 4 hours and shaded the system for 4 hours and continue irradiation for 4 hours finally detected the yield by GC.

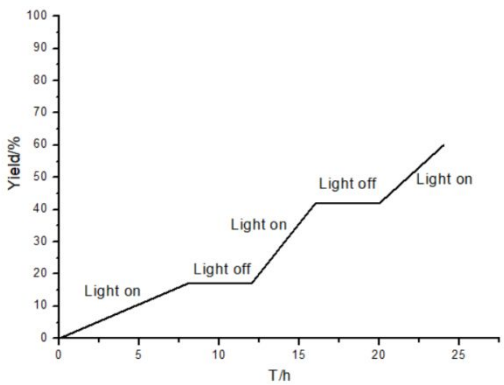


Fig. 4. Light on/off experiments

3.5 . Procedure for gram-scale synthesis experiment

A solution of isoquinoline **1a** (10 mmol, 1.29 g), cyclohexane **2a** (15 mL), selectfluor (20 mmol, 2 equiv., 7.08 g), 2,2,2-trifluoroacetic acid (15 mmol, 1.5 equiv., 1.71 g), in degassed dry CH_3CN were stirred under nitrogen atmosphere and irradiated by 3 W blue LEDs at 25 ˚C for 96 h. After completion of the reaction, the system was quenched by ethyl acetate and triethylamine. The solvent was removed under reduced pressure by rotary evaporation. Then, the pure product **3a** was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10:1).

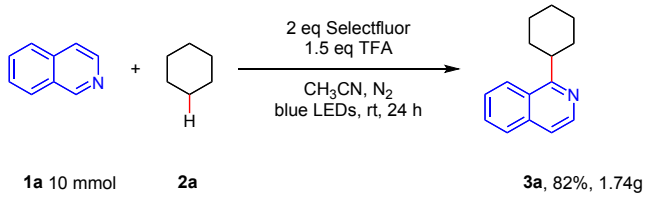
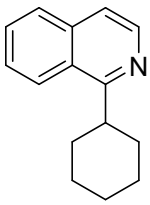


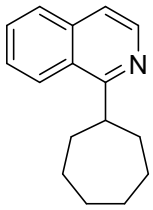
Fig. 4. The gram-scale synthesis experiment

4. Characterization of products



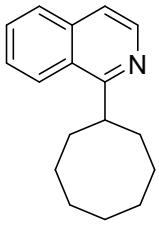
3a

Cyclohexylisoquinoline: 60.3 mg pale yellow liquid was obtained in 95% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 5.7 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.60 – 7.53 (m, 1H), 7.47 (d, *J* = 5.7 Hz, 1H), 3.70 – 3.43 (m, 1H), 2.05 – 1.89 (m, 4H), 1.89 – 1.76 (m, 3H), 1.61 – 1.46 (m, 2H), 1.45 – 1.35 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.40, 142.06, 136.65, 129.74, 127.76, 127.03, 126.17, 125.05, 118.97, 43.47, 34.84, 28.27, 27.78. **HRMS (ESI)** calcd for $C_{15}H_{18}N^+$, $[M+H]^+$, 212.1434, found 212.1434.



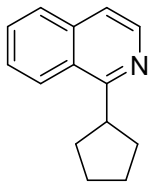
3b

1-Cycloheptylisoquinoline: 53.3 mg pale yellow liquid was obtained in 79% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 5.7 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.60 – 7.54 (m, 1H), 7.45 (d, *J* = 5.7 Hz, 1H), 3.80 – 3.61 (m, 1H), 2.11 – 1.88 (m, 6H), 1.81 – 1.60 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.96, 141.91, 136.60, 129.60, 127.68, 126.91, 126.04, 124.98, 118.82, 41.16, 33.22, 26.89, 26.41. **HRMS (ESI)** calcd for $C_{16}H_{19}N^{+}$, $[M+H]^{+}$, 225.1590, found 226.1596.[1]



3c

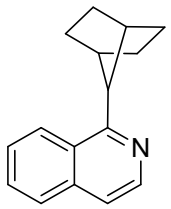
1-Cyclooctylisoquinoline: 41.6 mg pale yellow liquid was obtained in 58% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 5.7 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 5.6 Hz, 1H), 4.00 – 3.58 (m, 1H), 2.14 – 1.98 (m, 4H), 1.97 – 1.86 (m, 2H), 1.84 – 1.62 (m, 8H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.96, 141.91, 136.60, 129.60, 127.68, 126.91, 126.04, 124.98, 118.82, 41.16, 33.22, 26.89, 26.86, 26.41. **HRMS (ESI)** calcd for $C_{17}H_{21}N^{+}$, $[M+H]^{+}$, 240.1747, found 240.1748.



3d

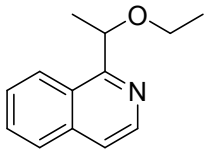
1-Cyclopentylisoquinoline: 46.5 mg pale yellow liquid was obtained in 79% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 5.7 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.64 (m,

1H), 7.60 – 7.55 (m, 1H), 7.47 (dd, *J* = 5.6, 0.9 Hz, 1H), 4.17 – 3.81 (m, 1H), 2.20 – 2.04 (m, 4H), 1.96 – 1.85 (m, 2H), 1.83 – 1.71 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.96, 142.02, 136.47, 129.80, 127.60, 127.41, 127.01, 125.47, 119.17, 43.22, 33.02, 26.29. **HRMS (ESI)** calcd for $C_{14}H_{16}N^+$, $[M+H]^+$, 198.1277, found 198.1277.



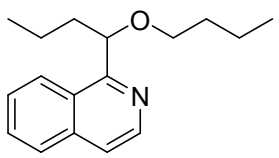
3e

1-(Bicyclo[2.2.1]heptan-2-yl)isoquinoline: 50.8 mg pale yellow liquid was obtained in 76% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 5.7 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.60 – 7.54 (m, 1H), 7.45 (d, *J* = 5.7 Hz, 1H), 3.58 (dd, *J* = 8.8, 5.2 Hz, 1H), 2.59 (d, *J* = 2.6 Hz, 1H), 2.43 (d, J = 4.4 Hz, 1H), 2.42 – 2.36 (m, 1H), 1.78 – 1.63 (m, 4H), 1.60 – 1.54 (m, 1H), 1.41 (dd, *J* = 5.4, 3.2 Hz, 1H), 1.22 – 1.16 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.46, 141.47, 136.52, 129.67, 127.62, 127.20, 126.96, 125.62, 119.06, 45.73, 43.19, 36.98, 36.33, 36.14, 30.46, 29.77. **HRMS (ESI)** calcd for $C_{16}H_{18}N^+$, $[M+H]^+$, 224.1434, found 224.1432.



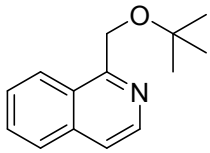
3f

1-(1-Ethoxyethyl)isoquinoline: 53.0 mg pale yellow liquid was obtained in 87% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.70 (d, *J* = 8.6 Hz, 1H), 8.47 (d, *J* = 5.7 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.63 – 7.53 (m, 2H), 5.18 (q, *J* = 6.7 Hz, 1H), 3.58 – 3.46 (m, 1H), 3.45 – 3.35 (m, 1H) , 1.71 (d, *J* = 6.7 Hz, 3H), 1.20 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.87, 140.62, 135.90, 129.00, 126.52, 125.98, 125.14, 124.65, 119.64, 79.18, 63.59, 20.77, 14.58. **HRMS (ESI)** calcd for $C_{13}H_{16}NO^+$, $[M+H]^+$, 202.1226, found 202.1232.



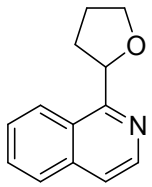
3g

1-(1-Butoxybutyl)isoquinoline: 76.7 mg pale yellow liquid was obtained in 99% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 8.5 Hz, 1H), 8.46 (d, *J* = 5.7 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.60 – 7.53 (m, 2H), 4.94 (dd, *J* = 8.5, 5.7 Hz, 1H), 3.44 – 3.25 (m, 2H), 2.22 – 2.07 (m, 1H), 1.95 – 1.82 (m, 1H), 1.65 – 1.49 (m, 3H), 1.40 – 1.24 (m, 3H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.92, 141.64, 136.99, 130.07, 127.50, 126.91, 126.54, 126.14, 120.63, 85.33, 69.38, 38.64, 32.23, 19.90, 19.55, 14.18, 14.07. **HRMS (ESI)** calcd for $C_{17}H_{24}NO^{+}$, $[M+H]^{+}$, 258.1852, found 258.1857.



3h

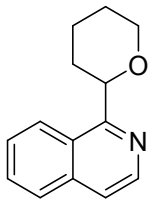
1-(Tert-butoxymethyl)isoquinoline: 65.1 mg pale yellow liquid was obtained in 99% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 5.8 Hz, 1H), 8.41 (d, *J* = 8.3, 1.0 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.72 – 7.67 (m, 1H), 7.65 – 7.59 (m, 2H), 5.05 (s, 2H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.43, 141.95, 136.81, 130.20, 127.80, 127.36, 127.28, 126.43, 121.16, 74.60, 65.94, 27.96. **HRMS (ESI)** calcd for $C_{14}H_{18}NO^{+}$, $[M+H]^{+}$, 216.1383, found 216.1386.



3i

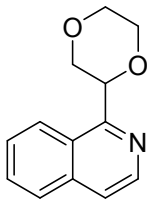
1-(Tetrahydrofuran-2-yl)isoquinoline: 55.4 mg pale yellow liquid was obtained in 94% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 5.7 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.61 – 7.53 (m, 2H), 5.71 (t, *J* = 7.1 Hz, 1H), δ 4.30 – 3.90 (m, 2H), 2.56

– 2.35 (m, 2H), 2.23 – 2.03 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.82, 141.71, 136.71, 130.08, 127.54, 127.35, 126.73, 125.44, 120.76, 79.27, 69.23, 31.11, 26.36. **HRMS (ESI)** calcd for $C_{13}H_{14}NO^+$, $[M+H]^+$, 200.1070, found 200.1075.



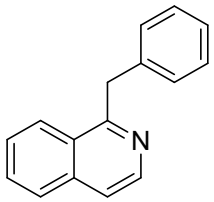
3j

1-(Tetrahydro-2H-pyran-2-yl)isoquinoline: 38.5 mg pale yellow liquid was obtained in 61% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 5.7 Hz, 1H), 8.37 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.63 – 7.56 (m, 2H), 5.21 (dd, *J* = 11.0, 2.2 Hz, 1H), 4.33 – 4.22 (m, 1H), 3.90 – 3.70 (m, 1H), 2.14 – 1.97 (m, 3H), 1.95 – 1.77 (m, 2H), 1.73 – 1.63 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.86, 141.98, 136.81, 129.95, 127.57, 127.19, 126.21, 125.39, 120.71, 79.44, 69.64, 31.31, 26.10, 24.09. **HRMS (ESI)** calcd for $C_{14}H_{16}NO^+$, $[M+H]^+$, 214.1226, found 214.1227.[3]



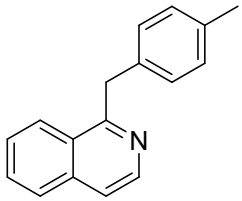
3k

1-(1,4-Dioxan-2-yl)isoquinoline: 56.5 mg white solid was obtained in 98% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 5.7 Hz, 1H), 8.30 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.65 – 7.59 (m, 2H), 5.48 (dd, *J* = 9.7, 2.9 Hz, 1H), 4.21 – 4.03 (m, 4H), 3.94 – 3.84 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.12, 141.99, 136.62, 130.21, 127.65, 126.64, 124.84, 121.24, 75.99, 70.46, 67.75, 66.68. **HRMS (ESI)** calcd for $C_{13}H_{14}NO_2^+$, $[M+H]^+$, 216.1019, found 216.1021.



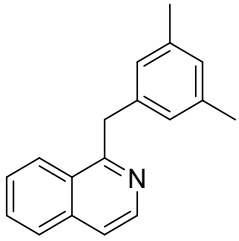
3l

1-Benzylisoquinoline: 31.9 mg pale yellow liquid was obtained in 48% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 5.8 Hz, 1H), 8.14 (d, *J* = 9.1 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.58 – 7.48 (m, 2H), 7.32 – 7.21 (m, 4H), 7.19 – 7.12 (m, 1H), 4.67 (s, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.21, 142.03, 139.51, 136.65, 129.97, 128.69, 128.61, 127.44, 127.33, 127.26, 126.36, 125.91, 119.95, 42.12. **HRMS (ESI)** calcd for $C_{16}H_{14}N^{+}$, $[M+H]^{+}$, 220.1121, found 220.1120.



3m

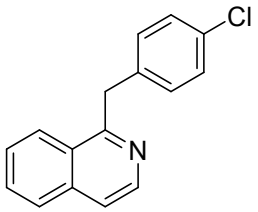
1-(4-Methylbenzyl)isoquinoline: 68.5 mg pale yellow liquid was obtained in 98% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 5.8 Hz, 1H), 8.14 (d, *J* = 9.3 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.55 – 7.46 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 4.62 (s, 2H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.59, 142.15, 136.79, 136.57, 135.96, 130.07, 129.44, 128.70, 127.55, 127.42, 127.38, 126.08, 120.01, 41.86, 21.23. **HRMS (ESI)** calcd for $C_{17}H_{16}N^{+}$, $[M+H]^{+}$, 234.1277, found 234.1278.



3n

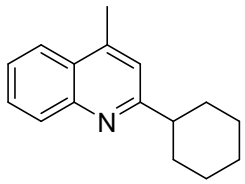
1-(3,5-Dimethylbenzyl)isoquinoline: 31.5 mg pale yellow liquid was obtained in 43% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 5.8 Hz, 1H), 8.17 (d, *J* = 10.1 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H),

7.65 – 7.59 (m, 1H), 7.56 – 7.48 (m, 2H), 6.90 (s, 2H), 6.80 (s, 1H), 4.59 (s, 2H), 2.22 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.58, 142.18, 139.50, 138.22, 136.79, 130.09, 128.23, 127.54, 127.46, 126.65, 126.16, 120.01, 42.15, 21.54. **HRMS (ESI)** calcd for $C_{18}H_{18}N^+$, $[M+H]^+$, 248.1434, found 248.1440.



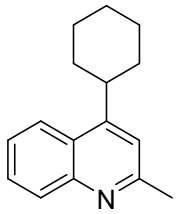
3o

1-(4-Chlorobenzyl)isoquinoline: 50.7 mg pale yellow liquid was obtained in 67% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 5.8 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.58 – 7.49 (m, 2H), 7.20 (s, 4H), 4.62 (s, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.78, 142.15, 138.05, 136.81, 132.31, 130.24, 130.18, 128.85, 127.68, 127.61, 127.26, 125.75, 120.27, 41.44. **HRMS (ESI)** calcd for $C_{16}H_{13}ClN^+$, $[M+H]^+$, 254.0731, found 254.0734.



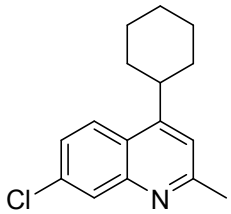
3p

2-Cyclohexyl-4-methylquinoline: 58.8 mg pale yellow liquid was obtained in 87% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 9.1 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.56 – 7.47 (m, 1H), 7.19 (s, 1H), 2.95 – 2.85 (m, 1H), 2.71 – 2.68 (m, 3H), 2.09 – 2.00 (m, 2H), 1.92 (dt, *J* = 12.6, 2.9 Hz, 2H), 1.85 – 1.78 (m, 1H), 1.72 – 1.59 (m, 2H), 1.56 – 1.44 (m, 2H), 1.42 – 1.31 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.89, 153.39, 148.18, 129.58, 128.87, 125.35, 125.22, 122.92, 118.40, 38.84, 33.63, 27.01, 26.40, 25.63. **HRMS (ESI)** calcd for $C_{16}H_{20}N^+$, $[M+H]^+$, 226.1590, found 226.1593.



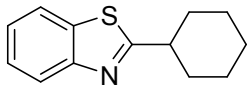
3q

4-Cyclohexyl-2-methylquinoline: 54.1 mg pale yellow liquid was obtained in 80% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.16 (s, 1H), 3.28 (m, 1H), 2.71 (s, 3H), 2.04 – 1.88 (m, 4H), 1.84 (d, *J* = 13.1 Hz, 1H), 1.59 – 1.48 (m, 4H), 1.39 – 1.26 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.00, 153.50, 148.31, 129.70, 128.99, 125.47, 125.35, 123.04, 118.52, 38.98, 33.76, 27.14, 26.53, 25.75. **HRMS (ESI)** calcd for $C_{16}H_{20}N^{+}$, $[M+H]^{+}$, 226.1590, found 226.1593.



3r

7-Chloro-4-cyclohexyl-2-methylquinoline: 71.7 mg colourless liquid was obtained in 92% yield. was obtained in 98%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 2.1 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.40 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.14 (s, 1H), 3.21 (m, 1H), 2.69 (s, 3H), 2.07 – 1.74 (m, 5H), 1.57 – 1.20 (m, 5H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.28, 153.56, 148.84, 134.72, 128.62, 126.29, 124.49, 123.78, 118.72, 39.06, 33.71, 27.05, 26.42, 25.70. **HRMS (ESI)** calcd for $C_{16}H_{16}ClN^{+}$, $[M+H]^{+}$, 260.1201, found 260.1176.[4]



3s

2-Cyclohexylbenzo[d]thiazole: 34.7 mg pale yellow liquid was obtained in 54% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 3.19 – 3.02 (m, 1H), 2.27 – 2.15 (m, 2H), 1.97 – 1.84 (m, 2H), 1.82 – 1.73 (m, 1H),

1.73 – 1.56 (m, 3H), 1.55 – 1.38 (m, 2H), 1.38 – 1.29 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.78, 153.18, 134.63, 125.92, 124.62, 122.64, 121.68, 43.56, 33.56, 26.19, 25.90. **HRMS (ESI)** calcd for $C_{13}H_{16}NS^+$, $[M+H]^+$, 218.0998, found 218.0997.[5]

5. References

1. Klauck, F. J. R.; James, M. J.; Glorius, F., *Angew. Chem., Int. Ed.* **2017**, *56*, 12336-12339.

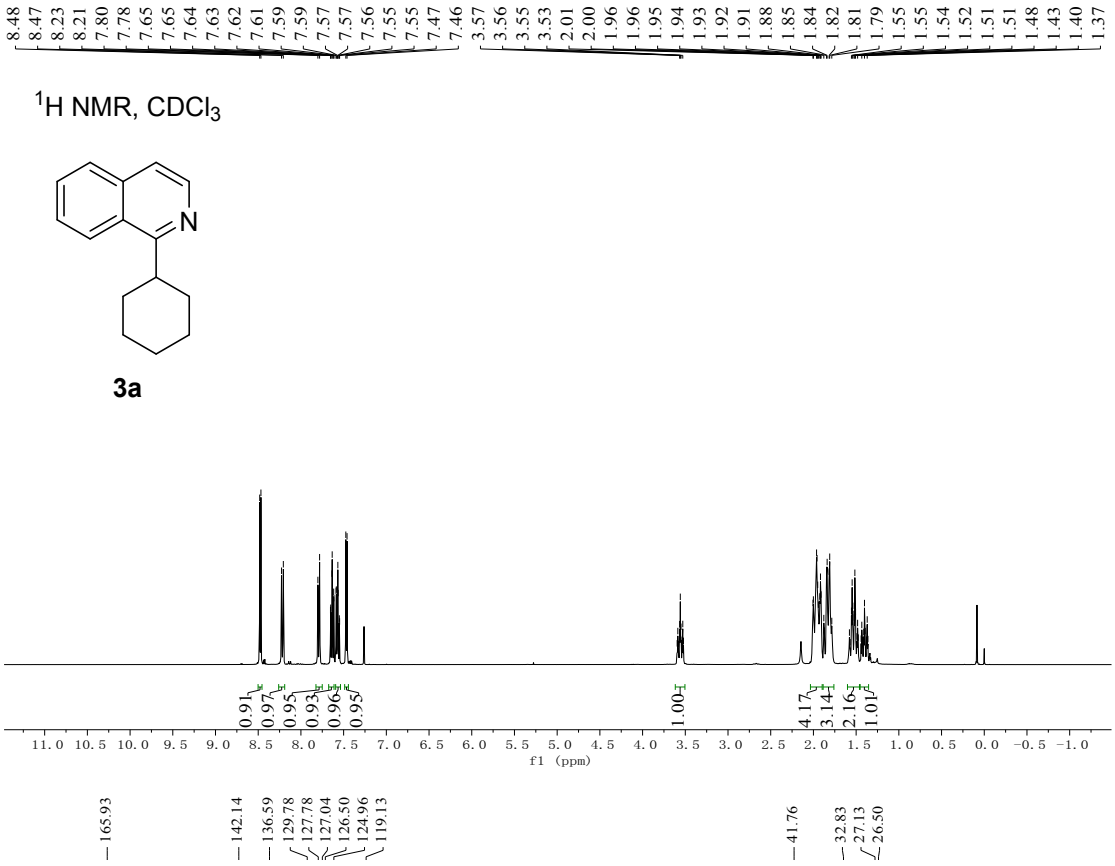
2. Tang, R.-J.; Kang, L.; Yang, L., *Adv. Synth. Catal.* **2015**, *357*, 2055-2060.

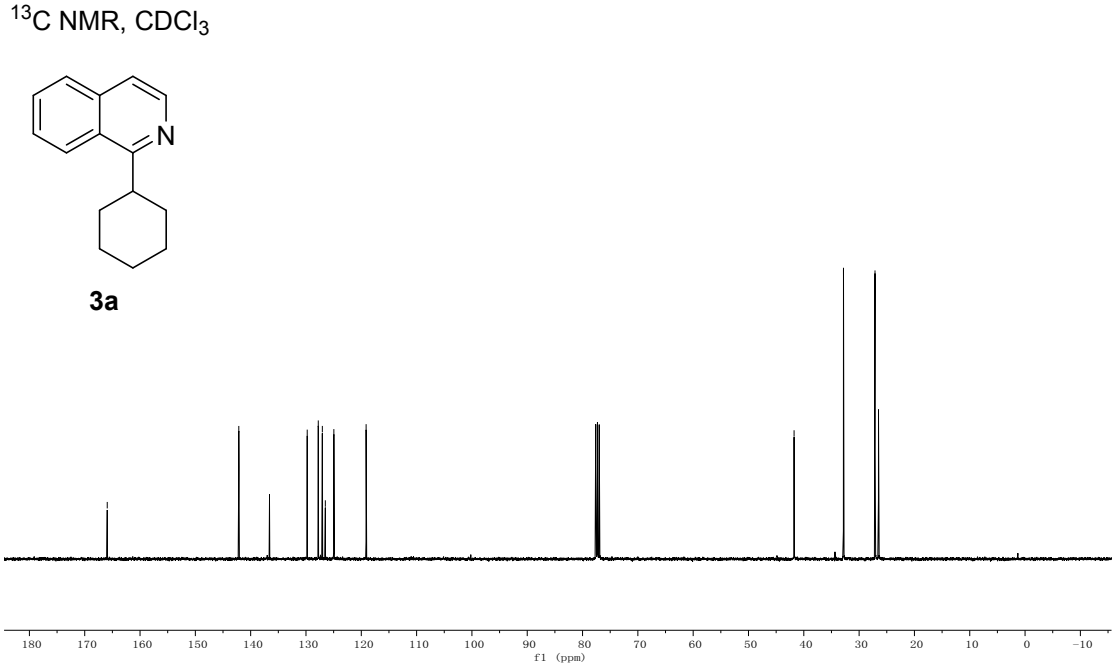
3. Liu, S.; Liu, A.; Zhang, Y.; Wang, W., *Chem. Sci.* **2017**, *8*, 4044-4050.

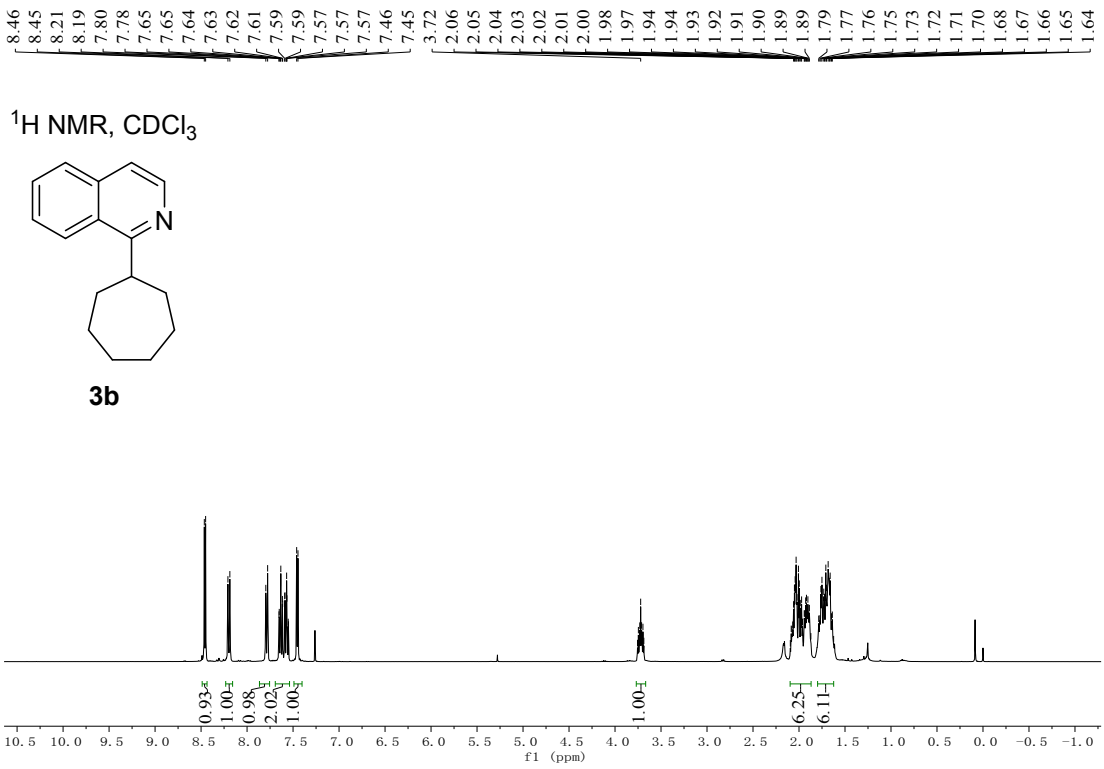
4. McCallum, T.; Barriault, L., *Chem. Sci.* **2016**, *7*, 4754-4758.

5. Liang, B.; Wang, Q.; Liu, Z. Q., A *Org. Lett.* **2017**, *19*, 6463-6465.

6. NMR spectra of products



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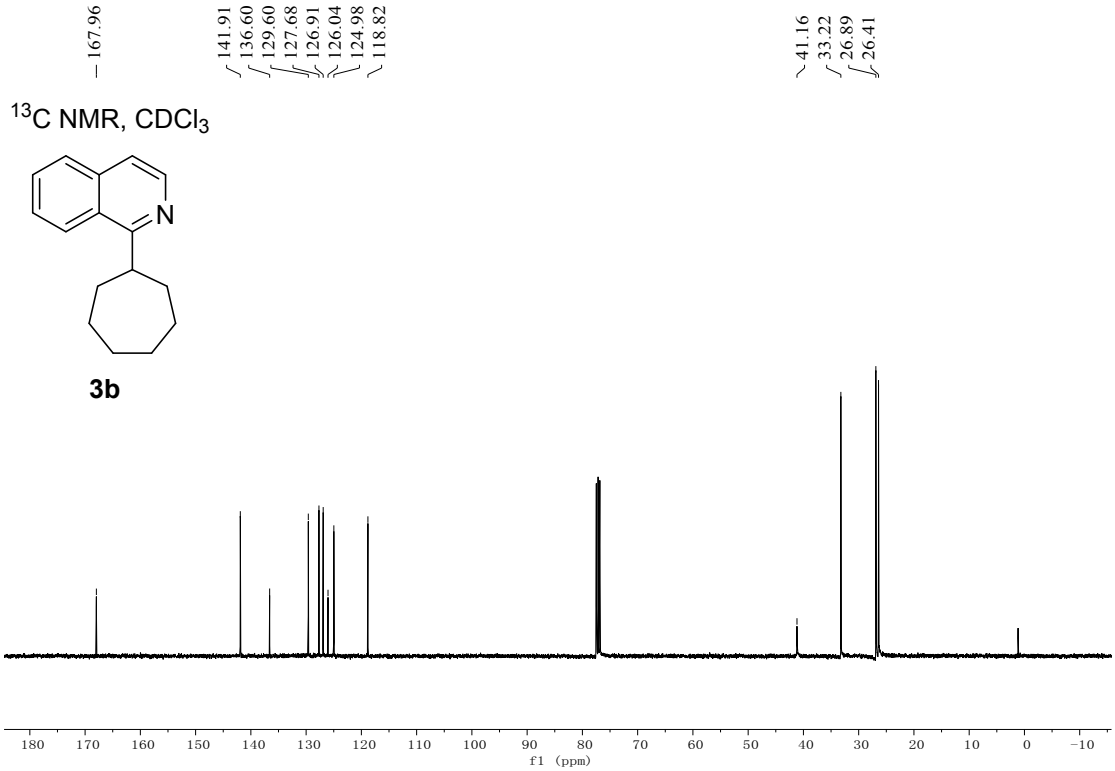
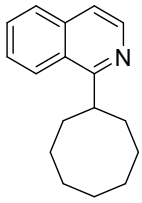
^{1}H NMR, $CDCl_3$
N
3b
0.93 1.00 0.98 2.02 1.00 1.00 6.25 6.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

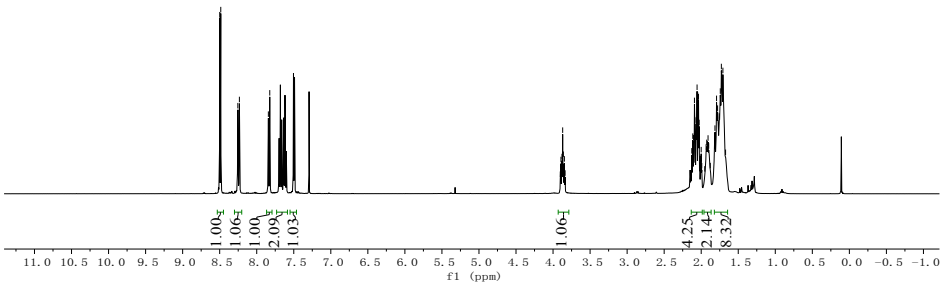

167.96
141.91 136.60 129.60 127.68 126.91 126.04 124.98 118.82
41.16 33.22 26.89 26.41
^{13}C NMR, $CDCl_3$
N
3b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

8.50 8.49 8.25 8.23 7.84 7.82 3.90 3.89 3.88 3.88 3.87 3.86 3.85 3.84 2.13 2.11 2.10 2.09 2.08 2.07 2.06 2.06 2.05 2.04 2.03 2.02 2.01 2.00 1.99 1.95 1.93 1.93 1.92 1.91 1.90 1.88 1.81 1.79 1.78 1.76 1.74 1.73 1.72 1.71 1.67

^{1}H NMR, $CDCl_3$



3c



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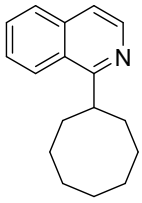
^{13}C NMR, $CDCl_3$



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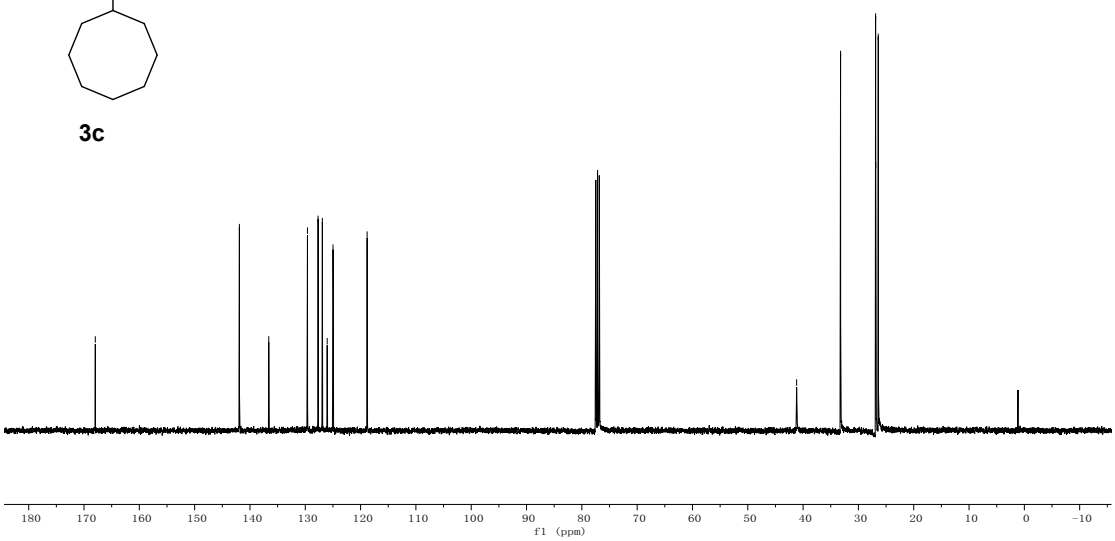

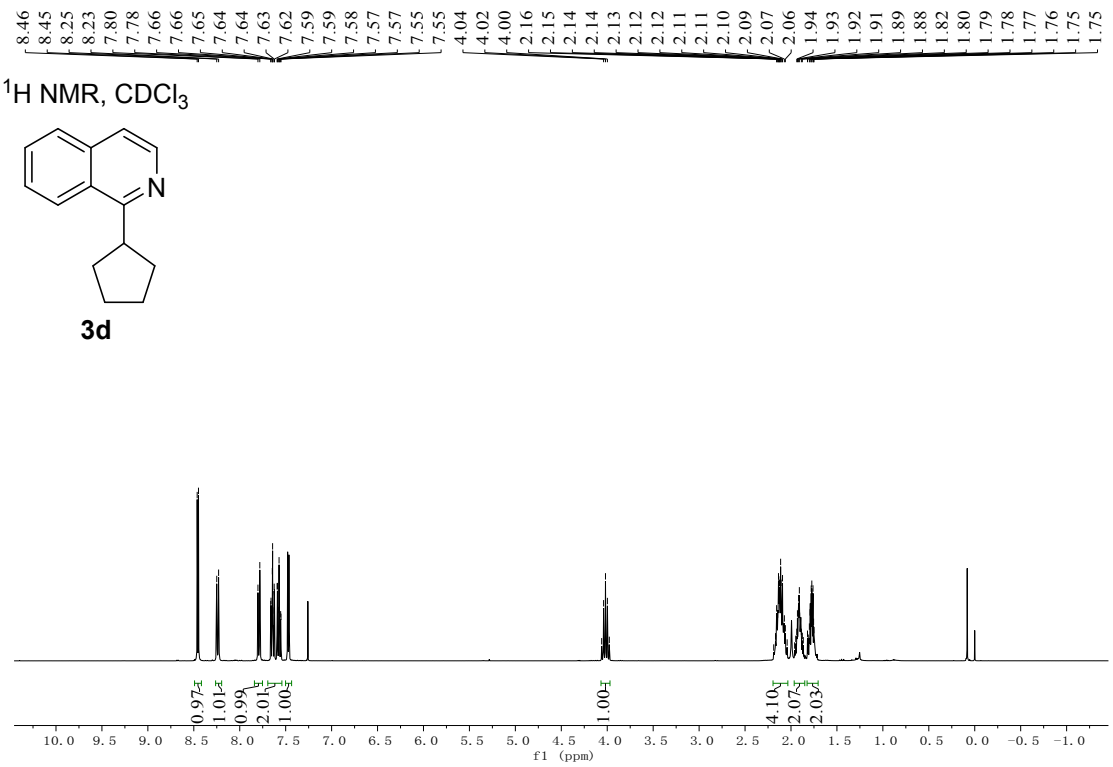
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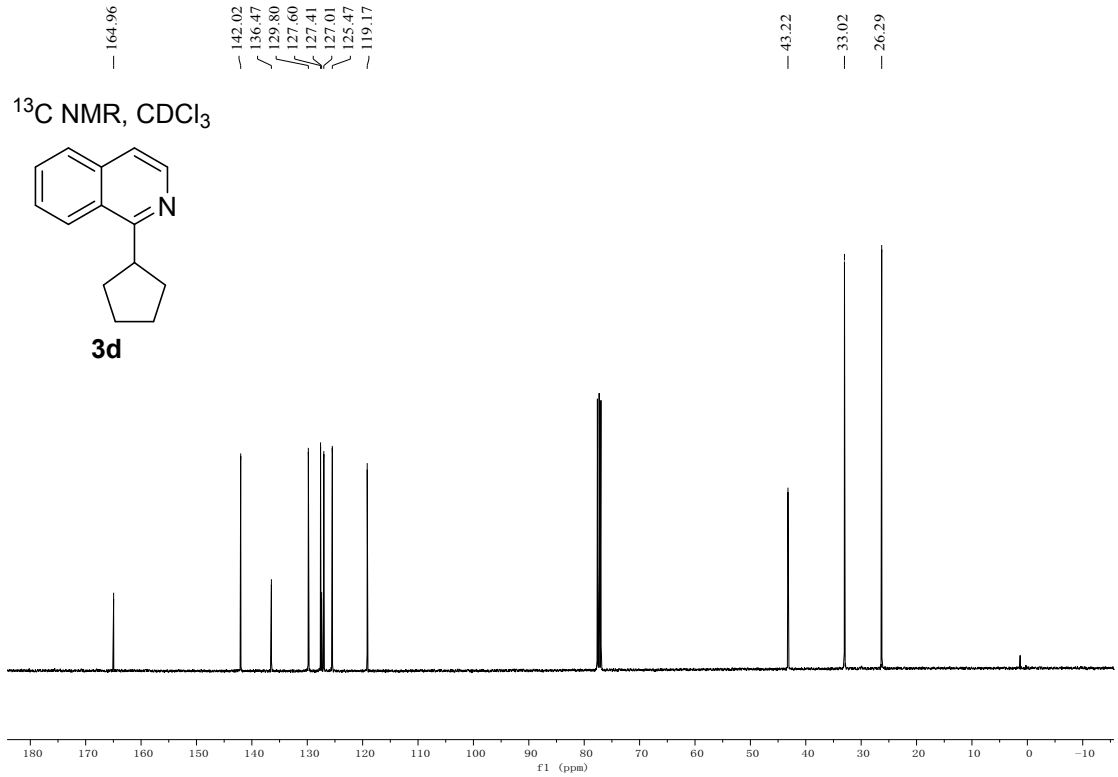
^{1}H NMR, $CDCl_3$
N
3d
0.97 1.01 0.99 2.01 1.00 1.00 4.10 2.07 2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)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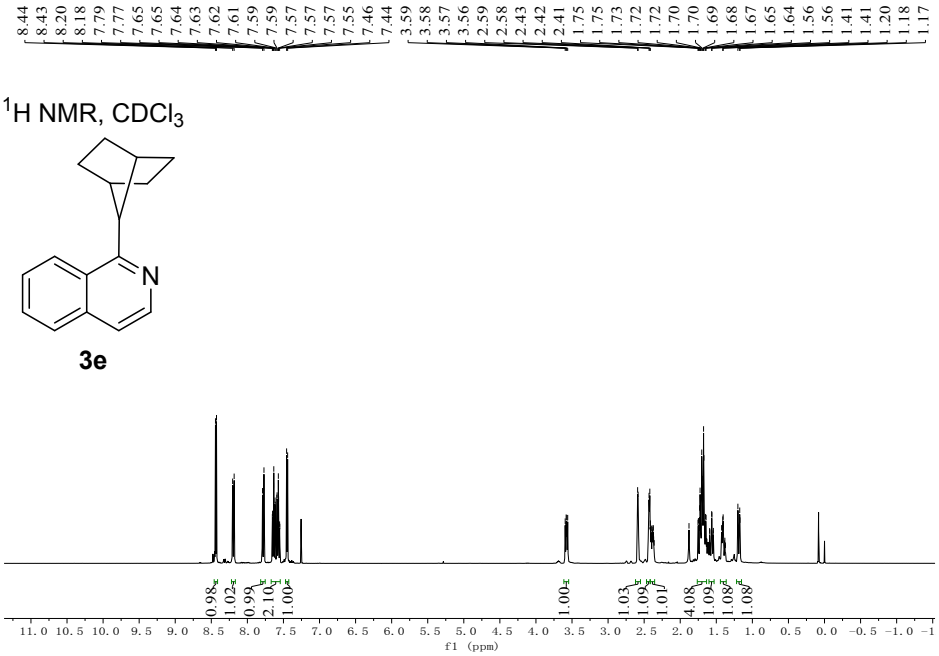
43.22 33.02 26.29
^{13}C NMR, $CDCl_3$
N
3d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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1.56
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1.41
1.20
1.18
1.17
^{1}H NMR, $CDCl_3$
N
3e
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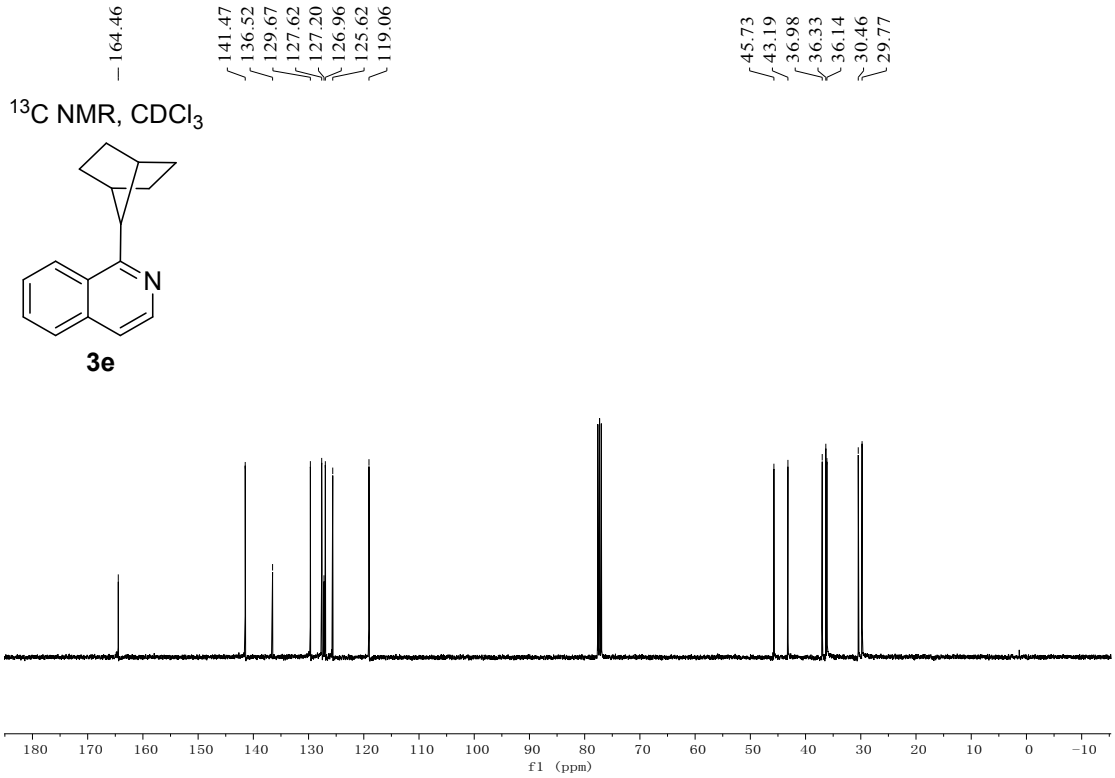
f1 (ppm)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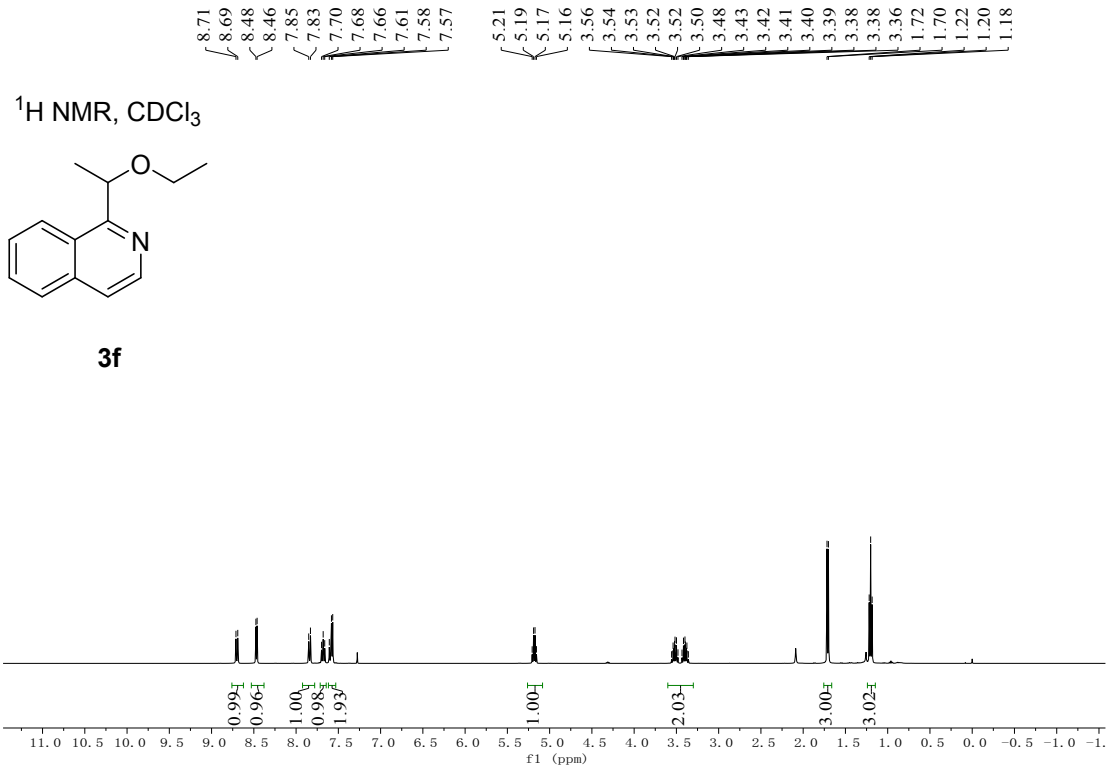
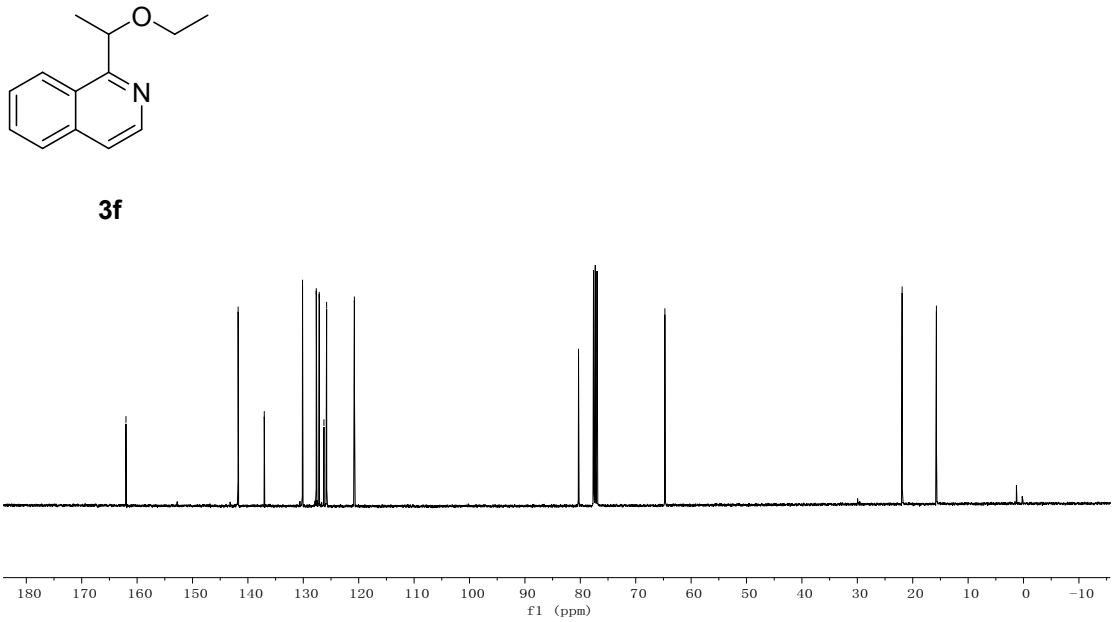
136.52
129.67
127.62
127.20
126.96
125.62
119.06
45.73
43.19
36.98
36.33
36.14
30.46
29.77
^{13}C NMR, $CDCl_3$
N
3e
f1 (ppm)

^{1}H NMR, $CDCl_3$

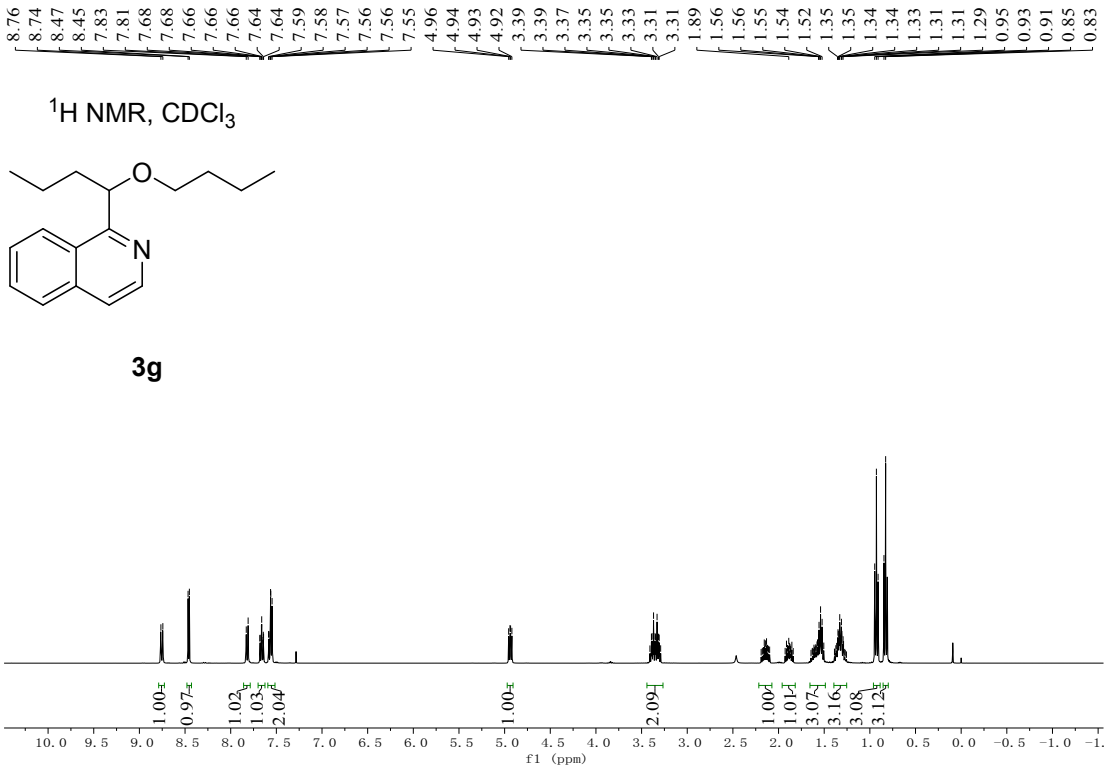


3f

^{13}C NMR, $CDCl_3$



3f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^{1}H NMR, $CDCl_3$
O
N
3g
1.00 0.97 1.02 1.03 2.04 1.00 2.09 1.00 1.01 3.07 3.16 3.08 3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.
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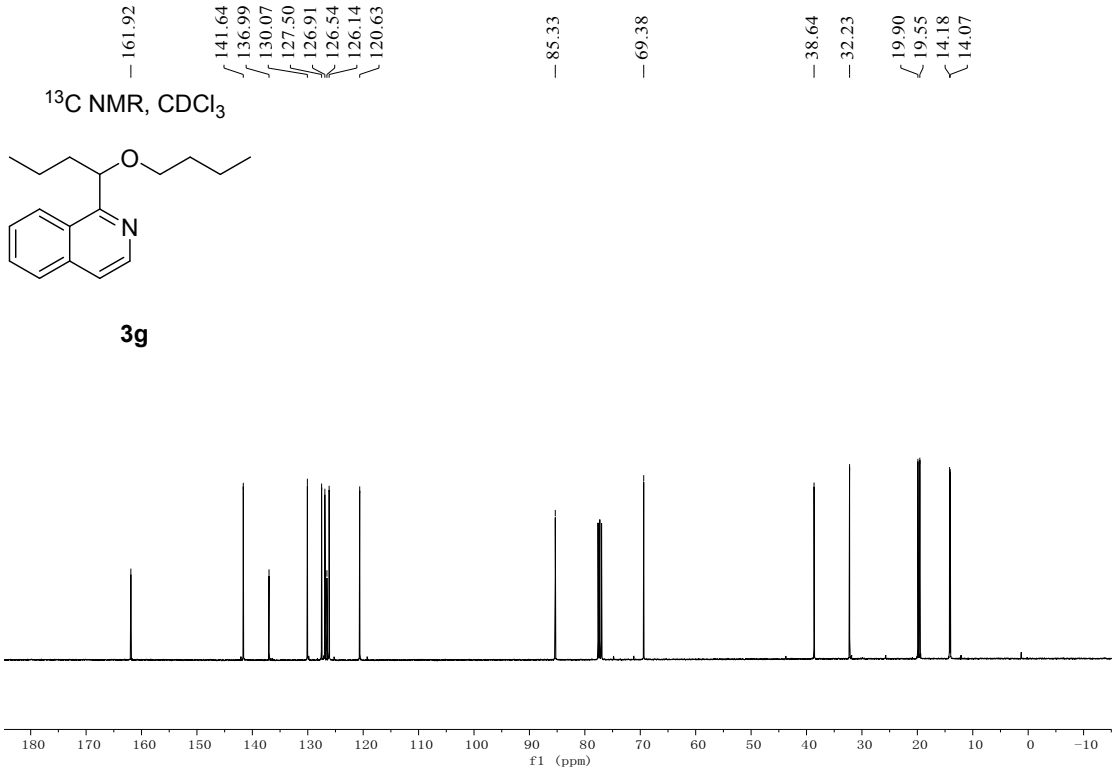
161.92 141.64 136.99 130.07 127.50 126.91 126.54 126.14 120.63 85.33 69.38 38.64 32.23 19.90 19.55 14.18 14.07
^{13}C NMR, $CDCl_3$
O
N
3g
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f1 (ppm)

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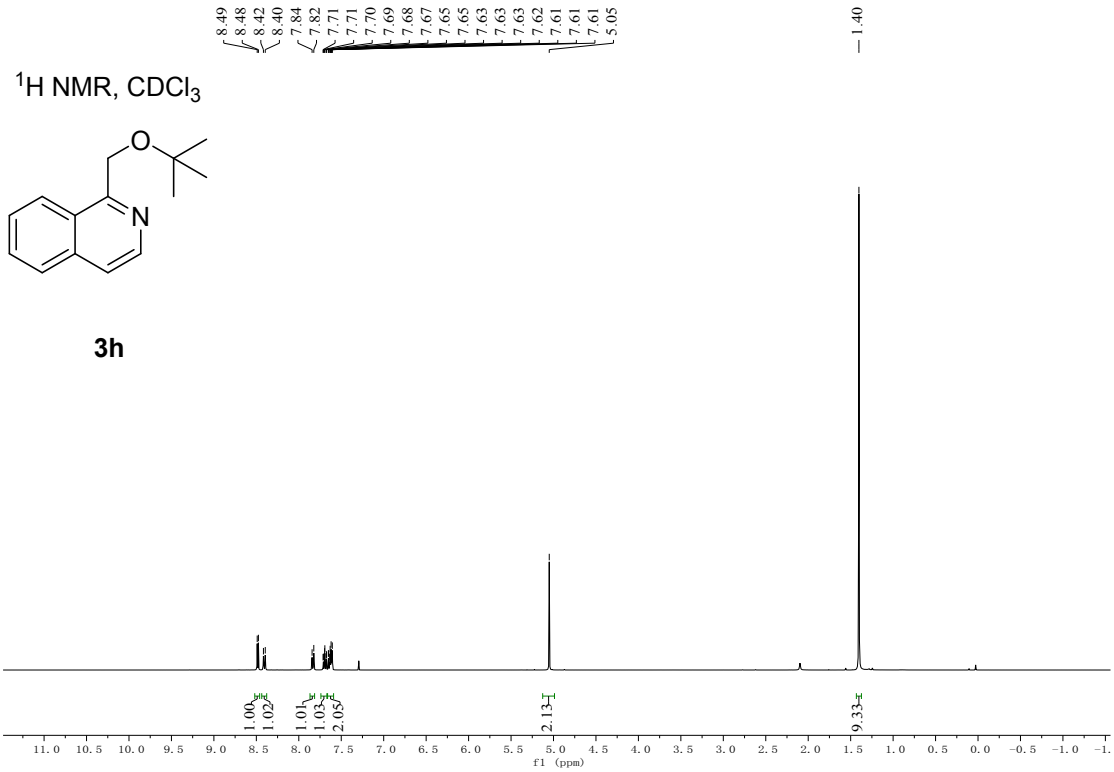
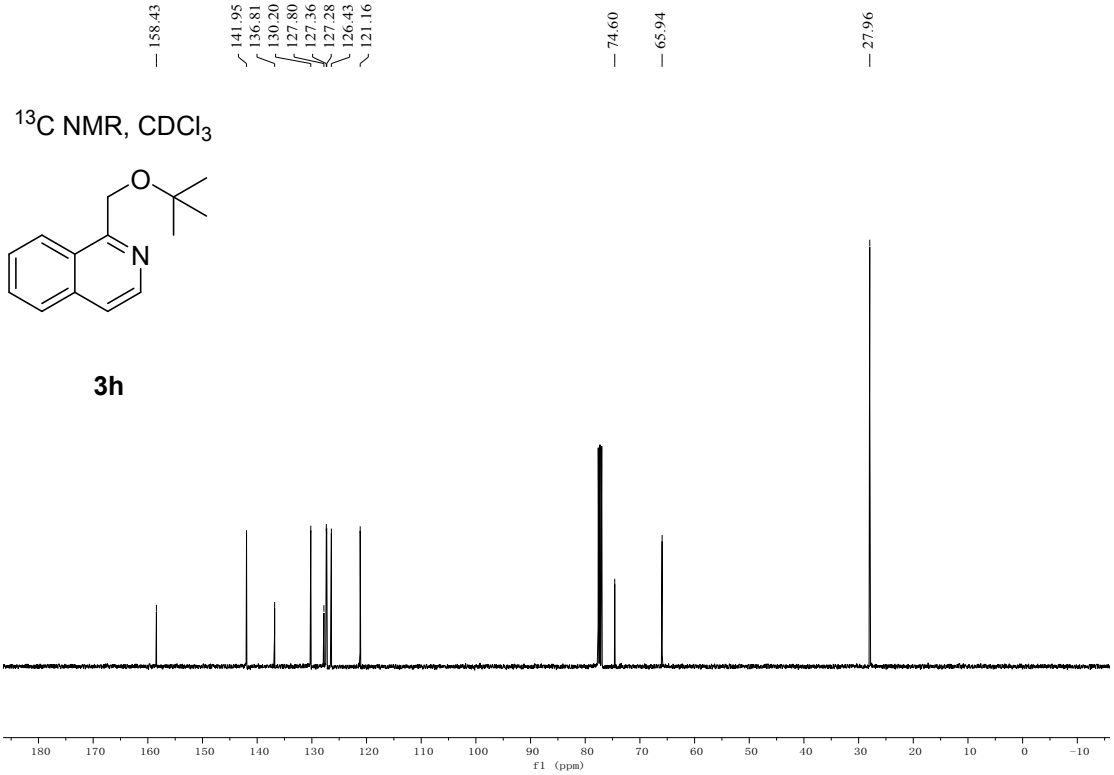
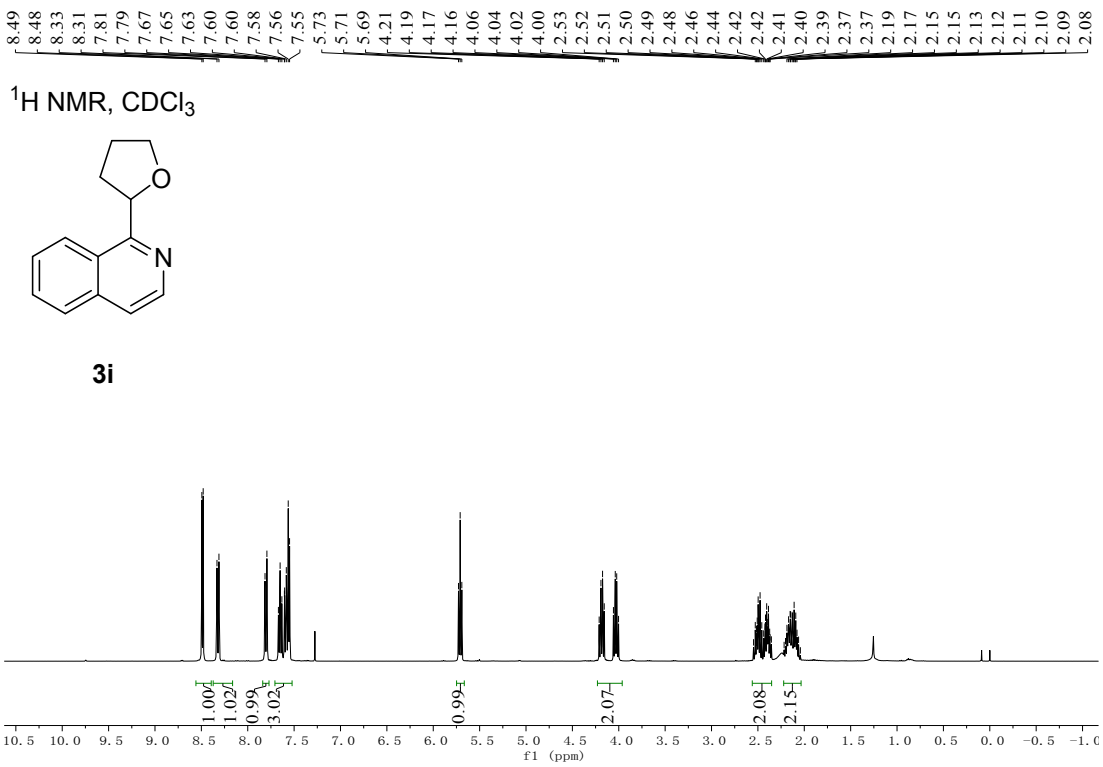


3h

^{13}C NMR, $CDCl_3$



3h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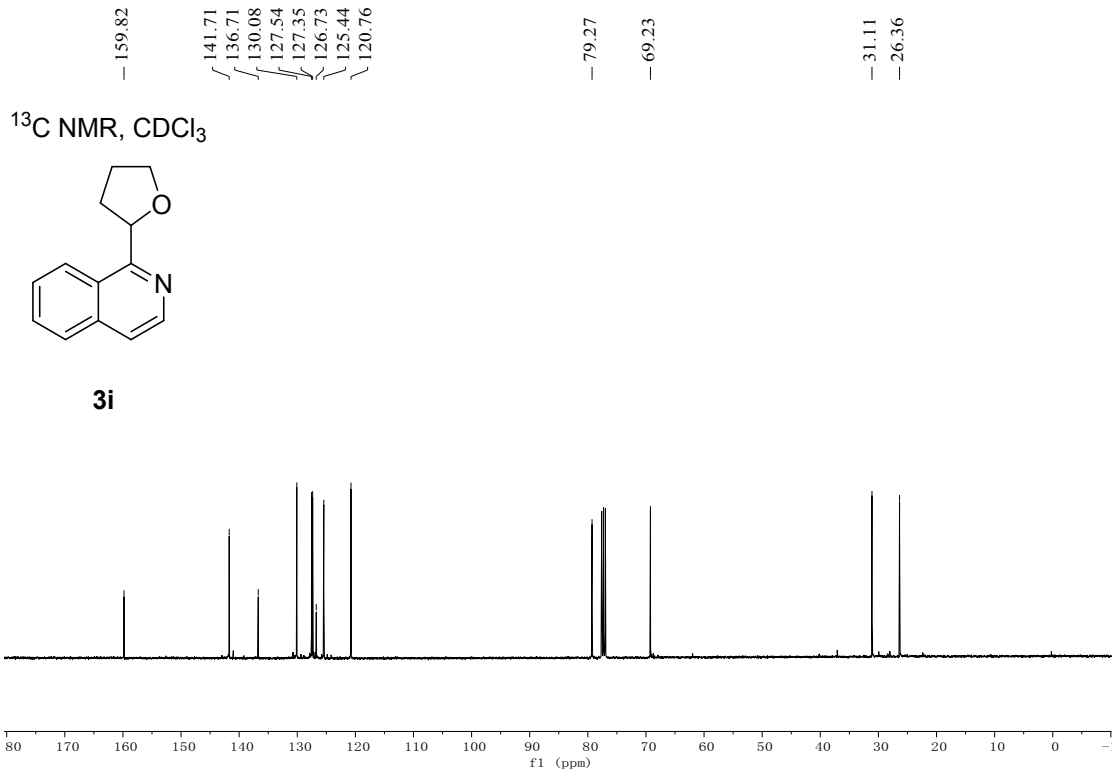
8.48
8.33
8.31
7.81
7.79
7.67
7.65
7.63
7.60
7.60
7.58
7.56
7.55
5.73
5.71
5.69
4.21
4.19
4.17
4.16
4.06
4.04
4.02
4.00
2.53
2.52
2.51
2.50
2.49
2.48
2.46
2.44
2.42
2.42
2.41
2.40
2.39
2.37
2.37
2.19
2.17
2.15
2.15
2.13
2.12
2.11
2.10
2.09
2.08
^{1}H NMR, $CDCl_3$
O
N
3i
1.00
1.02
0.99
3.02
0.99
2.07
2.08
2.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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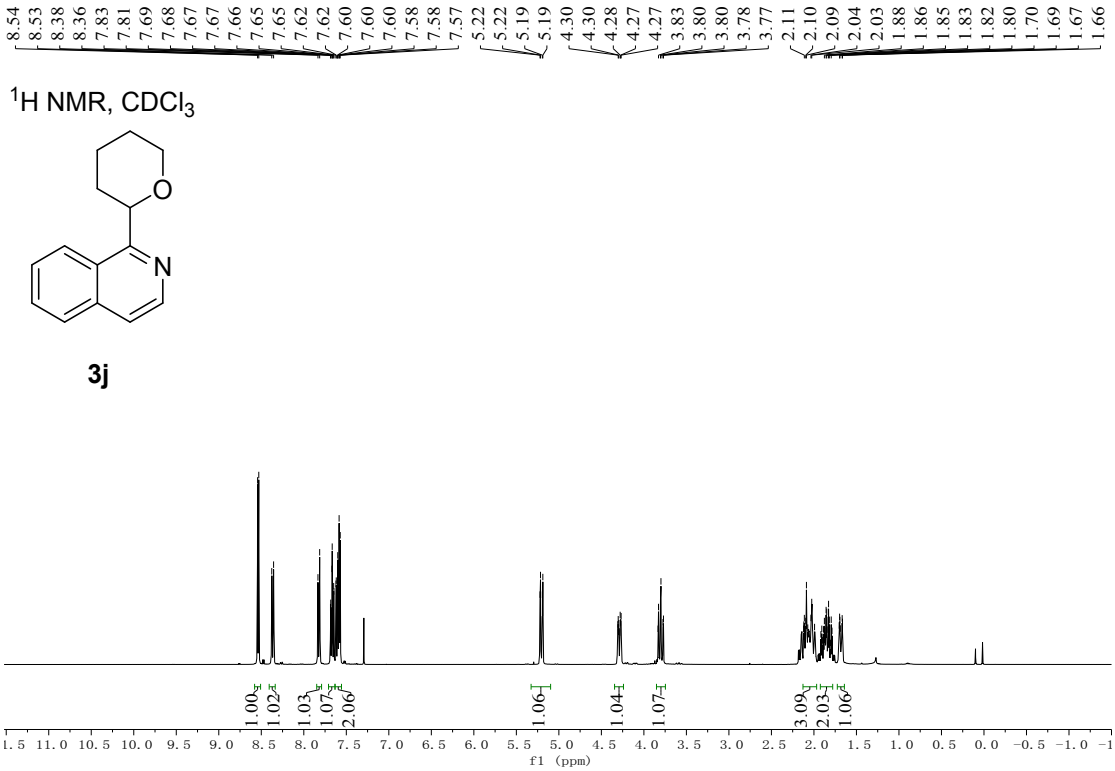
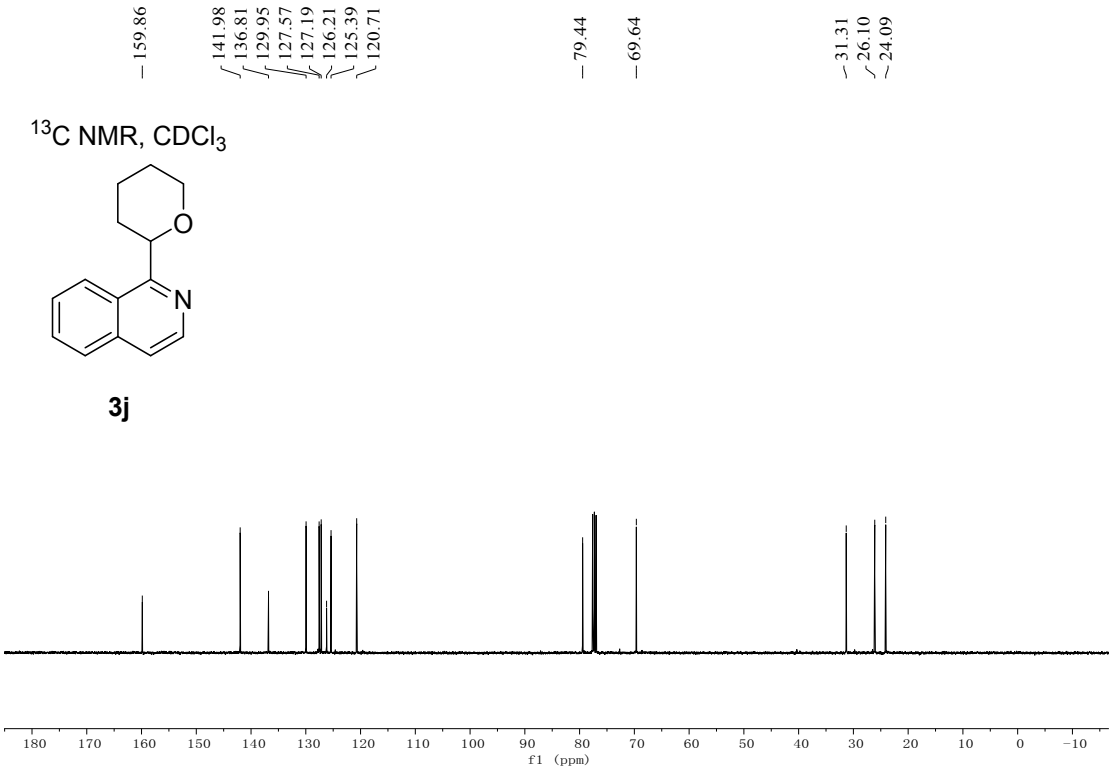
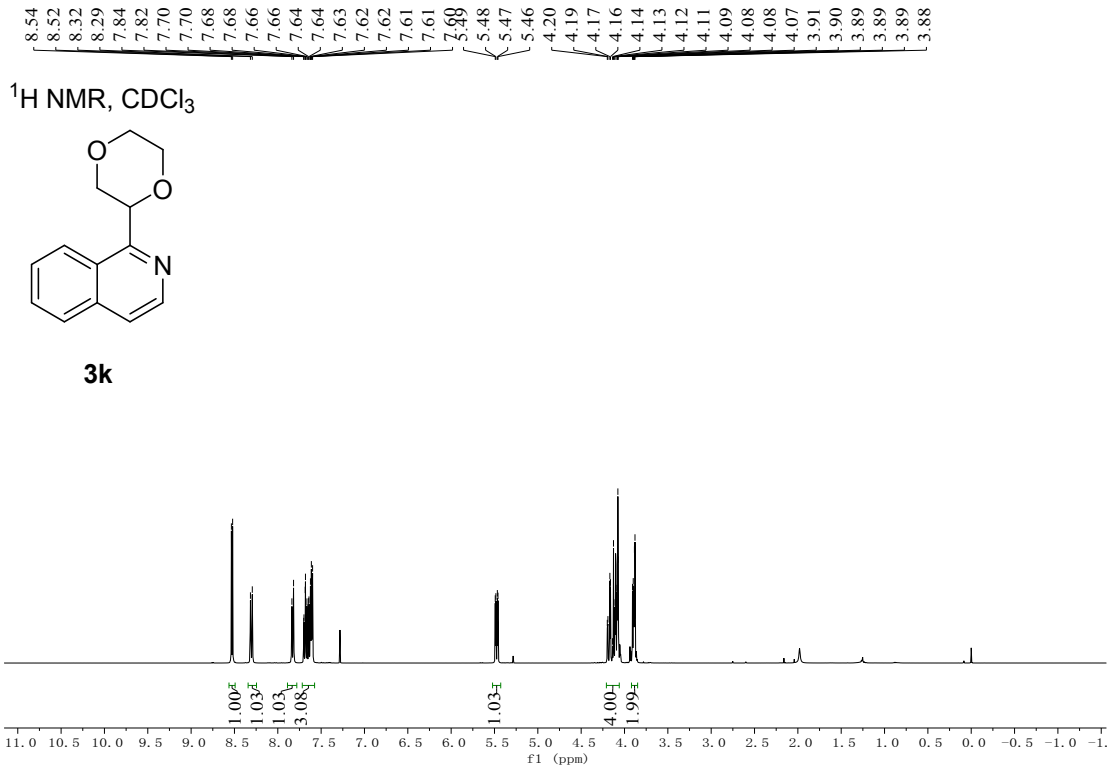
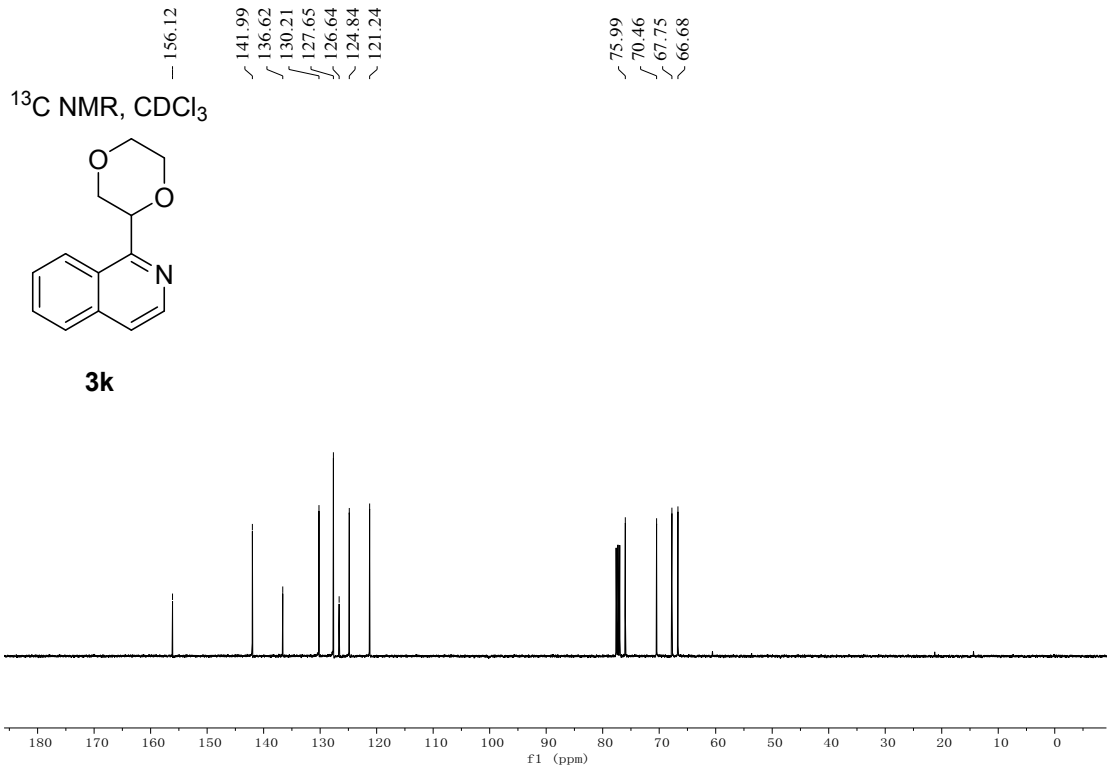
141.71
136.71
130.08
127.54
127.35
126.73
125.44
120.76
79.27
69.23
31.11
26.36
^{13}C NMR, $CDCl_3$
O
N
3i
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.54 8.53 8.38 8.36 7.83 7.81 7.69 7.68 7.67 7.67 7.66 7.65 7.65 7.62 7.62 7.60 7.60 7.60 7.58 7.58 7.57 5.22 5.22 5.19 5.19 4.30 4.30 4.28 4.27 4.27 3.83 3.80 3.80 3.78 3.77 2.11 2.10 2.09 2.04 2.03 1.88 1.86 1.85 1.83 1.82 1.80 1.70 1.69 1.67 1.66
^{1}H NMR, $CDCl_3$
O
N
3j
1.00 1.02 1.03 1.07 2.06 1.06 1.04 1.07 3.09 2.03 1.06
f1 (ppm)


159.86
141.98 136.81 129.95 127.57 127.19 126.21 125.39 120.71
79.44
69.64
31.31 26.10 24.09
^{13}C NMR, $CDCl_3$
O
N
3j
f1 (ppm)


8.54 8.52 8.32 8.29 7.84 7.82 7.70 7.70 7.68 7.68 7.66 7.66 7.64 7.64 7.63 7.62 7.62 7.61 7.61 7.60 5.49 5.48 5.47 5.46 4.20 4.19 4.17 4.16 4.14 4.13 4.12 4.11 4.09 4.08 4.08 4.07 3.91 3.90 3.89 3.89 3.89 3.88
^{1}H NMR, $CDCl_3$
O
O
N
3k
1.00 1.03 1.03 3.08 1.03 4.00 1.99
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)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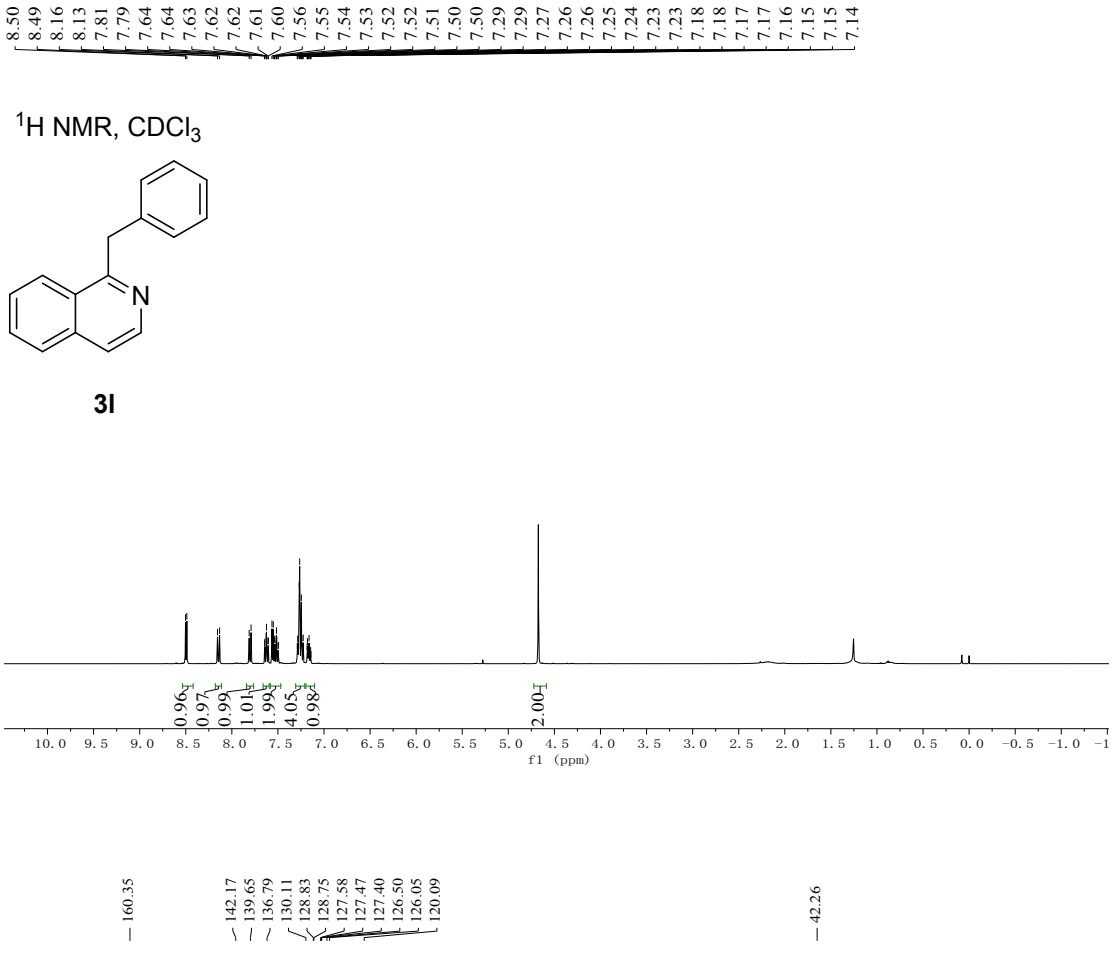
141.99 136.62 130.21 127.65 126.64 124.84 121.24
75.99 70.46 67.75 66.68
^{13}C NMR, $CDCl_3$
O
O
N
3k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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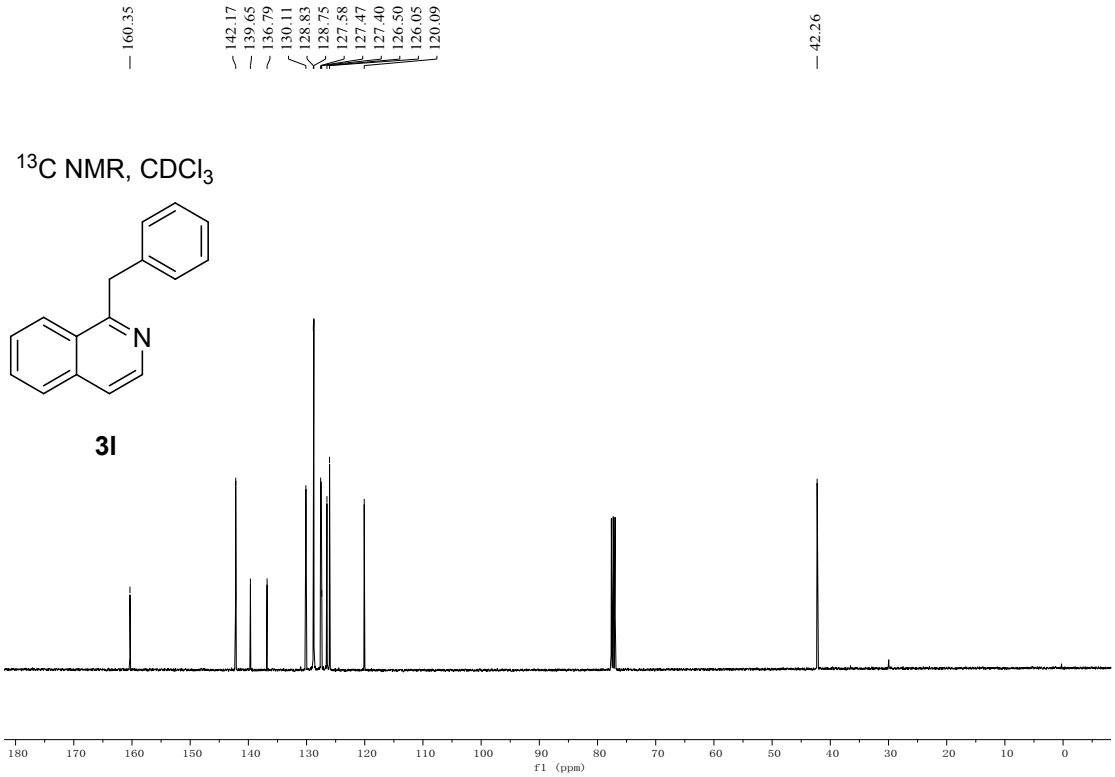
8.49
8.16
8.13
7.81
7.79
7.64
7.64
7.63
7.62
7.62
7.61
7.60
7.56
7.55
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.29
7.29
7.27
7.26
7.26
7.25
7.24
7.23
7.23
7.18
7.18
7.17
7.17
7.16
7.15
7.15
7.14
^{1}H NMR, $CDCl_3$
N
3l
0.96
0.97
0.99
1.01
1.99
4.05
0.98
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1
f1 (ppm)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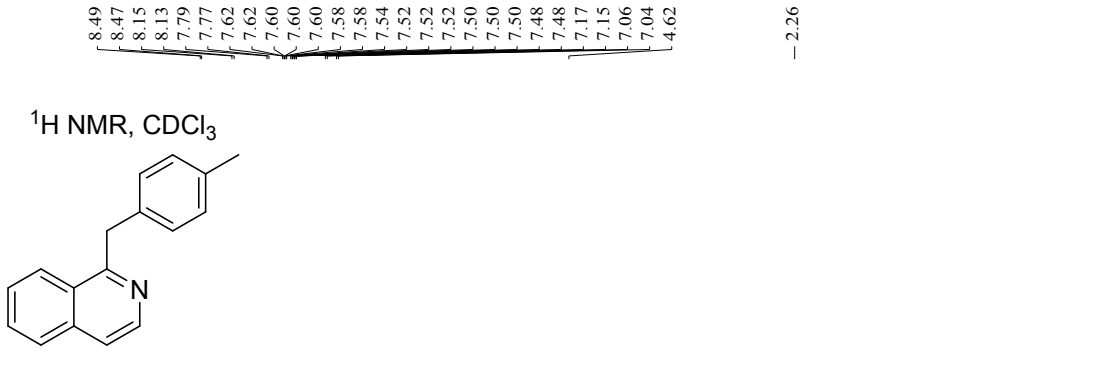
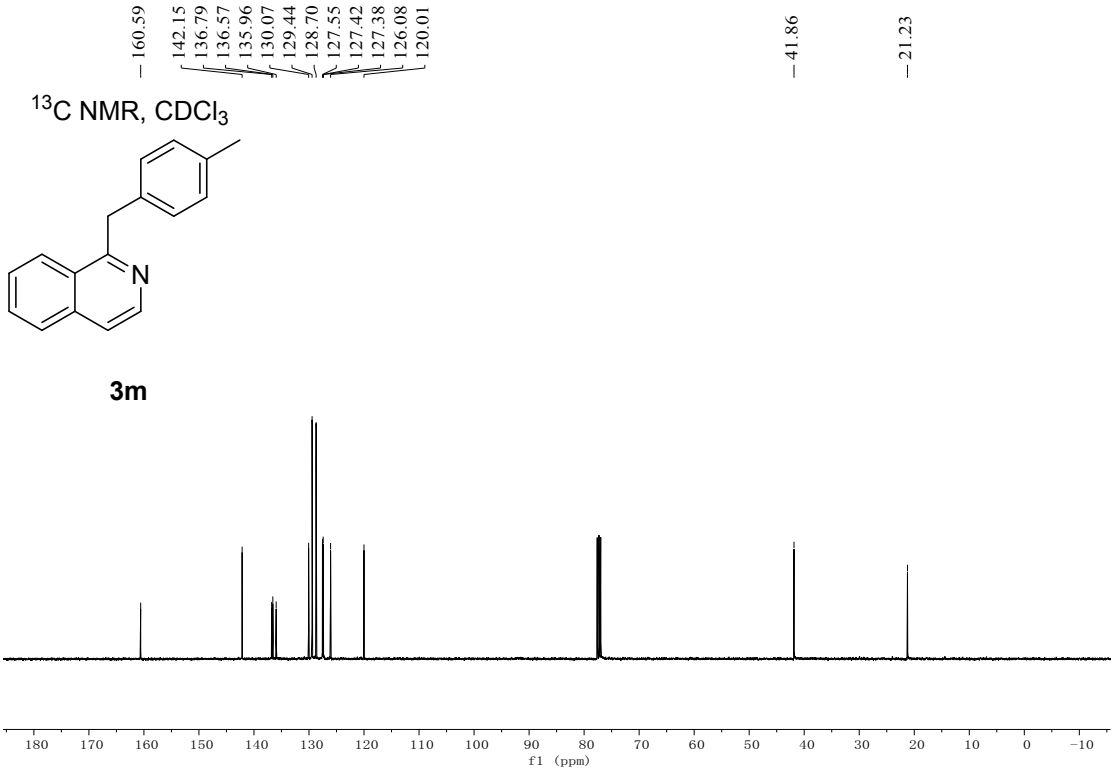
142.17
139.65
136.79
130.11
128.83
128.75
127.58
127.47
127.40
126.50
126.05
120.09
42.26
^{13}C NMR, $CDCl_3$
N
3l
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.49
8.47
8.15
8.13
7.79
7.77
7.62
7.62
7.60
7.60
7.60
7.58
7.58
7.54
7.52
7.52
7.52
7.50
7.50
7.50
7.48
7.48
7.17
7.15
7.06
7.04
4.62
2.26
^{1}H NMR, $CDCl_3$
N
3m
0.96
1.00
0.97
1.00
2.00
1.99
2.09
2.09
3.00
f1 (ppm)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142.15
136.79
136.57
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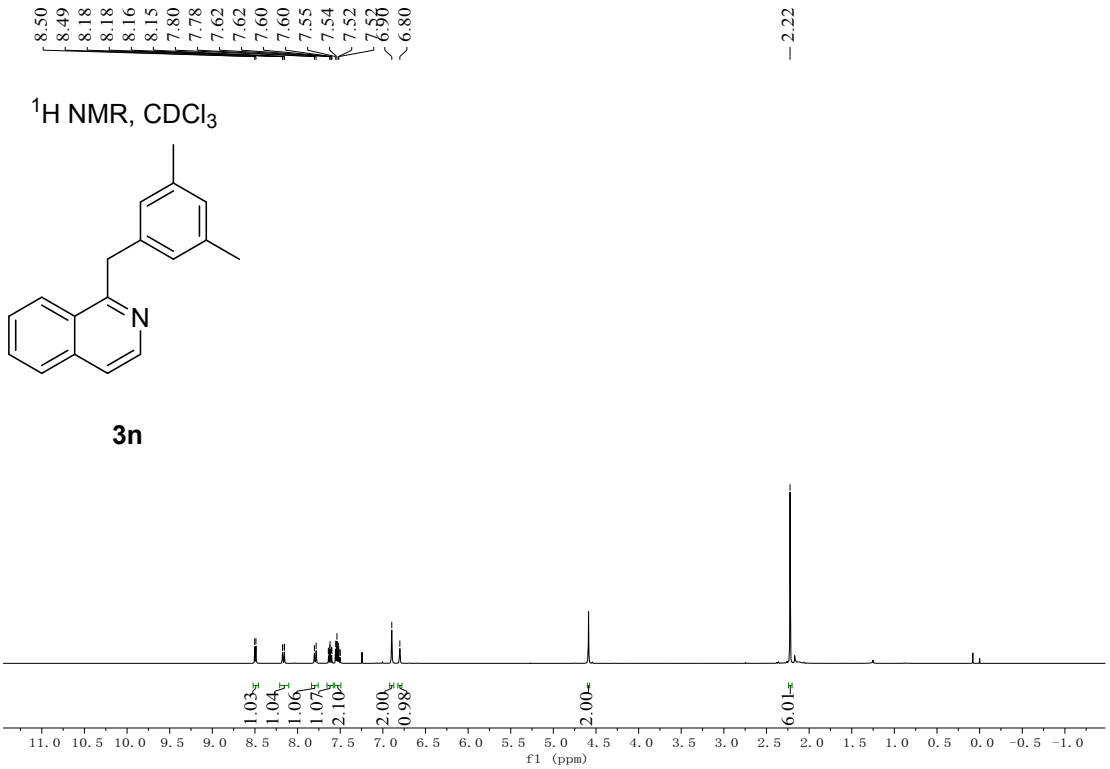
130.07
129.44
128.70
127.55
127.42
127.38
126.08
120.01
41.86
21.23
^{13}C NMR, $CDCl_3$
N
3m
f1 (ppm)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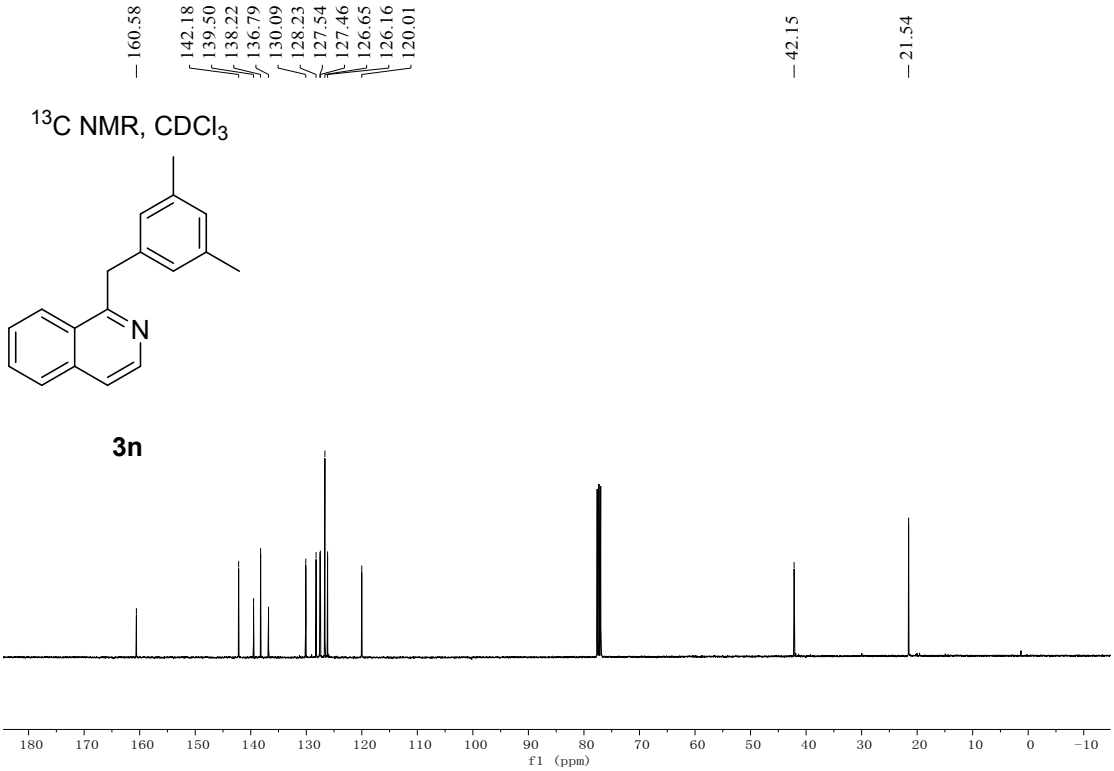
8.49
8.18
8.18
8.16
8.15
7.80
7.78
7.62
7.62
7.60
7.60
7.55
7.54
7.52
7.52
6.90
6.80
2.22
1H NMR, CDCl3
N
3n
1.03
1.04
1.06
1.07
2.10
2.00
0.98
2.00
6.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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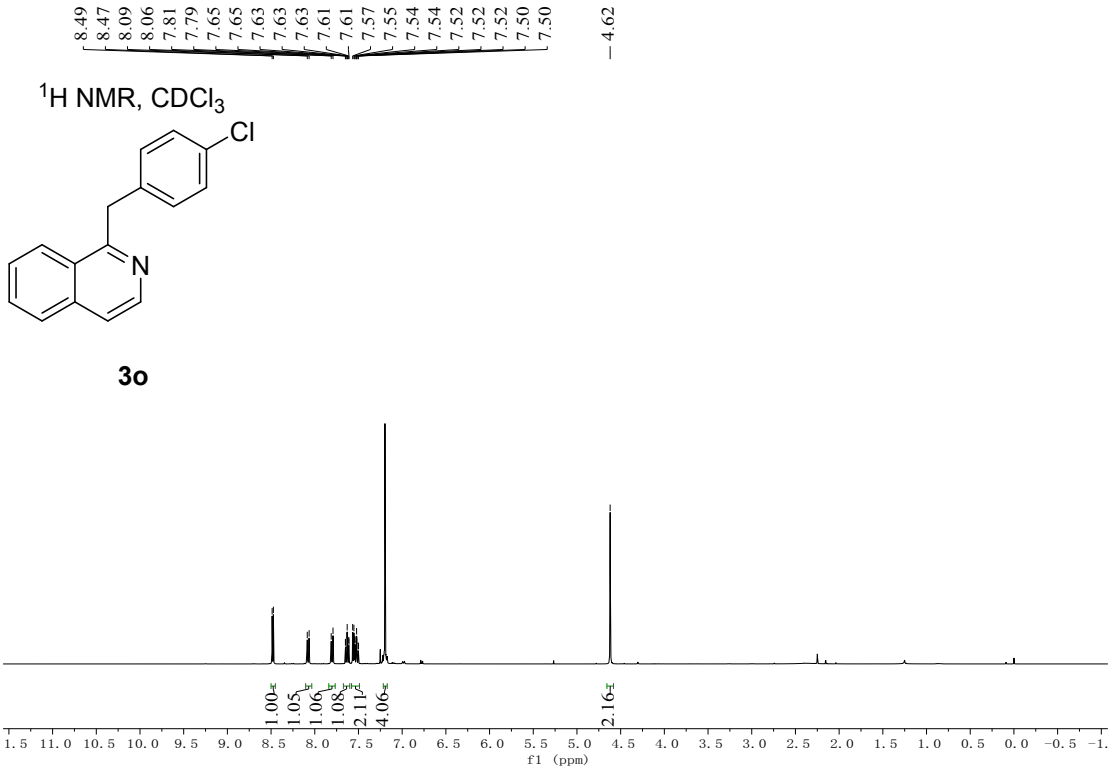
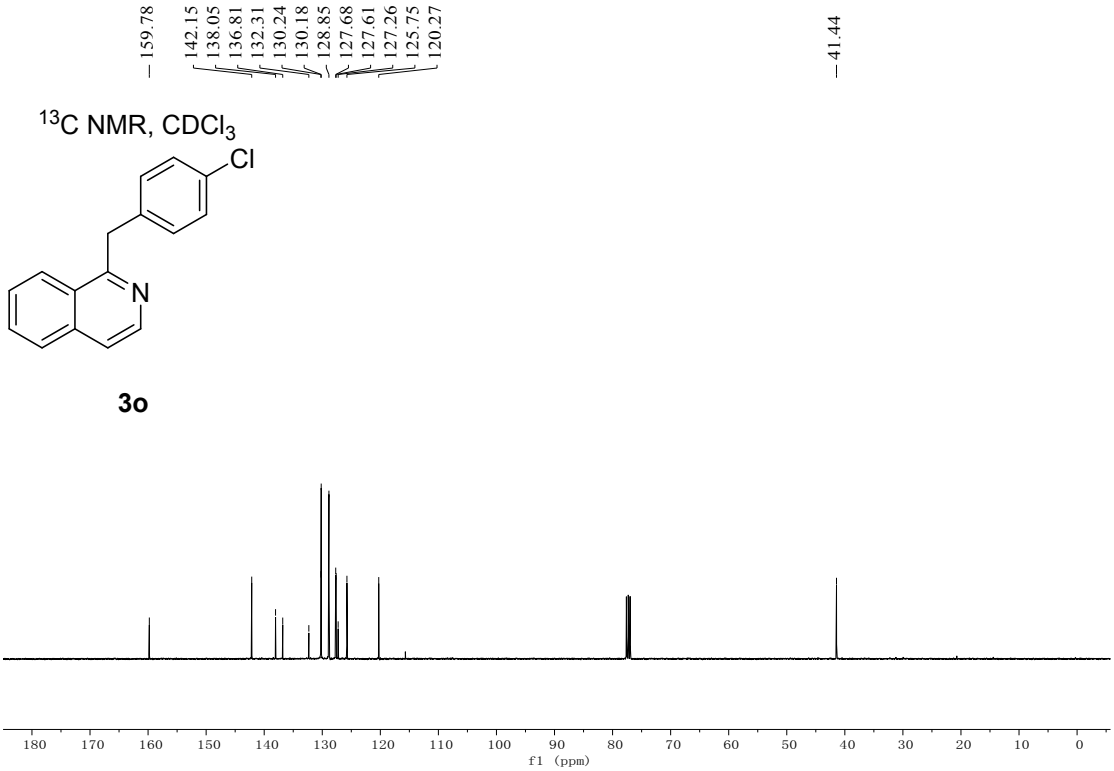
142.18
139.50
138.22
136.79
130.09
128.23
127.54
127.46
126.65
126.16
120.01
42.15
21.54
13C NMR, CDCl3
N
3n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.49
8.47
8.09
8.06
7.81
7.79
7.65
7.65
7.63
7.63
7.63
7.61
7.61
7.57
7.55
7.54
7.54
7.52
7.52
7.52
7.50
7.50
4.62
1H NMR, CDCl3
Cl
N
3o
1.00
1.05
1.06
1.08
2.11
4.06
2.16
f1 (ppm)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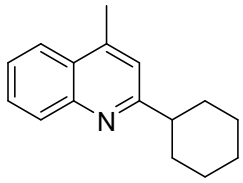
142.15
138.05
136.81
132.31
130.24
130.18
128.85
127.68
127.61
127.26
125.75
120.27
41.44
13C NMR, CDCl3
Cl
N
3o
f1 (ppm)

8.10 8.09 8.07 8.07 7.97 7.96 7.95 7.94 7.71 7.70 7.69 7.69 7.68 7.67 7.67 7.53 7.53 7.51 7.51 7.51 7.49 7.49 7.19 2.70 2.69 2.06 2.06 2.03 2.02 1.94 1.93 1.93 1.91 1.90 1.90 1.83 1.80 1.67 1.67 1.64 1.63 1.52 1.51 1.50 1.49 1.48 1.47 1.45 1.38 1.34

^{1}H NMR, $CDCl_3$



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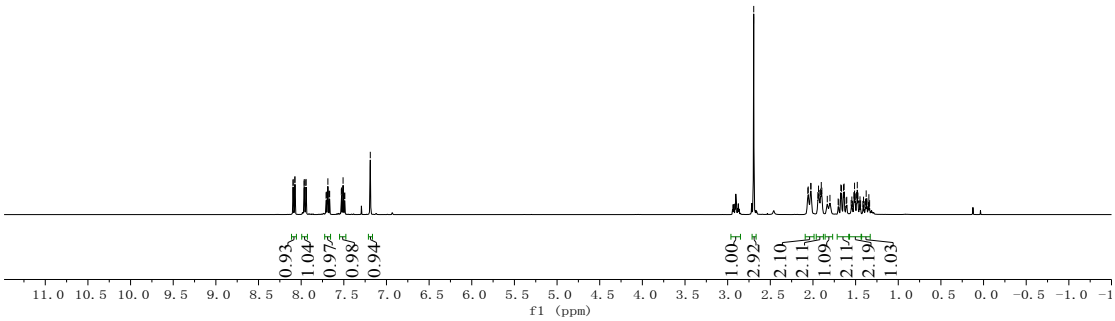
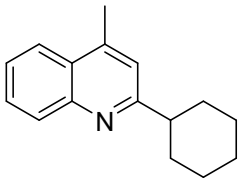


158.89 153.39 148.18 129.58 128.87 125.35 125.22 122.92 118.40 38.84 33.63 27.01 26.40 25.63

^{13}C NMR, $CDCl_3$



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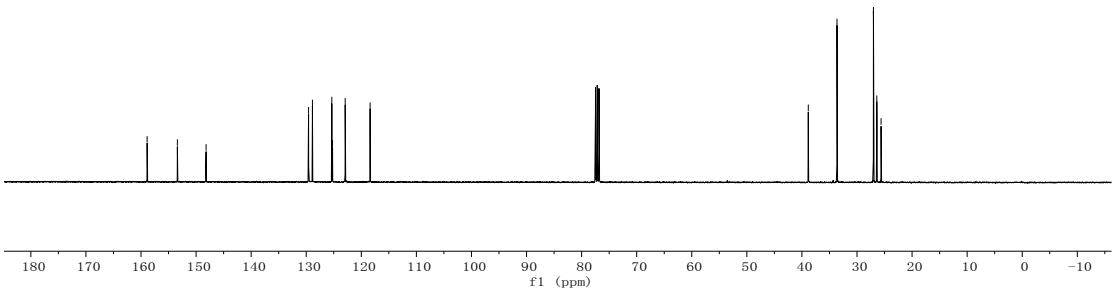
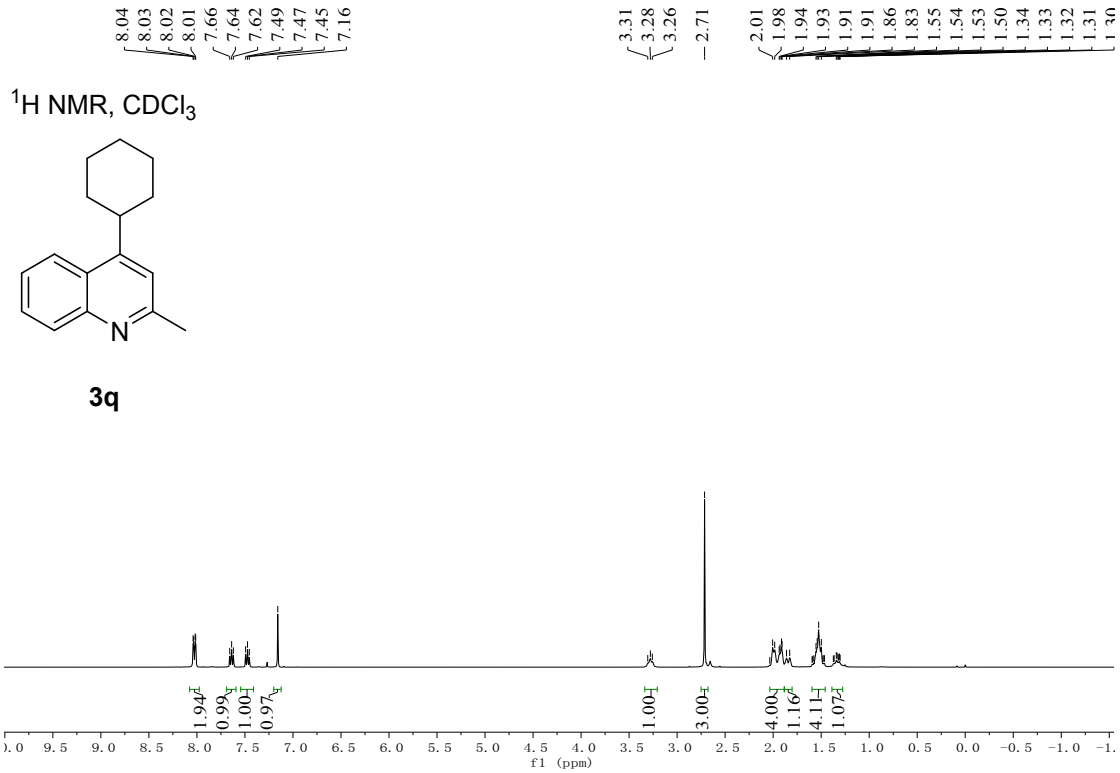


^{1}H NMR, $CDCl_3$



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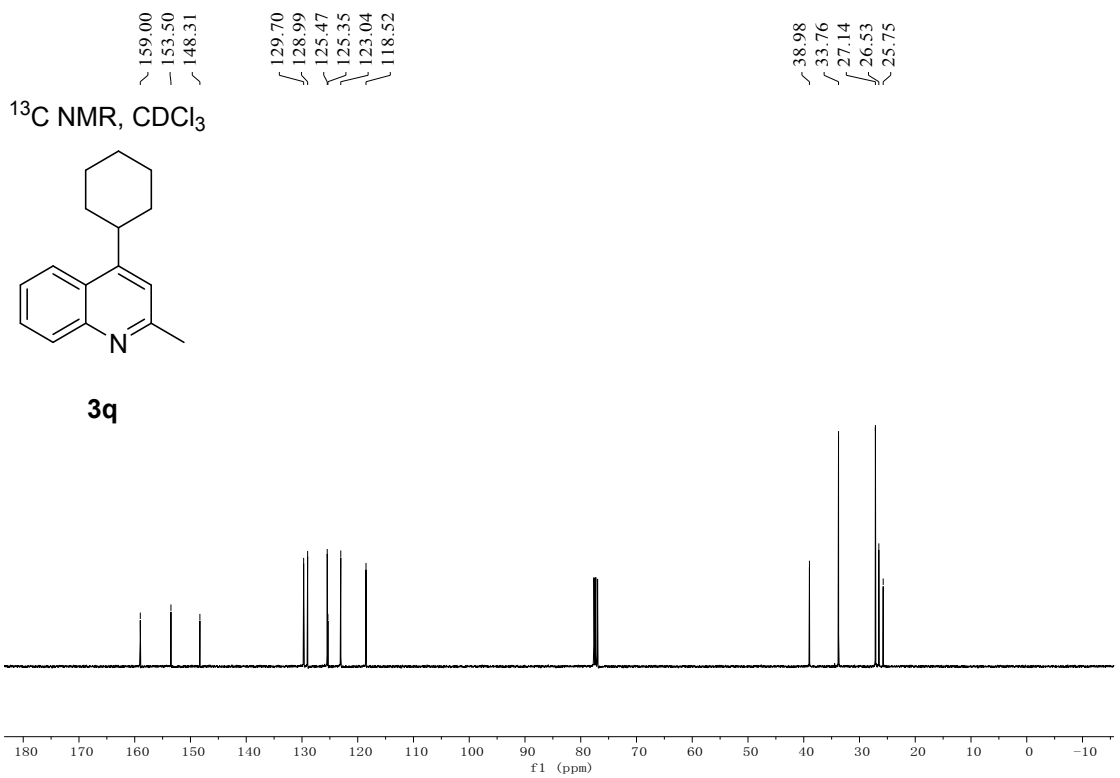
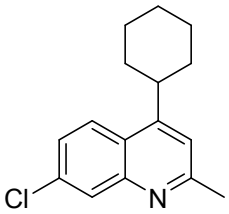
^{13}C NMR, $CDCl_3$



3q

^{1}H NMR, $CDCl_3$



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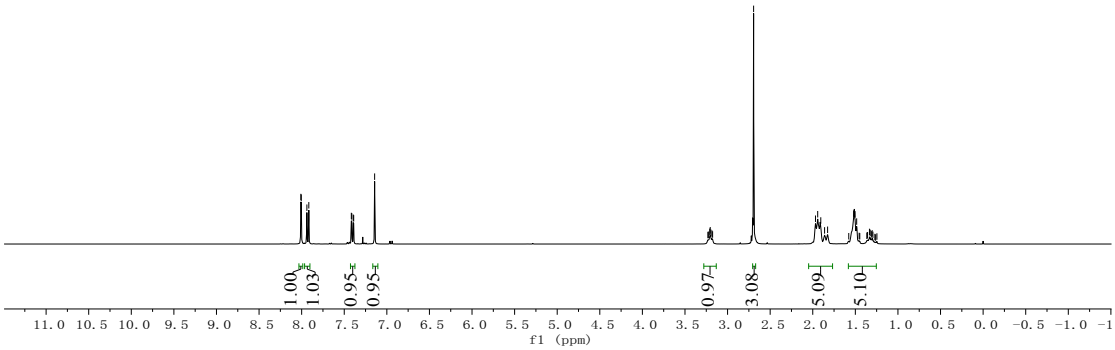
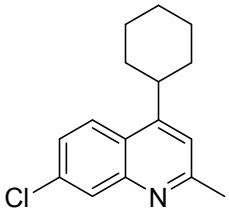


^{13}C NMR, $CDCl_3$



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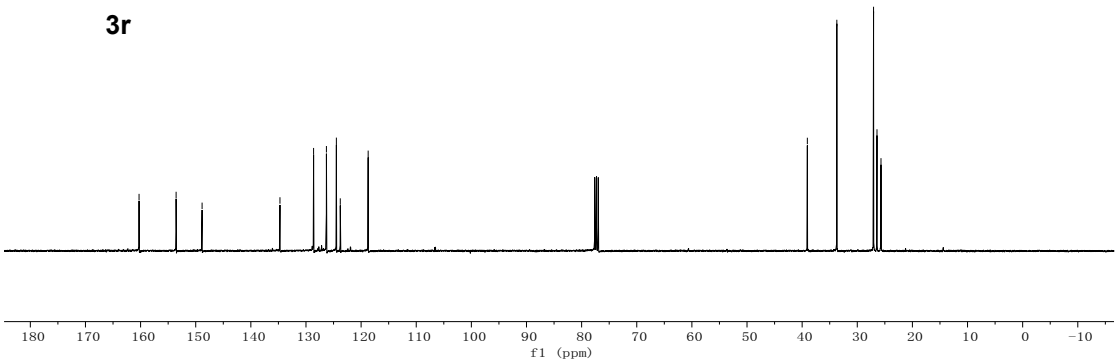
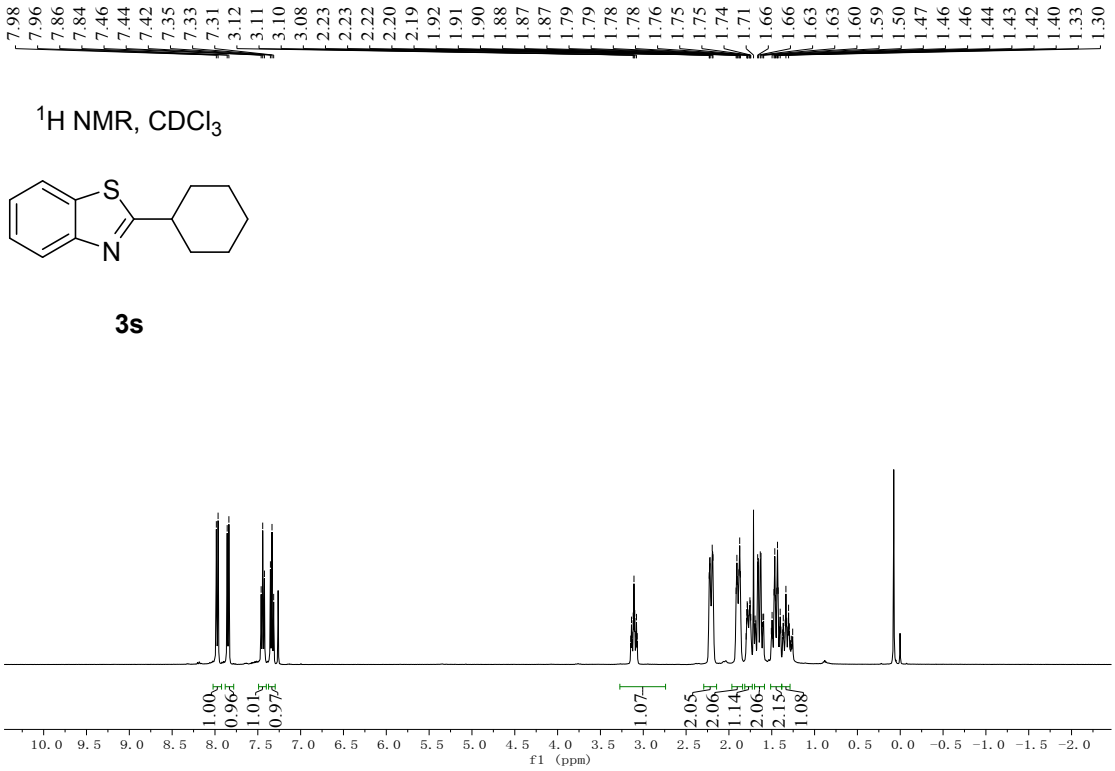
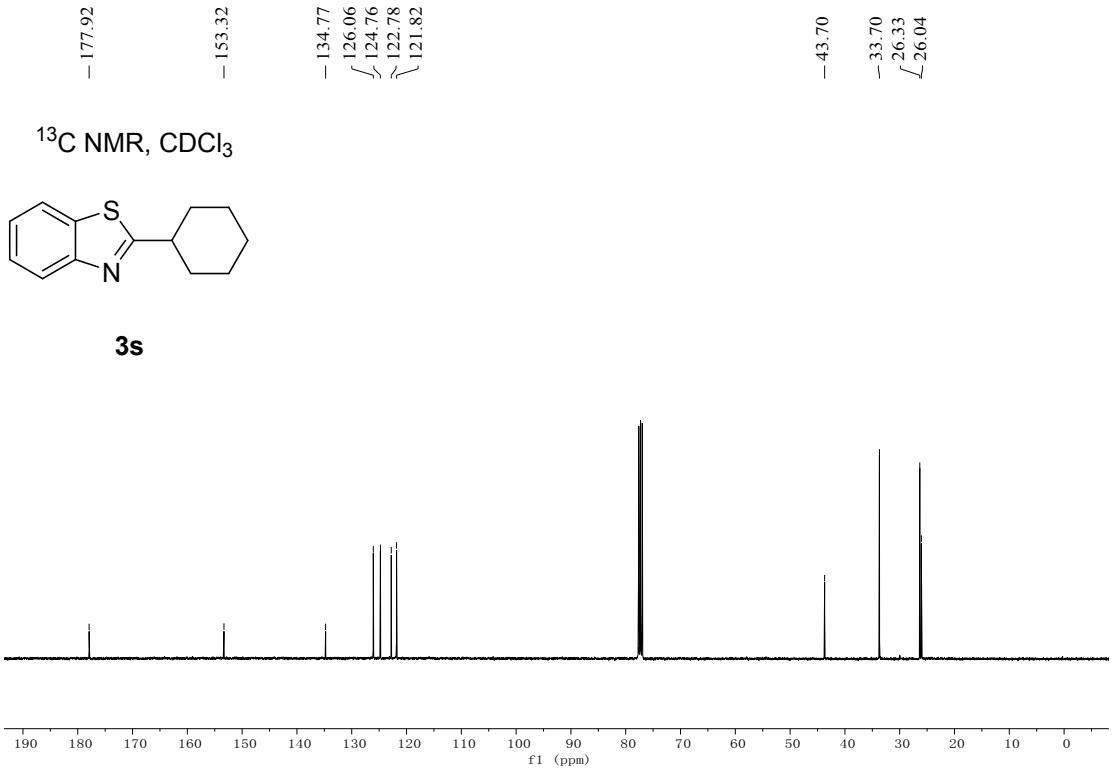



7.98 7.96 7.86 7.84 7.46 7.44 7.42 7.35 7.33 7.31 3.12 3.11 3.10 3.08 2.23 2.23 2.22 2.20 2.19 1.92 1.91 1.90 1.88 1.87 1.87 1.79 1.79 1.78 1.78 1.76 1.75 1.75 1.74 1.71 1.66 1.66 1.63 1.63 1.60 1.59 1.50 1.47 1.46 1.46 1.44 1.43 1.42 1.40 1.33 1.30
^{1}H NMR, $CDCl_3$
S
N
3s
1.00 0.96 1.01 0.97 1.07 2.05 2.06 1.14 2.06 2.15 1.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5 −2.0
f1 (ppm)

^{13}C NMR, $CDCl_3$

3s