Electronic Supplementary Information

Intramolecular Redox Cyclization Reaction Access to Cinnolines from 2-Nitrobenzyl Alcohol and Benzylamine via Intermediate 2-Nitrosobenzaldehyde

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Electronic Supplementary Information

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Experimental Section

1. General Methods

All substrates and reagents were commercial and used without further purification. TLC analysis was performed using precoated glass plates. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR spectra were determined at 25 °C on 500 or 600 MHz spectrometer. $^{13}C\{^{1}H\}$ NMR spectra were determined at 25 °C on 125 or 150 MHz spectrometer. Chemical shifts are given in ppm relative to the internal standard of tetramethylsilane (TMS). HRMS were obtained on an UPLC G2-XS Qtof MS equipped with an electrospray ionization (ESI) source. Melting points were determined using XT-4 apparatus and not corrected.

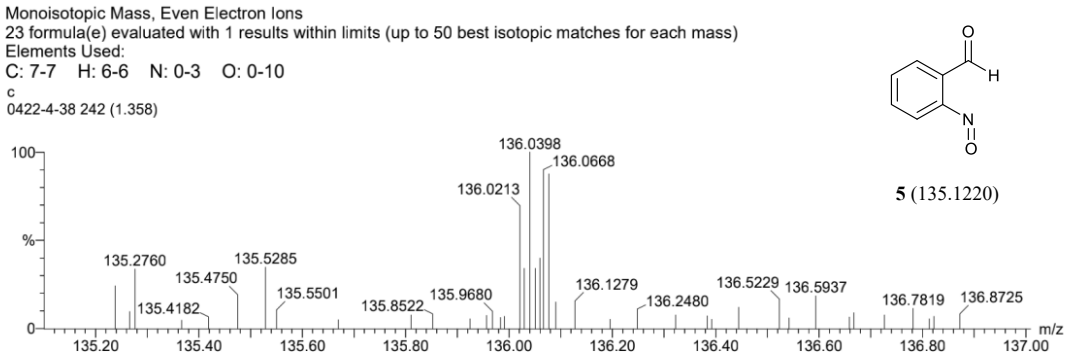
2. General Experimental Details

General procedure for the construction of **3aa-3aw,** and **3ba-3ia** (**3aa** as example).

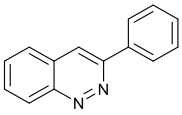
The mixture of 2-nitrobenzyl alcohol **1a** (153.1 mg, 1.0 mmol), benzylamine **2a** (321.5 mg, 3 mmol) and $CsOH{\cdot}H_2O$ (503.8 mg, 3.0 mmol) was added in EtOH/H_2O (4ml/2ml). Then, the resulting mixture was stirred at 100 °C for 3 h. After the reaction completed, added 200 mL water to the mixture, extracted with EtOAc three times (3×100 mL). Dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc =5/1) to afford the desired product **3aa** (167.1mg, 81%).

3. The MS Spectra of intermediate 5

A mixture of 2-nitrobenzyl alcohol **1a** (153.1 mg, 1.0 mmol) and $CsOH{\cdot}H_2O$ (503.8 mg, 3.0 mmol) was added in EtOH/H_2O (4ml/2ml) at 100 °C for 3 h. Then the mixture detected by HRMS. The following intermediate 2-Nitrosobenzaldehyde **5** (44.6mg, 33%) was captured.

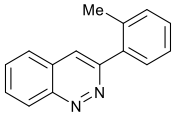


4. Spectroscopic Data



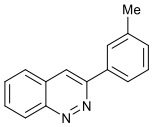
3-phenylcinnoline (**3aa**):[1]

Yield 81%; 167.1mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 107–108 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.58 (d, J = 8.4 Hz, 1H), 8.27 (d, J =7.8 Hz, 2H), 8.19 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.78 – 7.75 (m, 1H), 7.58 (t, J = 7.8 Hz, 2H), 7.51 (t, J = 7.8 Hz, 1H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 153.5, 149.9, 136.9, 131.3, 130.3, 129.8, 129.5, 129.1, 127.3, 127.0, 126.6, 118.9. **ITMS** (ESI, LCQ-fleet): *m/z* 208.10 (M+1, 23.87%), 207.14 (M, 100).



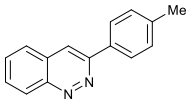
3-(o-tolyl) cinnoline (**3ab**):[1a]

Yield 62%; 137.0mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 54–57 °C; ^{1}**H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.59 (d, J = 9.5 Hz, 1H), 7.90 (s, 1H), 7.85 (t, J = 9.0 Hz, 2H), 7.76 (t, J = 8.0 Hz, 1H), 7.55 (d, J = 7.0 Hz, 1H), 7.41 – 7.34 (m, 3H), 2.44 (s, 3H); ^{13}**C**{^{1}H} **NMR** (125 MHz, $CDCl_3$): δ (ppm) 156.2, 149.3, 137.6, 136.6, 131.2, 130.9, 130.4, 130.3, 129.8, 128.9, 126.8, 126.1, 126.0, 122.2, 20.5. **ITMS** (ESI, LCQ-fleet): *m/z* 222.19 (M+1, 14.34%), 221.09 (M, 100).



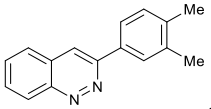
3-(m-tolyl) cinnoline (**3ac**):[1a, 1d, 2]

Yield 66%; 145.9mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 58–60 °C; ^{1}**H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.57 (d, J = 8.5 Hz, 1H), 8.17 (s, 1H), 8.11 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.82 (t, J = 9.5 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 2.50 (s, 3H); ^{13}**C**{^{1}H} **NMR** (125 MHz, $CDCl_3$): δ (ppm) 153.7, 149.8, 138.8, 136.9, 131.2, 130.2, 130.2, 129.8, 129.0, 128.1, 126.9, 126.6, 124.4, 118.8, 21.6. **ITMS** (ESI, LCQ-fleet): *m/z* 222.21 (M+1, 21.70%), 221.08 (M, 100).



3-(p-tolyl) cinnoline (**3ad**):[1a, 1c, 2]

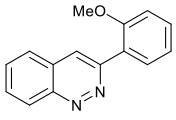
Yield 67%; 147.6mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 124–126 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.56 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 7.8 Hz, 2H), 8.15 (s, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.81 (t, J = 8.4 Hz, 1H), 7.74 (t, J = 7.8 Hz, 1H), 7.38 (d, J = 7.8 Hz, 2H), 2.46 (s, 3H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 153.5, 149.8, 139.6, 134.1, 131.2, 130.0, 129.8, 129.8, 127.1, 126.9, 126.6, 118.3, 21.3. **ITMS** (ESI, LCQ-fleet): *m/z* 222.19 (M+1, 14.11%), 221.08 (M, 100).



3-(3,4-dimethylphenyl) cinnoline (**3ae**):

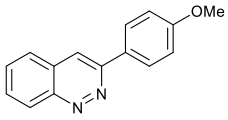
Yield 60%; 140.6mg; purified by column chromatography on silica gel (PE/EtOAc=4/1); yellow

solid; m.p. 105–107 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.54 (d, J = 8.4 Hz, 1H), 8.12 (s, 1H), 8.07 (s, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.78 (t, J = 8.4 Hz, 1H), 7.71 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 2.39 (s, 3H), 2.35 (s, 3H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 153.6, 149.8, 138.2, 137.3, 134.4, 131.1, 130.3, 129.9, 129.8, 128.4, 126.9, 126.6, 124.6, 118.2, 20.0, 19.7. **HRMS** (ESI, UPLC G2-XS Qtof): m/z [M+H]$^{+}$ calcd for $C_{16}H_{15}N_2$: 235.1235; found: 235.1237.



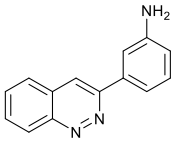
3-(2-methoxyphenyl) cinnoline (**3af**):

Yield 79%; 186.6mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 85–86 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.54 (d, J = 8.4 Hz, 1H), 8.40 (s, 1H), 8.19 (d, J = 7.2 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.79 (t, J = 7.8 Hz, 1H), 7.71 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 3.89 (s, 3H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 157.2, 152.0, 149.2, 131.6, 130.8, 130.5, 130.0, 129.5, 127.0, 126.1, 125.9, 123.4, 121.2, 111.3, 55.6. **HRMS** (ESI, UPLC G2-XS Qtof): m/z [M+H]$^{+}$ calcd for $C_{15}H_{13}N_2$: 237.1028; found: 237.1029.



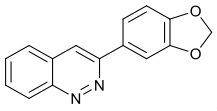
3-(4-methoxyphenyl) cinnoline (**3ag**):[1a, 1c, 2]

Yield 80%; 189.0mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 93–98 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.52 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 8.4 Hz, 2H), 8.07 (s, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.77 (t, J = 8.4 Hz, 1H), 7.70 (t, J = 7.2 Hz, 1H), 7.07 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 160.8, 153.1, 149.5, 131.1, 129.8, 129.7, 129.3, 128.5, 126.8, 126.6, 117.6, 114.4, 55.3. **ITMS** (ESI, LCQ-fleet): *m/z* 238.20 (M+1, 18.73%), 237.14 (M, 100).



3-(cinnolin-3-yl) aniline (**3ah**):

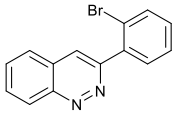
Yield 53%; 117.3mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 80–81 °C; ^{1}**H NMR** (600 MHz, DMSO-d_6): δ (ppm) 8.59 (s, 1H), 8.51 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.94 (t, J = 8.4 Hz, 1H), 7.89 (t, J = 7.8 Hz, 1H), 7.66 (s, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 5.40 (s, 2H); ^{13}**C**{^{1}H} **NMR** (150 MHz, DMSO-d_6): δ (ppm) 153.2, 149.4, 149.4, 137.1, 131.4, 130.7, 129.6, 128.8, 127.6, 126.1, 118.6, 115.1, 114.485, 112.3. **HRMS** (ESI, UPLC G2-XS Qtof): m/z [M+H]$^{+}$ calcd for $C_{14}H_{12}N_3$: 222.1031; found: 222.1033.



3-(benzo[d] [1,3] dioxol-5-yl) cinnoline (**3ai**):

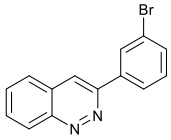
Yield 59%; 147.5mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 118–120 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.53 (d, J = 8.4 Hz, 1H), 8.06 (s, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.81 – 7.78 (m, 2H), 7.73 (t, J = 8.4 Hz, 2H), 6.99 (d, J = 7.8 Hz, 1H), 6.07 (s, 2H); ^{13}**C**{^{1}H} **NMR** (125 MHz, $CDCl_3$): δ (ppm) 153.1, 149.7, 148.9, 148.6, 131.2, 131.1,

130.0, 129.8, 126.8, 126.6, 121.4 118.0, 108.8, 107.6, 101.4. **HRMS** (ESI, UPLC G2-XS Qtof): m/z $[M+H]^+$ calcd for $C_{15}H_{11}N_2O_2$: 251.0821; found: 251.0826.



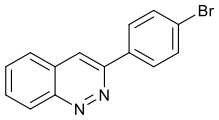
3-(2-bromophenyl) cinnoline (**3aj**):

Yield 51%; 145.4mg; purified by column chromatography on silica gel (PE/EtOAc=4/1); yellow solid; m.p. 83–86 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.59 (d, J = 9.0 Hz, 1H), 8.18 (s, 1H), 7.90 – 7.86 (m, 2H), 7.79 (d, J = 7.8 Hz, 1H), 7.77 – 7.74 (m, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H) ; ^{13}**C**$\{^1$H$\}$ **NMR** (150 MHz, $CDCl_3$): δ (ppm) 154.4, 149.5, 138.5, 133.4, 132.2, 131.3, 130.8, 130.3, 129.7, 127.7, 126.9, 125.4, 123.5, 122.4. **HRMS** (ESI, UPLC G2-XS Qtof): m/z $[M+H]^+$ calcd for $C_{14}H_{10}N_2Br$: 285.0027; found: 285.0028.



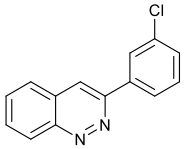
3-(3-bromophenyl) cinnoline (**3ak**):

Yield 54%; 153.9mg; purified by column chromatography on silica gel (PE/EtOAc=4/1); yellow solid; m.p. 88–89 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.59 (d, J = 9.0 Hz, 1H), 8.42 (s, 1H), 8.19 (d, J = 7.2 Hz, 1H), 8.17 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.86 (t, J = 7.8 Hz, 1H), 7.78 (t, J = 7.2 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H); ^{13}**C**$\{^1$H$\}$ **NMR** (150 MHz, $CDCl_3$): δ (ppm) 152.0, 150.0, 138.9, 132.3, 131.6, 130.7, 130.6, 130.2, 129.8, 127.0, 126.3, 125.8, 123.3, 119.1. **HRMS** (ESI, UPLC G2-XS Qtof): m/z $[M+H]^+$ calcd for $C_{14}H_{10}N_2Br$: 285.0027; found: 285.0026.



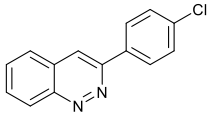
3-(4-bromophenyl) cinnoline (**3al**):[1a, 1c, 1d]

Yield 49%; 139.6mg; purified by column chromatography on silica gel (PE/EtOAc=4/1); yellow solid; m.p. 93–102 °C; ^{1}**H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.57 (d, J = 8.5 Hz, 1H), 8.16 (d, J = 3.0 Hz, 2H), 8.14 (s, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.85 (t, J = 8.5 Hz, 1H), 7.77 (t, J = 8.0 Hz, 1H), 7.70 (d, J = 9.0 Hz, 2H); ^{13}**C**$\{^1$H$\}$ **NMR** (125 MHz, $CDCl_3$): δ (ppm) 152.4, 150.0, 135.9, 132.3, 131.5, 130.5, 129.9, 128.8, 127.0, 126.4, 124.1, 118.6. **ITMS** (ESI, LCQ-fleet): *m/z* 287.11 (M+1, 52.73%), 285.03 (M, 100).



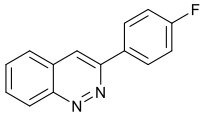
3-(3-chlorophenyl) cinnoline (**3am**):[1c, 2]

Yield 48%; 115.5mg; purified by column chromatography on silica gel (PE/EtOAc=4/1); yellow solid; m.p. 125–128 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.61 (d, J = 8.4 Hz, 1H), 8.28 (s, 1H), 8.20 (s, 1H), 8.16 (d, J = 7.2 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.88 (t, J = 7.8 Hz, 1H), 7.80 (t, J = 7.8 Hz, 1H), 7.53 – 7.48 (m, 2H); ^{13}**C**$\{^1$H$\}$ **NMR** (150 MHz, $CDCl_3$): δ (ppm) 152.1, 150.0, 138.6, 135.2, 131.6, 130.8, 130.3, 129.8, 129.5, 127.4, 127.0, 126.5, 125.4, 119.3. **HRMS** (ESI, UPLC G2-XS Qtof): m/z $[M+H]^+$ calcd for $C_{14}H_{10}N_2Cl$: 241.0533; found: 241.0537.



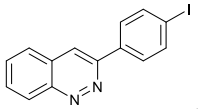
3-(4-chlorophenyl) cinnoline (**3an**):[1a, 1c, 1d, 2]

Yield 45%; 108.3mg; purified by column chromatography on silica gel (PE/EtOAc=4/1); yellow solid; m.p. 110–112 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.58 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 7.8 Hz, 2H), 8.17 (s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.85 (t, J = 7.8 Hz, 1H), 7.78 (t, J = 7.2 Hz, 1H), 7.55 (d, J = 7.8 Hz, 2H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 152.4, 150.0, 135.8, 135.4, 131.5, 130.5, 129.9, 129.3, 128.5, 126.9, 126.4, 118.7. **ITMS** (ESI, LCQ-fleet): *m/z* 243.15 (M+2, 50.66%), 242.06 (M+1, 23.46), 241.10 (M, 100).



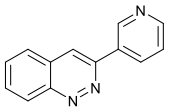
3-(4-fluorophenyl) cinnoline (**3ao**):[1a, 1c, 1d, 2]

Yield 60%; 134.5mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 95–105 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.52 (d, J = 8.4 Hz, 1H), 8.22 – 8.20 (m, 2H), 8.08 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.80 (t, J = 8.4 Hz, 1H), 7.72 (t, J = 7.2 Hz, 1H), 7.22 (t, J = 8.4 Hz, 2H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 163.7 (d, $J_{C\text{-}F}$=248.0 Hz), 152.4, 149.8, 133.0 (d, $J_{C\text{-}F}$=3.2 Hz), 131.3, 130.2, 129.7, 129.0 (d, $J_{C\text{-}F}$=8.3 Hz), 126.8, 126.3, 118.3, 115.9, (d, $J_{C\text{-}F}$=21.5 Hz). **ITMS** (ESI, LCQ-fleet): *m/z* 226.19 (M+1, 9.26%), 225.12 (M, 100).



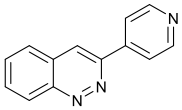
3-(4-iodophenyl) cinnoline (**3ap**):

Yield 52%; 172.7mg; purified by column chromatography on silica gel (PE/EtOAc=3/1); yellow solid; m.p. 106–110 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.55 (d, J = 8.4 Hz, 1H), 8.14 (s, 1H), 7.99 (d, J = 8.4 Hz, 2H), 7.90 – 7.86 (m, 3H), 7.84 (t, J = 8.4 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 152.4, 149.9, 138.2, 136.3, 131.5, 130.5, 129.8, 128.8, 126.9, 126.3, 118.6, 96.0. **HRMS** (ESI, UPLC G2-XS Qtof): m/z $[M+H]^+$ calcd for $C_{14}H_{10}N_2I$: 332.9889; found: 332.9893.



3-(pyridin-3-yl) cinnoline (**3aq**):

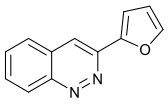
Yield 55%; 113.9mg; purified by column chromatography on silica gel (PE/EtOAc=1/1); yellow solid; m.p. 152–156 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 9.42 (s, 1H), 8.77 (s, 1H), 8.71 (d, J = 7.8 Hz, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.26 (s, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.90 (t, J = 7.2 Hz, 1H), 7.82 (t, J = 7.2 Hz, 1H), 7.57 – 7.55 (m, 1H). ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 150.8, 150.2, 150.0, 148.0, 135.1, 131.8, 131.0, 130.0, 127.0, 126.2, 124.1, 119.2, 117.2. **HRMS** (ESI, UPLC G2-XS Qtof): m/z $[M+H]^+$ calcd for $C_{13}H_{10}N_3$: 208.0875; found: 208.0883.



3-(pyridin-4-yl) cinnoline (**3ar**):

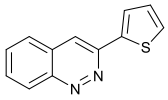
Yield 56%; 116.0mg; purified by column chromatography on silica gel (PE/EtOAc=1/1); yellow solid; m.p. 177–180 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.83 (d, J = 4.2 Hz, 2H), 8.61 (d, J = 8.4 Hz, 1H), 8.29 (s, 1H), 8.17 (d, J = 4.2 Hz, 2H), 7.94 (d, J = 8.4 Hz, 1H), 7.91 (t, J = 7.8 Hz,

1H), 7.82 (t, J = 7.8 Hz, 1H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 150.6, 150.6, 150.4, 144.1, 131.8, 131.3, 129.9, 127.1, 126.0, 121.2, 119.7. **HRMS** (ESI, UPLC G2-XS Qtof): m/z [M+H]$^{+}$calcd for $C_{13}H_{10}N_3$: 208.0875; found: 208.0879.



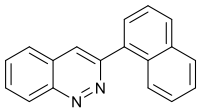
3-(furan-2-yl) cinnoline (**3as**):[1a]

Yield 45%; 88.3mg; purified by column chromatography on silica gel (PE/EtOAc=4/1); yellow solid; m.p. 93–95 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.52 (d, J = 8.4 Hz, 1H), 8.12 (s, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.80 – 7.77 (m, 1H), 7.74 – 7.71 (m, 1H), 7.63 (s, 1H), 7.49 (d, J = 3.6 Hz, 1H), 6.64 – 6.63 (m, 1H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 151.8, 149.6, 146.6, 144.0, 131.5, 130.0, 126.9, 126.3, 116.0, 112.5, 110.0. **HRMS** (ESI, UPLC G2-XS Qtof): m/z [M+H]$^{+}$ calcd for $C_{12}H_9N_2O$: 197.0715; found: 197.0719.



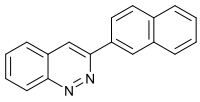
3-(thiophen-2-yl) cinnoline (**3at**):[1a]

Yield 48%; 101.2mg; purified by column chromatography on silica gel (PE/EtOAc=4/1); yellow solid; m.p. 111–113 °C; ^{1}**H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.52 (d, J = 8.5 Hz, 1H), 8.07 (s, 1H), 7.84 (d, J = 5.0 Hz, 2H), 7.80 – 7.77 (m, 1H), 7.73 (t, J = 8.0 Hz, 1H), 7.51 (d, J = 5.0 Hz, 1H), 7.22 – 7.20 (m, 1H); ^{13}**C**{^{1}H} **NMR** (125 MHz, $CDCl_3$): δ (ppm) 149.9, 149.5, 141.4, 131.6, 130.1, 130.0, 128.4, 128.2, 126.7, 126.4, 125.4, 116.5. **ITMS** (ESI, LCQ-fleet): *m/z* 216.42 (M+2, 14.52%), 214.04 (M+1, 19.28%), 212.91 (M, 100).



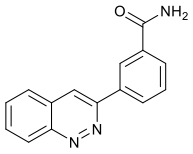
3-(naphthalen-1-yl) cinnoline (**3au**):

Yield 46%; 117.9mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 105–107 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.67 (d, J = 9.0 Hz, 1H), 8.11 (s, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 7.8 Hz, 1H), 7.91 (t, J = 7.8 Hz, 2H), 7.82 (t, J = 7.2 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.66 – 7.64 (m, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.51 – 7.48 (m, 1H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 155.4, 149.7, 135.7, 134.0, 131.4, 130.6, 129.9, 129.6, 128.7, 128.5, 126.9, 126.8, 126.2, 126.1, 125.4, 125.4, 123.5. **HRMS** (ESI, UPLC G2-XS Qtof): m/z [M+H]$^{+}$ calcd for $C_{18}H_{13}N_2$: 257.1079; found: 257.1077.



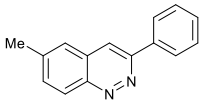
3-(naphthalen-2-yl) cinnoline (**3av**):[1c, 1d]

Yield 50%; 128.2mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 96–98 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.80 (s, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.39 – 8.37 (m, 1H), 8.34 (s, 1H), 8.05 (s, 1H), 8.04 – 8.01 (m, 1H), 7.94 – 7.92 (m, 2H), 7.86 – 7.84 (m, 1H), 7.78 (t, J = 7.8 Hz, 1H), 7.56 (d, J = 9.0 Hz, 2H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 153.4, 149.8, 134.1, 133.8, 133.6, 131.4, 130.4, 129.8, 128.9, 128.8, 127.8, 127.0, 127.0, 126.9, 126.7, 126.6, 124.5, 119.1, 77.23. **ITMS** (ESI, LCQ-fleet): *m/z* 258.06 (M+1, 16.48%), 257.12 (M, 100).



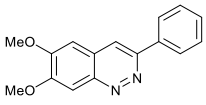
3-(cinnolin-3-yl) benzamide (**3aw**):

Yield 52%; 129.6mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 206–207 °C; ^{1}**H NMR** (600 MHz, DMSO-d_6): δ (ppm) 8.83 (d, J = 4.2 Hz, 2H), 8.55 – 8.51 (m, 2H), 8.22 (s, 1H), 8.16 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.99 (t, J = 8.4 Hz, 1H), 7.93 (t, J = 7.8 Hz, 1H), 7.72 (t, J = 7.8 Hz, 1H), 7.56 (s, 1H); ^{13}**C**{^{1}H} **NMR** (150 MHz, DMSO-d_6): δ (ppm) 168.1, 152.5, 150.0, 137.16, 135.7, 132.3, 131.6, 130.1, 129.6, 129.4, 128.9, 128.1, 126.6, 126.6, 119.9. **HRMS** (ESI, UPLC G2-XS Qtof): m/z $[M+H]^+$ calcd for $C_{15}H_{12}N_3O$: 250.0980; found: 250.0980.



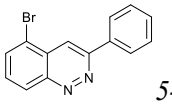
6-methyl-3-phenylcinnoline (**3ba**):[1d, 2]

Yield 63%; 69.4mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 119–123 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.41 (d, J = 8.4 Hz, 1H), 8.23 – 8.22 (m, 3H), 8.03 (s, 1H), 7.61 – 7.59 (m, 1H), 7.57 – 7.53 (m, 3H), 7.48 (t, J = 7.2 Hz, 1H), 2.56 (s, 3H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 153.4, 149.0, 141.9, 137.1, 132.8, 129.4, 129.3, 129.0, 127.2, 126.7, 125.3, 118.2, 22.09. **ITMS** (ESI, LCQ-fleet): *m/z* 222.15 (M+1, 17.82%), 221.07 (M, 100).



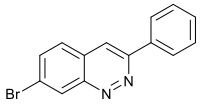
6,7-dimethoxy-3-phenylcinnoline (**3ca**):[1c]

Yield 51%; 67.9mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 117–118 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.20 (d, J = 7.2 Hz, 2H), 8.03 (s, 1H), 7.77 (s, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.48 (t, J = 7.8 Hz, 1H), 7.03 (s, 1H), 4.13 (s, 3H), 4.08 (s, 3H). ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 153.9, 153.3, 152.9, 147.9, 137.4, 129.1, 129.0, 127.1, 124.1, 117.9, 106.8, 103.0, 56.5. **ITMS** (ESI, LCQ-fleet): *m/z* 268.11 (M+1, 15.48%), 267.13 (M, 100).



5-bromo-3-phenylcinnoline (**3da**):[1a, 1d]

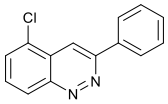
Yield 48%; 68.4mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 66–68 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.54 (d, J = 9.0 Hz, 1H), 8.42 (s, 1H), 8.30 – 8.29 (m, 2H), 7.99 (d, J = 7.8 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.59 (t, J = 7.8 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 154.7, 150.2, 136.5, 134.5, 130.5, 129.9, 129.7, 129.2, 127.5, 126.5, 121.3, 117.8. **ITMS** (ESI, LCQ-fleet): *m/z* 286.99 (M+2, 57.84%), 286.08 (M+1, 11.55), 285.11 (M, 100).



7-bromo-3-phenylcinnoline (**3ea**):[1a, 1d]

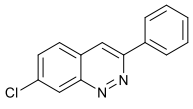
Yield 50%; 71.3mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 34–35 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.76 (s, 1H), 8.25 (d, J = 1.8 Hz, 2H), 8.15 (s, 1H), 7.83 – 7.82 (m, 1H), 7.78 (d, J = 9.0 Hz, 1H), 7.58 (t, J = 7.2 Hz, 2H), 7.52 (t, J = 7.2

Hz, 1H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 153.8, 150.0, 136.5, 135.1, 132.0, 129.8, 129.2, 128.4, 127.3, 125.2, 124.2, 118.6. **ITMS** (ESI, LCQ-fleet): *m/z* 285.03 (M+1, 79.50%), 286.96 (M, 100).



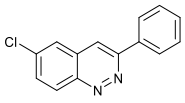
5-chloro-3-phenylcinnoline (**3fa**):[1a, 1d]

Yield 48%; 57.8mg; 58mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 102–106 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.53 – 8.51 (m, 2H), 8.31 – 8.30 (m, 2H), 7.82 (d, J = 7.8 Hz, 1H), 7.77 – 7.74 (m, 1H), 7.60 (t, J = 7.8 Hz, 2H), 7.53 (t, J = 7.8 Hz, 1H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 154.4, 150.0, 136.5, 130.9, 130.8, 129.9, 129.9, 129.2, 128.9, 127.5, 125.3, 115.4. **ITMS** (ESI, LCQ-fleet): *m/z* 243.13 (M+2, 40.05%), 242.10 (M+1, 13.79), 241.07 (M, 100).



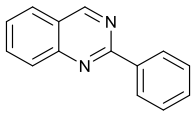
7-chloro-3-phenylcinnoline (**3ga**):[1a, 1d]

Yield 49%; 58.9mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 30–32 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.56 (s, 1H), 8.24 (d, J = 8.4 Hz, 2H), 8.15 (s, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.70 – 7.68 (m, 1H), 7.57 (t, J = 7.8 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 153.9 149.8, 136.5, 136.0, 132.6, 129.7, 129.2, 128.5, 128.5, 127.3, 125.0, 118.5. **ITMS** (ESI, LCQ-fleet): *m/z* 243.09 (M+1, 20.79%), 241.14 (M, 100).



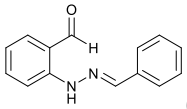
6-chloro-3-phenylcinnoline (**3ha**):[1a, 1d]

Yield 45%; 54.2mg; purified by column chromatography on silica gel (PE/EtOAc=5/1); yellow solid; m.p. 120–122 °C; ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.50 (d, J = 9.0 Hz, 1H), 8.23 (d, J = 7.2 Hz, 2H), 8.07 (s, 1H), 7.86 (d, J = 1.8 Hz, 1H), 7.74 – 7.72 (m, 1H), 7.57 (t, J = 8.4 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H); ^{13}**C**{^{1}H} **NMR** (150 MHz, $CDCl_3$): δ (ppm) 154.0, 148.2, 137.6, 136.4, 131.6, 131.5, 129.8, 129.1, 127.4, 127.2, 125.5, 117.6. **ITMS** (ESI, LCQ-fleet): *m/z* 242.98 (M+2, 30.90%), 242.17 (M+1, 12.58), 241.02 (M, 100).



2-phenylquinazoline (**4**)*:*

yellow solid; m.p. 78–80 °C; purified by column chromatography on silica gel (PE/EtOAc=10/1); ^{1}**H NMR** (600 MHz, $CDCl_3$): δ (ppm) 9.47 (s, 1H), 8.62 (d, J = 6.0 Hz, 2H), 8.09 (d, J = 8.4 Hz, 1H), 7.91 (q, J = 8.4 Hz, 2H), 7.61 (t, J =7.2 Hz, 1H), 7.55 – 7.51 (m, 3H). ^{13}**C**{^{1}H} **NMR** (150 MHz, CDCl3) δ 161.1, 160.5, 150.8, 138.0, 134.1, 130.6, 128.6, 128.6, 128.6, 127.3, 127.1, 123.6. **HRMS** (ESI, UPLC G2-XS Qtof): m/z $[M+H]^+$ calcd for $C_{14}H_{11}N_2$: 207.0922; found: 207.0925.



(E)-2-(2-benzylidenehydrazineyl) benzaldehyde (**6**)*:*

Yield 16%; 35.9mg; purified by column chromatography on silica gel (PE/EtOAc=20/1) ; yellow solid; m.p. 112–113 °C; ^{1}**H NMR** (500 MHz, $CDCl_3$): δ (ppm)11.53 (s, 1H), 9.90 (s, 1H), 7.95 (s, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.74 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 9.0 Hz, 1H), 7.54 (t, J = 8.5 Hz,

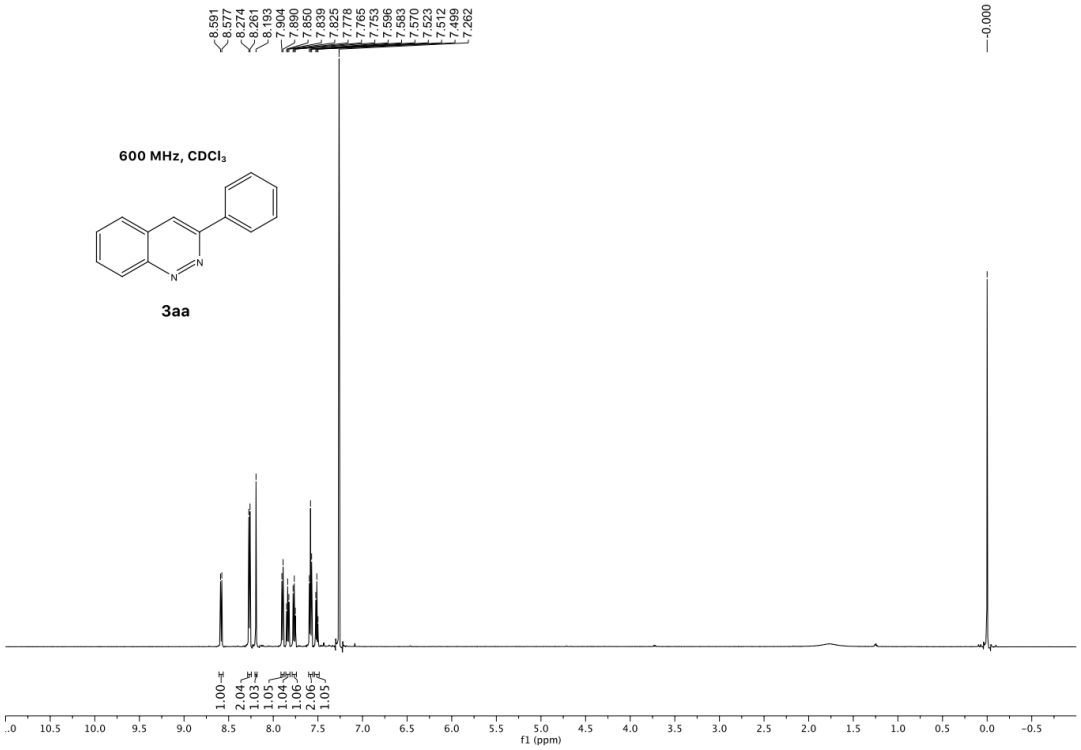
1H), 7.43 (t, J = 8.0 Hz, 2H), 7.37 (t, J = 7.5 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H); ^{13}**C**{^{1}H} **NMR** (125 MHz, $CDCl_3$): δ (ppm) 194.3, 147.2, 141.7, 136.0, 135.5, 134.8, 129.2, 128.7, 126.7, 118.0, 117.4, 113.3. **HRMS** (ESI, UPLC G2-XS Qtof): m/z $[M+H]^+$ calcd for $C_{14}H_{13}N_2O$: 225.1028; found: 225.1024.

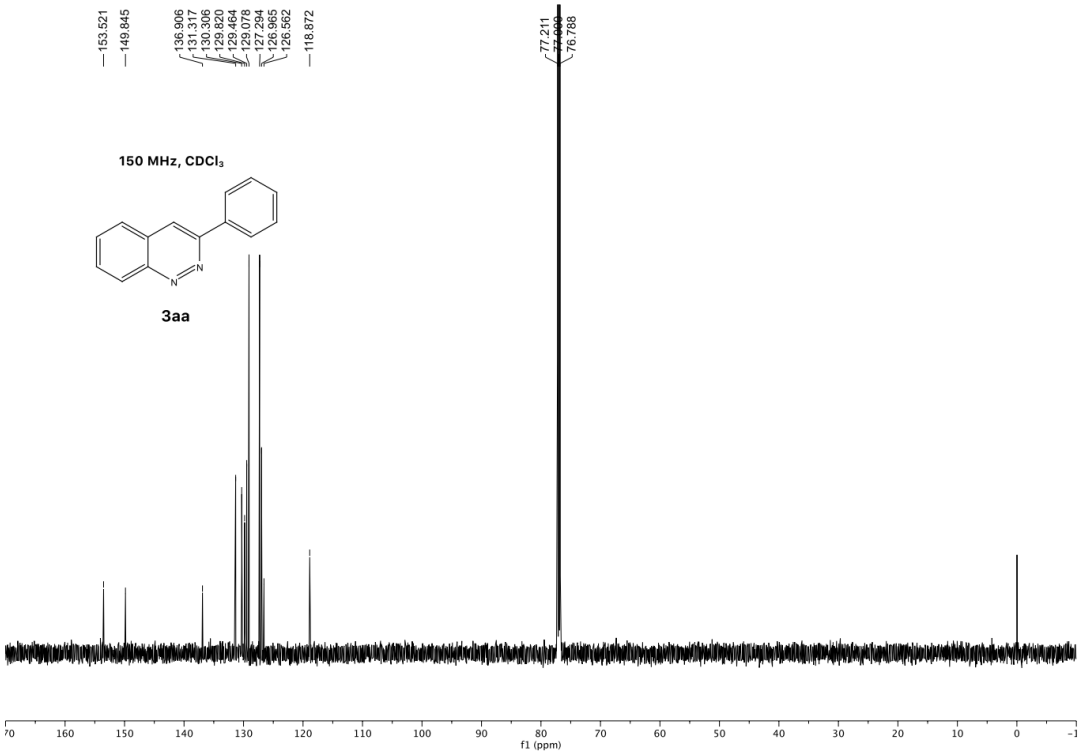
References and notes:

[1] (a) G. Zhang, J. Miao, Y. Zhao and H. Ge, *Angew. Chem. Int. Ed.*, 2012, **51**, 8318-8321. (b) D. Zhao, Q. Wu, X. Huang, F. Song, T. Lv and J. You, *Chem-Eur. J.*, 2013, **19**, 6239-6244. (c) W. M. Shu, J. R. Ma, K. L. Zheng and A. X. Wu, *Org. Lett.*, 2016, **18**, 196-199. (d) C. Lan, Z. Tian, X. Liang, M. Gao, W. Liu, Y. An, W. Fu, G. Jiao, J. Xiao and B. Xu, *Adv. Synth. Catal.*, 2017, **359**, 3735-3740.

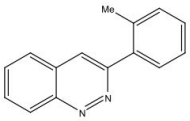
[2] C. J. Ball, J. Gilmore and M. C. Willis, *Angew. Chem. Int. Ed.* , 2012, **51**, 5718-5722.

6. Appendix: spectral copies of ^{1}H NMR, and $^{13}C\{^{1}H\}$ NMR

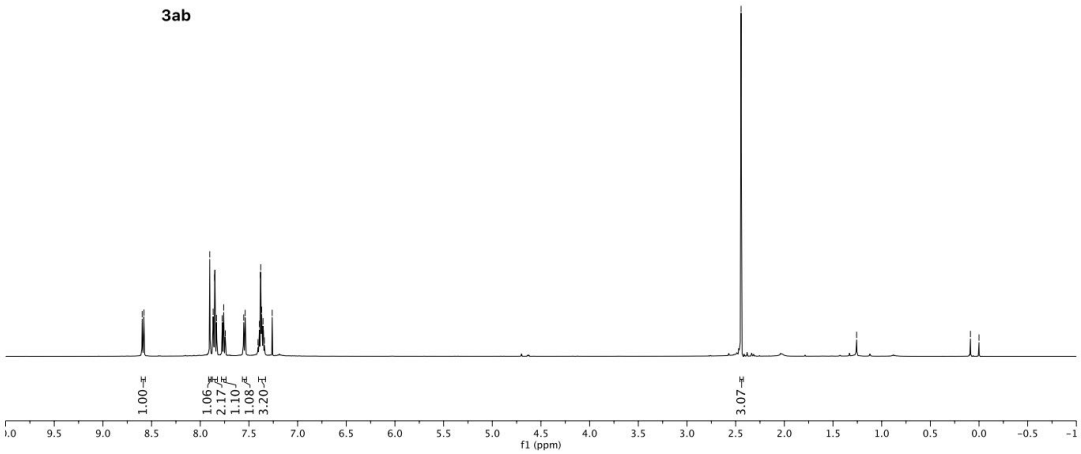




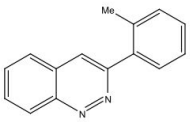
500 MHz, $CDCl_3$



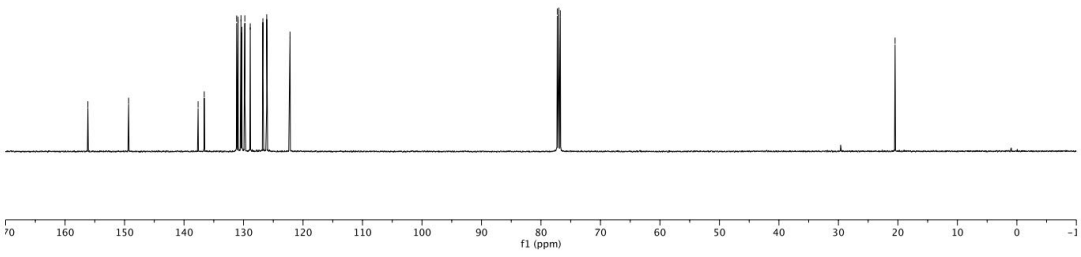
3ab

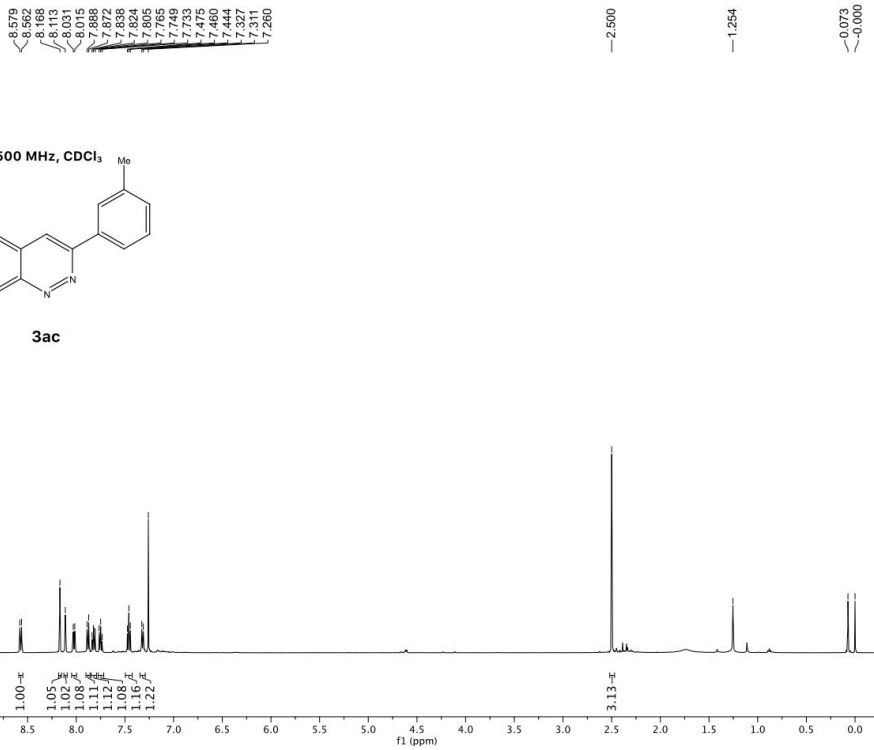


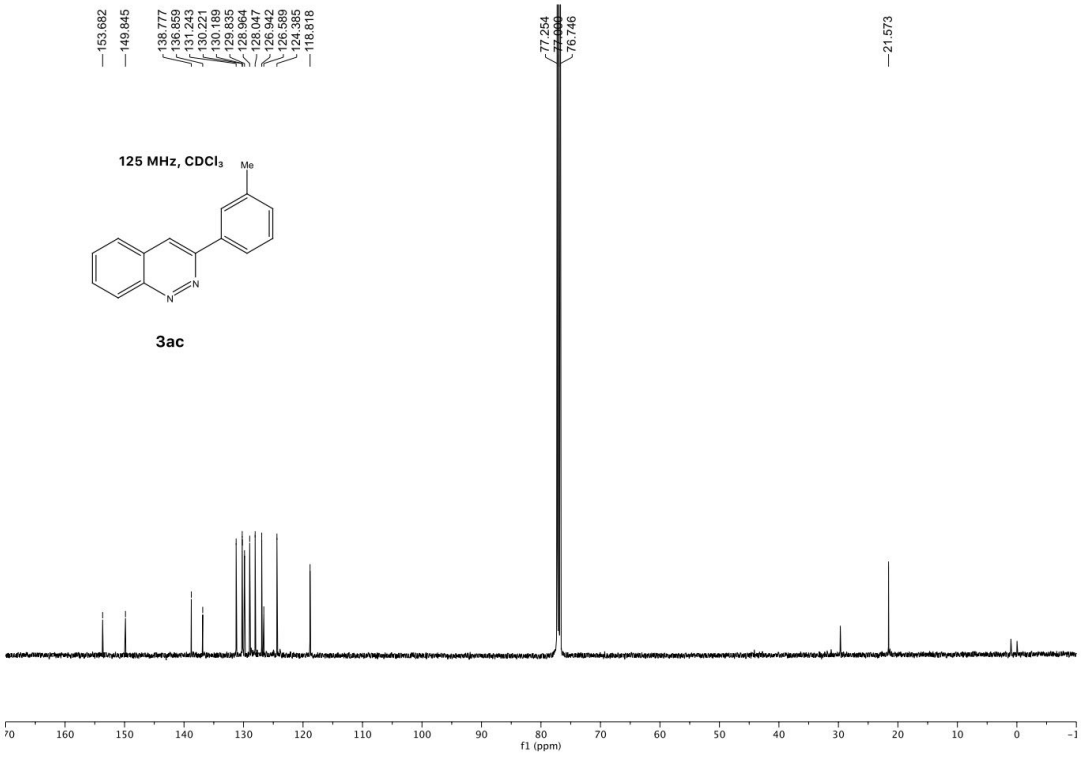
125 MHz, $CDCl_3$

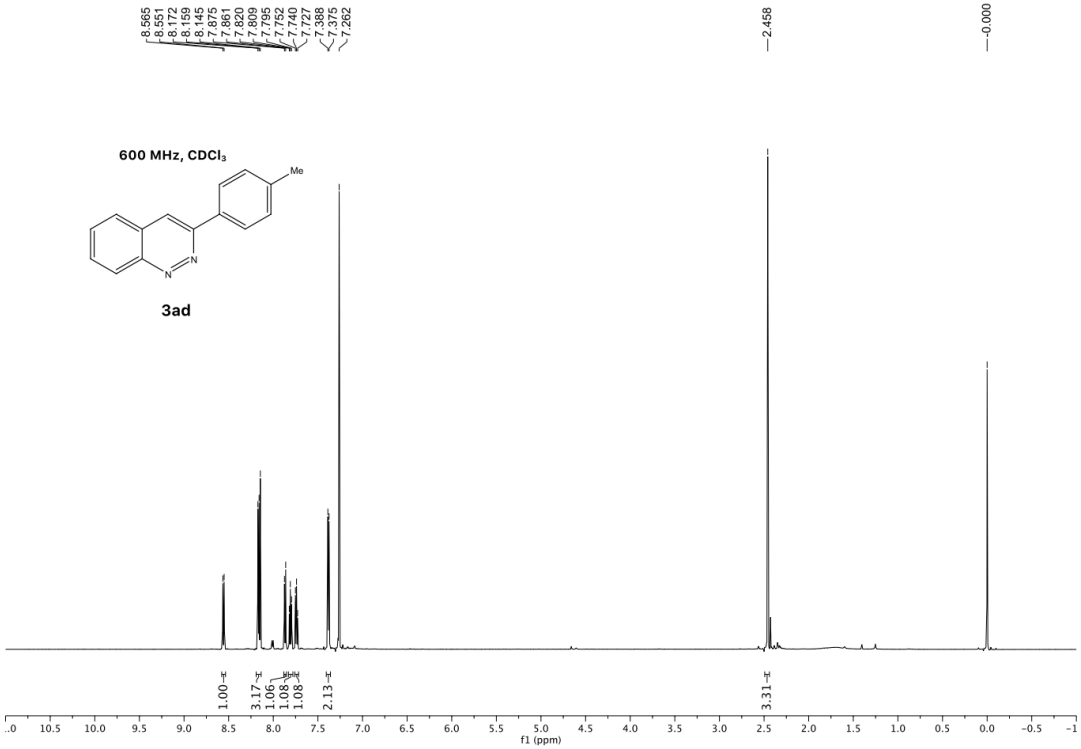


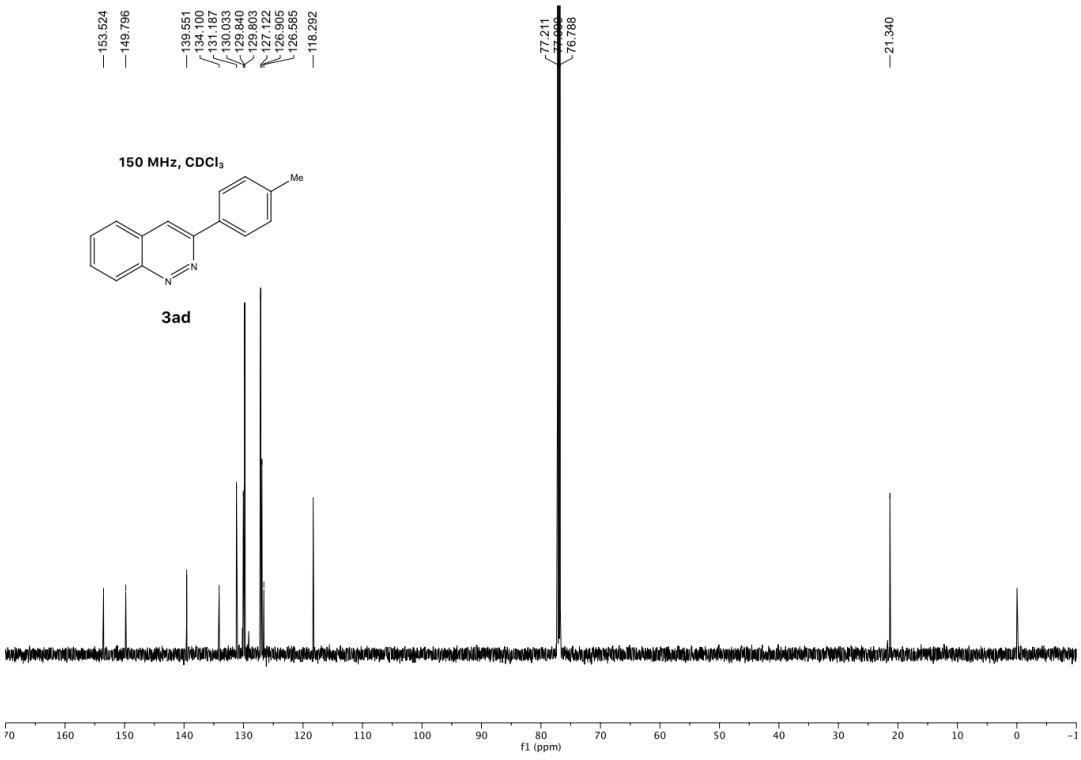
3ab




8.579
8.562
8.168
8.113
8.031
8.015
7.888
7.872
7.838
7.824
7.805
7.765
7.749
7.733
7.475
7.460
7.444
7.327
7.311
7.260
2.500
1.254
0.073
-0.000
500 MHz, CDCl3
Me
N
N
3ac
1.00
1.05
1.02
1.08
1.11
1.12
1.08
1.16
1.22
3.13
f1 (ppm)


153.682
149.845
138.777
136.859
131.243
130.221
130.189
129.835
128.964
128.047
126.942
126.589
124.385
118.818
77.254
77.000
76.746
21.573
125 MHz, CDCl3
Me
N
N
3ac
f1 (ppm)


8.565
8.551
8.172
8.159
8.145
7.875
7.861
7.820
7.809
7.795
7.752
7.740
7.727
7.398
7.375
7.262
2.458
0.000
600 MHz, CDCl3
Me
N
N
3ad
1.00
3.17
1.06
1.08
1.08
2.13
3.31
f1 (ppm)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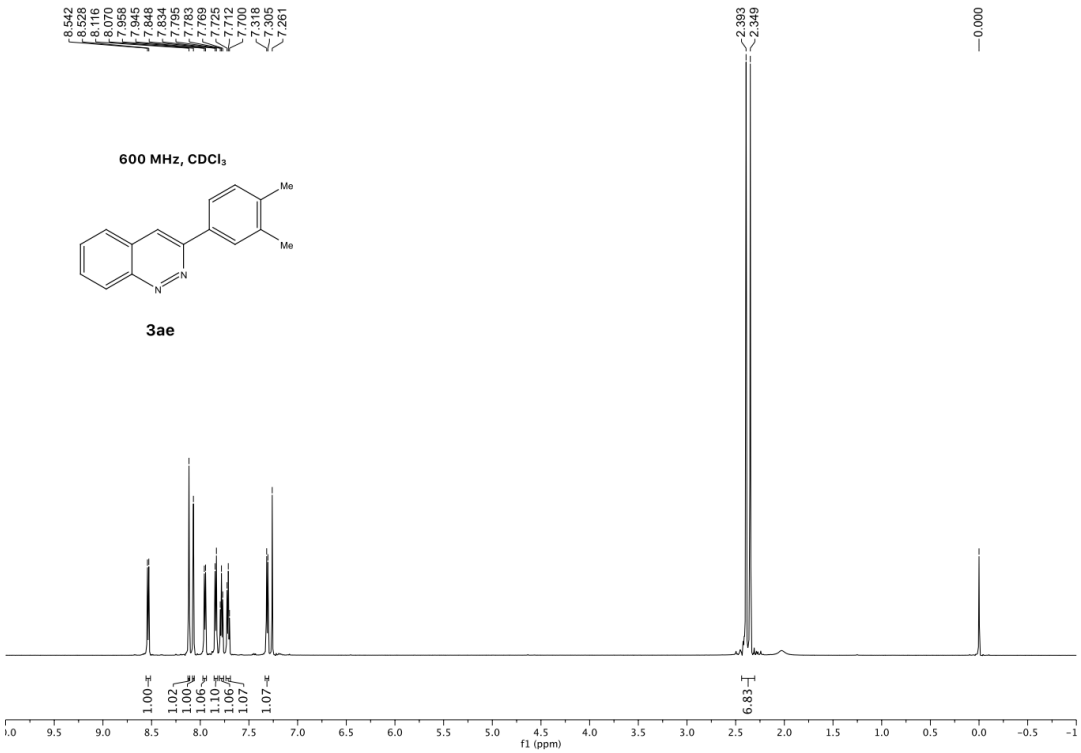
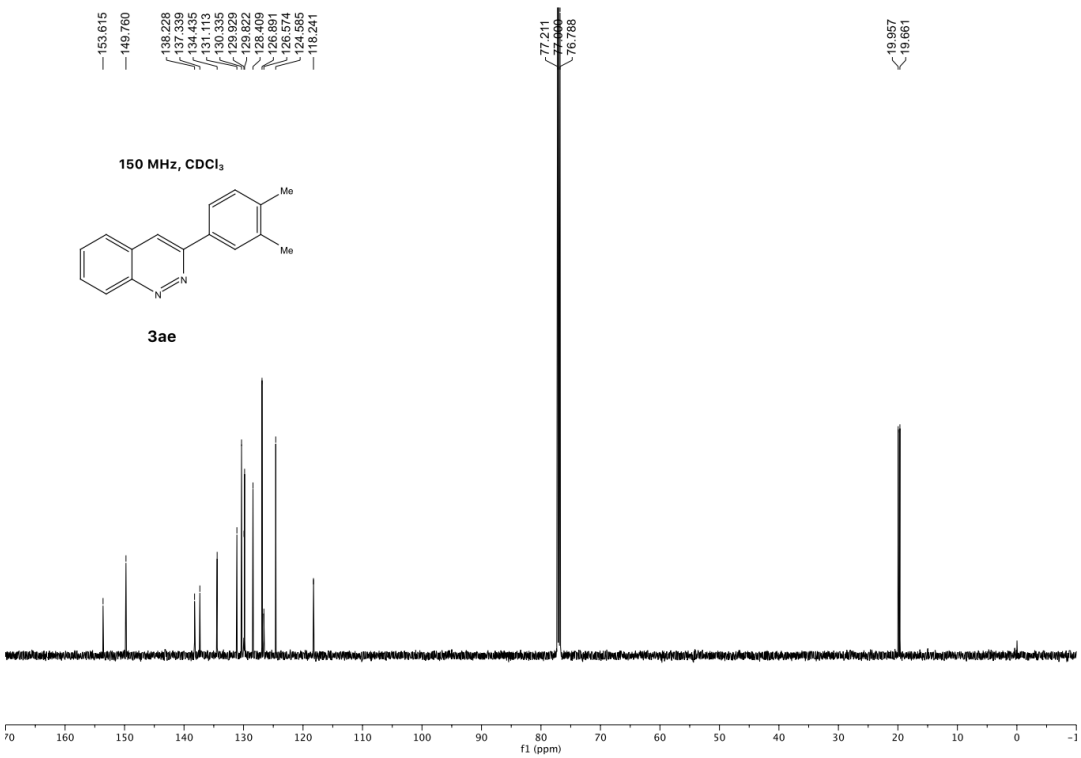
149.796
139.551
134.100
131.187
130.033
129.840
129.803
127.122
126.905
126.585
118.292
77.211
77.000
76.788
21.340
150 MHz, CDCl3
Me
N
N
3ad
f1 (ppm)


8.542
8.528
8.516
8.070
7.958
7.945
7.848
7.834
7.795
7.783
7.769
7.725
7.712
7.700
7.318
7.305
7.261
2.393
2.349
0.000
600 MHz, CDCl3
Me
Me
N
N
3ae
1.00
1.02
1.00
1.06
1.10
1.06
1.07
1.07
6.83
f1 (ppm)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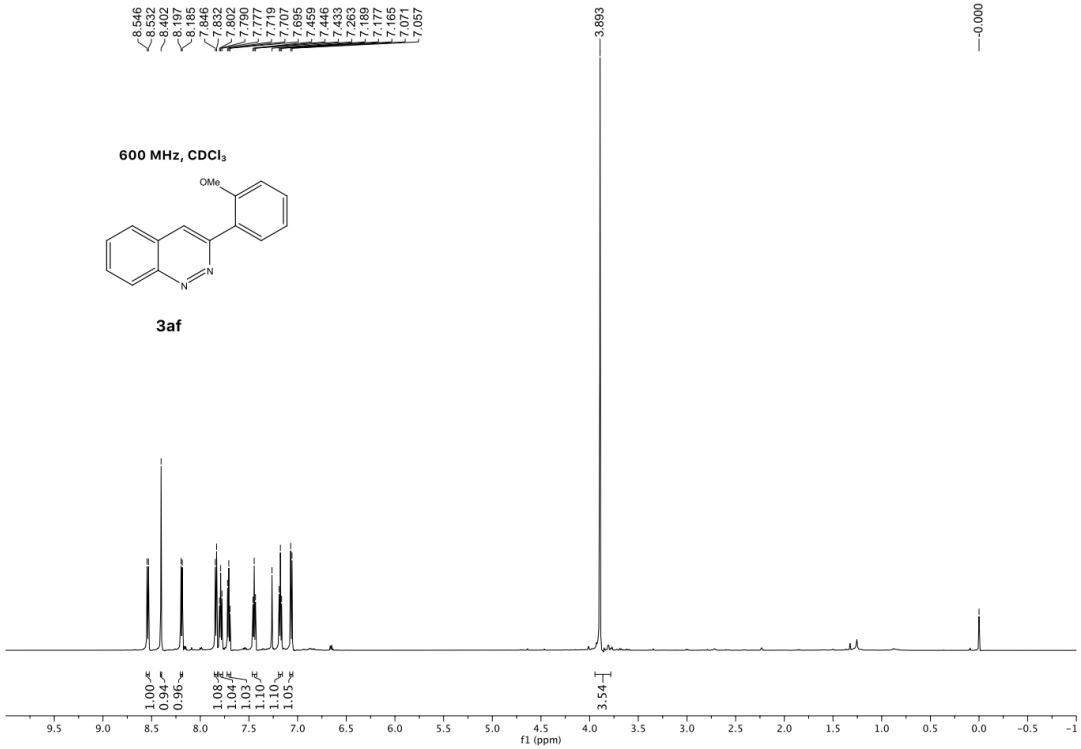
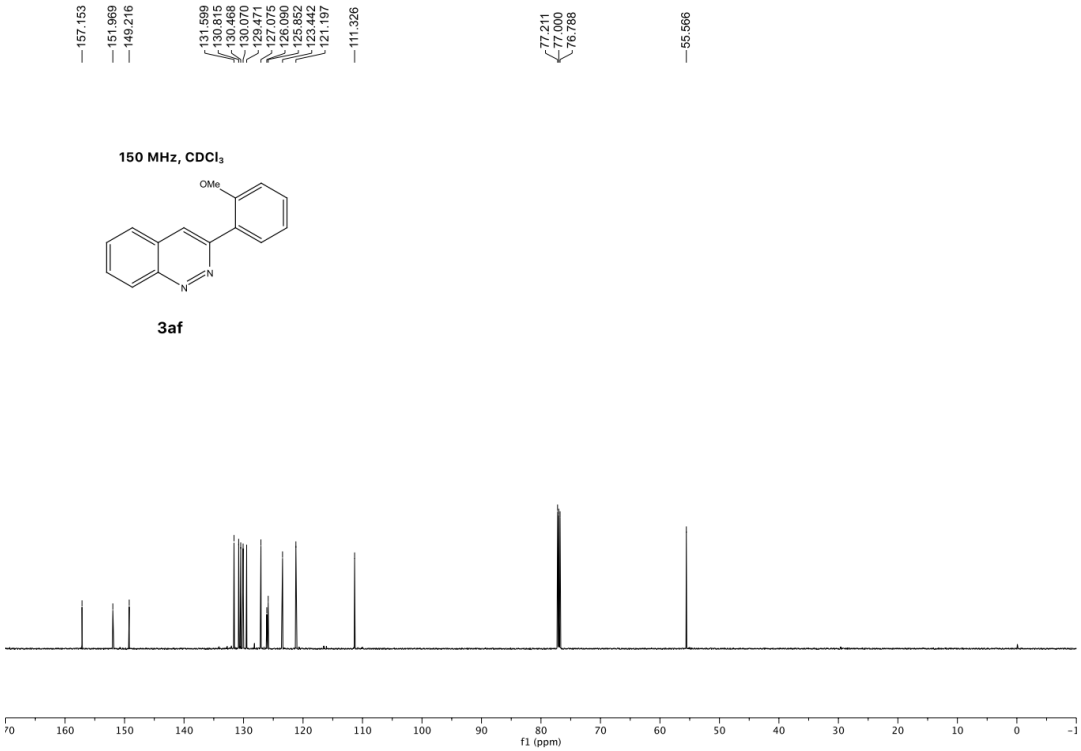
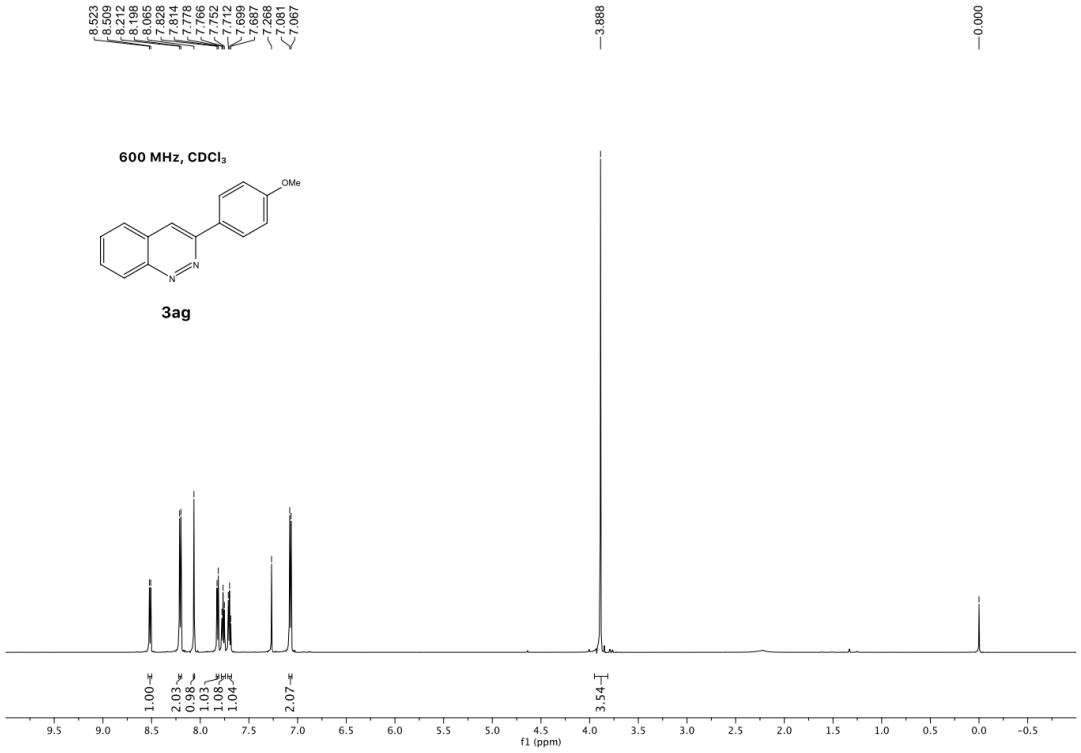
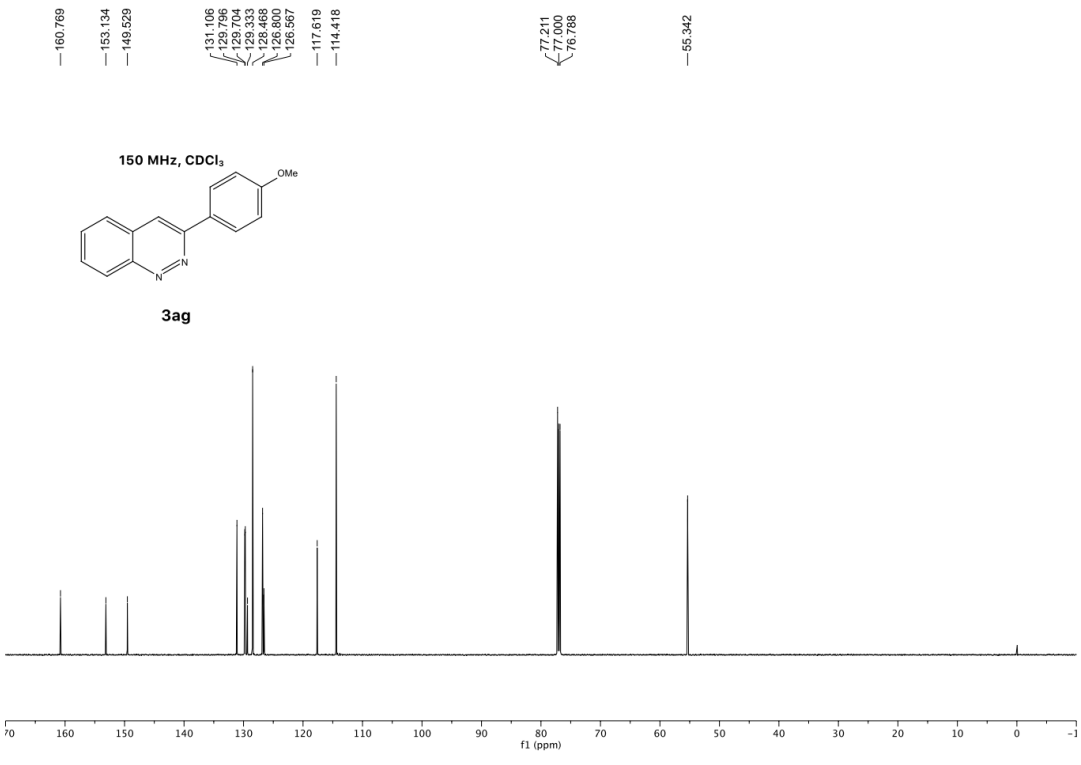
149.760
138.228
137.339
134.435
131.113
130.335
129.929
129.822
128.409
126.891
126.574
124.585
118.241
77.211
77.000
76.788
19.957
19.661
150 MHz, CDCl3
Me
Me
N
N
3ae
f1 (ppm)

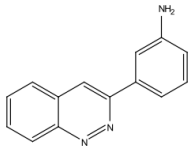

8.546
8.532
8.402
8.197
8.185
7.846
7.832
7.802
7.790
7.777
7.719
7.707
7.695
7.459
7.446
7.433
7.263
7.189
7.177
7.165
7.071
7.057
3.893
0.000
600 MHz, CDCl3
OMe
N
N
3af
1.00
0.94
0.96
1.08
1.04
1.03
1.10
1.10
1.05
3.54
f1 (ppm)


157.153
151.969
149.216
131.599
130.815
130.468
130.070
129.471
127.075
126.090
125.852
123.442
121.197
111.326
77.211
77.000
76.788
55.566
150 MHz, CDCl3
OMe
N
N
3af
f1 (ppm)

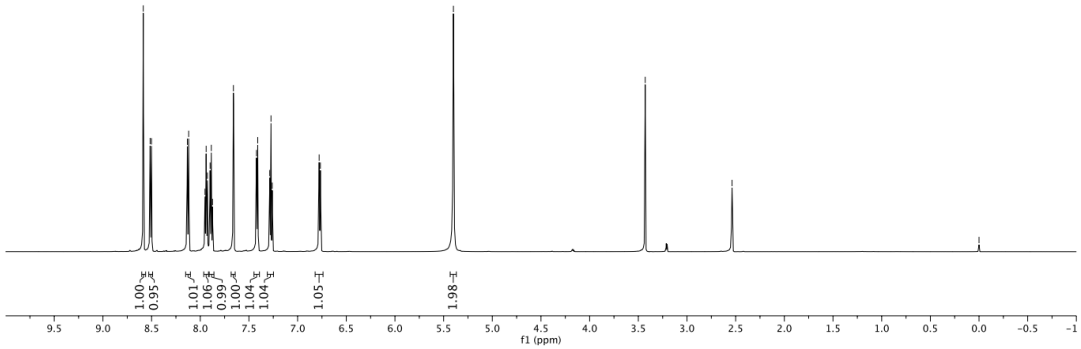

8.523
8.509
8.212
8.198
8.065
7.828
7.814
7.778
7.766
7.752
7.712
7.699
7.687
7.268
7.081
7.067
3.888
0.000
600 MHz, CDCl3
OMe
N
N
3ag
1.00
2.03
0.98
1.03
1.08
1.04
2.07
3.54
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

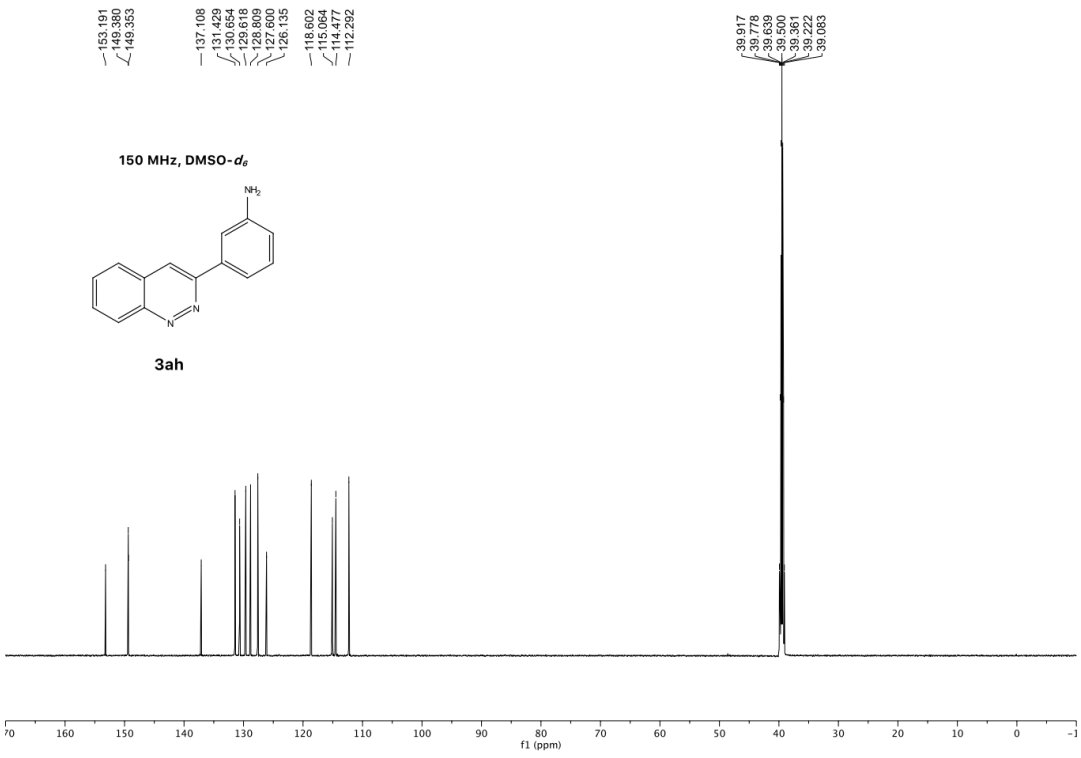

160.769
153.134
149.529
131.106
129.796
129.704
129.333
128.468
126.800
126.567
117.619
114.418
77.211
77.000
76.788
55.342
150 MHz, CDCl3
OMe
N
N
3ag
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

600 MHz, DMSO-d_6



3ah



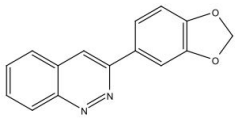


150 MHz, DMSO-d_6

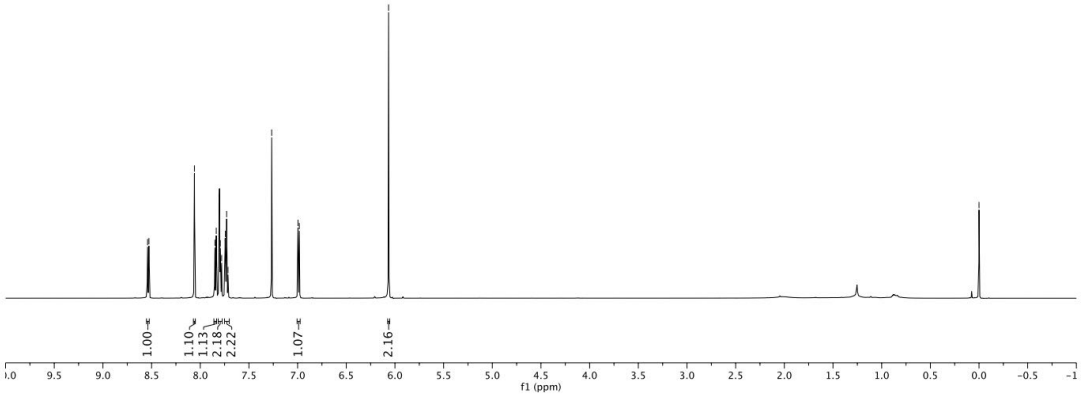
3ah

8.541
8.527
8.060
7.849
7.836
7.805
7.794
7.780
7.742
7.729
7.715
7.266
6.996
6.983
6.065
0.000

600 MHz, $CDCl_3$

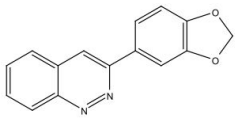


3ai

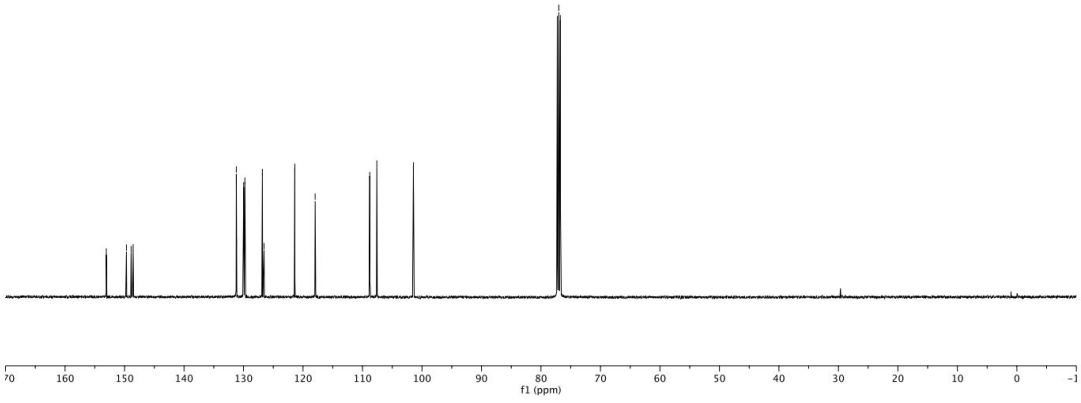


153.066
149.678
148.898
148.552
131.214
131.186
129.973
129.774
126.831
126.551
121.377
117.959
108.783
107.590
101.439
77.254
77.000
76.746

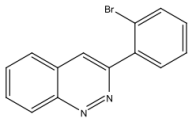
125 MHz, $CDCl_3$



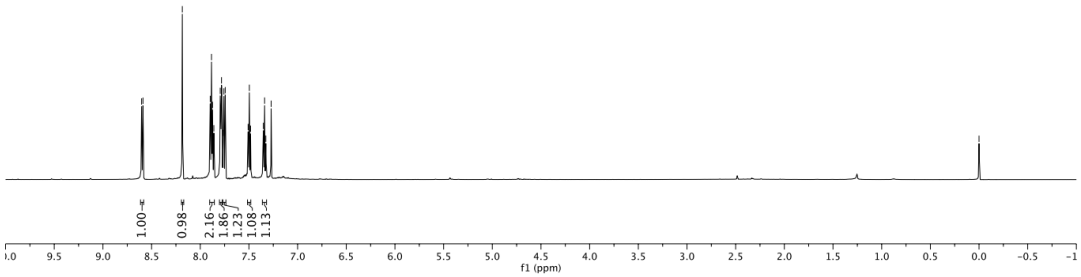
3ai



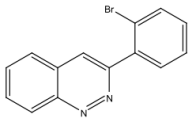
600 MHz, $CDCl_3$



3aj



150 MHz, $CDCl_3$



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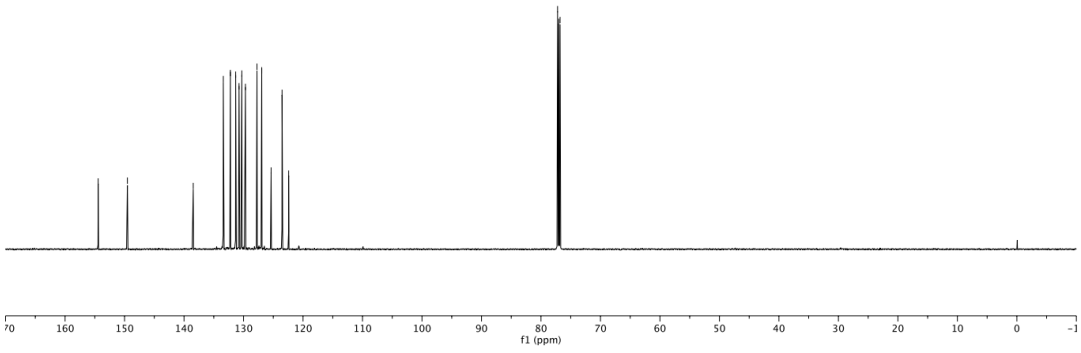
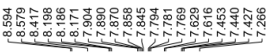
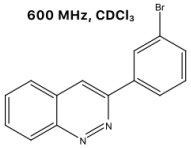
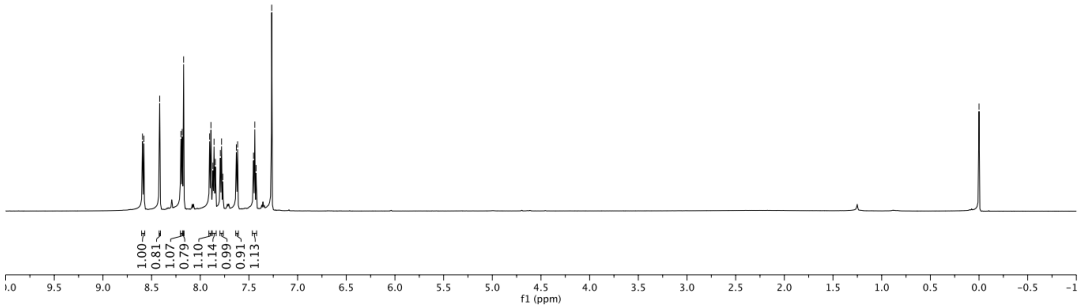


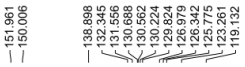


600 MHz, $CDCl_3$



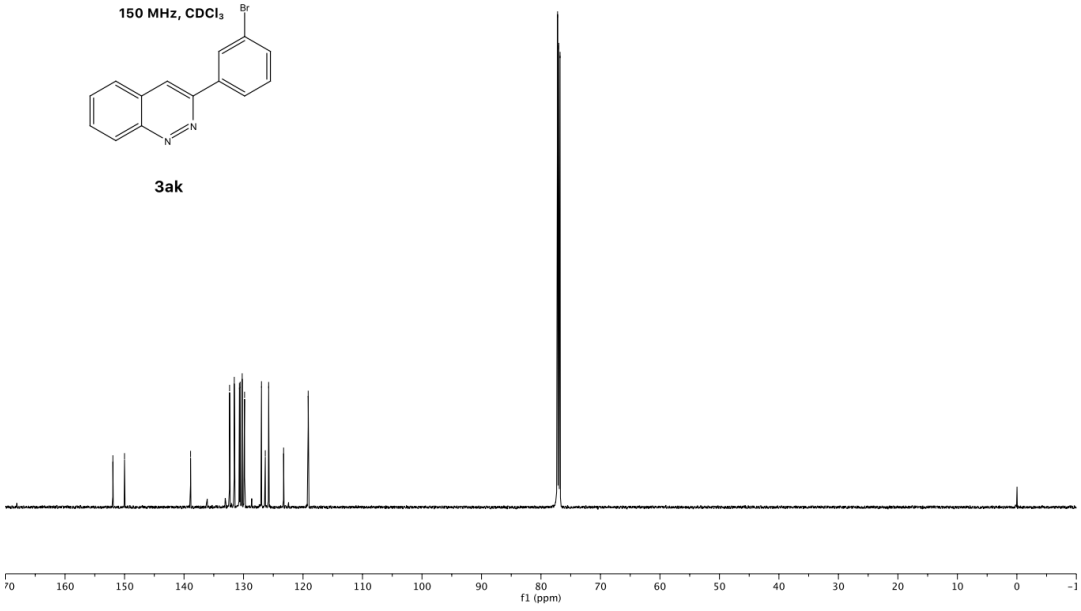
3ak

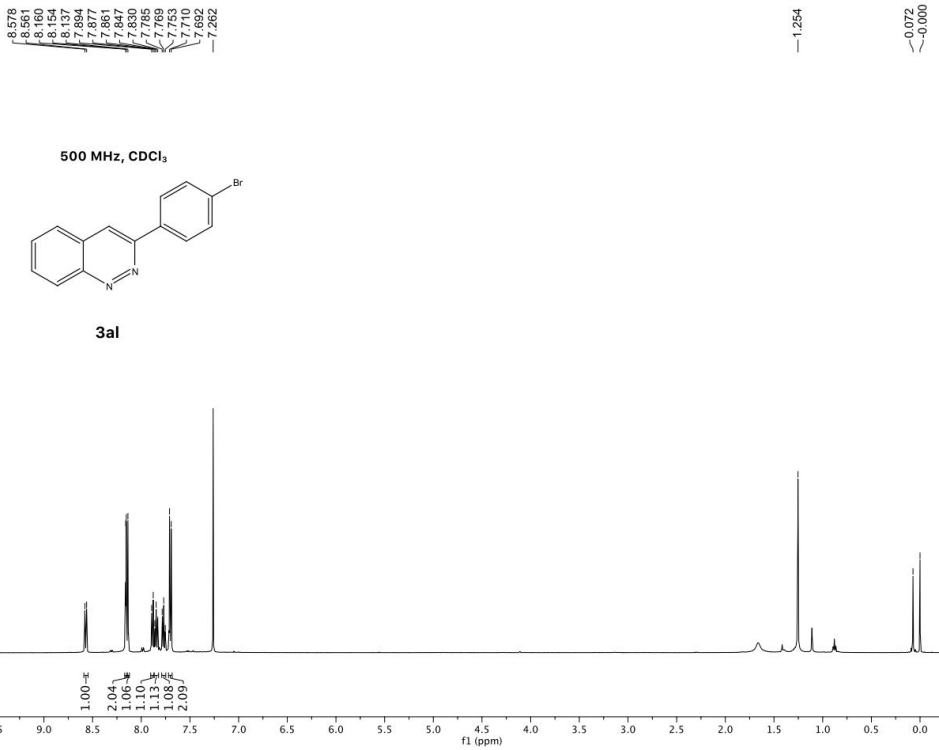


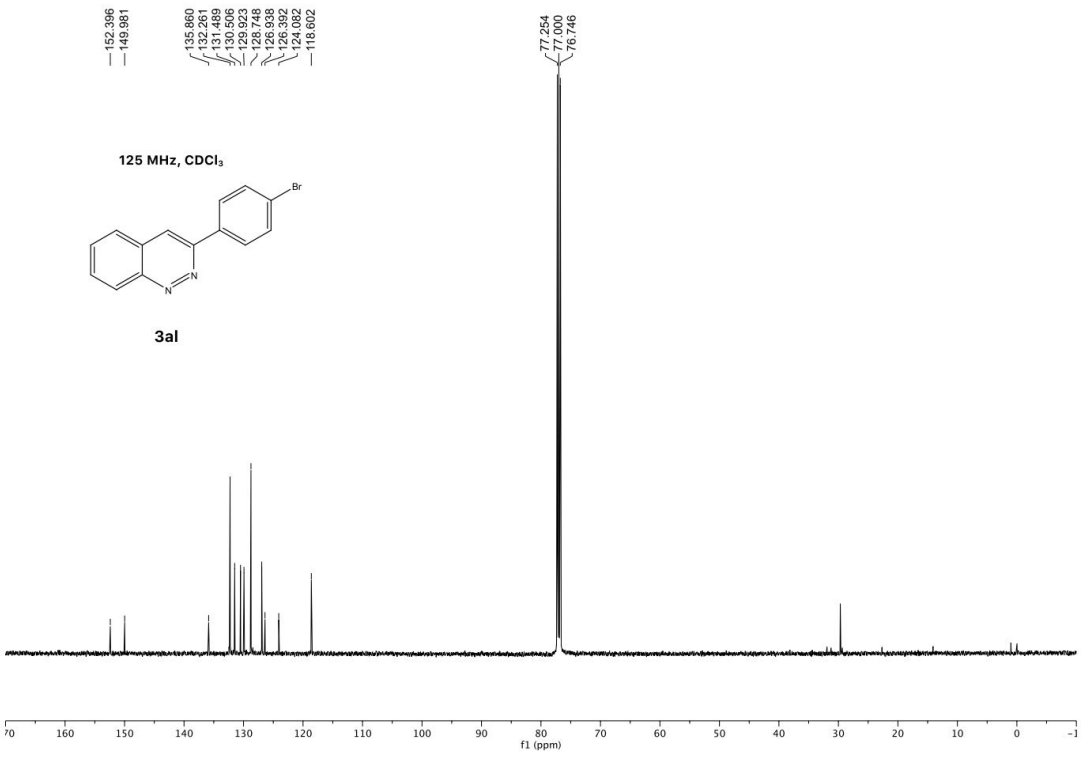


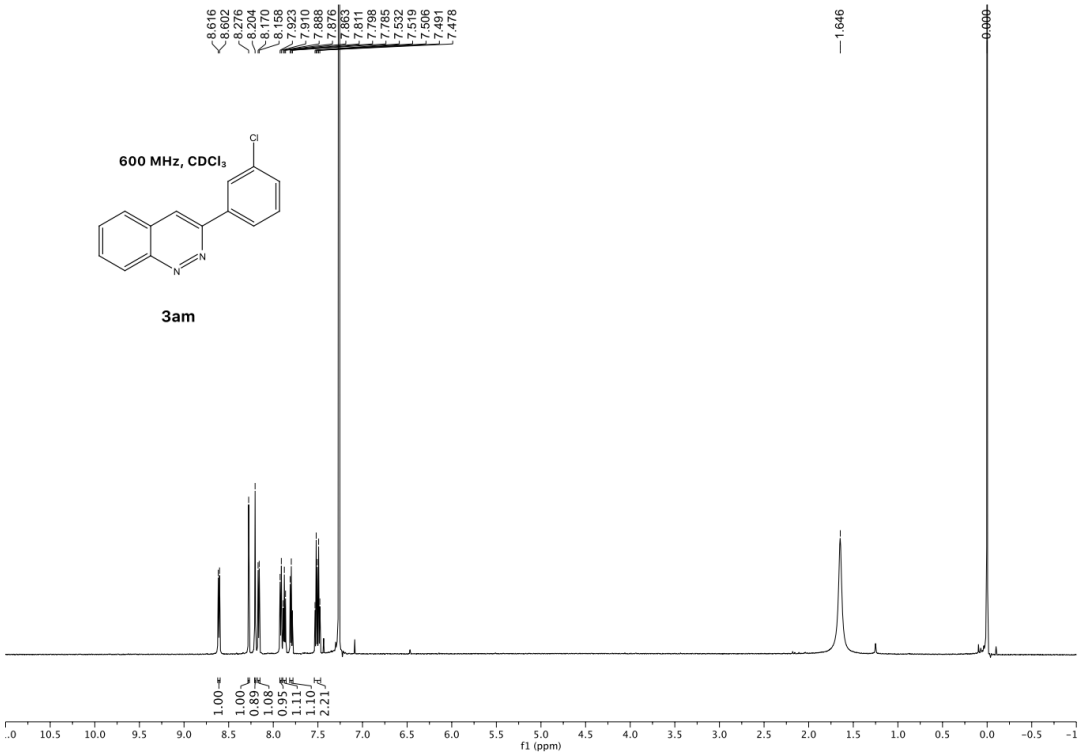
150 MHz, $CDCl_3$

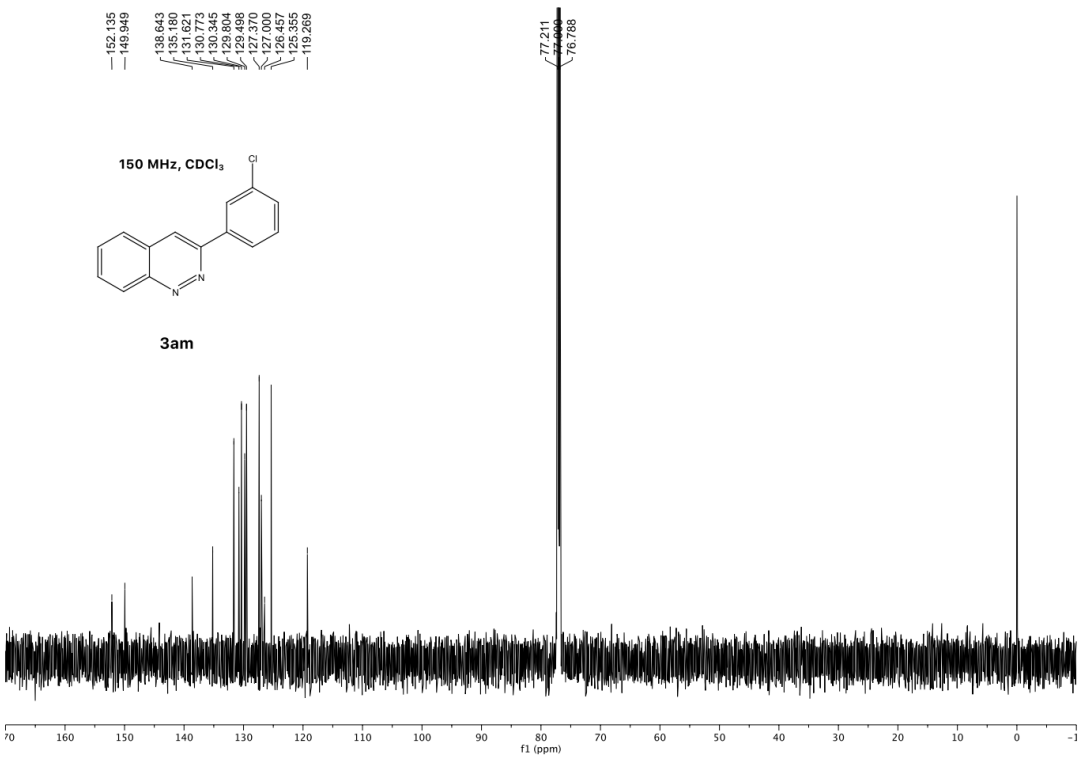
3ak

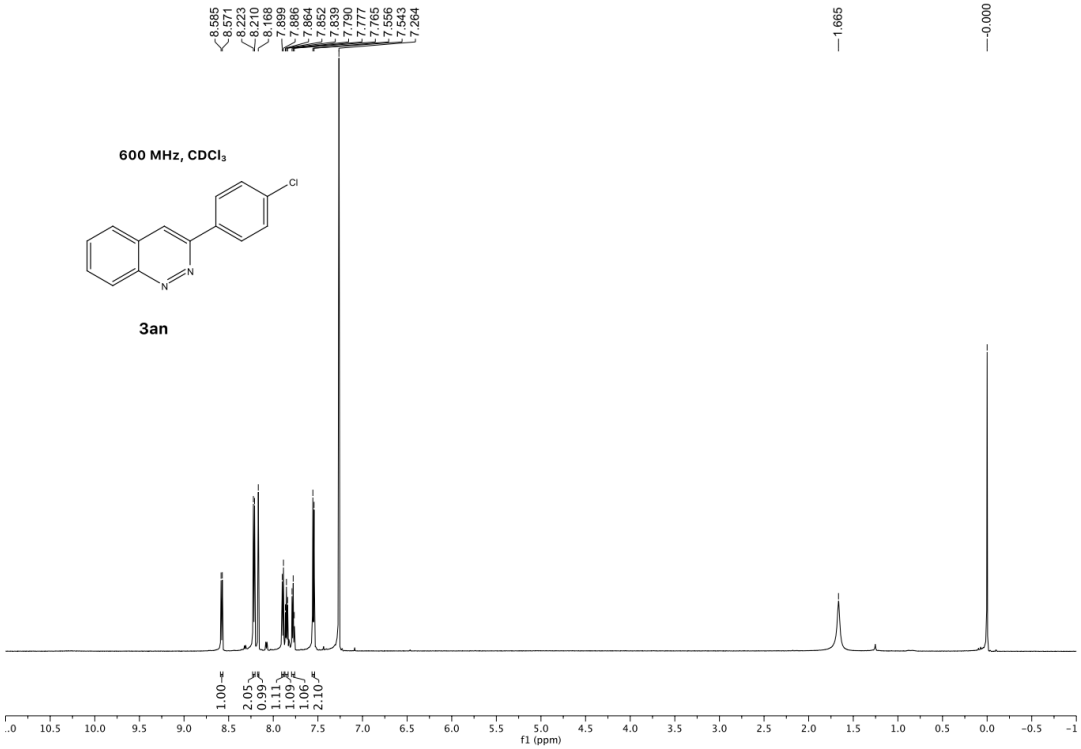


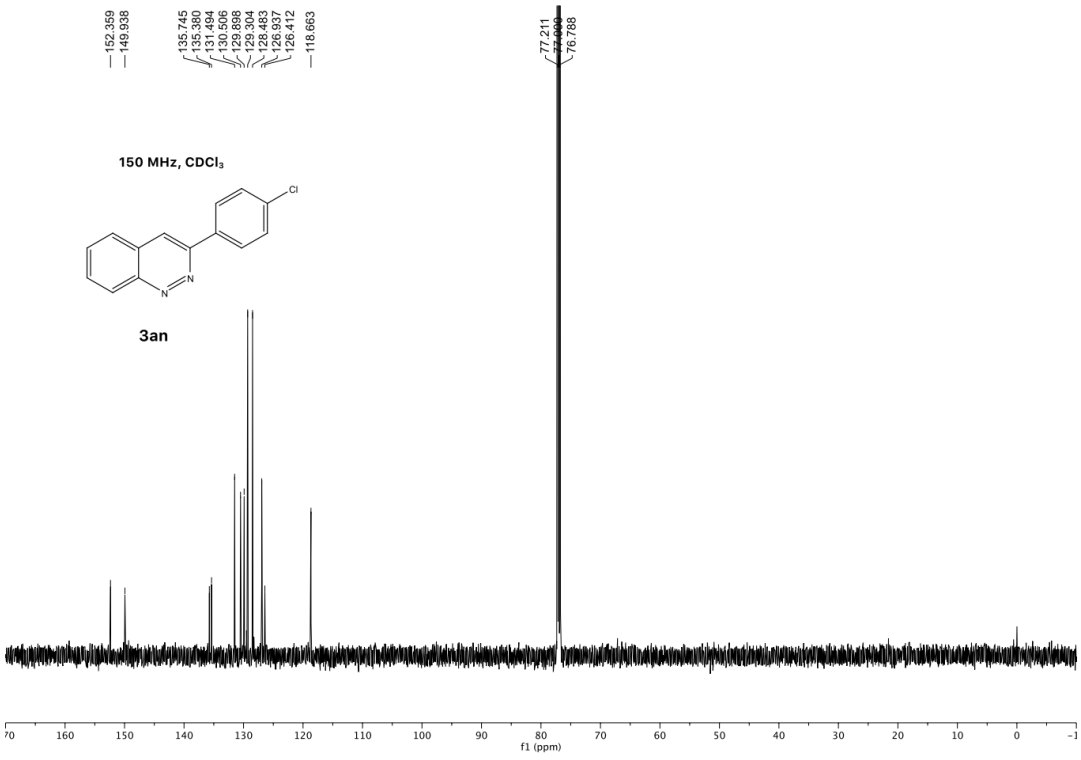

8.578
8.561
8.160
8.154
8.137
7.894
7.877
7.861
7.847
7.830
7.785
7.769
7.753
7.710
7.692
7.262
1.254
0.072
-0.000
500 MHz, CDCl3
Br
N
N
3al
1.00
2.04
1.06
1.10
1.13
1.08
2.09
f1 (ppm)


152.396
149.981
135.860
132.261
131.489
130.506
129.923
128.748
126.938
126.392
124.082
118.602
77.254
77.000
76.746
125 MHz, CDCl3
Br
N
N
3al
f1 (ppm)

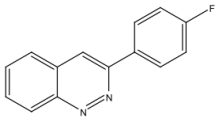

8.616
8.602
8.276
8.204
8.170
8.158
7.923
7.910
7.888
7.876
7.865
7.811
7.798
7.785
7.532
7.519
7.506
7.491
7.478
1.646
0.000
600 MHz, CDCl3
Cl
N
N
3am
1.00
1.00
0.89
1.08
0.95
1.11
1.10
2.21
f1 (ppm)


152.135
149.949
138.643
135.180
131.621
130.773
130.345
129.804
129.498
127.370
127.000
126.457
125.355
119.269
77.211
76.788
150 MHz, CDCl3
Cl
N
N
3am
f1 (ppm)

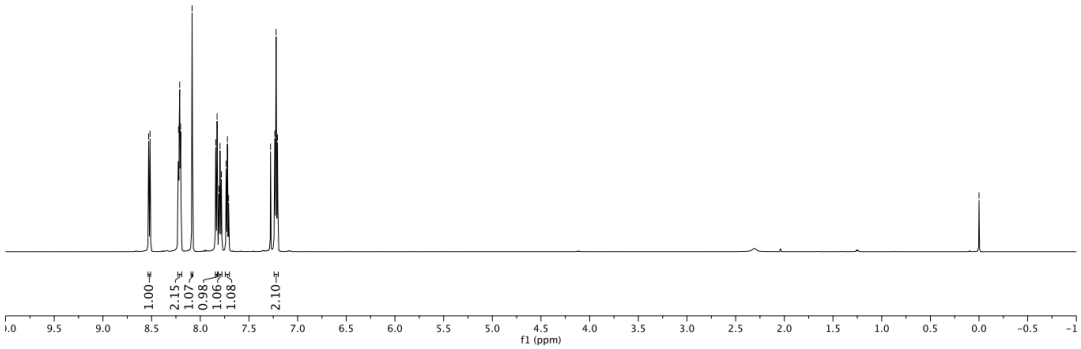

8.585
8.571
8.223
8.210
8.168
7.899
7.886
7.864
7.852
7.839
7.790
7.777
7.765
7.556
7.543
7.264
1.665
0.000
600 MHz, CDCl3
Cl
N
N
3an
1.00
2.05
0.99
1.11
1.09
1.06
2.10
f1 (ppm)


152.359
149.938
135.745
135.380
131.494
130.506
129.898
129.304
128.433
126.977
126.412
118.663
77.211
77.000
76.788
150 MHz, CDCl3
Cl
N
N
3an
f1 (ppm)

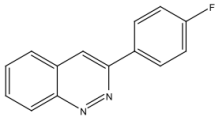
600 MHz, $CDCl_3$



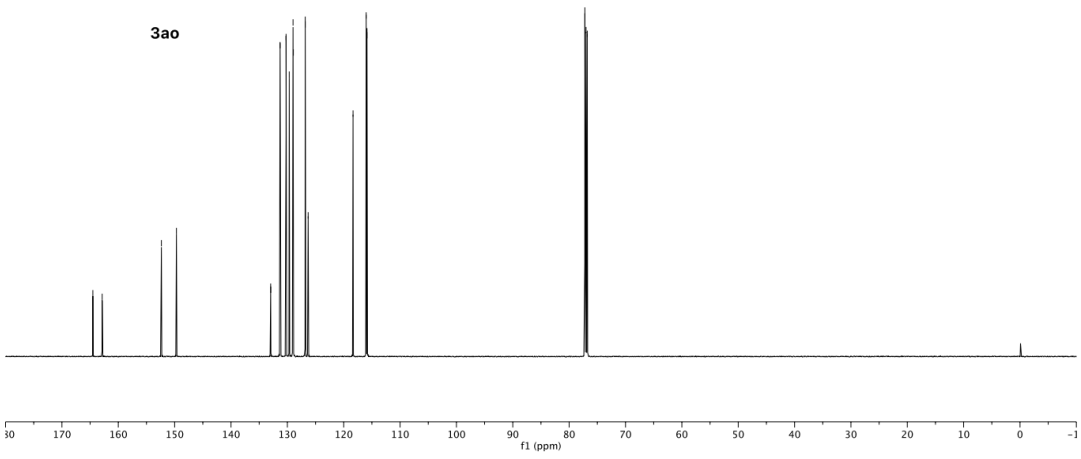
3ao



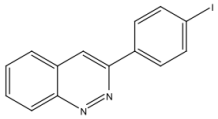
150 MHz, $CDCl_3$



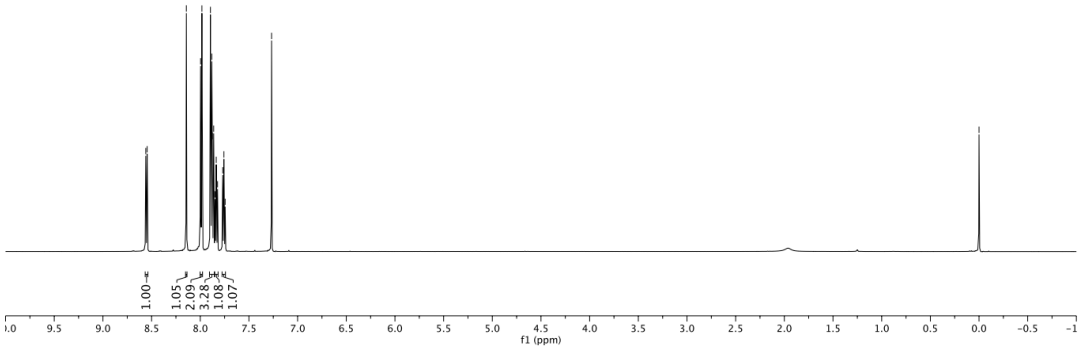
3ao

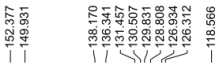


600 MHz, $CDCl_3$

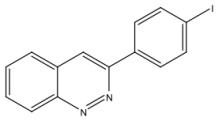


3ap

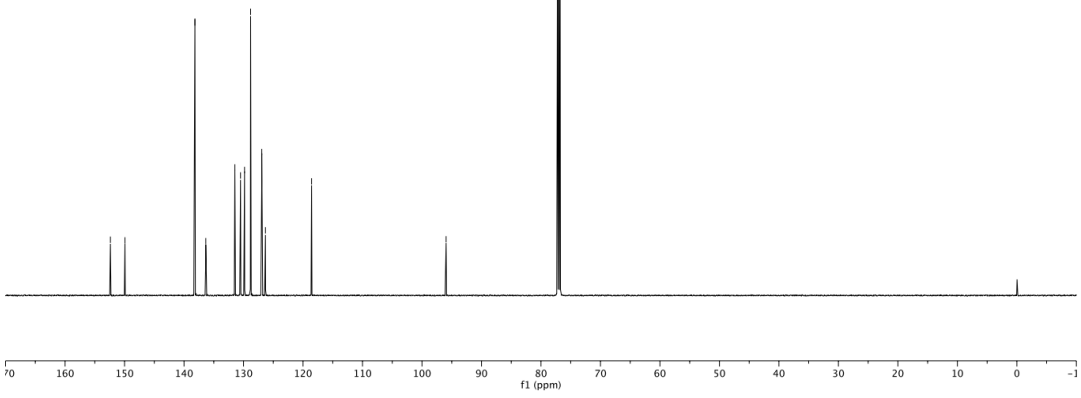


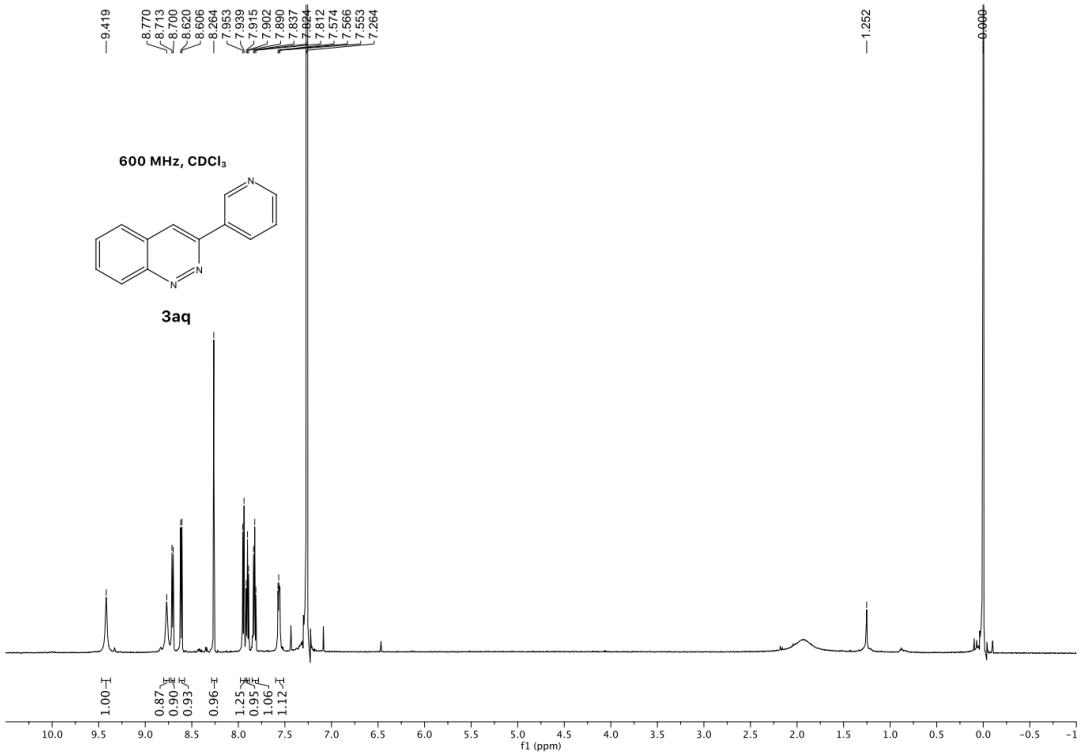


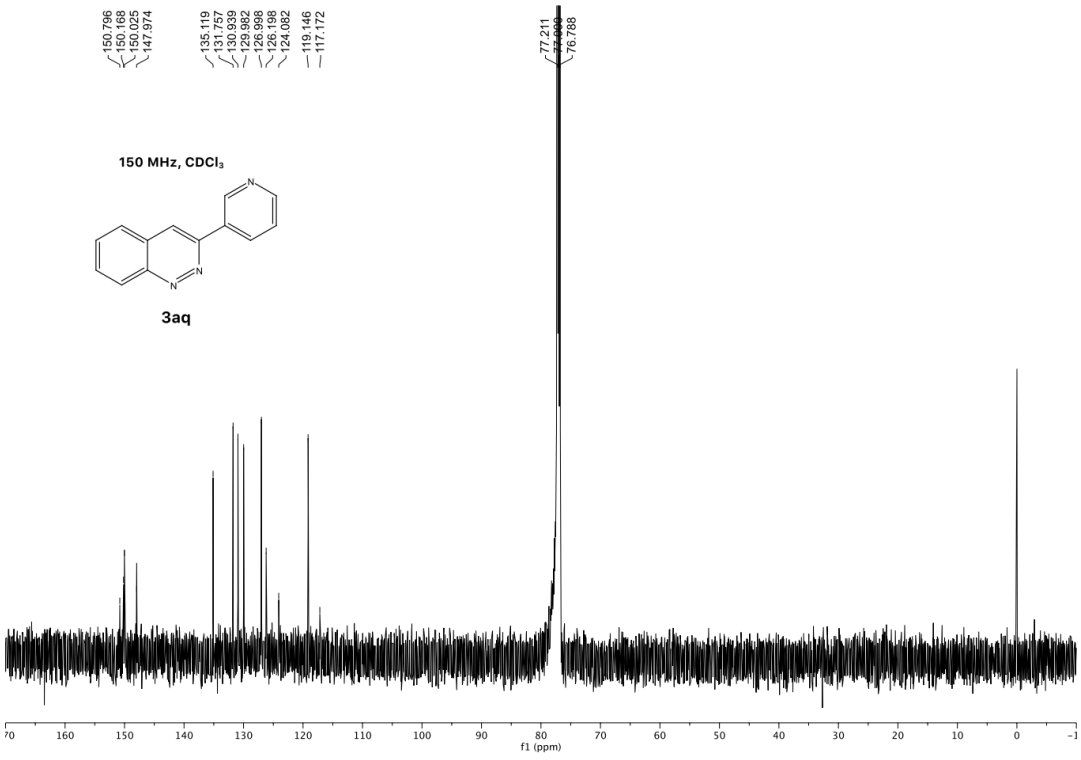
150 MHz, $CDCl_3$

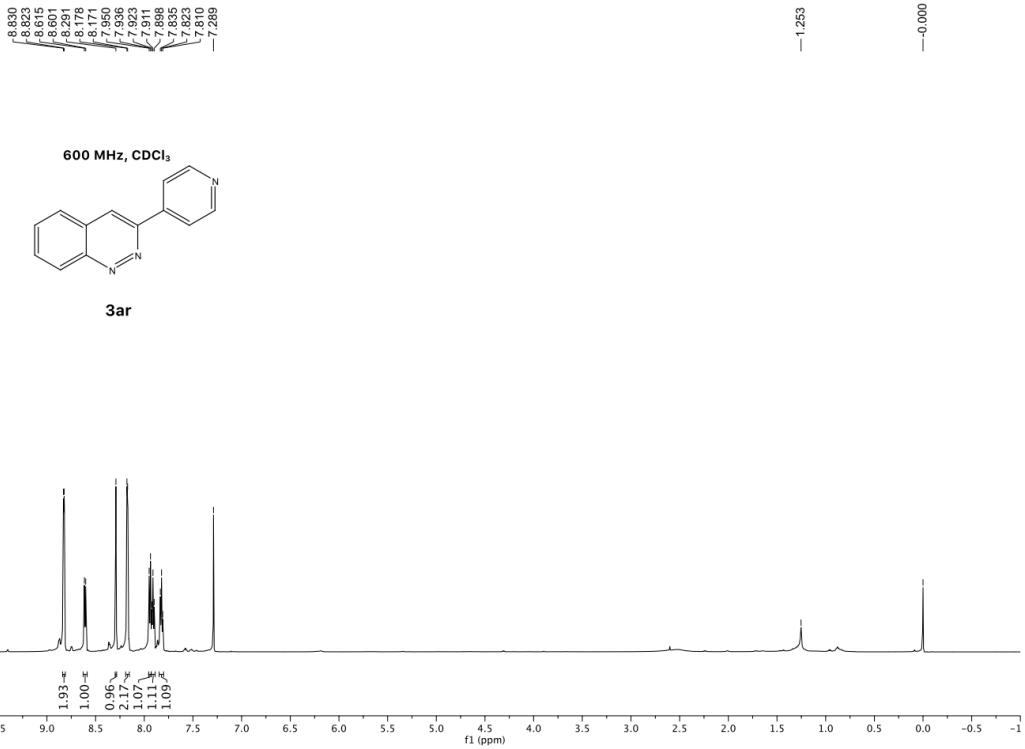


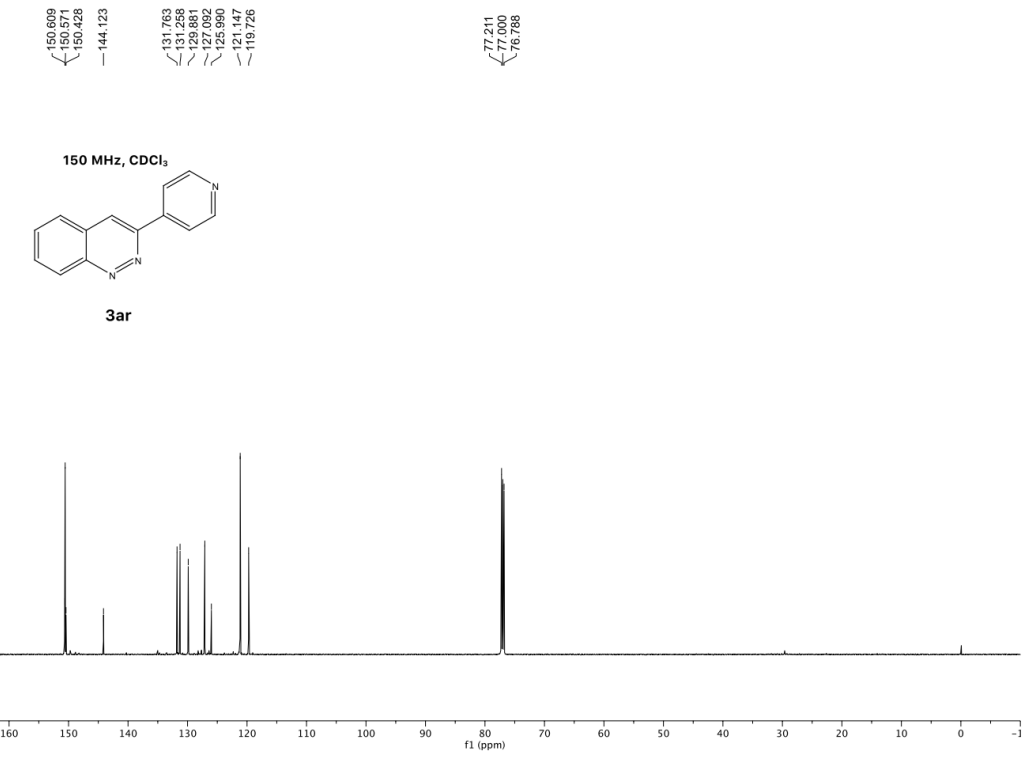
3ap

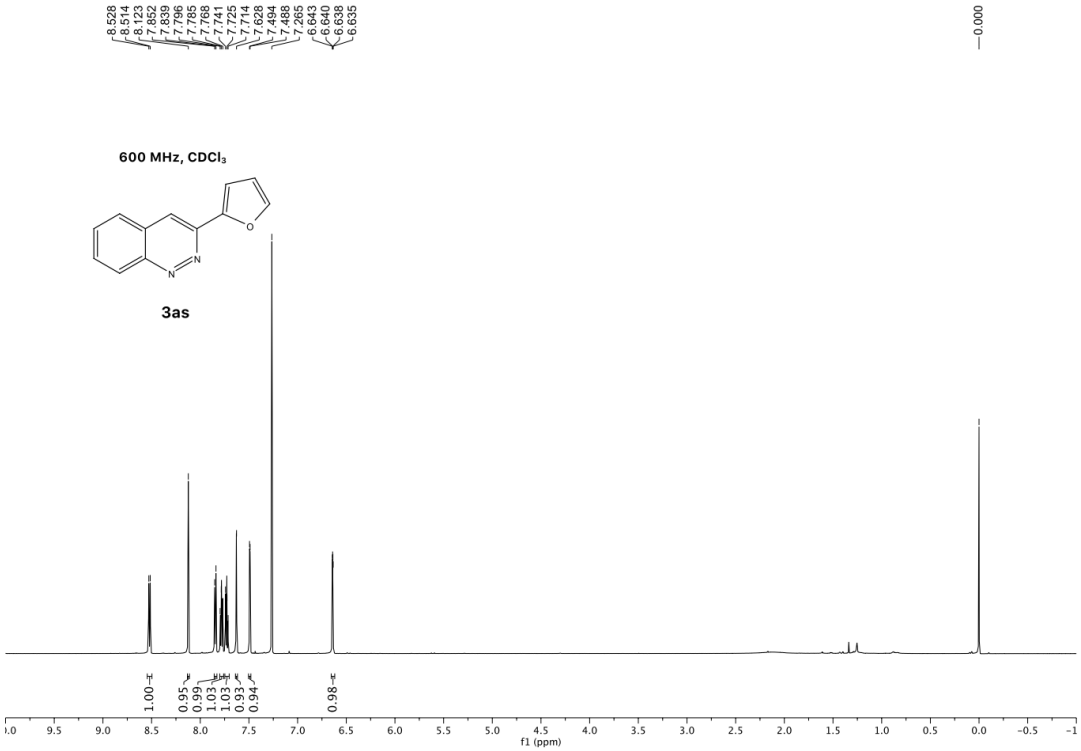


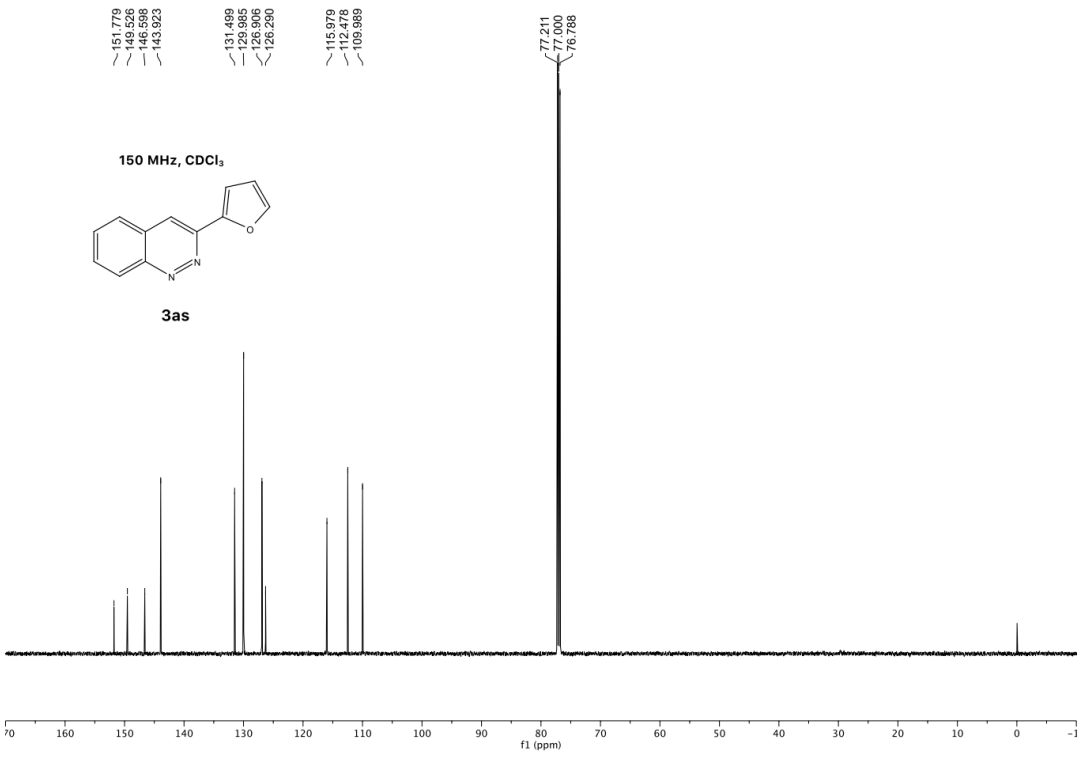

9.419
8.770
8.713
8.700
8.620
8.606
8.264
7.953
7.939
7.915
7.902
7.890
7.837
7.824
7.612
7.574
7.566
7.553
7.284
1.252
0.000
600 MHz, CDCl3
3aq
1.00
0.87
0.90
0.93
0.96
1.25
0.95
1.06
1.12
f1 (ppm)

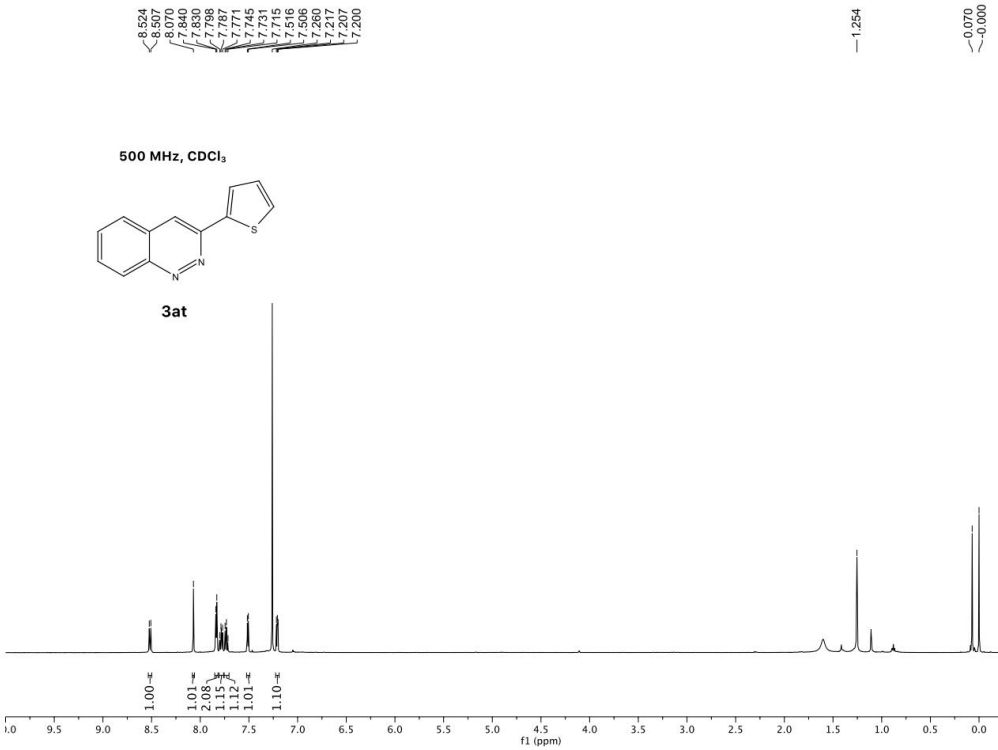

150.796
150.168
150.025
147.974
135.119
131.757
130.939
129.982
126.998
126.198
124.082
119.146
117.172
77.211
77.000
76.788
150 MHz, CDCl3
3aq
f1 (ppm)

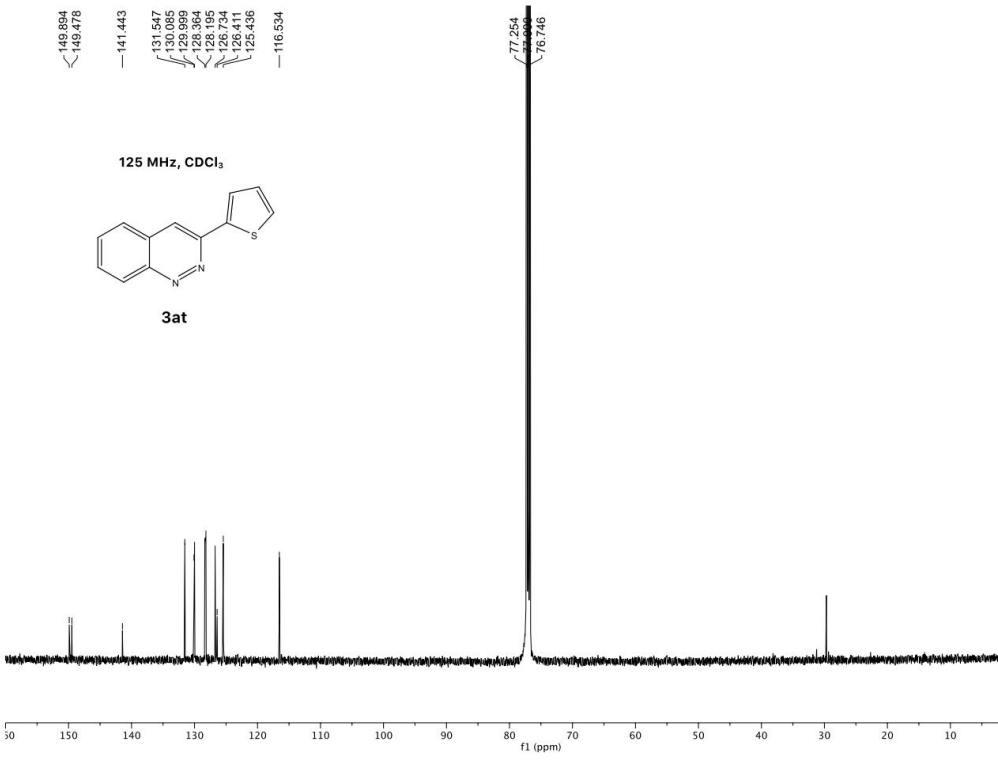

8.830
8.823
8.615
8.601
8.291
8.178
8.171
7.950
7.936
7.923
7.911
7.898
7.835
7.823
7.810
7.289
1.253
0.000
600 MHz, CDCl3
3ar
1.93
1.00
0.96
2.17
1.07
1.11
1.09
f1 (ppm)

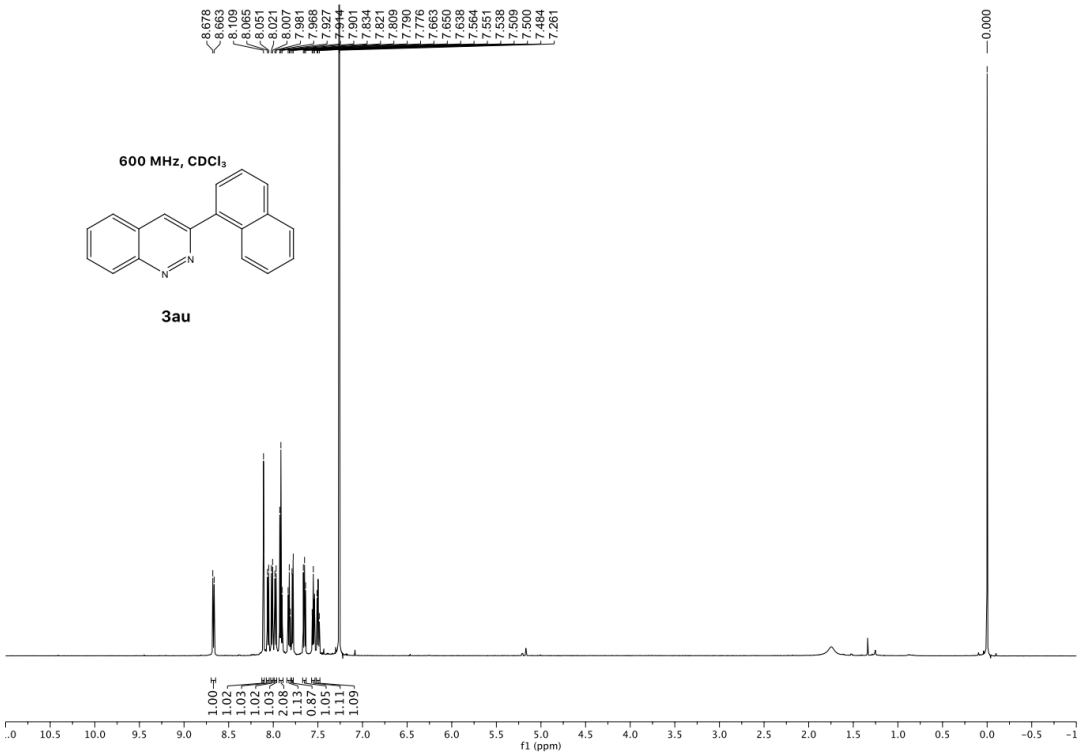

150.609
150.571
150.428
144.123
131.763
131.258
129.861
127.092
125.990
121.147
119.726
77.211
77.000
76.788
150 MHz, CDCl3
3ar
f1 (ppm)

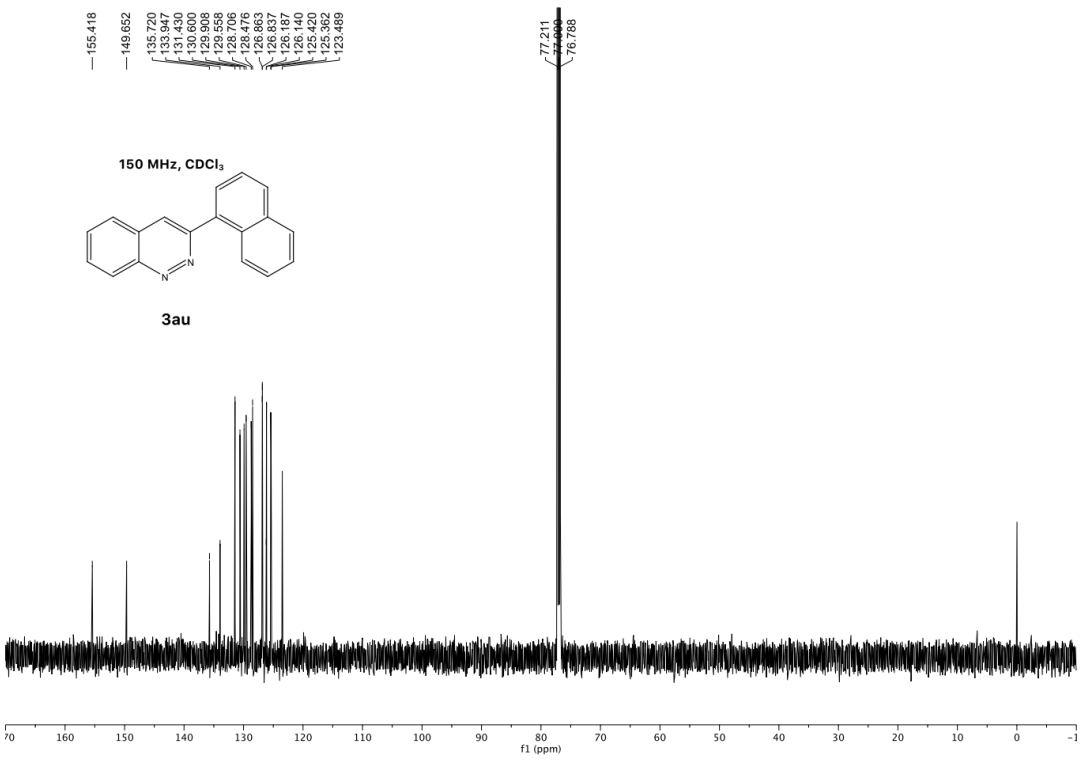

8.528
8.514
8.123
7.852
7.798
7.796
7.785
7.768
7.741
7.725
7.714
7.628
7.494
7.488
7.265
6.643
6.640
6.638
6.635
0.000
600 MHz, CDCl3
3as
1.00
0.95
0.99
1.03
1.03
0.93
0.94
0.98
f1 (ppm)

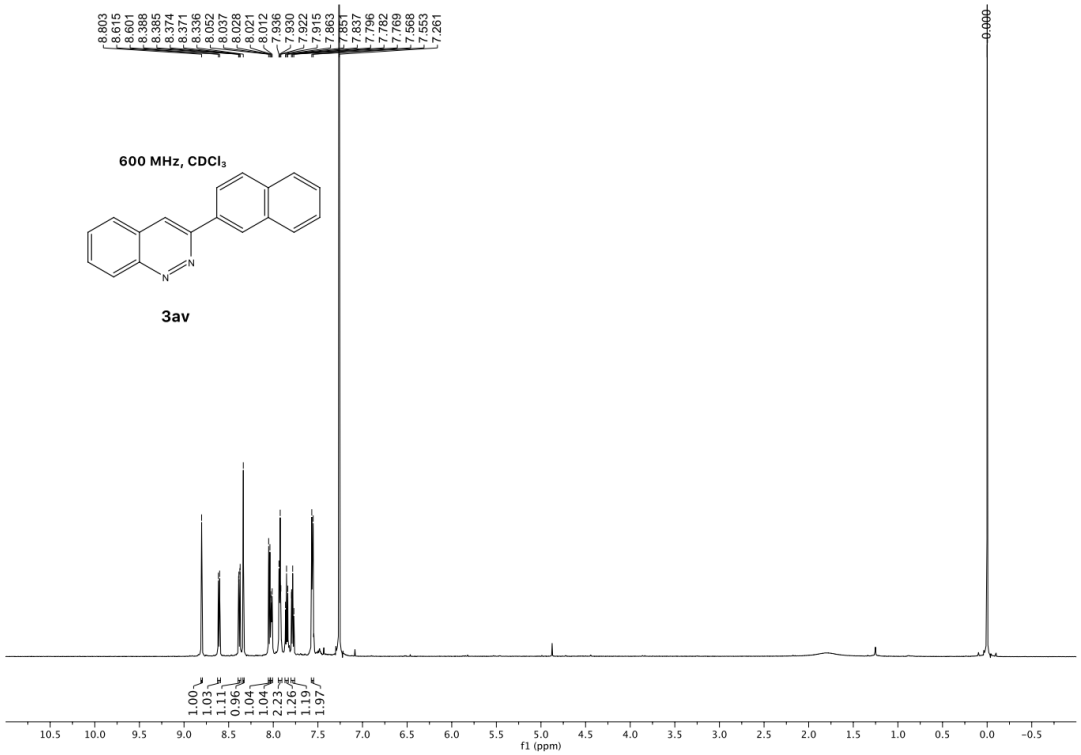

151.779
149.526
146.598
143.923
131.499
129.985
126.906
126.290
115.979
112.478
109.989
77.211
77.000
76.788
150 MHz, CDCl3
3as
f1 (ppm)

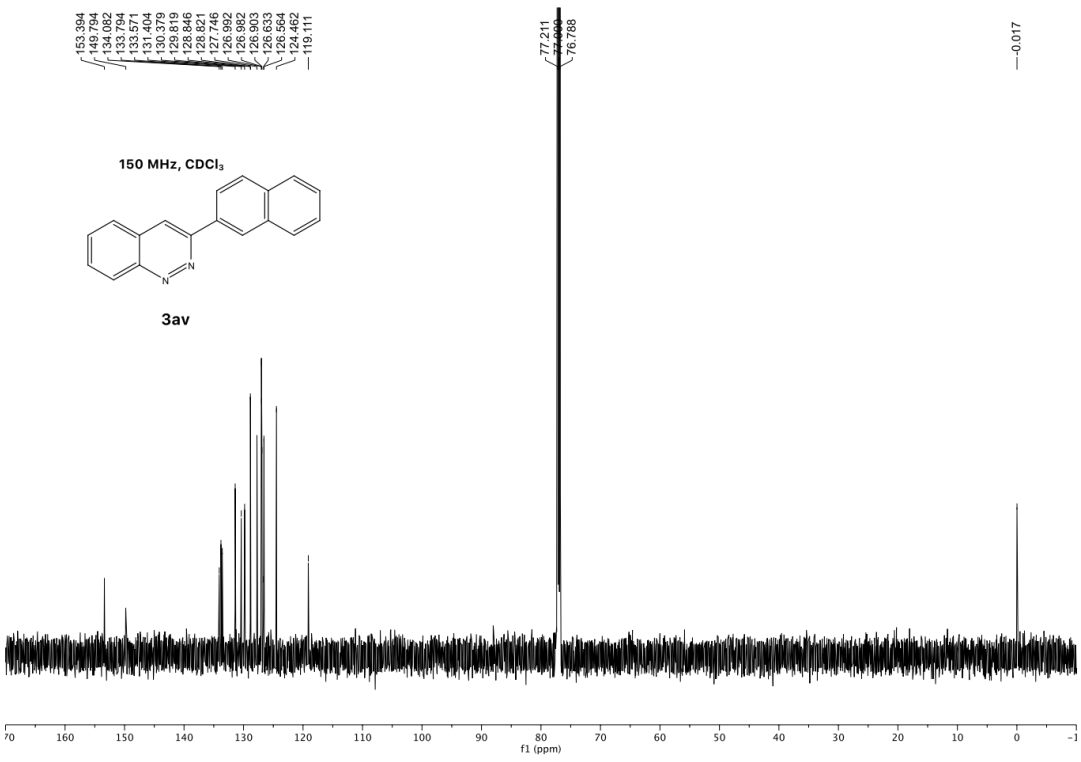

8.524
8.507
8.070
7.840
7.830
7.798
7.787
7.771
7.745
7.731
7.715
7.516
7.506
7.260
7.217
7.207
7.200
1.254
0.070
-0.000
500 MHz, CDCl3
3at
1.00
1.01
2.08
1.15
1.12
1.01
1.10
f1 (ppm)


149.894
149.478
141.443
131.547
130.085
129.999
128.364
128.195
126.734
126.411
125.436
116.534
77.254
76.746
125 MHz, CDCl3
3at
f1 (ppm)

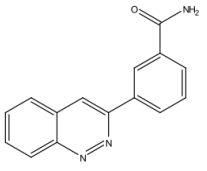

8.678
8.663
8.109
8.065
8.051
8.021
8.007
7.981
7.968
7.927
7.914
7.901
7.834
7.821
7.809
7.790
7.776
7.663
7.650
7.638
7.564
7.551
7.538
7.509
7.500
7.484
7.261
0.000
600 MHz, CDCl3
3au
1.00
1.02
1.03
1.02
1.03
2.08
1.13
0.87
1.05
1.11
1.09
f1 (ppm)


155.418
149.652
135.720
133.947
131.430
130.600
129.908
129.558
128.706
128.476
126.863
126.837
126.187
126.140
125.420
125.362
123.489
77.211
77.000
76.788
150 MHz, CDCl3
3au
f1 (ppm)

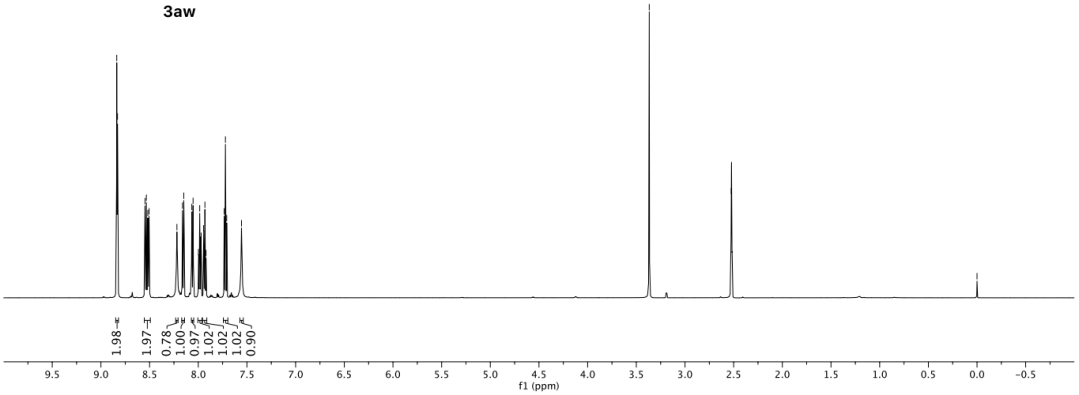

8.803
8.615
8.601
8.388
8.385
8.374
8.371
8.336
8.052
8.037
8.028
8.021
8.012
7.936
7.930
7.922
7.915
7.863
7.851
7.837
7.796
7.782
7.769
7.568
7.553
7.261
0.000
600 MHz, CDCl3
3av
1.00
1.03
1.11
0.96
1.04
1.04
2.23
1.26
1.19
1.97
f1 (ppm)


153.394
149.794
134.082
133.794
133.571
131.404
130.379
129.819
128.846
128.821
127.746
126.992
126.982
126.903
126.633
126.564
124.462
119.111
77.211
77.000
76.788
-0.017
150 MHz, CDCl3
3av
f1 (ppm)

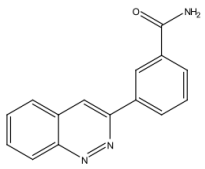
600 MHz, DMSO-d_6



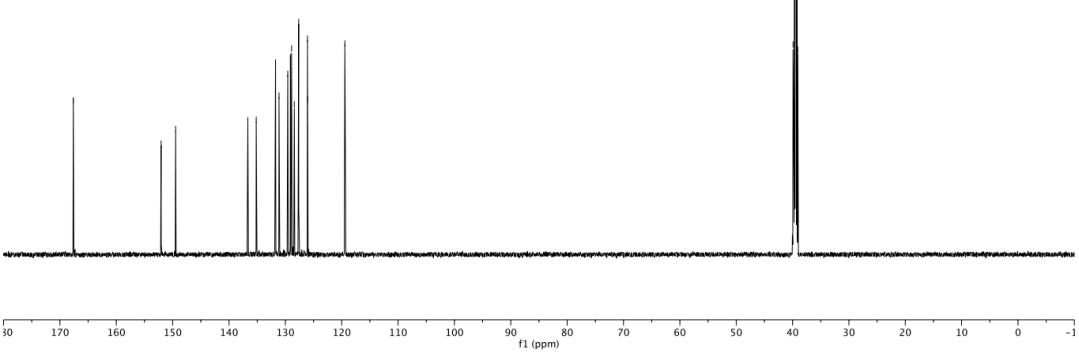
3aw

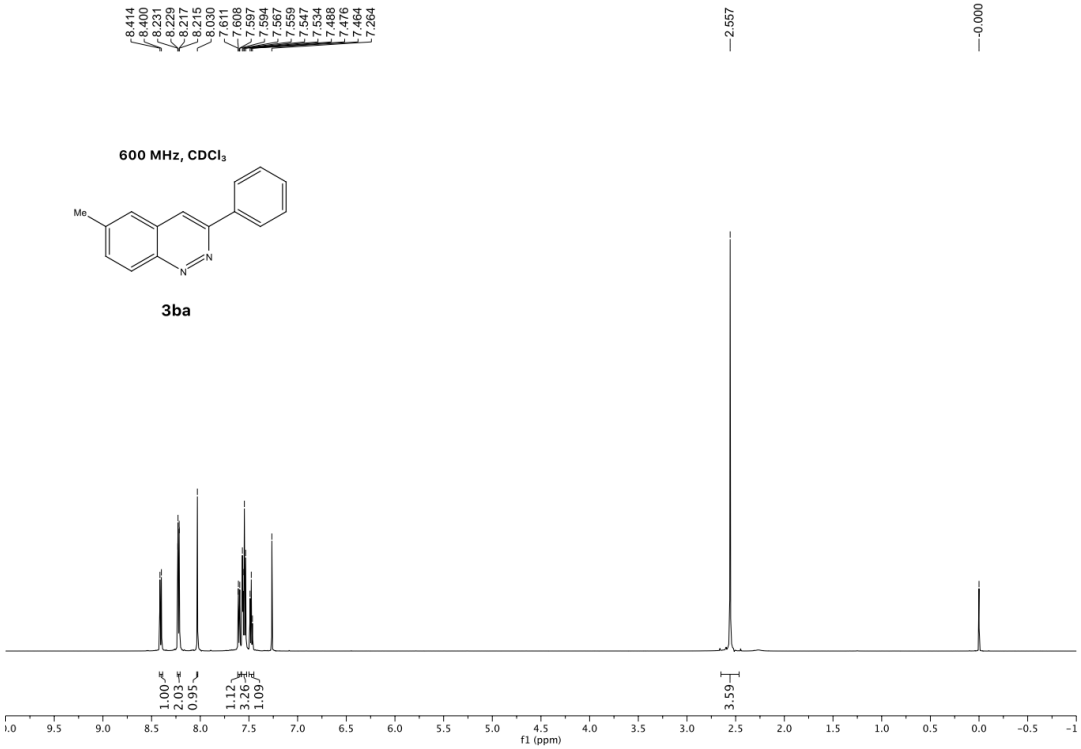


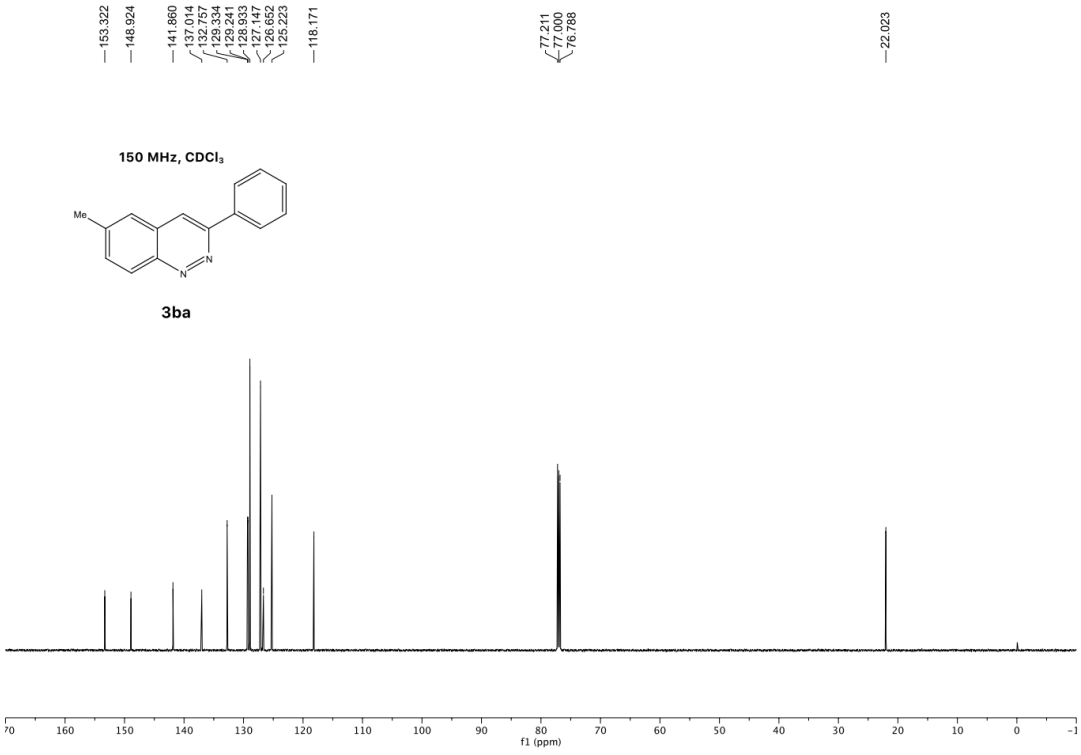
150 MHz, DMSO-d_6

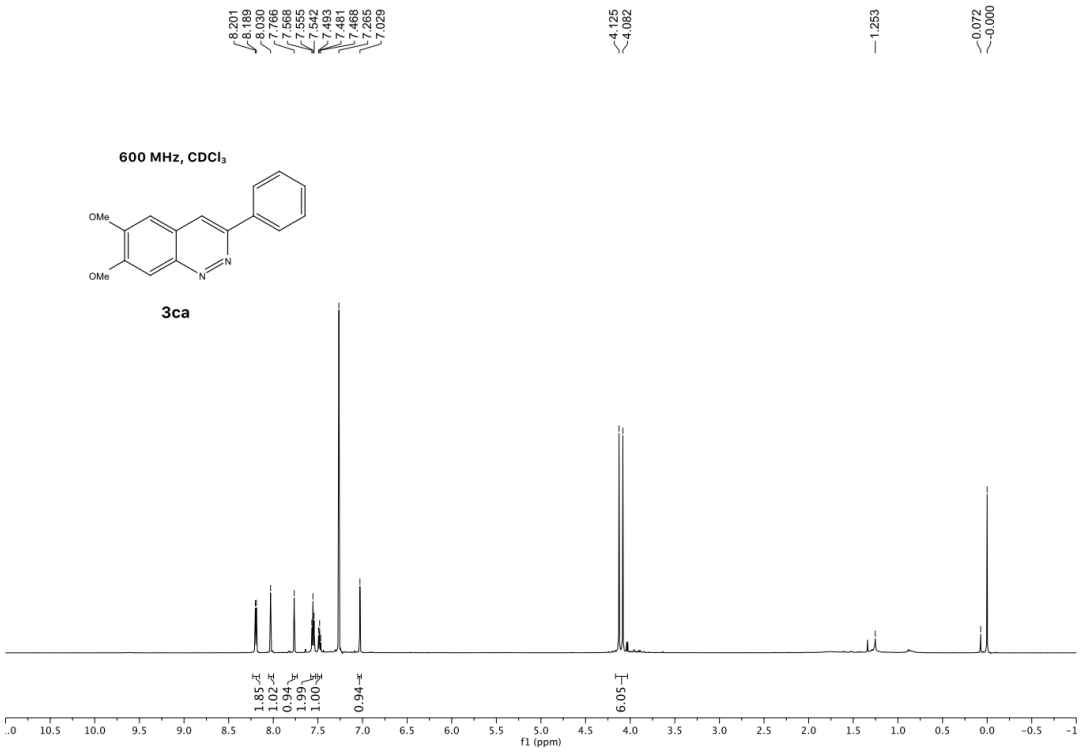


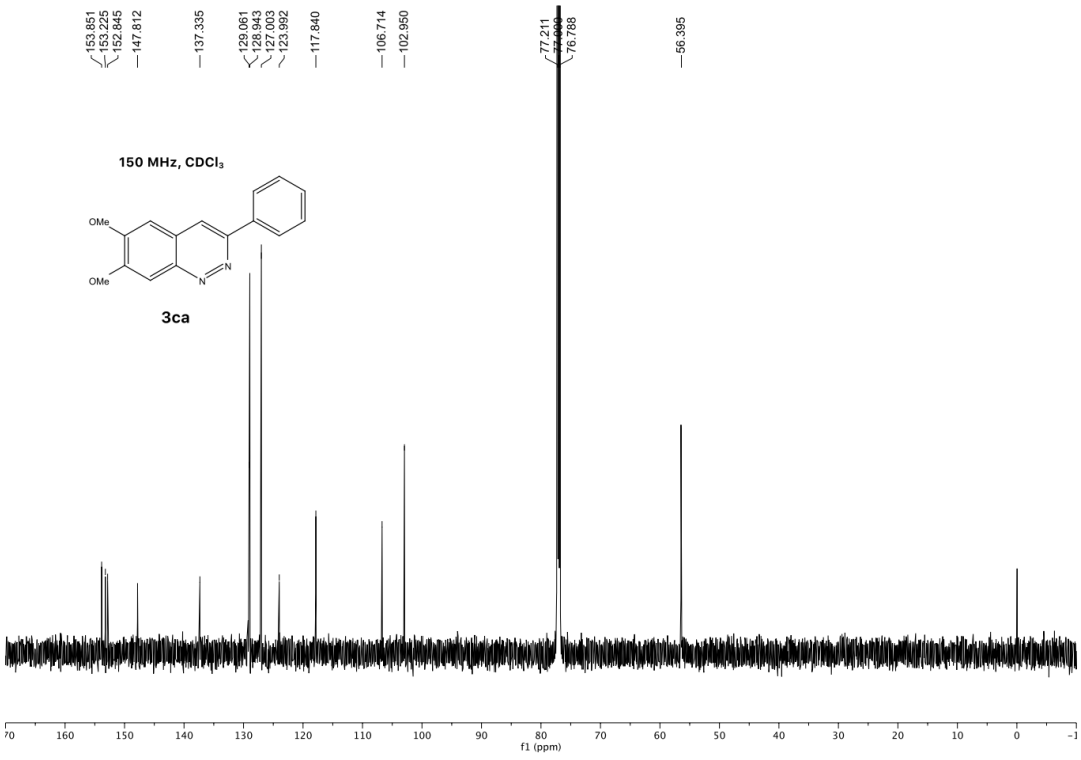
3aw




8.414
8.400
8.231
8.229
8.217
8.215
8.030
7.611
7.608
7.597
7.594
7.567
7.559
7.547
7.534
7.488
7.476
7.464
7.264
2.557
0.000
600 MHz, CDCl3
Me
N
N
3ba
1.00
2.03
0.95
1.12
3.26
1.09
3.59
f1 (ppm)


153.322
148.924
141.860
137.014
132.757
129.334
129.241
128.933
127.147
126.652
125.223
118.171
77.211
77.000
76.788
22.023
150 MHz, CDCl3
Me
N
N
3ba
f1 (ppm)

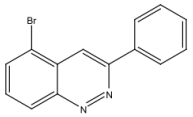

8.201
8.189
8.030
7.766
7.568
7.555
7.542
7.493
7.481
7.468
7.265
7.029
4.125
4.082
1.253
0.072
0.000
600 MHz, CDCl3
OMe
OMe
N
N
3ca
1.85
1.02
0.94
1.99
1.00
0.94
6.05
f1 (ppm)


153.851
153.225
152.845
147.812
137.335
129.061
128.943
127.003
123.992
117.840
106.714
102.950
77.211
76.788
56.395
150 MHz, CDCl3
OMe
OMe
N
N
3ca
f1 (ppm)

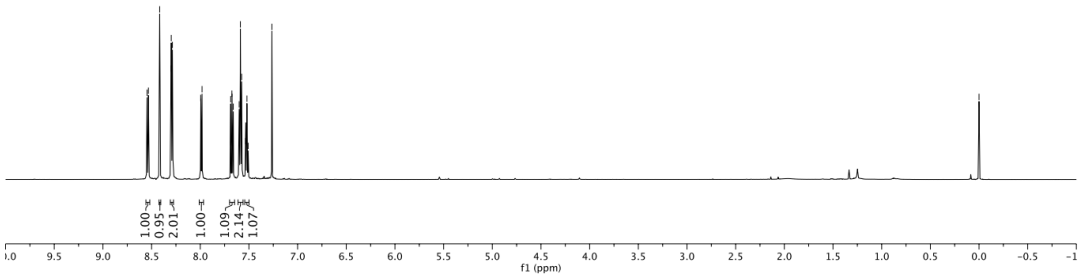
8.547
8.532
8.417
8.300
8.298
8.286
7.995
7.882
7.677
7.675
7.661
7.600
7.588
7.575
7.535
7.520
7.508
7.264

0.000

600 MHz, $CDCl_3$



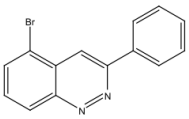
3da



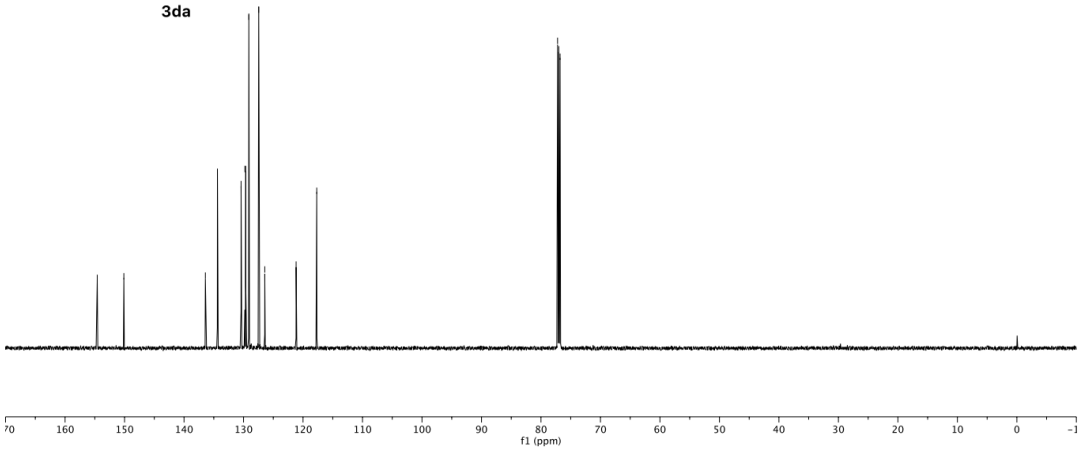
154.590
150.116
136.411
134.391
130.410
129.775
129.630
129.108
127.447
126.427
121.162
117.691

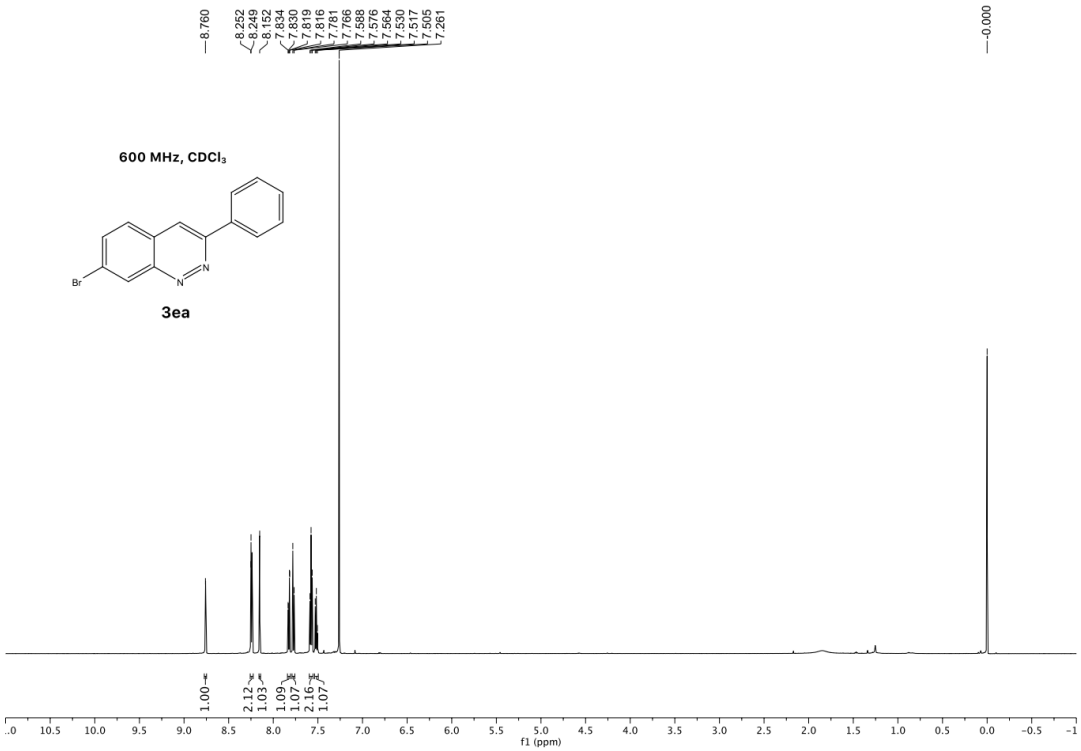
77.211
77.000
76.788

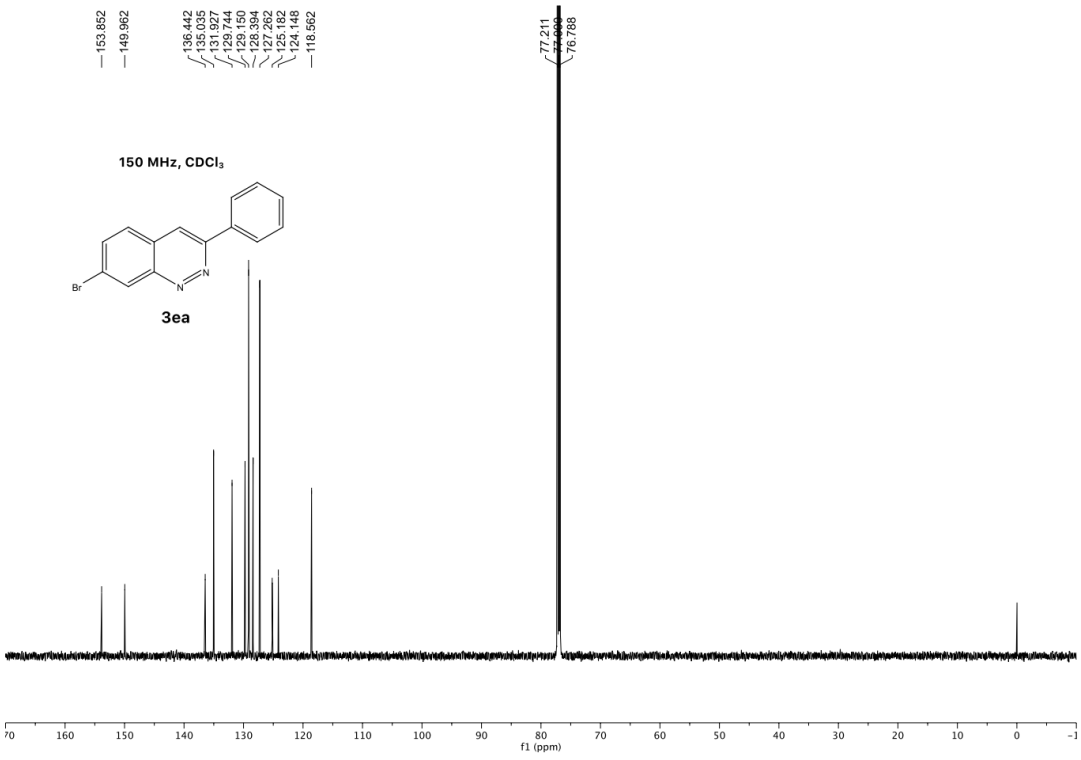
150 MHz, $CDCl_3$

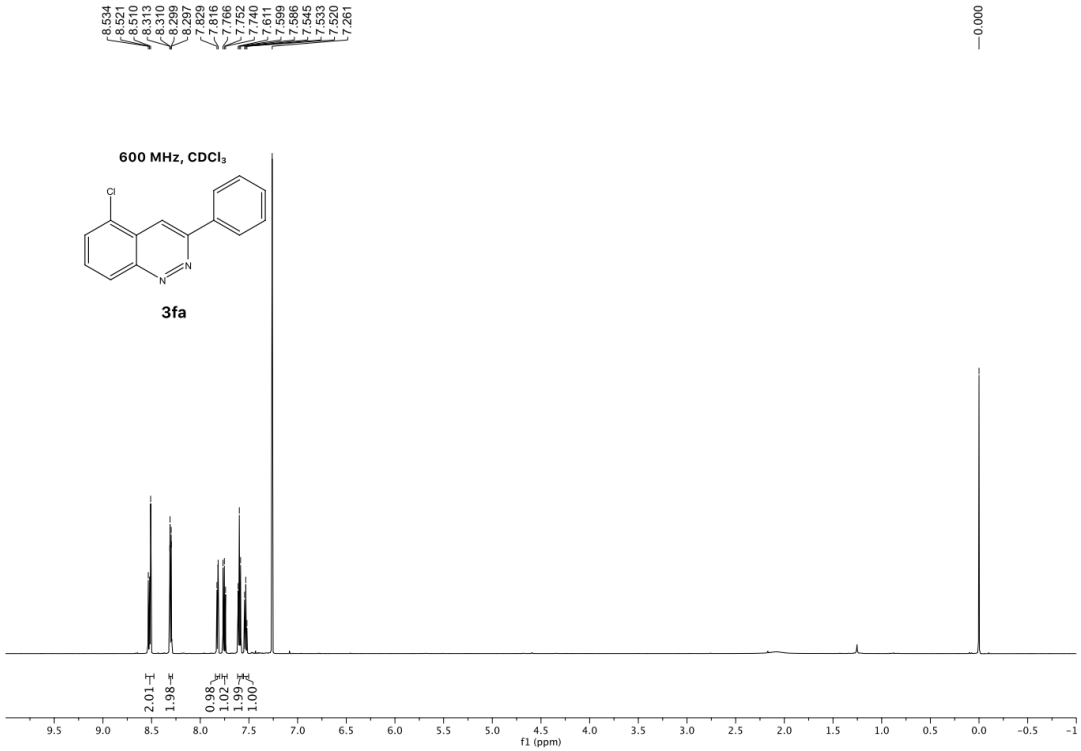


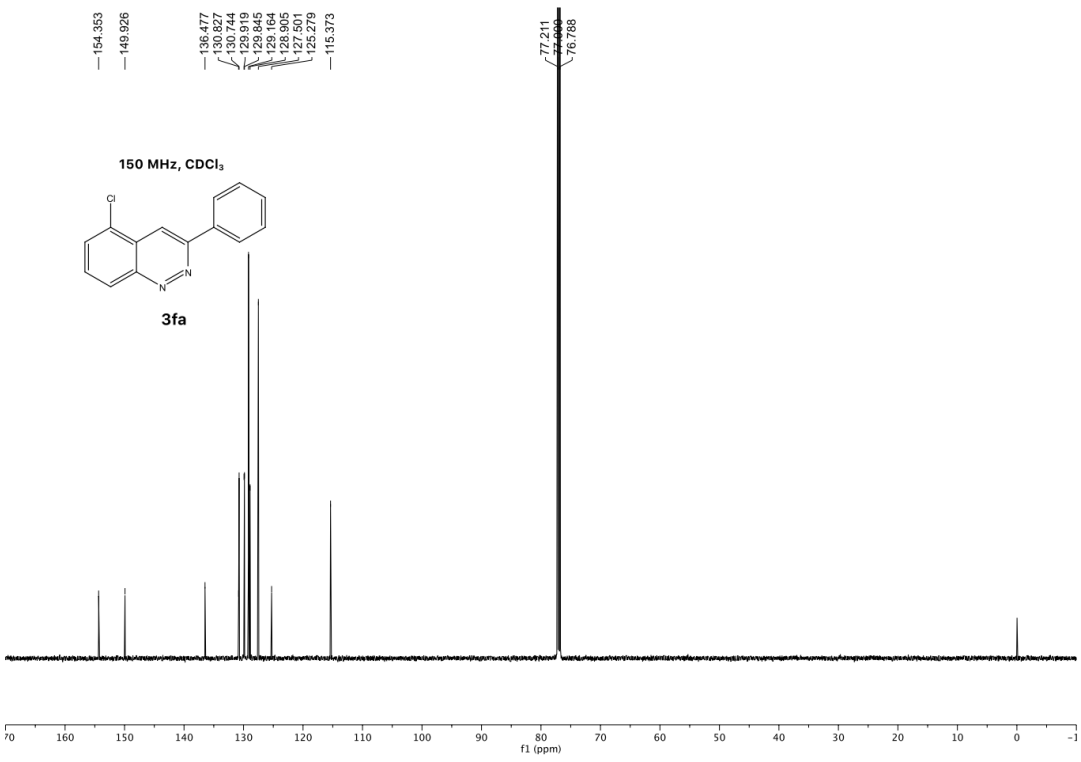
3da

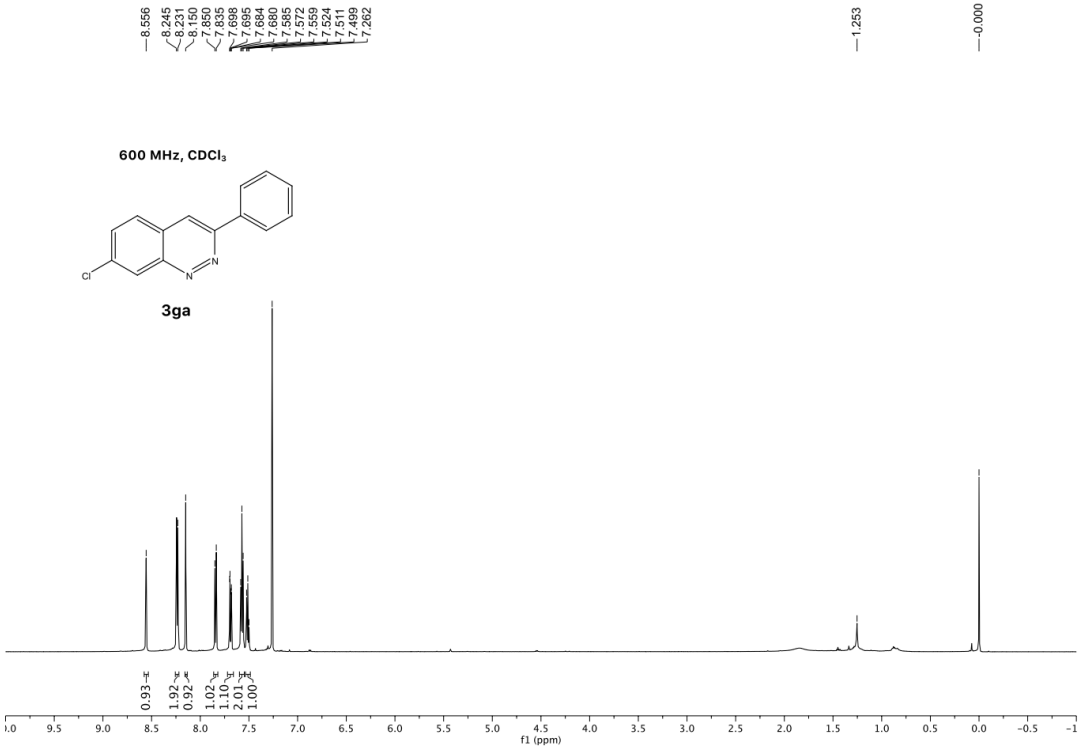


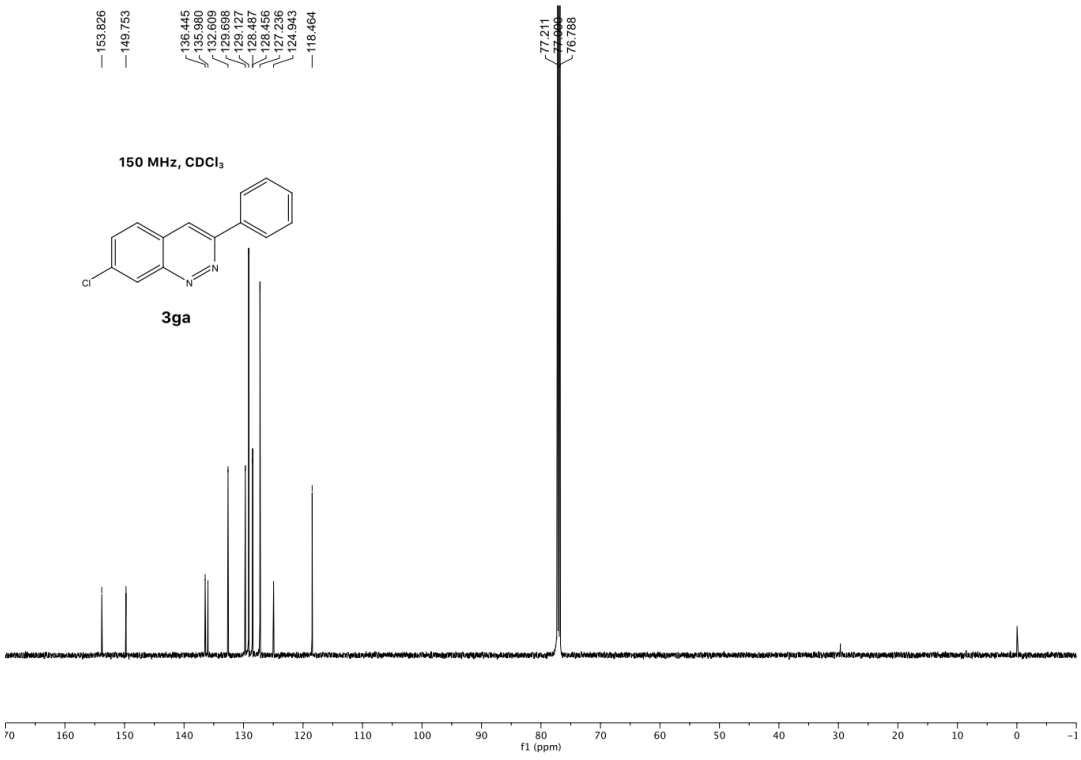

8.760
8.252
8.249
8.152
7.834
7.830
7.819
7.816
7.781
7.766
7.588
7.576
7.564
7.530
7.517
7.505
7.261
0.000
600 MHz, CDCl3
Br
N
N
3ea
1.00
2.12
1.03
1.09
1.07
2.16
1.07
f1 (ppm)


153.852
149.962
136.442
135.035
131.927
129.744
129.150
128.394
127.262
125.182
124.148
118.562
77.211
77.000
76.788
150 MHz, CDCl3
Br
N
N
3ea
f1 (ppm)

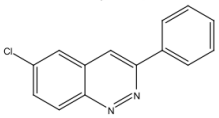

8.534
8.521
8.510
8.313
8.310
8.299
8.297
7.829
7.816
7.766
7.752
7.740
7.611
7.599
7.586
7.545
7.533
7.520
7.261
0.000
600 MHz, CDCl3
Cl
N
N
3fa
2.01
1.98
0.98
1.02
1.99
1.00
f1 (ppm)


154.353
149.926
136.477
130.827
130.744
129.919
129.845
129.164
128.905
127.501
125.279
115.373
77.211
77.000
76.788
150 MHz, CDCl3
Cl
N
N
3fa
f1 (ppm)

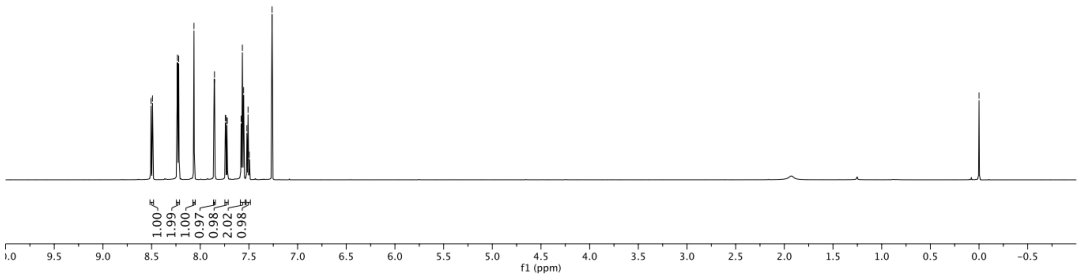

8.556
8.245
8.231
8.150
7.850
7.835
7.698
7.695
7.684
7.680
7.585
7.572
7.559
7.524
7.511
7.499
7.262
1.253
0.000
600 MHz, CDCl3
Cl
N
N
3ga
0.93
1.92
0.92
1.02
1.10
2.01
1.00
f1 (ppm)

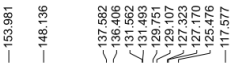

153.826
149.753
136.445
135.980
132.609
129.698
129.127
128.487
128.456
127.236
124.943
118.464
77.211
77.000
76.788
150 MHz, CDCl3
Cl
N
N
3ga
f1 (ppm)

600 MHz, $CDCl_3$

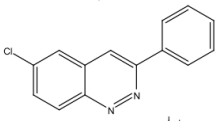


3ha

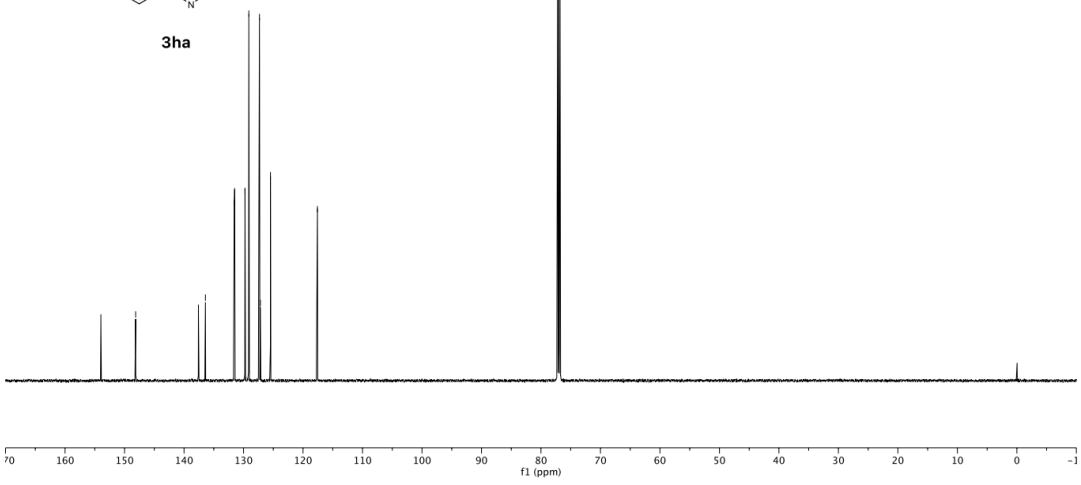




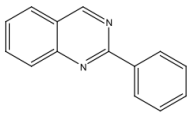
150 MHz, $CDCl_3$



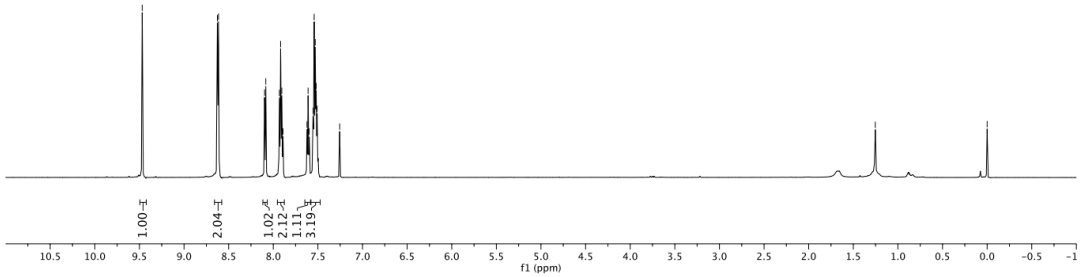
3ha

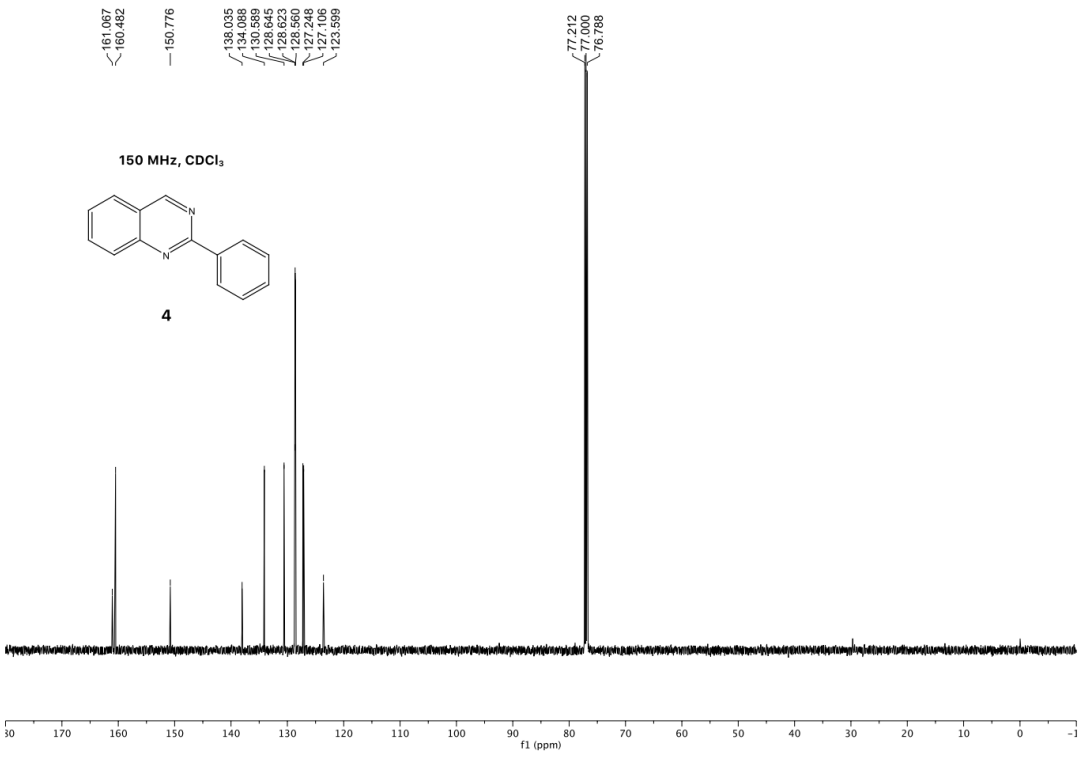


600 MHz, $CDCl_3$



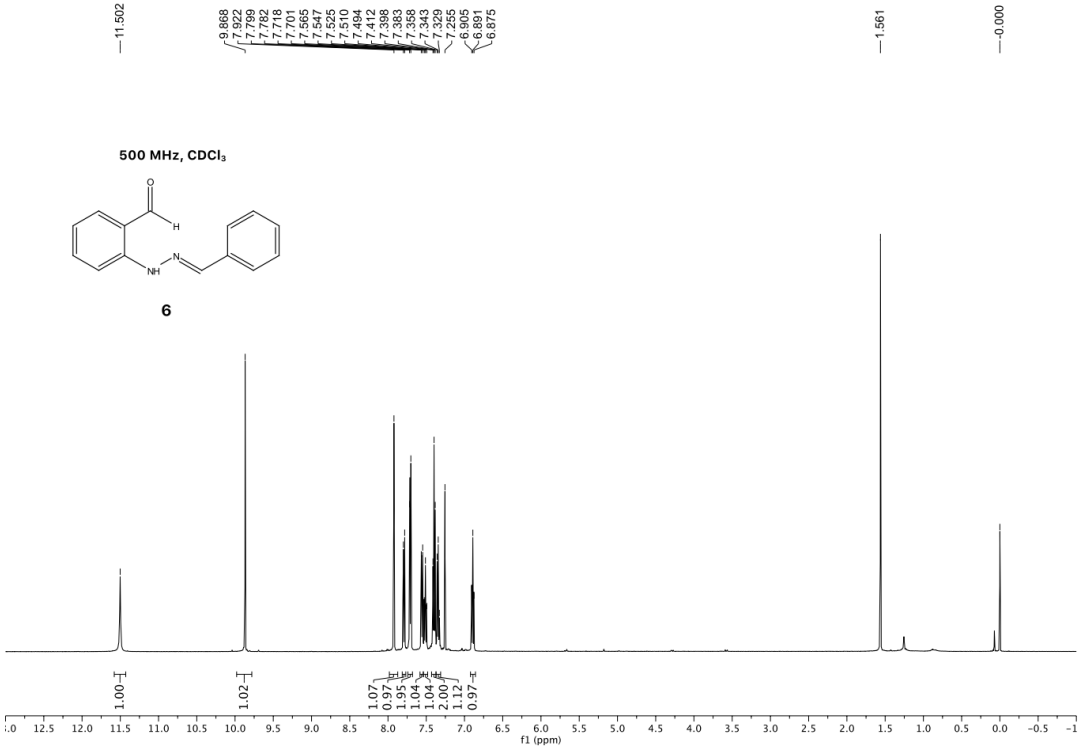
4

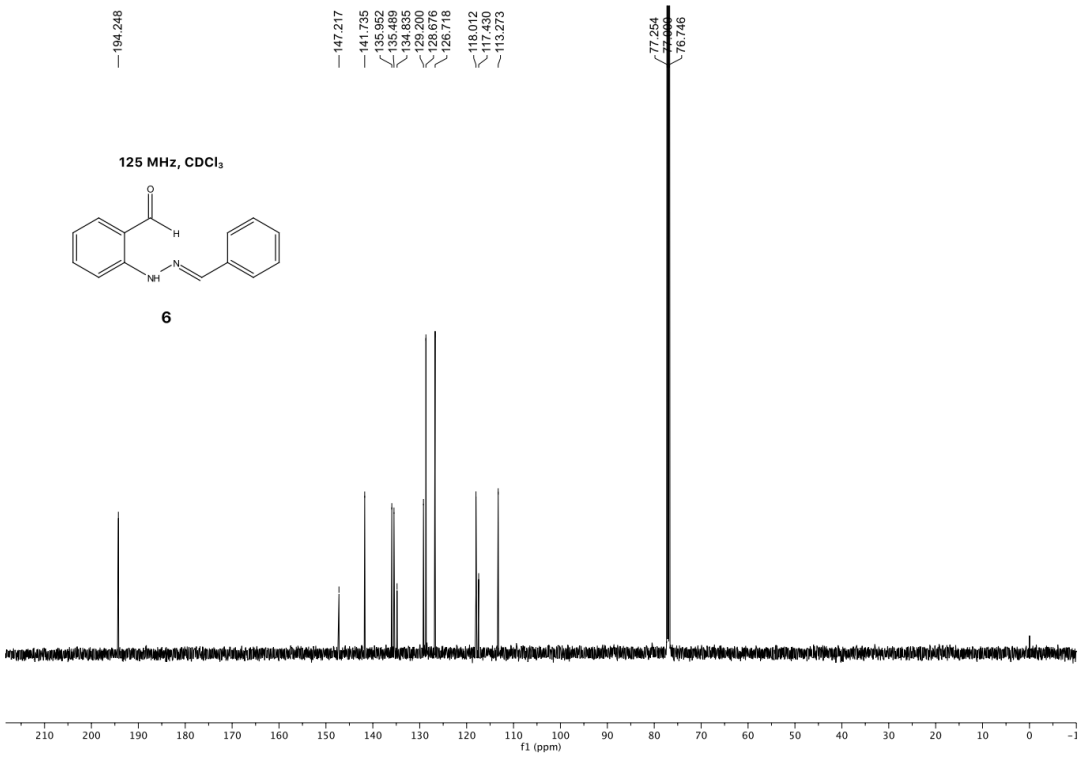




150 MHz, $CDCl_3$

4


11.502
9.868
7.922
7.799
7.782
7.718
7.701
7.565
7.547
7.525
7.510
7.494
7.412
7.398
7.383
7.358
7.343
7.329
7.255
6.905
6.891
6.875
1.561
0.000
500 MHz, CDCl3
O
H
N
NH
6
1.00
1.02
1.07
0.97
1.95
1.04
1.04
2.00
1.12
0.97
f1 (ppm)


194.248
147.217
141.735
135.952
135.489
134.835
129.200
128.676
126.718
118.012
117.430
113.273
77.254
77.000
76.746
125 MHz, CDCl3
O
H
N
NH
6
f1 (ppm)