Supporting Information

Zirconium catalysed intermolecular hydroamination reactions of secondary amines with alkynes

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General considerations

All manipulations of air- and/or moisture-sensitive compounds were performed under nitrogen atmosphere using standard Schlenk or glovebox techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 400 MHz spectrometer. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The FT-IR spectra were recorded with a Nicolet-550 FT-IR spectrometer as KBr pellets. X-ray crystallographic data were collected using a Bruker AXS D8 X-ray diffractometer. HR-MS data were recorded by Bruker ESI-TOF. Toluene and hexane were freshly distilled by refluxing over sodium/benzophenone ketyl and distilled prior to use. C_6H_5Cl, C_6D_6 and C_6D_5Cl were degassed and distilled over CaH_2. $[Ph_3C][B(C_6F_5)_4]$ purchased from Strem Chemicals, Inc. was used without purification. $ZrBn_4$, the ligand precursors L^1H_2 and L^2H_2, and complexes **1** and **2** were prepared according to reported procedures.[1] Amines were distilled over CaH_2. Alkynes were degassed, flushed with argon and stored over molecular sieves (4 Å).

Suitable single crystals of complexes **3** were sealed in a thin-walled glass capillary for determination the single-crystal structures. All data were collected with a Bruker AXS D8 X-ray diffractometer, using Mo-K_α radiation at 223(2) K with the SMART suite of Programs.[2] Data were processed and corrected for Lorentz and polarization effects with SAINT,[3] and for absorption effect with SADABS.[4] Structural solution and refinement were carried out with the SHELXTL suite of programs.[5] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H-atoms were put at calculated positions. A summary of the most important crystallographic data is given in Table S2.

Synthesis and characterization of complex 3

To a solution of $ZrBn_4$ (1.37 g, 3 mmol) in toluene (5 mL) was added dropwise L^2H_2 (1.53 g, 3 mmol) in toluene (5 mL) at room temperature over 15 min. After stirring for 2 hours, toluene was removed under reduced pressure and hexane (5 mL) was added to extract the residue. Complex **3** was obtained as colorless solid after the hexane solution was cooled to -30 °C (1.90 g, 2.7 mmol, 90%). Crystals suitable for X-ray diffraction analyses were grown from hexane solution at room temperature. IR (neat): v = 2958, 2905, 2868, 1479, 1442, 1415, 1386, 1267, 1239, 1240, 1203, 1171, 1132, 847, 753, 738, 551, 470 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.78 (d, 2H, J = 7.76 Hz, Ar-H), 7.58 (s, 2H, Ar-H), 7.32-7.28 (m, 2H, Ar-H), 7.15-7.13 (m, 1H, Ar-H), 6.96-6.93 (m, 4H, Ar-H), 6.78-6.74 (m, 2H, Ar-H), 6.65-6.62 (m, 1H, Ar-H), 3.32 (d, 2H, J = 16 Hz, $PhCH_2$), 3.02 (s, 2, NCH_2), 2.98 (d, 2H, J = 16 Hz, $PhCH_2$), 2.08 (m, 2H, NCH_2), 1.98 (s, 2, NCH_2C), 1.80 (s, 18H, o-$C(CH_3)_3$), 1.36 (s, 18H, p-$C(CH_3)_3$), 1.01 (m, 2H, $CCH_2C_2H_5$), 0.32 (m, 5H, CC_2H_5). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 156.8, 146.8, 140.5, 136.0, 135.4, 129.9, 128.0, 124.4, 124.0, 123.5, 121.2 (Ar-C), 59.4 ($PhCH_2$), 57.5 (NCH_2), 42.0 ($NCH_2C_3H_7$), 34.6 ($C(CH_3)_3$), 33.5 ($C(CH_3)_3$), 31.1 ($C(CH_3)_3$), 29.8 ($C(CH_3)_3$), 21.2 ($CH_2CH_2C_2H_5$), 18.7 ($C_2H_4CH_2CH_3$), 12.8 ($C_3H_6CH_3$). Anal. Calcd for $C_{48}H_{67}NO_2Zr$: C, 73.79; H, 8.64; N, 1.79. Found: C, 73.81; H, 8.66; N, 1.79.

General procedure for hydroamination reactions

In a glovebox filled with nitrogen, PhCl solution (1 mL) of $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.01 mmol) was added to PhCl solution (1 mL) of **3** (78 mg, 0.01 mmol) under stirring. A color change from orange to colorless was observed immediately. After 5 min, **4** (1 mmol) and **5** (2 mmol) were added to the mixture. The resulting solution was stirred at 110 °C for desired time. After the mixture was cooled to 0 °C, $LiAlH_4$ (76 mg, 2 mmol) was added, and the resulting mixture was stirred at 60 °C for 2 hours. The reaction was quenched by the aqueous solution of NaOH (6 M). The product was extracted with toluene (3 × 1 mL). The crude product obtained after removal of solvent was isolated by column chromatography (petroleum ether, silica gel, 0.5% NEt_3) as viscous colorless oil and characterized by ^1H and ^{13}C NMR spectroscopy and HR MS.

Characterizations of hydroamination products

1-(1-phenylethyl)-1,2,3,4-tetrahydroquinoline (6a). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.29 (m, 4H, Ar-H), 7.25-7.21 (m, 1H, Ar-H), 7.04-6.96. (m, 2H, Ar-H), 6.69 (d, 1H, J = 8.28 Hz, Ar-H), 6.59-6.55 (m, 2H, Ar-H), 5.12 (q, 1H, CH), 3.17-2.99 (m, 2H, NCH_2C), 2.83-2.70 (m, 2H, $NCCH_2C$), 1.89-1.82 (m, 2H, $NCCCH_2$), 1.57 (d, 3H, J = 6.96 Hz, $CHCH_3$). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): 145.6, 142.8, 129.3, 128.4, 127.2, 127.0, 126.8, 122.9, 115.5, 110.7 (Ar-C), 54.7(CH), 42.6, 28.6, 22.3 (CH_2), 16.0 (CH_3). HR MS (ESI+): Found 238.1594 $[M+H]^+$, calcd. for $C_{17}H_{20}N^+$: 238.1596.

1-(1-(2-fluorophenyl)ethyl)-1,2,3,4-tetrahydroquinoline (6b). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.35 (m, 1H, Ar-H), 7.22-7.04 (m, 5H, Ar-H), 6.68-6.63 (m, 2H, Ar-H), 5.35(q, 1H, CH), 3.43-3.31 (m, 2H, NCH_2C), 2.87-2.81 (m, 2H, $NCCH_2C$), 2.02-1.96 (m, 2H, $NCCCH_2$), 1.68 (d, 3H, J = 6.96 Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):162.1, 160.0, 145.0, 129.9, 129.5, 129.1, 128.5, 128.4, 127.9, 127.6, 127.2, 126.4, 126.0, 124.1, 122.7, 115.6, 110.9 (Ar-C), 50.8(CH), 43.1, 28.6, 22.5(CH_2), 17.3 (CH_3). HR MS (ESI+): Found 256.1503 $[M+H]^+$, calcd. for $C_{17}H_{19}FN^+$: 256.1502.

1-(1-(m-tolyl)ethyl)-1,2,3,4-tetrahydroquinoline (6c). ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.24-7.21 (m, 1H, Ar-H), 7.19-7.12 (m, 2H, Ar-H), 7.06-6.97 (m, 3H, Ar-H), 6.71-6.69 (m, 1H, Ar-H), 6.58-6.55 (m, 2H, Ar-H), 5.08 (q, 1H, CH), 3.13-3.00 (m, 2H, NCH_2C), 2.76-2.72 (m, 2H, $NCCH_2C$), 2.34 (s, 3H, Ar-CH_3), 1.86-1.83 (m, 2H, $NCCCH_2$), 1.55 (d, 3H, J = 6.96 Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): 145.7, 142.8, 138.0, 129.3, 127.7, 127.5, 127.2, 124.0, 122.8, 115.4, 110.6 (Ar-C), 54.6 (CH),

42.6, 28.6, 22.3 (CH_2), 21.6 ($ArCH_3$), 16.0 (CH_3). HR MS (ESI+): Found 252.1748 $[M+H]^+$, calcd. for $C_{18}H_{22}N^+$: 252.1752.

1-(1-(3-bromophenyl)ethyl)-1,2,3,4-tetrahydroquinoline (6d). ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (s, 1H, Ar-H), 7.39-7.37 (m, 1H, Ar-H), 7.20-7.13 (m, 3H, Ar-H), 7.06-7.00 (m, 2H, Ar-H), 6.68-6.60 (m, 2H, Ar-H), 5.08 (q, 1H, CH), 3.15-3.01(m, 2H, NCH_2C), 2.79-2.74 (m, 2H, $NCCH_2C$), 1.90-1.85 (m, 2H, $NCCCH_2$), 1.56 (d, 3H, J = 6.96 Hz, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): 145.7, 145.4, 144.0, 129.6, 128.4, 127.7, 127.3, 126.4, 125.7, 123.1, 122.9, 116.0, 111.0 (Ar-C), 54.6 (CH), 42.8, 28.6, 22.4 (CH_2), 16.2 (CH_3). HR MS (ESI+): Found 316.0703 $[M+H]^+$, calcd. for $C_{17}H_{19}BrN^+$: 316.0701.

1-(1-(p-tolyl)ethyl)-1,2,3,4-tetrahydroquinoline (6e). ^1H NMR (400 MHz, $CDCl_3$): δ 7.26-7.24 (m, 2H, Ar-H), 7.17-7.15 (m, 2H, Ar-H), 7.07-6.99 (m, 2H, Ar-H), 6.74-6.72 (m, 1H, Ar-H), 6.61-6.58 (m, 1H, Ar-H), 5.13 (q, 1H, CH), 3.15-3.02 (m, 2H, NCH_2C), 2.77-2.74 (m, 2H, $NCCH_2C$), 2.36 (s, 3H, $Ar\text{-}CH_3$), 1.88-1.84 (m, 2H, $NCCCH_2$), 1.58 (d, 3H, *J* = 6.96 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 145.7, 139.7, 136.3, 129.3, 129.1, 127.2, 127.0, 122.9, 115.4, 110.7 (Ar-C), 54.4 (CH), 42.5, 28.6, 22.3 (CH_2) 21.1 ($ArCH_3$), 16.0 (CH_3). HR MS (ESI+): Found 252.1749 $[M+H]^+$, calcd. for $C_{18}H_{22}N^+$: 252.1752.

1-(1-(4-fluorophenyl)ethyl)-1,2,3,4-tetrahydroquinoline (6f). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.27(m, 2H, Ar-H), 7.10-6.90 (m, 4H, Ar-H), 6.69-6.68 (m, 1H, Ar-H), 6.62-6.57 (m, 1H, Ar-H) , 5.09 (q, 1H, CH), 3.12-2.95 (m, 2H, NCH2C), 2.79-2.73 (m, 2H, NCCH2C),1.88-1.80 (m, 2H, NCCCH2), 1.56 (d, 3H, *J* = 6.96 Hz, CH_3).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): 145.5, 142.2, 131.1, 129.8, 129.5, 128.5, 128.4, 128.3, 127.2, 127.1, 125.4, 123.0, 122.2, 122.0, 115.7, 115.4, 115.3, 115.1, 110.7, 110.6 (Ar-C), 54.2 (CH), 42.5, 28.5, 22.3(CH_2), 16.1 (CH_3). HR MS (ESI+): Found 256.1503 $[M+H]^+$, calcd. for $C_{17}H_{19}FN^+$: 256.1502.

1-(1-(4-chlorophenyl)ethyl)-1,2,3,4-tetrahydroquinoline (6f). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.33 (m, 4H, Ar-H), 7.08-7.02 (m, 2H, Ar-H), 6.73-6.71 (m,1H, Ar-H), 6.67-6.63 (m, 1H, Ar-H), 5.14 (q, 1H, CH), 3.19-3.03(m, 2H, NCH_2C), 2.86-2.80 (m, 2H, $NCCH_2C$), 1.95-1.88 (m, 2H, $NCCCH_2$), 1.62 (d, 3H, J = 6.96 Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): 145.4, 141.4, 132.5, 129.4, 128.6, 128.4, 127.2, 123.0, 115.8, 110.7 (Ar-C), 54.3 (CH), 42.6, 28.5, 22.3 (CH_2), 16.0 (CH_3). HR MS (ESI+): Found 272.1206 $[M+H]^+$, calcd. for $C_{17}H_{19}ClN^+$: 272.1206.

1-(1-(4-bromophenyl)ethyl)-1,2,3,4-tetrahydroquinoline (6h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.49 (m, 1H, Ar-H), 7.40-7.39 (m, 1H, Ar-H), 7.28-7.26 (m, 2H, Ar-H), 7.09-7.04 (m, 2H, Ar-H), 6.75-6.70 (m, 2H, Ar-H), 6.66-6.62 (m, 2H, Ar-H), 5.22-5.09 (m, 1H, CH), 3.19-3.03 (m, 2H, NCH_2C), 2.88-2.79 (m, 2H, $NCCH_2C$), 1.94-1.90 (m, 2H, $NCCCH_2$), 1.63 (d, 3H, J = 6.96 Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): 157.8, 141.3, 136.2, 135.9, 128.6, 127.5, 127.1, 120.6, 119.9, 118.9, 115.1 (Ar-C), 149.2, 102.3 (CH_2), 45.7, 27.7, 22.5 (CH_2). HR MS (ESI+): Found 316.0704 $[M+H]^+$, calcd. for $C_{17}H_{19}BrN^+$: 316.0701.

1-(1-(4-methoxyphenyl)ethyl)-1,2,3,4-tetrahydroquinoline (6i). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.24 (m, 3H, Ar-H), δ 7.05-7.01 (m, 1H, Ar-H), δ 7.26-7.24 (m, 3H, Ar-H), 6.98-6.96 (m, 1H, Ar-H), 6.87-6.85 (m, 2H, Ar-H), 6.73-6.71 (m, 1H, Ar-

H), 6.59- 6.55 (m, 1H, Ar-H), 5.09 (q, 1H, CH), 3.79 (s, 3H, OCH_3), 3.08-2.96 (m, 2H, NCH_2C), 2.78-2.70 (m, 2H, $NCCH_2C$), 1.88-1.78 (m, 2H, $NCCCH_2$), 1.54 (d, 3H, J = 6.96 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 158.4, 145.7, 134.7, 129.3, 128.1, 127.1, 122.9, 115.4, 113.7, 110.7 (Ar-C), 55.3 (OCH_3), 54.0 (CH), 42.3, 28.6, 22.3 (CH_2), 15.3 (CH_3). HR MS (ESI+): Found 268.1704 $[M+H]^+$, calcd. for $C_{18}H_{22}N^+O$: 268.1701.

1-(1-(3,5-bis(trifluoromethyl)phenyl)ethyl)-1,2,3,4-tetrahydroquinoline (6j). ^1H NMR (400 MHz, $CDCl_3$): δ 7.80-7.78 (m, 2H, Ar-H), 7.22-7.20 (m, 1H, Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.67-6.64 (m, 2H, Ar-H), 5.19 (q, 1H, CH), 3.16-2.91 (m, 1H, NCH_2C), 2.85-2.75 (m, 2H, $NCCH_2C$), 1.90-1.87 (m, 2H, $NCCCH_2$), 1.63 (d, 3H, J = 6.96 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 146.6, 146.1, 145.0, 129.8, 129.7, 127.6, 127.3, 127.1, 123.5, 121.0, 116.8, 110.8 (Ar-C), 54.6 (CH), 42.8, 28.3, 22.2 (CH_2), 15.6 (CH_3). HR MS (ESI+): Found 374.1346 $[M+H]^+$, calcd. for $C_{19}H_{18}F_6N^+$: 374.1343.

1-(1-(pyridin-2-yl)vinyl)-1,2,3,4-tetrahydroquinoline (6k). ^1H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H, Ar-H), 8.21 (d, 1H, J = 13.52 Hz CH_2), 7.49-7.45 (m, 1H, Ar-H), 7.16 (d, 1H, J = 3.68 Hz Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.87-6.83 (m, 2H, Ar-H), 5.72 (d, 1H, J = 13.48 Hz CH_2), 3.58-3.55 (m, 2H, NCH_2C), 2.71-2.68 (m, 2H, $NCCH_2C$), 2.05-1.96 (m, 2H, $NCCCH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 147.8, 129.4, 128.4, 126.4, 116.8, 113.2 (Ar-C), 48.5 (CH), 37.1 ($CHCH_2CH_2$), 28.5 ($CHCH_2CH_2$), 22.9 ($CHCH_2CH_2$), 20.9 ($CHCH_2CH_2$), 14.3 (CH_3). HR MS (ESI+): Found 237.1390 $[M+H]^+$, calcd. for $C_{16}H_{17}N_2^+$: 237.1392.

1-(1-(thiophen-2-yl)ethyl)-1,2,3,4-tetrahydroquinoline (6l). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.52(m, 1H, Ar-H), 7.43-7.41 (m, 1H, Ar-H), 7.33-7.14 (m, 2H, Ar-H), 6.84-6.82 (m, 2H, Ar-H), 6.67-6.65 (m, 1H, Ar-H), 5.36 (m, 1H, CH), 3.16-3.13 (m, 2H, NCH_2C), 2.80-2.75(s, 2H, $NCCH_2C$), 1.91-1.87 (m, 2H, $NCCCH_2$), 1.65 (d, 3H, J = 6.96 Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): 146.6, 131.1, 129.8, 129.4, 128.3, 127.6, 127.1, 126.6, 125.9, 124.8, 124.1, 116.2, 111.1 (Ar-C), 51.8 (CH), 42.2, 28.4, 22.2 (CH_2), 16.9 (CH_3). HR MS (ESI+): Found 244.1157 $[M+H]^+$, calcd. for $C_{15}H_{18}NS^+$: 244.1160.

1-(1-phenylpropan-2-yl)-1,2,3,4-tetrahydroquinoline (6m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 -7.25(m, 2H, Ar-H), 7.21-7.16 (m, 4H, Ar-H), 7.07-7.03 (m, 1H, Ar-H), 6.95-6.93 (m, 1H, Ar-H), 6.76-6.74 (m, 1H, Ar-H), 6.60-6.58 (m, 1H, Ar-H), 4.23-4.14 (m, 1H, CH), 3.24-3.17 (m, 2H, NCH_2C), 3.00-2.97 (m, 1H, $ArCH_2$), 2.75-2.71(m, 2H, $NCCH_2C$), 2.73-2.71 (m, 1H, $ArCH_2$), 1.93-1.87 (m, 2H, $NCCCH_2$), 1.18 (d, 3H, J = 6.60 Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): 145.5, 139.8, 129.4, 129.1, 128.4, 127.1, 126.1, 123.3, 115.4, 110.7 (Ar-C), 53.3 (CH), 41.2, 39.3, 28.5, 22.4 (CH_2), 16.4(CH_3). HR MS (ESI+): Found 252.1758 $[M+H]^+$, calcd. for $C_{18}H_{22}N^+$: 252.1752.

1-(hexan-2-yl)-1,2,3,4-tetrahydroquinoline (6n). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05-7.02 (m, 1H, Ar-H), 6.95-6.93 (m, 1H, Ar-H), 6.68-6.66(m, 1H, Ar-H), 6.54-6.51 (m, 1H, Ar-H), 3.93-3.84 (m, 1H, CH), 3.12-3.09 (m, 2H, NCH_2C), 2.73-2.71 (m, 2H, $NCCH_2C$), 1.90-1.88 (m, 2H, $NCCCH_2$), 1.63-1.58 (m, 2H CH_2), 1.45-1.39 (m, 2H CH_2), 1.29-1.23 (m, 2H CH_2),1.11 (d, 3H, J = 6.56Hz, CH_3), 0.90-0.87 (m, 3H

CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 146.0, 129.3, 127.0, 122.9, 114.9, 110.5 (Ar-C), 51.2 (CH), 40.3, 33.7, 29.1, 28.6, 22.8, 22.4 (CH_2), 16.4, 14.2(CH_3). HR MS (ESI+): Found 218.1904 $[M+H]^+$, calcd. for $C_{15}H_{24}N^+$: 218.1909.

1-(1-phenylethyl)indoline (7d). ^1H NMR (400 MHz, $CDCl_3$): δ 7.44-7.43 (m, 2H, Ar-H), 7.38-7.34 (m, 2H, Ar-H), 7.29-7.28 (m, 1H, Ar-H), 7.08-7.07 (m, 1H, Ar-H), 6.99-6.98 (m, 1H, Ar-H), 6.62-6.60 (m, 1H, Ar-H), 6.39-6.37 (m, 1H, Ar-H), 4.75 (q, 1H, CH), 3.41-3.32 (m, 2H, CH_2), 2.99-2.95 (m, 2H, CH_2), 1.56 (d, 3H, J = 6.96 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 146.6, 131.1, 129.8, 128.4, 127.6, 127.1, 126.9, 124.4, 116.9, 107.2 (Ar-C), 54.6 (CH), 48.0, 28.2 (CH_2), 17.8 (CH_3). HR MS (ESI+): Found 224.1940 $[M+H]^+$, calcd. for $C_{16}H_{18}N^+$: 224.1939.

4-(1-phenylethyl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (7e). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.35 (m, 4H, Ar-H), 7.33-7.31 (m, 1H, Ar-H), 6.82-6.80 (m, 2H, Ar-H), 6.64-6.59 (m, 1H, Ar-H), 5.11 (q, 1H, CH), 4.17-4.07 (m, 2H, OCH_2), 3.22-3.00 (m, 2H, NCH_2), 1.55(d, 3H, J = 6.92 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 144.2, 141.8, 135.1, 128.6, 127.2, 121.6, 117.3, 116.5, 112.2 (Ar-C), 64.9 (CH), 54.5, 40.5 (CH_2), 15.0 (CH_3). HR MS (ESI+): Found 240.1381 $[M+H]^+$, calcd. for $C_{16}H_{18}NO^+$: 240.1388.

2-methyl-1-(1-phenylethyl)-1,2,3,4-tetrahydroquinoline (7f). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.34 (m, 1H, Ar-H), 7.37-7.28 (m, 1H, Ar-H), 7.05 (m, 2H, Ar-H), 6.47 (m, 1H, Ar-H), 6.62 (m, 1H, Ar-H), 5.51 (q, 1H, CH), 3.63-3.40 (m, 1H, CH), 2.92-2.69 (m, 2H, CH_2), 1.72-1.65 (d, 3H, J = 7.04 Hz, CH_3), 1.17-1.15 (d, 3H, J = 6.52 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 144.1, 143.9, 143.2, 142.9, 129.5,

128.3, 127.3, 127.1, 126.8, 126.1, 122.4, 121.9, 115.9, 115.3, 114.0, 112.7 (Ar-C), 57.6, 56.1 (CH), 48.6, 47.0 (CH), 27.4, 27.2 (CH_2), 20.1, 19.6 (CH_3),17.4, 16.3 (CH_3). HR MS (ESI+): Found 252.1751 $[M+H]^+$, calcd. for $C_{18}H_{22}N^+$: 252.1752.

2-methyl-1-(1-phenylethyl)indoline (7g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50-7.43 (m, 2H, Ar-H), 7.33-7.30 (m, 2H, Ar-H), 7.25-7.22 (m, 1H, Ar-H), 7.03-6.80 (m, 2H, Ar-H), 6.61-6.55 (s, 1H, Ar-H), 6.36-6.01 (m, 1H, Ar-H), 4.78-4.53 (q, 1H, CH), 4.06-3.78 (m, 1H, CH), 3.28-2.59 (m, 2H, CH_2), 1.63-1.55 (d, 3H, J = 7.12 Hz, CH_3), 1.38-1.04 (d, 3H, J = 6.12 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 151.6, 150.0, 144.1, 143.0, 128.4, 128.3, 127.3, 127.1, 126.9, 126.7, 124.2, 117.1, 116.7, 109.2, 107.1 (Ar-C), 58.2, 56.8, 54.5, 53.5 (CH), 37.9, 37.5 (CH_2), 22.8, 20.9 (CH_3), 16.3, 13.9 (CH_3).

2-phenyl-1-(1-phenylethyl)indoline (7h). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50-7.38 (m, 1H, Ar-H), 7.38-7.34 (m, 2H, Ar-H), 7.32-7.26 (m, 3H, Ar-H), 7.26-7.23 (m, 5H, Ar-H), 7.05-7.01 (m, 2H, Ar-H), 6.96-6.86 (m, 2H, Ar-H), 6.64 (m, 2H, Ar-H), 6.44-6.10 (m, 1H, Ar-H), 4.88-4.72 (t, 1H, CH), 4.88-4.72 (t, 1H, CH), 4.48-4.36 (q, 1H, CH), 3.48-2.94 (m, 2H, CH_2), 1.51-1.45 (d, 3H, J = 6.96 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 115.7, 146.7, 145.0, 143.2, 138.5, 131.1, 128.6, 128.4, 128.3, 128.2, 127.6, 127.5, 127.4, 127.3, 127.1, 127.0, 126.8, 126.6, 126.0, 124.2, 124.0, 117.8, 117.4, 109.6, 108.5 (Ar-C), 68.0, 67.7, 58.6, 57.0 (CH), 40.4, 39.7 (CH_2), 20.6 (CH_3). HR MS (ESI+): Found 238.1590 $[M+H]^+$, calcd. For $C_{17}H_{20}N^+$: 238.1596.

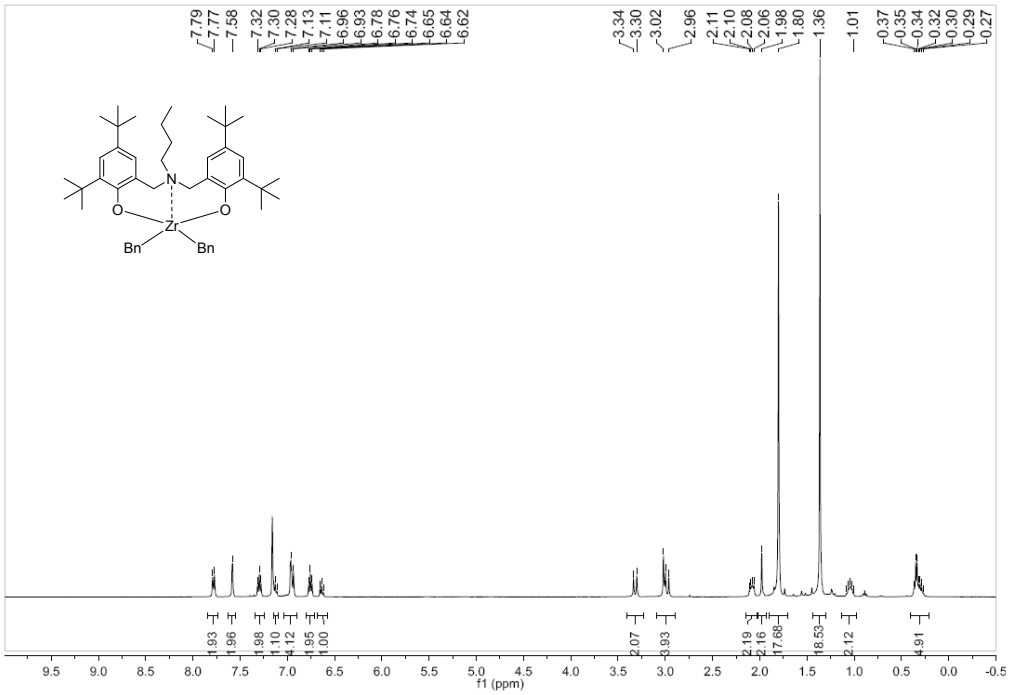
5-methyl-1-(1-phenylethyl)indoline (7i). ^1H NMR (400 MHz, $CDCl_3$): δ 7.42-

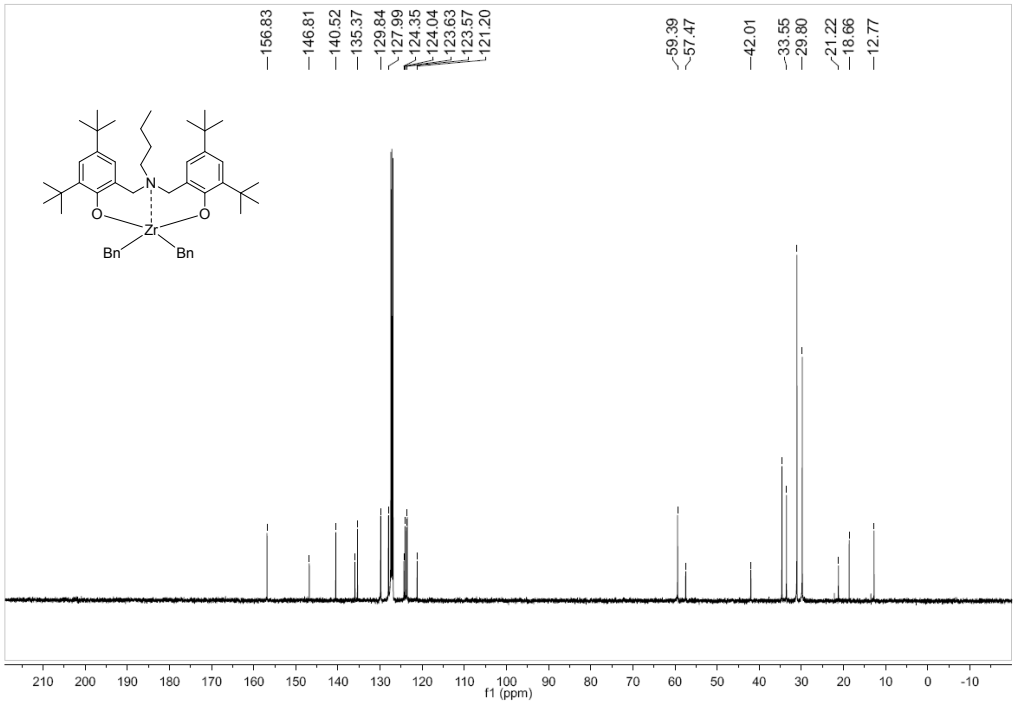
7.40 (m, 2H, Ar-H), 7.32-7.30 (m, 2H, Ar-H), 6.89 (s, 1H, Ar-H), 6.79-6.77 (m, 1H, Ar-H), 6.25-6.23 (m, 1H, Ar-H), 4.64 (q, 1H, CH), 3.32-3.27 (m, 2H, CH_2), 3.92-2.88 (m, 2H, CH_2), 2.22(s, 3H, $ArCH_3$), 1.51 (d, 3H, J = 6.96 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 149.4, 146.7, 143.2, 131.2, 130.6, 129.9, 128.4, 128.0, 127.6, 127.2, 126.9, 126.4, 126.0, 125.4, 117.4 (Ar-C), 55.1 (CH), 48.5, 28.4 (CH_2), 20.7, 16.7(CH_3). HR MS (ESI+): Found 238.1593 $[M+H]^+$, calcd. for $C_{17}H_{20}N^+$: 238.1596.

5-bromo-1-(1-phenylethyl)indoline (7j). ^1H NMR (400 MHz, $CDCl_3$): δ 7.41-7.39 (m, 2H, Ar-H), 7.34-7.31 (m, 3H, Ar-H), 7.04-7.02 (m, 1H, Ar-H), 7.01-7.00 (m, 1H, Ar-H), 6.36-6.34 (m, 1H, Ar-H), 4.71 (q, 1H, CH), 3.34-3.27 (m, 2H, CH_2), 2.98-2.92 (m, 2H, CH_2), 1.52 (d, 3H, J = 6.96 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 142.9, 137.0, 129.5, 128.4, 128.3, 127.2, 127.1, 126.9, 124.4, 117.0, 107.2 (Ar-C), 54.5 (CH), 48.0, 28.2 (CH_2), 16.5 (CH_3). HR MS (ESI+): Found 302.0539 $[M+H]^+$, calcd. for $C_{16}H_{17}BrN^+$: 302.0544.

^{1}H and ^{13}C NMR spectra of complex 3 and hydroamination products

Complex 3





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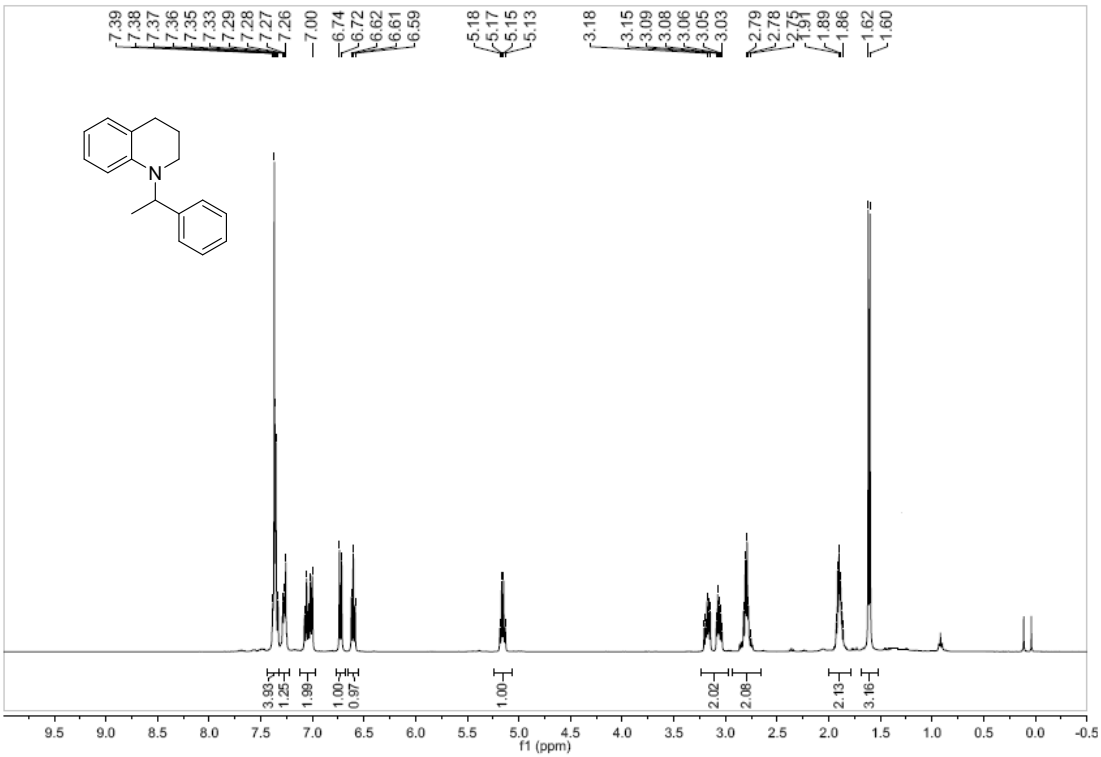
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3.15
3.09
3.08
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3.05
3.03
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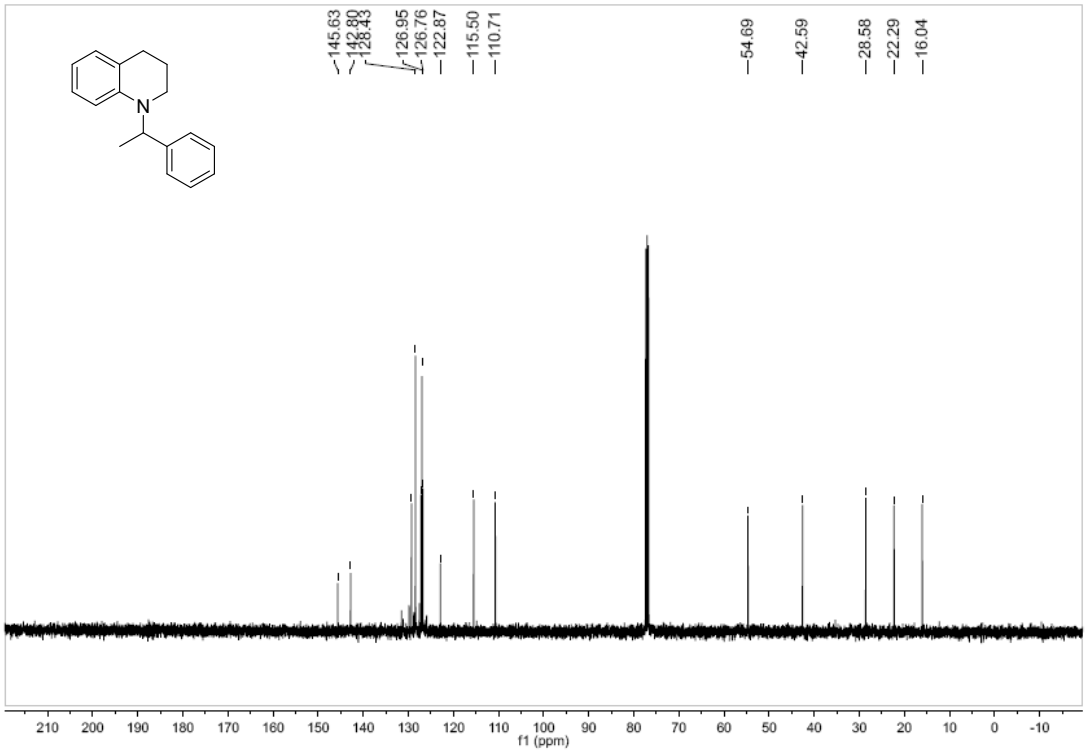
f1 (ppm)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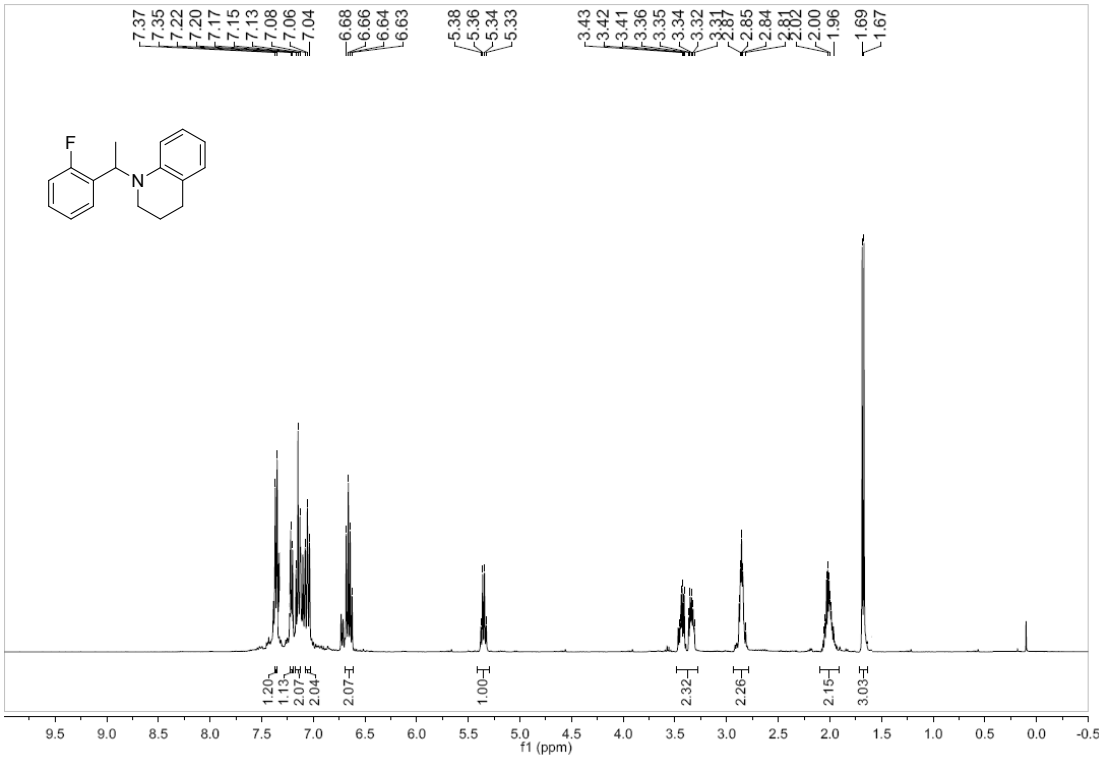
N
f1 (ppm)

6b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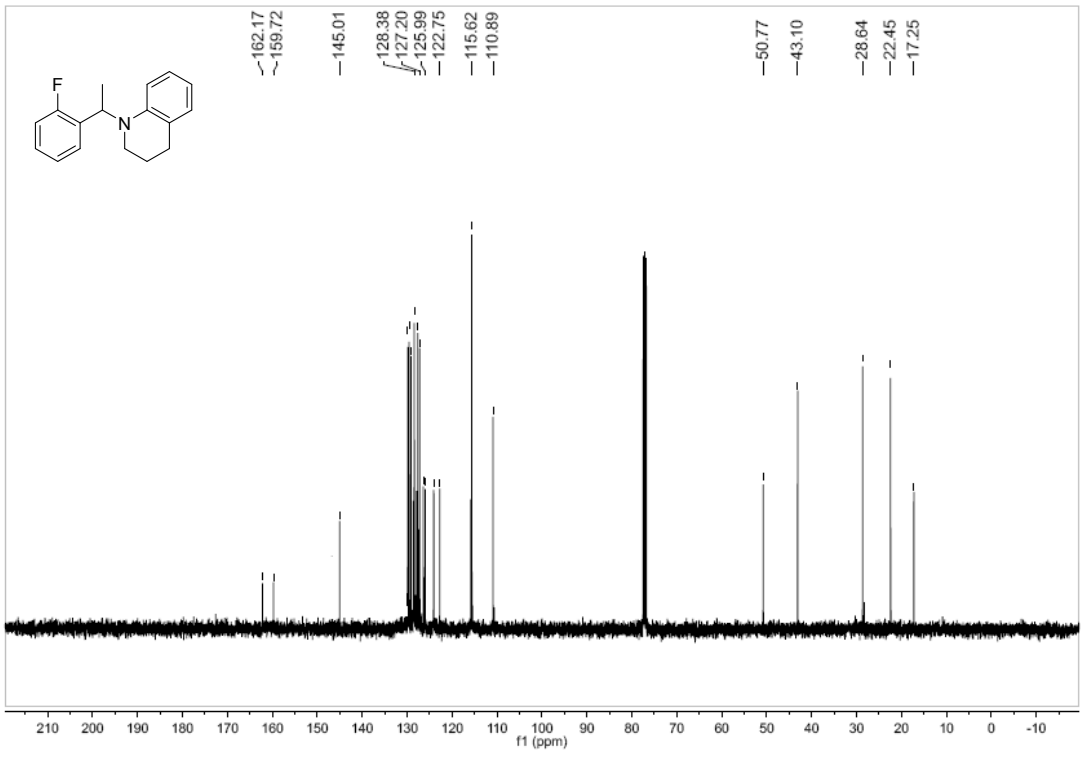
f1 (ppm)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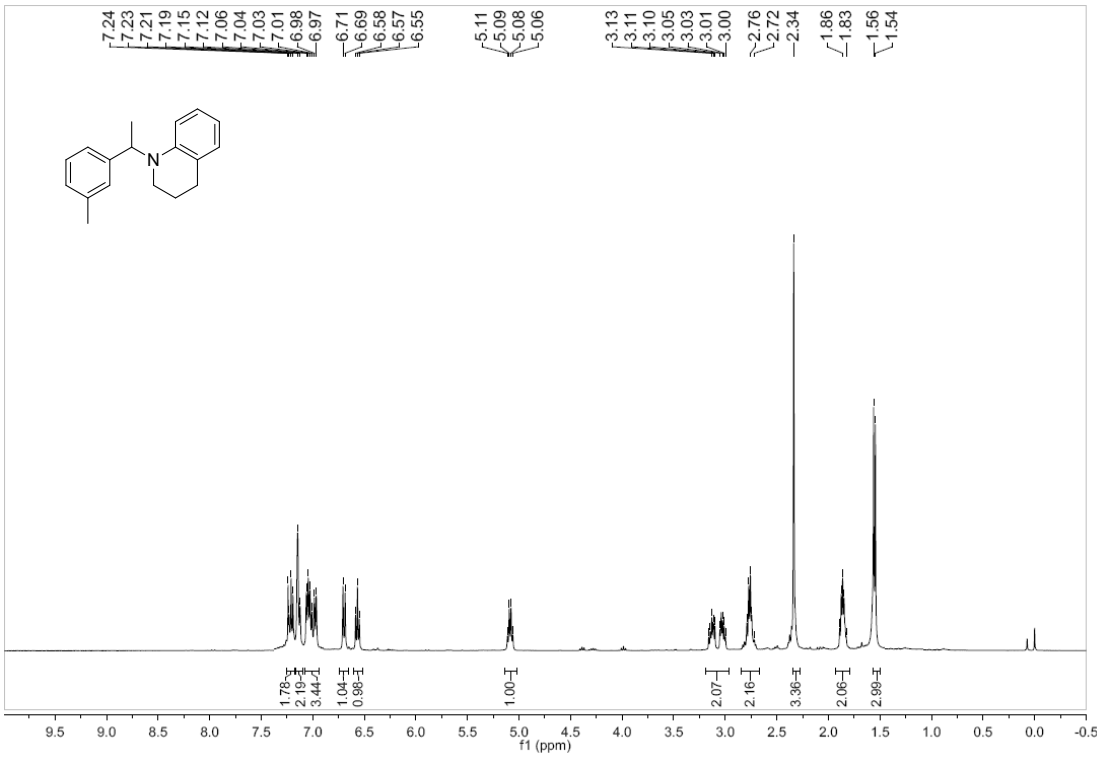
17.25
F
N
f1 (ppm)

6c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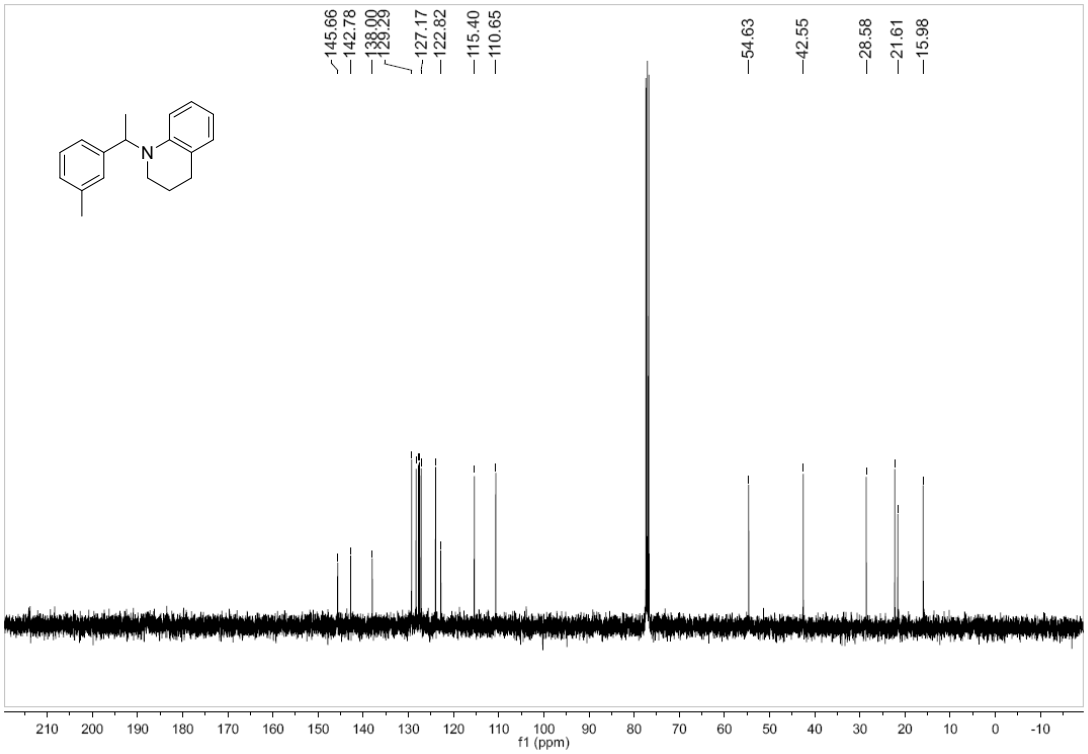
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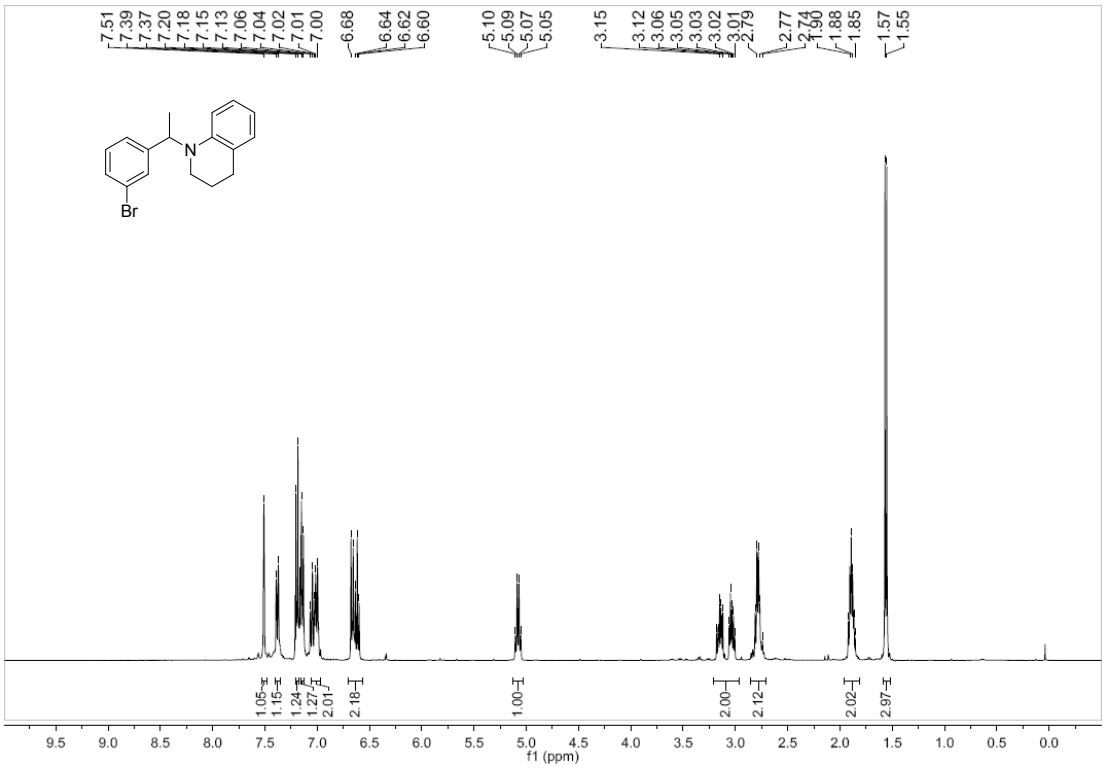
6d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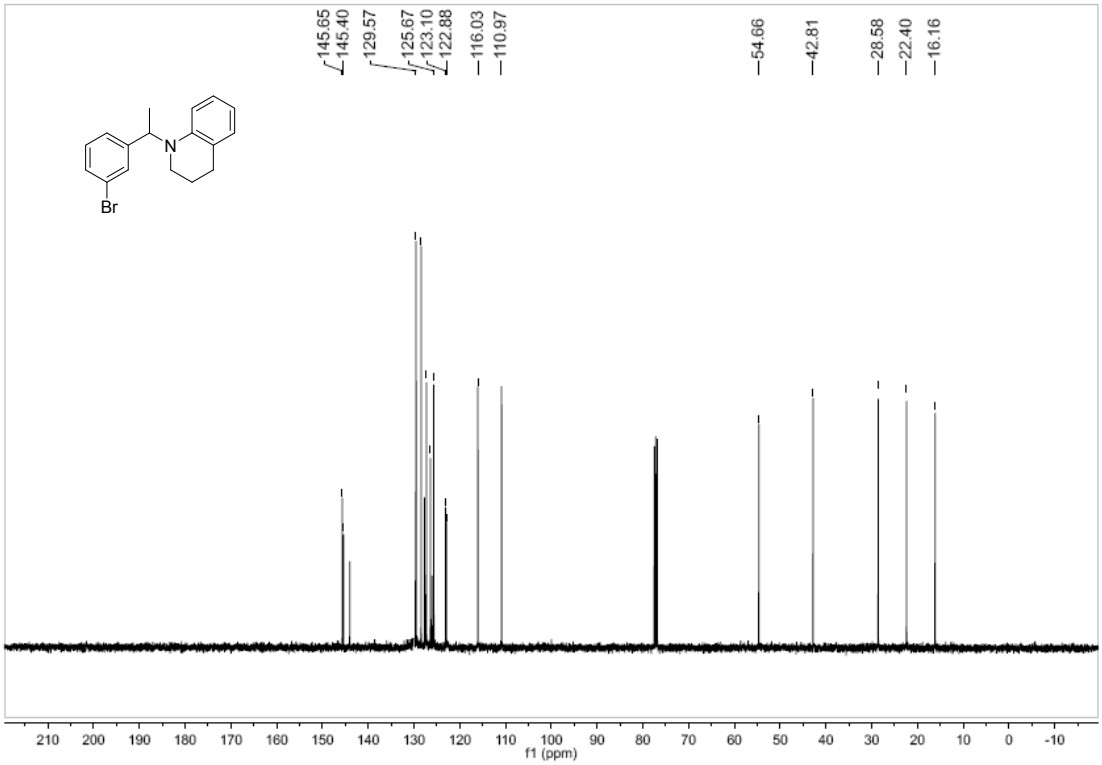
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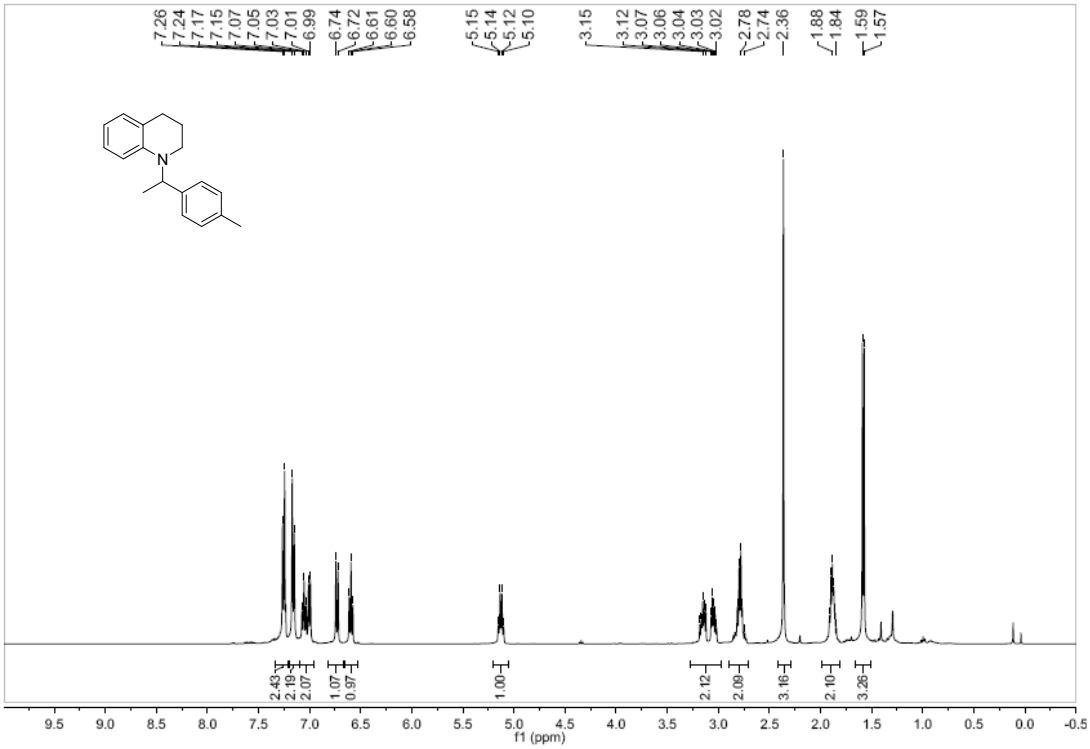
Br
f1 (ppm)

6e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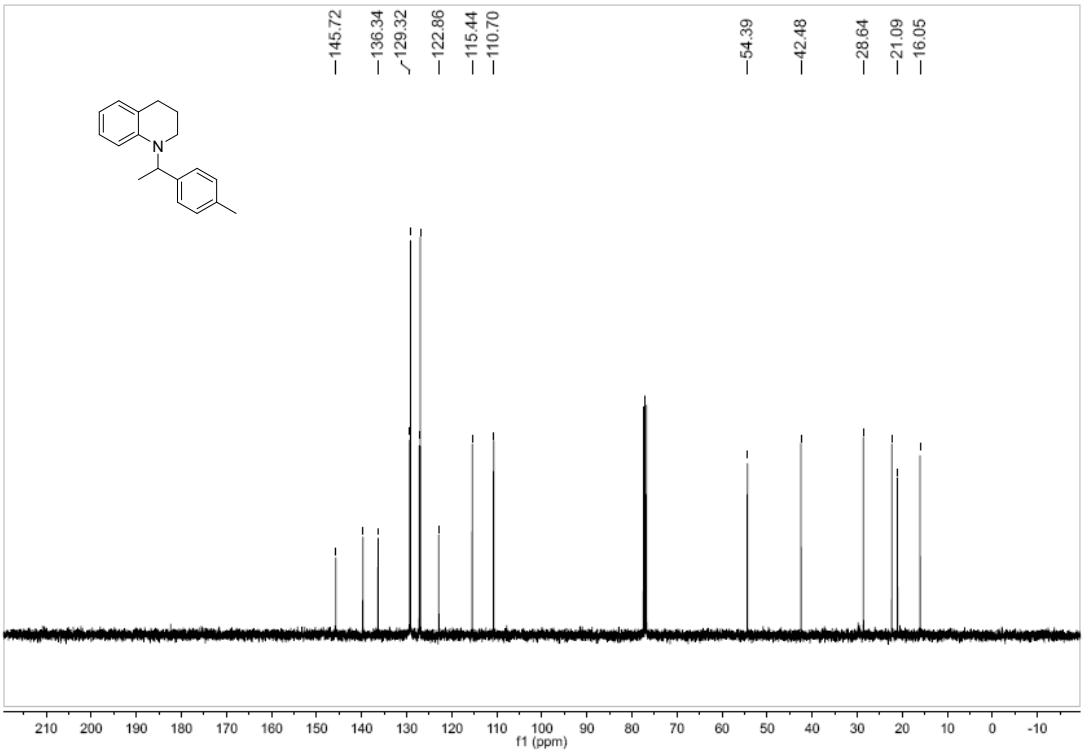
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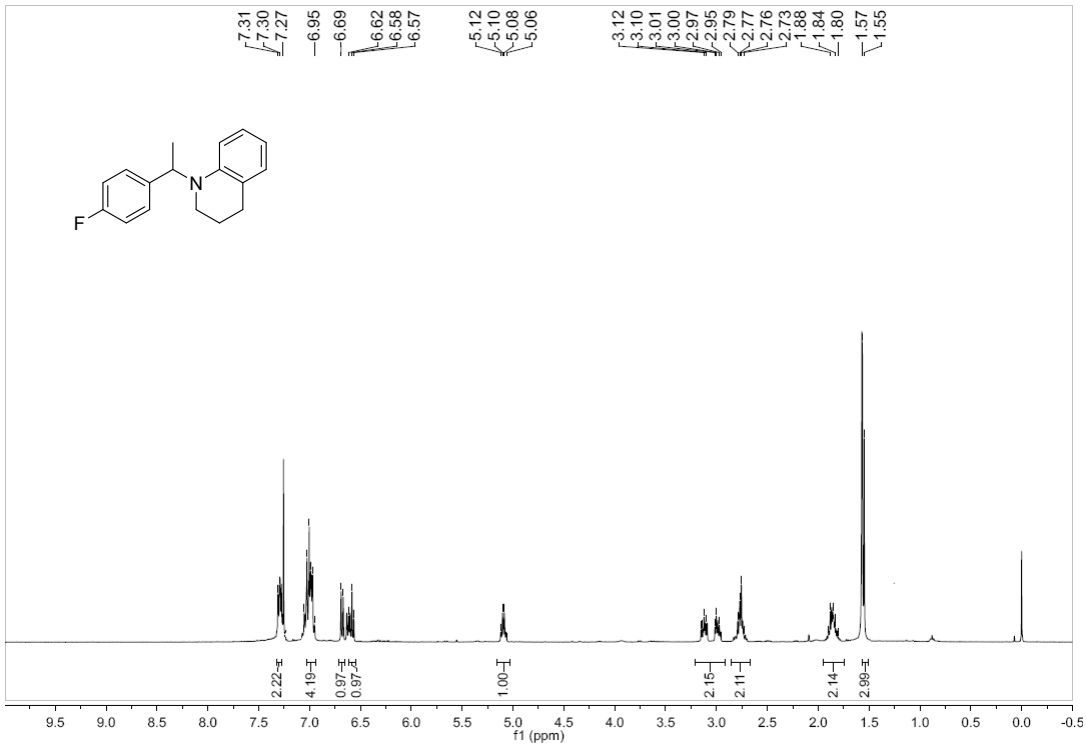
6f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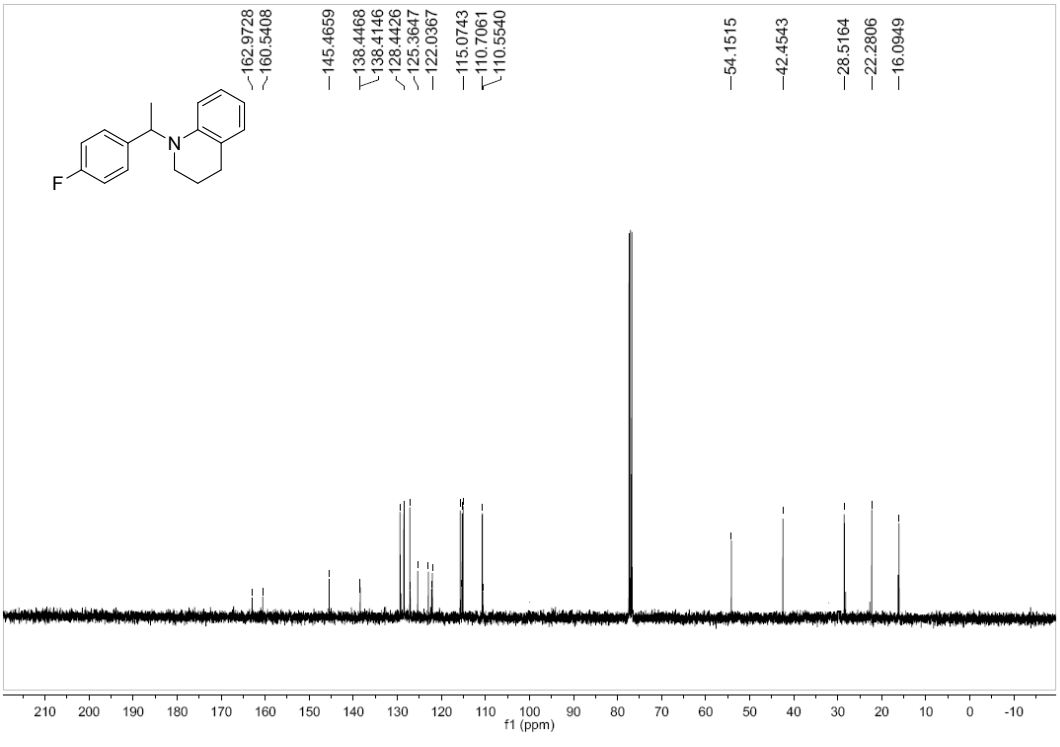
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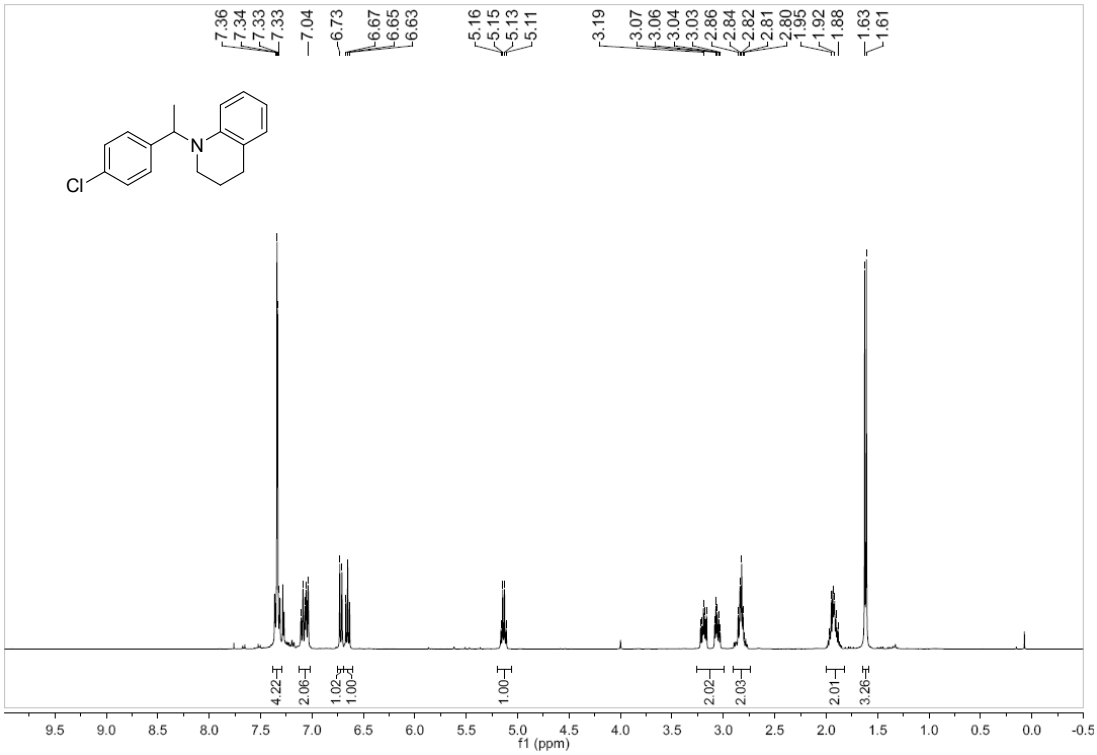
6g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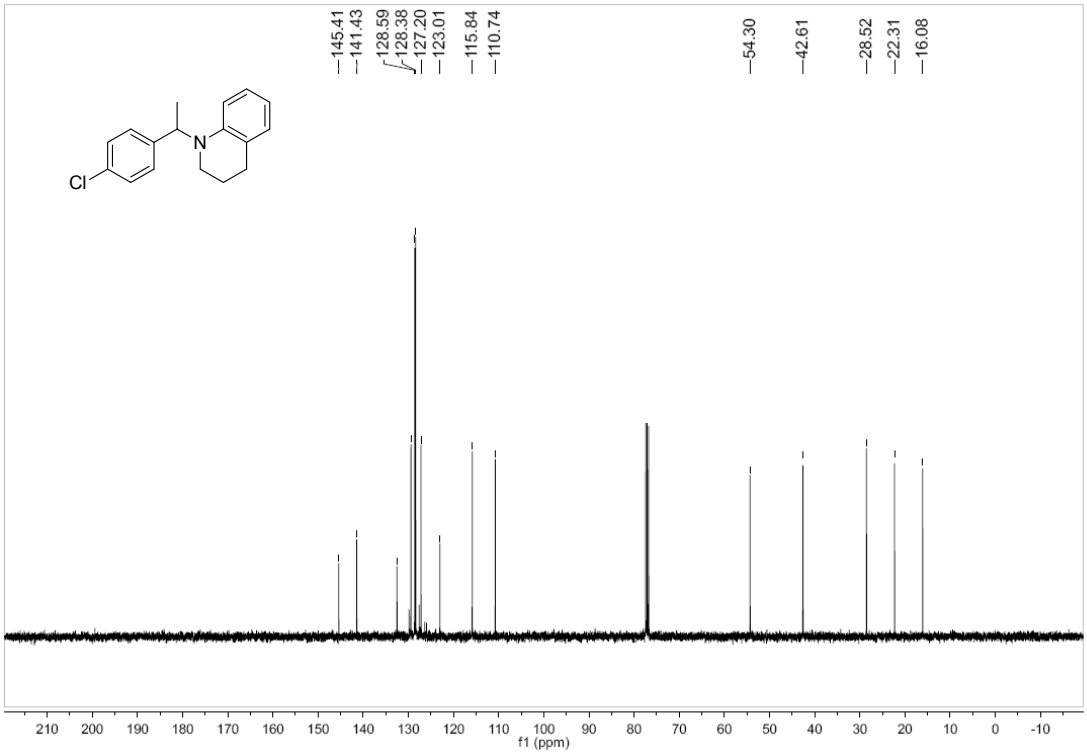
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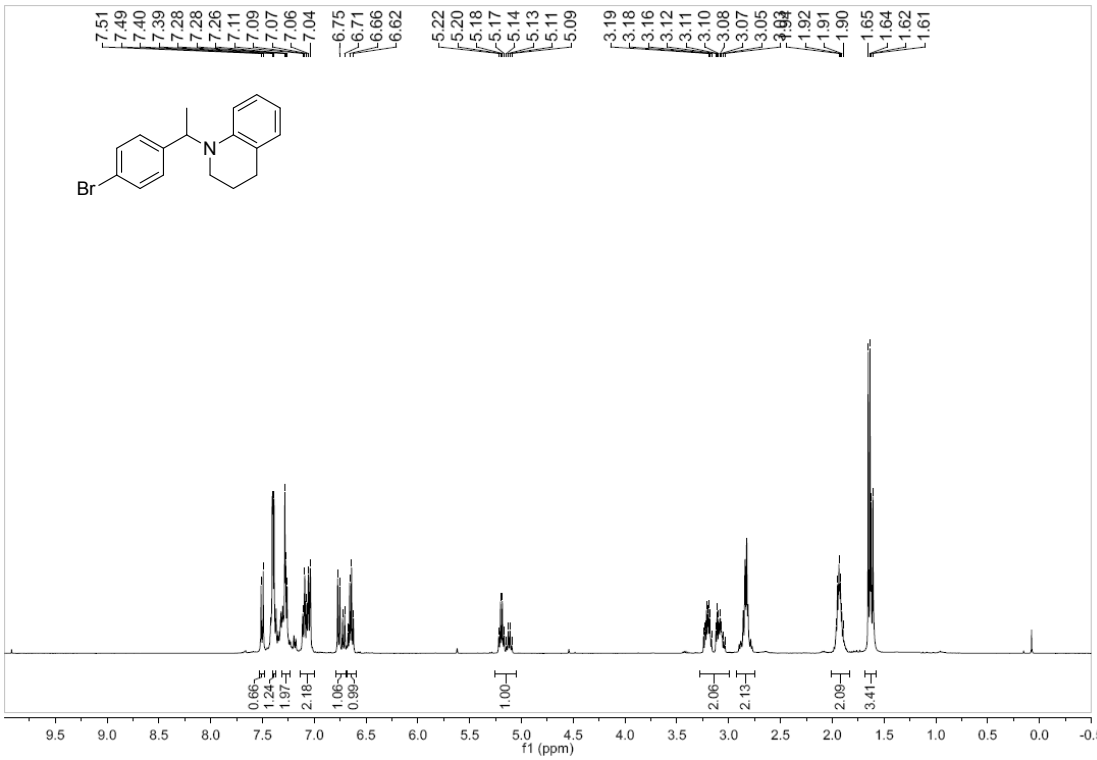
f1 (ppm)

6h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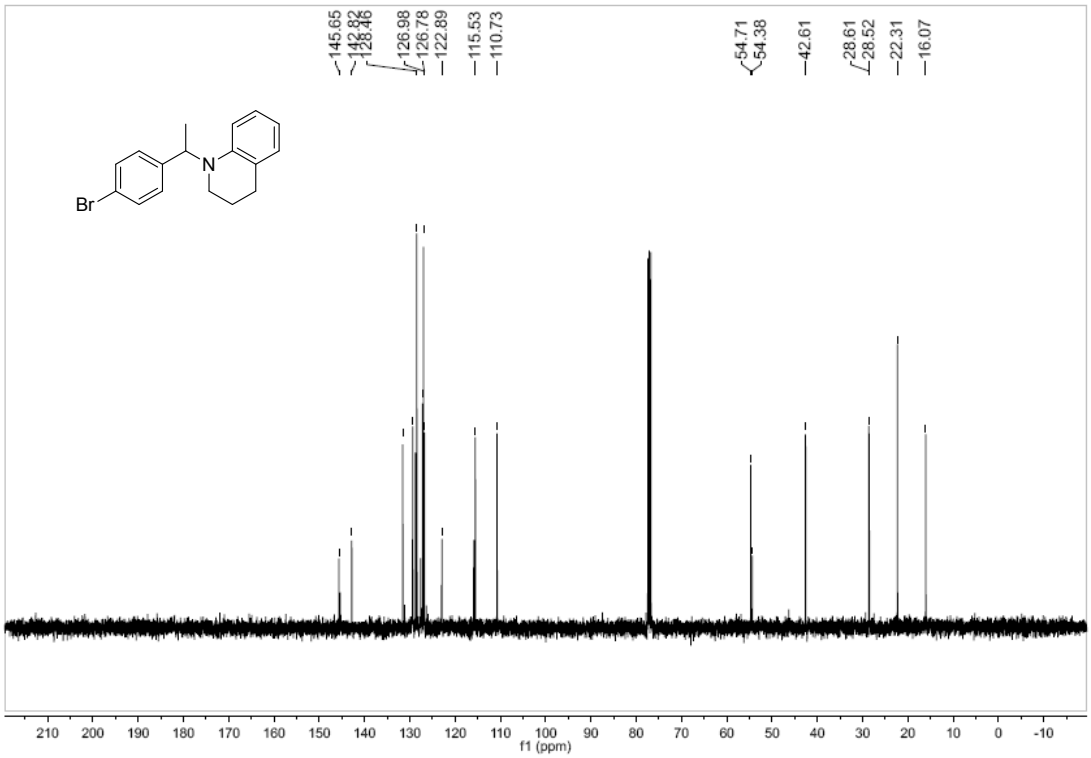
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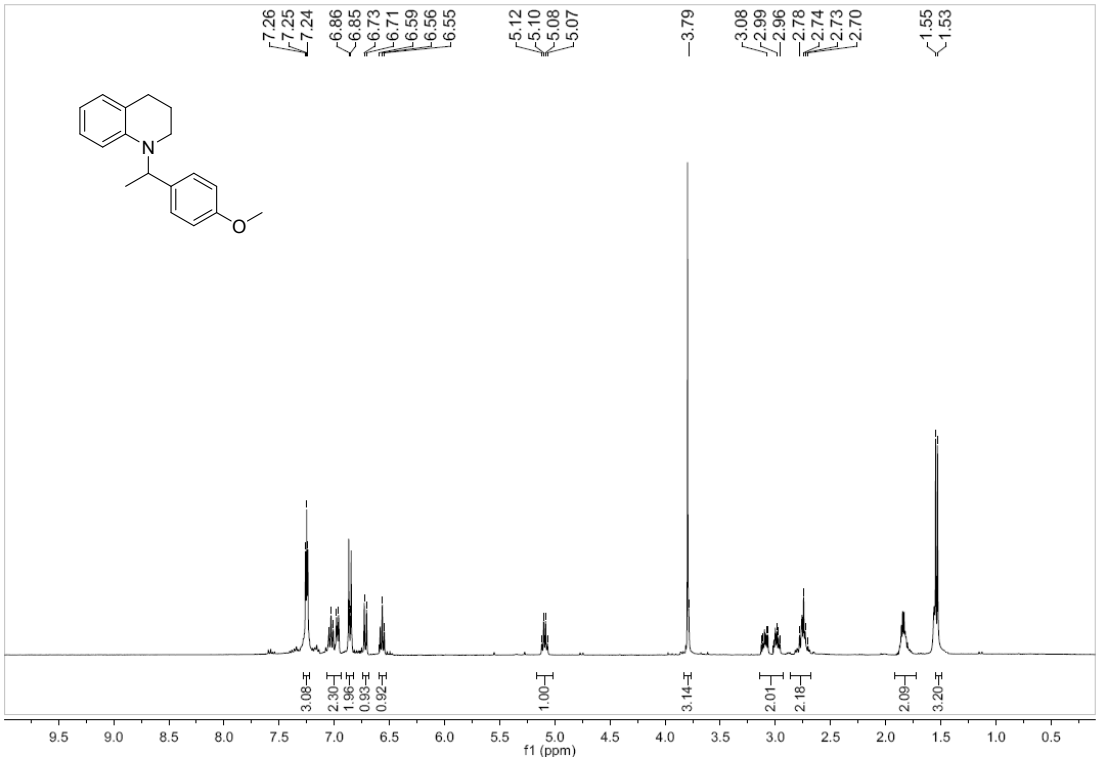
6i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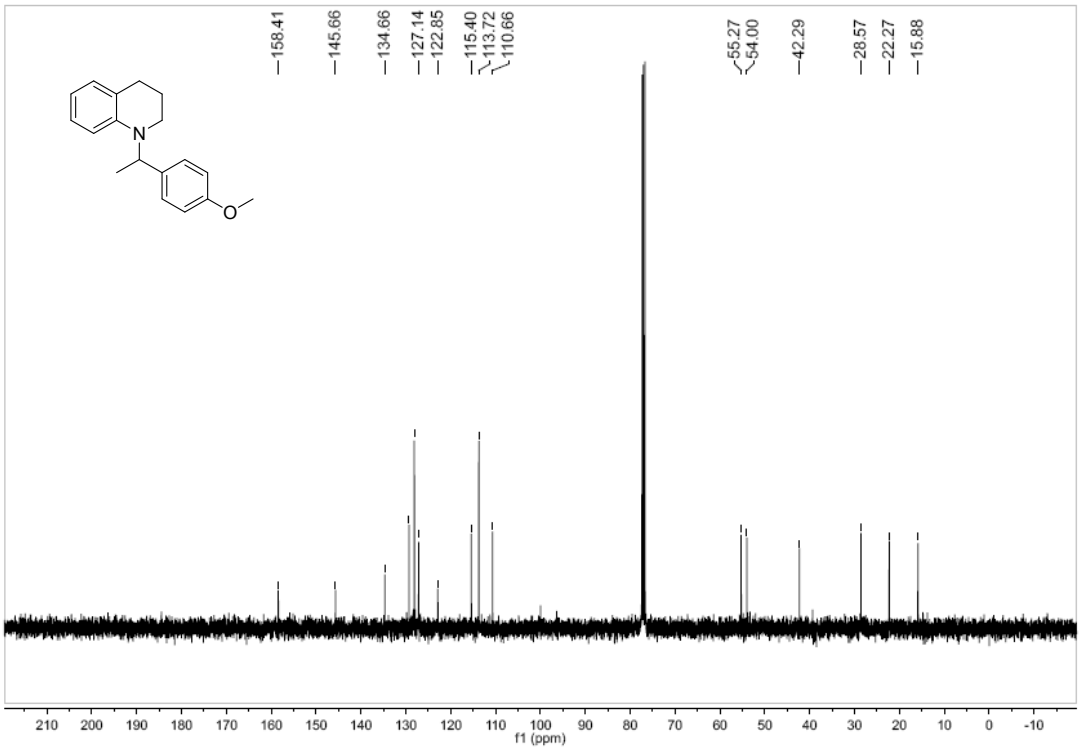
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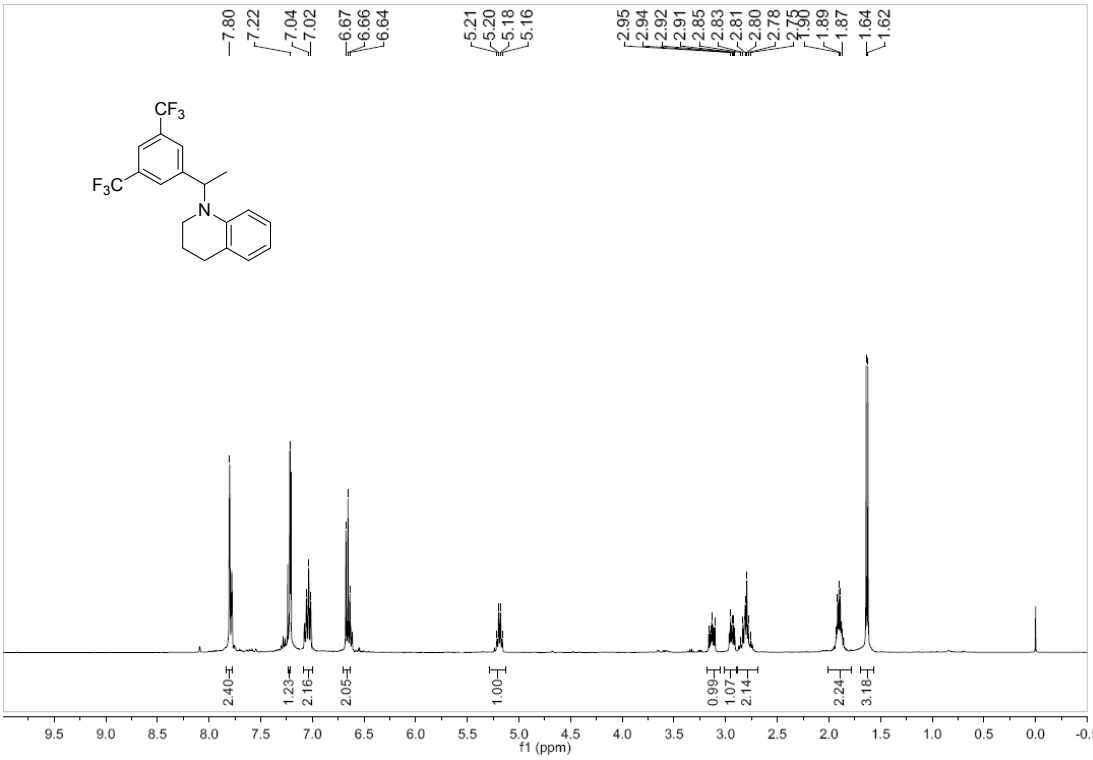
6j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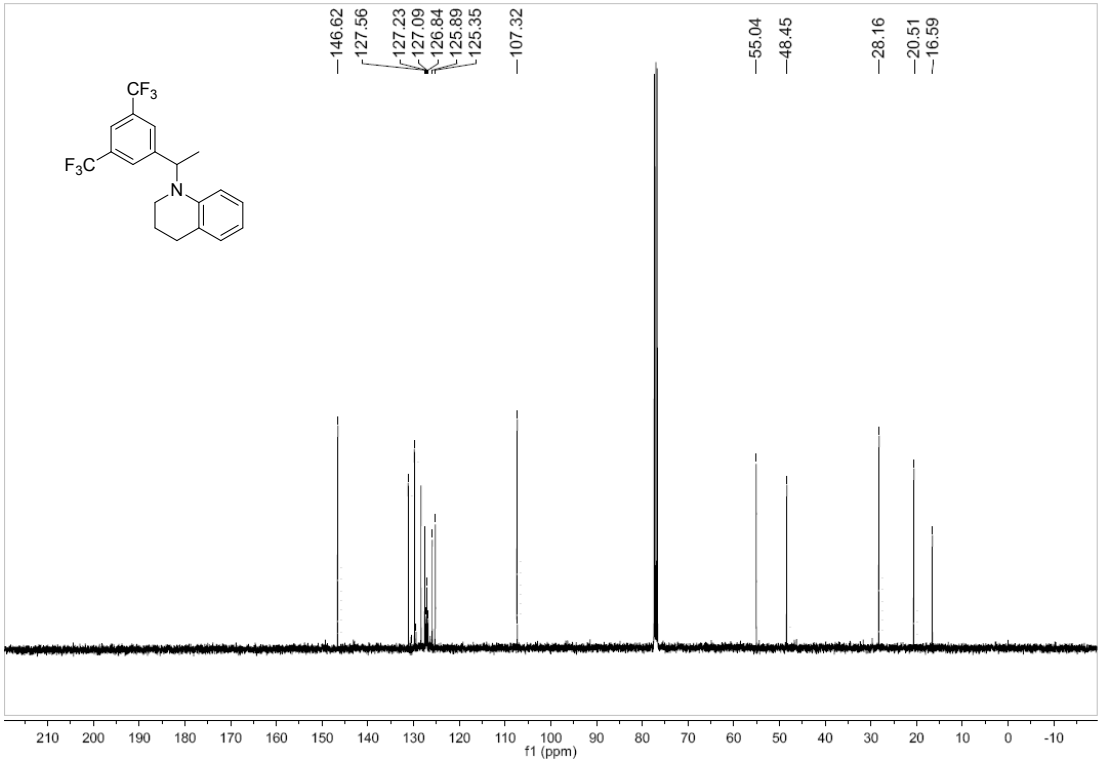
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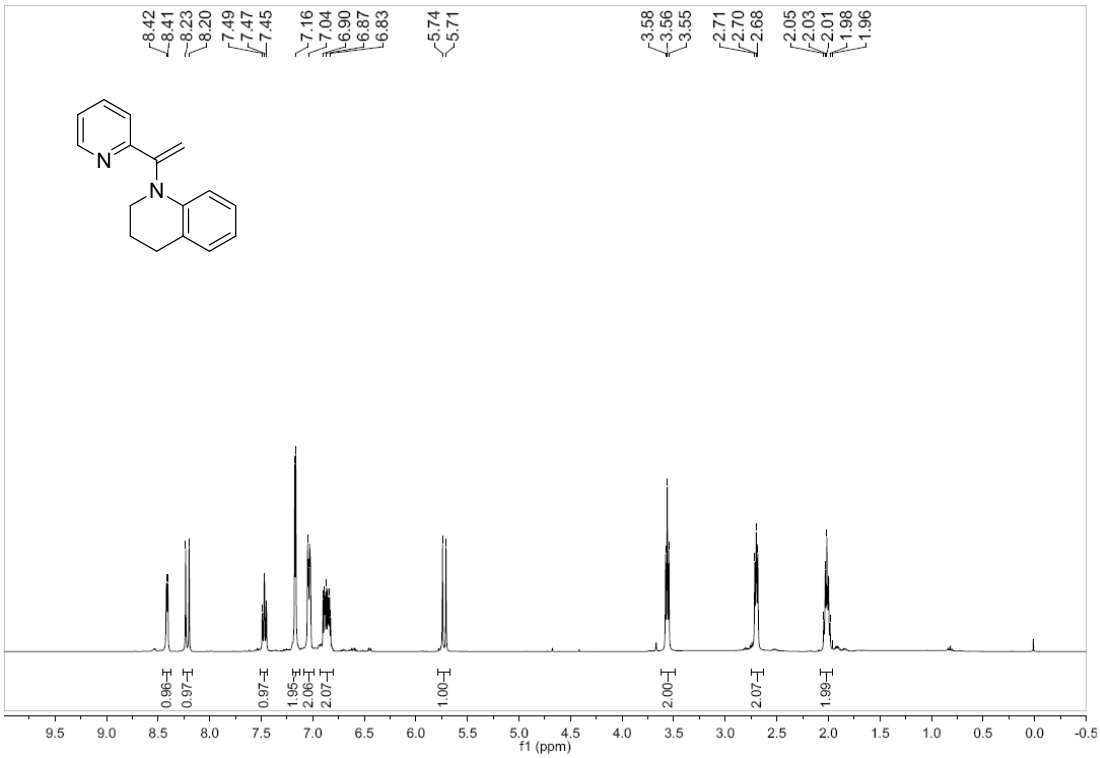
6k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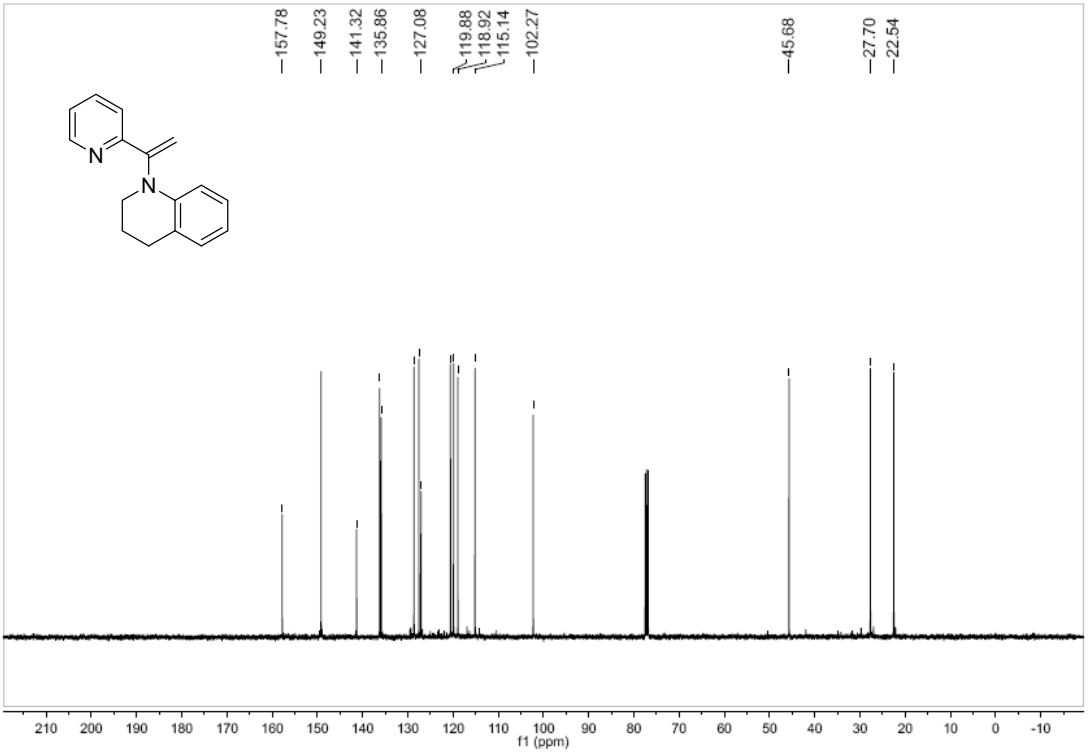
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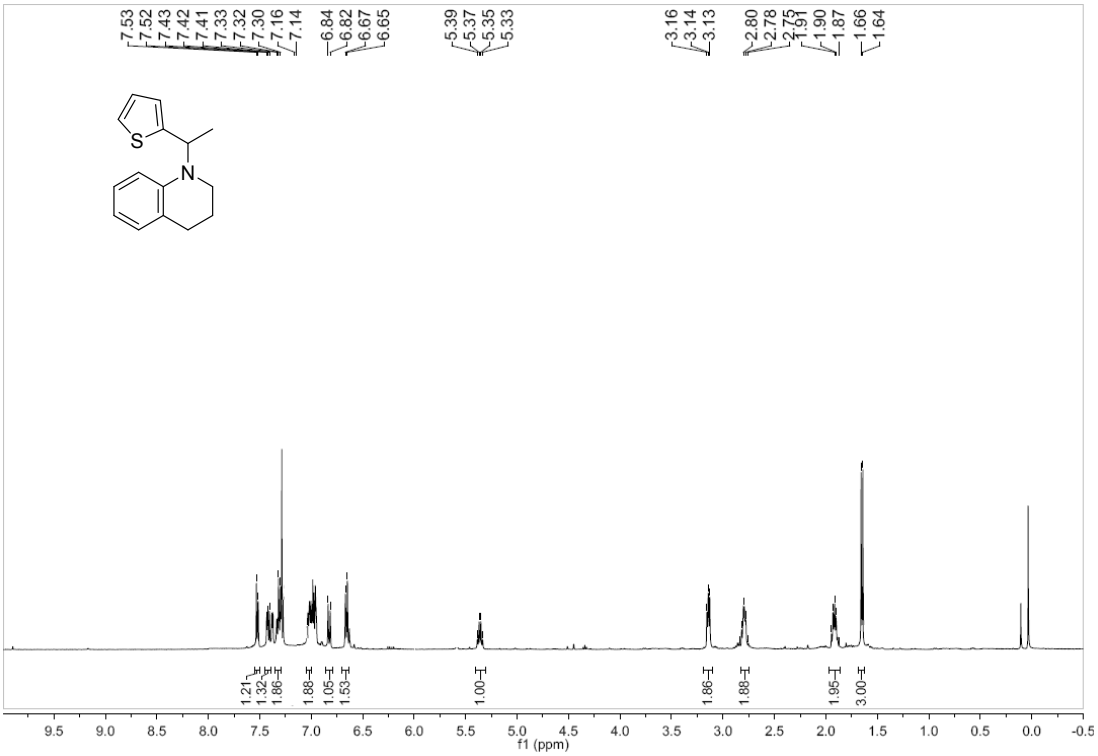
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5.37
5.35
5.33
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3.14
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1.64
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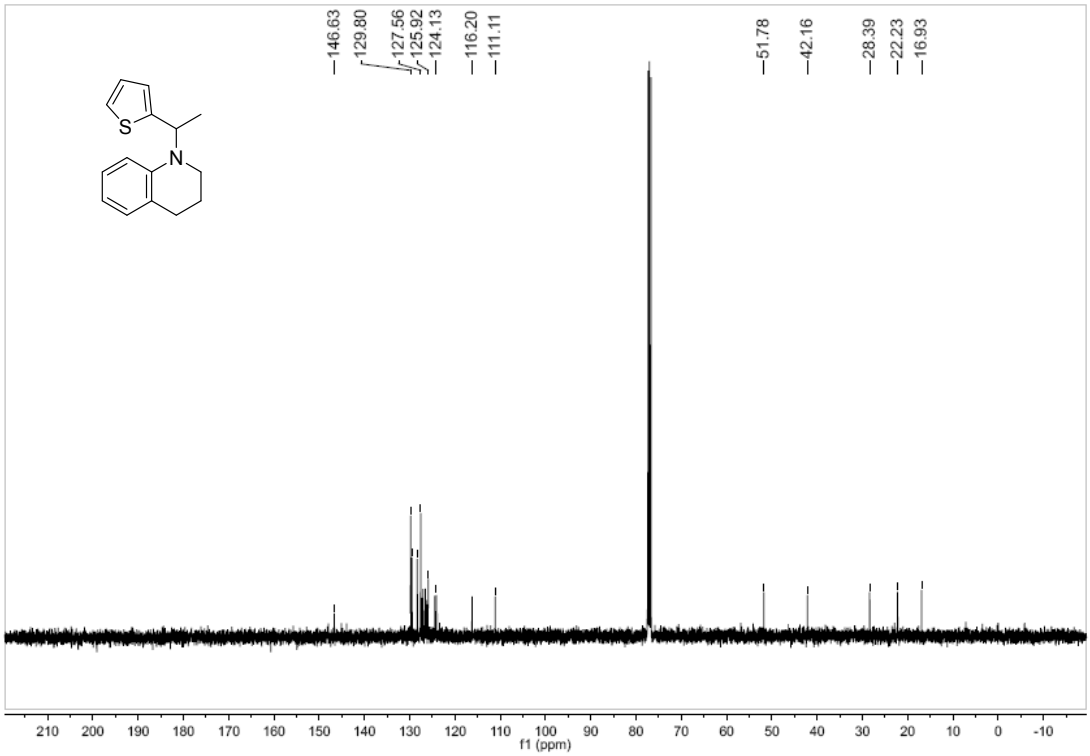
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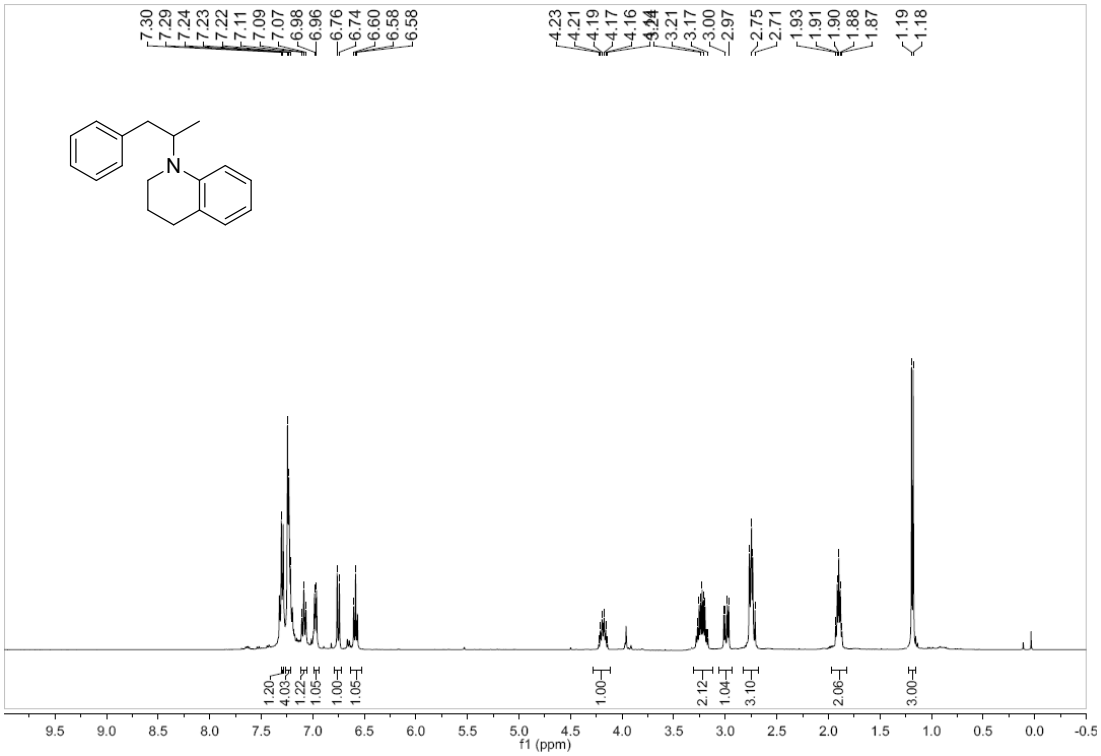
f1 (ppm)

6m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6.58
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4.19
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4.16
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1.93
1.91
1.90
1.88
1.87
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1.18
N
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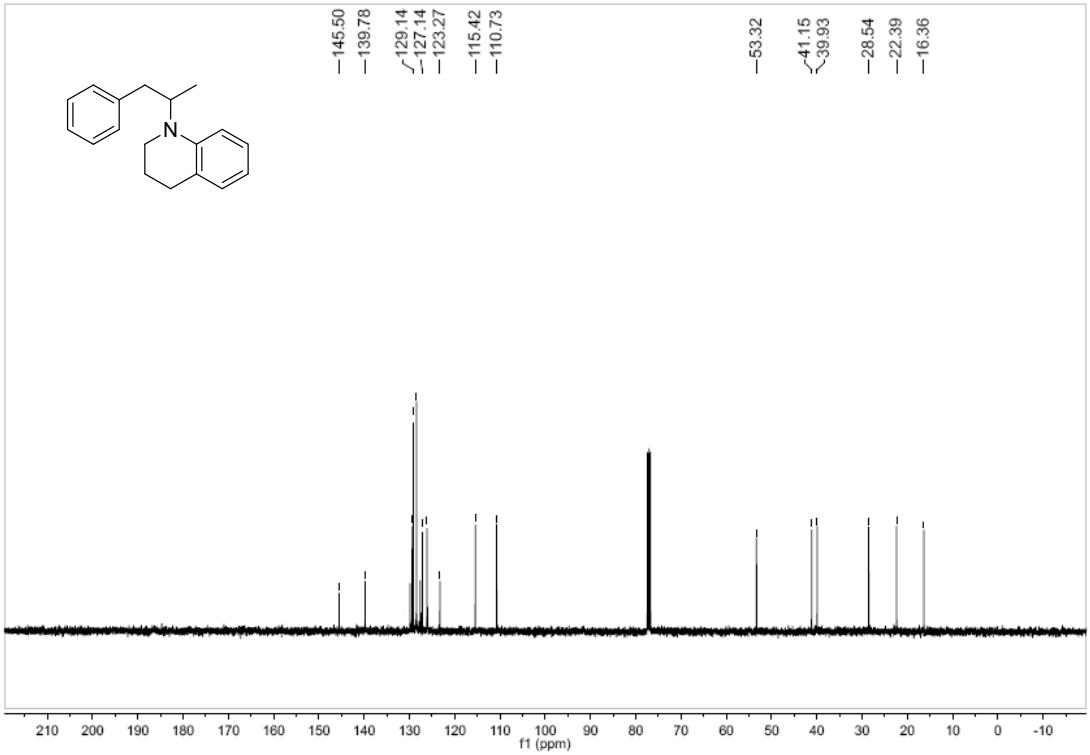
f1 (ppm)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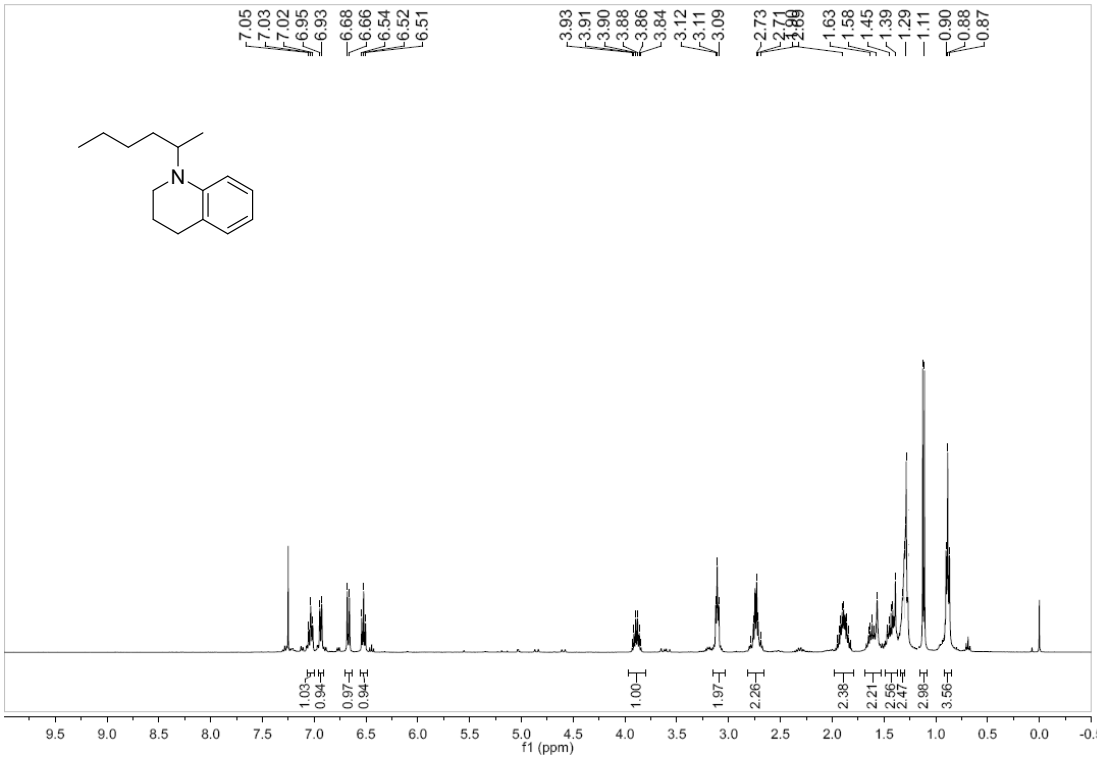
f1 (ppm)

6n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1.29
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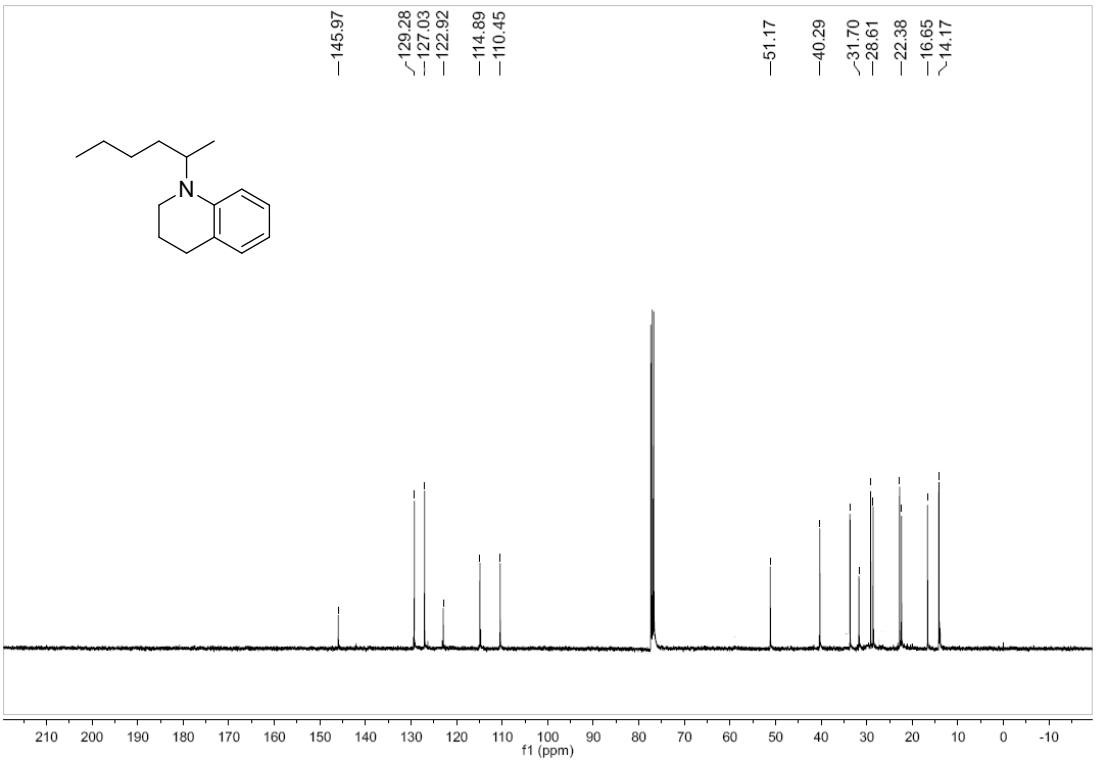
f1 (ppm)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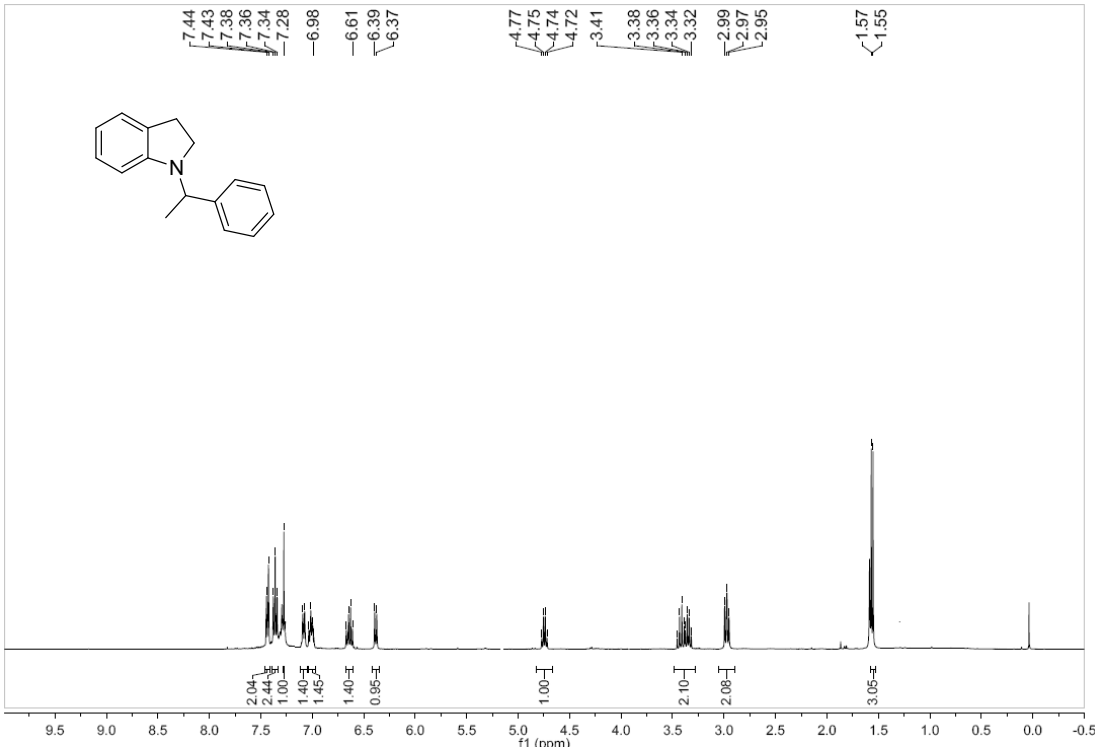
f1 (ppm)

7d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4.72
3.41
3.38
3.36
3.34
3.32
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2.97
2.95
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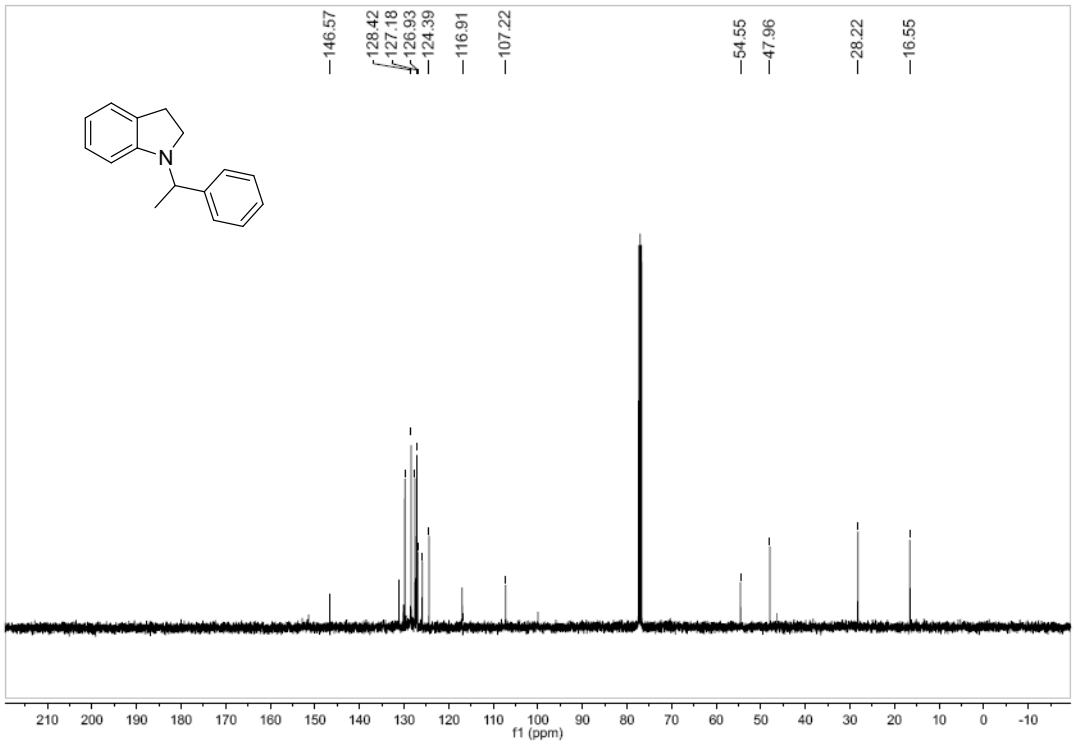
f1 (ppm)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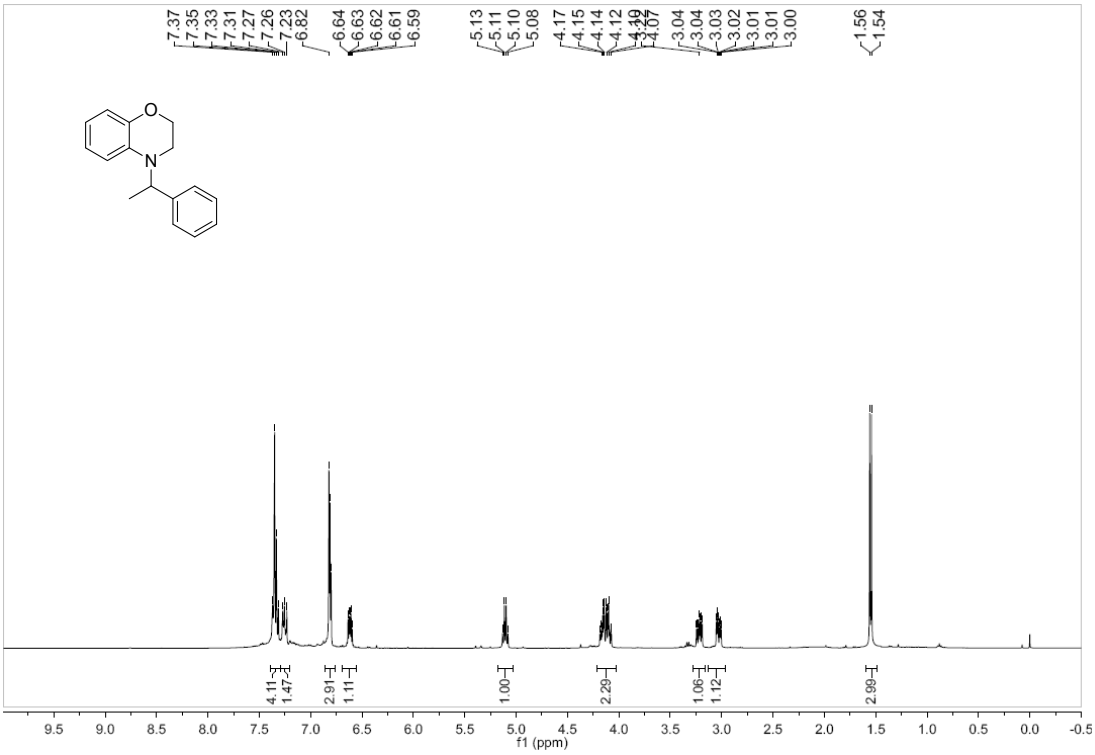
7e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6.59
5.13
5.11
5.10
5.08
4.17
4.15
4.14
4.12
3.04
3.04
3.03
3.02
3.01
3.01
3.00
1.56
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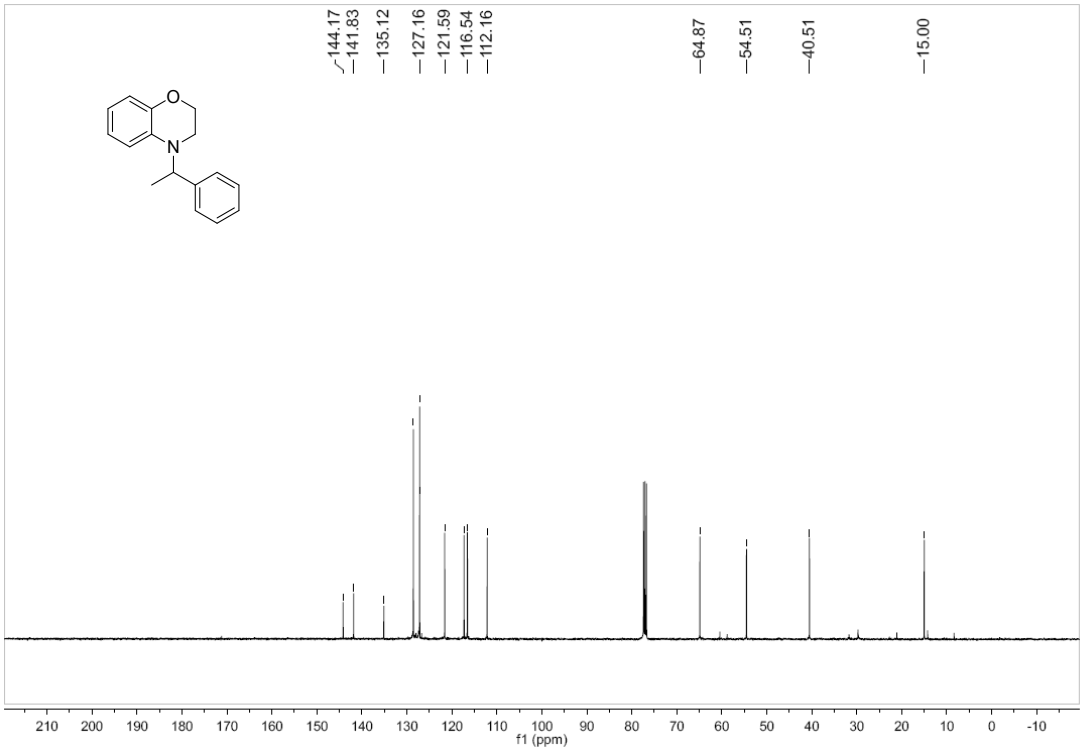
2.99
f1 (ppm)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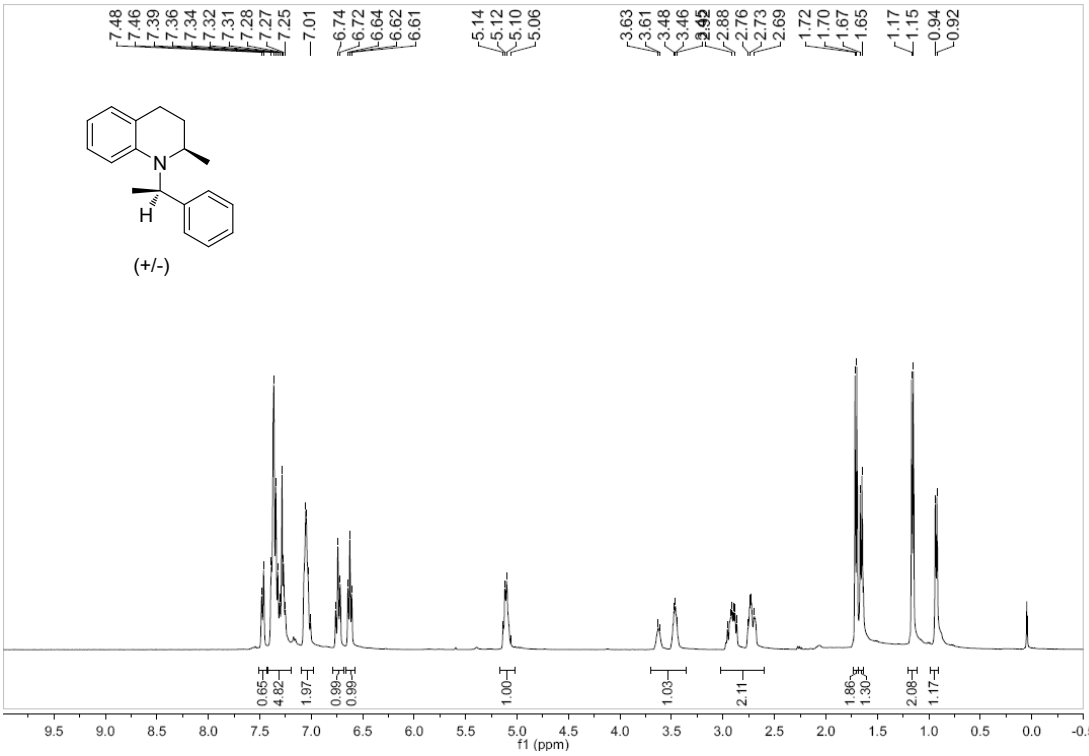
f1 (ppm)

7f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7.25
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6.64
6.62
6.61
5.14
5.12
5.10
5.06
3.63
3.61
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3.46
2.88
2.76
2.73
2.69
1.72
1.70
1.67
1.65
1.17
1.15
0.94
0.92
N
H
(+/-)
0.65
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1.00
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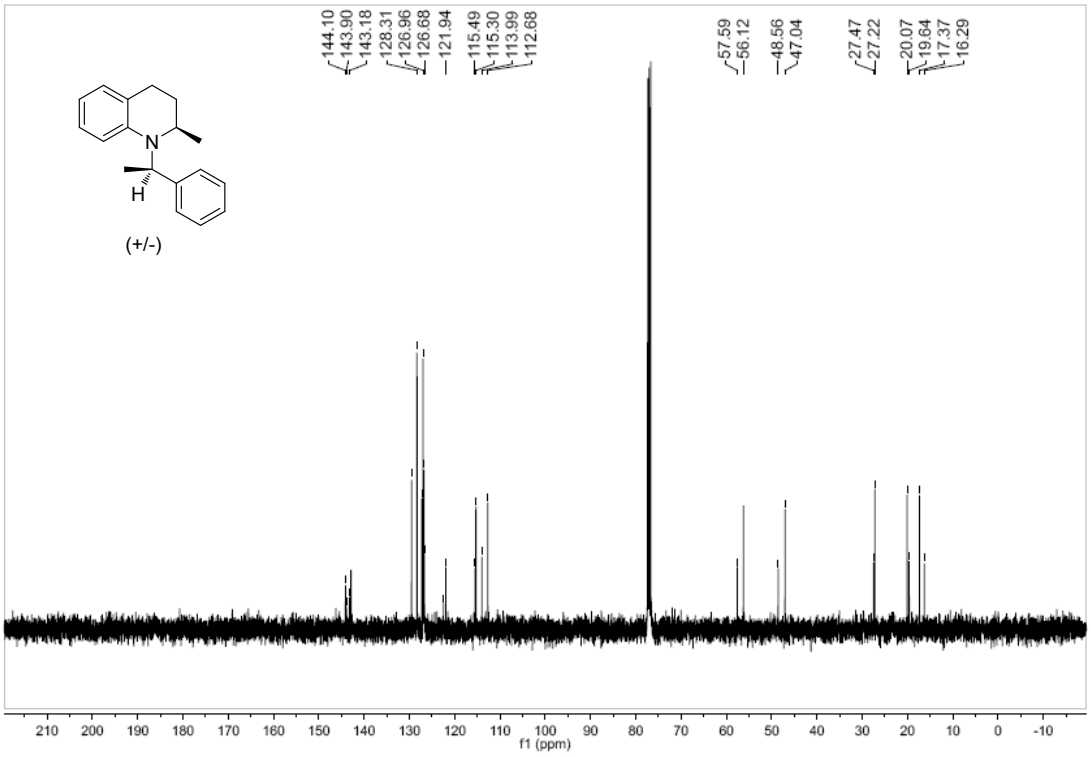
f1 (ppm)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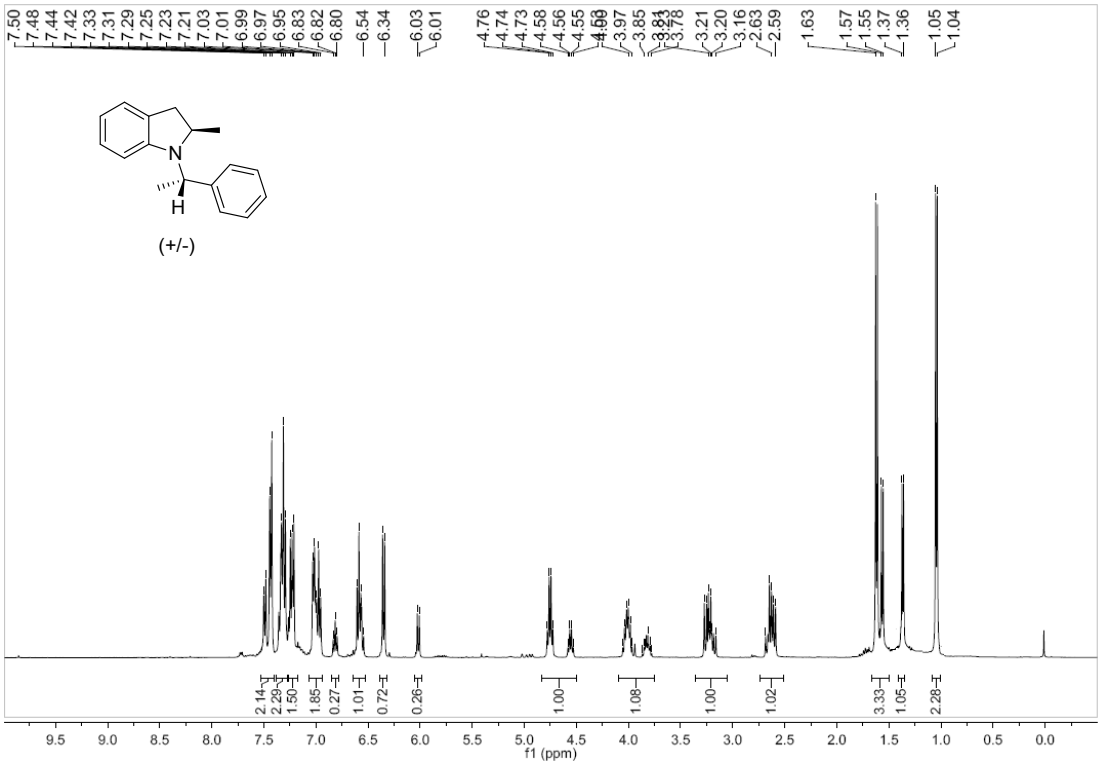
N
H
(+/-)
f1 (ppm)

7g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6.97
6.95
6.83
6.82
6.80
6.54
6.34
6.03
6.01
4.76
4.74
4.73
4.58
4.56
4.55
3.97
3.85
3.78
3.21
3.20
3.16
2.63
2.59
1.63
1.57
1.55
1.37
1.36
1.05
1.04
N
H
(+/-)
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2.29
1.50
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0.26
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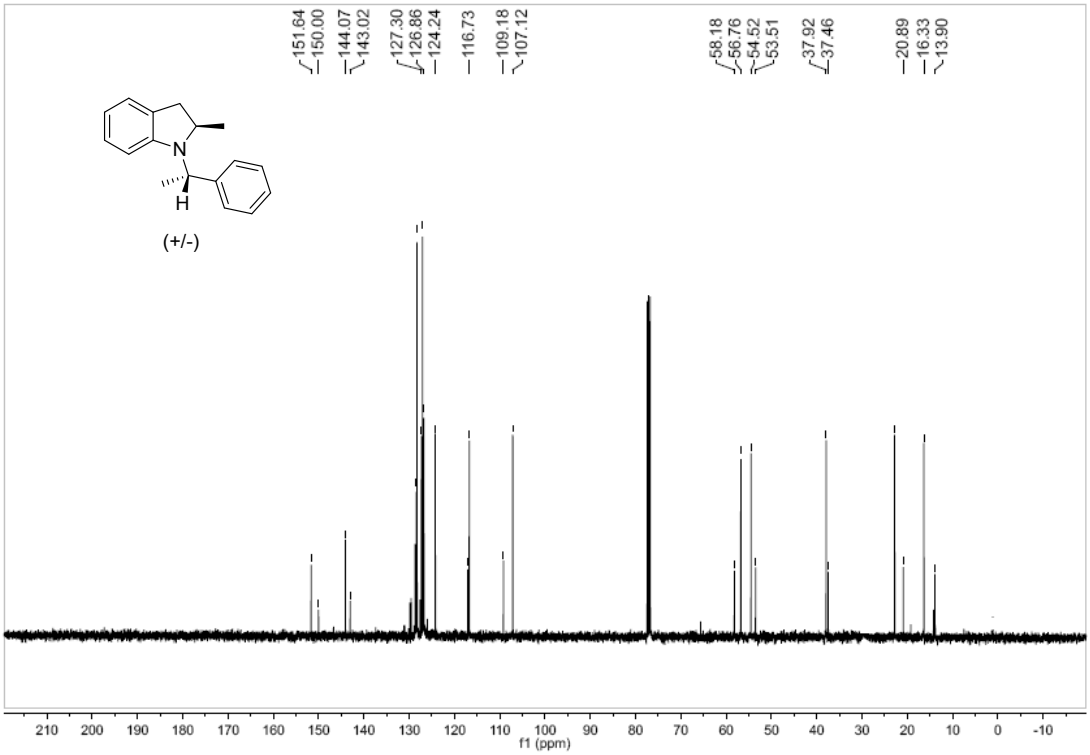
f1 (ppm)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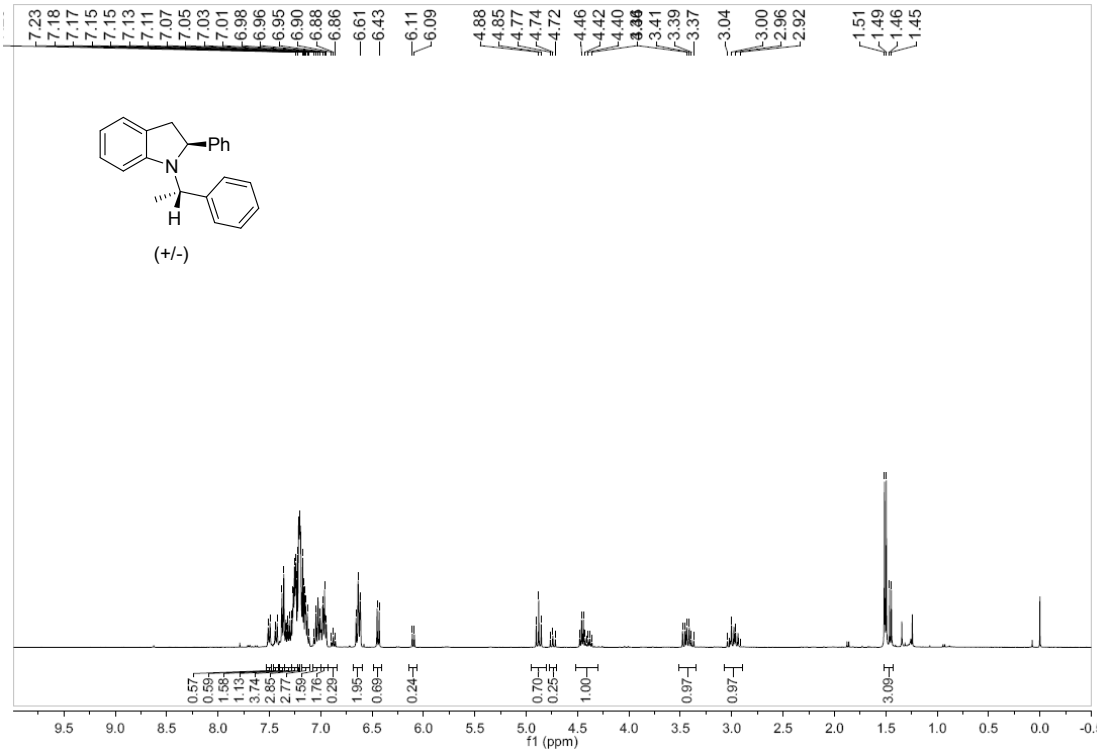
N
H
(+/-)
f1 (ppm)

7h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6.95
6.90
6.88
6.86
6.61
6.43
6.11
6.09
4.88
4.85
4.77
4.74
4.72
4.46
4.42
4.40
3.41
3.39
3.37
3.04
3.00
2.96
2.92
1.51
1.49
1.46
1.45
Ph
N
H
(+/-)
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3.74
2.85
2.77
1.59
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0.25
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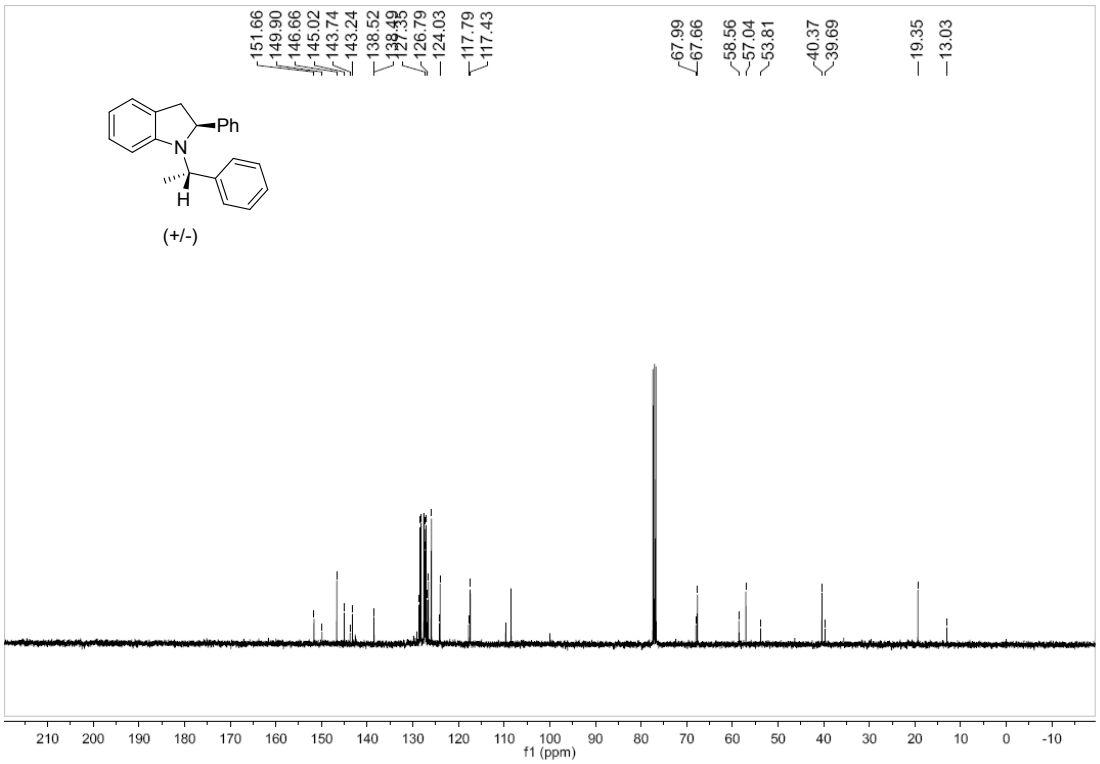
f1 (ppm)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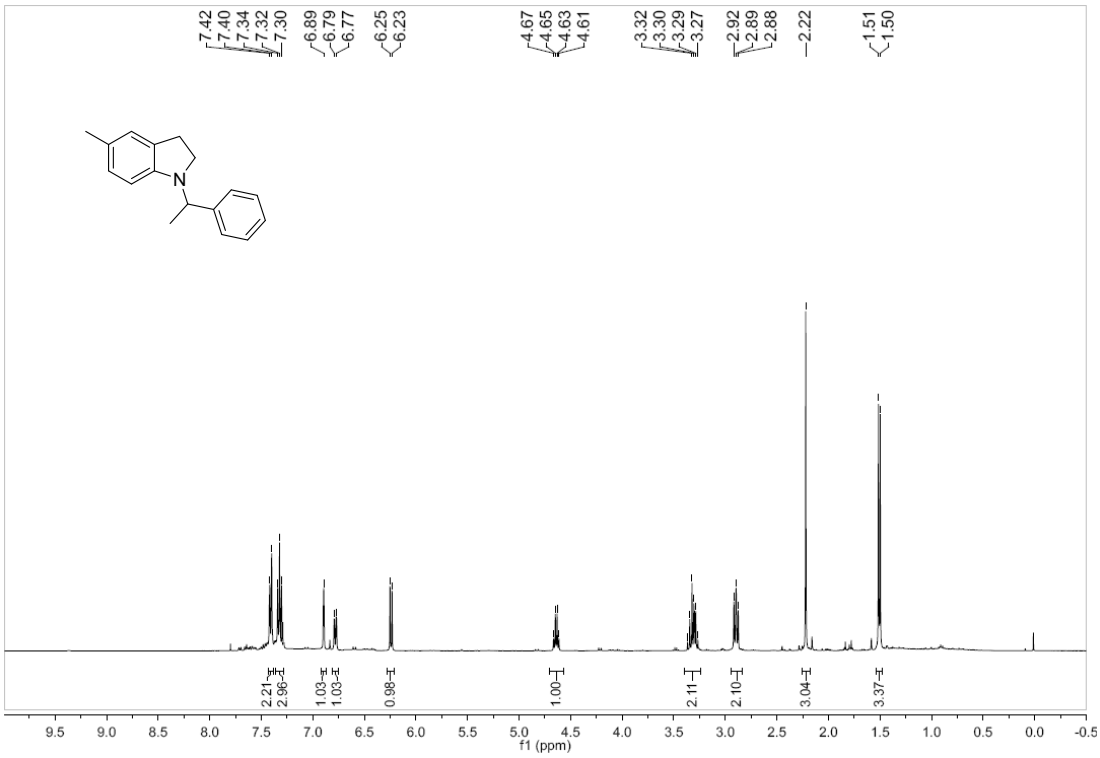
39.69
19.35
13.03
Ph
N
H
(+/-)
f1 (ppm)

7i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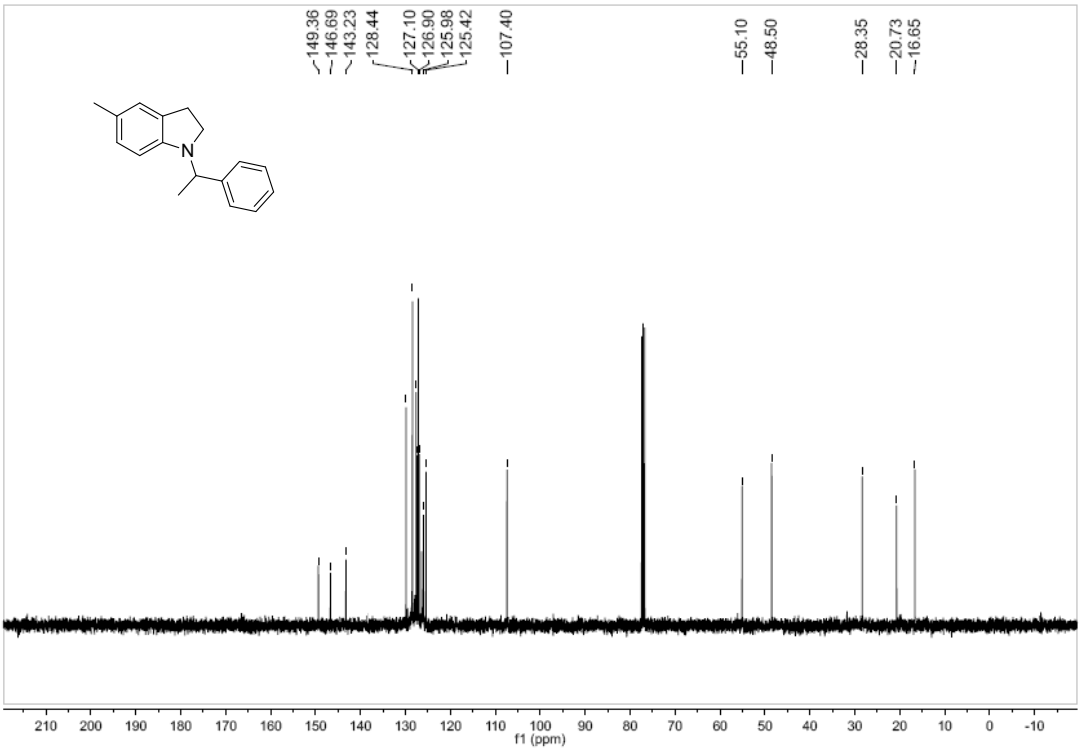
f1 (ppm)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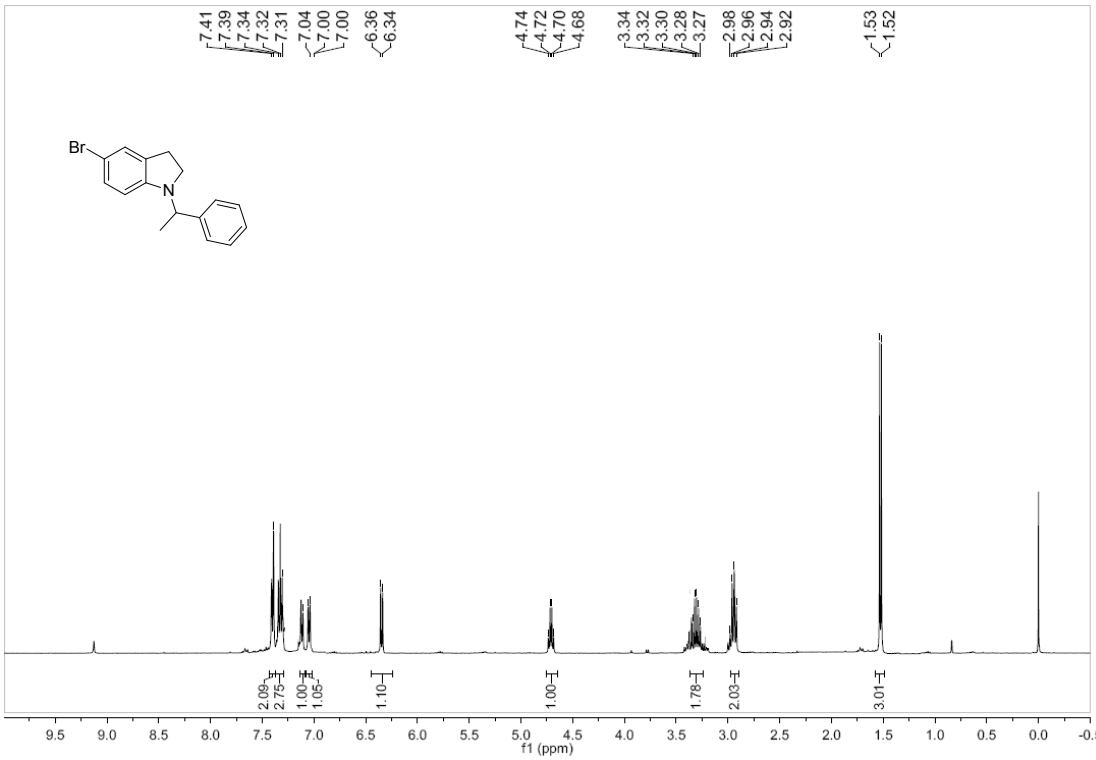
16.65
f1 (ppm)

7j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4.68
3.34
3.32
3.30
3.28
3.27
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2.96
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1.78
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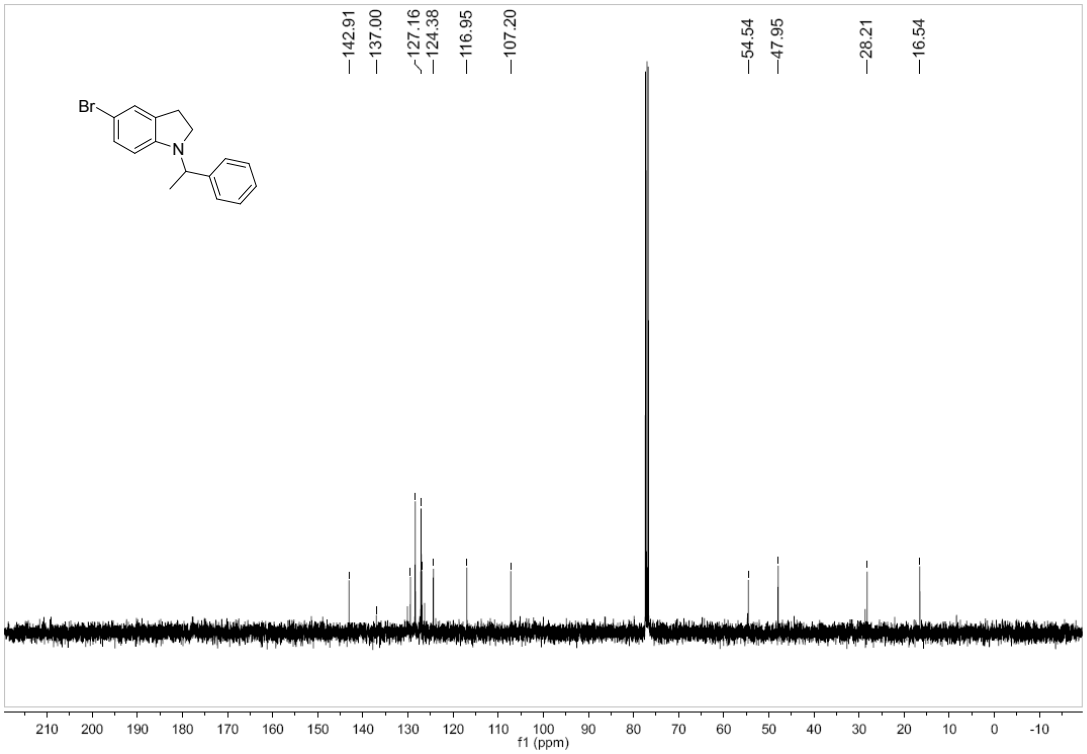
3.01
f1 (ppm)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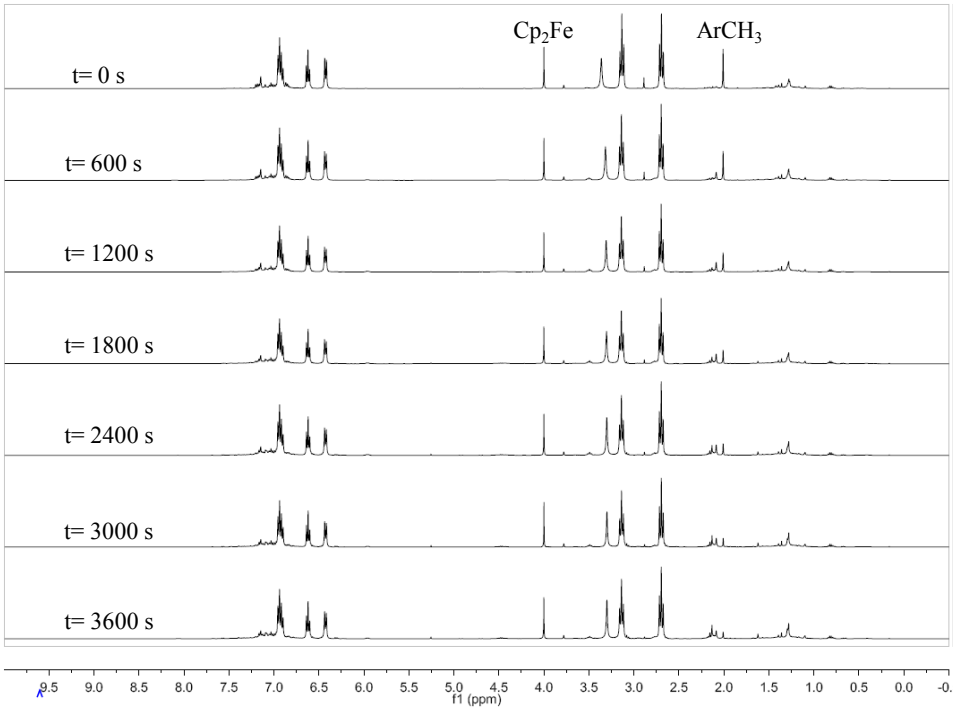
47.95
28.21
16.54
Br
N
f1 (ppm)

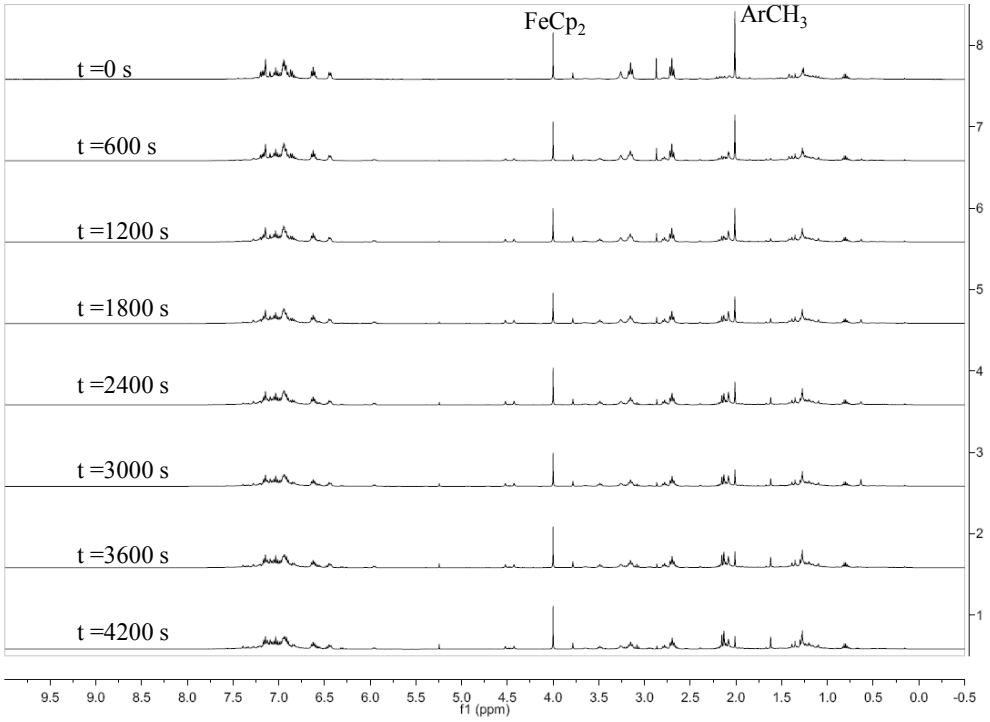
^{1}H NMR spectra (400 MHz, PhBr-d_5, ferrocene as internal standard) for kinetic study

Condition: $[\mathbf{4c}]_0$ = 0.3636 mol·L^{-1}, $[\mathbf{5d}]_0$ = 3.6374 mol·L^{-1}; 10 mol% of complex **3** and TB; 0.6 mL PhBr-d_5; 110 °C



The plot of ln[*m*-tolylacetylene]$_0$/[*m*-tolylacetylene] versus time (s) has been included in the maintext as Figure 2.

Condition: $[\mathbf{4c}]_0$ = 0.3636 mol·L^{-1}, $[\mathbf{5d}]_0$ = 0.3636 mol·L^{-1}; 10 mol% of complex **3** and TB; 0.6 mL PhBr-d_5; 110 °C



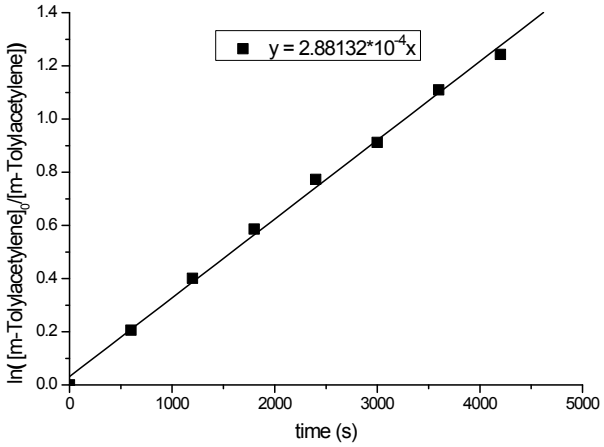
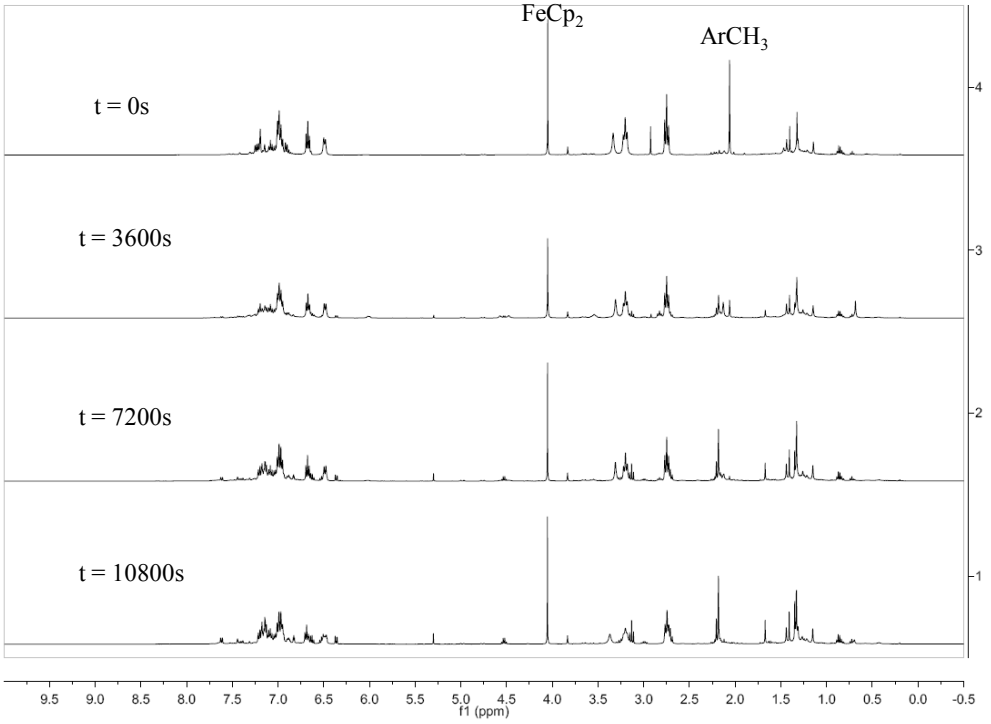


Figure S1. Plot of ln[*m*-tolylacetylene]$_0$/[*m*-tolylacetylene] versus time (s) for the hydroamination reaction of *m*-tolylacetylene **4c** and indoline **5d** catalyzed by complex **3** and TB. Conditions: $[\mathbf{4c}]_0$ = 0.3636 mol·L^{-1}, $[\mathbf{5d}]_0$ = 0.36363 mol·L^{-1}; 10 mol% of complex **3** and TB, PhBr-d_5, 110 °C.

Condition: $[\mathbf{4c}]_0$ = 0.3636 mol·L^{-1}, $[\mathbf{5d}]_0$ = 0.7272 mol·L^{-1}; 10 mol% of complex **3** and TB; 0.6 mL PhBr-d_5; 110 °C



Crystallographic data for complex 3

Table S1 Selected bond lengths (Å) and bond angles (deg) for complex **3**

Bond lengths	
Zr1-O1	1.995(2)
Zr1-O2	1.999(2)
Zr1-N1	2.351(3)
Zr1-C35	2.271(5)
Zr1-C42	2.291(5)
Bond angles	
O1-Zr1-O2	156.85(9)
O1-Zr1-C35	97.97(17)
O2-Zr1-C35	98.20(17)
O1-Zr1-C42	92.95(13)
O2-Zr1-C42	94.21(12)
C35-Zr1-C42	117.35(16)
O1-Zr1-N1	78.94(9)
O2-Zr1-N1	79.13(9),
C35-Zr1-N1	115.97(15)
C42-Zr1-N1	126.67(13)
O1-Zr1-C43	96.24(10)
O2-Zr1-C43	101.57(10)
C35-Zr1-C43	84.98(16)
C42-Zr1-C43	32.42(13)
N1-Zr1 -C43	158.87(11)

Table S2. Crystallographic data for complex **3**

	3
formula	$C_{48}H_{67}NO_2Zr$
fw	781.25
Temp (K)	223
cryst syst	Orthorhombic
color, habit	colorless，prism
cryst size(mm)	0.80×0.65×0.50
space group	$P2_1/c$
a (Å)	11.214(5)
b (Å)	17.371(6)
c (Å)	23.224(11)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	4524.0(3)
Z	4
D_{calcd} (g cm^{-3})	1.147
radiation used	Mo Kα
μ (mm^{-1})	0.278
F(000)	1672.0
θ_{max} (deg)	1.79-26.50
no. of unique data	9286
max, min transm	0.799, 1.000
No. of variables	445
final R indices (I > 2σ(I))	R_1 = 0.0469, wR_2 = 0.2061
R indices (all data)	R_1 = 0.1081, wR_2 = 0.1162
goodness-of-fit on F^2	1.048
Largest diff. peak, hole/e Å^{-3}	0.805, -0.613

References

1 (a) J. J. Felten, W. P. Anderson, *J. Organomet. Chem.* 1972, **36**, 87. (b) E. Y. Tshuva, I. Goldberg, M. Kol, *Organometallics* 2001, **20**, 3017. (c) E.Y. Tshuva, I. Goldberg, M. Kol, H. Weitmanb and Z. Goldschmidt, *Chem. Commun*. 2000, 379. (d) Q. Sun, Y. Wang, D. Yuan, Y. Yao and Q. Shen, *Organometallics* 2014, **33**, 994.

2 SMART version 5.628; Bruker AXS Inc.: Madison, WI, 2001.

3 *SAINT+ version 6.22a*; Bruker AXS Inc.: Madison, WI, 2001.

4 Sheldrick, G. W. *SADABS version 2.10*; University of Göttingen, 2001.

5 *SHELXTL version 6.14*; Bruker AXS Inc.: Madison, WI, 2000.