SUPPORTING INFORMATION
FOR

Efficient Synthesis of 2,4-Disubstituted Quinolines: Calixarene-Catalyzed Povarov-Hydrogen-Transfer Reaction Cascade

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GENERAL TECHNIQUES

Unless noted, all commercial reagents were used as purchased without further purification. Column chromatography was carried out using 0.063-0.2 mm silica gel (DavisilR LC60A 40-63 Micron) with the indicated solvent. Thin layer chromatography (tlc) was carried out using 0.2 mm Kieselgel F254 (Merck) silica plates and compounds visualized using UV irradiation at 365 nm. Infrared spectra were recorded as neat using a FT-IR Varian 660 Fourier Transform Infrared spectrometer. Values are expressed in wavenumbers (cm^{-1}) and recorded in a range of 4000 to 450 cm^{-1}. NMR spectra were recorded at 25 °C in $CDCl_3$ or D_2O on a *Varian* Mercury 300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C. All chemical shifts are reported in parts per million (ppm) and were measured relative to the solvent in which the sample was analyzed ($CDCl_3$ δ = 7.26 for ^1H NMR and δ = 77.0 for ^{13}C NMR) (D_2O δ = 4.67 for ^1H NMR). Coupling constants (*J*) are reported in Hertz (Hz).

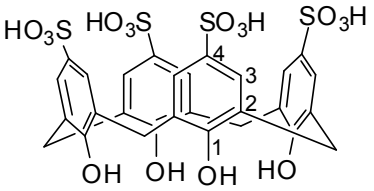
The analysis and monitoring by mass spectrometry was performed on a Shimadzu LCMS-IT-TOF instrument working at high-resolution and high mass accuracy (<5 ppm) under the following conditions: ESI ionization at 4.5 KV in simultaneous mode (positive and negative), nebulizer gas at 1.5 $L \cdot min^{-1}$, curved desorption line (CDL) interface at 200 °C, and drying gas at 200 kPa; octapole ion accumulation time of 100 ms, precursor ion selected width of 3.0 amu, CID collision time of 30 ms, collision energy of 50% (62.5 mV, waveform voltage from 0 to peak), unless specified otherwise of q=0.251. Full scan mass spectra from m/z = 50 to 500 were acquired with a scan time of 0.2 s. The samples were dissolved in methanol or acetonitrile and injected by direct infusion at a flow rate of 10 $\mu L\ min^{-1}$ with automatic syringe pump.

Diastereoselectivity was determined for gas chromatography coupled to mass spectrometer using a SHIMADZU CG-17A mass spectrometer and method with the following specifications, column DB-5, 30 meters, DI 0.25 mm; carrier gas helium; injector temperature: 250 ºC; oven temperature was: 120 °C (1 min), ramped at 15 °C min^{-1} up to 300 °C (held for 20 minutes).

EXPERIMENTAL PROCEDURES

Catalysts *p*-sulfonic acid calix[4]arene and *p*-sulfonic acid calix[6]arene were prepared according to published method.[1]

^{1}H NMR characterization for catalysts:

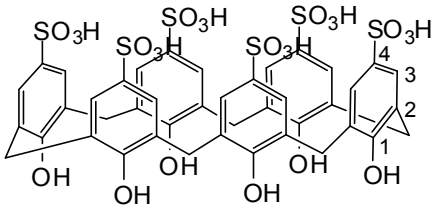


CX4SO$_3$H

***p*-sulfonic acid calix[4]arene**. White solid.

^{1}H NMR (300 MHz, D_2O): δ 3.88 (sl, 8H), 7.42 (sl, 8H).

^{13}C NMR (75 MHz, D_2O): δ 30.8 (Ar**C**H_2Ar), 126.7 (C-**2**), 128.3 (C-**3**), 135.8 (C-**4**), 151.9 (C-**1**).



CX6SO$_3$H

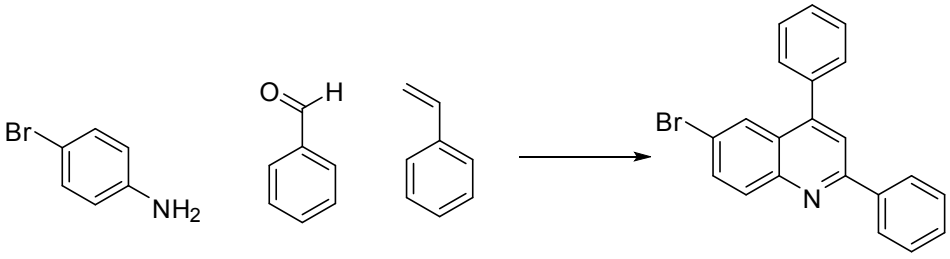
***p*-sulfonic acid calix[6]arene**. Gray solid.

^{1}H NMR (300 MHz, D_2O): δ 3.83 (s, 12H), 7.34 (s, 12H).

^{13}C NMR (75 MHz, D_2O): δ 30.8 (CH_2), 126.4 (C-**2**), 128.0 (C-**3**), 135.3 (C-**4**), 153.2 (C-**1**).

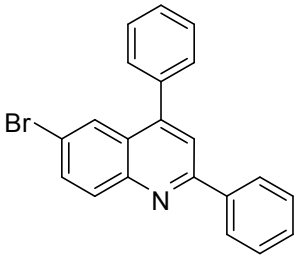
The NMR data for catalysts were in agreement with that reported in the literature.[1]

General procedure for the preparation of quinolines.



To a solution of *p*-sulfonic acid calix[4]arene (9.10 mg; 1 mol%) and aniline (1 mmol, 172 mg, 1 equiv) in acetonitrile (5 mL) was added styrene (0.175 mL; 1.5 mmol; 1.5 equiv) and benzaldehyde

(0.117 mL; 1.1 mmol; 1.1 equiv) at temperature of 80 ºC. The reaction mixture was stirred for 12 hours at 80 ºC, when TLC analyses revealed the consumption of all starting material. The reaction was quenched by addition of water (10 mL) and the product extracted with dichloromethane (4 x 10 mL). The combined organic extracts were washed with an aqueous solution of NH_4OH 0.1 mol L^{-1}, and subsequently dried over Na_2SO_4 and the solvent removed under reduced pressure in a rotary evaporator. The solid obtained was purified by silica gel column chromatography (hexane/dichloromethane of increasing polarity) or recrystallization to afford the required product.

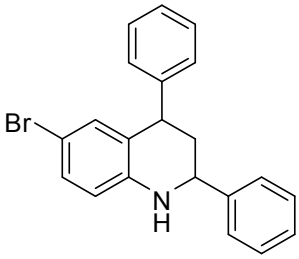


Chemical Formula: $C_{21}H_{14}BrN$
Exact Mass: 359,03

6-bromo-2,4-diphenylquinoline (4a). Recrystallized from hot methanol resulting in a solid as transparent crystal, afforded 229 mg. **m.p.**= 151.9-153.3 °C (literature 151°C)[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25–8.18 (m, 2H), 8.16 (d, J = 9.0 Hz, 1H), 8.05 (d, J = 2.2 Hz, 1H), 7.85 (s, 1H), 7.82 (dd, J = 9.0, 2.2 Hz, 1H), 7.61–7.50 (m, 8H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 157.30, 149.05, 147.18, 138.92, 137.76, 133.49, 131.71, 130.08, 129.67, 129.20, 129.11, 129.08, 128.06, 127.91, 127.21, 120.87, 120.41.

IV (cm^{-1}) $\bar{\nu}_{max}$**:** 3052, 1587, 1538, 1479, 1335, 778, 695, 541.
HRMS [ESI(+), IT-TOF] calculated for $[M+H]^+$ = 360.0388; found 360.0260



Chemical Formula: $C_{21}H_{18}BrN$
Exact Mass: 363,06

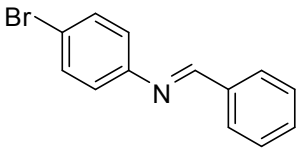
6-bromo-2,4-diphenyl-1,2,3,4-tetrahydroquinoline (5a). Column chromatography on silica gel (hexane/dichloromethane = 2:1 v/v) afforded 167 mg of title product in 46% yield as a yellow oil. (Table 1, Entry 9).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06–7.51 (m, 3H), 7.51–7.17 (m, 10H), 6.97–6.82 (m, 1H), 6.52 (d, J = 8.4 Hz, 1H), 4.69 (dd, J = 9.0, 3.2 Hz, 1H), 4.20 (dd, J = 12.0, 6.0 Hz, 1H), 2.41–2.01 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.96, 143.97, 143.80, 132.82, 132.33, 130.42, 129.06, 128.71, 127.58, 127.26, 127. 08, 118.83, 116.48, 111.94, 110.32, 77.65, 77.22, 76.80, 57.14, 44.74, 41.75.

IV (cm^{-1}) $\bar{\nu}_{max}$**:** 3346, 3031, 2213, 1603, 1453, 1301, 828, 753, 697, 503.

CG-MS (EI) *m/z* (abundance %); 365 (25, M^+); 363 (25, M+2); 284 (24); 206 (20); 193 (100); 193 (100); 179 (25); 165 (23); 102 (30); 91 (89); 77 (76).



Chemical Formula: $C_{13}H_{10}BrN$
Exact Mass: 259,00

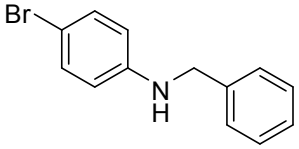
(*E*)-*N*-benzylidene-4-bromoaniline (6a). Isolated in various reaction like intermediates. **m.p.**= 65.8-66.6 °C (literature 65-66.5 °C)[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.96–7.84 (m, 2H), 7.56–7.43 (m, 5H), 7.14–7.05 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.99, 151.20, 136.14, 132.42, 131.89, 129.13, 129.06, 122.82, 119.55.

IV (cm^{-1}) $\bar{\nu}_{max}$**:** 3050, 2849, 1587, 1492, 1288, 1226, 1134, 1013, 965, 883, 813, 651, 509.

CG-MS (EI) *m/z* (abundance %); 259 (35, M^+); 261 (35, M+2); 260 (30); 258 (30); 179 (10); 155 (25); 91 (25); 77 (38); 76 (100); 55 (89).



Chemical Formula: $C_{13}H_{12}BrN$
Exact Mass: 261,02

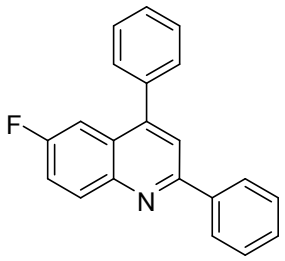
***N*-benzyl-4-bromoaniline (7a)** Isolated in various reaction like intermediates.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.05 (m, 7H), 6.51 (d, J = 8.9 Hz, 2H), 4.30 (s, 2H), 4.06 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.99, 138.81, 131.92, 128.69, 127.38, 127.37, 114.43, 109.15, 77.43, 77.01, 76.58, 48.24.

IV (cm^{-1}) $\bar{\nu}_{max}$**:** 3416, 1587, 1492, 1288, 1224, 1218, 1134, 1013, 965, 883, 813, 651, 509.

CG-MS (EI) *m/z* (abundance %); 261 (9, M^+); 263 (9, M+2); 91 (100); 65 (12).



Chemical Formula: $C_{21}H_{14}FN$
Exact Mass: 299,11

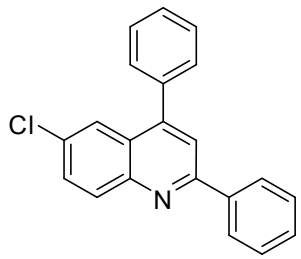
6-fluoro-2,4-diphenylquinoline (4b). Column chromatography on silica gel (hexane/dichloromethane = 1:1 v/v) afforded 179 mg of title product in 60% yield as a white solid. **m.p**. = 102.8-103.7 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (dd, J = 8.9, 5.5 Hz, 1H), 8.21–8.15 (m, 2H), 7.85 (s, 1H), 7.64–7.45 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.15, 158.88, 156.28, 148.67, 148.60, 145.86, 139.29, 137.87, 132.53, 132.41, 129.38, 129.31, 128.84, 128.75, 128.61, 127.41, 119.85, 119.82, 119.48, 109.17, 108.86.

IV (cm^{-1}) $\bar{\nu}_{max}$**:** 3042, 1623, 1547, 1462, 1359, 1228, 1193, 1077, 1028, 919, 889, 833, 712, 587, 556, 503.

HRMS [ESI(+), IT-TOF] calculated for $[M+H]^+$ = 300.1189; found 300.1091



Chemical Formula: $C_{21}H_{14}ClN$
Exact Mass: 315,08

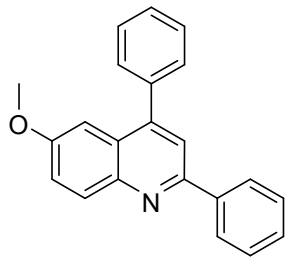
6-chloro-2,4-diphenylquinoline (4c). Recrystallized from hot methanol as transparent crystal, afforded 183 mg of title compound in 58% yield. **m. p.** = 122.3-123.3 °C (literature 124.4-125.3 °C).[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23–8.16 (m, 3H), 7.89 (d, J = 2.3 Hz, 1H), 7.85 (s, 1H), 7.67 (dd, J = 9.0, 2.4 Hz, 1H), 7.61–7.48 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.06, 148.45, 147.19, 139.16, 137.71, 132.21, 131.70, 130.47, 129.63, 129.47, 128.92, 128.84, 128.74, 127.56, 126.47, 124.49, 120.07, 77.54, 77.11, 76.69.

IV (cm^{-1}) $\bar{\nu}_{max}$**:** 3054, 1588, 1541, 1483, 1357, 1152, 1076, 1027, 891, 824, 780, 755, 699, 608, 546.

CG-MS (EI) *m/z* (abundance %); 315 (100, M^+); 316 (32, M+1); 280 (28); 236 (15); 201 (27); 176 (17); 139 (97); 77 (20).



Chemical Formula: $C_{22}H_{17}NO$
Exact Mass: 311,13

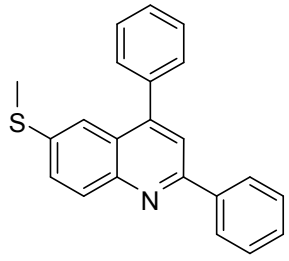
6-methoxy-2,4-diphenylquinoline (4d). Column chromatography on silica gel (hexane/dichloromethane = 2:1 v/v) afforded 186 mg of title compound in 60% yield as a yellow solid. **m. p.** = 119-120.6 °C (literature 116-117.1ºC).[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24–8.13 (m, 3H), 7.79 (s, 1H), 7.65–7.49 (m, 7H), 7.46 (d, J = 7.1 Hz, 1H), 7.41 (dd, J = 9.2, 2.7 Hz, 1H), 7.21 (d, J = 2.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.06, 148.45, 147.19, 139.16, 137.71, 132.21, 131.70, 130.47, 129.63, 129.47, 128.92, 128.84, 128.74, 127.56, 126.47, 124.49, 120.07, 77.54, 77.11, 76.69.

IV (cm^{-1}) $\bar{\nu}_{max}$ 3018, 2954, 2828, 16161, 1588, 1511, 1487, 1400, 1295, 1265, 1235, 1220, 1178, 1113, 1026, 891, 836, 784, 705, 587, 521.

HRMS [ESI(+), IT-TOF] calculated for $[M+H]^+$ = 312.1388; found 312.1309



Chemical Formula: $C_{22}H_{17}NS$
Exact Mass: 327,11

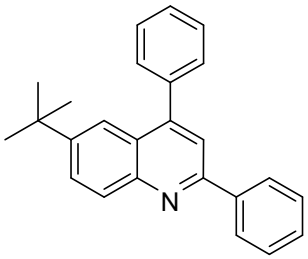
6-(methylthio)-2,4-diphenylquinoline (4e). Column chromatography on silica gel (hexane/dichloromethane = 2:1 v/v) afforded 209 mg of title compound in 64% yield as a cream solid. **m. p**. = 142.2-143 ºC

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (dd, J = 13.6, 6.6 Hz, 3H), 7.81 (s, 1H), 7.73–7.41 (m, 10H), 2.48 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.30, 148.07, 147.28, 139.73, 138.46, 137.28, 130.61, 129.70, 129.53, 129.14, 129.09, 128.94, 128.74, 127.67, 126.37, 121.19, 120.13, 16.01.

IV (cm^{-1}) $\bar{\nu}_{max}$**:** 3038, 2920, 1582, 1541, 1478, 1355, 1155, 1073, 1025, 830, 786, 760, 704, 588.

HRMS [ESI(+), IT-TOF] calculated for $[M+H]^+$ = 328.1160; found 328.1106



Chemical Formula: $C_{25}H_{23}N$
Exact Mass: 337,18

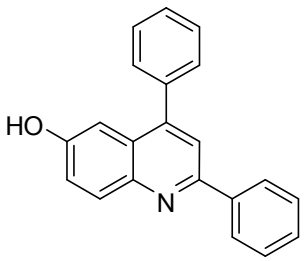
6-tert-butyl-2,4-diphenylquinoline (4f). Column chromatography on silica gel (hexane/dichloromethane = 2:1 v/v) afforded 209 mg of title product in 64% yield as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25–8.13 (m, 3H), 7.88 (s, 1H), 7.84 (dd, J = 8.8, 2.2 Hz, 1H), 7.80 (s, 1H), 7.64–7.41 (m, 9H), 1.36 (s, 10H). **m. p.** = 75.3-75.9 °C

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.60, 149.38, 149.19, 147.58, 140.10, 138.85, 129.86, 129.78, 129.36, 129.05, 128.81, 128.63, 128.58, 127.75, 125.45, 120.73, 119.72, 35.31, 31.40.

IV (cm^{-1}) $\bar{\nu}_{max}$ 3050, 2959, 2860, 1699, 1588, 1544, 1489, 1449, 1353, 1262, 1199, 1159, 1024, 893, 833, 765, 702, 666, 614, 583.

HRMS [ESI(+), IT-TOF] calculated for $[M+H]^+$ = 338.1909; found 338.1847



Chemical Formula: $C_{21}H_{15}NO$
Exact Mass: 297,12

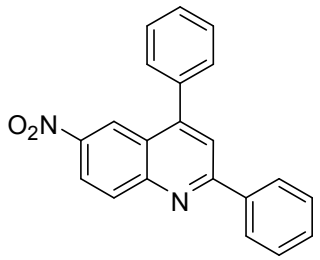
2,4-diphenylquinolin-6-ol (4g). Column chromatography on silica gel (hexane/dichloromethane = 1:1 v/v) afforded 208 mg of title product in 70% yield as a transparent crystal. **m. p**. = 224.7-225.8 ºC (literature 222-223 °C)[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, J = 8.6 Hz, 2H), 8.10 (d, J = 9.0 Hz, 1H), 8.06 (d, J = 2.1 Hz, 1H), 7.88–7.77 (m, 4H), 7.55 (ddd, J = 8.3, 7.1, 4.5 Hz, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.30, 155.12, 155.02, 154.75, 148.18, 144.48, 144.26, 142.44, 139.69, 138.59, 136.22, 131.49, 131.30, 129.58, 129.34, 129.06, 128.93, 128.84, 128.58, 127.83, 127.78, 127.45, 127.25, 122.62, 122.05, 120.37, 116.46, 116.29, 114.68, 107.66.

IV (cm^{-1}) $\bar{\nu}_{max}$ 3046, 1614, 1591, 1493, 1362, 1227, 1154, 1029, 889, 834, 760, 706, 696, 622, 589.

HRMS [ESI(+), IT-TOF] calculated for $[M+H]^+$ = 298.1232; found 298.1225



Chemical Formula: $C_{21}H_{14}N_2O_2$
Exact Mass: 326,11

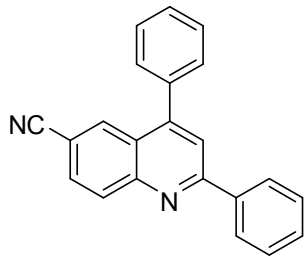
6-nitro-2,4-diphenylquinoline (4h). Column chromatography on silica gel (hexane/dichloromethane = 1:1 v/v) afforded 147 mg of title product in 45% yield as a yellow solid. **m. p**. = 255.5-257.0 °C (literature 256.5-258.2 °C).[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, J = 8.6 Hz, 2H), 8.10 (d, J = 9.0 Hz, 1H), 8.06 (d, J = 2.1 Hz, 1H), 7.88–7.77 (m, 4H), 7.64–7.45 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.98, 149.23, 147.57, 143.41, 137.48, 133.76, 132.89, 132.16, 129.62, 129.23, 129.18, 128.27, 128.14, 127.52, 121.68, 119.92, 118.98, 113.23.

IV (cm^{-1}) $\bar{\nu}_{max}$ 3030, 1601, 1531, 1473, 1282, 1109, 829, 751, 732, 697.

HRMS [ESI(+), IT-TOF] calculated for $[M+H]^+$ = 327.1134; found 327.1069



Chemical Formula: $C_{22}H_{14}N_2$
Exact Mass: 306,12

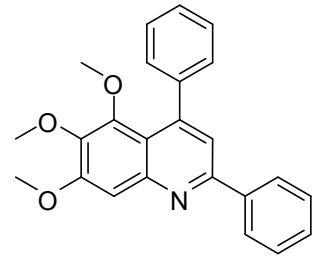
2,4-diphenylquinoline-6-carbonitrile (4i). Column chromatography on silica gel (hexane/dichloromethane = 1:1 v/v) afforded 122 mg of title product in 40% yield as a white solid. **m. p.** = 189.9-192 ºC (literature 189-190 °C)[6].

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39–8.24 (m, 2H), 8.10 (d, J = 9.0 Hz, 1H), 8.06 (d, J = 2.0 Hz, 1H), 7.82 (m, 4H), 7.62–7.50 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.73, 148.99, 147.36, 143.18, 137.26, 133.51, 132.63, 131.93, 128.98, 128.93, 128.66, 128.02, 127.89, 127.29, 121.43, 119.65, 118.70, 113.02.

IV (cm^{-1}) $\bar{\nu}_{max}$ 3078, 2221, 1599, 1588, 1538, 1481, 1353, 1152, 1058, 879, 835, 825, 690, 651, 624, 589.

HRMS [ESI(+), IT-TOF] calculated for $[M+H]^+$ = 307.1235; found 307.1161



Chemical Formula: $C_{24}H_{21}NO_3$
Exact Mass: 371,15

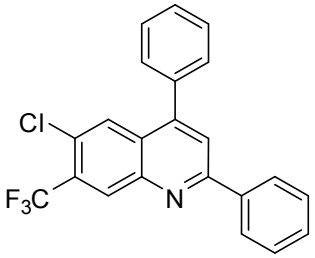
5,6,7-trimethoxy-2,4-diphenylquinoline (4j). Column chromatography on silica gel (hexane/dichloromethane = 2:1 v/v) afforded 148 mg of title product in 40% yield as a grey oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19–8.01 (dd, J = 6.90, 1H), 7.45 (m, 8H), 5.88 (s, 1H), 4.06 (s, 3H), 3.93 (s, 3H), 3.20 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.15, 129.41, 129.03, 128.91, 127.83, 127.62, 127.58, 127.40, 127.25, 120.06, 105.67, 90.54, 77.72, 77.29, 76.87, 61.42, 61.35, 60.92, 56.34, 49.10.

IV (cm^{-1}) $\bar{\nu}_{max}$ 3042, 2928, 2820, 1611, 1397, 1235, 1035, 999, 801, 772, 698, 633, 573, 546.

HRMS [ESI(+), IT-TOF] calculated for $[M+H]^+$ = 372.1600; found 372.1547



Chemical Formula: $C_{22}H_{13}ClF_3N$
Exact Mass: 383,07

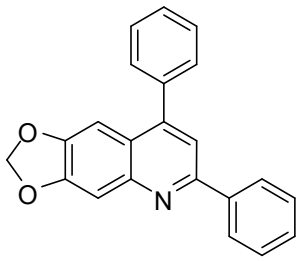
6-chloro-2,4-diphenyl-7-(trifluoromethyl)quinoline (4k). Recrystallized from hot methanol as transparent crystal, afforded 199 mg of title product in 52% yield. **m. p**. = 102.9-103.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.35–8.08 (m, 2H), 8.02 (s, 1H), 7.94 (s, 1H), 7.75–7.24 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.36, 148.35, 146.46, 146.19, 138.44, 138.07, 136.91, 130.13, 129.37, 129.12, 129.03, 127.57, 116.11, 111.65, 111.58, 111.50, 111.43.

IV (cm^{-1}) $\bar{\nu}_{max}$ 3054, 1592, 1543, 1483, 1357, 1303, 1154, 1123, 1101, 906, 786, 702, 687.

HRMS [ESI(+), IT-TOF] calculated for $[M+H]^+$ = 384.0767; found 384.0756



Chemical Formula: $C_{22}H_{15}NO_2$
Exact Mass: 325,11

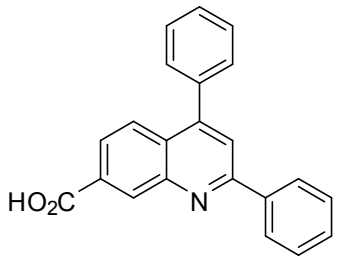
6,8-diphenyl-[1,3]dioxolo[4,5-g]quinoline (4l). Column chromatography on silica gel (hexane/dichloromethane = 2:1 v/v) afforded 198 mg of title product in 61% yield as a white solid. **m. p**. = 102.9-103.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 7.0 Hz, 2H), 7.67 (s, 1H), 7.57–7.41 (m, 9H), 7.16 (s, 1H), 6.08 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.15, 150.76, 148.28, 148.15, 147.40, 139.94, 139.10, 129.59, 129.19, 129.02, 128.88, 128.53, 127.51, 122.83, 118.11, 106.67, 101.93, 101.30, 77.71, 77.29, 76.87.

IV (cm^{-1}) $\bar{\nu}_{max}$ 3046, 2892, 2780, 1616, 1559, 1495,1459, 1360, 1242, 1209, 1151, 1037, 939, 861, 764, 711, 689. 660. 609, 574.

CG-MS (EI) *m/z* (abundance %): 325 (100, M^+), 367 (13), 163 (15), 134 (30), 119 (11), 77 (10).



Chemical Formula: $C_{22}H_{15}NO_2$
Exact Mass: 325,11

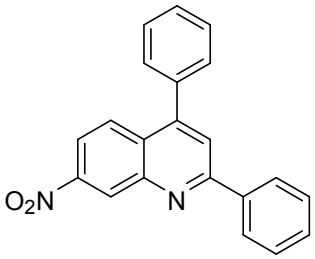
2,4-diphenylquinoline-7-carboxylic acid (4m). Column chromatography on silica gel (hexane/dichloromethane = 1:1 v/v) afforded 139 mg of title product in 43% yield as a white solid. **m. p**. = 167.9-168.8 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23–8.16 (m, 3H), 7.89 (d, J = 2.3 Hz, 1H), 7.85 (s, 1H), 7.67 (dd, J = 9.0, 2.4 Hz, 1H), 7.61–7.48 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.06, 148.45, 147.19, 139.16, 137.71, 132.21, 131.70, 130.47, 129.63, 129.47, 128.92, 128.84, 128.74, 127.56, 126.47, 124.49, 120.07.

IV (cm^{-1}) $\bar{\nu}_{max}$ 3411, 3050, 1691, 1580, 1544, 1485, 1449, 1354, 1250, 1159, 1028, 897, 833, 773, 694, 587.

HRMS [ESI(+), IT-TOF] calculated for $[M-H]^-$ = 324.1025; found 324.1064



Chemical Formula: $C_{21}H_{14}N_2O_2$
Exact Mass: 326,11

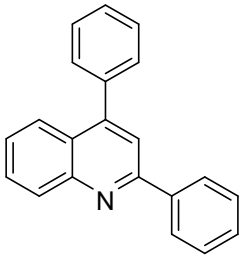
7-nitro-2,4-diphenylquinoline (4n). Column chromatography on silica gel (hexane/dichloromethane = 1:1 v/v) afforded 195 mg of title product in 60% yield as a yellow solid. **m. p**. = 180.9-182.8 °C (literature 180-182 °C)[7].

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.11 (d, J = 2.3 Hz, 1H), 8.28–8.17 (m, 3H), 8.05 (d, J = 9.2 Hz, 1H), 7.99 (s, 1H), 7.66–7.49 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.01, 149.36, 148.17, 147.94, 138.37, 137.18, 130.23, 129.44, 129.07, 129.02, 128.94, 127.64, 127.49, 126.11, 121.75, 119.45, 77.45, 77.02, 76.60.

IV (cm^{-1}) $\bar{\nu}_{max}$ 3042, 1611, 1598, 1397, 1235, 1035, 999, 801, 772, 698, 633, 573, 546.

HRMS [ESI(+), IT-TOF] calculated for $[M+H]^+$ = 327.1134; found 327.1067



Chemical Formula: $C_{21}H_{15}N$
Exact Mass: 281,12

2,4-diphenylquinoline (4o). Column chromatography on silica gel (hexane/dichloromethane = 4:1 v/v) afforded 107 mg of title product in 38% yield as a yellow oil.

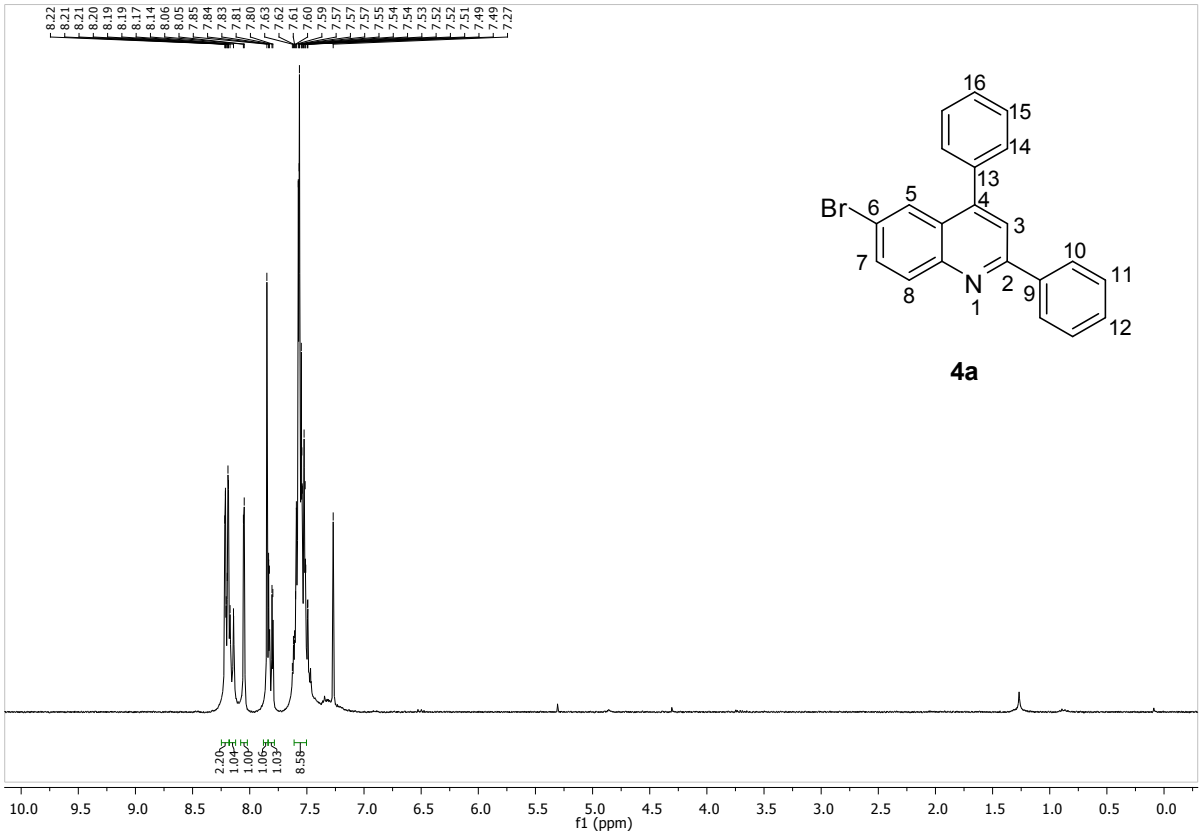
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22–8.10 (m, 3H), 7.88 (d, J = 2.3 Hz, 1H), 7.85 (s, 1H), 7.68 (dd, J = 9.0, 2.3 Hz, 1H), 7.62–7.42 (m, 8H), 7.35 (d, J = 4.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.07, 148.56, 147.09, 137.69, 132.24, 131.60, 130.50, 129.63, 129.42, 129.04, 128.89, 128.82, 128.73, 128.68, 127.55, 127.39, 127.34, 124.49, 120.08, 113.90, 77.43, 77.01, 76.58.

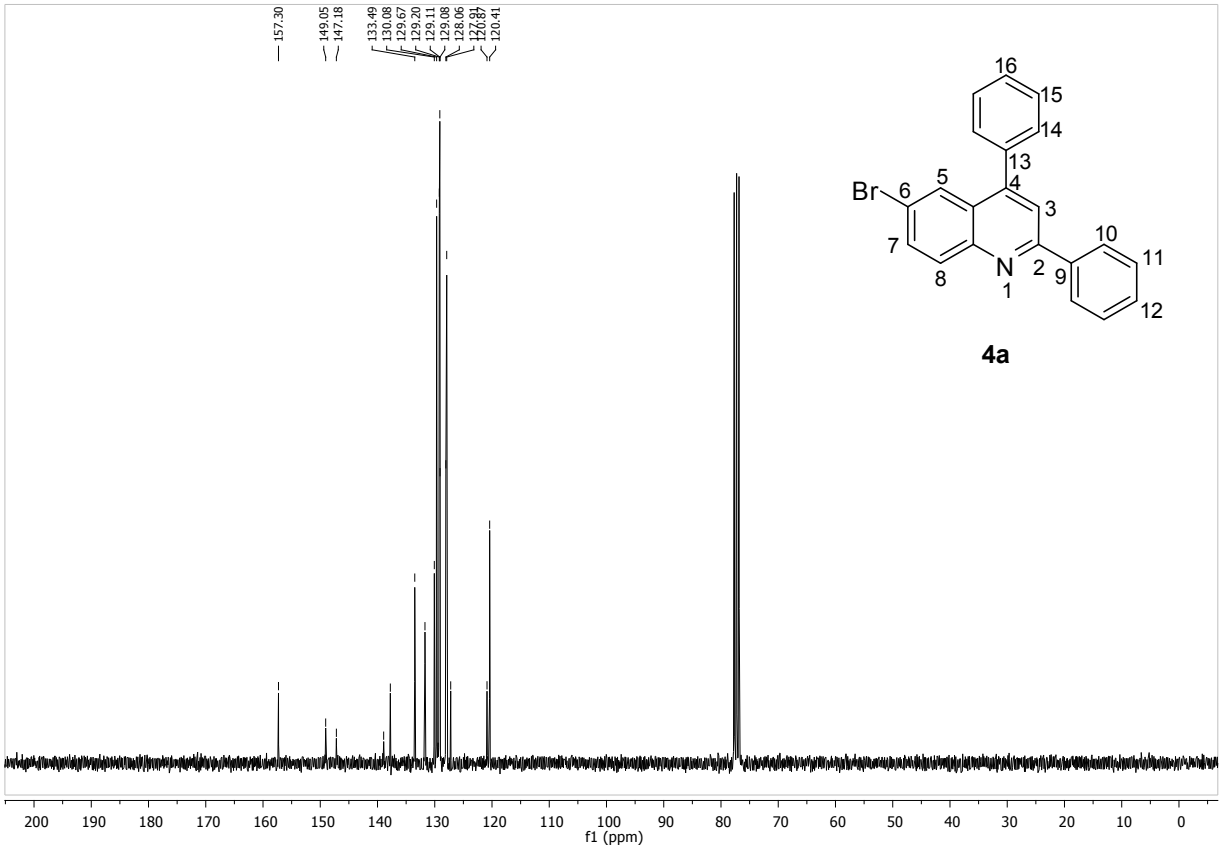
IV (cm^{-1}) $\bar{\nu}_{max}$ 3054, 1696. 1586, 1547, 1490, 1354, 1260, 1159, 1026, 894, 839, 772, 700, 590.

CG-MS (EI) *m/z* (abundance %): 281 (100, M^+), 204 (13), 203 (15), 129 (30), 127 (11), 77 (10).

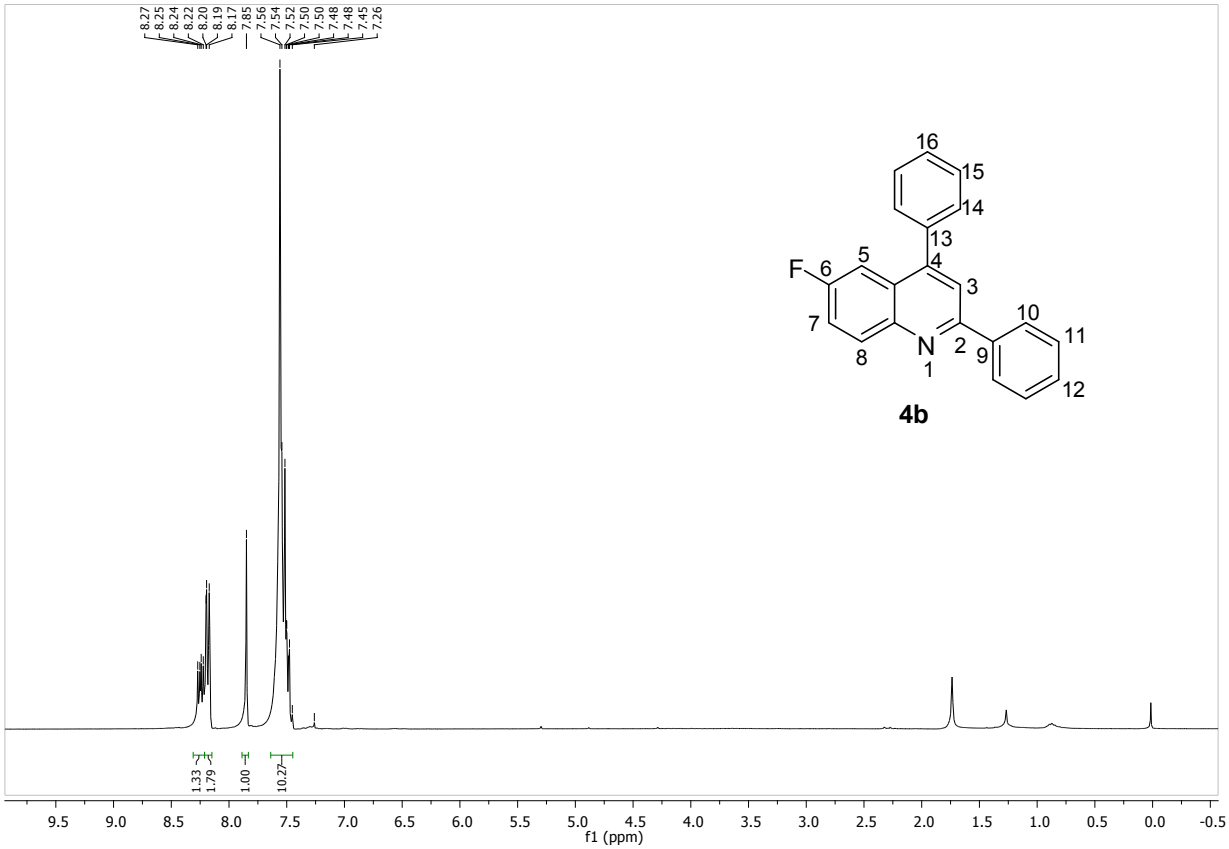
^{1}H NMR AND ^{13}C NMR SPECTRA FOR ALL COMPOUNDS



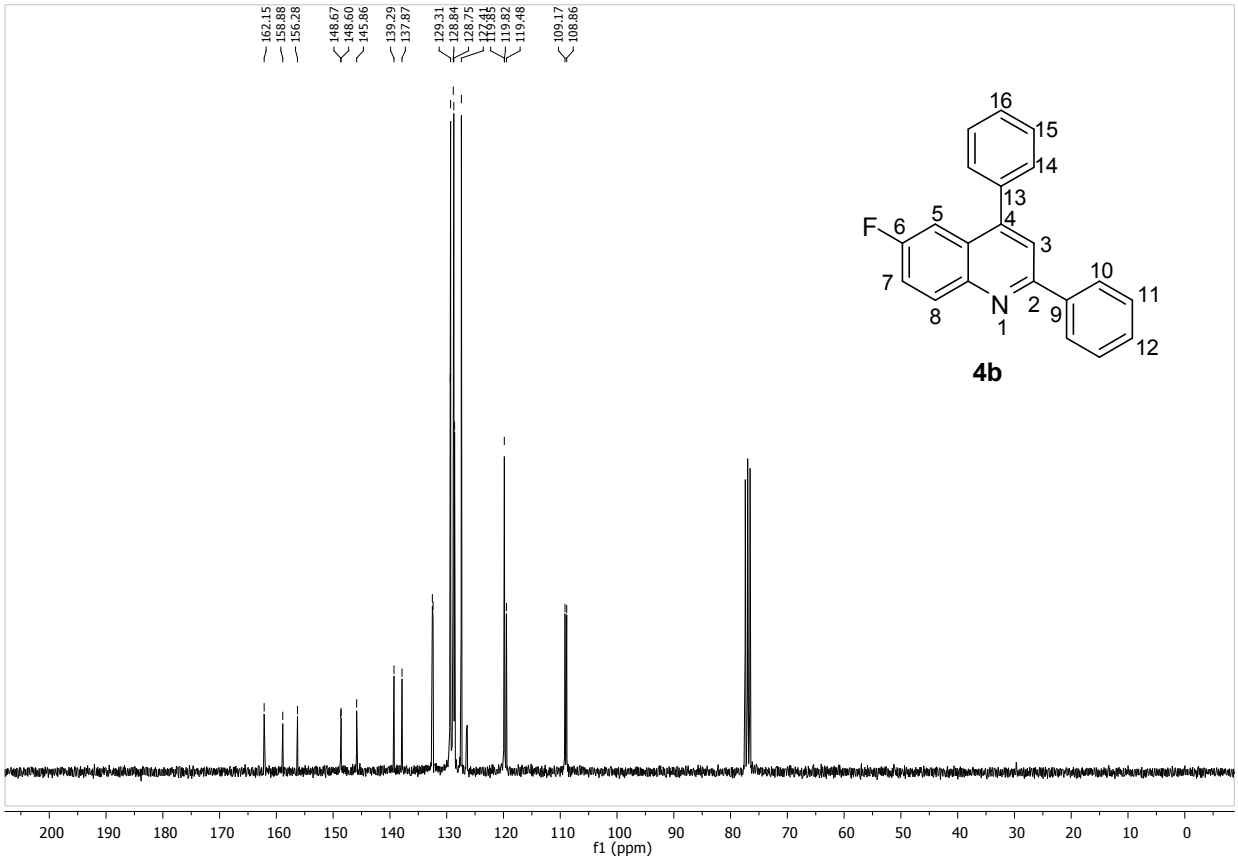
^{1}H NMR (300 MHz, $CDCl_3$) of **4a**.



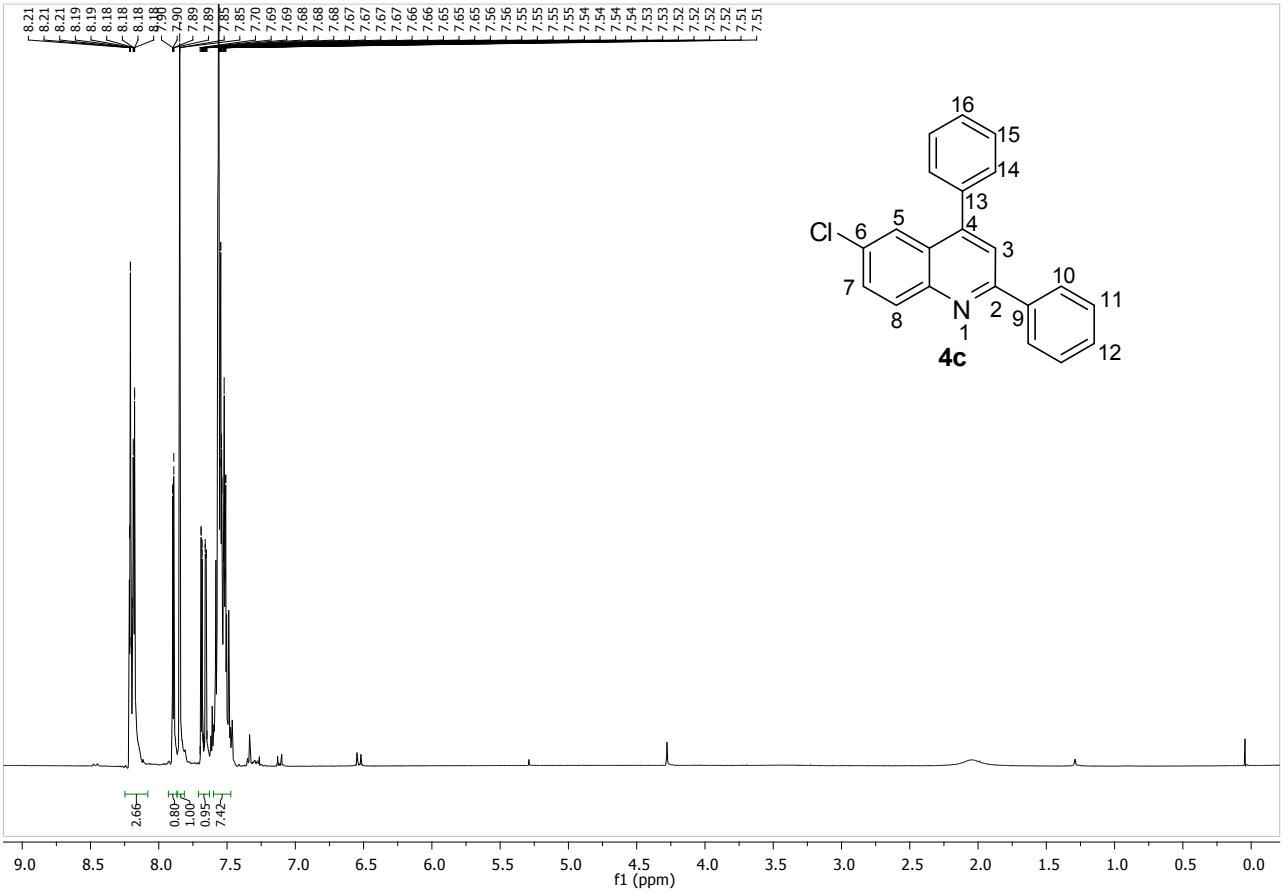
^{13}C NMR (75 MHz, $CDCl_3$) of **4a**.



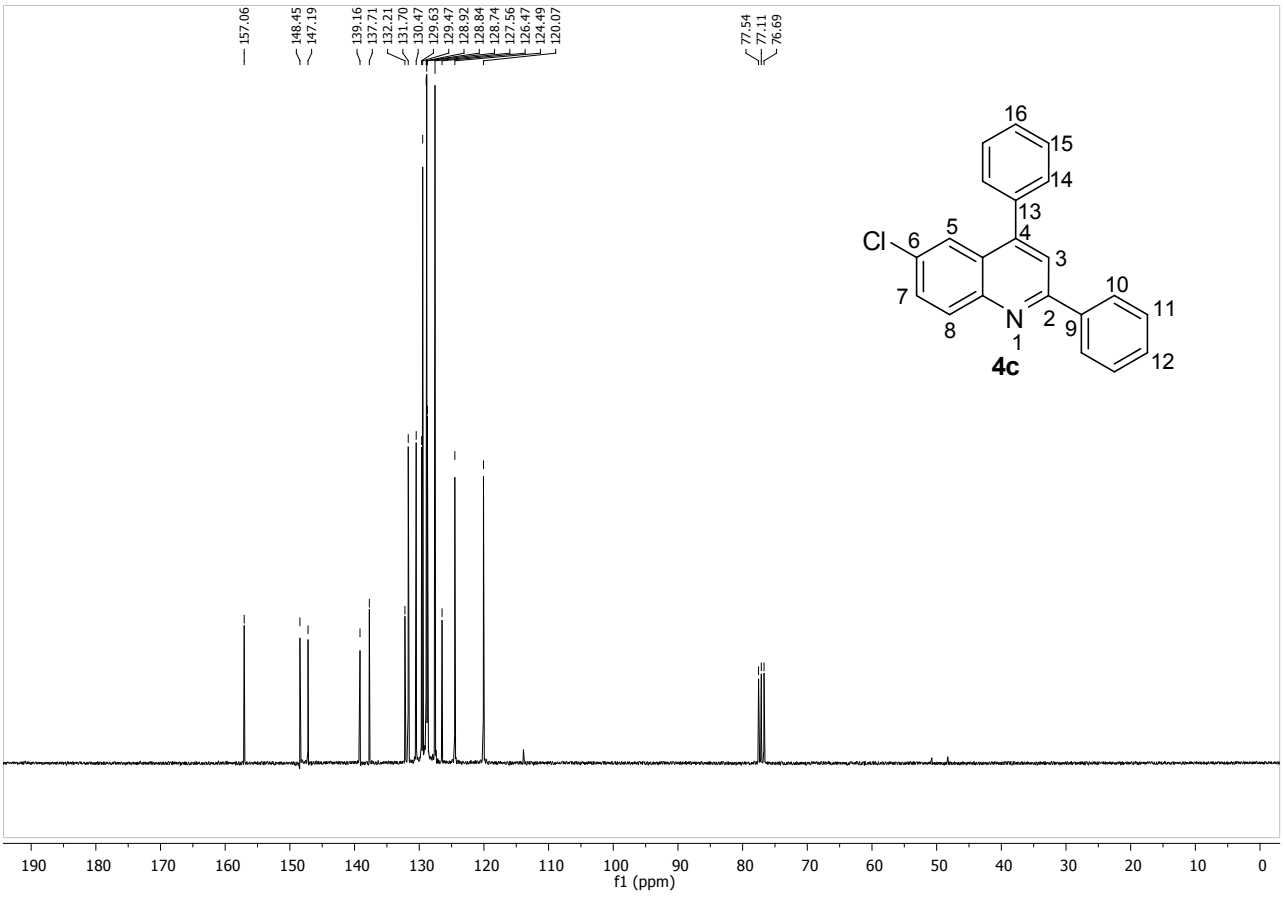
^{1}H NMR (300 MHz, $CDCl_3$) of **4b**.



^{13}C NMR (75 MHz, $CDCl_3$) of **4b**.

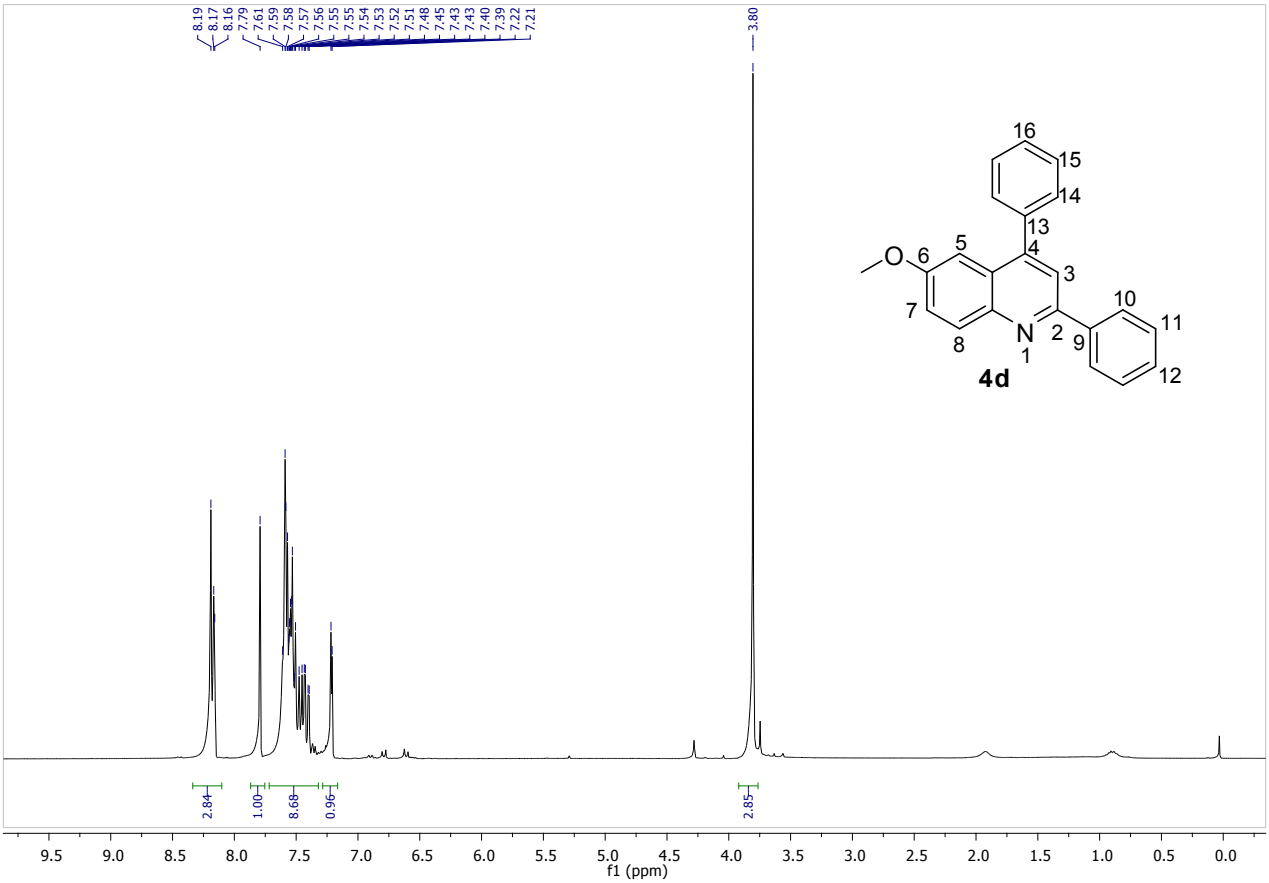


^{1}H NMR (300 MHz, $CDCl_3$) of **4c**.

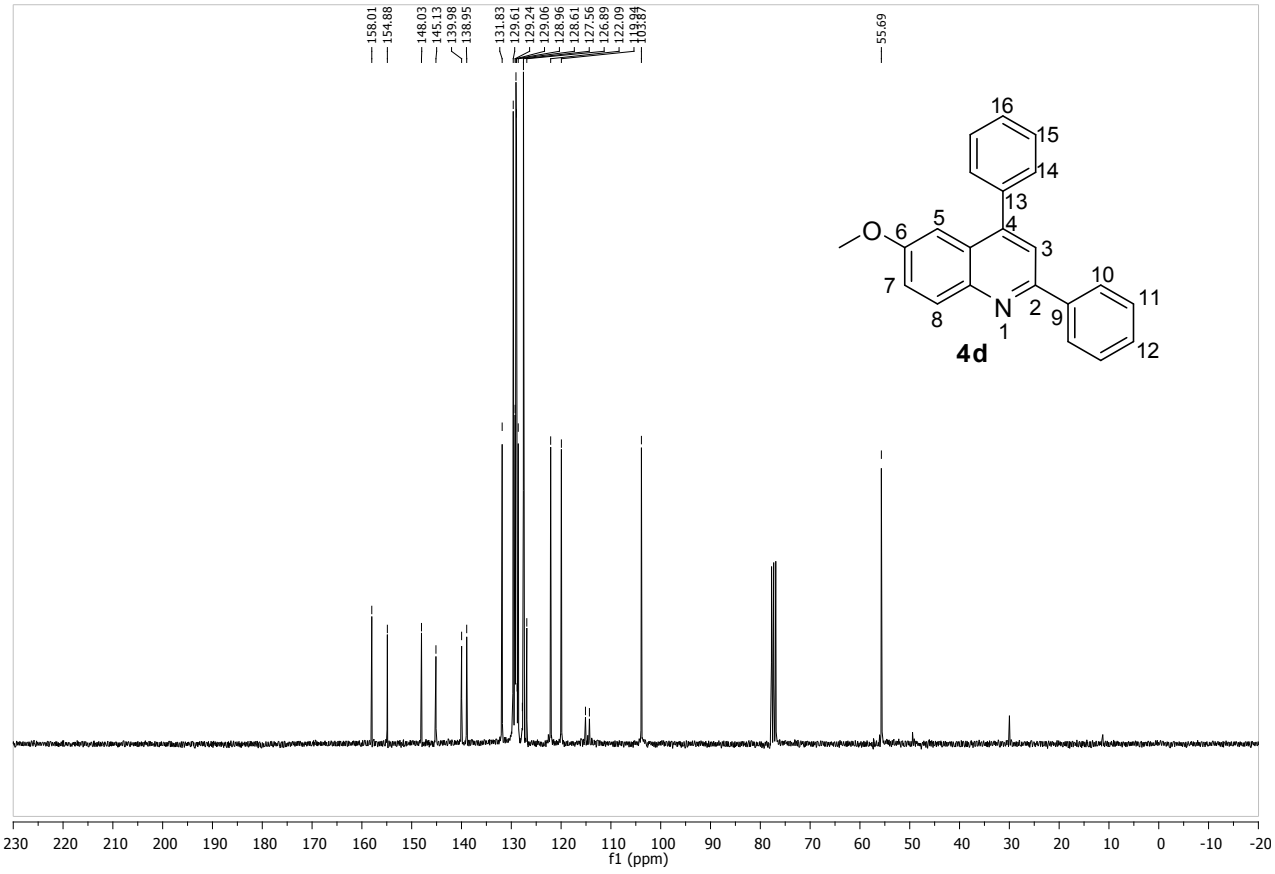


^{13}C NMR (75 MHz, $CDCl_3$) of **4c**.

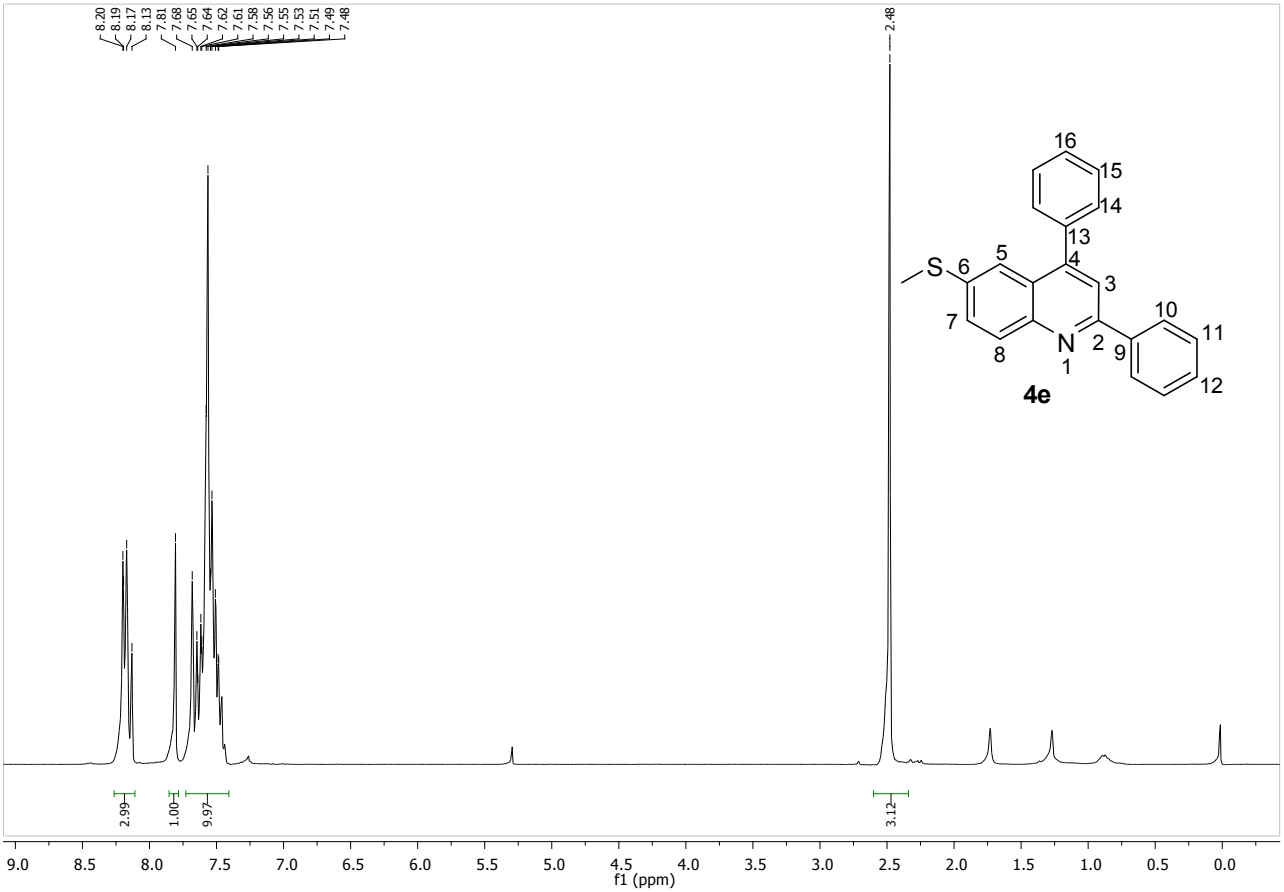
4d



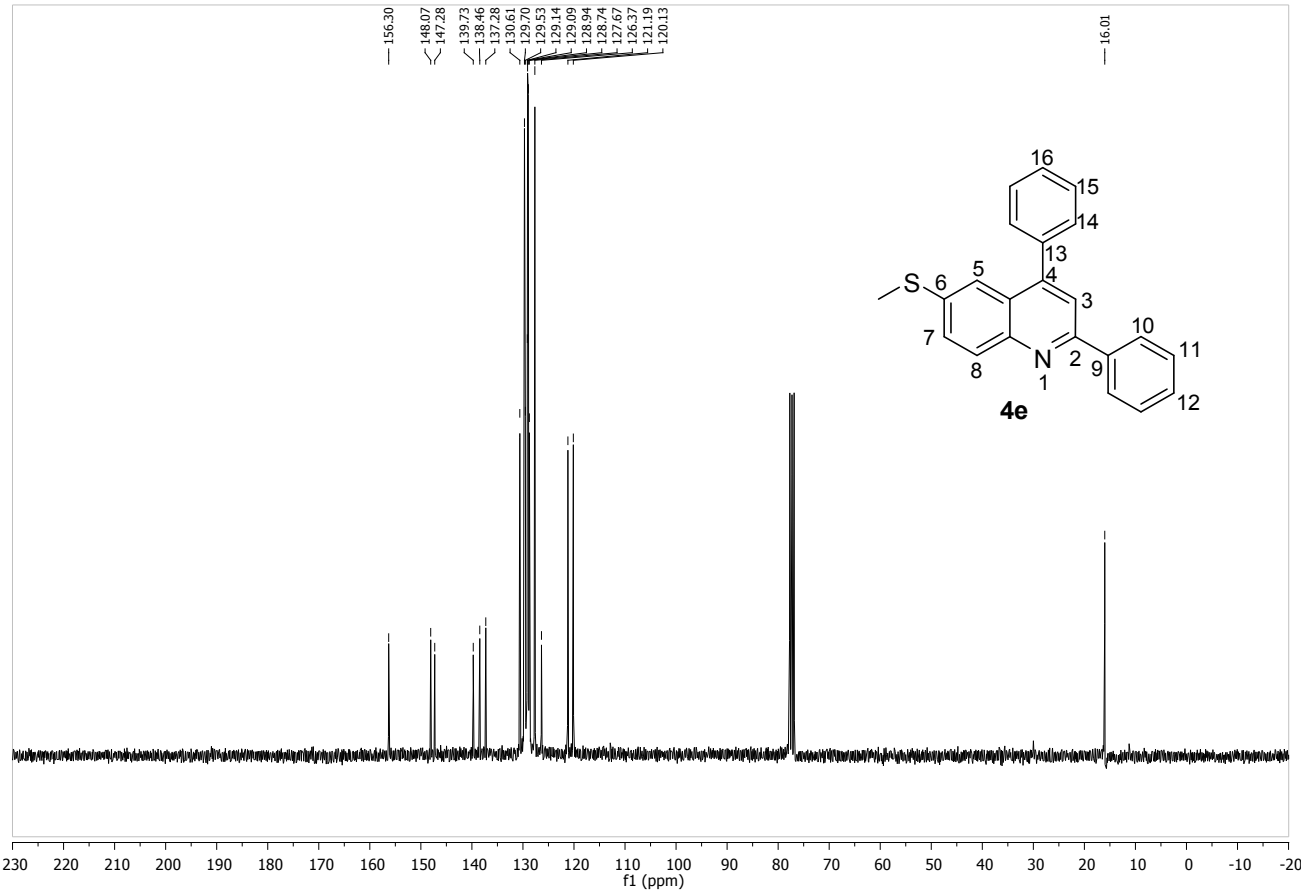
^{1}H NMR (300 MHz, $CDCl_3$) of **4d**.



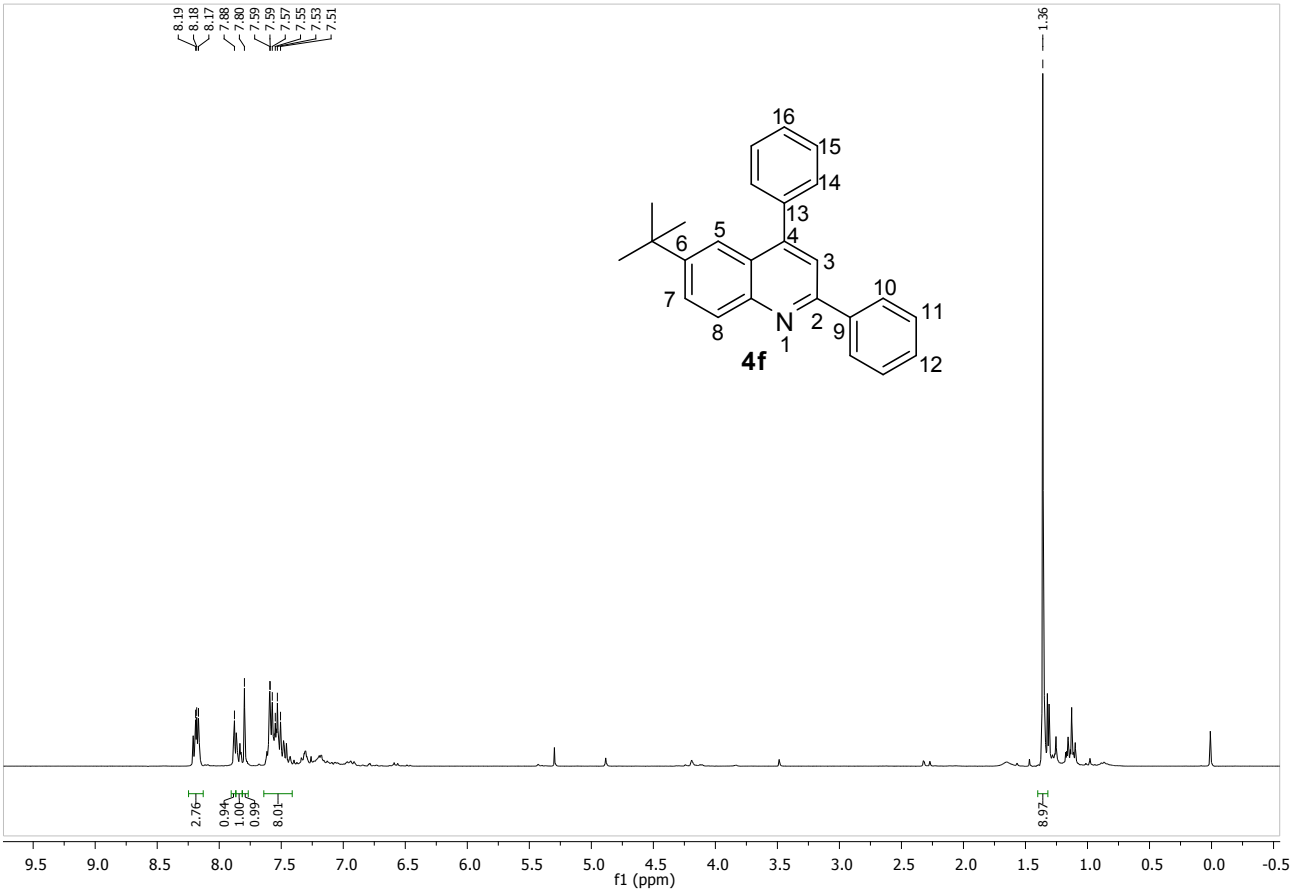
^{13}C NMR (75 MHz, $CDCl_3$) of **4d**.



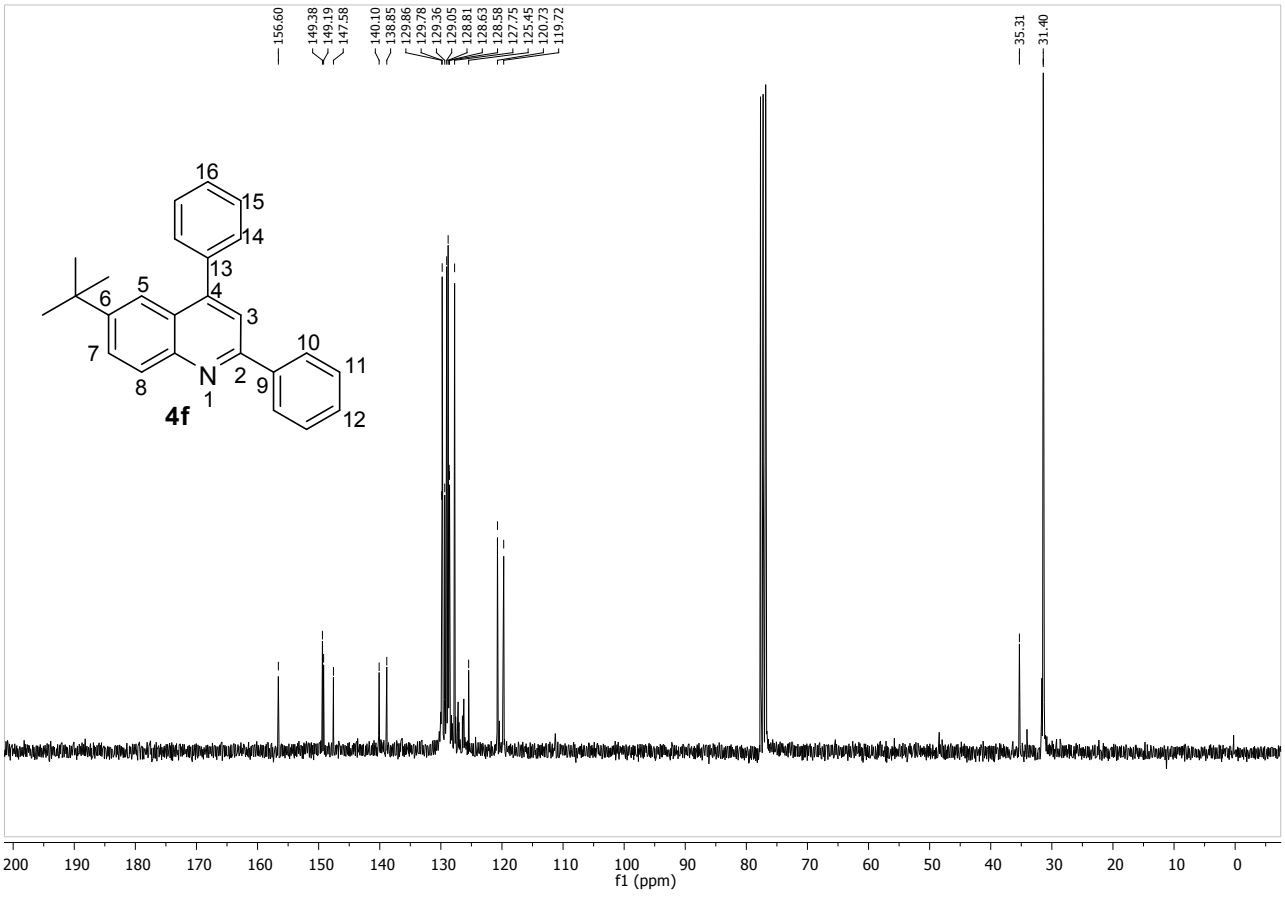
^{1}H NMR (300 MHz, $CDCl_3$) of **4e**.



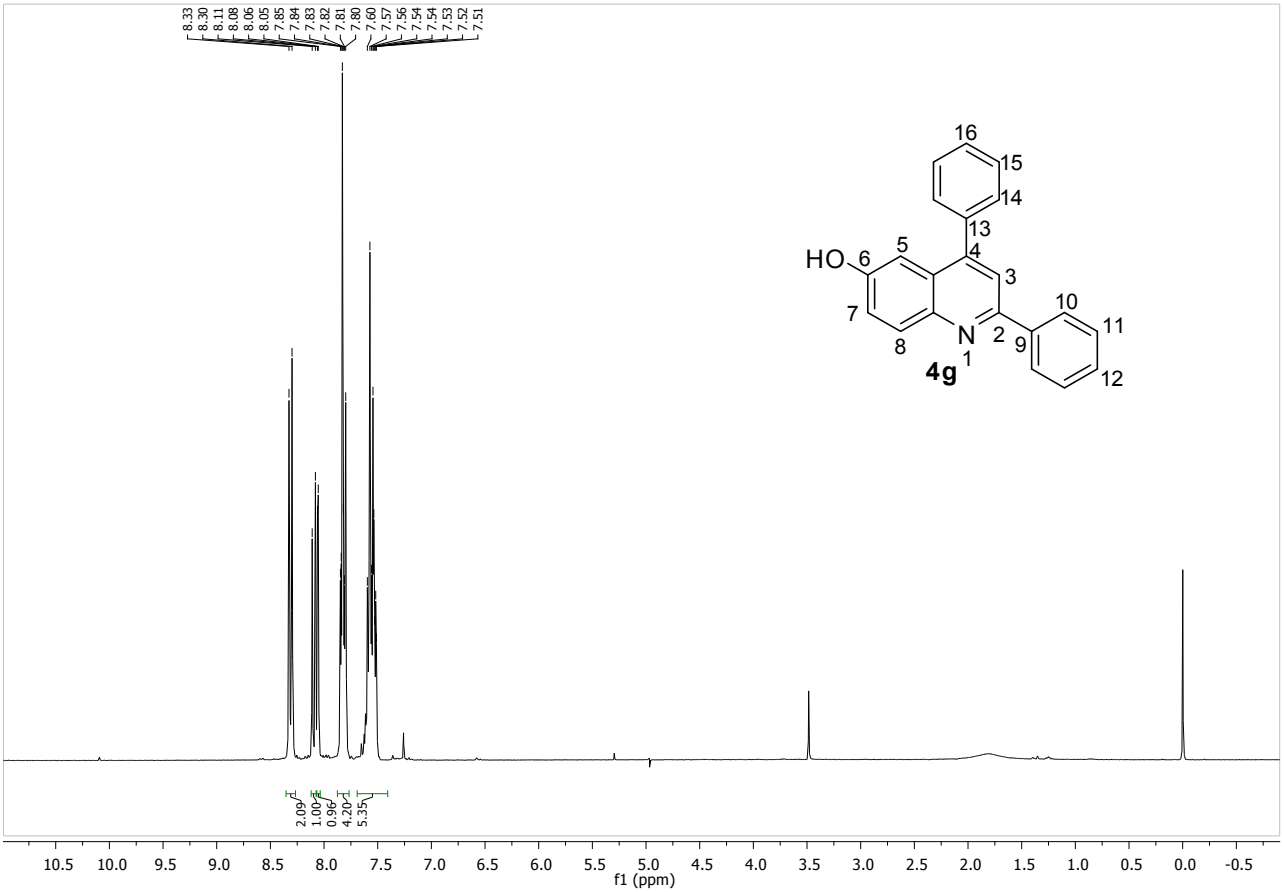
^{13}C NMR (75 MHz, $CDCl_3$) of **4e**.



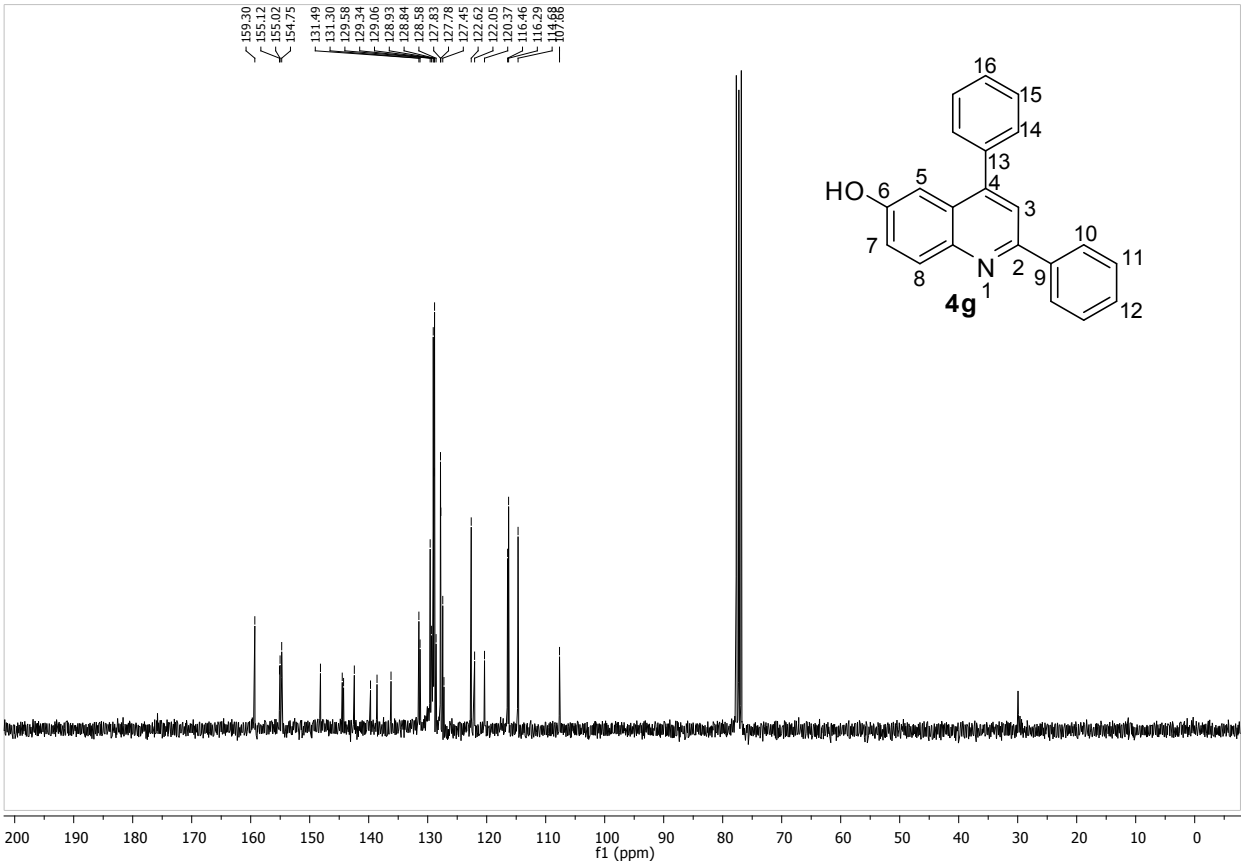
^{1}H NMR (300 MHz, $CDCl_3$) of **4f**.



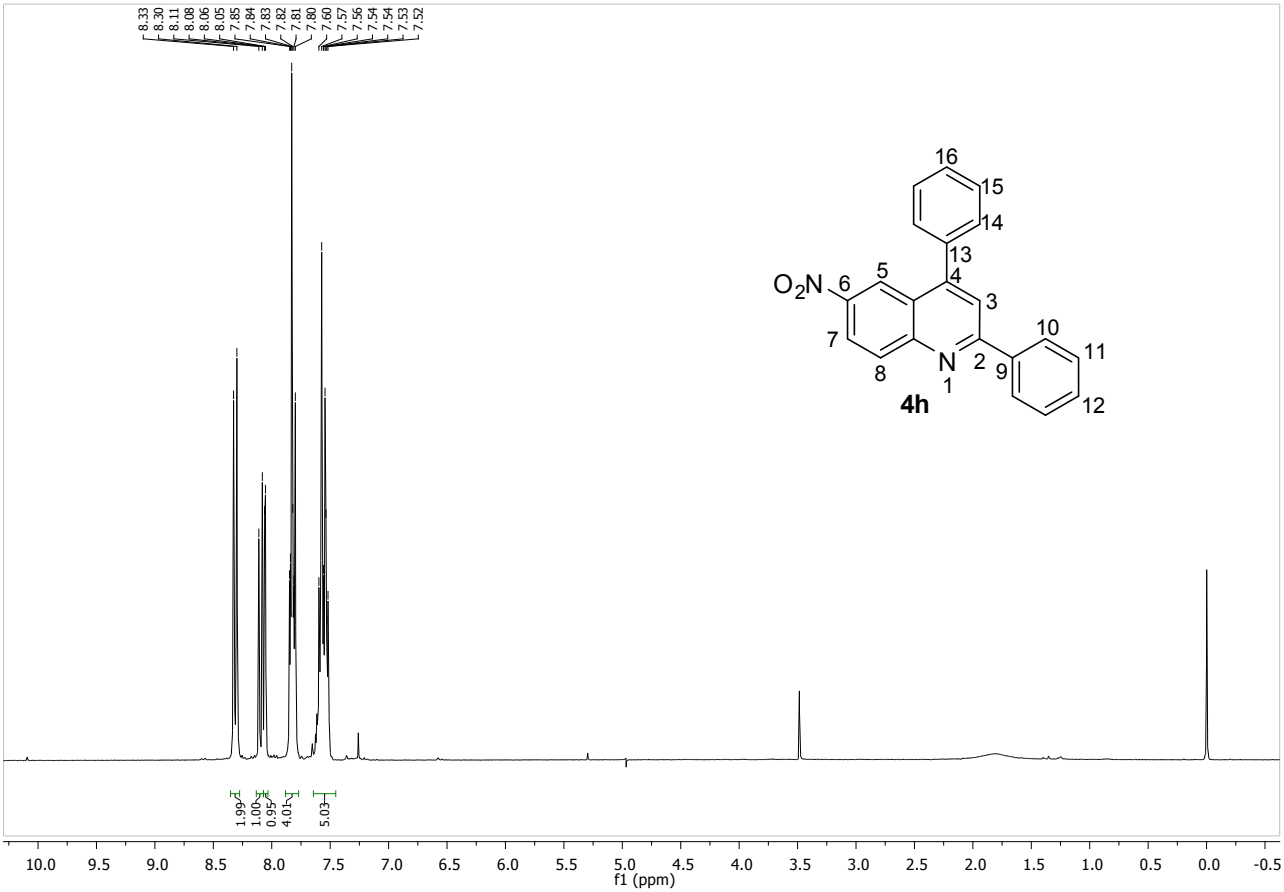
^{13}C NMR (75 MHz, $CDCl_3$) of **4f**.



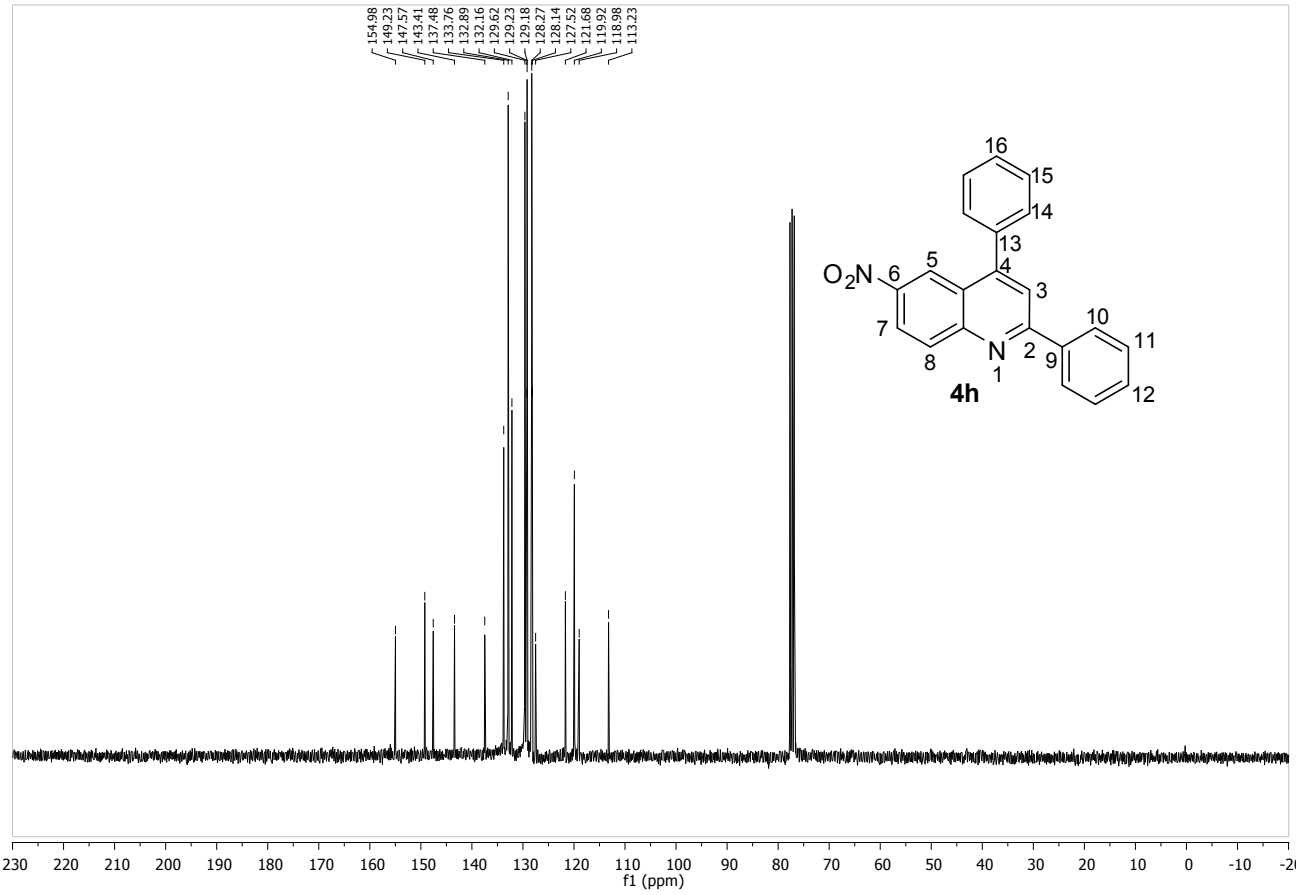
^{1}H NMR (300 MHz, $CDCl_3$) of **4g**.



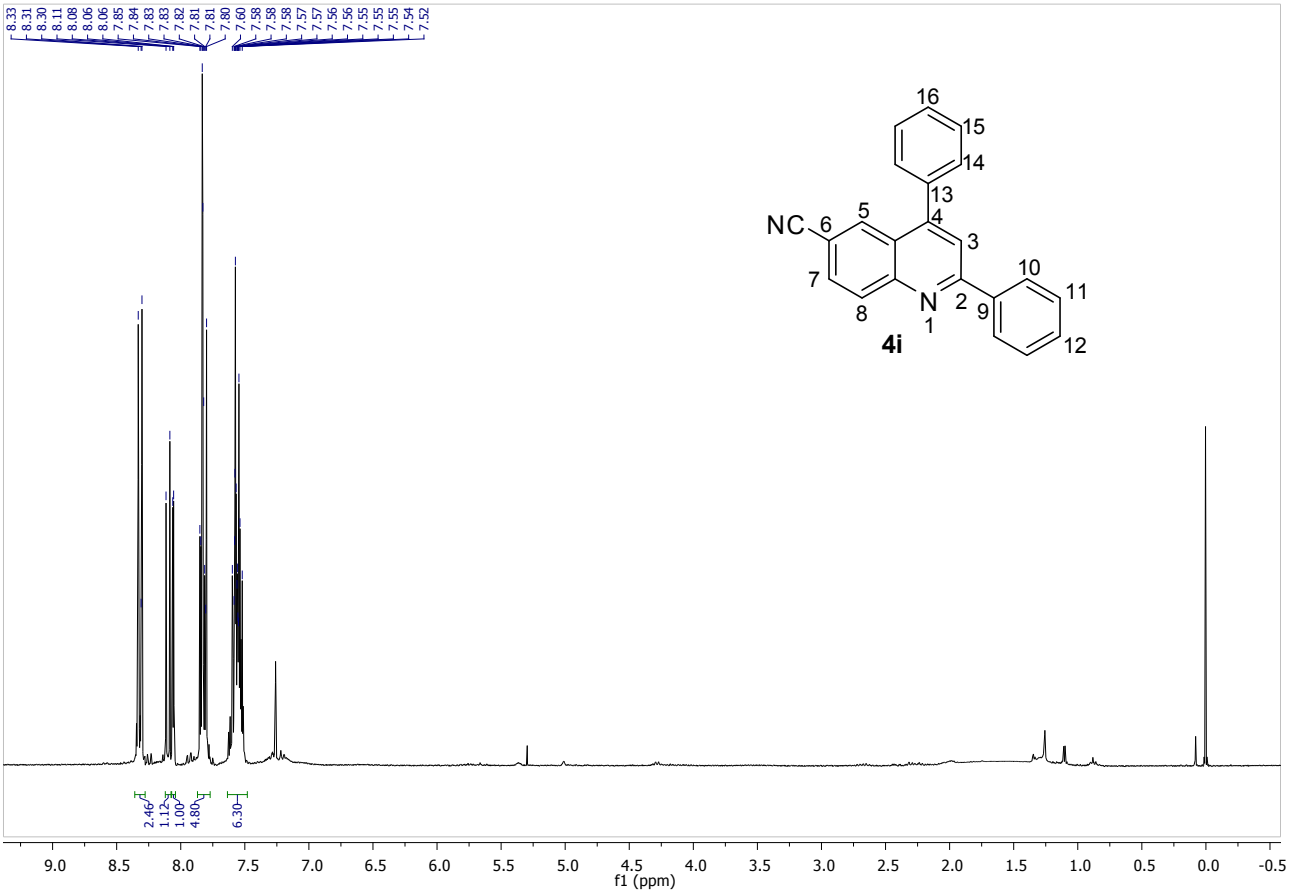
^{13}C NMR (75 MHz, $CDCl_3$) of **4g**.



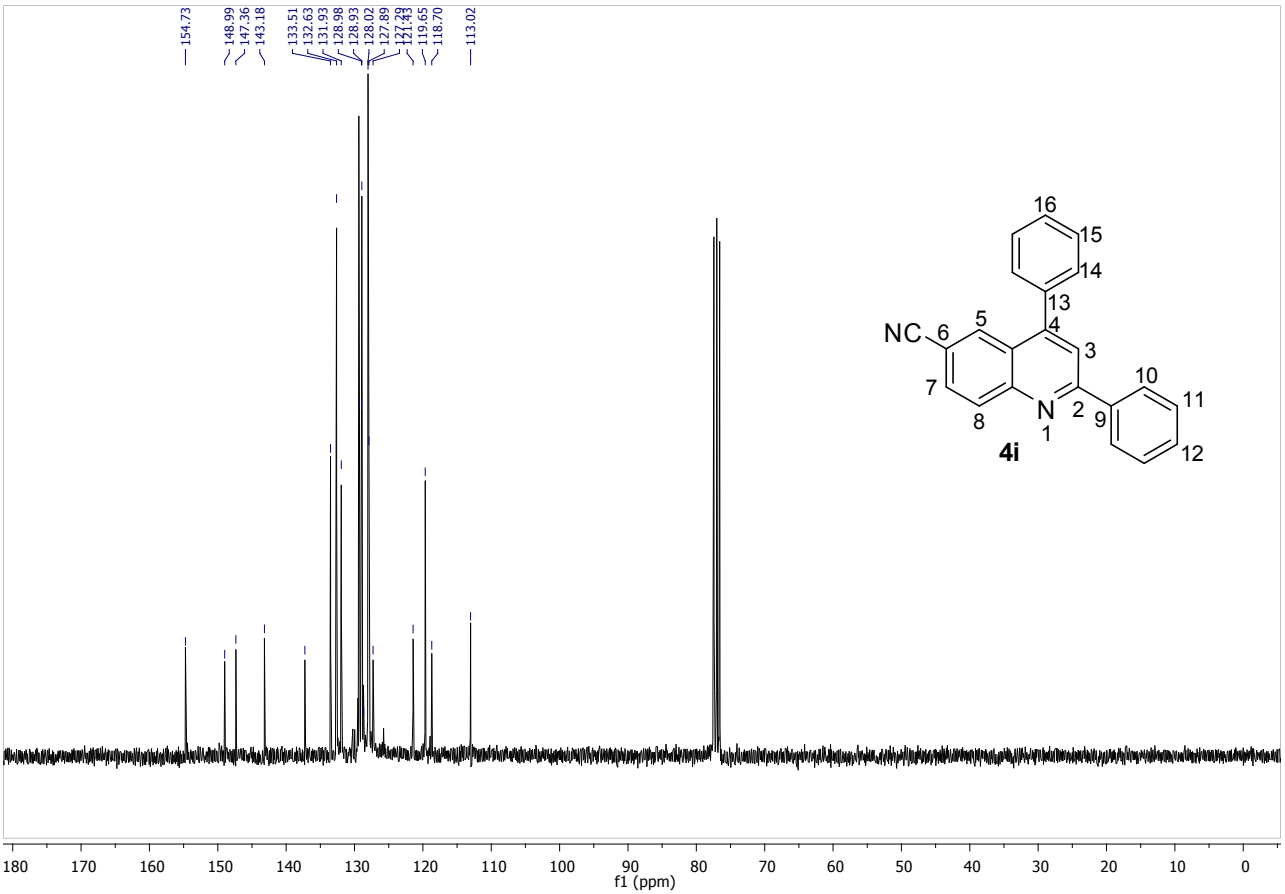
^{1}H NMR (300 MHz, $CDCl_3$) of **4h**.



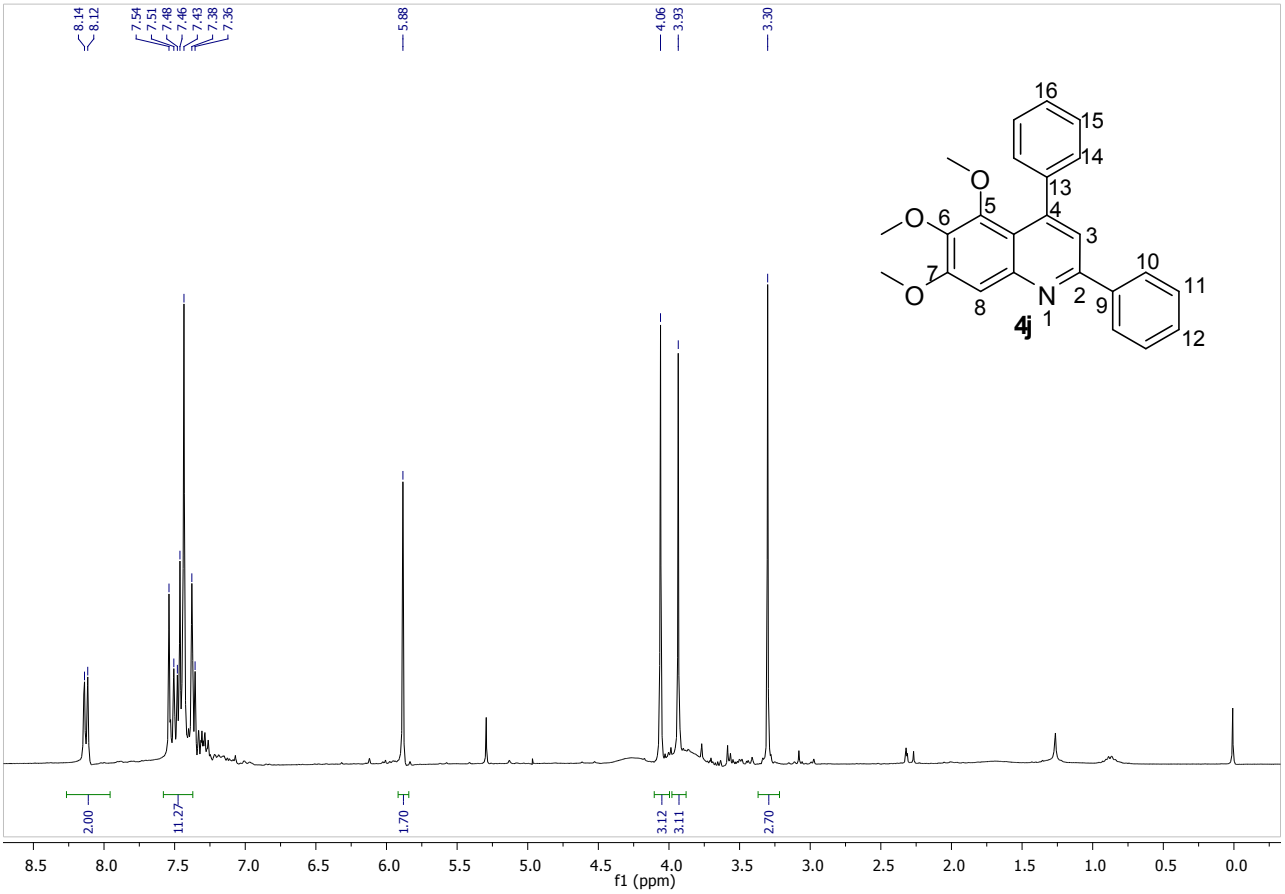
^{13}C NMR (75 MHz, $CDCl_3$) of **4h**.



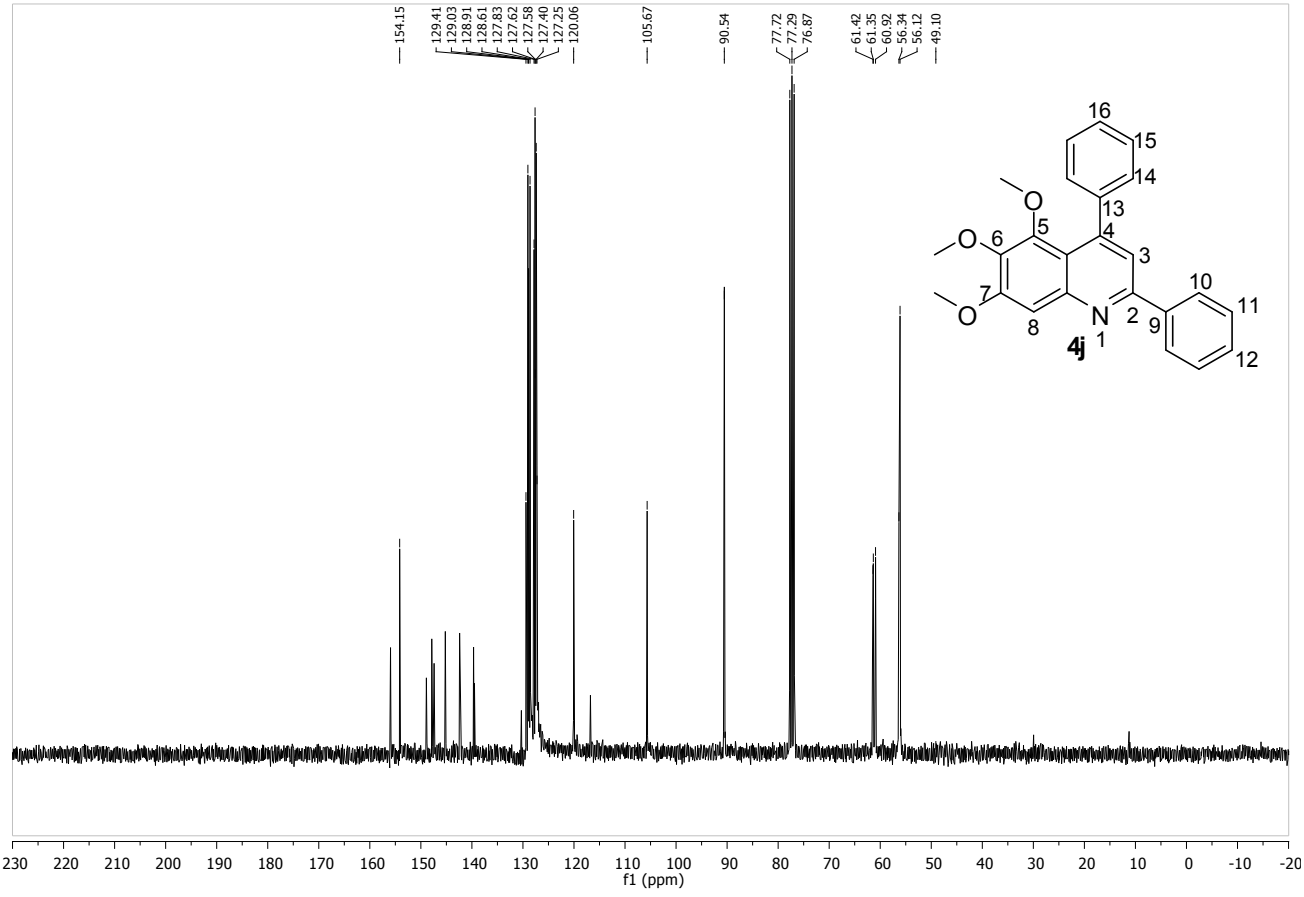
^{1}H NMR (300 MHz, $CDCl_3$) of **4i**.



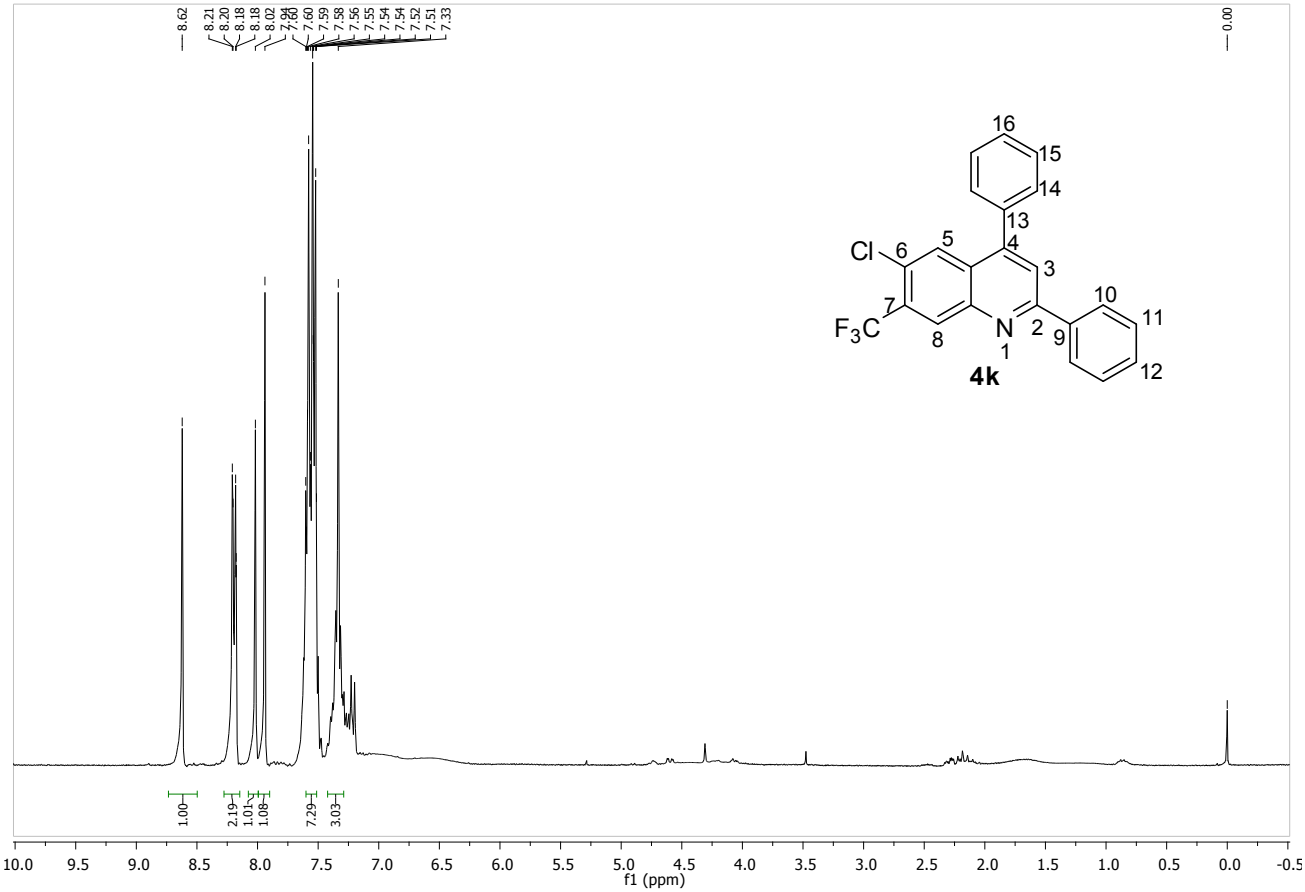
^{13}C NMR (75 MHz, $CDCl_3$) of **4i**.



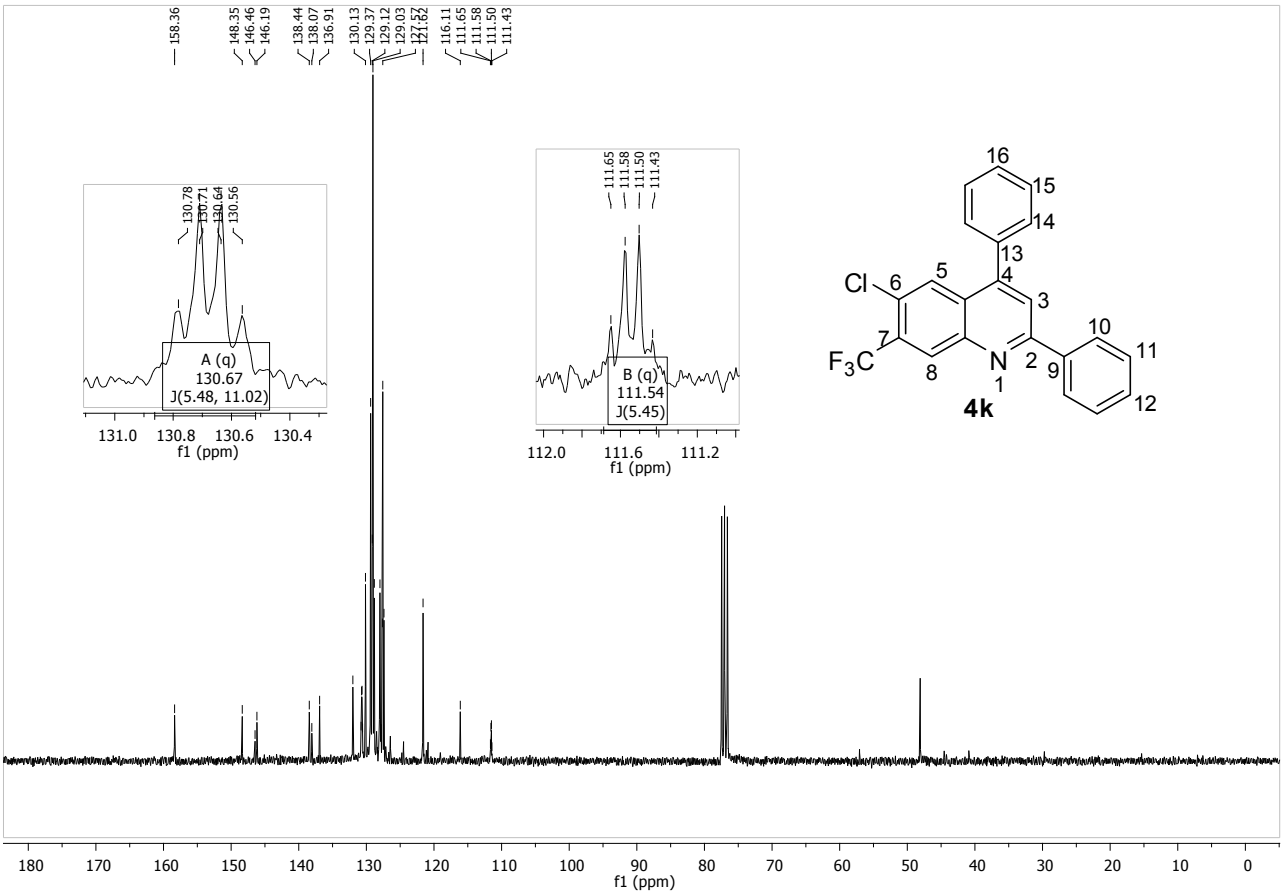
^{1}H NMR (300 MHz, $CDCl_3$) of **4j**.



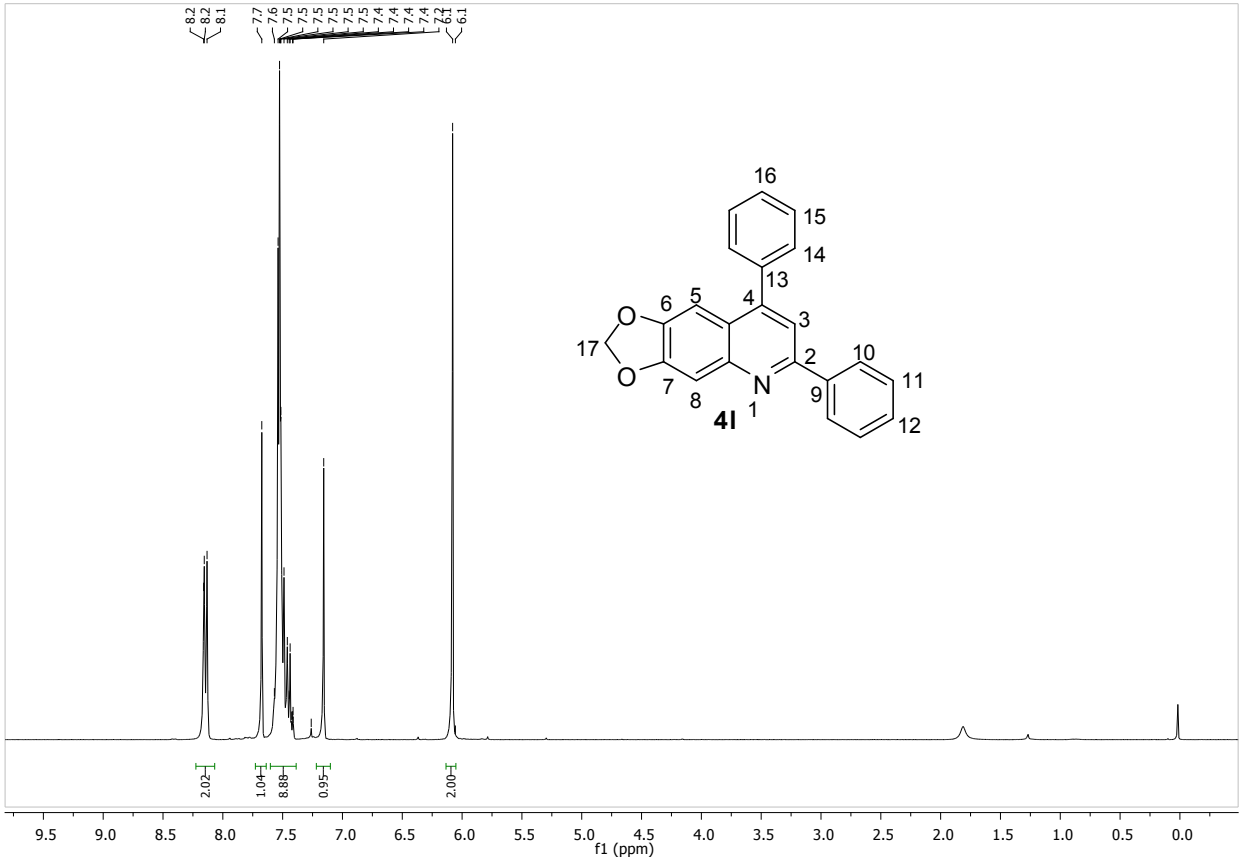
^{13}C NMR (75 MHz, $CDCl_3$) of **4j**.



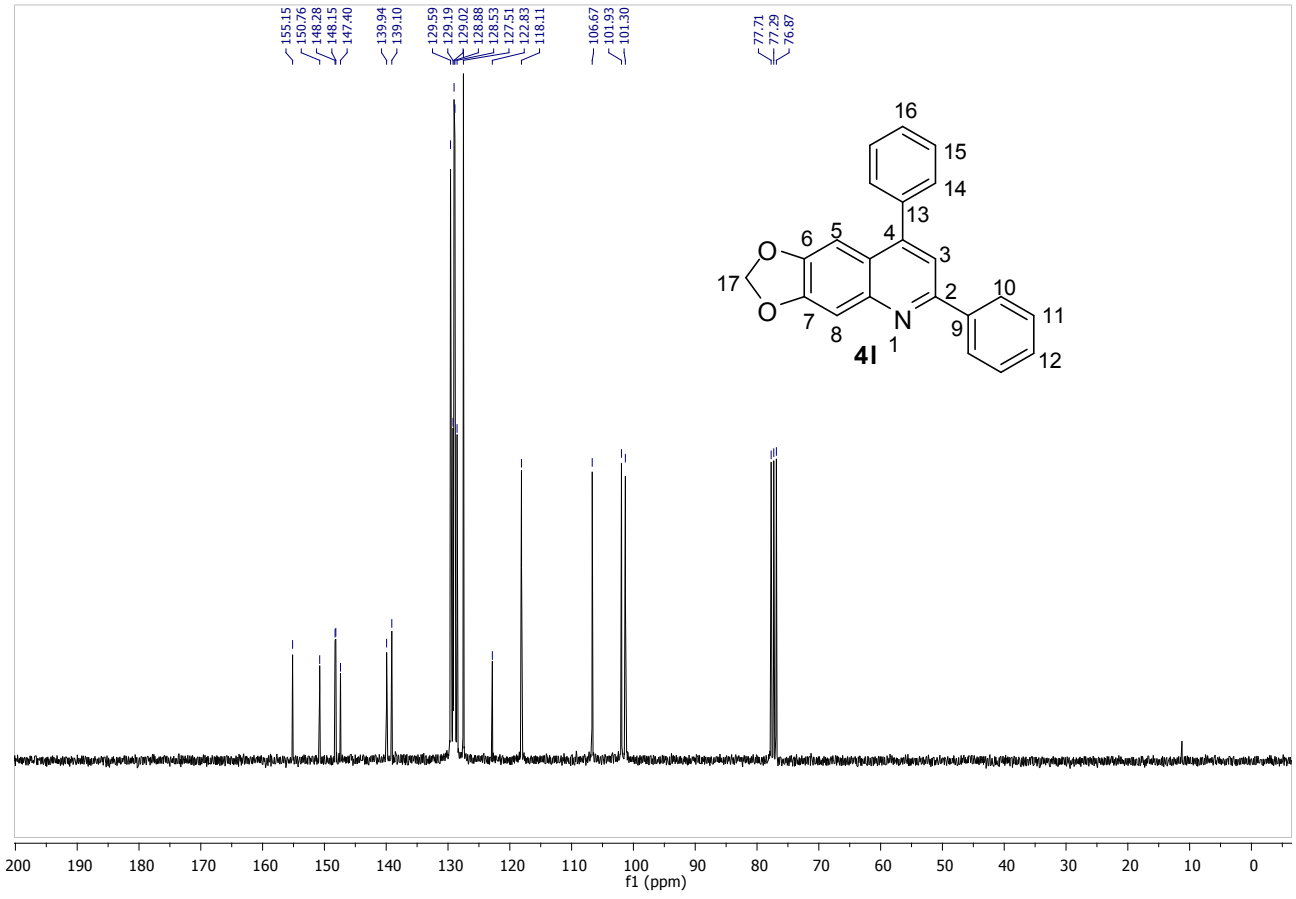
^{1}H NMR (300 MHz, $CDCl_3$) of **4k**.



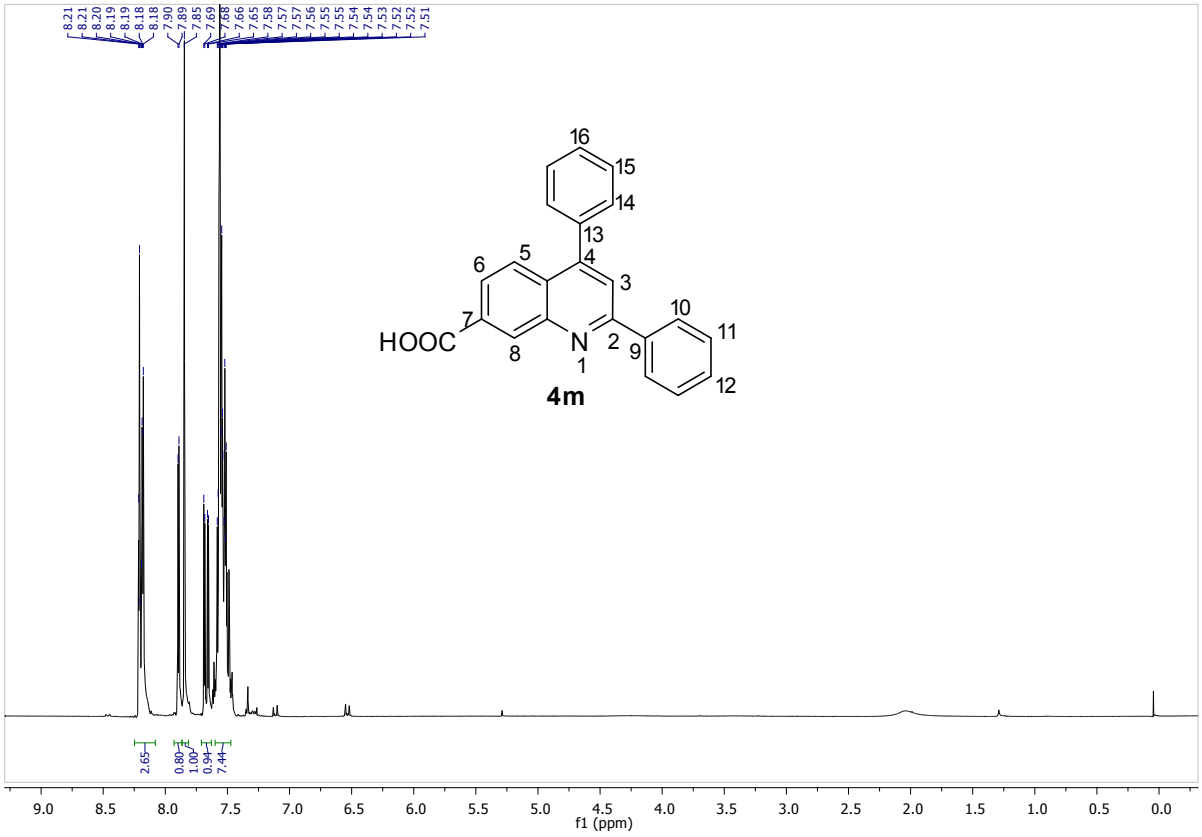
^{13}C NMR (75 MHz, $CDCl_3$) of **4k**.



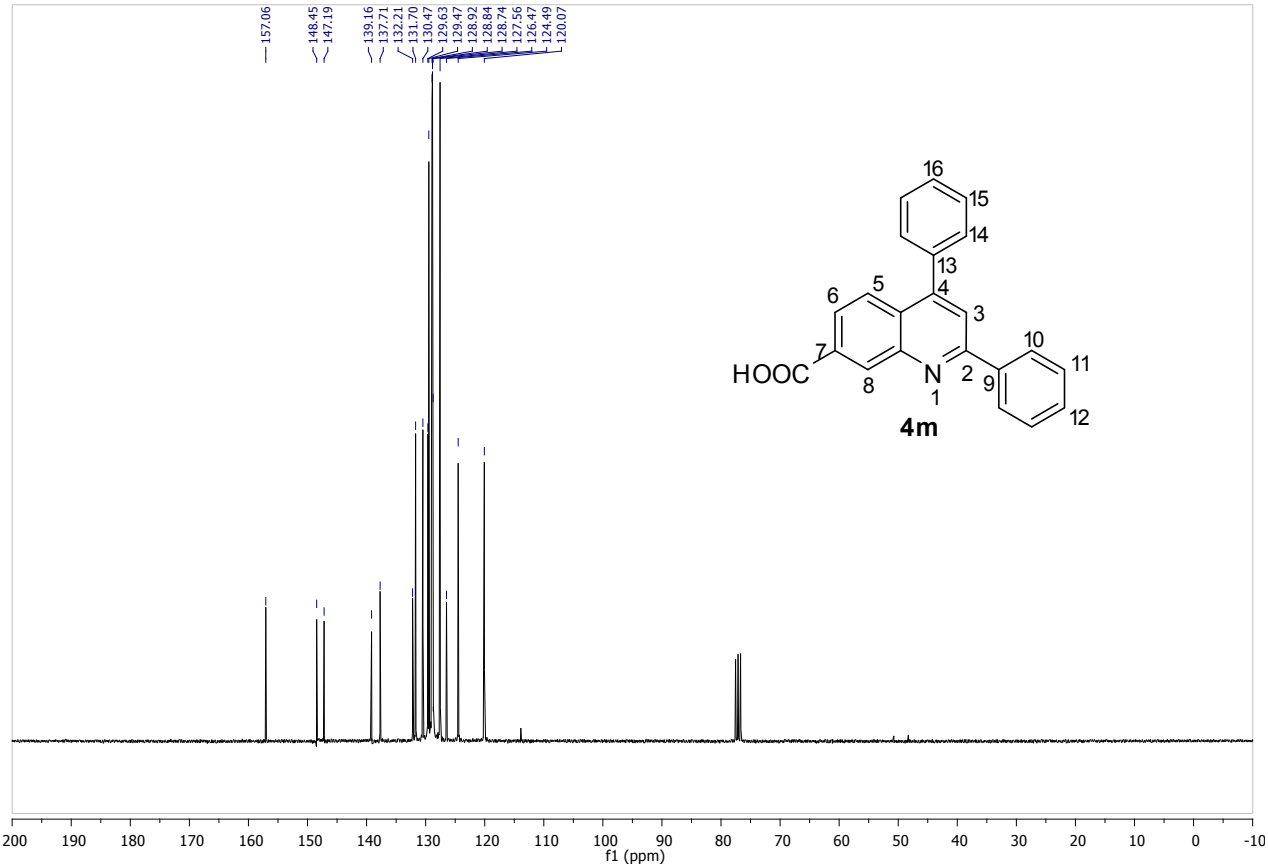
^{1}H NMR (300 MHz, $CDCl_3$) of **4l**.



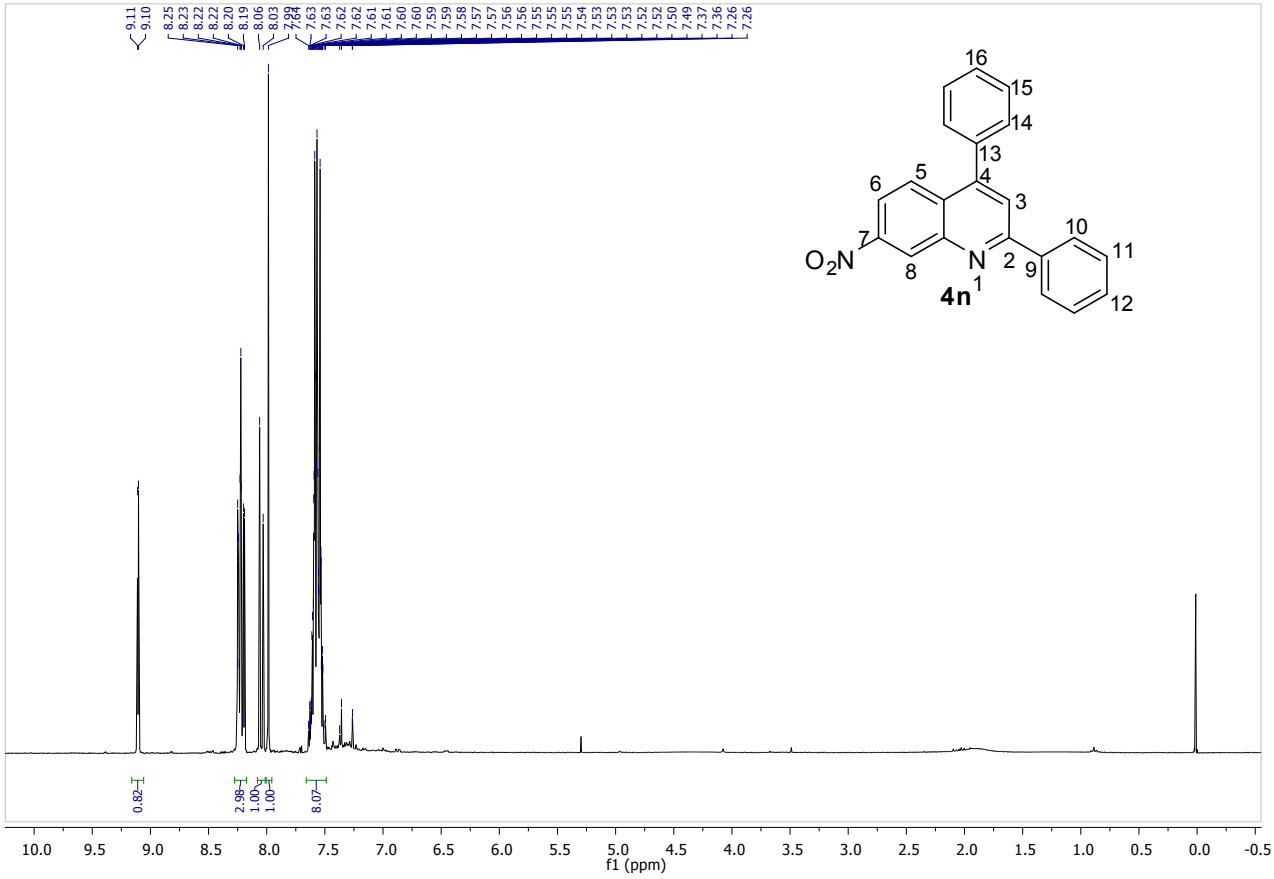
^{13}C NMR (75 MHz, $CDCl_3$) of **4l**.



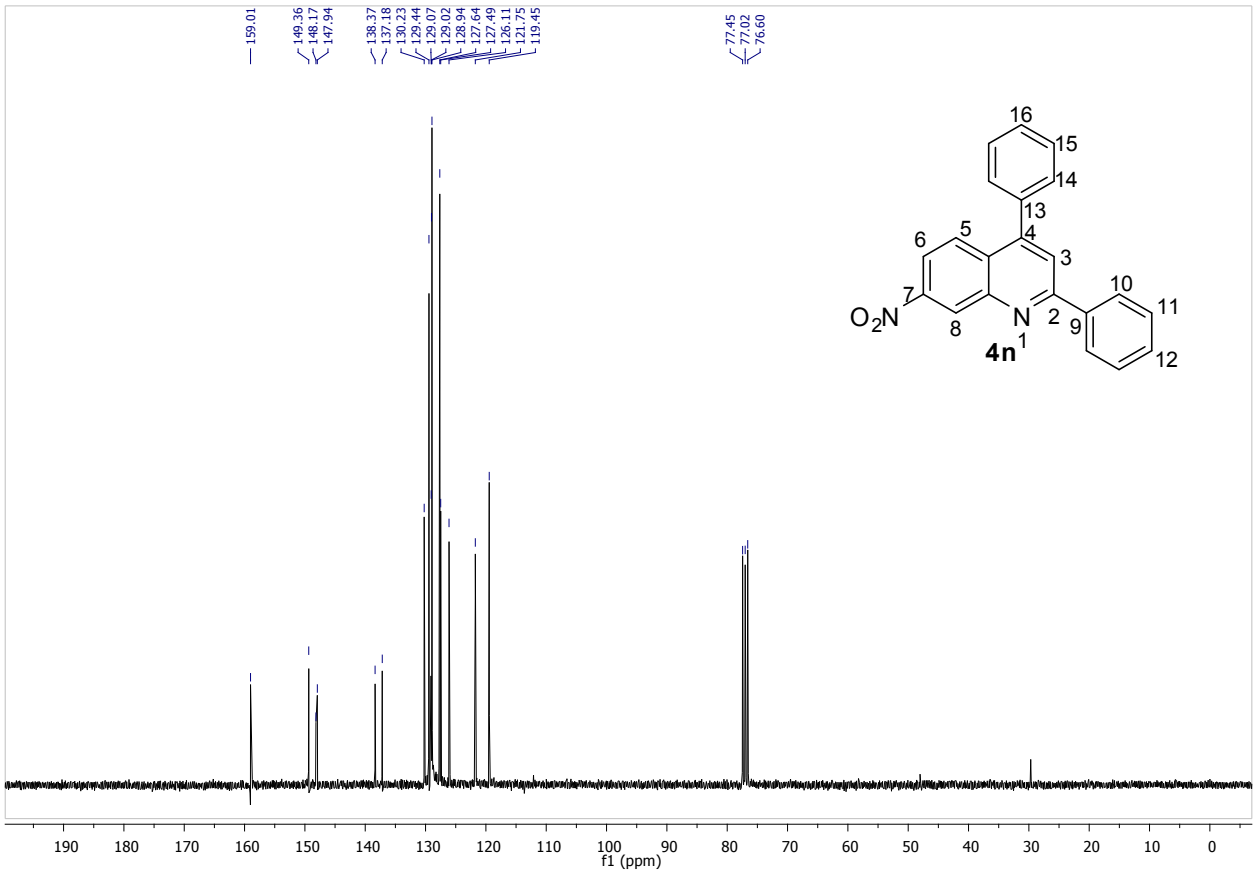
^{1}H NMR (300 MHz, $CDCl_3$) of **4m**.



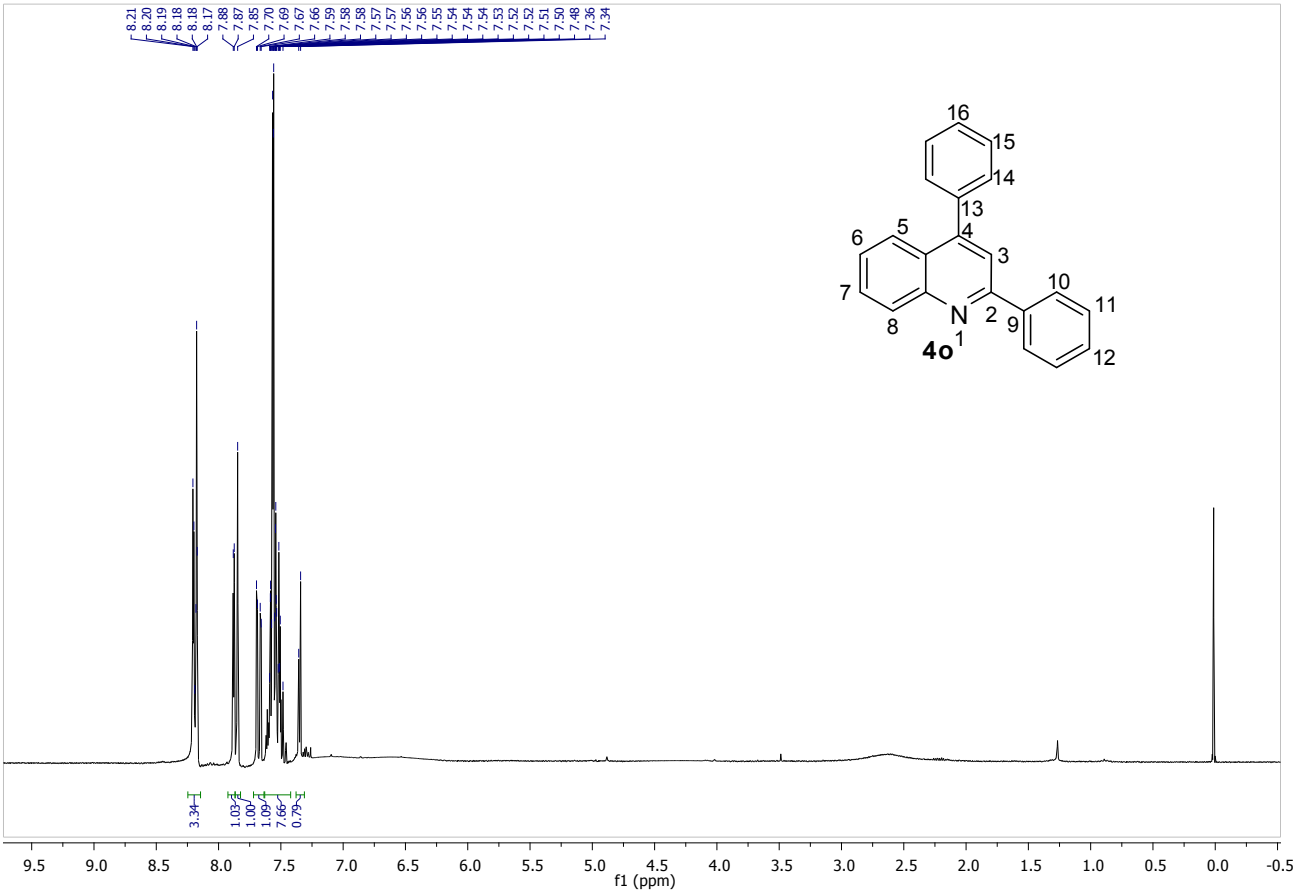
^{13}C NMR (75 MHz, $CDCl_3$) of **4m**.



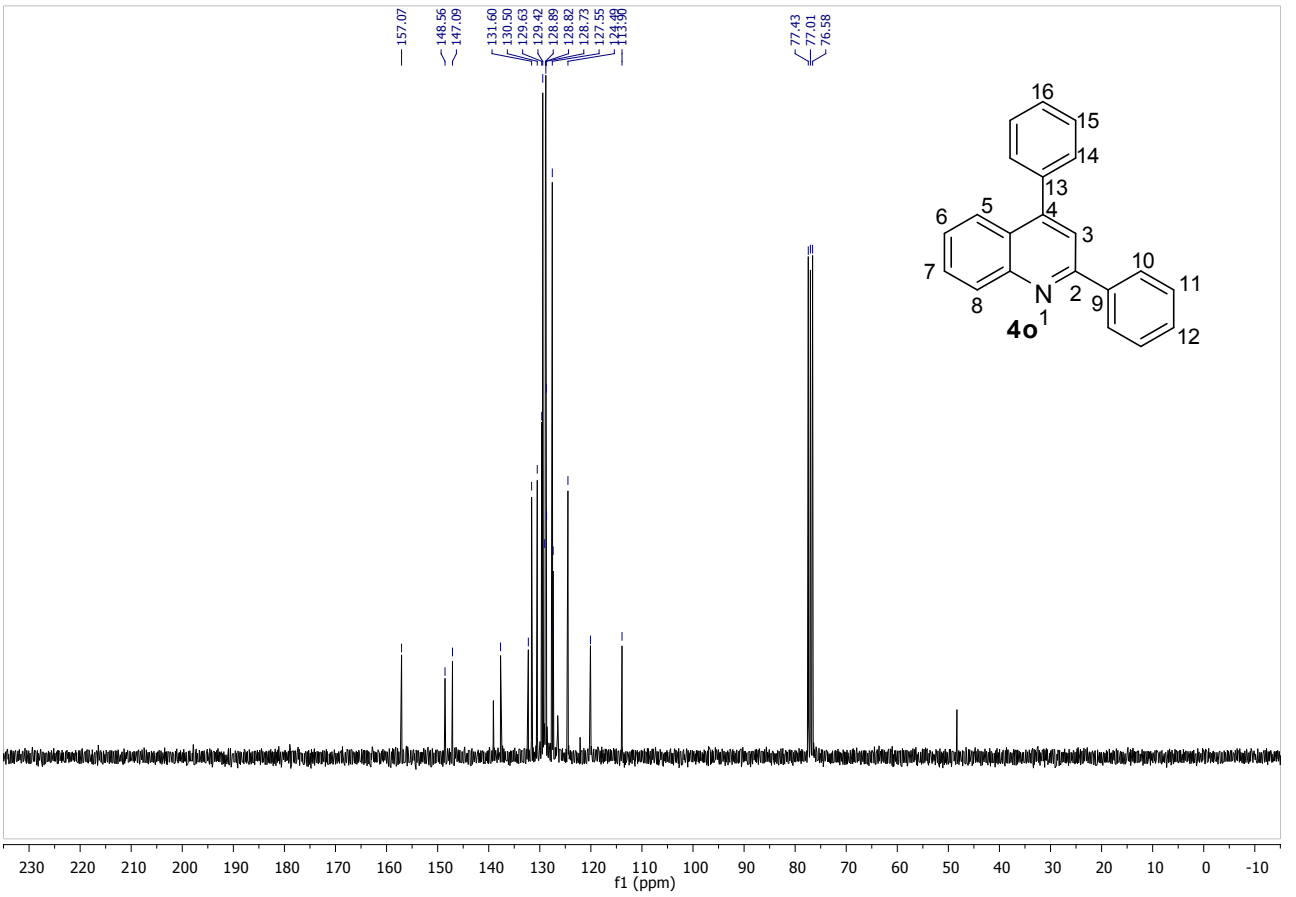
^{1}H NMR (300 MHz, $CDCl_3$) of **4n**.



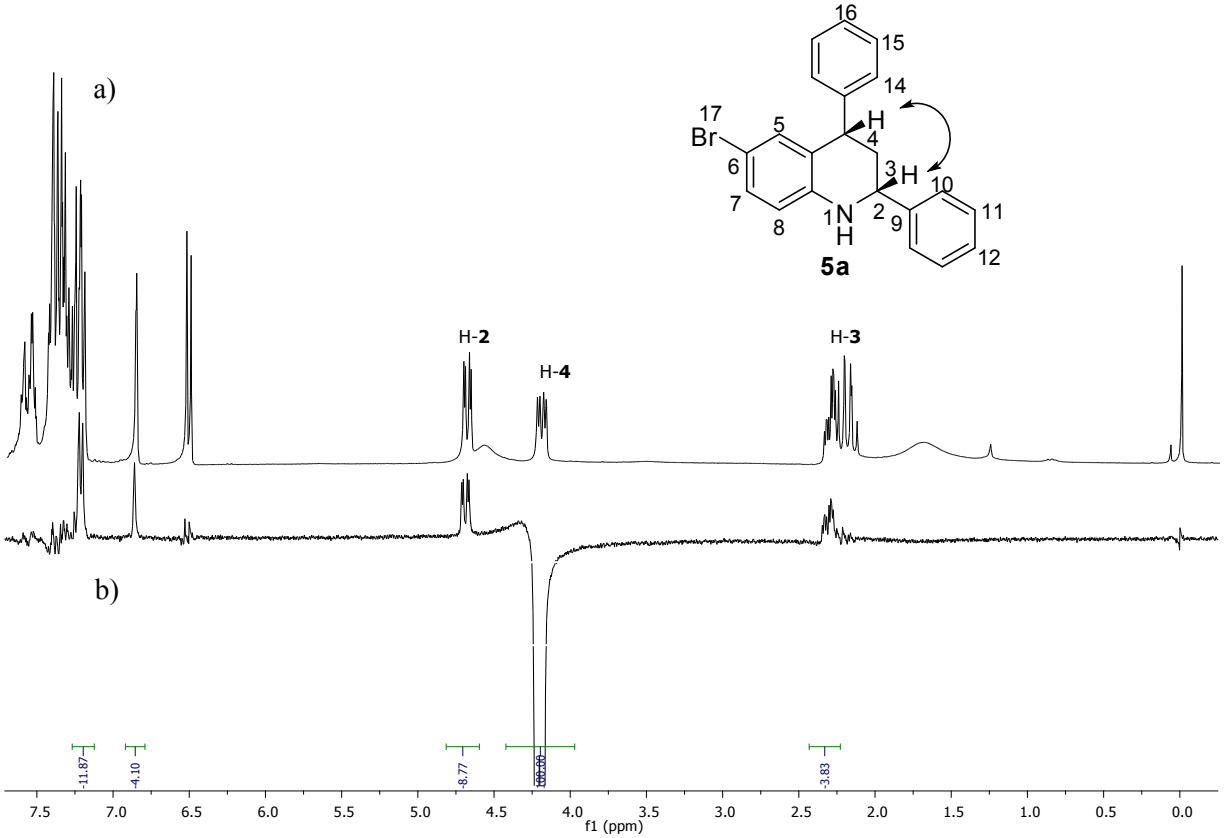
^{13}C NMR (75 MHz, $CDCl_3$) of **4n**.



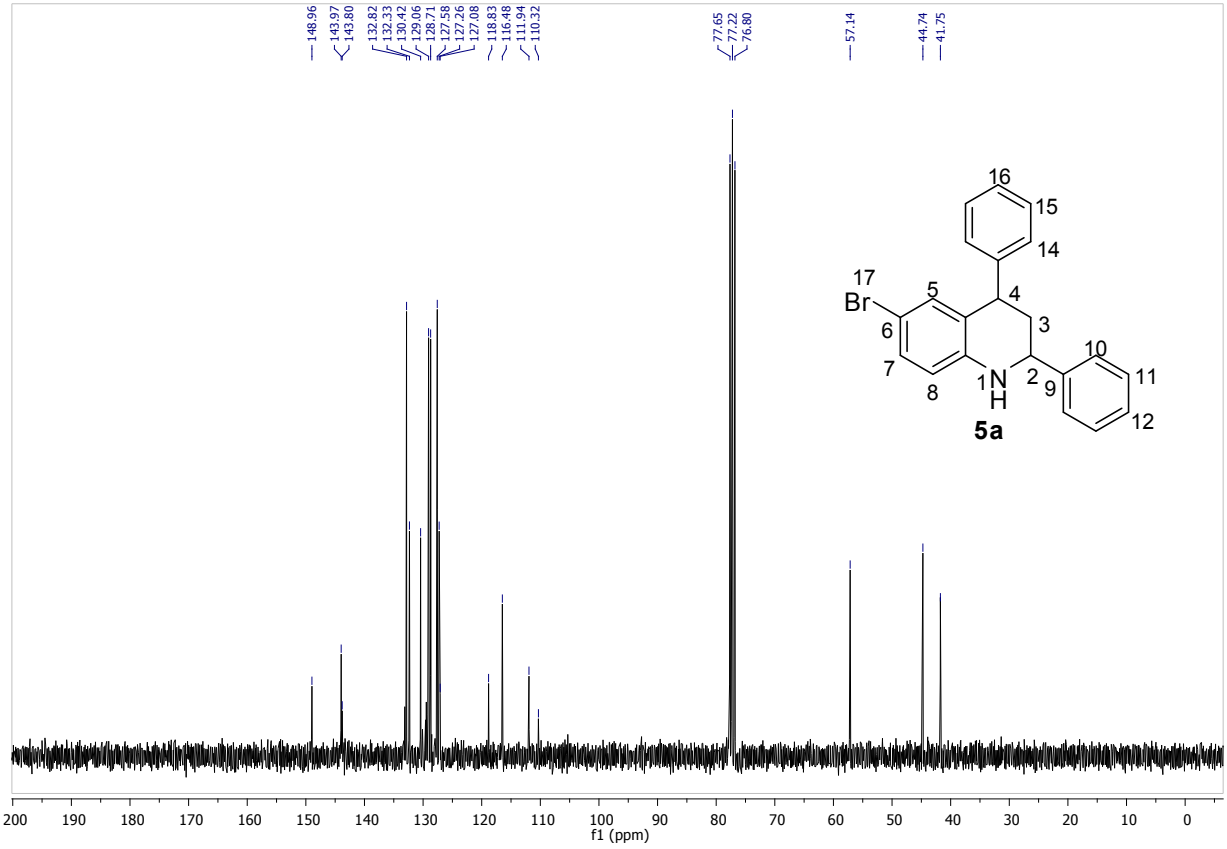
^{1}H NMR (300 MHz, $CDCl_3$) of **4o**.



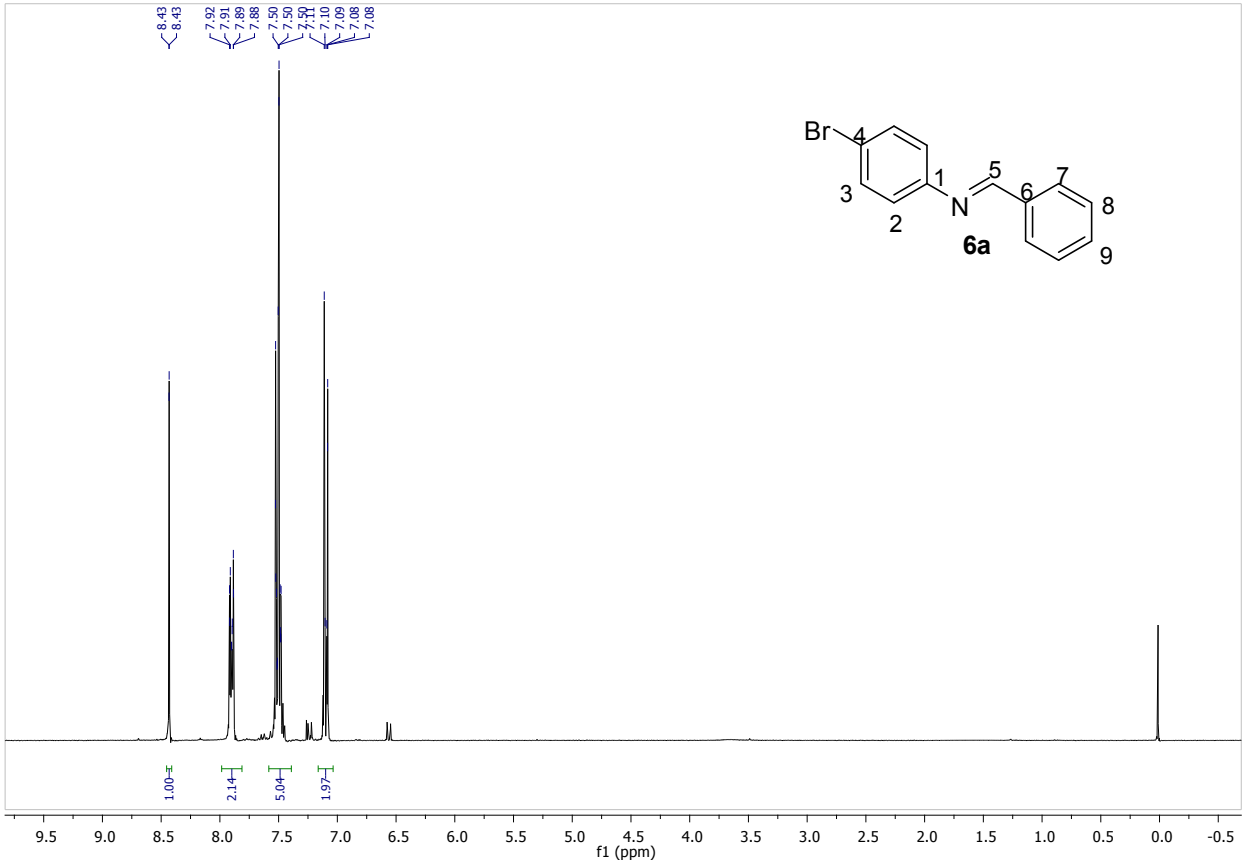
^{13}C NMR (75 MHz, $CDCl_3$) of **4o**.



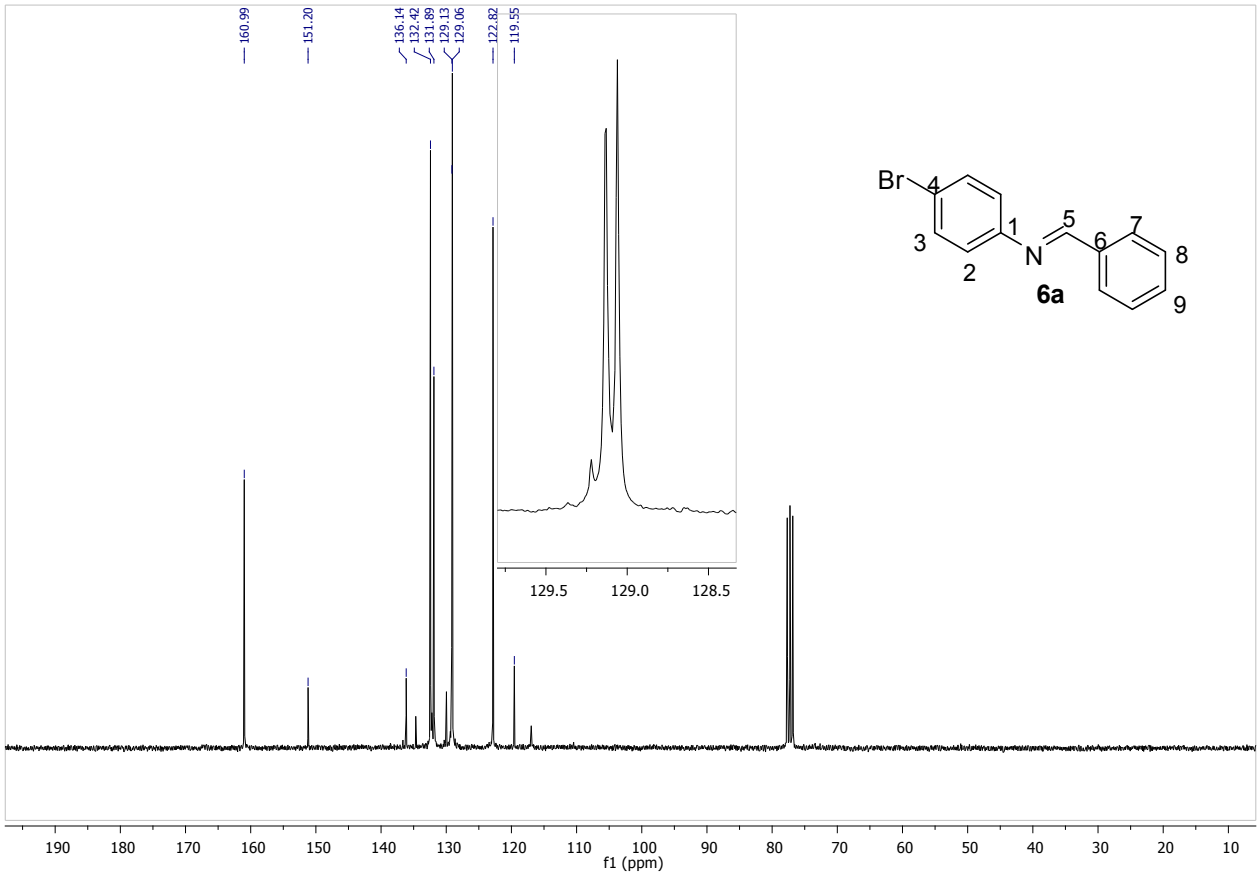
a) ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) of tetrahydroquinoline **5a**; b) Experiment NOEDiff selectively irradiating **H-4**.



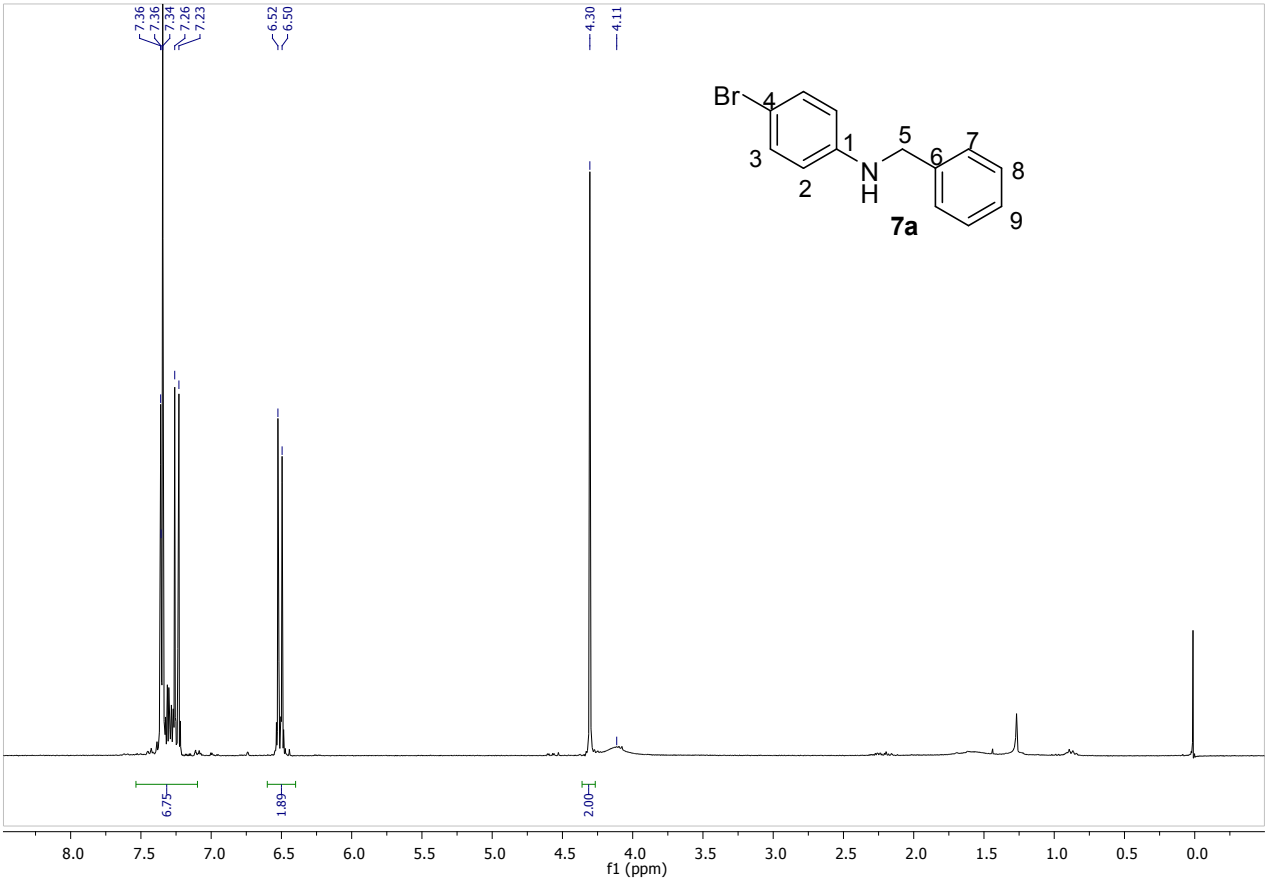
^{13}C NMR (75 MHz, $CDCl_3$) of **5a**.



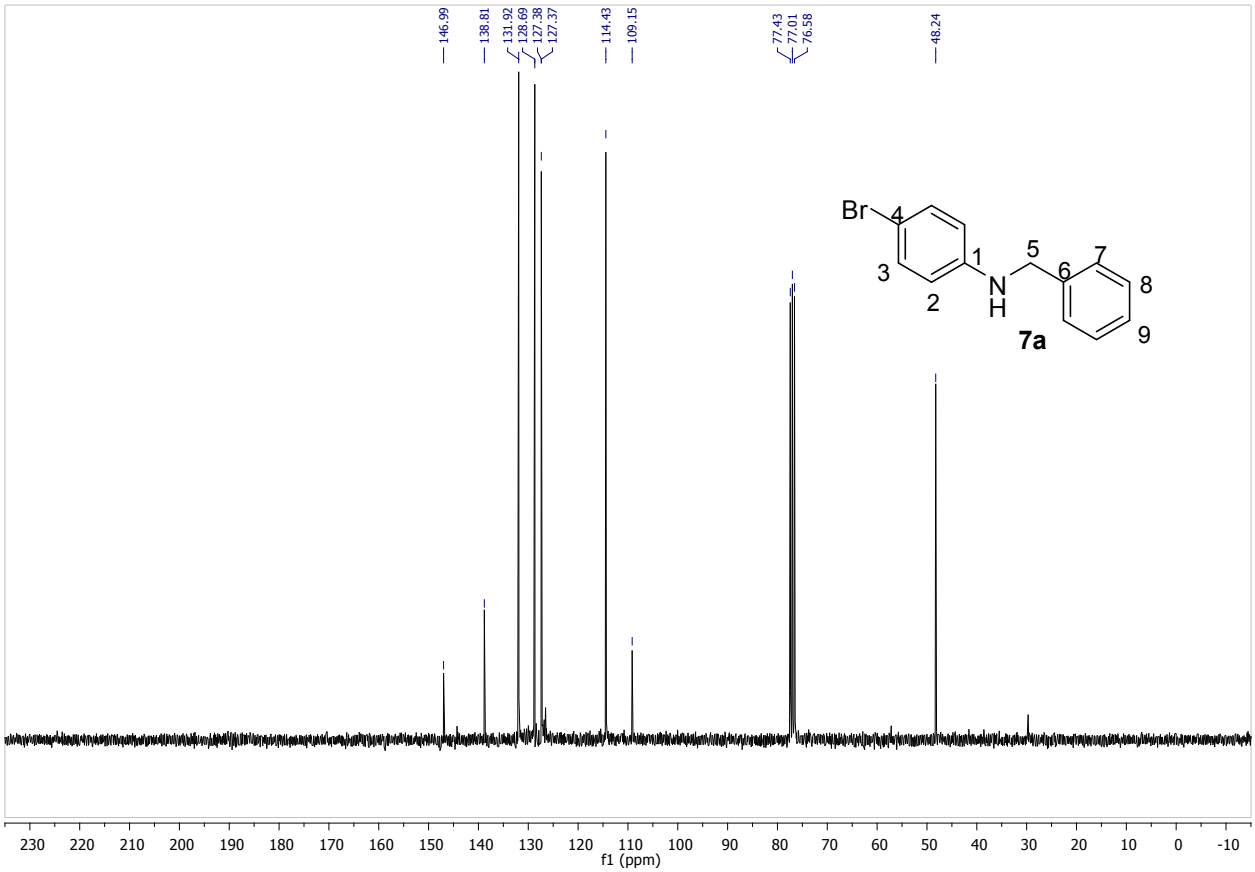
^{1}H NMR (300 MHz, $CDCl_3$) of **6a**.



13C NMR (75 MHz, $CDCl_3$) of **6a**.



^{1}H NMR (300 MHz, $CDCl_3$) of **7a**.



^{13}C NMR (75 MHz, $CDCl_3$) of **7a**.

RECOVERED AND REUSE OF CATALYST CX4SO$_3$H

Since we have proved that CX4SO$_3$H can efficiently catalyze the formation quinolines, the possibility of its recycle was evaluated. For this test the quinoline **4a** was obtained and the catalyst CX4SO$_3$H was recovered by liquid extraction with water. After removing the water by evaporation the catalyst was obtained as a solid residue in 95% crude yield. This was reused in successive reactions and after three cycles with a reduction catalyst recovery of 8% and only a marginal loss in yield (7%) was observed.

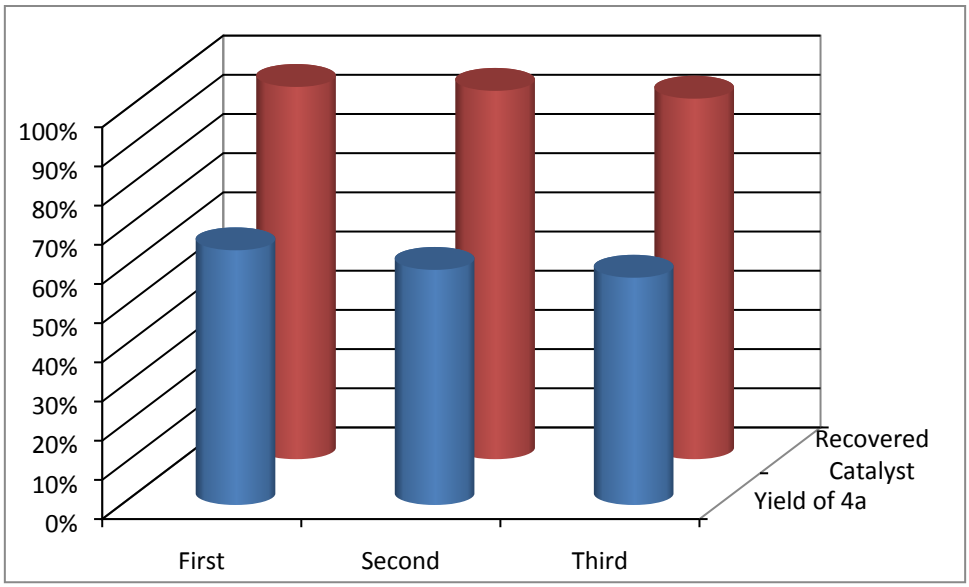


Figure 1 – Percentage of recovery of the catalyst CX4SO$_3$H from successive reactions of formation of **4a** and percentage of **4a** obtained reusing the catalyst CX4SO$_3$H recoved in successive cycles.

EXPERIMENTS IN DEUTERATED ACETONITRILE

To confirm the participation of acetonitrile in hydrogen-transfer process the following reactions were performed in acetonitrile deuterated in side NMR tube.

Tube 1 - The tetrahydroquinoline **5a** was solubilized in deuterated acetonitrile and maintained under temperature of 80 °C for 24 hours. ^{1}H NMR spectrum was obtained and showed only the signals affecting tetraidroquinolina and few signs related to impurities and decomposition products. (Figure 2 in paper).

Tube 2 - The tetrahydroquinoline **5a** was solubilized in deuterated acetonitrile and the catalyst $CX4SO_3H$ was added under temperature of 80 °C for 24 hours. The catalyst $CX4SO_3H$ remained insoluble and was filtrated in final reaction. ^{1}H NMR spectrum of filtrate was obtained and showed a broad signal in 2.90 ppm that was not present in the spectrum of tetrahydroquinoline **5a.** (Figure 2 in paper)

Tube 3 - The tetrahydroquinoline **5a** and the imine **6a** (1 equivalent) were solubilized in deuterated acetonitrile and the catalyst $CX4SO_3H$ was added under temperature of 80 °C for 24 hours. The catalyst $CX4SO_3H$ remained insoluble and was filtrated in final reaction. ^{1}H NMR spectrum of filtrate was obtained and showed a signal in 2.90 ppm and a signal in 4.30 ppm refers the group CH_2 of amine **7a** coming of reduction of **6a**. (Figure 2 in paper).

To prove that signal in 2.90 ppm is refers the NH group from of acetonitrile reduction, the ^{1}H NMR spectrum of amine **7a** in deuterated acetonitrile and in presence of $CX4SO_3H$ conducting under same reaction conditions (80 °C, 24 h) was obtained. This experiment showed that signal in 2.90 ppm is not refers the NH group of amine **7a** (**Figure 1**).

To prove that the signal in 2.90 ppm is not refers of catalyst $CX4SO_3H$, this was added in deuterated acetonitrile, as $CX4SO_3H$ was insoluble, was obtained the spectrum of filtrate, that not showed the signal in 2.90 ppm. Thus we conclusion that signal is refers the acetonitrile reduction forming the bond N–H (**Figure 2**). ^{1}H NMR spectrum of $CX4SO_3H$ in CD3CN not corresponding the structure of $CX4SO_3H$ that is confirming in ^{1}H NMR spectrum in D_2O. Probable this signal in ^{1}H NMR spectrum in CD3CN corresponding the impurities.

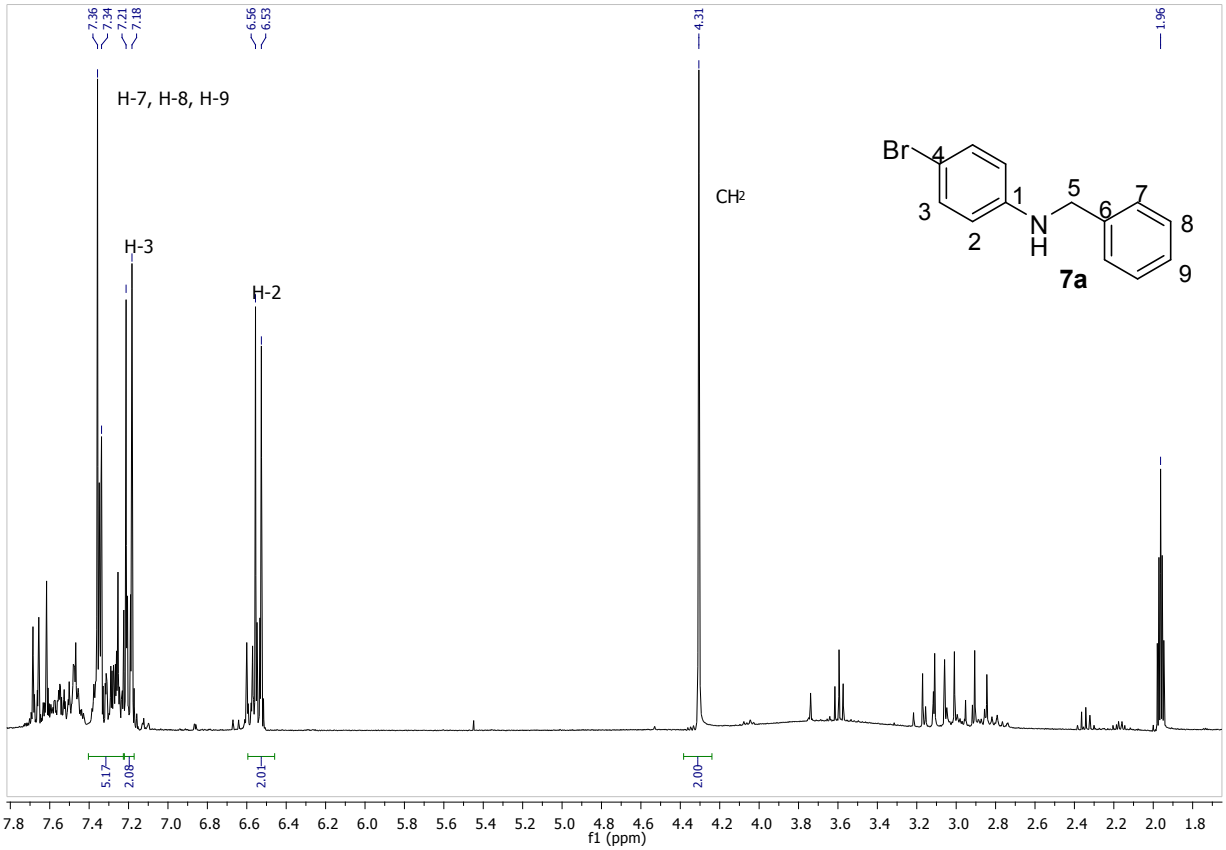


Figure 1 - ^{1}H NMR (300 MHz, CD_3CN) of amine **7a**.

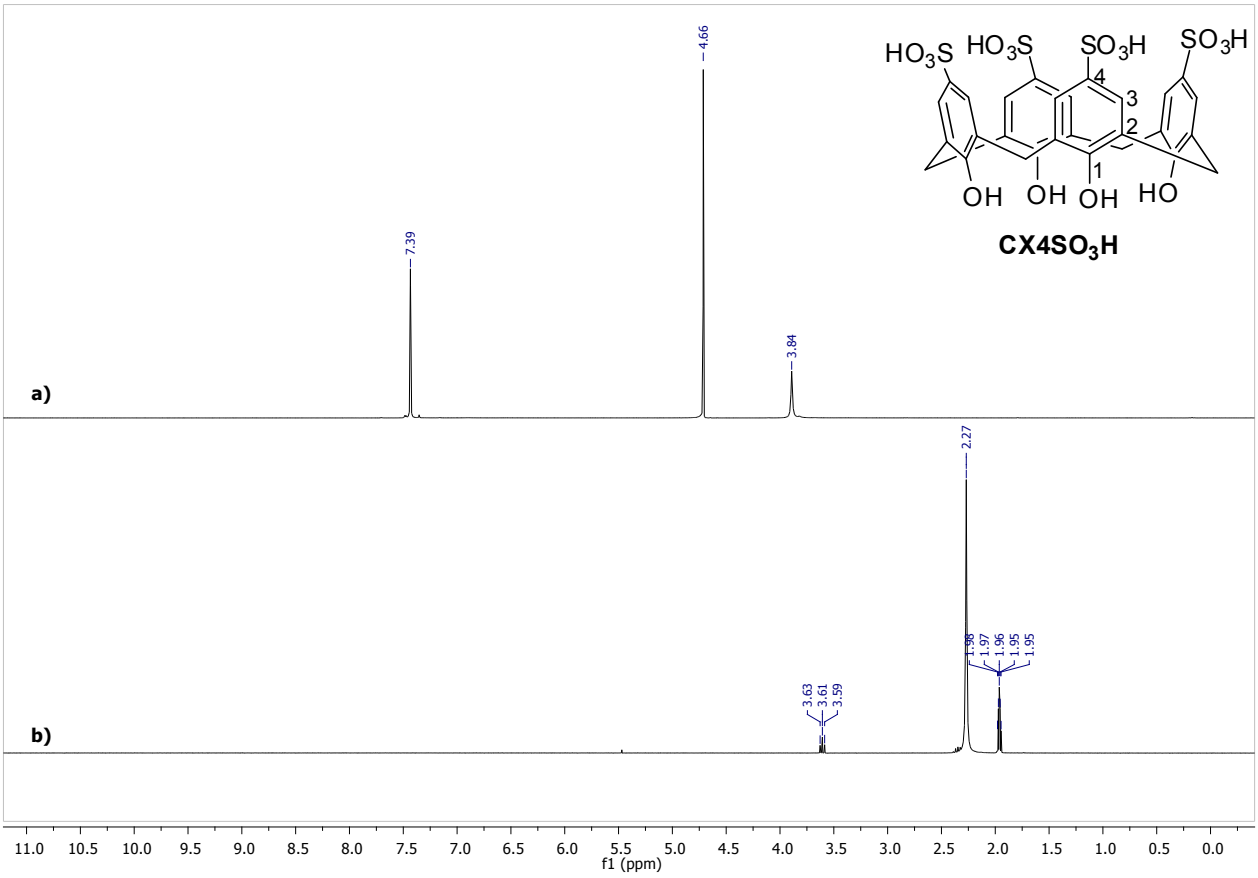


Figure 2–a) ^{1}H NMR (300 MHz, D_2O) of **$CX4SO_3H$**. **b)** ^{1}H NMR (300 MHz, CD_3CN) of **$CX4SO_3H$.**

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