Supporting Information for Publication

Copper-catalyzed synthesis of 2-substituted quinolines *via* transmetalation/cyclization of (*E*)-2-(2-(trimethylsilyl)vinyl)anilines and aldehydes

Archana Chutia, Ankita Pradhan, Manas Kumar Barik and Anil K. Saikia*

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, India, e-mail: asaikia@iitg.ac.in

Table of Content:

General Information

All the reagents were of reagent grade (AR grade) and were used as purchased without further purification. Silica gel (60−120 mesh size) was used for column chromatography. Reactions were monitored by TLC on silica gel GF254 (0.25 mm). Melting points were recorded in an open capillary tube and are uncorrected. Fourier transform-infrared (FT-IR) spectra were recorded as neat liquid or KBr pellets. NMR spectra were recorded in $CDCl_3$ and MeOD-d_4 with tetramethylsilane as the internal standard for ^1H (600, 500 and 400 MHz) or $^{13}C\{^1H\}$ (150 and 125 MHz) NMR. Chemical shifts (δ) are reported in ppm, and spin−spin coupling constants (*J*) are given in Hz. HRMS spectra were recorded using a Q-TOF mass spectrometer.

The starting material **1** was synthesized using 2-iodoaniline derivatives which were purchased directly from BLDPharm, which were used without additional purification. The starting materials **2** were also purchased directly from BLDPharm and used without further purification.

The starting material **1a-1k** and **1b′** were synthesized according to literature reports.[1] Attempts were made to prepare *Z*-configured or *E*/*Z* mixtures of vinylsilanes following previously reported literature procedures.[2] However, these substrates were found to be difficult to obtain in our system. This may be attributed to the steric hindrance of the aniline moiety present in the 2-((trimethylsilyl)ethynyl)aniline framework, which disfavors the formation of the corresponding *Z*-configured isomer.

The experimental procedure and the characterization data of the starting materials **1a**-**1k** and **1b′** are provided here.

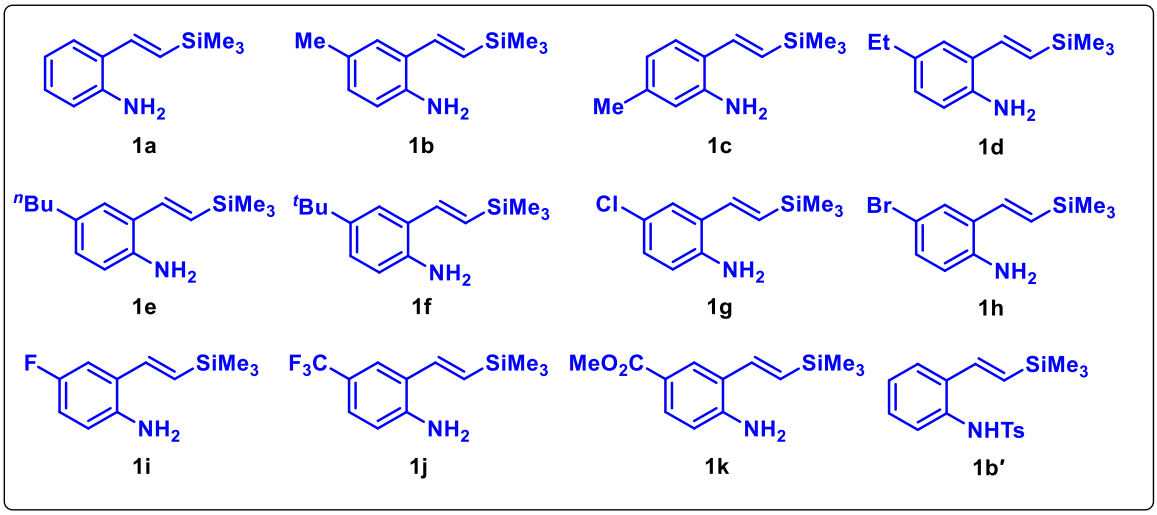


Figure S1: (*E*)-2-(2-(trimethylsilyl)vinyl)anilines employed in the reaction

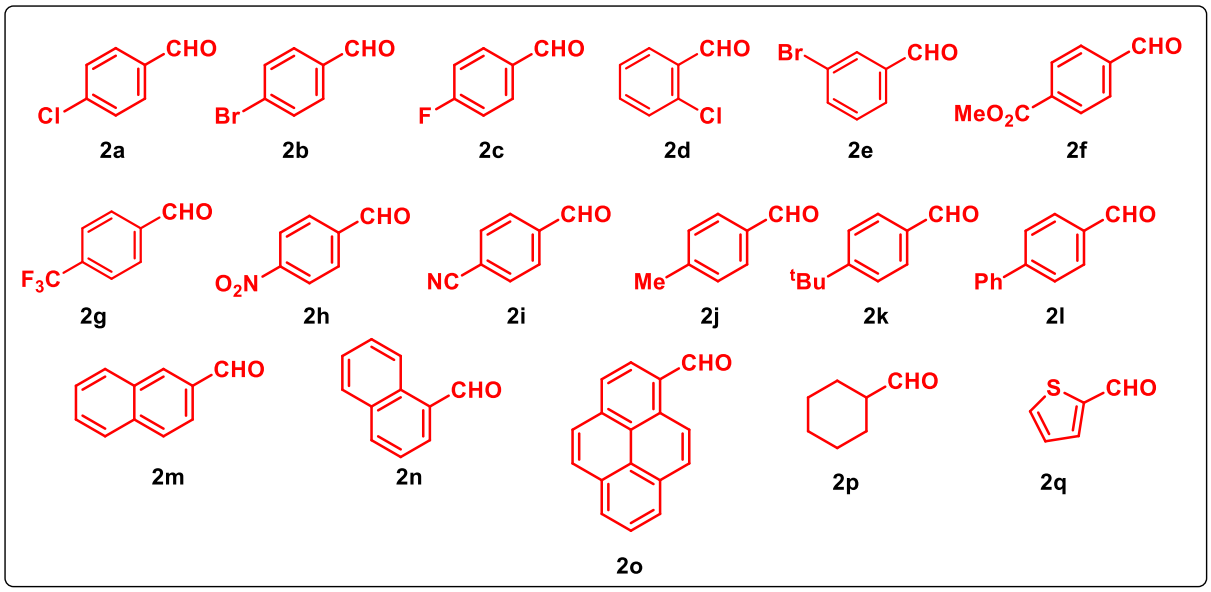
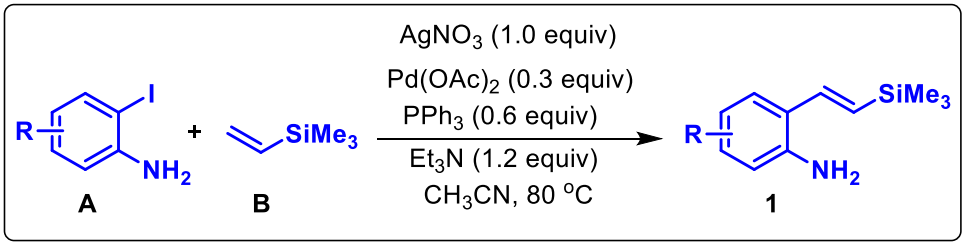


Figure S2: Aldehydes employed in the reaction

General Experimental Procedure and Characterization Data of Compounds 1a-1k:

Schematic representation of preparation of starting materials **1a-1k:**



To a stirred suspension of 2-iodoaniline derivative **A** (1.37 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.41 mmol, 30 mol %), $AgNO_3$ (1.37 mmol, 1.0 equiv), PPh_3 (0.82 mmol, 0.6 equiv) in CH_3CN

under nitrogen atmosphere, was added triethylamine (1.64 mmol, 1.2 equiv) and then trimethyl(vinyl)silane **B** (2.74 mmol, 2.0 equiv) slowly over a period of 5 min. The reaction mixture was then stirred at room temperature for 5–10 minutes before being heated to 80 °C in an oil bath. The progress of the reaction was monitored by TLC analysis (using hexane/ethyl acetate = 9:1 as eluents). After completion of the reaction (12 h), the reaction mixture was allowed to filter through Celite and washed with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated using a rotary evaporator to give the crude product, which was then subjected to column chromatography over silica gel to provide the desired starting material **1**.

Characterization Data of Compounds 1a-1k:

(*E*)-2-(2-(Trimethylsilyl)vinyl)aniline (1a):

Brown liquid; R_f (Hexane/EtOAc, 9:1) 0.50. Yield 157 mg, 60%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.0 Hz, 1 H), 6.66 (t, *J* = 8.0 Hz, 1 H), 6.87 (d, *J* = 19.0 Hz, 1 H), 6.69 (t, *J* = 8.0 Hz, 1 H), 6.58 (d, *J* = 10.0 Hz, 1 H), 6.28 (d, *J* = 19.1 Hz, 1 H), 3.64 (s, 2 H), 0.09 (s, 9 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.7, 139.2, 131.7, 129.0, 127.3, 125.3, 119.2, 116.5, -0.9; IR (KBr, neat) 3379, 2953, 1619, 1487, 1455, 1246, 834, 744, 690 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{18}NSi$ $(M + H)^+$ 192.1203, found 192.1231.

(*E*)-4-Methyl-2-(2-(trimethylsilyl)vinyl)aniline (1b):

Brown liquid; R_f (Hexane/EtOAc, 9:1) 0.50. Yield 177 mg, 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1 H), 6.97 (d, *J* = 19.2 Hz, 1 H), 6.91 (dd, *J* = 8.0, 2.0 Hz, 1 H), 6.62 (d, *J* = 8.0 Hz, 1 H), 6.37 (d, *J* = 18.8 Hz, 1 H), 3.62 (s, 2 H), 2.27 (s, 3 H), 0.18 (s, 9 H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 140.9, 139.2, 131.5, 129.7, 128.7, 127.6, 125.5, 116.9, 20.7, -0.9; IR (KBr, neat) 3277, 2919, 2857, 1633, 1525, 1162, 591 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{20}NSi$ $(M + H)^+$ 206.1360, found 206.1359.

(*E*)-5-Methyl-2-(2-(trimethylsilyl)vinyl)aniline (1c):

Brown liquid; R_f (Hexane/EtOAc, 9:1) 0.50. Yield 160 mg, 57%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.0 Hz, 1 H), 6.84 (d, *J* = 19.2 Hz, 1 H), 6.51 (d, *J* = 7.6 Hz, 1 H), 6.41 (s, 1 H), 6.22 (d, *J* = 19.2 Hz, 1 H), 3.64 (s, 2 H), 2.18 (s, 3 H), 0.08 (s, 9 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 143.6, 139.1, 139.0, 130.4, 127.3, 122.6, 120.2, 117.1, 21.4, -0.88 ; IR (KBr, neat) 3269, 2912, 2856, 1631, 1621, 1099, 595 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{20}NSi$ $(M + H)^+$ 206.1360, found 206.1373.

(*E*)-4-Ethyl-2-(2-(trimethylsilyl)vinyl)aniline (1d):

Brown liquid; R_f (Hexane/EtOAc, 9:1) 0.60. Yield 180 mg, 60%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 1 H), 6.78 – 6.72 (m, 2 H), 6.41 (d, *J* = 7.0 Hz, 1 H), 6.17 (d, *J* = 19.5 Hz, 1 H), 3.38 (s, 2 H), 2.36 (q, *J* = 7.0 Hz, 2 H), 1.01 (t, *J* = 7.5 Hz, 3 H), -0.02 (s, 9 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 141.5, 139.4, 135.0, 131.3, 128.5, 126.5, 125.3, 116.8, 28.3, 16.2, -0.9 ; IR (KBr, neat) 3291, 2955, 2877, 1593, 1525, 1162, 781, 699 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_{22}NSi$ $(M + H)^+$ 220.1516, found 220.1529.

(*E*)-4-Butyl-2-(2-(trimethylsilyl)vinyl)aniline (1e):

Brown liquid; R_f (Hexane/EtOAc, 9:1) 0.60. Yield 200 mg, 59%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (s, 1 H), 6.97 (d, *J* = 19.0 Hz, 1 H), 6.92 (d, *J* = 8.0 Hz, 1 H), 6.62 (d, *J* = 8.0 Hz, 1 H), 6.37 (d, *J* = 19.0 Hz, 1 H), 3.59 (s, 2 H), 2.53 (t, *J* = 8.0 Hz, 2 H), 1.61 – 1.55 (m, 2 H), 1.40 – 1.33(m, 2 H), 0.94 (t, *J* = 8.0 Hz, 3 H), 0.18 (s, 9 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 141.5, 139.4, 133.7, 131.3, 129.1, 127.0, 125.2, 116.7, 35.1, 34.2, 22.6, 14.2, -0.9; IR (KBr, neat) 2966, 2921, 2864, 1510, 1254, 877, 678 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{26}NSi$ $(M + H)^+$ 248.1829, found 248.1837.

(*E*)-4-(*Tert*-butyl)-2-(2-(trimethylsilyl)vinyl)aniline (1f):

Brown liquid; R_f (Hexane/EtOAc, 9:1) 0.60. Yield 196 mg, 58%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 2.4 Hz, 1 H), 7.13 (dd, *J* = 8.0, 2.0 Hz, 1 H), 6.98 (d, *J* = 18.8 Hz, 1 H), 6.65 (d, *J* = 8.4 Hz, 1 H), 6.37 (d, *J* = 18.8 Hz, 1 H), 3.64 (s, 2 H), 1.32 (s, 9 H), 0.19 (s, 9 H); $^{13}C\{^1H\}$

NMR (125 MHz, $CDCl_3$) δ 142.0, 141.3, 139.9, 131.2, 126.1, 124.7, 123.9, 116.5, 34.2, 31.7, -0.8; IR (KBr, neat) 2956, 2923, 2864, 1504, 1250, 839 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{26}NSi$ $(M + H)^+$ 248.1829, found 248.1832.

(*E*)-4-Chloro-2-(2-(trimethylsilyl)vinyl)aniline (1g):

Brown liquid; R_f (Hexane/EtOAc, 9:1) 0.50. Yield 164 mg, 53%; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (s, 1 H), 6.98 (dd, *J* = 8.5, 2.0 Hz, 1 H), 6.81 (d, *J* = 18.5 Hz, 1 H), 6.55 (d, *J* = 8.5 Hz, 1 H), 6.34 (d, *J* = 19.0 Hz, 1 H), 3.67 (s, 2 H), 0.14 (s, 9 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 142.2, 137.8, 133.4, 128.5, 126.9, 126.7, 123.9, 117.6, -1.0; IR (KBr, neat) 2951, 2873, 1498, 839, 681, 531 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{17}ClNSi$ $(M + H)^+$ 226.0813, found 226.0817.

(*E*)-4-bromo-2-(2-(trimethylsilyl)vinyl)aniline (1h):

Brown liquid; R_f (Hexane/EtOAc, 9:1) 0.50. Yield 189 mg, 51%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 2.4 Hz, 1 H), 7.14 (dd, *J* = 8.4, 2.4 Hz, 1 H), 6.83 (d, *J* = 18.8 Hz, 1 H), 6.55 (d, *J* = 8.8 Hz, 1 H), 6.37 (d, *J* = 18.8 Hz, 1 H), 3.76 (s, 2 H), 0.17 (s, 9 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 142.6, 137.7, 133.5, 131.4, 129.8, 127.2, 118.0, 111.1, -1.0; IR (KBr, neat) 2978, 2871, 1578, 1123, 767, 687, 531 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{17}BrNSi$ $(M + H)^+$ 270.0308, found 270.0281.

(*E*)-4-Fluoro-2-(2-(trimethylsilyl)vinyl)aniline (1i):

Brown liquid; R_f (Hexane/EtOAc, 9:1) 0.50. Yield 135 mg, 47%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.05 (dd, *J* = 10.0, 3.2 Hz, 1 H), 6.89 (dd, *J* = 18.8, 1.6 Hz, 1 H), 6.81 – 6.76 (m, 1 H), 6.61 (dd, *J* = 8.7, 4.8 Hz, 1 H), 6.36 (d, *J* = 18.9 Hz, 1 H), 3.57 (s, 2 H), 0.16 (s, 9 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 157.0 (d, *J* = 234.6 Hz), 139.7 (d, *J* = 1.88 Hz), 138.1, (d, *J* = 2.13 Hz), 133.1, 126.6 (d, *J* = 6.75 Hz), 117.6 (d, *J* = 7.63 Hz), 115.5 (d, *J* = 22.8 Hz), 113.1, (d, *J* = 22.5 Hz), -1.0; ^{19}F NMR (470 MHz, $CDCl_3$/ C_6F_6) *δ* –129.3 (s, –CF–); IR (KBr, neat) 2925, 2854, 1487, 1248, 840, 749 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{17}FNSi$ $(M + H)^+$ 210.1109, found 210.1112.

(*E*)-4-(Trifluoromethyl)-2-(2-(trimethylsilyl)vinyl)aniline (1j):

Brown liquid; R_f (Hexane/EtOAc, 9:1) 0.50. Yield 145 mg, 41%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1 H), 7.11 (d, *J* = 8.5 Hz, 1 H), 6.70 (d, *J* = 19.0 Hz, 1 H), 6.49 (d, *J* = 8.5 Hz, 1 H), 6.25 (d, *J* = 19.0 Hz, 1 H), 3.85 (s, 2 H), 0.00 (s, 9 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 146.5, 137.9, 134.1, 126.1, 125.7 (q, *J* = 3.8 Hz), 124.8 (q, *J* = 3.9 Hz), 124.0, 120.8 (q, *J* = 32.3 Hz), 115.8, -1.1; ^{19}F NMR (470 MHz, $CDCl_3$/ C_6F_6) *δ* –64.4 (s, –CF–); IR (KBr, neat) 3236, 2921, 2812, 1546, 1248, 876, 749, 622 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{17}F_3NSi$ $(M + H)^+$ 260.1077, found 260.1082.

Methyl (*E*)-4-amino-3-(2-(trimethylsilyl)vinyl)benzoate (1k):

Brown liquid; R_f (Hexane/EtOAc, 4:1) 0.60. Yield 143 mg, 42%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1 H), 7.74 (d, *J* = 6.0 Hz, 1 H), 6.86 (d, *J* = 19.0 Hz, 1 H), 6.63 (d, *J* = 7.5 Hz, 1 H), 6.43 (d, *J* = 18.5 Hz, 1 H), 4.26 (s, 2 H), 3.85 (s, 3 H), 0.16 (s, 9 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.5, 148.1, 138.1, 133.4, 130.6, 129.6, 124.1, 120.1, 115.3, 51.8, -1.1; IR (KBr, neat) 3374, 2951, 1697, 1453, 1379, 1024, 987, 840, 727, 702 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_{20}NO_2Si$ $(M + H)^+$ 250.1258, found 250.1249.

General Experimental Procedure and Characterization Data of Compound 1b′:

To a solution of (*E*)-2-(2-(trimethylsilyl)vinyl)aniline (1.57 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 was added TsCl (1.88 mmol, 1.2 equiv) and pyridine (1.88 mmol, 1.2 equiv) at room temperature and the reaction mixture was stirred for 12.0 h. The progress of the reaction was monitored by TLC analysis (using hexane/ethyl acetate = 9:1 as eluents). After the completion of the reaction, the solvent was removed under reduced pressure. The combined organic layer was washed with brine, extracted with CH_2Cl_2 (3 x 30 mL), and dried over anhydrous Na_2SO_4. The crude was then purified using column chromatography over silica gel to get the corresponding product **1b′** in 71% yield.

Characterization Data of Compound 1b′:

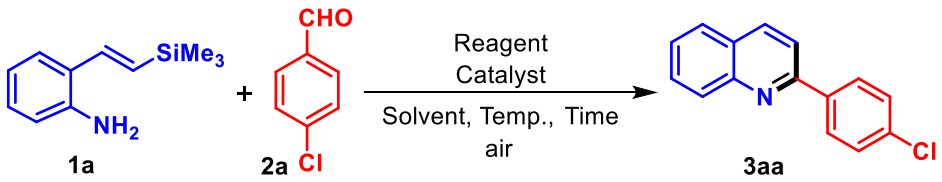
(*E*)-4-Methyl-*N*-(2-(2-(trimethylsilyl)vinyl)phenyl)benzenesulfonamide (1b′):

Brown Solid; R_f (Hexane/EtOAc, 4:1) 0.50; mp 100–102 °C. Yield 213 mg, 71%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2 H), 7.46 (t, *J* = 8.0 Hz, 2 H), 7.26 (s, 1 H), 7.23 (d, *J* = 7.5 Hz, 3 H), 6.72 (d, *J* = 19.0 Hz, 1 H), 6.30 (d, *J* = 19.0 Hz, 1 H), 2.40 (s, 3H), 0.14 (s, 9 H).; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.8, 137.7, 136.7, 134.5, 134.2, 133.0, 129.7, 128.6, 127.2, 126.8, 126.6, 126.6, 21.6, -1.22 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{24}NO_2SSi$ $(M + H)^+$ 346.1292, found 346.1284.

Optimization Studies:

Our investigation commenced with (*E*)-2-(2-(trimethylsilyl)vinyl)aniline (**1a**) and 4-chlorobenzaldehyde (**2a**) as model substrates, using CuI (0.2 equiv) as the catalyst and $BF_3{\cdot}OEt_2$ (1.2 equiv) as the Lewis acid in CH_3CN under an air atmosphere. At room temperature, no product formation was observed (Table S1, entry 1). In contrast, heating the reaction to 80 °C furnished the product 2-(4-chlorophenyl)quinoline (**3aa**) in 78% yield within 12 h (Table S1, entry 2), with the structure confirmed by ^{1}H and ^{13}C NMR spectroscopy and HRMS analysis. Encouraged by this result, various Lewis and Brønsted acids were evaluated. Replacement of $BF_3{\cdot}OEt_2$ with TMSOTf afforded only 20% yield (Table S1, entry 3), while metal triflates such as $In(OTf)_3$ and $Bi(OTf)_3$, as well as Brønsted acids including TfOH and *p*-TsOH, were ineffective (Table S1, entries 4–7). Variation of $BF_3{\cdot}OEt_2$ loading revealed that 1.0 equiv was optimal, delivering **3aa** in 82% yield, whereas lower loadings resulted in reduced efficiency (Table S1, entries 8 and 9). Notably, decreasing the CuI loading to 0.1 equiv improved the yield to 85% (Table S1, entry 10), while higher catalyst loadings offered no further enhancement in the yield (Table S1, entry 11). Lowering the reaction temperature to 50 °C led to a comparatively lower conversion (Table S1, entry 12). Screening of alternative copper salts like CuBr, CuCl, and $CuCl_2$ did not improve the outcome (Table S1, entries 13–15). We also

Table S1. Optimization of the reaction conditions[a].



entry	reagent (equiv)	catalyst (equiv)	solvent	T(°C)	time(h)	%yield[b]
1	BF_3·OEt_2 (1.2)	CuI (0.2)	CH_3CN	rt	24.0	[c]nr
2	BF_3·OEt_2 (1.2)	CuI (0.2)	CH_3CN	80	12.0	78
3	TMSOTf (1.2)	CuI (0.2)	CH_3CN	80	24.0	20
4	$In(OTf)_3$ (0.3)	CuI (0.2)	CH_3CN	80	24.0	[c]nr
5	$Bi(OTf)_3$ (0.3)	CuI (0.2)	CH_3CN	80	24.0	[c]nr
6	TfOH (1.2)	CuI (0.2)	CH_3CN	80	24.0	[c]nr
7	*P*-TsOH (1.2)	CuI (0.2)	CH_3CN	80	12.0	[c]nr
8	BF_3·OEt_2 (1.0)	CuI (0.2)	CH_3CN	80	12.0	82
9	BF_3·OEt_2 (0.5)	CuI (0.2)	CH_3CN	80	24.0	67
10	**BF_3·OEt_2 (1.0)**	**CuI (0.1)**	**CH_3CN**	**80**	**12.0**	**85**
11	BF_3·OEt_2 (1.0)	CuI (0.3)	CH_3CN	80	12.0	81
12	BF_3·OEt_2 (1.0)	CuI (0.1)	CH_3CN	50	24.0	74
13	BF_3·OEt_2 (1.0)	CuBr (0.1)	CH_3CN	80	24.0	57
14	BF_3·OEt_2 (1.0)	CuCl (0.1)	CH_3CN	80	24.0	36
15	BF_3·OEt_2 (1.0)	$CuCl_2$ (0.1)	CH_3CN	80	24.0	[c]nr
16	BF_3·OEt_2 (1.0)	CuI (0.1)	DCE	80	24.0	[c]nr
17	BF_3·OEt_2 (1.0)	CuI (0.1)	DCM	40	24.0	[c]nr
18	BF_3·OEt_2 (1.0)	CuI (0.1)	Toluene	110	12.0	30
19	BF_3·OEt_2 (1.0)	CuI (0.1)	DMF	110	24.0	[c]nr
20	BF_3·OEt_2 (1.0)	CuI (0.1)	CH_3CN	80	12.0	[d]68

[a]Reaction conditions: **1a** (0.43 mmol, 1.2 equiv), **2a** (0.36 mmol, 1.0 equiv), solvent 3.0 mL, [b]Isolated yield, [c]nr = No reaction, [d]N_2 atmosphere.

examined the reaction with different solvents like DCE, DCM, toluene and DMF (Table S1, entries 16–19). In DCE and DCM the reaction did not afford the desired product (Table S1, entries 16 and 17), while toluene furnished an inferior 30% yield (Table S1, entry 18). Besides, in DMF, the starting materials were decomposed under the proposed reaction conditions (Table

S1, entry 19), with CH_3CN remaining the solvent of optimal yield. Then, we performed the reaction under nitrogen atmosphere but it resulted in comparatively less yield (Table S1, entry 20). Collectively, from all these observations it is concluded that 1.0 equiv of $BF_3{\cdot}OEt_2$ and 0.1 equiv of CuI in CH_3CN at 80 °C are the optimal conditions for this reaction.

General Experimental Procedure and Spectral Data of Compounds 3aa-3aq, 3ba, 3bl, 3cb, 3da,3ea, 3fa, 3ga, 3ha, and 3ik:

To a mixture of (*E*)-2-(2-(trimethylsilyl)vinyl)aniline **1** (0.85 mmol, 1.2 equiv), aldehyde derivatives **2** (0.71 mmol, 1.0 equiv) and CuI (0.07 mmol, 0.1 equiv) in CH_3CN, $BF_3{\cdot}OEt_2$ (0.71 mmol, 1.0 equiv) was added slowly at 0 ^oC under air atmosphere. The mixture was then stirred at room temperature for 5–10 min before being heated to 80 °C in an oil bath. The progress of the reaction was monitored by TLC (using hexane/ethyl acetate = 19:1 as eluents). After completion of the reaction (12–14 h), the mixture was cooled to room temperature. The solvent was removed in vacuo in a rotary evaporator and then the residue was diluted with ethyl acetate, saturated $NaHCO_3$, and saturated brine solution. The aqueous phase was extracted with ethyl acetate (3 × 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated using a rotary evaporator. The resulting crude product was purified by column chromatography over silica gel to yield the desired product **3**.

Characterization Data of Compounds 3aa-3aq, 3ba, 3bl, 3cb, 3da, 3ea, 3fa, 3ga, 3ha and 3ik:

2-(4-Chlorophenyl)quinoline (3aa):

White solid; R_f (Hexane/EtOAc, 19:1) 0.50; mp 106–108 ^oC. Yield 145 mg, 85%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 1 H), 8.05 (d, *J* = 8.4 Hz, 2 H), 8.00 (d, *J* = 8.4 Hz, 1 H), 7.72 – 7.69 (m, 2 H), 7.62 (d, *J* = 8.4 Hz, 1 H), 7.49 (d, *J* = 7.6 Hz, 1 H), 7.44 (d, *J* = 8.4 Hz, 2 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.3, 148.5, 138.3, 137.2, 135.8, 130.1, 129.9,

129.3, 129.1, 127.7, 127.5, 126.8, 118.8; IR (KBr, neat) 3236, 2912, 1453, 1379, 1024, 752, 727, 702, 463 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{11}ClN$ $(M + H)^+$ 240.0575, found 240.0572.

2-(4-Bromophenyl)quinoline (3ab):

White solid; R_f (Hexane/EtOAc, 19:1) 0.50; mp 114–116 °C. Yield 167 mg, 83%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1 H), 8.09 (d, *J* = 8.4 Hz, 1 H), 8.01 (d, *J* = 8.4 Hz, 2 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.72 – 7.69 (m, 2 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 7.53 – 7.49 (m, 1 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.3, 148.4, 138.7, 137.2, 132.2, 130.1, 129.9, 129.3, 127.7, 127.5, 126.8, 124.2, 118.7; IR (KBr, neat) 3223, 2955, 1543, 1430, 1024, 752, 720, 478 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{11}BrN$ $(M + H)^+$ 284.0069, found 284.0086.

2-(4-Fluorophenyl)quinoline (3ac):

White solid; R_f (Hexane/EtOAc, 19:1) 0.40; mp 112–114 °C. Yield 127 mg, 80%; ^1H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 1 H), 8.18 – 8.16 (m, 3 H), 7.83 (d, *J* = 8.4 Hz, 2 H), 7.74 (t, *J* = 8.4 Hz, 1 H), 7.54 (t, *J* = 7.8 Hz, 1 H), 7.21 (t, *J* = 8.4 Hz, 2 H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 164.1 (d, *J* = 247.5 Hz), 156.5, 148.4, 137.2, 136.0, (d, *J* = 3.2 Hz), 130.1, 129.8, 129.7 (d, *J* = 8.7 Hz), 127.7, 127.3, 126.6, 118.9, 116.0 (d, *J* = 21.5 Hz); ^{19}F NMR (470 MHz, $CDCl_3$/ C_6F_6) *δ* –115.6 (s, –CF–); IR (KBr, neat) 3318, 2971, 1670, 1430, 1124, 810, 782, 701 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{11}FN$ $(M + H)^+$ 224.0870, found 224.0888.

2-(2-Chlorophenyl)quinoline (3ad):

White solid; R_f (Hexane/EtOAc, 19:1) 0.50; mp 102–104 °C. Yield 134 mg, 79%; ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 14.5, 8.5 Hz, 2 H), 7.88 (d, *J* = 8.5 Hz, 1 H), 7.76 (d, *J* = 9.0 Hz, 2 H), 7.71 (d, *J* = 6.5 Hz, 1 H), 7.59 (t, *J* = 7.5 Hz, 1 H), 7.52 (d, *J* = 7.5 Hz, 1 H), 7.44 – 7.37 (m, 2 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 157.6, 148.3, 139.8, 136.0, 132.6, 132.0, 130.3, 130.1, 130.0, 129.9, 127.8, 127.4, 127.4, 127.1, 123.0; IR (KBr, neat) 3329, 3039, 1650, 1456, 1024, 877, 751, 707, 678 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{11}ClN$ $(M + H)^+$ 240.0575, found 240.0577.

2-(3-Bromophenyl)quinoline (3ae):

White solid; R_f (Hexane/EtOAc, 19:1) 0.50; mp 108–110 ^oC. Yield 165 mg, 82%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (t, *J* = 1.6 Hz, 1 H), 8.24 (d, *J* = 8.8 Hz, 1 H), 8.18 (d, *J* = 8.8 Hz, 1 H), 8.08 (d, *J* = 7.6 Hz, 1 H), 7.84 (d, *J* = 8.8 Hz, 2 H), 7.77 – 7.73 (m, 1 H), 7.61 – 7.53 (m, 2 H), 7.40 (t, *J* = 8.0 Hz, 1 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.8, 148.4, 141.9, 137.2, 132.4, 130.8, 130.5, 130.1, 130.0, 127.7, 127.6, 126.9, 126.3, 123.4, 118.9; IR (KBr, neat) 3304, 2967, 1634, 1530, 1184, 890, 712, 645 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{11}BrN$ $(M + H)^+$ 284.0069, found 284.0069.

Methyl 4-(quinolin-2-yl)benzoate (3af):

White solid; R_f (Hexane/EtOAc, 4:1) 0.60; mp 142–144 ^oC. Yield 189 mg, 84%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 3.6 Hz, 1 H), 8.25 (d, *J* = 3.2 Hz, 2 H), 8.19 (d, *J* = 8.4 Hz, 3 H), 7.92 (d, J = 8.4 Hz, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.78 – 7.73 (m, 1 H), 7.56 (d, *J* = 7.2 Hz, 1 H), 3.96 (s, 3 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 167.2, 156.3, 148.4, 143.9, 137.4, 130.9, 130.4, 130.3, 130.0, 127.8, 127.8, 127.7, 127.1, 119.3, 52.5; IR (KBr, neat) 3374, 2950, 1720, 1277, 1107, 824, 774, 705 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{14}NO_2$ $(M + H)^+$ 264.1019, found 264.1009.

2-(4-(Trifluoromethyl)phenyl)quinoline (3ag):

White solid; R_f (Hexane/EtOAc, 19:1) 0.50; mp 112–114 ^oC. Yield 165 mg, 85%; ^1H NMR (500 MHz, $CDCl_3$) δ 8.27 (q, *J* = 8.5 Hz, 3 H), 8.19 (d, *J* = 8.5 Hz, 1 H), 7.89 – 7.84 (m, 2 H), 7.79 – 7.75 (m, 3 H), 7.57 (t, *J* = 7.5 Hz, 1 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.9, 148.5, 143.2, 137.4, 131.3 (q, *J* = 32.1 Hz), 130.2, 130.1, 128.1, 127.8, 127.7, 127.1, 126.0 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 270.4 Hz), 119.0; ^{19}F NMR (470 MHz, $CDCl_3/C_6F_6$) *δ* –65.7 (s, –CF_3–); IR (KBr, neat) 3441, 3236, 1432, 1379, 1074, 819, 790, 760 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{11}F_3N$ $(M + H)^+$ 274.0838, found 274.0839.

2-(4-Nitrophenyl)quinoline (3ah):

White solid; R_f (Hexane/EtOAc, 4:1) 0.50; mp 118–120 °C. Yield 156 mg, 88%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 4 H), 8.30 (d, *J* = 8.5 Hz, 1 H), 8.20 (d, *J* = 8.5 Hz, 1 H), 7.92 (d, *J* = 8.5 Hz, 1 H), 7.87 (d, *J* = 8.5 Hz, 1 H), 7.78 (t, *J* = 8.0 Hz, 1 H), 7.60 (t, *J* = 7.5 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.8, 148.6, 148.5, 145.6, 137.6, 130.5, 130.1, 128.6, 127.8, 127.5, 124.3, 124.2, 119.0; IR (KBr, neat) 3341, 3236, 1534, 1458,1124, 1021, 878, 766 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{11}N_2O_2$ $(M + H)^+$ 251.0815, found 251.0827.

4-(Quinolin-2-yl)benzonitrile (3ai):

White solid; R_f (Hexane/EtOAc, 4:1) 0.60; mp 114–116 °C. Yield 146 mg, 89%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.0 Hz, 3 H), 8.19 (d, *J* = 8.5 Hz, 1 H), 7.88 (t, *J* = 9.0 Hz, 2 H), 7.82 (d, *J* = 8.5 Hz, 2 H), 7.78 (t, *J* = 7.5 Hz, 1 H), 7.59 (t, *J* = 8.0 Hz, 1 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.2, 148.4, 143.9, 137.6, 132.9, 130.5, 130.1, 128.3, 127.8, 127.8, 127.4, 119.1, 118.9, 113.0; IR (KBr, neat) 3236, 2978, 2234, 2178, 1453, 1379, 1024, 865, 752, 727, 656 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{11}N_2$ $(M + H)^+$ 231.0917, found 231.0923.

2-(*P*-tolyl)quinoline (3aj):

White solid; R_f (Hexane/EtOAc, 19:1) 0.60; mp 85–87 °C. Yield 121 mg, 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 1 H), 8.15 (d, *J* = 8.8 Hz, 1 H), 8.12 (d, *J* = 8.0 Hz, 2 H), 7.84 (d, *J* = 8.8 Hz, 1 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.74 (t, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.2 Hz, 1 H), 7.36 (d, *J* = 7.6 Hz, 2 H), 2.46 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 148.5, 139.7, 137.1, 136.9, 129.8, 129.8, 127.7, 127.3, 126.3, 119.2, 21.6; IR (KBr, neat) 3256, 2971, 1543, 1432, 1371, 1055, 822, 730, 623 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{14}N$ $(M + H)^+$ 220.1121, found 220.1136.

2-(4-(*Tert*-butyl)phenyl)quinoline (3ak):

White solid; R_f (Hexane/EtOAc, 19:1) 0.60; mp 80–82 °C. Yield 154 mg, 83%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 12.0, 9.0 Hz, 2 H), 8.10 (d, *J* = 8.5 Hz, 2 H), 7.87 (d, *J* = 9.0 Hz, 1 H), 7.82 (d, J = 8.0 Hz, 1 H), 7.72 (t, *J* = 8.5 Hz, 1 H), 7.56 (d, *J* = 8.5 Hz, 2 H), 7.52 (t, *J* =

8.5 Hz, 1 H), 1.39 (s, 9 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 157.4, 152.6, 148.3, 136.9, 136.7, 129.7, 129.6, 127.5, 127.3, 127.1, 126.1, 125.9, 119.0, 34.8, 31.3; IR (KBr, neat) 3273, 2911, 1557, 1486, 1371, 878, 787, 673 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{20}N$ $(M + H)^+$ 262.1590, found 262.1607.

2-([1,1'-Biphenyl]-4-yl)quinoline (3al):

White solid; R_f (Hexane/EtOAc, 19:1) 0.50; mp 152–154 °C. Yield 170 mg, 85%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.0 Hz, 2 H), 8.23 (t, *J* = 9.0 Hz, 2 H), 7.93 (d, *J* = 8.5 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 2 H), 7.74 (d, *J* = 7.0 Hz, 1 H), 7.69 (d, *J* = 7.0 Hz, 2 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 7.49 (t, *J* = 8.0 Hz, 2 H), 7.40 (t, *J* = 7.5 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 157.1, 148.5, 142.3, 140.8, 138.7, 137.1, 130.0, 129.9, 129.1, 128.2, 127.8, 127.8, 127.7, 127.4, 127.4, 126.5, 119.1; IR (KBr, neat) 3036, 2923, 1951, 1568, 1208, 767, 619 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{16}N$ $(M + H)^+$ 282.1277, found 282.1290.

2-(Naphthalen-2-yl)quinoline (3am):

White solid; R_f (Hexane/EtOAc, 19:1) 0.50; mp 156–158 °C. Yield 156 mg, 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1 H), 8.38 (dd, *J* = 8.8, 2.0 Hz, 1 H), 8.28 – 8.25 (m, 2 H), 8.04 (d, *J* = 8.4 Hz, 1 H), 8.02 – 8.00 (m, 2 H), 7.92 – 7.89 (m, 1 H), 7.85 (d, *J* = 7.6 Hz, 1 H), 7.78 – 7.74 (m, 1 H), 7.57 – 7.52 (m, 3 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 157.4, 148.5, 137.2, 137.0, 134.1, 133.7, 130.0, 129.9, 129.1, 128.8, 128.0, 127.7, 127.5, 127.0, 126.6, 126.6, 125.3, 119.4; IR (KBr, neat) 3234, 2945, 1596, 1277, 1163, 820, 712 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{14}N$ $(M + H)^+$ 256.1121, found 256.1129.

2-(Naphthalen-1-yl)quinoline (3an):

White solid; R_f (Hexane/EtOAc, 19:1) 0.50; mp 147–149 °C. Yield 143 mg, 79%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.25 (m, 2 H), 8.14 (d, *J* = 8.0 Hz, 1 H), 7.98 – 7.91 (m, 3 H), 7.79 (t, *J* = 7.5 Hz, 1 H), 7.75 – 7.71 (m, 2 H), 7.61 (t, *J* = 7.5 Hz, 2 H), 7.54 – 7.47 (m, 2 H);

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 159.6, 148.3, 138.9, 136.5, 134.2, 131.5, 130.0, 129.9, 129.4, 128.6, 128.0, 127.8, 127.2, 126.8, 126.8, 126.2, 125.9, 125.6, 123.5; IR (KBr, neat) 3245, 2951, 1544, 1346, 1134, 1105, 834, 708 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{14}N$ $(M + H)^+$ 256.1121, found 256.1139.

2-(Pyren-1-yl)quinoline (3ao):

White solid; R_f (Hexane/EtOAc, 19:1) 0.50; mp 138–140 °C. Yield 189 mg, 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 9.2 Hz, 1 H), 8.34 – 8.28 (m, 4 H), 8.24 – 8.18 (m, 2 H), 8.14 (s, 2 H), 8.09 (d, *J* = 9.2 Hz, 1 H), 8.03 (t, *J* = 7.6 Hz, 1 H), 7.94 (d, *J* = 8.8 Hz, 1 H), 7.85 (d, *J* = 8.4 Hz, 1 H), 7.83 – 7.80 (m, 1 H), 7.63 (t, *J* = 8.0 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 159.9, 148.4, 136.5, 136.0, 131.8, 131.6, 131.1, 130.1, 129.9, 129.0, 128.4, 128.2, 128.0, 127.8, 127.6, 127.1, 126.9, 126.3, 125.6, 125.4, 125.1, 125.0, 124.0; IR (KBr, neat) 3040, 1595, 1498, 1424, 837, 760, 721 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{16}N$ $(M + H)^+$ 330.1277, found 330.1295.

2-Cyclohexylquinoline (3ap):

Brown liquid; R_f (Hexane/EtOAc, 19:1) 0.60. Yield 101 mg, 67%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.5, 3.5 Hz, 2 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.67 (t, *J* = 7.0 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 1 H), 7.32 (d, *J* = 8.5 Hz, 1 H), 2.96 – 2.89 (m, 1 H), 2.03 (d, *J* = 13.0 Hz, 2 H), 1.92 – 1.87 (m, 2 H), 1.79 (d, *J* = 12.0 Hz, 1 H), 1.67 – 1.59 (m, 2 H), 1.52 – 1.43 (m, 2 H), 1.38 – 1.26 (m, 1 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 167.0, 148.0, 136.5, 129.4, 129.1, 127.6, 127.2, 125.8, 119.8, 47.8, 33.0, 26.7, 26.3; IR (KBr, neat) 3057, 2922, 2850, 1600, 1501, 823, 753 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{18}N$ $(M + H)^+$ 212.1434, found 212.1446.

2-Methylquinoline (3aq):

White liquid; R_f (Hexane/EtOAc, 9:1) 0.40. Yield 38 mg, 37%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (t, *J* = 10.0 Hz, 2 H), 7.72 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.66 – 7.62 (m, 1 H), 7.46 – 7.42 (m, 1 H), 7.23 (d, *J* = 8.4 Hz, 1 H), 2.71 (s, 3 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 159.2, 148.1,

136.4, 129.7, 128.8, 127.7, 126.7, 125.9, 122.3, 25.6; IR (KBr, neat) 3050, 2922, 1601, 1506, 1423, 1220, 1116, 819, 745 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{10}N$ $(M + H)^+$ 144.0808, found 144.0814.

2-(Thiophen-2-yl)quinoline (3ar):

White solid; R_f (Hexane/EtOAc, 19:1) 0.60; mp 124–126 °C. Yield 97 mg, 65%; ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2 H), 7.77 (t, *J* = 9.0 Hz, 2 H), 7.73 (d, *J* = 4.0 Hz, 1 H), 7.70 (t, *J* = 7.0 Hz, 1 H), 7.50 – 7.47 (m, 2 H), 7.16 (t, *J* = 5.0 Hz, 1 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 152.5, 148.3, 145.6, 136.8, 130.0, 129.4, 128.8, 128.3, 127.7, 127.4, 126.3, 126.1, 117.8; IR (KBr, neat) 3345, 2967, 1578, 1497, 1370, 787, 678 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_{10}NS$ $(M + H)^+$ 212.0528, found 212.0517.

2-(4-Chlorophenyl)-6-methylquinoline (3ba):

White solid; R_f (Hexane/EtOAc, 19:1) 0.60; mp 108–110 °C. Yield 160 mg, 89%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 3 H), 8.05 (d, *J* = 8.4 Hz, 1 H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.58 – 7.55 (m, 2 H), 7.50 – 7.47 (m, 2 H), 2.55 (s, 3 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.4, 147.0, 138.4, 136.7, 136.5, 135.6, 132.4, 129.6, 129.2, 128.9, 127.5, 126.6, 118.8, 21.8; IR (KBr, neat) 3236, 2987, 1553, 1434, 1125, 878, 727, 688 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{13}ClN$ $(M + H)^+$ 254.0731, found 254.0732.

2-([1,1'-Biphenyl]-4-yl)-6-methylquinoline (3bl):

White solid; R_f (Hexane/EtOAc, 19:1) 0.50; mp 148–150 °C. Yield 189 mg, 90%; ^1H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 2 H), 8.12 (dd, *J* = 14.0, 9.0 Hz, 2 H), 7.88 (d, *J* = 8.5 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 2 H), 7.69 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 11.0 Hz, 2 H), 7.49 (t, *J* = 7.5 Hz, 2 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 2.56 (s, 3 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.2, 147.1, 142.1, 140.8, 138.8, 136.4, 136.4, 132.2, 129.6, 129.1, 128.1, 127.8, 127.7, 127.5, 127.4, 126.6, 119.1, 21.8; IR (KBr, neat) 3034, 2961, 1901, 1567, 1322, 781, 650 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{18}N$ $(M + H)^+$ 296.1434, found 296.1428.

2-(4-Bromophenyl)-7-methylquinoline (3cb):

White solid; R_f (Hexane/EtOAc, 19:1) 0.60; mp 112–114 °C. Yield 180 mg, 85%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 1 H), 8.04 (t, *J* = 9.0 Hz, 3 H), 7.78 (d, *J* = 8.5 Hz, 1 H), 7.64 (d, *J* = 6.5 Hz, 2 H), 7.57 (d, *J* = 10.5 Hz, 2 H), 2.55 (s, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.4, 147.0, 138.8, 136.7, 136.6, 132.4, 132.2, 129.6, 129.2, 127.5, 126.6, 123.9, 118.7, 21.9; IR (KBr, neat) 3221, 2980, 1567, 1488, 1409, 1055, 878, 653 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{13}BrN$ $(M + H)^+$ 298.0226, found 298.0219.

2-(4-Chlorophenyl)-6-ethylquinoline (3da):

White solid; R_f (Hexane/EtOAc, 19:1) 0.60; mp 114–116°C. Yield 191 mg, 86%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 9.0 Hz, 1 H), 8.10 (t, *J* = 8.5 Hz, 3 H), 7.81 (d, *J* = 8.5 Hz, 1 H), 7.61 (s, 2 H), 7.49 (d, *J* = 8.5 Hz, 2 H), 2.86 (q, *J* = 7.5 Hz, 2 H), 1.35 (t, *J* = 7.5 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.4, 147.1, 143.0, 138.3, 136.8, 135.6, 131.4, 129.6, 129.2, 129.0, 127.5, 125.3, 118.8, 29.1, 15.6; IR (KBr, neat) 3278, 2945, 1667, 1456, 1123, 878, 727, 644 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{15}ClN$ $(M + H)^+$ 268.0888, found 268.0881.

6-Butyl-2-(4-chlorophenyl)quinoline (3ea):

White solid; R_f (Hexane/EtOAc, 19:1) 0.60; mp 104–106 °C. Yield 193 mg, 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1 H), 8.12 – 8.06 (m, 3 H), 7.79 (d, *J* = 8.8 Hz, 1 H), 7.60 – 7.58 (m, 2 H), 7.50 – 7.47 (m, 2 H), 2.81 (t, *J* = 7.6 Hz, 2 H), 1.75 – 1.68 (m, 3 H), 1.46 – 1.37 (m, 2 H), 0.97 (t, *J* = 7.2 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.4, 147.2, 141.6, 138.4, 136.7, 135.5, 131.7, 129.6, 129.2, 129.0, 127.5, 126.0, 118.8, 35.8, 33.6, 22.6, 14.2; IR (KBr, neat) 3265, 2922, 1567, 1456, 1105, 890, 727, 644 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{19}ClN$ $(M + H)^+$ 296.1201, found 296.1217.

6-(*Tert*-butyl)-2-(4-chlorophenyl)quinoline (3fa):

White solid; R_f (Hexane/EtOAc, 19:1) 0.60; mp 98–100 °C. Yield 174 mg, 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 1 H), 8.10 (d, *J* = 8.8 Hz, 3 H), 7.85 – 7.80 (m, 2 H), 7.74

(d, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 2 H), 1.44 (s, 9 H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 155.7, 149.7, 147.0, 138.4, 137.3, 135.6, 129.4, 129.2, 129.1, 129.0, 127.2, 122.7, 118.8, 35.2, 31.4; IR (KBr, neat) 3277, 2919, 2851, 1710, 1633, 1525, 989, 678 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{19}ClN$ $(M + H)^+$ 296.1201, found 296.1222.

6-Chloro-2-(4-chlorophenyl)quinoline (3ga):

White solid; R_f (Hexane/EtOAc, 19:1) 0.50; mp 134–136 °C. Yield 156 mg, 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.07 (m, 4 H), 7.87 (d, *J* = 8.8 Hz, 1 H), 7.82 (d, J = 2.4 Hz, 1 H), 7.67 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.52 – 7.48 (m, 2 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.5, 146.8, 137.8, 136.3, 136.1, 132.4, 131.5, 131.0, 129.3, 129.0, 128.0, 126.4, 119.6; IR (KBr, neat) 3287, 2910, 2851, 1703, 1525, 989, 878, 678 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{10}Cl_2N$ $(M + H)^+$ 274.0185, found 274.0194.

6-Bromo-2-(4-chlorophenyl)quinoline (3ha):

White solid; R_f (Hexane/EtOAc, 19:1) 0.50; mp 142–144 °C. Yield 167 mg, 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 3 H), 7.99 (d, *J* = 8.8 Hz, 1 H), 7.96 (d, *J* = 2.4 Hz, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H), 7.78 (dd, *J* = 8.8, 2.0 Hz, 1 H), 7.48 (d, *J* = 8.4 Hz, 2 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.6, 147.0, 137.7, 136.3, 136.2, 133.6, 131.6, 129.8, 129.4, 129.0, 128.5, 120.6, 119.6; IR (KBr, neat) 3281, 2934, 1703, 1525, 1178, 923, 887, 677 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{10}BrClN$ $(M + H)^+$ 317.9680, found 317.9683.

2-(4-(*Tert*-butyl)phenyl)-6-fluoroquinoline (3ik):

White solid; R_f (Hexane/EtOAc, 19:1) 0.60; mp 115–117 °C. Yield 133 mg, 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1 H), 8.17 – 8.12 (m, 3 H), 7.84 (dd, *J* = 9.2, 2.4 Hz, 1 H), 7.80 (d, *J* = 8.4 Hz, 1 H), 7.74 (d, *J* = 2.4 Hz, 1 H), 7.20 (t, *J* = 8.4 Hz, 2 H), 1.44 (s, 9 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 164.0 (d, *J* = 247.3 Hz), 155.9, 149.6, 146.8, 137.3, 136.1, 129.6 (d, *J* = 8.4 Hz), 129.2 (d, *J* = 11.1 Hz), 127.0, 124.3 (d, *J* = 252.4 Hz), 122.7, 118.9, 116.0 (d, *J* = 21.4 Hz), 35.2, 31.5; (d, *J* = 21.5 Hz); ^{19}F NMR (470 MHz, $CDCl_3$/ C_6F_6)

δ –119.6 (s, –CF–); IR (KBr, neat) 3277, 2956, 1633, 1567, 1425, 1256, 923, 678 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{19}FN$ $(M + H)^+$ 280.1496, found 280.1495.

Experimental Procedure for Control Experiments:

Experimental Procedure for Scheme 3a: Radical Trapping Experiment

To a mixture of (*E*)-2-(2-(trimethylsilyl)vinyl)aniline **1a** (0.85 mmol, 1.2 equiv), 4-chlorobenzaldehyde **2a** (0.71 mmol, 1.0 equiv), CuI (0.07 mmol, 0.1 equiv) and TEMPO or BHT (1.42 mmol, 2.0 equiv) in CH_3CN, $BF_3{\cdot}OEt_2$ (0.71 mmol, 1.0 equiv) was added slowly at 0 ^oC under air atmosphere. The mixture was then stirred at room temperature for 5–10 min before being heated to 80 °C in an oil bath. The progress of the reaction was monitored by TLC (using hexane/ethyl acetate = 19:1 as eluents). After completion of the reaction (12 h), the mixture was cooled to room temperature. The solvent was removed in vacuo in a rotary evaporator and then the residue was diluted with ethyl acetate, saturated $NaHCO_3$, and saturated brine solution. The aqueous phase was extracted with ethyl acetate (3 × 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated using a rotary evaporator. The crude was subjected to column chromatography over silica gel to give the corresponding desired product **3aa** with 72% yield for TEMPO, 77% yield for BHT. This observation suggests non-involvement of any radical path.

Experimental Procedure for Scheme 3b: Reaction Without CuI

To a mixture of (*E*)-2-(2-(trimethylsilyl)vinyl)aniline **1a** (0.85 mmol, 1.2 equiv), 4-chlorobenzaldehyde **2a** (0.71 mmol, 1.0 equiv) in CH_3CN, $BF_3{\cdot}OEt_2$ (0.71 mmol, 1.0 equiv) was added slowly at 0 ^oC under air atmosphere. The mixture was then stirred at room temperature for 5–10 min before being heated to 80 °C in an oil bath. The progress of the reaction was monitored by TLC (using hexane/ethyl acetate = 19:1 as eluents). No product formation was observed even after 12 hours, instead, decomposition of the starting

materials occurred. This outcome highlights the crucial role of CuI in facilitating the reaction.

Experimental Procedure for Scheme 3c: Reaction Without $BF_3 \cdot OEt_2$

To a mixture of (*E*)-2-(2-(trimethylsilyl)vinyl)aniline **1a** (0.85 mmol, 1.2 equiv), 4-chlorobenzaldehyde **2a** (0.71 mmol, 1.0 equiv) and CuI (0.07 mmol, 0.1 equiv), CH_3CN was added under air atmosphere. The mixture was then stirred at room temperature for 5–10 min before being heated to 80 °C in an oil bath. The progress of the reaction was monitored by TLC (using hexane/ethyl acetate = 49:1 as eluents). After completion of the reaction (12 h), the mixture was cooled to room temperature. The solvent was then removed in vacuo in a rotary evaporator and, the residue was diluted with ethyl acetate, saturated $NaHCO_3$, NH_4Cl, and brine solution. The aqueous phase was extracted with ethyl acetate (3 × 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated using a rotary evaporator. The resulting crude product was then purified by column chromatography over silica gel to isolate the imine intermediate **A** in 71% yield.

Characterization Data of Intermediate A:

(*E*)-1-(4-Chlorophenyl)-*N*-(2-((*E*)-2-(trimethylsilyl)vinyl)phenyl)methanimine (A):

White solid; R_f (Hexane/EtOAc, 49:1) 0.50; mp. Yield 158 mg, 71%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1 H), 7.86 (d, *J* = 8.4 Hz, 2 H), 7.63 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.49 – 7.45 (m, 2 H), 7.40 (d, *J* = 19.2 Hz, 1 H), 7.29 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.24 – 7.20 (m, 1 H), 6.95 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.48 (d, *J* = 19.2 Hz, 1 H), 0.14 (s, 9 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.8, 149.5, 139.9, 137.6, 135.1, 132.3, 131.3, 130.1, 129.4, 129.0, 126.4, 125.9, 118.6, -1.0; IR (KBr, neat) 3379, 3236, 1619, 1487, 1455, 1379, 1246, 1024, 834, 744, 727, 690 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{21}ClNSi$ $(M + H)^+$ 314.1126, found 314.1105.

Experimental Procedure for Scheme 3d: To validate the role of H_2O

To a mixture of (*E*)-2-(2-(trimethylsilyl)vinyl)aniline **1a** (0.85 mmol, 1.2 equiv), 4-chlorobenzaldehyde **2a** (0.71 mmol, 1.0 equiv), CuI (0.07 mmol, 0.1 equiv) and oven dried MS 4 Å (20 mg) in CH_3CN, $BF_3{\cdot}OEt_2$ (0.71 mmol, 1.0 equiv) was added slowly at 0 ^oC under nitrogen atmosphere. The mixture was then stirred at room temperature for 5–10 min before being heated to 80 °C in an oil bath. The progress of the reaction was monitored by TLC (using hexane/ethyl acetate = 19:1 as eluents). After completion of the reaction (12 h), the mixture was cooled to room temperature. The solvent was removed in vacuo in a rotary evaporator and then the residue was diluted with ethyl acetate, saturated $NaHCO_3$, and saturated brine solution. The aqueous phase was extracted with ethyl acetate (3 × 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated using a rotary evaporator. The crude was subjected to column chromatography over silica gel, affording the corresponding product in only 16% yield, indicating that H_2O plays a crucial role in enabling the reaction.

Experimental Procedure for Scheme 3e: Reaction with Phenyl Substituted Alkene

To a mixture of (*E*)-2-styrylaniline **1a′** (0.85 mmol, 1.2 equiv), 4-chlorobenzaldehyde **2a** (0.71 mmol, 1.0 equiv) and CuI (0.07 mmol, 0.1 equiv) in CH_3CN, $BF_3{\cdot}OEt_2$ (0.71 mmol, 1.0 equiv) was added slowly at 0 ^oC under air atmosphere. The mixture was then stirred at room temperature for 5–10 min before being heated to 80 °C in an oil bath and monitored by TLC (using hexane/ethyl acetate = 19:1 as eluents). No product formation was observed, highlighting the crucial role of the silyl group in the reaction mechanism.

Experimental Procedure for Scheme 3f: *N* - Protected Experiment

To a mixture of (*E*)-4-methyl-*N*-(2-(2-(trimethylsilyl)vinyl)phenyl)benzenesulfonamide **1b′** (0.85 mmol, 1.2 equiv), 4-chlorobenzaldehyde **2a** (0.71 mmol, 1.0 equiv) and CuI (0.07 mmol, 0.1 equiv) in CH_3CN, $BF_3{\cdot}OEt_2$ (0.71 mmol, 1.0 equiv) was added slowly at 0 ^oC under air atmosphere. The mixture was then stirred at room temperature for 5–10 min before being

heated to 80 °C in an oil bath. The progress of the reaction was monitored by TLC (using hexane/ethyl acetate = 19:1 as eluents). No expected product was observed even after 12 hours, highlighting the free *ortho*-amino (–NH_2) group is essential for smooth reaction progress.

Experimental Procedure for Gram-scale Synthesis of Compound 3aa:

To a mixture of (*E*)-2-(2-(trimethylsilyl)vinyl)aniline **1a** (1.63 g, 8.54 mmol, 1.2 equiv), 4-chlorobenzaldehyde **2a** (1.0 g, 7.11 mmol, 1.0 equiv.), and CuI (135.16 mg, 0.71 mmol, 0.1 equiv) in CH_3CN (10 ml), $BF_3{\cdot}OEt_2$ (0.88 ml, 7.11 mmol, 1.0 equiv) was added slowly at 0 ^oC under air atmosphere. The mixture was then stirred at room temperature for 5–10 min before being heated to 80 °C in an oil bath. The progress of the reaction was monitored by TLC (using hexane/ethyl acetate = 19:1 as eluents). After completion of the reaction (12 h), the mixture was cooled to room temperature. The solvent was removed in vacuo in a rotary evaporator and then the residue was diluted with ethyl acetate, saturated $NaHCO_3$, and saturated brine solution. The aqueous phase was extracted with ethyl acetate (3 × 10 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated using a rotary evaporator. The crude was subjected to column chromatography over silica gel to give the corresponding product **3aa** in 74% yield (1.26 g).

Experimental Procedure and Characterization Data of Compounds 5aa, 5ab and 5ea:

To an oven-dried sealed tube, compound **3** (0.21 mmol, 1.0 equiv), diphenylacetylene **4** (0.21 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (0.004 mmol, 2 mol %), $AgBF_4$ (0.21 mmol, 1.0 equiv), and $Cu(OAc)_2{\cdot}H_2O$ (0.21 mmol, 1.0 equiv) in DCE (3.0 mL) were refluxed in a preheated oil bath at 80 °C. The reaction mixture was refluxed for 24 h (monitored by TLC analysis) before filtering through a short pad of Celite. The solids were washed with MeOH, and the combined filtrates were concentrated in a rotary evaporator. The crude product was then purified by column chromatography to provide the corresponding product **5**.

9-Chloro-6,7-diphenylisoquinolino[2,1-*a*]quinolin-5-ium Tetrafluoroborate (5aa):

Yellow solid; R_f (DCM:MeOH, 9:1) 0.40; mp 290–292 °C. Yield 81 mg, 92%; ^{1}H NMR (400 MHz, $CDCl_3$/ MeOD-d_4) δ 9.23 (s, 1 H), 9.10 (s, 1 H), 8.95 (s, 1 H), 8.16 (d, *J* = 7.6 Hz, 1 H), 7.96 (s, 1 H), 7.84 (d, *J* = 8.4 Hz, 1 H), 7.60 (d, *J* = 33.2 Hz, 3 H), 7.35 (s, 4 H), 7.14 – 7.05 (m, 4 H), 6.91 (s, 2 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$/ MeOD-d_4) δ 147.9, 143.2, 142.4, 141.5, 137.2, 137.1, 136.2, 135.7, 133.5, 132.5, 131.4, 130.7, 130.4, 130.3, 129.9, 129.7, 129.5, 129.4, 129.1, 129.0, 128.9, 126.9, 125.4, 123.9, 119.1; IR (KBr, neat) 3278, 2919, 1687, 1525, 1162, 927, 727 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{19}ClN$ $(M - BF_4)^+$ 416.1201, found 416.1203.

9-Bromo-6,7-diphenylisoquinolino[2,1-*a*]quinolin-5-ium Tetrafluoroborate (5ab):

Yellow solid; R_f (DCM:MeOH, 9:1) 0.40; mp 312–314 °C. Yield 91 mg, 94%; ^{1}H NMR (400 MHz, $CDCl_3$/ MeOD-d_4) δ 9.18 (d, *J* = 10.0 Hz, 1 H), 8.95 (d, *J* = 9.2 Hz, 1 H), 8.89 (d, *J* = 8.4 Hz, 1 H), 8.14 (d, *J* = 8.4 Hz, 1 H), 8.05 (d, *J* = 8.8 Hz, 1 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.75 (s, 1 H), 7.67 – 7.62 (m, 1 H), 7.37 – 7.32 (m, 4 H), 7.18 – 7.06 (m, 5 H), 6.93 (d, *J* = 8.0 Hz, 2 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$/ MeOD-d_4) δ 148.0, 142.4, 141.5, 137.1, 137.0, 136.1, 135.7, 135.2, 133.4, 132.1, 131.4 130.8, 130.6, 130.3, 130.2, 130.1, 129.8, 129.7, 129.5, 129.1, 129.0, 128.9, 125.3, 124.2, 118.9; IR (KBr, neat) 3277, 2919, 2851, 1525, 1162, 989, 591 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{19}BrN$ $(M - BF_4)^+$ 460.0695, found 460.0683.

2-Butyl-9-chloro-6,7-diphenylisoquinolino[2,1-*a*]quinolin-5-iumTetrafluoroborate (5ea):

Yellow solid; R_f (DCM:MeOH, 9:1) 0.40; mp 302–304 °C. Yield 94 mg, 95%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.24 (s, 1 H), 9.05 (s, 1 H), 8.82 (s, 1 H), 7.89 (s, 2 H), 7.80 (s, 1 H), 7.59 (s, 1 H), 7.41 (s, 3 H), 7.20 (d, *J* = 6.5 Hz, 3 H), 7.14 (s, 2 H), 7.02 (s, 2 H), 2.75 (t, *J* = 7.5 Hz, 2 H), 1.68 – 1.64 (s, 2 H), 1.37 – 1.32 (m, 2 H), 0.92 (t, *J* = 7.0 Hz, 3 H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.4, 145.3, 142.8, 142.4, 141.4, 137.2, 135.6, 135.5, 133.8, 132.5, 131.8, 130.7, 130.6, 129.6, 129.5, 129.2, 129.1, 129.0, 128.2, 126.9, 125.4, 124.1, 119.6, 35.1, 32.9,

22.5, 14.1; IR (KBr, neat) 2925, 2852, 1600, 1502, 1449, 1058, 825, 757 cm^{-1}; HRMS (ESI) calcd. for $C_{33}H_{27}ClN$ $(M - BF_4)^+$ 472.1827, found 472.1820

Photophysical Studies:

Photophysical studies, including UV-visible and photoluminescence analyses, were performed on the synthesized compounds in a 10.0 μM dichloromethane solution. Through detailed analysis in dichloromethane, compounds **5aa**, **5ab** and **5ea** exhibited a pair of fluorescent emission bands, covering the yellow-green (550–580 nm) region under 420–430 nm photoexcitation. The corresponding absorption (λ_{max}), emission (λ_{em}) spectra, and UV irradiation of the corresponding compounds are depicted in Figure 2 and Figure 3 (see MS), with detailed results are summarized in Table S2.

Table S2. UV-vis and photoluminescence parameters

entry	**compound**	**λ_{max} (nm)[a]**	**absorbance at λ_{max}**	**ε (1×10^4 M^{-1} cm^{-1})**	**λ_{em} (nm)[b]**
1	**5aa**	421	0.338	3.38	558
2	**5ab**	423	0.309	3.09	504
3	**5ea**	422	0.158	1.58	550

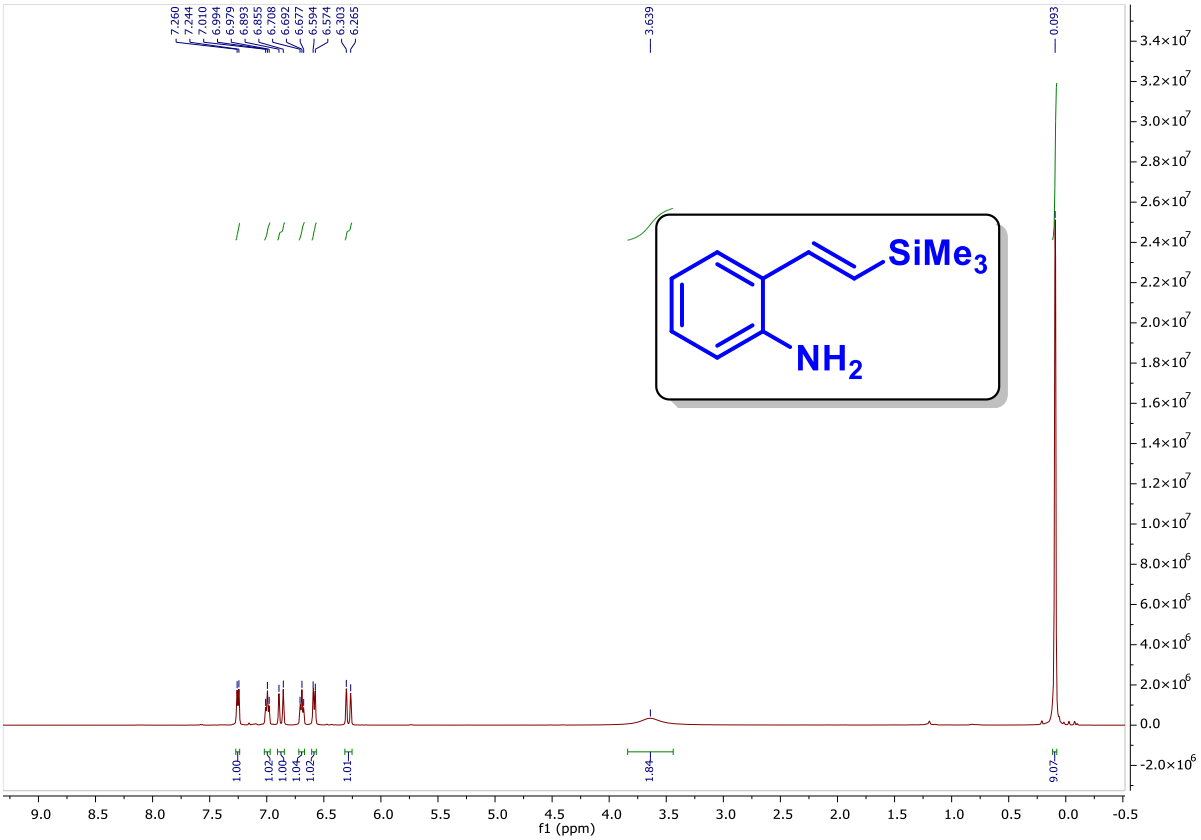
[a]Absorption wavelengths. [b]Emission wavelengths in DCM at a concentration of 1×10^{-5} M.

References:

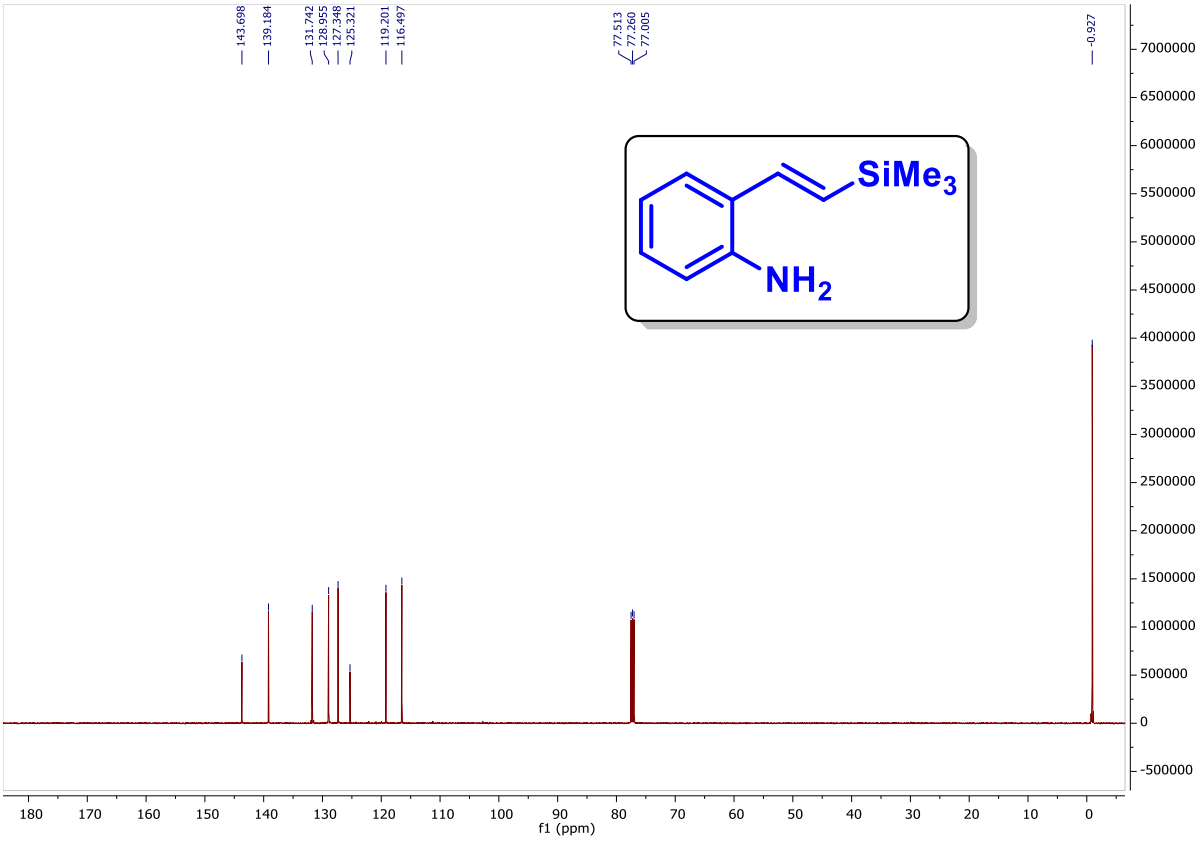
1. (a) Karabelas, K.; Hallberg, A. Synthesis of (*E*)-(2-arylethenyl) silanes by palladium-catalyzed arylation of vinylsilanes in the presence of silver nitrate. *J. Org. Chem.* **1986**, *51*, 5286-5290; (b) Zhang, J.; Li, X.; Li, X.; Shi, H.; Sun, F.; Du, Y. DMSO/$SOCl_2$-mediated C (sp 2)–H amination: switchable synthesis of 3-unsubstituted indole and 3-methylthioindole derivatives. *Chem. Commun.*, **2021**, *57*, 460-463.
2. (a) Miura, K.; Inoue, G.; Sasagawa, H.; Kinoshita, H.; Ichikawa, J.; Hosomi, A. Platinum-catalyzed nucleophilic addition of vinylsilanes at the β-position. *Org. Lett.*, **2009**, *11*, 5066–5069. (b) Niljianskul, N.; Zhu, S.; Buchwald, S. L. Enantioselective

Synthesis of α-Aminosilanes by Copper-Catalyzed Hydroamination of Vinylsilanes. *Angew. Chem.*, **2015**, *127*, 1658-1661. (c) Miller, R. B.; McGarvey, G. A highly stereoselective synthesis of vinyl bromides and chlorides via disubstituted vinylsilanes. *J.Org.Chem.*, **1978**, *43*, 4424-4431. (d) Obora, Y.;Moriya, H.; Tokunaga, M.; Tsuji, Y. Cross-coupling reaction of thermally stable titanium (ii)-alkyne complexes with aryl halides catalysed by a nickel complex. *Chem. Commun.*, **2003**, *22*, 2820-2821. (e) Carpita, A.; Ribecai, A.; Rossi, R.; Stabile, P. Synthesis of the racemic forms of carbon–carbon double bond locked analogues of strobilurins which are characterized by a 2-arylcyclopropane ring cis-substituted at C-1 by the methyl (*E*)-3-methoxypropenoate unit. *Tetrahedron*, **2002**, *58*, 3673-3680.

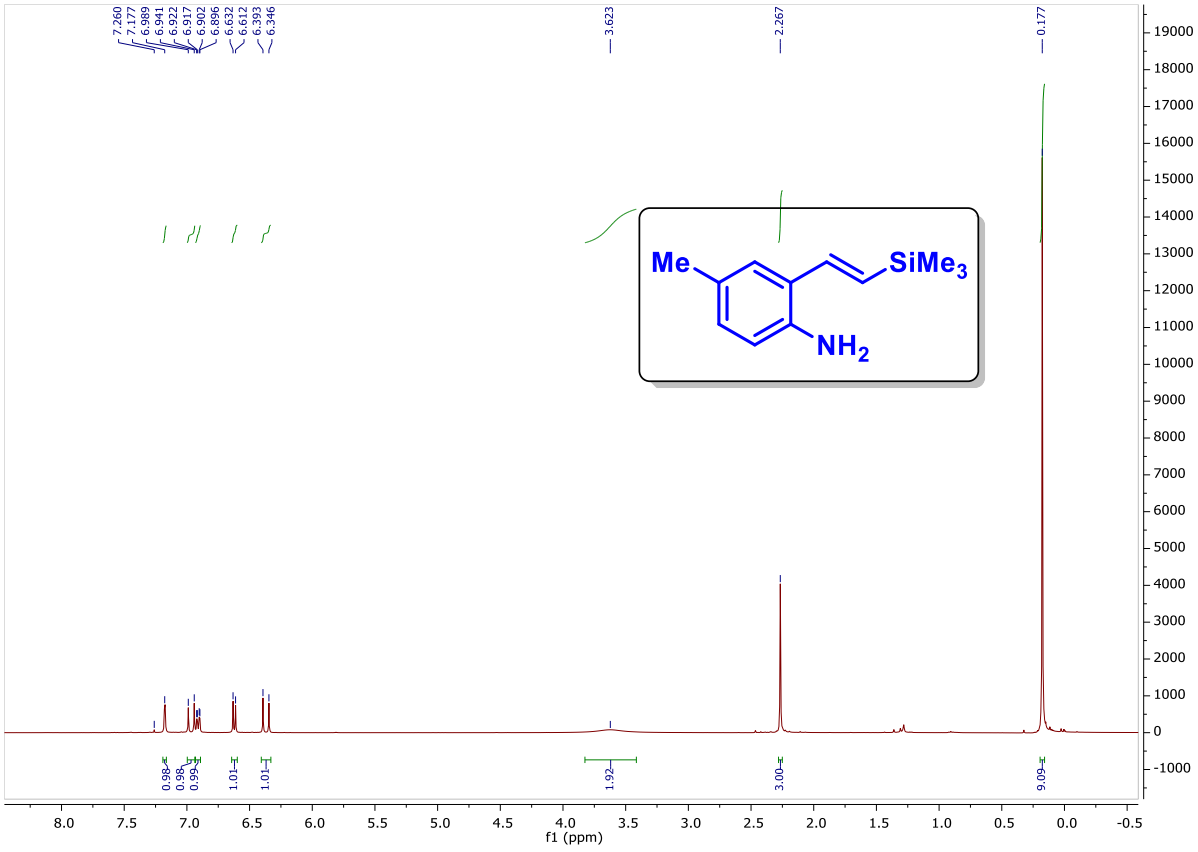
^{1}H spectrum of compound **1a** (500 MHz, $CDCl_3$)



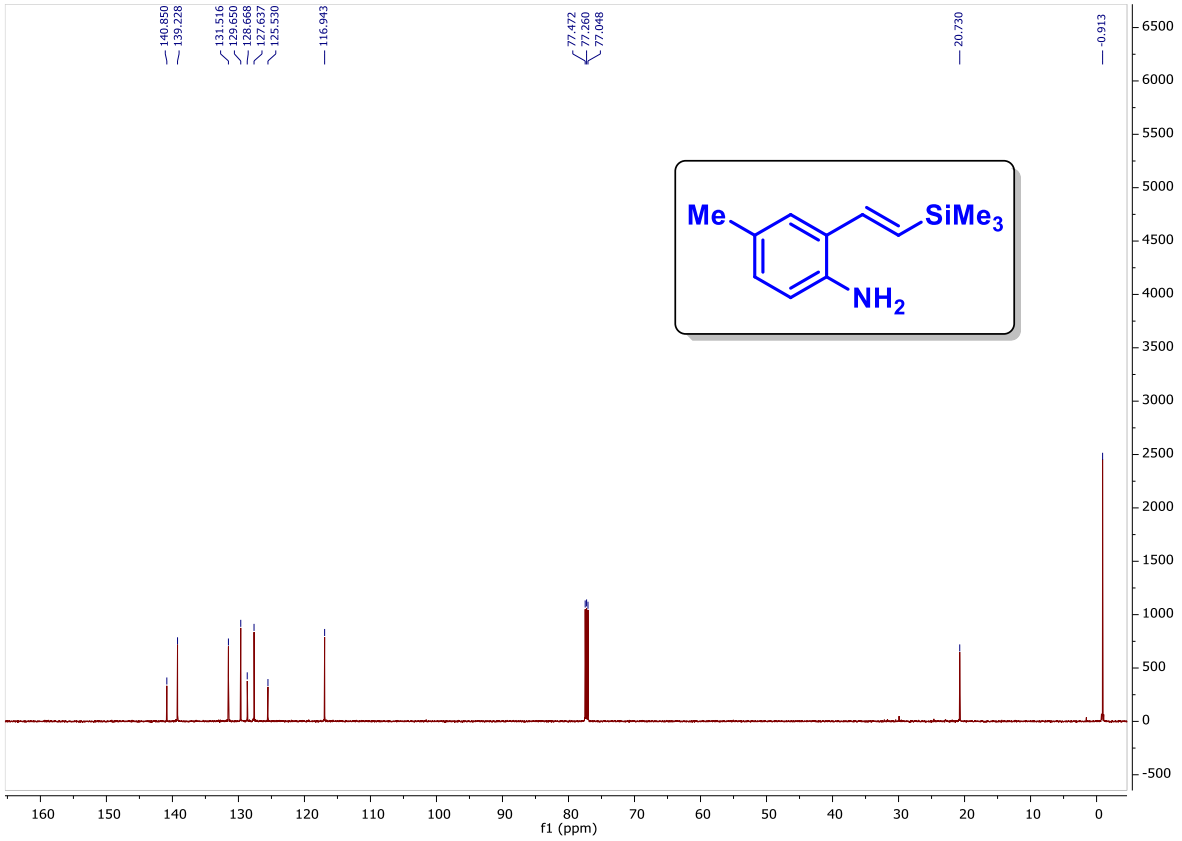
^{13}C{^{1}H} spectrum of compound **1a** (125 MHz, $CDCl_3$)



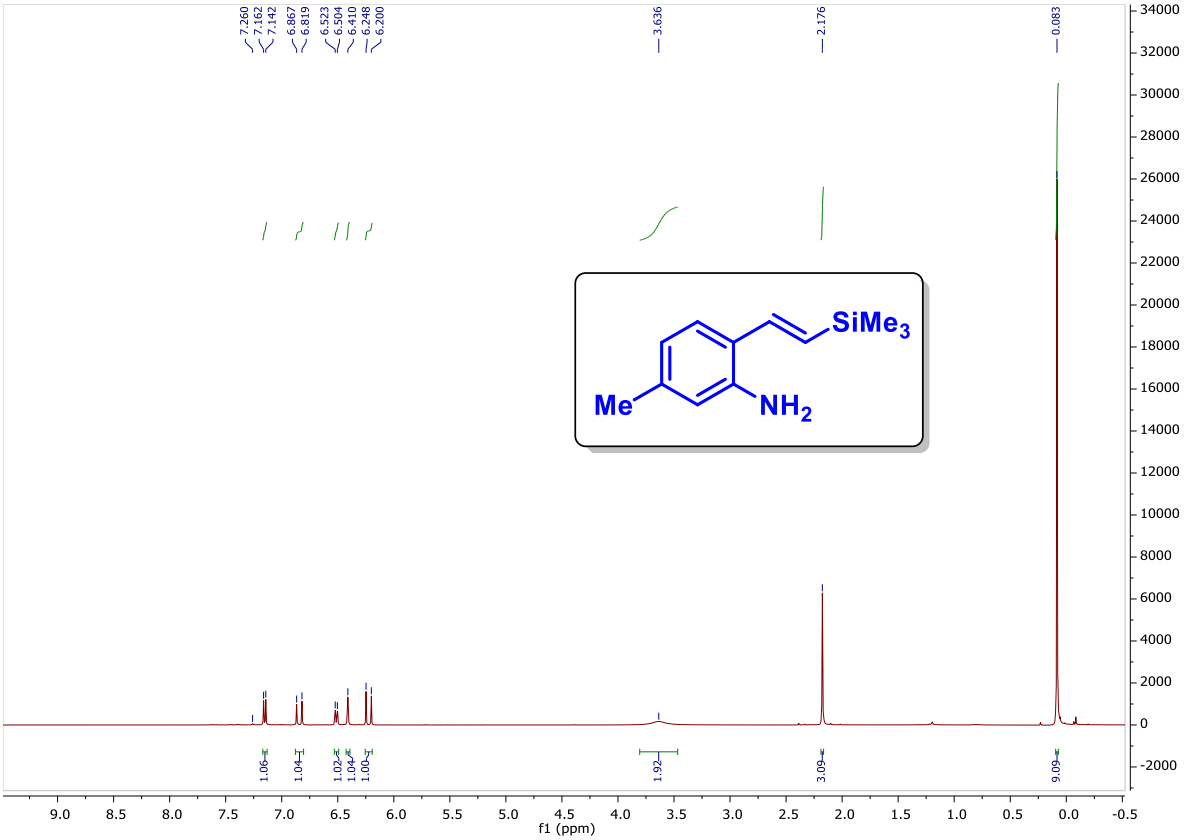
^{1}H spectrum of compound **1b** (400 MHz, $CDCl_3$)



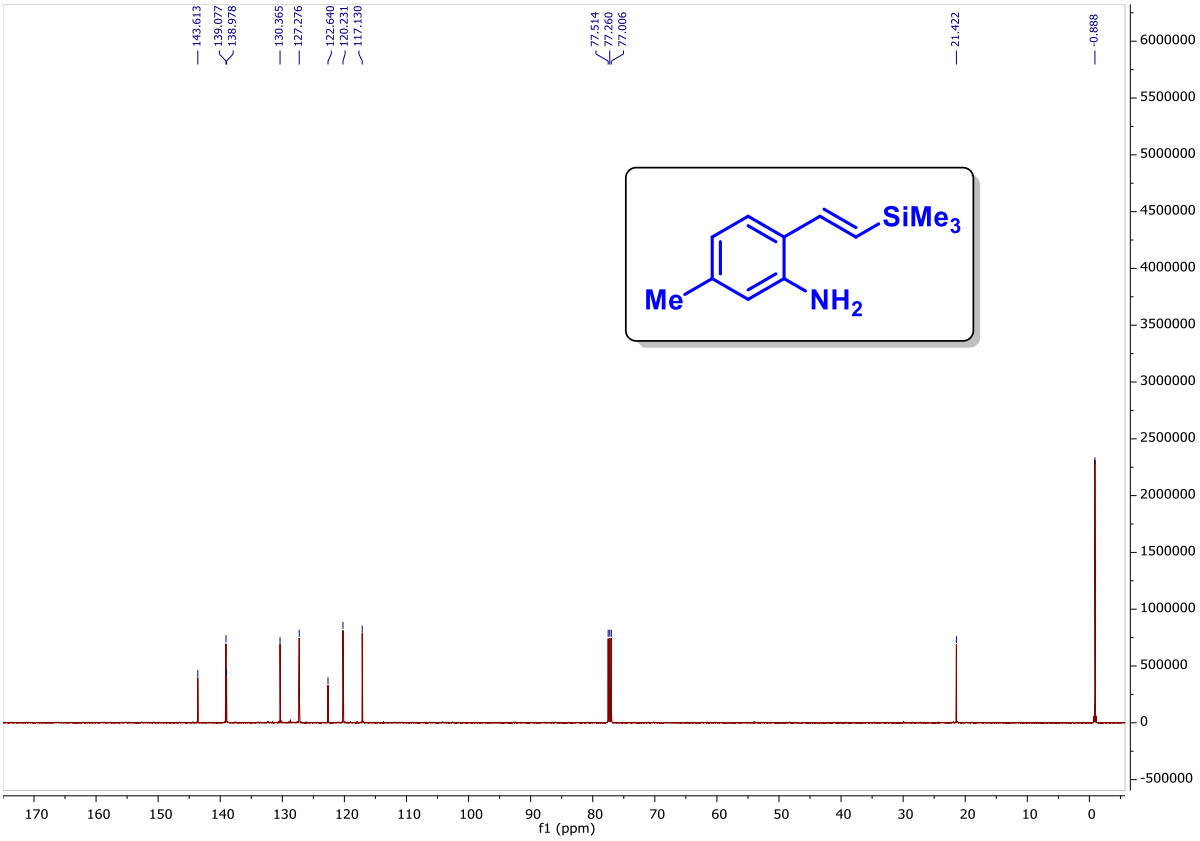
^{13}C{^{1}H} spectrum of compound **1b** (150 MHz, $CDCl_3$)



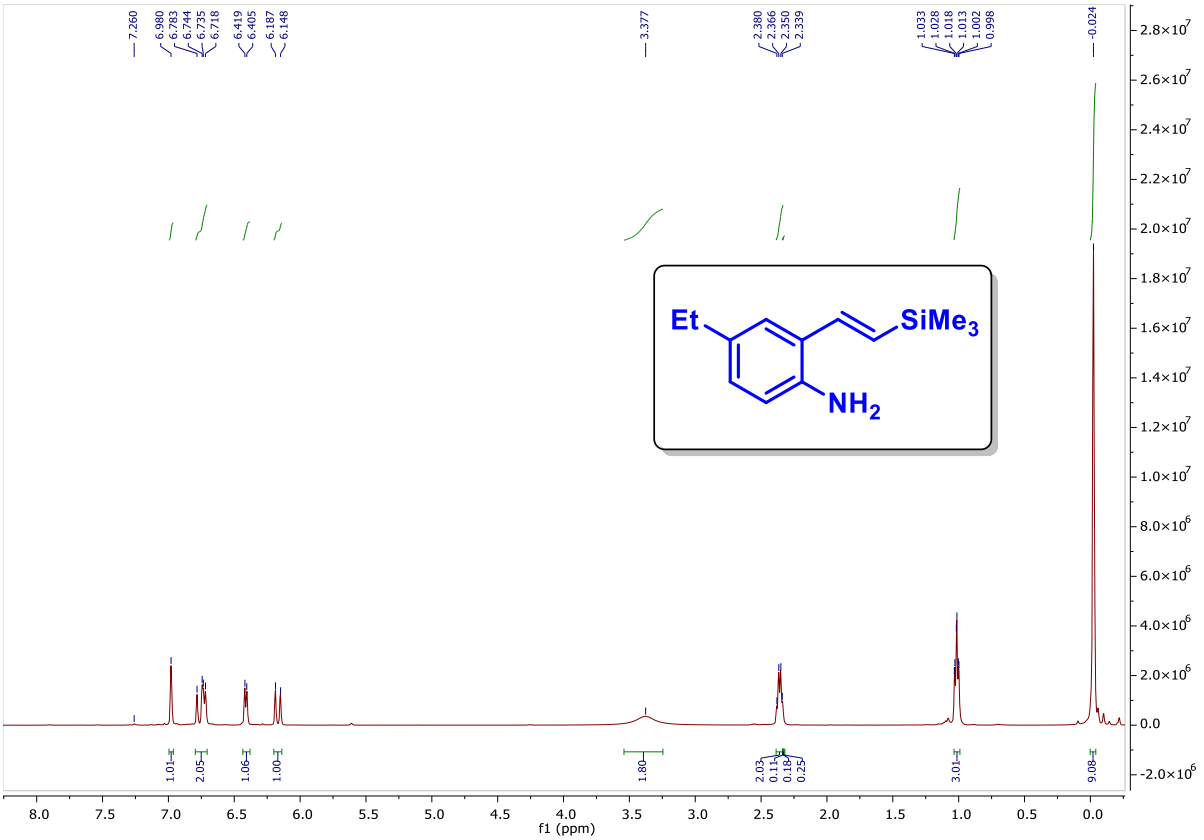
^{1}H spectrum of compound **1c** (400 MHz, $CDCl_3$)



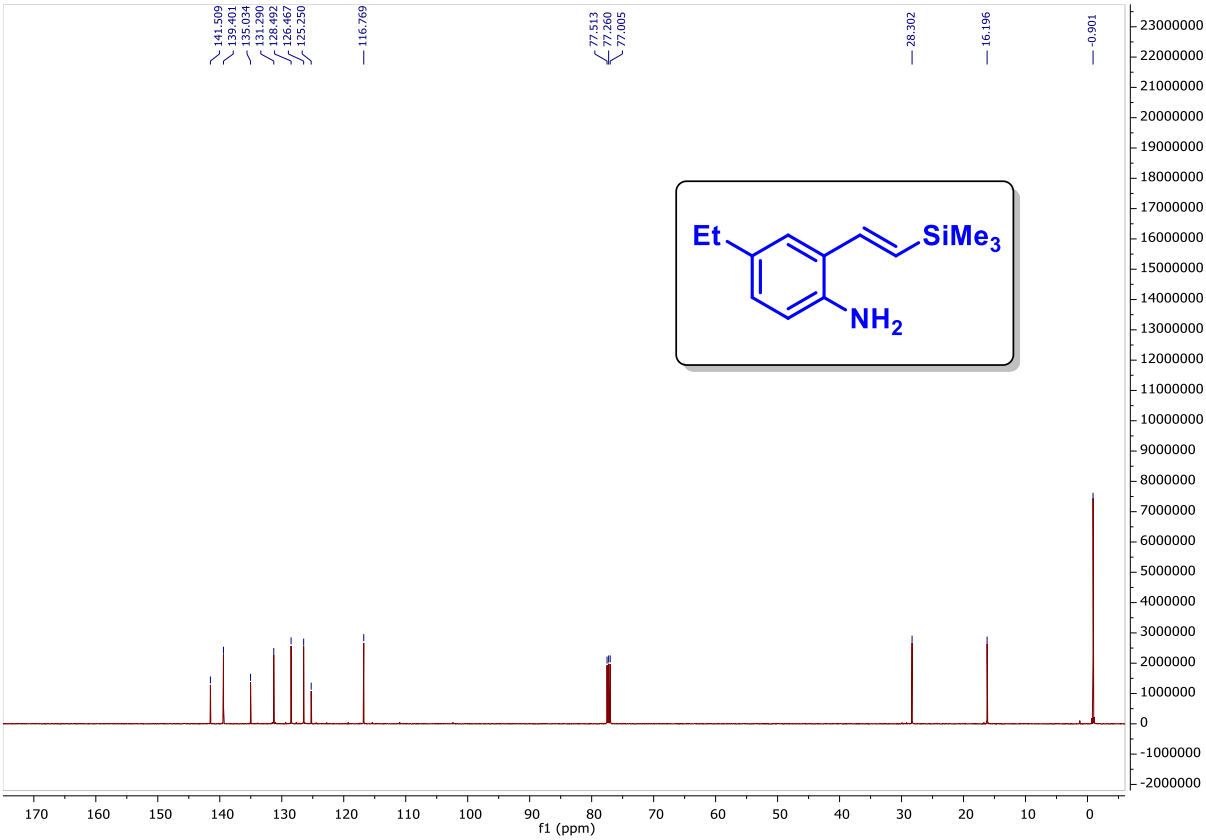
^{13}C{^{1}H} spectrum of compound **1c** (125 MHz, $CDCl_3$)



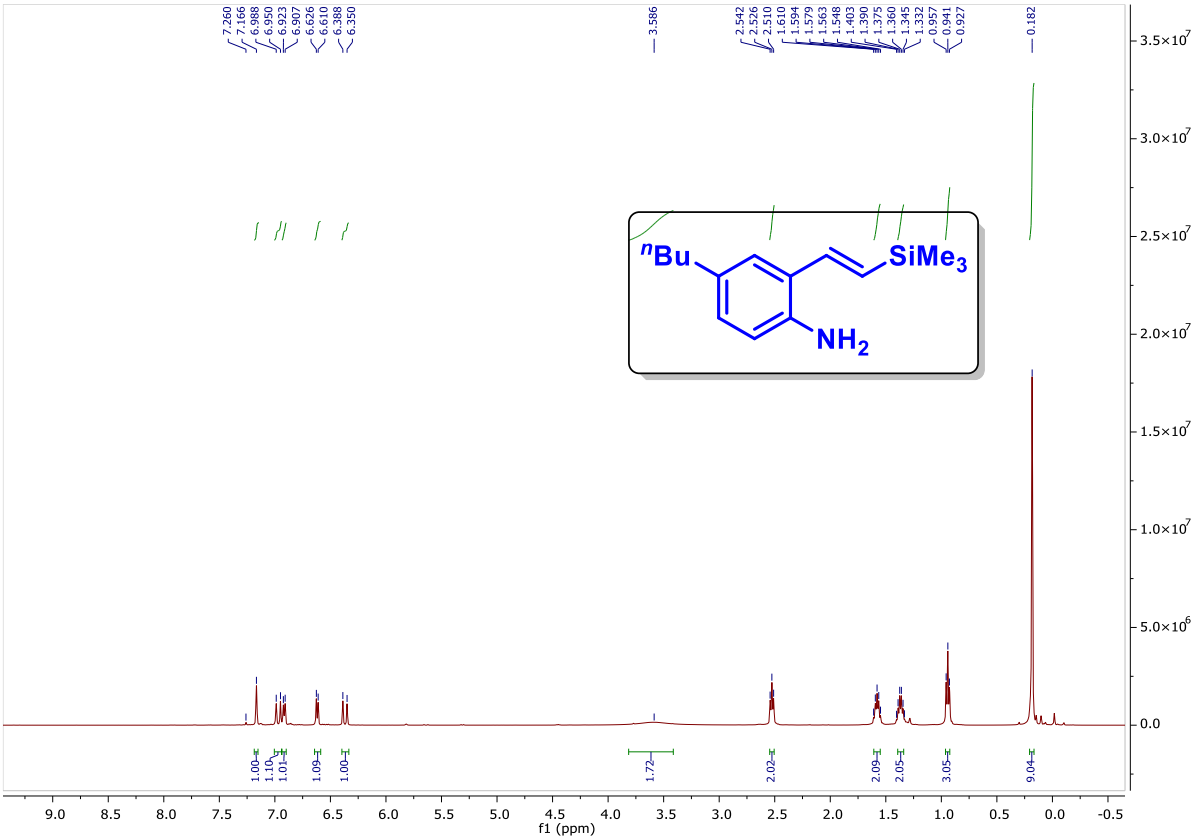
^{1}H spectrum of compound **1d** (500 MHz, $CDCl_3$)



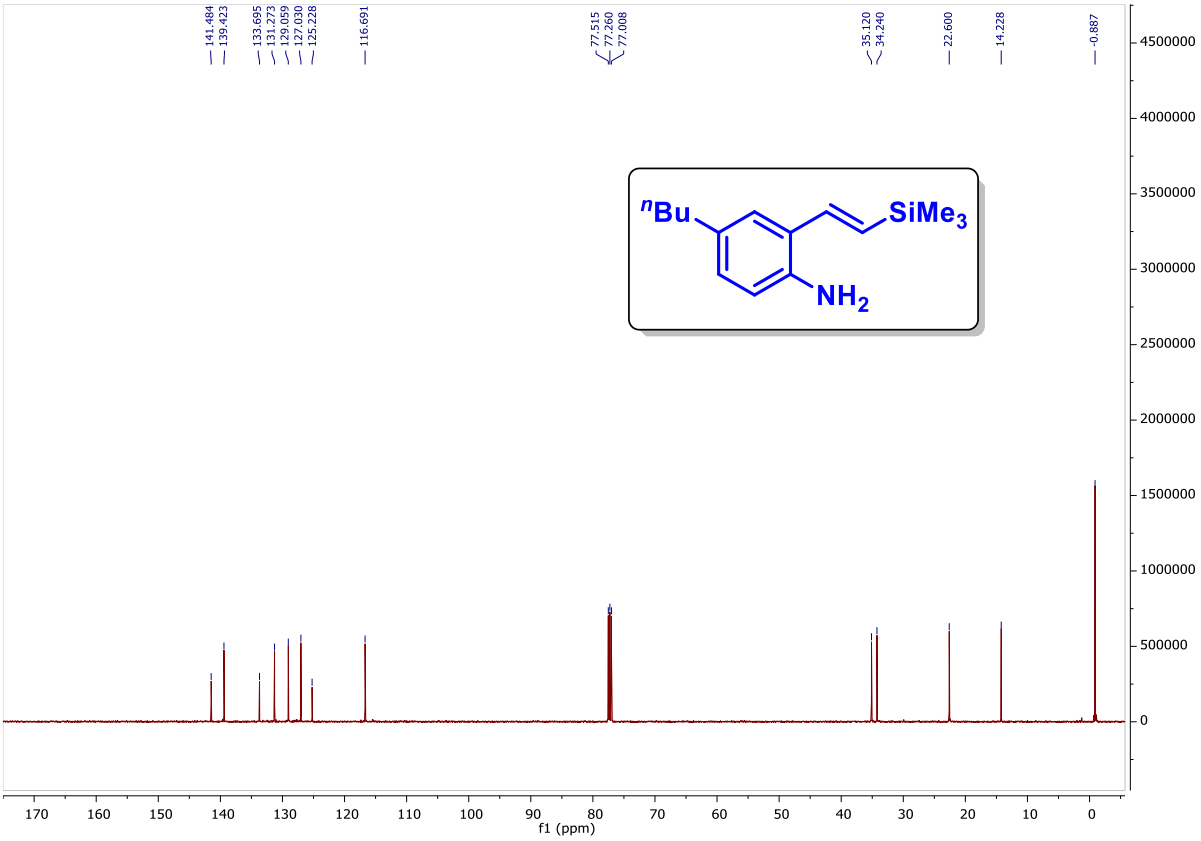
^{13}C{^{1}H} spectrum of compound **1d** (125 MHz, $CDCl_3$)



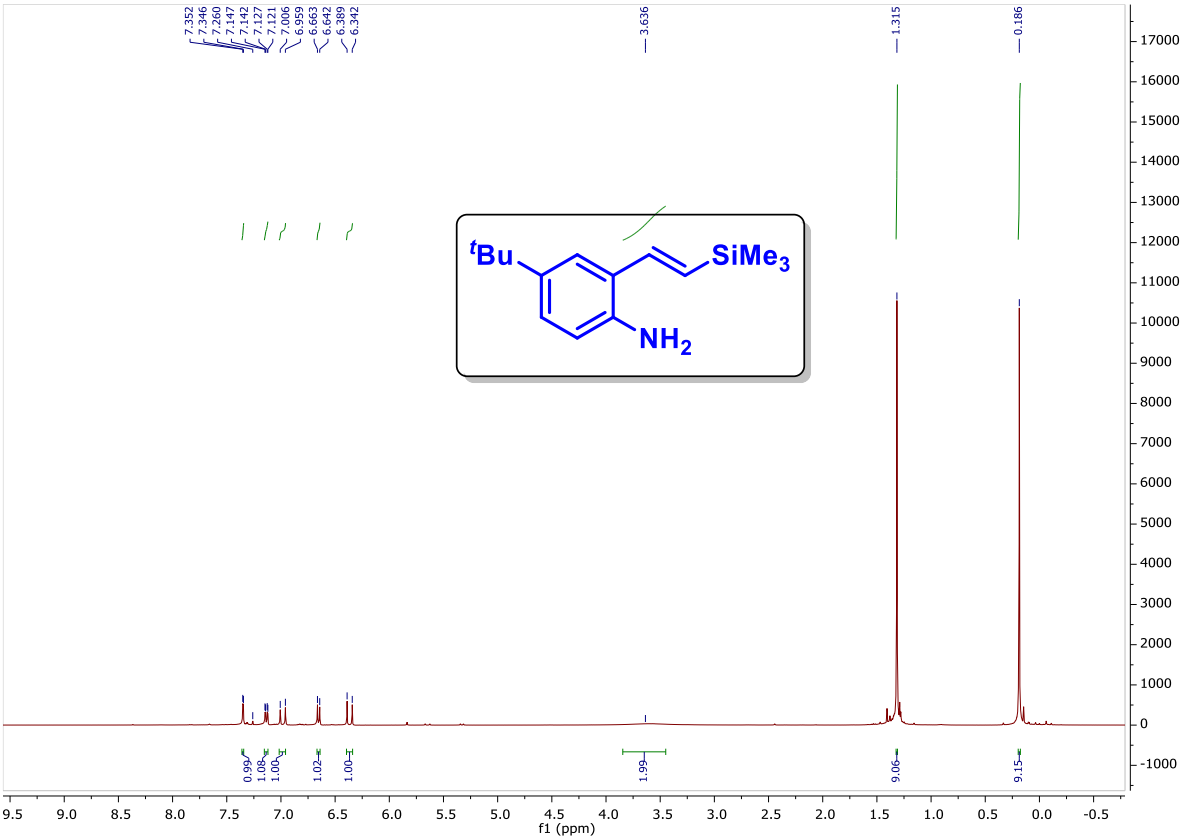
^{1}H spectrum of compound **1e** (500 MHz, $CDCl_3$)



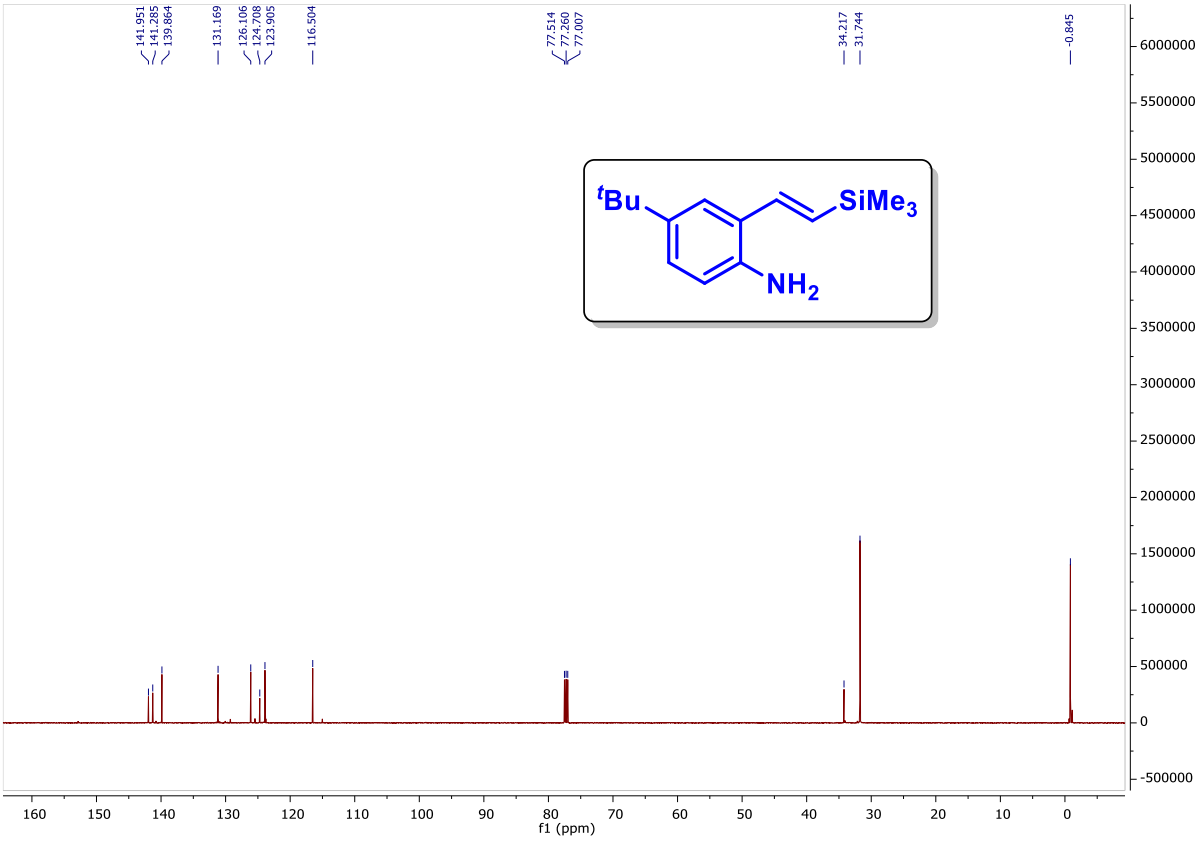
^{13}C{^{1}H} spectrum of compound **1e** (125 MHz, $CDCl_3$)



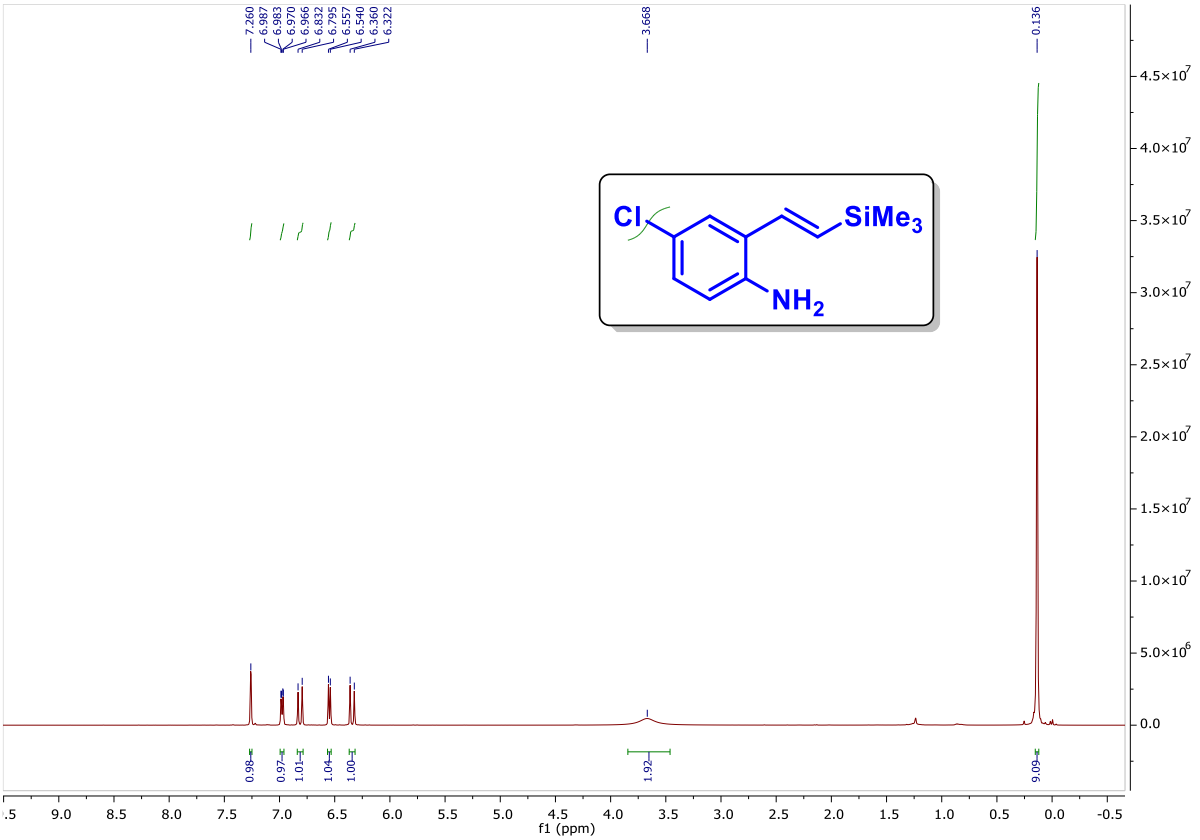
^{1}H spectrum of compound **1f** (400 MHz, $CDCl_3$)



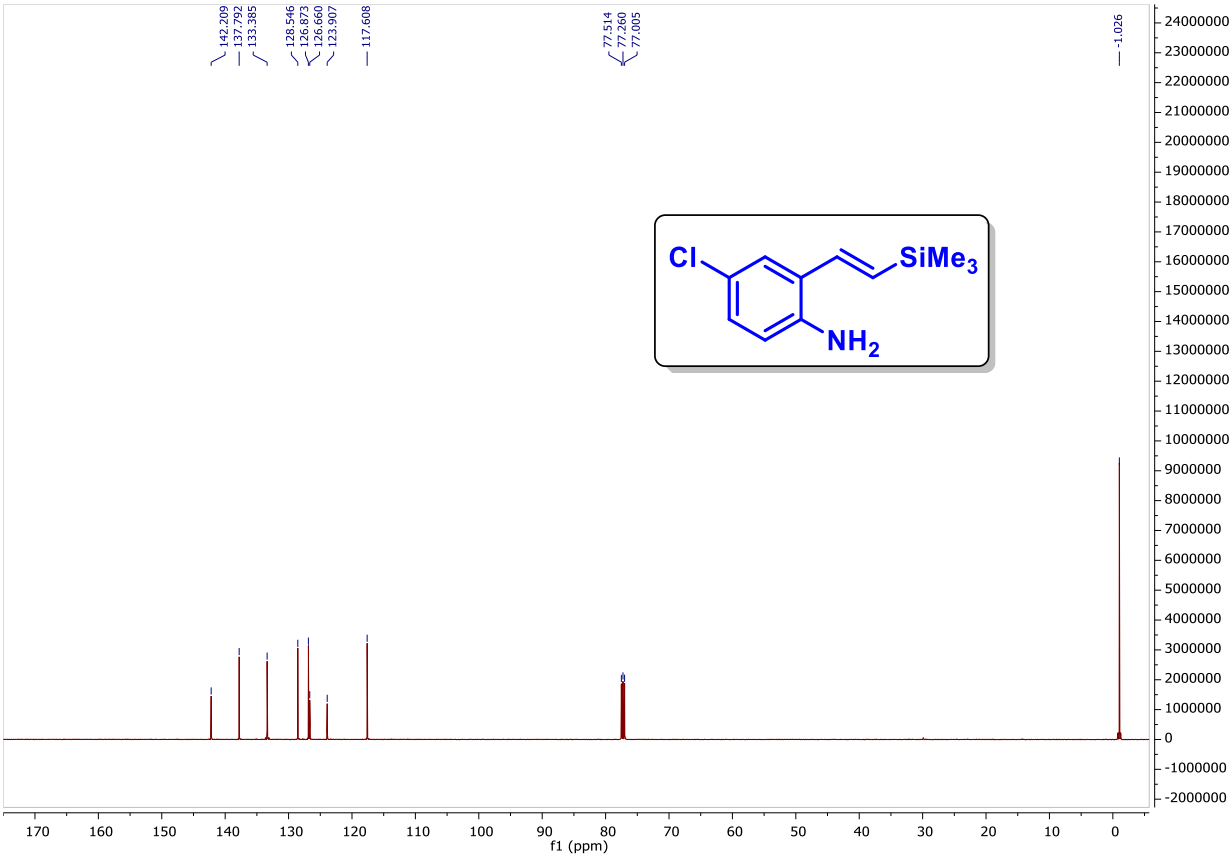
^{13}C{^{1}H} spectrum of compound **1f** (100 MHz, $CDCl_3$)



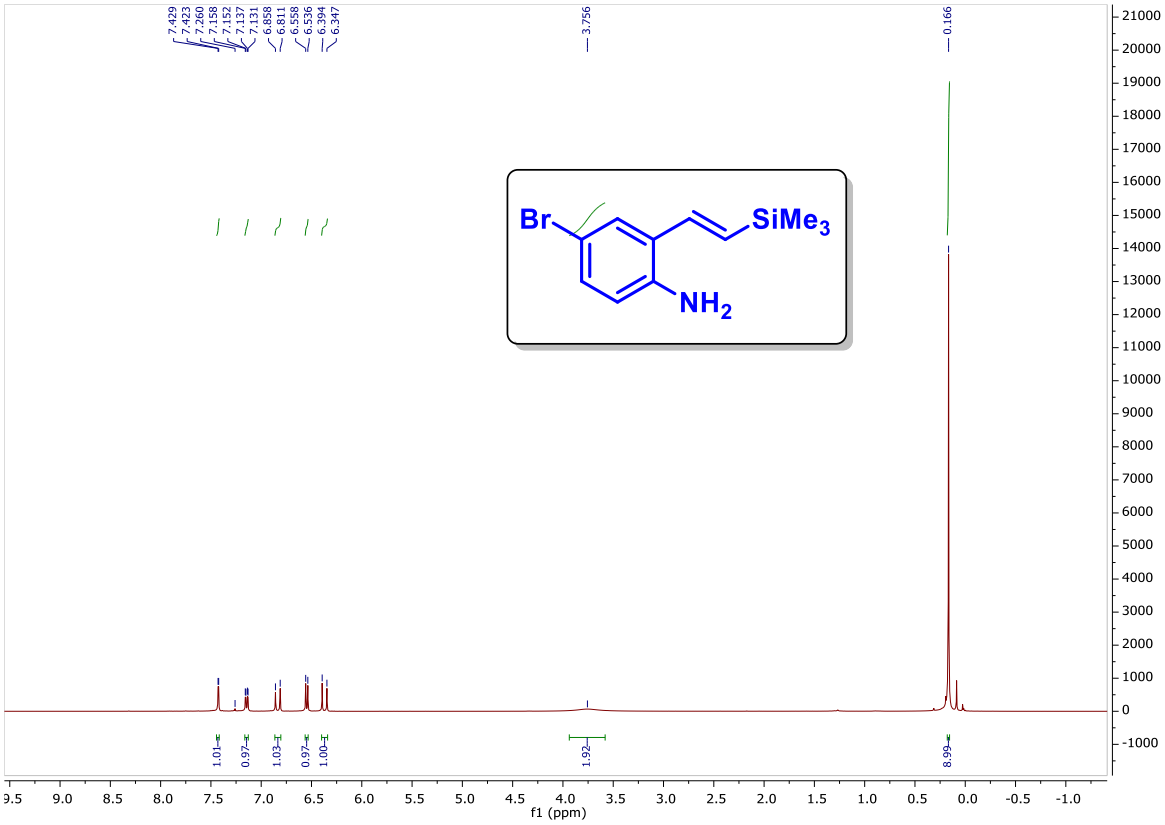
^{1}H spectrum of compound **1g** (500 MHz, $CDCl_3$)



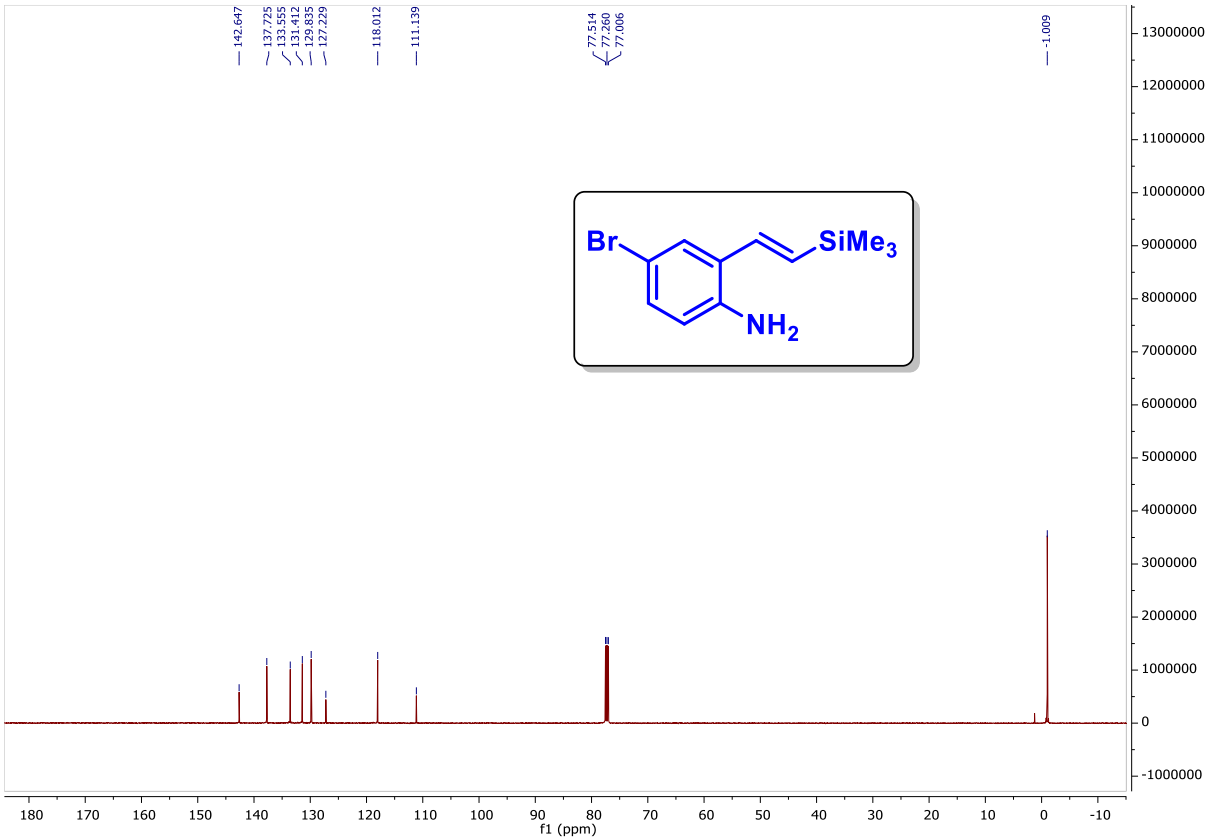
^{13}C{^{1}H} spectrum of compound **1g** (125 MHz, $CDCl_3$)



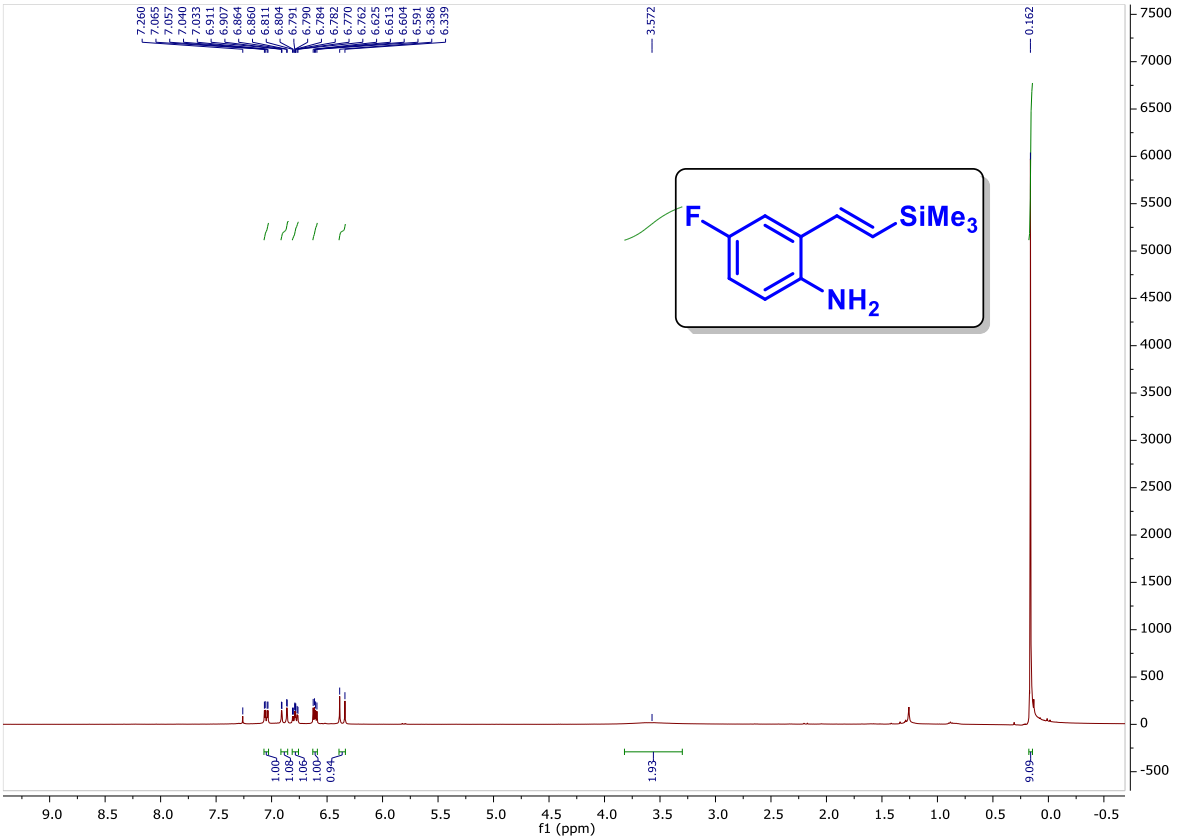
^{1}H spectrum of compound **1h** (400 MHz, $CDCl_3$)



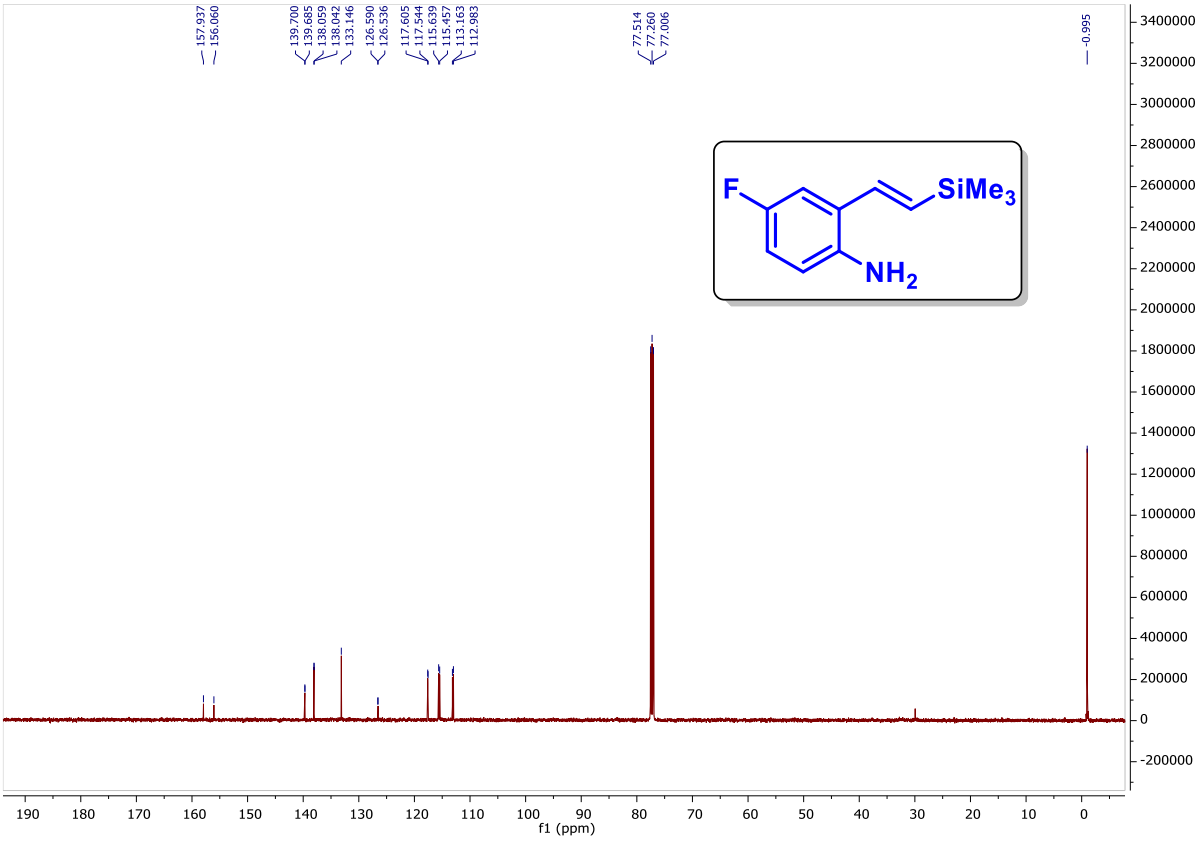
^{13}C{^{1}H} spectrum of compound **1h** (125 MHz, $CDCl_3$)



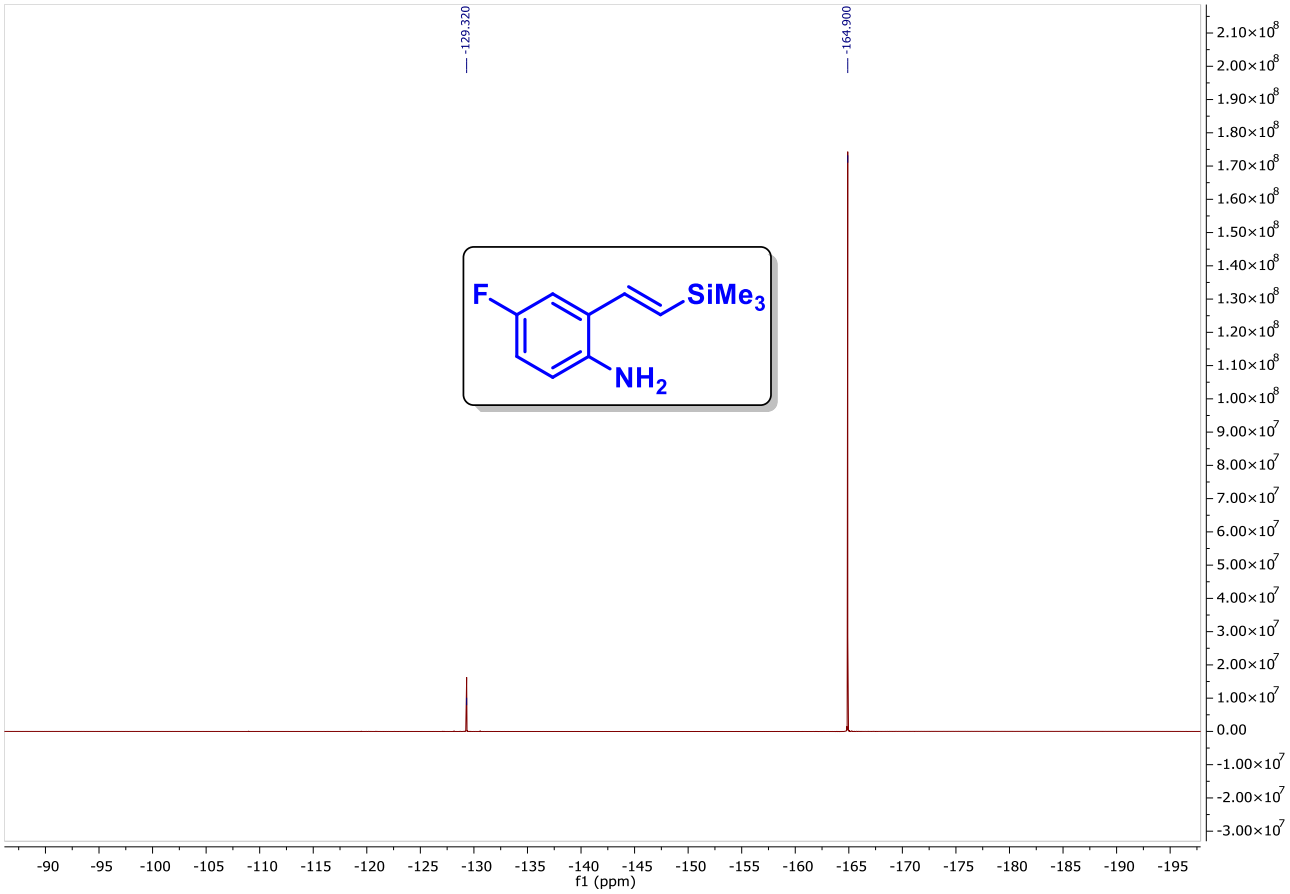
^{1}H spectrum of compound **1i** (400 MHz, $CDCl_3$)



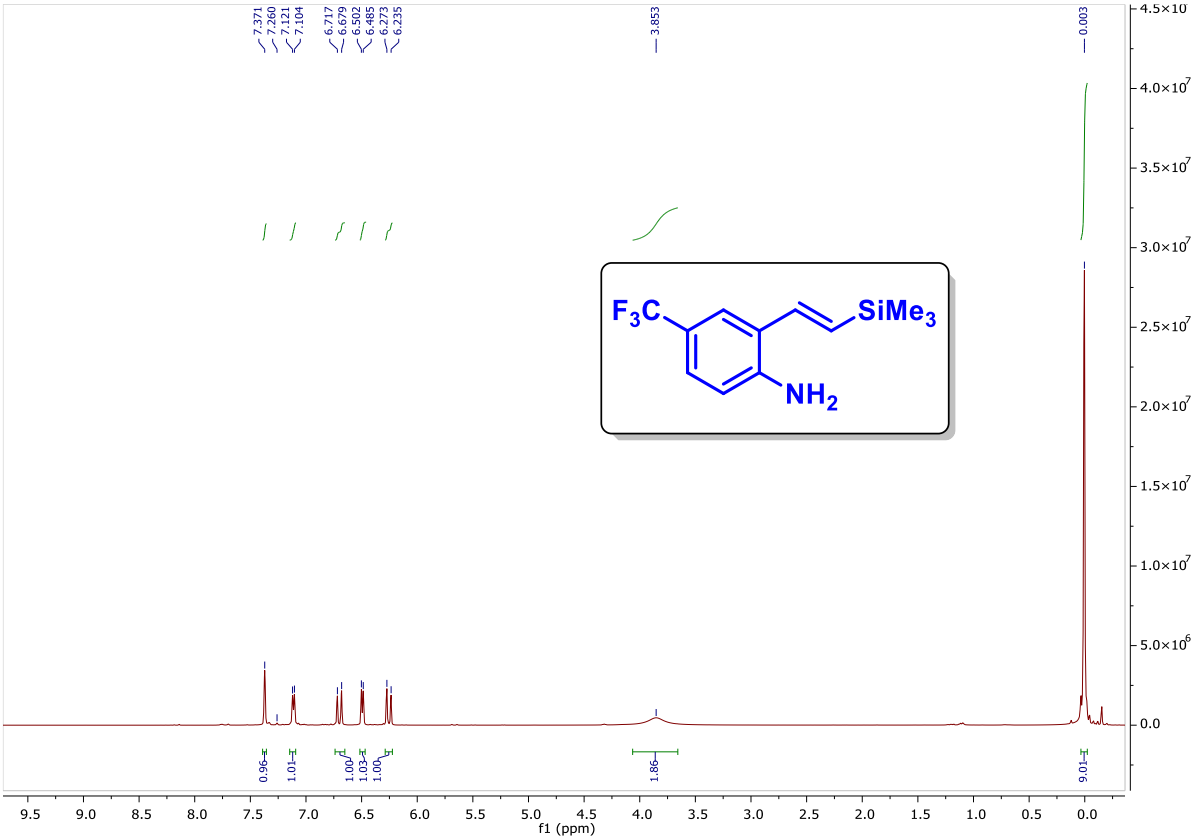
^{13}C{^{1}H} spectrum of compound **1i** (125 MHz, $CDCl_3$)



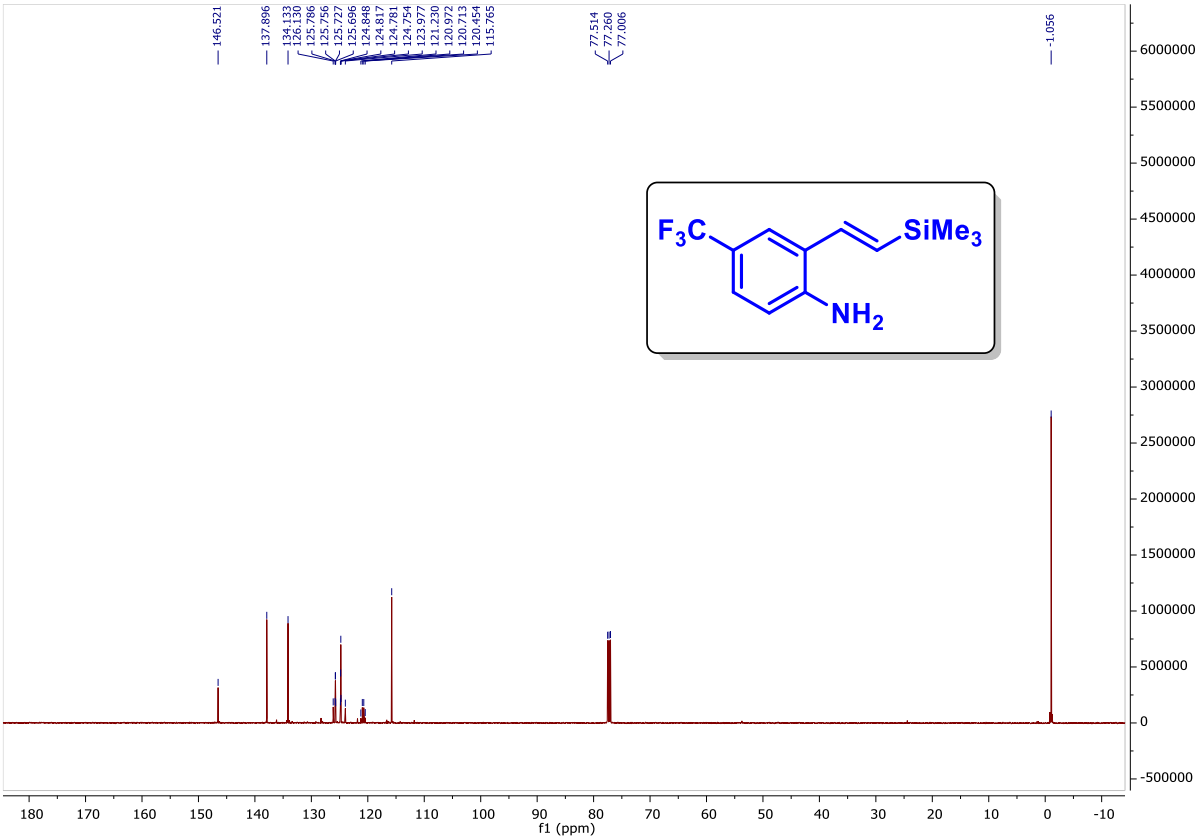
^{19}F spectrum of compound **1i** (470 MHz, $CDCl_3$ /C_6F_6)



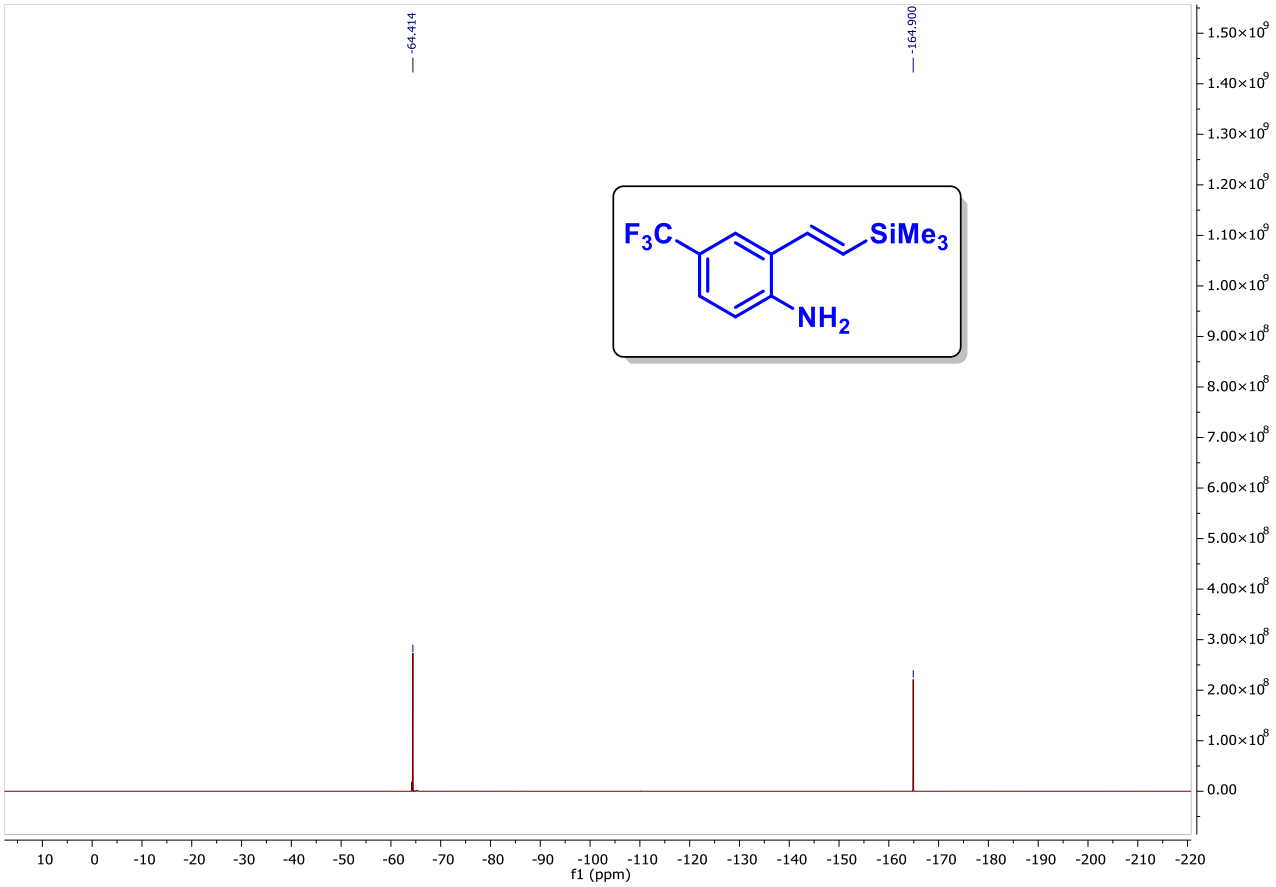
^{1}H spectrum of compound **1j** (500 MHz, $CDCl_3$)



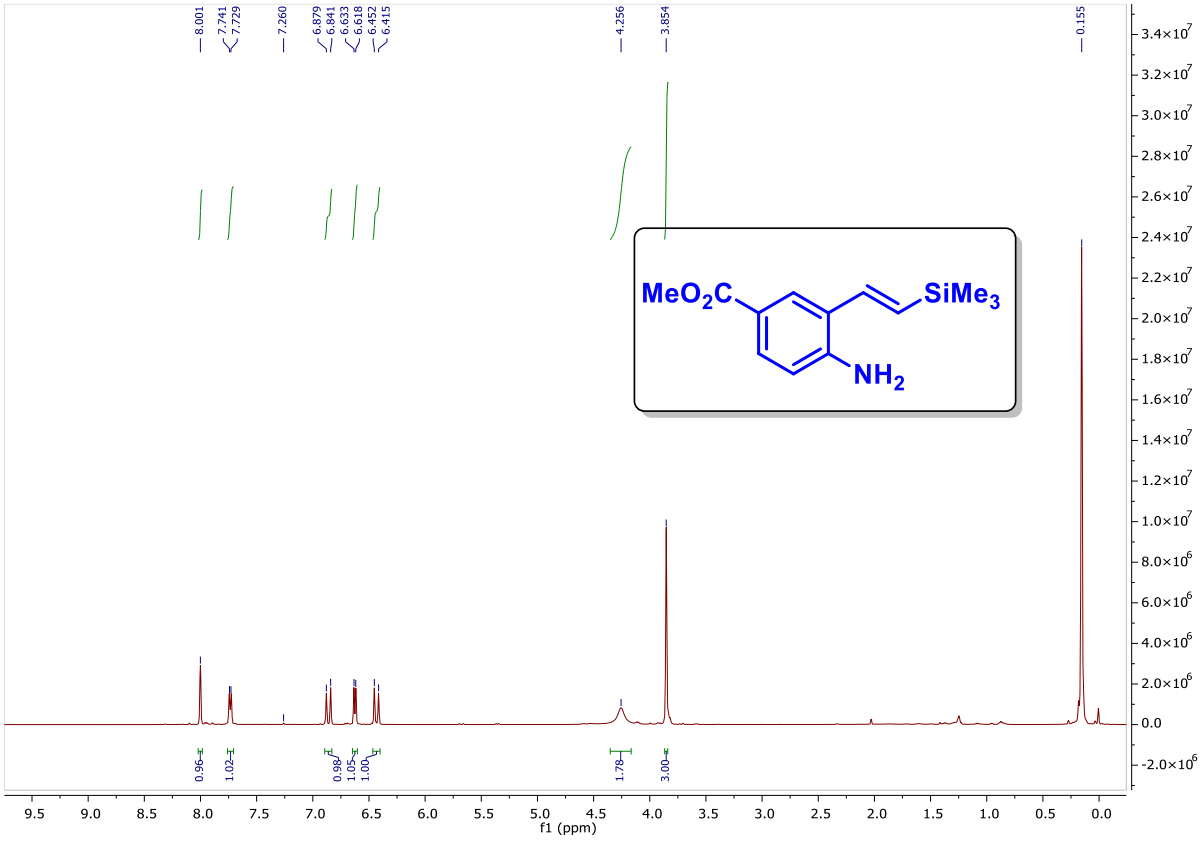
^{13}C{^{1}H} spectrum of compound **1j** (125 MHz, $CDCl_3$)



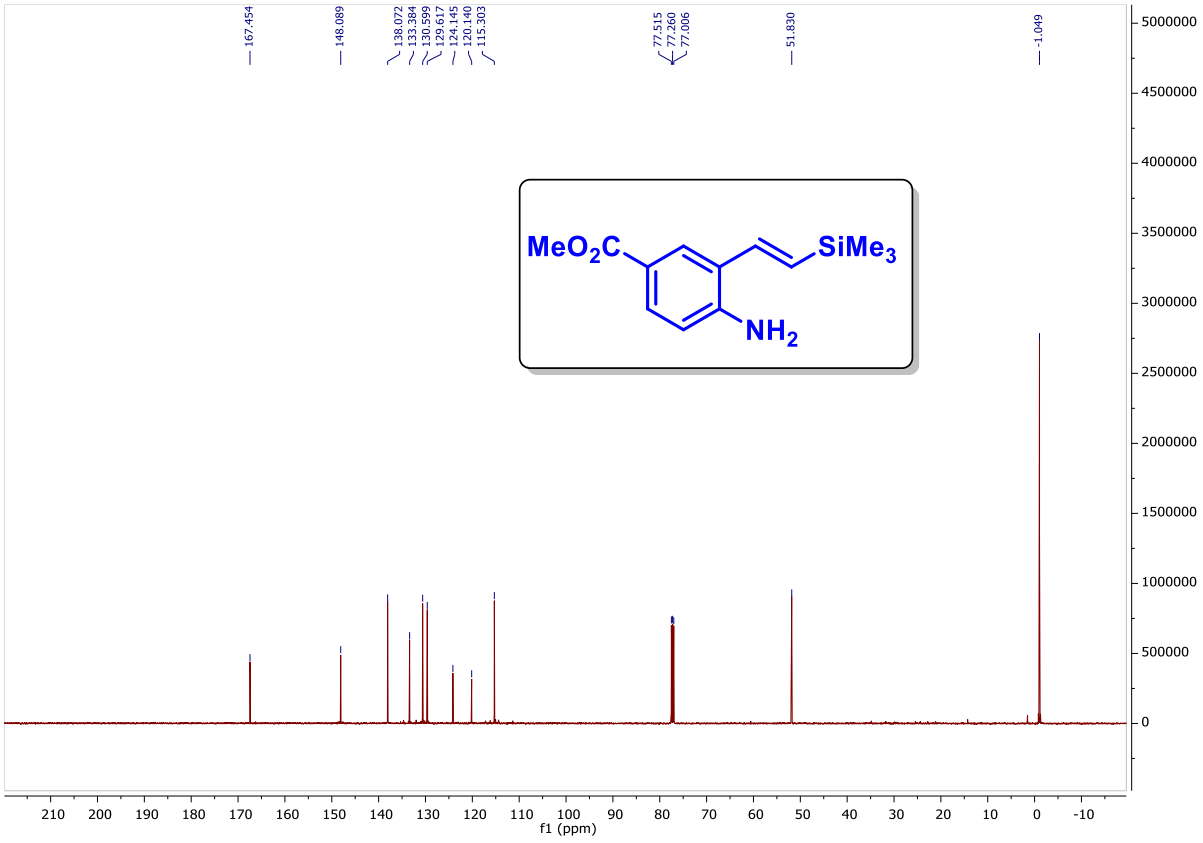
^{19}F spectrum of compound **1j** (470 MHz, $CDCl_3$ /C_6F_6)



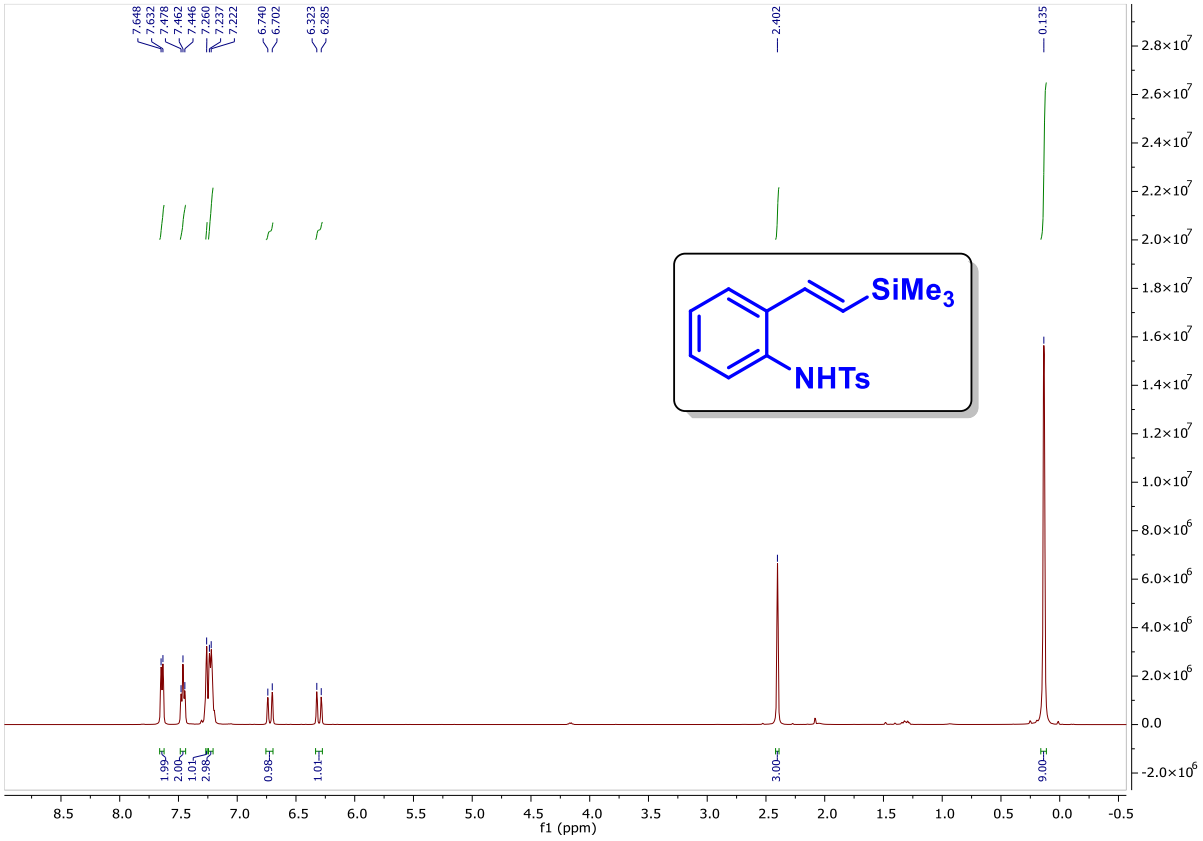
^{1}H spectrum of compound **1k** (500 MHz, $CDCl_3$)



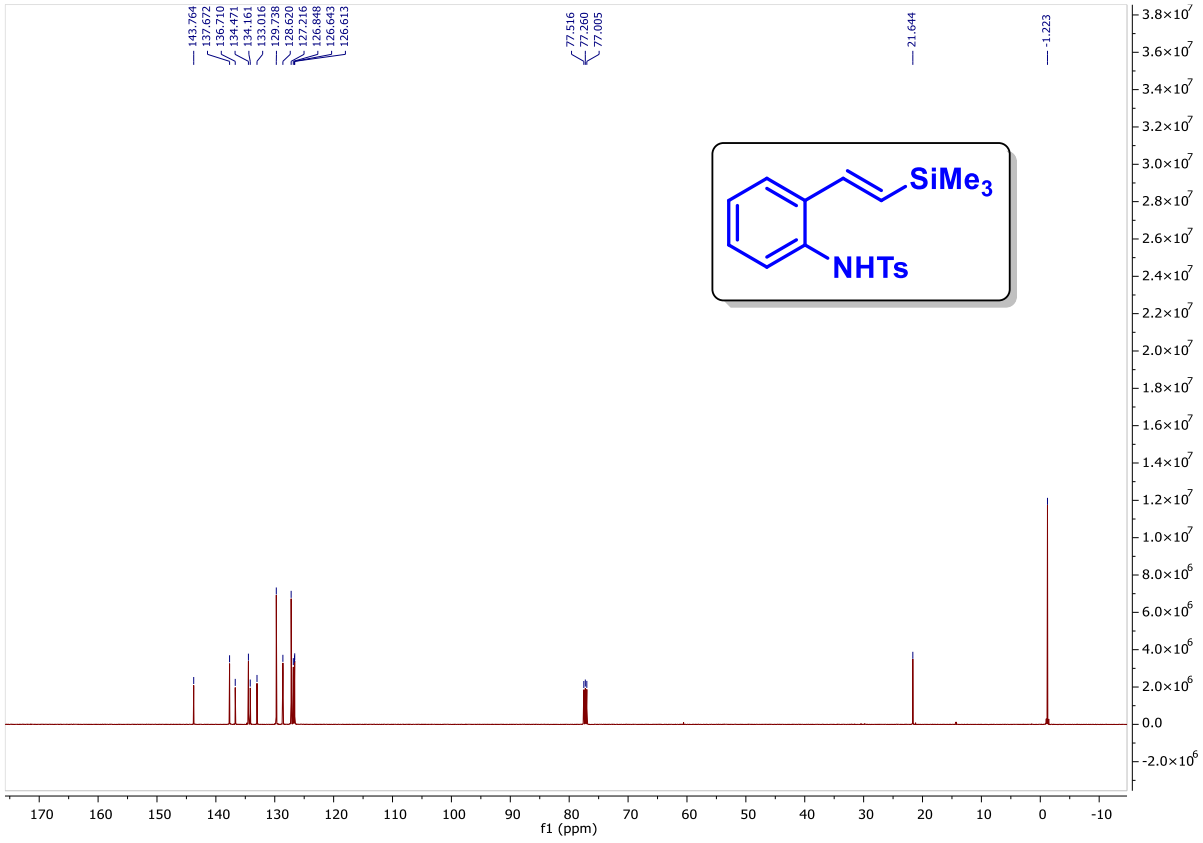
^{13}C{^{1}H} spectrum of compound **1k** (125 MHz, $CDCl_3$)



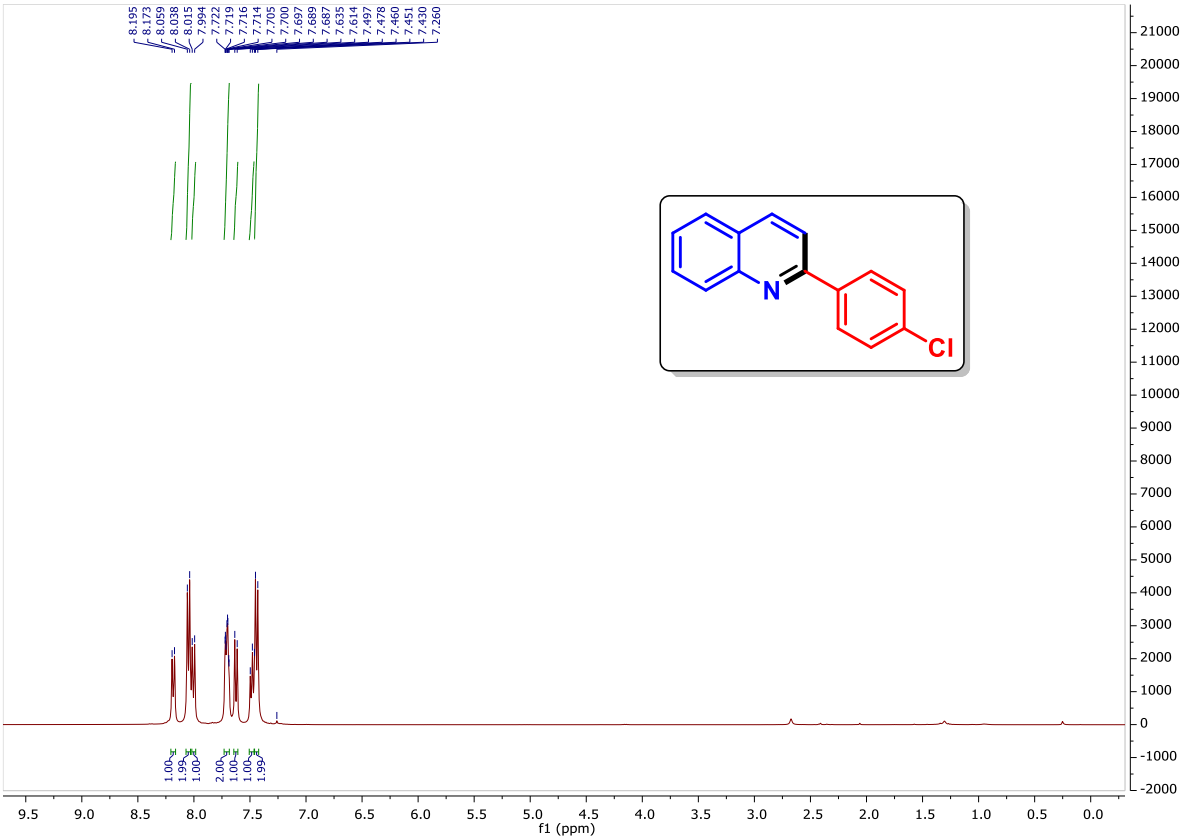
^{1}H spectrum of compound **1b′** (500 MHz, $CDCl_3$)



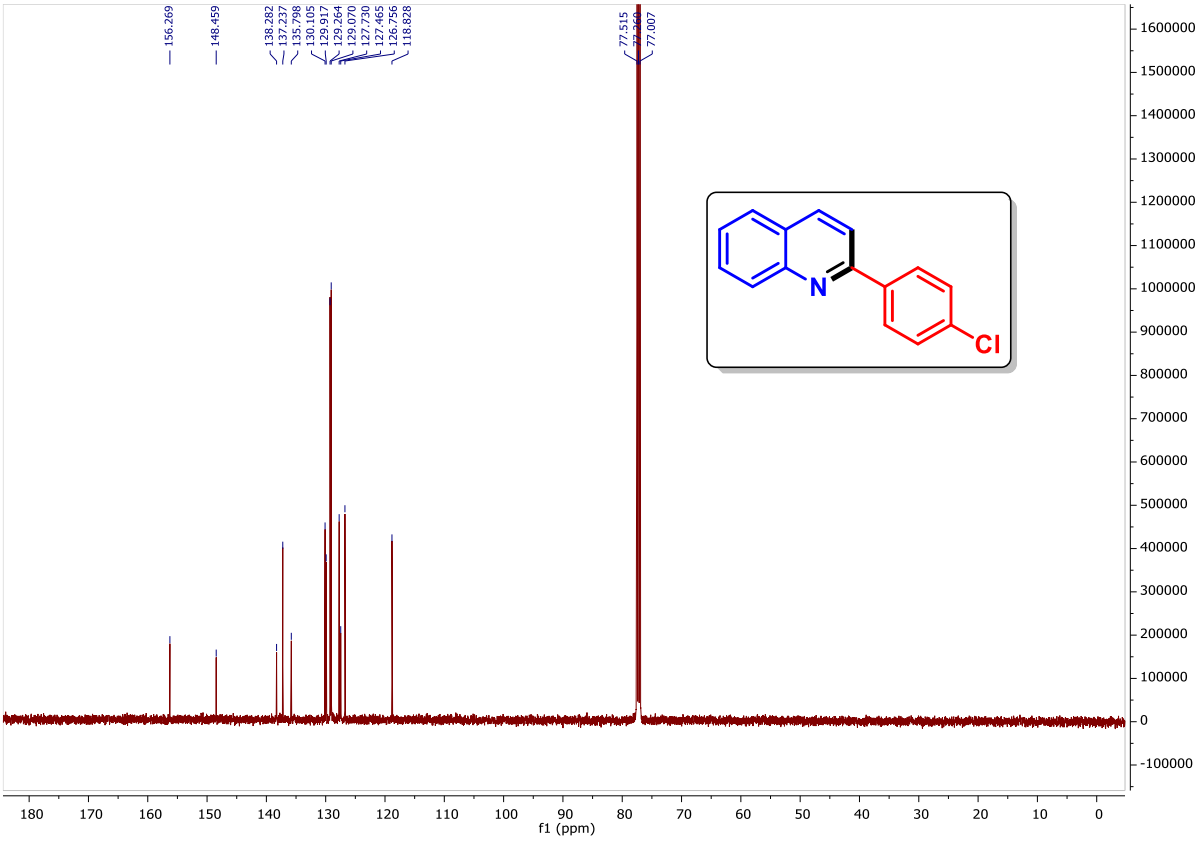
^{13}C{^{1}H} spectrum of compound **1b′** (125 MHz, $CDCl_3$)



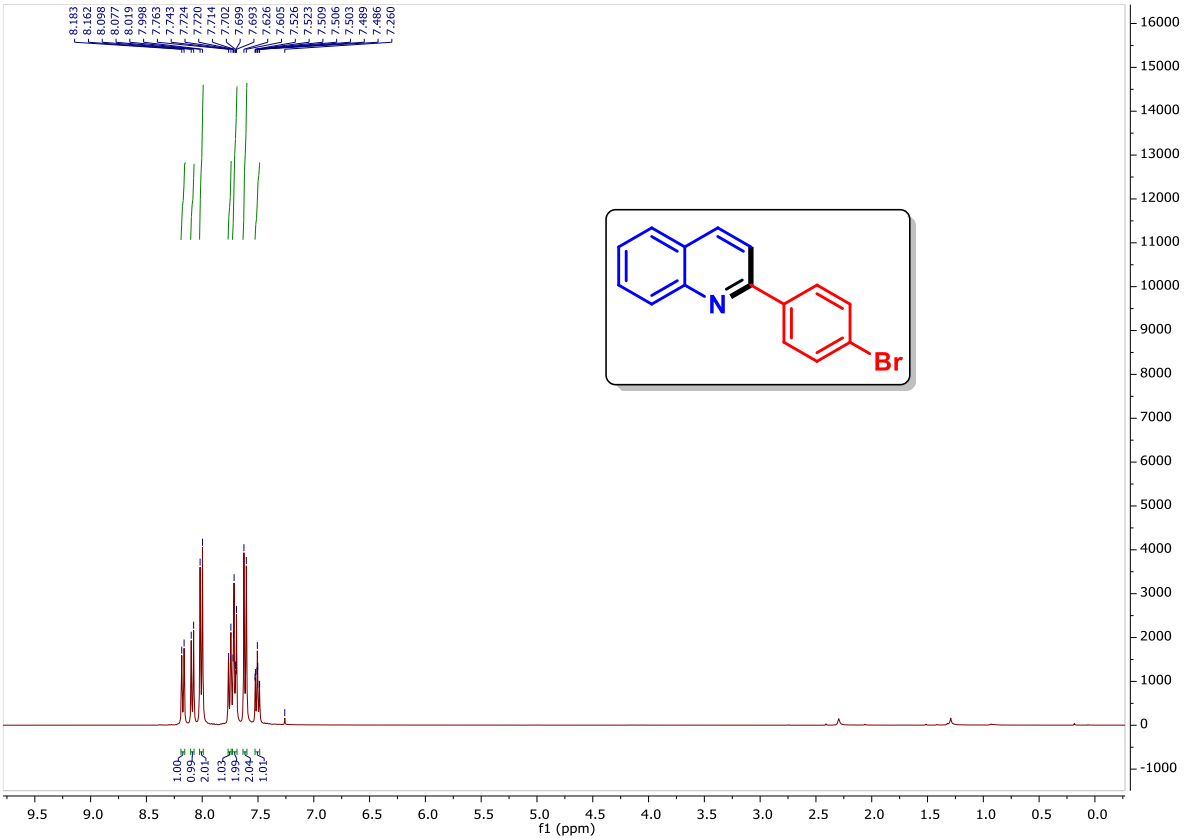
^{1}H spectrum of compound **3aa** (400 MHz, $CDCl_3$)



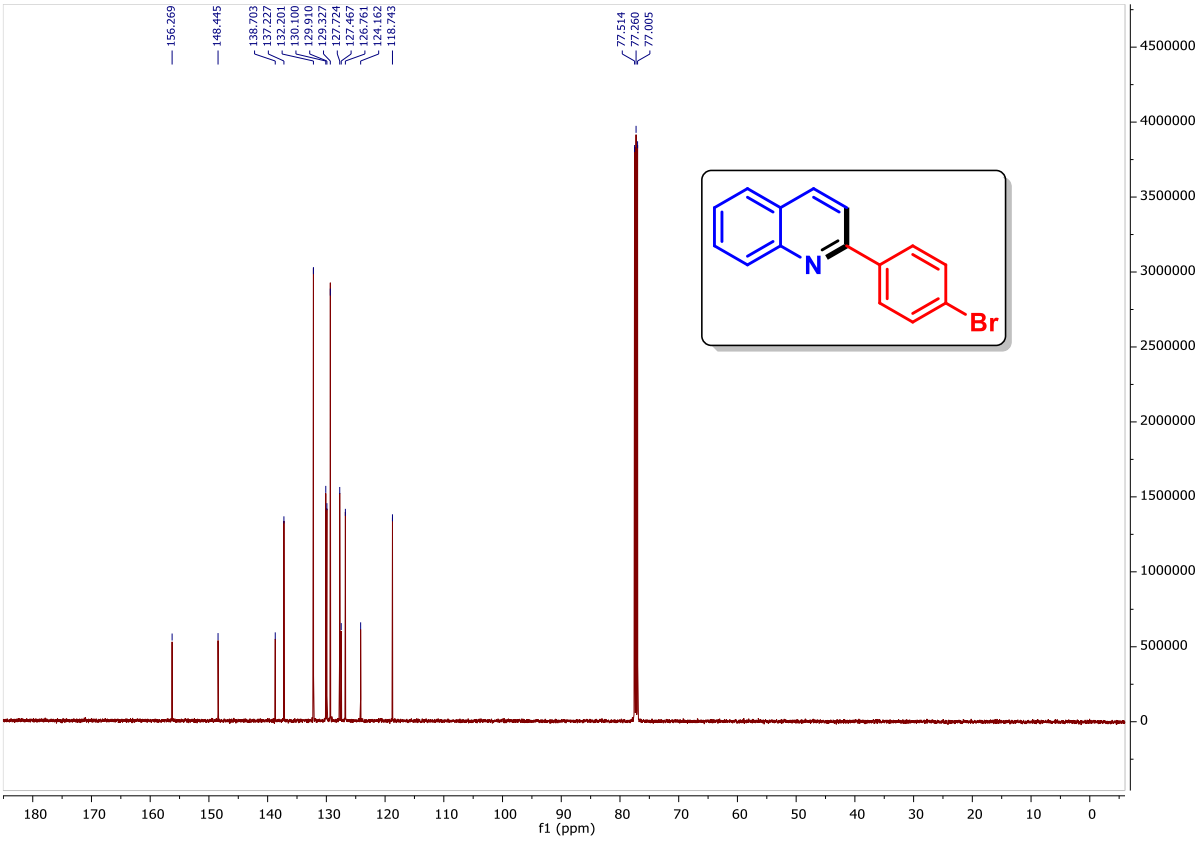
^{13}C{^{1}H} spectrum of compound **3aa** (125 MHz, $CDCl_3$)



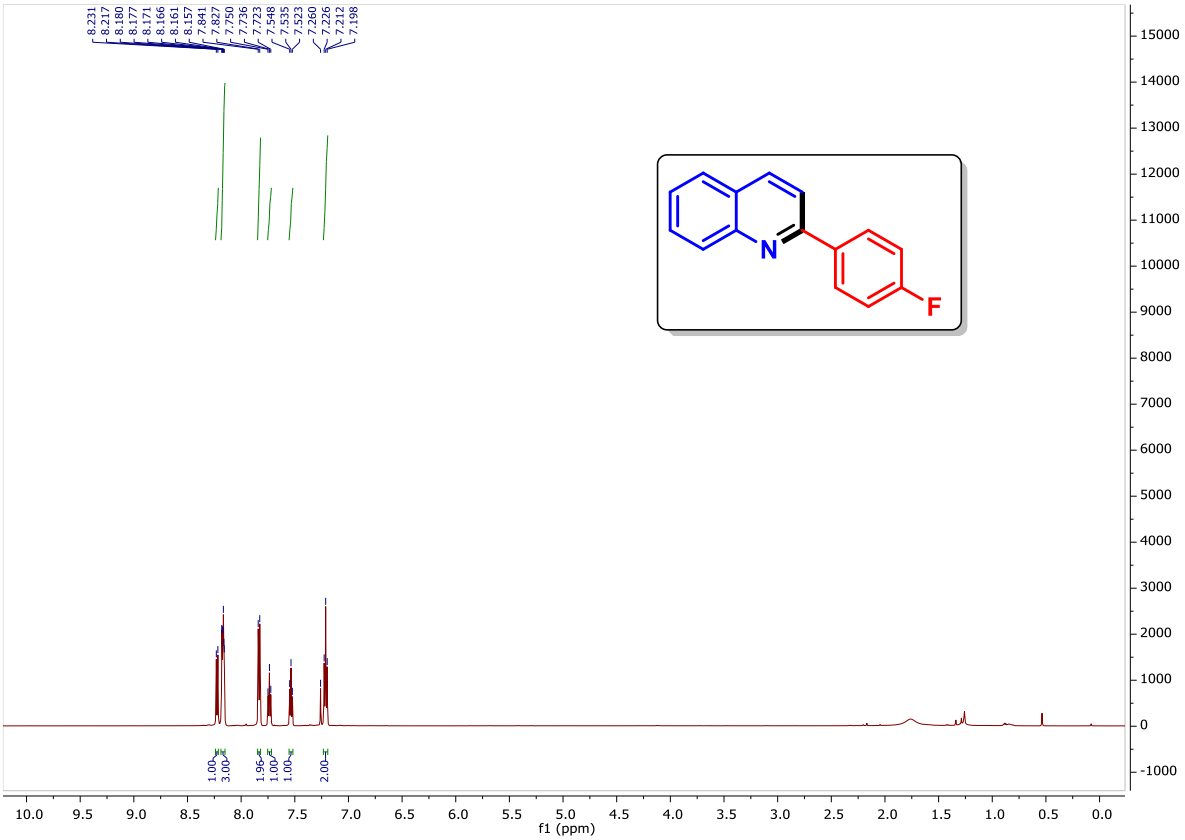
^{1}H spectrum of compound **3ab** (400 MHz, $CDCl_3$)



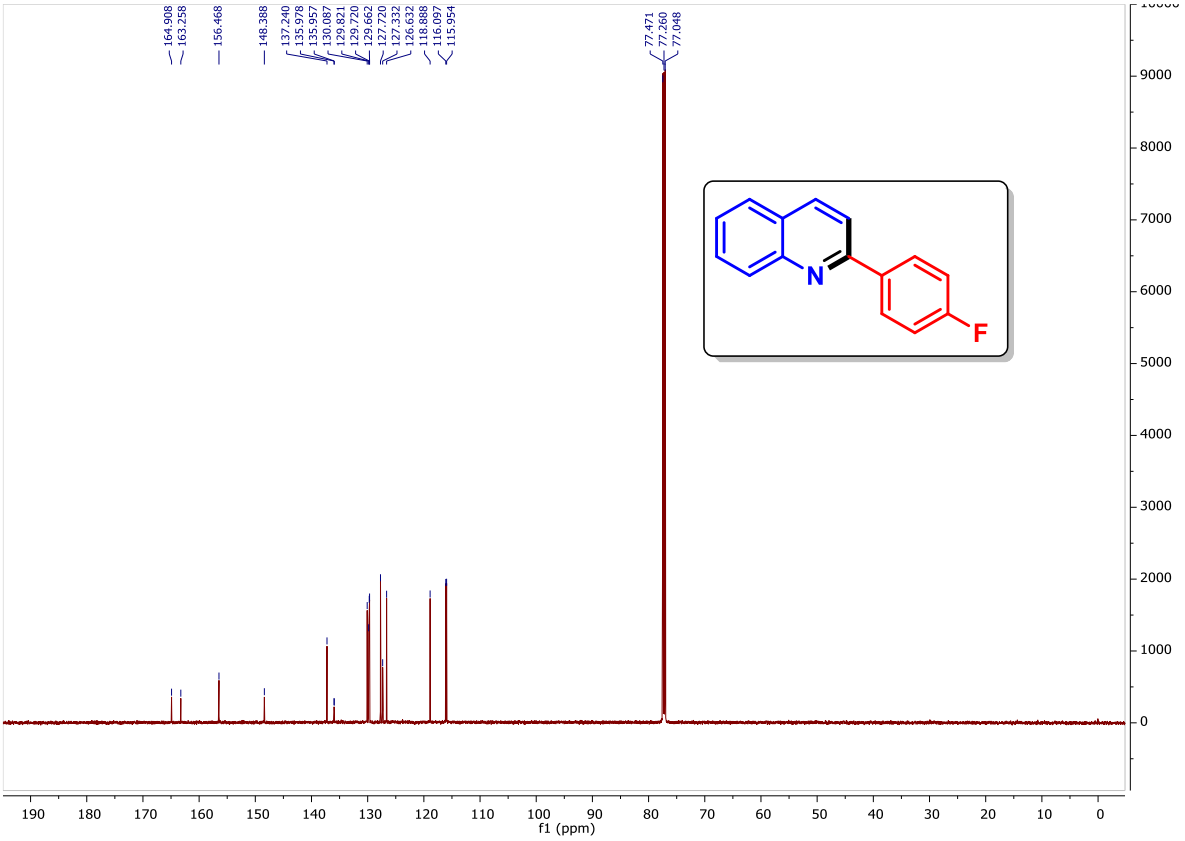
$^{13}C\{^{1}H\}$ spectrum of compound **3ab** (125 MHz, $CDCl_3$)



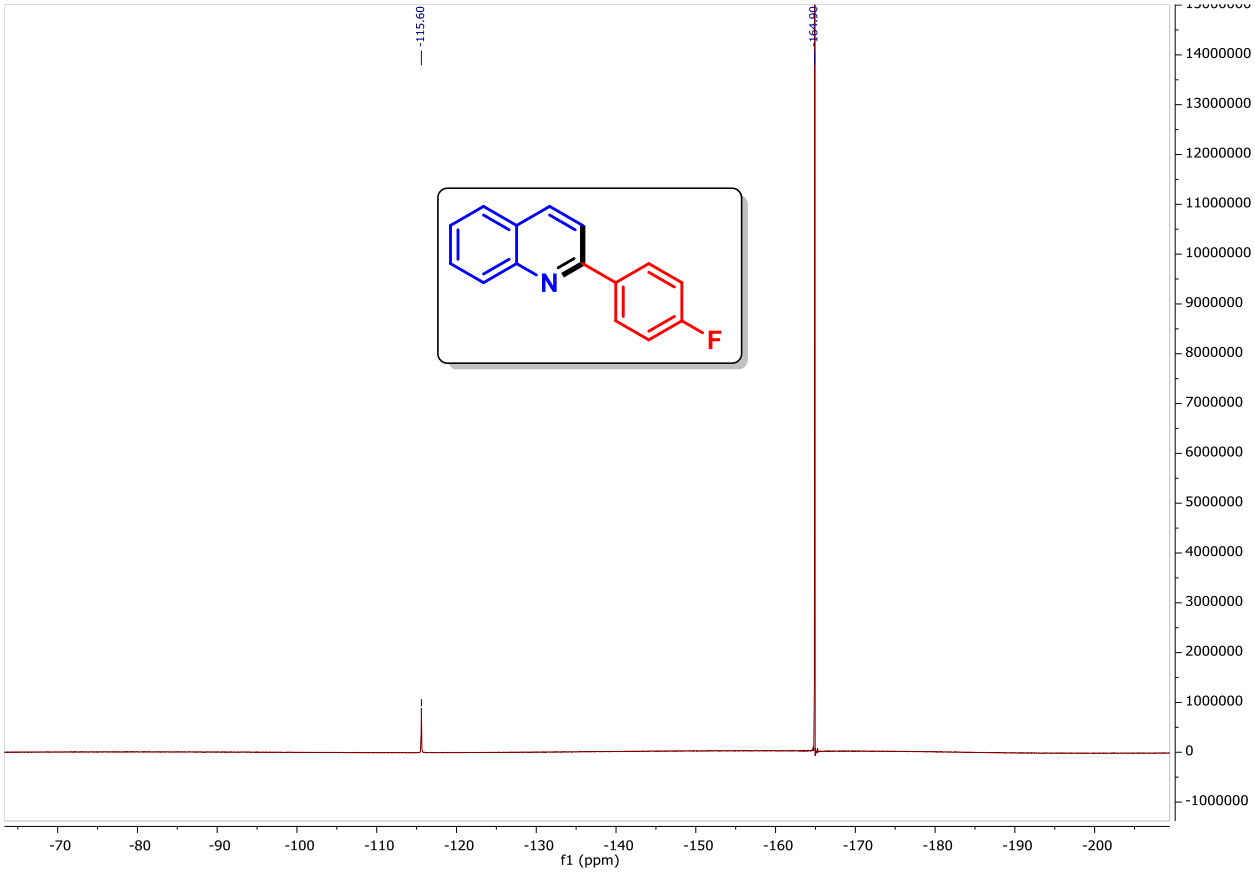
^{1}H spectrum of compound **3ac** (600 MHz, $CDCl_3$)



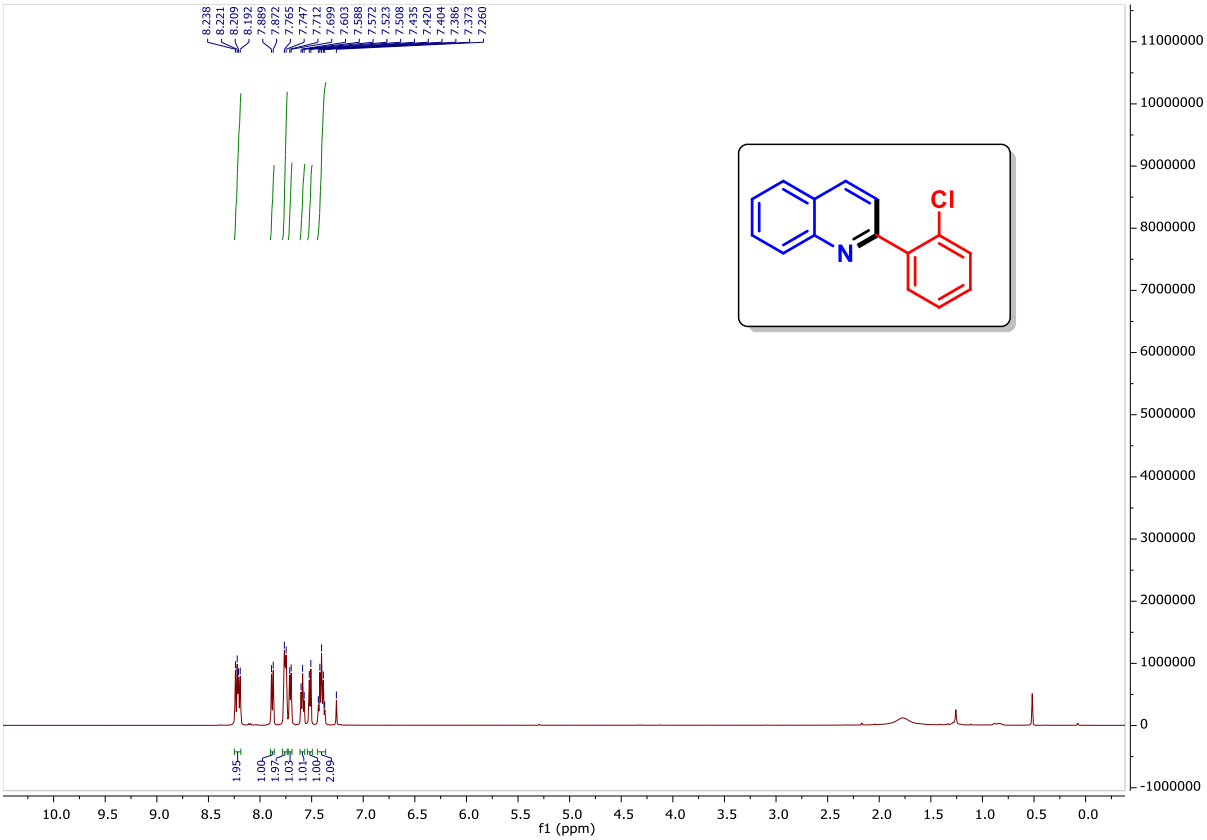
^{13}C{^{1}H} spectrum of compound **3ac** (150 MHz, $CDCl_3$)



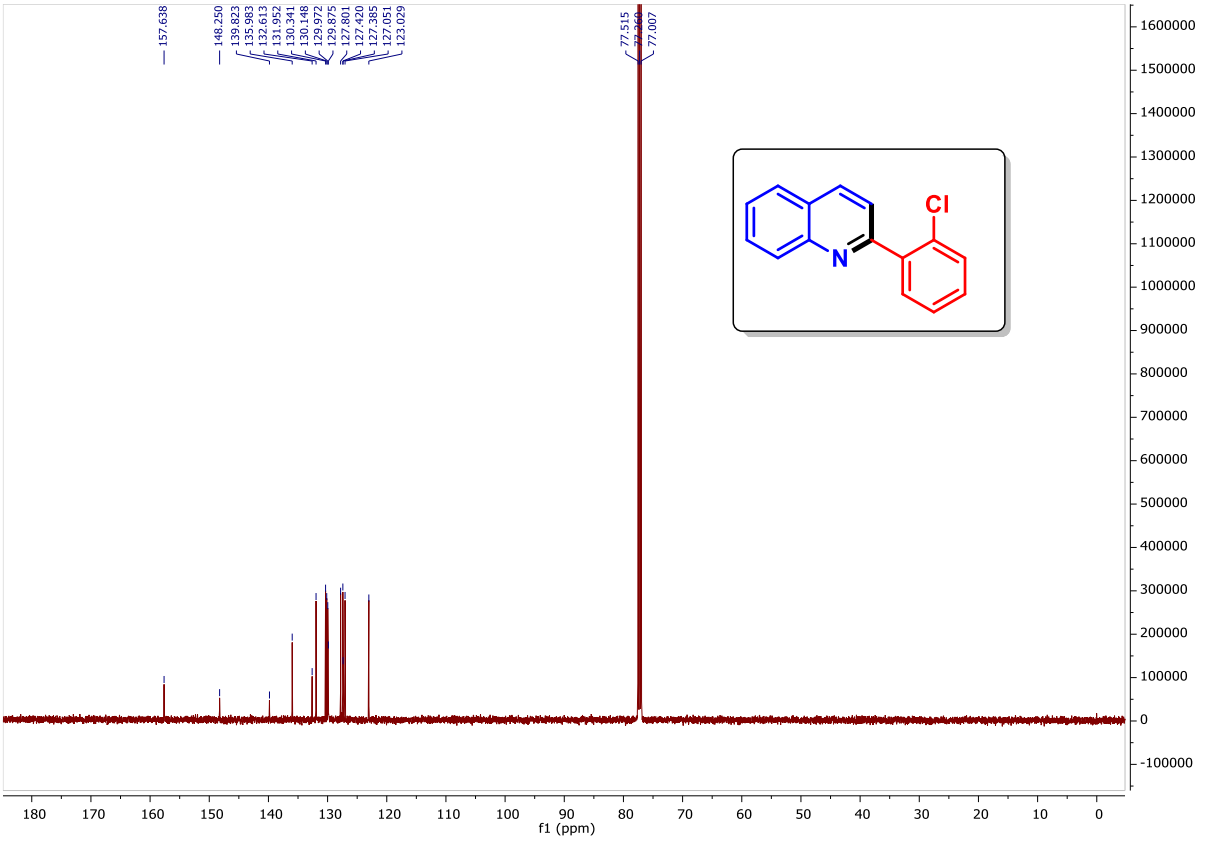
^{19}F spectrum of compound **3ac** (470 MHz, $CDCl_3$ /C_6F_6)



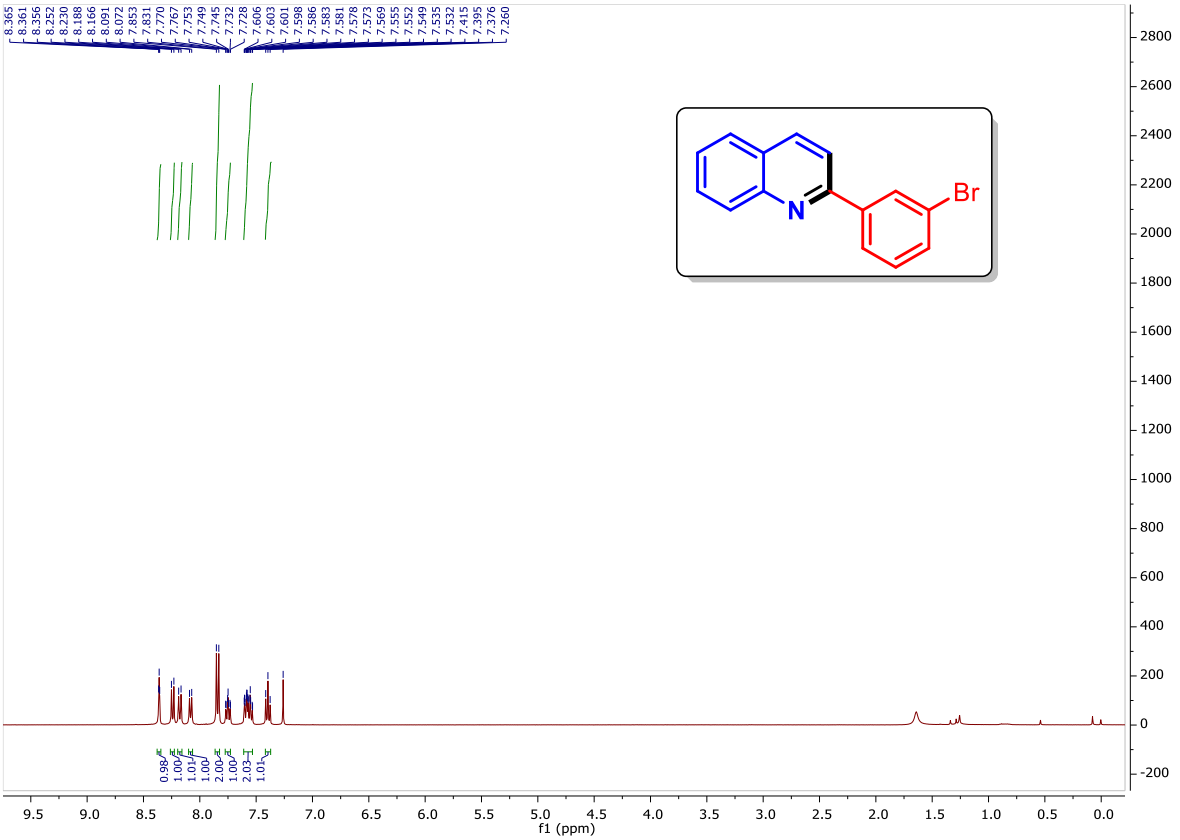
^{1}H spectrum of compound **3ad** (500 MHz, $CDCl_3$)



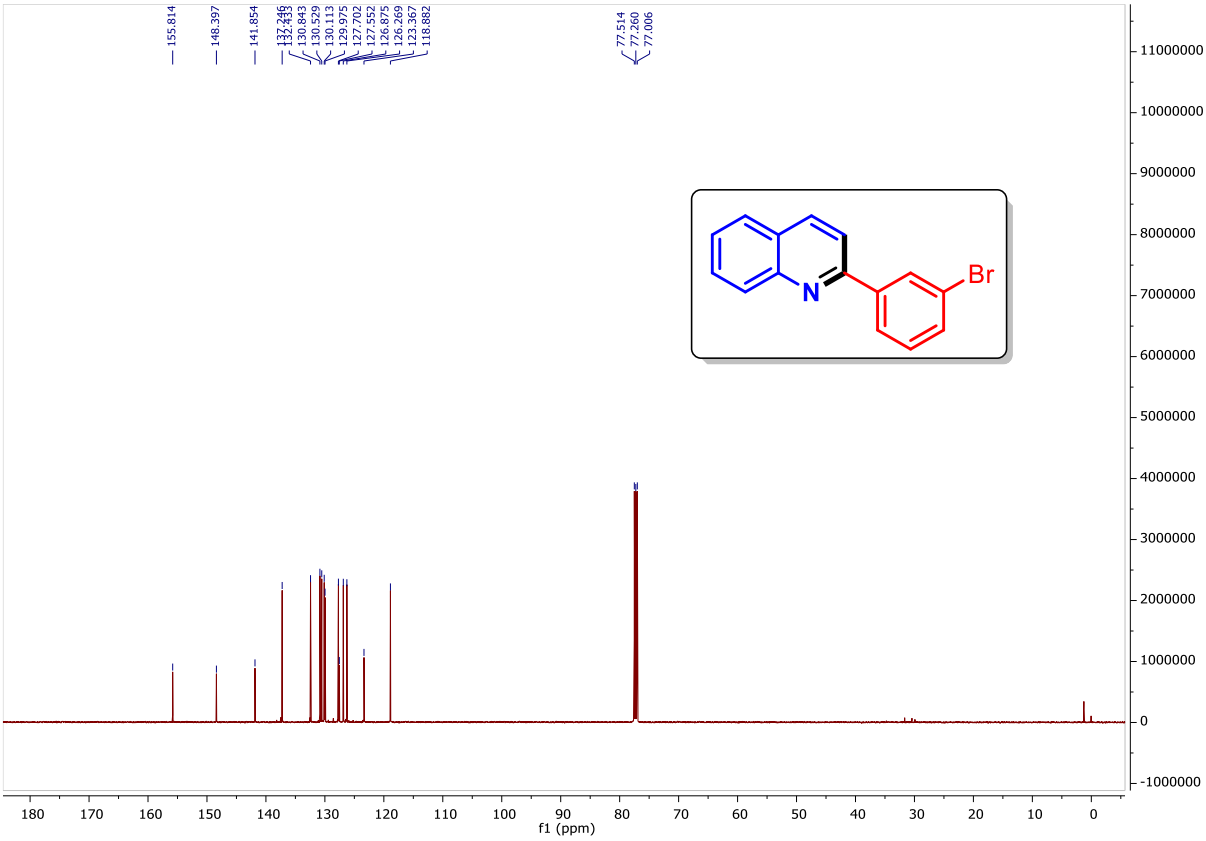
^{13}C{^{1}H} spectrum of compound **3ad** (125 MHz, $CDCl_3$)



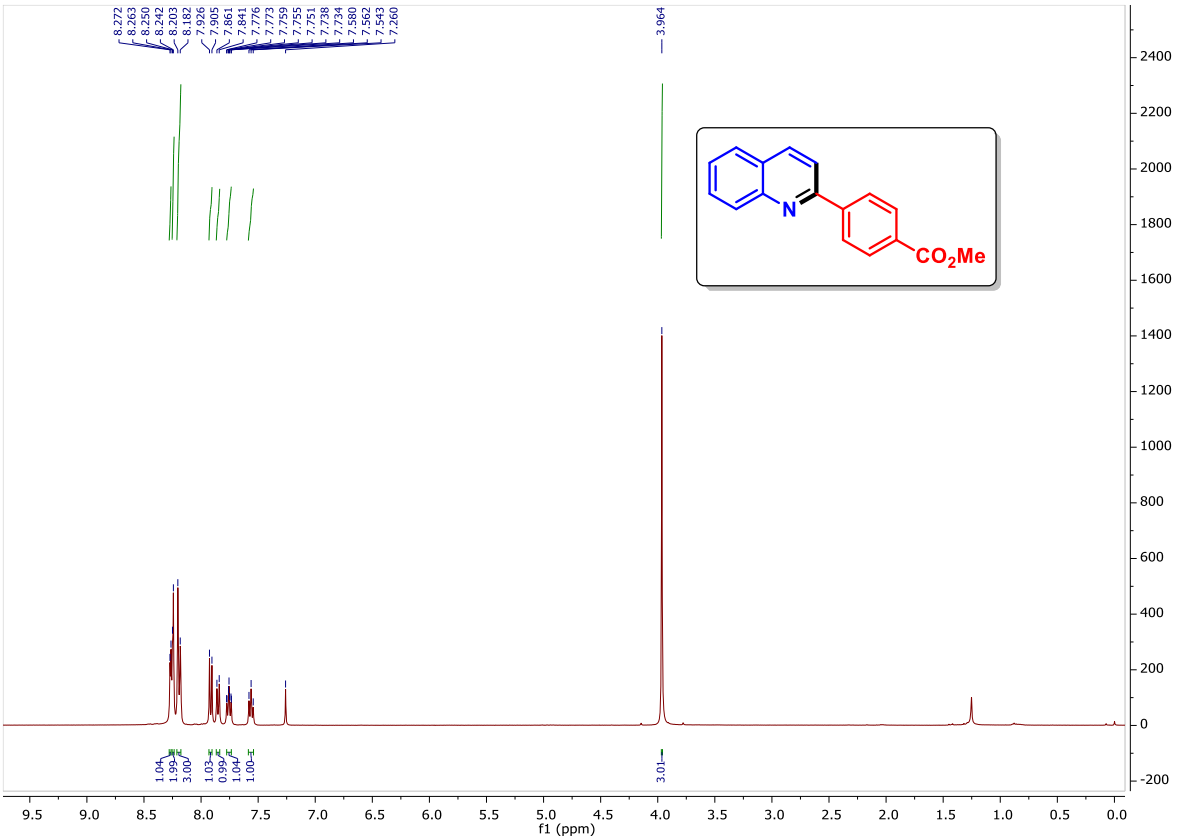
^{1}H spectrum of compound **3ae** (400 MHz, $CDCl_3$)



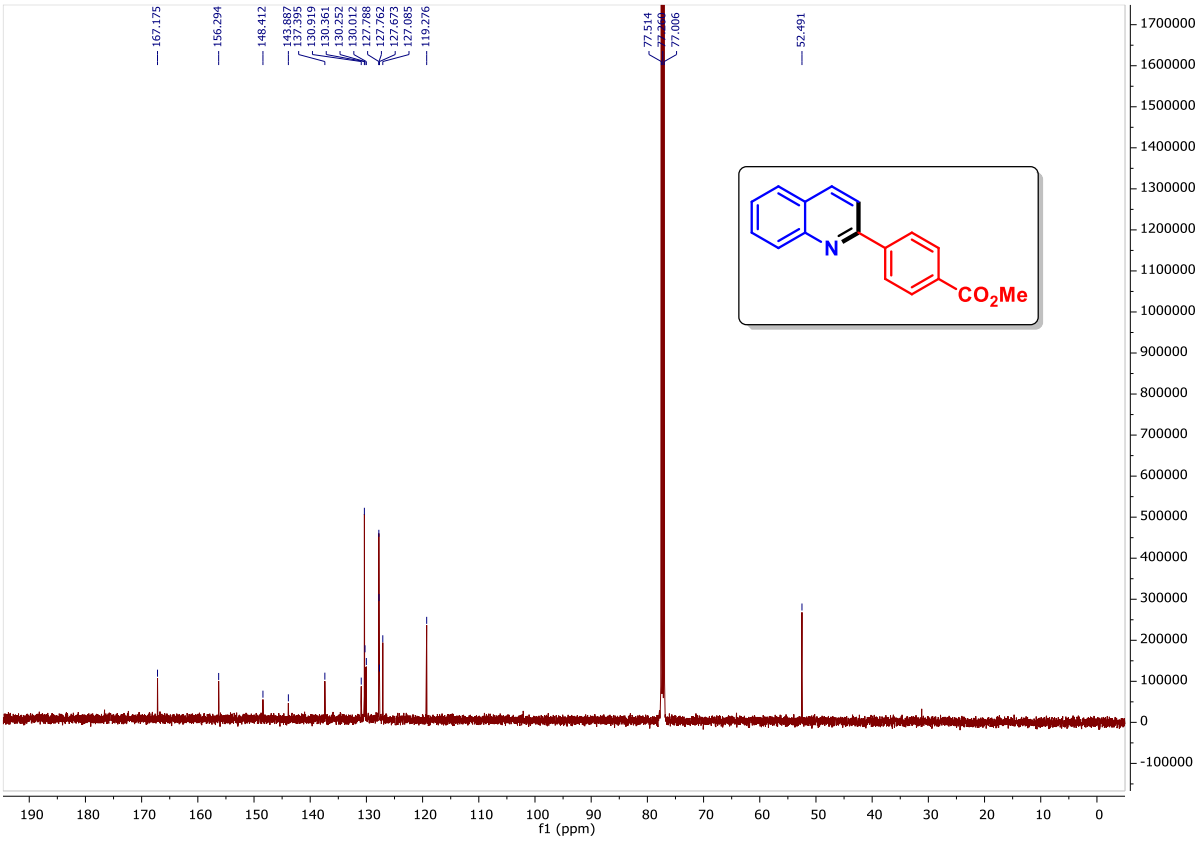
^{13}C{^{1}H} spectrum of compound **3ae** (125 MHz, $CDCl_3$)



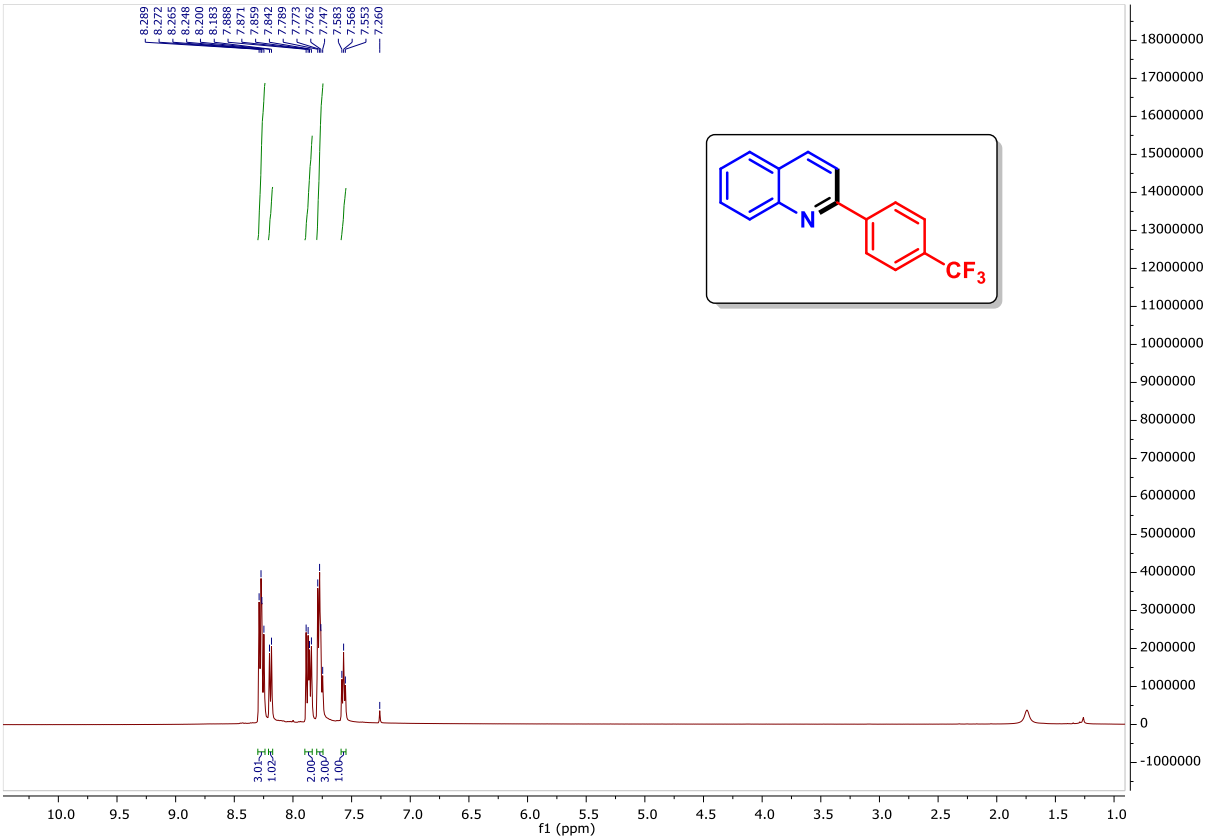
^{1}H spectrum of compound **3af** (400 MHz, $CDCl_3$)



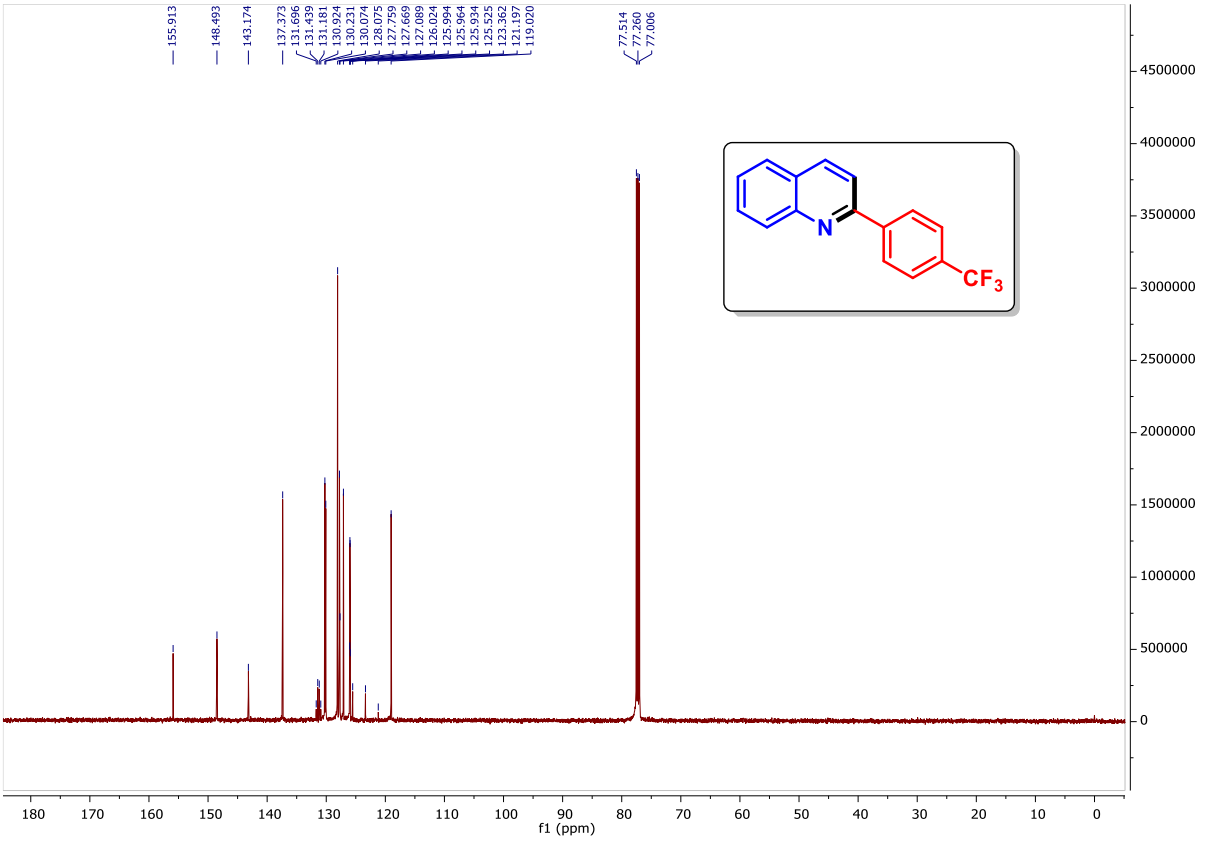
^{13}C{^{1}H} spectrum of compound **3af** (125 MHz, $CDCl_3$)



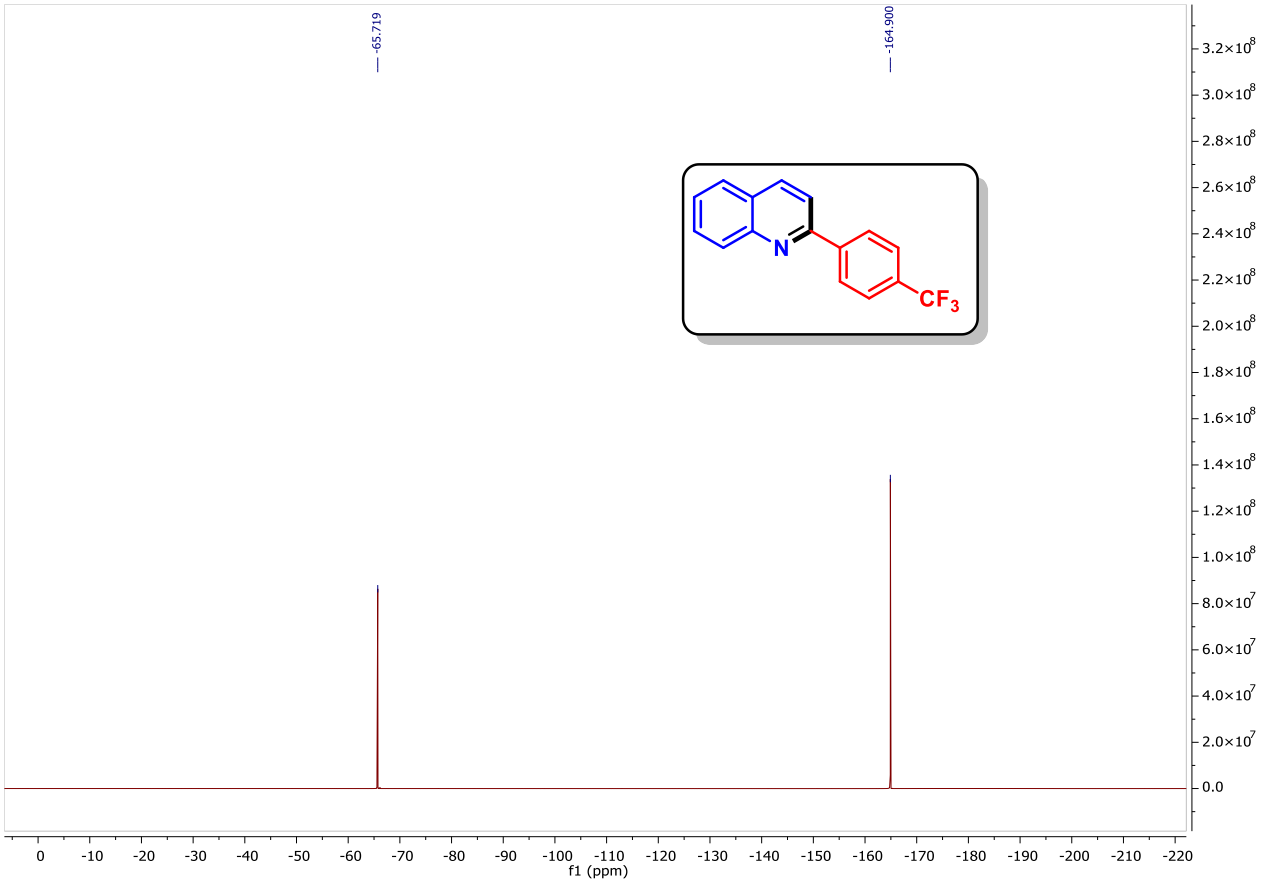
^{1}H spectrum of compound **3ag** (500 MHz, $CDCl_3$)



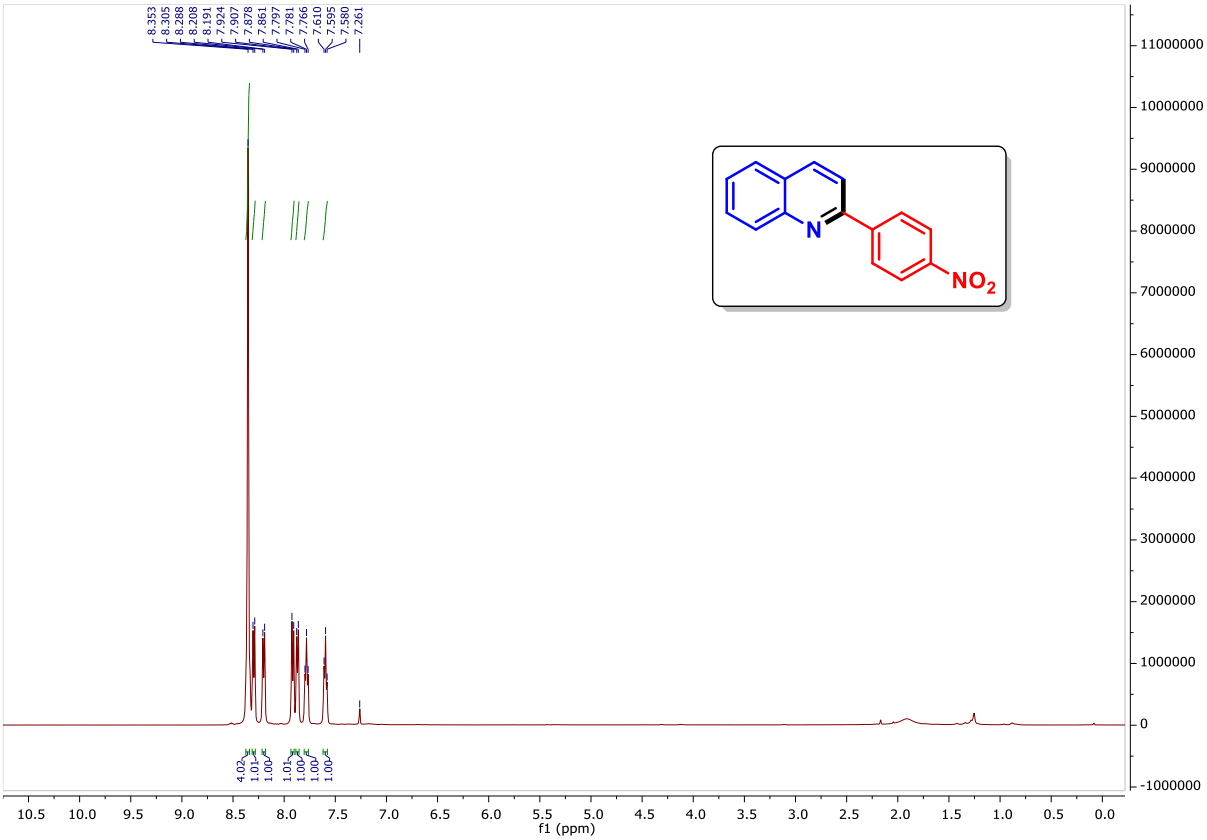
^{13}C{^{1}H} spectrum of compound **3ag** (125 MHz, $CDCl_3$)



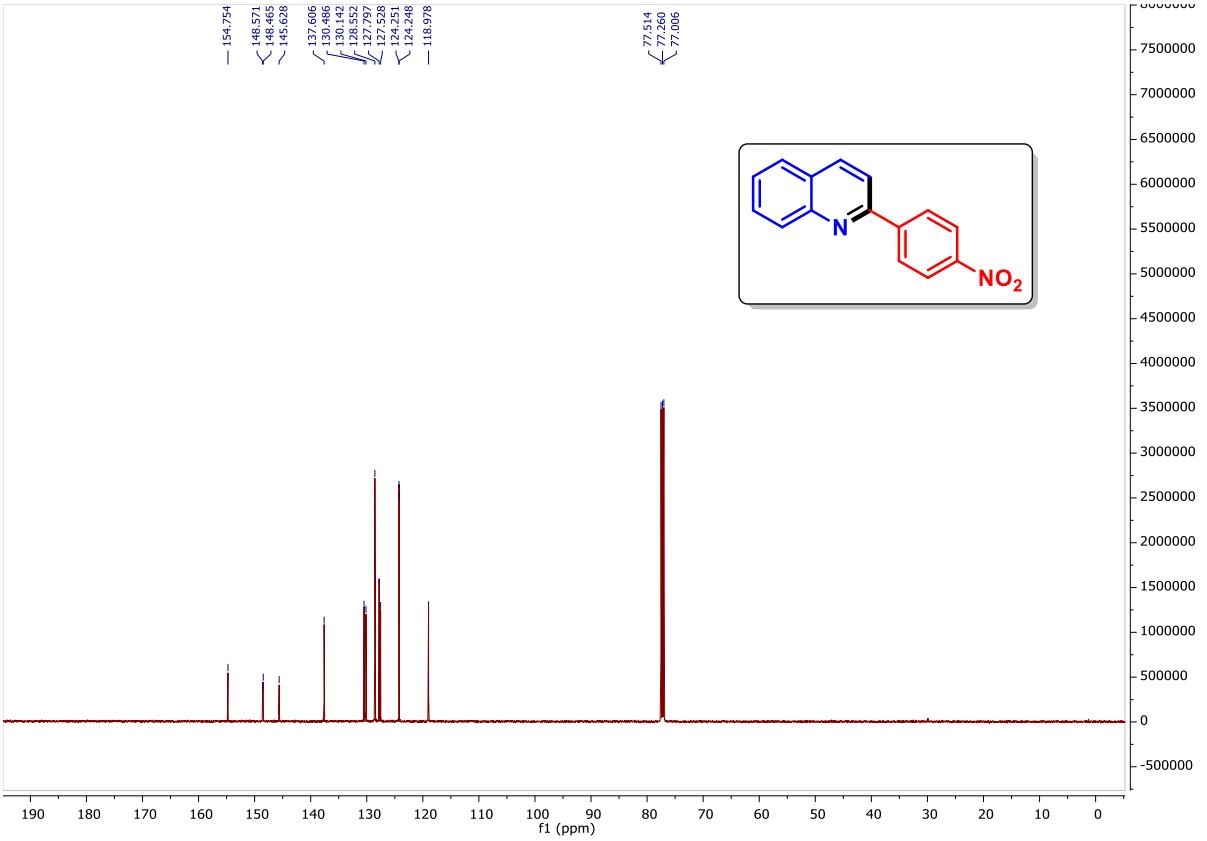
^{19}F spectrum of compound **3ag** (470 MHz, $CDCl_3$ /C_6F_6)



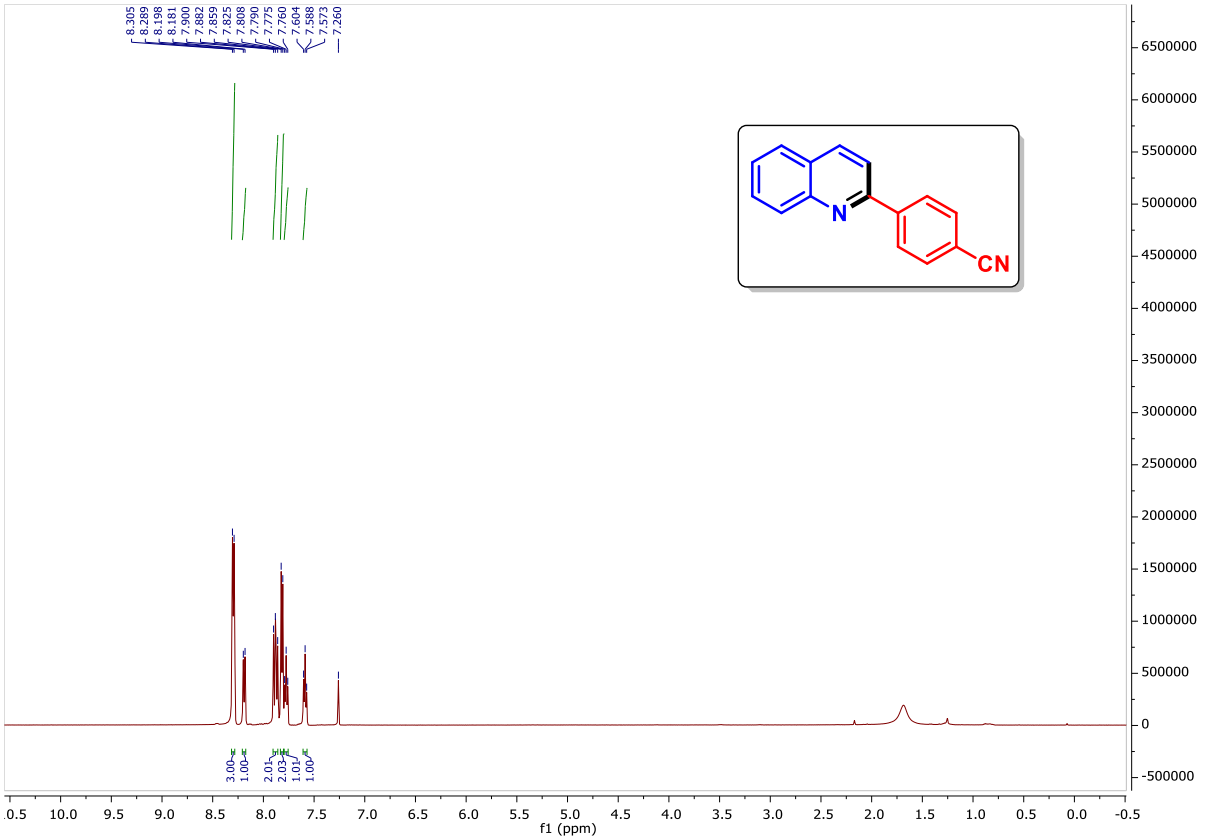
^{1}H spectrum of compound **3ah** (500 MHz, $CDCl_3$)



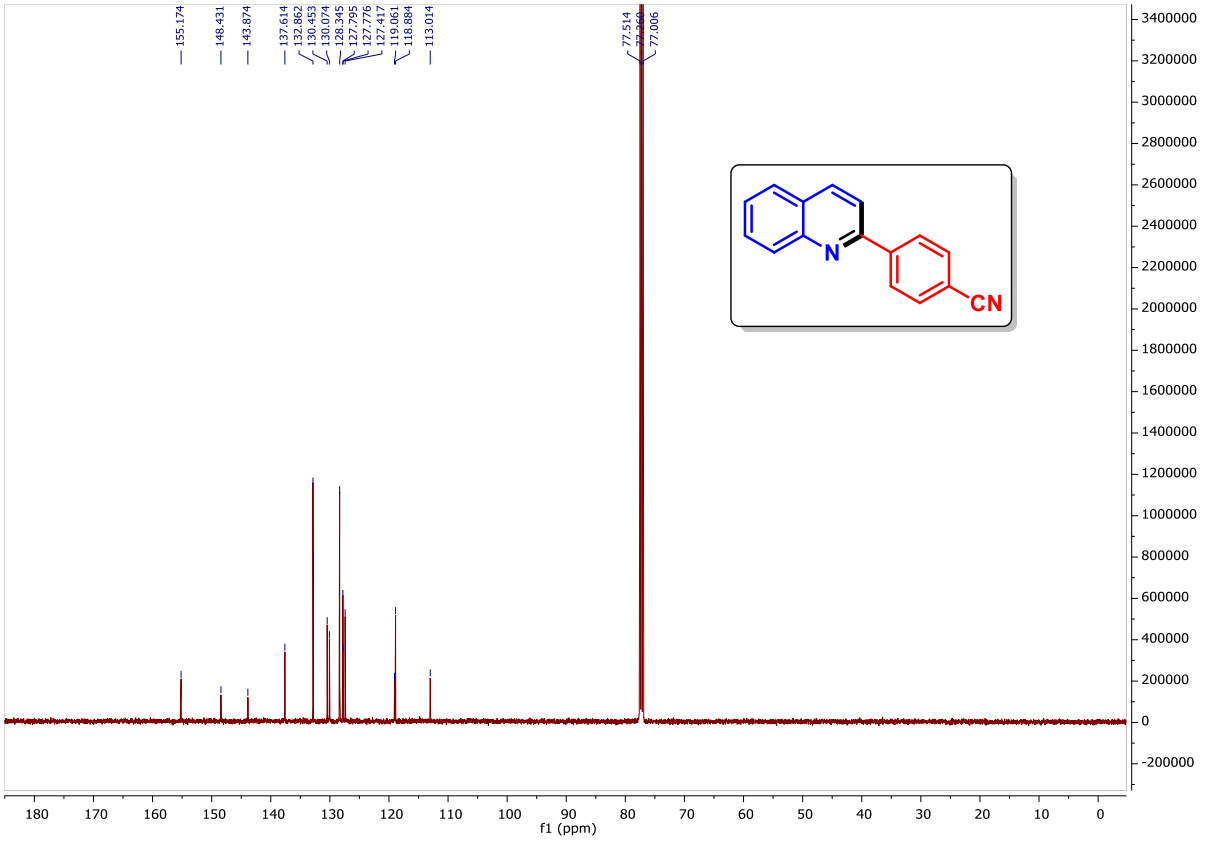
^{13}C{^{1}H} spectrum of compound **3ah** (125 MHz, $CDCl_3$)



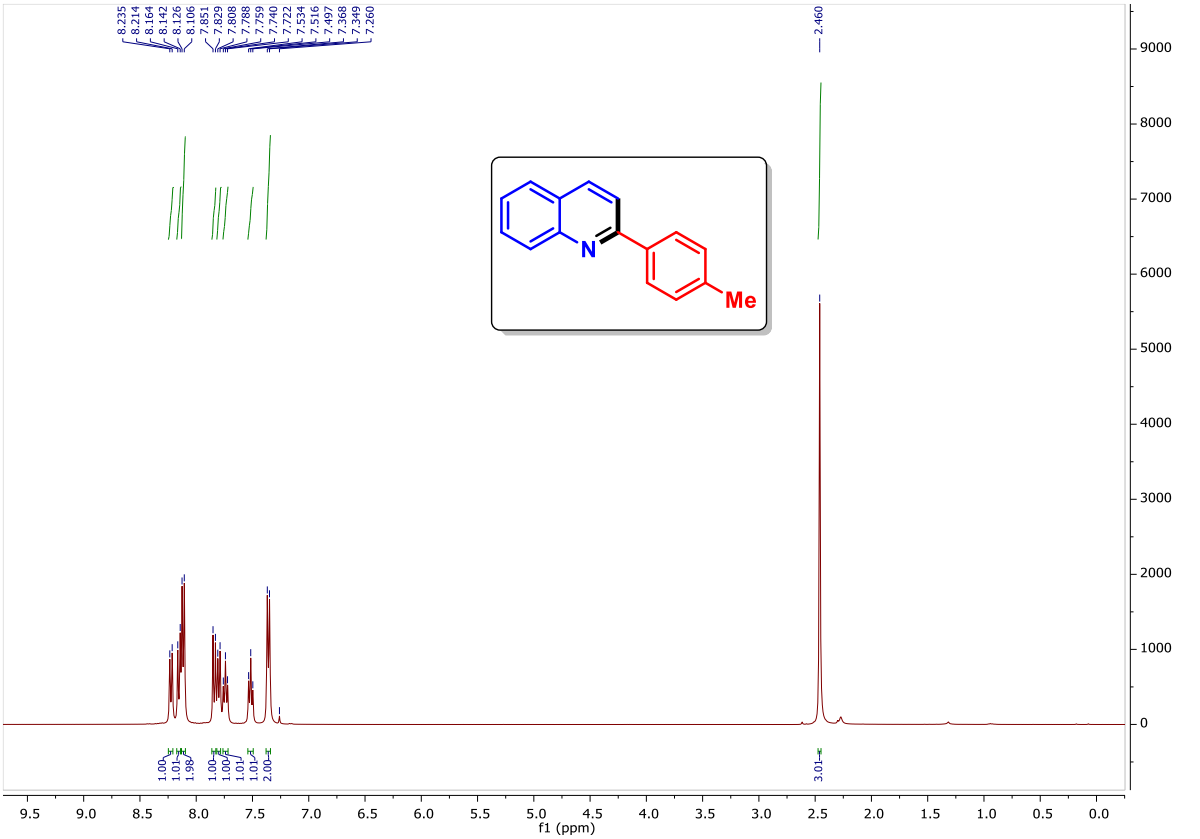
^{1}H spectrum of compound **3ai** (500 MHz, $CDCl_3$)



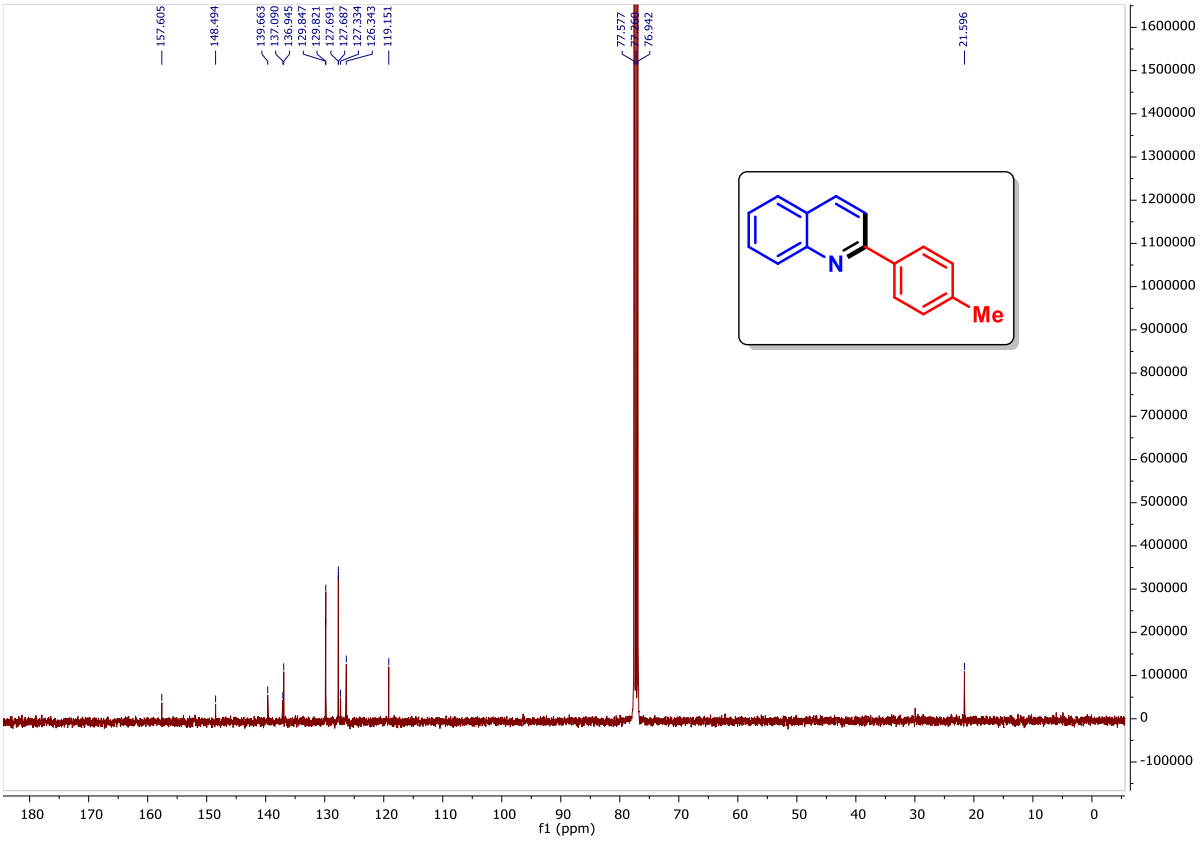
^{13}C{^{1}H} spectrum of compound **3ai** (125 MHz, $CDCl_3$)



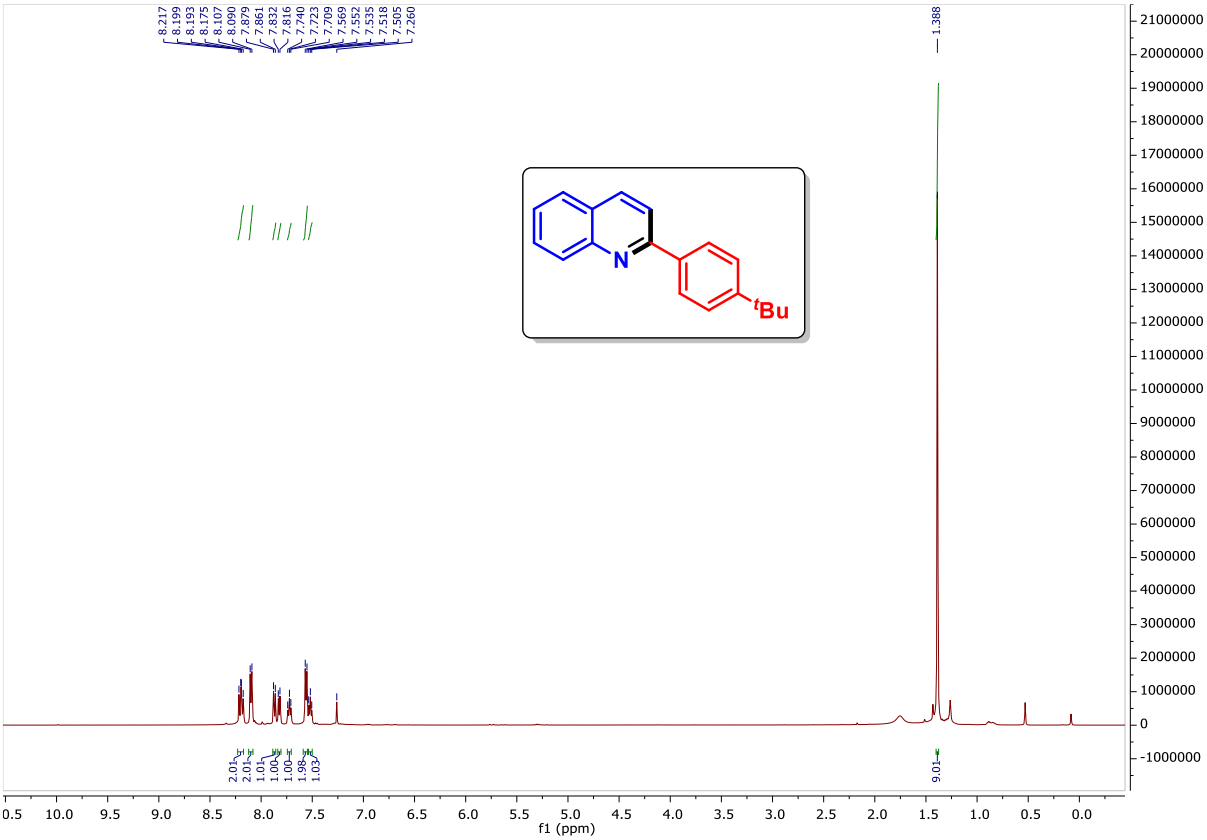
^{1}H spectrum of compound **3aj** (400 MHz, $CDCl_3$)



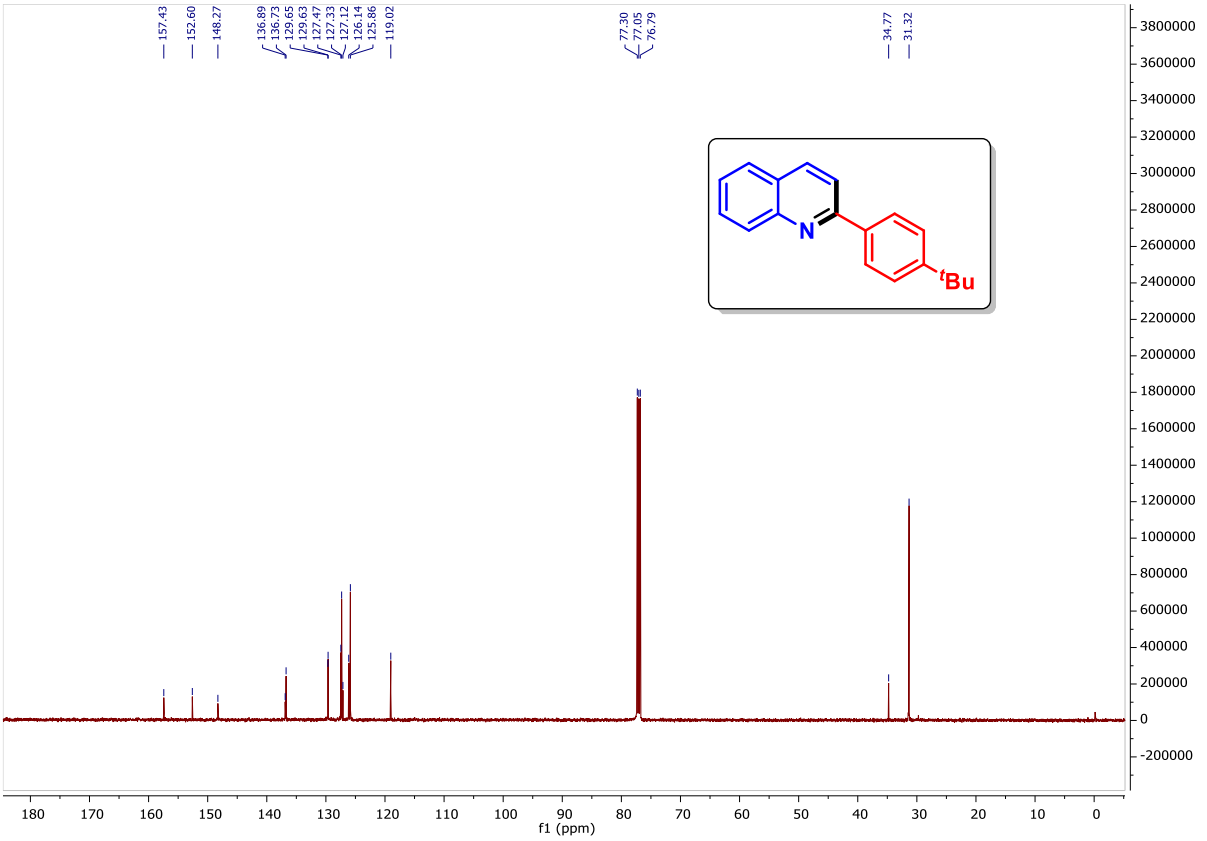
^{13}C{^{1}H} spectrum of compound **3aj** (100 MHz, $CDCl_3$)



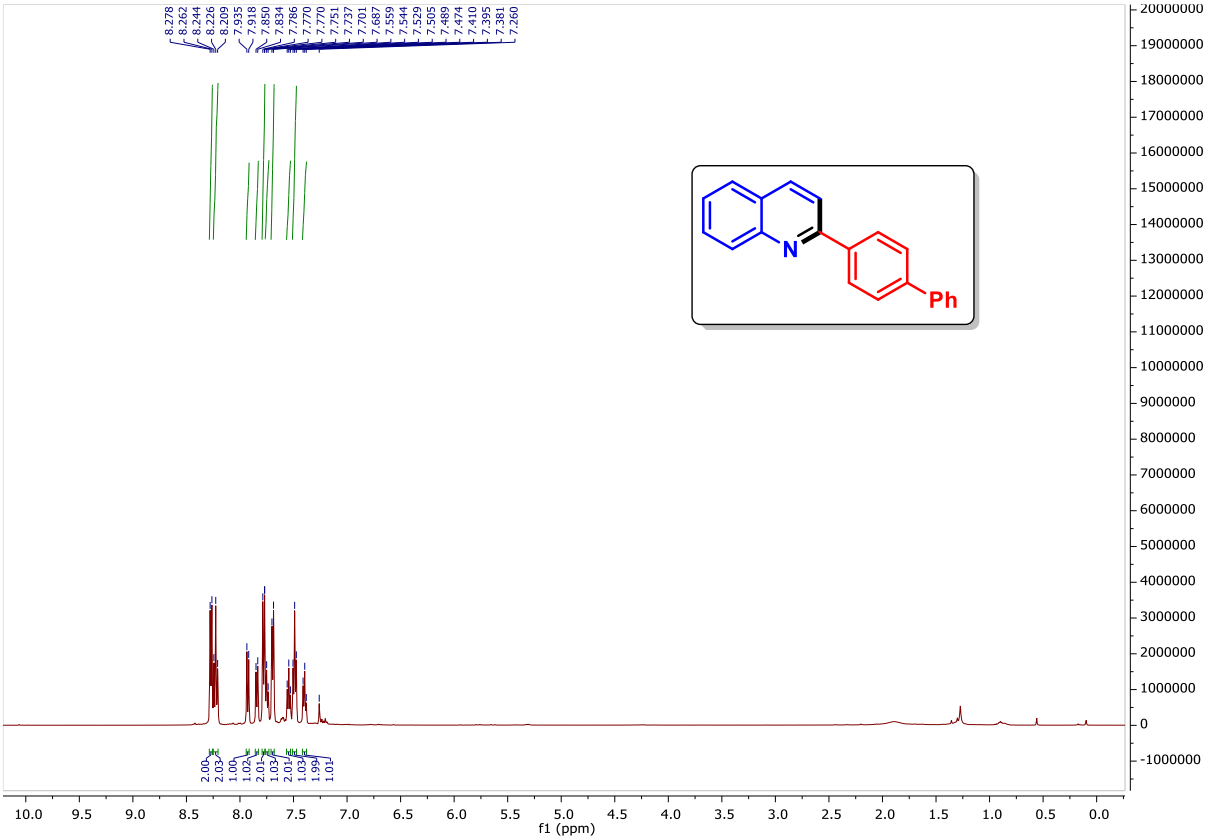
^{1}H spectrum of compound **3ak** (500 MHz, $CDCl_3$)



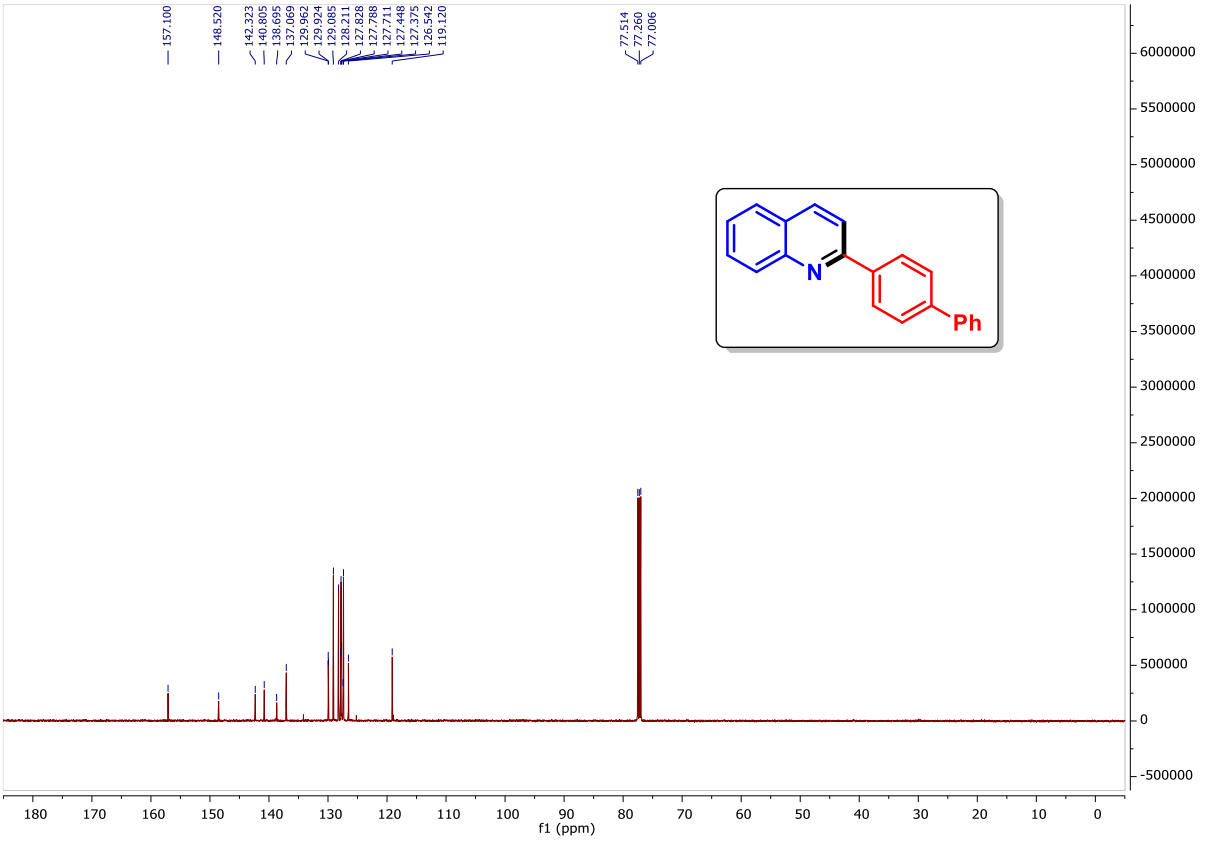
^{13}C{^{1}H} spectrum of compound **3ak** (125 MHz, $CDCl_3$)



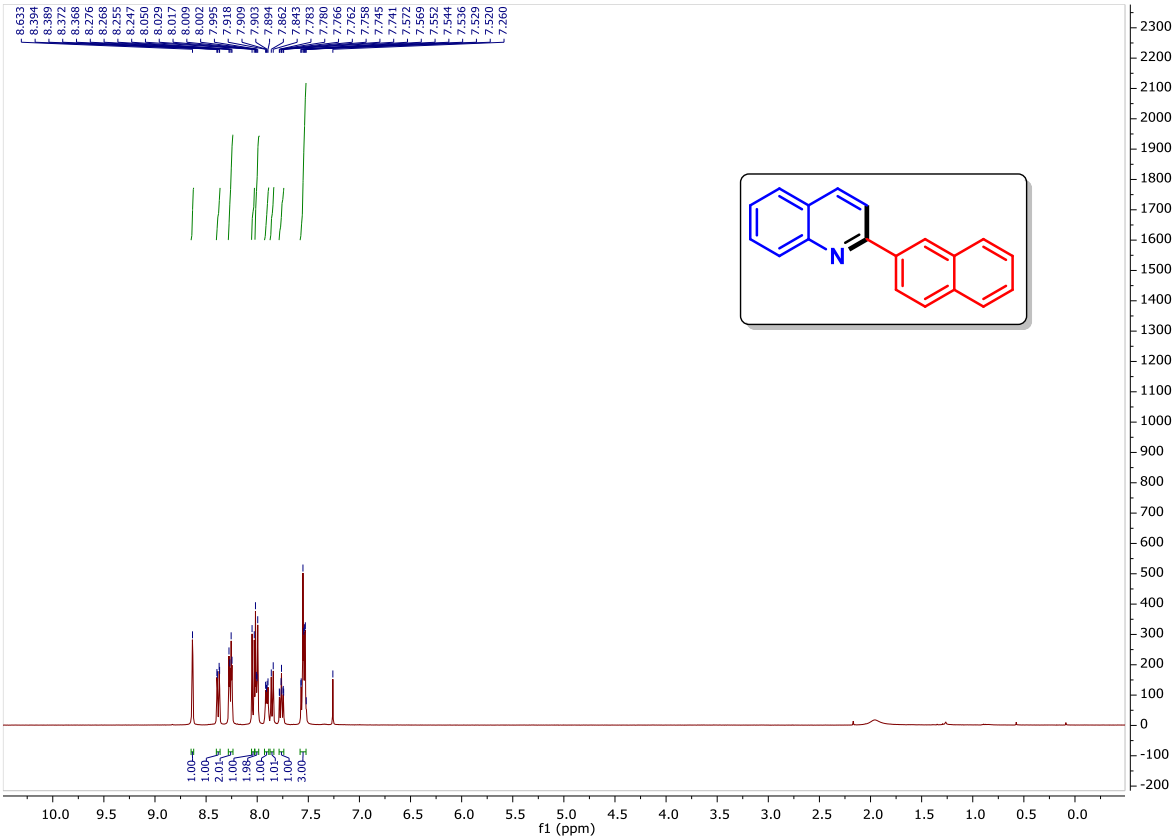
^{1}H spectrum of compound **3al** (500 MHz, $CDCl_3$)



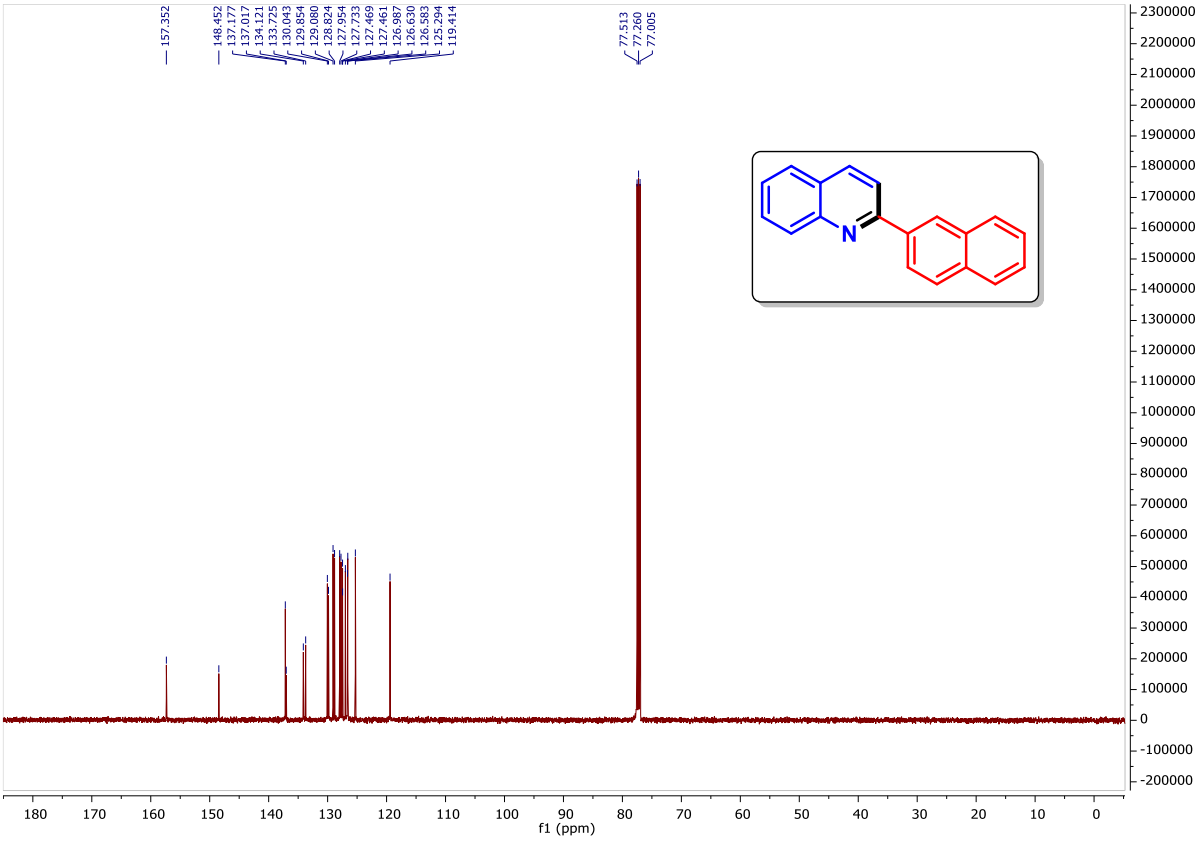
^{13}C{^{1}H} spectrum of compound **3al** (125 MHz, $CDCl_3$)



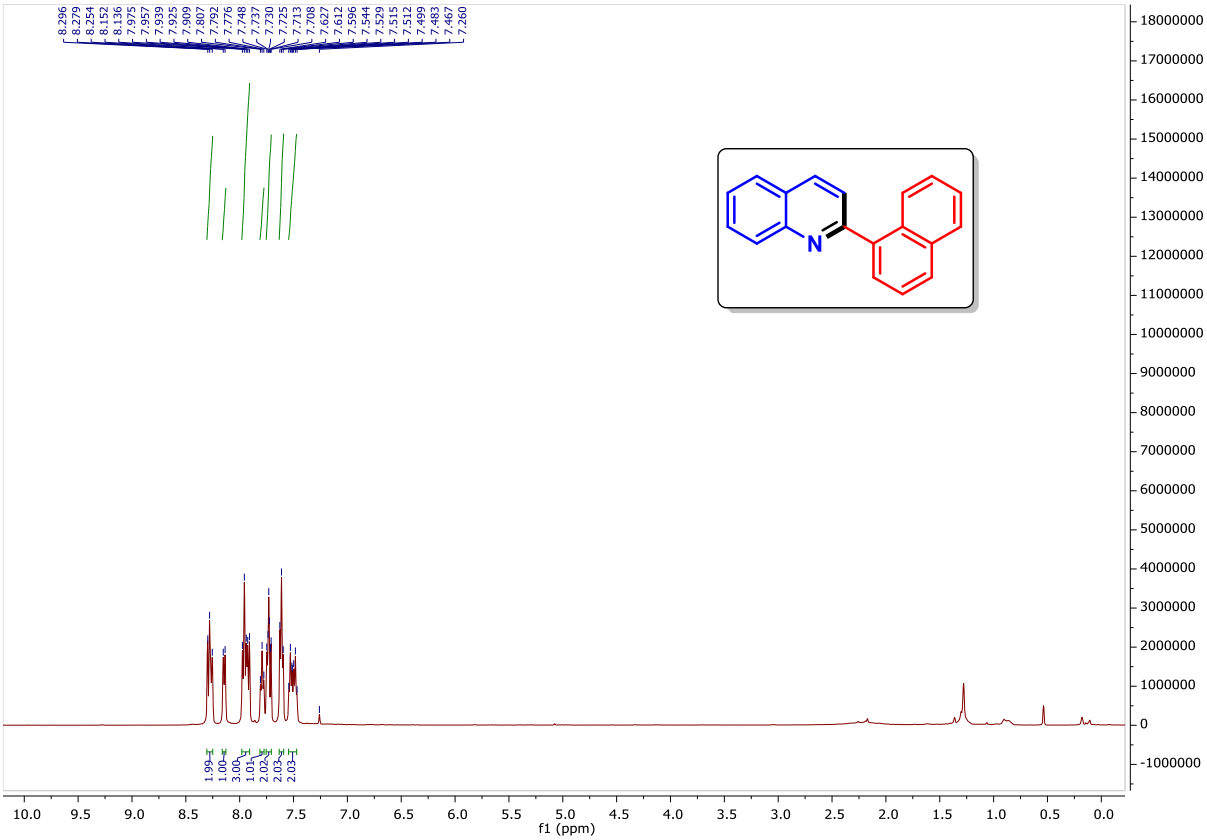
^{1}H spectrum of compound **3am** (400 MHz, $CDCl_3$)



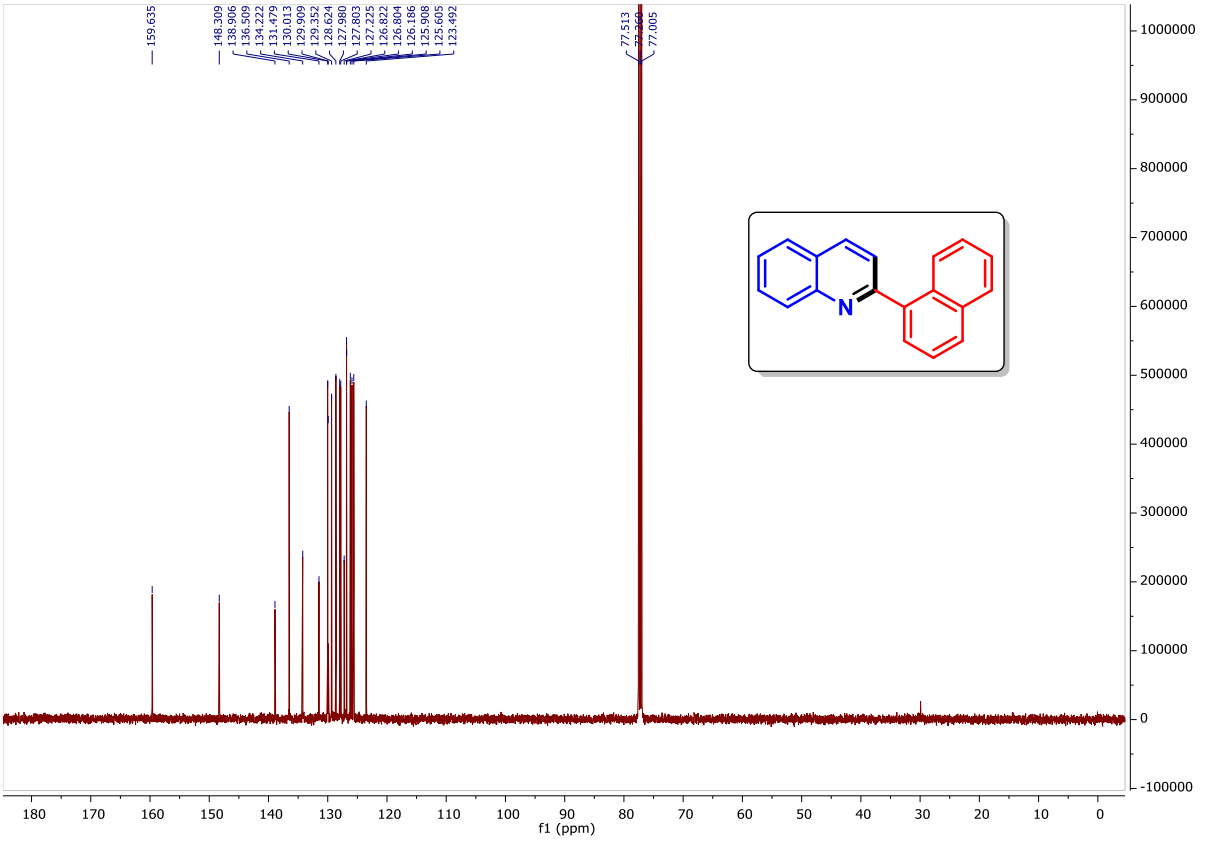
^{13}C{^{1}H} spectrum of compound **3am** (125 MHz, $CDCl_3$)



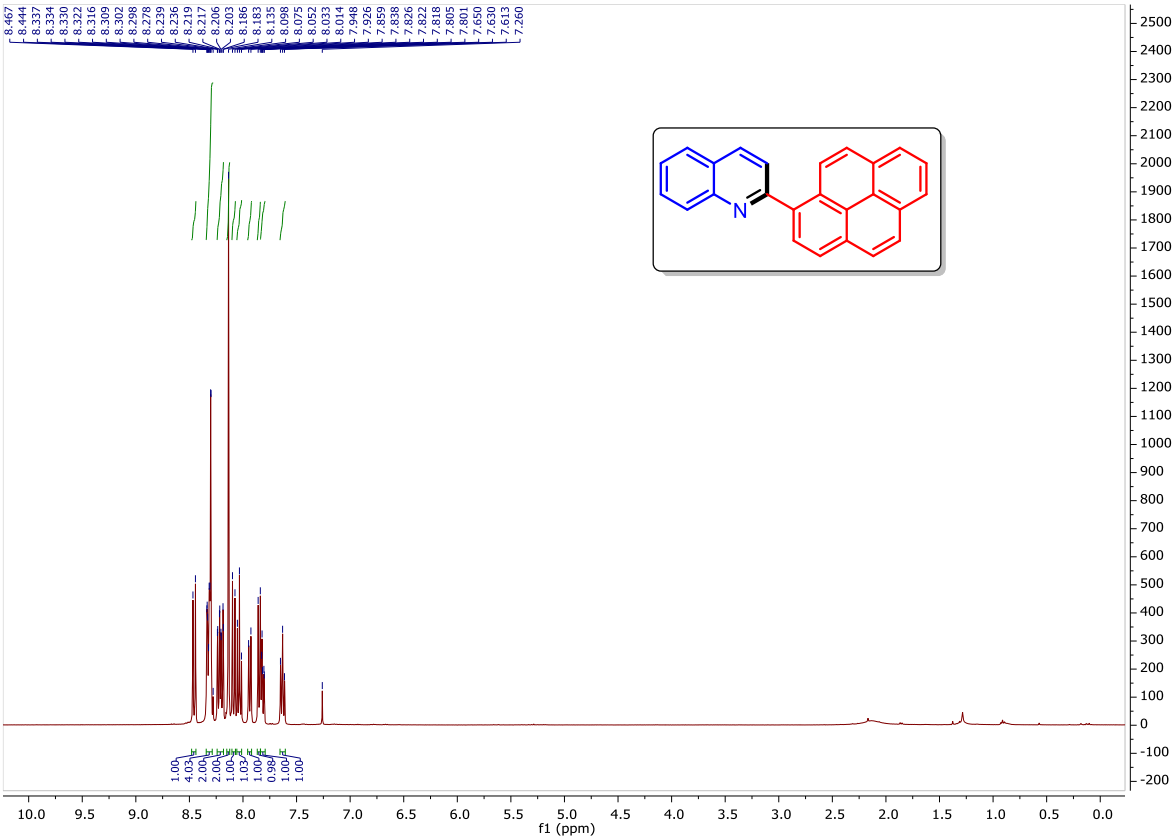
^{1}H spectrum of compound **3an** (500 MHz, $CDCl_3$)



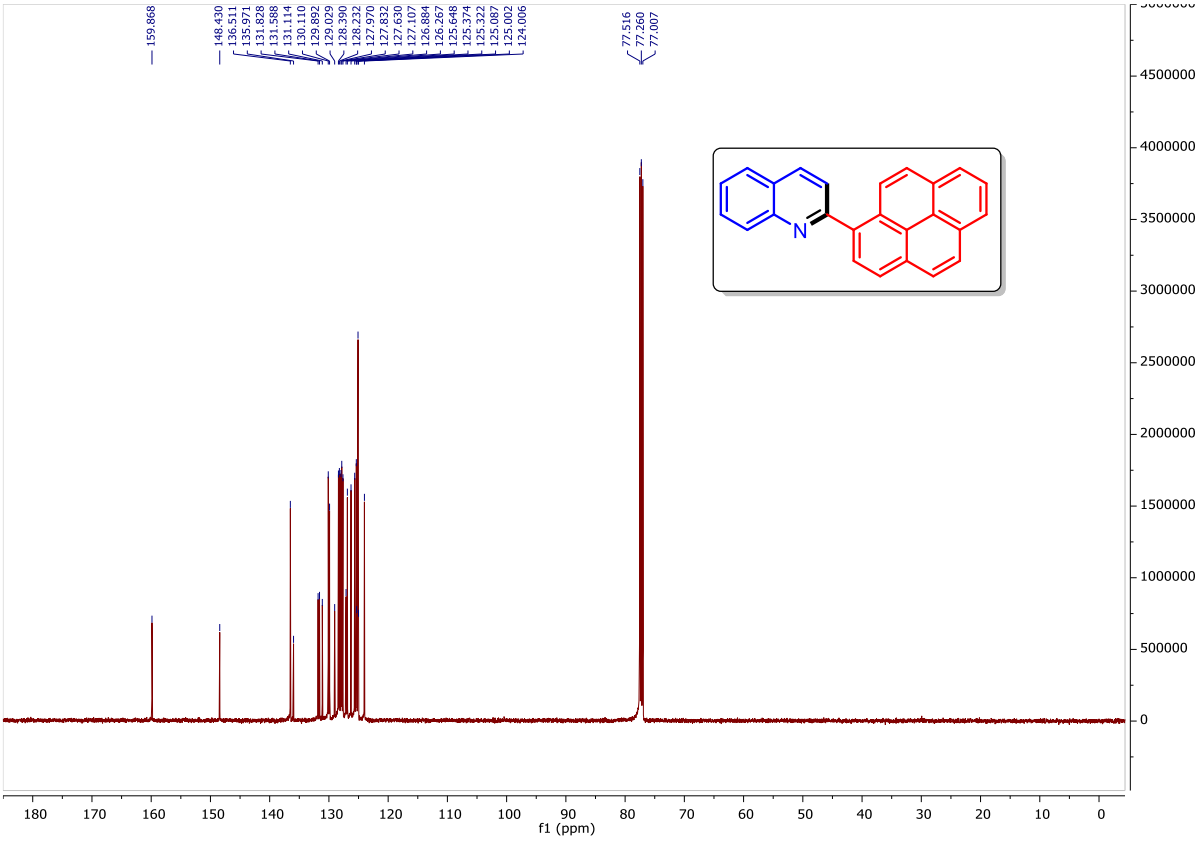
^{13}C{^{1}H} spectrum of compound **3an** (125 MHz, $CDCl_3$)



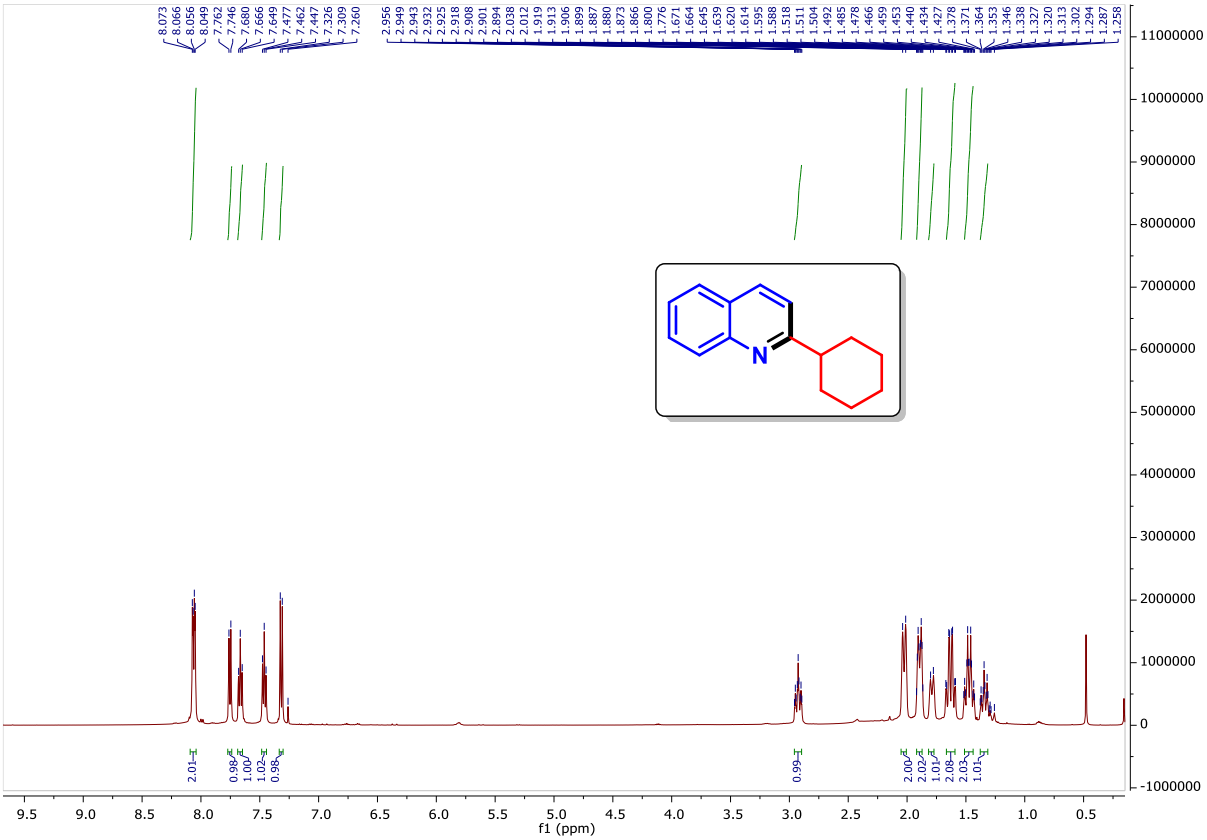
^{1}H spectrum of compound **3ao** (400 MHz, $CDCl_3$)



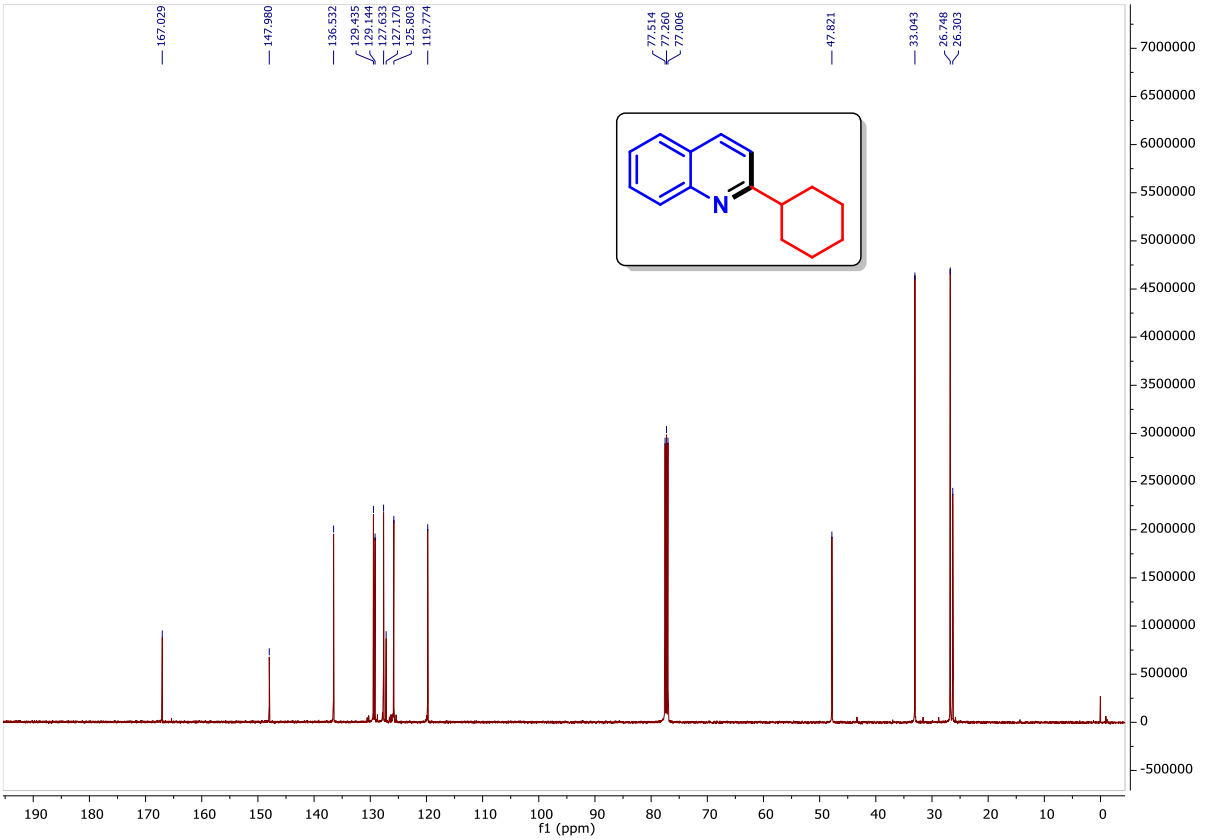
^{13}C{^{1}H} spectrum of compound **3ao** (125 MHz, $CDCl_3$)



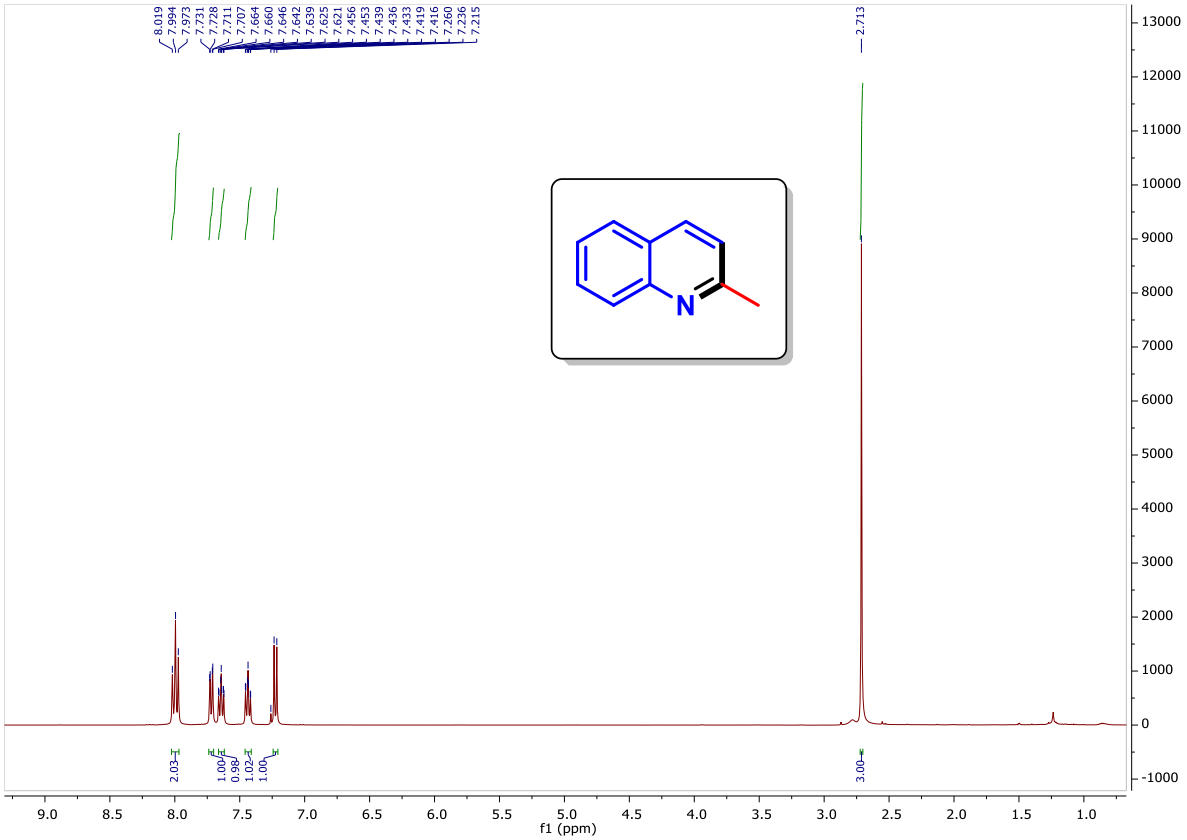
^{1}H spectrum of compound **3ap** (500 MHz, $CDCl_3$)



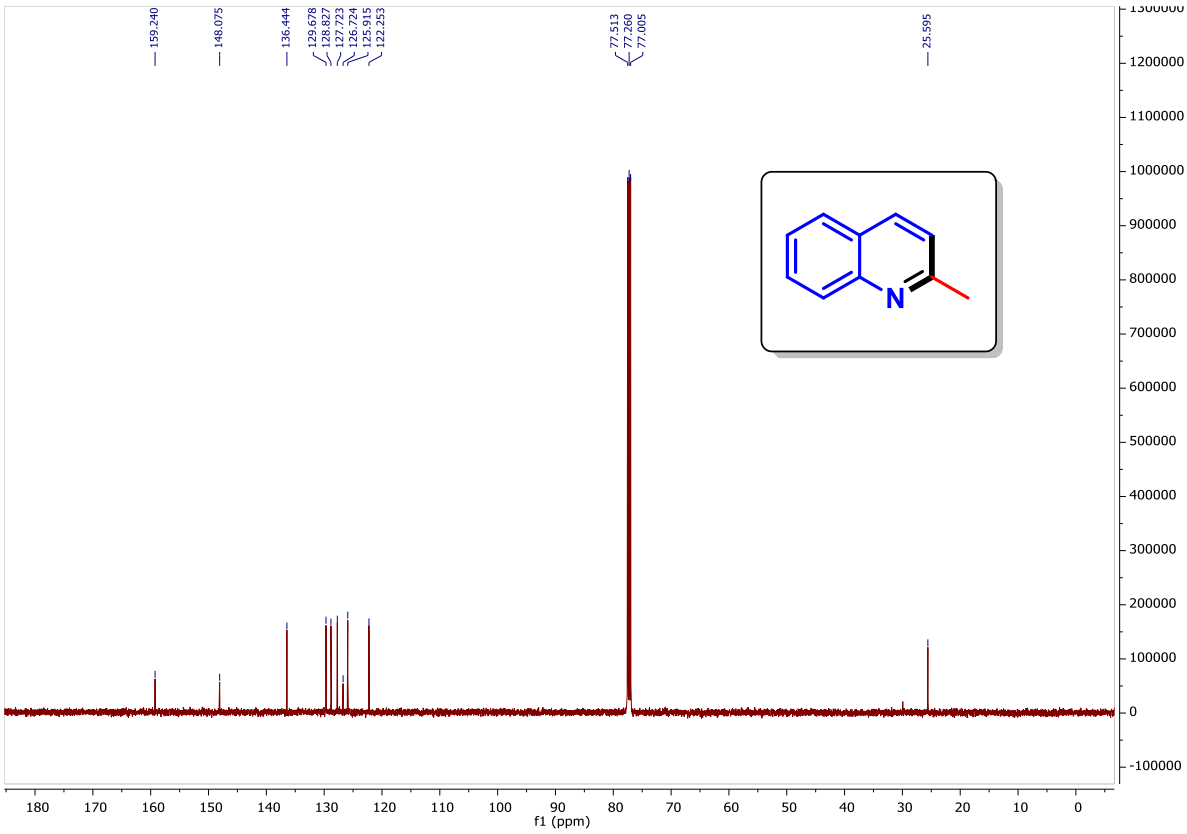
^{13}C{^{1}H} spectrum of compound **3ap** (125 MHz, $CDCl_3$)



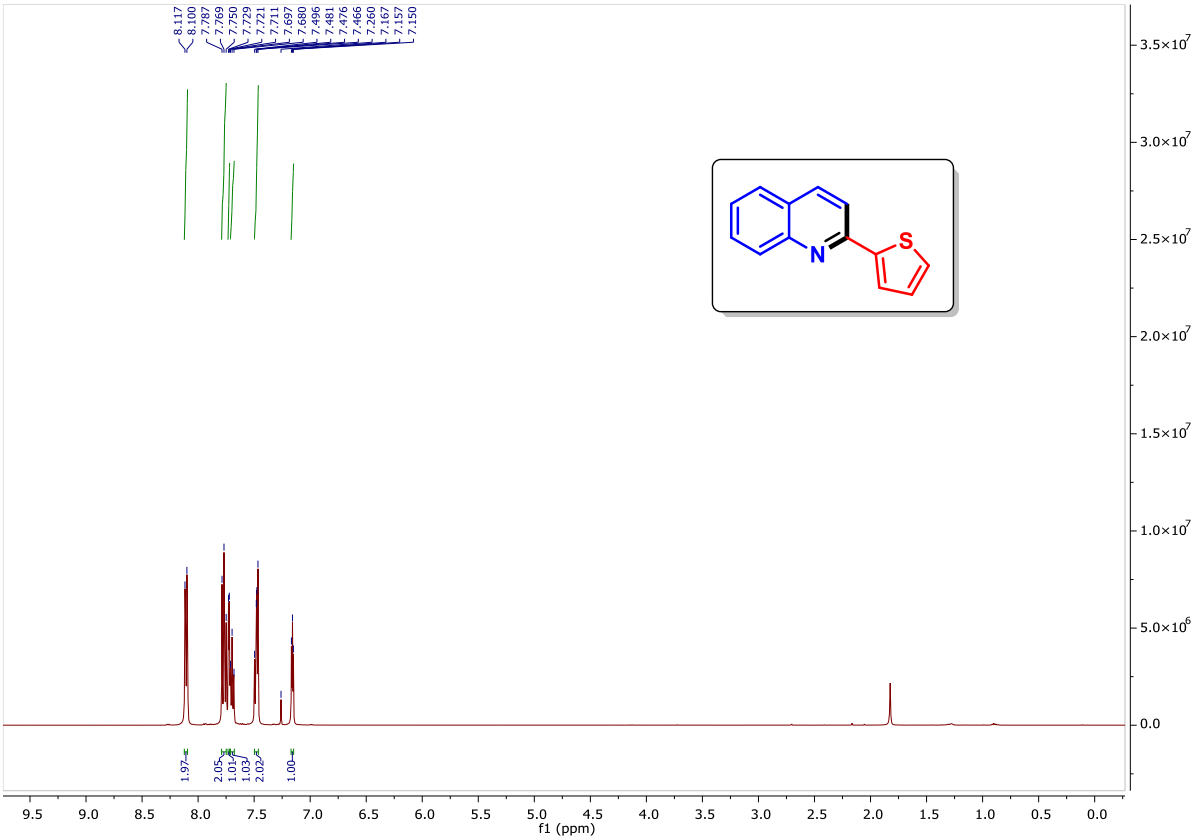
^{1}H spectrum of compound **3aq** (400 MHz, $CDCl_3$)



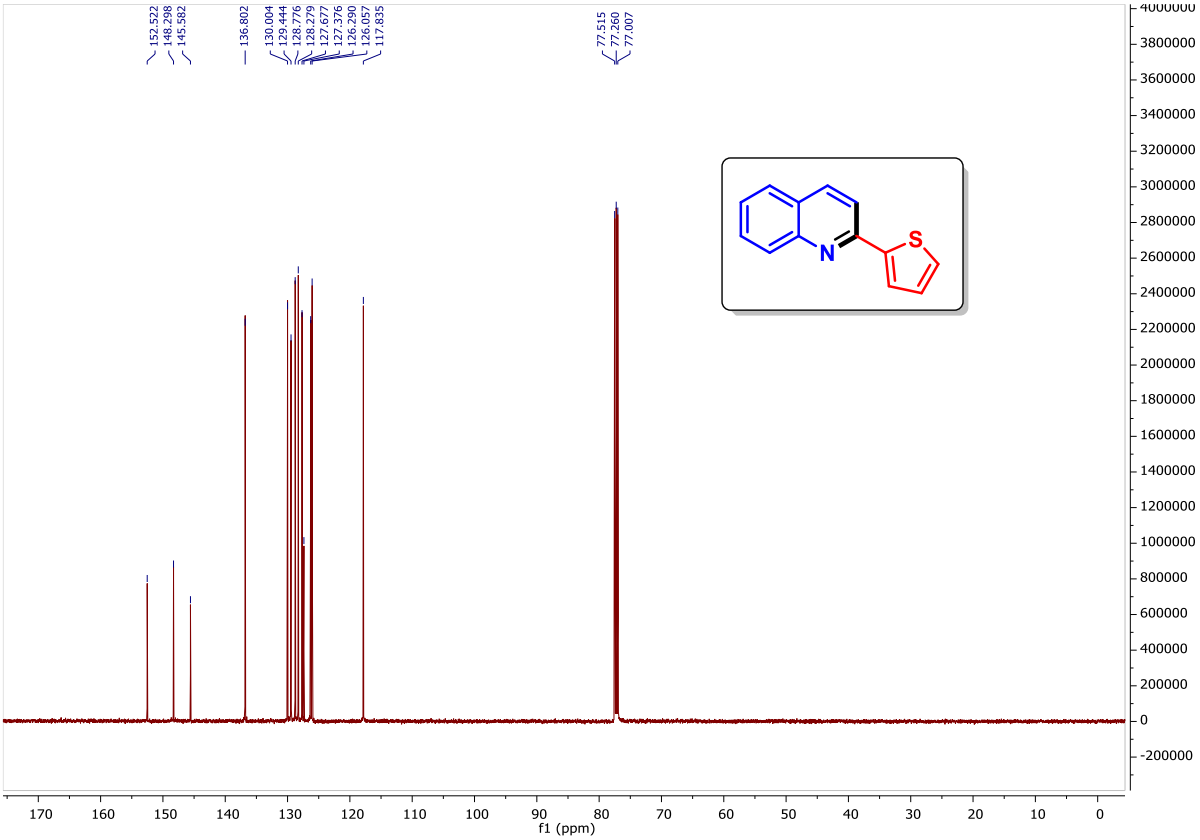
$^{13}C\{^{1}H\}$ spectrum of compound **3aq** (125 MHz, $CDCl_3$)



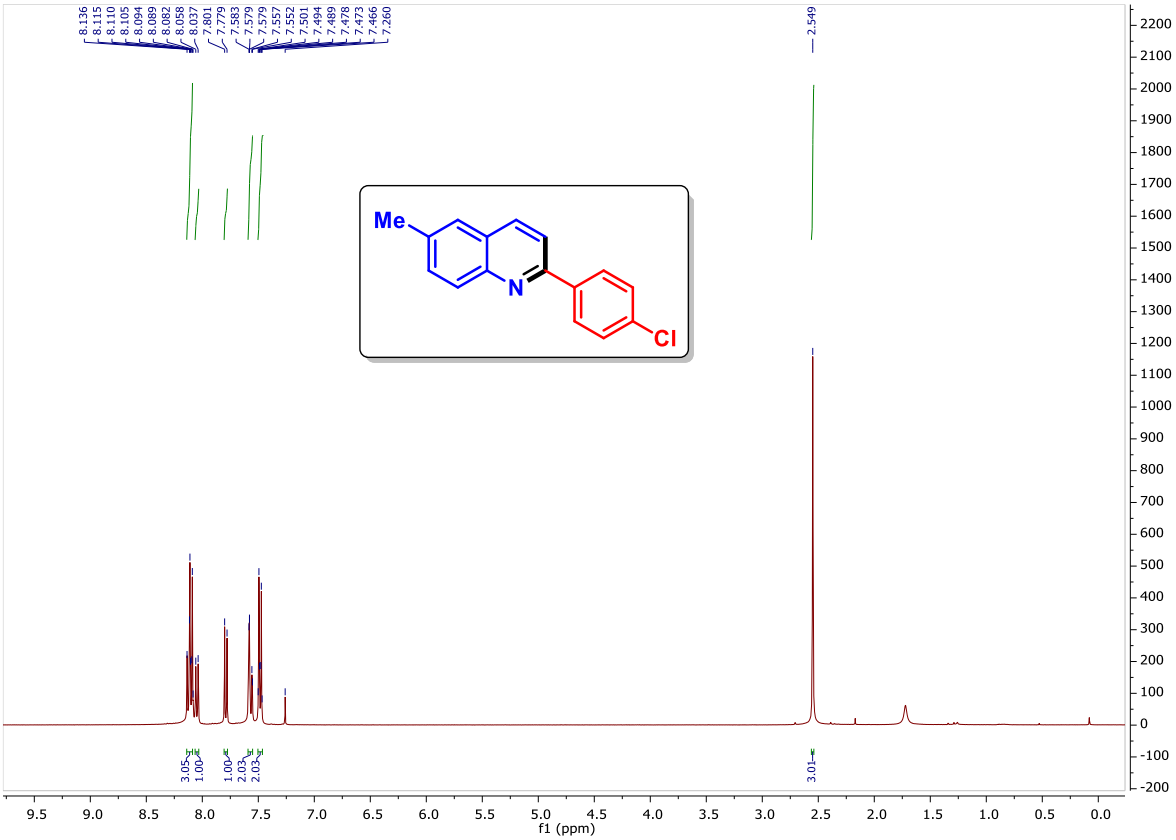
^{1}H spectrum of compound **3ar** (500 MHz, $CDCl_3$)



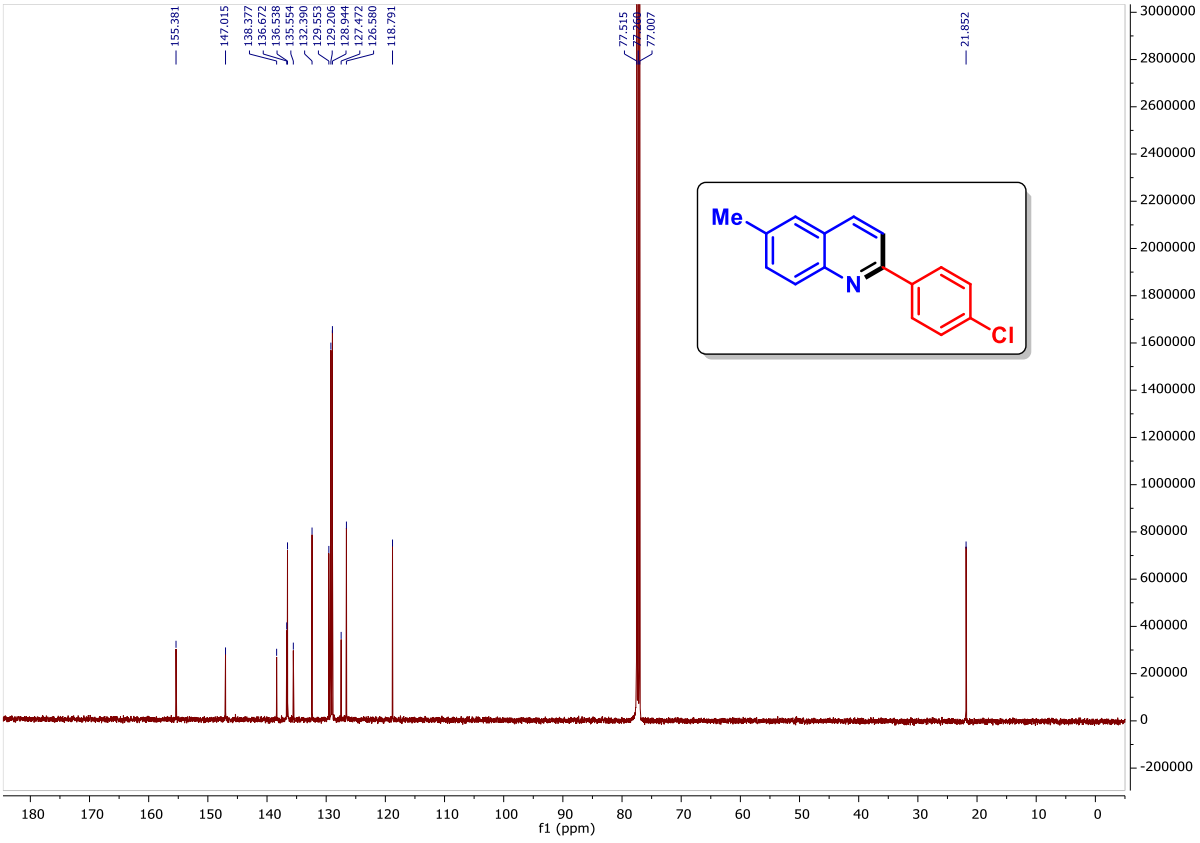
^{13}C{^{1}H} spectrum of compound **3ar**(125 MHz, $CDCl_3$)



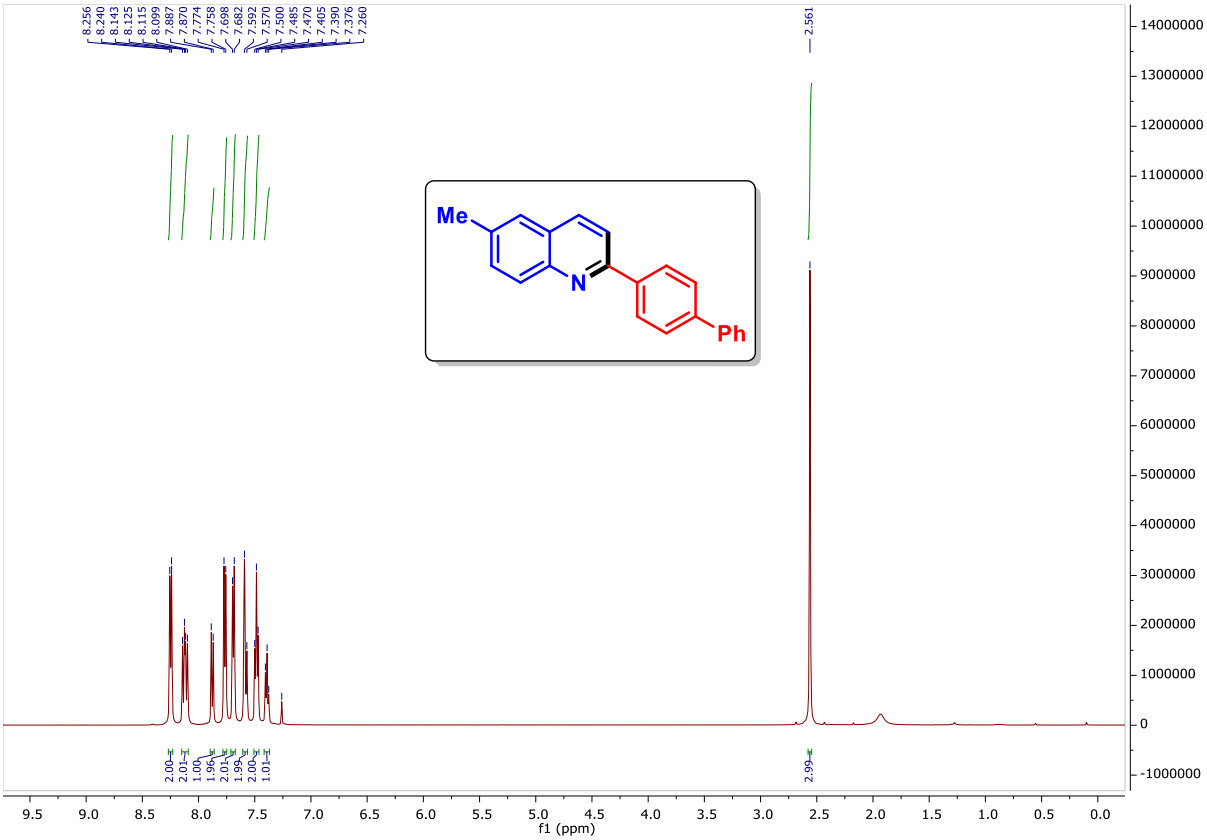
^{1}H spectrum of compound **3ba** (400 MHz, $CDCl_3$)



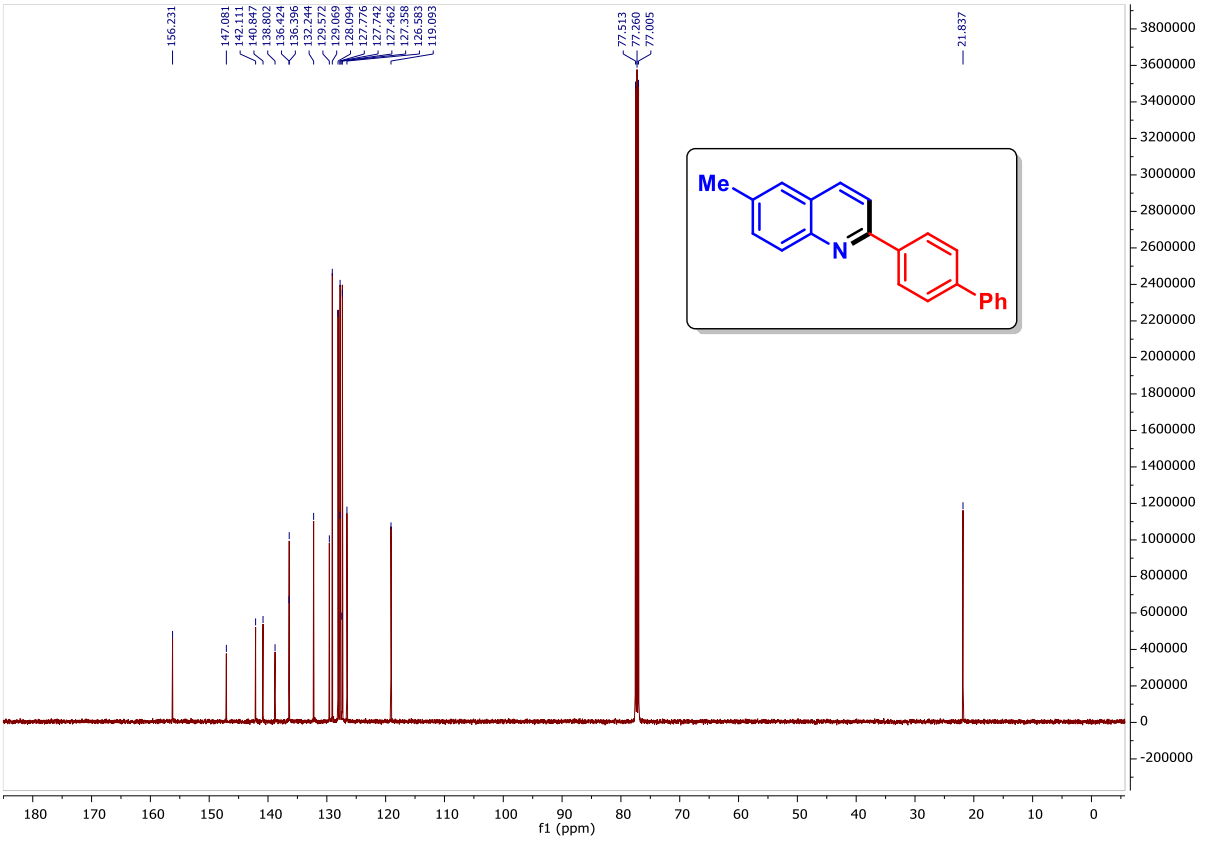
^{13}C{^{1}H} spectrum of compound **3ba** (125 MHz, $CDCl_3$)



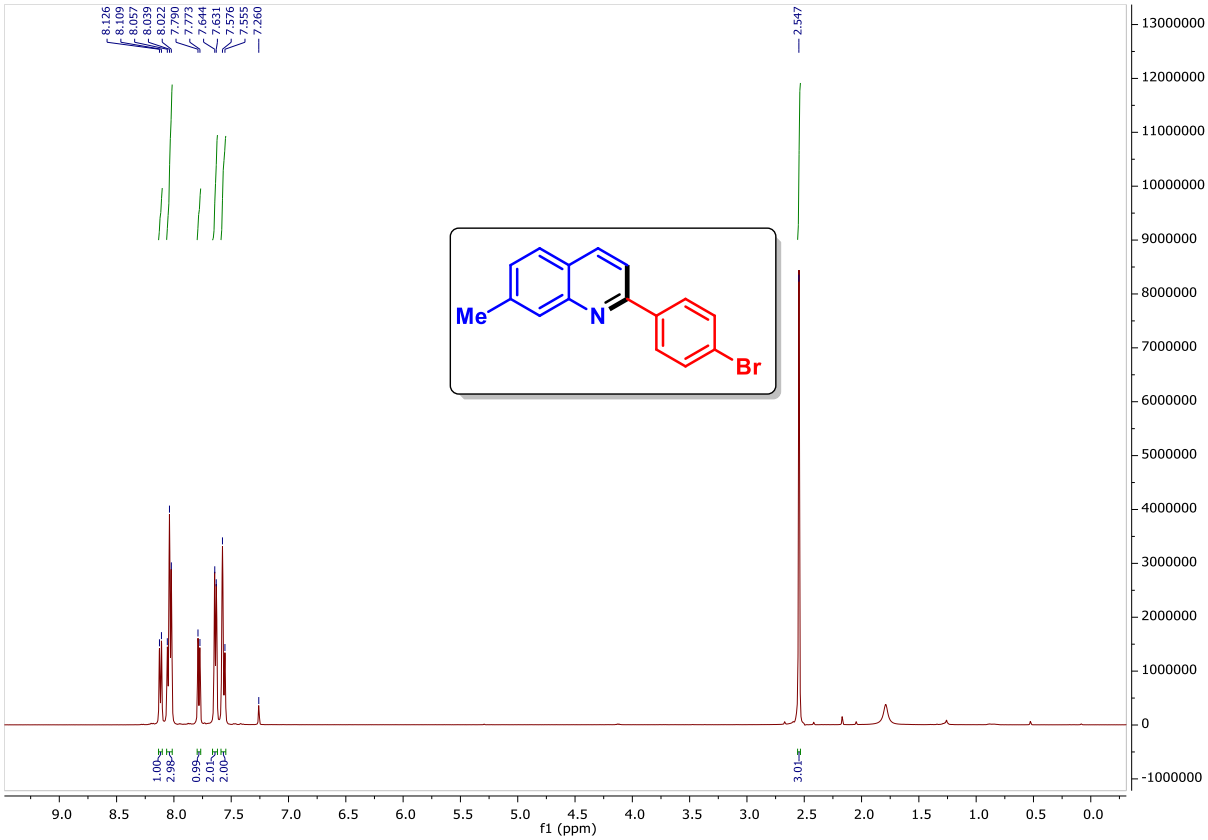
^{1}H spectrum of compound **3bl** (500 MHz, $CDCl_3$)



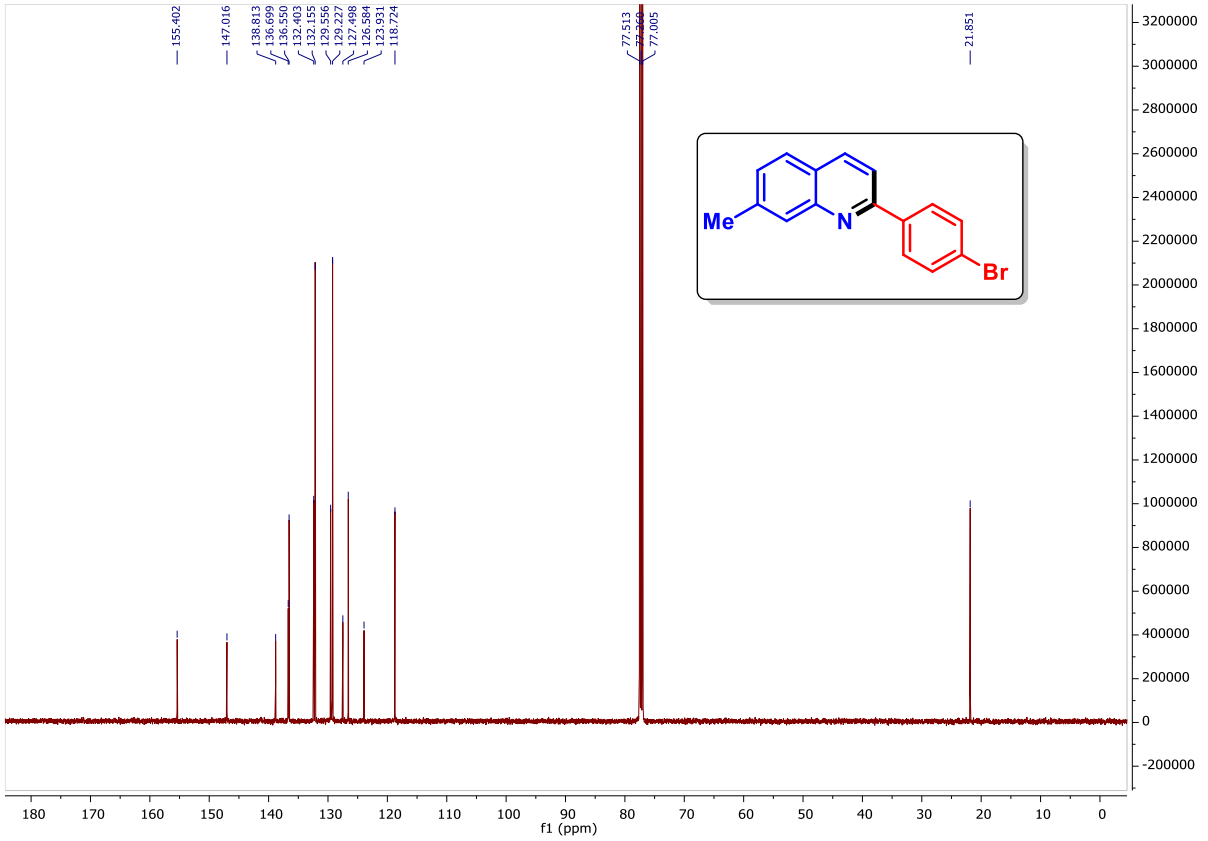
^{13}C{^{1}H} spectrum of compound **3bl** (125 MHz, $CDCl_3$)



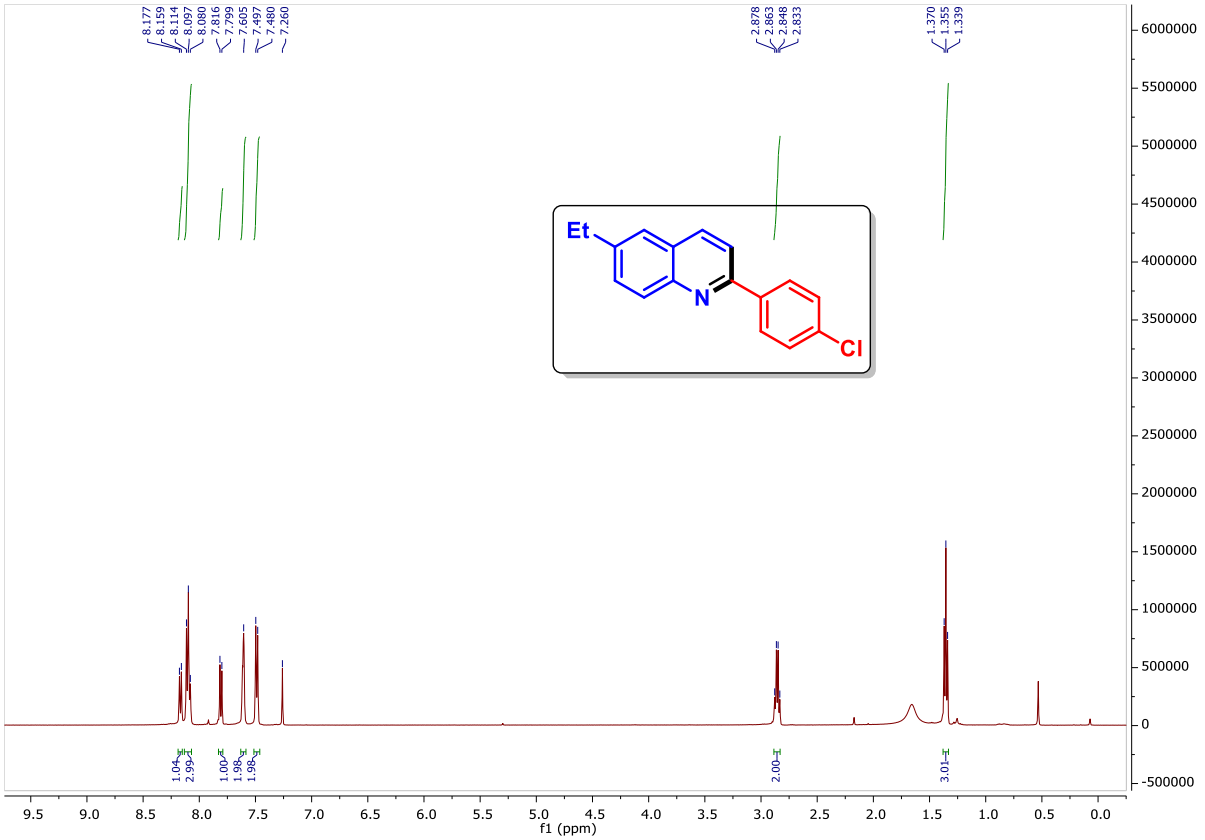
^{1}H spectrum of compound **3cb** (500 MHz, $CDCl_3$)



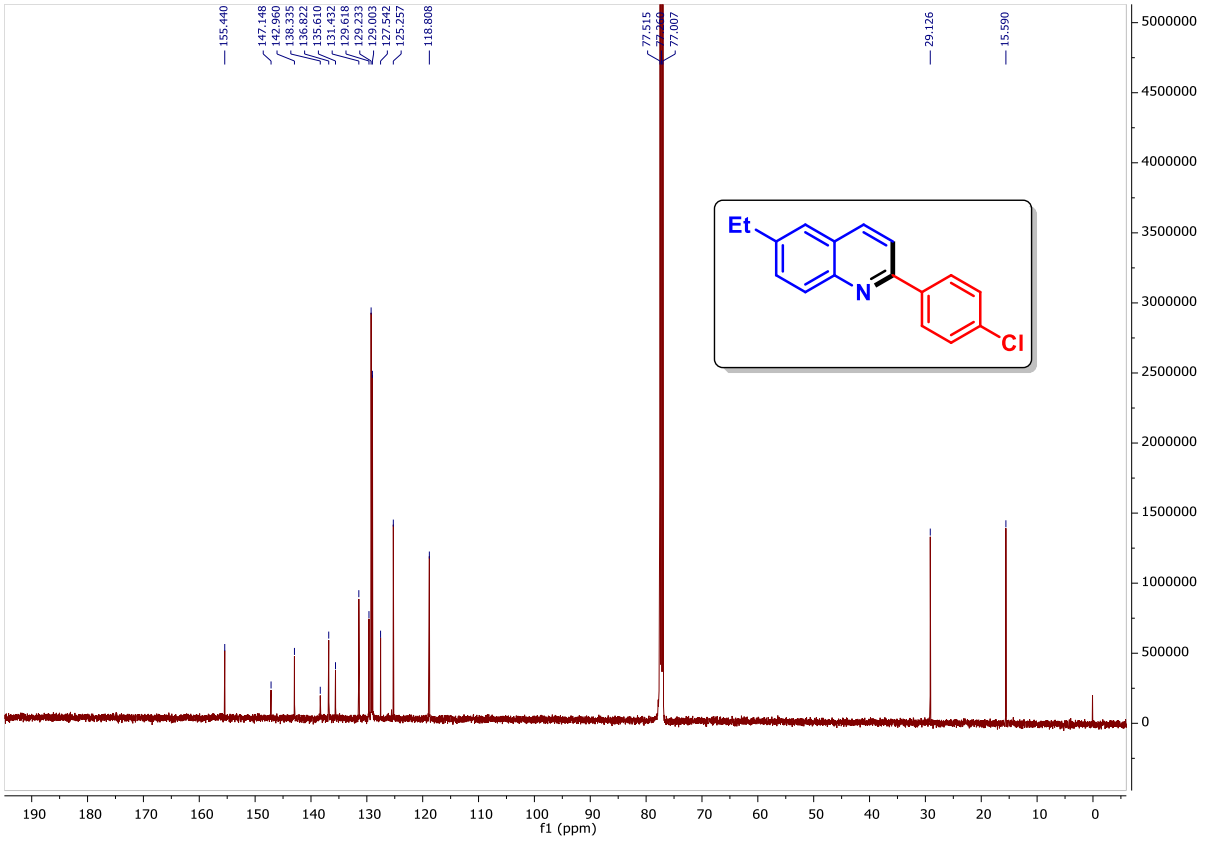
^{13}C{^{1}H} spectrum of compound **3cb** (125 MHz, $CDCl_3$)



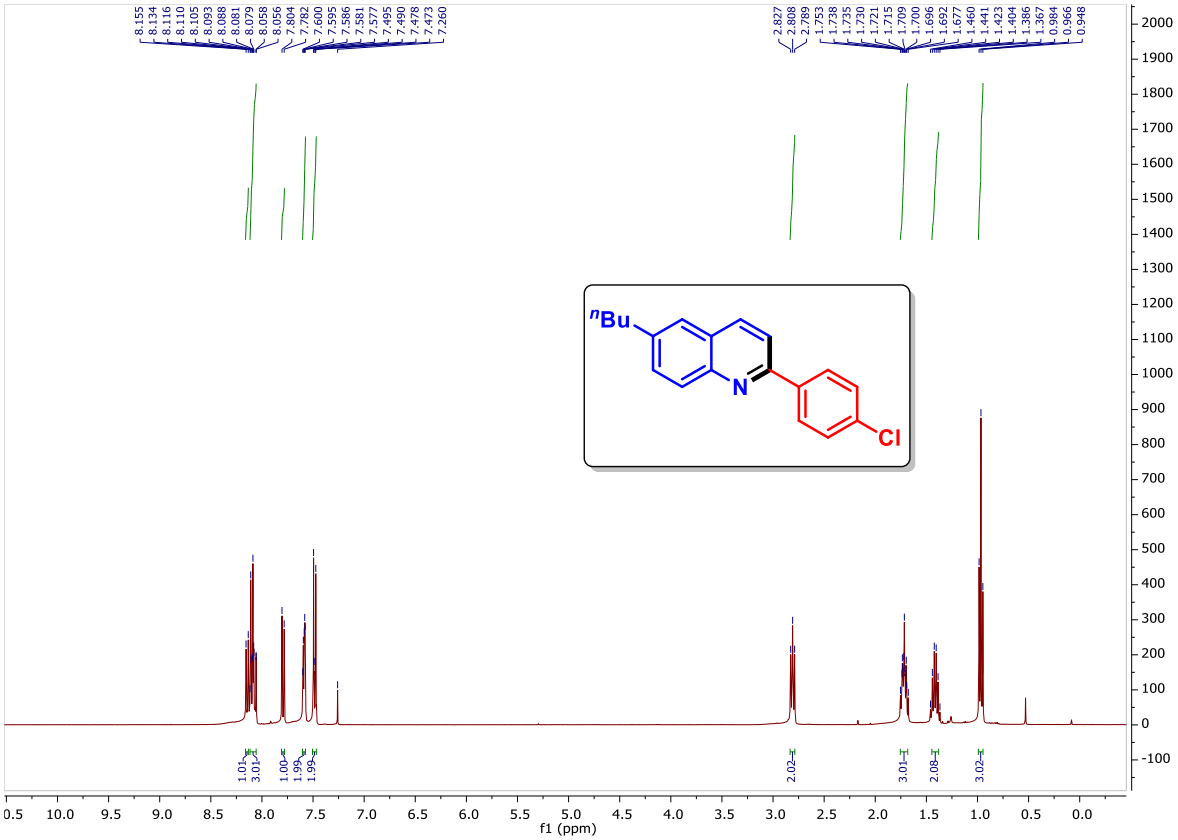
^{1}H spectrum of compound **3da** (500 MHz, $CDCl_3$)



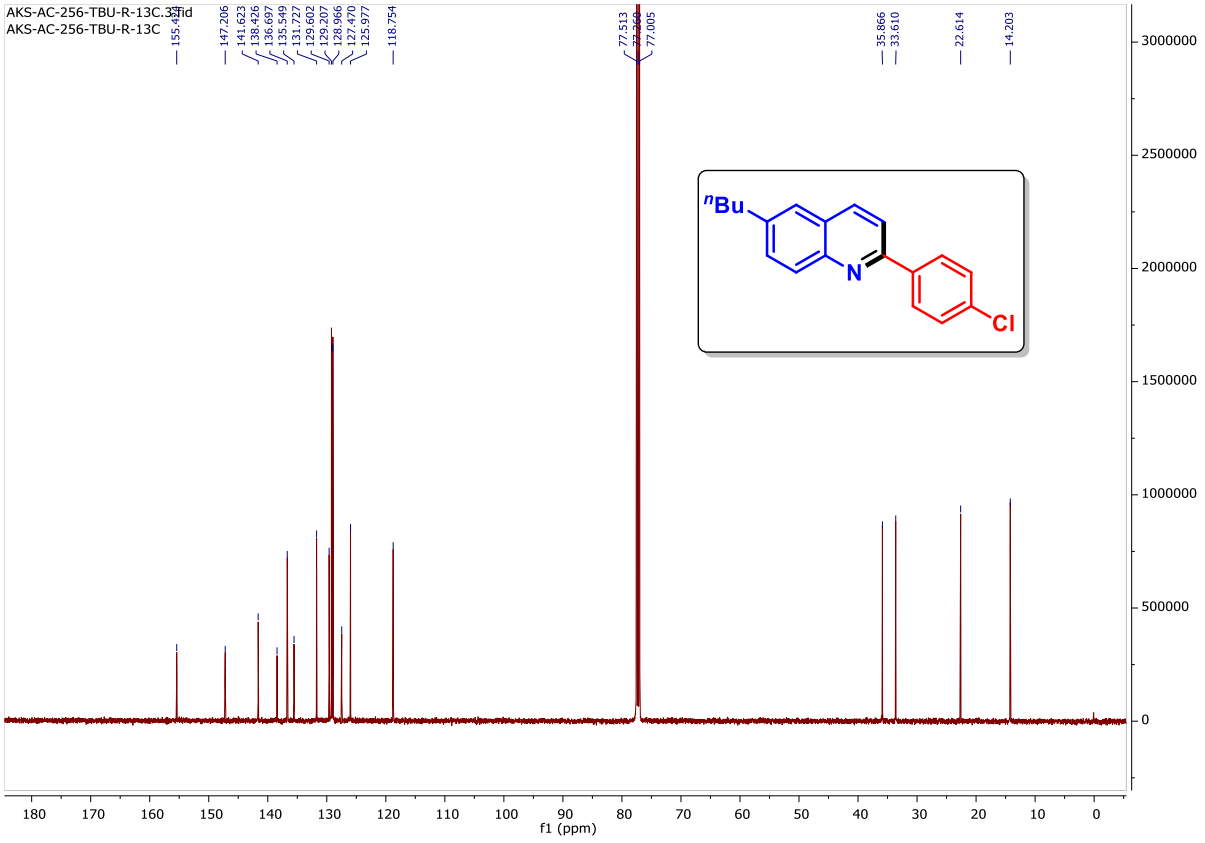
^{13}C{^{1}H} spectrum of compound **3da** (125 MHz, $CDCl_3$)



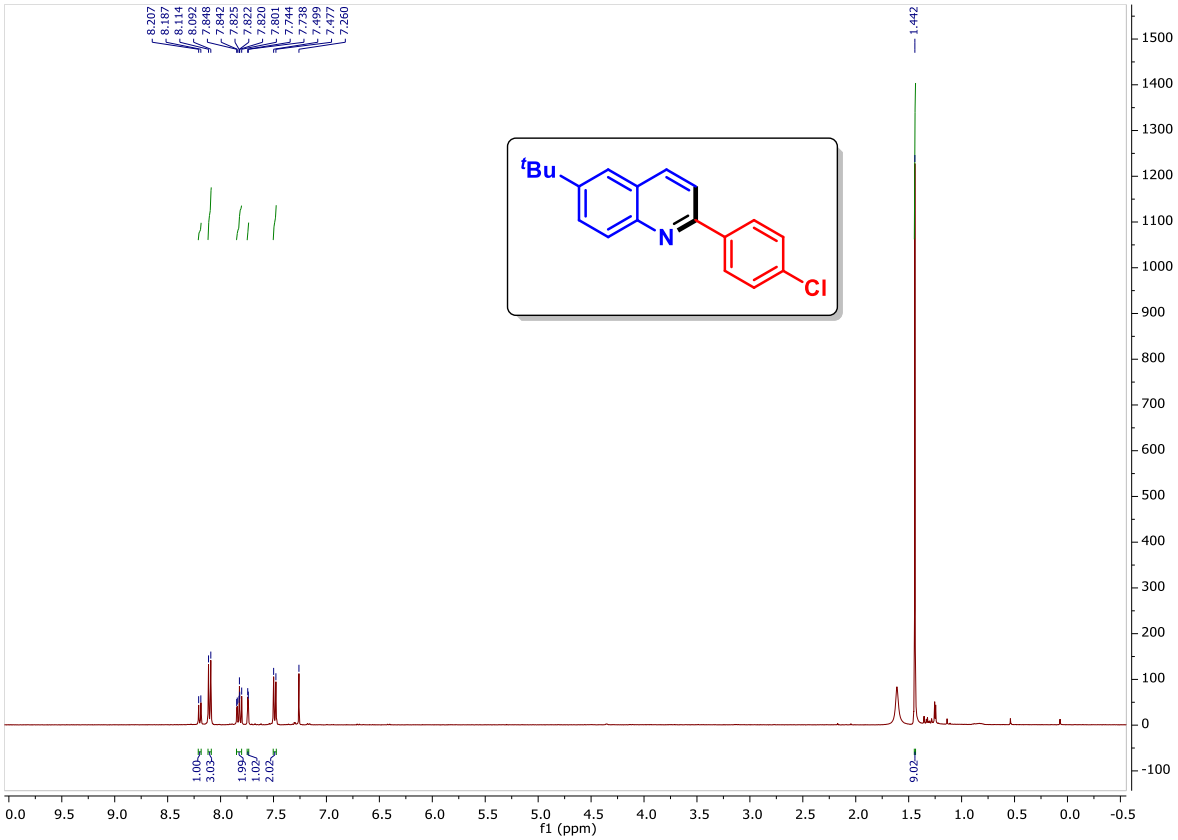
^{1}H spectrum of compound **3ea** (400 MHz, $CDCl_3$)



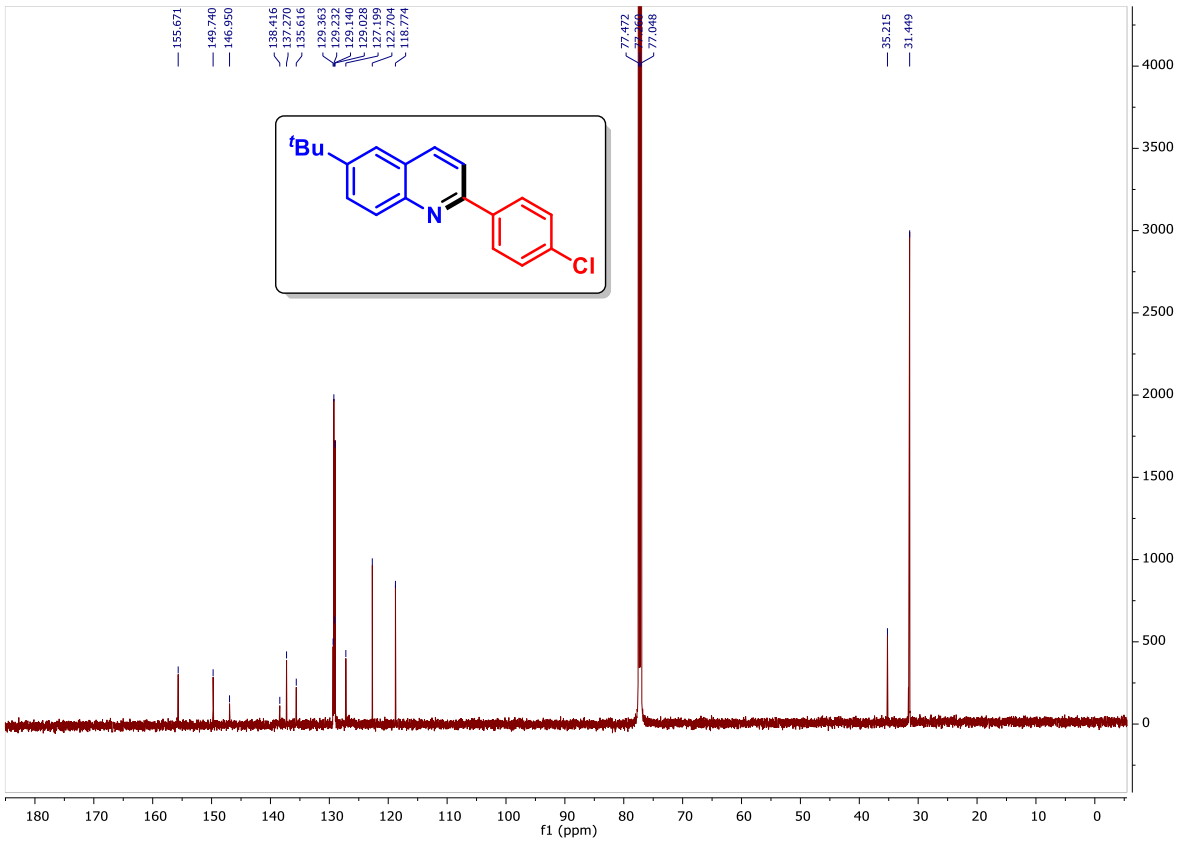
^{13}C{^{1}H} spectrum of compound **3ea** (125 MHz, $CDCl_3$)



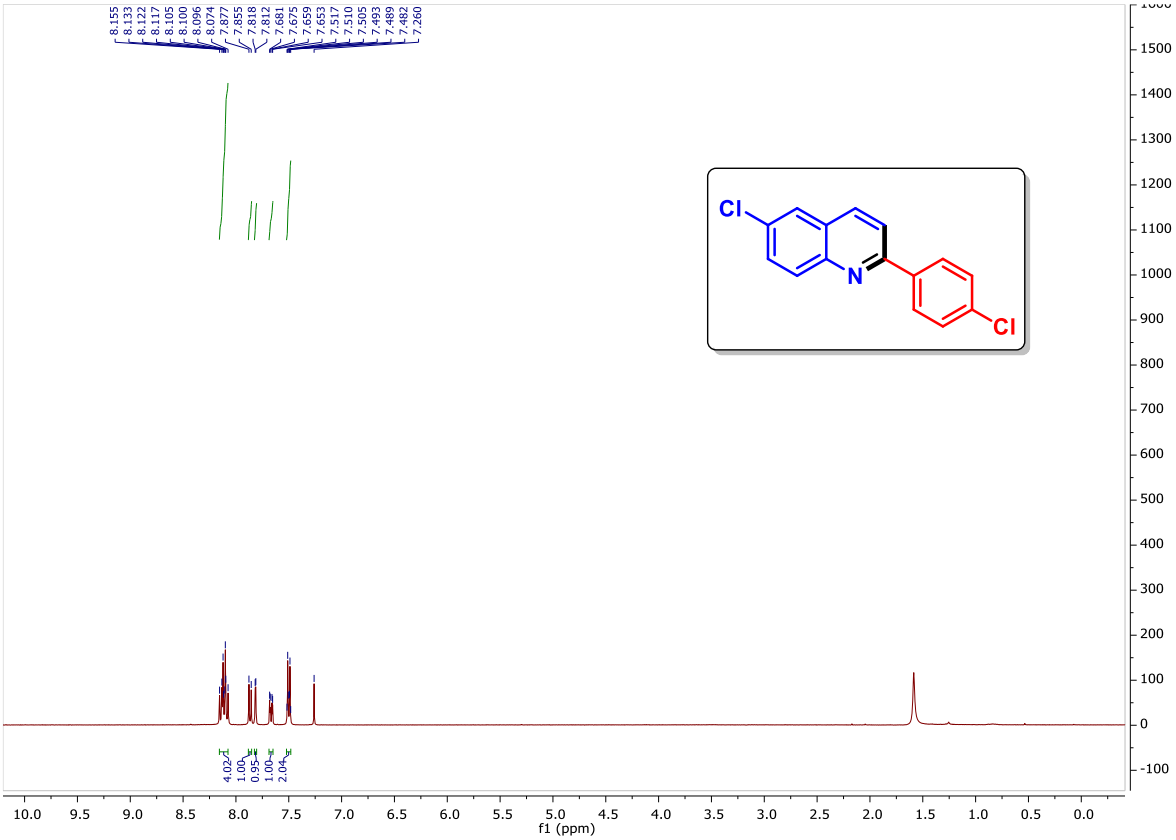
^{1}H spectrum of compound **3fa** (400 MHz, $CDCl_3$)



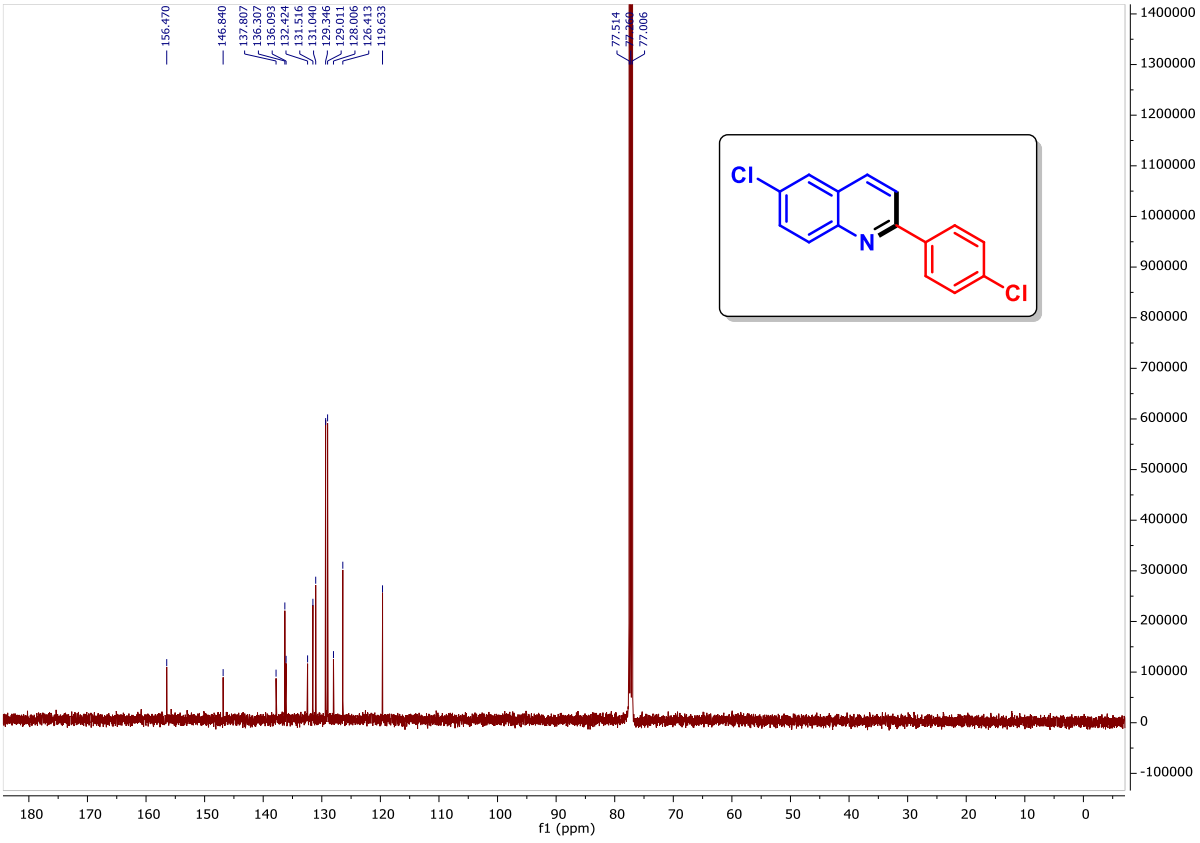
^{13}C{^{1}H} spectrum of compound **3fa** (150 MHz, $CDCl_3$)



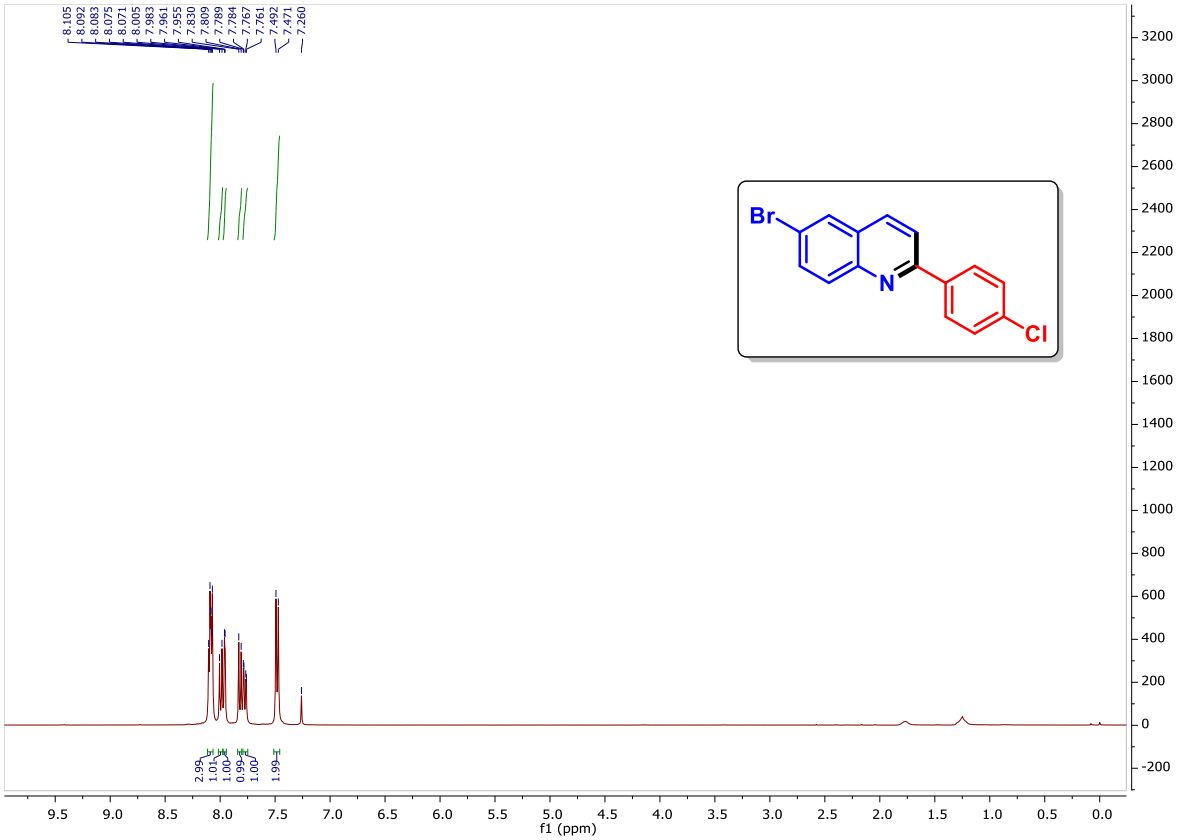
^{1}H spectrum of compound **3ga** (400 MHz, $CDCl_3$)



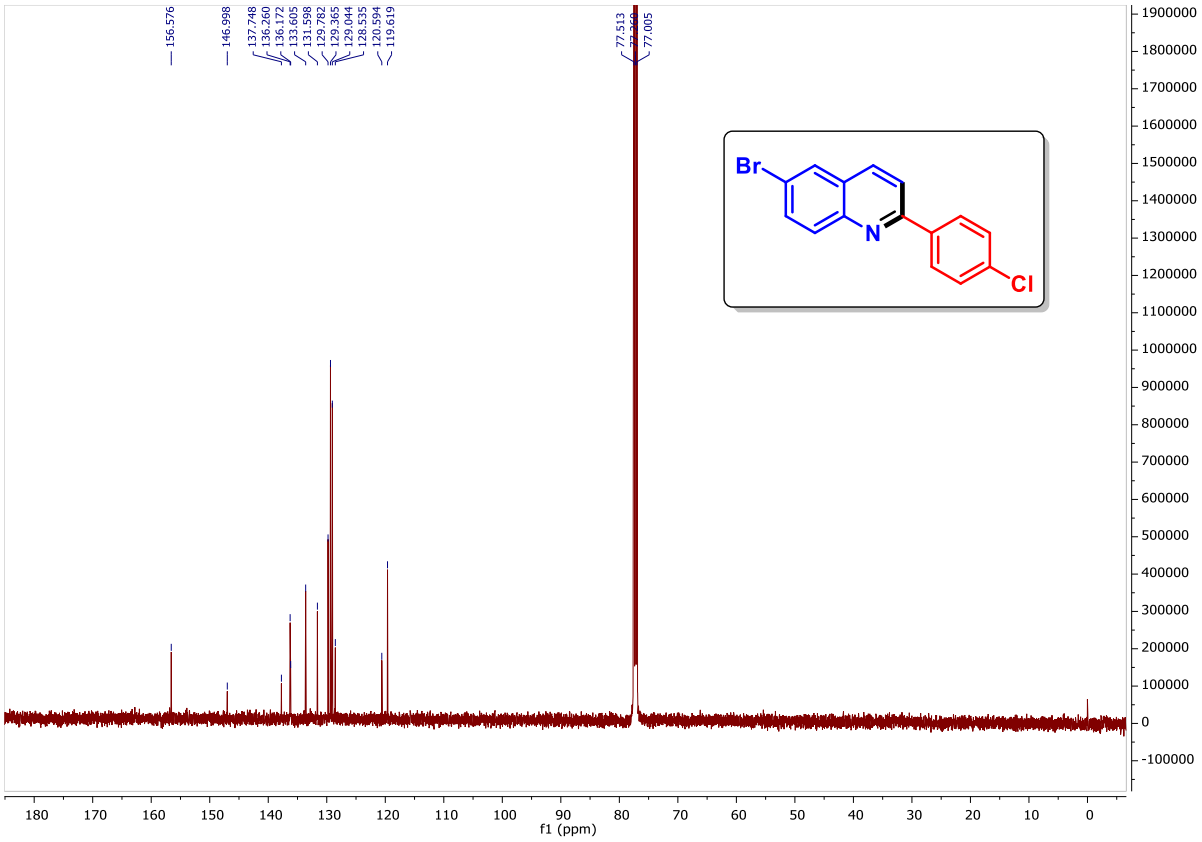
^{13}C{^{1}H} spectrum of compound **3ga** (125 MHz, $CDCl_3$)



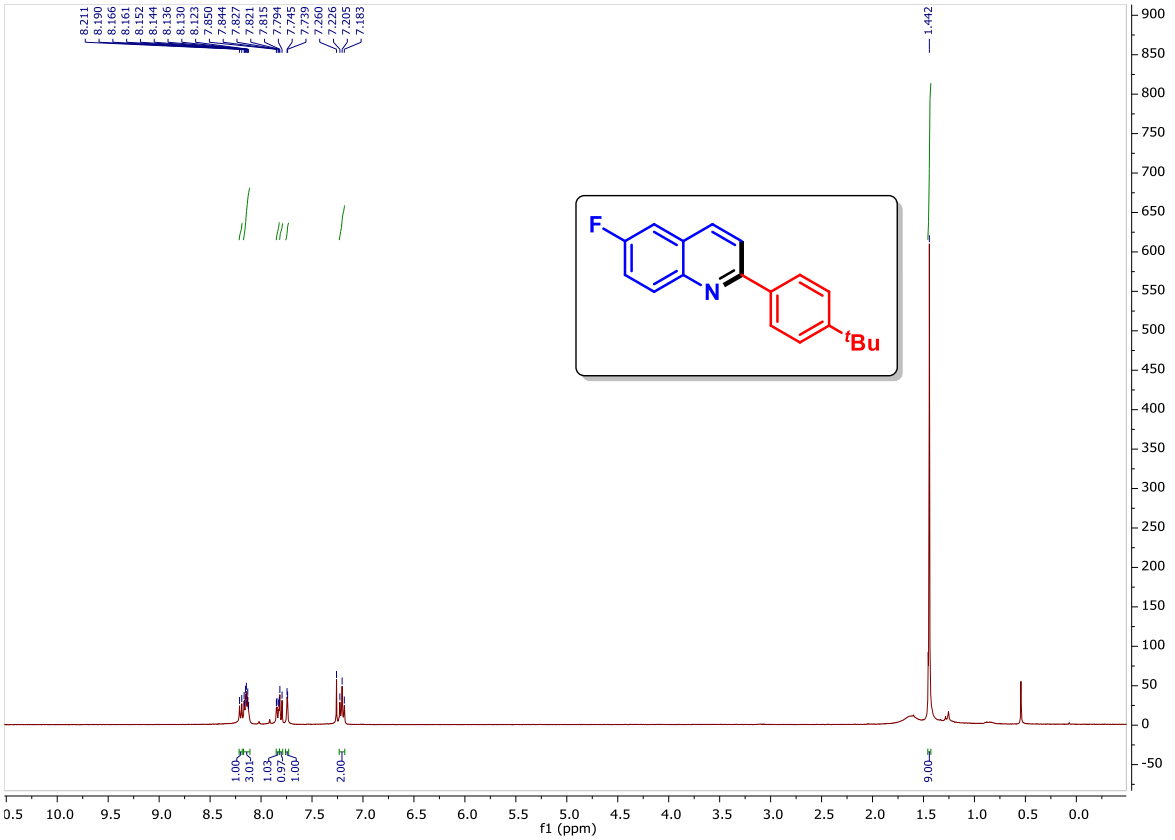
^{1}H spectrum of compound **3ha** (400 MHz, $CDCl_3$)



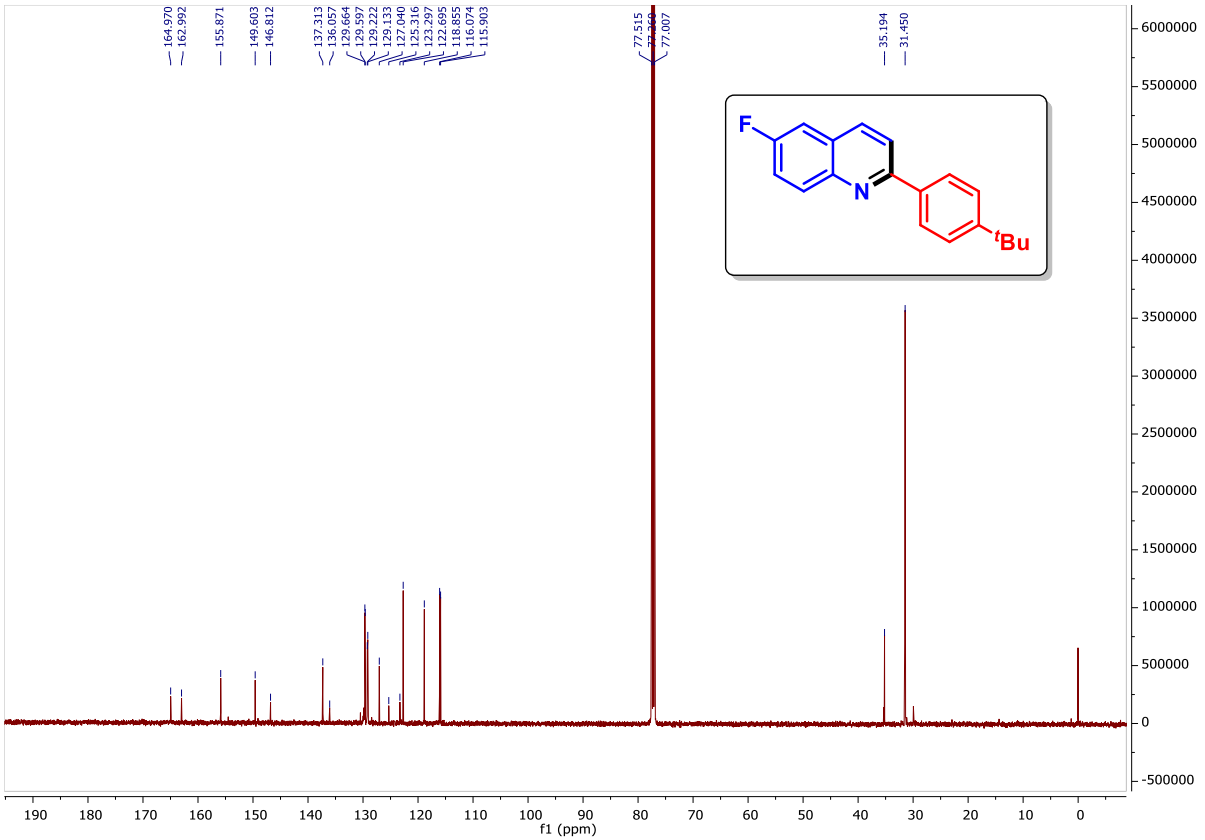
^{13}C{^{1}H} spectrum of compound **3ha** (125 MHz, $CDCl_3$)



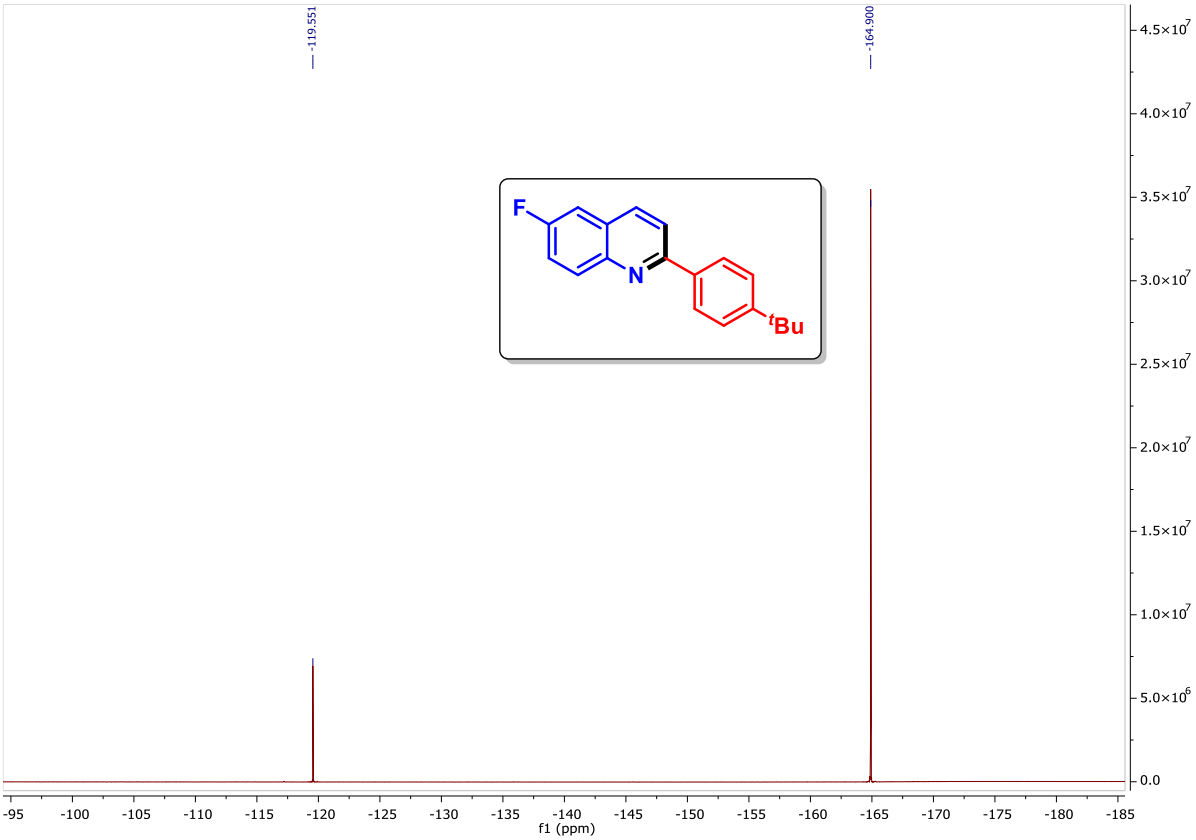
^{1}H spectrum of compound **3ik** (400 MHz, $CDCl_3$)



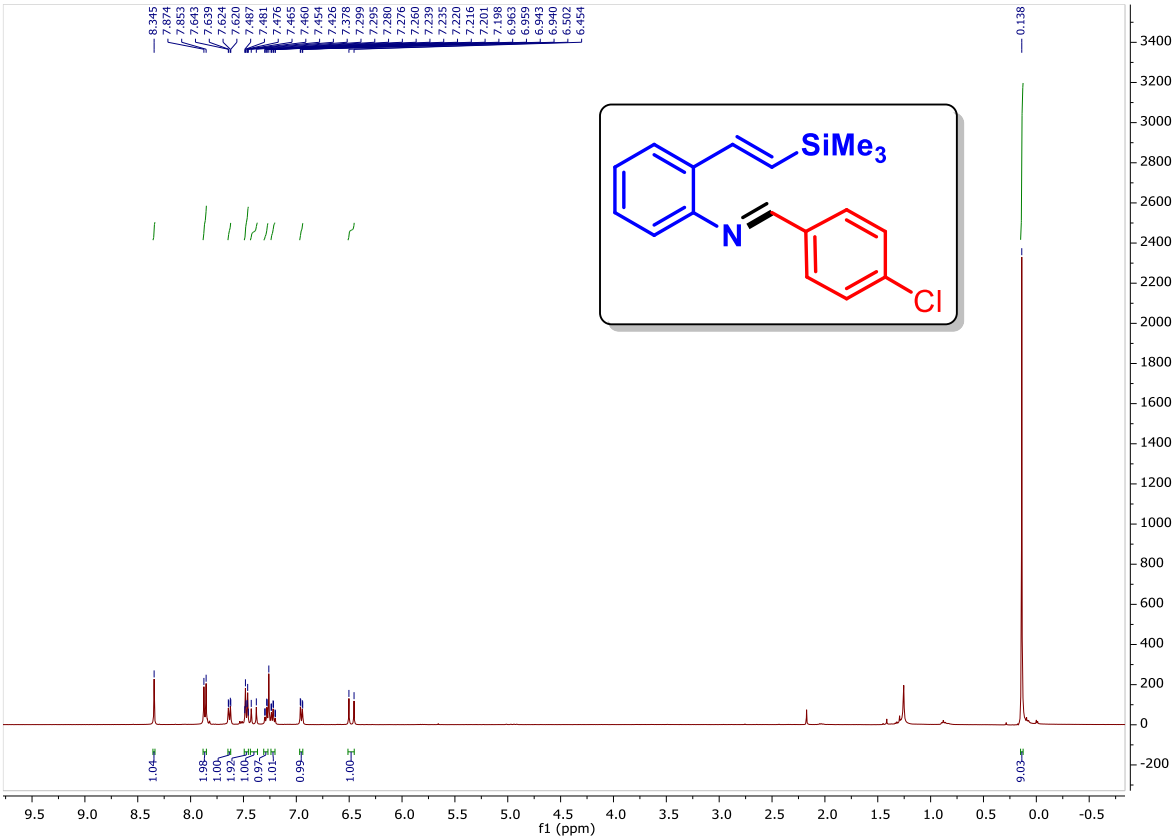
^{13}C{^{1}H} spectrum of compound **3ik** (125 MHz, $CDCl_3$)



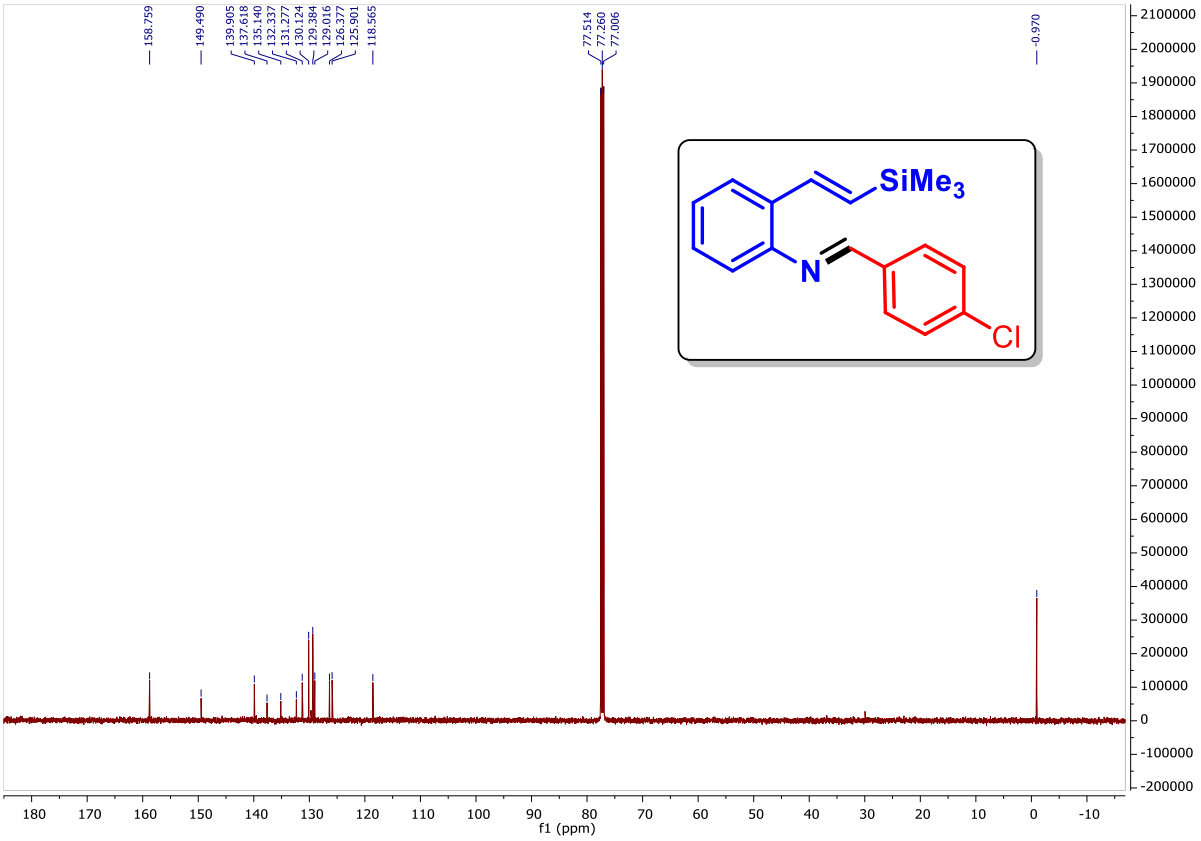
^{19}F spectrum of compound **3ik** (470 MHz, $CDCl_3$ /C_6F_6)



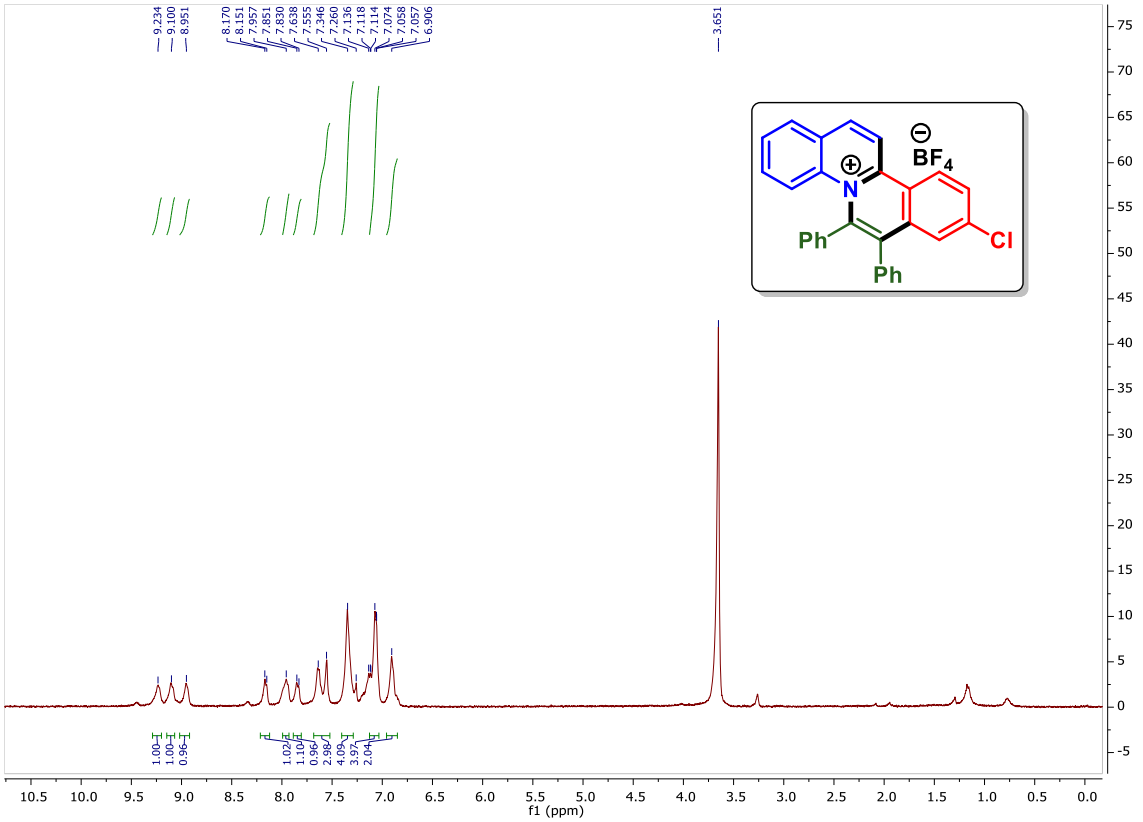
^{1}H spectrum of Intermediate **A** (400 MHz, $CDCl_3$)



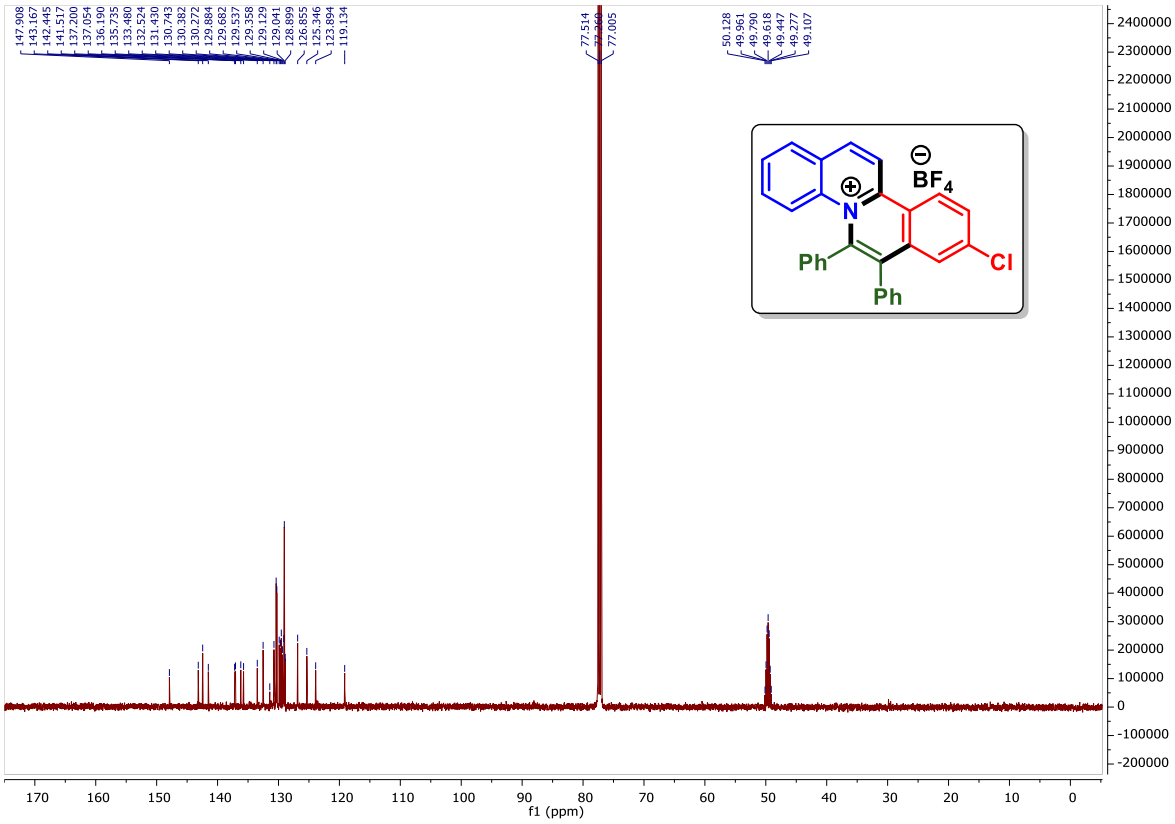
^{13}C{^{1}H} spectrum of Intermediate **A** (125 MHz, $CDCl_3$)



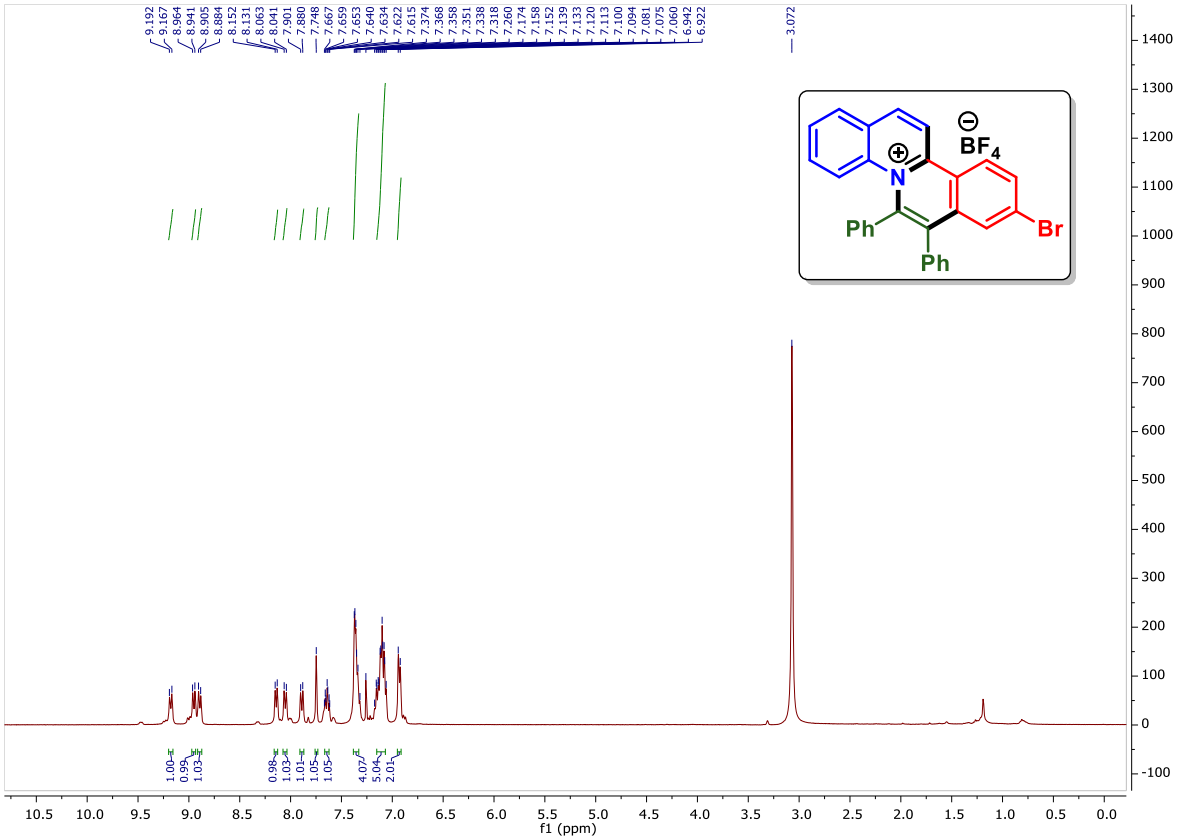
^{1}H spectrum of compound **5aa** (400 MHz, $CDCl_3$)/ MeOD-d_4)



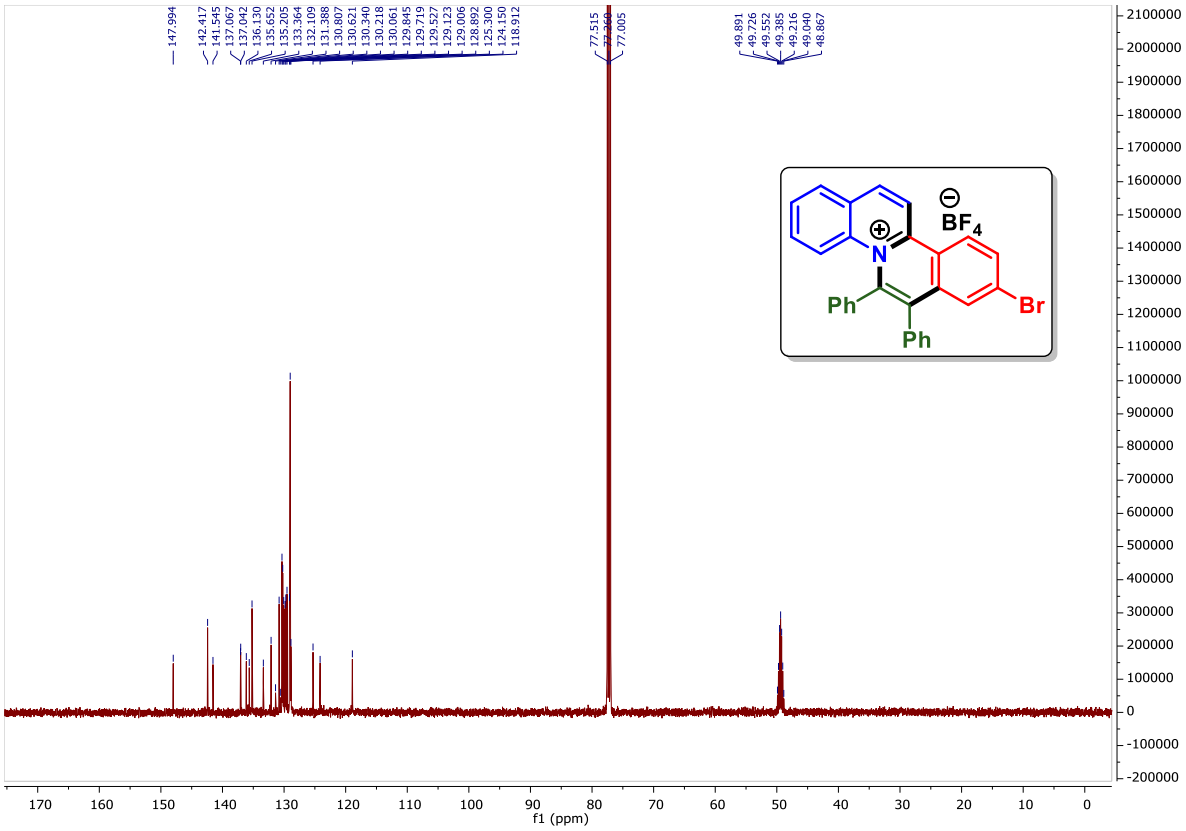
^{13}C{^{1}H} spectrum of compound **5aa** (125 MHz, $CDCl_3$/ MeOD-d_4)



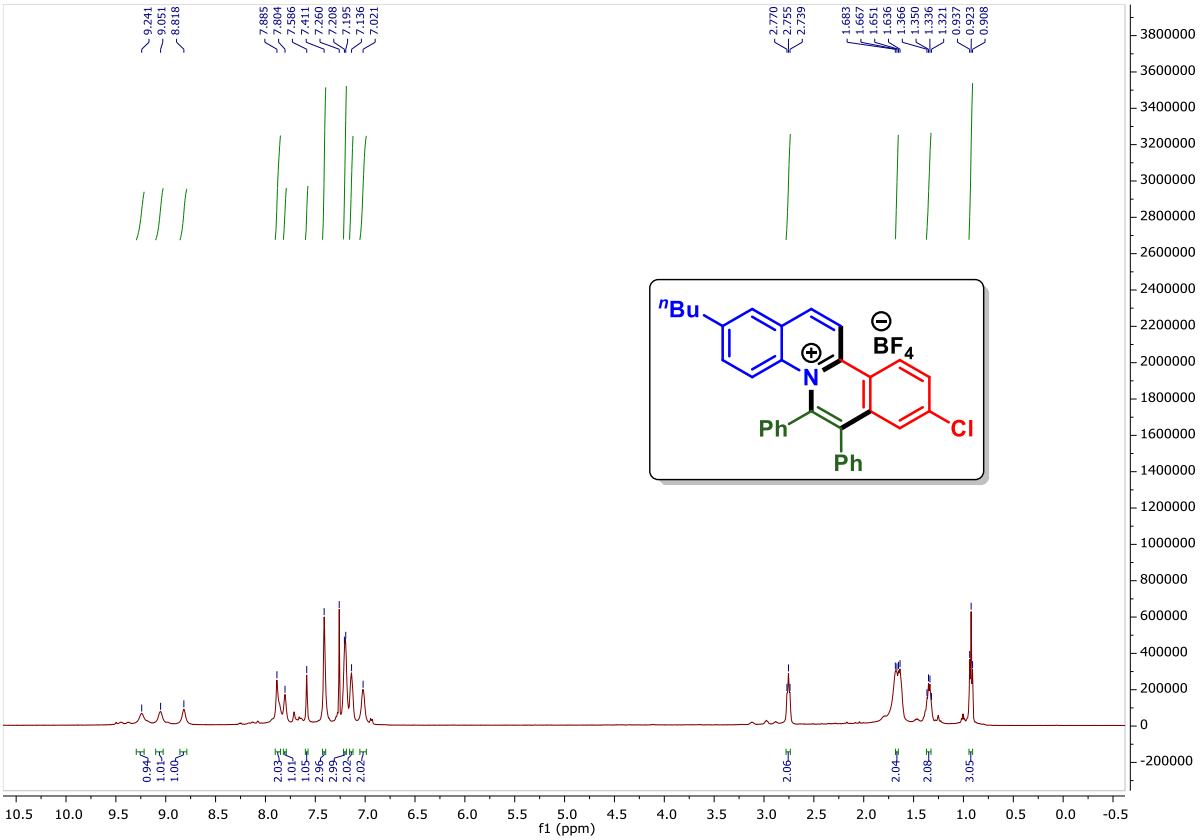
^{1}H spectrum of compound **5ab** (400 MHz, $CDCl_3$)/ MeOD-d_4)



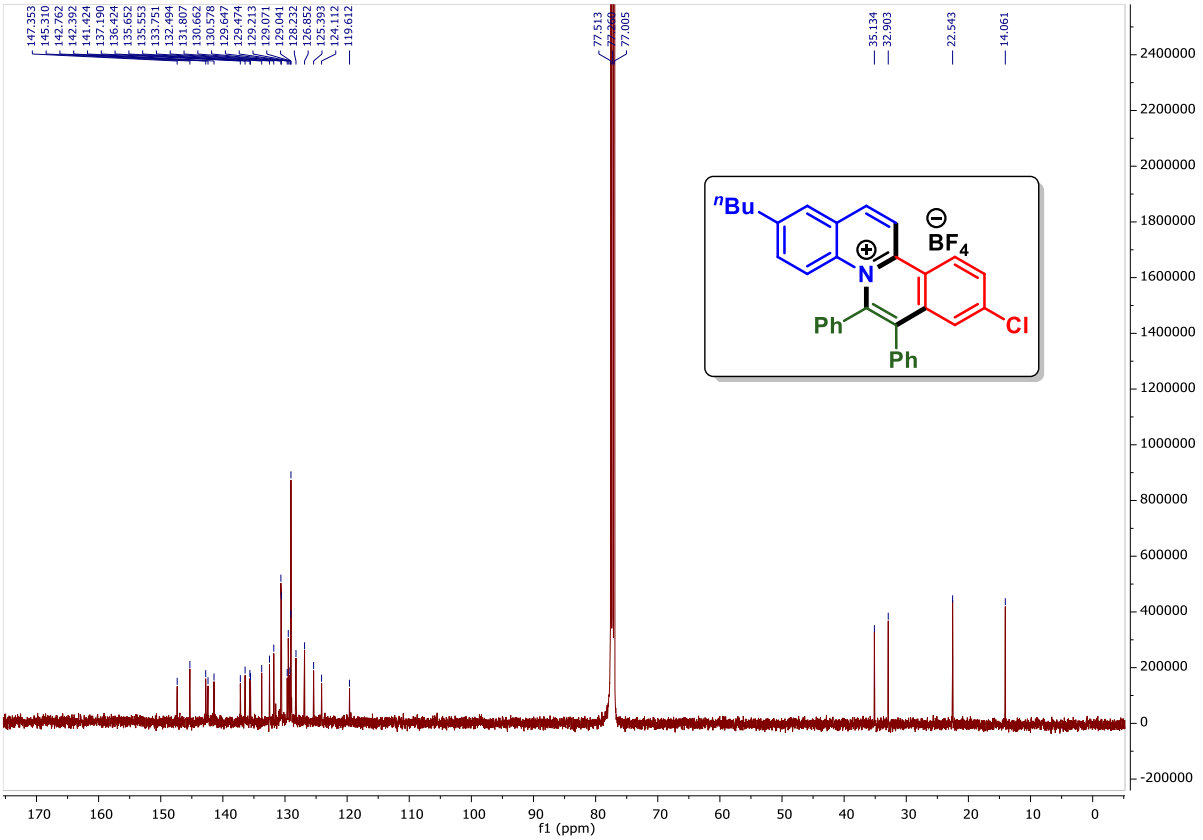
^{13}C{^{1}H} spectrum of compound **5ab** (125 MHz, $CDCl_3$/ MeOD-d_4)



^{1}H spectrum of compound **5ea** (500 MHz, $CDCl_3$)



^{13}C{^{1}H} spectrum of compound **5ea** (125 MHz, $CDCl_3$)



X-Ray Crystallographic Data and Structure of Compound 3ab:

Single crystal of compound **3ab** was obtained by slow evaporation of ethyl acetate and hexane solution (9:1). Bruker APEX-II CCD diffractometer was used to collect intensity data. The instrument is equipped with a fine focus 1.75 kW sealed tube Mo Kα radiation (λ = 0.71073 Å) at 295(2) K. The data acquisition was done with the APEX4 software. APEX4 software was implemented for data integration and reduction. Multi-scan empirical absorption corrections were employed to the data using the program APEX4. Structures were solved by direct methods using SHELXL-2019 and Olex2 1.5 software and refined with full-matrix least-squares on F2 using SHELXL-2019/1.[2] Structural illustrations have been drawn with ORTEP-3 for Windows.[3] The detailed data collection and structure refinement are summarized in Table S3. CCDC-2522737 contained supplementary crystallographic data for this paper.

References:

3. G. M. Sheldrick, SHELXS-2014, Program for the crystal structure solution; University of Göttingen: Göttingen, Germany, **2014**.

4. L. J. Farrugia, XRDIFF: simulation of X-ray diffraction patterns, *J. Appl. Crystallogr*., **1997**, *30*, 565.

Table S3. Crystal Parameters of Compound **3ab**

Entries	**CCDC 2522737**
Formula	$C_{15}H_{10}NBr$
Formula weight	284.15
T/K	295(2)
Crystal system	Monoclinic
Space group	P 1 21/c 1
a/Å	13.5714(14)
b/Å	14.8390(16)
c/Å	5.9416(7)
α/°	90.0
β/°	93.035(3)
γ/°	90.0
V/Å^3	1194.9(2)
Z	4
Abs. Coeff./mm^{-1}	3.414
Abs. Correction	none
GOF on F^2	1.799
Final *R* indices [$I > 2\sigma(I)$]	*R1* = 0.1784
	wR2 = 0.3256
R indices [all data]	*R1* = 0.1019
	wR2 = 0.2841

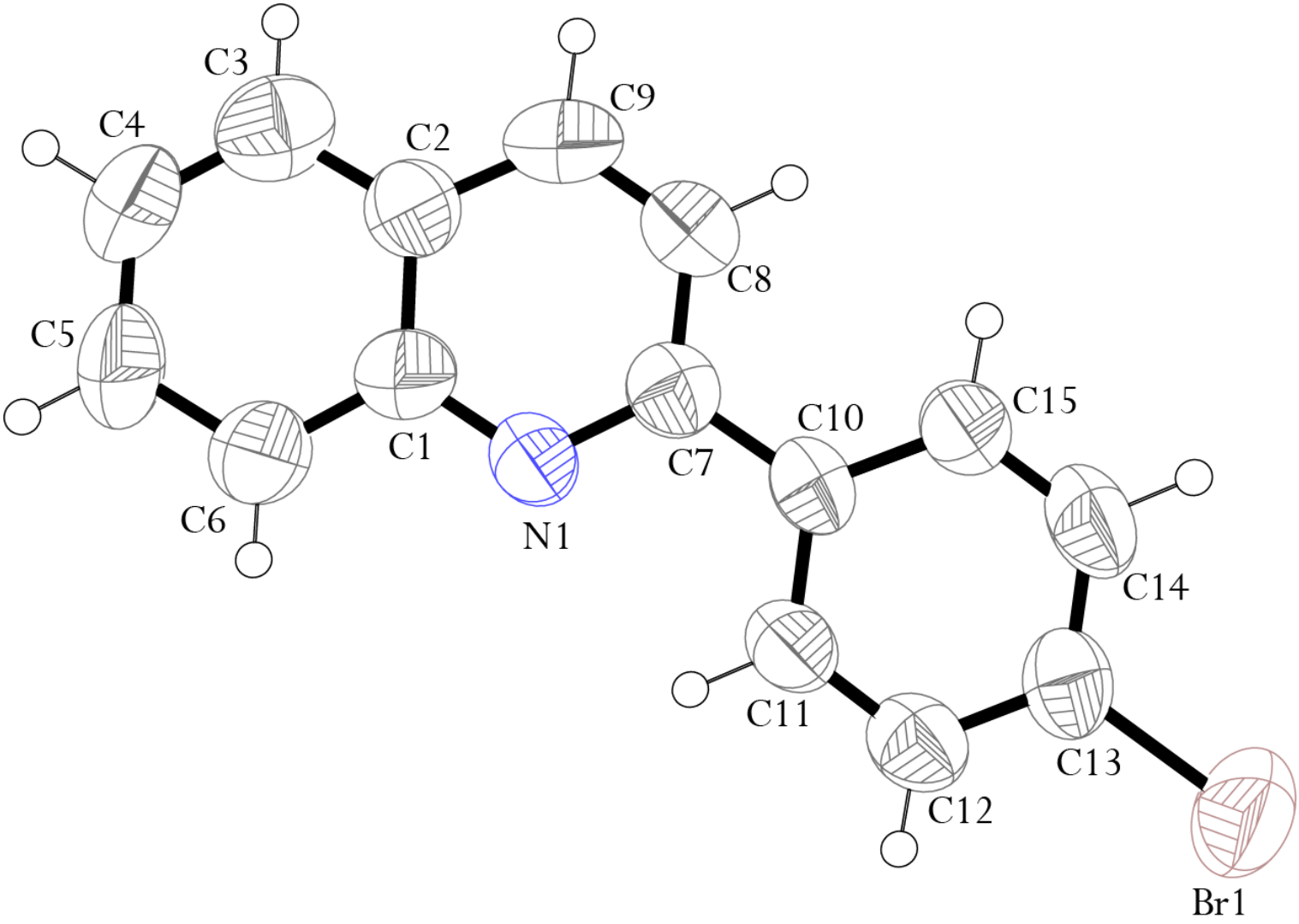


Figure S3: ORTEP diagram of compound **3ab** using thermal ellipsoids of 50% probability