Supporting Information

Blue-Light-Promoted Carbon-Carbon Double Bond Isomerization and Its Application in Syntheses of Quinolines

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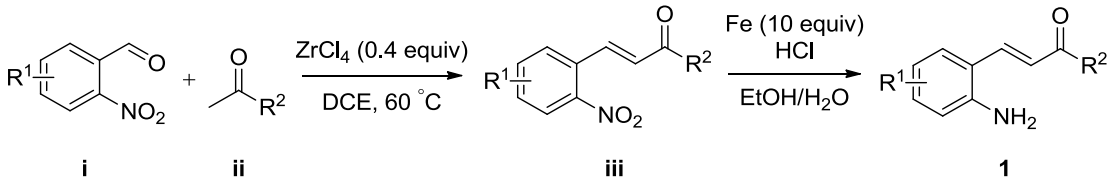
I. General Information

All reagents were purchased at the highest commercial quality and used as received unless otherwise noted. Anhydrous THF was distilled from sodium-benzophenone. Analytically pure ethanol was purchased and used as received, however no precautions were taken to exclude air or water from the solvent or reaction mixtures and reactions run with undried solvent proceed similarly. Thin-layer chromatography (TLC) was conducted with 0.25 mm Yantai silica gel plates (60F-254) and visualized by exposure to UV light (254 nm) or stained with $KMnO_4$. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Data for ^1H NMR spectra were reported as following: chemical shift (δ/ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.), coupling constant (*J*/Hz) and integration. Data for ^{13}C NMR and ^{19}F NMR spectra were reported in terms of the chemical shift. The UV-visible absorption spectra were recorded on Shimadzu UV-2600 UV-visible spectrophotometer. High-resolution mass spectrometry (HRMS) was conducted on Bruker Apex IV RTMS.

II. General procedure for preparation of *α, β*-unsaturated ketone substrates

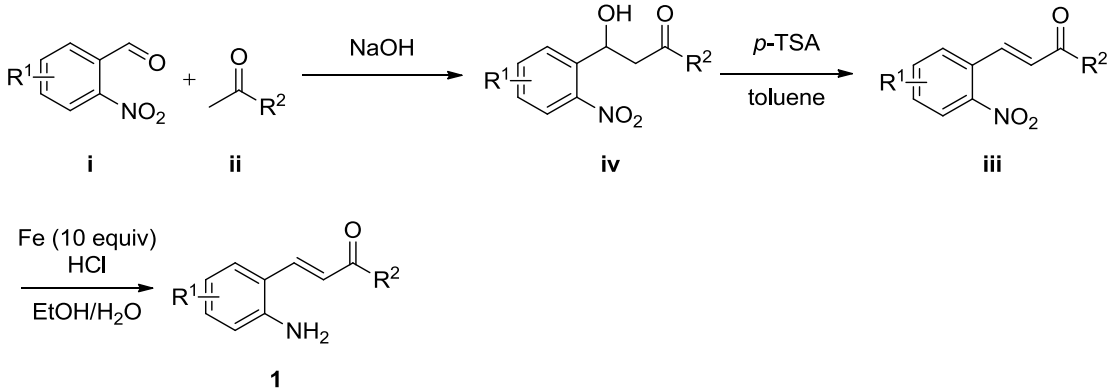
Method A:



i **ii** **iii** **1**

1) To a dry flask was added 2-nitrobenzaldehyde **i** (8.0 mmol) under argon. Then ketone **ii** (9.6 mmol), $ZrCl_4$ (3.2 mmol) and anyhydrous DCE (40 mL) were added. The mixture was maintained at 60°C until the complete disappearance of the substrates monitored by TLC. The reaction was quenched with H_2O. The mixture was extracted with DCM three times and the combined organic phases were washed with saturated brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford **iii**. (A modified method of Angela Patti, according to ref: Angela Patti *, Sonia Pedotti *Tetrahedron* **2010**, *66*, 5607-5611).
2) Iron powder (20.0 mmol, 10 equiv.) and concd. hydrochloric acid (ca. 10 mg) were added to a solution of **iii** (2.0 mmol) in EtOH (10 mL) and water (2.5 mL). The mixture was heated to reflux and monitored by TLC. After substrate **iii** was consumed, the mixture was cooled to room temperature and extracted with ethyl acetate three times. The combined organic phases were washed with saturated brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford **1**. (A modified method of Jens Christoffers, according to ref: Claas Lüder Diedrich, Wolfgang Frey and Jens Christoffers* *Eur. J. Org. Chem.* **2008**, 1811–1816).

Method B:



i **ii** **iv** **iii** **1**

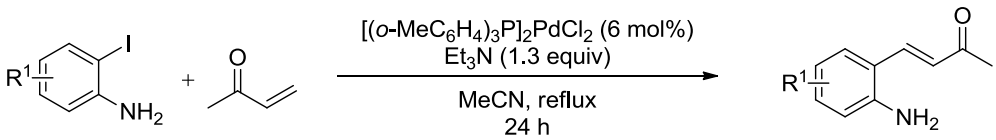
1) To a mixture of 2-nitrobenzaldehyde **i** (4.0 mmol), ketone **ii** (8.0 mmol) and H_2O (4.0 mL) was added 5% NaOH aqueous solution (0.4 mL). The reaction was maintained at 40℃ for 12 h before being cooled to room temperature and extracted

with ethyl acetate three times. The combined organic phases were washed with saturated brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford **iv**.

2) The aldol product **iv** (3.0 mmol) was dissolved in toluene, and a catalytic amount of *p*-toluenesulfonic acid (0.3 mmol) was added. The reaction was refluxed. After substrate **iv** was consumed, the mixture was cooled to room temperature. And the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to afford the *α, β*-unsaturated ketone products **iii**.

3) Iron powder (20.0 mmol, 10 equiv.) and concd. hydrochloric acid (ca. 10 mg) were added to a solution of **iii** (2.0 mmol) in EtOH (10 mL) and water (2.5 mL). The mixture was heated to reflux and monitored by TLC. After substrate **iii** was consumed, the mixture was cooled to room temperature and extracted with ethyl acetate three times. The combined organic phases were washed with saturated brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford **1**. (A modified method of Jens Christoffers, according to ref: Claas Lüder Diedrich, Wolfgang Frey and Jens Christoffers* *Eur. J. Org. Chem.* **2008**, 1811–1816).

Method C:



v **vi** **1**

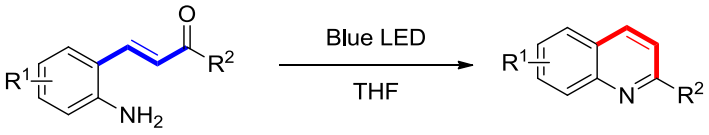
To a N_2-purged dry flask was added 2-iodoaniline **v** (1.0 mmol), dichlorobis(tri-*o*-tolylphosphine)palladium(II) (0.06 mmol), but-3-en-2-one **vi** (1.4 mmol), Et_3N (1.3 mmol) and MeCN (6.0 mL). The reaction was heated to reflux for 24 h. After 2-iodoaniline **v** was consumed, the mixture was cooled to room temperature and diluted with ethyl acetate. The organic layer was washed with water and brine. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford **1**. (A modified method of Naoto Chatani, according to ref: Mamoru Tobisu, Hirokazu Fujihara, Keika Koh and Naoto Chatani* *J. Org. Chem.* **2010**, *75*, 4841–4847).

Substrates **1b-1x** were prepared according to **Method A**.

Substrates **1a**, **1y-1ad, 1ak-1am** were prepared according to **Method B**.

Substrates **1ae-1aj** were prepared according to **Method C**.

III. General procedure for synthesis of quinolines



1 **2**

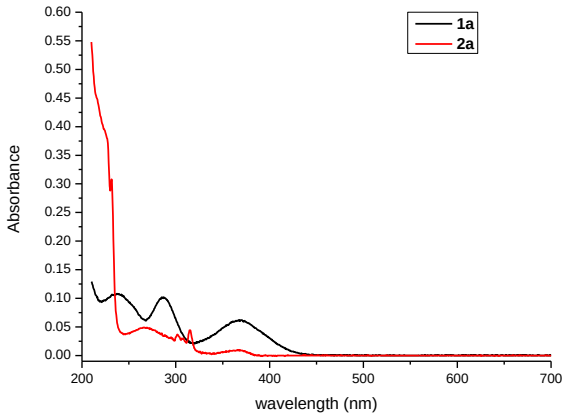
Fig. 1

Typical procedure: Substrate **1** (0.1 mmol) and anhydrous THF (1.0 mL) were added to a 5 mL flask. The solution was stirred under irradiation of blue LEDs (5 W LED light band was used, see **Fig. 1**). The reaction was monitored by TLC. After the consumption of starting materials, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford quinoline product **2**. (*Please Note: Low power blue LED light band (only 5 W) was used in the experiment. Exothermic effect was not obvious. The reactions were conducted at room temperature while the inside temperature was 1.5 ℃ higher than room temperature.*)

1a **2a**

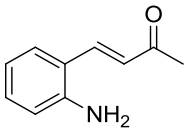
For gram-scale experiment: Substrate **1a** (1.79 g, 11.1 mmol) and anhydrous THF (50 mL) were added to a 100 mL flask. The solution was stirred under irradiation of blue LEDs (5 W LED light band was used, see **Fig. 1**). The reaction was monitored by TLC. After 5 days, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 10 : 1) to afford quinoline product **2a** (1.49 g, 10.4 mmol, 93%).

IV. UV-visible absorption spectra of 1a and 2a



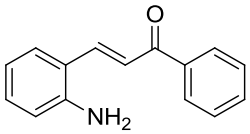
The UV-visible absorption spectra were recorded in MeCN in 1 cm path quartz cuvettes using a Shimadzu UV-2600 UV-visible spectrophotometer. The substrate concentrations are 10 μM in MeCN.

V. ^{1}H NMR and ^{13}C NMR spectra data of the substrates



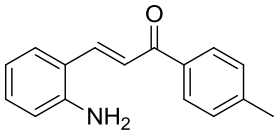
1a

(*E*)-4-(2-aminophenyl)but-3-en-2-one (**1a**): Following method B, compound **1a** was obtained in 42% yield (three steps, 1.79 g, yellow oil). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 2.37 (3.0H, s), 3.99 (2.0H, br), 6.67 (1.0H, d, *J*=15.95 Hz), 6.71 (1.0H, dd, *J*=0.85, 8.10 Hz), 6.78 (1.0H, t, *J*=7.58 Hz), 7.18 (1.0H, dd, *J*=1.48, 15.33 Hz), 7.39 (1.0H, dd, *J*=1.30, 7.80 Hz), 7.68 (1.0H, d, *J*=15.95 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 28.0, 116.9, 119.1, 119.9, 126.8, 128.2, 131.5, 138.6, 145.8, 198.1; HRMS calculated for $C_{10}H_{12}NO$ ($[M + H]^+$): 162.0919, found: 162.0914.



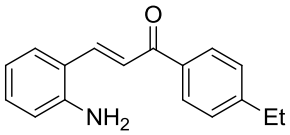
1b

(*E*)-3-(2-aminophenyl)-1-phenylprop-2-en-1-one (**1b**): Following method A, compound **1b** was obtained in 58% yield (two steps, 0.263 g, yellow solid, mp. 113–116 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.06 (2.0H, br), 6.73 (1.0H, d, *J*=8.04 Hz), 6.80 (1.0H, t, *J*=7.52 Hz), 7.21 (1.0H, m), 7.47-7.61 (5.0H, m), 7.97-8.04 (3.0H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 116.8, 118.9, 120.3, 121.8, 128.1, 128.4, 128.6, 131.7, 132.7, 138.3, 140.1, 146.2, 190.3; HRMS calculated for $C_{15}H_{14}NO$ ($[M + H]^+$): 224.1075, found: 224.1070.



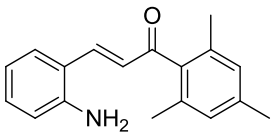
1c

(*E*)-3-(2-aminophenyl)-1-(p-tolyl)prop-2-en-1-one (**1c**): Following method A, compound **1c** was obtained in 76% yield (two steps, 0.294 g, yellow solid, mp. 125–128 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.44 (3.0H, s), 4.07 (2.0H, br), 6.73 (1.0H, d, *J*=8.08 Hz), 6.80 (1.0H, t, *J*=7.50 Hz), 7.17-7.22 (1.0H, m), 7.30 (2.0H, d, *J*=8.04 Hz), 7.47-7.54 (2.0H, m), 7.93-8.00 (3.0H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 21.6, 116.7, 118.9, 120.4, 121.9, 128.1, 128.6, 129.3, 131.5, 135.7, 139.6, 143. 6, 146.1, 189.8; HRMS calculated for $C_{16}H_{16}NO$ ($[M + H]^+$): 238.1232, found: 238.1228.



1d

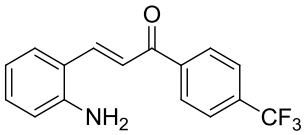
(*E*)-3-(2-aminophenyl)-1-(4-ethylphenyl)prop-2-en-1-one (**1d**): Following method A, compound **1d** was obtained in 47% yield (two steps, 0.215 g, yellow solid, mp. 91–94 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.28 (3.0H, t, *J*=7.60 Hz), 2.73 (2.0H, q, *J*=7.60 Hz), 4.07 (2.0H, br), 6.73 (1.0H, d, *J*=8.04 Hz), 6.80 (1.0H, t, *J*=7.52 Hz), 7.20 (1.0H, m), 7.33 (2.0H, d, *J*=8.12 Hz), 7.47-7.54 (2.0H, m), 7.96-8.00 (3.0H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 15.2, 28.9, 116.7, 118.9, 120.4, 121.9, 128.1, 128.1, 128.7, 131.5, 135.9, 139.6, 146.1, 149.7, 189.8; HRMS calculated for $C_{17}H_{17}NNaO$ ($[M + Na]^+$): 274.1208, found: 274.1202.



1e

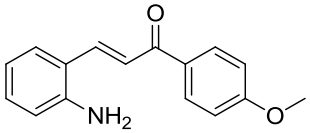
(*E*)-3-(2-aminophenyl)-1-mesitylprop-2-en-1-one (**1e**): Following method A, compound **1e** was obtained in 76% yield (two steps, 0.283 g, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.21 (6.0H, s), 2.32 (3.0H, s), 3.88 (2.0H, br), 6.68 (1.0H, d, *J*=8.08 Hz), 6.77 (1.0H, m), 6.87 (3.0H, m), 7.18 (1.0H, m), 7.41 (2.0H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 19.4,

21.1, 116.8, 119.0, 119.6, 128.0, 128.4, 131.9, 134.0, 137.4, 138.3, 141.7, 145.9, 201.0; HRMS calculated for $C_{18}H_{19}NNaO$ ([M + Na]$^+$): 288.1364, found: 288.1361.



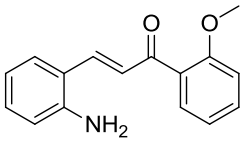
1f

(*E*)-3-(2-aminophenyl)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**1f**): Following method A, compound **1f** was obtained in 42% yield (two steps, 0.189 g, yellow solid, mp. 122–124 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =4.09 (2.0H, br), 6.74 (1.0H, dd, *J*=0.80, 8.12 Hz), 6.81 (1.0H, t, *J*=7.52 Hz), 7.23 (1.0H, t, *J*=8.38 Hz), 7.45 (1.0H, d, *J*=15.36 Hz), 7.54 (1.0H, dd, *J*=1.22, 7.86 Hz), 7.76 (2.0H, d, *J*=8.16 Hz), 8.03 (1.0H, d, *J*=15.41 Hz), 8.11 (2.0H, d, *J*=8.08 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 116.9, 119.0, 119.9, 121.0, 125.6 (q, ^3J(C,F) = 3.6 Hz), 128.2, 128.7, 132.1, 133.8, 134.0, 141.2, 141.3, 146.5, 189.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -63.0; HRMS calculated for $C_{16}H_{13}F_3NO$ ([M + H]$^+$): 292.0949, found: 292.0942.



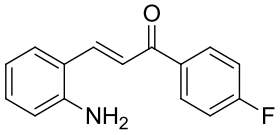
1g

(*E*)-3-(2-aminophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (**1g**): Following method A, compound **1g** was obtained in 72% yield (two steps, 0.258 g, yellow solid, mp. 122–125 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.88 (3.0H, s), 4.10 (2.0H, br), 6.72 (1.0H, d, *J*=8.04 Hz), 6.79 (1.0H, t, *J*=7.50 Hz), 6.97 (2.0H, d, *J*=8.80 Hz), 7.19 (1.0H, m), 7.50 (2.0H, m), 7.97 (1.0H, d, *J*=15.32 Hz), 8.04 (2.0H, d, *J*=8.76 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 55.4, 113.8, 116.7, 118.8, 120.4, 121.6, 128.0, 130.7, 131.1, 131.4, 139.2, 146.1, 163.3, 188.5; HRMS calculated for $C_{16}H_{16}NO_2$ ([M + H]$^+$): 254.1181, found: 254.1178.



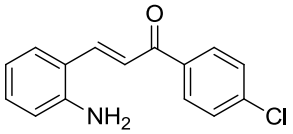
1h

(*E*)-3-(2-aminophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one (**1h**): Following method A, compound **1h** was obtained in 67% yield (two steps, 0.325 g, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =3.90 (3.0H, s), 4.05 (2.0H, br), 6.70 (1.0H, dd, *J*=0.84, 8.08 Hz), 6.77 (1.0H, t, *J*=7.50 Hz), 6.99 (1.0H, d, *J*=8.32 Hz), 7.04 (1.0H, m), 7.17 (1.0H, m), 7.33 (1.0H, d, *J*=15.69 Hz), 7.47 (2.0H, m), 7.65 (1.0H, dd, *J*=1.8, 7.53 Hz), 7.82 (1.0H, d, *J*=15.69 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 55.7, 111.6, 116.6, 118.7, 120.4, 120.7, 126.9, 128.3, 129.4, 130.4, 131.2, 132.9, 138.4, 146.1, 158.1, 192.5; HRMS calculated for $C_{16}H_{15}NNaO_2$ ([M + Na]$^+$): 276.1000, found: 276.0997.



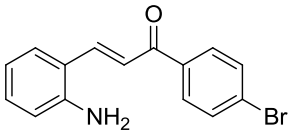
1i

(*E*)-3-(2-aminophenyl)-1-(4-fluorophenyl)prop-2-en-1-one (**1i**): Following method A, compound **1i** was obtained in 49% yield (two steps, 0.218 g, yellow solid, mp. 135–137 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =4.08 (2.0H, br), 6.73 (1.0H, d, *J*=8.08 Hz), 6.80 (1.0H, t, *J*=7.52 Hz), 7.14-7.22 (3.0H, m), 7.45 (1.0H, d, *J*=15.32 Hz), 7.52 (1.0H, dd, *J*=1.08, 7.84 Hz), 8.00 (1.0H, d, *J*=15.36 Hz), 8.06 (2.0H, dd, *J*=5.44, 8.84 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 115.7 (d, ^{2}J(C,F) = 21.7 Hz), 116.8, 118.9, 120.1, 121.2, 128.1, 131.0 (d, ^{3}J(C,F) = 9.2 Hz), 131.8, 134.6 (d, ^{4}J(C,F) = 3.0 Hz), 140.3, 146.3, 165.5 (d, ^{1}J(C,F) = 252.7 Hz), 188.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -105.7; HRMS calculated for $C_{15}H_{13}FNO$ ($[M + H]^+$): 242.0981, found: 242.0978.



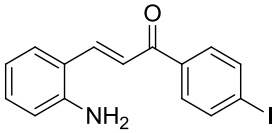
1j

(*E*)-3-(2-aminophenyl)-1-(4-chlorophenyl)prop-2-en-1-one (**1j**): Following method A, compound **1j** was obtained in 43% yield (two steps,0.171 g, yellow solid, mp. 120–123 ℃). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) =4.09 (2.0H, br), 6.73 (1.0H, d, *J*=7.95 Hz), 6.80 (1.0H, t, *J*=7.50 Hz), 7.21 (1.0H, t, *J*=8.28 Hz), -7.43 (1.0H, d, *J*=15.35 Hz), 7.47 (2.0H, d, *J*=8.55 Hz), 7.52 (1.0H, dd, *J*=0.85, 7.63 Hz), 7.96 (2.0H, d, *J*=8.50 Hz), 8.00 (1.0H, d, *J*=15.35 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 116.9, 118.9, 120.1 , 121.1, 128.1, 128.9, 129.8, 131.9, 136.6, 139.1, 140.6, 146.3, 188.9; HRMS calculated for $C_{15}H_{13}ClNO$ ($[M + H]^+$): 258.0686, found: 258.0675.



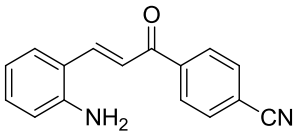
1k

(*E*)-3-(2-aminophenyl)-1-(4-bromophenyl)prop-2-en-1-one (**1k**): Following method A, compound **1k** was obtained in 48% yield (two steps, 0.204 g, orange solid, mp. 127–129 ℃). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.07 (2.0H, br), 6.73 (1.0H, d, *J*=8.10 Hz), 6.80 (1.0H, t, *J*=7.52 Hz), 7.22 (1.0H, m), 7.43 (1.0H, d, *J*=15.34 Hz), 7.52 (1.0H, d, *J*=7.11 Hz), 7.64 (2.0H, d, *J*=8.49 Hz), 7.89 (2.0H, d, *J*=8.52 Hz), 8.00 (1.0H, d, *J*=15.37 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) =116.9, 118.9, 120.0, 121.0, 127.8, 128.1, 129.9, 131.9, 137.0, 140.6, 146.3, 189.1; HRMS calculated for $C_{15}H_{13}BrNO$ ($[M + H]^+$): 302.0181, found: 302.0172.



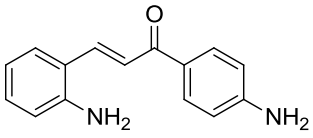
1l

(*E*)-3-(2-aminophenyl)-1-(4-iodophenyl)prop-2-en-1-one (**1l**): Following method A, compound **1l** was obtained in 34% yield (two steps, 0.364 g, orange solid, mp. 126–129 ℃). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.08 (2.0H, br), 6.73 (1.0H, d, *J*=8.10 Hz), 6.80 (1.0H, t, *J*=7.52 Hz), 7.21 (1.0H, t, *J*=8.34 Hz), 7.42 (1.0H, d, *J*=15.37 Hz), 7.52 (1.0H, dd, *J*=0.93, 7.83 Hz), 7.73 (2.0H, d, *J*=8.49 Hz), 7.86 (2.0H, d, *J*=8.49 Hz), 8.00 (1.0H, d, *J*=15.37 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 100.5, 116.9, 118.9, 120.0, 120.9, 128.1, 129.8, 131.9, 137.5, 137.9, 140.6, 146.3, 189.4; HRMS calculated for $C_{15}H_{13}INO$ ($[M + H]^+$): 350.0042, found: 350.0041.



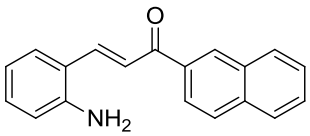
1m

(*E*)-4-(3-(2-aminophenyl)acryloyl)benzonitrile (**1m**): Following method A, compound **1m** was obtained in 54% yield (two steps, 0.285 g, orange solid, mp. 154–158 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.09 (2.0H, br), 6.74 (1.0H, dd, *J*=0.78, 8.14 Hz), 6.81 (1.0H, t, *J*=7.54 Hz), 7.23 (1.0H, t, *J*=6.94 Hz), 7.42 (1.0H, d, *J*=15.32 Hz), 7.53 (1.0H, dd, *J*=1.22, 7.86 Hz), 7.80 (2.0H, d, *J*=8.56 Hz), 8.04 (1.0H, d, *J*=15.32 Hz), 8.09 (2.0H, d, *J*=8.56 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) =115.9, 117.0, 118.0, 119.0, 119.7, 120.5, 128.2, 128. 8, 132.3, 132.5, 141.6, 141.7, 146.6, 188.8; HRMS calculated for $C_{16}H_{13}N_2O$ ([M + H]$^+$): 249.1028, found: 249.1016.



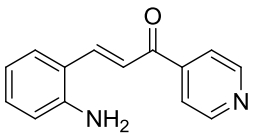
1n

(*E*)-3-(2-aminophenyl)-1-(4-aminophenyl)prop-2-en-1-one (**1n**): Following method A, compound **1n** was obtained in 50% yield (two steps, 0.213 g, yellow solid, mp. 176–178 ℃). ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 4.53 (2.0H, br), 4.84 (2.0H, br), 6.67-6.71 (3.0H, m), 6.73 (1.0H, dd, *J*=0.80, 8.08 Hz), 7.15 (1.0H, t, *J*=8.40 Hz), 7.52-7.59 (2.0H, q, *J*=8.15 Hz), 7.84-7.91 (3.0H, m); ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 114.2, 117.4, 118.74, 121.0, 122.4, 128.3, 128.7, 131.8, 132.0, 138.7, 148.3, 153.8, 188.0; HRMS calculated for $C_{15}H_{15}N_2O$ ([M + H]$^+$): 239.1184, found: 239.1179.



1o

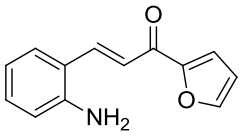
(*E*)-3-(2-aminophenyl)-1-(naphthalen-2-yl)prop-2-en-1-one (**1o**): Following method A, compound **1o** was obtained in 65% yield (two steps, 0.262 g, orange solid, mp. 143–145 ℃). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.11 (2.0H, br), 6.74 (1.0H, d, *J*=8.04 Hz), 6.83 (1.0H, t, *J*=7.49 Hz), 7.22 (1.0H, t, *J*=8.34 Hz), 7.62 (4.0H, m), 8.01 (5.0H, m), 8.54 (1.0H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 116.8, 118.9, 120.3, 121.8, 124.4, 126.7, 127.8, 128.2, 128.3, 128.5, 129.5, 129.8, 131.7, 132. 6, 135.4, 135.6, 140.0, 146.3, 190.0; HRMS calculated for $C_{19}H_{16}NO$ ([M + H]$^+$): 274.1232, found: 274.1225.



1p

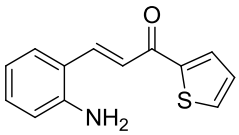
(*E*)-3-(2-aminophenyl)-1-(pyridin-4-yl)prop-2-en-1-one (**1p**): Following method A, compound **1p** was obtained in 8% yield (two steps, 83.0 mg, dark red solid, mp. 150–152 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.11 (2.0H, br), 6.73 (1.0H, dd, *J*=0.80, 8.12 Hz), 6.80 (1.0H, t, *J*=7.54 Hz), 7.23 (1.0H, t, *J*=8.42 Hz), 7.39 (1.0H, d, *J*=15.41 Hz), 7.53 (1.0H, dd, *J*=1.30, 7.86 Hz), 7.78 (2.0H, d, *J*=6.08 Hz), 8.03 (1.0H, d, *J*=15.41 Hz), 8.82 (2.0H, d, *J*=6.04 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)

= 117.0, 119.0, 119.6, 120.4, 121.4, 128.2, 132.4, 142.0, 144.5, 146.6, 150.8, 189.4; HRMS calculated for $C_{14}H_{13}N_2O$ ([M + H]$^+$): 225.1028, found: 225.1025.



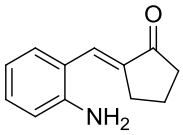
1q

(*E*)-3-(2-aminophenyl)-1-(furan-2-yl)prop-2-en-1-one (**1q**): Following method A, compound **1q** was obtained in 31% yield (two steps, 0.283 g, orange solid, mp. 127–128 ℃). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) =4.12 (2.0H, br), 6.58 (1.0H, dd, *J*=1.68, 3.53 Hz), 6.72 (1.0H, d, *J*=8.00 Hz), 6.78 (1.0H, t, *J*=7.50 Hz), 7.19 (1.0H, t, *J*=8.30 Hz), 7.31 (1.0H, d, *J*=3.55 Hz), 7.37 (1.0H, d, *J*=15.45 Hz), 7.53 (1.0H, d, *J*=6.95 Hz), 7.64 (1.0H, d, *J*=0.95 Hz), 8.03 (1.0H, d, *J*=15.50 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 112.4, 116.8, 117.3, 118.8, 119.9, 120.8, 128.1, 131.7, 139.2, 146.4, 146.4, 153.7, 178.0; HRMS calculated for $C_{13}H_{12}NO_2$ ([M +H]$^+$): 214.0868, found: 214.0862.



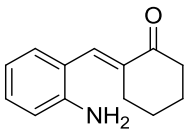
1r

(*E*)-3-(2-aminophenyl)-1-(thiophen-2-yl)prop-2-en-1-one (**1r**): Following method A, compound **1r** was obtained in 58% yield (two steps, 0.350 g, yellow solid, mp. 119–120 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =4.09 (2.0H, br), 6.73 (1.0H, d, *J*=8.08 Hz), 6.80 (1.0H, t, *J*=7.52 Hz), 7.17-7.23 (2.0H, m), 7.36 (1.0H, d, *J*=15.28 Hz), 7.52 (1.0H, d, *J*=7.80 Hz), 7.67 (1.0H, d, *J*=4.88 Hz), 7.85 (1.0H, d, *J*=3.76 Hz), 8.01 (1.0H, d, *J*=15.28 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) =116.8, 118.8, 120.0, 121.4, 128.1, 128.2, 131.6, 131.7, 133.7, 139.3, 145.7, 146.3, 182.0; HRMS calculated for $C_{13}H_{12}NOS$ ([M + H]$^+$): 230.0640, found: 230.0634.



1s

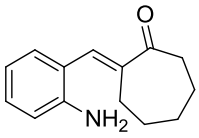
(*E*)-2-(2-aminobenzylidene)cyclopentanone (**1s**): Following method B, compound **1s** was obtained in 14% yield (three steps, 0.320 g, yellow solid, mp. 106–108 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.00 (2.0H, m), 2.41 (2.0H, t, *J*=7.78 Hz), 2.89 (2.0H, dt, *J*=2.60, 7.14 Hz), 3.96 (2.0H, br), 6.71 (1.0H, dd, *J*=0.92, 8.08 Hz), 6.77 (1.0H, t, *J*=7.52 Hz), 7.16 (1.0H, t, *J*=8.40 Hz), 7.30 (1.0H, dd, *J*=1.04, 7.76 Hz), 7.43 (1.0H, t, *J*=2.56 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 20.4, 29.4, 38.0, 116.0, 118.1, 120.4, 126.7, 129.3, 130.5, 136.4, 146.4, 207.9; HRMS calculated for $C_{12}H_{14}NO$ ([M + H]$^+$): 188.1075, found: 188.1069.



1t

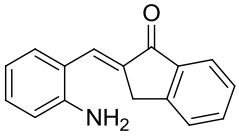
(*E*)-2-(2-aminobenzylidene)cyclohexanone (**1t**): Following method B, compound **1t** was obtained in 19% yield (three steps,

0.310 g, yellow solid, mp. 97–98 ℃). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.70-1.75 (2.0H, m), 1.90-1.95 (2.0H, m), 2.53 (2.0H, t, *J*=6.75 Hz), 2.71 (2.0H, dt, *J*=1.84, 6.50 Hz), 3.81 (2.0H, br), 6.70 (1.0H, d, *J*=8.00 Hz), 6.73 (1.0H, t, *J*=7.50 Hz), 7.08 (1.0H, d, *J*=7.60 Hz), 7.12 (1.0H, t, *J*=7.65 Hz), 7.39 (1.0H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 23.6, 24.0, 28.9, 40.4, 115.5, 117.7, 120.7, 129.7, 130.9, 138.0, 145.4, 201.7; HRMS calculated for $C_{13}H_{15}NNaO$ ($[M + Na]^+$): 224.1051, found: 224.1047.



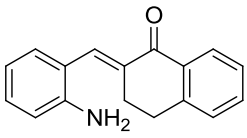
1u

(*E*)-2-(2-aminobenzylidene)cycloheptanone (**1u**): Following method B, compound **1u** was obtained in 16% yield (three steps, 0.302 g, yellow solid, mp. 136–137 ℃). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.70-1.79 (6.0H, m), 2.59-2.62 (2.0H, m), 2.70-2.72 (2.0H, m), 3.75 (2.0H, br), 6.71 (1.0H, d, *J*=8.05 Hz), 6.75 (1.0H, t, *J*=7.45 Hz), 7.04 (1.0H, d, *J*=7.55 Hz), 7.13 (1.0H, t, *J*=8.18 Hz), 7.47 (1.0H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 25.4, 28.0, 29.7, 31.1, 43.4, 124.8, 128.7, 131.0, 132.6, 132.8, 133.1, 141.5, 203.3; HRMS calculated for $C_{14}H_{18}NO$ ($[M + H]^+$): 216.1388, found: 216.1384.



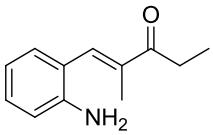
1v

(*E*)-2-(2-aminobenzylidene)-2,3-dihydro-1H-inden-1-one (**1v**): Following method B, compound **1v** was obtained in 27% yield (three steps, 0.136 g, yellow solid, mp. 181–183 ℃). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 4.03 (2.0H, br), 5.64 (2.0H, s), 6.63 (1.0H, t, *J*=7.44 Hz), 6.75 (1.0H, d, *J*=7.40 Hz), 7.11 (1.0H, t, *J*=8.24 Hz), 7.47 (1.0H, t, *J*=6.66 Hz), 7.54 (1.0H, d, *J*=7.12 Hz), 7.64-7.71 (3.0H, m), 7.78 (1.0H, d, *J*=7.60 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 32.0, 116.1, 116.2, 118.5, 123.3, 126.6, 127.5, 129.2, 129.4, 130.9, 133.1, 134.4, 137.7, 149.6, 149.9, 193.1; HRMS calculated for $C_{16}H_{14}NO$ ($[M + H]^+$): 236.1075, found: 236.1072.



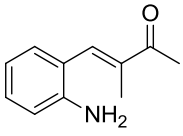
1w

(*E*)-2-(2-aminobenzylidene)-3,4-dihydronaphthalen-1(2H)-one (**1w**): Following method B, compound **1w** was obtained in 52% yield (three steps, 0.271 g, yellow solid, mp. 116–119 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.91-2.95 (2.0H, m), 3.00-3.03 (2.0H, m), 3.87 (2.0H, br), 6.74-6.80 (2.0H, m), 7.13-7.19 (2.0H, m), 7.25 (1.0H, d, *J*=7.52 Hz), 7.37 (1.0H, t, *J*=7.46 Hz), 7.49 (1.0H, t, *J*=7.42 Hz), 7.79 (1.0H, s), 8.15 (1.0H, d, *J*=7.72 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 27.5, 29.1, 115.6, 117.9, 120.9, 127.0, 128.2, 128.2, 129.7, 129.9, 132.4, 133.3, 133.4, 136.6, 143.5, 145.4, 187.8; HRMS calculated for $C_{17}H_{16}NO$ ($[M + H]^+$): 250.1232, found: 250.1226.



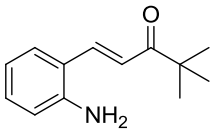
1x

(*E*)-1-(2-aminophenyl)-2-methylpent-1-en-3-one (**1x**): Following method B, compound **1x** was obtained in 41% yield (three steps, 0.383 g, yellow solid, mp. 60–62 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =1.17 (3.0H, t, *J*=7.28 Hz), 1.96 (3.0H, d, *J*=1.32 Hz), 2.84 (2.0H, q, *J*=7.27 Hz), 3.71 (2.0H, br), 6.74 (1.0H, d, *J*=8.00 Hz), 6.80 (1.0H, t, *J*=7.10 Hz), 7.10-7.17 (2.0H, m), 7.45 (1.0H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 8.7, 13.4, 31.0, 115.7, 118.3, 121.5, 129.5, 129.6, 134.2, 138.5, 144.2, 202.7; HRMS calculated for $C_{12}H_{16}NO$ ($[M + H]^+$): 190.1232, found: 190.1228.



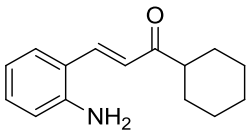
1y

(*E*)-4-(2-aminophenyl)-3-methylbut-3-en-2-one (**1y**): Following method B, compound **1y** was obtained in 83% yield (three steps, 0.480 g, yellow solid, mp. 50–54 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =1.95 (3.0H, d, *J*=1.36 Hz), 2.46 (3.0H, s), 3.73 (2.0H, br), 6.75 (1.0H, dd, *J*=0.78, 8.02 Hz), 6.78-6.82 (1.0H, m), 7.11-7.18 (2.0H, m), 7.46 (1.0H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 13.2, 26.0, 115.7, 118.3, 121.4, 129.6, 129.7, 135.7, 139.1, 144.2, 200.1; HRMS calculated for $C_{11}H_{14}NO$ ($[M + H]^+$): 176.1075, found: 176.1070.



1z

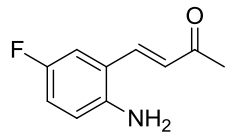
(*E*)-1-(2-aminophenyl)-4,4-dimethylpent-1-en-3-one (**1z**): Following method B, compound **1z** was obtained in 17% yield (three steps, 0.157 g, yellow solid, mp. 89–92 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.23 (9.0H, s), 3.99 (2.0H, br), 6.70 (1.0H, dd, *J*=0.90, 8.10 Hz), 6.77 (1.0H, t, *J*=7.30 Hz), 7.04 (1.0H, d, *J*=15.36 Hz), 7.15-7.20 (1.0H, m), 7.43 (1.0H, dd, *J*=1.34, 7.82 Hz), 7.83 (1.0H, d, *J*=15.32 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 26.4, 43.1, 116.6, 118.8, 120.3, 120.9, 127.9, 131.2, 138.1, 145.9, 204.4; HRMS calculated for $C_{13}H_{18}NO$ ($[M + H]^+$): 204.1388, found: 204.1384.



1aa

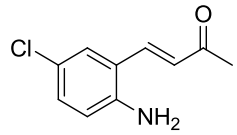
(*E*)-3-(2-aminophenyl)-1-cyclohexylprop-2-en-1-one (**1aa**): Following method B, compound **1aa** was obtained in 22% yield (three steps, 0.240 g, yellow solid, mp. 82–85 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =1.19-1.48 (5.0H, m), 1.69-1.1.73 (1.0H, m), 1.80-1.85 (2.0H, m), 1.90 (2.0H, d, *J*=13.40 Hz), 2.59 (1.0H, tt, *J*=3.36, 11.22 Hz), 3.98 (2.0H, br), 6.70 (1.0H, dd, *J*=0.88, 8.08 Hz), 6.74-6.78 (2.0H, m), 7.15-7.20 (1.0H, m), 7.42 (1.0H, dd, *J*=1.34, 7.82 Hz), 7.76 (1.0H, d, *J*=15.65 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.8, 25.9, 28.7, 50.0, 116.7, 118.9, 120.1, 124.5, 128.0, 131.3, 137.5, 145.9, 203.0; HRMS

calculated for $C_{15}H_{20}NO$ ([M + H]$^+$): 230.1545, found: 230.1540.



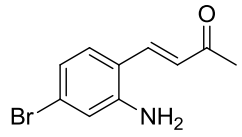
1ab

(*E*)-4-(2-amino-5-fluorophenyl)but-3-en-2-one (**1ab**): Following method A, compound **1ab** was obtained in 17% yield (two steps, 0.109 g, yellow solid, mp. 128–130 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.36 (3.0H, s), 3.86 (2.0H, br), 6.63 (1.0H, d, *J*=15.89 Hz), 6.66 (1.0H, dd, *J*=4.68, 8.80 Hz), 6.91 (1.0H, td, *J*=2.92, 8.91 Hz), 7.09 (1.0H, dd, *J*=2.86, 9.50 Hz), 7.61 (1.0H, dd, *J*=1.00, 15.89 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 28.3, 113.3 (d, ^2J(C,F) = 22.7 Hz), 118.1 (d, ^3J(C,F) = 7.7 Hz), 118.4, 118.6, 120.9 (d, ^3J(C,F) = 7.1 Hz), 127.5, 137.2 (d, ^4J(C,F) = 2.32 Hz), 142.0, 156.3 (d, ^1J(C,F) = 235.7 Hz), 197.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -125.8; HRMS calculated for $C_{10}H_{11}FNO$ ([M + H]$^+$): 180.0825, found: 180.0820.



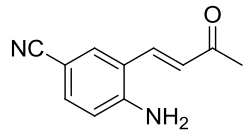
1ac

(*E*)-4-(2-amino-4-chlorophenyl)but-3-en-2-one (**1ac**): Following method A, compound **1ac** was obtained in 20% yield (two steps, 36.5 mg, yellow solid, mp. 76–79 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.35 (3.0H, s), 4.04 (2.0H, s), 6.62 (1.0H, d, *J*=2.52 Hz), 6.65 (1.0H, d, *J*=4.64 Hz), 7.11 (1.0H, dd, *J*=2.36, 8.60 Hz), 7.34 (1.0H, d, *J*=2.32 Hz), 7.57 (1.0H, d, *J*=15.89 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 28.4, 118.0, 121.0, 123.7, 127.2, 127.3, 131.1, 136.9, 144.4, 197.8; HRMS calculated for $C_{10}H_{11}ClNO$ ([M + H]$^+$): 196.0529, found: 196.0526.



1ad

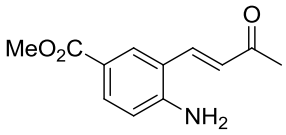
(*E*)-4-(2-amino-4-bromophenyl)but-3-en-2-one (**1ad**): Following method A, compound **1ad** was obtained in 17% yield (two steps, 0.166 g, pale yellow solid, mp. 130–132 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =2.35 (3.0H, s), 4.06 (2.0H, br), 6.65 (1.0H, d, *J*=15.89 Hz), 6.87-6.90 (2.0H, m), 7.23 (1.0H, d, *J*=9.00 Hz), 7.57 (1.0H, d, *J*=15.93 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 28.3, 118.7, 119.3, 122.1, 125.4, 126.9, 129.3, 137.4, 146.8, 197.9; HRMS calculated for $C_{10}H_{11}BrNO$ ([M + H]$^+$): 240.0024, found: 240.0021.



1ae

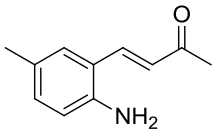
(*E*)-4-amino-3-(3-oxobut-1-en-1-yl)benzonitrile (**1ae**): Following method C, compound **1ae** was obtained in 43% (79.1 mg, yellow solid, mp. 142–143 ℃). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 2.37 (3.0H, s), 4.51 (2.0H, br), 6.71-6.67 (2.0H, m), 7.40 (1.0H, q, *J*=3.42 Hz), 7.54 (1.0H, d, *J*=15.80 Hz), 7.65 (1.0H, d, *J*=1.60 Hz);^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) =

28.8, 101.4, 116.4, 119.2, 119.7, 128.4, 132.6, 134.3, 135.7, 149.1, 197.2; HRMS calculated for $C_{11}H_{10}N_2NaO$ ([M + Na]$^+$): 209.0691, found: 209.0681.



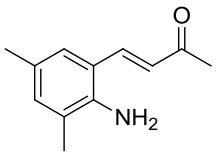
1af

(*E*)-methyl 4-amino-3-(3-oxobut-1-en-1-yl)benzoate (**1af**): Following method C, compound **1af** was obtained in 51% (112.7 mg, yellow solid, mp. 139–140 ℃). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 2.37 (3.0H, s), 3.87 (3.0H, s), 4.42 (2.0H, br), 6.68 (1.0H, d, *J*=8.50 Hz), 6.76 (1.0H, d, *J*=15.80 Hz), 7.62 (1.0H, d, *J*=15.80 Hz), 7.84 (1.0H, q, *J*=3.38 Hz), 8.11 (1.0H, d, *J*=1.45 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 28.6, 51.8, 115.8, 118.7, 120.4, 127.5, 130.4, 132.7, 137.1, 149.6, 166.6, 197.7; HRMS calculated for $C_{12}H_{13}NNaO_3$ ([M + Na]$^+$): 242.0793, found: 242.0792.



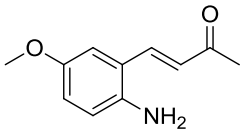
1ag

(*E*)-4-(2-amino-5-methylphenyl)but-3-en-2-one (**1ag**): Following method C, compound **1ag** was obtained in 49% (86.0 mg, yellow oil). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 2.24 (3.0H, s), 2.35 (3.0H, s), 3.86 (2.0H, br), 6.67-6.62 (2.0H, m), 7.00 (1.0H, q, *J*=3.28 Hz), 7.21 (1.0H, s), 7.66 (1.0H, d, *J*=15.95 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 20.3, 28.0, 117.1, 120.0, 126.6, 128.3, 128.3, 132.5, 138.7, 143.6, 198.1; HRMS calculated for $C_{11}H_{14}NO$ ([M + H]$^+$): 176.1070, found: 176.1066.



1ah

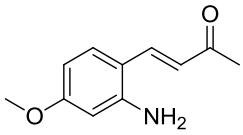
(*E*)-4-(2-amino-3,5-dimethylphenyl)but-3-en-2-one (**1ah**): Following method C, compound **1ah** was obtained in 37% (69.4 mg, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.16 (3.0H, s), 2.22 (3.0H, s), 2.36 (3.0H, s), 3.87 (2.0H, br), 6.65 (1.0H, d, *J*=15.85 Hz), 6.93 (1.0H, s), 7.10 (1.0H, s), 7.71 (1.0H, d, *J*=15.89 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 17.5, 20.3, 28.1, 119.4, 123.4, 125.9, 126.5, 127.4, 133.7, 139.0, 141.9, 198.2; HRMS calculated for $C_{12}H_{16}NO$ ([M + H]$^+$): 190.1226, found: 190.1227.



1ai

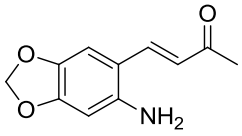
(*E*)-4-(2-amino-5-methoxyphenyl)but-3-en-2-one (**1ai**): Following method C, compound **1ai** was obtained in 21% (40.8 mg, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.37 (3H, s), 3.73 (2H, br), 3.76 (3H, s), 6.68-6.62 (2H, m), 6.82 (1.0H, dd, *J*=2.90, 8.74 Hz), 6.92 (1.0H, d, *J*=2.84 Hz), 7.67 (1.0H, d, J=15.97 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 27.9, 55.7, 111.3, 118.5, 119.0, 120.8, 126.9, 138.5, 139.9, 152.9, 198.2; HRMS calculated for $C_{11}H_{14}NO_2$ ([M + H]$^+$): 192.1019,

found: 192.1018.



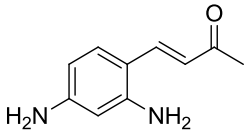
1aj

(*E*)-4-(2-amino-4-methoxyphenyl)but-3-en-2-one (**1aj**): Following method C, compound **1aj** was obtained in 28% (53.9 mg, yellow solid, mp. 122–123 ℃). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.36 (3.0H, s), 3.81 (3.0H, s), 4.08 (2.0H, br), 6.23 (1.0H, d, *J*=2.46 Hz), 6.39 (1.0H, q, *J*=3.72 Hz), 6.59 (1.0H, d, *J*=15.82 Hz), 7.38 (1.0H, d, *J*=8.73 Hz), 7.65 (1.0H, d, *J*=15.85 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 28.1, 55.3, 101.2, 106.2, 113.0, 124.1, 129.9, 138.4, 147.8, 162.7, 198.2; HRMS calculated for $C_{11}H_{13}NNaO_2$ ($[M + Na]^+$): 214.0844, found: 214.0838.



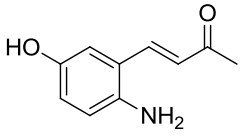
1ak

(*E*)-4-(6-aminobenzo[*d*][1,3]dioxol-5-yl)but-3-en-2-one (**1ak**): Following method A, compound **1ak** was obtained in 12% yield (two steps, 81.0 mg, yellow solid, mp. 102–103 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.33 (3.0H, s), 3.91 (2.0H, br), 5.90 (2.0H, s), 6.25 (1.0H, s), 6.49 (1.0H, d, *J*=15.65 Hz), 6.87 (1.0H, s), 7.63 (1.0H, d, *J*=15.65 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 28.2, 98.2, 101.2, 105.6, 112.1, 123.6, 137.8, 141.4, 142.9, 151.0, 198.0; HRMS calculated for $C_{11}H_{12}NO_3$ ($[M + H]^+$): 206.0817, found: 206.0812.



1al

(*E*)-4-(2,4-diaminophenyl)but-3-en-2-one (**1al**): Following method A, compound **1al** was obtained in 13% yield (two steps, 0.127 g, dark brown oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.65 (3.0H, s), 3.84 (4.0H, br), 6.89 (1.0H, dd, *J*=2.12, 8.64 Hz), 7.00 (1.0H, d, *J*=8.24 Hz), 7.16 (1.0H, d, *J*=1.88 Hz), 7.53 (1.0H, d, *J*=8.60 Hz), 7.86 (1.0H, d, *J*=8.24 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 26.7, 109.8, 118.9, 128.8, 129.8, 138.5, 148.7, 155.2, 163.6, 198.3; HRMS calculated for $C_{10}H_{13}N_2O$ ($[M + H]^+$): 177.1028, found: 177.1023.

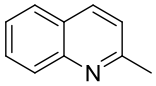


1am

(*E*)-4-(2-amino-5-hydroxyphenyl)but-3-en-2-one (**1am**): Following method A, compound **1am** was obtained in 23% yield (two steps, 89.8 mg, brown solid, mp. 109–111 ℃). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.32 (3.0H, s), 5.13 (2.0H, br), 6.38 (1.0H, d, *J*=16.05 Hz), 6.56-6.65 (2.0H, m), 6.80 (1.0H, d, *J*=2.68 Hz), 7.75 (1.0H, d, *J*=16.09 Hz), 8.61 (1.0H, s); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 26.9, 111.3, 117.9, 118.3, 120.4, 125.0, 139.7, 141.6, 148.4, 198.1; HRMS calculated

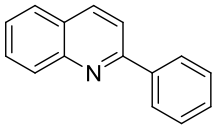
for $C_{10}H_{12}NO_2$ ([M + H]$^+$): 178.0868, found: 178.0862.

VI. ^{1}H NMR and ^{13}C NMR spectra data of the products



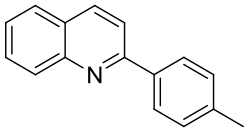
2a

2-methylquinoline (**2a**): 99% (20.5 mg, pale yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =2.75 (3.0H, s), 7.28 (1.0H, d, *J*=8.36 Hz), 7.48 (1.0H, t, *J*=7.18 Hz), 7.68 (1.0H, t, *J*=8.36 Hz), 7.77 (1.0H, d, *J*=8.07 Hz), 8.03 (2.0H, t, *J*=8.90 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.4, 122.0, 125.6, 126.5, 127.5, 128.6, 129.4, 136.1, 147.9, 159.0; HRMS calculated for $C_{10}H_{10}N$ ([M + H]$^+$): 144.0813, found: 144.0807.



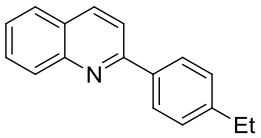
2b

2-phenylquinoline (**2b**): 97% (21.1 mg, white solid, mp. 73–76 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.48 (1.0H, t, *J*=7.24 Hz), 7.51-7.56 (3.0H, m), 7.74 (1.1H, t, *J*=8.36 Hz), 7.83 (1.0H, d, *J*=8.12 Hz), 7.88 (1.0H, d, *J*=8.60 Hz), 8.17-8.23 (4.0H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 119.0, 126.2, 127.2, 127.4, 127.5, 128.8, 129.3, 129.6, 129.7, 136.7, 139. 7, 148.3, 157.3; HRMS calculated for $C_{15}H_{12}N$ ([M + H]$^+$): 206.0970, found: 206.0963.



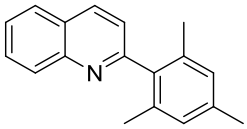
2c

2-(*p*-tolyl)quinoline (**2c**): 99% (20.9 mg, white solid, mp. 72–75 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =2.44 (3.0H, s), 7.34 (2.0H, d, *J*=7.92 Hz), 7.51 (1.0H, t, *J*=6.96 Hz), 7.72 (1.0H, t, *J*=8.34 Hz), 7.81 (1.0H, d, *J*=7.24 Hz), 7.86 (1.0H, d, *J*=8.64 Hz), 8.09 (2.0H, d, *J*=8.16 Hz), 8.18 (2.0H, d, *J*=15.77 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 21.3, 118.8, 126.0, 127.1, 127.4, 129.5, 129.6, 136.6, 136.8, 139.3, 148.3, 157.3; HRMS calculated for $C_{16}H_{14}N$ ([M + H]$^+$): 220.1126, found: 220.1121.



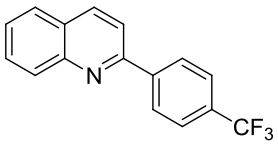
2d

2-(4-ethylphenyl)quinoline (**2d**): 94% (16.0 mg, white solid, mp. 48–49 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.30 (3.0H, t, *J*=7.60 Hz), 2.74 (2.0H, q, *J*=7.60 Hz), 7.37 (2.0H, d, *J*=8.12 Hz), 7.52 (1.0H, t, *J*=7.46 Hz), 7.72 (1.0H, t, *J*=8.30 Hz), 7.82 (1.0H, d, *J*=8.32 Hz), 7.87 (1.0H, d, *J*=8.56 Hz), 8.10 (2.0H, d, *J*=8.16 Hz), 8.19 (2.0H, t, *J*=9.66 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 15.5, 28.7, 118.9, 126.0, 127.1, 127.4, 127.5, 128.4, 129.5, 129.7, 136.6, 137.1, 145.7, 148.3, 157.4; HRMS calculated for $C_{17}H_{16}N$ ([M + H]$^+$): 234.1283, found: 234.1277.



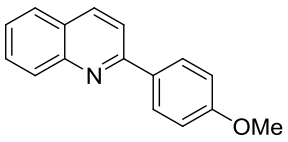
2e

2-mesitylquinoline (**2e**): 61% (28.7 mg, pale yellow oil). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 2.06 (6.0H, s), 2.35 (3.0H, s), 6.98 (2.0H, s), 7.36 (1.0H, d, *J*=8.35 Hz), 7.58 (1.0H, t, *J*=7.85 Hz), 7.74 (1.0H, t, *J*=8.28 Hz), 7.88 (1.0H, d, *J*=8.05 Hz), 8.17 (1.0H, d, *J*=8.45 Hz), 8.21 (1.0H, d, *J*=8.35 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 20.1, 21.1, 122.9, 126.3, 126.7, 127.5, 128.4, 129.4, 129.5, 135.6, 136.1, 137.6, 137.9, 148.2, 160.6; HRMS calculated for $C_{18}H_{18}N$ ([M + H]$^+$): 248.1439, found: 248.1435.



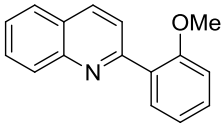
2f

2-(4-(trifluoromethyl)phenyl)quinoline (**2f**): 71% (17.3 mg, white solid, mp. 122–124 ℃). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) =7.57 (1.0H, t, *J*=8.00 Hz), 7.74-7.79 (3.0H, m), 7.85 (1.0H, d, *J*=8.05 Hz), 7.89 (1.0H, d, *J*=8.55 Hz), 8.19 (1.0H, d, *J*=8.50 Hz), 8.26 (1.0H, d, *J*=8.65 Hz), 8.29 (2.0H, d, *J*=8.15 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 118.7, 123.1, 125.3, 125.7 (q, ^{3}J(C,F) = 3.5 Hz), 126.8, 127.4, 127.5, 127.8, 129.9, 131.1, 137.1, 143.0, 148.3, 155.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -62.6; HRMS calculated for $C_{16}H_{11}F_3N$ ([M + H]$^+$): 274.0844, found: 274.0839.



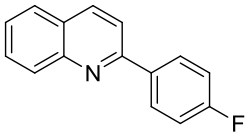
2g

2-(4-methoxyphenyl)quinoline (**2g**): 91% (20.0 mg, white solid, mp. 118–119 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.89 (3.0H, s), 7.05 (2.0H, d, *J*=8.84 Hz), 7.50 (1.0H, t, *J*=7.10 Hz), 7.71 (1.0H, t, *J*=8.36 Hz), 7.80 (1.0H, dd, *J*=1.00, 8.28 Hz), 7.83 (1.0H, d, *J*=8.60 Hz), 8.13-8.18 (4.0H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 55.4, 114.2, 118.5, 125.9, 126.9, 127.4, 128.8, 129.5, 132.2, 136.6, 148.3, 156.9, 160.8; HRMS calculated for $C_{16}H_{14}NO$ ([M + H]$^+$): 236.1075, found: 236.1069.



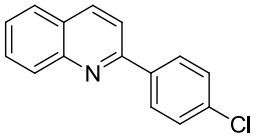
2h

2-(2-methoxyphenyl)quinoline (**2h**): 96% (22.0 mg, pale yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.87 (3.0H, s), 7.04 (1.0H, d, *J*=8.20 Hz), 7.14 (1.0H, dt, *J*=0.89, 7.47 Hz), 7.40-7.45 (1.0H, m), 7.53 (1.0H, t, *J*=8.02 Hz), 7.71 (1.0H, t, *J*=8.38 Hz), 7.83 (1.0H, d, *J*=8.12 Hz), 7.86 (1.0H, dd, *J*=1.76, 7.56 Hz), 7.89 (1.0H, d, *J*=8.56 Hz), 8.14 (1.0H, d, *J*=8.60 Hz), 8.18 (1.0H, d, *J*=8.48 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 55.6, 111.4, 121.2, 123.4, 126.1, 127.0, 127.3, 129.1, 129.6, 129.7, 130.3, 131.4, 135.0, 148.3, 157.1, 157.2; HRMS calculated for $C_{16}H_{14}NO$ ([M + H]$^+$): 236.1075, found: 236.1073.



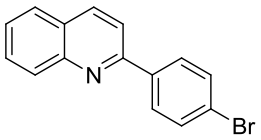
2i

2-(4-fluorophenyl)quinoline (**2i**): 90% (19.5 mg, white solid, mp. 90–91 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.21 (2.0H, t, *J*=8.70 Hz), 7.53 (1.0H, t, *J*=8.00 Hz), 7.73 (1.0H, dd, *J*=5.54, 8.42 Hz), 7.82 (2.0H, d, *J*=8.60 Hz), 8.14-8.21 (4.0H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 115.7 (d, ^{2}J(C,F) = 21.5 Hz), 118.6, 126.3, 127.1, 127.4, 129.4 (d, ^{3}J(C,F) = 8.5 Hz), 129.6, 129.7, 135.8 (d, ^{4}J(C,F) = 3.0 Hz), 136.9, 148.2, 156.2, 163.8 (d, ^{1}J(C,F) = 247.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -112.5; HRMS calculated for $C_{15}H_{11}FN$ ($[M + H]^+$): 224.0876, found: 224.0870.



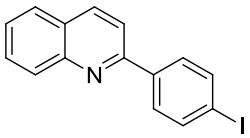
2j

2-(4-chlorophenyl)quinoline (**2j**): 96% (22.0 mg, white solid, mp. 106–110 ℃). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.49 (2.0H, d, *J*=8.58 Hz), 7.55 (1.0H, d, *J*=7.86 Hz), 7.74 (1.0H, t, *J*=8.31 Hz), 7.83 (2.0H, d, *J*=8.58 Hz), 8.12 (2.0H, d, *J*=8.58 Hz), 8.16 (1.0H, d, *J*=8.94 Hz), 8.21 (1.0H, d, *J*=8.64 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 118.5, 126.5, 127.2, 127.4, 128.8, 129.0, 129.6, 129.8, 135.5, 136.9, 138.0, 148.2, 155.9; HRMS calculated for $C_{15}H_{11}ClN$ ($[M + H]^+$): 240.0580, found: 240.0578.



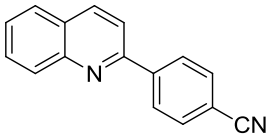
2k

(*E*)-4-(2-amino-4-bromophenyl)but-3-en-2-one (**2k**): 97% (29.5 mg, white solid, mp. 113–116 ℃). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.54 (1.0H, t, *J*=7.23 Hz), 7.65 (2.0H, d, *J*=8.50 Hz), 7.74 (1.0H, t, *J*=8.23 Hz), 7.83 (2.0H, d, *J*=8.60 Hz), 8.06 (2.0H, d, *J*=8.50 Hz), 8.16 (1.0H, d, *J*=8.50 Hz), 8.21 (1.0H, d, *J*=8.60 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 118.4, 123.9, 126.5, 127.2, 127.5, 129.1, 129.7, 129.8, 131.9, 136.9, 138.5, 148.2, 156.0; HRMS calculated for $C_{15}H_{11}BrN$ ($[M + H]^+$): 284.0075, found: 284.0061.



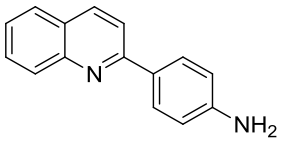
2l

2-(4-iodophenyl)quinoline (**2l**): 94% (17.9 mg, white solid, mp. 138–141 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.54 (1.0H, t, *J*=8.04 Hz), 7.74 (1.0H, t, *J*=8.42 Hz), 7.82 (2.0H, d, *J*=8.60 Hz), 7.86 (2.0H, d, *J*=8.64 Hz), 7.92 (2.0H, d, *J*=8.64 Hz), 8.16 (1.0H, d, *J*=8.60 Hz), 8.21 (1.0H, d, *J*=8.64 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 95.9, 118.4, 126.5, 127.2, 127.5, 129.2, 129.7, 129.8, 136.9, 137.9, 139.1, 148.2, 156.1; HRMS calculated for $C_{15}H_{11}IN$ ($[M + H]^+$): 331.9936, found: 331.9927.



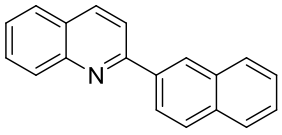
2m

4-(quinolin-2-yl)benzonitrile (**2m**): 30% (5.9 mg, white solid, mp. 90–94 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =7.59 (1.0H, t, *J*=7.18 Hz), 7.77 (1.0H, t, *J*=8.32 Hz), 7.82 (2.0H, d, *J*=8.32 Hz), 7.88 (2.0H, t, *J*=9.12 Hz), 8.18 (1.0H, d, *J*=8.52 Hz), 8.27-8.30 (3.0H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 112.7, 118.6, 118.8, 127.1, 127.5, 128.1, 129.9, 130.1, 132.6, 137.3, 143.7, 148.2, 154.9; HRMS calculated for $C_{16}H_{11}N_2$ ([M + H]$^+$): 231.0922, found: 231.0915.



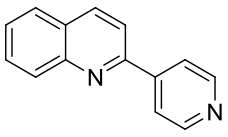
2n

4-(quinolin-2-yl)aniline (**2n**): 80% (16.6 mg, white solid, mp. 105–108 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.88 (2.0H, br), 6.81 (2.0H, d, *J*=8.68 Hz), 7.47 (1.0H, t, *J*=8.06 Hz), 7.69 (1.0H, t, *J*=8.42 Hz), 7.78 (1.0H, d, *J*=8.44 Hz), 7.80 (1.0H, d, *J*=8.80 Hz), 8.03 (2.0H, d, *J*=8.68 Hz), 8.13 (2.0H, t, *J*=7.28 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 115.1, 118.3, 125.5, 126.7, 127.3, 128.8, 129.3, 129.4, 129.9, 136.4, 147.8, 148.3, 157.2; HRMS calculated for $C_{15}H_{13}N_2$ ([M + H]$^+$): 221.1079, found: 221.1074.



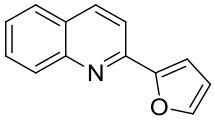
2o

2-(naphthalen-2-yl)quinoline (**2o**): 97% (23.5 mg, white solid, mp. 141–144 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =7.53-7.57 (3.0H, m), 7.76 (1.0H, t, *J*=8.28 Hz), 7.85 (1.0H, dd, *J*=1.36, 8.12 Hz), 7.91 (1.0H, dd, *J*=3.44, 5.96 Hz), 8.00-8.04 (3.0H, m), 8.25 (2.0H, d, *J*=8.44 Hz), 8.39 (1.0H, dd, *J*=1.82, 8.62 Hz), 8.63 (1.0H, d, *J*=0.88 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 119.1, 125.0, 126.3, 126.7, 127.1, 127.2, 127.5, 127.7, 128.5, 128.8, 129.7, 129.7, 133.5, 133.8, 136.8, 136.9, 148.3, 157.1; HRMS calculated for $C_{19}H_{14}N$ ([M + H]$^+$): 256.1126, found: 256.1120.



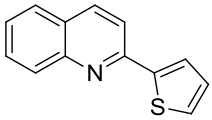
2p

2-(pyridin-4-yl)quinoline (**2p**): 34% (6.4 mg, white solid, mp. 80–83 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.59 (1.0H, t, *J*=7.94 Hz), 7.78 (1.0H, t, *J*=8.36 Hz), 7.87 (1.0H, d, *J*=8.16 Hz), 7.91 (1.0H, d, *J*=8.56 Hz), 8.07 (2.0H, d, *J*=6.04 Hz), 8.20 (1.0H, d, *J*=8.48 Hz), 8.30 (1.0H, d, *J*=8.56 Hz), 8.79 (2.0H, d, *J*=5.52 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 118.4, 121.6, 127.2, 127.5, 127.8, 130.0, 130.1, 137.3, 146.7, 148.3, 150.5, 154.5; HRMS calculated for $C_{14}H_{11}N_2$ ([M + H]$^+$): 207.0922, found: 207.0918.



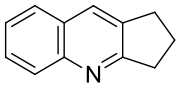
2q

2-(furan-2-yl)quinoline (**2q**): 65% (12.6 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =6.59 (1.0H, dd, *J*=1.74, 3.38 Hz), 7.22 (1.0H, d, *J*=3.40 Hz), 7.50 (1.0H, t, *J*=7.46 Hz), 7.63 (1.0H, d, *J*=1.00 Hz), 7.70 (1.0H, t, *J*=8.34 Hz), 7.78 (1.0H, d, *J*=8.12 Hz), 7.82 (1.0H, d, *J*=8.60 Hz), 8.13 (1.0H, d, *J*=8.56 Hz), 8.16 (1.0H, d, *J*=8.72 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 110.1, 112.2, 117.4, 126.2, 127.1, 127.5, 129.3, 129.8, 136.6, 144.1, 148.1, 149.0, 153.7; HRMS calculated for $C_{13}H_{10}NO$ ($[M + H]^+$): 196.0762, found: 196.0759.



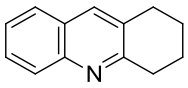
2r

2-(thiophen-2-yl)quinoline (**2r**): 99% (20.7 mg, white solid, mp. 124–127 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =7.16 (1.0H, q, *J*=2.91 Hz), 7.46-7.50 (2.0H, m), 7.67-7.80 (4.0H, m), 8.08-8.13 (2.0H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 117.6, 125.8, 126.1, 127.1, 127.4, 128.0, 128.5, 129.2, 129.8, 136.6, 145.4, 148.1, 152.3; HRMS calculated for $C_{13}H_{10}NS$ ($[M + H]^+$): 212.0534, found: 212.0531.



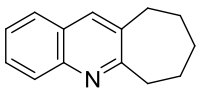
2s

2,3-dihydro-1H-cyclopenta[b]quinoline (**2s**): 99% (19.7 mg, pale yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.15-2.23 (2.0H, m), 3.07 (2.0H, dt, *J*=1.30, 7.41 Hz), 3.15 (2.0H, t, *J*=7.64 Hz), 7.44 (1.0H, t, *J*=8.00 Hz), 7.60 (1.0H, t, *J*=8.36 Hz), 7.71 (1.0H, dd, *J*=0.94, 8.10 Hz), 7.87 (1.0H, s), 8.01 (1.0H, d, *J*=8.40 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 23.6, 30.5, 34.6, 125.5, 127.3, 127.4, 128.3, 128.5, 130.3, 135.6, 147.5, 167.9; HRMS calculated for $C_{12}H_{12}N$ ($[M + H]^+$): 170.0970, found: 170.0962.



2t

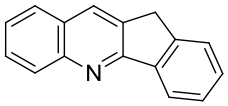
1,2,3,4-tetrahydroacridine (**2t**): 99% (20.6 mg, colorless solid, mp. 38–40 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.85-1.91 (2.0H, m), 1.95-2.01 (2.0H, m), 2.96 (2.0H, t, *J*=6.26 Hz), 3.12 (2.0H, t, *J*=6.54 Hz), 7.42 (1.0H, t, *J*=8.02 Hz), 7.59 (1.0H, t, *J*=8.38 Hz), 7.68 (1.0H, d, *J*=8.12 Hz), 7.78 (1.0H, s), 7.97 (1.0H, d, *J*=8.44 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.9, 23.2, 29.2, 33.5, 125.5, 126.8, 127.2, 128.2, 128.4, 130.9, 134.9, 146.5, 159.3; HRMS calculated for $C_{13}H_{14}N$ ($[M + H]^+$): 184.1126, found: 184.1119.



2u

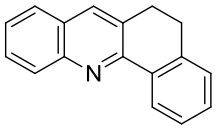
7,8,9,10-tetrahydro-6H-cyclohepta[b]quinoline (**2u**): 94% (18.7 mg, colorless solid, mp. 57–62 ℃). ^{1}H NMR (500 MHz,

$CDCl_3$): δ (ppm) = 1.74-1.92 (6.0H, m), 2.94 (2.0H, d, *J*=11.05 Hz), 3.21 (2.0H, d, *J*=11.20 Hz), 7.44 (1.0H, t, *J*=7.93 Hz), 7.61 (1.0H, t, *J*=8.33 Hz), 7.70 (1.0H, d, *J*=8.10 Hz), 7.79 (1.0H, s), 7.99 (1.0H, d, *J*=8.45 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 27.0, 28.8, 32.2, 35.4, 40.0, 125.7, 126.8, 127.3, 128.4, 128.5, 134.5, 136.5, 146.3, 164.6; HRMS calculated for $C_{14}H_{16}N$ ($[M + H]^+$): 198.1283, found: 198.1277.



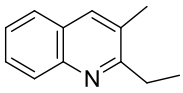
2v

11*H*-indeno[1,2-b]quinoline (**2v**): 63% (13.5 mg, colorless solid, mp. 154–157 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.04 (2.0H, s), 7.48-7.53 (3.0H, m), 7.60-7.62 (1H, m), 7.70 (1.1H, t, *J*=8.38 Hz), 7.83 (1.0H, dd, *J*=1.12, 8.08 Hz), 8.18-8.21 (2.0H, m), 8.30-8.32 (1.0H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 34.0, 122.1, 125.4, 125.7, 127.4, 127.5, 127.7, 128.8, 129.1, 130.0, 131.2, 134.6, 140.3, 145.1, 148.0, 161.7; HRMS calculated for $C_{16}H_{12}N$ ($[M + H]^+$): 218.0970, found: 218.0966.



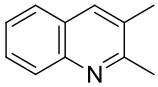
2w

5,6-dihydrobenzo[c]acridine (**2w**): 99% (24.9 mg, colorless solid, mp. 60–62 ℃). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.02 (2.0H, t, *J*=6.95 Hz), 3.14 (2.0H, t, *J*=6.90 Hz), 7.28 (1.0H, d, *J*=7.45 Hz), 7.37 (1.0H, dt, *J*=1.38, 7.36 Hz), 7.41-7.44 (1.0H, m), 7.46-7.49 (1.0H, m), 7.63-7.66 (1.0H, m), 7.75 (1.0H, d, *J*=7.45 Hz), 7.93 (1.0H, s), 8.13 (1.0H, d, *J*=8.45 Hz), 8.58 (1.0H, dd, *J*=1.00, 7.70 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 28.4, 28.9, 126.0, 126.1, 126.9, 127.3, 127.9, 128.6, 129.5, 129.7, 130.6, 133.6, 134.8, 139.4, 147.7, 153.4; HRMS calculated for $C_{17}H_{14}N$ ($[M + H]^+$): 232.1126, found: 232.1123.



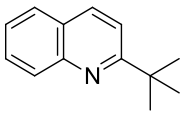
2x

2-ethyl-3-methylquinoline (**2x**): 95% (16.6 mg, colorless solid, mp. 66–68 ℃). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) =1.37 (3.0H, t, *J*=7.55 Hz), 2.48 (3.0H, d, *J*=0.65 Hz), 2.99 (2.0H, q, *J*=7.55 Hz), 7.44 (1.0H, t, *J*=7.98 Hz), 7.60 (1.0H, t, *J*=8.35 Hz), 7.69 (1.0H, d, *J*=7.30 Hz), 7.82 (1.0H, s), 8.02 (1.0H, d, *J*=8.45 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 12.8, 19.1, 29.5, 125.6, 126.6, 127.3, 128.2, 128.5, 129.4, 135.7, 146.6, 163.3; HRMS calculated for $C_{12}H_{14}N$ ($[M + H]^+$): 172.1126, found: 172.1122.



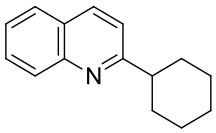
2y

2,3-dimethylquinoline (**2y**): 92% (15.0 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =2.43 (3.0H, d, *J*=0.48 Hz), 2.68 (3.0H, s), 7.41-7.46 (1.0H, m), 7.58-7.63 (1.0H, m), 7.69 (1.0H, d, *J*=8.08 Hz), 7.82 (1.0H, s), 7.99 (1.0H, d, *J*=8.44 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 19.6, 23.6, 125.6, 126.7, 127.4, 128.3, 128.3, 130.0, 135.2, 146.5, 159.0; HRMS calculated for $C_{11}H_{12}N$ ($[M + H]^+$): 158.0970, found: 158.0965.



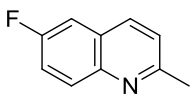
2z

2-(tert-butyl)quinoline (**2z**): 99% (20.2 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =1.48 (9.0H, s), 7.45-7.50 (1.0H, m), 7.53 (1.0H, d, *J*=8.64 Hz), 7.65-7.69 (1.0H, m), 7.77 (1.0H, dd, *J*=1.24, 8.08 Hz), 8.07 (2.0H, d, *J*=8.52 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 30.1, 38.1, 118.2, 125.6, 126.4, 127.2, 129.0, 129.4, 135.8, 147.4, 169.2; HRMS calculated for $C_{13}H_{16}N$ ($[M + H]^+$): 186.1283, found: 186.1278.



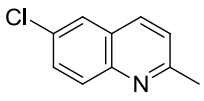
2aa

2-cyclohexylquinoline (**2aa**): 90% (19.1 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =1.31-1.39 (1.0H, m), 1.47 (2.0H, tq, *J*=3.23, 12.74 Hz), 1.63 (2.0H, dq, *J*=3.05, 12.50 Hz), 1.76-1.81 (1.0H, m), 1.87-1.91 (2.0H, m), 2.00-2.04 (2.0H, m), 2.92 (1.0H, tt, *J*=3.43, 11.97 Hz), 7.32 (1.0H, d, *J*=8.48 Hz), 7.45-7.49 (1.0H, m), 7.65-7.69 (1.0H, m), 7.76 (1.0H, dd, *J*=1.12, 8.12 Hz), 8.03-8.08 (2.0H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 26.1, 26.5, 32.8, 47.6, 119.5, 125.6, 126.9, 127.4, 128.9, 129.2, 136.3, 147.8, 166.8; HRMS calculated for $C_{15}H_{18}N$ ($[M + H]^+$): 212.1439, found: 212.1433.



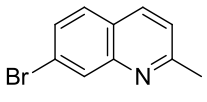
2ab

6-fluoro-2-methylquinoline (**2ab**): 52% (11.2 mg, yellow solid, mp. 39–42 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.73 (3.0H, s), 7.29 (1.0H, d, *J*=8.52 Hz), 7.38 (1.0H, q, *J*=3.89 Hz), 7.41-7.46 (1.0H, m), 7.97-8.01 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.2, 110.5 (d, ^{2}J(C,F) = 21.5 Hz), 119.4 (d, ^{2}J(C,F) = 25.4 Hz), 122.7, 126.9 (d, ^{3}J(C,F) = 10.0 Hz), 131.0 (d, ^{3}J(C,F) = 9.0 Hz), 135.5 (d, ^{4}J(C,F) = 5.3 Hz), 144.9, 158.3 (d, ^{4}J(C,F) = 2.6 Hz), 159.9 (d, ^{1}J(C,F) = 245.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) = -115.0; HRMS calculated for $C_{10}H_9FN$ ($[M + H]^+$): 162.0719, found: 162.0715.



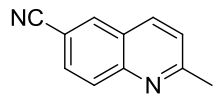
2ac

6-chloro-2-methylquinoline (**2ac**): 95% (13.4 mg, white solid, mp. 80–82 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.73 (3.0H, s), 7.30 (1.0H, d, *J*=8.44 Hz), 7.60 (1.0H, dd, *J*=2.36, 9.00 Hz), 7.74 (1.0H, d, *J*=2.32 Hz), 7.93 (1.0H, d, *J*=3.40 Hz), 7.96 (1.0H, d, *J*=2.80 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.3, 122.9, 126.1, 127.0, 130.2, 130.2, 131.3, 135.2, 146.2, 159.3; HRMS calculated for $C_{10}H_9ClN$ ($[M + H]^+$): 178.0424, found: 178.0417.



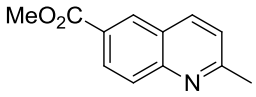
2ad

7-bromo-2-methylquinoline (**2ad**): 96% (18.8 mg, white solid, mp. 51–53 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.73 (3.0H, s), 7.28 (1.0H, d, *J*=8.40 Hz), 7.55 (1.0H, q, *J*=3.51 Hz), 7.62 (1.0H, d, *J*=8.64 Hz), 7.99 (1.0H, d, *J*=8.40 Hz), 8.19 (1.0H, d, *J*=1.72 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.4, 122.3, 123.4, 125.0, 128.7, 129.2, 131.1, 135.9, 148.5, 160.1; HRMS calculated for $C_{10}H_9BrN$ ($[M + H]^+$): 221.9918, found: 221.9912.



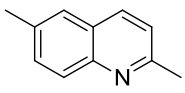
2ae

2-methylquinoline-6-carbonitrile (**2ae**): 86% (14.5 mg, white solid, mp. 164–165 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.78 (3.0H, s), 7.41 (1.0H, d, J=8.52 Hz), 7.81 (1.0H, q, *J*=3.52 Hz), 8.07 (1.0H, d, *J*=5.08 Hz), 8.09 (1.0H, d, *J*=4.68 Hz), 8.17 (1.0H, d, *J*=1.72 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.6, 109.3, 118.6, 123.7, 125.8, 130.1, 130.2, 133.7, 136.2, 148.8, 162.5; HRMS calculated for $C_{11}H_9N_2$ ($[M + H]^+$): 169.0760, found: 169.0758.



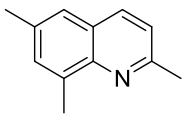
2af

methyl 2-methylquinoline-6-carboxylate (**2af**): 76% (15.2 mg, white solid, mp. 95–96 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.76 (3.0H, s), 3.97 (3.0H, s), 7.34 (1.0H, d, *J*=8.40 Hz), 8.03 (1.0H, d, *J*=8.80 Hz), 8.13 (1.0H, d, *J*=8.44 Hz), 8.26 (1.0H, q, *J*=3.57 Hz), 8.53 (1.0H, d, *J*=1.80 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.5, 52.3, 122.7, 125.5, 127.2, 128.8, 128.9, 130.6, 137.2, 149.7, 161.5, 166.7; HRMS calculated for $C_{12}H_{12}NO_2$ ($[M + H]^+$): 202.0863, found: 202.0867.



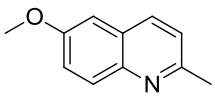
2ag

2,6-dimethylquinoline (**2ag**): 64% (10.0 mg, pale yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.51 (3.0H, s), 2.72 (3.0H, s), 7.24 (1.0H, d, *J*=8.40 Hz), 7.49-7.52 (2.0H, m), 7.91 (1.0H, d, *J*=8.48 Hz), 7.95 (1.0H, d, *J*=8.44 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 21.4, 25.2, 121.9, 126.3, 126.4, 128.2, 131.6, 135.3, 135.5, 146.4, 157.9; HRMS calculated for $C_{11}H_{12}N$ ($[M + H]^+$): 158.0964, found: 158.0962.



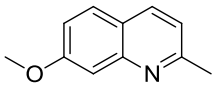
2ah

2,6,8-trimethylquinoline (**2ah**): 81% (13.9 mg, pale yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.47 (3.0H, s), 2.73 (3.0H, s), 2.77 (3.0H, s), 7.22 (1.0H, d, *J*=8.36 Hz), 7.37 (2.0H, s), 7.91 (1.0H, d, *J*=8.32 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 17.7, 21.4, 25.5, 121.5, 124.3, 126.4, 131.7, 134.7, 135.5, 136.0, 145.5, 156.8; HRMS calculated for $C_{12}H_{14}N$ ($[M + H]^+$): 172.1121, found: 172.1113.



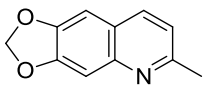
2ai

6-methoxy-2-methylquinoline (**2ai**): 60% (10.3 mg, pale yellow oil). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 2.70 (3.0H, s), 3.91 (3.0H, s), 7.04 (1.0H, d, *J*=2.80 Hz), 7.24 (1.0H, d, *J*=8.40 Hz), 7.33 (1.0H, q, *J*=3.98 Hz), 7.92 (1.0H, d, *J*=9.25 Hz), 7.94 (1.0H, d, *J*=8.50 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 25.0, 55.5, 105.3, 121.8, 122.2, 127.3, 130.0, 135.0, 143.9, 156.3, 157.2; HRMS calculated for $C_{11}H_{12}NO$ ($[M + H]^+$): 174.0913, found: 174.0916.



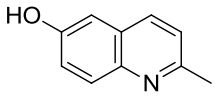
2aj

7-methoxy-2-methylquinoline (**2aj**): 74% (12.8 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.70 (3.0H, s), 3.93 (3.0H, s), 7.11-7.15 (2.0H, m), 7.35 (1.0H, d, *J*=2.48 Hz), 7.63 (1.0H, d, *J*=8.88 Hz), 7.94 (1.0H, d, *J*=8.28 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.2, 55.4, 106.7, 118.6, 119.7, 121.5, 128.4, 135.8, 149.4, 159.1, 160.7; HRMS calculated for $C_{11}H_{12}NO$ ($[M + H]^+$): 174.0913, found: 174.0914.



2ak

6-methyl-[1,3]dioxolo[4,5-g]quinoline (**2ak**): 61% (11.5 mg, white solid, mp. 144–145 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.66 (3.0H, s), 6.07 (2.0H, s), 7.00 (1.0H, s), 7.12 (1.0H, d, *J*=8.28 Hz), 7.31 (1.0H, s), 7.83 (1.0H, d, *J*=8.28 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 24.9, 101.5, 102.6, 105.3, 120.1, 123.1, 135.0, 146.0, 147.1, 150.5, 156.6; HRMS calculated for $C_{11}H_{10}NO_2$ ($[M + H]^+$): 188.0712, found: 188.0705.



2am

2-methylquinolin-6-ol (**2am**): 20% (3.3 mg, light pink oil). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.57 (3.0H, s), 7.08 (1.0H, d, *J*=2.68 Hz), 7.24 (1.0H, dd, *J*=2.72, 9.04 Hz), 7.27 (1.0H, d, *J*=8.48 Hz), 7.75 (1.0H, d, *J*=9.00 Hz), 8.01 (1.0H, d, *J*=8.44 Hz), 9.84 (1.0H, s); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 24.5, 108.3, 121.5, 122.0, 127.4, 129.6, 134.4, 142.5, 154.8, 155.0; HRMS calculated for $C_{10}H_{10}NO$ ($[M + H]^+$): 160.0762, found: 160.0757.

VII. ^{1}H and ^{13}C NMR Spectra

Fig. S1. ^{1}H NMR Spectrum of 1a (500 MHz, $CDCl_3$).

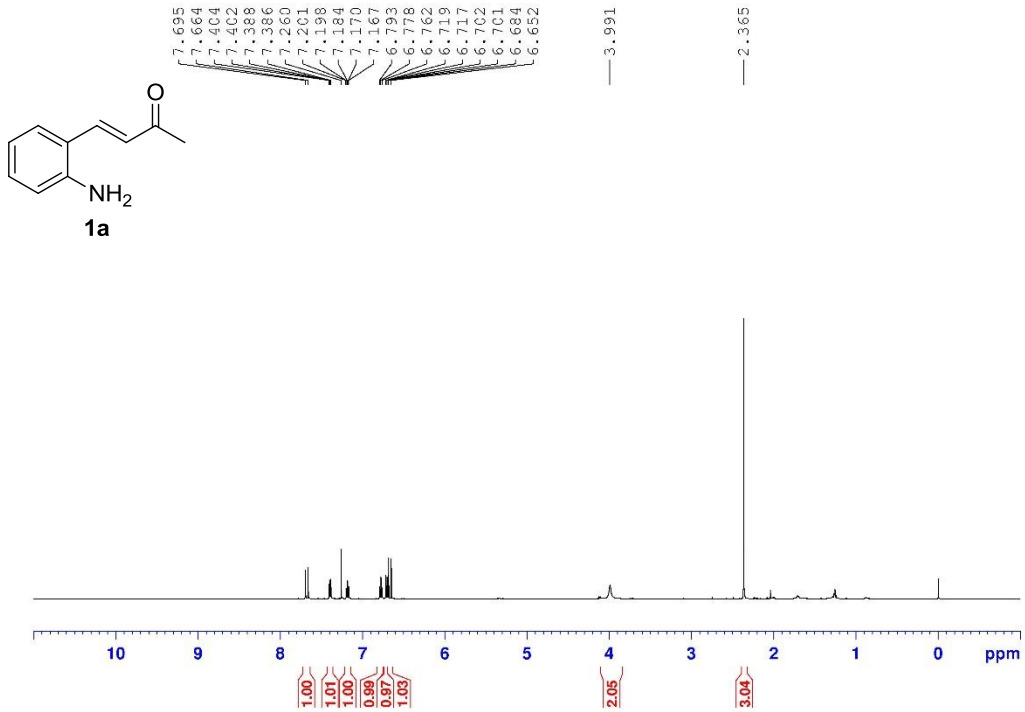


Fig. S2. ^{13}C NMR Spectrum of 1a (125 MHz, $CDCl_3$).

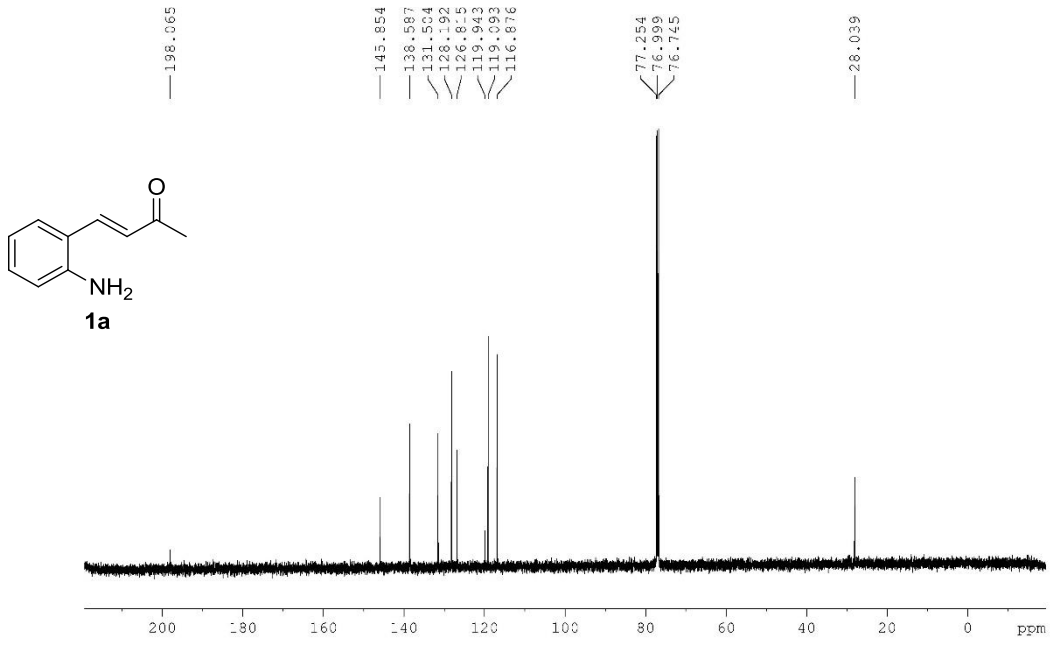


Fig. S3. ^{1}H NMR Spectrum of 1b (400 MHz, $CDCl_3$).

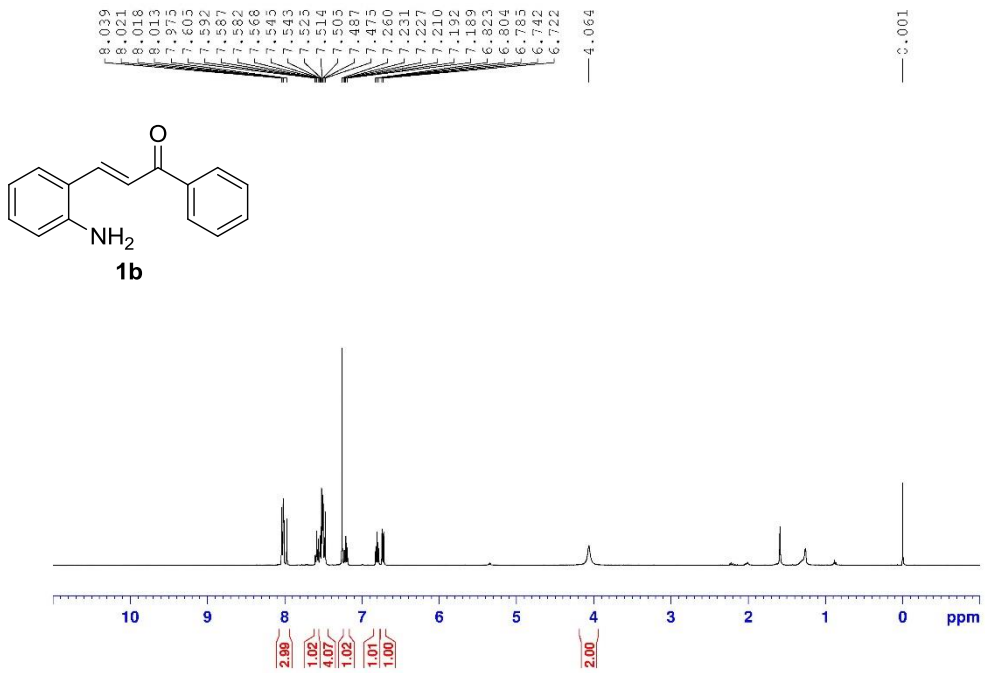


Fig. S4. ^{13}C NMR Spectrum of 1b (100 MHz, $CDCl_3$).

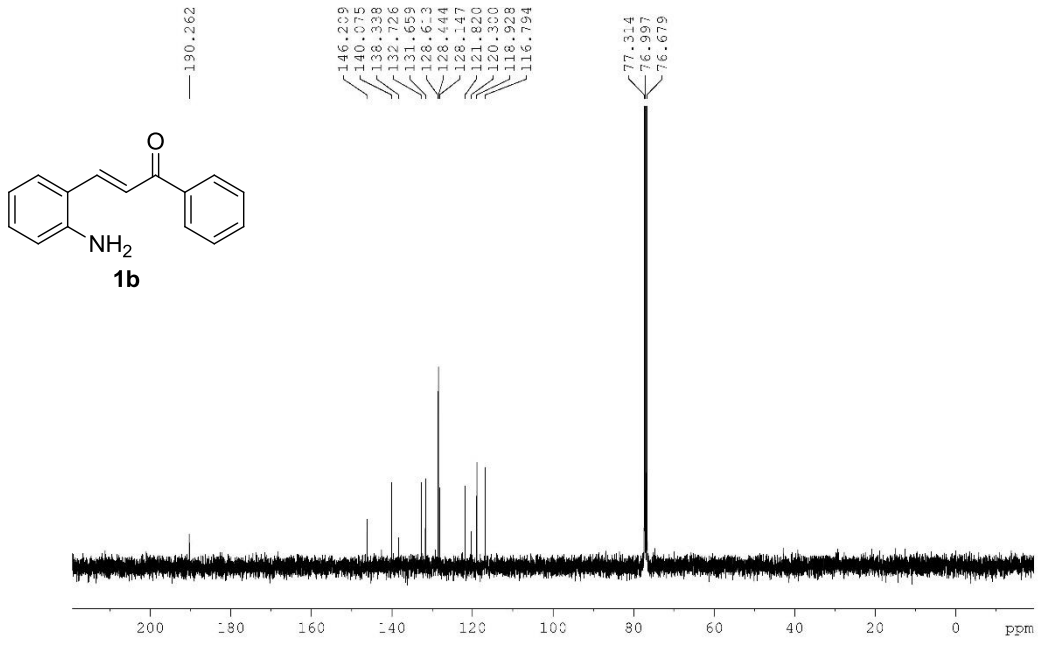


Fig. S5. ^{1}H NMR Spectrum of 1c (400 MHz, $CDCl_3$).

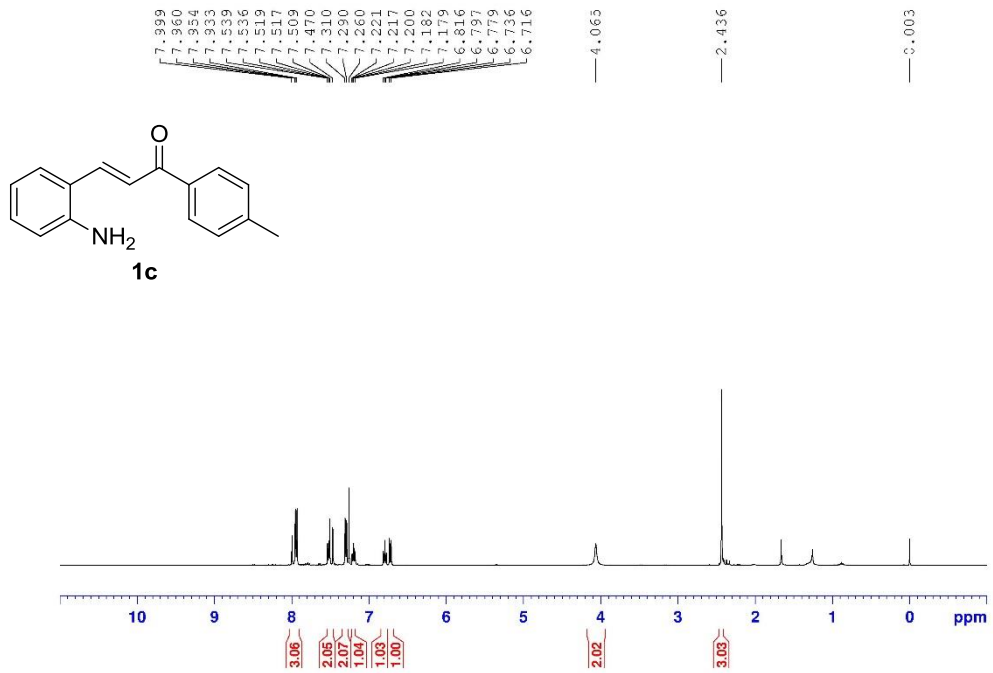


Fig. S6. ^{13}C NMR Spectrum of 1c (100 MHz, $CDCl_3$).

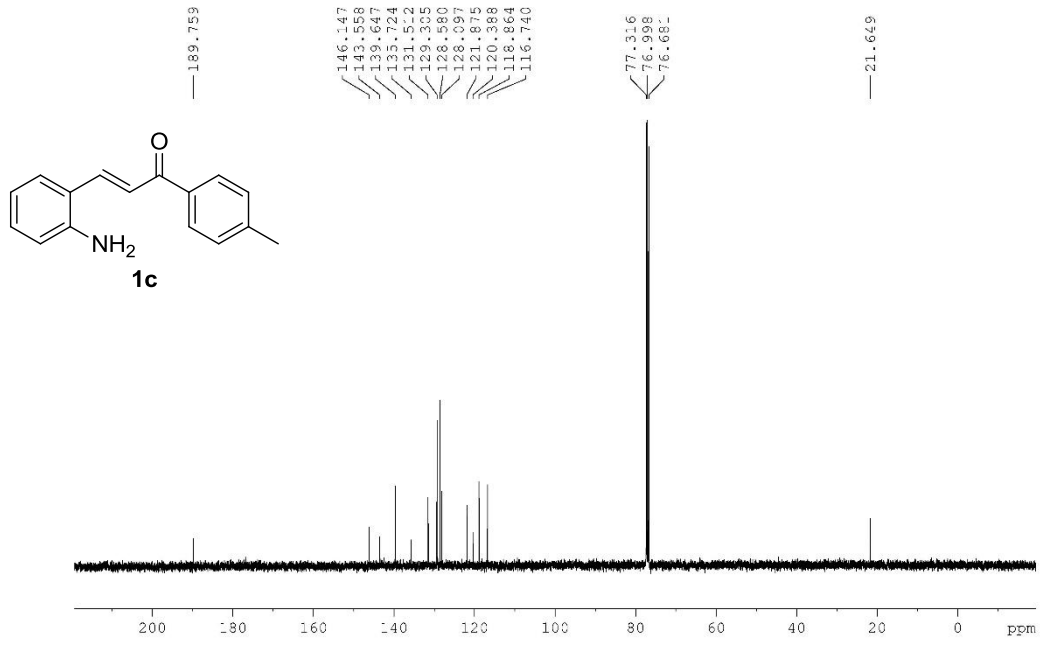


Fig. S7. ^{1}H NMR Spectrum of 1d (400 MHz, $CDCl_3$).

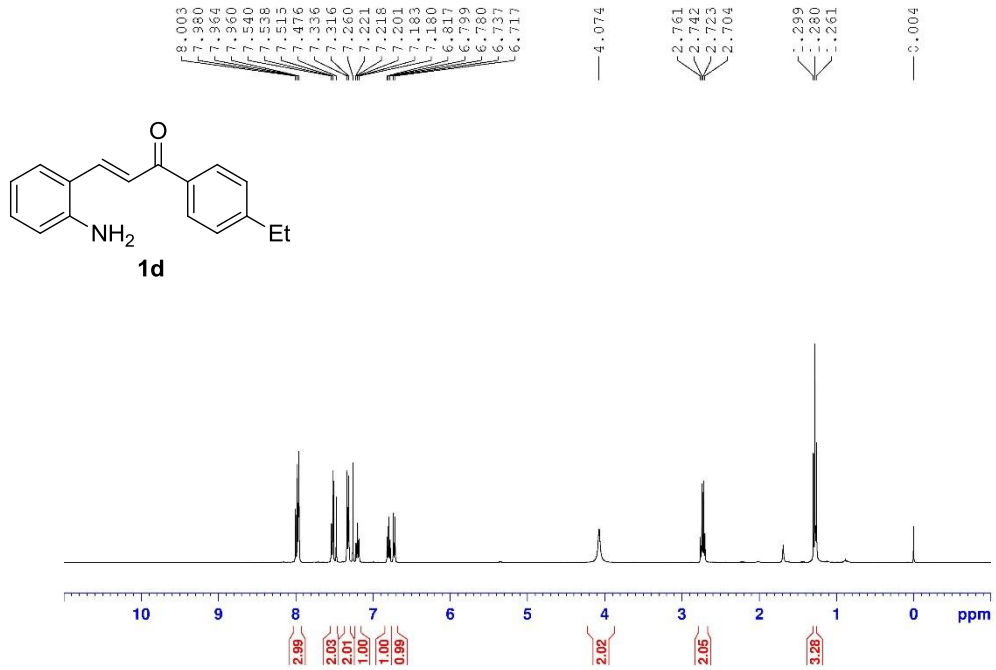


Fig. S8. ^{13}C NMR Spectrum of 1d (100 MHz, $CDCl_3$).

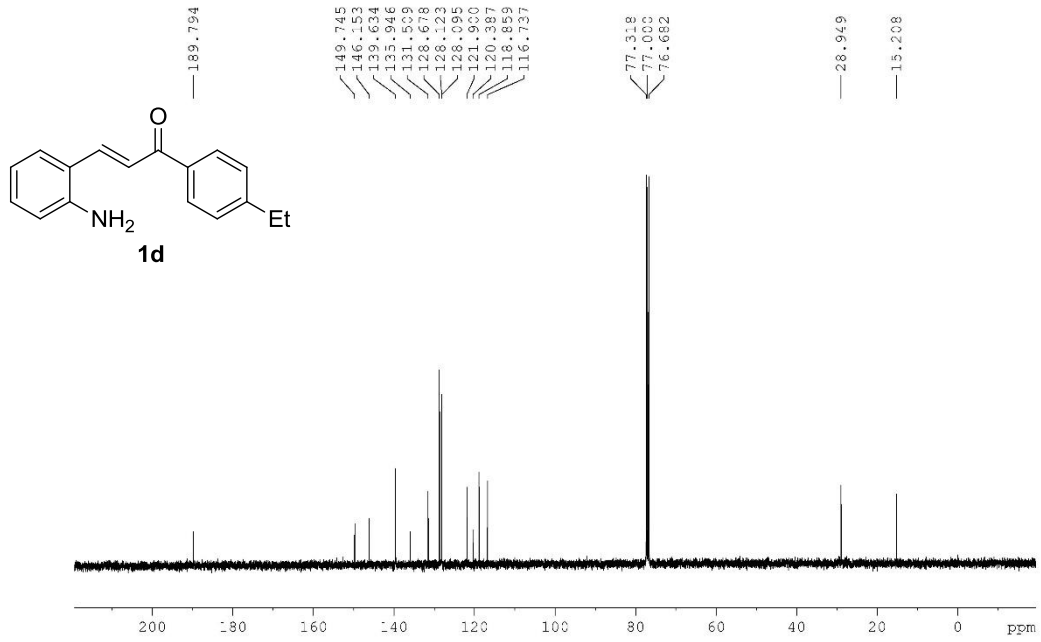


Fig. S9. ^{1}H NMR Spectrum of 1e (400 MHz, $CDCl_3$).

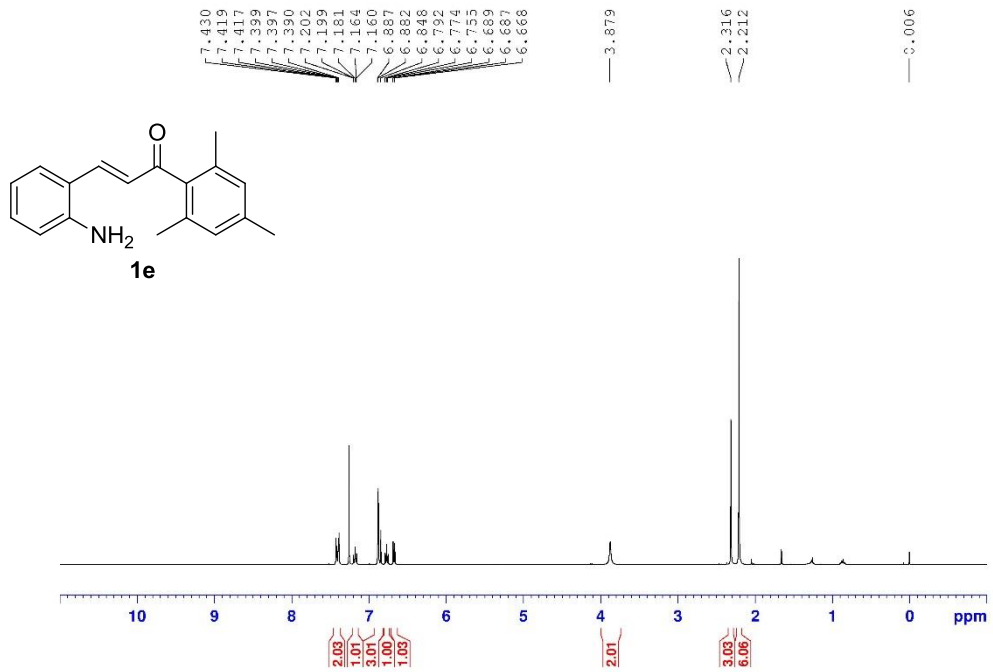


Fig. S10. ^{13}C NMR Spectrum of 1e (100 MHz, $CDCl_3$).

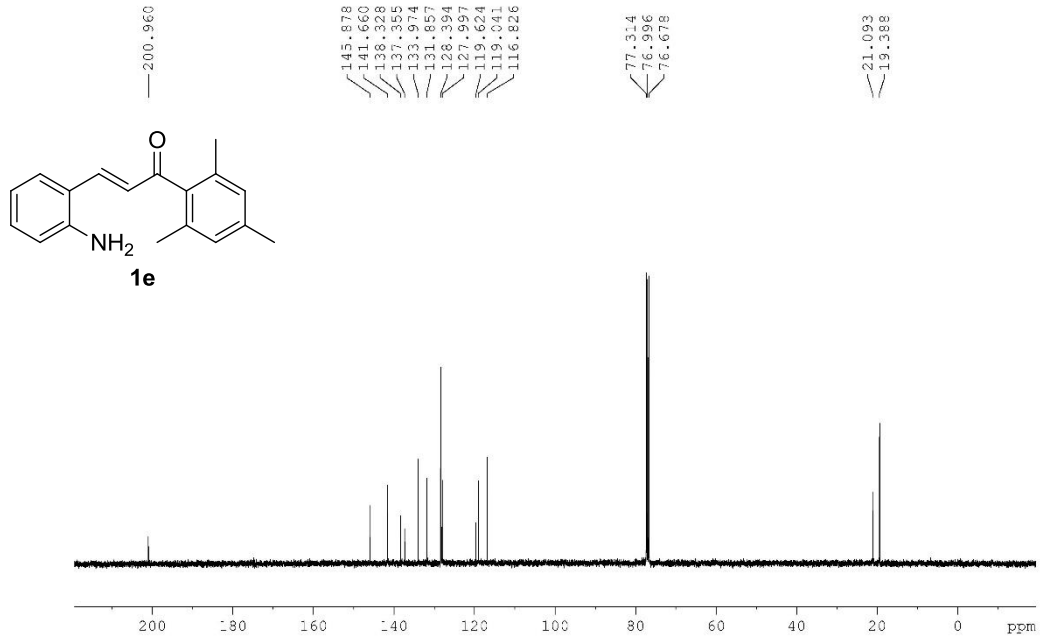


Fig. S11. ^{1}H NMR Spectrum of 1f (400 MHz, $CDCl_3$).

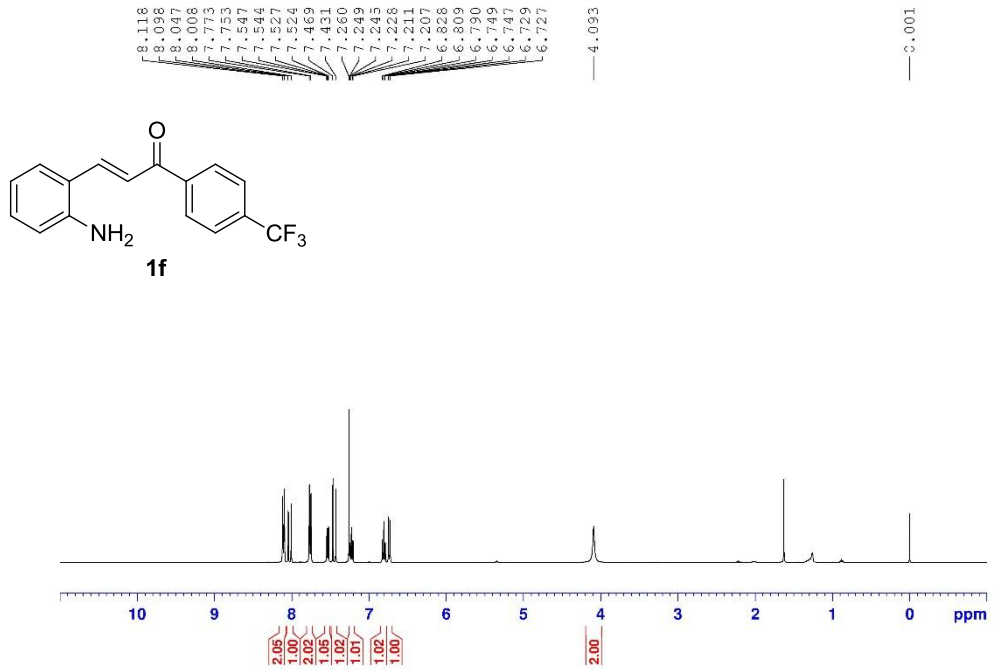


Fig. S12. ^{13}C NMR Spectrum of 1f (100 MHz, $CDCl_3$).

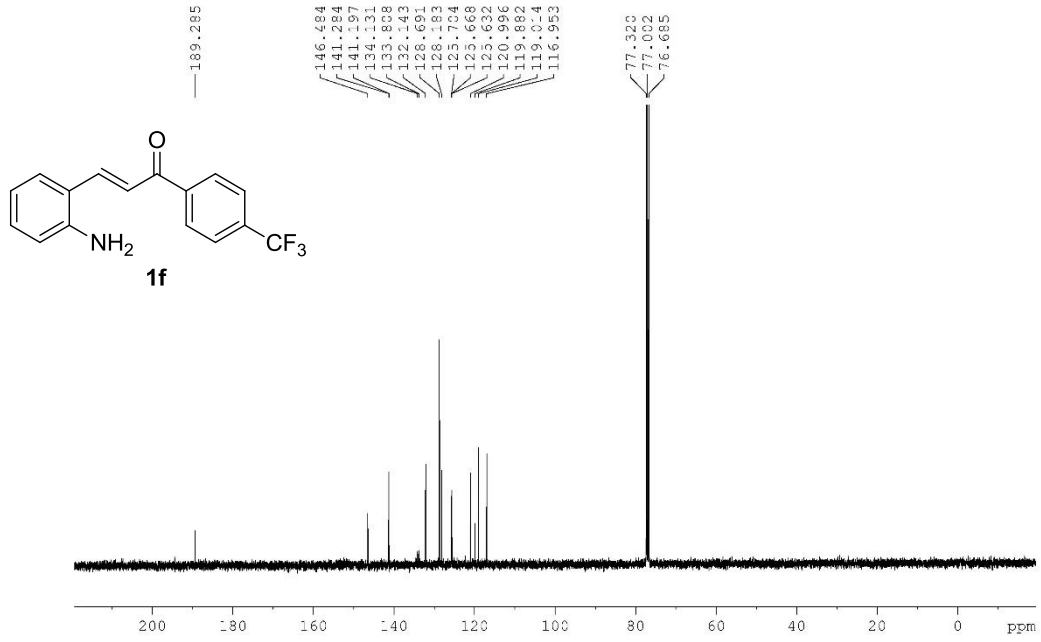


Fig. S13. ^{19}F NMR Spectrum of 1f (376 MHz, $CDCl_3$).

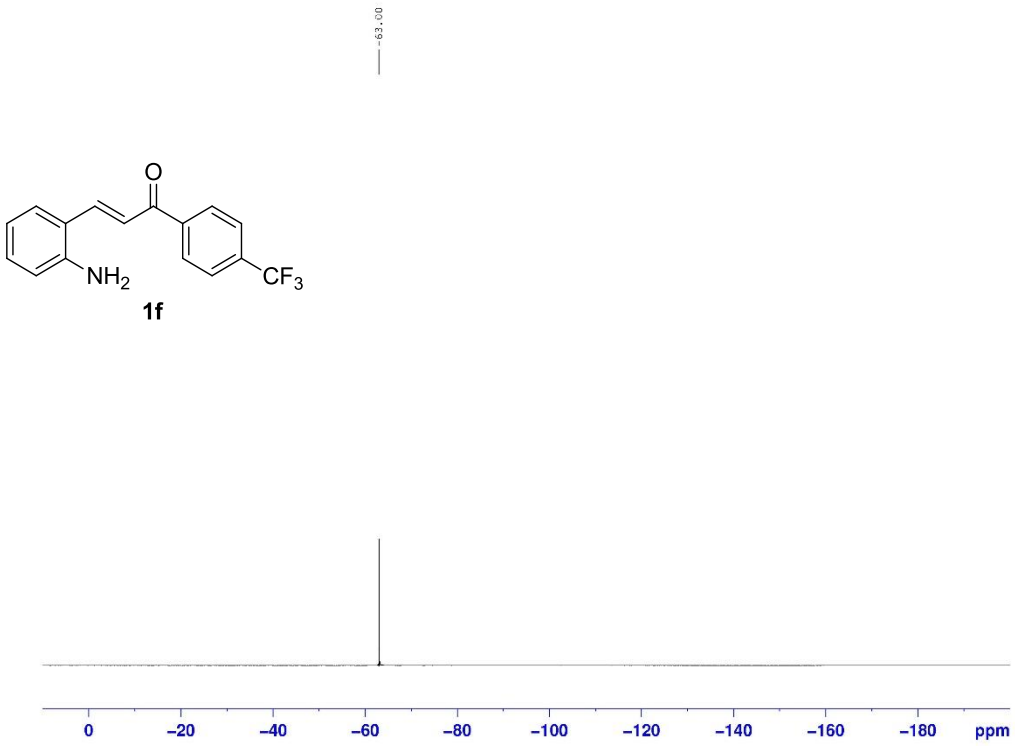


Fig. S14. ^{1}H NMR Spectrum of 1g (400 MHz, $CDCl_3$).

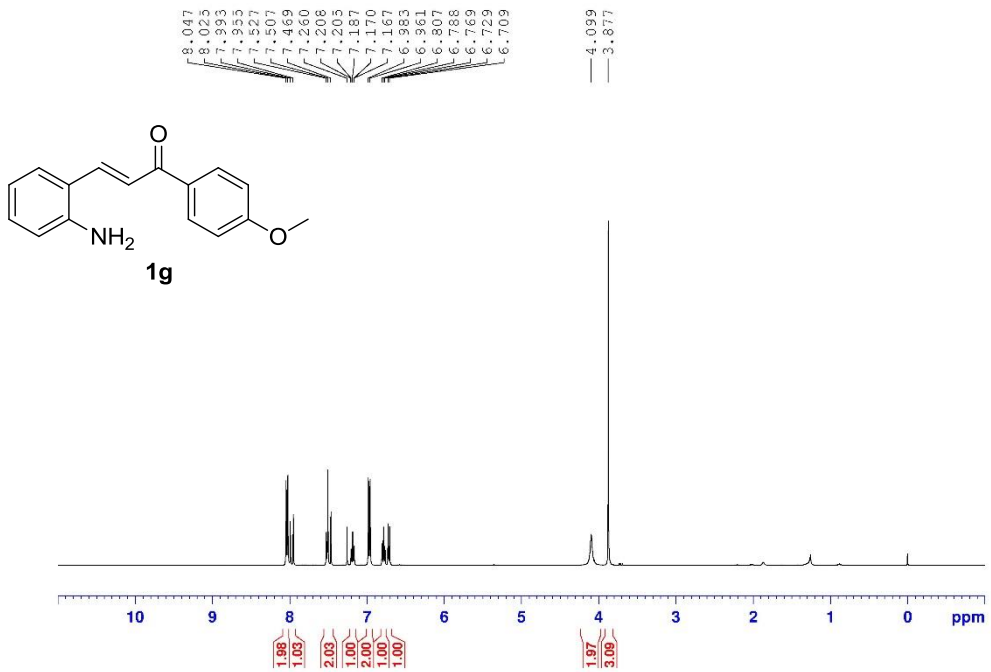


Fig. S15. ^{13}C NMR Spectrum of 1g (100 MHz, $CDCl_3$).

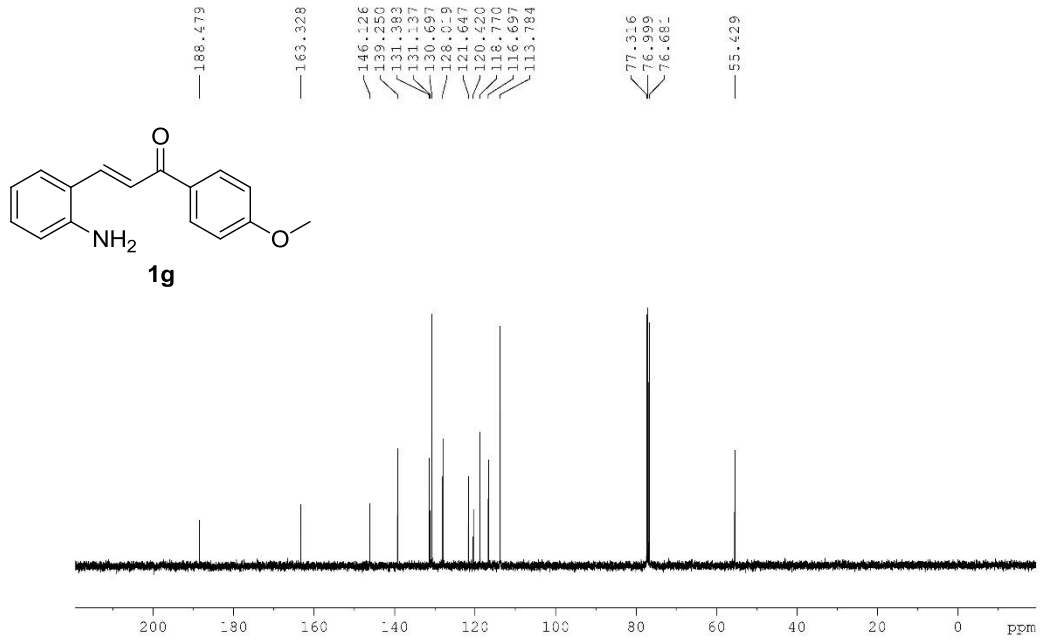


Fig. S16. ^{1}H NMR Spectrum of 1h (400 MHz, $CDCl_3$).

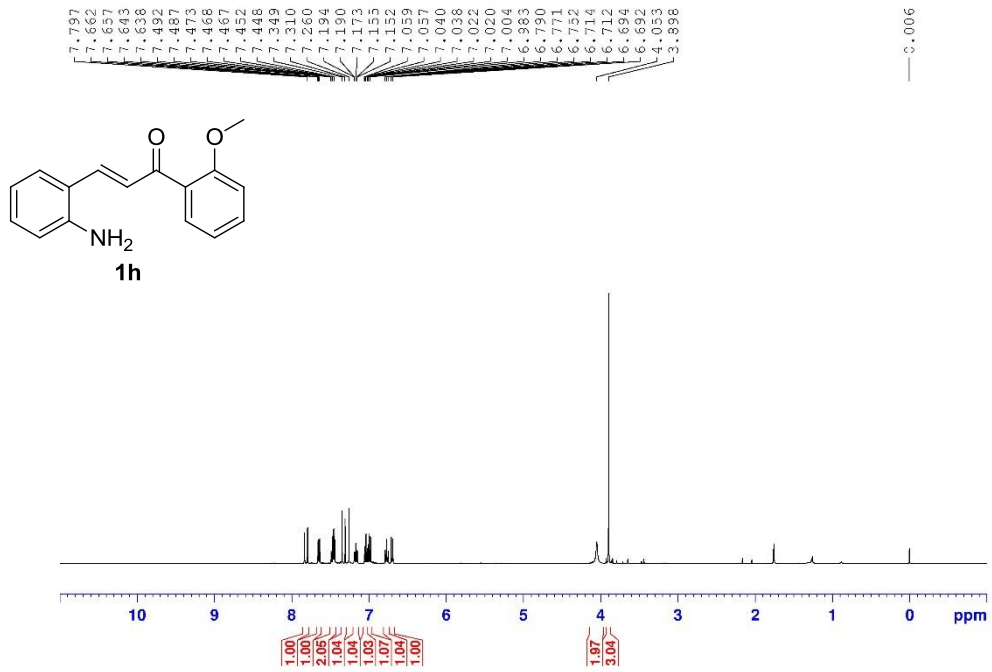


Fig. S17. ^{13}C NMR Spectrum of 1h (100 MHz, $CDCl_3$).

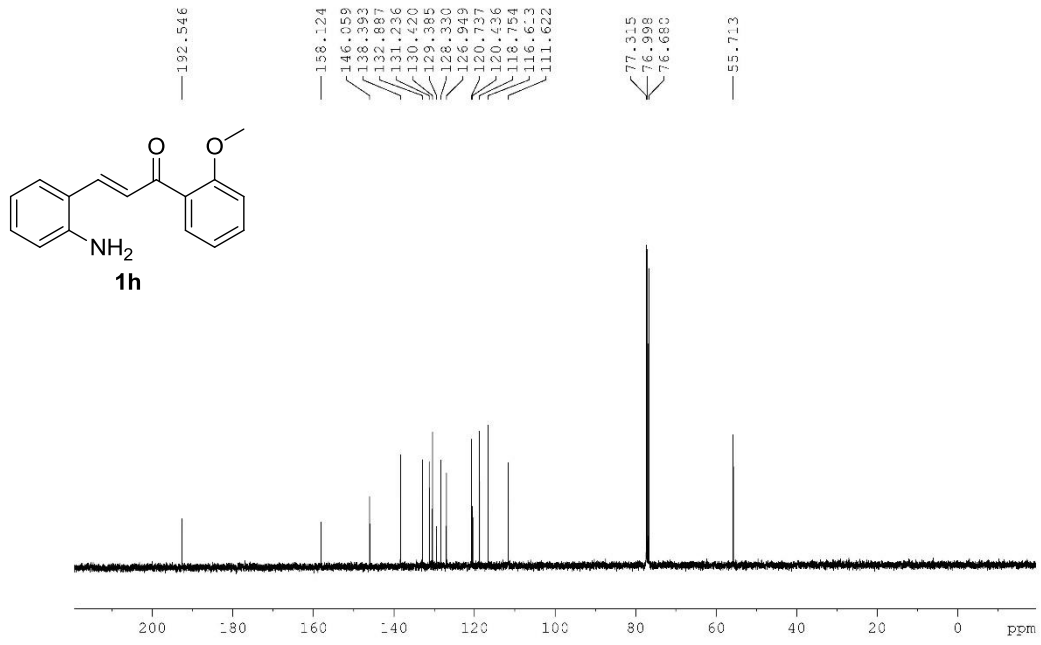


Fig. S18. ^{1}H NMR Spectrum of 1i (400 MHz, $CDCl_3$).

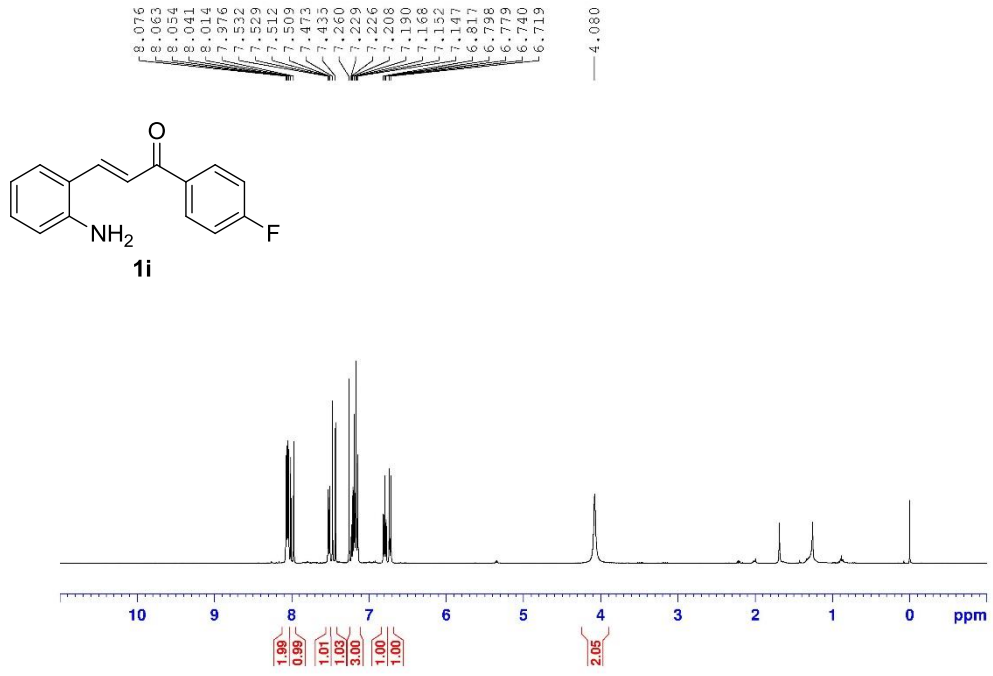


Fig. S19. ^{13}C NMR Spectrum of 1i (100 MHz, $CDCl_3$).

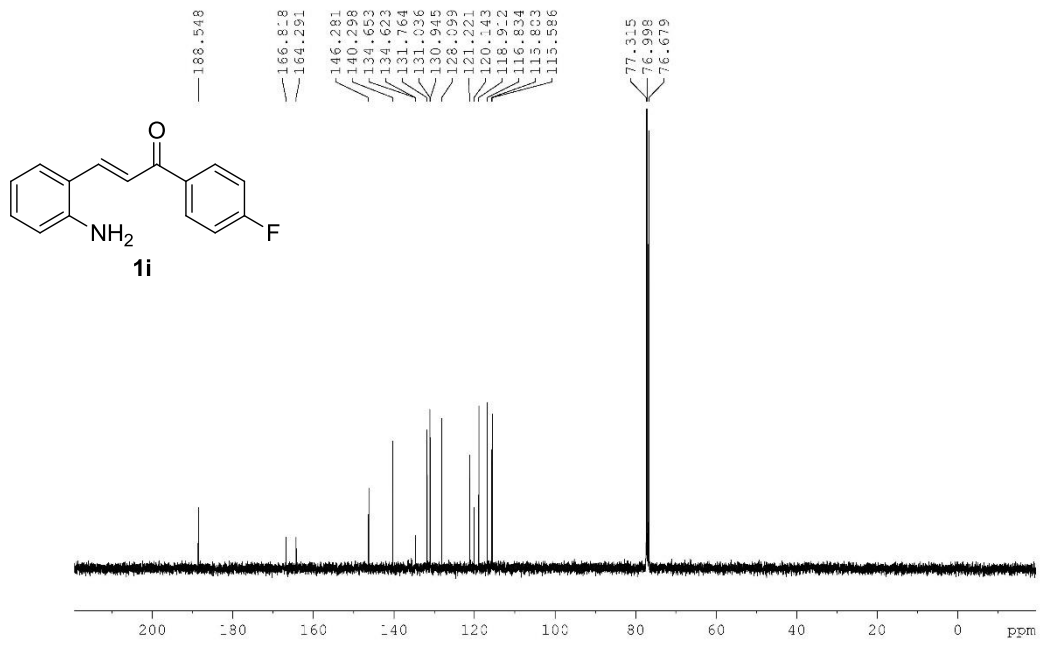


Fig. S20. ^{19}F NMR Spectrum of 1i (376 MHz, $CDCl_3$).

Fig. S21. ^{1}H NMR Spectrum of 1j (500 MHz, $CDCl_3$).

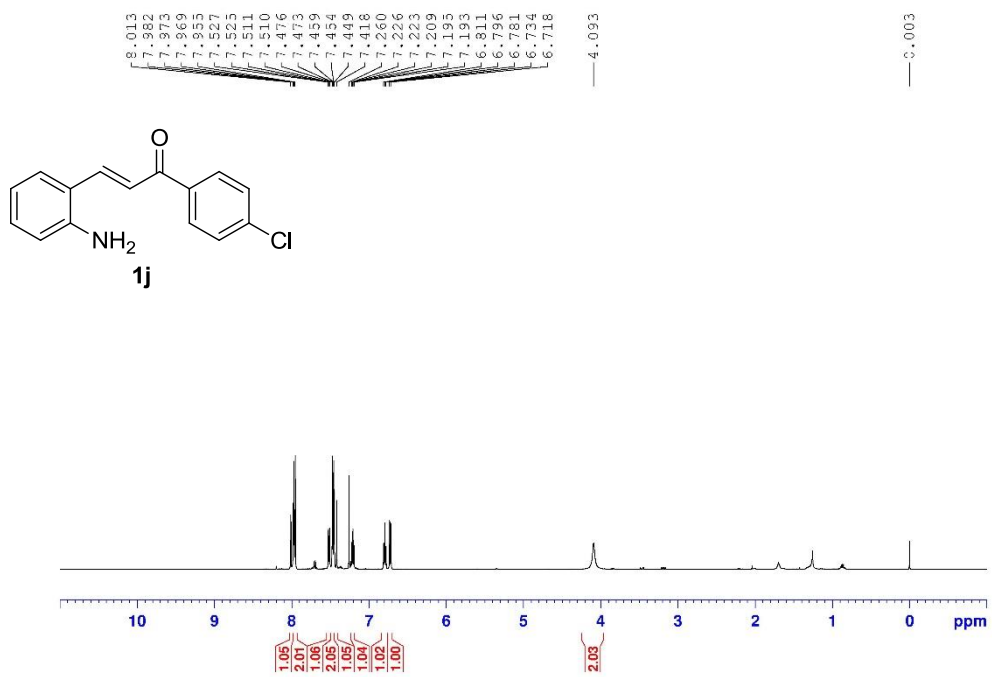


Fig. S22. ^{13}C NMR Spectrum of 1j (125 MHz, $CDCl_3$).

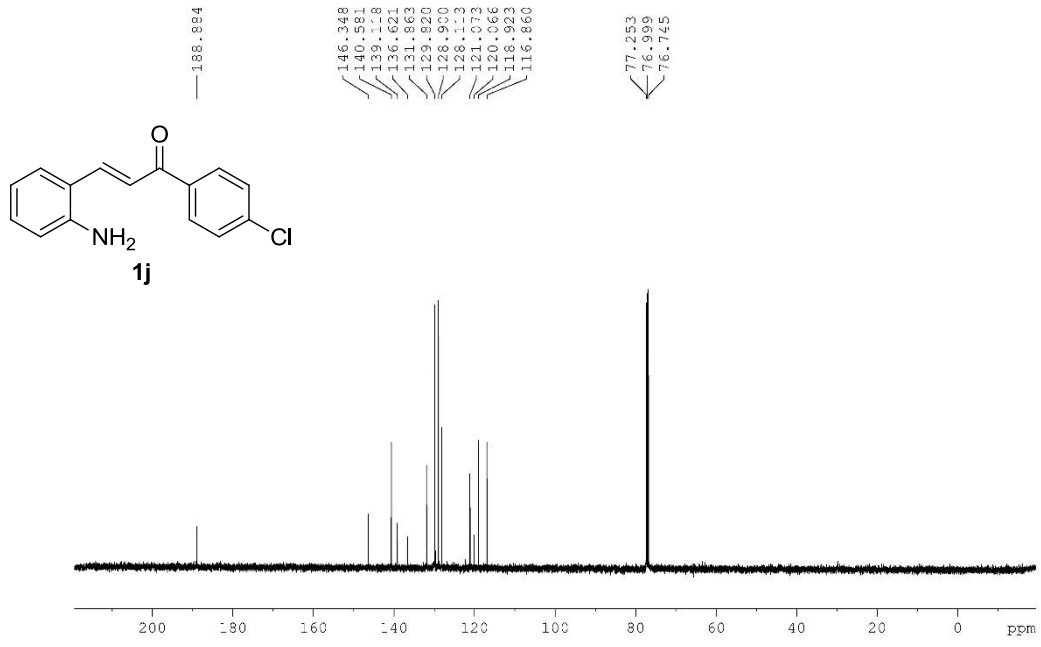


Fig. S23. ^{1}H NMR Spectrum of 1k (300 MHz, $CDCl_3$).

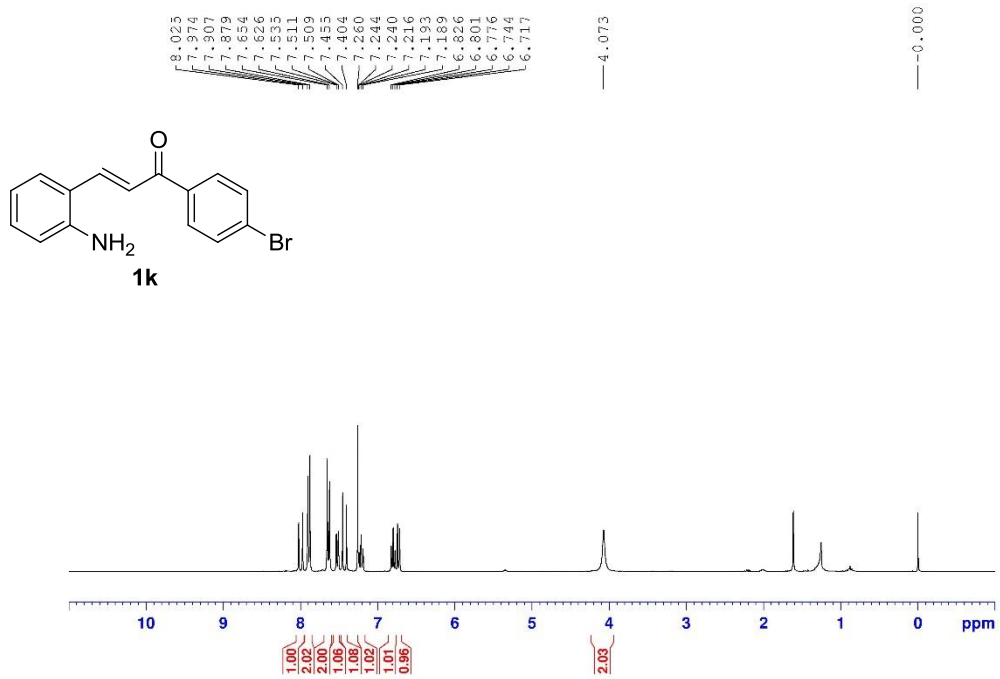


Fig. S24. ^{13}C NMR Spectrum of 1k (75 MHz, $CDCl_3$).

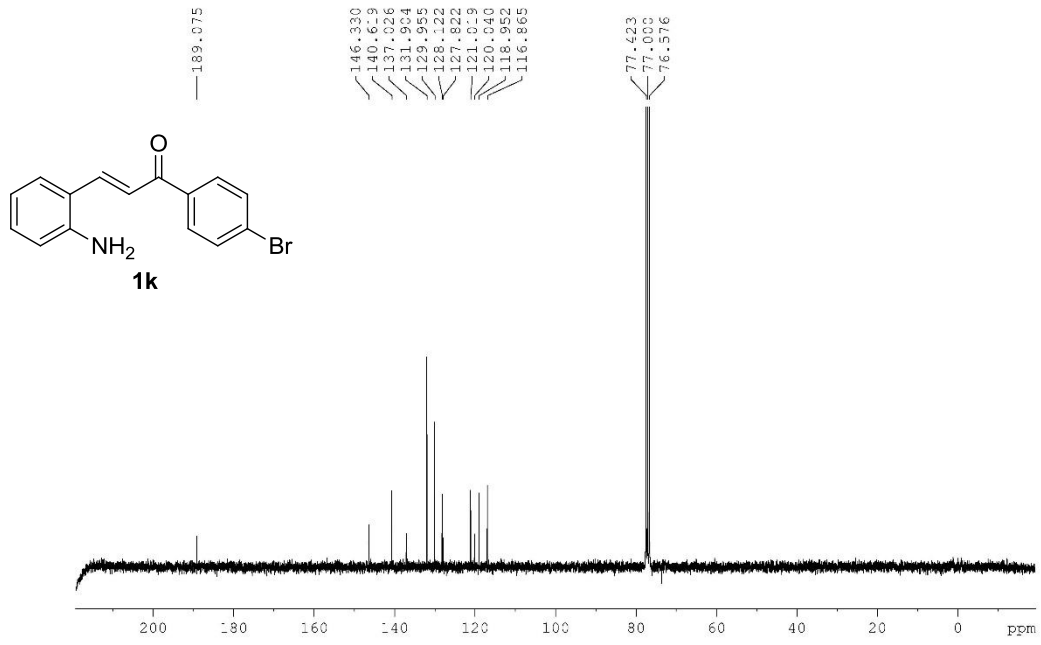


Fig. S25. ^{1}H NMR Spectrum of 1l (300 MHz, $CDCl_3$).

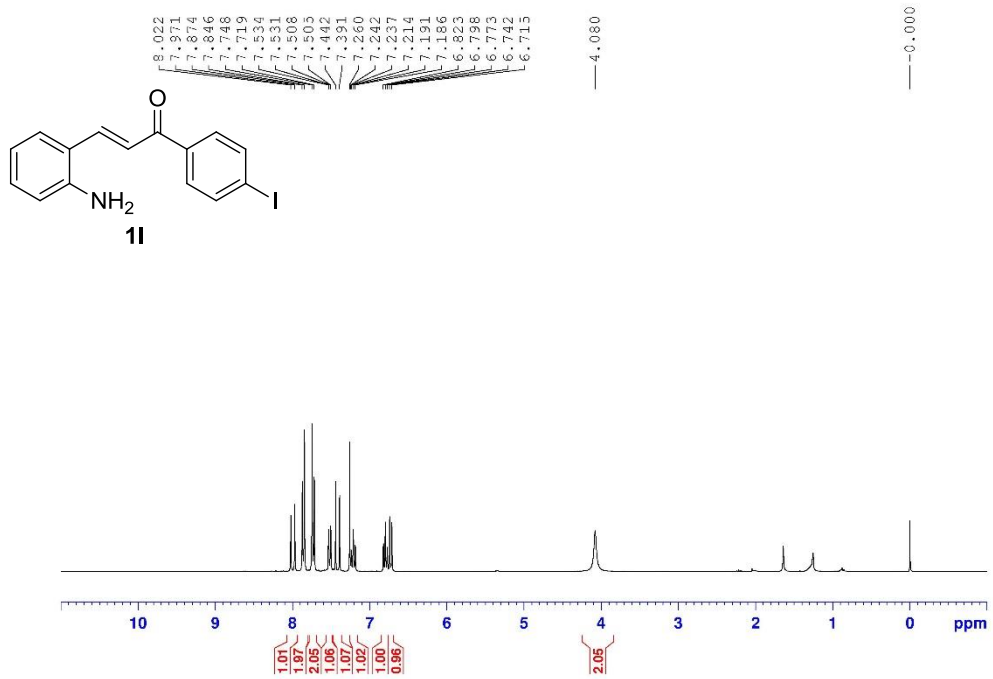


Fig. S26. ^{13}C NMR Spectrum of 1l (75 MHz, $CDCl_3$).

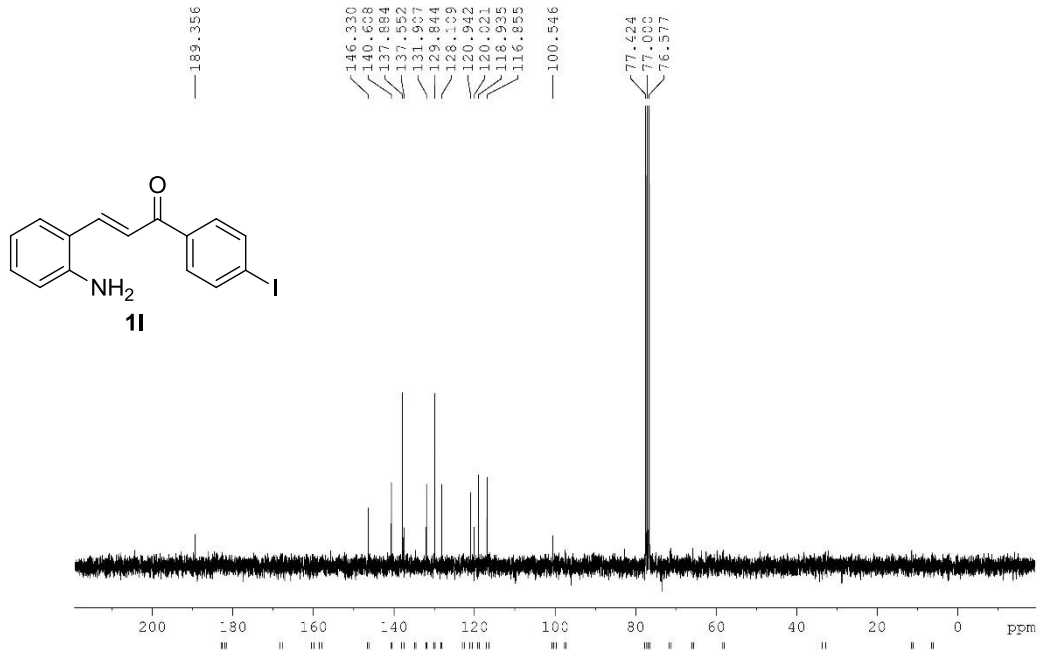


Fig. S27. ^{1}H NMR Spectrum of 1m (400 MHz, $CDCl_3$).

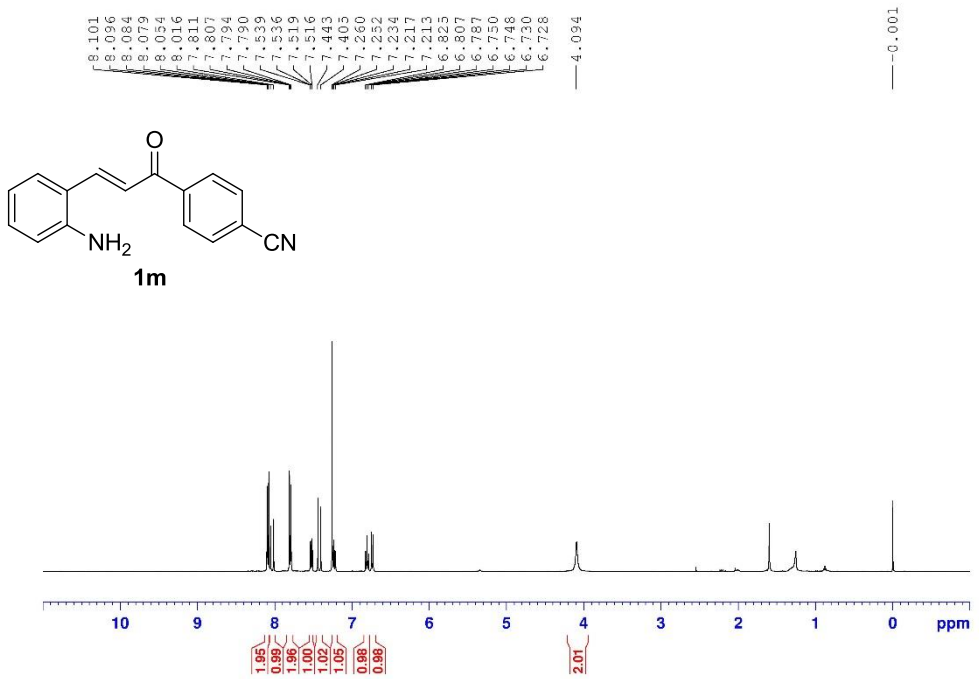


Fig. S28. ^{13}C NMR Spectrum of 1m (100 MHz, $CDCl_3$).

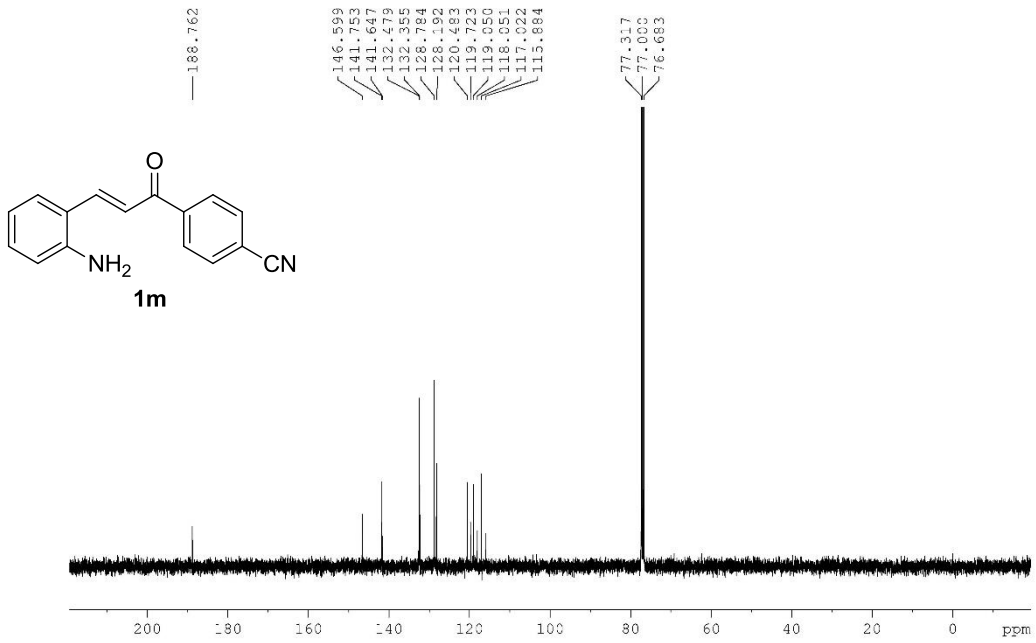


Fig. S29. ^{1}H NMR Spectrum of 1n (400 MHz, CD_3CN).

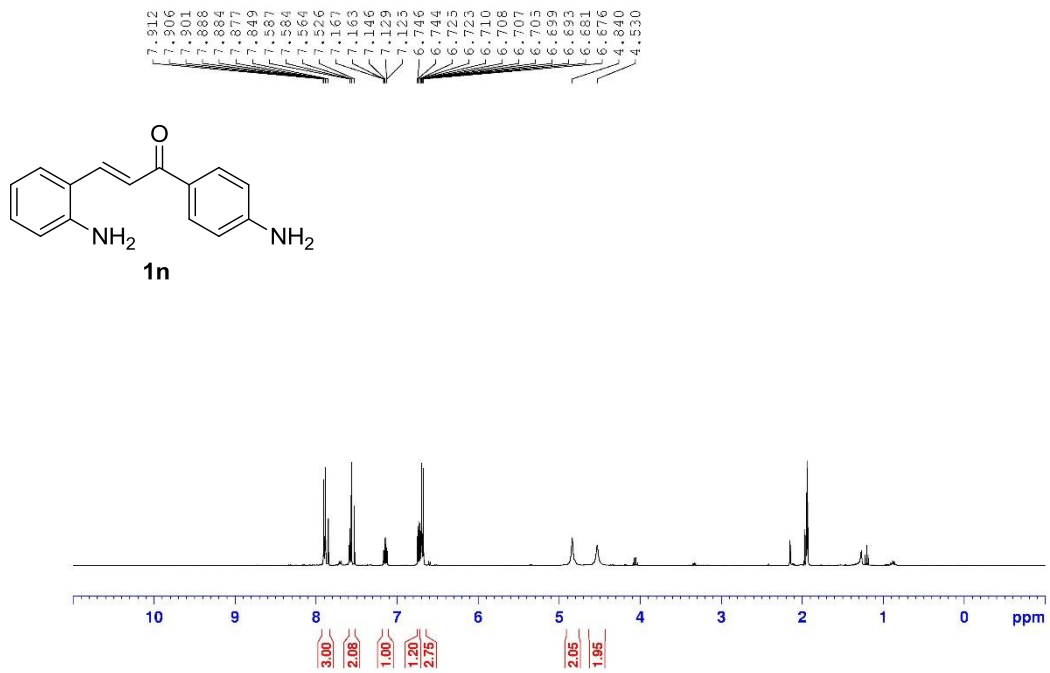


Fig. S30. ^{13}C NMR Spectrum of 1n (100 MHz, CD_3CN).

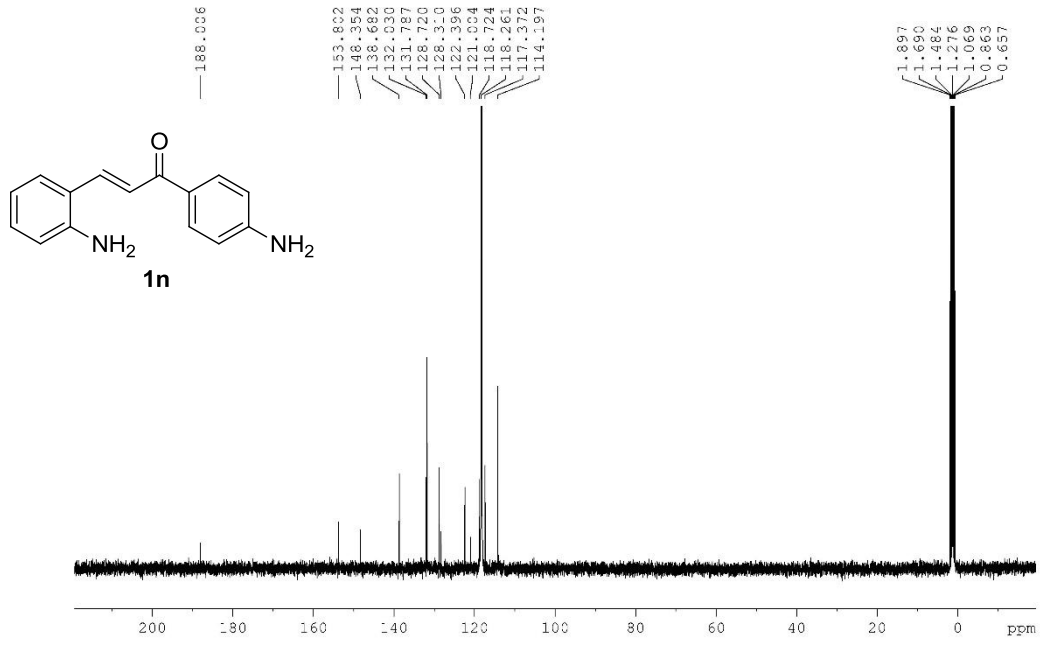


Fig. S31. ^{1}H NMR Spectrum of 1o (300 MHz, $CDCl_3$).

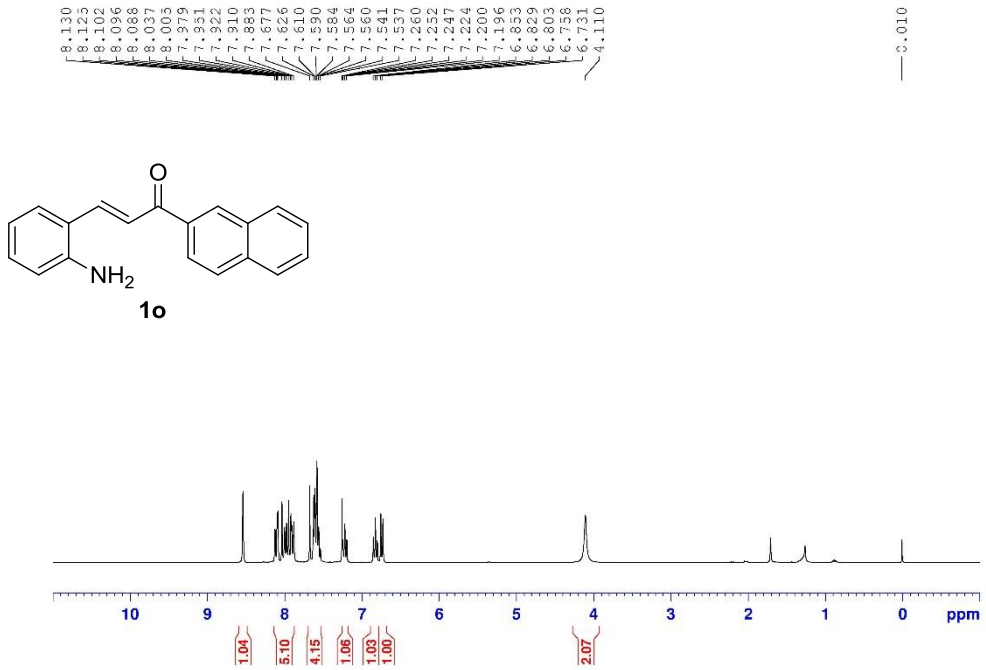


Fig. S32. ^{13}C NMR Spectrum of 1o (75 MHz, $CDCl_3$).

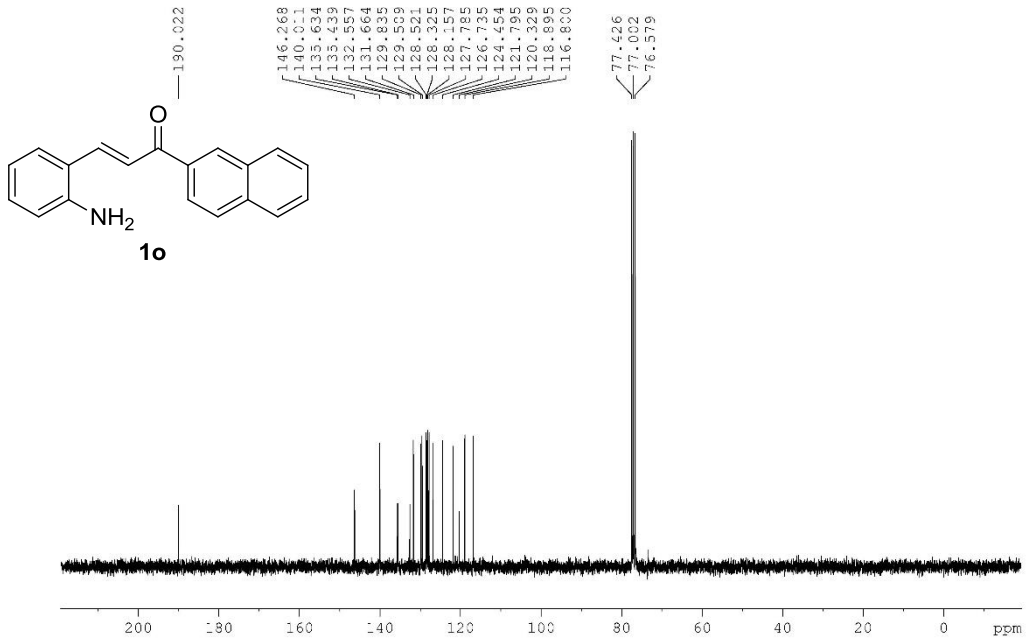


Fig. S33. ^{1}H NMR Spectrum of 1p (400 MHz, $CDCl_3$).

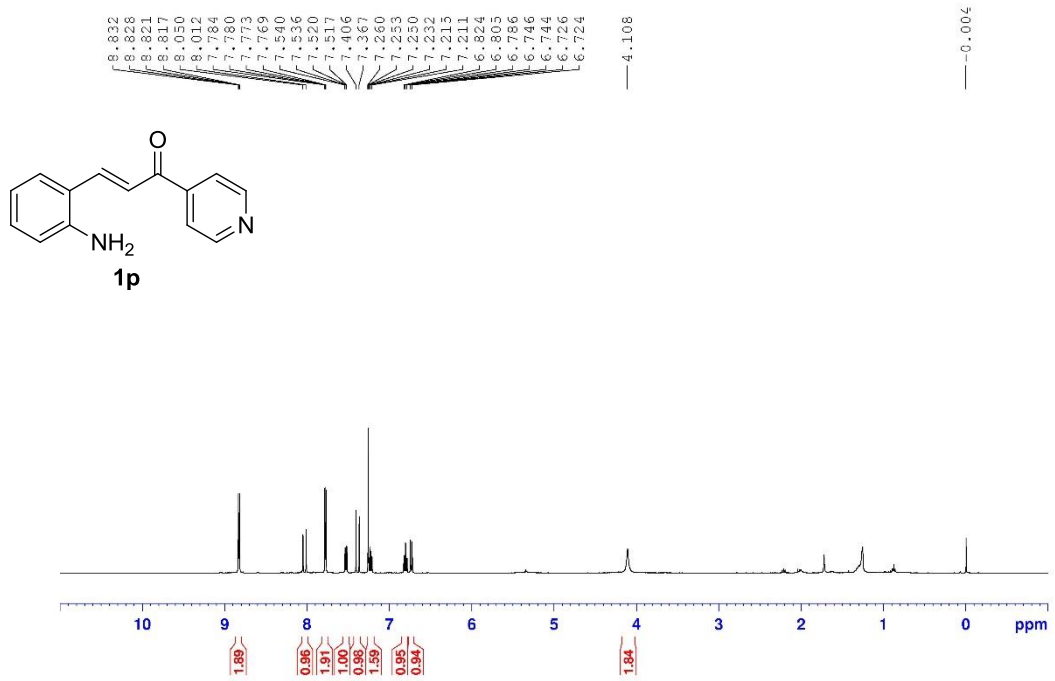


Fig. S34. ^{13}C NMR Spectrum of 1p (100 MHz, $CDCl_3$).

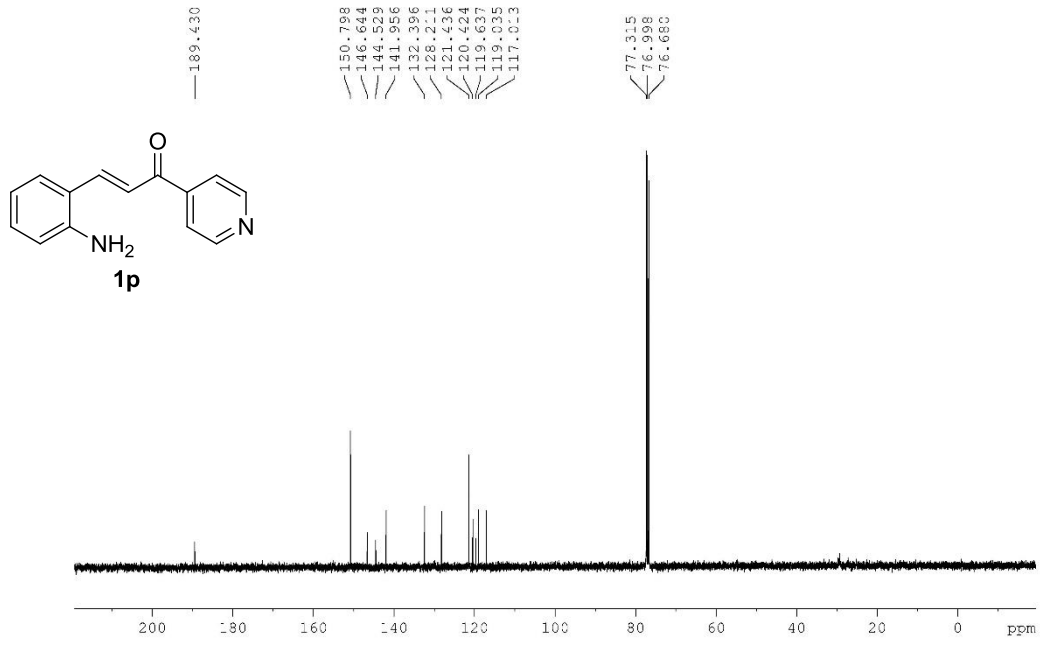


Fig. S35. ^{1}H NMR Spectrum of 1q (500 MHz, $CDCl_3$).

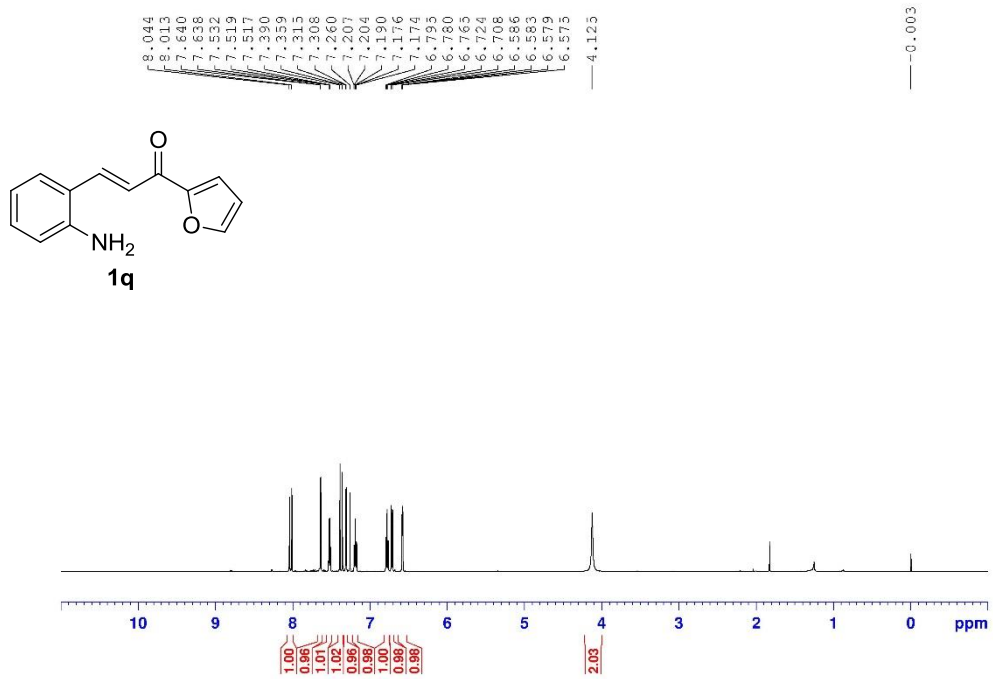


Fig. S36. ^{13}C NMR Spectrum of 1q (125 MHz, $CDCl_3$).

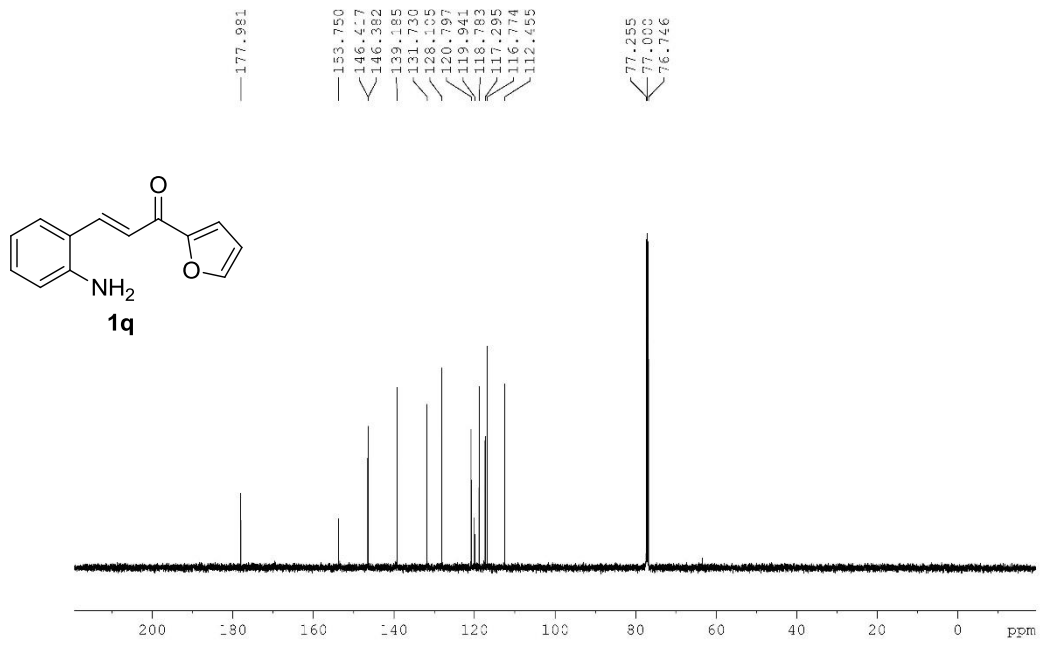


Fig. S37. ^{1}H NMR Spectrum of 1r (400 MHz, $CDCl_3$).

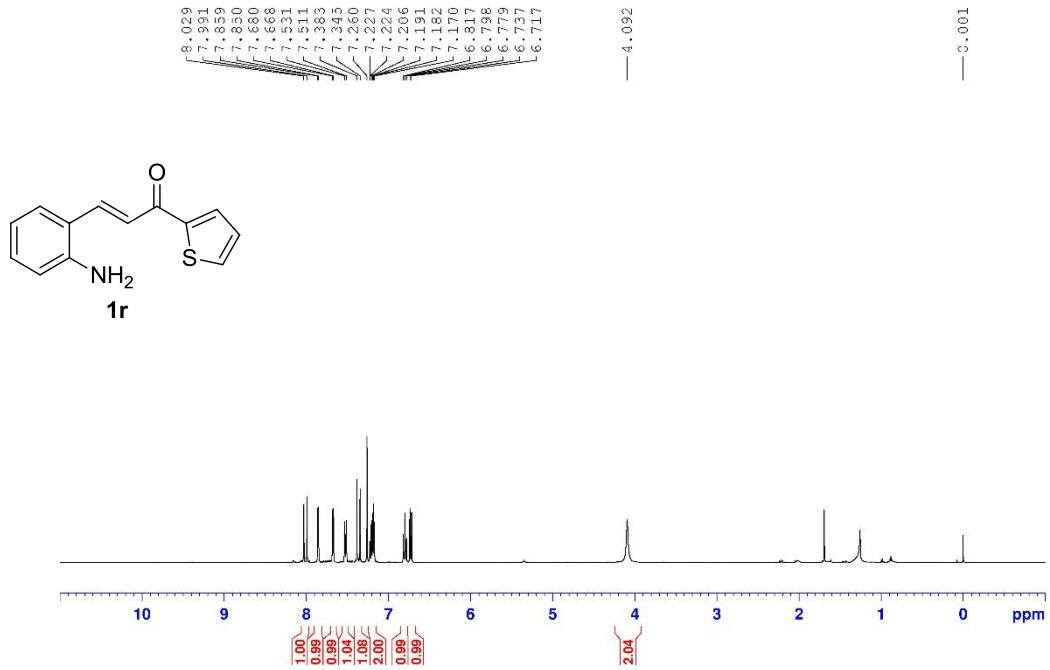


Fig. S38. ^{13}C NMR Spectrum of 1r (100 MHz, $CDCl_3$).

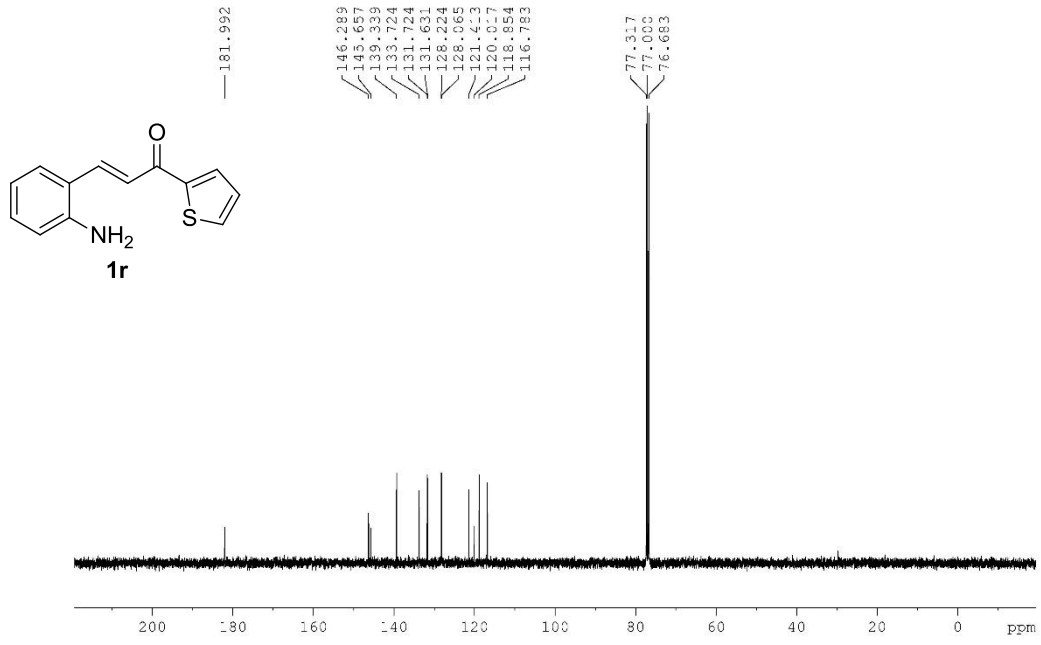


Fig. S39. ^{1}H NMR Spectrum of 1s (400 MHz, $CDCl_3$).

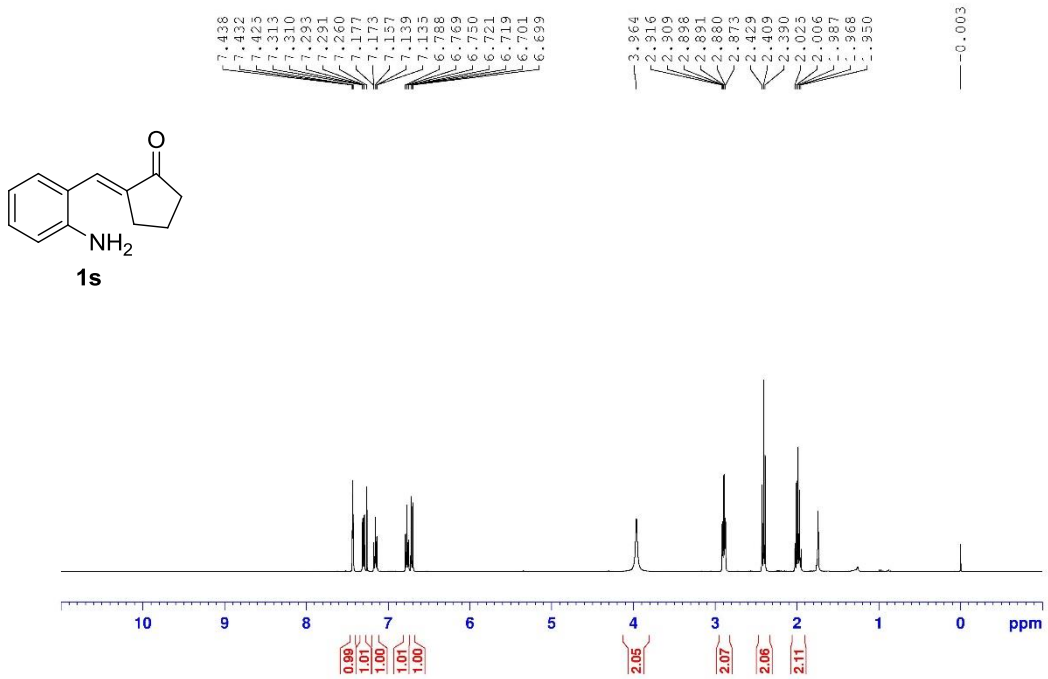


Fig. S40. ^{13}C NMR Spectrum of 1s (100 MHz, $CDCl_3$).

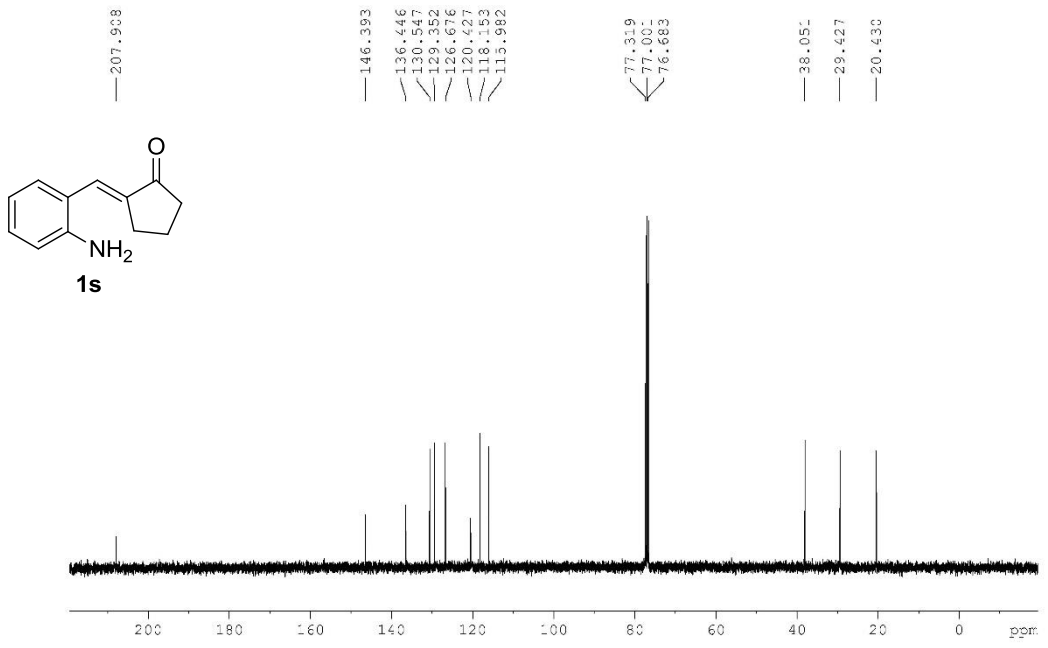


Fig. S41. ^{1}H NMR Spectrum of 1t (500 MHz, $CDCl_3$).

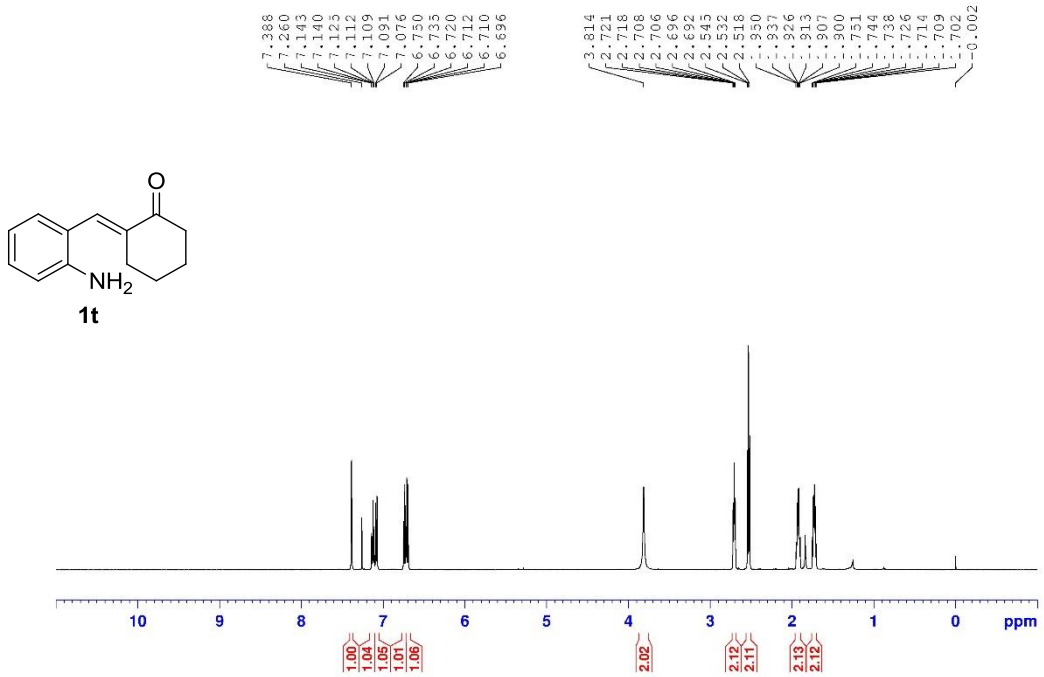


Fig. S42. ^{13}C NMR Spectrum of 1t (125 MHz, $CDCl_3$).

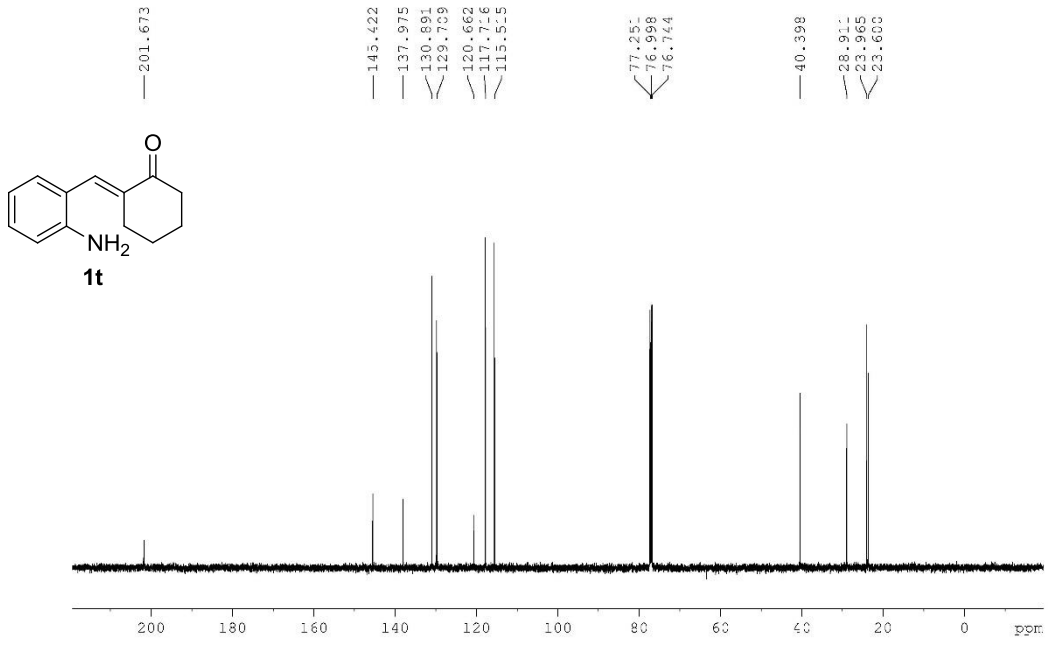


Fig. S43. ^{1}H NMR Spectrum of 1u (500 MHz, $CDCl_3$).

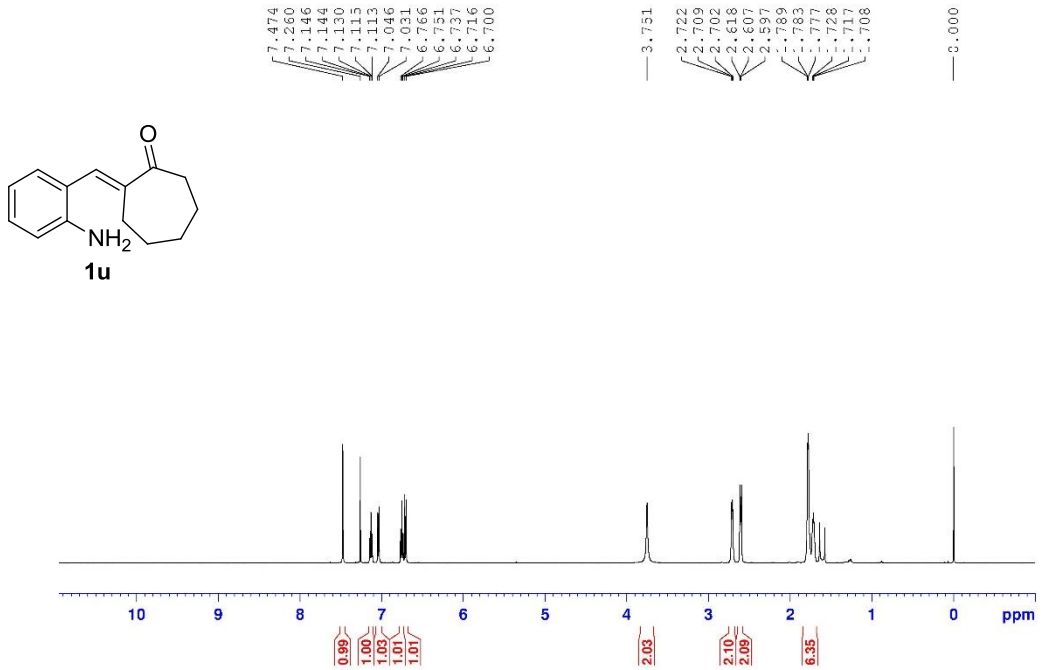


Fig. S44. ^{13}C NMR Spectrum of 1u (125 MHz, $CDCl_3$).

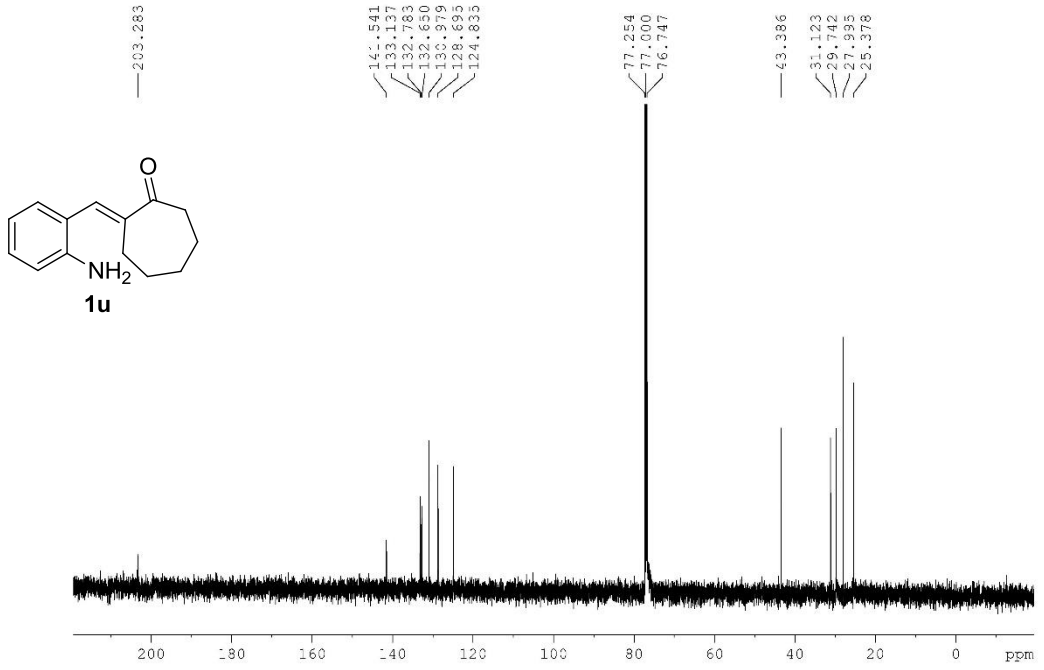


Fig. S45. ^{1}H NMR Spectrum of 1v (400 MHz, DMSO-d_6**).**

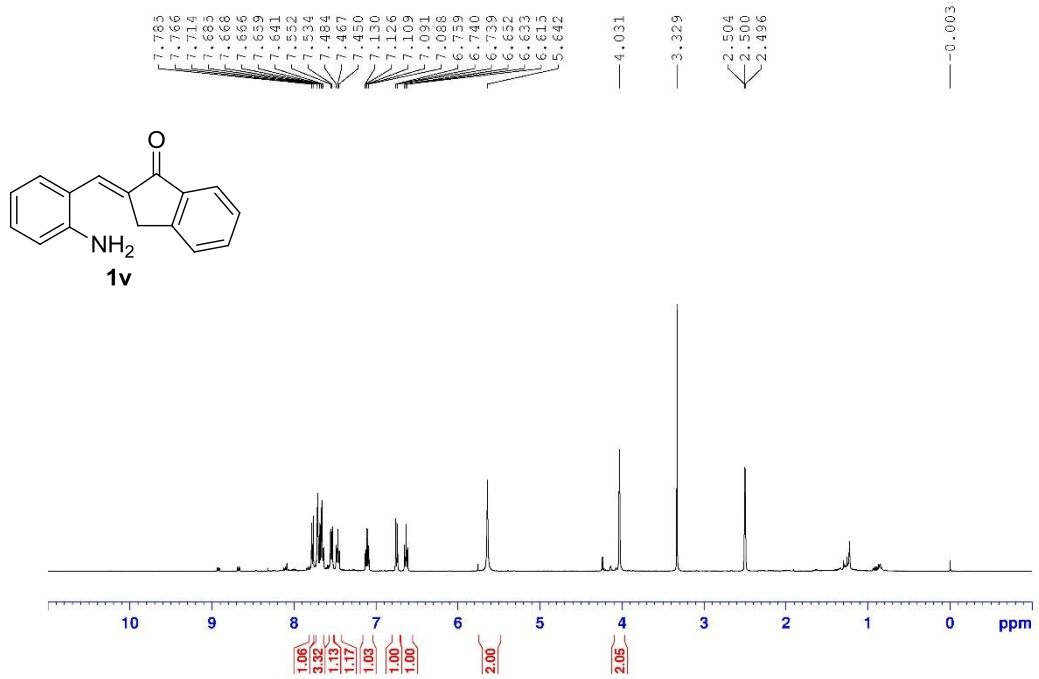


Fig. S46. ^{13}C NMR Spectrum of 1v (100 MHz, DMSO-d_6**).**

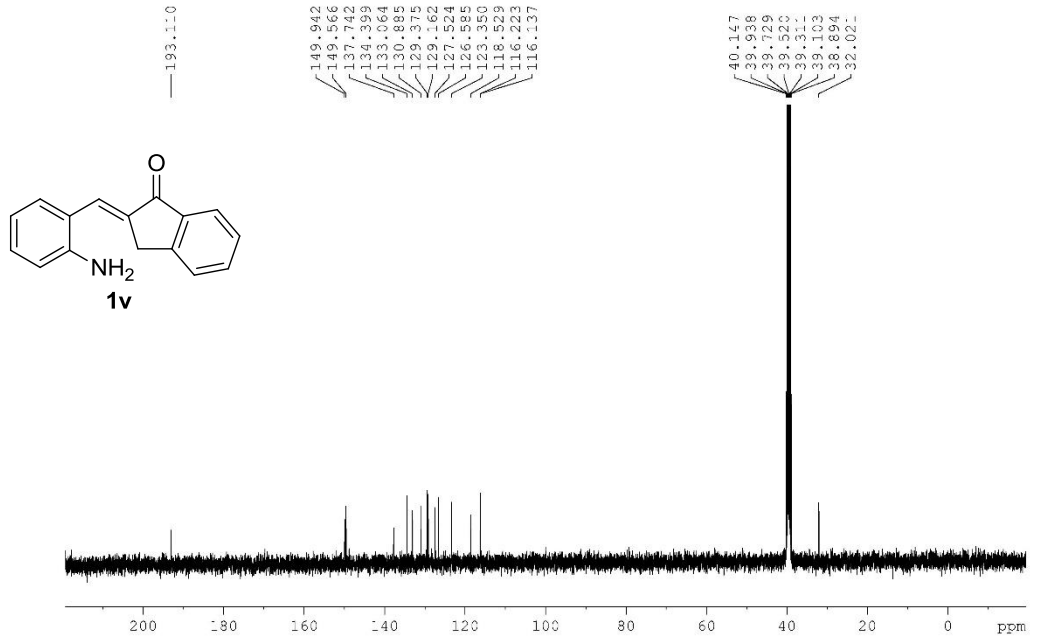


Fig. S47. ^{1}H NMR Spectrum of 1w (400 MHz, $CDCl_3$).

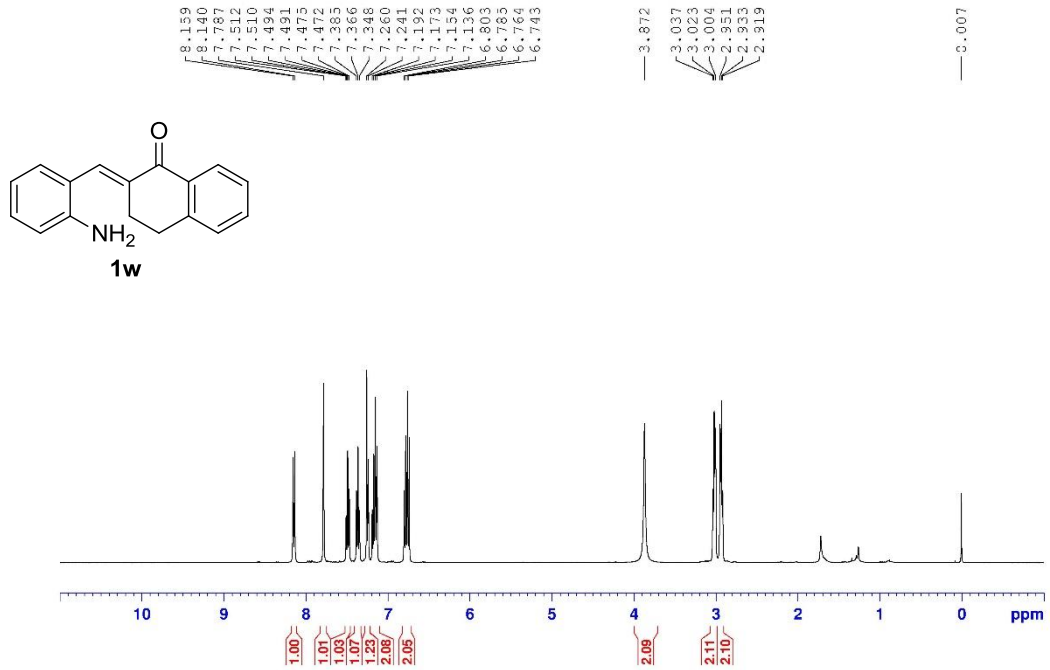


Fig. S48. ^{13}C NMR Spectrum of 1w (100 MHz, $CDCl_3$).

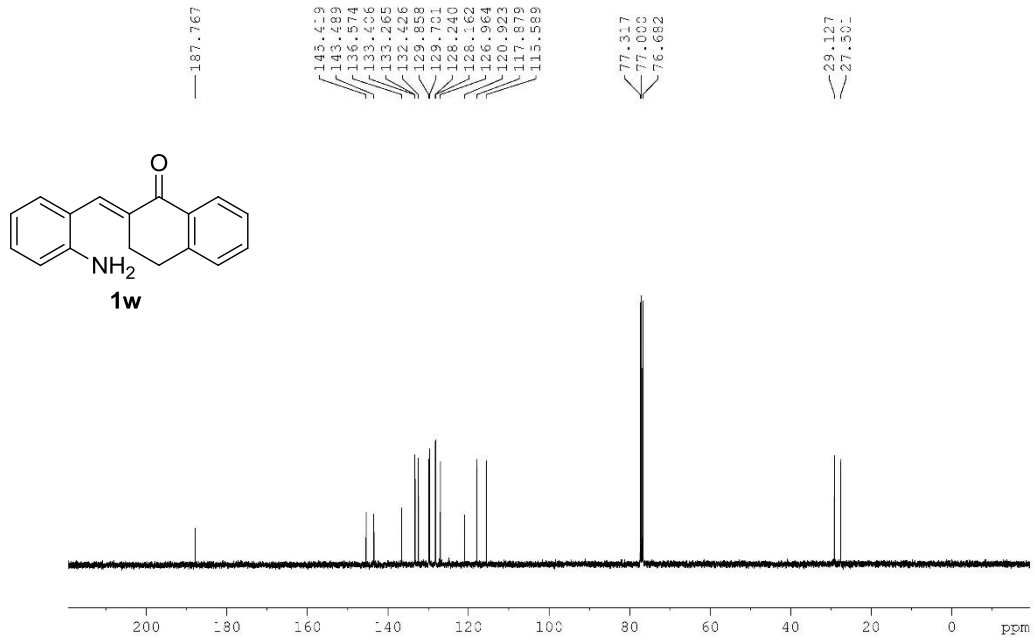


Fig. S49. ^{1}H NMR Spectrum of 1x (400 MHz, $CDCl_3$).

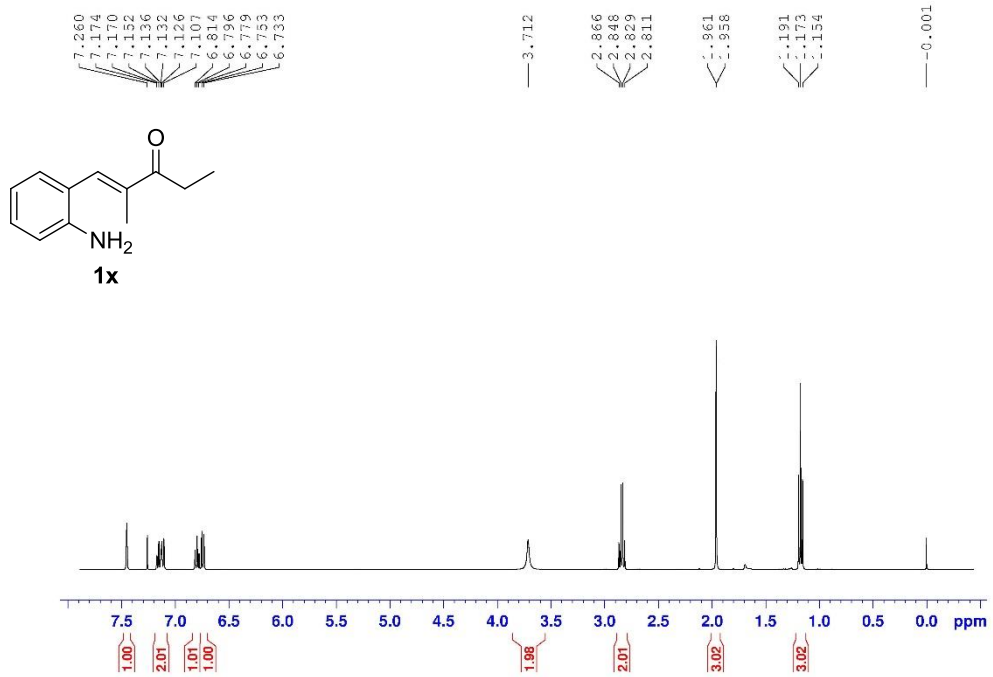


Fig. S50. ^{13}C NMR Spectrum of 1x (100 MHz, $CDCl_3$).

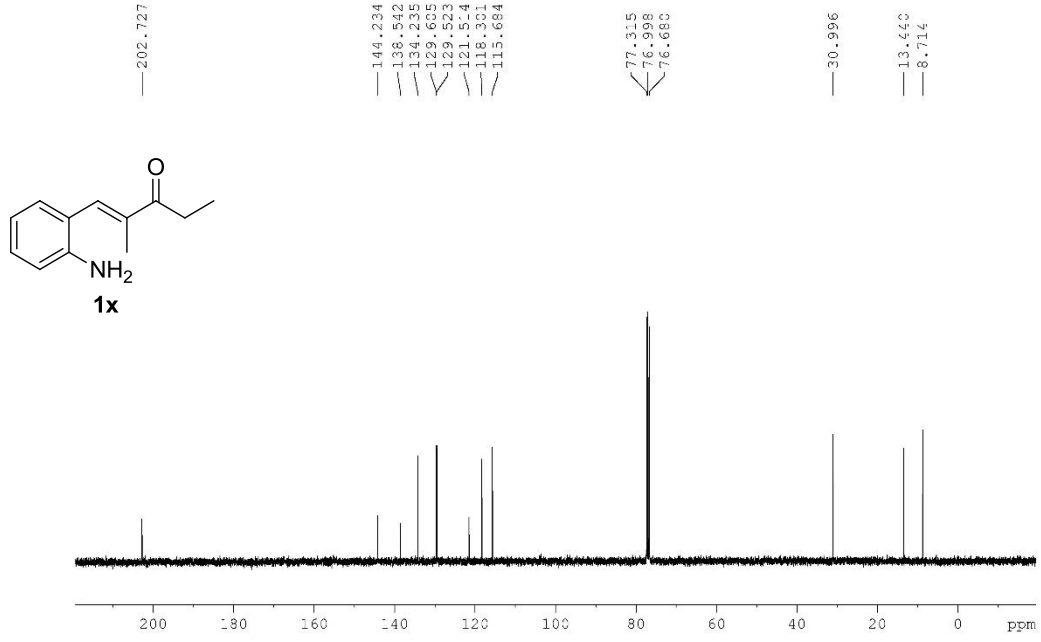


Fig. S51. ^{1}H NMR Spectrum of 1y (400 MHz, $CDCl_3$).

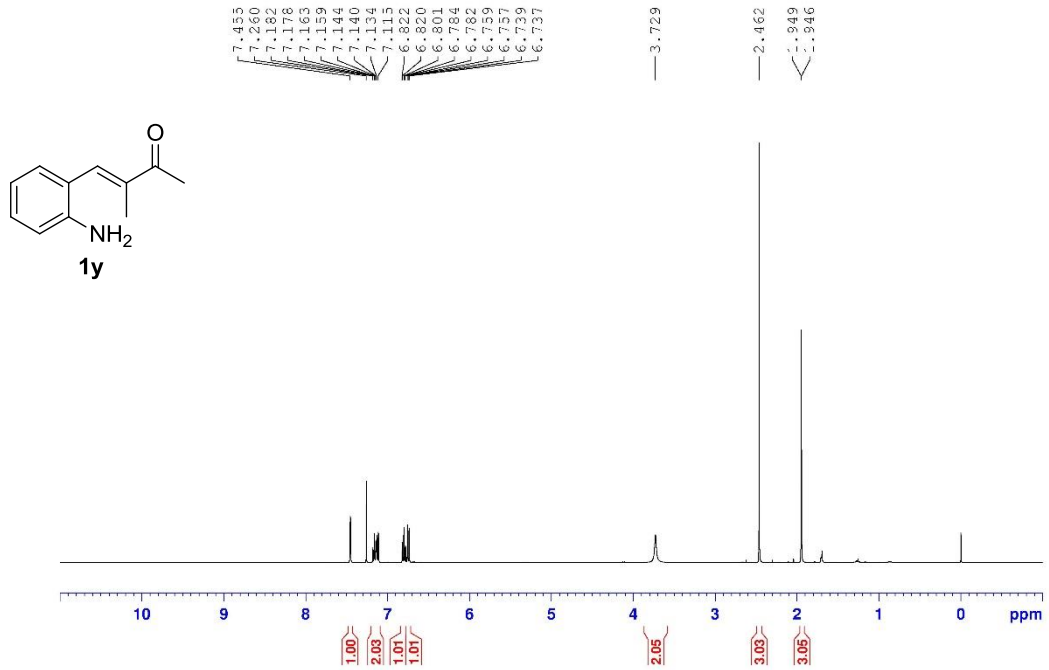


Fig. S52. ^{13}C NMR Spectrum of 1y (100 MHz, $CDCl_3$).

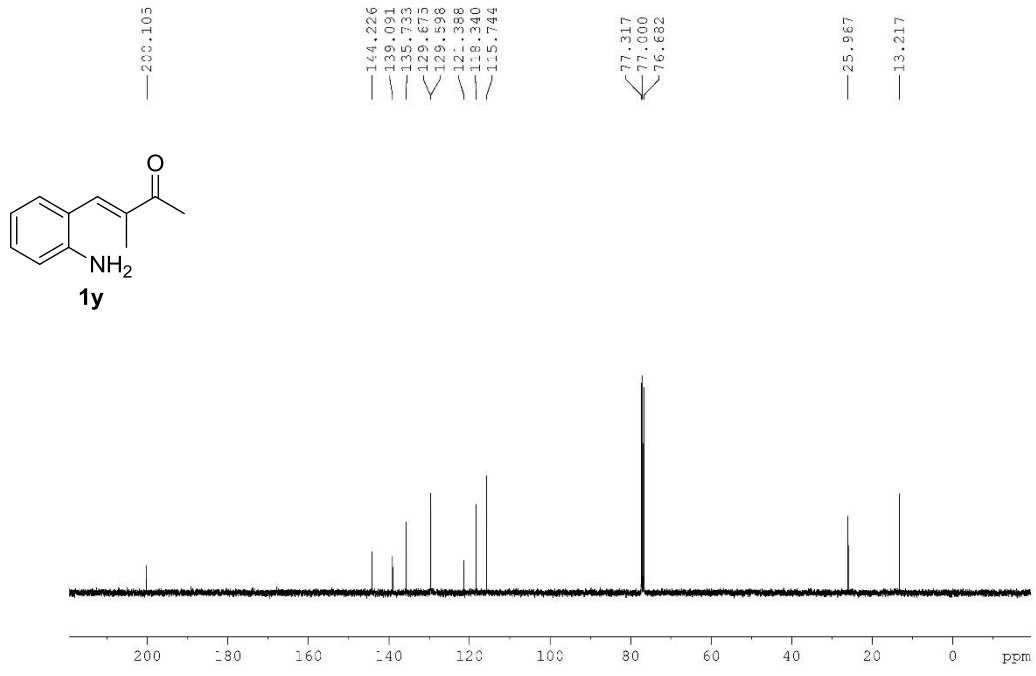


Fig. S53. ^{1}H NMR Spectrum of 1z (400 MHz, $CDCl_3$).

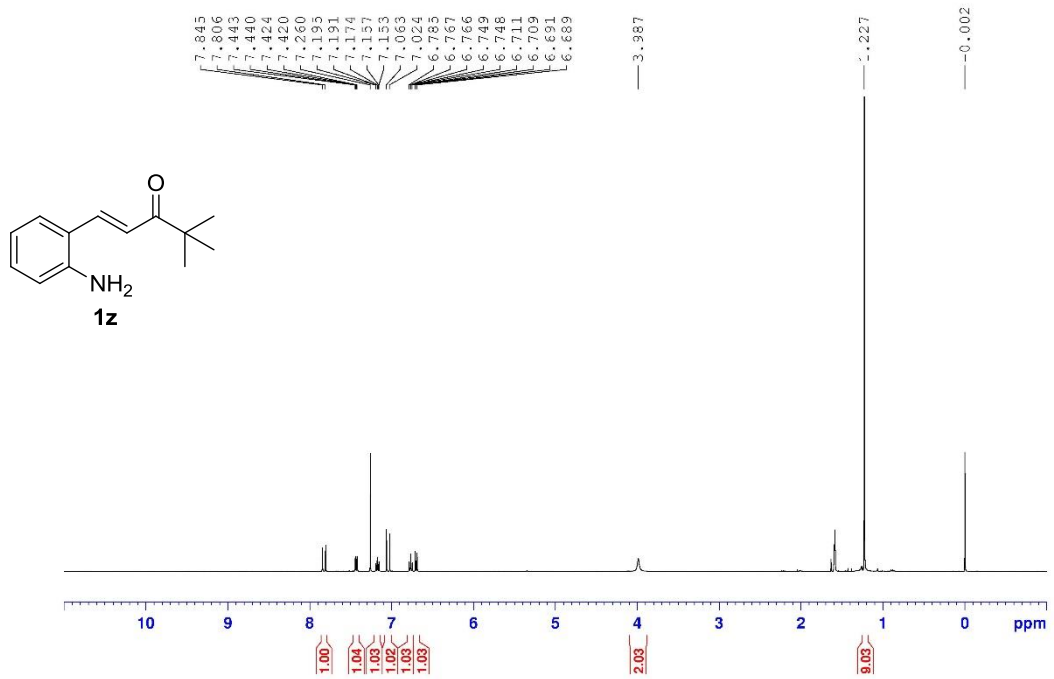


Fig. S54. ^{13}C NMR Spectrum of 1z (100 MHz, $CDCl_3$).

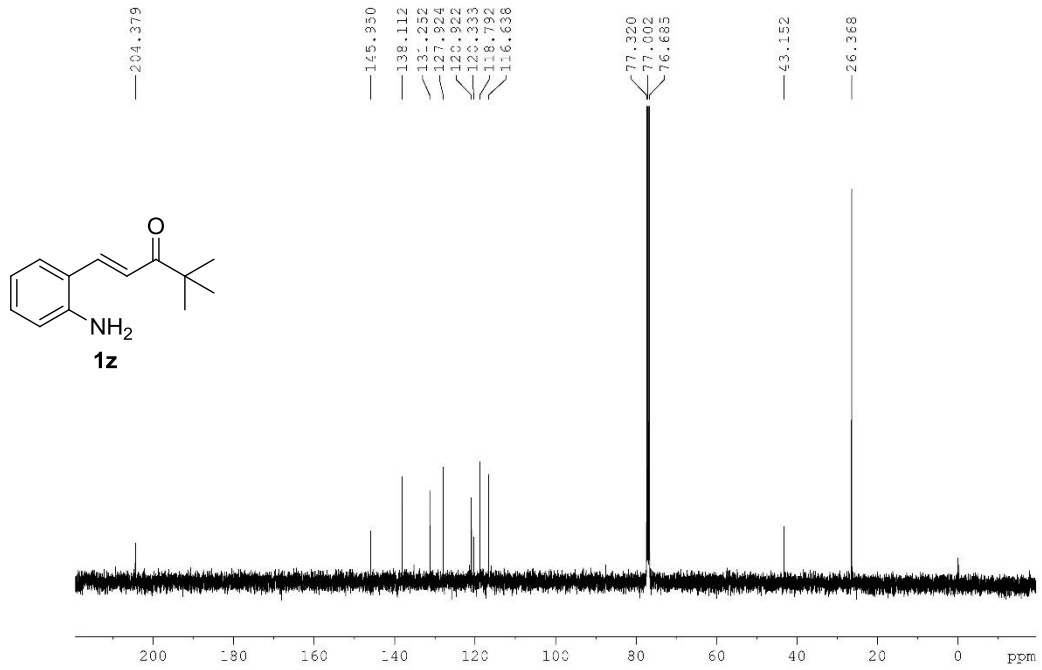


Fig. S55. ^{1}H NMR Spectrum of 1aa (400 MHz, $CDCl_3$).

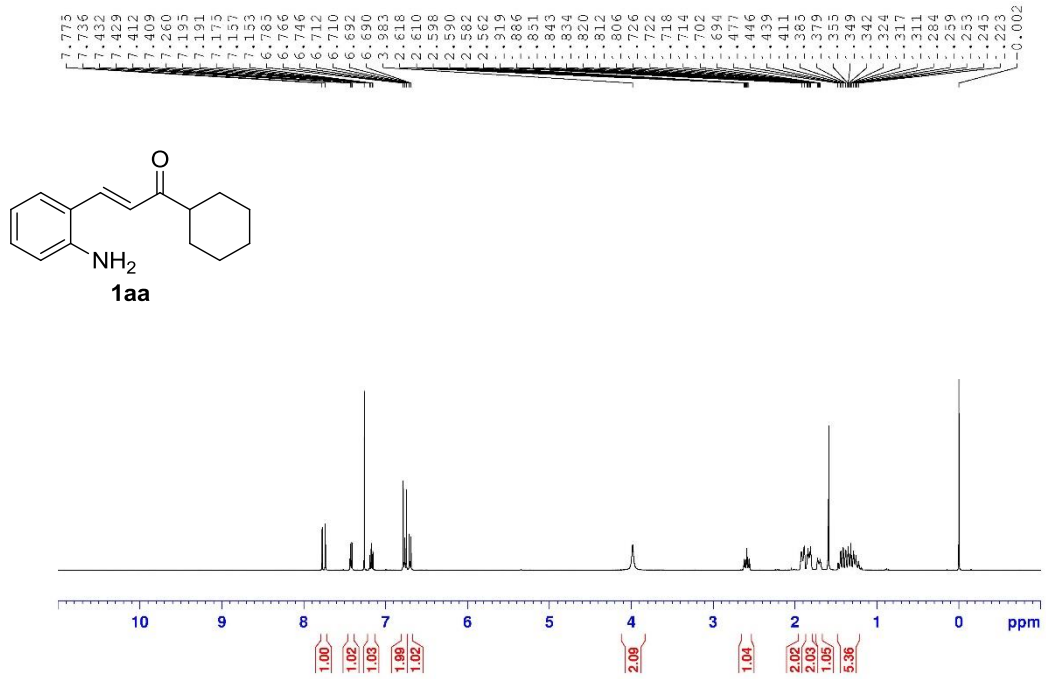


Fig. S56. ^{13}C NMR Spectrum of 1aa (100 MHz, $CDCl_3$).

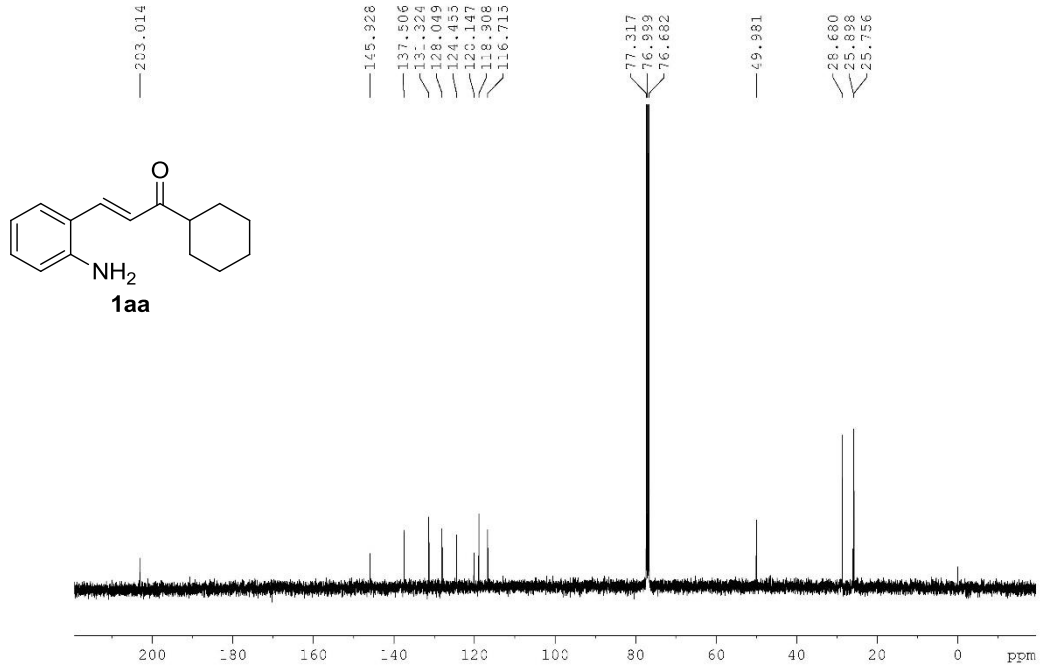


Fig. S57. ^{1}H NMR Spectrum of 1ab (400 MHz, $CDCl_3$).

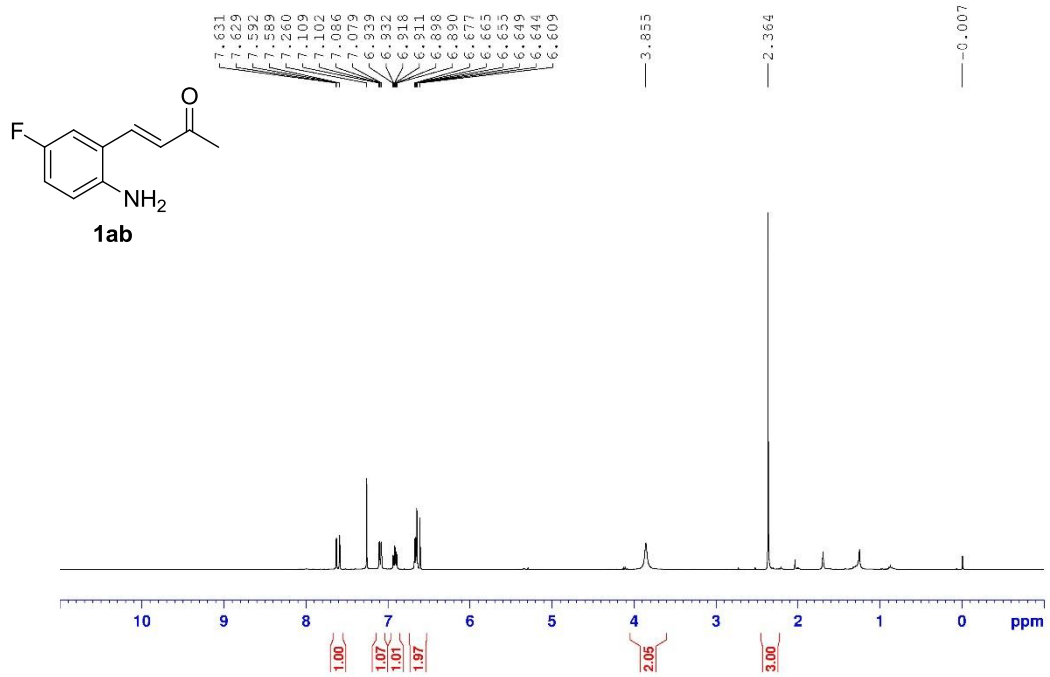


Fig. S58. ^{13}C NMR Spectrum of 1ab (100 MHz, $CDCl_3$).

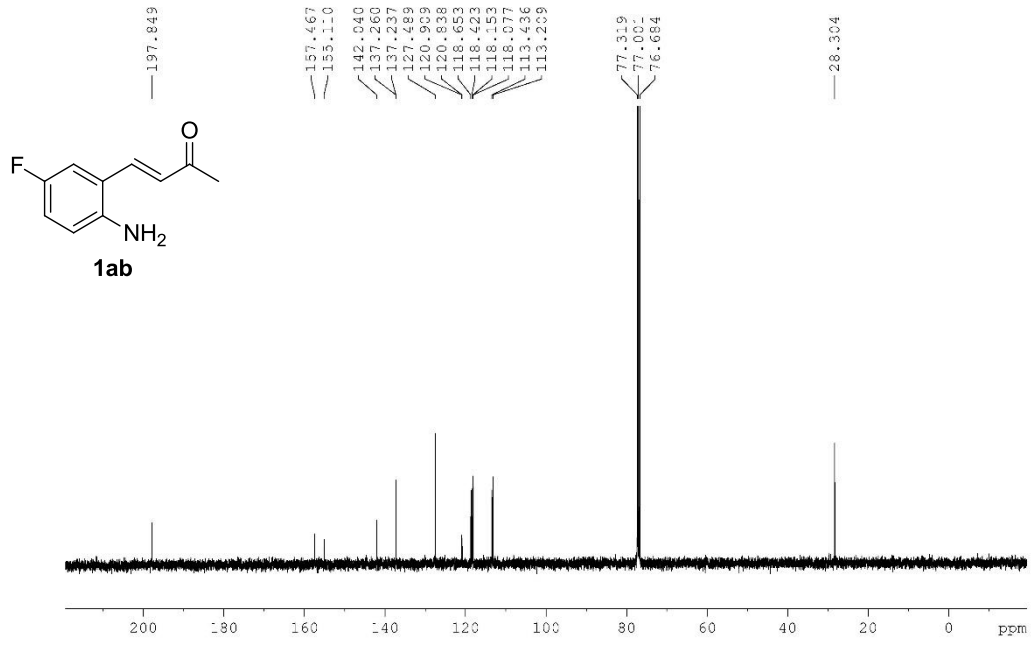


Fig. S59. ^{19}F NMR Spectrum of 1ab (376 MHz, $CDCl_3$).

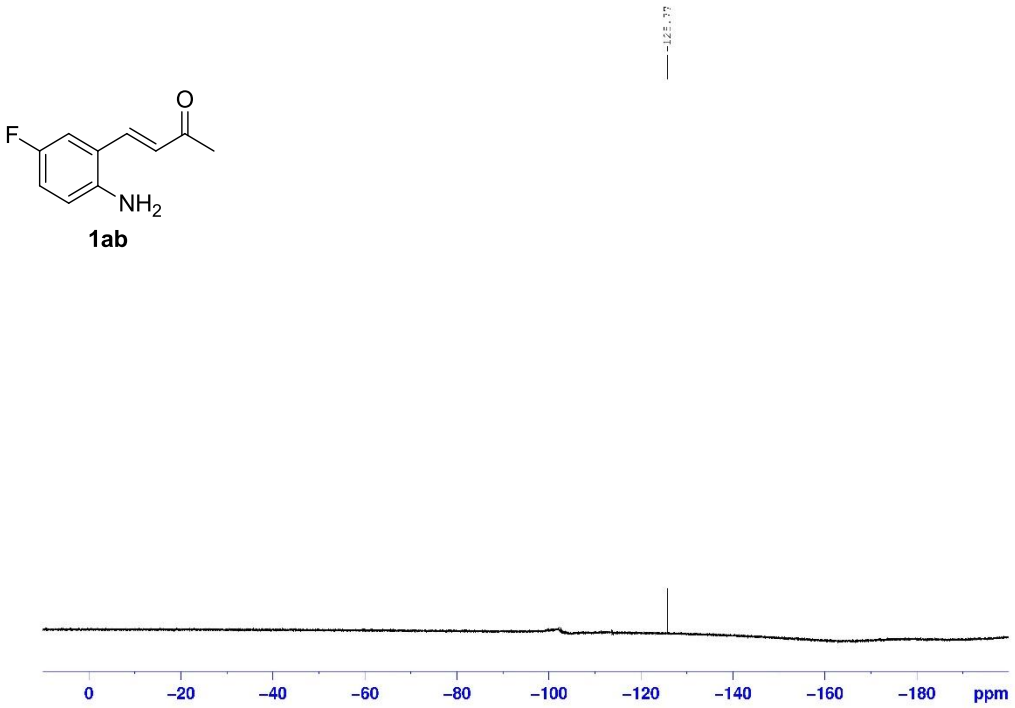


Fig. S60. ^{1}H NMR Spectrum of 1ac (400 MHz, $CDCl_3$).

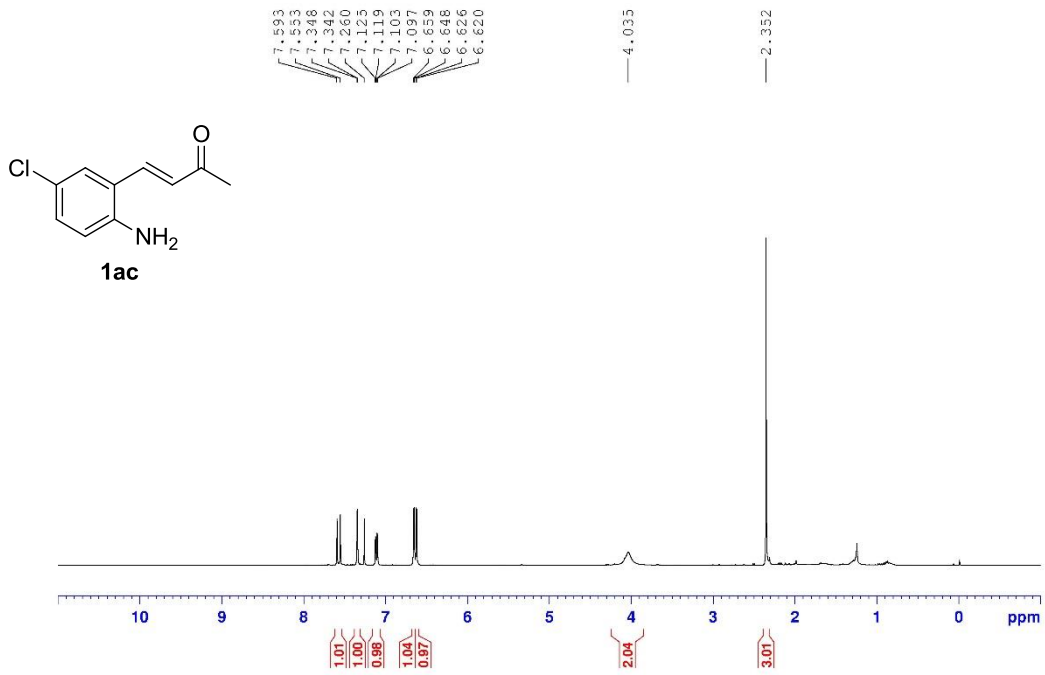


Fig. S61. ^{13}C NMR Spectrum of 1ac (100 MHz, $CDCl_3$).

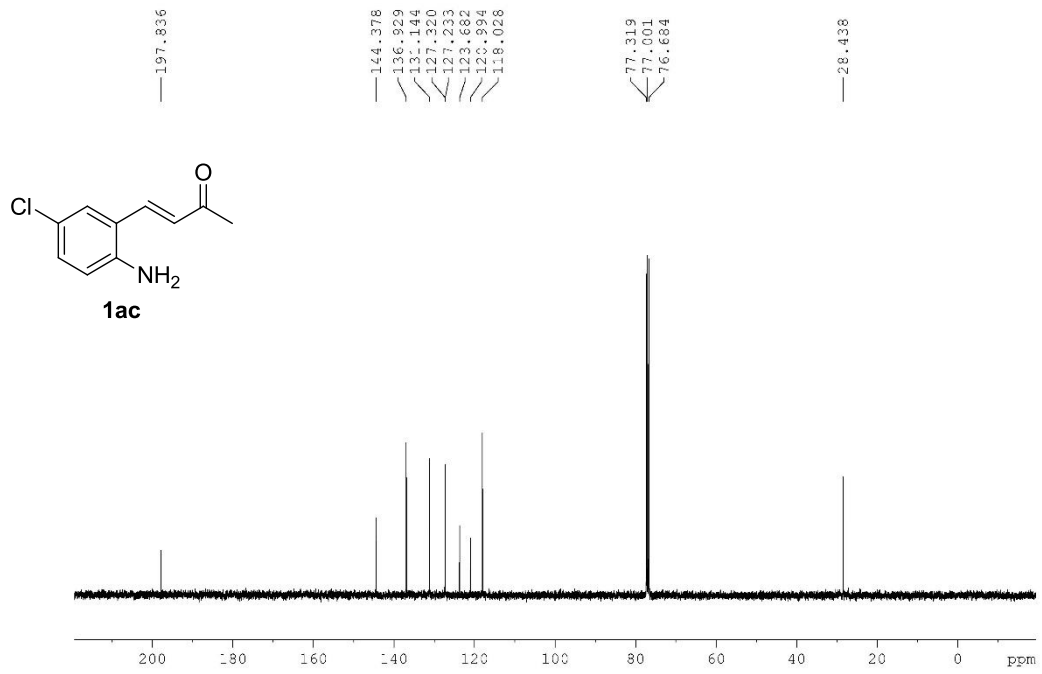


Fig. S62. ^{1}H NMR Spectrum of 1ad (400 MHz, $CDCl_3$).

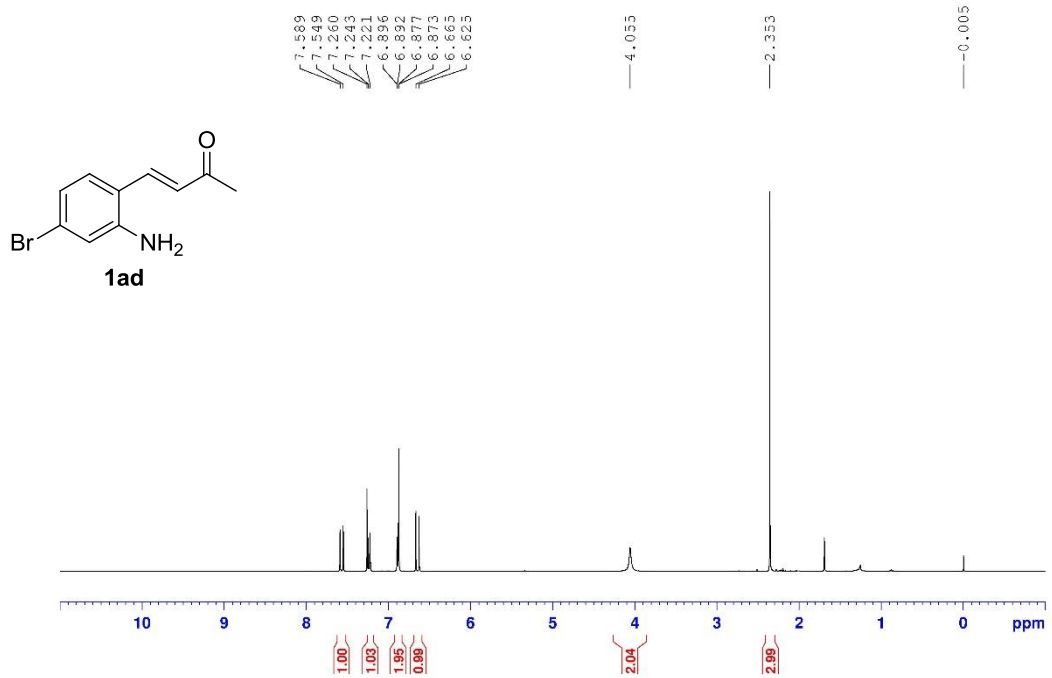


Fig. S63. ^{13}C NMR Spectrum of 1ad (100 MHz, $CDCl_3$).

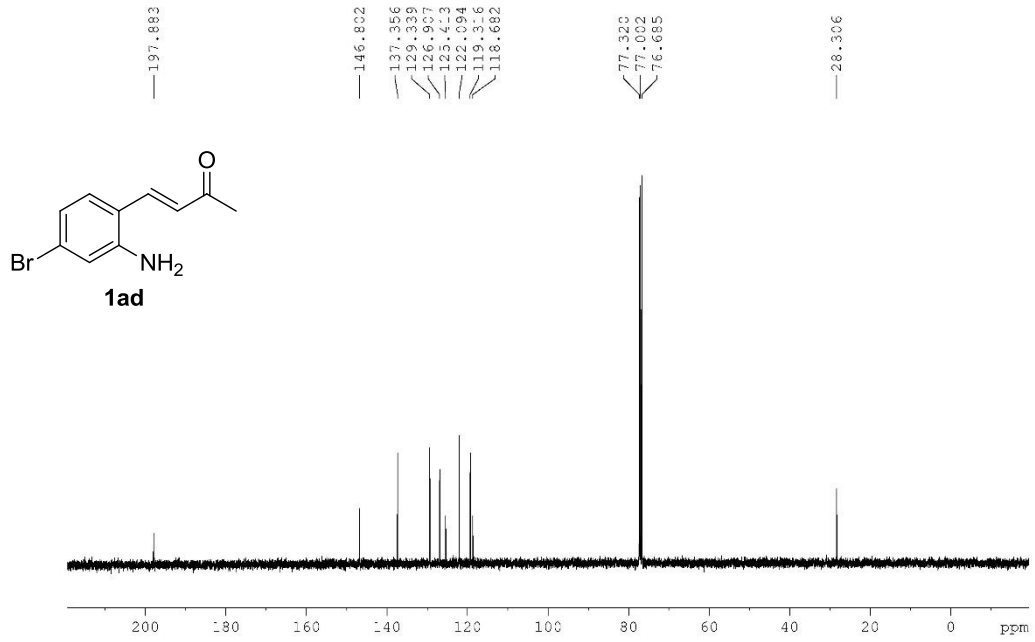


Fig. S64. ^{1}H NMR Spectrum of 1ae (500 MHz, $CDCl_3$).

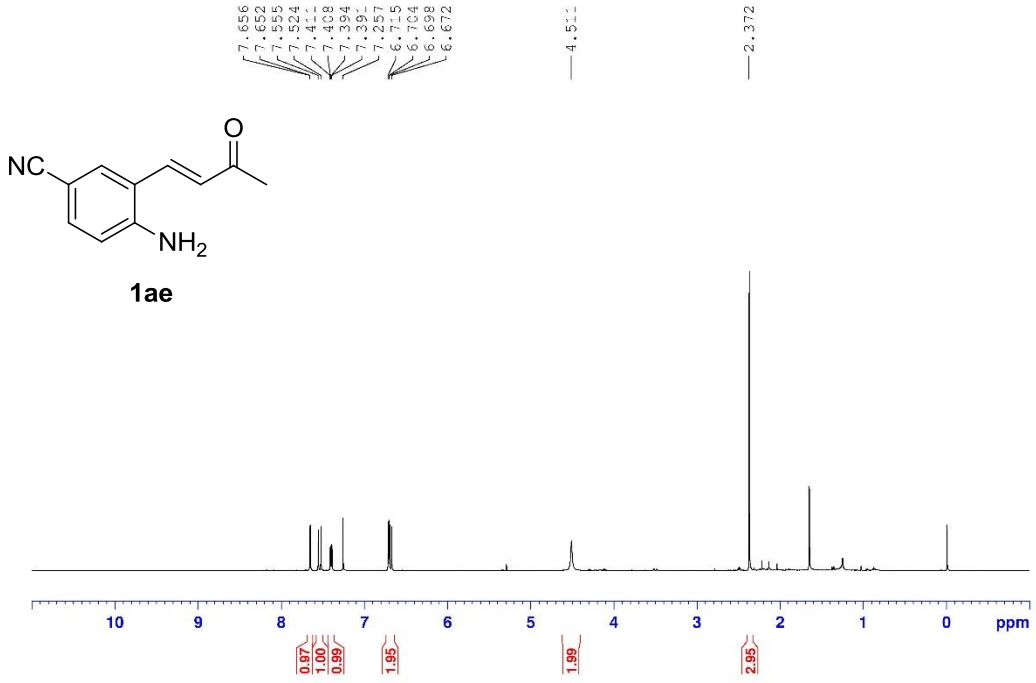


Fig. S65. ^{13}C NMR Spectrum of 1ae (125 MHz, $CDCl_3$).

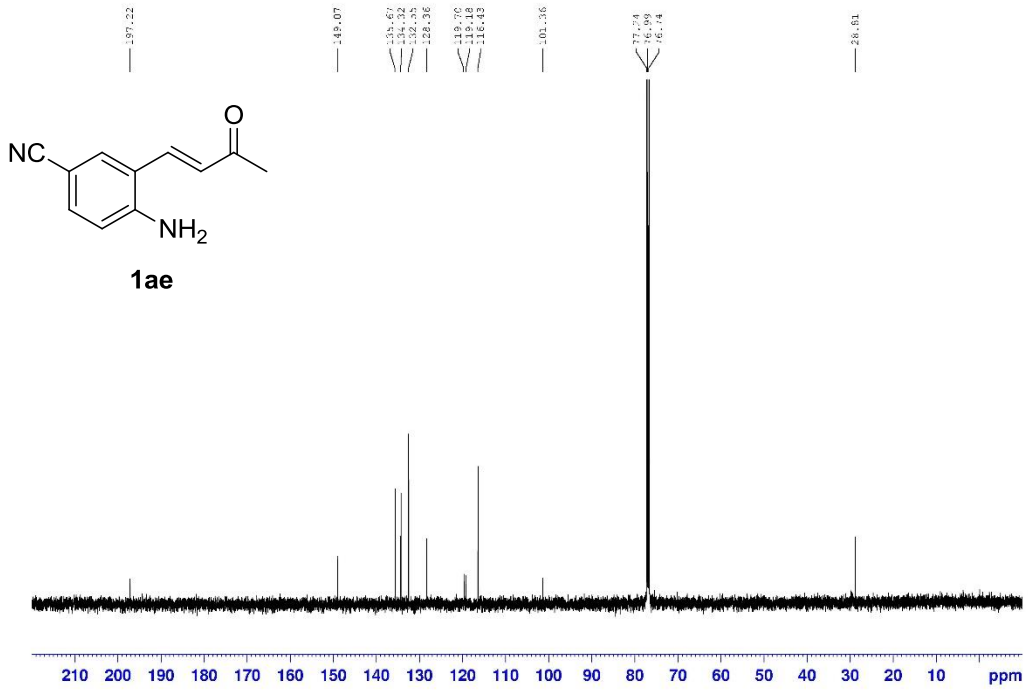


Fig. S66. ^{1}H NMR Spectrum of 1af (500 MHz, $CDCl_3$).

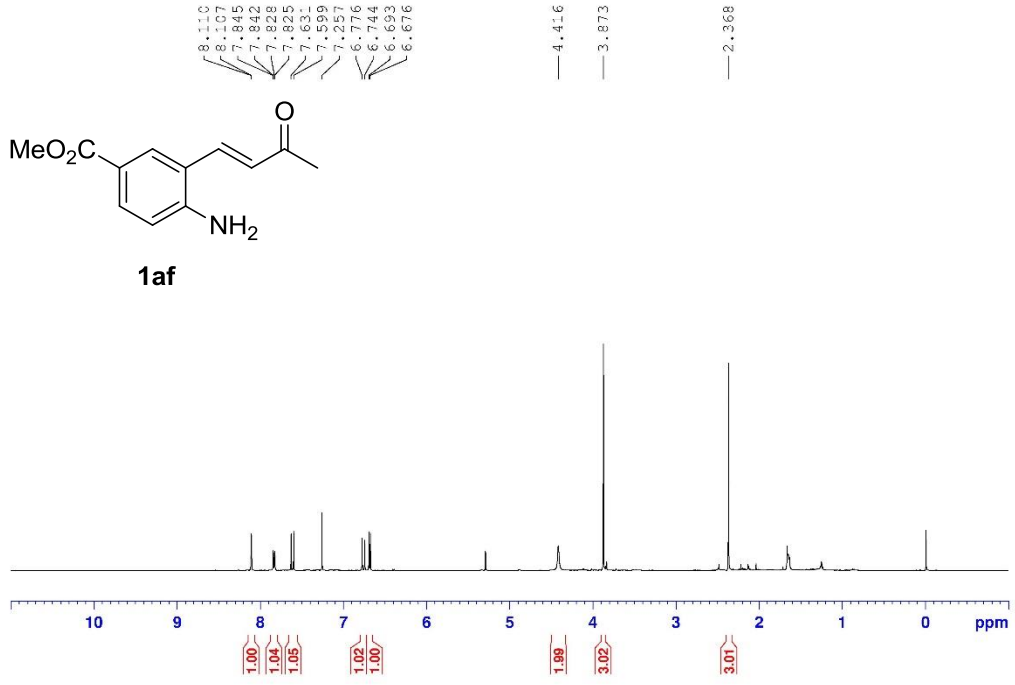


Fig. S67. ^{13}C NMR Spectrum of 1af (125 MHz, $CDCl_3$).

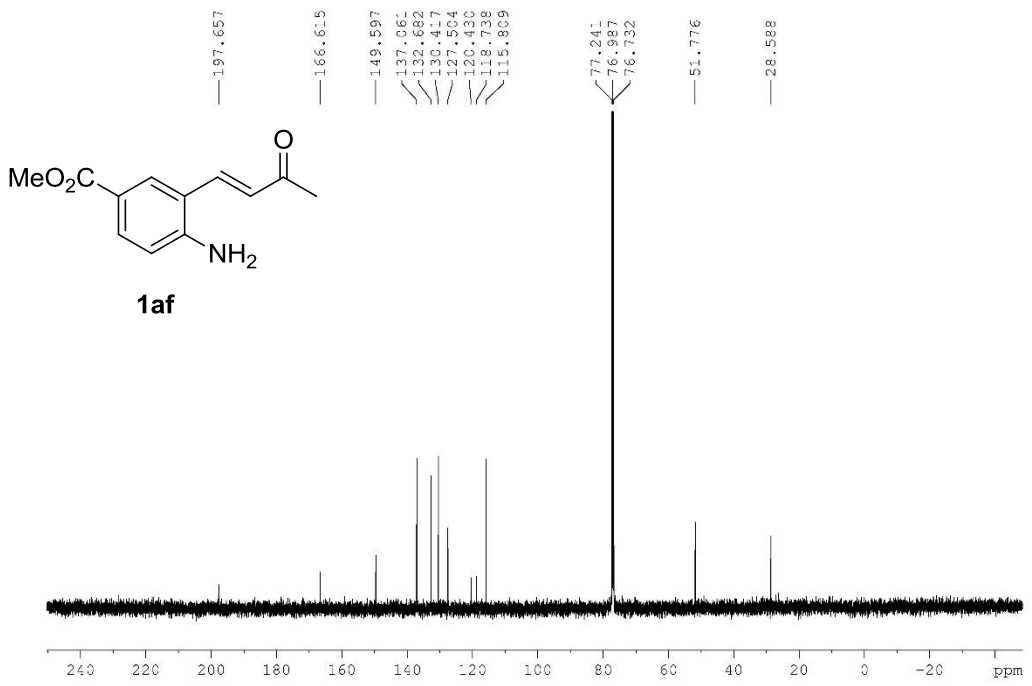


Fig. S68. ^{1}H NMR Spectrum of 1ag (500 MHz, $CDCl_3$).

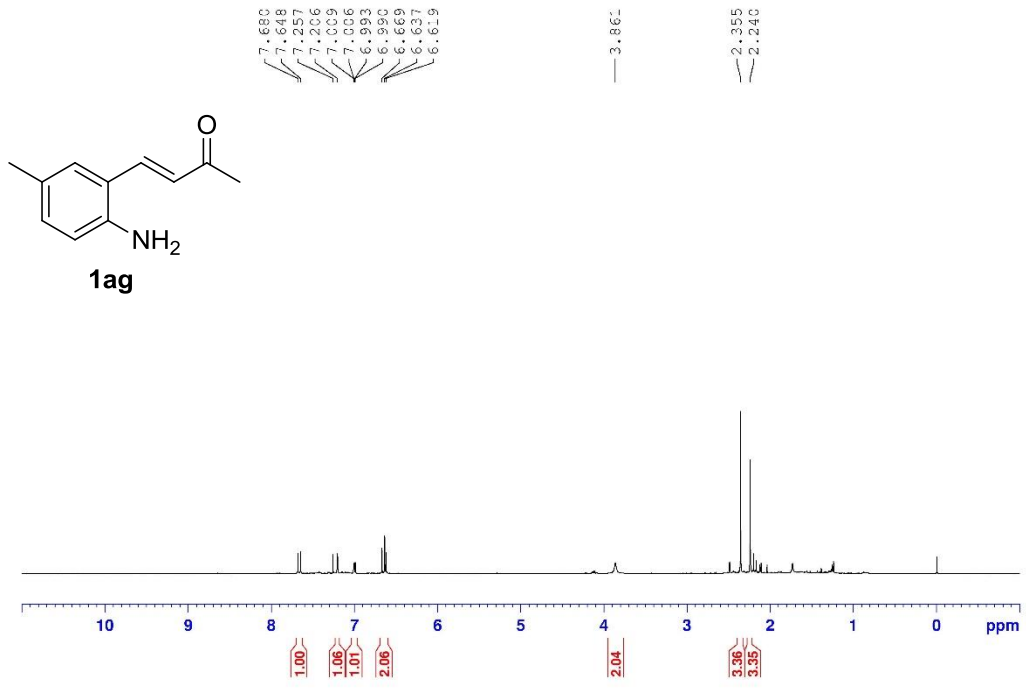


Fig. S69. ^{13}C NMR Spectrum of 1ag (125 MHz, $CDCl_3$).

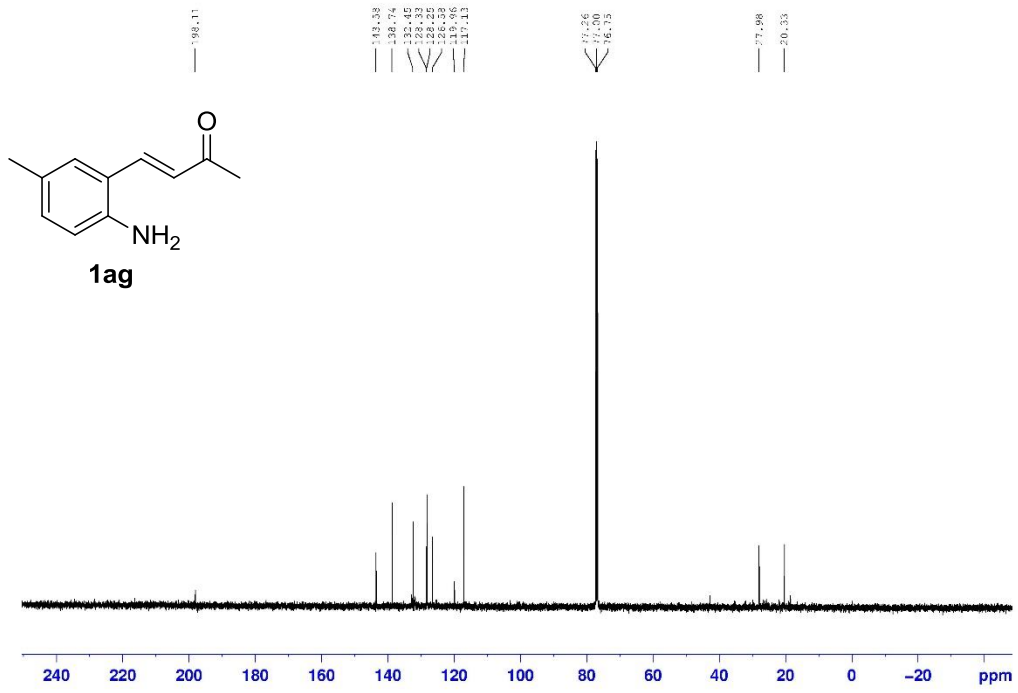


Fig. S70. ^{1}H NMR Spectrum of 1ah (400 MHz, $CDCl_3$).

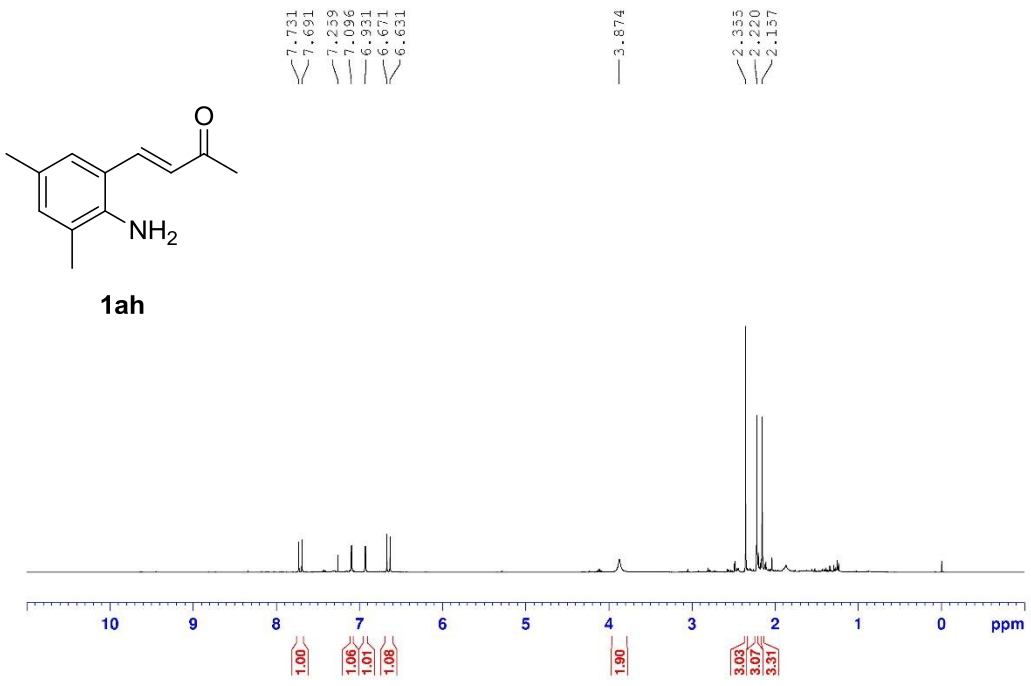


Fig. S71. ^{13}C NMR Spectrum of 1ah (100 MHz, $CDCl_3$).

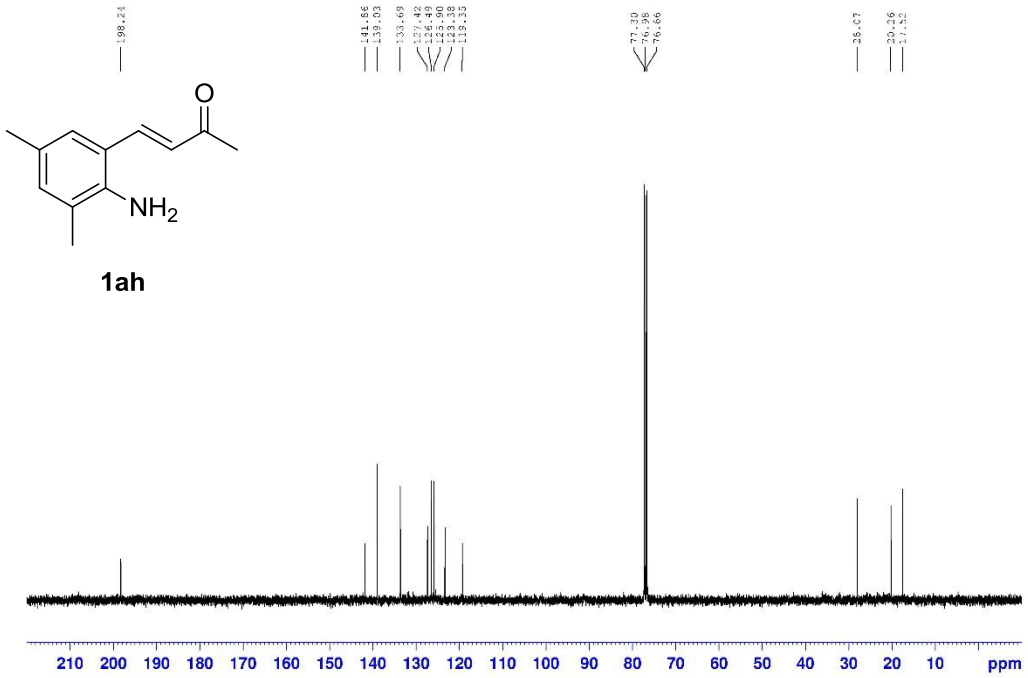


Fig. S72. ^{1}H NMR Spectrum of 1ai (400 MHz, $CDCl_3$).

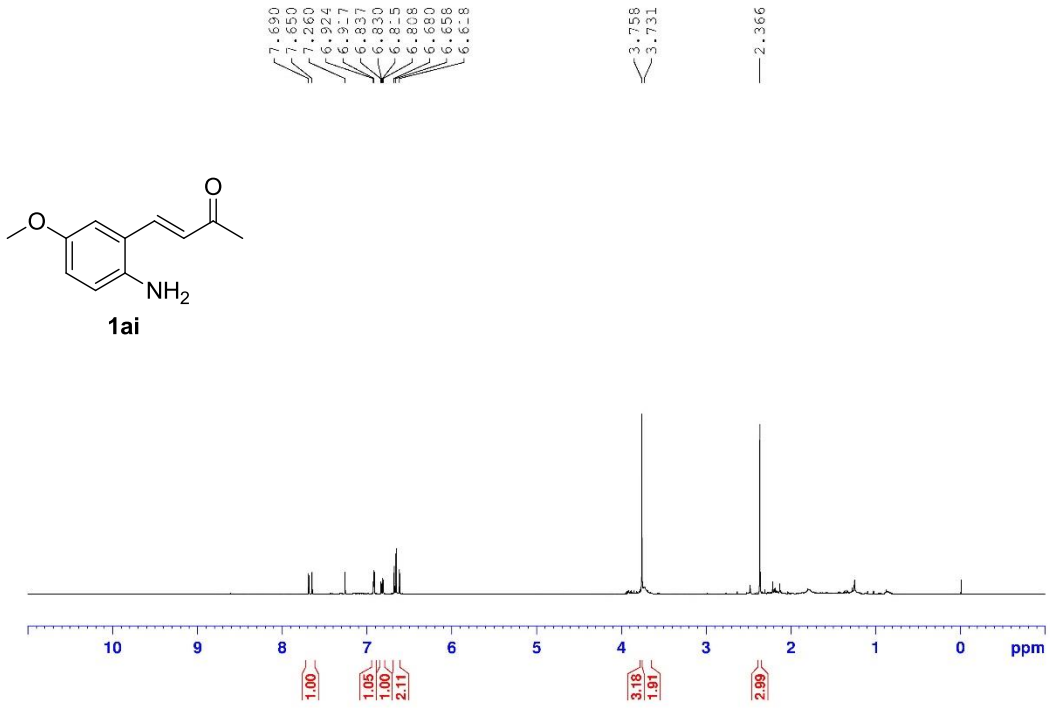


Fig. S73. ^{13}C NMR Spectrum of 1ai (100 MHz, $CDCl_3$).

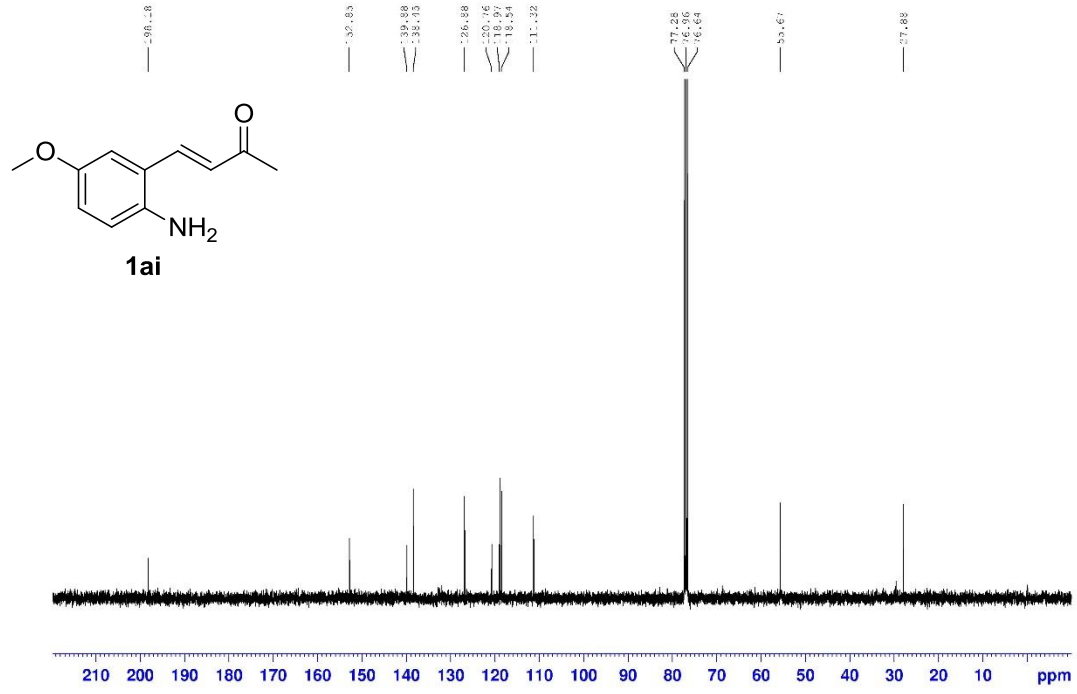


Fig. S74. ^{1}H NMR Spectrum of 1aj (300 MHz, $CDCl_3$).

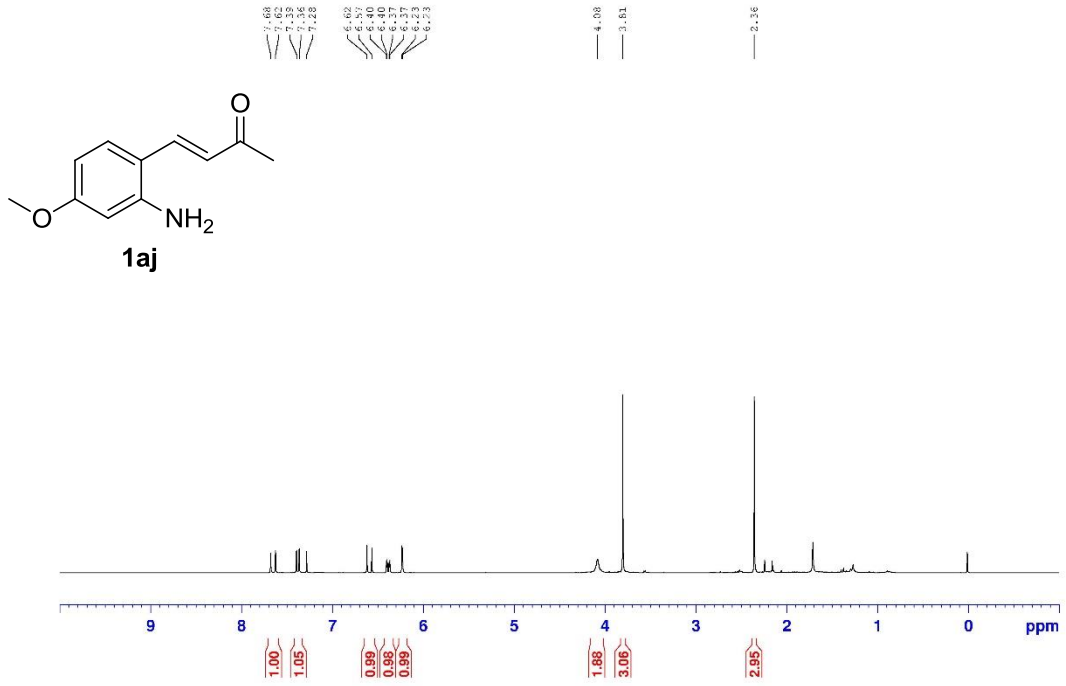


Fig. S75. ^{13}C NMR Spectrum of 1aj (75 MHz, $CDCl_3$).

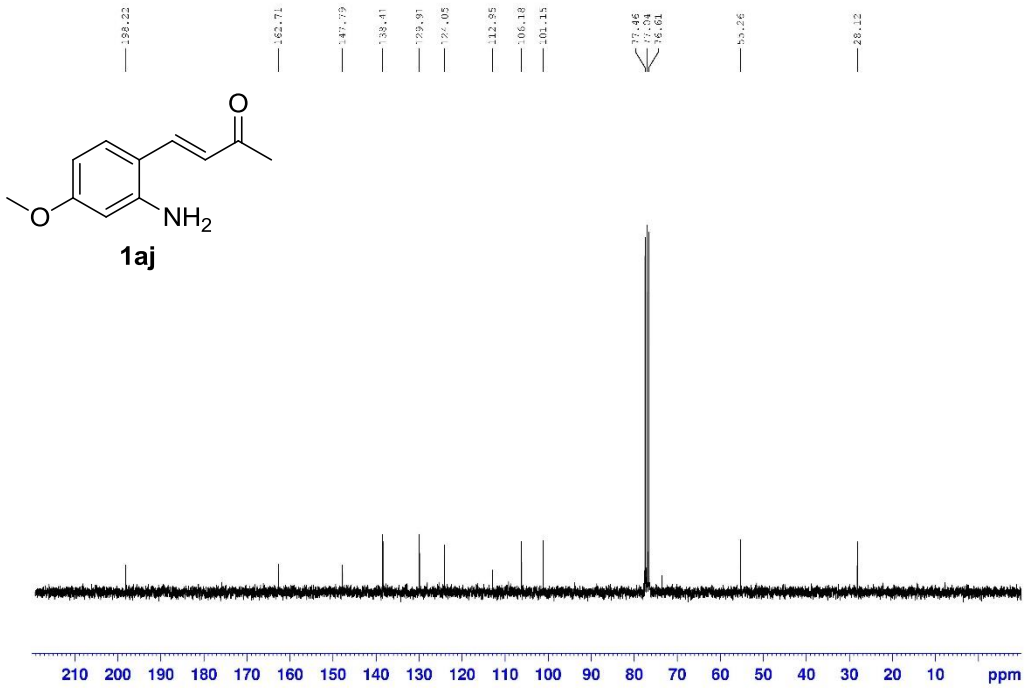


Fig. S76. ^{1}H NMR Spectrum of 1ak (400 MHz, $CDCl_3$).

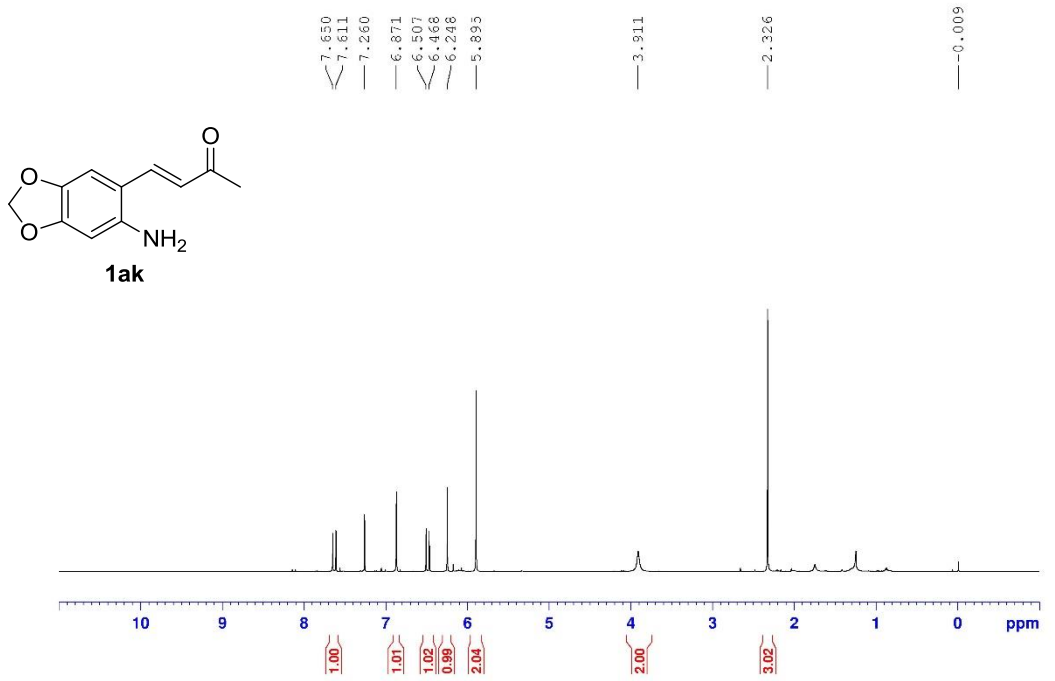


Fig. S77. ^{13}C NMR Spectrum of 1ak (100 MHz, $CDCl_3$).

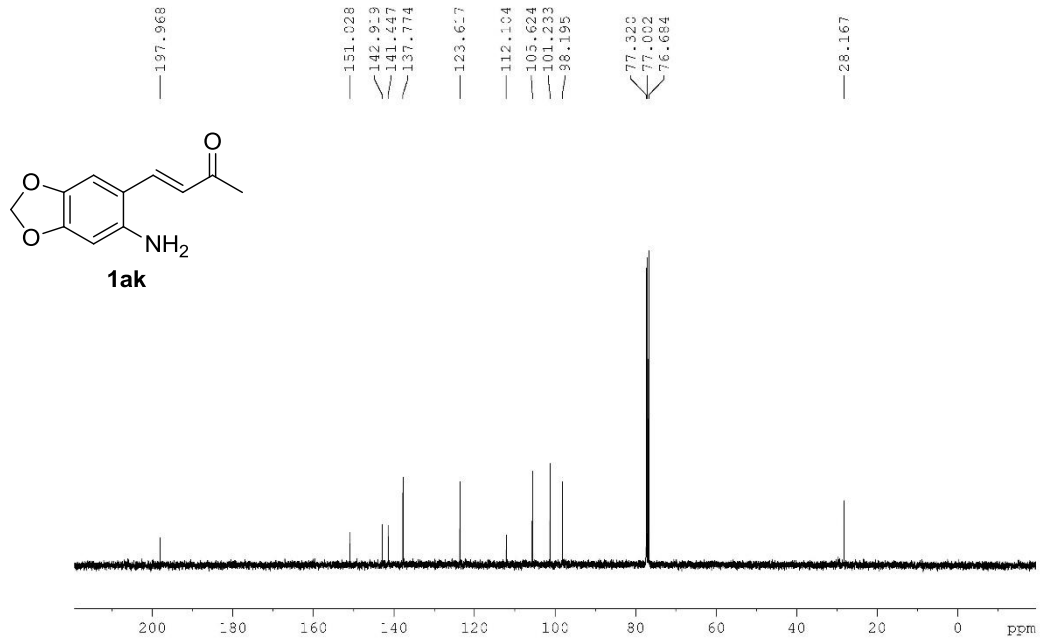


Fig. S78. ^{1}H NMR Spectrum of 1al (400 MHz, $CDCl_3$).

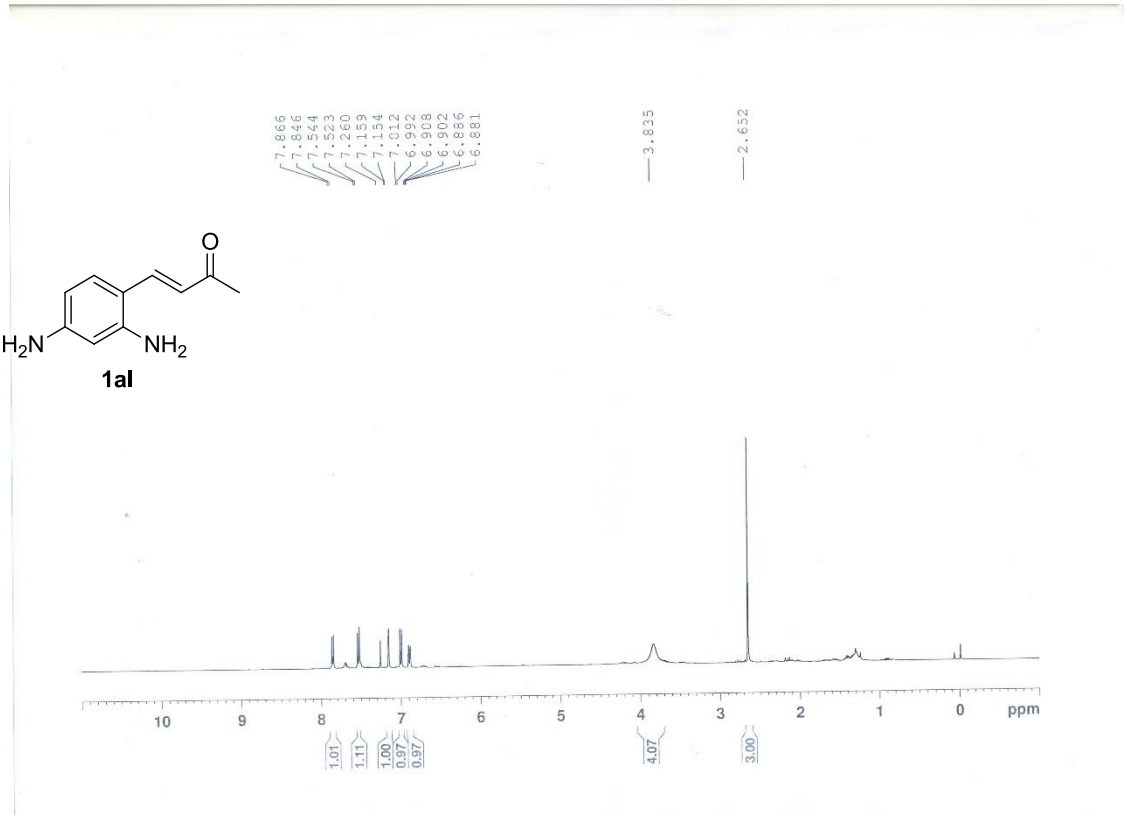


Fig. S79. ^{13}C NMR Spectrum of 1al (100 MHz, $CDCl_3$).

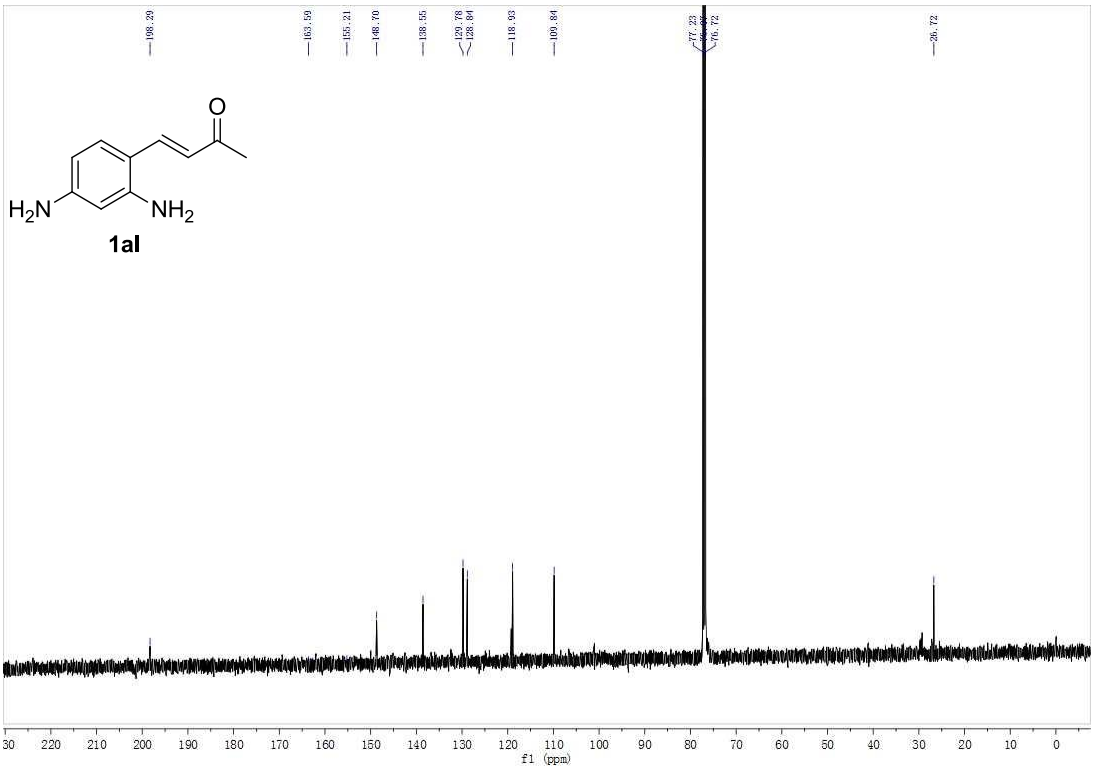


Fig. S80. ^{1}H NMR Spectrum of 1am (400 MHz, DMSO-d_6).

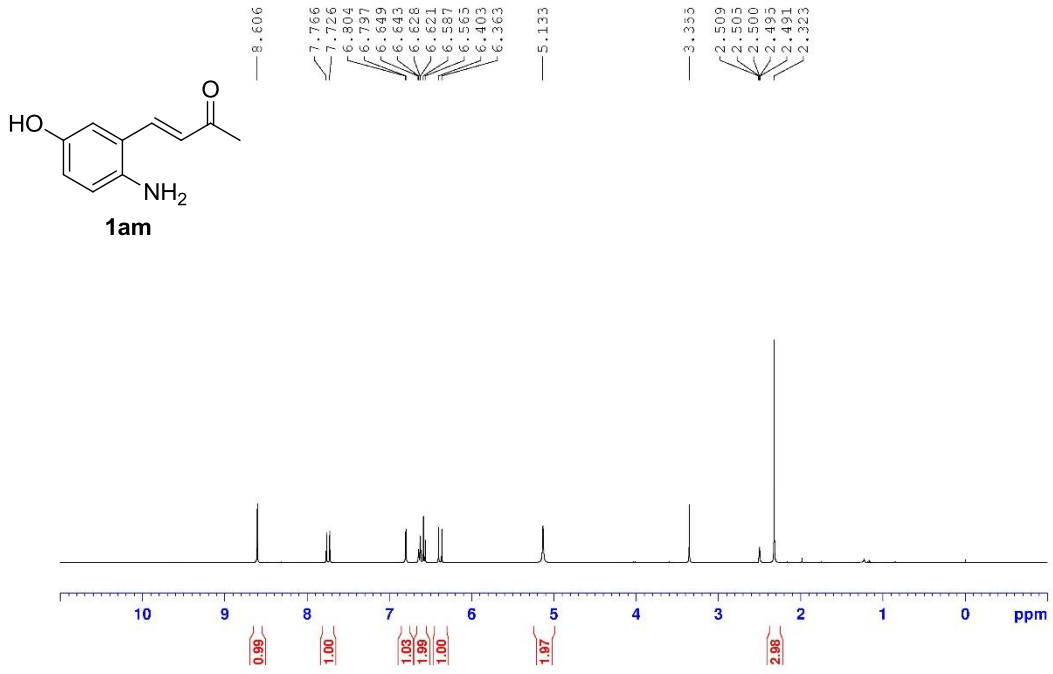


Fig. S81. ^{13}C NMR Spectrum of 1am (100 MHz, DMSO-d_6).

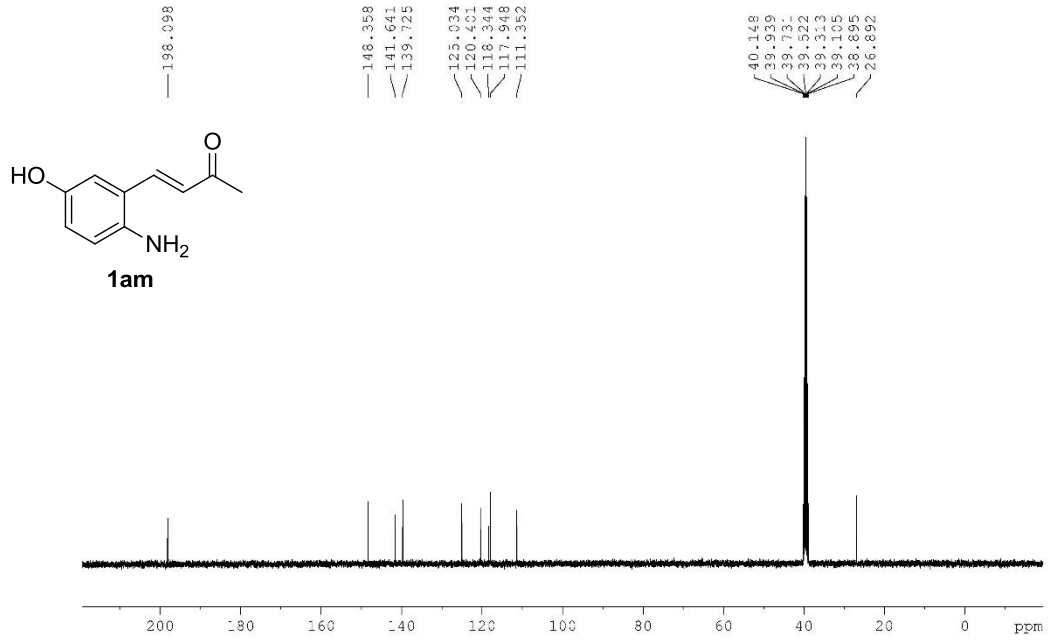


Fig. S82. ^{1}H NMR Spectrum of 2a (400 MHz, $CDCl_3$).

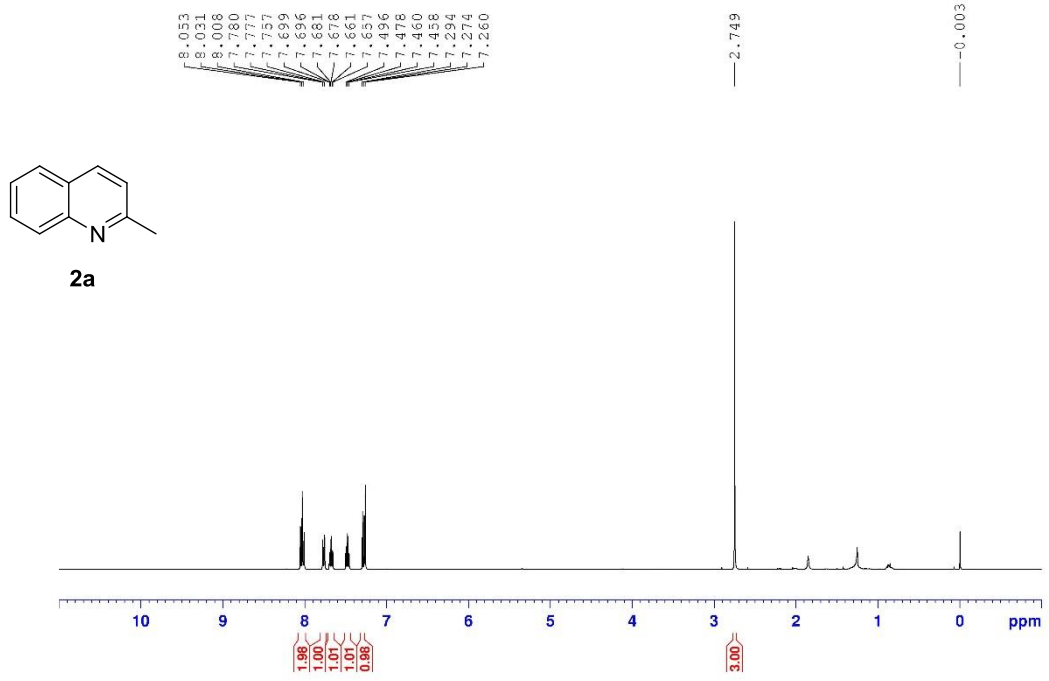


Fig. S83. ^{13}C NMR Spectrum of 2a (100 MHz, $CDCl_3$).

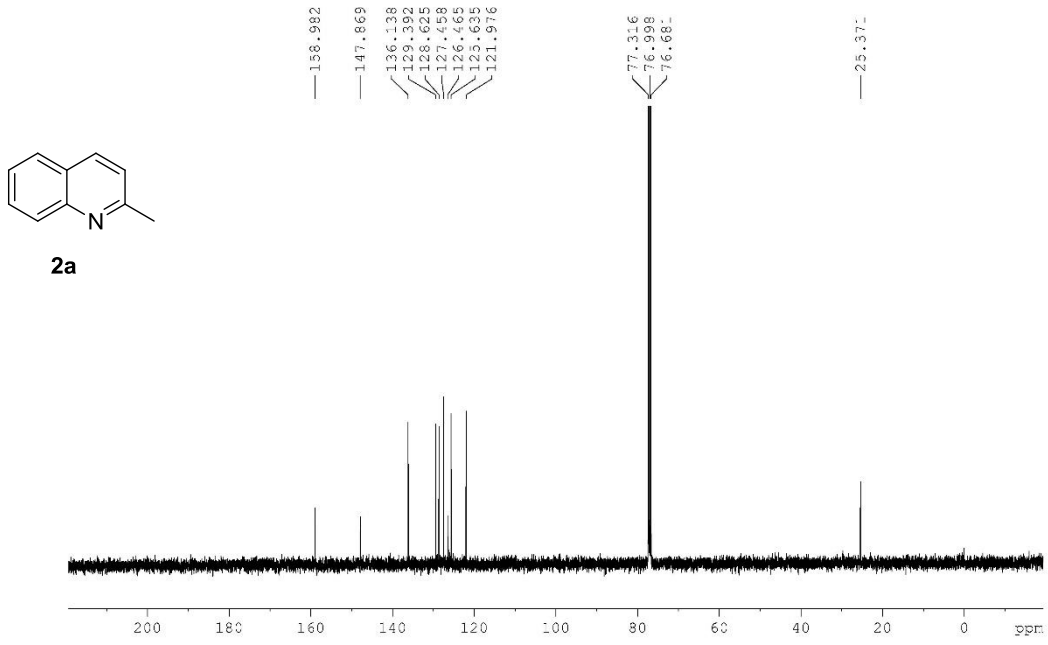


Fig. S84. ^{1}H NMR Spectrum of 2b (400 MHz, $CDCl_3$).

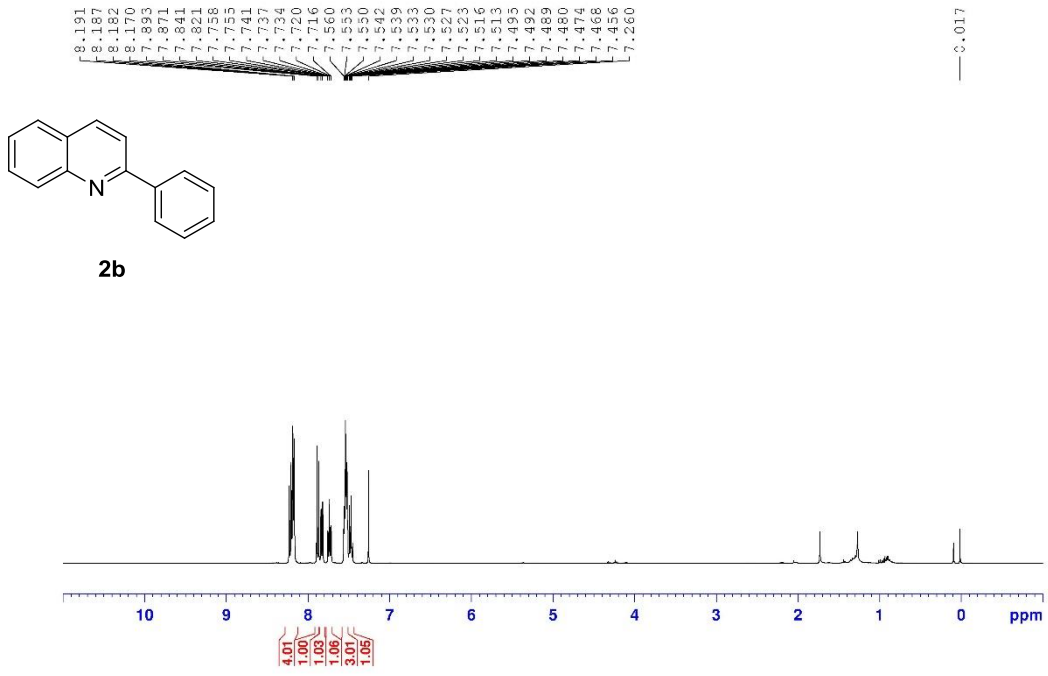


Fig. S85. ^{13}C NMR Spectrum of 2b (100 MHz, $CDCl_3$).

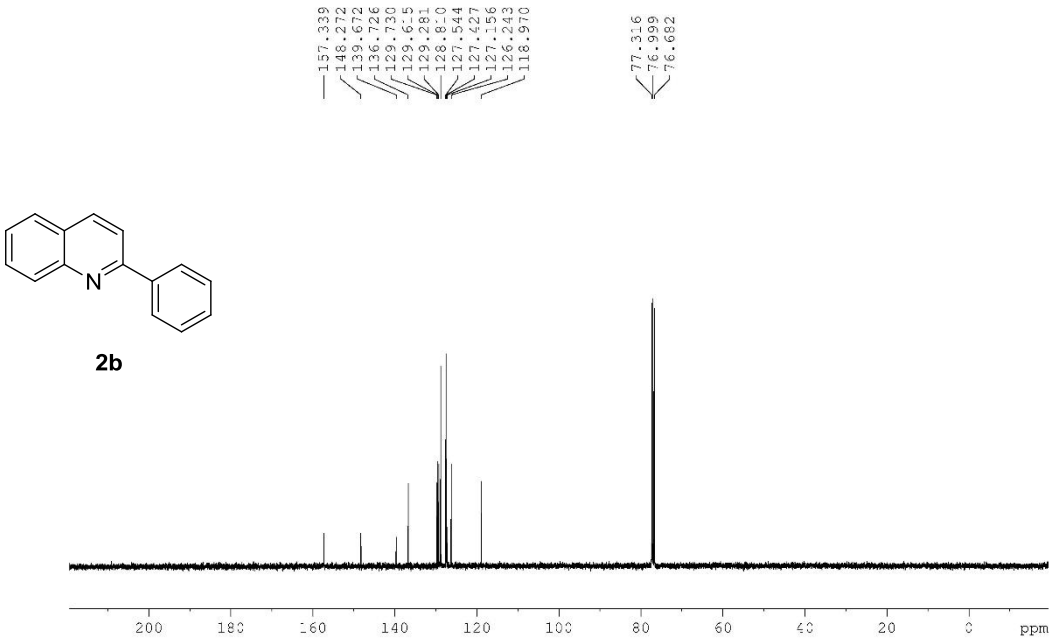


Fig. S86. ^{1}H NMR Spectrum of 2c (400 MHz, $CDCl_3$).

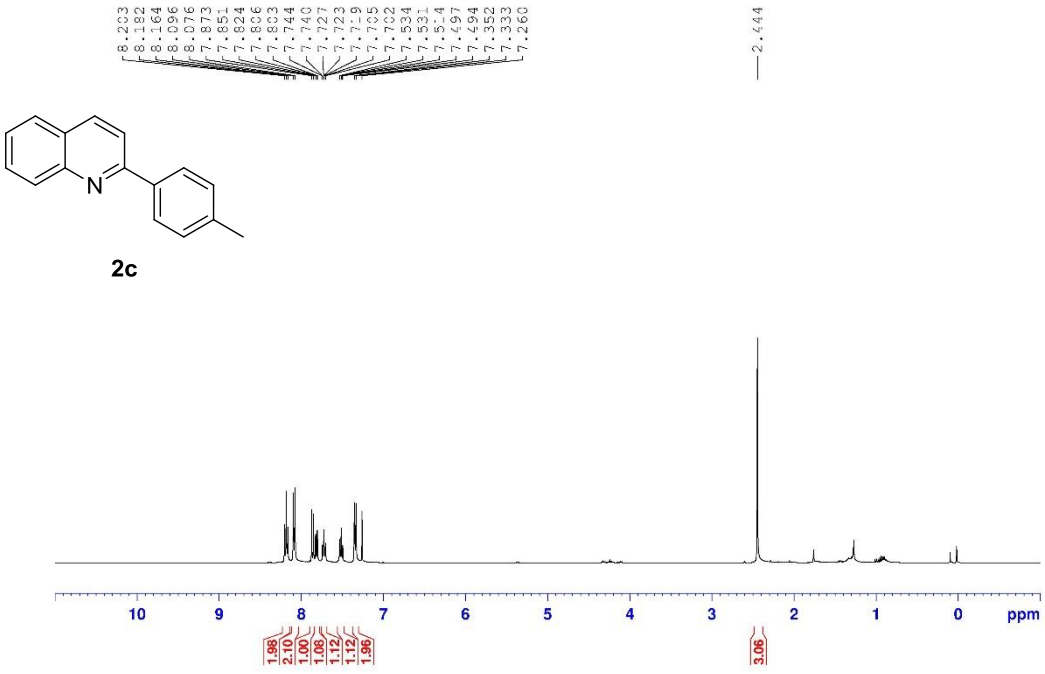


Fig. S87. ^{13}C NMR Spectrum of 2c (100 MHz, $CDCl_3$).

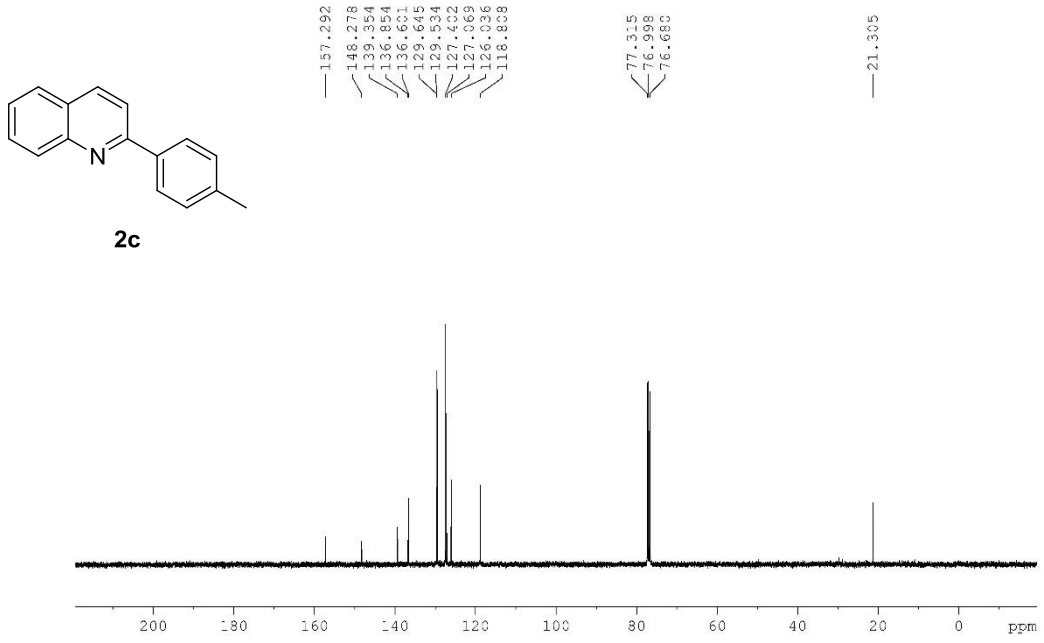


Fig. S88. ^{1}H NMR Spectrum of 2d (400 MHz, $CDCl_3$).

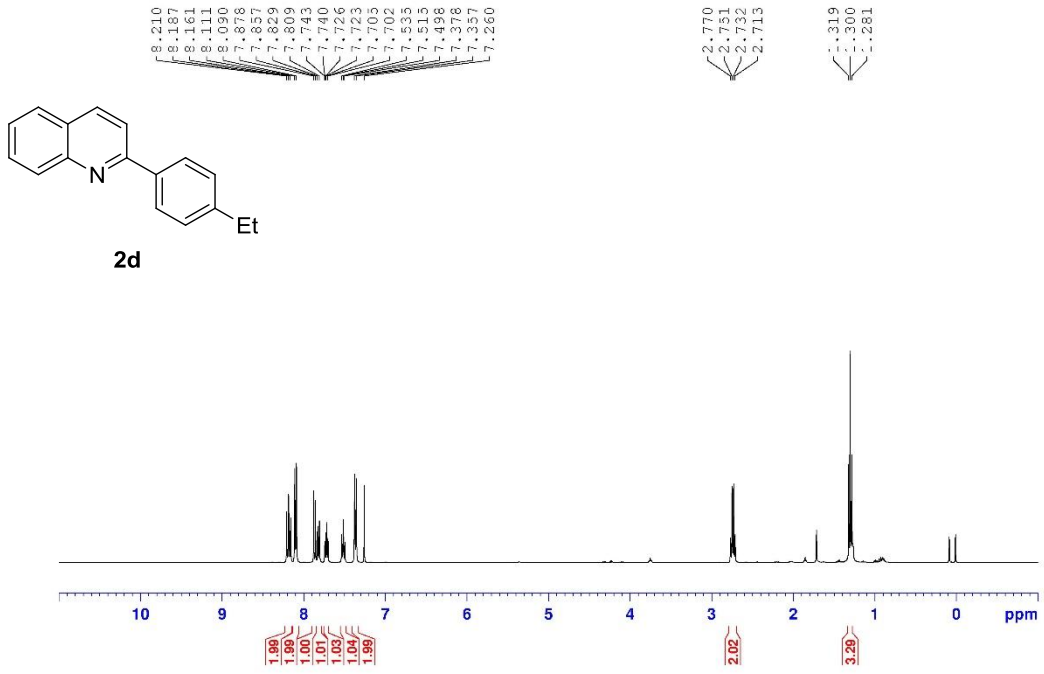


Fig. S89. ^{13}C NMR Spectrum of 2d (100 MHz, $CDCl_3$).

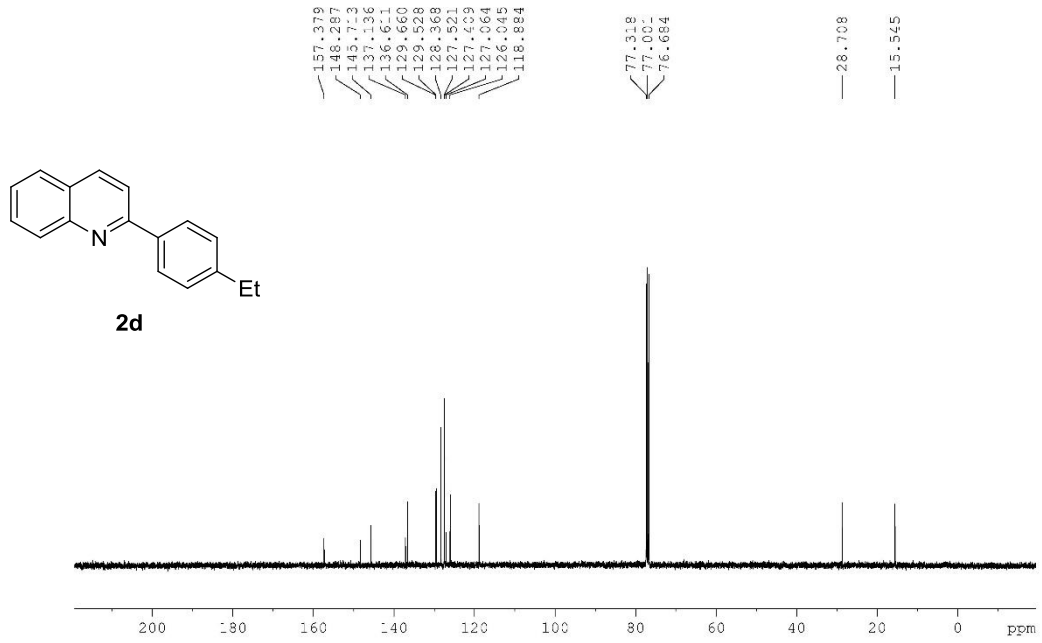


Fig. S90. ^{1}H NMR Spectrum of 2e (500 MHz, $CDCl_3$).

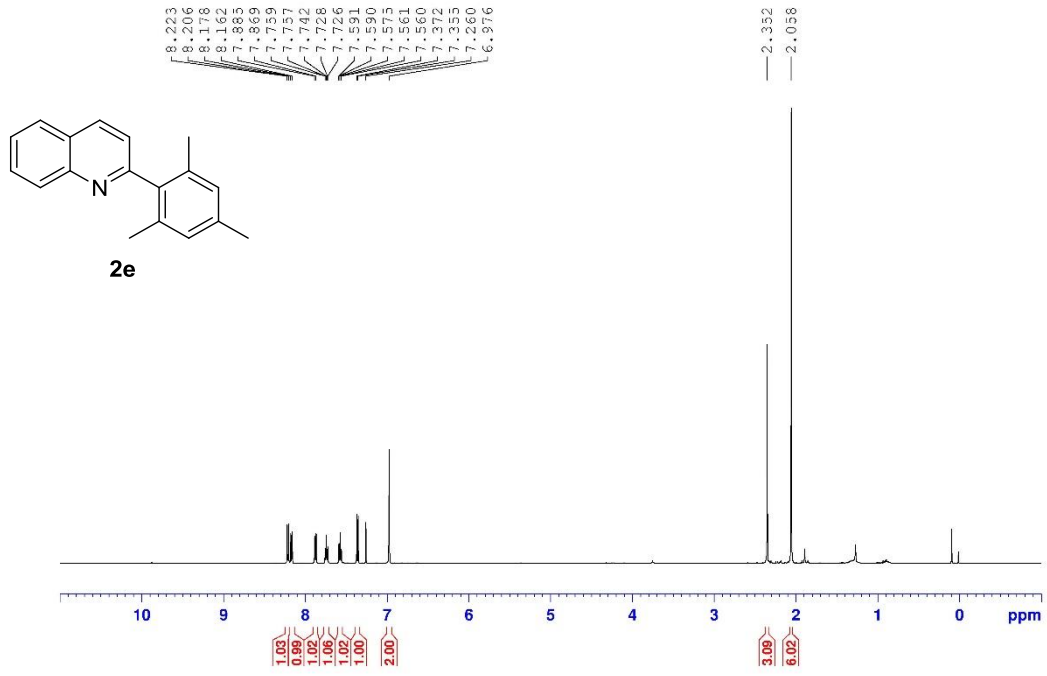


Fig. S91. ^{13}C NMR Spectrum of 2e (125 MHz, $CDCl_3$).

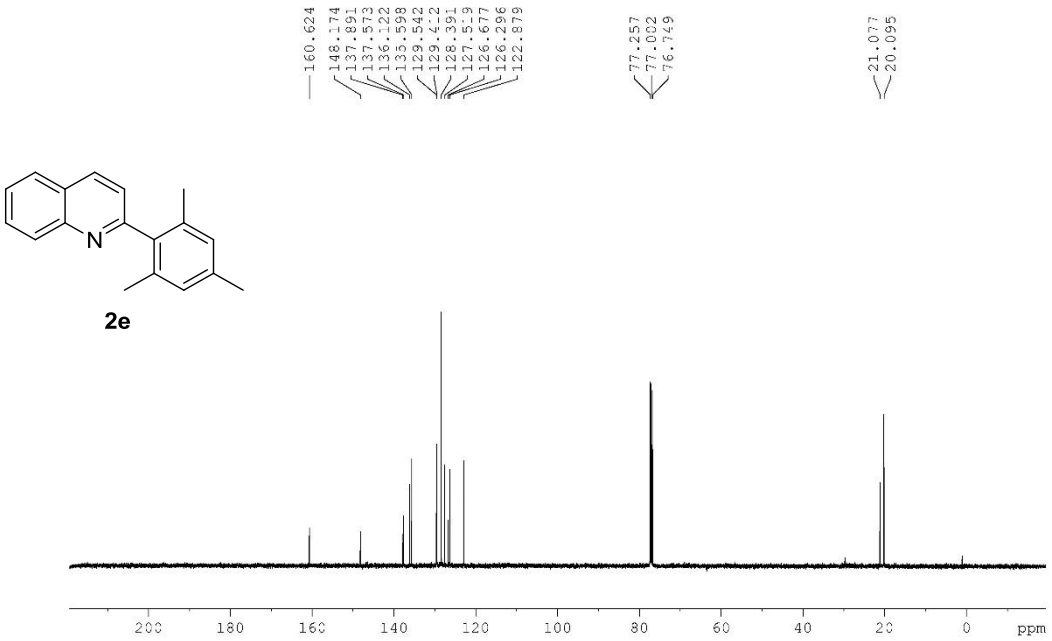


Fig. S92. ^{1}H NMR Spectrum of 2f (500 MHz, $CDCl_3$).

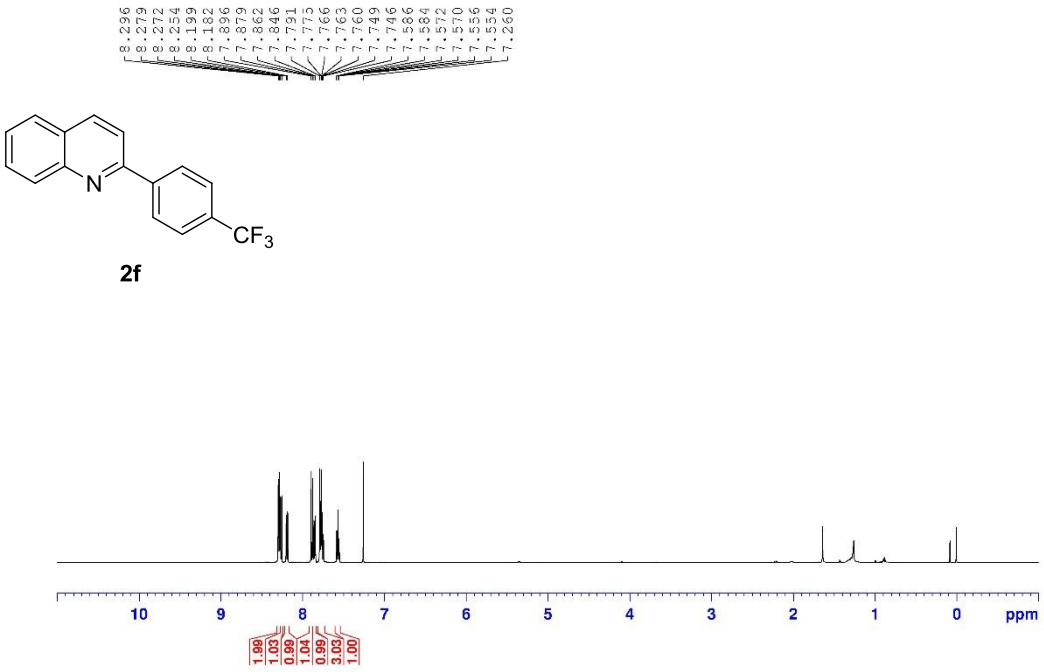


Fig. S93. ^{13}C NMR Spectrum of 2f (125 MHz, $CDCl_3$).

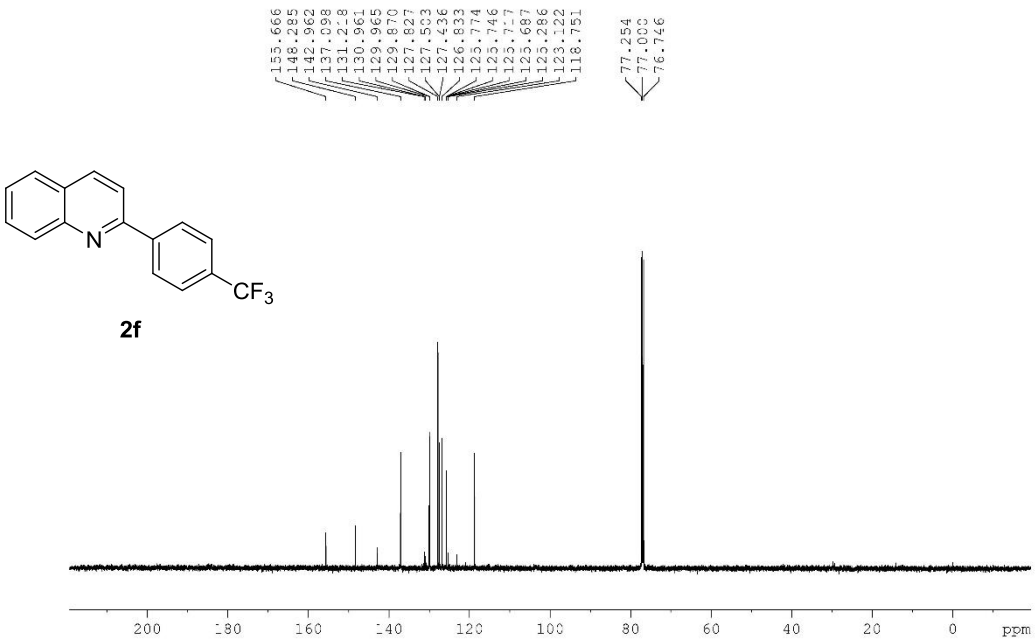


Fig. S94. ^{19}F NMR Spectrum of 2f (376 MHz, $CDCl_3$).

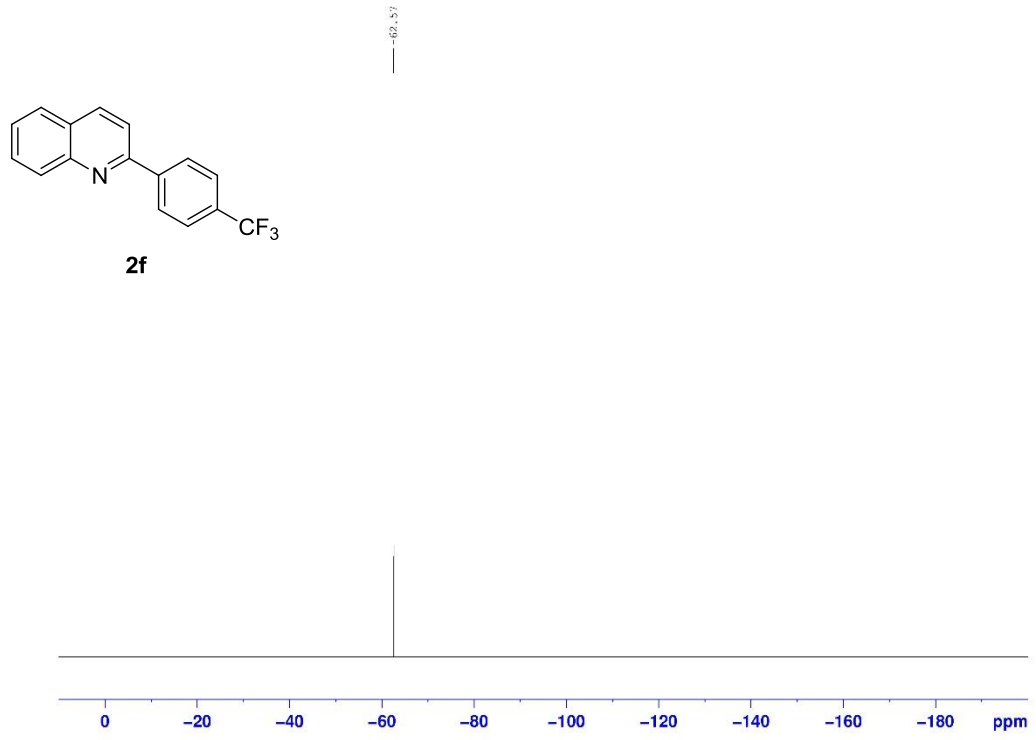


Fig. S95. ^{13}C NMR Spectrum of 2g (400 MHz, $CDCl_3$).

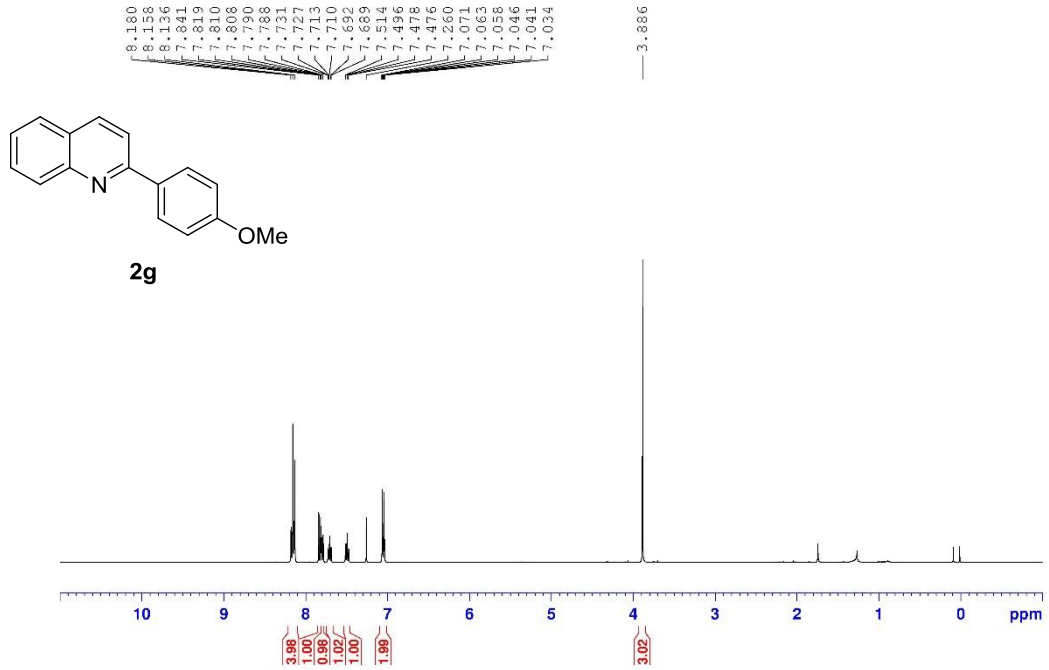


Fig. S96. ^{13}C NMR Spectrum of 2g (100 MHz, $CDCl_3$).

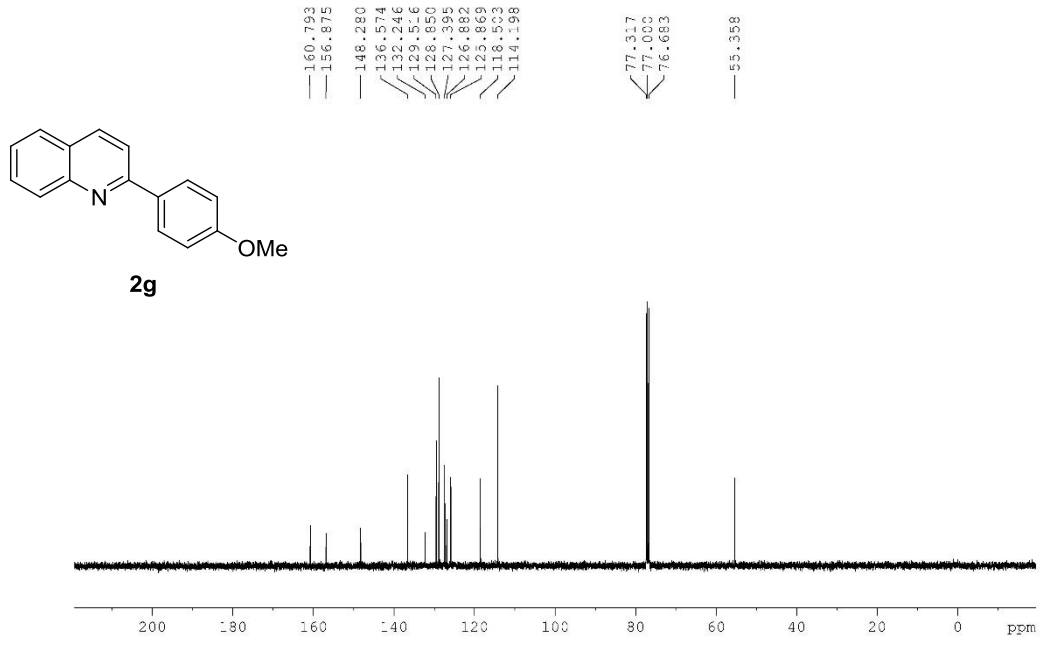


Fig. S97. ^{1}H NMR Spectrum of 2h (400 MHz, $CDCl_3$).

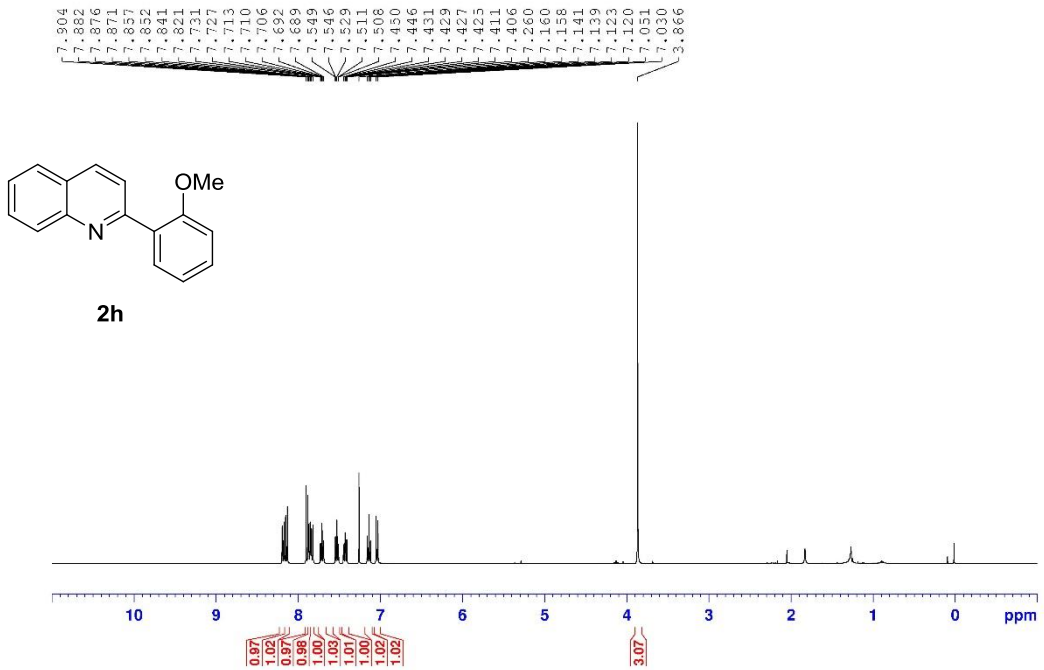


Fig. S98. ^{13}C NMR Spectrum of 2h (100 MHz, $CDCl_3$).

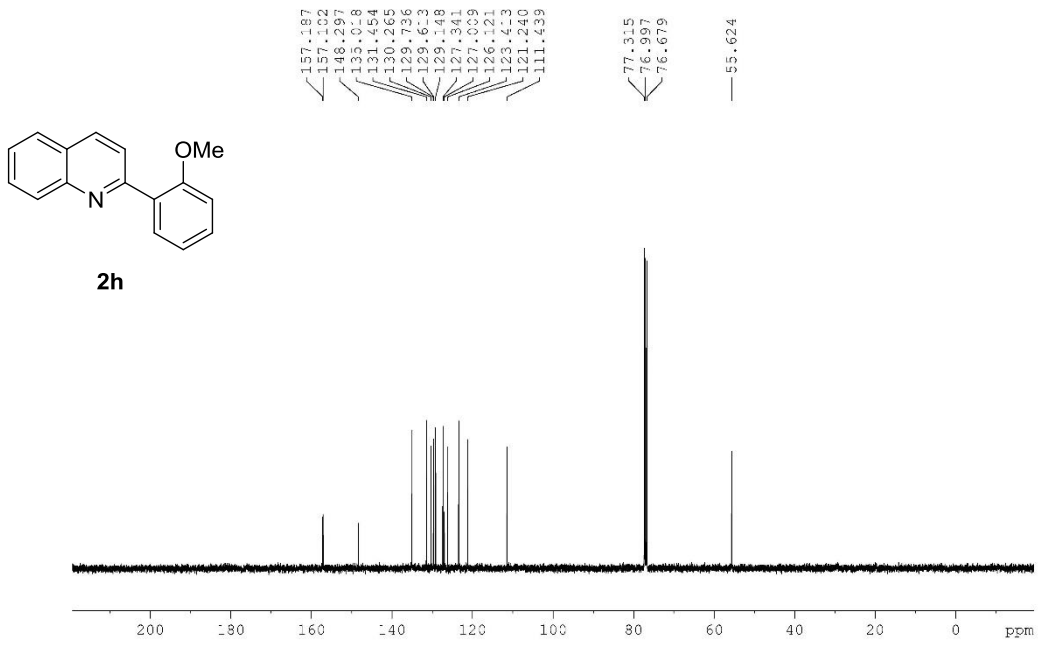


Fig. S99. ^{1}H NMR Spectrum of 2i (400 MHz, $CDCl_3$).

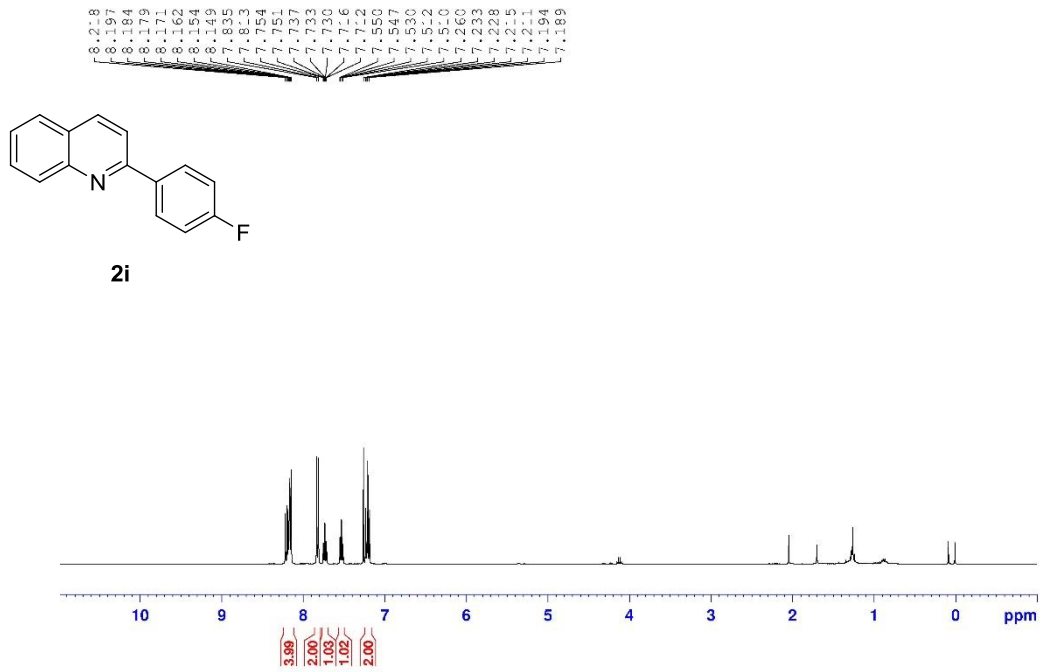


Fig. S100. ^{13}C NMR Spectrum of 2i (100 MHz, $CDCl_3$).

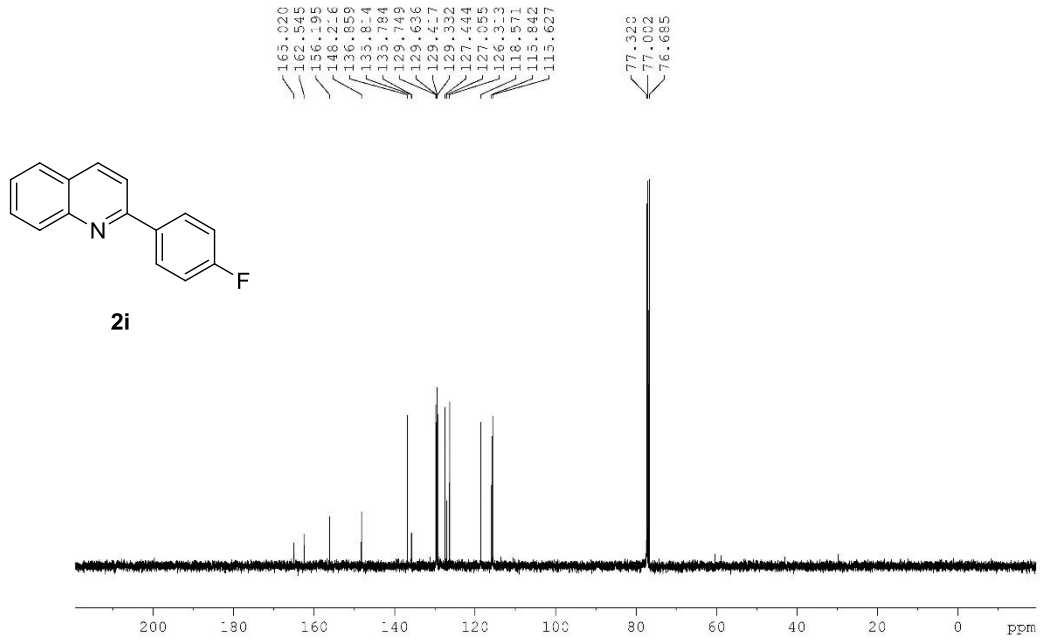


Fig. S101. ^{19}F NMR Spectrum of 2i (376 MHz, $CDCl_3$).

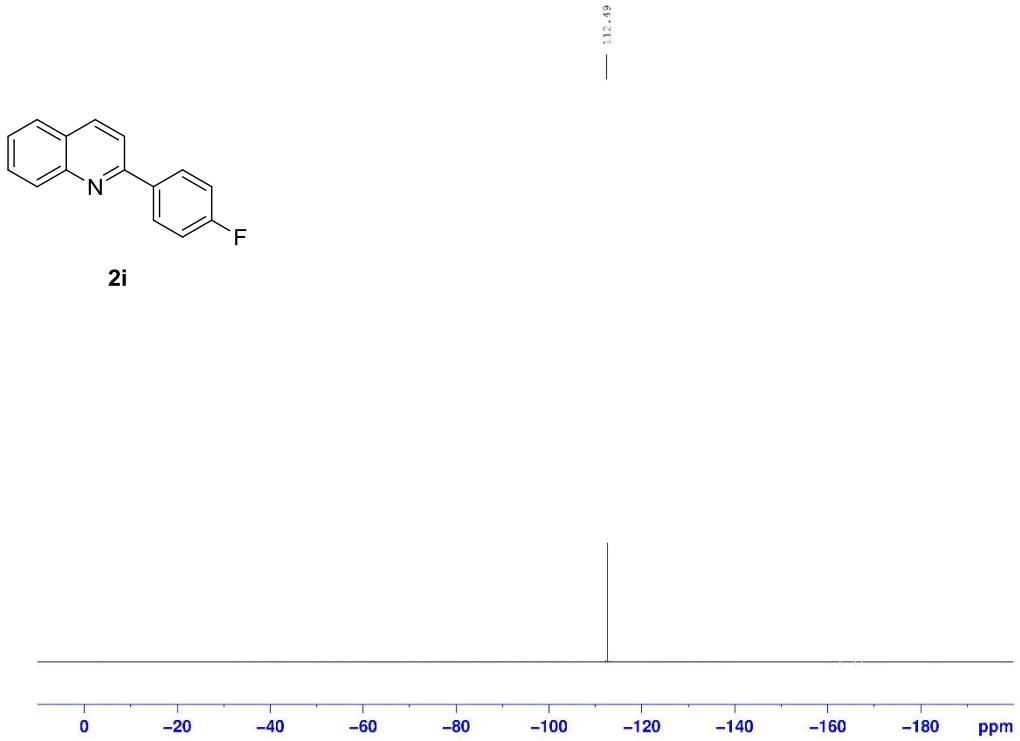


Fig. S102. ^{1}H NMR Spectrum of 2j (300 MHz, $CDCl_3$).

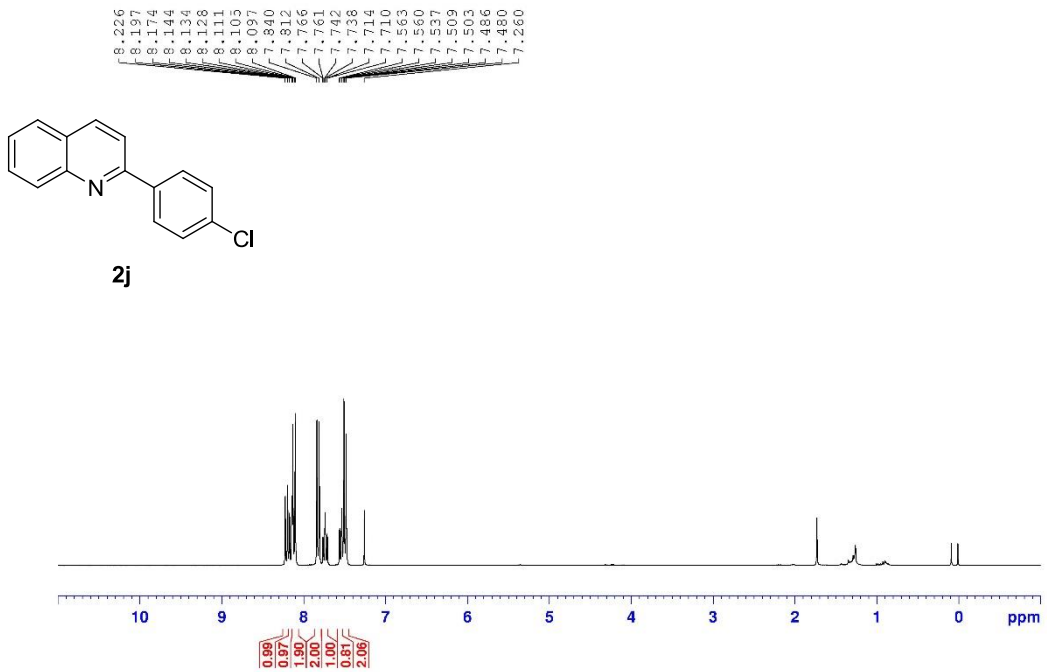


Fig. S103. ^{13}C NMR Spectrum of 2j (75 MHz, $CDCl_3$).

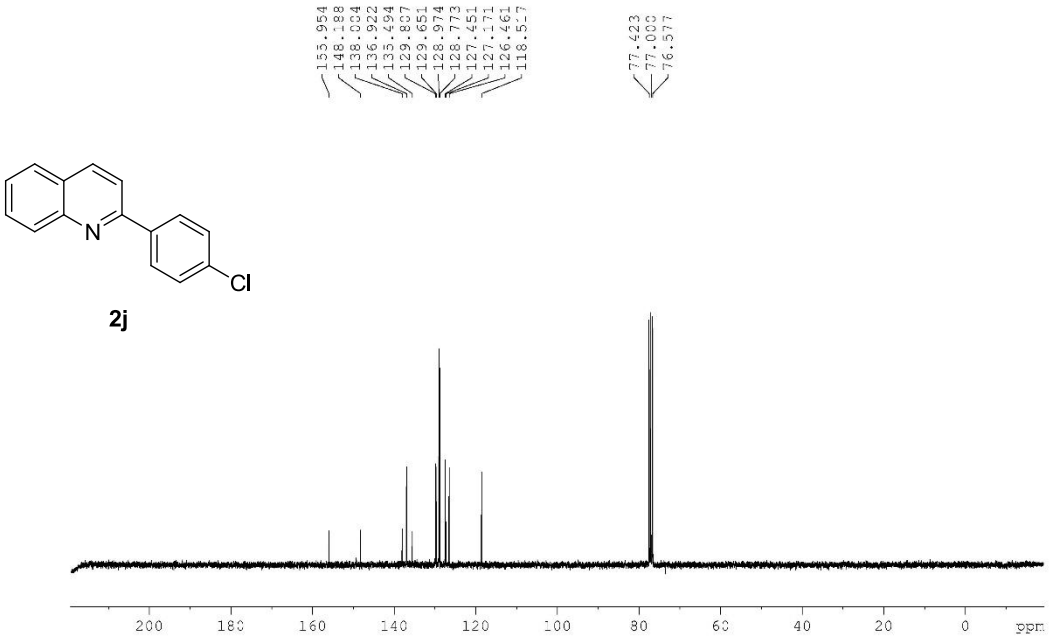


Fig. S104. ^{1}H NMR Spectrum of 2k (500 MHz, $CDCl_3$).

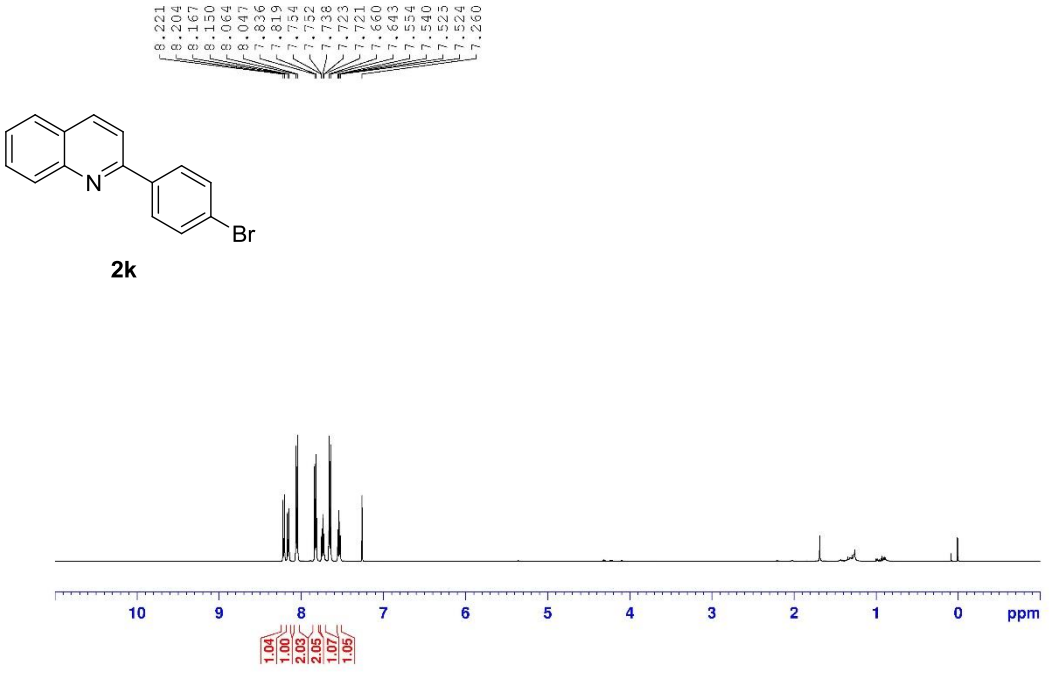


Fig. S105. ^{13}C NMR Spectrum of 2k (125 MHz, $CDCl_3$).

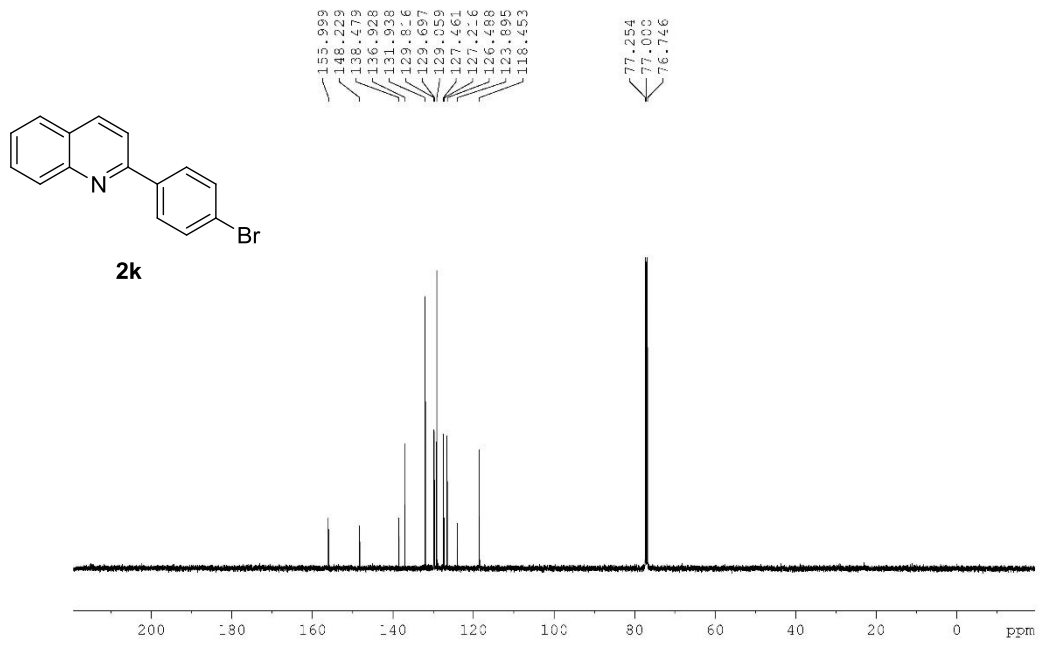


Fig. S106. ^{1}H NMR Spectrum of 2l (400 MHz, $CDCl_3$).

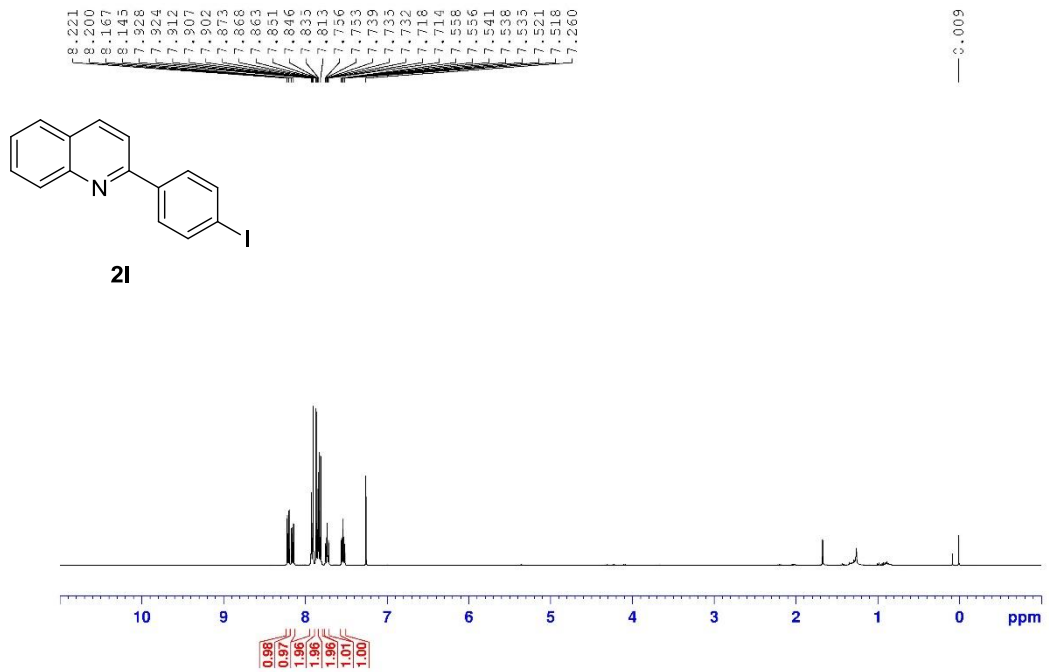


Fig. S107. ^{13}C NMR Spectrum of 2l (100 MHz, $CDCl_3$).

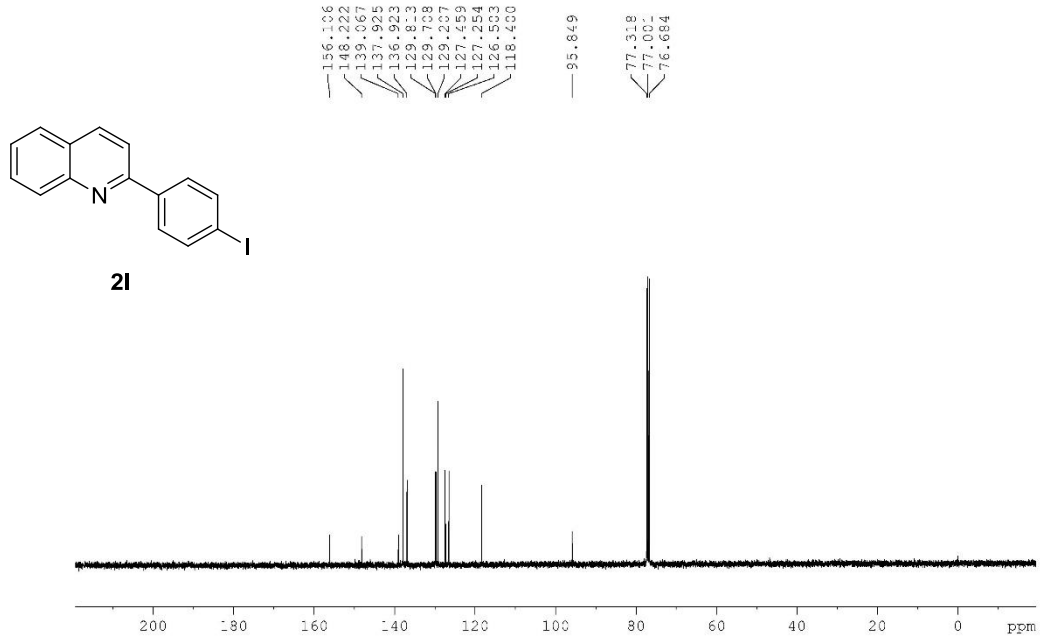


Fig. S108. ^{1}H NMR Spectrum of 2m (400 MHz, $CDCl_3$).

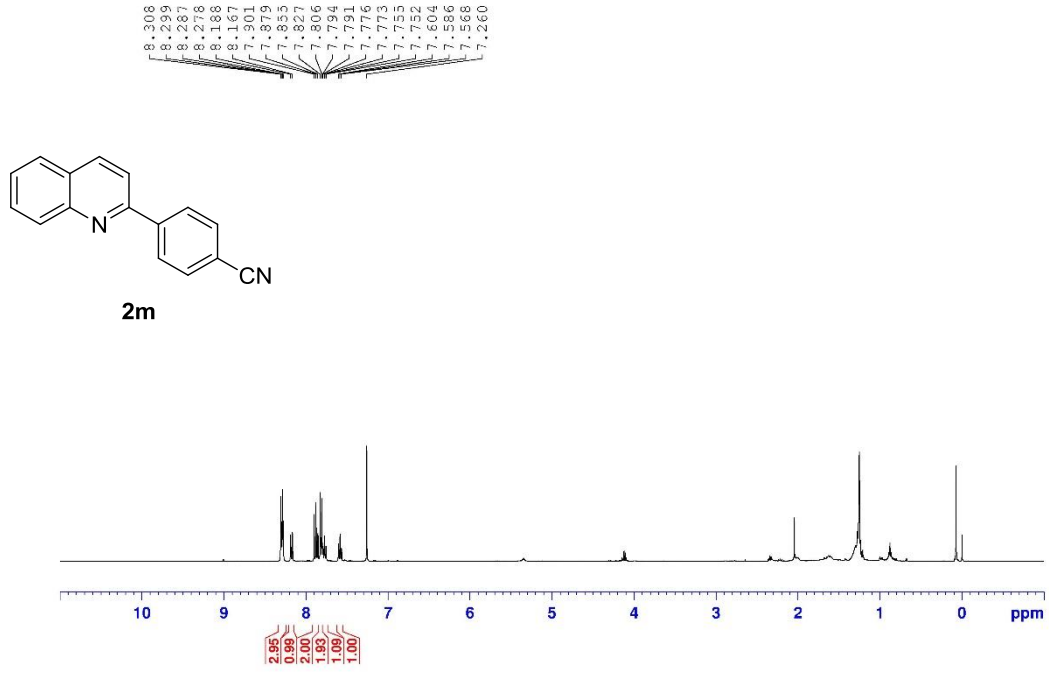


Fig. S109. ^{13}C NMR Spectrum of 2m (100 MHz, $CDCl_3$).

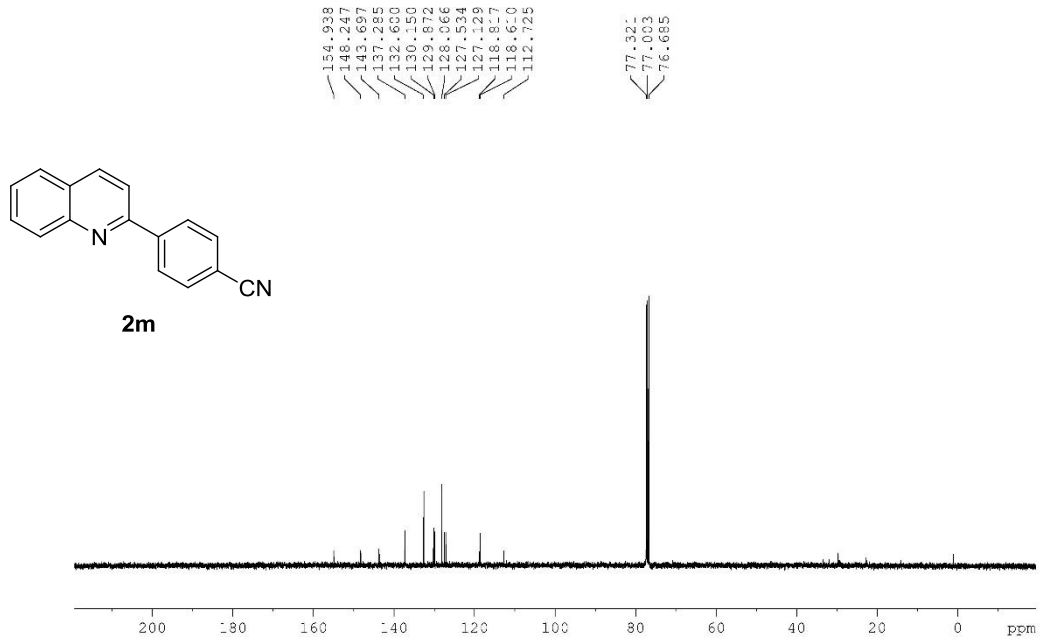


Fig. S110. ^{1}H NMR Spectrum of 2n (400 MHz, $CDCl_3$).

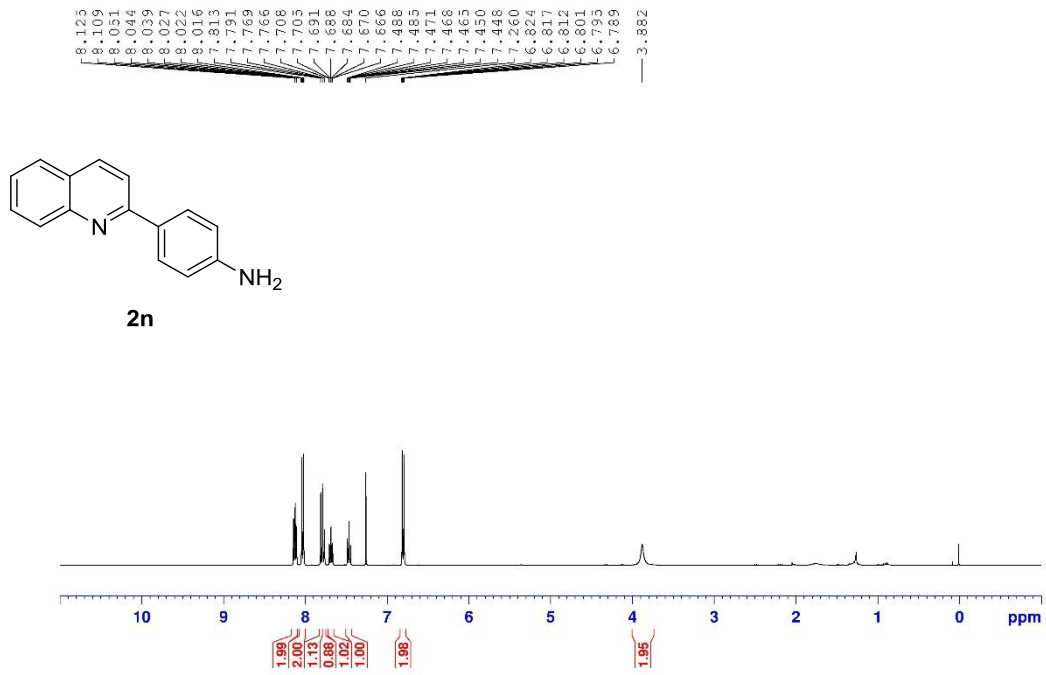


Fig. S111. ^{13}C NMR Spectrum of 2n (100 MHz, $CDCl_3$).

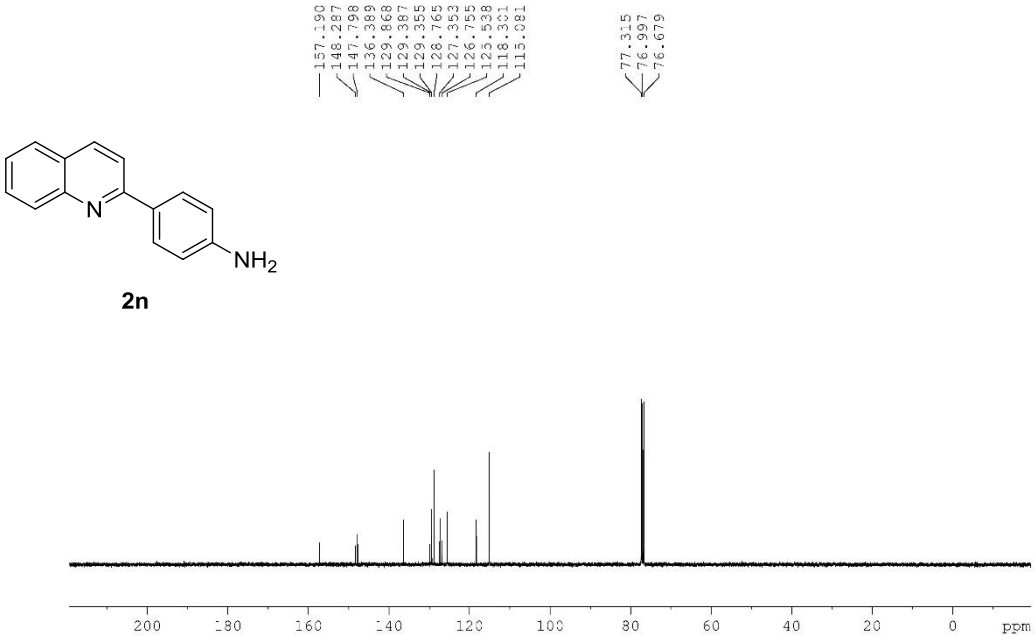


Fig. S112. ^{1}H NMR Spectrum of 2o (400 MHz, $CDCl_3$).

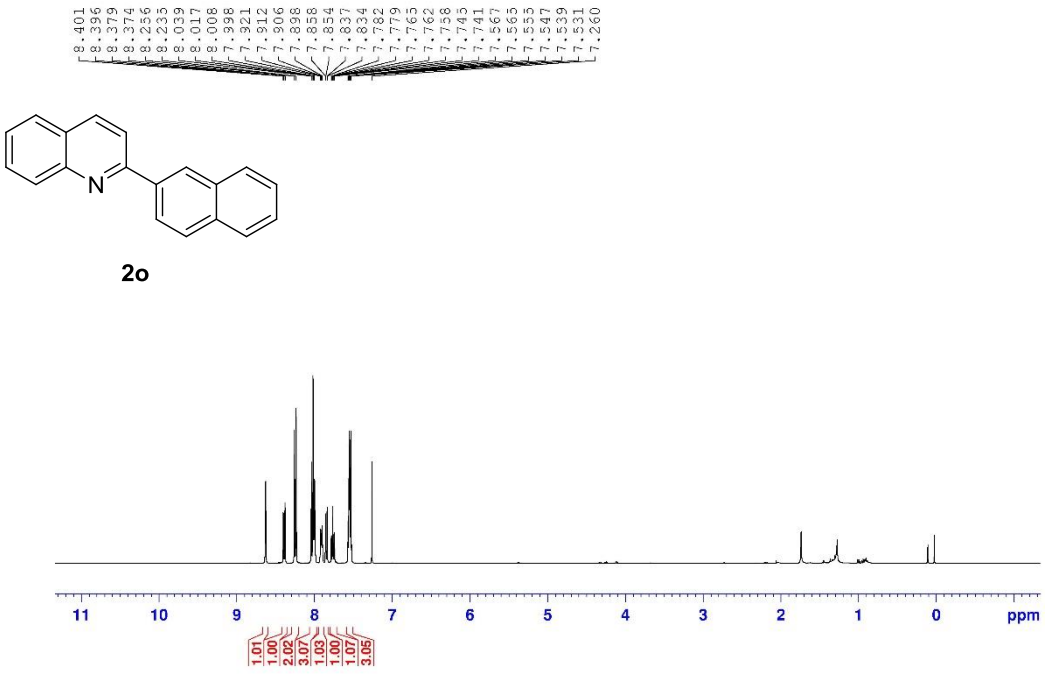


Fig. S113. ^{13}C NMR Spectrum of 2o (100 MHz, $CDCl_3$).

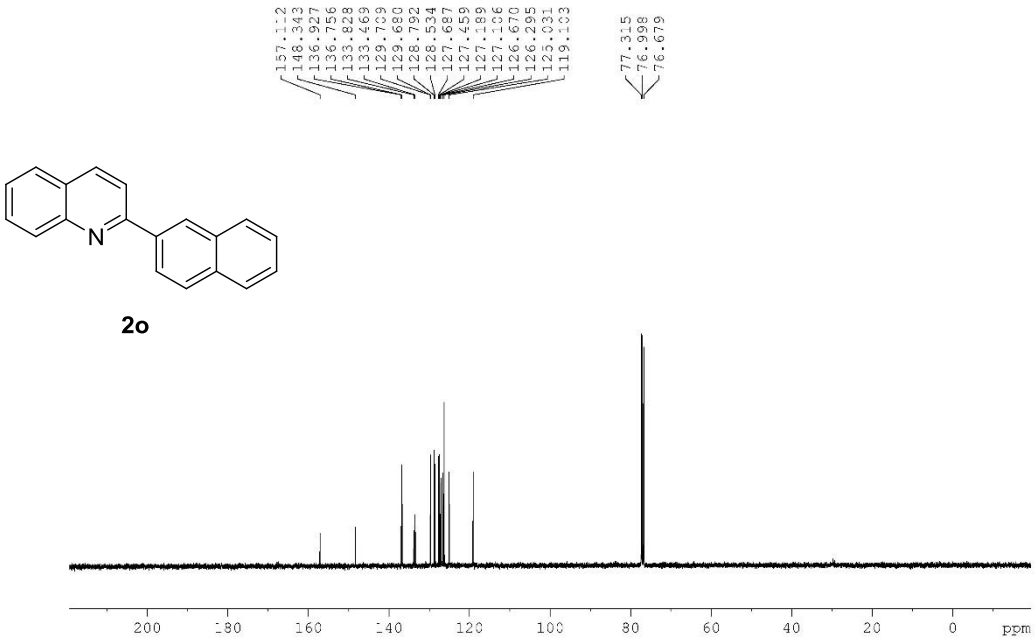


Fig. S114. ^{1}H NMR Spectrum of 2p (400 MHz, $CDCl_3$).

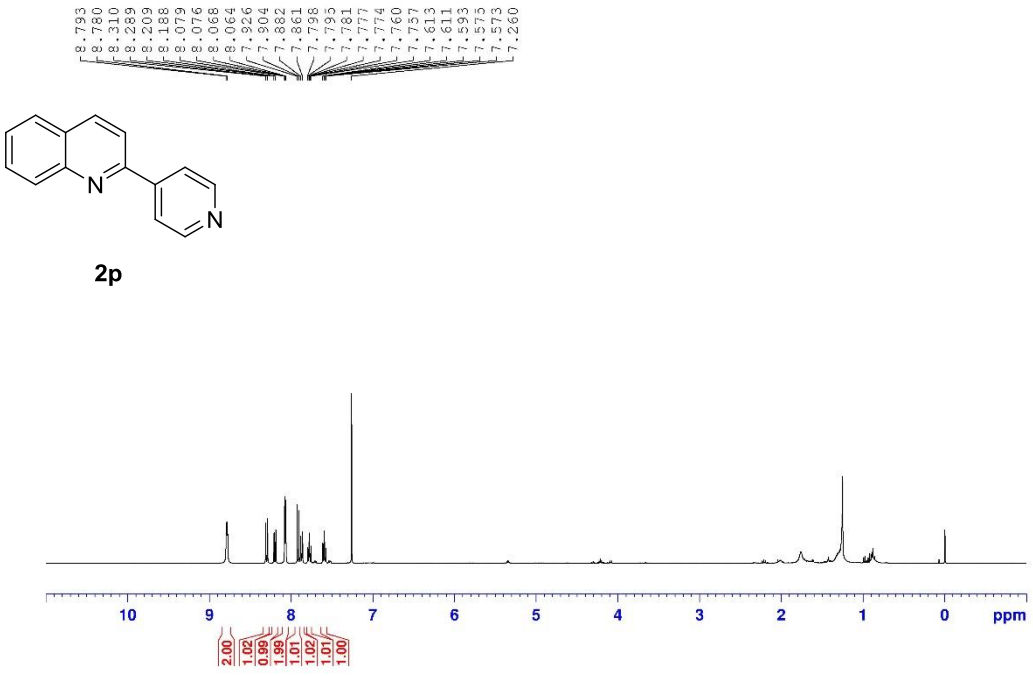


Fig. S115. ^{13}C NMR Spectrum of 2p (100 MHz, $CDCl_3$).

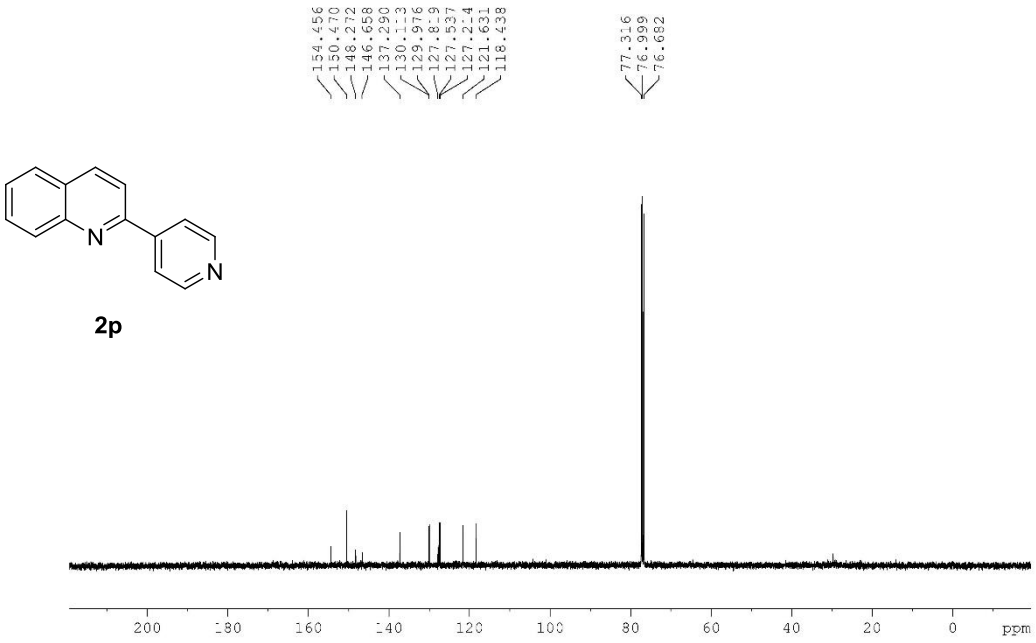


Fig. S116. ^{1}H NMR Spectrum of 2q (400 MHz, $CDCl_3$).

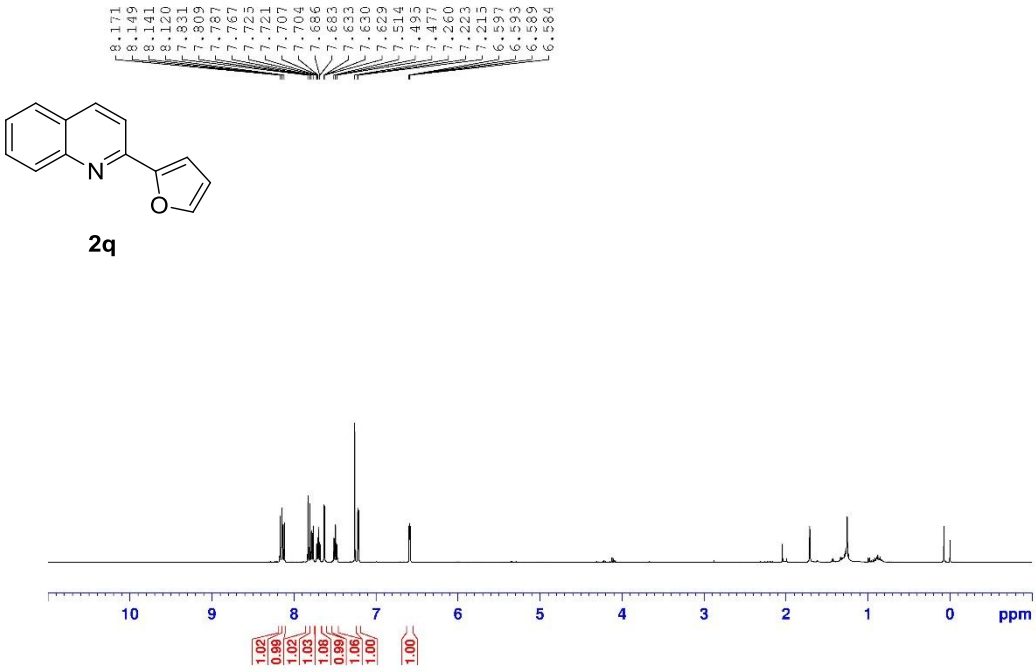


Fig. S117. ^{13}C NMR Spectrum of 2q (100 MHz, $CDCl_3$).

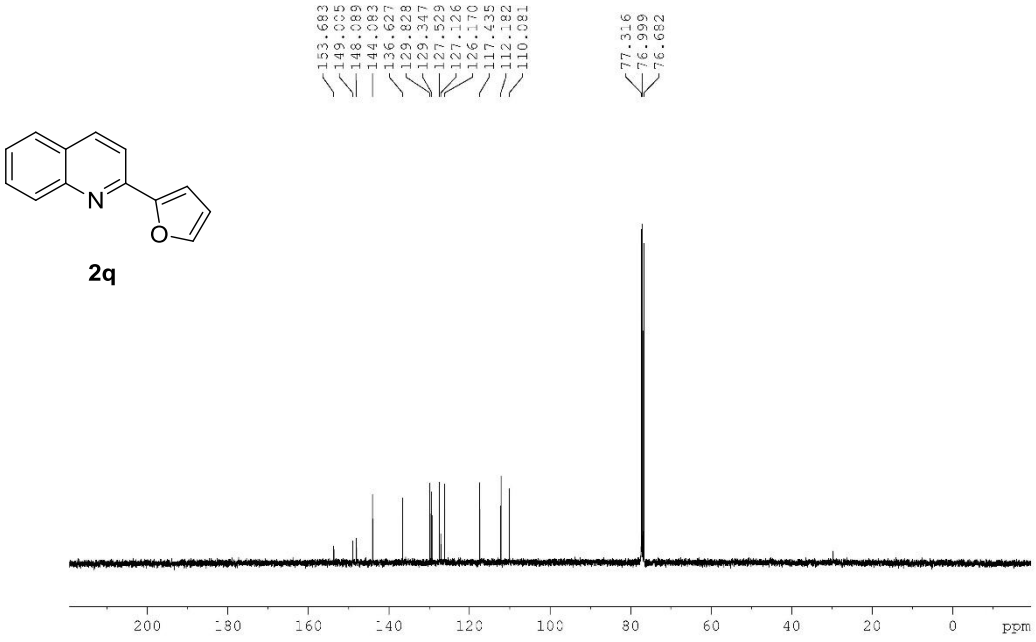


Fig. S118. ^{1}H NMR Spectrum of 2r (400 MHz, $CDCl_3$).

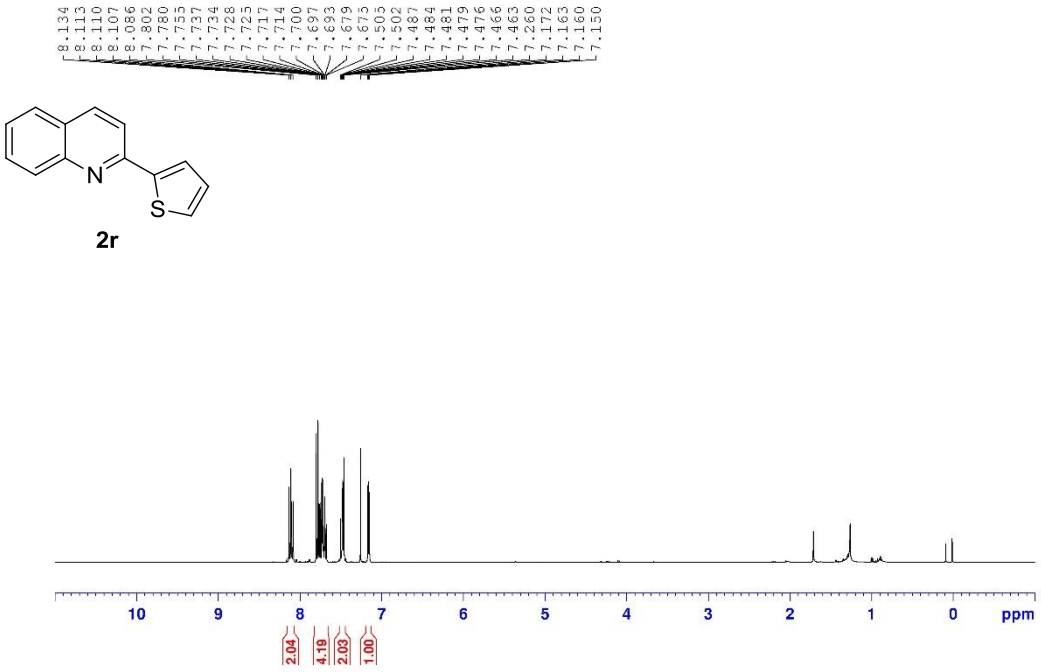


Fig. S119. ^{13}C NMR Spectrum of 2r (100 MHz, $CDCl_3$).

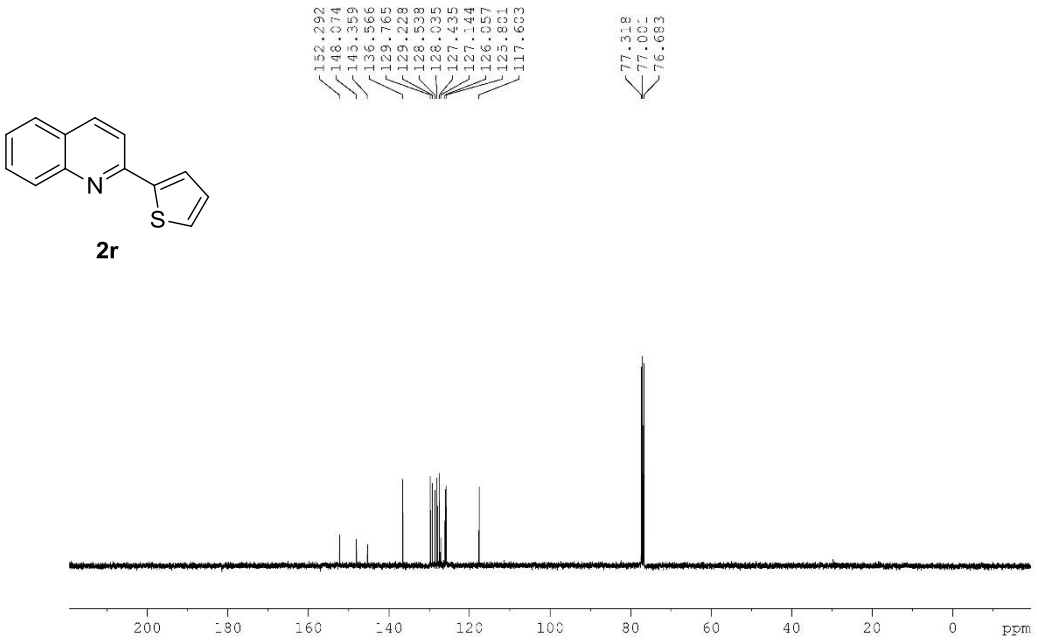


Fig. S120. ^{1}H NMR Spectrum of 2s (400 MHz, $CDCl_3$).

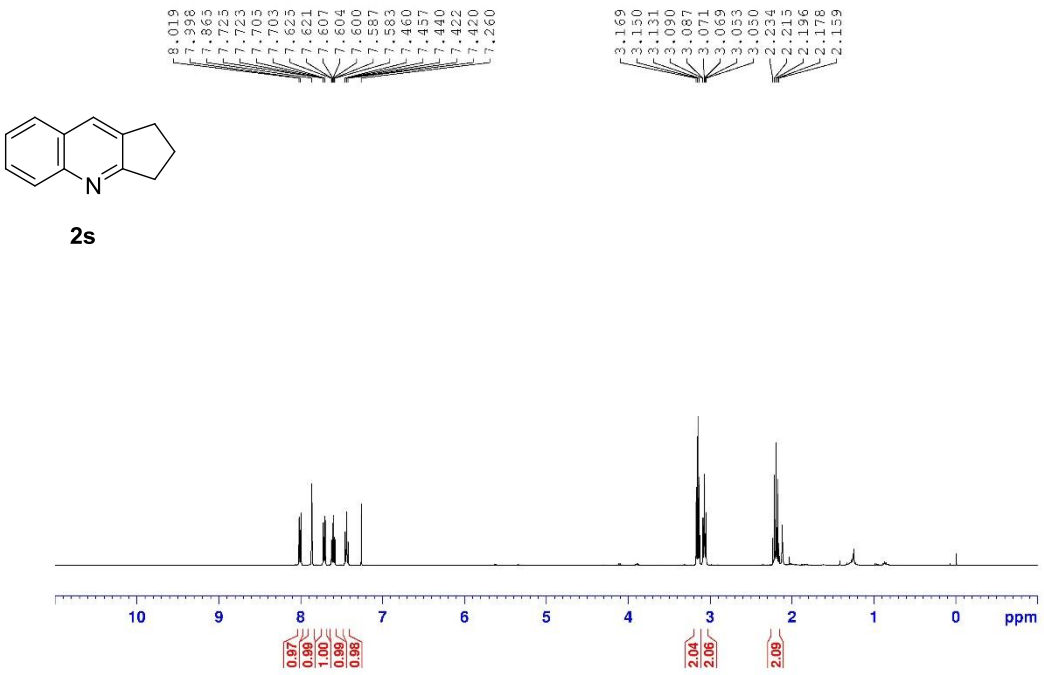


Fig. S121. ^{13}C NMR Spectrum of 2s (100 MHz, $CDCl_3$).

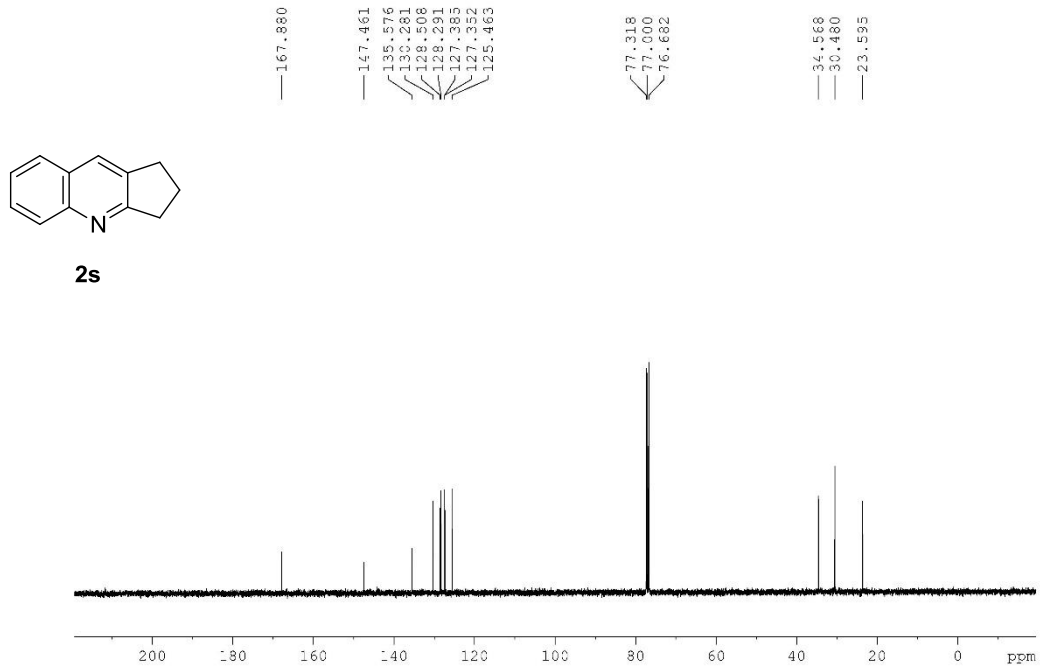


Fig. S122. ^{1}H NMR Spectrum of 2t (400 MHz, $CDCl_3$).

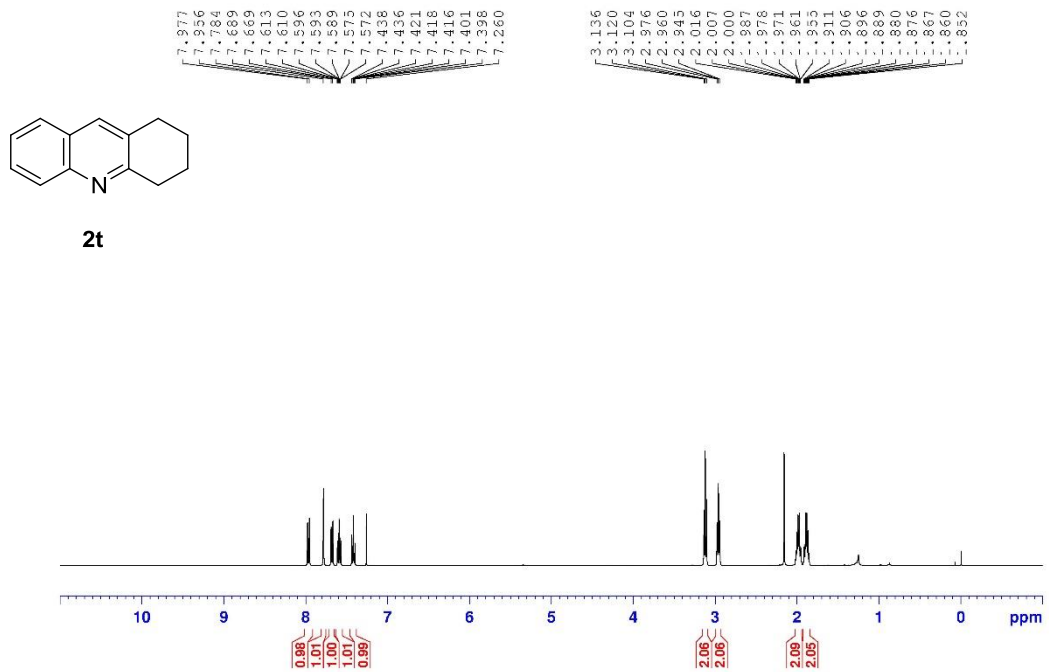


Fig. S123. ^{13}C NMR Spectrum of 2t (100 MHz, $CDCl_3$).

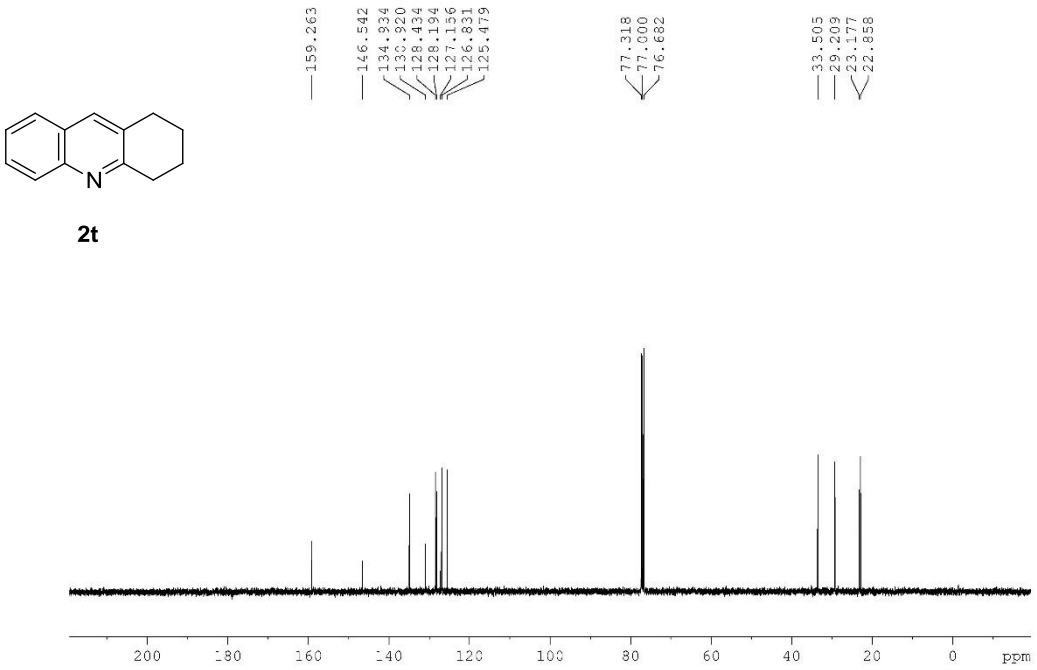


Fig. S124. ^{1}H NMR Spectrum of 2u (500 MHz, $CDCl_3$).

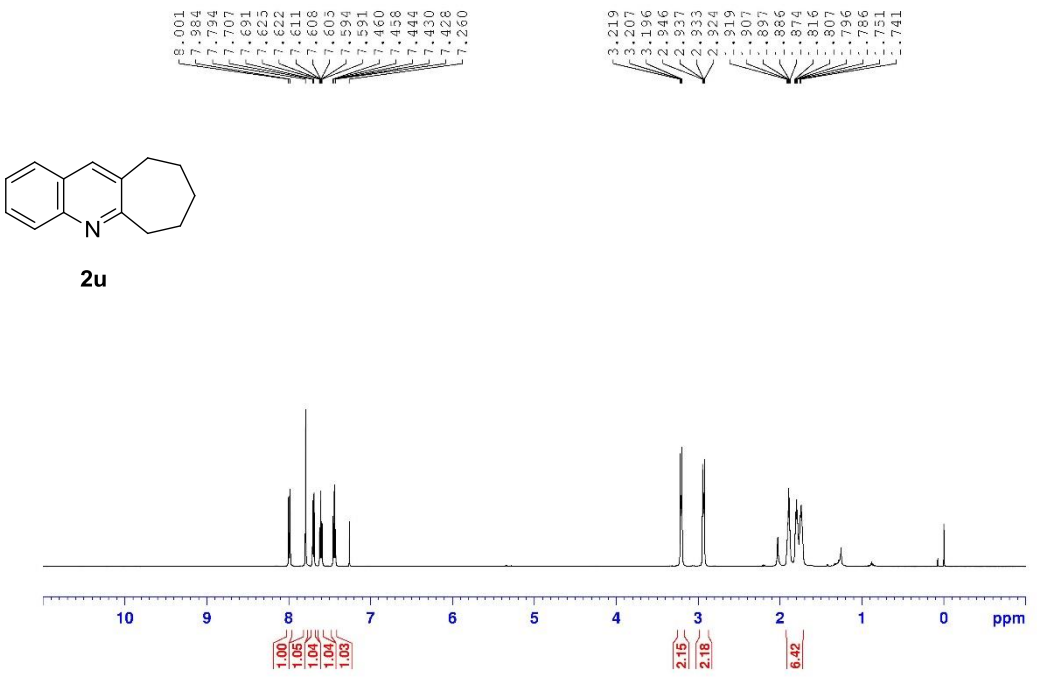


Fig. S125. ^{13}C NMR Spectrum of 2u (125 MHz, $CDCl_3$).

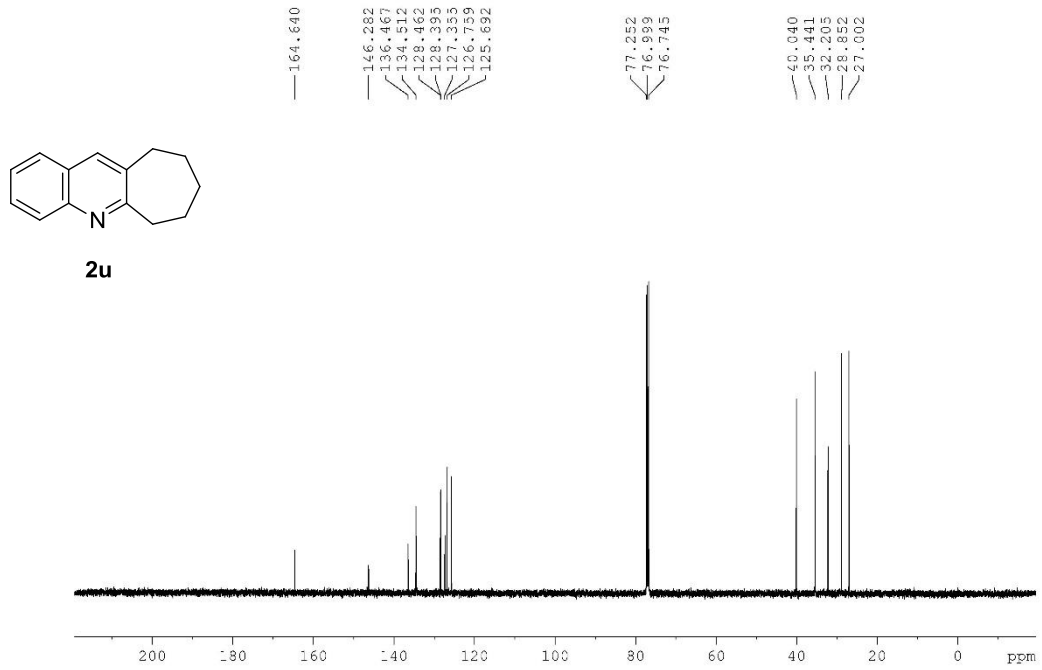


Fig. S126. ^{1}H NMR Spectrum of 2v (400 MHz, $CDCl_3$).

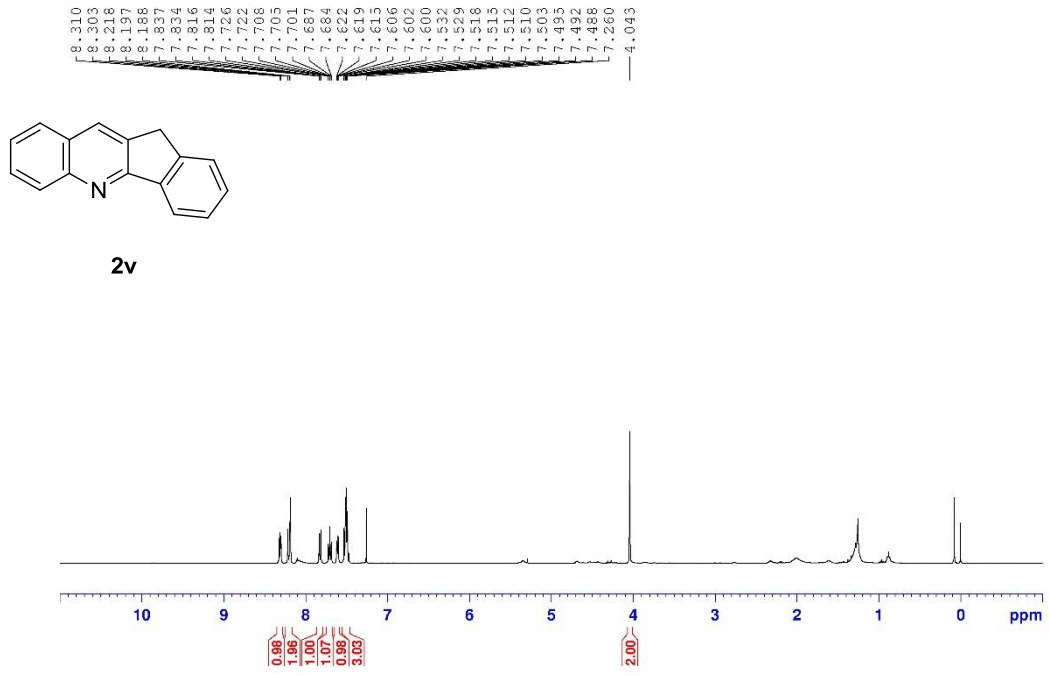


Fig. S127. ^{13}C NMR Spectrum of 2v (100 MHz, $CDCl_3$).

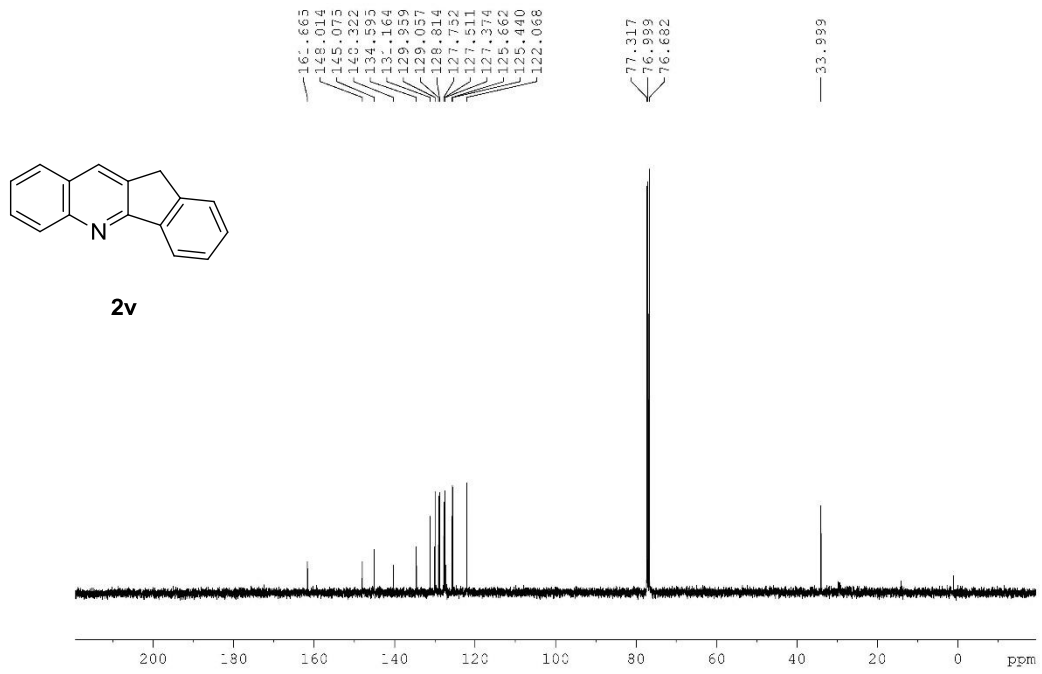


Fig. S128. ^{1}H NMR Spectrum of 2w (500 MHz, $CDCl_3$).

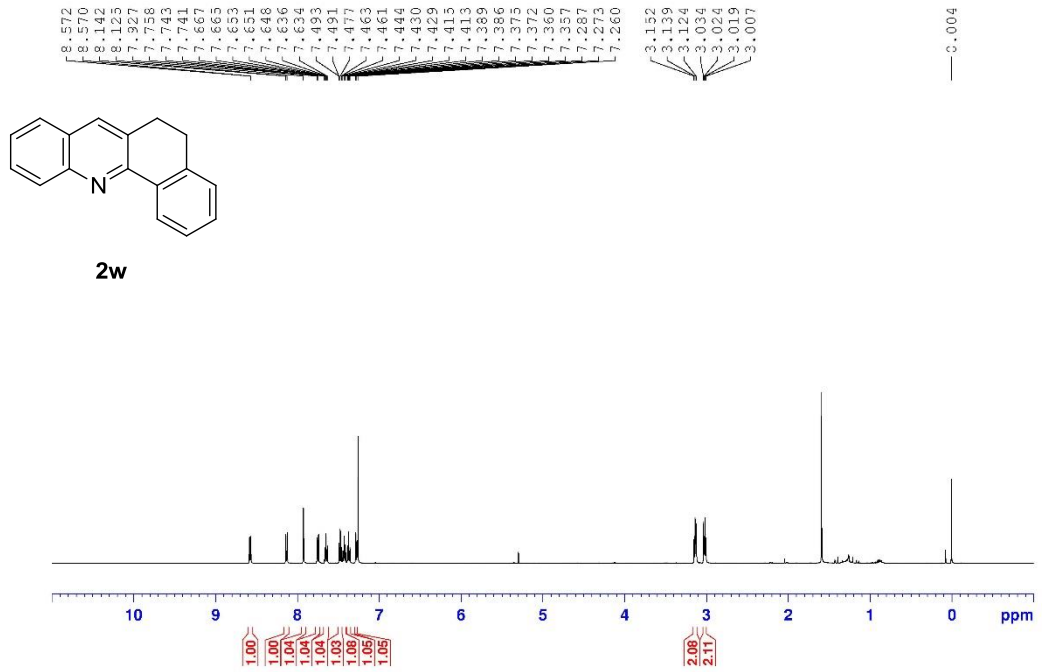


Fig. S129. ^{13}C NMR Spectrum of 2w (100 MHz, $CDCl_3$).

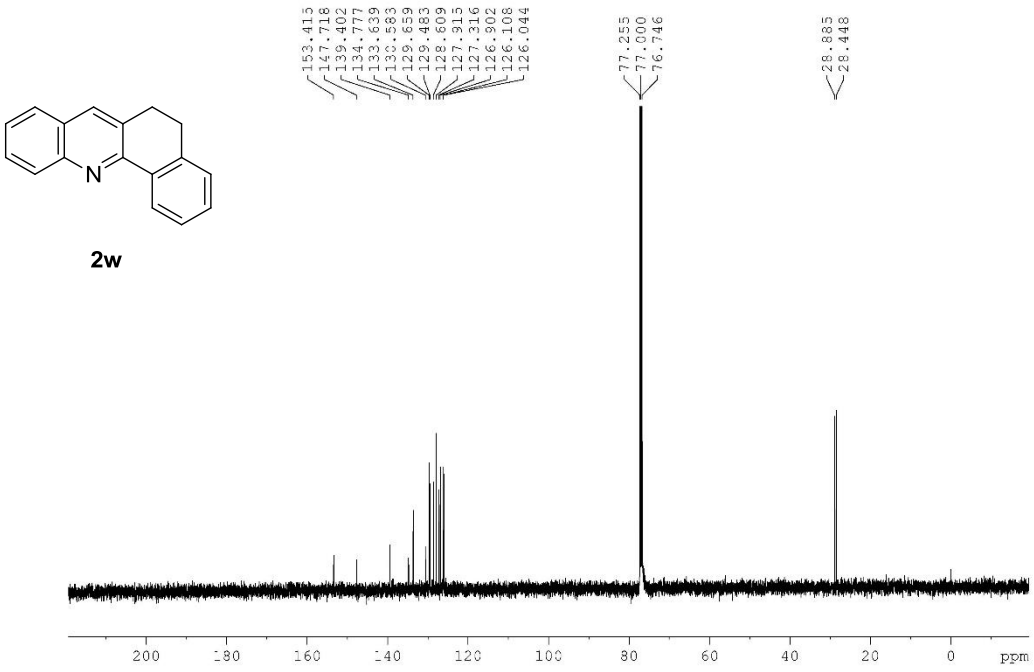


Fig. S130. ^{1}H NMR Spectrum of 2x (500 MHz, $CDCl_3$).

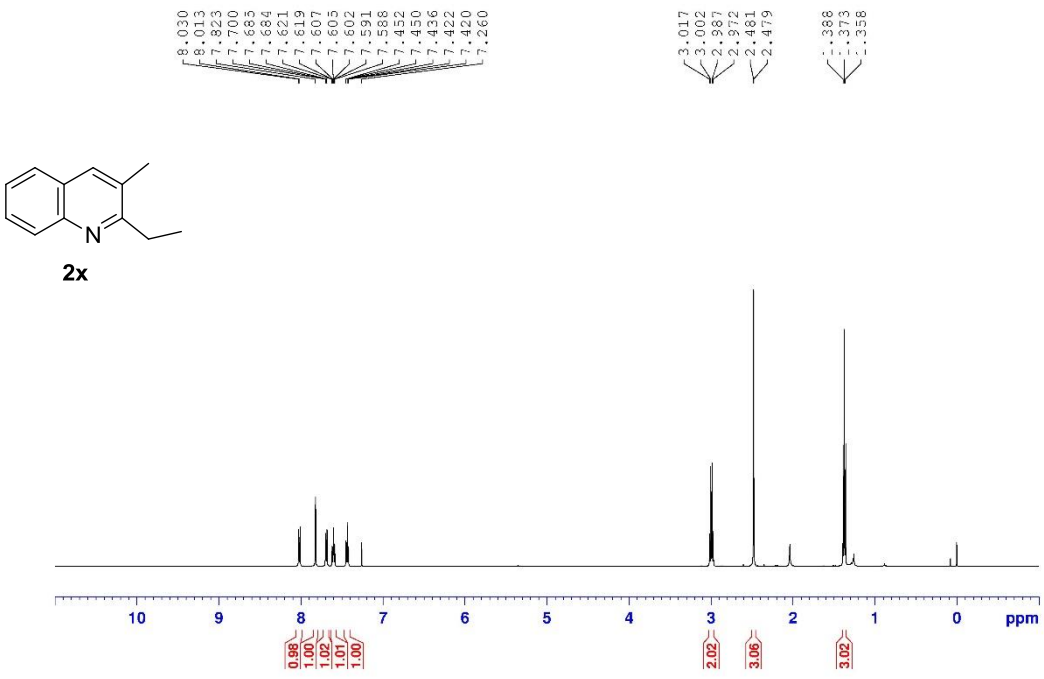


Fig. S131. ^{13}C NMR Spectrum of 2x (100 MHz, $CDCl_3$).

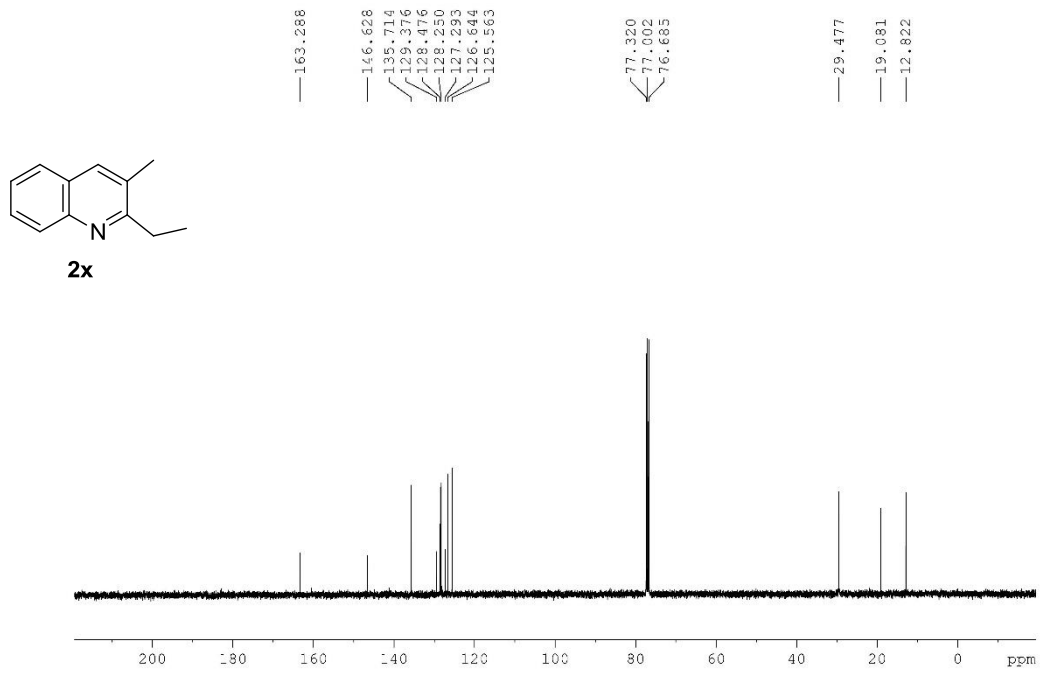


Fig. S132. ^{1}H NMR Spectrum of 2y (400 MHz, $CDCl_3$).

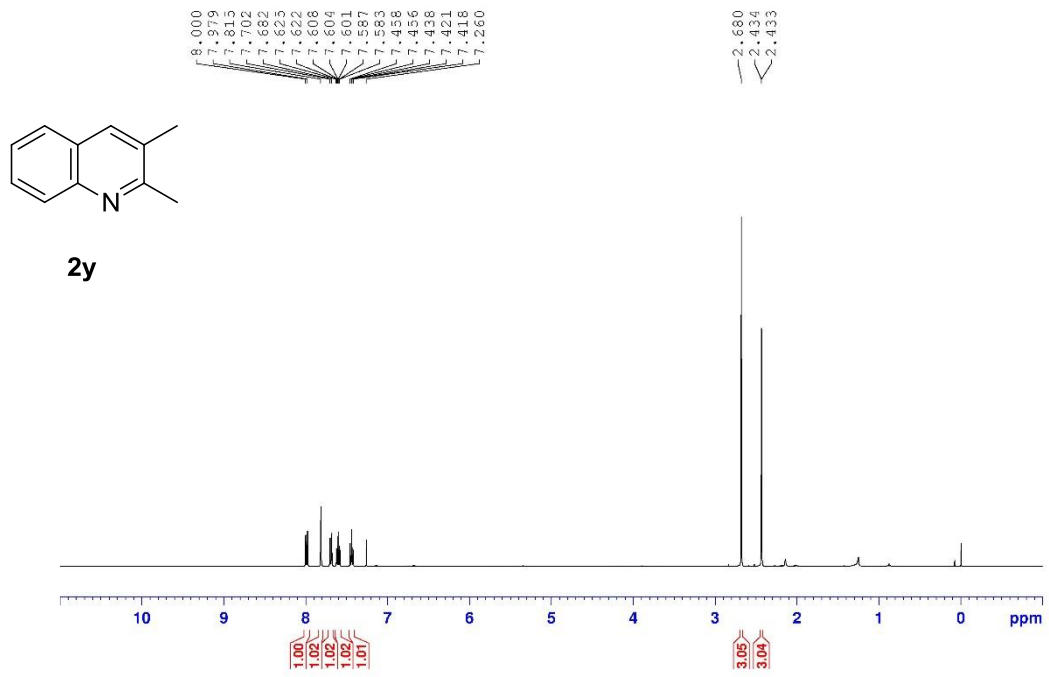


Fig. S133. ^{13}C NMR Spectrum of 2y (100 MHz, $CDCl_3$).

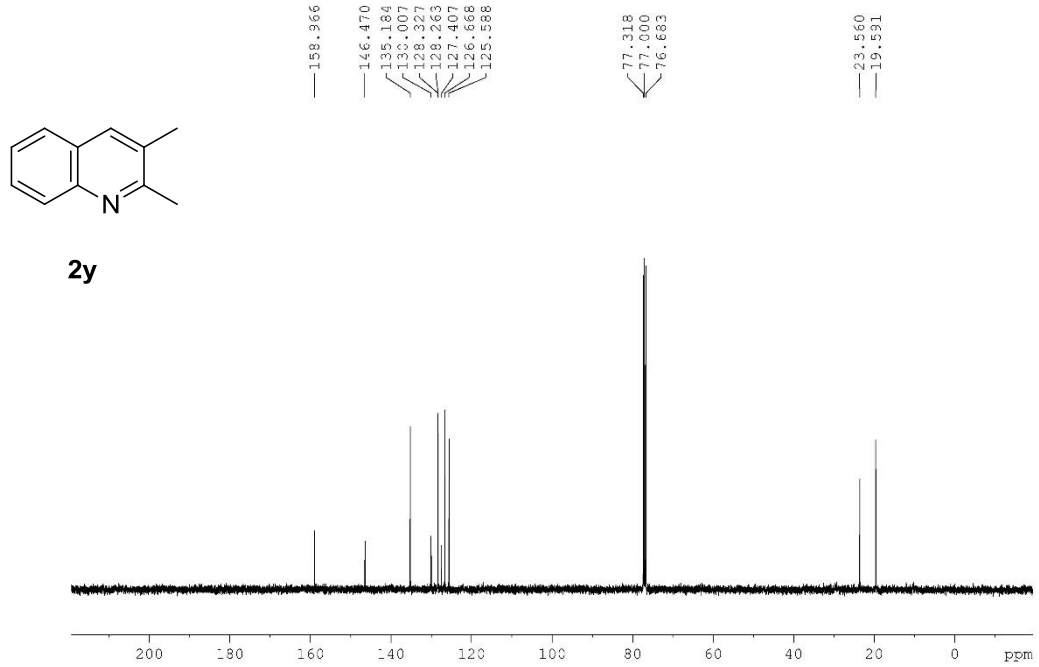


Fig. S134. ^{1}H NMR Spectrum of 2z (400 MHz, $CDCl_3$).

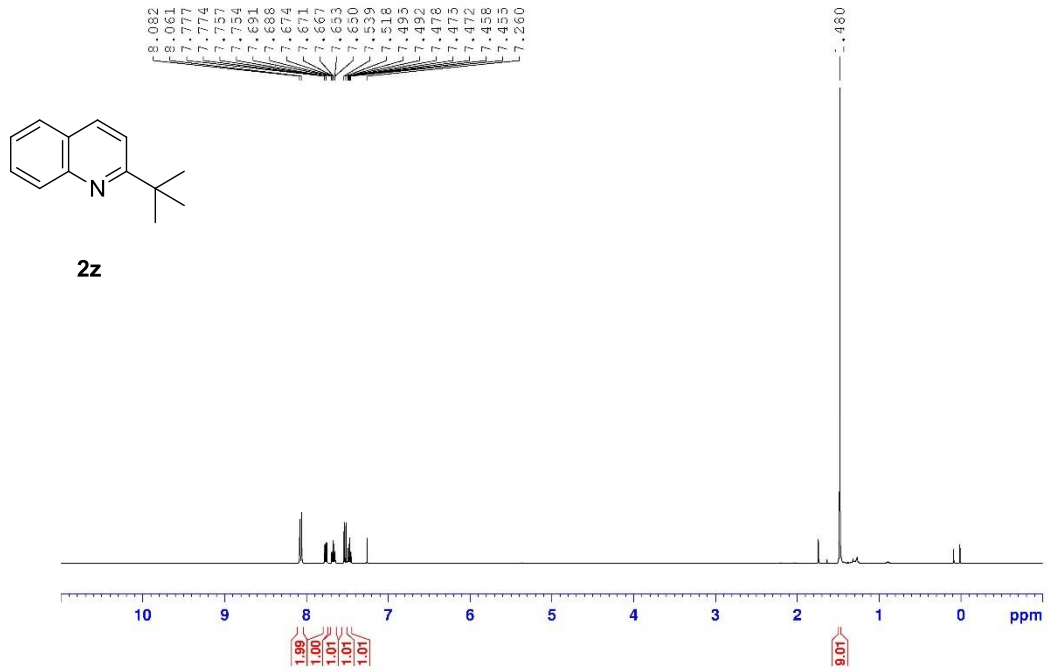


Fig. S135. ^{13}C NMR Spectrum of 2z (100 MHz, $CDCl_3$).

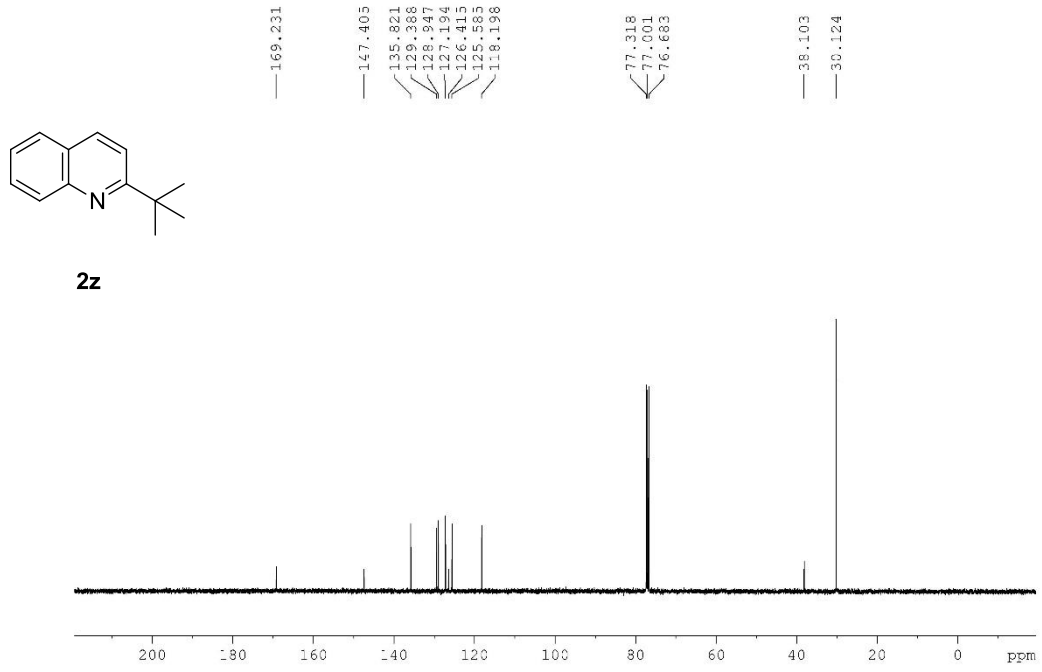


Fig. S136. ^{1}H NMR Spectrum of 2aa (400 MHz, $CDCl_3$).

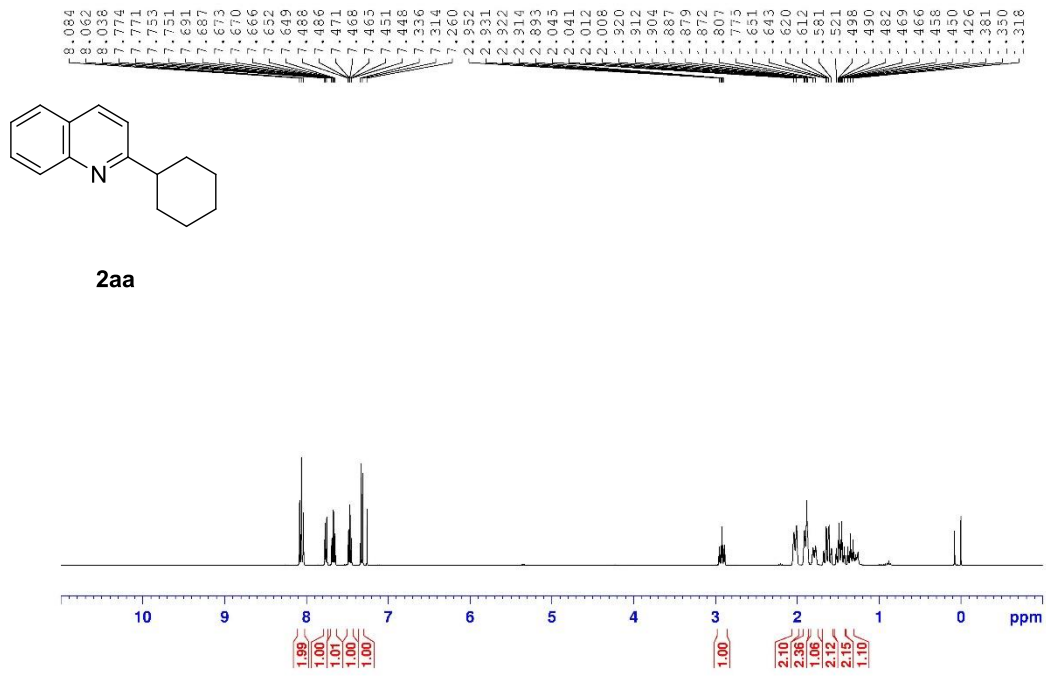


Fig. S137. ^{13}C NMR Spectrum of 2aa (100 MHz, $CDCl_3$).

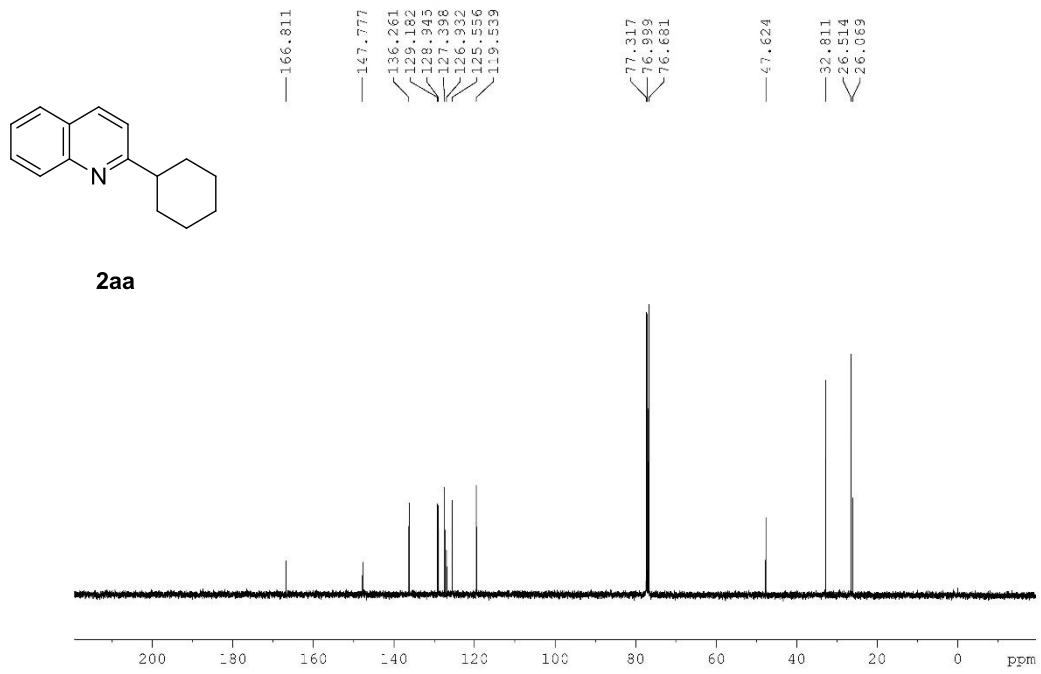


Fig. S138. ^{1}H NMR Spectrum of 2ab (400 MHz, $CDCl_3$).

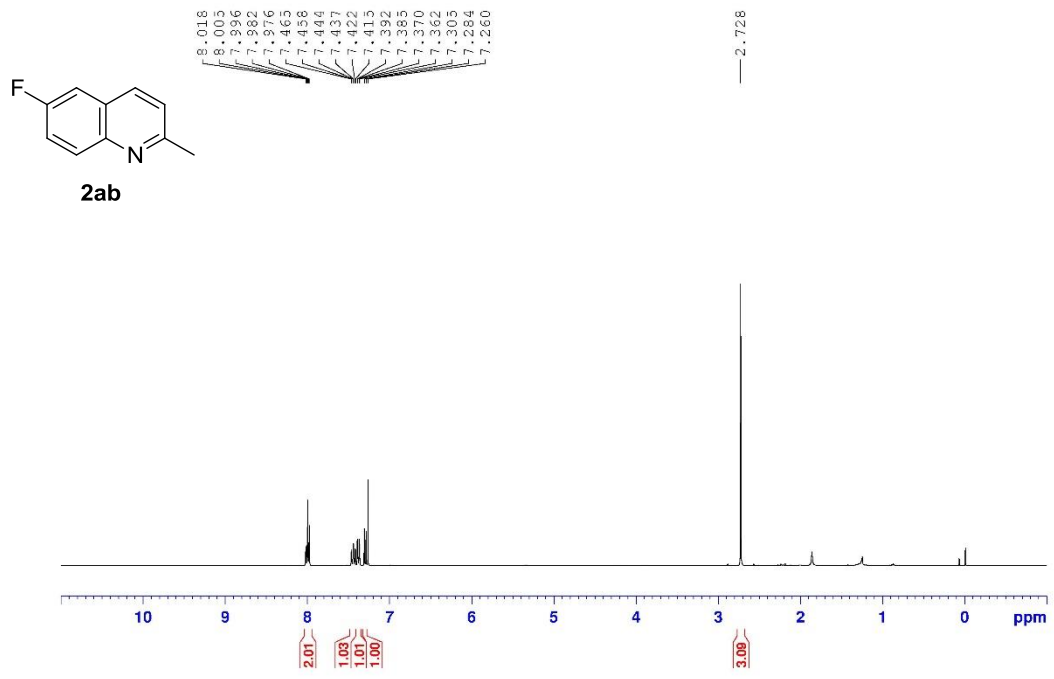


Fig. S139. ^{13}C NMR Spectrum of 2ab (100 MHz, $CDCl_3$).

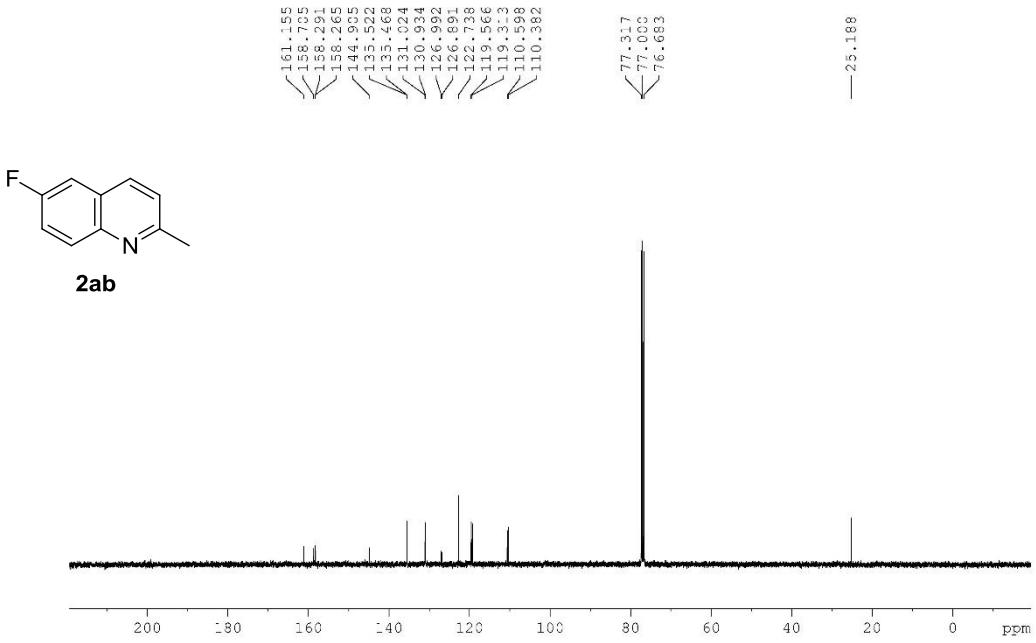


Fig. S140. ^{19}F NMR Spectrum of 2ab (376 MHz, $CDCl_3$).

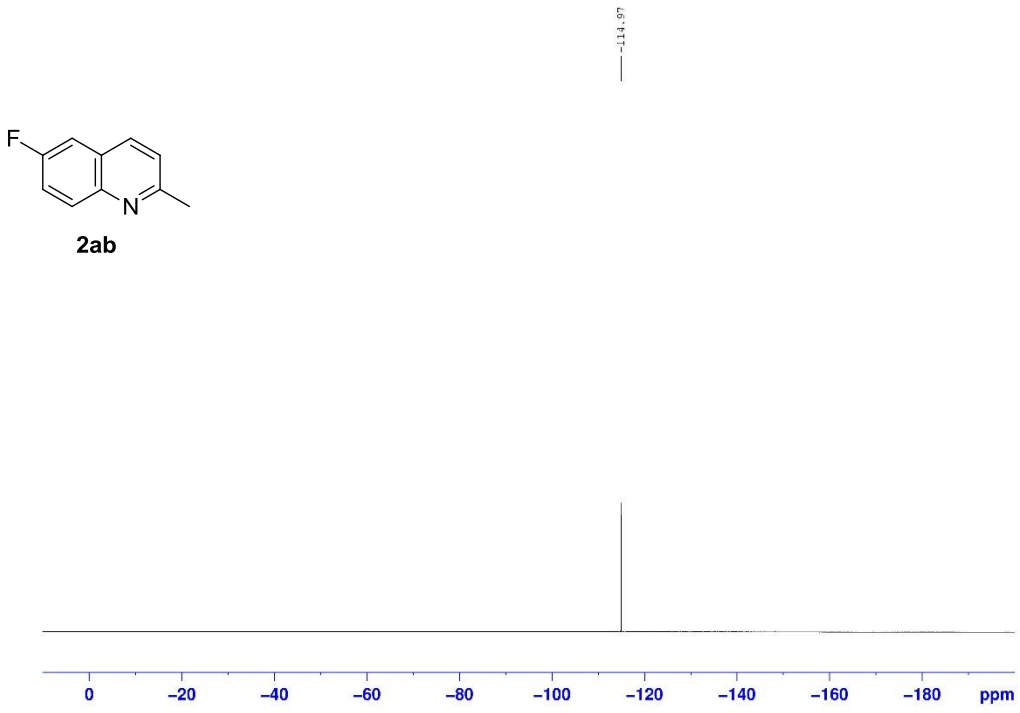


Fig. S141. ^{1}H NMR Spectrum of 2ac (400 MHz, $CDCl_3$).

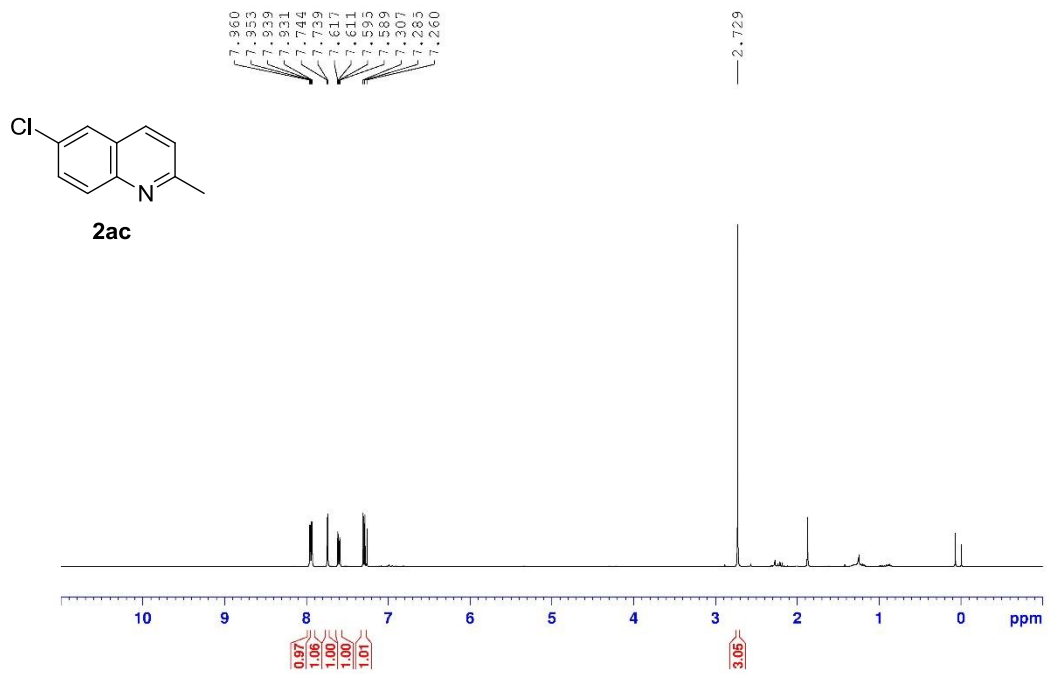


Fig. S142. ^{13}C NMR Spectrum of 2ac (100 MHz, $CDCl_3$).

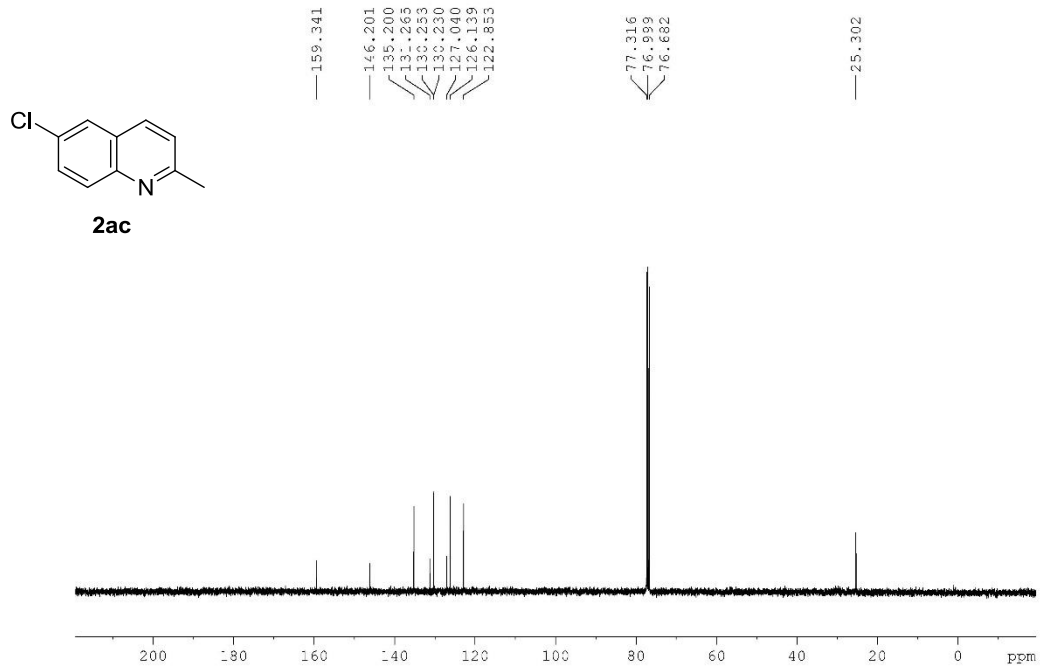


Fig. S143. ^{1}H NMR Spectrum of 2ad (400 MHz, $CDCl_3$).

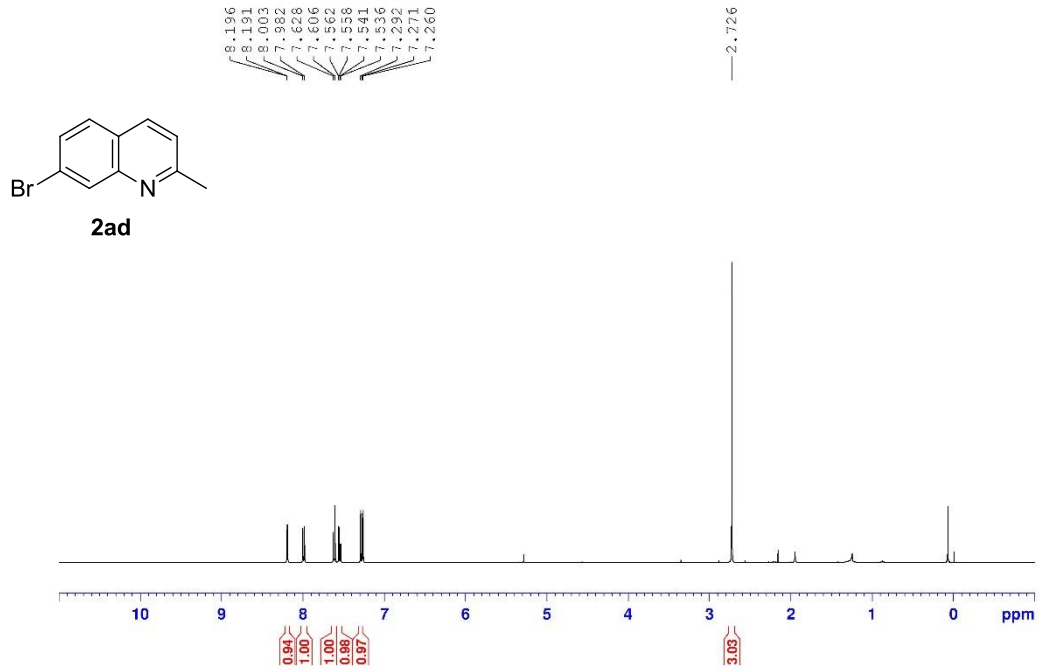


Fig. S144. ^{13}C NMR Spectrum of 2ad (100 MHz, $CDCl_3$).

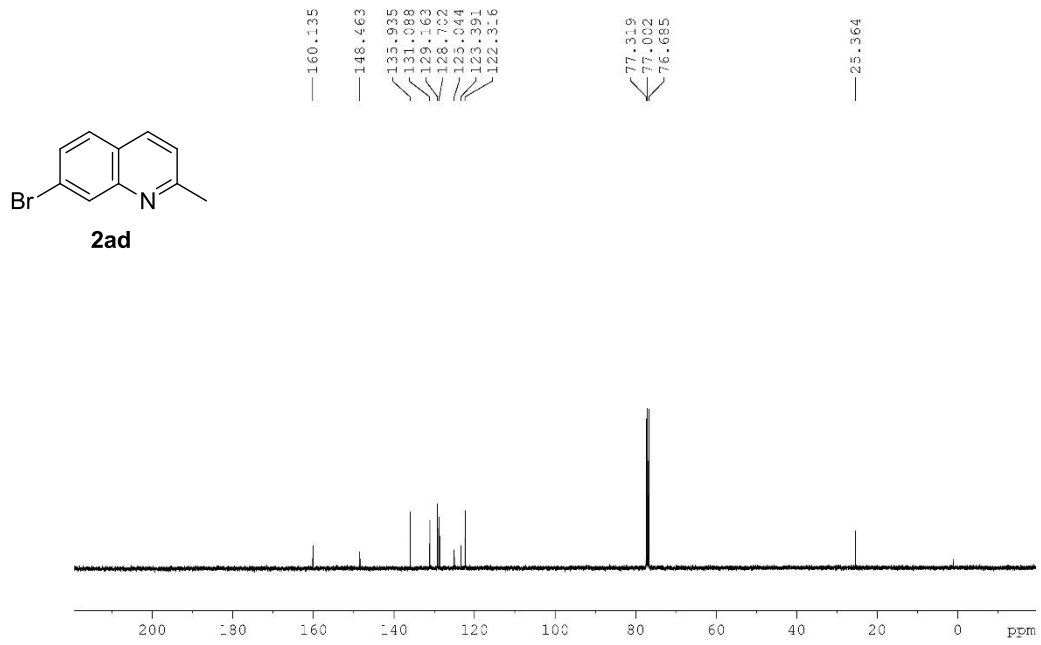


Fig. S145. ^{1}H NMR Spectrum of 2ae (400 MHz, $CDCl_3$).

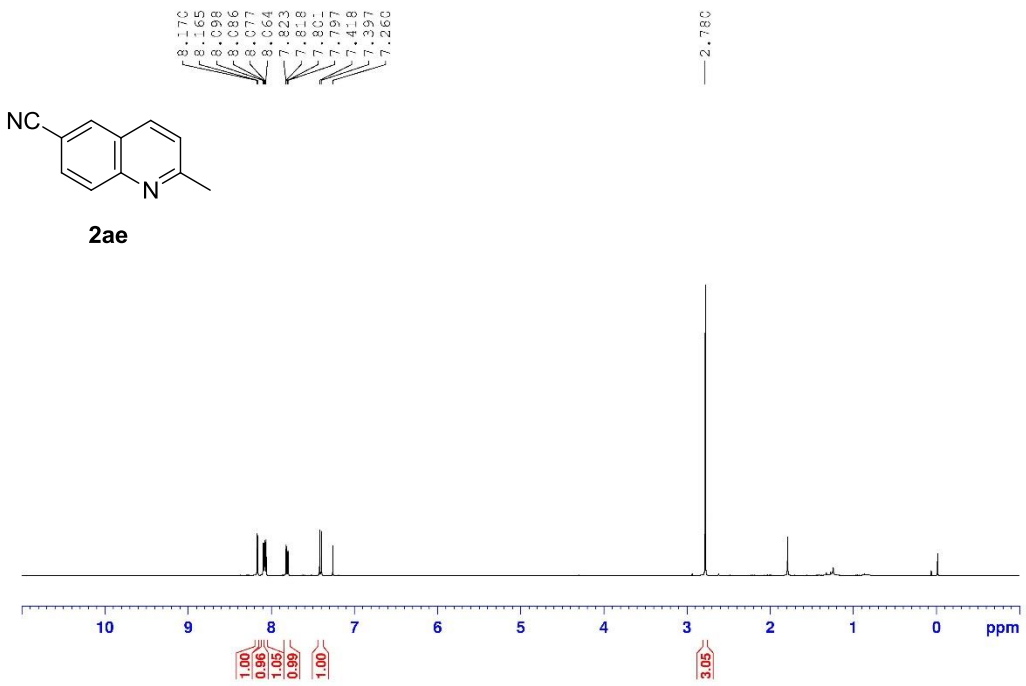


Fig. S146. ^{13}C NMR Spectrum of 2ae (100 MHz, $CDCl_3$).

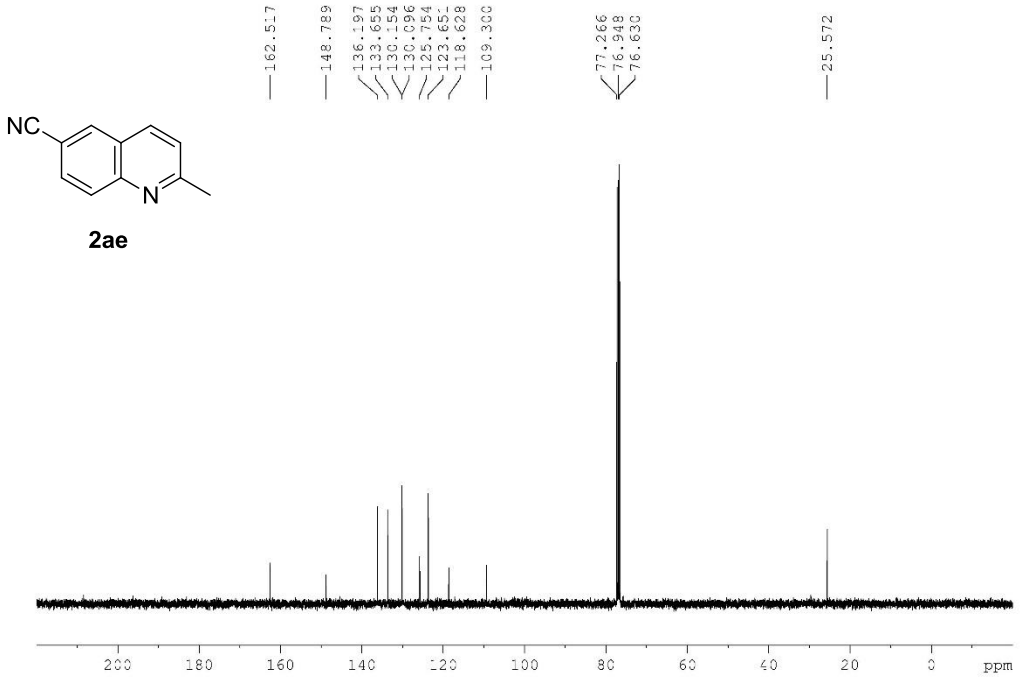


Fig. S147. ^{1}H NMR Spectrum of 2af (400 MHz, $CDCl_3$).

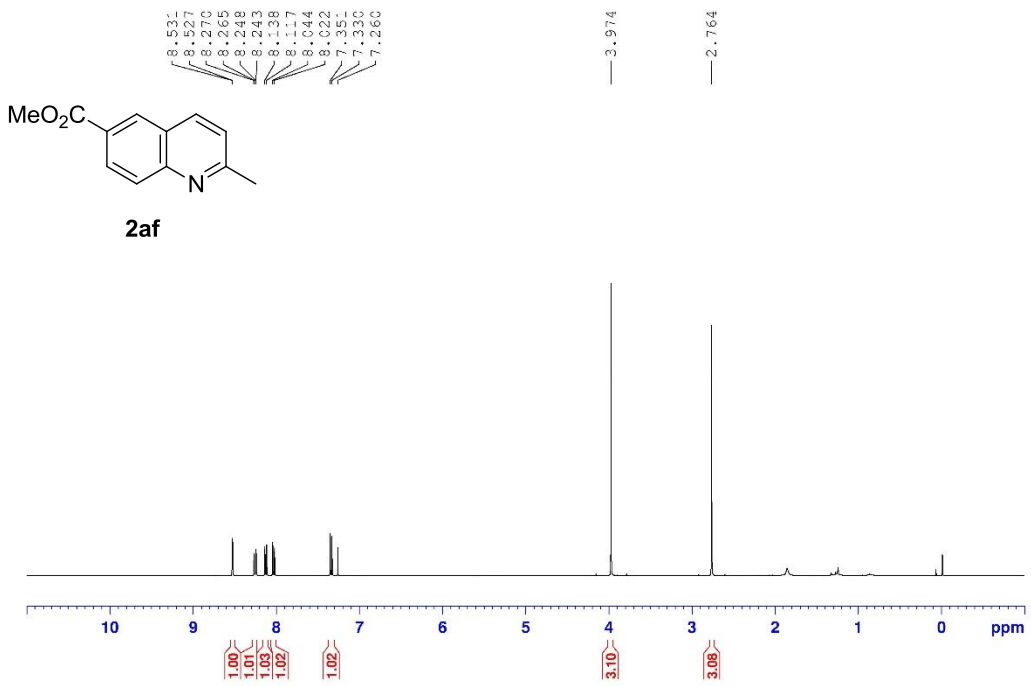


Fig. S148. ^{13}C NMR Spectrum of 2af (100 MHz, $CDCl_3$).

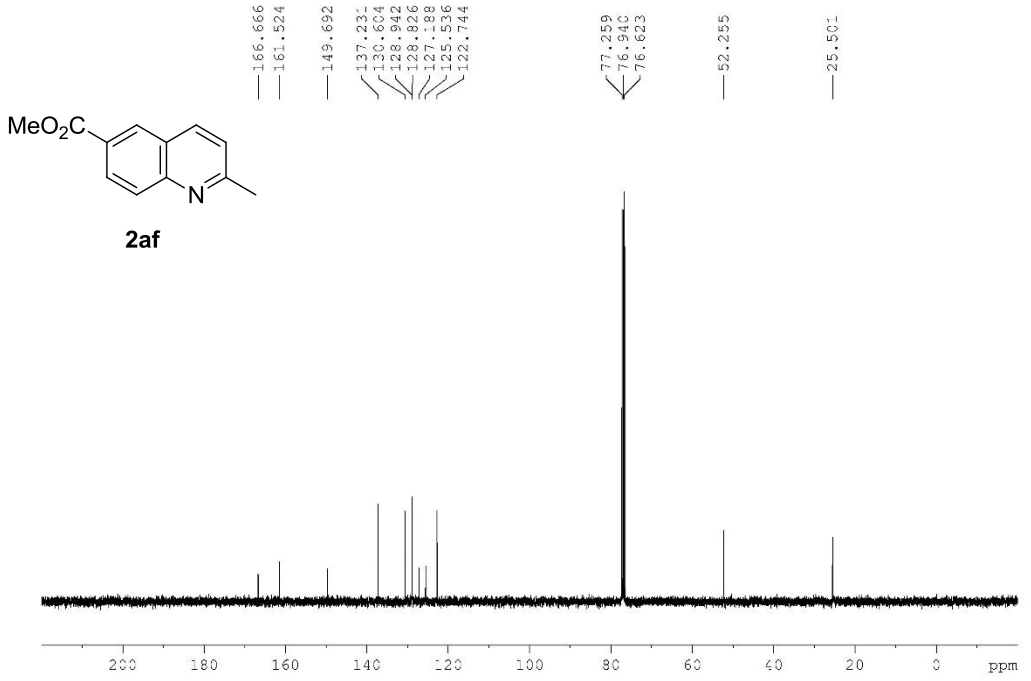


Fig. S149. ^{1}H NMR Spectrum of 2ag (400 MHz, $CDCl_3$).

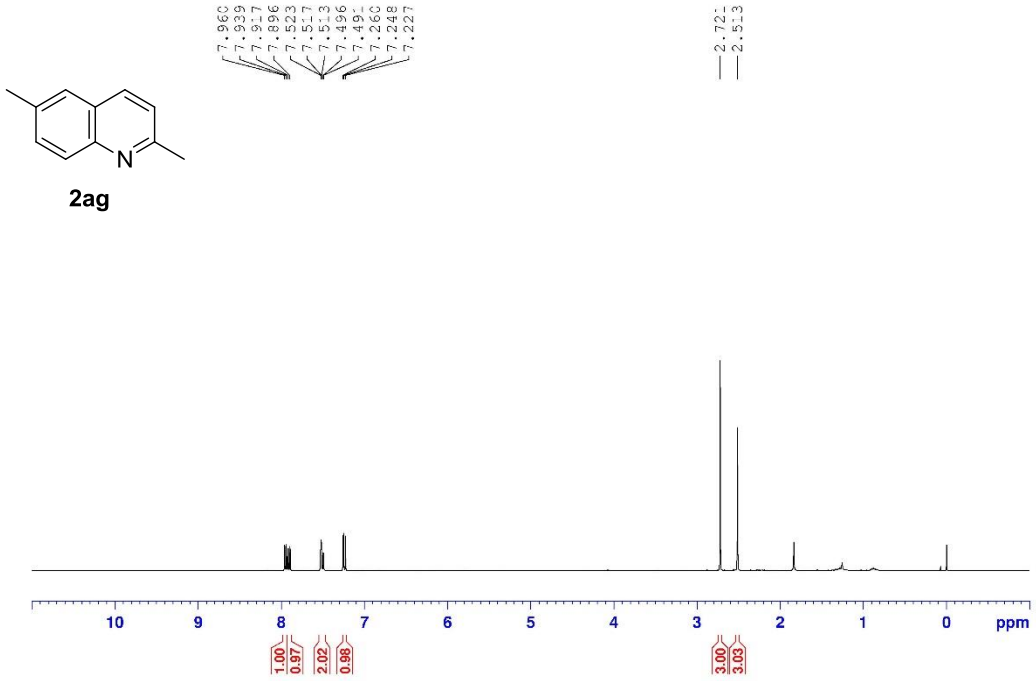


Fig. S150. ^{13}C NMR Spectrum of 2ag (100 MHz, $CDCl_3$).

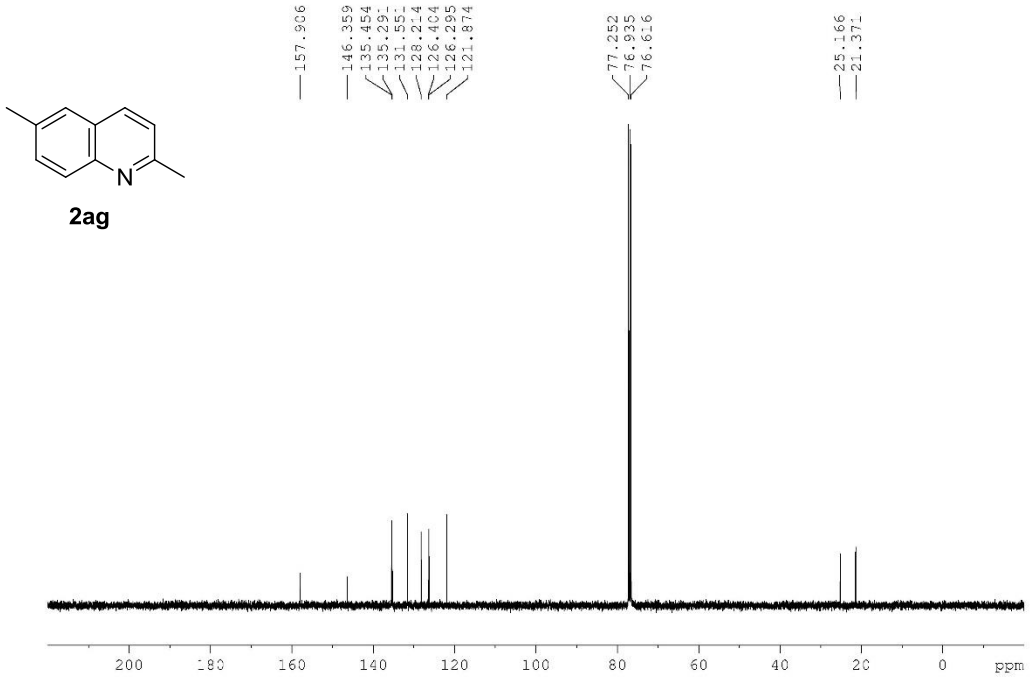


Fig. S151. ^{1}H NMR Spectrum of 2ah (400 MHz, $CDCl_3$).

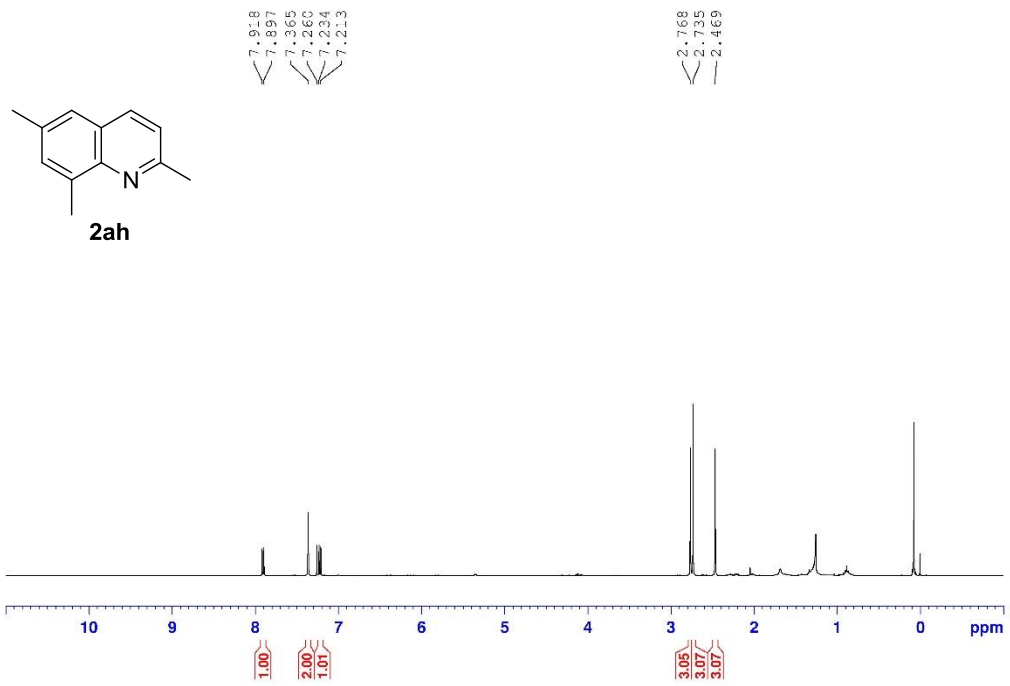


Fig. S152. ^{13}C NMR Spectrum of 2ah (100 MHz, $CDCl_3$).

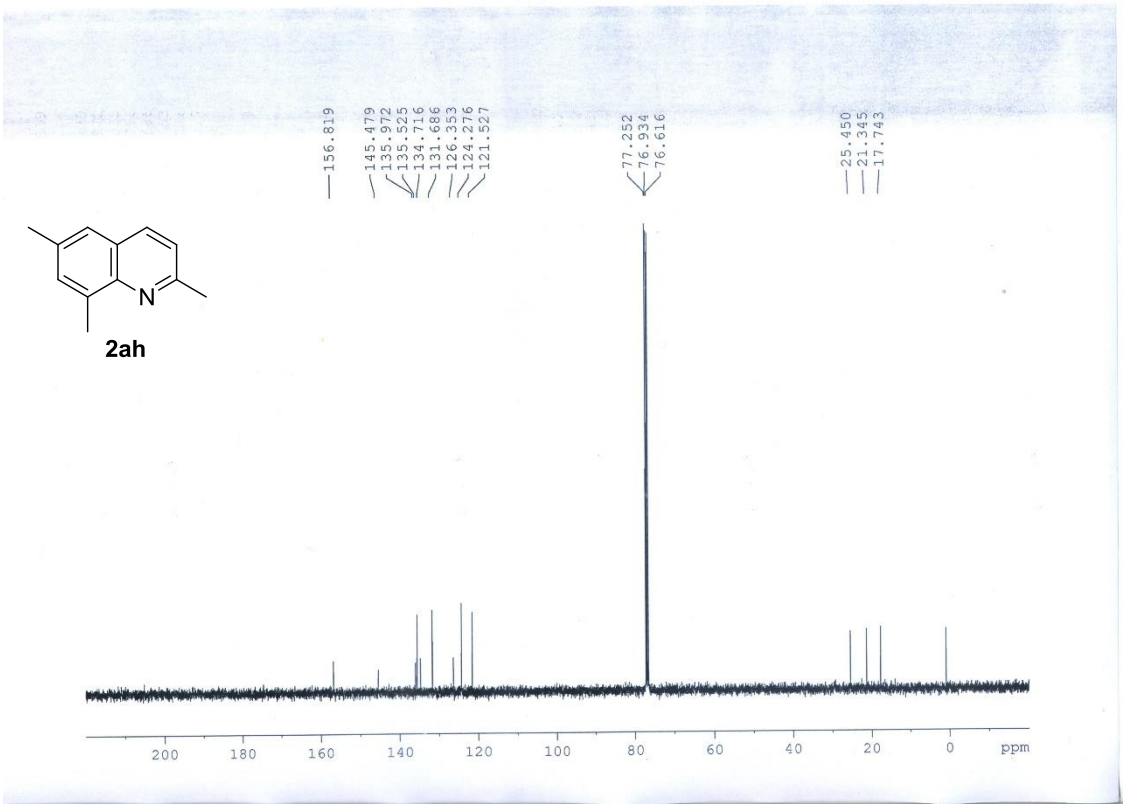


Fig. S153. ^{1}H NMR Spectrum of 2ai (500 MHz, $CDCl_3$).

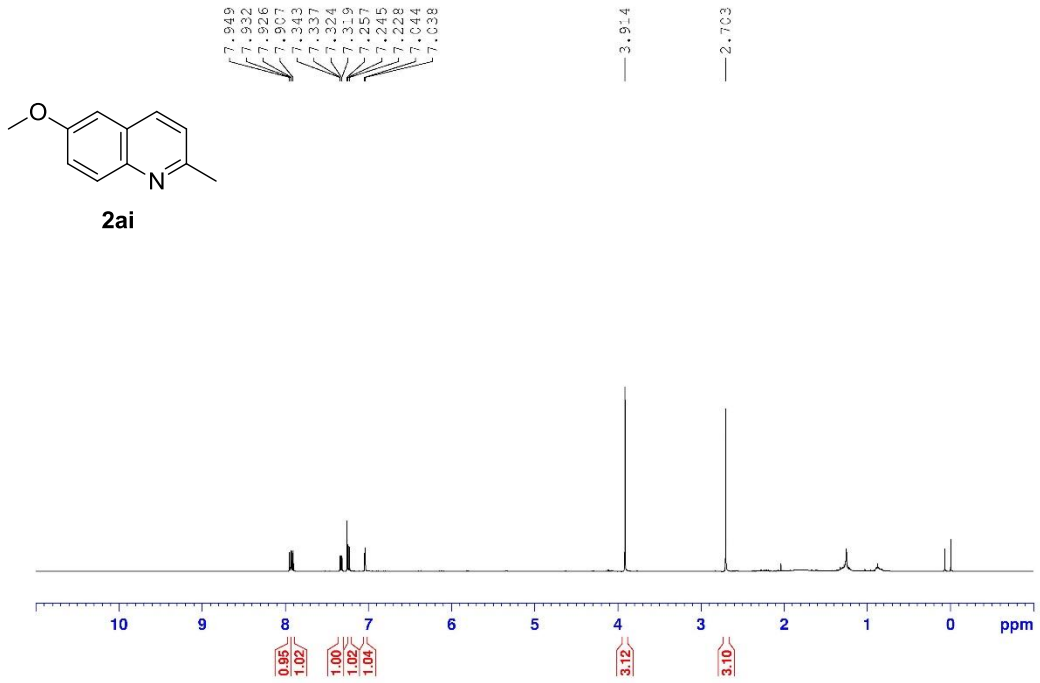


Fig. S154. ^{13}C NMR Spectrum of 2ai (125 MHz, $CDCl_3$).

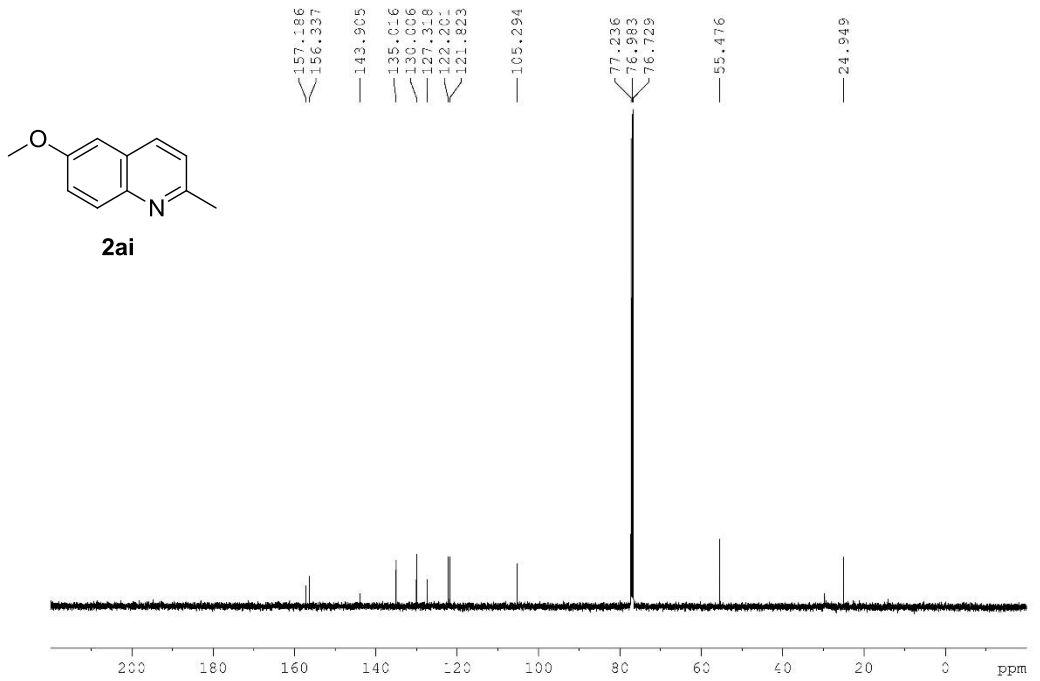


Fig. S155. ^{1}H NMR Spectrum of 2aj (400 MHz, $CDCl_3$).

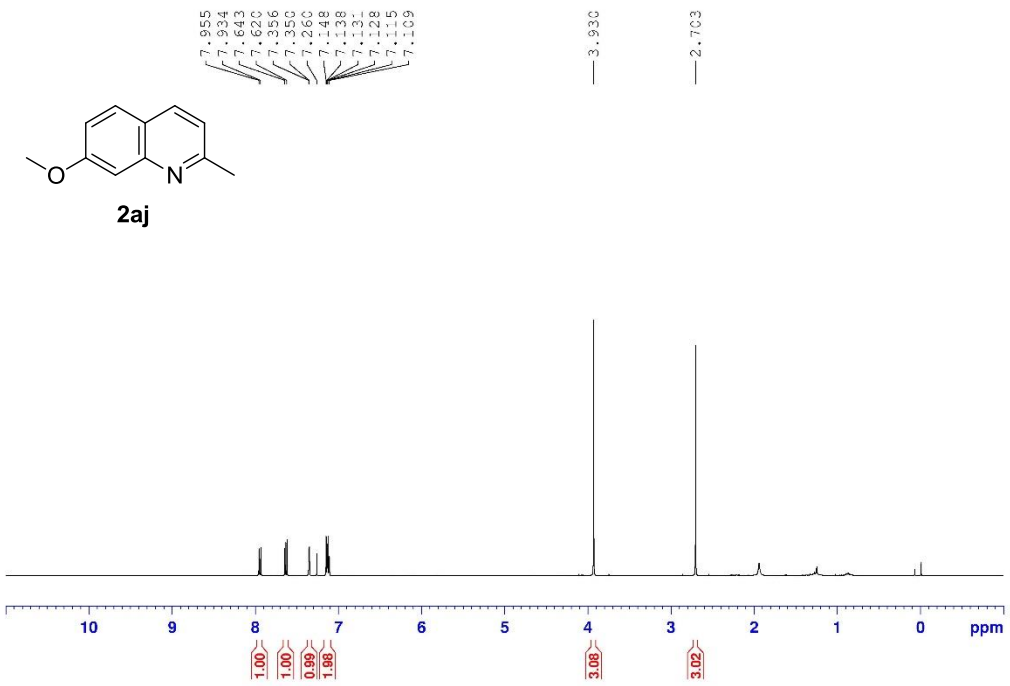


Fig. S156. ^{13}C NMR Spectrum of 2aj (100 MHz, $CDCl_3$).

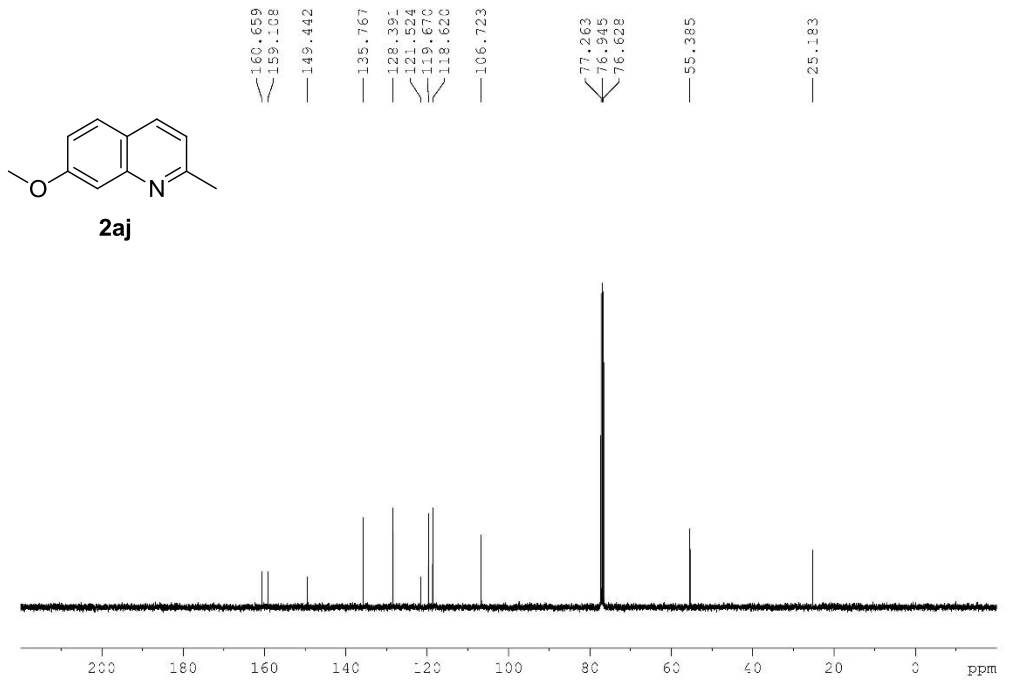


Fig. S157. ^{1}H NMR Spectrum of 2ak (400 MHz, $CDCl_3$).

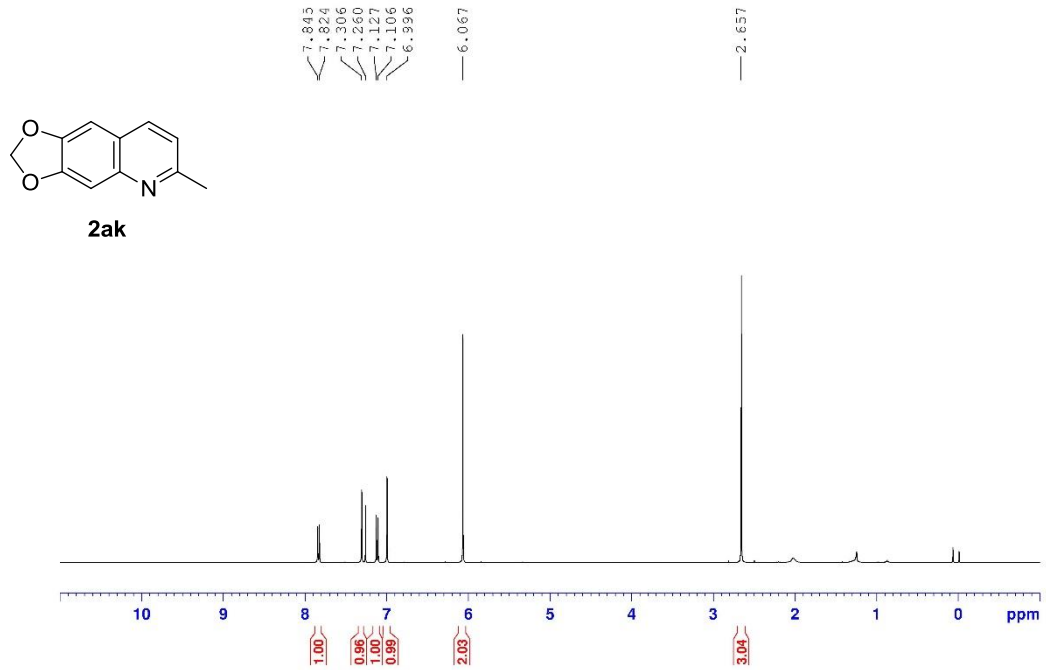


Fig. S158. ^{13}C NMR Spectrum of 2ak (100 MHz, $CDCl_3$).

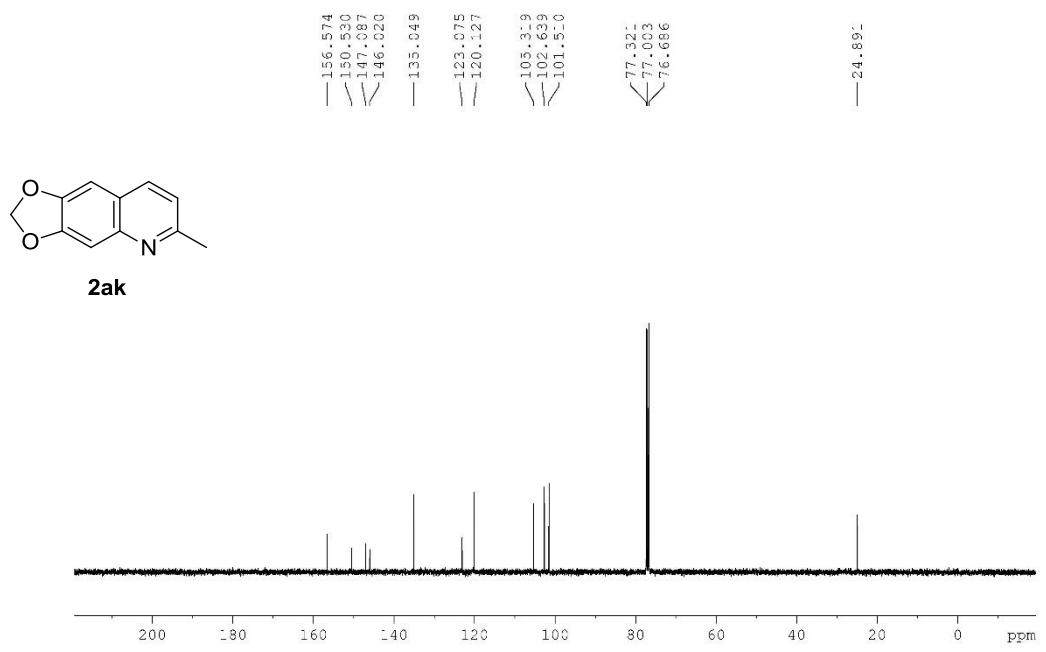


Fig. S159. ^{1}H NMR Spectrum of 2am (400 MHz, DMSO-d_6**).**

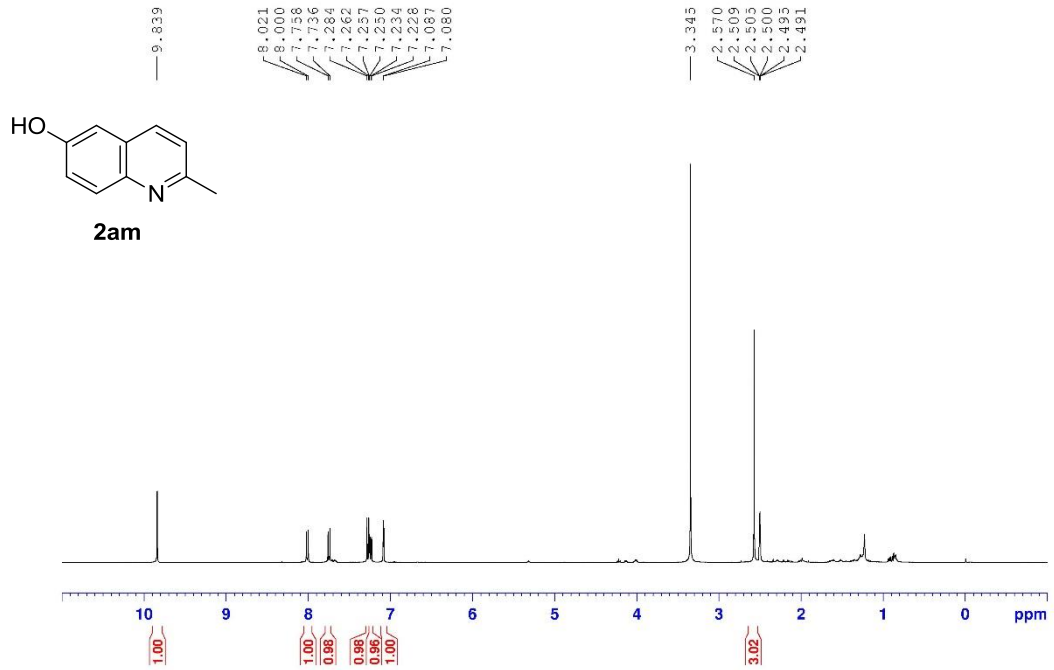


Fig. S160. ^{13}C NMR Spectrum of 2am (100 MHz, DMSO-d_6**).**