Supporting Information

Photochemical oxidative dehydrogenation of saturated *N*-heterocycles by an iminoquinone

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1. General remarks

All starting compounds employed in this study were procured from commercial suppliers. Glassware was dried overnight at 160 °C. Potassium tert-butoxide, sodium tert-butoxide, and potassium hydroxide were purchased from Avra Synthesis Private. Ltd. Deuterated solvents were purchased from Sigma Aldrich. Solvents such as acetonitrile were used as received from the suppliers. Toluene was dried by heating over sodium with benzophenone as the indicator. For thin layer chromatography (TLC), silica-coated aluminium foil with fluorescent indicator 254 nm (from Merck) was used. Column chromatography was performed using 60-120 mesh using a gradient of ethyl acetate and hexane as mobile phase. High-resolution mass spectra were recorded on a Waters QTOF mass spectrometer. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a 400 MHz Bruker Biospin Advance III FT-NMR spectrometer. NMR shifts are reported as delta (δ) units in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). Chemical shifts (δ) are quoted to the nearest 0.01 ppm relative to the residual protons in $CDCl_3$ (δ 7.26 ppm). Carbon chemical shifts are internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm).

Caution: *The reaction is set under 1 atm pressure of O_2 filled in a balloon. The reaction also generates some amount of H_2O_2. Precaution should be taken and perfomed in small scale.*

2. Synthesis of PA

The molecule was prepared following a literature-reported procedure from our group.[1] In a 50 mL round bottom flask, 1 mmol of pyrene dione was taken in 10 mL acetic acid. The mixture was heated at 60 ^{o}C for 30 min. Later, the solution of phenyl hydrazine (4 mmol) in 2 mL acetic acid was added dropwise to the mixture. The resulting dark red solution was stirred at 60 ^{o}C for 4 h. The reaction mixture was poured into an ice bath and was neutralized to pH = 7-8. The precipitate obtained was filtered and washed with water (3 times) to afford pure product as dark red solid in 54% yield. It is important to note that the imine form (from the condensation of pyrene dione and phenyl hydrazine) can tautomerize, but the iminoquinone form is predominant. The NMR spectroscopic data is in agreement with the literature[1] and justifies the almost exclusive presence of the iminoqunone form.

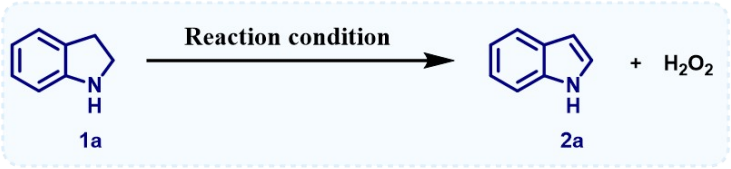
3. Experimental Procedures

3A. Preparation of starting materials: Starting materials were prepared following the literature procedure.[2,3]

3B. Synthesis of intermediate compounds: Intermediates **14**, **15** were synthesized by the literature procedure.[4,5]

4. Optimization of reaction conditions

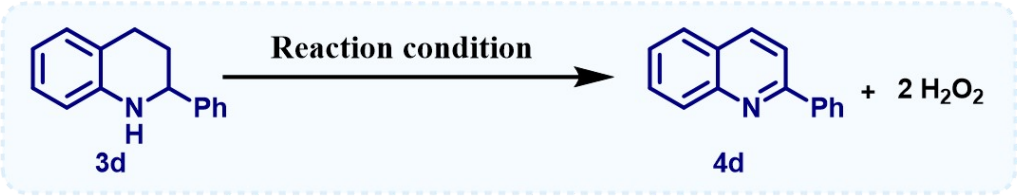
Table S1. Optimization for dehydrogenation of Indoline:



entry	catalyst loading	base loading	yield%
1	5 mol%	KO^{t}Bu (50 mol%)	68
2	7 mol%	KO^{t}Bu (50 mol%)	62
3	10 mol%	KO^{t}Bu (50 mol%)	58
4	2.5 mol%	KO^{t}Bu (50 mol%)	46
5	-	KO^{t}Bu (50 mol%)	n.r.
6	5 mol%	KO^{t}Bu (30 mol%)	74
7	5 mol%	KO^{t}Bu (25 mol%)	80
8	5 mol%	NaO^{t}Bu (50 mol%)	n.r.
9	5 mol%	KOH (50 mol%)	n.r.
10	5 mol%	NaOH (50 mol%)	n.r.
11	5 mol%	-	n.r.
12[a]	5 mol%	KO^{t}Bu (25 mol%)	n.r.
13[b]	5 mol%	KO^{t}Bu (25 mol%)	n.r.
14[c]	5 mol%	KO^{t}Bu (25 mol%)	trace
15[d]	5 mol%	KO^{t}Bu (25 mol%)	n.r.

Reaction conditions: **PA** (x mol%), base (y mmol%), indoline (1 mmol), in 3 mL toluene, O_2 balloon, blue LED, 50 ^{o}C for 12 h. [a]: solvent: acetonitrile, [b]: solvent: DMF, DMSO, [c]: no light source, [d]: under argon atmosphere.

Table S2. Optimization for the dehydrogenation of 2-phenyl-1,2,3,4-tetrahydroquinoline:

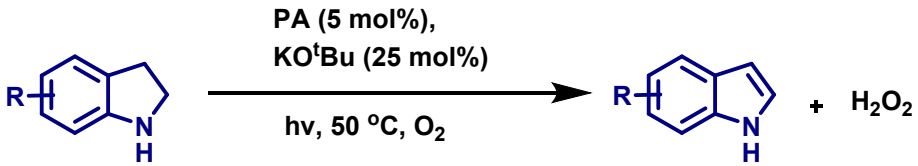


entry	catalyst Loading (mol%)	base loading (mol%)	yield (%)
1	5 mol%	KO^{t}Bu (100 mol%)	72
2	7 mol%	KO^{t}Bu (100 mol%)	70
3	10 mol%	KO^{t}Bu (100 mol%)	65
4	5 mol%	KO^{t}Bu (50 mol%)	78
5	5 mol%	KO^{t}Bu (70 mol%)	74
6	5 mol%	NaO^{t}Bu (100 mol%)	n.r.
7	5 mol%	KOH (100 mol%)	n.r.
8	5 mol%	NaOH (100 mol%)	n.r.
9	-	KO^{t}Bu (100 mol%)	n.r.
10	5 mol%	-	n.r.
11[a]	5 mol%	KO^{t}Bu (25 mol%)	n.r.
12[b]	5 mol%	KO^{t}Bu (25 mol%)	n.r.
13[c]	5 mol%	KO^{t}Bu (25 mol%)	trace
14[d]	5 mol%	KO^{t}Bu (25 mol%)	n.r.

Reaction conditions: **PA** (x mol%), base (y mmol%), 2-phenyl-1,2,3,4-tetrahydroquinoline (1 mmol), in 3 mL toluene, O_2 balloon, blue LED, 70 ^oC for 24 h. [a]: solvent: acetonitrile, [b]: solvent: DMF, DMSO, [c]: no light source, [d]: under argon atmosphere.

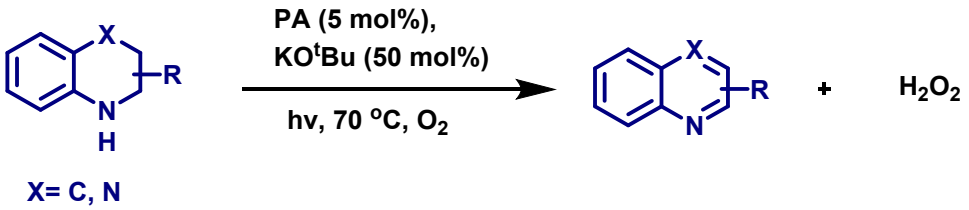
5. General procedure

5A) Procedure for dehydrogenation of indolines catalyzed by PA:



A 10-mL reaction vial was charged with **PA** (5 mol%), KO^{t}Bu (25 mol%), substituted indoline (1 mmol) in 3mL toluene. The reaction mixture was stirred at 50 °C in an oil bath for 12 h under blue LED light. Oxygenated environment was provided for the reaction by an oxygen-filled balloon. The reaction mixture was cooled and concentrated *in vacuo*. The crude mixture was purified by column chromatography using hexane/ethyl acetate (10:1) as eluent. The desired products were well-characterized by ^{1}H, ^{13}C NMR spectroscopies.

5B) Procedure for dehydrogenation of tetrahydroquinolines and tetrahydroquinoxalines catalyzed by PA:



A 10 mL reaction vial was charged with **PA** (5 mol%), KO^{t}Bu (50 mol%), substituted tetrahydroquinoline and quinoxaline (1 mmol) in 3 mL toluene. The reaction mixture was stirred at 70 °C in an oil bath and stirred for 24 h under blue LED light. Oxygenated environment was provided for the reaction by an oxygen-filled balloon. The reaction mixture was cooled and concentrated *in vacuo*. The crude mixture was purified by column chromatography using hexane/ethyl acetate (10:1) as eluent. The desired products were well-characterized by ^{1}H, ^{13}C NMR spectroscopies.

The same reaction when conducted under open air, rather than the O_2-filled balloon afforded slightly deceased yield of the desired product.

6. Mechanistic investigation

6A. Radical quenching experiment

A 10 mL reaction vial was charged with **PA** (5 mol%), KO^{t}Bu (25 mol%), indoline (1 mmol), and galvinoxyl radical (0.5 mmol) in 1.5 mL toluene. The reaction mixture was stirred at 50 ^{o}C in an oil bath for 12 h under blue LED light. The samples were subjected to GC-MS for quantification. The reaction afforded only 9% product, while complete quenching happens with the addition of 1.2 equiv. of the radical quencher.

Table S3: Product formation after addition of galvinoxyl radical

S. No.	Galvinoxyl equivalence	Yield (%)
1.	0.5 eq	9
2.	1.2 eq	-

6B. Procedure for intercepting ketyl radical intermediate

A 10 mL reaction vial was charged with **PA** (5 mol%), KO^{t}Bu (50 mol%), 2-phenyl-1,2,3,4-tetrahydroquinoline (0.2 mmol) in 1 mL toluene. The solution was stirred for 5 min. Later, 0.5 equiv. butylated hydroxy toluene (BHT) was added, and the reaction mixture was stirred for 4 h at 70 ^{o}C under blue light. The BHT-trapped intermediate was detected by HRMS (ESI, m/z) calcd. for $C_{30}H_{36}NO$ [M + H] $^+$: 426.2797; found 426.2778.

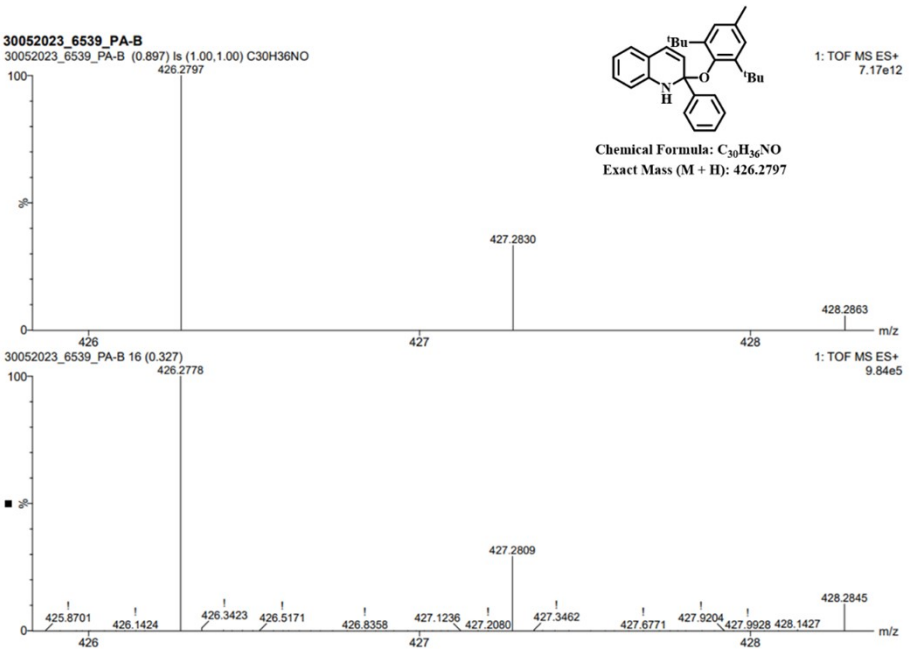


Figure S1. HRMS spectrum of carbon-based radical intercepted by BHT.

6C. New reaction flask and stirring bead test

A trace amount of metal contamination can catalyze some organocatalytic reactions through uncleaned glassware or stir-bars[6]. This test was done to nullify any effect of metal contamination. A 10-mL pristine reaction vial was charged with **PA** (5 mol%), KO^{t}Bu (25 mol%), indoline (1 mmol) in 3 mL toluene. In this reaction a fresh magnetic bead was used. The reaction mixture was stirred at 50 ^{o}C in an oil bath for 12 h under blue LED light. At the end of the reaction, the reaction mixture was cooled and concentrated *in vacuo*. The crude mixture was purified by column chromatography using hexane/ethyl acetate (10:1) as eluent. The desired products were well-characterized by ^{1}H, ^{13}C NMR spectroscopies. Indole was isolated by using the standard procedure described above in 70% yield.

Table S4: **ICP-MS analysis to determine contents (in ppm) of transition metals in KO^{t}Bu**

Entry	Parameter	Results	
		Result-1	Result-2
1.	Copper	BDL (MDL: 0.1 mg/kg)	BDL (MDL: 0.1 mg/kg)
2.	Palladium	BDL (MDL: 0.1 mg/kg)	BDL (MDL: 0.1 mg/kg)
3.	Iron	2.26 mg/kg	2.26 mg/kg
4.	Nickel	BDL (MDL: 0.1 mg/kg)	BDL (MDL: 0.1 mg/kg)
5.	Cobalt	BDL (MDL: 0.1 mg/kg)	BDL (MDL: 0.1 mg/kg)

BDL: Below Detection Limit, MDL: Method Detection Limit

6D. Detection of H_2O_2 during indoline dehydrogenation

During the dehydrogenation of indoline, presence of H_2O_2 in the reaction mixture was traced by UV−Vis spectroscopy[7] using the iodometric assay based on peak of I_3^- at λ_{max} = 345 nm; ε = 26 000 M^{-1} cm^{-1} upon reaction with KI.

A 10 mL reaction vial was charged with **PA** (5 mol%), KO^{t}Bu (25 mol%), indoline (1 mmol) in 3 mL toluene. The reaction mixture was stirred at 50 ^{o}C in an oil bath for 6 h under blue LED light. To the reaction mixture, 10 mL of water + 10 mL of DCM was added.

The aqueous part was then separated. To the separated aqueous layer dilute H_2SO_4 (pH = 2) was added to stop further oxidation. Then, 1 mL of a 10% solution of KI and a few drops of a 3% solution of ammonium molybdate was added.

The produced H_2O_2 oxidizes I^- to I_2, which reacts with an excess of I^- to form I_3^-. The chemical reactions are as follows[7]:

(i) $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$

(ii) I_2 (aq) + $I^- \rightarrow I_3^-$

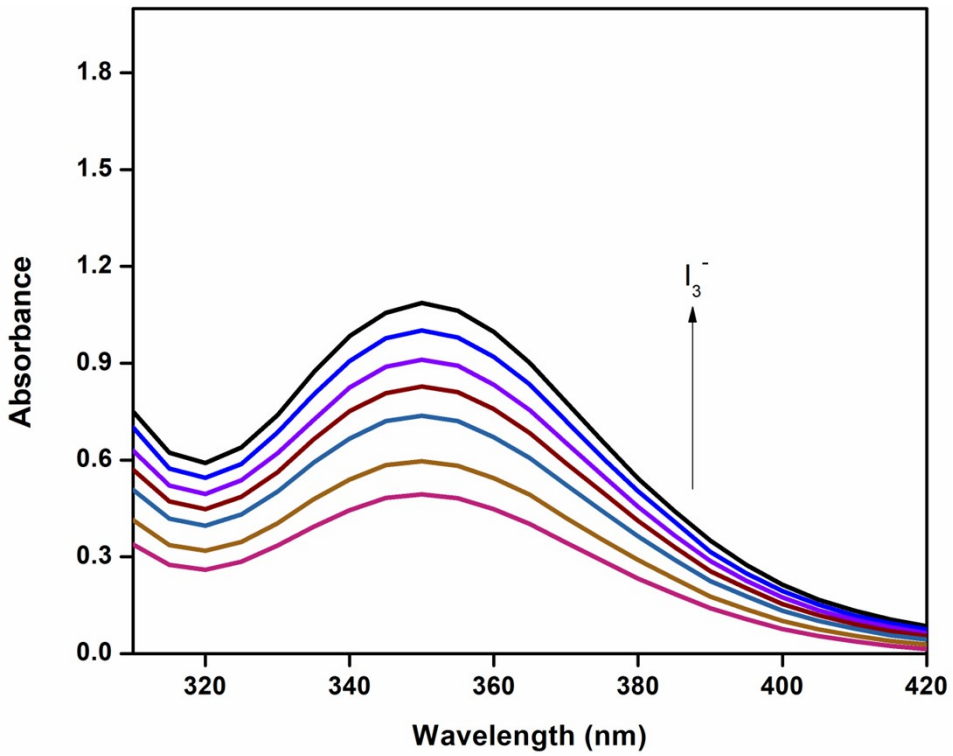


Figure S2. UV-Visible spectrum of I_3^- ion formation in the presence of H_2O_2.

7. ^1H and ^{13}C NMR spectra for compounds synthesized

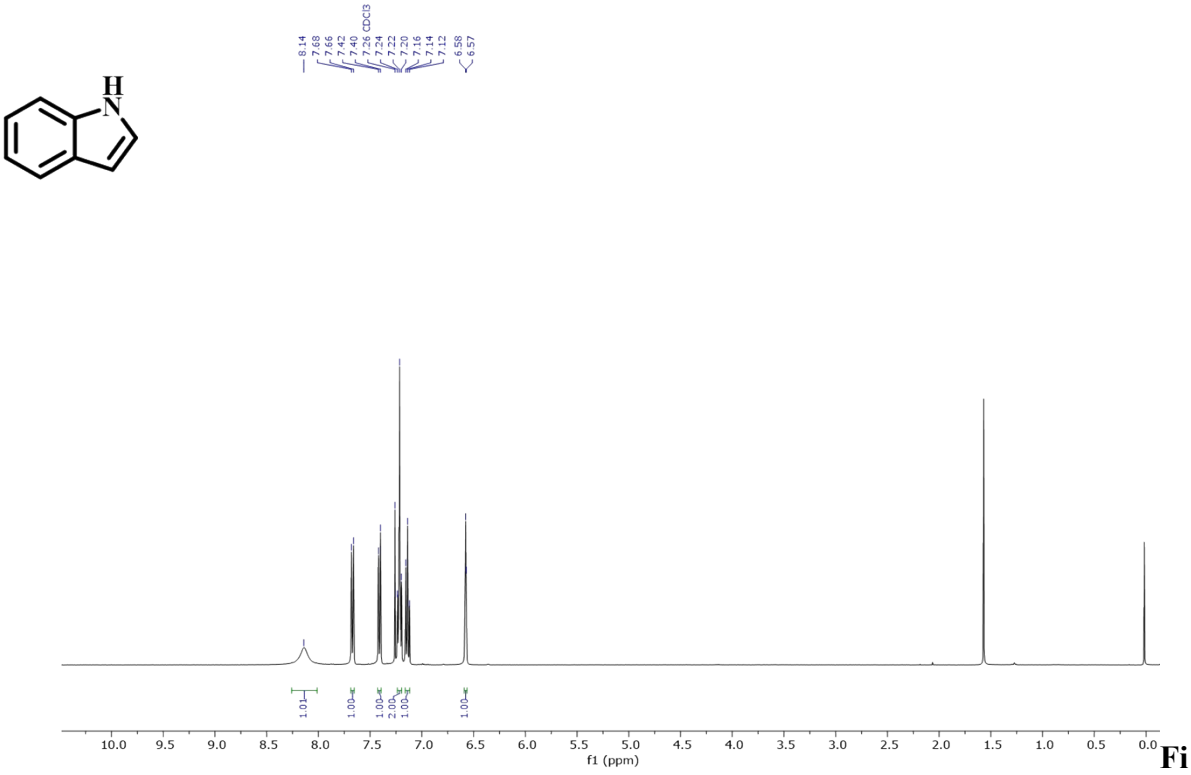


Figure S3. ^{1}H NMR spectrum (400 MHz) of **2a** in $CDCl_3$.

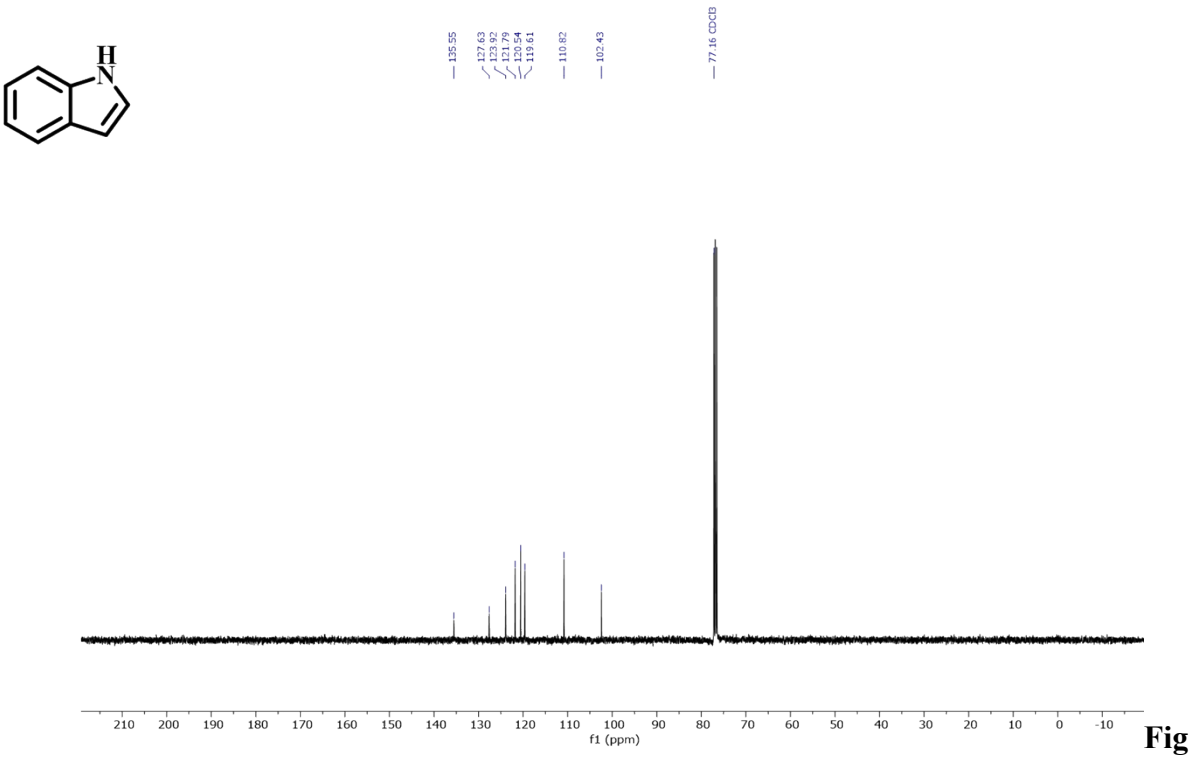


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2a** in $CDCl_3$.

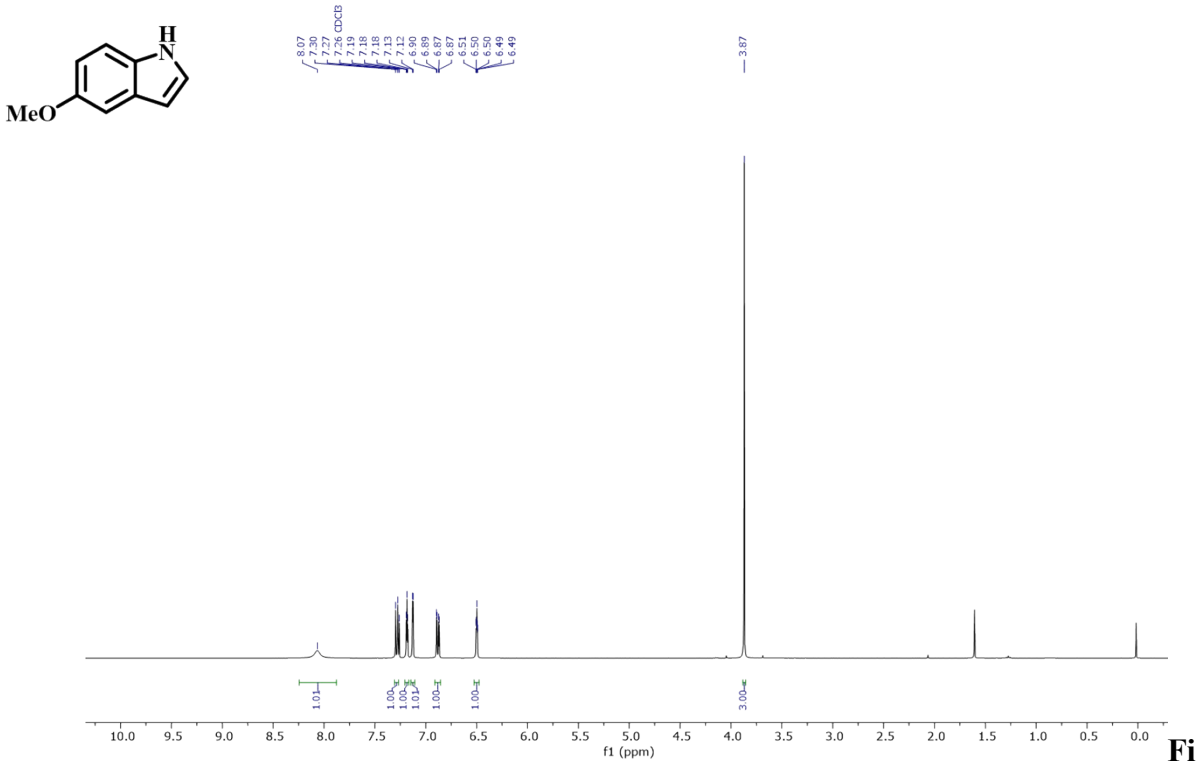


Figure S5. ^{1}H NMR spectrum (400 MHz) of **2b** in $CDCl_3$.

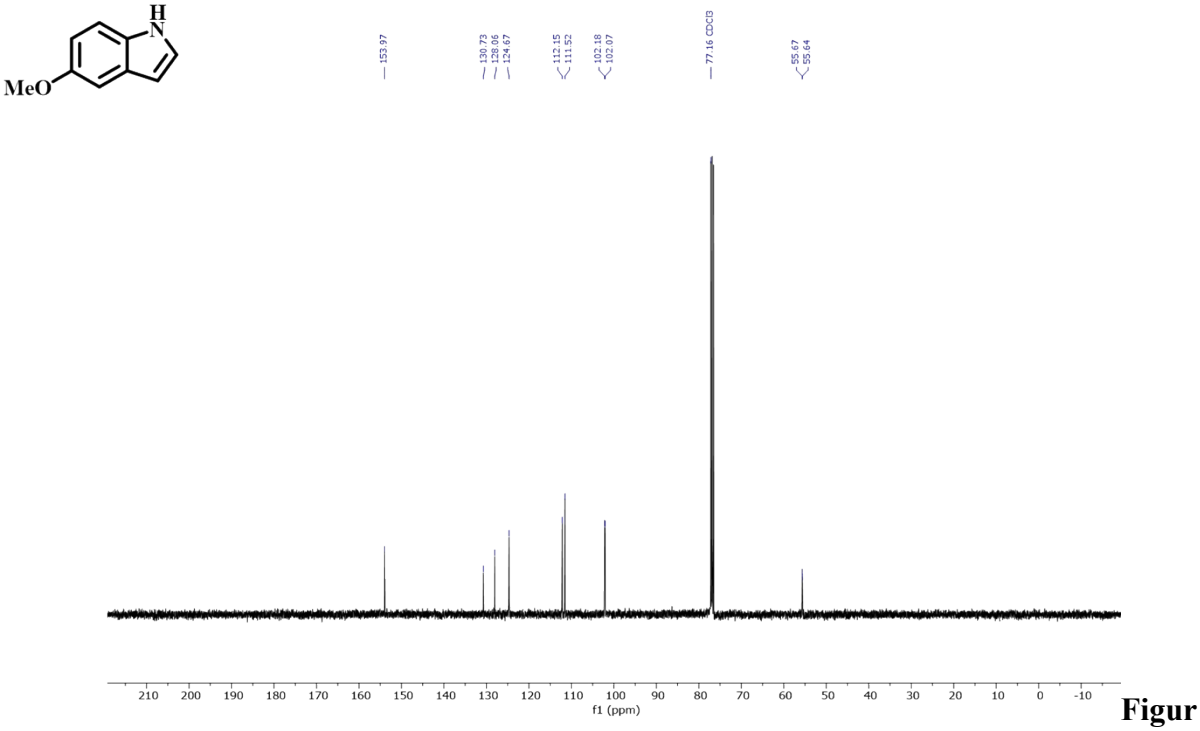


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2b** in $CDCl_3$.

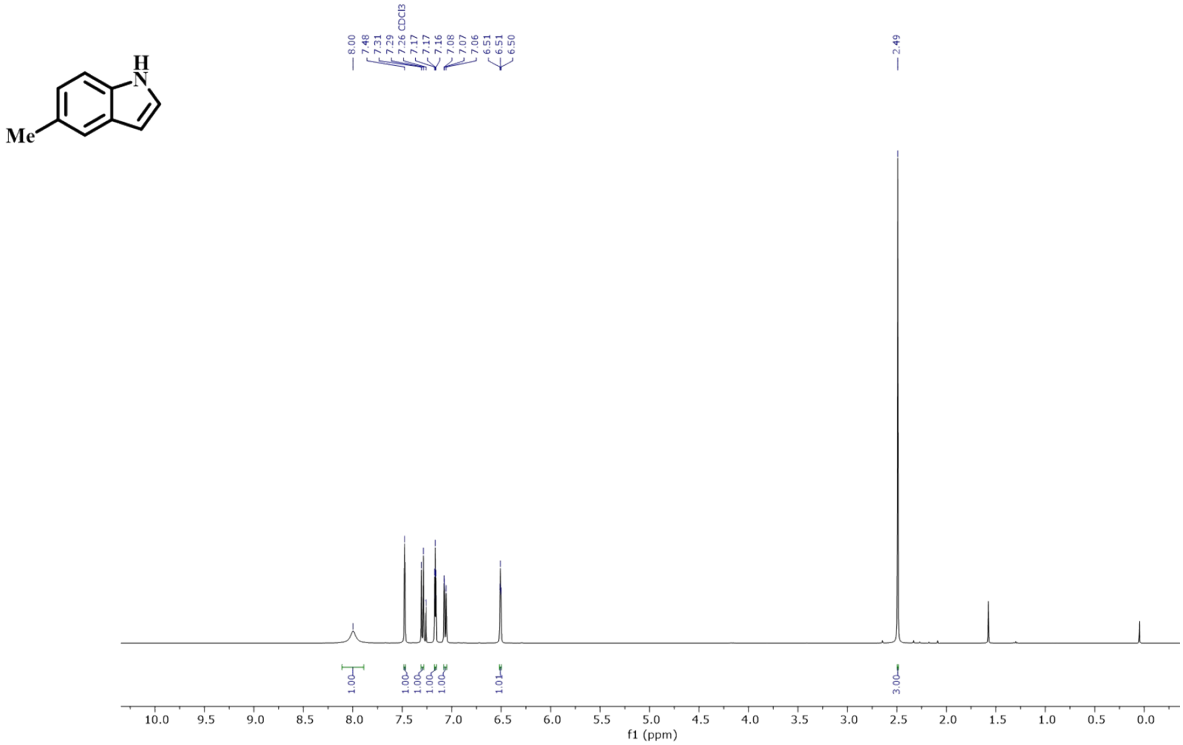


Figure S7. ^{1}H NMR spectrum (400 MHz) of **2c** in $CDCl_3$.

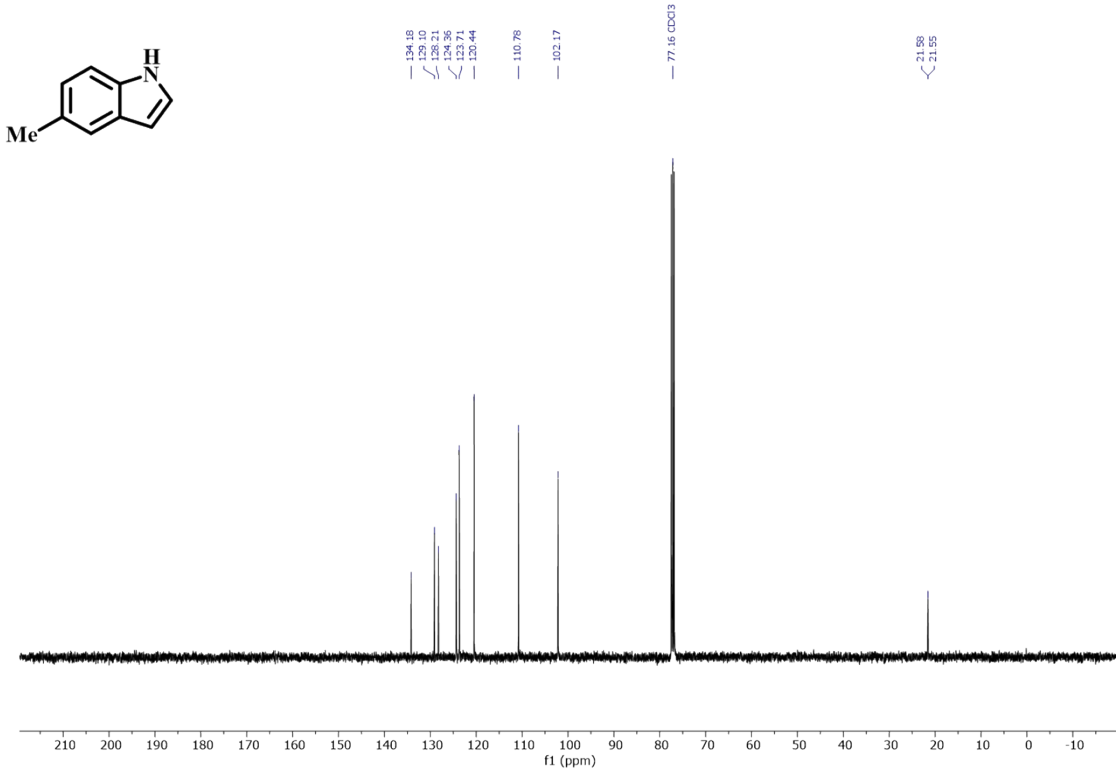


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2c** in $CDCl_3$.

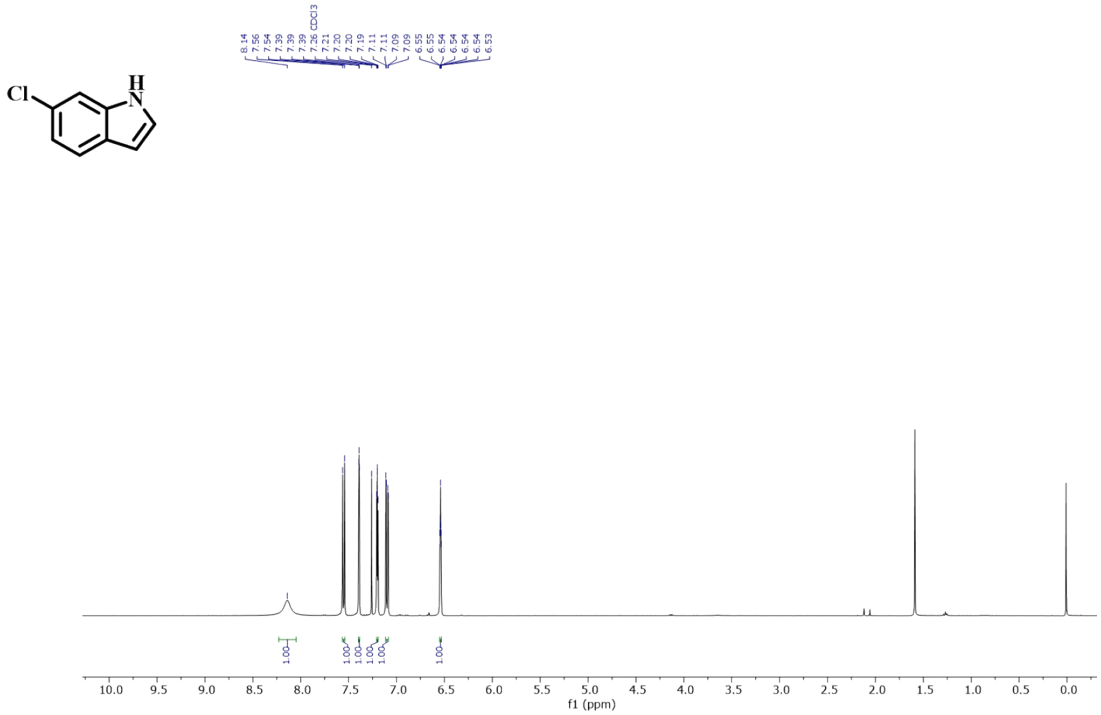


Figure S9. ^{1}H NMR spectrum (400 MHz) of **2d** in $CDCl_3$.

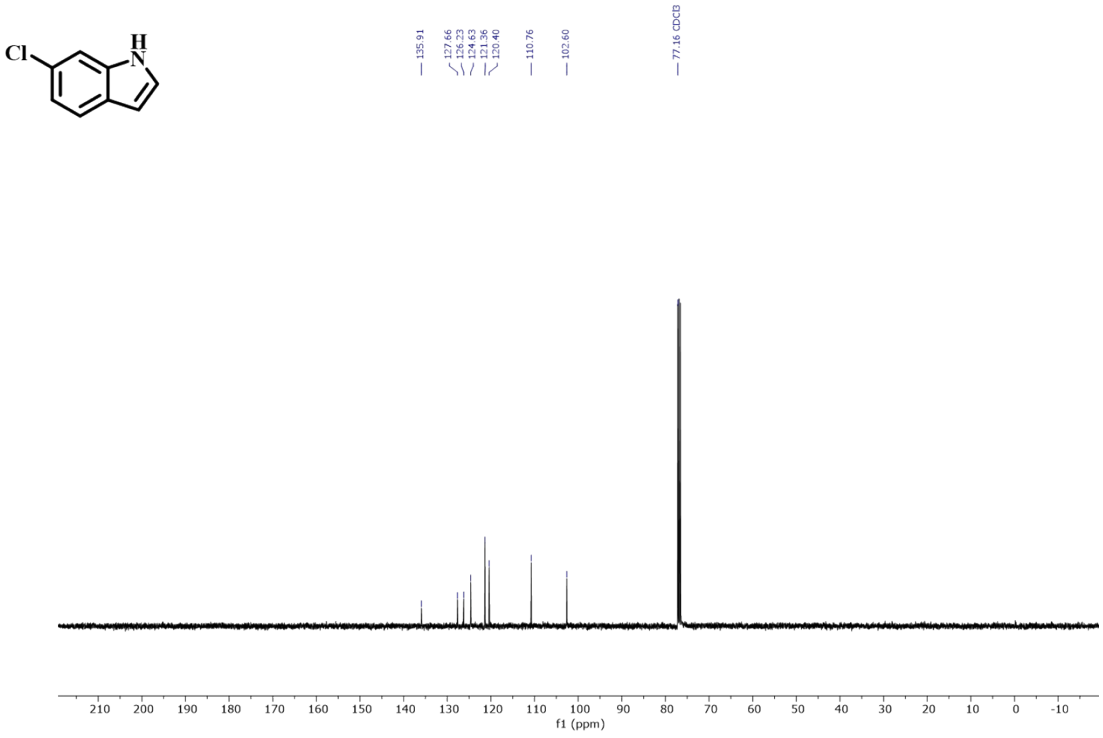


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2d** in $CDCl_3$

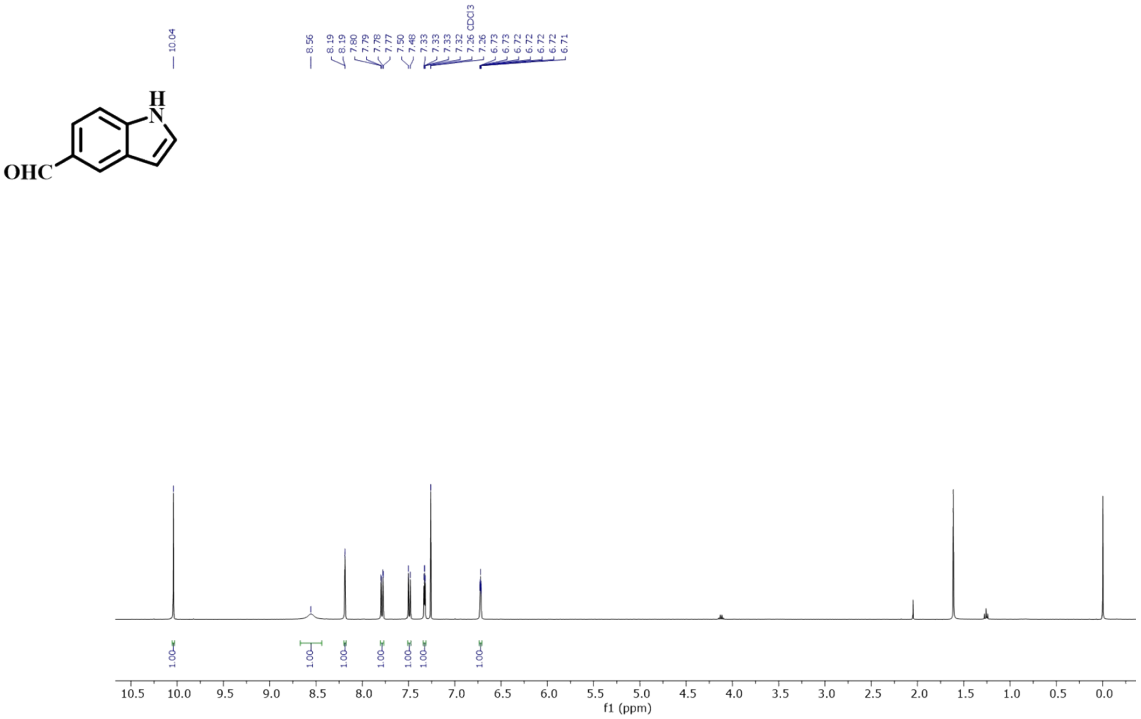


Figure S11. ^{1}H NMR spectrum (400 MHz) of **2e** in $CDCl_3$.

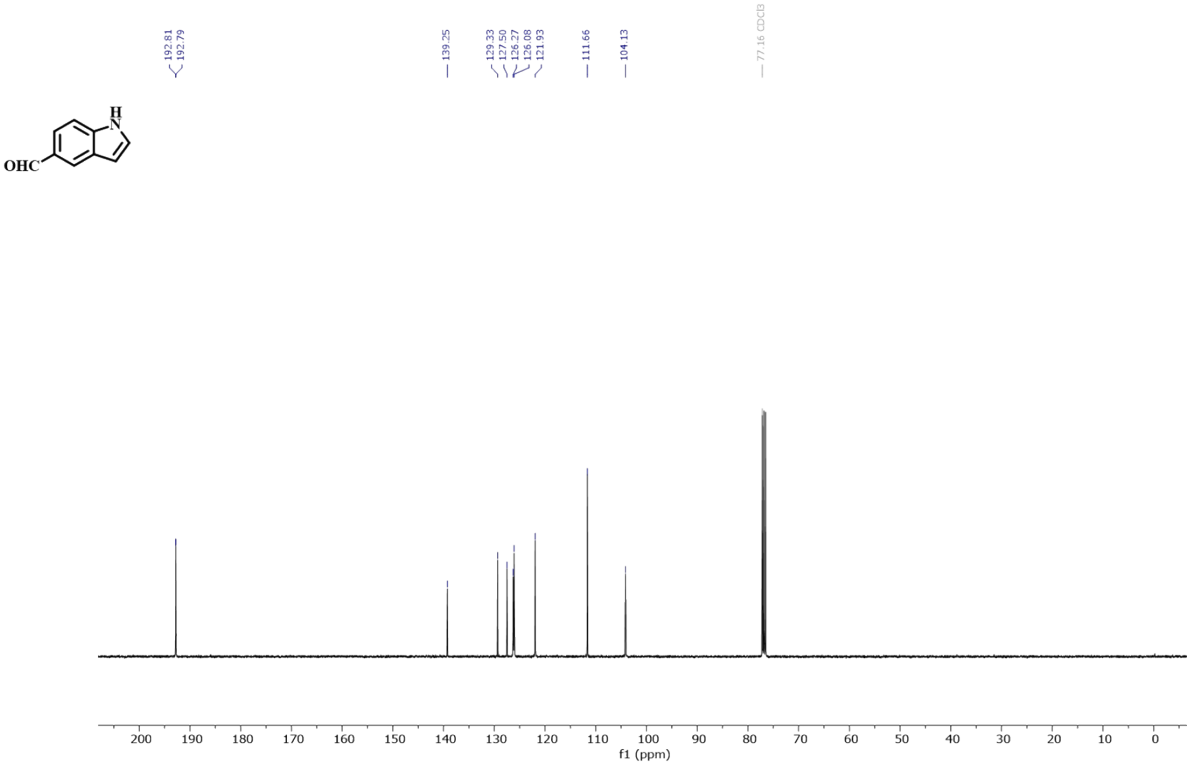


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2e** in $CDCl_3$.

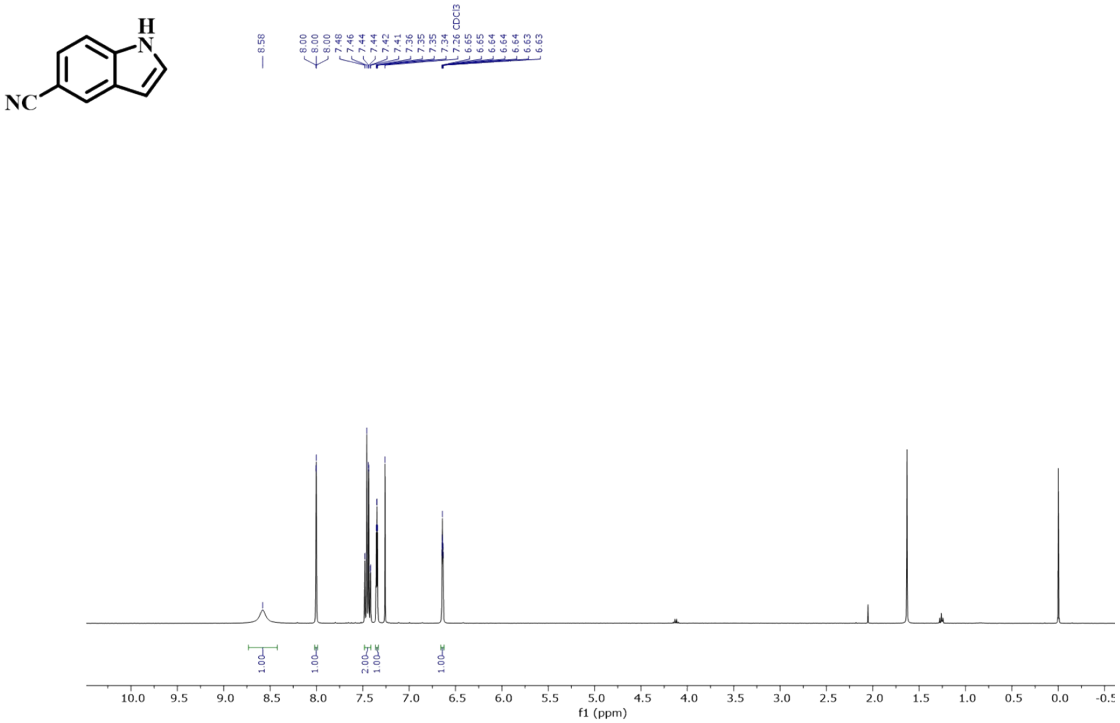


Figure S13. ^{1}H NMR spectrum (400 MHz) of **2f** in $CDCl_3$.

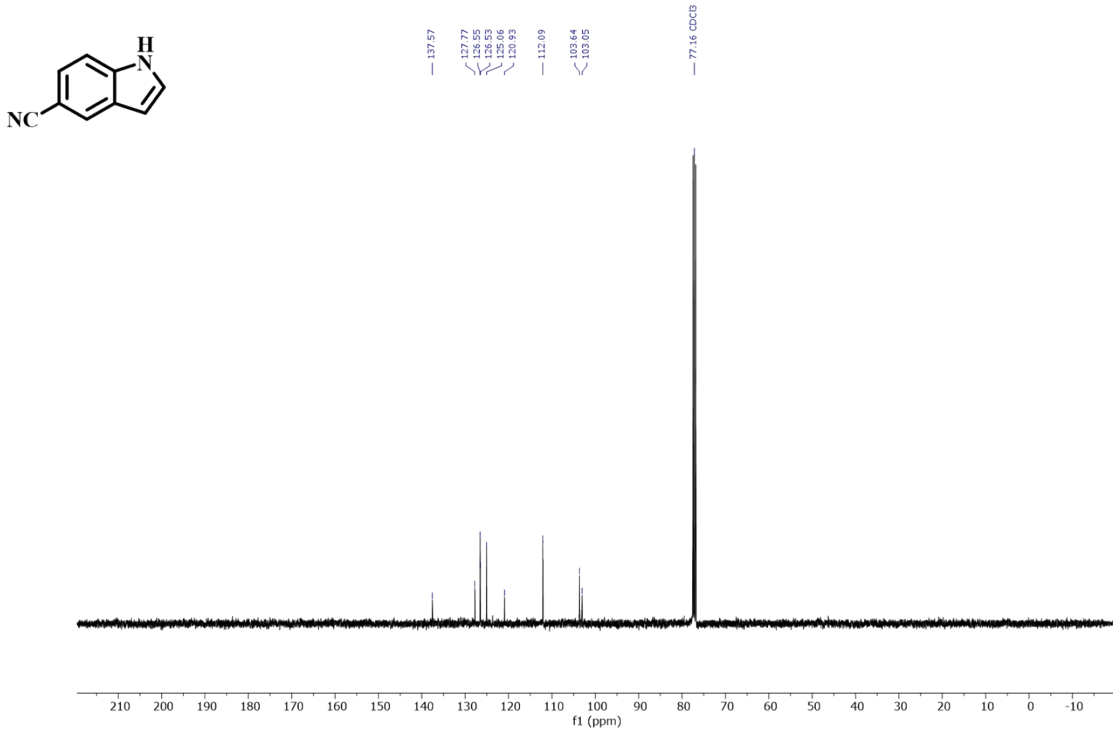


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2f** in $CDCl_3$.

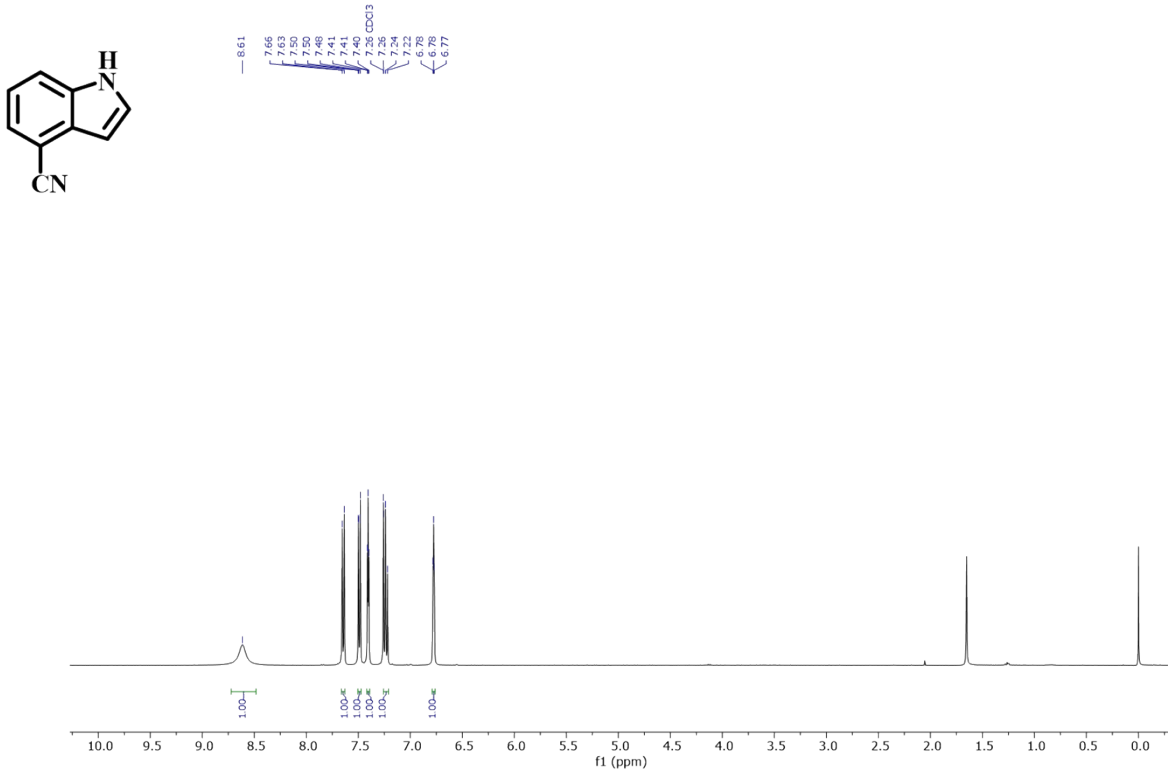


Figure S15. ^{1}H NMR spectrum (400 MHz) of **2g** in $CDCl_3$.

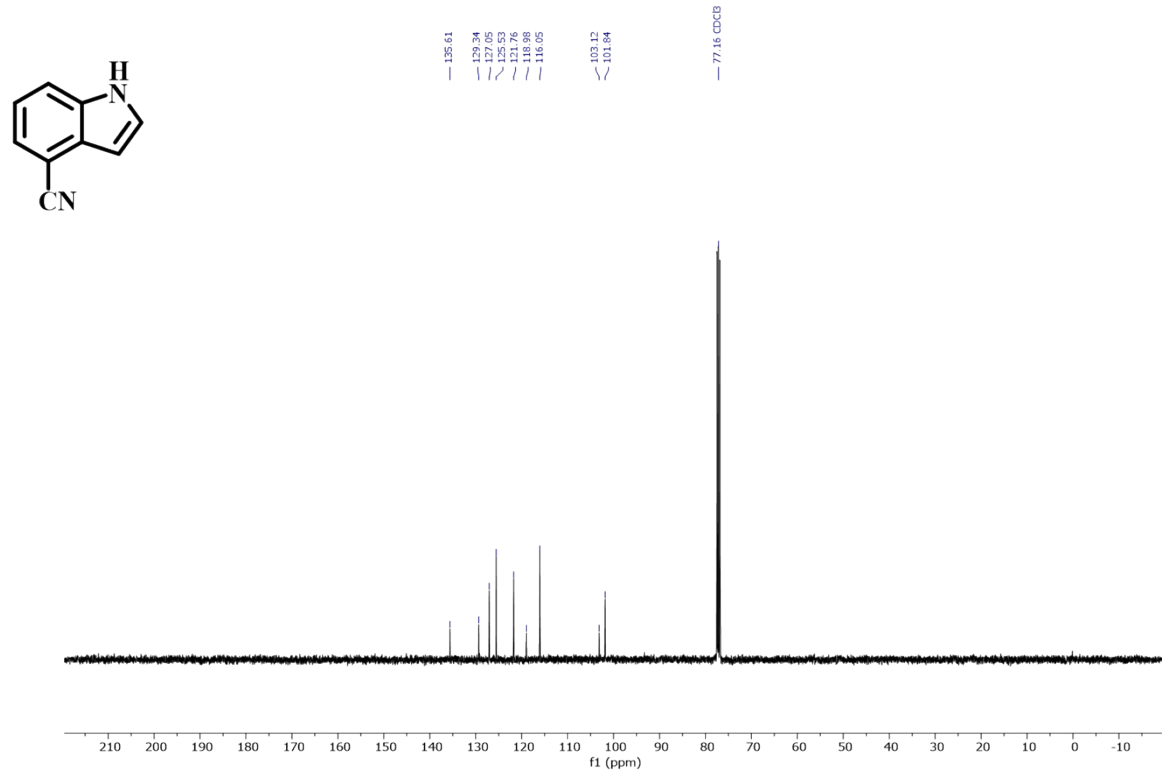


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2g** in $CDCl_3$

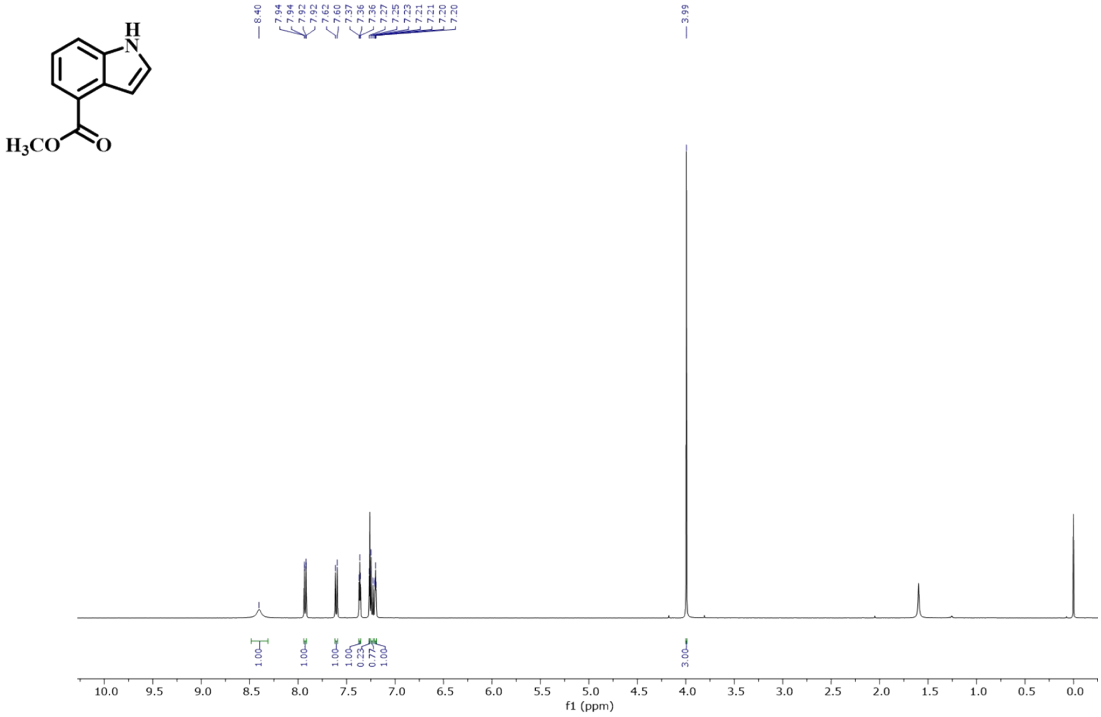


Figure S17. ^{1}H NMR spectrum (400 MHz) of **2h** in $CDCl_3$.

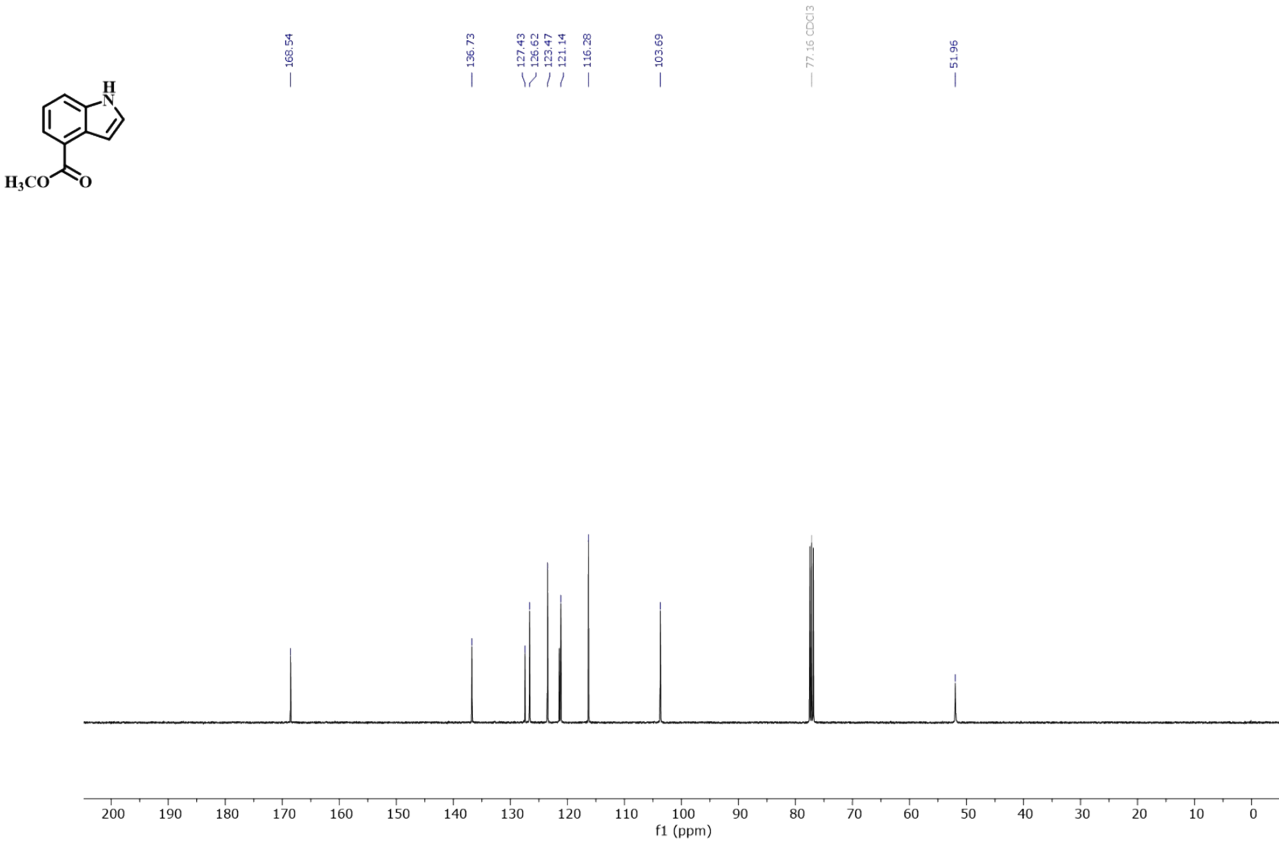


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2h** in $CDCl_3$

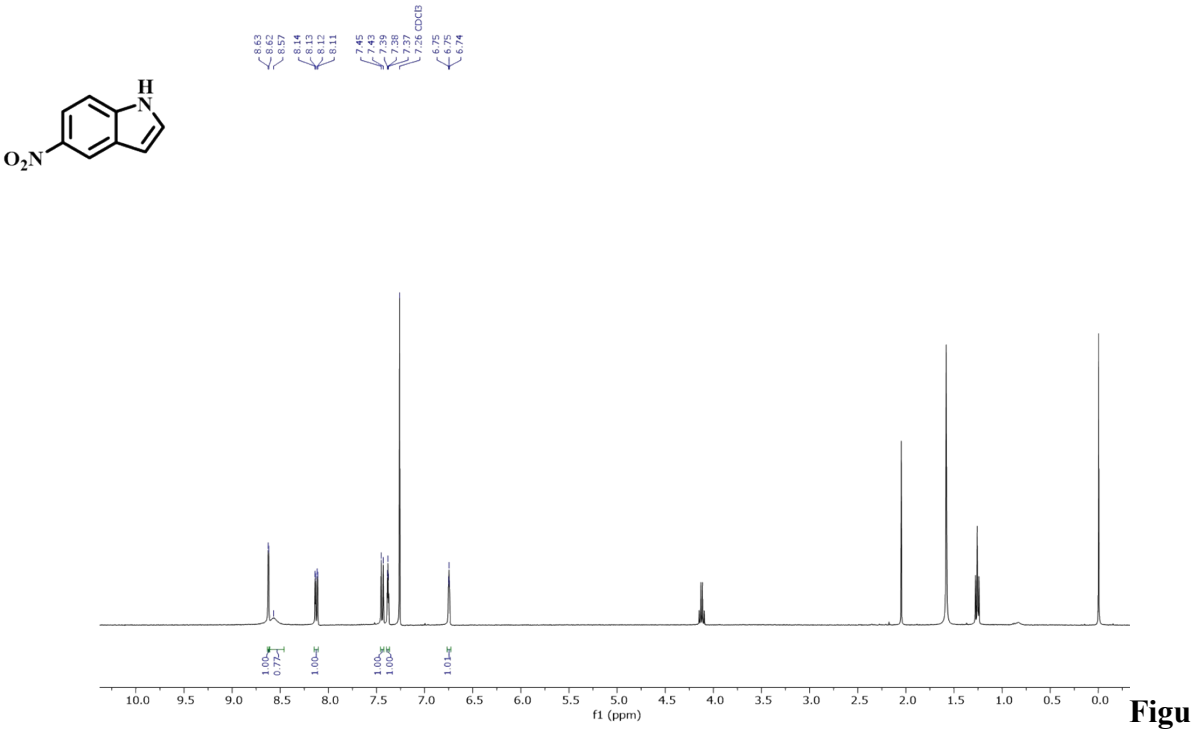


Figure S19. ^{1}H NMR spectrum (400 MHz) of **2i** in $CDCl_3$.

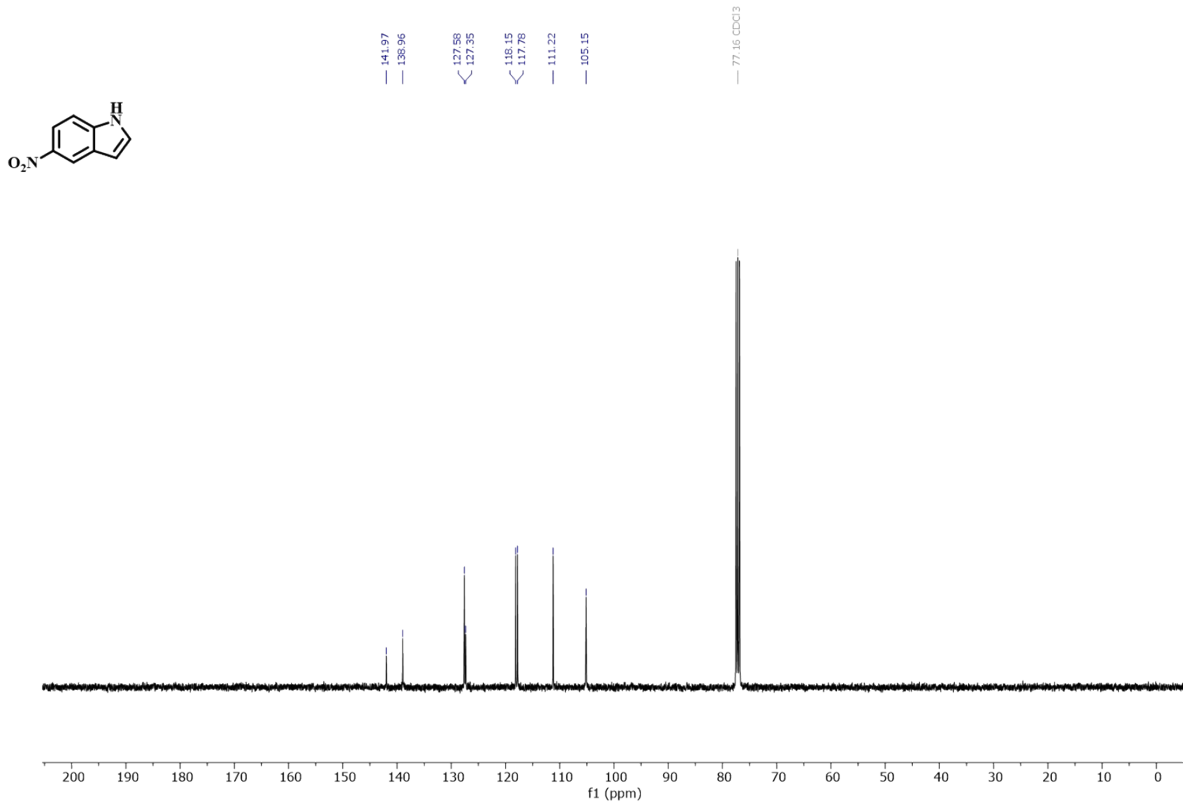


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2i** in $CDCl_3$

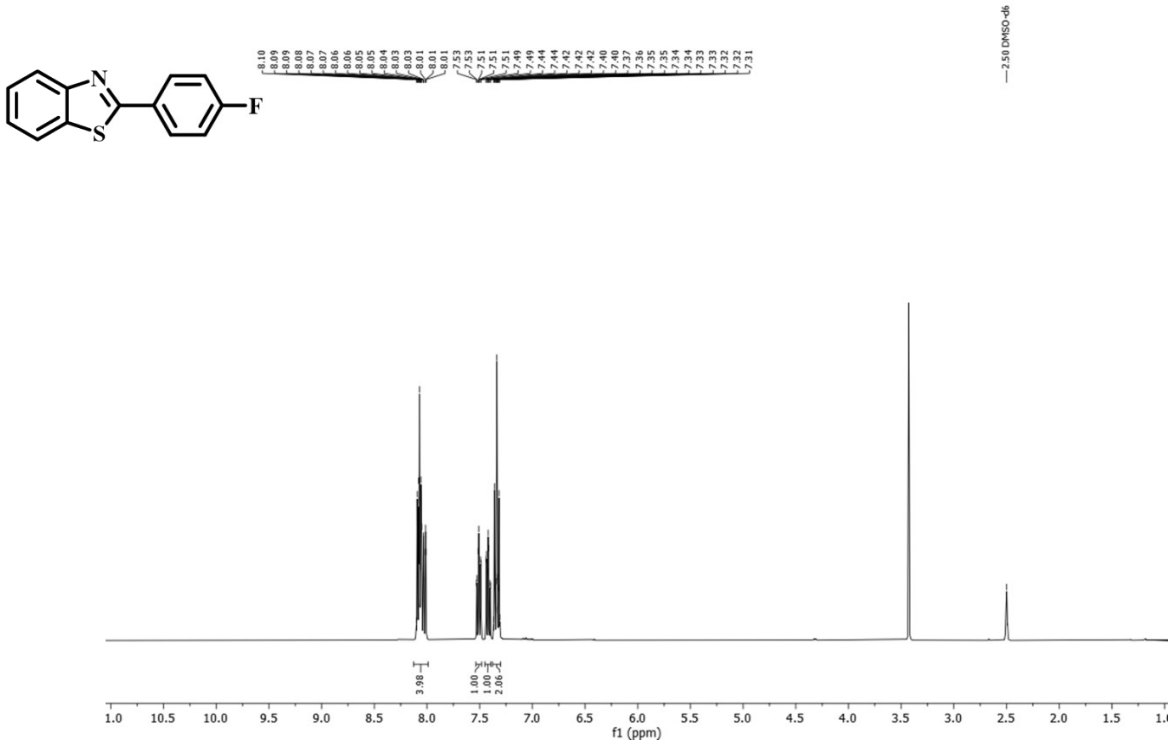


Figure S21: ^{1}H NMR spectrum (4 00 MHz) of **2j** in DMSO-d_6.

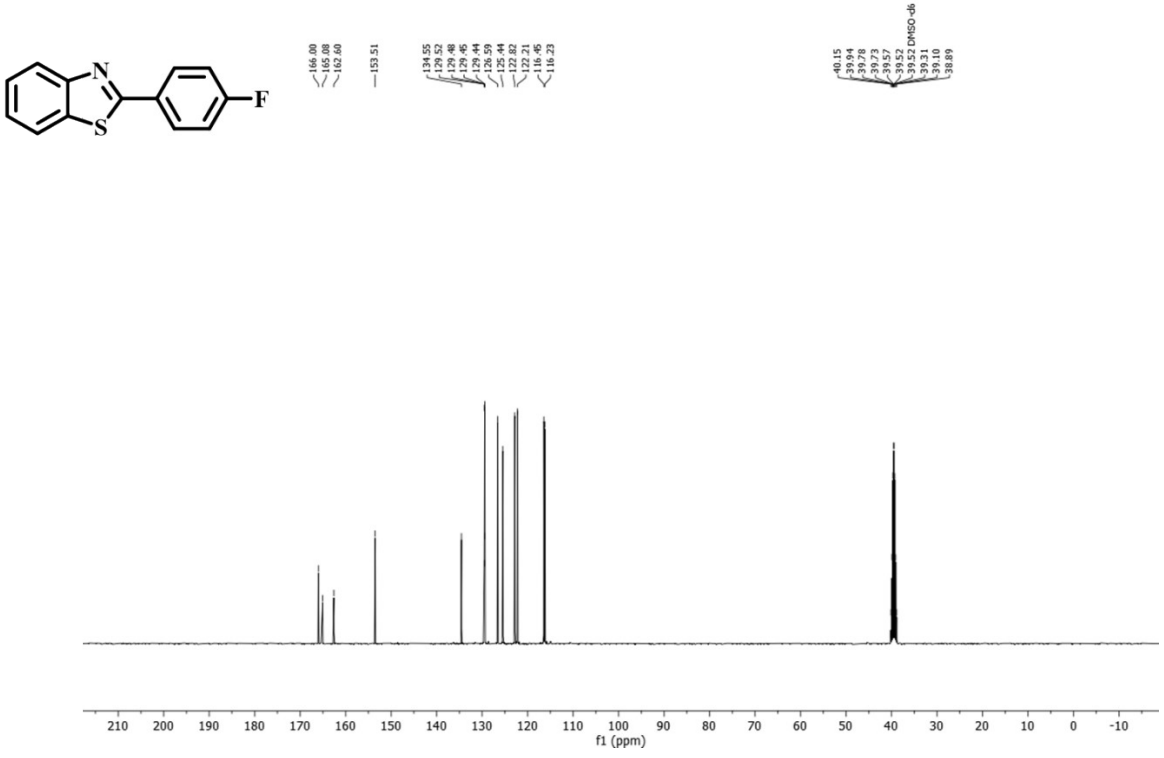


Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2j** in DMSO-d_6.

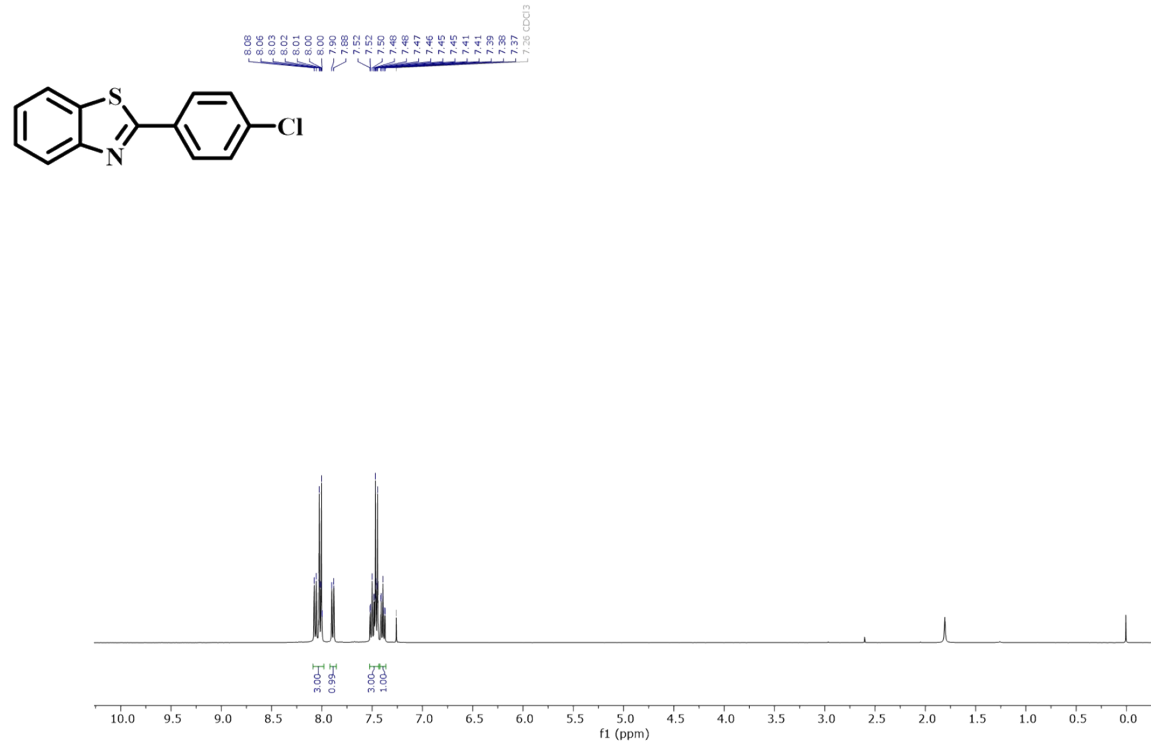


Figure S23. ^{1}H NMR spectrum (400 MHz) of **2k** in $CDCl_3$.

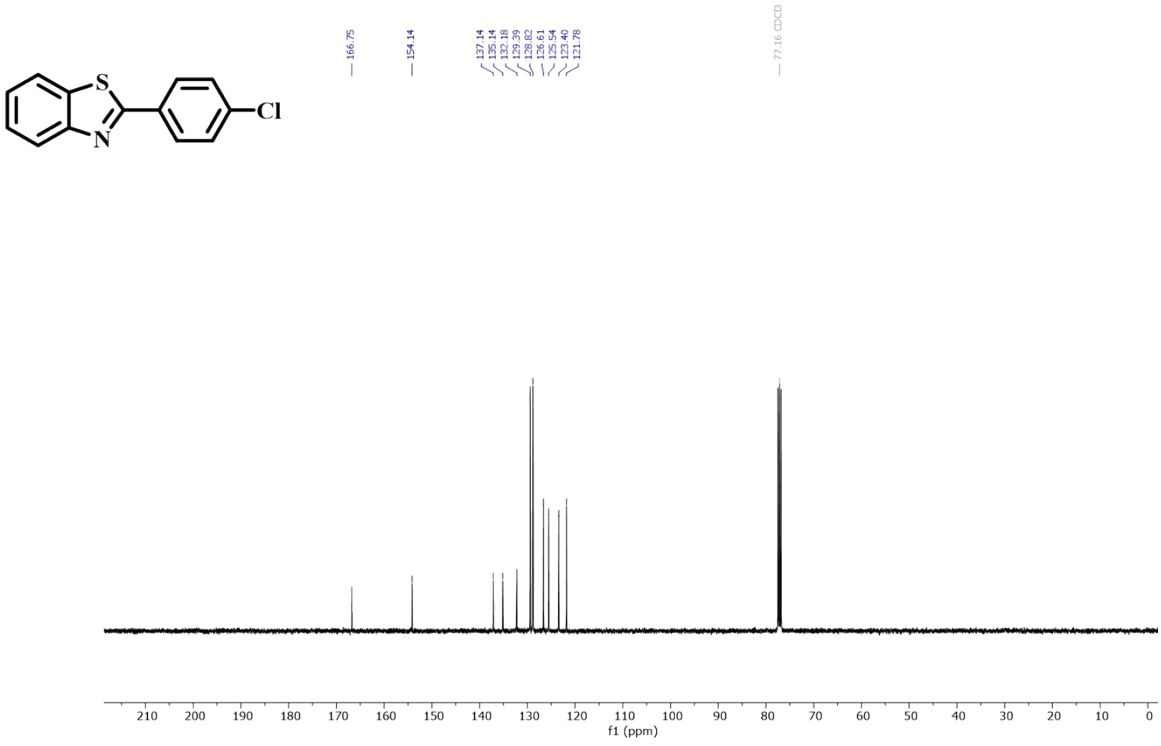


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2k** in $CDCl_3$

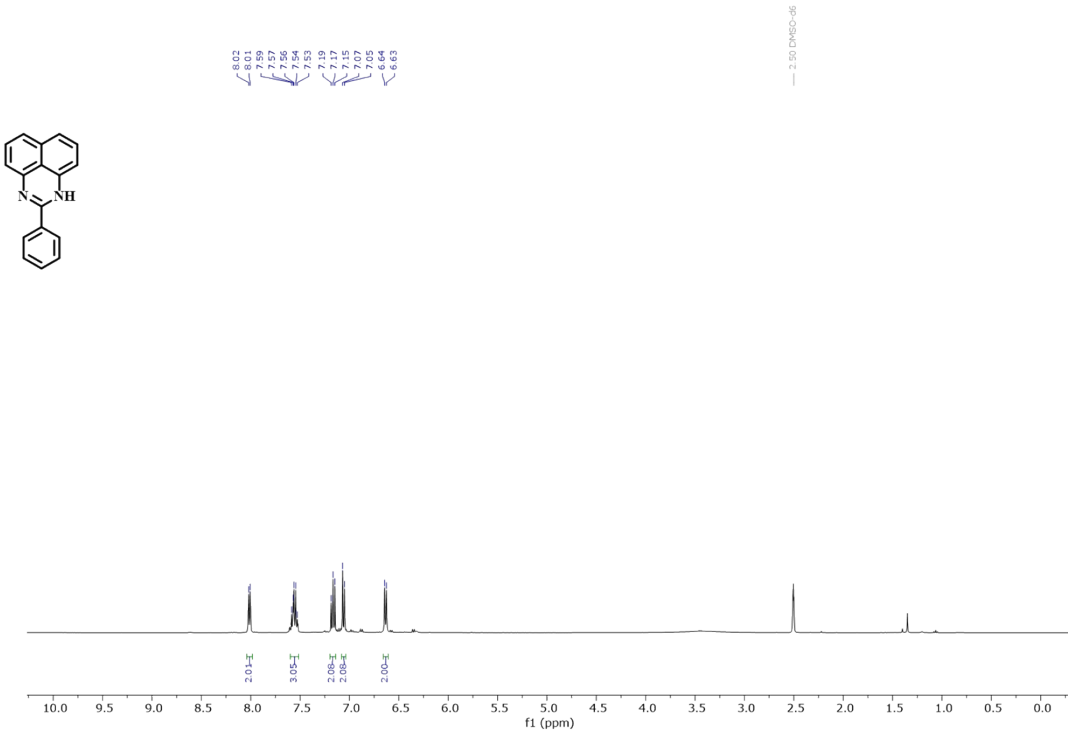


Figure S25. ^{1}H NMR spectrum (400 MHz) of **2l** in DMSO-d6.

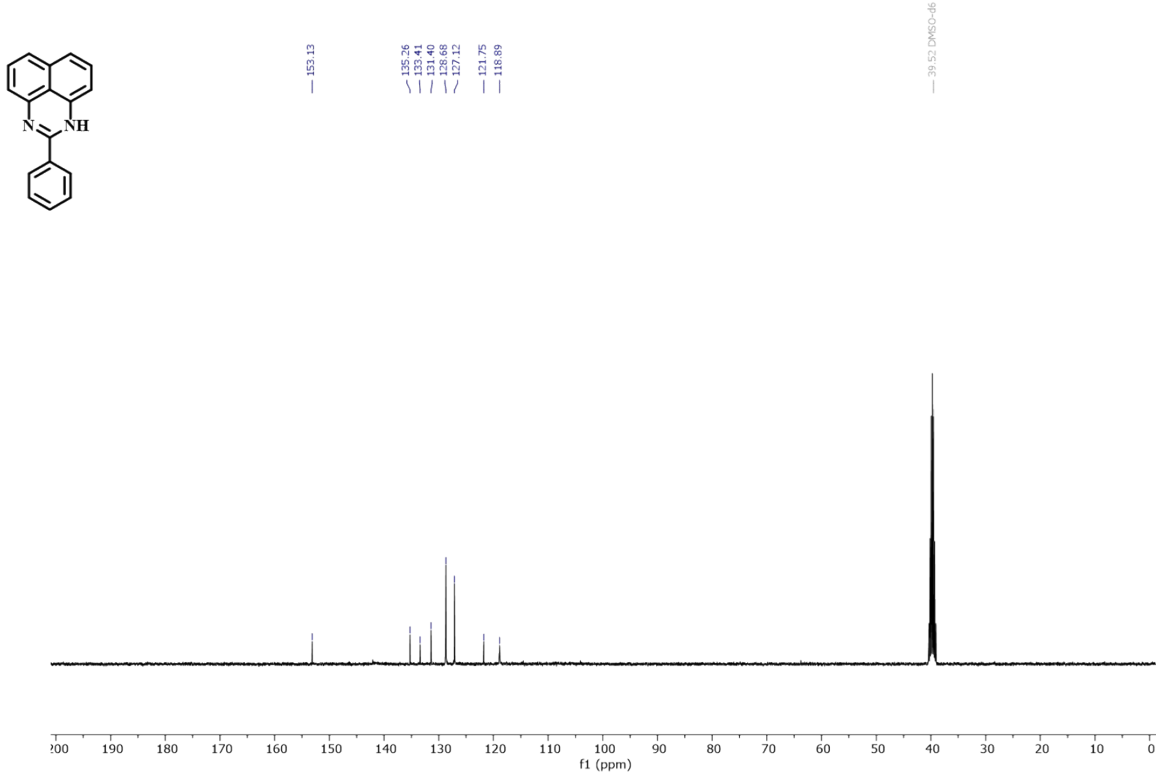


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2l** in DMSO-d6.

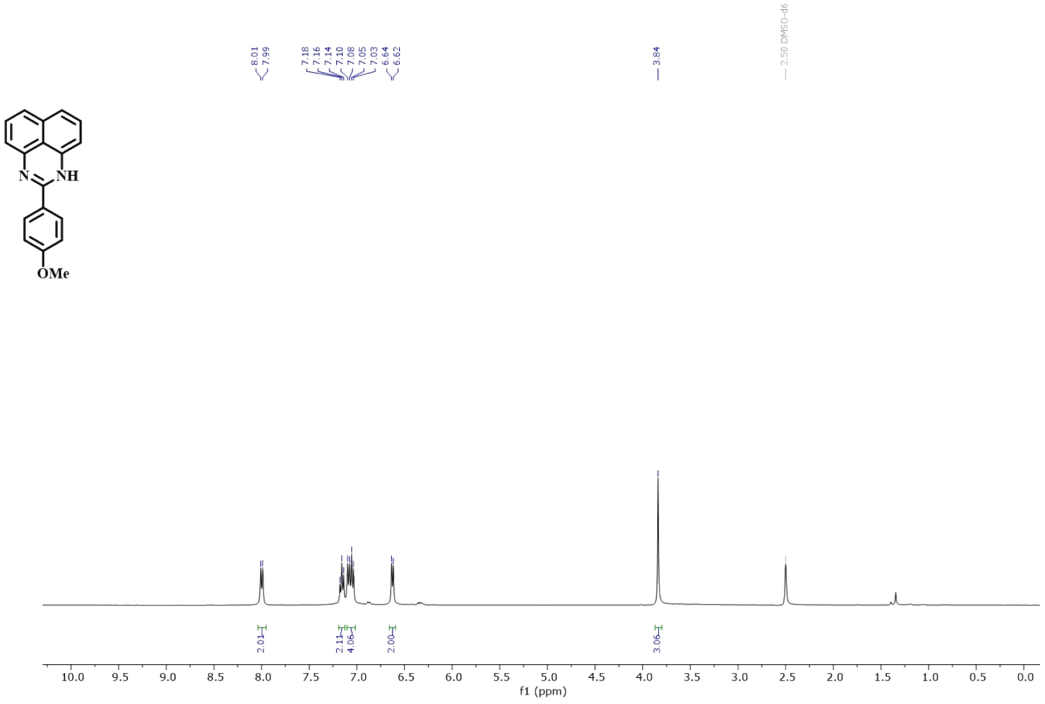


Figure S27. ^{1}H NMR spectrum (400 MHz) of **2m** in DMSO-d6

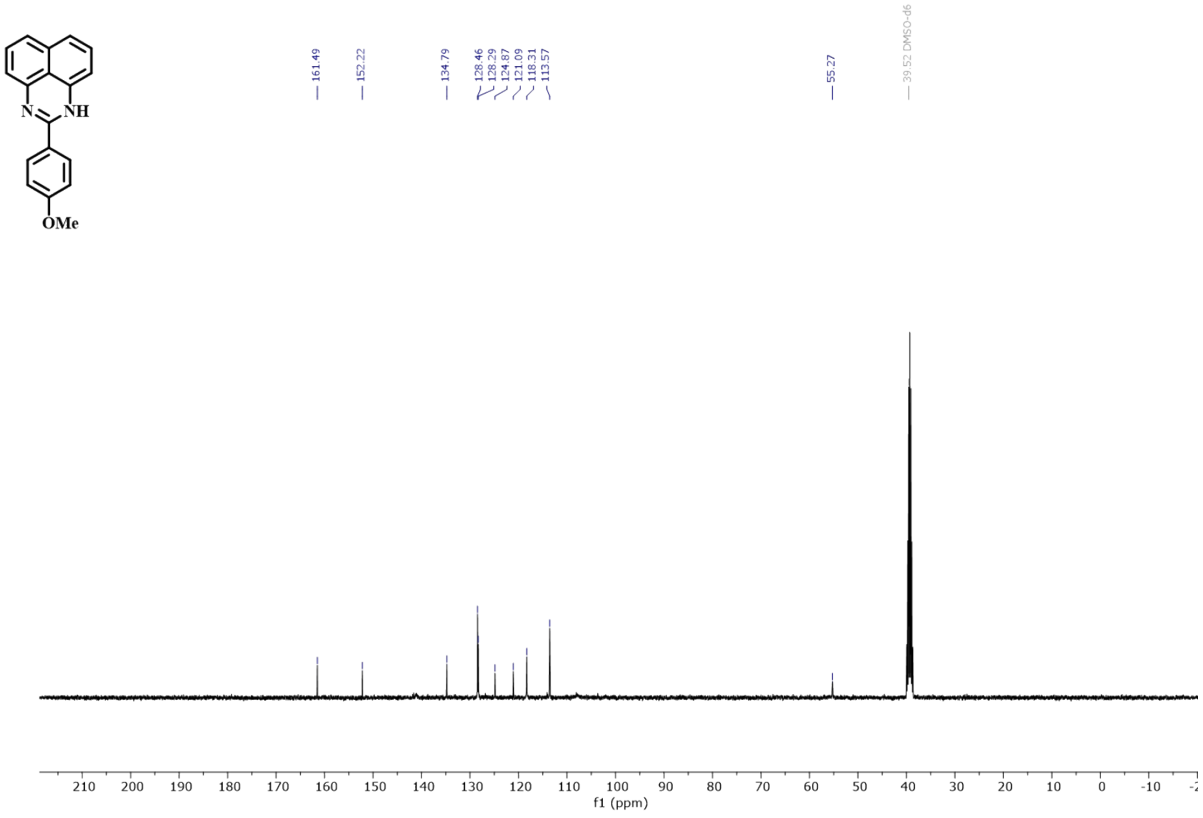


Figure S28. ^{13}C{^{1}H} NMR spectrum (100 MHz) of **2m** in DMSO-d6.

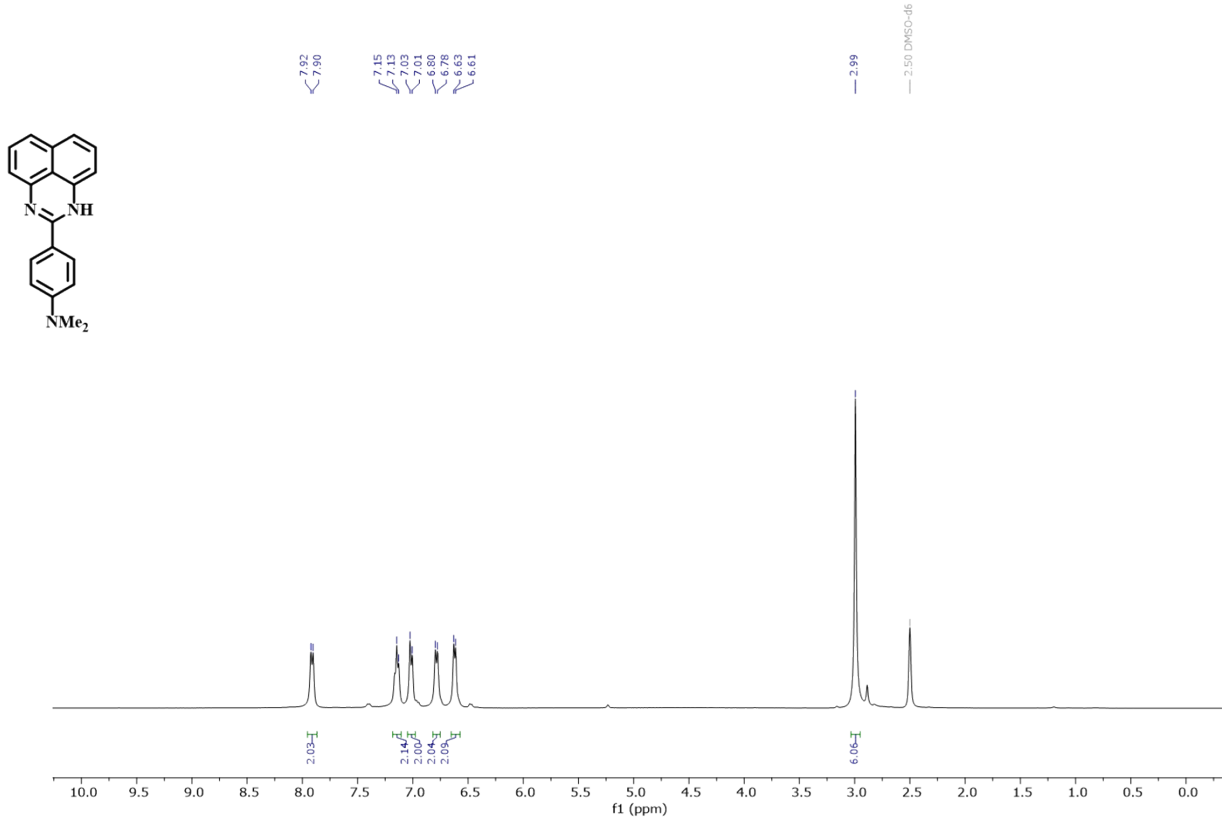


Figure S29. ^{1}H NMR spectrum (400 MHz) of **2n** in DMSO-d6.

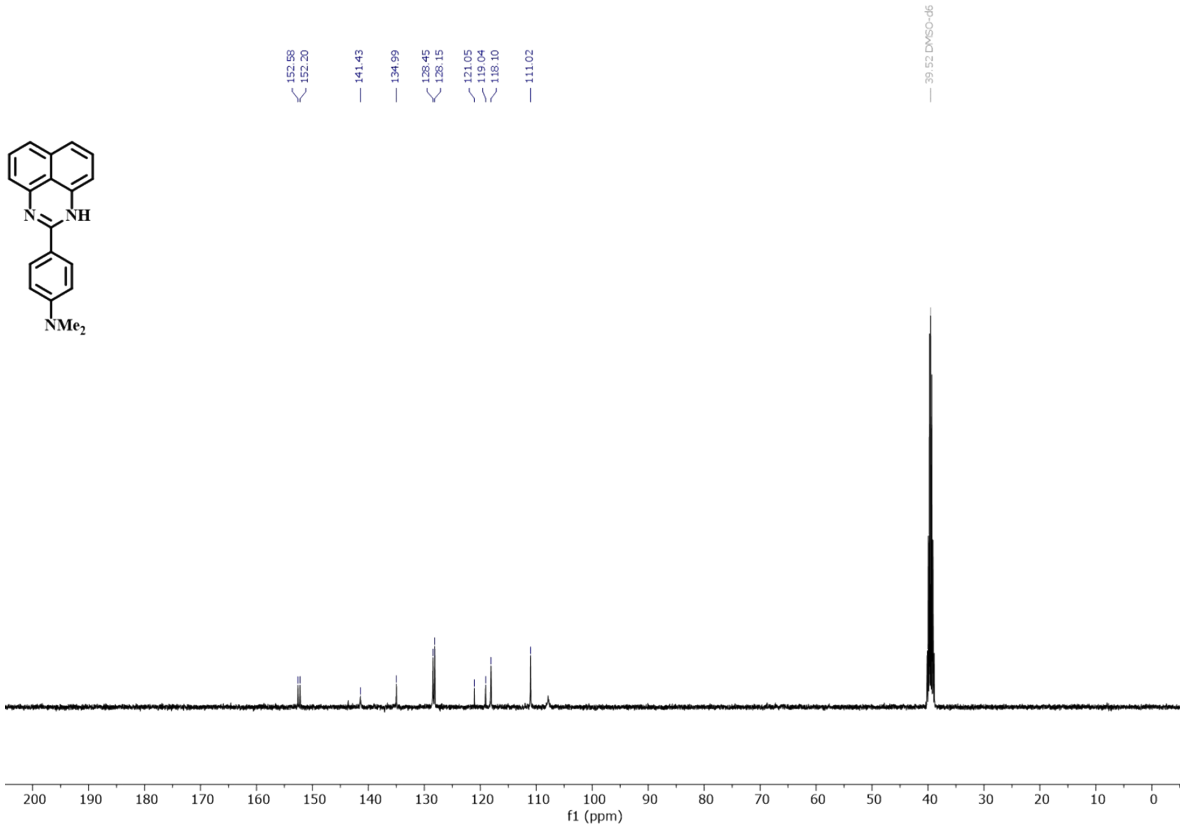


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **2n** in DMSO-d6.

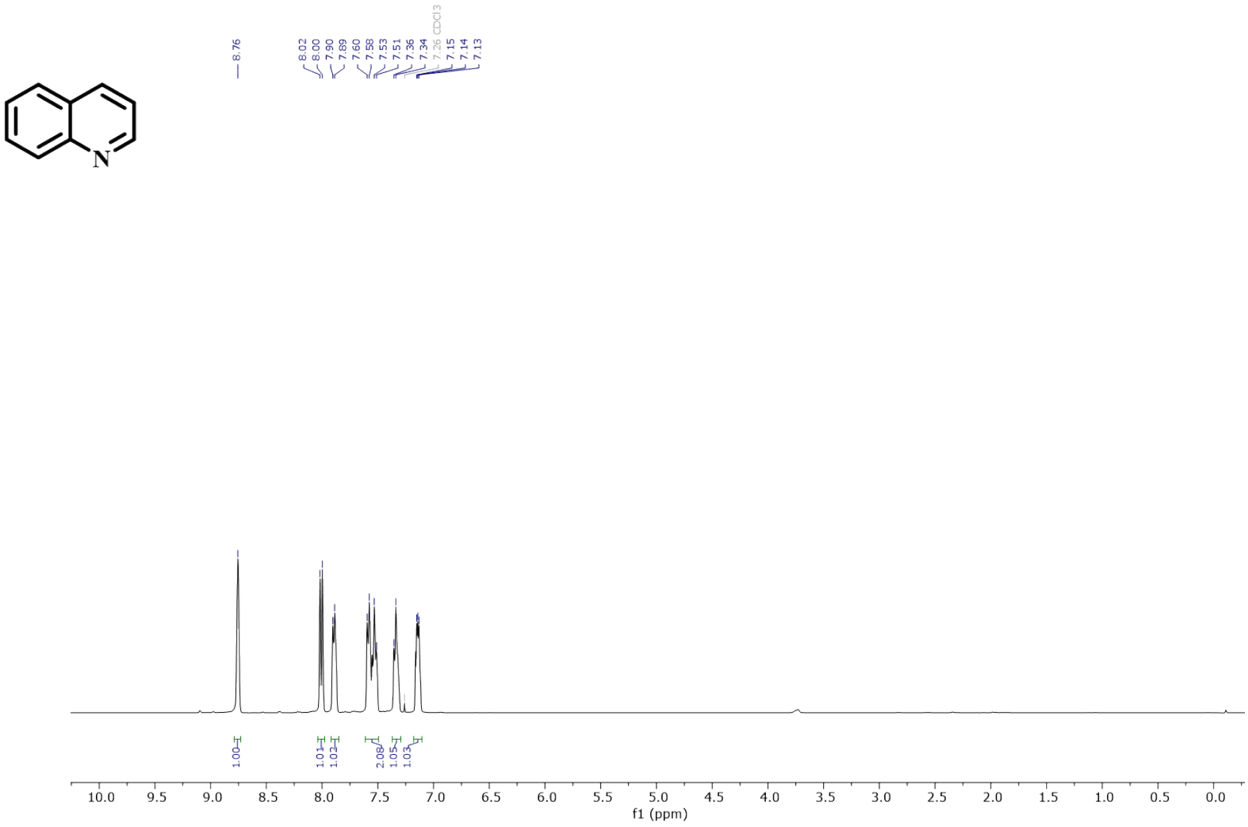


Figure S31. ^{1}H NMR spectrum (400 MHz) of **4a** in $CDCl_3$.

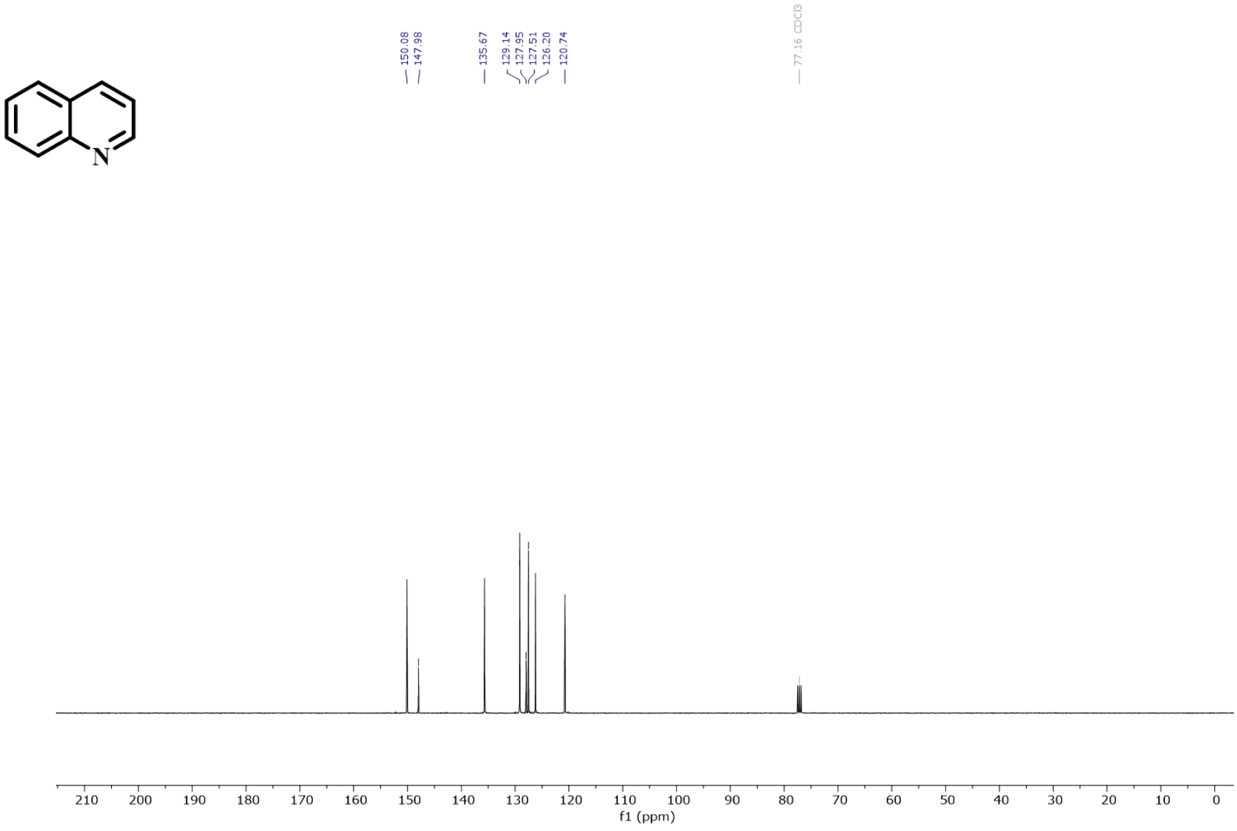


Figure $^{13}C\{^{1}H\}$. ^{13}C NMR spectrum (100 MHz) of **4a** in $CDCl_3$

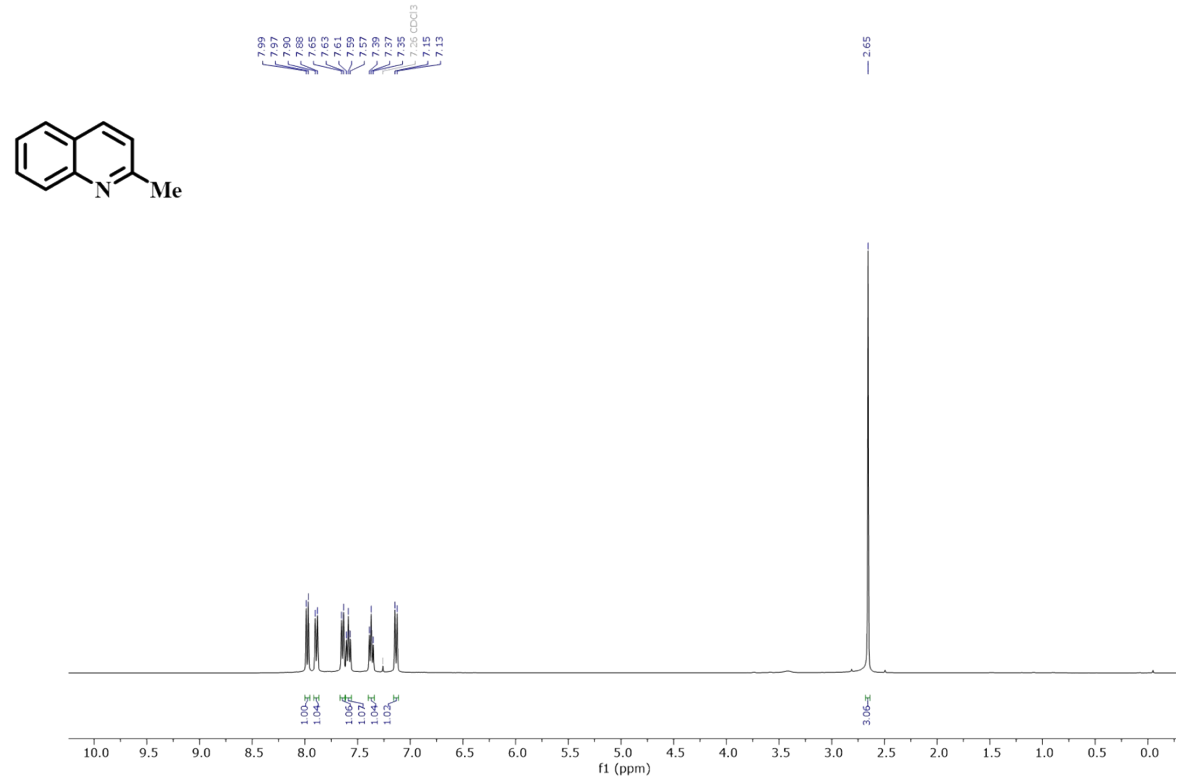


Figure S33. ^{1}H NMR spectrum (400 MHz) of **4b** in $CDCl_3$.

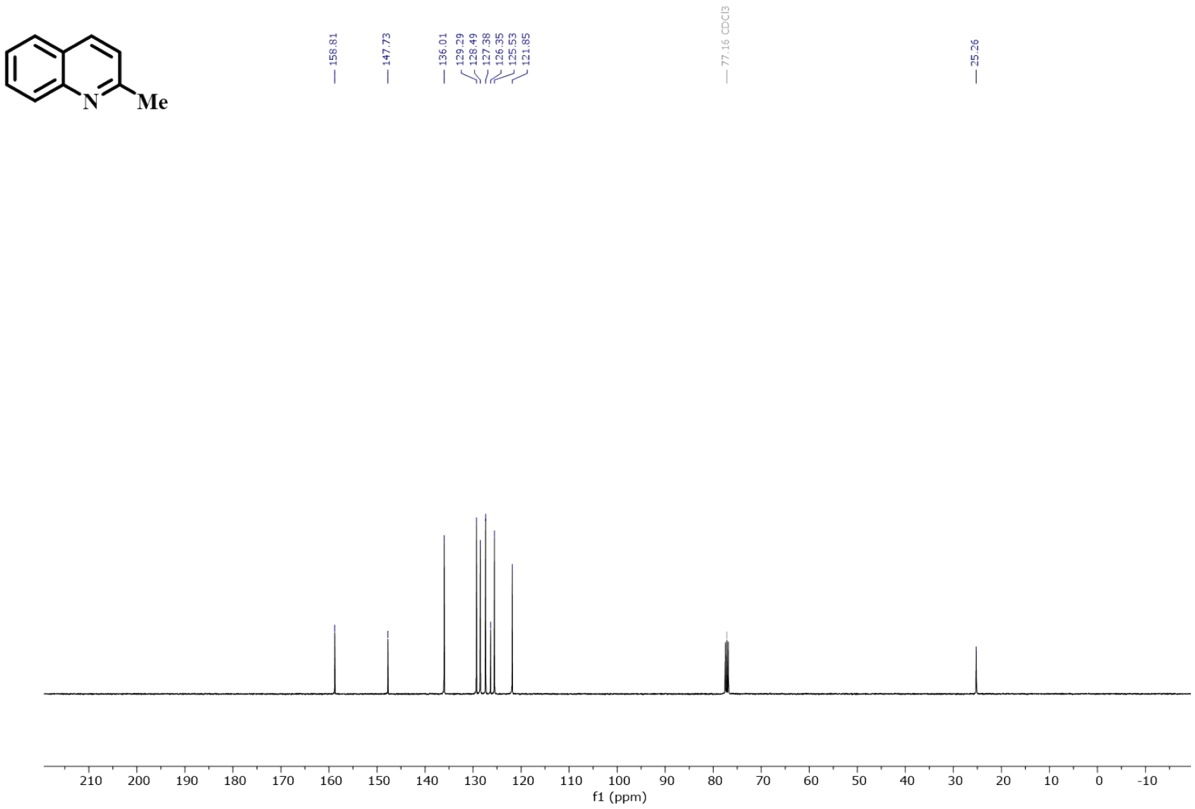


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **4b** in $CDCl_3$

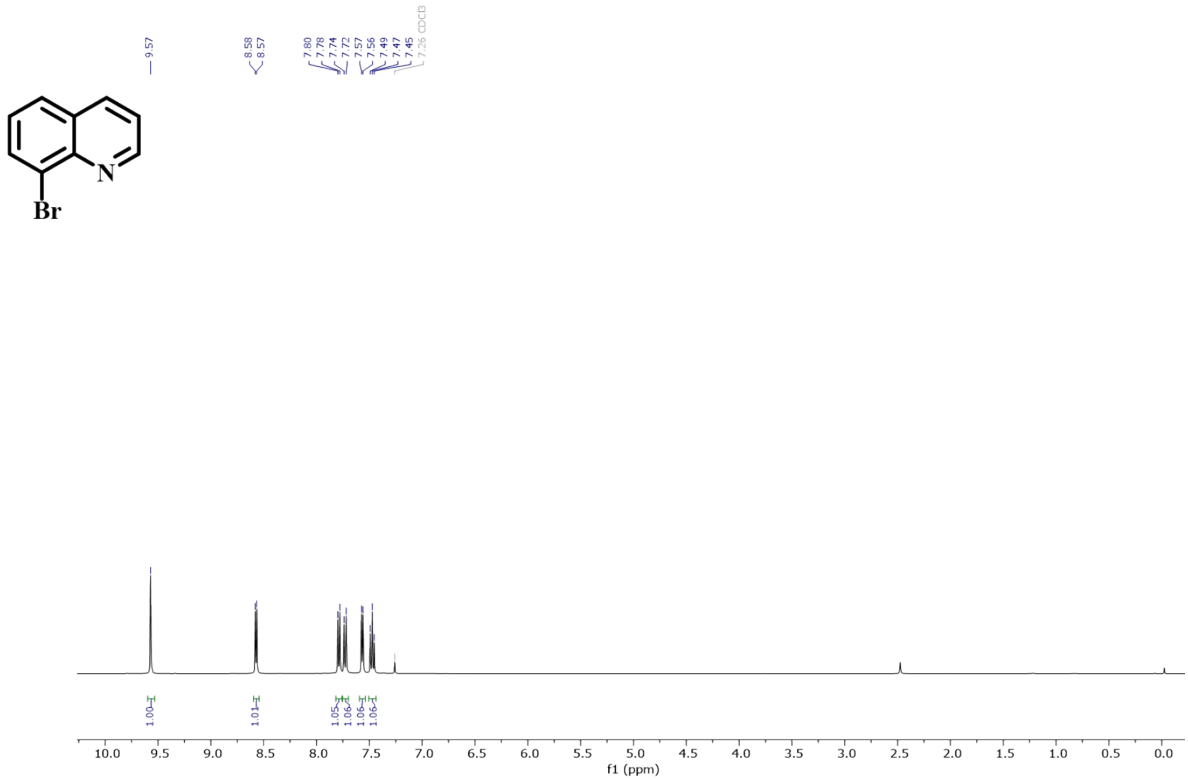


Figure S35. ^{1}H NMR spectrum (400 MHz) of **4c** in $CDCl_3$.

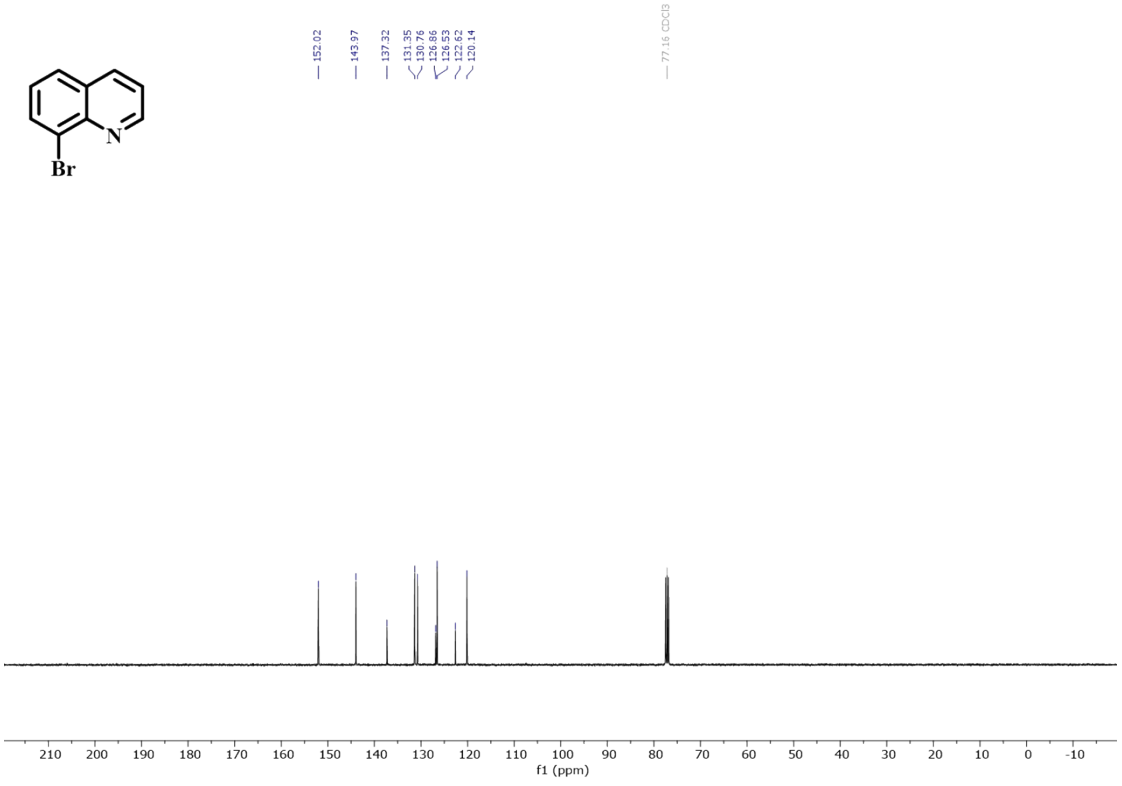


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **4c** in $CDCl_3$

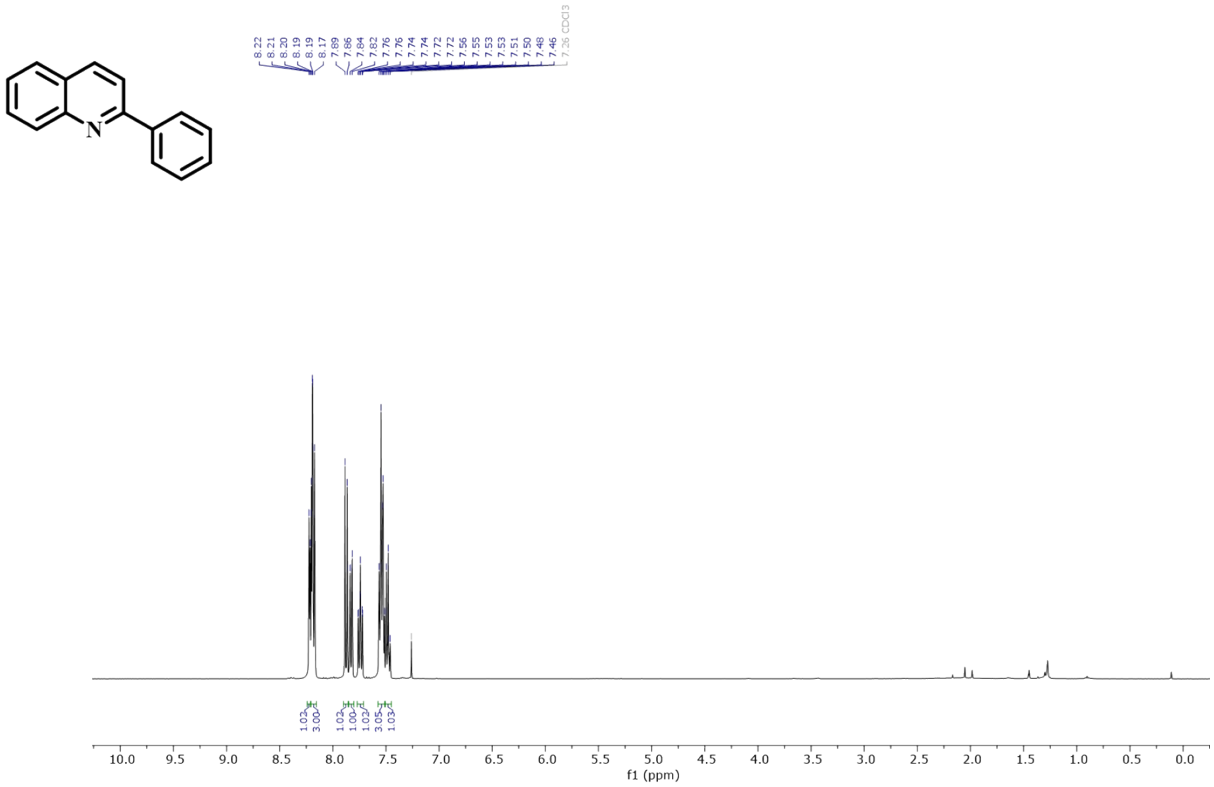


Figure S37. ^{1}H NMR spectrum (400 MHz) of **4d** in $CDCl_3$.

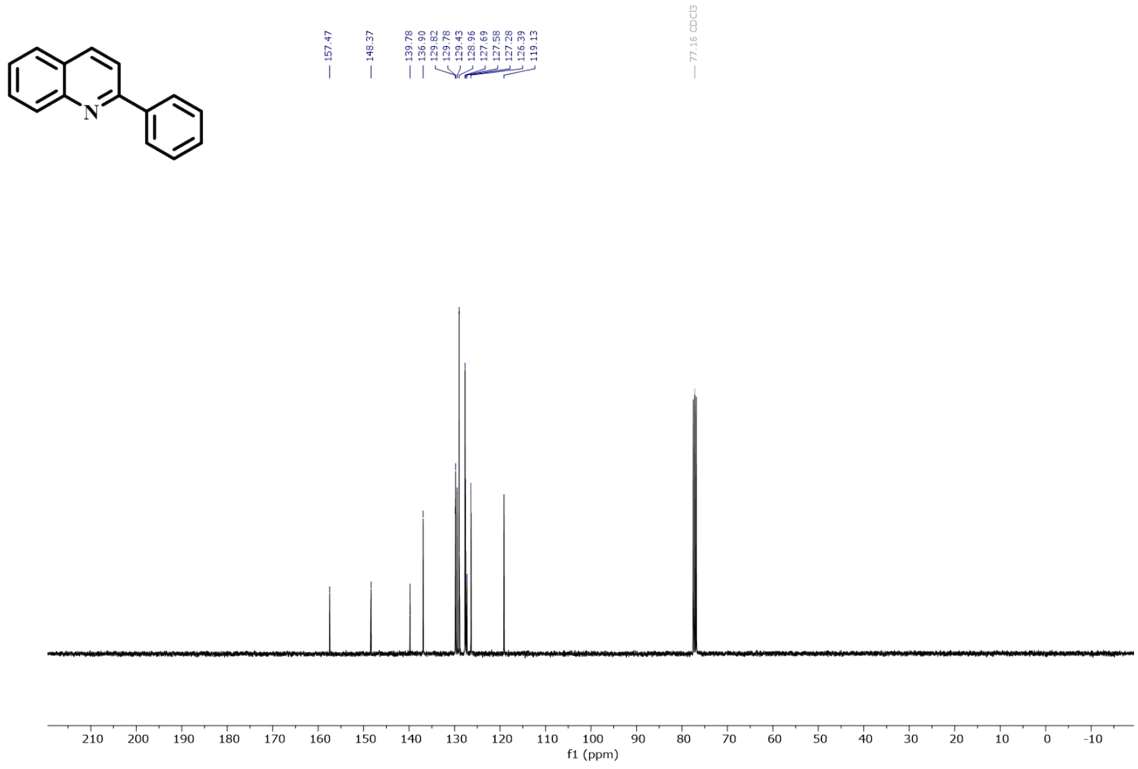


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **4d** in $CDCl_3$

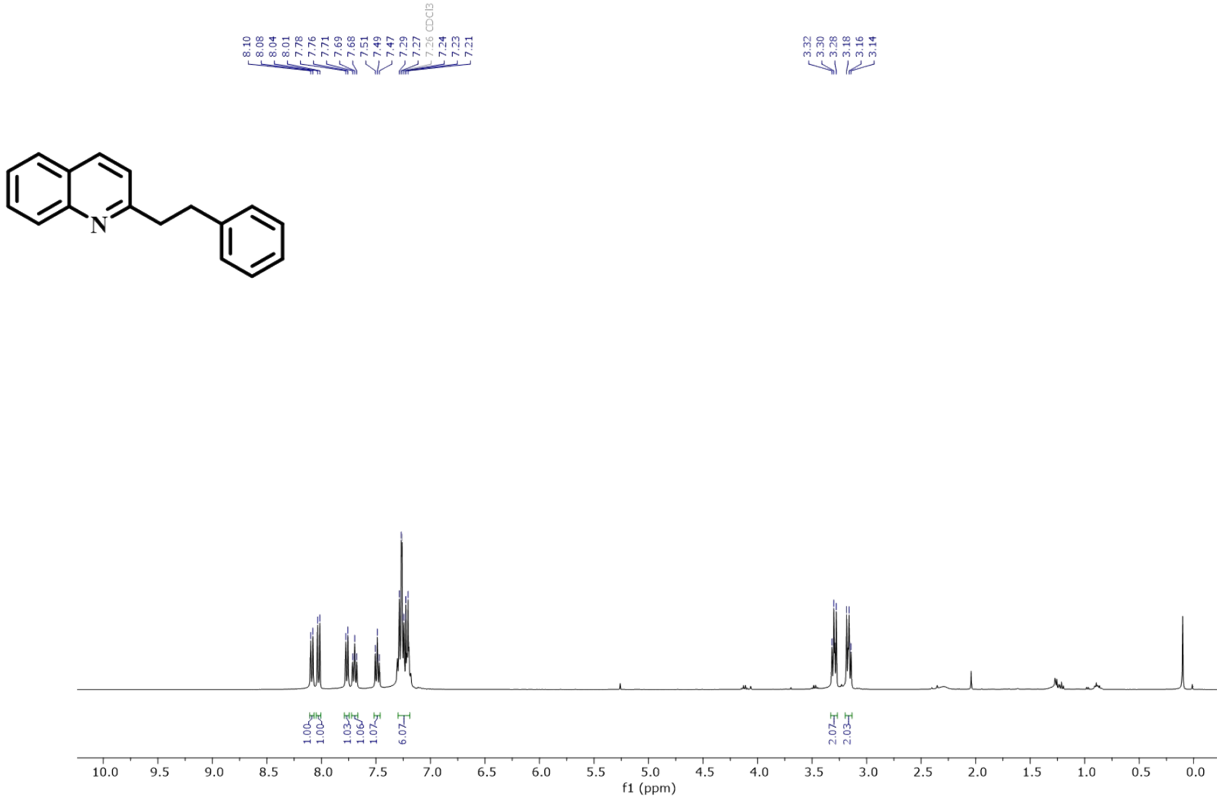


Figure S39. ^{1}H NMR spectrum (400 MHz) of **4e** in $CDCl_3$.

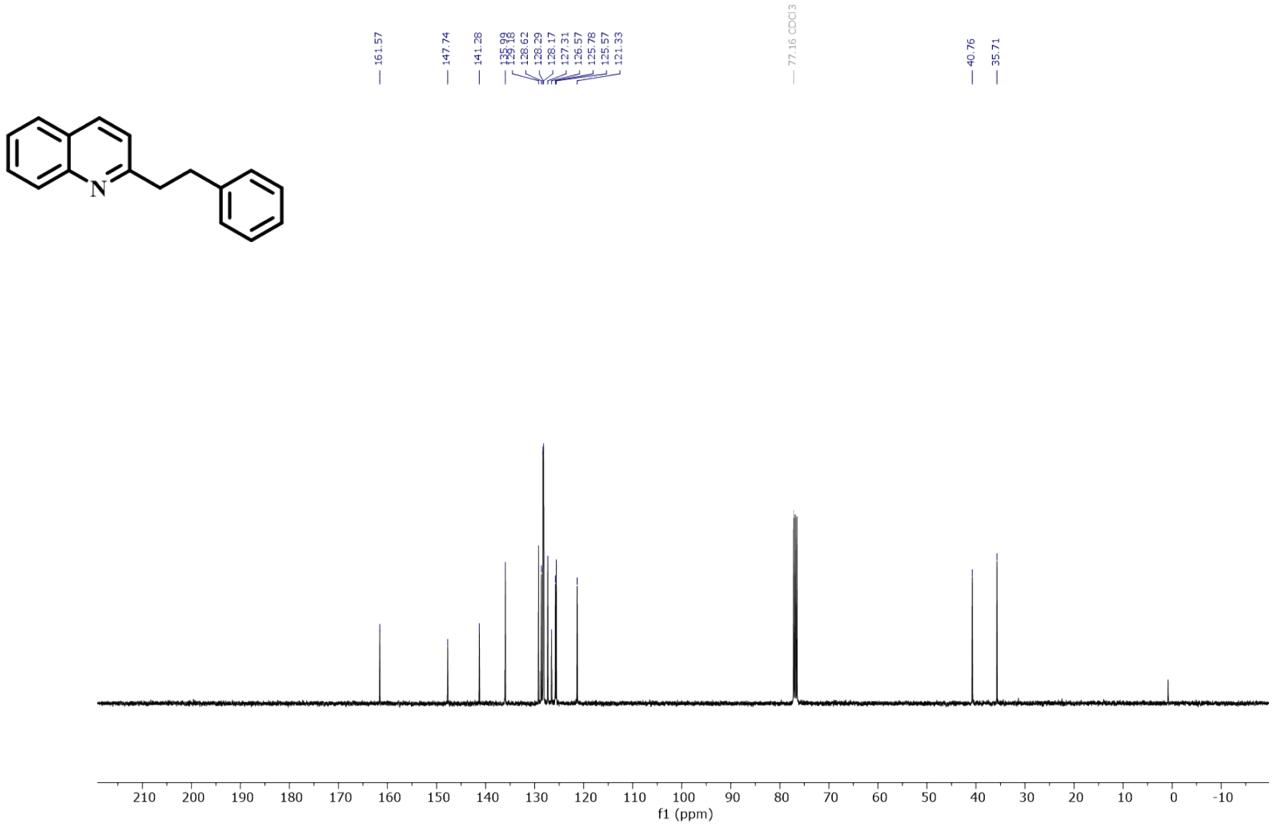


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **4e** in $CDCl_3$

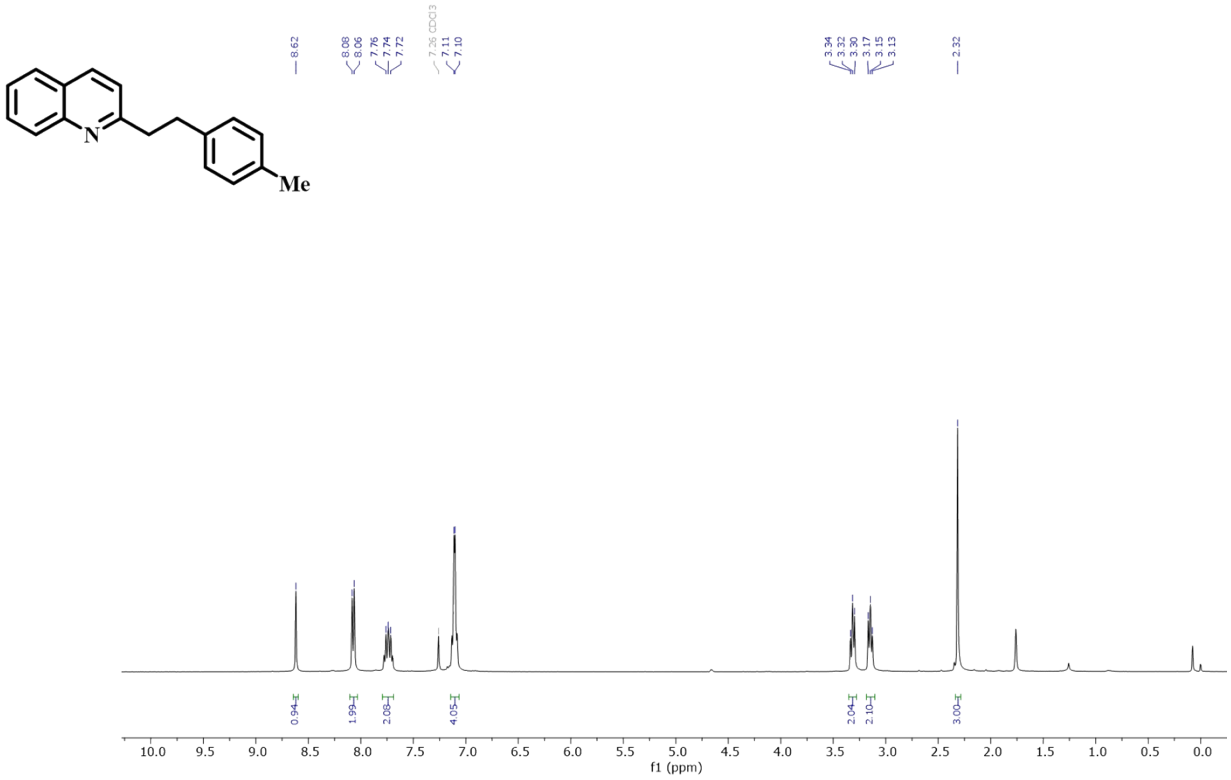


Figure S41. ^{1}H NMR spectrum (400 MHz) of **4f** in $CDCl_3$.

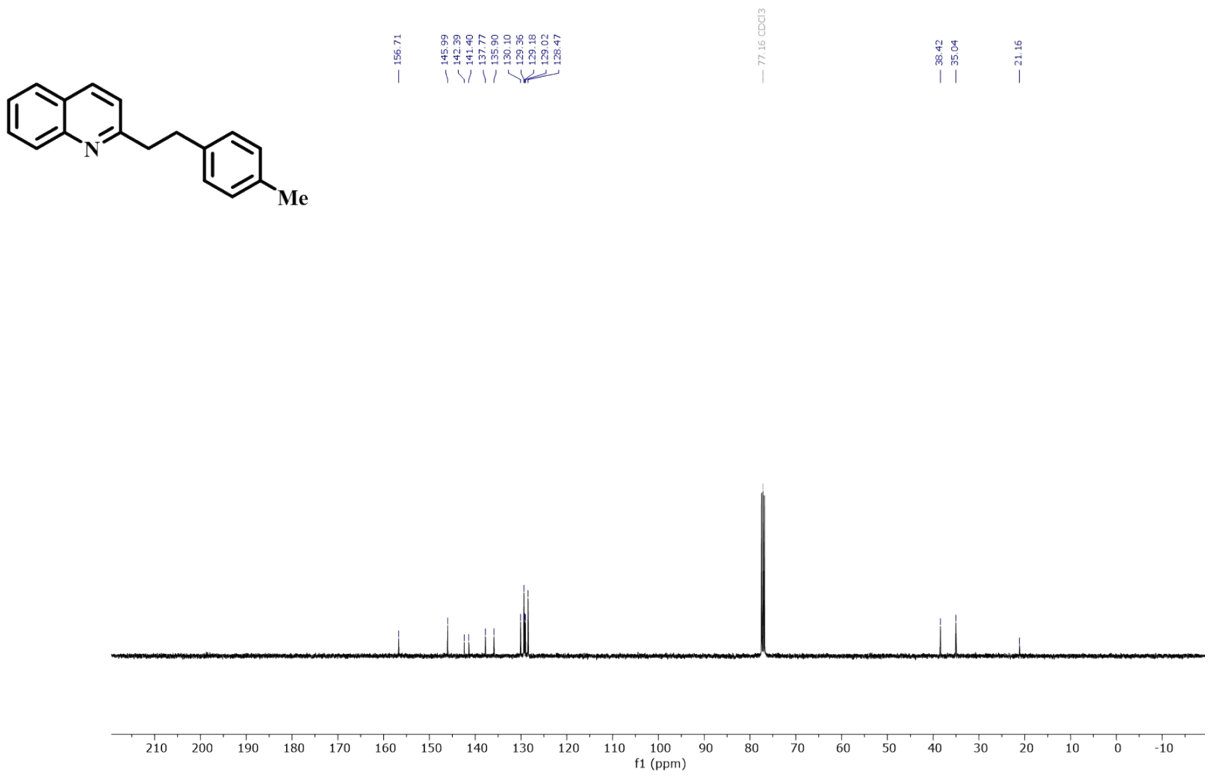


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **4f** in $CDCl_3$

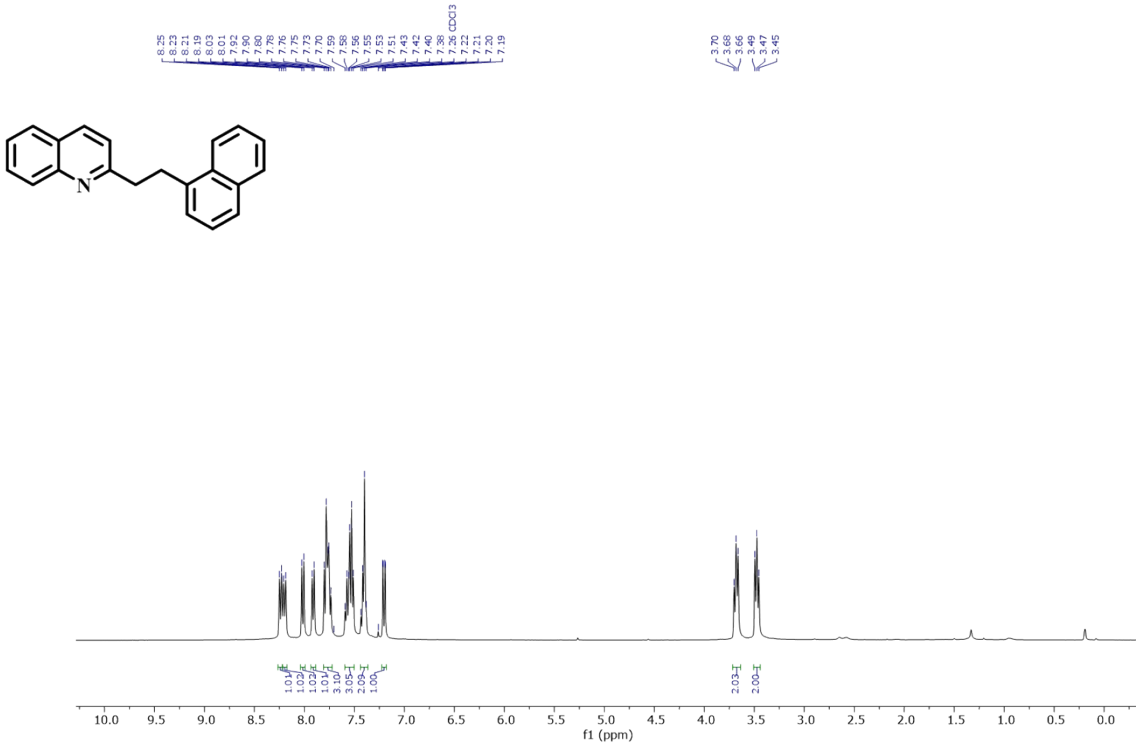


Figure S43. ^{1}H NMR spectrum (400 MHz) of **4g** in $CDCl_3$.

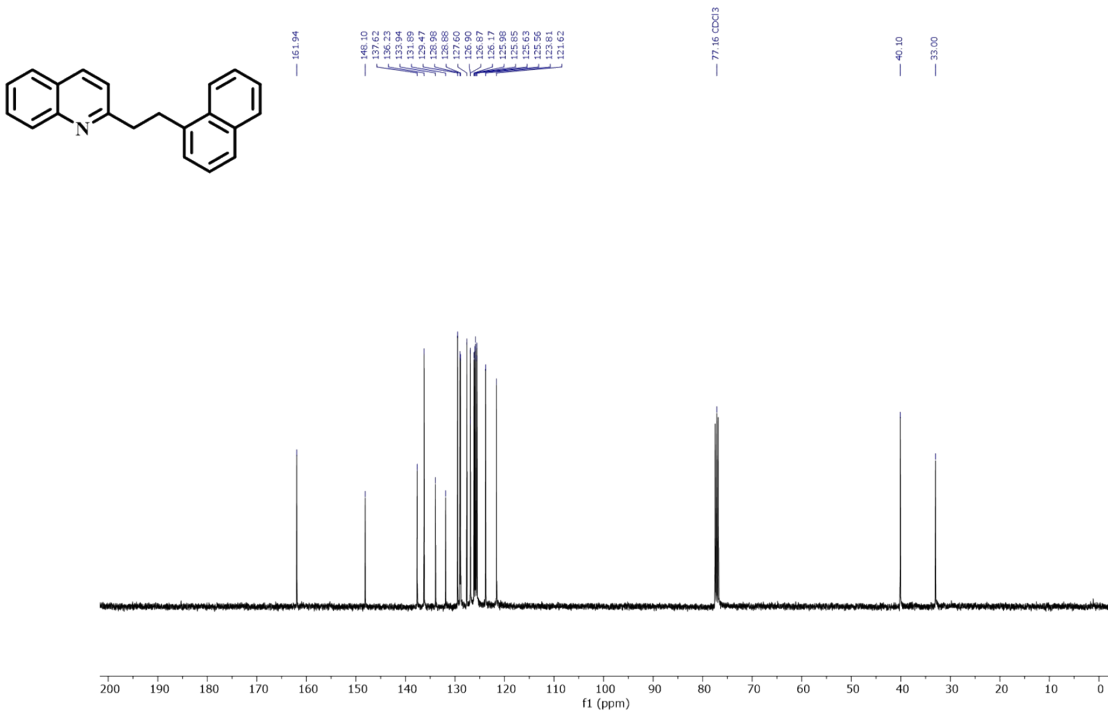


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **4g** in $CDCl_3$

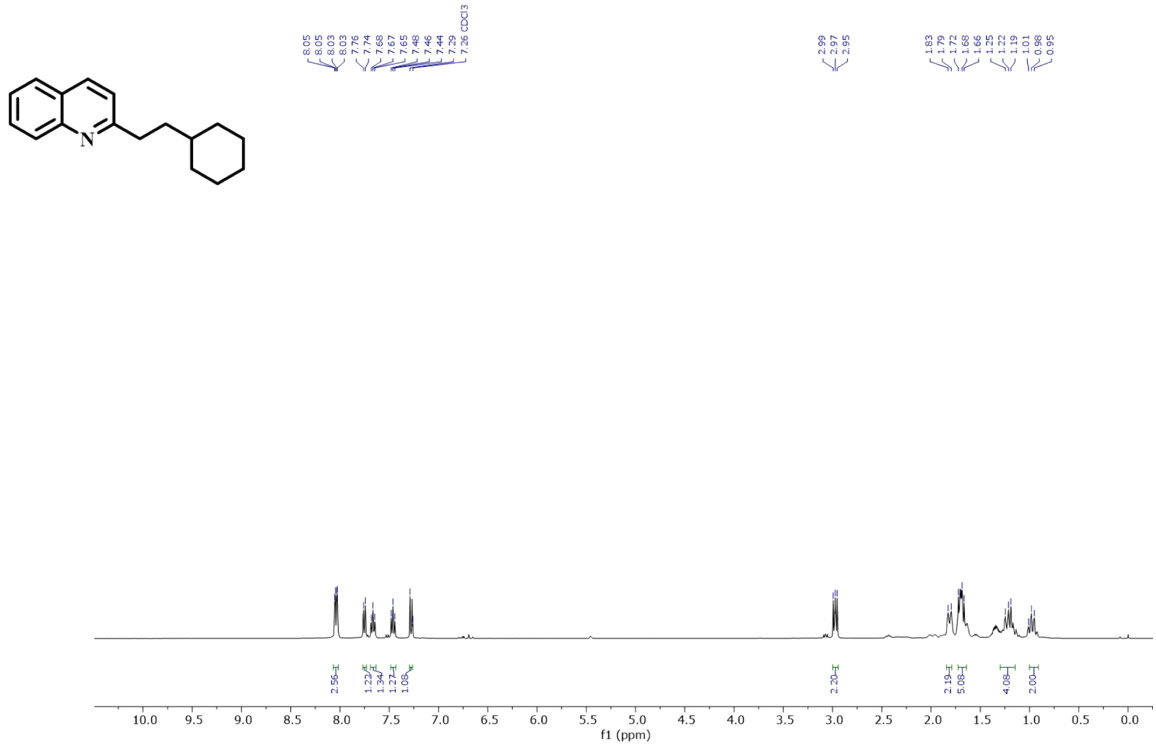


Figure S45. ^{1}H NMR spectrum (400 MHz) of **4h** in $CDCl_3$.

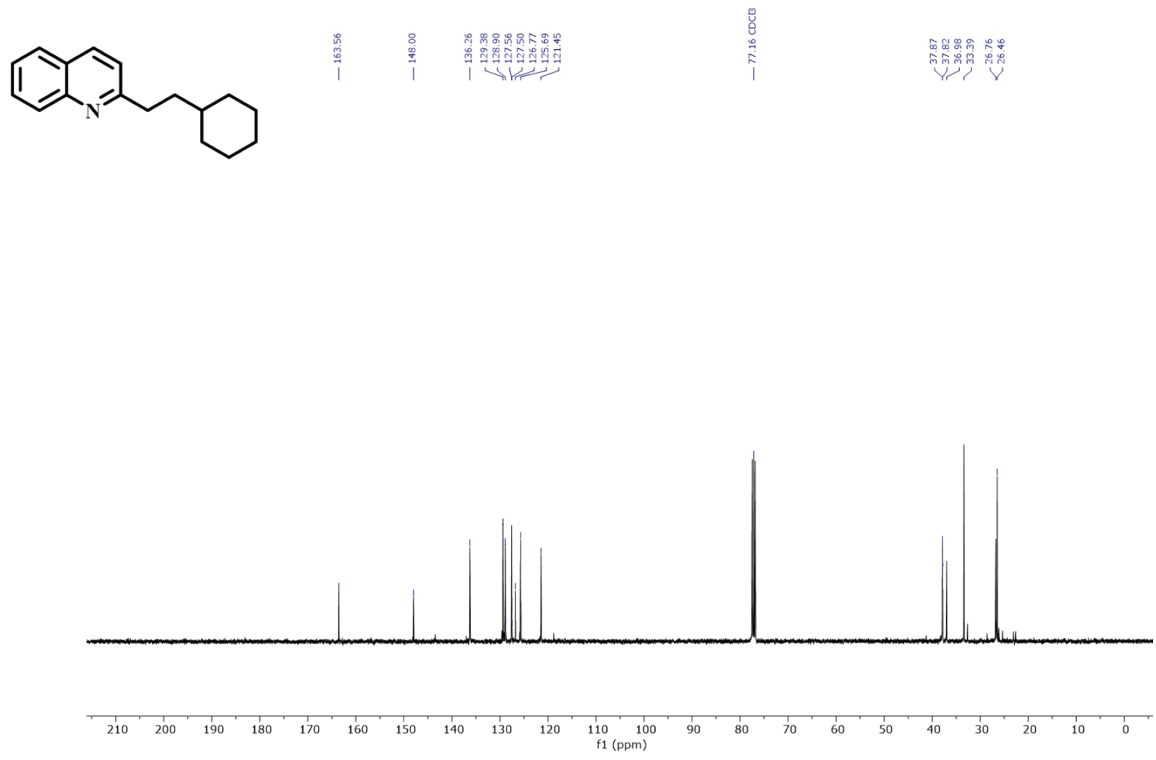


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **4h** in $CDCl_3$

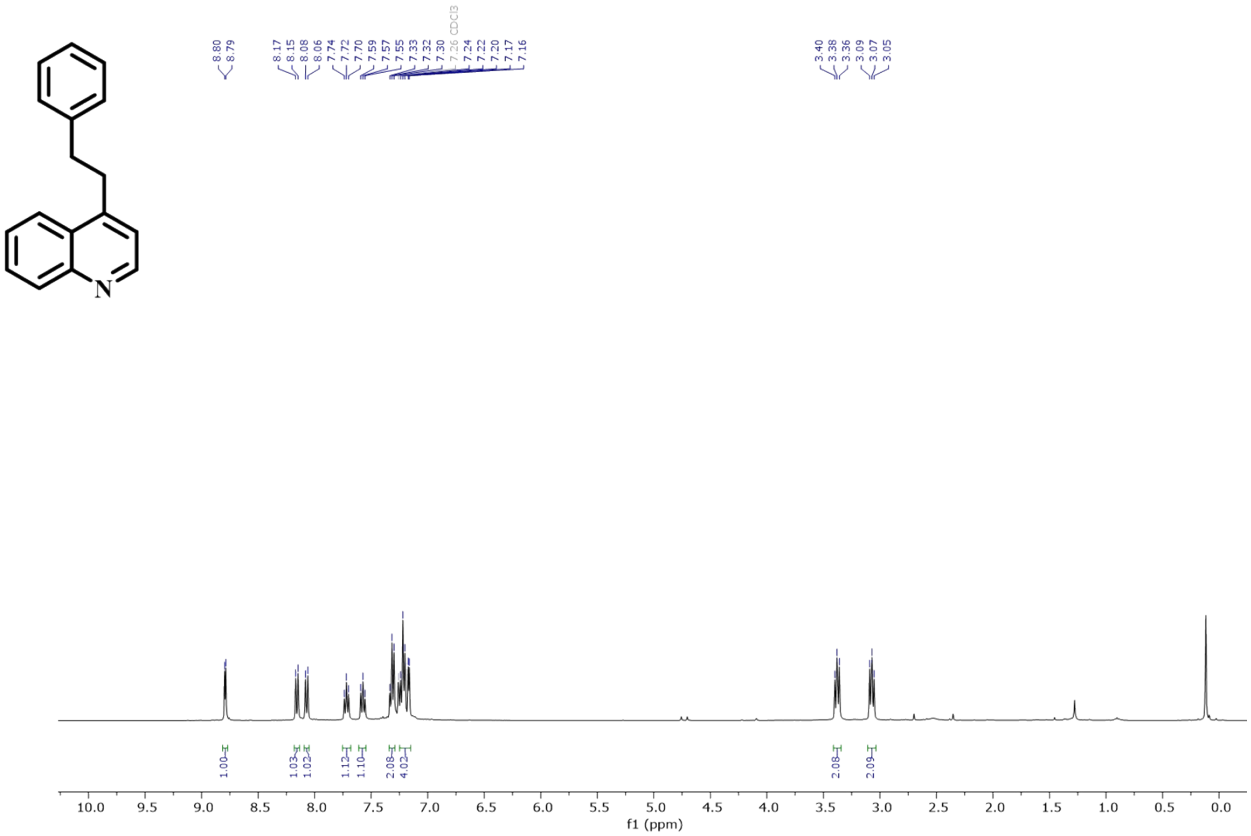


Figure S47. ^{1}H NMR spectrum (400 MHz) of **4i** in $CDCl_3$.

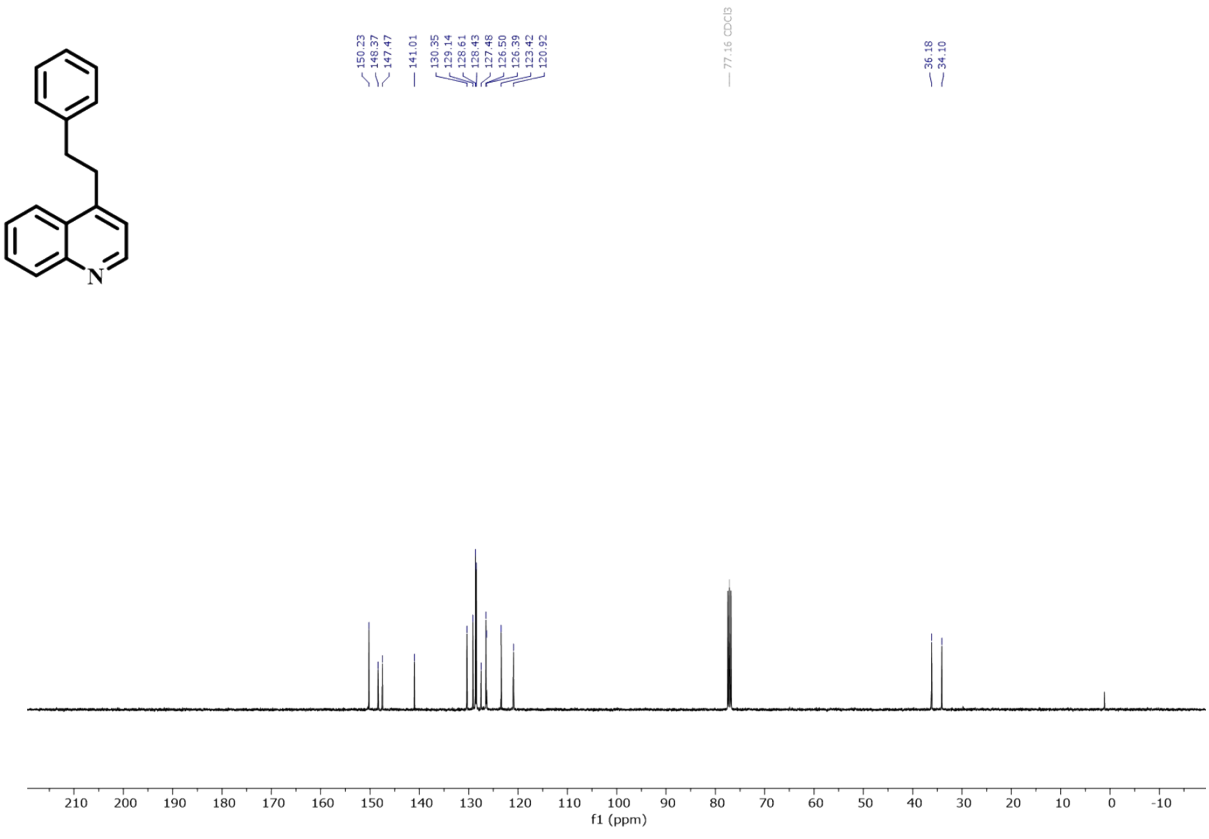


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **4i** in $CDCl_3$

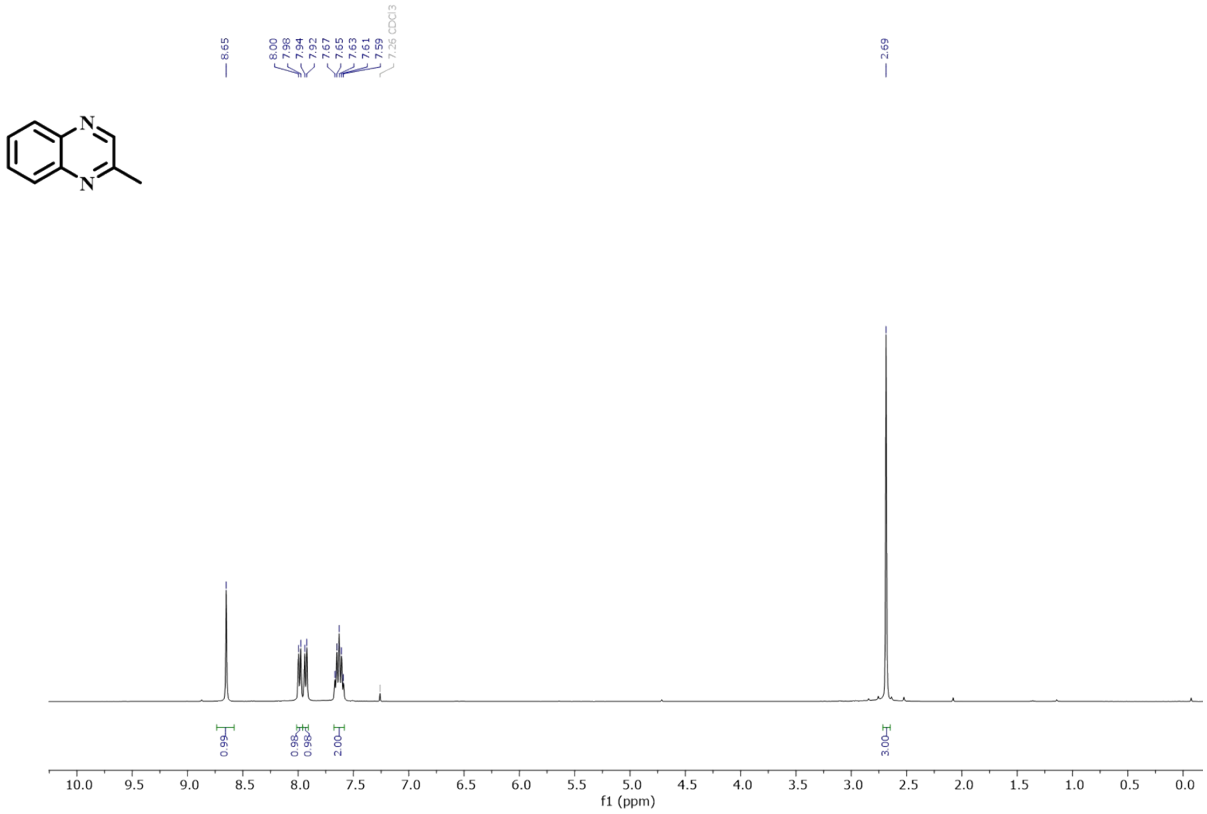


Figure S49. ^{1}H NMR spectrum (400 MHz) of **6a** in $CDCl_3$.

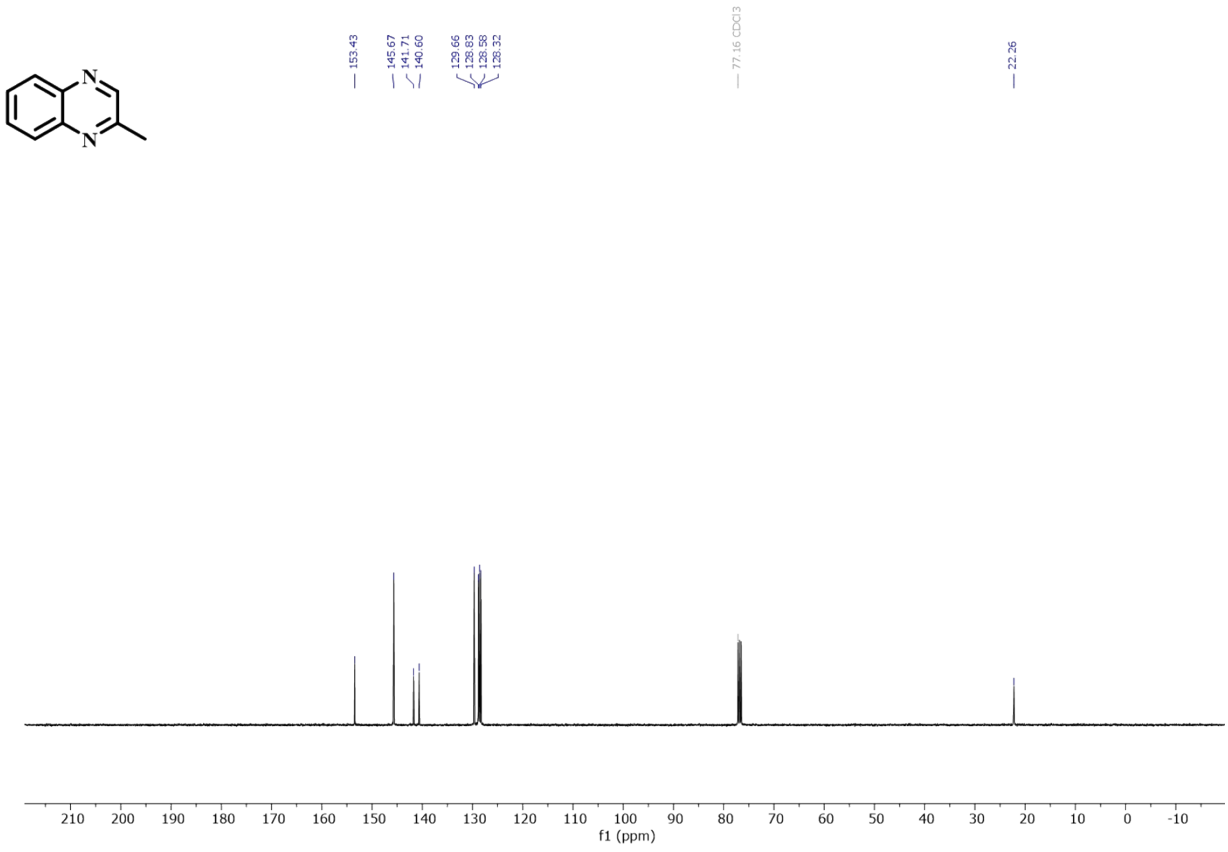


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **6a** in $CDCl_3$

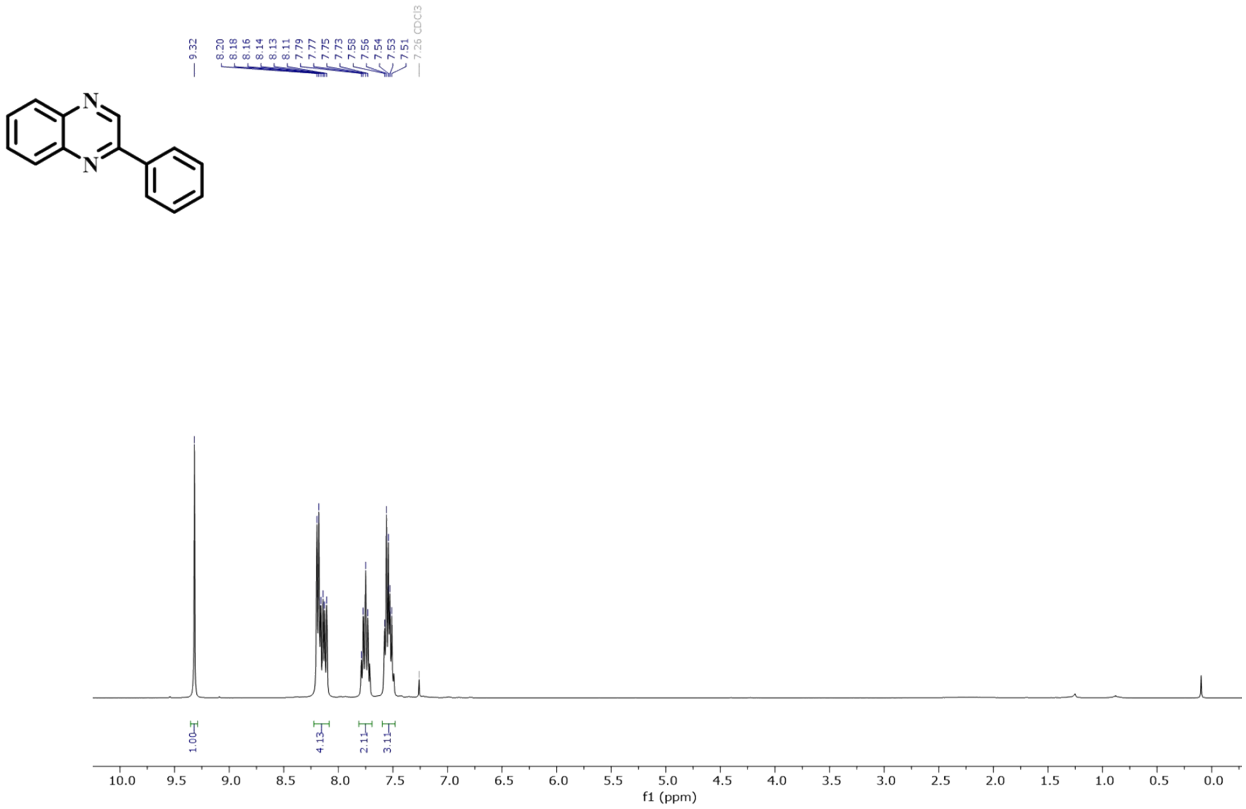


Figure S51. ^{1}H NMR spectrum (400 MHz) of **6b** in $CDCl_3$.

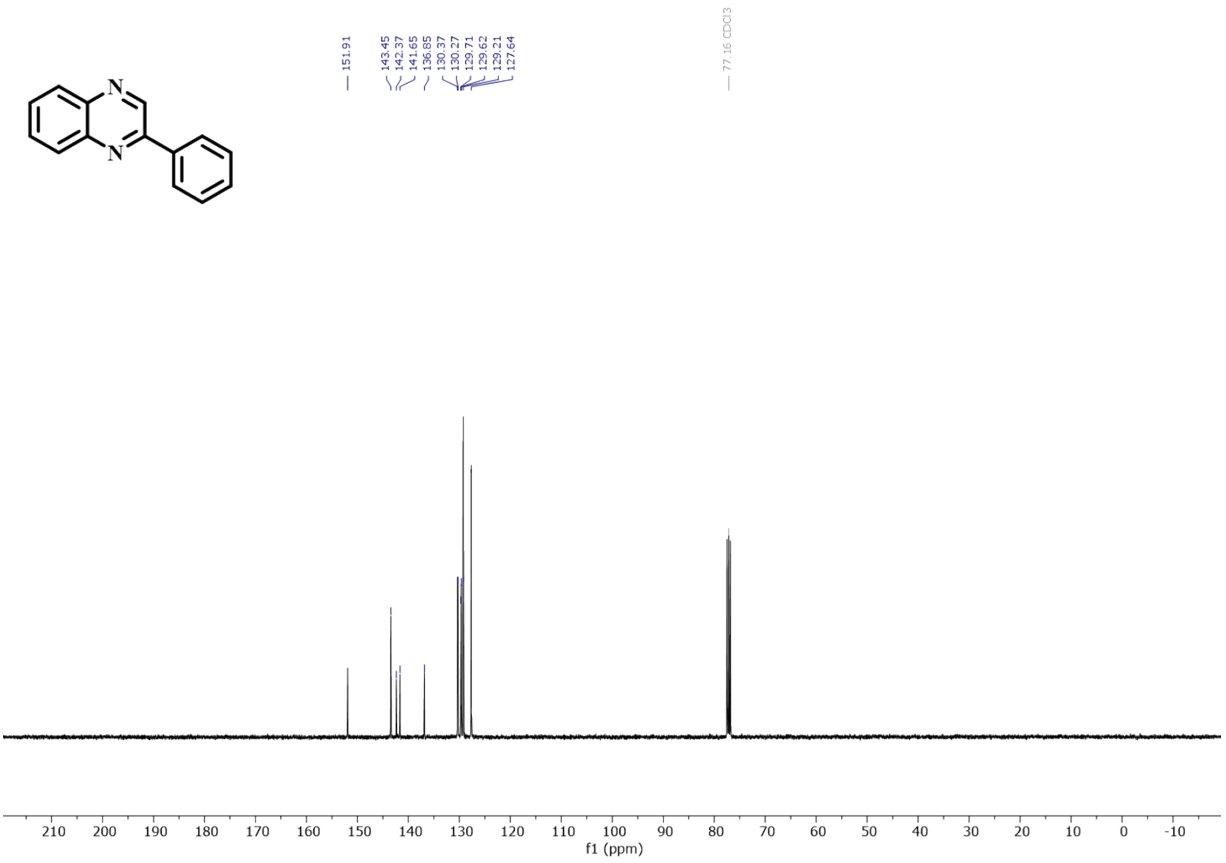


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **6b** in $CDCl_3$

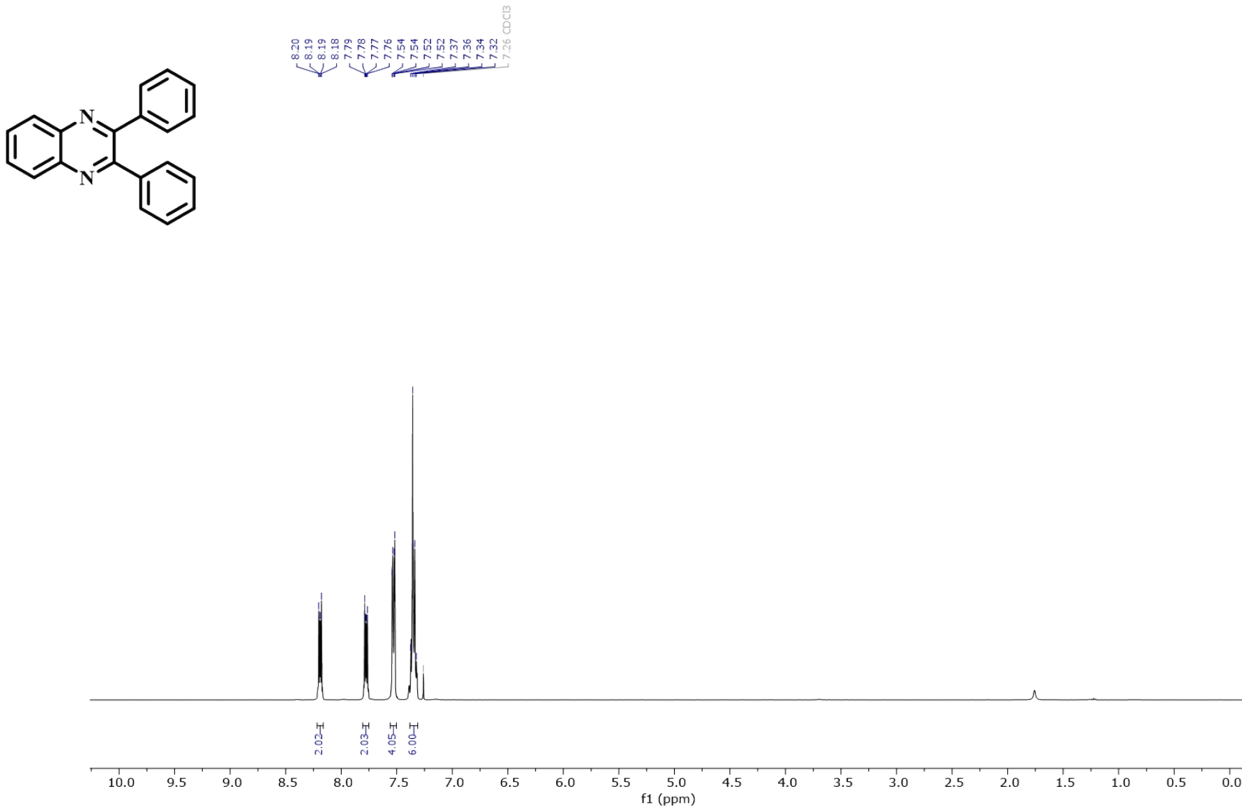


Figure S53. ^{1}H NMR spectrum (400 MHz) of **6c** in $CDCl_3$.

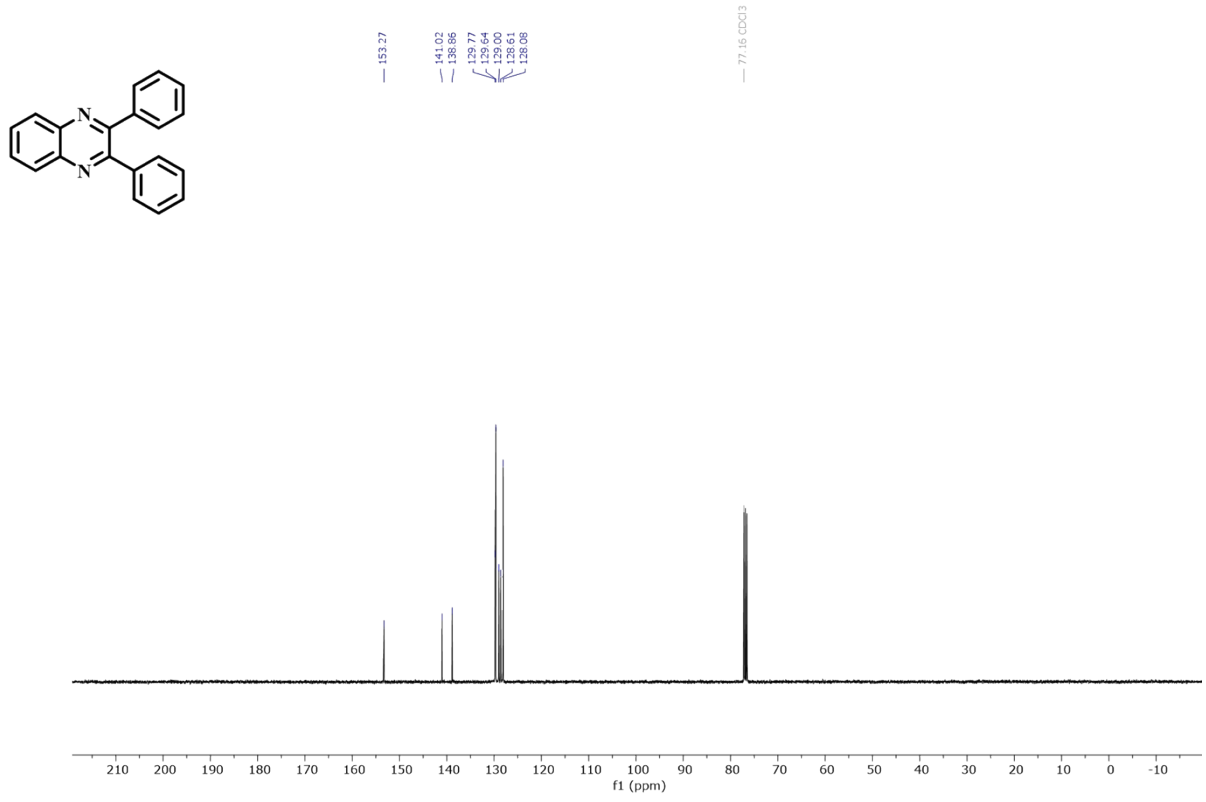


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **6c** in $CDCl_3$

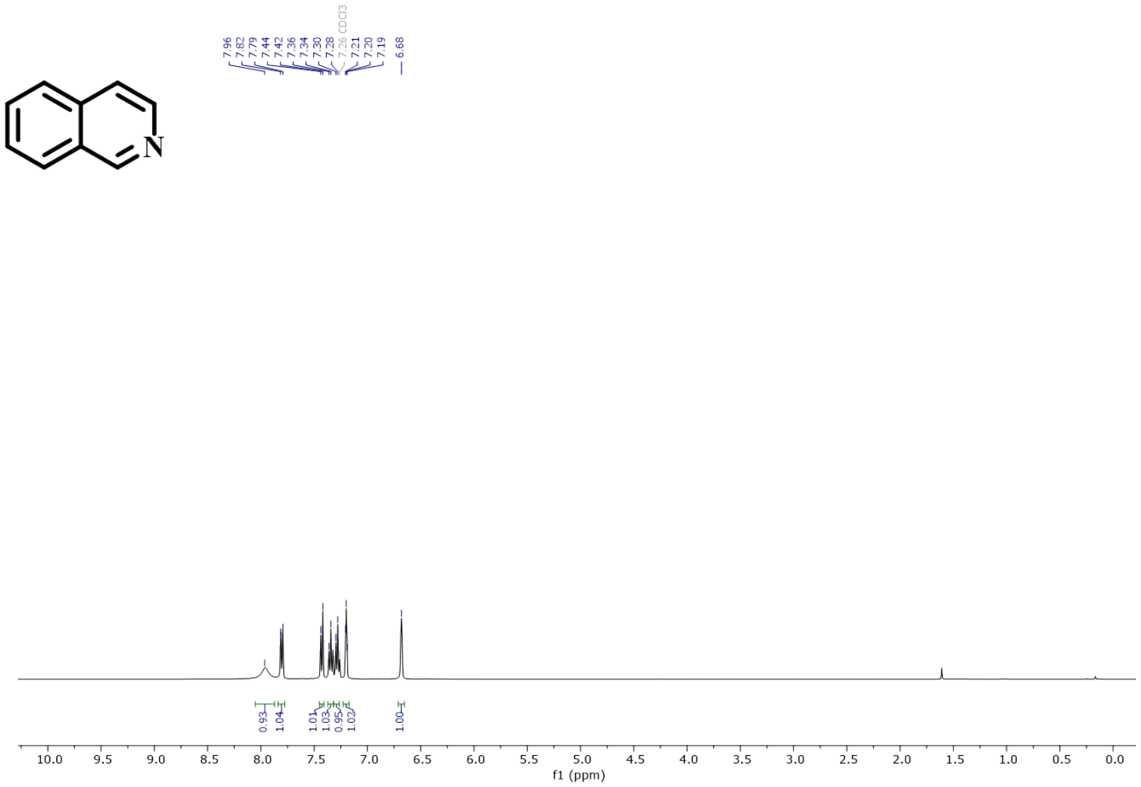


Figure S55. ^{1}H NMR spectrum (400 MHz) of **6d** in $CDCl_3$.

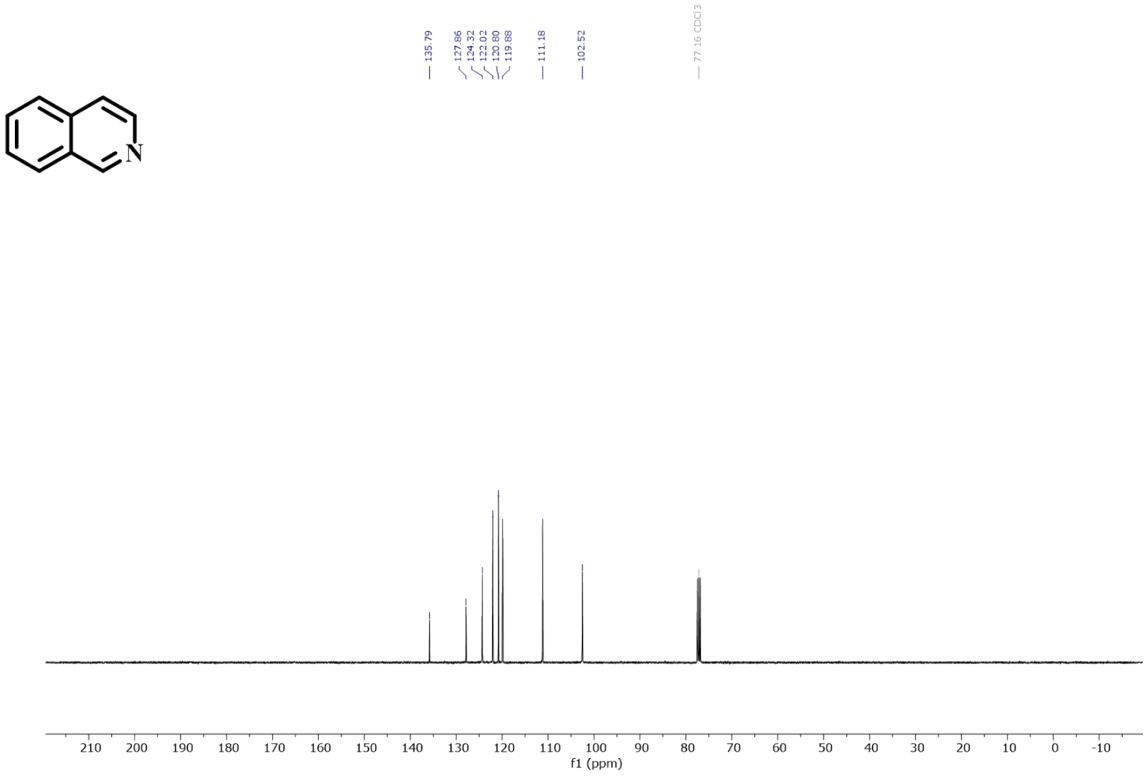


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **6d** in $CDCl_3$

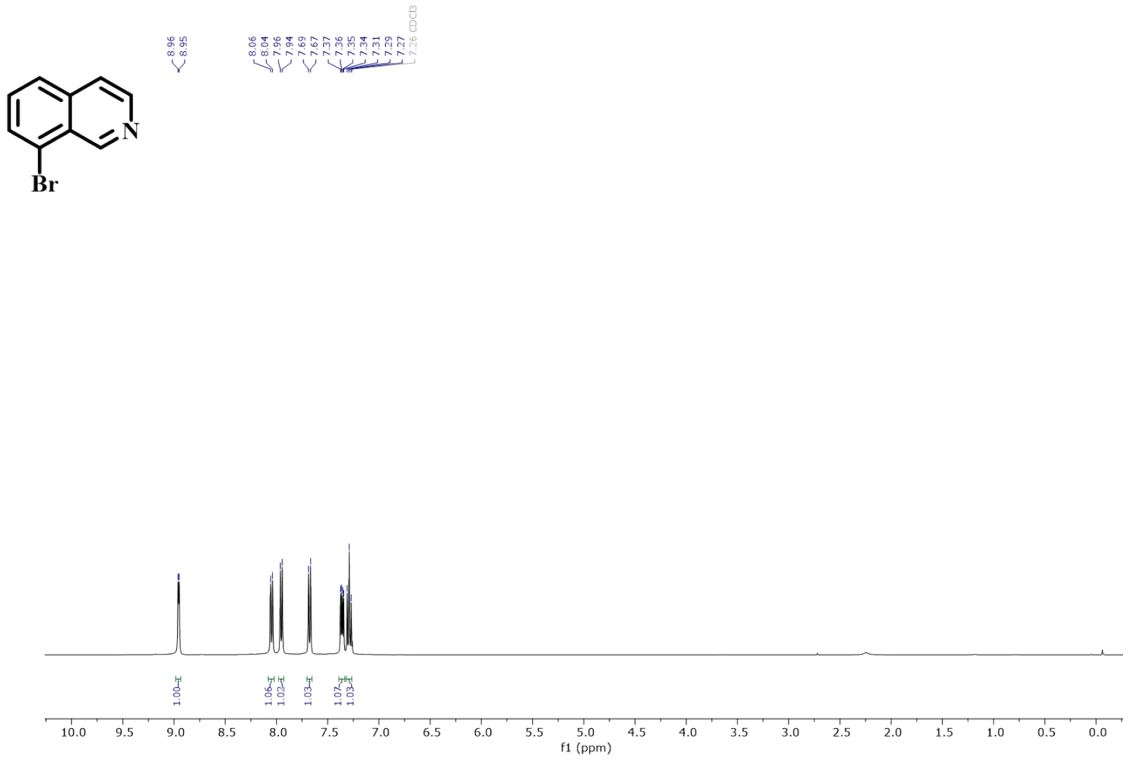


Figure S57. ^{1}H NMR spectrum (400 MHz) of **6e** in $CDCl_3$.

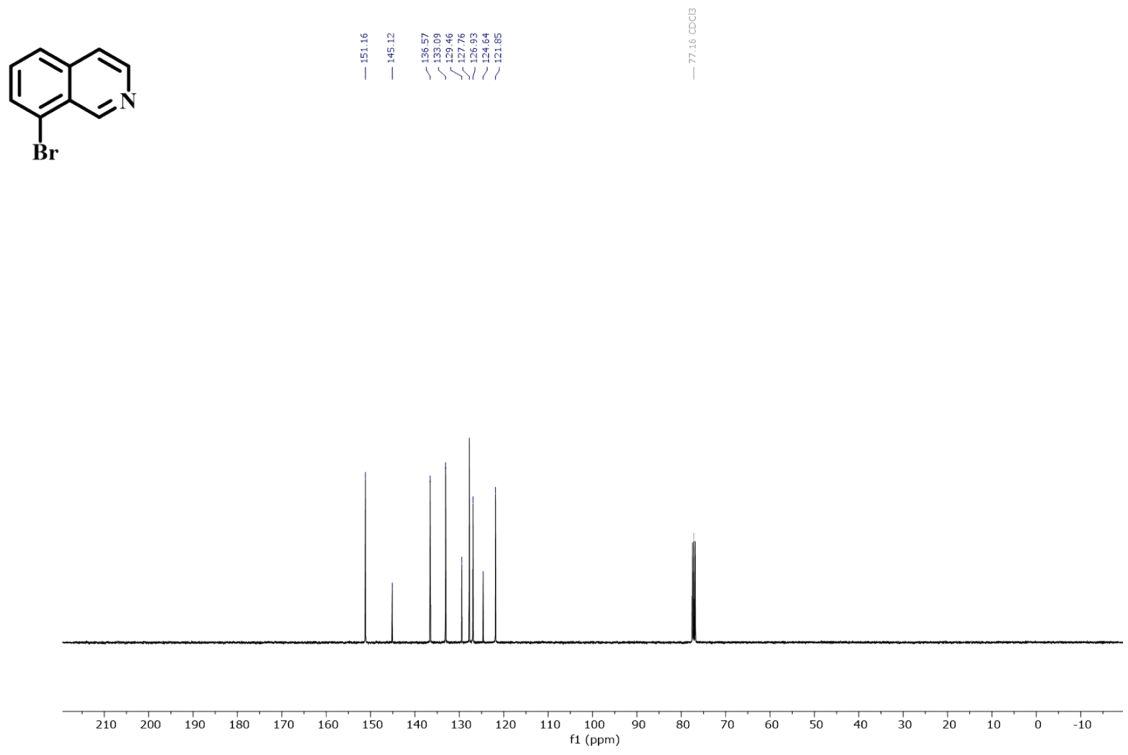


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **6e** in $CDCl_3$

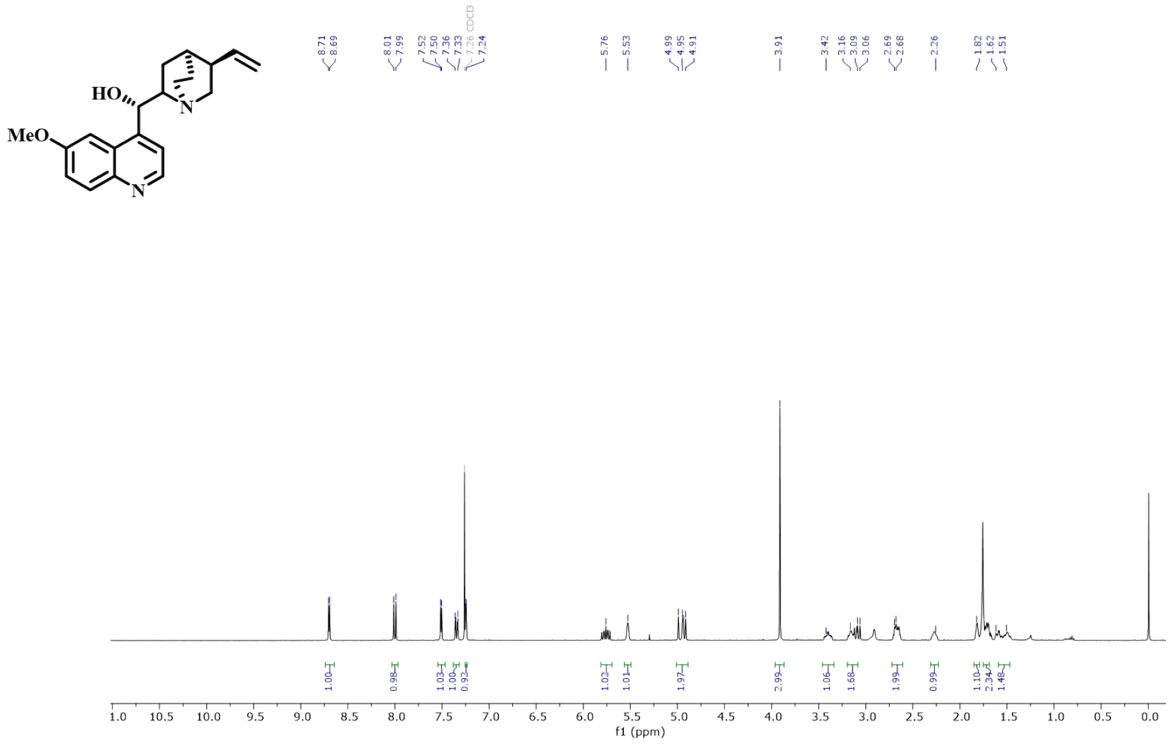


Figure S59. ^{1}H NMR spectrum (400 MHz) of **8** in $CDCl_3$

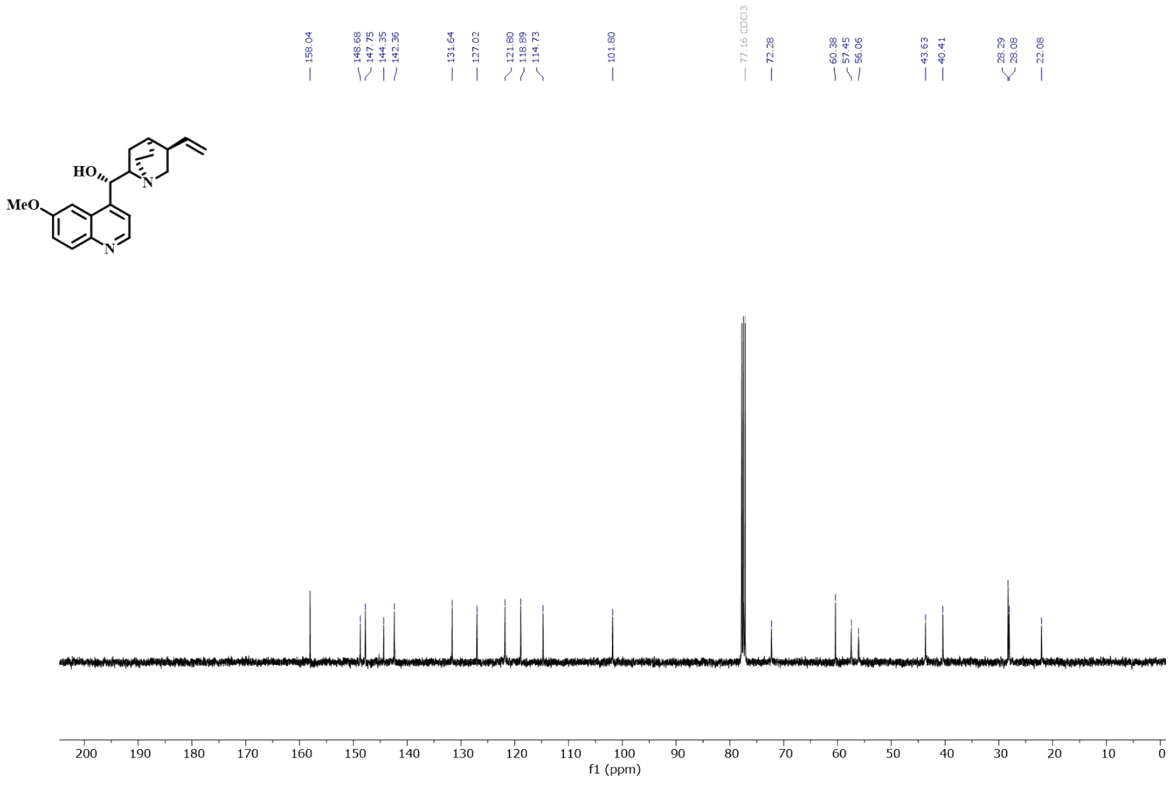
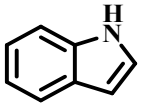
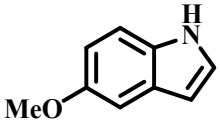


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **8** in $CDCl_3$

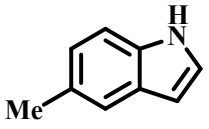
8. **Analytical data**



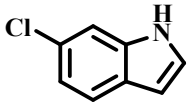
1*H*-indole (2a)[2]: white solid, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.6, 127.6, 123.9, 121.8, 120.5, 119.6, 110.8, 102.4.



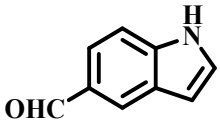
5-methoxy-1*H*-indole (2b)[2] : White solid, 81% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.18 (t, *J* = 2.8 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.52 – 6.48 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.00, 130.7, 128.1, 124.7, 112.2, 111.5, 102.2, 102.1, 55.7, 55.6.



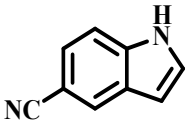
5-methyl-1*H*-indole (2c)[8] : White solid, 77% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.48 (s, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.18 – 7.16 (m, 1H), 7.08 – 7.05 (m, 1H), 6.51 (t, *J* = 2.1 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.2, 129.1, 128.2, 124.4, 123.7, 120.4, 110.8, 102.2, 21.6, 21.6.



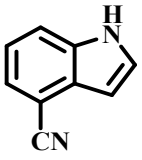
6-chloro-1*H*-indole (2d)[8] : White solid**,** 67% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.40 – 7.38 (m, 1H), 7.20 (dd, *J* = 3.1, 2.5 Hz, 1H), 7.10 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.54 (ddd, *J* = 3.1, 2.0, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.9, 127.7, 126.2, 124.6, 121.4, 120.4, 110.8, 102.6.



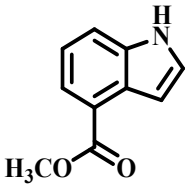
1*H*-indole-5-carbaldehyde (2e)[9] : White solid, 73% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.04 (s, 1H), 8.56 (s, 1H), 8.20 – 8.17 (m, 1H), 7.79 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.34 – 7.31 (m, 1H), 6.72 (ddd, *J* = 3.0, 2.0, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.4, 129.6, 127.5, 126.1, 125.8, 122.2, 111.5, 104.3.



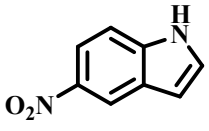
1*H*-indole-5-carbonitrile (2f)[9] **:** White soild, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 8.02 – 7.99 (m, 1H), 7.48 – 7.41 (m, 2H), 7.36 – 7.33 (m, 1H), 6.64 (ddd, *J* = 3.0, 2.0, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.6, 127.8, 126.6, 126.5, 125.1, 120.9, 112.1, 103.6, 103.1.



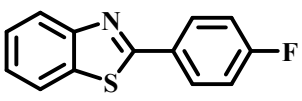
1*H*-indole-4-carbonitrile (2g)[10] **:** White solid, 62% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.41 (t, *J* = 2.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 6.79 – 6.76 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.6, 129.3, 127.1, 125.5, 121.8, 119.0, 116.1, 103.1, 101.9.



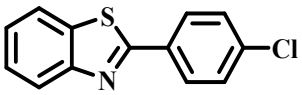
methyl 1*H*-indole-4-carboxylate (2h)[11] **:** white solid, 60% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 7.93 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.36 (t, *J* = 2.8 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.20 (dd, *J* = 3.7, 1.5 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 136.4, 127.2, 126.0, 123.3, 121.4, 121.0, 115.7, 103.8, 51.6.



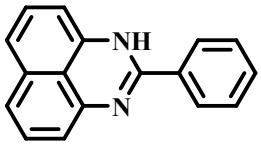
5-nitro-1*H*-indole (2i)[12] **:** White solid, 65% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 2.1 Hz, 1H), 8.57 (s, 1H), 8.12 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.44 (d, *J* = 9.0 Hz, 1H), 7.40 – 7.36 (m, 1H), 6.77 – 6.73 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 127.1, 127.1, 117.9, 117.6, 110.8, 105.0.



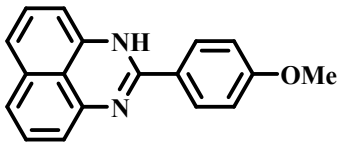
2-(4-fluorophenyl)benzo[*d*]thiazole (2j)[13] **:** White solid, 73% yield. ^{1}H NMR (400 MHz), DMSO-d_6) δ 8.10-8.01 (m, 4H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), ppm. 166.0, 165.1, 162.6, 153.5, 134.6, 129.6, 129.5, 129.4, 126.6, 125.4, 122.3 116.4 ppm



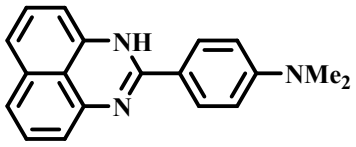
2-(4-chlorophenyl)benzo[*d*]thiazole (2k)[14] **:** White solid, 72% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 7.98 (m, 3H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.42 – 7.36 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 154.1, 137.1, 135.1, 132.2, 129.4, 128.8, 126.6, 125.5, 123.4, 121.8.



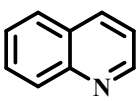
2-phenyl-1*H*-perimidine (2l)[15] **:** Brown yellowish solid, 70% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (d, *J* = 6.6 Hz, 2H), 7.60 – 7.51 (m, 3H), 7.20 – 7.14 (m, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.63 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.13, 133.41, 131.40, 128.68, 127.12, 121.75.



2-(4-methoxyphenyl)-1*H*-perimidine (2m)[15] **:** Orange solid, 72% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.07 (dd, *J* = 17.0, 8.4 Hz, 4H), 6.63 (d, *J* = 7.2 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.49, 152.22, 134.79, 128.46, 128.29, 124.87, 121.09, 113.57, 55.27.

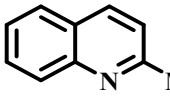


N,N-dimethyl-4-(1*H*-perimidin-2-yl)aniline (2n)[15] **:** yellow solid, 64% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.62 (d, *J* = 6.8 Hz, 2H), 2.99 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.58, 152.20, 141.43, 134.99, 128.45, 128.15, 121.05, 119.04, 118.10, 111.02.

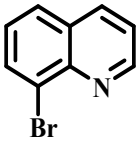


quinoline (4a)[2] **:** Colorless liquid, 70% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 (s, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 6.5 Hz, 1H), 7.61 – 7.49 (m, 2H), 7.35 (d,

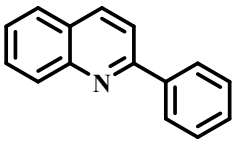
J = 7.0 Hz, 1H), 7.18 – 7.10 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 135.7, 129.1, 127.9, 127.5, 126.2, 120.7.



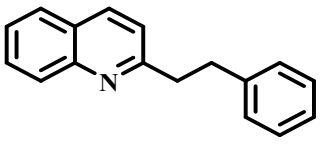
2-methylquinoline (4b)[2] **:** Yellow oil, 73% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.8, 147.7, 136.0, 129.3, 128.5, 127.4, 126.4, 125.5, 121.9, 25.3.



8-bromoquinoline (4c)[16] **:** Brownish liquid, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.57 (s, 1H), 8.57 (d, *J* = 5.7 Hz, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 5.7 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.0, 137.3, 131.4, 130.8, 126.9, 126.5, 122.6, 120.1.

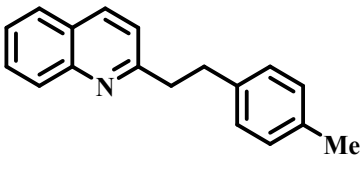


2-phenylquinoline (4d)[17] **:** White solid, 78% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 3.7 Hz, 1H), 8.21 – 8.15 (m, 3H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.58 – 7.51 (m, 3H), 7.48 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.5, 148.4, 139.8, 136.9, 129.8, 129.8, 129.4, 129.0, 127.7, 127.6, 127.3, 126.4, 119.1.

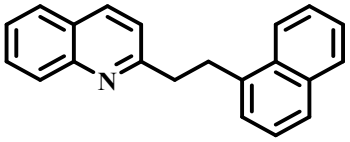


2-phenethylquinoline (4e)[2] **:** Yellow oil, 52% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.30 – 7.19 (m, 6H), 3.33 – 3.27 (m,

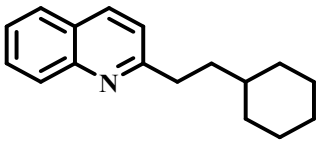
2H), 3.20 – 3.13 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.6, 147.8, 141.3, 136.0, 129.2, 128.6, 128.3, 128.2, 127.3, 126.6, 125.8, 125.6, 121.3, 40.8, 35.7.



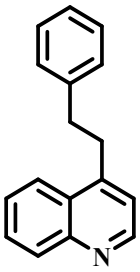
2-(4-methylphenethyl)quinoline (4f)[18] **:** Brown oil, 55% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.79 – 7.69 (m, 2H), 7.11 (d, *J* = 3.8 Hz, 4H), 3.32 (t, *J* = 7.8 Hz, 2H), 3.15 (t, *J* = 7.8 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.7, 146.0, 142.4, 141.4, 137.8, 135.9, 130.1, 129.4, 129.2, 129.0, 128.5, 38.4, 35.0, 21.2.



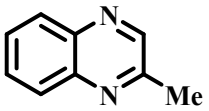
2-(2-(naphthalen-1-yl)ethyl)quinoline (4g)[2] **:** Yellow oil, 60% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.3 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.81 – 7.72 (m, 3H), 7.55 (dt, *J* = 18.8, 7.3 Hz, 3H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.20 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.72 – 3.64 (m, 2H), 3.47 (t, *J* = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.9, 148.1, 137.6, 136.2, 133.9, 131.9, 129.5, 129.0, 128.9, 127.6, 126.9, 126.9, 126.2, 126.0, 125.9, 125.6, 125.6, 123.8, 121.6, 40.1, 33.0.



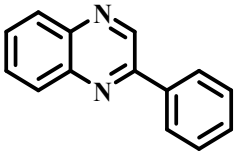
2-(2-cyclohexylethyl)quinoline (4h)[18]**:** Pale yellow oil, 41% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 8.3, 2.6 Hz, 3H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.29 (s, 1H), 3.00 – 2.94 (m, 2H), 1.81 (d, *J* = 12.6 Hz, 2H), 1.72 – 1.64 (m, 5H), 1.30 – 1.15 (m, 4H), 0.97 (d, *J* = 11.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6, 148.0, 136.3, 129.4, 128.9, 127.6, 126.8, 125.7, 121.5, 37.9, 37.8, 37.0, 33.4, 26.8, 26.5.



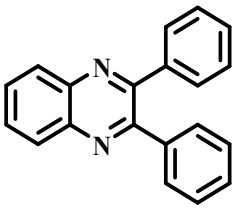
4-phenethylquinoline (4i)[18] **:** Colorless oil, 46% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.79 (d, *J* = 4.4 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.15 (m, 4H), 3.41 – 3.34 (m, 2H), 3.11 – 3.04 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2, 148.4, 147.5, 141.0, 130.4, 129.1, 128.6, 128.4, 127.5, 126.6, 126.4, 123.4, 120.9, 36.2, 34.1.



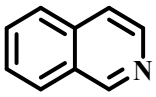
2-methylquinoxaline (6a)[2] **:** oil**,** 71% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.63 (dt, *J* = 15.3, 6.8 Hz, 2H), 2.69 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.4, 145.7, 141.7, 140.6, 129.7, 128.8, 128.6, 128.3, 22.3.



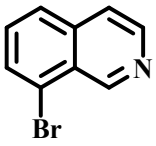
2-phenylquinoxaline (6b)[10] **:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 (s, 1H), 8.22 – 8.08 (m, 4H), 7.81 – 7.69 (m, 2H), 7.54 (dt, *J* = 12.4, 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.9, 143.5, 142.4, 141.7, 136.9, 130.4, 130.3, 129.7, 129.6, 129.2, 127.6.



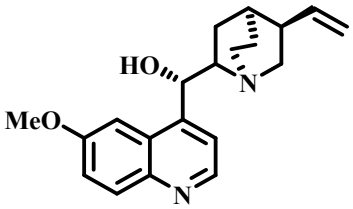
2,3-diphenylquinoxaline (6c)[17] **:** White solid, 77% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 6.4, 3.4 Hz, 2H), 7.78 (dd, *J* = 6.4, 3.4 Hz, 2H), 7.53 (dd, *J* = 7.7, 1.8 Hz, 4H), 7.35 (d, *J* = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.3, 141.0, 138.9, 129.8, 129.6, 129.0, 128.6, 128.1.



isoquinoline (6d)[2] **:** White solid, 53% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.82 (s, 1H), 7.44 (s, 1H), 7.35 (d, *J* = 7.1 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 2.6 Hz, 1H), 6.68 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.8, 127.9, 124.3, 122.0, 120.8, 119.9, 111.2, 102.5.



8-bromoisoquinoline (6e)[19] **:** Beige solid, 48% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.96 (d, *J* = 3.9 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.36 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.1, 136.6, 133.1, 129.5, 127.8, 124.6, 121.9.



(1S)-(6-methoxyquinolin-4-yl)((1S,4S,5R)-5-vinylquinuclidin-2-yl)methanol(8)[2] **:** White solid, 25% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 (d, *J* = 4.5 Hz, 1H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.51 (d, *J* = 4.5 Hz, 1H), 7.35 (d, *J* = 11.9 Hz, 1H), 7.24 (s, 1H), 5.76 (s, 1H), 5.53 (s, 1H), 5.01 – 4.89 (m, 2H), 3.91 (s, 3H), 3.42 (s, 1H), 3.13 (d, *J* = 30.9 Hz, 2H), 2.69 (d, *J* = 6.7 Hz, 2H), 2.26 (s, 1H), 1.82 (s, 1H), 1.75 – 1.69 (m, 2H), 1.51 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.04, 148.68, 147.75, 144.35, 142.36, 131.64, 127.02, 121.80, 118.89, 114.73, 101.80, 72.28, 60.38, 57.45, 56.06, 43.63, 40.41, 28.29, 28.08, 22.08.

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