Supporting Information for

Organophotoelectrocatalytic C(sp^2)–H alkylation of heteroarenes with unactivated C(sp^3)–H compounds

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1. General Considerations

Unless otherwise noted, chemicals and materials were purchased from commercial suppliers and used without further purification. All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 or 500 MHz Bruker FT-NMR spectrometer. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) or $CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 ppm) for ^{1}H NMR and $CDCl_3$ (77.2 ppm) or DMSO-d_6 (40.0 ppm) for ^{13}C NMR. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). X-Ray data were collected on a Bruker SMART APEX Ⅱ instrument with an IμS Mo microsource (λ = 0.7107 A). Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2. XINRUI® DJS-292B potentiostat made in China was used as a power supply device. The reticulated vitreous carbon (RVC) anode and Pt plate cathode are commercially available from Gaoss Union in China.

2. General Procedure and Setup of Photoelectrosynthesis

General Procedure for the C–H Alkylation: A 20 mL tube (Figure S1A, height: 9.5 cm, outer diameter: 2.5 cm, inner diameter: 2.2 cm) equipped with a reticulated vitreous carbon (RVC, 100 PPI, 1.2 cm x 0.8 cm x 0.8 cm) anode and a platinum plate (1 cm x 1 cm x 0.1 mm) cathode (Figure S1B) was charged with heteroarene (0.3 mmol, 1 equiv.), cyclohexane (162 μL, 1.5 mmol, 5 equiv.), PQ (6.2 mg, 10 mol%), $LiClO_4$ (32 mg, 0.3 mmol, 1 equiv.). Then MeCN (6 mL) and TFA (46 μL, 0.6 mmol, 2 equiv.) were added and the solution was purged with argon for 10 min. The RVC was fixed on a sharpened graphite rod (diameter: 0.6 cm) and the distance between RVC electrode and platinum electrode was about 0.5 cm. The reaction was carried out at room temperature (cooled by water) using a constant current of 2 mA under irradiation with 420–425 nm LEDs (10 W) for 16 h (Figure S1C). The reaction

mixture was concentrated and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product.

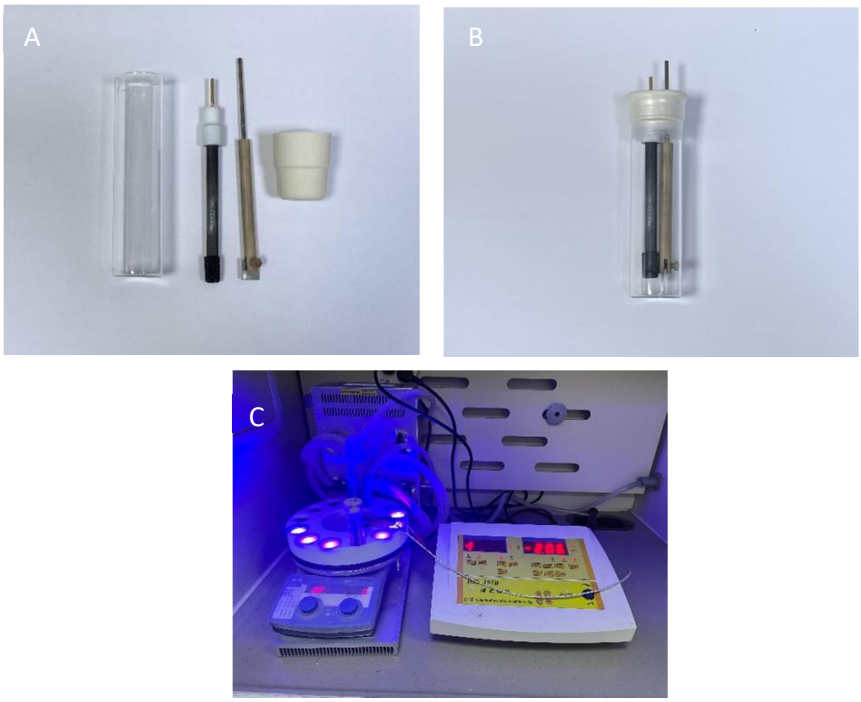


Figure S1. Setup of photoelectrosynthesis.

3. Amplification Synthesis of 3

The amplification reaction between **1** and **2** was performed on a 1.5 mmol scale by utilizing large electrodes. The reaction was irradiated by a 20 W LED emitting at 427 nm for 35 h, ultimately leading to the formation of **3** with a yield of 53% (Figure S2).

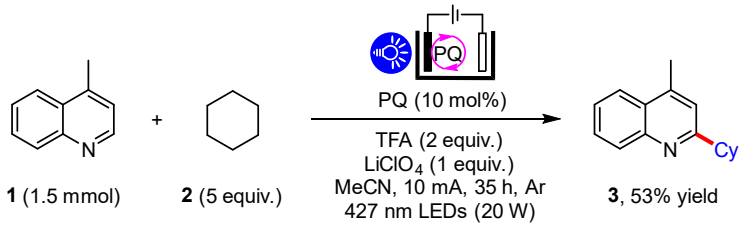


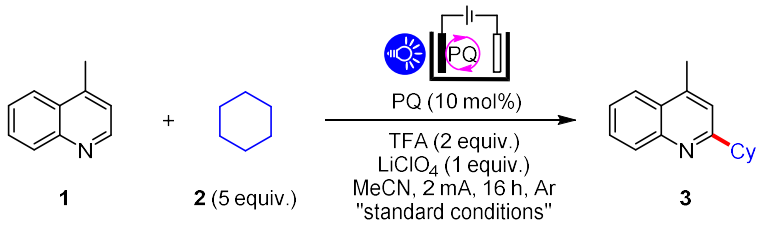
Figure S2. Amplification synthesis of **3**.

The amplification synthesis of **3** was conducted on 1.5 mmol at 10 mA under irradiation with Kessil PR160L LED lamp (427 nm, 20 W) for 35 h by using a piece of RVC (1.2 cm x 2 cm x 2 cm) as the anode and a Pt plate (1.5 cm x 1.5 cm x 0.3 mm) as the cathode. The reaction mixture consisted **1** (198 μL, 1.5 mmol, 1 equiv), **2**

(0.81 mL, 7.5 mmol, 5 equiv), PQ (31 mg, 10 mol%), $LiClO_4$ (160 mg, 0.3 mmol, 1 equiv), TFA (230 μL, 3.0 mmol, 2 equiv) and MeCN (14 mL). When the reaction was completed, the reaction mixture was concentrated under reduced pressure. Then the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product **3** as a colorless oil (179 mg, 53% yield).

4. Optimization of the Reaction Conditions

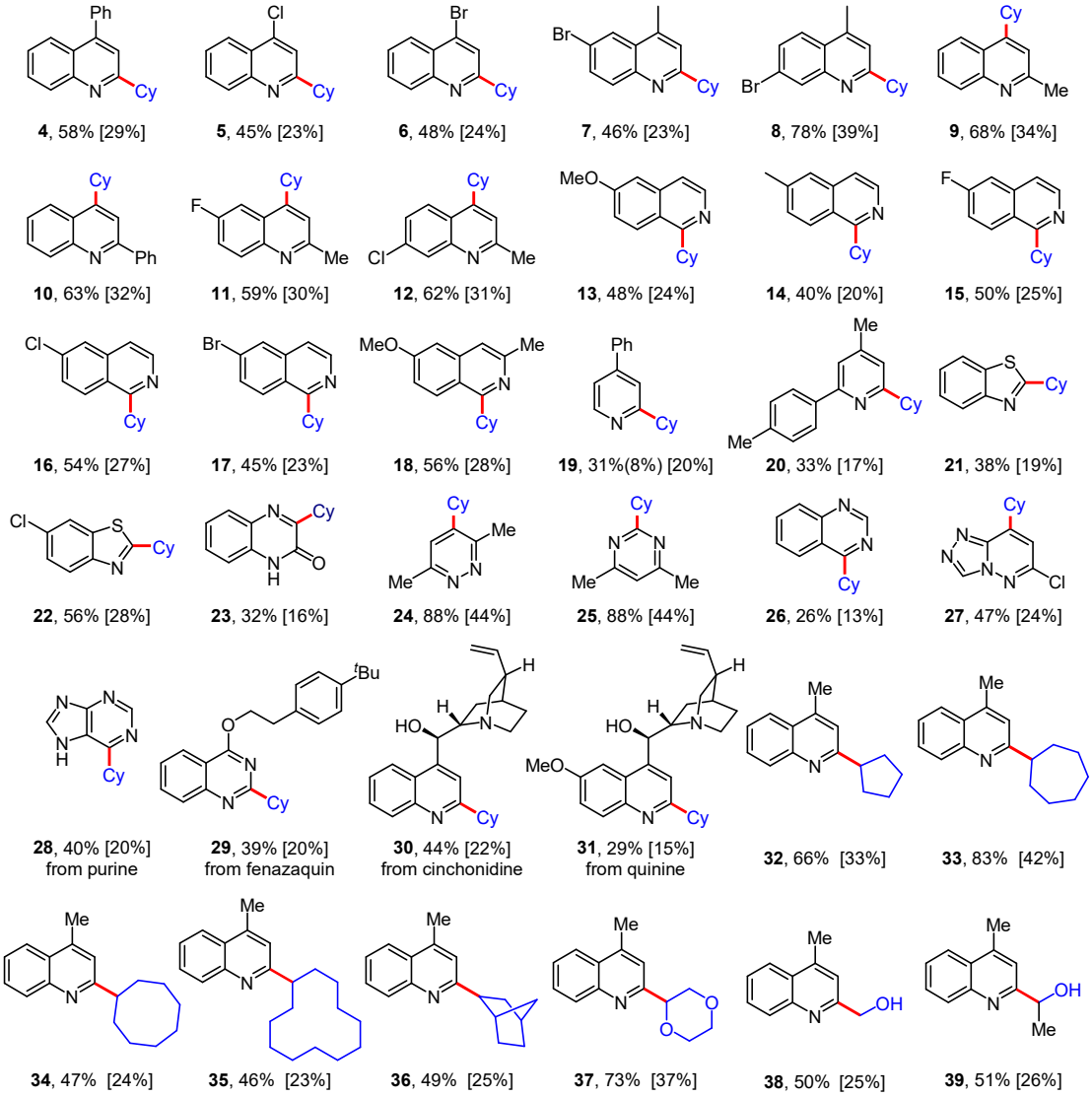
Table 1 Optimization of the reaction conditions[a]



Entry	Variation from the standard conditions	Yield (%)[b]
1	none	72[c]
2	PQ (5 mol%)	55
3	no PQ	0
4	no electricity	14
5	no light	0
6	TFA (1 equiv.)	65
7	no TFA	21
8	no $LiClO_4$	60
9	**2** (3 equiv.)	39
10	under air	32
11	12 h	54
12	3 mA, 12 h	65

[a]Reaction conditions: undivided cell, 4-methylquinoline (**1**, 0.3 mmol), cyclohexane (**2**, 1.5 mmol), PQ (10 mol%), TFA (0.6 mmol), $LiClO_4$ (0.3 mmol), MeCN (6 mL), 2 mA, LEDs (420–425 nm, 10 W), rt, 16 h (4 F•mol^{-1}). [b]Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. [c]Isolated yield.

5. Faraday Efficiencies of the Reactions



4, 58% [29%] **5**, 45% [23%] **6**, 48% [24%] **7**, 46% [23%] **8**, 78% [39%] **9**, 68% [34%]

10, 63% [32%] **11**, 59% [30%] **12**, 62% [31%] **13**, 48% [24%] **14**, 40% [20%] **15**, 50% [25%]

16, 54% [27%] **17**, 45% [23%] **18**, 56% [28%] **19**, 31%(8%) [20%] **20**, 33% [17%] **21**, 38% [19%]

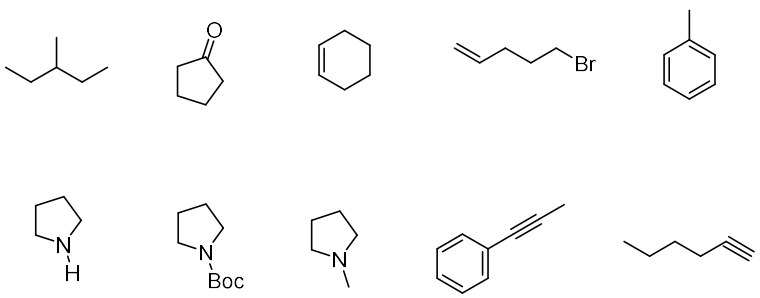
22, 56% [28%] **23**, 32% [16%] **24**, 88% [44%] **25**, 88% [44%] **26**, 26% [13%] **27**, 47% [24%]

28, 40% [20%] from purine **29**, 39% [20%] from fenazaquin **30**, 44% [22%] from cinchonidine **31**, 29% [15%] from quinine **32**, 66% [33%] **33**, 83% [42%]

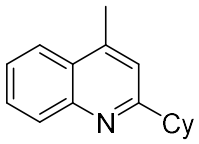
34, 47% [24%] **35**, 46% [23%] **36**, 49% [25%] **37**, 73% [37%] **38**, 50% [25%] **39**, 51% [26%]

Faraday Efficiencies of the reactions were afford in square brackets.

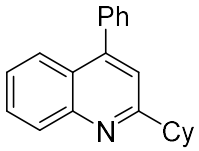
6. Unsuccessful C(sp^3)−H Substrates



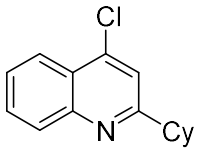
7. Characterization Data for the Products



2-Cyclohexyl-4-methylquinoline (3).[1] The title compound was obtained by eluting with petroleum ether : ethyl acetate 20:1 to 10:1 as a colorless oil (48 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.16 (s, 1H), 2.91–2.83 (m, 1H), 2.67 (s, 3H), 2.03–1.98 (m, 2H), 1.91–1.86 (m, 2H), 1.81–1.76 (m, 1H), 1.67–1.57 (m, 2H), 1.52–1.41 (m, 2H), 1.39–1.31 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 147.8, 144.4, 129.6, 129.1, 127.2, 125.5, 123.7, 120.4, 47.8, 33.0, 26.7, 26.3, 19.0.

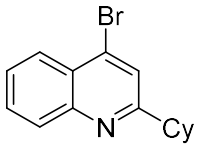


2-Cyclohexyl-4-phenylquinoline (4).[1] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to 20:1 as a colorless oil (50 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 8.5, 1.2 Hz, 1H), 7.87 (dd, J = 8.5, 1.2 Hz, 1H), 7.68 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.57–7.46 (m, 5H), 7.43 (ddd, J = 8.2, 6.7, 1.3 Hz, 1H), 7.28 (s, 1H), 3.00–2.93 (m, 1H), 2.10–2.05 (m, 2H), 1.93–1.87 (m, 2H), 1.82–1.77 (m, 1H), 1.72–1.62 (m, 2H), 1.54–1.43 (m, 2H), 1.39–1.30 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 148.8, 148.4, 138.7, 129.7, 129.5, 129.3, 128.6, 128.4, 125.8, 125.7, 125.7, 120.0, 47.8, 33.0, 26.7, 26.3.

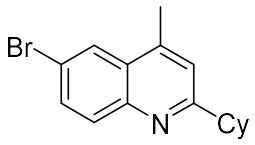


4-Chloro-2-cyclohexylquinoline (5).[2] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a yellow oil (33 mg, 45% yield);

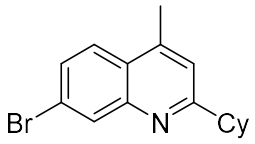
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, J = 8.4, 1.2 Hz, 1H), 8.05 (dt, J = 8.4, 1.2 Hz, 1H), 7.74–7.70 (m, 1H), 7.59–7.54 (m, 1H), 7.42 (s, 1H), 2.93–2.85 (m, 1H), 2.05–1.99 (m, 2H), 1.93–1.86 (m, 2H), 1.82–1.76 (m, 1H), 1.66–1.56 (m, 2H), 1.51–1.40 (m, 2H), 1.38–1.29 (m, 1H); ^{13}C NMR 101 MHz, $CDCl_3$) δ 167.0, 148.8, 142.8, 130.3, 129.5, 126.8, 125.3, 124.1, 120.0, 47.6, 32.9, 26.6, 26.2.



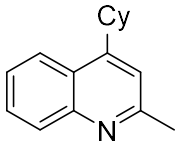
4-Bromo-2-cyclohexylquinoline (6).[2] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to 20:1 as a colorless oil (42 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J = 8.3, 1.4 Hz, 1H), 8.05–8.01 (m, 1H), 7.71 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.62 (s, 1H), 7.56 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 2.88 (tt, J = 12.0, 3.4 Hz, 1H), 2.05–1.99 (m, 2H), 1.93–1.86 (m, 2H), 1.81–1.76 (m, 1H), 1.66–1.56 (m, 2H), 1.50–1.41 (m, 2H), 1.38–1.28 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 148.6, 134.4, 130.3, 129.6, 127.0, 126.7, 126.6, 123.9, 47.4, 32.9, 26.6, 26.1.



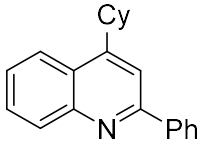
6-Bromo-2-cyclohexyl-4-methylquinoline (7).[3] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to 20:1 as a white solid (42 mg, 46% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 2.2 Hz, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.71 (dd, J = 9.0, 2.2 Hz, 1H), 7.17 (s, 1H), 2.84 (tt, J = 12.0, 3.5 Hz, 1H), 2.63 (s, 3H), 2.02–1.97 (m, 2H), 1.91–1.86 (m, 2H), 1.81–1.76 (m, 1H), 1.66–1.56 (m, 2H), 1.51–1.41 (m, 2H), 1.36–1.28 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 146.5, 143.5, 132.4, 131.5, 128.5, 126.2, 121.3, 119.4, 47.7, 32.9, 26.7, 26.2, 18.9.



7-Bromo-2-cyclohexyl-4-methylquinoline (8).[3] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to 20:1 as a white solid (71 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 2.0 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.54 (dd, J = 8.8, 2.0 Hz, 1H), 7.15 (d, J = 1.1 Hz, 1H), 2.83 (tt, J = 11.9, 3.4 Hz, 1H), 2.64 (s, 3H), 2.01–1.95 (m, 2H), 1.92–1.85 (m, 2H), 1.81–1.75 (m, 1H), 1.66–1.56 (m, 2H), 1.50–1.42 (m, 2H), 1.36–1.29 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 148.6, 144.4, 132.0, 128.8, 125.8, 125.2, 123.1, 121.0, 47.6, 32.8, 26.7, 26.2, 18.9.

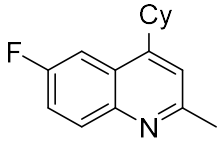


4-Cyclohexyl-2-methylquinoline (9).[1] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to 20:1 as a colorless oil (46 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 2H), 7.66–7.62 (m, 1H), 7.50–7.46 (m, 1H), 7.16 (s, 1H), 3.32–3.25 (m, 1H), 2.72 (s, 3H), 2.01–1.91 (m, 4H), 1.87–1.82 (m, 1H), 1.58–1.48 (m, 4H), 1.38–1.31 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 153.4, 148.3, 129.7, 128.9, 125.4, 125.3, 123.0, 118.4, 38.9, 33.7, 27.1, 26.5, 25.7.

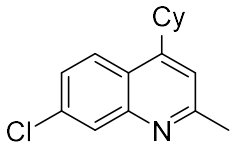


4-Cyclohexyl-2-phenylquinoline (10).[1] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a colorless oil (54 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.14 (m, 3H), 8.10 (dd, J = 8.5, 1.3 Hz, 1H), 7.76 (s, 1H), 7.74–7.69 (m, 1H), 7.56–7.52 (m, 3H), 7.49–7.44 (m, 1H), 3.38 (tt, J = 11.5, 3.2 Hz, 1H), 2.11–2.08 (m, 2H), 1.99–1.94 (m, 2H), 1.92–1.86 (m, 1H), 1.68–1.56 (m, 4H), 1.41–1.33 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 154.1,

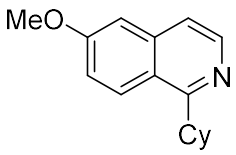
148.8, 140.5, 130.9, 129.3, 129.2, 128.9, 127.8, 127.7, 126.0, 123.0, 115.7, 39.3, 33.8, 27.1, 26.5.



4-Cyclohexyl-6-fluoro-2-methylquinoline (11).[4] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a yellow oil (43 mg, 59% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 9.2, 5.7 Hz, 1H), 7.60 (dd, J = 10.6, 2.8 Hz, 1H), 7.40 (ddd, J = 9.2, 7.9, 2.8 Hz, 1H), 7.16 (s, 1H), 3.11 (tt, J = 7.5, 3.1 Hz, 1H), 2.69 (s, 3H), 1.99–1.91 (m, 4H), 1.87–1.82 (m, 1H), 1.59–1.48 (m, 4H), 1.37–1.30 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2 (d, $J_{C–F}$ = 245.1 Hz), 158.3 (d, $J_{C–F}$ = 2.5 Hz), 152.9 (d, $J_{C–F}$ = 5.5 Hz), 145.4, 132.0 (d, $J_{C–F}$ = 9.1 Hz), 126.0 (d, $J_{C–F}$ = 8.9 Hz), 119.1, 118.8 (d, $J_{C–F}$ = 25.4 Hz), 106.8 (d, $J_{C–F}$ = 22.5 Hz), 39.2, 33.6, 27.0, 26.4, 25.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ –114.8.

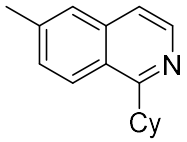


7-Chloro-4-cyclohexyl-2-methylquinoline (12).[5] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to 20:1 as a colorless oil (48 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 2.2 Hz, 1H), 7.92 (d, J = 9.0 Hz, 1H), 7.40 (dd, J = 9.0, 2.2 Hz, 1H), 7.13 (s, 1H), 3.21 (td, J = 8.4, 4.3 Hz, 1H), 2.68 (s, 3H), 1.97–1.90 (m, 4H), 1.86–1.81 (m, 1H), 1.54–1.48 (m, 4H), 1.36–1.29 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 153.5, 148.9, 134.7, 128.6, 126.3, 124.4, 123.7, 118.7, 39.0, 33.7, 27.0, 26.4, 25.7.

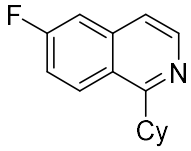


1-Cyclohexyl-6-methoxyisoquinoline (13).[6] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a colorless oil (35 mg, 48%

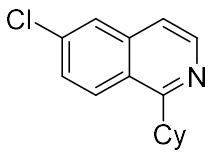
yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 5.7 Hz, 1H), 8.12 (d, J = 9.2 Hz, 1H), 7.37 (d, J = 5.7, 1H), 7.19 (dd, J = 9.2, 2.6 Hz, 1H), 7.05 (d, J = 2.6 Hz, 1H), 3.93 (s, 3H), 3.52–3.44 (m, 1H), 1.97–1.90 (m, 4H), 1.84–1.77 (m, 3H), 1.55–1.47 (m, 2H), 1.43–1.35 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 160.3, 142.8, 138.6, 126.8, 122.1, 119.6, 118.5, 105.2, 55.6, 41.7, 32.7, 27.0, 26.4.



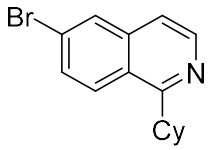
1-Cyclohexyl-6-methylisoquinoline (14).[6] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to 20:1 as a brown oil (27 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 5.7 Hz, 1H), 8.10 (d, J = 8.7 Hz, 1H), 7.56 (s, 1H), 7.41–7.38 (m, 2H), 3.52 (tt, J = 11.7, 3.2 Hz, 1H), 2.52 (s, 3H), 1.99–1.90 (m, 4H), 1.86–1.76 (m, 3H), 1.57–1.47 (m, 2H), 1.44–1.36 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 142.2, 139.9, 136.9, 129.2, 126.6, 124.8, 124.7, 118.6, 41.7, 32.7, 27.1, 26.4, 21.9.



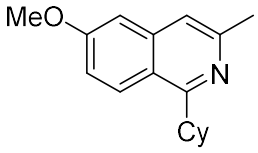
1-Cyclohexyl-6-fluoroisoquinoline (15).[6] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a colorless solid (35 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 5.4 Hz, 1H), 8.24 (dd, J = 9.3, 5.4 Hz, 1H), 7.44–7.39 (m, 2H), 7.36–7.31 (m, 1H), 3.54–3.47 (m, 1H), 1.99–1.91 (m, 4H), 1.87–1.80 (m, 3H), 1.56–1.47 (m, 2H), 1.44–1.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (d, $J_{C–F}$ = 1.4 Hz), 162.8 (d, $J_{C–F}$ = 251.7 Hz), 143.1, 138.2 (d, $J_{C–F}$ = 10.2 Hz), 128.1 (d, $J_{C–F}$ = 9.5 Hz), 123.7, 118.7 (d, $J_{C–F}$ = 5.0 Hz), 117.2 (d, $J_{C–F}$ = 25.0 Hz), 110.8 (d, $J_{C–F}$ = 20.2 Hz), 41.9, 32.8, 27.0, 26.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ –109.1.



6-Chloro-1-cyclohexylisoquinoline (16).[6] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to 20:1 as a colorless oil (40 mg, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 5.7 Hz, 1H), 8.14 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 2.2 Hz, 1H), 7.49 (dd, J = 9.0, 2.2 Hz, 1H), 7.38 (d, J = 5.7 Hz, 1H), 3.48 (tt, J = 11.7, 3.3 Hz, 1H), 1.97–1.89 (m, 4H), 1.85–1.76 (m, 3H), 1.56–1.47 (m, 2H), 1.42–1.33 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 143.2, 137.4, 135.8, 127.9, 126.8, 126.4, 124.6, 118.1, 41.8, 32.7, 27.0, 26.3.

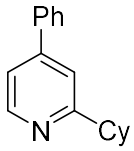


6-Bromo-1-cyclohexylisoquinoline (17).[6] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a colorless oil (39 mg, 45% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 5.7 Hz, 1H), 8.08 (d, J = 9.0 Hz, 1H), 7.97 (d, J = 2.0 Hz, 1H), 7.64 (dd, J = 9.0, 2.0 Hz, 1H), 7.38 (d, J = 5.7 Hz, 1H), 3.49 (tt, J = 11.7, 3.3 Hz, 1H), 1.97–1.91 (m, 4H), 1.86–1.77 (m, 3H), 1.57–1.47 (m, 2H), 1.43–1.35 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 143.2, 137.8, 130.5, 129.8, 126.8, 124.9, 124.4, 118.0, 41.8, 32.7, 27.0, 26.3.

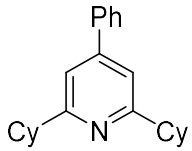


1-Cyclohexyl-6-methoxy-3-methylisoquinoline (18). The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to 20:1 as a colorless oil (43 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 9.3 Hz, 1H), 7.20 (s, 1H), 7.10 (dd, J = 9.3, 2.6 Hz, 1H), 6.95 (d, J = 2.6 Hz, 1H), 3.91 (s, 3H), 3.45 (tt, J = 11.4, 3.4 Hz, 1H), 2.62 (s, 3H), 1.95–1.89 (m, 4H), 1.86–1.77 (m, 3H), 1.53–1.37 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 160.2, 151.4, 139.3, 126.7, 120.2, 118.5,

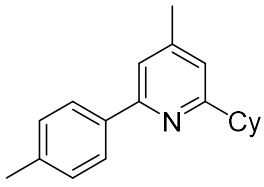
116.3, 104.6, 55.5, 41.8, 32.6, 27.0, 26.3, 24.7; ESI HRMS *m/z* $(M + H)^+$ calcd 256.1696, obsd 256.1695.



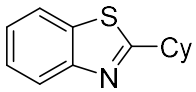
2-Cyclohexyl-4-phenylpyridine (19).[7] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to petroleum ether : ethyl acetate 30:1 as a colorless oil (22 mg, 31% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 5.1 Hz, 1H), 7.64–7.61 (m, 2H), 7.50–7.40 (m, 3H), 7.36 (d, J = 1.8 Hz, 1H), 7.31 (dd, J = 5.1, 1.8 Hz, 1H), 2.77 (tt, J = 12.0, 3.4 Hz, 1H), 2.03–1.97 (m, 2H), 1.91–1.86 (m, 2H), 1.80–1.71 (m, 1H), 1.64–1.54 (m, 2H), 1.49–1.38 (m, 2H), 1.34–1.28 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 149.6, 149.0, 139.0, 129.2, 129.0, 127.2, 119.4, 119.2, 46.9, 33.2, 26.8, 26.3.



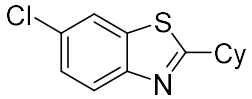
2,6-Dicyclohexyl-4-phenylpyridine (19').[7] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to petroleum ether : ethyl acetate 30:1 as a colorless oil (8 mg, 8% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.60 (m, 2H), 7.4–7.38 (m, 3H), 7.17 (s, 2H), 2.75 (tt, J = 11.8, 3.4 Hz, 2H), 2.05–1.99 (m, 4H), 1.88–1.83 (m, 4H), 1.79–1.73 (m, 2H), 1.58–1.42 (m, 8H), 1.35–1.31 (m, 1H), 1.28–1.25 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 149.2, 139.8, 129.1, 128.7, 127.3, 116.2, 46.9, 33.4, 26.8, 26.4.



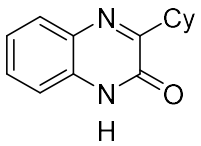
2-Cyclohexyl-4-methyl-6-(*p*-tolyl)pyridine (20). The title compound was obtained by eluting with petroleum ether : ethyl acetate 20:1 to 10:1 as a colorless oil (25 mg, 33% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.89 (m, 2H), 7.32 (s, 1H), 7.26 (s, 1H), 7.23 (s, 1H), 6.89 (s, 1H), 2.73 (tt, J = 11.9, 3.5 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 2.05–1.97 (m, 2H), 1.89–1.83 (m, 2H), 1.78–1.73 (m, 1H), 1.56–1.52 (m, 1H), 1.47–1.38 (m, 2H), 1.34–1.25 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 156.6, 147.7, 138.5, 137.5, 129.5, 127.1, 120.0, 118.7, 46.7, 33.2, 26.8, 26.4, 21.5, 21.; ESI HRMS *m/z* $(M + H)^+$ calcd 266.1903, obsd 266.1903.



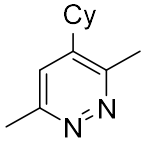
2-Cyclohexylbenzo[*d*]thiazole (21).[5] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a colorless oil (24 mg, 38% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.96 (m, 1H), 7.86–7.84 (m, 1H), 7.44 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 7.34 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 3.15–3.07 (tt, J = 11.7, 3.6 Hz, 1H), 2.24–2.17 (m, 2H), 1.93–1.86 (m, 2H), 1.80–1.74 (m, 1H), 1.69–1.62 (m, 2H), 1.50–1.43 (m, 2H), 1.34–1.30 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 153.3, 134.7, 126.0, 124.7, 122.7, 121.7, 43.6, 33.6, 26.3, 26.0.



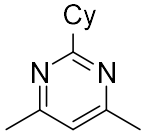
6-Chloro-2-cyclohexylbenzo[*d*]thiazole (22).[8] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to petroleum ether : ethyl acetate 30:1 as a white solid (42 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 2.2 Hz, 1H), 7.38 (dd, J = 8.7, 2.2 Hz, 1H), 3.07 (tt, J = 11.7, 3.6 Hz, 1H), 2.21–2.15 (m, 2H), 1.91–1.84 (m, 2H), 1.79–1.72 (m, 1H), 1.66–1.56 (m, 2H), 1.48–1.37 (m, 2H), 1.35–1.28 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 151.8, 135.9, 130.5, 126.7, 123.4, 121.3, 43.5, 33.5, 26.2, 25.9.



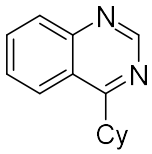
3-Cyclohexylquinoxalin-2(1*H*)-one (23).[5] The title compound was obtained by eluting with petroleum ether : ethyl acetate 5:1 to 3:1 as a white solid (22 mg, 32% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.32 (s, 1H), 7.70 (dd, J = 8.3, 1.4 Hz, 1H), 7.46 (td, J = 7.6, 1.4 Hz, 1H), 7.28–7.23 (m, 2H), 3.16 (tt, J = 11.4, 3.2 Hz, 1H), 1.88–1.78 (m, 4H), 1.73–1.69 (m, 1H), 1.49–1.34 (m, 4H), 1.27–1.18 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 154.6, 132.1, 131.9, 129.8, 128.6, 123.5, 115.6, 30.5, 26.3, 26.2.



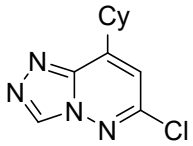
4-Cyclohexyl-3,6-dimethylpyridazine (24). The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a brown oil (50 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 1H), 2.63 (s, 3H), 2.59 (s, 3H), 2.57–2.52 (m, 1H), 1.87–1.83 (m, 2H), 1.79–1.74 (m, 3H), 1.38–1.34 (m, 2H), 1.30–1.22 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 156.7, 145.1, 123.4, 39.2, 32.6, 26.6, 26.0, 22.1, 19.6; ESI HRMS m/z $(M + H)^+$ calcd 191.1543, obsd 191.1543.



2-Cyclohexyl-4,6-dimethylpyrimidine (25).[9] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to 20:1 as a white solid (50 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 3.59 (tt, J = 11.8, 3.5 Hz, 1H), 2.82 (s, 6H), 2.06–2.01 (m, 2H), 1.90–1.83 (m, 2H), 1.80–1.67 (m, 3H), 1.56–1.45 (m, 2H), 1.36–1.28 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 119.9, 43.1, 31.1, 25.4 (2C).

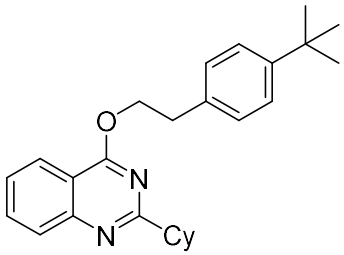


2-Cyclohexylquinazoline (26).[4] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a colorless oil (16 mg, 26% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.87 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.63 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 3.56 (tt, J = 11.6, 3.3 Hz, 1H), 1.99–1.93 (m, 4H), 1.87–1.77 (m, 3H), 1.57–1.47 (m, 2H), 1.43–1.34 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 155.0, 150.3, 133.4, 129.5, 127.5, 124.3, 123.5, 41.5, 32.2, 26.7, 26.2.

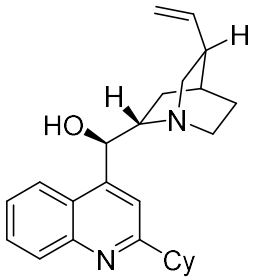


6-Chloro-8-cyclohexyl-[1,2,4]triazolo[4,3-*b*]pyridazine (27). The title compound was obtained by eluting with petroleum ether : ethyl acetate 20:1 to 10:1 as a yellow solid (33 mg, 47% yield); m.p. = 188.5−186.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 6.89 (d, J = 0.9 Hz, 1H), 3.37–3.30 (m, 1H), 2.17–2.12 (m, 2H), 1.94–1.88 (m, 2H), 1.85–1.77 (m, 2H), 1.60–1.55 (m, 2H), 1.54–1.51 (m, 1H), 1.36–1.28 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 148.2, 143.4, 138.9, 118.0, 39.6, 31.8, 26.2, 25.9; ESI HRMS m/z $(M+H)^+$ calcd 237.0902, obsd 237.0907.

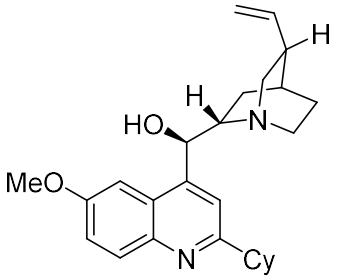
6-Cyclohexyl-purine (28).[10] The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to 20:1 as a white solid (24 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.66 (s, 1H), 8.99 (s, 1H), 8.33 (s, 1H), 3.53–3.48 (m, 1H), 2.04–1.99 (m, 2H), 1.92–1.85 (m, 4H), 1.81–1.76 (m, 1H), 1.51–1.42 (m, 2H), 1.38–1.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 142.1, 42.2, 31.5, 26.4, 26.1.



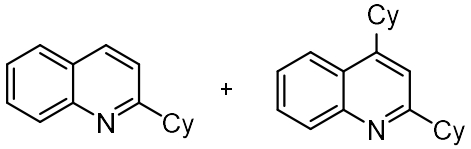
4-(4-(*tert*-Butyl)phenethoxy)-2-cyclohexylquinazoline (29). The title compound was obtained by eluting with petroleum ether : ethyl acetate 10:1 to 5:1 as a colorless oil (45 mg, 39% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (ddd, J = 8.2, 1.5, 0.9 Hz, 1H), 7.87 (dt, J = 8.2, 0.9 Hz, 1H), 7.77 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.48 (ddd, J = 8.4, 6.9, 1.2 Hz, 1H), 7.40–7.37 (m, 2H), 7.32–7.29 (m, 2H), 4.79 (t, J = 7.2 Hz, 2H), 3.20 (t, J = 7.2 Hz, 2H), 2.92–2.84 (m, 1H), 2.07–2.01 (m, 2H), 1.91–1.85 (m, 2H), 1.80–1.71 (m, 3H), 1.51–1.39 (m, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 166.7, 151.6, 149.6, 135.2, 133.3, 129.0, 127.4, 126.0, 125.6, 123.5, 115.2, 67.5, 48.1, 34.9, 34.6, 31.9, 31.5, 26.4, 26.3; ESI HRMS *m/z* $(M+H)^+$ calcd 389.2587, obsd 389.2587.



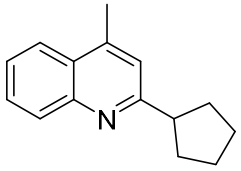
(*R*)-(2-Cyclohexylquinolin-4-yl)((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methanol (30).[1] The title compound was obtained by eluting with dichloromethane : methanol 30:1 to 10:1 as a brown solid (50 mg, 44% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 8.4, 6.6 Hz, 2H), 7.59 (s, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.29–7.25 (m, 1H), 6.15 (s, 1H), 5.57–5.49 (m, 1H), 5.05–4.99 (m, 2H), 4.4 6–4.38 (m, 1H), 3.62–3.56 (m, 1H), 3.45 (t, J = 9.1 Hz, 1H), 3.30–3.21 (m, 2H), 2.86–2.69 (m, 2H), 2.24–2.06 (m, 3H), 1.96–1.73 (m, 6H), 1.63–1.51 (m, 2H), 1.42–1.25 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 147.5, 145.3, 137.2, 129.6, 129.3, 126.7, 123.2, 121.9, 117.6, 117.2, 67.4, 61.2, 55.6, 47.8, 45.2, 37.2, 32.9, 32.8, 26.9, 26.6, 26.1, 24.4, 18.4.



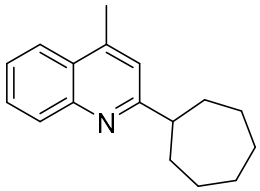
(*R*)-(2-Cyclohexyl-6-methoxyquinolin-4-yl)((1*S*,2*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methanol (31).[1] The title compound was obtained by eluting with dichloromethane : methanol 30:1 to dichloromethane : methanol 10:1 as a brown solid (35 mg, 29% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 9.2 Hz, 1H), 7.57 (s, 1H), 7.02 (dd, J = 9.2, 2.6 Hz, 1H), 6.80 (d, J = 2.6 Hz, 1H), 6.13 (s, 1H), 5.59–5.51 (m, 1H), 5.05–5.03 (m, 1H), 5.01–5.00 (m, 1H), 4.49–4.41 (m, 1H), 3.63 (s, 3H), 3.55 (dd, J = 13.4, 10.6 Hz, 1H), 3.35 (t, J = 9.0 Hz, 1H), 3.22–3.08 (m, 2H), 2.85–2.78 (m, 1H), 2.69 (s, 1H), 2.26–2.07 (m, 3H), 2.02–1.75 (m, 7H), 1.57 (td, J = 12.2, 3.3 Hz, 2H), 1.48–1.39 (m, 2H), 1.35–1.30 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 157.9, 143.8, 143.6, 137.4, 131.2, 124.0, 122.1, 117.6, 117.2, 99.3, 67.1, 60.7, 56.4, 55.5, 47.5, 44.9, 37.4, 33.1, 33.0, 27.0, 26.7 (2C), 26.2, 24.5, 18.4.



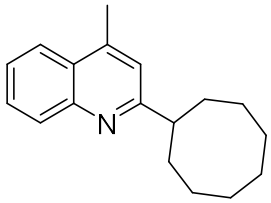
2-Cyclohexylquinoline (32) and 2,4-dicyclohexylquinoline (33).[11] **32**:**33** = 5:1; The title compounds were obtained by eluting with petroleum ether : ethyl acetate 50:1 to petroleum ether : ethyl acetate 20:1 as a colorless oil (16 mg, 26% yield); Characterization Data for **32**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.6 Hz, 1H), 8.05 (d, J = 8.6 Hz, 1H), 7.77 (d, J = 6.7 Hz, 1H), 7.69–7.65 (m, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 8.6 Hz, 1H), 2.96–2.88 (m, 1H), 2.05–2.01 (m, 2H), 1.92–1.87 (m, 2H), 1.82–1.76 (m, 1H), 1.65–1.59 (m, 2H), 1.51–1.43 (m, 2H), 1.38–1.31 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 148.0, 136.5, 129.4, 129.2, 127.6, 127.2, 125.8, 119.8, 47.8, 33.0, 26.7, 26.3.



2-Cyclopentyl-4-methylquinoline (34).[1] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a colorless oil (42 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.4, 1.2 Hz, 1H), 7.93 (dd, J = 8.4, 1.2 Hz, 1H), 7.66 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.49 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.17 (s, 1H), 3.38–3.29 (m, 1H), 2.68 (s, 3H), 2.20–2.13 (m, 2H), 1.92–1.86 (m, 4H), 1.79–1.72 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 147.7, 144.2, 129.7, 129.1, 127.1, 125.5, 123.7, 120.8, 49.0, 33.7, 26.2, 19.0.

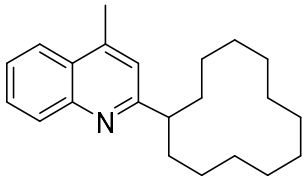


2-Cycloheptyl-4-methylquinoline (35).[12] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a colorless oil (58 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.13 (s, 1H), 3.06–2.99 (m, 1H), 2.67 (s, 3H), 2.07–2.00 (m, 2H), 1.89–1.71 (m, 6H), 1.68–1.61 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 147.5, 144.5, 129.5, 129.1, 127.1, 125.5, 123.7, 120.4, 49.7, 35.2, 28.1, 27.6, 19.0.

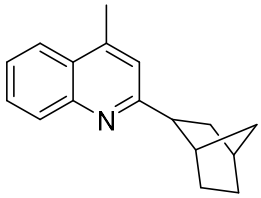


2-Cyclooctyl-4-methylquinoline (36).[13] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a colorless oil (36 mg, 47% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.12 (s, 1H), 3.14–3.07 (m, 1H),

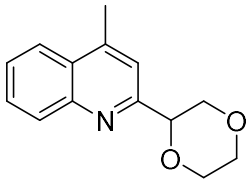
2.67 (s, 3H), 2.01–1.94 (m, 2H), 1.93–1.81 (m, 4H), 1.74–1.61 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 147.5, 144.5, 129.6, 129.1, 127.0, 125.5, 123.7, 120.8, 47.7, 33.7, 26.7, 26.5, 26.3, 19.0.



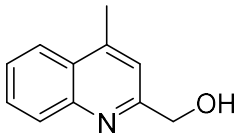
2-Cyclododecyl-4-methylquinoline (37).[1] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a colorless oil (44 mg, 46% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.13 (s, 1H), 3.13–3.07 (m, 1H), 2.68 (s, 3H), 1.95–1.87 (m, 2H), 1.74–1.67 (m, 2H), 1.58–1.32 (m, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 147.8, 144.0, 129.7, 129.0, 127.1, 125.4, 123.7, 121.6, 43.2, 30.3, 24.1, 24.0, 23.8, 23.5, 23.1, 19.0.



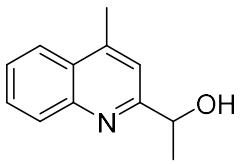
2-(Bicyclo[2.2.1]heptan-2-yl)-4-methylquinoline (38).[1] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a colorless oil (35 mg, 49% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.9 Hz, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.18 (s, 1H), 2.99–3.03 (m, 1H), 2.67 (s, 3H), 2.56 (d, J = 4.2 Hz, 1H), 2.42 (d, J = 4.2 Hz, 1H), 2.28–2.21 (m, 1H), 1.77–1.60 (m, 4H), 1.50–1.45 (m, 1H), 1.36–1.34 (m, 1H), 1.21–1.17 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 147.6, 143.9, 129.8, 128.9, 126.9, 125.4, 123.6, 121.7, 50.2, 43.2, 36.9, 36.4, 36.2, 30.7, 29.3, 18.9.



2-(1,4-Dioxan-2-yl)-4-methylquinoline (39).[1] The title compound was obtained by eluting with petroleum ether : ethyl acetate 10:1 to 5:1 as a yellow oil (50 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.4, 1.4 Hz, 1H), 7.96 (dd, J = 8.4, 1.4 Hz, 1H), 7.68 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.53 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.45 (s, 1H), 4.88 (dd, J = 10.1, 2.9 Hz, 1H), 4.23 (dd, J = 11.6, 2.9 Hz, 1H), 4.01–3.98 (m, 2H), 3.85–3.74 (m, 2H), 3.63 (dd, J = 11.6, 10.1 Hz, 1H), 2.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 147.4, 145.3, 129.9, 129.4, 127.7, 126.3, 123.8, 119.2, 78.9, 71.2, 67.2, 66.5, 19.0.

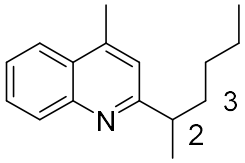


(4-Methylquinolin-2-yl)methanol (40).[1] The title compound was obtained by eluting with petroleum ether : ethyl acetate 5:1 to 3:1 as a colorless oil (26 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.71 (t, J = 7.7 Hz, 1H), 7.57–7.54 (m, 1H), 7.12 (s, 1H), 4.87 (s, 2H), 2.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 146.6, 145.3, 129.6, 129.3, 127.8, 126.3, 124.0, 119.1, 64.1, 19.0.

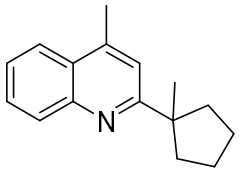


(4-Methylquinolin-2-yl)methanol (41).[1] The title compound was obtained by eluting with petroleum ether : ethyl acetate 5:1 to 3:1 as a colorless oil (29 mg, 51% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.72–7.68 (m, 1H), 7.57–7.53 (m, 1H), 7.18 (s, 1H), 4.98 (q, J = 6.6 Hz, 1H), 2.70 (s,

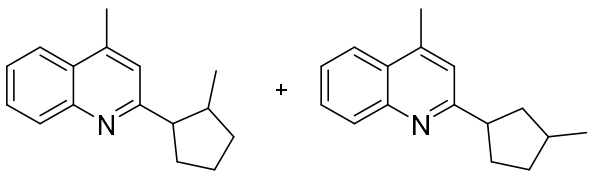
3H), 1.56 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 146.3, 145.5, 129.6, 129.4, 127.6, 126.3, 123.9, 118.7, 68.8, 24.2, 19.1.



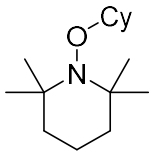
2-(Hexan-2-yl)-4-methylquinoline (42).[14] C2:C3 = 1.9:1; The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to petroleum ether : ethyl acetate 50:1 as a colorless oil (15 mg, 22% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–8.04(m, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.69–7.64 (m, 1H), 7.52–7.48 (m, 1H), 7.13–7.10 (m, 1H), 3.07–32.98 (m, 0.66 H), 2.86–2.79 (m, 0.34 H), 2.69 (s, 3H), 1.85–1.67 (m, 3H), 1.35–1.24 (m, 5H), 0.88–0.80 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 147.8, 144.4, 129.7, 129.1, 127.2, 125.5, 123.8, 120.9, 120.3, 43.1, 37.9, 37.0, 30.1, 28.7, 23.0, 21.0, 19.1, 14.4, 14.2.



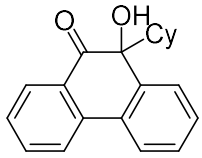
4-Methyl-2-(1-methylcyclopentyl)quinoline (43).[1] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to petroleum ether : ethyl acetate 50:1 as a Colorless oil (12 mg, 17% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.4, 1.5 Hz, 1H), 7.93 (dd, J = 8.4, 1.5 Hz, 1H), 7.65 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.49 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.29 (s, 1H), 2.68 (s, 3H), 2.35–2.28 (m, 2H), 1.85–1.71 (m, 6H), 1.41 (s, 3H).



4-Methyl-2-(2-methylcyclopentyl)quinoline (44) and 4-Methyl-2-(3-methylcyclopentyl)quinoline (45).[1] **44**:**45** = 1:1; The title compounds were obtained by eluting with petroleum ether : ethyl acetate 100:1 to petroleum ether : ethyl acetate 50:1 as a colorless oil (15 mg, 22% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53–8.48 (m, 1H), 8.02–7.99 (m, 1H), 7.782–7.77 (m, 1H), 7.65–7.60 (m, 1H), 7.34–7.30 (m, 1H), 3.92–3.83 (m, 0.5H), 3.25–3.23 (m, 0.5 H), 2.79–2.78 (m, 3H), 2.42–2.25 (m, 2H), 2.19–1.99 (m, 2H), 1.95–1.82 (m, 2H), 1.51–1.35 (m, 2H), 1.09 (d, *J* = 6.8 Hz, 1H), 1.04 (d, *J* = 6.5 Hz, 1H).



1-(Cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (46).[15] The title compound was obtained by eluting with petroleum ether : ethyl acetate 100:1 to 50:1 as a colorless oil (10 mg, 14% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.58 (tt, *J* = 9.9, 4.0 Hz, 1H), 2.07–2.01 (m, 2H), 1.77–1.70 (m, 2H), 1.55–1.44 (m, 6H), 1.27–1.09 (m, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 81.9, 59.8, 40.4, 34.6, 33.1, 26.1, 25.3, 20.5, 17.5; ESI HRMS *m/z* $(M+H)^+$ calcd 240.2322, obsd 240.2325.



10-Cyclohexyl-10-hydroxyphenanthren-9(10*H*)-one (47).[16] A 25 mL flask was charged with PQ (62 mg, 1 equiv.), cyclohexane (1 mL). Then MeCN (6 mL) was added and the solution was purged with argon for 10 min. The reaction was carried out at room temperature under irradiation with 420–425 nm LEDs (10 W) for 16 h. The reaction mixture was concentrated and the residue was chromatographed through silica gel. The title compound was obtained by eluting with petroleum ether : ethyl acetate 50:1 to 20:1 as a colorless oil (44 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.89 (d, *J* = 8.0, 1H), 7.85 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.80–7.78 (m, 1H), 7.69–7.64

(m, 2H), 7.43–7.35 (m, 3H), 4.03 (s, 1H), 1.75–1.58 (m, 3H), 1.56–1.49 (m, 2H), 1.37–1.22 (m, 3H), 1.09–0.95 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.3, 139.9, 138.0, 135.0, 129.9, 129.4, 128.5, 128.4, 128.0, 127.6, 127.0, 124.3, 123.2, 82.4, 48.4, 27.4, 26.5, 26.4, 26.3, 26.0.

References

1. Laze, L.; Quevedo-Flores, B.; Bosque, I.; Gonzalez-Gomez, J. C. Alkanes in Minisci-Type Reaction under Photocatalytic Conditions with Hydrogen Evolution. *Org. Lett.* **2023**, *25*, 8541–8546.

2. Zhang, L.; Pfund, B.; Wenger, O.; Hu, X. Oxidase-Type C–H/C–H Coupling Using an Isoquinoline-Derived Organic Photocatalyst. *Angew. Chem., Int. Ed.* **2022**, *61*, e202202649.

3. Rio-Rodriguez, R. D.; Fragoso-Jarillo, L.; Alema, J. General Electrochemical Minisci Alkylation of *N*-Heteroarenes with Alkyl Halides. *Chem*. *Sci.* **2022**, *13*, 6512–6518.

4. Sutherland, D. R.; Veguillas, M.; Lee, A.-L. Metal-, Photocatalyst-, and Light-Free, Late-Stage C–H Alkylation of Heteroarenes and 1,4-Quinones Using Carboxylic Acids. *Org. Lett.* **2018**, *20*, 6863–6867.

5. Liang, X.-A.; Niu, L.; Wang, S.; Lei, A. Visible-Light-Induced C(sp^3)–H Oxidative Arylation with Heteroarenes. *Org. Lett.* **2019**, *21*, 2441–2444.

6. Cai, R.-N.; Qiao, J.; Gan, Q.-B.; Wu, L.-Z. Aliphatic C–H Arylation with Heteroarenes without Photocatalysts. *Green Chem.* **2023**, *25*, 8500–2504.

7. Li, D.-S.; Liu, T.; Wu, J. Stop-Flow Microtubing Reactor-Assisted Visible Light-Induced Hydrogen-Evolution Cross Coupling of Heteroarenes with C(sp^3)–H Bonds. *ACS Catal.* **2022**, *12*, 4473–4480.

8. Li, Z.-L.; Jin, L.-K.; Cai, C. Efficient Synthesis of 2-Substituted Azoles: Radical C–H Alkylation of Azoles with Dicumyl Peroxide, Methylarenes and Cycloalkanes under Metal-Free Condition. *Org. Chem. Front*. **2017**, *4*, 2039-2043.

9. Zhang, X.-Y.; Wang, W.-Z.; Yang, H.; Zhang, B. Visible-Light-Initiated,

Photocatalyst-Free Decarboxylative Coupling of Carboxylic Acids with *N*-Heterocycles. *Org. Lett.* **2018**, *20*, 2686–2690.

10. Liu, G.; Mu, X.; Tian, M.; Zou, C.; Yu, M. Metal-Free, Light-Mediated, Site-Specific, Radical C6–H Alkylation of Purines with Alcohols Intervened by Oxalates without Catalysts. *Eur. J. Org. Chem.* **2023**, *26*, e202201491.

11. Garza-Sanchez, R. A.; Tavakoli, G.; Glorius, F. Visible Light-Mediated Direct Decarboxylative C-H Functionalization of Heteroarenes. *ACS Catal.* **2017**, *7*, 4057–4061.

12. Pan, Z.-T.; Shen, L.-M.; Jian, J.-X.; Tong, Q.-X. Minisci Reaction of Heteroarenes and Unactivated C(sp^3)–H Alkanes via a Photogenerated Chlorine Radical. *Chem. Common.* **2023**, *59*, 1637–1640.

13. Bhakat, M.; Khatua, B.; Guin, J. Metal-, Photocatalytic Aerobic Coupling of Azaarenes and Alkanes via Nontraditional $Cl^{\bullet}$ Generation. *Org. Lett.* **2022**, *24*, 5276–5280.

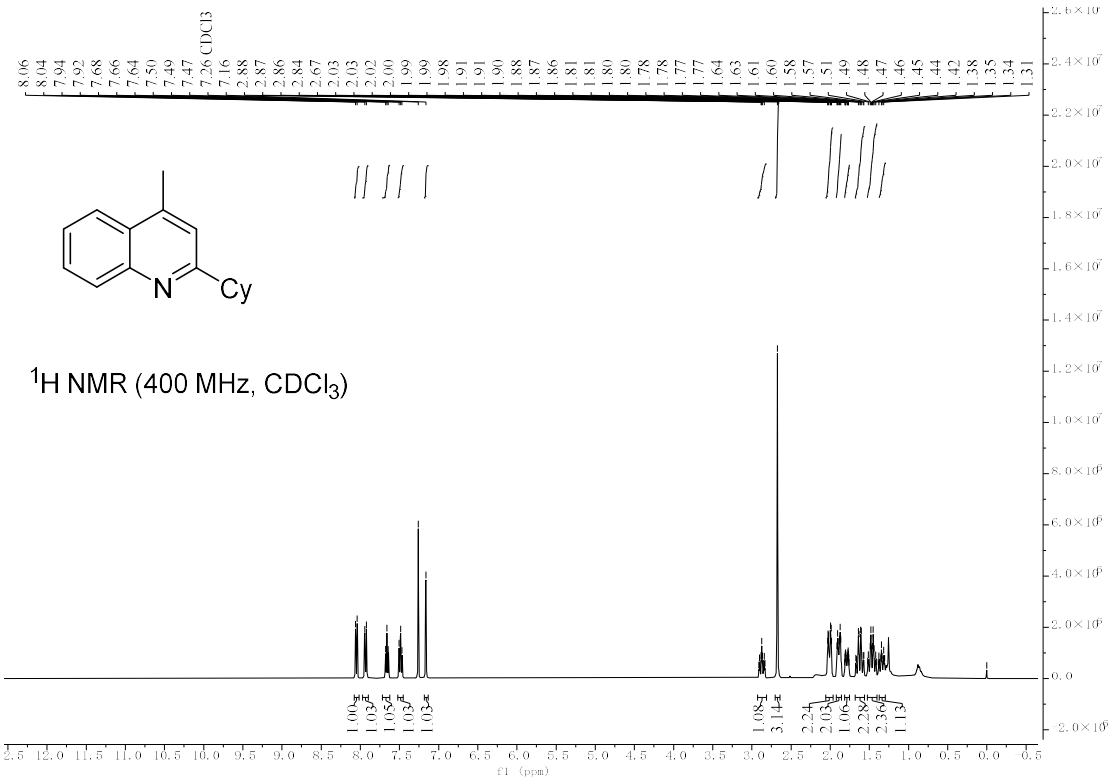
14. Liu, Y.; Shi, B.; Qi, X.; Lei, A. Time-Resolved EPR Revealed the Formation, Structure, and Reactivity of *N*-Centered Radicals in an Electrochemical C(sp^3)-H Arylation Reaction. *J. Am. Chem. Soc.* **2021**, *143*, 20863–20872.

15. Lv, X.-Y.; Martin, R. Cu-Catalyzed C(sp^3) Amination of Unactivated Secondary Alkyl Iodides Promoted by Diaryliodonium Salts. *Org. Lett.* **2023**, *25*, 3750–3754.

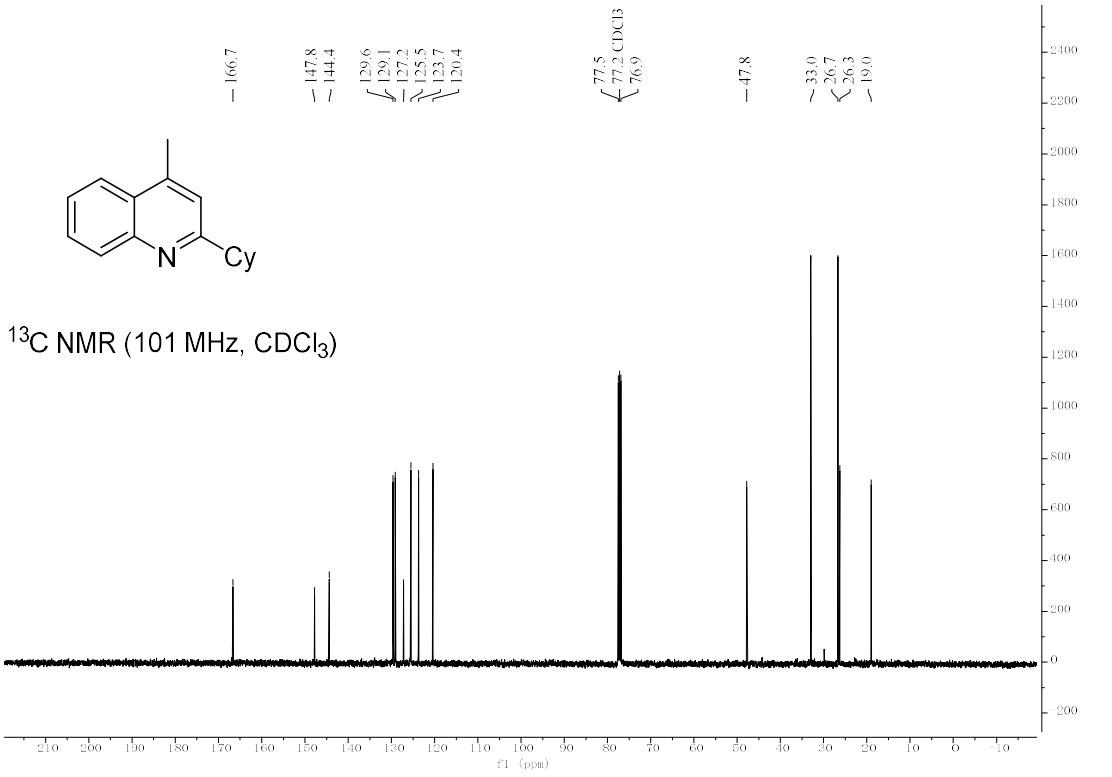
16. Wang, X.-Y.; He, Y.-Q.; Zhou, Y.; Xiao, Q. Photoalkylation/-Arylation of *ortho*-Diketones with Unactivated Organic Halides. *Org. Lett.* **2023**, *25*, 3847–3852.

8. NMR Spectra for the Products

Compound 3

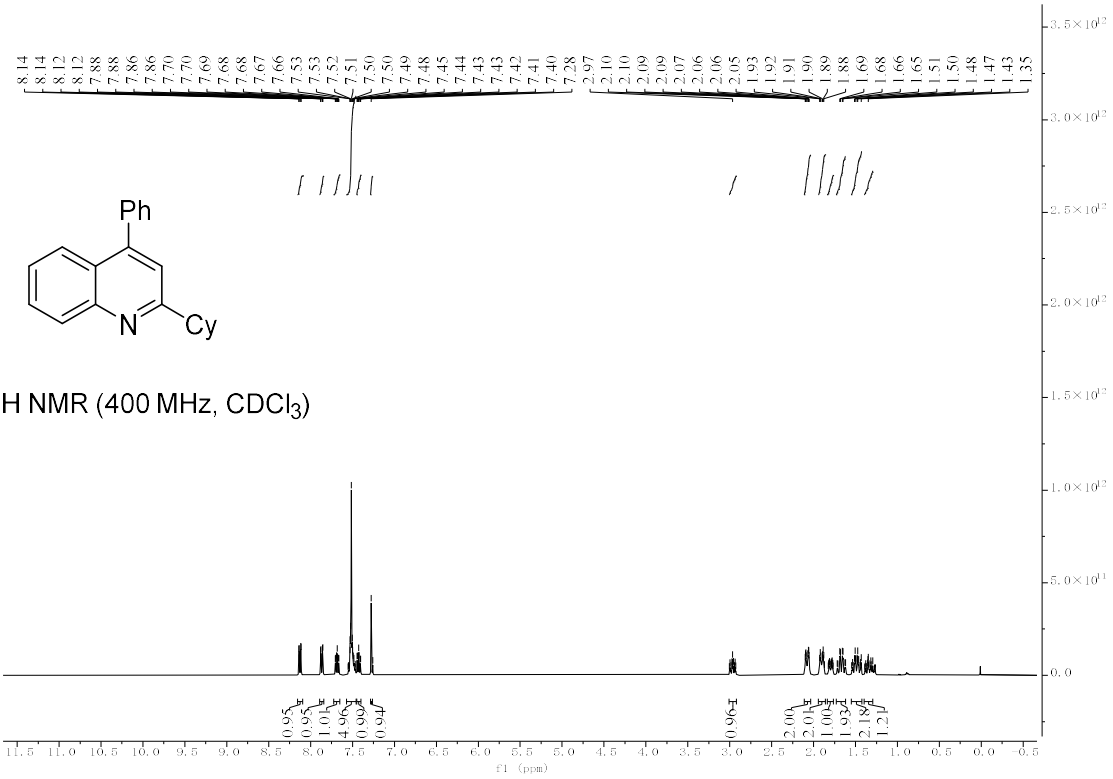


^{1}H NMR (400 MHz, $CDCl_3$)

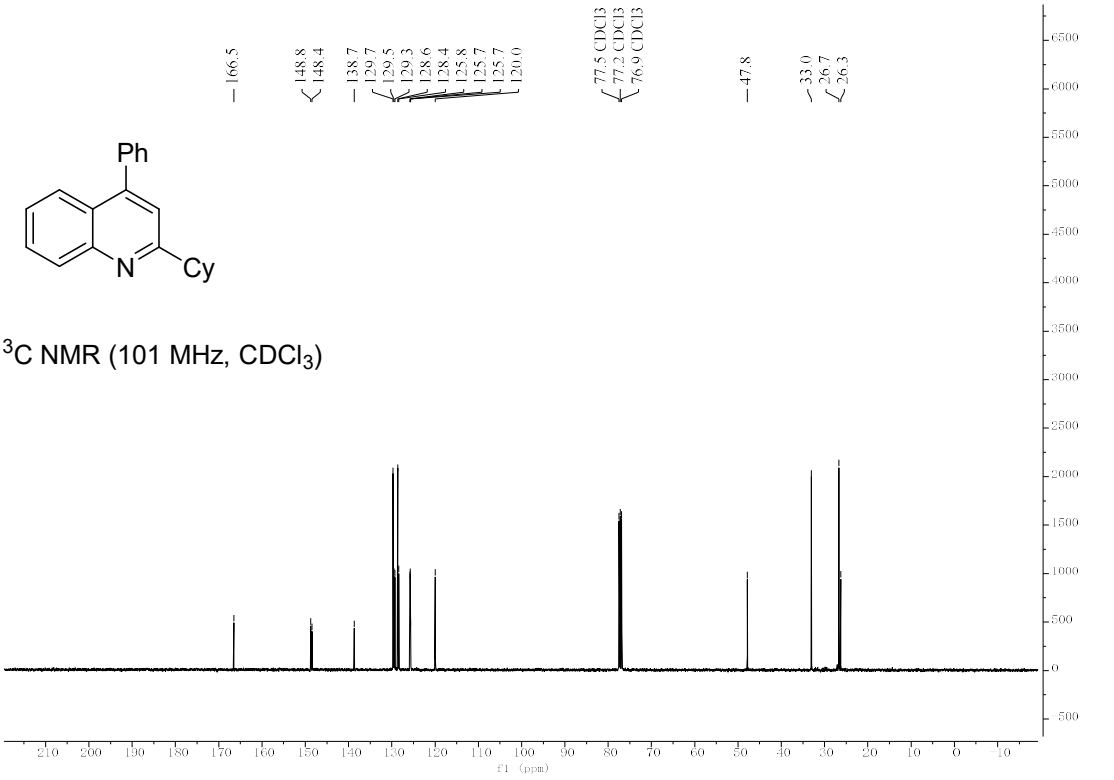


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 4

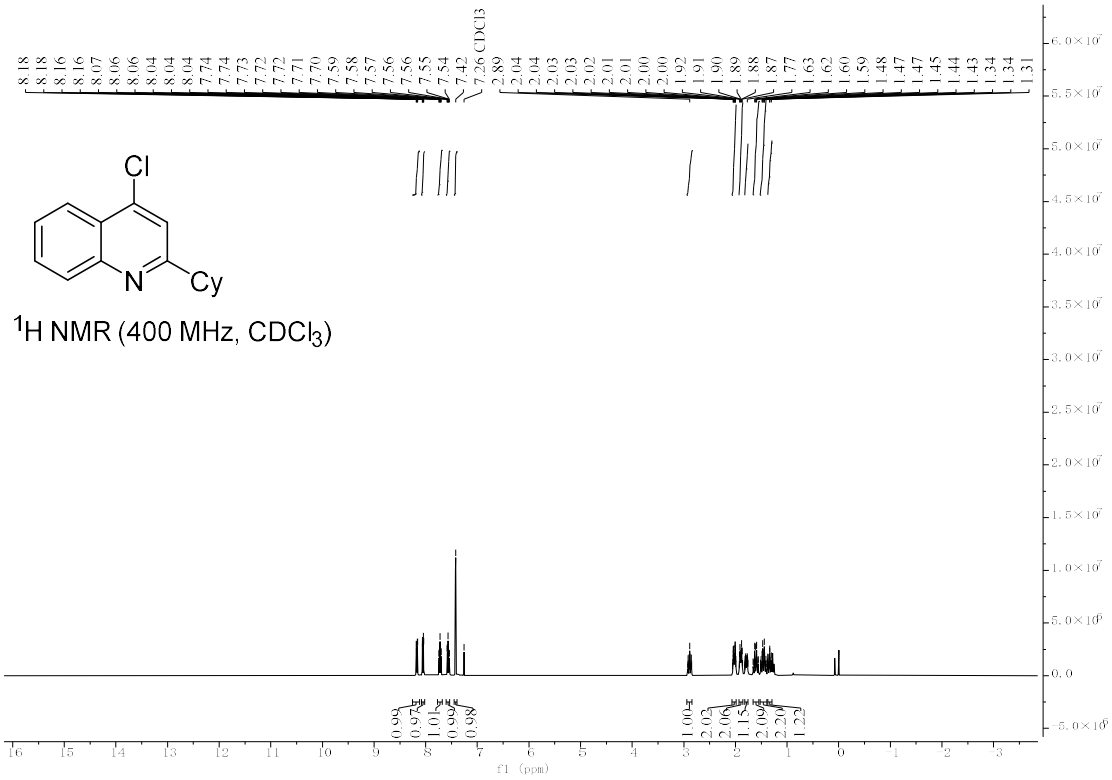


^{1}H NMR (400 MHz, $CDCl_3$)

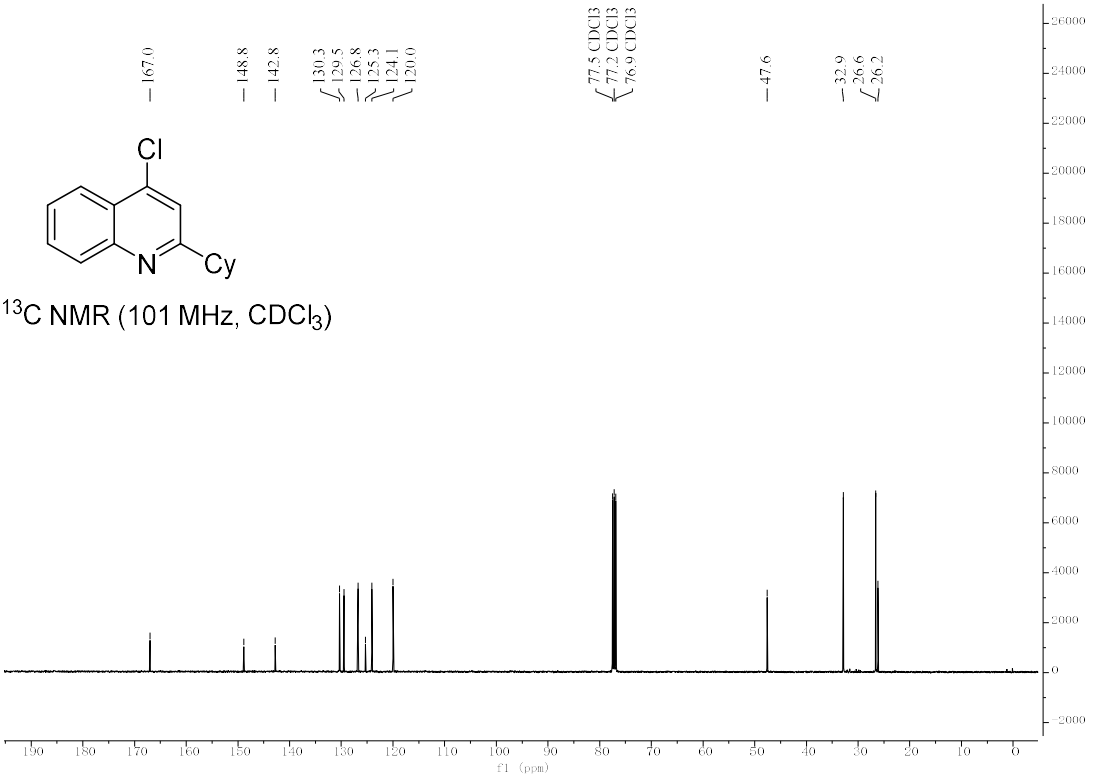


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 5

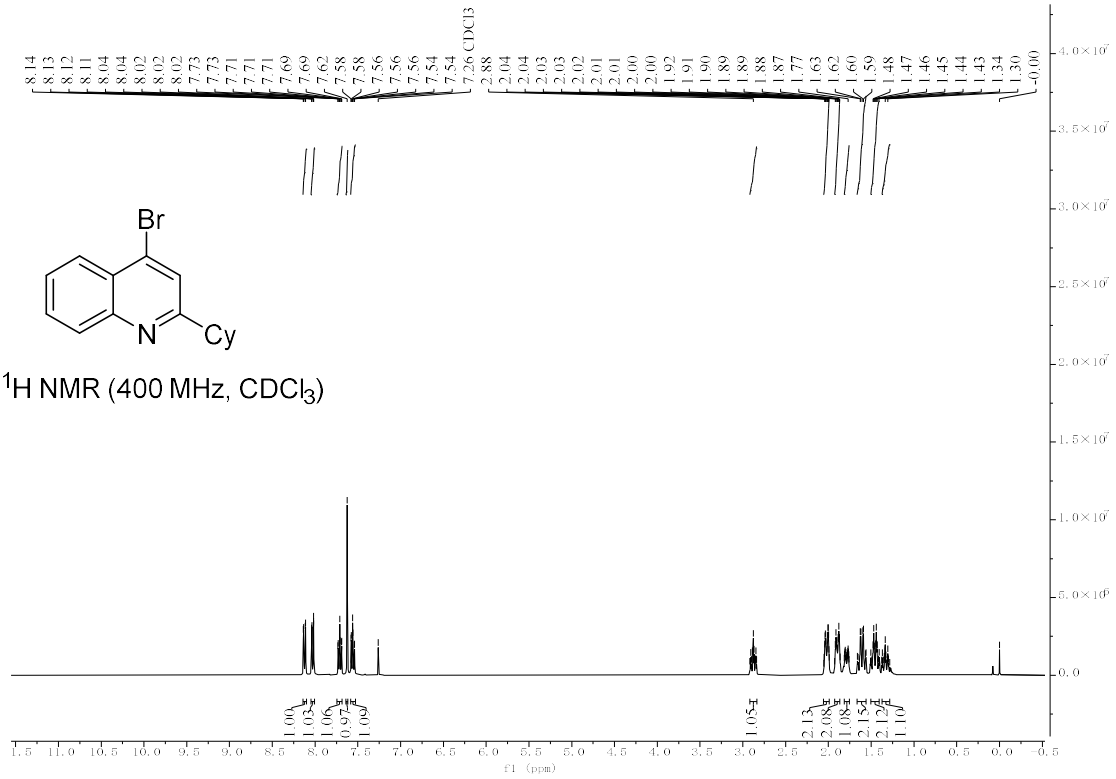


^{1}H NMR (400 MHz, $CDCl_3$)

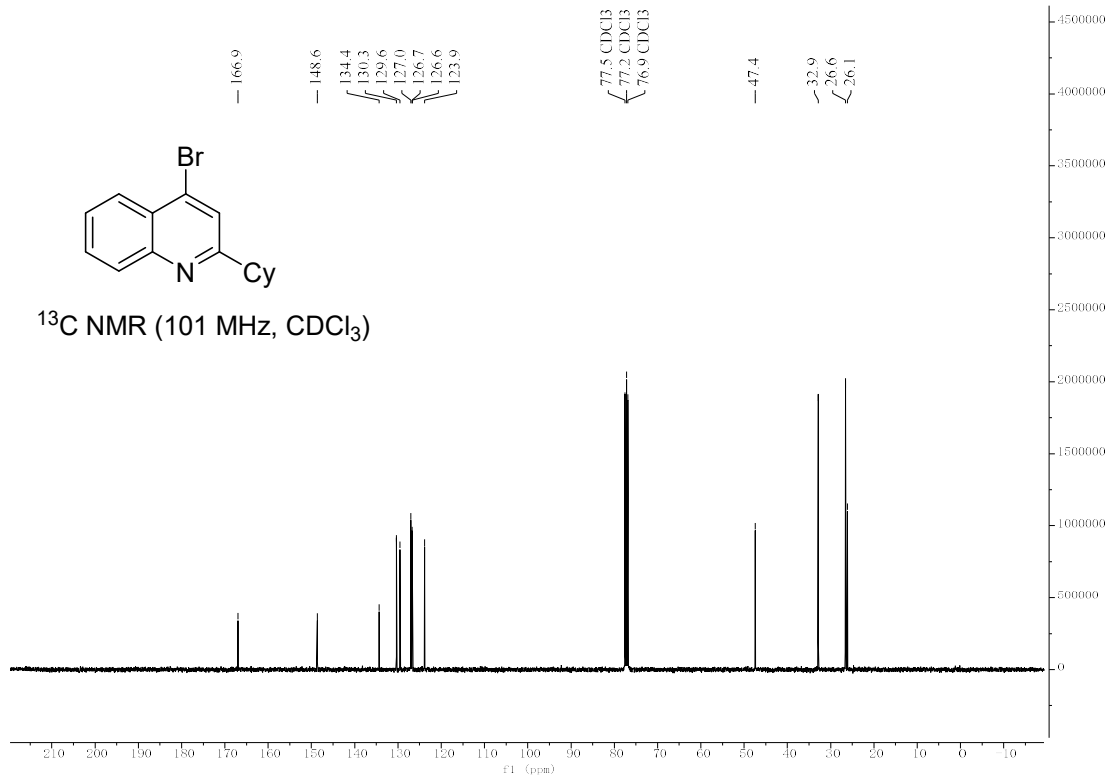


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 6

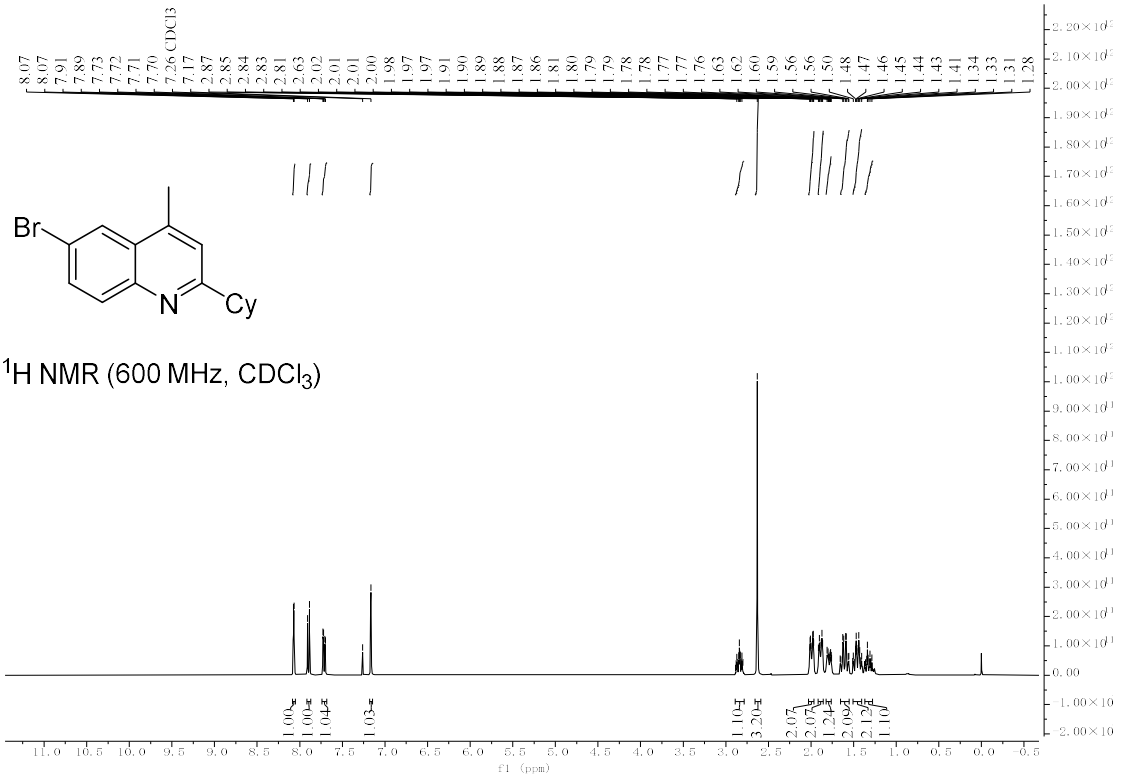


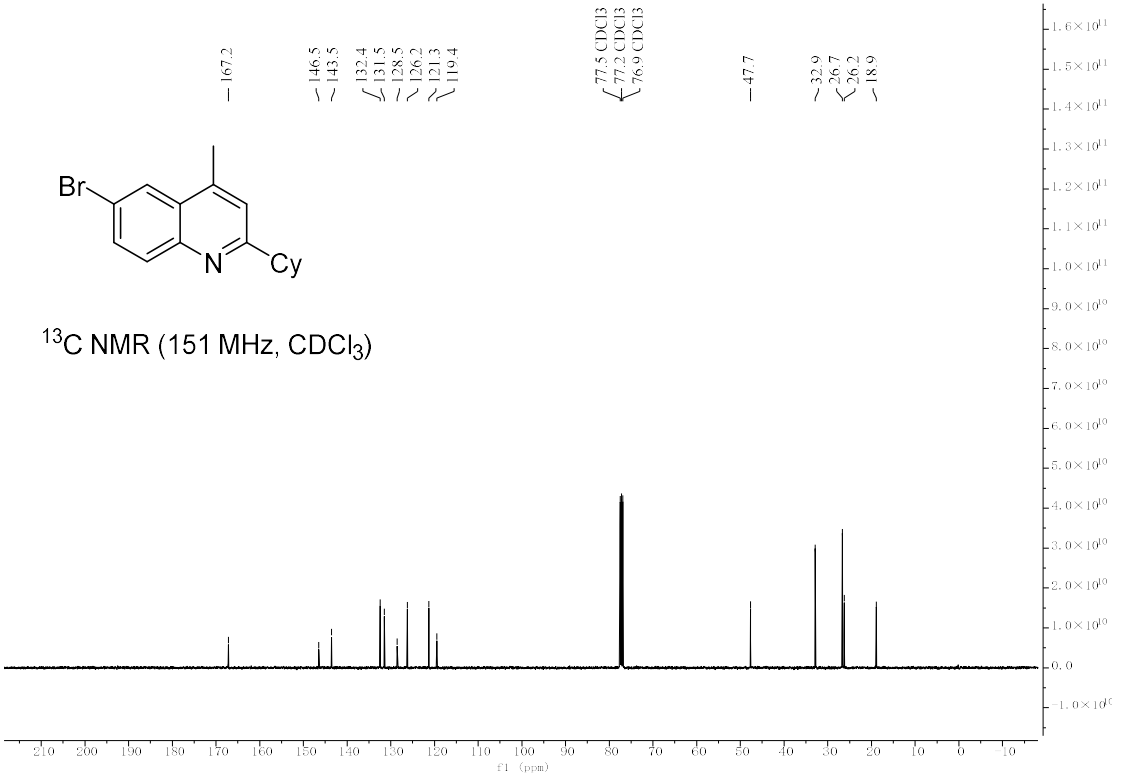
^{1}H NMR (400 MHz, $CDCl_3$)



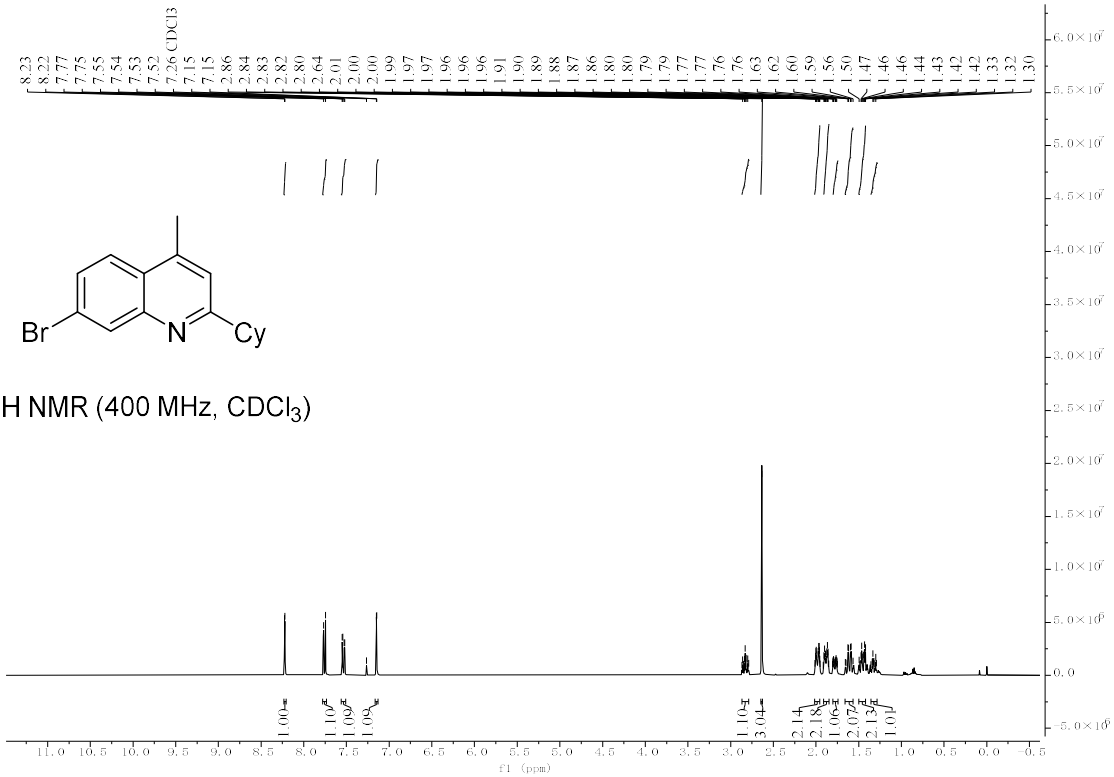
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 7

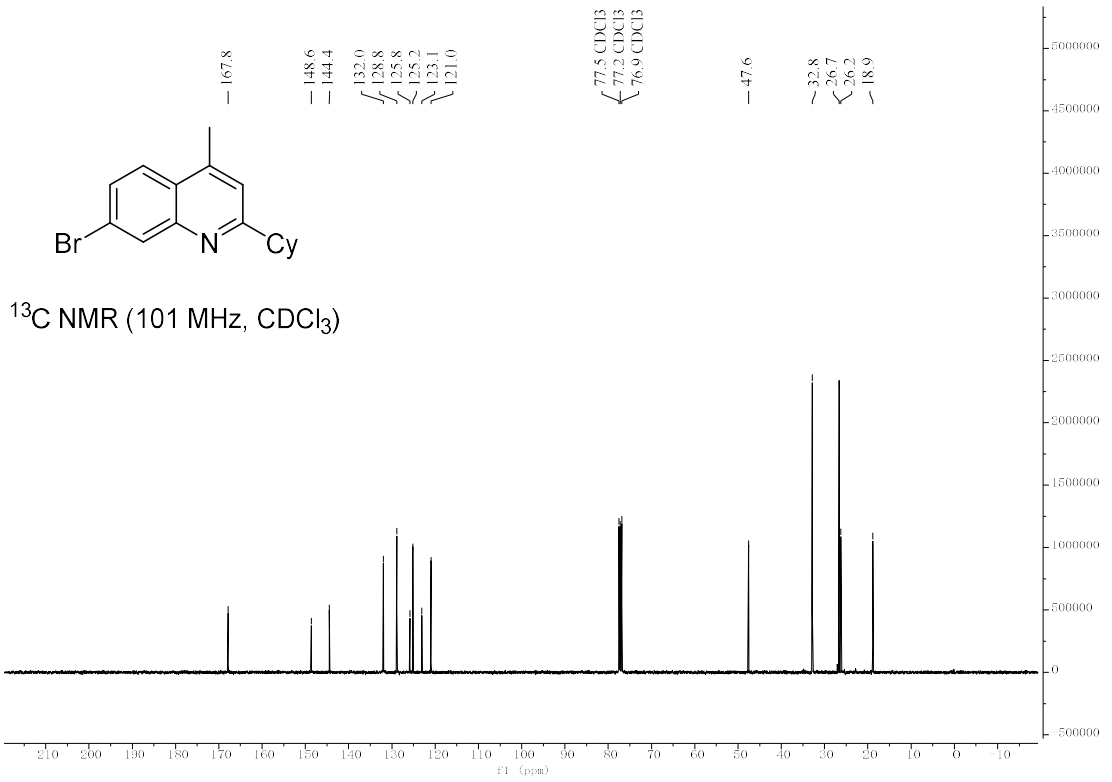




Compound 8

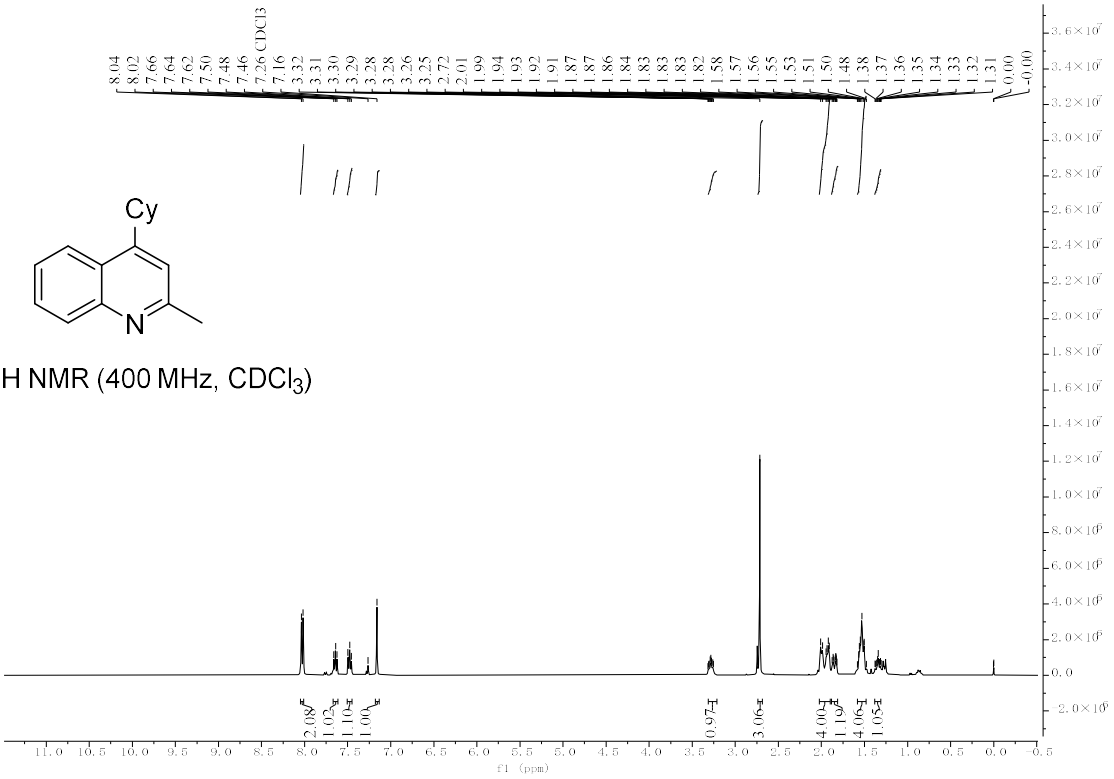


^{1}H NMR (400 MHz, $CDCl_3$)

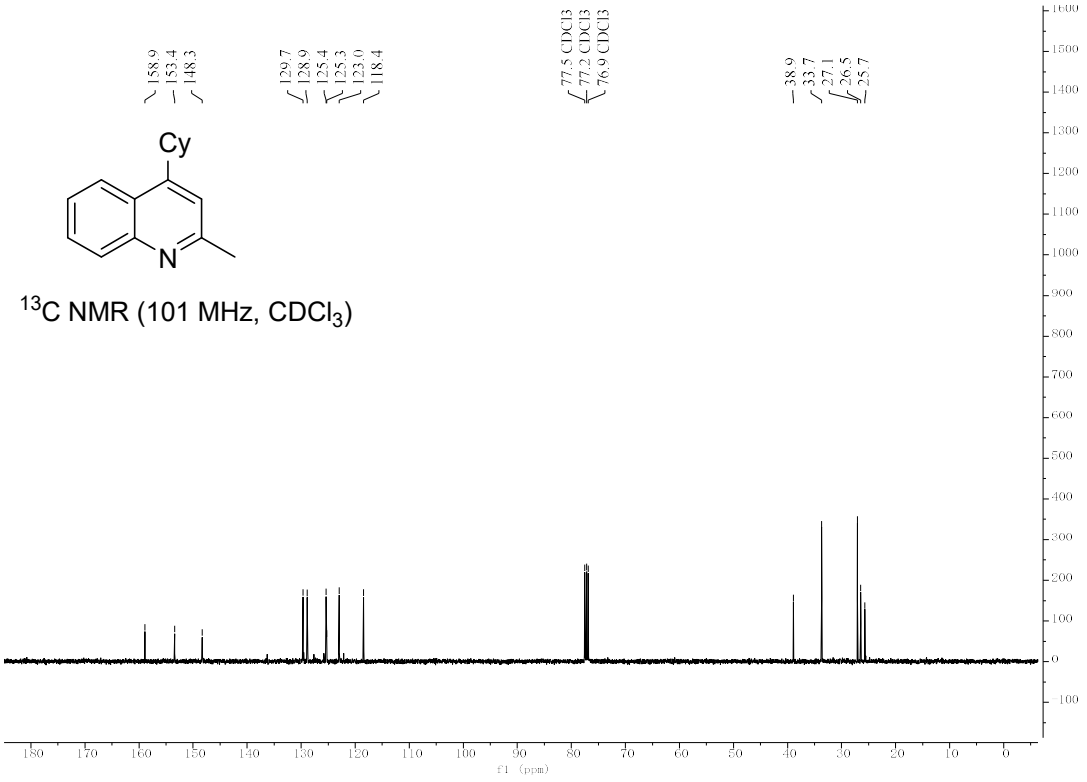


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 9

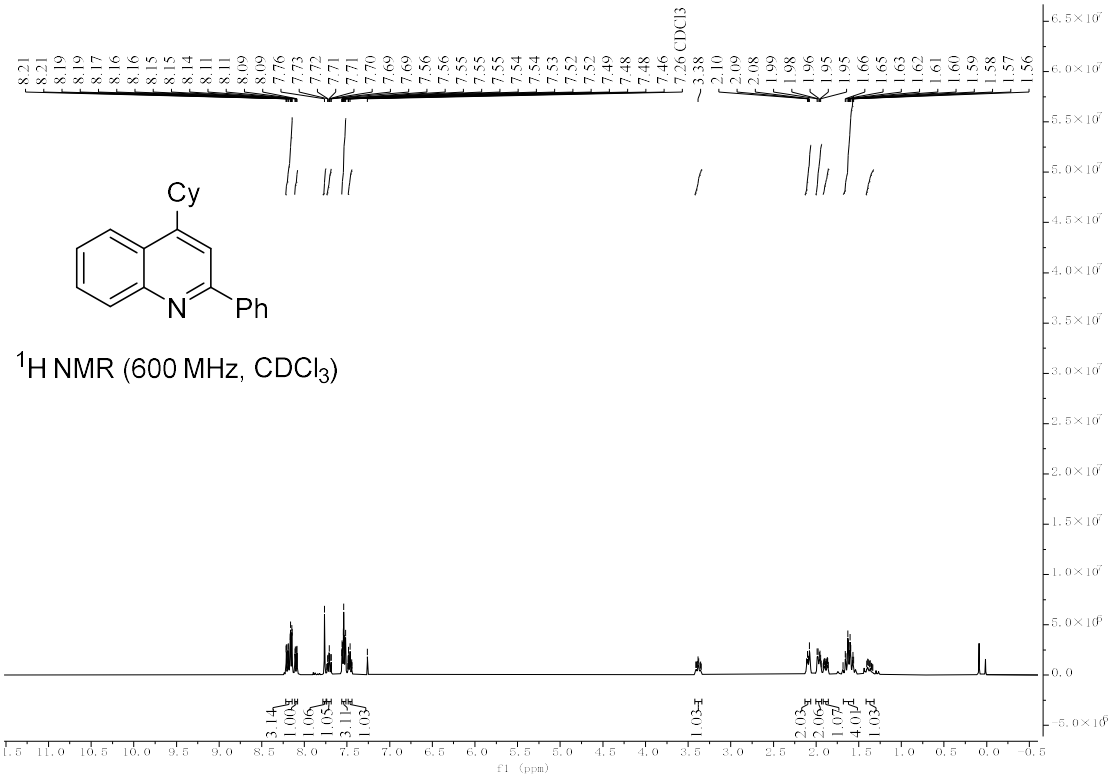


^{1}H NMR (400 MHz, $CDCl_3$)

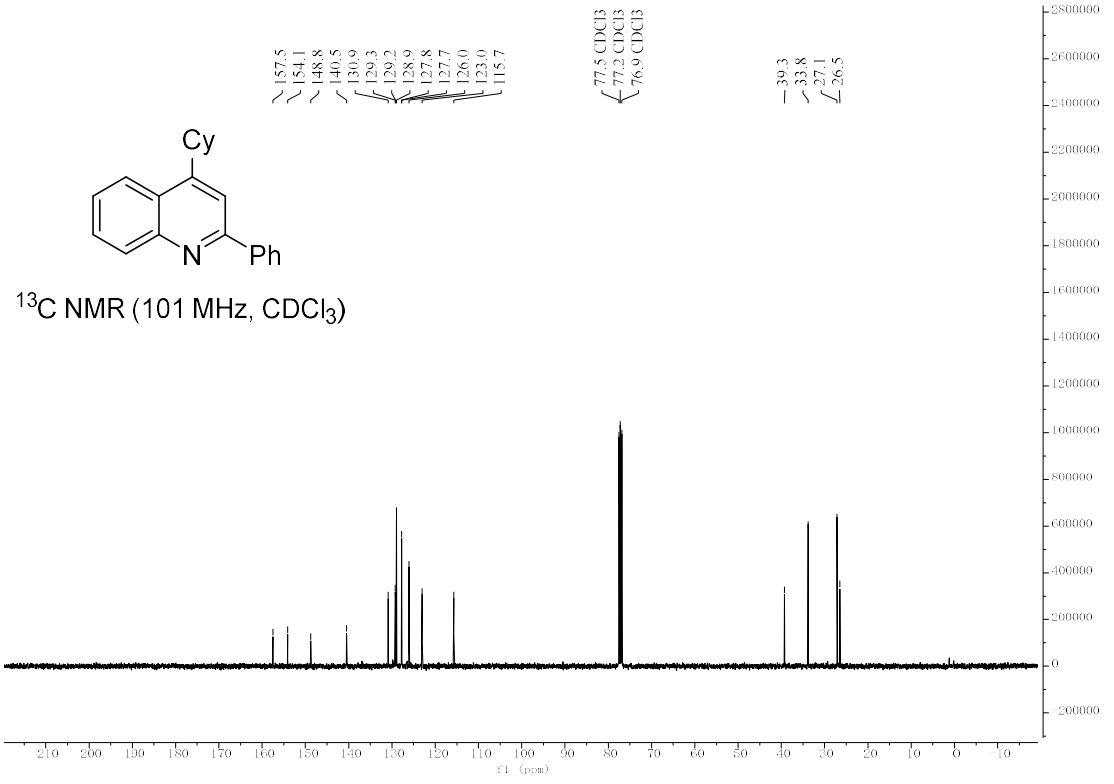


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 10

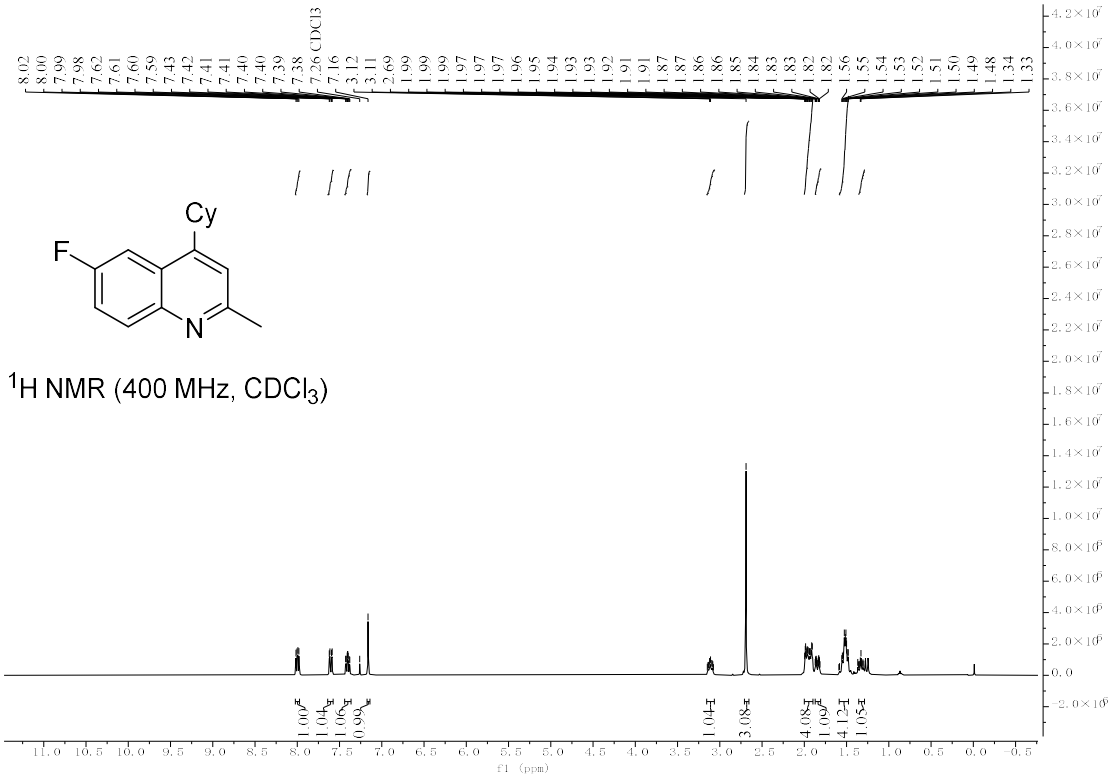


^{1}H NMR (600 MHz, $CDCl_3$)

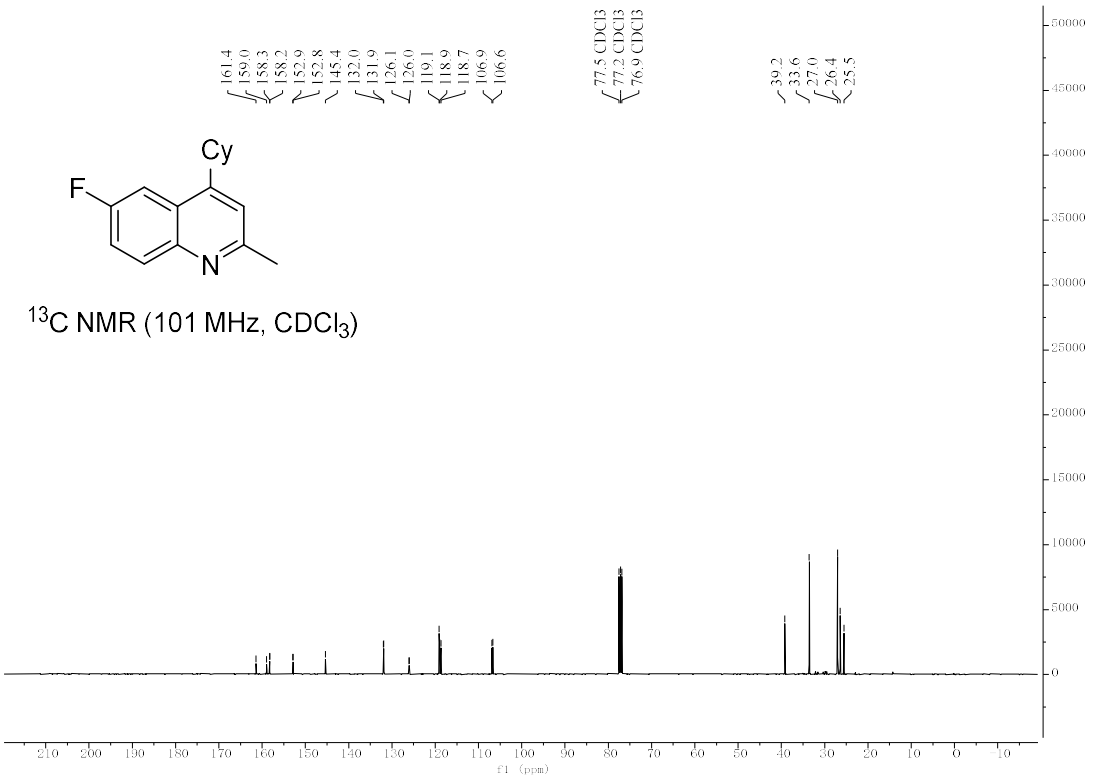


^{13}C NMR (101 MHz, $CDCl_3$)

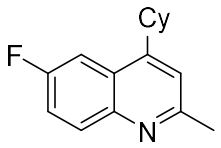
Compound 11



^{1}H NMR (400 MHz, $CDCl_3$)

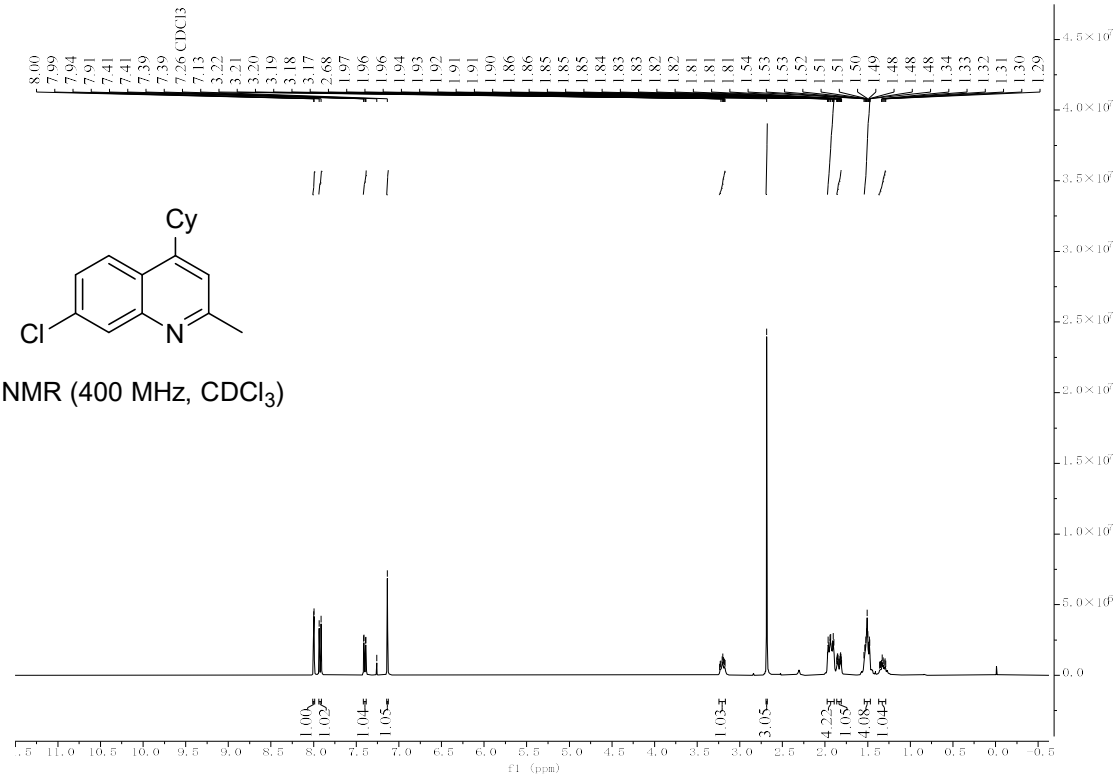


^{13}C NMR (101 MHz, $CDCl_3$)

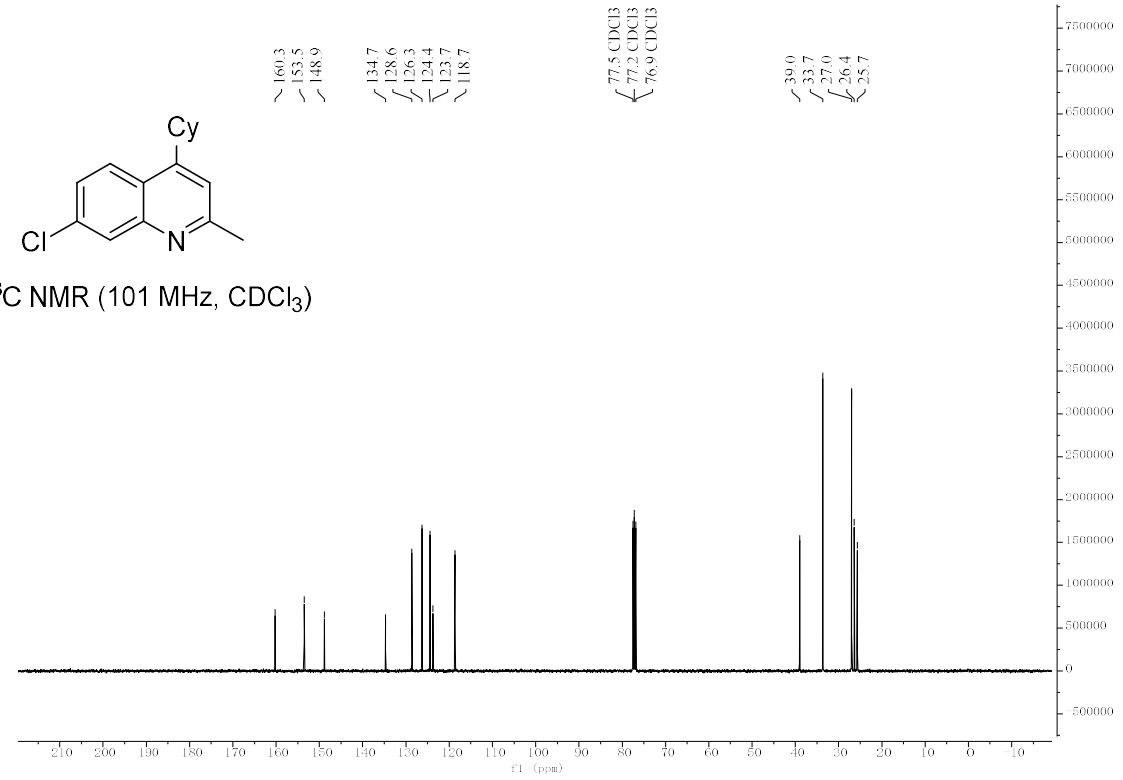


^{19}F NMR (377 MHz, $CDCl_3$)

Compound 12

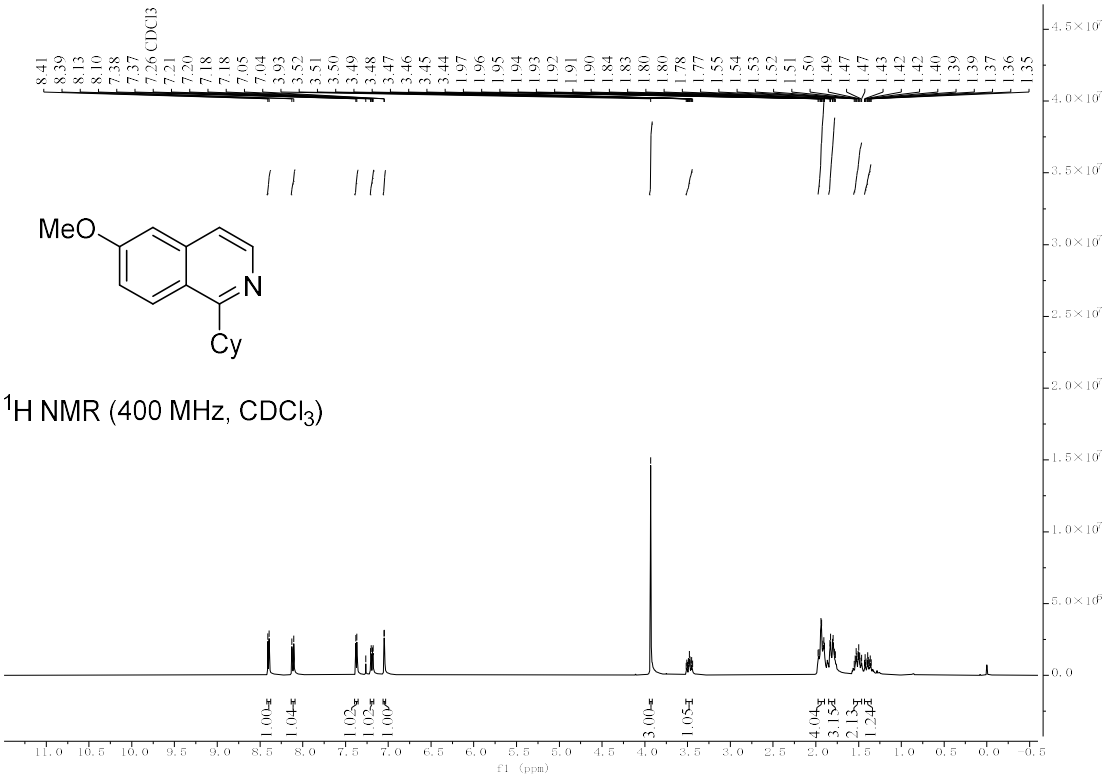


^{1}H NMR (400 MHz, $CDCl_3$)

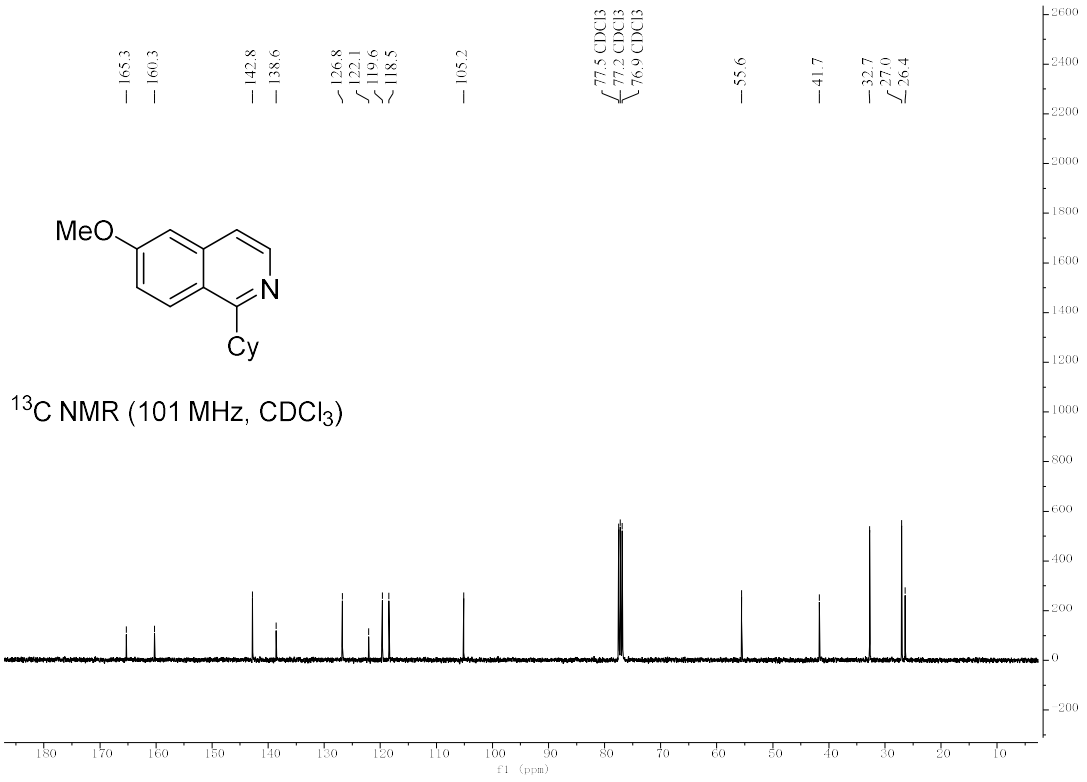


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 13

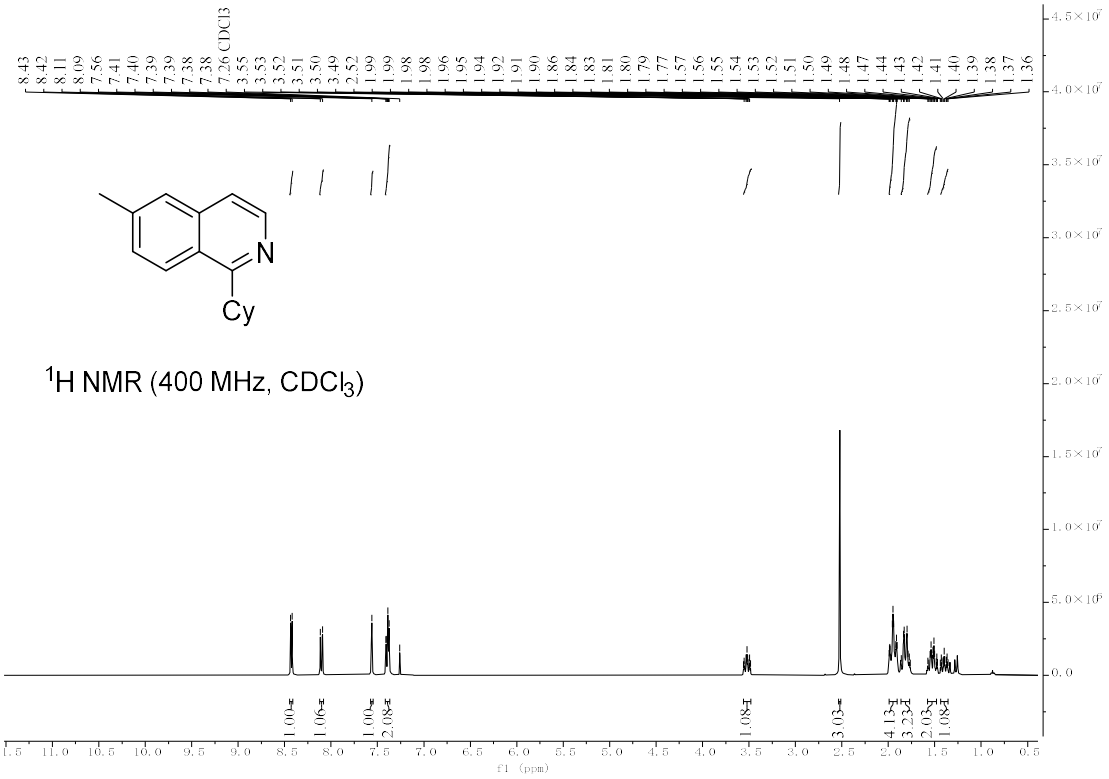


^{1}H NMR (400 MHz, $CDCl_3$)

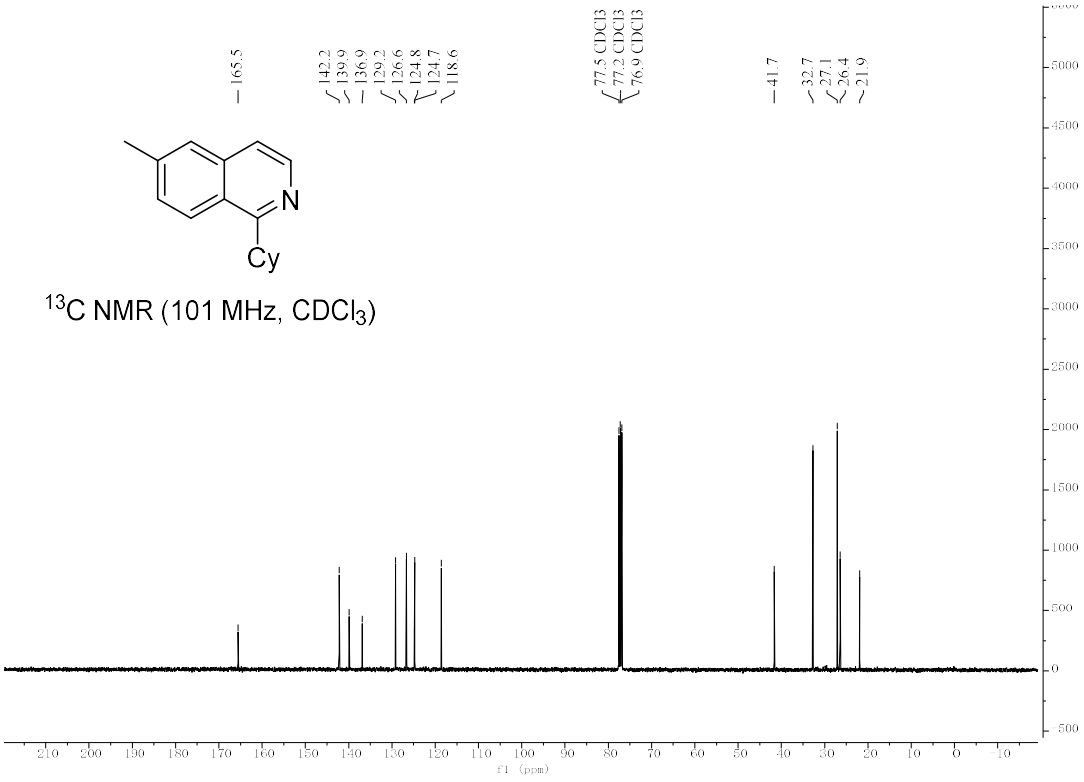


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 14

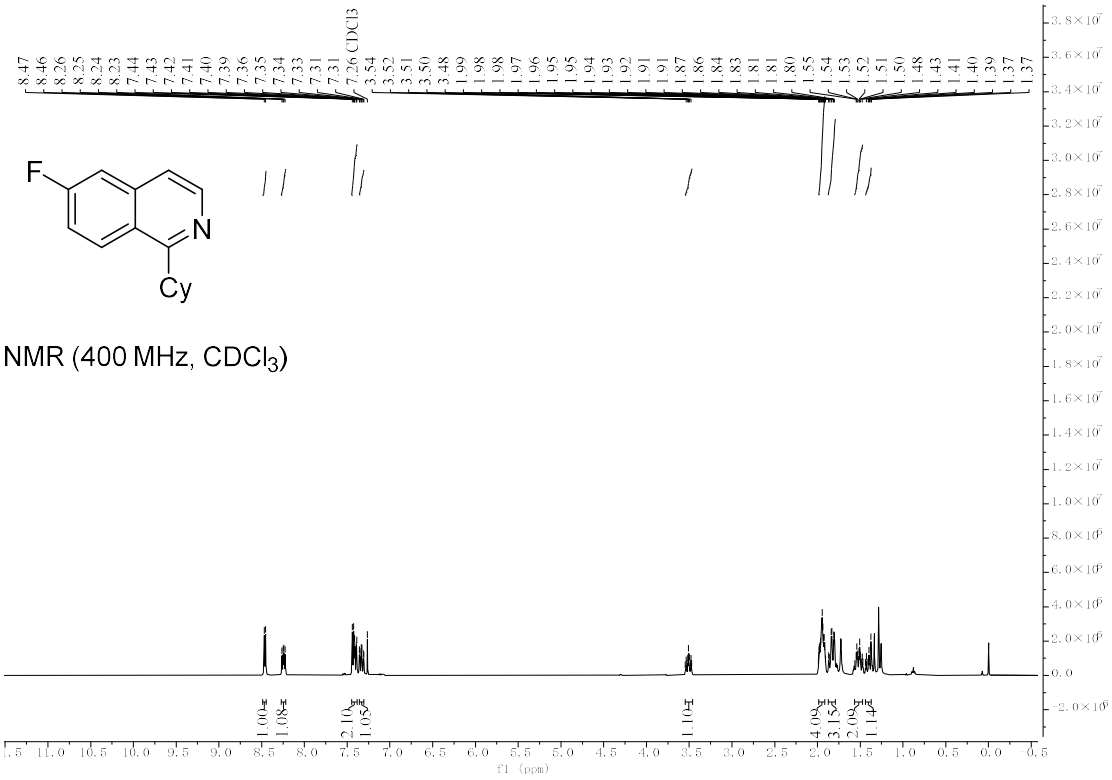


^{1}H NMR (400 MHz, $CDCl_3$)

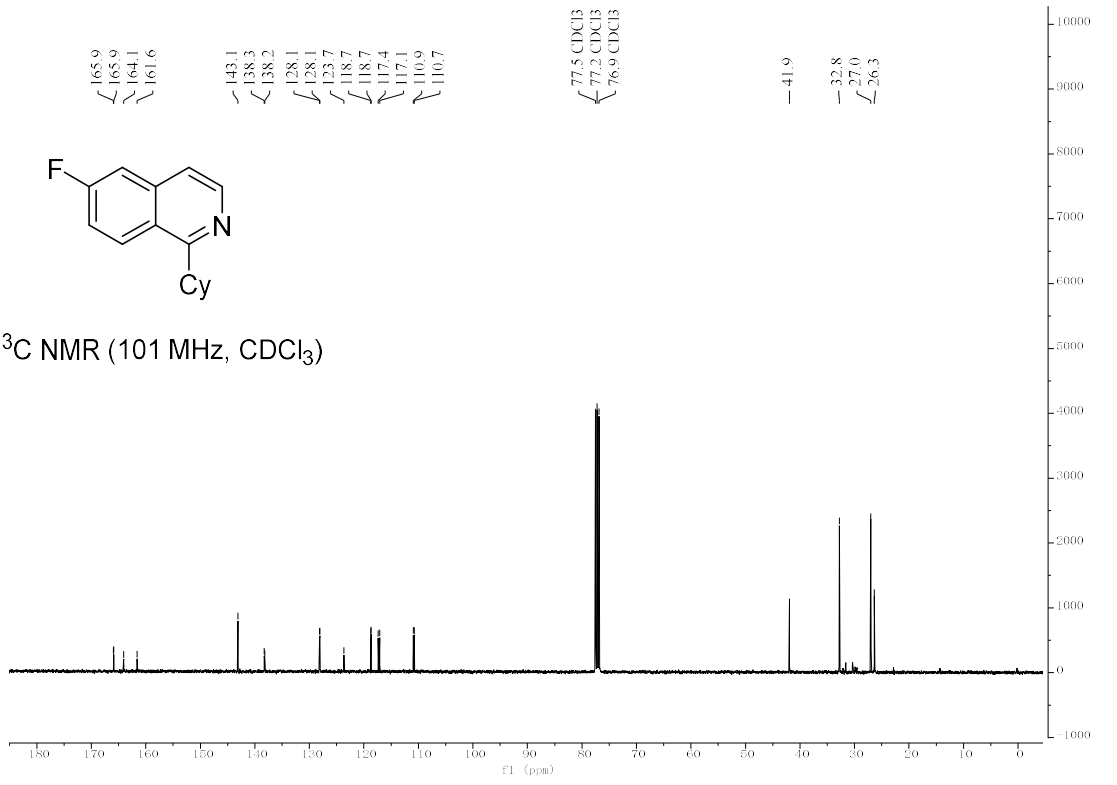


^{13}C NMR (101 MHz, $CDCl_3$)

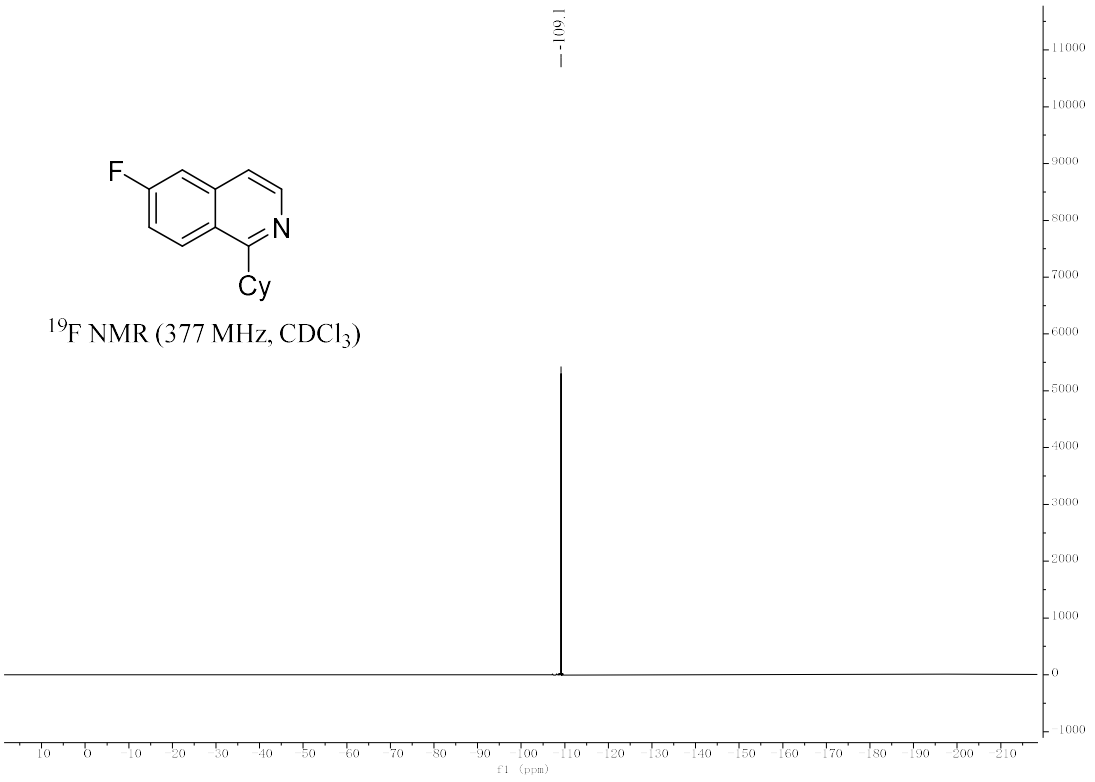
Compound 15



^{1}H NMR (400 MHz, $CDCl_3$)

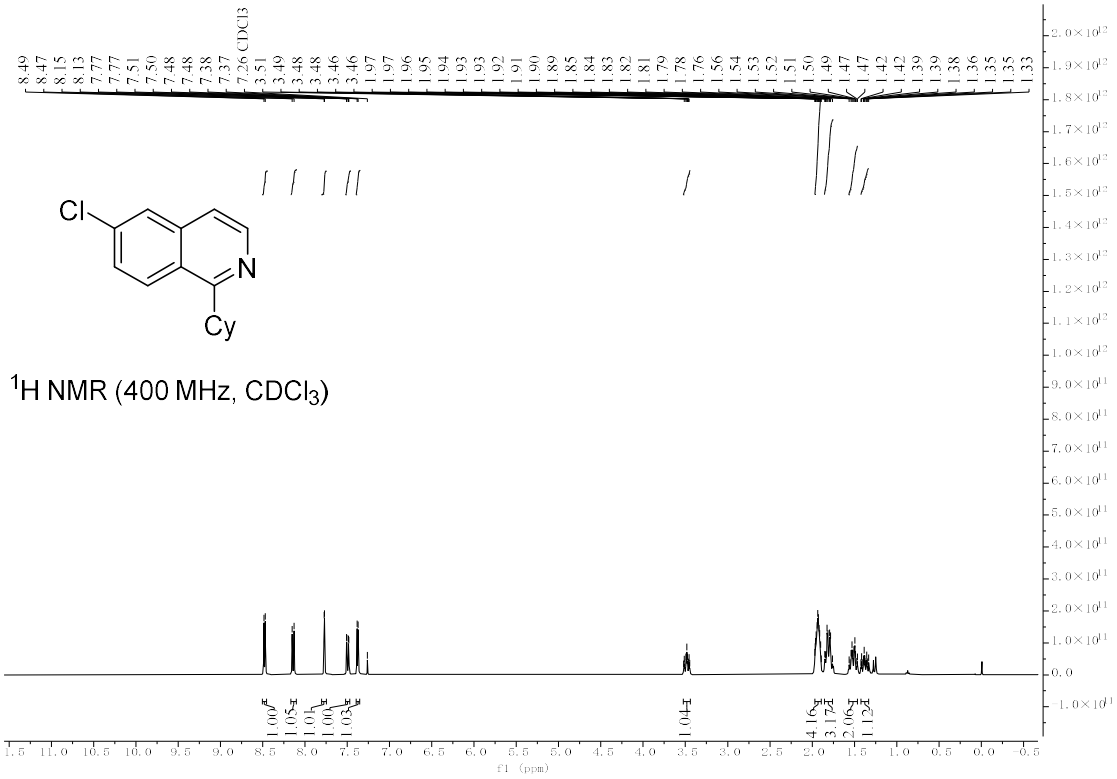


^{13}C NMR (101 MHz, $CDCl_3$)

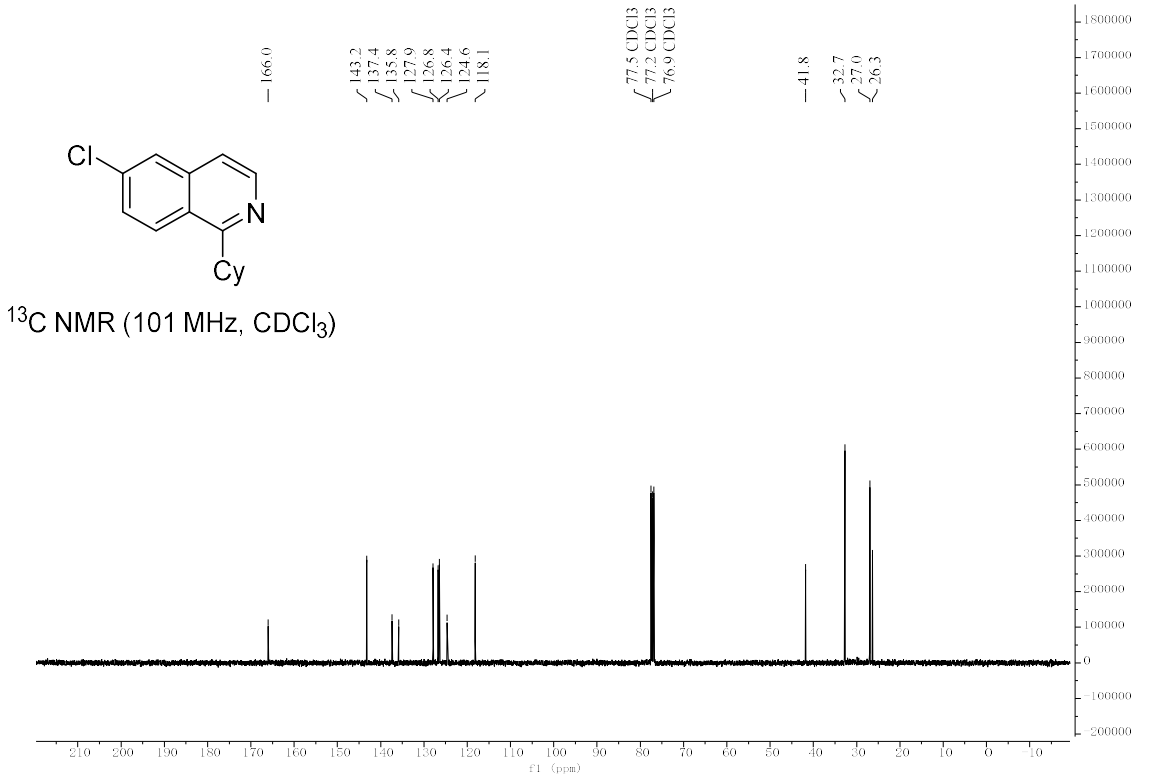


^{19}F NMR (377 MHz, $CDCl_3$)

Compound 16

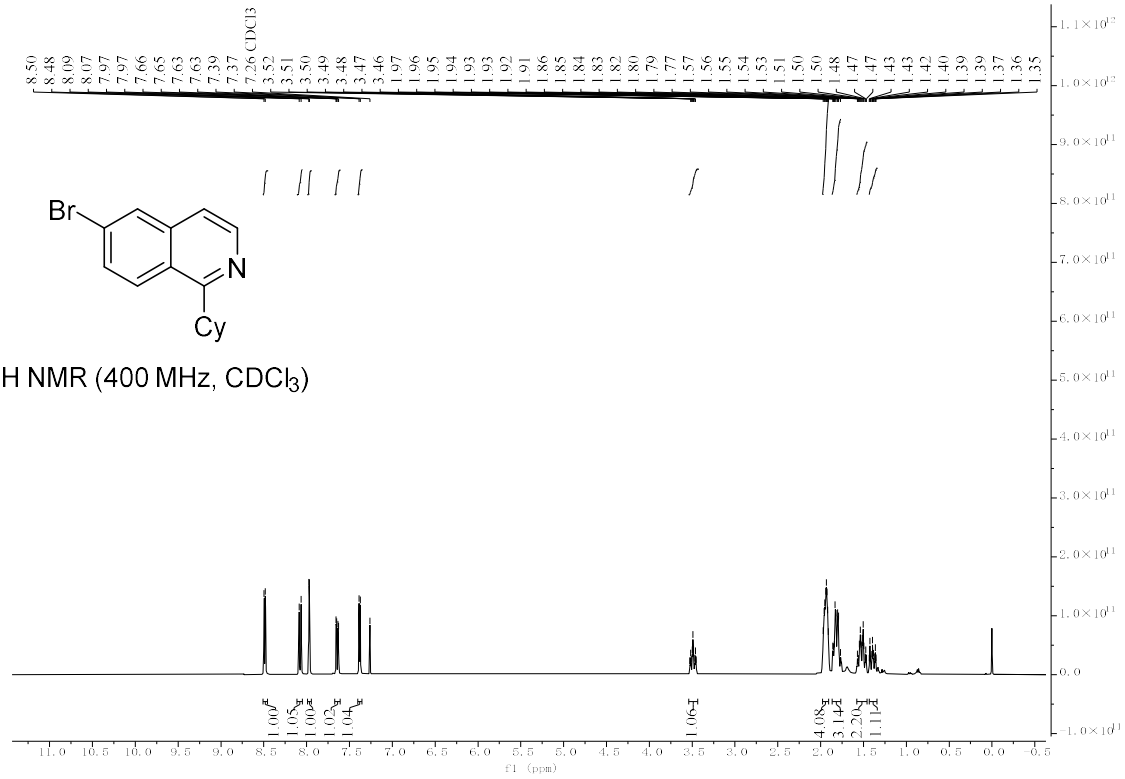


^{1}H NMR (400 MHz, $CDCl_3$)

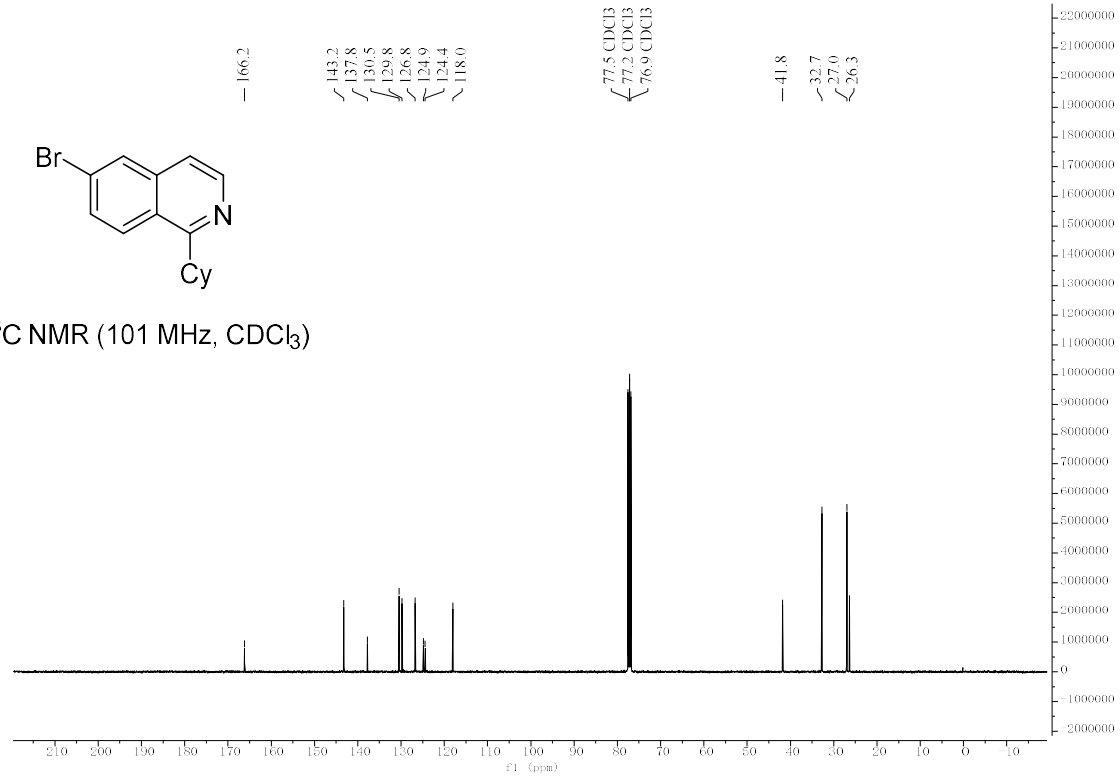


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 17

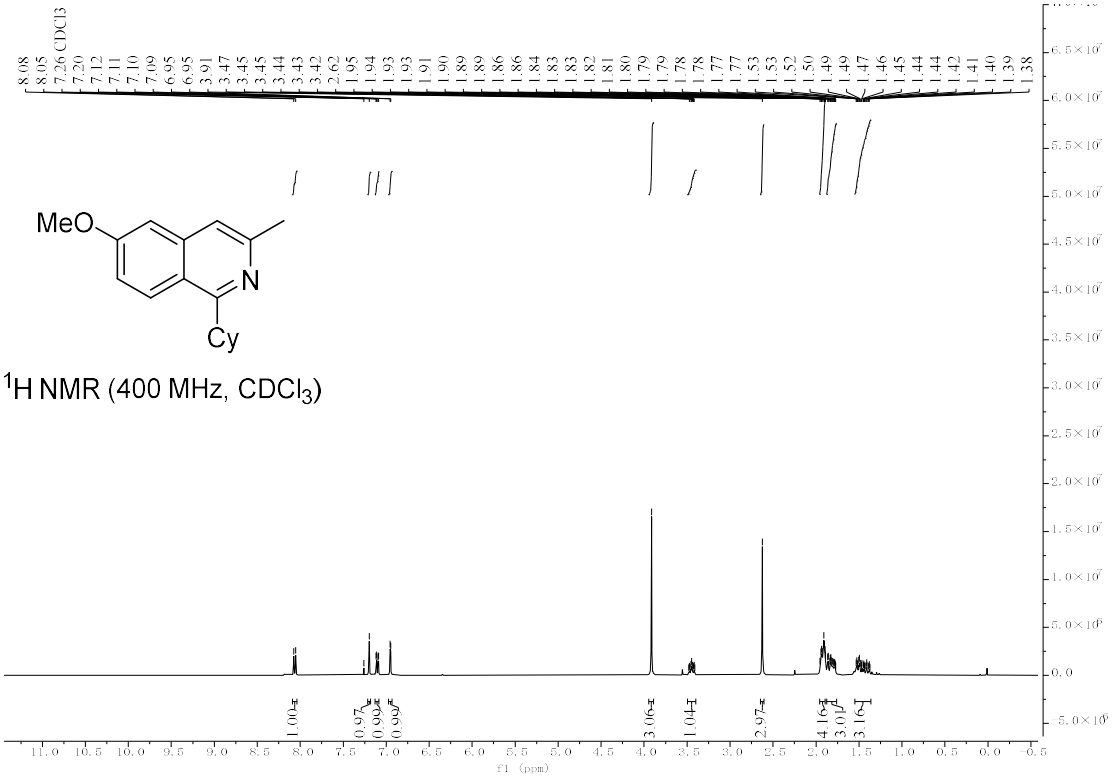


^{1}H NMR (400 MHz, $CDCl_3$)

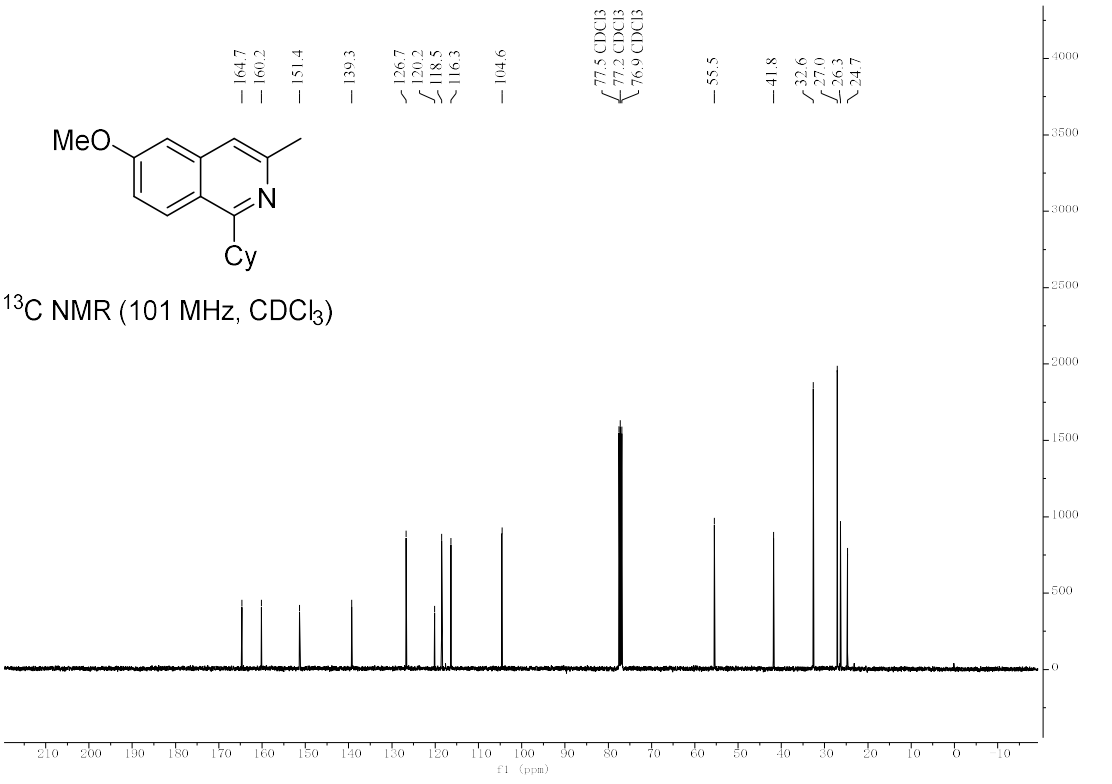


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 18

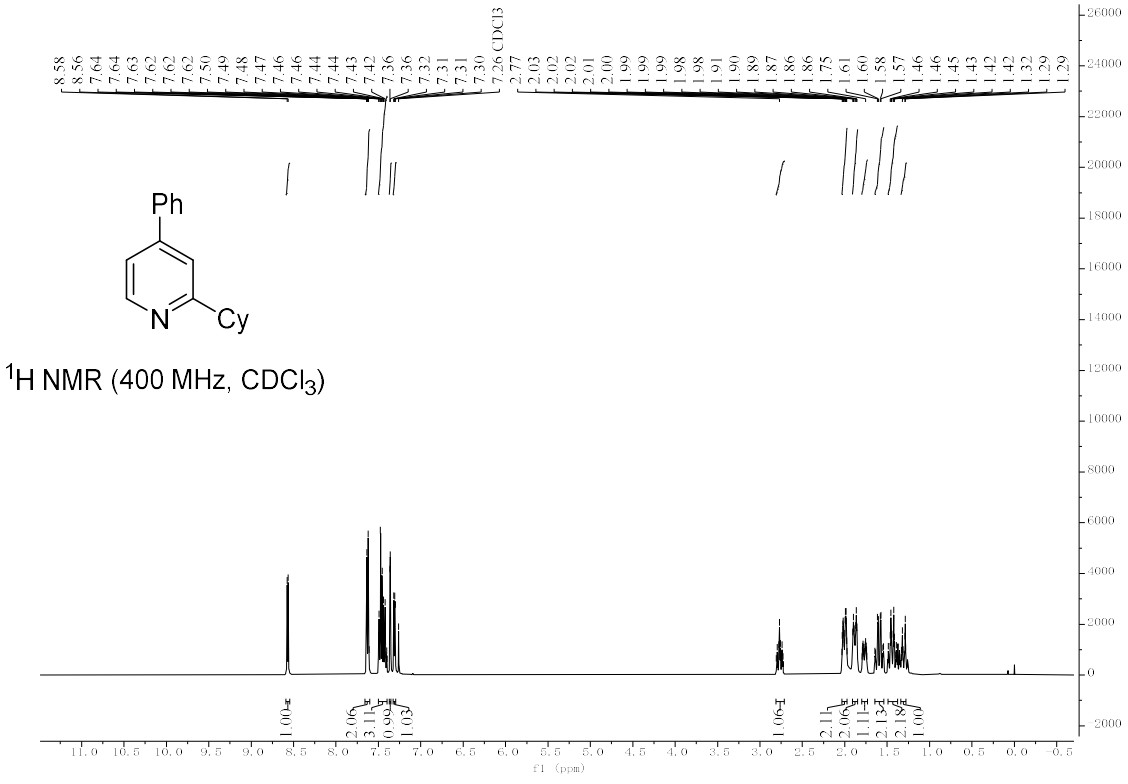


^{1}H NMR (400 MHz, $CDCl_3$)

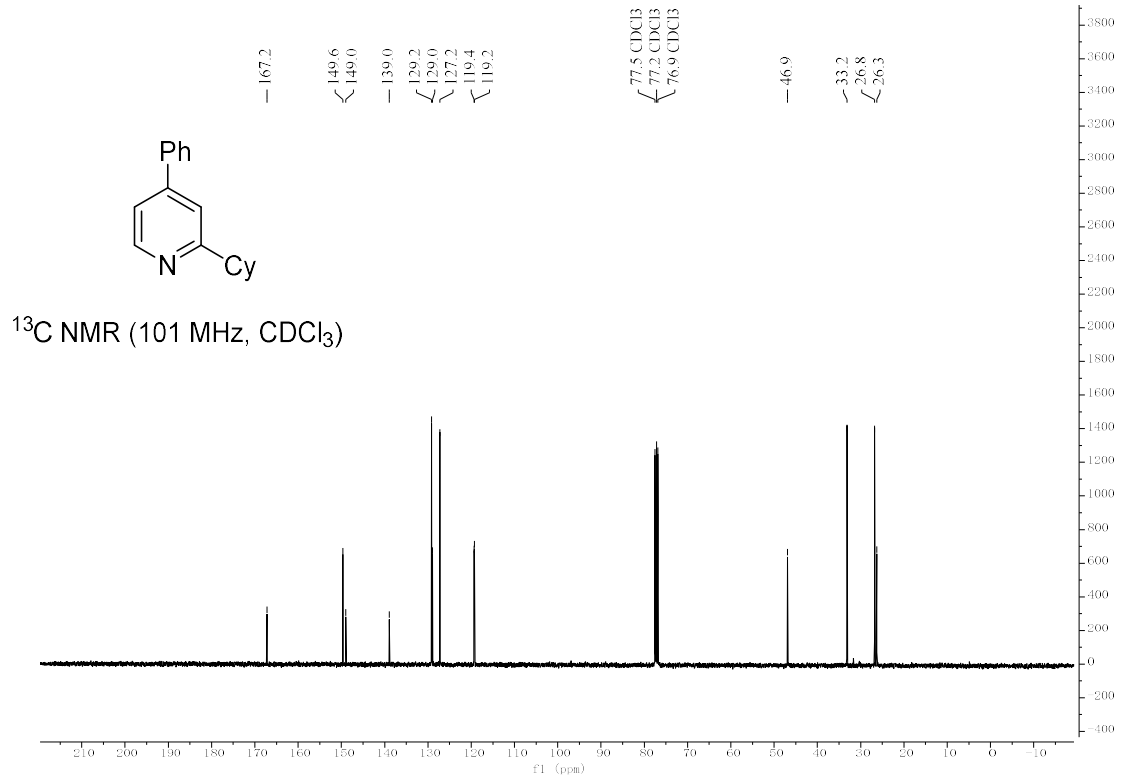


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 19

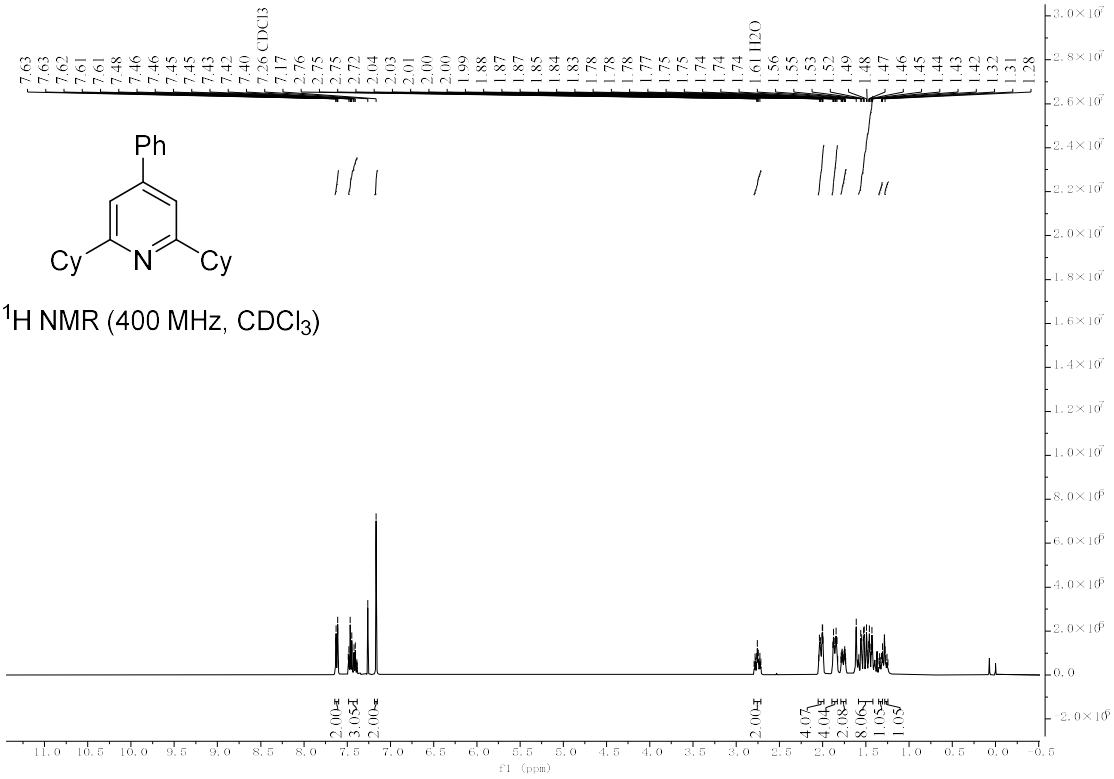


^{1}H NMR (400 MHz, $CDCl_3$)

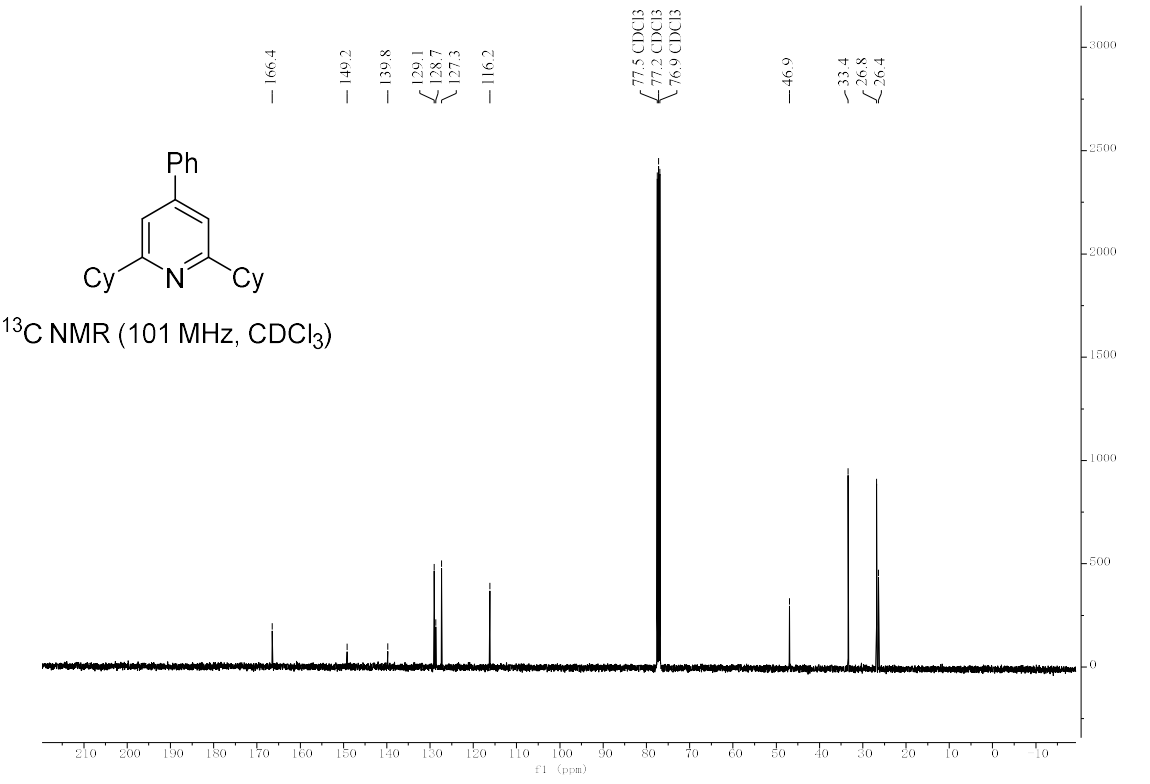


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 19'

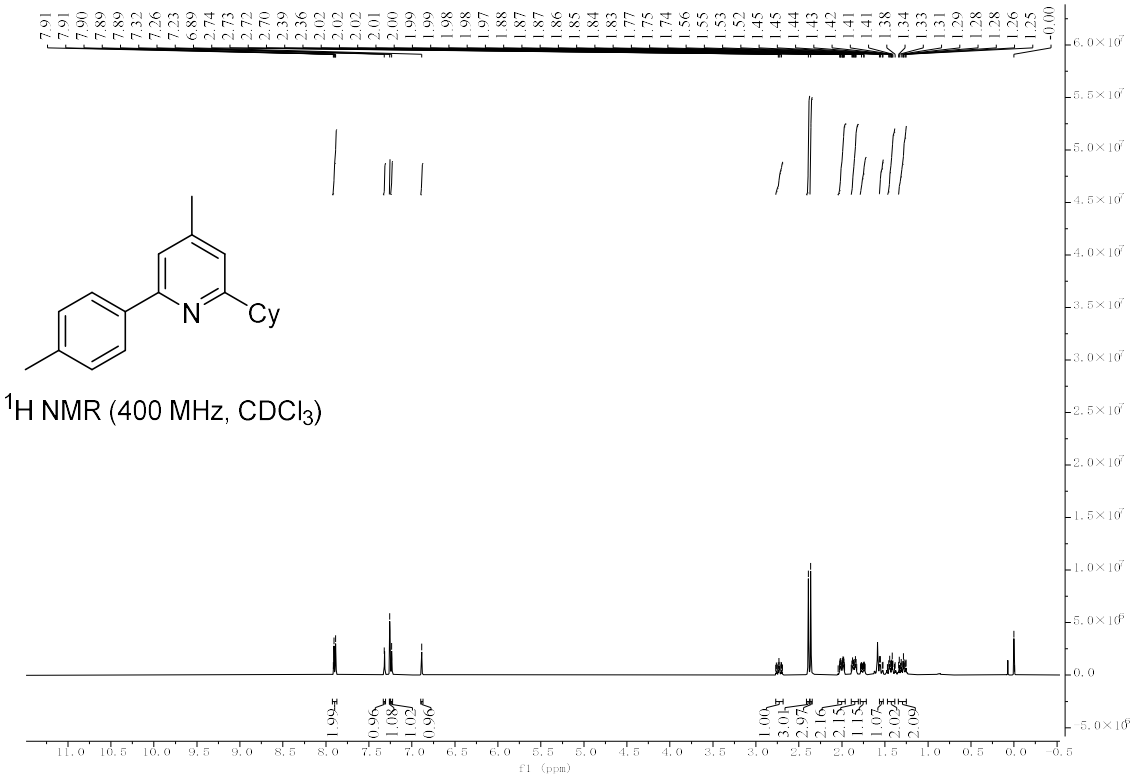


^{1}H NMR (400 MHz, $CDCl_3$)

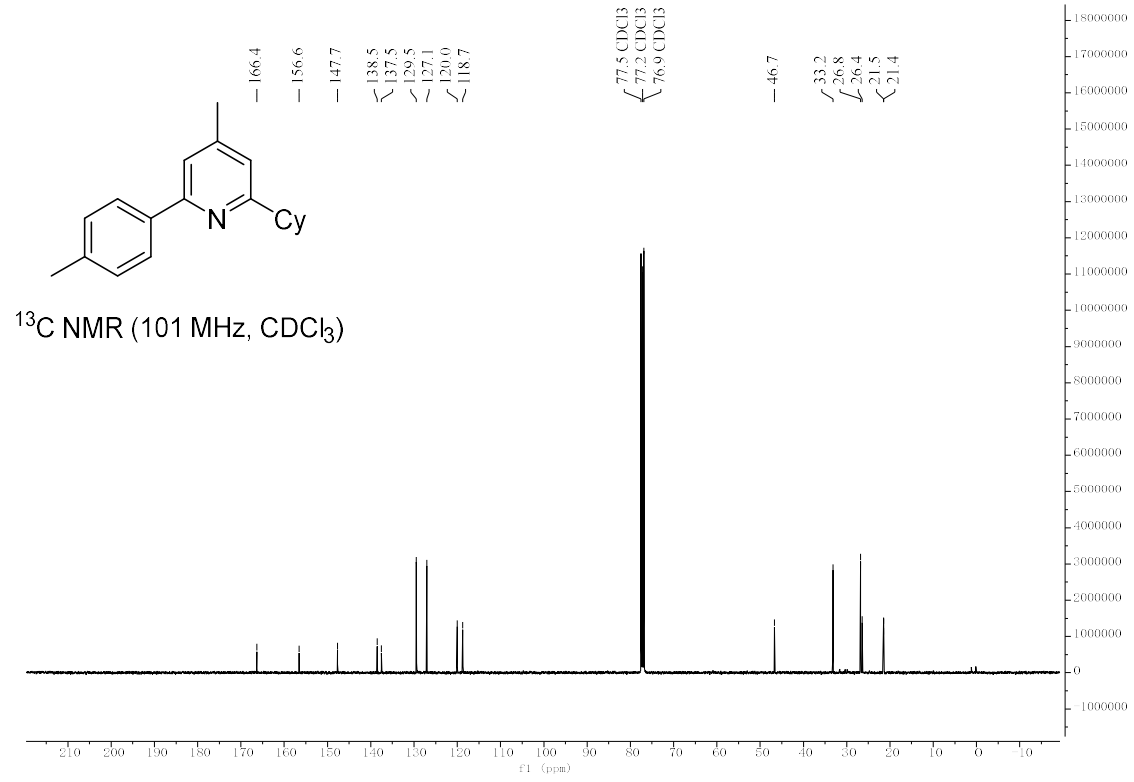


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 20

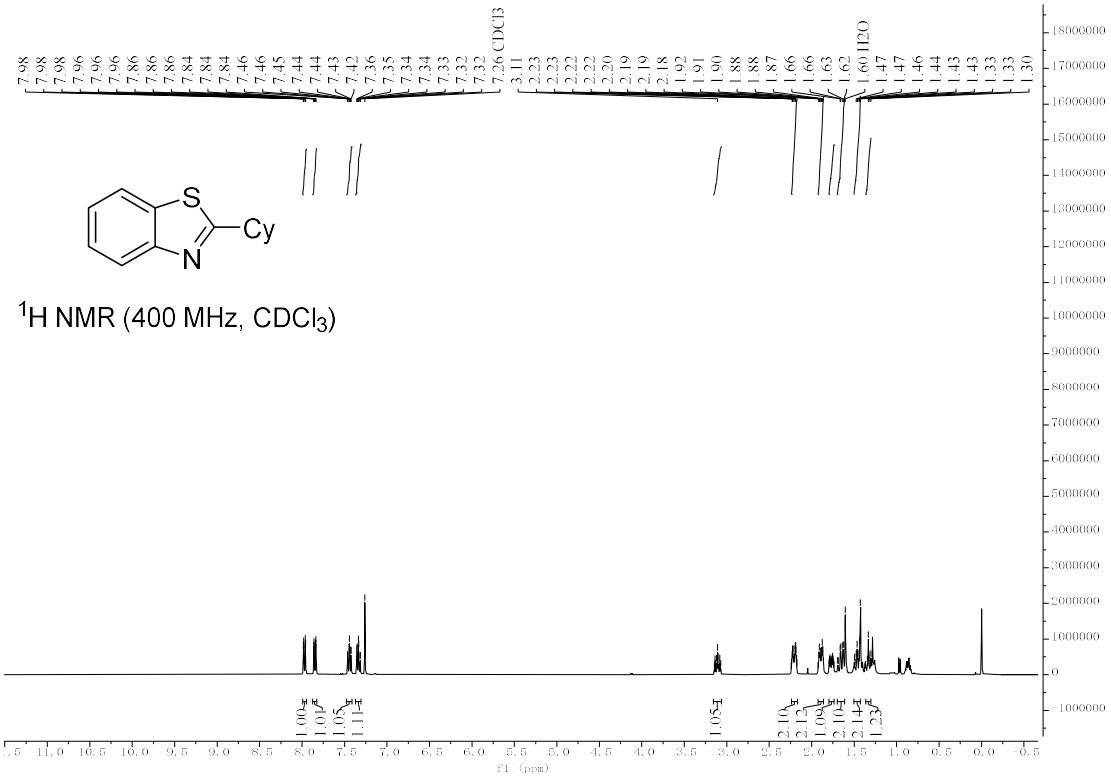


^{1}H NMR (400 MHz, $CDCl_3$)

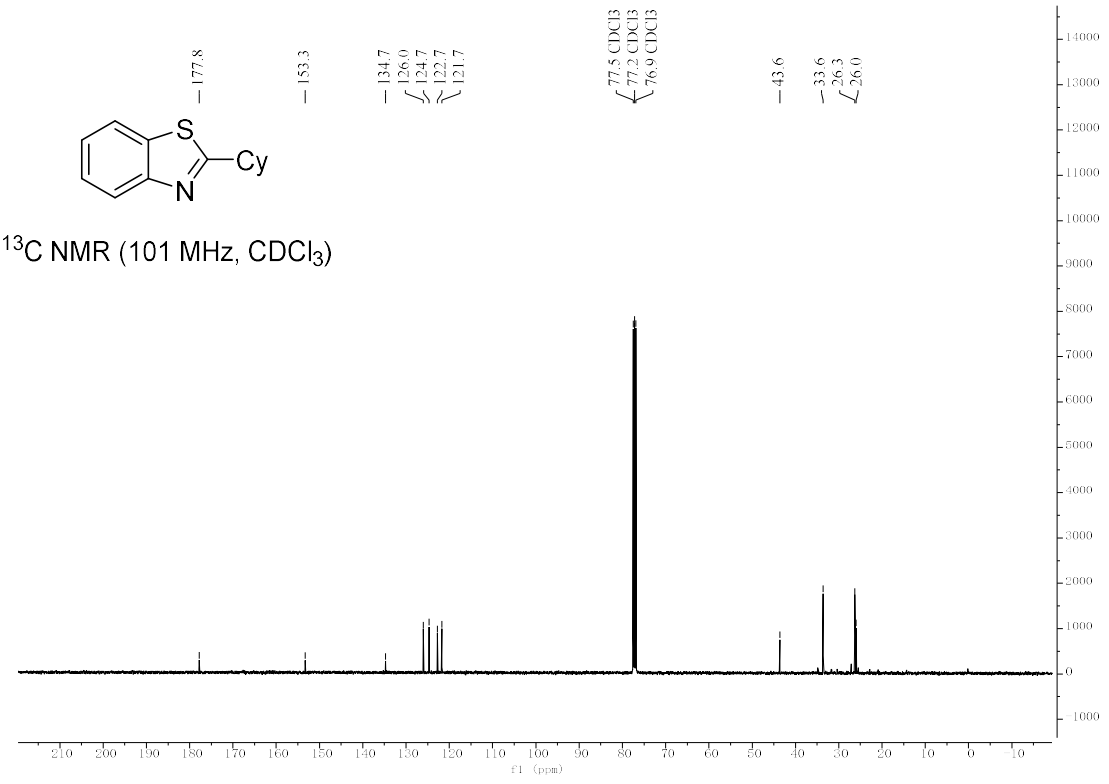


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 21

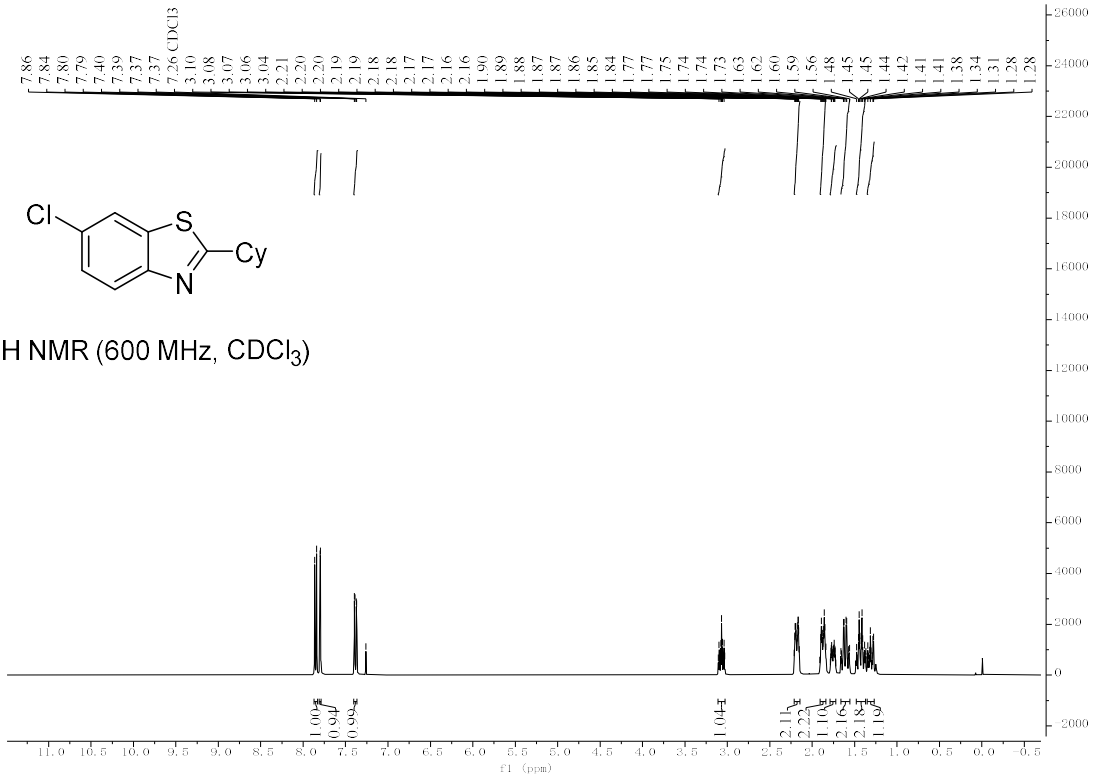


^{1}H NMR (400 MHz, $CDCl_3$)

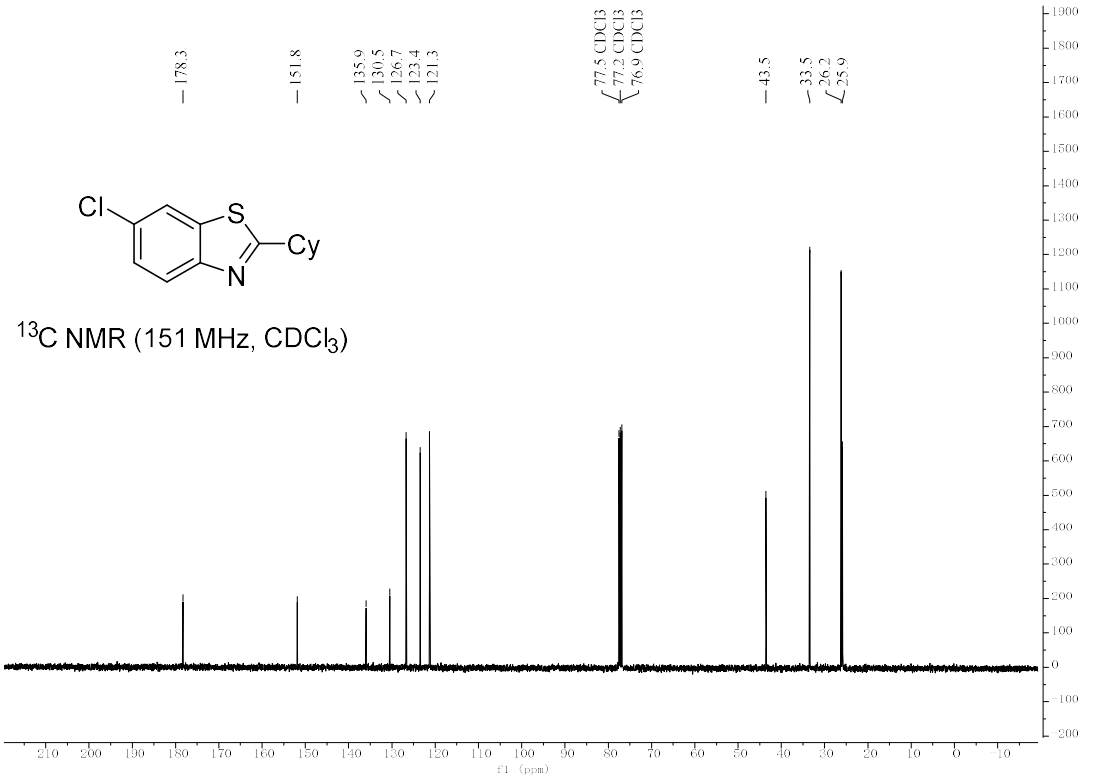


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 22

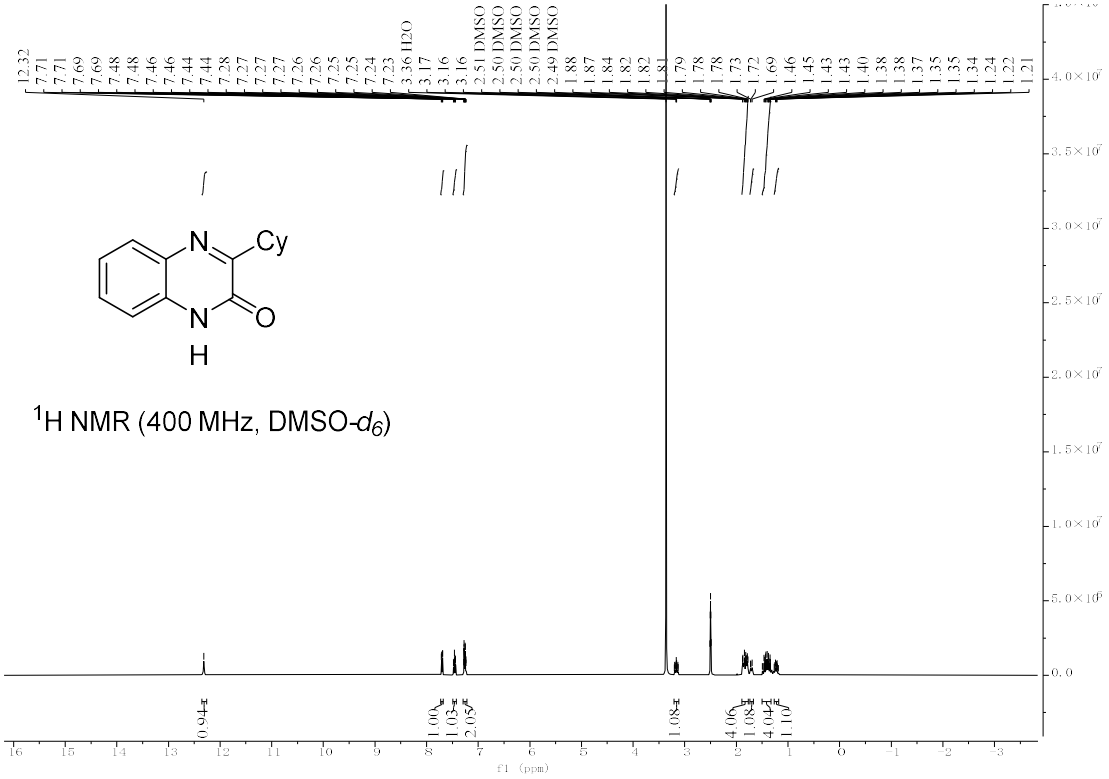


^{1}H NMR (600 MHz, $CDCl_3$)

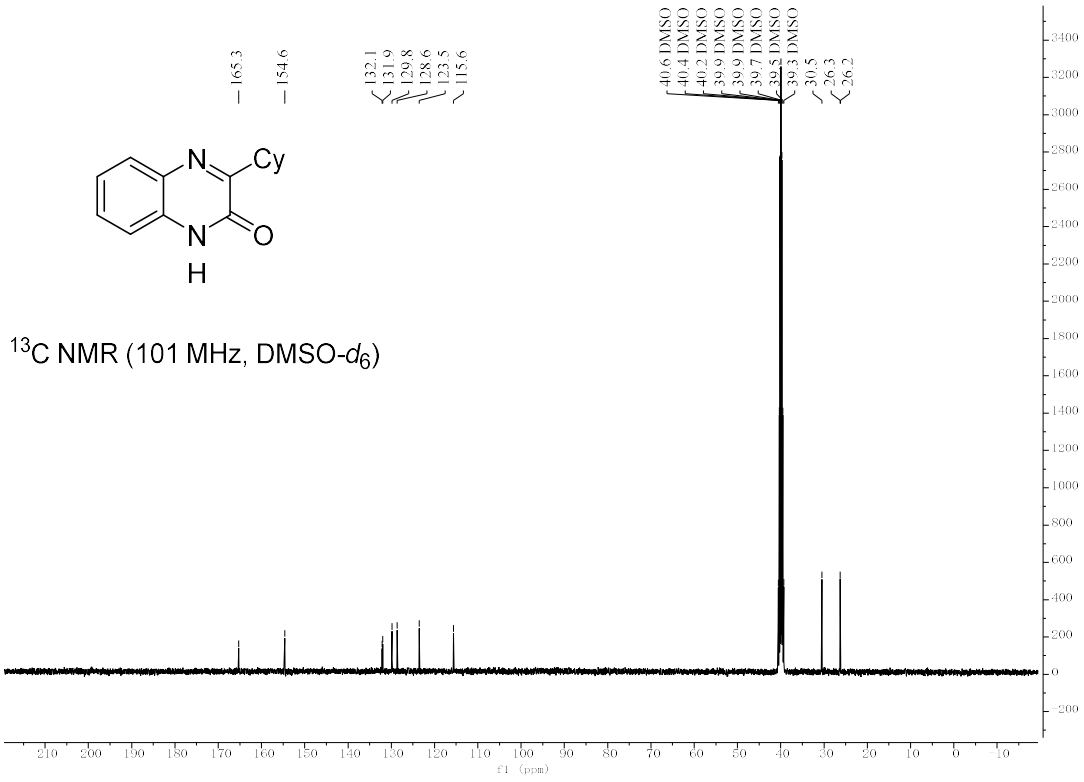


^{13}C NMR (151 MHz, $CDCl_3$)

Compound 23

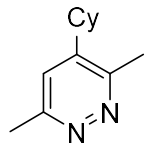


^{1}H NMR (400 MHz, DMSO-d_6)

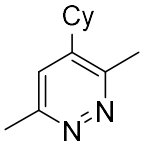


^{13}C NMR (101 MHz, DMSO-d_6)

Compound 24

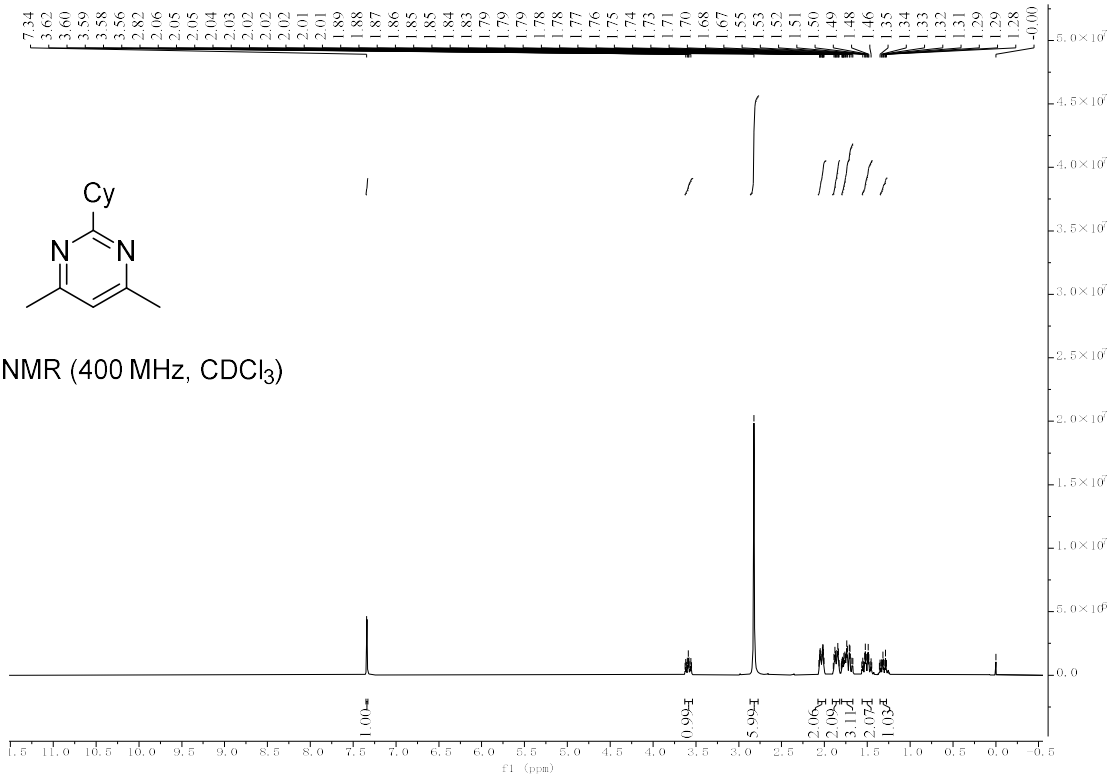


^{1}H NMR (400 MHz, $CDCl_3$)

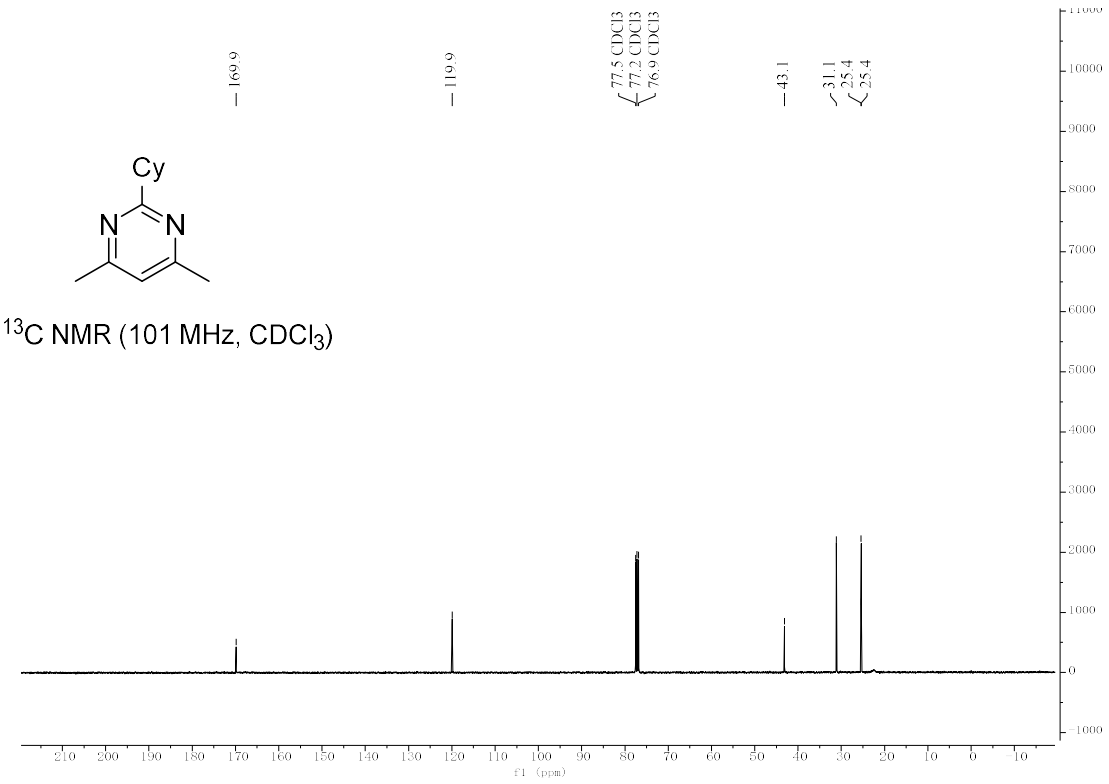


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 25

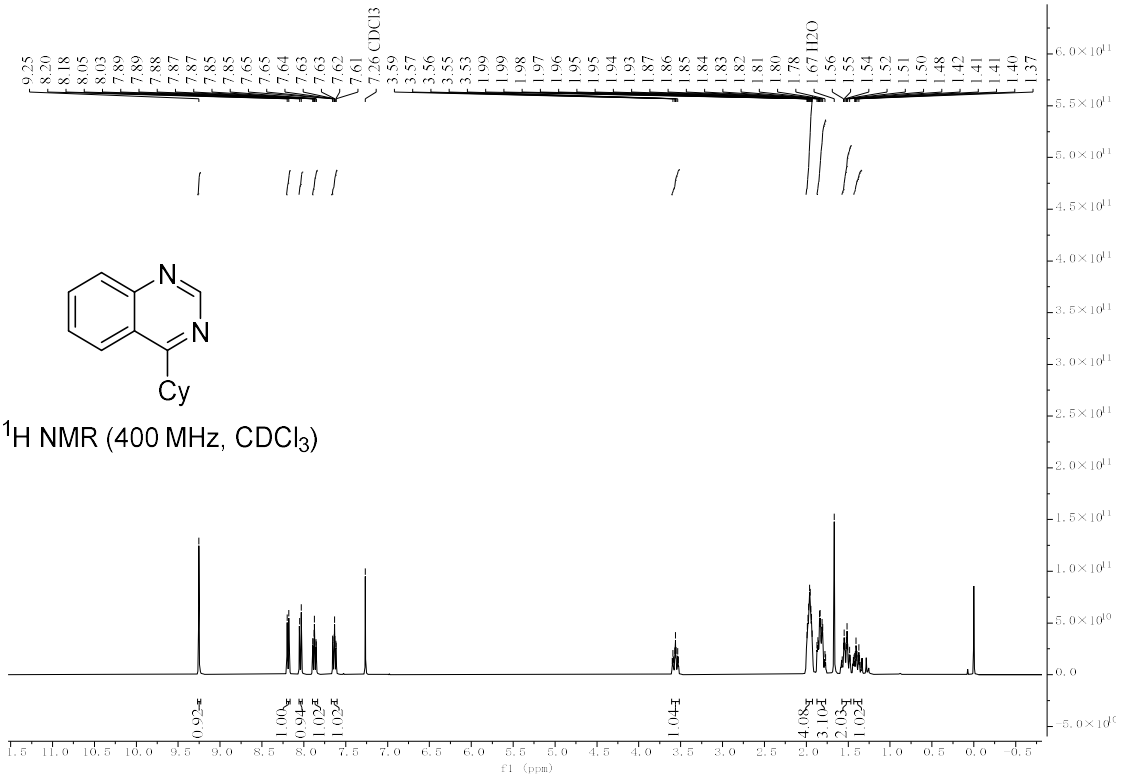


^{1}H NMR (400 MHz, $CDCl_3$)

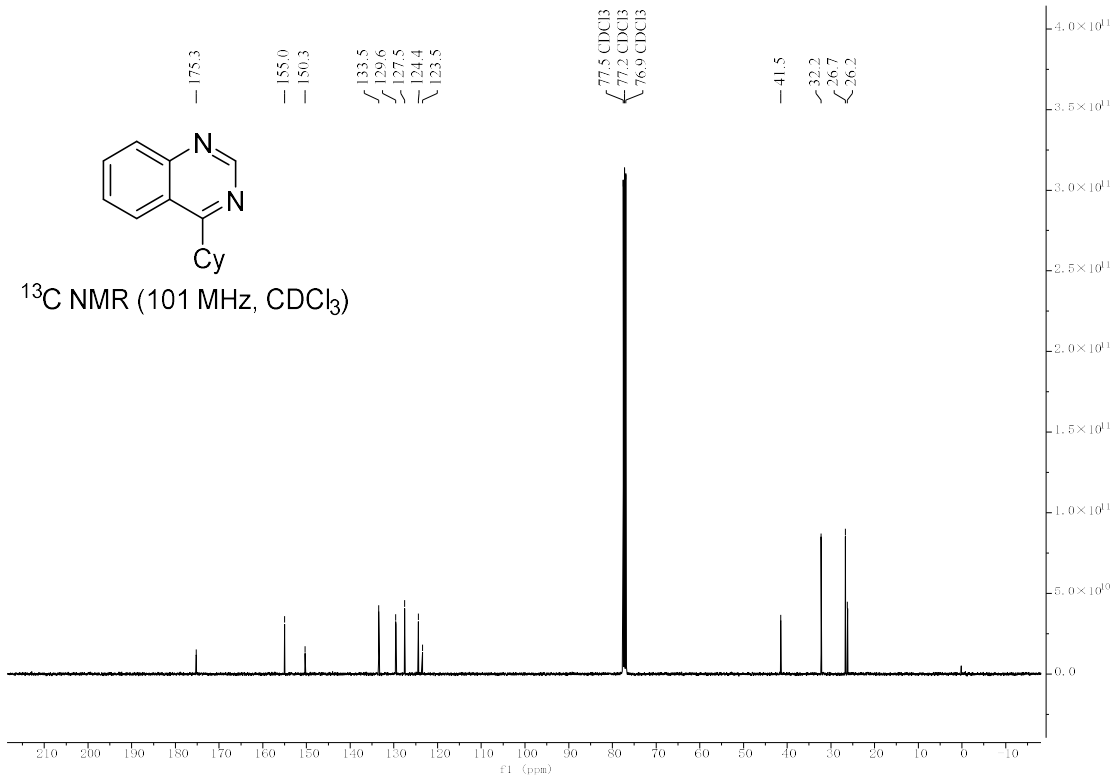


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 26

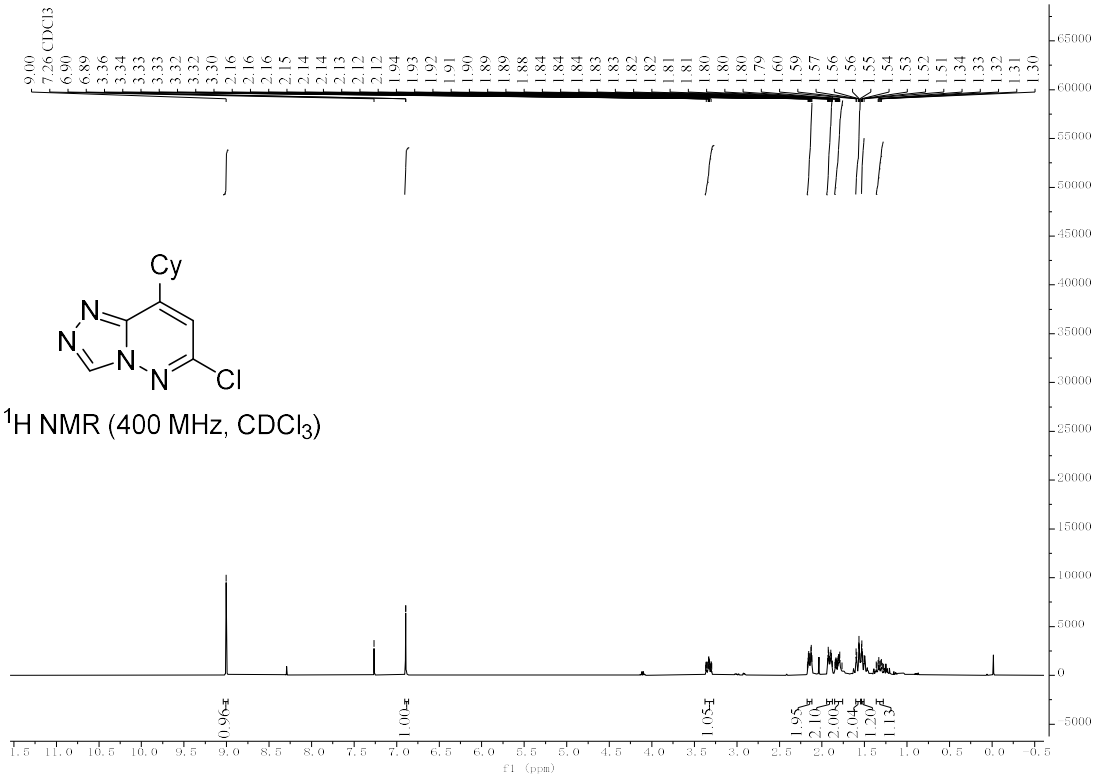


^{1}H NMR (400 MHz, $CDCl_3$)

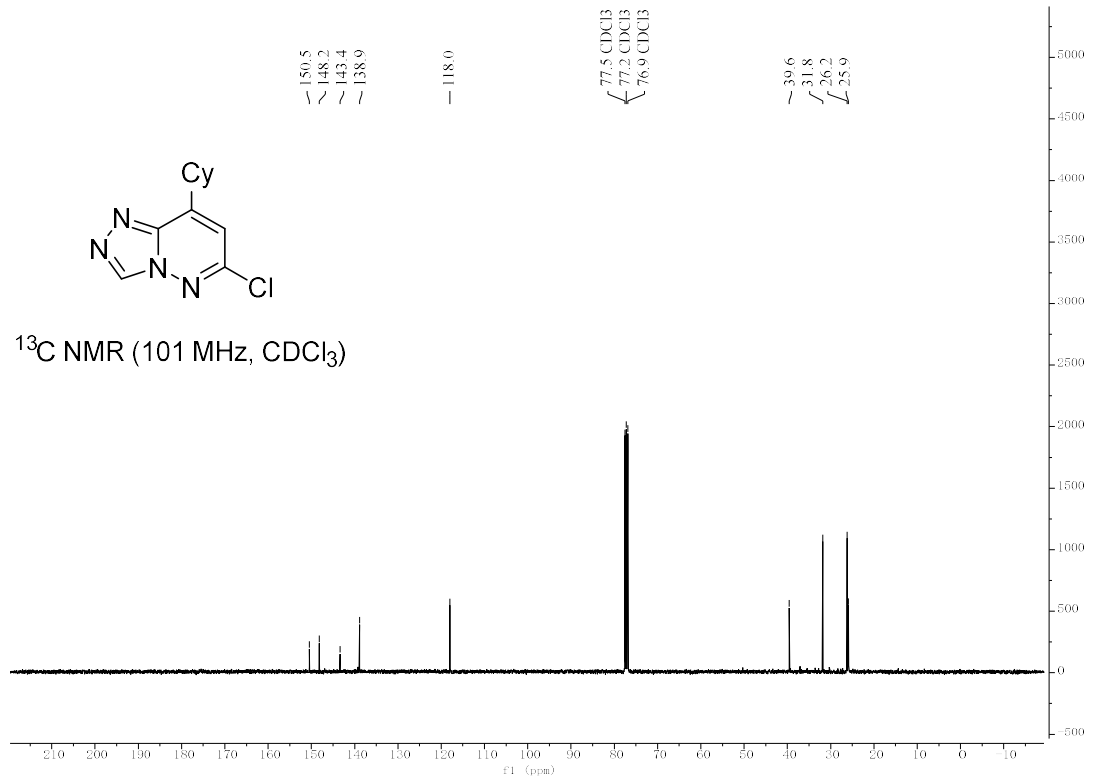


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 27

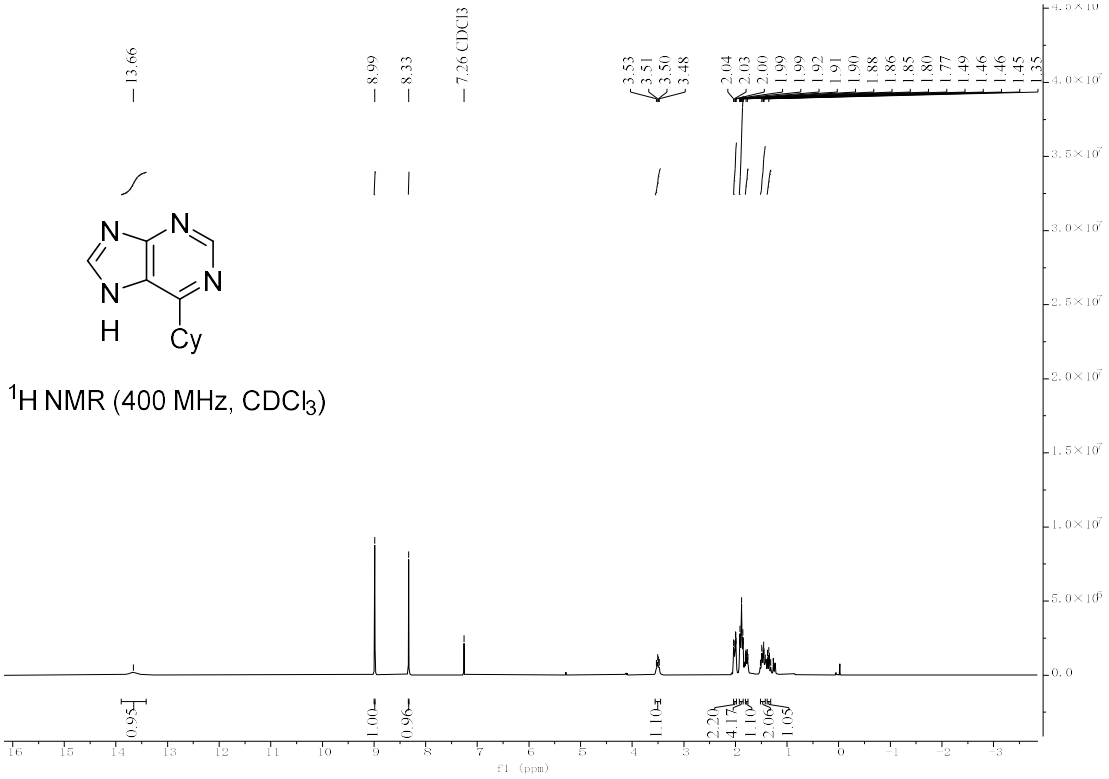


^{1}H NMR (400 MHz, $CDCl_3$)

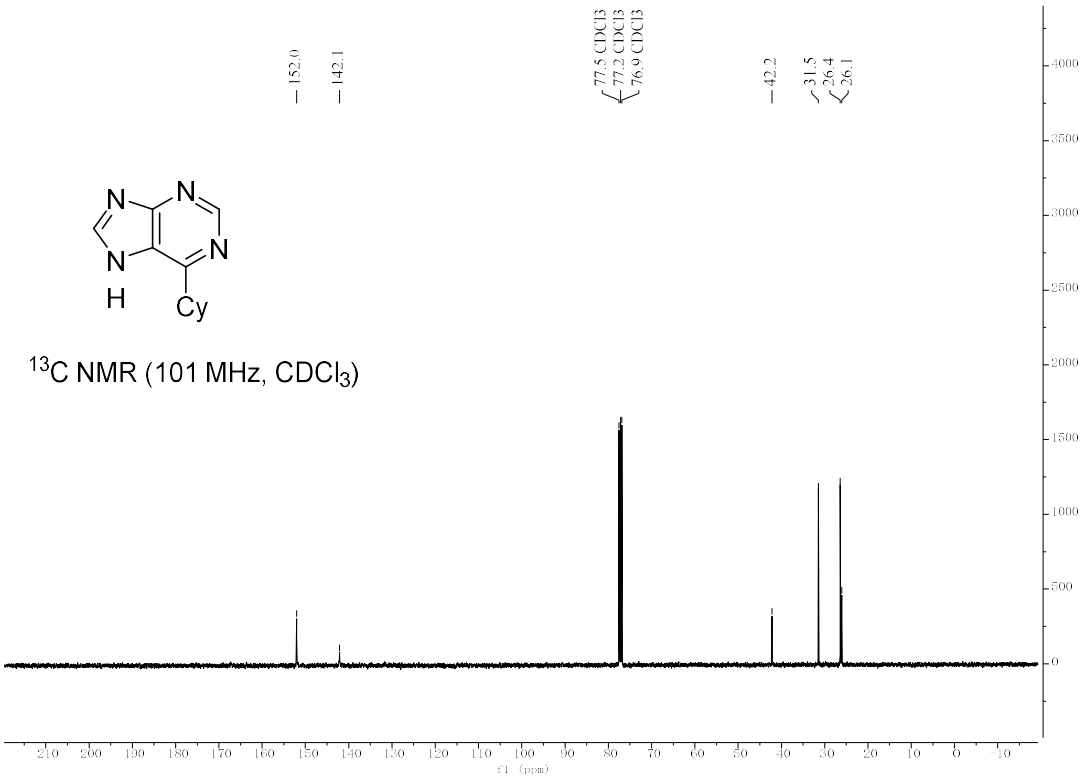


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 28

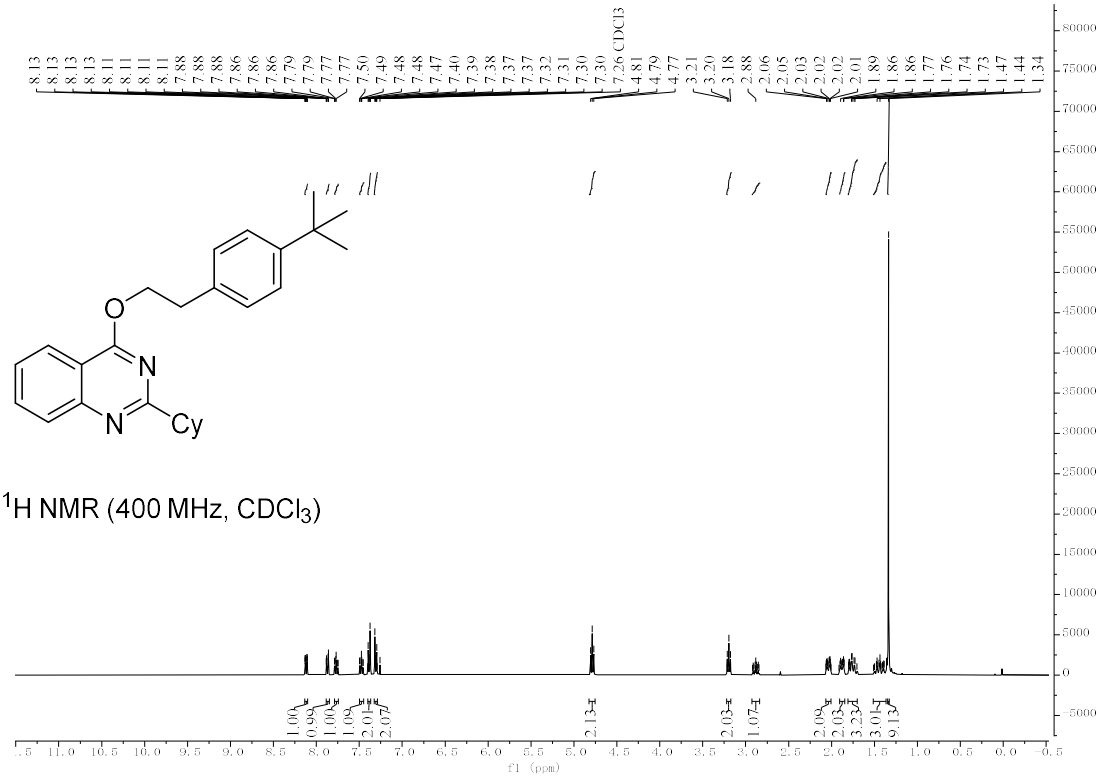


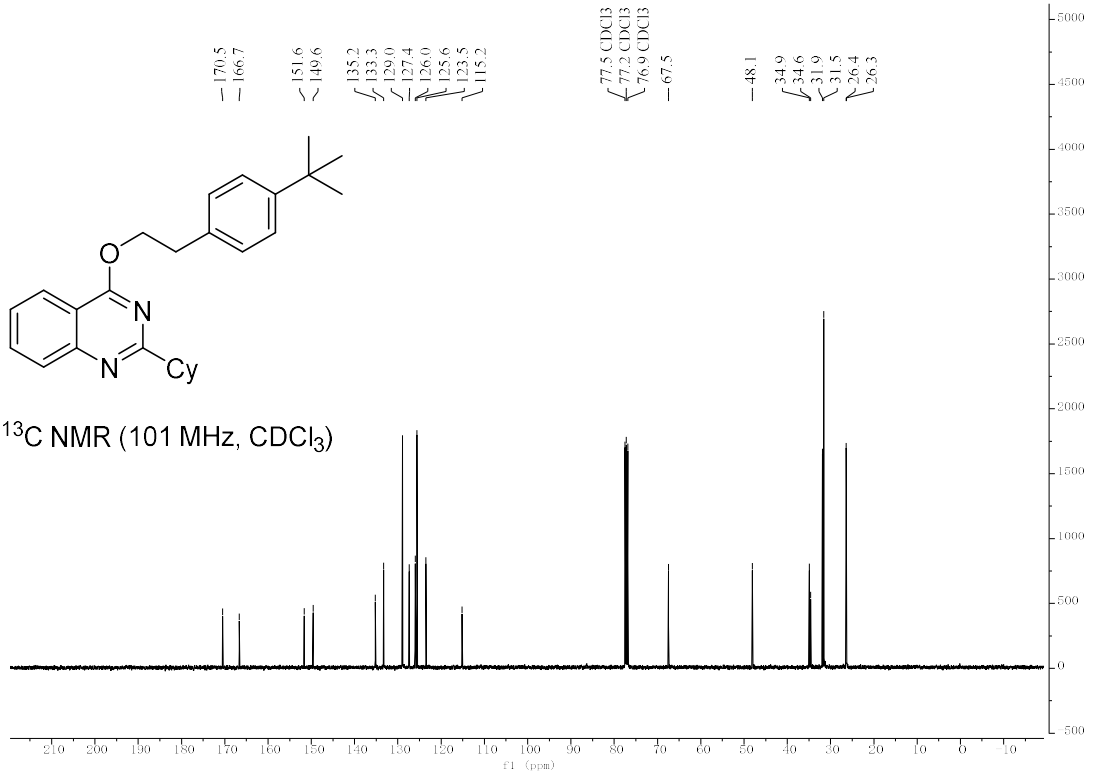
^{1}H NMR (400 MHz, $CDCl_3$)



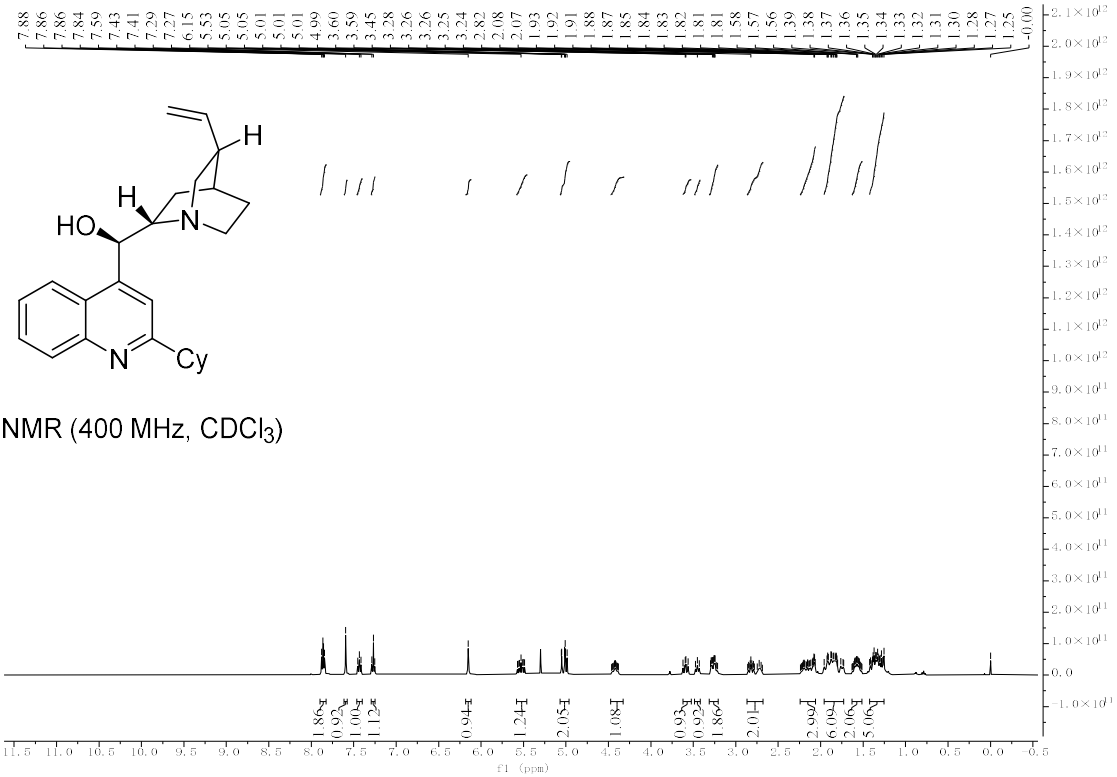
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 29

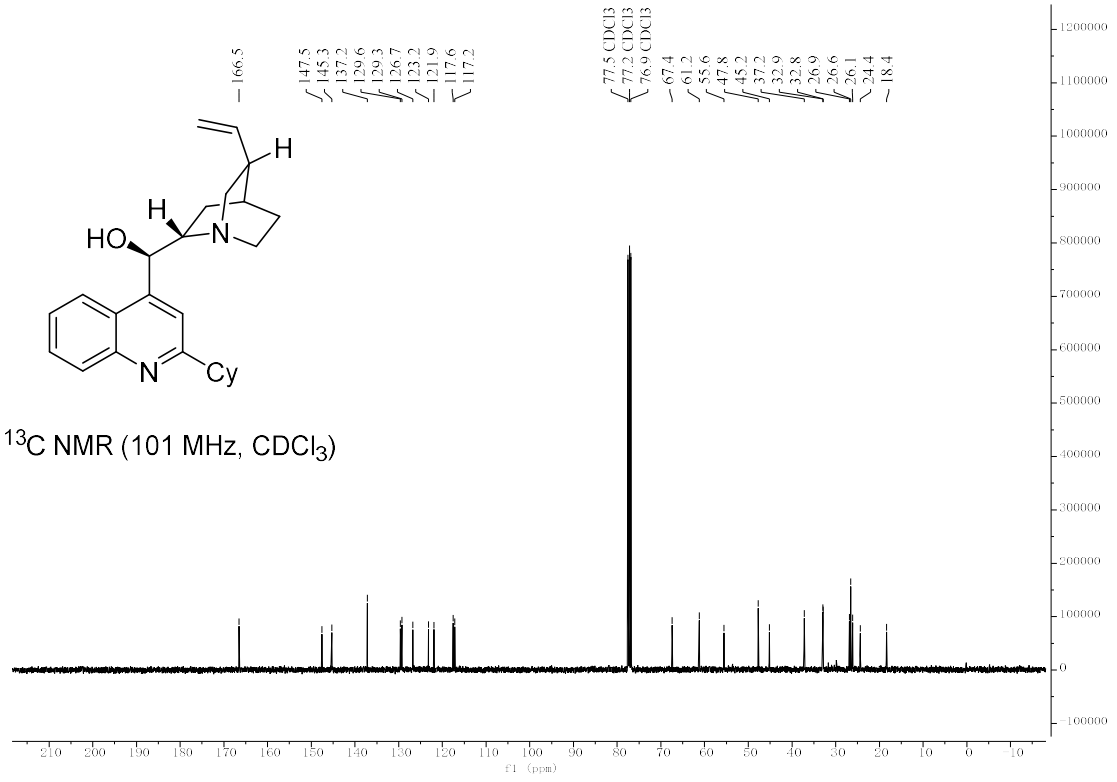




Compound 30

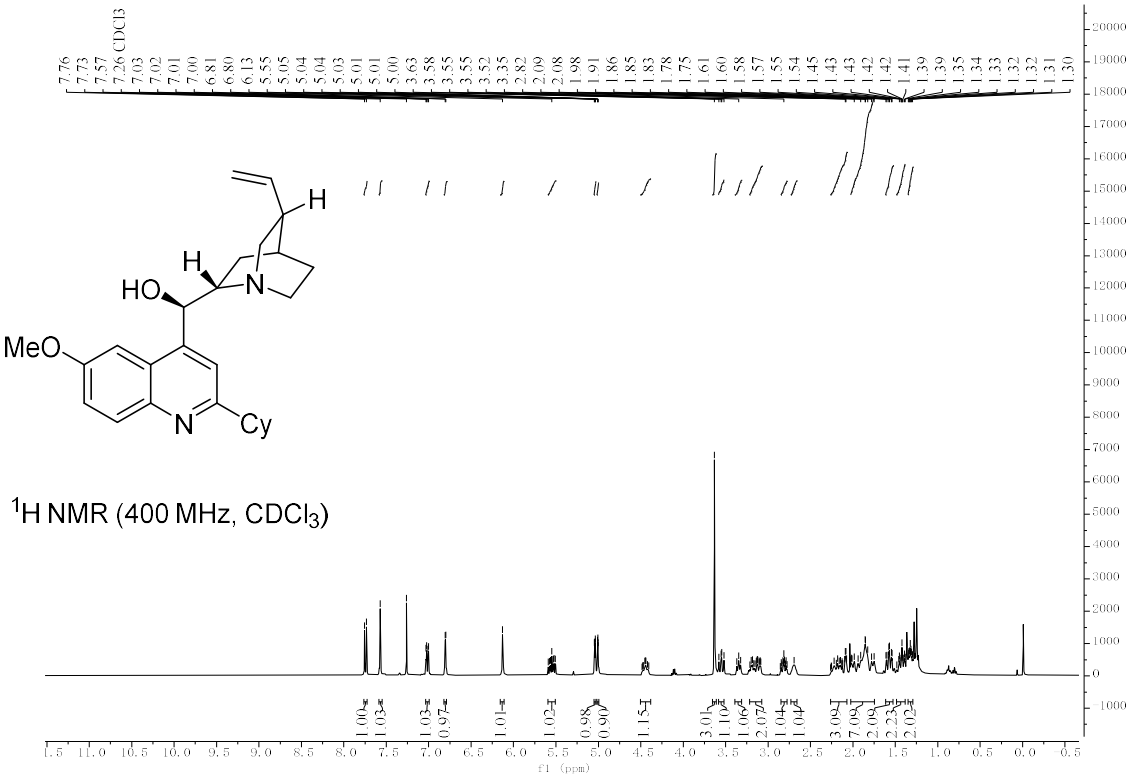


^{1}H NMR (400 MHz, $CDCl_3$)

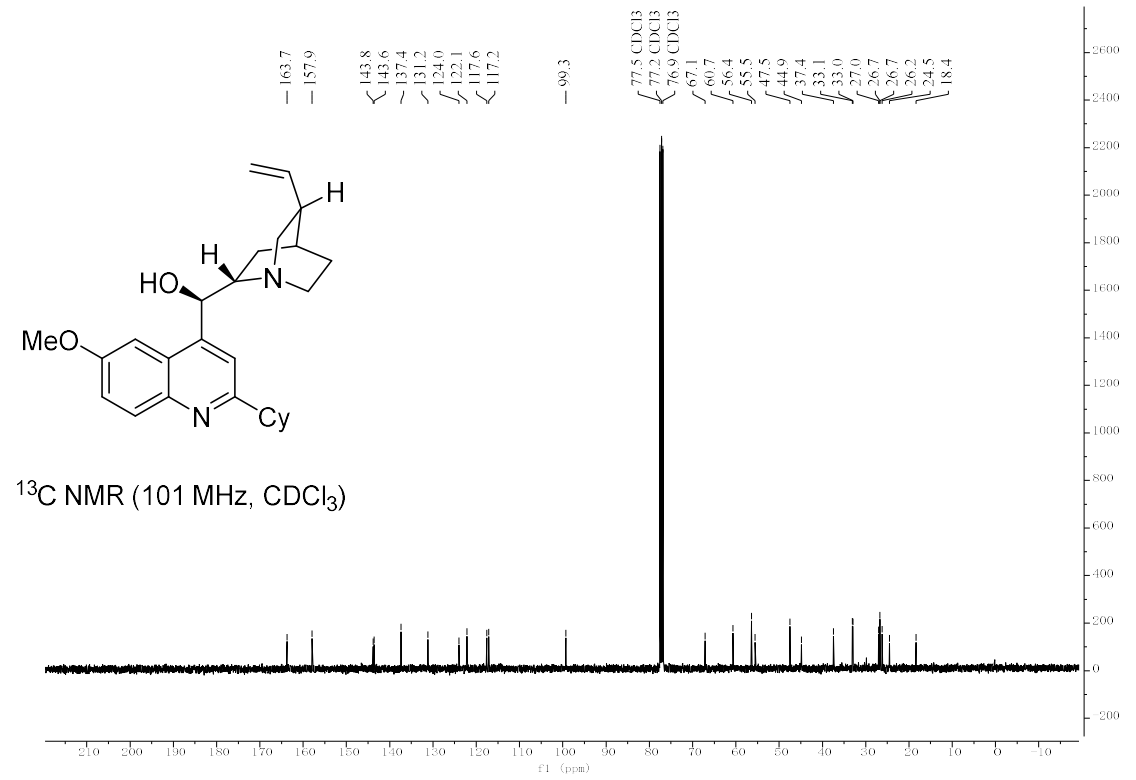


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 31

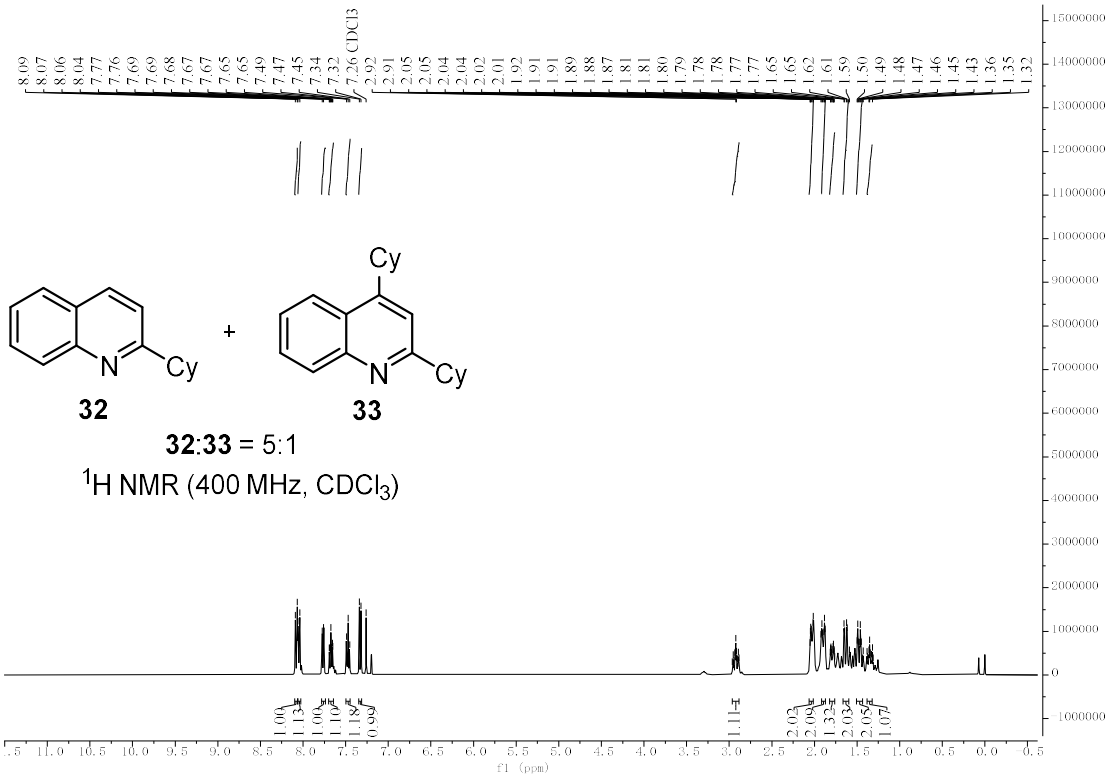


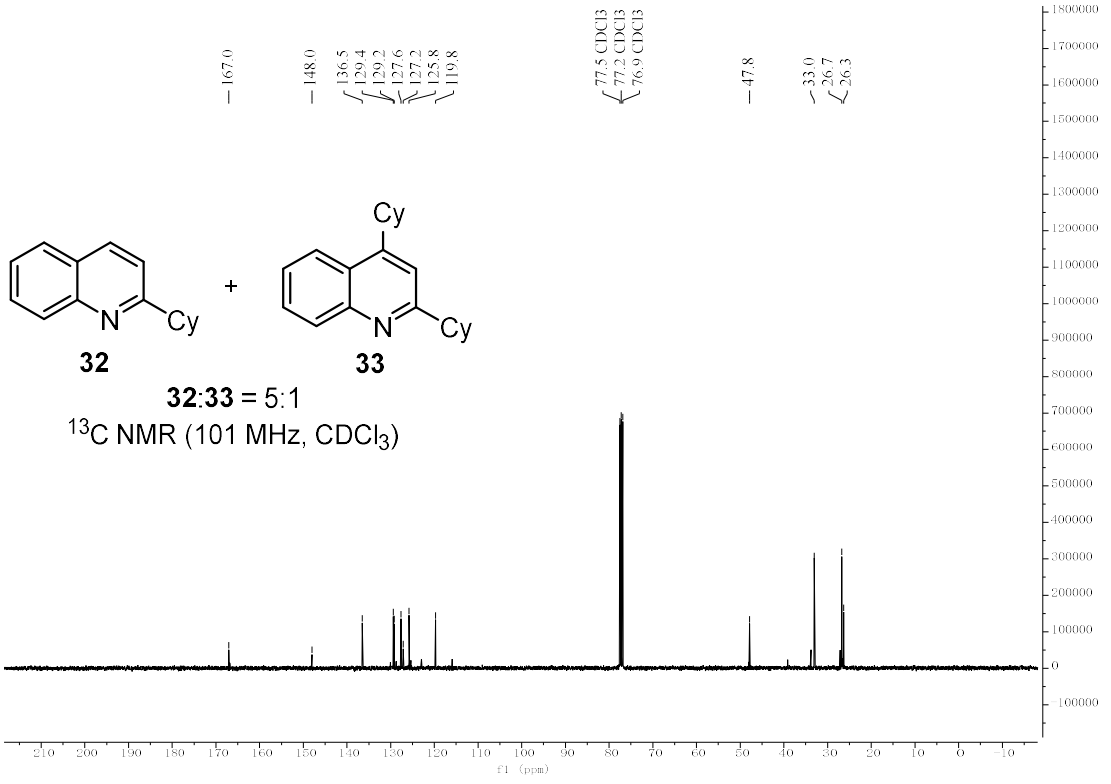
^{1}H NMR (400 MHz, $CDCl_3$)



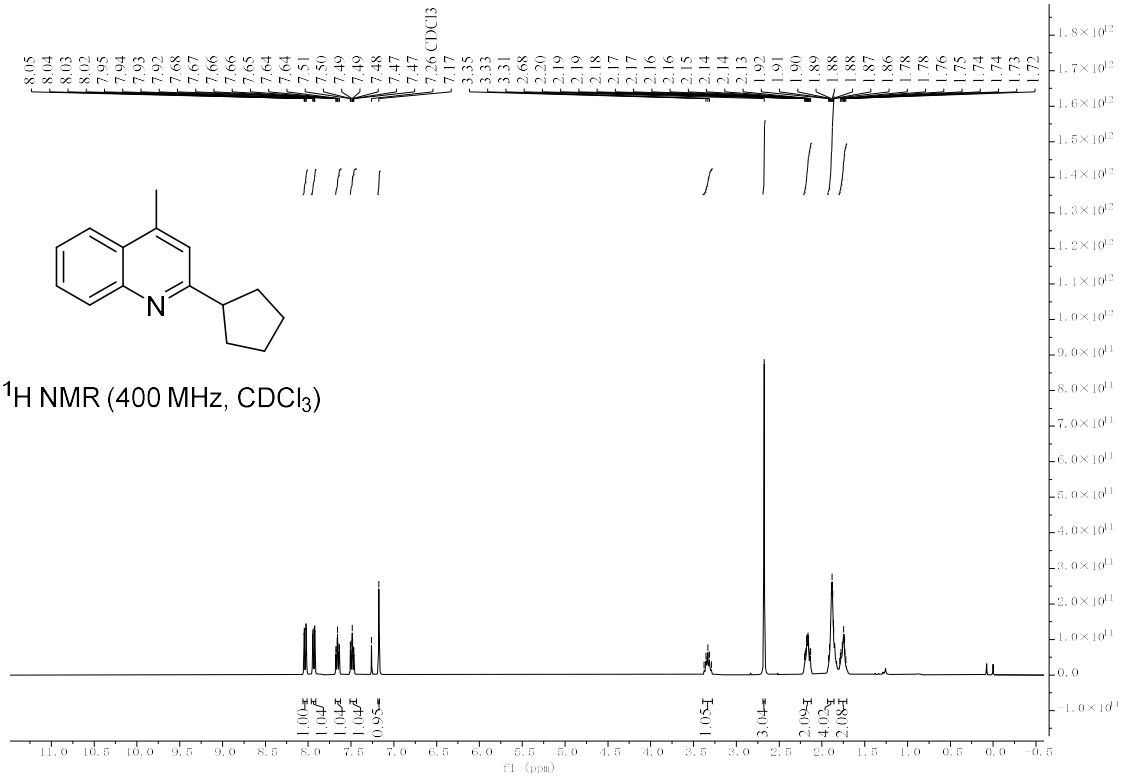
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 32 and 33

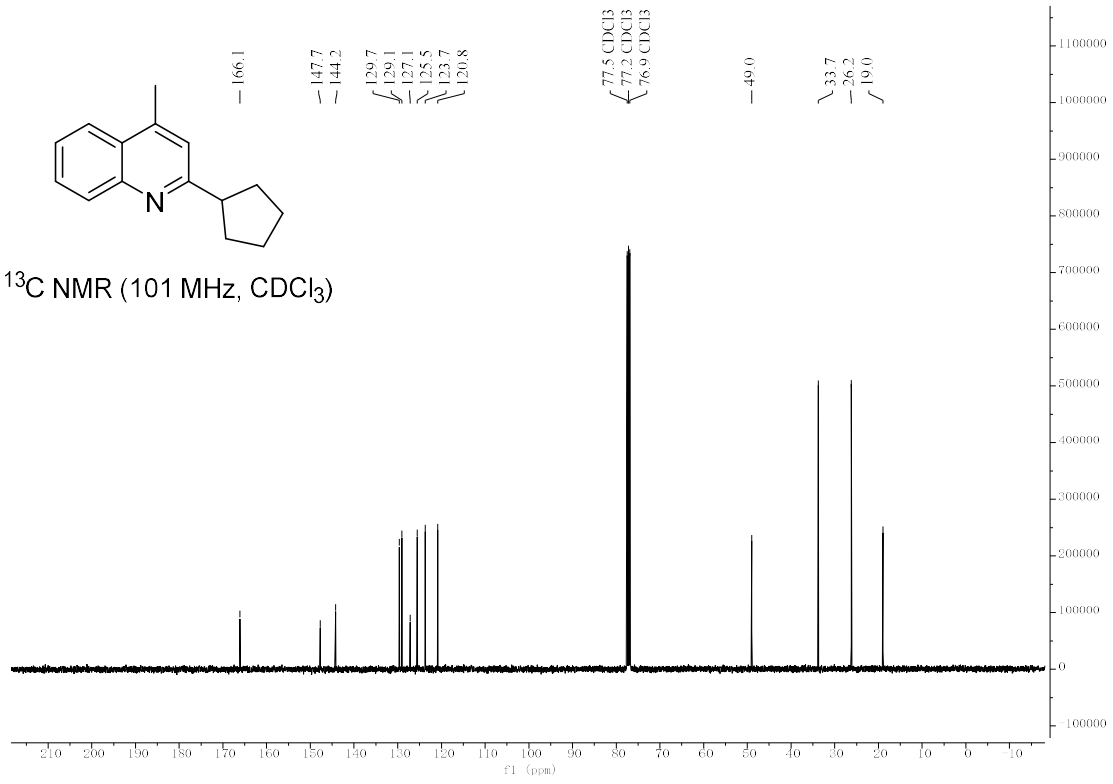




Compound 34

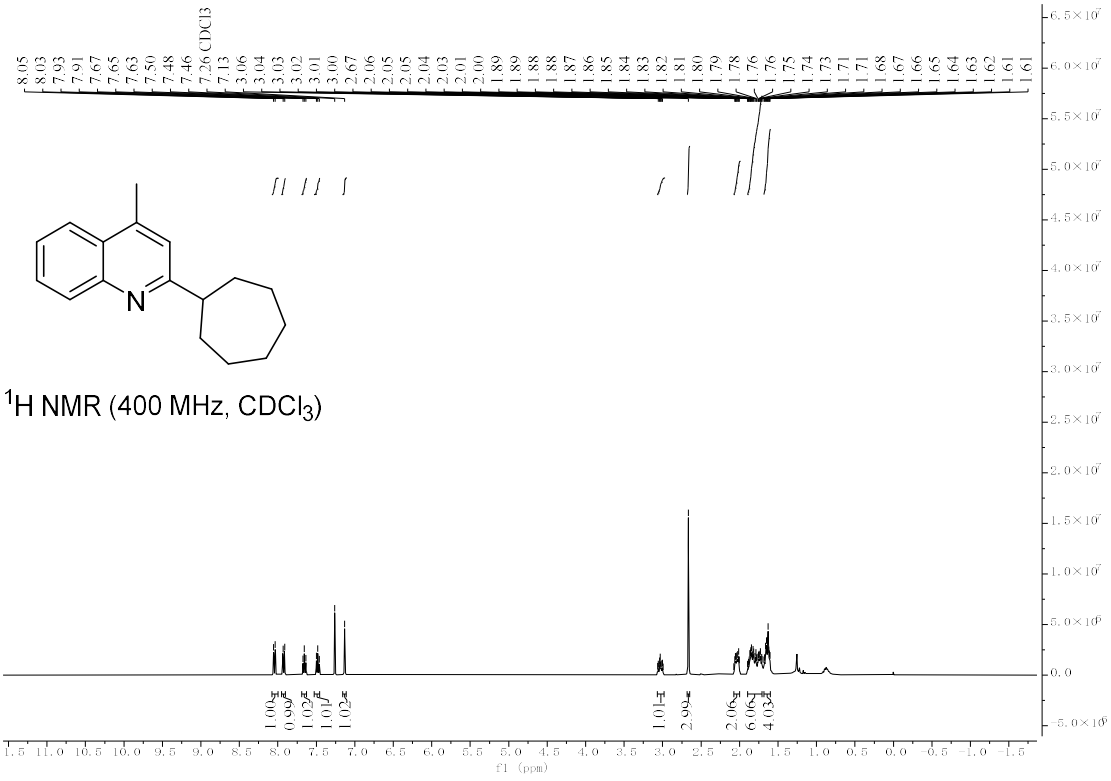


^{1}H NMR (400 MHz, $CDCl_3$)

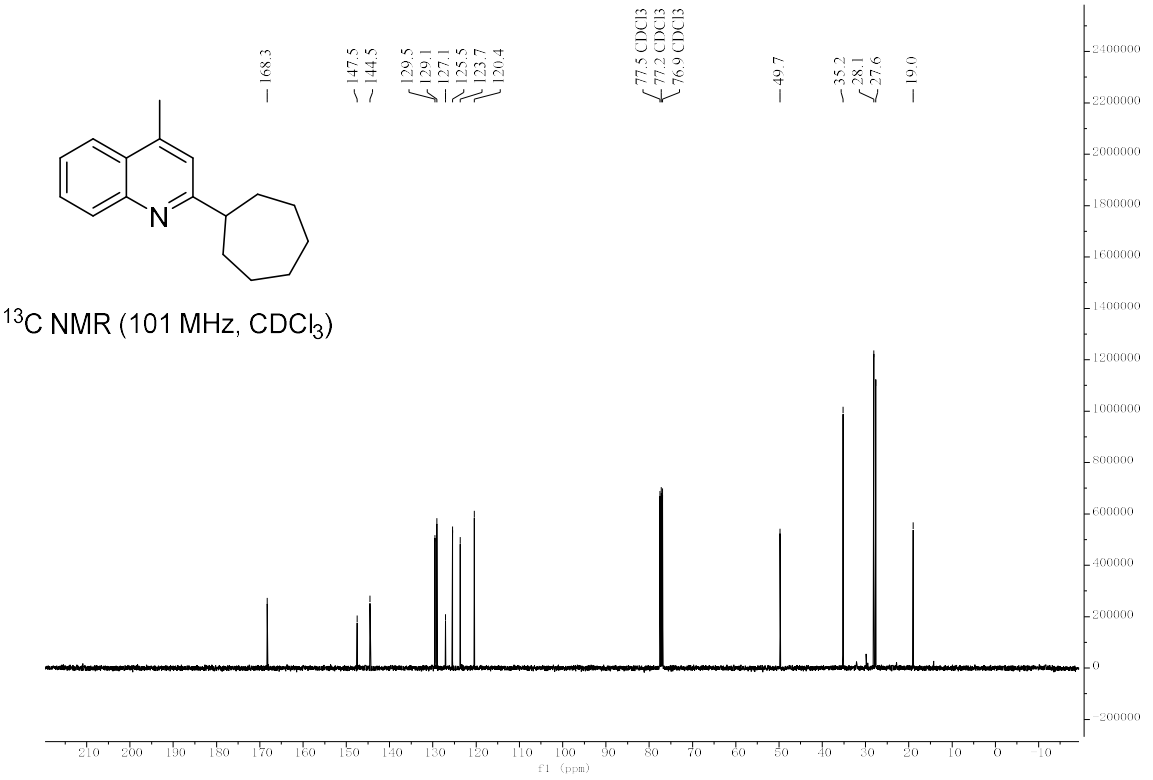


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 35

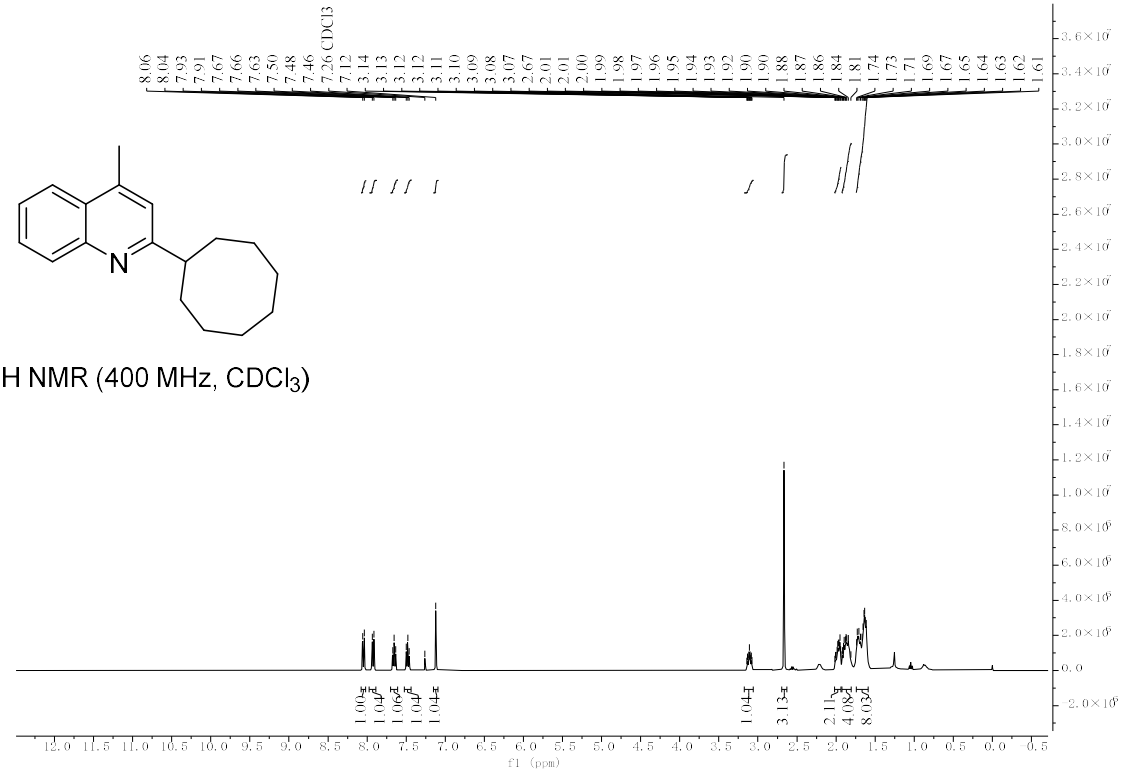


^{1}H NMR (400 MHz, $CDCl_3$)

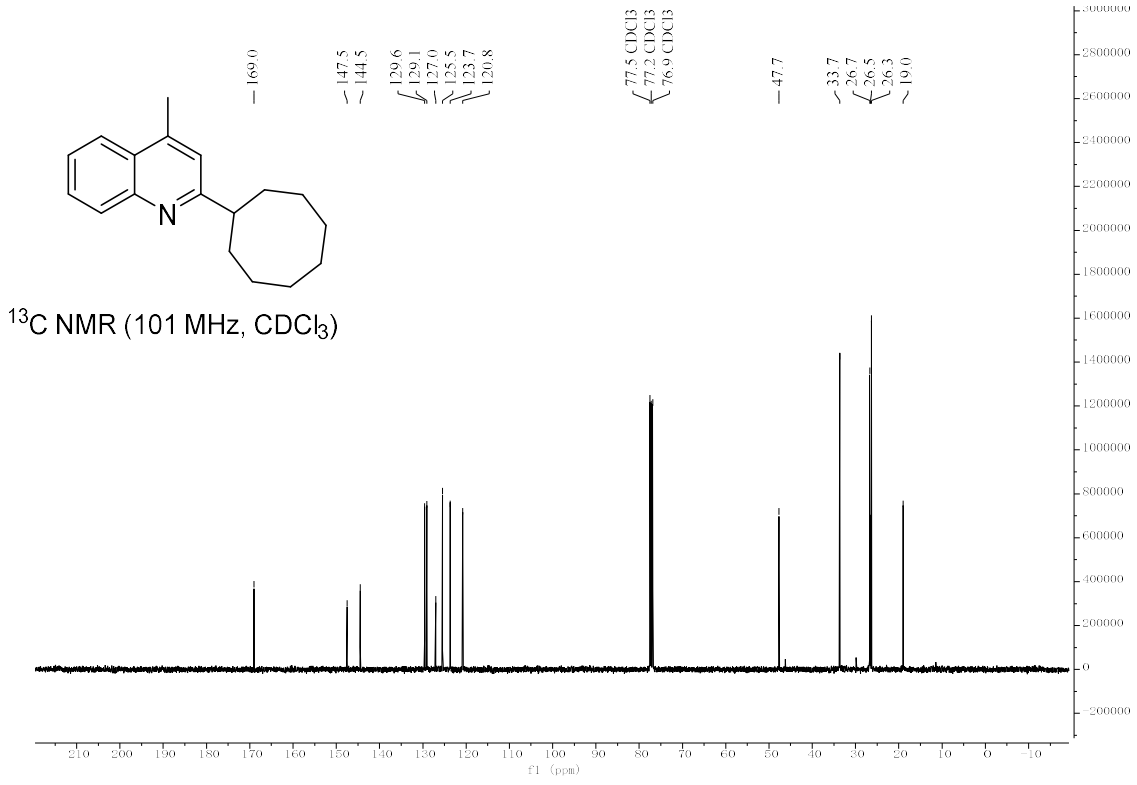


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 36

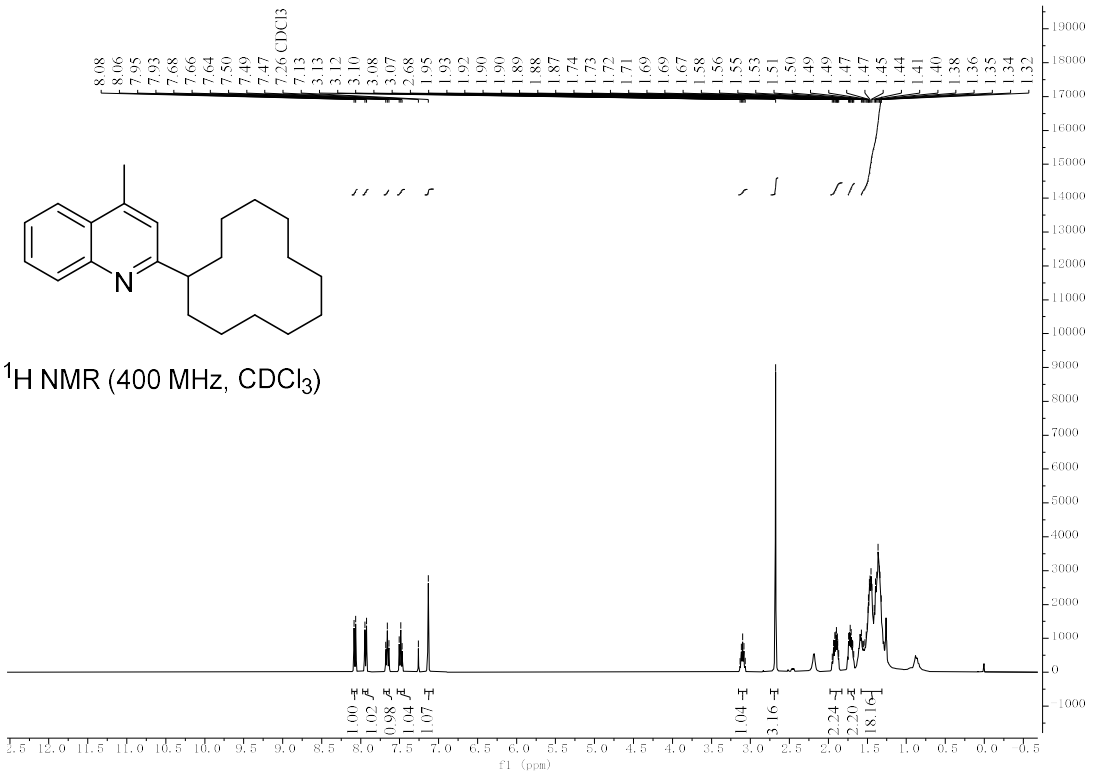


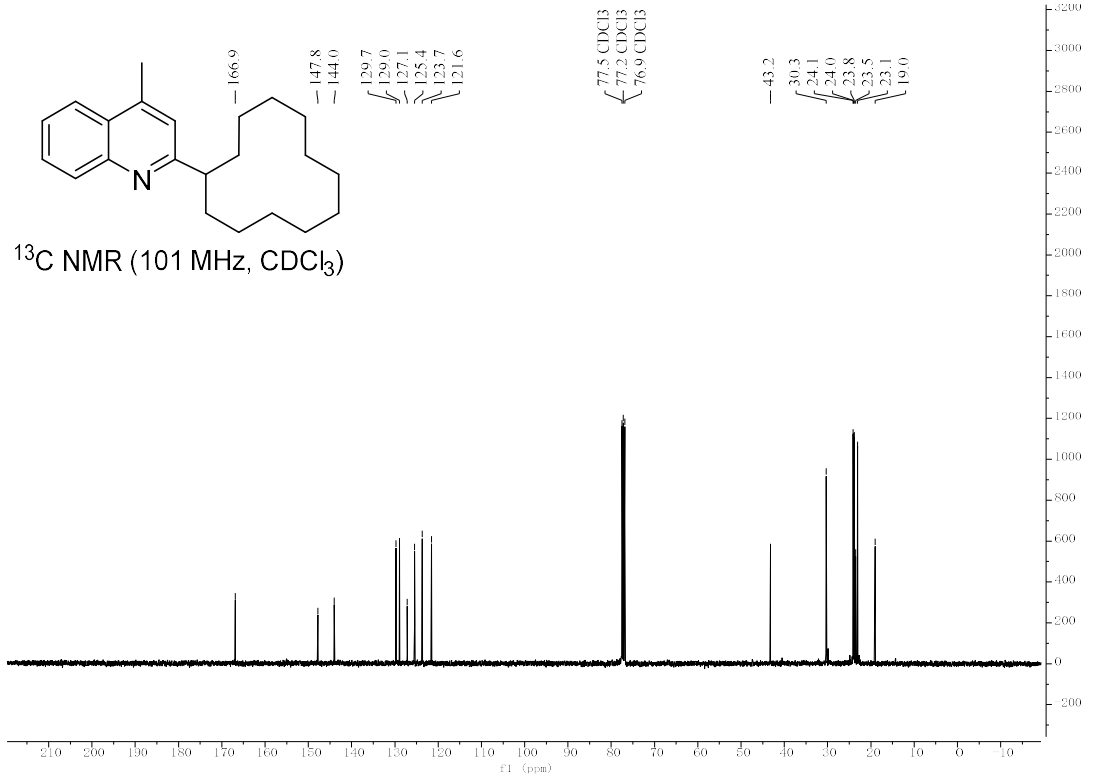
^{1}H NMR (400 MHz, $CDCl_3$)



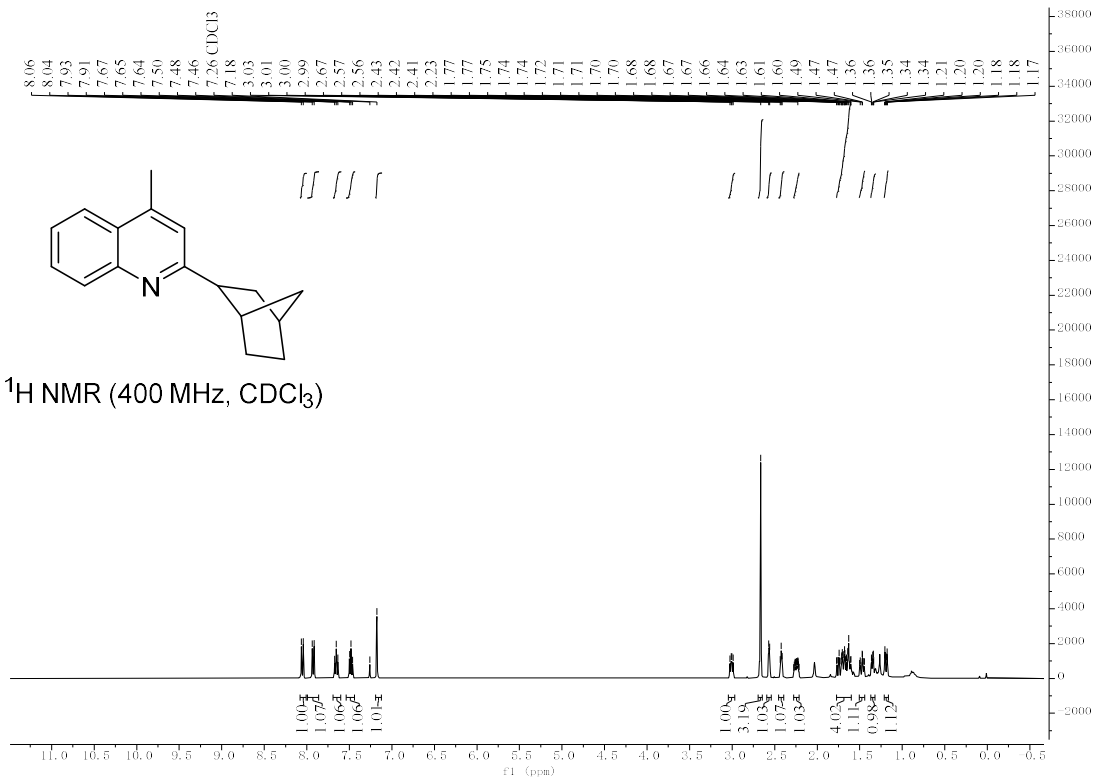
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 37

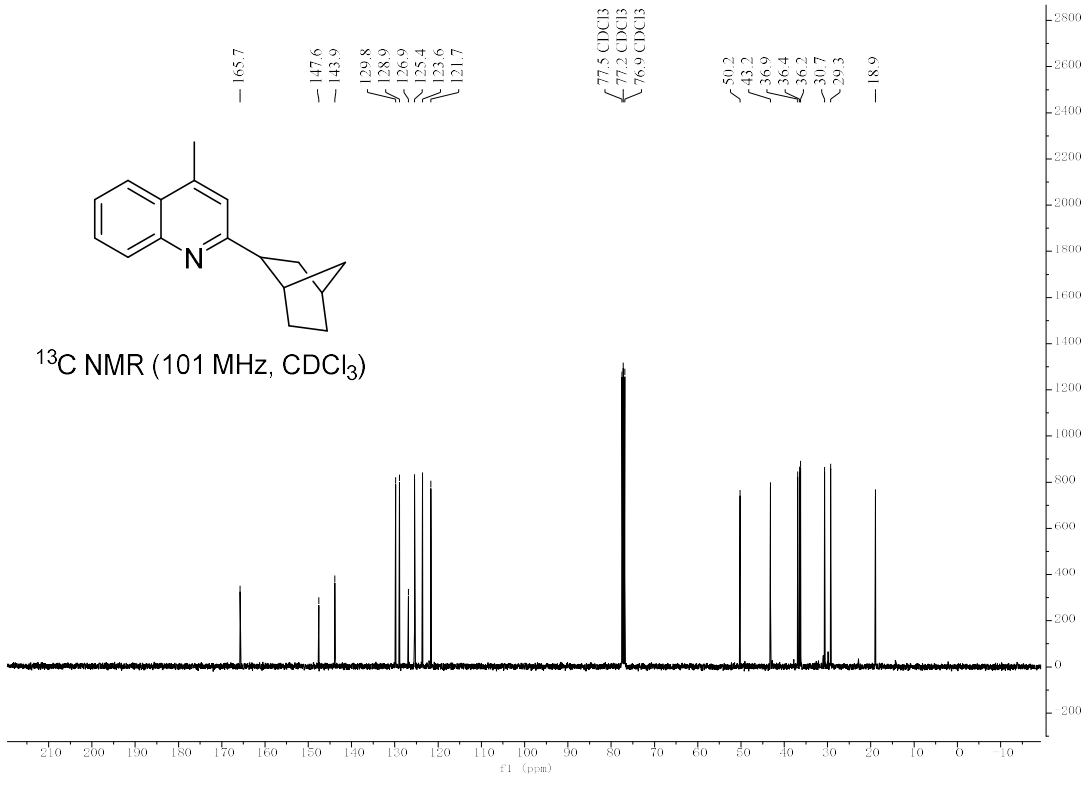

8.08
8.06
7.95
7.93
7.68
7.66
7.64
7.50
7.49
7.47
7.26 CDCl3
7.13
3.13
3.12
3.10
3.08
3.07
2.68
1.95
1.93
1.92
1.90
1.90
1.89
1.88
1.87
1.74
1.73
1.72
1.71
1.69
1.69
1.67
1.58
1.56
1.55
1.53
1.51
1.50
1.49
1.49
1.47
1.47
1.45
1.44
1.41
1.40
1.38
1.36
1.35
1.34
1.32
N
1H NMR (400 MHz, CDCl3)
1.00
1.02
0.98
1.04
1.07
1.04
3.16
2.24
2.20
18.16
f1 (ppm)


166.9
147.8
144.0
129.7
129.0
127.1
125.4
123.7
121.6
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
43.2
30.3
24.1
24.0
23.8
23.5
23.1
19.0
N
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 38

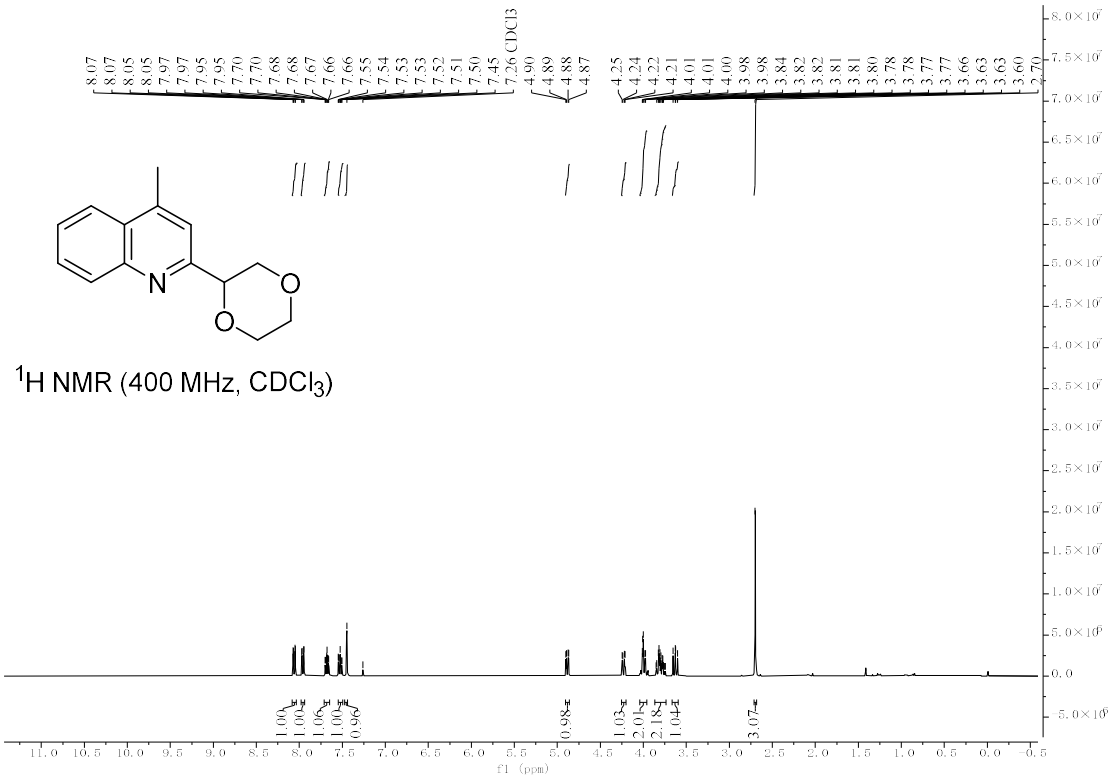


^{1}H NMR (400 MHz, $CDCl_3$)

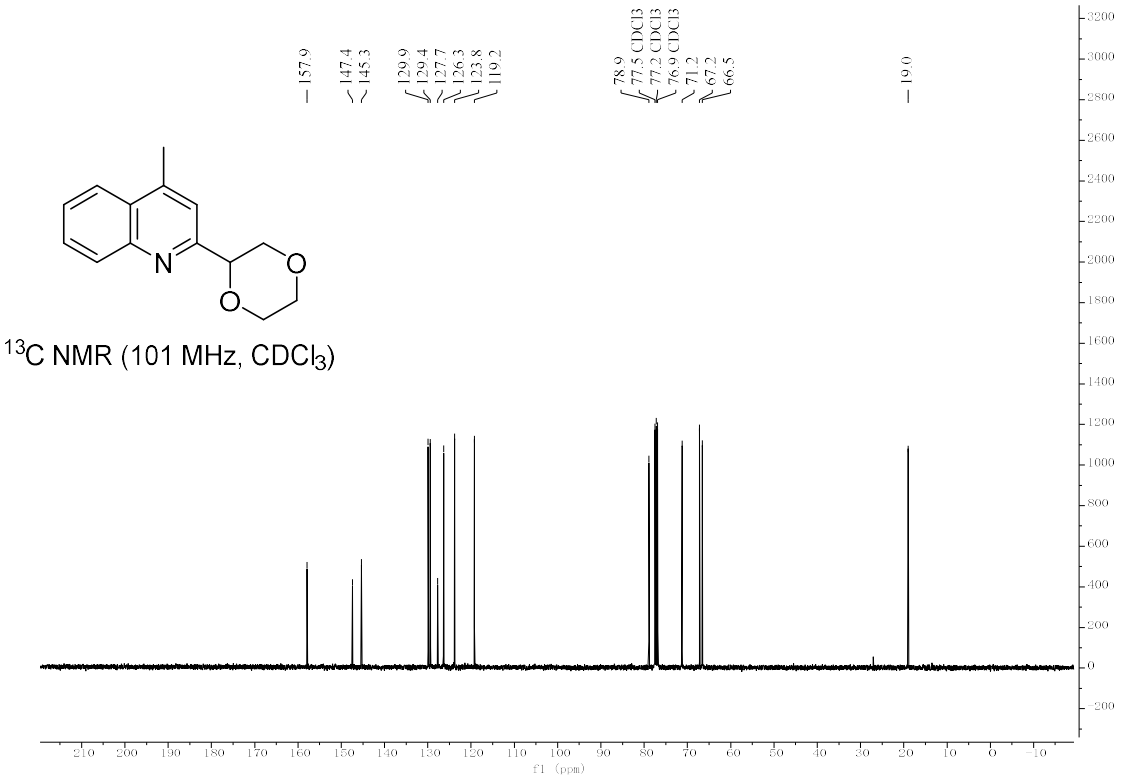


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 39

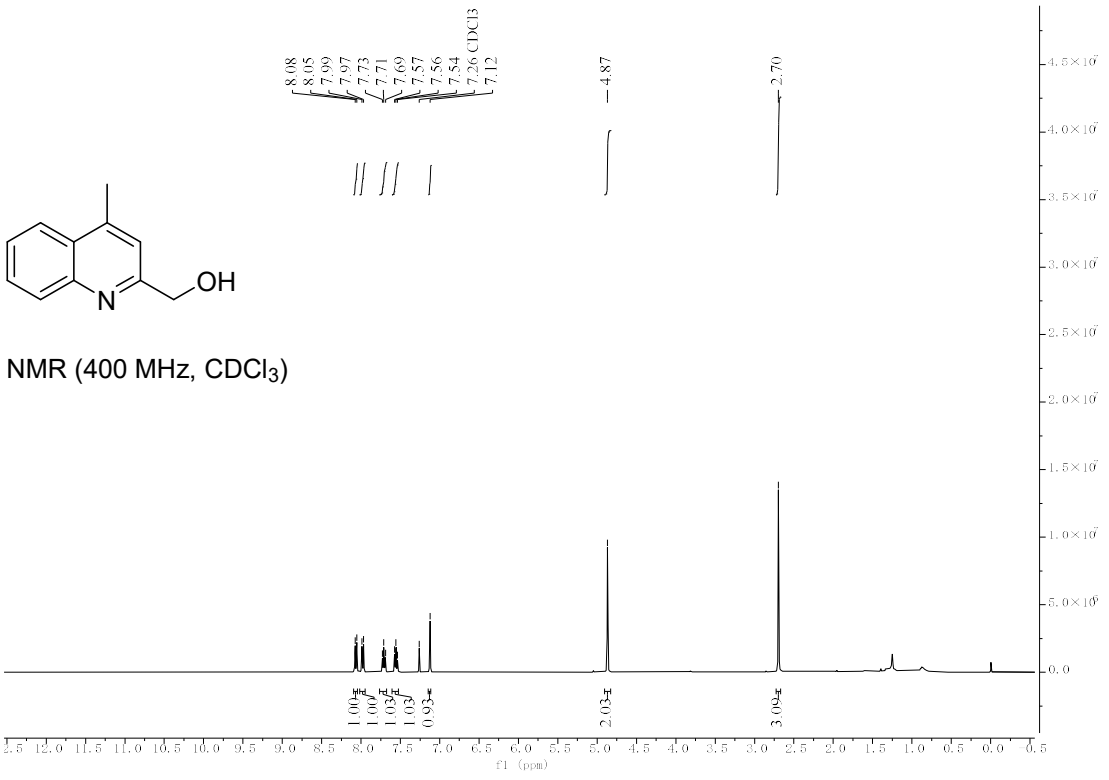


^{1}H NMR (400 MHz, $CDCl_3$)

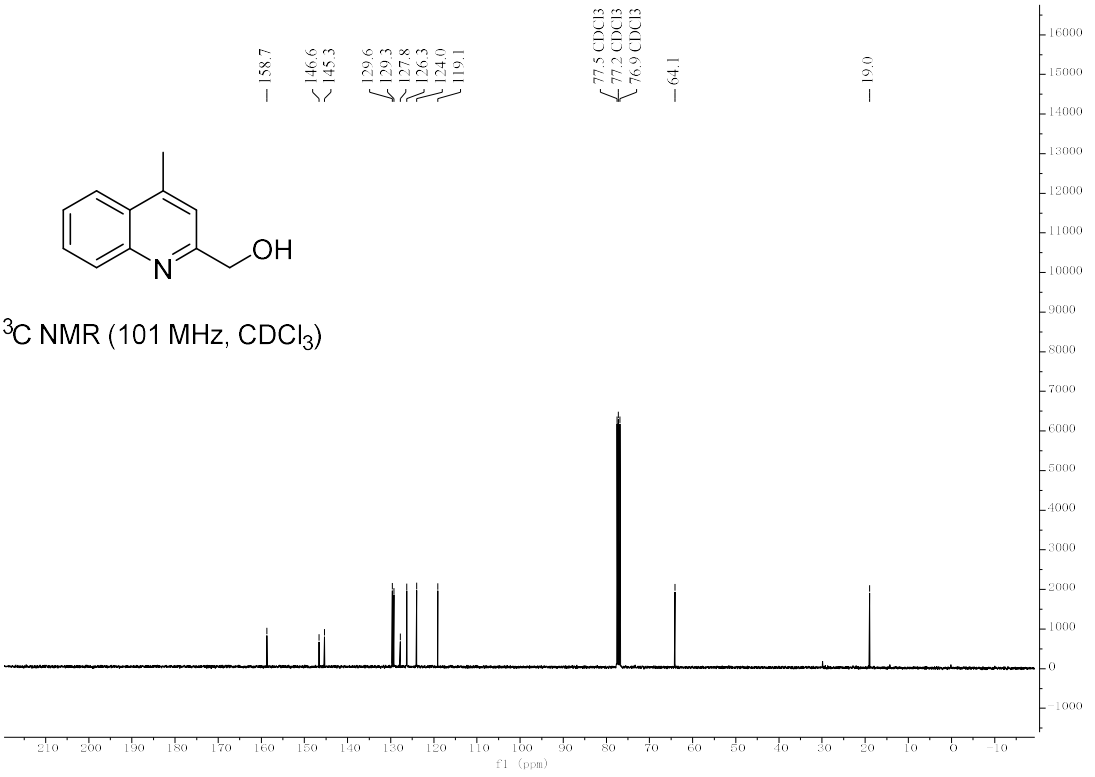


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 40

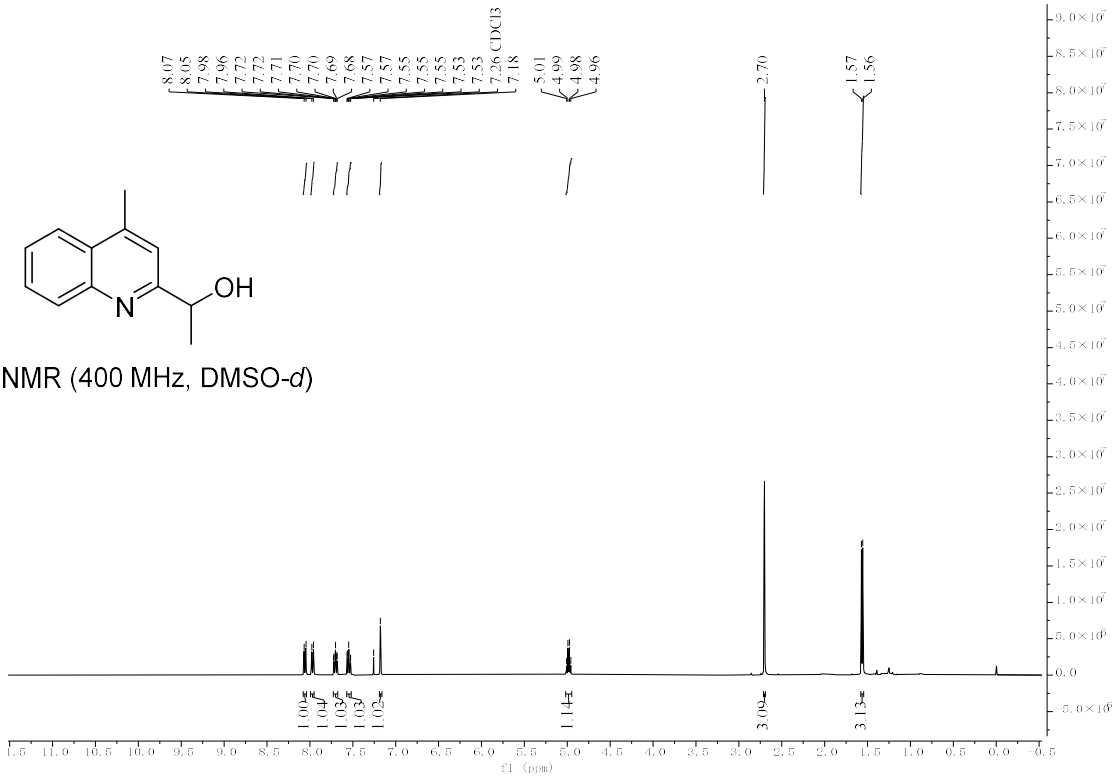


^{1}H NMR (400 MHz, $CDCl_3$)

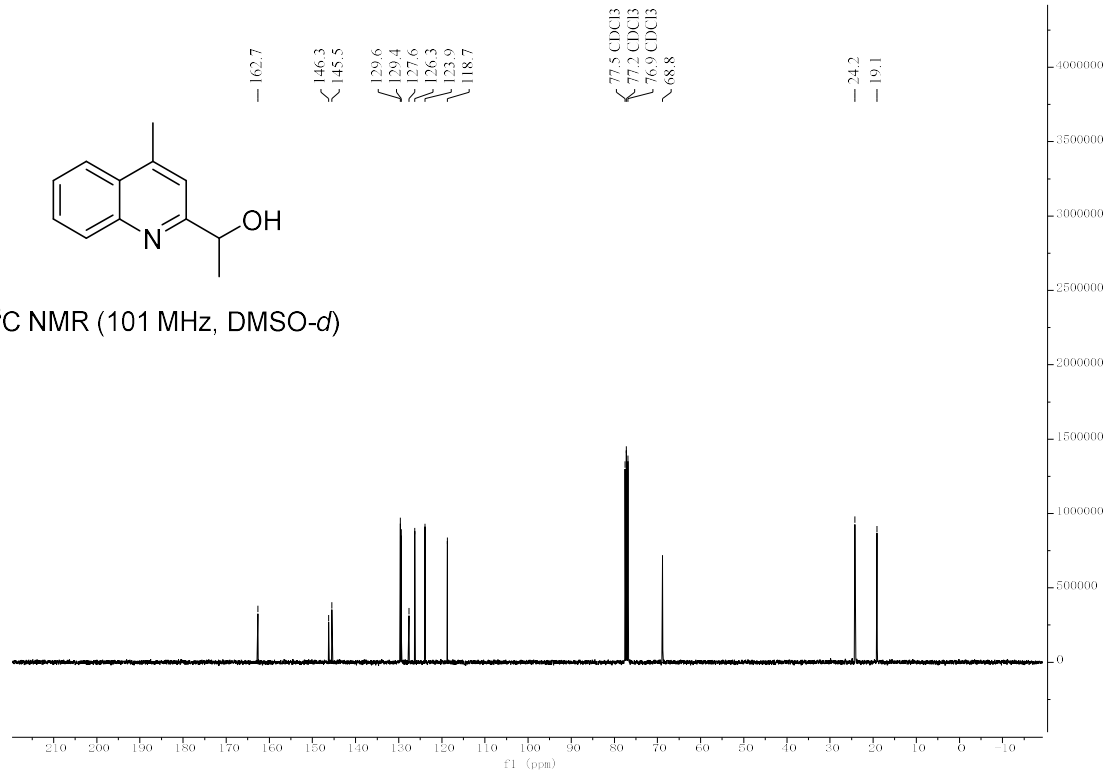


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 41

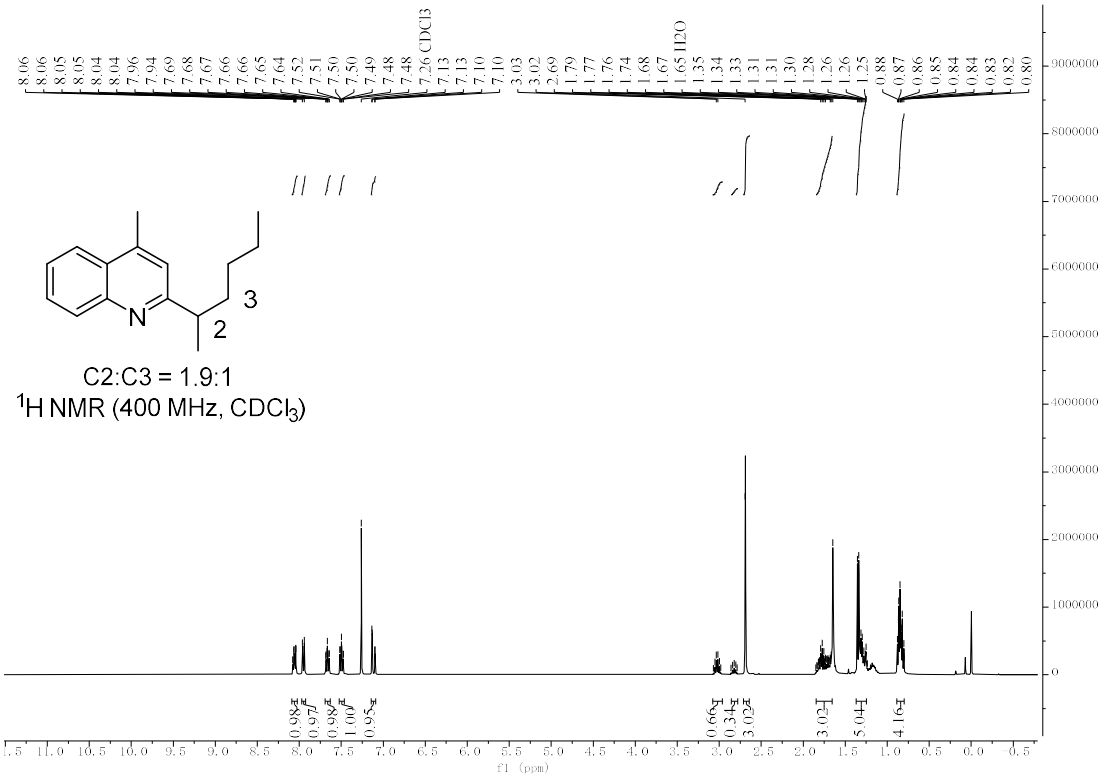


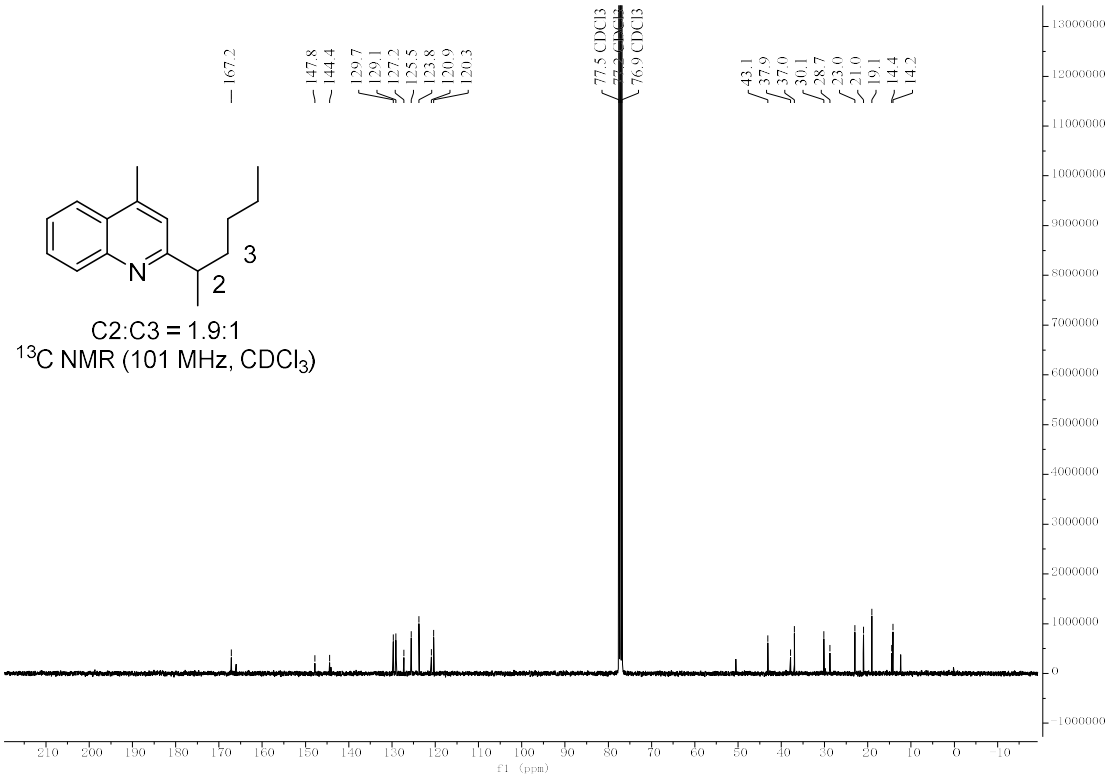
^{1}H NMR (400 MHz, DMSO-*d*)



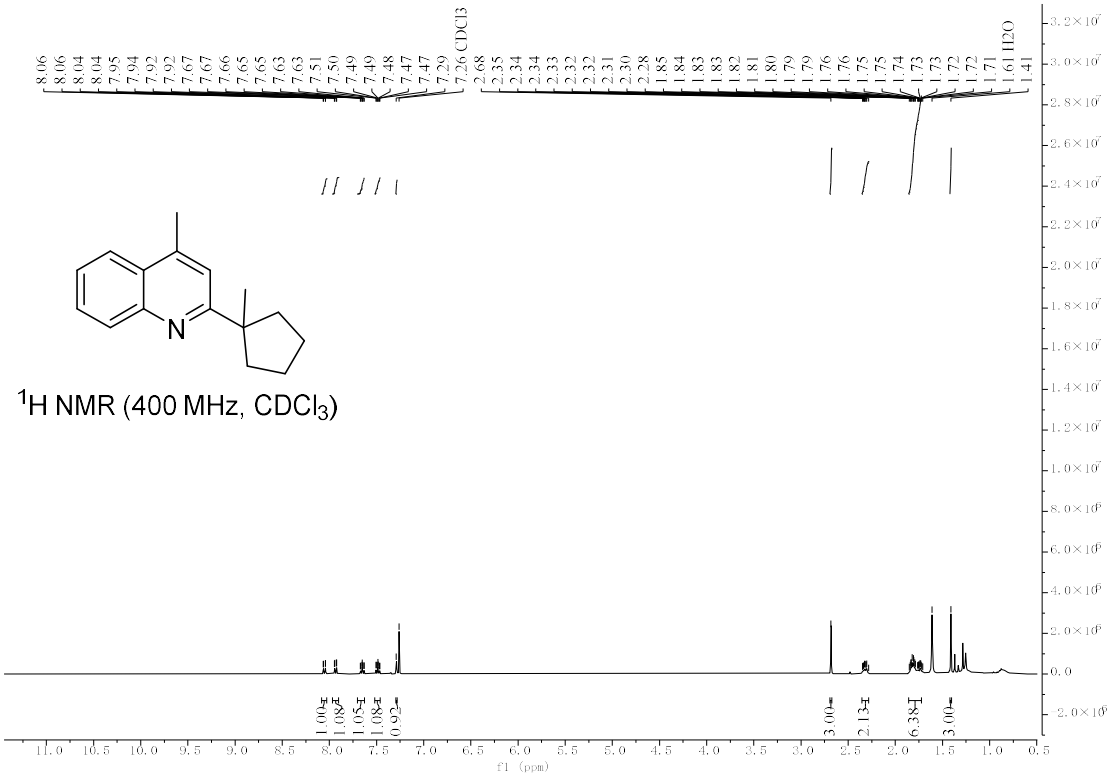
^{13}C NMR (101 MHz, DMSO-*d*)

Compound 42



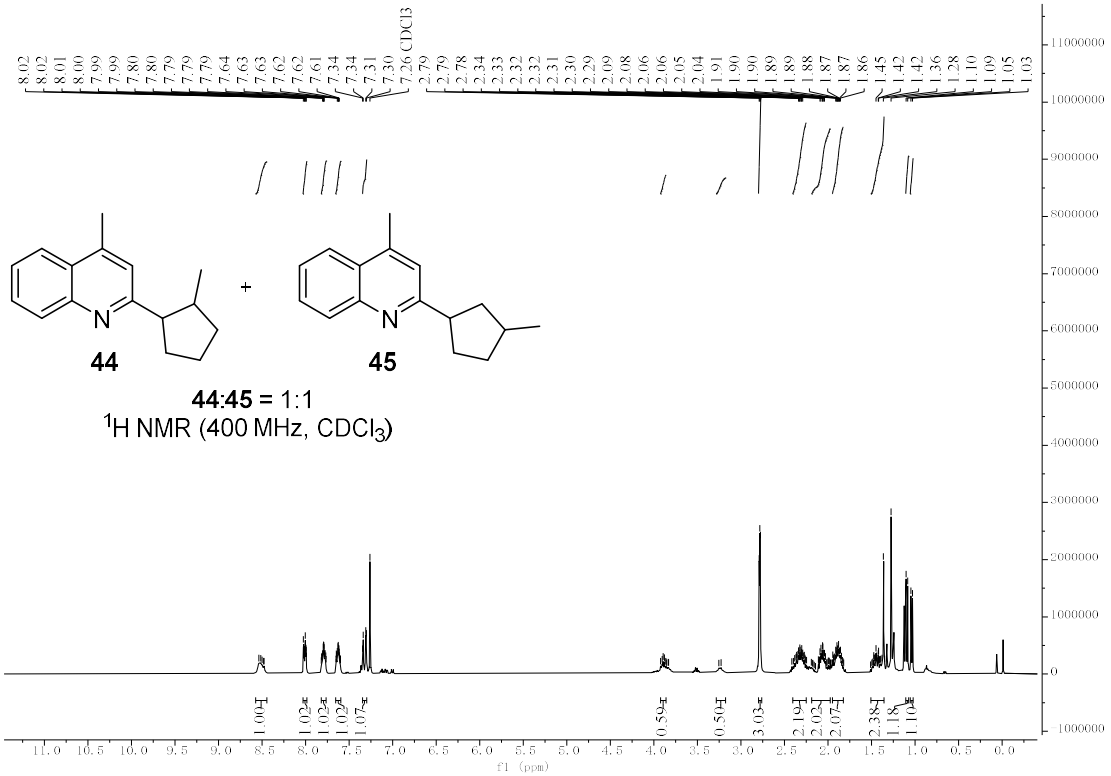


Compound 43



^{1}H NMR (400 MHz, $CDCl_3$)

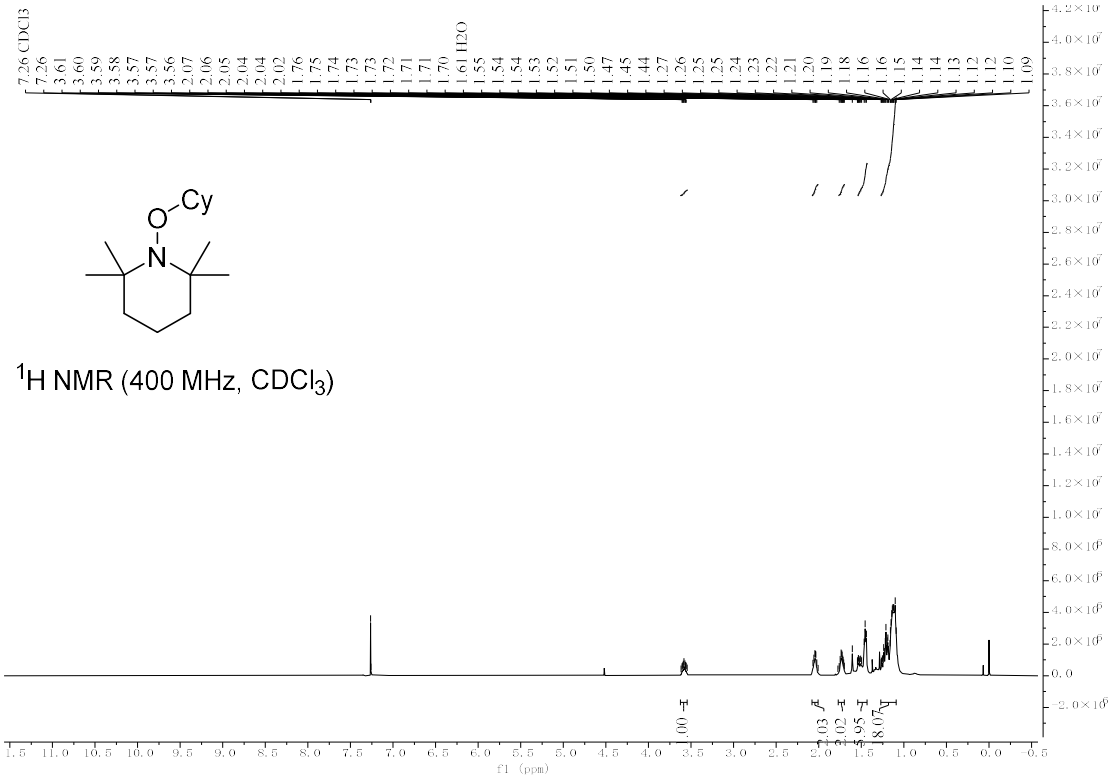
Compound 44 and 45



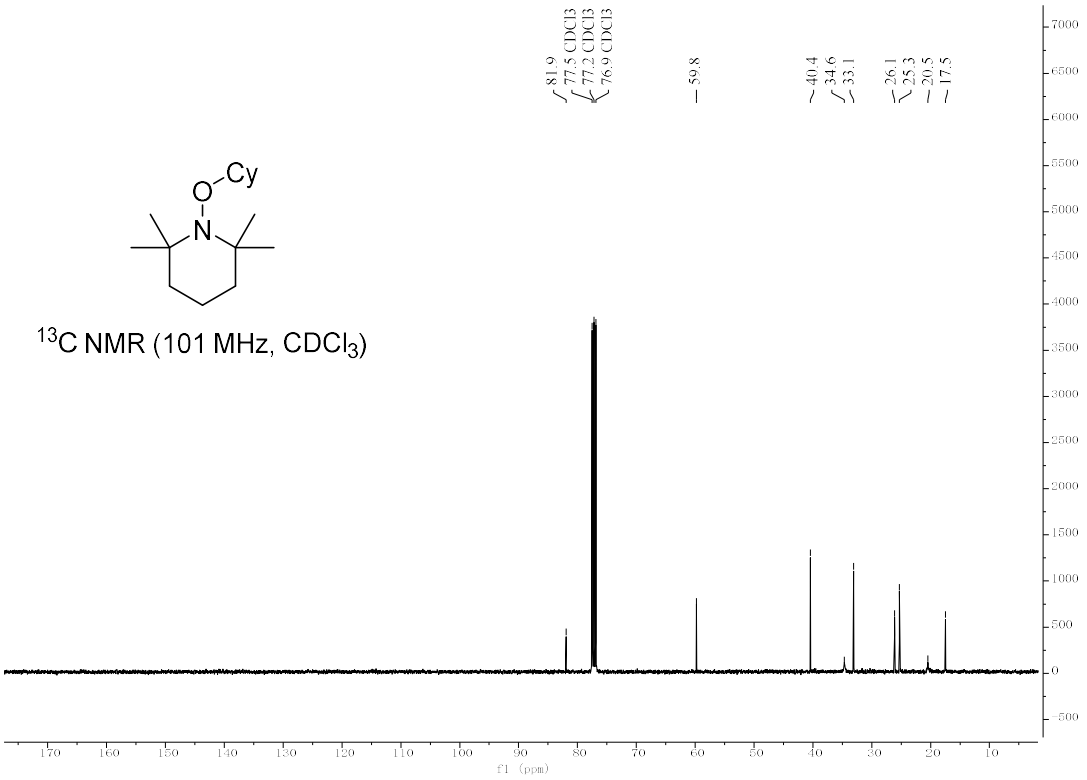
44:**45** = 1:1

^{1}H NMR (400 MHz, $CDCl_3$)

Compound 46

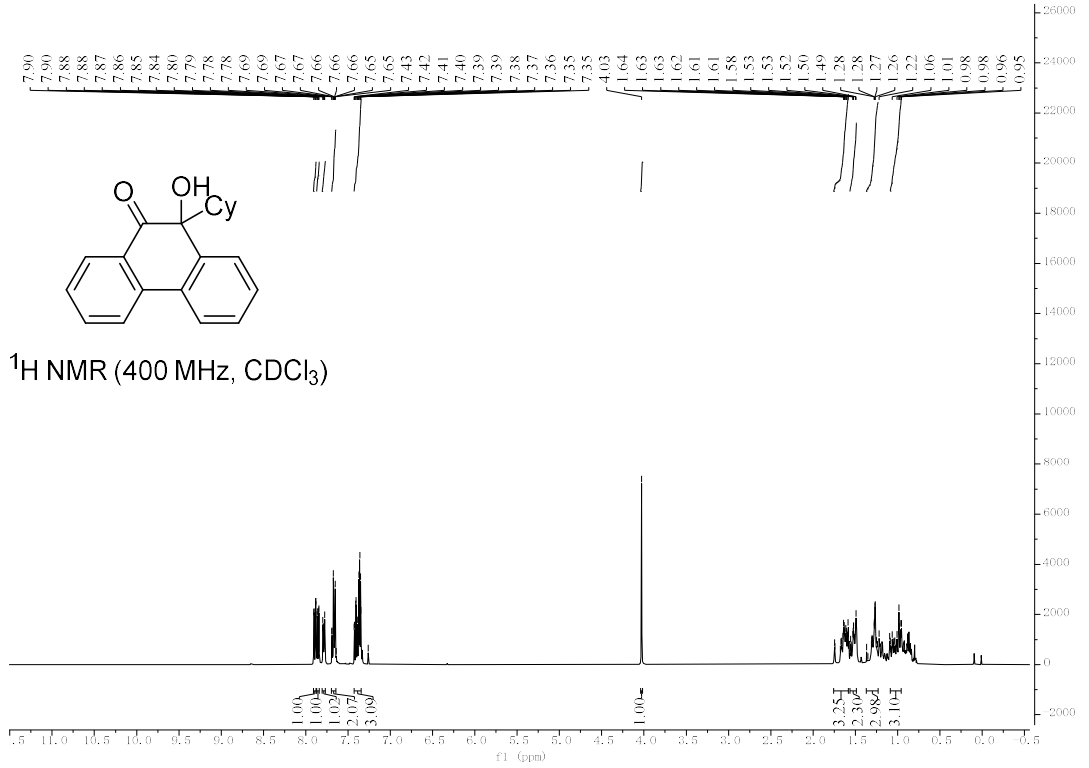


^{1}H NMR (400 MHz, $CDCl_3$)

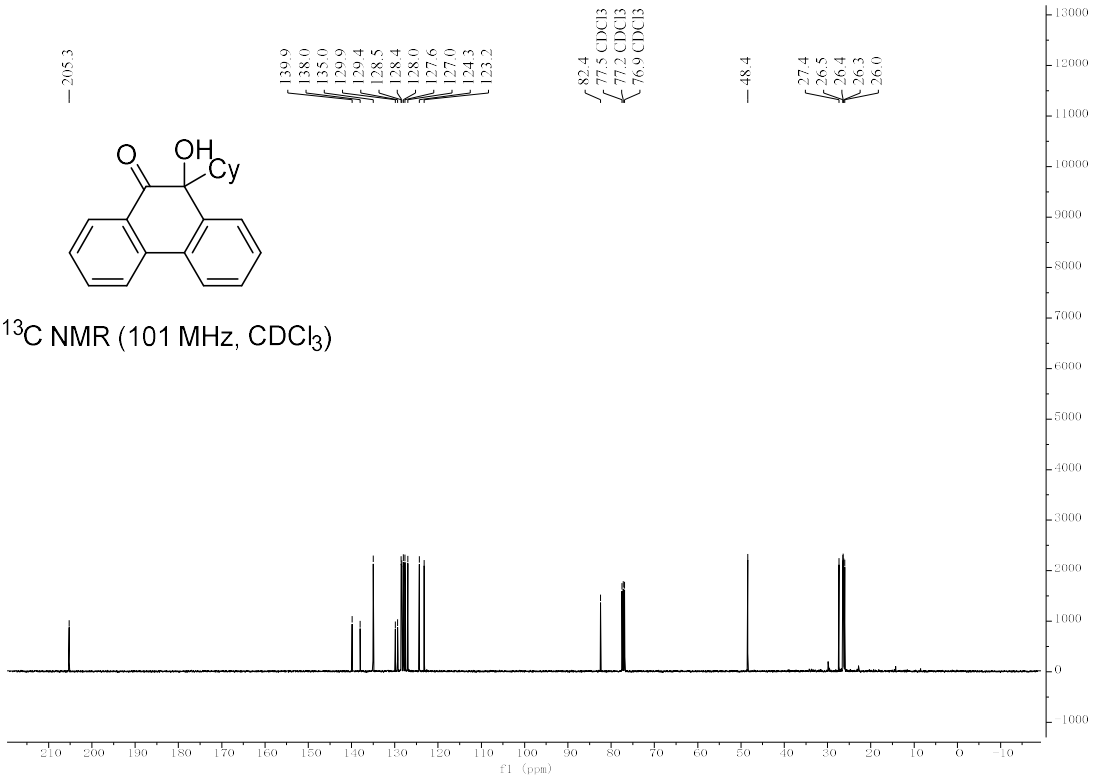


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 47



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)