

Supporting Information

Palladium-catalyzed regioselective hydrofunctionalization of methylenecyclopropanes (MCPs) with azaaryl alcohols as latent C(sp³)-nucleophiles

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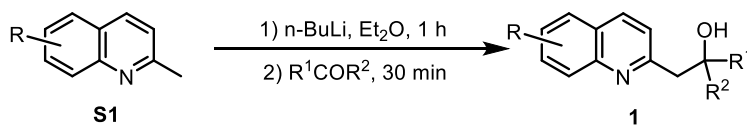
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1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. An oil bath was used for reactions requiring heating. Temperatures quoted are external. All reactions were carried out at inert atmosphere using reaction tubes and were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV-light at 254 nm and 365 nm. Flash column chromatography was performed using Yantai Yinlong flash silica gel (200-300 mesh). Melting points were recorded on an Electrothermal digital melting point apparatus. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on Bruker 400 MHz or Agilent 600 MHz spectrometer in CDCl_3 with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quarter; p = pentet; m = multiplet; br = broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ , ppm). Data for ^{19}F NMR are reported in terms of chemical shift (δ , ppm). HRMS spectra were obtained by using BRUKER microTOF-Q III instrument with ESI, EI or CI source. The crystal was measured by using Agilent or Bruker instrument. IR spectra were recorded on a BRUKER VERTEX 70 spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}).

2. Preparation of quinoline derivatives and methylenecyclopropanes (MCPs)

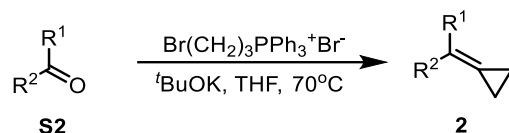
2.1 Preparation of quinoline derivatives



The quinoline derivatives was synthesized according to the literature^[1]: To a stirred solution of quinoline derivatives (10 mmol, 1 equiv) in anhydrous Et₂O (50 mL) at 0 °C under nitrogen was added a 1.6 M solution of n-butyllithium in hexanes (6.8 mL, 10.8 mmol, 1.08 equiv). The resulting yellow solution was stirred at 0 °C for 10 min and then at room temperature for 1 h. After cooling to below -30 °C, diisopropyl ketone (1.370 g, 12 mmol, 1.2 equiv) was added and the mixture was stirred for 20 min. The reaction was quenched with saturated aqueous NH₄Cl solution (20 mL) and warmed to room temperature. The

mixture was extracted with EtOAc (3 × 30 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the quinoline derivatives.

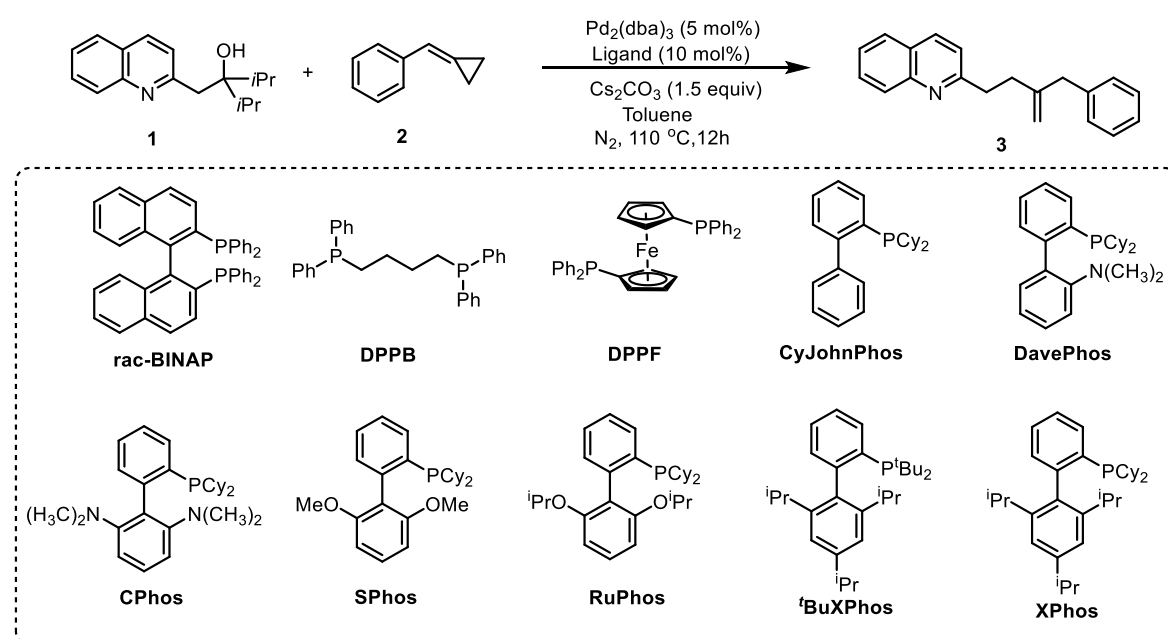
2.2 Preparation of methylenecyclopropanes (MCPs)



The methylenecyclopropanes was synthesized according to the literature^[2]: To a suspension of 1-bromopropyl-3-triphenylphosphonium bromide (1.5 equiv) in THF (2 mL/mmol of phosphonium) under argon atmosphere was added a solution of ^tBuOK (3 equiv) in THF (1 mL/mmol of ^tBuOK) via cannula, and the reaction mixture turned to bright orange. The reaction mixture was then heated at reflux with an oil bath for 90 min and the aldehyde or ketone (1 equiv) was then added. The reflux was continued for 16 h for ketones and 2 h for aldehydes, and the reaction mixture was cooled down to room temperature. The reaction mixture was then poured in a large Erlenmeyer containing a large amount of pentane (10 mL/mmol) and the precipitates were filtered. The filtrate was concentrated and the residue was purified on a silica gel chromatography.

3. Optimization of reaction conditions

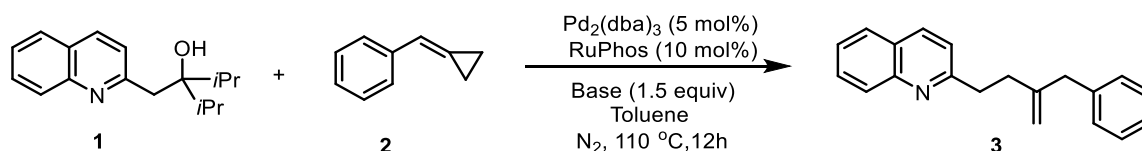
Table S1: Ligand screening^{a,b}



Entry	Ligand	Yield(%) ^b
1	PPh ₃	17
2	^t BuPh ₂ P	32
3	rac-BINAP	trace
4	DPPB	5
5	DPPF	9
6	CyJohnPhos	trace
7	DavePhos	42
8	CPhos	27
9	SPhos	46
10	^t BuXPhos	trace
11	XPhos	48
12	RuPhos	52

^aReaction conditions: **1** (0.10 mmol), **2** (0.12 mmol), Pd₂(dba)₃ (5.0 mol %), Cs₂CO₃ (1.5 equiv) and ligand (10.0 mol %) in toluene (1.0 mL) at 110 °C for 12 h. ^bDetermined by LC analysis using biphenyl as an internal standard.

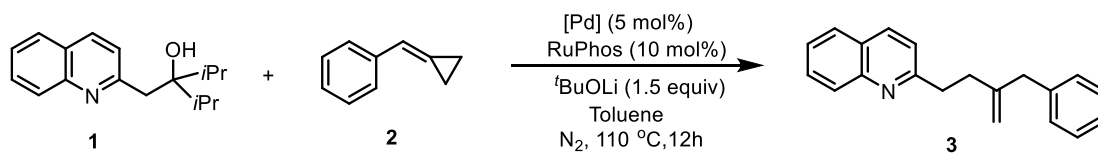
Table S2: Base screening^{a,b}



entry	Base	Yield (%) ^b
13	Cs ₂ CO ₃	52
14	NaOAc	47
15	NaOH	38
16	^t BuOK	N.R.
17	^tBuOLi	59
18	K ₂ CO ₃	50
19	KOH	51
20	K ₃ PO ₄	19
21	DMAP	40

^aReaction conditions: **1** (0.10 mmol), **2** (0.12 mmol), Pd₂(dba)₃ (5.0 mol %), Base (1.5 equiv) and RuPhos (10.0 mol %) in toluene (1.0 mL) at 110 °C for 12 h. ^bDetermined by LC analysis using biphenyl as an internal standard.

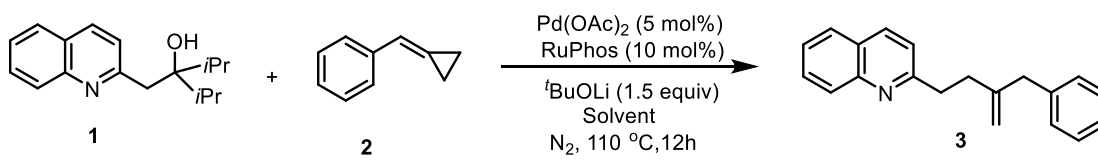
Table S3: Catalyst screening^{a,b}



Entry	[Pd]	Yield (%) ^b
22	Pd ₂ (dba) ₃	59
23	PdCl ₂	N.R.
24	Pd(OAc)₂	62
25	Pd(acac) ₂	41
26	Pd(TFA) ₂	7
27	Pd(alkyl) ₂ Cl ₂	trace
28	Pd(PPh ₃) ₄	15
29	Pd(PPh ₃) ₂ Cl ₂	trace
30	Pd(MeCN) ₄ (OTf) ₂	28

^aReaction conditions: **1** (0.10 mmol), **2** (0.12 mmol), [Pd] (5.0 mol %), ^tBuOLi (1.5 equiv) and RuPhos (10.0 mol %) in Toluene (1.0 mL) at 110 °C for 12 h. ^bDetermined by LC analysis using biphenyl as an internal standard.

Table S4: Solvent screening^{a,b,c}



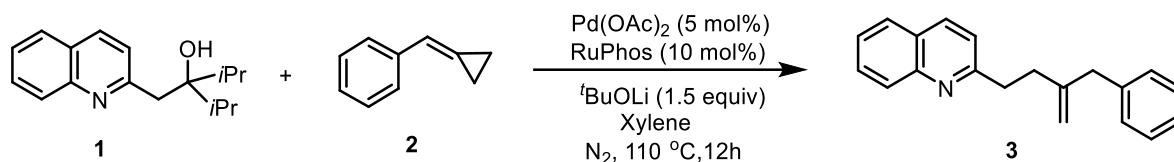
Entry	Solvent	Yield (%) ^b
31	Toluene	62
32	Xylene	72(70)^c
33	MeCN	trace
34	DMA	N.R.
35	Dioxane	64

36	NMP	N.R.
37	DCM	42
38	EA	trace
39	EtOH	N.R.
40	THF	36

^aReaction conditions: **1** (0.10 mmol), **2** (0.12 mmol), Pd(OAc)₂ (5.0 mol %), ^tBuOLi (1.5 equiv) and RuPhos (10.0 mol %) in Solvent (1.0 mL) at 110 °C for 12 h. ^bDetermined by LC analysis using biphenyl as an internal standard. ^cIsolated yield.

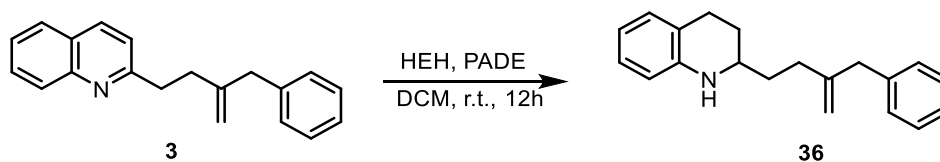
4. Experimental procedures

4.1 Typical procedure for the synthesis of **3**

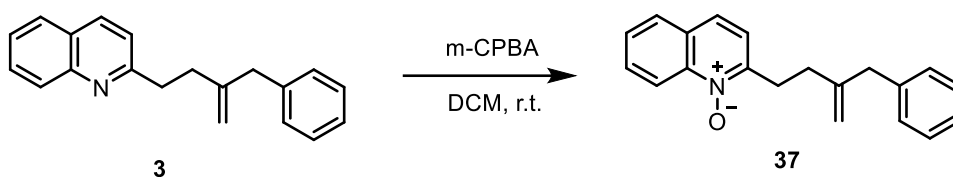


In a glovebox, an 8 mL glass reaction vial was sequentially charged with 2-quinolinyl tertiary alcohol **1** (0.2 mmol, 1.0 equiv), methylenecyclopropane substrate **2** (0.24 mmol, 1.2 equiv), Pd(OAc)₂ (0.01 mmol, 5 mol%), RuPhos (0.02 mmol, 10 mol%), ^tBuOLi (0.3 mmol, 1.5 equiv), and xylene (2 mL). The reaction mixture was stirred at 110 °C for 12 h. After cooling, the mixture was filtered through Celite, and the solution was concentrated under reduced pressure by rotary evaporation. The residue was purified by column chromatography (PE/EtOAc = 40:1-30:1) to afford product **3**.

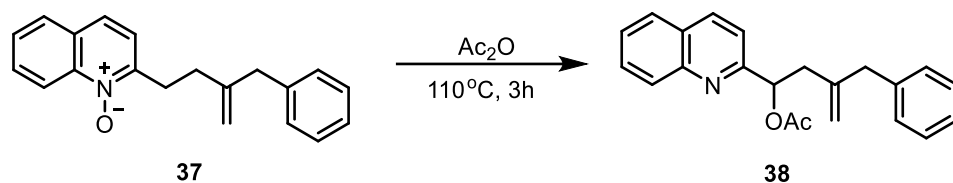
4.2 Further transformation of **3**



To an 8 mL vial equipped with a magnetic stir bar were added **3** (0.2 mmol, 1.0 equiv), PADE (0.02 mmol, 10 mol%), and HEH (0.48 mmol, 2.4 equiv). Dichloromethane (4 mL) was added under an air atmosphere, and the mixture was stirred at 30 °C for 12 h. After completion of the reaction, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc = 60:1 to 40:1) to afford a yellow liquid **36** (50 mg, 90%).



3 (0.2 mmol, 1.0 equiv) was dissolved in DCM. *m*-CPBA (0.3 mmol, 1.5 equiv) was added slowly at room temperature, and the mixture was stirred for 6 h. The reaction was quenched with saturated aqueous sodium thiosulfate, extracted with DCM three times, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography (DCM/MeOH = 40:1-20:1) to give compound **37** as a colorless oil (28 mg, 48%).



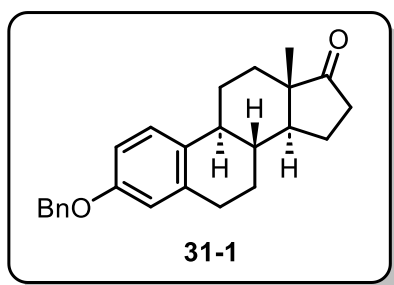
To a 25 mL Schlenk tube equipped with a magnetic stir bar was sealed, and the system was purged with nitrogen gas three times. Quinoline N-oxide derivative **37** (0.2 mmol, 1.0 equiv.) and acetic anhydride (4 mL) were added. The mixture was heated and stirred at 110 °C for 3 h. After completion of the reaction, the solvent was removed under reduced pressure. The crude product was purified by a column chromatography on a silica gel (PE/EtOAc = 40:1-20:1) to afford the product **38** as a yellow liquid (28 mg, 42%).

5. References

- [1] M. M. López, N. Jamey, A. Pinet, B. Figadère and L. Ferrié, *Org. Lett.*, 2021, **23**, 1626-1631.
- [2] D.-W. Wang, X.-B. Wang, D.-S. Wang, S.-M. Lu, Y.-G. Zhou and Y.-X. Li, *J. Org. Chem.*, 2009, **74**, 2780-2787.

6. Analytic and characterization data for the products

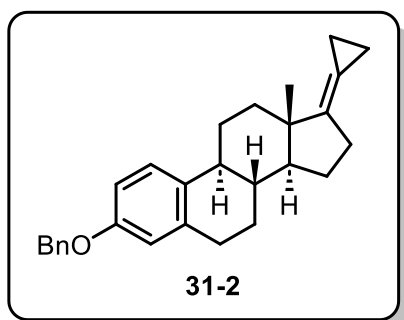
(8R,9S,13S,14S)-3-(benzyloxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (31-1)



To a dried reaction tube were added estrone (5.0 mmol) and anhydrous potassium carbonate (10.0 mmol). The tube was evacuated and backfilled with nitrogen three times. Acetone (15 mL) was added, and the mixture was stirred at room temperature for 10 min. The reaction mixture was heated to reflux at 56 °C and stirred for 48 h.

After cooling to room temperature, the mixture was filtered to remove inorganic salts, and the filtrate was concentrated under reduced pressure to give a crude product. The crude product was purified by column chromatography to afford a white solid (1.45 g, 80% yield). **m.p.** = 123.8-124.5 °C. **¹H NMR (400 MHz, CDCl₃)** δ 7.45 - 7.41 (m, 2H), 7.40 - 7.35 (m, 2H), 7.34 - 7.29 (m, 1H), 7.20 (dd, *J* = 8.7, 1.1 Hz, 1H), 6.79 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.73 (d, *J* = 2.7 Hz, 1H), 5.03 (s, 2H), 2.93 - 2.86 (m, 2H), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.42 - 2.36 (m, 1H), 2.30 - 2.22 (m, 1H), 2.19 - 2.09 (m, 1H), 2.08 - 1.93 (m, 3H), 1.68 - 1.60 (m, 1H), 1.58 - 1.41 (m, 5H), 0.91 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.9, 137.8, 137.3, 132.3, 128.6, 127.9, 127.5, 126.4, 114.9, 112.4, 70.0, 50.4, 48.0, 44.0, 38.4, 35.9, 31.6, 29.7, 26.6, 25.9, 21.6, 13.9. **HRMS (ESI)** calcd for [M+Na]⁺ C₂₅H₂₈NaO₂⁺, *m/z*: 383.1987, found: 383.1985. **FT-IR (ATR)**: 2919, 2866, 2051, 2029, 1734, 1601, 1495, 1228, 1022, 818, 751, 728, 694 cm⁻¹.

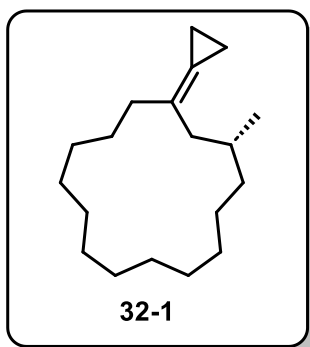
(8S,9S,13S,14S)-3-(benzyloxy)-17-cyclopropylidene-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene (31-2)



According to the general procedure, **31-2** was obtained as a white solid (0.82 g, 53% yield). **m.p.** = 87.9-89.9 °C. **¹H NMR (400 MHz, CDCl₃)** δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.72 (d, *J* = 2.8 Hz, 1H), 5.03 (s, 2H), 2.95 - 2.80 (m, 2H), 2.60 - 2.49 (m, 1H), 2.41 - 2.30 (m, 2H), 2.28 - 2.18 (m, 1H), 2.18 - 2.10 (m, 1H), 1.99 - 1.91 (m, 1H), 1.91 - 1.82 (m, 1H), 1.54 (d, *J* = 8.9 Hz, 2H), 1.49 - 1.41 (m, 2H), 1.40 - 1.28 (m, 2H), 1.14 - 1.01 (m, 2H), 0.85 (s, 4H), 0.84 - 0.79 (m, 1H). **¹³C NMR (101 MHz, CDCl₃)** δ 157.3, 139.7, 138.7, 138.0, 133.9, 129.1, 128.4, 128.0, 126.9, 115.4, 112.8, 107.8, 70.6, 54.9, 45.6, 44.9, 39.5, 36.9, 30.5, 29.6, 28.3, 27.3, 25.0, 18.4, 2.1,

0.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{28}H_{33}O^+$, m/z : 385.2531, found: 385.2532. **FT-IR** (ATR): 2913, 2848, 2180, 2145, 1962, 1495, 1278, 1027, 730, 693 cm^{-1} .

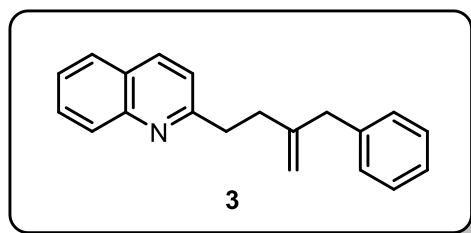
(R)-1-cyclopropylidene-3-methylcyclopentadecane (32-1)



According to the general procedure, **32-1** was obtained as a yellow oil (0.84 g, 64% yield). **1H NMR (400 MHz, $CDCl_3$)** δ 2.22 - 2.09 (m, 3H), 1.93 (dd, $J = 13.4, 7.7$ Hz, 1H), 1.77 - 1.68 (m, 1H), 1.60 - 1.51 (m, 1H), 1.47 - 1.20 (m, 20H), 1.14 - 1.06 (m, 1H), 1.05 - 1.00 (m, 2H), 0.98 - 0.92 (m, 2H), 0.82 (d, $J = 6.6$ Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 125.7, 114.1, 40.8, 33.5, 32.1, 28.1, 25.8, 25.1, 24.8, 24.8, 24.7, 24.6, 24.5, 23.3, 18.5, 0.5,

0.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{19}H_{35}^+$, m/z : 263.2739, found: 263.2739. **FT-IR** (ATR): 2922, 2853, 1456, 1373, 1350, 992, 716 cm^{-1} .

2-(3-benzylbut-3-en-1-yl)quinoline (3)



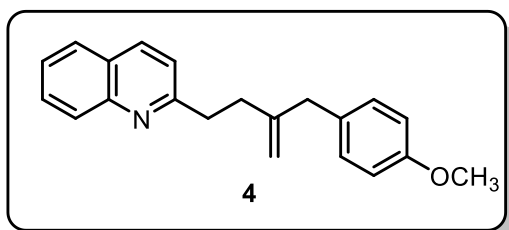
According to the general procedure, **3** was obtained as a yellow liquid (38 mg, 70% yield). **1H NMR (400 MHz, $CDCl_3$)** δ 8.05 (dd, $J = 16.0, 8.4$ Hz, 2H), 7.75 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.70 - 7.65 (m, 1H), 7.49 - 7.45 (m, 1H), 7.30 - 7.24 (m, 2H), 7.20 (t, $J =$

7.7 Hz, 4H), 4.92 (d, $J = 1.6$ Hz, 1H), 4.79 (d, $J = 1.4$ Hz, 1H), 3.41 (s, 2H), 3.18 - 3.11 (m, 2H), 2.51 (t, $J = 8.0$ Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.1, 148.0, 147.6, 139.6,

136.5, 129.6, 129.1, 128.7, 128.3, 127.5, 126.8, 126.1, 125.9, 121.3, 111.9, 43.3, 37.2, 35.2.

HRMS (ESI) calcd for $[M+H]^+$ $C_{20}H_{20}N^+$, m/z : 274.1596, found: 274.1594. **FT-IR** (ATR): 2923, 1599, 1500, 1445, 1113, 823, 745 cm^{-1} .

2-(3-(4-methoxybenzyl)but-3-en-1-yl)quinoline (4)



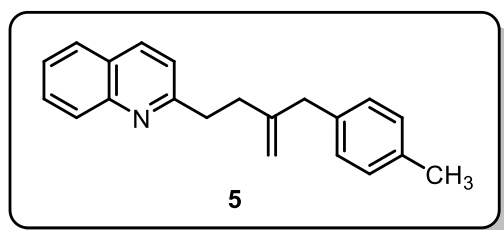
According to the general procedure, **4** was obtained as a yellow liquid (38 mg, 62% yield).

1H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, $J = 8.6, 3.2$ Hz, 2H), 7.75 (dd, $J = 8.2, 1.5$ Hz, 1H), 7.70 - 7.64 (m, 1H), 7.49 - 7.45 (m, 1H), 7.26 (d, $J = 8.4$

Hz, 1H), 7.12 (s, 4H), 4.90 (d, $J = 1.4$ Hz, 1H), 4.53 (d, $J = 1.9$ Hz, 1H), 3.40 (s, 2H), 3.19 -

3.14 (m, 2H), 2.61 - 2.54 (m, 2H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.2, 148.0, 147.1, 137.7, 136.9, 136.3, 130.2, 130.1, 129.4, 128.9, 127.5, 126.8, 126.4, 125.9, 125.8, 121.3, 111.3, 40.6, 38.0, 36.1, 19.4. HRMS (ESI) calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{21}\text{H}_{22}\text{NO}^+$, m/z : 304.1696, found: 304.1694. FT-IR (ATR): 2982, 1731, 1597, 1284, 1156, 1031, 907, 725, 645 cm^{-1} .

2-(3-(4-methylbenzyl)but-3-en-1-yl)quinoline (5)

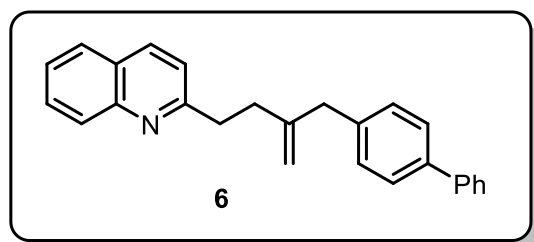


According to the general procedure, **5** was obtained as a yellow liquid (28 mg, 48% yield).

^1H NMR (400 MHz, CDCl_3) δ 8.04 (dd, $J = 8.3$, 2.5 Hz, 2H), 7.77 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.70 - 7.65 (m, 1H), 7.50 - 7.46 (m, 1H), 7.24 (d, $J = 8.4$

Hz, 1H), 7.09 (s, 4H), 4.90 (s, 1H), 4.79 (s, 1H), 3.38 (s, 2H), 3.18 - 3.09 (m, 2H), 2.50 (t, $J = 8.0$ Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.6, 148.3, 147.3, 136.5, 136.2, 135.6, 129.4, 129.0, 128.9, 128.8, 127.5, 126.8, 125.8, 121.3, 111.6, 42.9, 37.4, 35.5, 21.1. HRMS (ESI) calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{21}\text{H}_{22}\text{N}^+$, m/z : 288.1747, found: 288.1749. FT-IR (ATR): 2916, 1599, 1495, 1447, 1315, 1118, 888, 829, 737, 699 cm^{-1} .

2-(3-([1,1'-biphenyl]-4-ylmethyl)but-3-en-1-yl)quinoline (6)

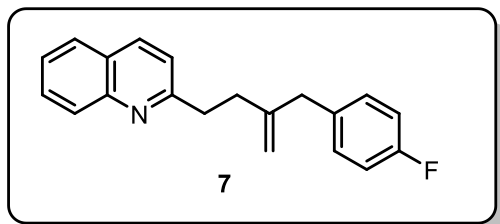


According to the general procedure, **6** was obtained as a yellow liquid (45 mg, 65% yield).

^1H NMR (400 MHz, CDCl_3) δ 8.02 (dd, $J = 14.4$, 8.5 Hz, 2H), 7.73 (dd, $J = 8.2$, 1.5 Hz, 1H), 7.67 - 7.63 (m, 1H), 7.59 - 7.55 (m, 2H), 7.52 - 7.48 (m, 2H), 7.47 - 7.38 (m, 3H), 7.33 - 7.28

(m, 1H), 7.28 - 7.24 (m, 2H), 7.21 (d, $J = 8.4$ Hz, 1H), 4.95 (s, 1H), 4.84 (s, 1H), 3.45 (s, 2H), 3.18 - 3.12 (m, 2H), 2.53 (t, $J = 8.1$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.2, 148.0, 148.0, 141.1, 139.1, 138.8, 136.3, 129.5, 129.4, 128.9, 128.8, 127.6, 127.1, 127.1, 126.8, 125.8, 121.34, 112.0, 43.0, 37.4, 35.2. HRMS (ESI) calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{26}\text{H}_{24}\text{N}^+$, m/z : 350.1903, found: 350.1903. FT-IR (ATR): 2924, 1604, 1437, 1373, 1117, 891, 825, 759 cm^{-1} .

2-(3-(4-fluorobenzyl)but-3-en-1-yl)quinoline (7)

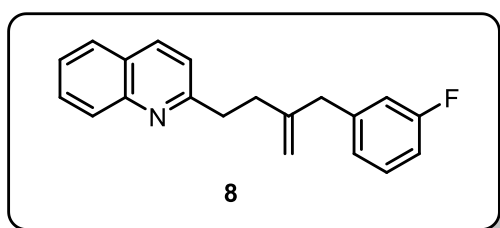


According to the general procedure, **7** was obtained as a yellow liquid (41 mg, 57% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.03 (t, *J* = 7.7 Hz, 2H), 7.77 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.70 - 7.64 (m, 1H), 7.52 - 7.46 (m, 1H), 7.23 (d, *J* = 8.5 Hz, 1H),

7.18 - 7.11 (m, 2H), 7.01 - 6.91 (m, 2H), 4.92 (d, *J* = 1.7 Hz, 1H), 4.77 (d, *J* = 1.8 Hz, 1H), 3.38 (s, 2H), 3.16 - 3.10 (m, 2H), 2.49 (t, *J* = 8.1 Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.4 (d, *J*_{C-F} = 67.5 Hz), 160.3, 148.0 (d, *J*_{C-F} = 7.1 Hz), 136.3, 135.2, 135.1, 130.4 (d, *J*_{C-F} = 10.1 Hz), 129.5, 128.8, 127.5, 126.8, 125.8, 121.3, 115.1 (d, *J*_{C-F} = 8.0 Hz), 111.9, 42.5, 37.3, 35.1. **¹⁹F NMR (376 MHz, CDCl₃)** δ -117.4. **HRMS (ESI)** calcd for [M+H]⁺ C₂₀H₁₉FN⁺, *m/z*: 292.1496, found: 292.1491. **FT-IR (ATR)**: 2918, 1602, 1503, 1430, 1219, 820, 757 cm⁻¹.

2-(3-(3-fluorobenzyl)but-3-en-1-yl)quinoline (8)

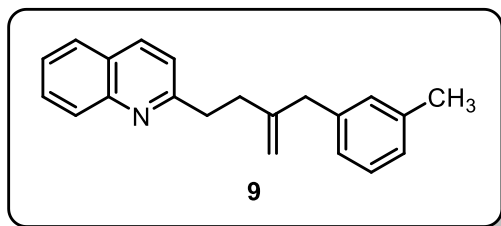


According to the general procedure, **8** was obtained as a yellow liquid (43 mg, 74% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.78 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.73 - 7.67 (m, 1H), 7.53 - 7.46 (m, 1H), 7.26 - 7.19 (m, 2H),

6.97 (d, *J* = 7.6 Hz, 1H), 6.93 - 6.85 (m, 2H), 4.95 (d, *J* = 1.6 Hz, 1H), 4.81 (d, *J* = 1.7 Hz, 1H), 3.41 (s, 2H), 3.19 - 3.12 (m, 2H), 2.51 (t, *J* = 8.0 Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 165.4, 161.8 (d, *J*_{C-F} = 24.6 Hz), 147.9, 146.8, 142.2 (d, *J*_{C-F} = 7.3 Hz), 136.3, 129.7 (d, *J*_{C-F} = 8.3 Hz), 129.4, 128.9, 127.5, 126.8, 125.8, 124.8 (d, *J*_{C-F} = 2.8 Hz), 121.3, 115.8 (d, *J*_{C-F} = 21.2 Hz), 113.1 (d, *J*_{C-F} = 21.2 Hz), 112.3, 43.0 (d, *J*_{C-F} = 1.8 Hz), 37.3, 35.1. **¹⁹F NMR (376 MHz, CDCl₃)** δ -113.8. **HRMS (ESI)** calcd for [M+H]⁺ C₂₀H₁₉FN⁺, *m/z*: 292.1496, found: 292.1492. **FT-IR (ATR)**: 2919, 1604, 1498, 1437, 1265, 821, 737 cm⁻¹.

2-(3-(3-methylbenzyl)but-3-en-1-yl)quinoline (9)

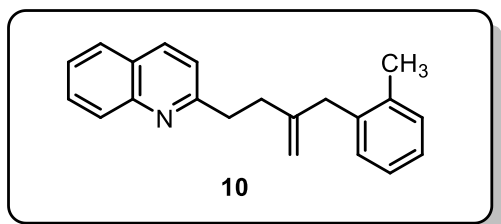


According to the general procedure, **9** was obtained as a yellow liquid (24 mg, 42% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.05 - 8.00 (m, 2H), 7.74 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.69 - 7.64 (m, 1H), 7.49 - 7.44 (m, 1H), 7.21 (d, *J* = 8.5 Hz,

1H), 7.18 - 7.14 (m, 1H), 7.00 (d, *J* = 5.8 Hz, 3H), 4.91 (dd, *J* = 3.2, 1.6 Hz, 1H), 4.80 (dd, *J* = 2.6, 1.3 Hz, 1H), 3.38 (s, 2H), 3.17 - 3.09 (m, 2H), 2.50 (t, *J* = 6.0 Hz, 2H), 2.31 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.9, 148.1, 147.9, 134.0, 137.9, 136.2, 129.8, 129.40, 128.8, 128.2, 127.5, 126.9, 126.8, 126.1, 125.8, 121.0, 111.7, 43.3, 37.4, 35.2, 21.4. **HRMS (ESI)** calcd for [M+H]⁺ C₂₁H₂₂N⁺, *m/z*: 288.1747, found: 288.1742. **FT-IR (ATR)**: 2915, 1602, 1499, 1431, 1310, 890, 821, 749 cm⁻¹.

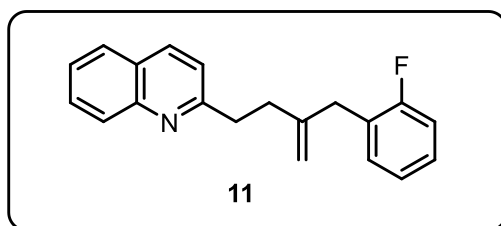
2-(3-(2-methylbenzyl)but-3-en-1-yl)quinoline (10)



According to the general procedure, **10** was obtained as a yellow liquid (33 mg, 57% yield). **¹H NMR (400 MHz, CDCl₃)** δ 8.04 (dd, *J* = 8.5, 2.8 Hz, 2H), 7.75 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.69 - 7.65 (m, 1H), 7.49 - 7.44 (m, 1H), 7.26 (d, *J* = 8.5 Hz,

1H), 7.12 (s, 4H), 4.90 (dd, *J* = 2.6, 1.3 Hz, 1H), 4.53 (d, *J* = 1.9 Hz, 1H), 3.40 (d, *J* = 1.3 Hz, 2H), 3.20 - 3.14 (m, 2H), 2.61 - 2.55 (m, 2H), 2.24 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.2, 148.0, 147.1, 137.7, 136.9, 136.3, 130.2, 130.1, 129.4, 128.9, 127.5, 126.8, 126.4, 125.9, 125.8, 121.3, 111.3, 40.6, 38.1, 36.1, 19.4. **HRMS (ESI)** calcd for [M+H]⁺ C₂₁H₂₂N⁺, *m/z*: 288.1747, found: 288.1746. **FT-IR (ATR)**: 2923, 1600, 1446, 1330, 1165, 1124, 824, 754, 704 cm⁻¹.

2-(3-(2-fluorobenzyl)but-3-en-1-yl)quinoline (11)

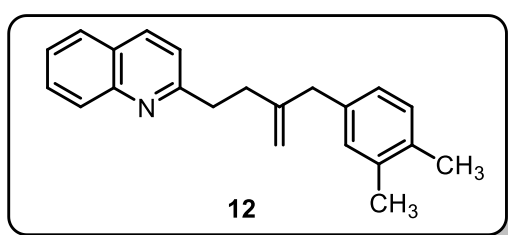


According to the general procedure, **11** was obtained as a yellow liquid (49 mg, 84% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.99 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.70 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.66 - 7.57 (m, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.19 (d,

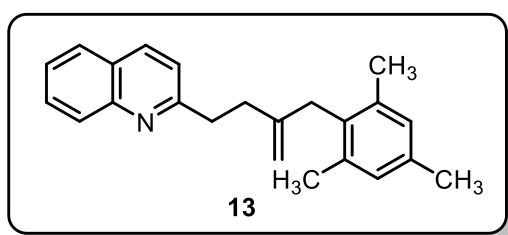
$J = 2.1$ Hz, 1H), 7.17 - 7.06 (m, 2H), 7.02 - 6.89 (m, 2H), 4.84 (s, 1H), 4.66 (s, 1H), 3.38 (s, 2H), 3.14 - 3.06 (m, 2H), 2.48 (t, $J = 8.1$ Hz, 2H). **^{13}C NMR (101 MHz, CDCl_3)** δ 162.4 (d, $J_{\text{C-F}} = 34.6$ Hz), 160.0, 148.3, 146.8, 136.3, 131.3 (d, $J_{\text{C-F}} = 4.7$ Hz), 129.4, 128.8, 128.0 (d, $J_{\text{C-F}} = 8.1$ Hz), 127.5, 126.8, 126.5 (d, $J_{\text{C-F}} = 14.8$ Hz), 125.8, 124.0 (d, $J_{\text{C-F}} = 3.6$ Hz), 121.4, 115.3 (d, $J_{\text{C-F}} = 22.5$ Hz), 111.8, 37.4, 35.7 (d, $J_{\text{C-F}} = 2.9$ Hz), 35.6. **^{19}F NMR (376 MHz, CDCl_3)** δ -118.2. **HRMS (ESI)** calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{20}\text{H}_{19}\text{FN}^+$, m/z : 292.1496, found: 292.1491. **FT-IR (ATR)**: 2920, 1599, 1493, 1438, 1226, 895, 823, 751 cm^{-1} .

2-(3-(3,5-dimethylbenzyl)but-3-en-1-yl)quinoline (12)



According to the general procedure, **12** was obtained as a yellow liquid (39 mg, 64% yield). **^1H NMR (400 MHz, CDCl_3)** δ 8.03 (d, $J = 8.4$ Hz, 2H), 7.78 - 7.73 (m, 1H), 7.69 - 7.64 (m, 1H), 7.49 - 7.45 (m, 1H), 7.23 (d, $J = 8.8$ Hz, 1H), 7.06 - 7.02 (m, 1H), 6.97 - 6.91 (m, 2H), 4.90 (s, 1H), 4.80 (s, 1H), 3.35 (s, 2H), 3.17 - 3.09 (m, 2H), 2.50 (t, $J = 8.0$ Hz, 2H), 2.22 (s, 6H). **^{13}C NMR (400 MHz, CDCl_3)** δ 162.3, 148.3, 147.9, 137.0, 136.4, 136.2, 134.2, 130.3, 129.6, 129.4, 128.8, 127.5, 126.8, 126.4, 125.7, 121.4, 111.5, 42.9, 37.4, 35.2, 19.8, 19.4. **HRMS (ESI)** calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{22}\text{H}_{24}\text{N}^+$, m/z : 302.1903, found: 302.1902. **FT-IR (ATR)**: 2956, 1599, 1434, 1362, 1248, 886, 821, 751 cm^{-1} .

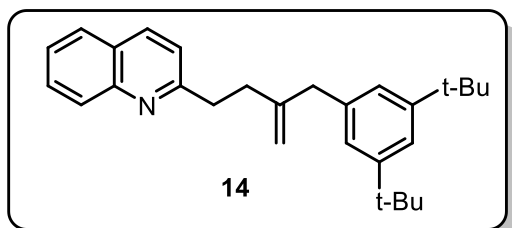
2-(3-(2,4,6-trimethylbenzyl)but-3-en-1-yl)quinoline (13)



According to the general procedure, **13** was obtained as a yellow liquid (58 mg, 92% yield). **^1H NMR (400 MHz, CDCl_3)** δ 7.96 (dd, $J = 8.4$, 5.1 Hz, 2H), 7.66 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.60 - 7.55 (m, 1H), 7.40 - 7.34 (m, 1H), 7.22 (d, $J = 8.4$ Hz, 1H), 6.73 (s, 2H), 4.67 (dd, $J = 3.0$, 1.5 Hz, 1H), 4.13 (dd, $J = 3.8$, 1.9 Hz, 1H), 3.24 (d, $J = 1.9$ Hz, 2H), 3.18 - 3.11 (m, 2H), 2.61 - 2.54 (m, 2H), 2.15 (s, 3H), 2.09 (s, 6H). **^{13}C NMR (400 MHz, CDCl_3)** δ 162.2, 148.0, 146.1, 137.0, 136.3, 135.3, 133.3, 129.5, 128.9, 128.7, 127.6, 126.8, 125.8, 121.3, 109.4, 37.8, 37.2, 35.8, 20.9, 19.8. **HRMS (ESI)** calcd for

$[M+H]^+$ $C_{23}H_{26}N^+$, m/z : 316.2060, found: 316.2055. **FT-IR** (ATR): 2915, 1602, 1502, 1429, 1309, 894, 825, 759 cm^{-1} .

2-(3-(3,5-di-tert-butylbenzyl)but-3-en-1-yl)quinoline (14)

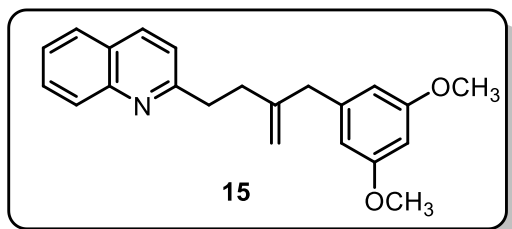


According to the general procedure, **14** was obtained as a yellow liquid (39 mg, 51% yield).

1H NMR (400 MHz, $CDCl_3$) δ 8.05 - 7.99 (m, 2H), 7.74 (dd, $J = 8.2, 1.4$ Hz, 1H), 7.68 - 7.64 (m, 1H), 7.48 - 7.43 (m, 1H), 7.27 (t, $J = 1.9$ Hz,

1H), 7.20 (d, $J = 8.4$ Hz, 1H), 7.05 (d, $J = 1.9$ Hz, 2H), 4.91 (d, $J = 1.6$ Hz, 1H), 4.81 (d, $J = 2.0$ Hz, 1H), 3.42 (s, 2H), 3.17 - 3.10 (m, 2H), 2.56 - 2.50 (m, 2H), 1.31 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.4, 150.6, 148.4, 148.0, 138.6, 136.2, 129.4, 128.9, 127.5, 126.8, 125.7, 123.3, 121.3, 120.0, 111.7, 43.8, 37.6, 35.4, 34.8, 31.6. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{28}H_{36}N^+$, m/z : 386.2842, found: 386.2839. **FT-IR** (ATR): 2923, 2253, 1643, 1600, 1445, 1377, 1038, 893, 823, 751 cm^{-1} .

2-(3-(3,5-dimethoxybenzyl)but-3-en-1-yl)quinoline (15)



According to the general procedure, **15** was obtained as a yellow liquid (48 mg, 72% yield).

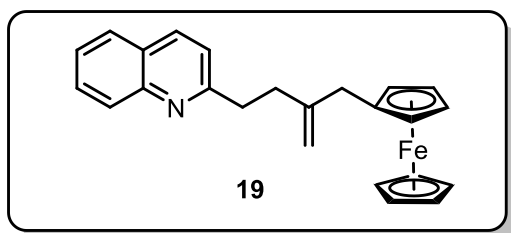
1H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, $J = 8.6, 2.8$ Hz, 2H), 7.75 (dd, $J = 8.2, 1.5$ Hz, 1H), 7.68 - 7.64 (m, 1H), 7.48 - 7.44 (m, 1H), 7.22 (d, $J =$

8.4 Hz, 1H), 6.36 (d, $J = 2.3$ Hz, 2H), 6.31 (t, $J = 2.3$ Hz, 1H), 4.93 (d, $J = 1.2$ Hz, 1H), 4.84 (d, $J = 1.6$ Hz, 1H), 3.75 (s, 6H), 3.35 (s, 2H), 3.16 - 3.08 (m, 2H), 2.51 (t, $J = 8.0$ Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.2, 160.8, 147.9, 147.6, 142.0, 136.2, 129.4, 128.8, 127.5, 126.8, 125.8, 121.3, 112.0, 107.1, 98.2, 55.3, 43.6, 37.4, 35.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{24}NO_2^+$, m/z : 334.1802, found: 334.1799. **FT-IR** (ATR): 2929, 1595, 1459, 1200, 1149, 1061, 825, 753 cm^{-1} .

2-(3-((2,2-difluorobenzo[d][1,3]dioxol-5-yl)methyl)but-3-en-1-yl)quinoline (16)

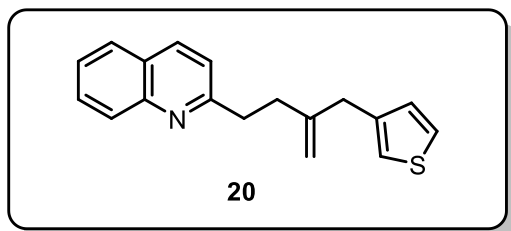
- 7.40 (m, 3H), 7.33 (dd, $J = 8.4, 1.8$ Hz, 1H), 7.18 (d, $J = 8.4$ Hz, 1H), 4.97 (d, $J = 1.6$ Hz, 1H), 4.87 - 4.83 (m, 1H), 3.57 (s, 2H), 3.18 - 3.12 (m, 2H), 2.56 - 2.50 (t, $J = 8.4$ Hz, 2H). **^{13}C NMR (101 MHz, CDCl_3)** δ 162.1, 147.9, 147.9, 137.1, 136.3, 133.6, 132.2, 129.4, 128.8, 127.9, 127.7, 127.7, 127.6, 127.5, 127.4, 126.8, 125.9, 125.8, 125.3, 121.3, 112.1, 43.5, 37.4, 35.3. **HRMS (ESI)** calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{24}\text{H}_{22}\text{N}^+$, m/z : 324.1747, found: 324.1751. **FT-IR (ATR)**: 2914, 1599, 1503, 1430, 1310, 893, 778 cm^{-1} .

2-(3-((ferrocenyl)methyl)but-3-en-1-yl)quinoline (19)



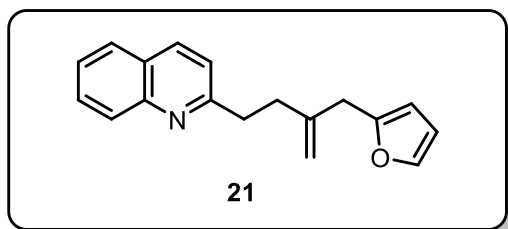
According to the general procedure, **19** was obtained as a yellow liquid (46 mg, 60% yield). **^1H NMR (400 MHz, CDCl_3)** δ 8.05 (dd, $J = 8.4, 1.6$ Hz, 2H), 7.77 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.70 - 7.66 (m, 1H), 7.50 - 7.46 (m, 1H), 7.26 (d, $J = 8.4$ Hz, 1H), 4.74 (d, $J = 1.6$ Hz, 1H), 4.68 (d, $J = 1.7$ Hz, 1H), 4.18 - 4.12 (m, 1H), 4.09 (s, 6H), 4.06 (t, $J = 1.8$ Hz, 2H), 3.16 (s, 2H), 3.12 - 3.02 (m, 2H), 2.51 (t, $J = 8.0$ Hz, 2H). **^{13}C NMR (101 MHz, CDCl_3)** δ 162.3, 148.9, 147.9, 136.2, 129.4, 128.8, 127.5, 126.8, 125.8, 121.4, 110.3, 86.3, 69.1, 68.6, 67.5, 37.5, 37.4, 35.6. **HRMS (ESI)** calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{24}\text{H}_{24}\text{FeN}^+$, m/z : 382.1247, found: 382.1242. **FT-IR (ATR)**: 2918, 1602, 1498, 1432, 892, 823, 743 cm^{-1} .

2-(3-(thiophen-3-ylmethyl)but-3-en-1-yl)quinoline (20)



According to the general procedure, **20** was obtained as a yellow liquid (38 mg, 68% yield). **^1H NMR (400 MHz, CDCl_3)** δ 8.07 - 8.03 (m, 2H), 7.77 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.71 - 7.66 (m, 1H), 7.51 - 7.46 (m, 1H), 7.33 (dd, $J = 1.9, 0.9$ Hz, 1H), 7.26 (d, $J = 8.4$ Hz, 1H), 6.30 (dd, $J = 3.2, 1.9$ Hz, 1H), 6.08 (dd, $J = 3.1, 0.9$ Hz, 1H), 4.93 (d, $J = 1.8$ Hz, 1H), 4.86 (dd, $J = 2.2, 1.1$ Hz, 1H), 3.44 (s, 2H), 3.16 - 3.09 (m, 2H), 2.55 (t, 2H). **^{13}C NMR (101 MHz, CDCl_3)** δ 162.6, 153.5, 147.8, 146.1, 141.4, 135.8, 129.4, 128.4, 127.5, 126.8, 125.8, 121.3, 112.2, 110.3, 106.5, 37.3, 35.6, 35.3. **HRMS (ESI)** calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{18}\text{H}_{18}\text{NS}^+$, m/z : 280.1154, found: 280.1156. **FT-IR (ATR)**: 3362, 2920, 2851, 1718, 1659, 1426, 1263, 734, 704 cm^{-1} .

2-(3-(furan-2-ylmethyl)but-3-en-1-yl)quinoline (21)

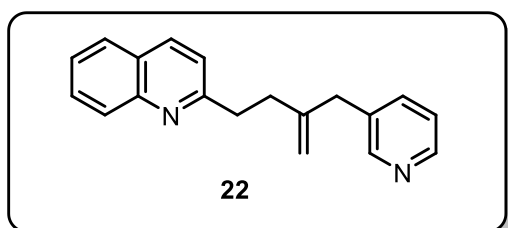


According to the general procedure, **21** was obtained as a yellow liquid (22 mg, 42% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.08 - 8.00 (m, 2H), 7.76 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.70 - 7.65 (m, 1H), 7.50 - 7.45 (m, 1H), 7.26 - 7.24 (m, 1H),

7.23 (t, *J* = 2.5 Hz, 1H), 6.99 - 6.96 (m, 1H), 6.92 (dd, *J* = 4.9, 1.3 Hz, 1H), 4.91 (d, *J* = 1.7 Hz, 1H), 4.82 (d, *J* = 1.3 Hz, 1H), 3.43 (s, 2H), 3.18 - 3.07 (m, 2H), 2.53 (t, *J* = 8.0 Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 161.2, 147.9, 147.2, 140.0, 135.9, 129.4, 128.8, 128.7, 127.5, 126.8, 125.8, 125.3, 121.4, 121.3, 111.5, 37.7, 37.4, 35.3. **HRMS (ESI)** calcd for [M+H]⁺ C₁₈H₁₈NO⁺, *m/z*: 264.1383, found: 264.1380. **FT-IR (ATR)**: 3053, 2922, 1600, 1504, 1427, 895, 818, 754 cm⁻¹.

2-(3-(pyridin-3-ylmethyl)but-3-en-1-yl)quinoline (22)

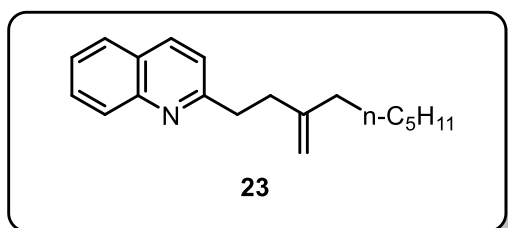


According to the general procedure, **22** was obtained as a yellow liquid (27 mg, 49% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.50 - 8.40 (m, 2H), 8.04 (dd, *J* = 8.5, 5.7 Hz, 2H), 7.76 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.70 - 7.65 (m, 1H), 7.52 - 7.44

(m, 2H), 7.26 - 7.15 (m, 2H), 4.96 (d, *J* = 1.6 Hz, 1H), 4.77 (d, *J* = 1.2 Hz, 1H), 3.39 (s, 2H), 3.18 - 3.09 (m, 2H), 2.51 (t, *J* = 8.0 Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 161.8, 150.4, 147.9, 147.7, 147.0, 136.5, 136.3, 134.9, 129.5, 128.8, 127.5, 126.8, 125.8, 123.3, 121.2, 112.5, 40.3, 37.2, 35.2. **HRMS (ESI)** calcd for [M+H]⁺ C₁₉H₁₉N₂⁺, *m/z*: 275.1543, found: 275.1539. **FT-IR (ATR)**: 3740, 3357, 2921, 2852, 1642, 1424, 748 cm⁻¹.

2-(3-methylenenonyl)quinoline (23)



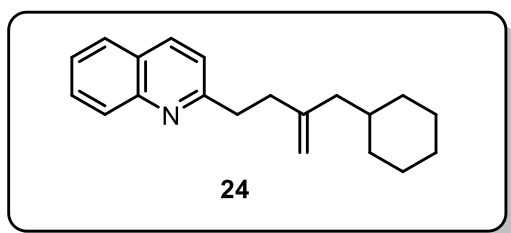
According to the general procedure, **23** was obtained as a yellow liquid (36 mg, 67% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.00 - 7.96 (m, 2H), 7.69 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.62 - 7.57 (m, 1H), 7.43 - 7.37 (m, 1H), 7.23 (d, *J* = 8.5 Hz,

1H), 4.72 (d, *J* = 1.7 Hz, 1H), 4.69 (d, *J* = 1.7 Hz, 1H), 3.09 - 3.01 (m, 2H), 2.49 - 2.41 (m,

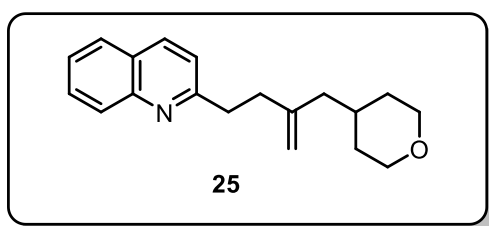
2H), 2.05 - 1.98 (m, 2H), 1.41 - 1.34 (m, 2H), 1.24 - 1.18 (m, 6H), 0.83 - 0.77 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.5, 149.7, 147.9, 136.2, 129.4, 128.8, 127.5, 126.8, 125.7, 121.4, 108.8, 37.6, 36.4, 35.9, 31.8, 29.1, 27.8, 22.7, 14.1. HRMS (ESI) calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{19}\text{H}_{26}\text{N}^+$, m/z : 268.2060, found: 268.2061. FT-IR (ATR): 2924, 1602, 1503, 1432, 1114, 887, 822, 752 cm^{-1} .

2-(3-(cyclohexylmethyl)but-3-en-1-yl)quinoline (24)



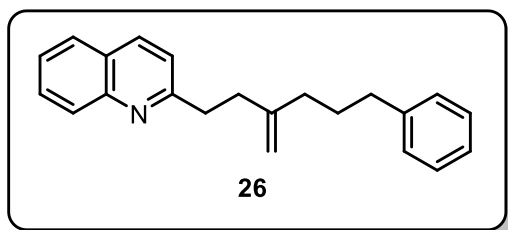
According to the general procedure, **24** was obtained as a yellow liquid (41 mg, 74% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.05 (dd, $J = 8.4$, 2.1 Hz, 2H), 7.77 (dd, $J = 8.1$, 1.5 Hz, 1H), 7.70 - 7.65 (m, 1H), 7.50 - 7.45 (m, 1H), 7.30 (d, $J = 8.4$ Hz, 1H), 4.83 (dd, $J = 3.6$, 1.6 Hz, 1H), 4.73 (dd, $J = 2.0$, 0.8 Hz, 1H), 3.15 - 3.09 (m, 2H), 2.51 (t, $J = 8.2$ Hz, 2H), 1.98 (dd, $J = 7.2$, 0.8 Hz, 2H), 1.72 - 1.65 (m, 4H), 1.51 - 1.42 (m, 1H), 1.30 - 1.08 (m, 4H), 0.90 - 0.79 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.5, 149.0, 147.3, 136.2, 129.4, 128.8, 127.5, 126.8, 125.7, 121.0, 110.7, 44.8, 37.5, 35.6, 35.6, 33.4, 26.6, 26.4. HRMS (ESI) calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{20}\text{H}_{26}\text{N}^+$, m/z : 280.2060, found: 280.2063. FT-IR (ATR): 2918, 1600, 1495, 1447, 1118, 890, 830, 700 cm^{-1} .

2-(3-((tetrahydro-2H-pyran-4-yl)methyl)but-3-en-1-yl)quinoline (25)



According to the general procedure, **25** was obtained as a yellow liquid (45 mg, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.96 (dd, $J = 8.4$, 2.3 Hz, 2H), 7.67 (dd, $J = 8.2$, 1.5 Hz, 1H), 7.61 - 7.56 (m, 1H), 7.40 - 7.36 (m, 1H), 7.20 (d, $J = 8.4$ Hz, 1H), 4.79 (d, $J = 1.6$ Hz, 1H), 4.67 (d, $J = 1.6$ Hz, 1H), 3.83 (dd, $J = 12.0$, 4.0 Hz, 2H), 3.24 (td, $J = 11.8$, 2.1 Hz, 2H), 3.07 - 3.00 (m, 2H), 2.44 (t, $J = 8.0$ Hz, 2H), 1.94 (d, $J = 7.2$ Hz, 2H), 1.65 - 1.55 (m, 1H), 1.49 - 1.45 (m, 2H), 1.18 - 1.11 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.2, 147.9, 146.2, 136.2, 129.4, 128.8, 127.5, 126.8, 125.8, 121.4, 111.4, 68.0, 44.2, 37.4, 35.5, 33.1, 32.9. HRMS (ESI) calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{19}\text{H}_{24}\text{NO}^+$, m/z : 282.1852, found: 282.1857. FT-IR (ATR): 2922, 1600, 1504, 1428, 894, 819, 752 cm^{-1} .

2-(3-methylene-6-phenylhexyl)quinoline (26)

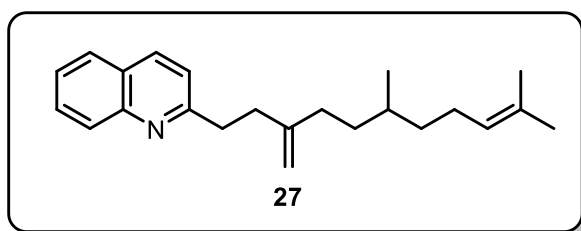


According to the general procedure, **26** was obtained as a yellow liquid (56 mg, 93% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.03 (dd, *J* = 12.3, 8.5 Hz, 2H), 7.74 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.68 - 7.63 (m, 1H), 7.48 - 7.43 (m, 1H), 7.26 (dd, *J* =

8.4, 6.2 Hz, 3H), 7.19 - 7.13 (m, 3H), 4.84 (d, *J* = 1.8 Hz, 1H), 4.79 (s, 1H), 3.15 - 3.07 (m, 2H), 2.61 (t, *J* = 7.8 Hz, 2H), 2.54 (t, *J* = 7.8 Hz, 2H), 2.14 (t, *J* = 7.8 Hz, 2H), 1.84 - 1.75 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 148.6, 147.6, 142.0, 136.3, 129.4, 128.9, 128.3, 127.6, 126.8, 125.8, 121.0, 109.7, 37.6, 35.9, 35.9, 35.6, 29.6. **HRMS (ESI)** calcd for [M+H]⁺ C₂₂H₂₄N⁺, *m/z*: 302.1903, found: 302.1900. **FT-IR (ATR)**: 2928, 1601, 1500, 1434, 822, 746, 699 cm⁻¹.

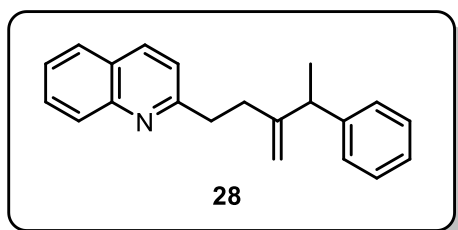
2-(6,10-dimethyl-3-methyleneundec-9-en-1-yl)quinoline (27)



According to the general procedure, **27** was obtained as a yellow liquid (40 mg, 62% yield). **¹H NMR (400 MHz, CDCl₃)** δ 8.05 (dd, *J* = 8.5, 2.9 Hz, 2H), 7.77 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.70 - 7.65 (m, 1H), 7.50 -

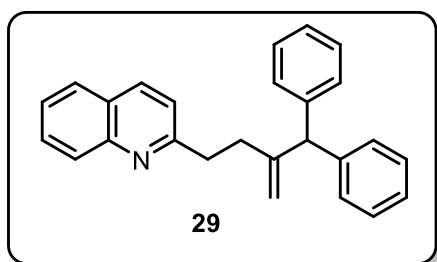
7.45 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 5.12 - 5.06 (m, 1H), 4.80 (d, *J* = 1.7 Hz, 1H), 4.77 (d, *J* = 1.7 Hz, 1H), 3.18 - 3.06 (m, 2H), 2.54 (t, *J* = 8.0 Hz, 2H), 2.14 - 2.05 (m, 2H), 2.02 - 1.90 (m, 2H), 1.70 - 1.66 (m, 4H), 1.60 (d, *J* = 1.3 Hz, 3H), 1.52-1.38 (m, 2H), 1.37- 1.25 (m, 2H), 1.19 - 1.10 (m, 1H), 0.89 (d, *J* = 6.4 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.8, 149.5, 147.9, 136.2, 131.1, 129.4, 128.9, 127.5, 126.8, 125.7, 124.2, 121.4, 109.1, 37.7, 37.1, 36.0, 35.1, 33.9, 32.3, 25.8, 25.6, 19.5, 17.7. **HRMS (ESI)** calcd for [M+H]⁺ C₂₃H₃₂N⁺, *m/z*: 322.2529, found: 322.2528. **FT-IR (ATR)**: 2921, 1509, 1418, 1098, 986, 852, 629 cm⁻¹.

2-(3-methylene-4-phenylpentyl)quinoline (28)



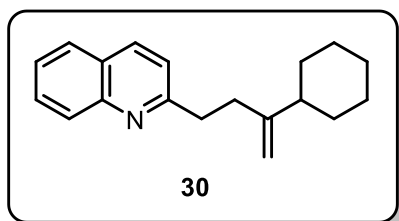
According to the general procedure, **28** was obtained as a yellow liquid (35 mg, 61% yield). **¹H NMR (400 MHz, CDCl₃)** δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.75 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.69 - 7.63 (m, 1H), 7.50 - 7.44 (m, 1H), 7.29 - 7.26 (m, 1H), 7.26 - 7.14 (m, 5H), 5.00 (d, *J* = 1.2 Hz, 2H), 3.49 (dd, *J* = 14.0, 7.2 Hz, 1H), 3.14 - 3.01 (m, 2H), 2.50 - 2.33 (m, 2H), 1.39 (d, *J* = 7.0 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.3, 152.1, 148.3, 145.2, 136.2, 129.4, 128.8, 128.3, 127.6, 127.5, 126.7, 126.2, 125.7, 121.3, 109.4, 45.6, 37.6, 34.7, 20.7. **HRMS (ESI)** calcd for [M+H]⁺ C₂₁H₂₂N⁺, *m/z*: 288.1752, found: 288.1754. **FT-IR (ATR)**: 2965, 2928, 1599, 1503, 1492, 1451, 898, 823, 751, 700 cm⁻¹.

2-(3-benzhydrylbut-3-en-1-yl)quinoline (**29**)



According to the general procedure, **29** was obtained as a yellow liquid (45 mg, 65% yield). **¹H NMR (400 MHz, CDCl₃)** δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.76 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.71 - 7.66 (m, 1H), 7.50 - 7.45 (m, 1H), 7.30 - 7.23 (m, 5H), 7.22 - 7.20 (m, 1H), 7.19 (d, *J* = 2.5 Hz, 1H), 7.18 - 7.14 (m, 4H), 5.18 (s, 1H), 4.86 (s, 1H), 4.54 (s, 1H), 3.22 - 3.12 (m, 2H), 2.59 (t, *J* = 8.0 Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.0, 150.9, 147.9, 142.3, 136.2, 129.4, 129.4, 128.8, 128.3, 127.5, 126.8, 126.3, 125.8, 121.3, 114.4, 57.6, 37.7, 35.9. **HRMS (ESI)** calcd for [M+H]⁺ C₂₆H₂₄N⁺, *m/z*: 350.1909, found: 350.1908. **FT-IR (ATR)**: 3057, 3025, 1598, 1497, 1427, 902, 824, 745, 699 cm⁻¹.

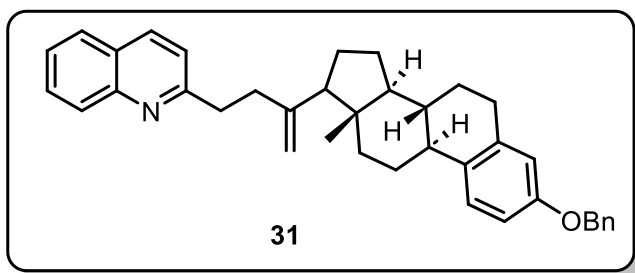
2-(3-cyclohexylbut-3-en-1-yl)quinoline (**30**)



According to the general procedure, **30** was obtained as a yellow liquid (24 mg, 45% yield). **¹H NMR (400 MHz, CDCl₃)** δ 8.06 (t, *J* = 8.3 Hz, 2H), 7.78 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.71 - 7.66 (m, 1H), 7.52 - 7.45 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 4.82 - 4.74 (m, 2H), 3.17 - 3.05 (m, 2H), 2.62 - 2.48 (m, 2H), 2.00 - 1.88 (m, 1H), 1.84 - 1.74 (m, 4H), 1.71 - 1.65 (m, 1H), 1.28 - 1.10 (m, 5H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.6, 154.5, 148.2, 136.2, 129.4, 128.8,

127.5, 126.8, 125.7, 121.4, 107.3, 44.5, 38.0, 34.8, 32.5, 26.8, 26.4. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{19}H_{24}N^+$, m/z : 266.1909, found: 266.1908. **FT-IR (ATR)**: 2924, 2852, 1640, 1600, 1503, 1447, 886, 825, 753 cm^{-1} .

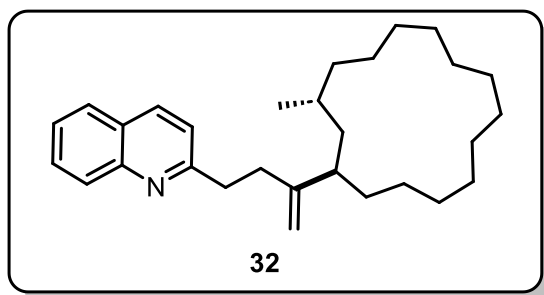
2-(3-(((8S,9S,13R,14S,17S)-3-(benzyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)methyl)but-3-en-1-yl)quinoline (31)



According to the general procedure, **31** was obtained as a white solid (51 mg, 47% yield). **m.p.** = 129.0-132.8 °C. **1H NMR (400 MHz, $CDCl_3$)** δ 8.06 (dd, J = 8.5, 2.6 Hz, 2H), 7.77 (dd, J = 8.1, 1.5 Hz, 1H), 7.71 - 7.65 (m, 1H), 7.50 - 7.45

(m, 1H), 7.44 - 7.40 (m, 2H), 7.39 - 7.34 (m, 2H), 7.33 - 7.28 (m, 2H), 7.18 (d, J = 8.5 Hz, 1H), 6.76 (dd, J = 8.6, 2.8 Hz, 1H), 6.71 (d, J = 2.8 Hz, 1H), 5.02 (s, 2H), 5.00 (d, J = 1.6 Hz, 1H), 4.87 (s, 1H), 3.21 - 3.10 (m, 2H), 2.89 - 2.78 (m, 2H), 2.70 - 2.59 (m, 1H), 2.56 - 2.46 (m, 1H), 2.30 - 2.16 (m, 3H), 1.97 (dd, J = 8.5, 2.6 Hz, 1H), 1.92 - 1.72 (m, 5H), 1.51 - 1.43 (m, 2H), 1.40 - 1.35 (m, 2H), 0.91 - 0.84 (m, 1H), 0.62 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.6, 156.7, 148.5, 148.0, 138.1, 137.4, 136.2, 133.2, 129.4, 128.9, 128.6, 127.9, 127.5, 127.5, 126.8, 126.3, 125.7, 121.5, 114.8, 112.3, 110.3, 70.0, 56.4, 55.4, 43.9, 43.7, 39.2, 38.9, 38.2, 37.6, 31.6, 29.9, 27.7, 26.8, 26.0, 23.9, 22.7, 14.2, 13.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{38}H_{42}NO^+$, m/z : 528.3266, found: 528.3270. **FT-IR (ATR)**: 2921, 2855, 1600, 1499, 1235, 1048, 888, 827, 734, 695 cm^{-1} .

2-(3-(((1S,3R)-3-methylcyclopentadecyl)methyl)but-3-en-1-yl)quinoline (32)

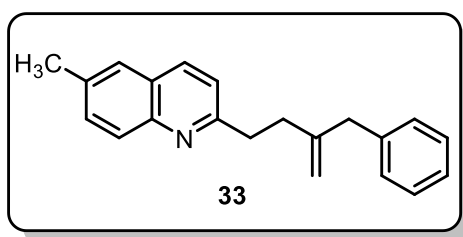


According to the general procedure, **32** was obtained as a yellow liquid (26 mg, 31% yield, d.r. \approx 1.5:1). **1H NMR (400 MHz, $CDCl_3$)** δ 8.06 (t, J = 9.0 Hz, 2H), 7.78 (dd, J = 8.0, 1.5 Hz, 1H), 7.71 - 7.66 (m, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.32 (dd, J = 8.4, 2.3 Hz, 1H), 4.87

(dd, J = 7.9, 1.7 Hz, 1H), 4.82 (s, 1H), 3.19 - 3.10 (m, 2H), 2.53 - 2.44 (m, 2H), 2.20 - 2.12 (m, 1H), 1.58 - 1.48 (m, 2H), 1.39 - 1.24 (m, 25H), 0.84 (dd, J = 6.7, 1.5 Hz, 3H). **^{13}C NMR**

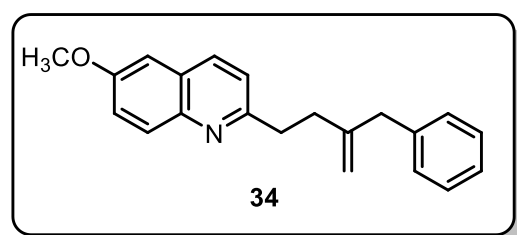
(101 MHz, CDCl₃) δ 162.6, 153.2(isomers), 152.4, 147.9, 136.2, 129.4, 128.8, 127.5, 126.8, 125.7, 121.4, 121.4(isomers), 109.1, 108.4(isomers), 43.9(isomers), 43.5, 42.7(isomers), 40.0, 37.7(isomers), 37.6, 35.2, 33.6(isomers), 33.2(isomers), 32.7, 32.6, 30.1(isomers), 29.8, 29.3, 27.5, 27.2(isomers), 27.1, 26.9(isomers), 26.8, 26.7(isomers), 26.7, 26.6(isomers), 26.6, 26.6(isomers), 25.5(isomers), 25.4, 24.8, 23.6, 21.4(isomers), 21.1. **HRMS (ESI)** calcd for [M+H]⁺ C₂₉H₄₄N⁺, m/z: 406.3474, found: 406.3475. **FT-IR (ATR):** 2923, 2854, 1601, 1502, 1457, 1312, 967, 887, 824, 750 cm⁻¹.

2-(3-benzylbut-3-en-1-yl)-6-methylquinoline (33)



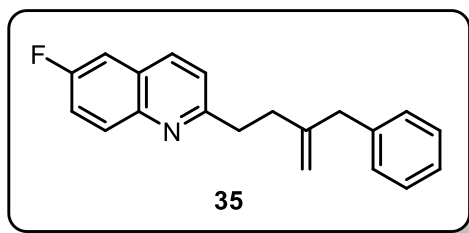
According to the general procedure, **33** was obtained as a yellow liquid (32 mg, 56% yield). **¹H NMR (400 MHz, CDCl₃)** δ 7.93 (dd, $J = 11.1, 8.4$ Hz, 2H), 7.54 - 7.48 (m, 2H), 7.31 - 7.26 (m, 2H), 7.22 - 7.17 (m, 4H), 4.91 (d, $J = 1.7$ Hz, 1H), 4.79 (d, $J = 1.8$ Hz, 1H), 3.41 (s, 2H), 3.14 - 3.08 (m, 2H), 2.51 (s, 3H), 2.48 (t, $J = 8.0, 2$ H). **¹³C NMR (101 MHz, CDCl₃)** δ 161.2, 148.1, 146.5, 139.6, 135.6, 135.5, 131.6, 129.1, 128.5, 128.3, 126.8, 126.4, 126.1, 121.3, 111.8, 43.3, 37.3, 35.3, 21.5. **HRMS (ESI)** calcd for [M+H]⁺ C₂₁H₂₂N⁺, m/z: 288.1747, found: 288.1742. **FT-IR (ATR):** 2917, 1597, 1492, 1440, 1315, 890, 824, 745, 699 cm⁻¹.

2-(3-benzylbut-3-en-1-yl)-6-methoxyquinoline (34)



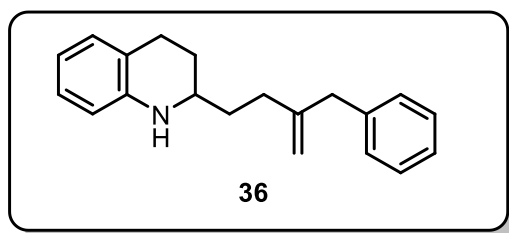
According to the general procedure, **34** was obtained as a yellow liquid (28 mg, 46% yield). **¹H NMR (400 MHz, CDCl₃)** δ 7.90 (t, $J = 8.1$ Hz, 2H), 7.28 (dd, $J = 9.2, 2.8$ Hz, 1H), 7.23 - 7.19 (m, 2H), 7.15 - 7.10 (m, 4H), 6.97 (d, $J = 2.8$ Hz, 1H), 4.84 (d, $J = 1.7$ Hz, 1H), 4.72 (d, $J = 1.8$ Hz, 1H), 3.85 (s, 3H), 3.34 (s, 2H), 3.08 - 3.02 (m, 2H), 2.42 (t, $J = 8.0$ Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 159.4, 157.4, 148.0, 143.5, 139.6, 135.6, 129.8, 129.1, 128.3, 127.7, 126.1, 122.2, 121.5, 111.9, 105.2, 55.5, 43.3, 36.8, 35.2. **HRMS (ESI)** calcd for [M+H]⁺ C₂₁H₂₂NO⁺, m/z: 304.1696, found: 304.1694. **FT-IR (ATR):** 2919, 1608, 1499, 1225, 1102, 869, 825, 738, 698 cm⁻¹.

2-(3-benzylbut-3-en-1-yl)-6-fluoroquinoline (35)



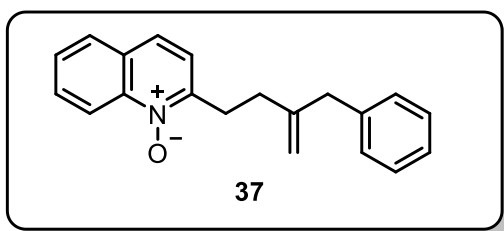
According to the general procedure, **35** was obtained as a yellow liquid (33 mg, 57% yield). **¹H NMR (400 MHz, CDCl₃)** δ 8.02 (dd, *J* = 9.3, 5.3 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.38 (td, *J* = 8.8, 2.9 Hz, 1H), 7.31 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.19 (t, 3H), 7.14 - 7.09 (m, 3H), 4.83 (d, *J* = 1.8 Hz, 1H), 4.72 (d, *J* = 1.8 Hz, 1H), 3.34 (s, 2H), 3.11 - 3.04 (m, 2H), 2.43 (t, *J* = 8.0 Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 161.38, 158.9, 147.8, 144.3, 139.5, 136.1 (d, *J*_{C-F} = 5.2 Hz), 130.8 (d, *J*_{C-F} = 9.1 Hz), 129.1, 128.3, 127.3 (d, *J*_{C-F} = 10.1 Hz), 126.2, 122.1, 119.8 (d, *J*_{C-F} = 25.8 Hz), 112.0, 110.5 (d, *J*_{C-F} = 21.7 Hz), 43.3, 36.8, 35.0. **¹⁹F NMR (376 MHz, CDCl₃)** δ -114.25. **HRMS (ESI)** calcd for [M+H]⁺ C₂₀H₁₉FN⁺, *m/z*: 292.1496, found: 292.1492. **FT-IR (ATR)**: 2918, 1608, 1498, 1225, 1141, 871, 829, 739, 699 cm⁻¹.

2-(3-benzylbut-3-en-1-yl)-1,2,3,4-tetrahydroquinoline (36)



According to the general procedure, **36** was obtained as a yellow liquid (50 mg, 90% yield). **¹H NMR (400 MHz, CDCl₃)** δ 7.22 - 7.17 (m, 2H), 7.14 - 7.08 (m, 3H), 6.88 - 6.81 (m, 2H), 6.50 (m, 1H), 6.32 (dd, *J* = 7.9, 1.2 Hz, 1H), 4.79 (d, *J* = 3.2 Hz, 1H), 4.72 (d, *J* = 1.8 Hz, 1H), 3.52 (s, 1H), 3.27 (s, 2H), 3.13 - 3.08 (m, 1H), 2.69 - 2.56 (m, 2H), 2.01 - 1.94 (m, 2H), 1.83 - 1.76 (m, 1H), 1.56 - 1.50 (m, 2H), 1.50 - 1.43 (m, 1H). **¹³C NMR (101 MHz, CDCl₃)** δ 148.6, 144.7, 140.5, 129.3, 129.1, 128.5, 126.8, 126.5, 121.9, 117.1, 114.2, 111.7, 51.3, 43.3, 34.5, 31.5, 28.0, 26.3. **HRMS (ESI)** calcd for [M+H]⁺ C₂₀H₂₄N⁺, *m/z*: 278.1909, found: 278.1907. **FT-IR (ATR)**: 2922, 1713, 1655, 1599, 1500, 1451, 1427, 1113, 824, 751, 700 cm⁻¹.

2-(3-benzylbut-3-en-1-yl)quinoline 1-oxide (37)

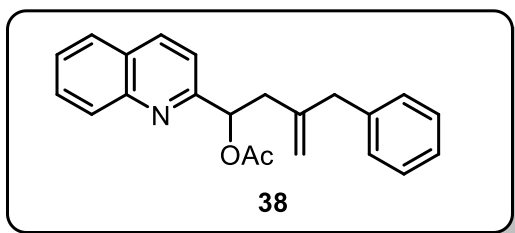


According to the general procedure, **37** was obtained as a colorless liquid (28 mg, 48% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, *J* = 8.7 Hz, 1H), 7.74 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.70 - 7.64 (m, 1H), 7.57 - 7.47 (m, 2H), 7.24 - 7.18 (m,

2H), 7.17 - 7.08 (m, 4H), 4.85 (d, *J* = 1.6 Hz, 1H), 4.77 (d, *J* = 1.8 Hz, 1H), 3.37 (s, 2H), 3.25 - 3.15 (m, 2H), 2.44 (t, *J* = 7.7 Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 148.6, 147.4, 141.7, 139.4, 130.3, 129.1, 128.4, 128.0, 127.8, 126.2, 125.1, 121.9, 119.7, 112.2, 43.3, 31.2, 29.7. **HRMS (ESI)** calcd for [M+H]⁺ C₂₀H₁₉NO⁺, *m/z*: 290.1545, found: 290.1547. **FT-IR (ATR)**: 2921, 1638, 1600, 1502, 1429, 1260, 1022, 891, 820, 752 cm⁻¹.

3-benzyl-1-(quinolin-2-yl)but-3-en-1-yl acetate (**38**)



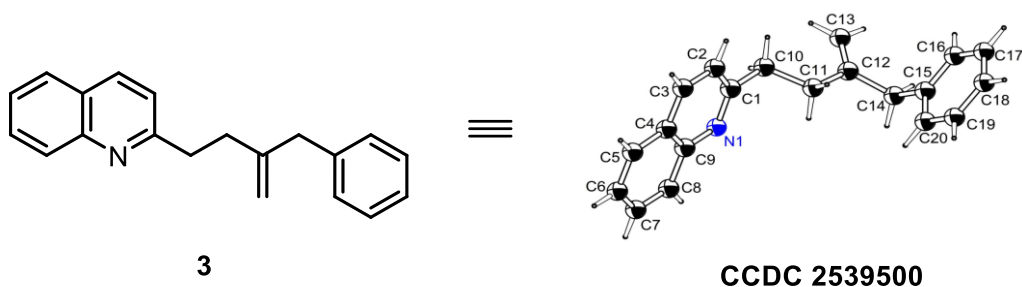
According to the general procedure, **38** was obtained as a yellow liquid (28 mg, 42% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.14 - 8.08 (m, 2H), 7.79 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.73 - 7.68 (m, 1H), 7.55 - 7.50 (m, 1H), 7.40 (d, *J* = 8.5 Hz,

1H), 7.30 - 7.27 (m, 1H), 7.26 - 7.25 (m, 1H), 7.21 - 7.16 (m, 3H), 6.18 (t, *J* = 7.0 Hz, 1H), 4.92 (dd, *J* = 2.6, 1.0 Hz, 1H), 4.80 (dd, *J* = 3.0, 1.4 Hz, 1H), 3.41 (d, *J* = 4.6 Hz, 2H), 2.72 (dd, *J* = 7.1, 1.0 Hz, 2H), 2.13 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 170.4, 159.4, 149.0, 144.3, 139.2, 136.8, 129.6, 129.4, 129.2, 128.4, 127.5, 126.6, 126.2, 118.6, 115.0, 75.4, 43.0, 40.8, 21.2. **HRMS (ESI)** calcd for [M+H]⁺ C₂₂H₂₂NO⁺, *m/z*: 332.1651, found: 332.1651. **FT-IR (ATR)**: 2925, 1594, 1493, 1452, 1243, 1112, 894, 758, 733 cm⁻¹.

7. Crystal data and structure refinement for **3**

Crystal of **3** was prepared in a mixture solvent system (dichloromethane and hexane), the solution was evaporated at 0°C for about two week, sing crystals were formed.



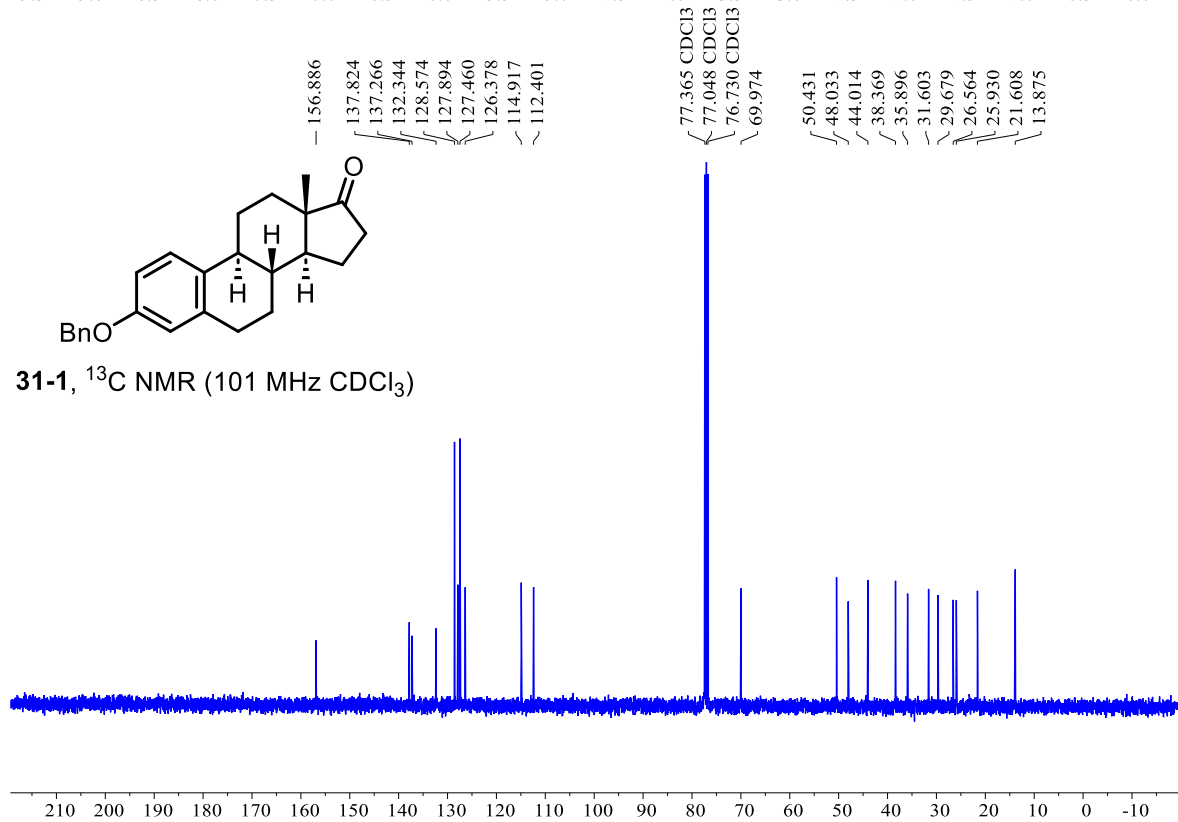
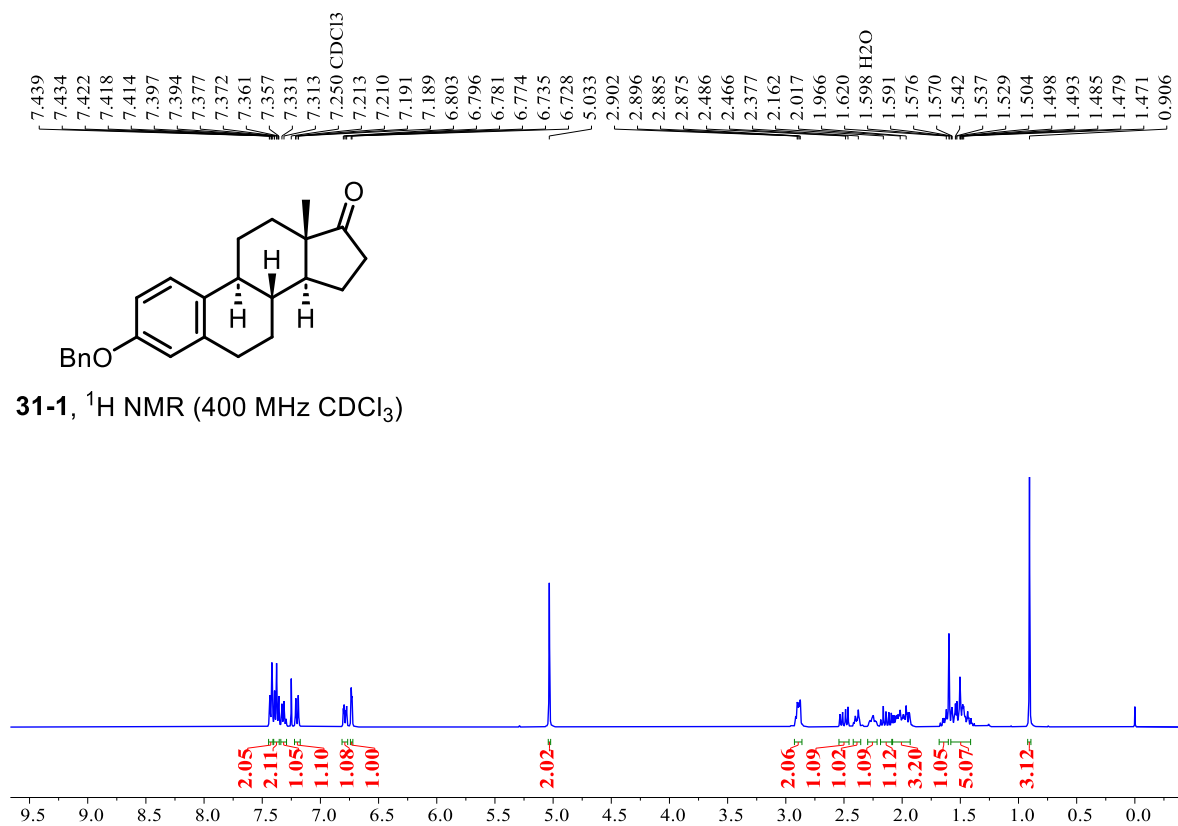
The thermal ellipsoid was drawn at the 50% probability level.

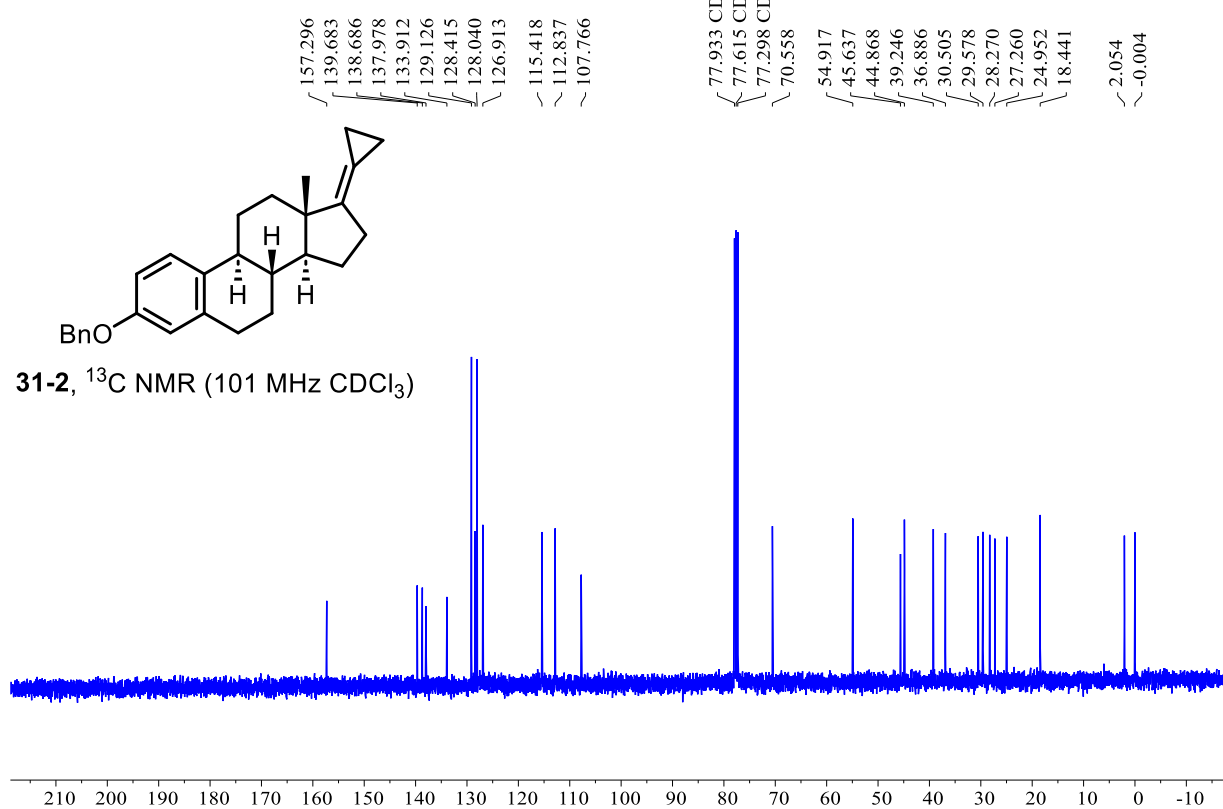
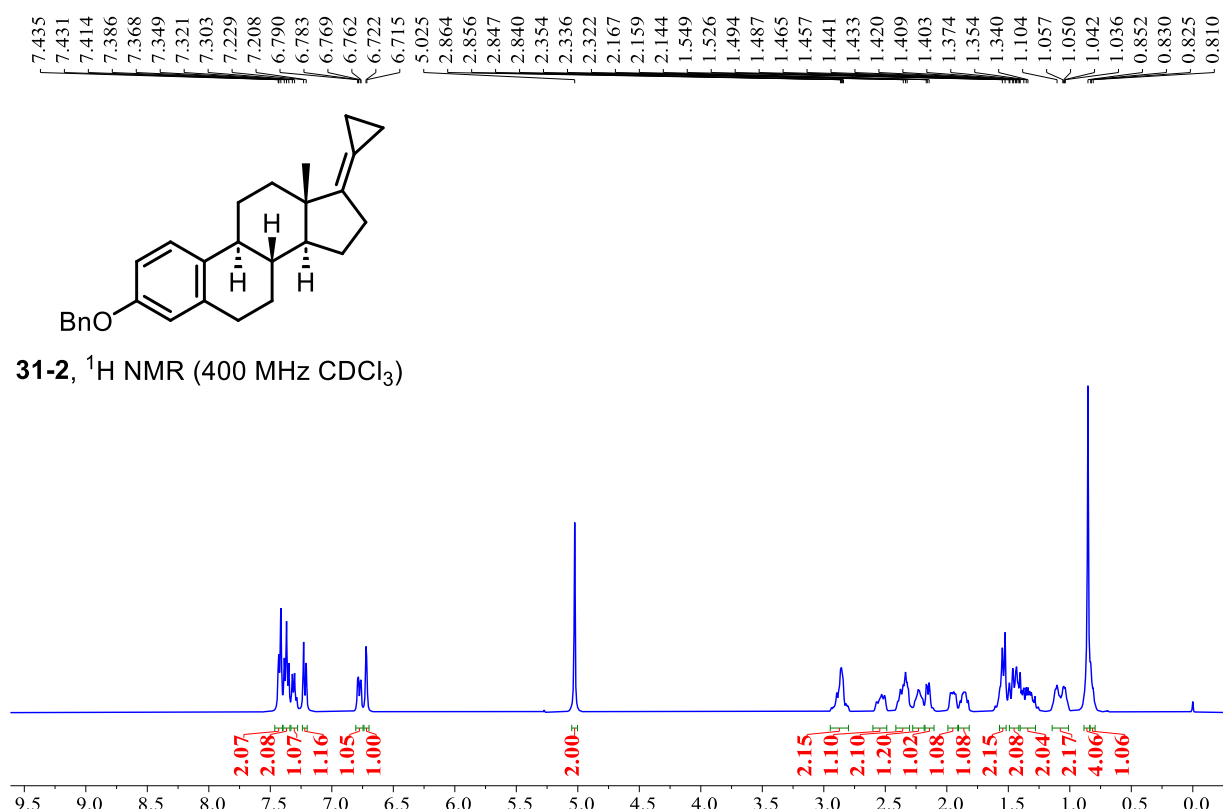
Crystal data and structure refinement for **3**

CCDC	2539500
dentification code	PHY325
Empirical formula	C ₂₀ H ₁₉ N
Formula weight	273.36
Temperature/K	223.00
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	6.0064(2)
b/Å	10.9329(4)
c/Å	23.1967(9)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1523.27(10)

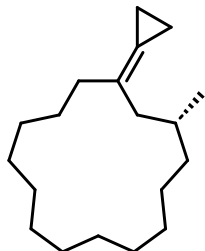
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.192
μ/mm^{-1}	0.069
F(000)	584.0
Crystal size/ mm^3	$0.5 \times 0.4 \times 0.2$
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/ $^\circ$	4.118 to 54.964
Index ranges	$-7 \leq h \leq 7, -13 \leq k \leq 14, -30 \leq l \leq 30$
Reflections collected	17746
Independent reflections	3500 [$R_{\text{int}} = 0.0391, R_{\text{sigma}} = 0.0304$]
Data/restraints/parameters	3500/0/190
Goodness-of-fit on F ²	0.978
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0357, wR_2 = 0.1180$
Final R indexes [all data]	$R_1 = 0.0420, wR_2 = 0.1265$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.14/-0.12
Flack parameter	-0.7(10)

8. ^1H , ^{13}C , ^{19}F NMR spectra of new substrates and all products

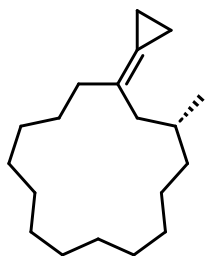
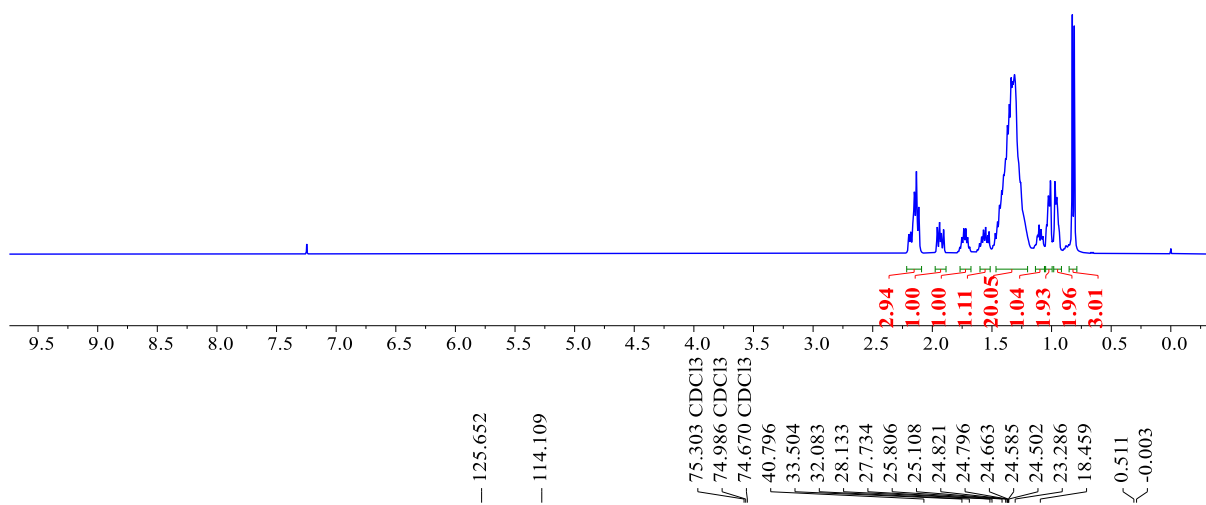




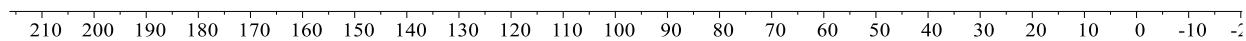
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2.133
2.114
1.959
1.939
1.925
1.906
1.736
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1.570
1.553
1.535
1.524
1.472
1.458
1.453
1.438
1.433
1.426
1.419
1.404
1.389
1.370
1.354
1.344
1.339
1.328
1.315
1.307
1.298
1.276
1.274
1.257
1.240
1.229
1.219
1.116
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1.088
1.043
1.026
1.009
0.971
0.955
0.938
0.826
0.809



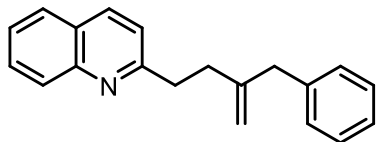
32-1, ^1H NMR (400 MHz CDCl_3)



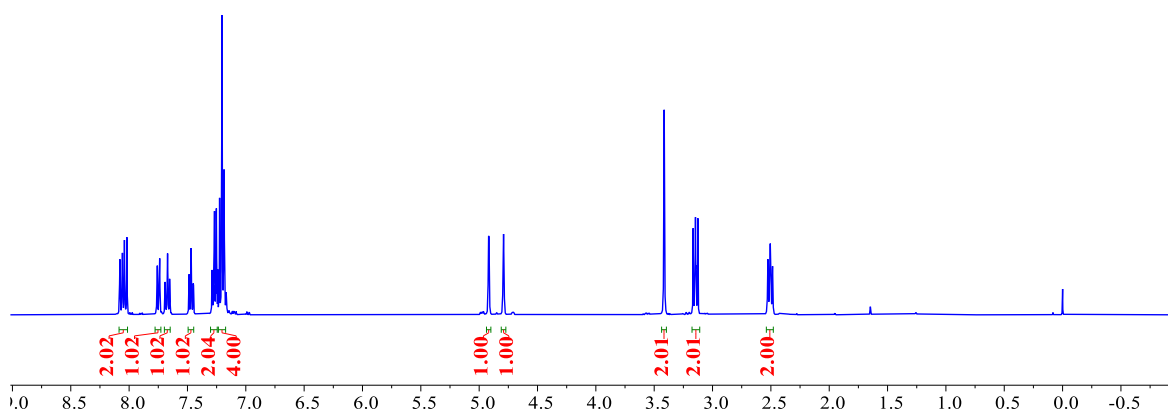
32-1, ^{13}C NMR (101 MHz CDCl_3)



8.080
8.059
8.040
8.019
7.762
7.758
7.742
7.738
7.691
7.688
7.674
7.670
7.666
7.653
7.649
7.488
7.486
7.471
7.468
7.465
7.451
7.448
7.292
7.289
7.285
7.279
7.276
7.271
7.268
7.259
7.252
7.239
7.225
7.204 CDCl₃
7.186
6.152
4.919
4.793
3.414
3.166
3.153
3.149
3.146
3.142
3.126
2.526
2.505
2.485



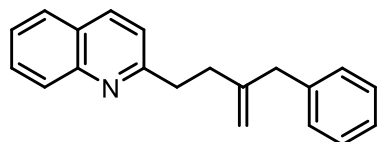
3, ¹H NMR (400 MHz CDCl₃)



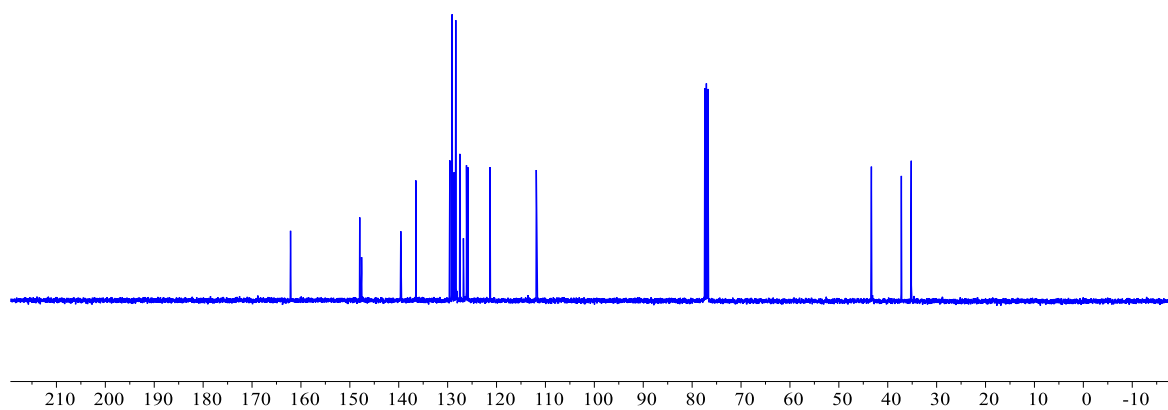
162.126
147.980
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139.585
136.499
129.555
129.085
128.651
128.343
128.299
128.057
127.511
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126.097
125.874
121.318
111.866

77.403 CDCl₃
77.085 CDCl₃
76.768 CDCl₃

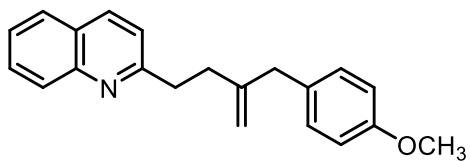
43.344
37.212
35.183



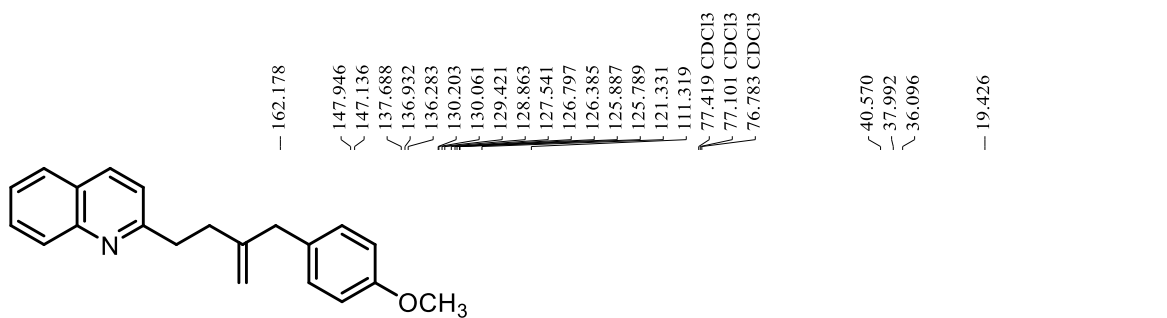
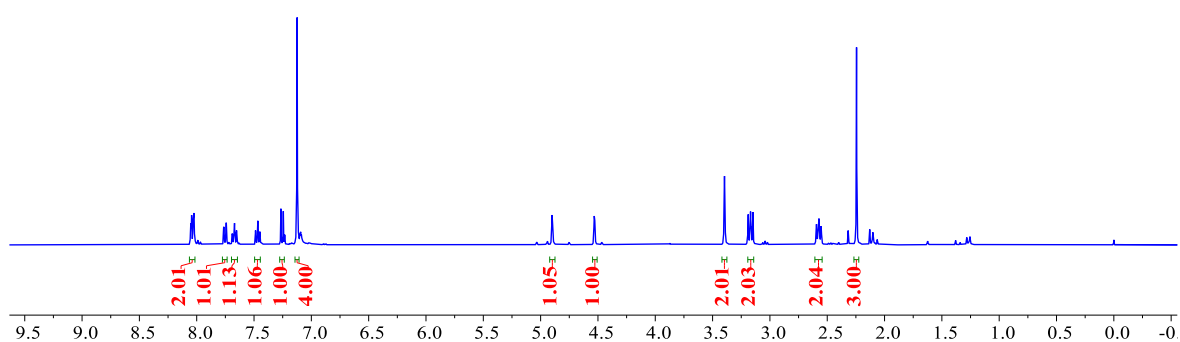
3, ¹³C NMR (101 MHz CDCl₃)



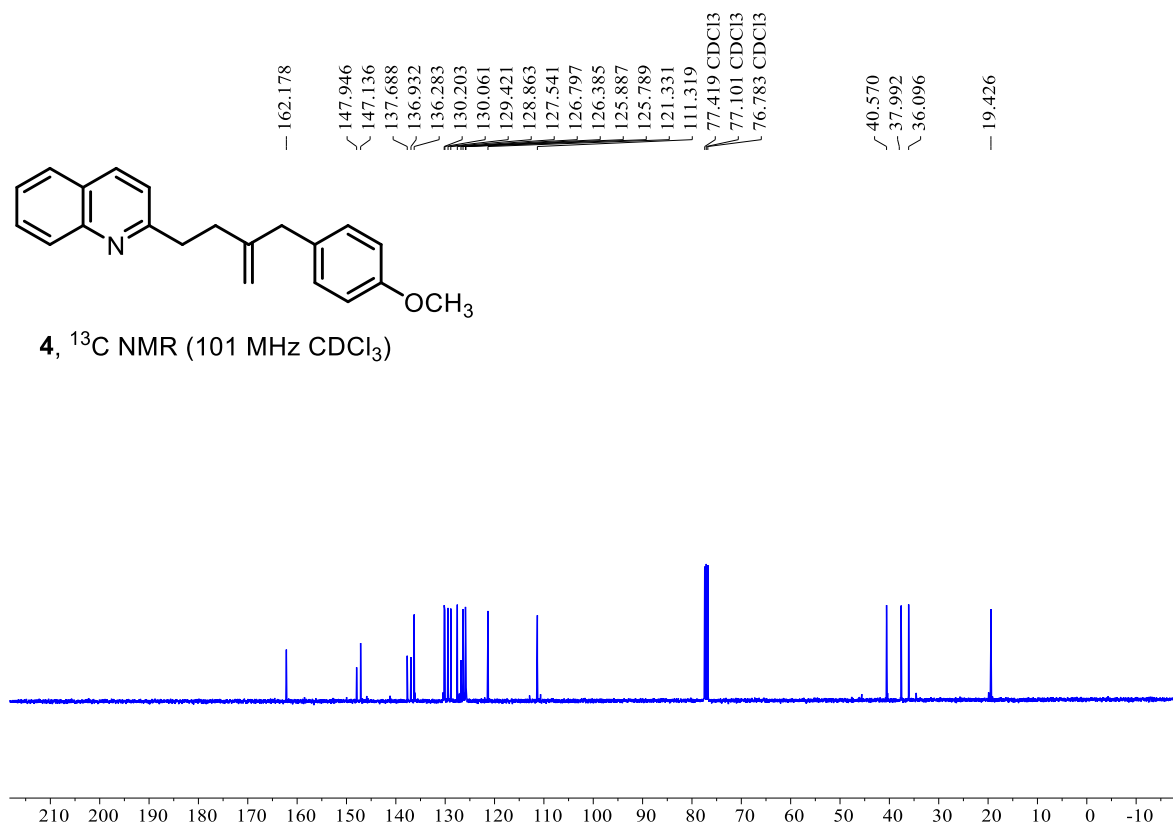
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8.051
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8.023
8.014
7.765
7.762
7.745
7.741
7.691
7.688
7.681
7.674
7.670
7.666
7.653
7.649
7.645
7.487
7.484
7.470
7.467
7.464
7.449
7.446
7.432
7.266
7.245
7.233 CDCl₃
7.124
4.904
4.900
4.897
4.893
4.533
4.528
3.551
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3.160
3.148
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2.574
2.553
2.244

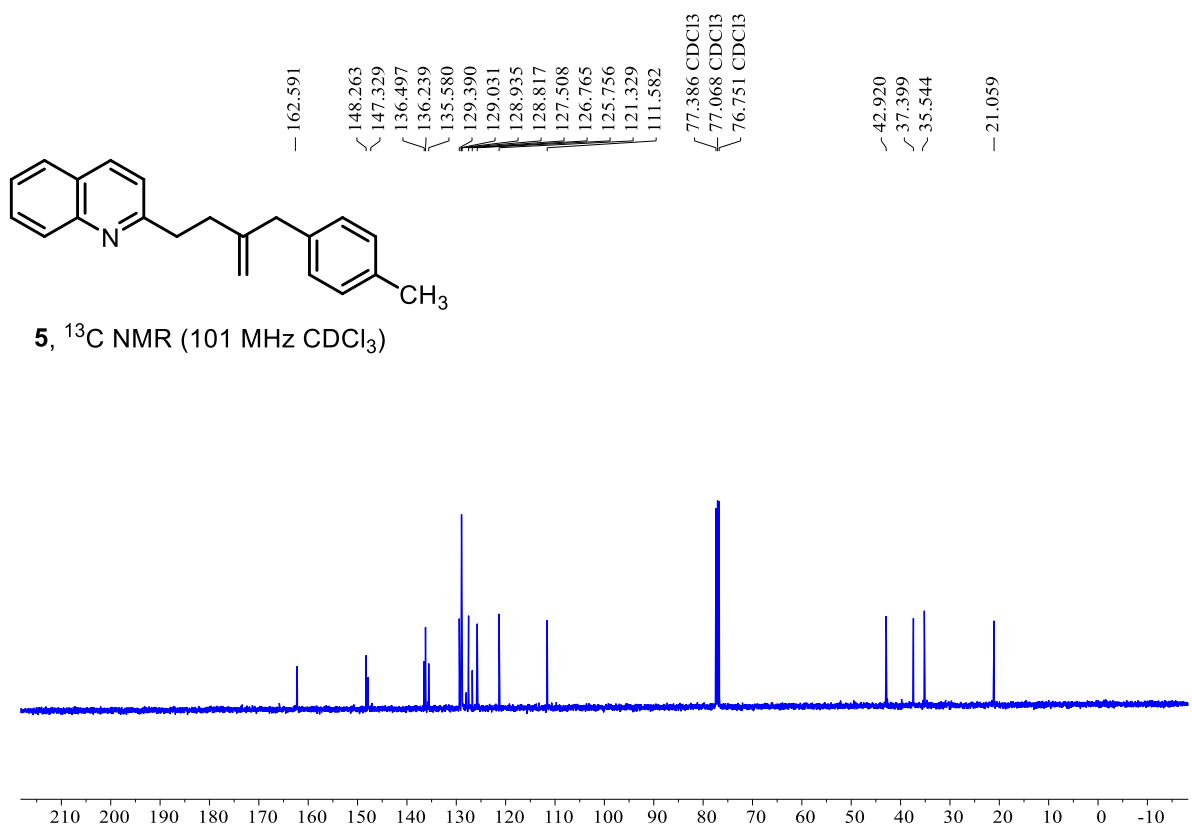
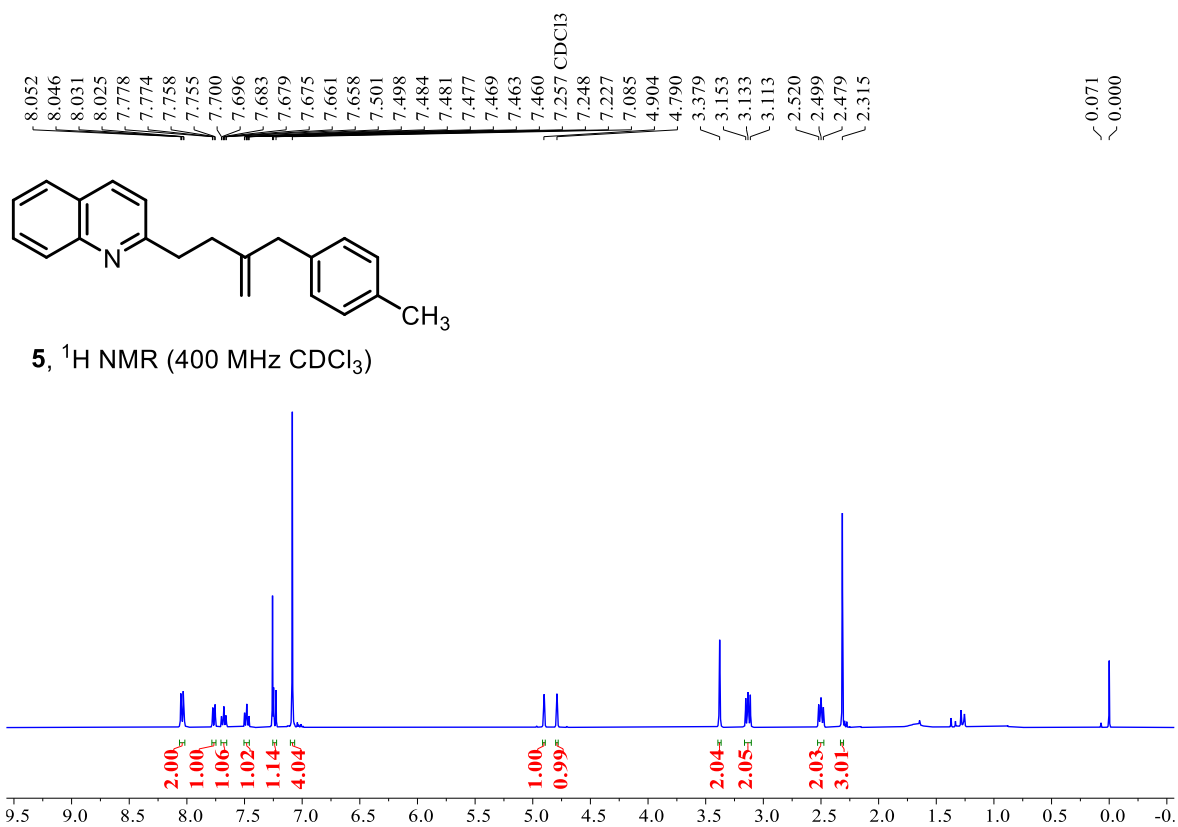


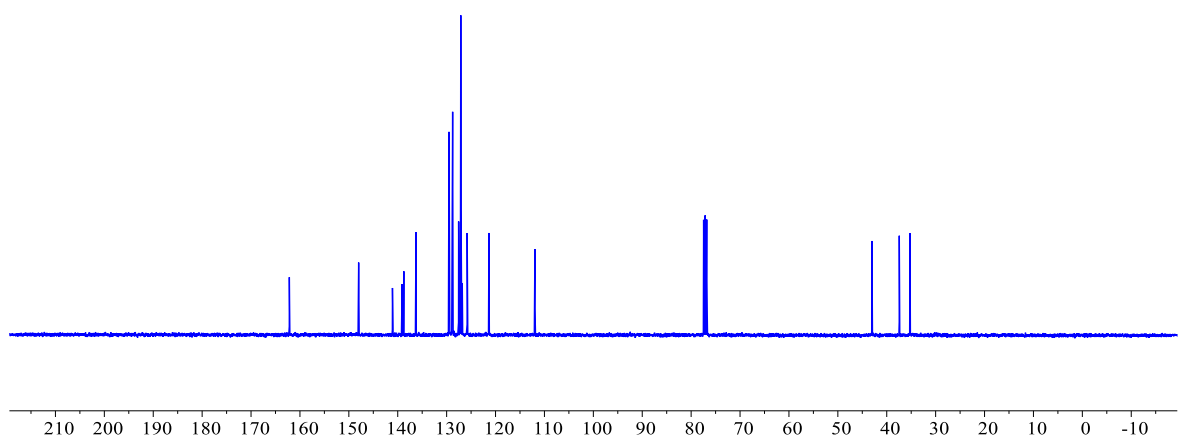
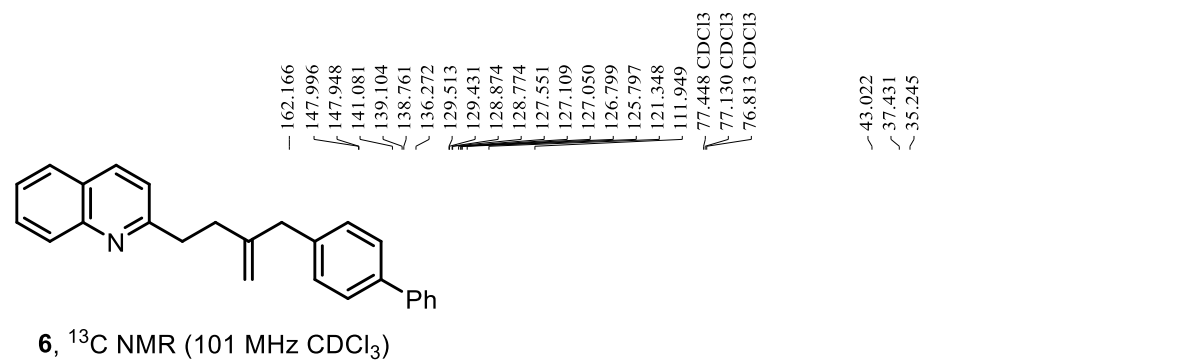
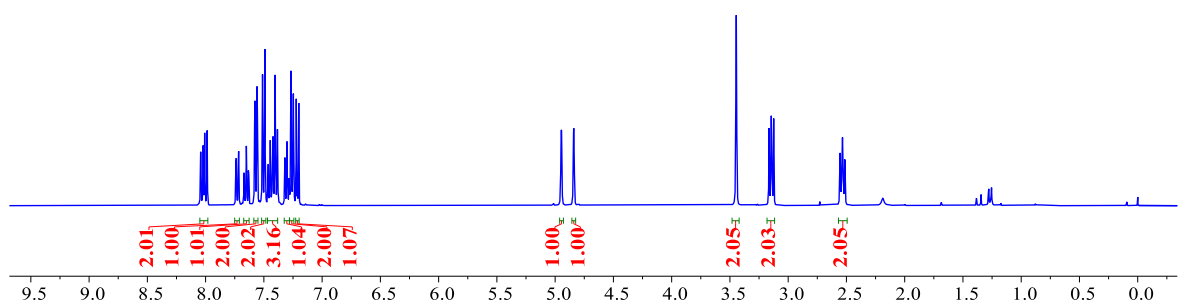
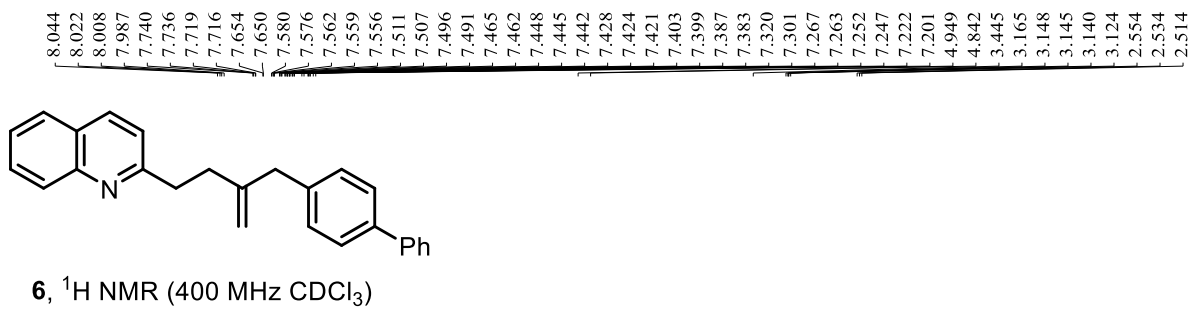
4, ¹H NMR (400 MHz CDCl₃)

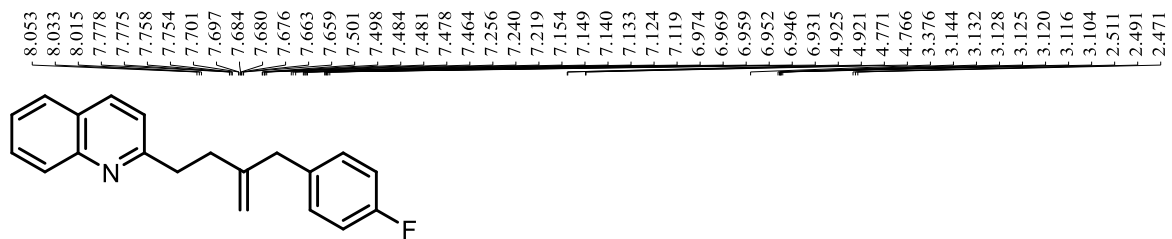


4, ¹³C NMR (101 MHz CDCl₃)

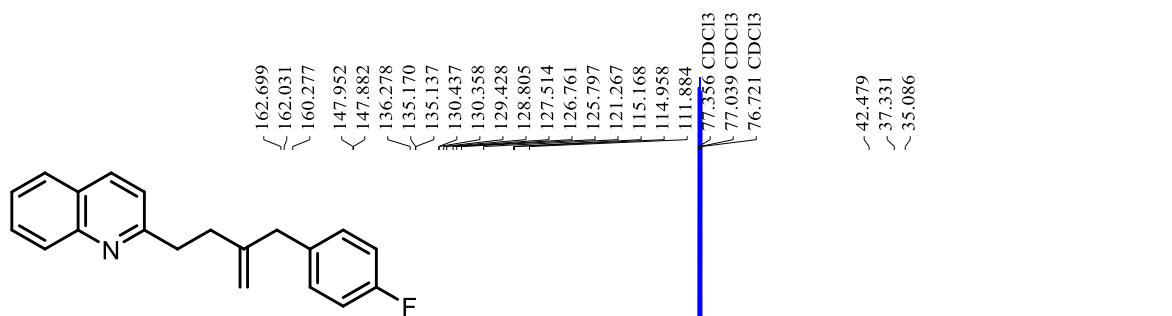
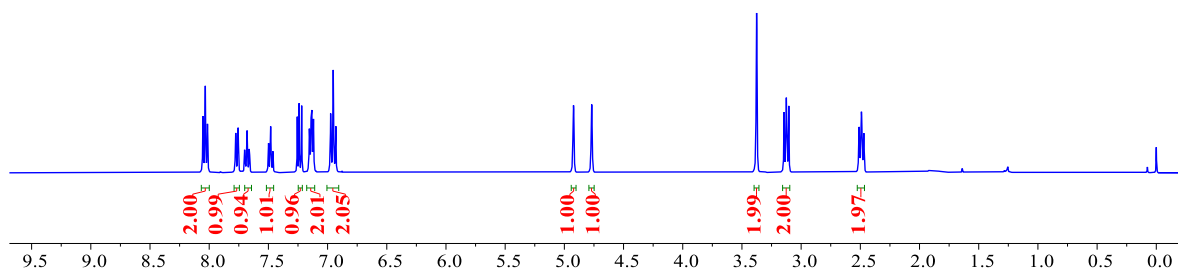




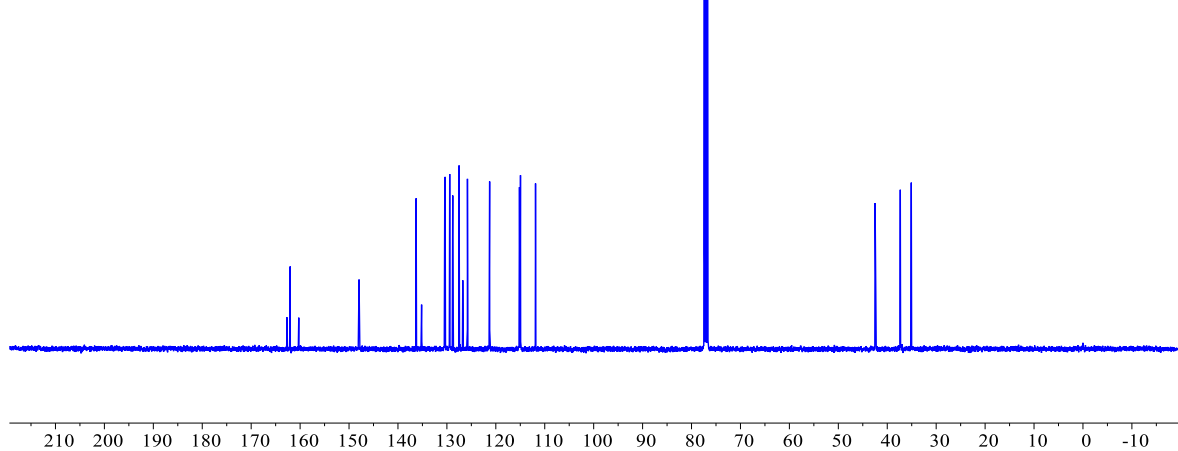


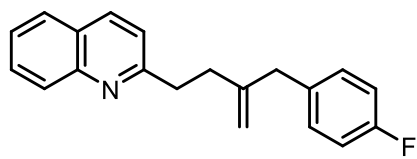


7, ^1H NMR (400 MHz CDCl_3)

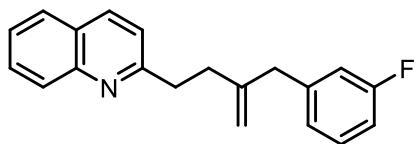
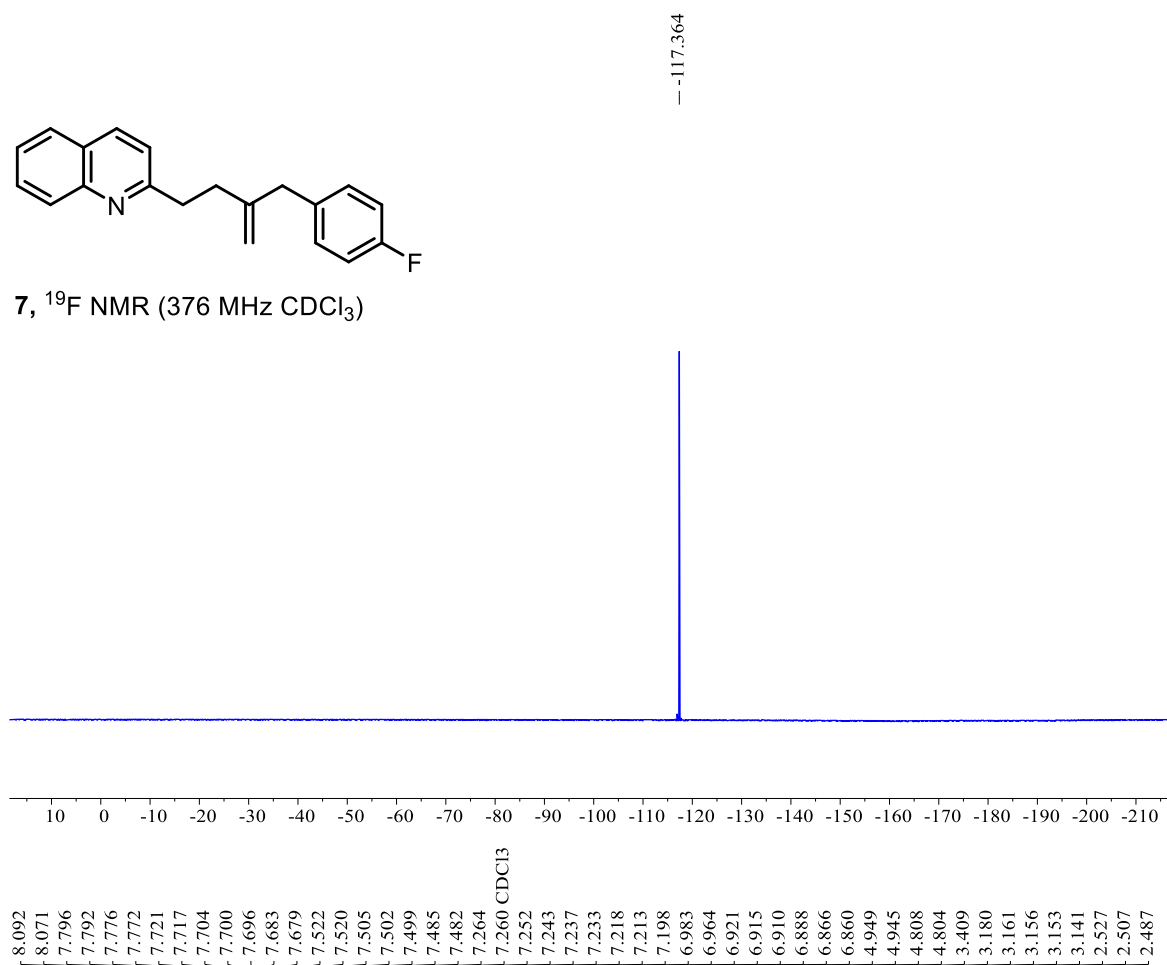


7, ^{13}C NMR (101 MHz CDCl_3)

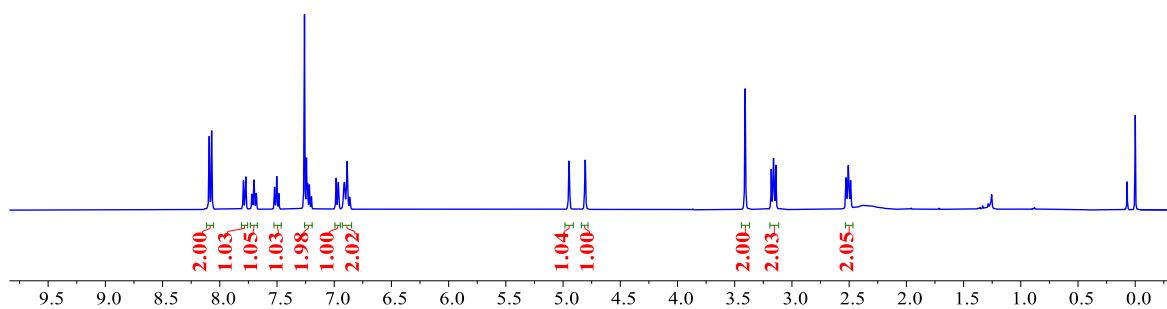


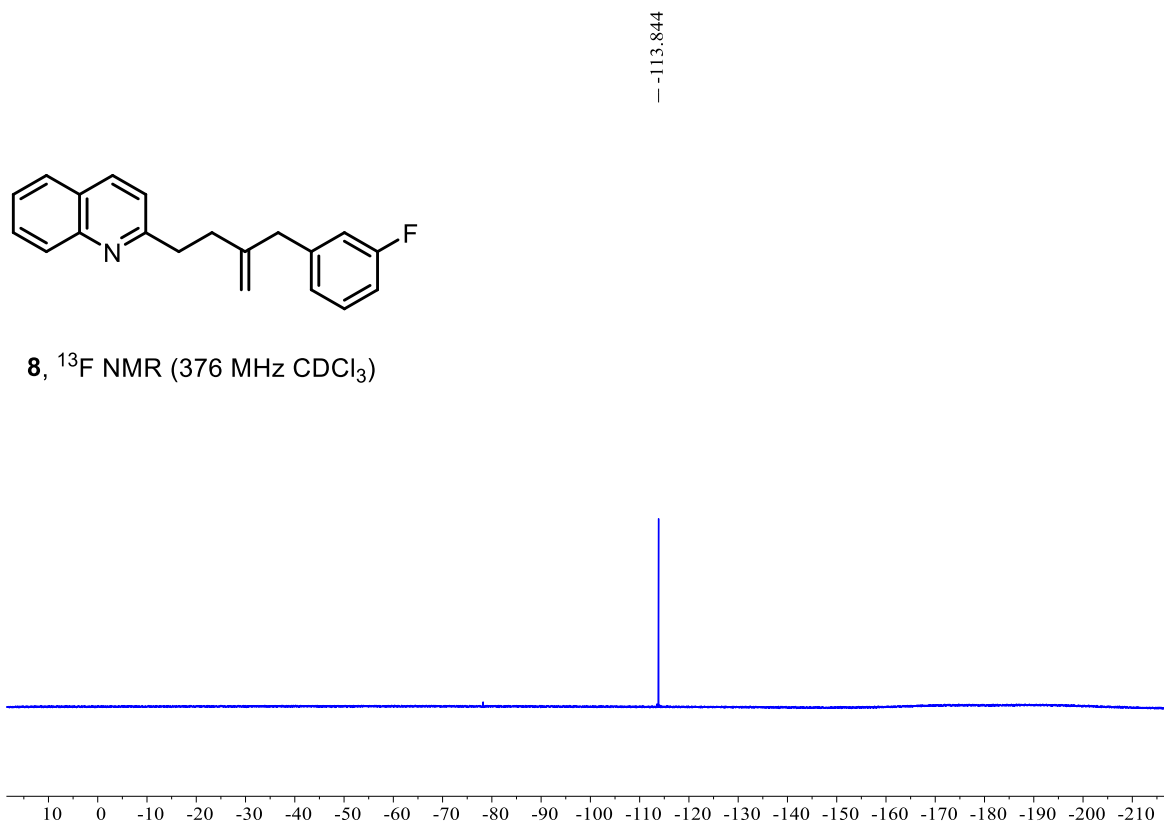
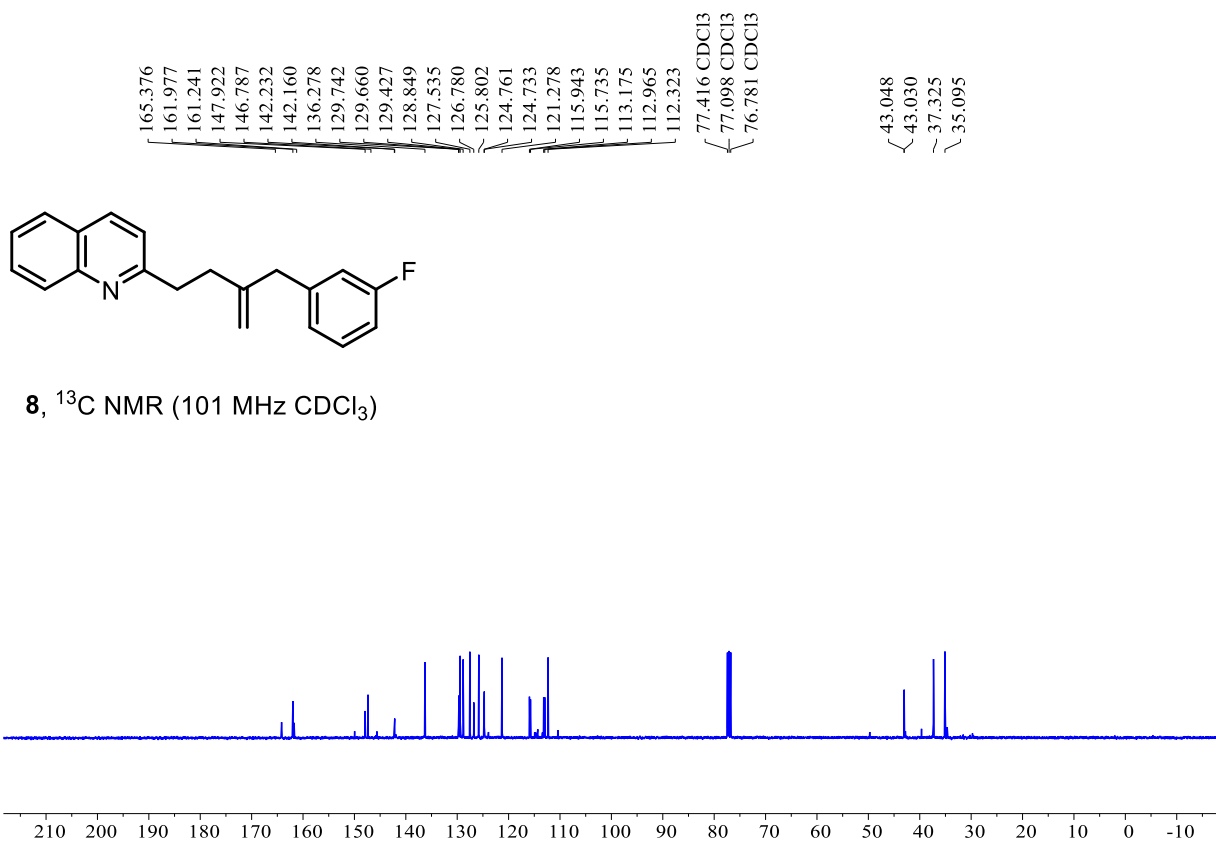


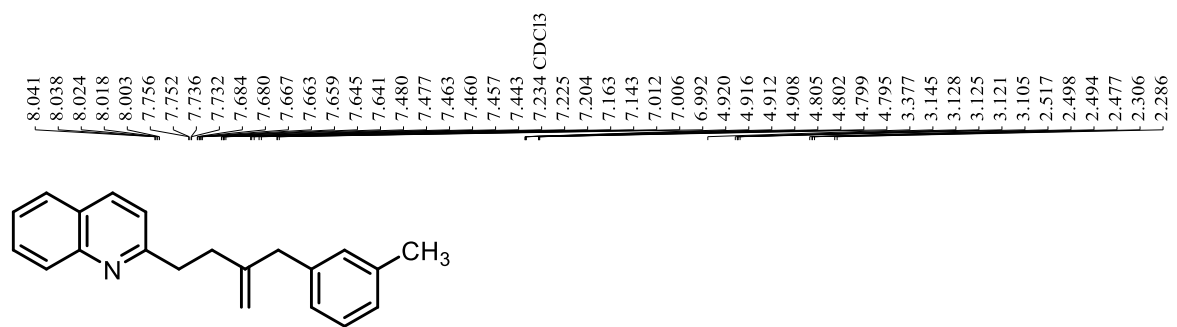
7, ^{19}F NMR (376 MHz CDCl_3)



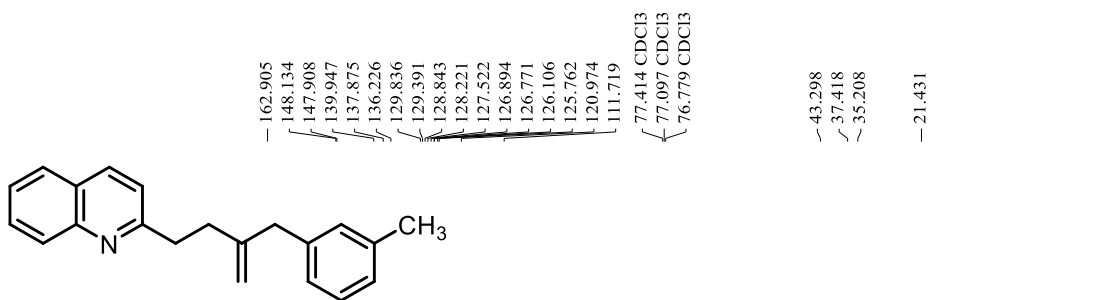
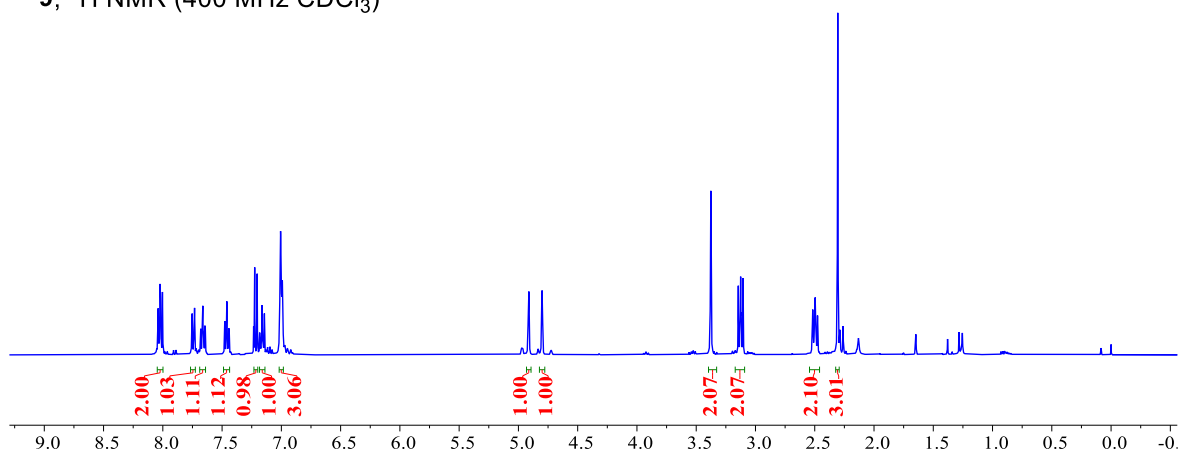
8, ^1H NMR (400 MHz CDCl_3)



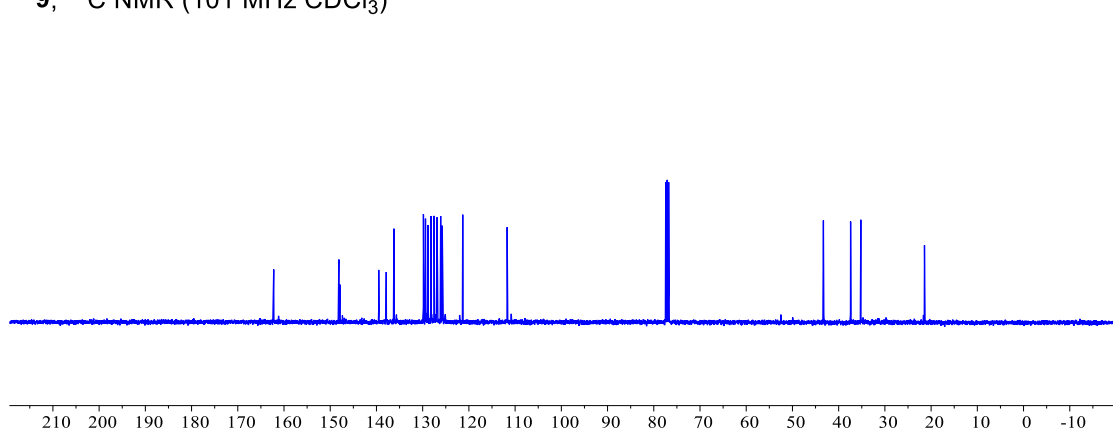




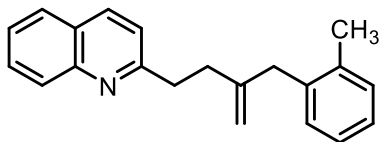
9, ¹H NMR (400 MHz CDCl₃)



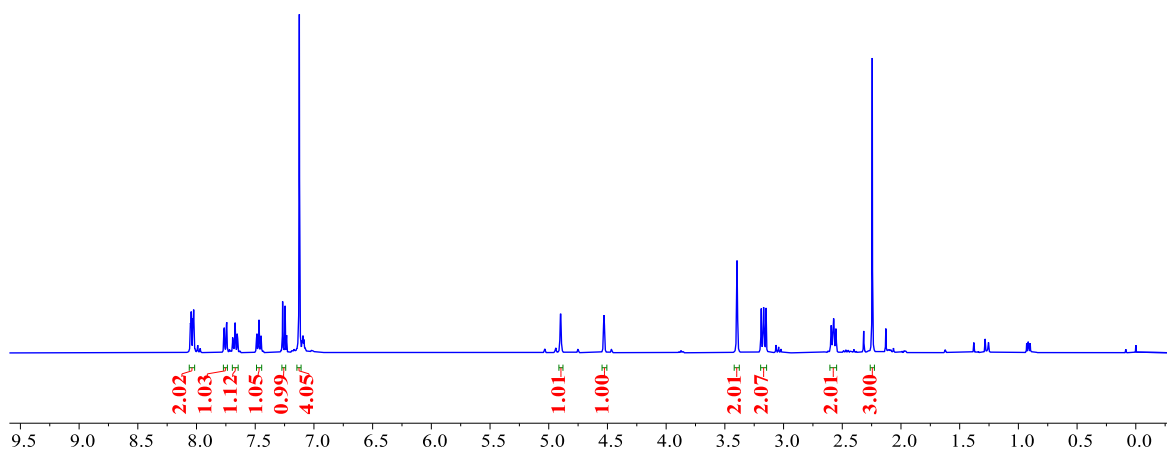
9, ¹³C NMR (101 MHz CDCl₃)



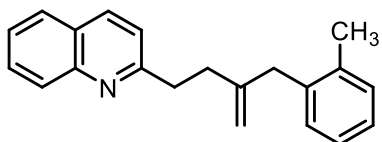
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7.667
7.654
7.650
7.646
7.488
7.485
7.471
7.468
7.465
7.451
7.447
7.267
7.259
7.246
7.233 CDCl₃
7.124
4.907
4.904
4.901
4.897
4.894
4.531
4.526
3.399
3.396
3.393
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3.161
3.149
2.621
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2.554
2.245



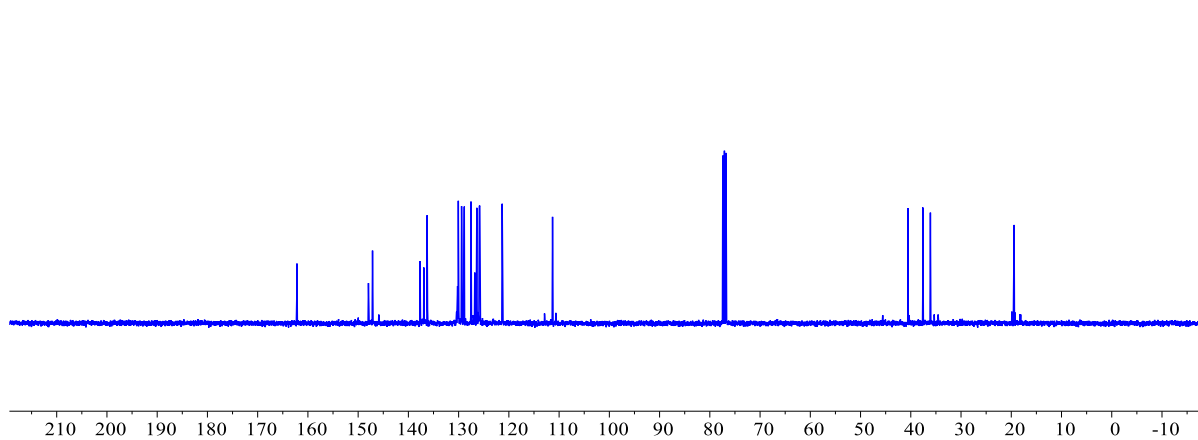
10, ¹H NMR (400 MHz CDCl₃)



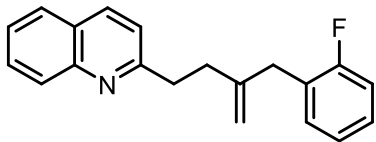
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137.685
136.930
136.272
130.197
130.058
129.414
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127.539
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126.380
125.883
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77.095 CDCl₃
76.777 CDCl₃
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38.054
36.095
19.425



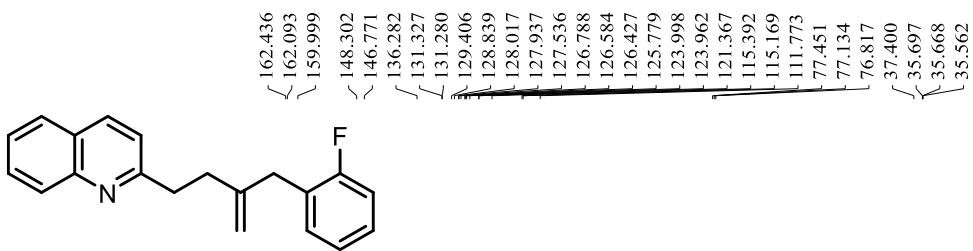
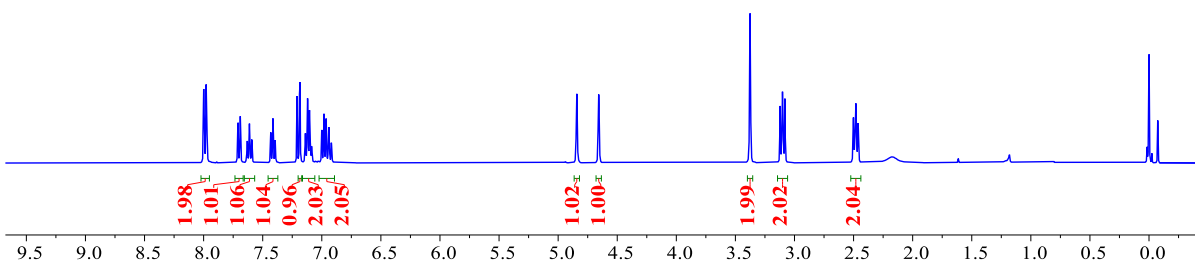
10, ¹³C NMR (101 MHz CDCl₃)



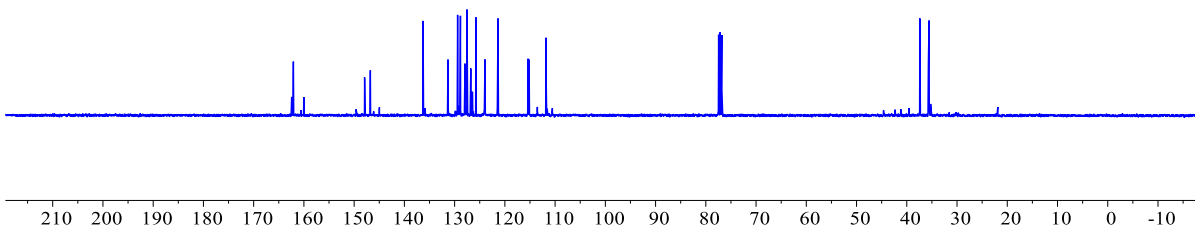
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7.974
7.974
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7.709
7.692
7.688
7.633
7.629
7.616
7.612
7.607
7.594
7.591
7.432
7.413
7.394
7.210 CDCl₃
7.189
7.184
7.144
7.139
7.124
7.120
7.104
7.100
7.094
7.086
7.082
7.001
6.982
6.963
6.945
6.940
6.919
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2.461

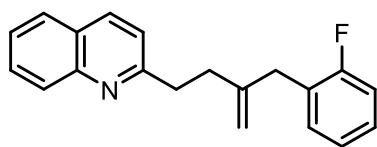


11, ¹H NMR (400 MHz CDCl₃)

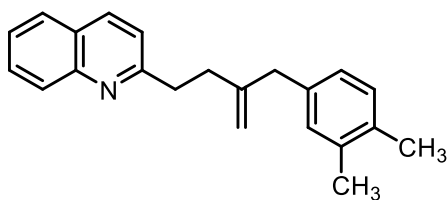
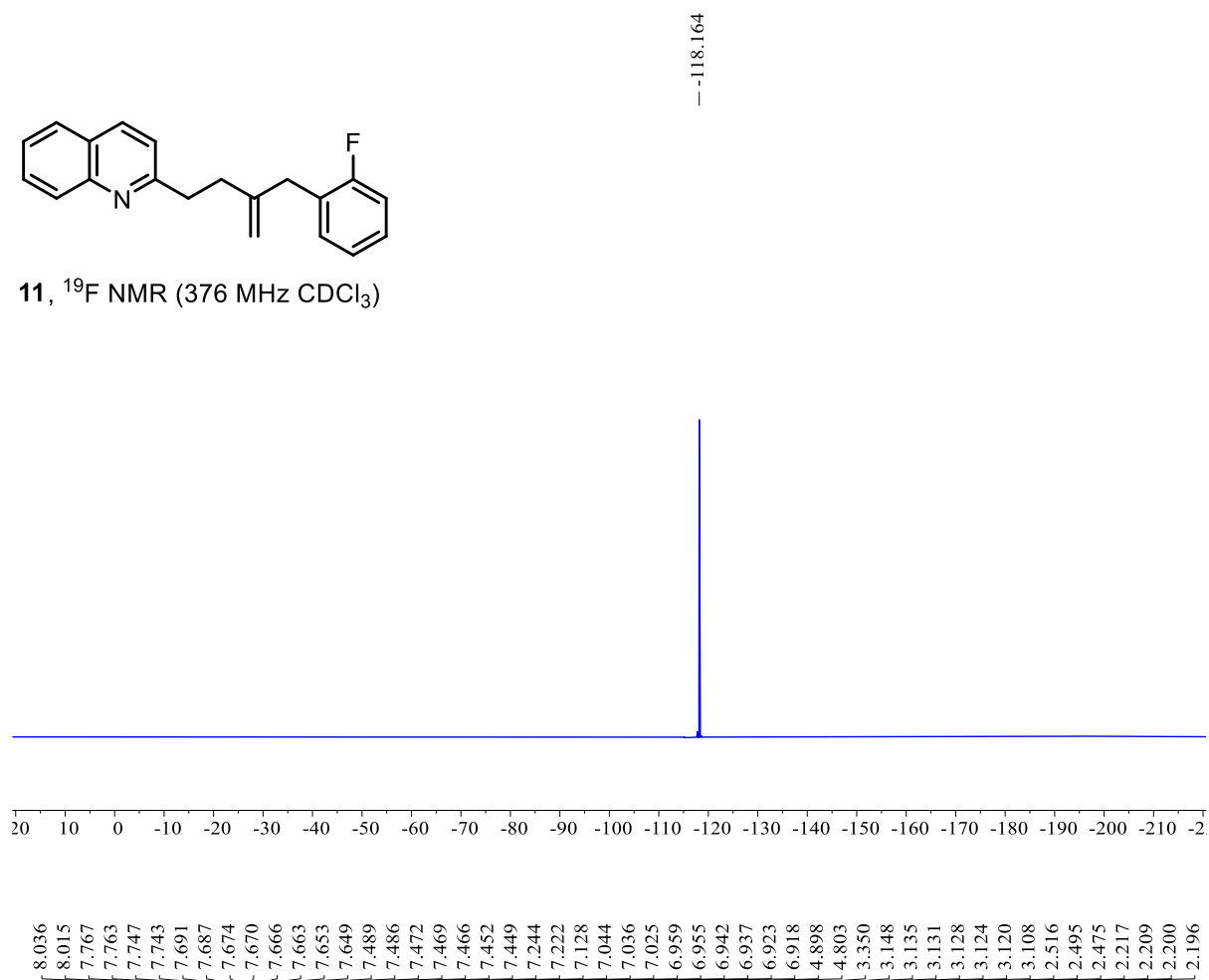


11, ¹³C NMR (101 MHz CDCl₃)

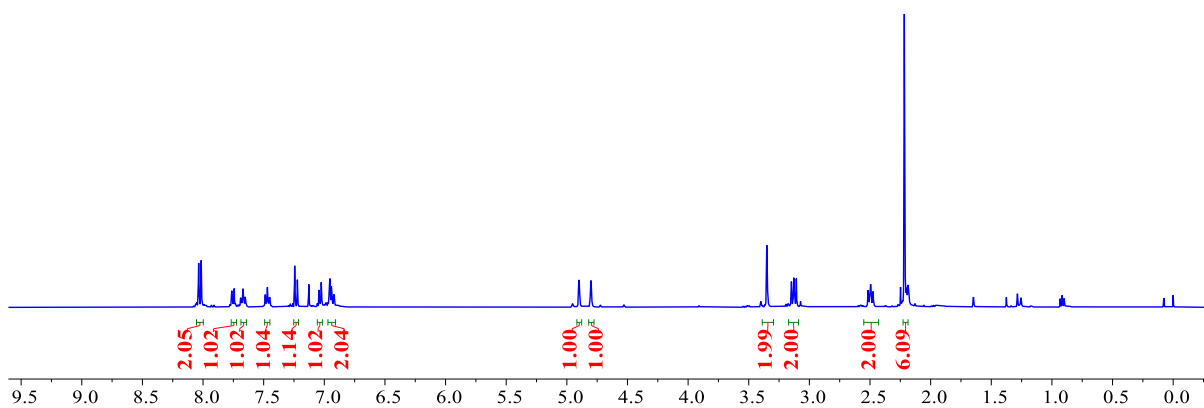


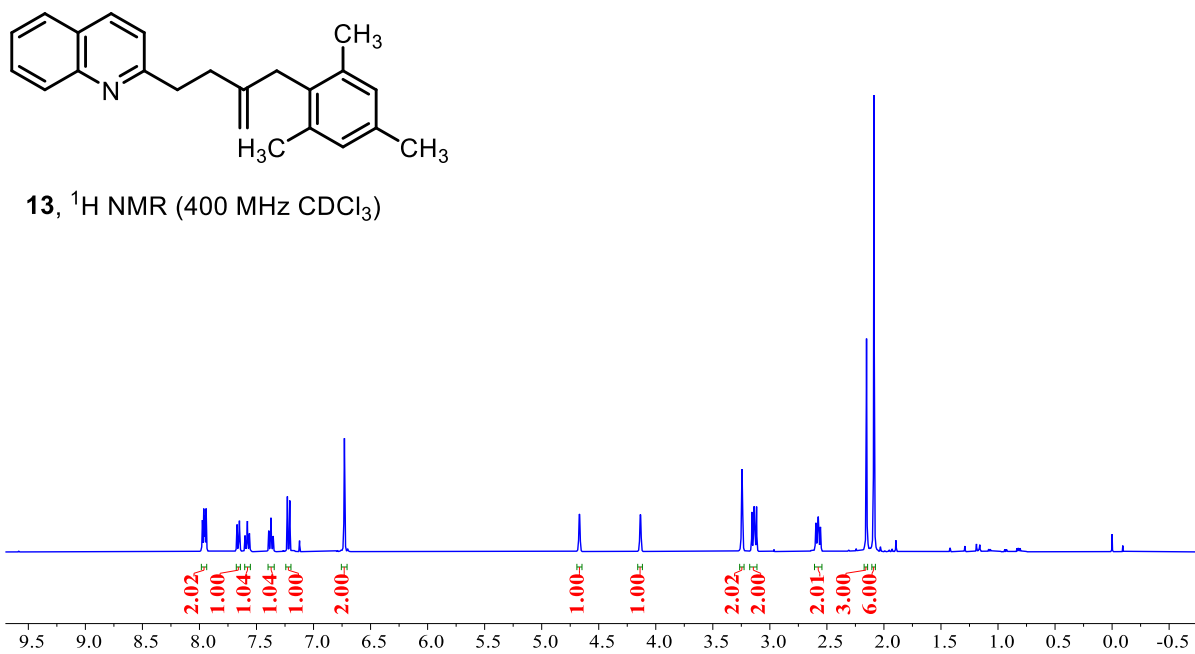
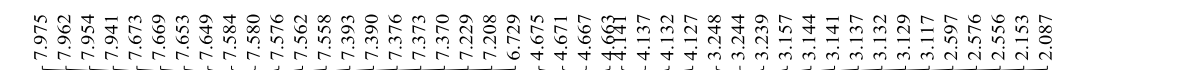
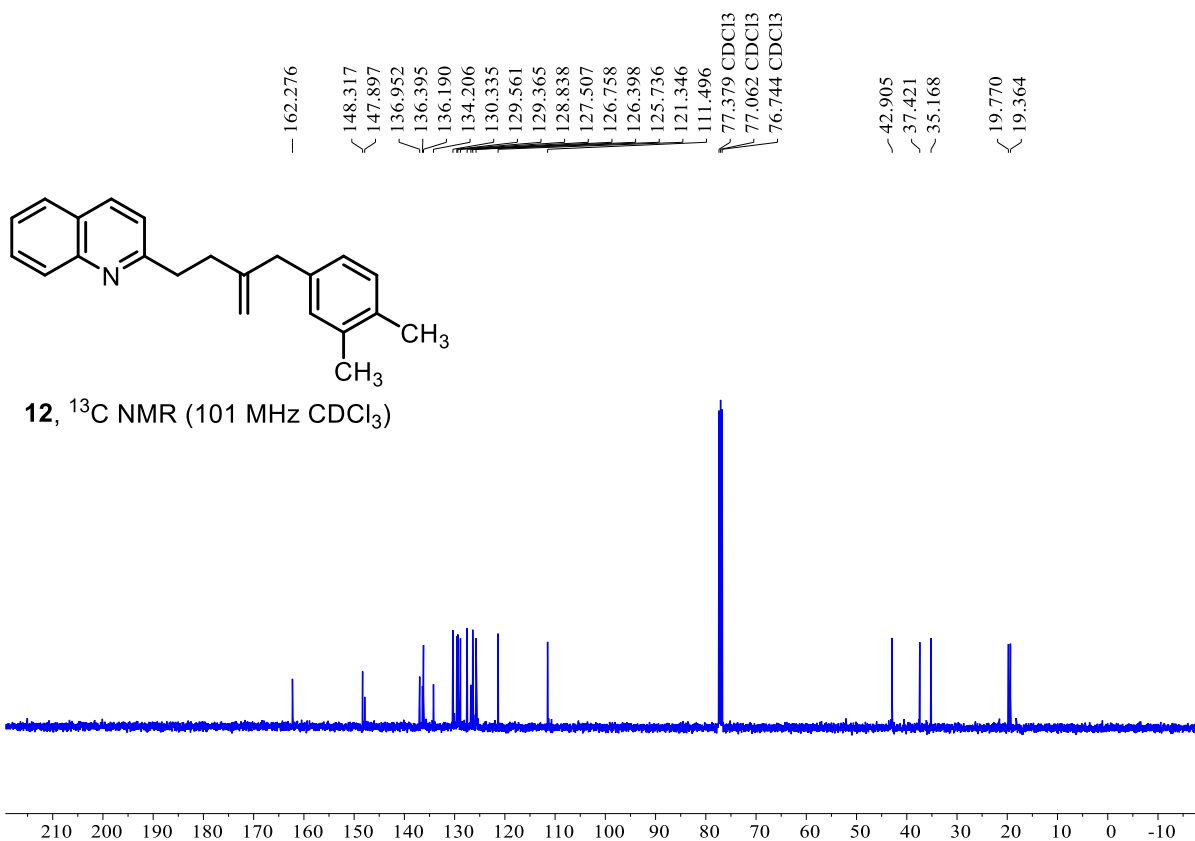


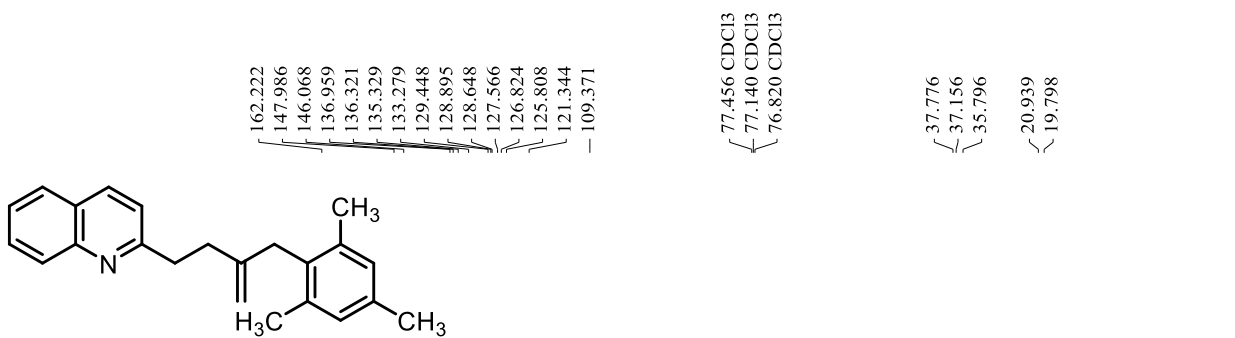
11, ^{19}F NMR (376 MHz CDCl_3)



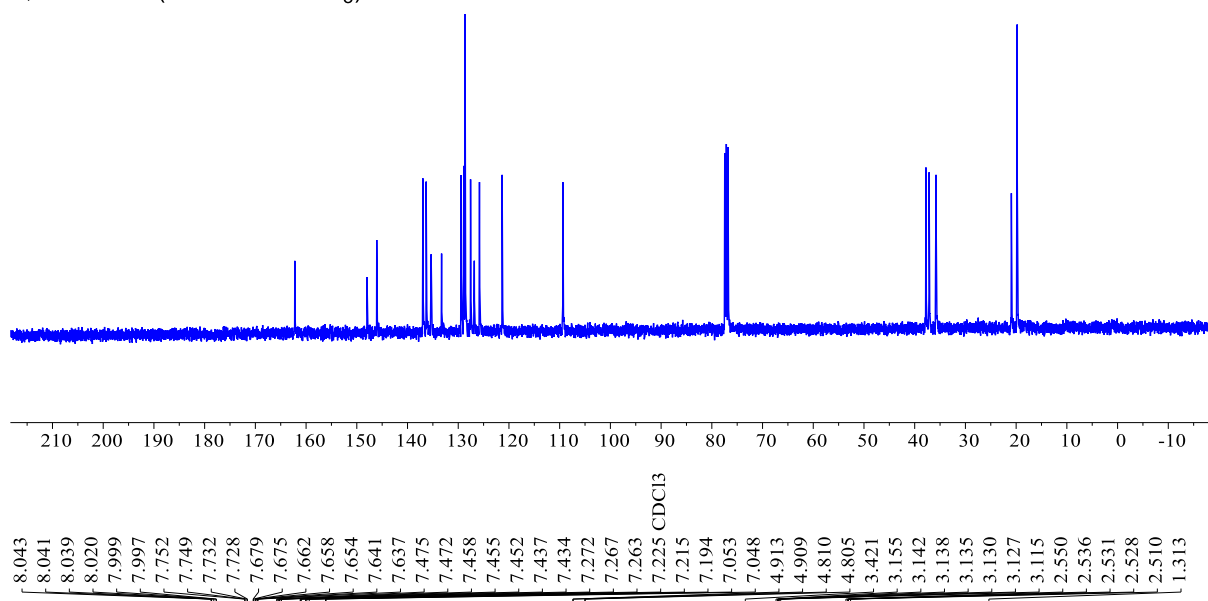
12, ^1H NMR (400 MHz CDCl_3)



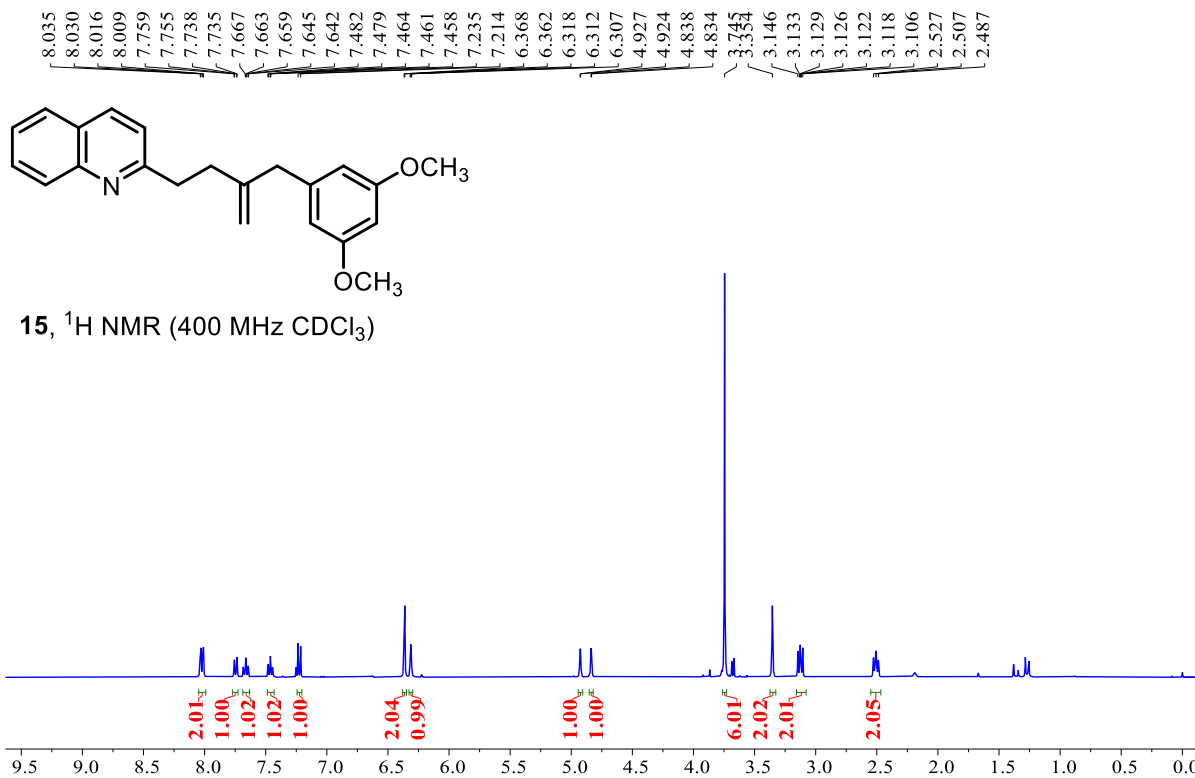
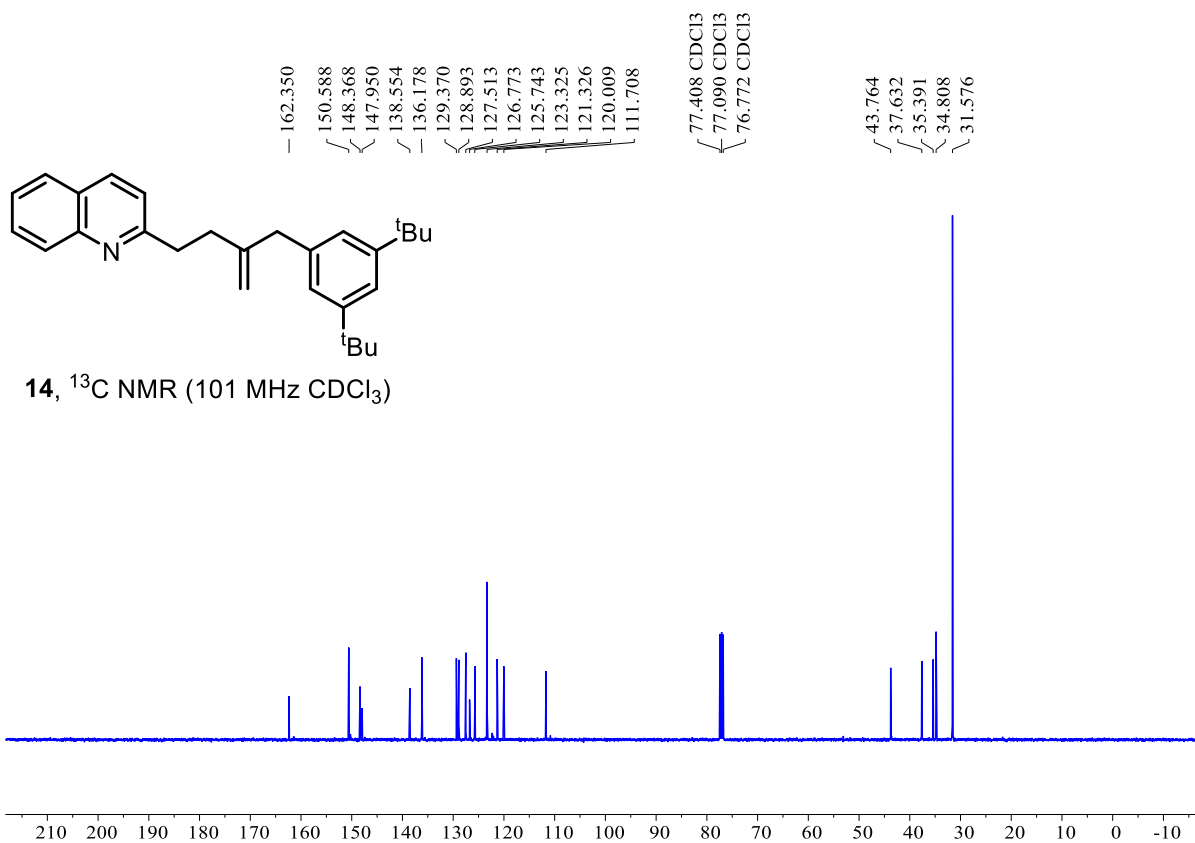


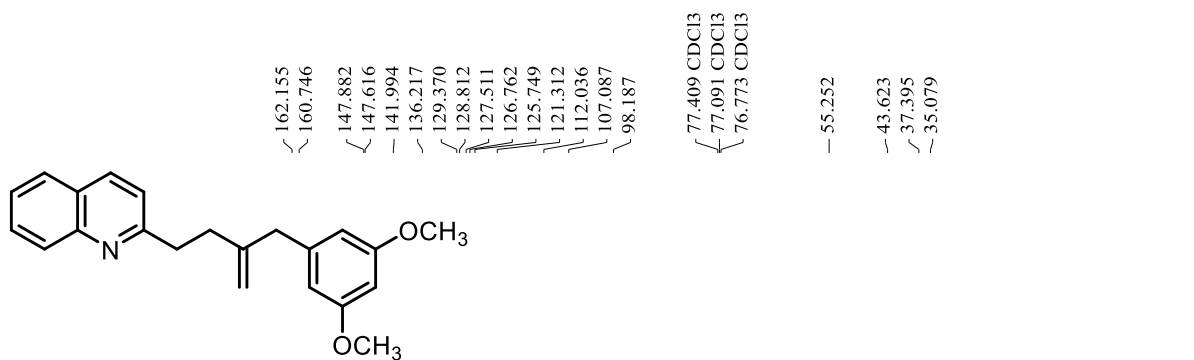


13, ¹³C NMR (101 MHz CDCl₃)

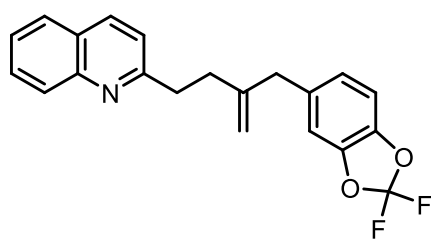
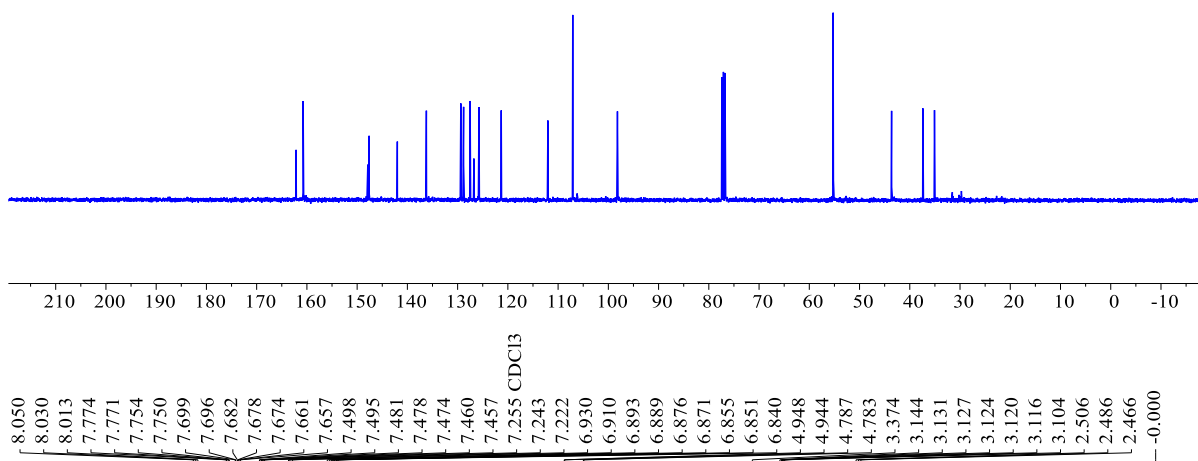


14, ¹H NMR (400 MHz CDCl₃)

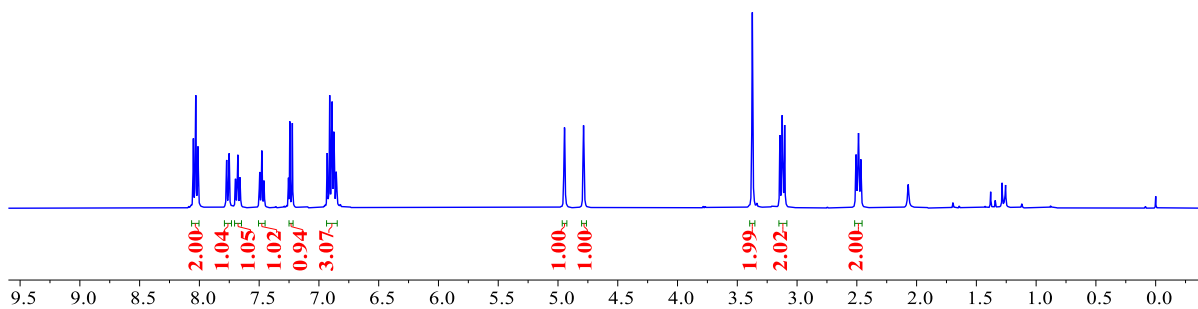


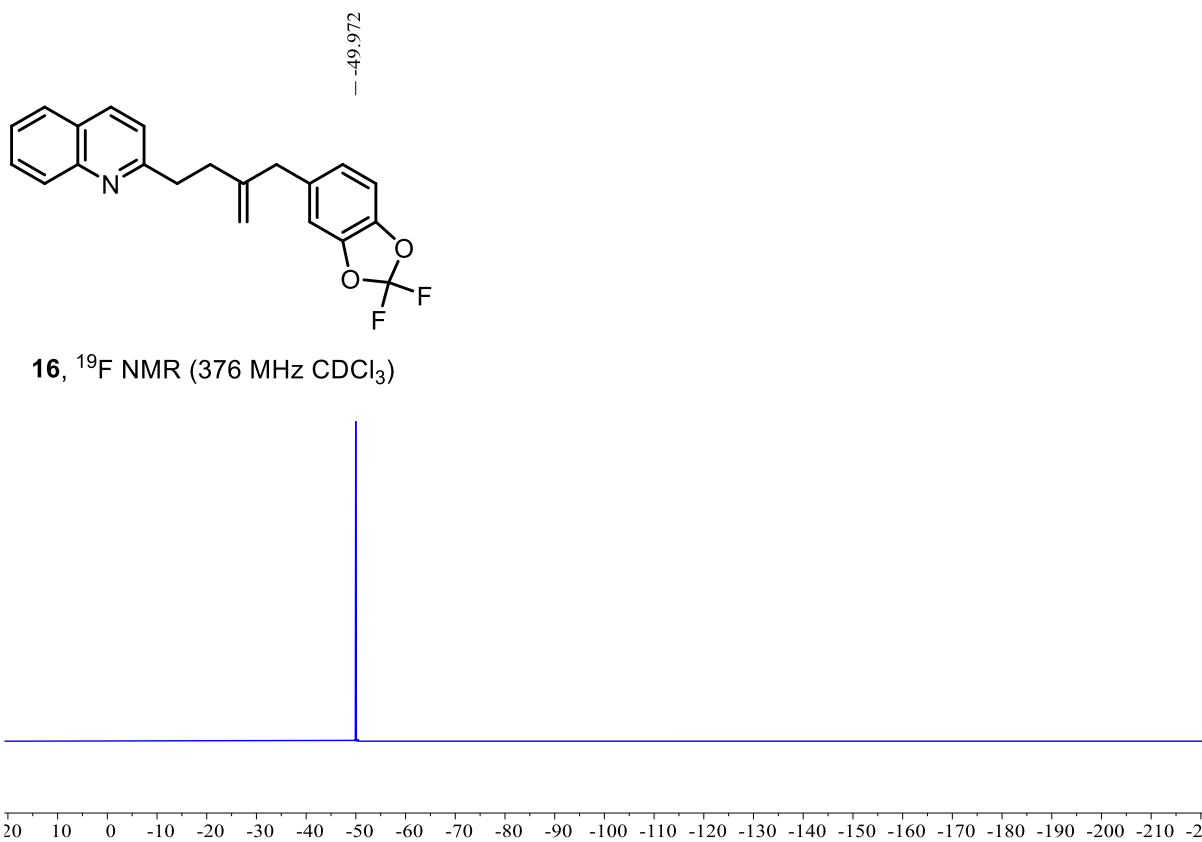
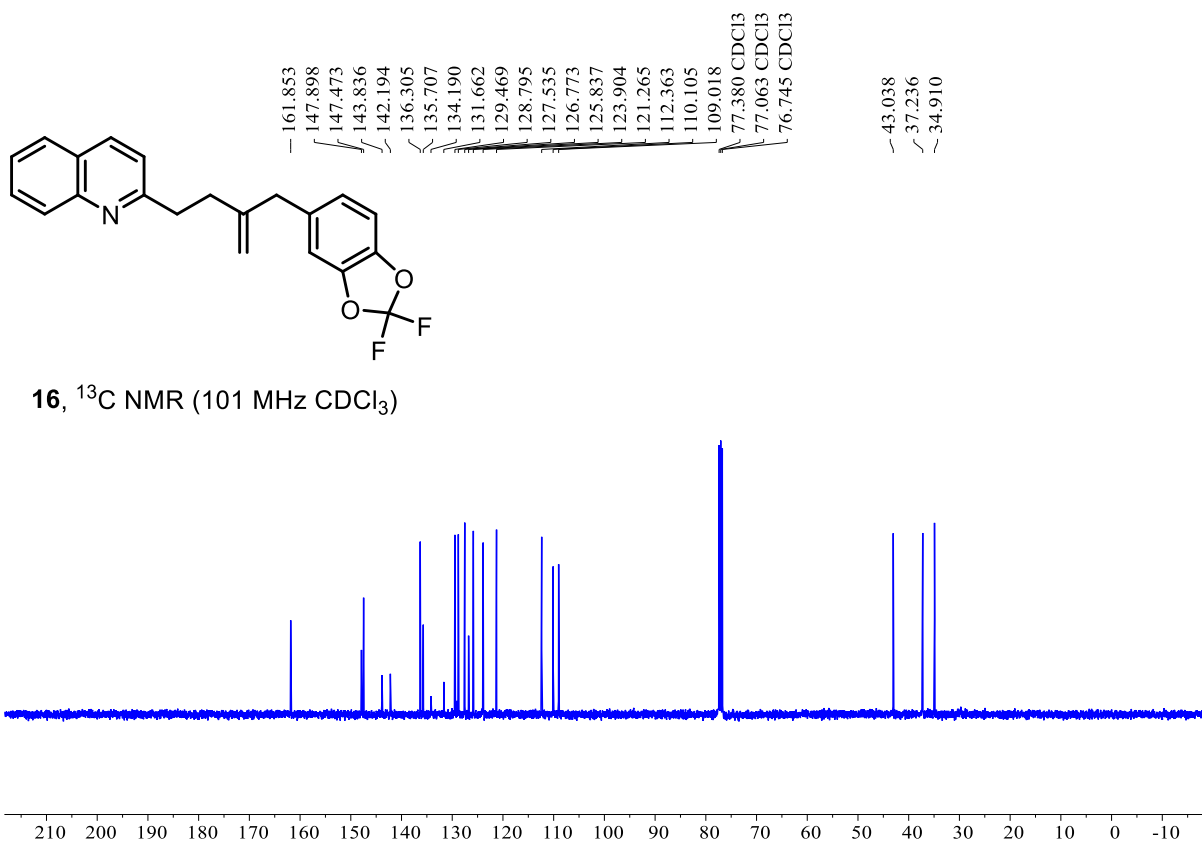


15, ¹³C NMR (101 MHz CDCl₃)

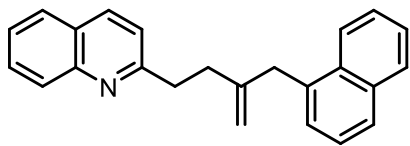


16, ¹H NMR (400 MHz CDCl₃)

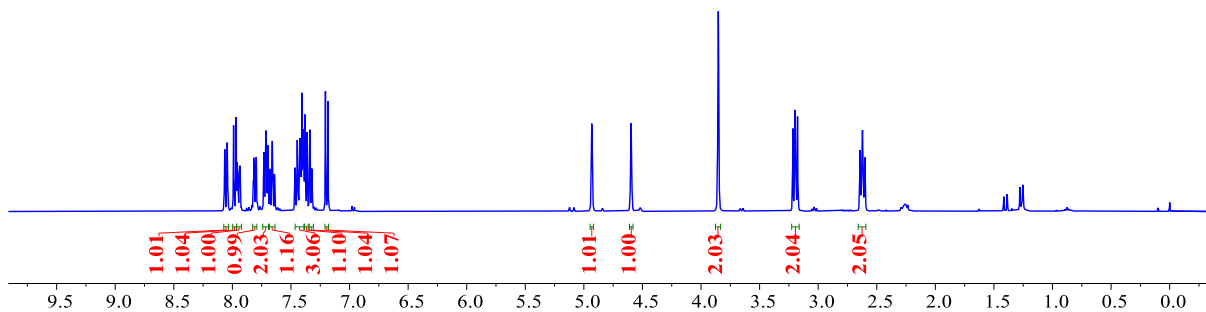




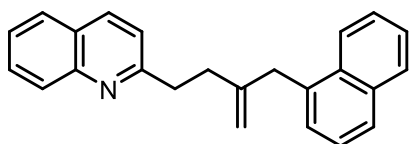
8.065
8.044
7.990
7.969
7.958
7.940
7.935
7.819
7.814
7.799
7.795
7.733
7.730
7.718
7.713
7.709
7.697
7.680
7.663
7.659
7.466
7.463
7.449
7.446
7.442
7.429
7.425
7.419
7.414
7.407
7.400
7.394
7.389
7.382
7.362
7.340
7.337
7.323
7.206
7.185
4.933
4.599
3.853
3.216
3.192
3.176
2.642
2.622
2.602



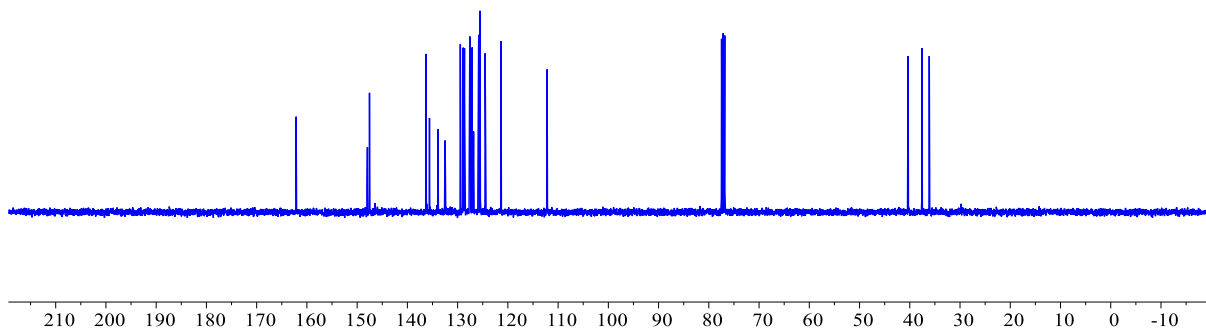
17, ¹H NMR (400 MHz CDCl₃)

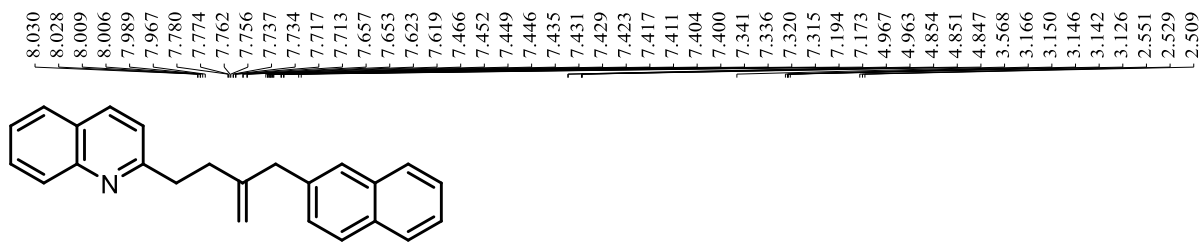


162.137
147.957
147.539
136.304
135.601
133.897
132.492
129.458
128.895
128.630
127.579
127.478
127.115
126.823
125.825
125.789
125.549
125.532
124.520
121.360
112.178
77.467 CDCl₃
77.149 CDCl₃
76.832 CDCl₃
40.338
37.581
36.117

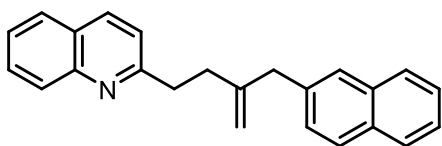
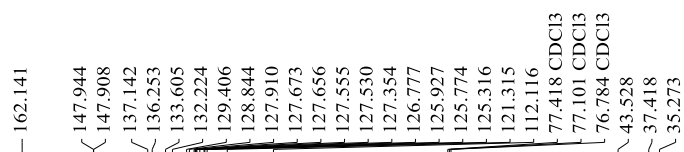
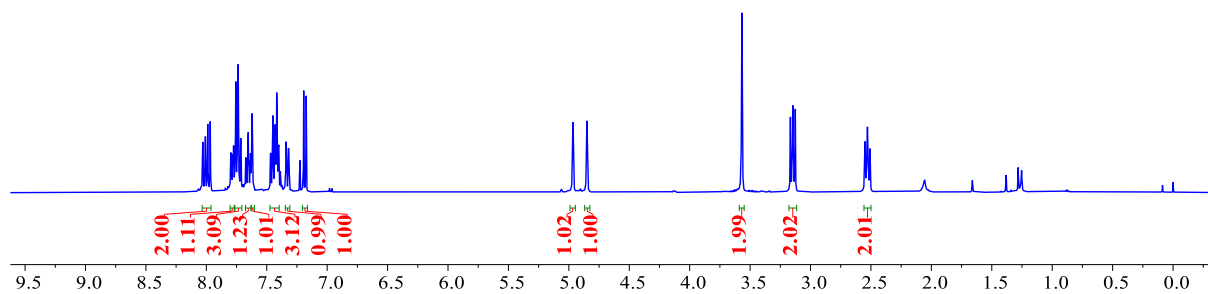


17, ¹³C NMR (101 MHz CDCl₃)

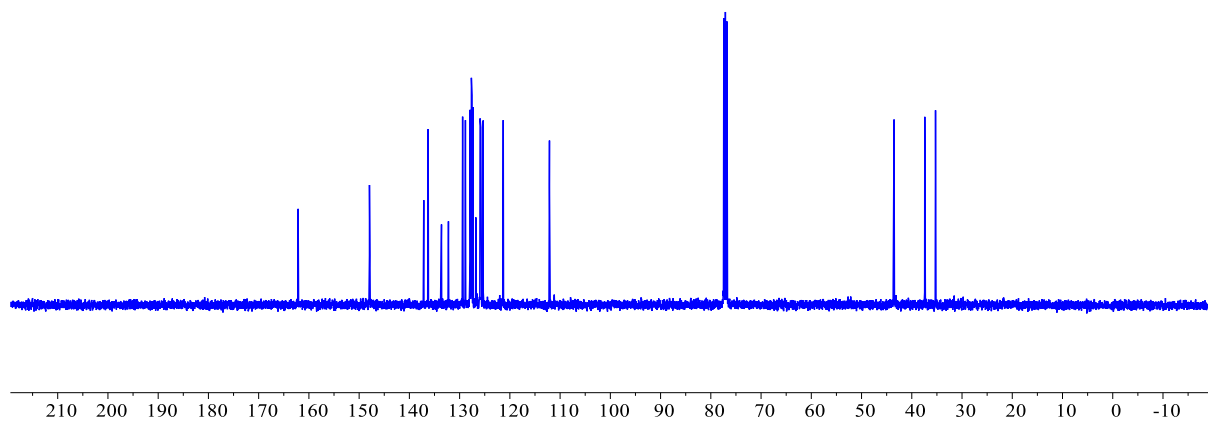


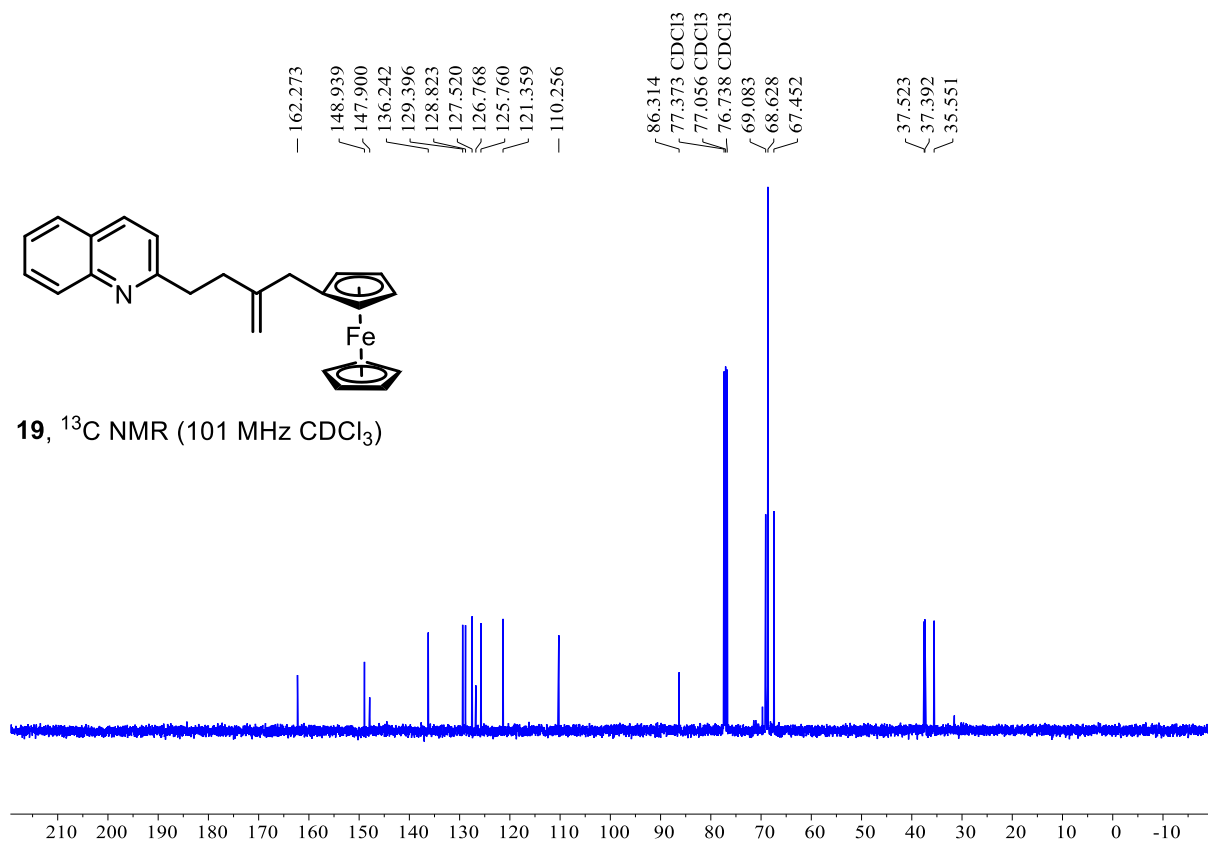
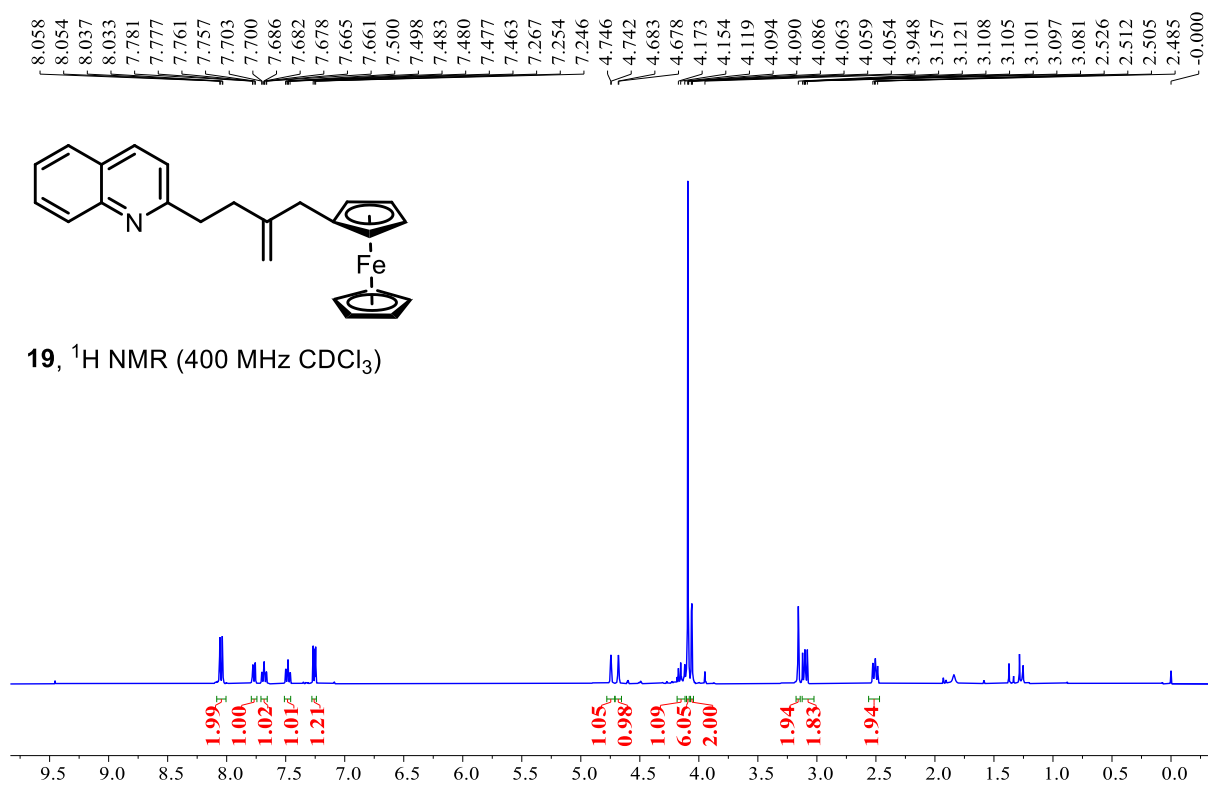


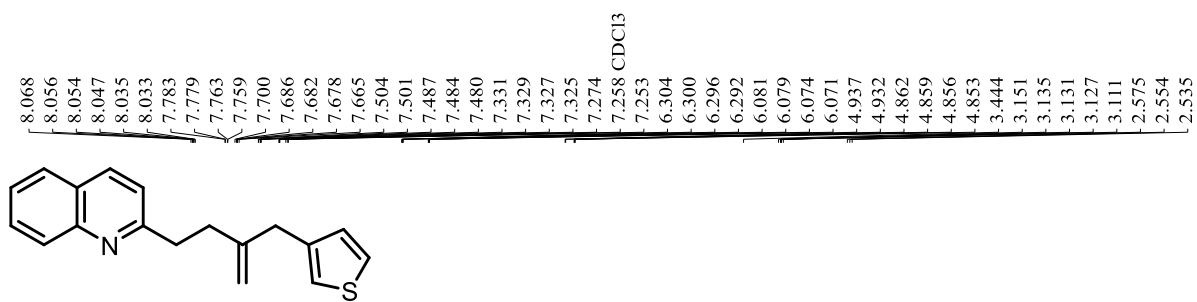
18, ^1H NMR (400 MHz CDCl_3)



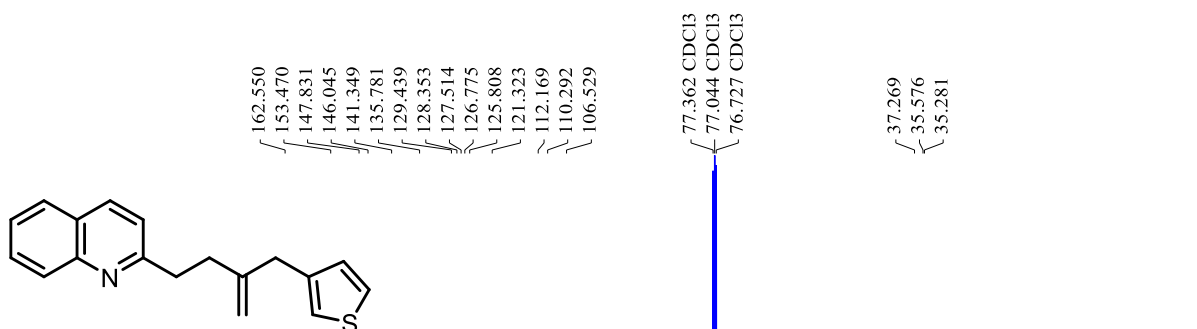
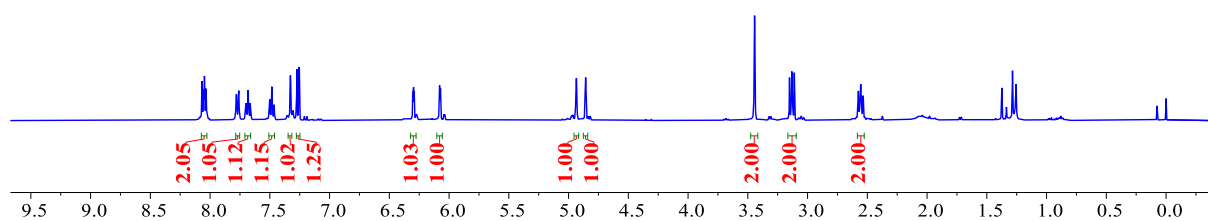
18, ^{13}C NMR (101 MHz CDCl_3)



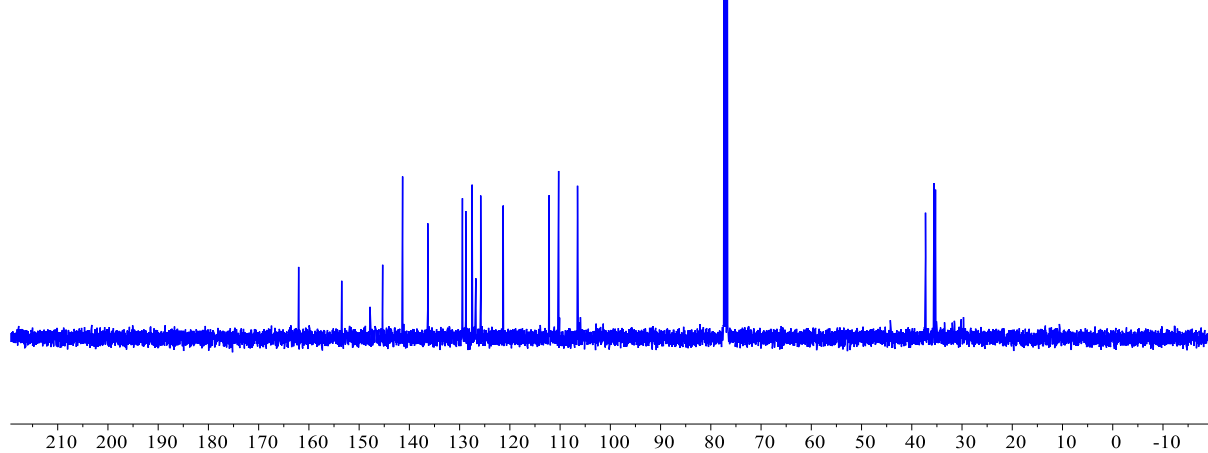




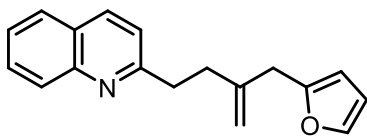
20, ¹H NMR (400 MHz CDCl₃)



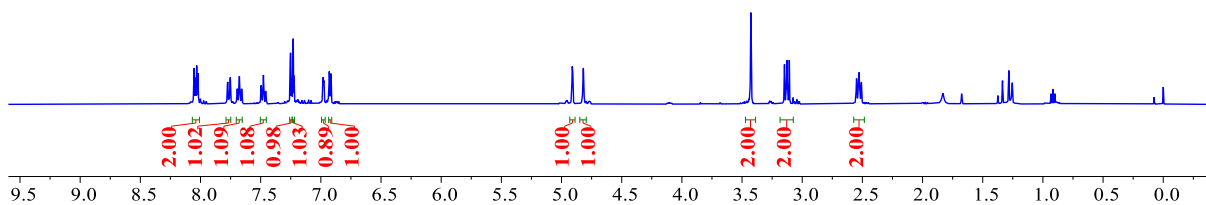
20, ¹³C NMR (101 MHz CDCl₃)



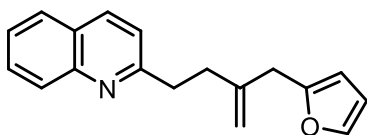
8.053
8.043
8.041
8.032
8.022
8.019
7.777
7.773
7.756
7.753
7.698
7.694
7.681
7.677
7.673
7.660
7.656
7.498
7.495
7.481
7.477
7.474
7.460
7.254
7.250
7.242
7.235
7.229
7.223
6.983
6.980
6.976
6.973
6.930
6.927
6.918
6.914
4.911
4.907
4.821
4.817
3.427
3.147
3.131
3.128
3.123
3.107
2.548
2.528
2.508



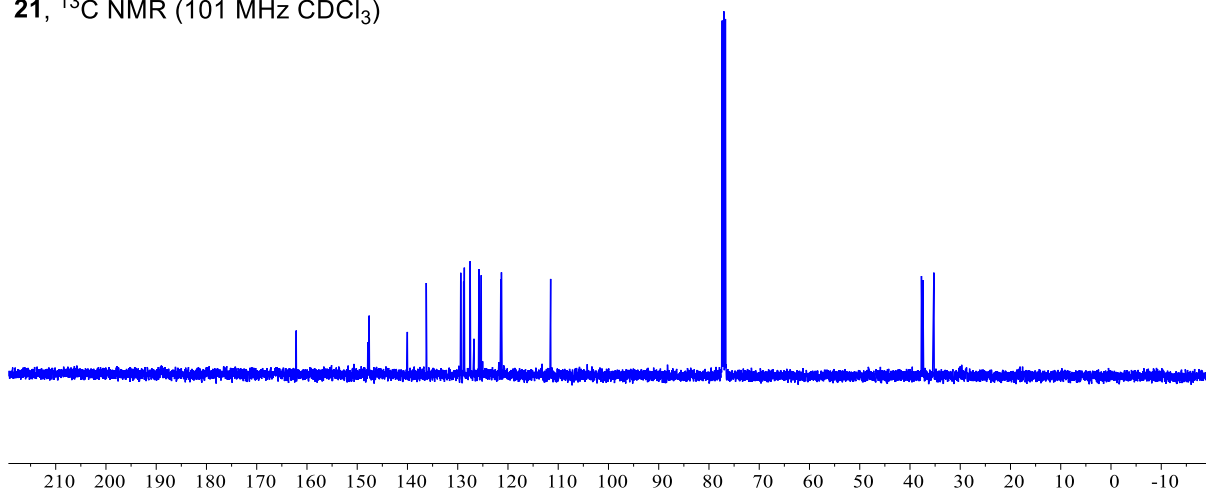
21, ^1H NMR (400 MHz CDCl_3)



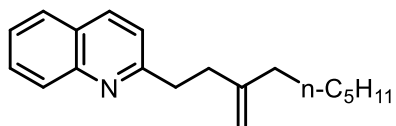
161.227
147.897
147.215
140.025
135.899
129.402
128.823
128.680
127.514
126.765
125.771
125.312
121.429
121.297
111.510
77.365 CDCl_3
77.047 CDCl_3
76.729 CDCl_3
37.717
37.421
35.248



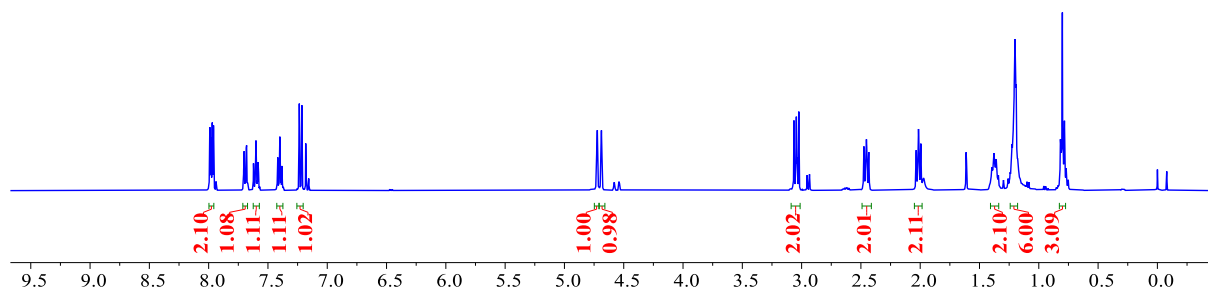
21, ^{13}C NMR (101 MHz CDCl_3)



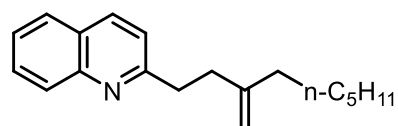
7.991
7.982
7.980
7.970
7.960
7.704
7.700
7.683
7.679
7.605
7.601
7.420
7.417
7.400
7.397
7.236
7.214
4.726
4.722
4.690
4.686
3.065
3.048
3.044
3.039
3.024
2.474
2.456
2.452
2.434
2.035
2.032
2.014
1.996
1.993
1.378
1.231
1.226
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1.191
1.178
0.818
0.814
0.808
0.801
0.784



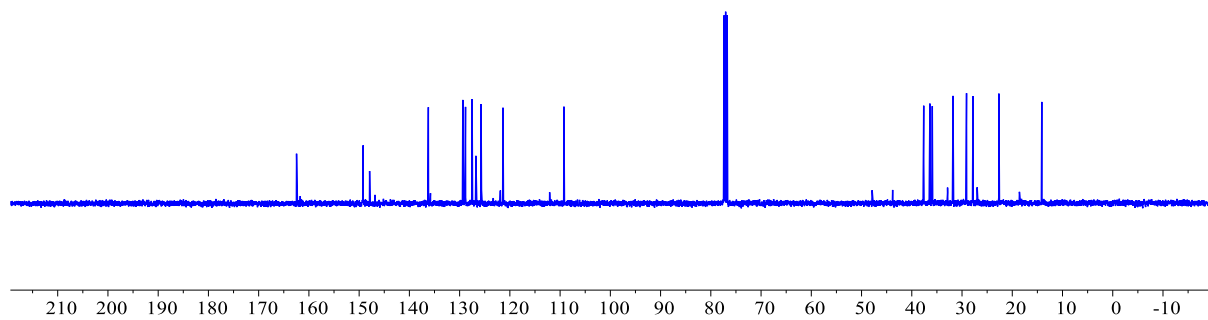
23, ^1H NMR (400 MHz CDCl_3)

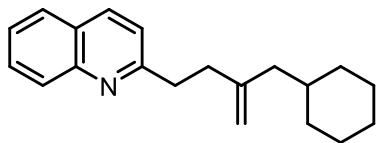
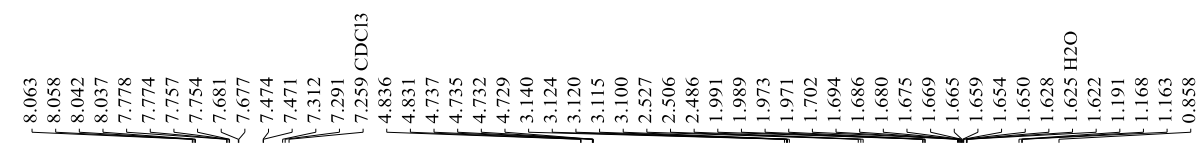


162.458
149.690
147.919
136.220
129.366
128.827
127.506
126.759
125.723
121.369
108.790
77.369 CDCl_3
77.051 CDCl_3
76.733 CDCl_3
37.629
36.395
35.912
31.793
29.102
27.811
22.660
14.129

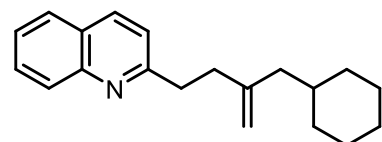
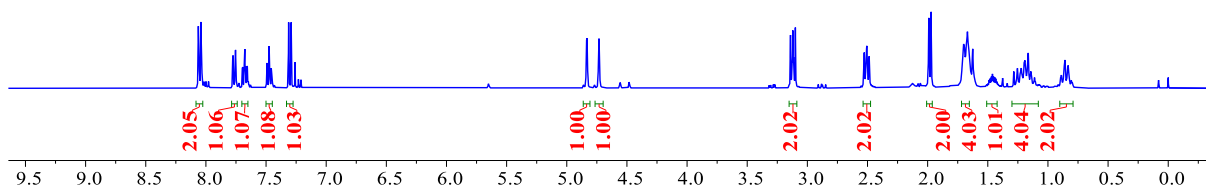


23, ^{13}C NMR (101 MHz CDCl_3)

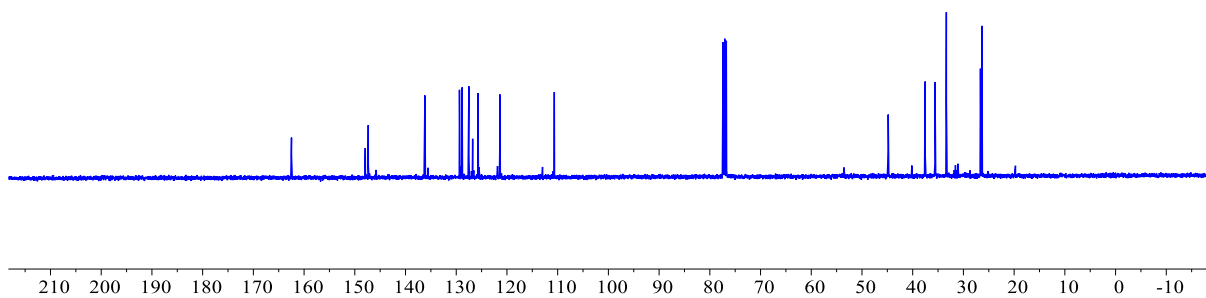




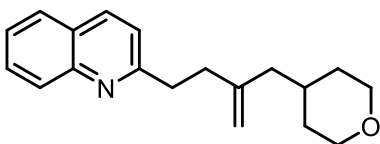
24, ¹H NMR (400 MHz CDCl₃)



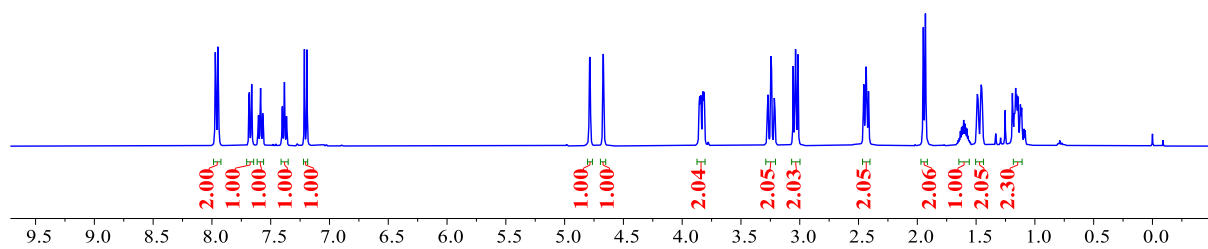
24, ¹³C NMR (101 MHz CDCl₃)



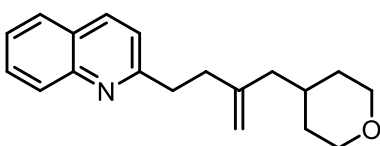
7.971
7.966
7.950
7.945
7.685
7.681
7.664
7.661
7.586
7.383
7.213
7.192
4.788
4.784
4.672
4.668
3.851
3.845
3.840
3.827
3.822
3.816
3.811
3.275
3.270
3.246
3.241
3.216
3.211
3.055
3.039
3.036
3.031
3.015
2.456
2.435
2.415
1.949
1.931
1.489
1.484
1.461
1.457
1.451
1.447
1.191
1.164
1.156
1.152
1.145



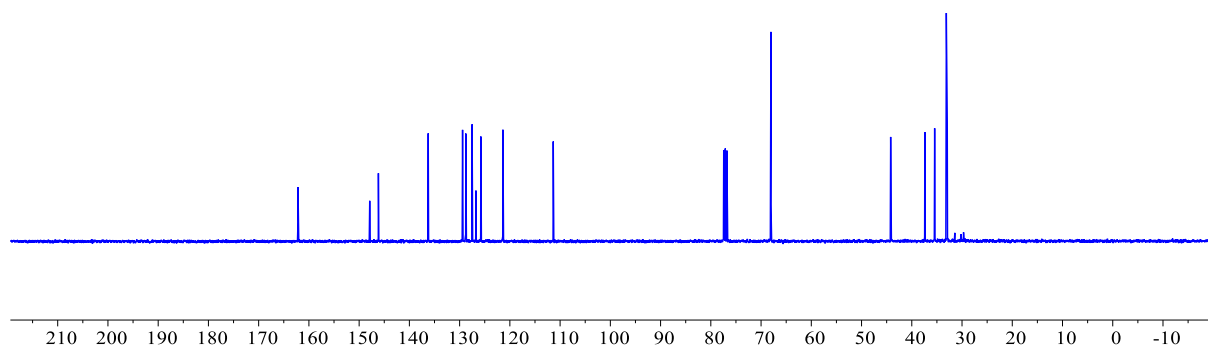
25, ^1H NMR (400 MHz CDCl_3)



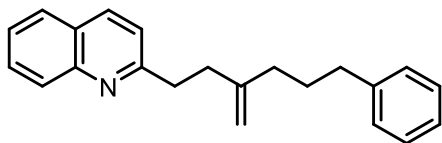
162.171
147.898
146.164
136.245
129.414
128.771
127.514
126.751
125.777
121.385
111.362
77.437 CDCl_3
77.119 CDCl_3
76.802 CDCl_3
68.035
44.205
37.407
35.449
33.124
32.933



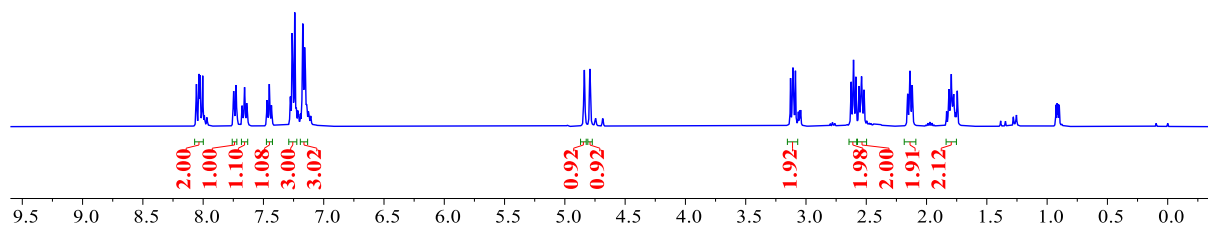
25, ^{13}C NMR (101 MHz CDCl_3)



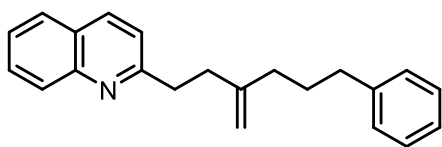
8.056
8.035
8.025
8.004
7.749
7.746
7.729
7.726
7.661
7.657
7.652
7.639
7.472
7.468
7.454
7.451
7.448
7.277
7.262
7.256
7.240
7.176
7.173
7.158
7.153
7.144
7.141
4.841
4.836
4.792
3.128
3.115
3.111
3.108
3.103
3.087
2.625
2.606
2.586
2.560
2.539
2.519
2.157
2.138
2.118
1.818
1.813
1.795
1.775
1.745



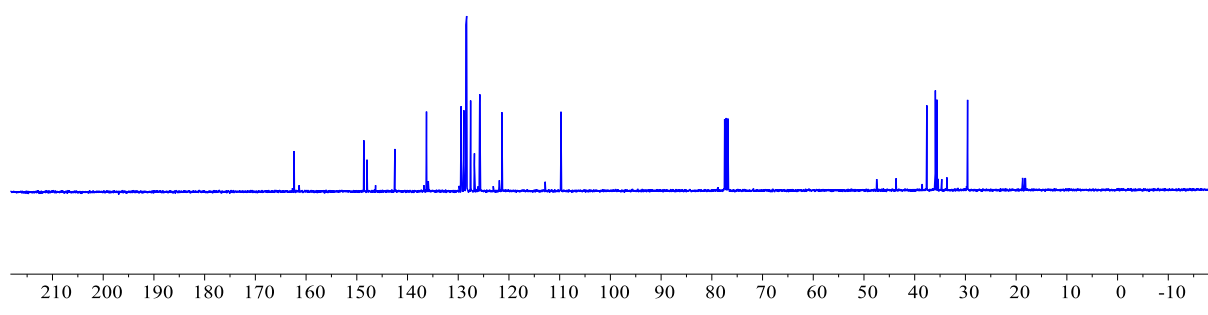
26, ^1H NMR (400 MHz CDCl_3)

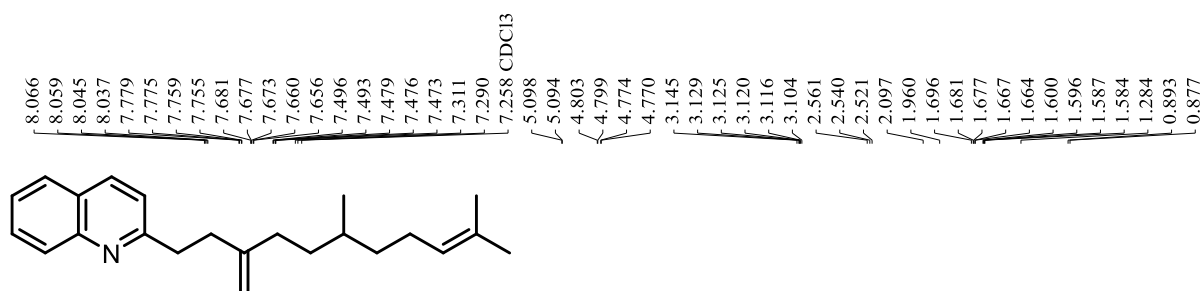


148.620
147.588
142.009
136.256
129.420
128.897
128.339
127.560
126.802
125.780
121.031
- 109.742
77.473 CDCl_3
77.155 CDCl_3
76.837 CDCl_3
37.616
35.944
35.922
35.619
29.570

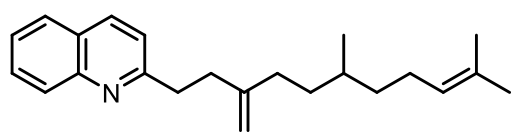
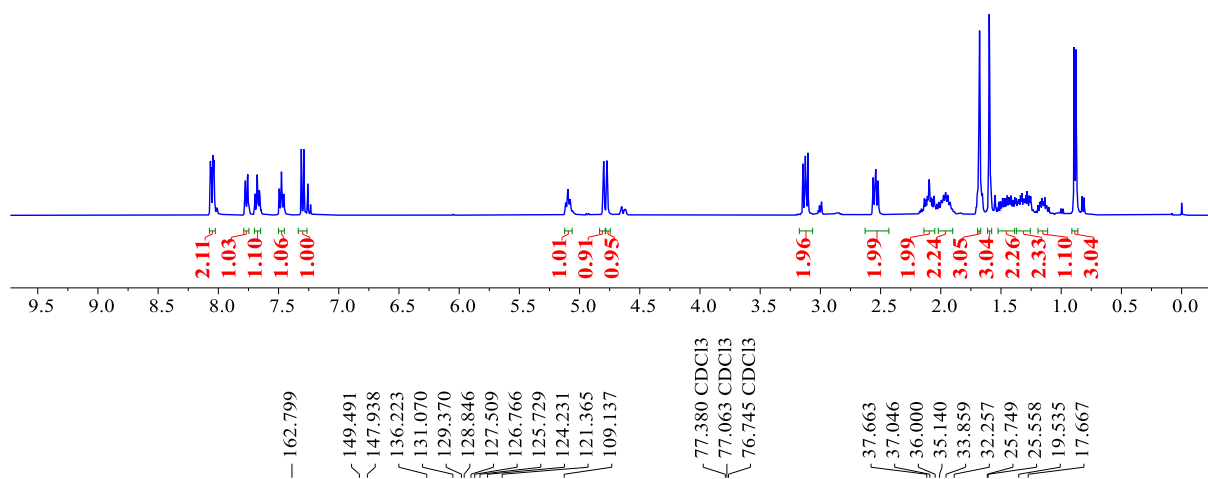


26, ^{13}C NMR (101 MHz CDCl_3)

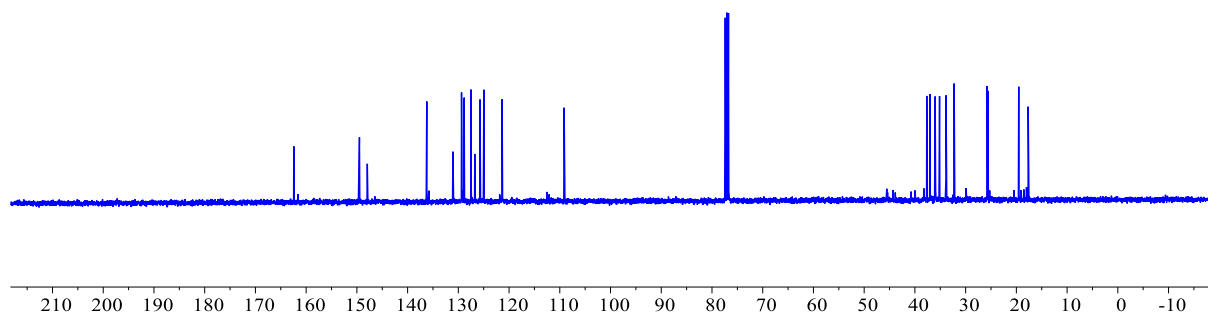


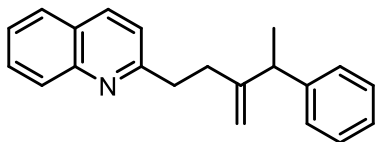
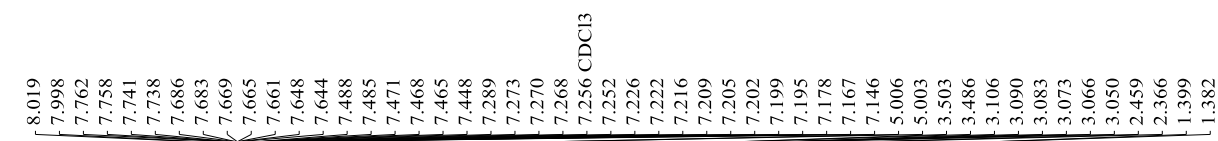


27, $^1\text{H NMR}$ (400 MHz CDCl_3)

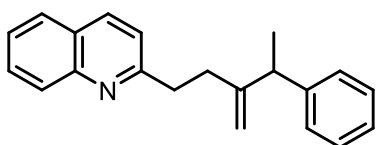
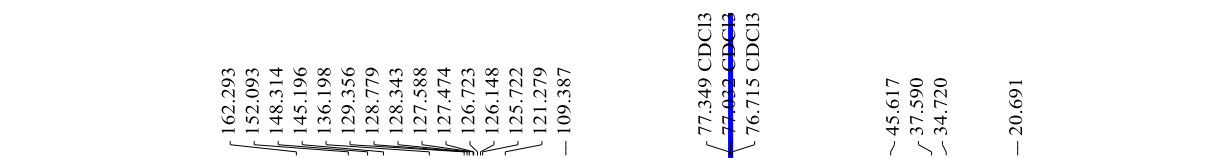
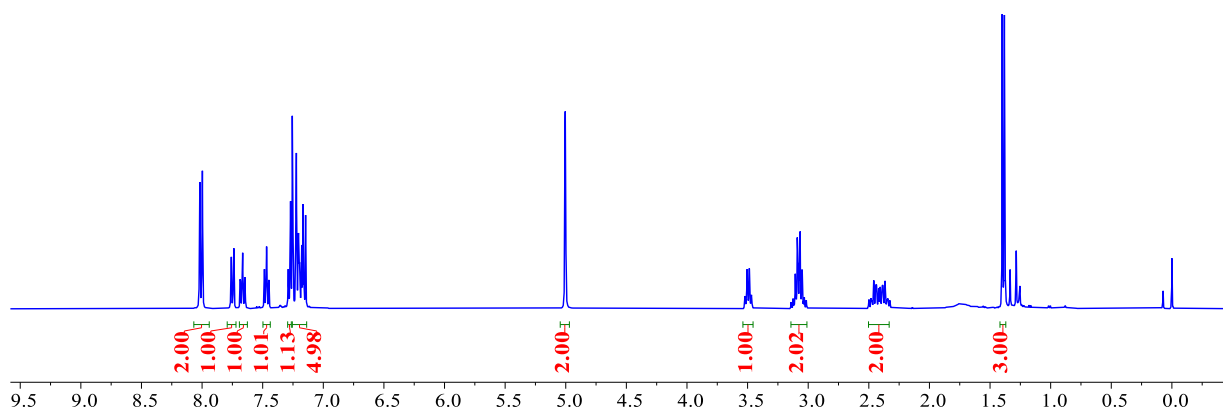


27, $^{13}\text{C NMR}$ (101 MHz CDCl_3)

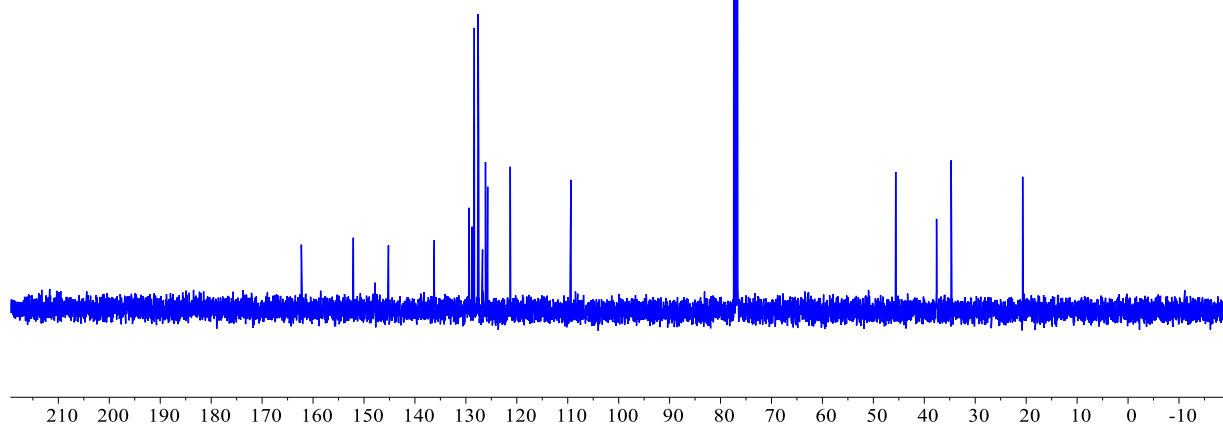


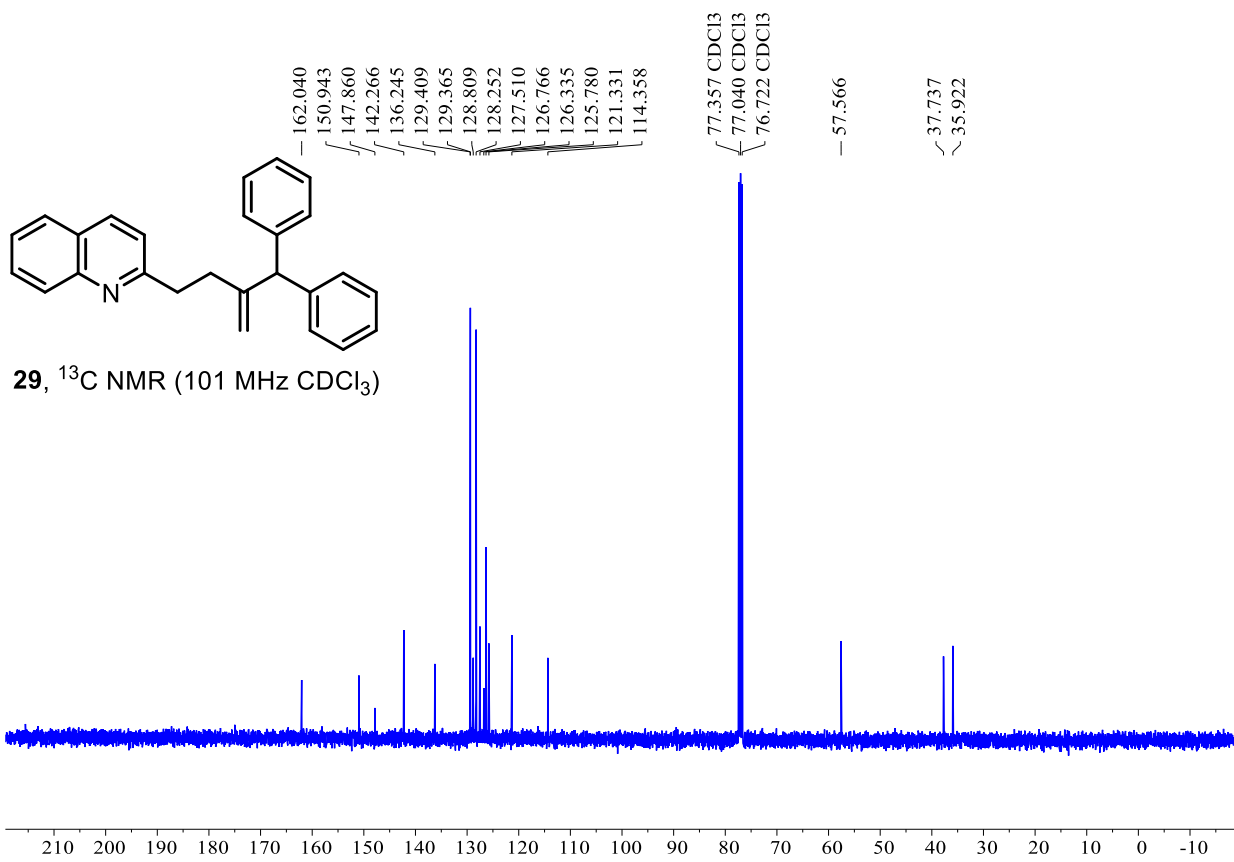
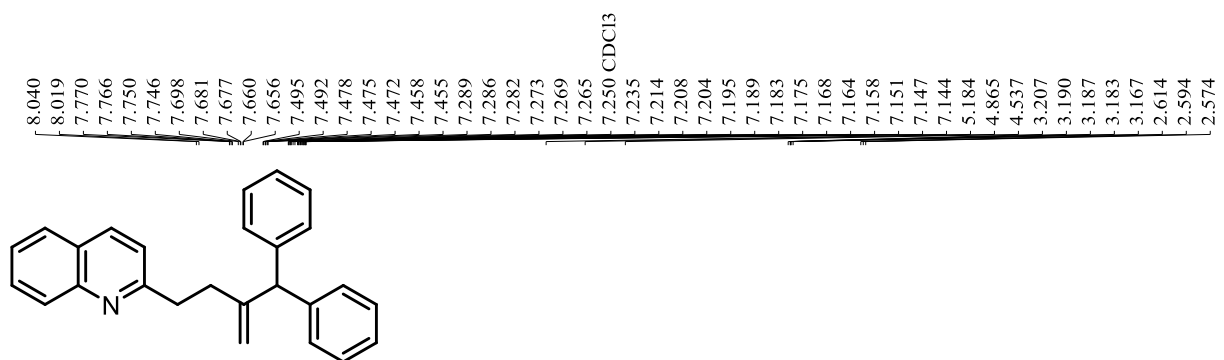


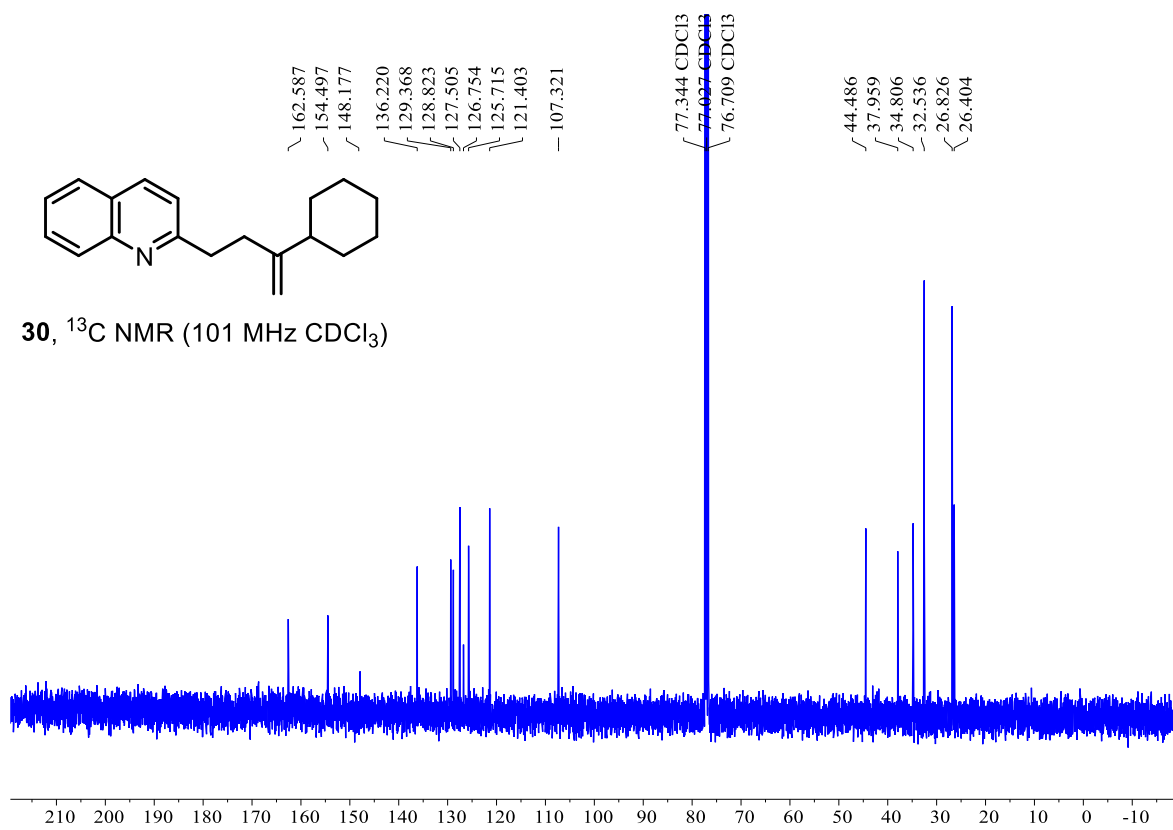
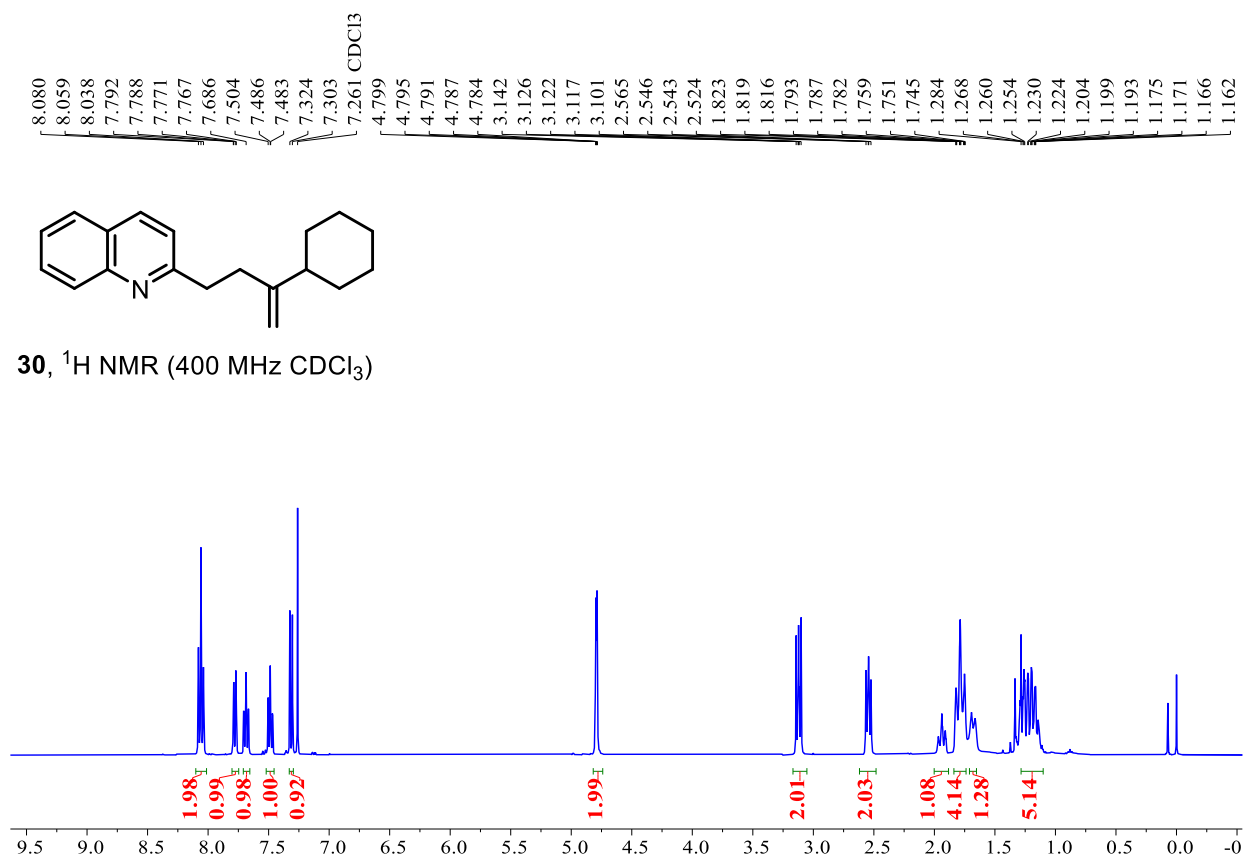
28, ¹H NMR (400 MHz CDCl₃)

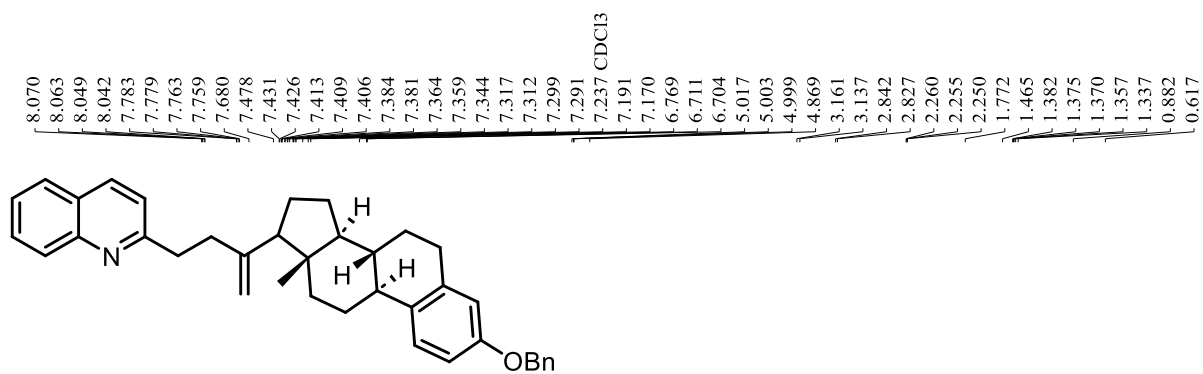


28, ¹³C NMR (101 MHz CDCl₃)

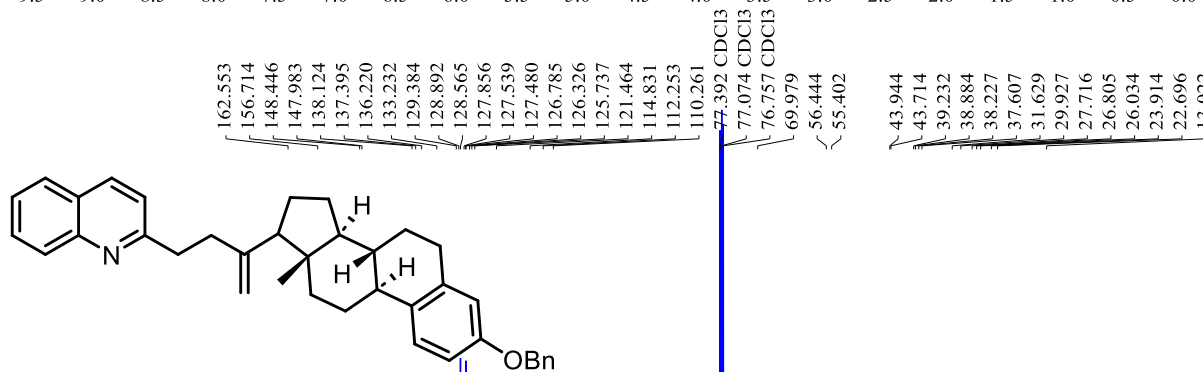
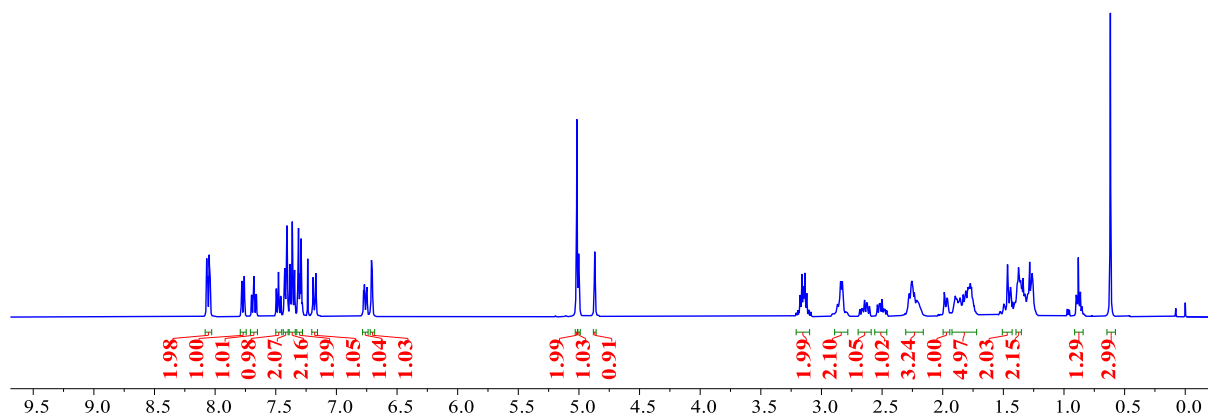




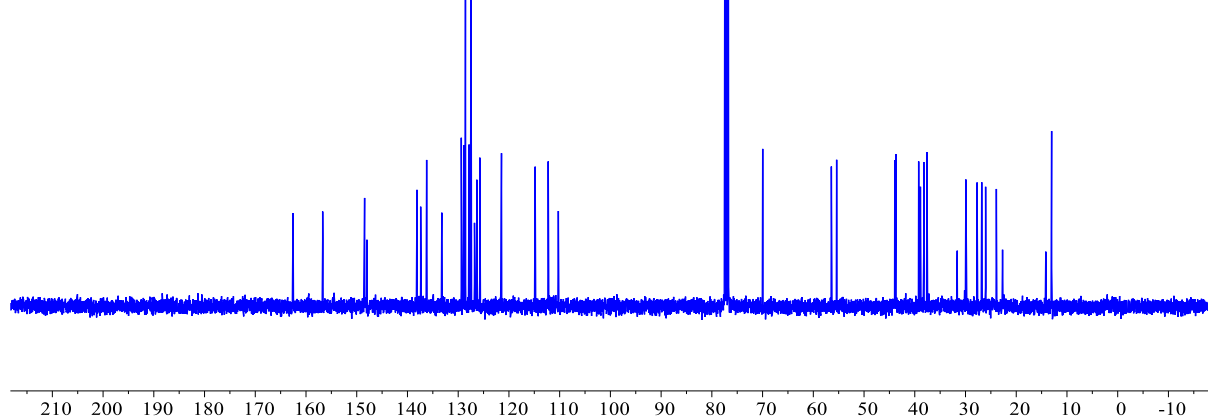


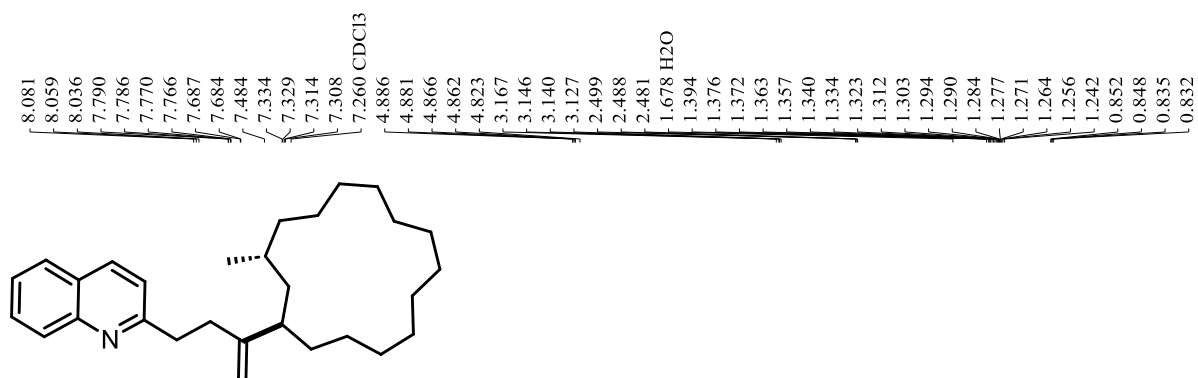


31, ¹H NMR (400 MHz CDCl₃)

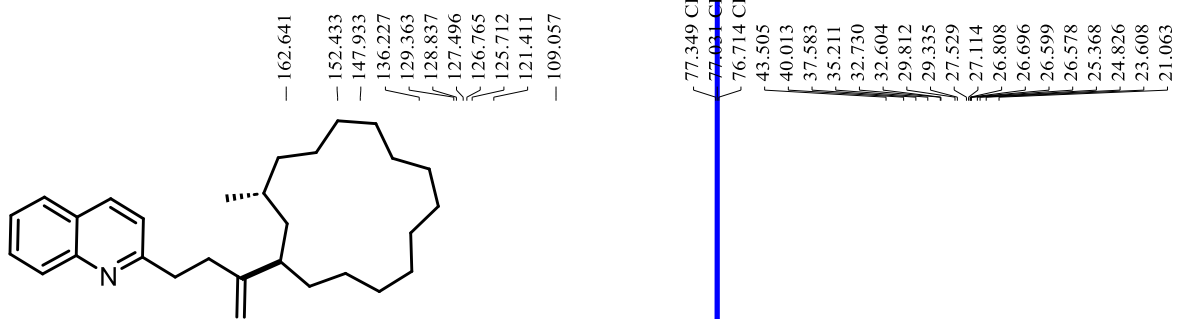
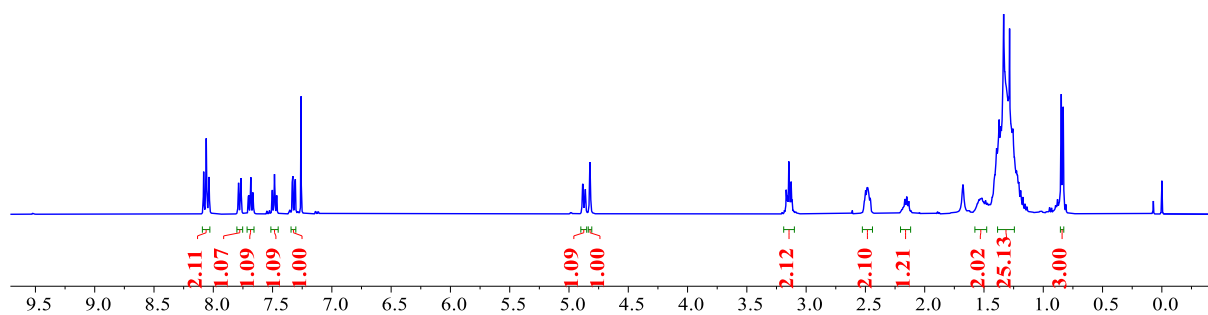


31, ¹³C NMR (101 MHz CDCl₃)

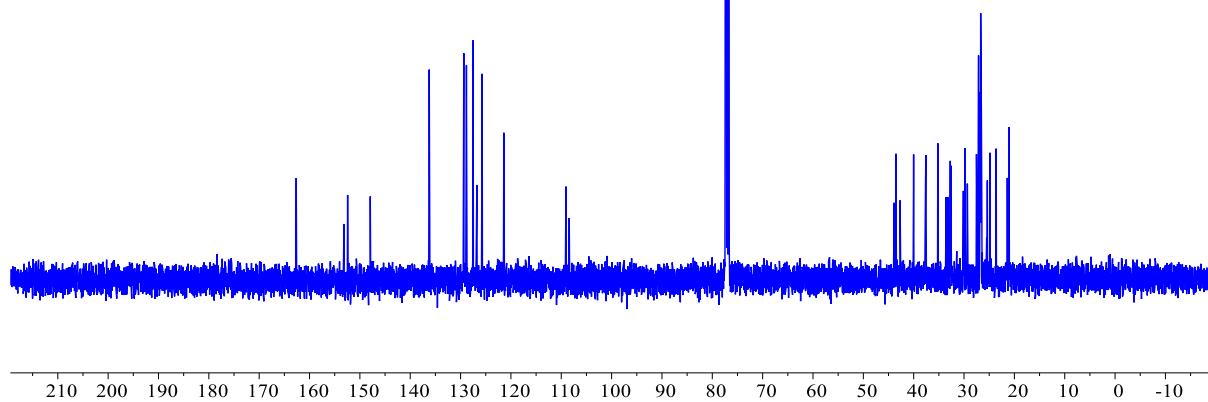


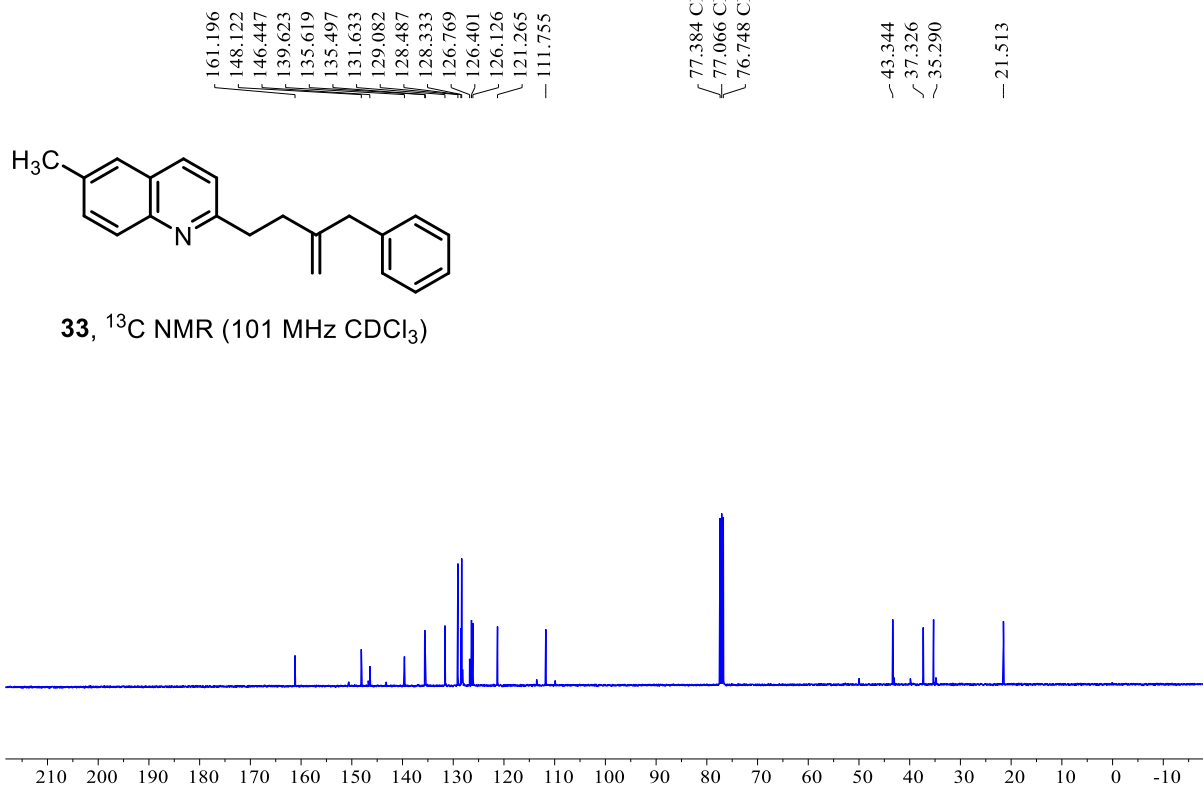
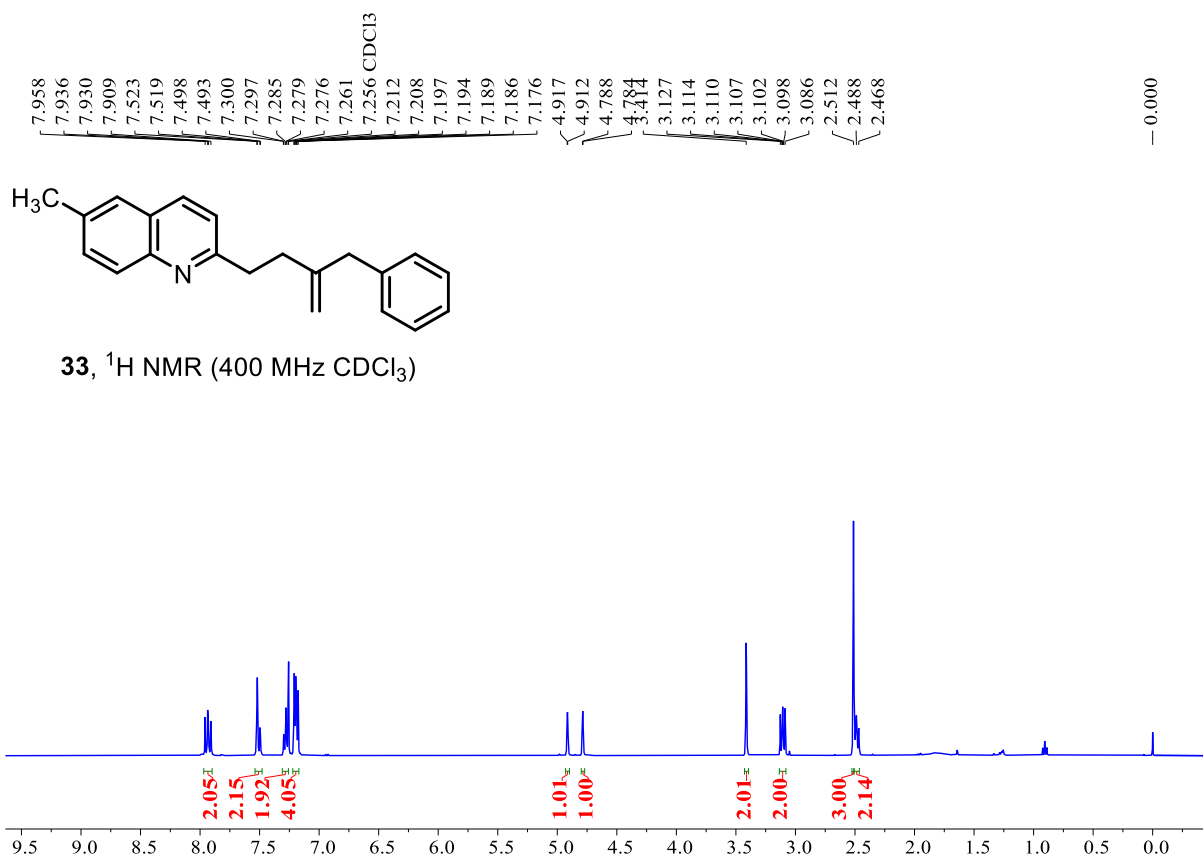


32, ¹H NMR (400 MHz CDCl₃)

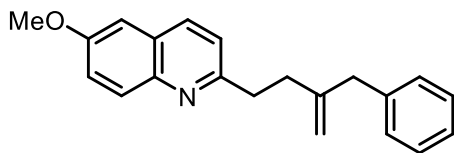


32, ¹³C NMR (101 MHz CDCl₃)

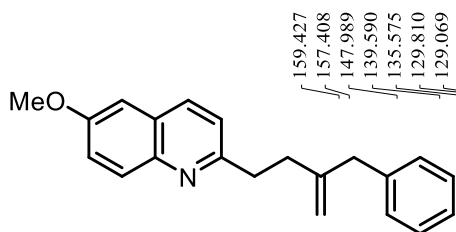
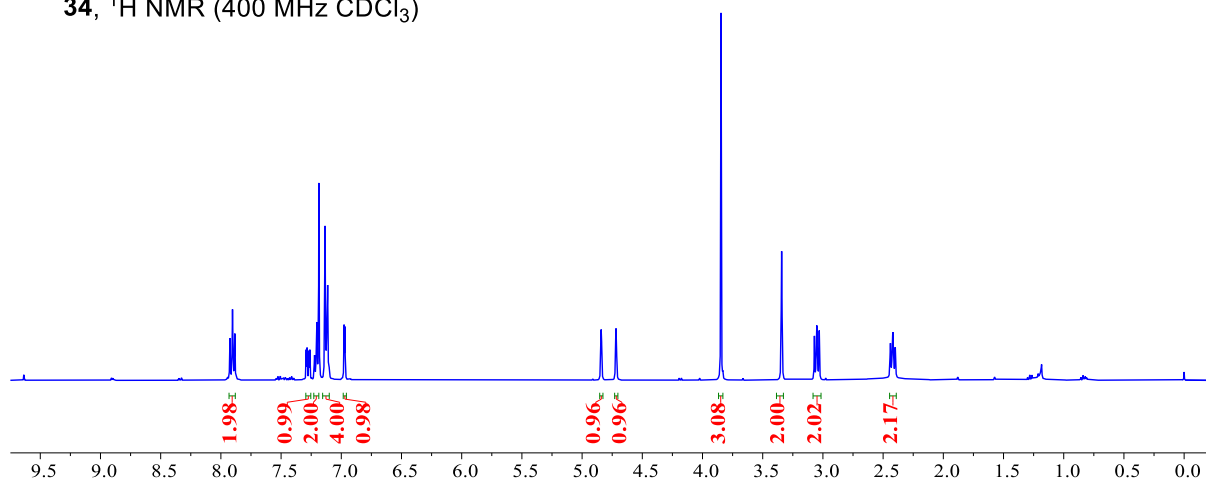




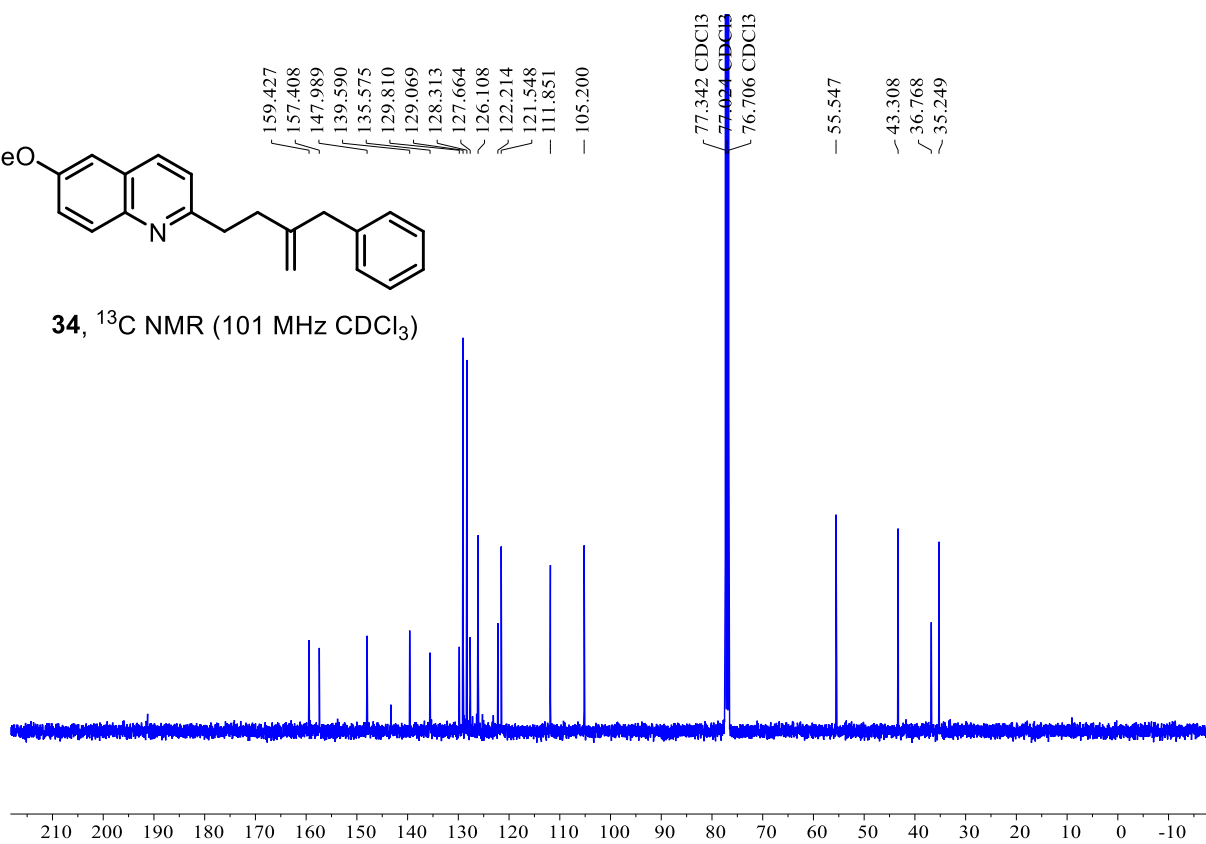
7.925
7.904
7.884
7.291
7.284
7.268
7.261
7.225
7.222
7.218
7.210
7.204
7.201
7.186 CDCl₃
7.138
7.134
7.127
7.119
7.113
7.105
7.101
6.977
6.970
4.843
4.839
4.720
4.715
3.855
3.846
3.831
3.343
3.070
3.058
3.054
3.051
3.046
3.042
3.030
2.440
2.419
2.399

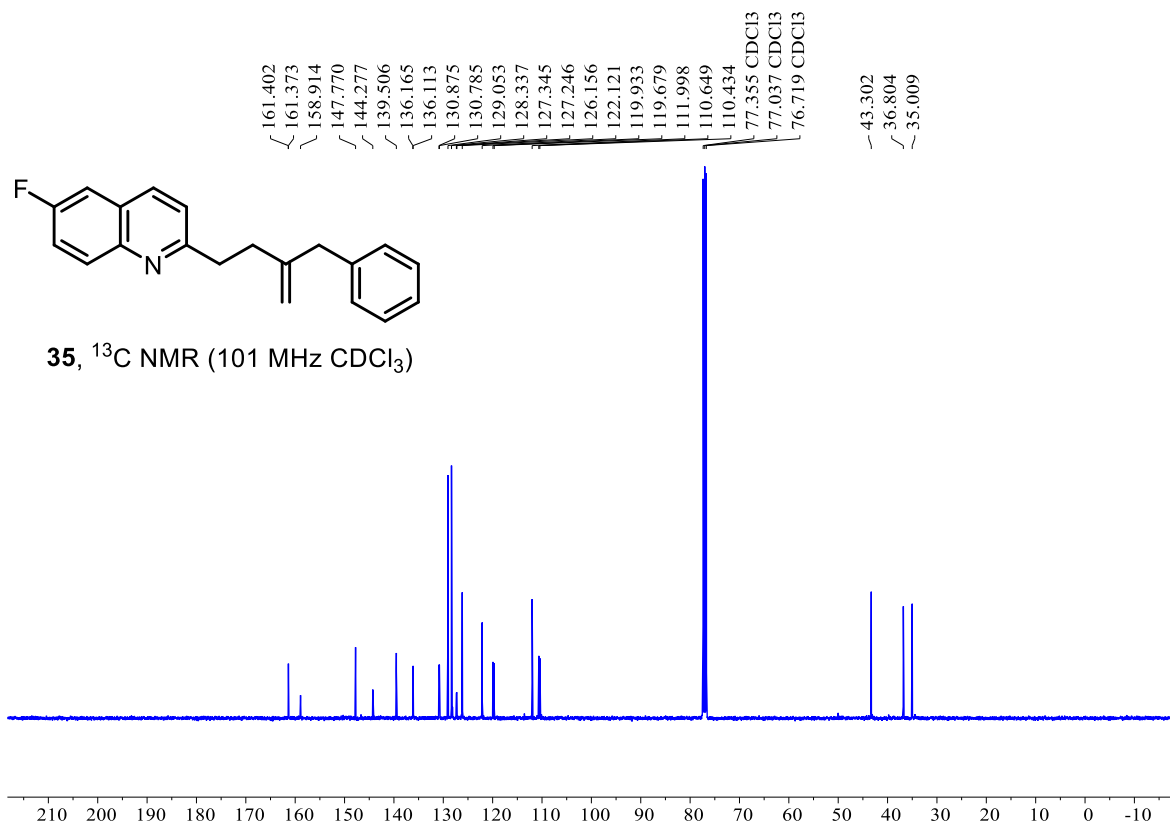
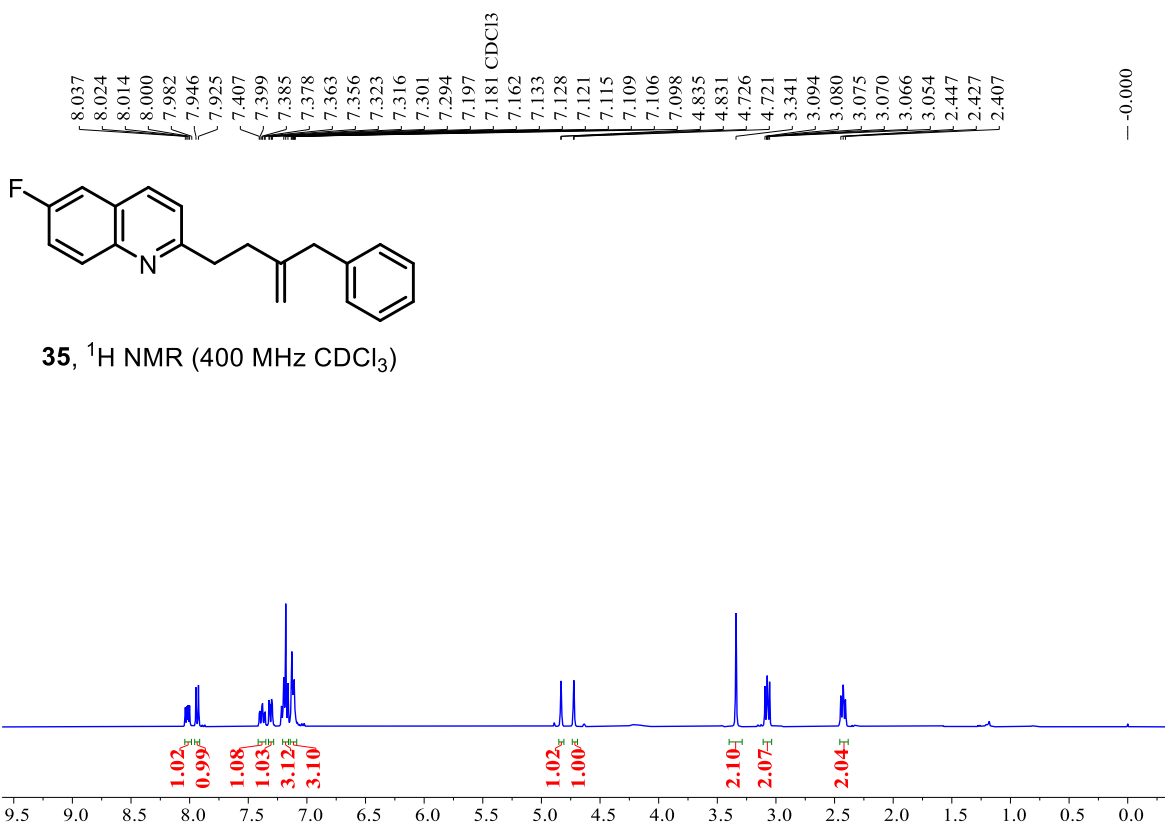


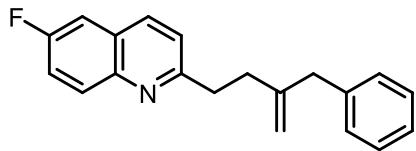
34, ¹H NMR (400 MHz CDCl₃)



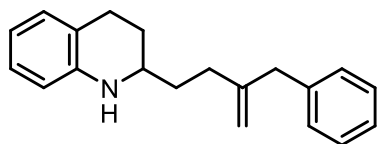
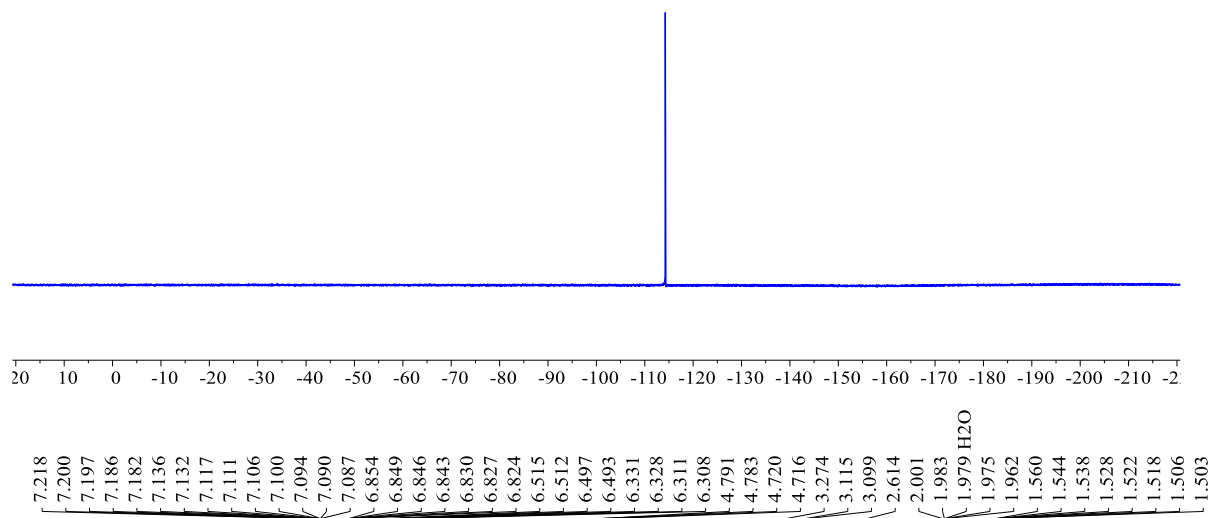
34, ¹³C NMR (101 MHz CDCl₃)







35, ¹⁹F NMR (376 MHz CDCl₃)



36, ¹H NMR (400 MHz CDCl₃)

