# Supplementary Information

***for***

## Nickel-Catalyzed Reductive Difunctionalization of BN-heterocyclic Olefins

Chaokun Li, Kui Yu, Kai Yang*, Qiuling Song*

*Key Laboratory of Molecule Synthesis and Function Discovery, Fujian Province University, College of Chemistry at Fuzhou University, Fuzhou, Fujian, 350108, China*

*Corresponding author. Email: kyang@fzu.edu.cn; qsong@fzu.edu.cn

# Table of Contents

## 1. General Methods

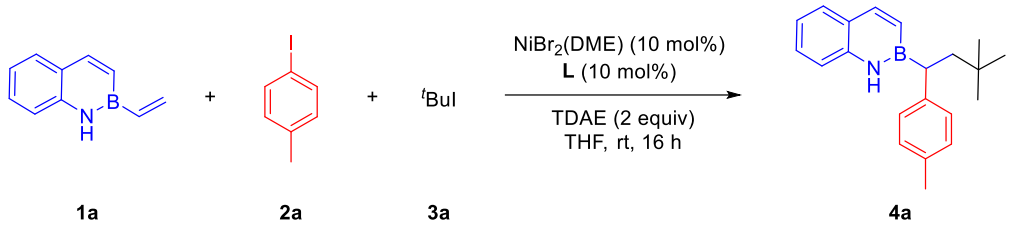
**General Experimental Procedures:** All reactions dealing with air- or moisture-sensitive compounds were performed by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere or in the argon-filled glove box. Flash column chromatography was performed over silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was accomplished by UV light (254 nm) and phosphomolybdic acid followed by heating, also by Gas chromatograph-Mass spectrometer analysis (GC-MS).

**Materials:** Unless noted otherwise, all reagents and starting materials were purchased from commercial sources and used as received. $CDCl_3$, was purchased from *Energy Chemical*. The reaction solvent is dry solvent and was purchased from *Energy Chemical*. Metal catalysts are purchased from *Bide Pharmaceutical* and *Energy Chemical*.

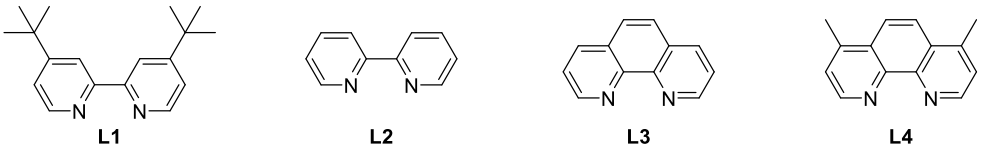
**Instrumentation:** $^{1}H$ NMR, $^{11}B$ NMR, $^{13}C$ NMR and $^{19}F$ NMR spectra were recorded at ambient temperature using Bruker AscendTM 400 (400 MHz) spectrometer or JNM-ECZ500R/S1 (500 MHz) spectrometer $^{1}H$ NMR chemical shifts (in ppm) were referenced to $CDCl_3$ ($\delta$ = 7.26 ppm) as internal standards. $^{13}C$ NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ ($\delta$ = 77.0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd, = double doublet, dt = double triplet, td = triple doublet, m = multiplet. GC analysis was performed at Shimadzu GC-2030. High-resolution mass spectroscopy (HR-MS) analysis was performed at an Exactive Plus (Thermo Scientific) with an ESI source or Agilent 8890-7250 GC-MS with EI mode.

## 2. Optimization of Experimental Conditions

**Table S1**




1a 2a 3a 4a

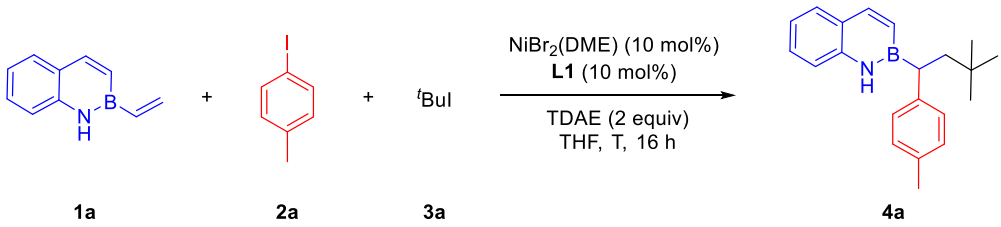


L1 L2 L3 L4

| entry | ligand | **4a** yield (%) |
|---|---|---|
| 1 | L1 | 94 |
| 2 | L2 | 37[b] |
| 3 | L3 | 34[b] |
| 4 | L4 | 30[b] |

[a] Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (0.12 mmol, 1.2 equiv), **3a** (0.3 mmol, 3 equiv), $NiBr_2$(DME) (10 mol%), **L** (10 mol%), TDAE (2 equiv) in 1 mL THF under argon at room temperature for 16 h. [b] Determined by GC analysis using dodecane as an internal standard.

**Table S2**



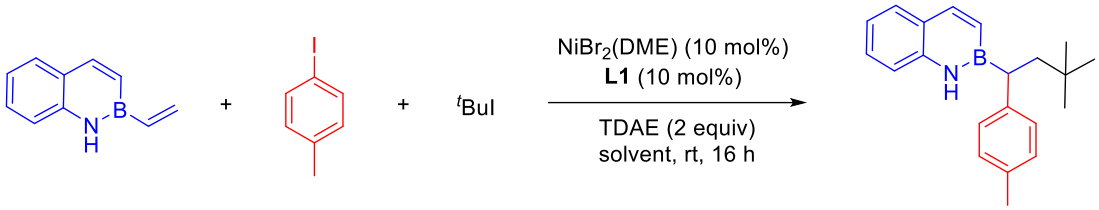

1a 2a 3a 4a

| entry | T / °C | **4a** yield (%)[b] |
|---|---|---|
| 1 | 30 | 86 |
| 2 | 40 | 82 |

| | | |
|---|---|---|
| 3 | 0 | 76 |

[a] Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (0.12 mmol, 1.2 equiv), **3a** (0.3 mmol, 3 equiv), $NiBr_2(DME)$ (10 mol%), **L1** (10 mol%), TDAE (2 equiv) in 1 mL THF under argon at T for 16 h. [b] Determined by GC analysis using dodecane as an internal standard.

**Table S3**

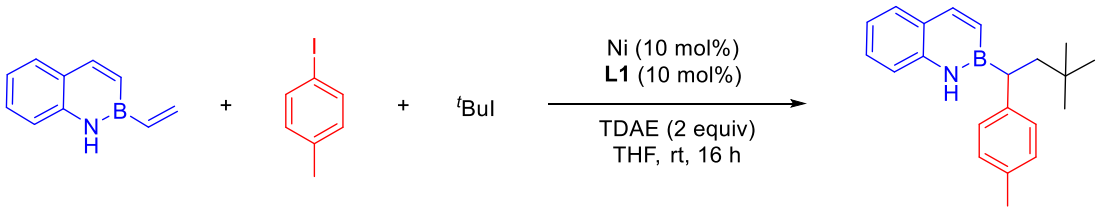



**1a** **2a** **3a** **4a**

| entry | solvent | **4a** yield (%)[b] |
|---|---|---|
| 1 | DCM | 29 |
| 2 | $CH_3CN$ | 38 |
| 3 | DMF | 36 |
| 4 | toluene | 44 |
| 5 | 1,4-dioxane | 62 |
| 6 | CPME | 51 |

[a] Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (0.12 mmol, 1.2 equiv), **3a** (0.3 mmol, 3 equiv), $NiBr_2(DME)$ (10 mol%), **L1** (10 mol%), TDAE (2 equiv) in 1 mL solvent under argon at room temperature for 16 h. [b] Determined by GC analysis using dodecane as an internal standard.

**Table S4**

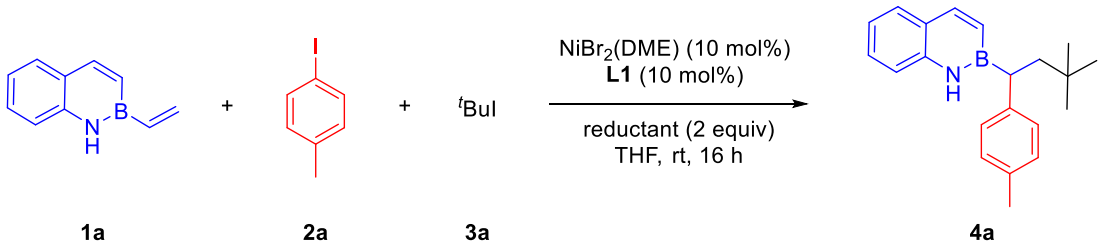



**1a** **2a** **3a** **4a**

| entry | Ni | **4a** yield (%)[b] |
|---|---|---|
| 1 | $NiCl_2(DME)$ | 63 |
| 2 | $NiCl_2(py)_4$ | trace |
| 3 | $NiCl_2(acac)_2$ | trace |

[a] Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (0.12 mmol, 1.2 equiv), **3a** (0.3 mmol, 3 equiv), Ni (10 mol%), **L1** (10 mol%), TDAE (2 equiv) in 1 mL THF under argon at room temperature for 16 h. [b] Determined by GC analysis using dodecane as an internal standard.

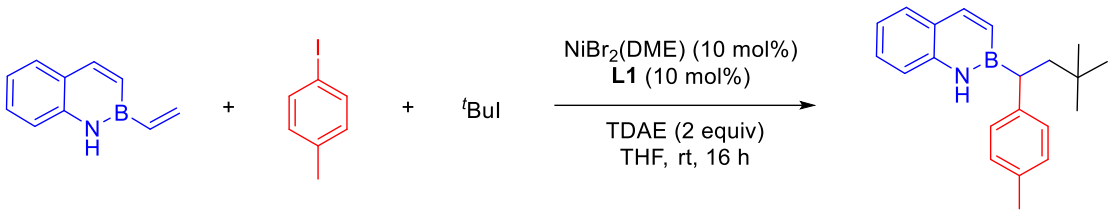
**Table S5**




| entry | reductant | **4a** yield (%)[b] |
|---|---|---|
| 1 | Mn | 62 |
| 2 | Zn | 40 |

[a] Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (0.12 mmol, 1.2 equiv), **3a** (0.3 mmol, 3 equiv), $NiBr_2(DME)$ (10 mol%), **L1** (10 mol%), reductant (2 equiv) in 1 mL THF under argon at room temperature for 16 h. [b] Determined by GC analysis using dodecane as an internal standard.

**Table S6**



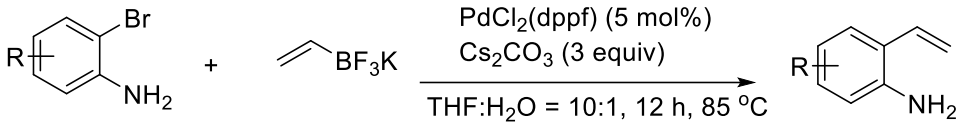

**1a** **2a** (x equiv) **3a** **4a**

| entry | x equiv | **4a** yield (%)[b] |
|---|---|---|
| 1 | 1 | 84 |
| 2 | 1.1 | 90 |
| 3 | 1.3 | 92 |
| 4 | 1.5 | 88 |

[a] Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (x mmol, x equiv), **3a** (0.3 mmol, 3 equiv), $NiBr_2$(DME) (10 mol%), **L1** (10 mol%), TDAE (2 equiv) in 1 mL THF under argon at room temperature for 16 h. [b] Determined by GC analysis using dodecane as an internal standard.

## 3. General procedure for the preparation of the starting material

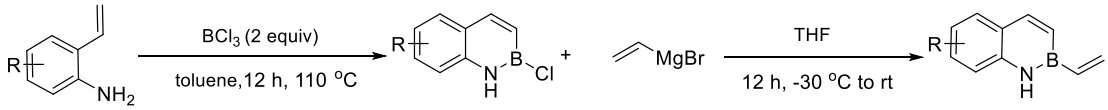
### 3.1 General procedure A




Prepared following a literature procedure [1]. To a 100 mL Schlenk flask equipped with a stir bar were added $Pd(dppf)Cl_2$ (5 mol%), $Cs_2CO_3$ (3.0 equiv), and potassium vinyltrifluoroborate (1.5 equiv). The flask was evacuated and filled with argon for three cycles. THF and $H_2O$ was added under argon, followed N-benzyl-2-bromo-4-(trifluoromethoxy)aniline (1.0 equiv). The resulting mixture was heated to 85 °C and stirred until full consumption of N-benzyl-2-bromo-4-(trifluoromethoxy)aniline was observed by TLC (12-18 h). The reaction mixture was cooled to RT, diluted with EtOAc, and filtered over Celite. The filtrate was dried over anhydrous $Na_2SO_4$ and evaporated

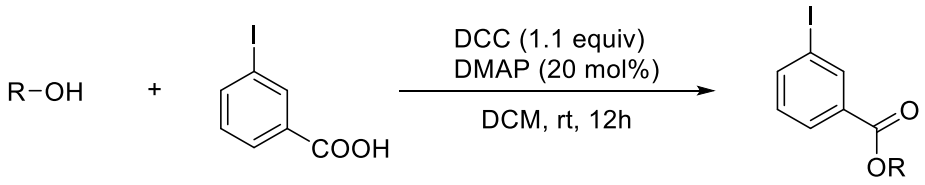
to dryness in vacuo. The residue was purified by flash column chromatography on silica gel to give corresponding product.

### 3.2 General procedure B



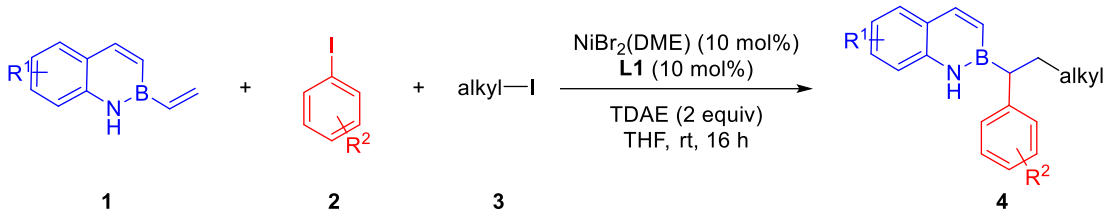

Prepared following a literature procedure [2]. To a stirred solution of 2-vinylaniline (1.0 equiv) in dry toluene, cold boron trichloride solution (1.0 M in hexane, 2.0 equiv) was added dropwise at -30 °C under an argon atmosphere. At the conclusion of the addition, the reaction mixture was allowed to warm to room temperature over 1 hour, and then it was refluxed. After being stirred for 4 hours, the mixture was concentrated under reduced pressure to afford the B-Cl intermediate. Under argon, dry THF (0.2 M) was added to dilute the B-Cl intermediate, and the mixture was cooled to –30 °C. Vinylmagnesium bromide solution (1.0 M in $Et_2O$, 2.0 equiv) was slowly added dropwise using a syringe and allow the reaction mixture to warm to room temperature. The mixture was stirred for 18 hours at same temperture. After completion (TLC), concentrated under reduced pressure. The residue was purified by silica gel chromatography to obtain the corresponding product.

### 3.3 General procedure C




Alcohol (1.0 equiv), DMAP (0.2 equiv) and 3-iodobenzoic acid (1.0 equiv) were added to dichloromethane. DCC (1.1 equiv) was added and the reaction mixture was allowed to stir at RT for 12 h before concentrating under reduced pressure. The crude residue was purified by flash column chromatography to afford the corresponding ester.

### 3.4 General procedure D

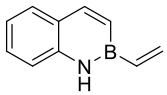



1 2 3 4

To a 25 mL Young tube were added **1** (0.1 mmol, 1 equiv), **2** (0.12 mmol, 1.2 equiv), **3** (0.3 mmol, 3 equiv), $NiBr_2$(DME) (10 mol%), **L1** (10 mol%), TDAE (2 equiv) and 1 mL THF under argon and the resulting mixture was stirred at room temperature for 16 h. The reaction mixture was diluted with EtOAC and washed with water and brine. The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was then purified by flash column chromatography.

## 4. Characterization of Starting Materials

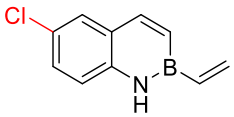
### 2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (1a)



The product as a white solid. Yield: 82%. TCL PE $R_f$ = 0.7.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 8.04 (d, *J* = 11.5 Hz, 1H), 7.79 – 7.75 (m, 1H), 7.62 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.41 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.18 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 7.07 (dd, *J* = 11.6, 2.0 Hz, 1H), 6.51 (s, 1H), 6.25 (dd, *J* = 19.6, 3.6 Hz, 1H), 6.06 (dd, *J* = 13.3, 3.6 Hz, 1H).

### 6-chloro-2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (1b)

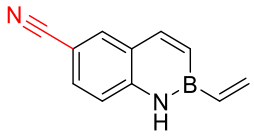


The product as a white solid. Yield: 73%. TCL PE $R_f$ = 0.7.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.91 (d, *J* = 11.6 Hz, 1H), 7.74 (s, 1H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.34 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 1H), 7.08 (dd, *J* =

11.5, 1.9 Hz, 1H), 6.46 (dd, *J* = 19.6, 13.2 Hz, 1H), 6.24 (dd, *J* = 19.6, 3.6 Hz, 1H), 6.06 (dd, *J* = 13.1, 3.6 Hz, 1H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 32.51. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 143.8, 138.3, 132.7, 128.4, 126.6, 125.9, 119.3. **HRMS (EI)** calcd for $C_{10}H_9BClN$ [M]: 189.0517, found:189.0520.

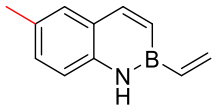
**2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine-6-carbonitrile(1c)**




The product as a white solid. Yield: 48%. TCL PE $R_f$ = 0.4.

**$^{1}$H NMR (400 MHz, Chloroform-*d*)** δ 8.00 – 7.90 (m, 3H), 7.60 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.14 (dd, *J* = 11.6, 1.9 Hz, 1H), 6.48 (dd, *J* = 19.6, 13.2 Hz, 1H), 6.28 (dd, *J* = 19.6, 3.6 Hz, 1H), 6.11 (dd, *J* = 13.1, 3.5 Hz, 1H).**$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 33.77. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 143.8, 142.6, 134.3, 134.1, 130.6, 125.5, 119.3, 119.0, 104.1. **HRMS (EI)** calcd for $C_{11}H_9BN_2$ [M]: 180.0859, found: 180.0860.

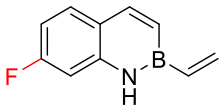
**6-methyl-2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (1d)**




The product as a white solid. Yield: 76%. TCL PE $R_f$ = 0.7.

**$^{1}$H NMR (500 MHz, Chloroform-*d*)** δ 7.98 (d, *J* = 11.5 Hz, 1H), 7.73 (s, 1H), 7.43 – 7.39 (m, 1H), 7.26 – 7.21 (m, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.03 (dd, *J* = 11.5, 1.9 Hz, 1H), 6.49 (dd, *J* = 19.6, 13.3 Hz, 1H), 6.23 (dd, *J* = 19.6, 3.6 Hz, 1H), 6.03 (dd, *J* = 13.2, 3.6 Hz, 1H), 2.44 (s, 3H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 32.12. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 144.7, 138.0, 131.8, 130.1, 129.5, 129.1, 125.68, 117.8, 20.8. **HRMS (EI)** calcd for $C_{11}H_{12}BN$ [M]: 169.1063, found: 169.1065.

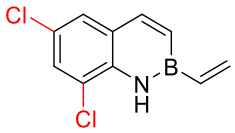
**7-fluoro-2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (1e)**



The product as a white solid. Yield: 67%. TCL PE $R_f$ = 0.7.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.98 (d, *J* = 11.6 Hz, 1H), 7.75 (s, 1H), 7.56 (dd, *J* = 8.6, 6.2 Hz, 1H), 7.01 – 6.85 (m, 3H), 6.47 (dd, *J* = 19.6, 13.2 Hz, 1H), 6.23 (dd, *J* = 19.6, 3.6 Hz, 1H), 6.05 (dd, *J* = 13.1, 3.6 Hz, 1H).**$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 32.79. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 163.7, 161.3, 144.4, 141.1 (d, *J* = 11.0 Hz), 132.7, 131.0 (d, *J* = 10.2 Hz), 122.5, 109.3 (d, *J* = 22.9 Hz), 103.9 (d, *J* = 23.8 Hz). **$^{19}$F NMR (376 MHz, Chloroform-*d*)** δ -112.33. **HRMS (EI)** calcd for $C_{10}H_9BFN$ [M]: 173.0812, found: 173.0815.

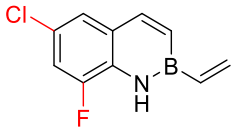
**6,8-dichloro-2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (1f)**



The product as a white solid. Yield: 75%. TCL PE $R_f$ = 0.65.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 8.24 (s, 1H), 7.88 (dd, *J* = 11.6, 1.4 Hz, 1H), 7.48 (q, *J* = 2.1 Hz, 2H), 7.13 (dd, *J* = 11.5, 1.8 Hz, 1H), 6.51 (dd, *J* = 19.6, 13.3 Hz, 1H), 6.28 (dd, *J* = 19.6, 3.4 Hz, 1H), 6.11 (dd, *J* = 13.3, 3.5 Hz, 1H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 32.9. **$^{13}$C NMR (126 MHz, CHLOROFORM-D)** δ 143.6, 134.8, 133.6, 127.2, 125.3, 122.7, 77.2, 77.0, 76.7. **HRMS (EI)** calcd for $C_{10}H_8BCl_2N$ [M]: 223.0127, found: 223.0130.

**6-chloro-8-fluoro-2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (1g)**

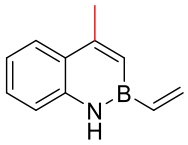


The product as a white solid. Yield: 75%. TCL PE $R_f$ = 0.65.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.97 (s, 1H), 7.89 (dd, *J* = 11.5, 1.9 Hz, 1H),

7.39 – 7.34 (m, 1H), 7.16 (ddd, *J* = 21.3, 11.0, 2.1 Hz, 2H), 6.48 (dd, *J* = 19.6, 13.2 Hz, 1H), 6.26 (dd, *J* = 19.6, 3.5 Hz, 1H), 6.09 (dd, *J* = 13.2, 3.5 Hz, 1H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 32.57. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 152.7, 150.3, 143.0 (d, *J* = 3.2 Hz), 133.4, 127.8 (d, *J* = 4.1 Hz), 127.6, 124.7, 124.6, 123.8 (d, *J* = 3.6 Hz), 113.9, 113.7. **$^{19}$F NMR (376 MHz, Chloroform-*d*)** δ -134.67 (d, *J* = 10.2 Hz). **HRMS (EI)** calcd for $C_{10}H_8BClFN$ [M]: 207.0422, found: 207.0423.

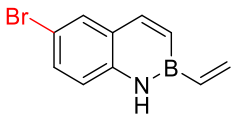
**4-methyl-2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (1h)**




The product as a colorless oil. Yield: 84%. TCL PE $R_f$ = 0.7.

**$^{1}$H NMR (400 MHz, Chloroform-*d*)** δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.41 – 7.33 (m, 1H), 7.21 – 7.11 (m, 2H), 6.84 (s, 1H), 6.44 (dd, *J* = 19.6, 13.2 Hz, 1H), 6.18 (dd, *J* = 19.5, 3.7 Hz, 1H), 5.99 (dd, *J* = 13.4, 3.6 Hz, 1H), 2.59 – 2.55 (m, 3H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 32.03. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 151.0, 140.2, 131.7, 127.9, 125.8, 125.6, 120.8, 118.6, 22.9. **HRMS (EI)** calcd for $C_{11}H_{12}BN$ [M]: 169.1063, found: 169.1065.

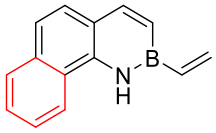
**6-bromo-2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (1i)**




The product as a white solid. Yield: 60%. TCL PE $R_f$ = 0.7.

**$^{1}$H NMR (400 MHz, Chloroform-*d*)** δ 7.91 (d, *J* = 11.5 Hz, 1H), 7.73 (d, *J* = 2.3 Hz, 1H), 7.46 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.20 – 7.01 (m, 2H), 6.46 (dd, *J* = 19.6, 13.2 Hz, 1H), 6.23 (dd, *J* = 19.6, 3.6 Hz, 1H), 6.06 (dd, *J* = 13.3, 3.5 Hz, 1H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 32.53. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 143.7, 138.7, 132.8, 131.5, 130.9, 127.2, 119.6, 113.2. **HRMS (EI)** calcd for $C_{10}H_9BBrN$ [M]: 233.0011, found: 233.0014.

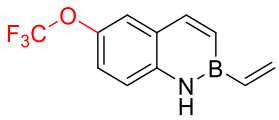
**2-vinyl-1,2-dihydronaphtho[2,1-e][1,2]azaborinine (1j)**



The product as a pink solid. Yield: 68%. TCL PE $R_f$ = 0.5.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 8.67 (s, 1H), 8.08 (t, *J* = 9.9 Hz, 2H), 7.83 – 7.76 (m, 1H), 7.61 – 7.39 (m, 4H), 7.13 (dd, *J* = 11.5, 1.8 Hz, 1H), 6.57 (dd, *J* = 19.6, 13.3 Hz, 1H), 6.25 (dd, *J* = 19.6, 3.5 Hz, 1H), 6.04 (dd, *J* = 13.3, 3.6 Hz, 1H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 32.42. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 145.6, 135.6, 133.3, 131.8, 128.8, 127.6, 126.4, 125.7, 123.7, 121.4, 121.0, 119.5. **HRMS (EI)** calcd for $C_{14}H_{12}BN$ [M]: 205.1063, found: 205.1066.

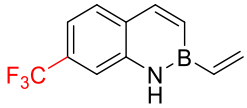
**6-(trifluoromethoxy)-2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (1k)**



The product as a white solid. Yield: 46%. TCL PE $R_f$ = 0.65.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 11.6 Hz, 1H), 7.77 (s, 1H), 7.47 – 7.42 (m, 1H), 7.29 – 7.19 (m, 2H), 7.10 (dd, *J* = 11.5, 1.9 Hz, 1H), 6.45 (dd, *J* = 19.6, 13.2 Hz, 1H), 6.23 (dd, *J* = 19.6, 3.6 Hz, 1H), 6.05 (dd, *J* = 13.2, 3.6 Hz, 1H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 32.64. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 144.10, 142.81 (d, *J* = 2.0 Hz), 138.4, 132.9, 125.9, 121.9, 121.6, 121.0, 119.0. **$^{19}$F NMR (376 MHz, Chloroform-*d*)** δ -58.15. **HRMS (EI)** calcd for $C_{11}H_9BF_3NO$ [M]: 239.0729, found: 239.0724.

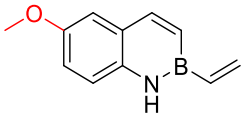
**7-(trifluoromethyl)-2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (1l)**



The product as a white solid. Yield: 42%. TCL PE $R_f$ = 0.6.

**$^{1}$H NMR (400 MHz, Chloroform-*d*)** δ 7.83 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.50 (s, 1H), 7.41 – 7.37 (m, 1H), 7.17 (dd, *J* = 11.7, 1.9 Hz, 1H), 6.48 (dd, *J* = 19.6, 13.2 Hz, 1H), 6.27 (dd, *J* = 19.6, 3.6 Hz, 1H), 6.10 (dd, *J* = 13.2, 3.6 Hz, 1H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 32.81. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 144.0, 139.3, 133.2, 129.9, 129.6, 127.8, 125.5, 122.7, 117.2 (q, *J* = 3.6 Hz), 115.15 (q, *J* = 4.2 Hz). **$^{19}$F NMR (376 MHz, Chloroform-*d*)** δ -62.16. **HRMS (EI)** calcd for $C_{11}H_9BF_3N$ [M]: 223.0780, found: 223.0782.

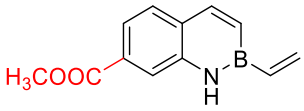
**6-methoxy-2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine (1m)**




The product as a white solid. Yield: 78%. TCL PE $R_f$ = 0.6.

**$^{1}$H NMR (400 MHz, Chloroform-*d*)** δ 7.99 (d, *J* = 11.5 Hz, 1H), 7.73 (s, 1H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.11 – 7.03 (m, 3H), 6.49 (dd, *J* = 19.6, 13.3 Hz, 1H), 6.22 (dd, *J* = 19.7, 3.7 Hz, 1H), 6.03 (dd, *J* = 13.3, 3.7 Hz, 1H), 3.87 (s, 2H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 31.83. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 153.8, 144.3, 134.6, 131.6, 126.0, 118.9, 117.4, 110.7, 55.6. **HRMS (EI)** calcd for $C_{11}H_{12}BNO$ [M]: 185.1012, found: 185.1016.

**Methyl 2-vinyl-1,2-dihydrobenzo[e][1,2]azaborinine-7-carboxylate (1n)**

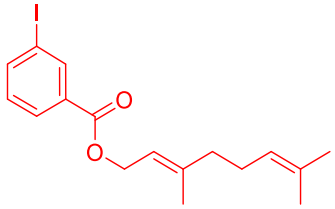



The product as a white solid. Yield: 53%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.4.

**$^{1}$H NMR (400 MHz, Chloroform-*d*)** δ 8.09 – 7.87 (m, 3H), 7.79 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.17 (dd, *J* = 11.6, 1.9 Hz, 1H), 6.49 (dd, *J* = 19.6, 13.2 Hz, 1H), 6.25 (dd, *J* = 19.6, 3.5 Hz, 1H), 6.07 (dd, *J* = 13.3, 3.6 Hz, 1H), 3.96 (s, 3H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 32.81. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 167.0, 144.1, 139.4, 132.9, 129.3, 128.9, 121.3, 119.7, 52.2. **HRMS (EI)** calcd for

$C_{12}H_{12}BNO_2$ [M]: 213.0961, found: 213.0963.

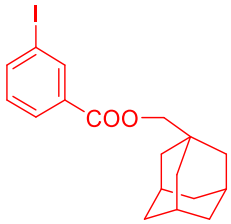
**(E)-3,7-dimethylocta-2,6-dien-1-yl 3-iodobenzoate (1o)**



The product as a white solid. Yield: 83%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.4.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 8.37 (s, 1H), 8.00 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.17 (t, *J* = 7.9 Hz, 1H), 5.45 (ddt, *J* = 7.1, 5.8, 1.3 Hz, 1H), 5.09 (tdd, *J* = 5.5, 3.0, 1.5 Hz, 1H), 4.83 (d, *J* = 7.1 Hz, 2H), 2.17 – 2.04 (m, 4H), 1.76 (d, *J* = 1.3 Hz, 3H), 1.67 (d, *J* = 1.4 Hz, 3H), 1.60 (d, *J* = 1.3 Hz, 3H).

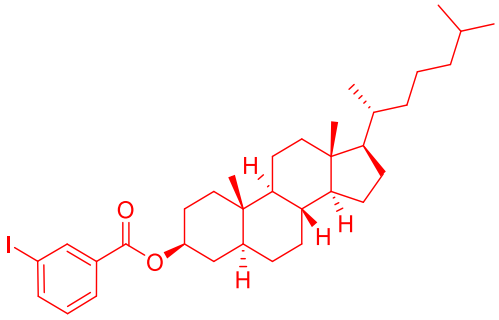
**((3r,5r,7r)-adamantan-1-yl)methyl 3-iodobenzoate (1p)**



The product as a white solid. Yield: 76%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.5.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 8.36 (t, *J* = 1.7 Hz, 1H), 8.00 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.87 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 3.92 (s, 2H), 2.01 (p, *J* = 3.1 Hz, 3H), 1.75 (dt, *J* = 12.4, 3.0 Hz, 3H), 1.71 – 1.65 (m, 3H), 1.62 (d, *J* = 2.9 Hz, 6H).

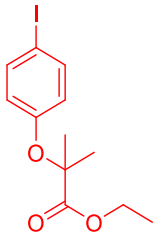
**(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-iodobenzoate (1q)**




The product as a white solid. Yield: 74%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 8.35 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 4.93 (tt, *J* = 11.0, 4.9 Hz, 1H), 2.06 – 1.41 (m, 12H), 1.30 (dhept, *J* = 24.8, 12.6, 11.6 Hz, 10H), 1.14 – 0.92 (m, 9H), 0.91 – 0.69 (m, 12H), 0.65 (s, 3H).

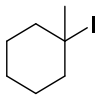
**Ethyl 2-(4-iodophenoxy)-2-methylpropanoate (1r)**




The product as a white solid. Yield: 85%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.5.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.54 – 7.47 (m, 2H), 6.63 – 6.57 (m, 2H), 4.21 (dd, *J* = 7.2, 1.5 Hz, 2H), 1.57 (d, *J* = 1.7 Hz, 6H), 1.27 – 1.19 (m, 3H).

**1-iodo-1-methylcyclohexane (1s)**

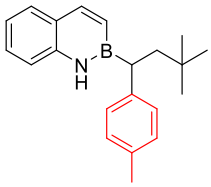



The product as a white solid. Yield: 65%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 2.27 – 1.99 (m, 4H), 1.73 – 1.55 (m, 5H), 1.27 – 1.17 (m, 1H), 1.03 – 0.92 (m, 2H), 0.88 – 0.75 (m, 1H).

## 5. Characterization of Products

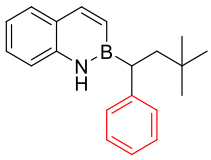
**2-(3,3-dimethyl-1-(p-tolyl)butyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4a)**



The product as a colorless oil. Yield: 94%. TCL PE $R_f$ = 0.55.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.96 (d, *J* = 11.5 Hz, 1H), 7.56 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.35 (td, *J* = 7.5, 7.0, 1.5 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.07 (m, 4H), 6.91 (dd, *J* = 11.5, 2.0 Hz, 1H), 2.89 (dd, *J* = 7.6, 5.6 Hz, 1H), 2.33 (s, 3H), 2.11 (dd, *J* = 13.9, 5.6 Hz, 1H), 1.93 (dd, *J* = 13.9, 7.6 Hz, 1H), 0.90 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 37.33. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 144.6, 144.0, 139.7, 133.8, 129.2, 129.1, 127.9, 127.9, 125.1, 120.6, 117.9, 46.7, 32.7, 30.3, 20.9. **HRMS (EI)** calcd for $C_{21}H_{26}BN$ [M]: 303.2158, found: 303.2150.

**2-(3,3-dimethyl-1-phenylbutyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4b)**

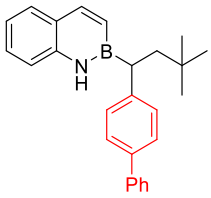


The product as a colorless oil. Yield: 70%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.93 (d, *J* = 11.5 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.36 (s, 1H), 7.31 (s, 1H), 7.29 – 7.25 (m, 2H), 7.25 – 7.22 (m, 2H), 7.15 – 7.06 (m, 3H), 6.88 (dd, *J* = 11.6, 2.0 Hz, 1H), 2.90 (dd, *J* = 7.8, 5.4 Hz, 1H), 2.12 – 2.02 (m, 1H), 1.93 (dd, *J* = 14.0, 7.8 Hz, 1H), 0.87 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 37.3. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 147.3, 144.6, 139.7, 129.2, 128.5, 128.1, 127.9, 125.1, 124.5, 120.7, 117.9, 46.7, 32.2, 30.2. **HRMS (EI)** calcd for $C_{20}H_{24}BN$ [M]: 289.2002, found: 289.1997.

**2-(1-([1,1'-biphenyl]-4-yl)-3,3-dimethylbutyl)-1,2-**

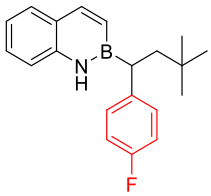
**dihydrobenzo[e][1,2]azaborinine (4c)**




The product as a colorless oil. Yield: 83%. TCL PE $R_f$ = 0.5.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.99 (d, *J* = 11.5 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.59 – 7.52 (m, 3H), 7.47 – 7.41 (m, 3H), 7.35 (dddd, *J* = 10.7, 6.1, 5.0, 1.9 Hz, 4H), 7.17 – 7.10 (m, 2H), 6.95 (dt, *J* = 11.6, 1.7 Hz, 1H), 2.98 (dd, *J* = 7.5, 5.7 Hz, 1H), 2.16 (ddd, *J* = 14.0, 5.6, 1.4 Hz, 1H), 1.99 (ddd, *J* = 13.9, 7.6, 1.4 Hz, 1H), 0.93 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 35.19. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 146.5, 144.7, 141.0, 139.7, 137.3, 129.2, 128.6, 128.5, 128.0, 127.2, 126.8, 125.1, 120.8, 118.0, 46.8, 32.2, 30.3. **HRMS (EI)** calcd for $C_{26}H_{28}BN$ [M]: 365.2315, found: 365.2319.

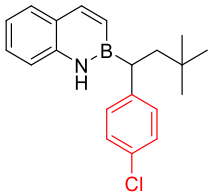
**2-(1-(4-fluorophenyl)-3,3-dimethylbutyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4d)**




The product as a colorless oil. Yield: 75%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.95 (d, *J* = 11.6 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.39 – 7.32 (m, 2H), 7.22 – 7.16 (m, 2H), 7.13 (dt, *J* = 7.0, 2.9 Hz, 2H), 7.01 – 6.94 (m, 2H), 6.86 (dd, *J* = 11.6, 2.0 Hz, 1H), 2.89 (dd, *J* = 8.0, 5.4 Hz, 1H), 2.08 (dd, *J* = 14.0, 5.4 Hz, 1H), 1.88 (dd, *J* = 13.9, 7.9 Hz, 1H), 0.87 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.17. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 144.8, 142.8, 139.6, 129.2, 128.1, 125.1, 120.9, 118.0, 115.2, 46.9, 32.1, 30.2. **HRMS (EI)** calcd for $C_{20}H_{23}BFN$ [M]: 307.1908, found: 307.1899.

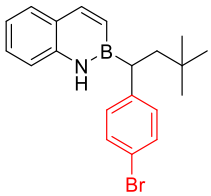
**2-(1-(4-chlorophenyl)-3,3-dimethylbutyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4e)**




The product as a colorless oil. Yield: 84%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 11.5 Hz, 1H), 7.54 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.34 (td, *J* = 7.5, 7.1, 1.6 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.13 – 7.07 (m, 2H), 6.83 (dd, *J* = 11.6, 2.0 Hz, 1H), 2.88 (dd, *J* = 8.0, 5.2 Hz, 1H), 2.06 (dd, *J* = 14.0, 5.2 Hz, 1H), 1.88 (dd, *J* = 14.0, 8.0 Hz, 1H), 0.86 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 37.76. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 145.8, 144.9, 139.6, 130.1, 129.4, 129.2, 128.6, 128.1, 125.1, 120.9, 117.9, 46.7, 32.2, 30.2. **HRMS (EI)** calcd for $C_{20}H_{23}BClN$ [M]: 323.1612, found: 323.1617.

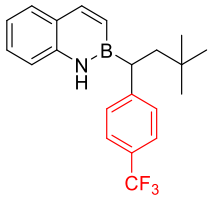
**2-(1-(4-bromophenyl)-3,3-dimethylbutyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4f)**




The product as a colorless oil. Yield: 83%. TCL PE $R_f$ = 0.55.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.96 (d, *J* = 11.5 Hz, 1H), 7.56 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.36 (td, *J* = 7.4, 1.5 Hz, 2H), 7.18 – 7.06 (m, 4H), 6.85 (dd, *J* = 11.5, 2.0 Hz, 1H), 2.89 (dd, *J* = 8.0, 5.2 Hz, 1H), 2.11 – 2.04 (m, 1H), 1.90 (dd, *J* = 14.0, 8.1 Hz, 1H), 0.88 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 35.16. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 146.4, 144.9, 139.6, 131.5, 129.8, 129.2, 128.1, 125.1, 120.9, 118.1, 118.0, 46.7, 32.2, 30.2. **HRMS (EI)** calcd for $C_{20}H_{23}BBrN$ [M]: 367.1107, found: 367.1100.

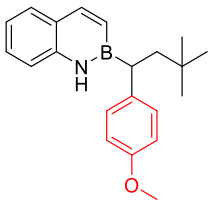
**2-(3,3-dimethyl-1-(4-(trifluoromethyl)phenyl)butyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4g)**



The product as a colorless oil. Yield: 84%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.97 (d, *J* = 11.4 Hz, 1H), 7.56 (dd, *J* = 12.3, 7.9 Hz, 3H), 7.37 (d, *J* = 7.3 Hz, 4H), 7.15 (d, *J* = 7.7 Hz, 2H), 6.86 (dd, *J* = 11.6, 2.1 Hz, 1H), 3.01 (dd, *J* = 7.8, 5.3 Hz, 1H), 2.12 (dd, *J* = 14.0, 5.3 Hz, 1H), 1.96 (dd, *J* = 14.0, 7.8 Hz, 1H), 0.89 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 36.95. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 151.8, 145.1, 139.5, 129.3, 128.2 (d, *J* = 6.0 Hz), 125.5 (d, *J* = 4.0 Hz), 125.1, 121.0, 118.0, 46.6, 32.2, 30.1. **$^{19}$F NMR (376 MHz, Chloroform-*d*)** δ -62.02. **HRMS (EI)** calcd for $C_{21}H_{23}BF_3N$ [M]: 357.1876, found: 357.1881.

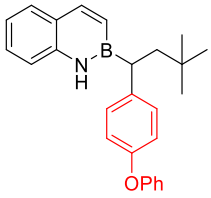
**2-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4h)**



The product as a colorless oil. Yield: 83%. TCL PE $R_f$ = 0.55.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.95 (d, *J* = 11.6 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.40 – 7.30 (m, 2H), 7.19 – 7.13 (m, 2H), 7.12 (dd, *J* = 7.2, 1.0 Hz, 2H), 6.89 (dd, *J* = 11.6, 2.0 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.85 (dd, *J* = 7.8, 5.5 Hz, 1H), 2.08 (dd, *J* = 13.9, 5.5 Hz, 1H), 1.92 – 1.83 (m, 1H), 0.88 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 37.32. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 156.8, 144.6, 139.8, 139.1, 129.1, 128.9, 127.9, 125.1, 120.7, 117.9, 114.0, 55.1, 46.9, 32.1, 30.2. **HRMS (EI)** calcd for $C_{21}H_{26}BNO$ [M]: 319.2107, found: 319.2098.

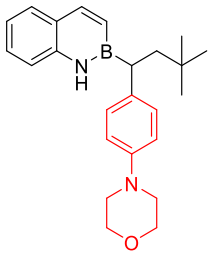
**2-(3,3-dimethyl-1-(4-phenoxyphenyl)butyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4i)**




The product as a colorless oil. Yield: 87%. TCL PE $R_f$ = 0.5.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.96 (d, *J* = 11.5 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.41 (s, 1H), 7.38 – 7.34 (m, 1H), 7.31 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.16 – 7.11 (m, 2H), 7.06 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.98 (dt, *J* = 7.8, 1.1 Hz, 2H), 6.96 – 6.92 (m, 2H), 6.89 (dd, *J* = 11.5, 2.0 Hz, 1H), 2.89 (dd, *J* = 7.7, 5.7 Hz, 1H), 2.09 (dd, *J* = 13.9, 5.7 Hz, 1H), 1.90 (dd, *J* = 13.9, 7.6 Hz, 1H), 0.89 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 36.71. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 157.7, 154.0, 144.7, 142.3, 139.7, 129.6, 129.2, 129.2, 128.0, 125.1, 122.7, 120.8, 119.3, 118.3, 117.9, 47.0, 32.1, 30.2. **HRMS (EI)** calcd for $C_{26}H_{28}BNO$ [M]: 381.2264, found: 381.2263.

**4-(4-(1-(benzo[e][1,2]azaborinin-2(1H)-yl)-3,3-dimethylbutyl)phenyl)morpholine (4j)**

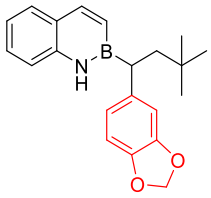



The product as a colorless oil. Yield: 72%. TCL PE $R_f$ = 0.45.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 11.6 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.39 (s, 1H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.18 – 7.06 (m, 4H), 6.92 – 6.83 (m, 3H), 3.90 – 3.83 (m, 4H), 3.16 – 3.09 (m, 4H), 2.83 (dd, *J* = 7.7, 5.6 Hz, 1H), 2.07 (dd, *J* = 13.9, 5.6 Hz, 1H), 1.88 (dd, *J* = 13.9, 7.7 Hz, 1H), 0.88 (s, 9H). **$^{11}$B NMR (128 MHz,**

**Chloroform-*d*)** δ 38.71. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 148.3, 144.5, 139.80, 138.8, 129.1, 128.7, 127.9, 125.1, 120.7, 117.9, 116.2, 67.0, 49.7, 46.9, 32.1, 30.2. **HRMS (EI)** calcd for $C_{24}H_{31}BN_2O$ [M]: 374.2529, found: 374.2524.

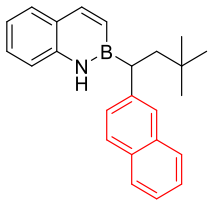
**2-(1-(benzo[d][1,3]dioxol-5-yl)-3,3-dimethylbutyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4j)**



The product as a colorless oil. Yield: 91%. TCL PE $R_f$ = 0.45.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.96 (d, *J* = 11.6 Hz, 1H), 7.56 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.42 (s, 1H), 7.35 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 1H), 7.18 – 7.08 (m, 2H), 6.88 (dd, *J* = 11.5, 2.0 Hz, 1H), 6.78 – 6.73 (m, 2H), 6.70 (dd, *J* = 8.0, 1.7 Hz, 1H), 5.92 (s, 2H), 2.84 (dd, *J* = 7.9, 5.4 Hz, 1H), 2.06 (dd, *J* = 13.9, 5.5 Hz, 1H), 1.86 (dd, *J* = 13.9, 7.8 Hz, 1H), 0.89 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.23. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 147.7, 144.7, 141.1, 139.7, 129.1, 128.0, 125.1, 120.8, 120.6, 117.9, 108.5, 108.3, 100.6, 46.9, 32.1, 30.2. **HRMS (EI)** calcd for $C_{21}H_{24}BNO_2$ [M]: 333.1900, found: 333.1905.

**2-(3,3-dimethyl-1-(naphthalen-2-yl)butyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4l)**

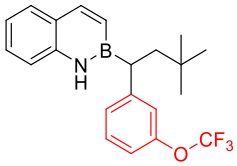


The product as a colorless oil. Yield: 88%. TCL PE $R_f$ = 0.45.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.97 (d, *J* = 11.6 Hz, 1H), 7.80 (t, *J* = 8.5 Hz, 3H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.56 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46 (ddd, *J* = 8.4, 6.7, 1.3 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.32 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 1H), 7.15 – 7.04 (m, 2H),

6.95 (dd, $J$ = 11.6, 1.9 Hz, 1H), 3.12 (dd, $J$ = 8.1, 5.1 Hz, 1H), 2.19 (dd, $J$ = 14.0, 5.1 Hz, 1H), 2.14 – 2.04 (m, 1H), 0.92 (d, $J$ = 1.1 Hz, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.46. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 144.9, 144.7, 139.7, 134.0, 131.4, 129.2, 128.0 (d, $J$ = 4.6 Hz), 127.6 (d, $J$ = 6.0 Hz), 127.2, 125.8, 125.6, 125.1, 124.6, 120.8, 118.0, 46.8, 32.3, 30.2. **HRMS (EI)** calcd for $C_{24}H_{26}BN$ [M]: 339.2158, found: 339.2159.

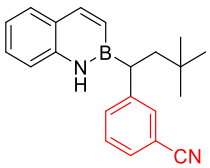
**2-(3,3-dimethyl-1-(3-(trifluoromethoxy)phenyl)butyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4m)**




The product as a colorless oil. Yield: 69%. TCL PE $R_f$ = 0.6.

**$^{1}$H NMR (400 MHz, Chloroform-*d*)** δ 7.95 (d, $J$ = 11.6 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.39 – 7.31 (m, 2H), 7.31 – 7.23 (m, 1H), 7.23 – 7.08 (m, 4H), 7.00 – 6.94 (m, 1H), 6.84 (dd, $J$ = 11.5, 2.1 Hz, 1H), 2.94 (dd, $J$ = 8.1, 5.2 Hz, 1H), 2.06 (dd, $J$ = 14.0, 5.2 Hz, 1H), 1.90 (dd, $J$ = 14.0, 8.1 Hz, 1H), 0.86 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 37.87. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 149.9, 149.5, 145.0, 139.6, 129.7, 129.2, 128.1, 126.6, 125.1, 121.0, 120.5, 118.0, 116.9, 46.65 32.2, 30.1.**$^{19}$F NMR (376 MHz, Chloroform-*d*)** δ -57.60. **HRMS (EI)** calcd for $C_{21}H_{23}BF_3NO$ [M]: 373.1825, found: 373.1823.

**3-(1-(benzo[e][1,2]azaborinin-2(1H)-yl)-3,3-dimethylbutyl)benzonitrile (4n)**

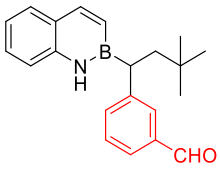



The product as a colorless oil. Yield: 91%. TCL PE $R_f$ = 0.3.

**$^{1}$H NMR (400 MHz, Chloroform-*d*)** δ 7.97 (d, $J$ = 11.6 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.50 (dt, $J$ = 7.6, 1.7 Hz, 1H), 7.45 (s, 1H), 7.42 – 7.31 (m, 3H), 7.22 – 7.11 (m, 2H),

6.82 (dd, *J* = 11.5, 2.0 Hz, 1H), 2.96 (dd, *J* = 7.5, 5.7 Hz, 1H), 2.12 (dd, *J* = 14.0, 5.7 Hz, 1H), 1.91 (dd, *J* = 13.9, 7.6 Hz, 1H), 0.87 (s, 9H). **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 149.0, 145.3, 139.5, 132.7, 131.4, 129.3, 129.2, 128.4, 128.2, 125.1, 121.1, 119.2, 118.0, 112.4, 46.6, 32.1, 30.1. **HRMS (EI)** calcd for $C_{21}H_{23}BN_2$ [M]: 314.1954, found: 314.1950.

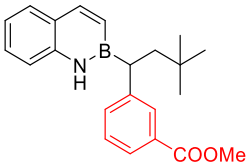
**3-(1-(benzo[e][1,2]azaborinin-2(1H)-yl)-3,3-dimethylbutyl)benzaldehyde (4o)**




The product as a colorless oil. Yield: 89%. TCL PE $R_f$ = 0.5.

**$^{1}$H NMR (500 MHz, Chloroform-*d*)** δ 9.98 (s, 1H), 7.94 (d, *J* = 11.5 Hz, 1H), 7.78 (t, *J* = 1.9 Hz, 1H), 7.61 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.46 – 7.39 (m, 2H), 7.34 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 1H), 7.16 – 7.07 (m, 2H), 6.85 (dd, *J* = 11.6, 2.0 Hz, 1H), 3.01 (dd, *J* = 7.5, 5.8 Hz, 1H), 2.14 (dd, *J* = 14.0, 5.7 Hz, 1H), 1.96 (dd, *J* = 14.0, 7.6 Hz, 1H), 0.87 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 37.1. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 192.8, 148.7, 145.1, 139.6, 136.6, 134.4, 129.2, 129.1, 128.6, 128.1, 126.8, 125.1, 121.0, 118.0, 46.6, 32.2, 30.2. **HRMS (EI)** calcd for $C_{21}H_{24}BNO$ [M]: 317.1951, found: 317.1956.

**Methyl 3-(1-(benzo[e][1,2]azaborinin-2(1H)-yl)-3,3-dimethylbutyl)benzoate (4p)**

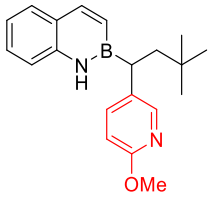



The product as a colorless oil. Yield: 87%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.45.

**$^{1}$H NMR (400 MHz, Chloroform-*d*)** δ 7.99 – 7.91 (m, 2H), 7.80 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.55 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.38 – 7.30 (m, 2H), 7.16 – 7.08 (m, 2H), 6.87 (dd, *J* = 11.5, 2.0 Hz, 1H), 3.91 (s, 3H), 2.99 (dd, *J* = 7.8, 5.5 Hz, 1H), 2.13 (dd, *J* = 14.0, 5.5 Hz, 1H), 1.97 (dd, *J* = 14.0, 7.8

Hz, 1H), 0.87 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.25. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 167.4, 147.8, 144.9, 139.6, 132.7, 130.2, 129.2, 129.1, 128.5, 128.0, 125.9, 125.1, 120.9, 118.0, 52.0, 46.6, 32.2, 30.2. **HRMS (EI)** calcd for $C_{22}H_{26}BNO_2$ [M]: 347.2057, found: 347.2053.

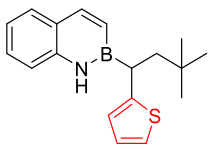
**2-(1-(6-methoxypyridin-3-yl)-3,3-dimethylbutyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4q)**




The product as a colorless oil. Yield: 85%. TCL PE $R_f$ = 0.45.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 8.05 (d, *J* = 2.5 Hz, 1H), 7.95 (d, *J* = 11.5 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.48 – 7.41 (m, 2H), 7.39 – 7.31 (m, 1H), 7.17 – 7.08 (m, 2H), 6.84 (dd, *J* = 11.6, 2.0 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 2.82 (dd, *J* = 7.8, 5.5 Hz, 1H), 2.08 (dd, *J* = 13.9, 5.6 Hz, 1H), 1.83 (dd, *J* = 13.9, 7.8 Hz, 1H), 0.87 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.27. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 161.9, 145.6, 145.0, 139.7, 138.6, 135.1, 129.2, 128.1, 125.1, 120.9, 117.9, 110.6, 53.2, 46.7, 32.1, 30.2. **HRMS (EI)** calcd for $C_{20}H_{25}BN_2O$ [M]: 320.2060, found: 320.2062.

**2-(3,3-dimethyl-1-(thiophen-2-yl)butyl)-1,2-dihydrobenzo[e][1,2]azaborinine (4r)**

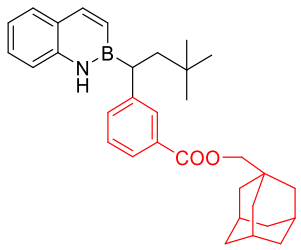



The product as a colorless oil. Yield: 72%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 11.5 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.41 (s, 1H), 7.37 – 7.28 (m, 1H), 7.27 – 7.22 (m, 1H), 7.14 – 7.07 (m, 2H), 6.94 (dd, *J* = 4.9, 1.3 Hz, 1H), 6.91 – 6.83 (m, 2H), 3.04 (dd, *J* = 7.7, 5.7 Hz, 1H), 2.03 (dd, *J* =

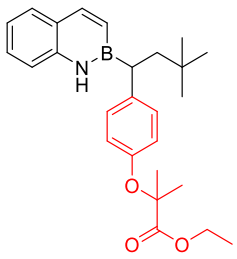
13.9, 5.7 Hz, 1H), 1.86 (dd, *J* = 13.9, 7.7 Hz, 1H), 0.87 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.07. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 147.3, 144.7, 139.7, 129.2, 128.2, 128.0, 125.3, 125.2, 120.7, 117.9, 117.9, 47.0, 31.9, 30.1. **HRMS (EI)** calcd for $C_{18}H_{22}BNS$ [M]: 295.1566, found: 295.1559.

**((3r,5r,7r)-adamantan-1-yl)methyl3-(1-(benzo[e][1,2]azaborinin-2(1H)-yl)-3,3-dimethylbutyl)benzoate (4s)**




The product as a colorless oil. Yield: 84%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.5. **$^{1}$H NMR (500 MHz, Chloroform-*d*)** δ 8.00 – 7.92 (m, 2H), 7.81 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.48 – 7.43 (m, 2H), 7.39 – 7.31 (m, 2H), 7.13 (ddd, *J* = 7.7, 6.8, 5.7 Hz, 2H), 6.89 (dd, *J* = 11.6, 2.0 Hz, 1H), 3.92 (d, *J* = 1.5 Hz, 2H), 3.00 (dd, *J* = 7.6, 5.7 Hz, 1H), 2.14 (dd, *J* = 13.9, 5.6 Hz, 1H), 2.02 (p, *J* = 3.2 Hz, 3H), 1.97 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.76 (dt, *J* = 12.1, 3.1 Hz, 3H), 1.72 – 1.67 (m, 3H), 1.65 (d, *J* = 3.0 Hz, 6H), 0.88 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 36.09. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 167.0, 147.7, 144.9, 139.6, 132.6, 130.7, 129.2 (d, *J* = 5.8 Hz), 128.5, 128.0, 125.8, 125.1, 120.9, 118.0, 74.3, 46.7, 39.4, 36.9, 33.5, 32.2, 30.2, 28.0.

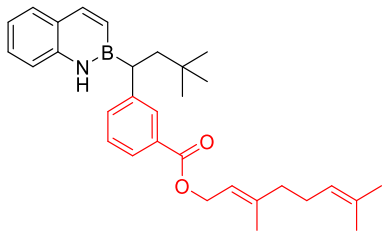
**Ethyl2-(4-(1-(benzo[e][1,2]azaborinin-2(1H)-yl)-3,3-dimethylbutyl)phenoxy)-2-methylpropanoate (4t)**



The product as a colorless oil. Yield: 83%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.5.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.96 (d, *J* = 11.5 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.13 (dd, *J* = 11.7, 7.9 Hz, 4H), 6.93 – 6.77 (m, 3H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.85 (dd, *J* = 8.1, 5.2 Hz, 1H), 2.06 (dd, *J* = 14.2, 5.1 Hz, 1H), 1.88 (dd, *J* = 14.1, 8.2 Hz, 1H), 1.59 (s, 6H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.87 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 35.31. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 174.4, 152.4, 144.5, 141.0, 139.7, 129.1, 128.6, 127.9, 125.1, 120.7, 119.7, 117.9, 79.1, 61.2, 46.8, 32.1, 30.1, 25.3, 14.0. **HRMS (EI)** calcd for $C_{26}H_{34}BNO_3$ [M]: 419.2632, found: 419.2638.

**(E)-3,7-dimethylocta-2,6-dien-1-yl3-(1-(benzo[e][1,2]azaborinin-2(1H)-yl)-3,3-dimethylbutyl)benzoate (4u)**

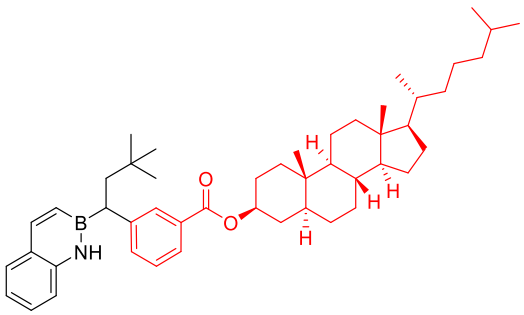


The product as a colorless oil. Yield: 74%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.4.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.97 – 7.91 (m, 2H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.30 (m, 3H), 7.13 (d, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 11.6 Hz, 1H), 5.48 (t, *J* = 7.1 Hz, 1H), 5.12 – 5.08 (m, 1H), 4.84 (d, *J* = 7.0 Hz, 2H), 2.99 (t, *J* = 6.5 Hz, 1H), 2.15 – 2.07 (m, 4H), 1.96 (dd, *J* = 14.0, 7.7 Hz, 1H), 1.77 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H), 0.87 (s, 9H).**$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 35.1. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 167.0, 147.7, 144.9, 142.1, 139.6, 132.6, 131.8, 130.6, 129.1 (d, *J* = 9.1 Hz), 128.4, 128.0, 125.9, 125.1,

123.7, 120.9, 118.4, 118.0, 61.8, 46.6, 39.5, 32.2, 30.2, 26.2, 25.6, 17.6, 16.5. **HRMS (EI)** calcd for $C_{31}H_{40}BNO_2$ [M]: 469.3152, found: 469.3156.

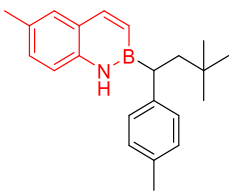
**(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl3-(1-(benzo[e][1,2]azaborinin-2(1H)-yl)-3,3-dimethylbutyl)benzoate (4v)**




The product as a colorless oil. Yield: 88%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.95 (d, *J* = 11.2 Hz, 2H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.12 (t, *J* = 8.1 Hz, 2H), 6.89 (d, *J* = 11.6 Hz, 1H), 4.95 (tt, *J* = 10.9, 5.0 Hz, 1H), 2.99 (t, *J* = 6.6 Hz, 1H), 2.18 – 2.04 (m, 1H), 2.04 – 1.42 (m, 14H), 1.37 – 1.20 (m, 9H), 1.18 – 0.98 (m, 9H), 0.95 – 0.85 (m, 21H), 0.67 (s, 3H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 36.01. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 166.5, 147.6, 144.8, 139.6, 132.4, 131.0, 129.2, 129.1, 128.8, 128.0, 125.8, 125.1, 120.8, 118.0, 74.2, 56.3, 56.1, 54.1, 46.6, 44.6, 42.5, 39.9, 39.4, 36.7, 36.1, 35.7, 35.4, 35.4, 34.0, 32.2, 31.9, 30.2, 28.5, 28.2, 27.9, 27.5, 24.1, 23.8, 22.8, 22.5, 21.1, 18.6, 12.2, 12.0.

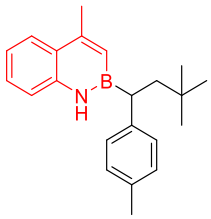
**2-(3,3-dimethyl-1-(p-tolyl)butyl)-6-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (5a)**




The product as a colorless oil. Yield: 79%. TCL PE $R_f$ = 0.6.

**$^{1}$H NMR (500 MHz, Chloroform-*d*)** δ 7.89 (d, *J* = 11.5 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 2H), 7.19 – 7.12 (m, 3H), 7.09 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.87 (dd, *J* = 11.5, 1.9 Hz, 1H), 2.86 (dd, *J* = 7.7, 5.5 Hz, 1H), 2.39 (s, 3H), 2.32 (s, 3H), 2.08 (dd, *J* = 13.9, 5.5 Hz, 1H), 1.90 (dd, *J* = 13.9, 7.7 Hz, 1H), 0.88 (d, *J* = 0.8 Hz, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.23. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 144.3, 144.2, 137.8, 133.8, 129.8, 129.2, 128.9, 128.0, 125.0, 117.7, 46.9, 32.1, 30.2, 20.9, 20.7. **HRMS (EI)** calcd for $C_{22}H_{28}BN$ [M]: 317.2315, found: 317.2311.

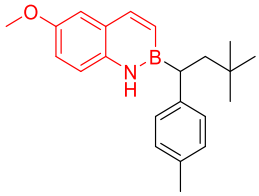
**2-(3,3-dimethyl-1-(p-tolyl)butyl)-4-methyl-1,2-dihydrobenzo[e][1,2]azaborinine (5b)**




The product as a colorless oil. Yield: 76%. TCL PE $R_f$ = 0.6.

**$^{1}$H NMR (500 MHz, Chloroform-*d*)** δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.24 (d, *J* = 6.9 Hz, 1H), 7.15 – 7.08 (m, 4H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.70 – 6.66 (m, 1H), 2.81 (dd, *J* = 7.7, 5.5 Hz, 1H), 2.53 (d, *J* = 1.3 Hz, 3H), 2.29 (s, 3H), 2.05 (dd, *J* = 14.0, 5.5 Hz, 1H), 1.88 (dd, *J* = 13.9, 7.6 Hz, 1H), 0.86 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.14. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 150.6, 144.2, 140.0, 133.7, 129.2, 127.9, 127.6, 125.4, 125.1, 120.6, 118.6, 46.8, 32.1, 30.2, 22.9, 20.9. **HRMS (EI)** calcd for $C_{22}H_{28}BN$ [M]: 317.2315, found:317.2312.

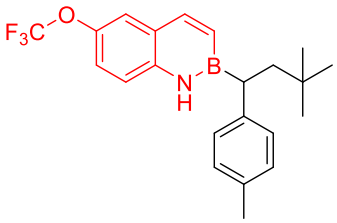
**2-(3,3-dimethyl-1-(p-tolyl)butyl)-6-methoxy-1,2-dihydrobenzo[e][1,2]azaborinine (5c)**



The product as a colorless oil. Yield: 88%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.89 (d, *J* = 11.6 Hz, 1H), 7.32 (s, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 7.04 – 6.96 (m, 3H), 6.90 (dd, *J* = 11.5, 1.9 Hz, 1H), 3.84 (s, 3H), 2.86 (dd, *J* = 7.8, 5.4 Hz, 1H), 2.32 (s, 3H), 2.07 (dd, *J* = 13.9, 5.5 Hz, 1H), 1.91 (dd, *J* = 13.9, 7.7 Hz, 1H), 0.88 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 37.48. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 153.7, 144.2, 144.1, 134.4, 133.8, 129.2, 127.9, 125.6, 125.5, 118.9, 117.1, 110.6, 55.6, 46.9, 32.1, 30.2, 20.9. **HRMS (EI)** calcd for $C_{22}H_{28}BNO$ [M]: 333.2264, found: 333.2268.

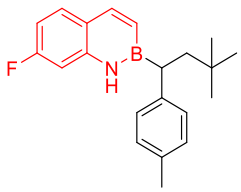
**2-(3,3-dimethyl-1-(p-tolyl)butyl)-6-(trifluoromethoxy)-1,2-dihydrobenzo[e][1,2]azaborinine (5d)**




The product as a colorless oil. Yield: 84%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.89 (d, *J* = 11.6 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.20 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.16 – 7.06 (m, 5H), 6.98 (dd, *J* = 11.6, 1.9 Hz, 1H), 2.87 (dd, *J* = 7.6, 5.6 Hz, 1H), 2.31 (s, 3H), 2.07 (dd, *J* = 13.9, 5.6 Hz, 1H), 1.90 (dd, *J* = 13.9, 7.6 Hz, 1H), 0.88 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.9. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 143.8, 143.6, 142.8, 138.2, 134.0, 129.3, 127.9, 125.3, 121.9, 121.3, 120.9, 119.3, 118.9, 46.7, 32.1, 30.2, 20.9.**$^{19}$F NMR (376 MHz, Chloroform-*d*)** δ -58.20. **HRMS (EI)** calcd for $C_{22}H_{25}BF_3NO$ [M]: 387.1981, found: 387.1985.

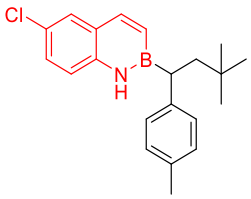
**2-(3,3-dimethyl-1-(p-tolyl)butyl)-7-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (5e)**



The product as a colorless oil. Yield: 73%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.90 (d, *J* = 11.5 Hz, 1H), 7.49 (dd, *J* = 8.6, 6.2 Hz, 1H), 7.36 (s, 1H), 7.16 – 7.07 (m, 4H), 6.83 (qd, *J* = 10.6, 9.5, 2.4 Hz, 3H), 2.86 (dd, *J* = 7.7, 5.5 Hz, 1H), 2.32 (s, 3H), 2.07 (dd, *J* = 13.9, 5.5 Hz, 1H), 1.90 (dd, *J* = 13.9, 7.7 Hz, 1H), 0.88 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.74. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 163.6, 161.1, 144.1, 143.8, 141.0, 140.9, 134.0, 130.8, 130.7, 129.3, 127.9, 121.8 (d, *J* = 1.9 Hz), 109.1, 108.9, 104.0, 103.7, 46.8, 32.1, 30.2, 20.9.**$^{19}$F NMR (376 MHz, )** δ -112.88. **HRMS (EI)** calcd for $C_{21}H_{25}BFN$ [M]: 321.2064, found: 321.2069.

**6-chloro-2-(3,3-dimethyl-1-(p-tolyl)butyl)-1,2-dihydrobenzo[e][1,2]azaborinine (5f)**

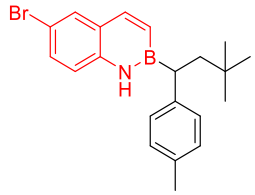


The product as a colorless oil. Yield: 65%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.82 (d, *J* = 11.6 Hz, 1H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.34 (s, 1H), 7.29 – 7.22 (m, 1H), 7.09 (d, *J* = 4.5 Hz, 4H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.92 (dd, *J* = 11.6, 1.9 Hz, 1H), 2.84 (dd, *J* = 7.8, 5.4 Hz, 1H), 2.30 (s, 3H), 2.04 (dd, *J* = 13.7, 5.3 Hz, 1H), 1.88 (dd, *J* = 14.0, 7.8 Hz, 1H), 0.86 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 35.7. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 143.7, 143.6, 138.2, 134.0, 129.3, 128.8, 127.9, 126.0, 125.6, 119.2, 46.7, 32.1, 30.2, 20.9. **HRMS (EI)** calcd for $C_{21}H_{25}BClN$ [M]: 337.1769, found: 337.1762.

**6-bromo-2-(3,3-dimethyl-1-(p-tolyl)butyl)-1,2-dihydrobenzo[e][1,2]azaborinine**

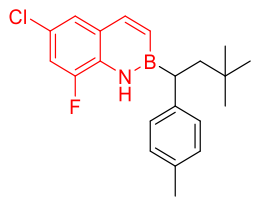
**(5g)**




The product as a colorless oil. Yield: 64%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.83 (d, *J* = 11.6 Hz, 1H), 7.67 (d, *J* = 2.3 Hz, 1H), 7.40 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.35 (s, 1H), 7.15 – 7.07 (m, 4H), 6.99 (d, *J* = 8.7 Hz, 1H), 6.93 (dd, *J* = 11.5, 1.9 Hz, 1H), 2.85 (dd, *J* = 7.7, 5.4 Hz, 1H), 2.31 (s, 3H), 2.05 (dd, *J* = 13.9, 5.4 Hz, 1H), 1.89 (dd, *J* = 14.0, 7.7 Hz, 1H), 0.87 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 35.71. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 143.8, 143.4, 138.6, 134.0, 131.2, 130.6, 129.3, 127.9, 126.6, 119.5, 113.0, 46.7, 32.1, 30.1, 20.9. **HRMS (EI)** calcd for $C_{21}H_{25}BBrN$ [M]: 381.1263, found: 381.1263.

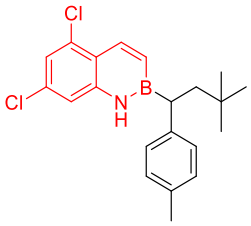
**6-chloro-2-(3,3-dimethyl-1-(p-tolyl)butyl)-8-fluoro-1,2-dihydrobenzo[e][1,2]azaborinine (5h)**




The product as a colorless oil. Yield: 82%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.81 (dd, *J* = 11.7, 1.8 Hz, 1H), 7.69 (s, 1H), 7.32 (t, *J* = 1.9 Hz, 1H), 7.18 – 7.12 (m, 3H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.00 (dd, *J* = 11.6, 1.9 Hz, 1H), 2.88 (t, *J* = 6.7 Hz, 1H), 2.30 (s, 3H), 2.07 (dd, *J* = 13.8, 6.0 Hz, 1H), 1.91 (dd, *J* = 13.9, 7.2 Hz, 1H), 0.88 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.68. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 152.6, 150.1, 143.3, 142.8 (d, *J* = 3.2 Hz), 134.1, 129.3, 127.9, 127.5, 127.4, 127.2 (d, *J* = 4.2 Hz), 124.5, 124.4, 123.6 (d, *J* = 3.5 Hz), 113.7, 113.5, 46.7, 32.1, 30.2, 20.9.**HRMS (EI)** calcd for $C_{21}H_{24}BClFN$ [M]: 355.1674, found: 355.1679.

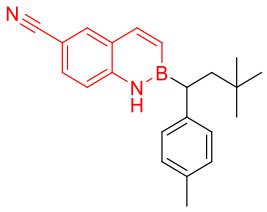
**5,7-dichloro-2-(3,3-dimethyl-1-(p-tolyl)butyl)-1,2-dihydrobenzo[e][1,2]azaborinine (5i)**




The product as a colorless oil. Yield: 74%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.82 (d, *J* = 11.5 Hz, 1H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.34 (s, 1H), 7.29 – 7.23 (m, 1H), 7.15 – 7.05 (m, 4H), 7.02 (d, *J* = 8.6 Hz, 1H), 2.84 (dd, *J* = 7.8, 5.4 Hz, 1H), 2.30 (s, 3H), 2.04 (dd, *J* = 13.9, 5.5 Hz, 1H), 1.88 (dd, *J* = 13.9, 7.7 Hz, 1H), 0.86 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.57. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 143.7, 143.5, 138.2, 134.0, 129.4, 128.1, 127.9, 126.0, 125.7, 119.2, 46.7, 32.1, 30.1, 20.9. **HRMS (EI)** calcd for $C_{21}H_{24}BCl_2N$ [M]: 371.1379, found: 371.1378.

**2-(3,3-dimethyl-1-(p-tolyl)butyl)-1,2-dihydrobenzo[e][1,2]azaborinine-6-carbonitrile (5j)**

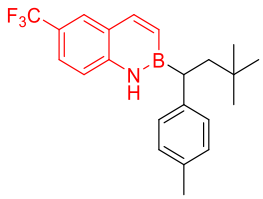



The product as a colorless oil. Yield: 80%. TCL PE $R_f$ = 0.35.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.96 – 7.84 (m, 2H), 7.57 – 7.50 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.14 – 7.06 (m, 4H), 7.02 (dd, *J* = 11.6, 1.9 Hz, 1H), 2.88 (dd, *J* = 7.6, 5.7 Hz, 1H), 2.31 (s, 3H), 2.11 – 1.96 (m, 1H), 1.90 (dd, *J* = 13.9, 7.6 Hz, 1H), 0.87 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 40.1. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 143.6, 143.0, 142.4, 134.3, 134.1, 130.4, 129.4, 127.9, 125.0, 119.3, 119.0, 104.0, 46.5, 32.1, 30.1, 20.9. **HRMS (EI)** calcd for $C_{22}H_{25}BN_2$ [M]: 328.2111,

found: 328.2117.

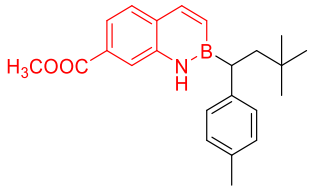
**2-(3,3-dimethyl-1-(p-tolyl)butyl)-6-(trifluoromethyl)-1,2-dihydrobenzo[e][1,2]azaborinine (5k)**




The product as a colorless oil. Yield: 70%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.95 (d, *J* = 11.6 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.48 (s, 1H), 7.38 (s, 1H), 7.33 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.20 – 7.08 (m, 4H), 7.03 (dd, *J* = 11.6, 1.9 Hz, 1H), 2.89 (dd, *J* = 7.7, 5.6 Hz, 1H), 2.32 (s, 3H), 2.07 (dd, *J* = 13.9, 5.5 Hz, 1H), 1.91 (dd, *J* = 13.9, 7.6 Hz, 1H), 0.88 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 35.49. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 143.8, 143.4, 139.2, 134.2, 129.8, 129.4, 127.9, 127.2, 117.0 (d, *J* = 3.6 Hz), 115.1 (d, *J* = 4.1 Hz), 46.6, 32.1, 30.2, 20.9.**$^{19}$F NMR (376 MHz, Chloroform-*d*)** δ -62.11. **HRMS (EI)** calcd for $C_{22}H_{25}BF_3N$ [M]: 371.2032, found: 371.2034.

**Methyl2-(3,3-dimethyl-1-(p-tolyl)butyl)-1,2-dihydrobenzo[e][1,2]azaborinine-7-carboxylate (5l)**

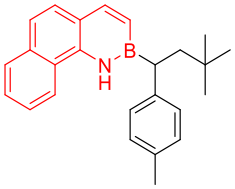



The product as a colorless oil. Yield: 80%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.45.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 11.5 Hz, 1H), 7.84 – 7.80 (m, 1H), 7.73 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.47 (s, 1H), 7.16 – 7.07 (m, 4H), 7.01 (dd, *J* = 11.5, 1.9 Hz, 1H), 3.92 (s, 3H), 2.87 (dd, *J* = 7.8, 5.4 Hz, 1H), 2.31 (s, 3H), 2.05 (dd, *J* = 14.1, 5.3 Hz, 1H), 1.90 (dd, *J* = 14.0, 7.7 Hz, 1H), 0.87 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 36.57. **$^{13}$C NMR (101 MHz, Chloroform-*d*)**

δ 167.0, 143.9, 143.6, 139.2, 134.0, 129.3, 129.1, 129.1, 128.3, 127.9, 121.2, 119.6, 52.2, 46.6, 32.1, 30.1, 20.9. **HRMS (EI)** calcd for $C_{23}H_{28}BNO_2$ [M]: 361.2213, found: 361.2218.

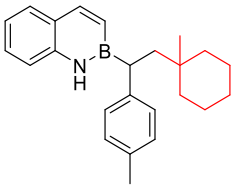
**2-(3,3-dimethyl-1-(p-tolyl)butyl)-1,2-dihydronaphtho[2,1-e][1,2]azaborinine (5m)**



The product as a colorless oil. Yield: 82%. TCL PE $R_f$ = 0.45.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 8.45 (s, 1H), 8.11 (d, *J* = 11.5 Hz, 1H), 7.93 – 7.82 (m, 2H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.57 – 7.44 (m, 3H), 7.30 – 7.21 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.06 (dd, *J* = 11.5, 1.9 Hz, 1H), 3.04 (dd, *J* = 8.3, 4.8 Hz, 1H), 2.37 (s, 3H), 2.16 (dd, *J* = 14.0, 4.8 Hz, 1H), 2.02 (dd, *J* = 14.0, 8.3 Hz, 1H), 0.94 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 38.79. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 145.4, 144.3, 135.5, 133.9, 133.4, 129.4, 128.8, 128.0, 127.4, 126.3, 125.8, 123.8, 120.8, 120.7, 119.4, 47.0, 32.3, 30.2, 20.9. **HRMS (EI)** calcd for $C_{25}H_{28}BN$ [M]: 353.2315, found: 353.2314.

**2-(2-(1-methylcyclohexyl)-1-(p-tolyl)ethyl)-1,2-dihydrobenzo[e][1,2]azaborinine (5n)**



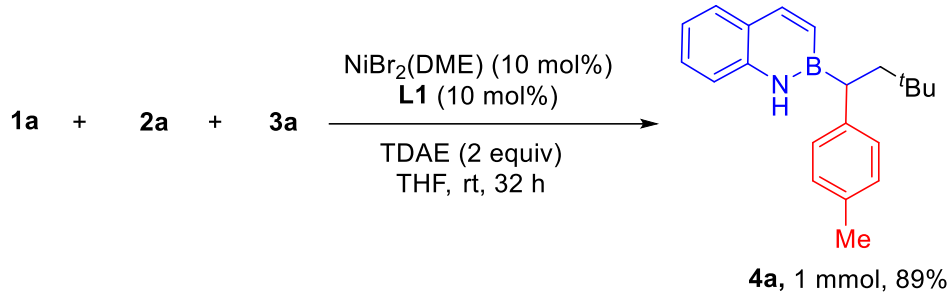
The product as a colorless oil. Yield: 68%. TCL PE $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (d, *J* = 11.5 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.40 – 7.29 (m, 2H), 7.18 – 7.03 (m, 6H), 6.90 (dd, *J* = 11.6, 1.9 Hz, 1H), 2.88 (t, *J* = 6.4 Hz, 1H), 2.31 (s, 3H), 2.09 (dd, *J* = 14.0, 5.6 Hz, 1H), 1.93 (dd, *J* = 14.0, 7.3 Hz, 1H), 1.51 – 1.33 (m, 5H), 1.31 – 1.20 (m, 5H), 0.84 (s, 3H). **$^{11}$B NMR (128 MHz,**

**Chloroform-*d*)** δ 30.62. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 144.5, 144.3, 139.7, 133.8, 129.2, 129.1, 128.0, 127.9, 125.1, 120.7, 117.9, 38.5, 38.4, 34.5, 26.5, 25.3, 22.1 (d, $J$ = 9.1 Hz), 20.92. **HRMS (EI)** calcd for $C_{24}H_{30}BN$ [M]: 343.2471, found: 343.2475.

## 6. Scale-up reactions and synthetic applications.

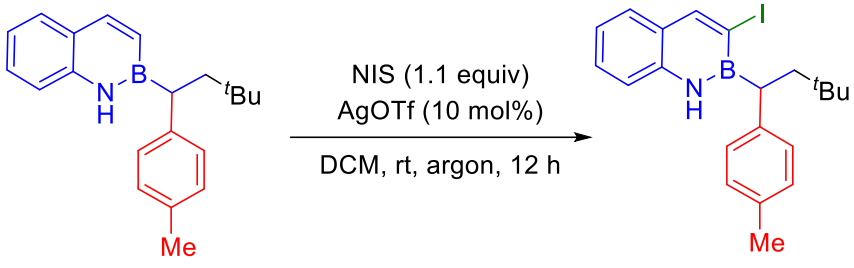
### 6.1 Scale-up reactions




**4a,** 1 mmol, 89%

To a 25 mL Young tube were added **1a** (1 mmol, 1 equiv), **2a** (1.2 mmol, 1.2 equiv), **3a** (3 mmol, 3 equiv), $NiBr_2$(DME) (10 mol%), **L1** (10 mol%), TDAE (2 mmol, 2 equiv) and 10 mL THF under argon and the resulting mixture was stirred at room temperature for 32 h. The reaction mixture was diluted with EtOAC and washed with water and brine. The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude product was then purified by flash column chromatography.

### 6.2 Synthetic applications

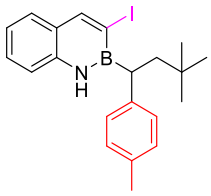



**4a** **6a**, 73%

By analogy to a modified literature procedure [3]. In argon, a 25 mL Schlenk tube was charged with **4a** (0.2 mmol, 1 equiv), AgOTf (10 mol%) and dry DCM (2 mL). Then,

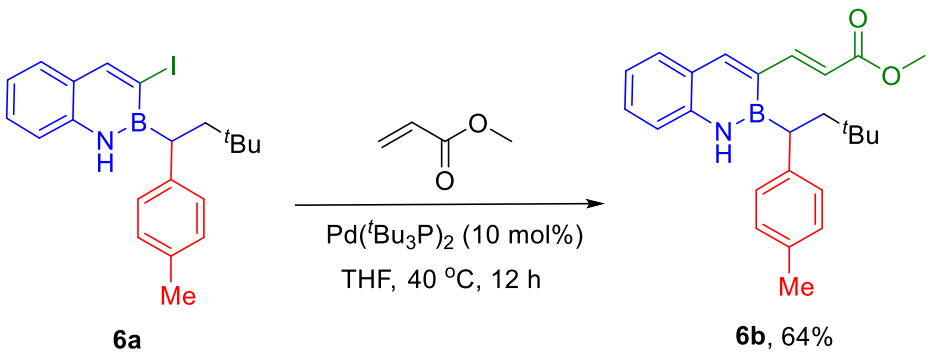
NIS (0.44 mmol, 1.1 equiv) in dry DCM (1 mL) was slowly added dropwise. The mixture was stirred at room temperature for 12 h. Upon completion, proper amount of silica gel was added to the reaction mixture. After removal of the solvent, the crude reaction mixture was purified on silica gel to afford product **6a**.

**2-(3,3-dimethyl-1-(p-tolyl)butyl)-3-iodo-1,2-dihydrobenzo[e][1,2]azaborinine (6a)**



The product as a colorless oil. Yield: 73%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.6.

**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 8.59 (s, 1H), 7.47 – 7.28 (m, 3H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.17 – 6.99 (m, 4H), 3.29 (t, *J* = 7.1 Hz, 1H), 2.29 (s, 3H), 1.96 (dd, *J* = 13.9, 6.4 Hz, 1H), 1.82 (dd, *J* = 13.9, 7.6 Hz, 1H), 0.89 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 37.4. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 153.2, 142.6, 139.3, 134.2, 129.4, 128.6, 128.2, 127.5, 125.8, 121.3, 118.0, 45.7, 32.3, 30.4, 20.9. **HRMS (EI)** calcd for $C_{21}H_{25}BIN$ [M]: 429.1125, found: 429.1124.

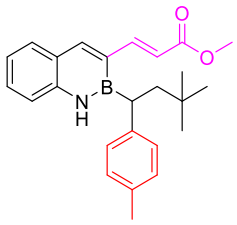



**6a** **6b**, 64%

By analogy to a modified literature procedure [4]. A 25 mL Young tube was charged with **6a** (0.2 mmol, 1 equiv) and $Pd(tBu_3P)_2$ (5 mol%). The tube was evacuated and filled with argon for three cycles, then added methyl acrylate (2 equiv) and dry THF (2 mL) in argon. The mixture was stirred at 40 °C for 12 h. Upon completion, proper amount of silica gel was added to the reaction mixture. After removal of the solvent,

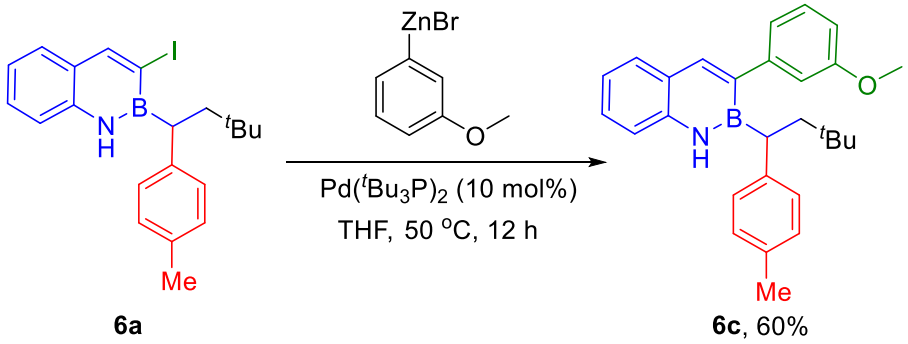
the crude reaction mixture was purified on silica gel to afford product **6b**.

**Methyl(E)-3-(2-(3,3-dimethyl-1-(p-tolyl)butyl)-1,2-dihydrobenzo[e][1,2]azaborinin-3-yl)acrylate (6b)**



The product as a colorless oil. Yield: 64%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.3.

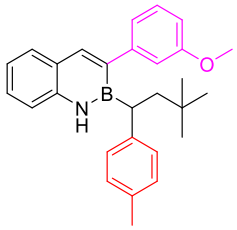
**$^1$H NMR (400 MHz, Chloroform-*d*)** δ 8.19 – 8.09 (m, 2H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.52 (s, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.13 (q, *J* = 7.7, 7.2 Hz, 6H), 6.37 (d, *J* = 15.7 Hz, 1H), 3.83 (s, 3H), 3.31 (dd, *J* = 8.3, 5.2 Hz, 1H), 2.31 (s, 3H), 1.86 (d, *J* = 5.2 Hz, 1H), 1.49 (d, *J* = 13.7 Hz, 1H), 0.87 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 34.11. **$^{13}$C NMR (101 MHz, Chloroform-*d*)** δ 167.7, 147.4, 142.7, 142.5, 140.2, 134.2, 129.9, 129.4, 129.2, 127.8, 124.3, 121.4, 117.9, 117.3, 51.5, 45.7, 32.4, 30.3, 20.9.




**6a** **6c**, 60%

By analogy to a modified literature procedure [5]. In a glove box, a 25 mL Schlenk tube was charged with zinc chloride (0.64 mmol, 3.2 equiv) (0.32 mmol, 1.6 equiv). Then, the mixture was charged with **6a** (0.2 mmol, 1.0 equiv), bis(tri-tert-butylphosphine)palladium (5 mol%) and 2 mL of THF. The tube was removed from glove box, and stirred at 50 °C for 12 h. Upon completion, the solvent was concentrated under reduced pressure and rapidly purified by column chromatography to obtain product **6c**.

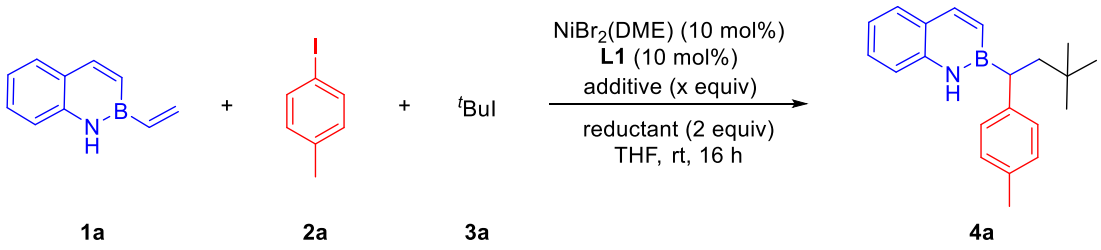
**2-(3,3-dimethyl-1-(p-tolyl)butyl)-3-(3-methoxyphenyl)-1,2-dihydrobenzo[e][1,2]azaborinine (6c)**



The product as a colorless oil. Yield: 60%. TCL (PE:EtOAc = 20:1) $R_f$ = 0.7.

**$^1$H NMR (500 MHz, Chloroform-*d*)** δ 7.79 (s, 1H), 7.61 – 7.53 (m, 2H), 7.39 – 7.32 (m, 2H), 7.22 – 7.11 (m, 2H), 7.06 (q, *J* = 8.0 Hz, 4H), 6.98 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.93 – 6.86 (m, 2H), 3.86 (s, 3H), 3.29 (dt, *J* = 7.6, 3.8 Hz, 1H), 2.31 (s, 3H), 1.73 (dd, *J* = 14.1, 8.8 Hz, 1H), 1.64 (dd, *J* = 14.1, 4.7 Hz, 1H), 0.62 (s, 9H). **$^{11}$B NMR (128 MHz, Chloroform-*d*)** δ 36.02. **$^{13}$C NMR (126 MHz, Chloroform-*d*)** δ 159.5, 146.4, 143.2, 142.6, 139.3, 133.8, 129.2 (d, *J* = 4.1 Hz), 129.1, 127.9, 127.8, 124.6, 121.0, 117.7, 113.9, 111.6, 55.2, 45.3, 32.1, 30.0, 20.9. **HRMS (EI)** calcd for $C_{28}H_{32}BNO$ [M]: 409.2577, found: 409.2579.

## 7. Control experiments




**1a** **2a** **3a** **4a**

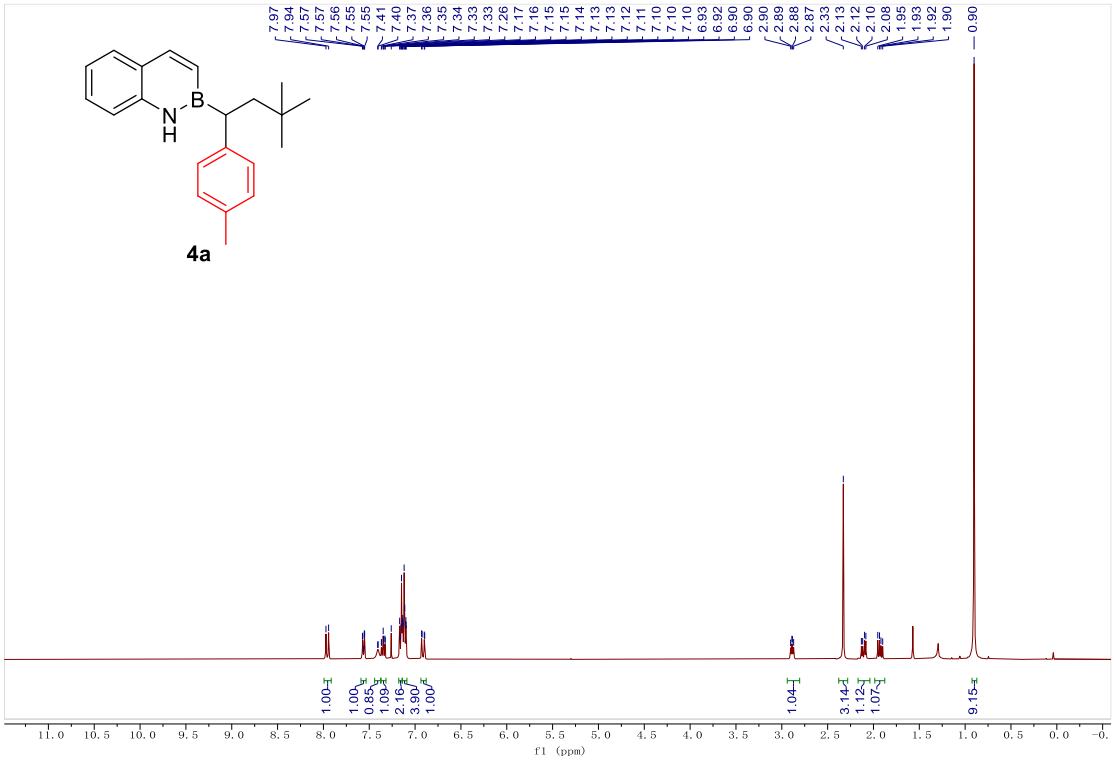
| additive | x equiv | yield (%)[a] |
|---|---|---|
| BHT | 1 | 93% |
| | 3 | 0 |
| TEMPO | 1 | 0 |
| | 3 | 0 |
| 1,1-Diphenylethylene | 1 | 39% |

| | | |
|---|---|---|
| | 3 | trace |

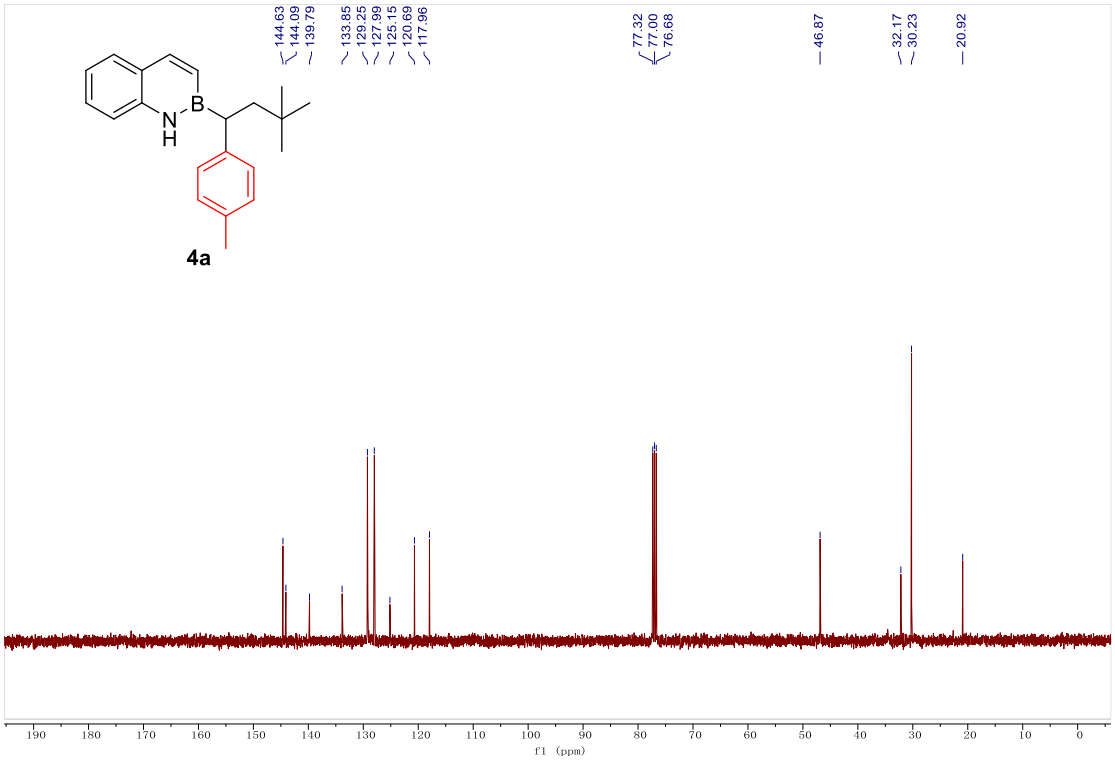
Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (0.12 mmol, 1.2 equiv), **3a** (0.3 mmol, 3 equiv), $NiBr_2$(DME) (10 mol%), **L1** (10 mol%), additive (x mmol, x equiv), TDAE (2 equiv) in 1 mL THF under argon at room temperature for 16 h. [a] Determined by GC analysis using dodecane as an internal standard.

## 8. NMR Spectroscopic Data

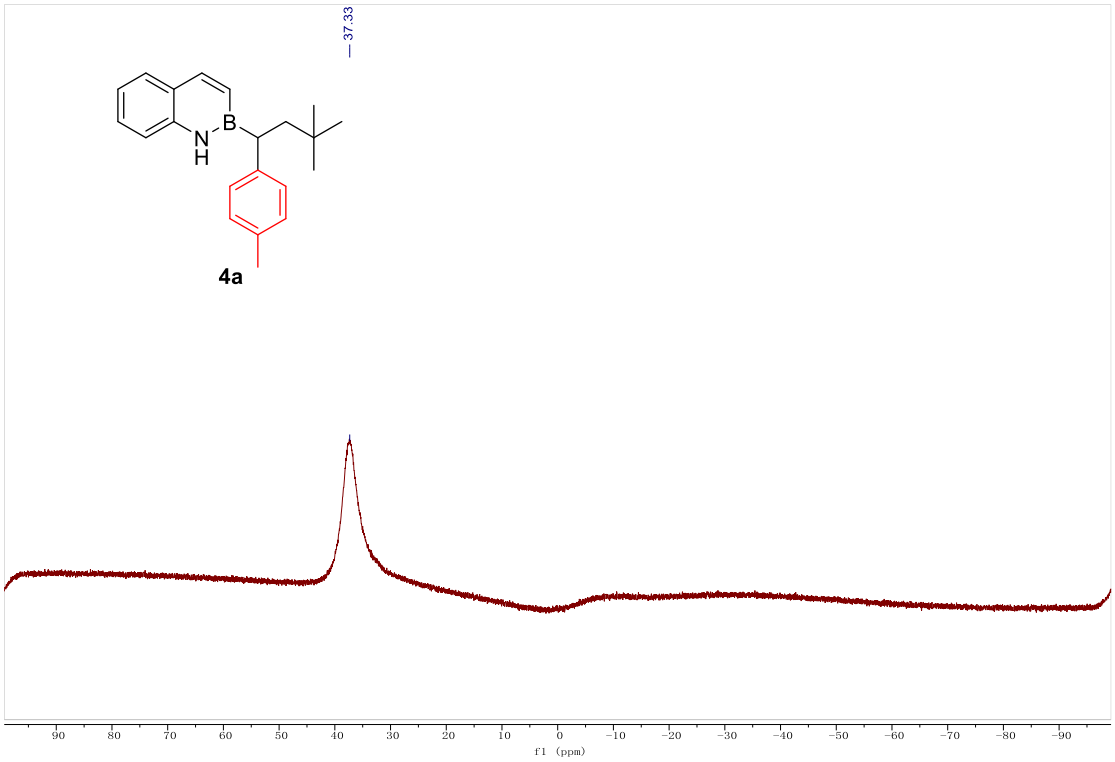
$^{1}$H NMR of **4a** (400 MHz, $CDCl_3$)



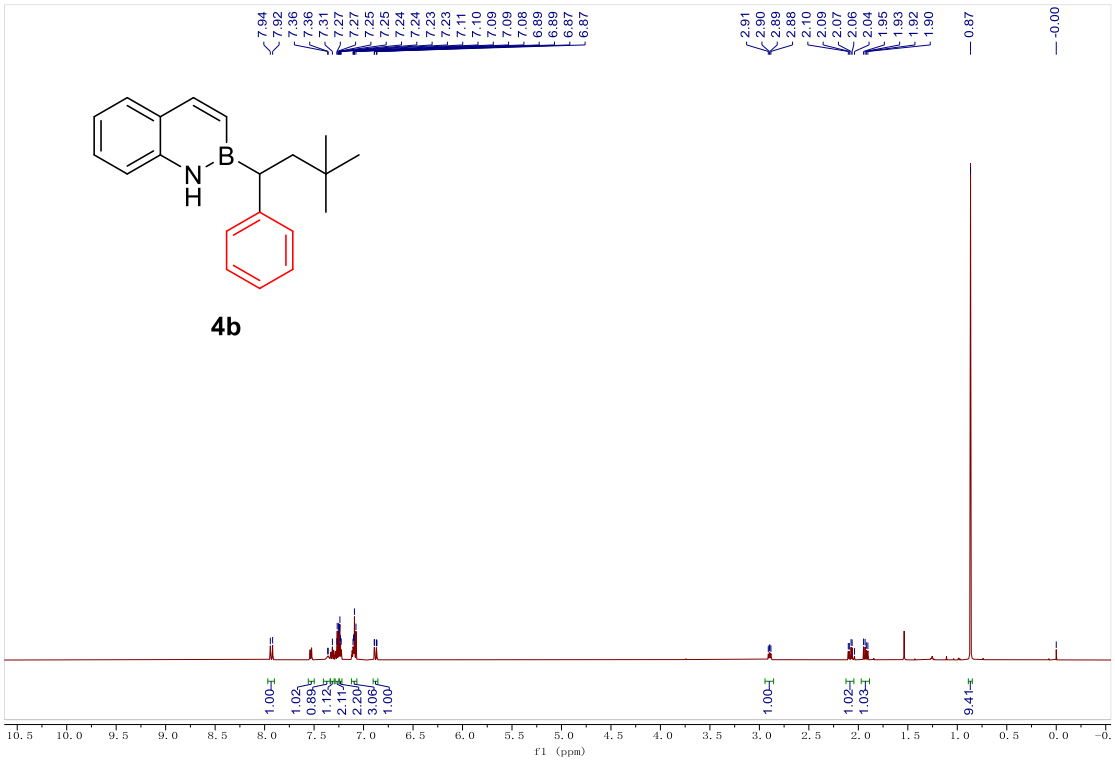

$^{13}$C NMR of **4a** (101 MHz, $CDCl_3$)



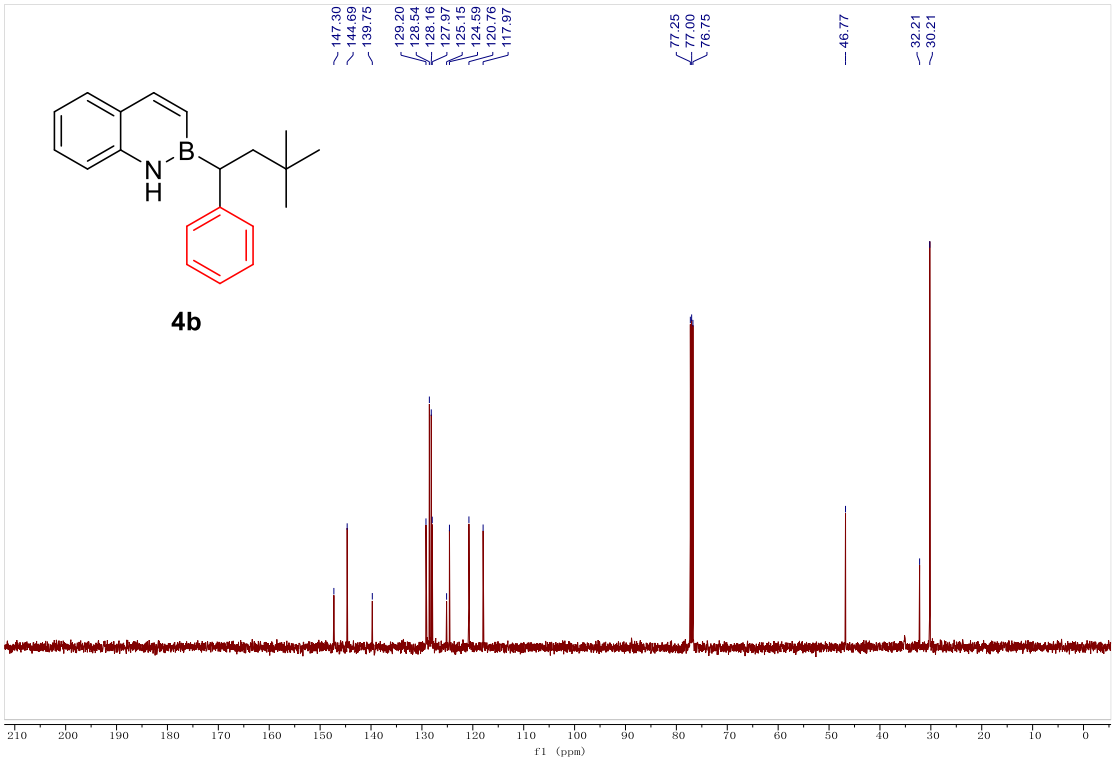
$^{11}$B NMR of **4a** (128 MHz, $CDCl_3$)



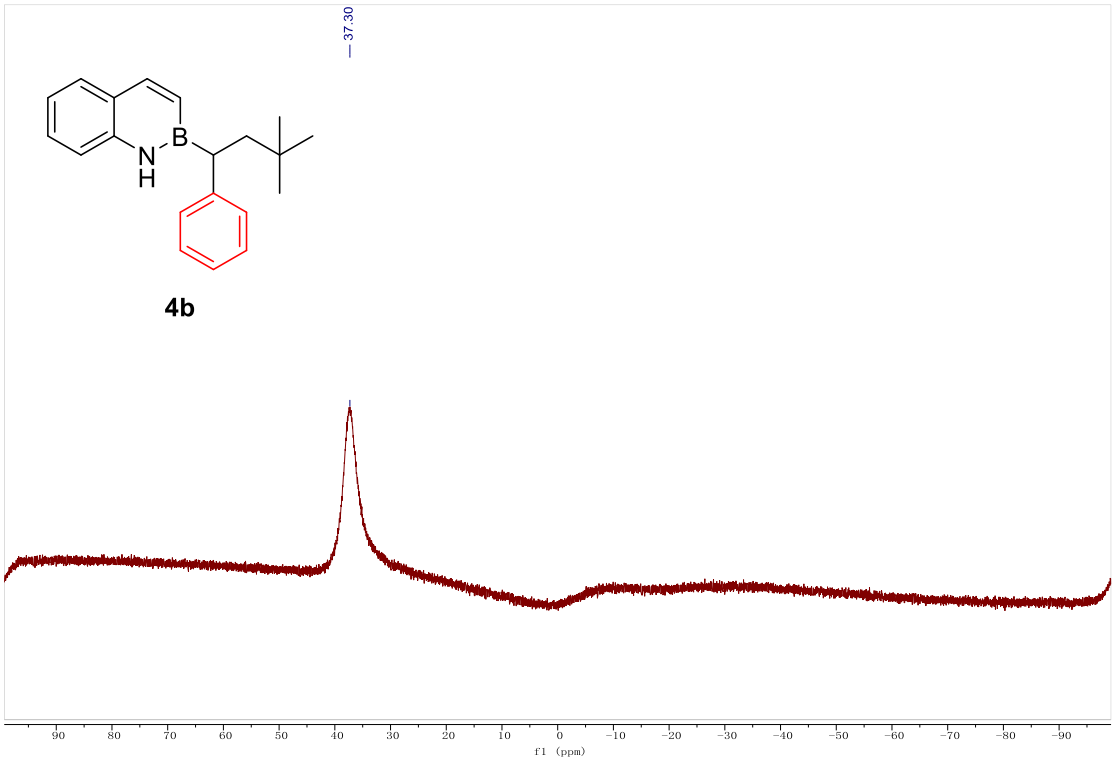

$^{1}$H NMR of **4b** (500 MHz, $CDCl_3$)



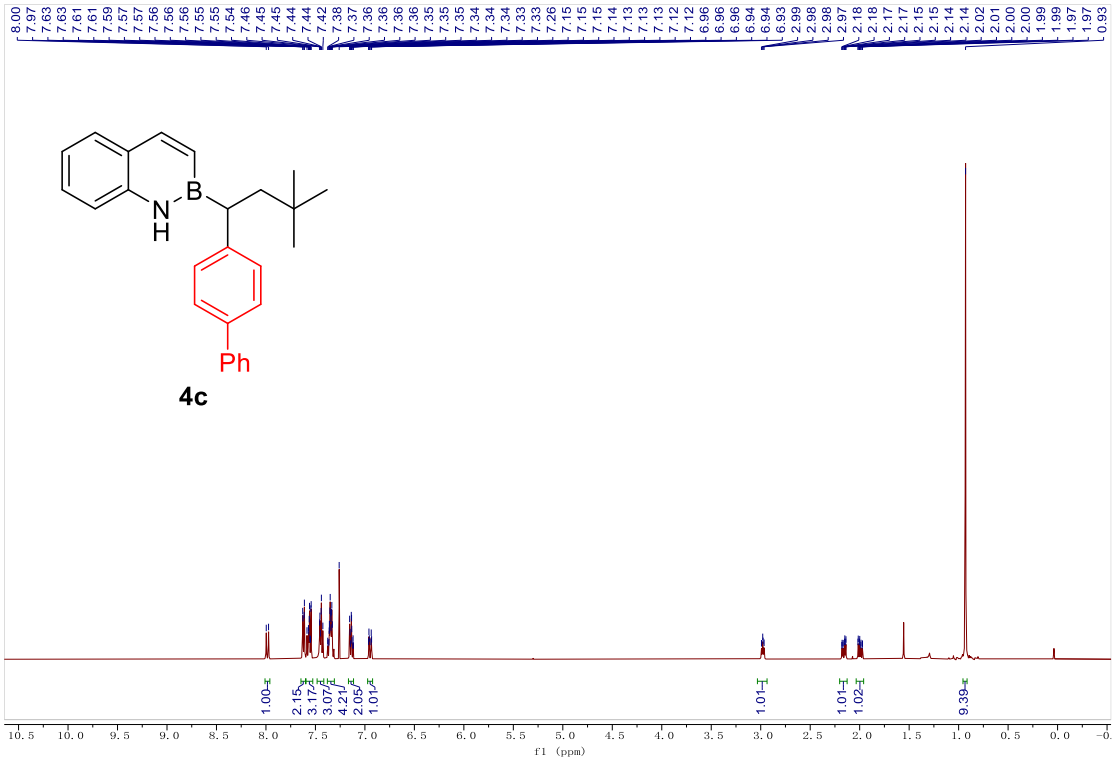
$^{13}$C NMR of **4b** (126 MHz, $CDCl_3$)



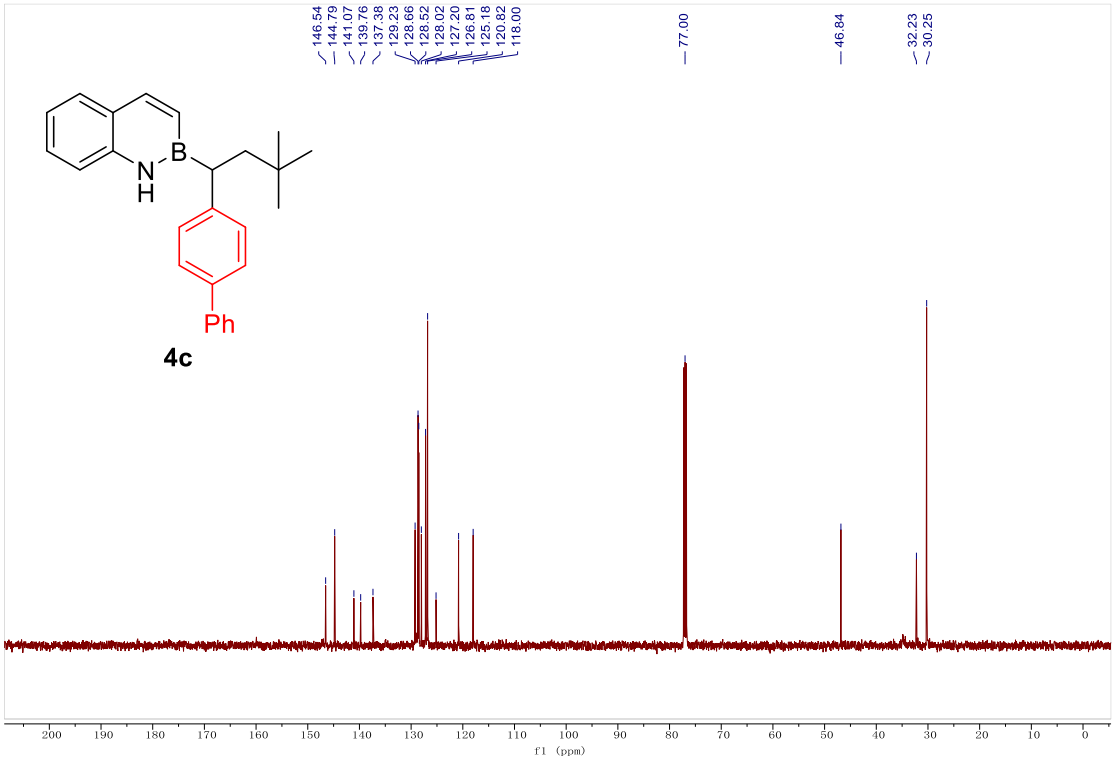

$^{11}$B NMR of **4b** (128 MHz, $CDCl_3$)



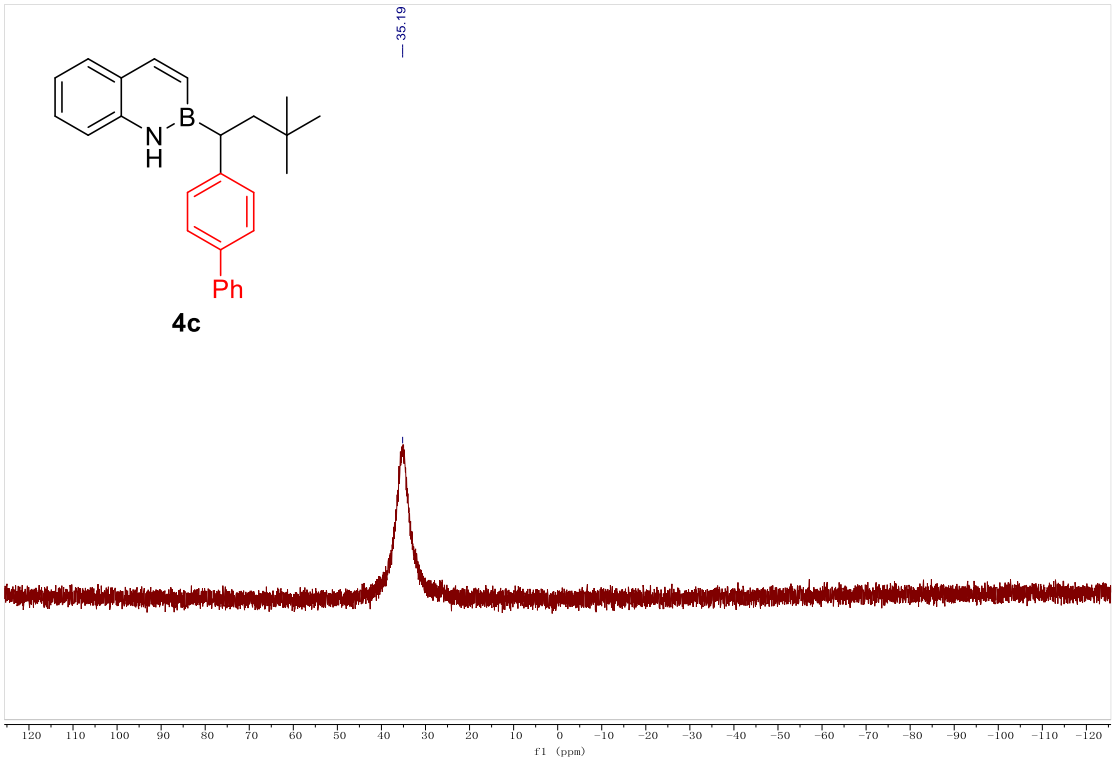
$^{1}$H NMR of **4c** (500 MHz, $CDCl_3$)



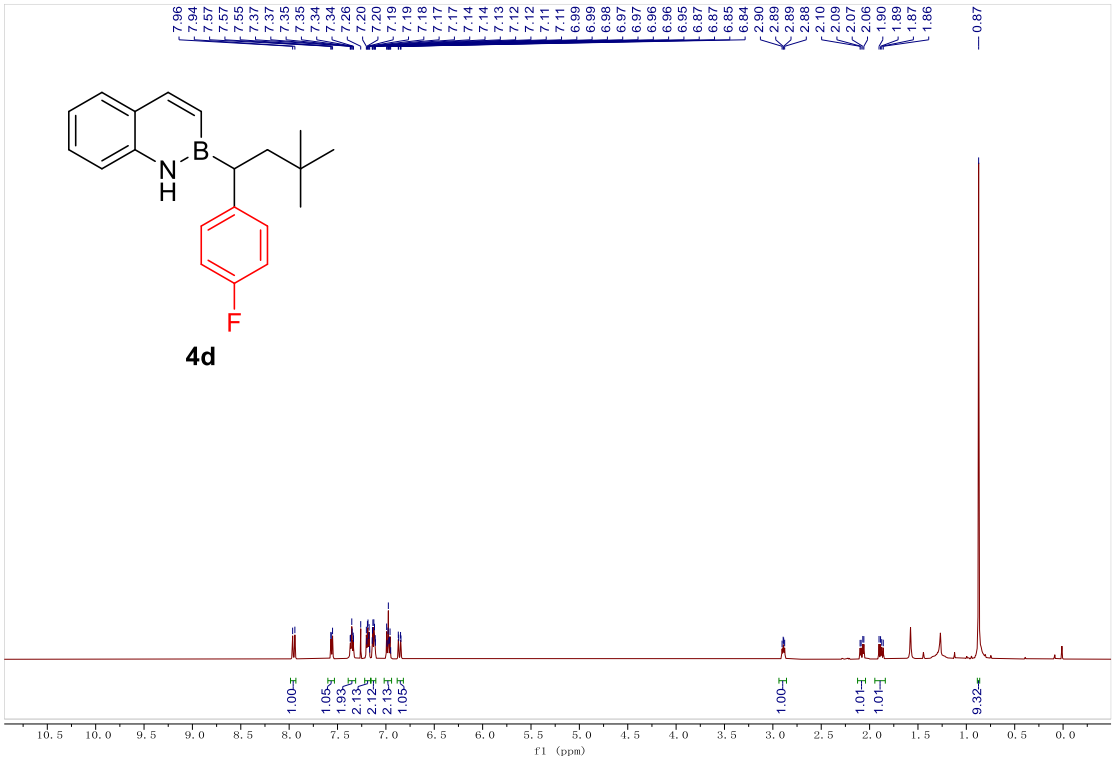

$^{13}$C NMR of **4c** (126 MHz, $CDCl_3$)



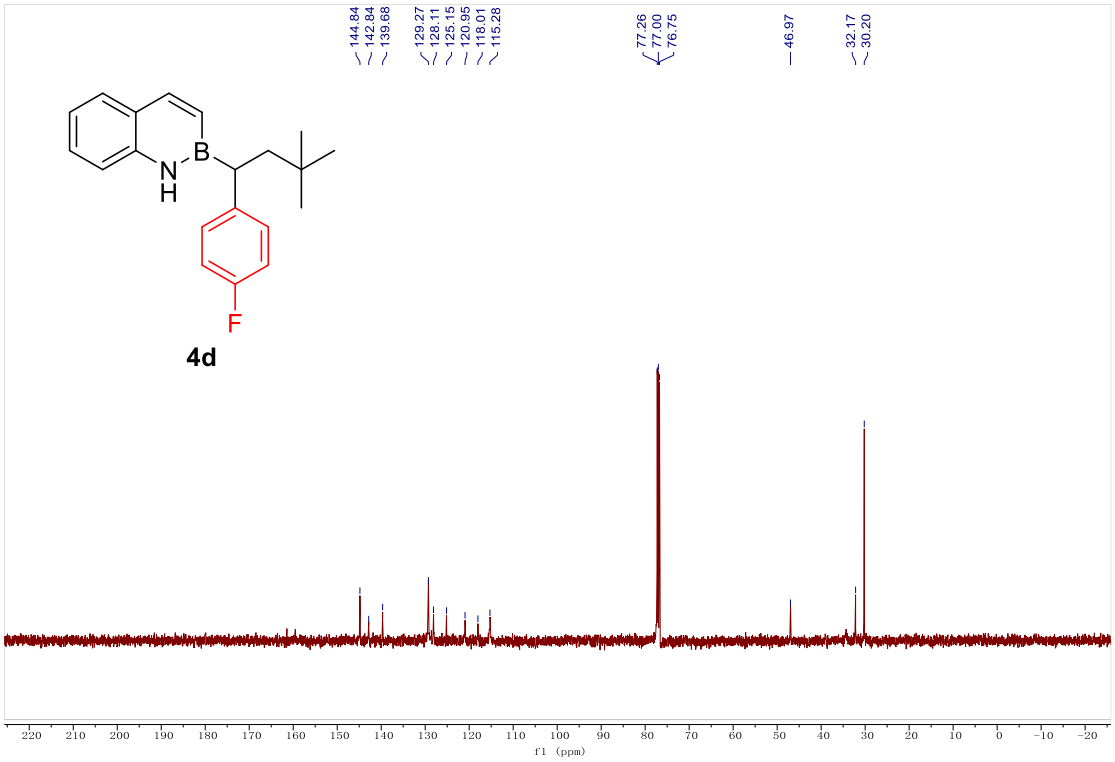
$^{11}$B NMR of **4c** (128 MHz, $CDCl_3$)



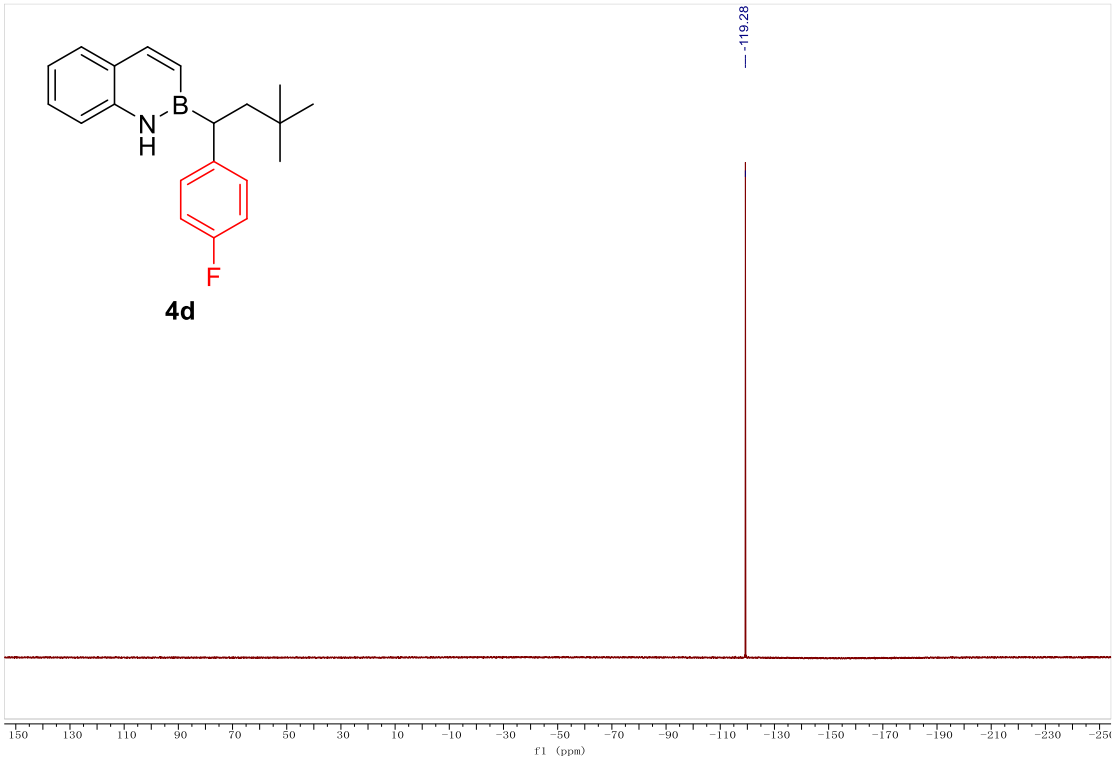

$^{1}$H NMR of **4d** (500 MHz, $CDCl_3$)



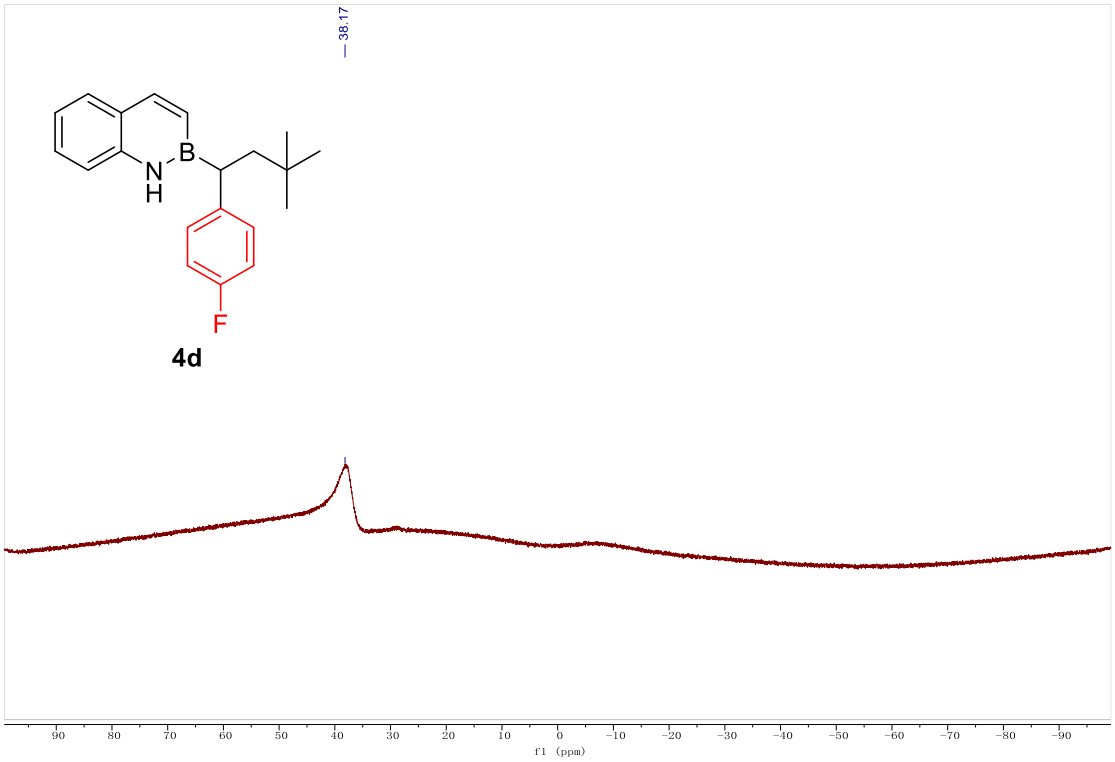
$^{13}$C NMR of **4d** (126 MHz, $CDCl_3$)



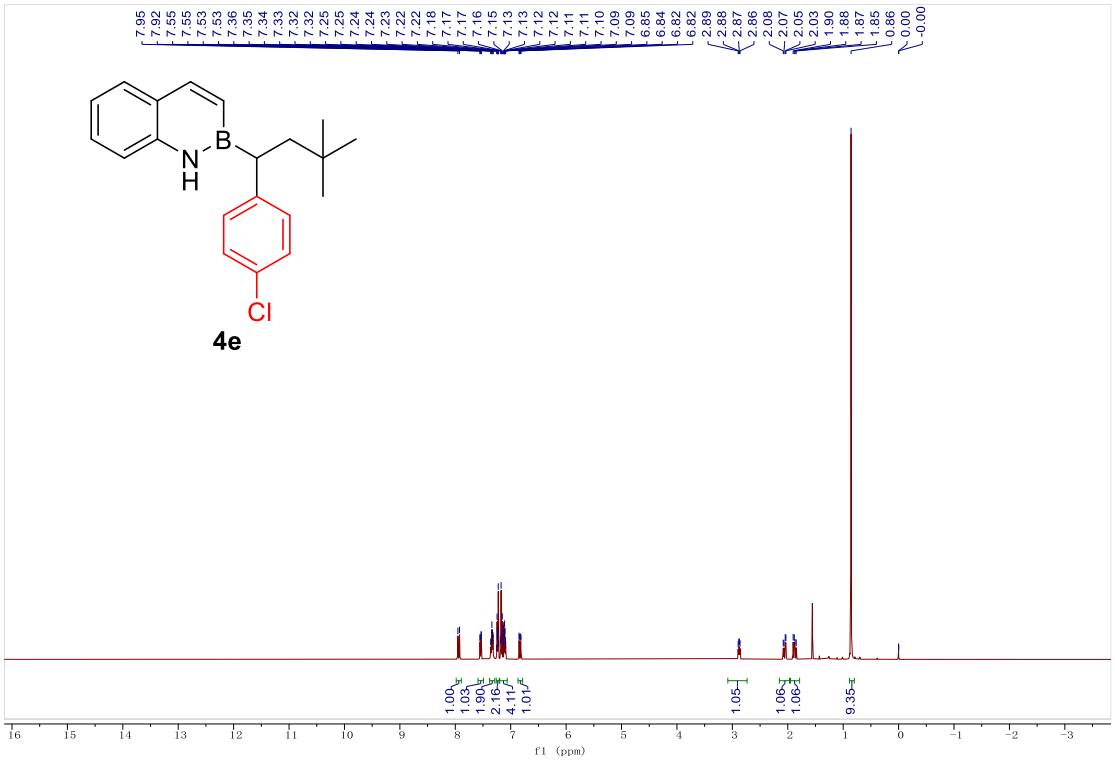

$^{19}$F NMR of **4d** (376 MHz, $CDCl_3$)



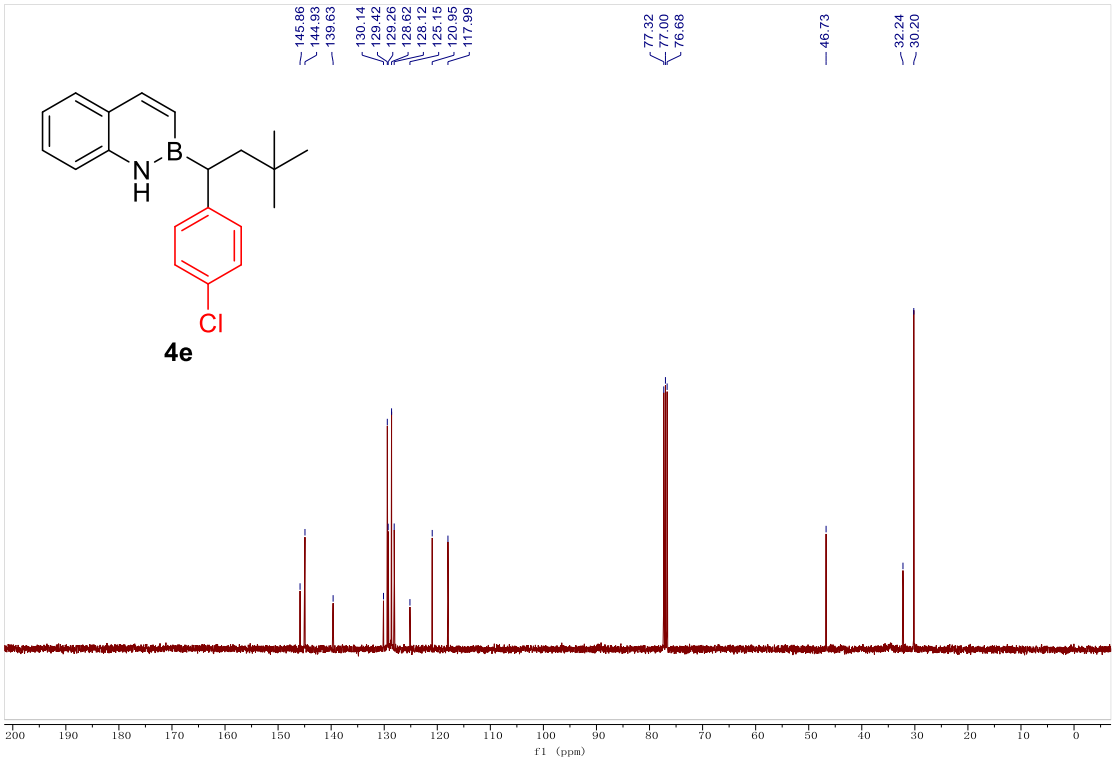
$^{11}$B NMR of **4d** (128 MHz, $CDCl_3$)



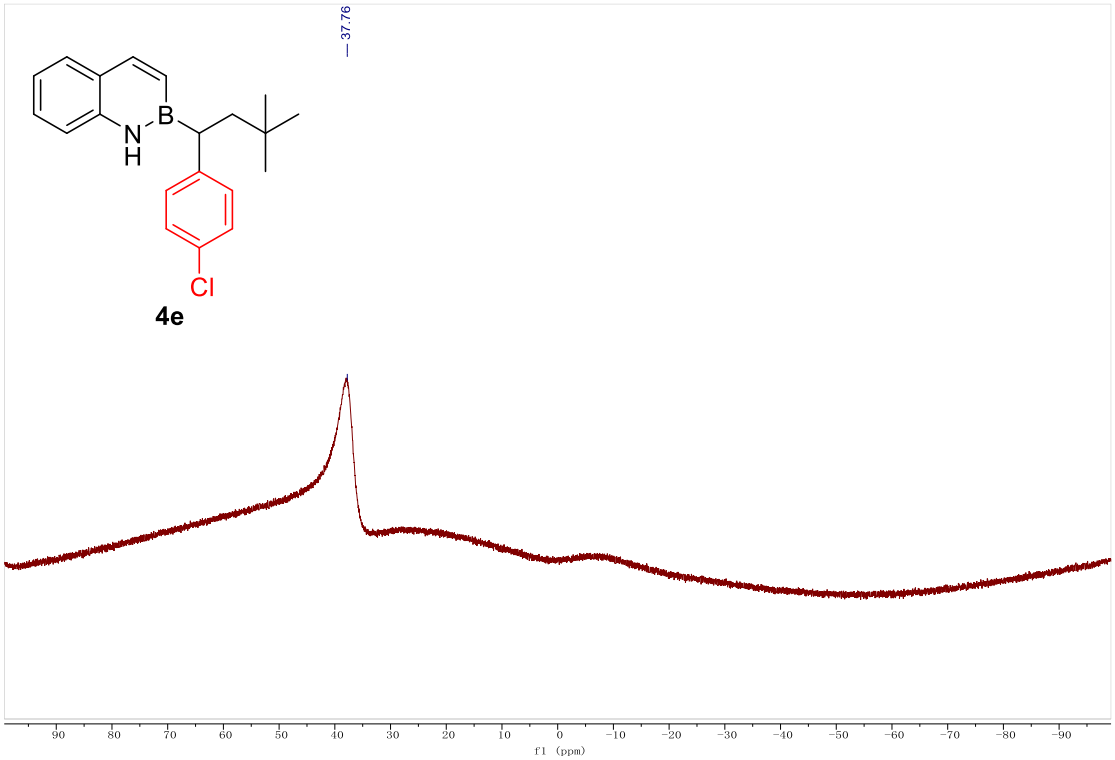

$^{1}$H NMR of **4e** (400 MHz, $CDCl_3$)



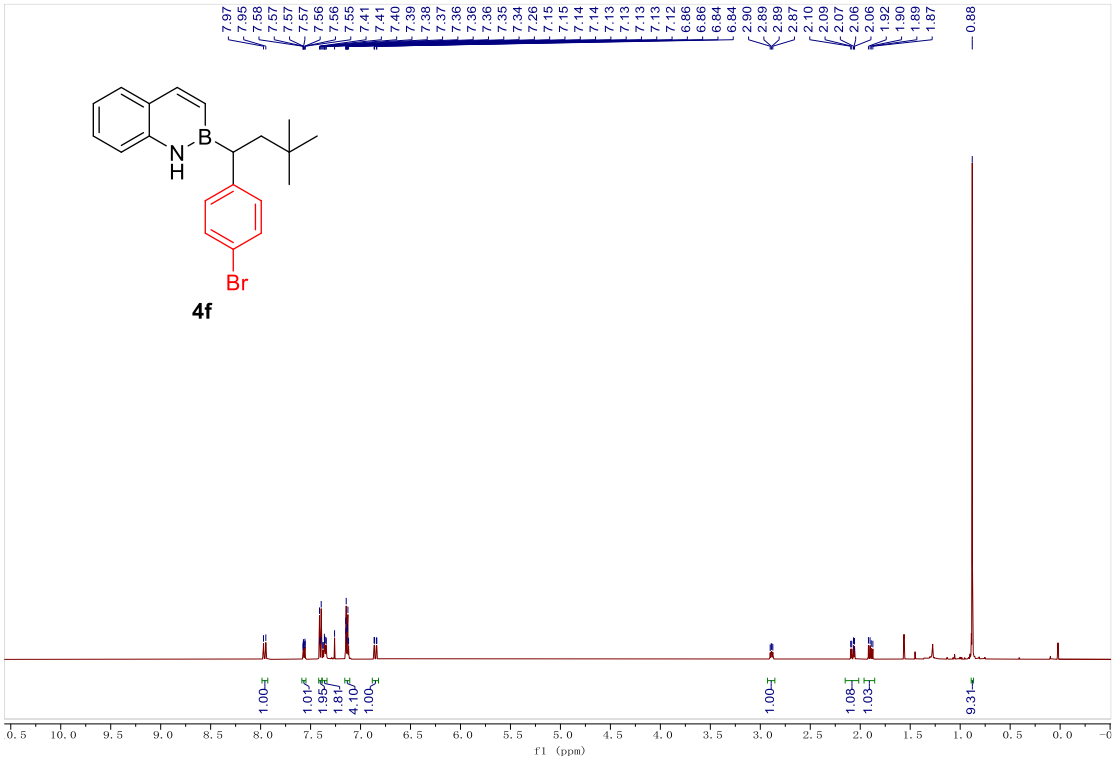
$^{13}$C NMR of **4e** (101 MHz, $CDCl_3$)



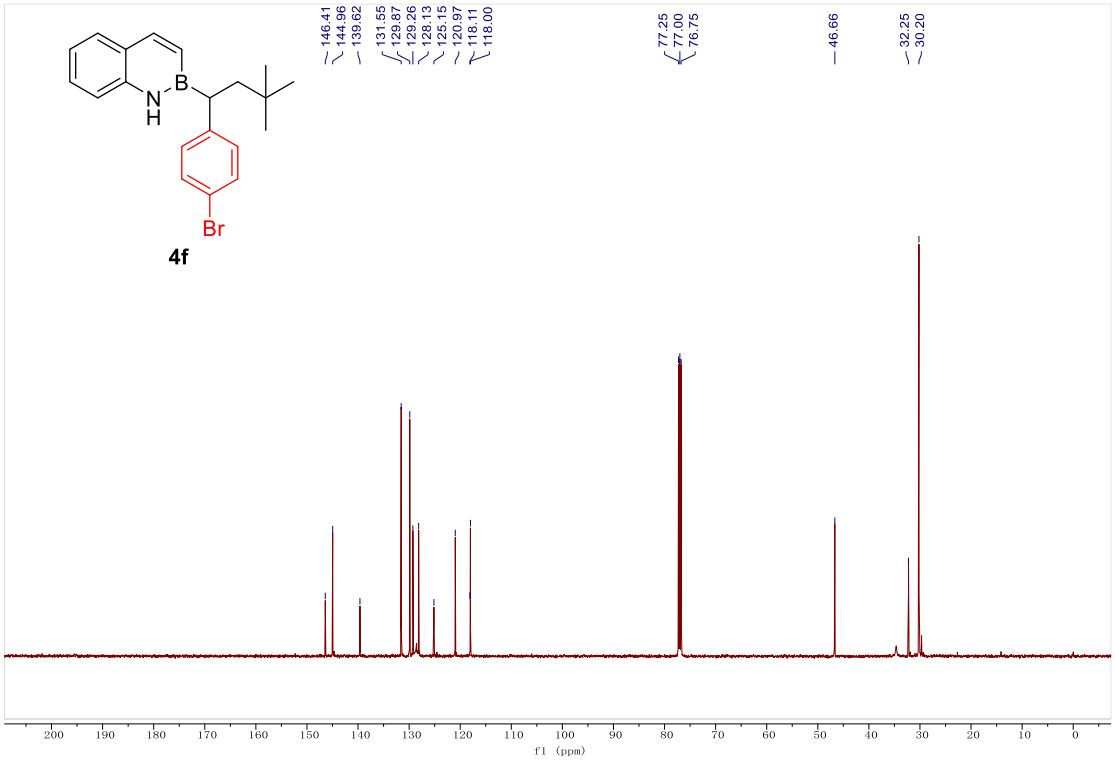

$^{11}$B NMR of **4e** (128 MHz, $CDCl_3$)



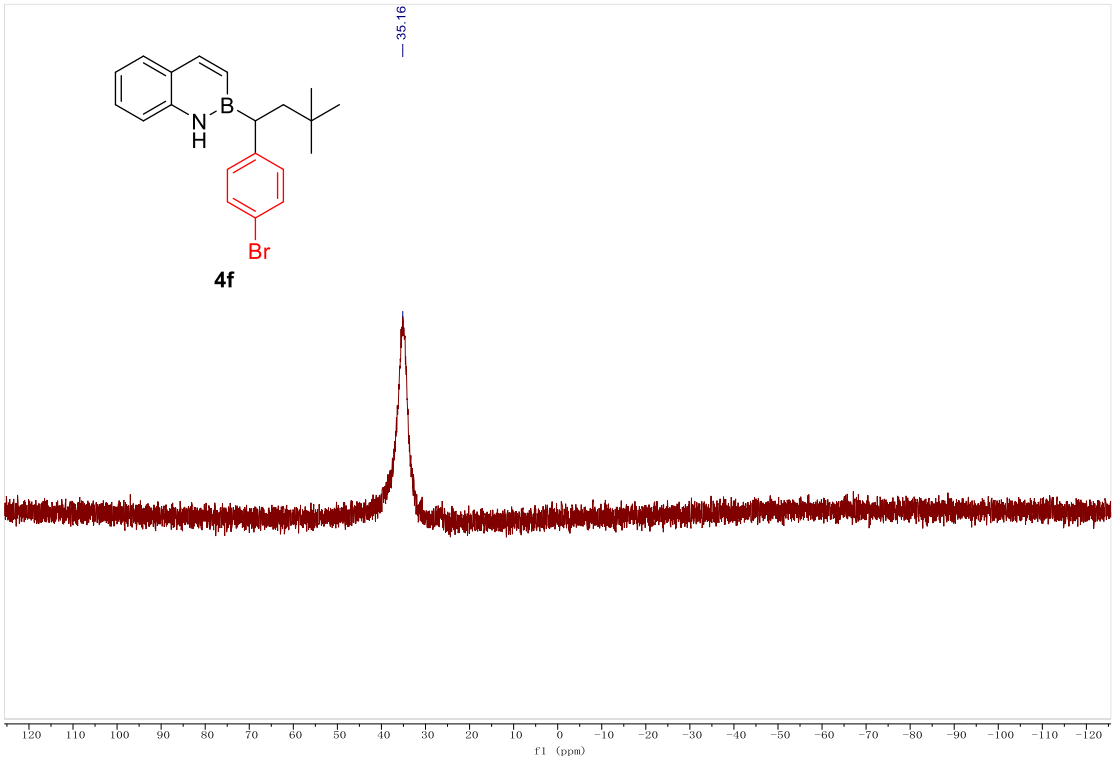
$^{1}$H NMR of **4f** (500 MHz, $CDCl_3$)



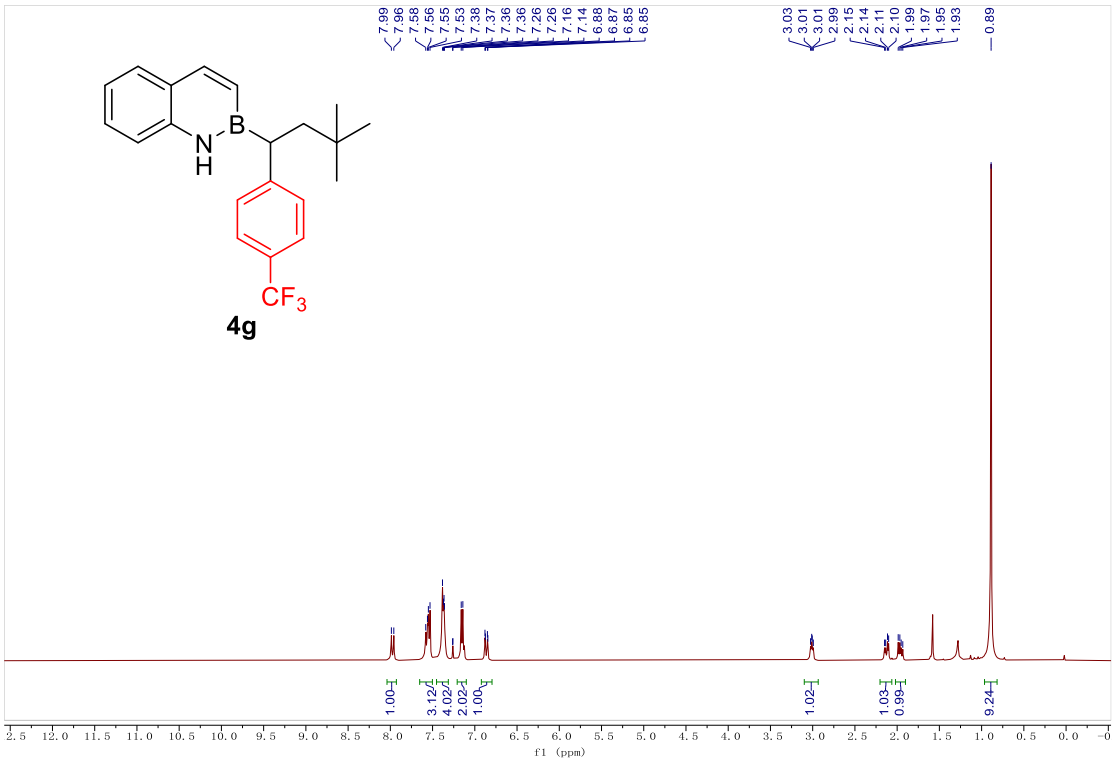

$^{13}$C NMR of **4f** (126 MHz, $CDCl_3$)



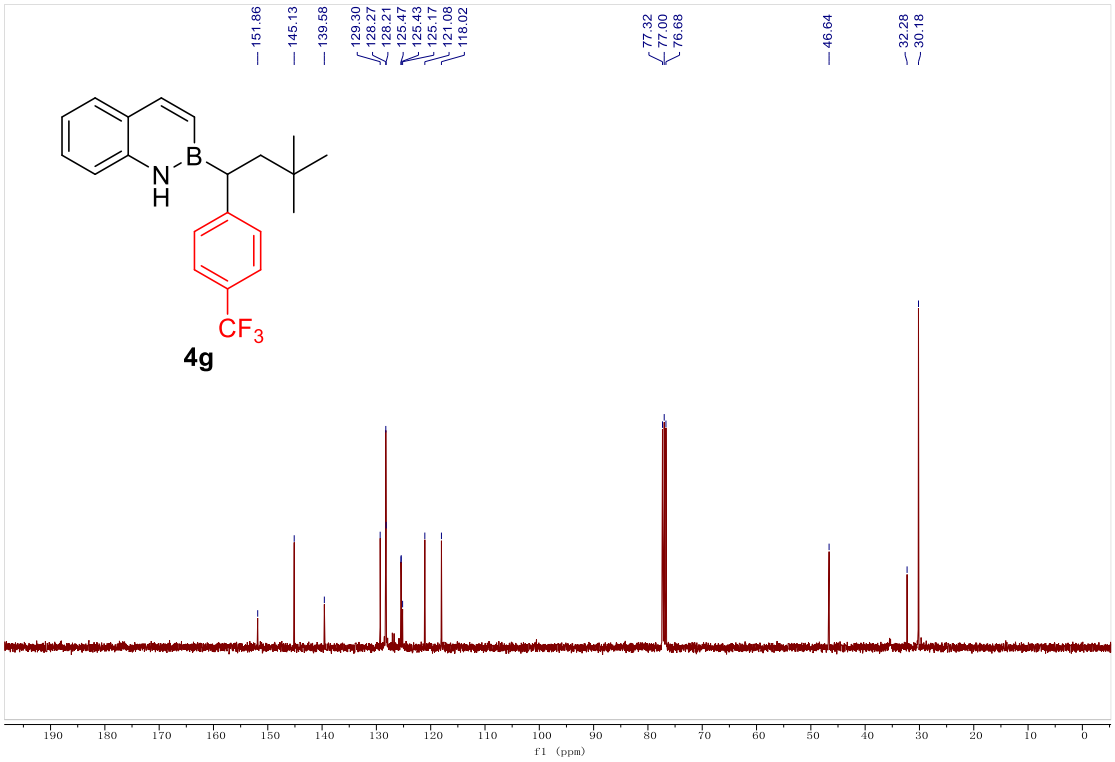
$^{11}$B NMR of **4f** (128 MHz, $CDCl_3$)



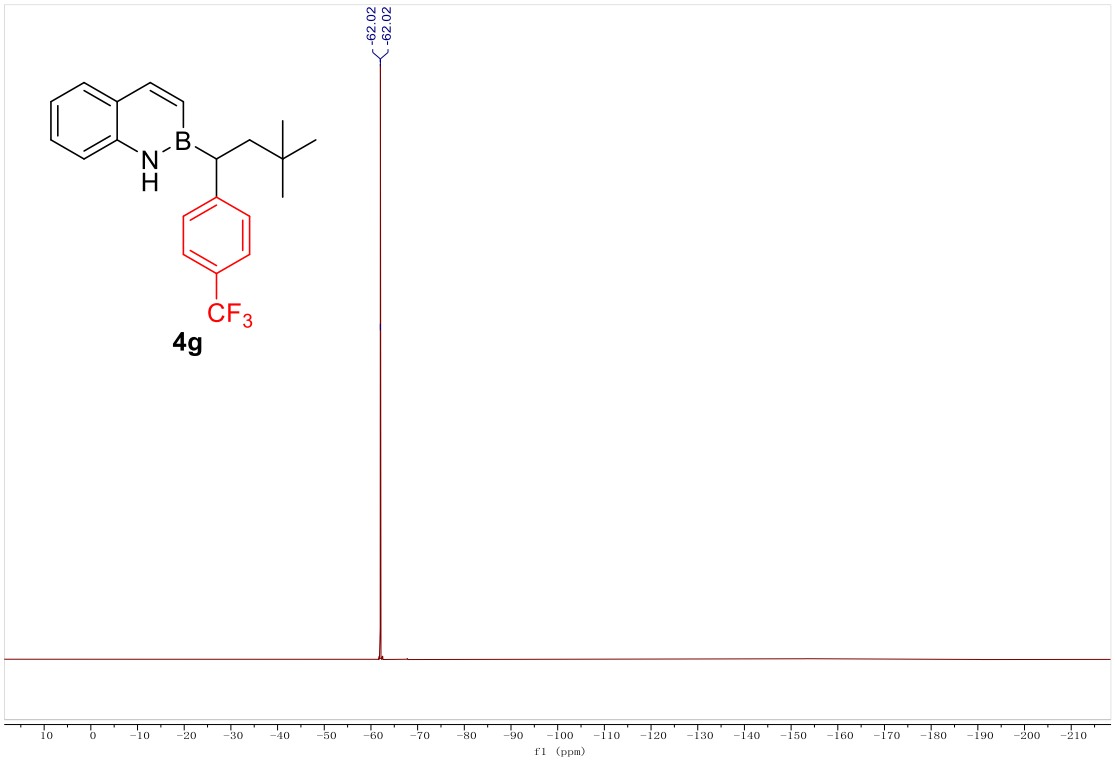

$^{1}$H NMR of **4g** (400 MHz, $CDCl_3$)



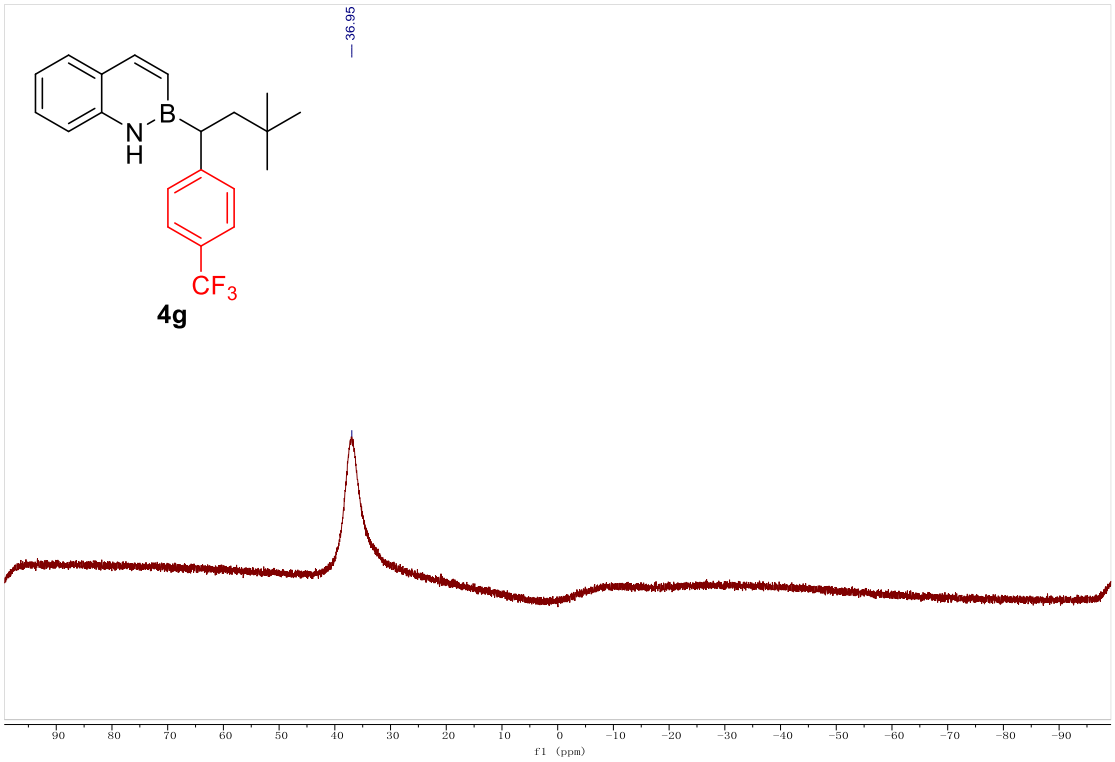
$^{13}$C NMR of **4g** (101 MHz, $CDCl_3$)



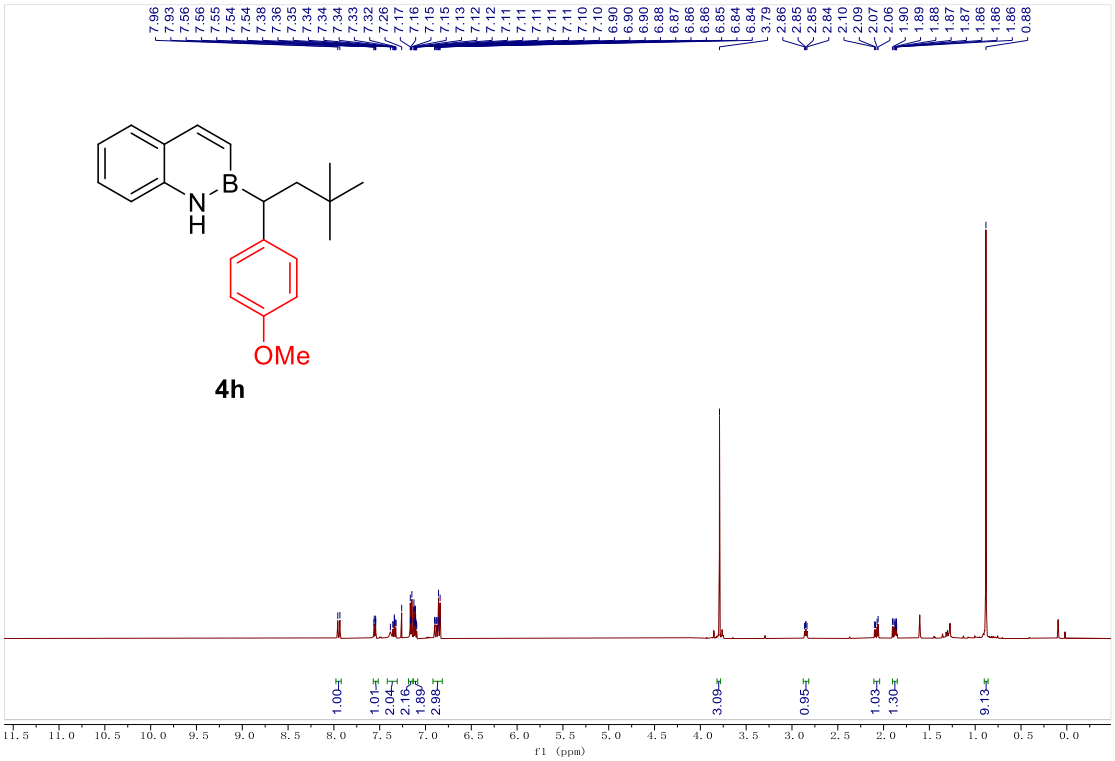

$^{19}$F NMR of **4g** (376 MHz, $CDCl_3$)



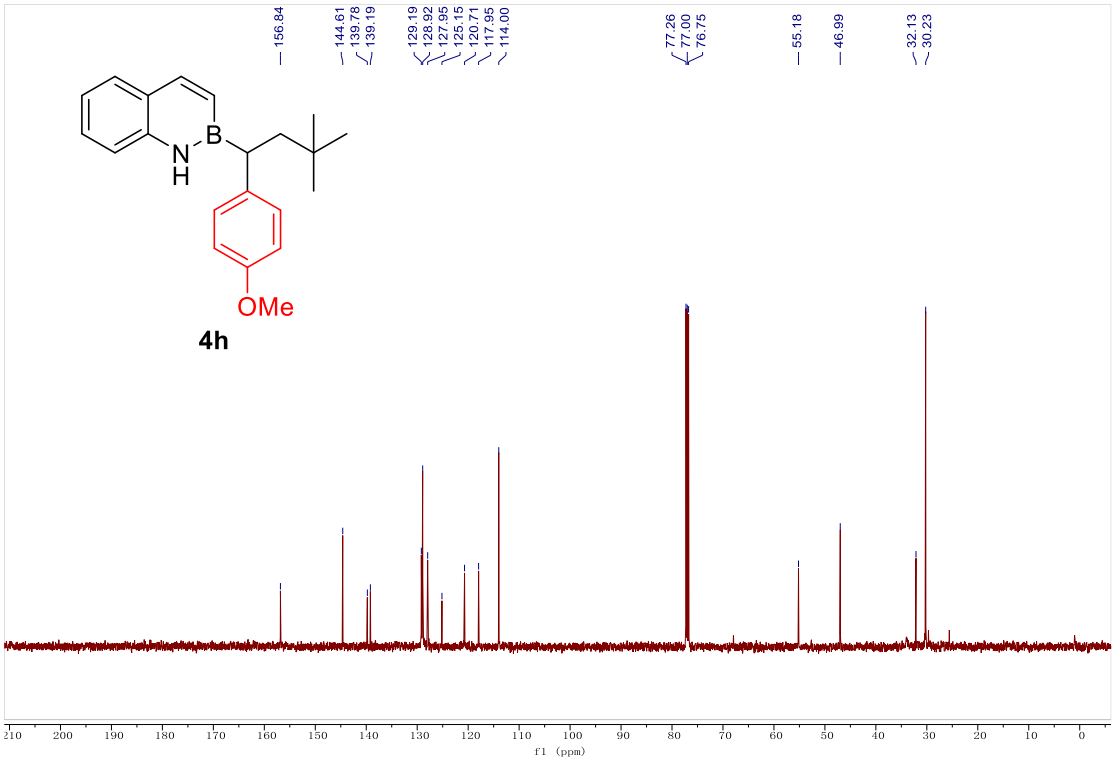
$^{11}$B NMR of **4g** (128 MHz, $CDCl_3$)



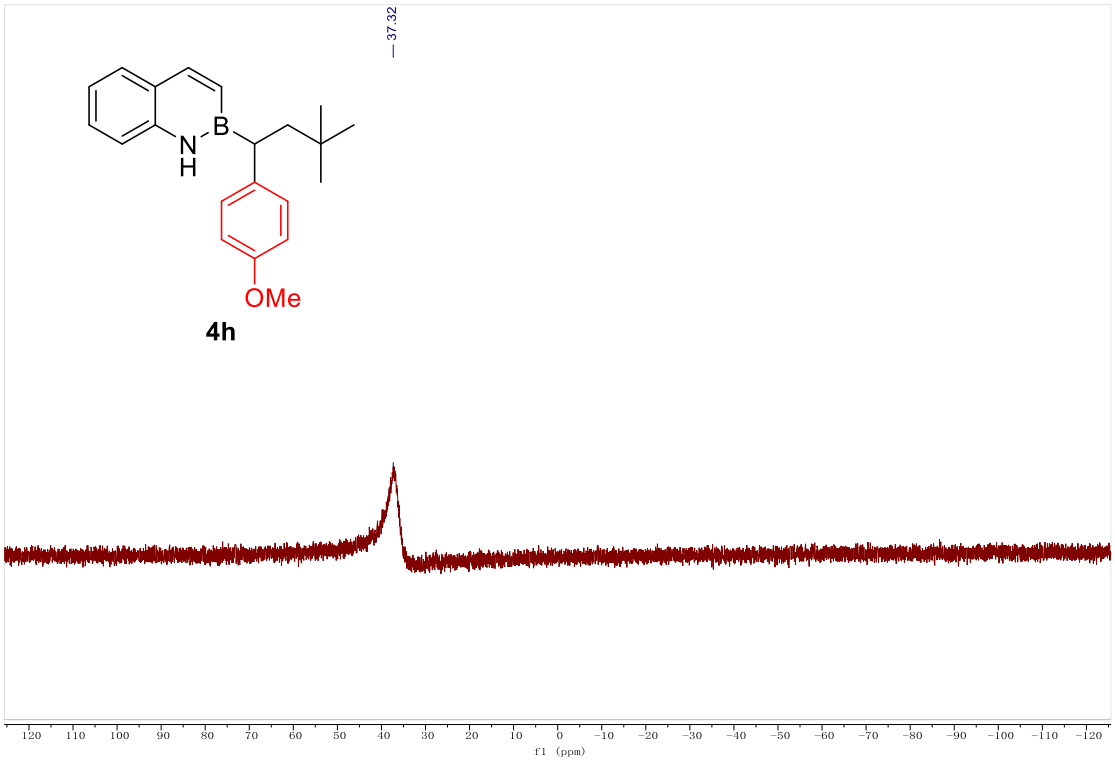

$^{1}$H NMR of **4h** (500 MHz, $CDCl_3$)



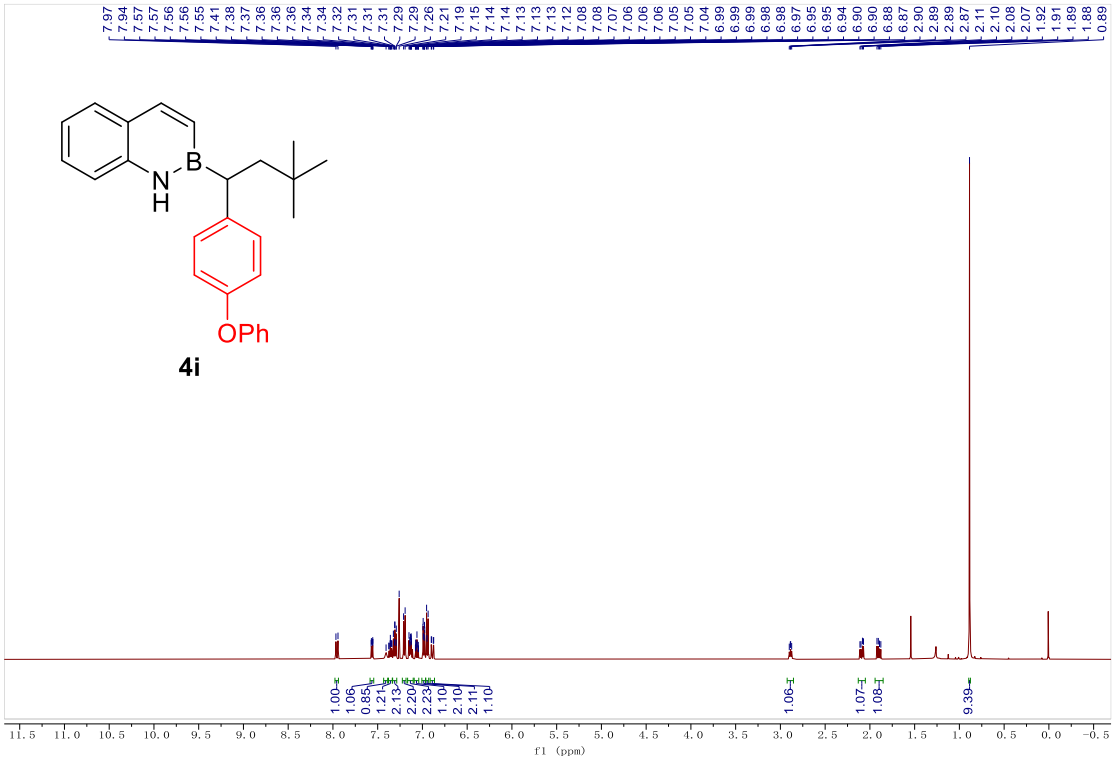
$^{13}$C NMR of **4h** (126 MHz, $CDCl_3$)



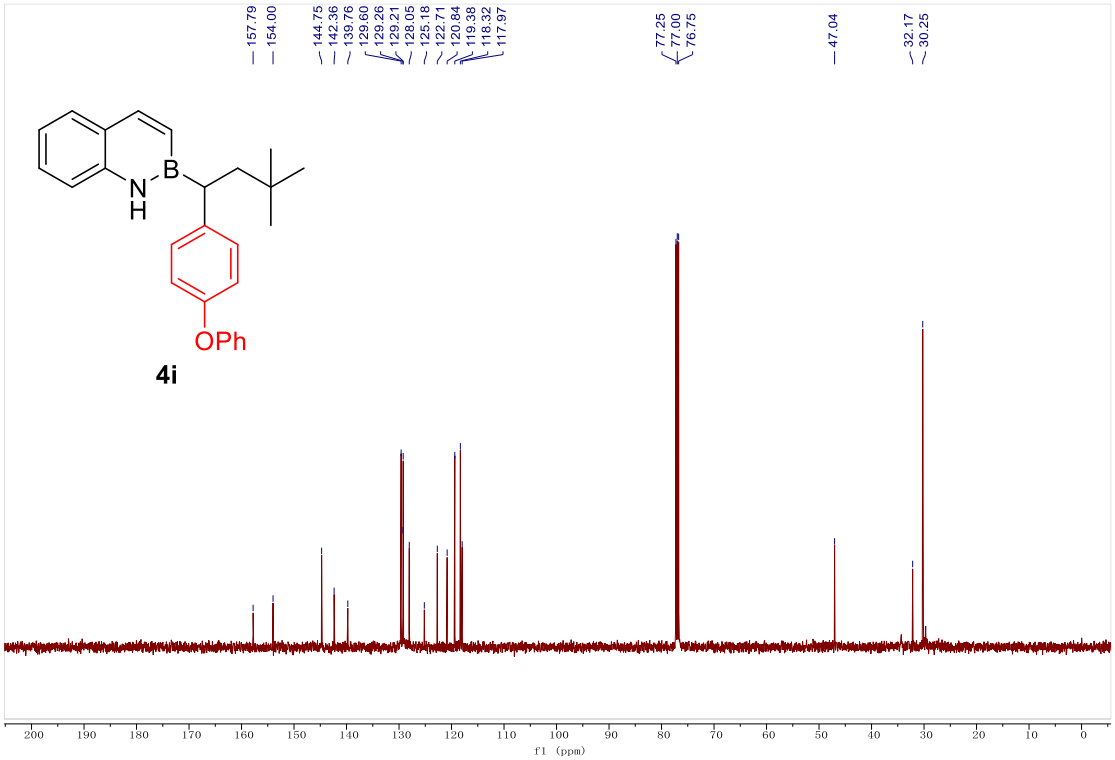

$^{11}$B NMR of **4h** (128 MHz, $CDCl_3$)



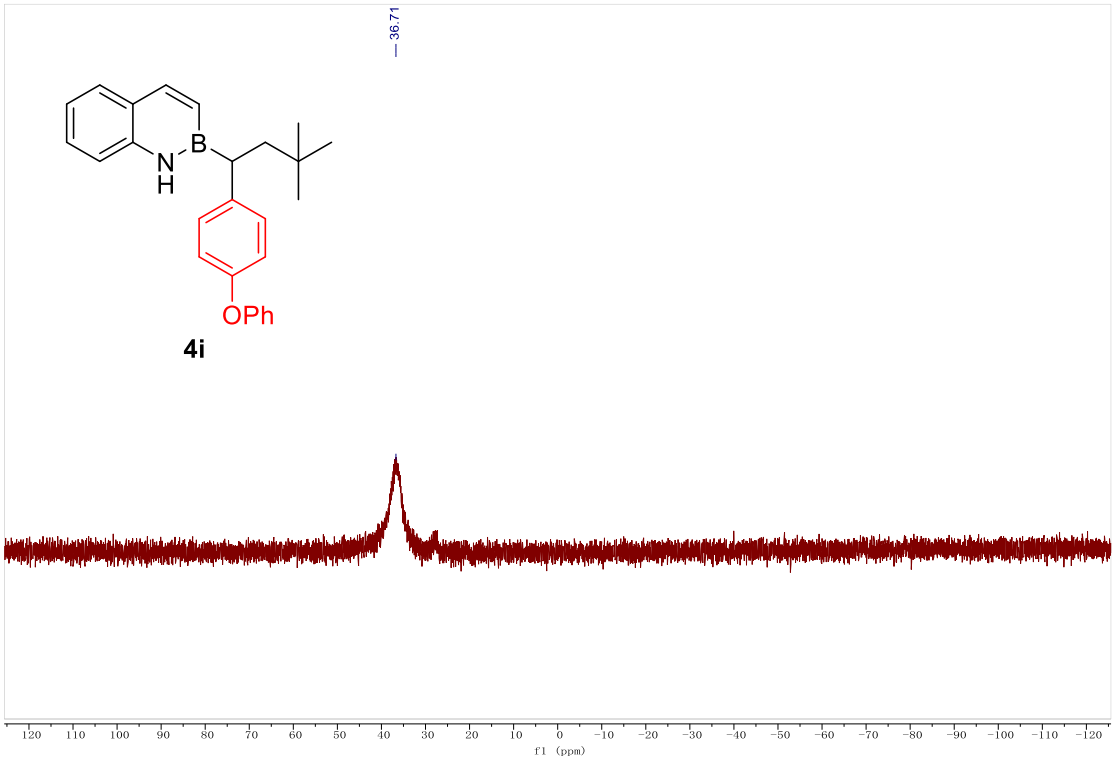
$^{1}$H NMR of **4i** (500 MHz, $CDCl_3$)



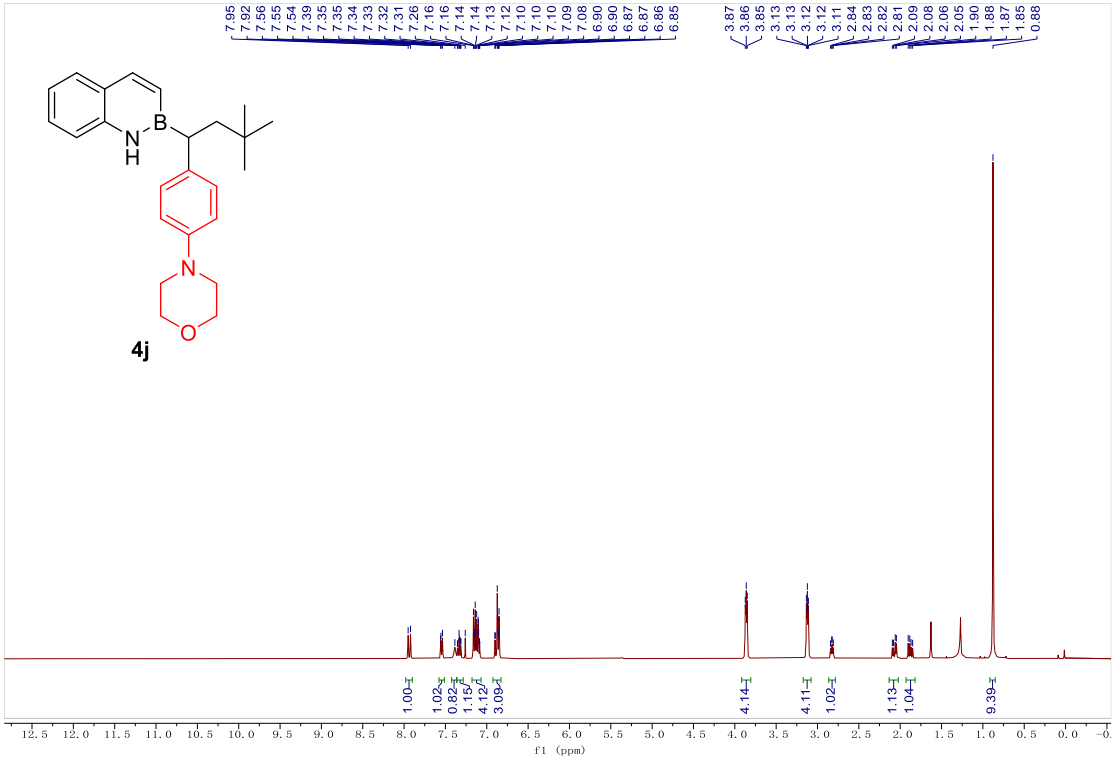

$^{13}$C NMR of **4i** (126 MHz, $CDCl_3$)



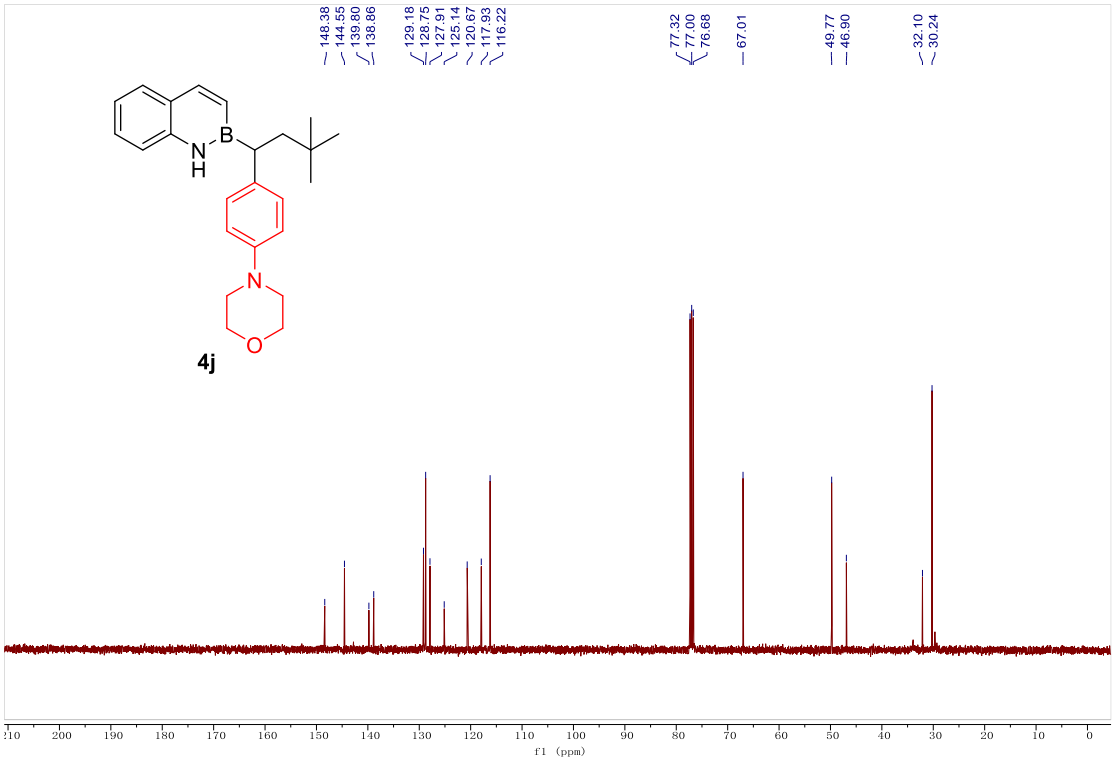
$^{11}$B NMR of **4i** (128 MHz, $CDCl_3$)



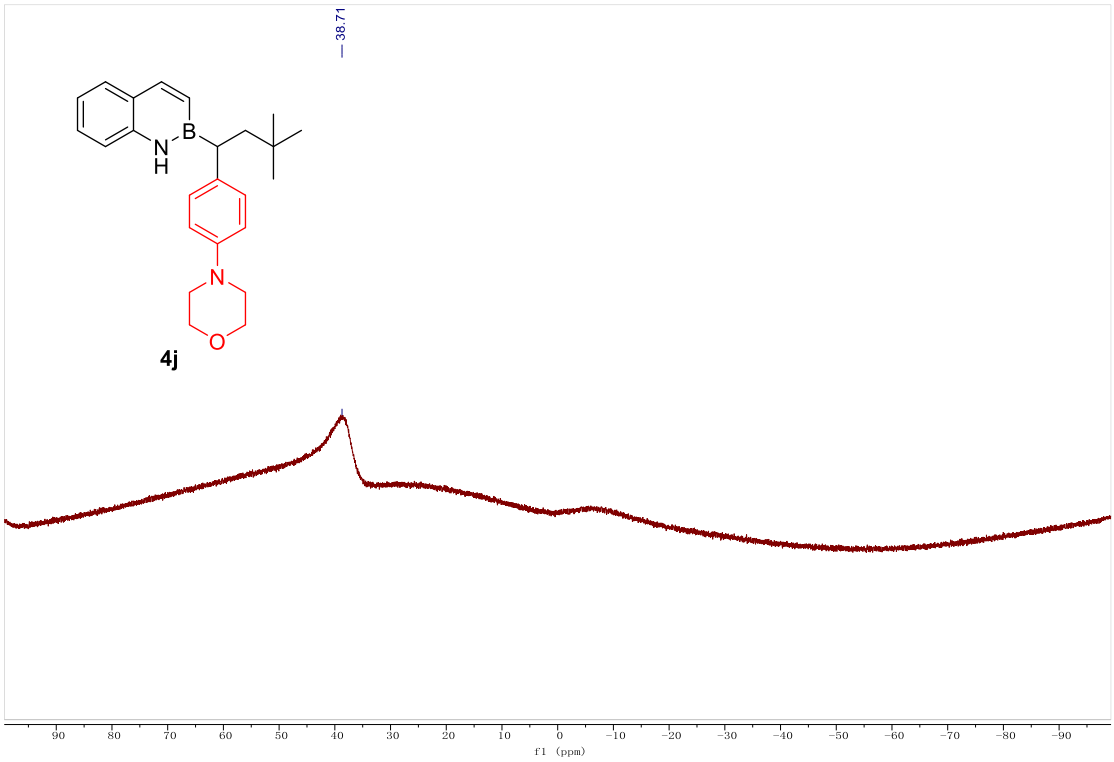

$^{1}$H NMR of **4j** (400 MHz, $CDCl_3$)



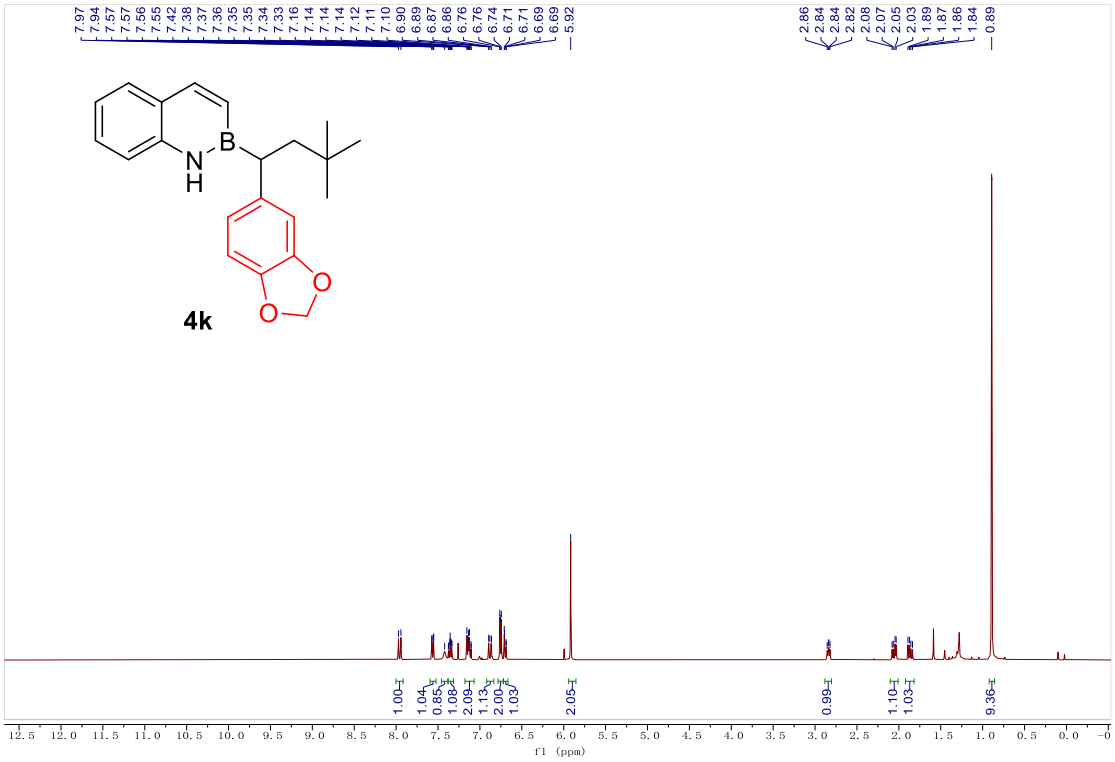
$^{13}$C NMR of **4j** (101 MHz, $CDCl_3$)



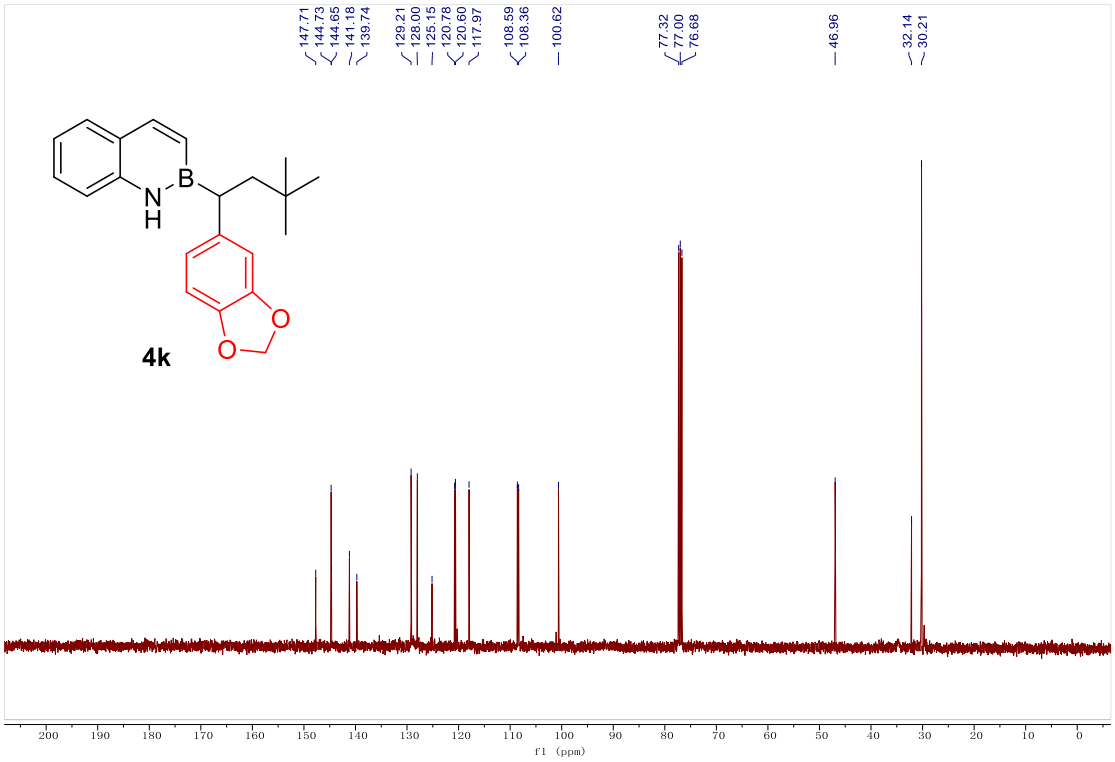

$^{11}$B NMR of **4j** (128 MHz, $CDCl_3$)



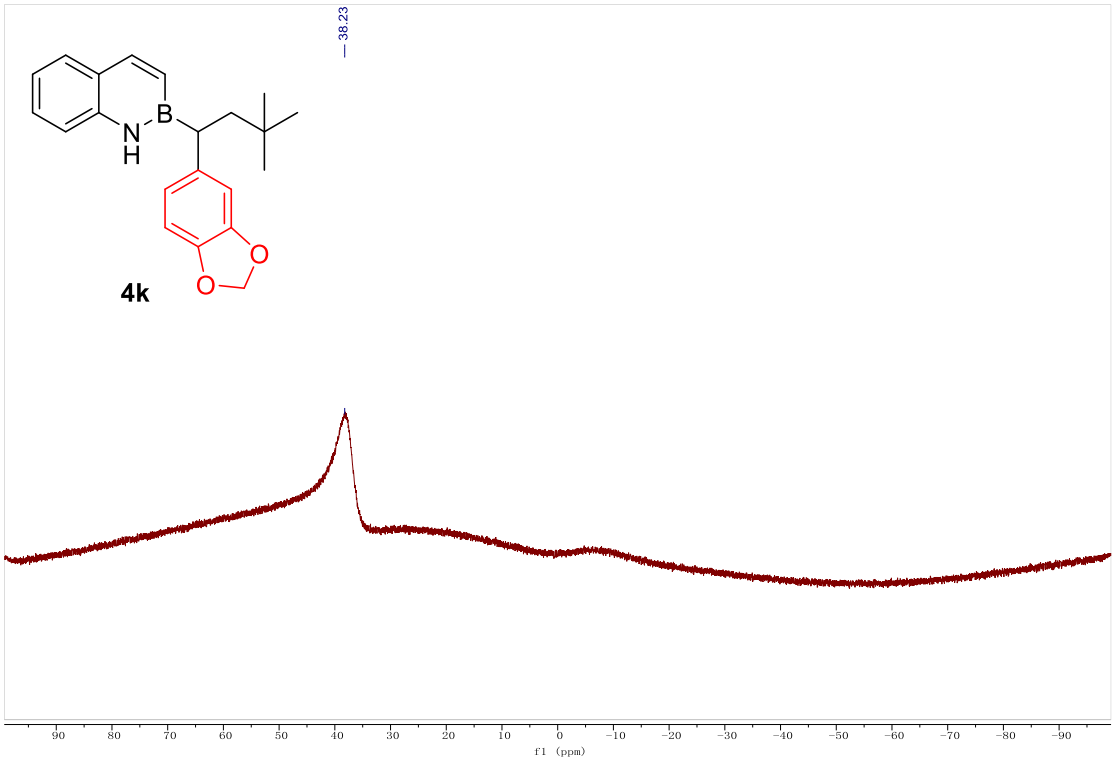
$^{1}$H NMR of **4k** (400 MHz, $CDCl_3$)



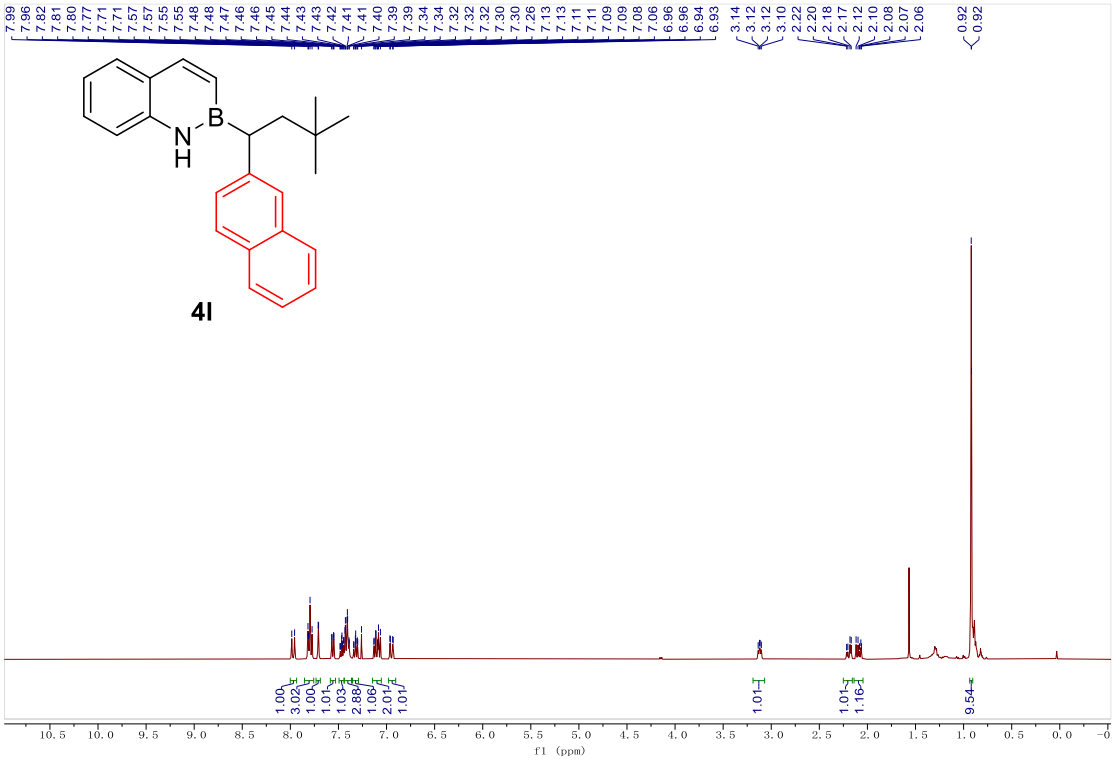

$^{13}$C NMR of **4k** (101 MHz, $CDCl_3$)



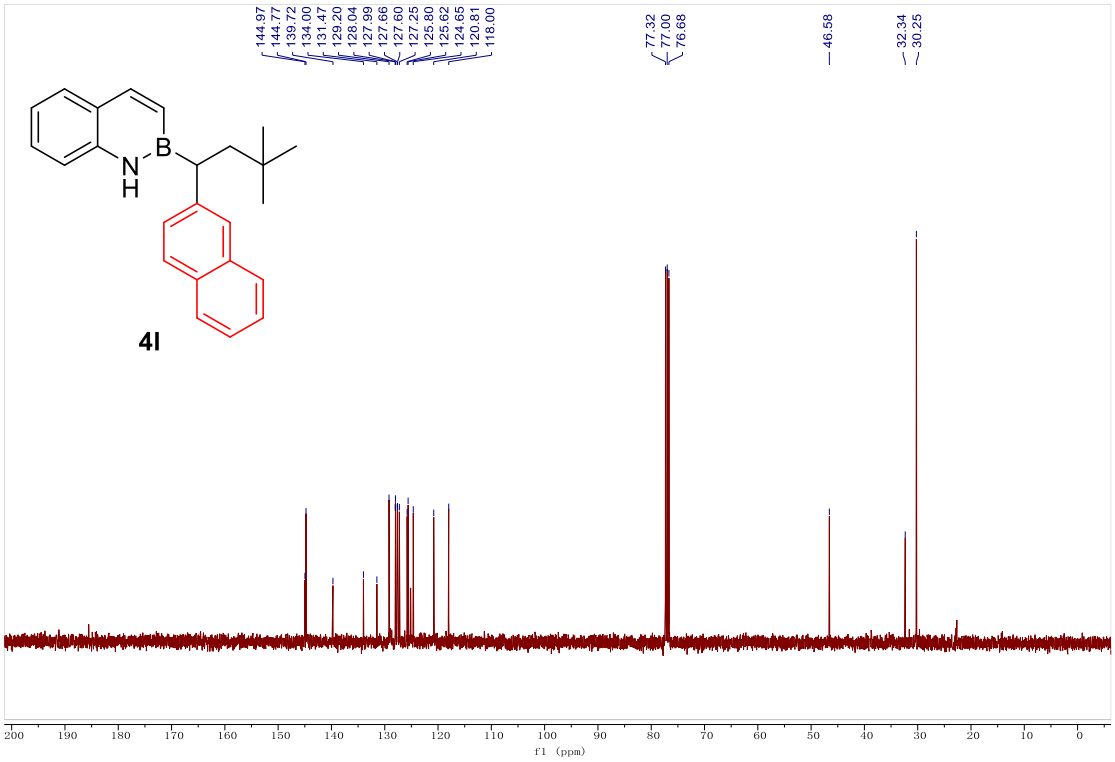
$^{11}$B NMR of **4k** (128 MHz, $CDCl_3$)



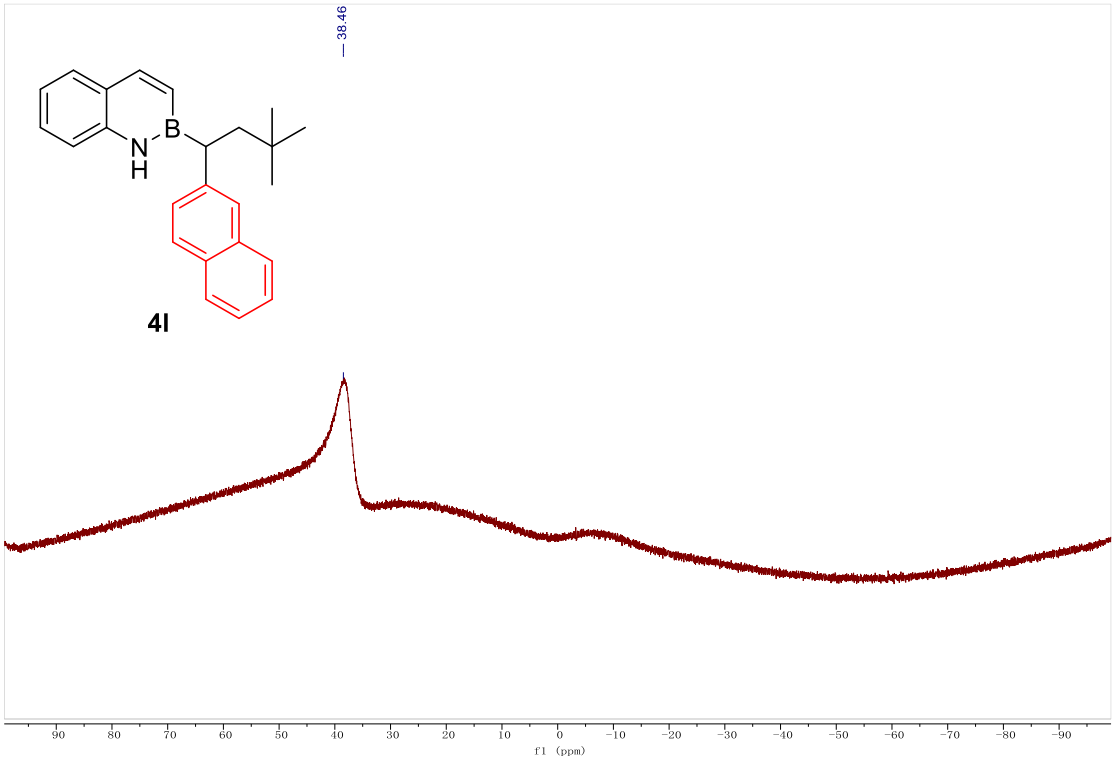

$^{1}$H NMR of **4l** (400 MHz, $CDCl_3$)



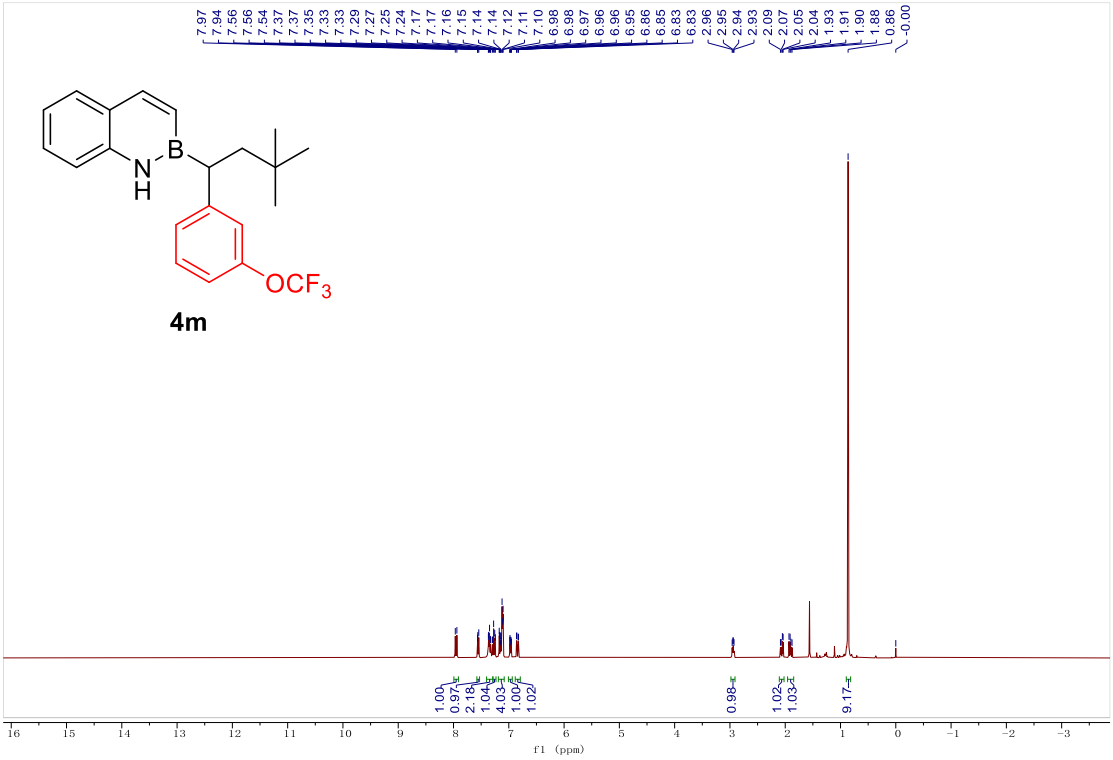
$^{13}$C NMR of **4l** (101 MHz, $CDCl_3$)



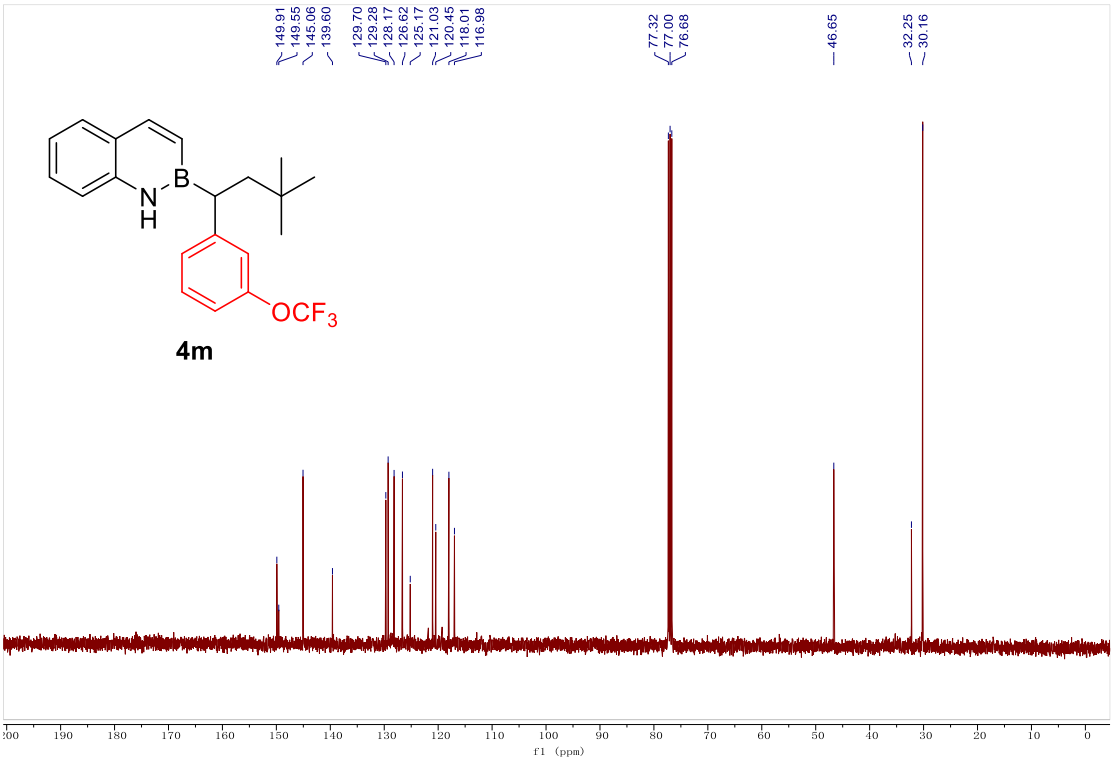

$^{11}$B NMR of **4l** (128 MHz, $CDCl_3$)



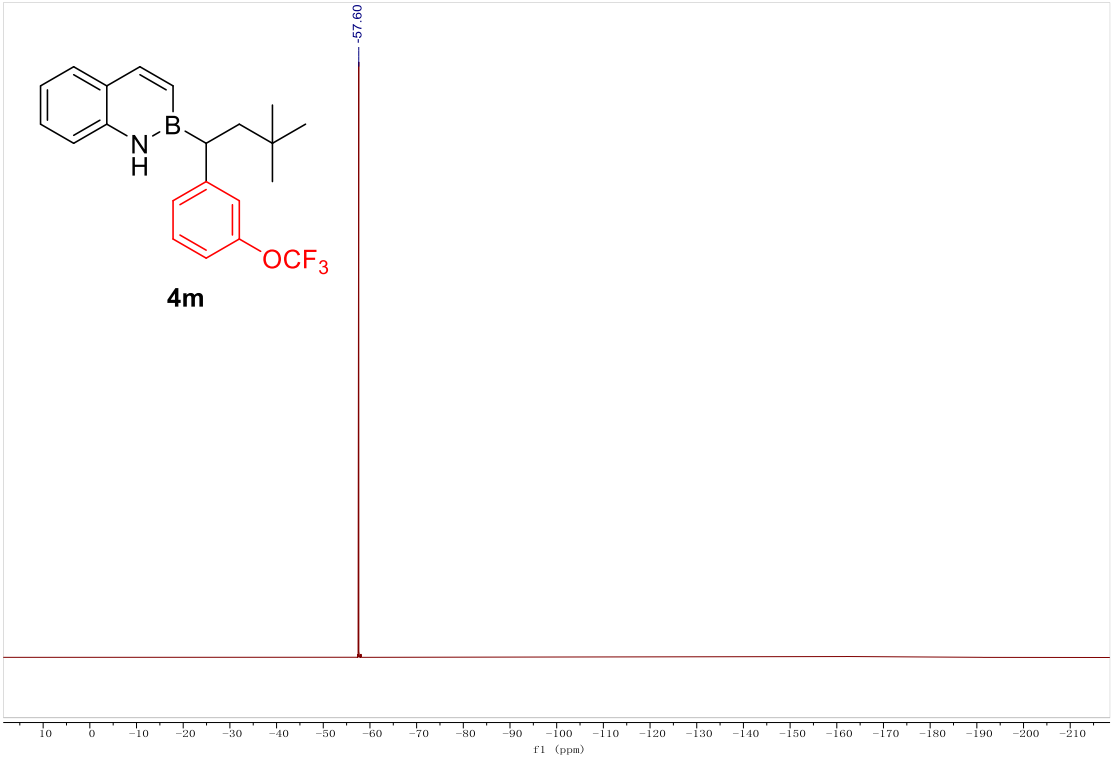
$^{1}$H NMR of **4m** (400 MHz, $CDCl_3$)



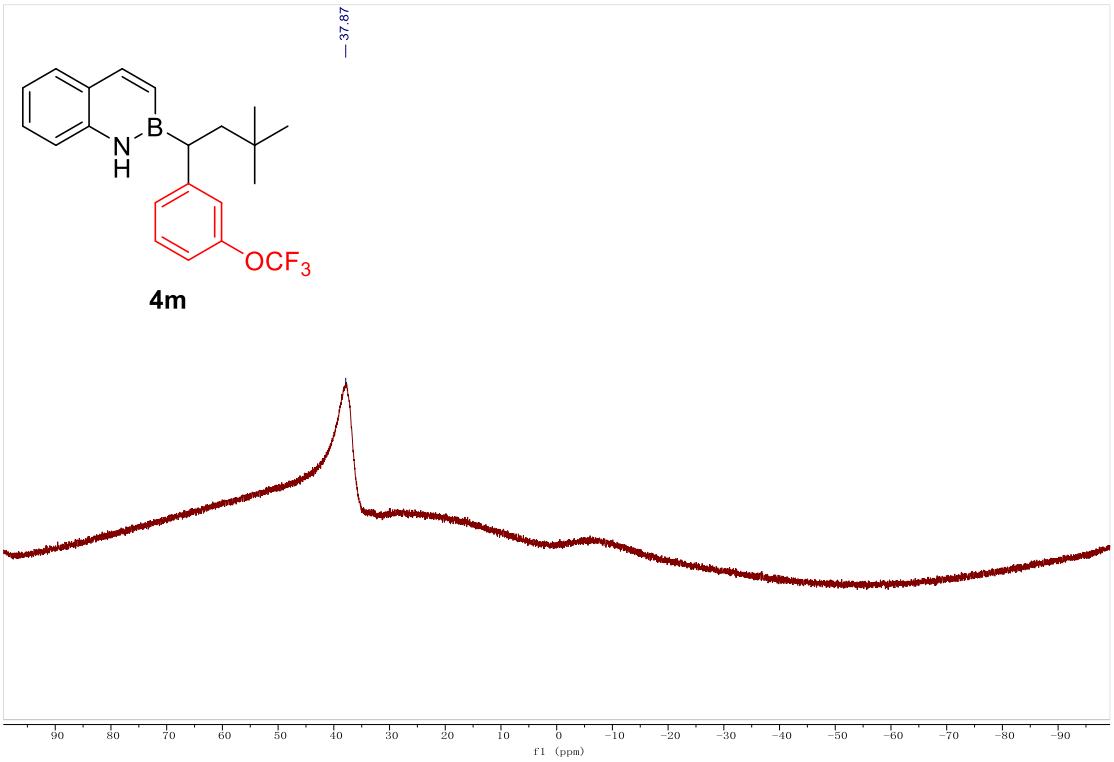

$^{13}$C NMR of **4m** (101 MHz, $CDCl_3$)



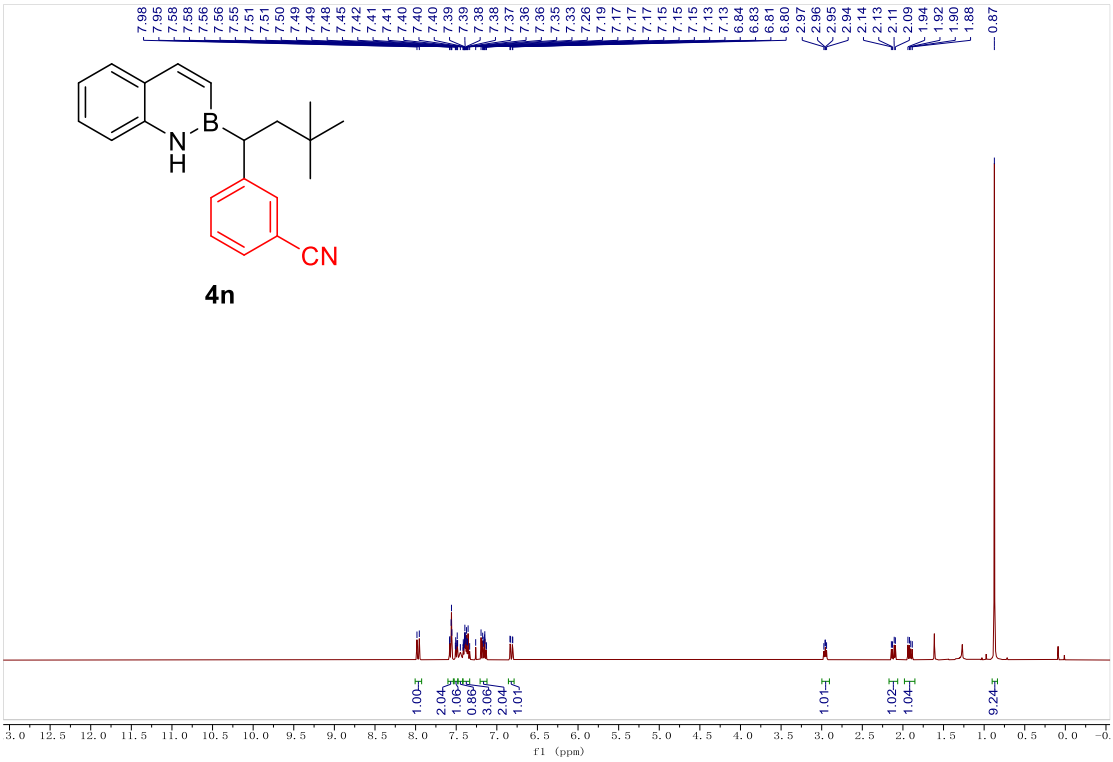
$^{19}$F NMR of **4m** (376 MHz, $CDCl_3$)



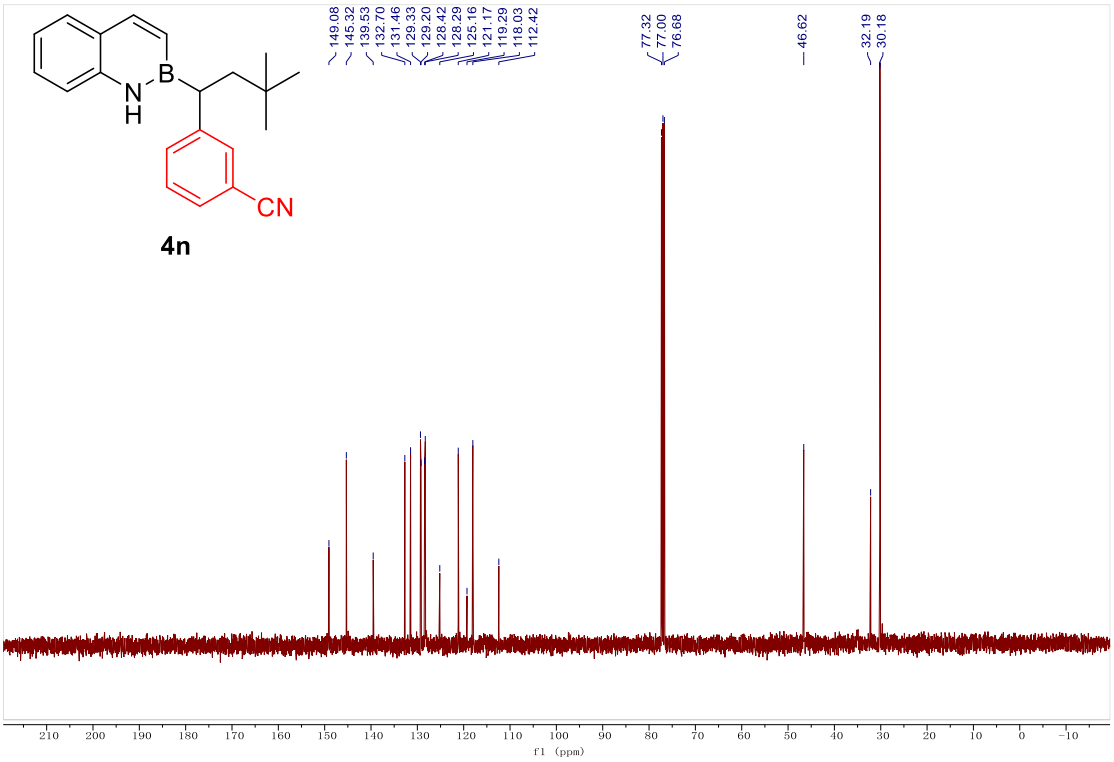

$^{11}$B NMR of **4m** (128 MHz, $CDCl_3$)



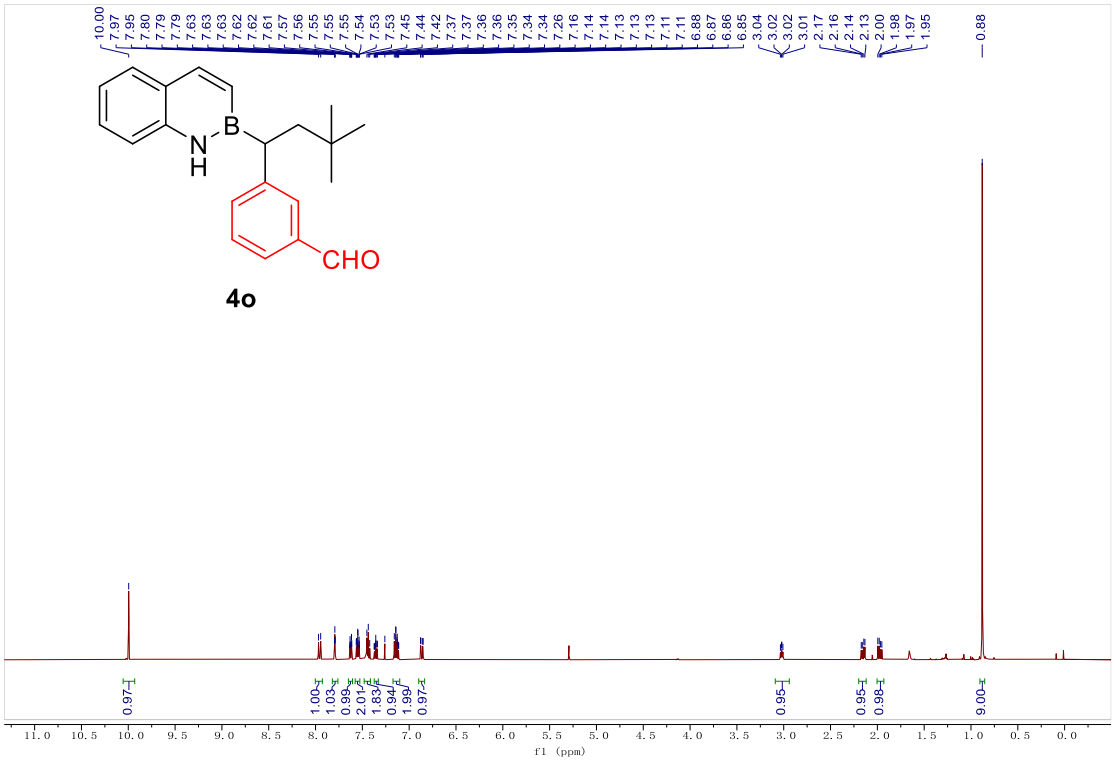
$^{1}$H NMR of **4n** (400 MHz, $CDCl_3$)



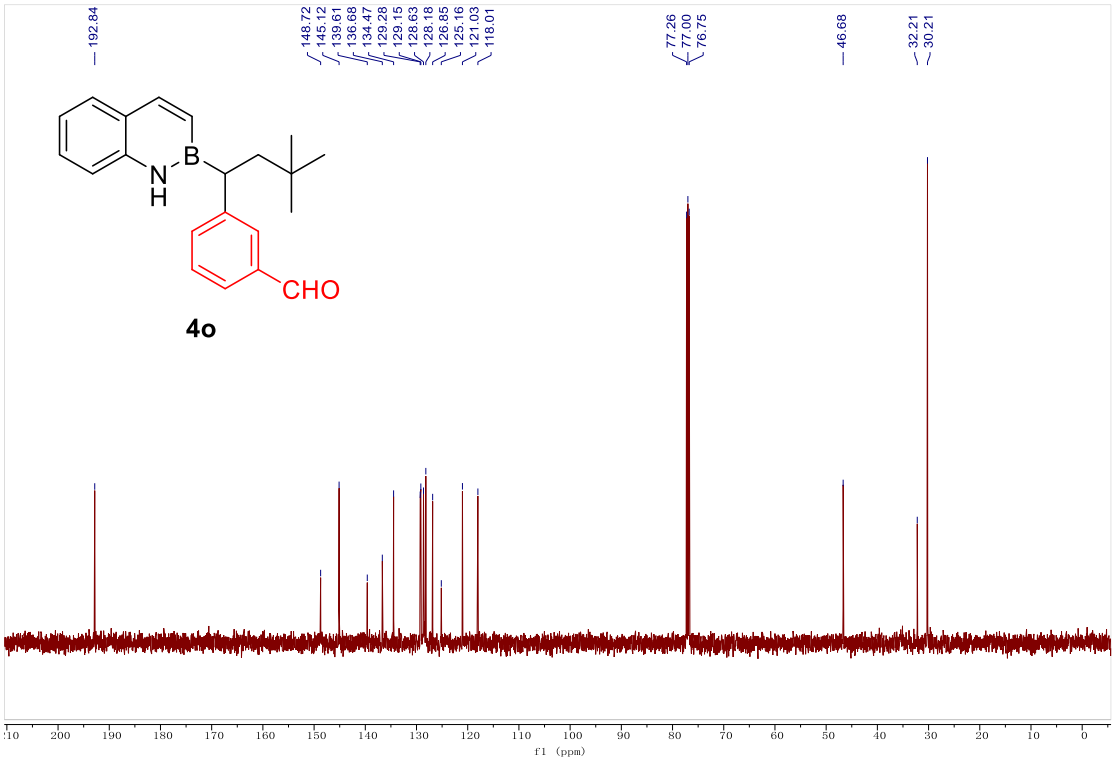

$^{13}$C NMR of **4n** (101 MHz, $CDCl_3$)



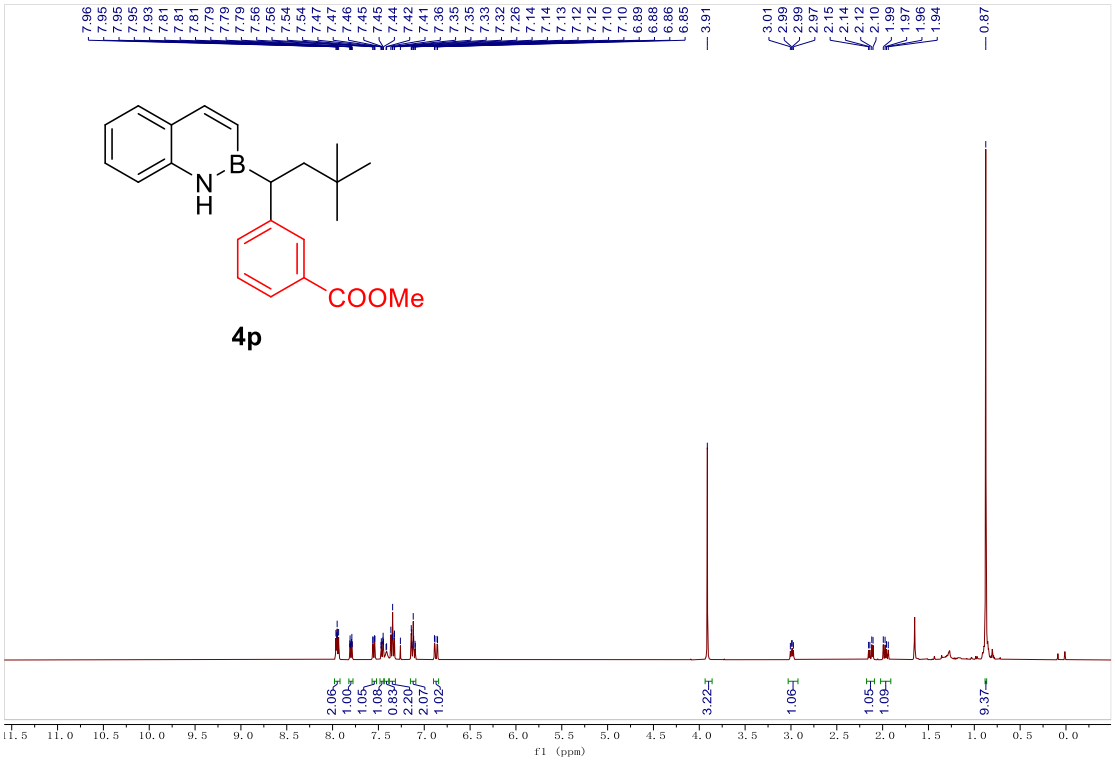
$^{1}$H NMR of **4o** (500 MHz, $CDCl_3$)



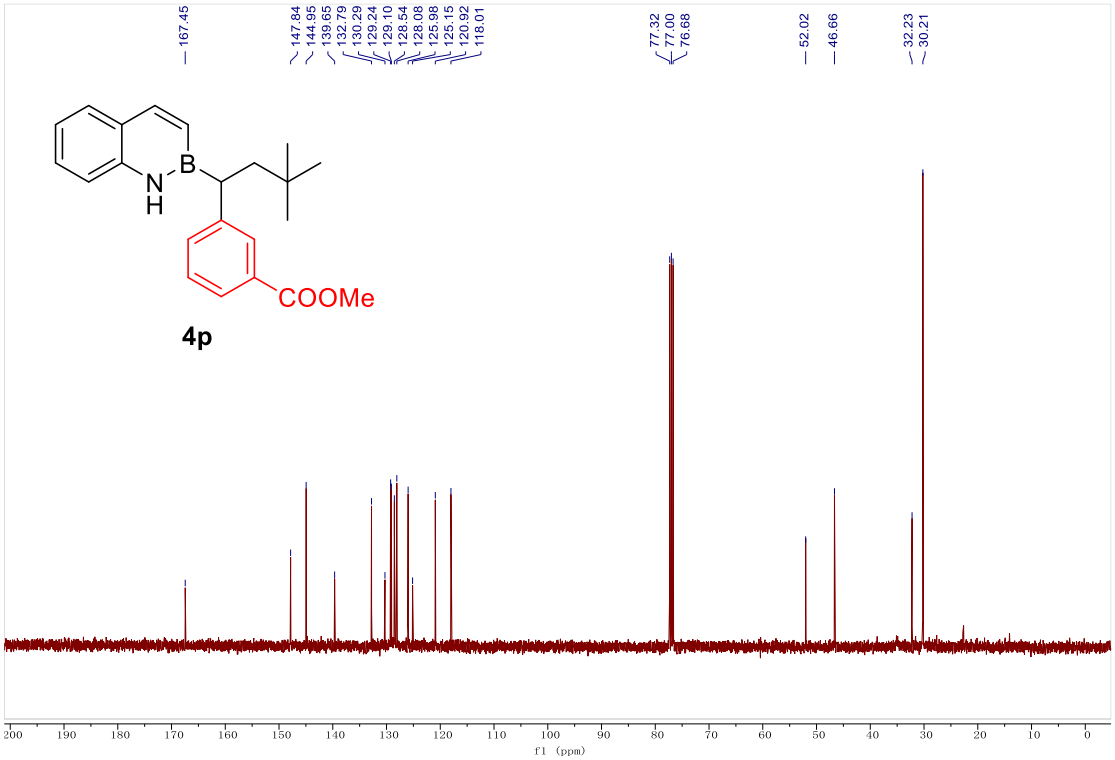

$^{13}$C NMR of **4o** (126 MHz, $CDCl_3$)



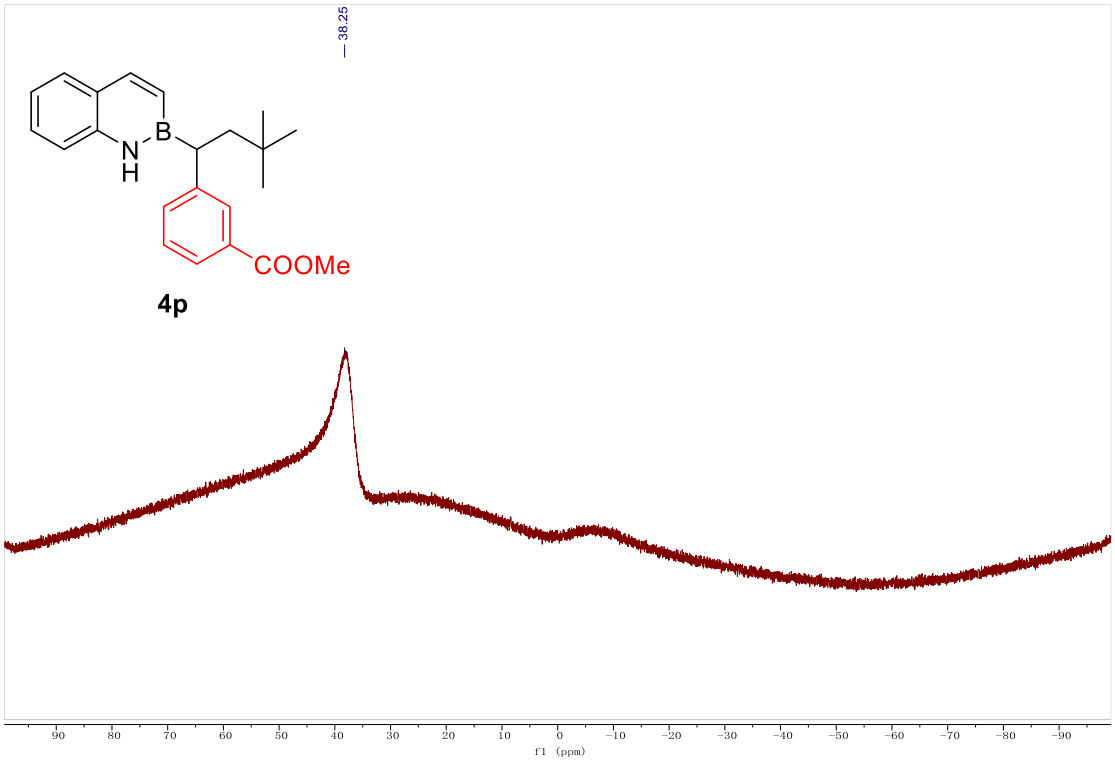
$^{1}$H NMR of **4p** (400 MHz, $CDCl_3$)



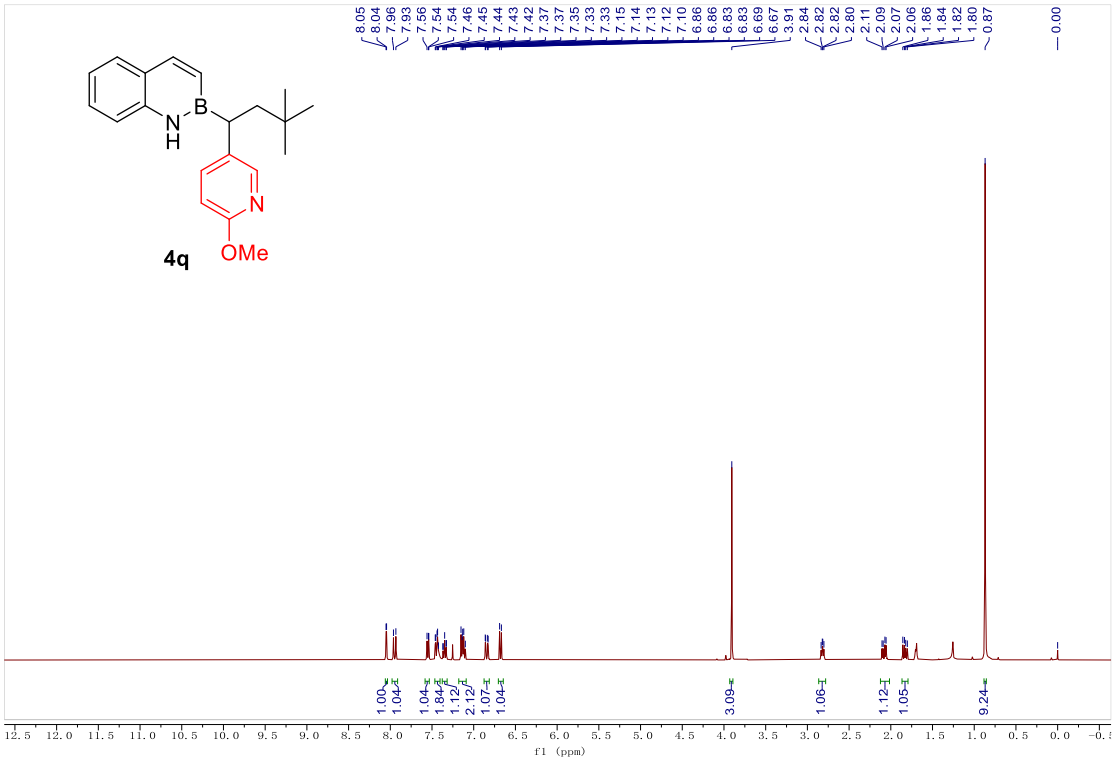

$^{13}$C NMR of **4p** (101 MHz, $CDCl_3$)



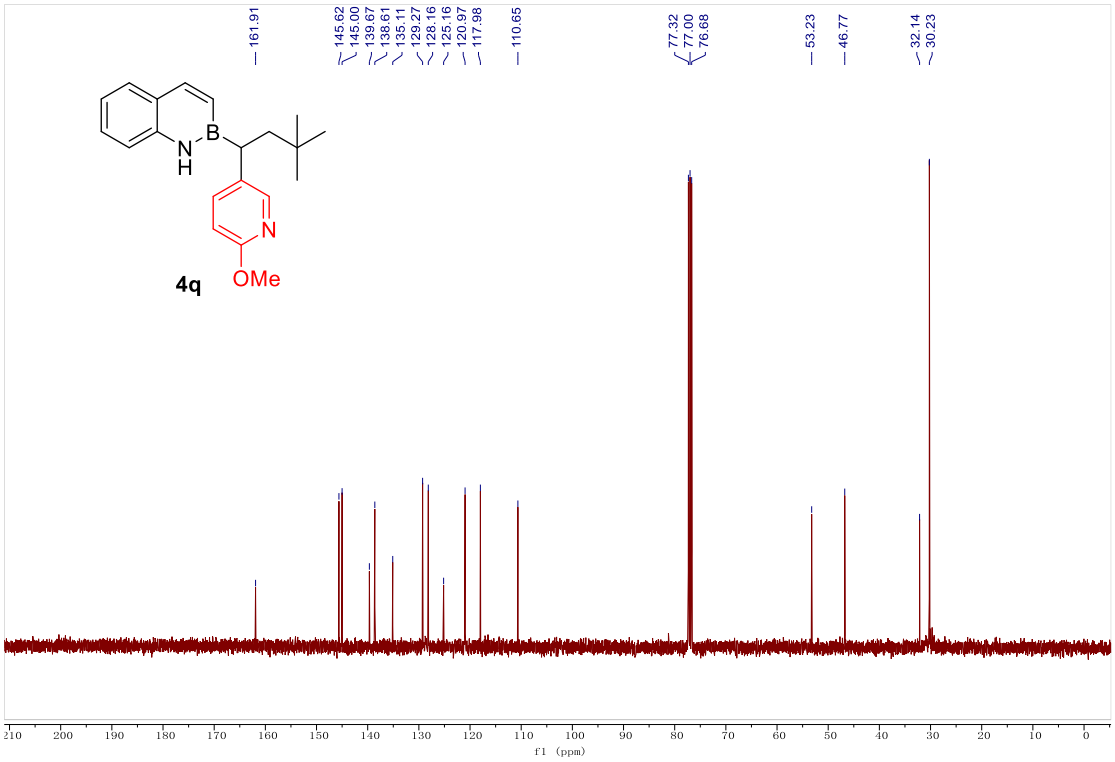
$^{11}$B NMR of **4p** (128 MHz, $CDCl_3$)



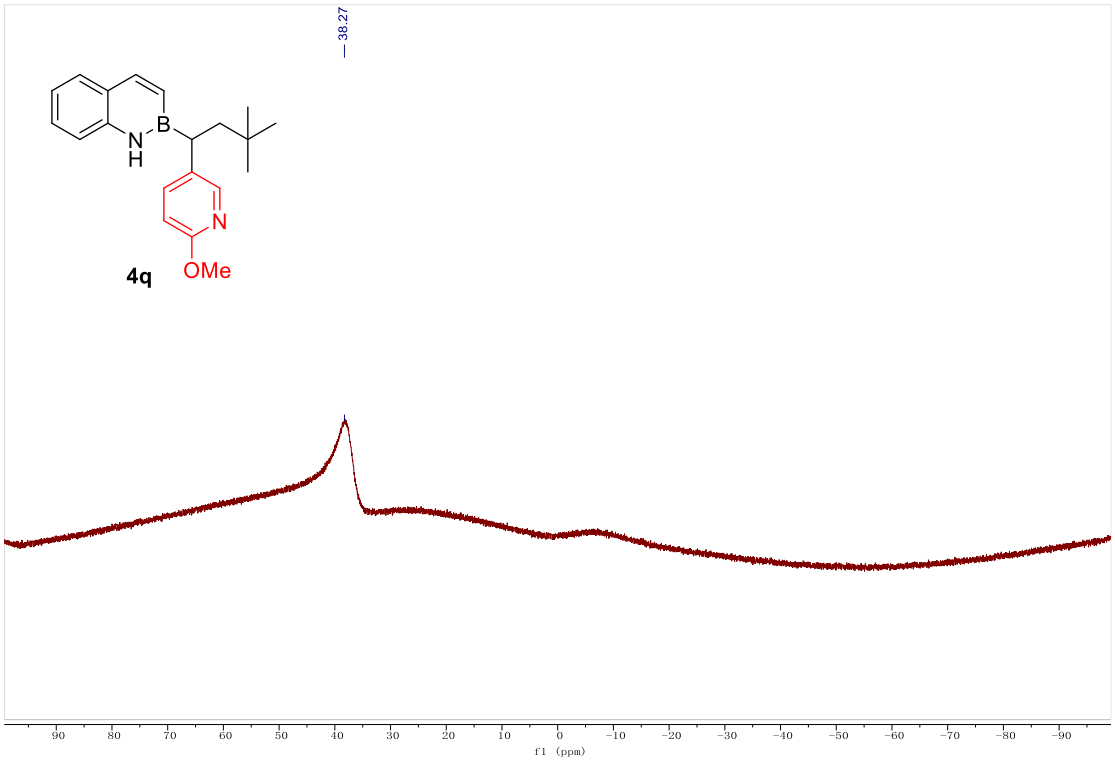

$^{1}$H NMR of **4q** (400 MHz, $CDCl_3$)



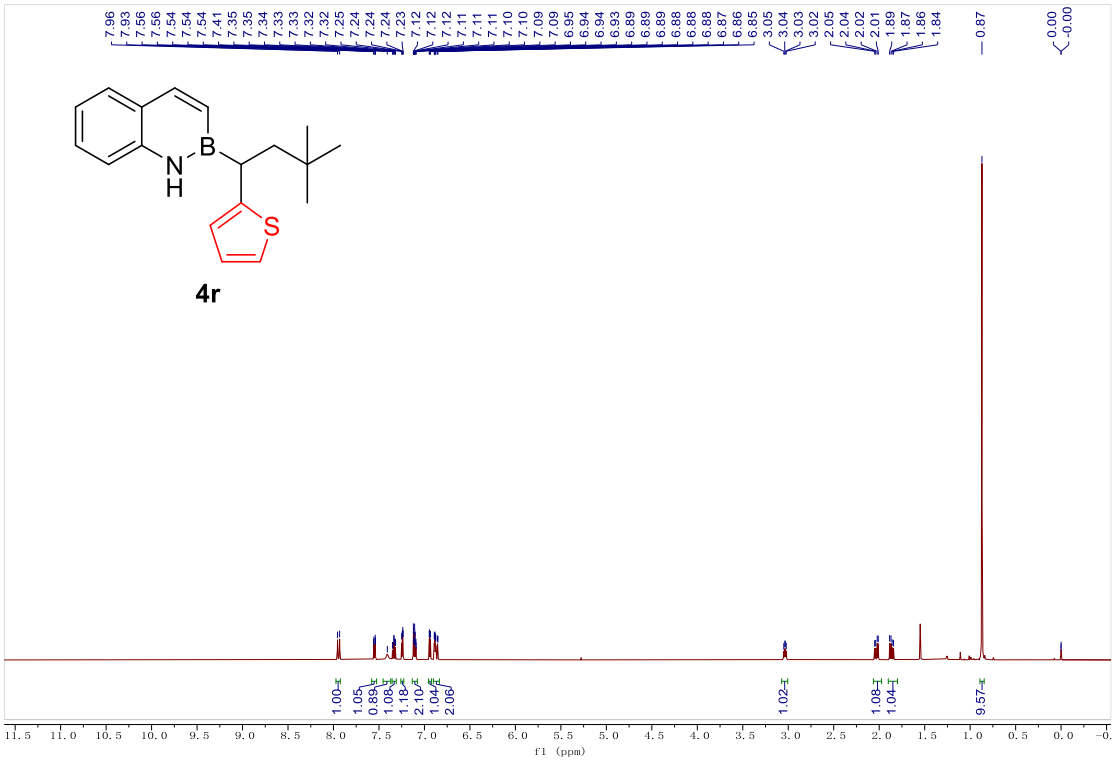
$^{13}$C NMR of **4q** (101 MHz, $CDCl_3$)



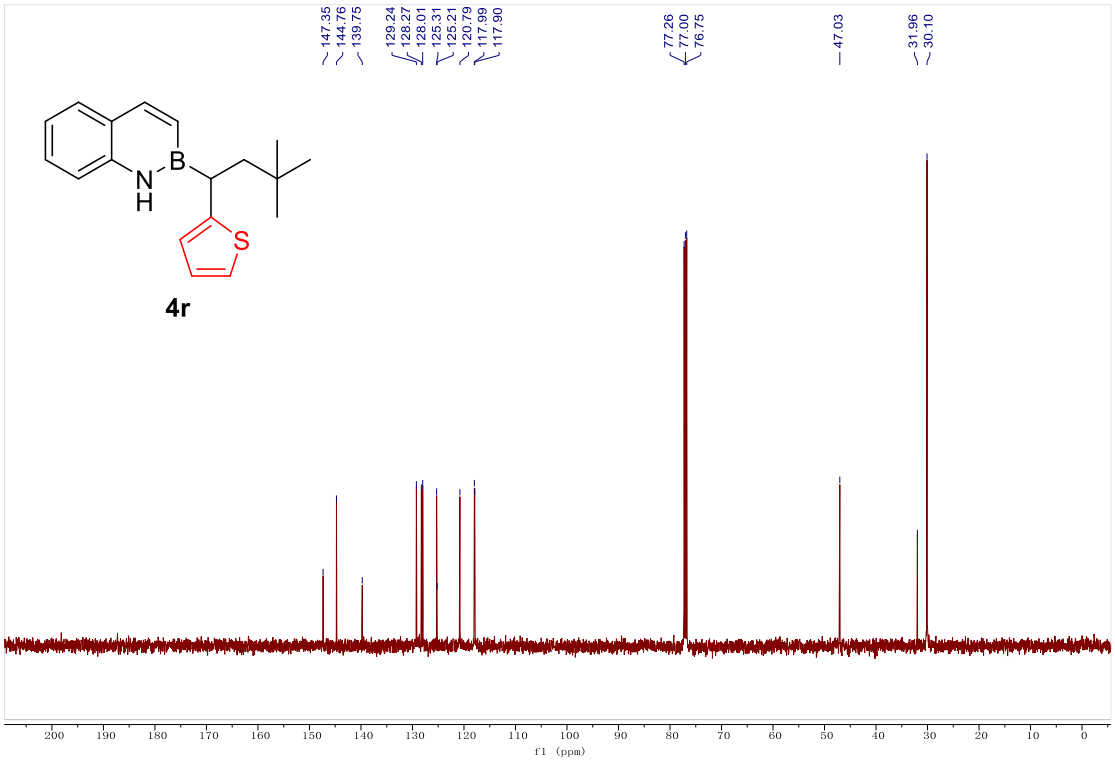

$^{11}$B NMR of **4q** (128 MHz, $CDCl_3$)



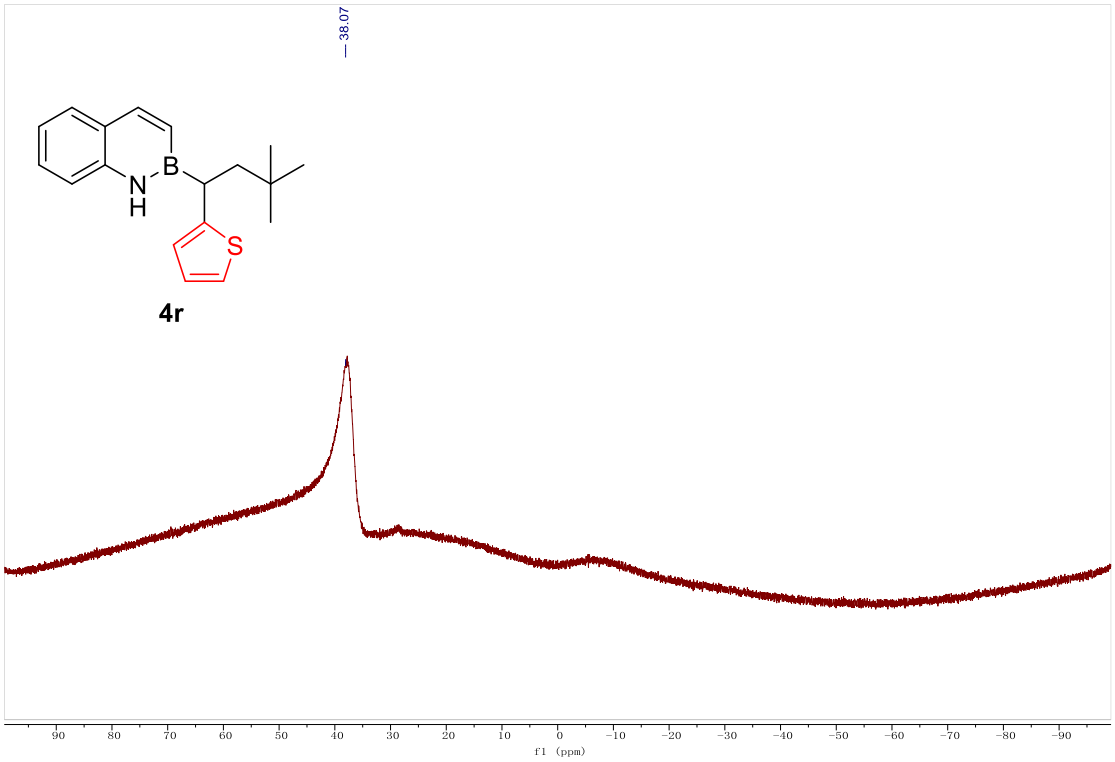
$^{1}$H NMR of **4r** (500 MHz, $CDCl_3$)



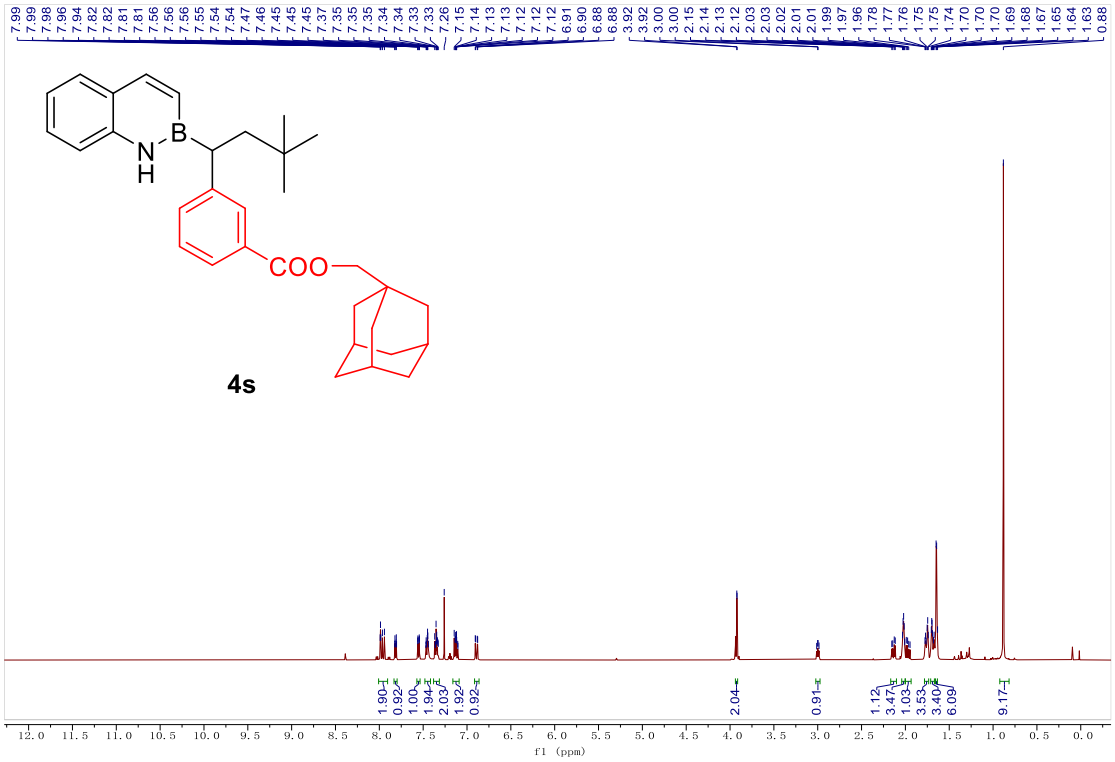

$^{13}$C NMR of **4r** (126 MHz, $CDCl_3$)



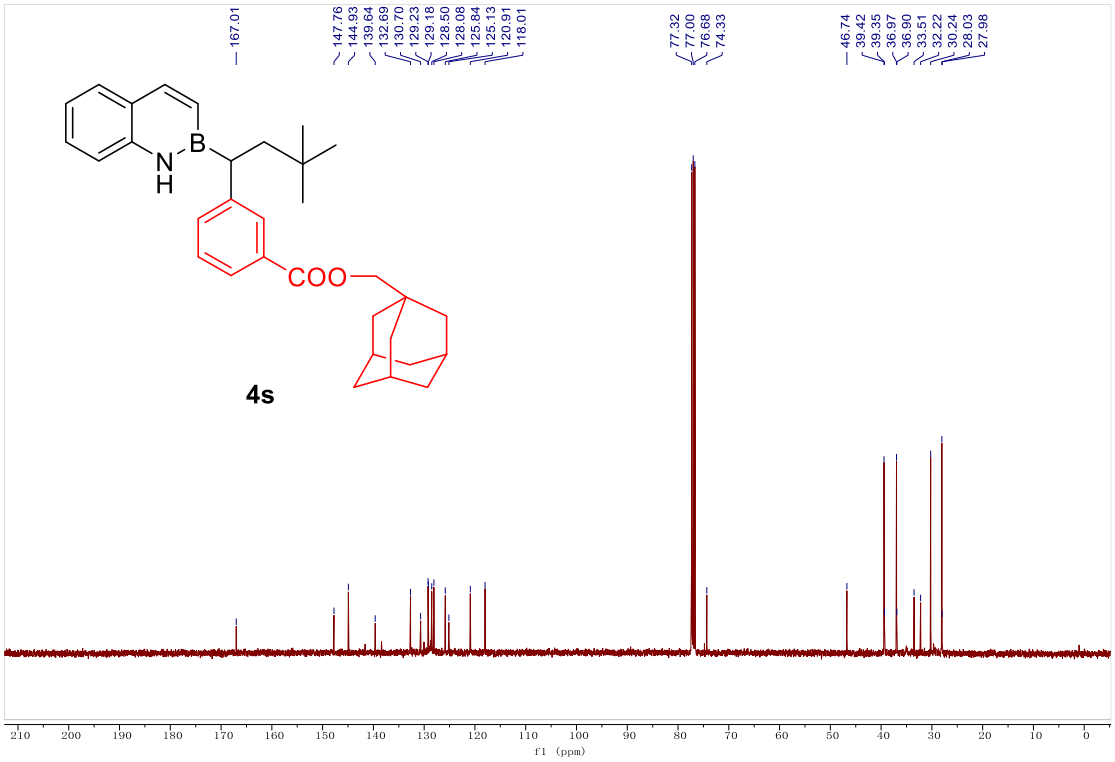
$^{11}$B NMR of **4r** (128 MHz, $CDCl_3$)



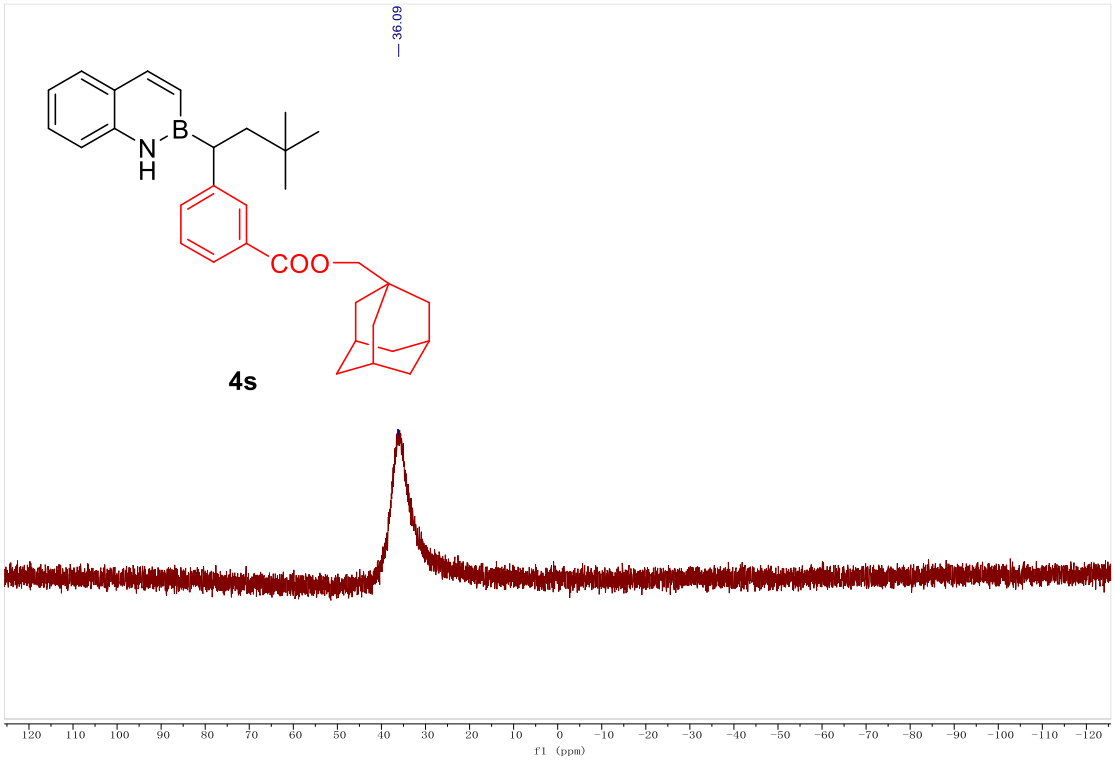

$^{1}$H NMR of **4s** (500 MHz, $CDCl_3$)



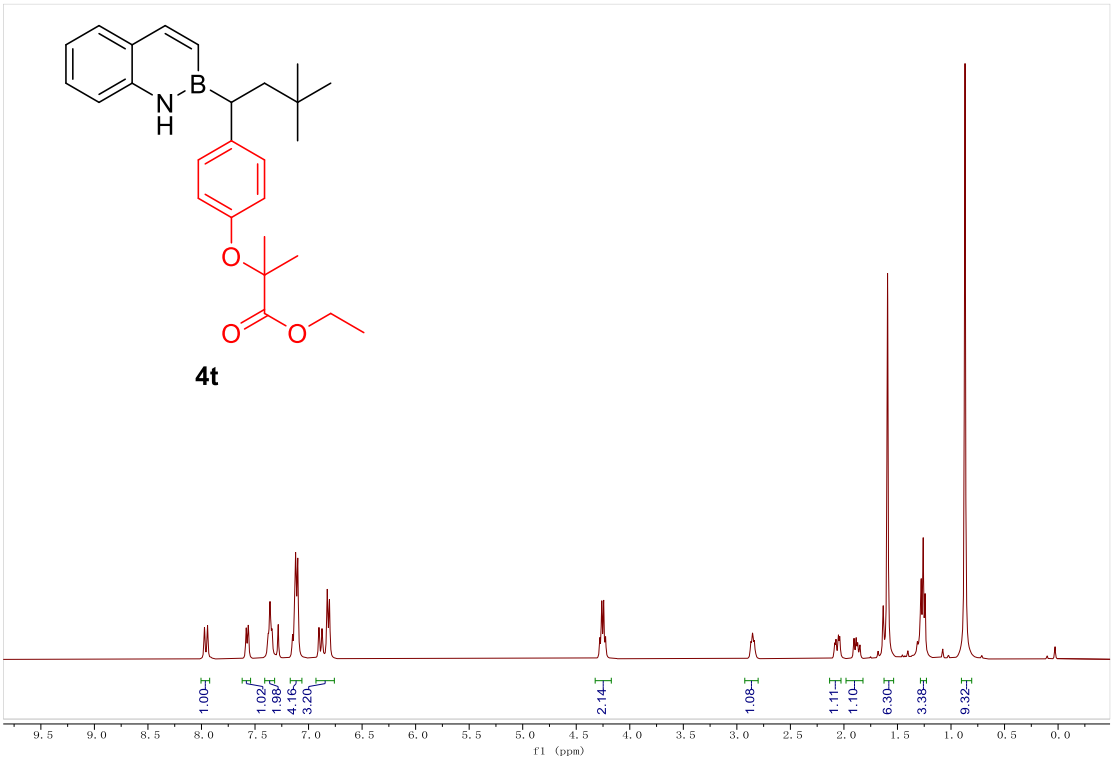
$^{13}$C NMR of **4s** (101 MHz, $CDCl_3$)



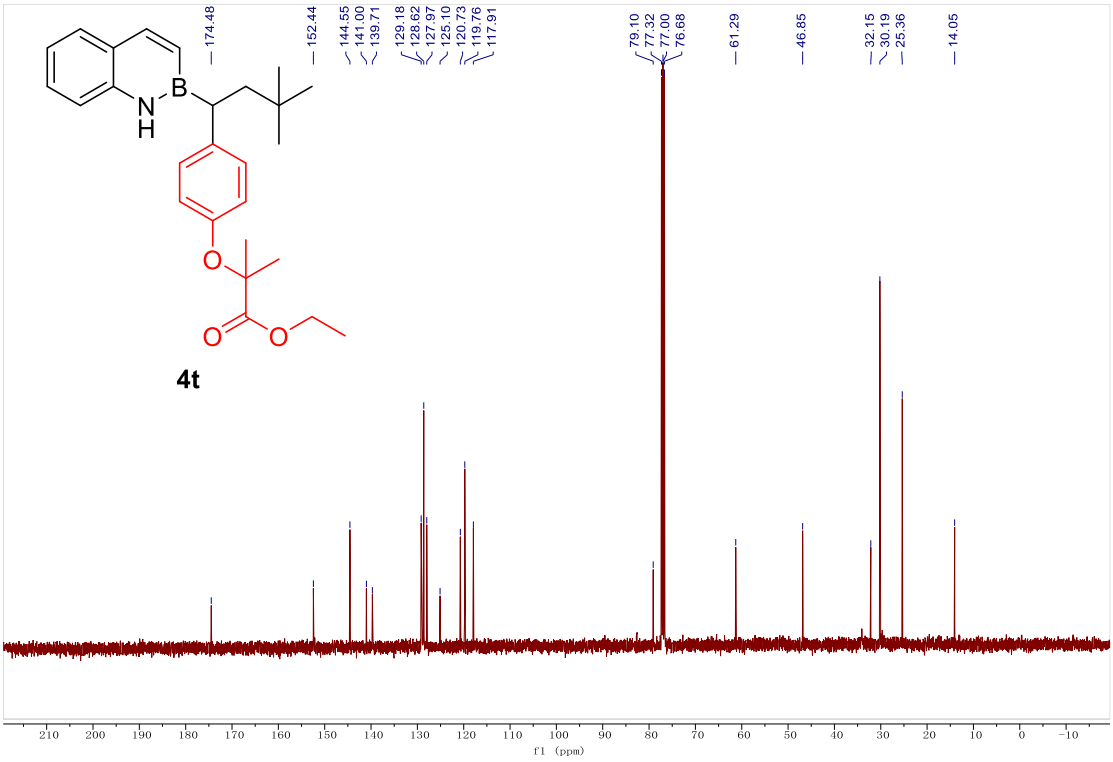

$^{11}$B NMR of **4s** (128 MHz, $CDCl_3$)



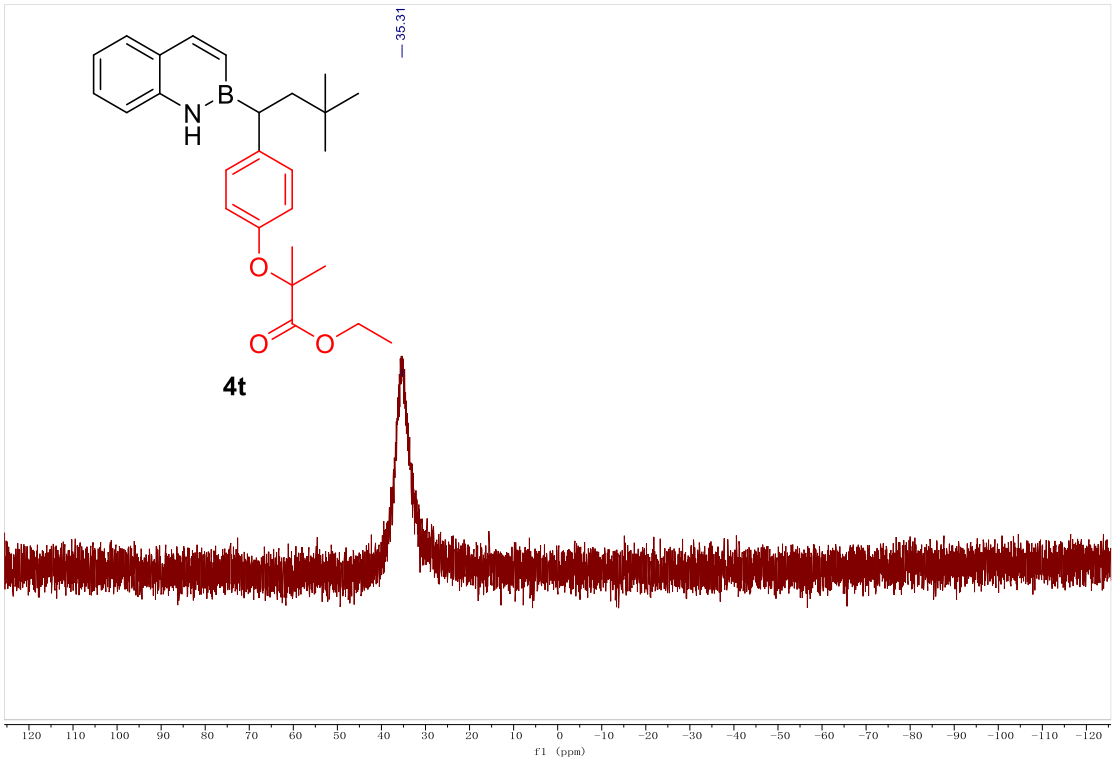
$^{1}$H NMR of **4t** (400 MHz, $CDCl_3$)



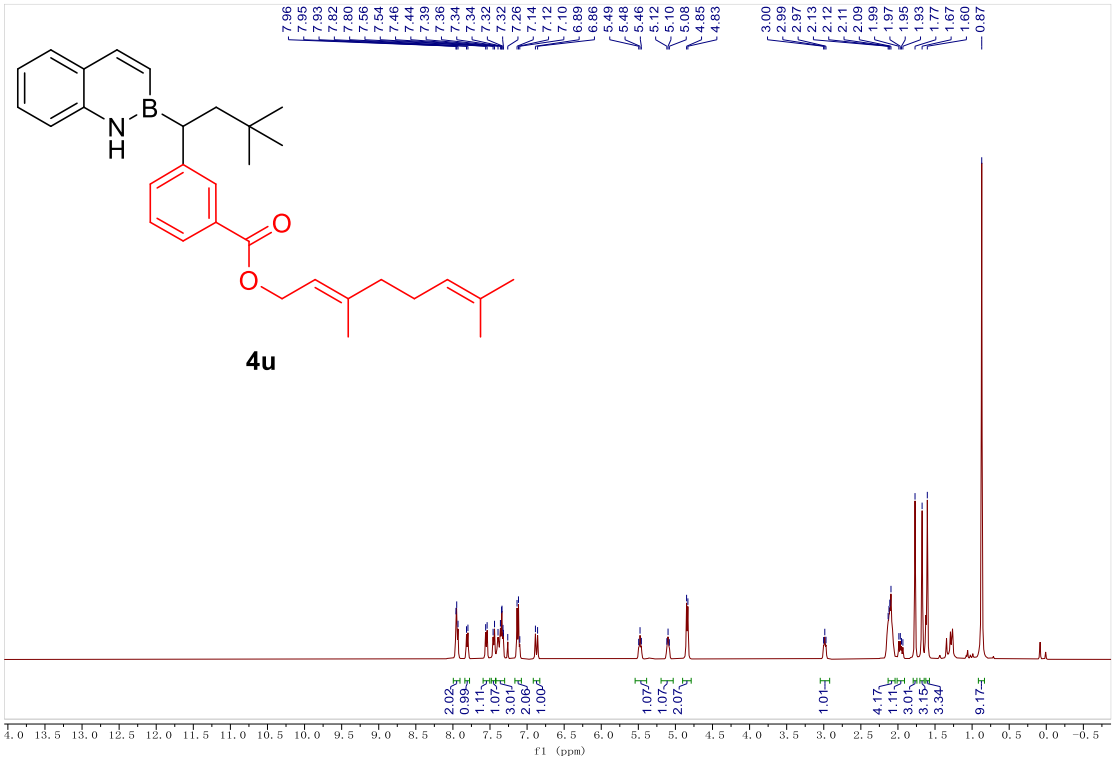

$^{13}$C NMR of **4t** (101 MHz, $CDCl_3$)



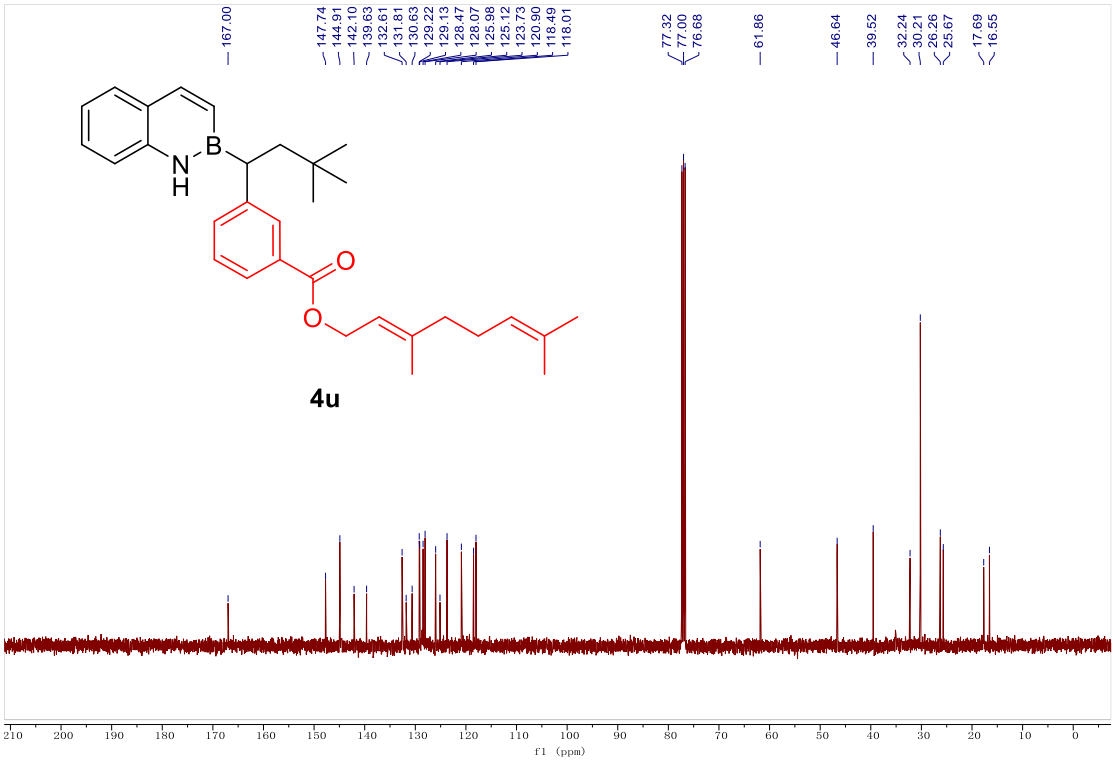
$^{11}$B NMR of **4t** (128 MHz, $CDCl_3$)



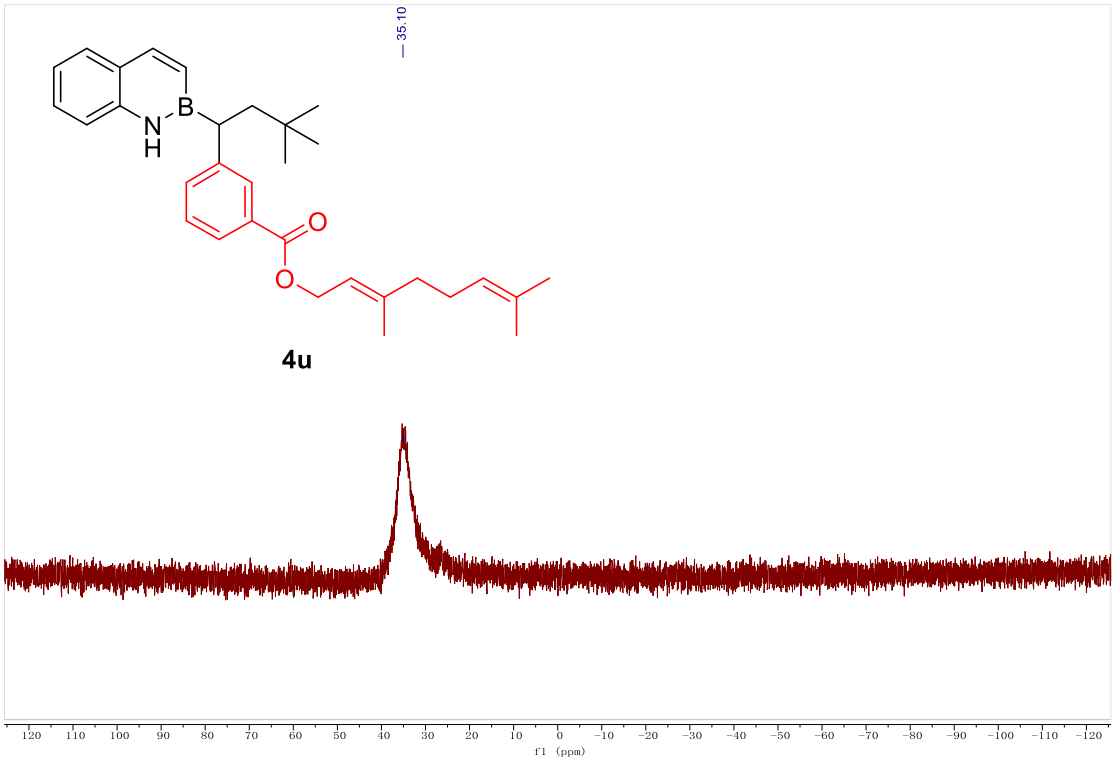

$^{1}$H NMR of **4u** (400 MHz, $CDCl_3$)



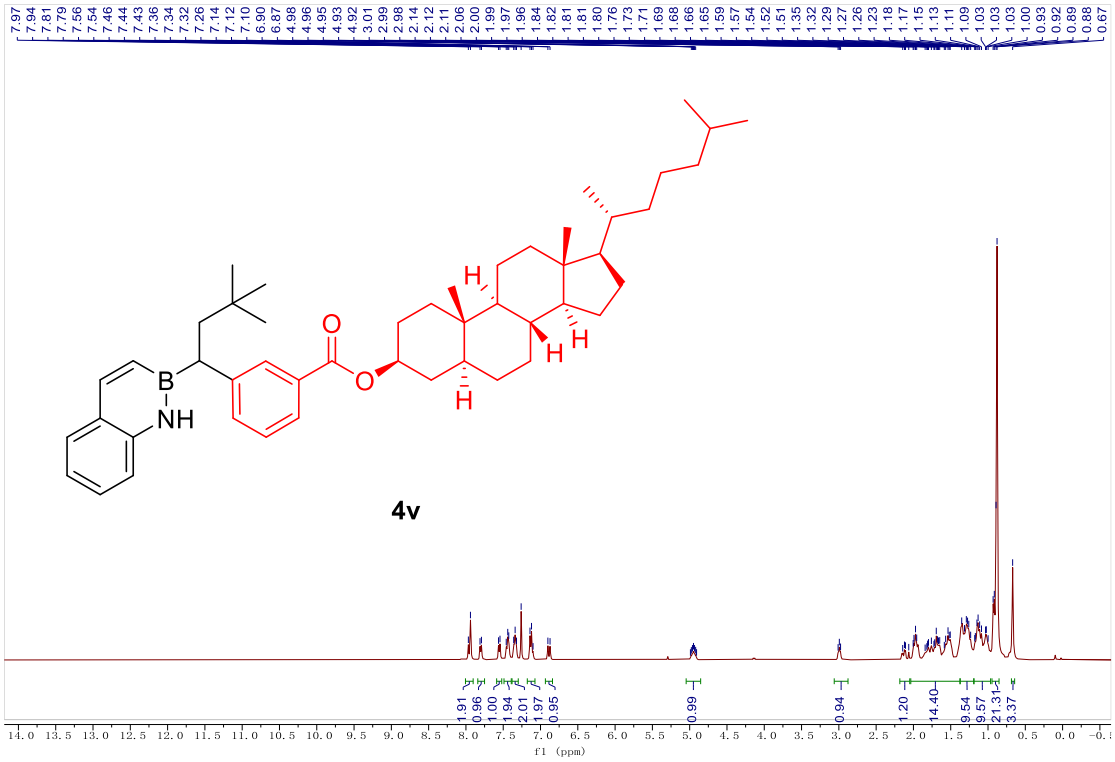
$^{13}$C NMR of **4u** (101 MHz, $CDCl_3$)



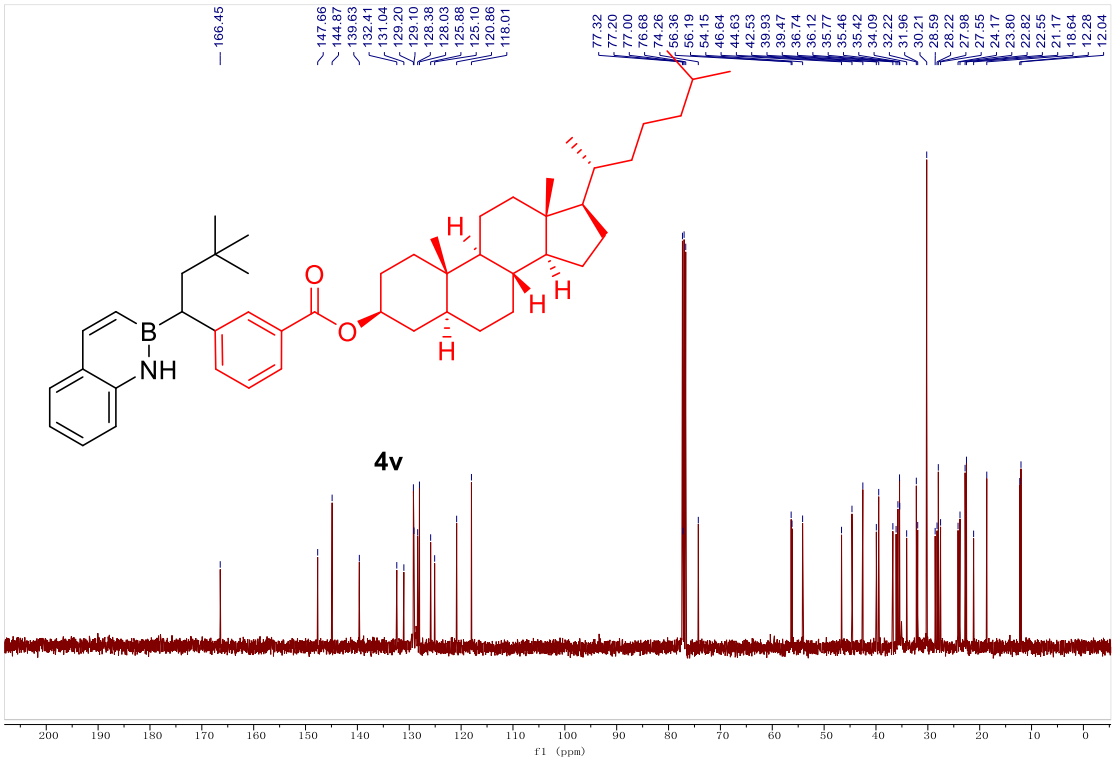

$^{11}$B NMR of **4u** (128 MHz, $CDCl_3$)



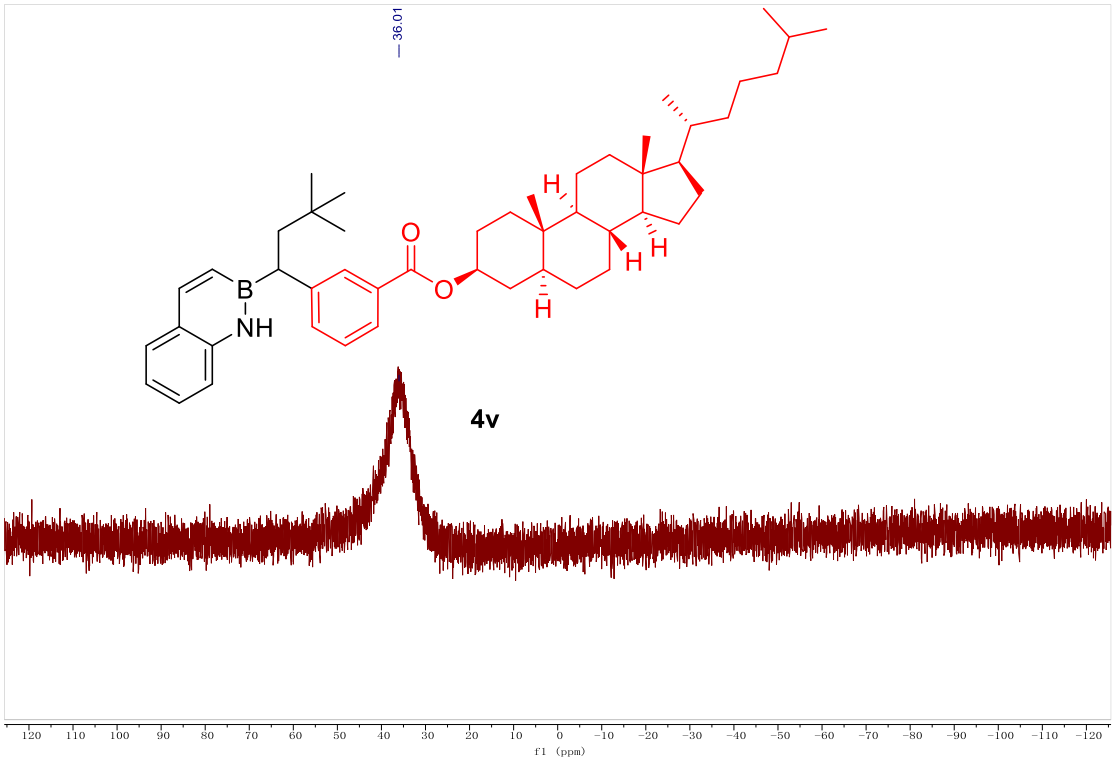
$^{1}$H NMR of **4v** (400 MHz, $CDCl_3$)



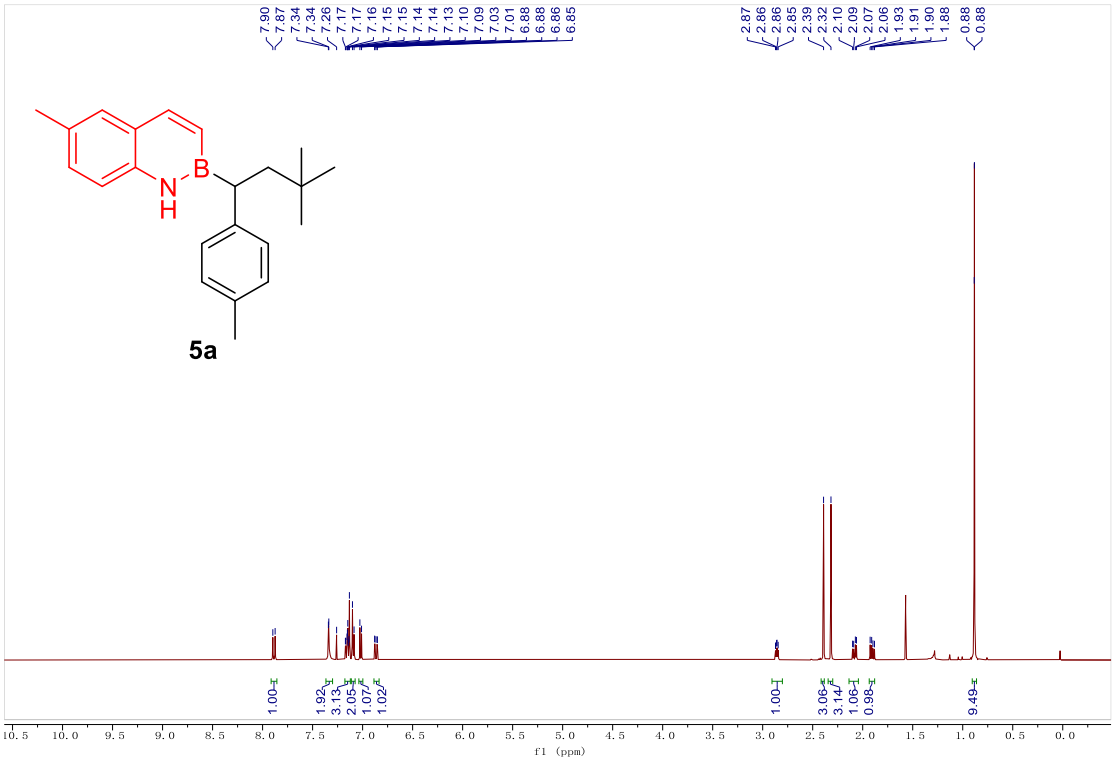

$^{13}$C NMR of **4v** (101 MHz, $CDCl_3$)



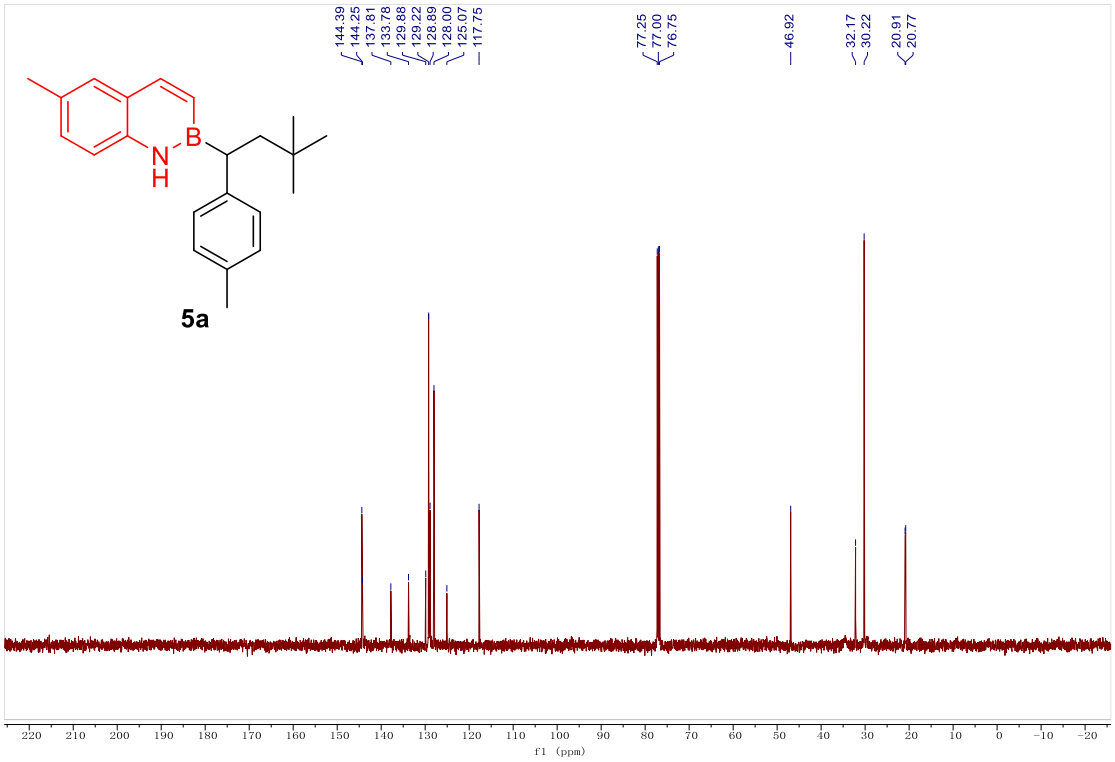
$^{11}$B NMR of **4v** (128 MHz, $CDCl_3$)



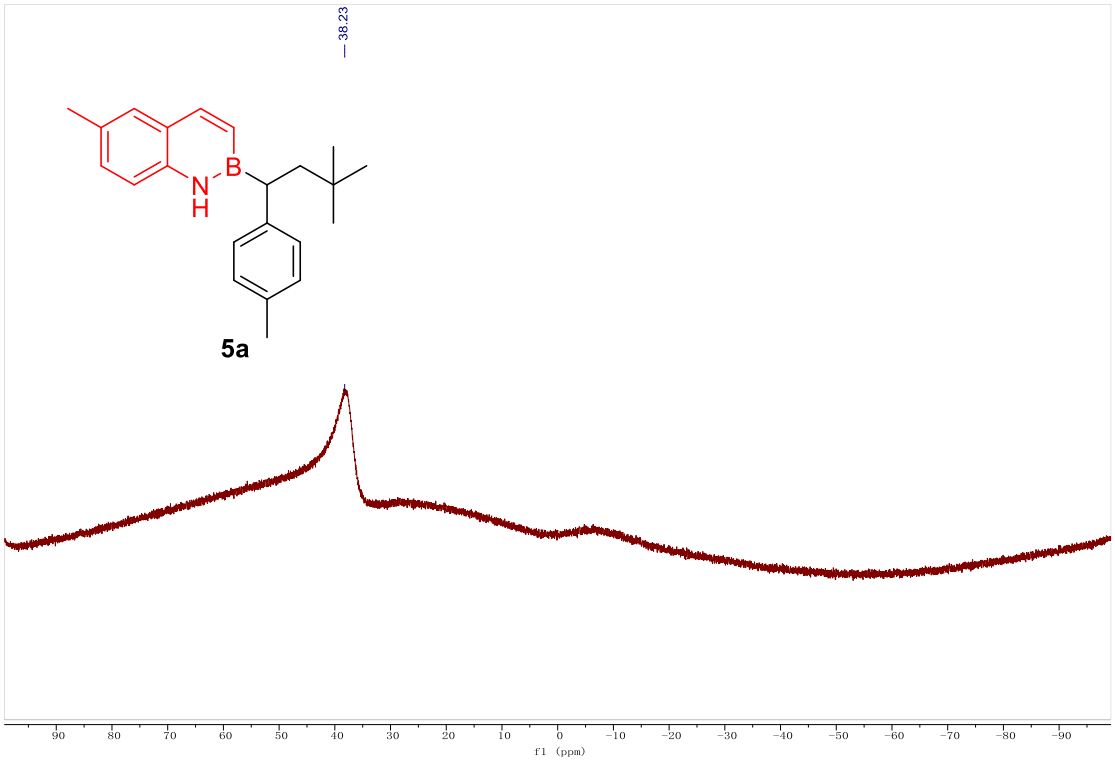

$^{1}$H NMR of **5a** (500 MHz, $CDCl_3$)



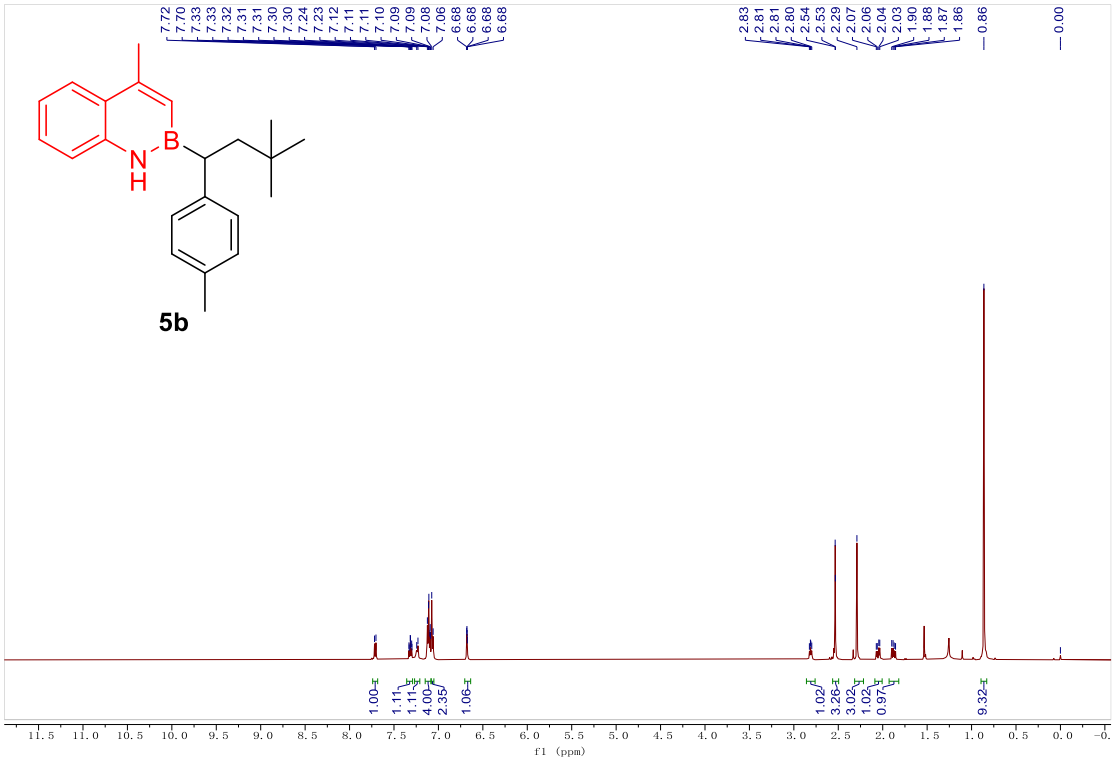
$^{13}$C NMR of **5a** (126 MHz, $CDCl_3$)



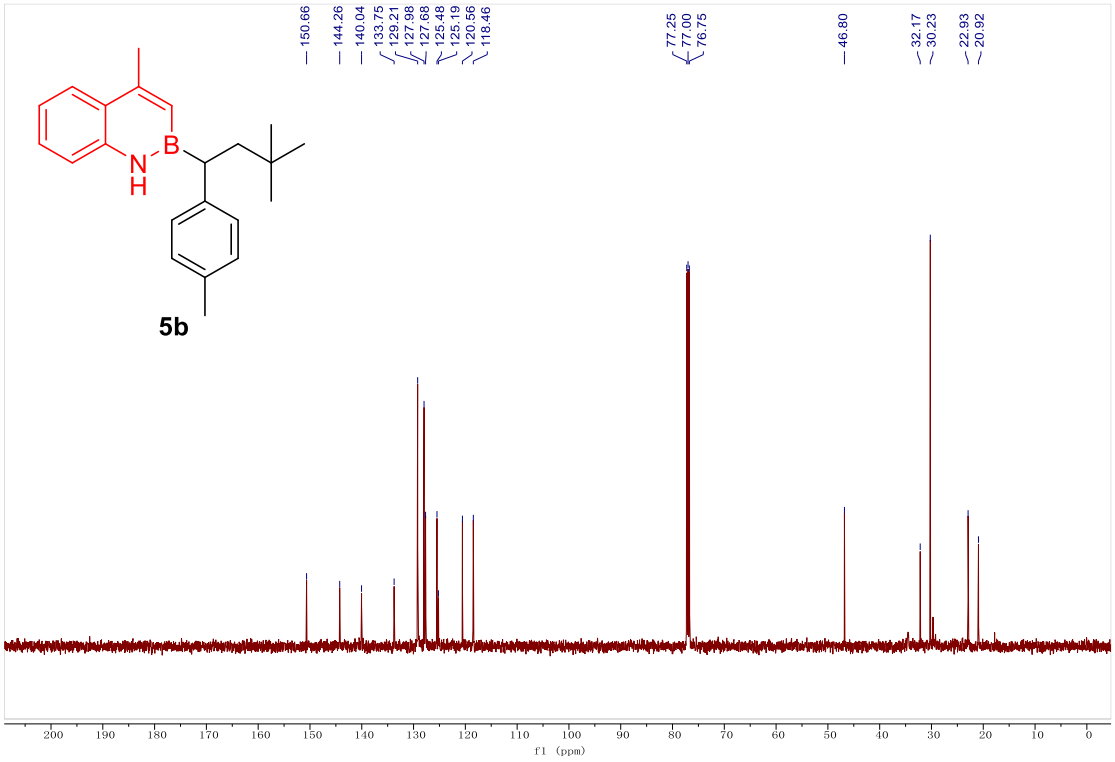

$^{11}$B NMR of **5a** (128 MHz, $CDCl_3$)



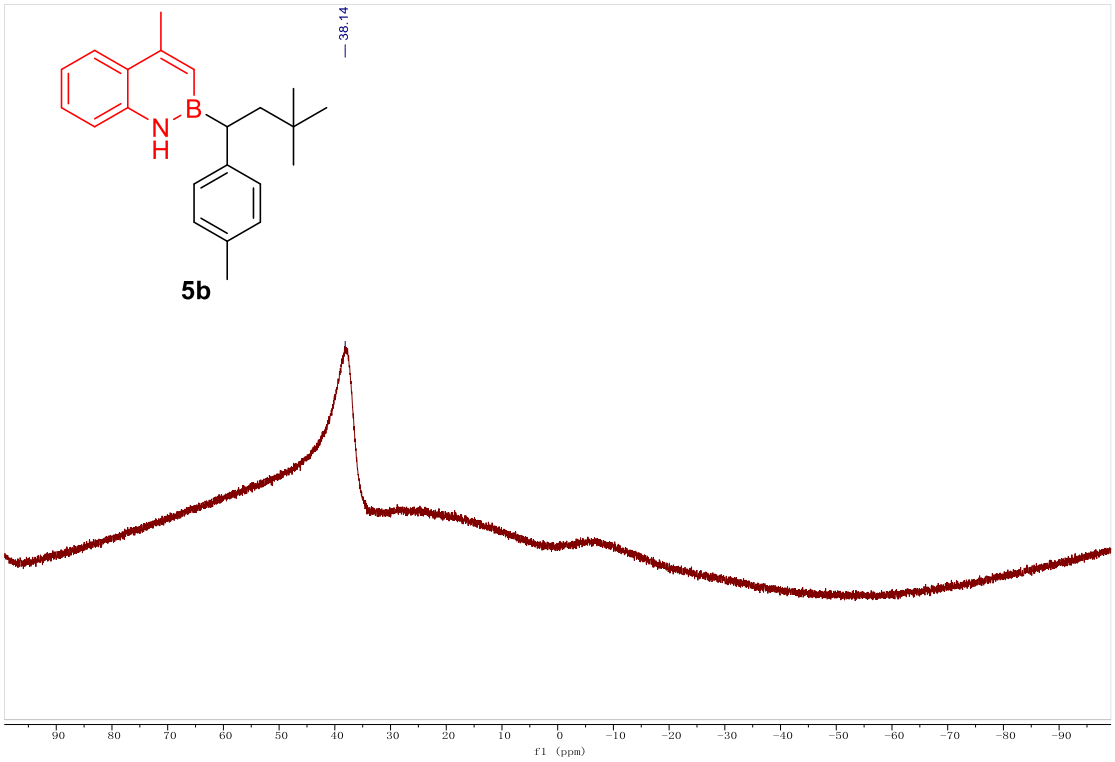
$^{1}$H NMR of **5b** (500 MHz, $CDCl_3$)



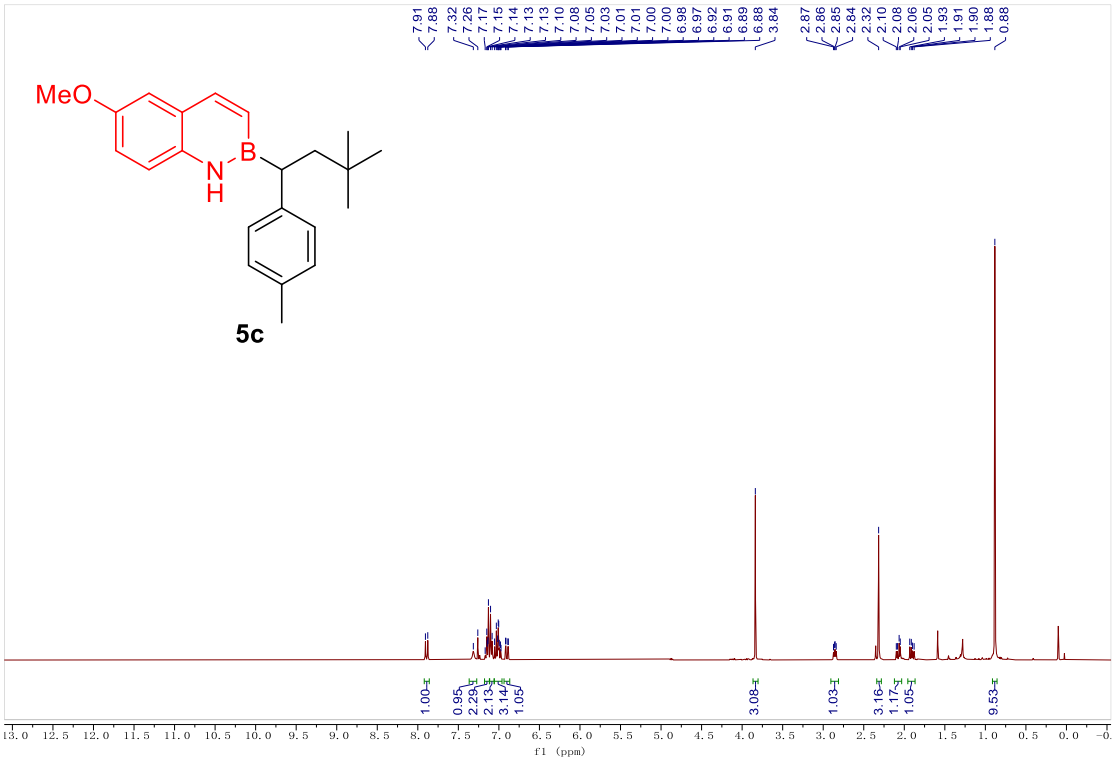

$^{13}$C NMR of **5b** (126 MHz, $CDCl_3$)



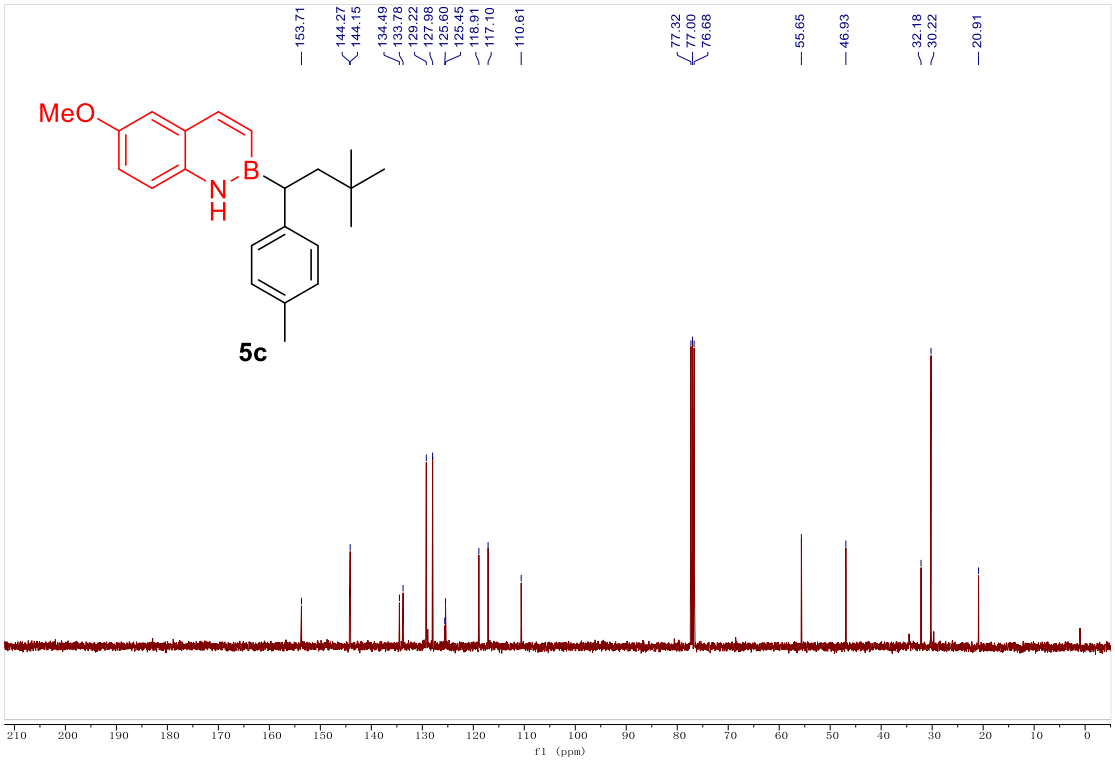
$^{11}$B NMR of **5b** (128 MHz, $CDCl_3$)



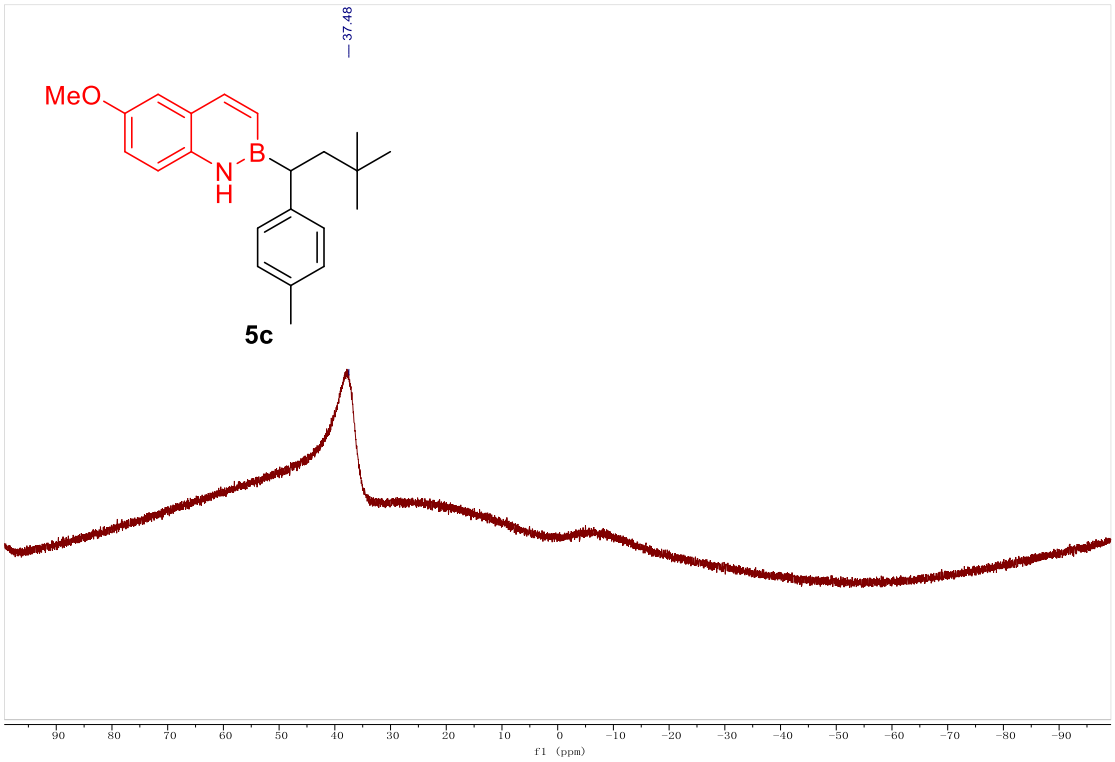

$^{1}$H NMR of **5c** (400 MHz, $CDCl_3$)



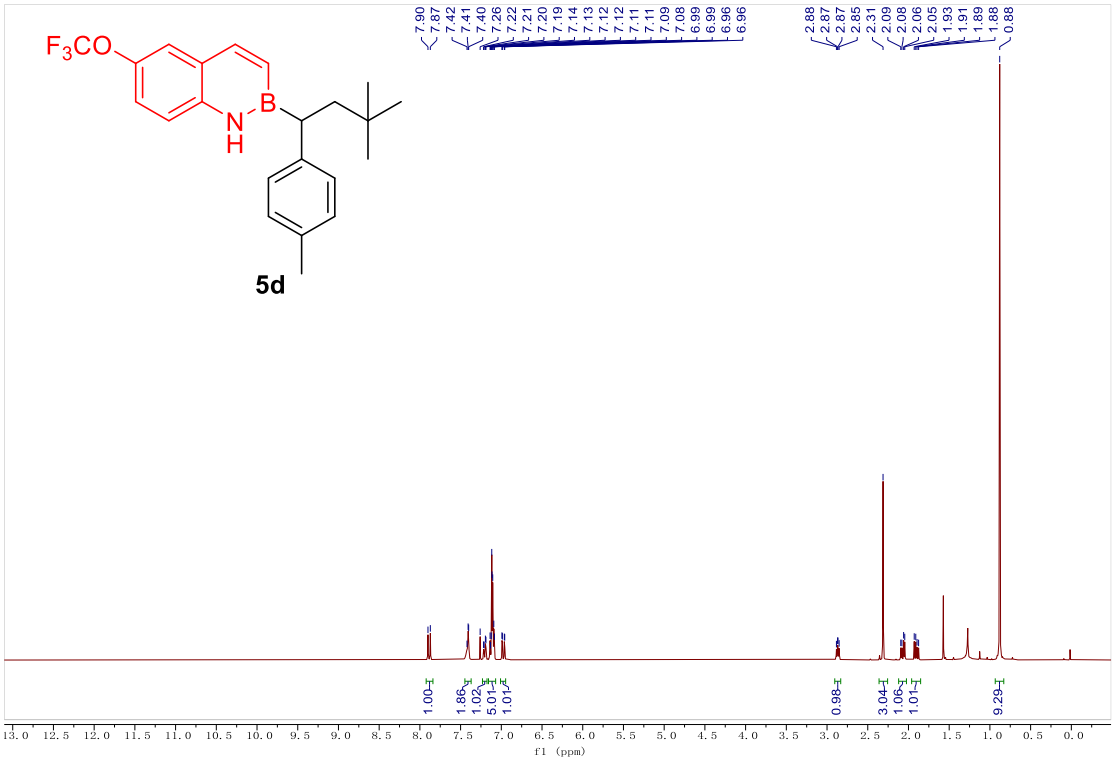
$^{13}$C NMR of **5c** (101 MHz, $CDCl_3$)



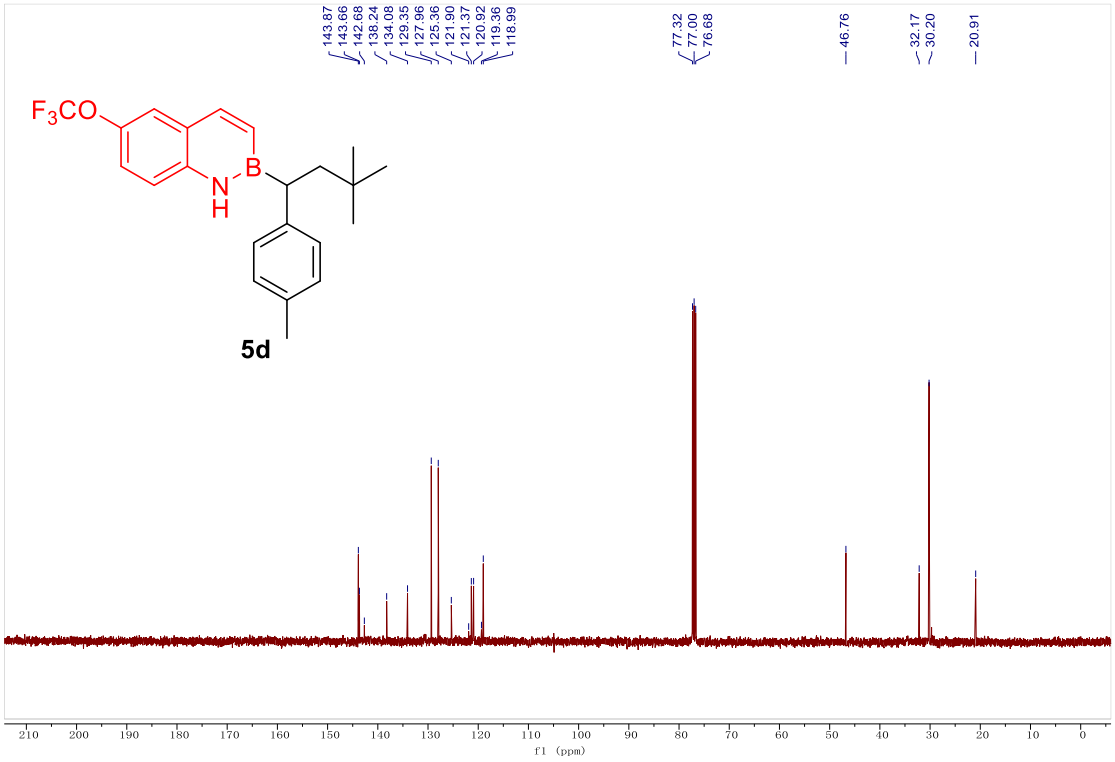

$^{11}$B NMR of **5c** (128 MHz, $CDCl_3$)



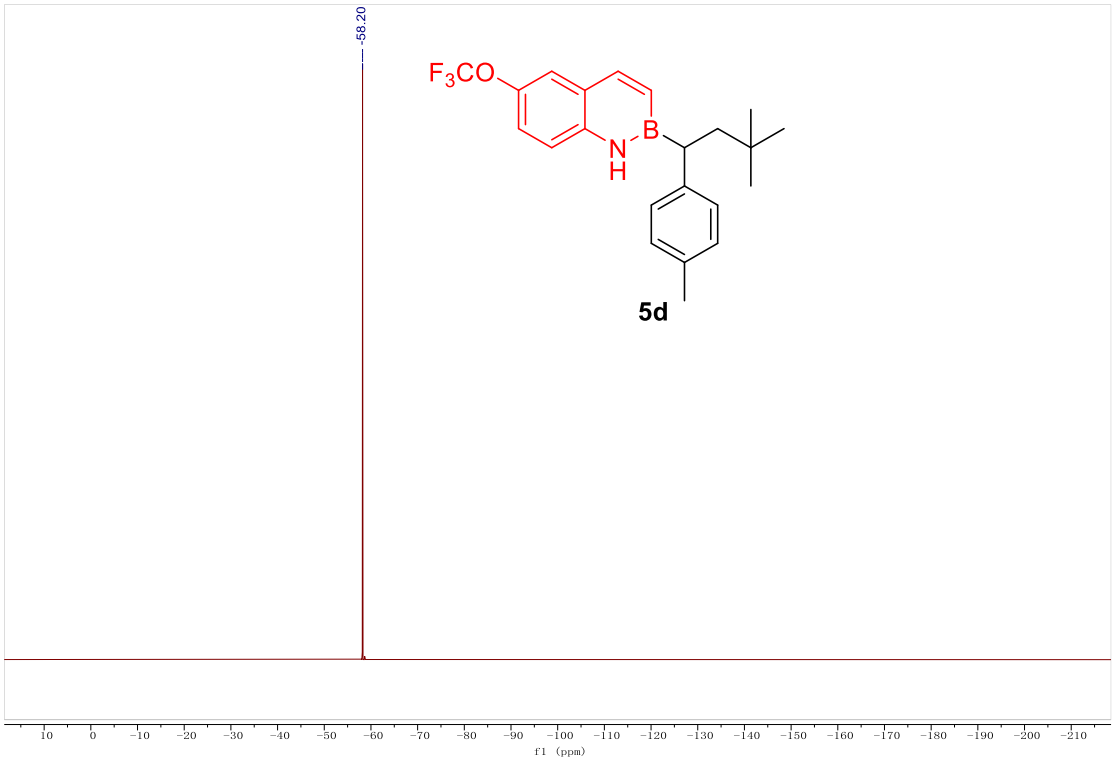
$^{1}$H NMR of **5d** (400 MHz, $CDCl_3$)



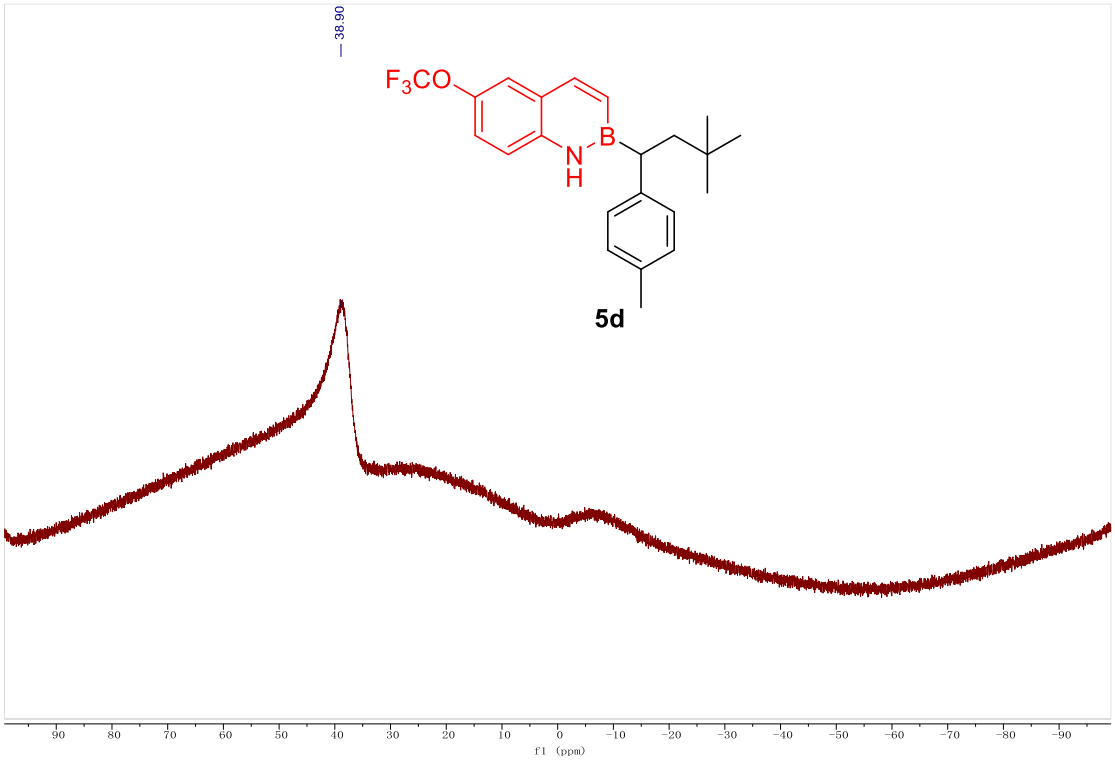

$^{13}$C NMR of **5d** (101 MHz, $CDCl_3$)



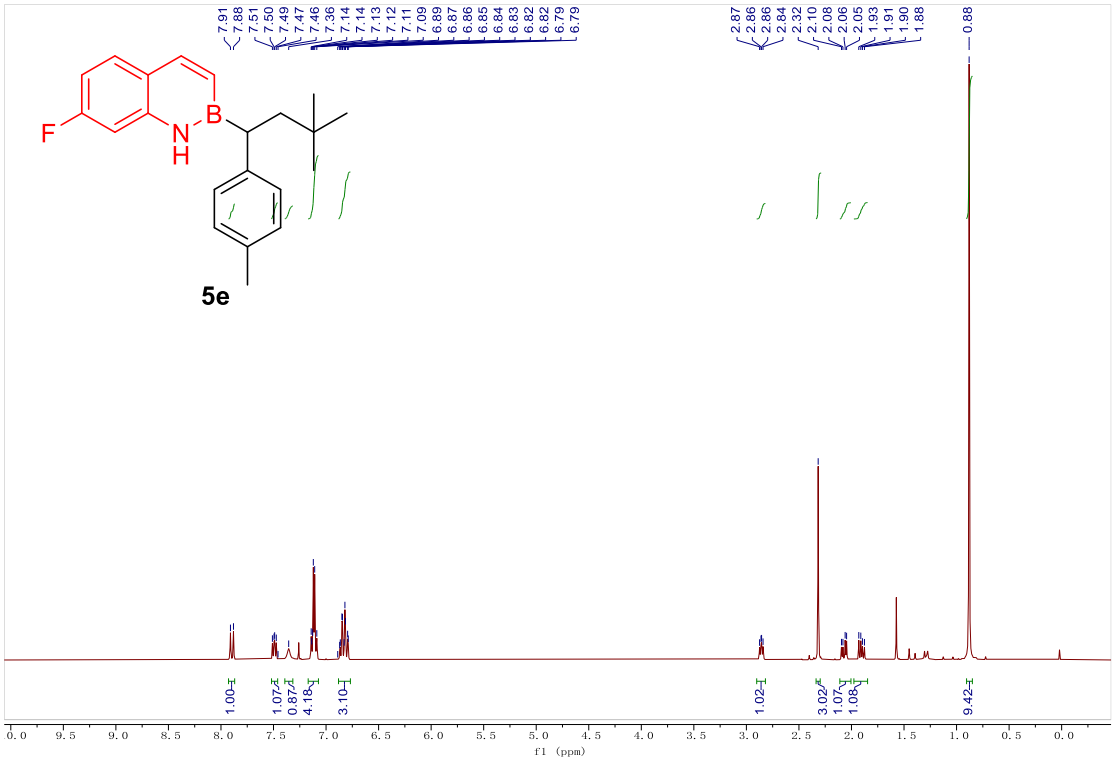
$^{19}$F NMR of **5d** (376 MHz, $CDCl_3$)



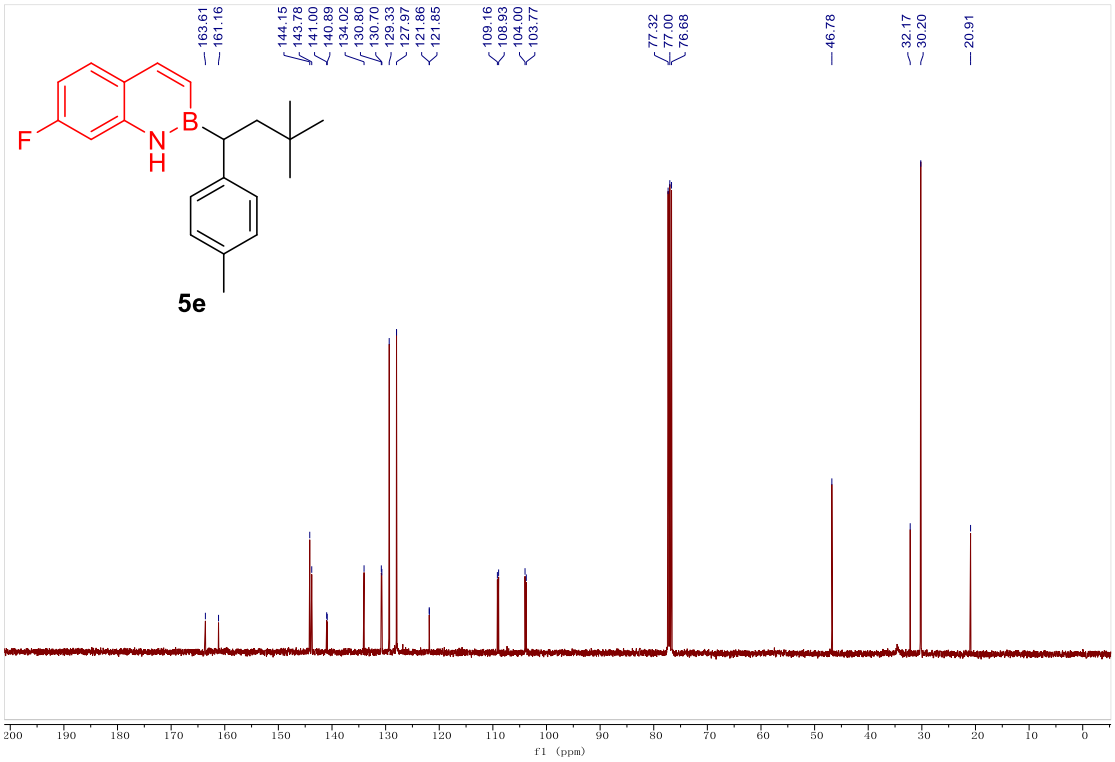

$^{11}$B NMR of **5d** (128 MHz, $CDCl_3$)



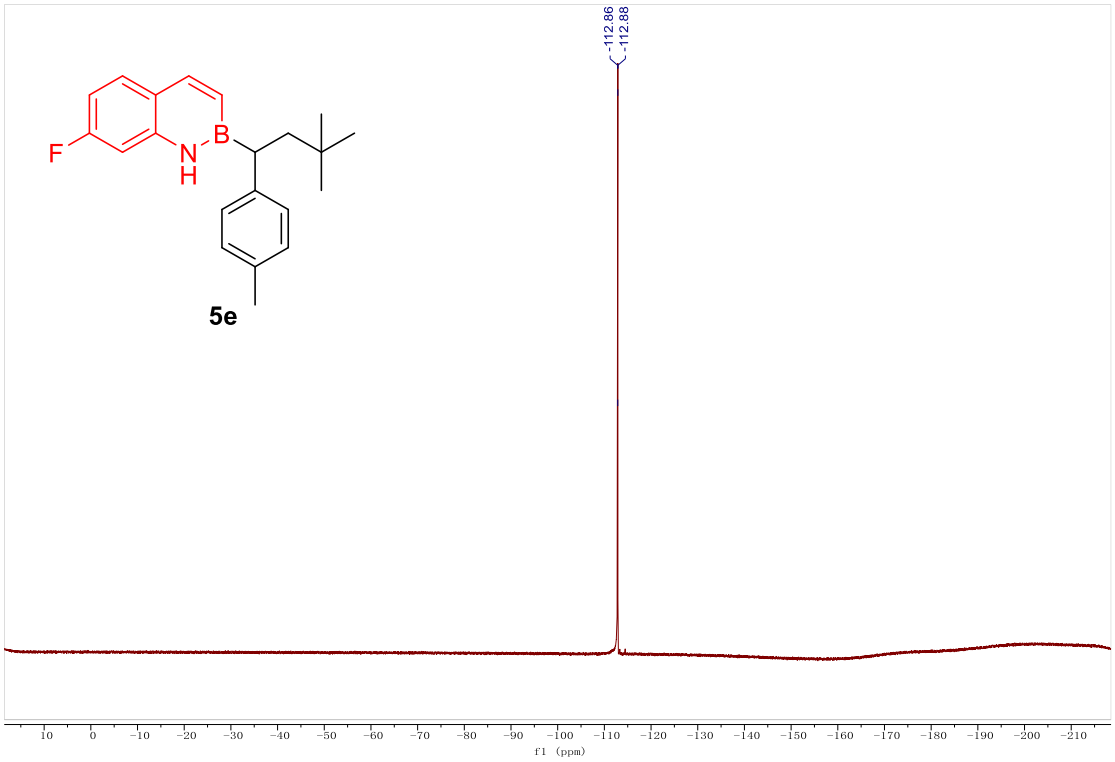
$^{1}$H NMR of **5e** (400 MHz, $CDCl_3$)



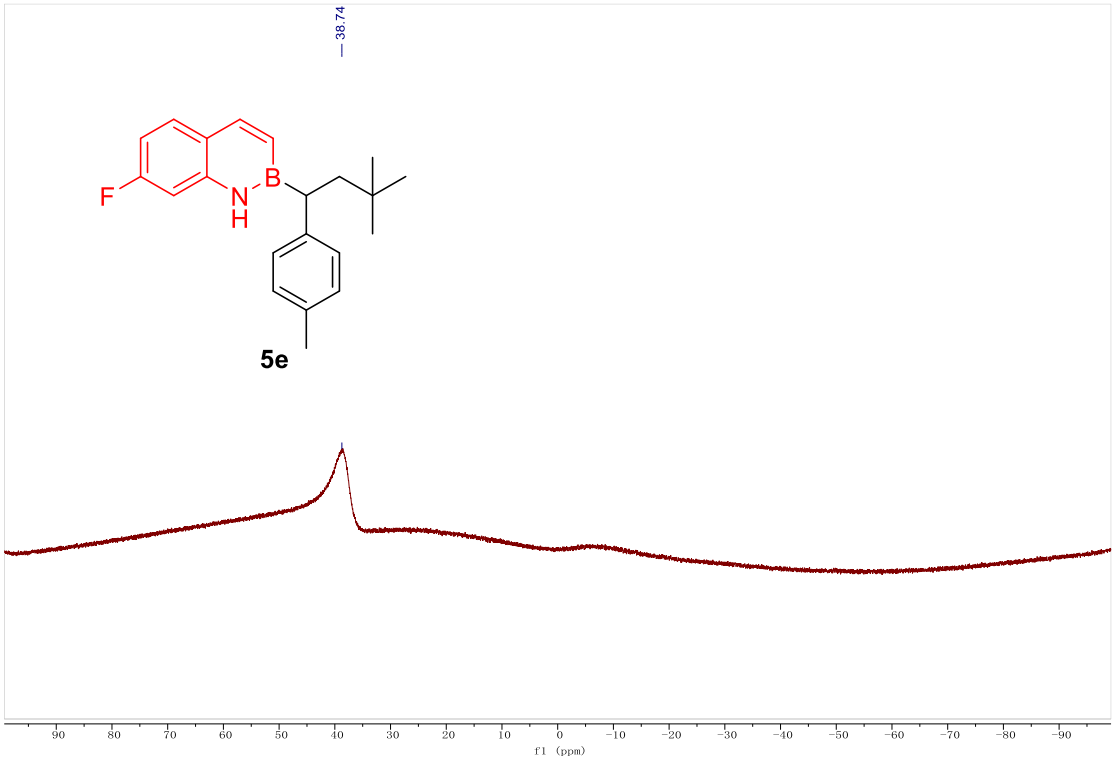

$^{13}$C NMR of **5e** (101 MHz, $CDCl_3$)



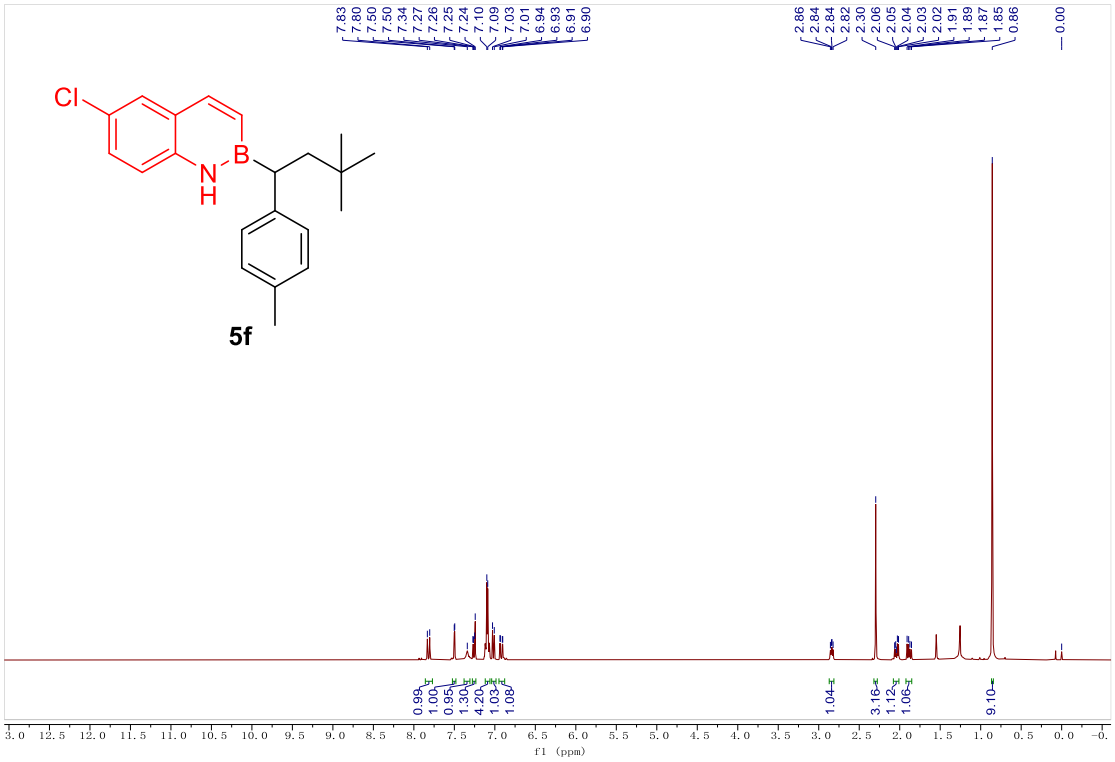
$^{19}$F NMR of **5e** (376 MHz, $CDCl_3$)



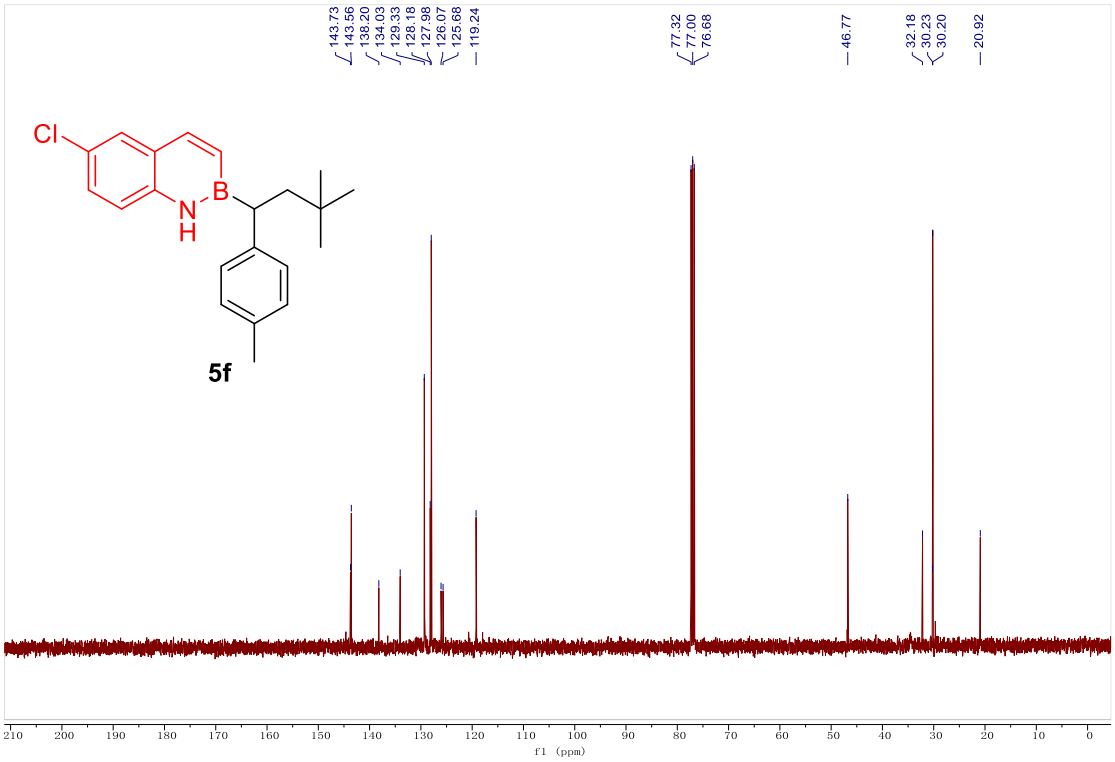

$^{11}$B NMR of **5e** (128 MHz, $CDCl_3$)



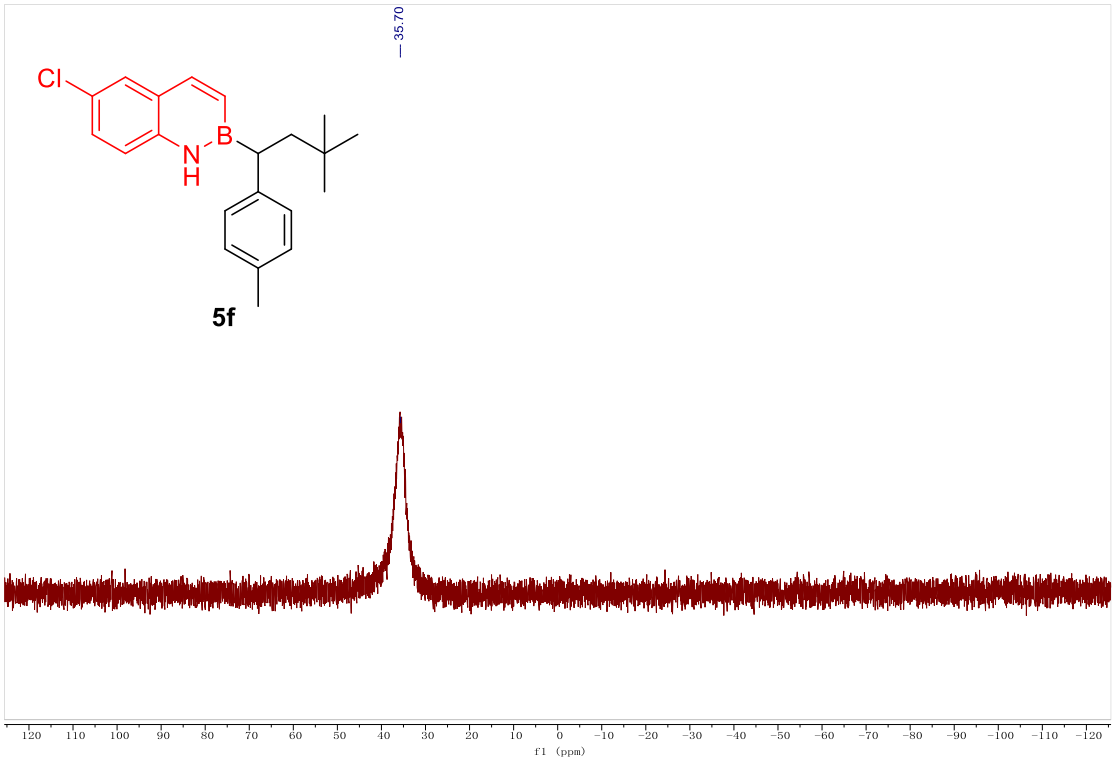
$^{1}$H NMR of **5f** (400 MHz, $CDCl_3$)



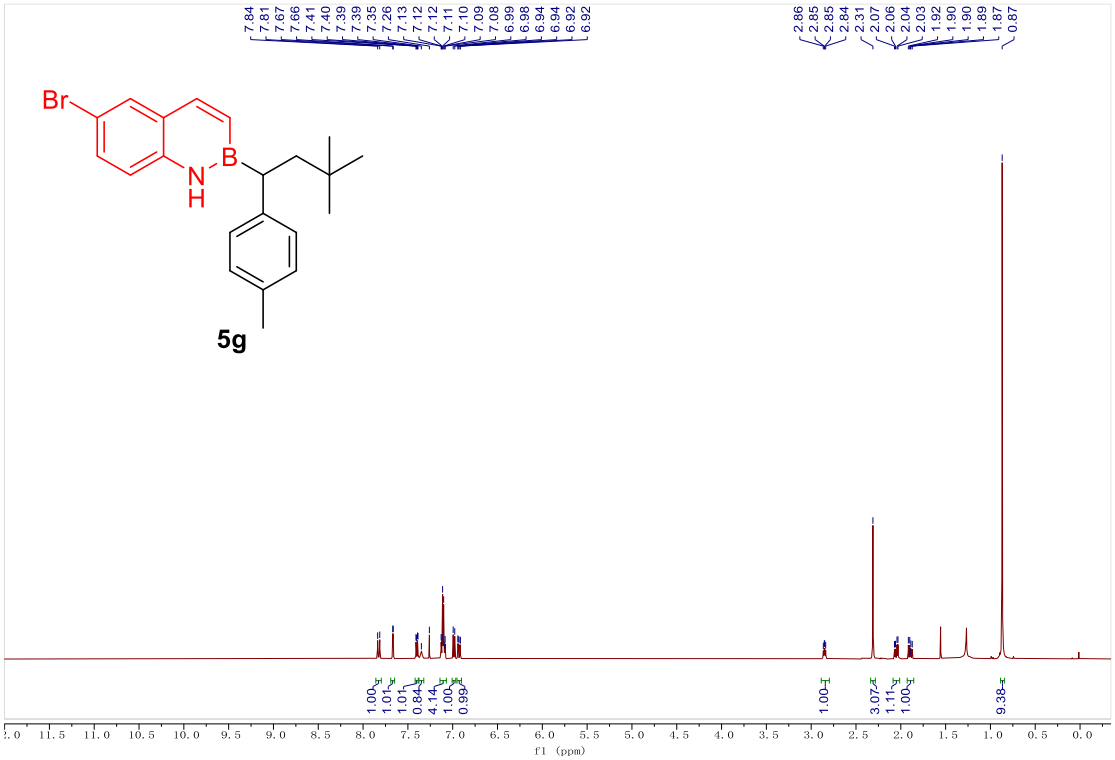

$^{13}$C NMR of **5f** (101 MHz, $CDCl_3$)



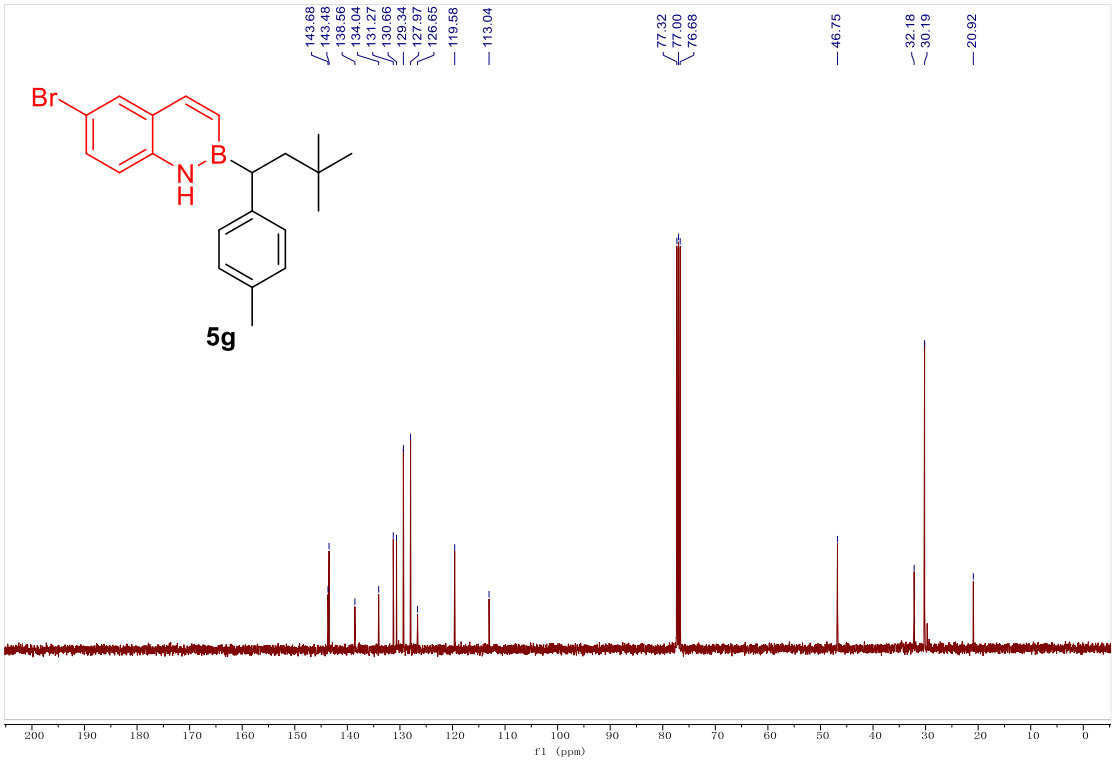
$^{11}$B NMR of **5f** (128 MHz, $CDCl_3$)



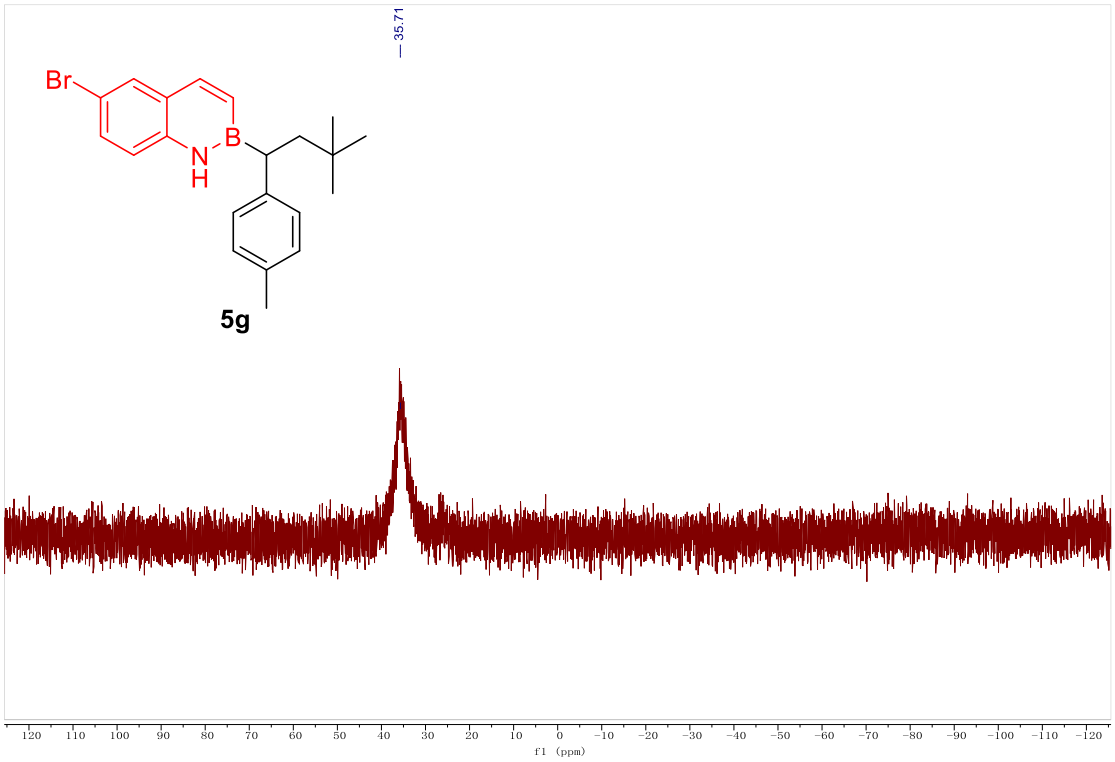

$^{1}$H NMR of **5g** (500 MHz, $CDCl_3$)



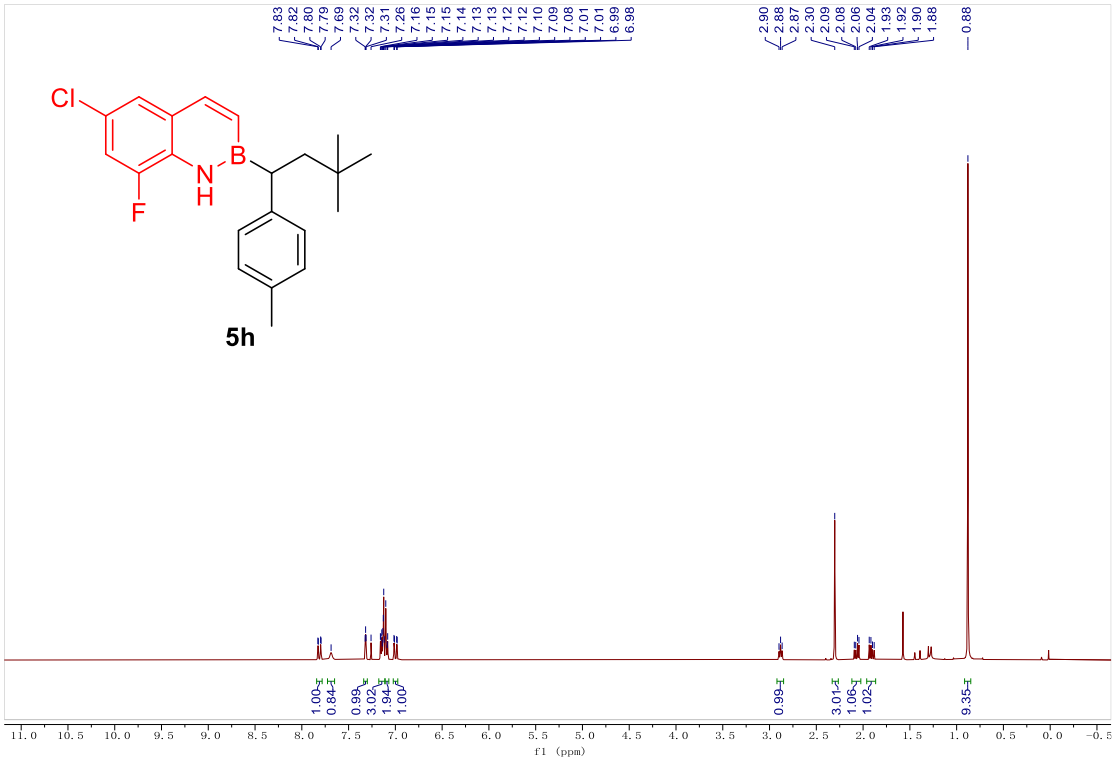
$^{13}$C NMR of **5g** (126 MHz, $CDCl_3$)



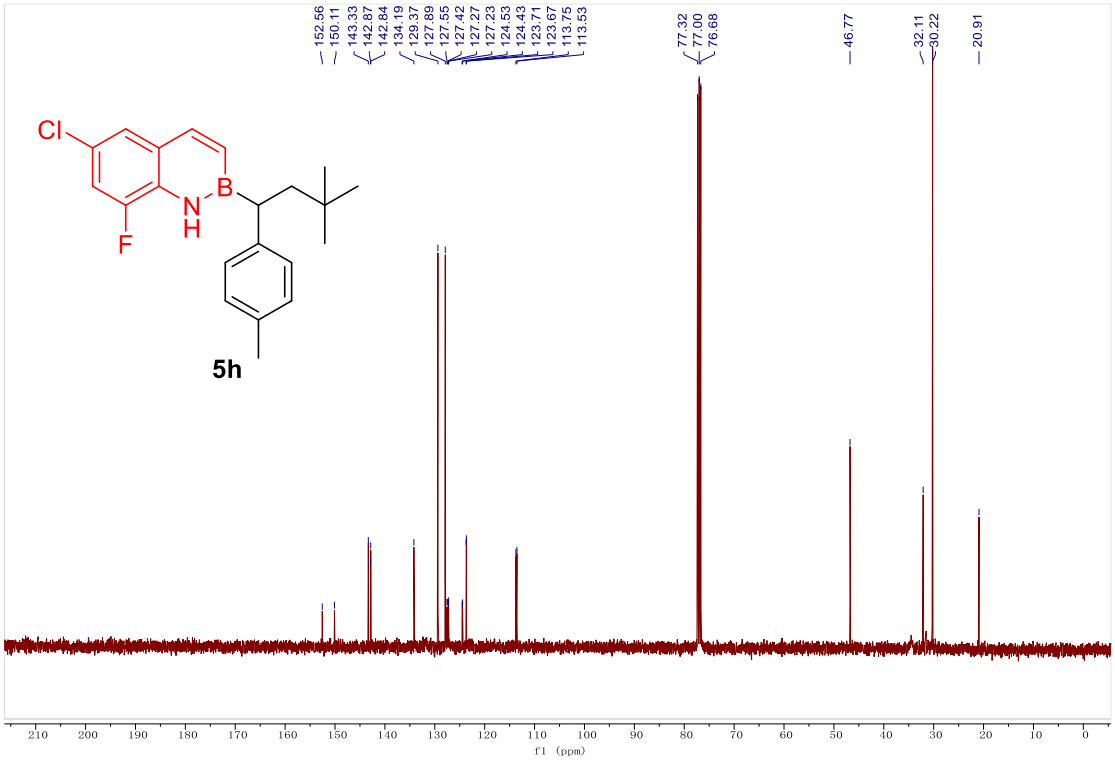

$^{11}$B NMR of **5g** (128 MHz, $CDCl_3$)



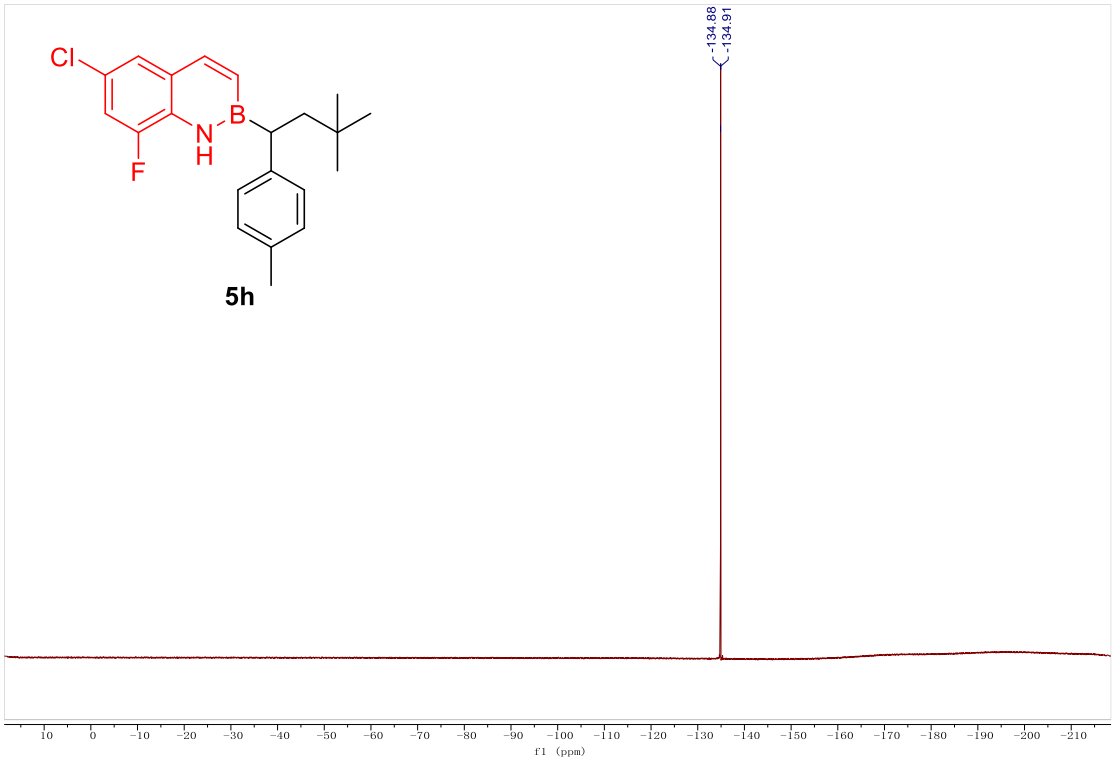
$^{1}$H NMR of **5h** (400 MHz, $CDCl_3$)



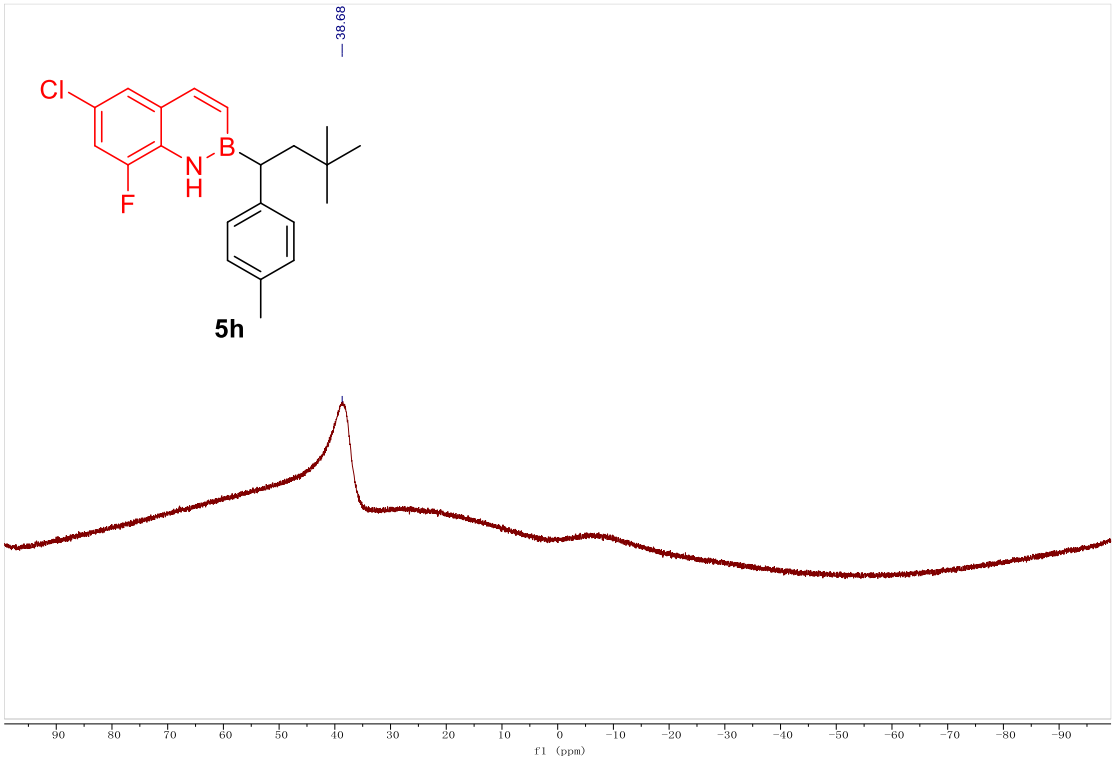

$^{13}$C NMR of **5h** (101 MHz, $CDCl_3$)



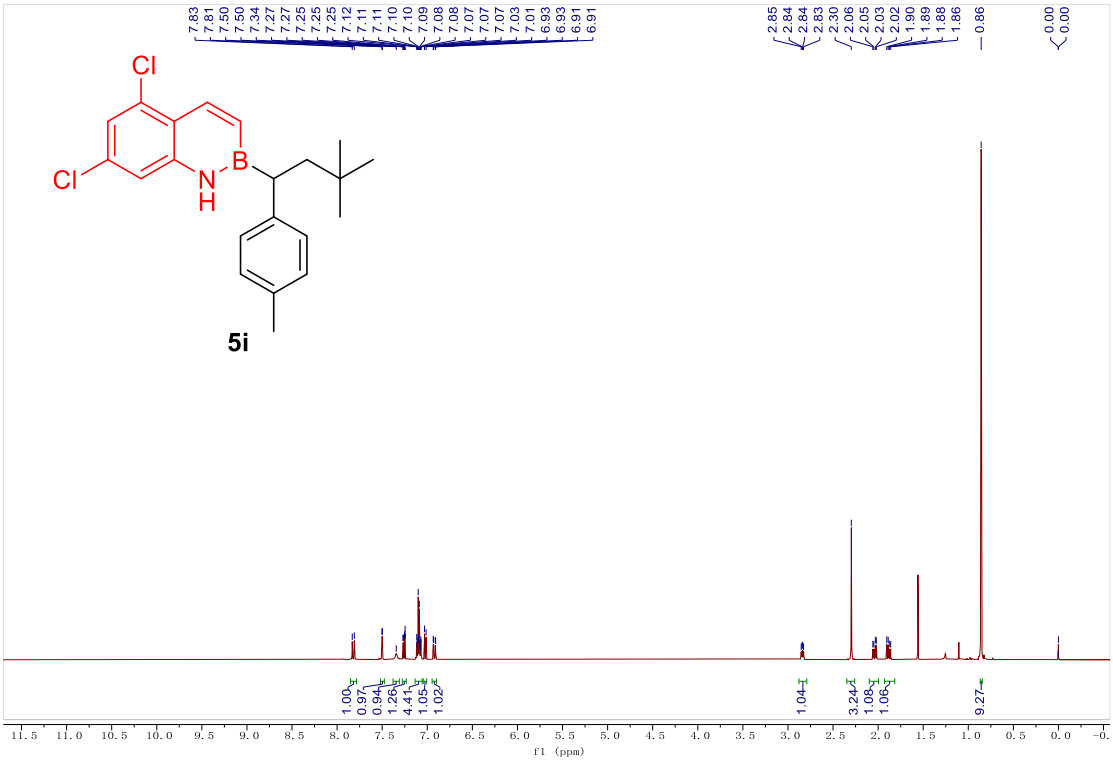
$^{19}$F NMR of **5h** (376 MHz, $CDCl_3$)



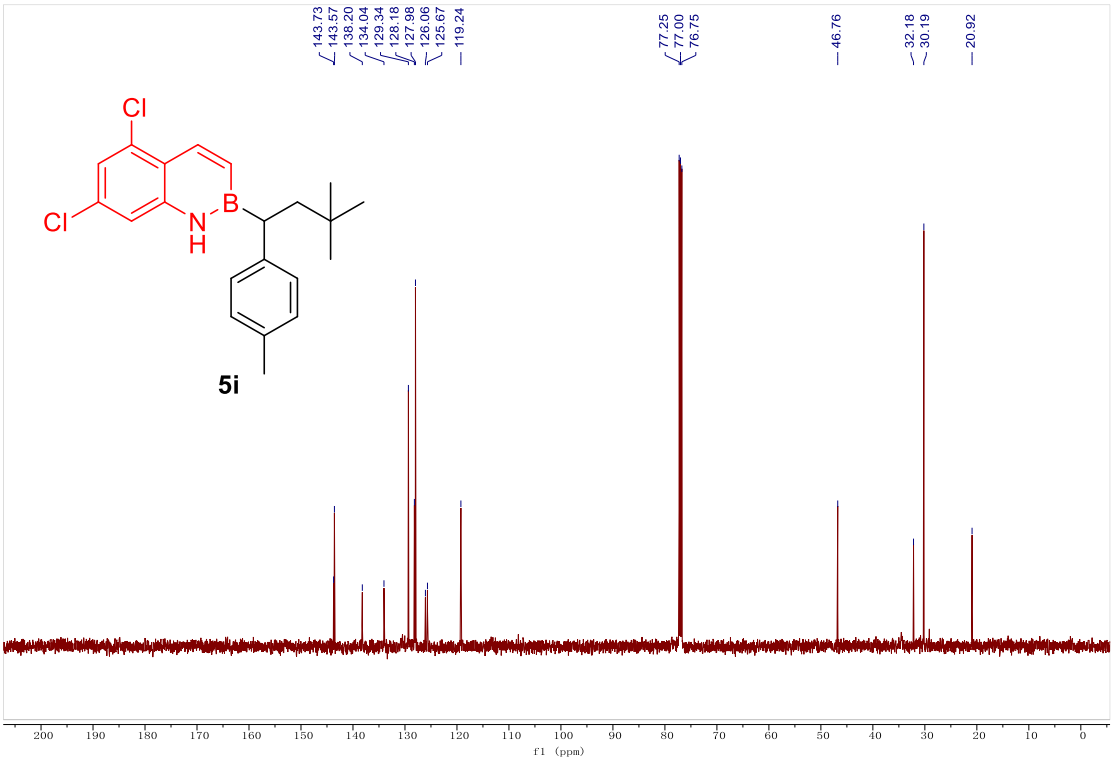

$^{11}$B NMR of **5h** (128 MHz, $CDCl_3$)



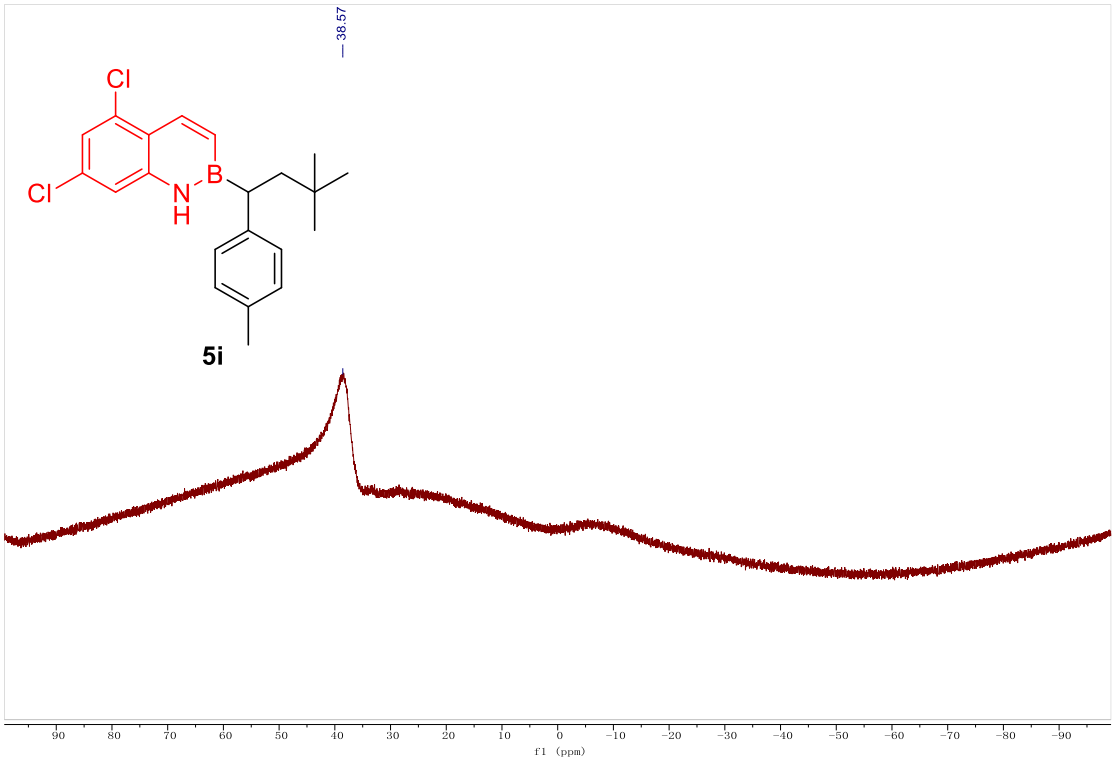
$^{1}$H NMR of **5i** (500 MHz, $CDCl_3$)



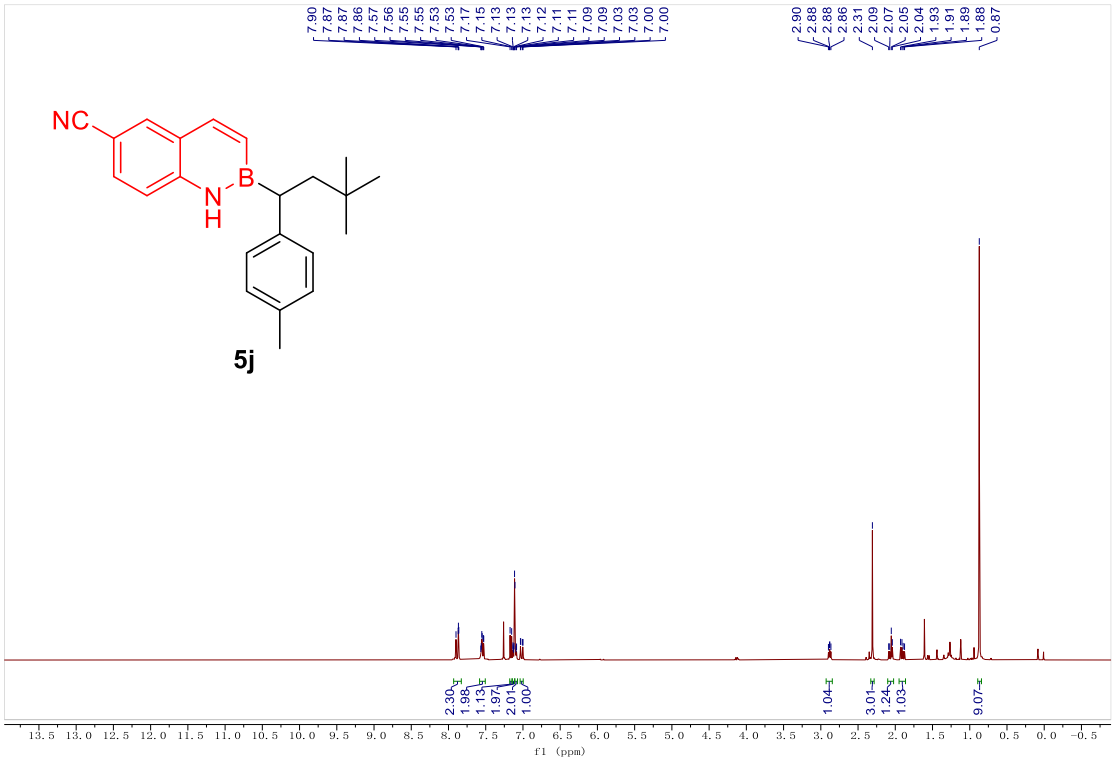

$^{13}$C NMR of **5i** (126 MHz, $CDCl_3$)



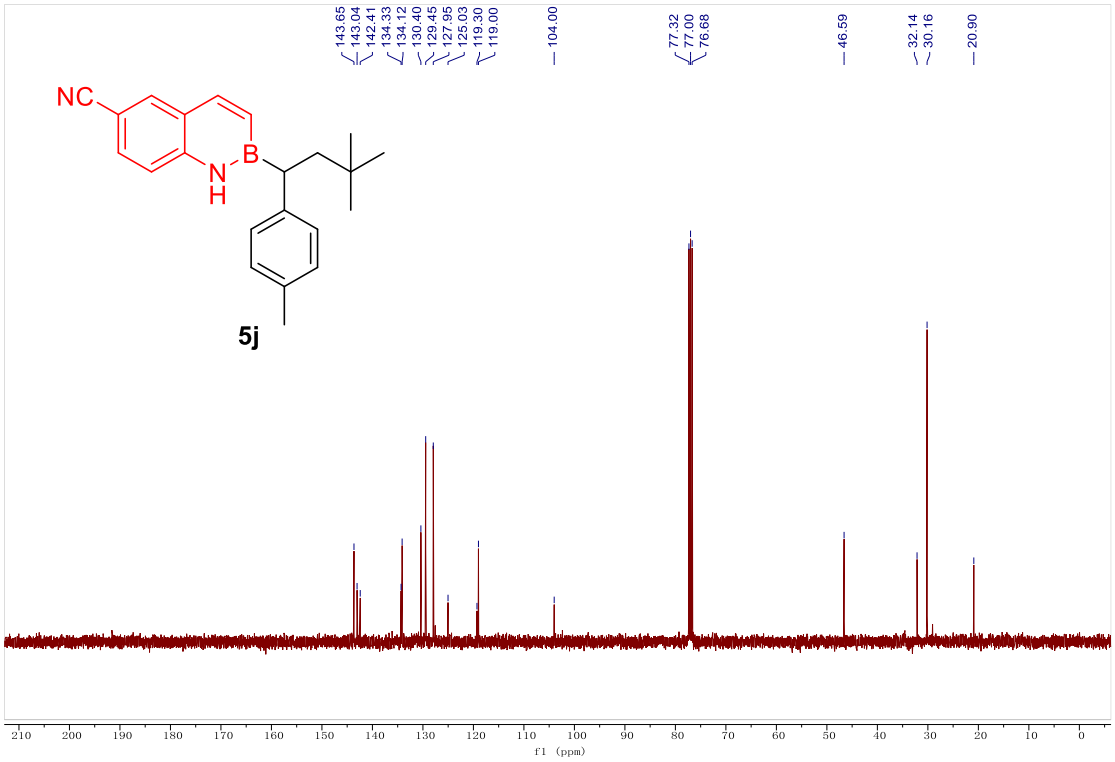
$^{11}$B NMR of **5i** (128 MHz, $CDCl_3$)



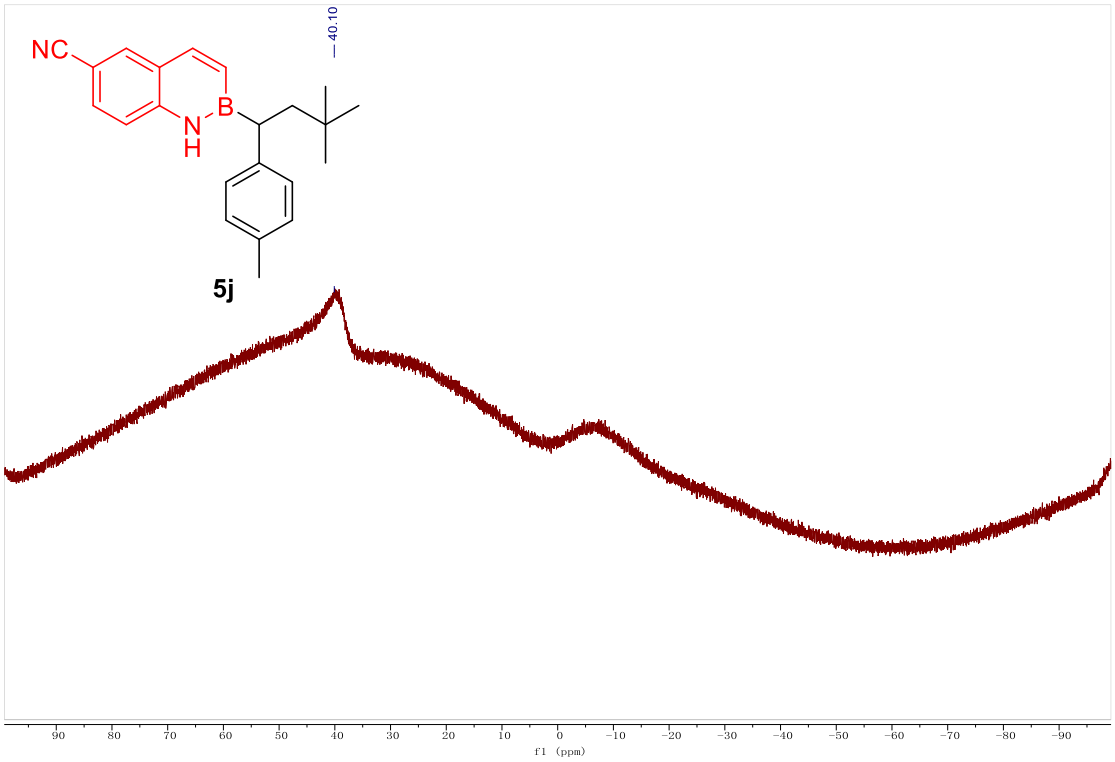

$^{1}$H NMR of **5j** (400 MHz, $CDCl_3$)



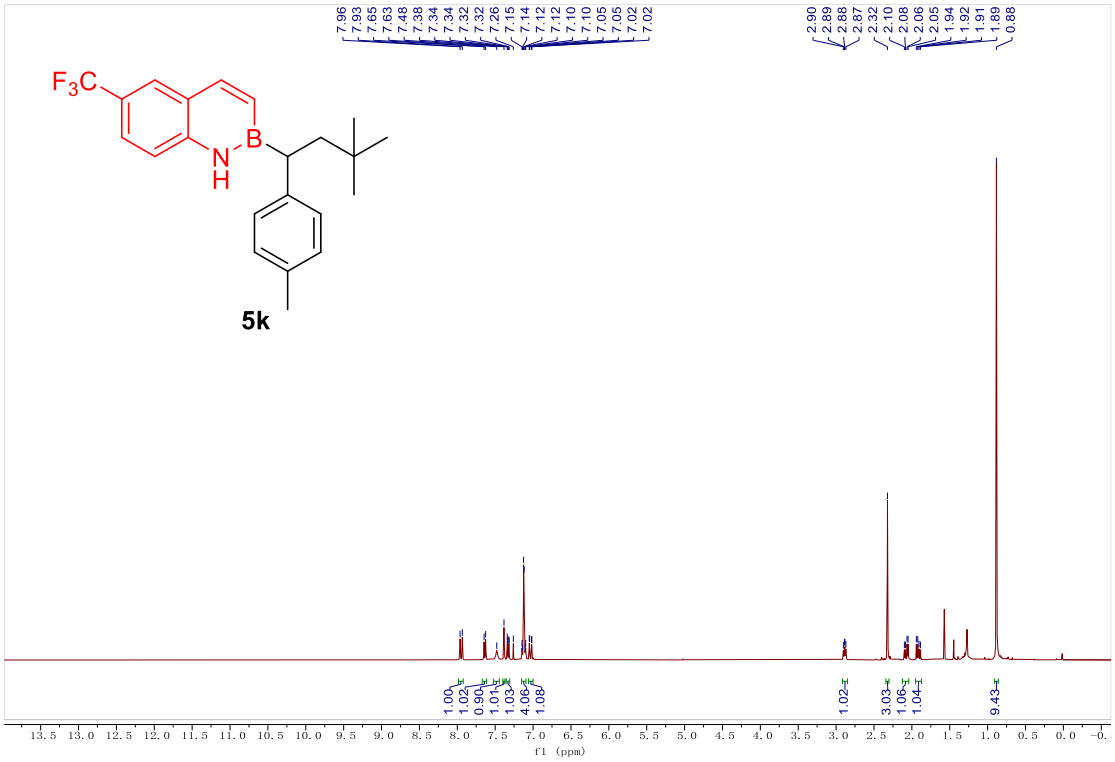
$^{13}$C NMR of **5j** (101 MHz, $CDCl_3$)



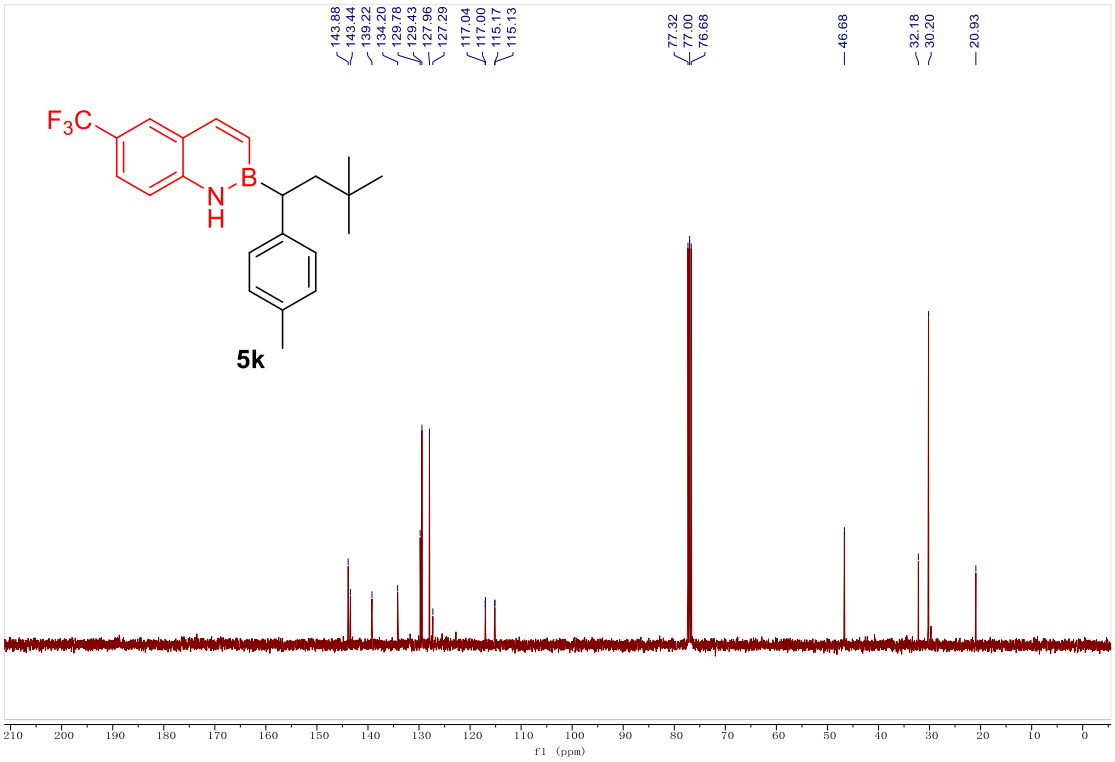

$^{11}$B NMR of **5j** (128 MHz, $CDCl_3$)



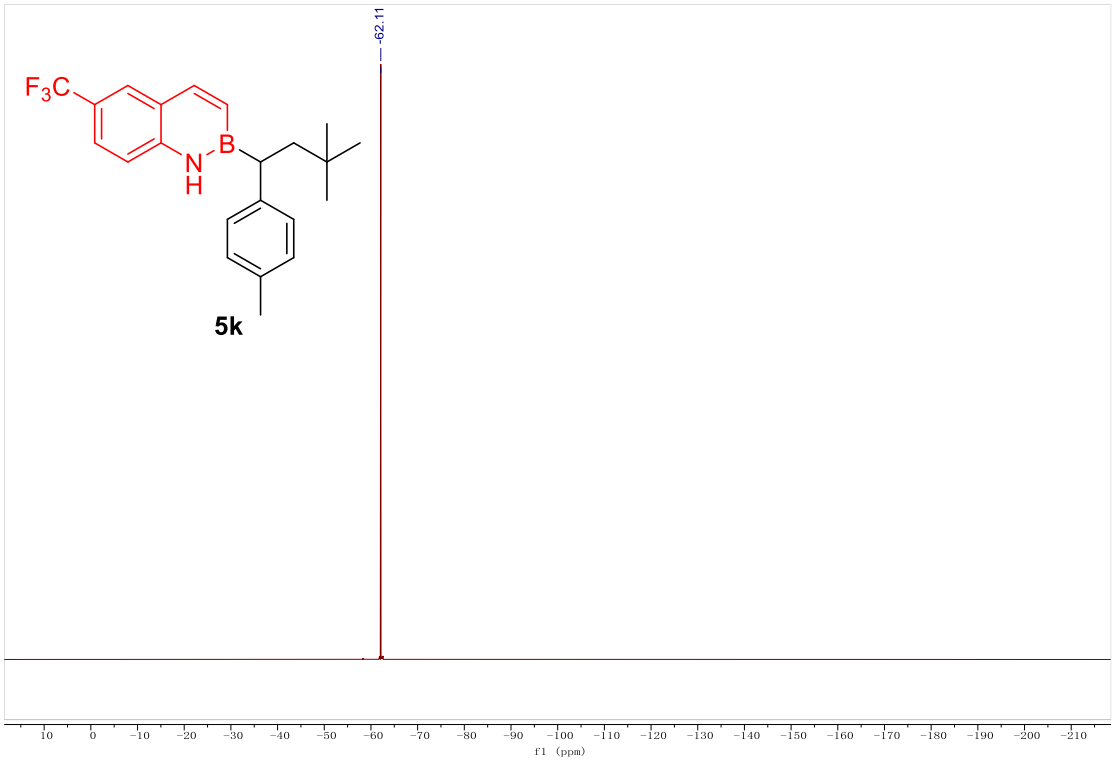
$^{1}$H NMR of **5k** (400 MHz, $CDCl_3$)



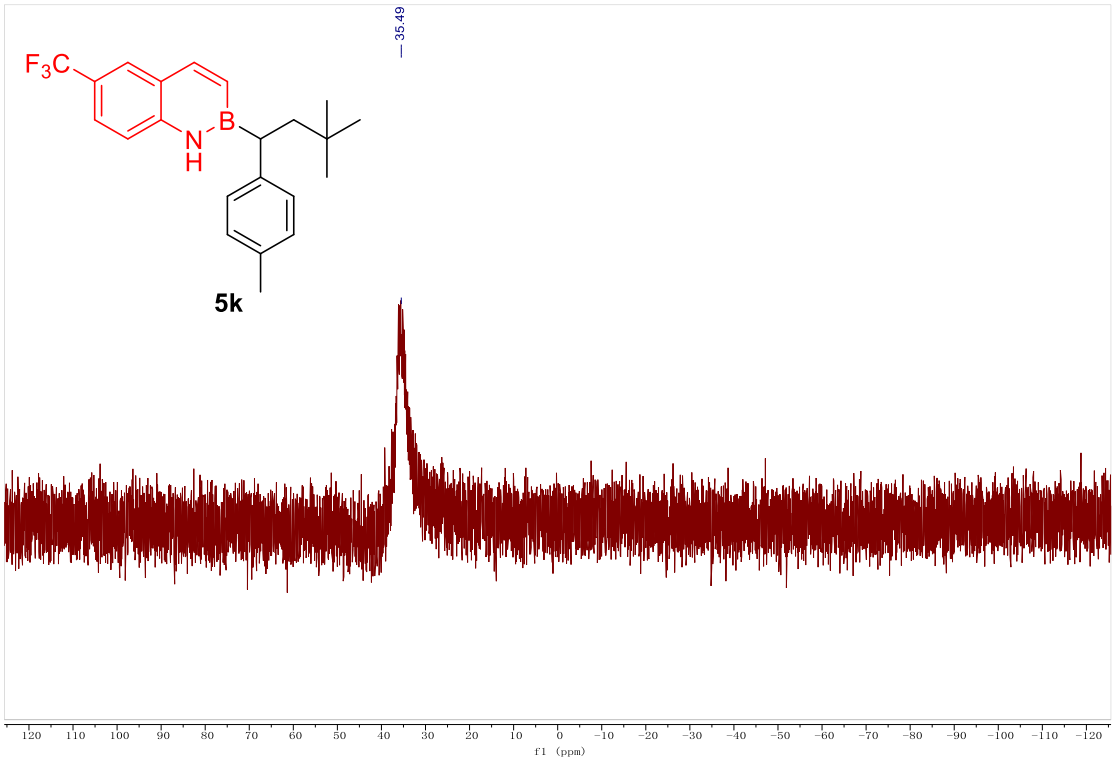

$^{13}$C NMR of **5k** (101 MHz, $CDCl_3$)



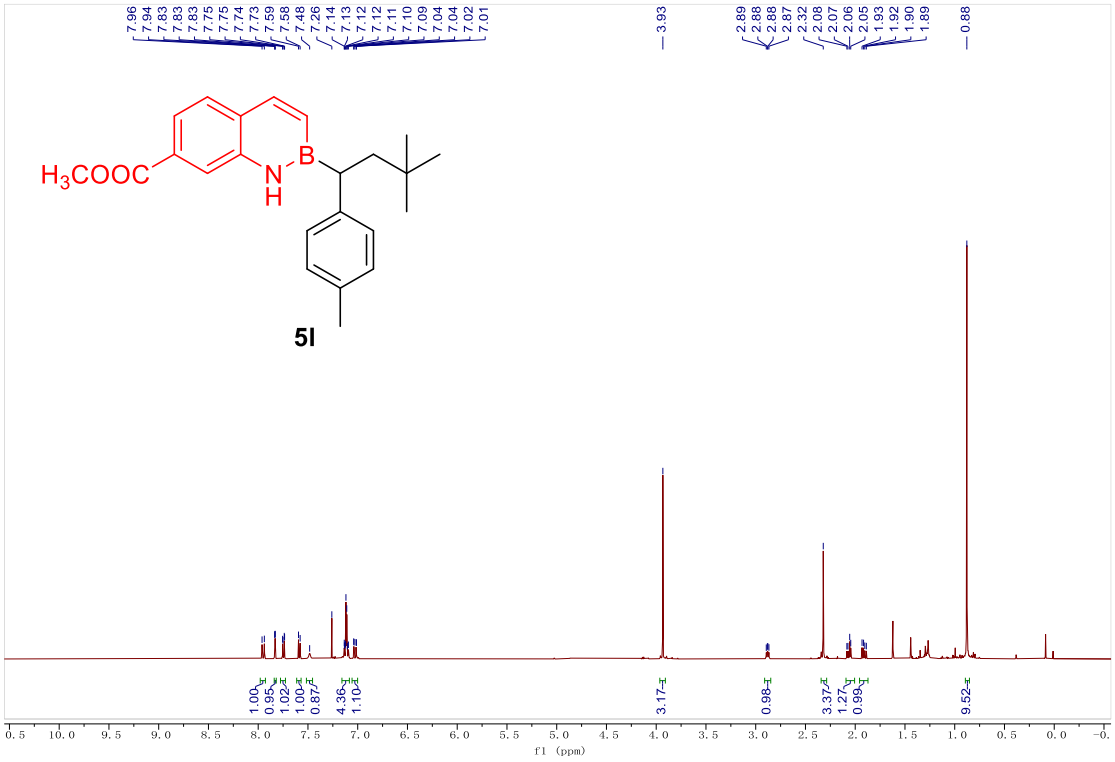
$^{19}$F NMR of **5k** (376 MHz, $CDCl_3$)



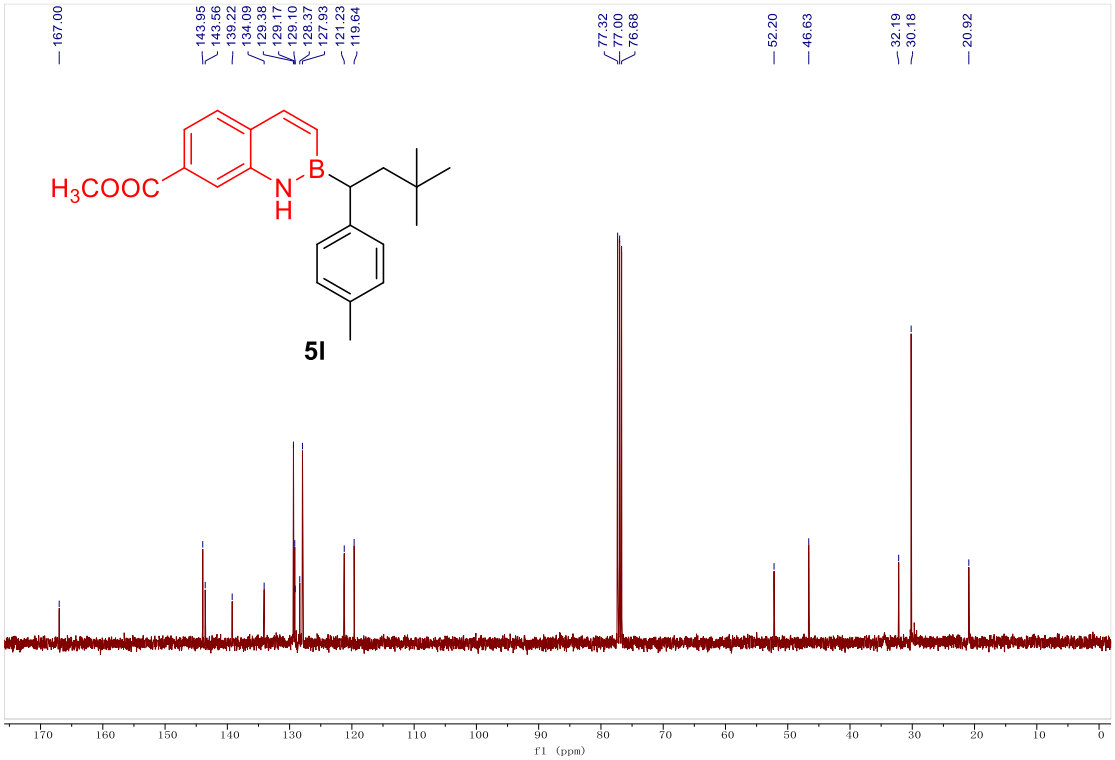

$^{11}$B NMR of **5k** (128 MHz, $CDCl_3$)



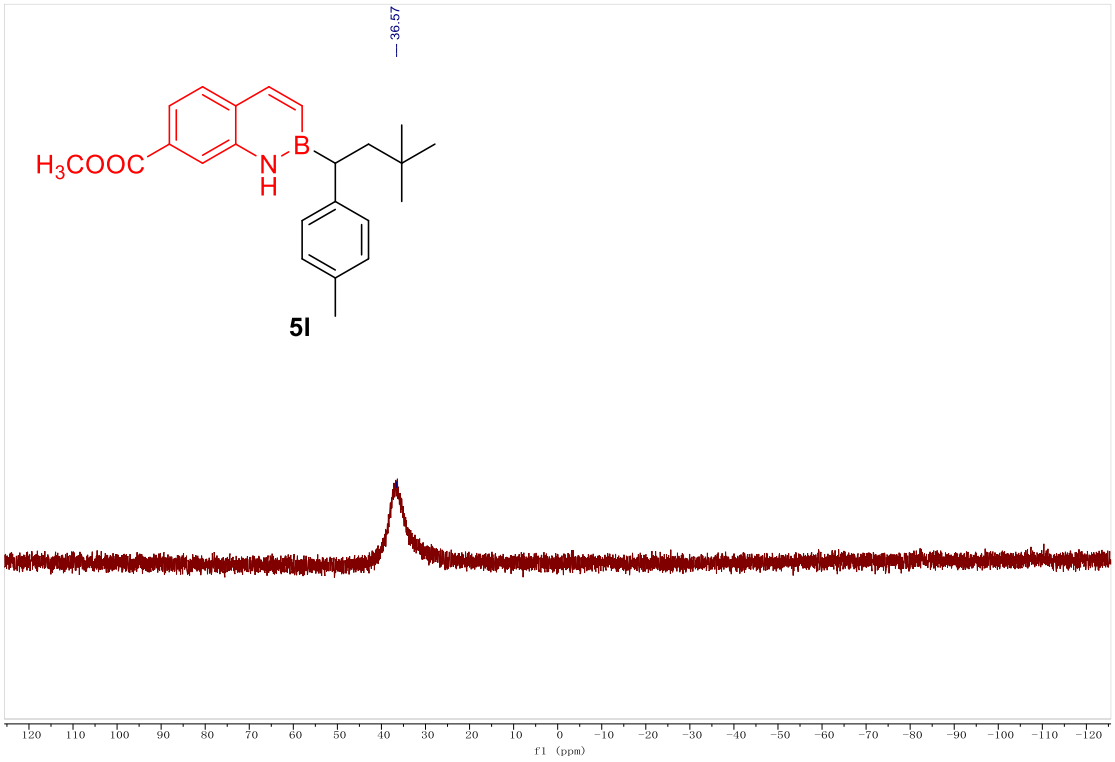
$^{1}$H NMR of **5l** (500 MHz, $CDCl_3$)



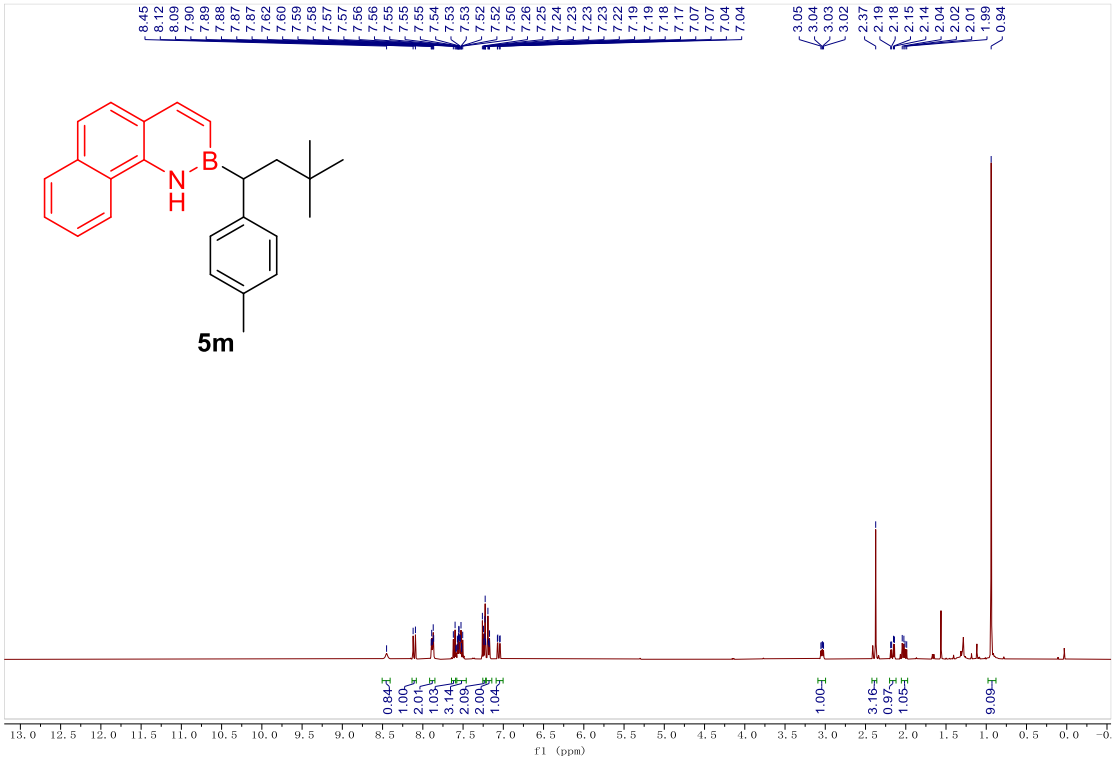

$^{13}$C NMR of **5l** (126 MHz, $CDCl_3$)



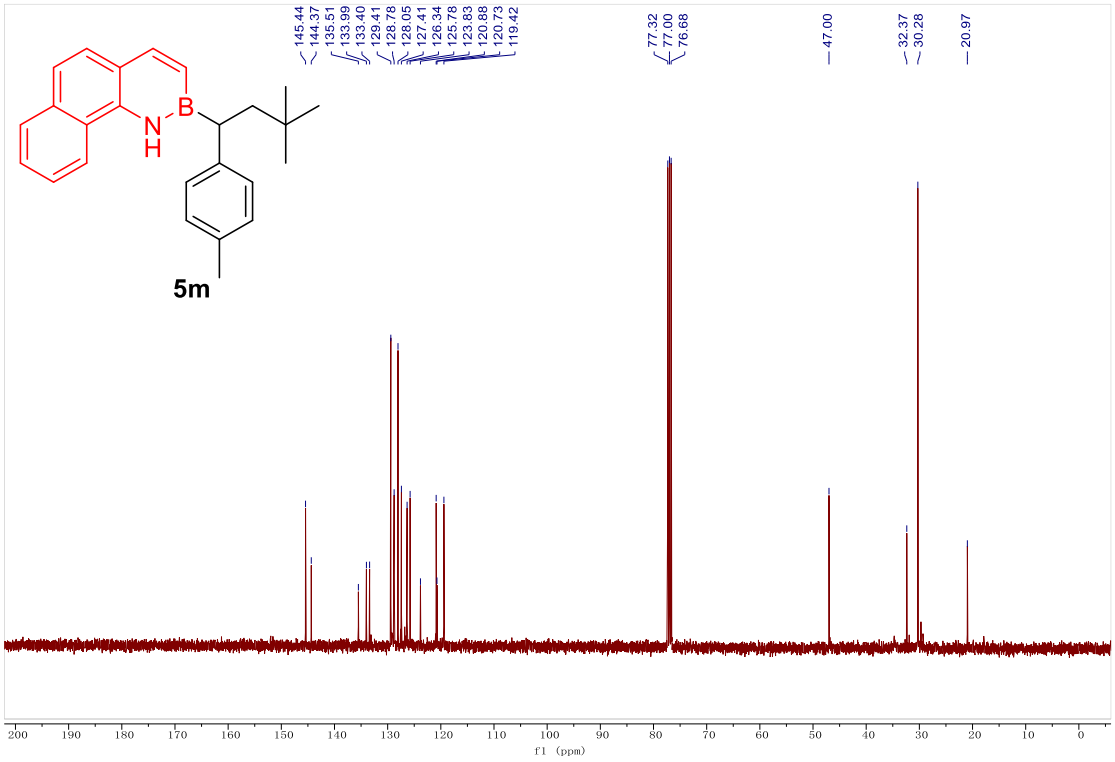
$^{11}$B NMR of **5l** (128 MHz, $CDCl_3$)



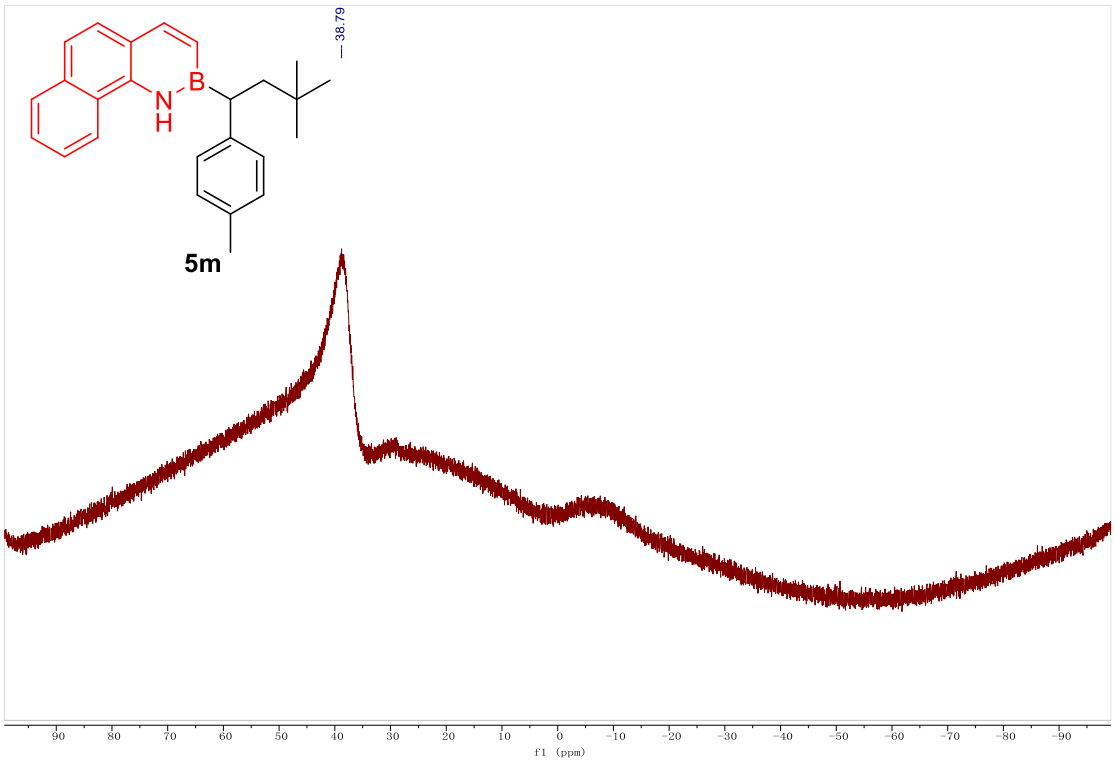

$^{1}$H NMR of **5m** (400 MHz, $CDCl_3$)



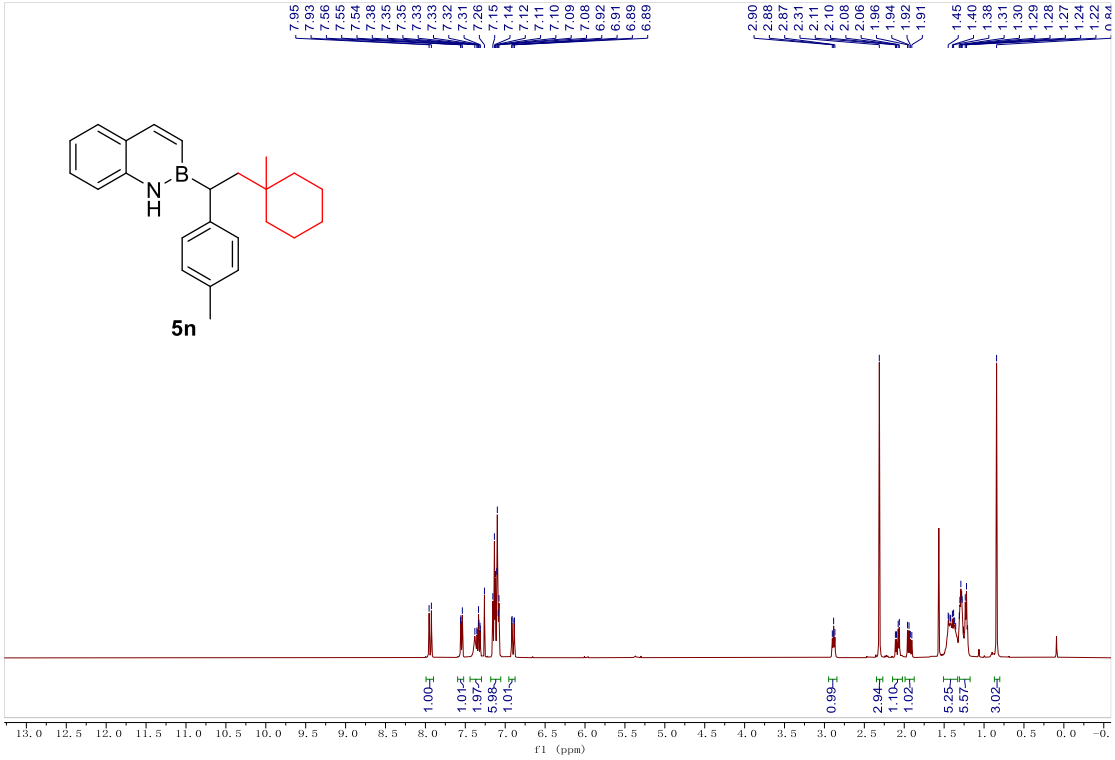
$^{13}$C NMR of **5m** (101 MHz, $CDCl_3$)



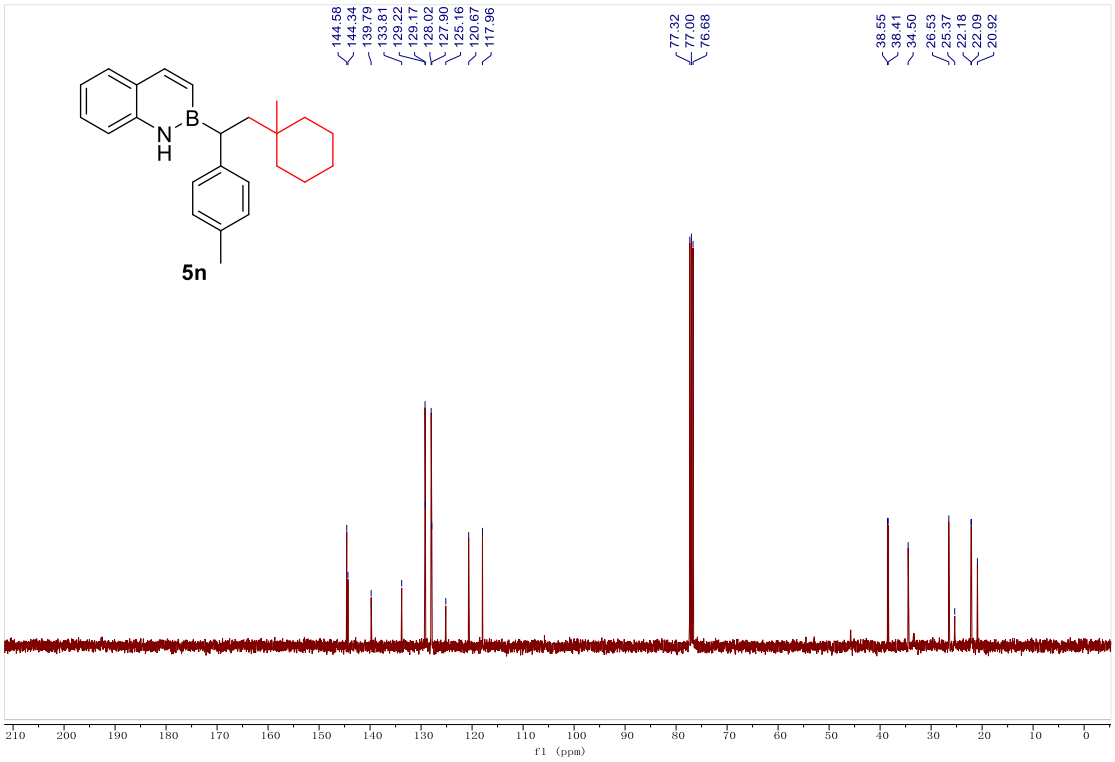

$^{11}$B NMR of **5m** (128 MHz, $CDCl_3$)



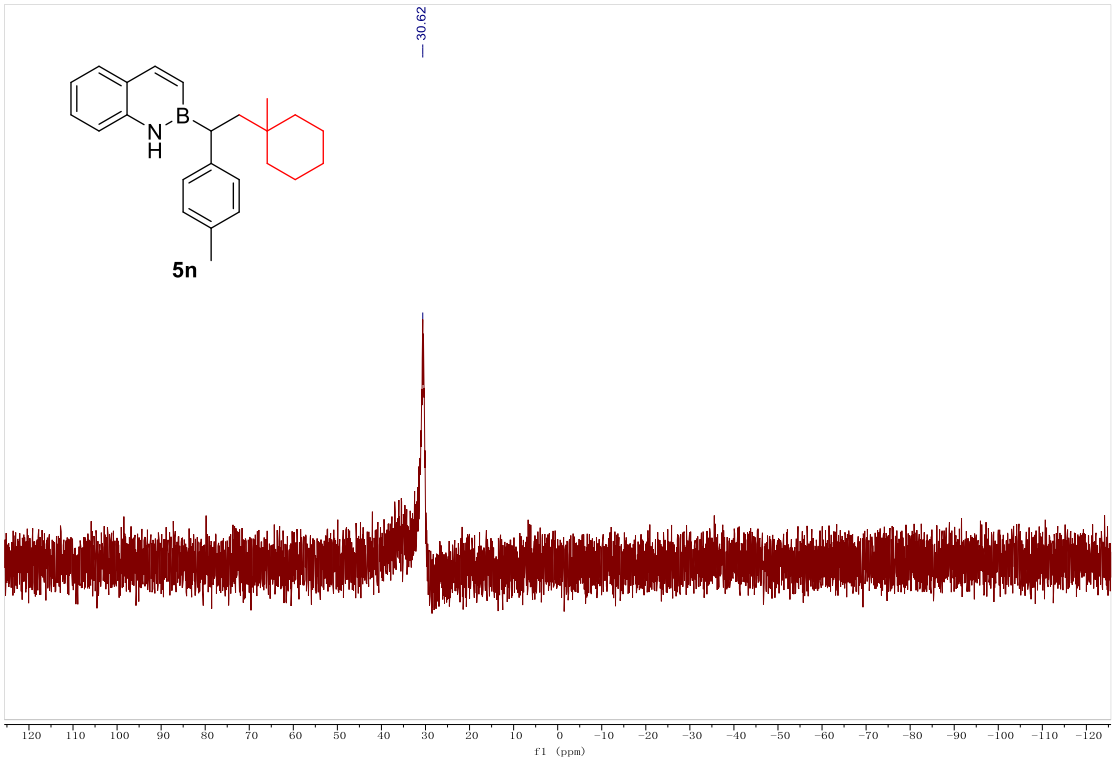
$^{1}$H NMR of **5n** (400 MHz, $CDCl_3$)



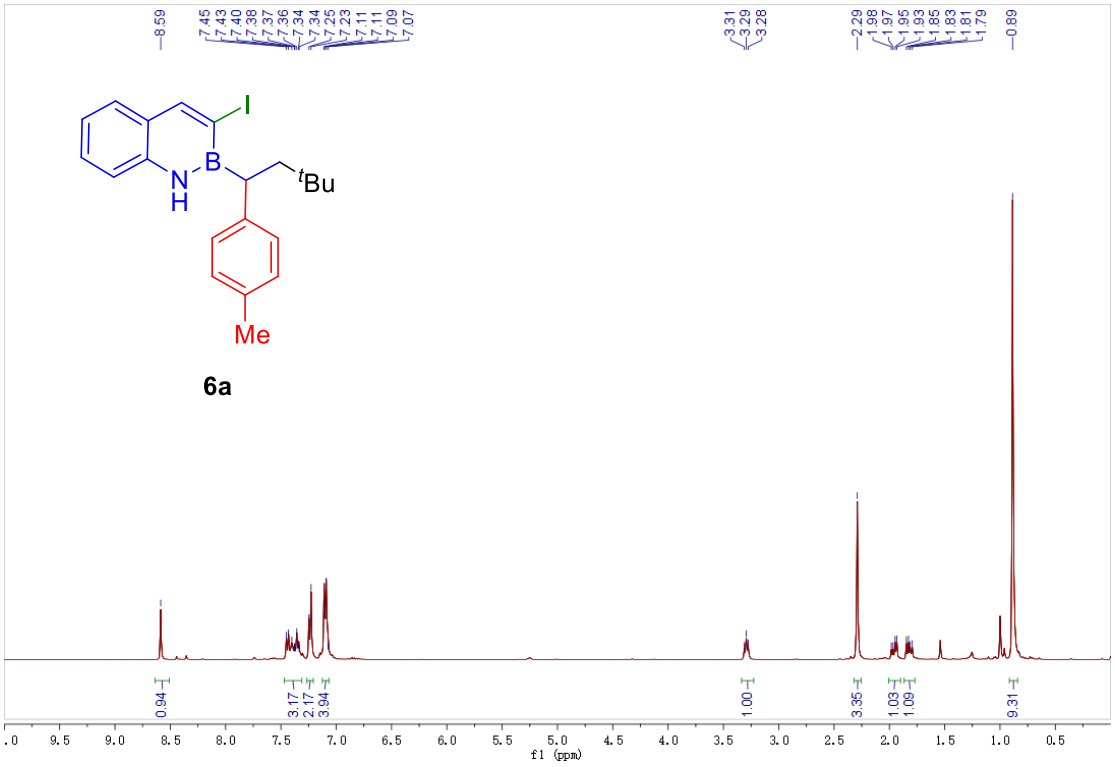

$^{13}$C NMR of **5n** (101 MHz, $CDCl_3$)



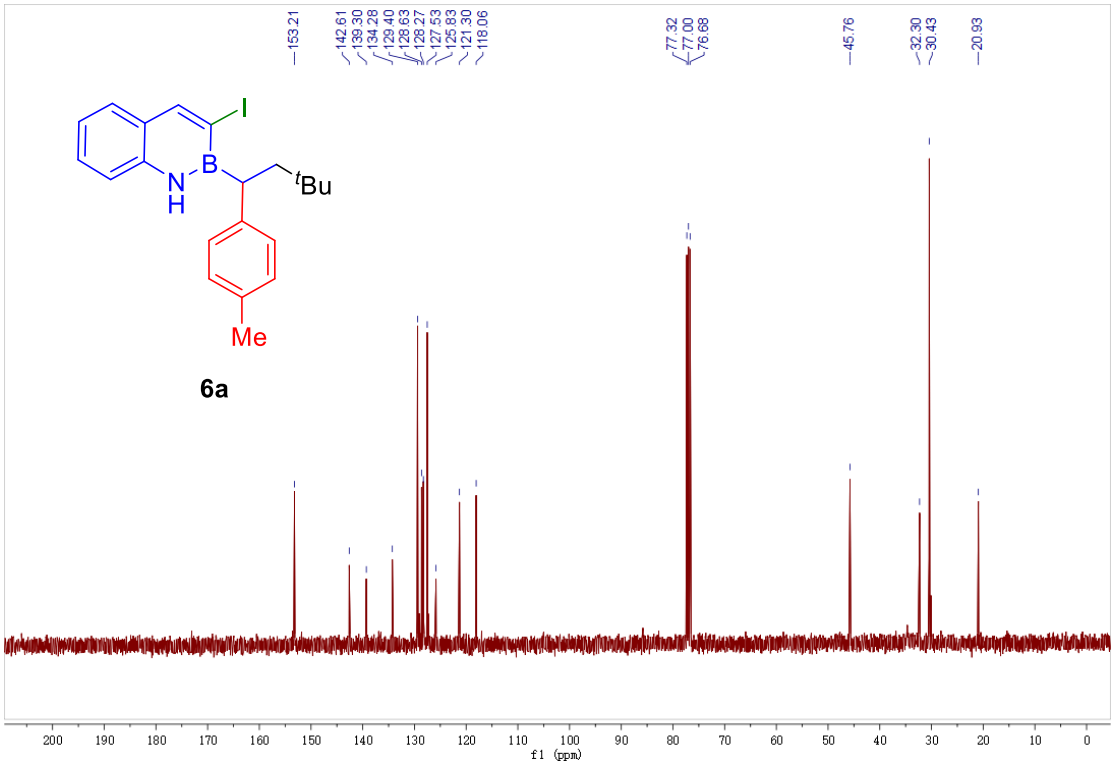
$^{11}$B NMR of **5n** (128 MHz, $CDCl_3$)



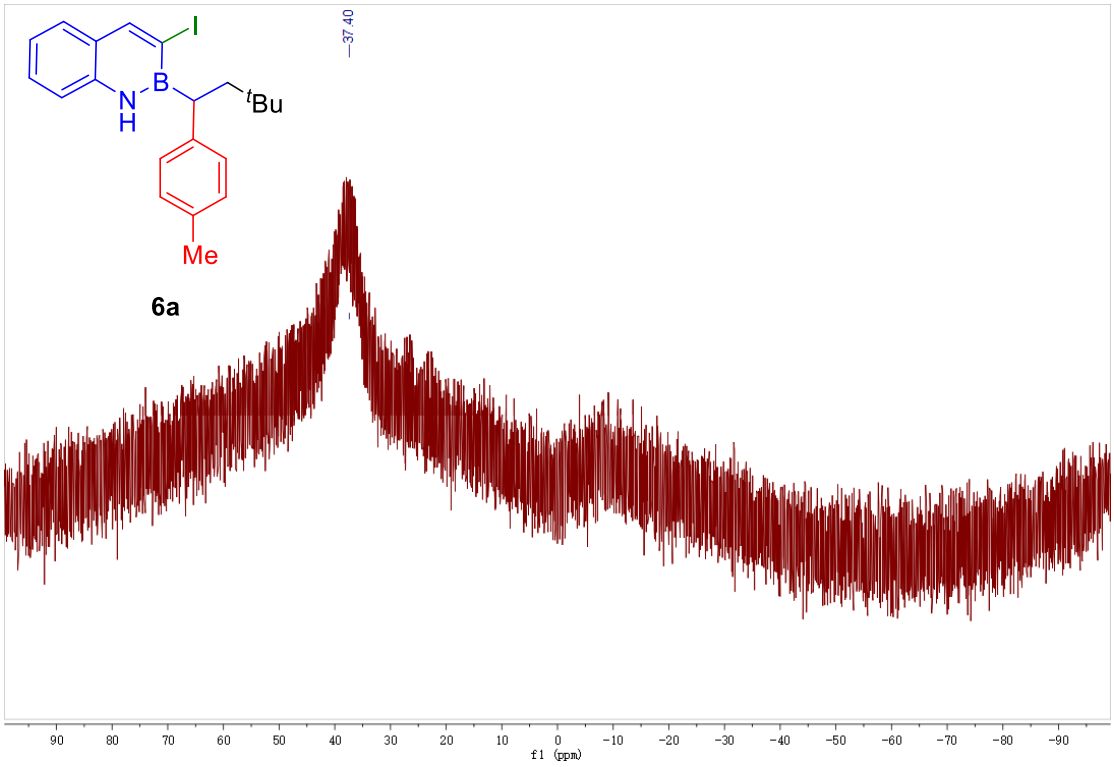

$^{1}$H NMR of **6a** (400 MHz, $CDCl_3$)



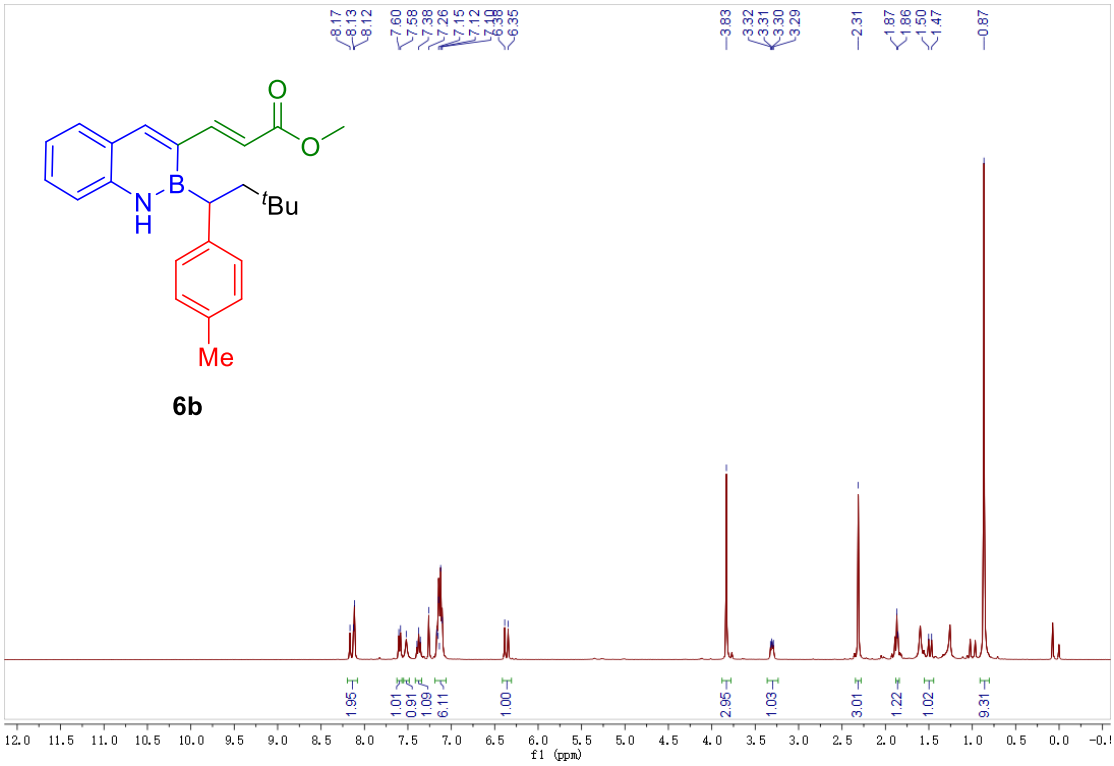
$^{13}$C NMR of **6a** (101 MHz, $CDCl_3$)



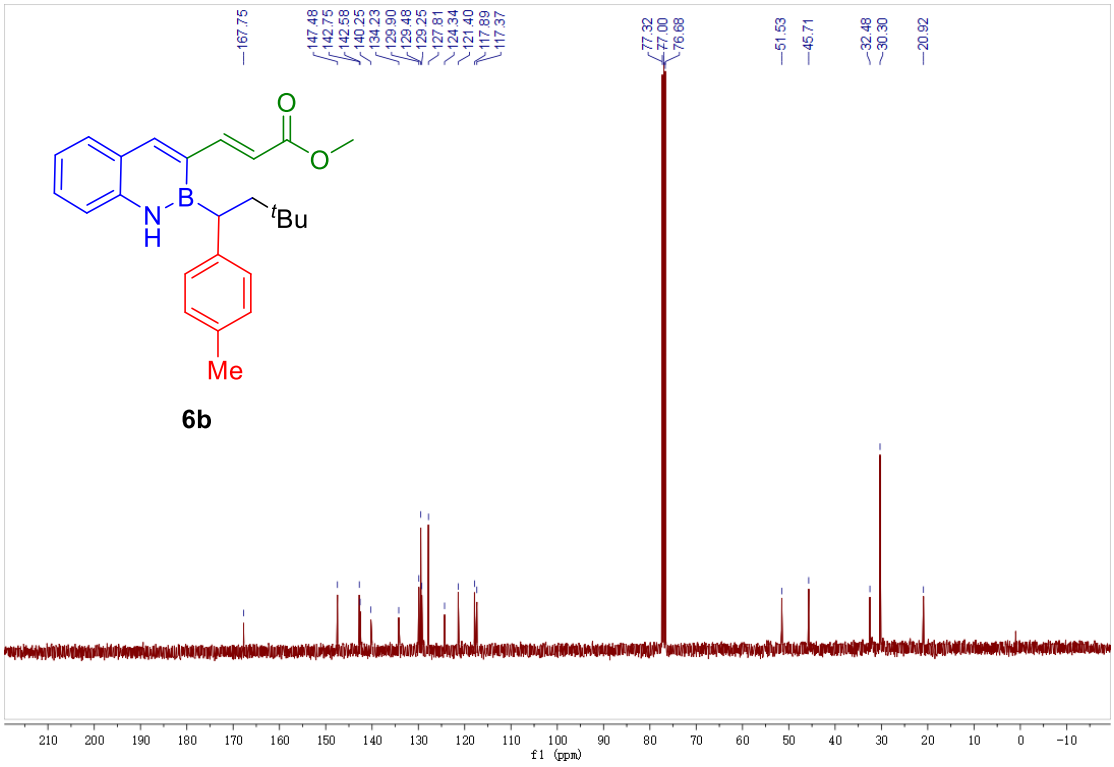

$^{11}$B NMR of **6a** (128 MHz, $CDCl_3$)



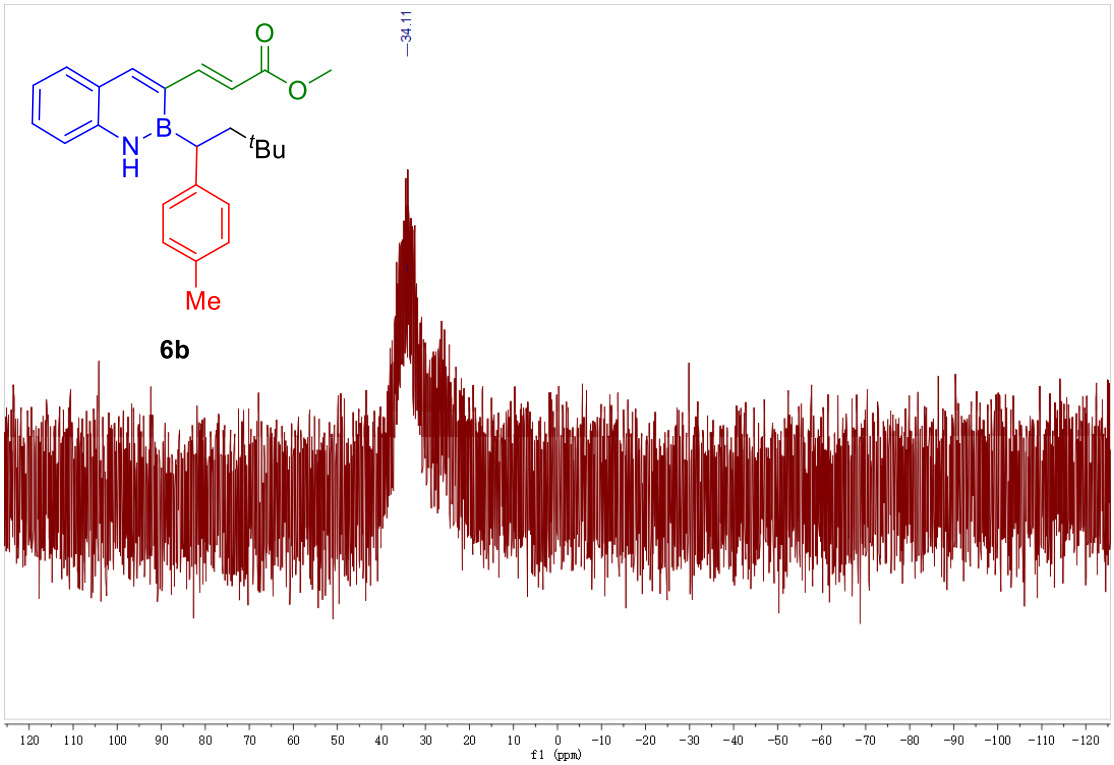
$^{1}$H NMR of **6b** (400 MHz, $CDCl_3$)



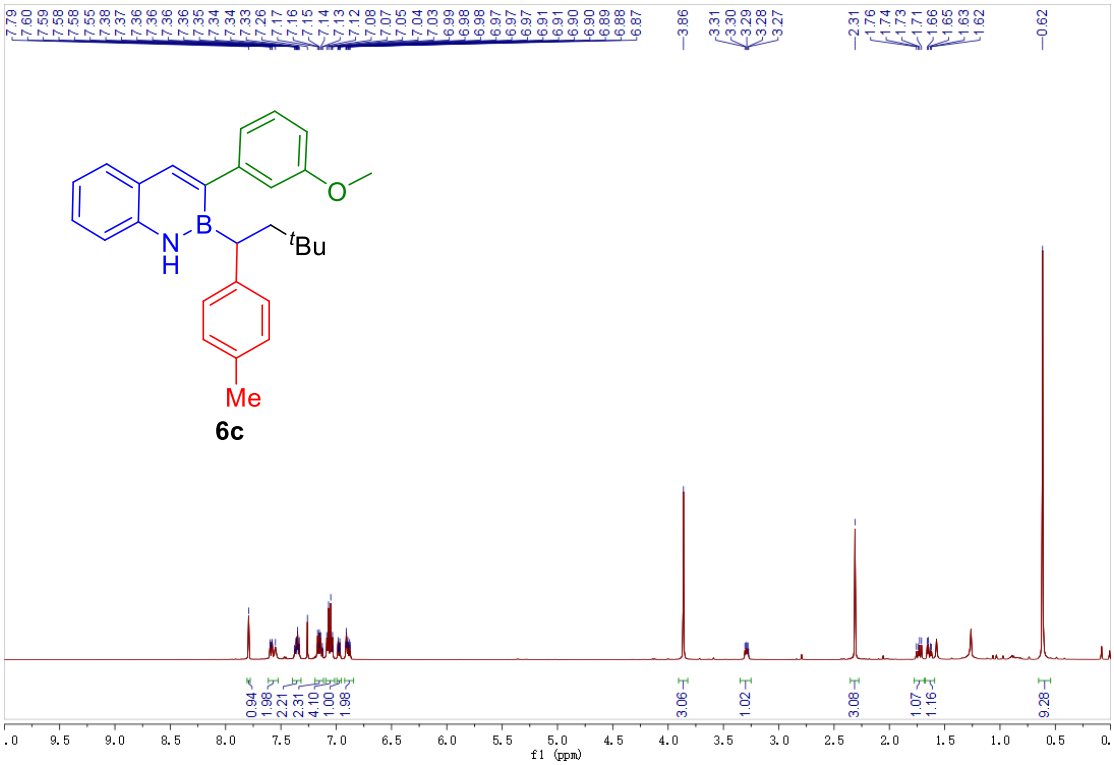

$^{13}$C NMR of **6b** (101 MHz, $CDCl_3$)



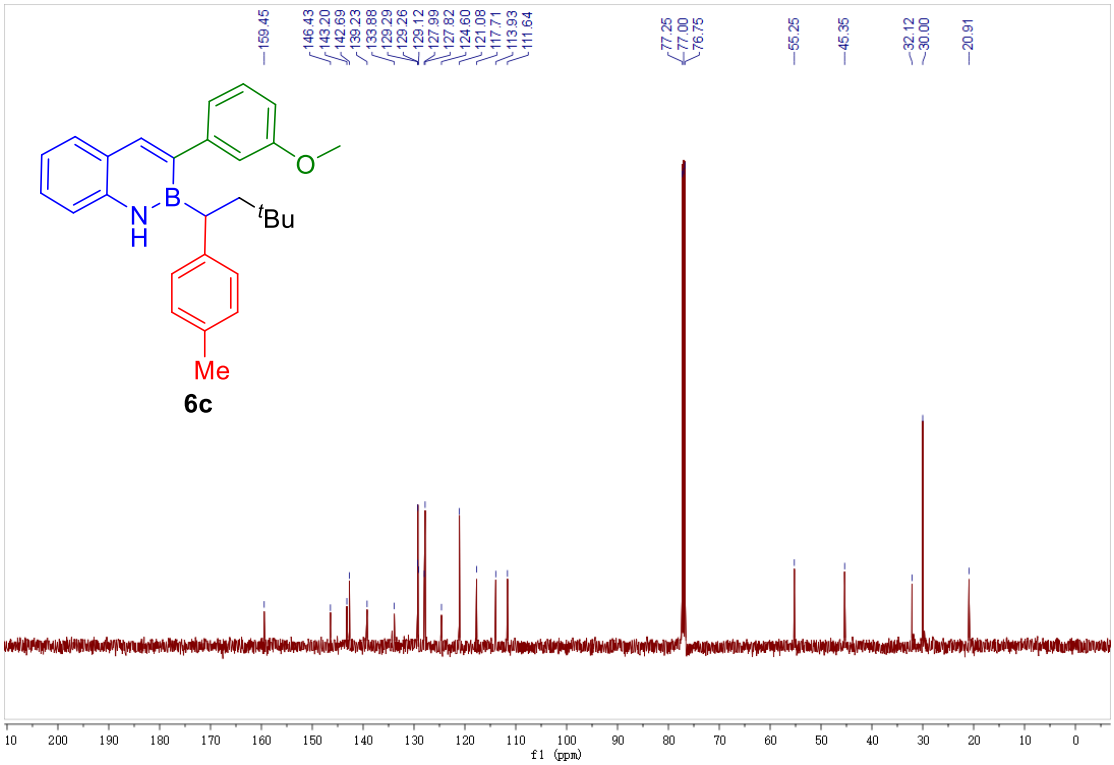
$^{11}$B NMR of **6b** (128 MHz, $CDCl_3$)



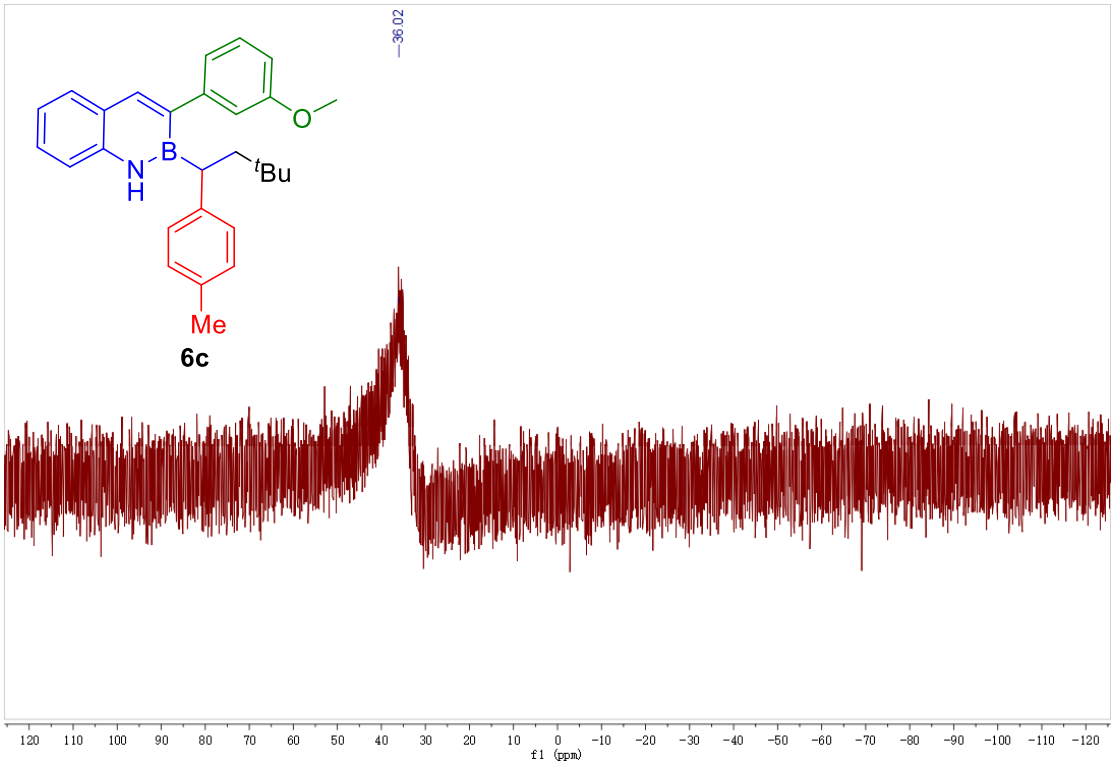

$^{1}$H NMR of **6c** (500 MHz, $CDCl_3$)



$^{13}$C NMR of **6c** (126 MHz, $CDCl_3$)




$^{11}$B NMR of **6c** (128 MHz, $CDCl_3$)



## 9. Supplementary References

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