Synthesis of ^{10}B-enriched 2,1-Borazaronaphthalenes from *o*-Aminostyrenes and $^{10}BF_3$

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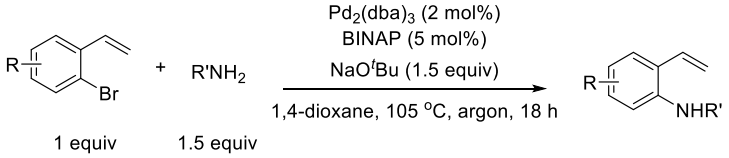
1. General information

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Flash column chromatography was performed over silica gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded at ambient temperature using Bruker 400M and JEOL 500M spectrometers, chemical shifts (in ppm) were referenced to $CDCl_3$ (δ = 7.26 ppm) as internal standards. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.0 ppm). Data for ^{1}H NMR are recorded as following abbreviations: multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (J, Hz). High resolution mass spectroscopy (HRMS) analysis was performed at an Exactive Plus (Thermo Scientific) or Agilent 8890-7250.

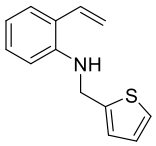
2. General Procedure for the Synthesis of 2-Aminostyrenes.

1a[1], **1n**[1], **1p**[1], **1q**[2], **1r**[3] and **1t**[9] is a known compound, **1m, 1o, 1s** are synthesized as follows:



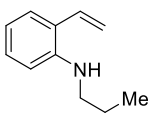
By analogy to a modified literature procedure.[1] To a 50 mL Schlenk flask equipped with a stir bar were added $Pd_2(dba)_3$ (2 mol%), BINAP (5 mo%), and NaO^{t}Bu (1.5 equiv). The flask was evacuated and filled with argon for three cycles. Dioxane was added under argon, followed by 2-bromostyrene (5.0 mmol, 1 equiv), and the corresponding amine (1.5 equiv). The resulting mixture was heated to 105 °C and stirred until full consumption of 2-bromostyrene was observed by TLC (12~18 h). The reaction mixture was cooled to rt., diluted with EtOAc, and filtered over Celite. After removal of the solvent, the crude reaction mixture was purified by flash column chromatography to afford the desired products **1m** and **1o**.

***N*-(thiophen-2-ylmethyl)-2-vinylaniline (1m)**

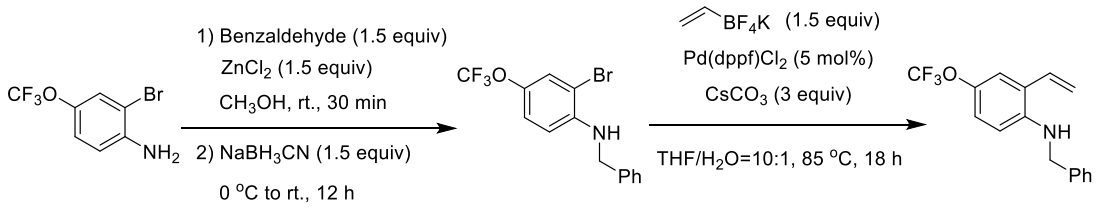


Yellow liquid. Yield: 79% (849.2 mg), R_f = 0.46 (silica gel, PE: EtOAc = 20:1).**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.27 (d, *J* = 7.5 Hz, 1H), 7.17 (dd, *J* = 19.2, 6.2 Hz, 2H), 7.01 – 6.89 (m, 2H), 6.80 – 6.62 (m, 3H), 5.61 (d, *J* = 17.4 Hz, 1H), 5.30 (d, *J* = 11.0 Hz, 1H), 4.50 (s, 2H), 4.17 (s, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 144.5, 142.7, 132.7, 128.9, 127.4, 126.8, 125.0, 124.6, 124.6, 118.0, 116.5, 111.1, 77.3, 77.0, 76.7, 43.5. **HRMS (EI)** calcd for $C_{13}H_{13}NS$ [M]: 215.0769, found: 215.0763.

***N*-propyl-2-vinylaniline (1o)**



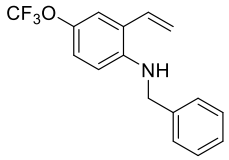
Yellow liquid. Yield: 85 % (685.3 mg), R_f = 0.6 (silica gel, PE: EtOAc = 20:1).**^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.31 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.84 – 6.73 (m, 2H), 6.69 (d, *J* = 8.1 Hz, 1H), 5.66 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.36 (dd, *J* = 11.0, 1.6 Hz, 1H), 3.83 (s, 1H), 3.15 (t, *J* = 7.1 Hz, 2H), 1.78 – 1.66 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.4, 132.9, 128.9, 127.4, 124.0, 116.9, 116.1, 110.5, 45.7, 22.6, 11.7. **HRMS (EI)** calcd for $C_{11}H_{15}N$ [M]: 161.1204, found: 161.1199.



By analogy to a modified literature procedure.[2] To a 100 mL Schlenk flask equipped with a stir bar were added $ZnCl_2$ (15 mmol, 1.5equiv), The flask was evacuated and filled with argon for three cycles. CH_3OH (30 mL) was added under argon, followed by 2-bromoaniline (10 mmol, 1.0 equiv) and benzaldehyde (15 mmol, 1.5 equiv). The mixture was stirred at room temperature for 30 min, then cool to 0 °C and added $NaBH_3CN$ (15 mmol, 1.5 equiv). Allow reaction to rise to room temperature overnight. The reaction was quenched by saturated NH_4Cl solution, the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4. Removal of the solvent, the crude reaction mixture was purified by flash column chromatography to afford *N*-benzyl-2-bromo-4-(trifluoromethoxy)aniline (3.08 g, 89%).

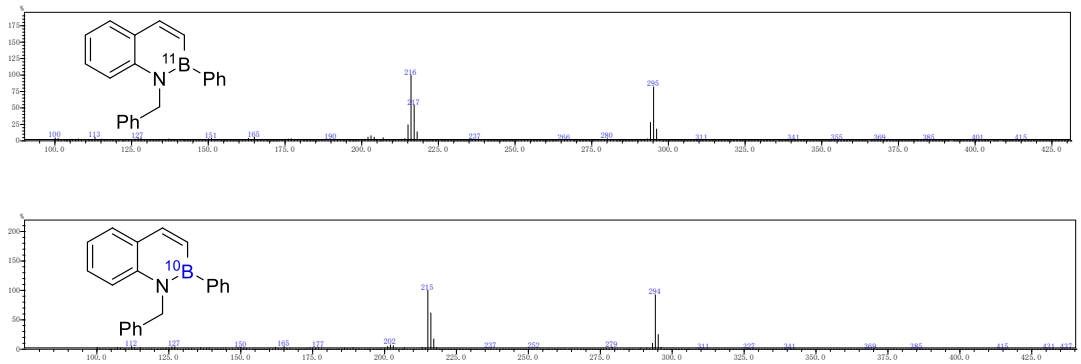
By analogy to a modified literature procedure.[1] To a 50 mL Schlenk flask equipped with a stir bar were added $Pd(dppf)Cl_2$ (0.25 mmol, 5 mol%), $CsCO_3$ (15 mmol, 3 equiv), and Potassium vinyltrifluoroborate (7.5 mmol, 1.5 equiv). The flask was evacuated and filled with argon for three cycles. THF (20 mL) and H_2O (2 mL) was added under argon, followed N-benzyl-2-bromo-4-(trifluoromethoxy)aniline (5 mmol, 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 were dried over anhydrous Na_2SO_4. Removal of the solvent, the crude reaction mixture was purified by flash column chromatography to afford **1s** (1.0841g, 74%).

***N*-benzyl-4-(trifluoromethoxy)-2-vinylaniline (1s)**



Borwn liquid. Yield: 74% (1.0841 g), R_f = 0.4 (silica gel, PE:EA = 20:1).**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.41 – 7.24 (m, 5H), 7.14 (s, 1H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.70 (dd, *J* = 17.2, 11.0 Hz, 1H), 6.54 (d, *J* = 8.8 Hz, 1H), 5.63 (d, *J* = 17.3 Hz, 1H), 5.36 (d, *J* = 11.0 Hz, 1H), 4.32 (s, 2H), 4.17 (s, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -58.29. **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 143.7, 140.5, 138.7, 131.6, 128.7, 127.4, 127.4, 125.0, 121.7, 120.7 (q, *J* = 255.5 Hz), 120.4, 117.8, 111.2, 48.4. **HRMS (EI)** calcd for $C_{16}H_{14}F_3NO$ [M]: 293.1027, found: 293.1027.

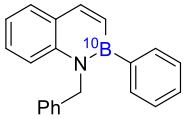
3. Comparison of GC-MS data between ^{11}B-3a and ^{10}B-3a



4. General procedure for the synthesis of ^{10}B-enriched 2,1-borazaronaphthalenes

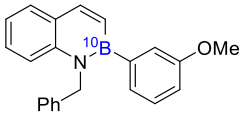
In argon, 2-Aminostyrene (0.5 mmol,1.0 equiv) was transferred to the 25 mL Young tube with 1.5 mL dry toluene and then added to $^{10}BF_3 \cdot OEt_2$ (0.5 mmol, 1.0 equiv), DIPEA (1.0 mmol, 2.0 equiv), $SiCl_4$ (0.5 mmol, 1.0 equiv). The resulting mixture was heated to 90 °C. After stirring for 5 hours, the mixture was cooled to -30 °C, then added RMgBr (1.5 mmol, 3.0 equiv) in argon. The resulting mixture allow to rise to room temperature and stir for 12 h. The reaction was quenched by saturated NH_4Cl solution, the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4. Removal of the solvent, the crude reaction mixture was purified by flash column chromatography to afford the desired products **3a-3s**.

1-benzyl-2-phenyl-1,2-dihydrobenzo[e][1,2]azaborinine-2-^{10}*B* (3a)



White solid, mp: 100 - 102 °C. Yield: 87% (128.4 mg). R_f = 0.6 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.11 (d, *J* = 11.3 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.35 – 7.24 (m, 7H), 7.23 – 7.14 (m, 2H), 7.12 (s, 1H), 7.10 (s, 1H), 7.05 (d, *J* = 11.3 Hz, 1H), 5.42 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.4, 141.1, 139.3, 132.5, 130.2, 128.7, 128.5, 127.9, 127.7, 127.3, 126.8, 125.7, 121.0, 117.0, 52.4. **HRMS (EI)** calcd for $C_{21}H_{18}{}^{10}BN$ [M]: 294.1569, found: 294.1570.

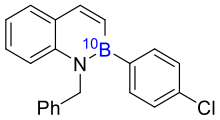
1-benzyl-2-(3-methoxyphenyl)-1,2-dihydrobenzo[e][1,2]azaborinine-2-^{10}*B* (3b)



White solid, mp: 99 - 101 °C. Yield: 85% (137.47 mg). R_f = 0.5 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.12 (d, *J* = 11.3 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 3.7 Hz, 2H), 7.31 – 7.16 (m, 5H), 7.14 – 7.09 (m, 3H), 7.08 – 7.01 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.43 (s,

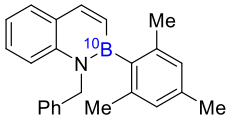
2H), 3.59 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 158.8, 145.4, 141.2, 139.3, 130.3, 128.9, 128.7, 128.6, 127.3, 126.8, 125.7, 124.9, 121.0, 117.1, 117.0, 114.1, 54.8, 52.5. **HRMS (EI)** calcd for $C_{22}H_{20}{}^{10}BNO$ [M]: 324.1674, found: 324.1671.

1-benzyl-2-(4-chlorophenyl)-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3c)



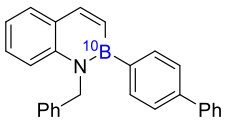
White solid, mp: 118 - 120 °C. Yield: 77% (126.7 mg). R_f = 0.6 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.19 (d, *J* = 11.3 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 2H), 7.43 – 7.33 (m, 6H), 7.32 – 7.24 (m, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 11.3 Hz, 1H), 5.45 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.7, 141.1, 139.0, 134.2, 133.9, 130.3, 128.8, 128.7, 127.9, 127.3, 126.9, 125.6, 121.2, 117.0, 52.4. **HRMS (EI)** calcd for $C_{21}H_{17}{}^{10}BClN$ [M]: 328.1179, found: 328.1174.

1-benzyl-2-mesityl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3d)



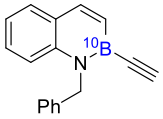
Yellow oil. Yield: 45% (76.2 mg). R_f = 0.6 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.08 (d, *J* = 11.3 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.32 (s, 2H), 7.22 – 7.07 (m, 4H), 7.01 – 6.88 (m, 3H), 6.86 – 6.75 (m, 2H), 5.25 (s, 2H), 2.28 (s, 3H), 2.10 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.1, 141.3, 139.2, 138.6, 136.9, 130.3, 128.4, 128.2, 127.3, 127.3, 126.5, 125.9, 120.9, 117.1, 51.9, 22.6, 21.1. **HRMS (EI)** calcd for $C_{24}H_{24}{}^{10}BN$ [M]: 336.2038, found: 336.2037.

2-([1,1'-biphenyl]-4-yl)-1-benzyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3e)



White solid, mp: 207 - 209 °C. Yield: 67% (128.4 mg). R_f = 0.5 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.14 (d, *J* = 11.4 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.58 (m, 4H), 7.58 – 7.55 (m, 2H), 7.45 – 7.38 (m, 2H), 7.36 – 7.28 (m, 5H), 7.25 – 7.17 (m, 2H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 11.3 Hz, 1H), 5.48 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.4, 141.2, 141.1, 140.6, 139.3, 133.2, 130.3, 128.8, 128.7, 128.6, 127.3, 127.2, 127.0, 126.8, 126.4, 125.7, 121.0, 117.0, 52.5. **HRMS (ESI)** calcd for $C_{27}H_{22}{}^{10}BN$ $[M+H]^+$: 371.1955, found: 371.1947.

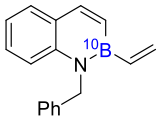
1-benzyl-2-ethynyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3f)



White solid, mp: 75 - 76 °C. Yield: 77% (93.3 mg). R_f = 0.6 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.05 (d, *J* = 11.4 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.30 – 7.24 (m, 2H), 7.23 – 7.12 (m, 4H), 7.03 (d, *J* = 11.4 Hz, 1H), 5.64 (s, 2H), 3.03 (s, 1H). **^{13}C NMR**

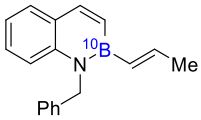
(101 MHz, Chloroform-*d*) δ 145.6, 140.8, 138.3, 130.3, 128.8, 128.6, 127.1, 127.0, 126.1, 121.3, 116.5, 95.9, 53.6. **HRMS (EI)** calcd for $C_{17}H_{14}{}^{10}BN$ [M]: 242.1256, found: 242.1257.

1-benzyl-2-vinyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3g)



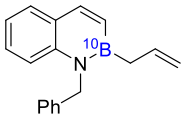
White solid, mp: 52 - 54 ºC. Yield: 58% (70.7 mg). R_f = 0.6 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.02 (d, *J* = 11.5 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.17 (m, 5H), 7.17 – 7.09 (m, 4H), 6.63 (dd, *J* = 19.4, 13.6 Hz, 1H), 6.26 (dd, *J* = 19.4, 3.6 Hz, 1H), 6.05 (dd, *J* = 13.5, 3.4 Hz, 1H), 5.38 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.0, 141.4, 138.6, 133.7, 130.1, 128.7, 128.4, 127.2, 126.9, 125.8, 120.7, 116.1, 51.1. **HRMS (EI)** calcd for $C_{17}H_{16}{}^{10}BN$ [M]: 244.1412, found: 244.1410.

(*E*)-1-benzyl-2-(prop-1-en-1-yl)-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3h)



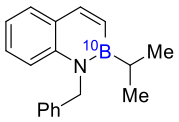
White solid, mp: 57 - 59 ºC. Yield: 70% (89.7 mg). R_f = 0.6 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.05 (d, *J* = 11.4 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.37 – 7.27 (m, 4H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.19 – 7.12 (m, 3H), 7.06 (d, *J* = 11.4 Hz, 1H), 6.39 – 6.30 (m, 1H), 6.12 – 6.07 (m, 1H), 5.37 (s, 2H), 1.91 (dd, *J* = 6.8, 1.5 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 144.4, 141.5, 139.4, 138.6, 130.1, 128.6, 128.3, 126.9, 126.8, 125.8, 120.6, 116.1, 51.7, 18.5. **HRMS (EI)** calcd for $C_{18}H_{18}{}^{10}BN$ [M]:258.1569, found: 258.1561.

2-allyl-1-benzyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3i)



Colorless oil. Yield: 67% (87.0 mg). R_f = 0.6 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.98 (d, *J* = 11.4 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.24 (m, 4H), 7.22 – 7.17 (m, 1H), 7.14 – 7.06 (m, 3H), 6.94 (d, *J* = 11.4 Hz, 1H), 6.18 – 6.02 (m, 1H), 5.31 (s, 2H), 5.05 – 4.90 (m, 2H), 2.26 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 144.9, 141.5, 138.3, 137.4, 130.2, 128.7, 128.4, 126.9, 126.8, 125.7, 120.6, 116.0, 114.0, 50.5. **HRMS (EI)** calcd for $C_{18}H_{18}{}^{10}BN$ [M]: 258.1569, found: 258.1563.

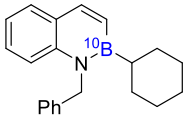
1-benzyl-2-isopropyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3j)



White solid, mp: 66 - 68 ºC. Yield: 67% (87.9 mg). R_f = 0.7 (silica gel, PE: EtOAc = 20:1).**^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.01 (d, *J* = 11.5 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.24 (m, 4H), 7.22 – 7.16 (m, 1H), 7.14 – 7.06 (m, 3H), 6.99 (d, *J* = 11.5 Hz, 1H), 5.35 (s, 2H), 1.70 – 1.56 (m, 1H), 1.13 (d, *J* = 7.1 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.2, 141.3, 138.9, 130.1, 128.7, 128.2,

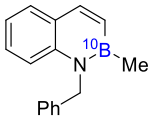
126.8, 126.8, 125.7, 120.5, 116.3, 50.2, 20.6. **HRMS (EI)** calcd for $C_{18}H_{20}{}^{10}BN$ [M]: 260.1725, found: 260.1723.

1-benzyl-2-cyclohexyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3k)



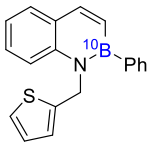
Colorless oil, Yield: 75% (113.3 mg). R_f = 0.7 (silica gel, PE: EtOAc = 20:1).**^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.99 (d, *J* = 11.6 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.28 – 7.22 (m, 4H), 7.19 (dd, *J* = 8.7, 6.5 Hz, 1H), 7.10 – 7.06 (m, 3H), 7.00 (d, *J* = 11.5 Hz, 1H), 5.34 (s, 2H), 1.78 – 1.67 (m, 6H), 1.54 – 1.44 (m, 2H), 1.32 – 1.24 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.0, 141.3, 139.0, 130.0, 128.7, 128.2, 126.8, 126.8, 125.7, 120.4, 116.4, 50.3, 30.3, 27.8, 27.0. **HRMS (EI)** calcd for $C_{21}H_{24}{}^{10}BN$ [M]: 300.2038, found: 300.2034.

1-benzyl-2-methyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3l)



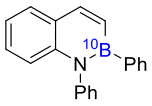
White solid, mp: 57 - 59 ºC. Yield: 79% (92.1 mg). R_f = 0.7 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 (d, *J* = 11.3 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.21 (m, 4H), 7.20 – 7.15 (m, 1H), 7.08 (d, *J* = 7.3 Hz, 3H), 6.87 (d, *J* = 11.3 Hz, 1H), 5.27 (s, 2H), 0.83 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 144.1, 141.7, 138.5, 130.1, 128.7, 128.2, 126.8, 125.8, 120.3, 115.8, 50.9. **HRMS (EI)** calcd for $C_{16}H_{16}{}^{10}BN$ [M]: 232.1422, found: 232.1411.

2-phenyl-1-(thiophen-2-ylmethyl)-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3m)



Brown solid, mp: 92 - 94 ºC. Yield: 61% (91.9 mg). R_f = 0.6 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.08 (d, *J* = 11.3 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.43 – 7.32 (m, 4H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 5.0 Hz, 1H), 7.00 (d, *J* = 11.3 Hz, 1H), 6.91 – 6.86 (m, 1H), 6.77 (s, 1H), 5.52 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.4, 143.2, 141.0, 132.5, 130.3, 128.6, 128.0, 127.7, 127.3, 127.0, 124.2, 123.9, 121.2, 116.4, 48.2. **HRMS (EI)** calcd for $C_{19}H_{16}{}^{10}BNS$ [M]: 300.1133, found: 300.1133.

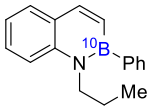
1,2-diphenyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3n)



White solid, mp: 119 - 121 ºC. Yield: 76% (106.2 mg). R_f = 0.6 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.15 (d, *J* = 11.4 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.27 (m, 4H), 7.24 – 7.09 (m, 9H), 6.94 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.2, 143.8,

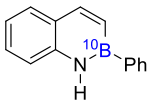
142.7, 133.8, 129.7, 129.4, 129.3, 128.2, 127.6, 127.1, 127.1, 126.1, 121.2, 117.6. **HRMS (EI)** calcd for $C_{20}H_{16}{}^{10}BN$ [M]: 280.1412, found: 280.1416.

2-phenyl-1-propyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3o)



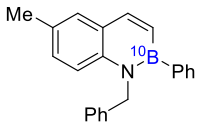
Colorless oil. Yield: 73% (89.5 mg). R_f = 0.65 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.02 (d, *J* = 11.3 Hz, 1H), 7.69 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.60 – 7.48 (m, 4H), 7.44 – 7.39 (m, 2H), 7.39 – 7.34 (m, 1H), 7.25 – 7.20 (m, 1H), 6.90 (d, *J* = 11.3 Hz, 1H), 4.15 – 4.05 (m, 2H), 1.86 – 1.76 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 144.7, 140.9, 132.2, 130.5, 128.4, 127.6, 127.4, 127.2, 120.7, 115.6, 49.5, 23.4, 11.2. **HRMS (EI)** calcd for $C_{17}H_{18}{}^{10}BN$ [M]: 246.1569, found: 246.1566.

2-phenyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3p)



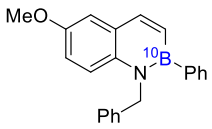
White solid, mp: 134 - 136 ºC. Yield: 45% (45.5 mg). R_f = 0.5 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.12 (d, *J* = 11.3 Hz, 2H), 7.90 (d, *J* = 6.2 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.39 (m, 4H), 7.33 – 7.24 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.5, 140.1, 132.7, 129.6, 129.4, 128.4, 128.2, 125.7, 121.0, 118.2. **HRMS (EI)** calcd for $C_{14}H_{12}{}^{10}BN$ [M]: 204.1099, found: 204.1095.

1-benzyl-6-methyl-2-phenyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3q)



White solid, mp: 76 - 78 ºC. Yield: 91% (141.2 mg). R_f = 0.6 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.07 (d, *J* = 11.3 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.51 (s, 2H), 7.34 – 7.25 (m, 5H), 7.22 (d, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 3H), 7.04 – 6.92 (m, 2H), 5.40 (s, 2H), 2.31 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 145.1, 141.2, 139.4, 138.7, 132.5, 130.1, 128.7, 127.8, 127.6, 126.7, 125.7, 125.1, 122.4, 117.1, 52.3, 22.2. **HRMS (EI)** calcd for $C_{22}H_{20}{}^{10}BN$ [M]: 308.1725, found: 308.1723.

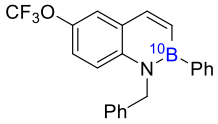
1-benzyl-6-methoxy-2-phenyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3r)



White solid, mp: 88 - 90 ºC. Yield: 66% (107.4 mg). R_f = 0.5 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.06 (d, *J* = 11.3 Hz, 1H), 7.52 (s, 2H), 7.36 – 7.18 (m, 7H), 7.16 – 7.03 (m, 4H), 6.96 (dd, *J* = 9.2, 2.5 Hz, 1H), 5.41 (s, 2H), 3.84 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)**

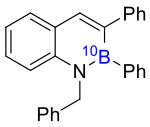
δ 153.7, 144.8, 139.4, 135.7, 132.6, 128.7, 128.0, 127.8, 127.7, 126.8, 125.7, 118.2, 117.2, 111.7, 55.5, 52.5. **HRMS (EI)** calcd for $C_{22}H_{10}{}^{10}BNO$ [M]: 324.1674 found: 324.1674.

1-benzyl-2-phenyl-6-(trifluoromethoxy)-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3s)



Colorless oil. Yield: 71% (133.6 mg). R_f = 0.6 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.05 (d, *J* = 11.4 Hz, 1H), 7.59 – 7.46 (m, 3H), 7.36 – 7.27 (m, 6H), 7.27 – 7.21 (m, 1H), 7.18 (d, *J* = 9.3 Hz, 1H), 7.15 – 7.08 (m, 3H), 5.42 (s, 2H). **^{19}F NMR (471 MHz, Chloroform-*d*)** δ -57.86. **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 144.6, 142.9, 139.6, 138.7, 132.5, 128.9, 128.2, 127.9, 127.8, 127.1, 125.6, 124.4, 121.9, 121.6, 121.5, 119.3, 118.4, 116.8, 52.7. **HRMS (EI)** calcd for $C_{22}H_{17}{}^{10}BF_3NO$ [M]: 378.1392, found: 378.1390.

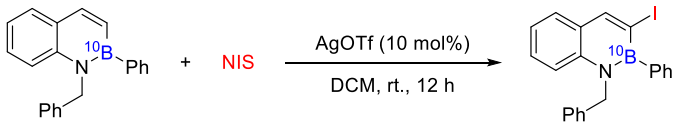
1-benzyl-2,3-diphenyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}B (3t)



Yellow oil, yield: 31% (57.7 mg). R_f = 0.5 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.09 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.34 (s, 2H), 7.29 – 7.08 (m, 16H), 5.36 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 144.3, 143.4, 140.4, 139.1, 132.1, 130.4, 128.9, 128.7, 128.5, 127.6, 127.4, 127.3, 126.8, 126.7, 125.7, 125.7, 121.4, 117.0, 52.9. **HRMS (EI)** calcd for $C_{27}H_{22}{}^{10}BN$ [M]: 370.1882, found: 370.1880.

5. Synthetic transformations

1-benzyl-3-iodo-2-phenyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (4)

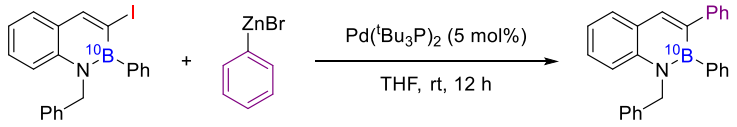


3a **4**

By analogy to a modified literature procedure.[4] In argon, a 50 mL Schlenk tube was charged with **3a** (2.0 mmol, 1 equiv), AgOTf (10 mol%) and dry DCM (5 mL). Then, NIS (2.2 mmol, 1.1 equiv) in dry DCM (15 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 **4**.

White solid, mp: 136 - 138 °C. Yield: 91% (766.8 mg). R_f = 0.6 (silica gel, PE: EtOAc = 20:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.81 (s, 1H), 7.59 (dd, J = 7.8, 1.4 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.35 – 7.27 (m, 5H), 7.26 – 7.21 (m, 2H), 7.20 – 7.13 (m, 2H), 7.02 (d, J = 7.2 Hz, 2H), 5.29 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.4, 140.4, 138.3, 131.3, 129.4, 129.2, 128.7, 128.0, 128.0, 127.6, 126.9, 125.5, 121.7, 117.3, 53.9. **HRMS (EI)** calcd for $C_{21}H_{17}{}^{10}BIN$ [M]: 420.0535, found: 420.0539.

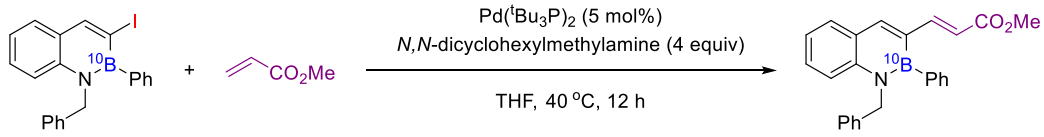
1-benzyl-2,3-diphenyl-1,2-dihydrobenzo[*e*][1,2]azaborinine-2-^{10}*B* (3t)



4 **3t**

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) and phenylmagnesium bromide (in THF (1M), 0.32 mmol, 1.6 equiv). The mixture was stirred for 30 minutes. Then, the mixture was charged with **4** (0.2 mmol, 1.0 equiv), bis(tri-tert-butylphosphine)palladium (0.005 mmol, 5 mol%), 2 mL of THF and phenylzinc solution prepared in the previous step. The tube was removed from glove box, and stirred for 12 h at room temperature. Upon completion, the solvent was concentrated under reduced pressure and rapidly purified by column chromatography to obtain product **3t** (63.7 mg, 86% yield).

methyl (*E*)-3-(1-benzyl-2-phenyl-1,2-dihydrobenzo[*e*][1,2] azaborinin-3-yl-2-^{10}*B*)acrylate (5)

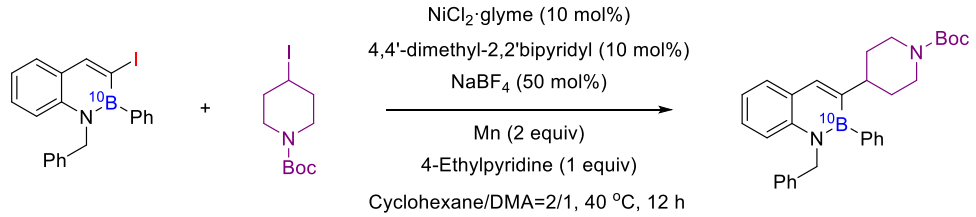


4 **5**

By analogy to a modified literature procedure.[6] A 25 mL Young tube was charged with **4** (0.2 mmol, 1 equiv) and Pd(^{t}Bu$_3$P)$_2$ (5 mol%). and *N,N*-dicyclohexylmethylamine (4 equiv). The tube was evacuated and filled with argon for three cycles, then added methyl acrylate (2 equiv), N, N-dicyclohexylmethylamine (4 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 **5**.

Yellow solid, mp: 73 - 75 °C. Yield: 79% (59.9 mg). R_f = 0.3 (silica gel, PE: EtOAc = 10:1). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.27 (s, 1H), 7.75 – 7.68 (m, 2H), 7.40 – 7.17 (m, 12H), 7.04 (d, J = 7.2 Hz, 2H), 5.90 (d, J = 15.9 Hz, 1H), 5.29 (s, 2H), 3.67 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 167.9, 148.7, 145.3, 141.4, 138.6, 131.2, 131.1, 129.9, 128.7, 128.0, 127.9, 126.8, 126.3, 125.6, 121.7, 118.2, 117.1, 52.6, 51.4. **HRMS (ESI)** calcd for $C_{25}H_{22}{}^{10}BNO_2$ $[M+H]^+$: 379.1853, found: 379.1859.

tert-butyl 4-(1-benzyl-2-phenyl-1,2-dihydrobenzo[*e*][1,2] azaborinin-3-yl-2-^{10}*B*)piperidine-1-carboxylate (6)



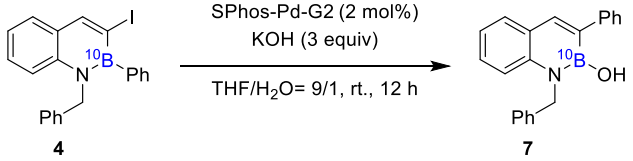
4 **6**

By analogy to a modified literature procedure.[7] A 25 mL Young tube was charged with **4** (0.2 mmol, 1equiv), alkyl iodide (2.4 mmol, 1.2 equiv), $NiCl_2$·glyme (0.02 mmol, 10 mol%), 4,4'-dimethy-2,2'-bipyridyl (0.02 mmol, 10 mol%), $NaBF_4$ (0.1 mmol, 50 mol%), Mn (0.4 mmol, 2 equiv). The tube was

evacuated and filled with argon for three cycles, then added 4-Ethylpyridine (0.2 mmol, 1 equiv), dry Cyclohexane (1 mL) and dry DMA (0.5 mL) in argon. The mixture was stirred at 40 °C for 12 h. Upon completion, removal of the solvent, the crude reaction mixture was purified on silica gel to afford product **6**.

Colorless oil. Yield: 93% (87.9 mg). R_f = 0.3 (silica gel, PE: EtOAc = 10:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.86 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.12 (m, 11H), 7.02 (d, *J* = 7.4 Hz, 2H), 5.23 (s, 2H), 4.11 (s, 2H), 2.59 – 2.40 (m, 3H), 1.74 – 1.63 (m, 2H), 1.56 – 1.36 (m, 11H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.8, 139.8, 139.6, 138.9, 130.9, 129.9, 128.5, 127.9, 127.7, 127.3, 126.9, 126.7, 125.6, 121.2, 116.7, 79.1, 52.8, 44.6, 39.8, 33.0, 28.5. **HRMS (ESI)** calcd for $C_{31}H_{35}{}^{10}BN_2O_2$ $[M+H]^+$: 478.2901, found: 478.2908.

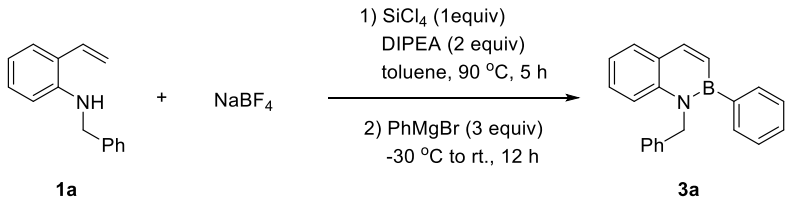
1-benzyl-3-phenylbenzo[*e*][1,2]azaborinin-2(1*H*)-ol-2-^{10}*B* (7)



By analogy to a modified literature procedure.[8] A 25 mL Schlenk tube was charged with **4** (0.2 mmol, 1 equiv), SPhos-Pd-G2 (0.004 mmol, 2 mol%), KOH (0.6 mmol, 3 equiv), The tube was evacuated and filled with argon for three cycles, then added THF (0.9 mL) and H_2O (0.1 mL) in argon. The mixture was stirred at room temperature for 12 h. Upon completion, anhydrous sodium sulfate was added, then diatomite and a small amount of silica gel filtration. The desired product **7** is obtained by removing the solvent.

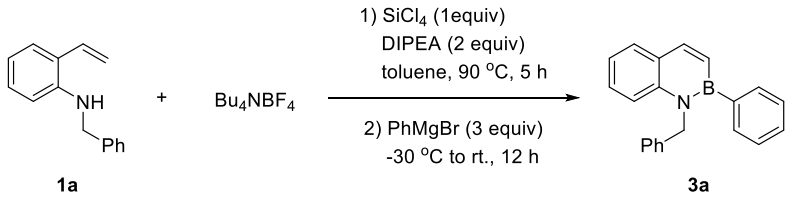
Brown oil, yield: 99% (61.4 mg). R_f = 0.5 (silica gel, PE:EtOAc = 5:1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.82 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.43 (m, 4H), 7.34 – 7.16 (m, 8H), 7.03 (d, *J* = 5.9 Hz, 1H), 5.26 (s, 2H), 4.56 (s, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 143.5, 142.4, 141.6, 138.8, 130.2, 129.3, 128.6, 128.6, 127.3, 126.8, 126.7, 126.3, 124.4, 119.7, 115.0, 46.8. **HRMS (EI)** calcd for $C_{21}H_{18}{}^{10}BNO$ [M]: 310.1518, found: 310.1519.

6. Control experiments



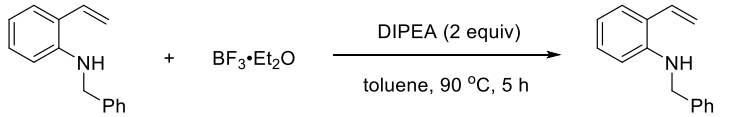
In argon, 2-Aminostyrene (0.5 mmol, 1.0 equiv) was transferred to the 25 mL Young tube with 1.5 ml dry toluene and then added to $NaBF_4$ (0.5 mmol, 1.0 equiv), DIPEA (1.0 mmol, 2.0 equiv), $SiCl_4$ (0.5 mmol, 1.0 equiv). The resulting mixture was heated to 90 °C. After stirring for 5 hours, the mixture was cooled to -30 °C, then added PhMgBr (1.5 mmol, 3.0 equiv) in argon. The resulting mixture allow to rise to room temperature and stir for 12 h. The reaction was quenched by saturated NH_4Cl solution, the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous

Na_2SO_4. Removal of the solvent, the crude reaction mixture was purified by flash column chromatography to afford the desired products **3a** (119.7 mg, 81% yield).



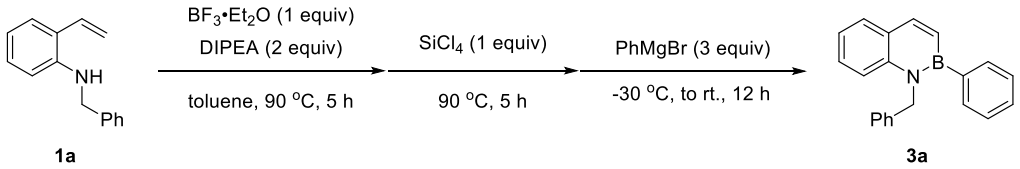
1a **3a**

In argon, 2-Aminostyrene (0.5 mmol, 1.0 equiv) was transferred to a 25 mL Young tube with 1.5 ml dry toluene and then added to Bu_4NBF_4 (0.5 mmol, 1.0 equiv), DIPEA (1.0 mmol, 2.0 equiv), $SiCl_4$ (0.5 mmol, 1.0 equiv). The resulting mixture was heated to 90 °C. After stirring for 5 hours, the mixture was cooled to -30 °C, then added PhMgBr (1.5 mmol, 3.0 equiv) in argon. The resulting mixture allow to rise to room temperature and stir for 12 h. The reaction was quenched by saturated NH_4Cl solution, the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4. Removal of the solvent, the crude reaction mixture was purified by flash column chromatography to afford the desired products **3a** (122.5 mg, 83% yield).



1a **1a** recovery: 89%

In argon, 2-Aminostyrene **1a** (0.5 mmol, 1.0 equiv) was transferred to the 25 mL Young tube with 1.5 ml dry toluene and then added to $BF_3 \cdot Et_2O$ (0.5 mmol, 1.0 equiv), DIPEA (1.0 mmol, 2.0 equiv). The resulting mixture was heated to 90 °C. After stir for 5 hours, The mixture was cooled to room temperature. Removal of the solvent, the crude reaction mixture was purified by flash column chromatography to recover **1a** (93.5 mg, 89%).



1a **3a**

In argon, 2-Aminostyrene **1a** (0.5 mmol, 1.0 equiv) was transferred to a 25 mL Young tube with 1.5 ml dry toluene and then added to $BF_3 \cdot Et_2O$ (0.5 mmol, 1.0 equiv), DIPEA (1.0 mmol, 2.0 equiv). The resulting mixture was heated to 90 °C. After stirring for 5 hours, the mixture was cooled to room temperature, then $SiCl_4$ (0.5 mmol, 1.0 equiv) was added. The resulting mixture was heated to 90 °C and stir for another 5 hours. The mixture was cooled to -30 °C and added PhMgBr (1.5 mmol, 3.0 equiv) in argon. The resulting mixture allow to rise to room temperature and stir for 12 h. The reaction was quenched by saturated NH_4Cl solution, the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4. Removal of the solvent, the crude reaction mixture was purified by flash column chromatography to afford the desired product **3a** (116.4 mg, 79% yield).

7. References

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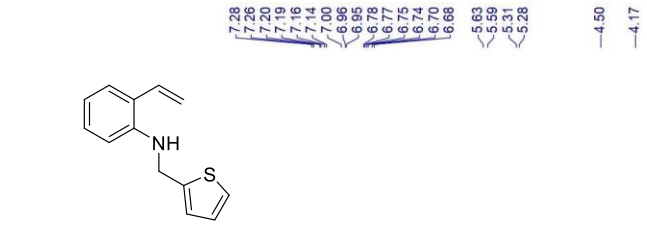
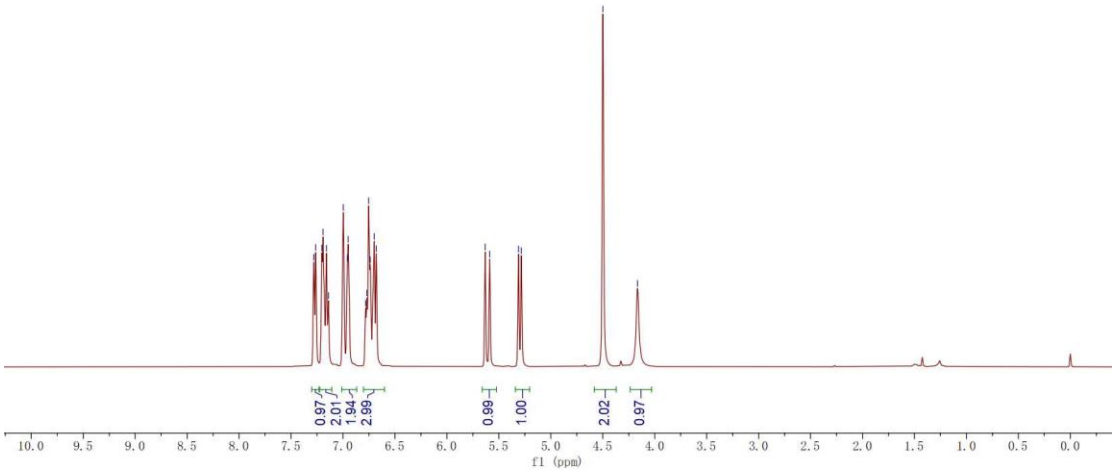
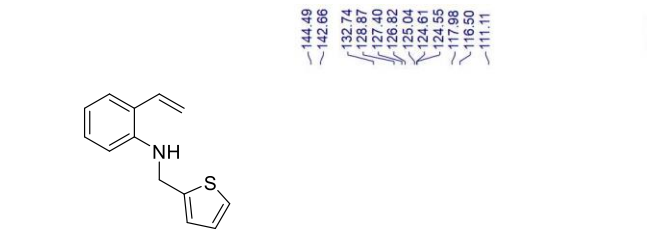
8. NMR Spectra



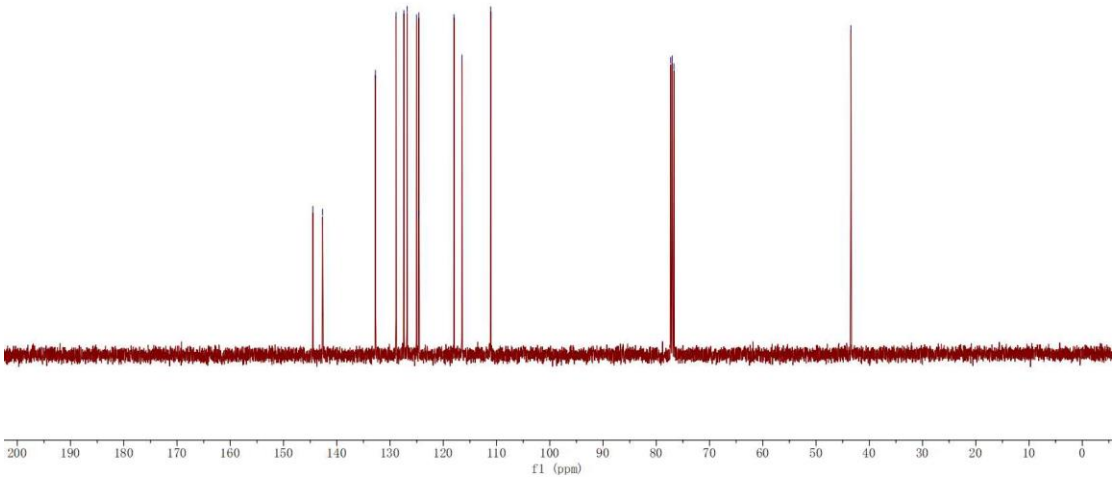
^{1}H NMR (400 MHz, Chloroform-*d*)



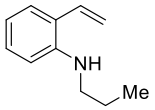
^{1}H NMR spectrum of **1m**



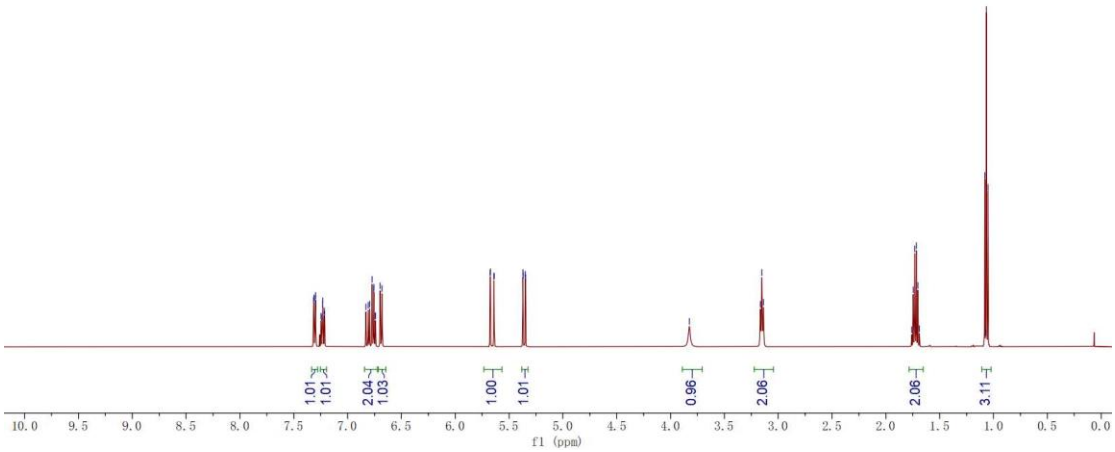
^{13}C NMR (101 MHz, Chloroform-*d*)



^{13}C NMR spectrum of **1m**



^{1}H NMR (500 MHz, Chloroform-*d*)



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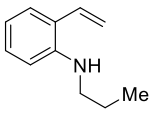

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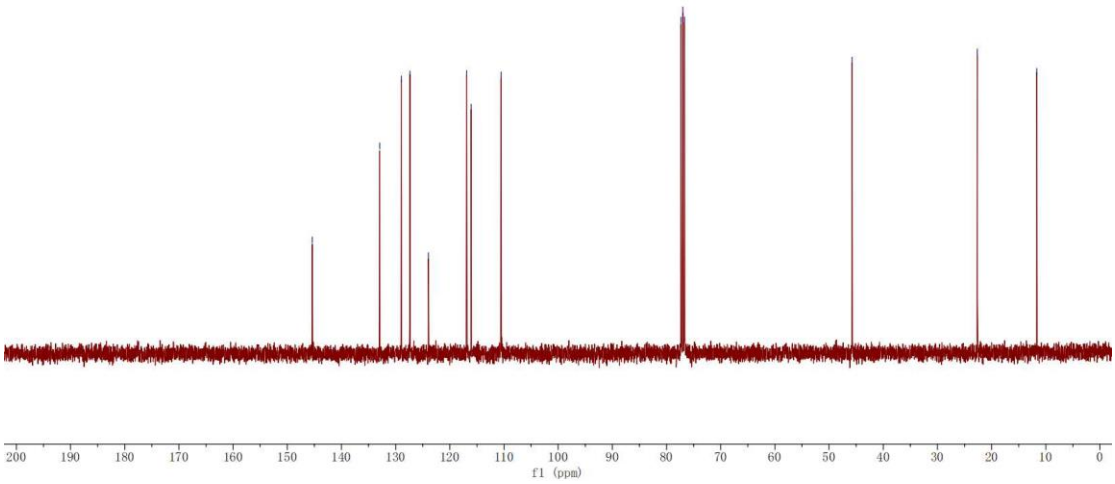

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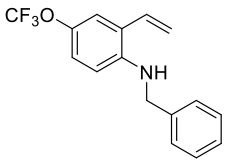

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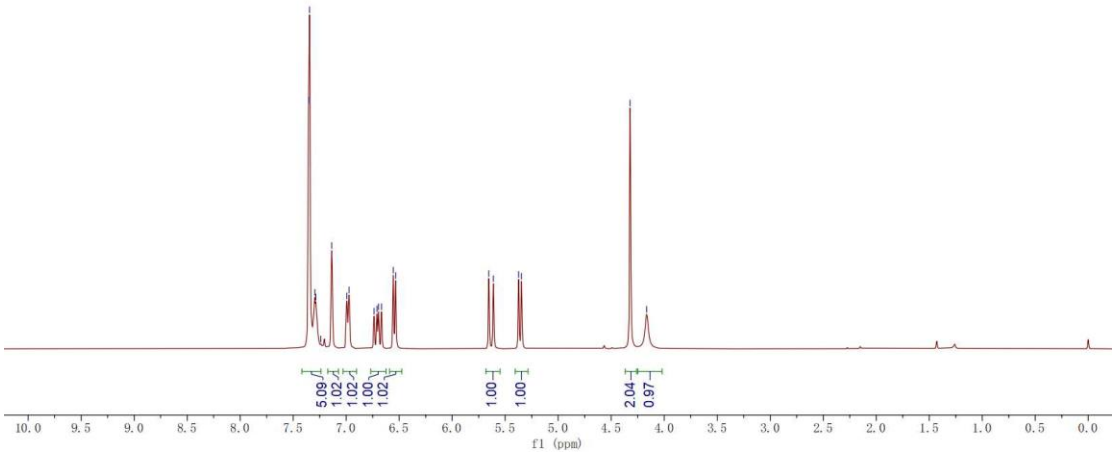

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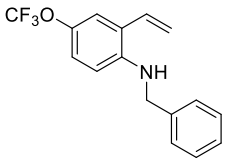

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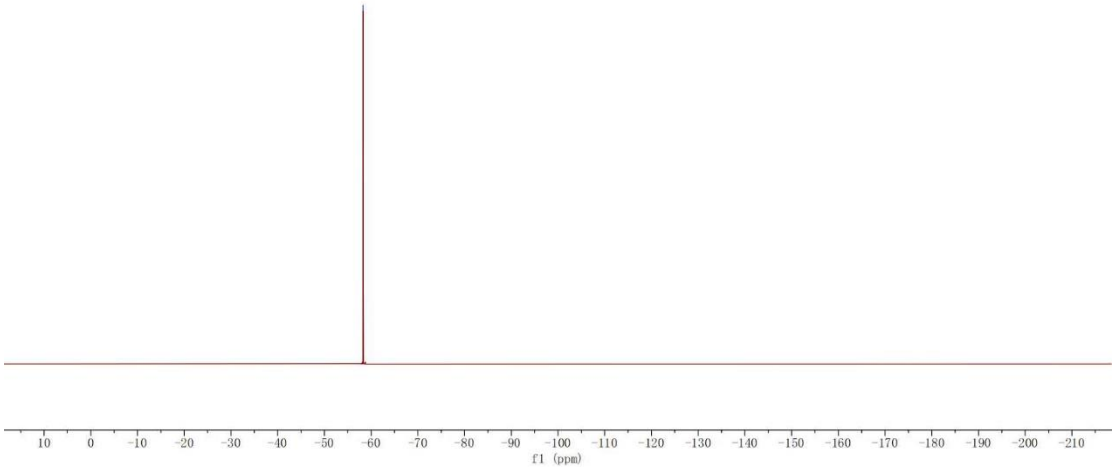
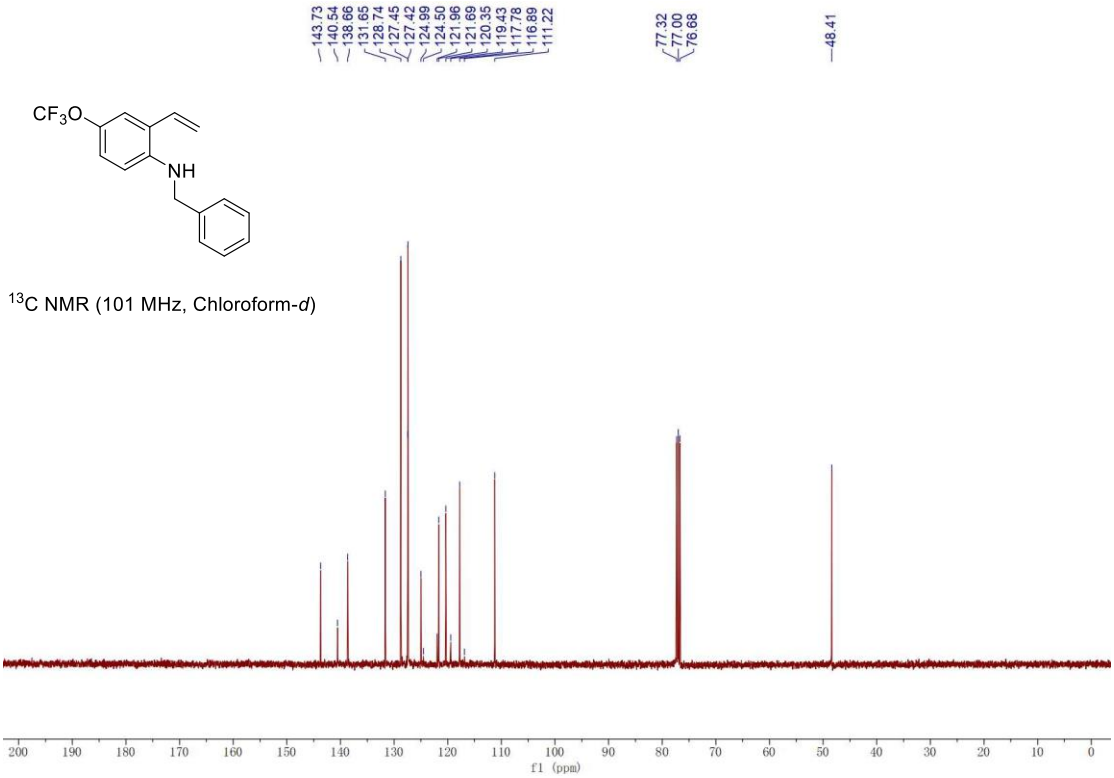
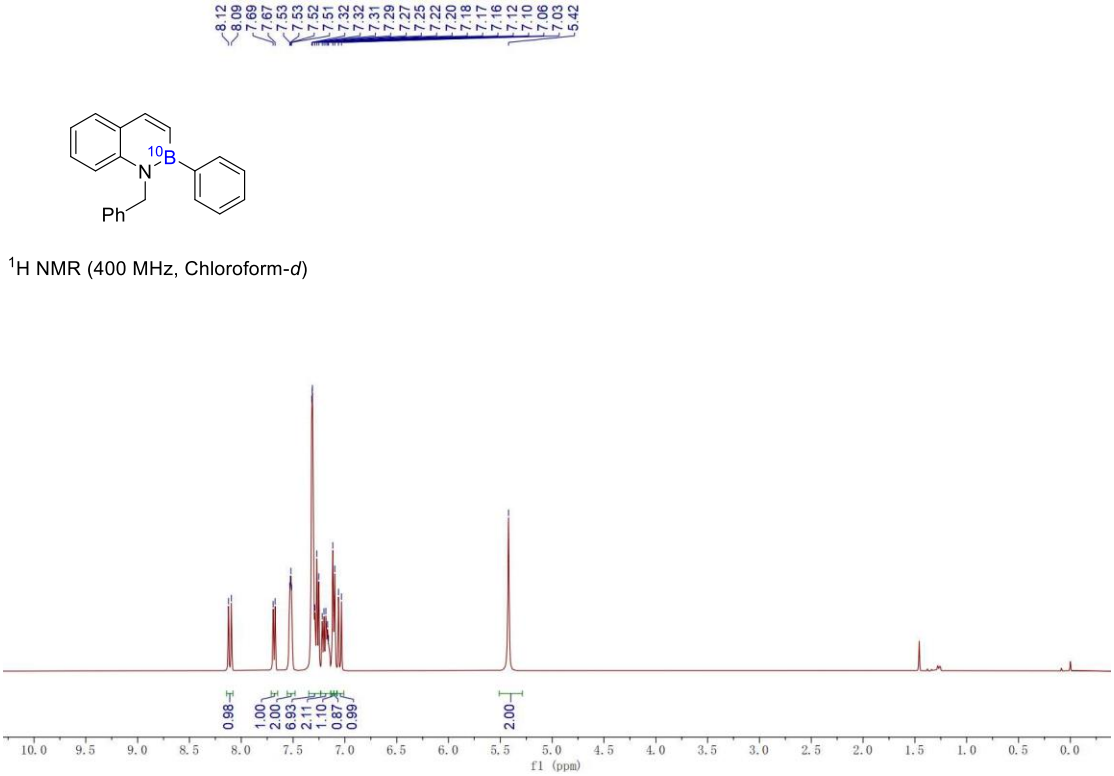


^{19}**F** NMR spectrum of **1s**



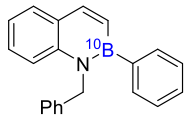
^{13}C NMR (101 MHz, Chloroform-*d*)

^{13}C NMR spectrum of **1s**



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

^{1}H NMR spectrum of **3a**



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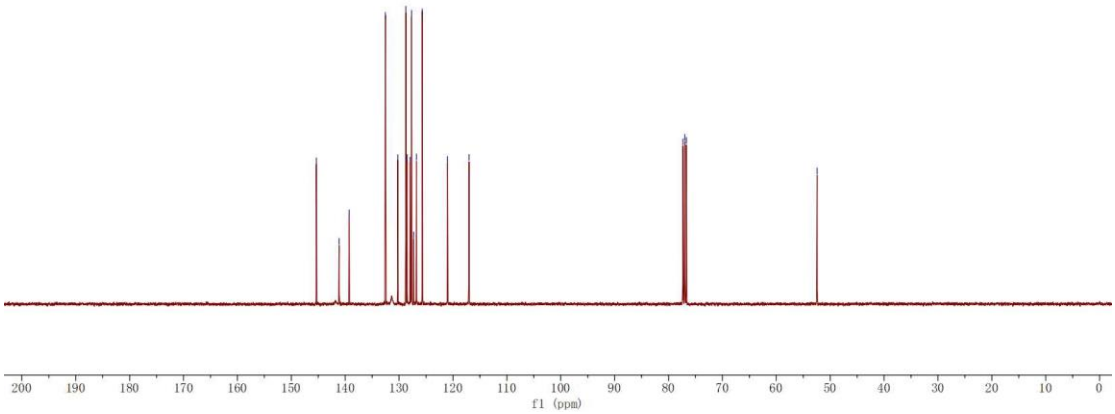
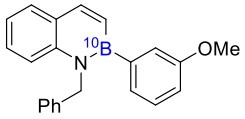


^{13}C NMR spectrum of **3a**



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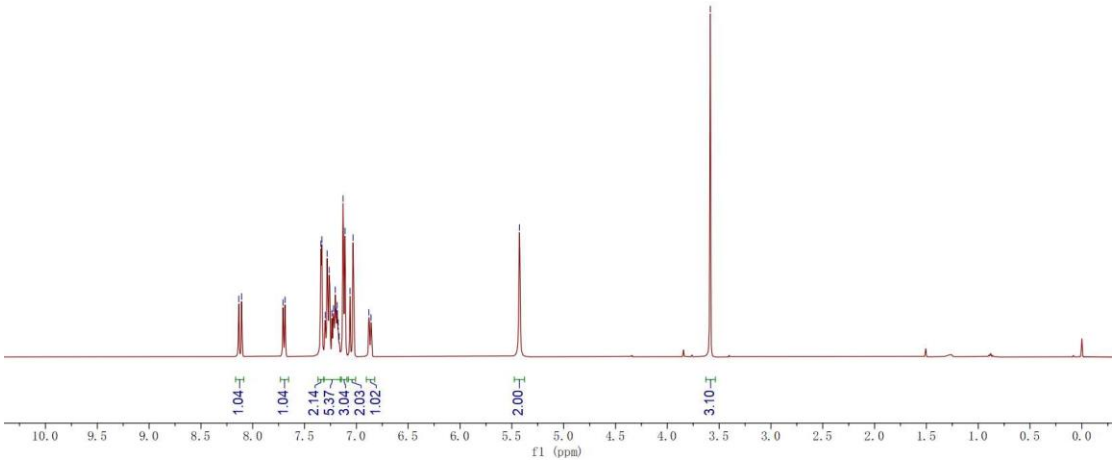
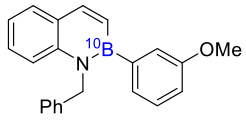


^{1}H NMR spectrum of **3b**



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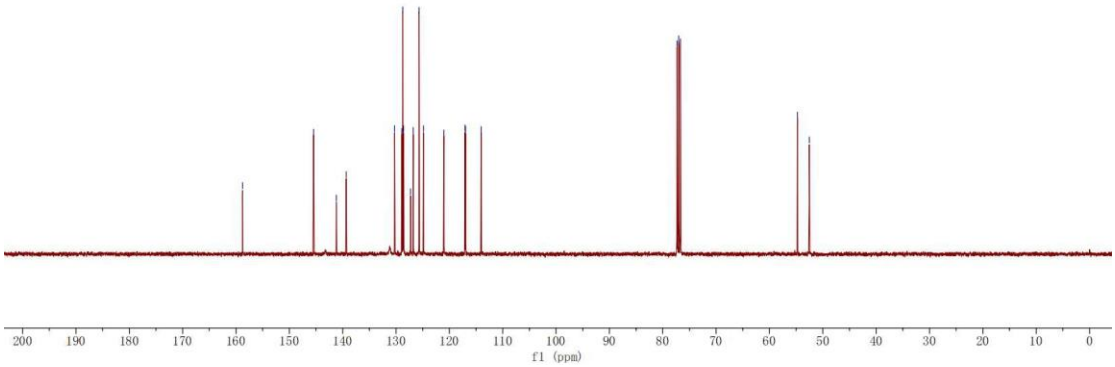

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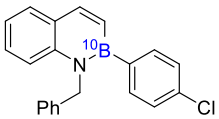

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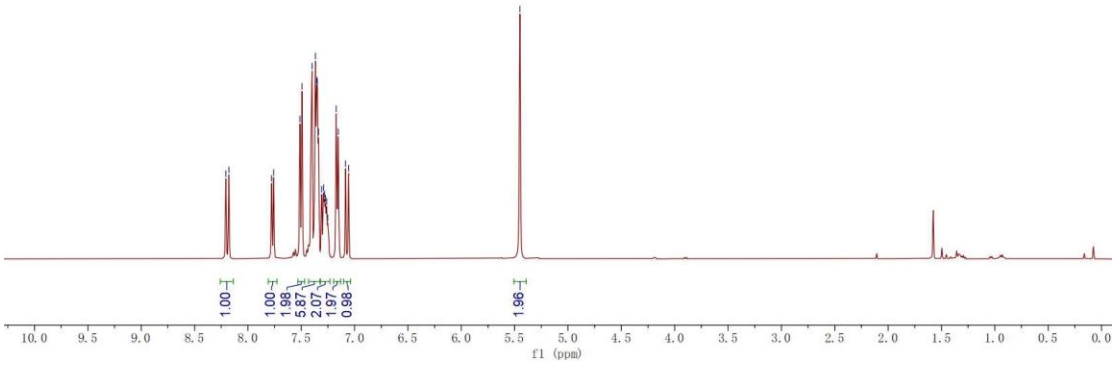

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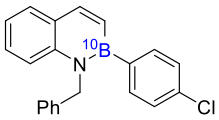

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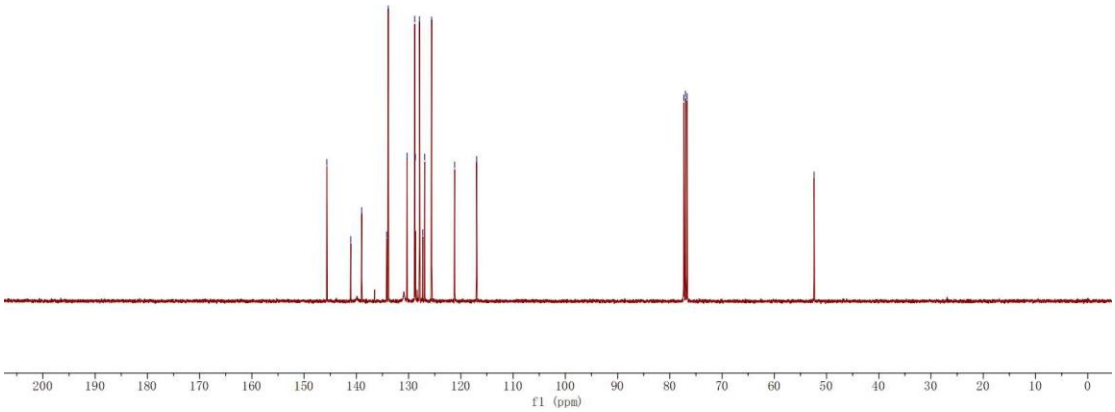
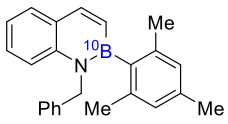


^{13}C NMR spectrum of **3c**



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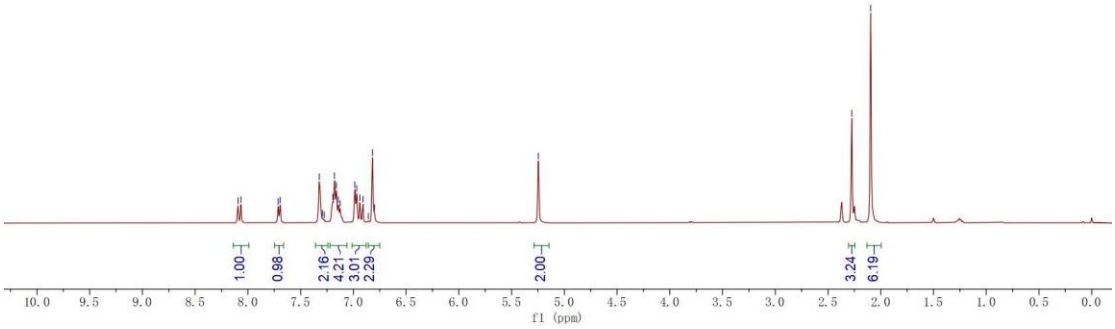

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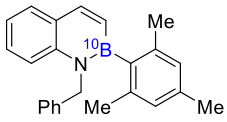

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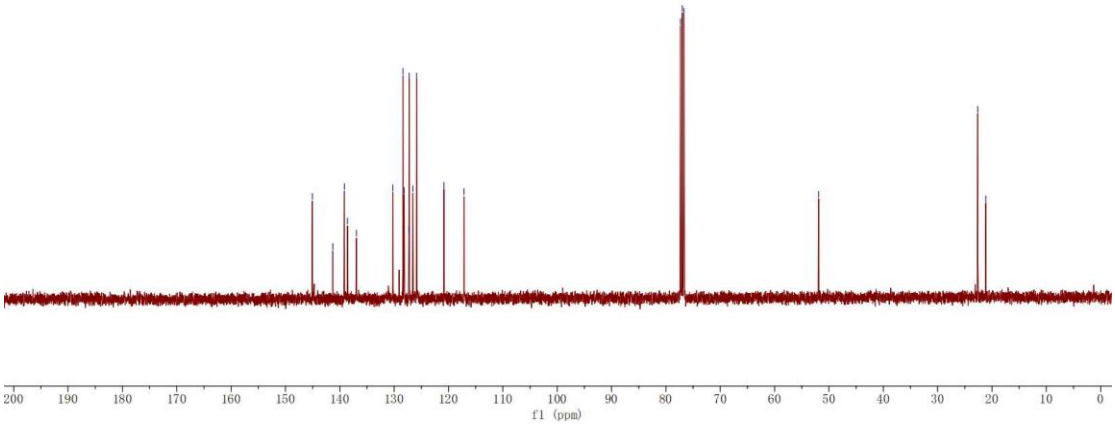

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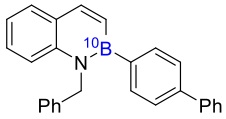

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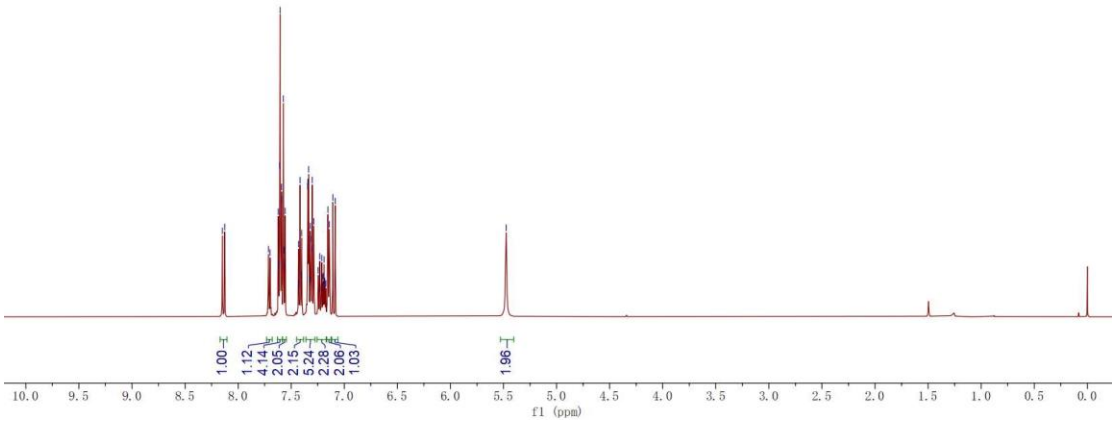

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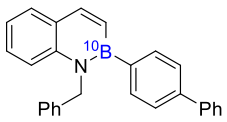

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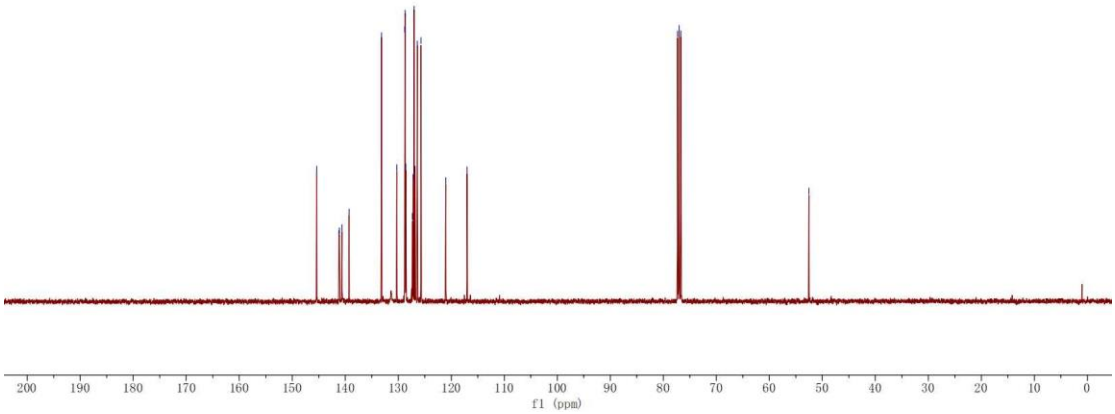

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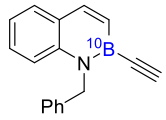

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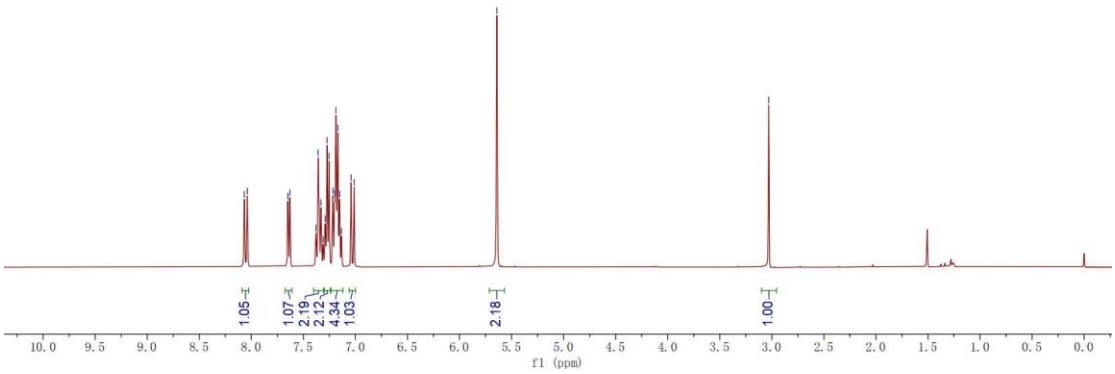

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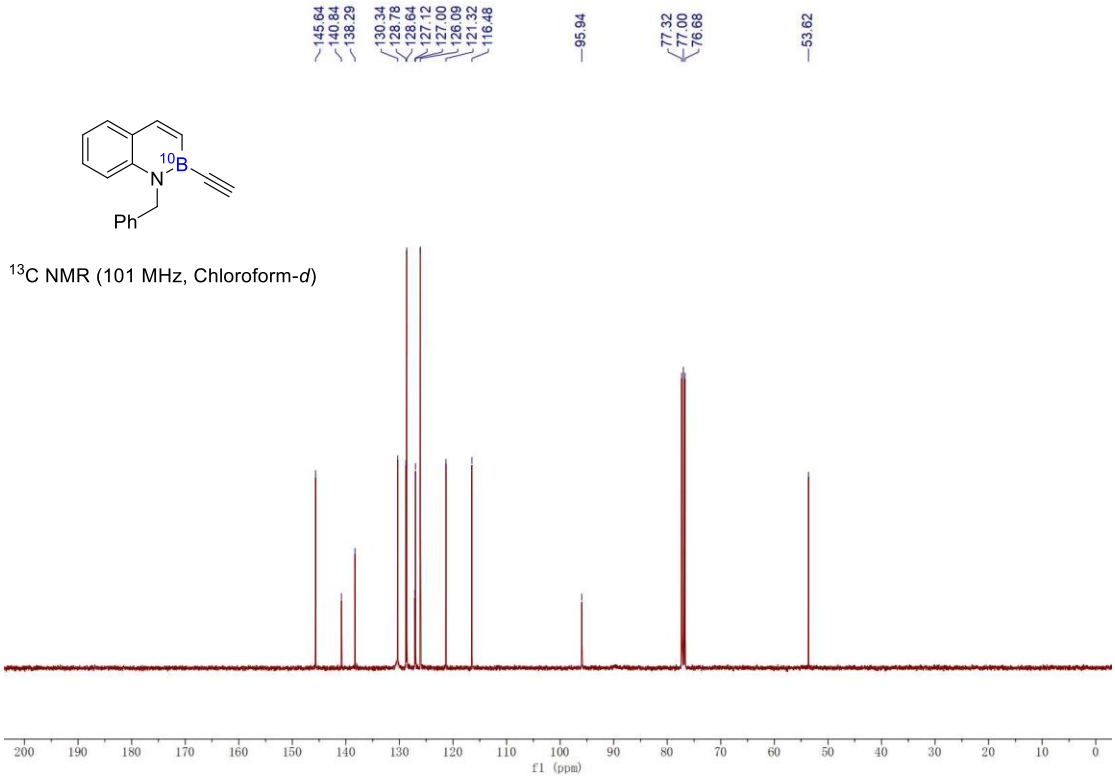

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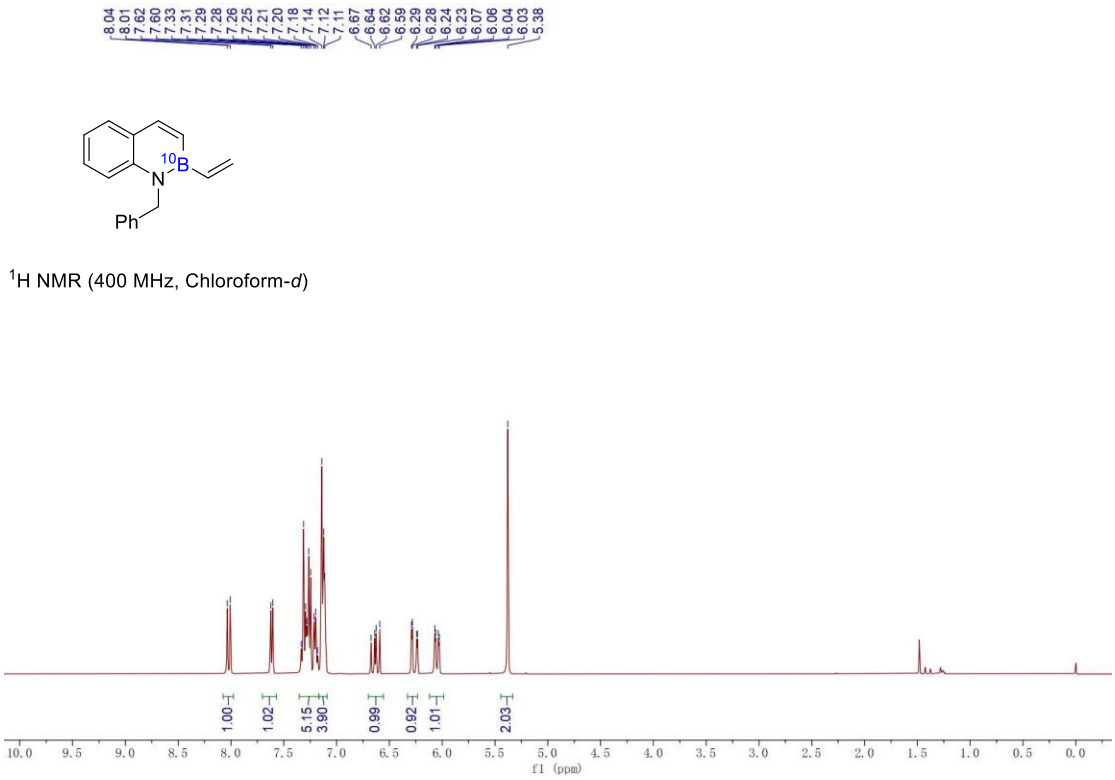
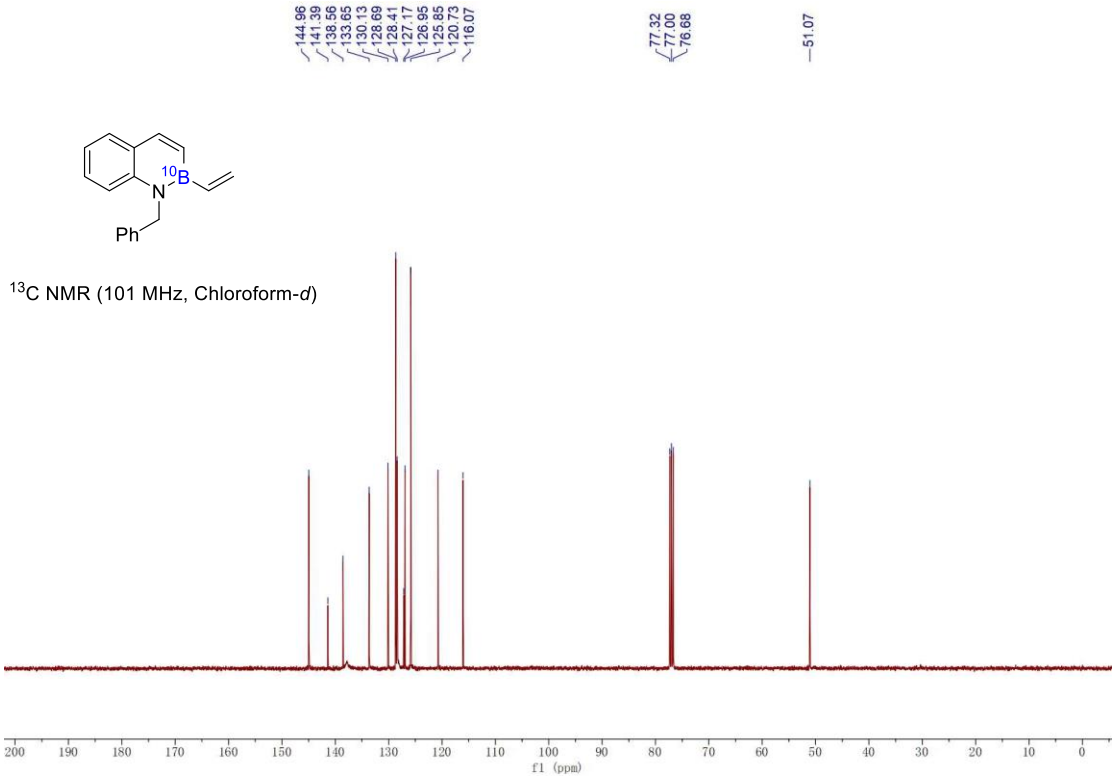


^{1}H NMR spectrum of **3g**



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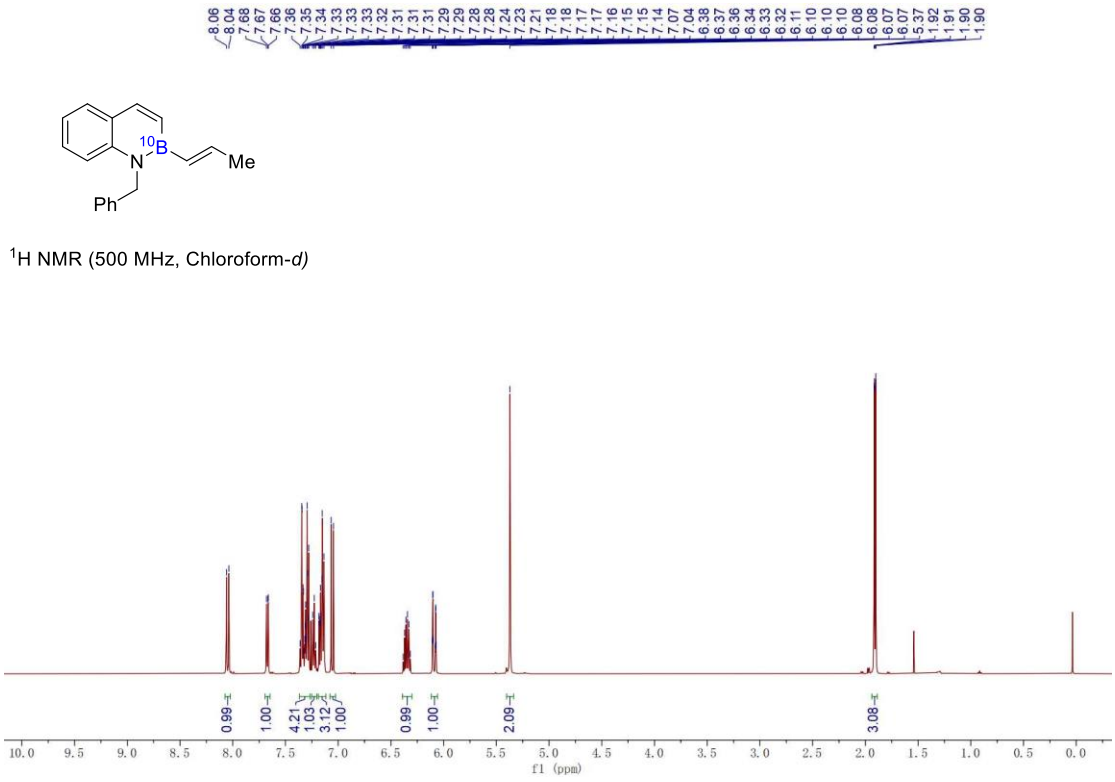
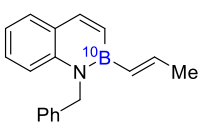


^{1}H NMR spectrum of **3h**



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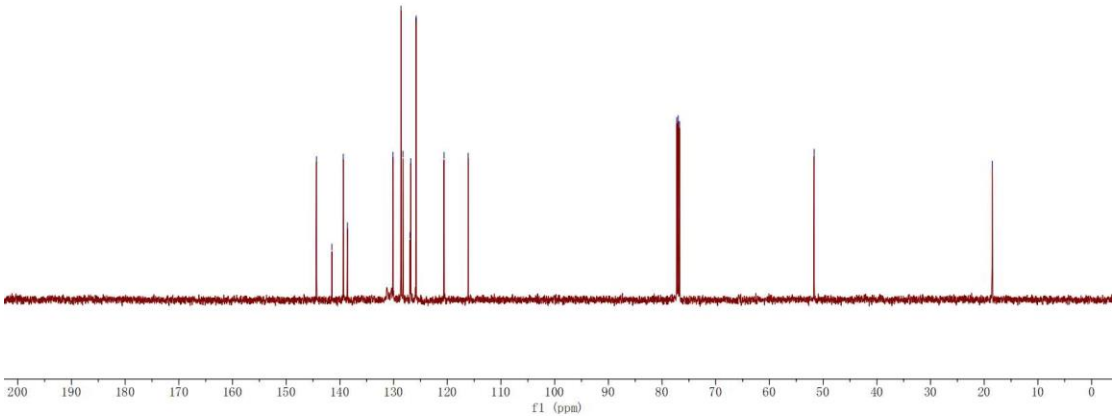
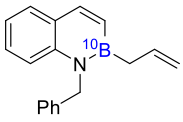
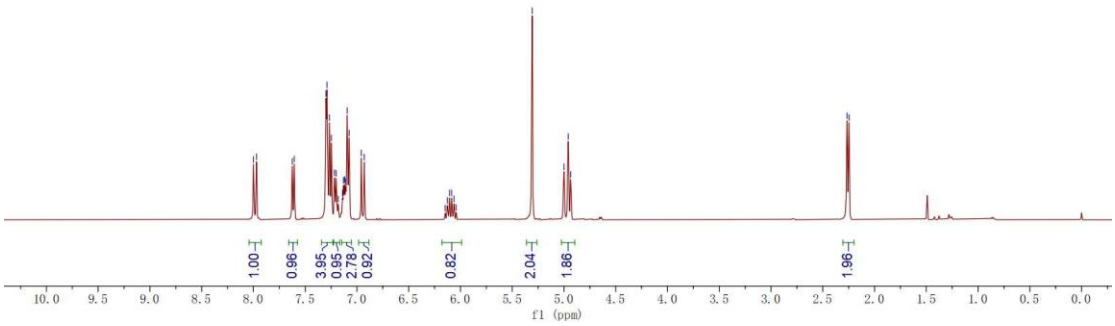


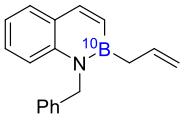
^{13}C NMR spectrum of **3h**



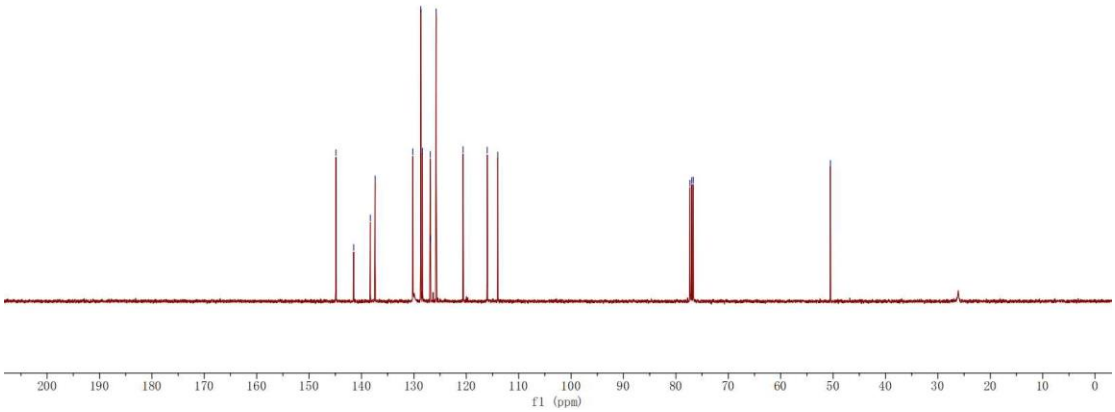
^{1}H NMR (400 MHz, Chloroform-*d*)



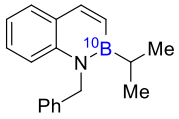
^{1}H NMR spectrum of **3i**



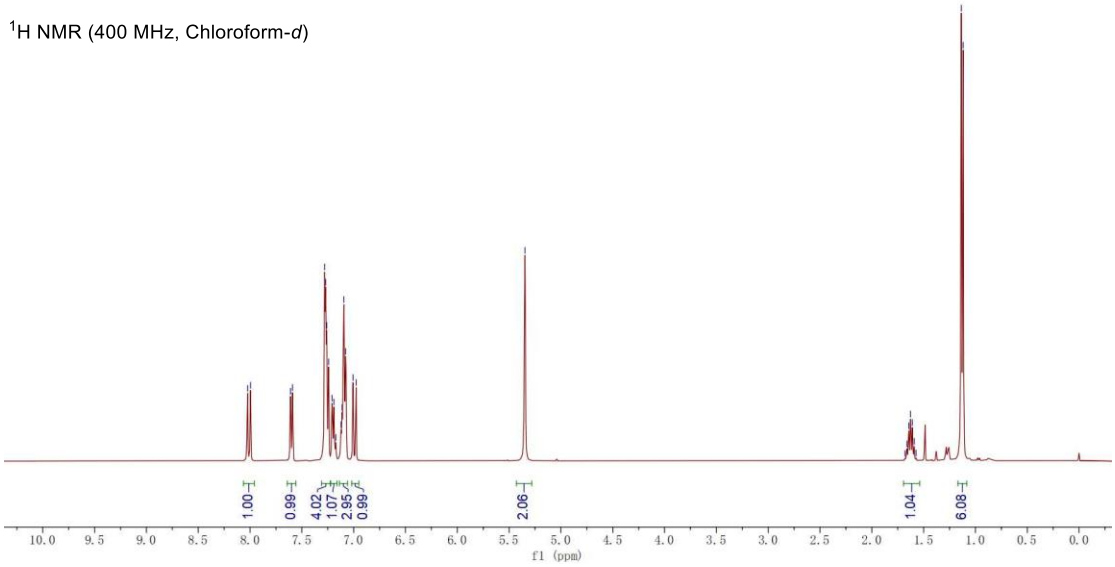
^{13}C NMR (101 MHz, Chloroform-*d*)



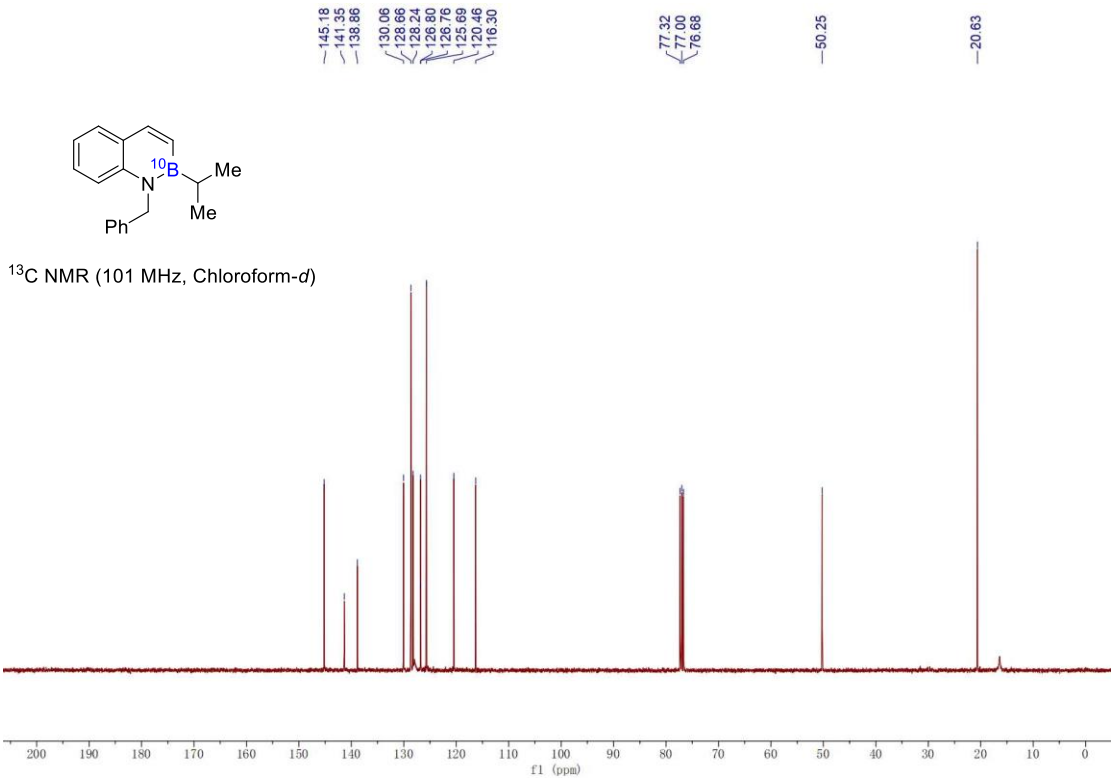
^{13}C NMR spectrum of **3i**



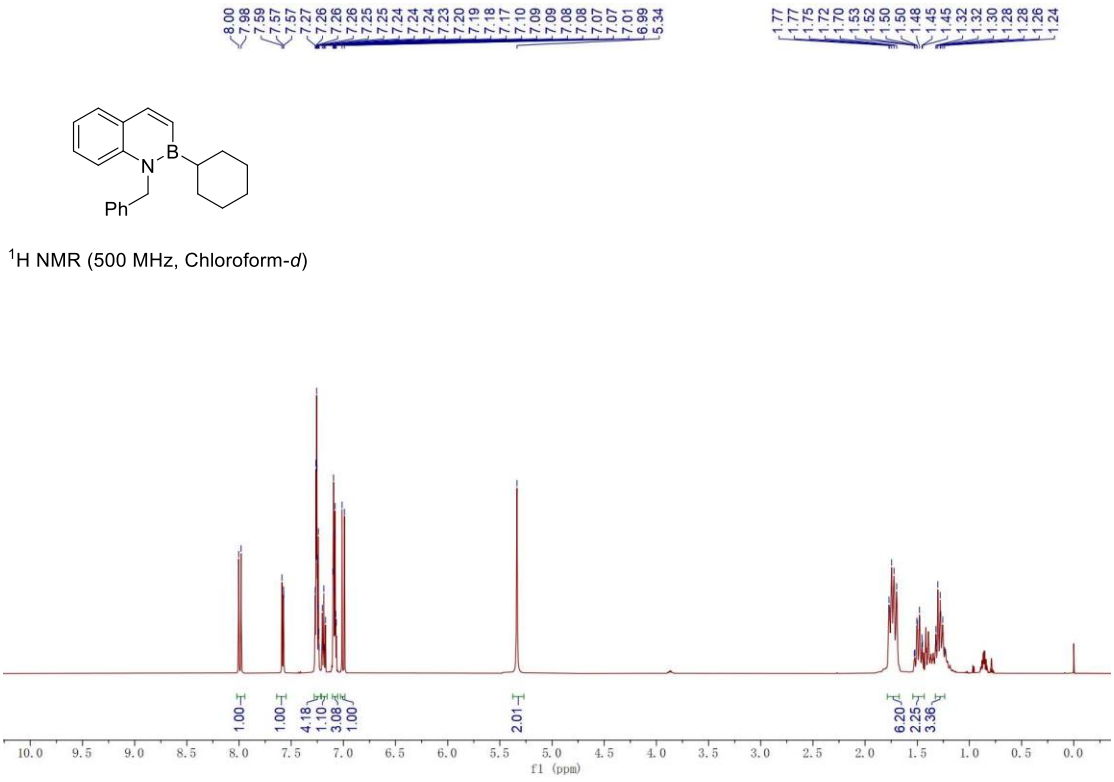
^{1}H NMR (400 MHz, Chloroform-*d*)



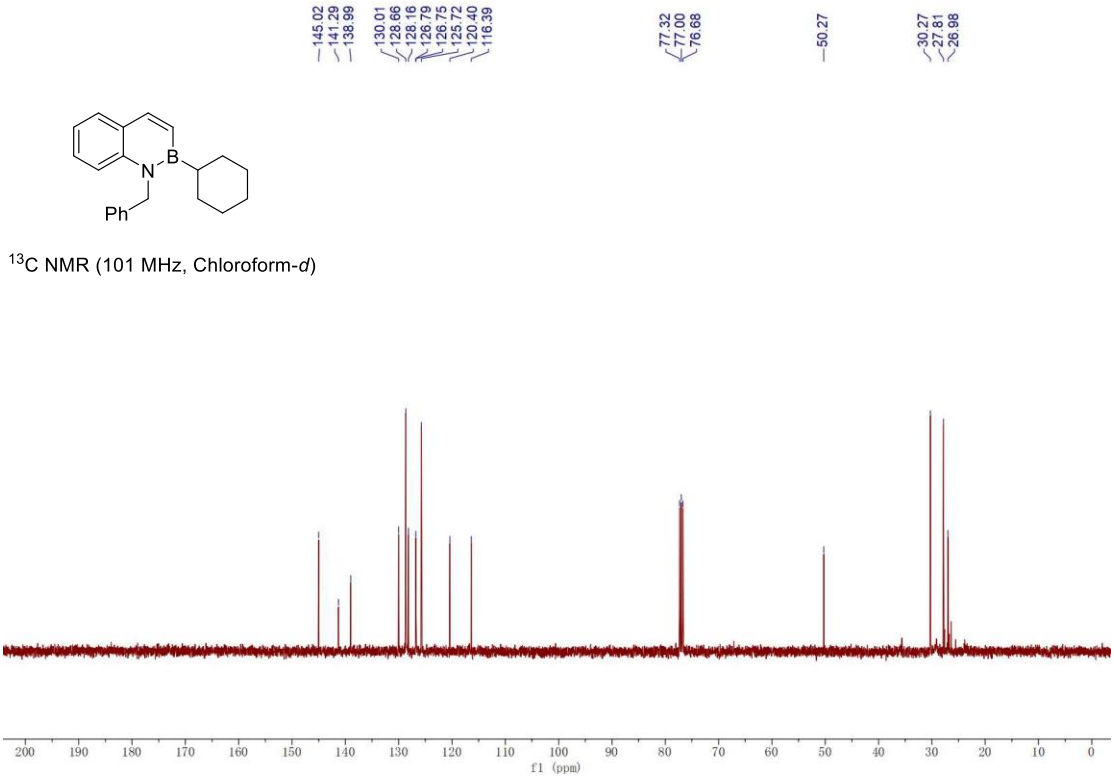
^{1}H NMR spectrum of **3j**



^{13}C NMR spectrum of **3j**

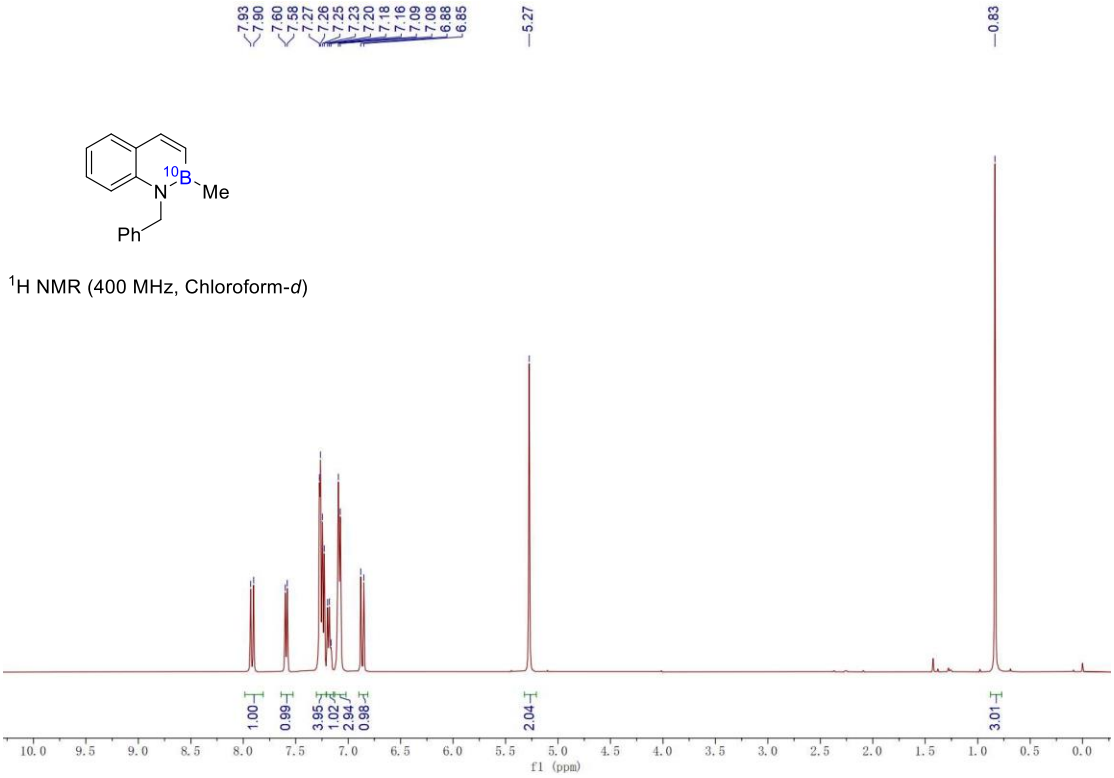


^{1}H NMR spectrum of **3k**



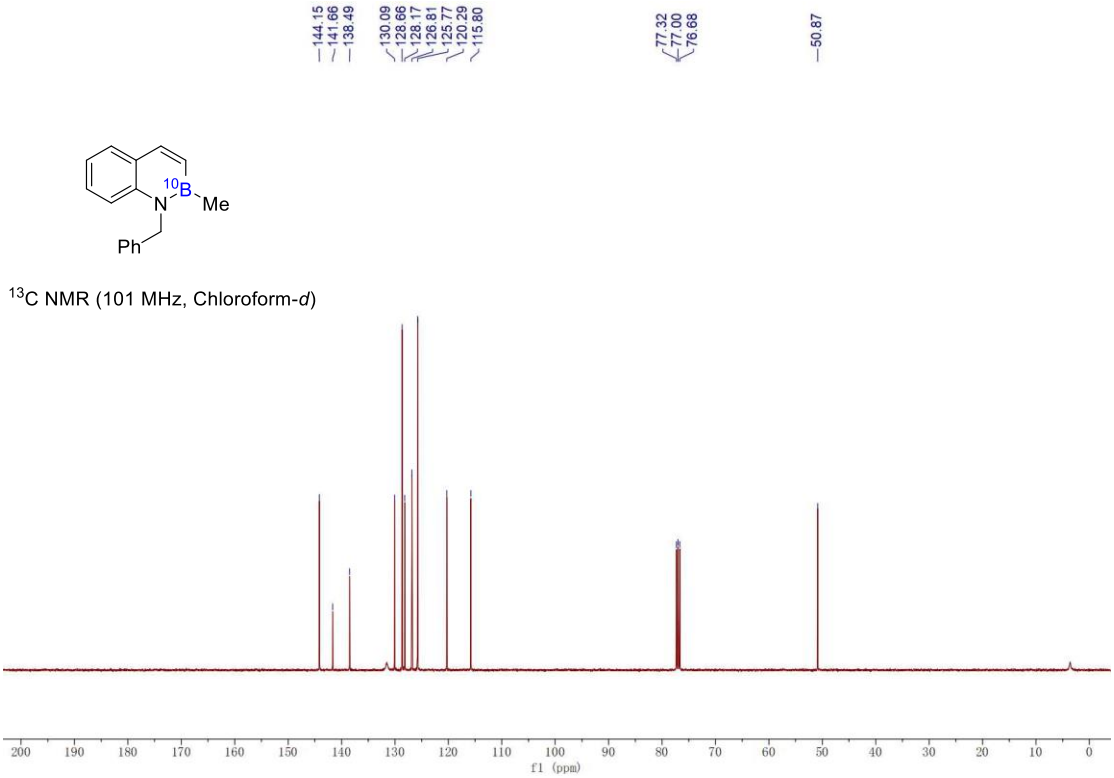
^{13}C NMR (101 MHz, Chloroform-*d*)

^{13}C NMR spectrum of **3k**

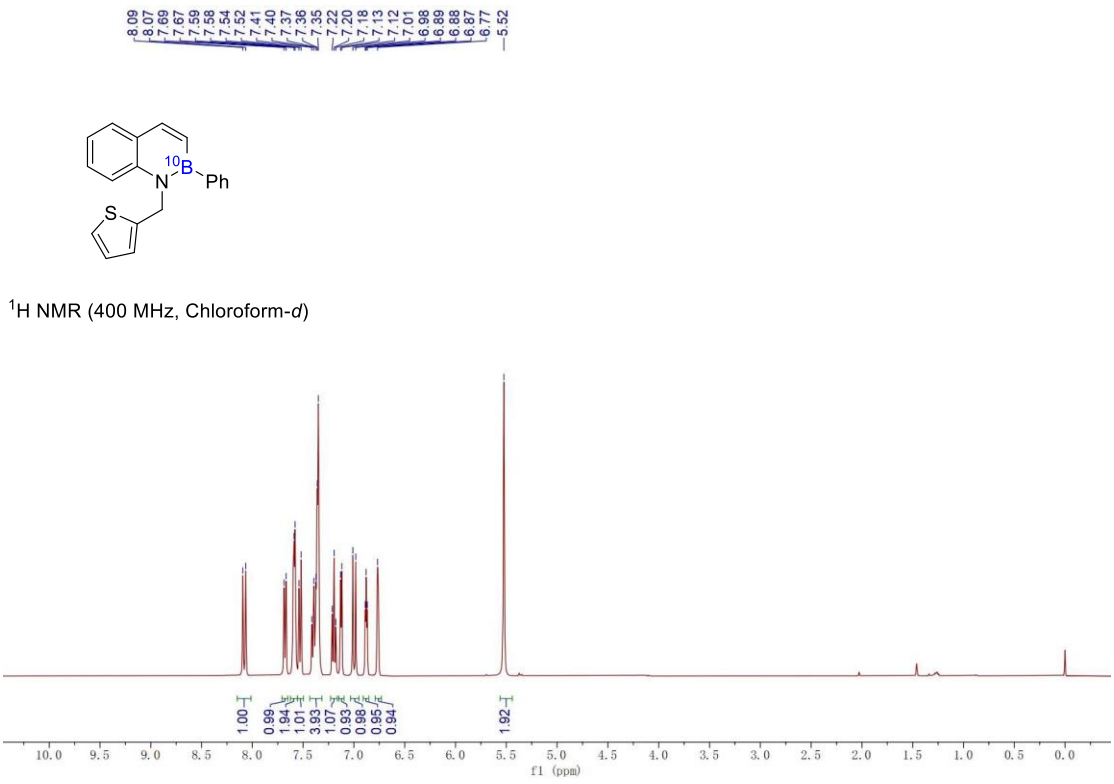


^{1}H NMR (400 MHz, Chloroform-*d*)

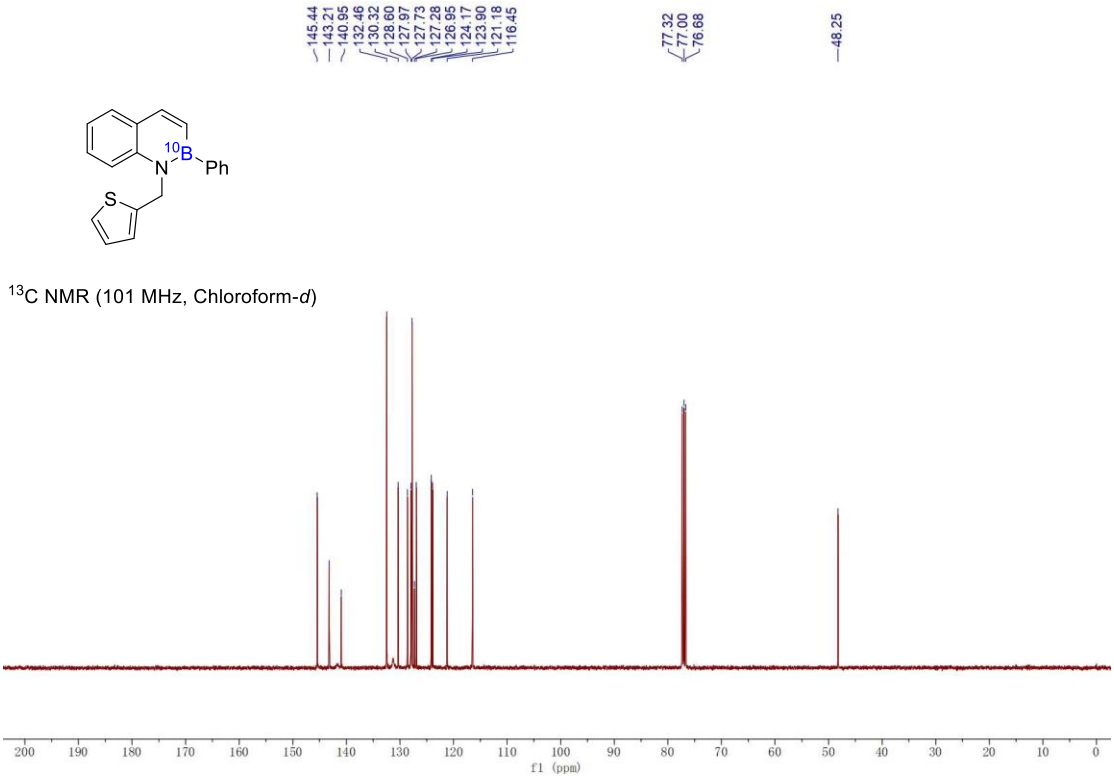
^{1}H NMR spectrum of **3l**



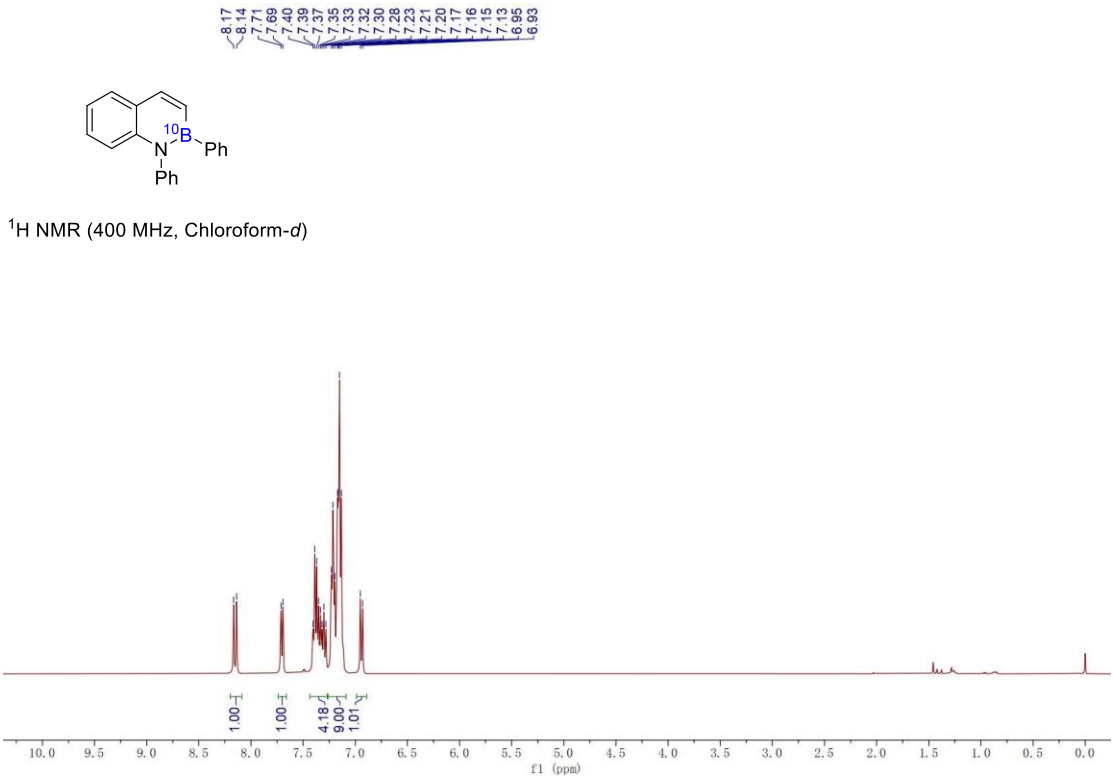
^{13}C NMR spectrum of **3l**



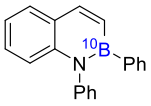
^{1}H NMR spectrum of **3m**



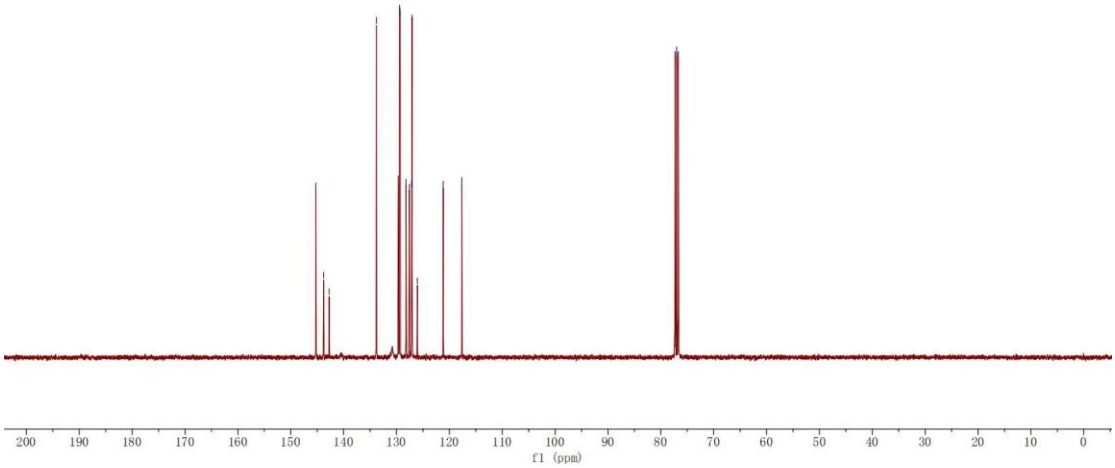
^{13}C NMR spectrum of **3m**



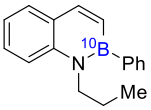
^{1}H NMR spectrum of **3n**



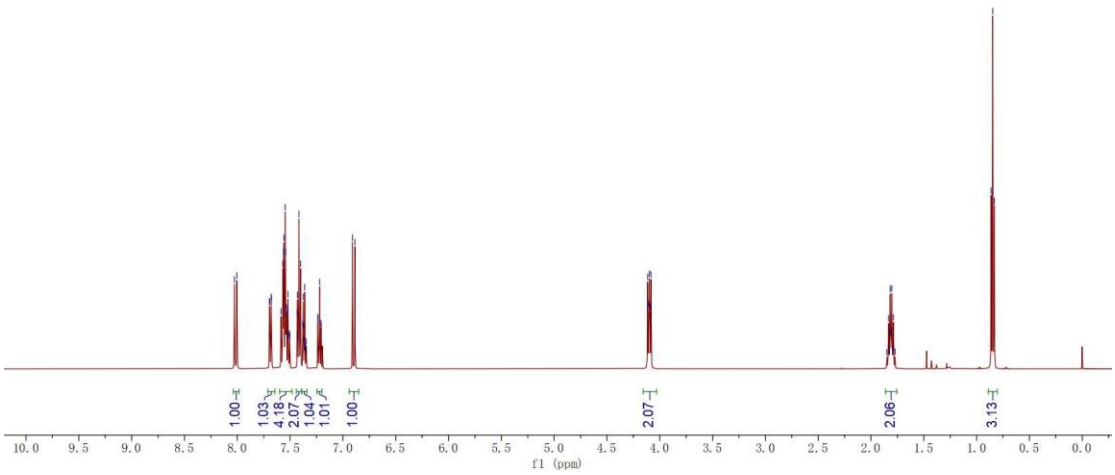
^{13}C NMR (101 MHz, Chloroform-*d*)



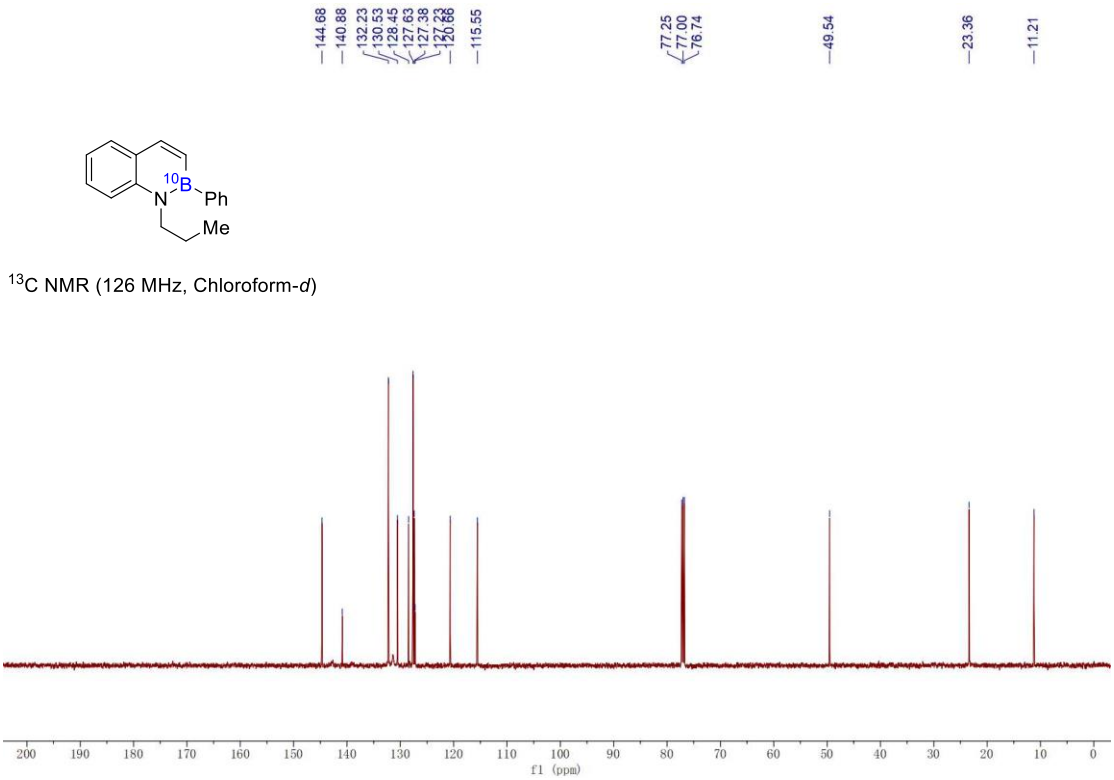
^{13}C NMR spectrum of **3n**



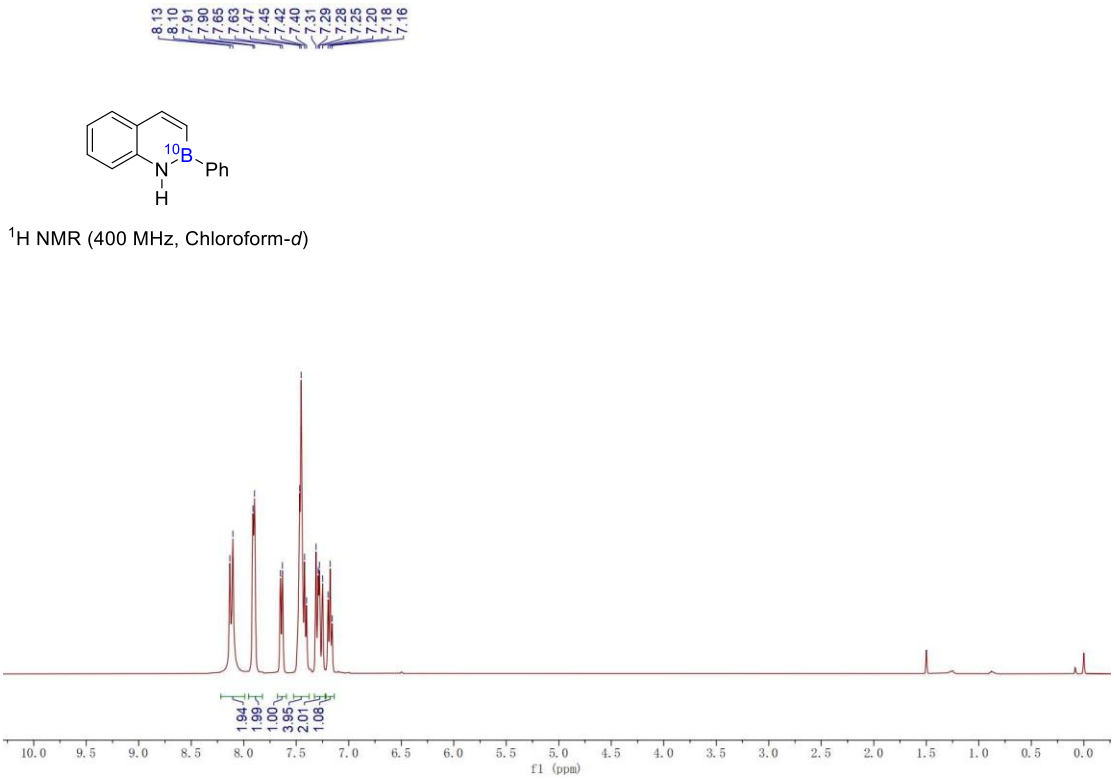
^{1}H NMR (500 MHz, Chloroform-*d*)



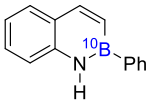
^{1}H NMR spectrum of **3o**



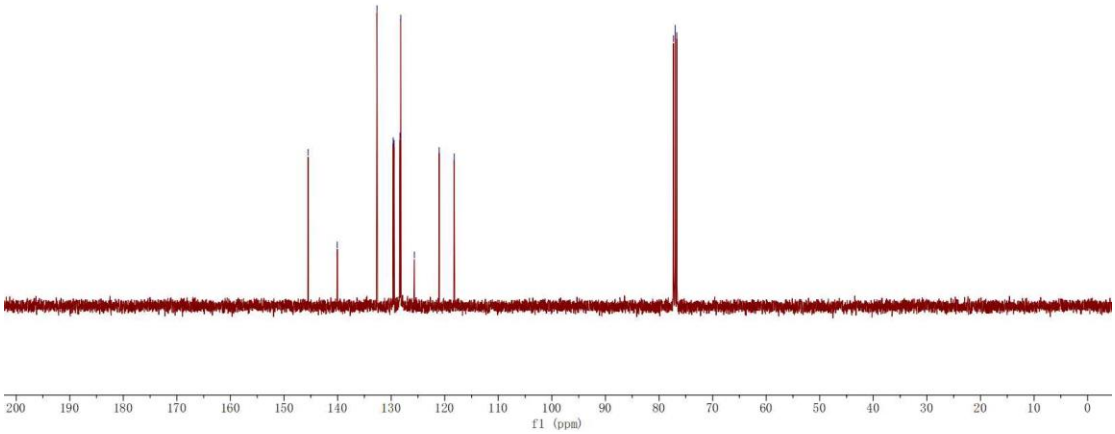
^{13}C NMR spectrum of **3o**



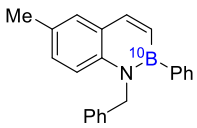
^{1}H NMR spectrum of **3p**



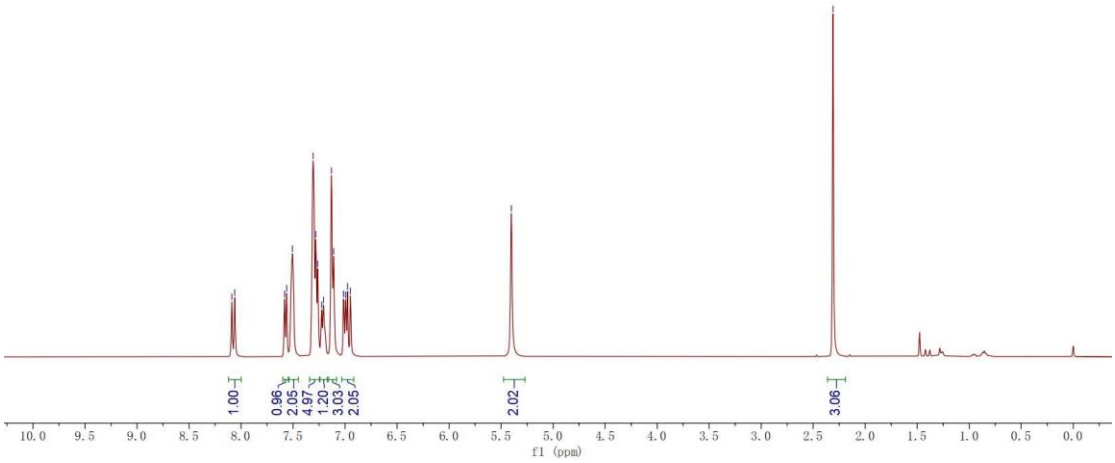
^{13}C NMR (101 MHz, Chloroform-*d*)



^{13}C NMR spectrum of **3p**

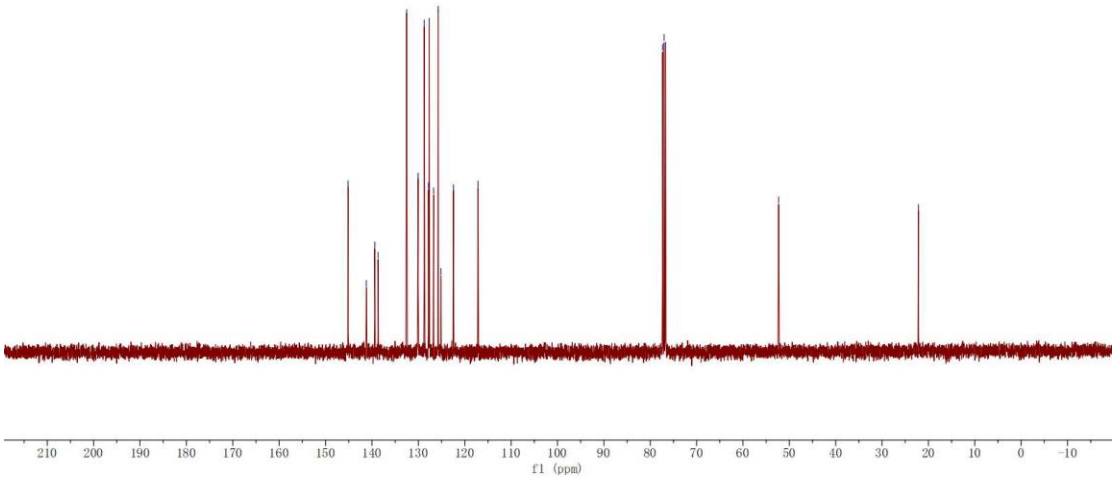


^{1}H NMR (400 MHz, Chloroform-*d*)

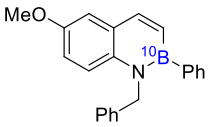


^{1}H NMR spectrum of **3q**

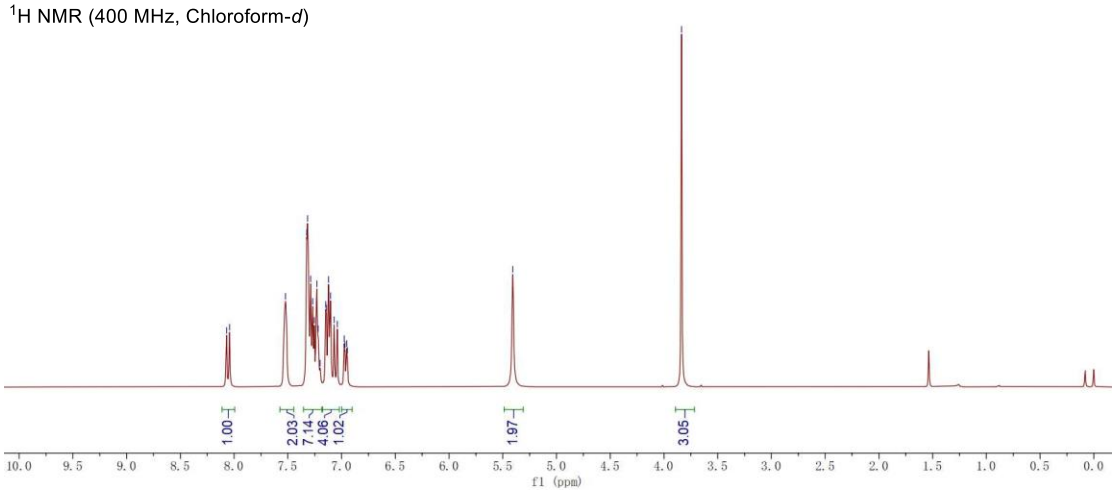
^{13}C NMR (101 MHz, Chloroform-*d*)



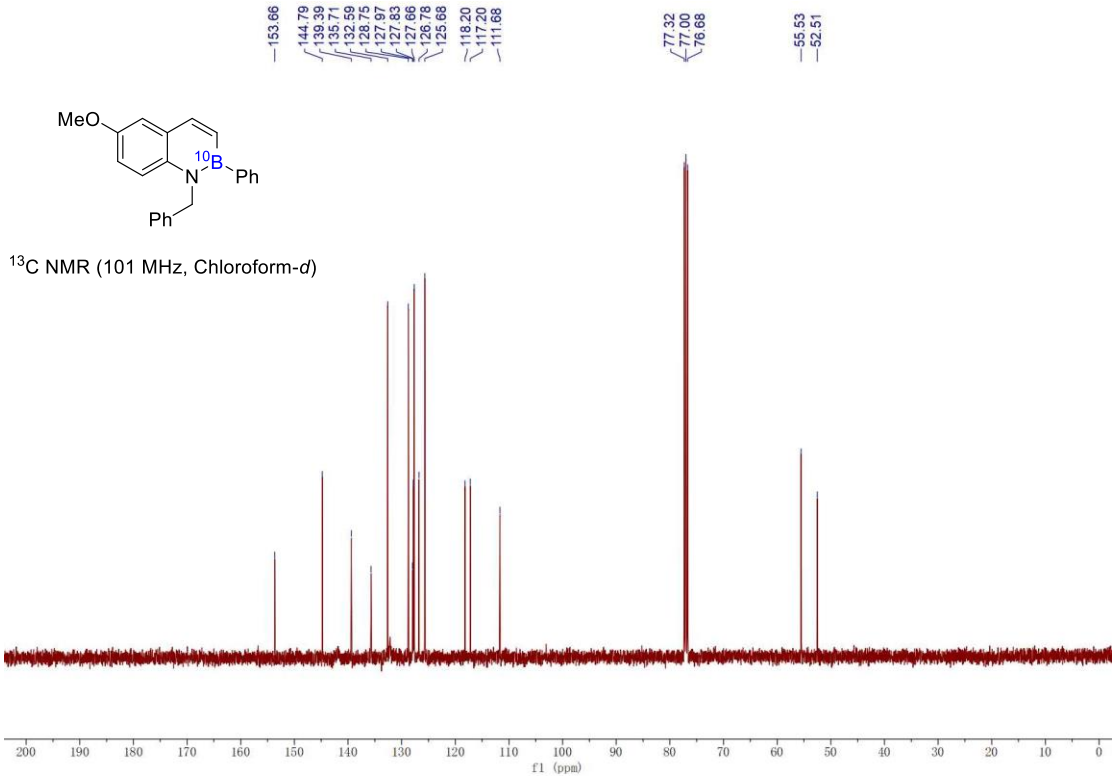
^{13}C NMR spectrum of **3q**



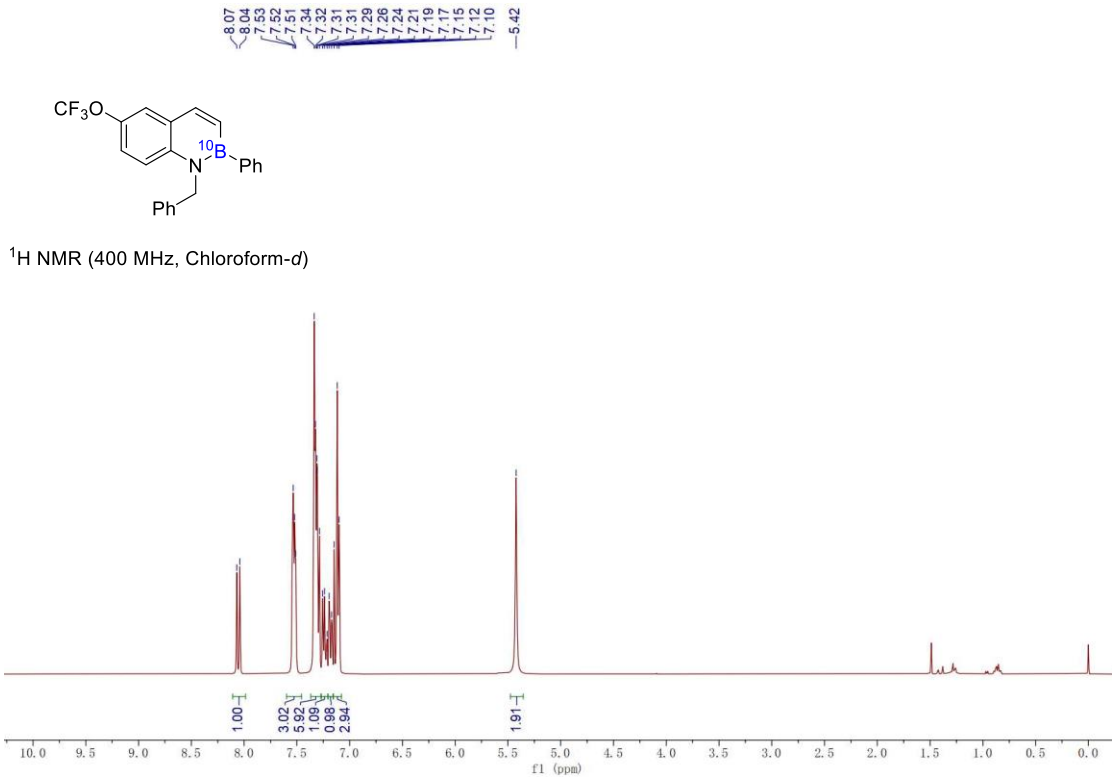
^{1}H NMR (400 MHz, Chloroform-*d*)



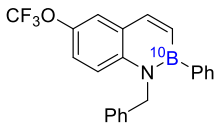
^{1}H NMR spectrum of **3r**



^{13}C NMR spectrum of **3r**

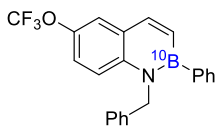


^{1}H NMR spectrum of **3s**



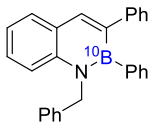
^{19}F NMR (471 MHz, Chloroform-*d*)

^{19}F NMR spectrum of **3s**

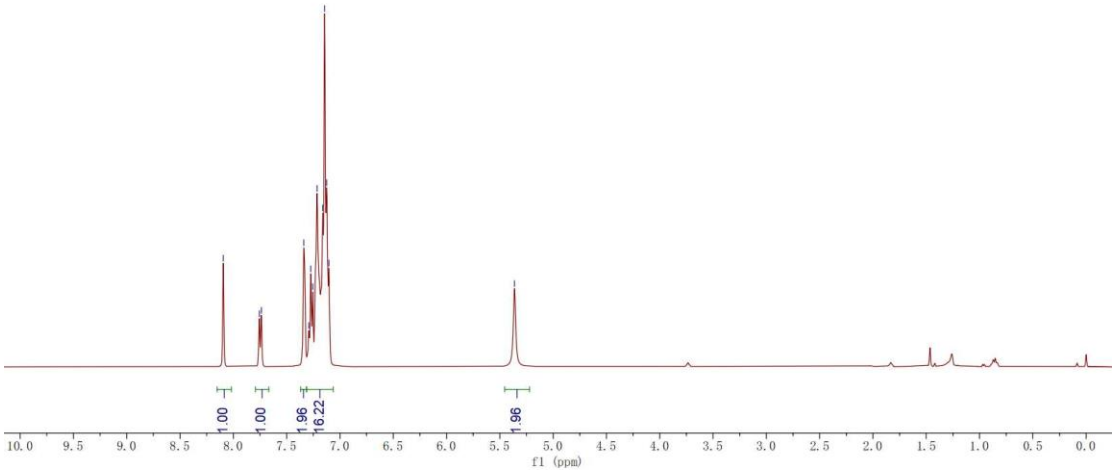


^{13}C NMR (101 MHz, Chloroform-*d*)

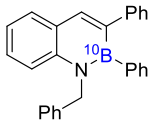
^{13}C NMR spectrum of **3s**



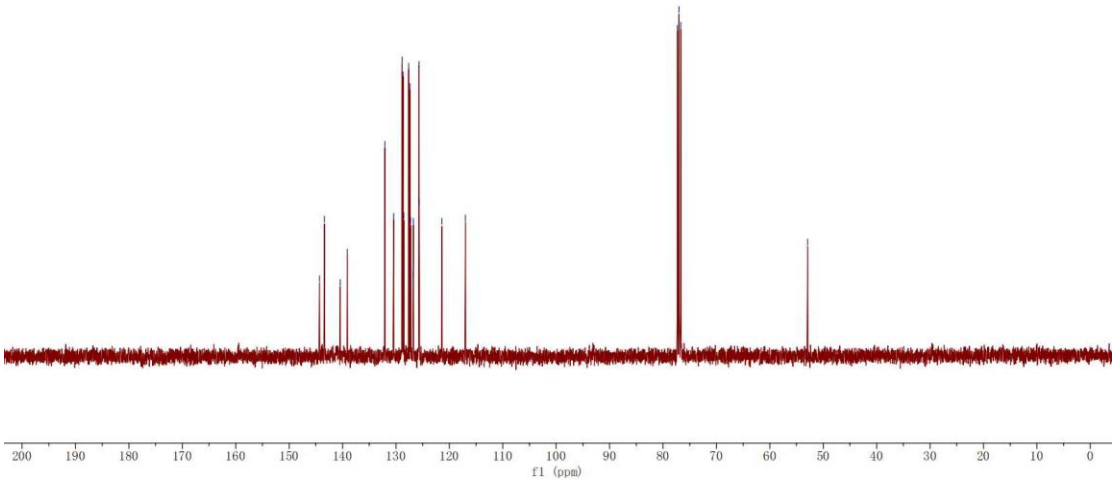
^{1}H NMR (400 MHz, Chloroform-*d*)



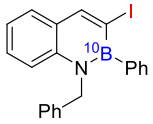
^{1}H NMR spectrum of **3t**



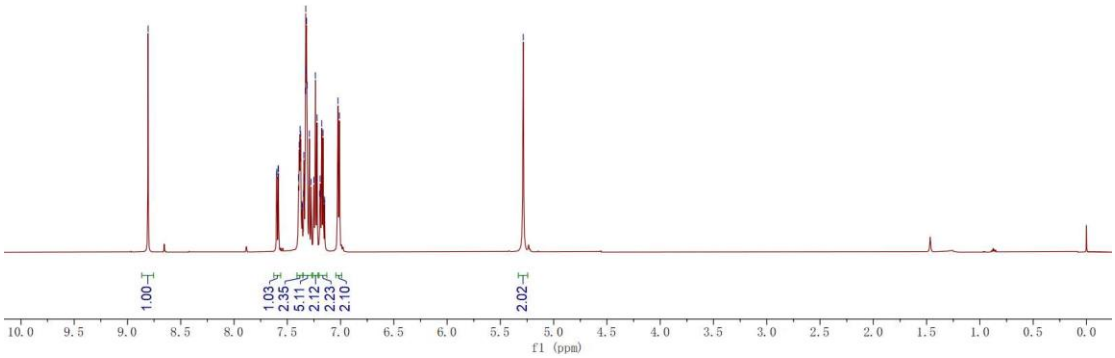
^{13}C NMR (101 MHz, Chloroform-*d*)



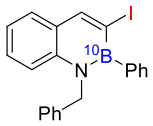
^{13}C NMR spectrum of **3t**



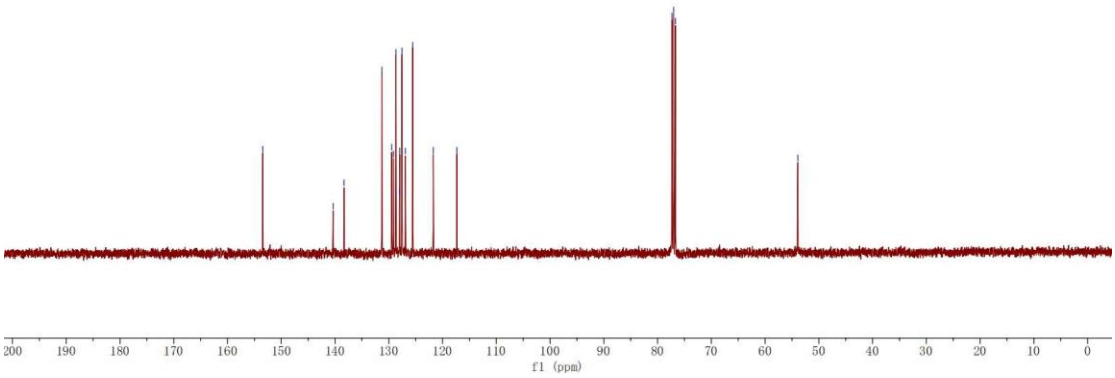
^{1}H NMR (500 MHz, Chloroform-*d*)



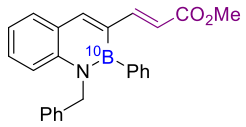
^{1}H NMR spectrum of **4**



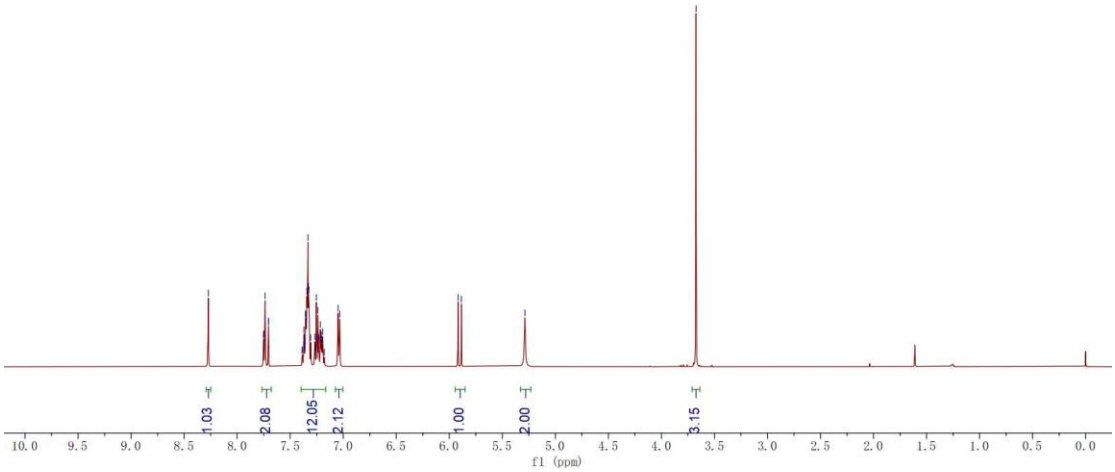
^{13}C NMR (101 MHz, Chloroform-*d*)



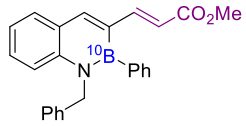
^{13}C NMR spectrum of **4**



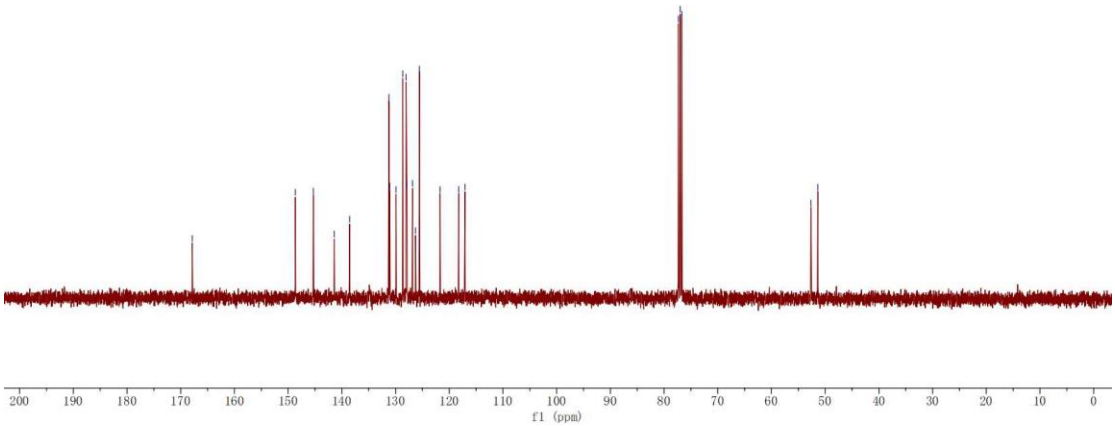
^{1}H NMR (500 MHz, Chloroform-*d*)



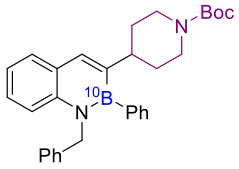
^{1}H NMR spectrum of **5**



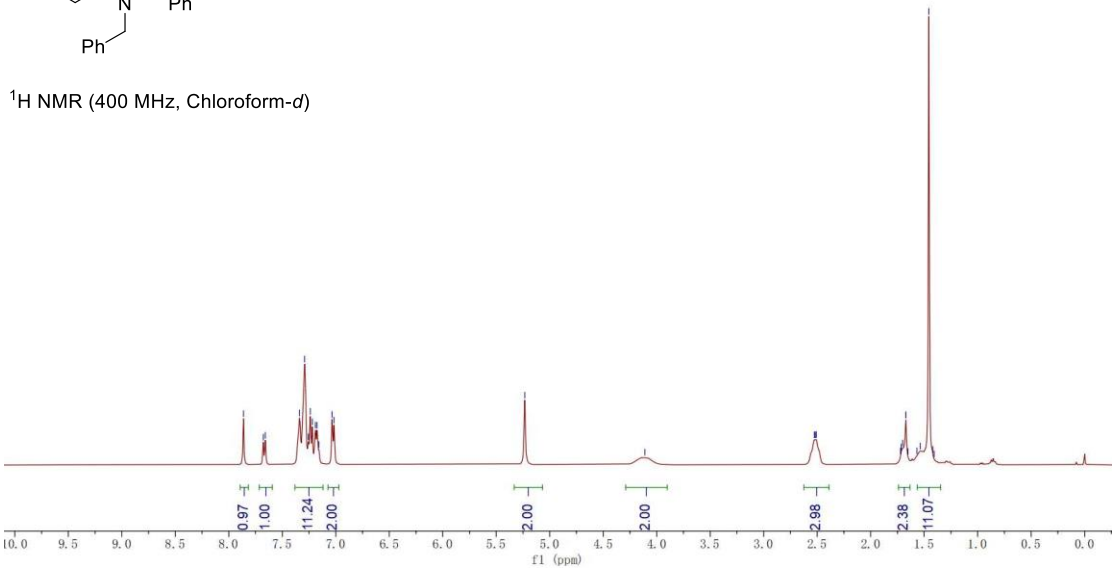
^{13}C NMR (101 MHz, Chloroform-*d*)



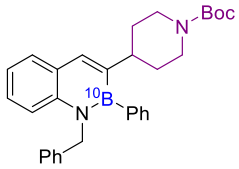
^{13}C NMR spectrum of **6**



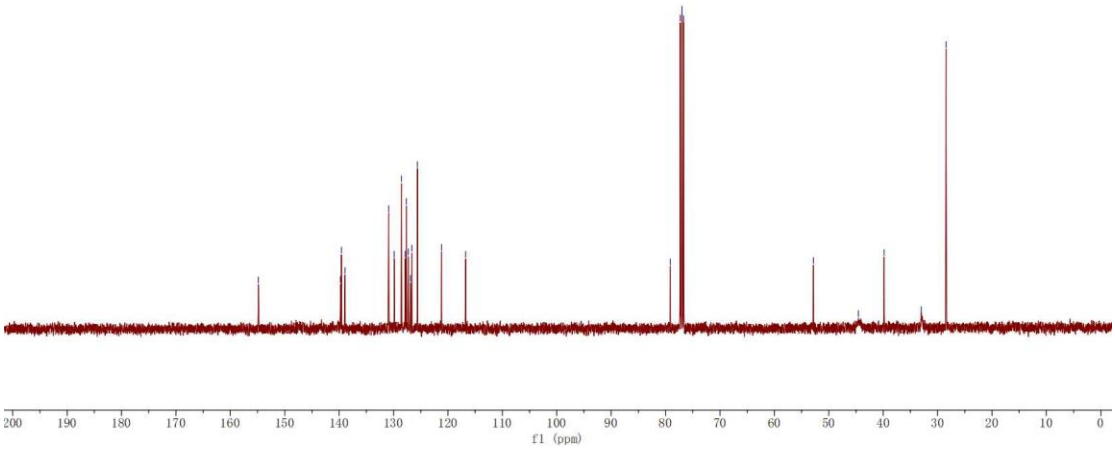
^{1}H NMR (400 MHz, Chloroform-*d*)



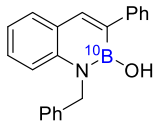
^{1}H NMR spectrum of **6**



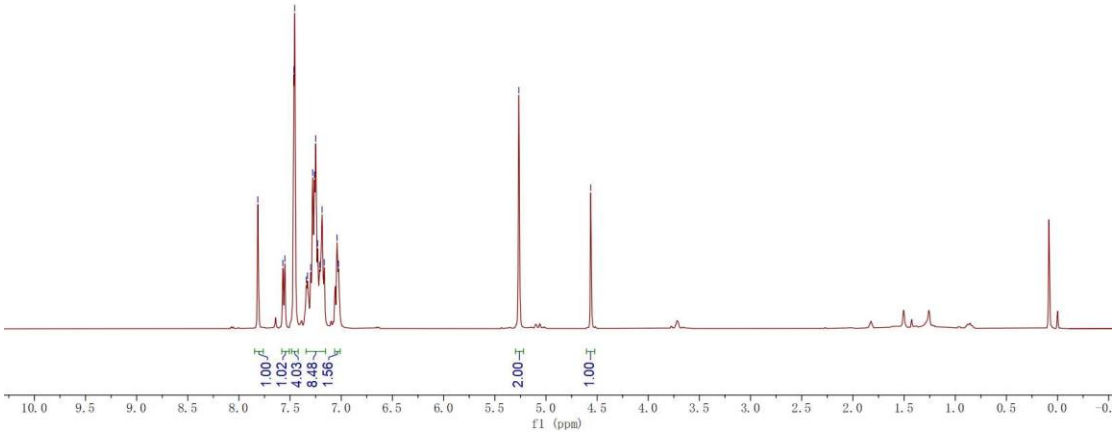
^{13}C NMR (101 MHz, Chloroform-*d*)



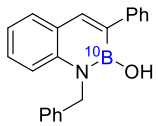
^{13}C NMR spectrum of **6**



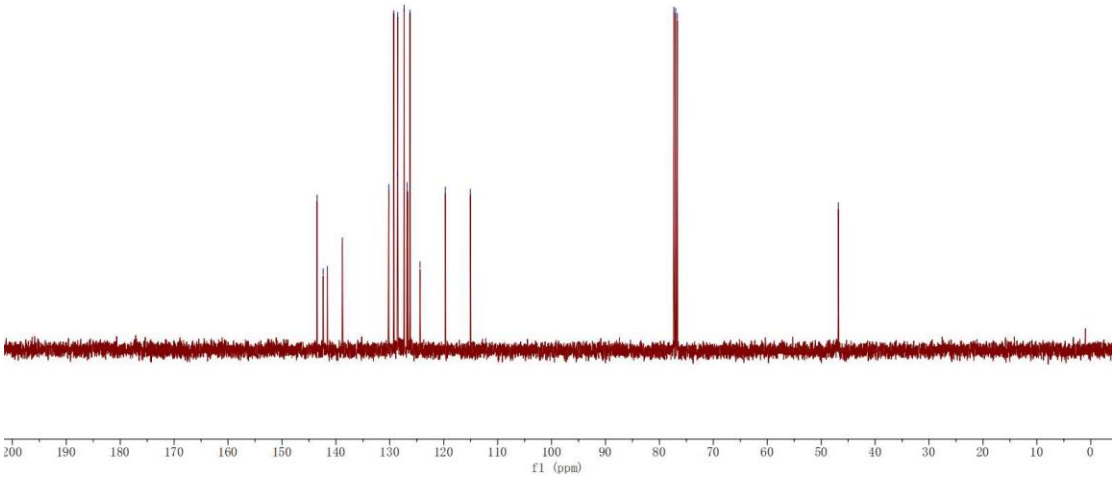
^{1}H NMR (400 MHz, Chloroform-*d*)



^{1}H NMR spectrum of **7**



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



^{13}C NMR spectrum of **7**