Supplementary Information (SI) for ChemComm.
This journal is © The Royal Society of Chemistry 2025

Cu-Catalyzed Selective Coupling of Alkynes with danB-Bpai

Qi Li,[a] Dezhao Zhang,[a] Tanyu Song,[a] Xiaodong Tang,[a] Jun-An Ma[b] and Chun Zhang*[,a,c]

[a.] *Institute of Molecular Plus, Department of Chemistry, State Key Laboratory of Synthetic Biology, School of Pharmaceutical Science and Technology, Faculty of Medicine, Tianjin University, 92 Weijin Road, Tianjin 300072, China.*

[b.] *Department of Chemistry, State Key Laboratory Synthetic Biology, Tianjin University, Tianjin 300072, China.*

[c.] *Tianjin Key Laboratory for Modern Drug Delivery & High-Efficiency, Tianjin University, Tianjin 300072, P. R. China.*

**E-mail: chunzhang@tju.edu.cn.*

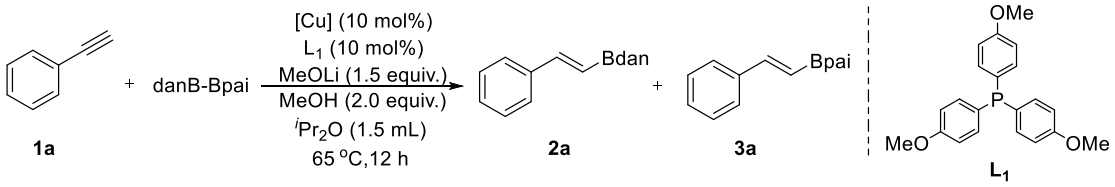
Table of Contents

1. General Considerations

All manipulations were conducted with Schlenk tube. **^{1}H-NMR** spectra were recorded on BrukerAVIII-400 spectrometers, JNM-ECZ400S/L1 and JNM-ECZ600R/S1 spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard and DMSO-D_6 (δ = 2.5 ppm). **^{13}C-NMR** spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm) and DMSO-D_6 (δ = 39.52 ppm).**^{11}B-NMR** spectra were obtained by using the same NMR spectrometers. **^{19}F-NMR** spectra were obtained by the same NMR High resolution mass spectrometry (**HRMS**) data were obtained on a QTOF mass analyzer with electrospray ionization (ESI) through a Waters Acquity UPLC Class I/Xevo G2 Q-Tof. Substrates were purchased from Aldrich, TCI, Acros, Energy, Aladdin, or synthesized according to the procedures outlined below. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. The effect of different reaction conditions

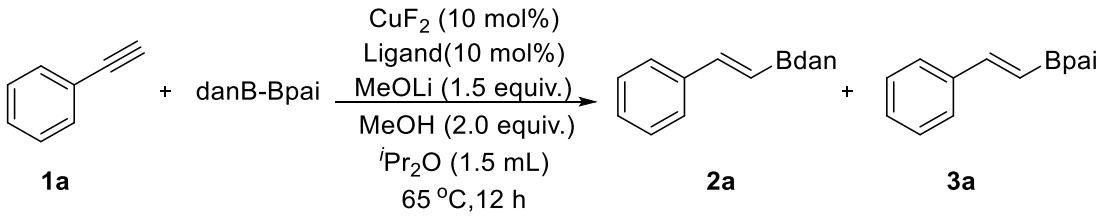
Table S1 The effect of different copper catalyst[a]

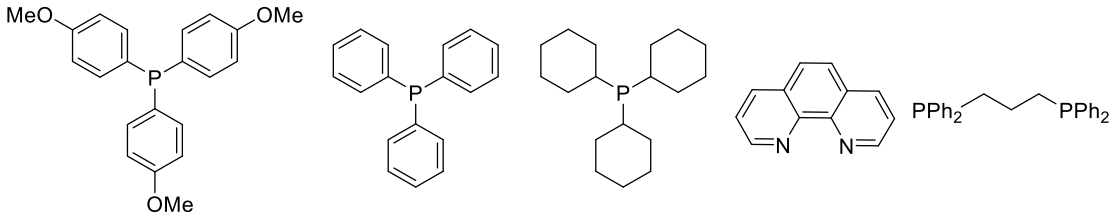


Entry	[Cu]	**2a** yield%[b]	**3a** yield%[b]
1	CuBr·SMe$_2$	57	18
2	CuCN	12	2
3	Cu(OAc)$_2$	33	0
4	CuO	0	0
5	CuF$_2$	89	trace
6	CuCl$_2$	70	10
7	CuBr$_2$	56	30
8	Cu(acac)$_2$	86	0

[a] **1a** (0.2 mmol, 1.0 equiv.), danB-Bpai (0.24 mmol, 1.2 equiv.), Copper catalyst (0.02 mmol, 10 mol%), L_1(0.02 mmol, 10 mol%), MeOLi (0.3 mmol, 1.5 equiv.), MeOH (0.4 mmol, 2.0 equiv.), ^{i}Pr$_2$O (1.5 mL), 65 ^{o}C, 12 h. [b] Isolated yield.

Table S2. The effect of different ligands on the formation of alkenyl Bdan[a]



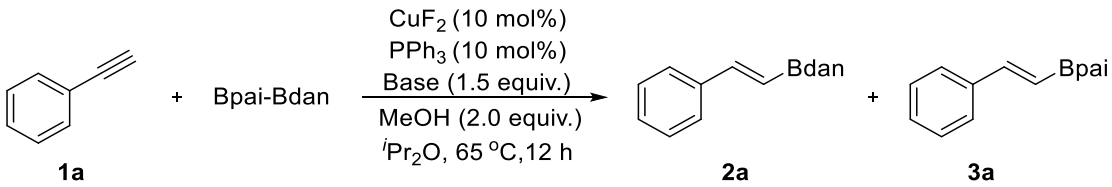


L_1 L_2 L_3 L_4 L_5

Entry	Ligand	**2a** yield%[b]	**3a** yield%[b]
1	L_1	89	trace
2	L_2	90	0
3	L_3	82	trace
4	L_4	0	0
5	L_5	49	5

[a] **1a** (0.2 mmol, 1.0 equiv.), danB-Bpai (0.24 mmol, 1.2 equiv.), CuF_2 (0.02 mmol, 10 mol%), Ligand (0.02 mmol, 10 mol%), MeOLi (0.3 mmol, 1.5 equiv.), MeOH (0.4 mmol, 2.0 equiv.), $^iPr_2O$ (1.5 mL), 65 °C, 12 h. [b] Isolated yield.

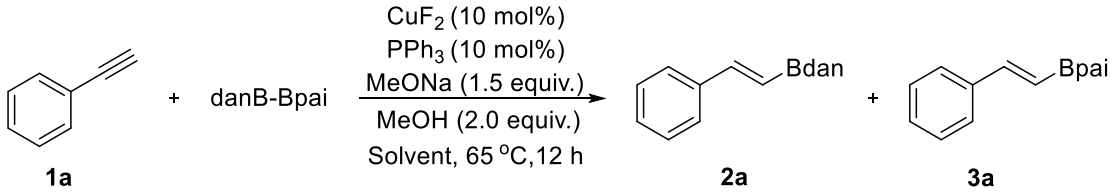
Table S3. The effect of different base on the formation of alkenyl Bdan[a]



Entry	Base	**2a** yield%[b]	**3a** yield%[b]
1	MeOLi	90	trace
2	MeONa	93	trace
3	MeOK	0	0
4	^{t}BuOLi	65	trace
5	^{t}BuONa	30	trace
6	^{t}BuOK	0	0

[a] **1a** (0.2 mmol, 1.0 equiv.), danB-Bpai (0.24 mmol, 1.2 equiv.), CuF_2 (0.02 mmol, 10 mol%), PPh_3 (0.02 mmol, 10 mol%), Base (0.3 mmol, 1.5 equiv.), MeOH (0.4 mmol, 2.0 equiv.), $^{i}Pr_2O$ (1.5 mL), 65 °C, 12 h. [b] Isolated yield.

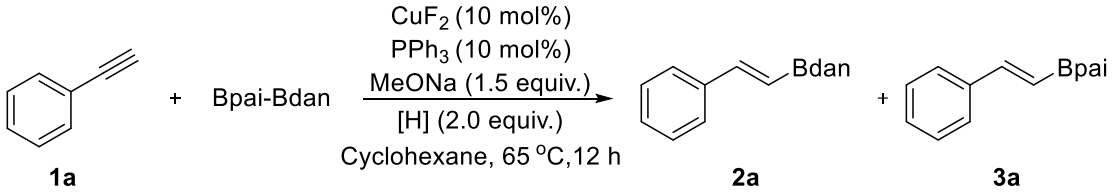
Table S4. The effect of different solvent on the formation of alkenyl Bdan[a]



Entry	Solvent	**2a** yield%[b]	**3a** yield%[b]
1	$^{i}Pr_2O$	93	trace
2	DME	61	trace
3	Dioxane	25	trace
4	THF	88	trace
5	$ClCH_2CH_2Cl$	82	trace
6	Cyclohexane	96	trace
7	DMA	29	trace
8	CH_3CN	49	trace

[a] **1a** (0.2 mmol, 1.0 equiv.), danB-Bpai (0.24 mmol, 1.2 equiv.), CuF_2 (0.02 mmol, 10 mol%), PPh_3 (0.02 mmol, 10 mol%), MeONa (0.3 mmol, 1.5 equiv.), MeOH (0.4 mmol, 2.0 equiv.), Solvent (1.5 mL), 65 °C, 12 h. [b] Isolated yield.

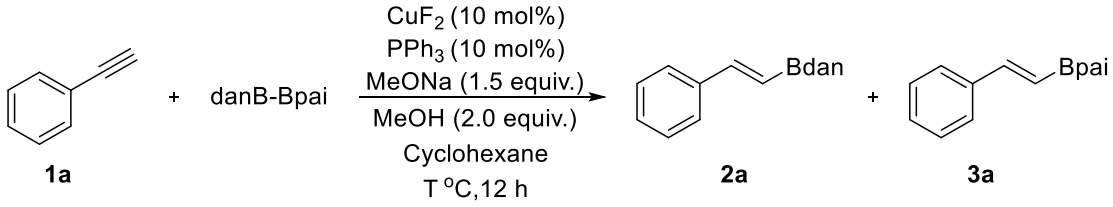
Table S5. The effect of different proton source on the formation of alkenyl Bdan[a]



Entry	[H]	**2a** yield%[b]	**3a** yield%[b]
1	MeOH	96	trace
2	EtOH	96	trace
3	^{i}PrOH	92	trace
4	CH_3COOH	8	11

[a] **1a** (0.2 mmol, 1.0 equiv.), danB-Bpai (0.24 mmol, 1.2 equiv.), CuF_2 (0.02 mmol, 10 mol%), PPh_3 (0.02 mmol, 10 mol%), MeONa (0.3 mmol, 1.5 equiv.), [H] (0.4 mmol, 2.0 equiv.), Cyclohexane (1.5 mL), 65 °C, 12 h. [b] Isolated yield.

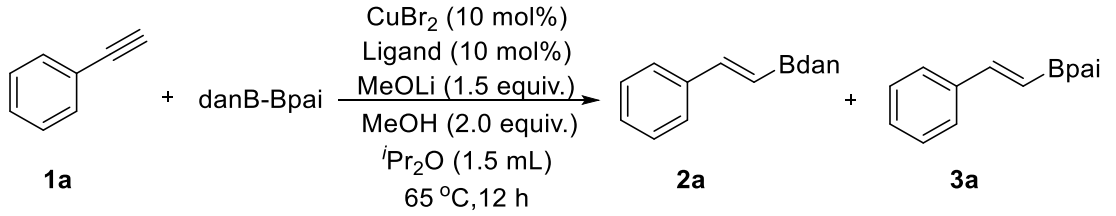
Table S6. The effect of different temperature on the formation of alkenyl Bdan[a]



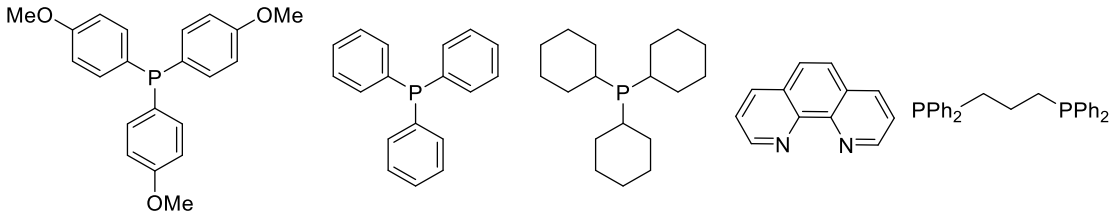
Entry	T °C	**2a** yield%[b]	**3a** yield%[b]
1	65	96	trace
2	55	96	trace
3	45	96	trace
4	35	96	trace
5	25	87	trace

[a] **1a** (0.2 mmol, 1.0 equiv.), danB-Bpai (0.24 mmol, 1.2 equiv.), CuF_2 (0.02 mmol, 10 mol%), PPh_3 (0.02 mmol, 10 mol%), MeONa (0.3 mmol, 1.5 equiv.), MeOH (0.4 mmol, 2.0 equiv.), Cyclohexane (1.5 mL),T °C, 12 h. [b] Isolated yield.

Table S7. The effect of different ligands on the formation of alkenyl Bpai[a]



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

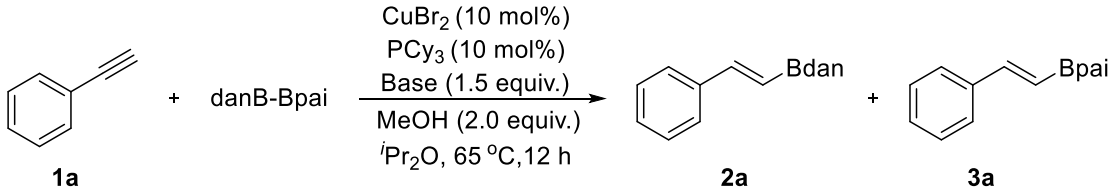


L_1 L_2 L_3 L_4 L_5

Entry	L	**2a** yield%[b]	**3a** yield%[b]
1	L_1	56	30
2	L_2	59	27
3	L_3	8	77
4	L_4	42	trace
5	L_5	57	trace
6	Xantphos	53	47

[a] **1a** (0.2 mmol, 1.0 equiv.), danB-Bpai (0.24 mmol, 1.2 equiv.), $CuBr_2$ (0.02 mmol, 10 mol%), L (0.02 mmol, 10 mol%), MeOLi (0.3 mmol, 1.5 equiv.), MeOH (0.4 mmol, 2.0 equiv.), $^{i}Pr_2O$ (1.5 mL), 65 °C, 12 h. [b] Isolated yield.

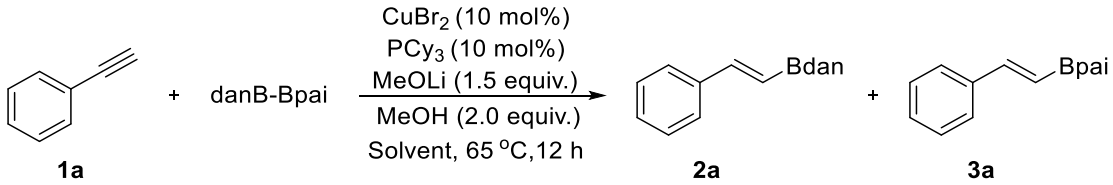
Table S8. The effect of different base on the formation of alkenyl Bpai[a]



Entry	Base	**2a** yield%[b]	**3a** yield%[b]
1	MeOLi	8	77
2	MeONa	70	0
3	MeOK	58	0
4	^{t}BuOLi	8	60
5	^{t}BuONa	66	0
6	^{t}BuOK	28	trace

[a] **1a** (0.2 mmol, 1.0 equiv.), danB-Bpai (0.24 mmol, 1.2 equiv.), $CuBr_2$ (0.02 mmol, 10 mol%), PCy_3 (0.02 mmol, 10 mol%), Base (0.3 mmol, 1.5 equiv.), MeOH (0.4 mmol, 2.0 equiv.), $^{i}Pr_2O$ (1.5 mL), 65 °C, 12 h. [b] Isolated yield.

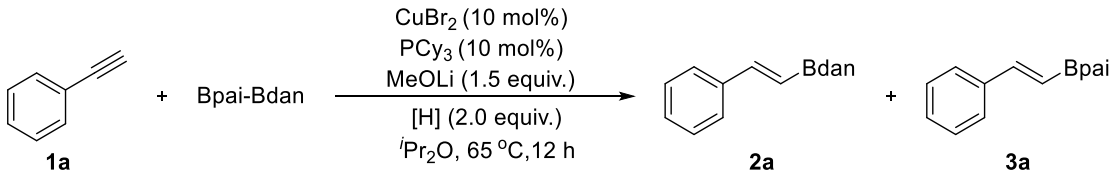
Table S9. The effect of different solvent on the formation of alkenyl Bpai[a]



Entry	Solvent	**2a** yield%[b]	**3a** yield%[b]
1	$^{i}Pr_2O$	8	77
2	DME	17	7
3	Dioxane	0	0
4	THF	21	trace
5	$ClCH_2CH_2Cl$	7	49
6	Cyclohexane	17	44
7	DMA	41	0
8	CH_3CN	12	5

[a] **1a** (0.2 mmol, 1.0 equiv.), danB-Bpai (0.24 mmol, 1.2 equiv.), $CuBr_2$ (0.02 mmol, 10 mol%), PCy_3 (0.02 mmol, 10 mol%), MeOLi (0.3 mmol, 1.5 equiv.), MeOH (0.4 mmol, 2.0 equiv.), Solvent (1.5 mL), 65 °C, 12 h. [b] Isolated yield.

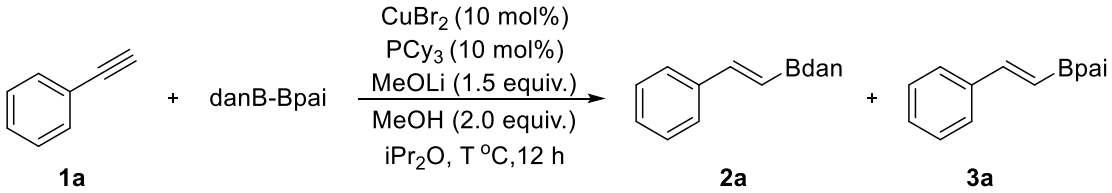
Table S10. The effect of different proton source on the formation of alkenyl Bpai[a]



Entry	[H]	**2a** yield%[b]	**3a** yield%[b]
1	MeOH	8	77
2	H_2O	14	13
3	EtOH	18	46
4	^{i}PrOH	12	23
5	CH_3COOH	0	0

[a] **1a** (0.2 mmol, 1.0 equiv.), danB-Bpai (0.24 mmol, 1.2 equiv.), $CuBr_2$ (0.02 mmol, 10 mol%), PCy_3 (0.02 mmol, 10 mol%), MeOLi (0.3 mmol, 1.5 equiv.), [H] (0.4 mmol, 2.0 equiv.), $^{i}Pr_2O$ (1.5 mL), 65 °C, 12 h. [b] Isolated yield.

Table S11. The effect of different temperature on the formation of alkenyl Bpai[a]



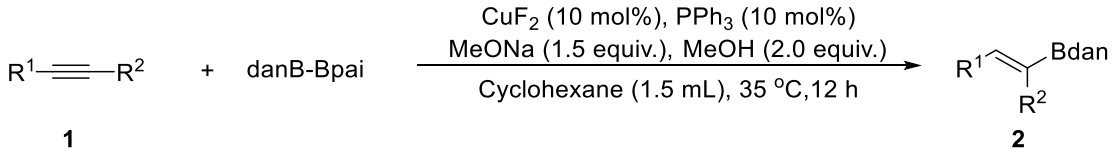
1a **2a** **3a**

Entry	T °C	**2a** yield%[b]	**3a** yield%[b]
1	70	5	31
2	65	8	77
3	55	8	73
4	45	10	57
5	35	6	10

[a] **1a** (0.2 mmol, 1.0 equiv.), danB-Bpai (0.24 mmol, 1.2 equiv.), $CuBr_2$ (0.02 mmol, 10 mol%), PCy_3 (0.02 mmol, 10 mol%), MeOLi (0.3 mmol, 1.5 equiv.), MeOH (0.4 mmol, 2.0 equiv.), $^{i}Pr_2O$ (1.5 mL), T °C, 12 h. [b] Isolated yield.

3. General procedure for making products

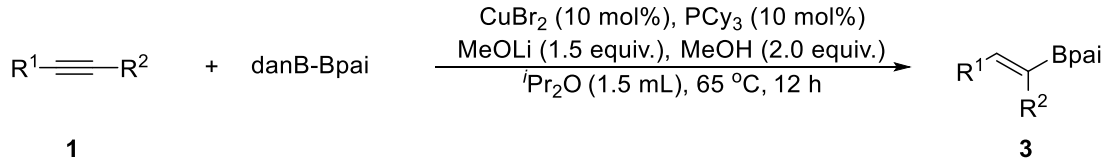
General procedure A:



1 **2**

In a 25 mL dry Schlenk tube, which contained a stirring bar, was charged with danB-Bpai (83.04 mg, 0.24 mmol, 1.2 equiv.), CuF_2 (2.1 mg, 0.02 mmol, 10 mol%), PPh_3 (5.3 mg, 0.02 mmol, 10 mol%), and MeONa (16.2 mg, 0.3 mmol, 1.5 equiv.). The tube was then evacuated and back-filled under N_2 flow (this sequence was repeated three times). Anhydrous Cyclohexane (1.5 mL), alkenyl (0.2 mmol, 1.0 equiv.), and MeOH (12.8 mg, 0.4 mmol, 2.0 equiv.) were added subsequently under N_2. The tube was stirred at 35 ℃ for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (PE/EA) to afford the product **2**.

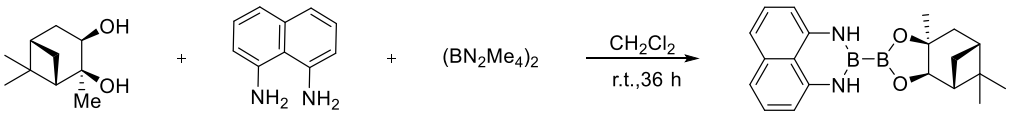
General procedure B:



1 **3**

In a 25 mL dry Schlenk tube, which contained a stirring bar, was charged with danB-Bpai (83.04 mg, 0.24 mmol, 1.2 equiv.), $CuBr_2$ (4.5 mg, 0.02 mmol, 10 mol%), PCy_3 (5.6 mg, 0.02 mmol, 10 mol%), and MeOLi (11.4 mg, 0.3 mmol, 1.5 equiv.). The tube was then evacuated and back-filled under N_2 flow (this sequence was repeated three times). Anhydrous *i*Pr_2O (1.5 mL), alkenyl (0.2 mmol, 1.0 equiv.), and MeOH (12.8 mg, 0.4 mmol, 2.0 equiv.) were added subsequently under N_2. The tube was stirred at 65 ℃ for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (PE/EA) to afford the product **3**.

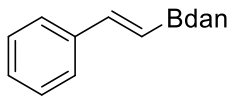
4. General Procedure for danB-Bpai



danB-Bpai

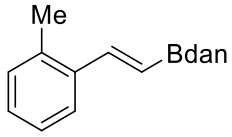
A 100 mL round-bottom flask equipped with a stirring bar was charged with (1S,2S,3R,5S)-(+)-2,3-pinanediol (1.7 g, 10 mmol, 1.0 equiv.) and tetrakis(dimethylamino)diboron (4.0 g, 20 mmol, 2.0 equiv.) in CH_2Cl_2 (40 mL). The reaction mixture was stirred at room temperature for 4 hours, after which 1,8-diaminonaphthalene (4.7 g, 30 mmol, 3.0 equiv.) was added to the system and stirring was continued at room temperature for 6 hours. The reaction mixture was concentrated by rotary evaporation and purified by silica gel chromatography (PE/EA) to afford the product **danB-Bpai** with 1.8g (53% yield). TLC (PE:EA): $\mathbf{R_f}$ = 0.7; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 (dd, *J* = 8.3, 7.2 Hz, 2H), 6.98 (dd, *J* = 8.4, 1.0 Hz, 2H), 6.26 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.18 (s, 2H), 4.28 (dd, *J* = 8.8, 1.9 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.22 (m, 1H), 2.07 (t, *J* = 5.5 Hz, 1H), 1.96 – 1.85 (m, 2H), 1.42 (s, 3H), 1.31 (s, 3H), 1.10 (d, *J* = 10.9 Hz, 1H), 0.87 (s, 3H)ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.5, 136.4, 127.5, 121.1, 117.6, 105.5, 86.2, 77.6, 51.1, 39.6, 38.0, 35.3, 28.8, 27.1, 26.6, 24.0 ppm; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 28.3 (large singlets) ppm ; $\mathbf{[\alpha]_D^{25}}$ = + 11.2 (c=1.0, CH_2Cl_2), **HRMS** (ESI) m/z calcd for $C_{20}H_{25}B_2N_2O_2$ $(M + H)^+$:347.2102, found 347.2109. This compound can be separated by silica gel column chromatography and does not deteriorate when stored at room temperature.

5. Analytical data for compounds



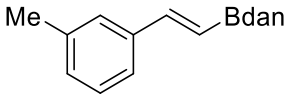
2a

(E)-2-styryl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2a)[1] **:** The general procedure was followed, using **phenylacetylene** (**1a**, 20.4 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2a** as a yellow solid (52.0 mg, 96% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.13 (d, *J* = 1.1 Hz, 1H), 7.12 – 7.08 (m, 2H), 7.02 (dd, *J* = 8.3, 1.1 Hz, 2H), 6.33 (dd, *J* = 7.3, 1.1 Hz, 2H), 6.28 (d, *J* = 18.6 Hz, 1H), 5.80 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 141.1, 137.5, 136.3, 128.7, 127.6, 126.8, 119.8, 117.6, 105.8 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.5 (large singlets) ppm.



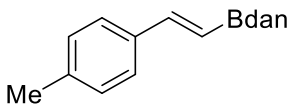
2b

(E)-2-(2-methylstyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2b)[2]**:** The general procedure was followed, using **2-methylphenylacetylene** (**1b**, 23.2 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2b** as a yellow solid (55.7 mg, 98% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 5.4, 3.7 Hz, 1H), 7.37 (d, *J* = 18.5 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.12 (dd, *J* = 8.2, 7.2 Hz, 2H), 7.02 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.36 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.20 (d, *J* = 18.4 Hz, 1H), 5.82 (s, 2H), 2.44 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.2, 141.1, 136.8, 136.3, 135.8, 130.5, 128.4, 127.6, 126.2, 125.6, 119.8, 117.6, 105.8, 19.9 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.7 (large singlets) ppm.



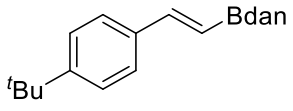
2c

(E)-2-(3-methylstyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2c)[: The general procedure was followed, using **3-methylphenylacetylene** (**1c**, 23.2 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2c** as a yellow solid (55.7 mg, 98% yield); $\mathbf{R_f}$ = 0.2 (PE : EA= 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 3H), 7.15 – 7.06 (m, 4H), 7.02 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.33 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.27 (d, *J* = 18.6 Hz, 1H), 5.80 (s, 2H), 2.37 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 141.1, 138.2, 137.4, 136.3, 129.5, 128.5, 127.6, 127.5, 123.9, 119.8, 117.5, 105.7, 21.4 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.6 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{19}H_{18}BN_2$ $(M + H)^+$:285.1563, found 285.1566.



2d

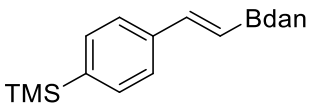
(E)-2-(4-methylstyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2d)[2]**:** The general procedure was followed, using **4-methylphenylacetylene** (**1d**, 23.2 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2d** as a yellow solid (54.9 mg, 96% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.13 – 7.06 (m, 3H), 7.01 (dd, *J* = 8.4, 1.0 Hz, 2H), 6.33 (dd, *J* = 7.2, 1.0 Hz, 2H), 6.22 (d, *J* = 18.5 Hz, 1H), 5.80 (s, 2H), 2.35 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 141.1, 138.7, 136.3, 134.8, 129.4, 127.6, 126.7, 119.8, 117.5, 105.7, 21.3 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.5 (large singlets) ppm.



2e

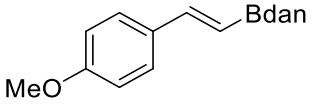
(E)-2-(4-(tert-butyl)styryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2e)[3]**:** The general procedure was followed, using **4-(tert-butyl)phenylacetylene** (**1e**, 31.6 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2e** as a yellow solid (63.9 mg, 98% yield); $\mathbf{R_f}$ = 0.3 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.08 (m, 3H), 7.02 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.36 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.28 (d, *J* = 18.6 Hz, 1H), 5.85 (s, 2H), 1.34 (s, 9H)ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.0, 143.5, 141.2, 136.3,

134.8, 127.6, 126.5, 125.6, 119.8, 117.5, 105.7, 34.7, 31.2 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.3 (large singlets) ppm.



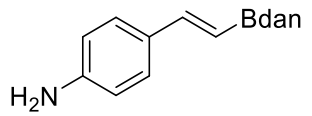
2f

(E)-2-(4-(trimethylsilyl)styryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2f): The general procedure was followed, using **(4-Ethynylphenyl)trimethylsilane** (**1f**, 34.9 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2f** as a yellow solid (67.1 mg, 98% yield); $\mathbf{R_f}$ = 0.3 (PE : EA =50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.45 (m, 4H), 7.15 (d, *J* = 10.4 Hz, 1H), 7.13 – 7.09 (m, 2H), 7.02 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.38 – 6.31 (m, 3H), 5.85 (s, 2H), 0.28 (s, 9H)ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 141.4, 141.1, 137.8, 136.3, 133.7, 127.6, 126.0, 119.8, 117.6, 105.7, -1.2 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.4 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{21}H_{24}BN_2Si$ $(M + H)^+$:343.1802, found 343.1806.



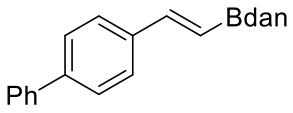
2g

(E)-2-(4-methoxystyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2g)[4]**:** The general procedure was followed, using **4-Ehynylanisole** (**1g**, 26.4 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 20 : 1) afforded product **2g** as a yellow solid (55.4 mg, 92% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 10 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 7.16 – 7.05 (m, 3H), 7.01 (dd, *J* = 8.4, 1.0 Hz, 2H), 6.94 – 6.86 (m, 2H), 6.35 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.14 (d, *J* = 18.5 Hz, 1H), 5.82 (s, 2H), 3.82 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1, 143.2, 141.2, 136.3, 130.4, 128.1, 127.6, 119.8, 117.5, 114.1, 105.7, 55.3 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 28.3 (large singlets) ppm.



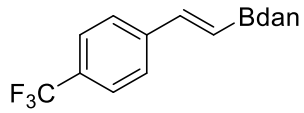
2h

(E)-3-(2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)vinyl)aniline (2h): The general procedure was followed, using **4-Ethynylaniline** (**1h**, 23.4 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 5 : 1) afforded product **2h** as a yellow solid (56.0 mg, 98% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 2 : 1); **^{1}H NMR** (400 MHz, DMSO-D_6) δ 7.99 (s, 2H), 7.33 – 7.21 (m, 3H), 7.05 (t, *J* = 7.8 Hz, 2H), 6.85 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.67 – 6.55 (m, 2H), 6.45 (dd, *J* = 7.4, 1.0 Hz, 2H), 6.00 (d, *J* = 18.5 Hz, 1H), 5.43 (s, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-D_6) δ 149.6, 144.7, 142.7, 136.1, 127.9, 127.7, 125.7, 119.5, 115.8, 113.9, 105.1 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, DMSO-D_6) δ 31.5 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{18}H_{17}BN_3$ $(M + H)^+$:286.1515, found 286.1519.



2i

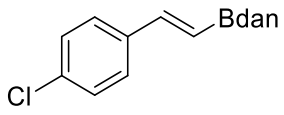
(E)-2-(2-([1,1'-biphenyl]-3-yl)vinyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2i): The general procedure was followed, using **4-biphenylacetylene** (**1i**, 35.7 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 50 : 1) afforded product **2i** as a yellow solid (65.2 mg, 94% yield); $\mathbf{R_f}$ = 0.1 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 4H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.39 – 7.33 (m, 1H), 7.21 – 7.09 (m, 3H), 7.03 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.39 – 6.31 (m, 3H), 5.85 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 141.4, 141.1, 140.5, 136.5, 136.3, 128.8, 127.6, 127.5, 127.4, 127.2, 127.0, 119.8, 117.6, 105.8 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 28.3 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{24}H_{20}BN_2$ $(M + H)^+$:347.1719, found 347.1724.



2j

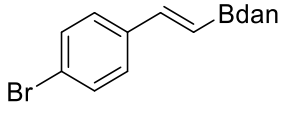
(E)-2-(4-(trifluoromethyl)styryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2j)[4]**:** The general procedure was followed, using **4-(Trifluoromethyl)phenylacetylene** (**1j**, 30.4 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 50 : 1) afforded product **2j** as a yellow solid (65.6 mg, 97% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 20 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.14 – 7.01 (m, 5H), 6.40 – 6.30 (m, 3H), 5.80 (s, 2H) ppm; **^{13}C NMR** (101

MHz, $CDCl_3$) δ 141.9, 140.9, 136.3, 130.3, 130.0, 127.6, 126.8, 125.6 (q, *J* = 14.7 Hz), 122.7, 119.9, 117.8, 105.9 ppm (the carbon next to boron could not be detected); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.5 ppm; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.7 (large singlets) ppm.



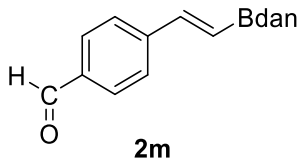
2k

(E)-2-(4-chlorostyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2k)[4]**:** The general procedure was followed, using **4-Chlorophenylacetylene** (**1k**, 27.3 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2k** as a yellow solid (50.2 mg, 82% yield); **R_f** = 0.1 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.36 – 7.31 (m, 2H), 7.14 – 7.01 (m, 5H), 6.36 (dd, *J* = 7.2, 1.1 Hz, 2H), 6.27 (d, *J* = 18.6 Hz, 1H), 5.83 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.2, 141.0, 136.3, 136.0, 134.3, 128.9, 127.9, 127.6, 119.8, 117.7, 105.8 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.6 (large singlets) ppm.



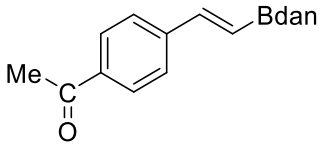
2l

(E)-2-(4-bromostyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2l)[4]**:** The general procedure was followed, using **4-Bromophenylacetylene** (**1l**, 36.2 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2l** as a yellow solid (68.4 mg, 98% yield); **R_f** = 0.1 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.12 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.05 – 7.01 (m, 3H), 6.35 (dd, *J* = 7.3, 1.1 Hz, 2H), 6.29 (d, *J* = 18.5 Hz, 1H), 5.82 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.3, 141.0, 136.4, 136.3, 131.8, 128.2, 127.6, 122.6, 119.8, 117.7, 105.8 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.6 (large singlets) ppm.



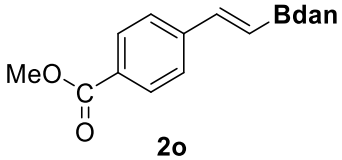
2m

(E)-4-(2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)vinyl)benzaldehyde (2m): The general procedure was followed, using **4-Ethynylbenzaldehyde** (**1m**, 26.0 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 10 : 1) afforded product **2m** as a yellow solid (60.6 mg, 97% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 5 : 1); **^{1}H NMR** (400 MHz, DMSO-D_6) δ 10.01 (s, 1H), 8.19 (s, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 18.4 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.57 (d, *J* = 18.6 Hz, 1H), 6.46 (d, *J* = 7.3 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-D_6) δ 192.6, 143.4, 142.6, 142.3, 136.1, 135.8, 130.2, 127.7, 127.1, 119.8, 116.2, 105.4 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, DMSO-D_6) δ 30.4 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{19}H_{16}BNO_2$ $(M + H)^+$:299.1355, found 299.1359.



2n

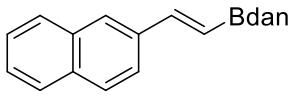
(E)-1-(4-(2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)vinyl)phenyl)ethan-1-one (2n)[2]**:** The general procedure was followed, using **4-Acetylphenylacetylene** (**1n** , 28.8 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 10 : 1) afforded product **2n** as a yellow solid (61.2 mg, 98% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 5 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.09 (m, 3H), 7.07 – 7.00 (m, 2H), 6.43 (d, *J* = 18.6 Hz, 1H), 6.36 (dd, *J* = 7.2, 1.0 Hz, 2H), 5.88 (s, 2H), 2.61 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.6, 142.3, 141.9, 140.9, 136.7, 136.3, 128.8, 127.6, 126.8, 119.9, 117.8, 105.9, 26.7 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 28.1 (large singlets) ppm.



2o

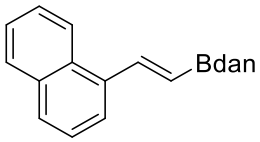
(E)-4-(2-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)vinyl) methyl benzoate (2o): The general procedure was followed, using **4-(Methoxycarbonyl)phenylacetylene** (**1o**, 32.0 mg, 0.2 mmol), **danB-Bpai** (83.04

mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 10 : 1) afforded product **2o** as a yellow solid (64.3 mg, 98% yield); $\mathbf{R_f}$ = 0.3 (PE : EA = 5 : 1); **^{1}H NMR** (400 MHz, DMSO-D_6) δ 8.17 (s, 2H), 8.04 – 7.97 (m, 2H), 7.69 – 7.62 (m, 2H), 7.49 (d, *J* = 18.6 Hz, 1H), 7.06 (dd, *J* = 8.2, 7.4 Hz, 2H), 6.87 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.52 (d, *J* = 18.7 Hz, 1H), 6.45 (dd, *J* = 7.4, 1.0 Hz, 2H), 3.86 (s, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-D_6) δ 166.0, 142.6, 142.3, 142.2, 136.1, 129.9, 129.1, 127.7, 126.7, 119.8, 116.2, 105.4, 52.2 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, DMSO-D_6) δ 31.9 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{20}H_{18}BN_2O_2$ $(M + H)^+$:329.1461, found 329.1465.



2p

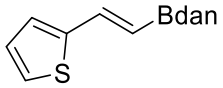
(E)-2-(2-(naphthalen-2-yl)vinyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2p): The general procedure was followed, using **2-Ethynyl-naphthalene** (**1p**, 30.4 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 20 : 1) afforded product **2p** as a yellow solid (56.8 mg, 89% yield); $\mathbf{R_f}$ = 0.4 (PE : EA= 10 : 1); **^{1}H NMR** (400 MHz, DMSO-D_6) δ 8.20 (s, 2H), 8.01 – 7.89 (m, 4H), 7.78 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.63 (d, *J* = 18.6 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.08 (t, *J* = 7.8 Hz, 2H), 6.89 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.57 – 6.46 (m, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-D_6) δ 143.9, 142.5, 136.1, 135.3, 133.2, 133.1, 128.5, 128.3, 127.7, 127.7, 126.9, 126.6, 126.5, 123.5, 123.2, 119.8, 116.1, 105.3 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, DMSO-D_6) δ 31.3 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{22}H_{18}BN_2$ $(M + H)^+$:321.1563, found 321.1567.



2q

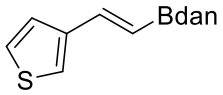
(E)-2-(2-(naphthalen-1-yl)vinyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2q): The general procedure was followed, using **1-Ethynyl-naphthalene** (**1q**, 30.4 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2q** as a yellow solid (58.1 mg, 91% yield); $\mathbf{R_f}$ = 0.2 (PE : EA= 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.95 – 7.81 (m, 3H), 7.71 (dt, *J* = 7.2, 1.0 Hz, 1H), 7.58 – 7.46 (m, 3H), 7.13 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.04 (dd, *J* = 8.3, 1.1 Hz, 2H), 6.40 – 6.33 (m, 3H), 5.89 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 140.6, 136.3, 135.5, 133.6, 131.0, 128.8, 128.6, 127.6, 126.3, 125.9, 125.6, 124.0, 123.5, 119.9, 117.6, 105.8 ppm (the carbon next to boron could not be detected); **^{11}B NMR**

(128 MHz, $CDCl_3$) δ 28.0 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{22}H_{18}BN_2$ $(M + H)^+$:321.1563, found 321.1567.



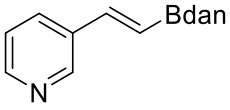
2r

(E)-2-(2-(thiophen-2-yl)vinyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2r): The general procedure was followed, using **2-Ethynylthiophene** (**1r**, 21.6 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 50 : 1) afforded product **2r** as a yellow solid (44.8 mg, 81% yield); $\mathbf{R_f}$ = 0.5 (PE : EA = 10 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 7.10 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.07 – 7.05 (m, 1H), 7.03 – 6.98 (m, 3H), 6.31 (dd, *J* = 7.2, 1.1 Hz, 2H), 6.04 (d, *J* = 18.3 Hz, 1H), 5.75 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 141.0, 136.3, 136.1, 127.7, 127.5, 127.1, 125.8, 119.8, 117.6, 105.8 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.6 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{16}H_{14}BN_2S$ $(M + H)^+$:277.0970, found 277.0974.



2s

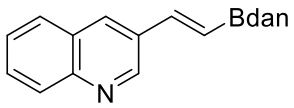
(E)-2-(2-(thiophen-3-yl)vinyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2s): The general procedure was followed, using **3-Ethynylthiophene** (**1s**, 21.6 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 50 : 1) afforded product **2s** as a yellow solid (51.6 mg, 93% yield); $\mathbf{R_f}$ = 0.1 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 3H), 7.13 – 7.05 (m, 3H), 7.01 (dd, *J* = 8.2, 1.1 Hz, 2H), 6.31 (dd, *J* = 7.2, 1.1 Hz, 2H), 6.04 (d, *J* = 18.5 Hz, 1H), 5.75 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 141.1, 137.3, 136.3, 127.5, 126.3, 124.8, 124.0, 119.7, 117.5, 105.7 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.9 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{16}H_{12}BN_2$ $(M - H)^-$:275.0814, found 275.0817.



2t

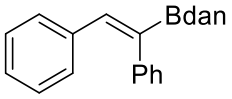
(E)-2-(2-(pyridin-3-yl)vinyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2t): The general procedure was followed, using **3-Ethynylpyridine** (**1t**, 20.6 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by

chromatography on silica gel (PE : EA = 5 : 1) afforded product **2t** as a yellow solid (26.2 mg, 48% yield); $\mathbf{R_f}$ = 0.5 (EA); **^{1}H NMR** (400 MHz, DMSO-D_6) δ 8.70 (d, J = 2.2 Hz, 1H), 8.52 (dd, J = 4.7, 1.6 Hz, 1H), 8.17 (s, 2H), 7.96 (d, J = 8.0 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.06 (t, J = 7.8 Hz, 2H), 6.88 (d, J = 8.2 Hz, 2H), 6.54 – 6.42 (m, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO-D_6) δ 149.4, 148.3, 142.3, 140.4, 136.1, 133.2, 132.8, 127.7, 124.1, 119.8, 116.1, 105.3 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.5 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{17}H_{15}BN_3$ $(M + H)^+$:272.1359, found 272.1362.



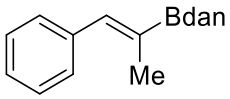
2u

(E)-2-(2-(quinolin-3-yl)vinyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2u): The general procedure was followed, using **3-Ethynylquinoline** (**1u**, 30.6 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 5 : 1) afforded product **2u** as a yellow solid (56.0 mg, 87% yield); $\mathbf{R_f}$ = 0.4 (PE : EA = 1 : 1); **^{1}H NMR** (400 MHz, DMSO-D_6) δ 9.14 (d, J = 2.2 Hz, 1H), 8.41 (d, J = 2.2 Hz, 1H), 8.23 (s, 2H), 8.09 – 8.00 (m, 2H), 7.76 (m, 1H), 7.69 – 7.59 (m, 2H), 7.07 (t, J = 7.8 Hz, 2H), 6.94 – 6.84 (m, 2H), 6.68 (d, J = 18.8 Hz, 1H), 6.49 (dd, J = 7.4, 1.0 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO-D_6) δ 149.2, 147.3, 142.4, 140.6, 136.1, 132.8, 130.6, 129.8, 128.7, 128.6, 127.7, 127.1, 125.9, 119.8, 116.2, 105.4 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, DMSO-D_6) δ 30.7 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{21}H_{17}BN_3$ $(M + H)^+$:322.1515, found 322.1519.



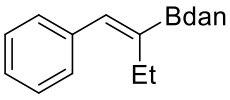
2v

(Z)-2-(1,2-diphenylvinyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2v)[1]**:** The general procedure was followed, using **Diphenylacetylene** (**1v**, 35.6 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2v** as a yellow solid (43.5 mg, 63% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 3H), 7.18 – 6.99 (m, 13H), 6.29 (dd, J = 7.2, 1.1 Hz, 2H), 5.68 (s, 2H) ppm ;**^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.0, 140.8, 137.3, 136.7, 136.3, 129.8, 129.0, 128.6, 128.0, 127.6, 127.5, 126.7, 119.7, 117.6, 105.9 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 28.9 (large singlets) ppm.



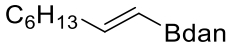
2w

(Z)-2-(1-phenylprop-1-en-2-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2w)[5]**:** The general procedure was followed, using **1-Phenylpropyne** (**1w**, 23.2 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2v** as a yellow solid (46.4 mg, 78% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.34 – 7.29 (m, 1H), 7.18 – 7.13 (m, 5H), 7.11 – 7.07 (m, 3H), 7.03 (dd, *J* = 7.3, 1.8 Hz, 3H), 7.00 (d, *J* = 1.1 Hz, 1H), 6.29 (dd, *J* = 7.2, 1.1 Hz, 2H), 5.68 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 137.7, 136.9, 136.3, 129.2, 128.1, 127.5, 127.0, 119.7, 117.5, 105.8, 15.8 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.6 (large singlets) ppm.



2x

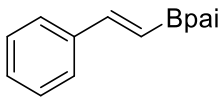
(Z)-2-(1-phenylbut-1-en-2-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2x)[5]**:** The general procedure was followed, using **1-Butynylbenzene** (**1x**, 26.0 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2x** as a yellow solid (42.1 mg, 74% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.34 – 7.26 (m, 3H), 7.12 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.03 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.95 (s, 1H), 6.37 (dd, *J* = 7.3, 1.0 Hz, 2H), 5.84 (s, 2H), 2.43 (qd, *J* = 7.5, 1.0 Hz, 2H), 1.15 (t, *J* = 7.5 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 137.8, 136.3, 136.1, 128.7, 128.2, 127.6, 127.0, 119.8, 117.6, 105.8, 22.7, 14.9 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.0 (large singlets) ppm.



2y

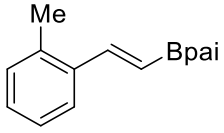
(E)-2-(oct-1-en-1-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (2y)[6]**:** The general procedure was followed, using **1-Octyne** (**1y**, 22.0 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **2y** as a pale yellow oil (49.5 mg, 89% yield); $\mathbf{R_f}$ = 0.3 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 6.94 (m, 4H), 6.38 – 6.23 (m, 3H), 5.66 (s, 2H), 5.52 (dt, *J* = 18.0, 1.6 Hz, 1H), 2.25 – 2.10 (m, 2H), 1.42 (q, *J* = 7.5 Hz, 2H), 1.37 – 1.22 (m, 6H), 0.96 – 0.83 (m, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.1, 141.2, 136.3, 127.5, 119.7, 117.3, 105.5, 35.9, 31.7,

28.9, 28.6, 22.6, 14.1 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 27.3 (large singlets) ppm.



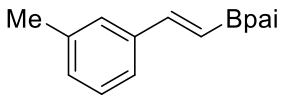
3a

(3aR,4R,6R,7aS)-3a,5,5-trimethyl-2-((E)-styryl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (3a)[7]: The general procedure was followed, using **phenylacetylene** (**1a**, 20.4 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3a** as a pale yellow oil (43.4 mg, 77% yield); $\mathbf{R_f}$ = 0.4 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.41 (d, *J* = 18.4 Hz, 1H), 7.36 – 7.27 (m, 3H), 6.20 (d, *J* = 18.5 Hz, 1H), 4.37 (dd, *J* = 8.8, 1.9 Hz, 1H), 2.38 (m, 1H), 2.24 (m, 1H), 2.11 (dd, *J* = 6.0, 4.8 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.45 (s, 3H), 1.30 (s, 3H), 1.20 (d, *J* = 10.9 Hz, 1H), 0.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 137.4, 128.8, 128.5, 127.0, 85.8, 77.8, 51.3, 39.5, 38.1, 35.5, 28.6, 27.1, 26.4, 24.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.5 (large singlets) ppm.



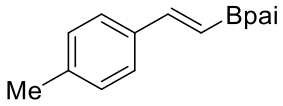
3b

(3aR,4R,6R,7aS)-3a,5,5-trimethyl-2-((E)-2-methylstyryl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (3b): The general procedure was followed, using **2-methylphenylacetylene** (**1b**, 23.2 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3b** as a pale yellow oil (43.4 mg, 73% yield); $\mathbf{R_f}$ = 0.3 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 18.3 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.21 – 7.17 (m, 2H), 7.16 – 7.13 (m, 1H), 6.11 (d, *J* = 18.3 Hz, 1H), 4.37 (dd, *J* = 8.8, 1.9 Hz, 1H), 2.42 (s, 3H), 2.40 – 2.34 (m, 1H), 2.29 – 2.21 (m, 1H), 2.11 (dd, *J* = 6.1, 4.8 Hz, 1H), 1.98 – 1.90 (m, 2H), 1.45 (s, 3H), 1.31 (s, 3H), 1.22 (d, *J* = 10.9 Hz, 1H), 0.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0, 136.7, 130.4, 128.6, 126.1, 125.7, 85.8, 77.8, 51.3, 39.5, 38.2, 35.5, 28.7, 27.1, 26.5, 24.0, 19.8 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.1 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{19}H_{26}BO_2$ $(M + H)^+$:297.2026, found 297.2029.



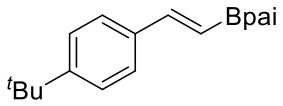
3c

(3aR,4R,6R,7aS)-3a,5,5-trimethyl-2-((E)-3-methylstyryl)hexahydro-4,6-methano benzo[d][1,3,2]dioxaborole (3c)： The general procedure was followed, using **3-methylphenylacetylene** (**1c**, 23.2 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3c** as a pale yellow oil (37.1 mg, 63% yield); $\mathbf{R_f}$ = 0.3 (PE : EA= 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 18.4 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.26 – 7.20 (m, 1H), 7.10 (dt, *J* = 7.3, 1.6 Hz, 1H), 6.17 (d, *J* = 18.4 Hz, 1H), 4.36 (dd, *J* = 8.7, 1.9 Hz, 1H), 2.43 – 2.37 (m, 1H), 2.36 – 2.33 (m, 3H), 2.24 (m, 1H), 2.11 (dd, *J* = 6.0, 4.8 Hz, 1H), 1.96 – 1.89 (m, 2H), 1.45 (s, 3H), 1.30 (s, 3H), 1.20 (d, *J* = 10.9 Hz, 1H), 0.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.6, 138.0, 137.4, 129.7, 128.4, 127.7, 124.2, 85.7, 77.8, 51.3, 39.5, 38.1, 35.5, 28.6, 27.1, 26.4, 24.0, 21.4 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.4 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{19}H_{26}BO_2$ $(M + H)^+$:297.2026, found 297.2029.



3d

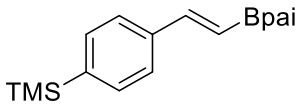
(3aR,4R,6R,7aS)-3a,5,5-trimethyl-2-((E)-4-methylstyryl)hexahydro-4,6-methano benzo[d][1,3,2]dioxaborole (3d): The general procedure was followed, using **4-methylphenylacetylene** (**1d**, 23.2 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3d** as a pale yellow solid (38.4 mg, 64% yield); $\mathbf{R_f}$ = 0.3(PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.13 (d, *J* = 18.4 Hz, 1H), 4.37 (dd, *J* = 8.7, 1.9 Hz, 1H), 2.43 – 2.36 (m, 1H), 2.35 (s, 3H), 2.28 – 2.21 (m, 1H), 2.11 (dd, *J* = 6.1, 4.9 Hz, 1H), 1.93 (m, 2H), 1.45 (s, 3H), 1.31 (s, 3H), 1.20 (d, *J* = 10.9 Hz, 1H), 0.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 139.0, 134.8, 129.3, 127.0, 85.7, 77.8, 51.4, 39.5, 38.2, 35.5, 28.7, 27.1, 26.4, 24.0, 21.3 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 30.8 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{19}H_{24}BO_2$ $(M - H)^-$:295.1870, found 295.1873.



3e

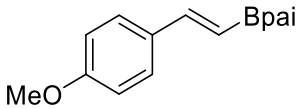
(3aR,4R,6R,7aS)-2-((E)-4-(tert-butyl)styryl)-3a,5,5-trimethylhexahydro-4,6-meth anobenzo[d][1,3,2]dioxaborole (3e): The general procedure was followed, using

4-(tert-butyl)phenylacetylene (**1e**, 31.6 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3e** as a colorless oil (42.8 mg, 63% yield); $\mathbf{R_f}$ = 0.4 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.6, 6.4 Hz, 3H), 7.38 – 7.35 (m, 2H), 6.15 (d, *J* = 18.4 Hz, 1H), 4.37 (dd, *J* = 8.7, 1.9 Hz, 1H), 2.43 – 2.34 (m, 1H), 2.28 – 2.20 (m, 1H), 2.11 (dd, *J* = 6.0, 4.8 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.45 (s, 3H), 1.31 (d, *J* = 4.0 Hz, 12H), 1.20 (d, *J* = 10.9 Hz, 1H), 0.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.1, 149.3, 134.8, 126.8, 125.5, 85.7, 77.8, 51.4, 39.5, 38.2, 35.5, 34.7, 31.2, 28.6, 27.1, 26.4, 24.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.5 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{22}H_{32}BO_2$ $(M + H)^+$:339.2495, found 339.2499.



3f

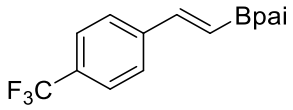
(4-((E)-2-((3aR,4R,6R,7aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)vinyl)phenyl) trimethyl silane (4t): The general procedure was followed, using **(4-Ethynylphenyl)trimethylsilane** (**1f**, 34.9 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3f** as a pale yellow oil (47.9 mg, 68% yield); $\mathbf{R_f}$ = 0.4 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 4H), 7.40 (d, *J* = 18.4 Hz, 1H), 6.22 (d, *J* = 18.4 Hz, 1H), 4.37 (dd, *J* = 8.7, 1.9 Hz, 1H), 2.38 (m, 1H), 2.23 (m, 1H), 2.11 (dd, *J* = 6.0, 4.8 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.45 (s, 3H), 1.30 (s, 3H), 1.21 (d, *J* = 10.9 Hz, 1H), 0.87 (s, 3H), 0.26 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.5, 141.5, 137.8, 133.6, 126.2, 85.8, 77.8, 51.3, 39.5, 38.1, 35.5, 28.6, 27.1, 26.4, 24.0, -1.2 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.2 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{21}H_{32}BO_2Si$ $(M + H)^+$:355.2264, found 355.2269.



3g

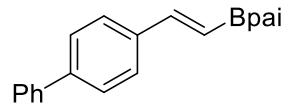
(3aR,4R,6R,7aS)-2-((E)-4-methoxystyryl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (3g)[7]: The general procedure was followed, using **4-Ehynylanisole** (**1g**, 26.4 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 50 : 1) afforded product **3g** as a pale yellow oil (31.2 mg, 50% yield); $\mathbf{R_f}$ = 0.4 (PE : EA = 20 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.36 (d, *J* = 18.4 Hz, 1H), 6.89 – 6.84 (m, 2H), 6.04 (d, *J* = 18.4 Hz, 1H), 4.36 (dd, *J* = 8.7, 1.9 Hz, 1H), 3.80 (s,

3H), 2.43 – 2.34 (m, 1H), 2.28 – 2.20 (m, 1H), 2.10 (dd, *J* = 6.0, 4.8 Hz, 1H), 1.97 – 1.89 (m, 2H), 1.44 (s, 3H), 1.30 (s, 3H), 1.20 (d, *J* = 10.9 Hz, 1H), 0.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2, 149.0, 130.3, 128.4, 113.9, 85.6, 77.7, 55.2, 51.3, 39.5, 38.1, 35.5, 28.6, 27.1, 26.4, 24.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.3 (large singlets) ppm.



3h

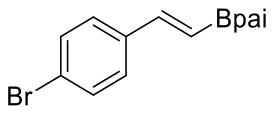
(3aR,4R,6R,7aS)-3a,5,5-trimethyl-2-((E)-4-(trifluoromethyl)styryl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (3h): The general procedure was followed, using **4-(Trifluoromethyl)phenylacetylene** (**1j**, 30.4 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3h** as a white solid (39.5 mg, 56% yield); **R_f** = 0.4 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 1.6 Hz, 4H), 7.41 (d, *J* = 18.5 Hz, 1H), 6.29 (d, *J* = 18.4 Hz, 1H), 4.39 (dd, *J* = 8.7, 1.8 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.29 – 2.22 (m, 1H), 2.12 (dd, *J* = 6.1, 4.9 Hz, 1H), 1.98 – 1.90 (m, 2H), 1.46 (s, 3H), 1.31 (s, 3H), 1.19 (d, *J* = 11.0 Hz, 1H), 0.88 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.6, 140.8, 127.1, 125.5 (q, 14.7 Hz), 86.0, 78.0, 51.3, 39.5, 38.2, 35.4, 28.6, 27.0, 26.4, 24.0 ppm (the carbon next to boron could not be detected); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.5 ppm; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.2 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{19}H_{23}BF_3O_2$ $(M + H)^+$:351.1743, found 351.1747.



3i

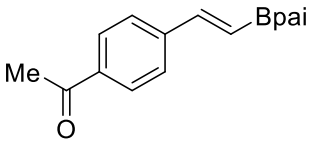
(3aR,4R,6R,7aS)-2-((E)-2-([1,1'-biphenyl]-4-yl)vinyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (3i): The general procedure was followed, using **4-biphenylacetylene** (**1i**, 35.7 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3i** as a white solid (43.0 mg, 60% yield); **R_f** = 0.5 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 6H), 7.48 – 7.40 (m, 3H), 7.36 – 7.32 (m, 1H), 6.23 (d, *J* = 18.4 Hz, 1H), 4.38 (dd, *J* = 8.7, 1.8 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.30 – 2.21 (m, 1H), 2.12 (dd, *J* = 6.1, 4.8 Hz, 1H), 1.99 – 1.91 (m, 2H), 1.46 (s, 3H), 1.31 (s, 3H), 1.22 (d, *J* = 10.9 Hz, 1H), 0.88 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.9, 141.5, 140.5, 136.4, 128.8, 127.5, 127.4, 127.2, 127.0, 85.8, 77.8,

51.3, 39.5, 38.2, 35.5, 28.6, 27.1, 26.4, 24.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.2 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{24}H_{26}BO_2$ $(M - H)^-$:357.2026, found 357.2030.



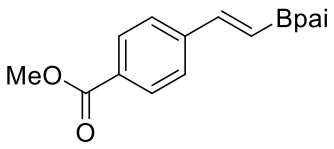
3j

(3aR,4R,6R,7aS)-2-((E)-4-bromostyryl)-3a,5,5-trimethylhexahydro-4,6-methano benzo[d][1,3,2]dioxaborole (3j): The general procedure was followed, using **4-Bromophenylacetylene** (**1l**, 36.2 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3j** as a pale yellow solid (43.2 mg, 60% yield); $\mathbf{R_f}$ = 0.4 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), 7.37 – 7.29 (m, 3H), 6.17 (d, *J* = 18.4 Hz, 1H), 4.37 (dd, *J* = 8.7, 1.9 Hz, 1H), 2.38 (m, 1H), 2.24 (m, 1H), 2.13 – 2.08 (m, 1H), 1.97 – 1.88 (m, 2H), 1.45 (s, 3H), 1.30 (s, 3H), 1.18 (d, *J* = 10.9 Hz, 1H), 0.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 136.3, 131.7, 128.5, 122.8, 85.9, 77.8, 51.3, 39.4, 38.1, 35.4, 28.6, 27.0, 26.4, 24.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.2 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{18}H_{23}BBrO_2$ $(M + H)^+$:361.0974, found 361.0978.



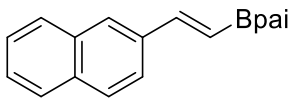
3k

1-(4-((E)-2-((3aR,4R,6R,7aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1, 3,2]dioxaborol-2-yl)vinyl)phenyl)ethan-1-one (3k): The general procedure was followed, using **4-Acetylphenylacetylene** (**1n** , 28.8 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 50 : 1) afforded product **3k** as a colorless oil (34.7 mg, 54% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 20 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.89 (m, 2H), 7.60 – 7.54 (m, 2H), 7.42 (d, *J* = 18.4 Hz, 1H), 6.32 (d, *J* = 18.4 Hz, 1H), 4.39 (dd, *J* = 8.7, 1.8 Hz, 1H), 2.60 (s, 3H), 2.40 (m, 1H), 2.25 (m, 1H), 2.12 (dd, *J* = 6.1, 4.9 Hz, 1H), 1.99 – 1.90 (m, 2H), 1.46 (s, 3H), 1.31 (s, 3H), 1.19 (d, *J* = 11.0 Hz, 1H), 0.88 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.57, 147.93, 141.80, 136.93, 128.70, 127.07, 86.02, 77.94, 51.28, 39.45, 38.17, 35.45, 28.61, 27.05, 26.65, 26.42, 24.01 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.88 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{20}H_{26}BO_3$ $(M + H)^+$:325.1975, found 325.1979.



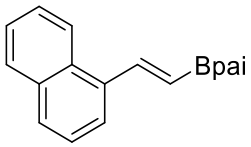
3l

4-((E)-2-((3aR,4R,6R,7aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)vinyl) methyl benzoate (3l): The general procedure was followed, using **4-(Methoxycarbonyl)phenylacetylene** (**1o**, 32.0 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 50 : 1) afforded product **3l** as a white solid (41.5 mg, 61% yield); $\mathbf{R_f}$ = 0.3 (PE : EA = 20 : 1); **^{11}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 18.5 Hz, 1H), 6.30 (d, *J* = 18.4 Hz, 1H), 4.38 (dd, *J* = 8.8, 1.8 Hz, 1H), 3.91 (s, 3H), 2.45 – 2.35 (m, 1H), 2.29 – 2.22 (m, 1H), 2.11 (dd, *J* = 6.1, 4.9 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.46 (s, 3H), 1.31 (s, 3H), 1.19 (d, *J* = 11.0 Hz, 1H), 0.88 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 148.1, 141.7, 130.1, 129.9, 126.9, 86.0, 77.9, 52.1, 51.3, 39.5, 38.2, 35.5, 28.6, 27.1, 26.4, 24.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.8 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{20}H_{26}BO_4$ $(M + H)^+$:341.1924, found 341.1928.



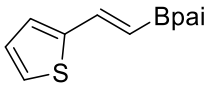
3m

(3aR,4R,6R,7aS)-3a,5,5-trimethyl-2-((E)-2-(naphthalen-2-yl)vinyl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (3m): The general procedure was followed, using **2-Ethynyl-naphthalene** (**1p**, 30.5 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3m** as a white solid (40.9 mg, 62% yield); $\mathbf{R_f}$ = 0.4 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 4H), 7.75 – 7.70 (m, 1H), 7.58 (d, *J* = 18.4 Hz, 1H), 7.49 – 7.41 (m, 2H), 6.32 (d, *J* = 18.4 Hz, 1H), 4.39 (dd, *J* = 8.7, 1.9 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.29 – 2.22 (m, 1H), 2.13 (dd, *J* = 6.0, 4.9 Hz, 1H), 1.99 – 1.92 (m, 2H), 1.46 (s, 3H), 1.30 (s, 3H), 1.23 (d, *J* = 11.0 Hz, 1H), 0.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 134.9, 133.7, 133.4, 128.4, 128.2, 128.0, 127.6, 126.4, 126.2, 123.3, 85.8, 77.8, 51.3, 39.5, 38.1, 35.5, 28.6, 27.1, 26.4, 24.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.2 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{22}H_{24}BO_2$ $(M - H)^-$:331.1870, found 331.1873.



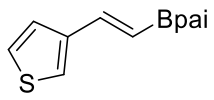
3n

(3aR,4R,6R,7aS)-3a,5,5-trimethyl-2-((E)-2-(naphthalen-1-yl)vinyl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (3n): The general procedure was followed, using **1-Ethynyl-naphthalene** (**1q**, 30.4 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3n** as a pale yellow oil (33.2 mg, 50% yield); $\mathbf{R_f}$ = 0.2 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 – 8.19 (m, 2H), 7.85 – 7.71 (m, 3H), 7.54 – 7.42 (m, 3H), 6.30 (d, *J* = 18.2 Hz, 1H), 4.40 (dd, *J* = 8.7, 1.9 Hz, 1H), 2.44 – 2.36 (m, 1H), 2.25 (m, 1H), 2.13 (dd, *J* = 6.0, 4.9 Hz, 1H), 2.01 – 1.90 (m, 2H), 1.48 (s, 3H), 1.34 – 1.24 (m, 4H), 0.86 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.3, 135.2, 133.5, 131.0, 129.0, 128.4, 126.1, 125.7, 125.5, 124.0, 123.7, 85.8, 77.8, 51.3, 39.5, 38.1, 35.5, 28.7, 27.1, 26.5, 24.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.2 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{22}H_{26}BO_2$ $(M + H)^+$:333.2026, found 333.2030.



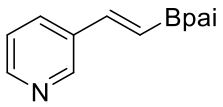
3o

(3aR,4R,6R,7aS)-3a,5,5-trimethyl-2-((E)-2-(thiophen-2-yl)vinyl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (3o): The general procedure was followed, using **2-Ethynylthiophene** (**1r**, 21.6 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3o** as a pale yellow oil (32.4 mg, 56% yield); $\mathbf{R_f}$ = 0.4 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 18.1 Hz, 1H), 7.23 (dt, *J* = 5.0, 1.0 Hz, 1H), 7.09 – 7.07 (m, 1H), 6.98 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.93 (d, *J* = 18.1 Hz, 1H), 4.35 (dd, *J* = 8.7, 1.8 Hz, 1H), 2.37 (m, 1H), 2.28 – 2.20 (m, 1H), 2.09 (dd, *J* = 6.1, 4.9 Hz, 1H), 1.96 – 1.87 (m, 2H), 1.43 (s, 3H), 1.30 (s, 3H), 1.18 (d, *J* = 11.0 Hz, 1H), 0.86 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 141.7, 127.6, 127.6, 126.2, 85.7, 77.8, 51.3, 39.4, 38.1, 35.5, 28.6, 27.0, 26.4, 24.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.3 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{16}H_{22}BO_2S$ $(M + H)^+$:289.1433, found 289.1436.



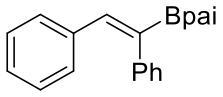
3p

(3aR,4R,6R,7aS)-3a,5,5-trimethyl-2-((E)-2-(thiophen-3-yl)vinyl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (3p): The general procedure was followed, using **3-Ethynylthiophene** (**1s**, 21.6 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3p** as a pale yellow oil (33.4 mg, 58% yield); $\mathbf{R_f}$ = 0.4 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 18.4 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.29 – 7.27 (m, 1H), 5.97 (d, *J* = 18.4 Hz, 1H), 4.36 (dd, *J* = 8.7, 1.8 Hz, 1H), 2.38 (m, 1H), 2.28 – 2.20 (m, 1H), 2.10 (dd, *J* = 6.1, 4.9 Hz, 1H), 1.97 – 1.89 (m, 2H), 1.44 (s, 3H), 1.30 (s, 3H), 1.19 (d, *J* = 11.1 Hz, 1H), 0.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 126.1, 125.0, 124.8, 85.8, 77.8, 51.4, 39.5, 38.2, 35.5, 28.6, 27.1, 26.4, 24.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.8 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{16}H_{20}BO_2S$ $(M - H)^-$:287.1277, found 287.1280.



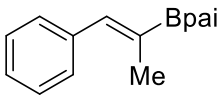
3q

3-((E)-2-((3aR,4R,6R,7aS)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)vinyl)pyridine (3q): The general procedure was followed, using **3-Ethynylpyridine** (**1t**, 20.6 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 10 : 1) afforded product **3q** as a colorless oil (31.9 mg, 56% yield); $\mathbf{R_f}$ = 0.4 (PE : EA =2 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 68.8 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.28 (m, 2H), 6.28 (d, *J* = 18.5 Hz, 1H), 4.39 (dd, *J* = 8.7, 1.8 Hz, 1H), 2.40 (m, 1H), 2.31 – 2.21 (m, 1H), 2.11 (dd, *J* = 6.1, 4.9 Hz, 1H), 1.99 – 1.86 (m, 2H), 1.46 (s, 3H), 1.31 (s, 3H), 1.19 (d, *J* = 10.9 Hz, 1H), 0.88 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.7, 149.0, 145.7, 133.1, 86.0, 77.9, 51.3, 39.4, 38.2, 35.4, 28.6, 27.0, 26.4, 24.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.9 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{17}H_{23}BNO_2$ $(M + H)^+$:284.1822, found 284.1825.



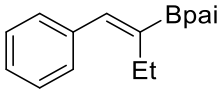
3r

(3aR,4R,6R,7aS)-2-((Z)-1,2-diphenylvinyl)-3a,5,5-trimethylhexahydro-4,6-metha nobenzo[d][1,3,2]dioxaborole (3r): The general procedure was followed, using **Diphenylacetylene** (**1v**, 35.6 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE : EA = 100 : 1) afforded product **3r** as a pale yellow oil (36.2 mg, 51% yield); $\mathbf{R_f}$ = 0.3 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.31 – 7.25 (m, 2H), 7.24 – 7.17 (m, 3H), 7.14 – 7.03 (m, 5H), 4.38 (dd, *J* = 8.7, 1.9 Hz, 1H), 2.39 – 2.22 (m, 2H), 2.11 (dd, *J* = 6.0, 4.8 Hz, 1H) 1.96 – 1.89 (m, 2H), 1.45 (s, 3H), 1.28 (d, *J* = 12.5 Hz, 4H), 0.85 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 140.5, 136.9, 129.9, 128.6, 128.3, 127.8, 127.6, 126.3, 86.1, 78.3, 51.3, 39.5, 38.1, 35.6, 28.6, 27.1, 26.6, 24.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.8 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{24}H_{28}BO_2$ $(M + H)^+$:359.2182, found 359.2187.



3s

(3aR,4R,6R,7aS)-3a,5,5-trimethyl-2-((Z)-1-phenylprop-1-en-2-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (3s): The general procedure was followed, using **1-Phenylpropyne** (**1w**, 23.2 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE) afforded product **3s** as a pale yellow oil (38.0 mg, 64% yield); $\mathbf{R_f}$ = 0.5 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 4H), 7.27 – 7.21 (m, 2H), 4.38 (dd, *J* = 8.7, 1.9 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.25 (m, 1H), 2.11 (dd, *J* = 6.1, 4.8 Hz, 1H), 2.01 (d, *J* = 1.9 Hz, 3H), 1.94 (m, 2H), 1.45 (s, 3H), 1.30 (s, 3H), 1.22 (d, *J* = 10.9 Hz, 1H), 0.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, CDCl3) δ 142.3, 137.9, 229.3, 128.0, 127.1, 85.9, 78.0, 51.3, 39.5, 38.1, 35.6, 28.7, 27.1, 26.5, 24.0, 16.0 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 23.0 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{19}H_{26}BO_2$ $(M + H)^+$:297.2026, found 297.2029.

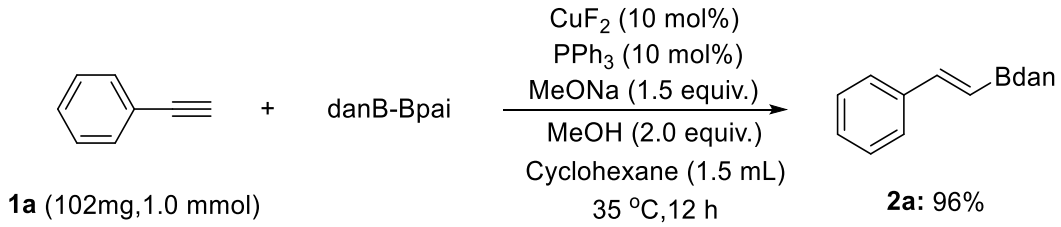


3t

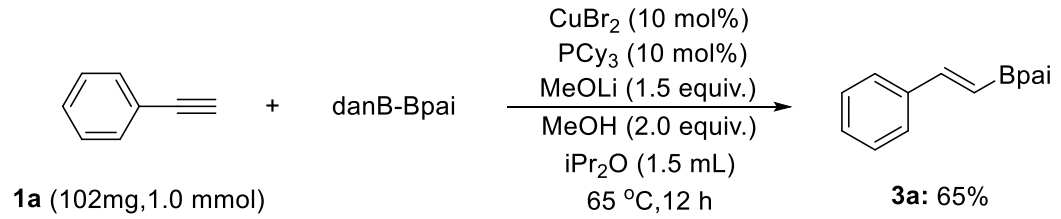
(3aR,4R,6R,7aS)-3a,5,5-trimethyl-2-((Z)-1-phenylbut-1-en-2-yl)hexahydro-4,6-m ethanobenzo[d][1,3,2]dioxaborole (3t): The general procedure was followed, using **1-Butynylbenzene** (**1x**, 26.0 mg, 0.2 mmol), **danB-Bpai** (83.04 mg, 0.24 mmol). Purification of this material by chromatography on silica gel (PE) afforded product **3t**

as a pale yellow oil (31.6 mg, 51% yield); $\mathbf{R_f}$ = 0.5 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 4.4 Hz, 4H), 7.23 (d, *J* = 8.2 Hz, 2H), 4.37 (dd, *J* = 8.7, 1.8 Hz, 1H), 2.40 (m, 3H), 2.29 – 2.22 (m, 1H), 2.15 – 2.09 (m, 1H), 1.99 – 1.89 (m, 2H), 1.49 – 1.42 (m, 3H), 1.30 (s, 3H), 1.22 (d, *J* = 10.9 Hz, 1H), 1.12 (t, *J* = 7.5 Hz, 3H), 0.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, CDCl3) δ 141.4, 137.8, 128.9, 128.1, 127.0, 85.8, 77.9, 51.3, 39.5, 38.1, 35.6, 28.7, 27.1, 26.5, 24.0, 22.7, 14.7 ppm (the carbon next to boron could not be detected); **^{11}B NMR** (128 MHz, $CDCl_3$) δ 23.0 (large singlets) ppm; **HRMS** (ESI) m/z calcd for $C_{20}H_{28}BO_2$ $(M + H)^+$:311.2182, found 311.2186.

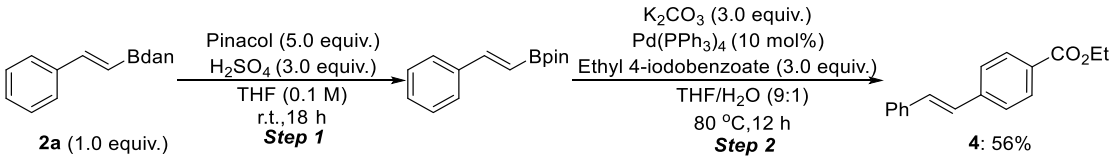
6. Product transformations



In a 50 mL dry Schlenk tube, which contained a stirring bar, was charged with danB-Bpai (415.2 mg, 1.2 mmol, 1.2 equiv.), CuF_2 (10.1 mg, 0.1 mmol, 10 mol%), PPh_3 (26.2 mg, 0.1 mmol, 10 mol%), and MeONa (81.0 mg, 1.5 mmol, 1.5 equiv.). The tube was then evacuated and back-filled under N_2 flow (this sequence was repeated three times). Anhydrous Cyclohexane (7.5 mL), Phenylacetylene (102 mg, 1.0 mmol, 1.0 equiv.), and MeOH (64.1 mg, 2.0 mmol, 2.0 equiv.) were added subsequently under N_2. The tube was stirred at 35℃ for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography to afford the product **2a** (260.7mg, 96% yield).



In a 50 mL dry Schlenk tube, which contained a stirring bar, was charged with danB-Bpai (415.2 mg, 1.2 mmol, 1.2 equiv.), $CuBr_2$ (22.3 mg, 0.1 mmol, 10 mol%), PCy_3 (28.0 mg, 0.1 mmol, 10 mol%), and MeOLi (57.0 mg, 1.5 mmol, 1.5 equiv.). The tube was then evacuated and back-filled under N_2 flow (this sequence was repeated three times). Anhydrous iPr_2O (7.5 mL), Phenylacetylene (102 mg, 1.0 mmol, 1.0 equiv.), and MeOH (64.1 mg, 2.0 mmol, 2.0 equiv.) were added subsequently under N_2. The tube was stirred at 65℃ for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography to afford the product **3a** (183.3 mg, 65% yield).

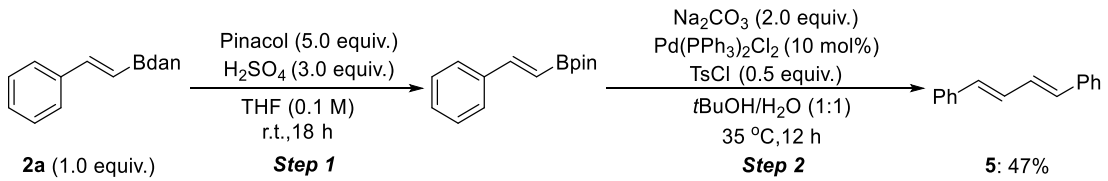


Step 1:

In a 25 mL Schlenk tube, which contained a stirring bar, was charged with **2a** (81.3 mg, 0.3 mmol, 1.0 equiv.) in THF (3.0 mL). 5M sulfuric acid (0.18 mL, 0.9 mmol, 3.0 equiv.) and pinacol (177.3 mg, 1.5 mmol, 5.0 equiv.) were added .The tube was stirred at room temperature for 18 hours. The reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation to afford the product (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane.

Step 2:

In a 25 mL Schlenk tube, which contained a stirring bar, was charged with $Pd(PPh_3)_4$ (34.7 mg, 0.03 mmol, 10 mol%) and K_2CO_3 (124.4 mg, 0.9 mmol, 3.0 equiv.). The tube was then evacuated and back-filled under N_2 flow (this sequence was repeated three times). To a solution of (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane in THF (1.8 mL), H_2O (0.2 mL), and Ethyl 4-iodobenzoate (248.5 mg, 0.9 mmol, 3.0 equiv.) were added subsequently under N_2. The tube was stirred at 85 ℃ for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (PE : EA = 100 : 1) to afford the product **4**[8] (42.4 mg, 56% yield) as a yellow solid; $\mathbf{R_f}$ = 0.3 (PE : EA = 50 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.50 (m, 4H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.21 (d, *J* = 16.3 Hz, 1H), 7.12 (d, *J* = 16.2 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 141.7, 136.7, 131.1, 123.0, 129.2, 128.7, 128.2, 127.6, 126.7, 126.2, 60.9, 14.3 ppm.



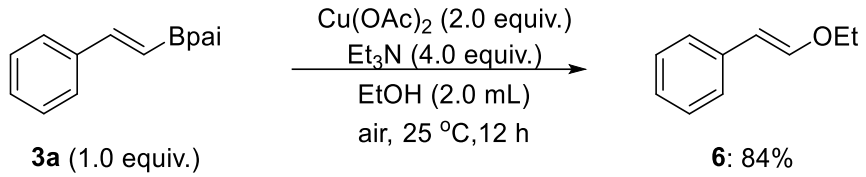
Step 1:

In a 25 mL Schlenk tube, which contained a stirring bar, was charged with **2a** (108.4 mg, 0.4 mmol, 1.0 equiv.) in THF (4.0 mL). 5M sulfuric acid (0.24 mL, 1.2

mmol, 3.0 equiv.) and pinacol (236.3 mg, 2.0 mmol, 5.0 equiv.) were added .The tube was stirred at room temperature for 18 hours. The reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation to afford the product (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane.

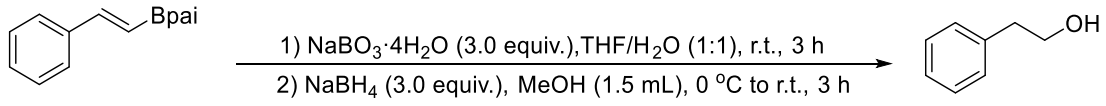
Step 2:

In a 25 mL Schlenk tube, which contained a stirring bar, was charged with $Pd(PPh_3)_2Cl_2$ (28.1mg, 0.04 mmol, 10 mol%) , Na_2CO_3 (84.8 mg, 0.8 mmol, 2.0 equiv.) and TsCl (38.1 mg, 0.2 mmol, 0.5 equiv.). The tube was then evacuated and back-filled under N_2 flow (this sequence was repeated three times). To a solution of (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane in *t*BuOH (1.5 mL) and H_2O (1.5 mL) were added subsequently under N_2. The tube was stirred at 35 ℃ for 12 hours. The reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (PE) to afford the product **5**[9] (19.4 mg, 47% yield) as a white solid; $\mathbf{R_f}$ = 0.5 (PE);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.3, 1.4 Hz, 4H), 7.33 (dd, *J* = 8.3, 6.9 Hz, 4H), 7.26 – 7.21 (m, 2H), 6.99 – 6.94 (m, 2H), 6.71 – 6.65 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.3, 132.8, 129.2, 128.6, 127.5, 126.4 ppm.



3a (1.0 equiv.) **6**: 84%

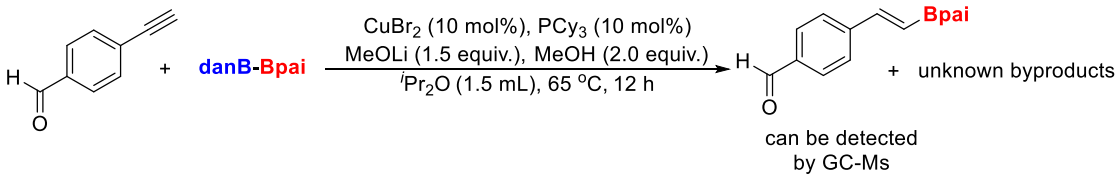
In a 25 mL Schlenk tube, which contained a stirring bar, was charged with **3a** (84.7 mg, 0.3 mmol, 1.0 equiv.), $Cu(OAc)_2$ (108.9 mg, 0.6 mmol, 2.0 equiv.), Et_3N (121.4 mg, 1.2 mmol, 4.0 equiv.), and EtOH (2.0 mL).The tube was stirred at 25 ℃ for 12 hours. The reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (PE) to afford the product **6**[9] (37.3mg, 84% yield) as a colorless oil; $\mathbf{R_f}$ = 0.4 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 4H), 7.15 – 7.09 (m, 1H), 6.98 (d, *J* = 12.9 Hz, 1H), 5.83 (d, *J* = 13.0 Hz, 1H), 3.89 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9, 136.5, 128.5, 125.5, 125.0, 105.8, 65.4, 14.8 ppm.



3a (1.0 equiv.) **7**: 53%

In a 25 m Schlenk tube, which contained a stirring bar, was charged with **3a** (84.7 mg, 0.3 mmol, 1.0 equiv.), $NaBO_3$ $4H_2O$ (138.5 mg, 0.9 mmol, 3.0 equiv.), THF (1.5 mL), and H_2O (2.0 mL).The tube was stirred at room temperature for 3 hours. The reaction mixture was diluted with EA and H_2O. Then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. At 0^oC, $NaBH_4$ (34.0 mg, 0.9 mmol, 3.0 equiv.) and MeOH (1.5 mL) were added. The tube was stirred at room temperature for 3 hours. The reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (PE : EA = 20 : 1) to afford the product **7**[10] (19.4 mg, 53% yield) as a colorless oil; $\mathbf{R_f}$ = 0.4 (PE : EA = 5 : 1); **^{1}HNMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.22 (td, *J* = 6.3, 1.6 Hz, 3H), 3.81 (t, *J* = 6.6 Hz, 2H), 2.84 (t, *J* = 6.6 Hz, 2H), 1.83 (s, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 129.0, 128.5, 126.4, 63.6 ppm.

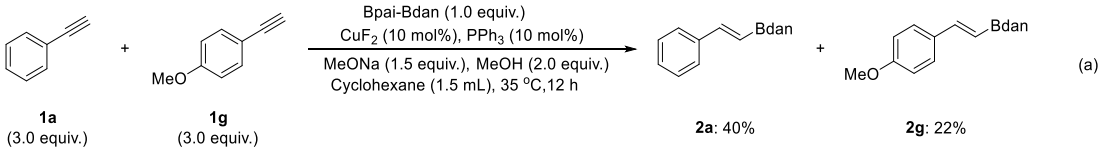
Failed example:



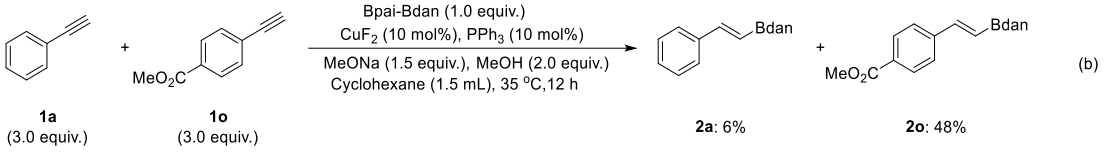
As shown above, using 4-ethynylbenzaldehyde as the starting material afforded the desired product but generated many unknown byproducts; this result suggested that the aldehyde group might not be compatible with the reaction conditions.

7. Mechanism experiment

7.1 The effect of substituent electricity:

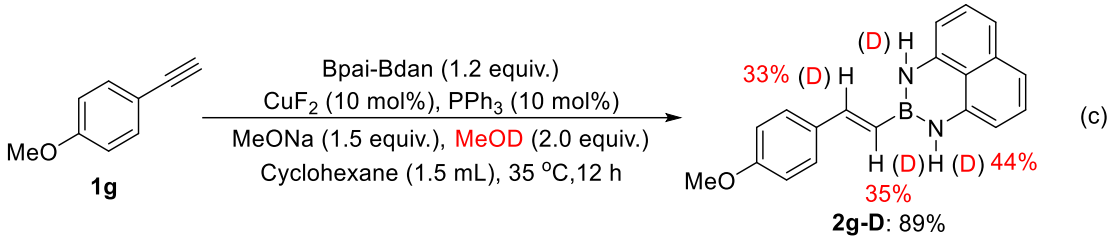


In a 25 mL dry Schlenk tube, which contained a stirring bar, was charged with danB-Bpai (69.2 mg, 0.2 mmol, 1.0 equiv.), 4-Ethynylanisole (79.3 mg, 0.6 mmol, 3.0 equiv.), CuF_2 (2.1 mg, 0.02 mmol, 10 mol%), PPh_3 (5.3 mg, 0.02 mmol, 10 mol%), and MeONa (16.2 mg, 0.3 mmol, 1.5 equiv.). The tube was then evacuated and back-filled under N_2 flow (this sequence was repeated three times). Anhydrous Cyclohexane (1.5 mL), Phenylacetylene (61.3 mg, 0.6 mmol, 3.0 equiv.), and MeOH (12.8 mg, 0.4 mmol, 2.0 equiv.) were added subsequently under N_2. The tube was stirred at 35 ℃ for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography to afford the product **2a** (21.3 mg, 40% yield) and **2g** (13.2 mg, 22% yield), **2a**:**2g** = 1.8:1.

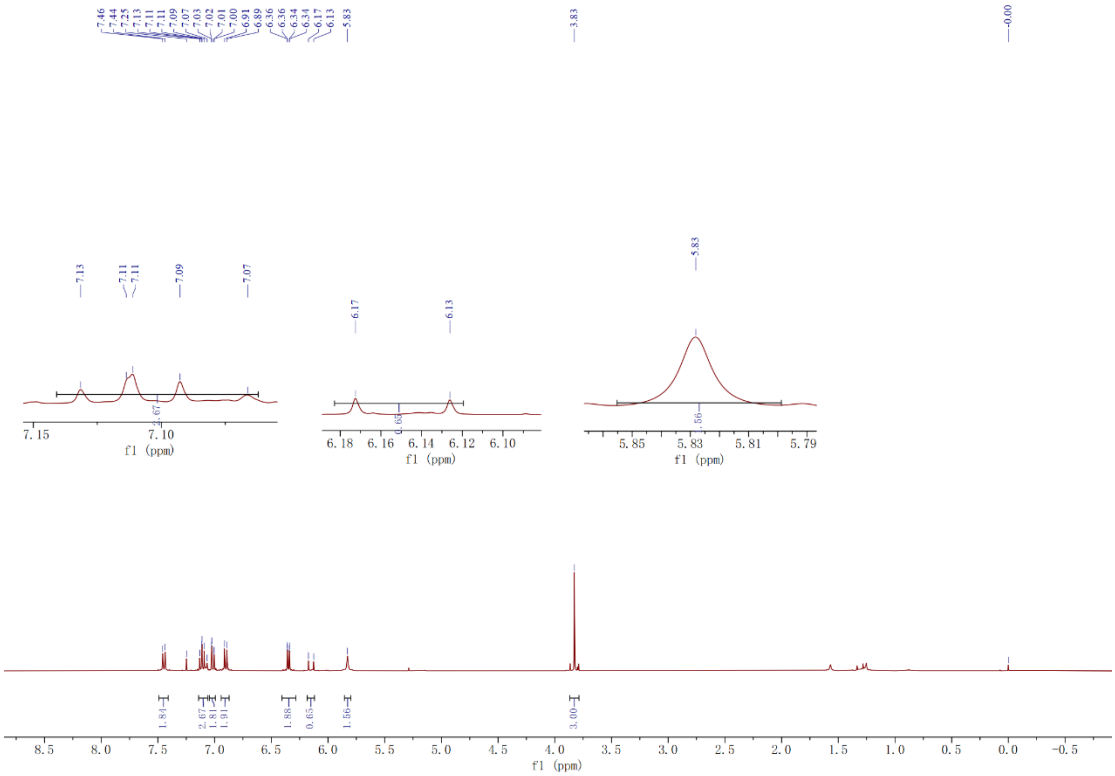


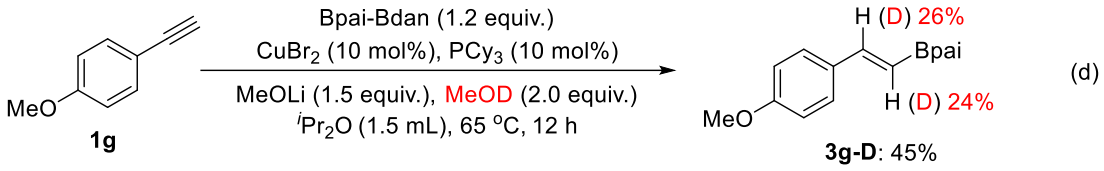
In a 25 mL dry Schlenk tube, which contained a stirring bar, was charged with danB-Bpai (69.2 mg, 0.2 mmol, 1.0 equiv.), 4-(Methoxycarbonyl)phenylacetylene (96.1 mg, 0.6 mmol, 3.0 equiv.), CuF_2 (2.1 mg, 0.02 mmol, 10 mol%), PPh_3 (5.3 mg, 0.02 mmol, 10 mol%), and MeONa (16.2 mg, 0.3 mmol, 1.5 equiv.). The tube was then evacuated and back-filled under N_2 flow (this sequence was repeated three times). Anhydrous Cyclohexane (1.5 mL), Phenylacetylene (61.3 mg, 0.6 mmol, 3.0 equiv.), and MeOH (12.8 mg, 0.4 mmol, 2.0 equiv.) were added subsequently under N_2. The tube was stirred at 35 ℃ for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography to afford the product **2a** (3.5 mg, 6% yield) and **2o** (31.7 mg, 48% yield), **2a**:**2o** = 1:8.

7.2 Deuterium experiments:

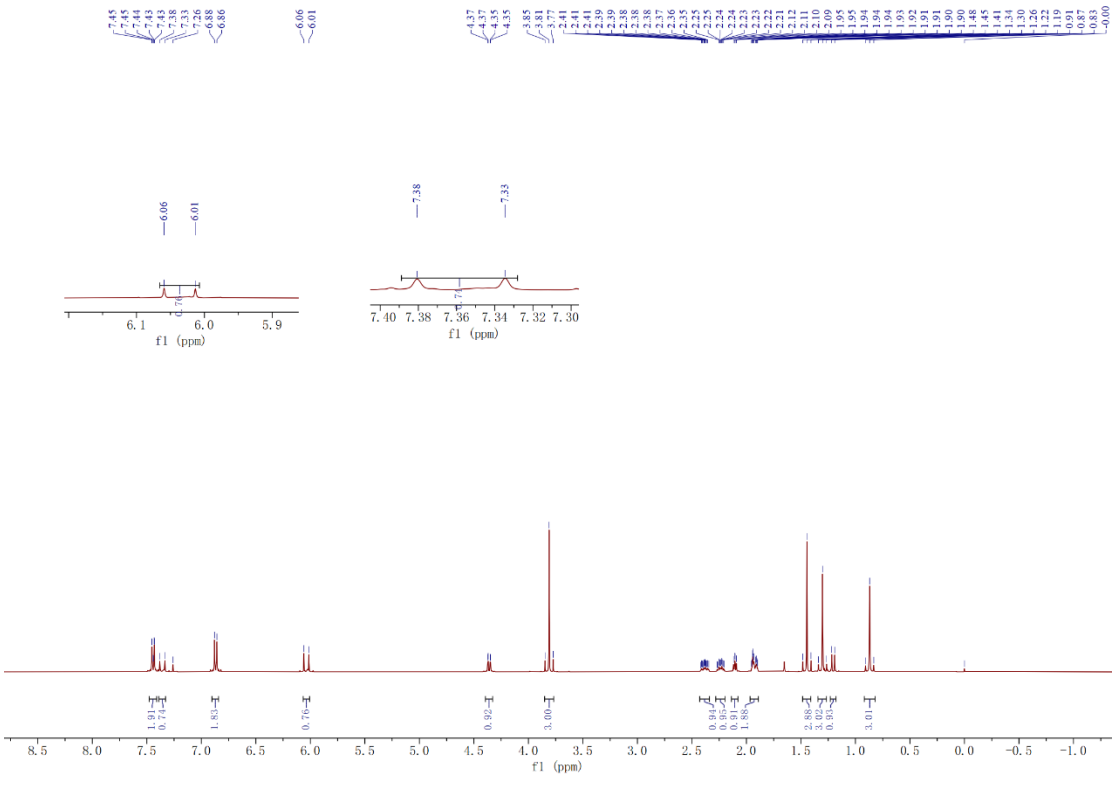


In a 25 mL dry Schlenk tube, which contained a stirring bar, was charged with danB-Bpai (83.04 mg, 0.2 mmol, 1.2 equiv.), 4-Ethynylanisole (26.4 mg, 0.6 mmol, 3.0 equiv.), CuF_2 (2.1 mg, 0.02 mmol, 10 mol%), PPh_3 (5.3 mg, 0.02 mmol, 10 mol%), and MeONa (16.2 mg, 0.3 mmol, 1.5 equiv.). The tube was then evacuated and back-filled under N_2 flow (this sequence was repeated three times). Anhydrous Cyclohexane (1.5 mL), and MeOH (12.8 mg, 0.4 mmol, 2.0 equiv.) were added subsequently under N_2. The tube was stirred at 35 ℃ for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography to afford the product **2g-D** (53.4 mg, 89% yield).





In a 25 mL dry Schlenk tube, which contained a stirring bar, was charged with danB-Bpai (83.04 mg, 0.24 mmol, 1.2 equiv.), 4-Ethynylanisole (26.4 mg, 0.6 mmol, 3.0 equiv.), $CuBr_2$ (4.5 mg, 0.02 mmol, 10 mol%), PCy_3 (5.6 mg, 0.02 mmol, 10 mol%), and MeOLi (11.4 mg, 0.3 mmol, 1.5 equiv.). The tube was then evacuated and back-filled under N_2 flow (this sequence was repeated three times). Anhydrous iPr_2O (1.5 mL), alkenyl (0.2 mmol, 1.0 equiv.), and MeOH (12.8 mg, 0.4 mmol, 2.0 equiv.) were added subsequently under N_2. The tube was stirred at 65 ℃ for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EA and H_2O, then extracted with EA. The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (PE/EA) to afford the product **3g-D** (28.1mg, 45% yield).



8. References

[1] Zhong, M.; Gagne, Y.; Hope, T. O.; Pannecoucke, X.; Frenette, M.; Jubault, P.; Poisson, T. *Angew. Chem. Int. Ed.* **2021**, *60*, 14498–14503.

[2] Iwadate, N.; Suginome, M. *Org. Lett.* **2009**, *11*, 1899–1902.

[3]Reid, W. B.; Spillane, J. J.; Krause, S. B.; Watson, D. A. *J. Am. Chem. Soc.* **2016**, *138*, 5539–5542.

[4] Jang, W. J.; Lee, W. L.; Moon, J. H.; Lee, J. Y.; Yun, J. *Org. Lett.* **2016**, *18*, 1390–1393.

[5] Yoshida, H.; Takemoto, Y.; Takaki, K. *Asian J. Org. Chem.* **2014**, *3*, 1204–1209.

[6] Birepinte, M.; Liautard, V.; Chabaud, L.; Pucheault, M. *Org. Lett.* **2020**, *22*, 2838–2843.

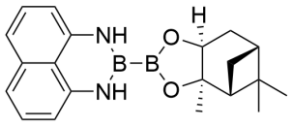
[7] Dominguez-Molano, P.; Bru, G.; Salvado, O.; Maza, R. J.; Carbó, J. J.; Fernández, E. *Chem. Commun.* **2021**, *57*, 13361–13364.

[8] Gong, D.; Hu, B.; Yang, W.; Kong, D.; Xia, H.; Chen, D. *Organometallics* **2020**, *39*, 862–869.

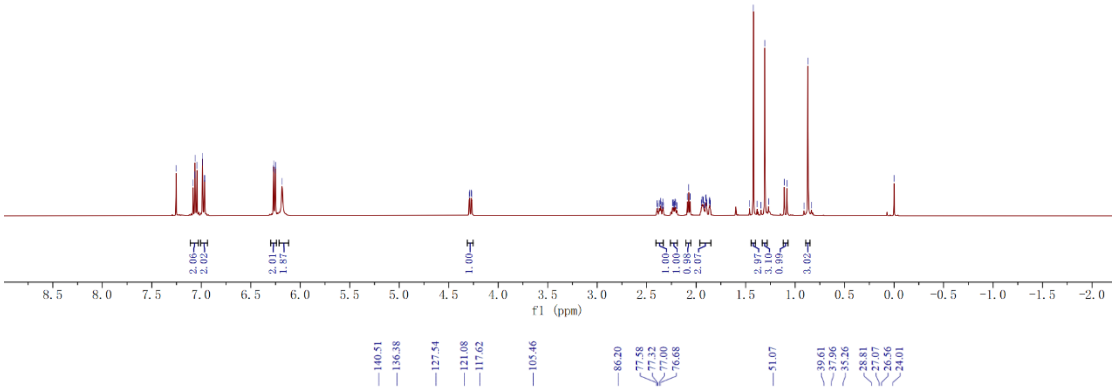
[9] Shi, X.; Li, S.; Wu, L. *Angew. Chem. Int. Ed.* **2019**, *58*, 16167–16171.

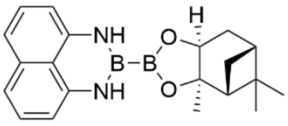
[10] Liu, X.; Sau, A.; Green, A. R.; Popescu, M. V.; Pompetti, N. F.; Li, Y.; Zhao, Y.; Paton, R. S.; Damrauer, N. H.; Miyake, G. M. *Nature* **2025**, *637*, 601–607.

9. NMR Spectra

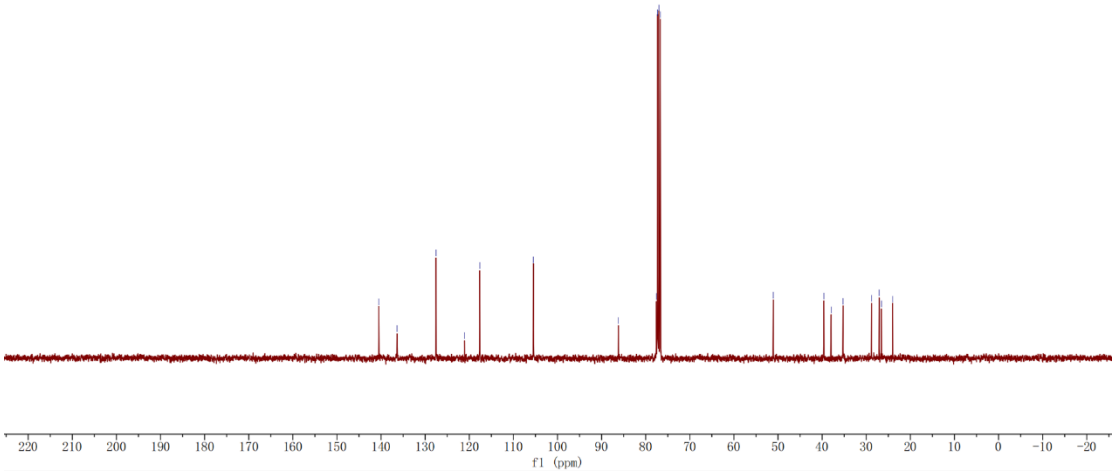


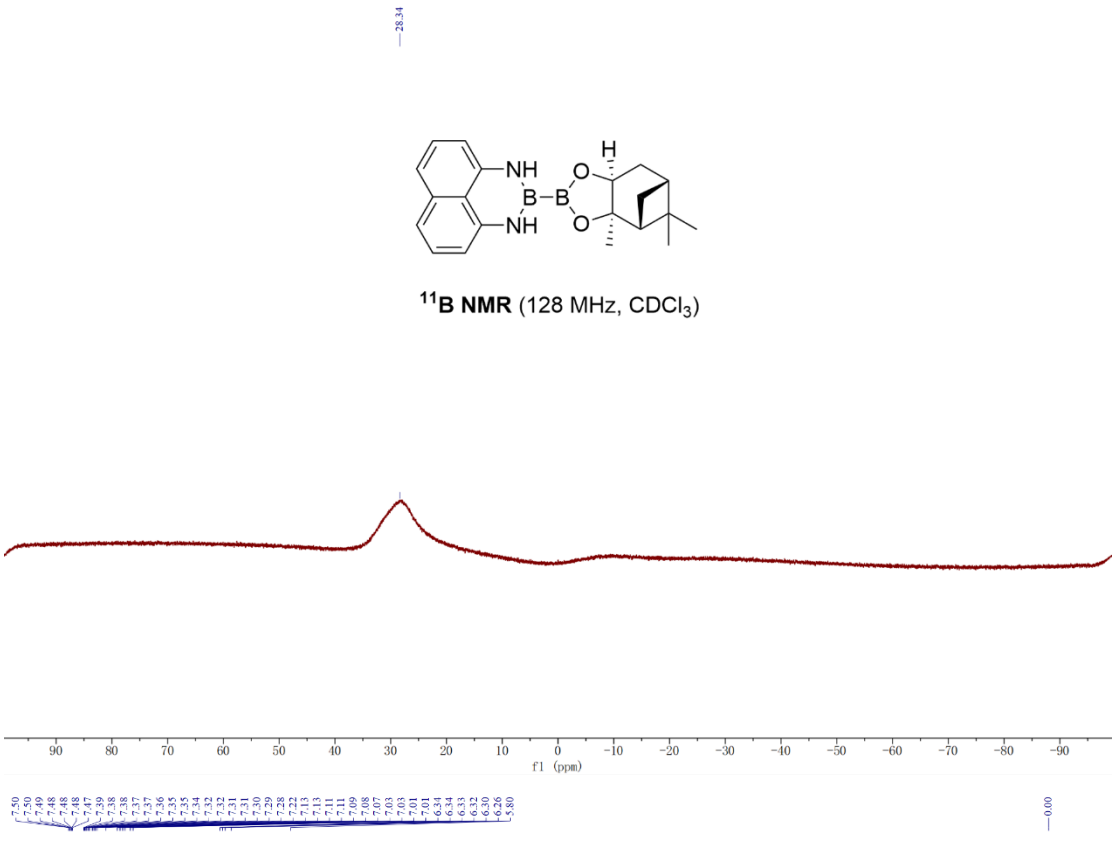
^{1}H NMR (400 MHz, $CDCl_3$)



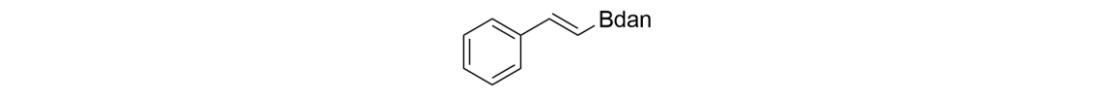


^{13}C NMR (101 MHz, $CDCl_3$)



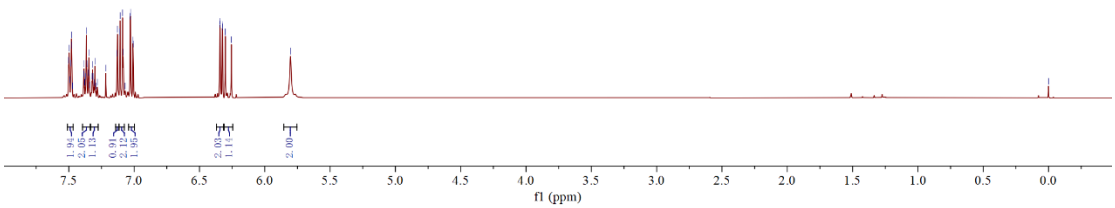


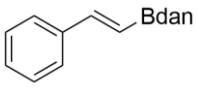
^{11}B NMR (128 MHz, $CDCl_3$)



2a

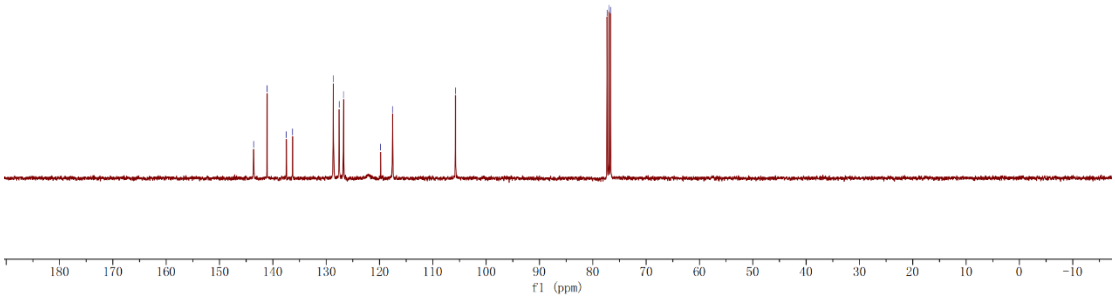
^{1}H NMR (400 MHz, $CDCl_3$)

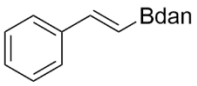




2a

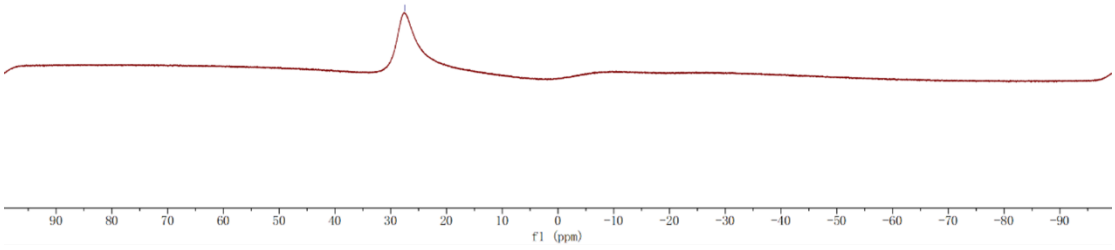
^{13}C NMR (101 MHz, $CDCl_3$)

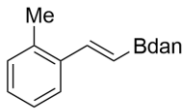




2a

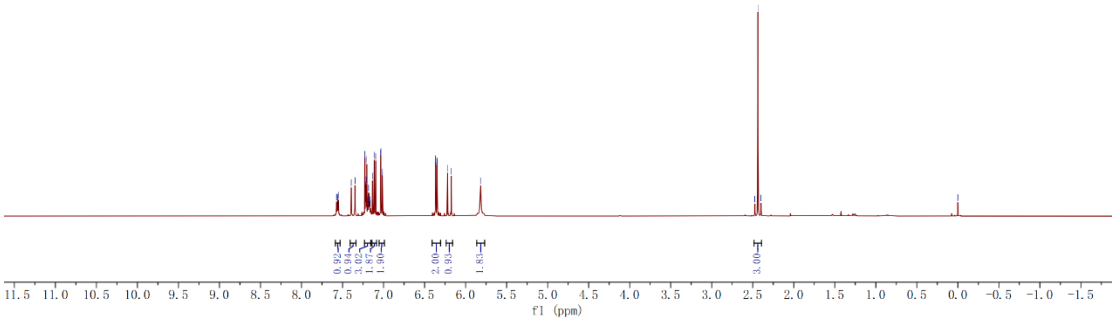
^{11}B NMR (128 MHz, $CDCl_3$)

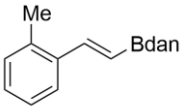




2b

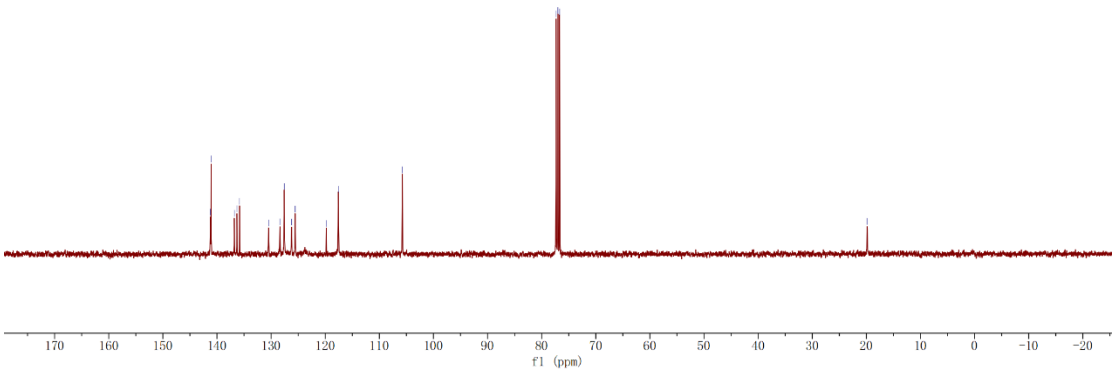
^{1}H NMR (400 MHz, $CDCl_3$)

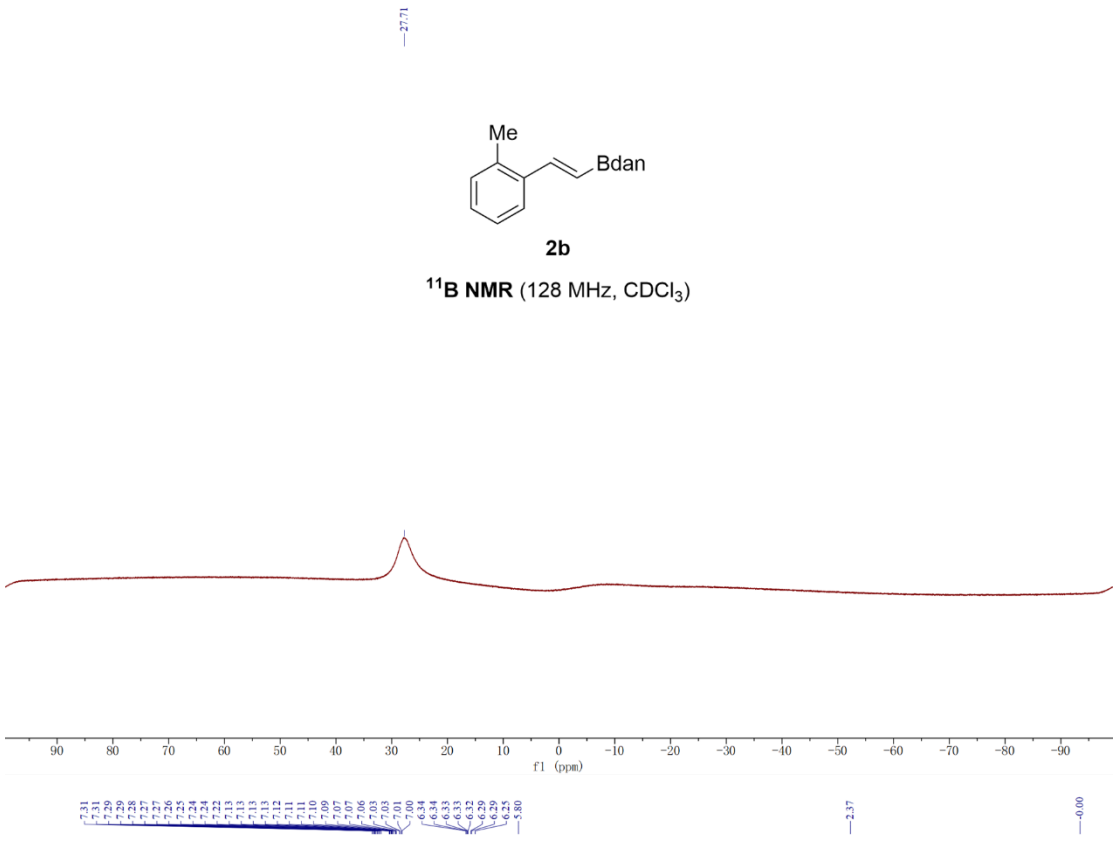




2b

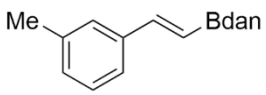
^{13}C NMR (101 MHz, $CDCl_3$)





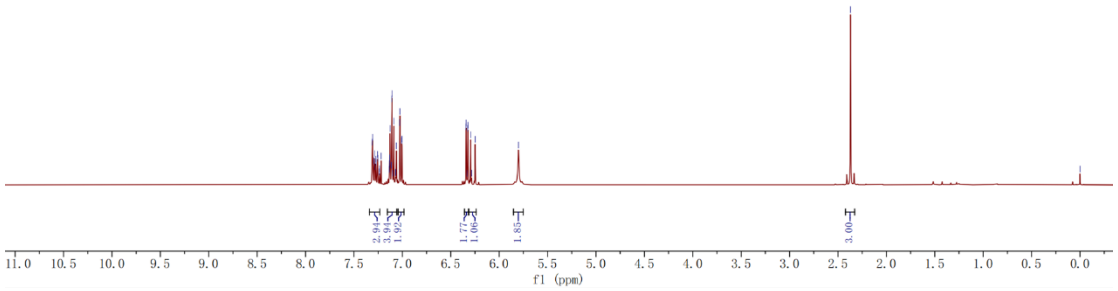
2b

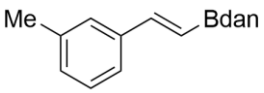
^{11}B NMR (128 MHz, $CDCl_3$)



2c

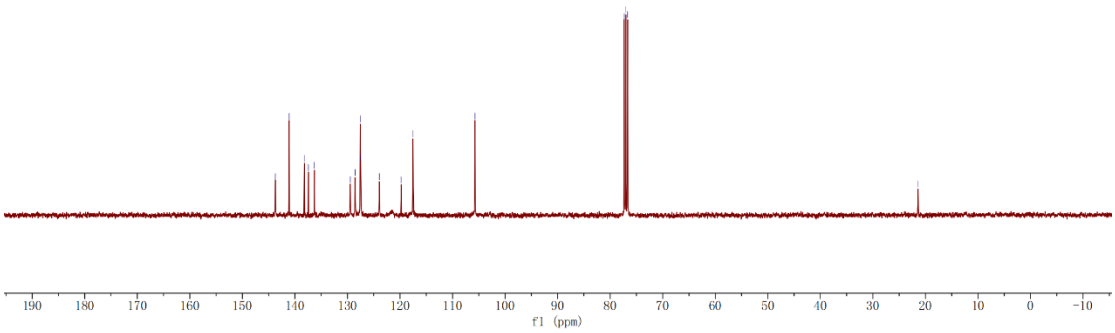
^{1}H NMR (400 MHz, $CDCl_3$)

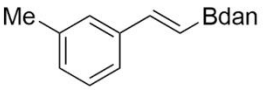




2c

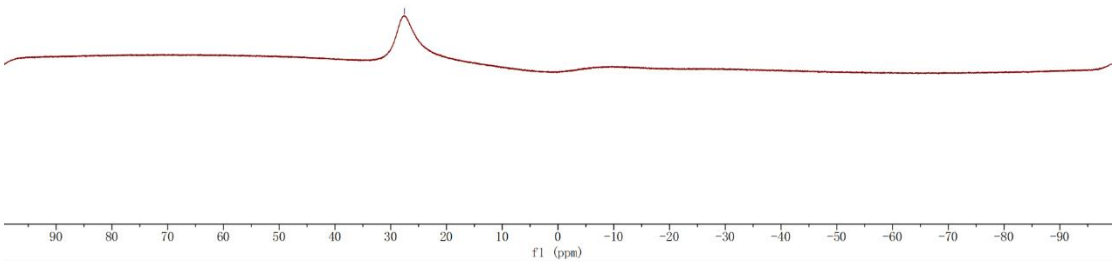
^{13}C NMR (101 MHz, $CDCl_3$)

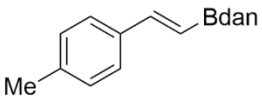




2c

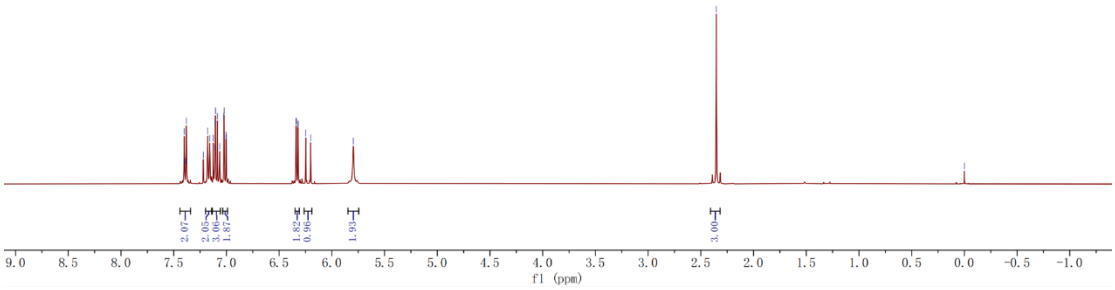
^{11}B NMR (128 MHz, $CDCl_3$)

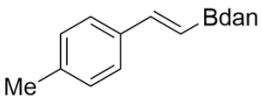




2d

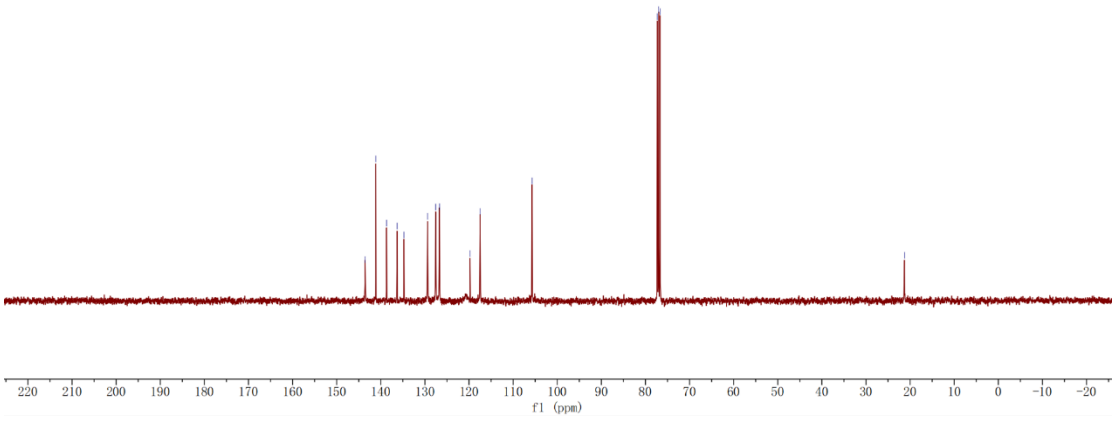
^{1}H NMR (400 MHz, $CDCl_3$)

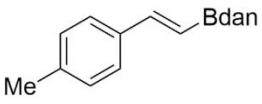




2d

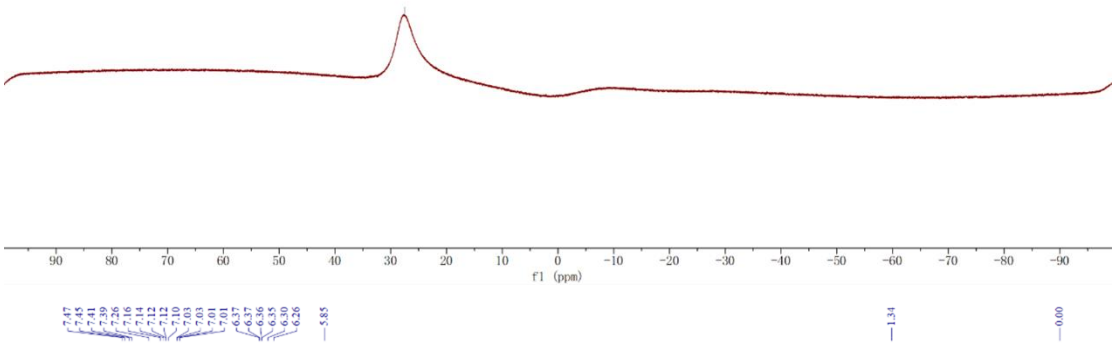
^{13}C NMR (101 MHz, $CDCl_3$)

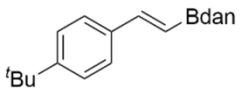




2d

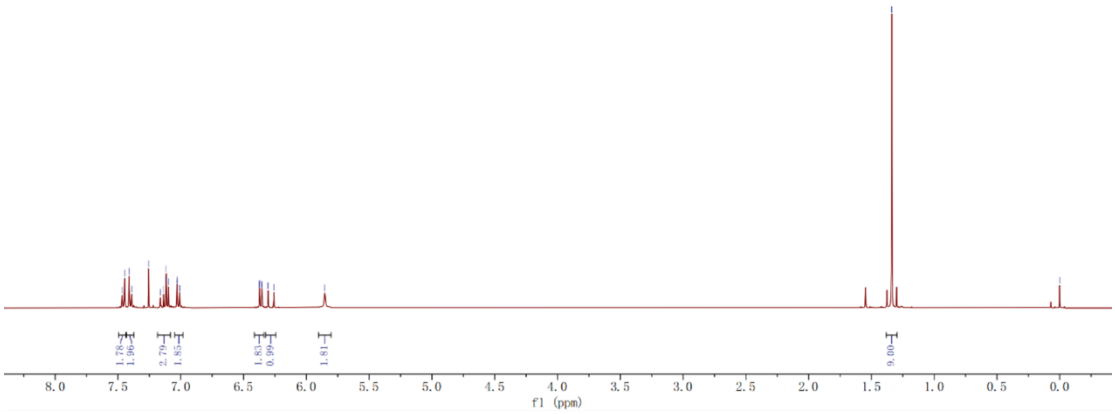
^{11}B NMR (128 MHz, $CDCl_3$)

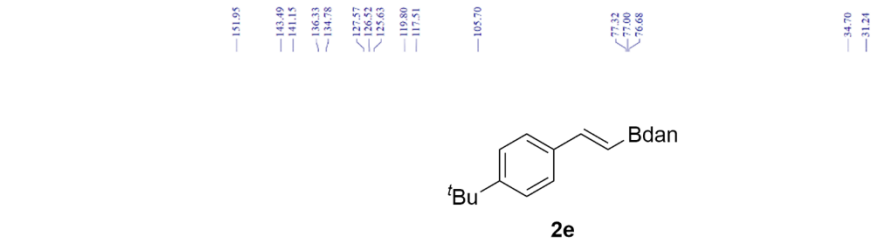




2e

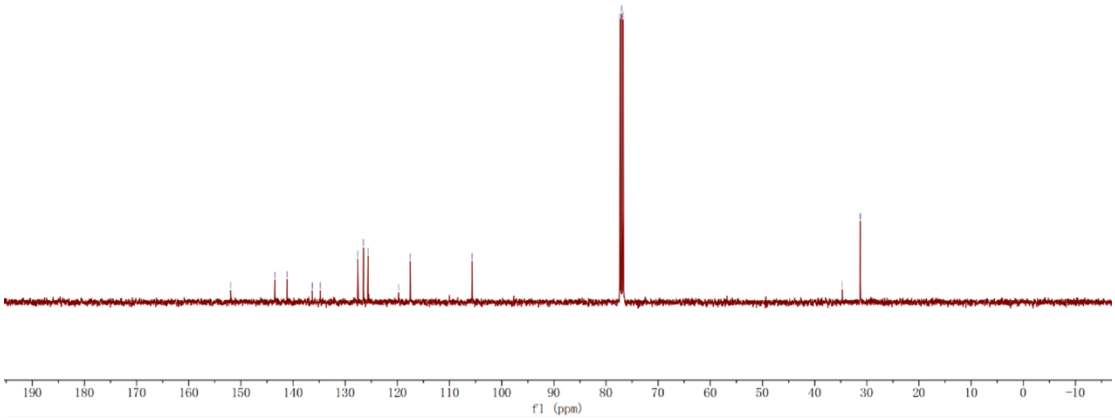
^{1}H NMR (400 MHz, $CDCl_3$)

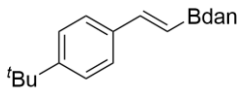




2e

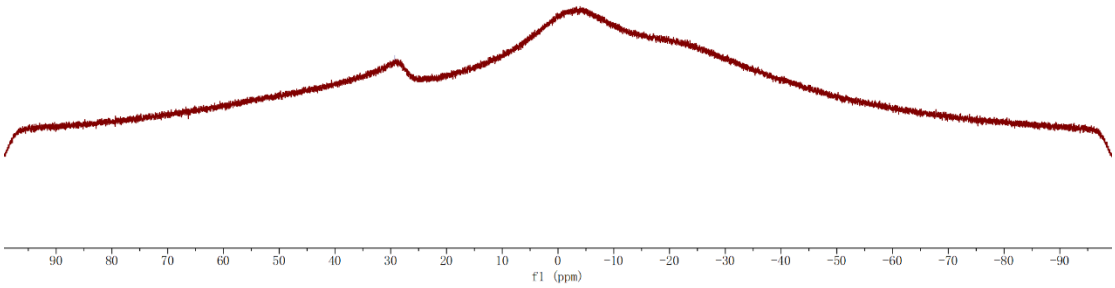
^{13}C NMR (101 MHz, $CDCl_3$)

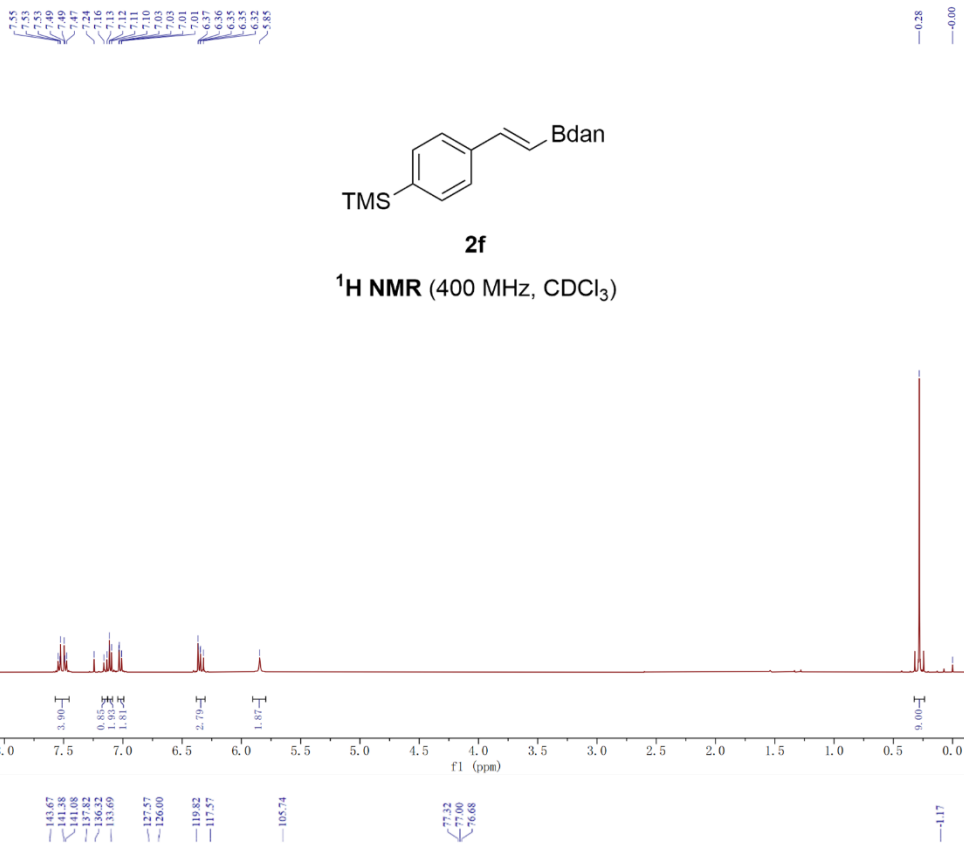




2e

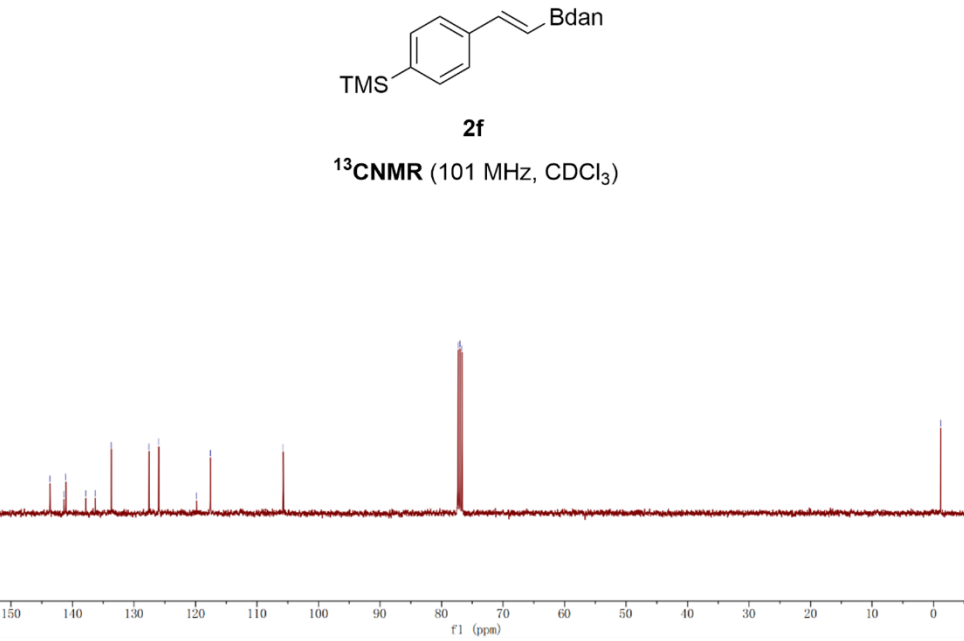
^{11}B NMR (128 MHz, $CDCl_3$)





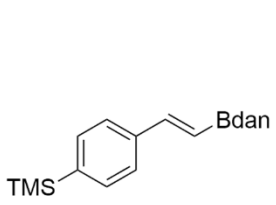
2f

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



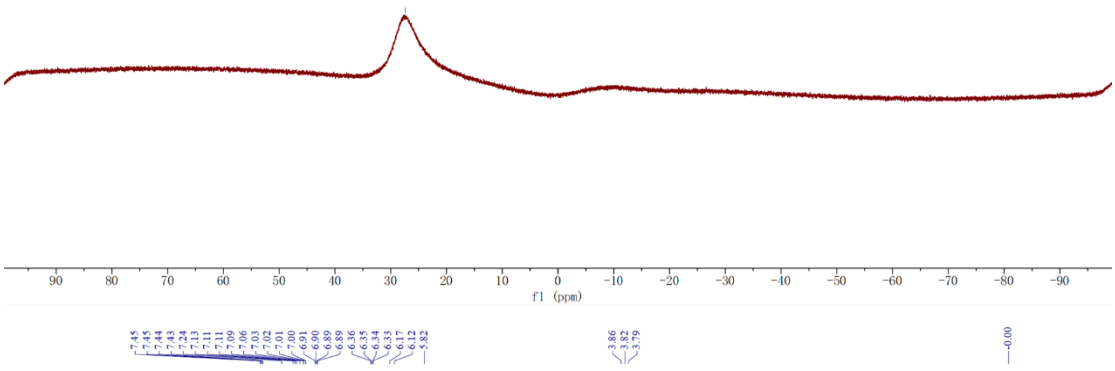
2f

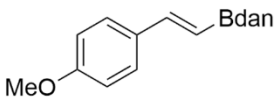
^{13}CNMR (101 MHz, $CDCl_3$)



2f

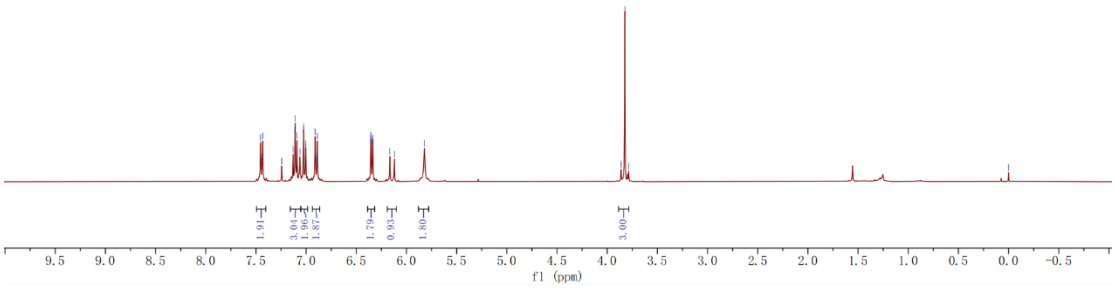
^{11}B NMR (128 MHz, $CDCl_3$)

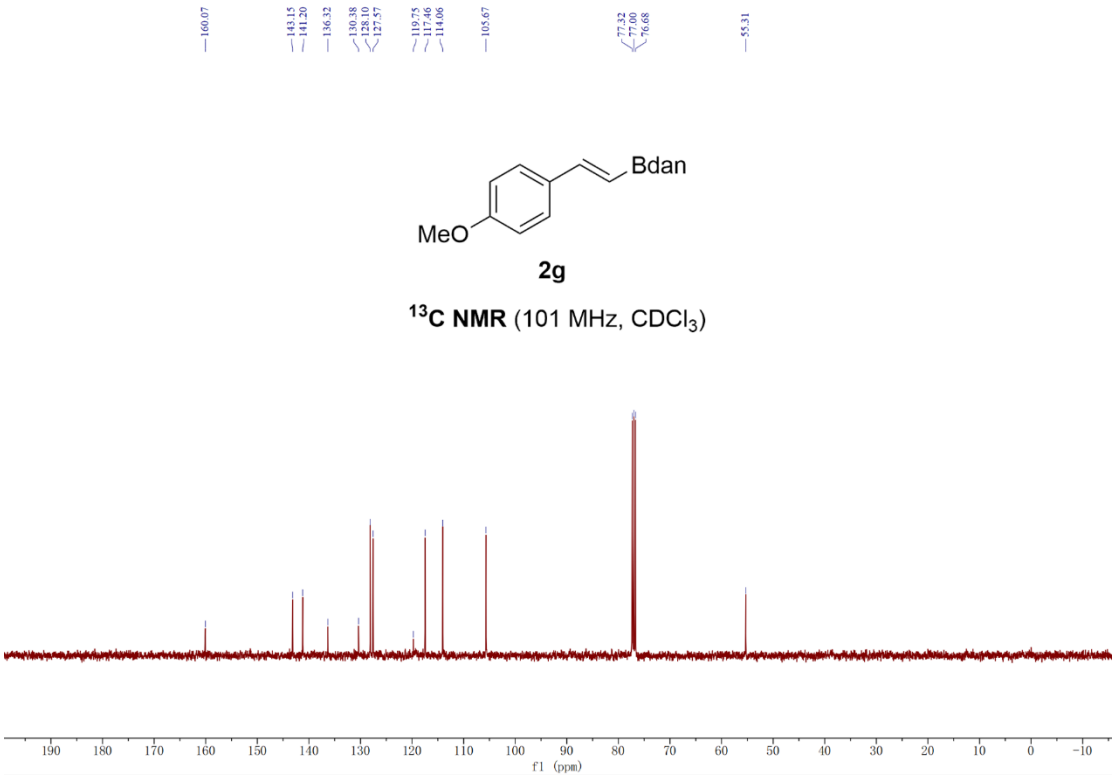




2g

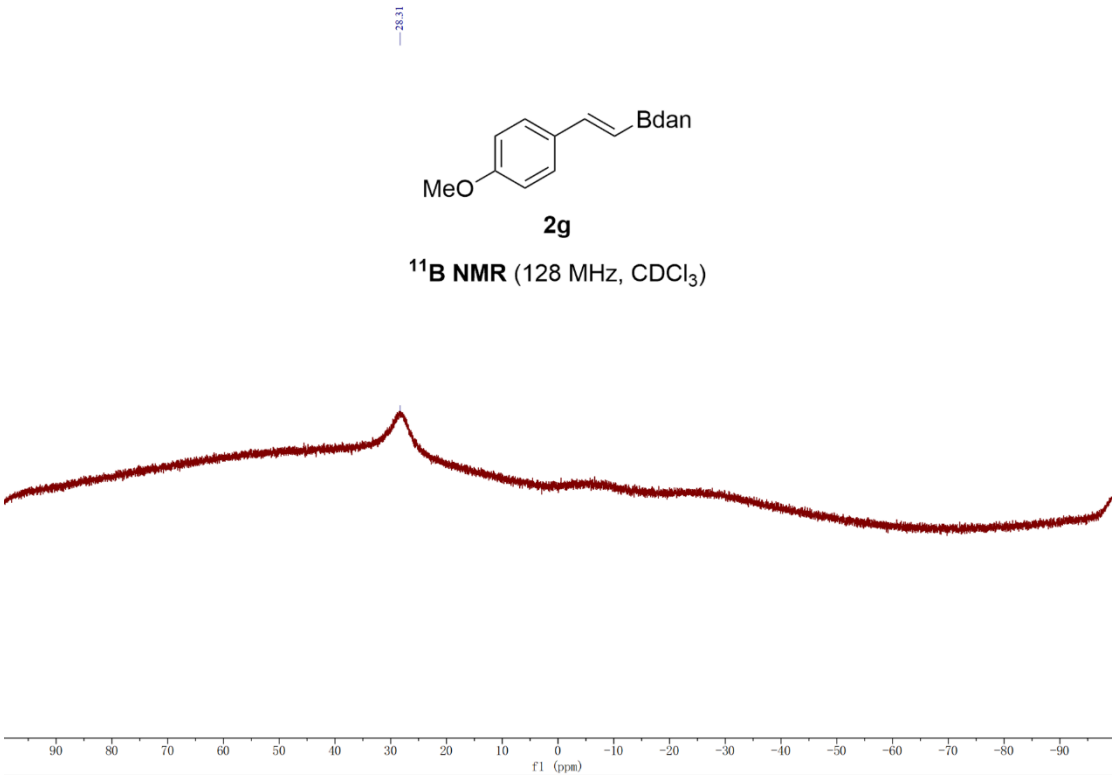
^{1}H NMR (400 MHz, $CDCl_3$)





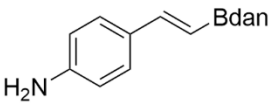
2g

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



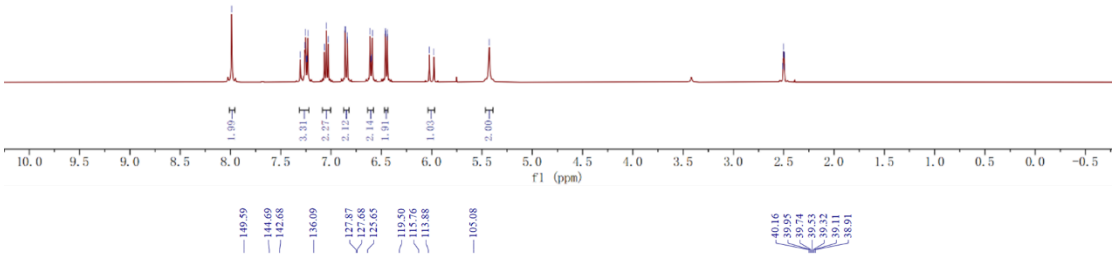
2g

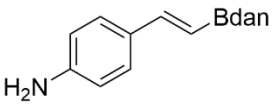
^{11}B NMR (128 MHz, $CDCl_3$)



2h

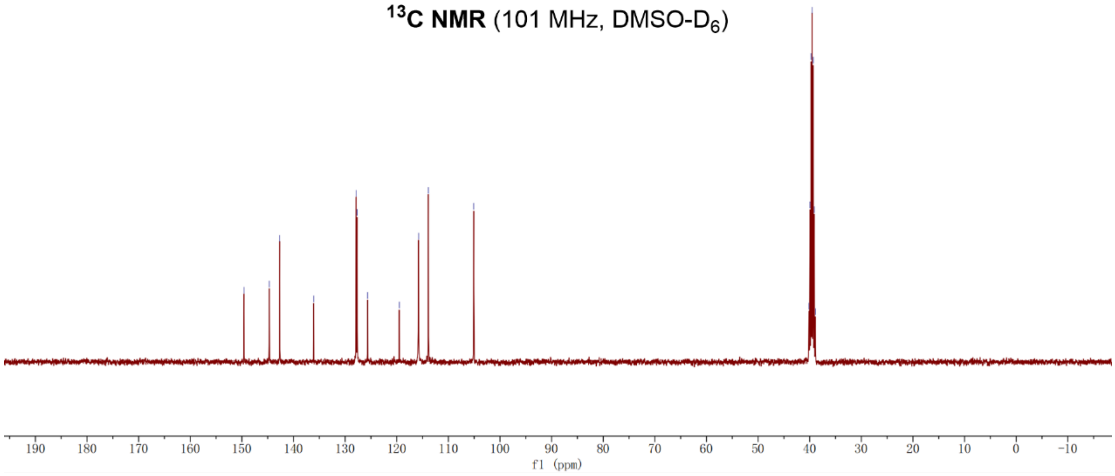
^{1}H NMR (400 MHz, DMSO-D_6)

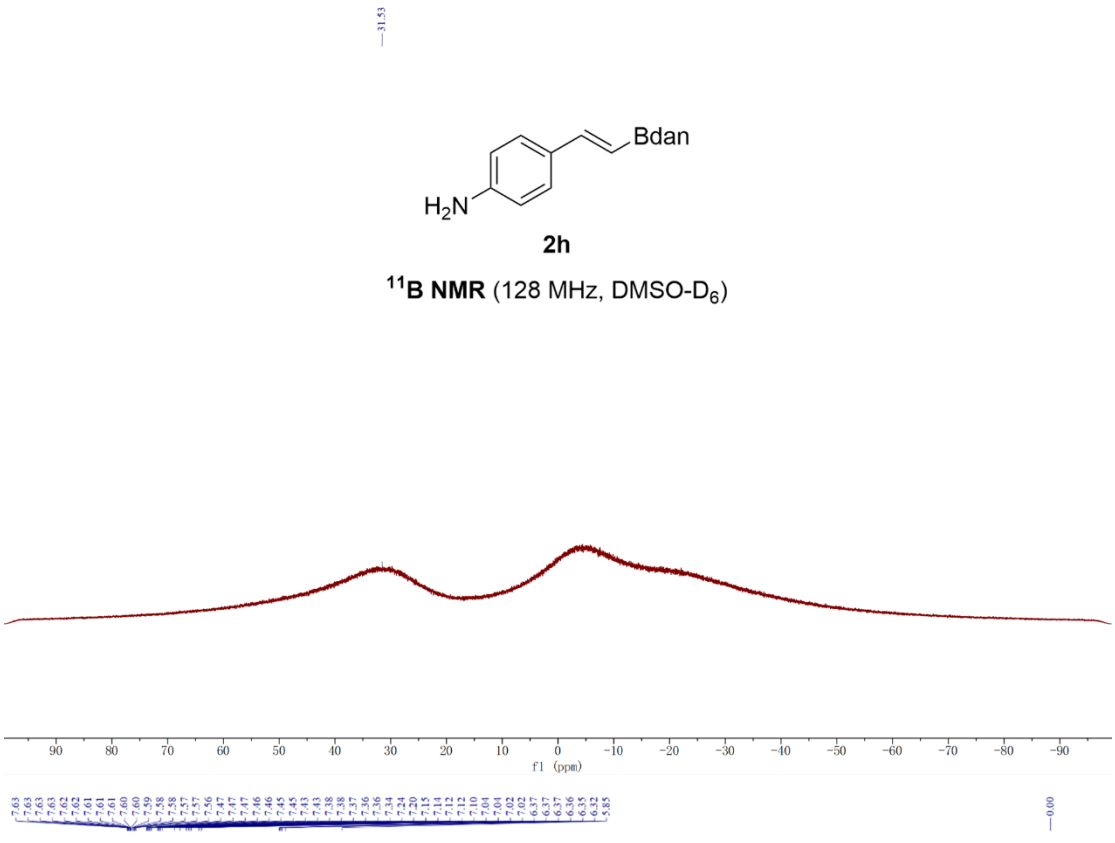




2h

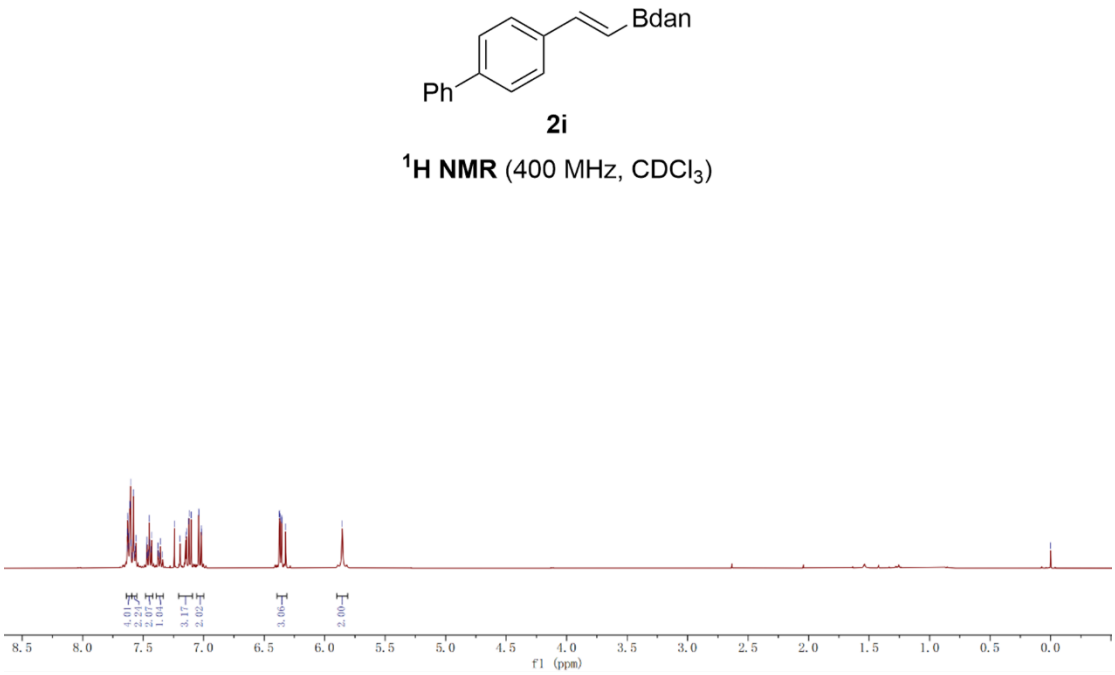
^{13}C NMR (101 MHz, DMSO-D_6)





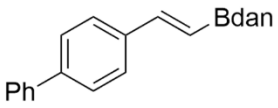
2h

^{11}B NMR (128 MHz, DMSO-D_6)



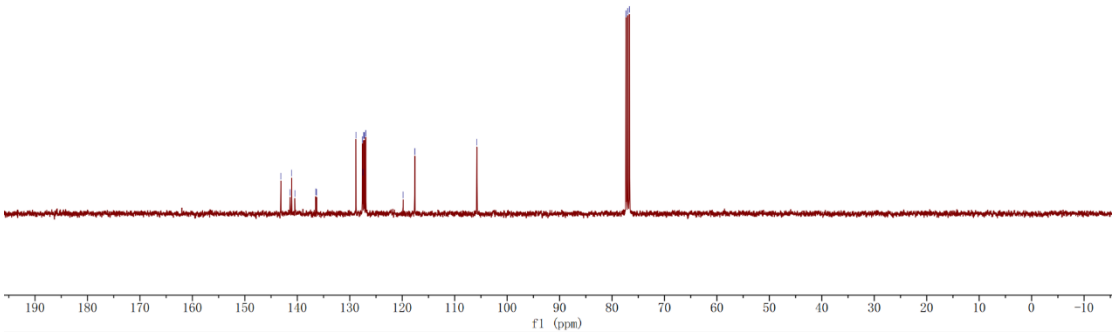
2i

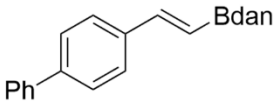
^{1}H NMR (400 MHz, $CDCl_3$)



2i

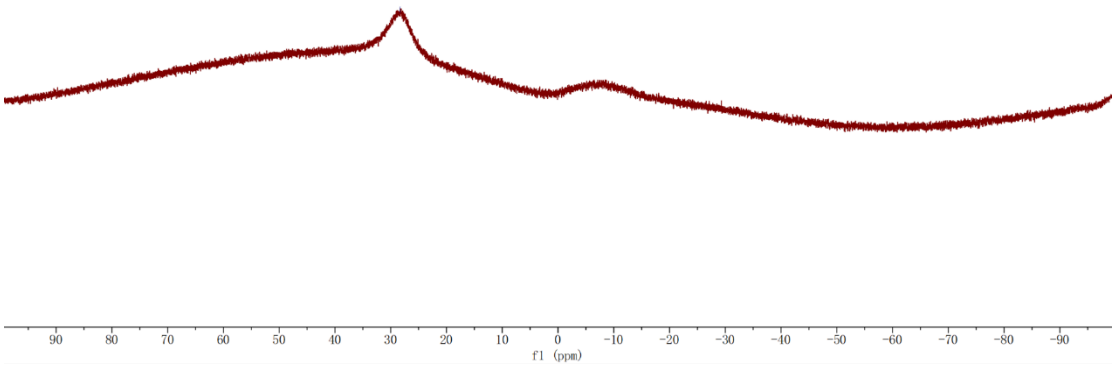
^{13}C NMR (101 MHz, $CDCl_3$)

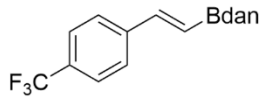




2i

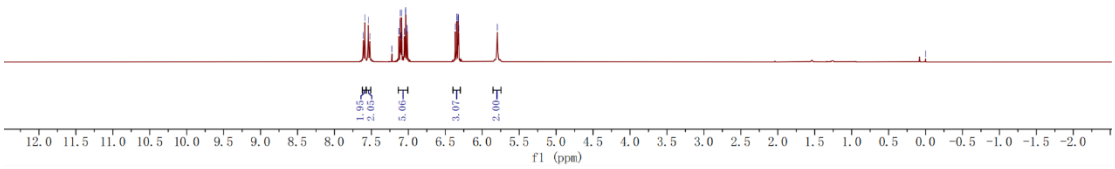
^{11}B NMR (128 MHz, $CDCl_3$)

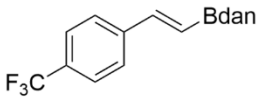




2j

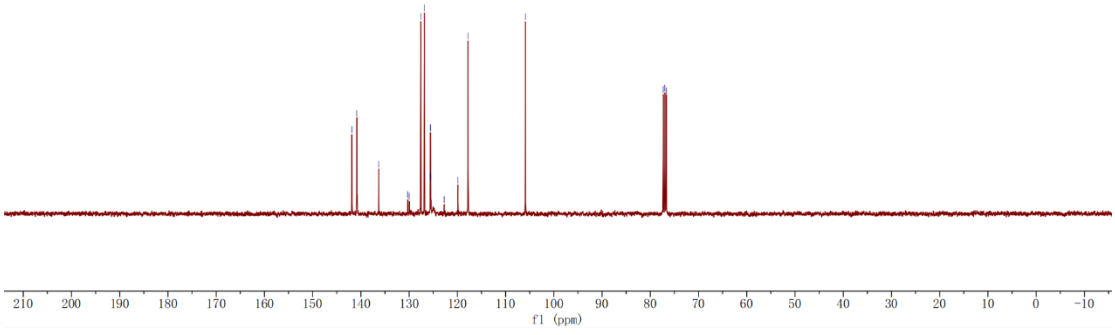
^{1}H NMR (400 MHz, $CDCl_3$)

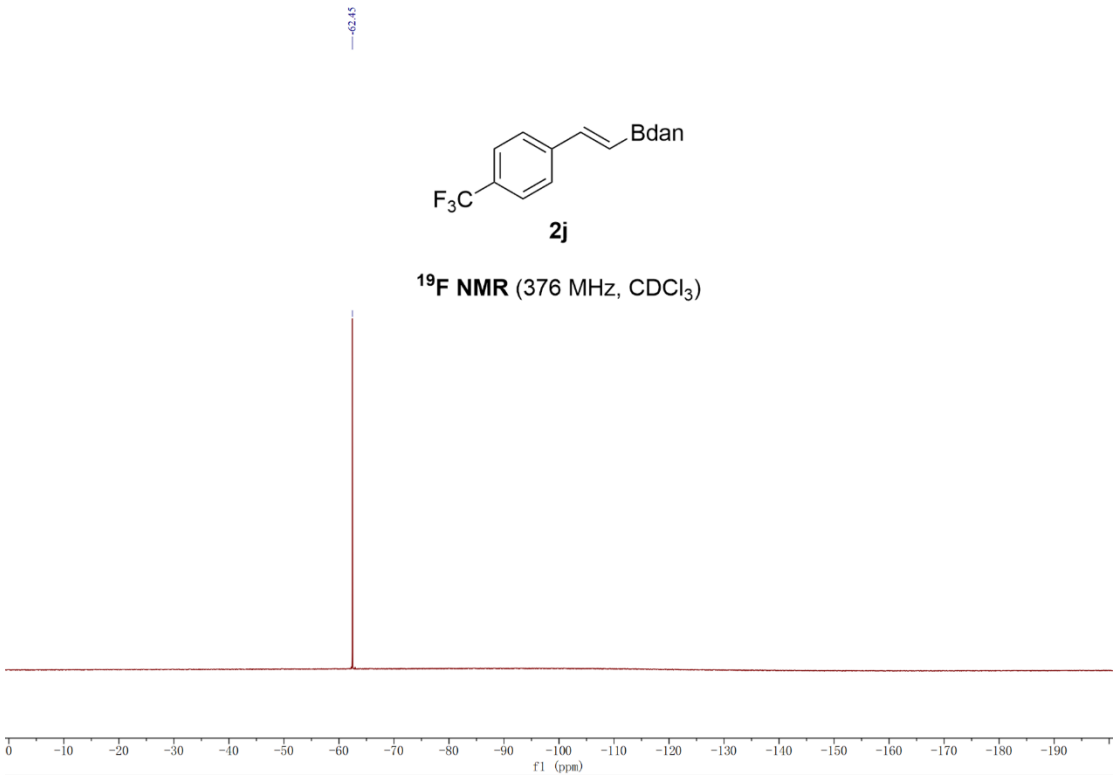




2j

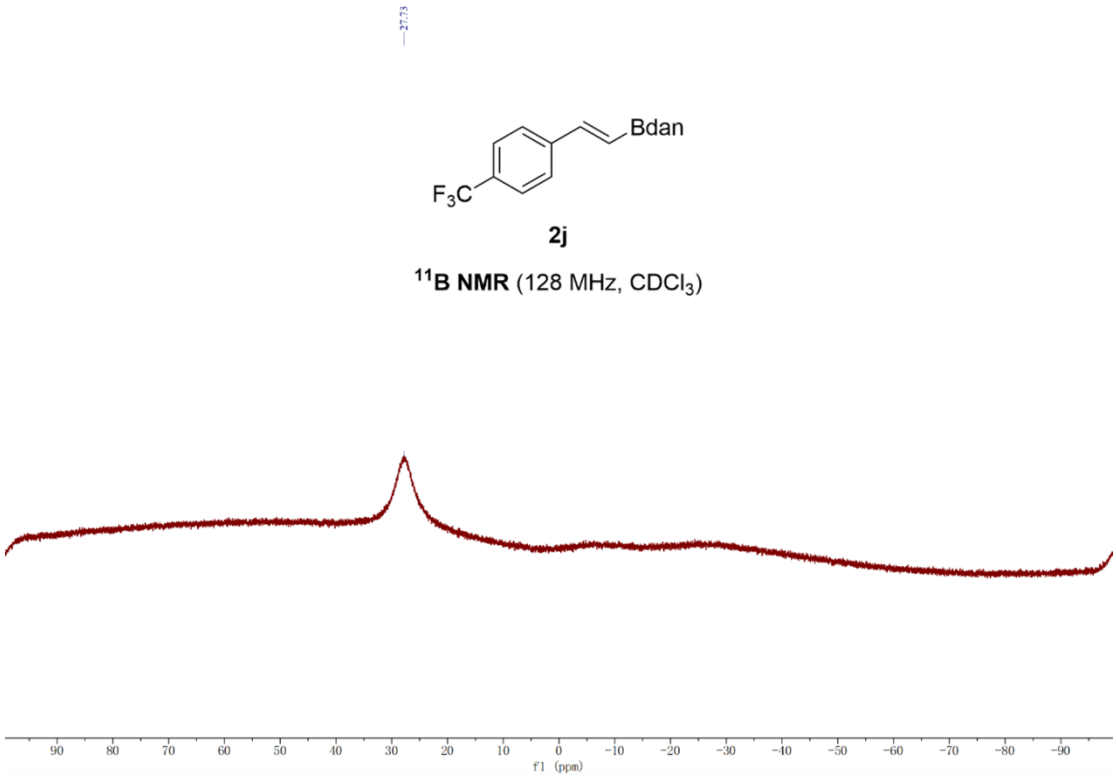
^{13}C NMR (101 MHz, $CDCl_3$)





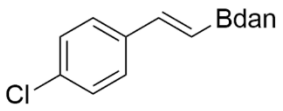
2j

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



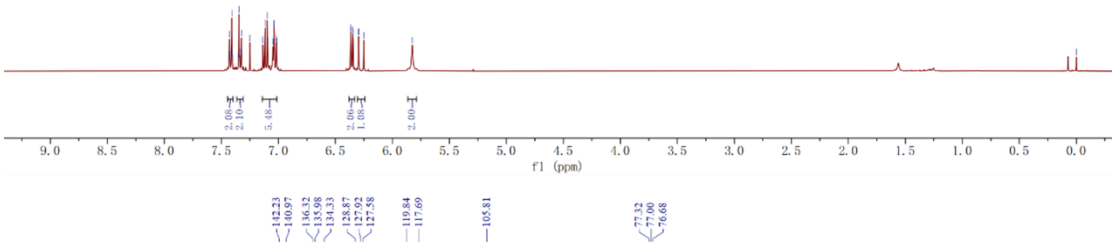
2j

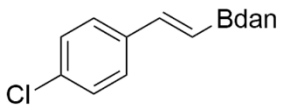
^{11}B NMR (128 MHz, $CDCl_3$)



2k

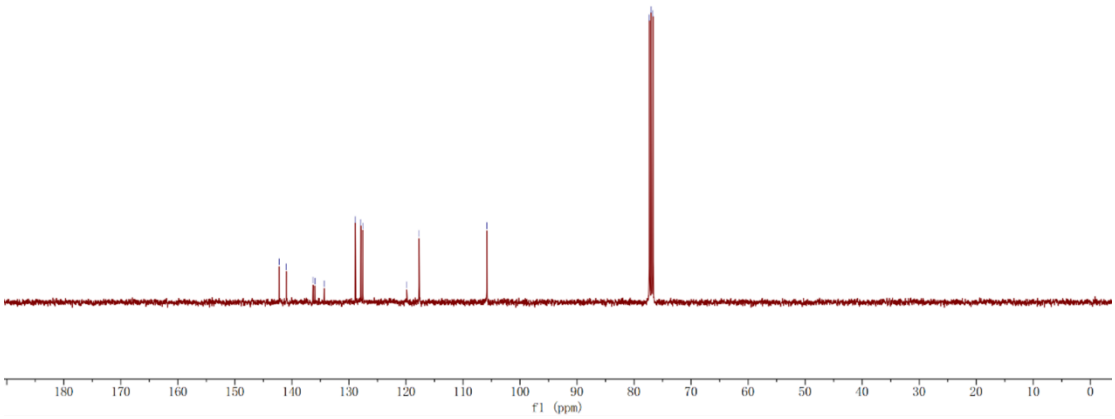
^{1}H NMR (400 MHz, $CDCl_3$)

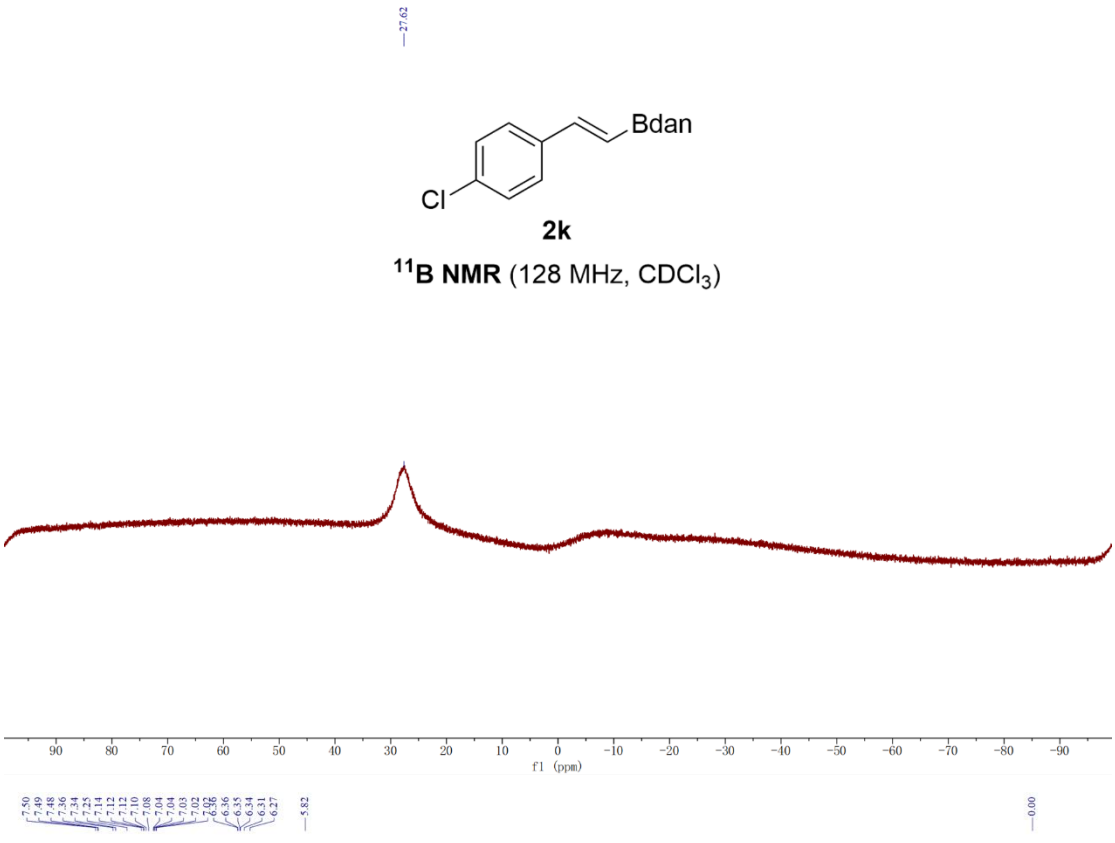




2k

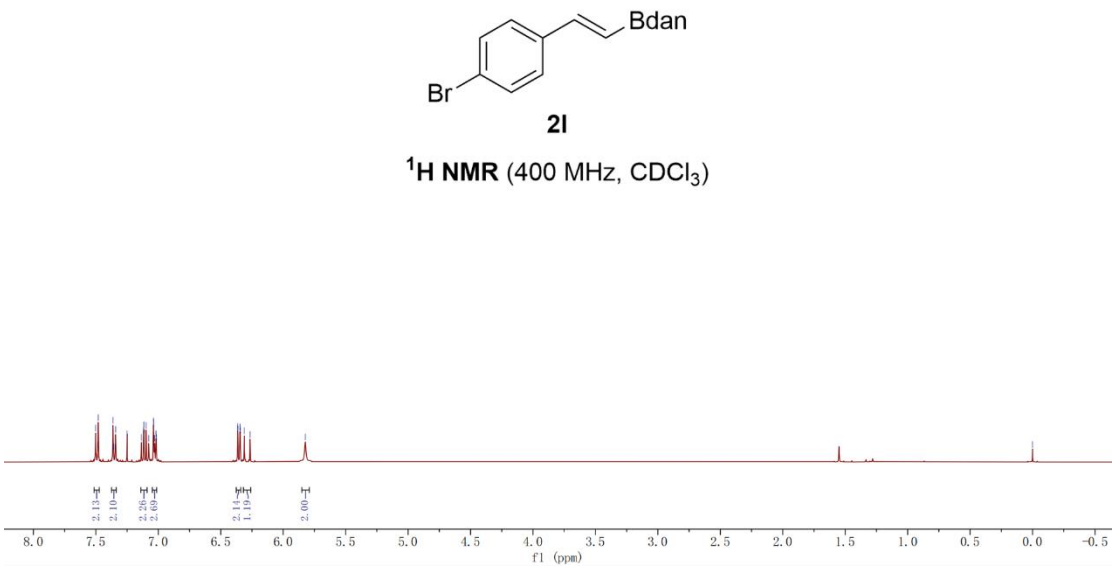
^{13}C NMR (101 MHz, $CDCl_3$)





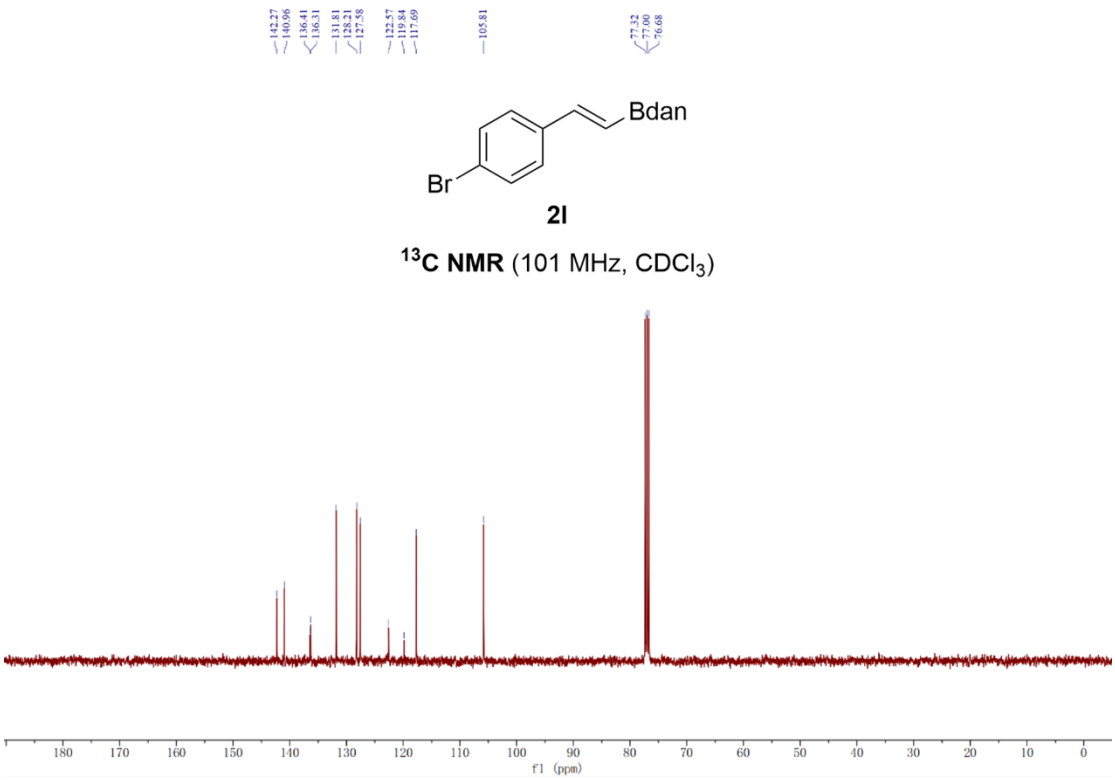
2k

^{11}B NMR (128 MHz, $CDCl_3$)



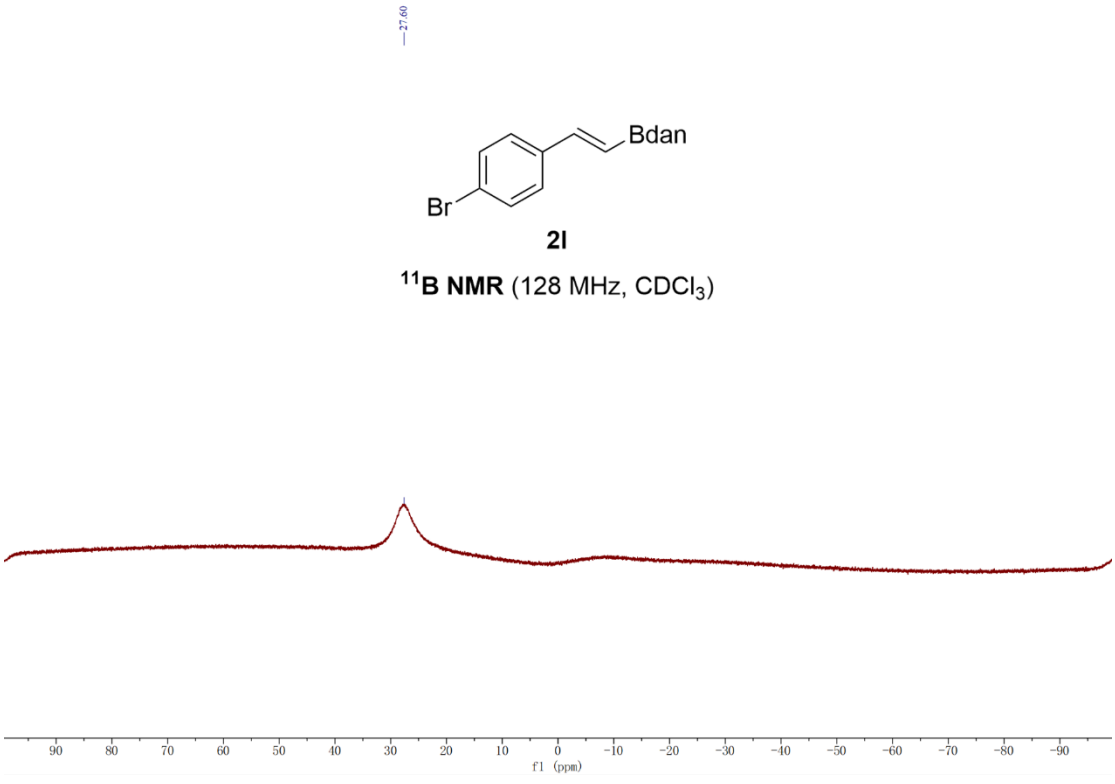
2l

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



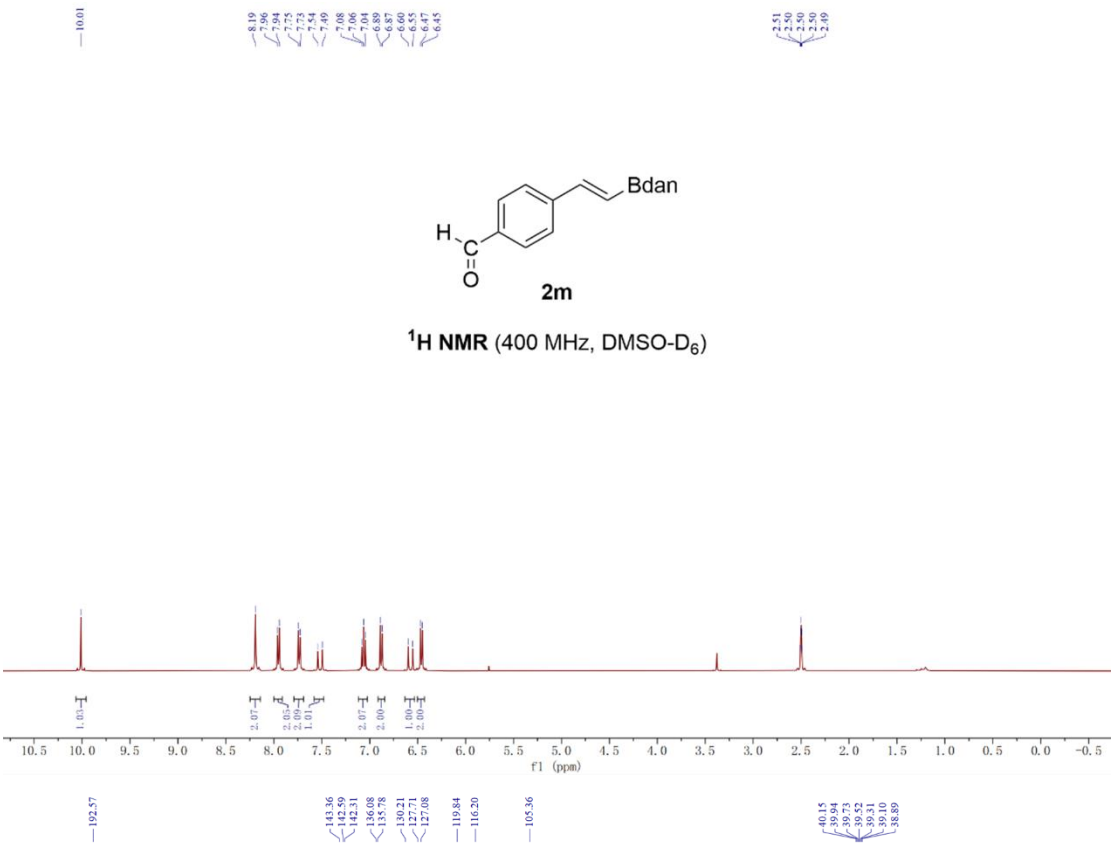
2l

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

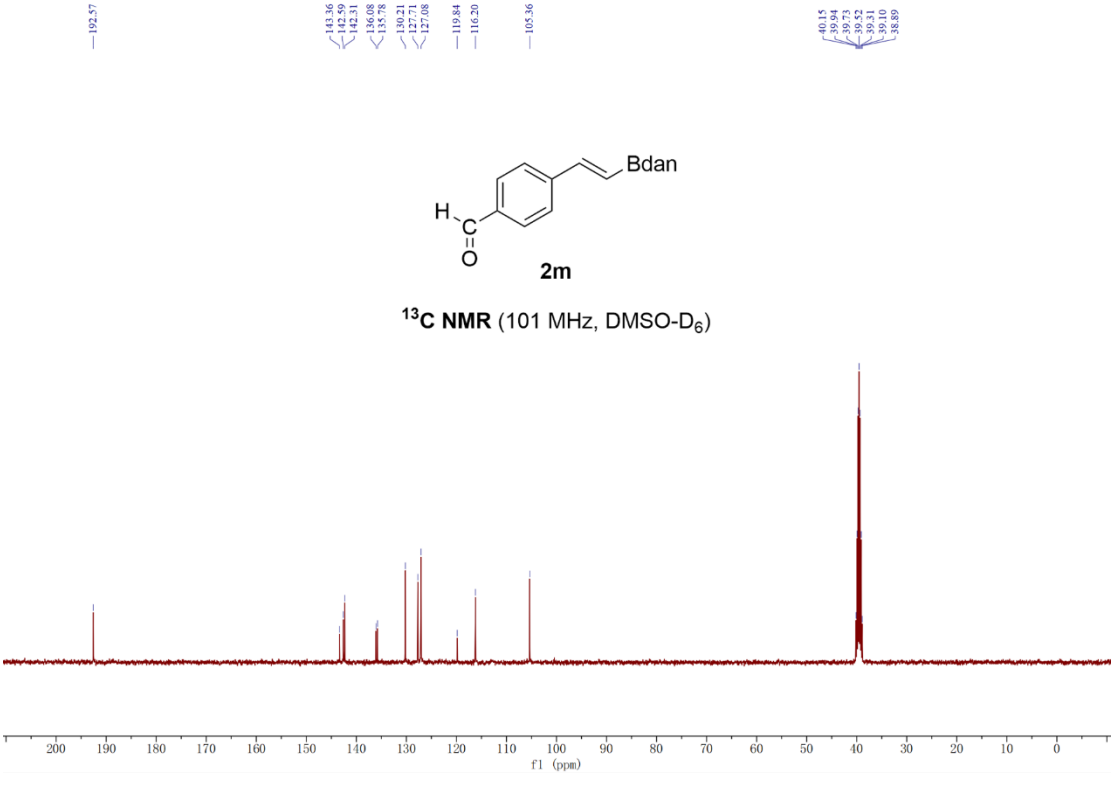


2l

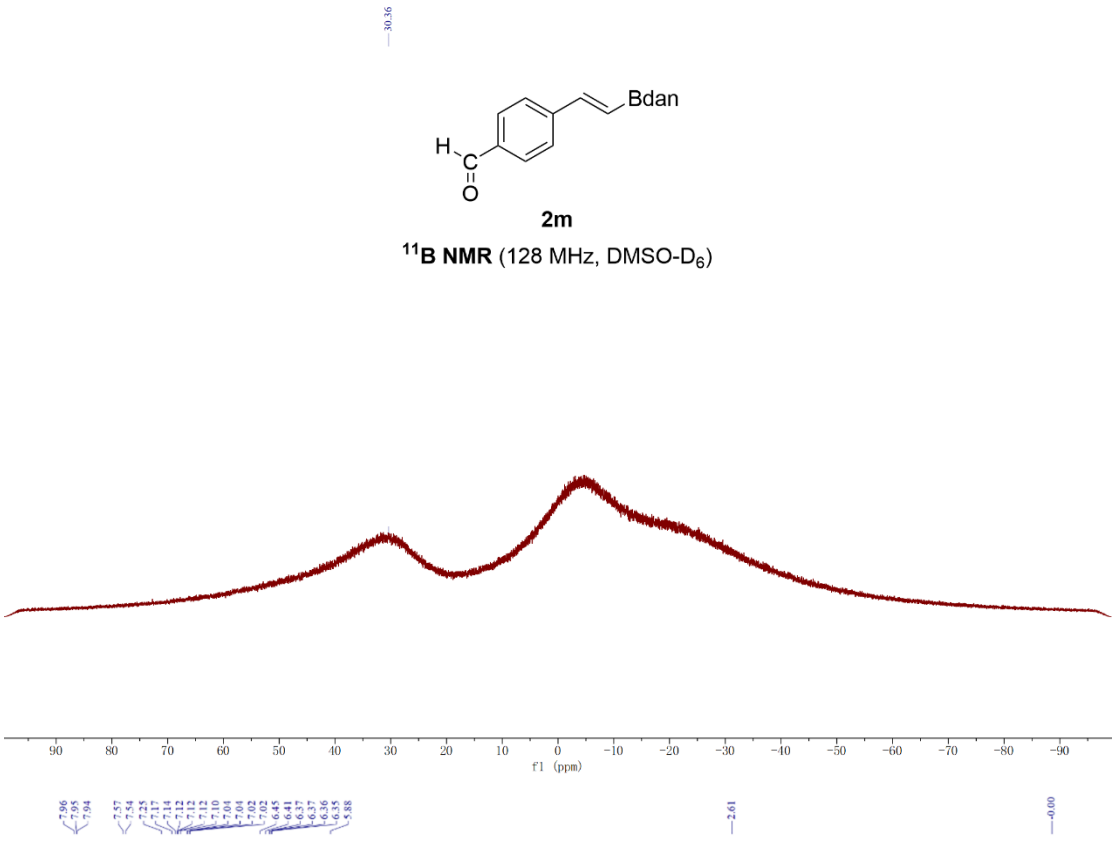
^{11}B NMR (128 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, DMSO-D_6)

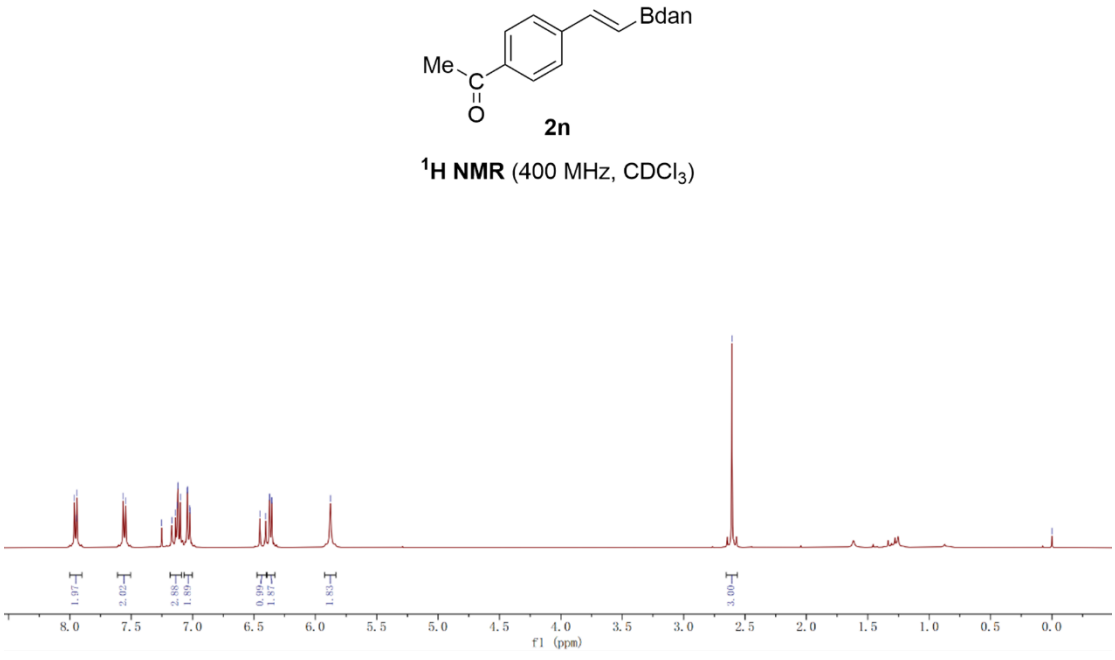


^{13}C NMR (101 MHz, DMSO-D_6)



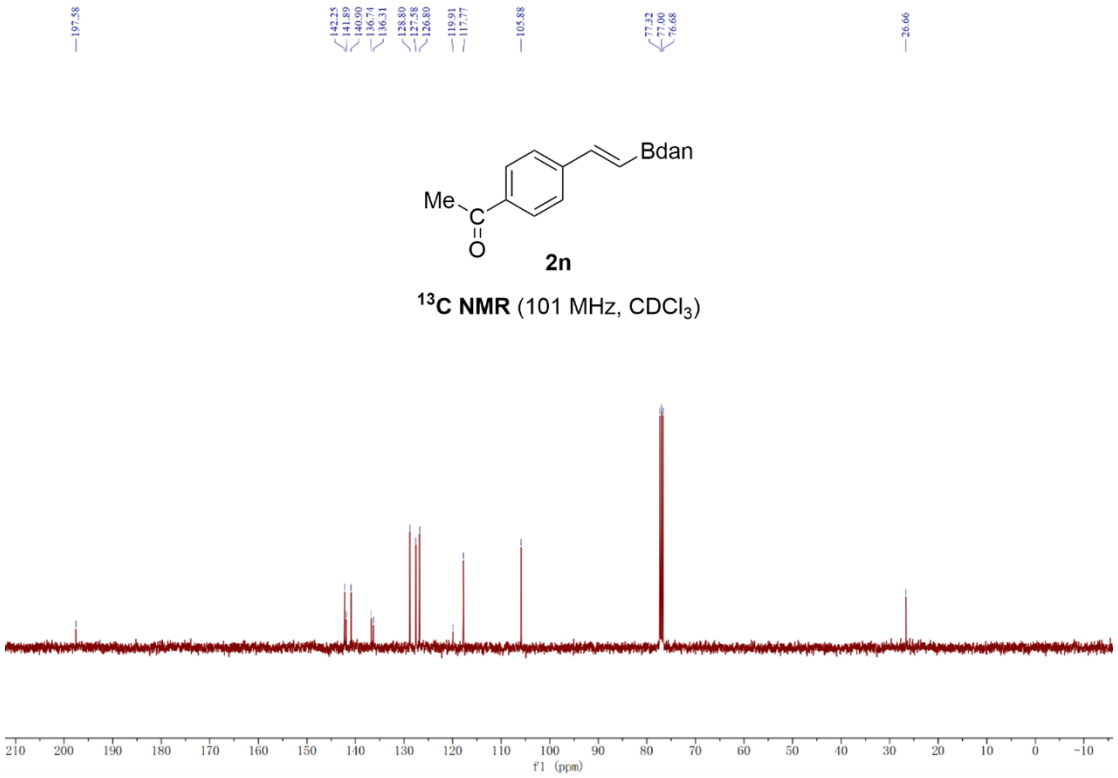
2m

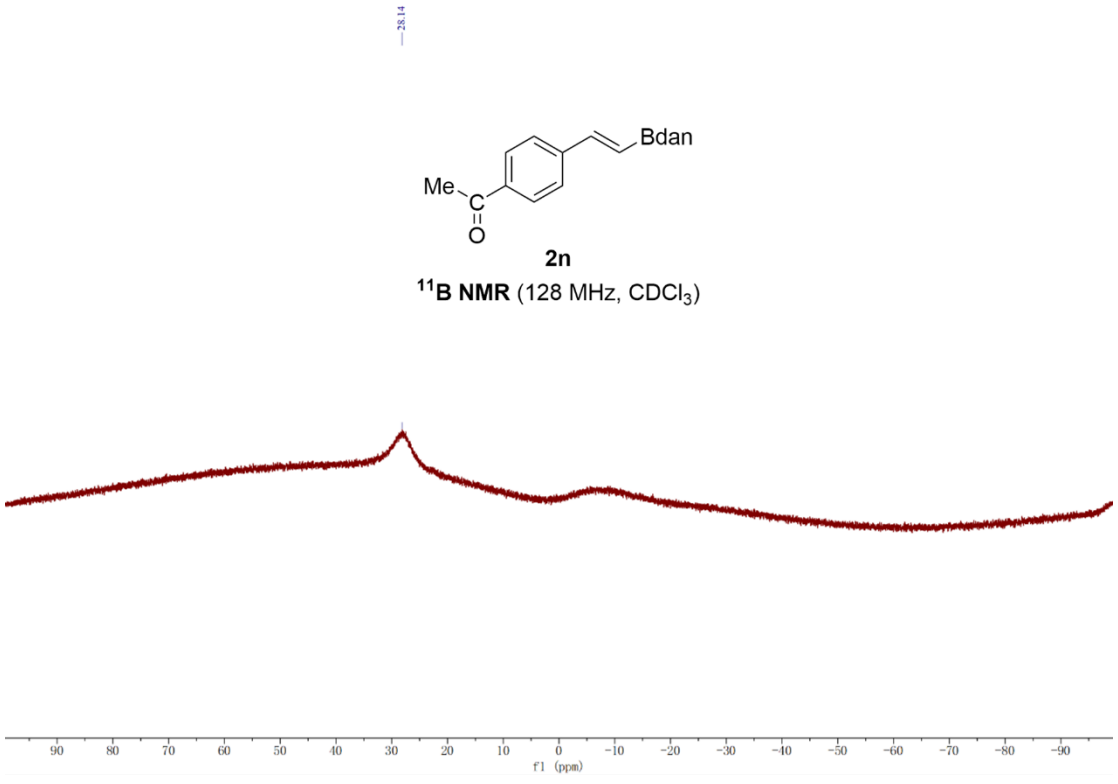
^{11}B NMR (128 MHz, DMSO-D_6)

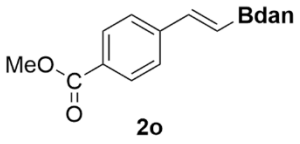


2n

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

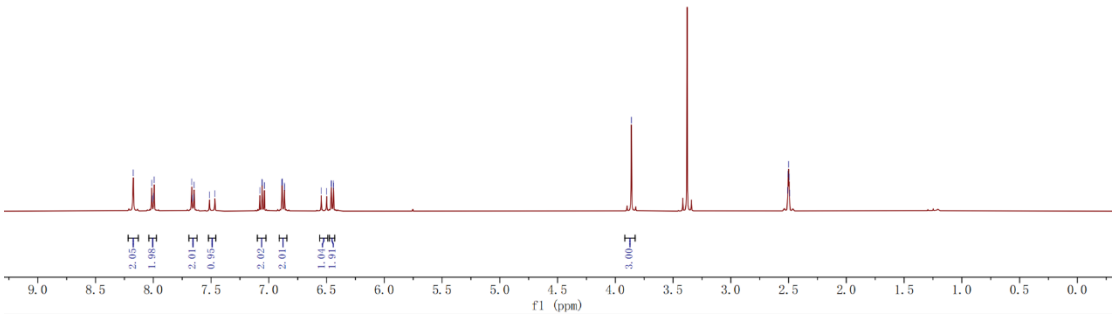

197.58
142.25
141.89
140.90
136.74
136.31
128.80
127.58
126.80
119.91
117.77
105.88
77.32
77.00
76.68
26.66
Bdan
Me
C
O
2n
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

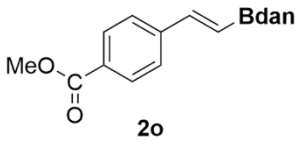

28.14
Bdan
Me
C
O
2n
11B NMR (128 MHz, CDCl3)
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)



2o

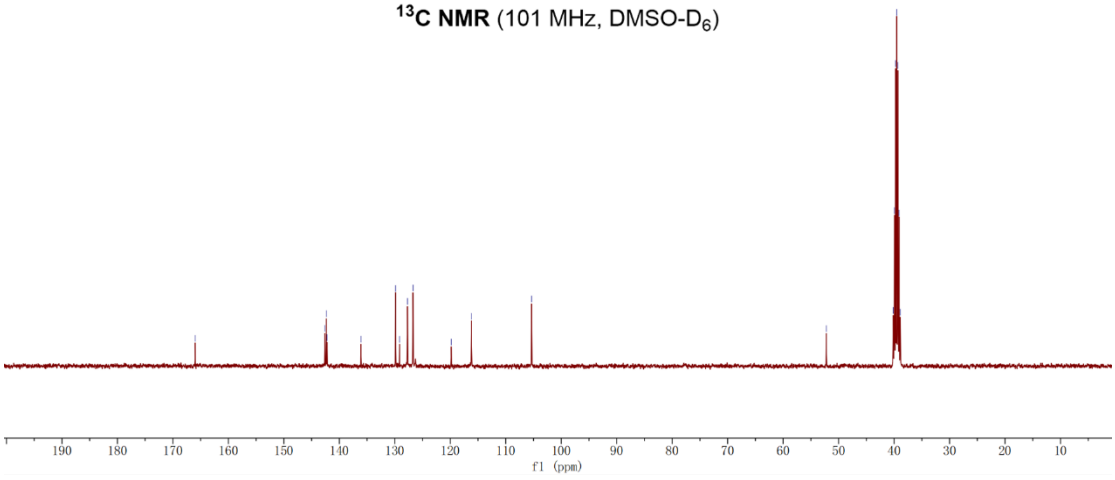
^{1}H NMR (400 MHz, DMSO-D_6)

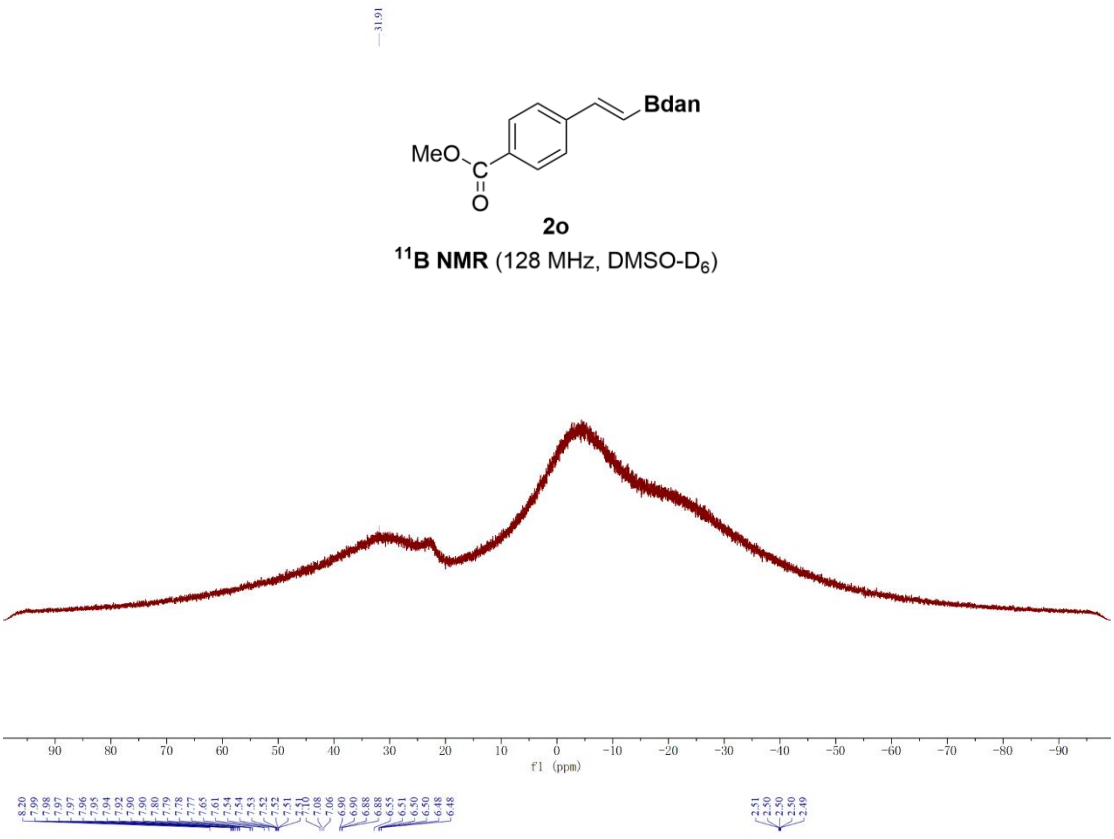




2o

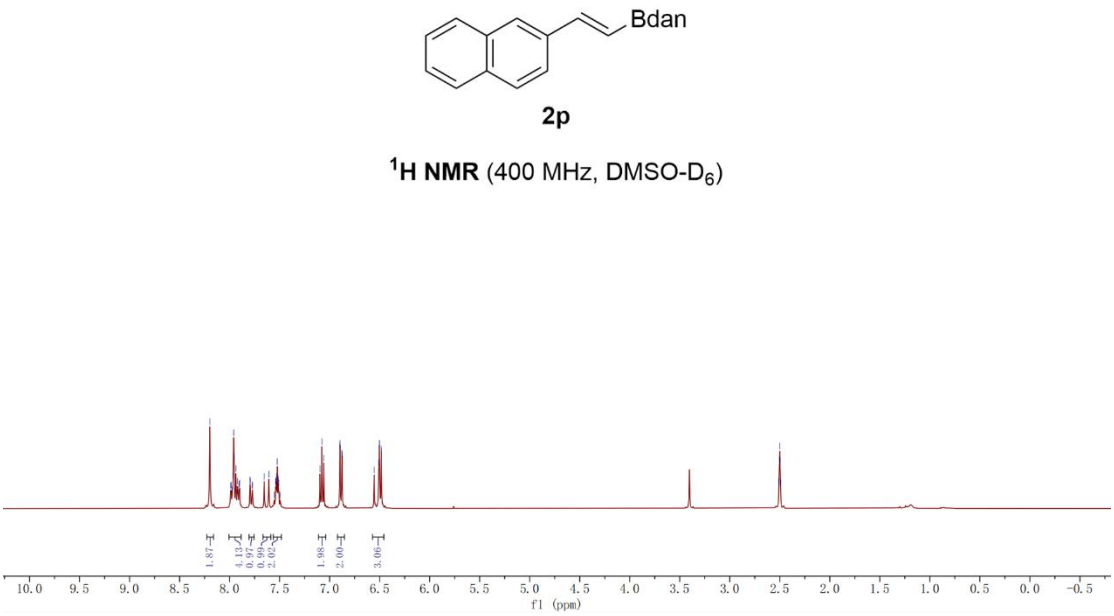
^{13}C NMR (101 MHz, DMSO-D_6)





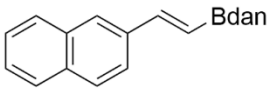
2o

^{11}B NMR (128 MHz, DMSO-D_6)



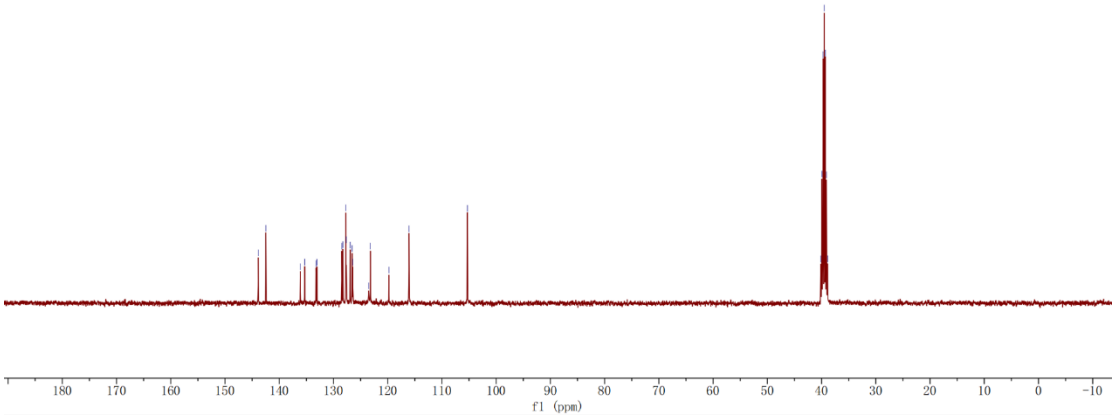
2p

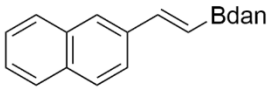
^{1}H NMR (400 MHz, DMSO-D_6)



2p

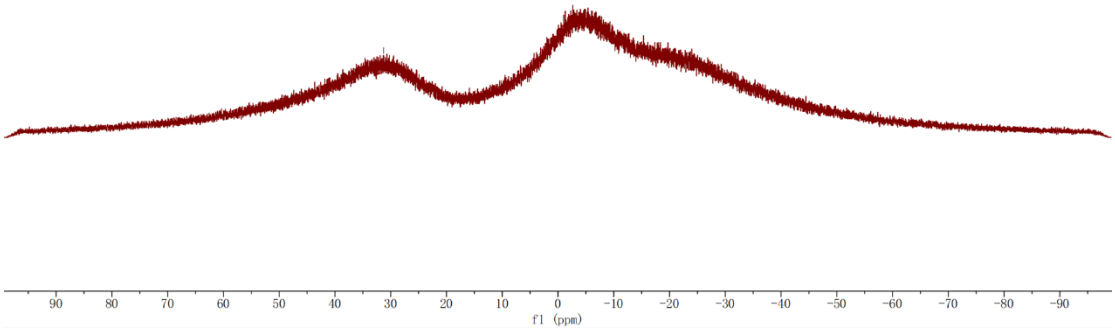
^{13}C NMR (101 MHz, DMSO-D_6)

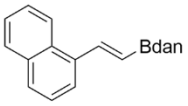




2p

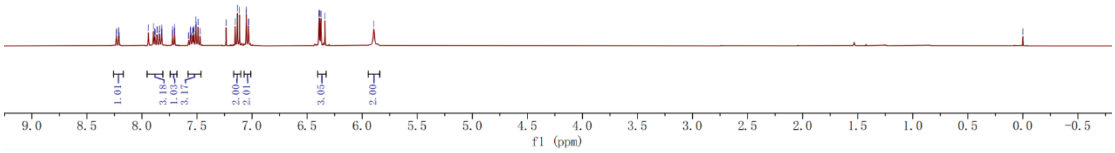
^{11}B NMR (128 MHz, DMSO-D_6)

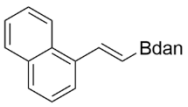




2q

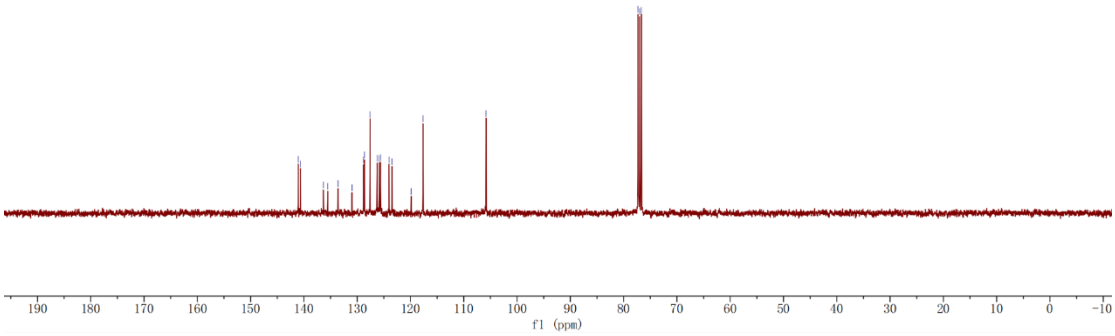
^{1}H NMR (400 MHz, $CDCl_3$)

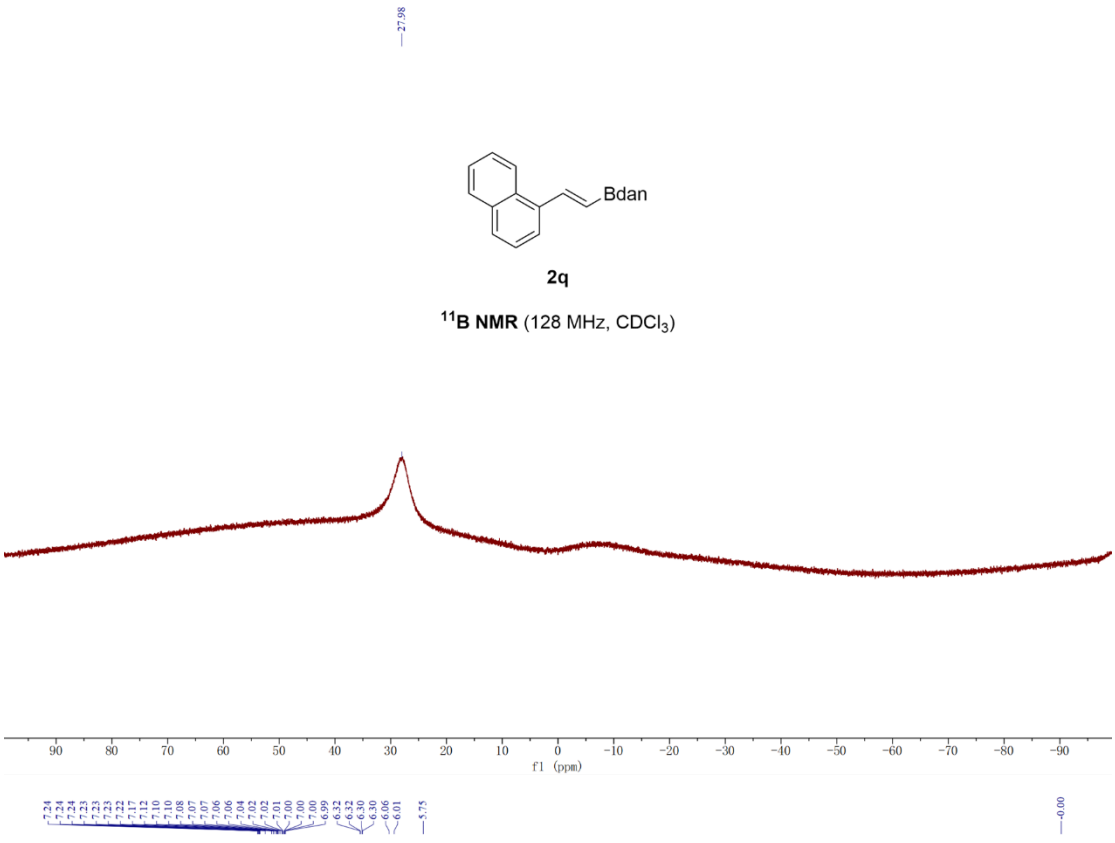




2q

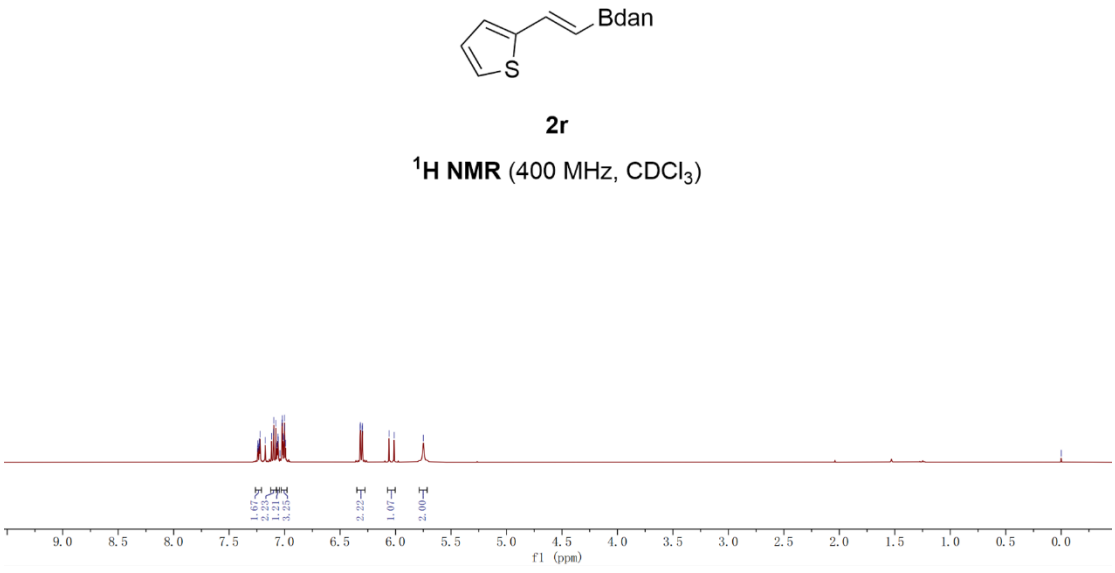
^{13}C NMR (101 MHz, $CDCl_3$)





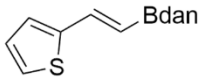
2q

^{11}B NMR (128 MHz, $CDCl_3$)



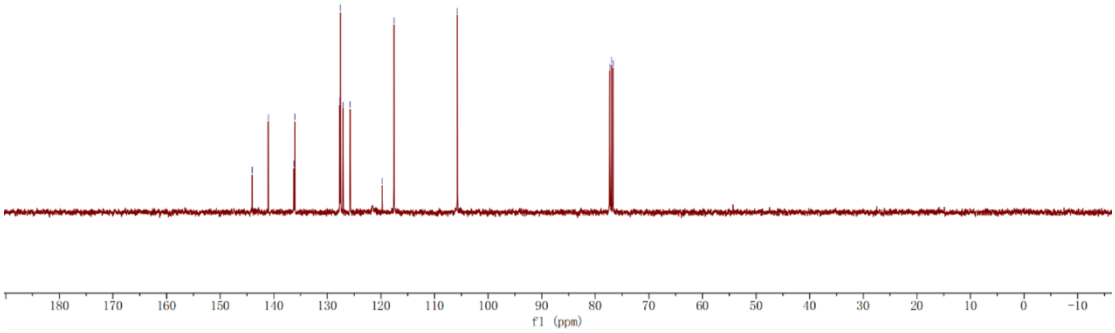
2r

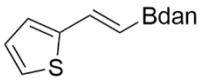
^{1}H NMR (400 MHz, $CDCl_3$)



2r

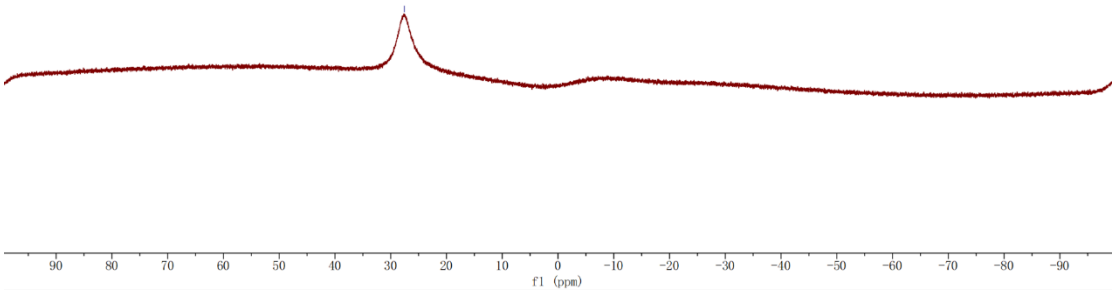
^{13}C NMR (101 MHz, $CDCl_3$)

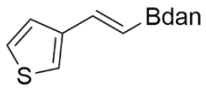




2r

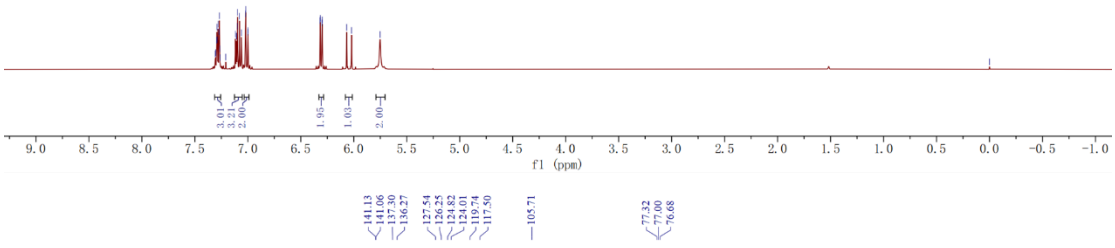
^{11}B NMR (128 MHz, $CDCl_3$)

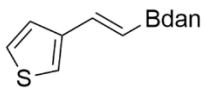




2s

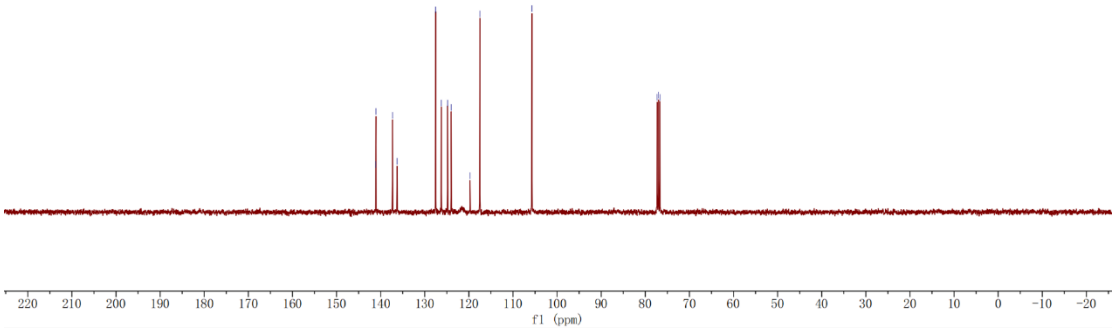
^{1}H NMR (400 MHz, $CDCl_3$)

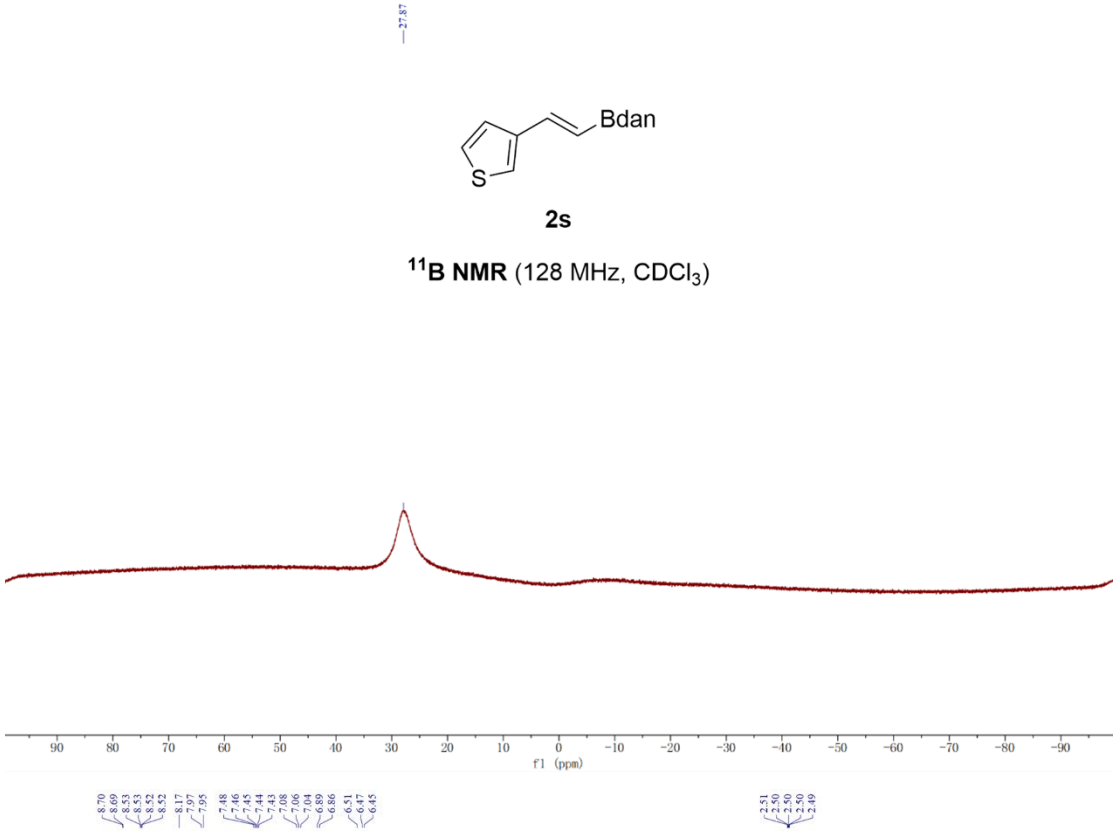




2s

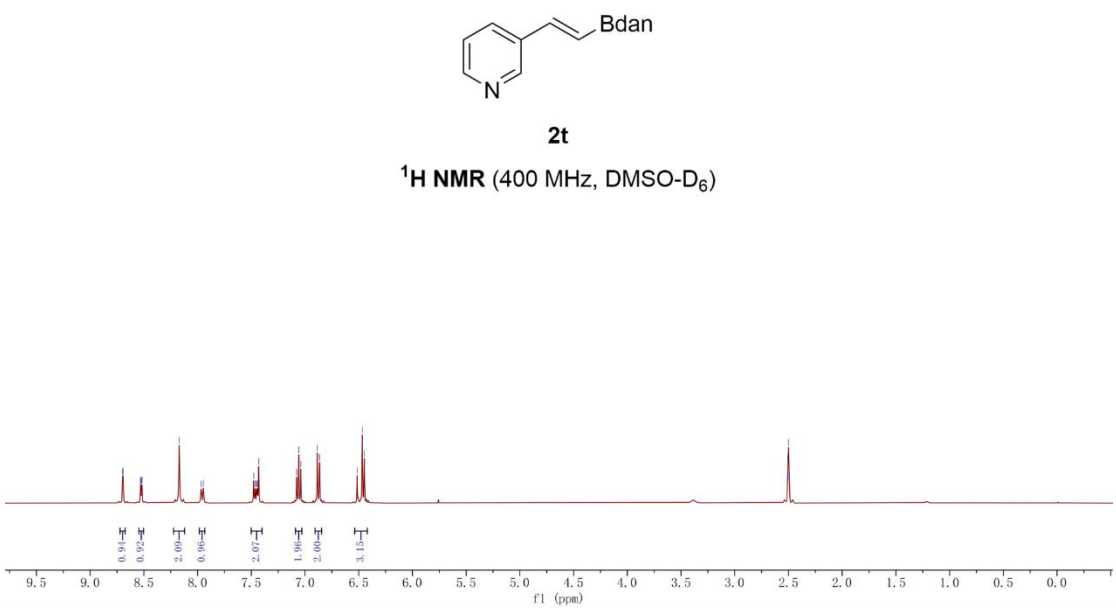
^{13}C NMR (101 MHz, $CDCl_3$)





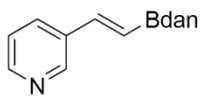
2s

^{11}B NMR (128 MHz, $CDCl_3$)



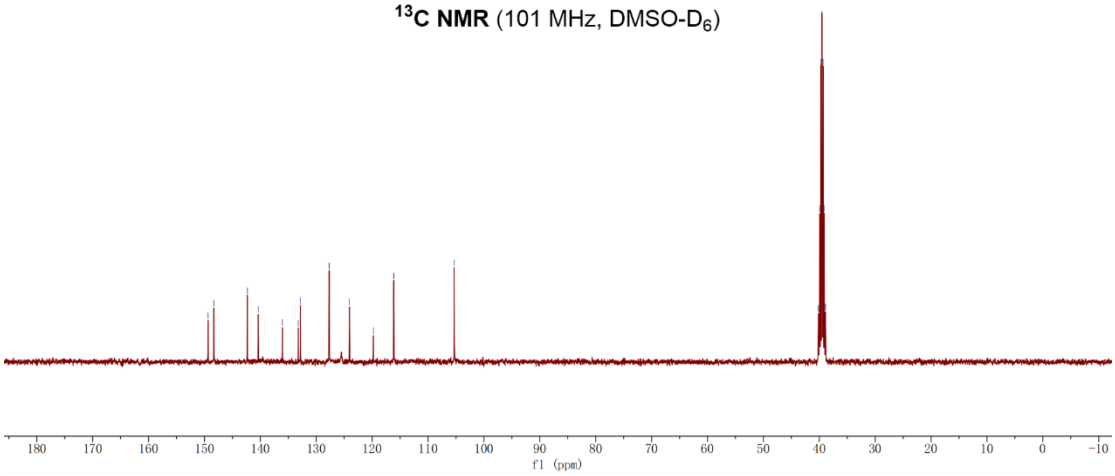
2t

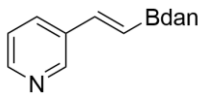
^{1}H NMR (400 MHz, DMSO-D_6)



2t

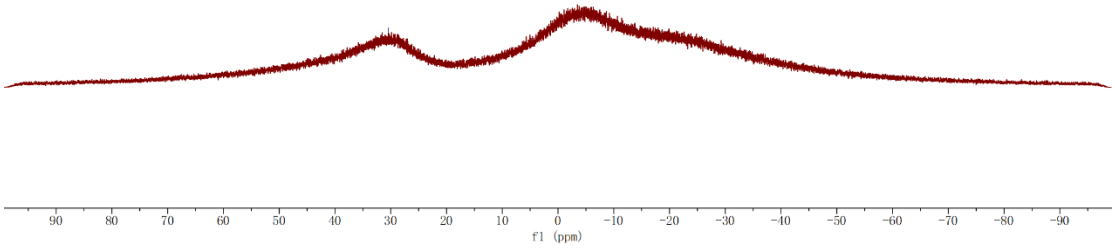
^{13}C NMR (101 MHz, DMSO-D_6)

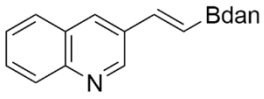




2t

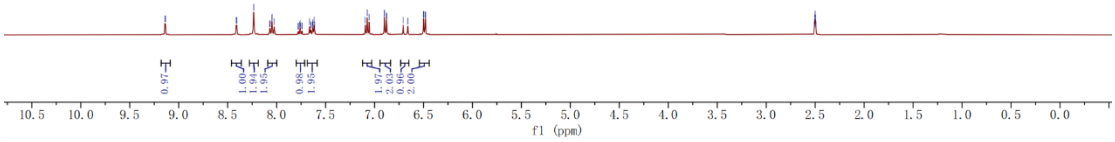
^{11}B NMR (128 MHz, DMSO-D_6)

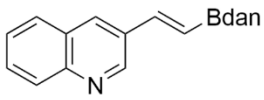




2u

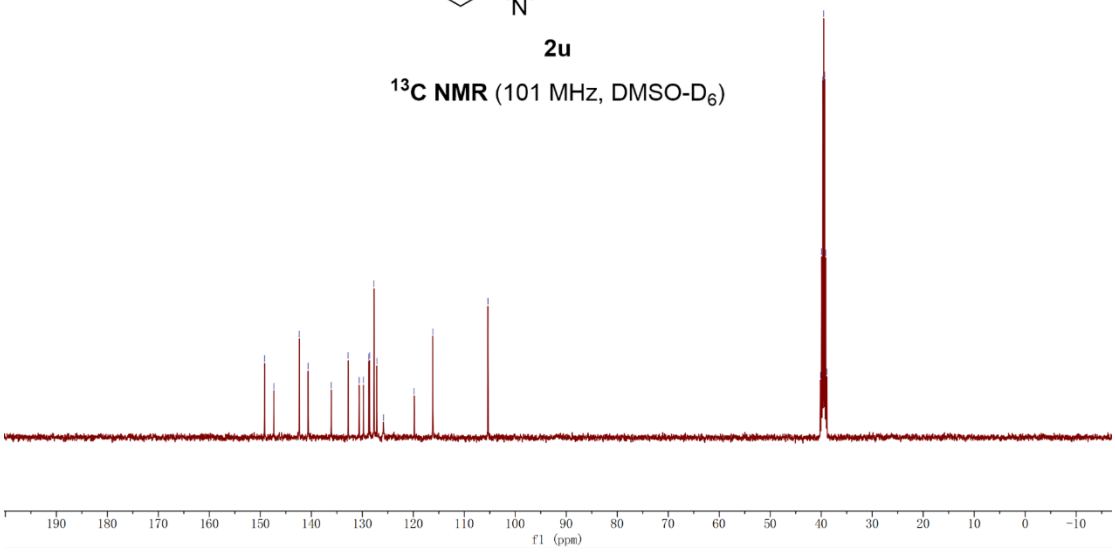
^{1}H NMR (400 MHz, DMSO-D_6)

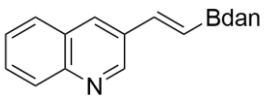




2u

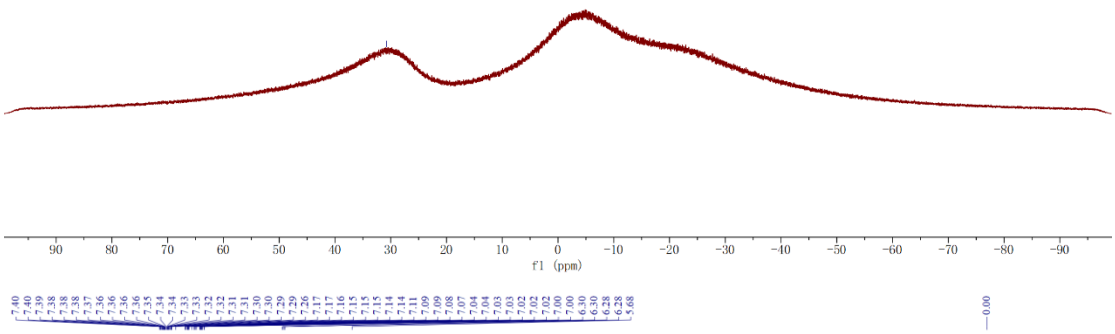
^{13}C NMR (101 MHz, DMSO-D_6)

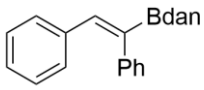




2u

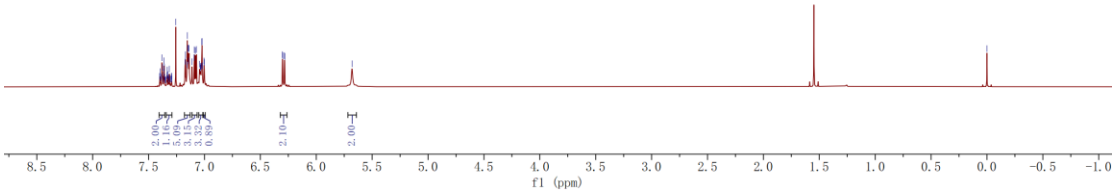
^{11}B NMR (128 MHz, DMSO-D_6)

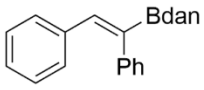




2v

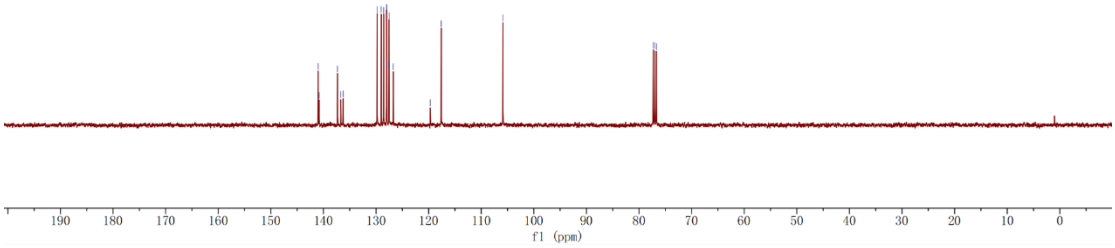
^{1}H NMR (400 MHz, $CDCl_3$)

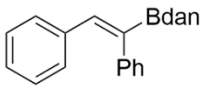




2v

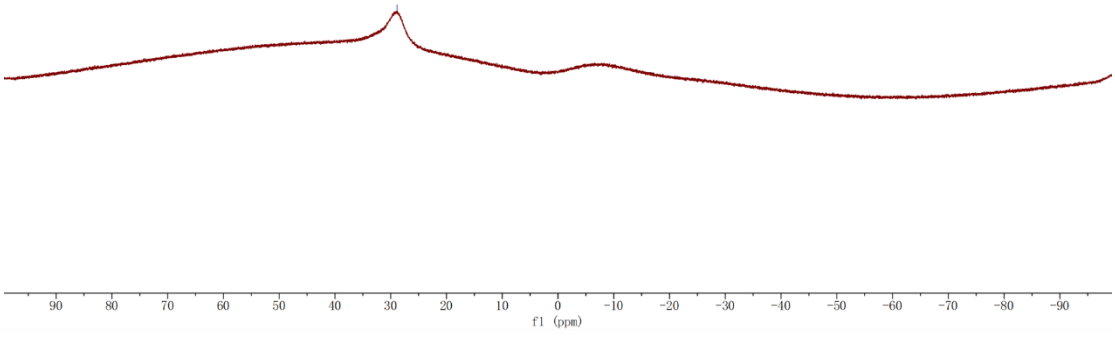
^{13}C NMR (101 MHz, $CDCl_3$)

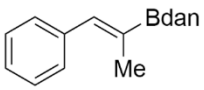




2v

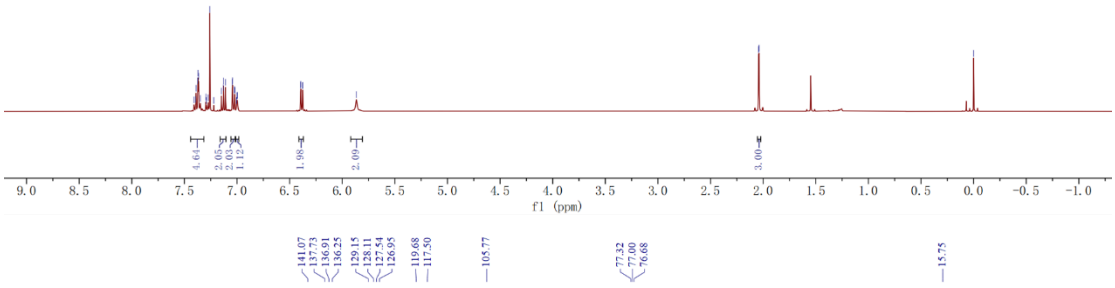
^{11}B NMR (128 MHz, $CDCl_3$)

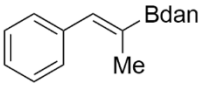




2w

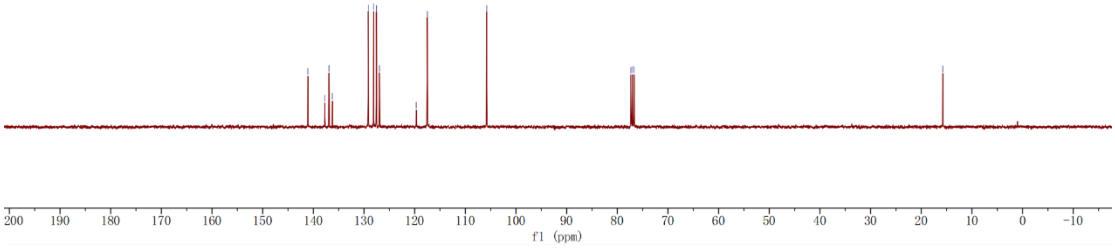
^{1}H NMR (400 MHz, $CDCl_3$)

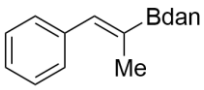




2w

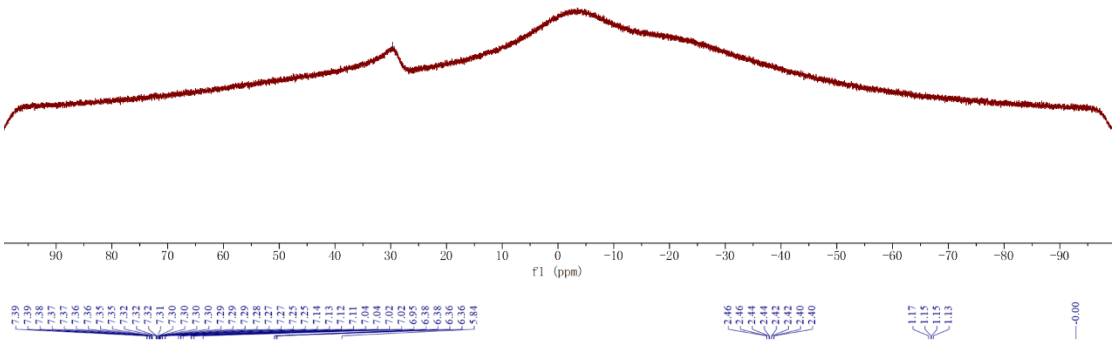
^{13}C NMR (101 MHz, $CDCl_3$)

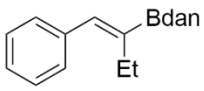




2w

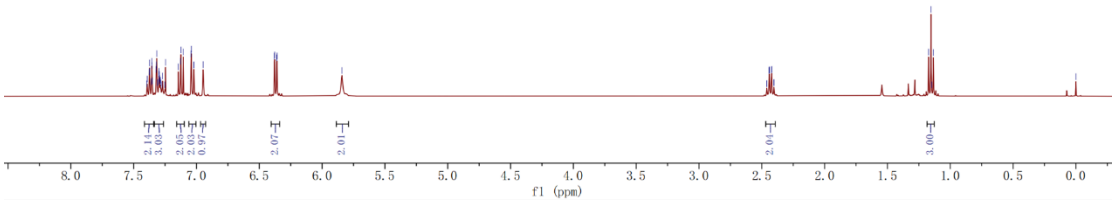
^{11}B NMR (128 MHz, $CDCl_3$)

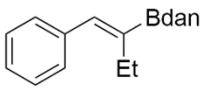




2x

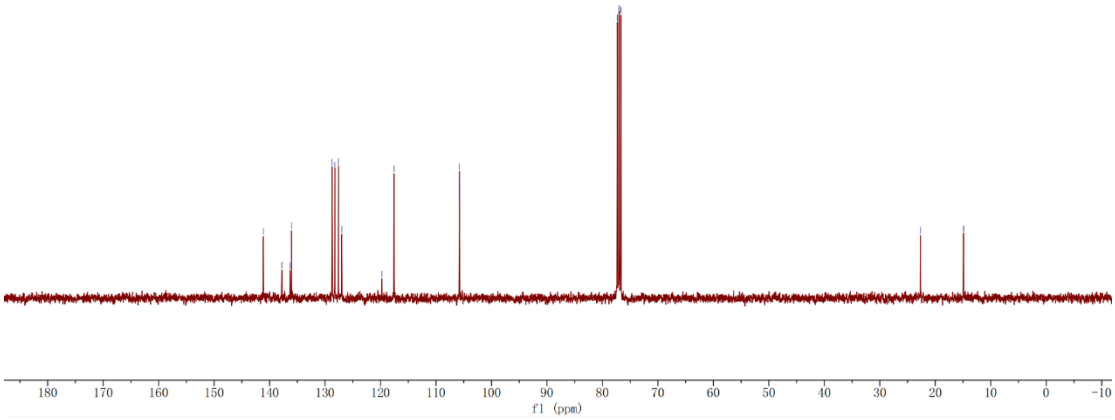
^{1}H NMR (400 MHz, $CDCl_3$)

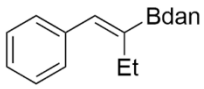




2x

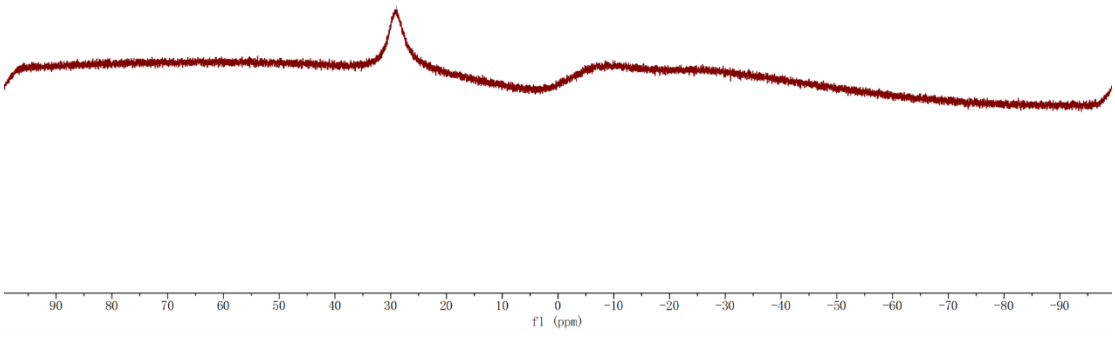
^{13}C NMR (101 MHz, $CDCl_3$)

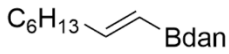




2x

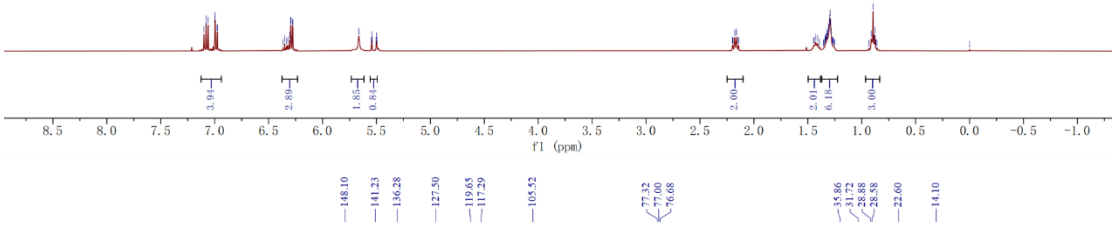
^{11}B NMR (128 MHz, $CDCl_3$)

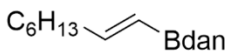




2y

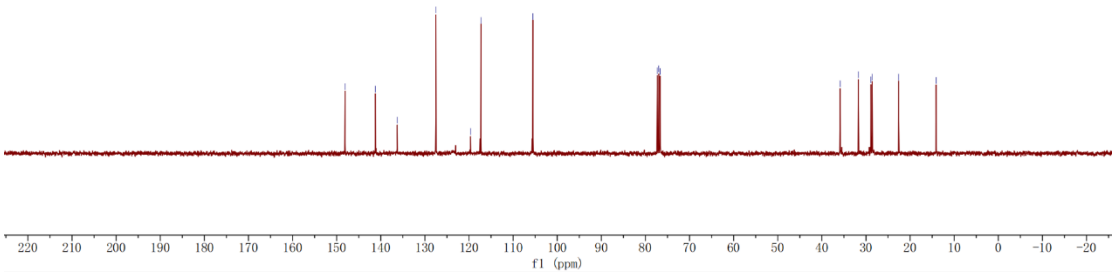
^{1}H NMR (400 MHz, $CDCl_3$)

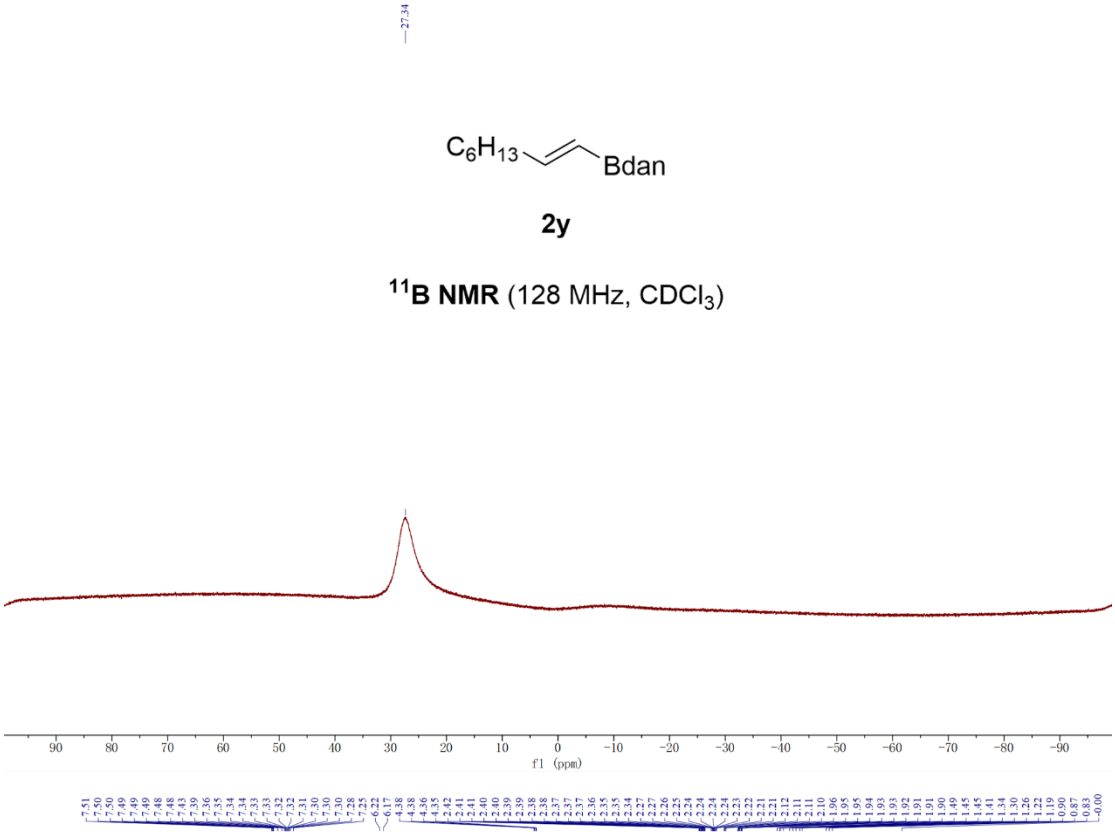




2y

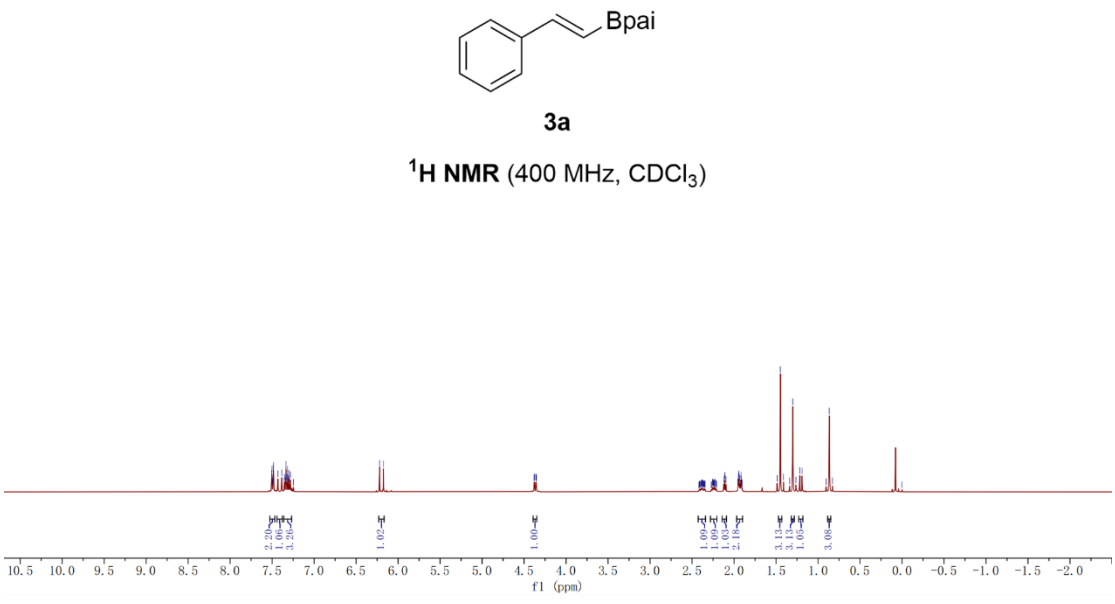
^{13}C NMR (101 MHz, $CDCl_3$)





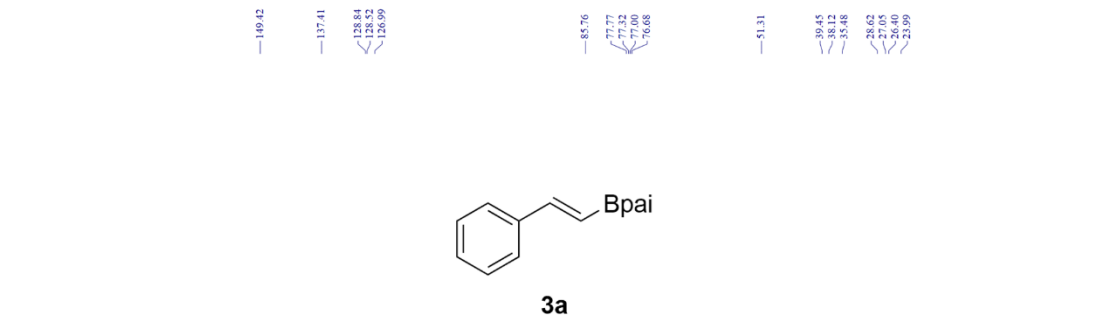
2y

^{11}B NMR (128 MHz, $CDCl_3$)



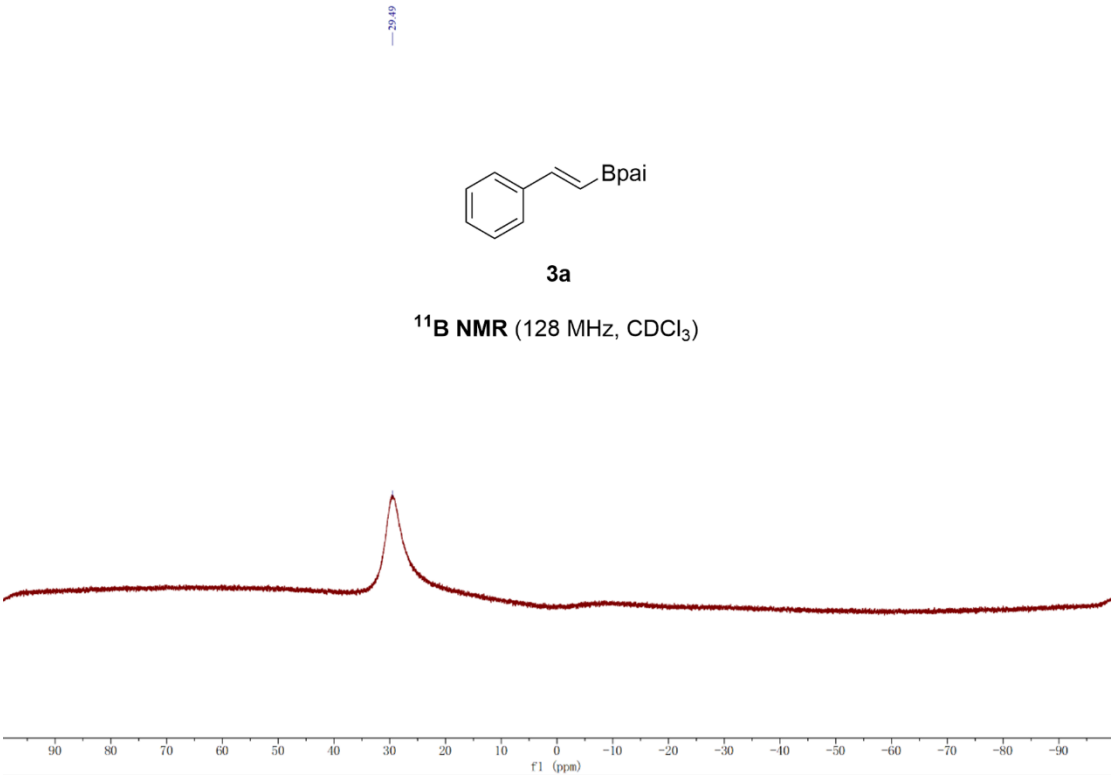
3a

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



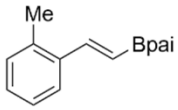
3a

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



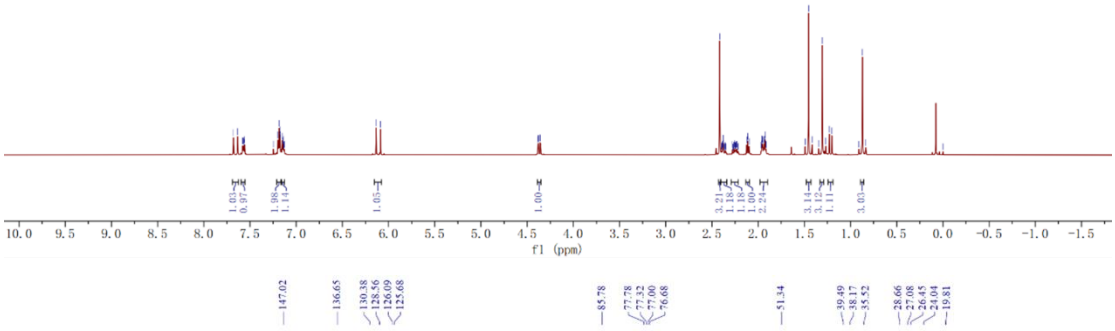
3a

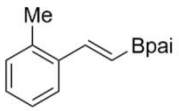
^{11}B NMR (128 MHz, $CDCl_3$)



3b

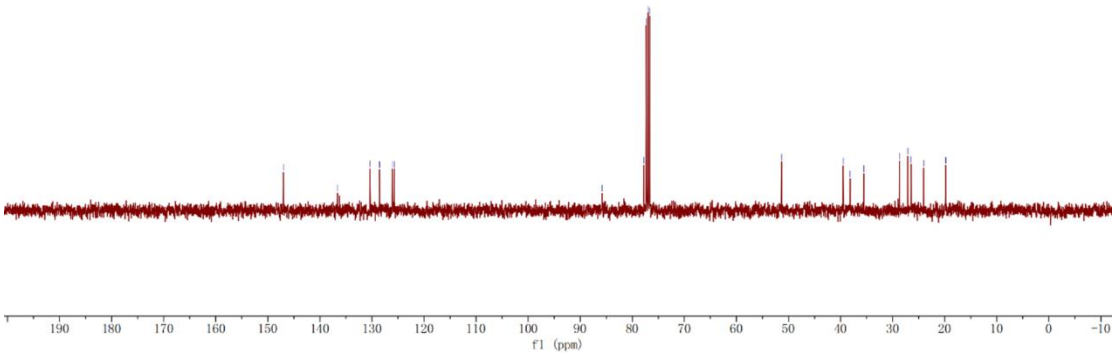
^{1}H NMR (400 MHz, $CDCl_3$)

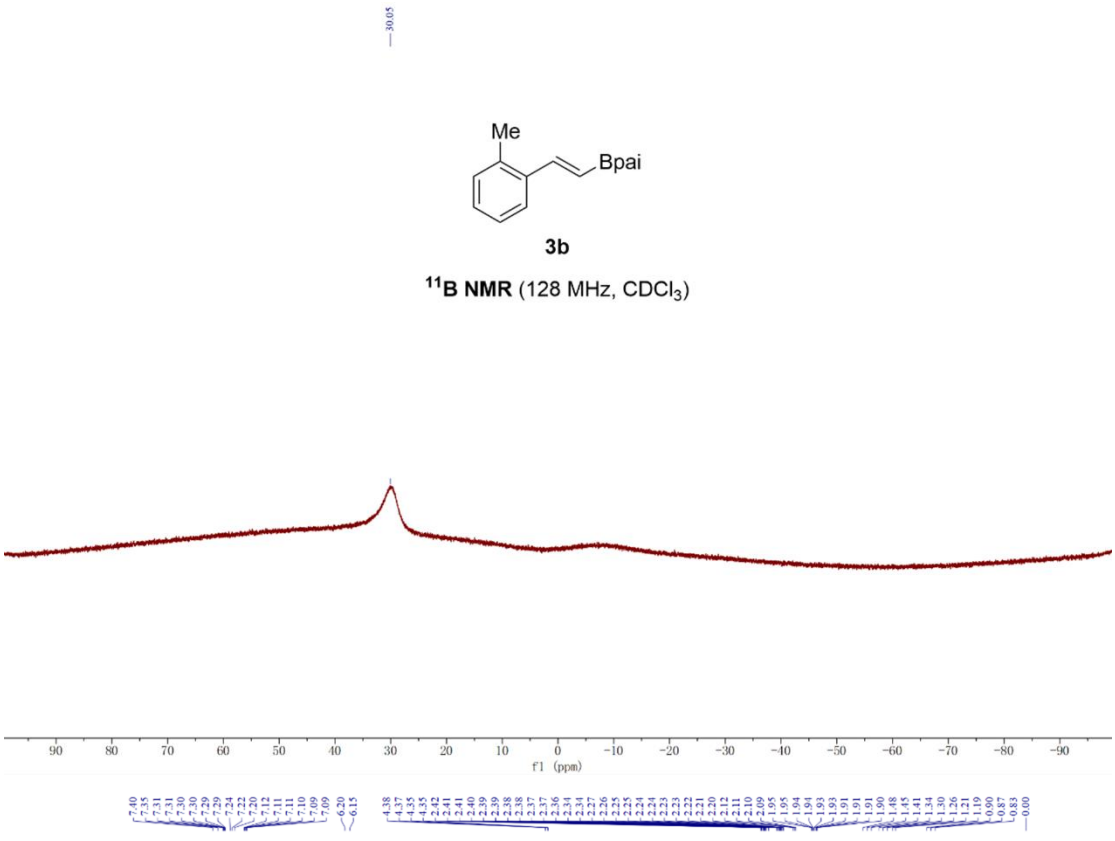




3b

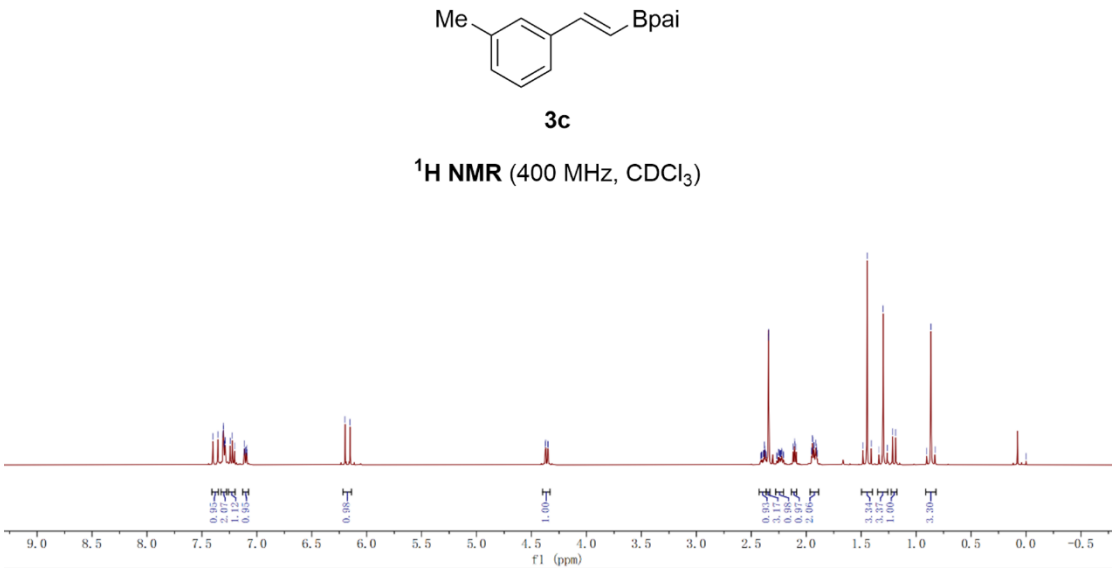
^{13}C NMR (101 MHz, $CDCl_3$)





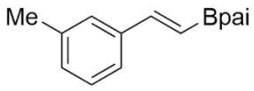
3b

^{11}B NMR (128 MHz, $CDCl_3$)



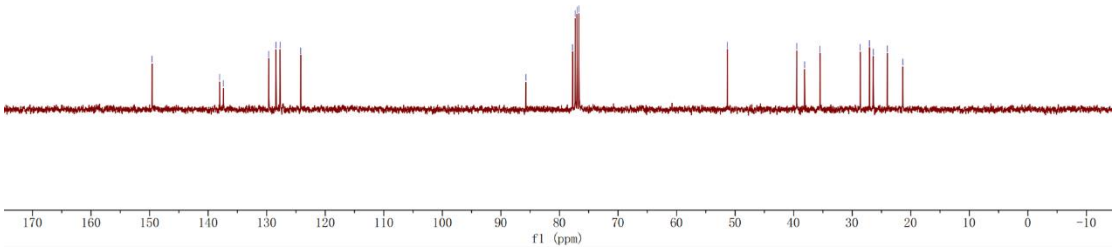
3c

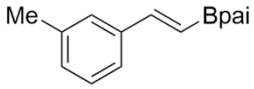
^{1}H NMR (400 MHz, $CDCl_3$)



3c

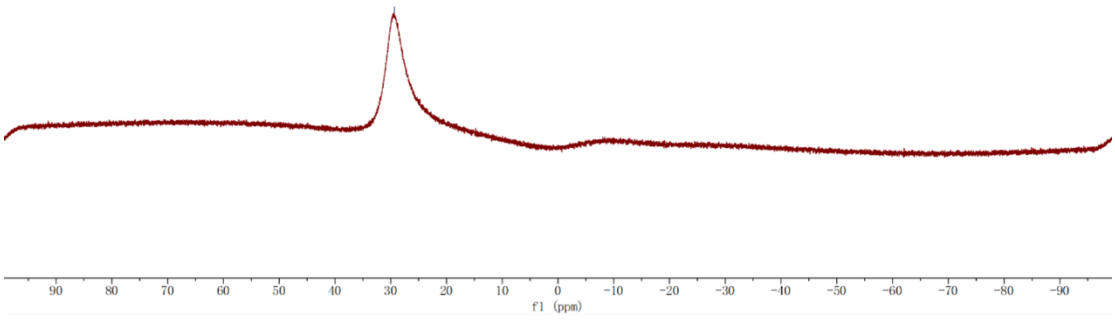
^{13}C NMR (101 MHz, $CDCl_3$)

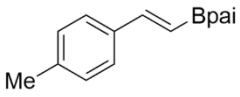




3c

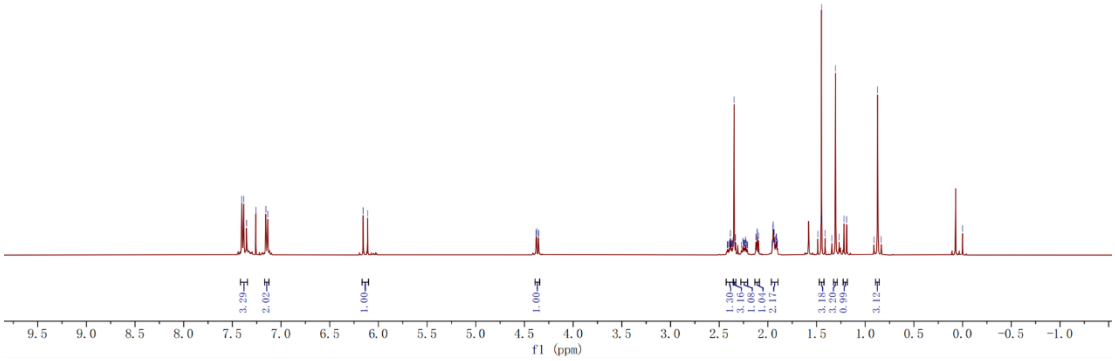
^{11}B NMR (128 MHz, $CDCl_3$)

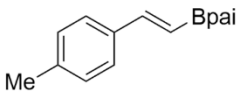




3d

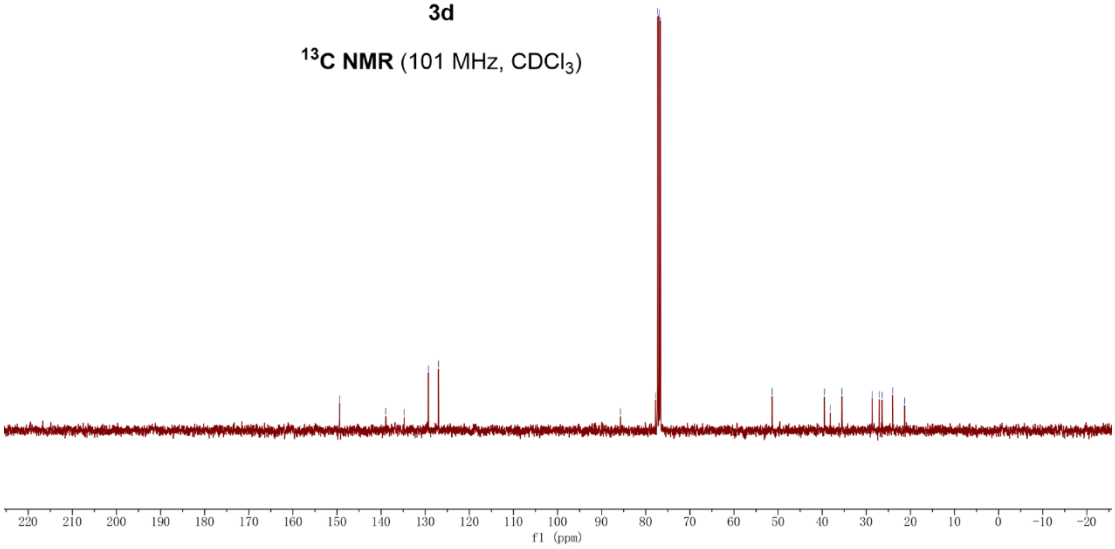
^{1}H NMR (400 MHz, $CDCl_3$)

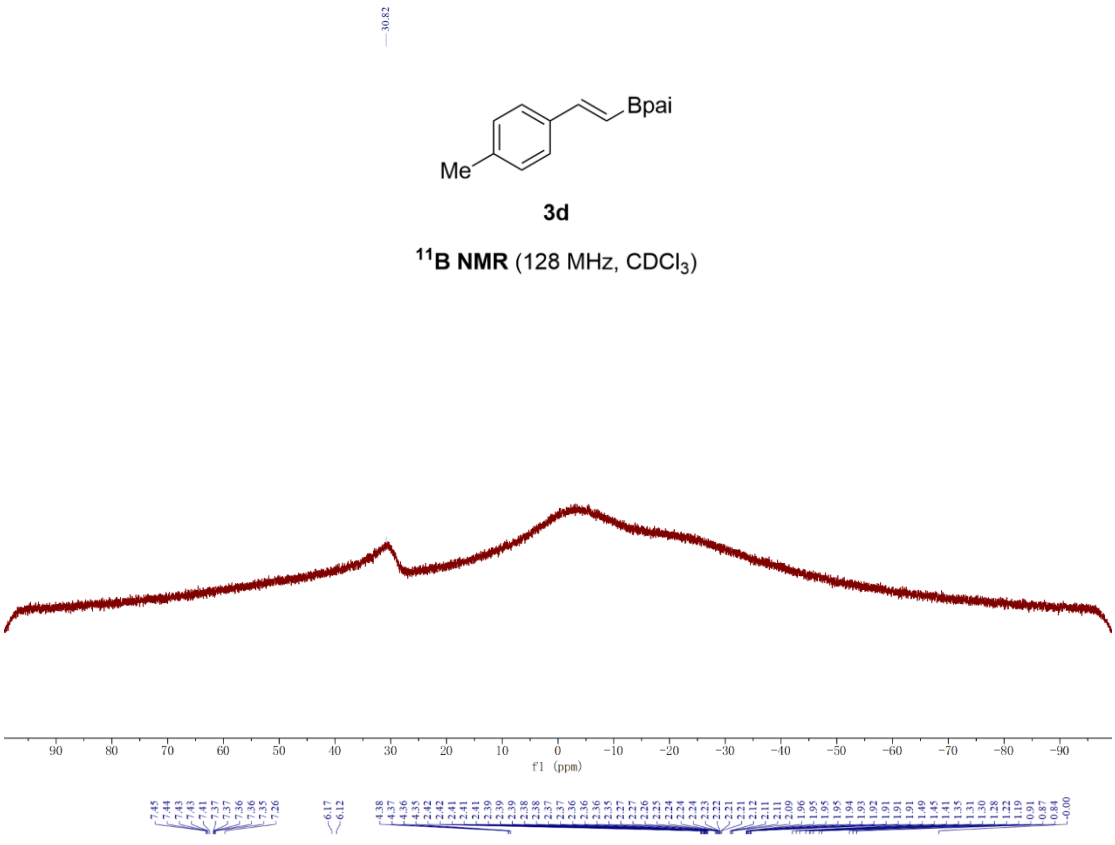


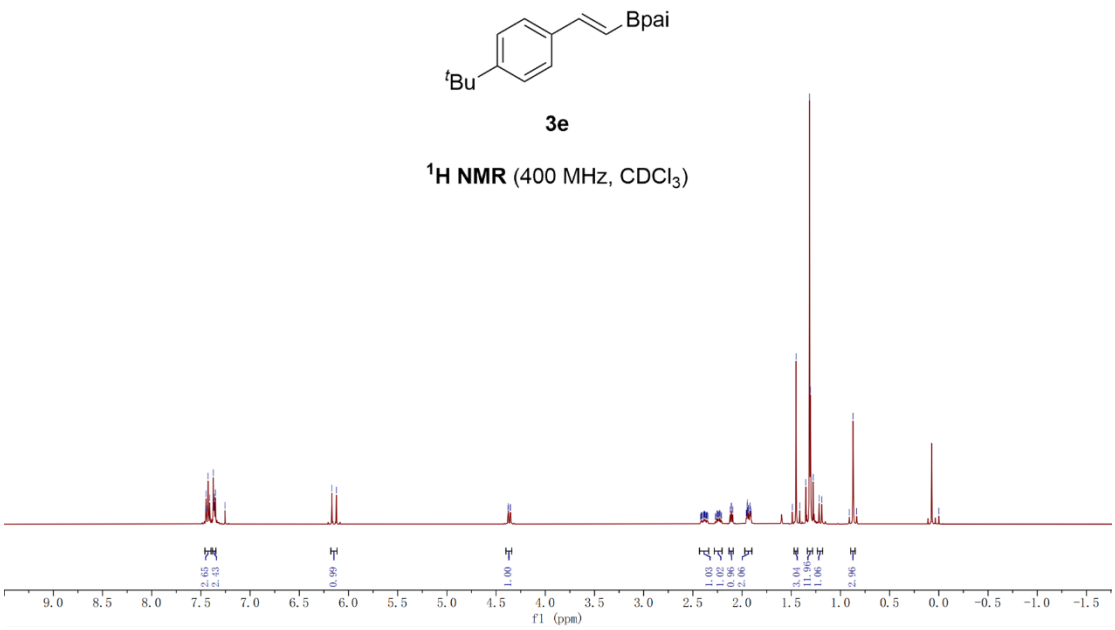


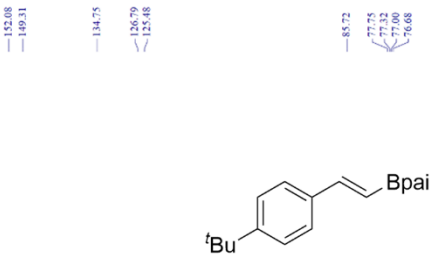
3d

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



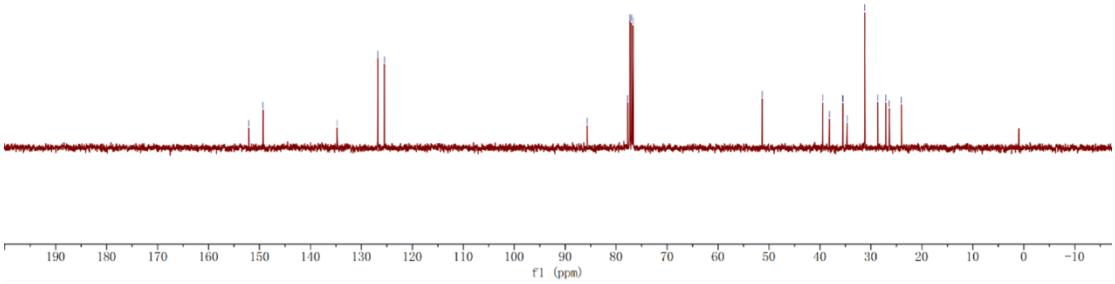

30.82
Bpai
Me
3d
11B NMR (128 MHz, CDCl3)
f1 (ppm)

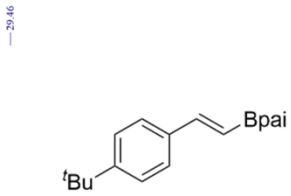

Bpai
tBu
3e
1H NMR (400 MHz, CDCl3)
f1 (ppm)



3e

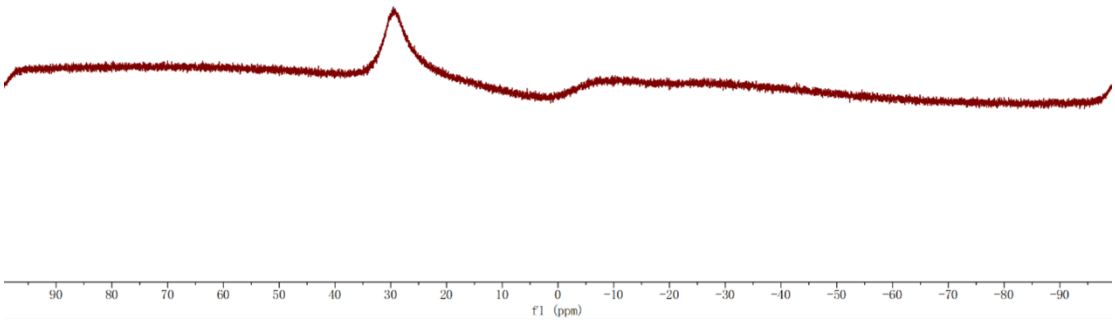
^{13}C NMR (101 MHz, $CDCl_3$)

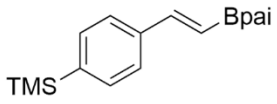




3e

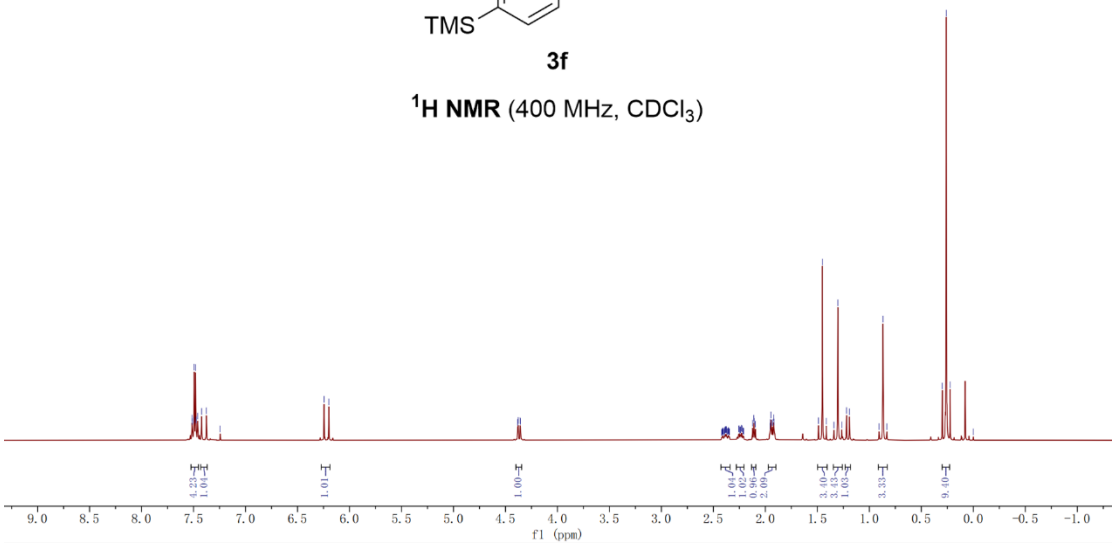
^{11}B NMR (128 MHz, $CDCl_3$)

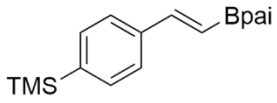




3f

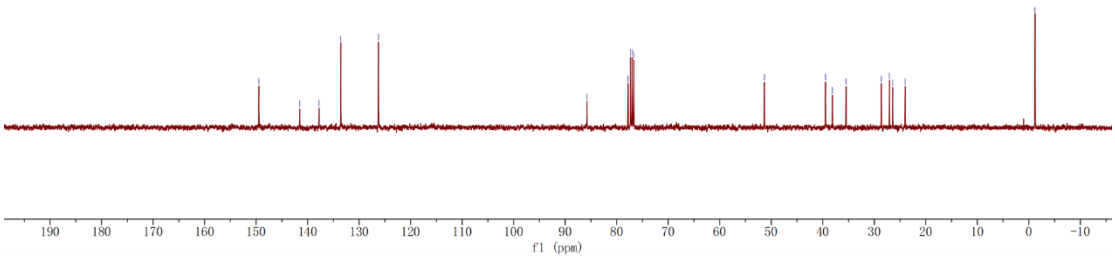
^{1}H NMR (400 MHz, $CDCl_3$)

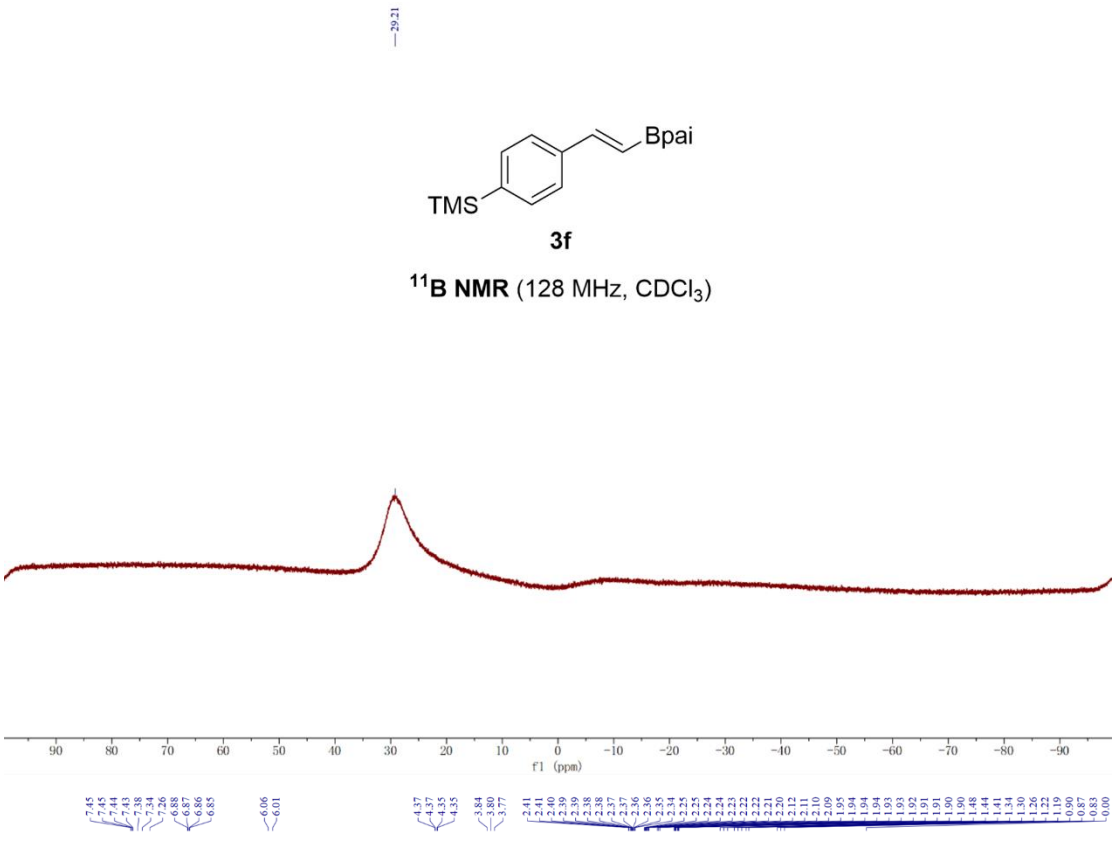




3f

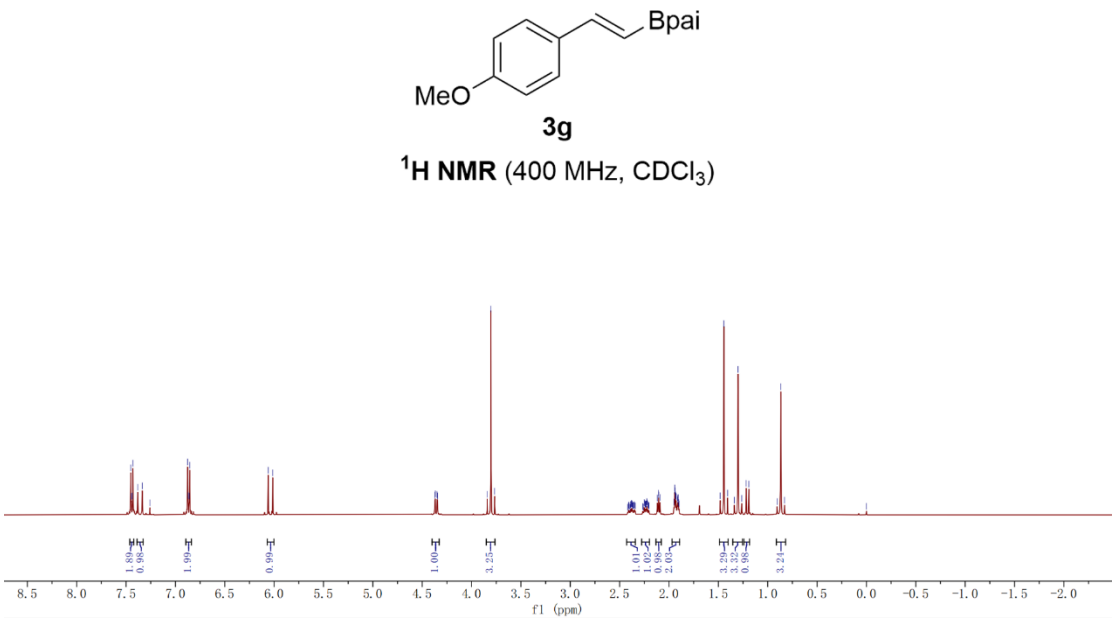
^{13}C NMR (101 MHz, $CDCl_3$)





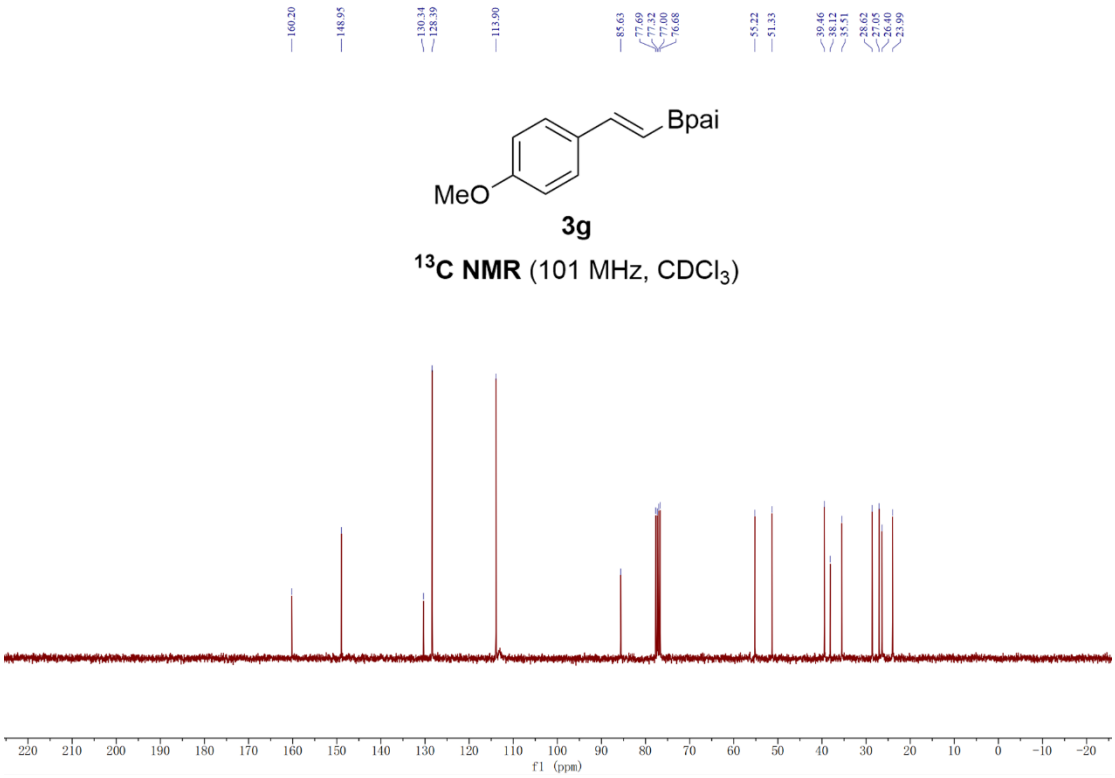
3f

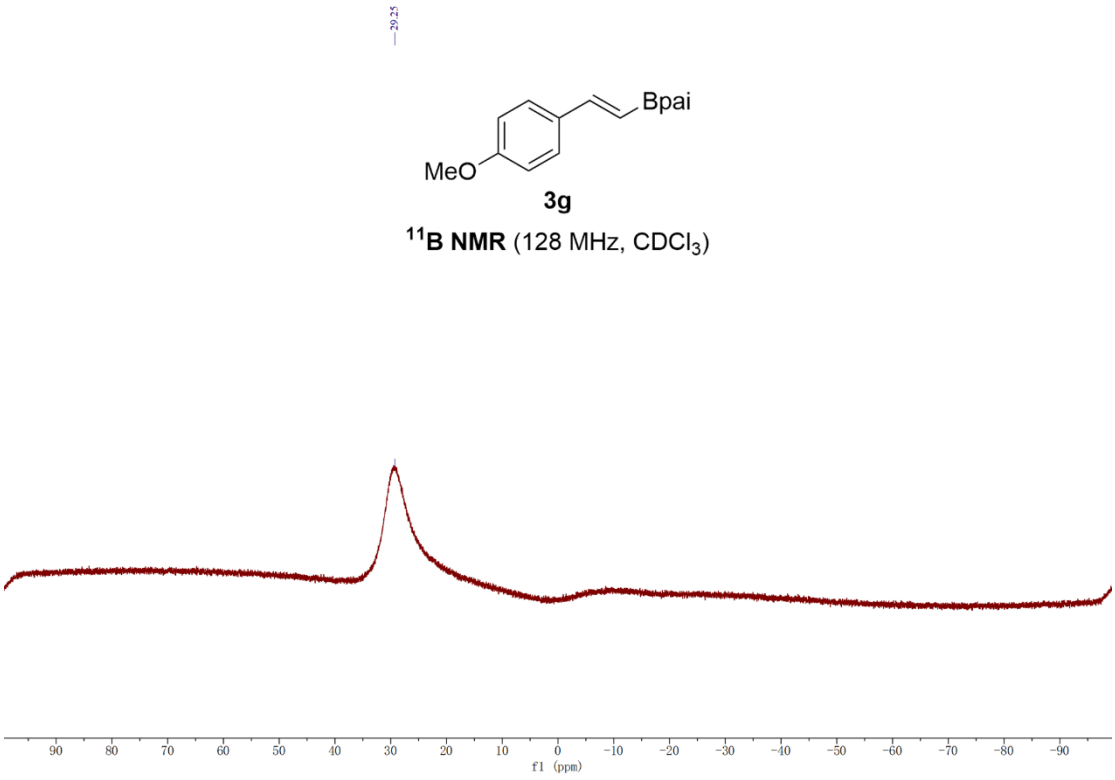
^{11}B NMR (128 MHz, $CDCl_3$)

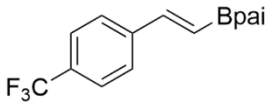


3g

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

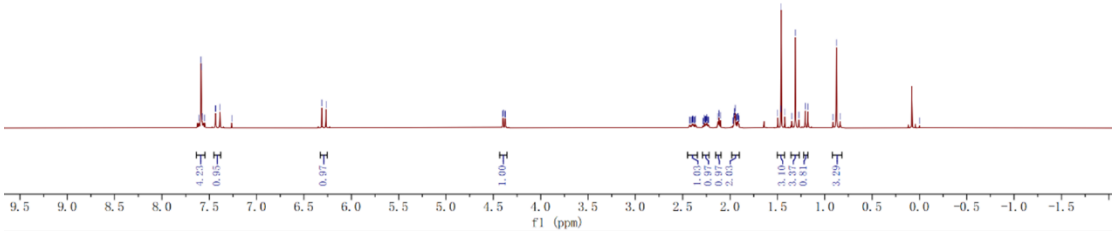

160.20
148.95
130.34
128.39
113.90
85.63
77.69
77.32
77.00
76.68
55.22
51.33
39.46
38.12
35.51
28.62
27.05
26.40
23.99
Bpai
MeO
3g
13C NMR (101 MHz, CDCl3)
f1 (ppm)

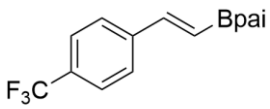

29.25
Bpai
MeO
3g
11B NMR (128 MHz, CDCl3)
f1 (ppm)



3h

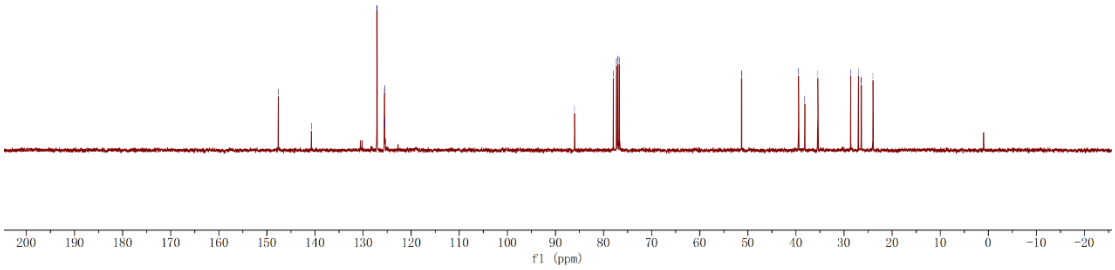
^{1}H NMR (400 MHz, $CDCl_3$)

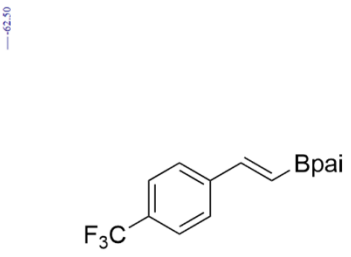




3h

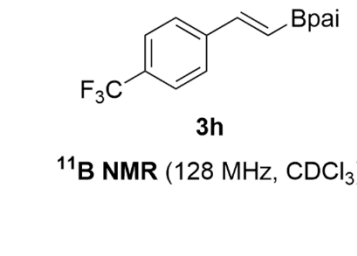
^{13}C NMR (101 MHz, $CDCl_3$)





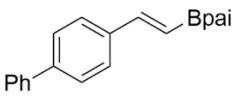
3h

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



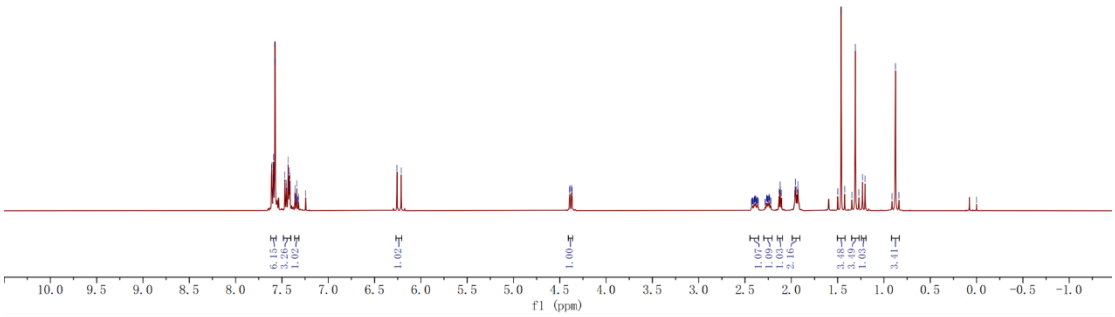
3h

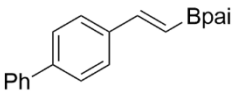
^{11}B NMR (128 MHz, $CDCl_3$)



3i

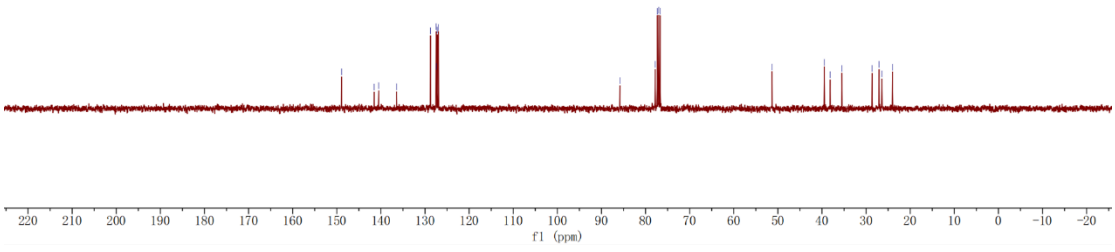
^{1}H NMR (400 MHz, $CDCl_3$)

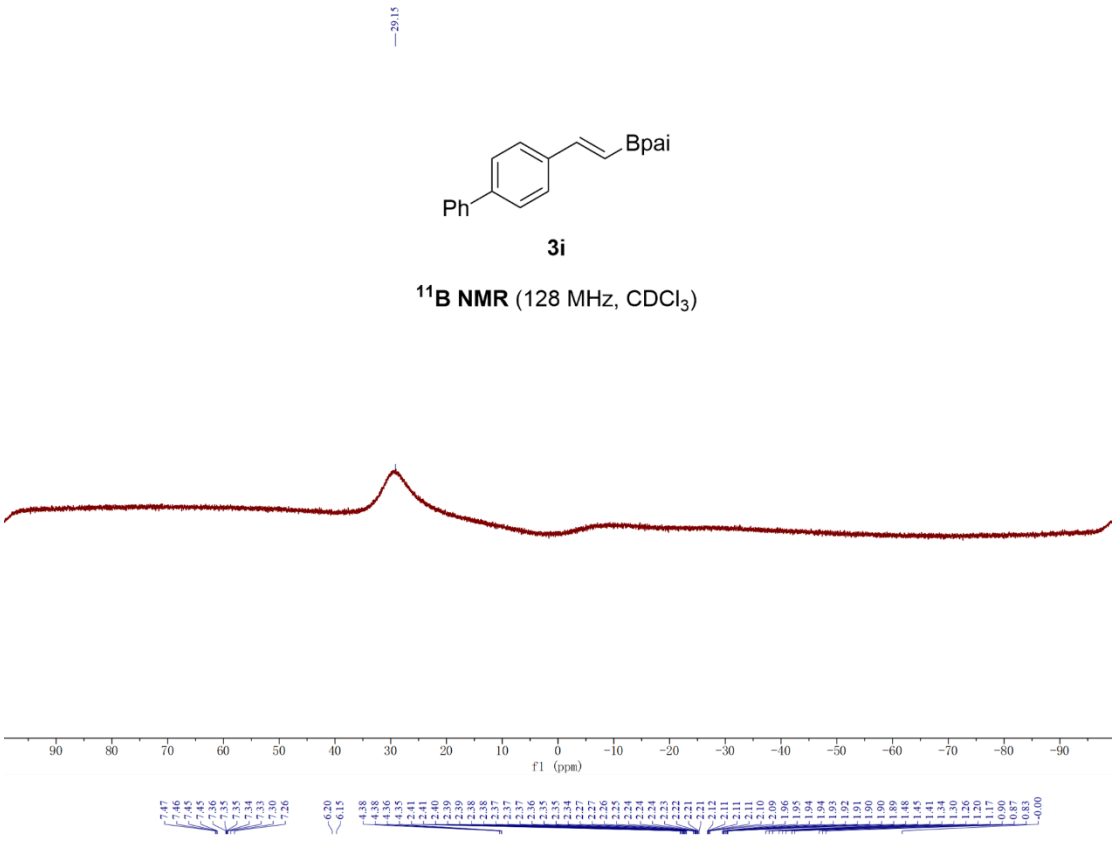




3i

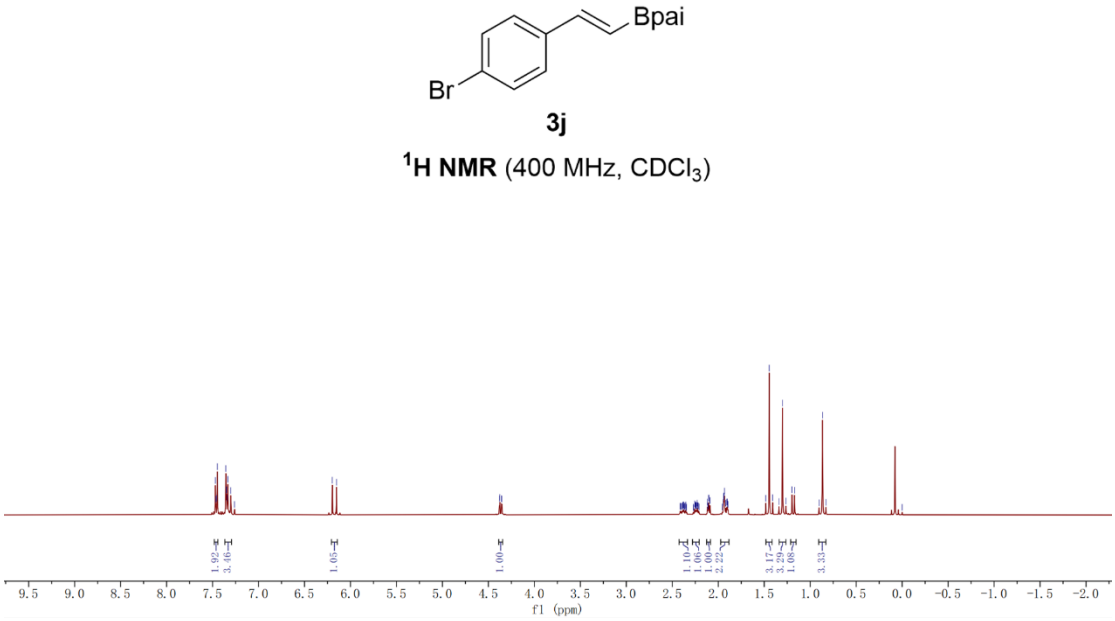
^{13}C NMR (101 MHz, $CDCl_3$)





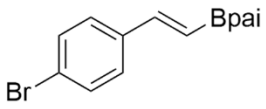
3i

^{11}B NMR (128 MHz, $CDCl_3$)



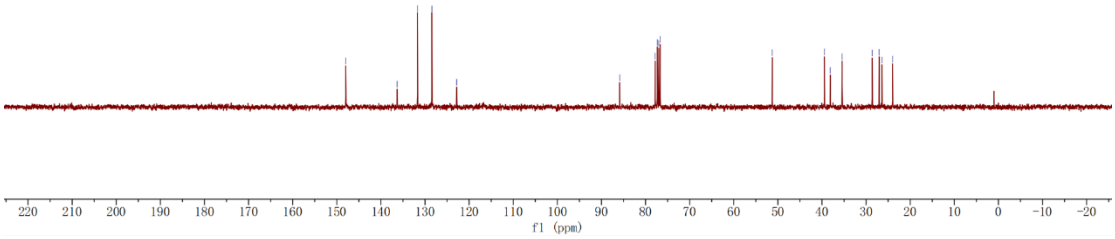
3j

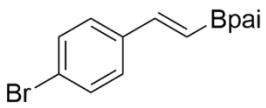
^{1}H NMR (400 MHz, $CDCl_3$)



3j

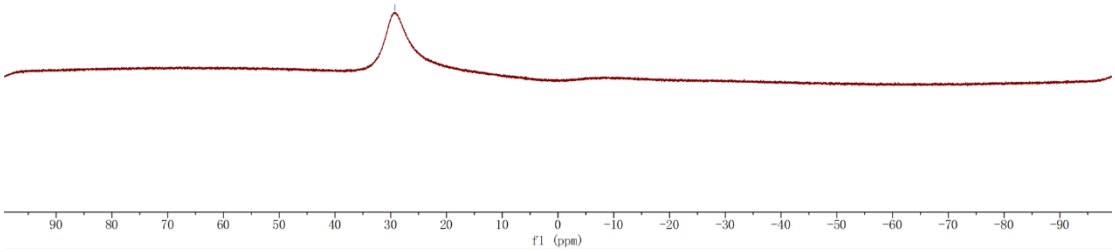
^{13}C NMR (101 MHz, $CDCl_3$)

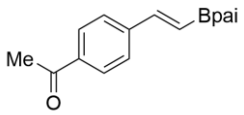




3j

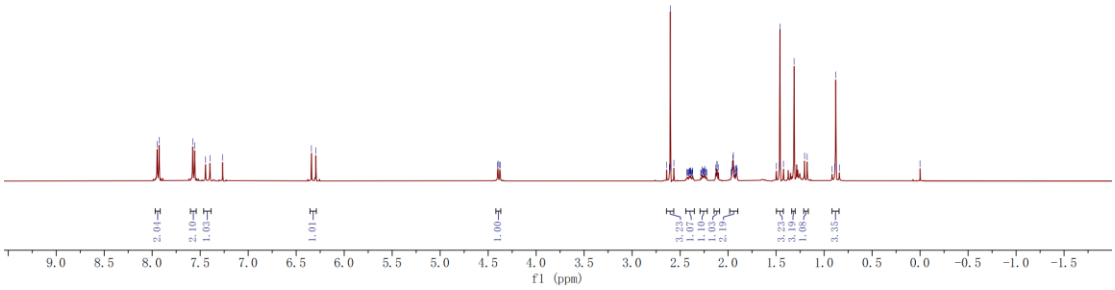
^{11}B NMR (128 MHz, $CDCl_3$)

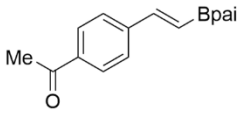




3k

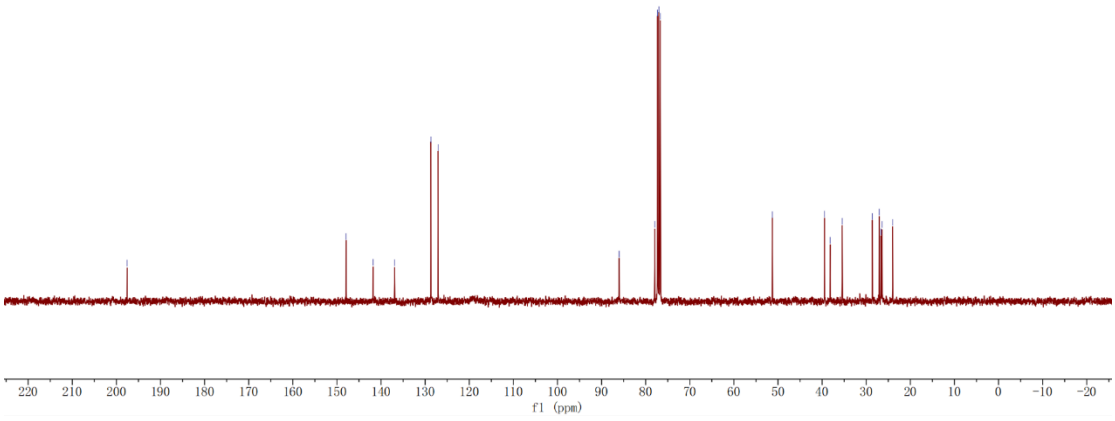
^{1}H NMR (400 MHz, $CDCl_3$)

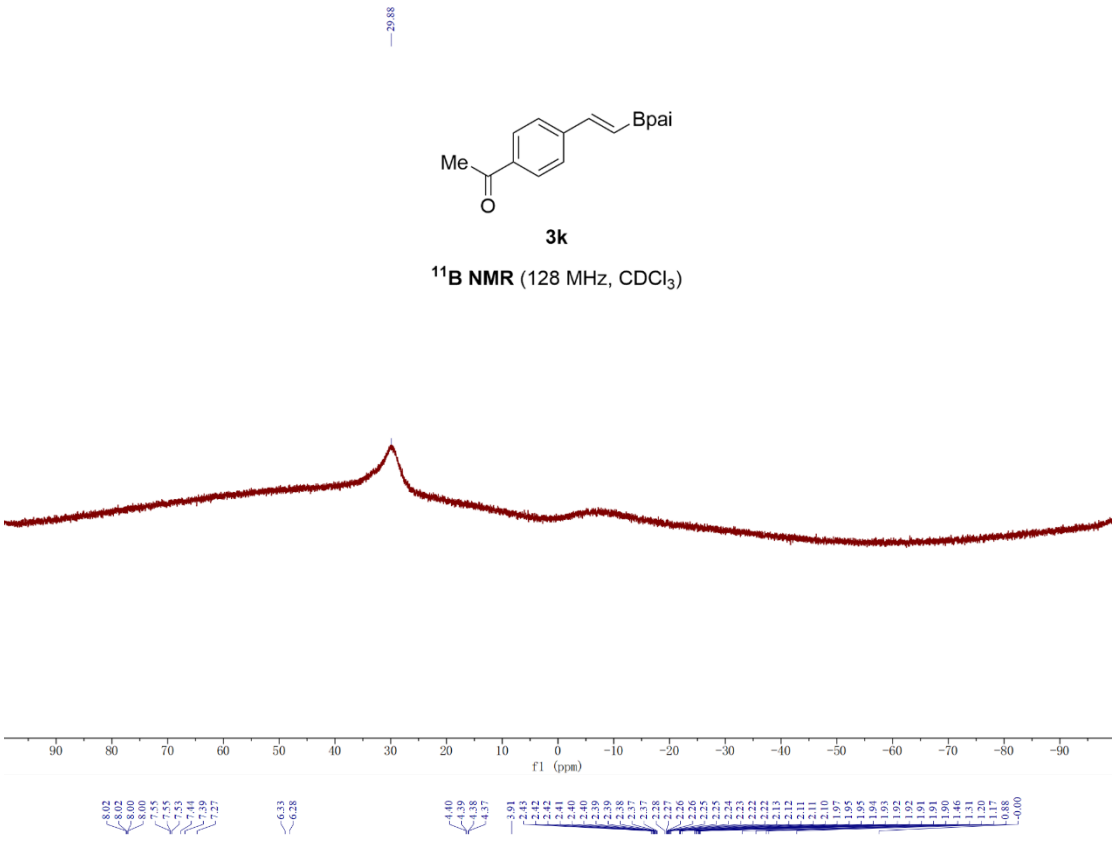




3k

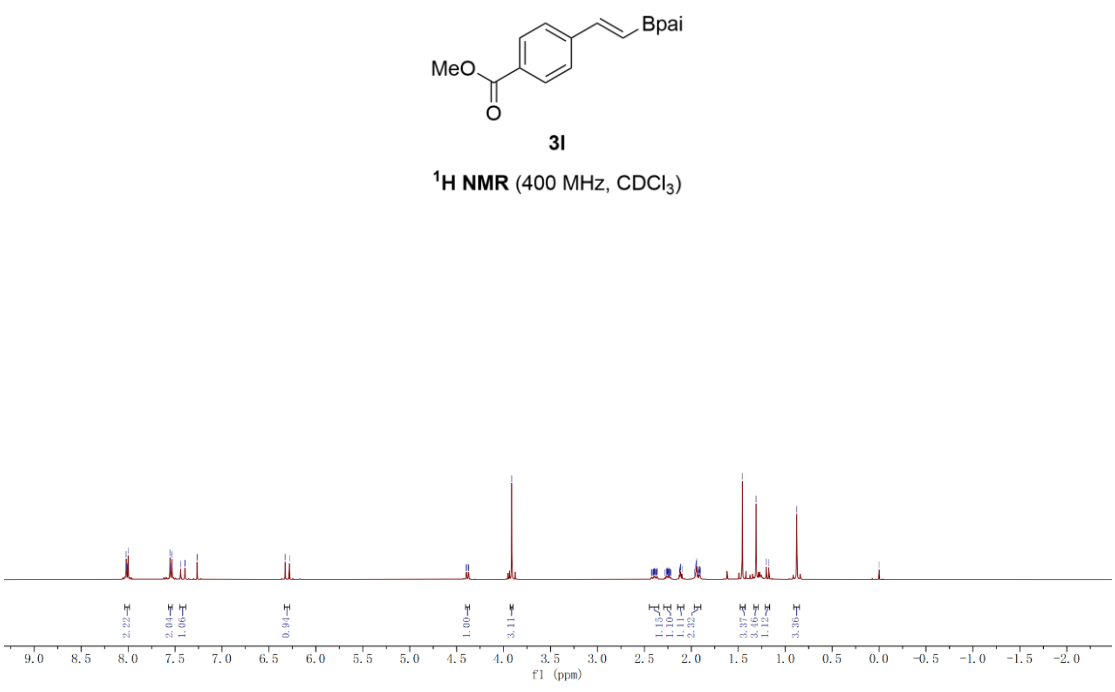
^{13}C NMR (101 MHz, $CDCl_3$)





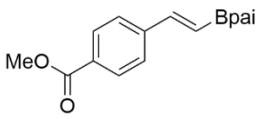
3k

^{11}B NMR (128 MHz, $CDCl_3$)



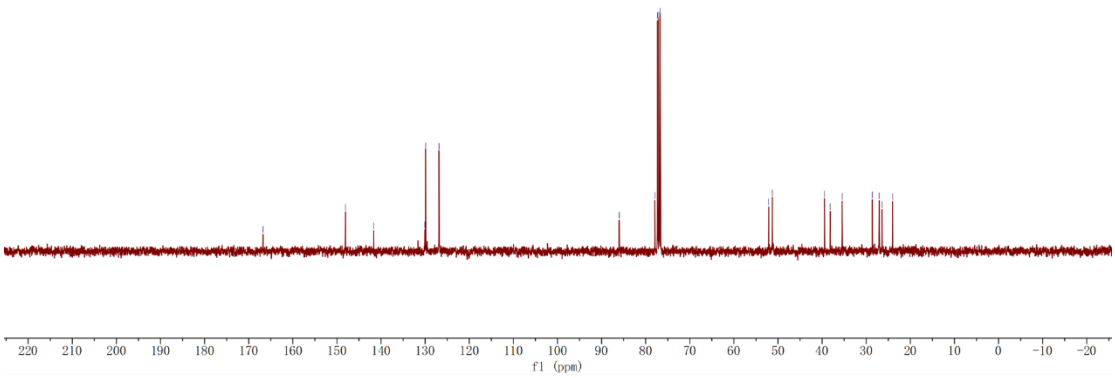
3l

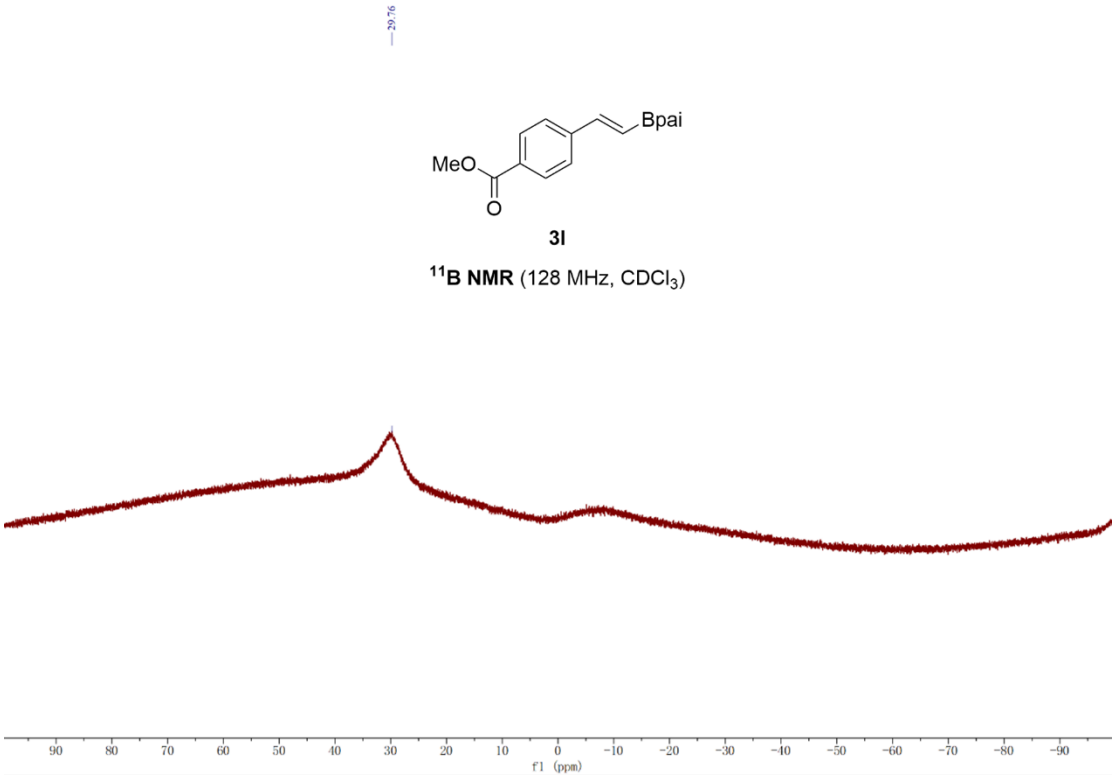
^{1}H NMR (400 MHz, $CDCl_3$)



3l

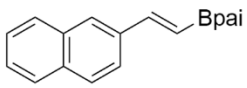
^{13}C NMR (101 MHz, $CDCl_3$)





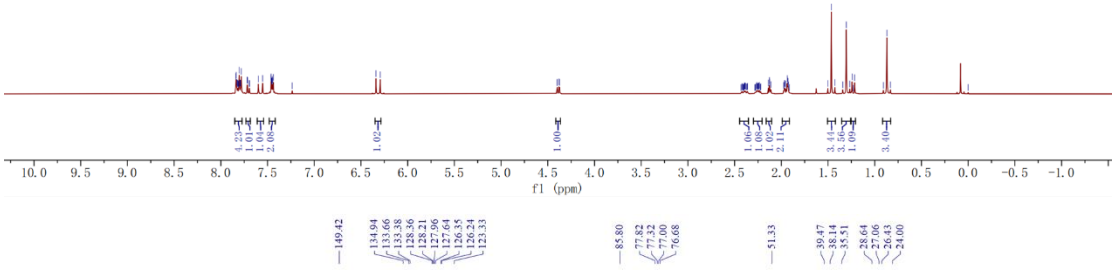
3l

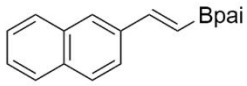
^{11}B NMR (128 MHz, $CDCl_3$)



3m

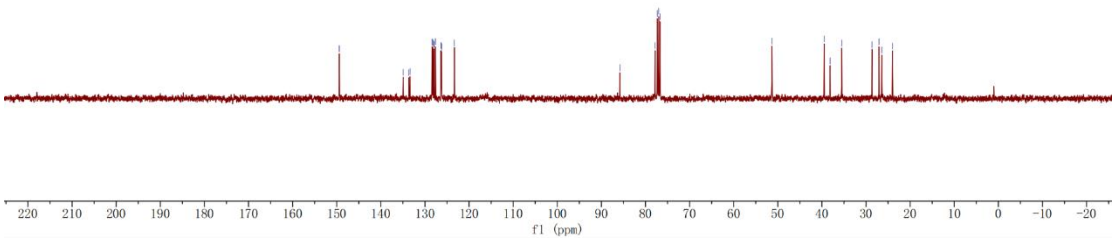
^{1}H NMR (400 MHz, $CDCl_3$)

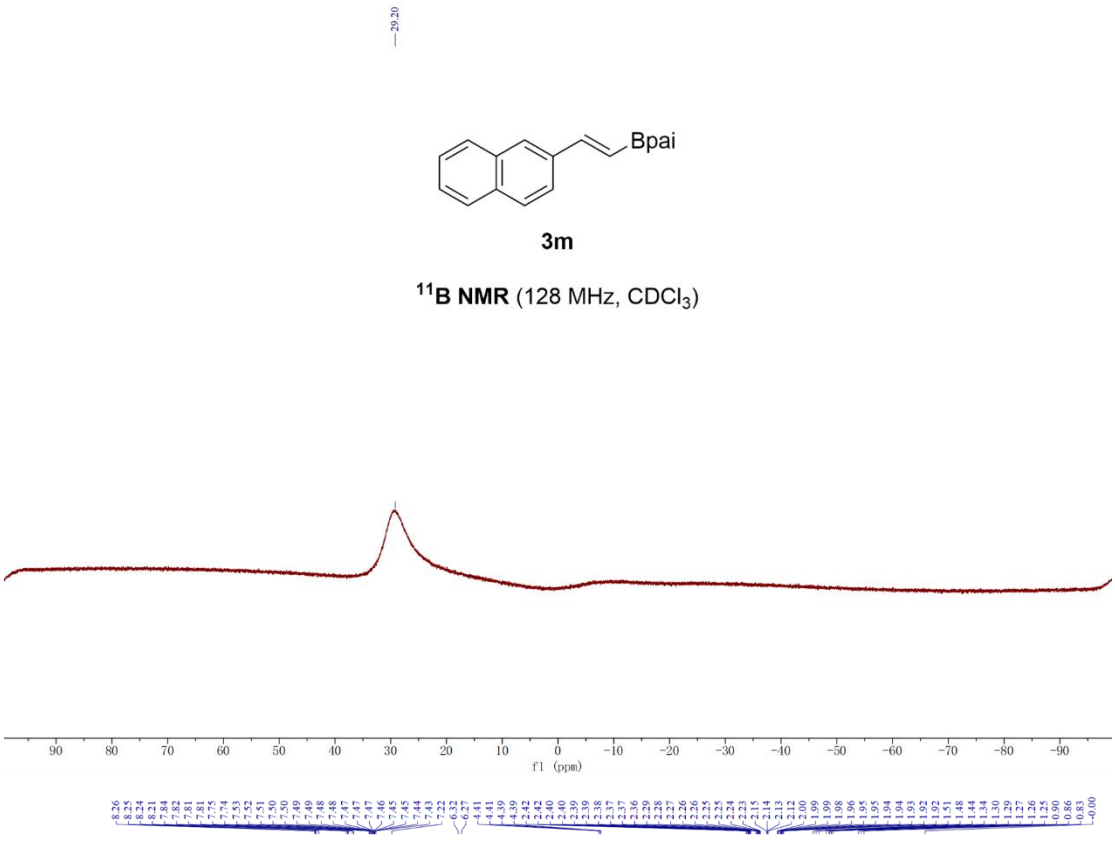




3m

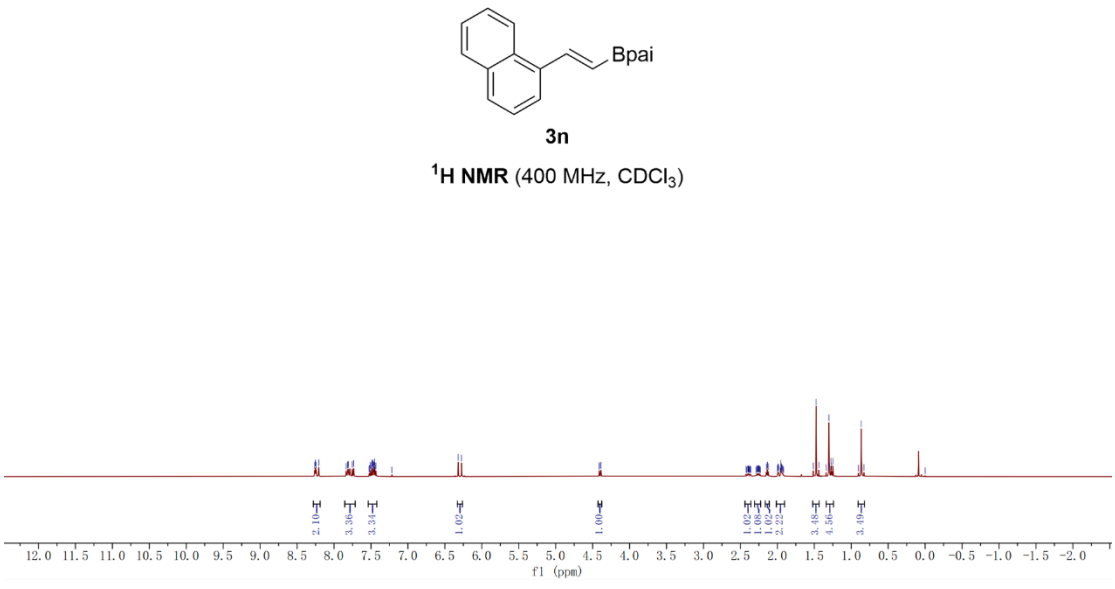
^{13}C NMR (101 MHz, $CDCl_3$)





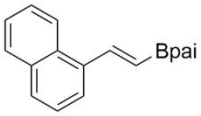
3m

^{11}B NMR (128 MHz, $CDCl_3$)



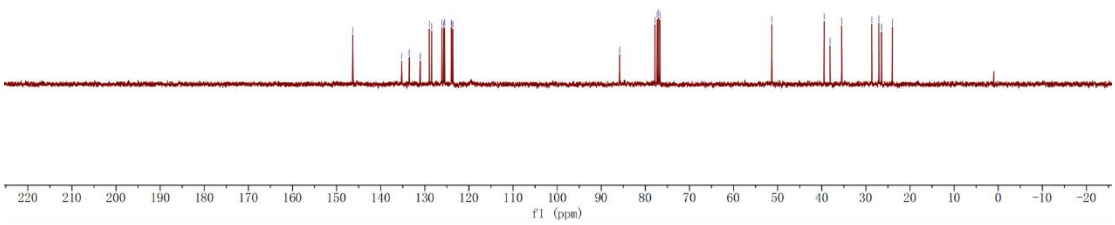
3n

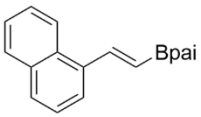
^{1}H NMR (400 MHz, $CDCl_3$)



3n

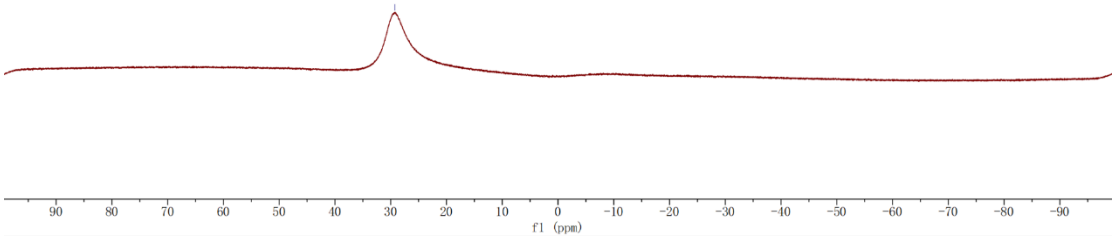
^{13}C NMR (101 MHz, $CDCl_3$)

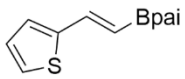




3n

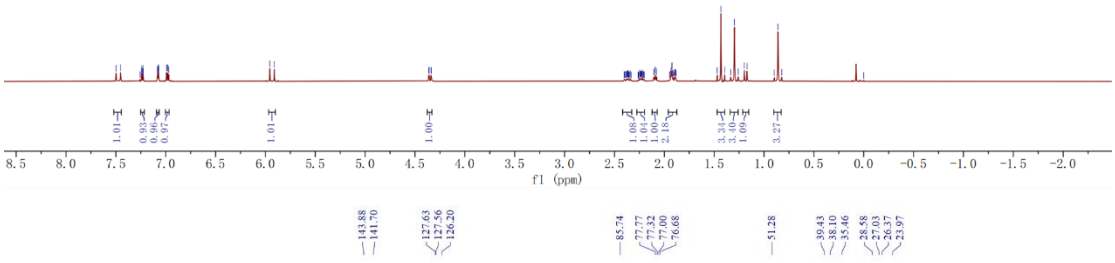
^{11}B NMR (128 MHz, $CDCl_3$)

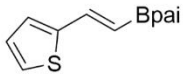




3o

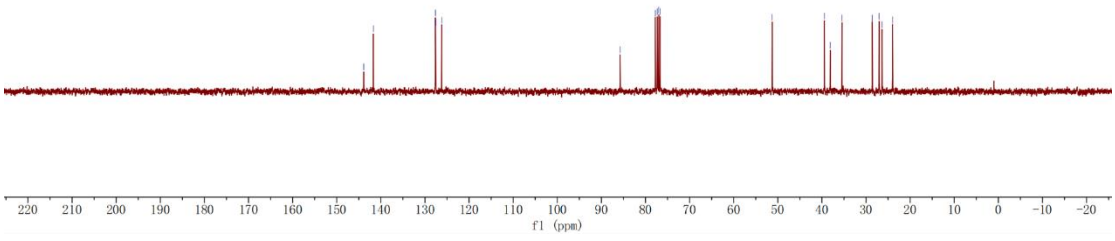
^{1}H NMR (400 MHz, $CDCl_3$)

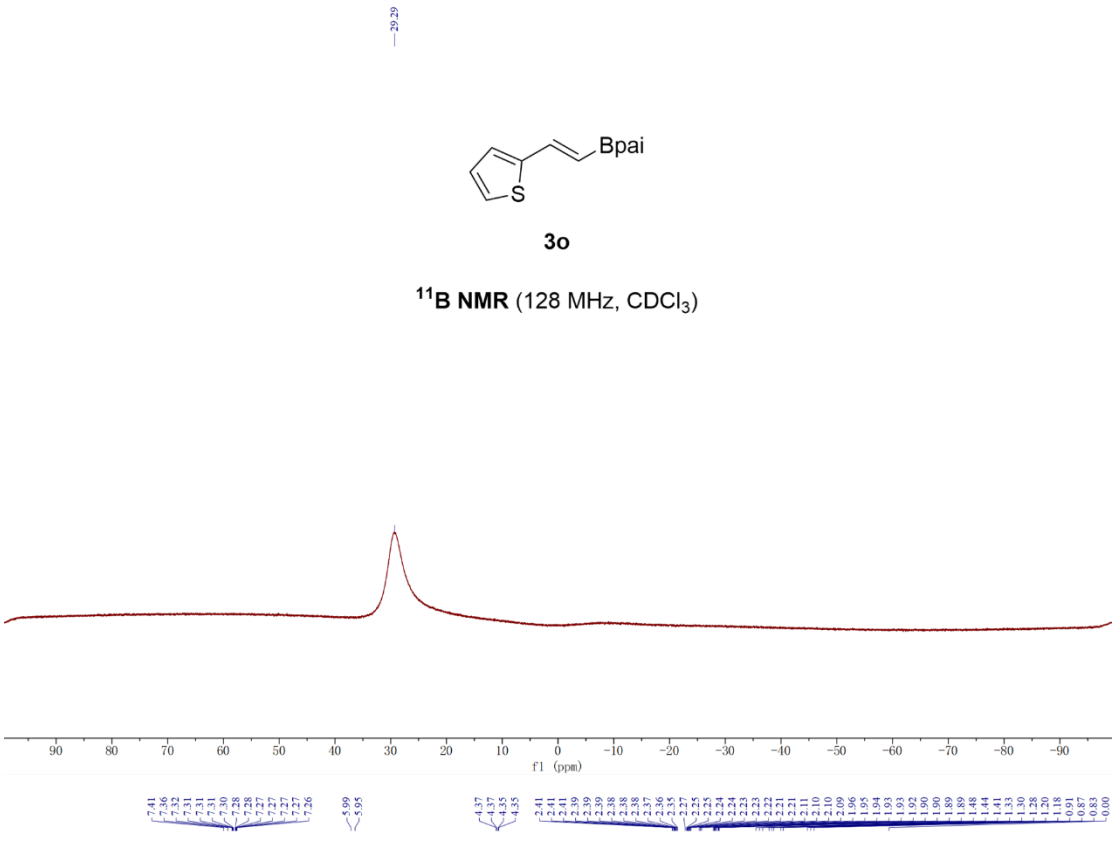




3o

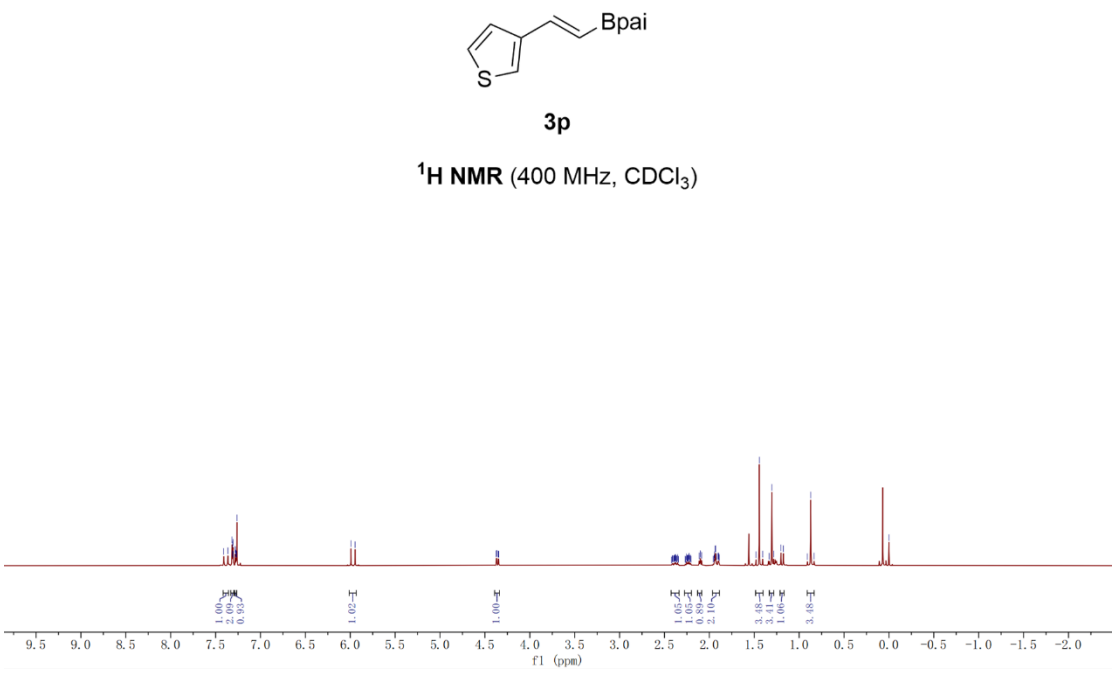
^{13}C NMR (101 MHz, $CDCl_3$)





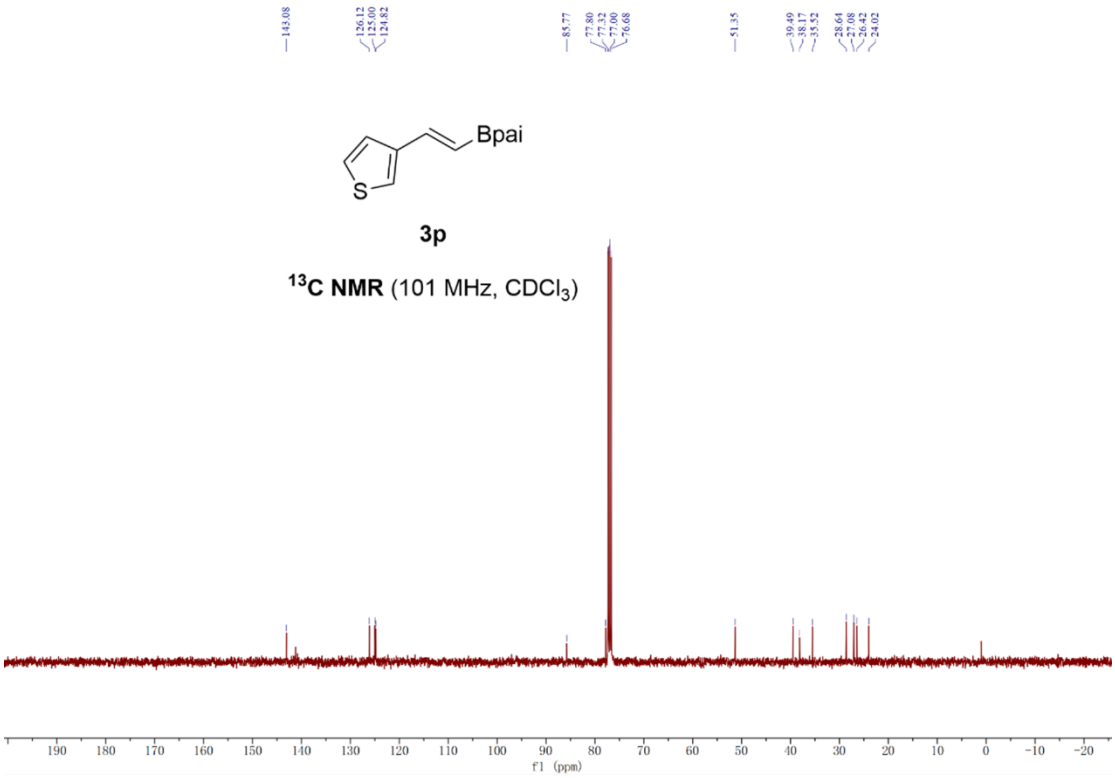
3o

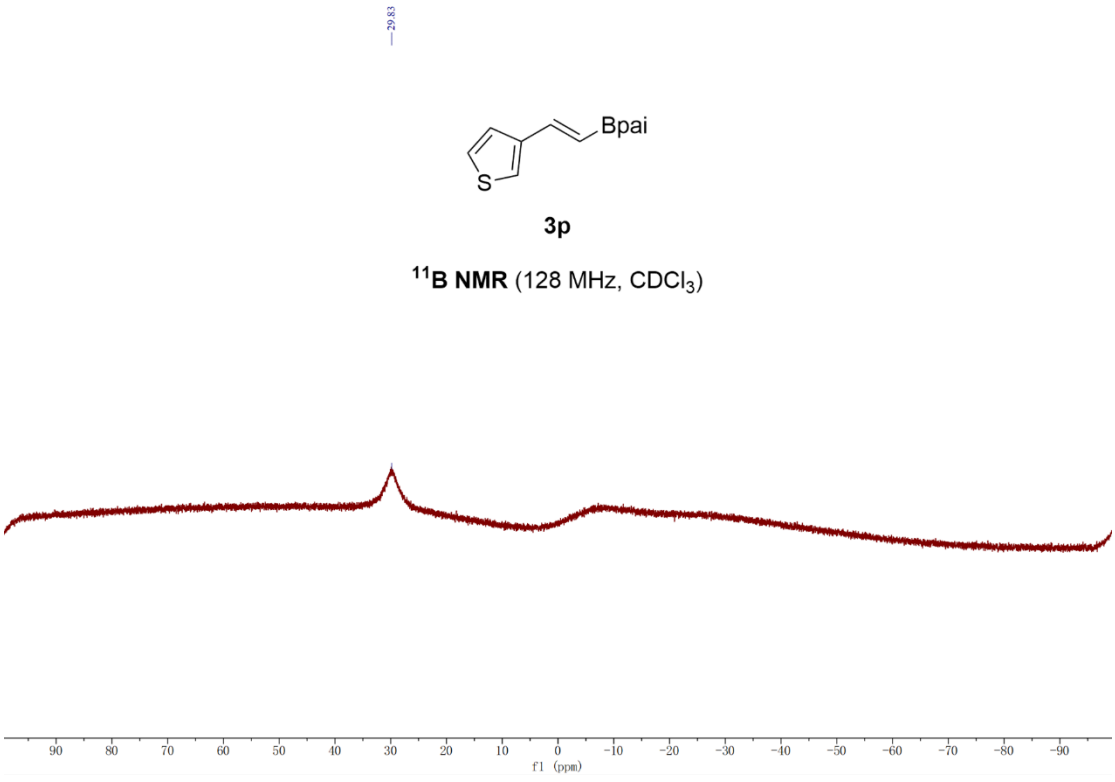
^{11}B NMR (128 MHz, $CDCl_3$)

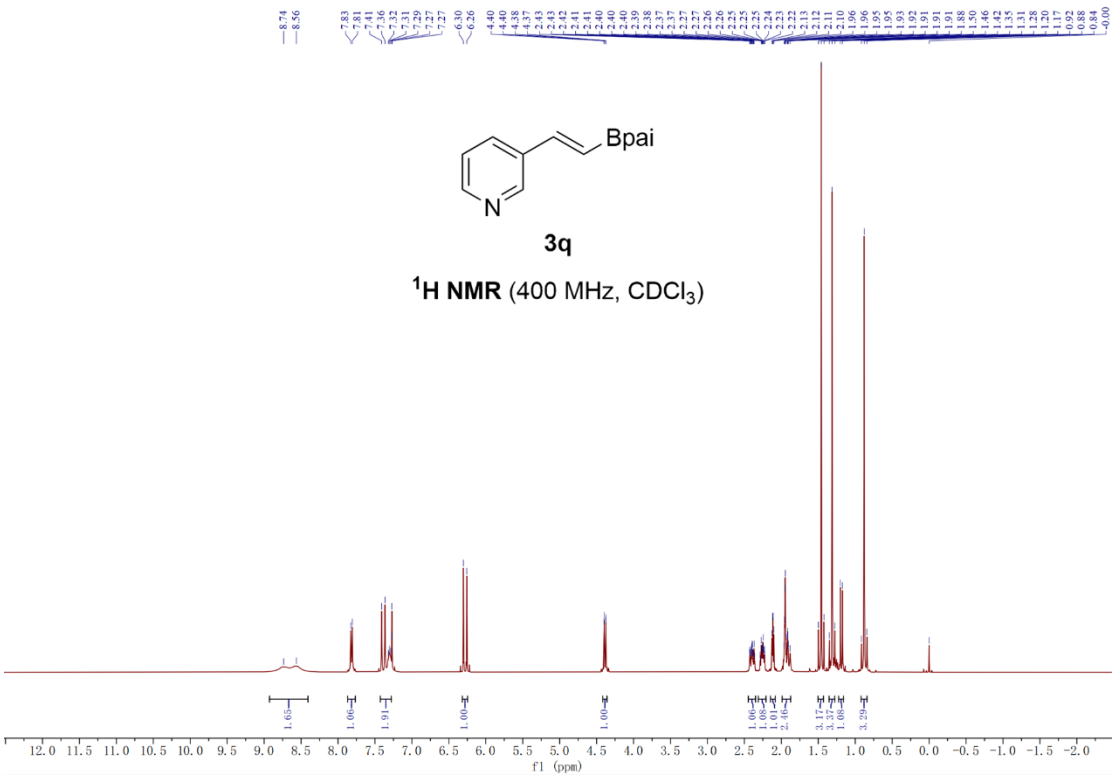


3p

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

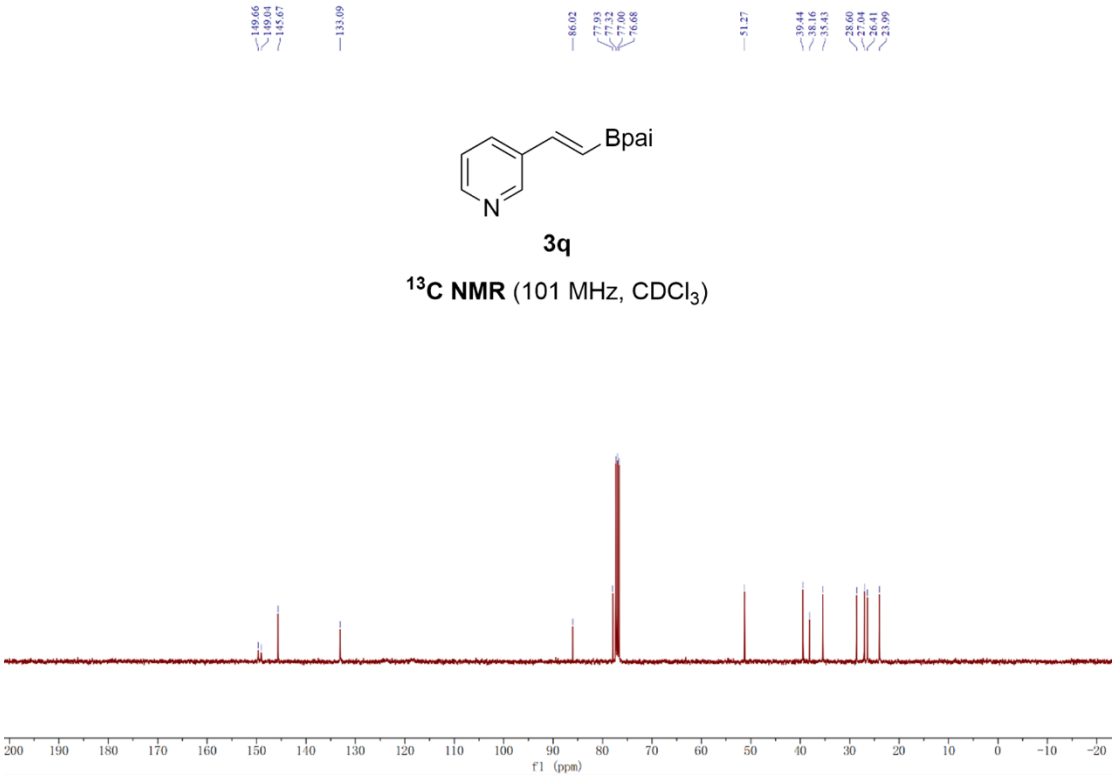

143.08
126.12
125.00
124.82
85.77
77.80
77.32
77.00
76.68
51.35
39.49
38.17
35.52
28.64
27.08
26.42
24.02
Bpai
S
3p
13C NMR (101 MHz, CDCl3)
f1 (ppm)


29.83
Bpai
S
3p
11B NMR (128 MHz, CDCl3)
f1 (ppm)



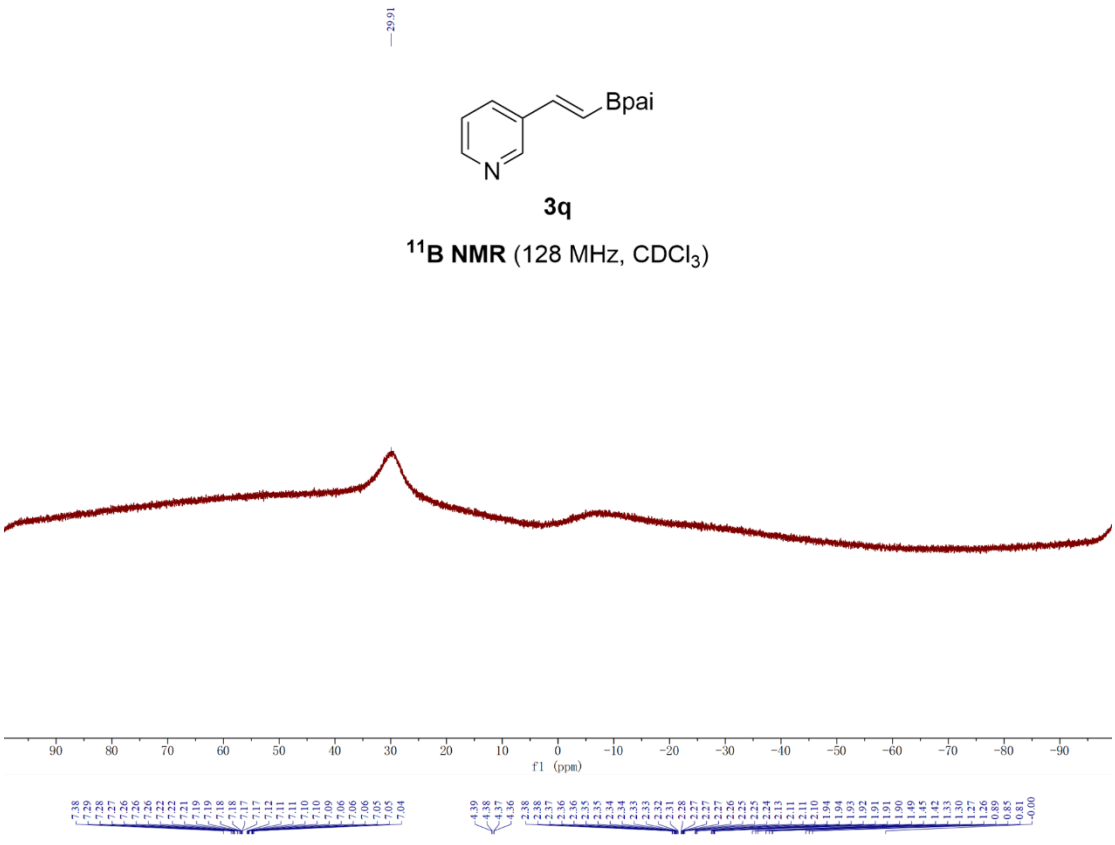
3q

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



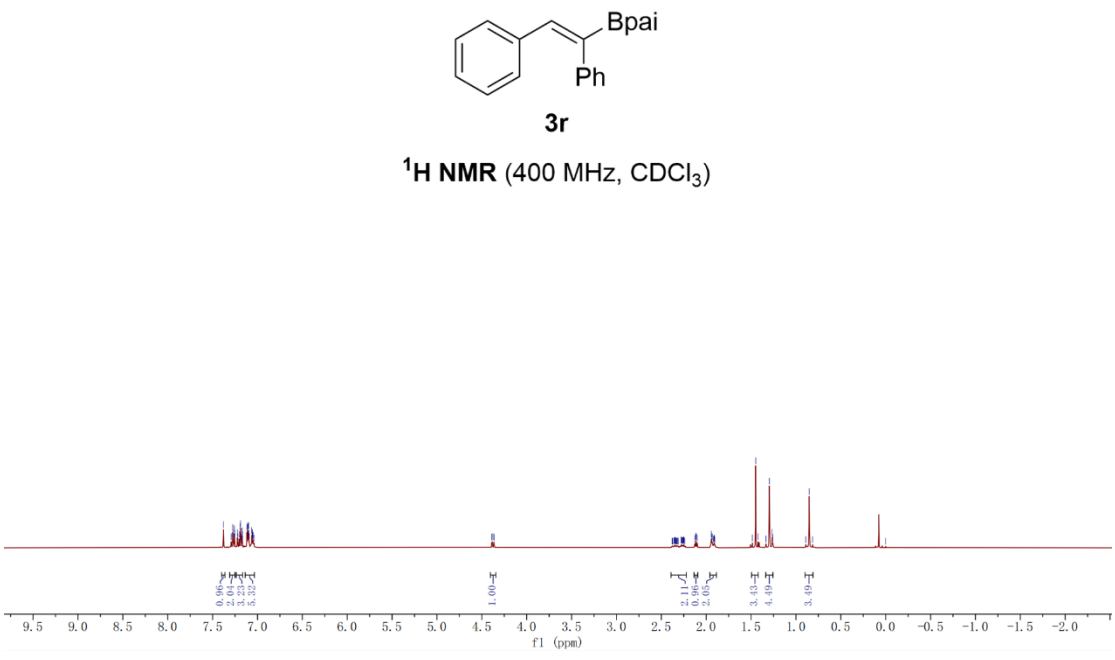
3q

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



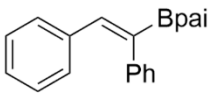
3q

^{11}B NMR (128 MHz, $CDCl_3$)



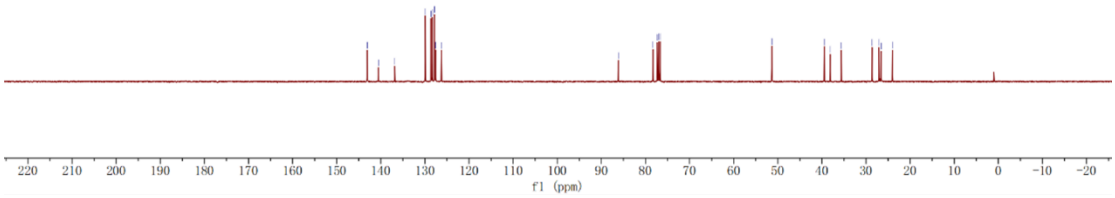
3r

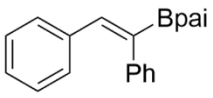
^{1}H NMR (400 MHz, $CDCl_3$)



3r

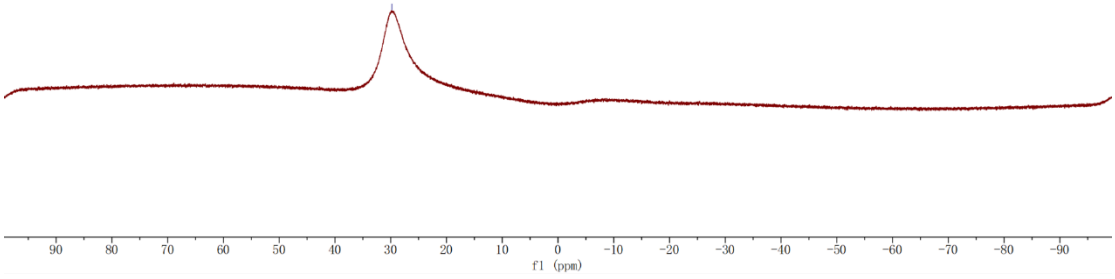
^{13}C NMR (101 MHz, $CDCl_3$)

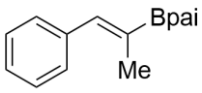




3r

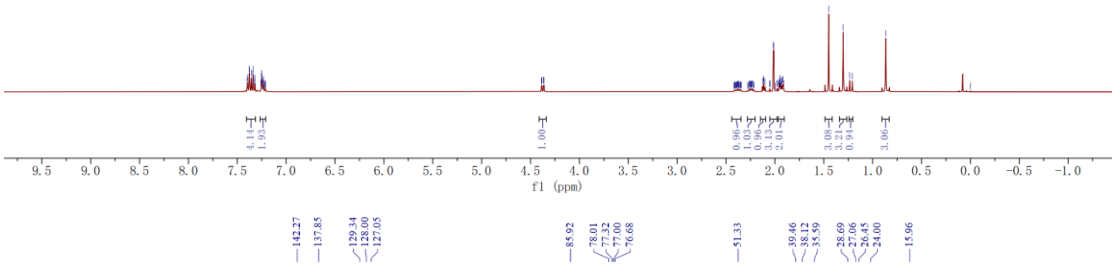
^{11}B NMR (128 MHz, $CDCl_3$)

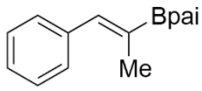




3s

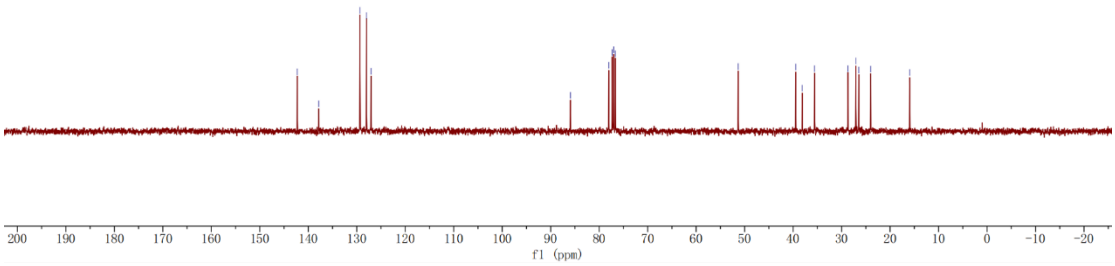
^{1}H NMR (400 MHz, $CDCl_3$)

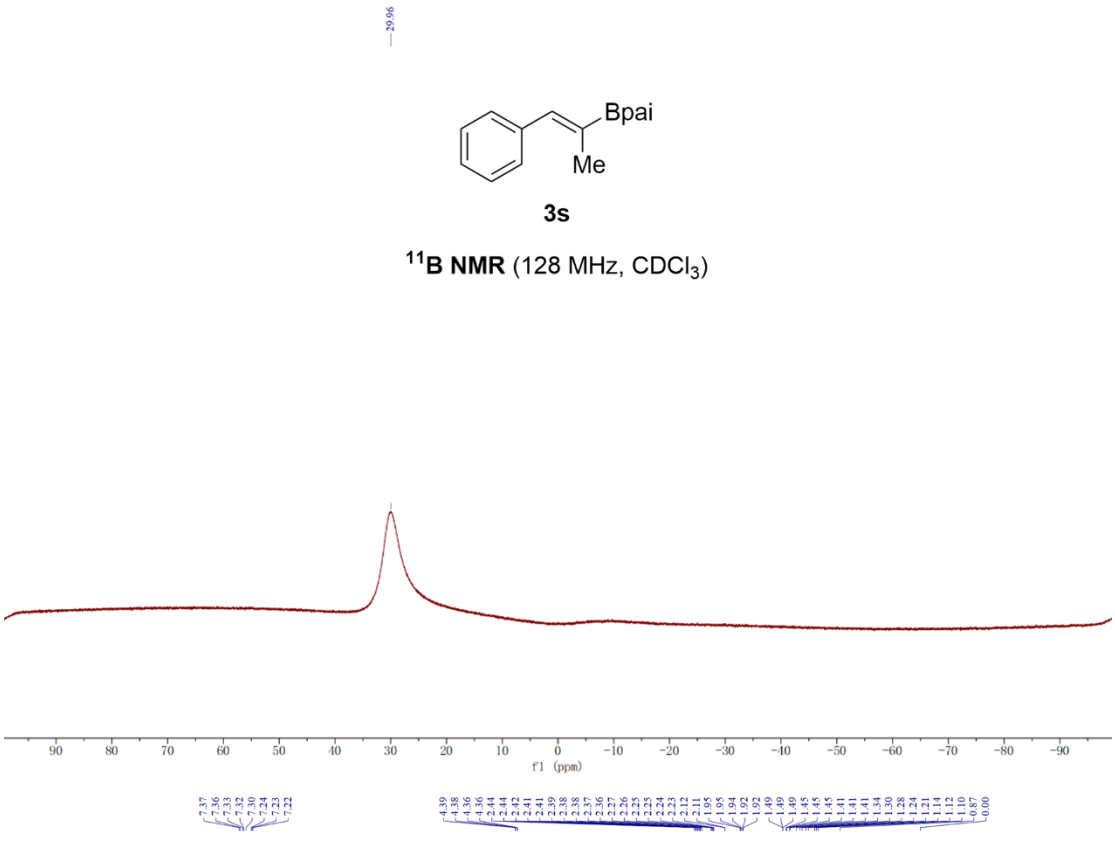




3s

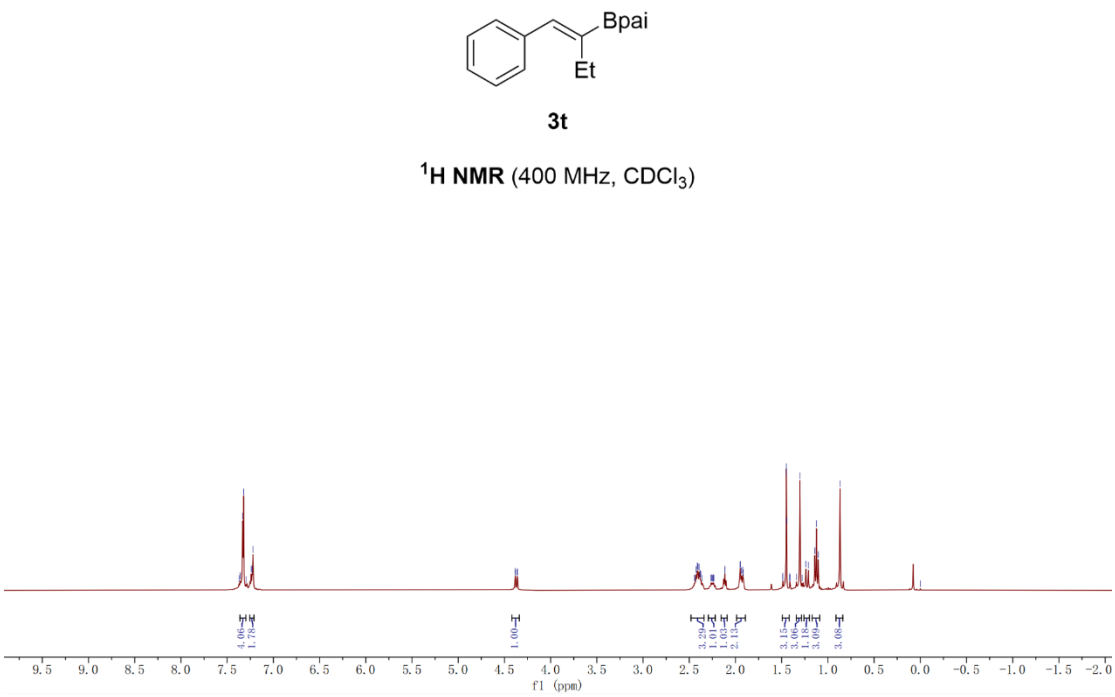
^{13}C NMR (101 MHz, $CDCl_3$)





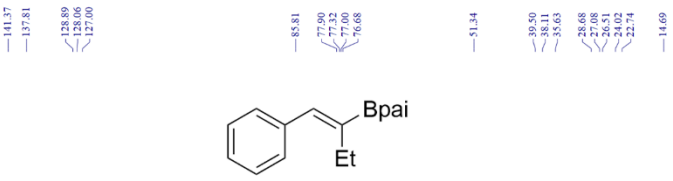
3s

^{11}B NMR (128 MHz, $CDCl_3$)



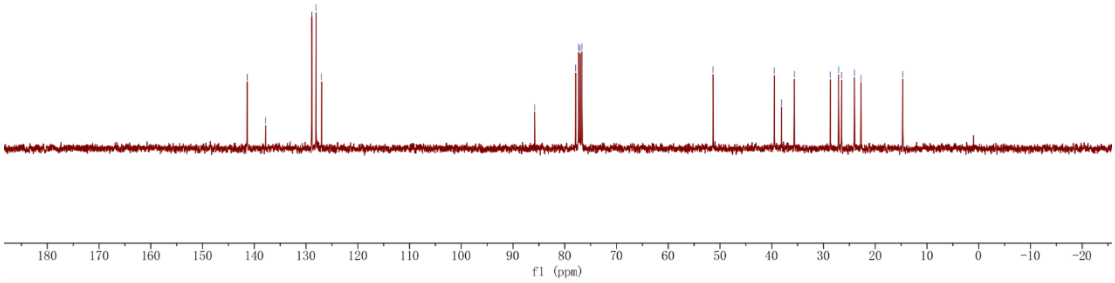
3t

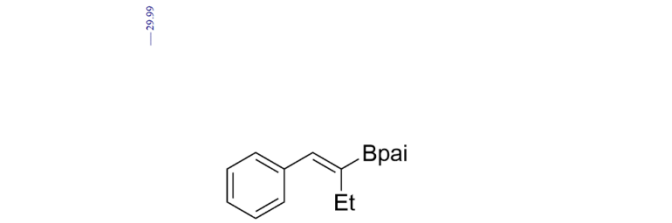
^{1}H NMR (400 MHz, $CDCl_3$)



3t

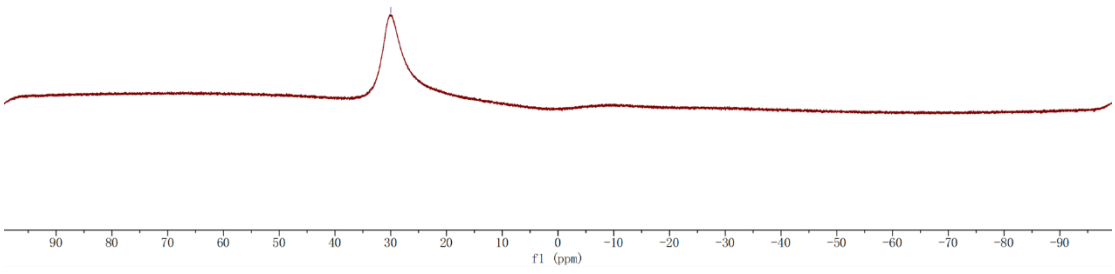
^{13}C NMR (101 MHz, $CDCl_3$)

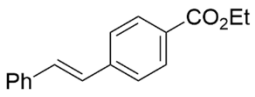




3t

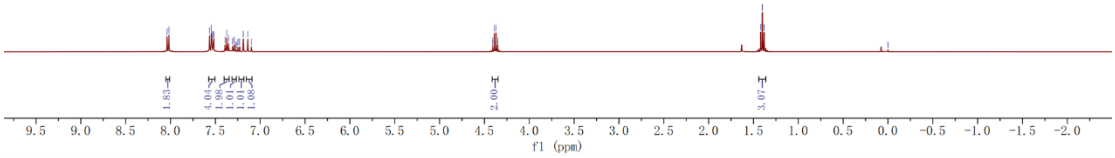
^{11}B NMR (128 MHz, $CDCl_3$)

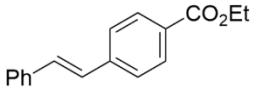




4

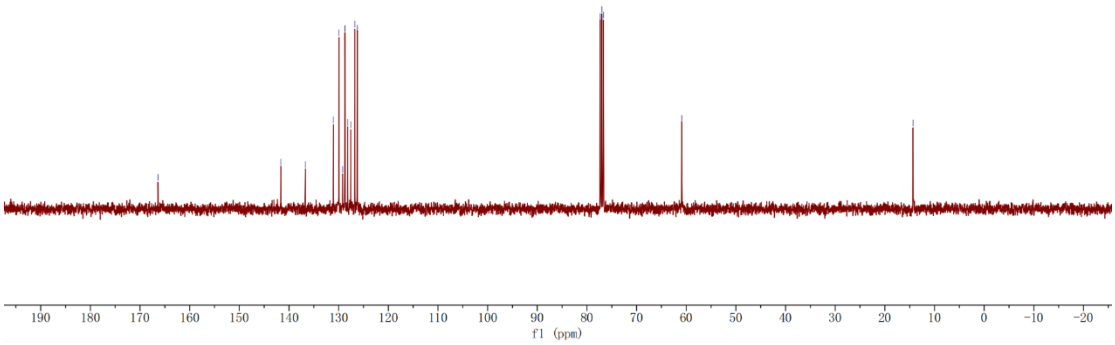
^{1}H NMR (400 MHz, $CDCl_3$)

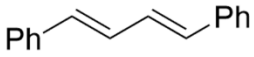




4

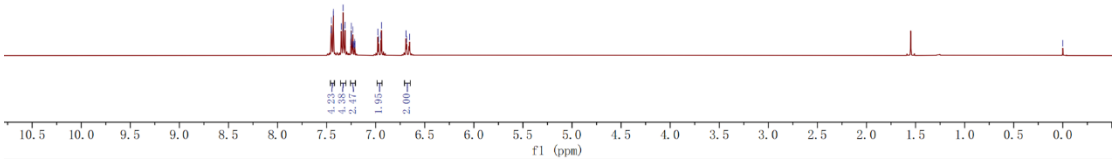
^{13}C NMR (101 MHz, $CDCl_3$)

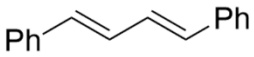




5

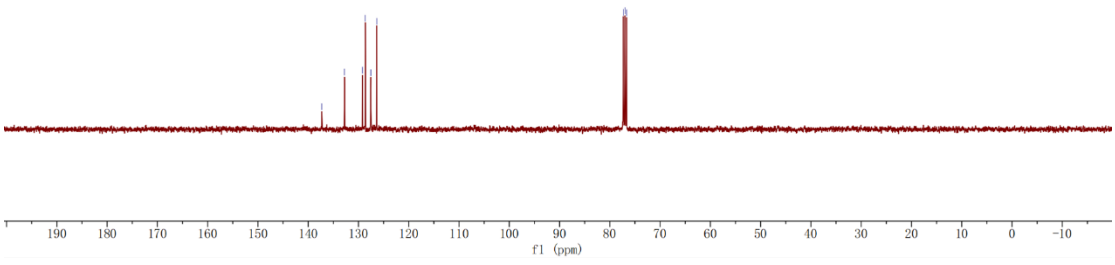
^{1}H NMR (400 MHz, $CDCl_3$)

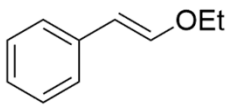




5

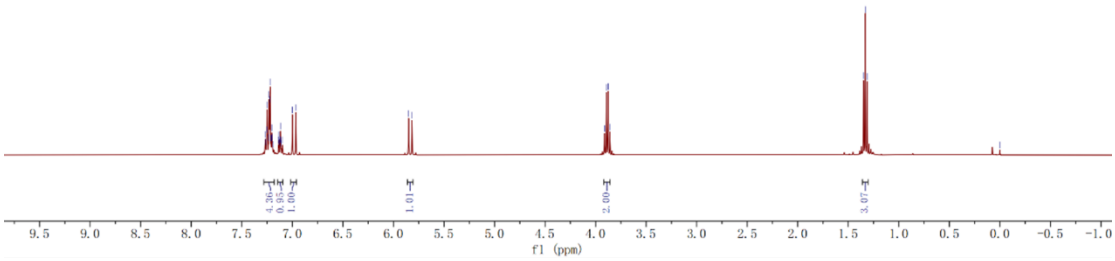
^{13}C NMR (101 MHz, $CDCl_3$)

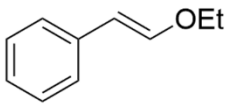




6

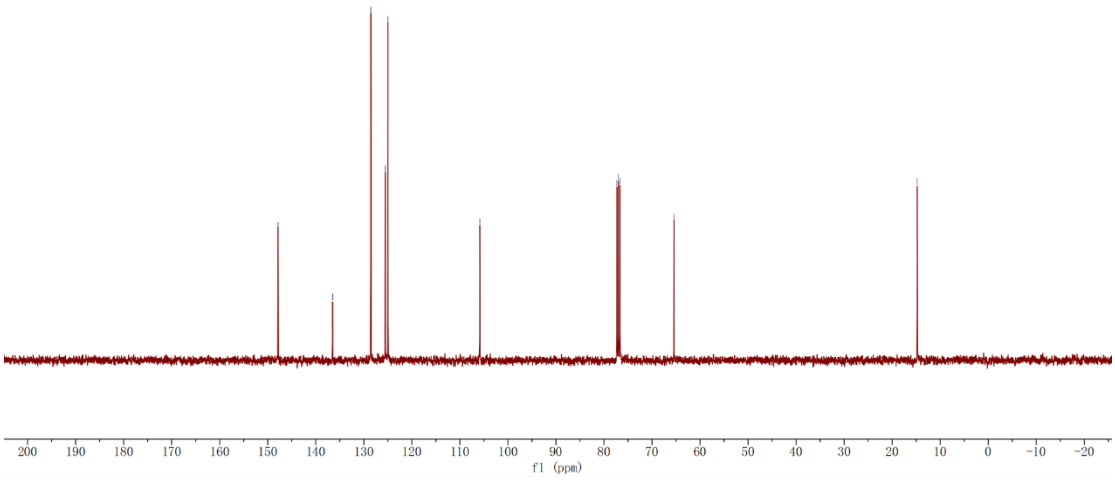
^{1}H NMR (400 MHz, $CDCl_3$)

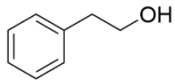




6

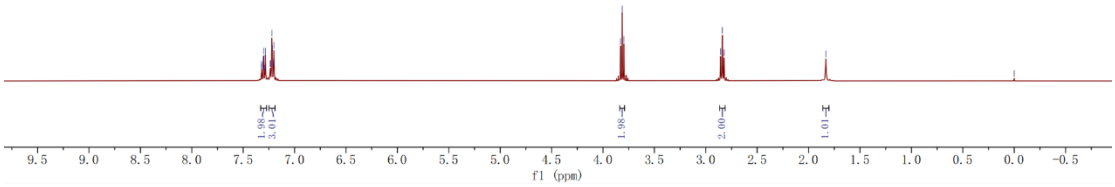
^{13}C NMR (101 MHz, $CDCl_3$)

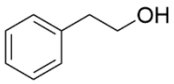




7

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





7

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