Supporting Information For:

Lewis Base/Alkali Metal Halide Co-catalyzed Allylic Alkylation of *gem*-Diborylalkanes with MBH Carbonates for the Construction of *tert*-Alkylboronic Esters

Zhen-Xu Yang,[a] Bing-Xia Yan,[a] Lei Shi,[a,*] Li-Dong Gong,[b,*] Zhi-Shi Ye[b,*]

[a]School of Chemistry, Dalian University of Technology, Dalian 116024, P. R. China
[b]School of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, 116029, P. R. China

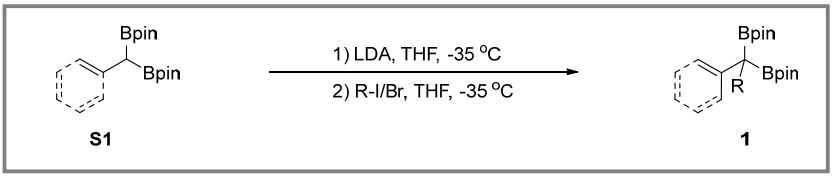
Table of Contents

1. General methods

All reactions were performed under an N_2 atmosphere with the standard Schlenk techniques, unless otherwise mentioned. Anhydrous diethyl ether, toluene and tetrahydrofuran were distilled over sodium benzophenone ketyl under nitrogen atmosphere. All other reagents were used as obtained from commercial sources without further purification. ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra were recorded at room temperature in $CDCl_3$ on Bruker AVANCE NEO 400 MHz spectrometers and Bruker AVANCE NEO 500 MHz spectrometers with tetramethylsilane (TMS) as internal standard. The high-resolution mass spectrometric detection was performed on a Q Exactive plus mass spectrometer (Thermo Scientific, Germany) equipped with a heated electrospray ionization (ESI) source and electrostatic field orbitrap mass analyzer. All X-ray crystallographic data were collected on a Bruker D8 Venture diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 120 (2) K. Flash column chromatography was performed on silica gel (200-300 mesh) using petroleum ether (PE, bp. 60-90 ºC), dichloromethane, ethyl acetate, triethylamine, and methanol as eluent. All reactions were monitored by TLC or NMR analysis.

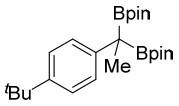
2. Representative procedures for synthesis of substrate 1

Substrates **1a-1b**, **1h-1i**, **1l**, **1p**[1], **1u**, **1y**, **1d′**[2], **1z**[3], **1k′**[4] were known compounds and all datas were in agreement with those reported literatures. Substrate **1k′** can be prepared according to the known literature procedures[4]. Compound **S1** can be prepared according to the known literature procedures[5,6]. Substrates **1a-1j′** were prepared according to the following method:



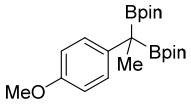
According to the reported procedures[7], under nitrogen atmosphere, a dried 50.0 mL reaction tube equipped with a magnetic stir bar was charged with **S1** (3.0 mmol, 1.0 equiv.) and anhydrous THF (20.0 mL). The reaction was cooled to -35 °C and stirred, followed by dropwise addition of LDA (3.3 mmol, 2M in THF, 1.1 equiv.) *via* syringe. The resulting mixture was maintained at -35 °C with vigorous stirring for 1 hour under nitrogen protection. Subsequently, the alkyl halide (3.6 mmol, 1.2 equiv.) was added dropwise, and the reaction was stirred at -35 °C for an additional 10 minutes. Upon completion (monitored by TLC), the reaction mixture was gradually warmed to room temperature and concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 50/1) on silica gel (200-300 mesh) to afford the desired compound **1**.

2,2′-(1-(4-(*tert*-Butyl)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1c):



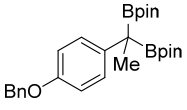
the reaction was conducted at 3.0 mmol scale from **S1**, 0.8266 g, 66% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 4H), 1.45 (s, 3H), 1.31 (s, 9H), 1.29-1.23 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.9, 142.3, 128.2, 125.1, 83.5, 34.4, 31.6, 24.86, 24.85, 19.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.53. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{24}H_{41}B_2O_4^+$ Calcd for 415.3185; Found 415.3181.

2,2′-(1-(4-Methoxyphenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1d):



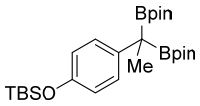
the reaction was conducted at 3.0 mmol scale from **S1**, 0.6755 g, 58% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 6.86-6.80 (m, 2H), 3.79 (s, 3H), 1.44 (s, 3H), 1.29-1.23 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9, 137.3, 129.2, 113.6, 83.4, 55.3, 24.8, 19.1. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.54. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{21}H_{35}B_2O_5^+$ Calcd for 389.2665; Found 389.2663.

2,2′-(1-(4-(Benzyloxy)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)



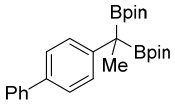
(1e): the reaction was conducted at 3.0 mmol scale from **S1**, 0.9345 g, 67% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 6.7 Hz, 2H), 7.44-7.38 (m, 2H), 7.35 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.32-7.25 (m, 2H), 6.95-6.88 (m, 2H), 5.05 (s, 2H), 1.45 (s, 3H), 1.32-1.19 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.2, 137.7, 137.6, 129.3, 128.7, 128.0, 127.7, 114.5, 83.5, 70.1, 24.8, 19.1. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.10. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{27}H_{39}B_2O_5^+$ Calcd for 465.2978; Found 465.2959.

(4-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenoxy)(*tert*-butyl)dimethyl-



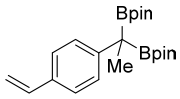
silane (1f): the reaction was conducted at 3.0 mmol scale from **S1**, 1.0716 g, 73% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23-7.14 (m, 2H), 6.77-6.68 (m, 2H), 1.42 (s, 3H), 1.30-1.20 (m, 24H), 0.99 (s, 9H), 0.19 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.7, 137.9, 129.3, 119.6, 83.4, 25.9, 24.81, 24.80, 19.5, 18.4, -4.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.35. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{26}H_{47}B_2O_5Si^+$ Calcd for 489.3373; Found 489.3362.

2,2′-(1-([1,1′-Biphenyl]-4-yl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1g):



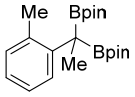
the reaction was conducted at 3.0 mmol scale from **S1**, 0.9639 g, 71% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.32 (t, *J* = 7.4 Hz, 1H), 1.53 (s, 3H), 1.37-1.19 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.5, 141.7, 137.2, 128.8, 128.7, 127.1, 126.8, 83.6, 24.8, 18.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.52. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{26}H_{37}B_2O_4^+$ Calcd for 435.2872; Found 435.2860.

2,2′-(1-(4-Vinylphenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1j): the



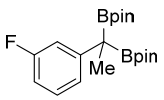
reaction was conducted at 3.0 mmol scale from **S1**, 0.5990 g, 52% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (s, 4H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.67 (d, *J* = 17.6 Hz, 1H), 5.13 (d, *J* = 10.9 Hz, 1H), 1.45 (s, 3H), 1.24-1.18 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.1, 137.3, 133.9, 128.4, 126.0, 112.2, 83.5, 24.8, 18.3. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.84. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{22}H_{35}B_2O_4^+$ Calcd for 385.2716; Found 385.2701.

2,2′-(1-(*o*-Tolyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1k): the reaction



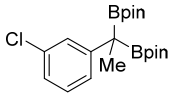
was conducted at 3.0 mmol scale from **S1**, 0.5917 g, 53% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.14-7.01 (m, 3H), 2.35 (s, 3H), 1.44 (s, 3H), 1.34-1.21 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.5, 137.2, 131.0, 129.2, 126.0, 125.3, 83.6, 25.2, 25.0, 21.4, 19.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.45. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{21}H_{35}B_2O_4^+$ Calcd for 373.2716; Found 373.2711.

2,2′-(1-(3-Fluorophenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1m):



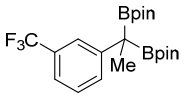
the reaction was conducted at 3.0 mmol scale from **S1**, 0.7224 g, 64% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.18 (m, 1H), 7.16-7.07 (m, 2H), 6.86-6.77 (m, 1H), 1.46 (s, 3H), 1.29-1.22 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{-}F}$ = 242.7 Hz), 147.9 (d, $J_{C\text{-}F}$ = 8.1 Hz), 129.0 (d, $J_{C\text{-}F}$ = 9.1 Hz), 123.9 (d, $J_{C\text{-}F}$ = 3.0 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.3 Hz), 111.3 (d, $J_{C\text{-}F}$ = 21.3 Hz), 83.7, 24.8, 18.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.06. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.97. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{20}H_{32}B_2FO_4^+$ Calcd for 377.2465; Found 377.2455.

2,2′-(1-(3-Chlorophenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1n): the

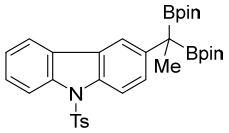


reaction was conducted at 3.0 mmol scale from **S1**, 0.7412 g, 69% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 1.9 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.12-

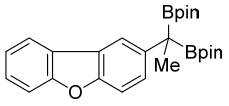
7.06 (m, 1H), 1.45 (s, 3H), 1.27-1.23 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 133.8, 129.0, 128.1, 126.9, 124.7, 83.7, 24.81, 24.77, 18.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.98. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{20}H_{32}B_2ClO_4^+$ Calcd for 393.2170; Found 393.2160.

2,2′-(1-(3-(Trifluoromethyl)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1o): 

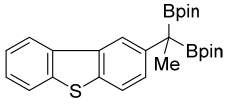
the reaction was conducted at 3.0 mmol scale from **S1**, 0.6519 g, 51% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.58-7.52 (m, 1H), 7.40-7.35 (m, 2H), 1.49 (s, 3H), 1.25 (s, 12H), 1.24 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.2, 132.0, 130.0 (q, $J_{C\text{-}F}$ = 31.5 Hz), 128.2, 125.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.8 (q, $J_{C\text{-}F}$ = 272.2 Hz), 121.4 (q, $J_{C\text{-}F}$ = 4.0 Hz), 83.8, 24.8, 24.7, 18.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.36. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.44. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{21}H_{32}B_2F_3O_4^+$ Calcd for 427.2433; Found 427.2455.

3-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-9-tosyl-9*H*-carbazole (1q): 

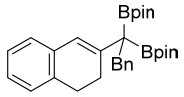
the reaction was conducted at 3.0 mmol scale from **S1**, 1.5544 g, 78% yield, white solid, new compound, yellow foam solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.7 Hz, 1H), 7.93-7.82 (m, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.53 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 2.28 (s, 3H), 1.55 (s, 3H), 1.33-1.22 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.7, 141.4, 138.7, 136.2, 135.4, 129.8, 129.0, 127.2, 126.9, 126.7, 126.4, 123.7, 120.0, 119.1, 115.2, 114.7, 83.7, 24.9, 24.8, 21.7, 19.4. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.02. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{33}H_{42}B_2NO_6S^+$ Calcd for 602.2913; Found 602.2903.

2,2′-(1-(Dibenzo[*b*,*d*]furan-2-yl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1r): 

the reaction was conducted at 3.0 mmol scale from **S1**, 1.0353 g, 77% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.90 (m, 2H), 7.59-7.40 (m, 4H), 7.36-7.29 (m, 1H), 1.59 (s, 3H), 1.37-1.20 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5, 154.2, 139.8, 128.6, 126.6, 125.1, 124.0, 122.4, 120.6, 119.4, 111.7, 111.0, 83.6, 24.84, 24.81, 19.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.83. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{26}H_{35}B_2O_5^+$ Calcd for 449.2665; Found 449.2653.

2,2′-(1-(Dibenzo[*b*,*d*]thiophen-2-yl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1s): 

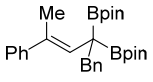
the reaction was conducted at 3.0 mmol scale from **S1**, 1.0305 g, 74% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.90-7.82 (m, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.55 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.47-7.38 (m, 2H), 1.61 (s, 3H), 1.29-1.28 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.7, 139.9, 136.2, 135.7, 135.6, 128.6, 126.3, 124.2, 123.0, 122.1, 121.5, 120.5, 83.6, 24.9, 24.8, 18.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.48. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{26}H_{35}B_2O_4S^+$ Calcd for 465.2437; Found 465.2426.

2,2′-(1-(3,4-Dihydronaphthalen-2-yl)-2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1t): 

the reaction was conducted at 2.0 mmol scale from **S1**, 0.4090 g, 42% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.5 Hz, 2H), 7.18-6.99 (m, 6H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.39 (s, 1H), 3.27 (s, 2H), 2.68 (t, *J* = 7.9 Hz, 2H), 2.30 (t, *J* = 8.0 Hz, 2H), 1.20

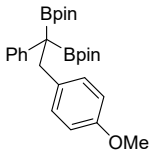
(s, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) 142.9, 142.1, 136.0, 134.9, 129.8, 127.7, 126.8, 126.2, 125.9, 125.7, 125.6, 124.4, 83.6, 36.7, 28.9, 28.8, 25.1, 24.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.95. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{30}H_{41}B_2O_4^+$ Calcd for 487.3185; Found 487.3172.

(*E*)-2,2'-(1,4-Diphenylpent-3-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1u):



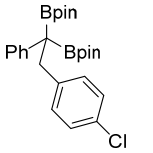
the reaction was conducted at 3.0 mmol scale from **S1**, 0.6630 g, 47% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 2H), 7.28-7.22 (m, 4H), 7.21-7.08 (m, 4H), 6.15 (s, 1H), 3.21 (s, 1H), 2.17-1.94 (m, 3H), 1.31-1.14 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.8, 142.3, 136.8, 130.5, 130.0, 128.0, 127.7, 126.4, 126.2, 125.7, 83.8, 38.2, 25.3, 24.9, 18.3. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.06. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{29}H_{41}B_2O_4^+$ Calcd for 475.3185; Found 475.3179.

2,2′-(2-(4-Methoxyphenyl)-1-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1w):



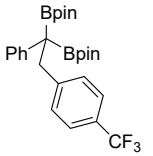
the reaction was conducted at 3.0 mmol scale from **S1**, 0.7272 g, 52% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.25-7.20 (m 2H), 7.17-7.11 (m, 1H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 8.5 Hz, 2H), 3.66 (s, 3H), 3.23 (s, 2H), 1.38-1.24 (m 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.5, 142.5, 133.7, 130.8, 130.7, 127.8, 124.9, 112.6, 83.5, 55.1, 39.2, 25.0, 24.6. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.94. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{27}H_{39}B_2O_5^+$ Calcd for 465.2978; Found 465.2967.

2,2′-(2-(4-Chlorophenyl)-1-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1x):



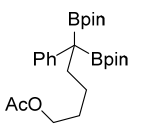
the reaction was conducted at 3.0 mmol scale from **S1**, 0.3361 g, 24% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23-7.14 (m, 4H), 7.13-7.07 (m, 1H), 7.05-6.98 (m, 2H), 6.81-6.73 (m, 2H), 3.24 (s, 2H), 1.30-1.22 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.1, 140.2, 131.33, 131.25, 130.9, 128.1, 127.4, 125.3, 83.9, 39.6, 25.1, 24.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.06. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{26}H_{36}B_2ClO_4^+$ Calcd for 469.2483; Found 469.2479.

2,2′-(1-Phenyl-2-(4-(trifluoromethyl)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1y):



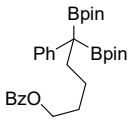
the reaction was conducted at 3.0 mmol scale from **S1**, 0.4518 g, 30% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.20-7.12 (m, 4H), 7.11-7.05 (m, 1H), 6.97-6.90 (m, 2H), 3.33 (s, 2H), 1.28-1.20 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.0, 141.9, 130.8, 130.2, 128.1, 127.8 (q, $J_{C\text{-}F}$ = 32.0 Hz), 125.4, 124.7 (q, $J_{C\text{-}F}$ = 271.8 Hz), 124.2 (q, $J_{C\text{-}F}$ = 3.7 Hz), 83.9, 40.0, 25.1, 24.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.99. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.18. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{27}H_{36}B_2F_3O_4^+$ Calcd for 503.2746; Found 503.2736.

5-Phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl acetate (1ba′):

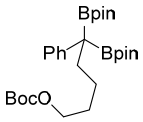


the reaction was conducted at 3.0 mmol scale from **S1**, 0.4372 g, 32% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 2H), 7.25-7.19 (m, 2H), 7.13-7.05 (m, 1H), 3.97 (t, *J* = 6.8 Hz, 2H), 2.01-1.90 (m, 5H), 1.57-1.53 (m, 2H), 1.27-1.14 (m, 26H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 143.2, 130.1, 128.2, 125.0, 83.6, 64.8, 34.0, 29.2, 24.9, 24.3, 21.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.60. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{25}H_{41}B_2O_6^+$ Calcd for 459.3084; Found 459.3081.

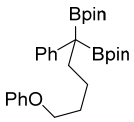
5-Phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl benzoate (1c′): the reaction was conducted at 3.0 mmol scale from **S1**, 0.4752 g, 30% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (q, *J* = 1.5 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42-7.33 (m, 4H), 7.24-7.19 (m, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 4.23 (t, *J* = 6.6 Hz, 2H), 2.04-1.96 (m, 2H), 1.69 (t, *J* = 7.2 Hz, 2H), 1.30-1.18 (m, 26H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 143.2, 132.9, 130.8, 130.2, 129.8, 128.4, 128.2, 125.0, 83.6, 65.3, 34.1, 29.4, 24.90, 24.85, 24.5. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.56. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{30}H_{43}B_2O_6^+$ Calcd for 521.3240; Found 521.3238.



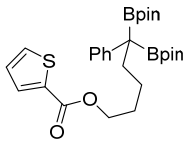
***tert*-Butyl (5-phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl) carbonate (1d′)**: the reaction was conducted at 3.0 mmol scale from **S1**, 0.7923 g, 51% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 2H), 7.24-7.18 (m, 2H), 7.12-7.04 (m, 1H), 3.96 (t, *J* = 7.1 Hz, 2H), 1.99-1.89 (m, 2H), 1.60-1.58 (m, 2H), 1.45 (s, 9H), 1.27-1.15 (m, 26H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.9, 143.1, 130.1, 128.2, 125.0, 83.6, 81.7, 67.4, 34.0, 29.4, 28.0, 24.9, 24.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.95. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{28}H_{47}B_2O_7^+$ Calcd for 517.3502; Found 517.3495.



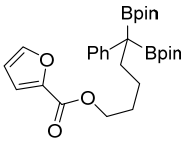
2,2′-(5-Phenoxy-1-phenylpentane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1f′): the reaction was conducted at 3.0 mmol scale from **S1**, 0.7923 g, 51% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 2H), 7.26-7.17 (m, 4H), 7.12-7.06 (m, 1H), 6.89 (t, *J* = 7.3 Hz, 1H), 6.85-6.80 (m, 2H), 3.86 (t, *J* = 6.7 Hz, 2H), 2.03-1.95 (m, 2H), 1.75-1.67 (m, 2H), 1.29-1.20 (m, 26H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 143.2, 134.6, 130.2, 129.5, 128.2, 124.9, 120.5, 114.7, 83.6, 68.0, 34.1, 30.0, 24.9, 24.5. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.90. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{29}H_{43}B_2O_5^+$ Calcd for 493.3291; Found 493.3290.

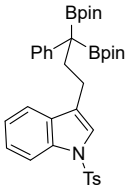


5-Phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl thiophene-2-carboxylate (1g′): the reaction was conducted at 3.0 mmol scale from **S1**, 0.7272 g, 46% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.51 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.38-7.34 (m, 2H), 7.23-7.19 (m, 2H), 7.11-7.05 (m, 2H), 4.21 (t, *J* = 6.7 Hz, 2H), 2.02-1.96 (m, 2H), 1.71-1.64 (m, 2H), 1.27-1.21 (m, 26H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5, 143.2, 134.5, 133.3, 132.2, 130.1, 128.2, 127.8, 124.9, 83.5, 65.5, 34.0, 29.4, 24.9, 24.8, 24.4. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.85. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{28}H_{41}B_2O_6S^+$ Calcd for 527.2804; Found 527.2800.

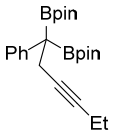


5-Phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl furan-2-carboxylate (1h′): the reaction was conducted at 3.0 mmol scale from **S1**, 0.6024 g, 39% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.23-7.18 (m, 2H), 7.11-7.05 (m, 2H), 6.47 (dd, *J* = 3.7, 1.9 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 2.01-1.95 (m, 2H), 1.71-1.64 (m, 2H), 1.26-1.21 (m, 26H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 146.2, 145.2, 143.2, 130.1, 128.2, 124.9, 117.7, 111.9, 83.6, 65.3, 34.0, 29.3, 24.9, 24.8, 24.4. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.19. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{28}H_{41}B_2O_7^+$ Calcd for 511.3033; Found 511.3002.

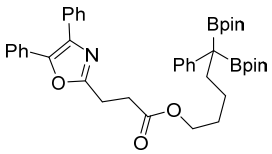


3-(3-Phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1-tosyl-1*H*-indole (1i′): 

the reaction was conducted at 3.0 mmol scale from **S1**, 0.9623 g, 50% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.46-7.39 (m, 3H), 7.29-7.24 (m, 4H), 7.20-7.13 (m, 4H), 2.50-2.41 (m, 2H), 2.32 (s, 3H), 2.28-2.21 (m, 2H), 1.30-1.22 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.7, 143.0, 135.5, 131.7, 130.3, 130.0, 128.4, 127.0, 125.3, 124.5, 124.4, 122.9, 122.6, 120.2, 113.7, 83.7, 34.5, 25.0, 24.9, 23.6, 21.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.76. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{36}H_{46}B_2NO_6S^+$ Calcd for 642.3226; Found 642.3220.

2,2′-(1-Phenylhex-3-yne-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1j′): 

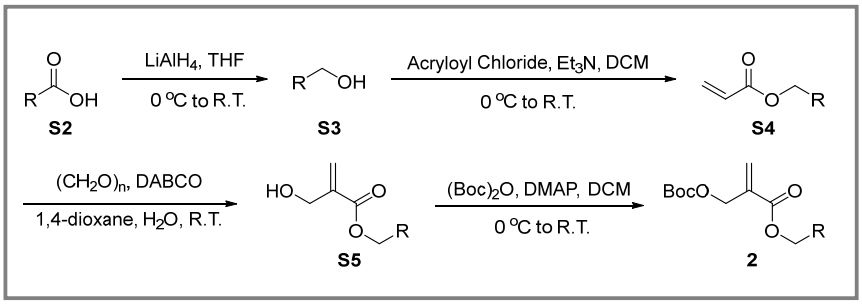
the reaction was conducted at 3.0 mmol scale from **S1**, 0.6782 g, 55% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 2.72 (s, 2H), 2.12-2.00 (m, 2H), 1.31-1.18 (m, 24H), 1.02 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.4, 129.8, 127.9, 125.1, 83.8, 82.3, 79.9, 24.9, 24.8, 23.6, 14.4, 12.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.73. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{24}H_{37}B_2O_4^+$ Calcd for 411.2872; Found 411.2859.

5-Phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl 3-(4,5-diphenyloxazol-2-yl) propanoate (1k′): 

the reaction was conducted at 3.0 mmol scale from **S1**, 0.8288 g, 40% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65-7.61 (m, 2H), 7.58-7.54 (m, 2H), 7.37-7.29 (m, 8H), 7.24-7.19 (m, 2H), 7.10-7.04 (m, 1H), 4.04 (t, *J* = 6.9 Hz, 2H), 3.12 (dd, *J* = 8.6, 6.7 Hz, 2H), 2.82 (dd, *J* = 8.6, 6.7 Hz, 2H), 2.00-1.90 (m, 2H), 1.57 (t, *J* = 7.2 Hz, 2H), 1.27-1.19 (m, 26H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 162.0, 145.6, 143.1, 135.3, 132.7, 130.2, 129.2, 128.8, 128.7, 128.6, 128.21, 128.16, 128.1, 126.7, 125.0, 83.6, 65.2, 34.0, 31.4, 29.2, 24.9, 24.3, 23.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.06. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{41}H_{52}B_2NO_7^+$ Calcd for 692.3924; Found 692.3919.

3. Representative procedures for synthesis of substrate 2

Substrates **2a**[8], **2b**[9], **2c**[10], **2d**[11], **2e**[12], **2a-OAc**, **2b-OAc**[13] were known compounds and all datas were in agreement with those reported literatures. Substrates **2h** is commercially available. Compound **S3**-**S5** can be prepared according to the known literature procedures[13-16]. Substrates **2f**-**2g** were prepared according to the following method:



According to the reported procedures[14], under nitrogen atmosphere, a dried 100.0 mL reaction tube equipped with a magnetic stir bar was charged with **S2** (20.0 mmol, 1.0 equiv.) and anhydrous THF (40.0 mL). The reaction was cooled to 0 °C and stirred, followed slowly addition of $LiAlH_4$ (30.0 mmol, 1.5 equiv.) stirring for 15 minutes under nitrogen protection. Then the reaction mixture was allowed to slowly warm to room temperature and stirred overnight. Upon completion (monitored by TLC), the mixture was treated with 1M NH_4Cl (aq.) and extracted with EtOAc. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 10/1) on silica gel (200-300 mesh) to afford the desired compound **S3**.

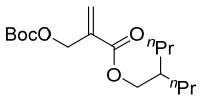
According to the reported procedures[15], under nitrogen atmosphere, a dried 100.0 mL reaction tube equipped with a magnetic stir bar was charged with **S3** (10.0 mmol, 1.0 equiv.), Et_3N (15.0 mmol, 1.5 equiv.) and anhydrous DCM (20.0 mL). The reaction was cooled to 0 °C and stirred, followed by dropwise addition of acryloyl chloride (12.0 mmol, 1.2 equiv.) *via* syringe. The reaction mixture was stirred for 15 minutes at 0 °C and allowed to slowly warm to room temperature. Then the resulting reaction mixture was stirred for an additional 3 hours. Upon completion (monitored by TLC), the mixture was gradually warmed to room temperature and concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 50/1) on silica gel (200-300 mesh) to afford the desired compound **S4**.

According to the reported procedures[16], under air atmosphere, a 50.0 mL reaction tube equipped with a magnetic stir bar was charged with **S4** (5.0 mmol, 1.0 equiv.), DABCO (5.0 mmol, 1.0 equiv.) and $(CH_2O)_n$ (15.0 mmol, 3.0 equiv.). 1,4-dioxane (10.0 mL) and water (10.0 mL) were added as solvent, and then the resulting reaction mixture was stirred at room temperature for 1 week. Upon completion (monitored by TLC), the mixture was extracted with EtOAc. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 10/1) on silica gel (200-300 mesh) to afford the desired compound **S5**.

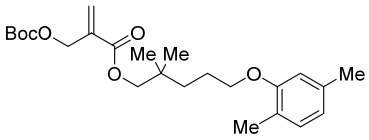
According to the reported procedures[17], under nitrogen atmosphere, a dried 25.0 mL reaction tube equipped with a magnetic stir bar was charged with **S5** (2.0 mmol, 1.0 equiv.), DMAP (0.2 mmol, 0.1 equiv.), and DCM (10.0 mL). The reaction was cooled to 0 °C and stirred, followed by dropwise addition of the solution of $(Boc)_2O$ (2.2 mmol, 0.5M in DCM, 1.1 equiv.) *via* syringe. The reaction mixture was stirred for 15 minutes under nitrogen protection and allowed to slowly

warm to room temperature. Then the resulting reaction mixture was stirred for an additional 3 hours. Upon completion (monitored by TLC), the mixture concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 100/1) on silica gel (200-300 mesh) to afford the desired compound **2**.

2-Propylpentyl 2-(((*tert*-butoxycarbonyl)oxy)methyl)acrylate (2f): the reaction was conducted at 2.0 mmol scale from **S5**, 0.3127 g, 50% yield, new compound, colorless liquid, R_f = 0.2 (PE/EtOAc 100/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.36 (d, *J* = 1.1 Hz, 1H), 5.87 (d, *J* = 1.3 Hz, 1H), 4.80 (t, *J* = 1.3 Hz, 2H), 4.09 (d, *J* = 5.6 Hz, 2H), 1.76-1.70 (m, 1H), 1.50 (s, 9H), 1.36-1.27 (m, 8H), 0.93-0.86 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 153.3, 135.6, 127.5, 82.7, 68.0, 65.0, 37.0, 33.8, 28.0, 20.1, 14.6. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{17}H_{31}O_5^+$ Calcd for 315.2166; Found 315.2175.

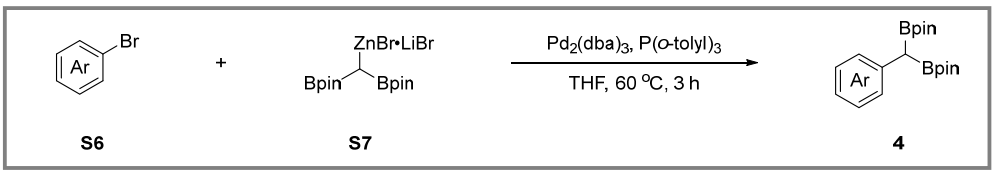


5-(2,5-Dimethylphenoxy)-2,2-dimethylpentyl 2-(((*tert*-butoxycarbonyl)oxy)methyl)acrylate (2g): the reaction was conducted at 2.0 mmol scale from **S5**, 0.0943 g, 22% yield, new compound, colorless liquid, R_f = 0.2 (PE/EtOAc 100/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.4 Hz, 1H), 6.61 (s, 1H), 6.39 (d, *J* = 1.2 Hz, 1H), 5.88 (t, *J* = 1.4 Hz, 1H), 4.80 (t, *J* = 1.3 Hz, 2H), 3.96-3.89 (m, 4H), 2.30 (s, 3H), 2.16 (s, 3H), 1.82-1.73 (m, 2H), 1.51-1.42 (m, 11H), 0.99 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 157.2, 153.3, 136.7, 135.5, 130.5, 127.7, 123.7, 120.9, 112.1, 82.7, 73.0, 68.4, 65.0, 35.7, 34.0, 27.9, 24.5, 24.3, 21.6, 16.0. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{24}H_{37}O_6^+$ Calcd for 421.2585; Found 421.2577.



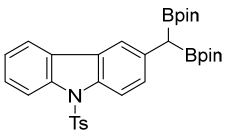
4. Representative procedures for synthesis of substrate 4

Substrates **4a-4b**, **4d**, **4f-4i**, **4k-4l**, **4p**, **4s**[5], **4c**[18], **4e**[19], **4j**, **4m**, **4o**[20], **4n**[21] were known compounds and all datas were in agreement with those reported literatures. Compound **S7** can be prepared according to the known literature procedures[5]. Substrates **4a-4s** were prepared according to the following method:



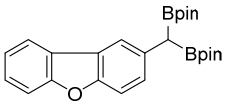
According to the reported procedures[5], in the nitrogen filled glovebox, a dried 100.0 mL Schlenk tube equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (0.1 mmol, 1.0 mol%), P(*o*-tolyl)$_3$ (0.2 mmol, 2.0 mol%), and anhydrous THF (10.0 mL). Then, the Schlenk tube was removed from the glovebox and stirred for 10 minutes, followed by the addition of aryl bromides **S6** (10.0 mmol, 1.0 equiv.); the mixture was then stirred for another 10 minutes under nitrogen protection. Subsequently, the organozinc reagent **S7** (15.0 mmol, 1M in THF, 1.5 equiv.) was added directly, and the reaction was stirred in 60 °C oil bath for 3 hours. Upon completion (monitored by TLC), the mixture was allowed to slowly cool to room temperature, followed by concentration under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 50/1) on silica gel (200-300 mesh), and recrystallized using PE at -35 °C to afford the desired compound **4**.

3-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-9-tosyl-9*H*-carbazole (4q): the



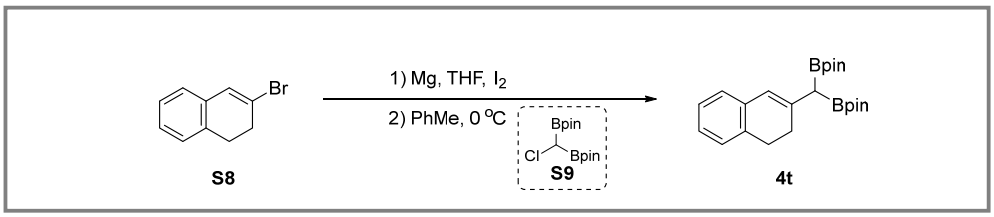
reaction was conducted at 10.0 mmol scale from **S6**, 4.6388 g, 79% yield, new compound, yellow foam solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 1.9 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.48-7.40 (m, 2H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 1H), 2.28 (s, 3H), 1.26 (s, 12H), 1.24 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.8, 138.7, 136.1, 135.5, 135.4, 129.7, 129.3, 127.1, 127.0, 126.8, 126.6, 123.8, 120.3, 120.2, 115.3, 114.8, 83.7, 24.9, 24.8, 21.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.69. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{32}H_{40}B_2NO_6S^+$ Calcd for 588.2757; Found 588.2749.

2,2′-(Dibenzo[*b*,*d*]furan-2-ylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4r): the



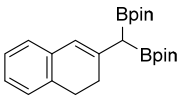
reaction was conducted at 10.0 mmol scale from **S6**, 1.7365 g, 40% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.45-7.35 (m, 3H), 7.33-7.27 (m, 1H), 2.46 (s, 1H), 1.29-1.18 (m, 24H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5, 154.3, 134.0, 128.8, 126.7, 124.9, 124.2, 122.5, 120.84, 120.80, 111.7, 111.1, 83.7, 24.9, 24.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.78. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{25}H_{33}B_2O_5^+$ Calcd for 435.2509; Found 435.2501.

Compound **S8**[22] and **S9**[6] can be prepared according to the known literature procedures. Substrates **4t** were prepared according to the following method:



According to the reported procedures[6], under nitrogen atmosphere, a dried 100.0 mL three-neck flask equipped with a magnetic stir bar and a constant-pressure dropping funnel was charged with Mg turnings (12.0 mmol, 1.2 equiv.) and I_2 (a crystal). Alkenyl bromide **S8** (10.0 mmol, 1.0 equiv.) dissolved in THF (10.0 mL) was added slowly (a small part and when the reaction started all the solution) from the dropping funnel. Then the reaction was stirred at room temperature for 1 hour. Under nitrogen atmosphere, a separate dried 100.0 mL reaction tube equipped with a magnetic stir bar was charged with **S9** (10.0 mmol, 1.0 equiv.) and PhMe (10.0 mL). The reaction was cooled to 0 °C and stirred, followed by dropwise addition of the reaction mixture in three-neck flask *via* syringe. Then the resulting reaction mixture was stirred at 0 °C for an additional 3 hours. Upon completion (monitored by TLC), the mixture was allowed to slowly warm to room temperature, followed by concentration under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc) on silica gel (200-300 mesh), and recrystallized using PE at -35 °C to afford the desired substrate **4t**.

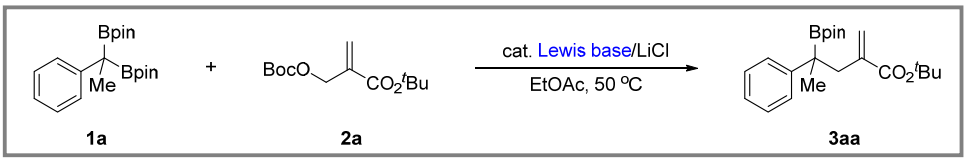
2,2′-((3,4-Dihydronaphthalen-2-yl)methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)



(4t): the reaction was conducted at 10.0 mmol scale from **S8**, 1.4772 g, 37% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11-6.99 (m, 3H), 6.93 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.26 (s, 1H), 2.78 (t, *J* = 8.1 Hz, 2H), 2.38 (t, *J* = 7.4 Hz, 2H), 1.95 (s, 1H), 1.26-1.22 (m, 24H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.7, 136.1, 134.6, 127.1, 126.4, 125.5, 125.3, 121.8, 83.5, 29.6, 28.8, 25.1, 24.8. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.99. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{23}H_{35}B_2O_4^+$ Calcd for 397.2716; Found 397.2711.

5. Optimization of the conditions of 3aa

Table S1: **Lewis base screening**[a]

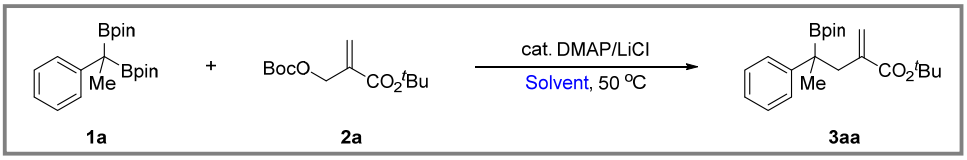


1a **2a** **3aa**

Entry	Lewis base	**3aa** Yield (%)[b]
1	DABCO	30
2	PPh_3	<5
3	PCy_3	15
4	$P(^tBu)_3$	20
5	$^iPr_2NEt$	<5
6	**DMAP**	**52**
7	DBU	14

[a] **1a** (0.10 mmol), **2a** (0.20 mmol), Lewis base (10.0 mol%), LiCl (10.0 mol%), EtOAc (2.0 mL), 50 °C, 16 h. [b] NMR yields (1,3,5-trimethoxybenzene as internal standard).

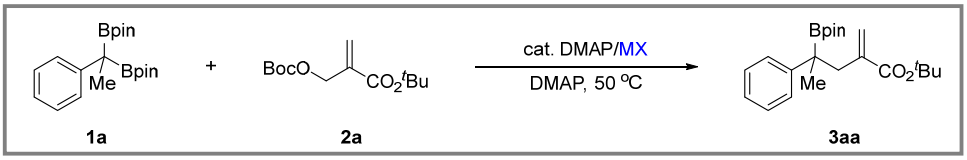
Table S2: **Solvent screening**[a]



Entry	Solvent	**3aa** Yield (%)[b]
1	EtOAc	52
2	THF	19
3	1,4-dioxane	<5
4	2-MeTHF	12
5	CPME	<5
6	DME	24
7	PhCl	<5
8	PhF	11
9	PhMe	<5
9	DCE	<5
11	DCM	<5
12	MeCN	21
13	**DMF**	**78**

[a] **1a** (0.10 mmol), **2a** (0.20 mmol), DMAP (10.0 mol%), LiCl (10.0 mol%), Solvent (2.0 mL), 50 °C, 16 h. [b] NMR yields (1,3,5-trimethoxybenzene as internal standard).

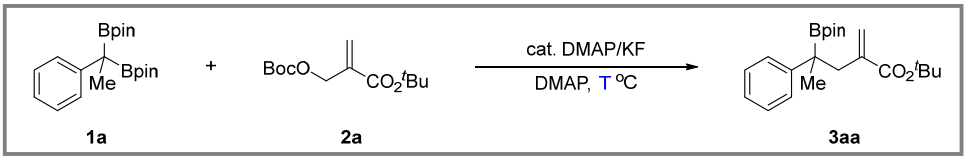
Table S3: **MX screening**[a]



Entry	MX	**3aa** Yield (%)[b]
1	LiCl	78
2	NaF	70
3	**KF**	**84**
4	KBr	66
5	KI	58
6	-	48

[a] **1a** (0.10 mmol), **2a** (0.20 mmol), DMAP (10.0 mol%), MX (10.0 mol%), DMF (2.0 mL), 50 °C, 16 h. [b] NMR yields (1,3,5-trimethoxybenzene as internal standard).

Table S4: Temperature screening[a]

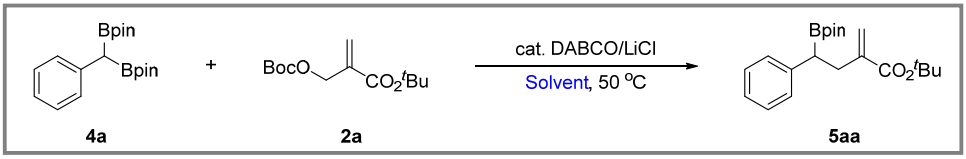


Entry	**T** (°C)	**3aa** Yield (%)[b]
1	50	84
2	40	80
3	**60**	**87**
4	70	82
5	25	66

[a] **1a** (0.10 mmol), **2a** (0.20 mmol), DMAP (10.0 mol%), KF (10.0 mol%), DMF (2.0 mL), T °C, 16 h.
[b] NMR yields (1,3,5-trimethoxybenzene as internal standard).

6. Optimization of the conditions of 5aa

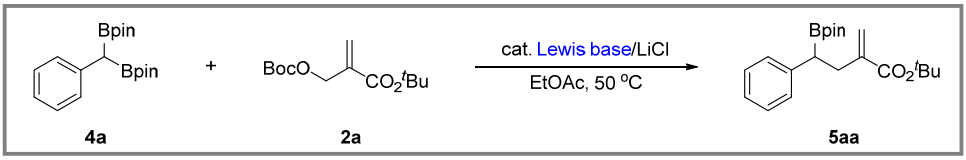
Table S5: **Solvent screening**[a]



Entry	Solvent	**5aa** Yield (%)[b]
1	DMF	35
2	DME	84
3	THF	82
4	1,4-dioxane	50
5	2-MeTHF	78
6	CPME	36
7	PhMe	32
8	PhCl	44
9	$PhCF_3$	34
10	**EtOAc**	**90**
11	DCE	39
12	DCM	32
13	MeCN	62
14	DMSO	<5

[a] **4a** (0.10 mmol), **2a** (0.20 mmol), DABCO (10.0 mol%), LiCl (10.0 mol%), Solvent (2.0 mL), 50 °C, 16 h. [b] NMR yields (1,3,5-trimethoxybenzene as internal standard).

Table S6: Lewis base screening[a]



Entry	Lewis base	**5aa** Yield (%)[b]
1	**DABCO**	**90**
2	PPh_3	<5
3	DMAP	15
4	Et_3N	<5
5	$^{i}Pr_2NEt$	<5
6	DBU	<5

[a] **4a** (0.10 mmol), **2a** (0.20 mmol), Lewis base (10.0 mol%), LiCl (10.0 mol%), EtOAc (2.0 mL), 50 °C, 16 h. [b] NMR yields (1,3,5-trimethoxybenzene as internal standard).

Table S7: MX screening[a]

Entry	MX	**5aa** Yield (%)[b]
1	**LiCl**	**90**
2	LiBr	67
3	LiI	65
4	KCl	56
5	KF	75
6	NaF	85
7	-	50

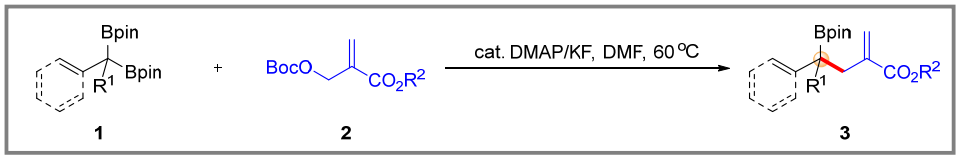
[a] **4a** (0.10 mmol), **2a** (0.20 mmol), DABCO (10.0 mol%), MX (10.0 mol%), EtOAc (2.0 mL), 50 °C, 16 h. [b] NMR yields (1,3,5-trimethoxybenzene as internal standard).

Table S8: Temperature screening[a]

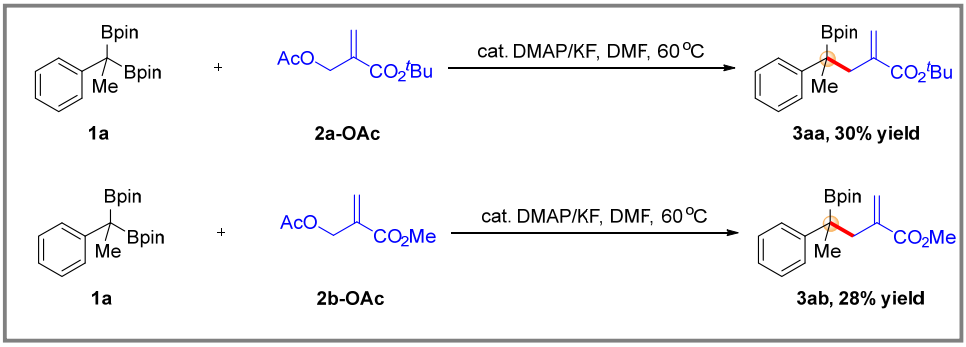
Entry	**T** (°C)	**5aa** Yield (%)[b]
1	**50**	**90**
2	40	84
3	60	85

[a] **4a** (0.10 mmol), **2a** (0.20 mmol), DABCO (10.0 mol%), LiCl (10.0 mol%), EtOAc (2.0 mL), T °C, 16 h. [b] NMR yields (1,3,5-trimethoxybenzene as internal standard).

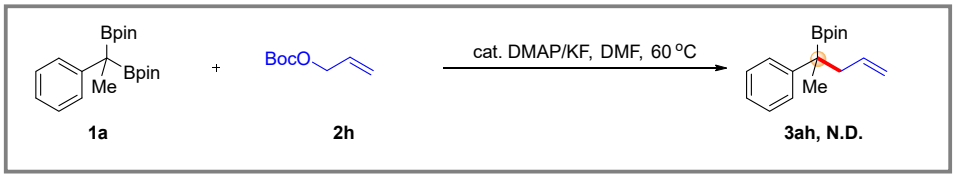
7. General procedure for synthesis of product 3



In the nitrogen filled glovebox, a dried 25.0 mL Schlenk tube was charged with DMAP (1.2 mg, 0.01 mmol, 10.0 mol%), KF (0.6 mg, 0.01 mmol, 10.0 mol%), **1** (0.10 mmol, 1.0 equiv.), **2** (0.20 mmol, 2.0 equiv.), and DMF (2.0 mL). Then, the Schlenk tube was removed from glovebox and stirred in a 60 °C oil bath. Upon completion (monitored by TLC), the mixture was allowed to slowly cool to room temperature, followed by concentration under reduced pressure in a 60 °C water bath. The crude product was purified by flash column chromatography (PE/EtOAc 60/1) on silica gel (200-300 mesh) to afford the target product **3**.



In the nitrogen filled glovebox, a dried 25.0 mL Schlenk tube was charged with DMAP (1.2 mg, 0.01 mmol, 10.0 mol%), KF (0.6 mg, 0.01 mmol, 10.0 mol%), **1a** (0.10 mmol, 1.0 equiv.), **2a-OAc** or **2b-OAc** (0.20 mmol, 2.0 equiv.), and DMF (2.0 mL). Then, the Schlenk tube was removed from glovebox and stirred in a 60 °C oil bath. Upon completion (monitored by TLC), the mixture was allowed to slowly cool to room temperature, followed by concentration under reduced pressure in a 60 °C water bath. The crude product was purified by flash column chromatography (PE/EtOAc 60/1) on silica gel (200-300 mesh) to afford the target product **3aa** and **3ab** in 30% and 28% yield.



In the nitrogen filled glovebox, a dried 25.0 mL Schlenk tube was charged with DMAP (1.2 mg, 0.01 mmol, 10.0 mol%), KF (0.6 mg, 0.01 mmol, 10.0 mol%), **1a** (0.10 mmol, 1.0 equiv.), **2h** (0.20 mmol, 2.0 equiv.), and DMF (2.0 mL). Then, the Schlenk tube was removed from glovebox and stirred in a 60 °C oil bath. Upon completion (monitored by TLC), the mixture was allowed to slowly cool to room temperature, followed by concentration under reduced pressure in a 60 °C water bath. The crude product was purified by flash column chromatography (PE/EtOAc 60/1) on silica gel (200-300 mesh), but the target product **3ah** was not isolated or detected.

***tert*-Butyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3aa)**: 31.9 mg, 86% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 4H), 7.18-7.07 (m, 1H), 5.98 (d, *J* = 2.0 Hz, 1H), 5.24 (d, *J* = 2.0 Hz, 1H), 2.98-2.80 (m, 1H), 2.82-2.70 (m, 1H), 1.40 (s, 9H), 1.31 (s, 3H), 1.27-1.17 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 146.2, 140.3, 128.2, 127.4, 126.1, 125.5, 83.7, 80.4, 39.5, 28.2, 25.0, 24.7, 20.6. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.98. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{22}H_{34}BO_4^+$ Calcd for 373.2545; Found 373.2539.

***tert*-Butyl 2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(*p*-tolyl)pentanoate (3ba)**: 28.4 mg, 74% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.17 (m, 2H), 7.07-7.03 (m, 2H), 5.99 (d, *J* = 2.1 Hz, 1H), 5.27 (s, 1H), 2.86-2.80 (m, 1H), 2.77-2.71 (m, 1H), 2.28 (s, 3H), 1.40 (s, 9H), 1.29 (s, 3H), 1.19 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 143.0, 140.4, 134.8, 128.9, 127.2, 126.1, 83.6, 80.3, 39.6, 28.1, 25.0, 24.7, 21.1, 20.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.52. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{23}H_{36}BO_4^+$ Calcd for 387.2701; Found 387.2697.

***tert*-Butyl 4-(4-(*tert*-butyl)phenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3ca)**: 32.7 mg, 76% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.21 (m 4H), 6.01 (d, *J* = 2.0 Hz, 1H), 5.30 (d, *J* = 2.0 Hz, 1H), 2.83-2.72 (m, 2H), 1.38 (s, 9H), 1.30 (s, 3H), 1.28 (s, 9H), 1.20 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 147.9, 143.0, 140.5, 126.9, 126.1, 125.0, 83.6, 80.2, 39.7, 34.4, 31.6, 28.2, 25.0, 24.7, 20.9. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.46. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{26}H_{42}BO_4^+$ Calcd for 429.3171; Found 429.3169.

***tert*-Butyl 4-(4-methoxyphenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3da)**: 23.5 mg, 58% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.18 (m, 2H), 6.84-6.77 (m, 2H), 5.98 (d, *J* = 2.1 Hz, 1H), 5.25 (s, 1H), 3.77 (s, 3H), 2.84-2.78 (m, 1H), 2.76-2.70 (m, 1H), 1.40 (s, 9H), 1.28 (s, 3H), 1.22-1.17 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 157.5, 140.4, 138.1, 128.3, 126.0, 113.6, 83.6, 80.3, 55.4, 39.7, 28.2, 24.9, 24.7, 20.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.87. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{23}H_{36}BO_5^+$ Calcd for 403.2650; Found 403.2643.

***tert*-Butyl 4-(4-(benzyloxy)phenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3ea)**: 28.2 mg, 59% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.31 (m, 5H), 7.25-7.21 (m, 2H), 6.91-6.84 (m, 2H), 5.99 (d, *J* = 2.0 Hz, 1H), 5.26 (d, *J* = 2.0 Hz, 1H), 5.02 (s, 2H), 2.85-2.78 (m, 1H), 2.76-2.70 (m, 1H), 1.40 (s, 9H), 1.28 (s, 3H), 1.22-1.17 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 156.8, 140.4, 138.4, 137.5, 128.7, 128.4, 128.1, 127.7, 126.1, 114.5, 83.6, 80.3, 70.2, 39.7, 28.2, 24.9, 24.7, 20.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.19. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{29}H_{40}BO_5^+$ Calcd for 479.2963; Found 479.2951.

***tert*-Butyl 4-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3fa)**: 17.7 mg, 35% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19-7.13 (m, 2H), 6.77-6.70 (m, 2H), 5.97 (d, *J* = 2.0 Hz, 1H), 5.21 (d, *J* = 2.0 Hz, 1H), 2.88-2.81 (m, 1H), 2.73-2.66 (m, 1H), 1.43 (s, 9H), 1.26 (s, 3H), 1.22-1.16 (m, 12H), 0.96 (s, 9H), 0.17 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 153.4, 140.4, 138.8, 128.2, 126.0, 119.7, 83.6, 80.3, 39.5, 28.2, 25.9, 24.9, 24.7, 20.5, 18.4, -4.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.11. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{28}H_{48}BO_5Si^+$ Calcd for 503.3359; Found 503.3353.

***tert*-Butyl 4-([1,1′-biphenyl]-4-yl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3ga)**: 34.3 mg, 76% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.55 (m, 2H), 7.53-7.47 (m, 2H), 7.45-7.34 (m, 4H), 7.34-7.27 (m, 1H), 6.02 (d, *J* = 2.0 Hz, 1H), 5.32 (d, *J* = 2.0 Hz, 1H), 2.98-2.72 (m, 2H), 1.38 (s, 9H), 1.35 (s, 3H), 1.25-1.17 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 145.3, 141.4, 140.3, 138.2, 128.9, 127.9, 127.13, 127.06, 126.8, 126.2, 83.8, 80.4, 39.6, 28.1, 25.0, 24.7, 20.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.93. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{28}H_{38}BO_4^+$ Calcd for 449.2858; Found 449.2863.

***tert*-Butyl 4-(4-fluorophenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3ha)**: 25.6 mg, 66% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.24 (m, 2H), 7.03-6.81 (m, 2H), 5.98 (d, *J* = 2.0 Hz, 1H), 5.25 (d, *J* = 1.9 Hz, 1H), 2.84-2.71 (m, 2H), 1.40 (s, 9H), 1.29 (s, 3H), 1.22-1.13 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 161.1 (d, $J_{C\text{-}F}$ = 243.3 Hz), 141.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 140.1, 128.9 (d, $J_{C\text{-}F}$ = 7.7 Hz), 126.2, 114.8 (d, $J_{C\text{-}F}$ = 20.8 Hz), 83.8, 80.4, 39.7, 28.1, 24.9, 24.7, 20.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.07. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.80. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{22}H_{33}BFO_4^+$ Calcd for 391.2450; Found 391.2449.

***tert*-Butyl 4-(4-chlorophenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3ia)**: 32.8 mg, 81% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.21 (m, 4H), 5.98 (d, *J* = 1.9 Hz, 1H), 5.25 (d, *J* = 1.9 Hz, 1H), 2.82-2.71 (m, 2H), 1.39 (s, 9H), 1.29 (s, 3H), 1.20 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 144.6, 140.0, 131.3, 129.0, 128.2, 126.2, 83.9, 80.5, 39.6, 28.1, 24.9, 24.7, 20.6. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.40. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{22}H_{33}BClO_4^+$ Calcd for 407.2155; Found 407.2151.

***tert*-Butyl 2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(4-vinylphenyl)-pentanoate (3ja)**: 20.8 mg, 52% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 4H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.98 (d, *J* = 2.0 Hz, 1H), 5.69 (dd, *J* = 17.6, 1.1 Hz, 1H), 5.26 (d, *J* = 2.2 Hz, 1H), 5.17 (dd, *J* = 10.8, 1.1 Hz, 1H), 2.89-2.81 (m, 1H), 2.80-2.74 (m, 1H), 1.39 (s, 9H), 1.30 (s, 3H), 1.22-1.17 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 146.0, 140.2, 137.0, 134.8, 127.6, 126.14, 126.07, 112.9, 83.7, 80.4, 39.4, 28.1, 24.9, 24.7, 20.5. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.57. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{24}H_{36}BO_4^+$ Calcd for 399.2701; Found 399.2696.

***tert*-Butyl 2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(*m*-tolyl)pentanoate (3la)**: 20.8 mg, 55% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17-7.08 (m, 3H), 6.97-6.91 (m, 1H), 5.99 (d, *J* = 2.0 Hz, 1H), 5.28 (d, *J* = 2.0 Hz, 1H), 2.89-2.82 (m, 1H), 2.78-2.71 (m, 1H), 2.31 (s, 3H), 1.41 (s, 9H), 1.29 (s, 3H), 1.19 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 146.1, 140.4, 137.4, 128.0, 126.3, 126.1, 124.5, 83.7, 80.3, 39.5, 28.2, 25.0, 24.7, 21.9, 20.6. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.68. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{23}H_{36}BO_4^+$ Calcd for 387.2701; Found 387.3693.

***tert*-Butyl 4-(3-fluorophenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3ma)**: 23.9 mg, 61% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.16 (m, 1H), 7.12-7.07 (m, 1H), 7.06-7.00 (m 1H), 6.87-6.77 (m, 1H), 5.99 (d, *J* = 1.9 Hz, 1H), 5.25 (d, *J* = 1.9 Hz, 1H), 2.86-2.80 (m, 1H), 2.79-2.73 (m, 1H), 1.41 (s, 9H), 1.29 (s, 3H), 1.22-1.17 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 163.0 (d, $J_{C\text{-}F}$ = 243.7 Hz), 149.1 (d, $J_{C\text{-}F}$ = 7.0 Hz), 140.0, 129.4 (d, $J_{C\text{-}F}$ = 8.2 Hz), 126.3, 123.2 (d, $J_{C\text{-}F}$ = 2.6 Hz), 114.5 (d, $J_{C\text{-}F}$ = 21.6 Hz), 112.3 (d, $J_{C\text{-}F}$ = 21.1 Hz), 83.9, 80.5, 39.5, 28.2, 24.9, 24.7, 20.5. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.30. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.00. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{22}H_{33}BFO_4^+$ Calcd for 391.2450; Found 391.2443.

***tert*-Butyl 4-(3-chlorophenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3na)**: 33.5 mg, 83% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.09 (m, 4H), 6.00 (d, *J* = 1.9 Hz, 1H), 5.27 (d, *J* = 1.8 Hz, 1H), 2.85-2.73 (m, 2H), 1.40 (s, 9H), 1.29 (s, 3H), 1.20 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 148.4, 140.0, 134.1, 129.3, 127.7, 126.3, 125.9, 125.7, 83.9, 80.5, 39.5, 28.1, 24.9, 24.7, 20.5. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.47. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{22}H_{33}BClO_4^+$ Calcd for 407.2155; Found 407.2147.

***tert*-Butyl 2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(3-(trifluoromethyl)phenyl)pentanoate (3oa)**: 35.2 mg, 80% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60-7.55 (m, 1H), 7.52-7.45 (m, 1H), 7.42-7.35 (m, 2H), 6.00 (d, *J* = 1.9 Hz, 1H), 5.30-5.25 (m, 1H), 2.86-2.76 (m, 2H), 1.38 (s, 9H), 1.33 (s, 3H), 1.20 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 147.2, 139.9, 130.9, 130.3 (q, $J_{C\text{-}F}$ = 31.7 Hz), 128.5, 126.4, 124.7 (q, $J_{C\text{-}F}$ = 272.5 Hz), 124.4 (q, $J_{C\text{-}F}$ = 3.9 Hz), 122.4 (q, $J_{C\text{-}F}$ = 4.0 Hz), 84.0, 80.5, 39.6, 28.1, 24.9, 24.7, 20.4. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.28. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.46. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{23}H_{33}BF_3O_4^+$ Calcd for 441.2419; Found 441.2411.

***tert*-Butyl 2-methylene-4-(naphthalen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3pa)**: 33.3 mg, 79% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.72 (m, 3H), 7.69-7.65 (m, 1H), 7.56-7.51 (m, 1H), 7.44-7.34 (m, 2H), 5.96 (d, *J* = 2.0 Hz, 1H), 5.26-5.20 (m, 1H), 2.98-2.86 (m, 2H), 1.42 (s, 3H), 1.33 (s, 9H), 1.20 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 143.6, 140.1, 133.8, 131.9, 128.1, 127.5, 127.4, 127.0, 126.1,

125.7, 125.2, 125.1, 83.8, 80.4, 39.2, 28.1, 24.9, 24.7, 20.4. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.77. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{26}H_{36}BO_4^+$ Calcd for 423.2701; Found 423.2694.

***tert*-Butyl 2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(9-tosyl-9*H*-carbazol-3-yl)pentanoate (3qa)**: 43.1 mg, 70% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31-8.27 (m, 1H), 8.22-8.17 (m, 1H), 7.90-7.85 (m, 1H), 7.82-7.78 (m, 1H), 7.69-6.65 (m, 2H), 7.52-7.41 (m, 2H), 7.37-7.31 (m, 1H), 7.09-7.05 (m, 2H), 5.95 (d, *J* = 1.9 Hz, 1H), 5.21 (s, 1H), 2.97-2.89 (m, 1H), 2.87-2.79 (m, 1H), 2.25 (s, 3H), 1.39 (s, 3H), 1.32 (s, 9H), 1.21-1.14 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 144.9, 142.2, 140.1, 138.8, 136.6, 135.2, 129.8, 127.4, 127.2, 127.1, 126.7, 126.5, 126.2, 123.9, 120.1, 118.3, 115.3, 114.8, 83.8, 80.4, 39.8, 28.1, 24.9, 24.7, 21.7, 20.6. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.19. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{35}H_{43}BNO_6S^+$ Calcd for 616.2899; Found 616.2897.

***tert*-Butyl 4-(dibenzo[*b*,*d*]furan-2-yl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3ra)**: 26.2 mg, 57% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96-7.90 (m, 1H), 7.89-7.85 (m, 1H), 7.57-7.50 (m, 1H), 7.49-7.37 (m, 3H), 7.34-7.28 (m, 1H), 5.98 (d, *J* = 2.0 Hz, 1H), 5.25 (d, *J* = 2.1 Hz, 1H), 2.98-2.91 (m, 1H), 2.90-2.84 (m, 1H), 1.42 (s, 3H), 1.35 (s, 9H), 1.23-1.17 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 156.7, 154.6, 140.7, 140.2, 127.2, 126.9, 126.2, 124.9, 124.1, 122.7, 120.7, 119.0, 111.8, 111.1, 83.8, 80.4, 40.0, 28.1, 25.0, 24.7, 20.9. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.15. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{28}H_{36}BO_5^+$ Calcd for 463.2650; Found 463.2646.

***tert*-Butyl 4-(dibenzo[*b*,*d*]thiophen-2-yl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3sa)**: 30.2 mg, 63% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17-8.11 (m, 1H), 8.10-8.06 (m, 1H), 7.87-7.78 (m, 1H), 7.77-7.70 (m, 1H), 7.50-7.40 (m, 3H), 5.98 (d, *J* = 2.0 Hz, 1H), 5.28 (d, *J* = 1.9 Hz, 1H), 2.99-2.85 (m, 2H), 1.44 (s, 3H), 1.33 (s, 9H), 1.25-1.19 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 142.7, 140.2, 140.0, 136.7, 136.1, 135.7, 127.0, 126.6, 126.2, 124.4, 123.0, 122.4, 121.7, 120.1, 83.9, 80.4, 39.8, 28.1, 25.0, 24.8, 20.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.31. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{28}H_{36}BO_4S^+$ Calcd for 479.2422; Found 479.2413.

***tert*-Butyl 4-(3,4-dihydronaphthalen-2-yl)-2-methylene-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3ta)**: 30.0 mg, 60% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23-7.11 (m, 6H), 7.09-7.05 (m, 2H), 6.99-6.95 (m, 1H), 6.31 (s, 1H), 6.12 (s, 1H), 5.65 (d, *J* = 1.8 Hz, 1H), 3.22-3.02 (m, 2H), 2.80-2.69 (m, 3H), 2.59-2.54 (m, 1H), 2.39-2.32 (m, 2H), 1.42 (s, 9H), 1.20 (s, 6H), 1.16 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.5, 144.2, 140.1, 139.7, 135.4, 135.0, 130.5, 128.0, 127.1, 126.5, 126.3, 126.2, 125.0, 123.9, 84.0, 80.5, 38.8, 32.6, 28.6, 28.3, 26.5, 25.3, 25.1. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 33.29. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{32}H_{42}BO_4^+$ Calcd for 501.3171; Found 501.3166.

***tert*-Butyl (*E*)-2-methylene-6-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-5-enoate (3ua)**: 14.8 mg, 30% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.29-7.26 (d, *J* = 7.3 Hz, 2H), 7.24-7.14 (m, 6H), 6.15 (d, *J* = 1.5 Hz, 1H), 5.71 (d, *J* = 1.7 Hz, 1H), 5.64 (d, *J* = 1.5 Hz, 1H), 3.14 (d, *J* = 13.4 Hz, 1H), 2.88 (d, *J* = 13.4 Hz, 1H), 2.78-2.60 (m, 2H), 1.87 (s, 3H), 1.41 (s, 9H), 1.24-1.19 (m, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.6, 145.3, 140.2, 139.7, 136.0, 133.7, 131.1, 128.2, 127.8, 126.6, 126.17, 126.15, 125.8, 83.9, 80.6, 42.4, 37.9, 28.3, 25.4, 25.4, 18.8. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.52. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{24}H_{36}BO_4^+$ Calcd for 399.2701; Found 399.2705.

***tert*-Butyl 2-methylene-4,5-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3va)**: 31.5 mg, 70% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.20 (m, 4H), 7.15-7.11 (m, 1H), 7.10-7.02 (m, 3H), 6.86-6.80 (m, 2H), 6.05 (d, *J* = 1.4 Hz, 1H), 5.28 (d, *J* = 1.6 Hz, 1H), 3.18 (s, 2H), 2.92-2.78 (m, 2H), 1.42 (s, 9H), 1.17 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 144.0, 139.7, 139.0, 130.5, 128.7, 127.9, 127.6, 126.0, 125.59, 125.55, 83.9, 80.4, 43.5, 35.5, 28.2, 25.03, 25.00. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.36. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{28}H_{38}BO_4^+$ Calcd for 449.2858; Found 449.2851.

***tert*-Butyl 5-(4-methoxyphenyl)-2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3wa)**: 36.5 mg, 87% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.20 (m, 4H), 7.16-7.10 (m, 1H), 6.75-6.69 (m, 2H), 6.65-6.59 (m, 2H), 6.07-6.02 (m, 1H), 5.30-5.25 (m, 1H), 3.72 (s, 3H), 3.15-3.07 (m, 2H), 2.90-2.78 (m, 2H), 1.43 (s, 9H), 1.26-1.15 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 158.0, 144.0, 139.7, 131.4, 131.0, 128.7, 127.9, 125.6, 125.5, 113.0, 83.8, 80.4, 55.3, 42.8, 35.5, 28.2, 25.1, 25.0. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.35. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{29}H_{40}BO_5^+$ Calcd for 479.2963; Found 479.2956.

***tert*-Butyl 5-(4-chlorophenyl)-2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3xa)**: 30.3 mg, 63% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.21 (m, 4H), 7.16-7.11 (m, 1H), 7.05-7.01 (m, 2H), 6.73-6.67 (m, 2H), 6.06 (s, 1H), 5.28 (d, *J* = 1.9 Hz, 1H), 3.18-3.09 (m, 2H), 2.88-2.76 (m, 2H), 1.44 (s, 9H), 1.20-1.15 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 143.6, 139.5, 137.5, 131.9, 131.8, 128.6, 128.1, 127.7, 125.73, 125.70, 84.0, 80.6, 43.0, 35.5, 28.2, 25.1, 25.0. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.78. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{28}H_{37}BClO_4^+$ Calcd for 483.2468; Found 483.2466.

***tert*-Butyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(4-(trifluoromethyl)phenyl)pentanoate (3ya)**: 43.0 mg, 81% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 7.29-7.25 (m, 4H), 7.20-7.15 (m, 1H), 6.925-6.90 (m, 2H), 6.10 (d, *J* = 1.4 Hz, 1H), 5.31 (d, *J* = 1.9 Hz, 1H), 3.27-7.19 (m, 2H), 2.94-2.78 (m, 2H), 1.46 (s, 9H), 1.20 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 143.5, 143.3, 139.5, 130.6, 128.5, 128.3 (q, J_{C-F} = 32.5 Hz), 128.1, 124.6 (q, J_{C-F} = 271.8 Hz), 124.4 (q, J_{C-F} =

3.8 Hz), 84.0, 80.6, 43.2, 35.5, 28.2, 25.1, 25.0. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.84. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.30. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{29}H_{37}BF_3O_4^+$ Calcd for 517.2732; Found 517.2726.

***tert*-Butyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanoate (3za)**: 34.3 mg, 81% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.21 (m, 4H), 7.14-7.06 (m, 1H), 5.93 (d, *J* = 1.9 Hz, 1H), 5.14 (d, *J* = 1.8 Hz, 1H), 2.85 (s, 2H), 1.88-1.65 (m, 2H), 1.37 (s, 9H), 1.28-1.12 (m, 16H), 0.85 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 145.0, 140.1, 128.2, 128.0, 125.7, 125.4, 83.7, 80.3, 36.4, 34.8, 28.2, 28.0, 25.02, 24.97, 23.7, 14.3. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.08. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{25}H_{40}BO_4^+$ Calcd for 415.3014; Found 415.3009.

***tert*-Butyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decanoate (3a′a)**: 35.4 mg, 80% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.19 (m, 4H), 7.14-7.06 (m, 1H), 5.92 (d, *J* = 1.8 Hz, 1H), 5.13 (d, *J* = 1.8 Hz, 1H), 2.85 (s, 2H), 1.76 (t, *J* = 7.8 Hz, 2H), 1.37 (s, 9H), 1.28-1.17 (m, 20H), 0.85 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 145.0, 140.1, 128.2, 128.0, 125.7, 125.4, 83.7, 80.2, 36.5, 35.1, 32.0, 30.4, 28.2, 25.7, 25.03, 24.99, 22.9, 14.3. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.03. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{27}H_{44}BO_4^+$ Calcd for 443.3327; Found 443.3322.

***tert*-Butyl 8-acetoxy-2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanoate (3b′a)**: 32.1 mg, 68% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 4H), 7.14-7.07 (m, 1H), 5.94 (d, *J* = 1.8 Hz, 1H), 5.16 (d, *J* = 1.8 Hz, 1H), 4.00 (t, *J* = 6.7 Hz, 2H), 2.85 (s, 2H), 2.00 (s, 3H), 1.83-1.75 (m, 2H), 1.64-1.51 (m, 2H), 1.38 (s, 9H), 1.29-1.19 (m, 14H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 167.3, 144.6, 139.9, 128.12, 128.06, 125.9, 125.5, 83.7, 80.3, 64.7, 36.4, 34.7, 29.5, 28.2, 25.0, 24.9, 22.1, 21.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.55. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{27}H_{42}BO_6^+$ Calcd for 473.3069; Found 473.3062.

7-(*tert*-Butoxycarbonyl)-5-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-en-1-yl benzoate (3c′a): 43.1 mg, 81% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07-7.93 (m, 2H), 7.56-7.48 (m, 1H), 7.45-7.37 (m, 2H), 7.30-7.20 (m, 4H), 7.15-7.06 (m, 1H), 5.94 (d, *J* = 1.8 Hz, 1H), 5.17 (d, *J* = 1.8 Hz, 1H), 4.27 (t, *J* = 6.5 Hz, 2H), 2.87 (s, 2H), 1.89-1.80 (m, 2H), 1.78-1.68 (m, 2H), 1.43-1.34 (m, 11H), 1.25-1.14 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 166.8, 144.7, 140.0, 132.9, 130.7, 129.8, 128.4, 128.13, 128.07, 125.9, 125.5, 83.7, 80.3, 65.2, 36.4, 34.8, 29.7, 28.2, 25.0, 24.9, 22.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.34. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{32}H_{44}BO_6^+$ Calcd for 535.3225; Found 535.3217.

***tert*-Butyl 8-((*tert*-butoxycarbonyl)oxy)-2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanoate (3d′a)**: 37.0 mg, 70% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.21 (m, 4H), 7.15-7.03 (m, 1H), 5.94 (d, *J* = 1.8 Hz, 1H), 5.17 (s, 1H), 3.99 (t, *J* = 6.9 Hz, 2H), 2.84 (s, 2H), 1.84-1.75 (m, 2H), 1.67-1.56 (m, 2H), 1.46 (s, 9H), 1.37 (s, 9H), 1.31-1.16 (m, 14H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 153.9, 144.6, 140.0, 128.13, 128.08,

125.9, 125.5, 83.8, 81.8, 80.3, 67.2, 36.4, 34.8, 29.6, 28.2, 28.0, 25.04, 24.96, 21.9. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 36.43. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{30}H_{48}BO_7^+$ Calcd for 531.3488; Found 531.3482.

***tert*-Butyl 8-((*tert*-butyldimethylsilyl)oxy)-2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanoate (3e′a)**: 45.8 mg, 84% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.21 (m, 4H), 7.17-7.07 (m, 1H), 5.93 (d, *J* = 1.8 Hz, 1H), 5.16 (d, *J* = 1.8 Hz, 1H), 3.55 (t, *J* = 6.7 Hz, 2H), 2.85 (s, 2H), 1.88-1.67 (m, 2H), 1.50-1.45 (m, 2H), 1.36 (s, 9H), 1.29-1.02 (m, 14H), 0.86 (s, 9H), 0.01 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 144.9, 140.0, 128.2, 128.1, 125.8, 125.4, 83.7, 80.3, 63.5, 36.4, 35.1, 34.0, 28.2, 26.2, 25.03, 24.99, 22.2, 18.6, -5.1. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.21. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{31}H_{54}BO_5Si^+$ Calcd for 545.3828; Found 545.3821.

***tert*-Butyl 2-methylene-8-phenoxy-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanoate (3f′a)**: 38.9 mg, 77% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.21 (m, 6H), 7.14-7.08 (m, 1H), 6.94-6.87 (m, 1H), 6.87-6.80 (m, 2H), 5.93 (d, *J* = 1.8 Hz, 1H), 5.17 (d, *J* = 1.8 Hz, 1H), 3.90 (t, *J* = 6.6 Hz, 2H), 2.87 (s, 2H), 1.90-1.80 (m, 2H), 1.79-1.71 (m, 2H), 1.43-1.33 (m, 11H), 1.22 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 159.3, 144.7, 140.0, 129.5, 128.13, 128.11, 125.9, 125.5, 120.6, 114.7, 83.7, 80.3, 67.8, 36.5, 34.9, 30.3, 28.2, 25.04, 24.96, 22.3. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.75. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{31}H_{44}BO_5^+$ Calcd for 507.3276; Found 507.3269.

7-(*tert*-Butoxycarbonyl)-5-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-en-1-yl thiophene-2-carboxylate (3g′a): 36.0 mg, 67% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.67 (m, 1H), 7.59-7.42 (m, 1H), 7.30-7.21 (m, 4H), 7.14-6.95 (m, 2H), 5.94 (d, *J* = 1.8 Hz, 1H), 5.18 (d, *J* = 1.8 Hz, 1H), 4.24 (t, *J* = 6.6 Hz, 2H), 2.86 (s, 2H), 1.94-1.78 (m, 2H), 1.74-1.63 (m, 2H), 1.42-1.32 (m, 11H), 1.24-1.10 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 162.5, 144.7, 140.0, 134.4, 133.4, 132.3, 128.13, 128.07, 127.8, 125.9, 125.5, 83.7, 80.3, 65.4, 36.4, 34.8, 29.7, 28.2, 25.01, 24.95, 22.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.00. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{30}H_{42}BO_6S^+$ Calcd for 541.2790; Found 541.2783.

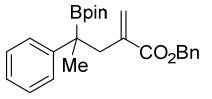
7-(*tert*-Butoxycarbonyl)-5-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-en-1-yl furan-2-carboxylate (3h′a): 37.5 mg, 72% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.48 (m, 1H), 7.29-7.22 (m, 4H), 7.16-7.03 (m, 2H), 6.51-6.45 (m, 1H), 5.94 (d, *J* = 1.8 Hz, 1H), 5.17 (s, 1H), 4.25 (t, *J* = 6.7 Hz, 2H), 2.86 (s, 2H), 1.90-1.77 (m, 2H), 1.74-1.65 (m, 2H), 1.40-1.32 (m, 11H), 1.25-1.16 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 159.0, 146.3, 145.1, 144.7, 140.0, 128.14, 128.07, 125.9, 125.5, 117.8, 111.9, 83.7, 80.3, 65.2, 36.4, 34.8, 29.6, 28.2, 25.0, 24.9, 22.1. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.08. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{30}H_{42}BO_7^+$ Calcd for 525.3018; Found 525.3012.

tert-Butyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(1-tosyl-1*H*-indol-3-yl)hexanoate (3i′a): 46.3 mg, 71% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.91 (m, 1H), 7.78-7.69 (m, 2H), 7.47-7.40 (m, 1H), 7.38-7.32 (m, 2H), 7.31-7.25 (m, 4H), 7.21-7.12 (m, 4H), 5.99 (d, *J* = 1.8 Hz, 1H), 5.23 (d, *J* = 1.8 Hz, 1H), 3.02-2.88 (m, 2H), 2.63-2.49 (m, 2H), 2.32 (s, 3H), 2.19-2.07 (m, 2H), 1.36 (s, 9H), 1.27-1.22 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 144.8, 144.4, 139.8, 135.7, 135.5, 131.4, 130.0, 128.3, 128.1, 127.0, 126.3, 125.7, 124.6, 124.2, 123.0, 122.5, 120.0, 113.8, 83.9, 80.5, 36.2, 34.8, 28.2, 25.1, 25.0, 21.7, 21.3. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.76. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{38}H_{47}BNO_6S^+$ Calcd for 656.3212; Found 656.3204.

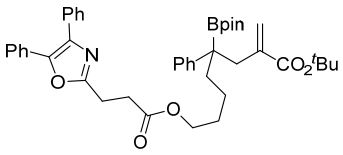
tert-Butyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-6-ynoate (3j′a): 26.9 mg, 63% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.15 (m, 4H), 7.14-7.07 (m, 1H), 5.99 (d, *J* = 2.1 Hz, 1H), 5.42 (dd, *J* = 2.2, 1.2 Hz, 1H), 3.12-3.02 (m, 1H), 3.00-2.91 (m, 1H), 2.71-2.57 (m, 2H), 2.19-2.09 (m, 2H), 1.29-1.20 (m, 21H), 1.10 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.1, 143.5, 139.4, 128.2, 127.7, 126.2, 125.8, 84.2, 83.9, 80.2, 78.3, 35.8, 28.0, 25.0, 24.8, 23.5, 14.4, 12.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.47. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{26}H_{38}BO_4^+$ Calcd for 425.2858; Found 425.2851.

Methyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3ab): 25.7 mg, 78% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.21 (m, 4H), 7.16-7.07 (m, 1H), 6.04 (d, *J* = 1.7 Hz, 1H), 5.29 (d, *J* = 1.7 Hz, 1H), 3.57 (s, 3H), 2.92-2.78 (m, 2H), 1.31 (s, 3H), 1.24-1.08 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 145.8, 138.7, 128.1, 127.5, 127.0, 125.6, 83.8, 51.9, 40.1, 24.9, 24.7, 20.6. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.25. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{19}H_{28}BO_4^+$ Calcd for 331.2075; Found 331.2069.

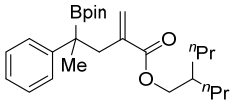
Ethyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3ac): 28.9 mg, 84% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 4H), 7.17-7.08 (m, 1H), 6.05 (d, *J* = 1.9 Hz, 1H), 5.29 (d, *J* = 1.7 Hz, 1H), 4.09-3.94 (m, 2H), 2.90-2.77 (m, 2H), 1.31 (s, 3H), 1.26-1.18 (m, 15H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 145.9, 139.1, 128.1, 127.5, 126.8, 125.6, 83.7, 60.7, 39.9, 24.9, 24.7, 20.7, 14.3. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.45. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{20}H_{30}BO_4^+$ Calcd for 345.2232; Found 345.2230.

Benzyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3ad): 

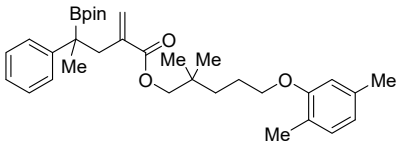
26.8 mg, 66% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.23 (m, 9H), 7.15-7.09 (m, 1H), 6.10 (d, *J* = 1.8 Hz, 1H), 5.32 (d, *J* = 1.8 Hz, 1H), 5.06-4.97 (m, 2H), 2.91-2.81 (m, 2H), 1.31 (s, 3H), 1.21-1.15 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 145.8, 138.8, 136.4, 128.7, 128.23, 128.15, 127.5, 127.3, 125.6, 83.8, 66.5, 40.0, 24.9, 24.8, 24.7, 20.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.31. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{25}H_{32}BO_4^+$ Calcd for 407.2388; Found 407.2381.

***tert*-Butyl 8-((3-(4,5-diphenyloxazol-2-yl)propanoyl)oxy)-2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanoate (3k′a)**: 

46.4 mg, 66% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.60 (m, 2H), 7.59-7.54 (m, 2H), 7.39-7.30 (m, 6H), 7.28-7.23 (m, 4H), 7.14-7.07 (m, 1H), 5.94 (d, *J* = 1.8 Hz, 1H), 5.17 (d, *J* = 1.9 Hz, 1H), 4.07 (t, *J* = 6.7 Hz, 2H), 3.19-3.12 (m, 2H), 2.93-2.78 (m, 4H), 1.86-1.73 (m, 2H), 1.63-1.53 (m, 2H), 1.38 (s, 9H), 1.28-1.19 (m, 14H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.3, 162.0, 145.6, 144.6, 140.0, 135.3, 132.7, 129.2, 128.84, 128.75, 128.6, 128.2, 128.14, 128.10, 128.05, 126.7, 125.9, 125.5, 83.7, 80.3, 65.1, 36.3, 34.8, 31.4, 29.5, 28.2, 25.0, 24.9, 23.8, 22.0. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 35.02. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{43}H_{53}BNO_7^+$ Calcd for 706.3910; Found 706.3902.

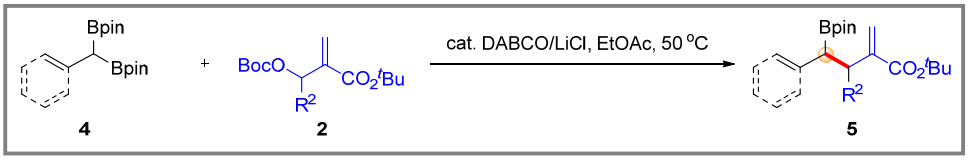
2-Propylpentyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3af): 

35.3 mg, 82% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 4H), 7.15-7.10 (m, 1H), 6.03 (d, *J* = 1.8 Hz, 1H), 5.27 (d, *J* = 1.8 Hz, 1H), 3.94-3.97 (m, 2H), 2.92-2.86 (m, 1H), 2.81-2.75 (m, 1H), 1.70-1.62 (m, 1H), 1.35-1.26 (m, 11H), 1.23-1.18 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 146.0, 139.1, 128.1, 127.4, 126.6, 125.5, 83.7, 67.6, 39.9, 37.1, 34.0, 24.9, 24.7, 20.7, 20.1, 14.6. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.56. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{26}H_{42}BO_4^+$ Calcd for 429.3171; Found 429.3168.

5-(2,5-Dimethylphenoxy)-2,2-dimethylpentyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (3ag): 

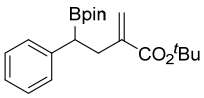
40.2 mg, 75% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 4H), 7.16-7.08 (m, 1H), 7.04-6.96 (m, 1H), 6.69-6.63 (m, 1H), 6.61 (s, 1H), 6.06 (d, *J* = 1.8 Hz, 1H), 5.29 (s, 1H), 3.91 (t, *J* = 6.4 Hz, 2H), 3.80-3.71 (m, 2H), 2.94-2.76 (m, 2H), 2.30 (s, 3H), 2.16 (s, 3H), 1.81-1.70 (m, 2H), 1.49-1.41 (m, 2H), 1.31 (s, 3H), 1.22-1.11 (m, 12H), 0.95 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 157.2, 146.0, 139.0, 136.7, 130.5, 128.2, 127.4, 126.7, 125.6, 123.8, 120.8, 112.1, 83.7, 72.6, 68.6, 39.8, 35.8, 33.9, 24.9, 24.7, 24.6, 24.3, 21.6, 20.7, 16.0. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.40. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{33}H_{48}BO_5^+$ Calcd for 535.3589; Found 535.3583.

8. General procedure for synthesis of product 5

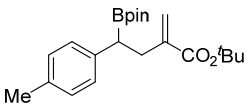


In the nitrogen filled glovebox, a dried 25.0 mL Schlenk tube was charged with DABCO (1.1 mg, 0.01 mmol, 10.0 mol%), LiCl (0.4 mg, 0.01 mmol, 10.0 mol%), **4** (0.10 mmol, 1.0 equiv.), **2** (0.20 mmol, 2.0 equiv.), and EtOAc (2.0 mL). Then, the Schlenk tube was removed from glove-box and stirred in a 50 °C oil bath. Upon completion (monitored by TLC), the mixture was allowed to slowly cool to room temperature, followed by concentration under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 60/1) on silica gel (200-300 mesh) to afford the target product **5**.

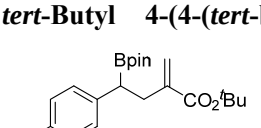
***tert*-Butyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5aa)**: 32.2 mg, 90% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 4H), 7.16-7.10 (m, 1H), 6.00 (d, *J* = 1.7 Hz, 1H), 5.38 (d, *J* = 1.8 Hz, 1H), 2.88-2.80 (m, 1H), 2.62-2.54 (m, 2H), 1.48 (s, 9H), 1.19 (s, 6H) 1.16 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 142.6, 141.6, 128.7, 128.5, 125.6, 124.6, 83.6, 80.5, 34.9, 28.3, 24.81, 24.79. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.24. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{21}H_{32}BO_4^+$ Calcd for 359.2388; Found 359.2381.



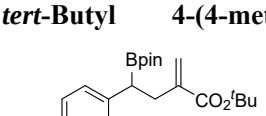
***tert*-Butyl 2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(*p*-tolyl)butanoate (5ba)**: 28.1 mg, 76% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14-7.00 (m, 4H), 6.00 (d, *J* = 1.7 Hz, 1H), 5.38 (d, *J* = 1.5 Hz, 1H), 2.87-2.75 (m, 1H), 2.60-2.49 (m, 2H), 2.29 (s, 3H), 1.48 (s, 9H), 1.24-1.15 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 141.7, 139.4, 134.9, 129.3, 128.6, 124.5, 83.5, 80.5, 35.1, 28.3, 24.9, 24.8, 21.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.88. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{22}H_{34}BO_4^+$ Calcd for 373.2545; Found 373.2541.



***tert*-Butyl 4-(4-(*tert*-butyl)phenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5ca)**: 25.5 mg, 62% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.23 (m, 2H), 7.15-7.10 (m, 2H), 6.02 (d, *J* = 1.8 Hz, 1H), 5.42 (d, *J* = 1.6 Hz, 1H), 2.84-2.74 (m, 1H), 2.60-2.52 (m, 2H), 1.47 (s, 9H), 1.29 (s, 9H), 1.22-1.15 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 148.1, 141.9, 139.3, 128.2, 125.4, 124.6, 83.5, 80.5, 35.1, 34.5, 31.6, 28.3, 24.9, 24.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.47. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{25}H_{40}BO_4^+$ Calcd for 415.3014; Found 415.3007.



***tert*-Butyl 4-(4-methoxyphenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5da)**: 30.9 mg, 80% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15-7.05 (m, 2H), 6.86-6.73 (m, 2H), 5.99 (d, *J* = 1.7 Hz, 1H), 5.36 (d, *J* = 1.5 Hz, 1H), 3.77 (s, 3H), 2.85-2.72 (m, 1H), 2.60-2.47 (m, 2H), 1.48 (s, 9H), 1.23-1.10 (m, 12H). **^{13}C NMR**



(100 MHz, $CDCl_3$) δ 166.7, 157.6, 141.7, 134.6, 129.6, 124.6, 114.0, 83.6, 80.5, 55.4, 35.2, 28.3, 24.84, 24.82. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.47. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{22}H_{34}BO_5^+$ Calcd for 389.2494; Found 389.2486.

***tert*-Butyl 4-(4-(benzyloxy)phenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5ea)**: 26.9 mg, 58% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.30 (m, 5H), 7.16-7.07 (m, 2H), 6.92-6.82 (m, 2H), 6.00 (d, *J* = 1.7 Hz, 1H), 5.37 (d, *J* = 1.6 Hz, 1H), 5.01 (s, 2H), 2.86-2.74 (m, 1H), 2.59-2.42 (m, 2H), 1.48 (s, 9H), 1.24-1.13 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 156.9, 141.6, 137.5, 134.9, 129.6, 128.7, 128.1, 127.8, 124.6, 114.9, 83.6, 80.5, 70.2, 35.2, 28.3, 24.84, 24.82. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.02. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{28}H_{38}BO_5^+$ Calcd for 465.2807; Found 465.2801.

***tert*-Butyl 4-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5fa)**: 40.5 mg, 83% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.07-7.02 (m, 2H), 6.75-6.69 (m, 2H), 5.99 (d, *J* = 1.7 Hz, 1H), 5.36 (d, *J* = 1.7 Hz, 1H), 2.84-2.75 (m, 1H), 2.56-2.49 (m, 2H), 1.48 (s, 9H), 1.21-1.13 (m, 12H), 0.96 (s, 9H), 0.17 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 153.5, 141.6, 135.1, 129.4, 124.5, 120.1, 83.5, 80.5, 35.0, 28.3, 25.9, 24.8, 18.4, -4.3. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.47. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{27}H_{46}BO_5Si^+$ Calcd for 489.3202; Found 489.3195.

***tert*-Butyl 4-([1,1′-biphenyl]-4-yl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5ga)**: 26.3 mg, 61% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60-7.55 (m, 2H), 7.51-7.46 (m, 2H), 7.44-7.38 (m, 2H), 7.36-7.29 (m, 1H), 7.28-7.25 (m, 2H), 6.02 (d, *J* = 1.7 Hz, 1H), 5.42 (d, *J* = 1.6 Hz, 1H), 2.92-2.81 (m, 1H), 2.68-2.57 (m, 2H), 1.48 (s, 9H), 1.25-1.16 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 141.8, 141.6, 141.3, 138.3, 129.1, 128.9, 127.2, 127.1, 124.7, 83.7, 80.6, 34.9, 28.3, 24.9, 24.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.56. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{27}H_{36}BO_4^+$ Calcd for 435.2701; Found 435.2693.

***tert*-Butyl 4-(4-fluorophenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-butanoate (5ha)**: 26.7 mg, 71% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18-7.09 (m, 2H), 6.98-6.87 (m, 2H), 5.99 (d, *J* = 1.7 Hz, 1H), 5.36 (d, *J* = 1.7 Hz, 1H), 2.85-2.74 (m, 1H), 2.61-2.47 (m, 2H), 1.48 (s, 9H), 1.24-1.14 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 161.2 (d, J_{C-F} = 242.7 Hz), 141.4, 138.2 (d, J_{C-F} = 3.2 Hz), 130.0 (d, J_{C-F} = 7.7 Hz), 124.8, 115.3 (d, J_{C-F} = 21.0 Hz), 83.7, 80.6, 35.1, 28.3, 24.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.30. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.43. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{21}H_{31}BFO_4^+$ Calcd for 377.2294; Found 377.2288.

***tert*-Butyl 4-(4-chlorophenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-butanoate (5ia)**: 30.0 mg, 76% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23-7.18 (m, 2H), 7.15-7.09 (m, 2H), 5.99 (d, *J* = 1.8 Hz, 1H), 5.35 (d, *J* = 1.4 Hz, 1H), 2.87-2.77 (m, 1H), 2.60-2.50 (m, 2H), 1.47 (s, 9H), 1.21-1.15 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 141.3, 141.1, 131.3, 130.0, 128.6, 124.9, 83.8, 80.7, 34.8, 28.3, 28.2, 24.8. **^{11}B NMR** (128

MHz, $CDCl_3$) δ 32.62. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{21}H_{31}BClO_4^+$ Calcd for 393.1998; Found 393.1992.

***tert*-Butyl 2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(4-vinylphenyl)-butanoate (5ja)**: 26.2 mg, 68% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 2H), 7.19-7.12 (m, 2H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.99 (d, *J* = 1.7 Hz, 1H), 5.69 (d, *J* = 17.6 Hz, 1H), 5.38 (s, 1H), 5.17 (d, *J* = 10.9 Hz, 1H), 2.88-2.78 (m, 1H), 2.63-2.52 (m, 2H), 1.48 (s, 9H), 1.22-1.13 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 142.4, 141.5, 137.0, 134.9, 128.8, 126.5, 124.7, 112.8, 83.6, 80.6, 34.8, 28.3, 24.84, 24.81. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.00. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{23}H_{34}BO_4^+$ Calcd for 385.2545; Found 385.2544.

***tert*-Butyl 2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(*o*-tolyl)butanoate (5ka)**: 25.0 mg, 70% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.21 (m, 1H), 7.14-7.07 (m, 2H), 7.06-7.00 (m, 1H), 5.97 (d, *J* = 1.8 Hz, 1H), 5.34 (s, 1H), 2.88-2.77 (m, 2H), 2.60-2.50 (m, 1H), 2.31 (s, 3H), 1.48 (s, 9H), 1.22-1.14 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 141.5, 140.9, 136.5, 130.4, 128.2, 126.1, 125.4, 124.7, 83.5, 80.5, 34.5, 28.3, 24.9, 24.8, 20.4. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.73. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{22}H_{34}BO_4^+$ Calcd for 373.2545; Found 373.2542.

***tert*-Butyl 2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(*m*-tolyl)butanoate (5la)**: 30.4 mg, 82% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.10 (m, 1H), 7.04-6.98 (m, 2H), 6.97-6.92 (m, 1H), 6.00 (d, *J* = 1.7 Hz, 1H), 5.40 (d, *J* = 1.7 Hz, 1H), 2.86-2.77 (m, 1H), 2.60-2.53 (m, 2H), 2.30 (s, 3H), 1.48 (s, 9H), 1.22-1.14 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 142.4, 141.7, 138.0, 129.5, 128.4, 126.4, 125.6, 124.6, 83.6, 80.5, 35.0, 28.3, 24.83, 24.76, 21.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.43. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{22}H_{34}BO_4^+$ Calcd for 373.2545; Found 373.2543.

***tert*-Butyl 4-(3-fluorophenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-butanoate (5ma)**: 29.0 mg, 77% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23-7.16 (m, 1H), 6.99-6.88 (m, 2H), 6.87-6.77 (m, 1H), 6.00 (d, *J* = 1.7 Hz, 1H), 5.37 (d, *J* = 1.5 Hz, 1H), 2.87-2.76 (m, 1H), 2.66-2.52 (m, 2H), 1.48 (s, 9H), 1.22-1.15 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 163.1 (d, $J_{C\text{-}F}$ = 244.8 Hz), 145.3 (d, $J_{C\text{-}F}$ = 7.2 Hz), 141.3, 129.8 (d, $J_{C\text{-}F}$ = 8.4 Hz), 124.9, 124.4 (d, $J_{C\text{-}F}$ = 2.8 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.1 Hz), 112.5 (d, $J_{C\text{-}F}$ = 21.1 Hz), 83.8, 80.7, 34.7, 28.3, 24.83, 24.81. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.29. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.91. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{21}H_{31}BFO_4^+$ Calcd for 377.2294; Found 377.2288.

***tert*-Butyl 4-(3-chlorophenyl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-butanoate (5na)**: 27.8 mg, 71% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.14 (m, 2H), 7.13-7.05 (m, 2H), 6.00 (d, *J* = 1.7 Hz, 1H), 5.37 (d, *J* = 1.5 Hz, 1H), 2.88-2.77 (m, 1H), 2.63-2.53 (m, 2H), 1.48 (s, 9H), 1.21-1.16 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$)

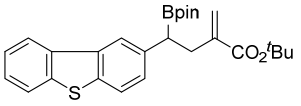
δ 166.5, 144.7, 141.2, 134.2, 129.7, 128.8, 126.9, 125.8, 124.9, 83.8, 80.7, 34.7, 28.3, 24.84, 24.80. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.40. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{21}H_{31}BClO_4^+$ Calcd for 393.1998 Found 393.1991.

***tert*-Butyl 2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(3-(trifluoromethyl)phenyl)butanoate (5oa)**: 28.3 mg, 66% yield, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.37-7.24 (m, 3H), 5.92 (d, *J* = 1.6 Hz, 1H), 5.30 (d, *J* = 1.6 Hz, 1H), 2.83-2.73 (m, 1H), 2.66-2.58 (m, 1H), 2.55-2.45 (m, 1H), 1.40 (s, 9H), 1.19-1.08 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 143.6, 141.1, 132.2, 130.7 (q, $J_{C\text{-}F}$ = 31.9 Hz), 128.9, 125.5 (q, $J_{C\text{-}F}$ = 4.0 Hz), 125.1, 124.5 (q, $J_{C\text{-}F}$ = 272.3 Hz), 122.5 (q, $J_{C\text{-}F}$ = 3.9 Hz), 83.9, 80.8, 34.9, 28.2, 24.8, 24.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.24. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.56. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{22}H_{31}BF_3O_4^+$ Calcd for 427.2262; Found 427.2255.

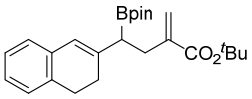
***tert*-Butyl 2-methylene-4-(naphthalen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5pa)**: 21.9 mg, 54% yield, new compound, white solid, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80-7.71 (m, 3H), 7.65-7.60 (m, 1H), 7.45-7.35 (m, 3H), 5.98 (d, *J* = 1.6 Hz, 1H), 5.40 (d, *J* = 1.7 Hz, 1H), 2.98-2.89 (m, 1H), 2.83-2.75 (m, 1H), 2.73-2.64 (m, 1H), 1.47 (s, 9H), 1.25-1.15 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 141.5, 140.2, 134.0, 132.1, 128.0, 127.7, 127.6, 126.7, 125.9, 125.1, 124.8, 83.7, 80.6, 34.7, 28.3, 24.9, 24.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.34. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{25}H_{34}BO_4^+$ Calcd for 409.2545; Found 409.2537.

***tert*-Butyl 2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(9-tosyl-9*H*-carbazol-3-yl)butanoate (5qa)**: 41.4 mg, 69% yield, new compound, yellow solid, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32-7.25 (m, 1H), 8.22-8.15 (m, 1H), 7.88-7.82 (m, 1H), 7.74-7.65 (m, 3H), 7.48-7.43 (m, 1H), 7.36-7.29 (m, 2H), 7.11-7.05 (m, 2H), 5.98 (d, *J* = 1.7 Hz, 1H), 5.38 (d, *J* = 1.4 Hz, 1H), 2.95-2.86 (m, 1H), 2.78-2.71 (m, 1H), 2.68-2.59 (m, 1H), 2.26 (s, 3H), 1.47 (s, 9H), 1.24-1.14 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 144.9, 141.5, 138.8, 138.5, 136.8, 135.2, 129.8, 128.3, 127.3, 126.9, 126.8, 126.7, 124.7, 124.0, 120.1, 119.7, 115.4, 115.3, 83.8, 80.7, 35.2, 28.3, 24.84, 24.78, 21.7. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 34.65. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{34}H_{41}BNO_6S^+$ Calcd for 602.2742; Found 602.2735.

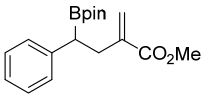
***tert*-Butyl 4-(dibenzo[*b*,*d*]furan-2-yl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5ra)**: 21.0 mg, 47% yield, new compound, yellow solid, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.80 (m, 1H), 7.73-7.68 (m, 1H), 7.49-7.43 (m, 1H), 7.39-7.31 (m, 2H), 7.26-7.20 (m, 2H), 5.92 (d, *J* = 1.7 Hz, 1H), 5.33 (d, *J* = 1.7 Hz, 1H), 2.91-2.81 (m, 1H), 2.75-2.67 (m, 1H), 2.62-2.50 (m, 1H), 1.41 (s, 9H), 1.19-1.09 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 156.4, 154.6, 141.3, 136.9, 127.8, 126.9, 124.6, 124.4, 124.3, 122.5, 120.6, 120.2, 111.6, 111.4, 83.5, 80.4, 35.2, 28.1, 24.7, 24.6. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.75. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{27}H_{34}BO_5^+$ Calcd for 449.2494; Found 449.2485.

***tert*-Butyl 4-(dibenzo[*b*,*d*]thiophen-2-yl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5sa)**: 

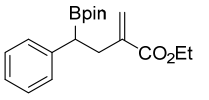
21.1 mg, 46% yield, new compound, yellow solid, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15-8.08 (m, 1H), 8.03-7.97 (m, 1H), 7.86-7.79 (m, 1H), 7.76-7.68 (d, *J* = 8.2 Hz, 1H), 7.46-7.40 (m, 2H), 7.36-7.30 (m, 1H), 6.00 (d, *J* = 1.7 Hz, 1H), 5.41 (d, *J* = 1.7 Hz, 1H), 3.00-2.90 (m, 1H), 2.84-2.76 (m, 1H), 2.73-2.63 (m, 1H), 1.48 (s, 9H), 1.25-1.16 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 141.5, 140.0, 139.0, 136.7, 136.0, 135.8, 127.9, 126.7, 124.8, 124.4, 123.0, 122.8, 121.7, 121.6, 83.8, 80.6, 35.3, 28.3, 24.9, 24.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.71. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{27}H_{34}BO_4S^+$ Calcd for 465.2265; Found 465.2259.

***tert*-Butyl 4-(3,4-dihydronaphthalen-2-yl)-2-methylene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5ta)**: 

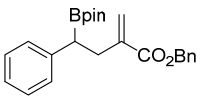
22.8 mg, 66% yield, new compound, yellow solid, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12-7.09 (m, 1H), 7.08-7.02 (m, 2H), 6.99-6.93 (m, 1H), 6.22 (d, *J* = 1.4 Hz, 1H), 6.03 (d, *J* = 1.6 Hz, 1H), 5.48 (q, *J* = 1.4 Hz, 1H), 2.76 (t, *J* = 8.3 Hz, 2H), 2.73-2.69 (m, 1H), 2.57-2.52 (m, 1H), 2.34-2.23 (m, 3H), 1.48 (s, 9H), 1.24-1.17 (m, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 142.3, 141.7, 135.5, 134.8, 127.3, 126.6, 126.1, 125.7, 124.5, 122.9, 83.7, 80.6, 31.6, 28.6, 28.4, 27.5, 25.0, 24.9. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 33.63. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{25}H_{36}BO_4^+$ Calcd for 411.2701; Found 411.2696.

Methyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5ab): 

26.5 mg, 84% yield, unknown compound, colorless oil, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.19 (m, 4H), 7.18-7.08 (m, 1H), 6.09 (d, *J* = 1.5 Hz, 1H), 5.47 (d, *J* = 1.5 Hz, 1H), 3.73 (s, 3H), 2.94-2.81 (m, 1H), 2.69-2.56 (m, 2H), 1.17 (d, *J* = 11.3 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 142.3, 140.0, 128.7, 128.6, 125.69, 125.66, 83.7, 52.0, 34.6, 24.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.82. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{18}H_{26}BO_4^+$ Calcd for 317.1919; Found 317.1912.

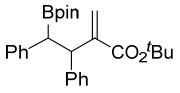
Ethyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5ac): 

26.3 mg, 80% yield, unknown compound, colorless oil, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.19 (m, 4H), 7.17-7.05 (m, 1H), 6.09 (d, *J* = 1.6 Hz, 1H), 5.46 (d, *J* = 1.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.99-2.80 (m, 1H), 2.70-2.57 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.18 (d, *J* = 11.4 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 142.4, 140.3, 128.6, 128.5, 125.6, 125.4, 83.6, 60.7, 34.7, 24.9, 24.8, 14.4. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.32. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{19}H_{28}BO_4^+$ Calcd for 331.2075; Found 331.2068.

Benzyl 2-methylene-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5ad): 

20.0 mg, 51% yield, unknown compound, colorless oil, R_f = 0.2 (PE/EtOAc 50/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 5H), 7.28-7.19 (m, 2H), 7.20-7.13 (m, 2H), 7.17-7.08 (m, 1H), 6.14 (d, *J* = 1.4 Hz, 1H), 5.49 (d, *J* = 1.6 Hz, 1H), 5.18 (d, *J* = 1.1 Hz, 2H), 2.96-2.84 (m, 1H), 2.71-2.59 (m, 2H), 1.17 (d, *J* = 11.6 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 142.3, 140.0, 136.4, 128.71, 128.68, 128.5, 128.3, 128.2, 126.1, 125.6, 83.7, 66.5, 34.8, 24.9, 24.8. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 33.42. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{24}H_{30}BO_4^+$ Calcd for 393.2232; Found 393.2221.

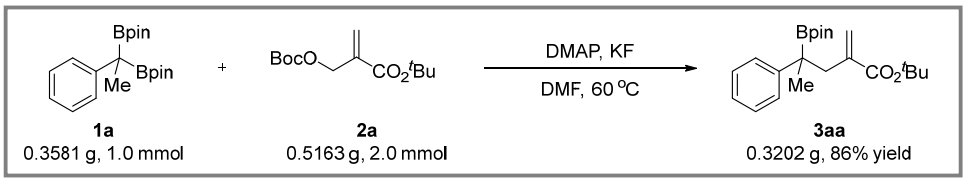
***tert*-Butyl 2-methylene-3,4-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (5ae)**: 34.3 mg, 84% yield, 4:1 dr, new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1).



Major product: 27.4 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09-6.93 (m, 10H), 6.31 (s, 1H), 5.87 (s, 1H), 4.30 (d, *J* = 12.8 Hz, 1H), 2.83 (d, *J* = 12.8 Hz, 1H), 1.37 (s, 9H), 1.19 (s, 6H), 1.33 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 146.5, 142.4, 140.2, 129.4, 128.3, 128.1, 127.8, 125.9, 125.5, 122.9, 83.7, 80.8, 48.9, 28.1, 24.8, 24.6. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.21. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{27}H_{36}BO_4^+$ Calcd for 435.2701; Found 435.2694.

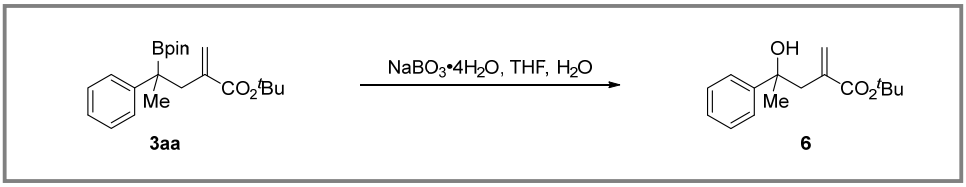
Minor product: 6.9 mg, 17% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H), 7.23-7.17 (m, 6H), 7.12-7.02 (m, 2H), 5.94 (s, 1H), 5.44 (s, 1H), 4.46 (d, *J* = 12.8 Hz, 1H), 3.06 (d, *J* = 12.8 Hz, 1H), 1.24 (s, 9H), 0.82 (s, 6H), 0.78 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 144.1, 143.2, 140.7, 129.1, 128.8, 128.5, 128.2, 126.6, 125.6, 124.2, 83.5, 80.7, 47.6, 28.1, 24.5, 24.2. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.50. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{27}H_{36}BO_4^+$ Calcd for 435.2701; Found 435.2695.

9. Scale up experiments of 3aa



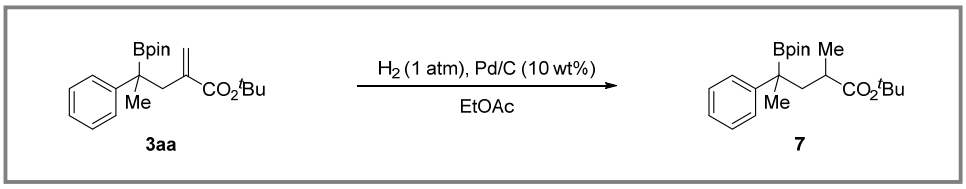
Scale up experiment of 3aa: In the nitrogen filled glovebox, a Schlenk tube was charged with DMAP (12.2 mg, 0.1 mmol, 10.0 mol%), KF (5.6 mg, 0.1 mmol, 10.0 mol%), **1a** (0.3581 g, 1.0 mmol, 1.0 equiv.), **2a** (0.5163 g, 2.0 mmol, 2.0 equiv.), and DMF (20.0 mL). Then, the Schlenk tube was removed from glovebox and stirred in a 60 °C oil bath. Upon completion (monitored by TLC), the mixture was allowed to slowly cool to room temperature, followed by concentration under reduced pressure in a 60 °C water bath. The crude product was purified by flash column chromatography (PE/EtOAc 60/1) on silica gel (200-300 mesh) to afford the target product **3aa** (0.3202 g, 86% yield).

10. Synthetic transformations of 3aa and 3ab



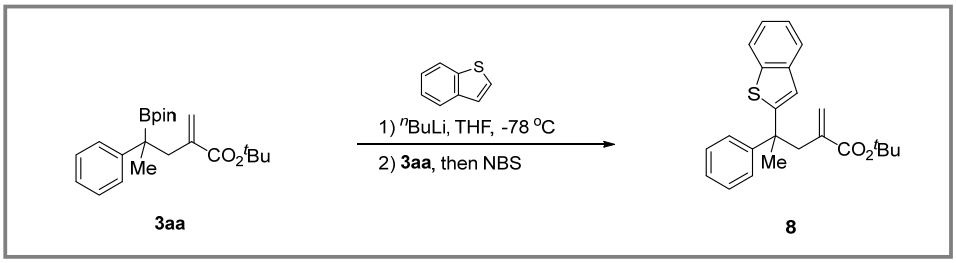
According to the reported procedures[23], under air atmosphere, a 25.0 mL reaction tube equipped with a magnetic stir bar was charged with **3aa** (104.2 mg, 0.28 mmol, 1.0 equiv.), THF (2.5 mL) and water (2.5 mL). Then, sodium perborate tetrahydrate (258.5 mg, 1.68 mmol, 6.0 equiv.) was added. The resulting reaction mixture was stirred at room temperature for 6 hours. Upon completion (monitored by TLC), the mixture was extracted with EtOAc. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 10/1) on silica gel (200-300 mesh) to afford the desired compound **6** (63.5 mg, 87% yield).

***tert*-Butyl 4-hydroxy-2-methylene-4-phenylpentanoate (6)**: known compound and all datas were in agreement with those reported literatures[24], colorless oil, R_f = 0.2 (PE/EtOAc 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.40 (m, 2H), 7.35-7.25 (m, 2H), 7.24-7.16 (m, 1H), 6.07 (d, *J* = 1.8 Hz, 1H), 5.38-5.32 (m, 1H), 3.93 (s, 1H), 2.84-2.74 (m, 2H), 1.53 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 148.0, 138.1, 128.7, 128.1, 126.5, 125.2, 81.7, 74.0, 46.6, 29.9, 28.1.



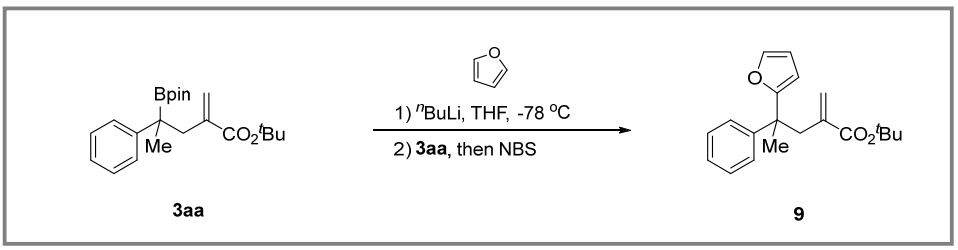
According to the reported procedures[23], under nitrogen atmosphere, a 25.0 mL reaction tube equipped with a magnetic stir bar was charged with **3aa** (74.4 mg, 0.20 mmol, 1.0 equiv.), Pd/C (2.1 mg, 10 wt%, 0.02 mmol, 0.1 equiv.) and EtOAc (4.0 mL). The reaction mixture was stirred overnight at room temperature under hydrogen atmosphere. Upon completion (monitored by TLC), the mixture concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 60/1) on silica gel (200-300 mesh) to give compound **7** (50.8 mg, 68% yield, 1:1.5 dr).

***tert*-Butyl 2-methyl-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (7)**: new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28-7.17 (m, 4H), 7.08-7.02 (m, 1H), 2.31-2.25 (m, 0.6H), 2.22-2.18 (m, 0.4H), 2.15-2.07 (m, 0.6H), 2.04-1.95 (m, 0.4H), 1.87-1.77 (m, 1H), 1.33 (s, 3.6H), 1.31-1.27 (m, 5.4H), 1.26 (s, 3H), 1.13-1.09 (m, 12H), 1.08-1.05 (m, 1.8H), 0.89-0.87 (m, 1.2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.6, 177.2, 147.2, 145.9, 128.3, 127.4, 127.0, 125.5, 125.4, 83.7, 83.6, 79.8, 79.7, 42.9, 42.0, 39.3, 37.3, 28.23, 28.20, 24.9, 24.82, 24.80, 24.7, 20.8, 20.5, 20.4, 20.2. **^{11}B NMR** (160 MHz, $CDCl_3$) δ 34.27. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{22}H_{36}BO_4^+$ Calcd for 375.2701; Found 375.2698.



According to the reported procedures[23], under nitrogen atmosphere, a 25.0 mL reaction tube equipped with a magnetic stir bar was charged with thianaphthene (53.7 mg, 0.40 mmol, 2.0 equiv.) and THF (0.8 mL). The reaction was cooled to -78 °C and stirred, followed by dropwise addition of ^{n}BuLi (0.40 mmol, 2.5M in THF, 2.0 equiv.) *via* syringe. The cooling bath was removed and the reaction was stirred at room temperature for 1 hour. Subsequently, the mixture was cooled back down to -78 °C, followed by slowly addition of the solution of **3aa** (74.4 mg, 0.20 mmol, 0.4M in THF, 1.0 equiv.) *via* syringe. The reaction mixture was stirred at -78 °C for an additional 1 hour, and then added the solution of *N*-bromosuccinimide (71.2 mg, 0.40 mmol, 0.4M in THF, 2.0 equiv.) *via* syringe. The resulting mixture was stirred at -78 °C for 1 hour under nitrogen protection. Upon completion (monitored by TLC), the mixture was treated with 1M sodium thiosulfate (aq.) and extracted with EtOAc. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 60/1) on silica gel (200-300 mesh) to give compound **8** (50.0 mg, 66% yield).

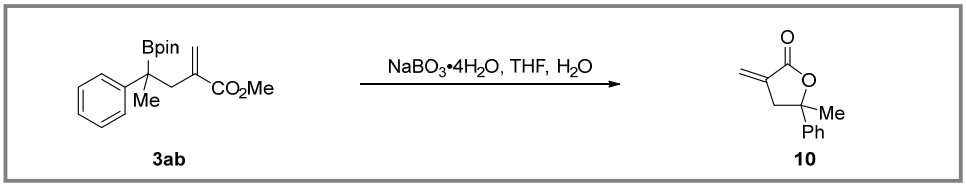
***tert*-Butyl 4-(benzo[*b*]thiophen-2-yl)-2-methylene-4-phenylpentanoate (8)**: new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74-7.64 (m, 2H), 7.35-7.21 (m, 7H), 7.12 (s, 1H), 6.01 (d, *J* = 1.6 Hz, 1H), 4.99 (d, *J* = 1.7 Hz, 1H), 3.36-3.23 (m, 2H), 1.72 (s, 3H), 1.37 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.2, 156.0, 147.2, 139.8, 138.3, 128.3, 128.0, 127.6, 126.8, 124.3, 124.0, 123.5, 122.3, 120.9, 80.8, 46.6, 42.6, 28.2, 27.7. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{24}H_{27}O_2S^+$ Calcd for 379.1726; Found 379.1726.



According to the reported procedures[23], under nitrogen atmosphere, a 25.0 mL reaction tube equipped with a magnetic stir bar was charged with furan (27.2 mg, 0.40 mmol, 2.0 equiv.) and THF (0.8 mL). The reaction was cooled to -78 °C and stirred, followed by dropwise addition of ^{n}BuLi (0.40 mmol, 2.5M in THF, 2.0 equiv.) *via* syringe. The cooling bath was removed and the reaction was stirred at room temperature for 1 hour. Subsequently, the mixture was cooled back down to -78 °C, followed by slowly addition of the solution of **3aa** (74.4 mg, 0.20 mmol, 0.4M in THF, 1.0 equiv.) *via* syringe. The reaction mixture was stirred at -78 °C for an additional 1 hour, and then added the solution of *N*-bromosuccinimide (71.2 mg, 0.40 mmol, 0.4M in THF, 2.0 equiv.) *via* syringe. The resulting mixture was stirred at -78 °C for 1 hour under nitrogen protection. Upon completion (monitored by TLC), the mixture was treated with 1M sodium thiosulfate

(aq.) and extracted with EtOAc. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 60/1) on silica gel (200-300 mesh) to give compound **9** (34.9 mg, 56% yield).

***tert*-Butyl 4-(furan-2-yl)-2-methylene-4-phenylpentanoate (9)**: new compound, colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37-7.33 (m, 1H), 7.29-7.26 (m, 2H), 7.22-7.16 (m, 3H), 6.34-6.27 (m, 1H), 6.17 (d, *J* = 3.2 Hz, 1H), 6.02 (d, *J* = 1.7 Hz, 1H), 4.90 (d, *J* = 1.6 Hz, 1H), 3.20-3.16 (m, 1H), 3.12-3.07 (m, 1H), 1.54 (s, 3H), 1.43 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.2, 160.4, 146.7, 141.4, 138.5, 128.3, 127.6, 126.9, 126.5, 110.1, 106.9, 80.6, 45.1, 40.2, 28.2, 24.8. **HRMS** (ESI-orbitrap) *m/z*: $[M+H]^+$ $C_{20}H_{25}O_3^+$ Calcd for 313.1798; Found 313.1790.

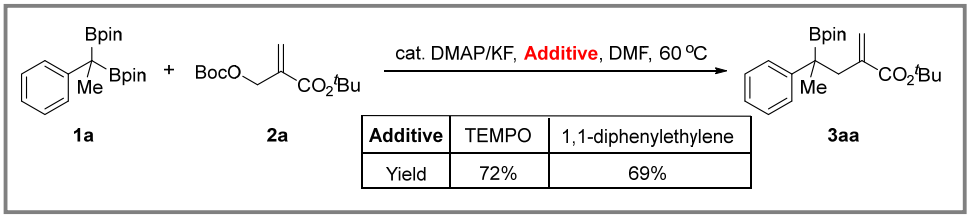


According to the reported procedures[23]. Under air atmosphere, a 50.0 mL reaction tube equipped with a magnetic stir bar was charged with **3ab** (169.3 mg, 0.50 mmol, 1.0 equiv.), THF (2.5 mL) and water (2.5 mL). Then, sodium perborate tetrahydrate (461.0 mg, 3.0 mmol, 6.0 equiv.) was added. The resulting reaction mixture was stirred at room temperature for 6 hours. Upon completion (monitored by TLC), the mixture was extracted with EtOAc. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 60/1) on silica gel (200-300 mesh) to afford the desired compound **10** (72.2 mg, 77% yield).

5-Methyl-3-methylene-5-phenyldihydrofuran-2(3*H*)-one (10): known compound and all datas were in agreement with those reported literatures[25], colorless oil, R_f = 0.2 (PE/EtOAc 60/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.33 (m, 4H), 7.32-7.26 (m, 1H), 6.29-6.23 (s, 1H), 5.64 (s, 1H), 3.21-3.13 (m, 2H), 1.73 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 144.7, 135.2, 128.8, 127.8, 124.3, 122.8, 84.1, 42.8, 30.2.

11. Mechanism investigation

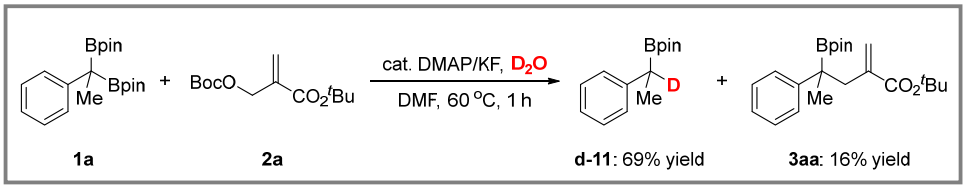
A. Radical capture experiments



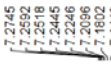
Additive	TEMPO	1,1-diphenylethylene
Yield	72%	69%

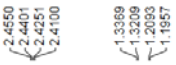
Same as the general procedure. TEMPO (0.10 mmol, 1.0 equiv.) or 1,1-diphenylethylene (0.10 mmol, 1.0 equiv.) was separately added with catalysts and substrates. After standard work-up, the mixture concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 60/1). The target product **3aa** was isolated in 72% and 69% yields, respectively.

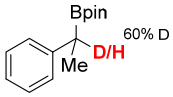
B. Carbanion capture experiments of 3aa



Same as the general procedure. **D_2O** (0.2 mg, 0.10 mmol, 1.0 equiv.) was added with catalysts and substrates. Upon completion (monitored by TLC), the mixture concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EtOAc 60/1) to give compound **11** (16.3 mg, 69% yield). The compound **11** was known compound and all datas were in agreement with those reported literatures.[26]

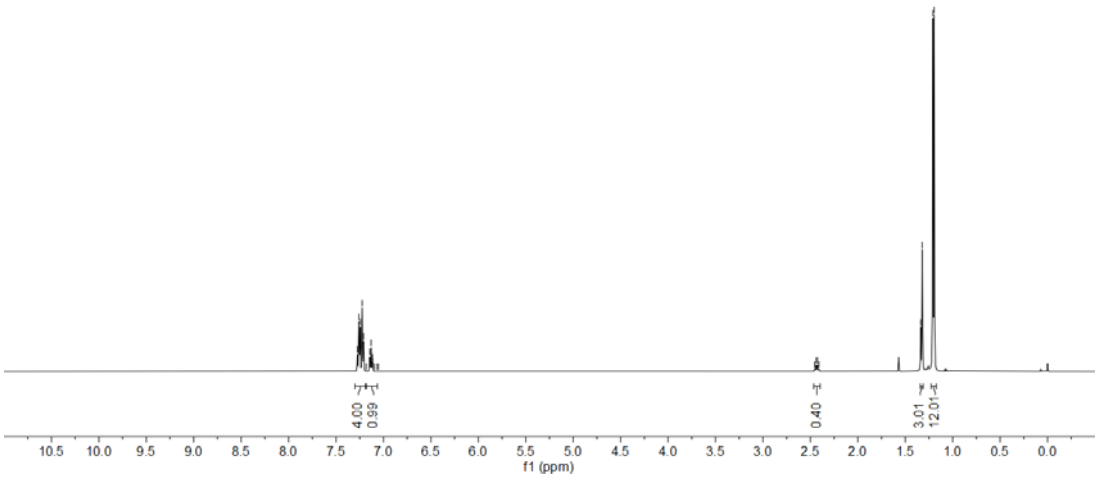




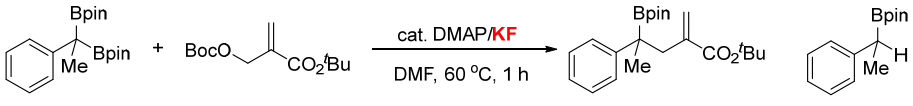


11

^{1}H NMR (500 MHz, $CDCl_3$)



C. Control experiments of catalyst KF



1a **2a** **3aa** **11**

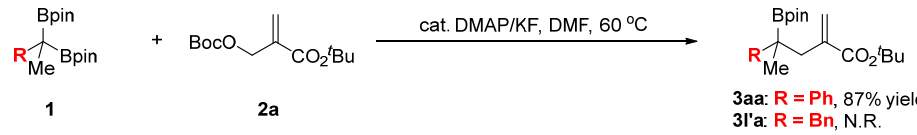
cat. KF	10.0 mol% KF	none KF	10.0 mol% KF 18-crown-6
Yield	82% **3aa**,10% **11**	18% **3aa**, 57% **11**	30% **3aa**, 45% **11**

Control experiments of catalyst KF (I): In the glovebox, a Schlenk tube was charged with DMAP (1.2 mg, 10.0 mol%), KF (0.6 mg, 10.0 mol%), **1a** (35.8 mg, 0.10 mmol, 1.0 equiv.), **2a** (51.6 mg, 0.20 mmol, 2.0 equiv.), and DMF (2.0 mL). Then, the Schlenk tube was removed from glovebox and stirred in a 60 °C oil bath for 1 hour. Subsequently, the mixture concentrated under reduced pressure, and crude product was purified by flash column chromatography (PE/EtOAc 60/1). The target product **3aa** was detected in 82% yield, and protonated product **11** was detected in 10% yield.

Control experiments of none catalyst KF (II): In the glovebox, a Schlenk tube was charged with DMAP (1.2 mg, 10.0 mol%), **1a** (35.8 mg, 0.10 mmol, 1.0 equiv.), **2a** (51.6 mg, 0.20 mmol, 2.0 equiv.), and DMF (2.0 mL). Then, the Schlenk tube was removed from glovebox and stirred in a 60 °C oil bath for 1 hour. Subsequently, the mixture concentrated under reduced pressure, and crude product was purified by flash column chromatography (PE/EtOAc 60/1). The target product **3aa** was detected in 18% yield, and protonated product **11** was detected in 57% yield.

Control experiments of catalyst KF and 18-crown-6 (III): In the glovebox, a Schlenk tube was charged with DMAP (1.2 mg, 10.0 mol%), KF (0.6 mg, 10.0 mol%), 18-crown-6 (2.6 mg, 10.0 mol%), **1a** (35.8 mg, 0.10 mmol, 1.0 equiv.), **2a** (51.6 mg, 0.20 mmol, 2.0 equiv.), and DMF (2.0 mL). Then, the Schlenk tube was removed from glovebox and stirred in a 60 °C oil bath for 1 hour. Subsequently, the mixture concentrated under reduced pressure, and crude product was purified by flash column chromatography (PE/EtOAc 60/1). The target product **3aa** was detected in 30% yield, and protonated product **11** was detected in 45% yield.

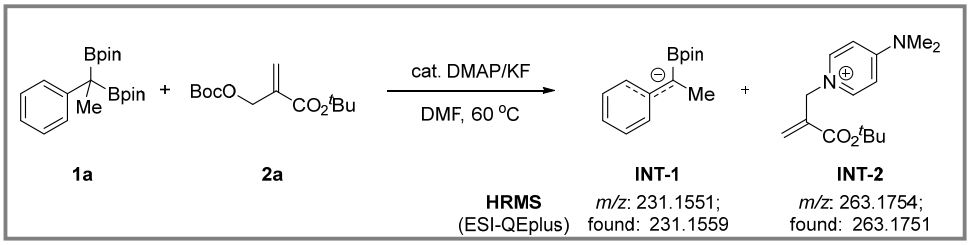
D. Experiments for influence of R group



1 **2a**

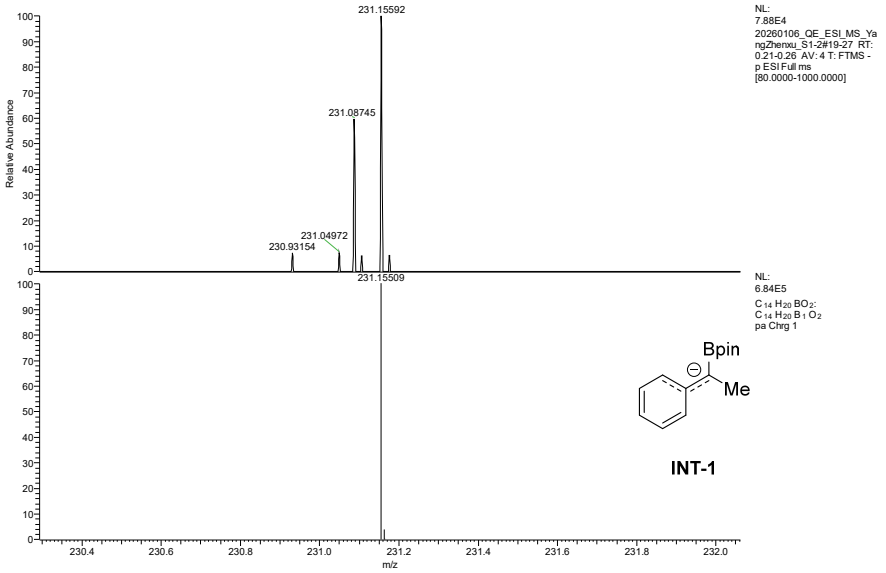
Same as the general procedure. Compound **1l′** (37.2 mg, 0.10 mmol, 1.0 equiv.), instead of **1a** as the *gem*-diborylalkanes substrate, was added to the Schlenk tube with the catalysts and **2a**. The Schlenk tube was stirred in a 60 °C oil bath for 16 hours. The target product 3**l′a** was not detected by TLC and NMR analysis. Most of substrate **1l′** (35.4 mg) was isolated and recovered by flash column chromatography (PE/EtOAc 60/1).

12. HRMS spectra of the proposed intermediate

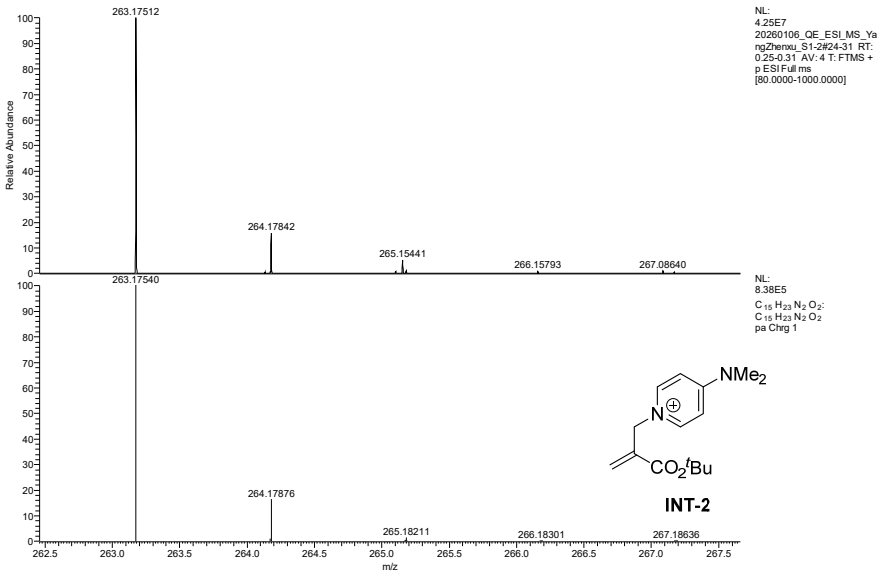


In the glovebox, a 25.0 mL Schlenk tube was charged with DMAP (1.2 mg, 10.0 mol%), KF (0.6 mg, 10.0 mol%), **1a** (0.10 mmol), **2a** (0.20 mmol), and DMF (2.0 mL). Then, the Schlenk tube was removed from glovebox and stirred in a 60 °C oil bath for 20 minutes. The mixture was filtered and diluted with MeCN, analyzed by HRMS immediately.

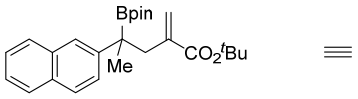
HRMS (ESI-orbitrap) *m/z*: $[M]^-$ $C_{14}H_{20}BO_2^-$ Calcd for 231.1551; Found 231.1559.



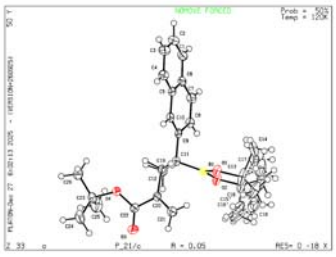
HRMS (ESI-orbitrap) *m/z*: $[M]^+$ $C_{15}H_{23}N_2O_2^+$ Calcd for 263.1754; Found 263.1751.



13. Crystallography data of 3pa



3pa



CCDC: 2519026

Procedure for recrystallization of 3pa: The hexane was slowly added to **3pa** in DCM, then the solution was cooled down to 0 °C. Then the single crystal of **3pa** was obtained after five days. The structure showed the absolute configuration of **3pa** is ***tert*-butyl 2-methylene-4-(naphthalen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate**. The CCDC number is **2519026**. These details can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Thermal ellipsoid plot for 3pa (50% probability level)

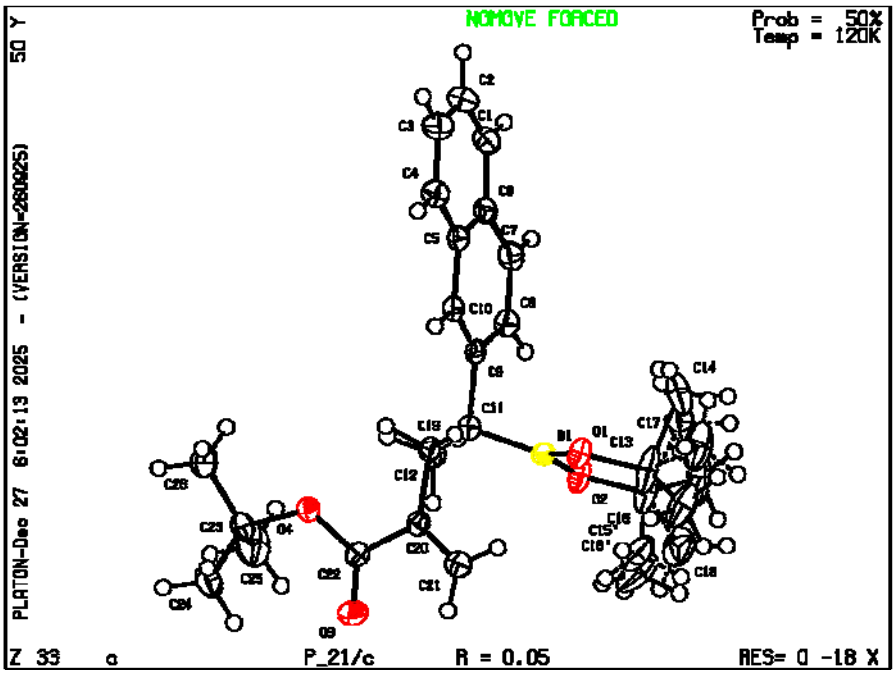


Table S9: Crystal data and structure refinement for 20251122S1.

Identification code	20251122S1	
Empirical formula	$C_{26}H_{35}BO_4$	
Formula weight	422.35	
Temperature	120.00 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	p_21/c	
Unit cell dimensions	a = 8.6140(5) Å	α = 90°.
	b = 13.7758(9) Å	β = 101.627(2) °.
	c = 21.2823(15) Å	γ = 90°.
Volume	2473.6(3) $Å^3$	
Z	4	
Density (calculated)	1.134 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	912.0	
Crystal size	0.050 x 0.090 x 0.100 mm^3	
Theta range for data collection	2.83 to 25.00°.	
Index ranges	-9<=h<=10, -16<=k<=16, -25<=l<=25	
Reflections collected	26564	
Independent reflections	4328 [R(int) = 0.0641]	
Completeness to theta = 25.00°	99.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4328 / 0 / 318	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1200	
R indices (all data)	R1 = 0.0624, wR2 = 0.1330	
Largest diff. peak and hole	0.323 and -0.264 e.$Å^{-3}$	

14. References

[1] Zhao, H.; Tong, M.; Wang, H. and Xu, S., Transition-Metal-Free Synthesis of 1,1-Diboronate Esters with a Fully Substituted Benzylic Center *via* Diborylation of Lithiated Carbamates, *Org. Biomol. Chem.,* 2017, **15**, 3418-3422.

[2] Dong, W.; Liu, Z.; Zhang, M.; Zhang, Z.; Wei, Y.; Liu, G. and Zhao, W., Copper-Catalyzed Regioselective Dihydroboration of Alkynes to Construct *gem*-Diborylalkanes, *Org. Lett.,* 2025, **27**, 3101-3106.

[3] Yao, T.; Wang, S.; Liu, Y.; Yin, G. and Li, Y., Nickel-Catalyzed 1,1-Carboboration of Polysubstituted Internal Alkenes, *Org. Lett.,* 2025, **27**, 3691-3696.

[4] Hwang, C.; Jo, W. and Cho, S. H., Base-Promoted, Deborylative Secondary Alkylation of N-heteroaromatic *N*-oxides with Internal *gem*-Bis[(pinacolato)boryl]alkanes: a Facile Derivatization of 2,2′-Bipyridyl Analogues, *Chem. Commun.,* 2017, **53**, 7573-7576.

[5] Lee, H.; Lee, Y. and Cho, S. H., Palladium-Catalyzed Chemoselective Negishi Cross-Coupling of Bis[(pinacolato)boryl]methylzinc Halides with Aryl (Pseudo)Halides, *Org. Lett.,* 2019, **21**, 5912-5916.

[6] Ning, P.-F.; Wei, Y.; Chen, X.-Y.; Yang, Y.-F.; Gao, F.-C. and Hong, K., A General Method to Access Sterically Encumbered Geminal Bis(boronates) *5* Formal Umpolung Transformation of Terminal Diboron Compounds, *Angew. Chem., Int. Ed.,* 2024, **63**, e202315232.

[7] Lee, B. and Chirik, P. J., Ketone Synthesis from Benzyldiboronates and Esters: Leveraging *α*-Boryl Carbanions for Carbon-Carbon Bond Formation, *J. Am. Chem. Soc.,* 2020, **142**, 2429-2437.

[8] Zhou, R.; Wang, J.; Song, H. and He, Z., Phosphine-Catalyzed Cascade [3 + 2] Cyclization-Allylic Alkylation, [2 + 2 + 1] Annulation, and [3 + 2] Cyclization Reactions between Allylic Carbonates and Enones, *Org. Lett.,* 2011, **13**, 580-583.

[9] Montgomery, T. P.; Hassan, A. H.; Park, B. Y. and Krische, M. J., Enantioselective Conversion of Primary Alcohols to *α-exo*-Methylene *γ*-Butyrolactones *via* Iridium-Catalyzed C-C Bond-Forming Transfer Hydrogenation: 2-(Alkoxycarbonyl)allylation, *J. Am. Chem. Soc.,* 2012, **134**, 11100-11103.

[10] Zheng, S. and Lu, X., A Phosphine-Catalyzed [3 + 2] Annulation Reaction of Modified Allylic Compounds and *N*-Tosylimines, *Org. Lett.,* 2008, **10**, 4481-4484.

[11] Yang, H.-B.; Zhao, Y.-Z.; Sang, R. and Shi, M., $(DHQ)_2AQN$-Catalyzed Asymmetric Substitution of Isatin-Derived Hydrazones with O-Boc-Protected Morita-Baylis-Hillman Adducts: A Strategy for Synthesizing Enantioenriched Azo Compounds Incorporating an Oxindole Scaffold, *J. Org. Chem.,* 2014, **79**, 3519-3528.

[12] Zhang, T.-Z.; Dai, L.-X. and Hou, X.-L., Enantioselective Allylic Substitution of Morita-Baylis-Hillman Adducts Catalyzed by Planar Chiral [2.2]Paracyclophane Monophosphines, *Tetrahedron: Asymmetry,* 2007, **18**, 1990-1994.

[13] Muthuraja, P.; Maharana, P. K.; Veerappan, T.; Kara, S. and Punniyamurthy, T., Pd-catalyzed Sequential Distal C-H Alkenylation and π-Allylic Amination of Arylacetic Acids Using MBH Acetates: Access to Macrocyclic Lactams, *Chem. Sci.,* 2026, **17**, 346-353.

[14] Zhang, W.; Lu, L.; Zhang, W.; Wang, Y.; Ware, S. D.; Mondragon, J.; Rein, J.; Strotman, N.; Lehnherr, D.; See, K. A. and Lin, S., Electrochemically Driven Cross-Electrophile Coupling of Alkyl Halides, *Nature,* 2022, **604**, 292-297.

[15] Sindhe, H.; Kamble, A.; Reddy, M. M.; Singh, A. and Sharma, S., Iridium(III)-Catalyzed β-Trifluoromethyl Enone Carbonyl-Directed Regioselective *ortho*-C(sp^2)-H Olefination. *Org. Biomol. Chem*., 2024, 22, 1162-1166.

[16] Bhattacharyya, H.; Saha, S.; Verma, K. and Punniyamurthy, T., Palladium-Catalyzed Substrate-Switchable C-H Alkenylation and Alkylation of Benzoic Acids Using MBH Alcohols, *Chem. Commun.,* 2025, **61**, 4200-4203.

[17] Roy, S.; Saha, S.; Bhattacharyya, H. and Punniyamurthy, T., Cascade C-H Functionalization/Annulation of 2-Aryl-1,3-Dicarbonyls with Morita-Baylis-Hillman Adducts: Access to α-Iso-/Benzochromenyl Acrylates, *Chem. Commun*., 2025, **61**, 9095-9098.

[18] Ghosh, P.; Schoch, R.; Bauer, M. and Wangelin, A. J. V., Selective Benzylic CH-Borylations by Tandem Cobalt Catalysis, *Angew. Chem., Int. Ed.,* 2022, **61**, e202110821.

[19] McDonald, T. R. and Rousseaux, S. A. L., Synthesis of 3-Borylated Cyclobutanols from Epihalohydrins or Epoxy Alcohol Derivatives, *Chem. Sci.,* 2023, **14**, 963-969.

[20] Zhang, X.-L.; Yan, B.-X. and Ye, Z.-S., Copper-Catalyzed Defluorinative C(sp^3)-C(sp^2) Cross-Coupling of Polyfluoroarenes with *gem*-Diborylalkanes, *Org. Lett.,* 2025, **27**, 5247-5252.

[21] Larsen, M. A.; Wilson, C. V. and Hartwig, J. F., Iridium-Catalyzed Borylation of Primary Benzylic C-H Bonds without a Directing Group: Scope, Mechanism, and Origins of Selectivity *J. Am. Chem. Soc.,* 2015, **137**, 8633-8643.

[22] Li, K.; Zu, B. and Mazet, C., Ni-Catalyzed Kumada-Corriu Cross-Coupling Reactions of Tertiary Grignard Reagents and Bromostyrenes, *Org. Lett.,* 2024, **26**, 6047-6052.

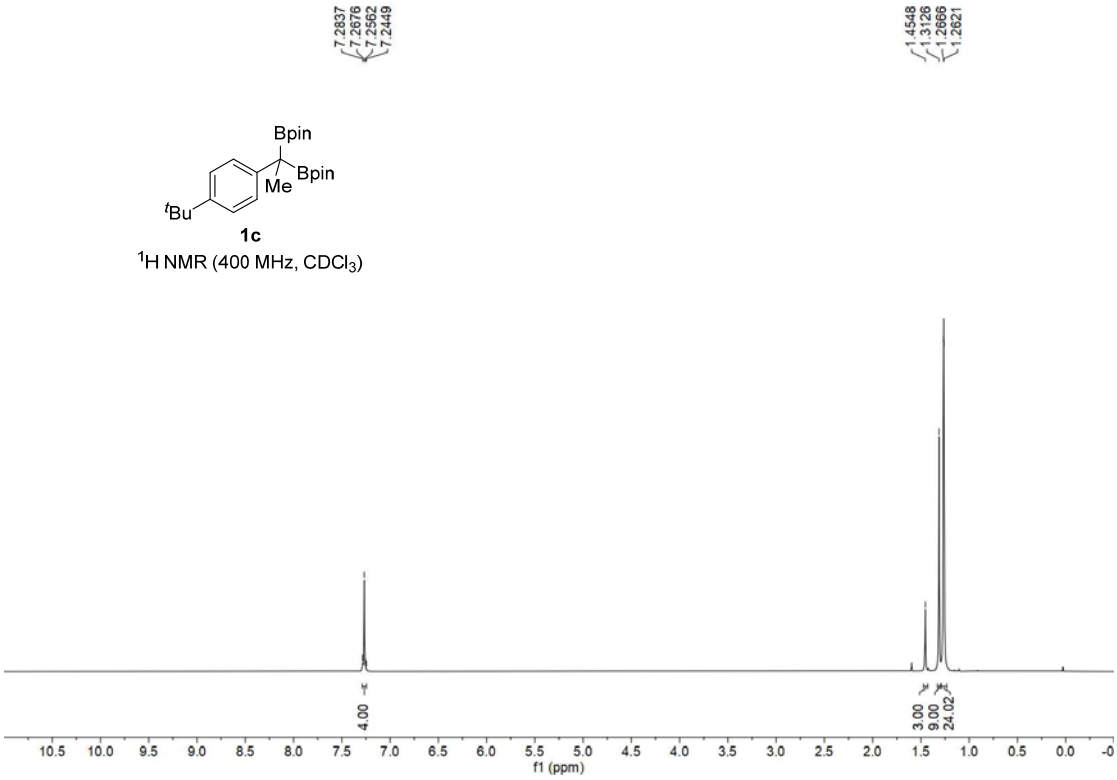
[23] Duran, J.; Rodríguez, P.; Vermeer, W. and Companyó, X., Organocatalytic Asymmetric Allylic Benzylborylation *via* Fluoride-Assisted Catalytic Generation of α-Boryl Carbanionic Intermediates, *Org. Lett.,* 2024, **26**, 8394-8399.

[24] Lazzarotto, M.; Hartmann, P.; Pletz, J.; Belaj, F.; Kroutil, W.; Payer, S. E. and Fuchs, M. Asymmetric Allylation Catalyzed by Chiral Phosphoric Acids: Stereoselective Synthesis of Tertiary Alcohols and a Reagent-Based Switch in Stereopreference, *Adv. Synth. Catal.,* 2021, **363**, 3138-3143.

[25] Nicponski, D. R., 4-(Dimethylamino)pyridine as a Catalyst for the Lactonization of 4-Hydroxy-2-Methylenebutanoate Esters, *Tetrahedron Lett.,* 2014, **55**, 2075-2077.

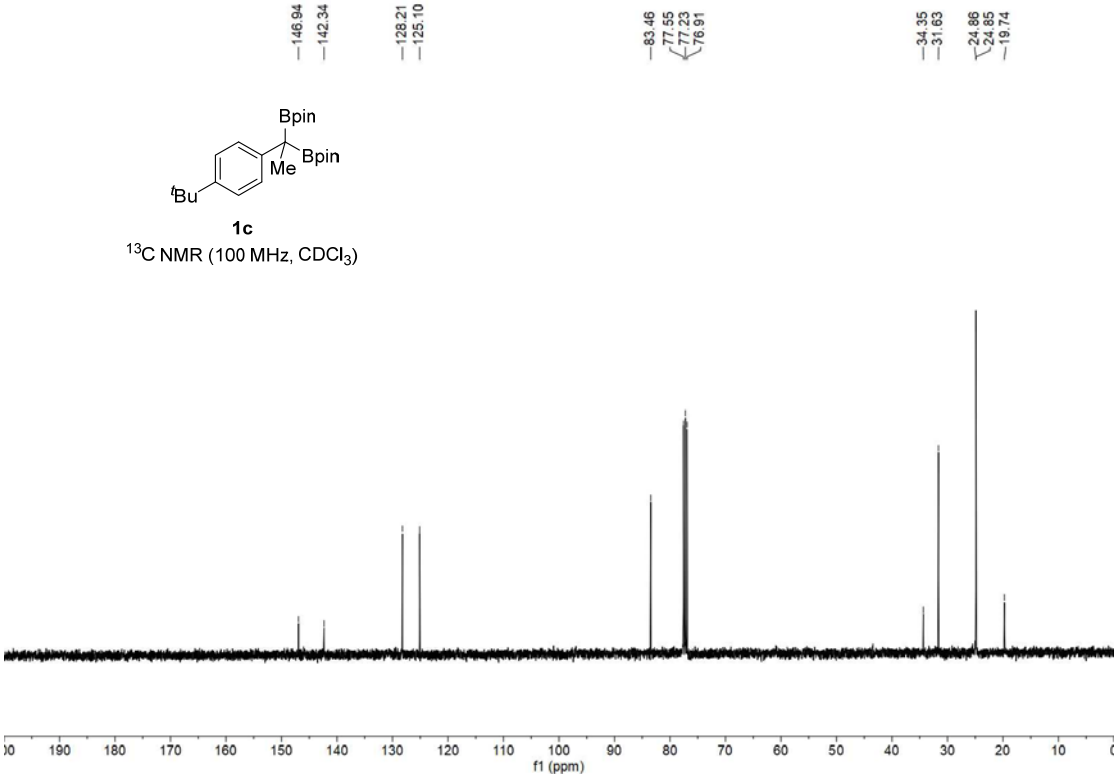
[26] Jin, H.; Han, J.; Liu, X.; Feng, C. and Zhan, M., Access to Diverse Organoborons by α-Deprotonation and Functionalization of Benzylboronates, *Org. Lett.,* 2023, **25**, 4168-4172.

12. Copy of NMR for compounds



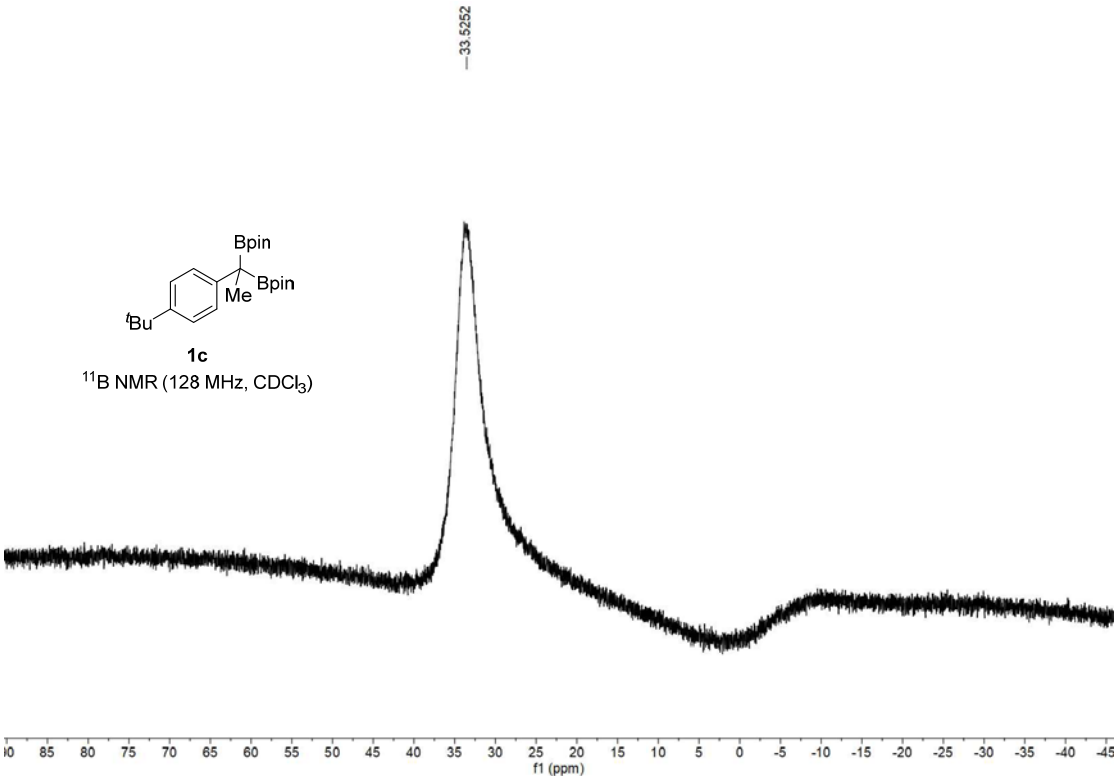
1c

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



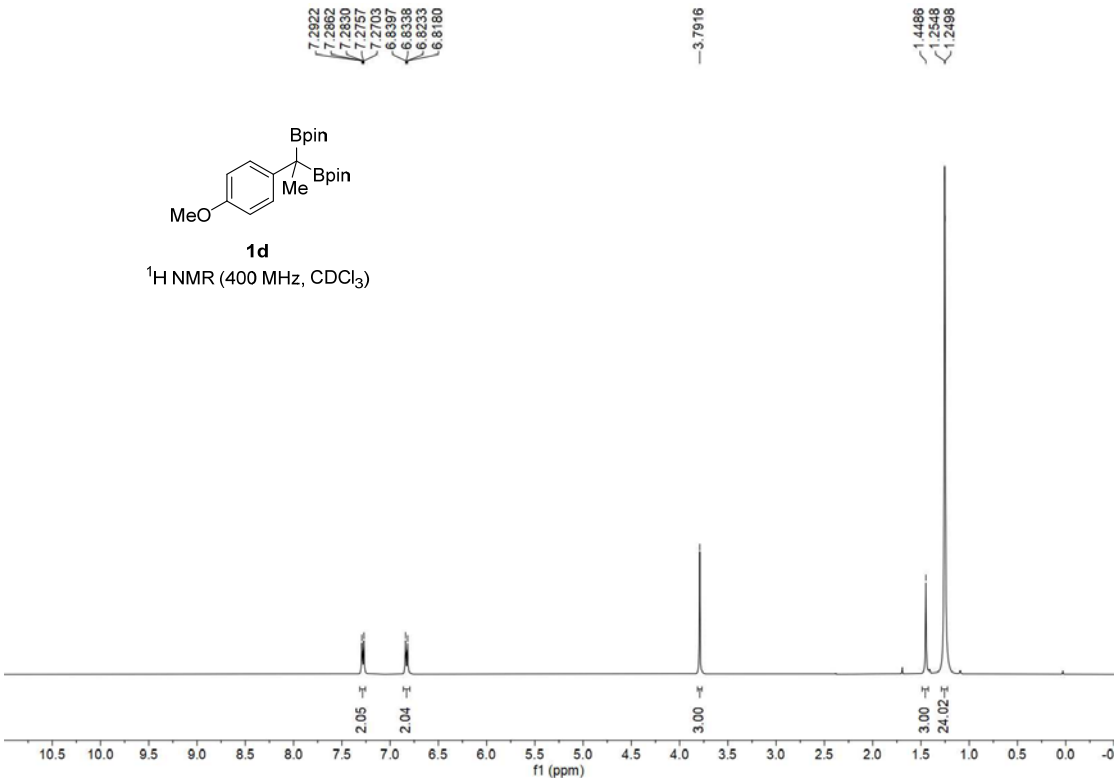
1c

^{13}C NMR (100 MHz, $CDCl_3$)



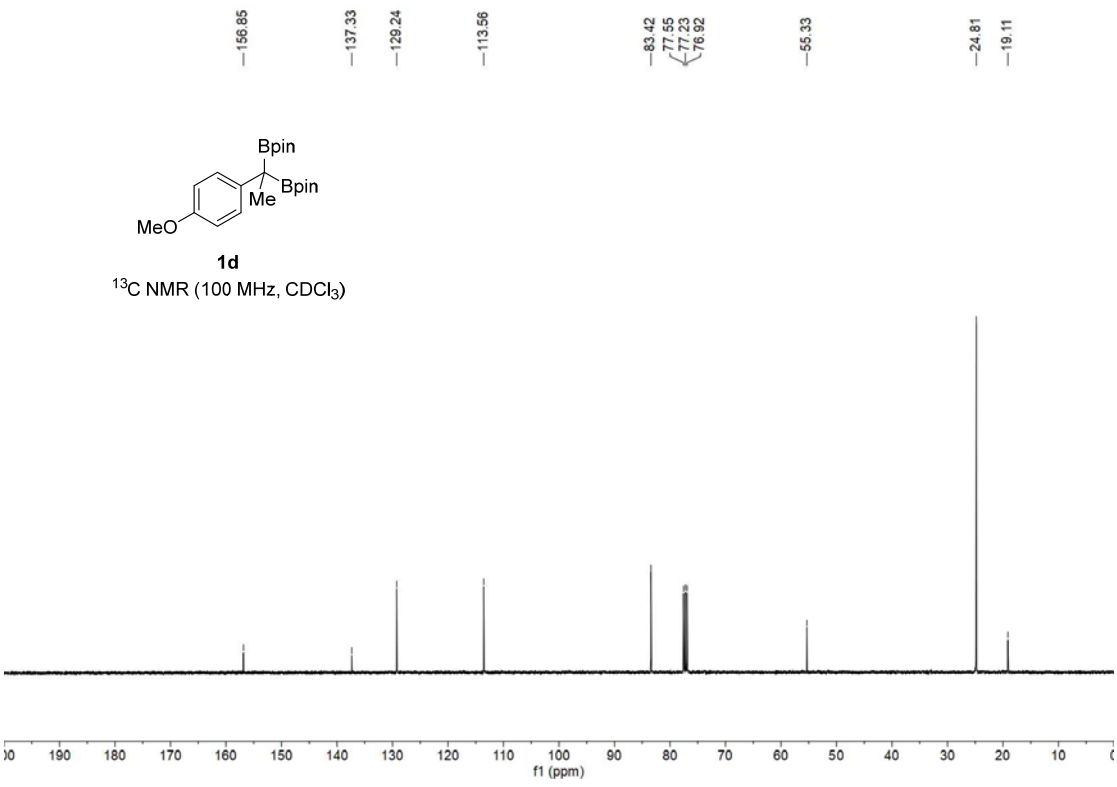
1c

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



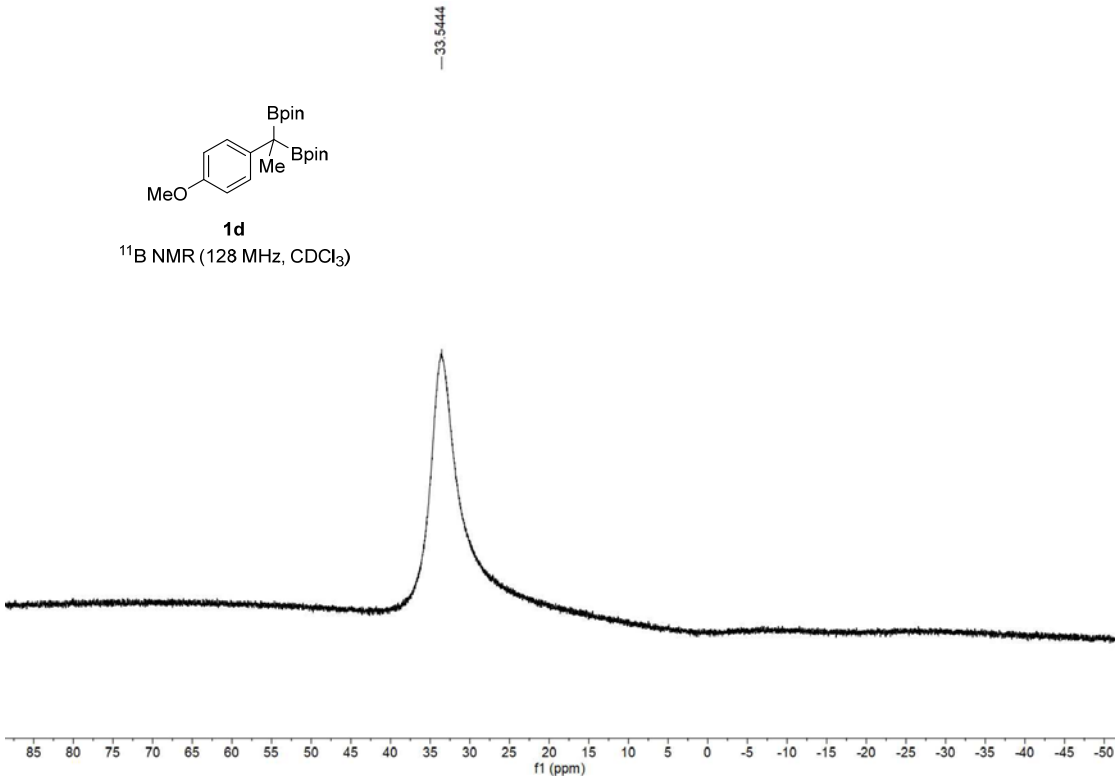
1d

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



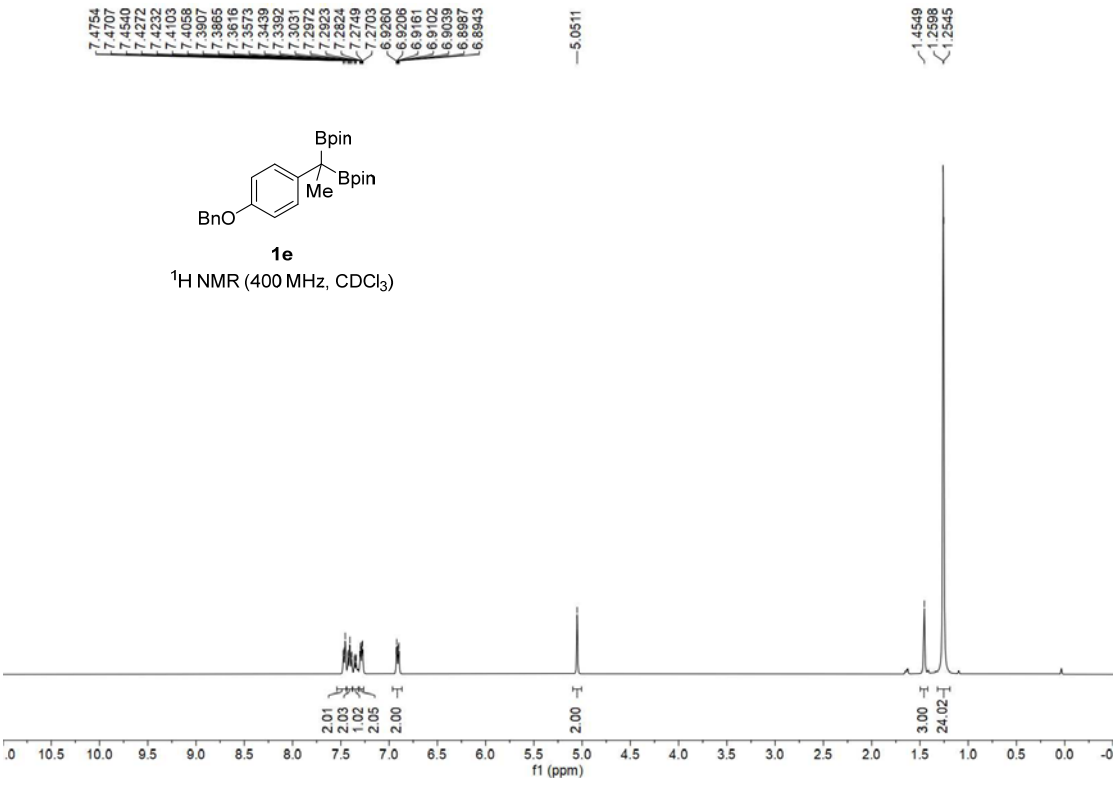
1d

^{13}C NMR (100 MHz, $CDCl_3$)



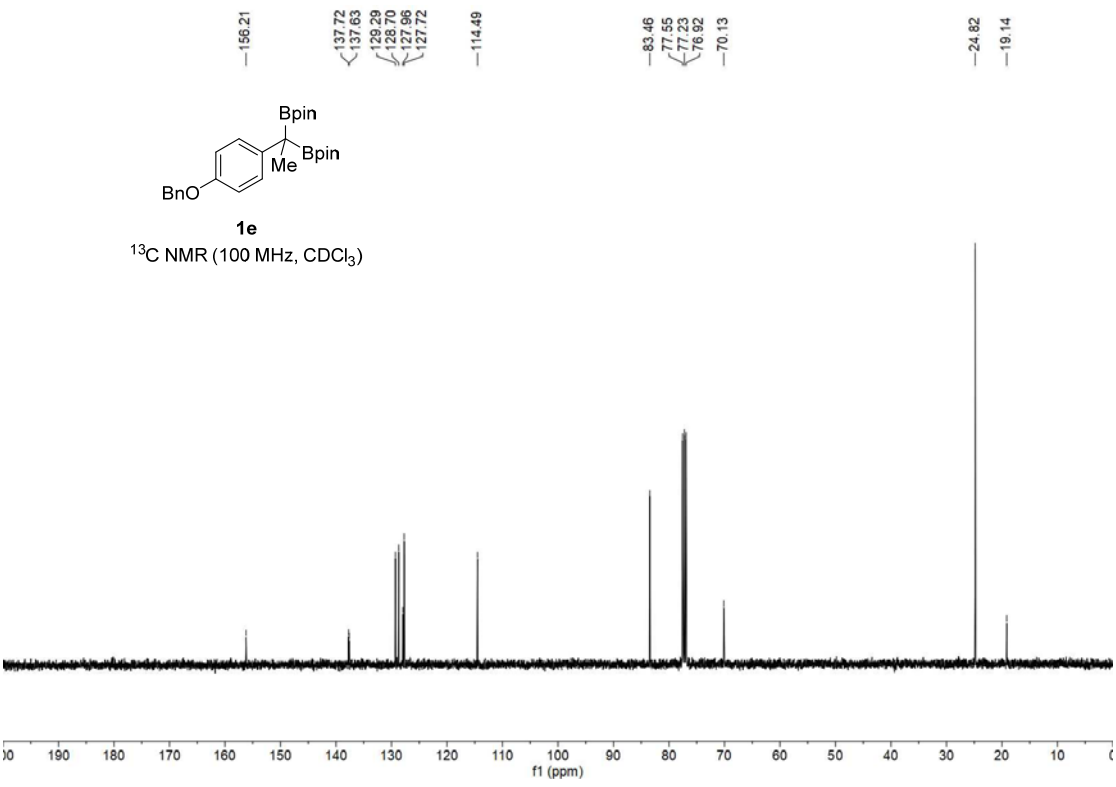
1d

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



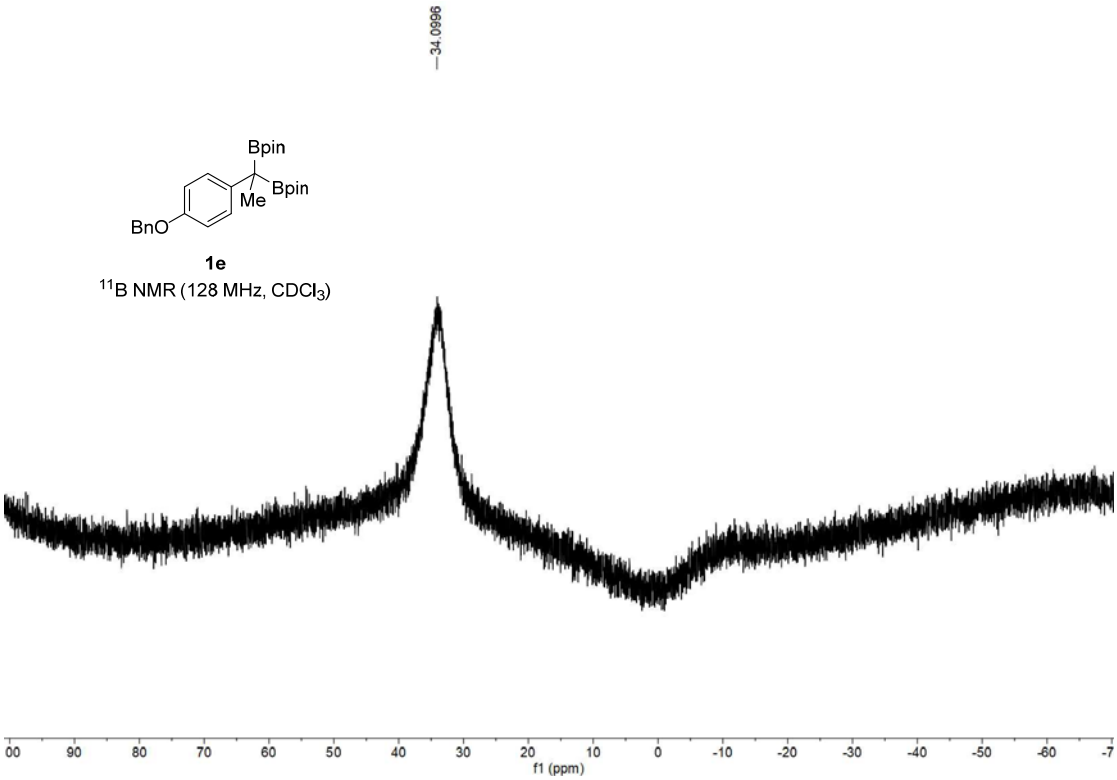
1e

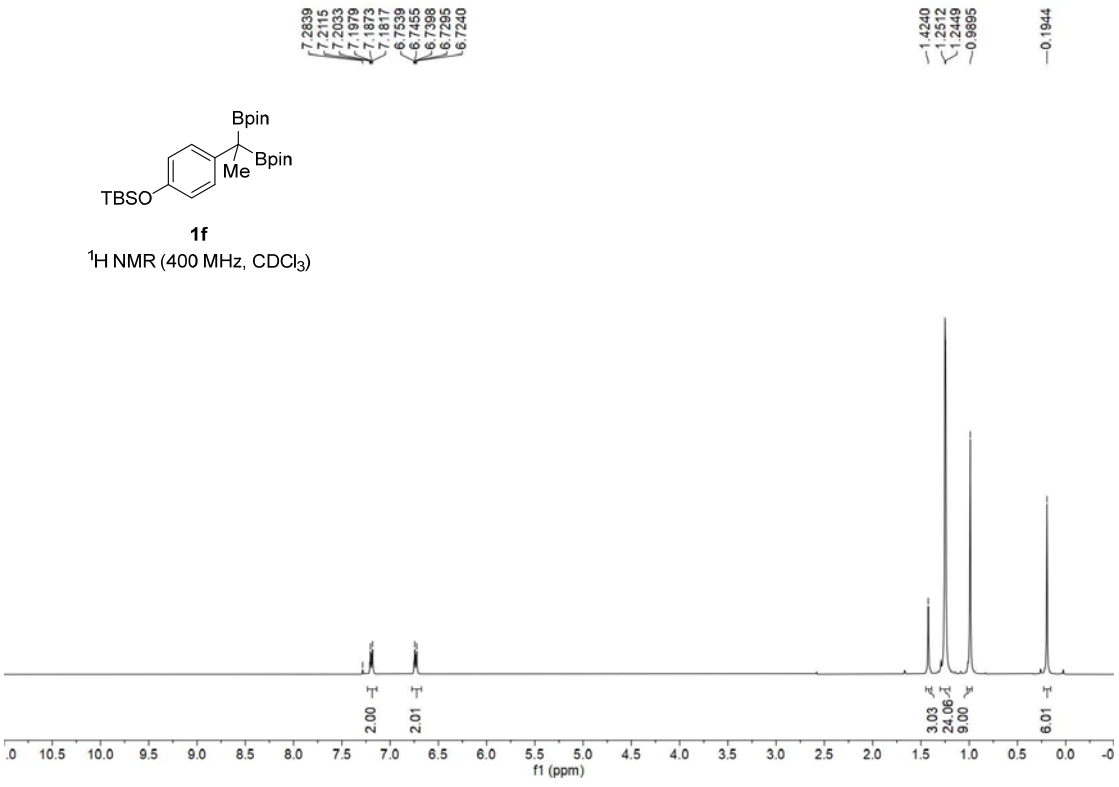
^{1}H NMR (400 MHz, $CDCl_3$)



1e

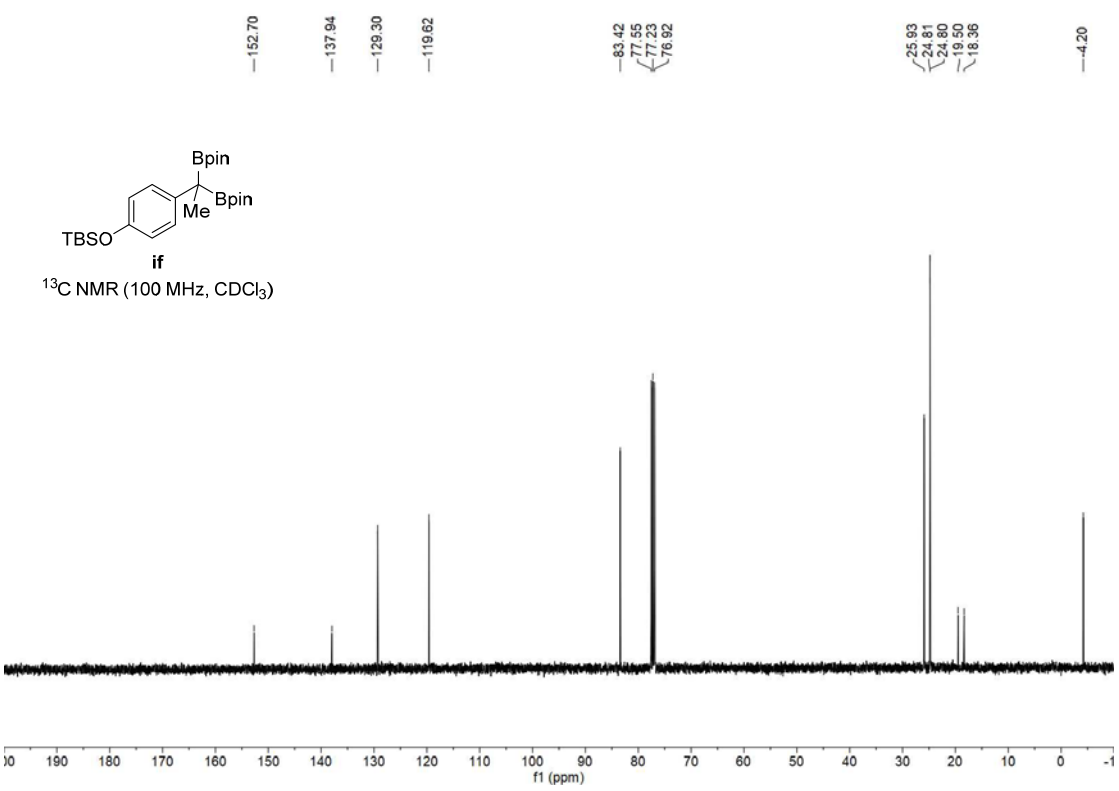
^{13}C NMR (100 MHz, $CDCl_3$)


34.0996
Bpin
Bpin
Me
BnO
1e
11B NMR (128 MHz, CDCl3)
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -7
f1 (ppm)



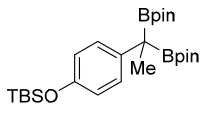
1f

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



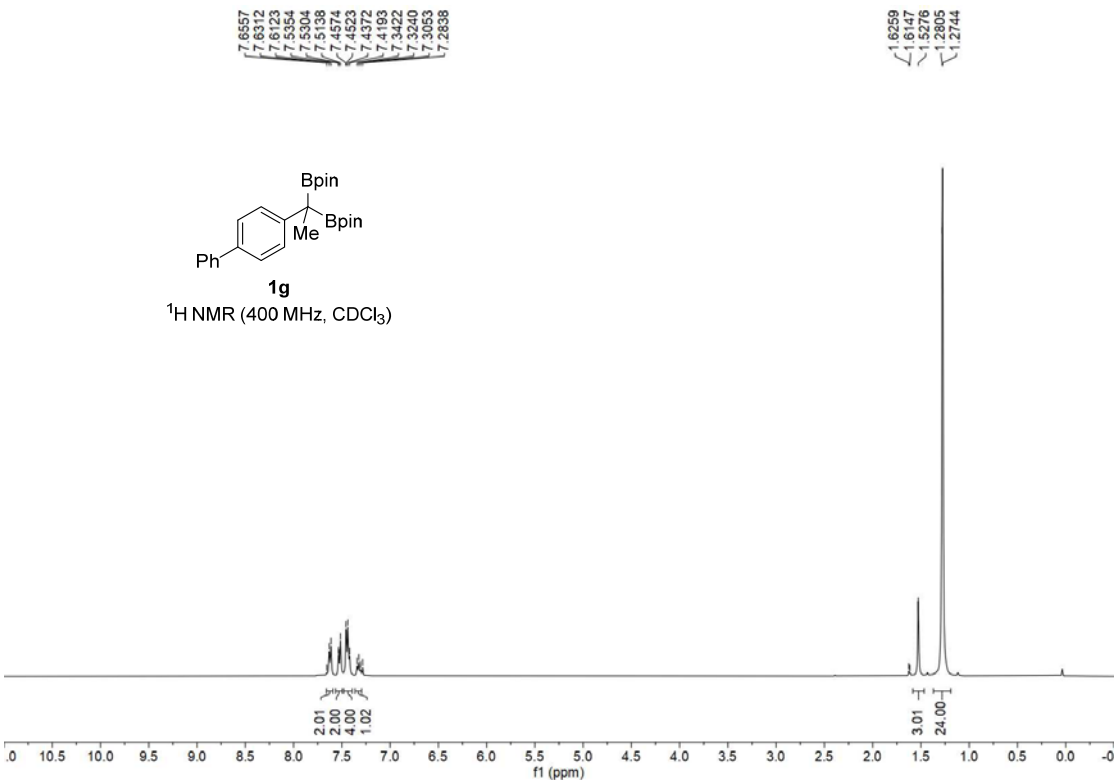
if

^{13}C NMR (100 MHz, $CDCl_3$)



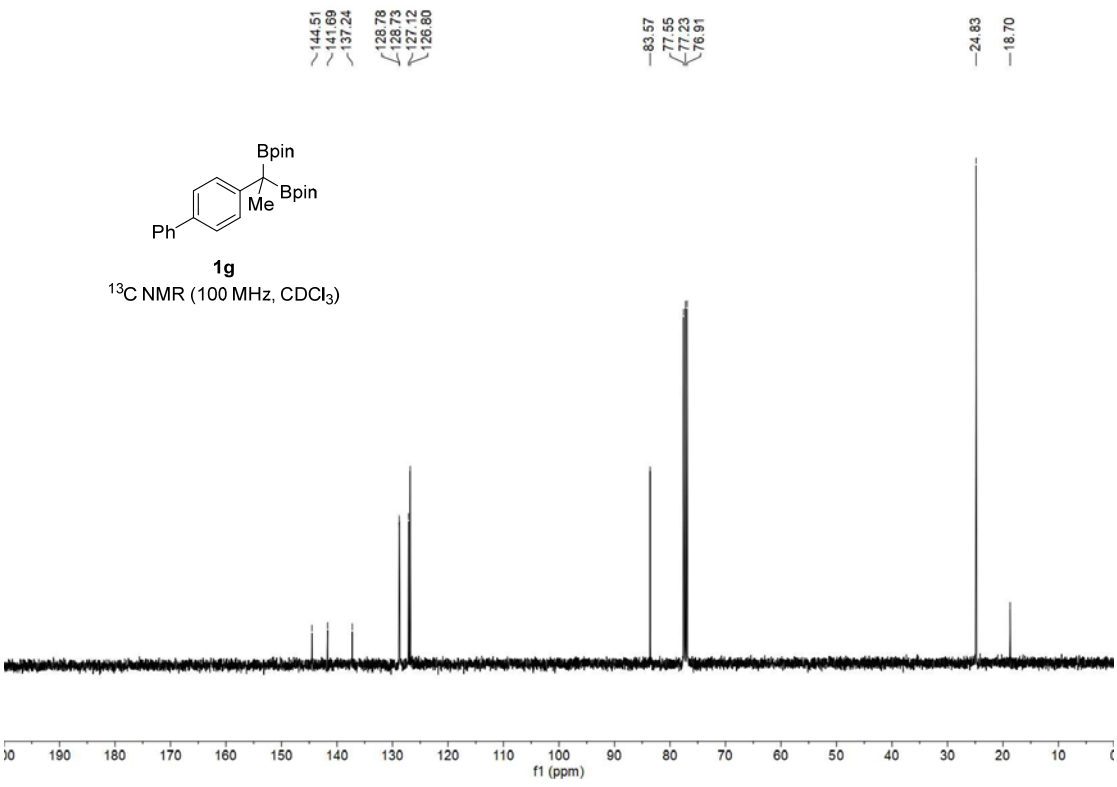
1f

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



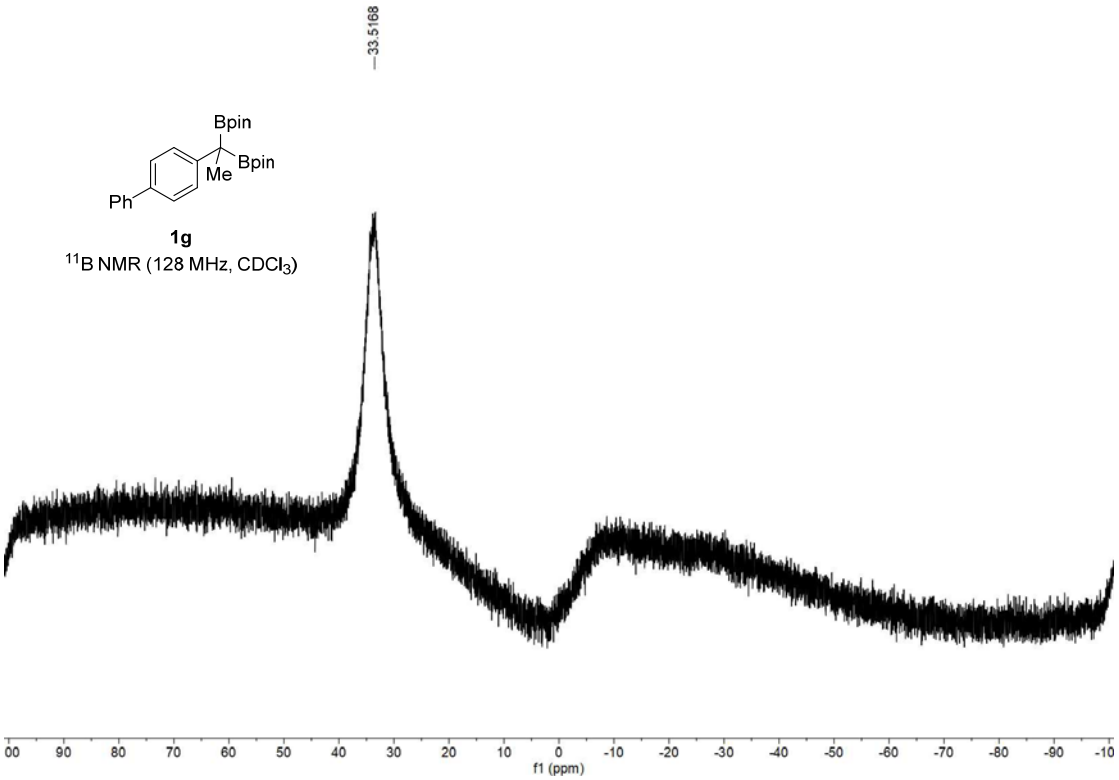
1g

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



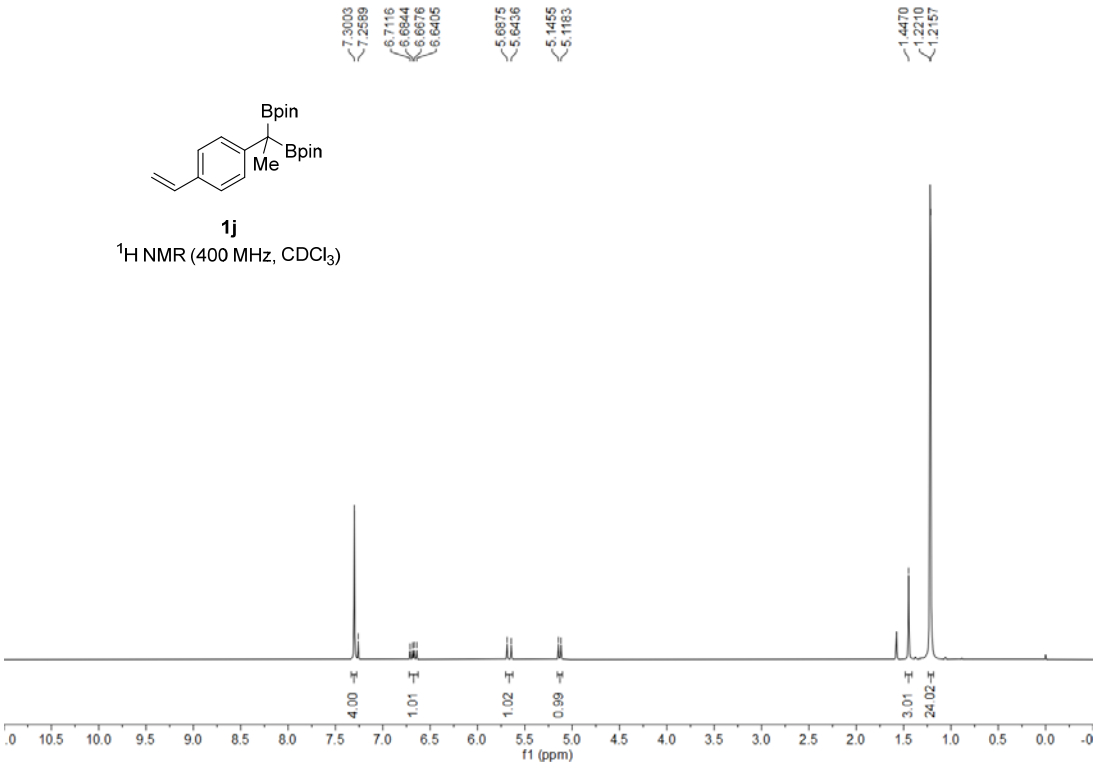
1g

^{13}C NMR (100 MHz, $CDCl_3$)



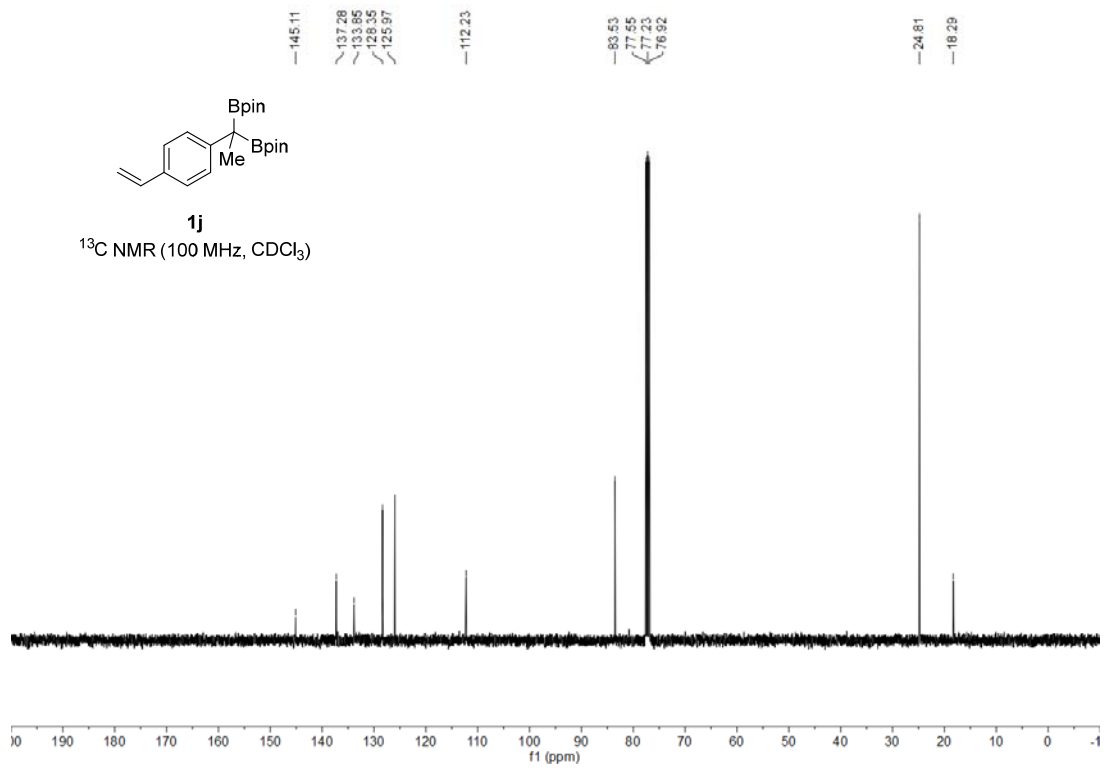
1g

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



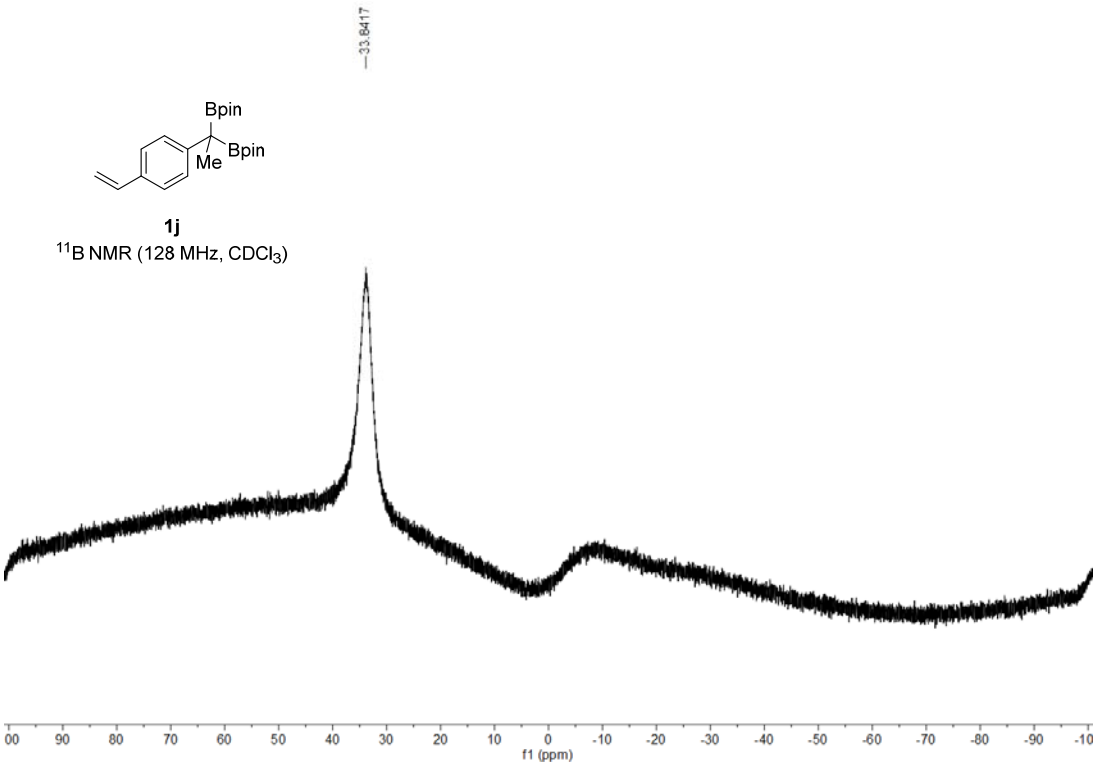
1j

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



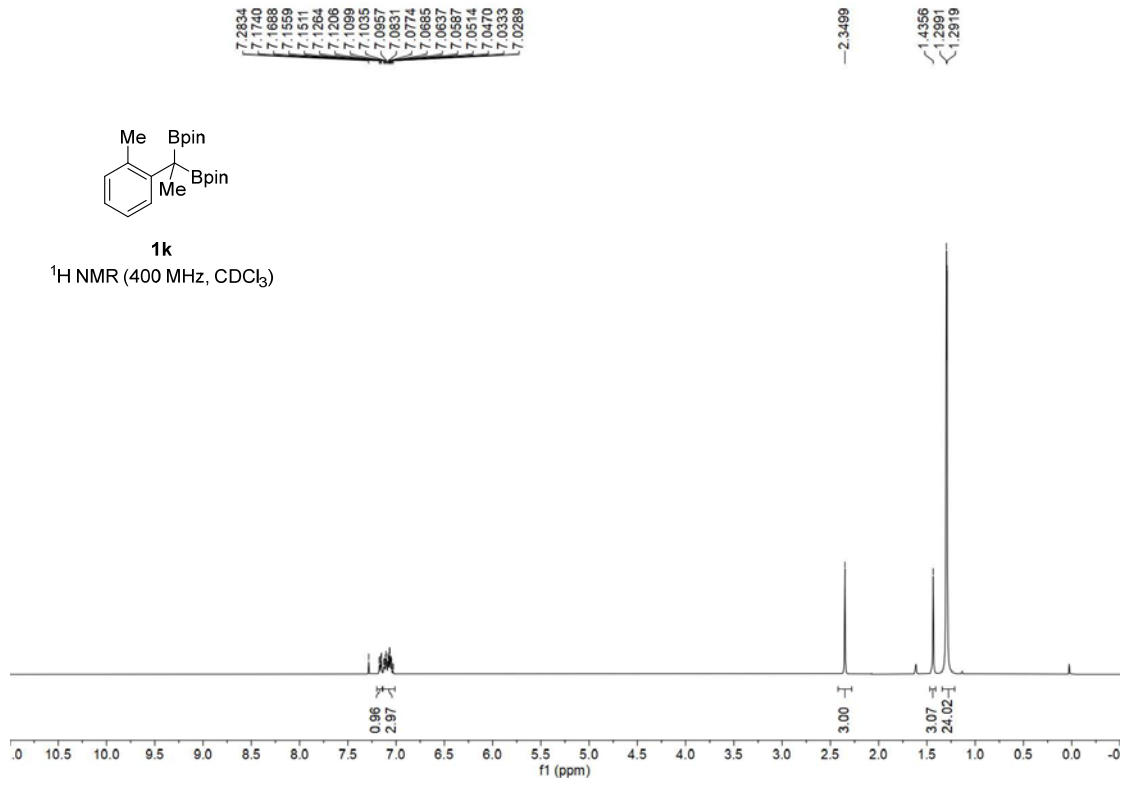
1j

^{13}C NMR (100 MHz, $CDCl_3$)



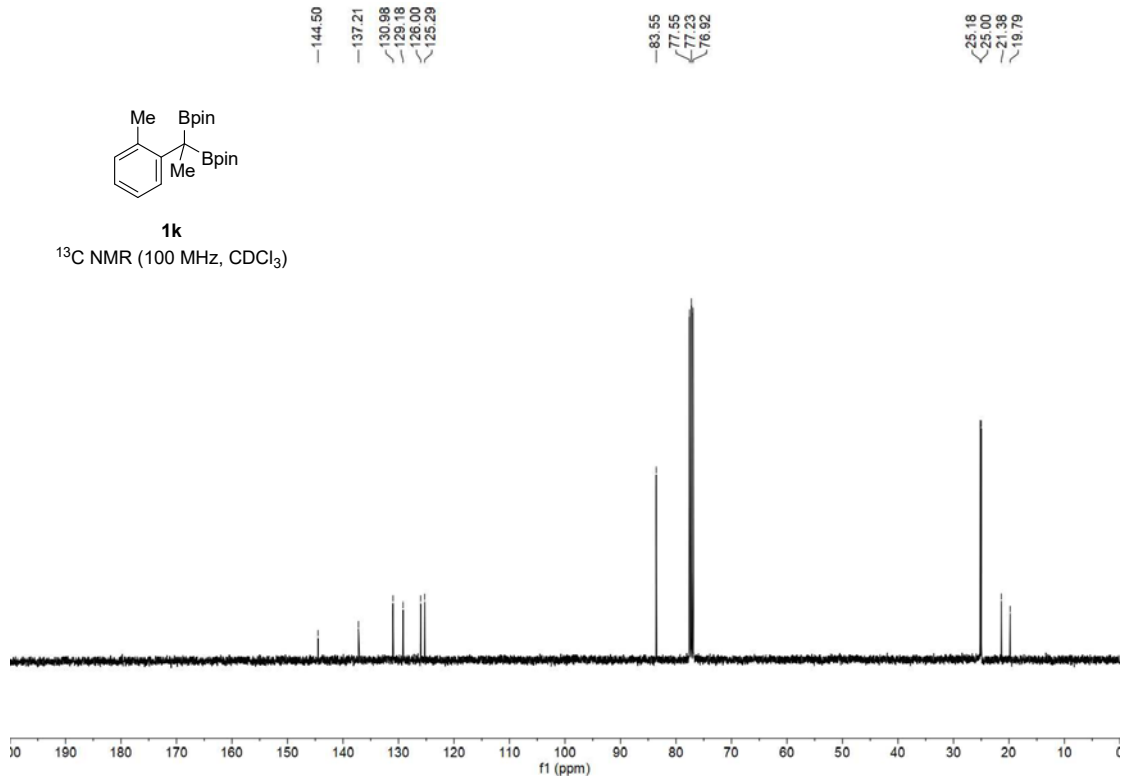
1j

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



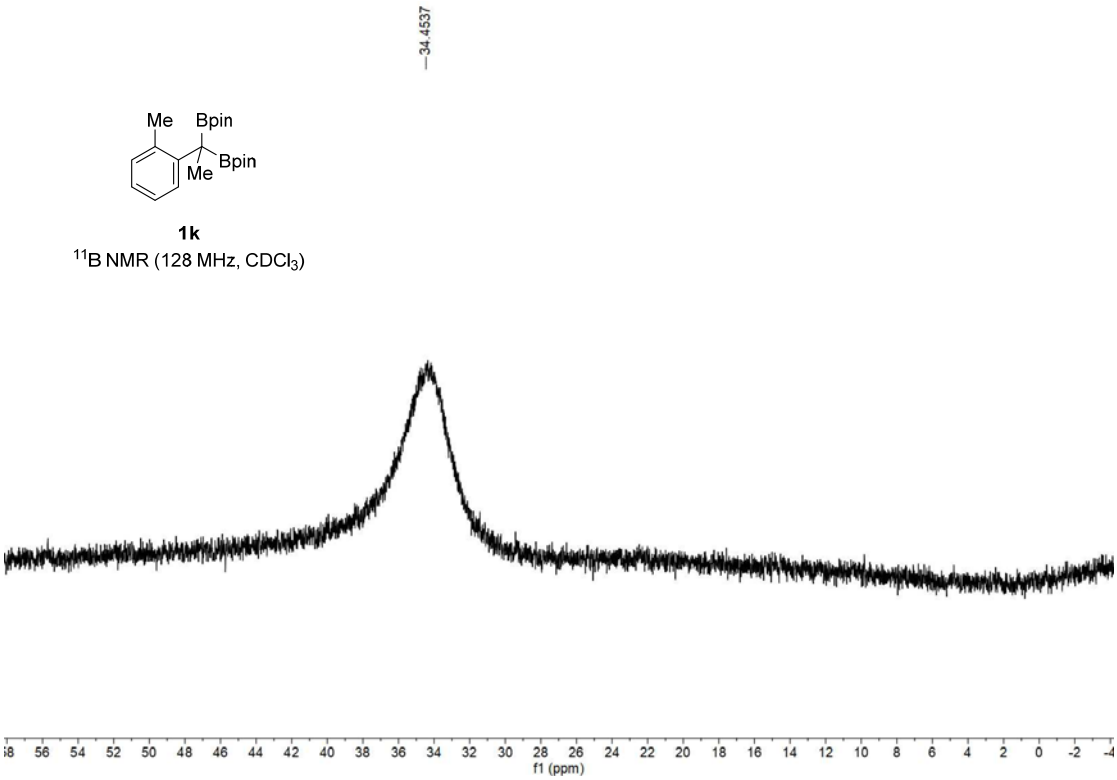
1k

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



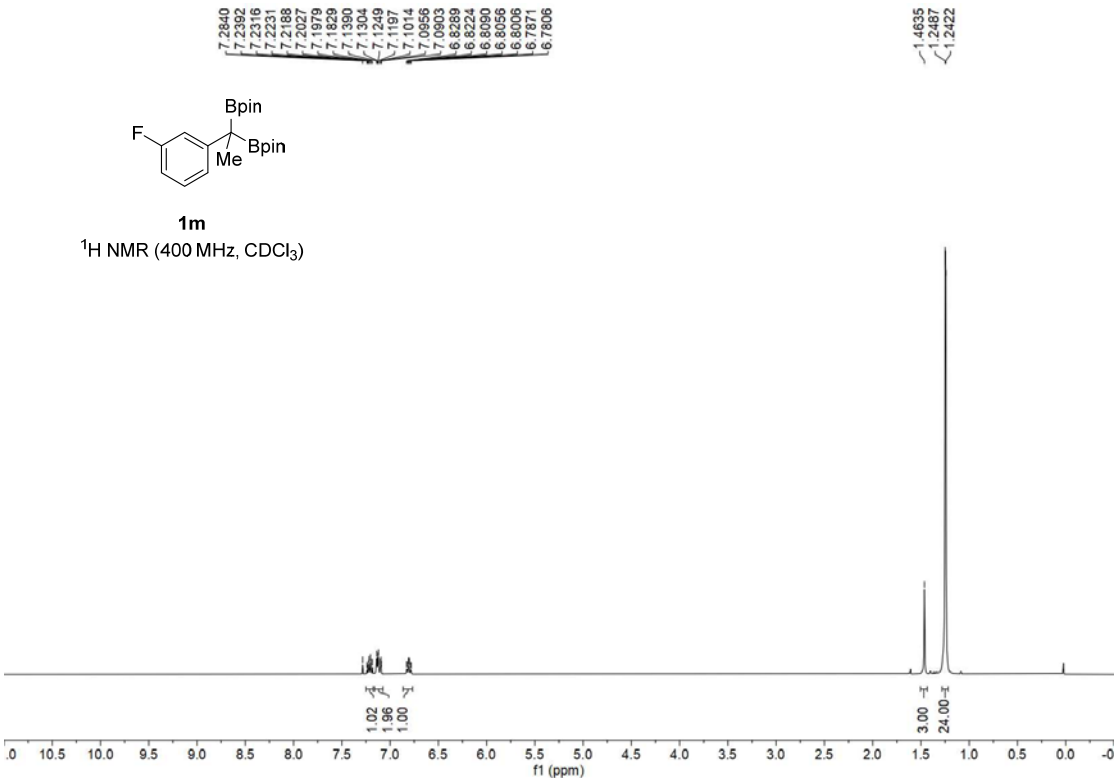
1k

^{13}C NMR (100 MHz, $CDCl_3$)



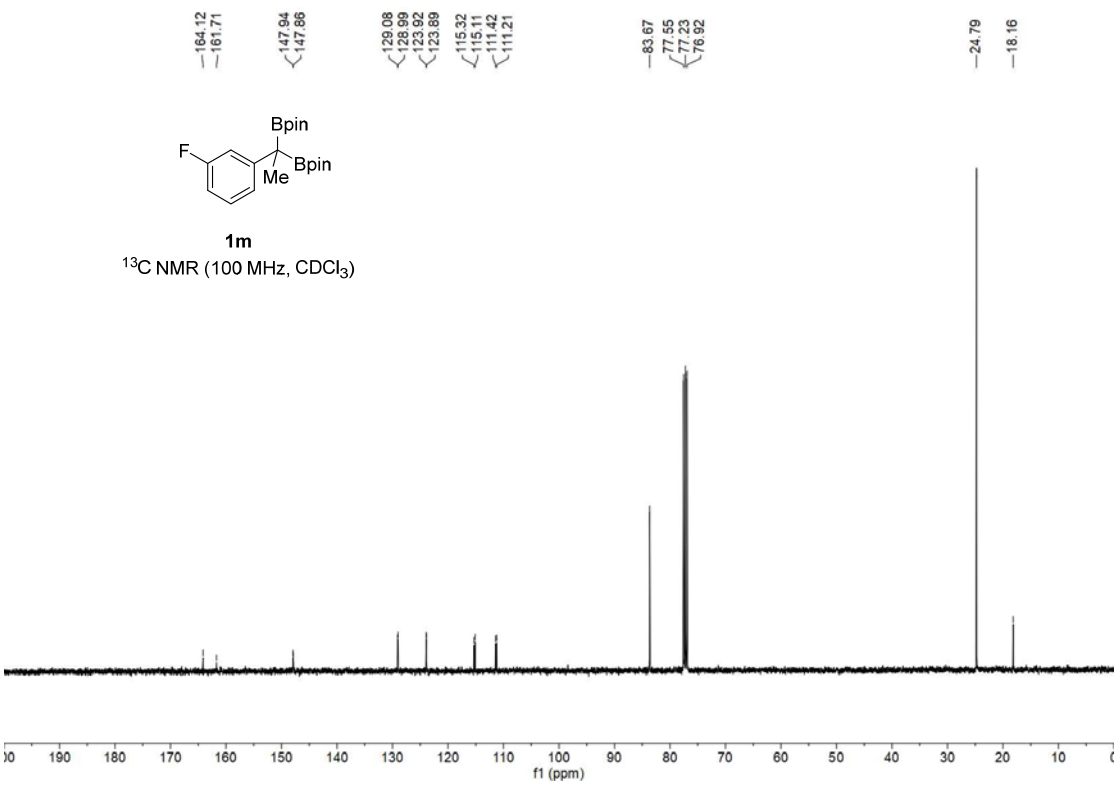
1k

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



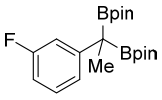
1m

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



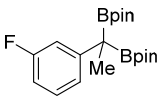
1m

^{13}C NMR (100 MHz, $CDCl_3$)



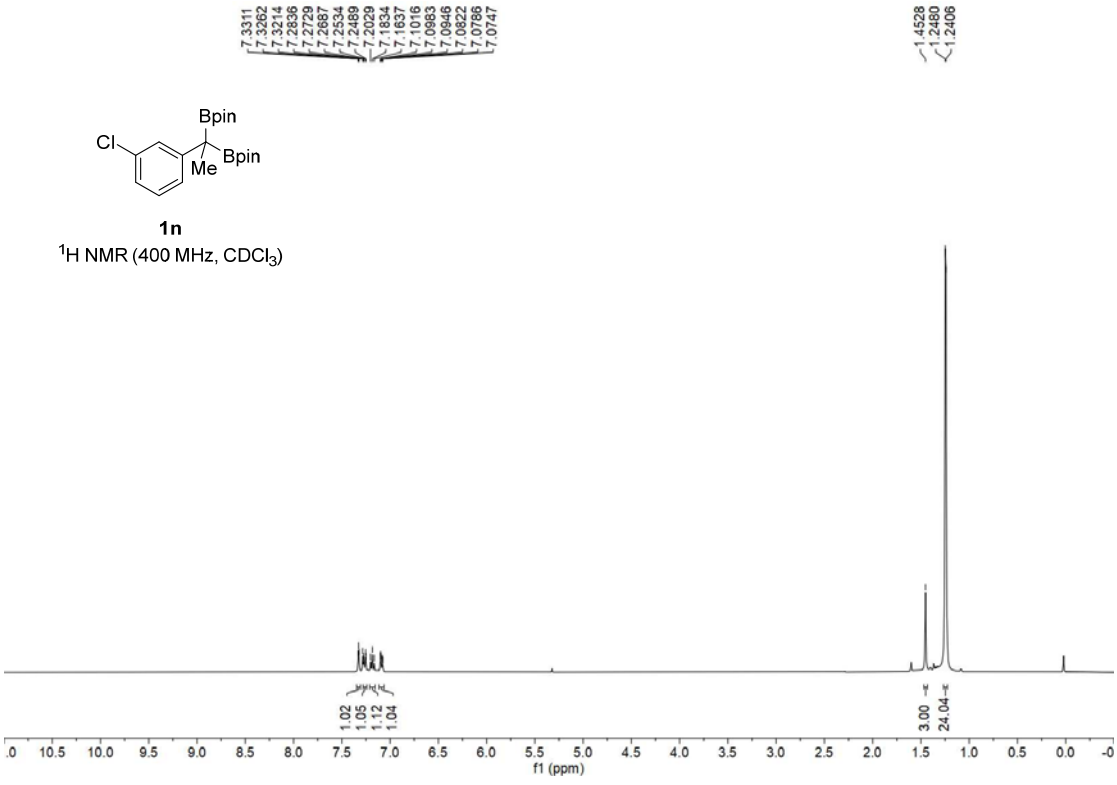
1m

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



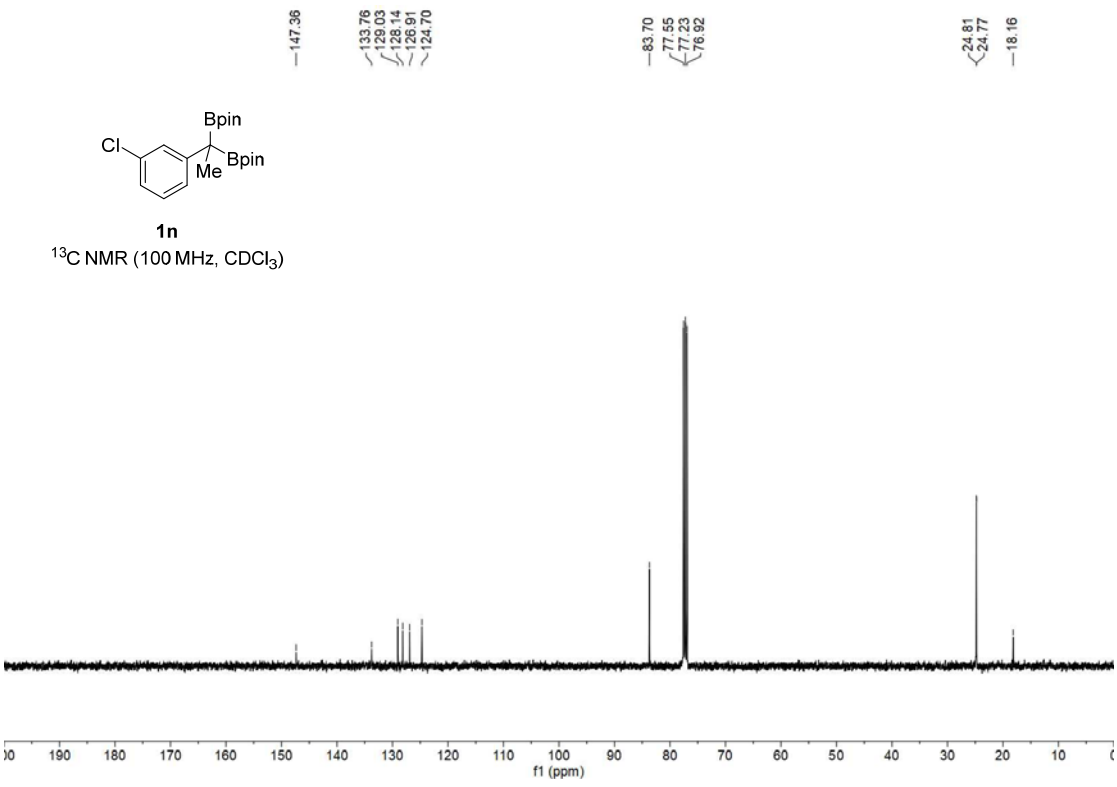
1m

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



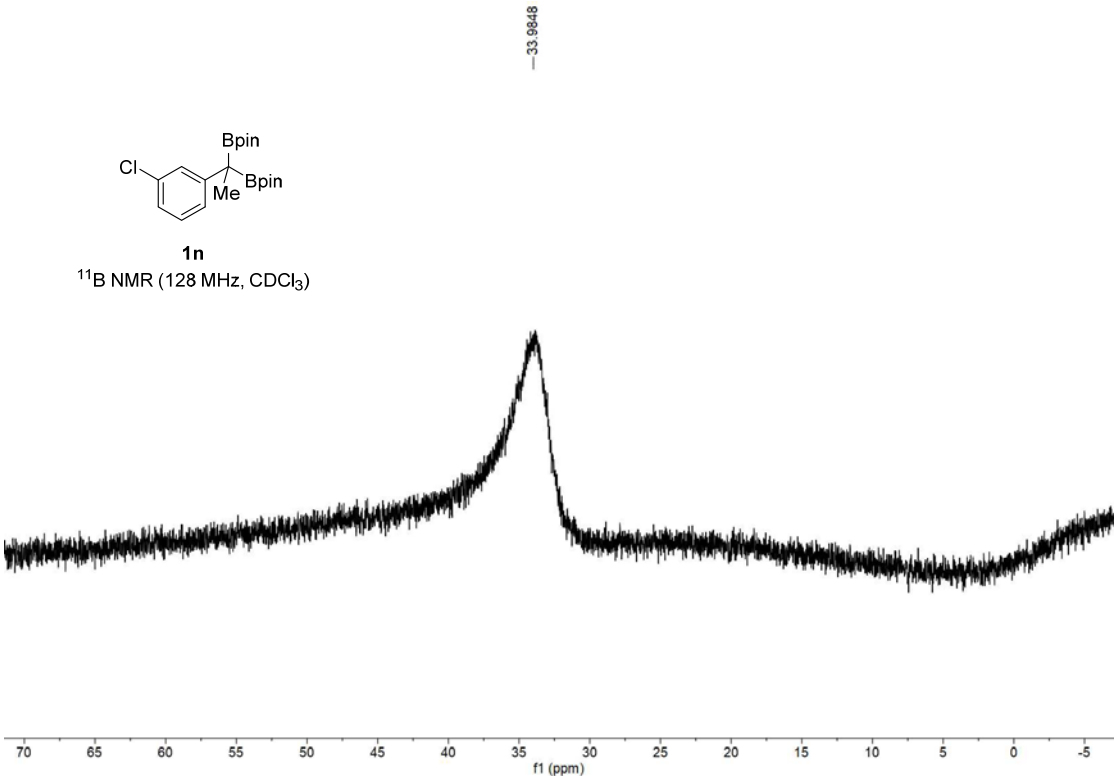
1n

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



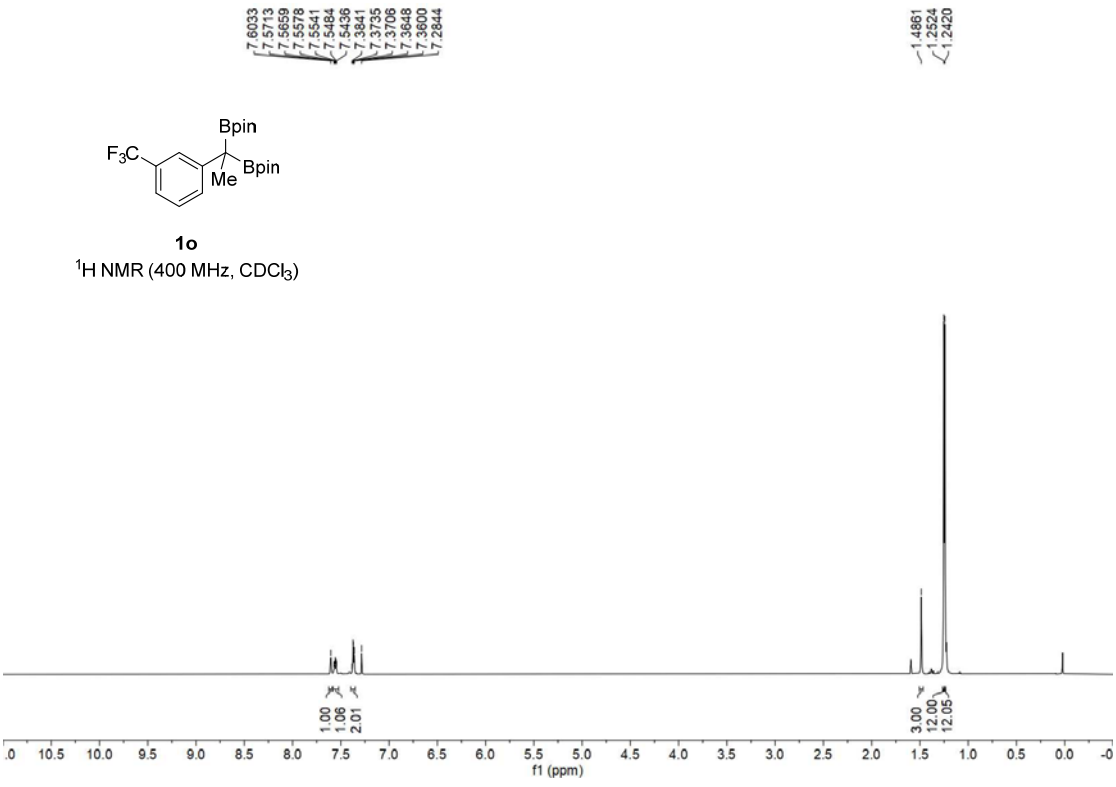
1n

^{13}C NMR (100 MHz, $CDCl_3$)



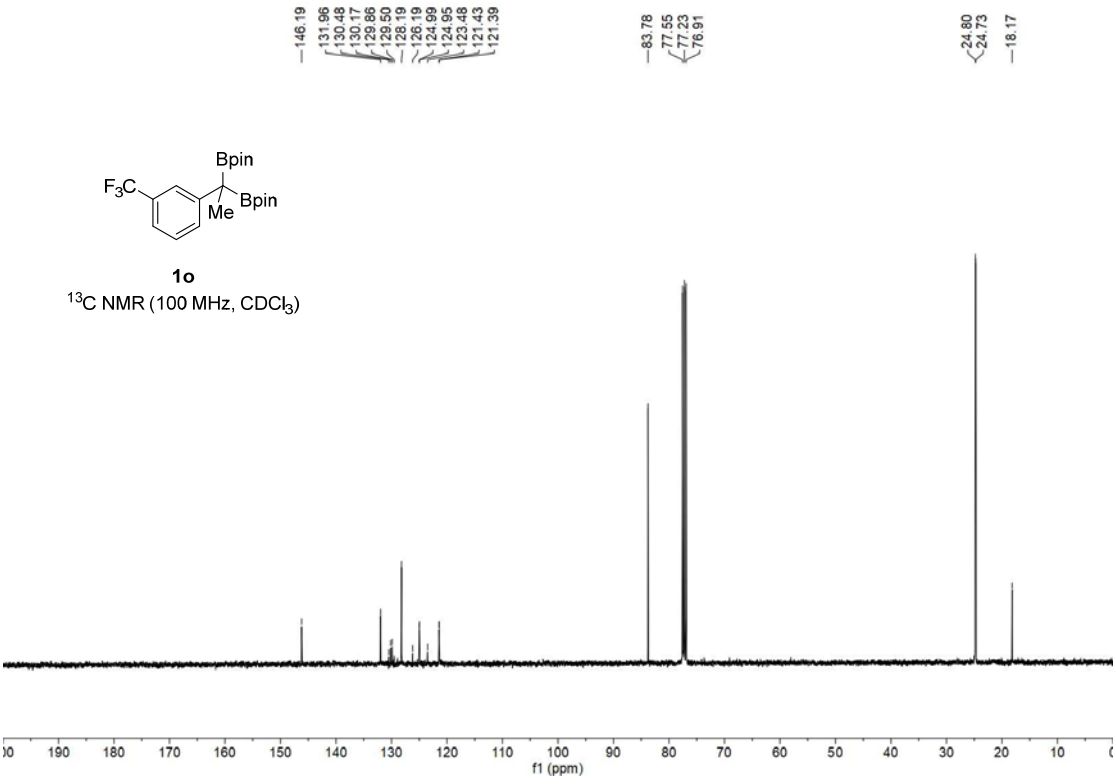
1n

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



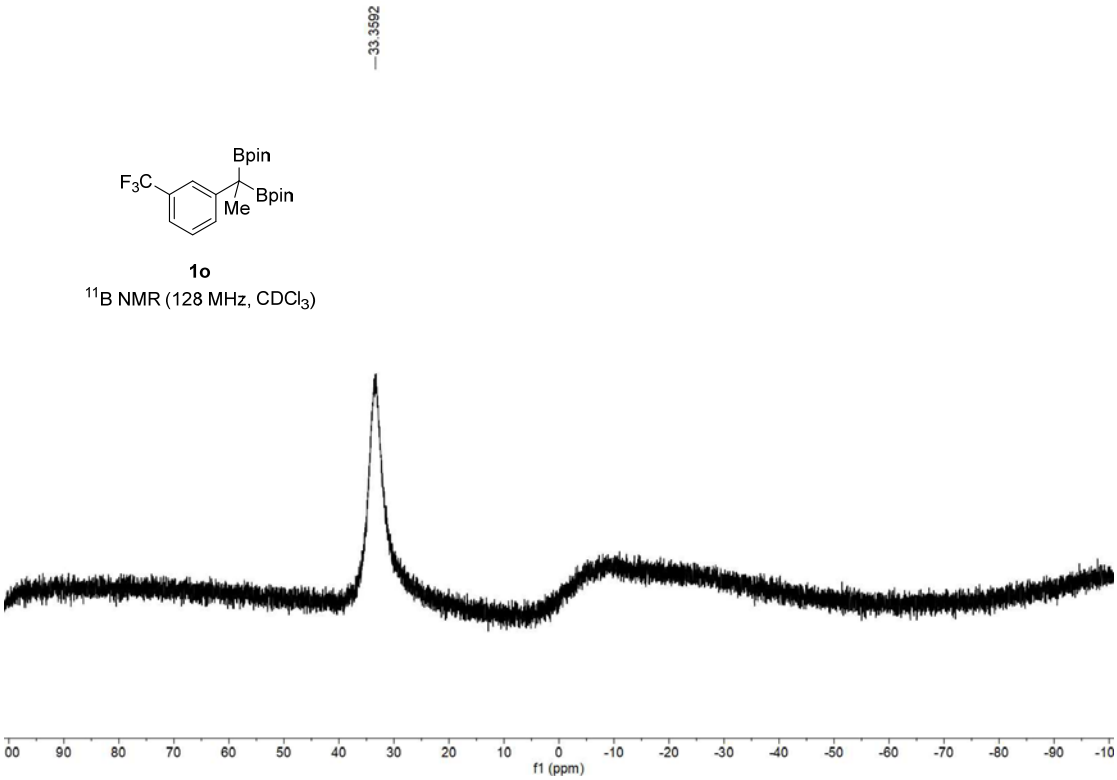
1o

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



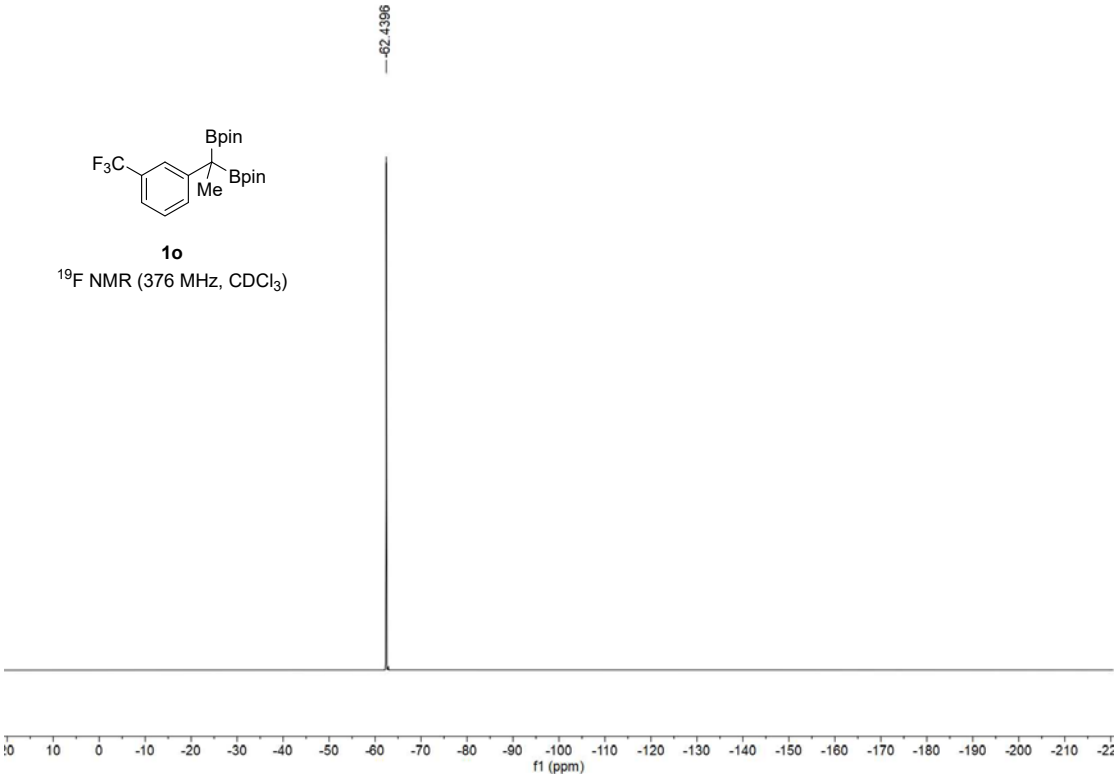
1o

^{13}C NMR (100 MHz, $CDCl_3$)



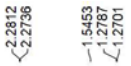
1o

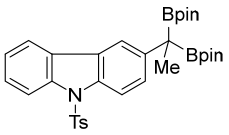
^{11}B NMR (128 MHz, $CDCl_3$)



1o

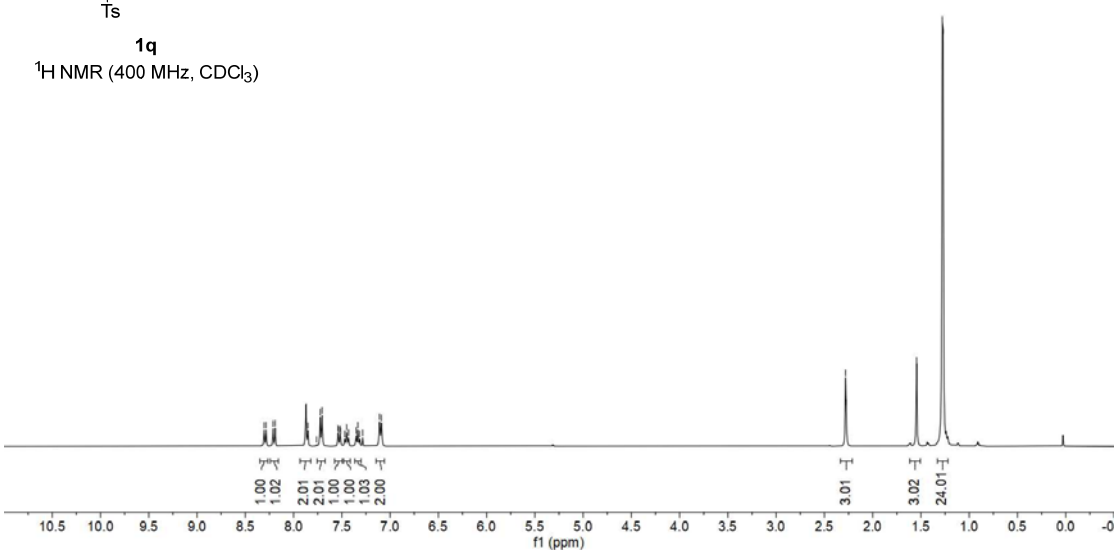
^{19}F NMR (376 MHz, $CDCl_3$)

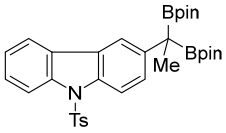




1q

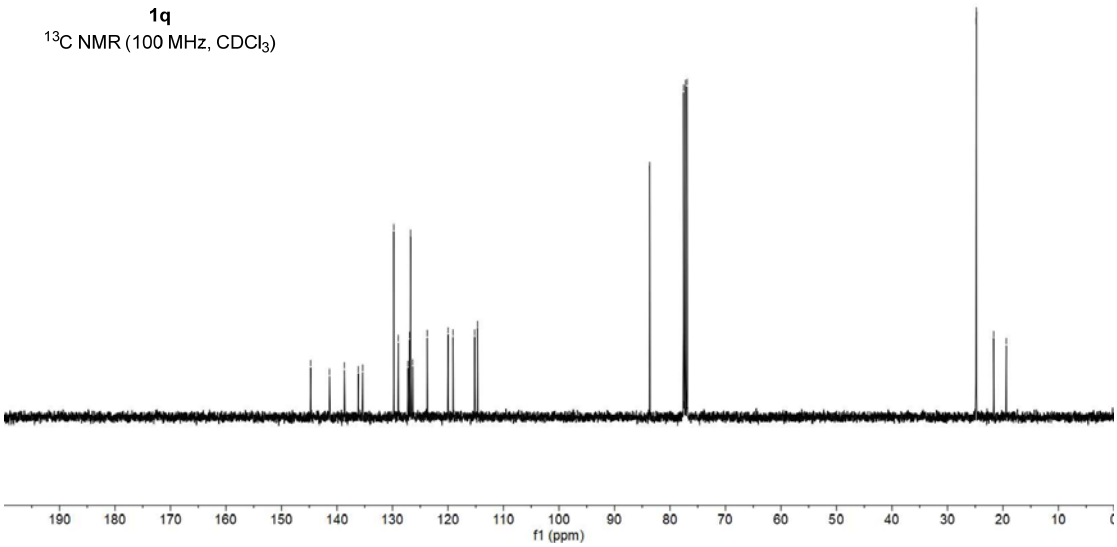
^{1}H NMR (400 MHz, $CDCl_3$)

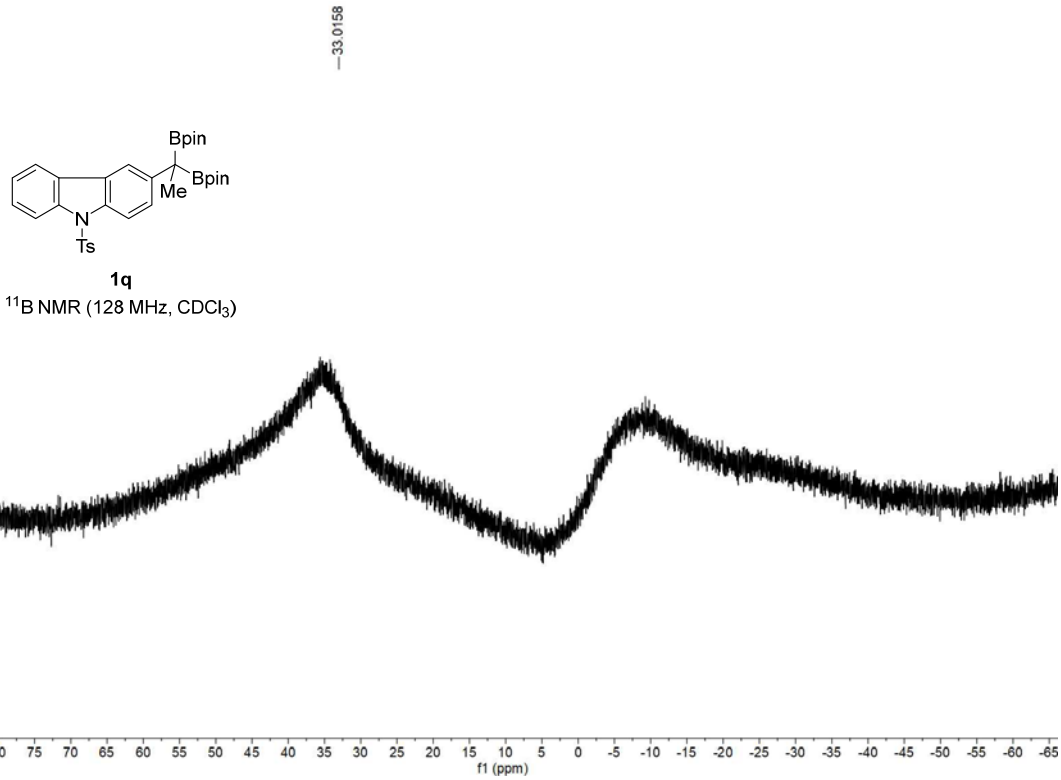




1q

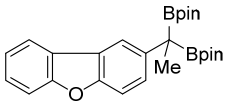
^{13}C NMR (100 MHz, $CDCl_3$)





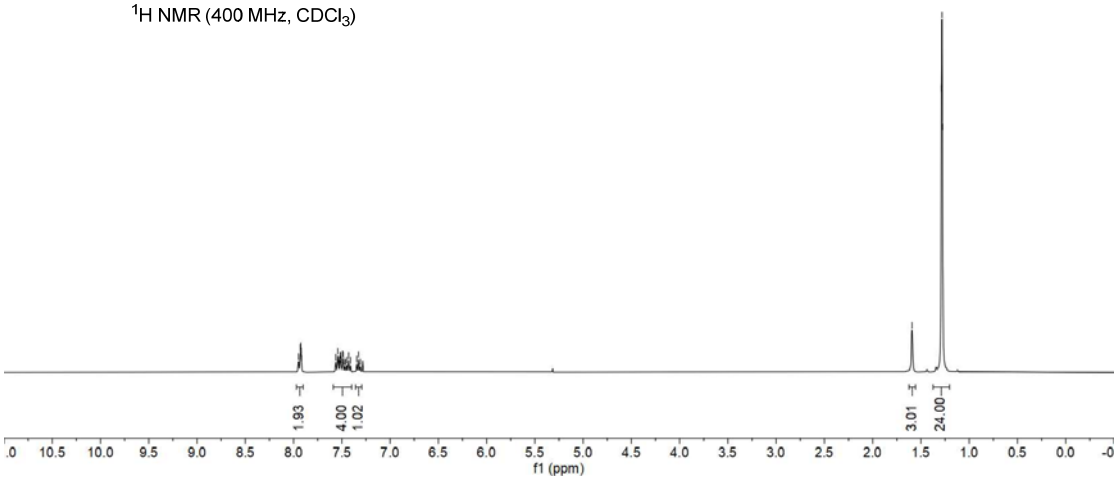
1q

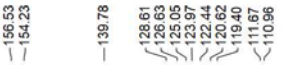
^{11}B NMR (128 MHz, $CDCl_3$)

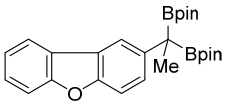


1r

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

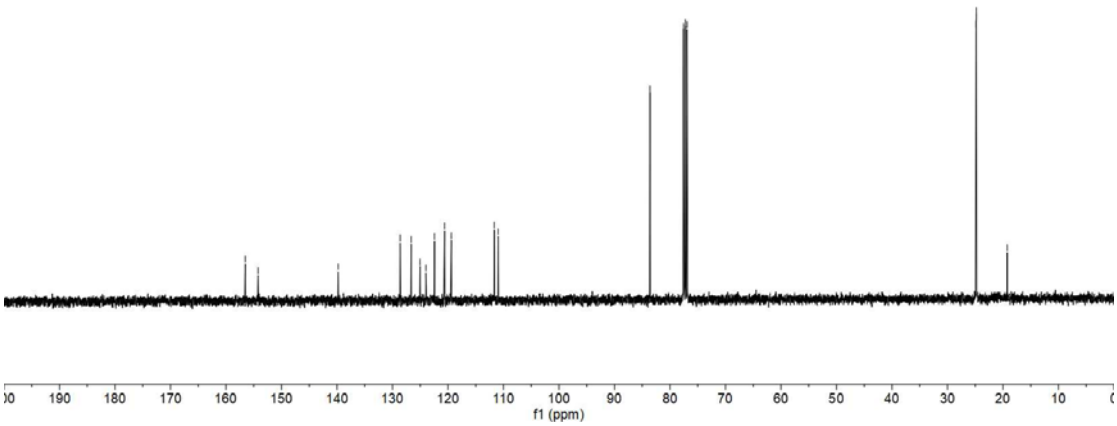


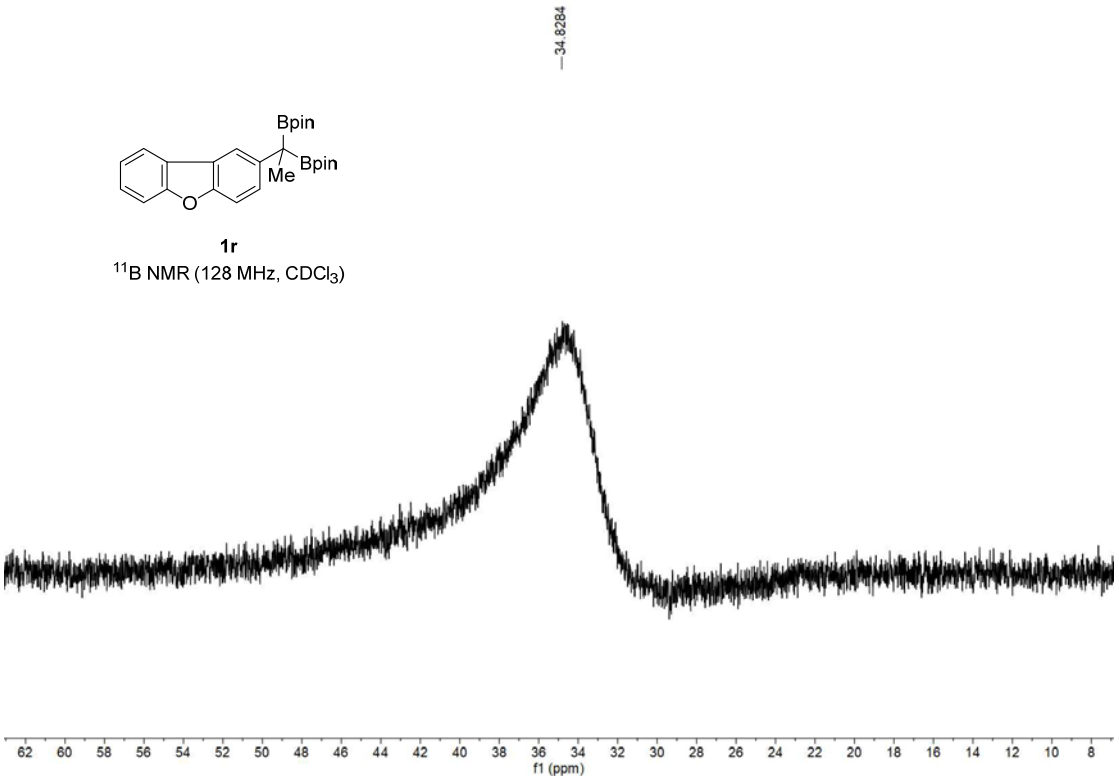




1r

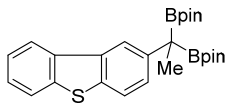
^{13}C NMR (100 MHz, $CDCl_3$)





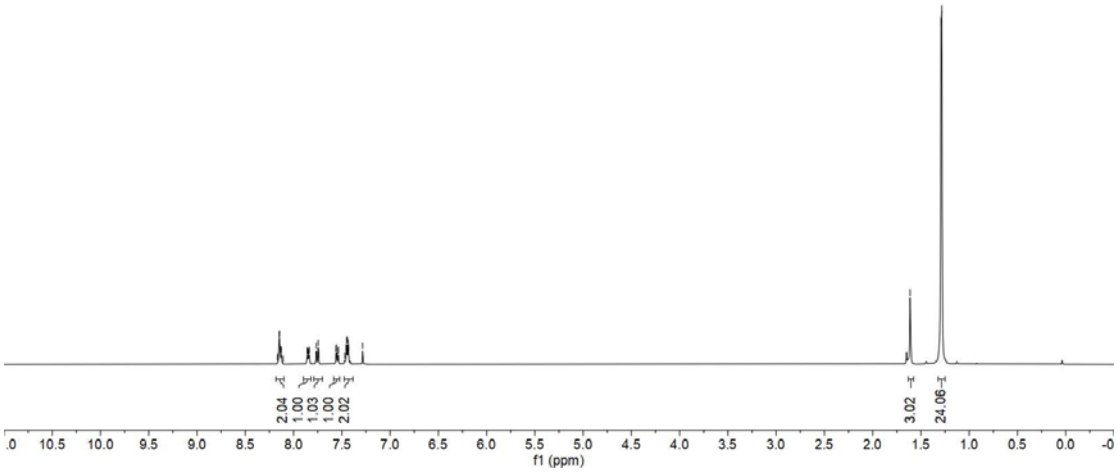
1r

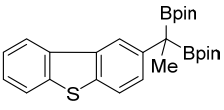
^{11}B NMR (128 MHz, $CDCl_3$)



1s

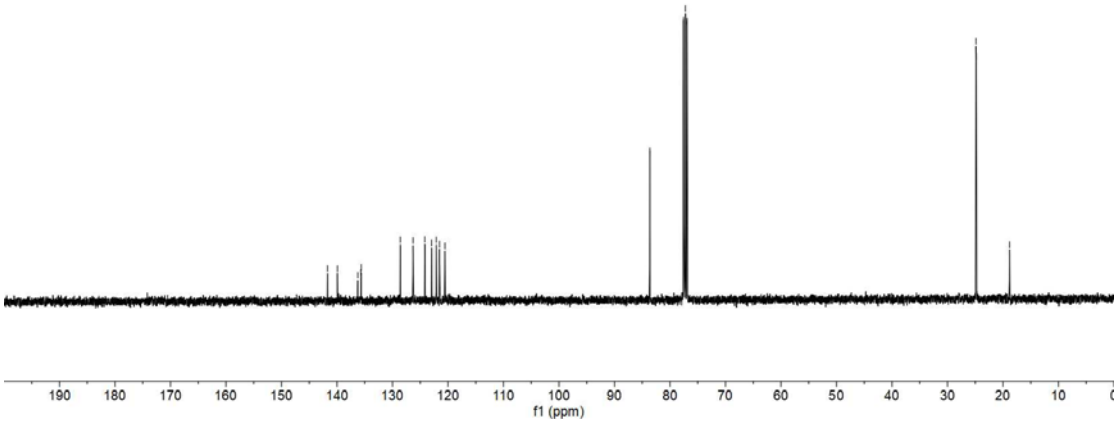
^{1}H NMR (400 MHz, $CDCl_3$)

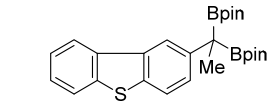




1s

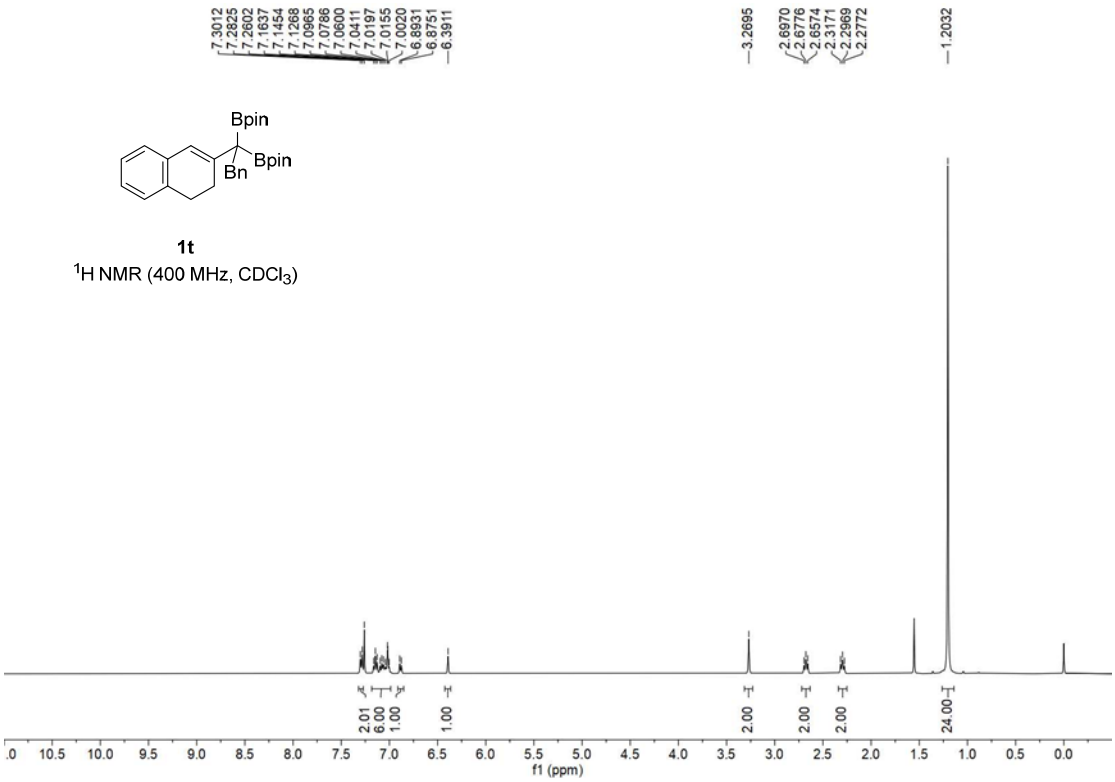
^{13}C NMR (100 MHz, $CDCl_3$)





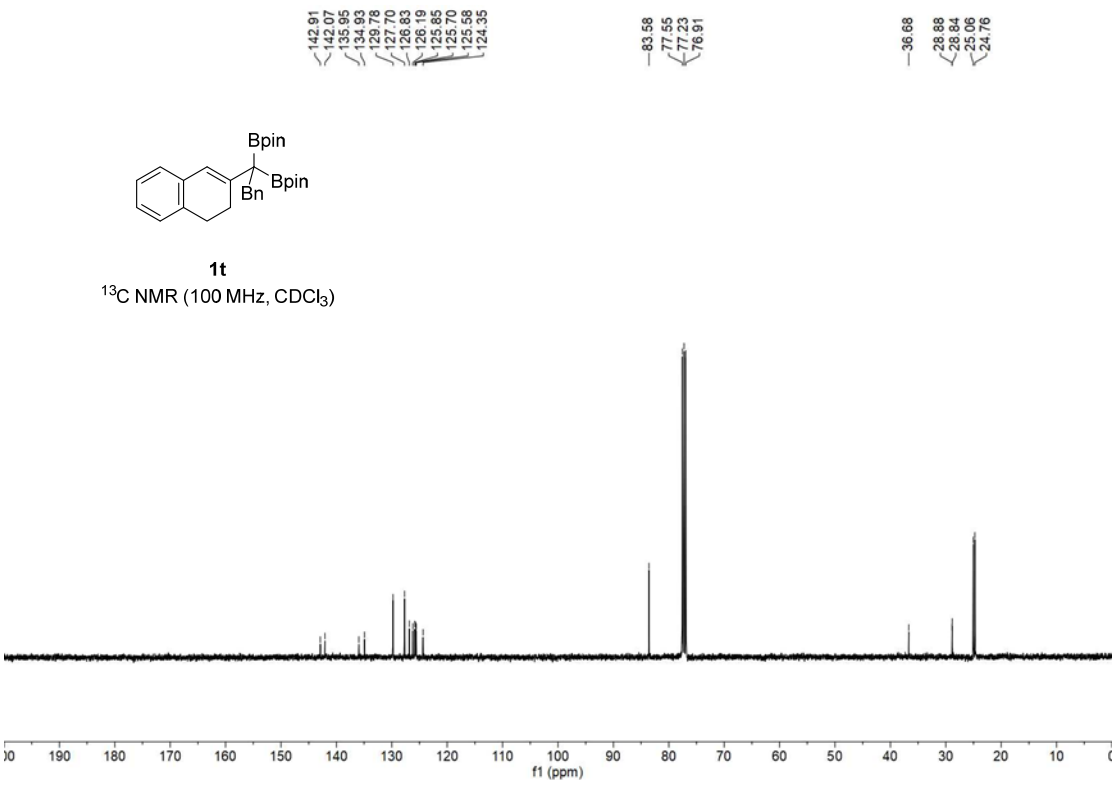
1s

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



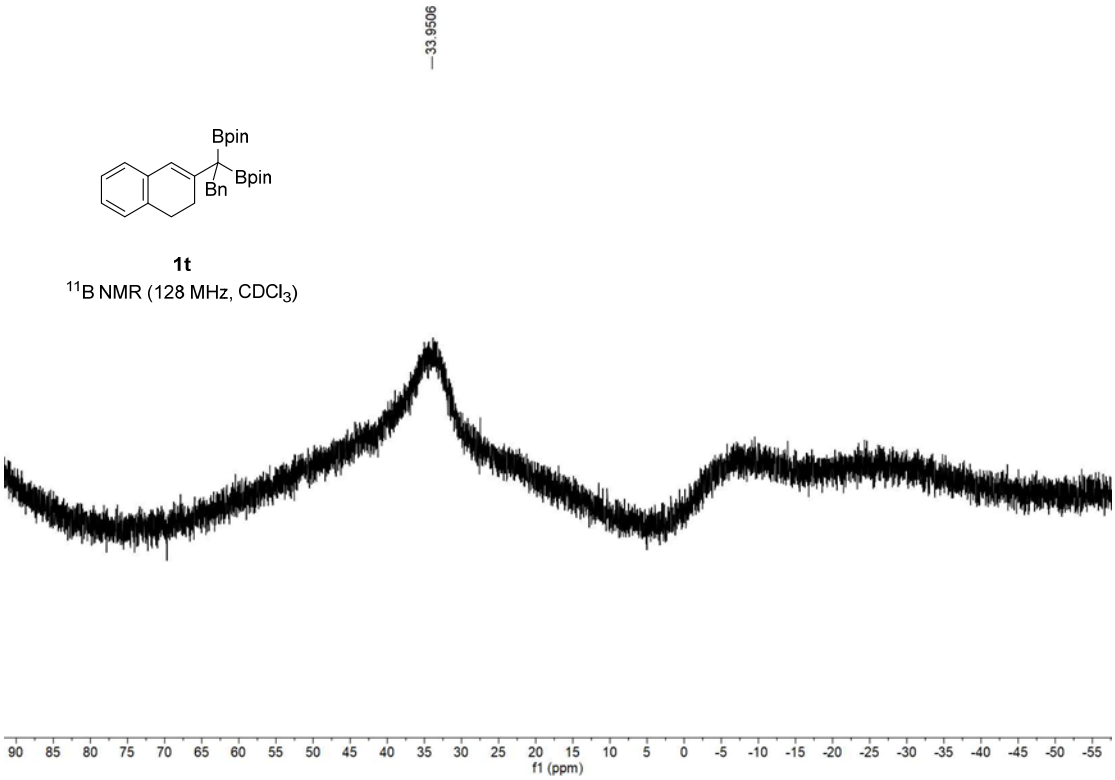
1t

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



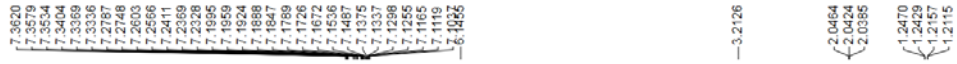
1t

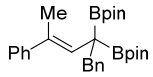
^{13}C NMR (100 MHz, $CDCl_3$)



1t

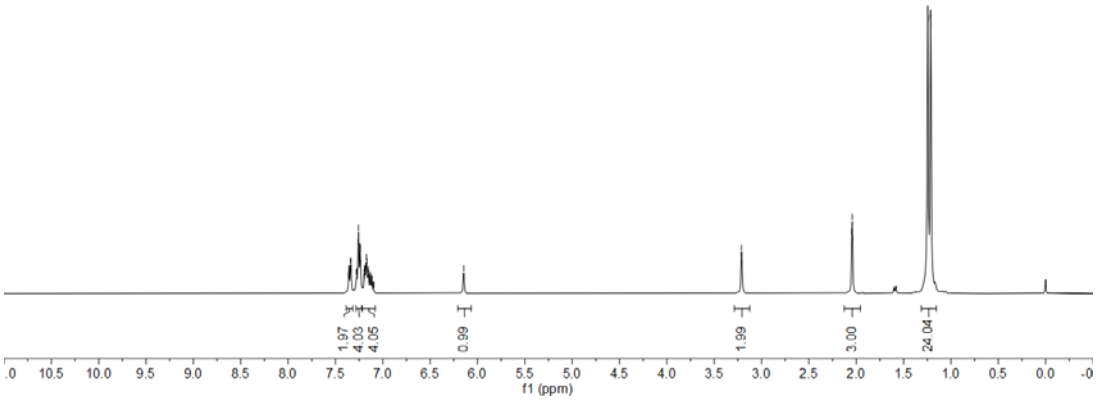
^{11}B NMR (128 MHz, $CDCl_3$)

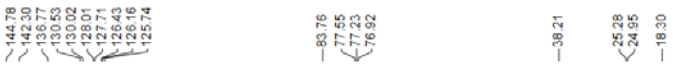


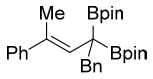


1u

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

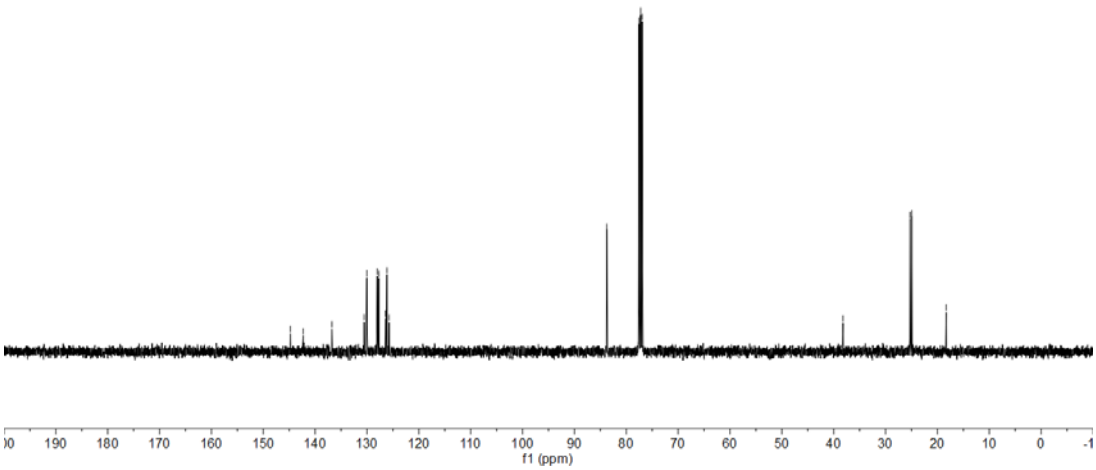






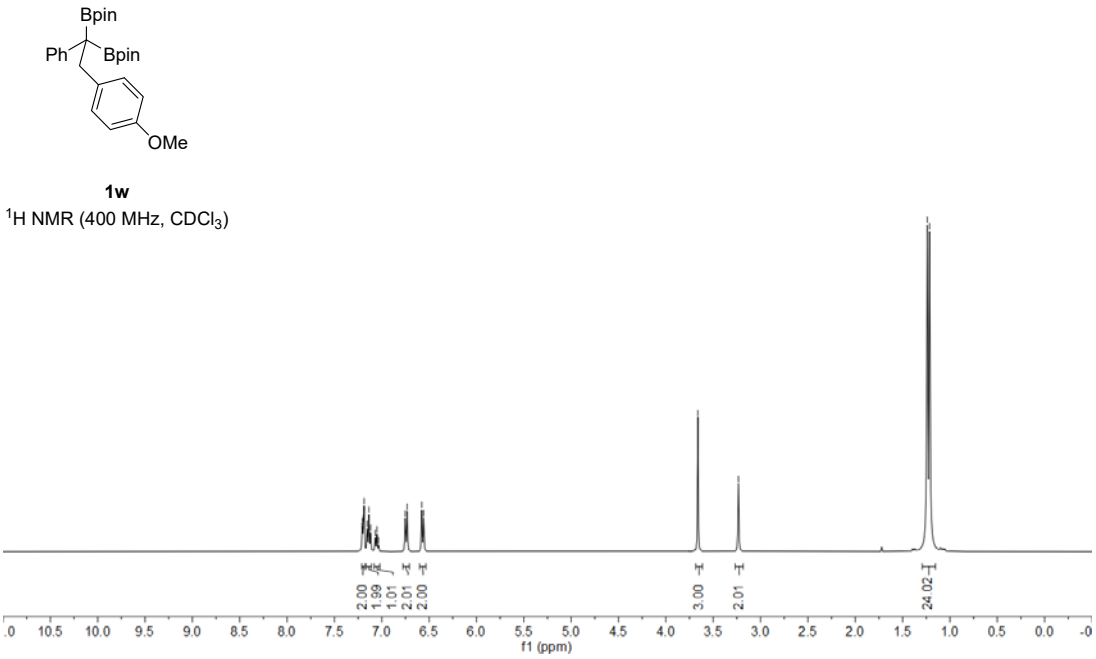
1u

^{13}C NMR (100 MHz, $CDCl_3$)



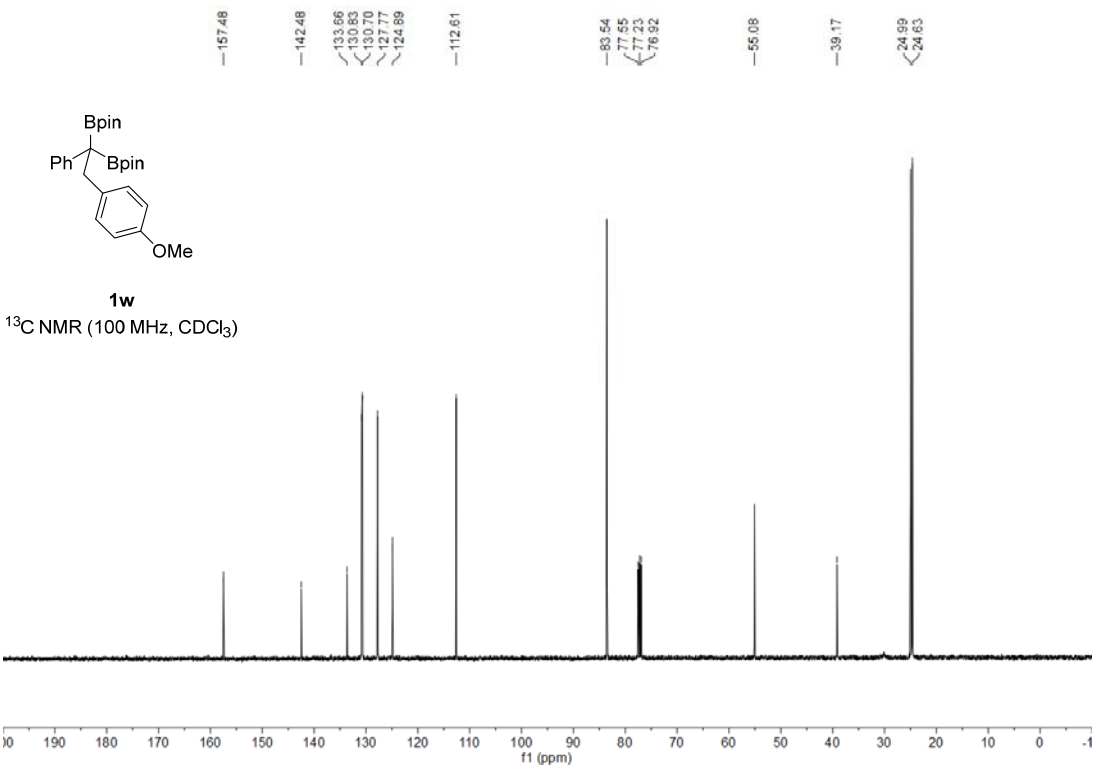
1u

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



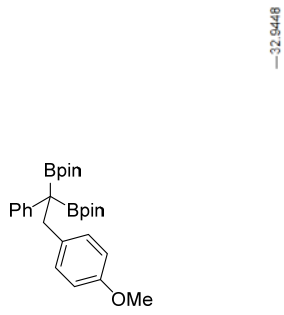
1w

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



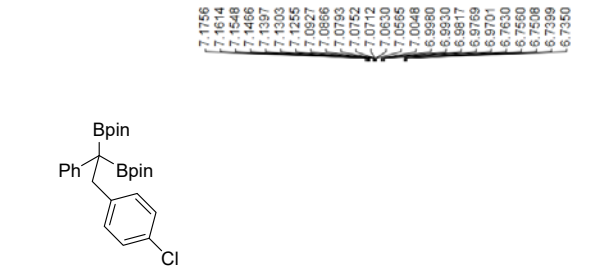
1w

^{13}C NMR (100 MHz, $CDCl_3$)



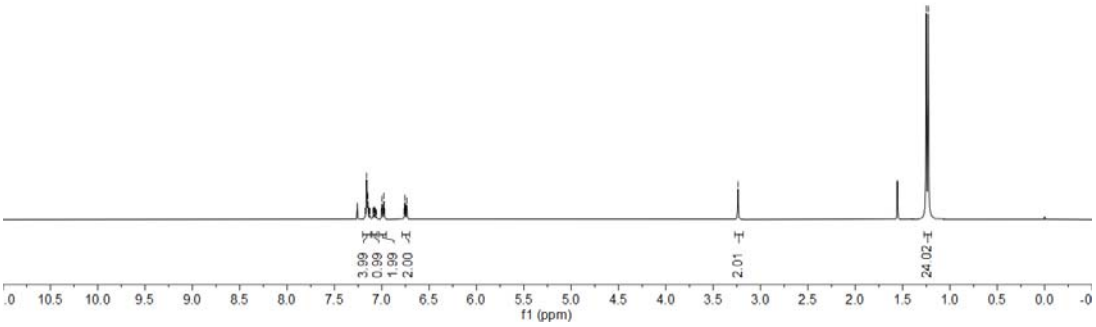
1w

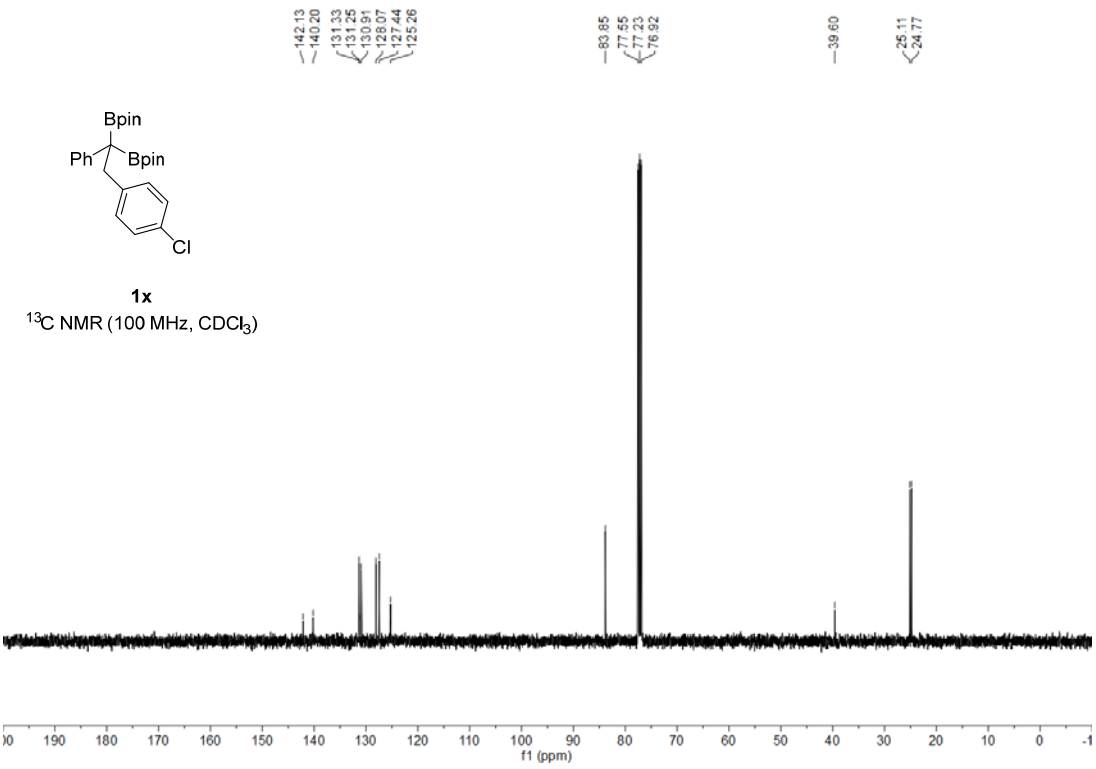
^{11}B NMR (128 MHz, $CDCl_3$)



1x

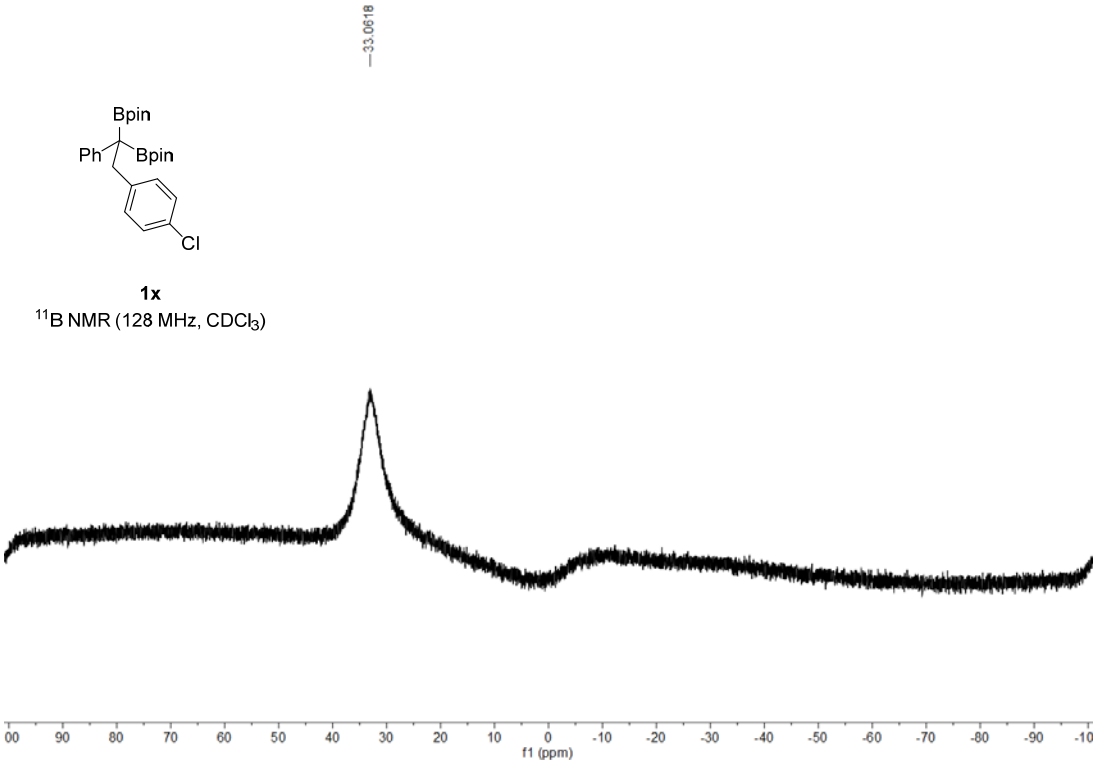
^{1}H NMR (400 MHz, $CDCl_3$)





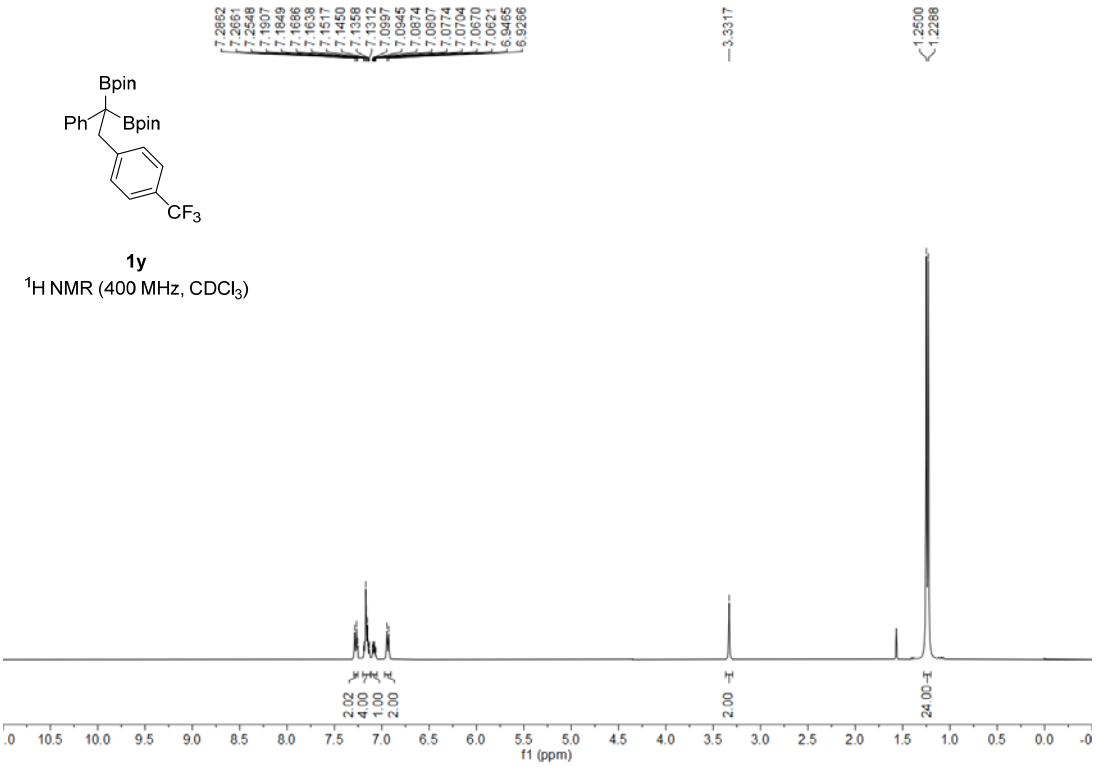
1x

^{13}C NMR (100 MHz, $CDCl_3$)



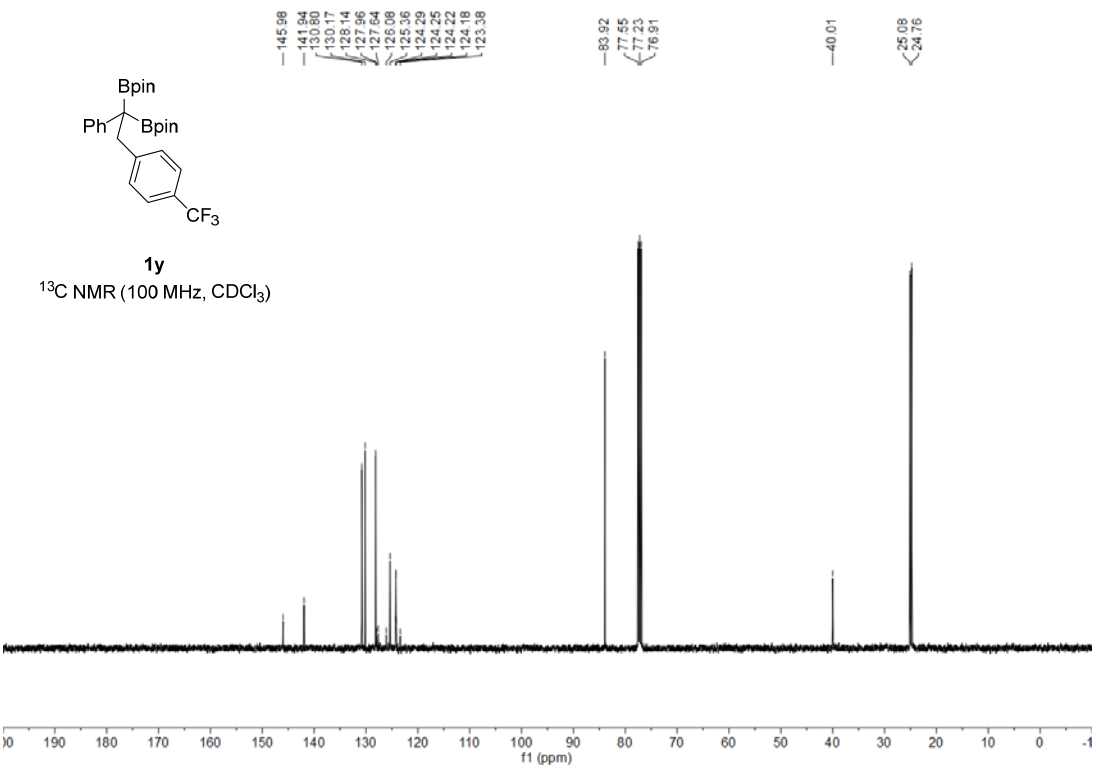
1x

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



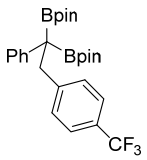
1y

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



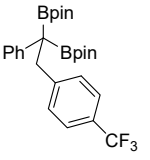
1y

^{13}C NMR (100 MHz, $CDCl_3$)



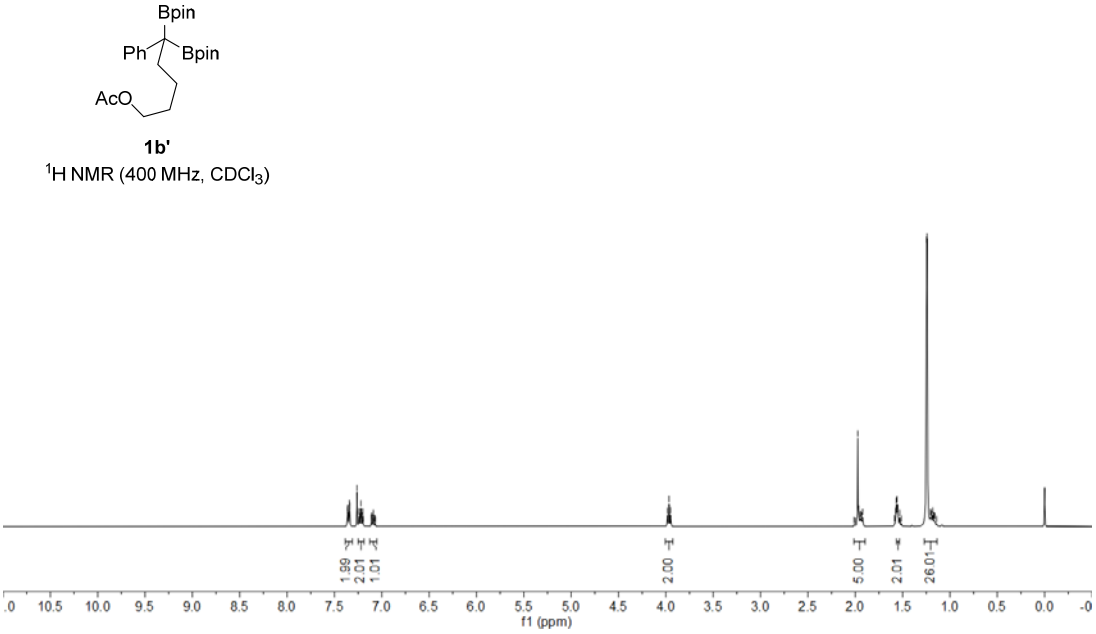
1y

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



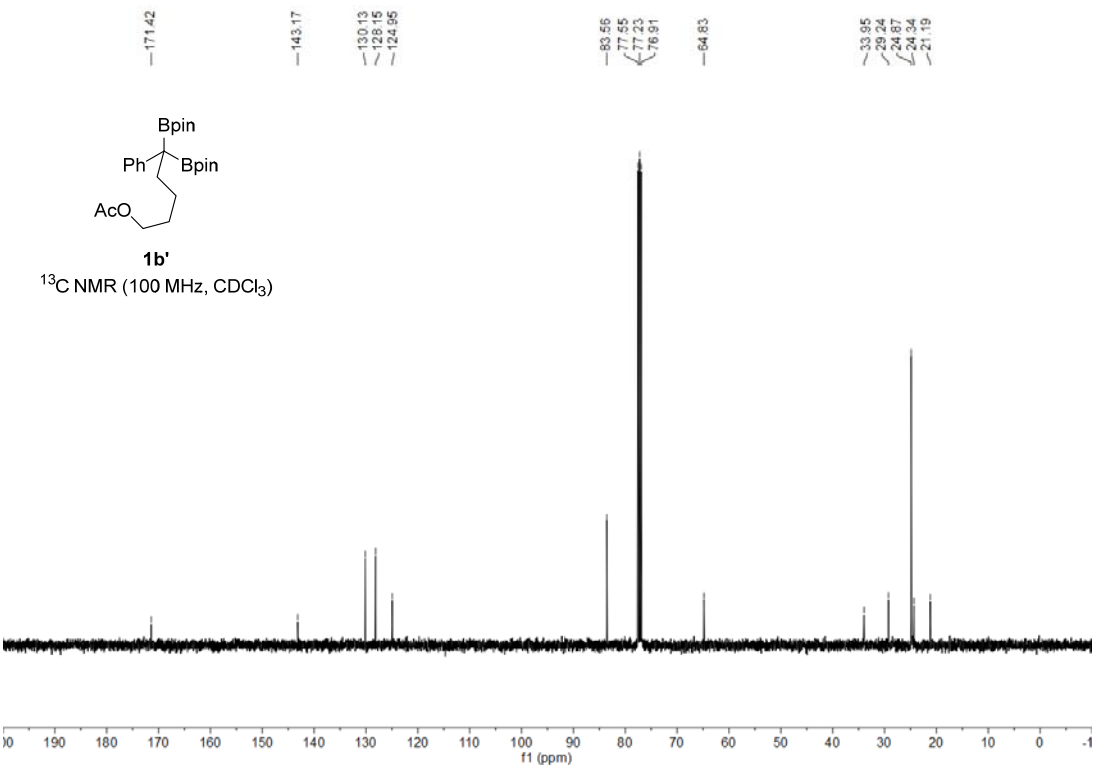
1y

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



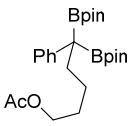
1b'

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



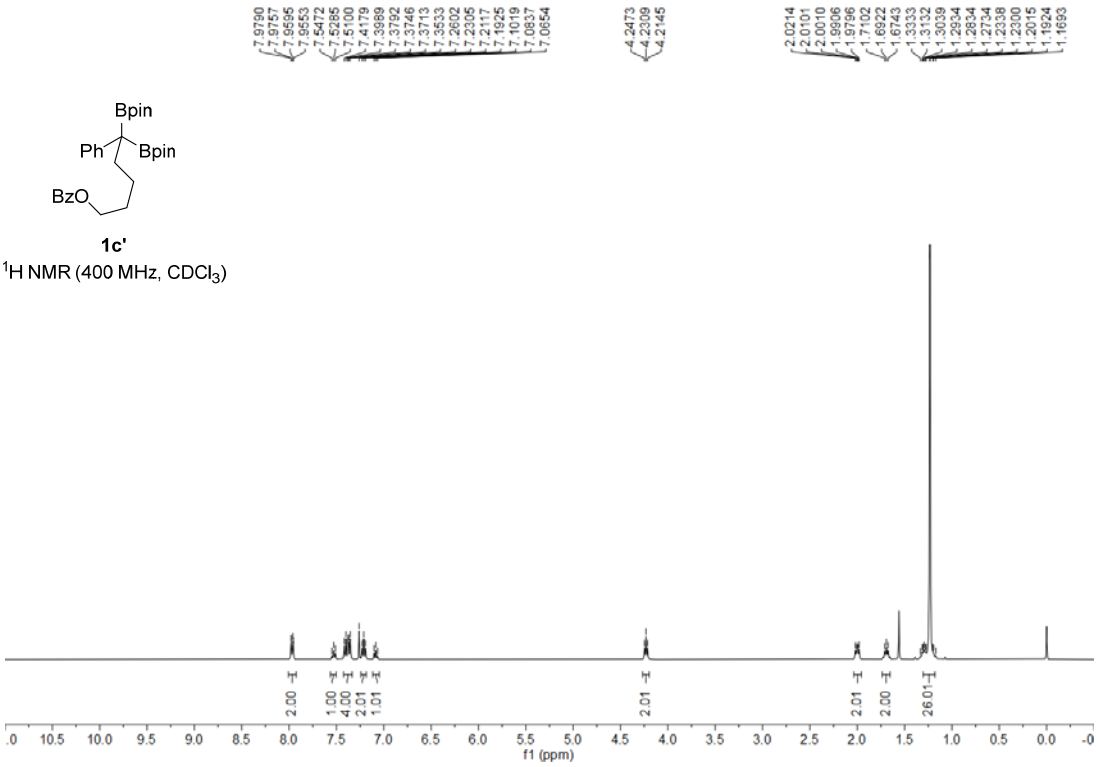
1b'

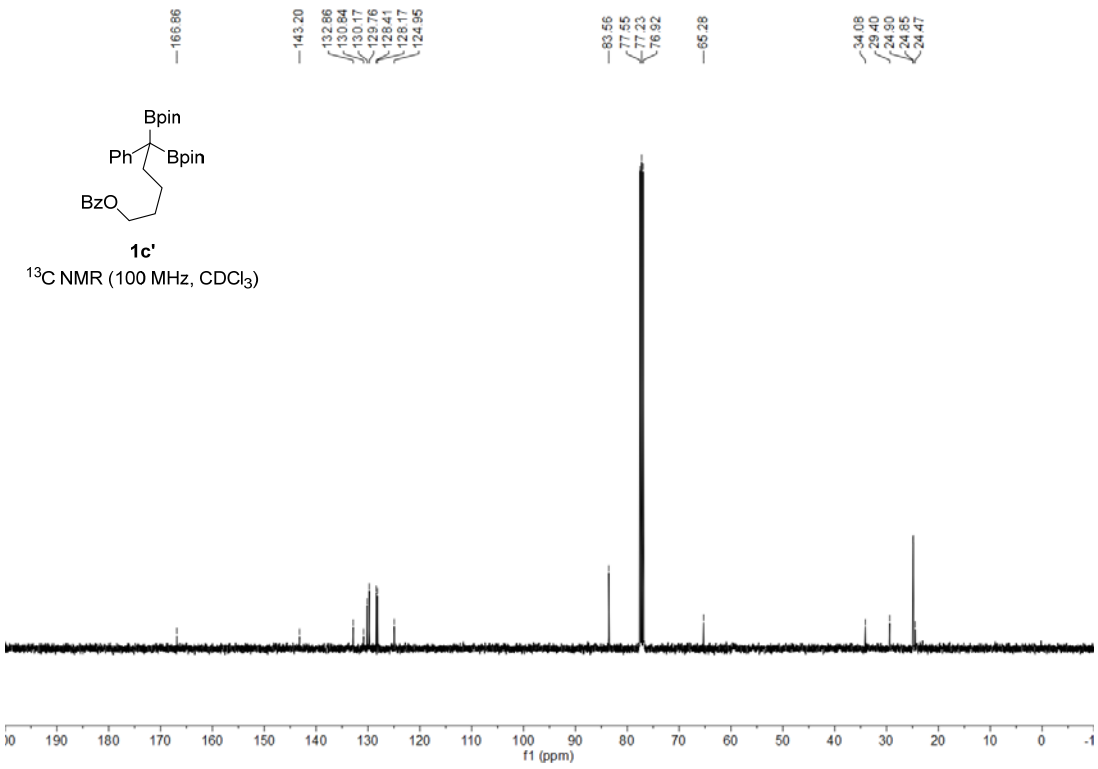
^{13}C NMR (100 MHz, $CDCl_3$)

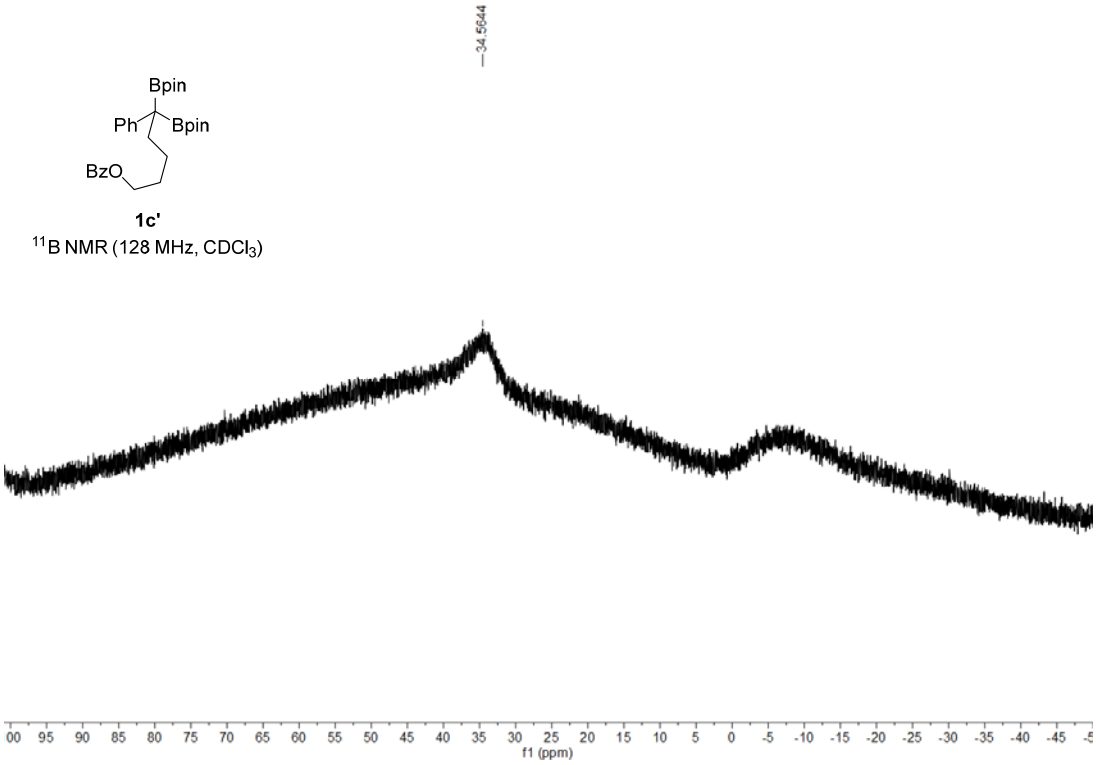


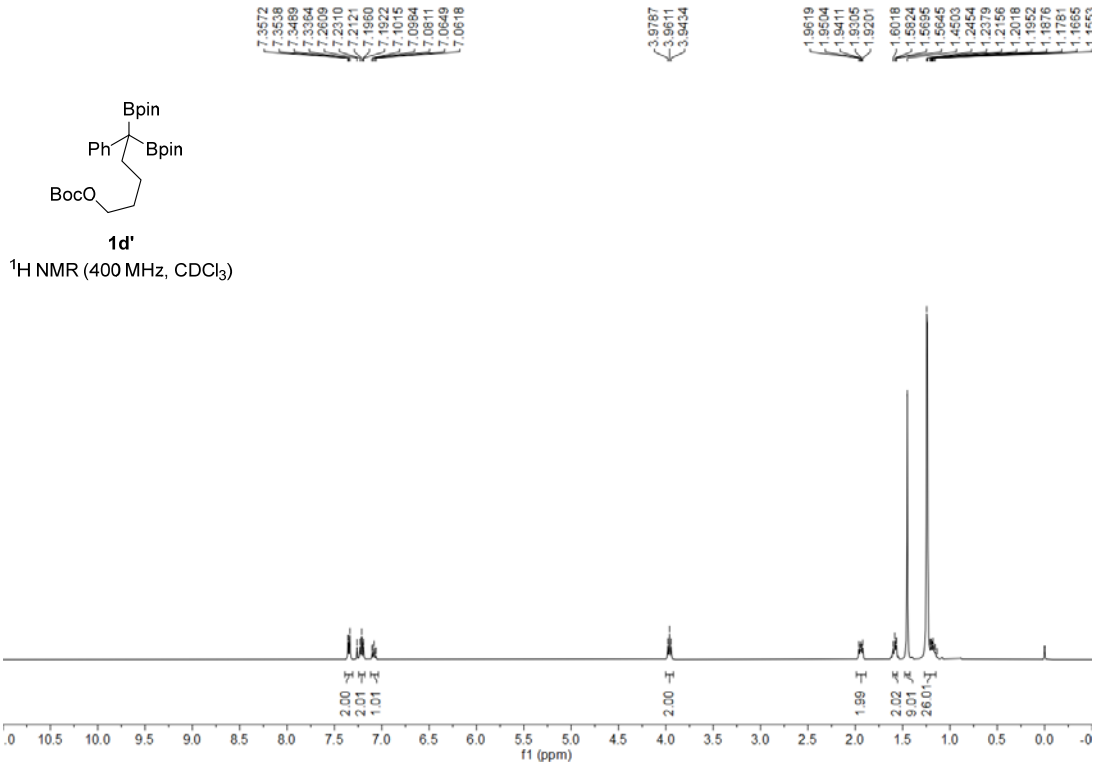
1b'

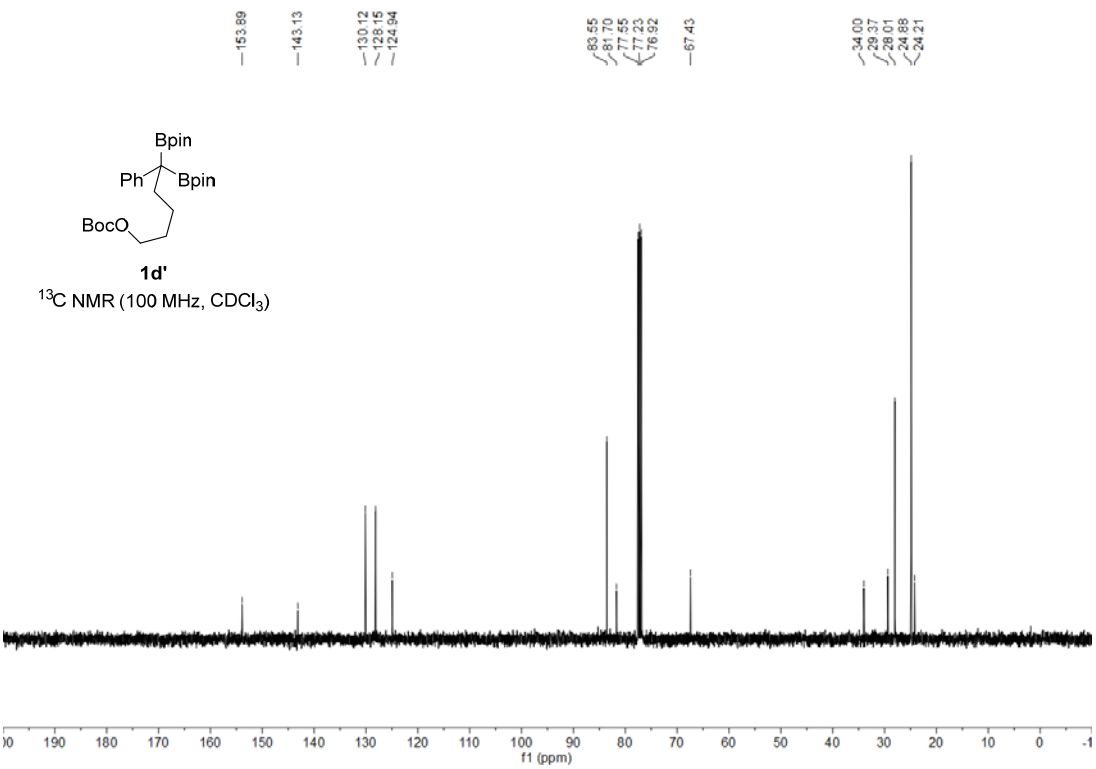
^{11}B NMR (128 MHz, $CDCl_3$)

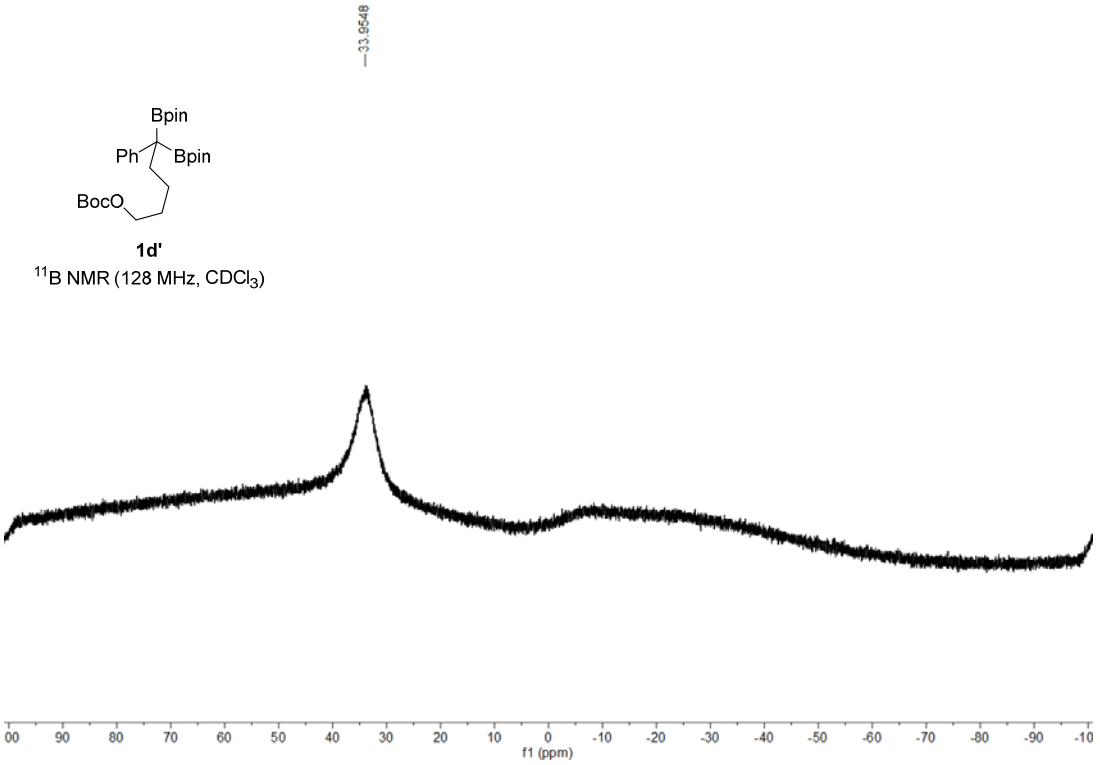

Bpin
Ph
Bpin
BzO
1c'
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Bpin
Ph
Bpin
BzO
1c'
13C NMR (100 MHz, CDCl3)
f1 (ppm)


34.5644
Bpin
Ph
Bpin
BzO
1c'
11B NMR (128 MHz, CDCl3)
f1 (ppm)

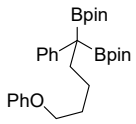

Bpin
Ph
Bpin
BocO
1d'
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Bpin
Ph
Bpin
BocO
1d'
13C NMR (100 MHz, CDCl3)
f1 (ppm)



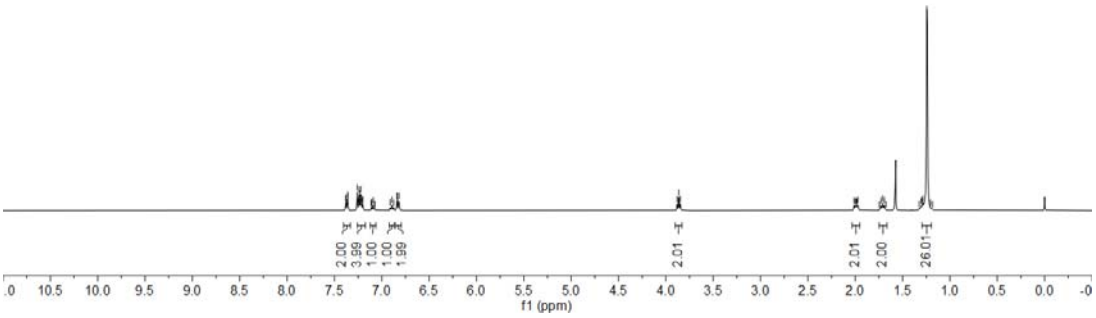
1d'

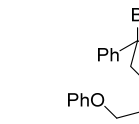
^{11}B NMR (128 MHz, $CDCl_3$)



1f'

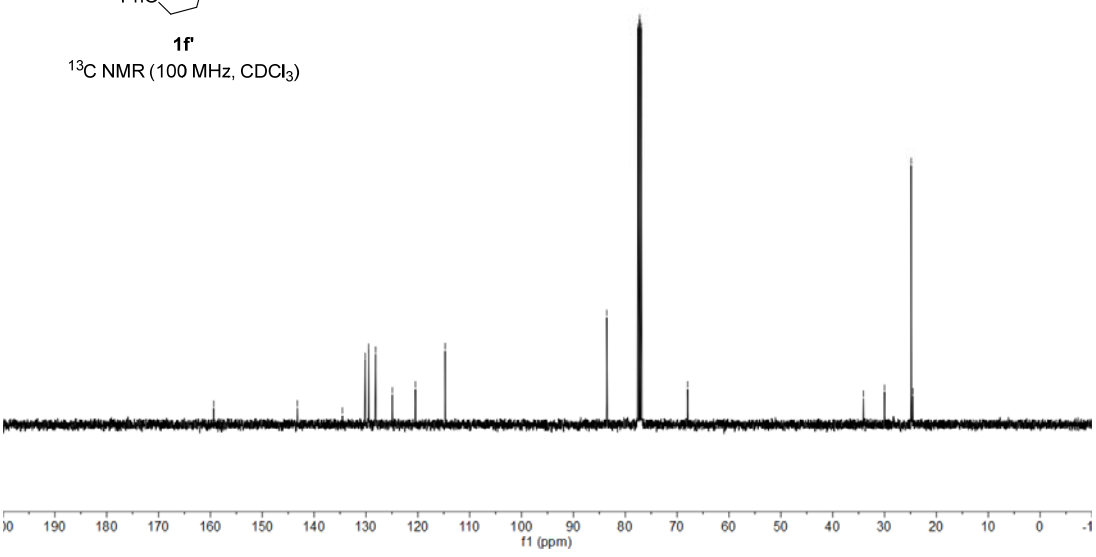
^{1}H NMR (400 MHz, $CDCl_3$)

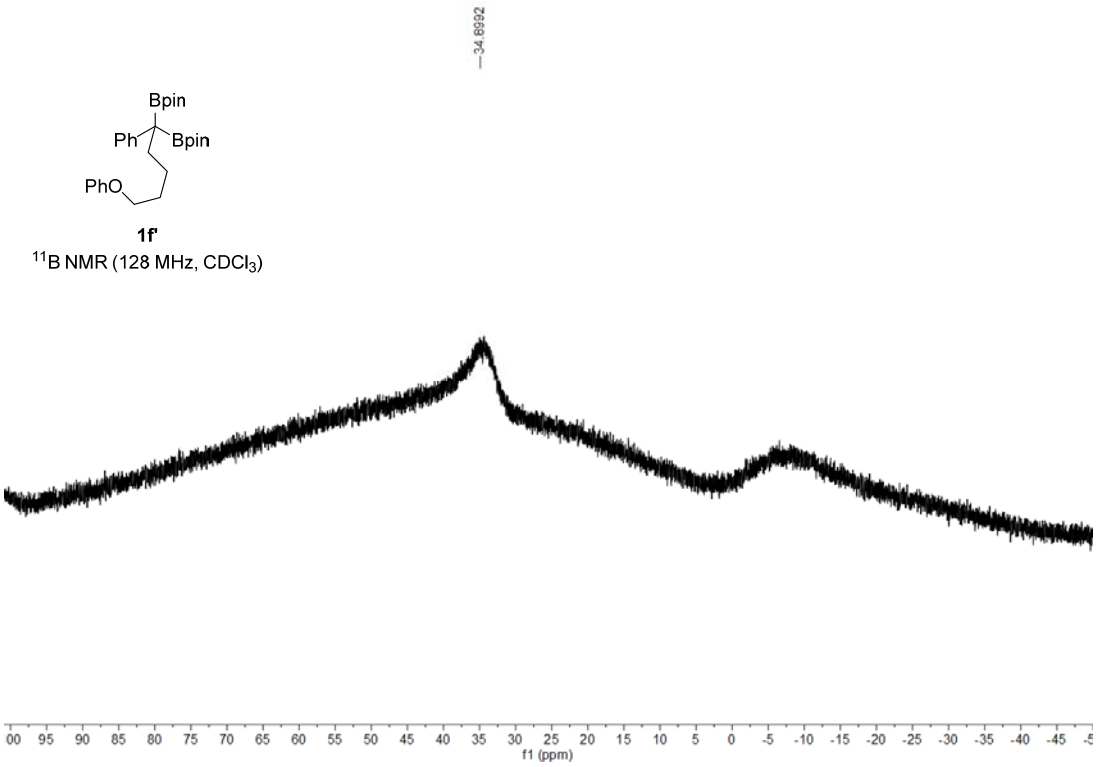




1f'

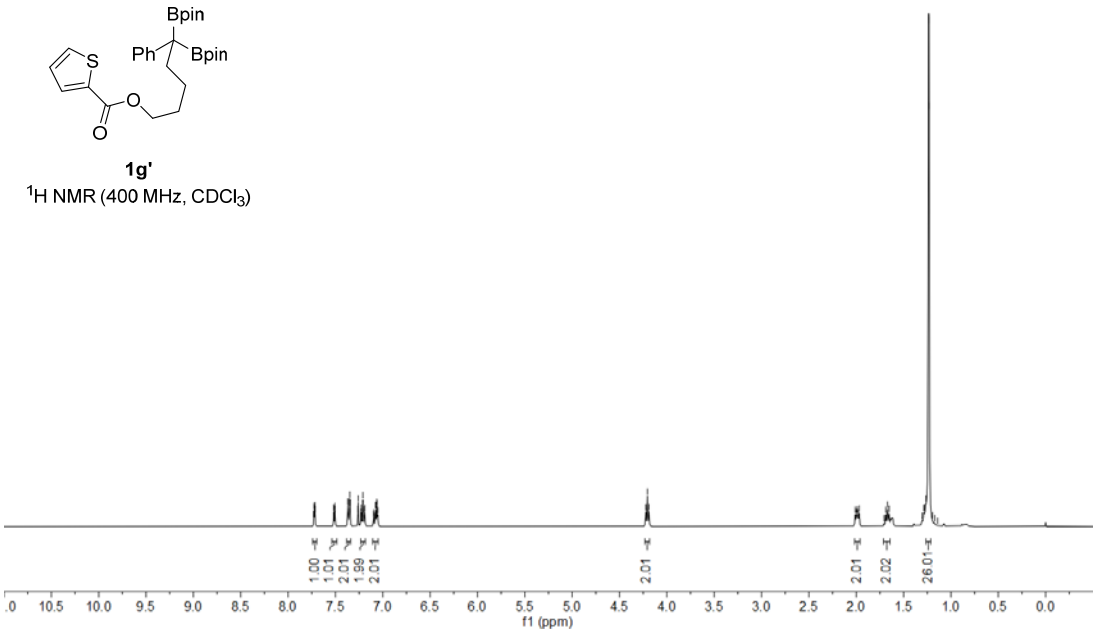
^{13}C NMR (100 MHz, $CDCl_3$)





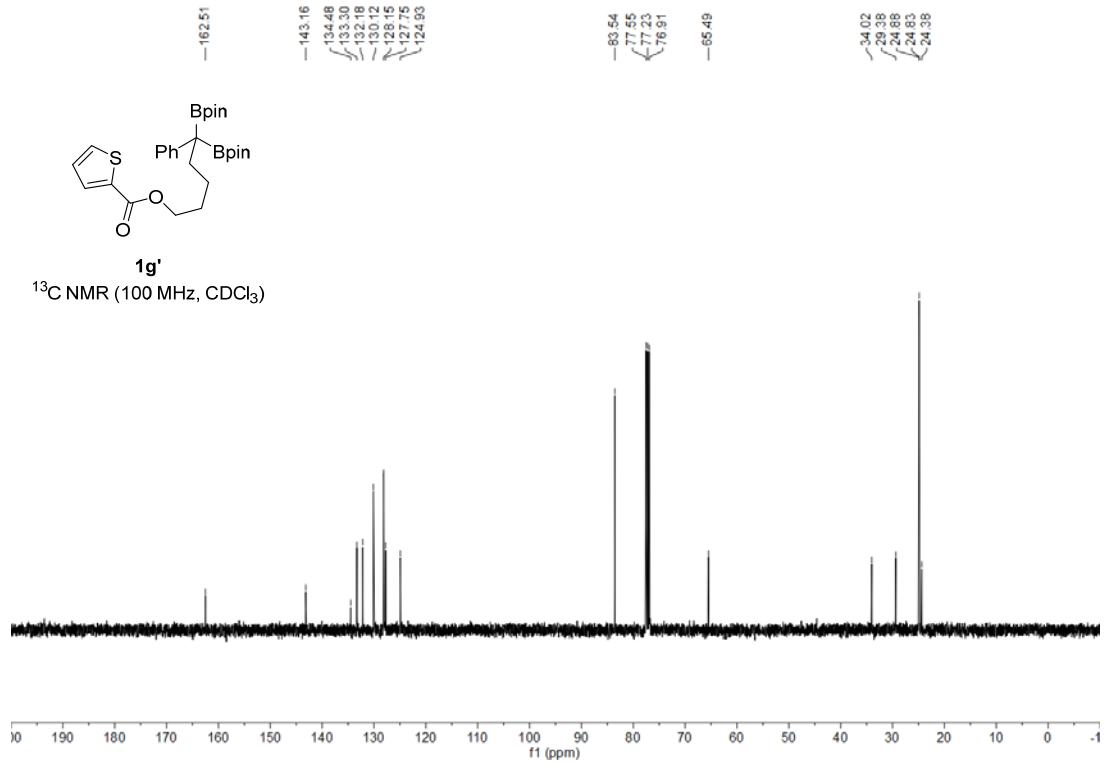
1f'

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



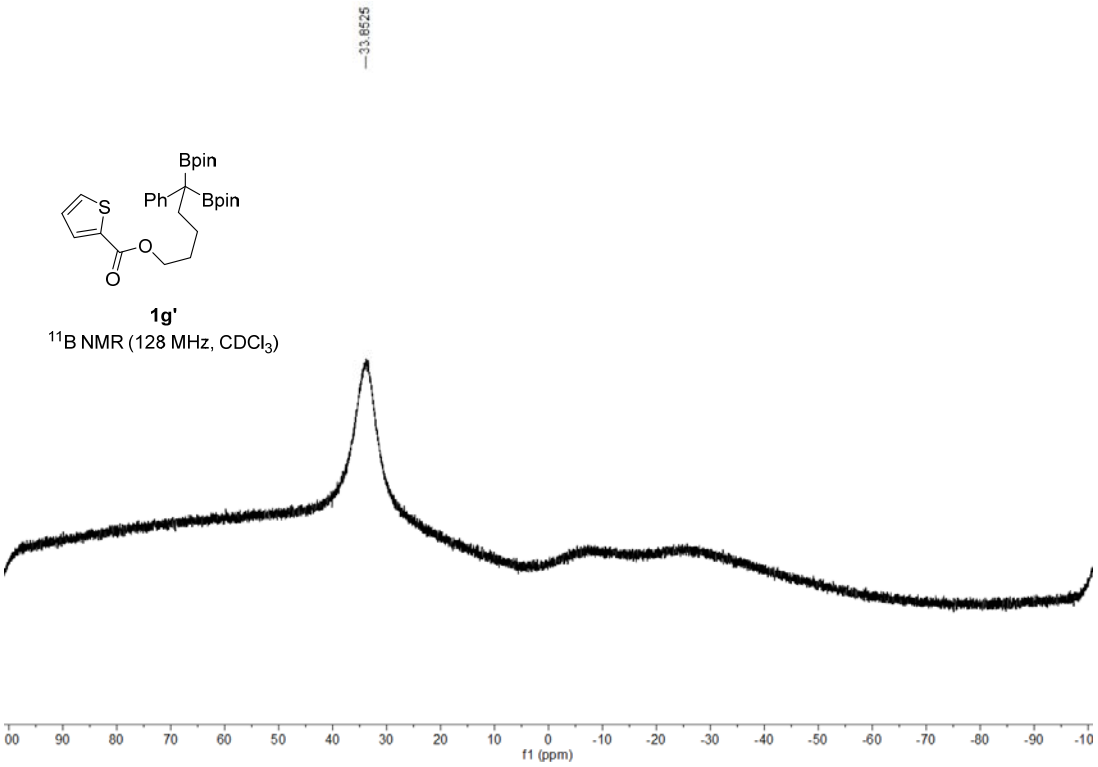
1g'

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



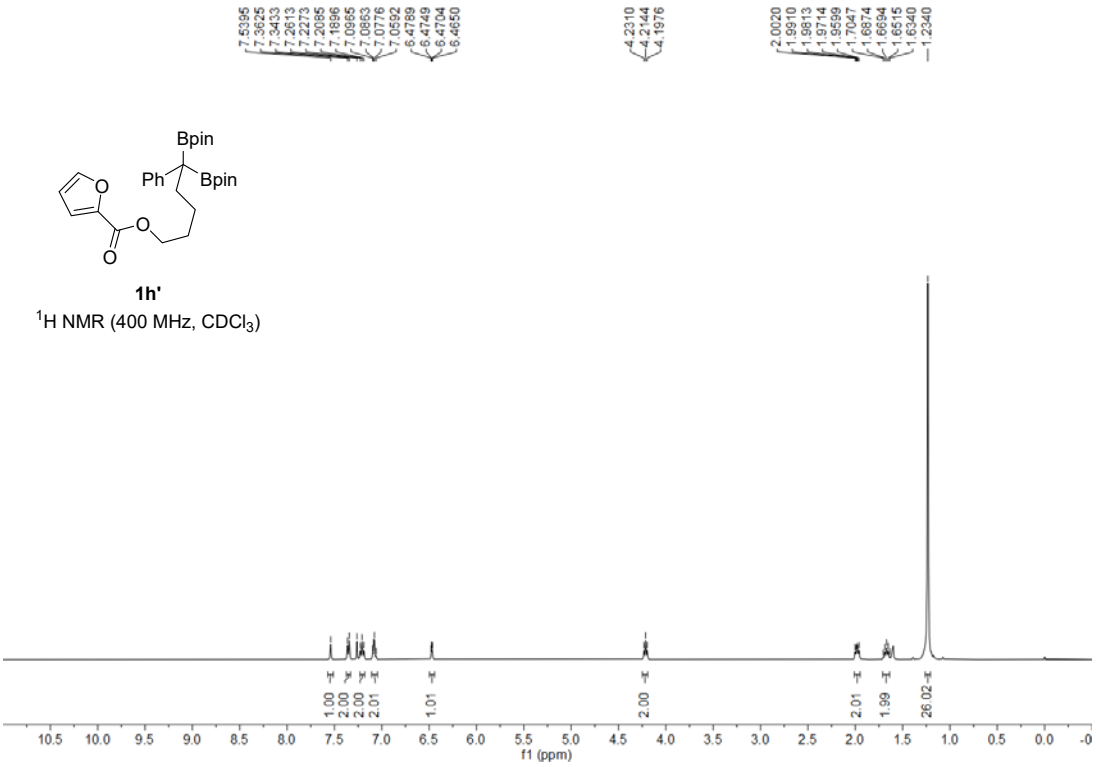
1g'

^{13}C NMR (100 MHz, $CDCl_3$)



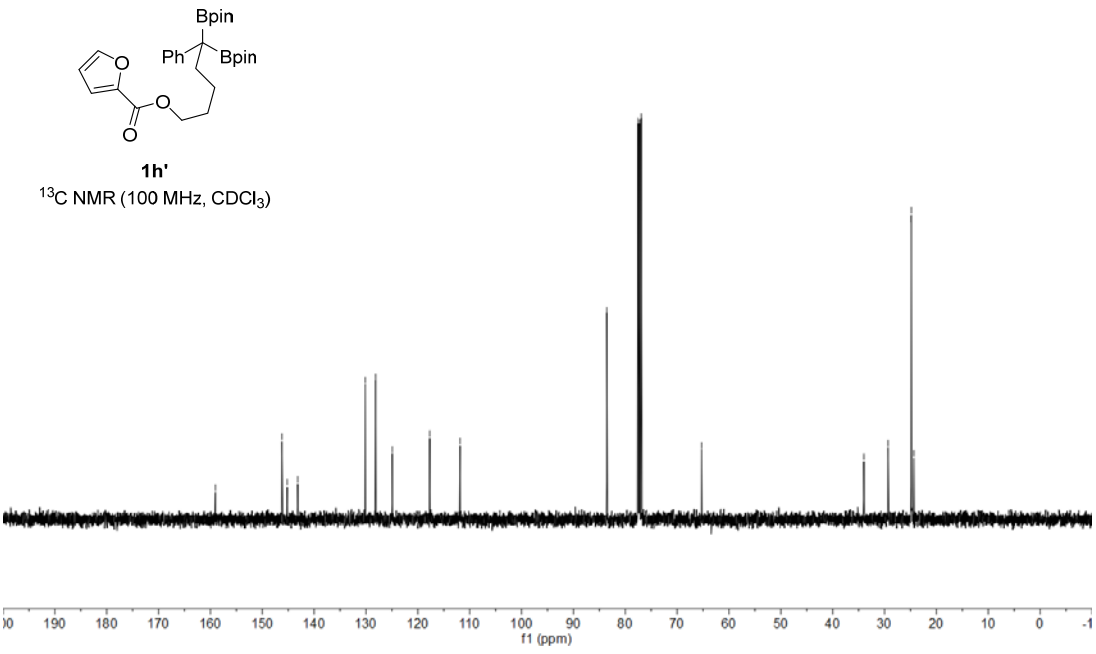
1g'

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



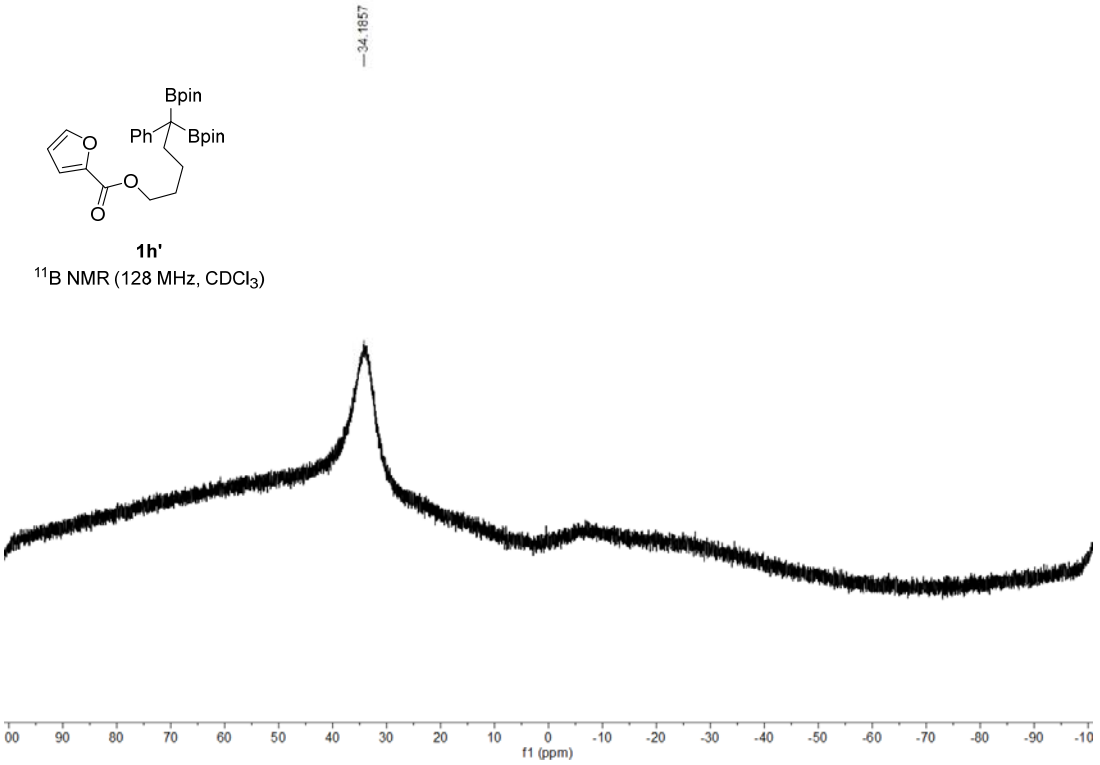
1h'

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



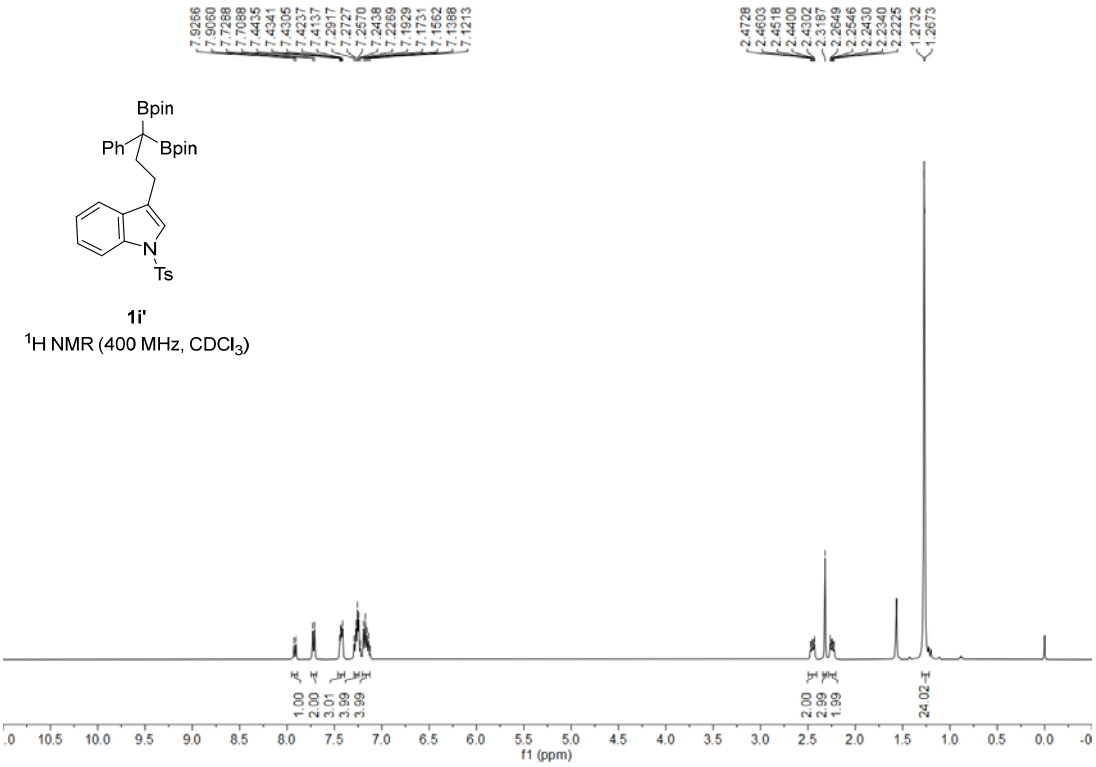
1h'

^{13}C NMR (100 MHz, $CDCl_3$)



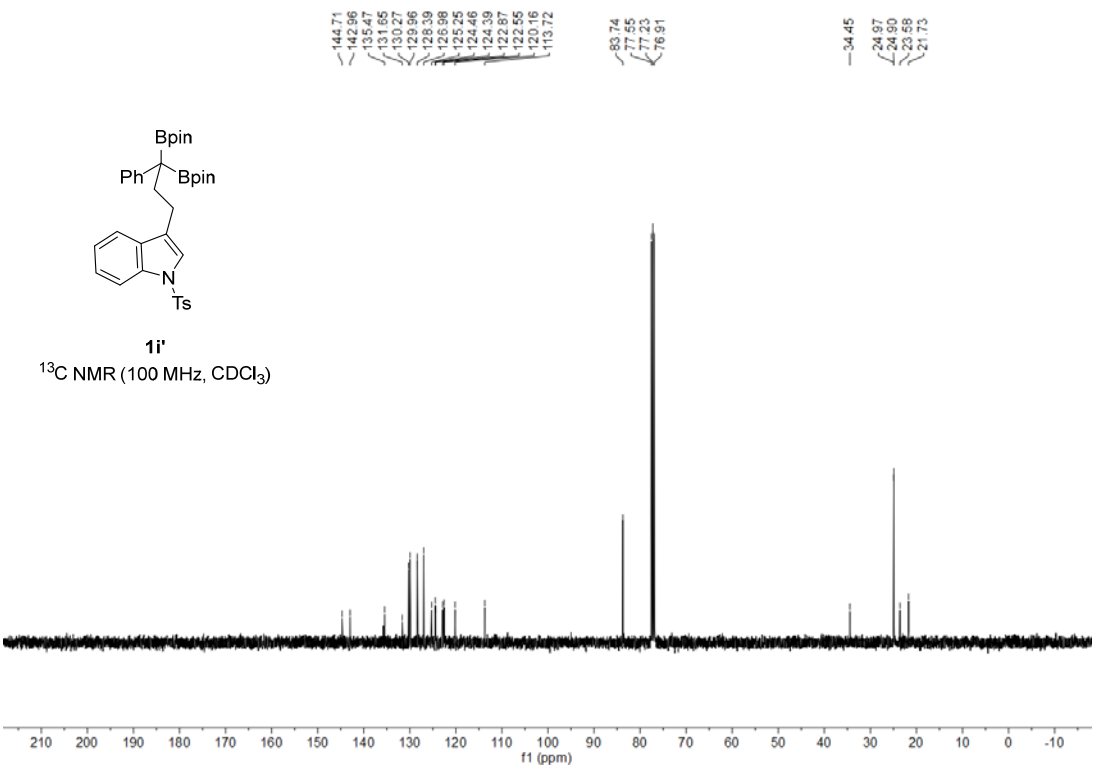
1h'

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



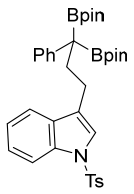
1i'

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



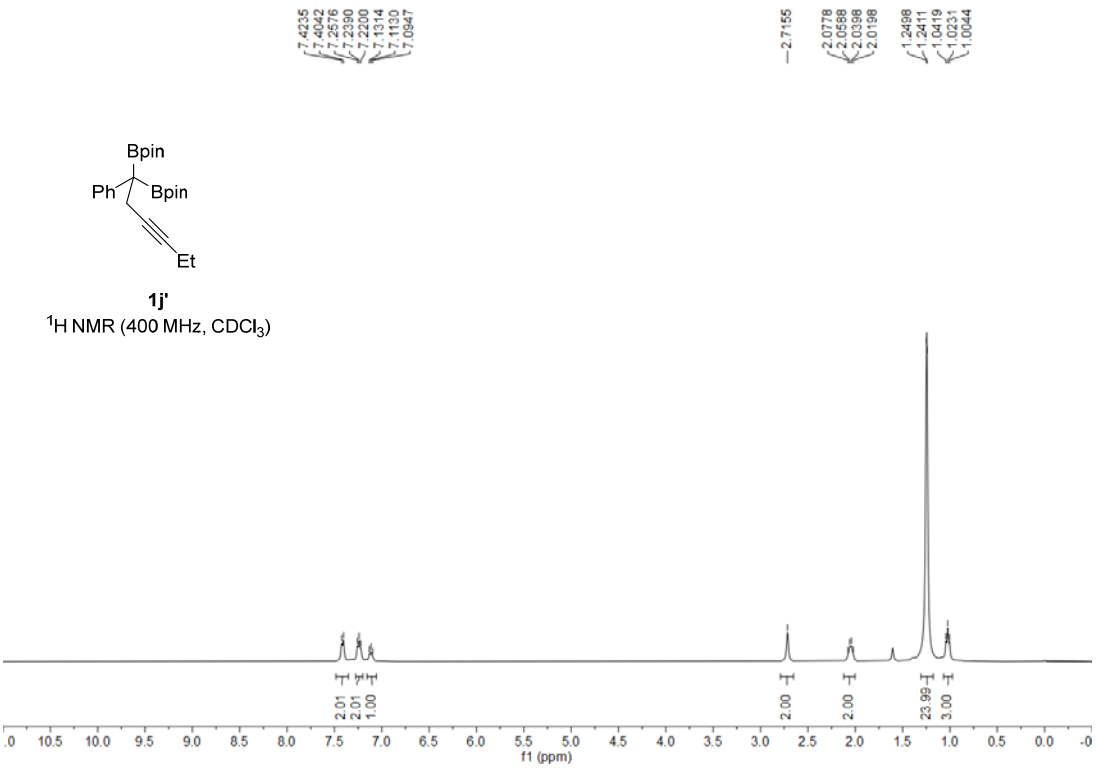
1i'

^{13}C NMR (100 MHz, $CDCl_3$)



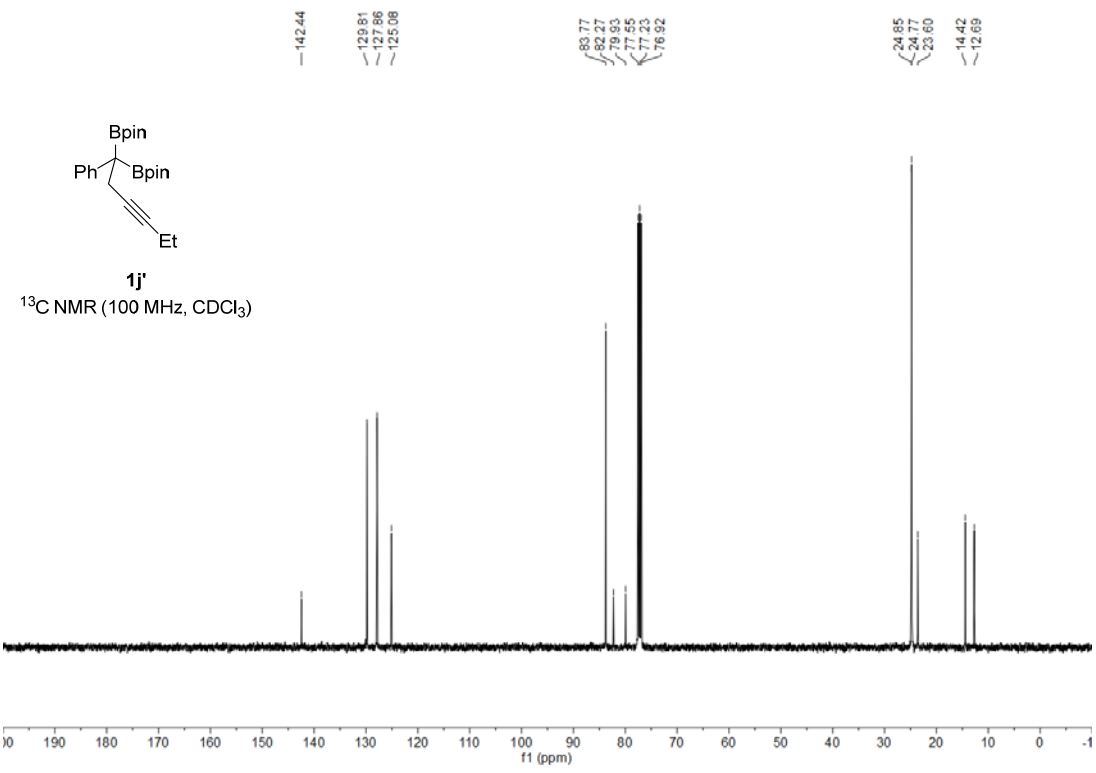
1i'

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



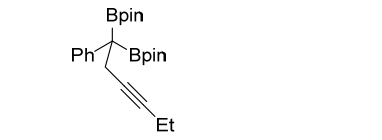
1j'

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



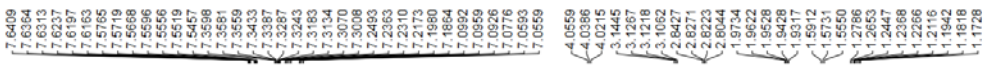
1j'

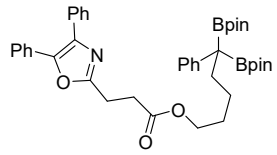
^{13}C NMR (100 MHz, $CDCl_3$)



1j'

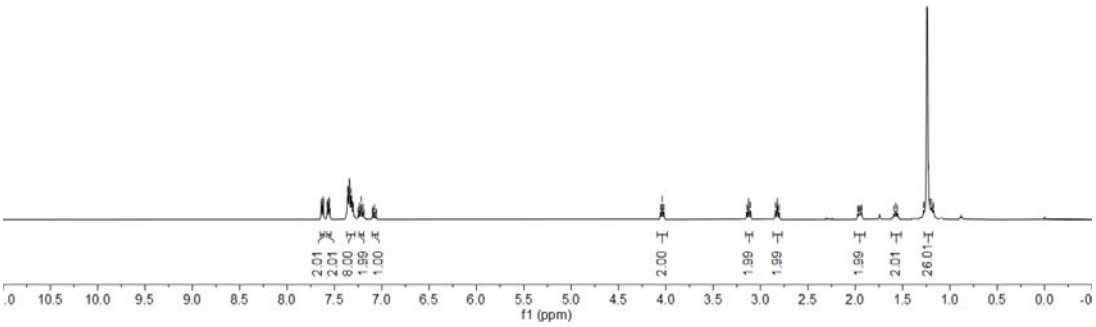
^{11}B NMR (128 MHz, $CDCl_3$)

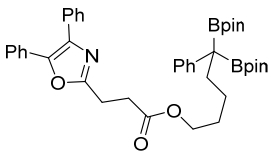




1k'

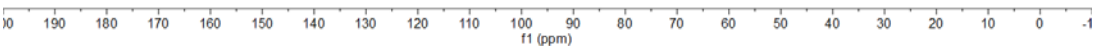
^{1}H NMR (400 MHz, $CDCl_3$)

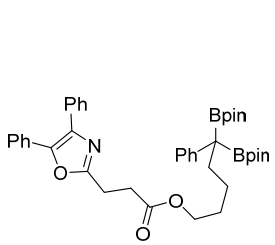




1k'

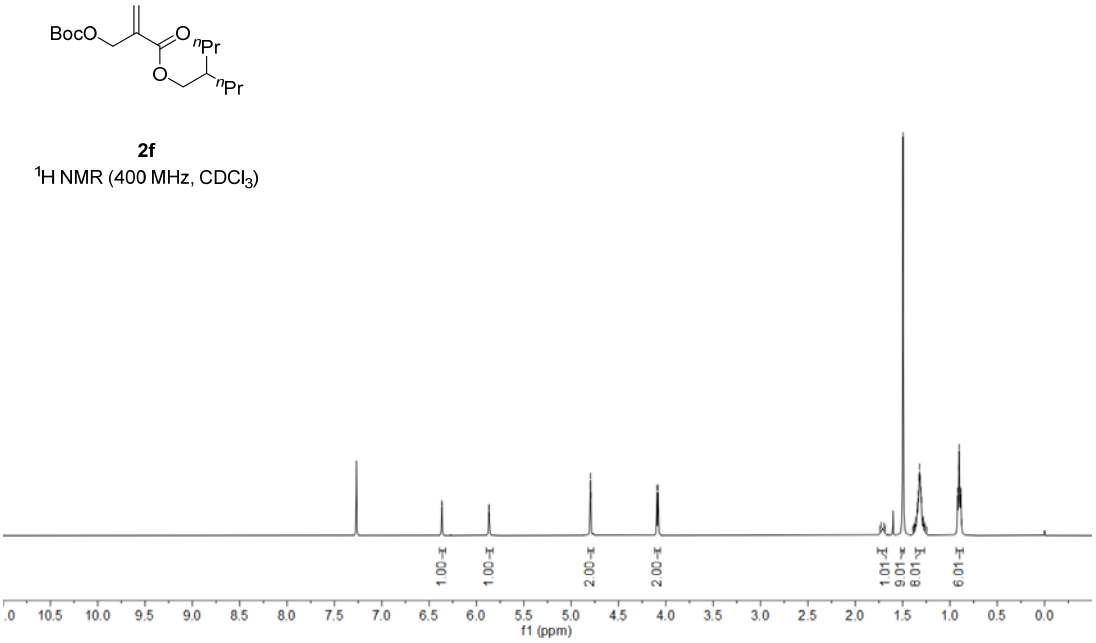
^{13}C NMR (100 MHz, $CDCl_3$)





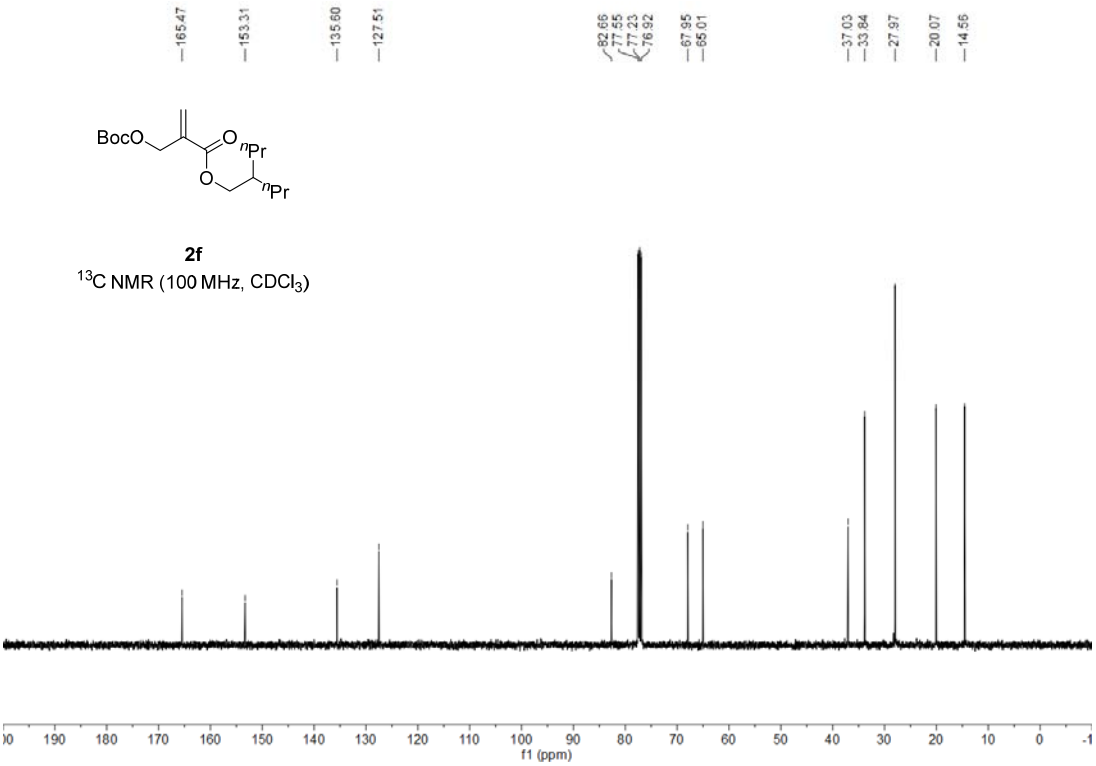
1k'

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



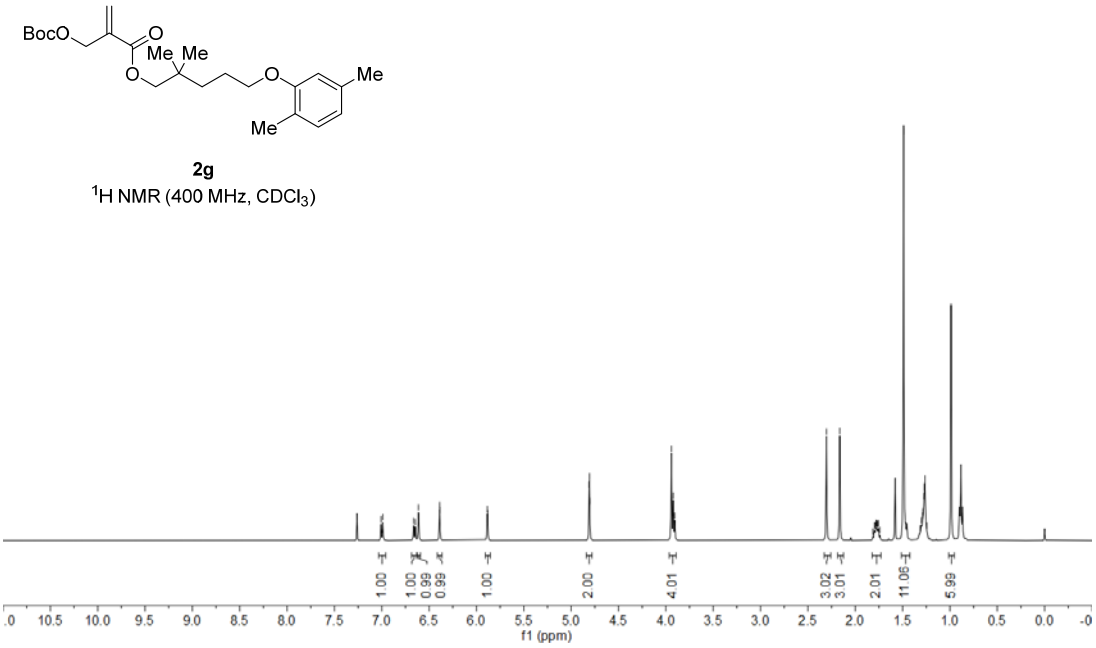
2f

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



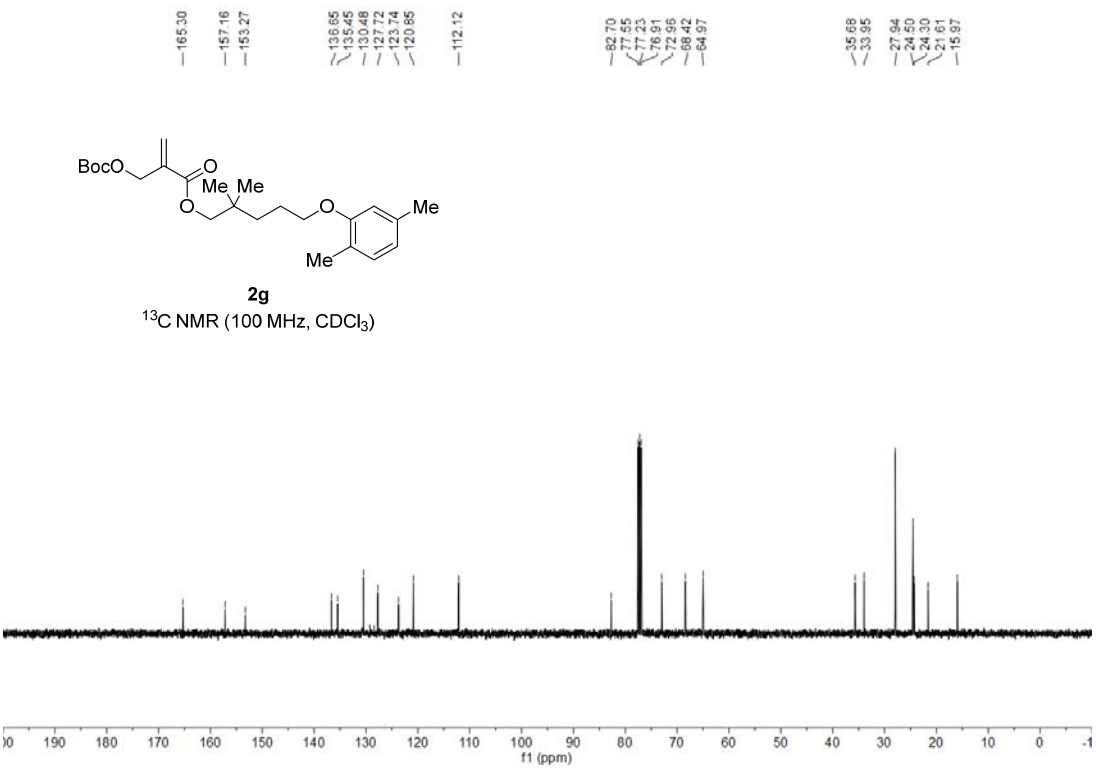
2f

^{13}C NMR (100 MHz, $CDCl_3$)



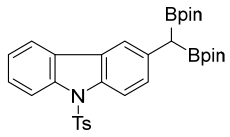
2g

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



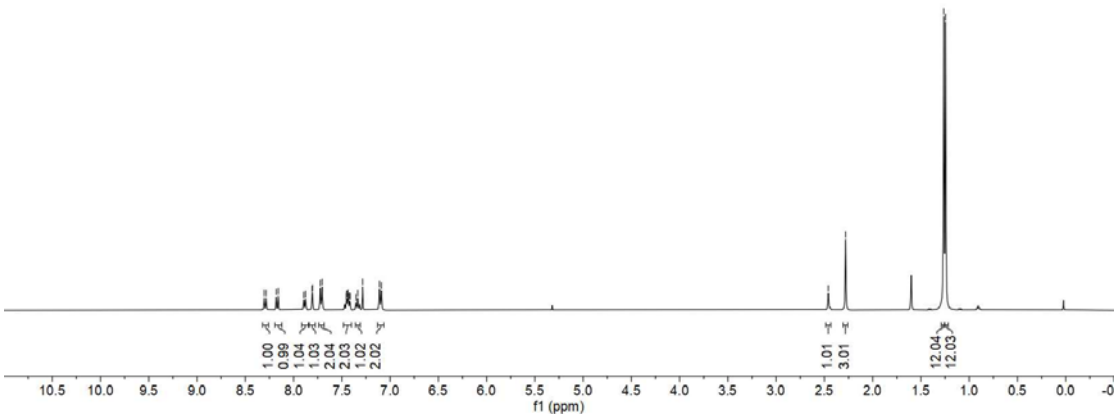
2g

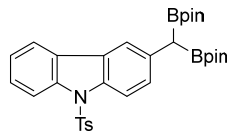
^{13}C NMR (100 MHz, $CDCl_3$)



4q

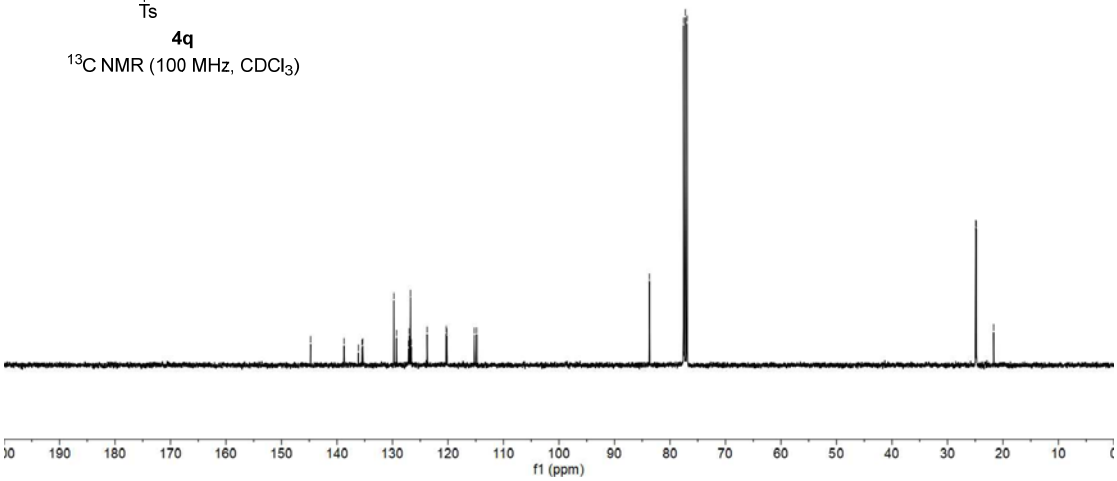
^{1}H NMR (400 MHz, $CDCl_3$)

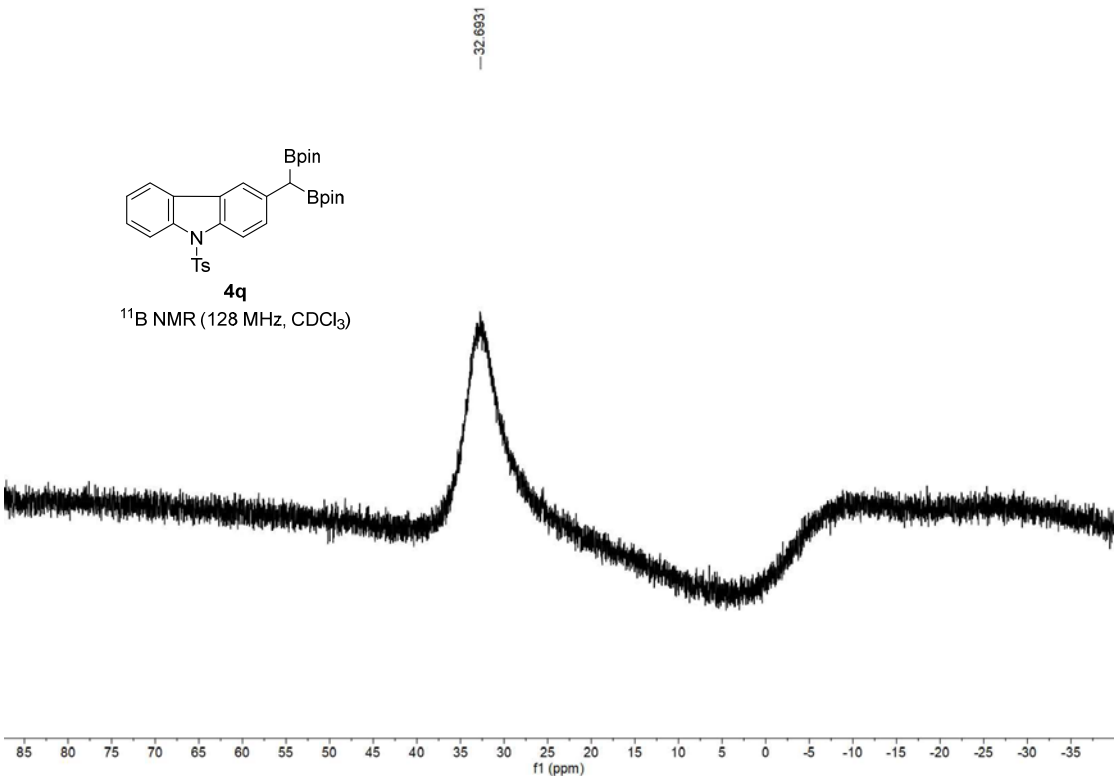




4q

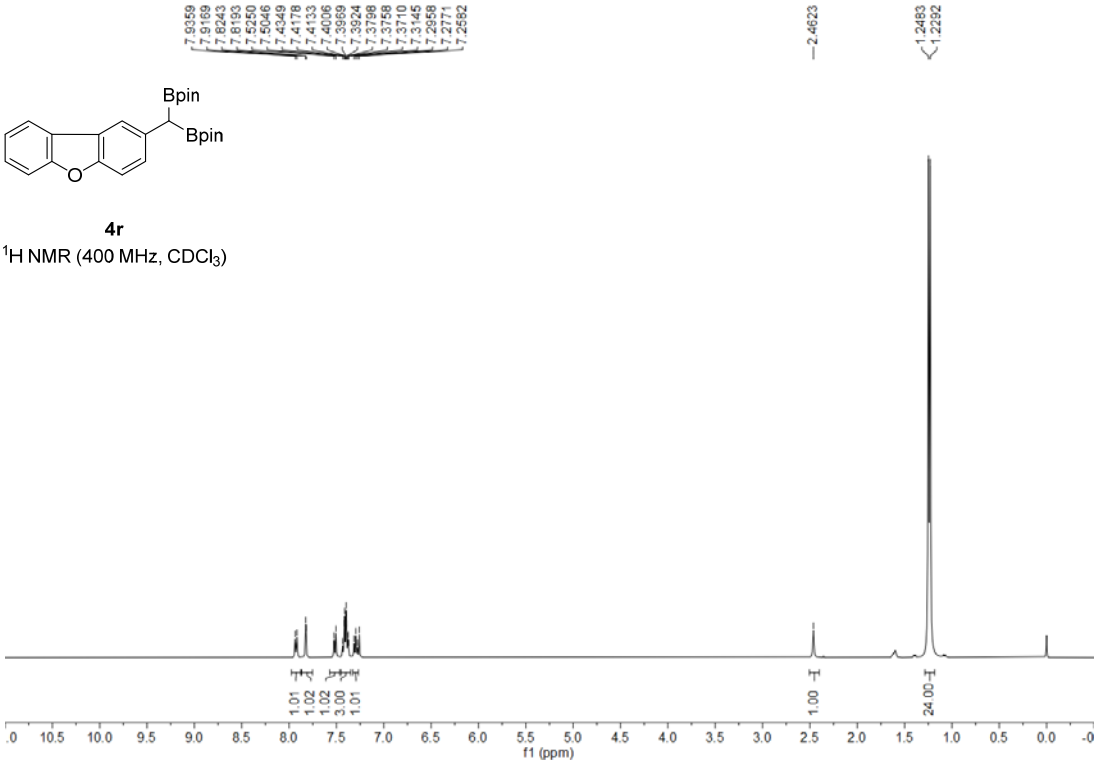
^{13}C NMR (100 MHz, $CDCl_3$)





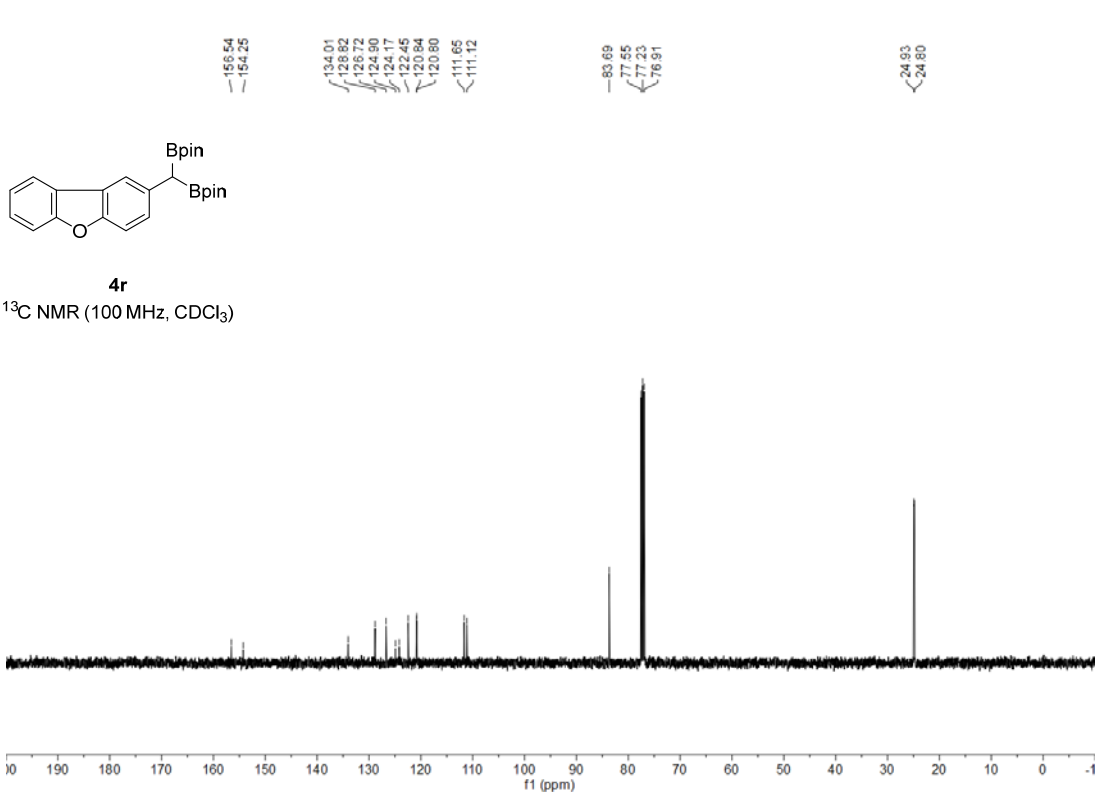
4q

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



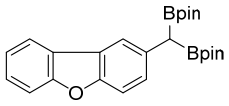
4r

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



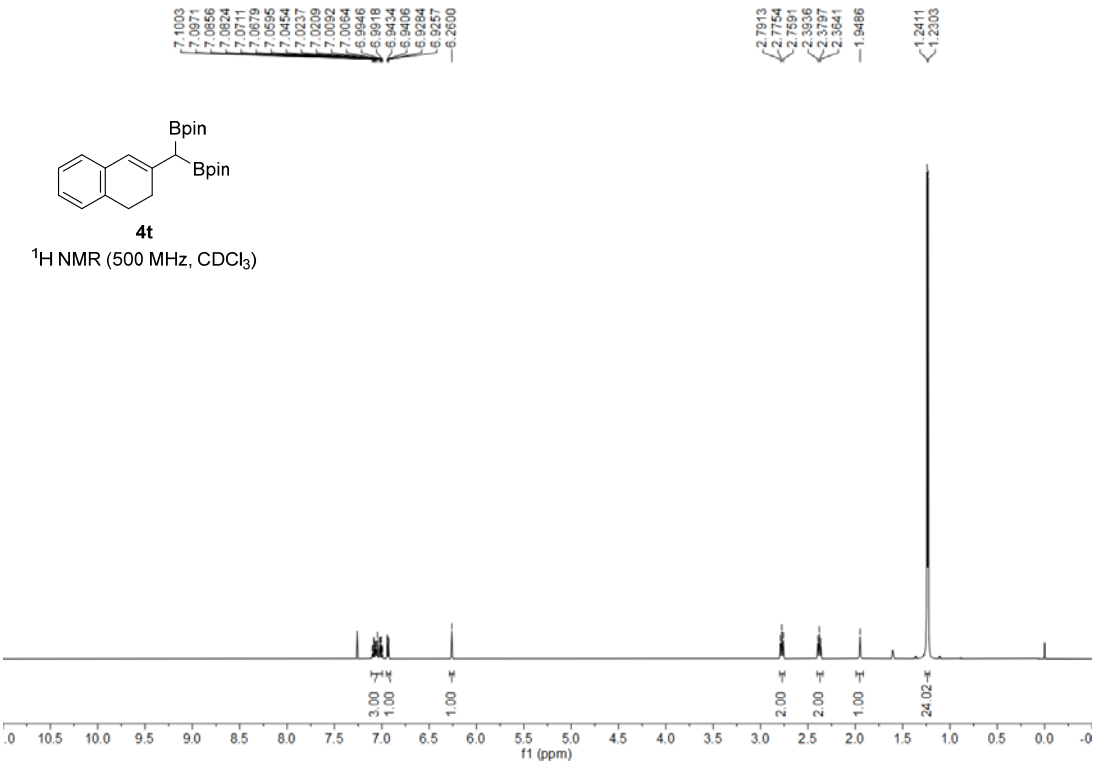
4r

^{13}C NMR (100 MHz, $CDCl_3$)



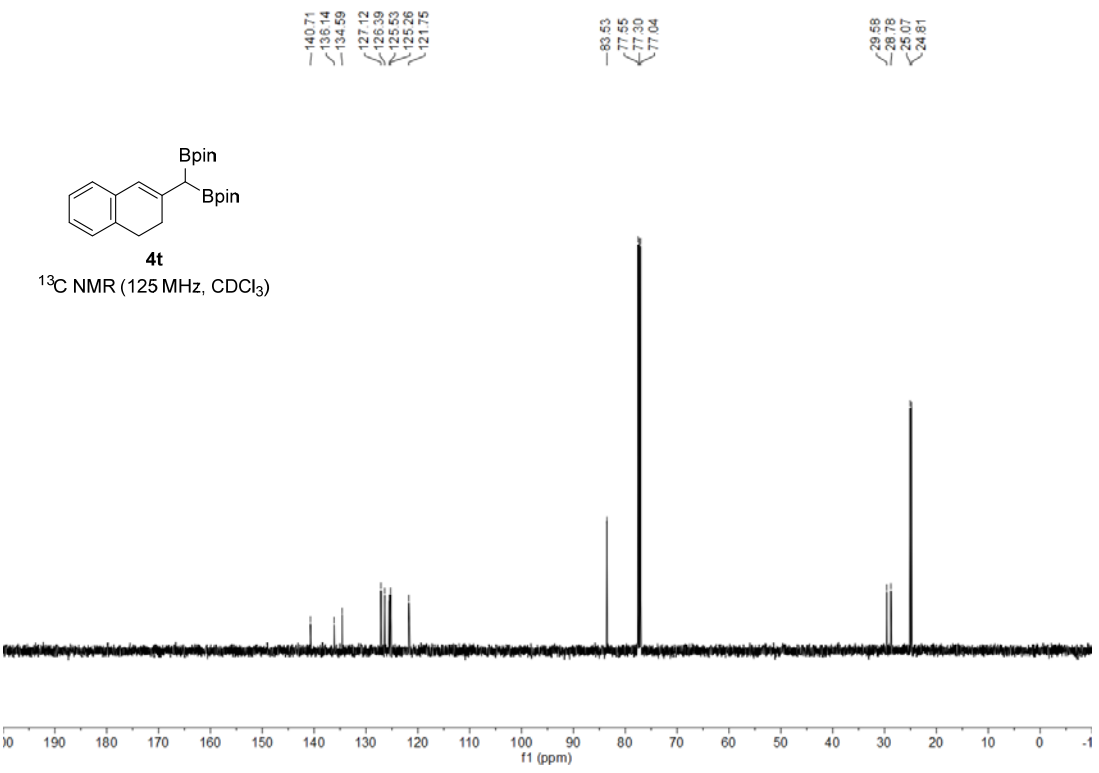
4r

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



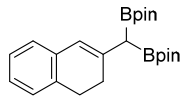
4t

^{1}H NMR (500 MHz, $CDCl_3$)



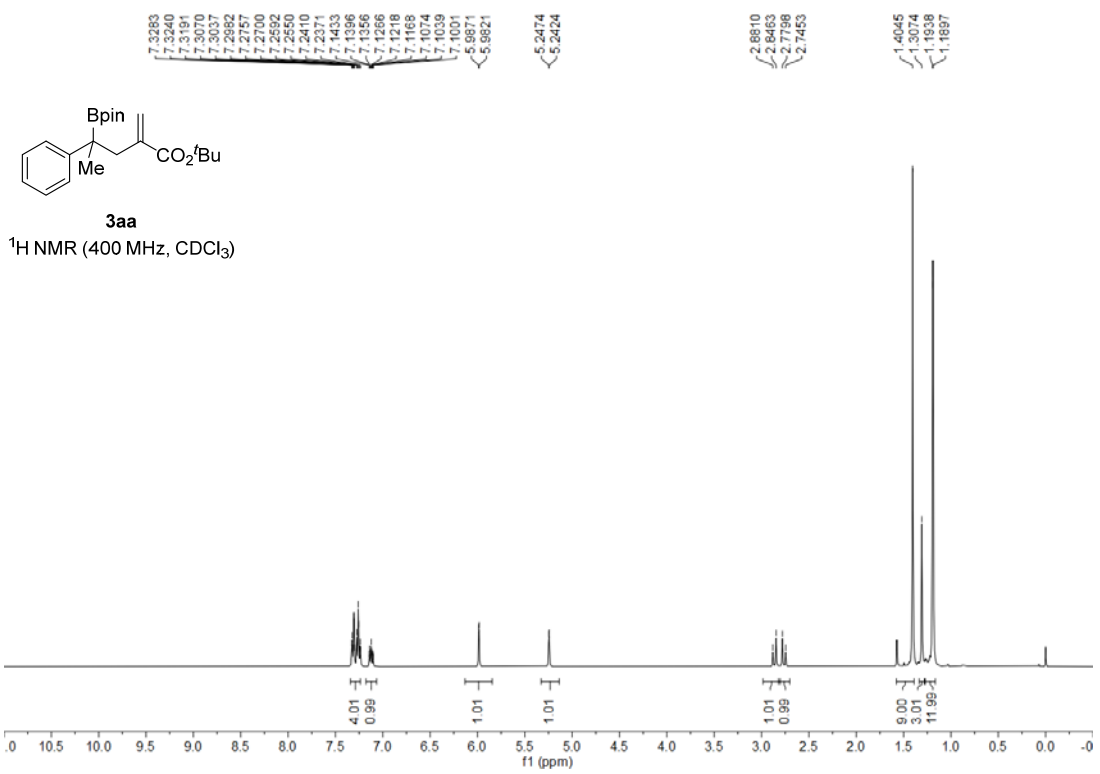
4t

^{13}C NMR (125 MHz, $CDCl_3$)



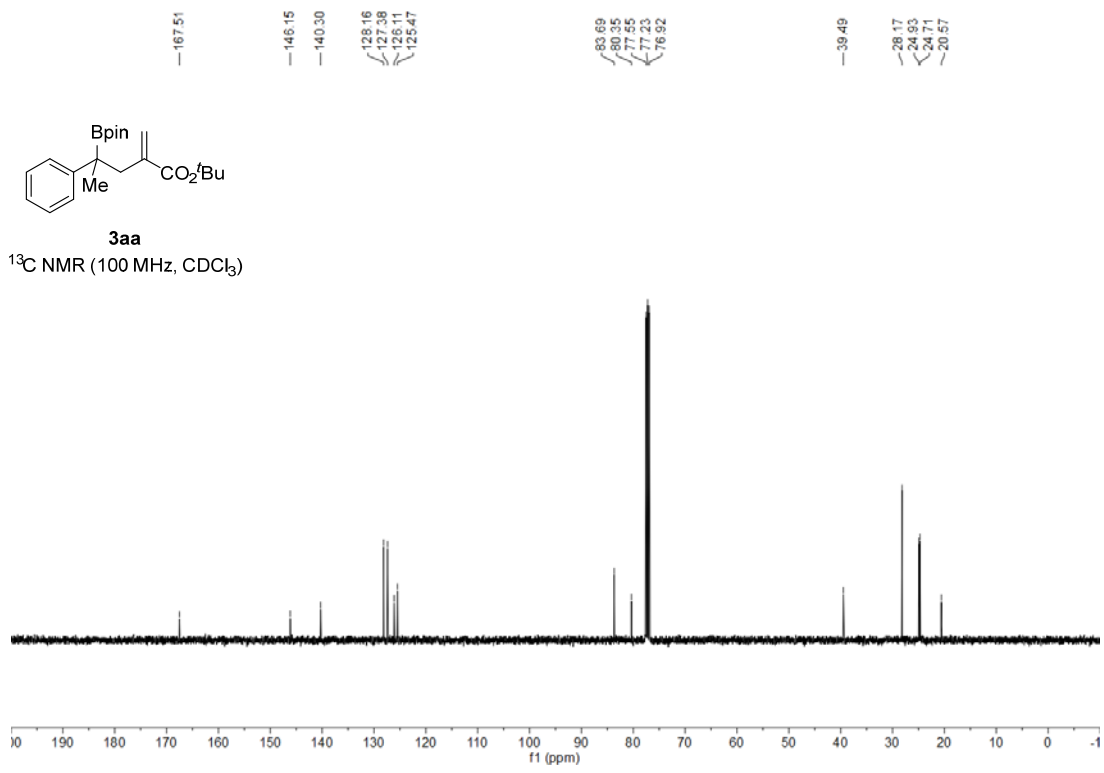
4t

^{11}B NMR (160 MHz, $CDCl_3$)



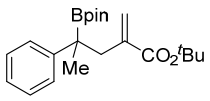
3aa

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



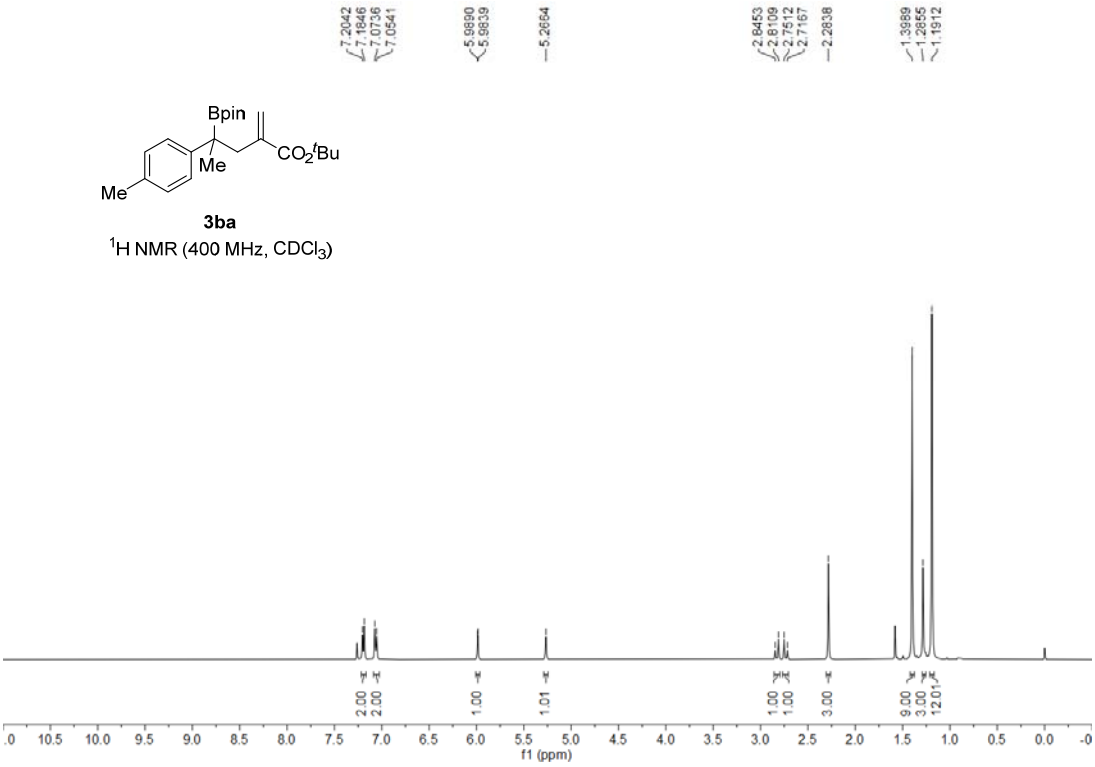
3aa

^{13}C NMR (100 MHz, $CDCl_3$)



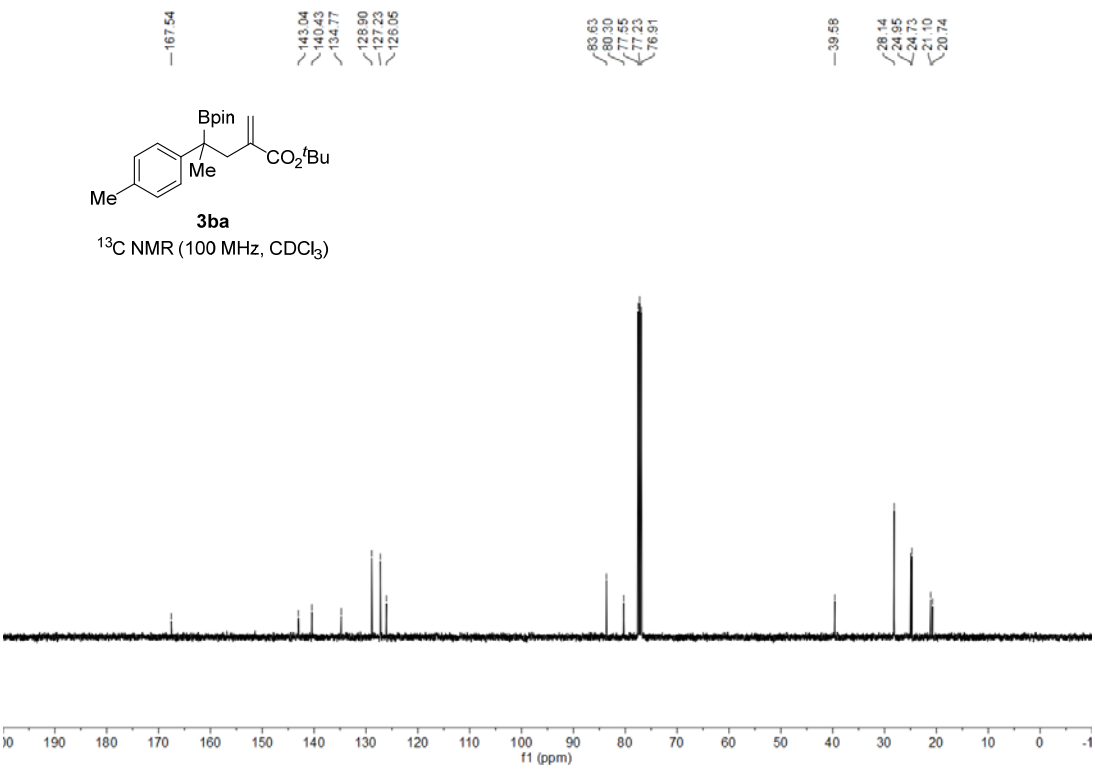
3aa

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



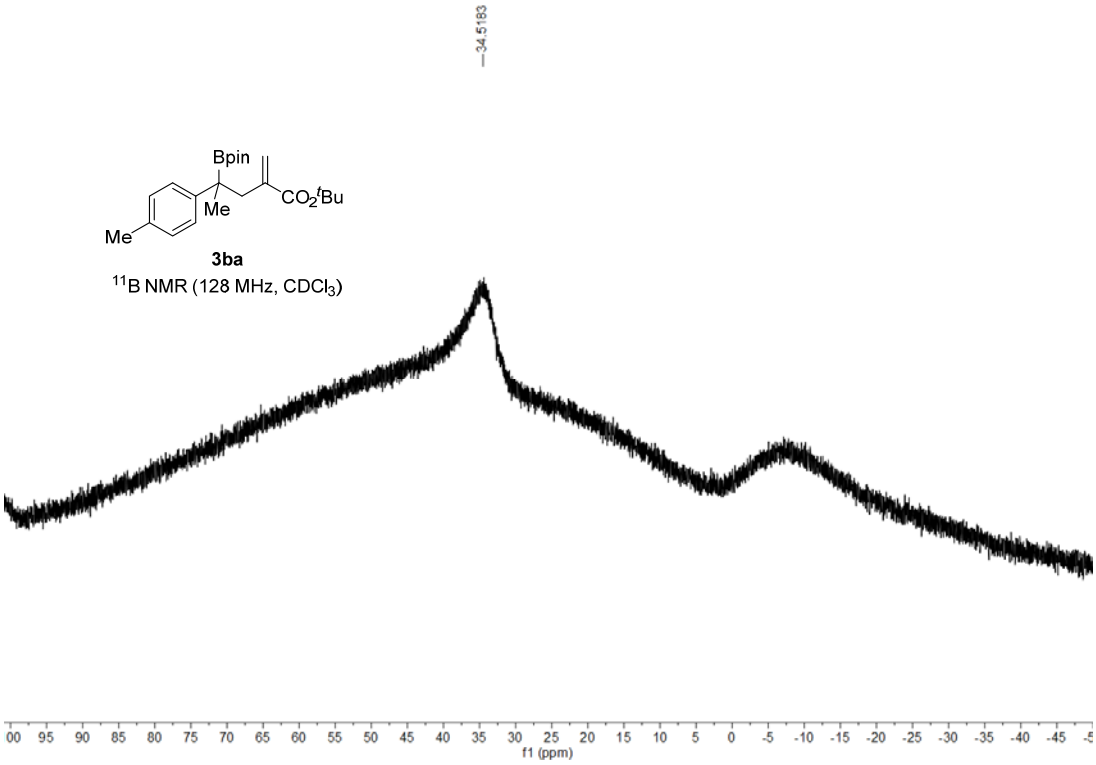
3ba

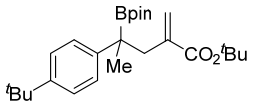
^{1}H NMR (400 MHz, $CDCl_3$)



3ba

^{13}C NMR (100 MHz, $CDCl_3$)


34.5183
Bpin
Me
CO2tBu
Me
3ba
11B NMR (128 MHz, CDCl3)
f1 (ppm)

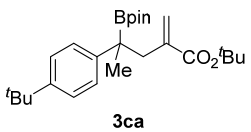


3ca

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

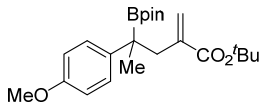
3ca

^{13}C NMR (100 MHz, $CDCl_3$)



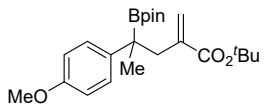
3ca

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



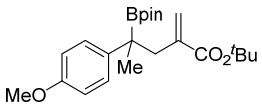
3da

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



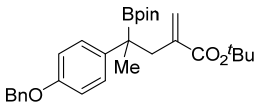
3da

^{13}C NMR (100 MHz, $CDCl_3$)



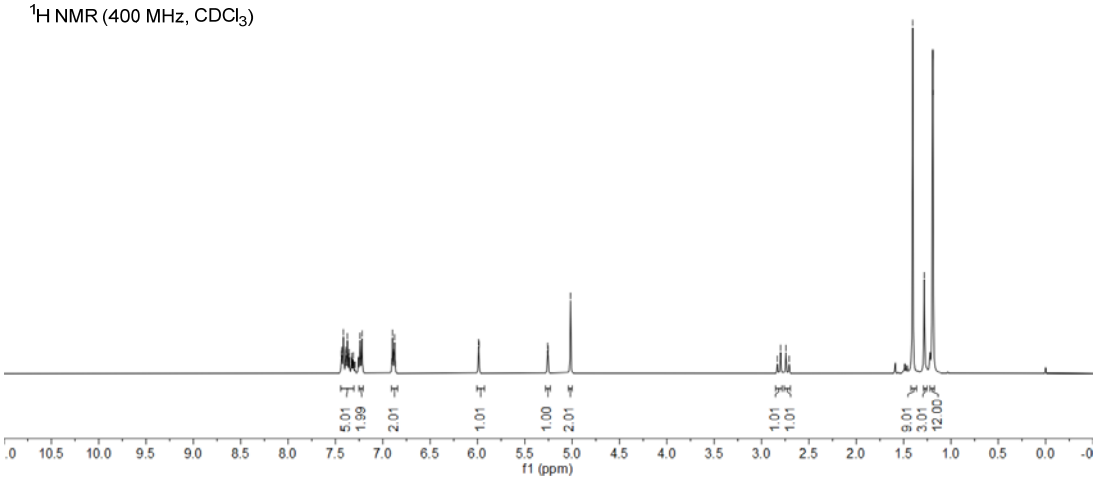
3da

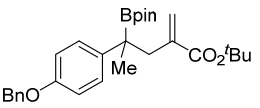
^{11}B NMR (128 MHz, $CDCl_3$)



3ea

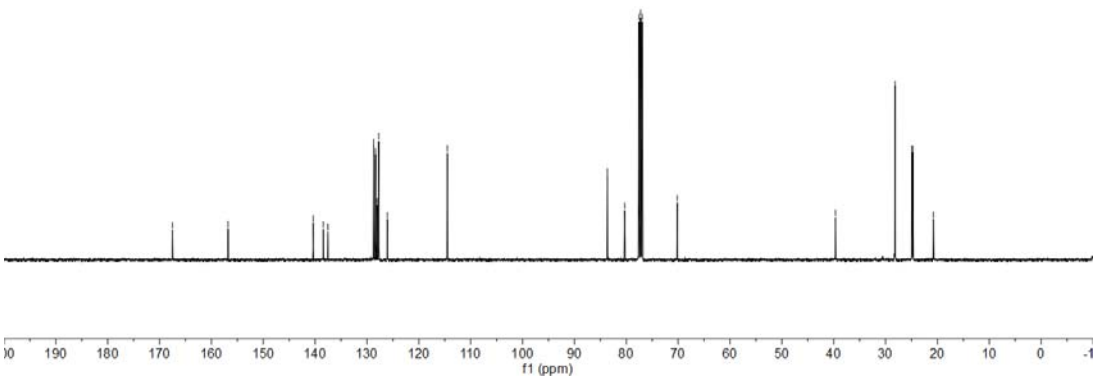
^{1}H NMR (400 MHz, $CDCl_3$)

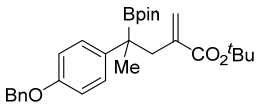




3ea

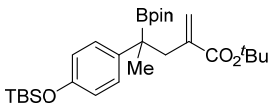
^{13}C NMR (100 MHz, $CDCl_3$)





3ea

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

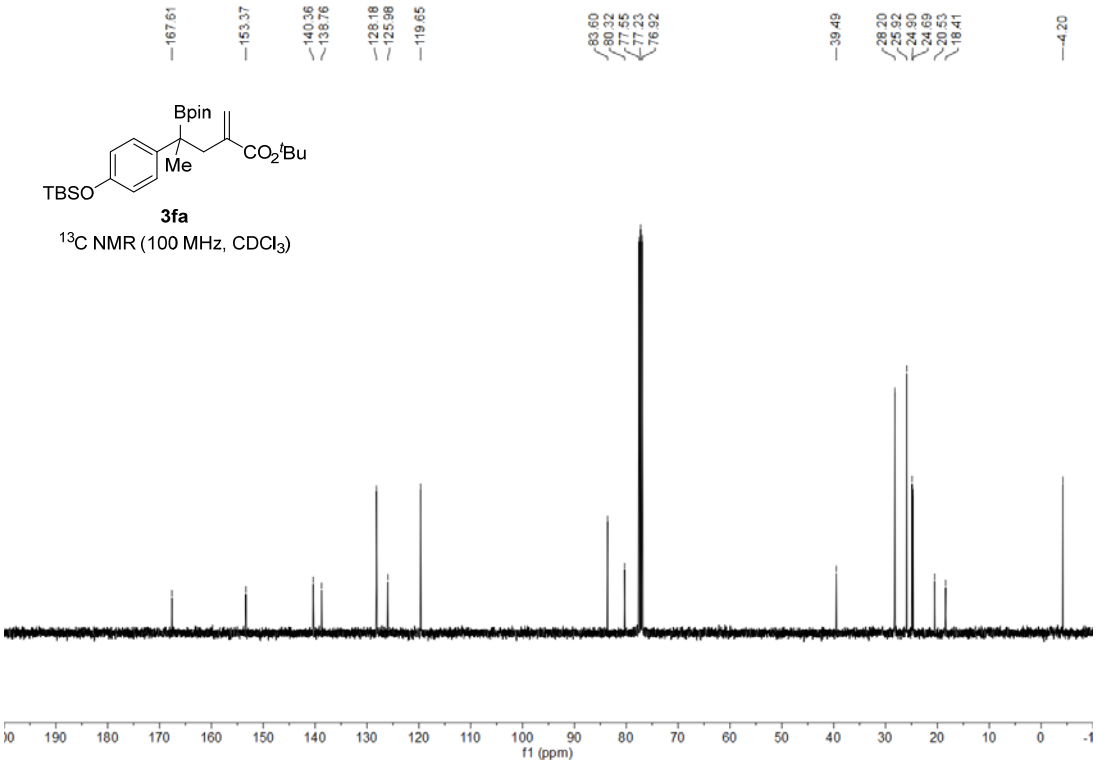


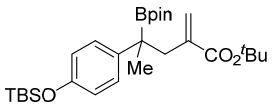
3fa

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

3fa

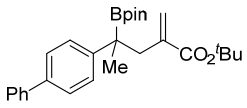
^{13}C NMR (100 MHz, $CDCl_3$)





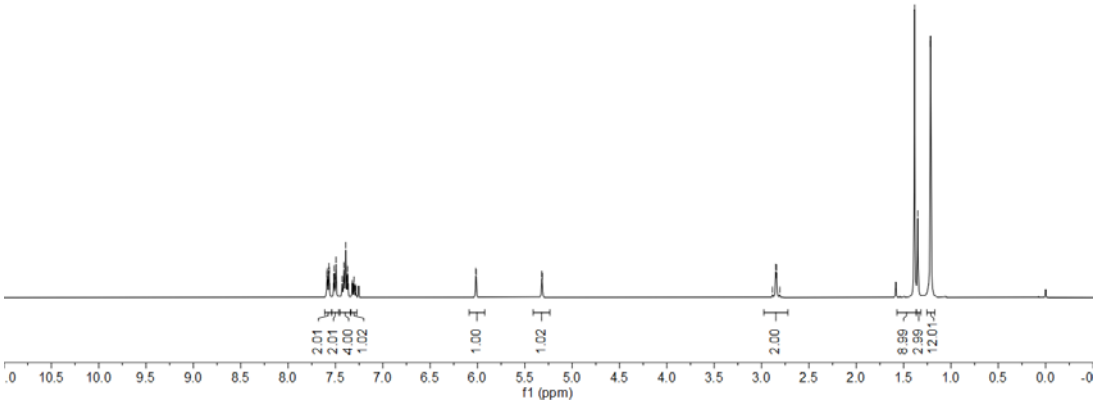
3fa

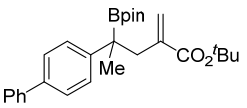
^{11}B NMR (128 MHz, $CDCl_3$)



3ga

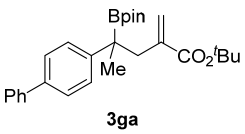
^{1}H NMR (400 MHz, $CDCl_3$)





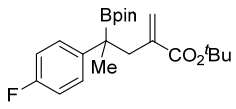
3ga

^{13}C NMR (100 MHz, $CDCl_3$)



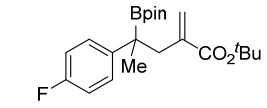
3ga

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



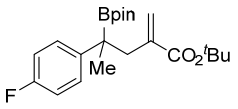
3ha

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



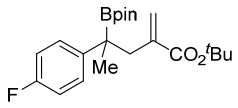
3ha

^{13}C NMR (100 MHz, $CDCl_3$)



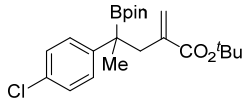
3ha

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



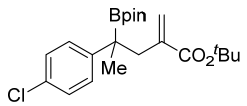
3ha

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



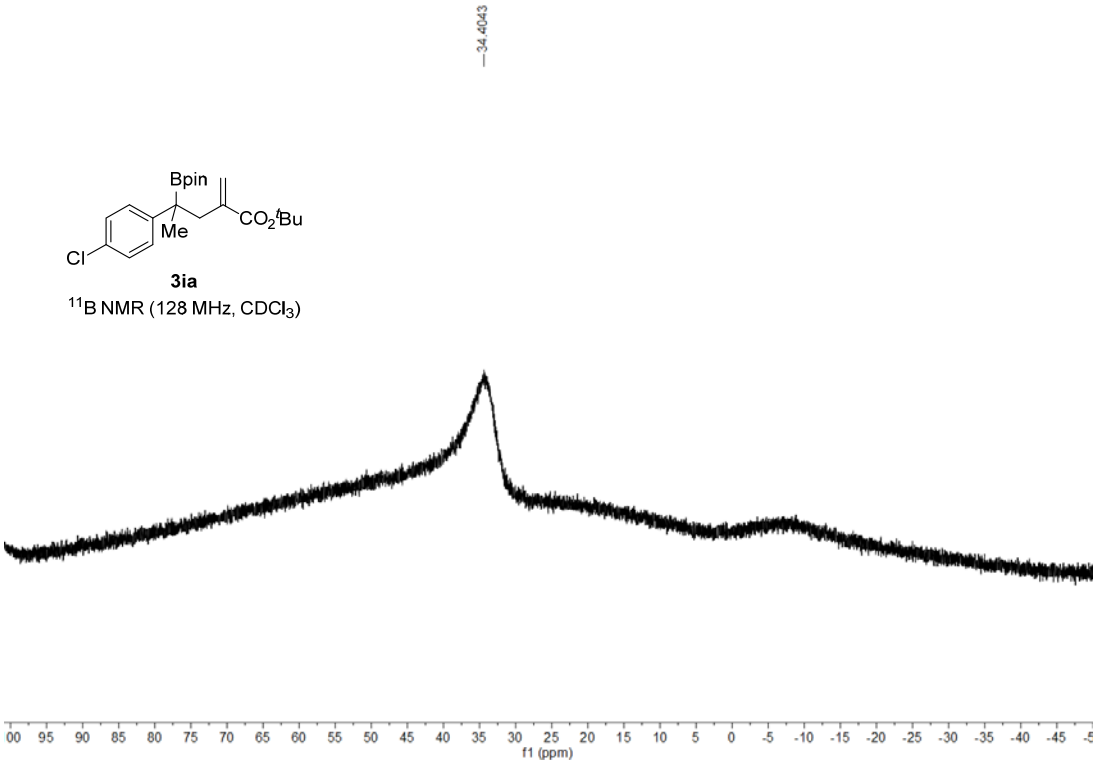
3ia

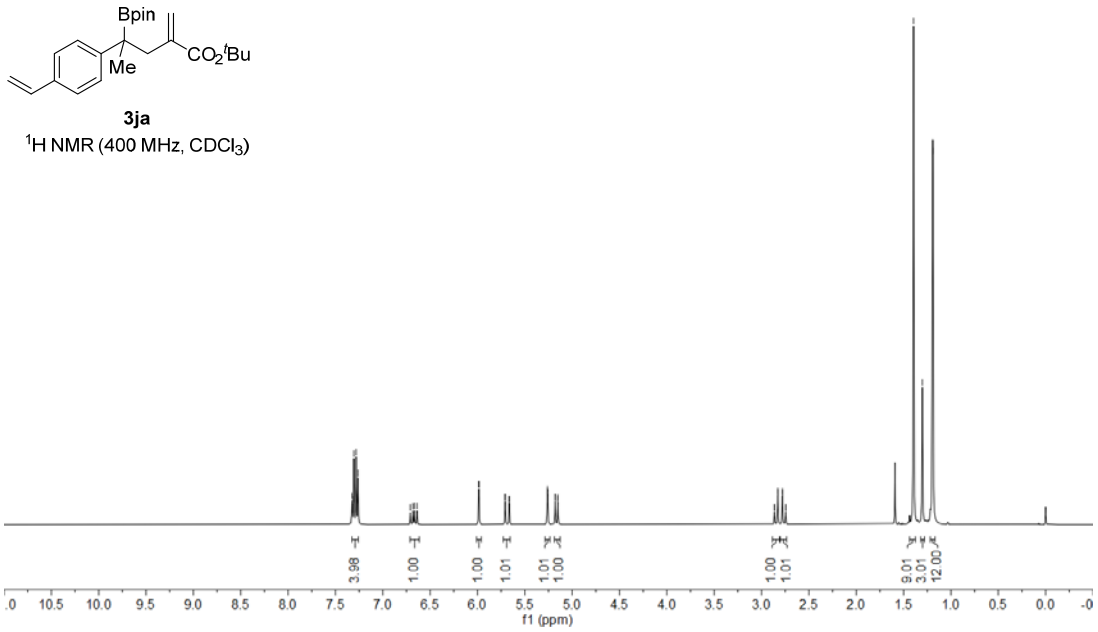
^{1}H NMR (400 MHz, $CDCl_3$)



3ia

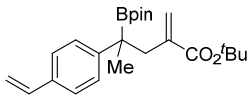
^{13}C NMR (100 MHz, $CDCl_3$)


34.4043
Bpin
Me
CO2tBu
Cl
3ia
11B NMR (128 MHz, CDCl3)
f1 (ppm)



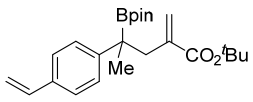
3ja

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



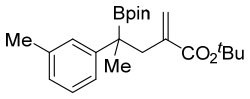
3ja

^{13}C NMR (100 MHz, $CDCl_3$)



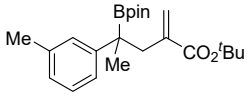
3ja

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



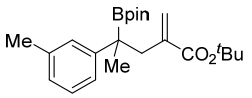
3la

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



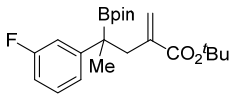
3la

^{13}C NMR (100 MHz, $CDCl_3$)



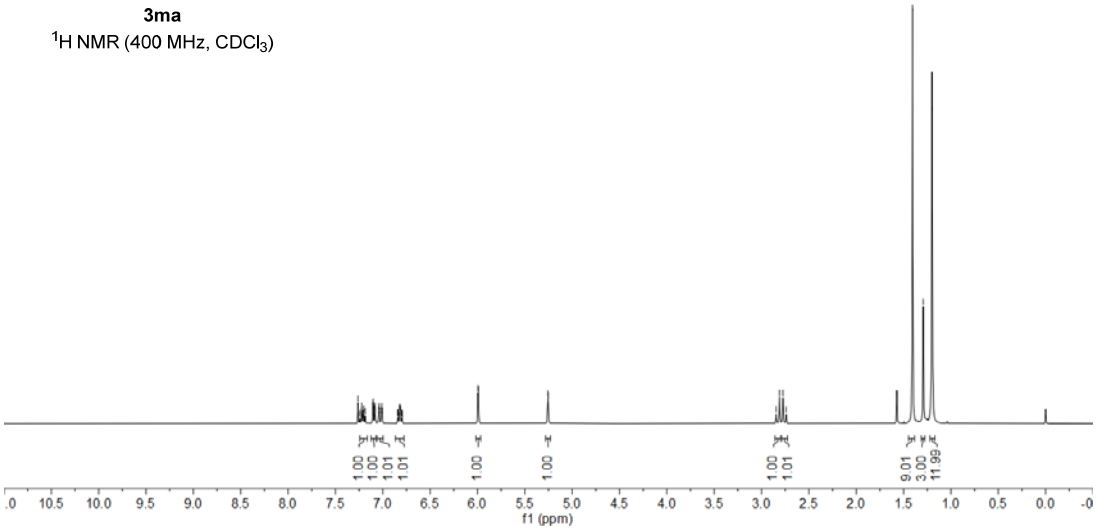
3la

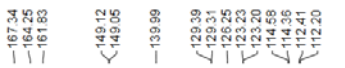
^{11}B NMR (128 MHz, $CDCl_3$)

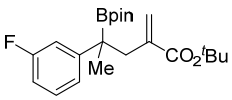


3ma

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

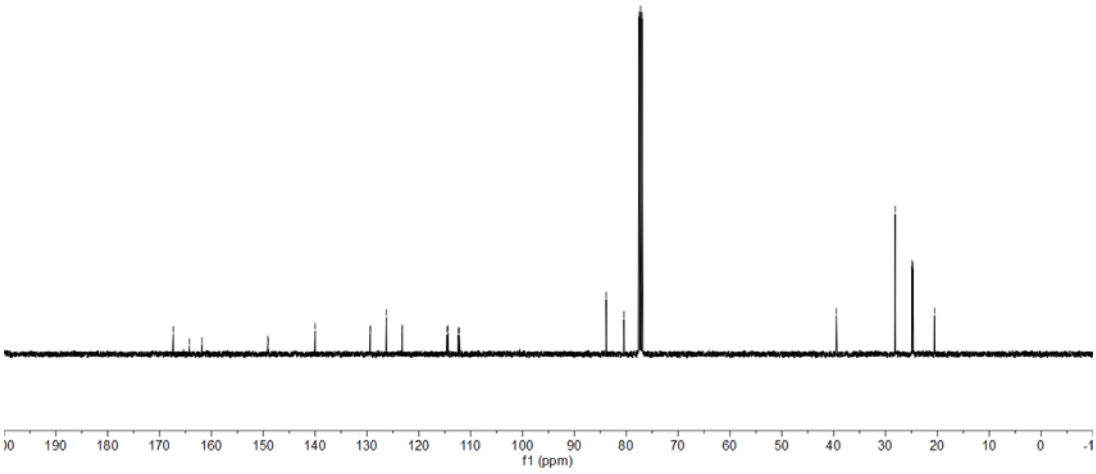


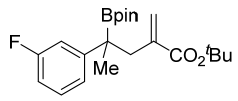




3ma

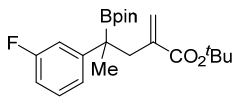
^{13}C NMR (100 MHz, $CDCl_3$)





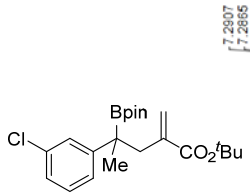
3ma

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



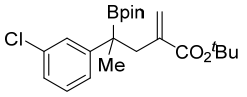
3ma

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



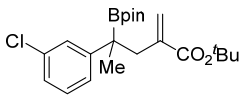
3na

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



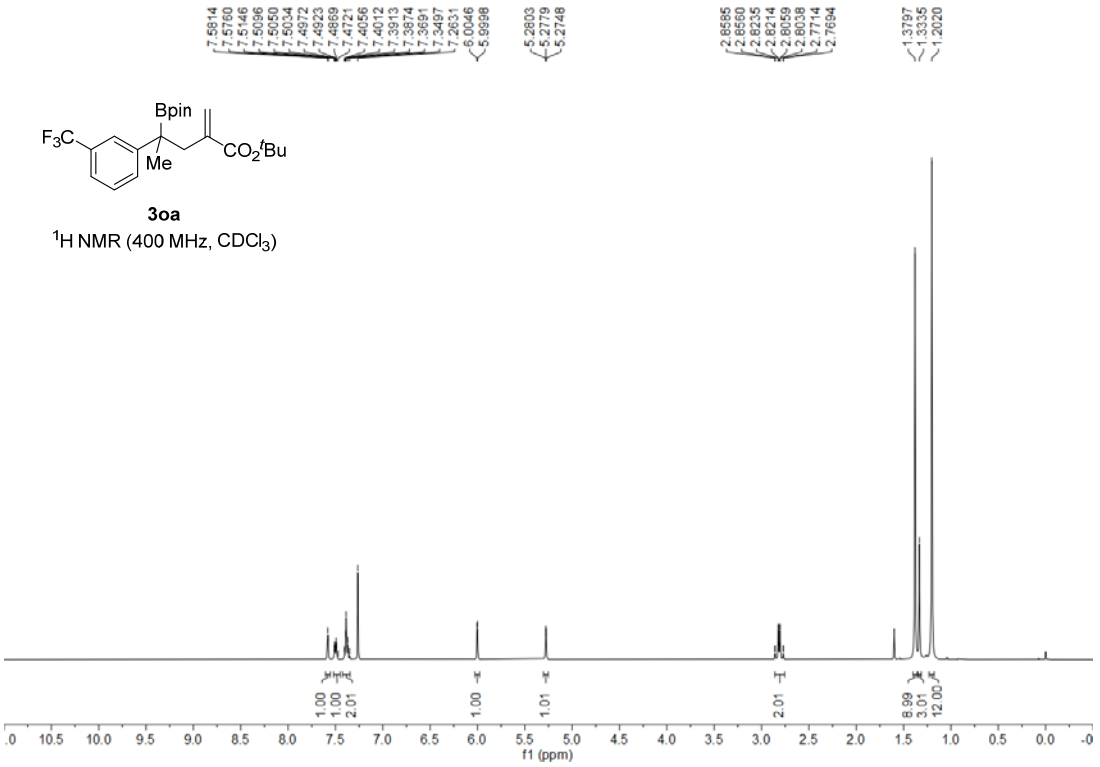
3na

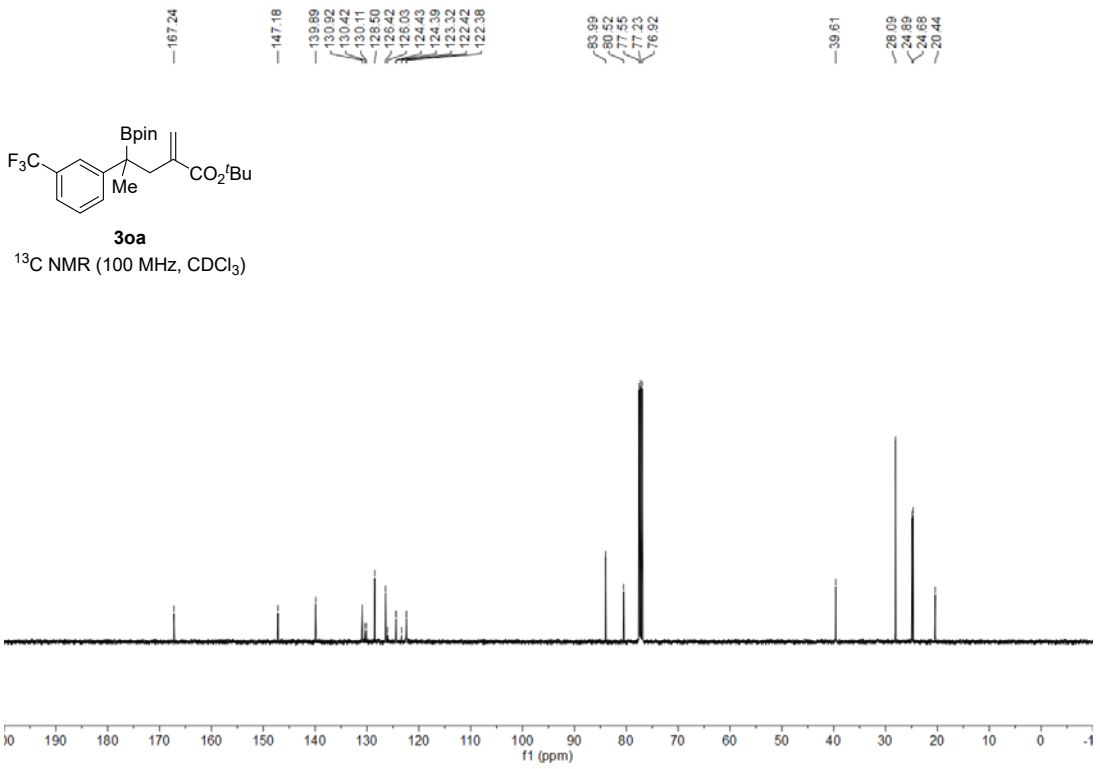
^{13}C NMR (100 MHz, $CDCl_3$)

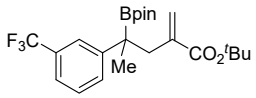


3na

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

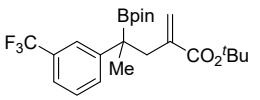

Bpin
F3C
Me
CO2tBu
3oa
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Bpin
F3C
Me
CO2tBu
3oa
13C NMR (100 MHz, CDCl3)
f1 (ppm)



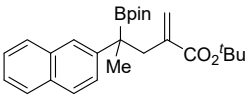
3oa

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



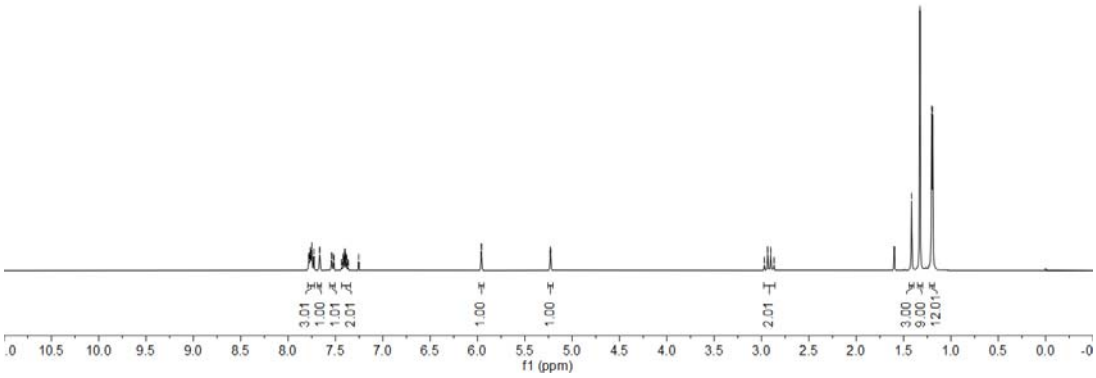
3oa

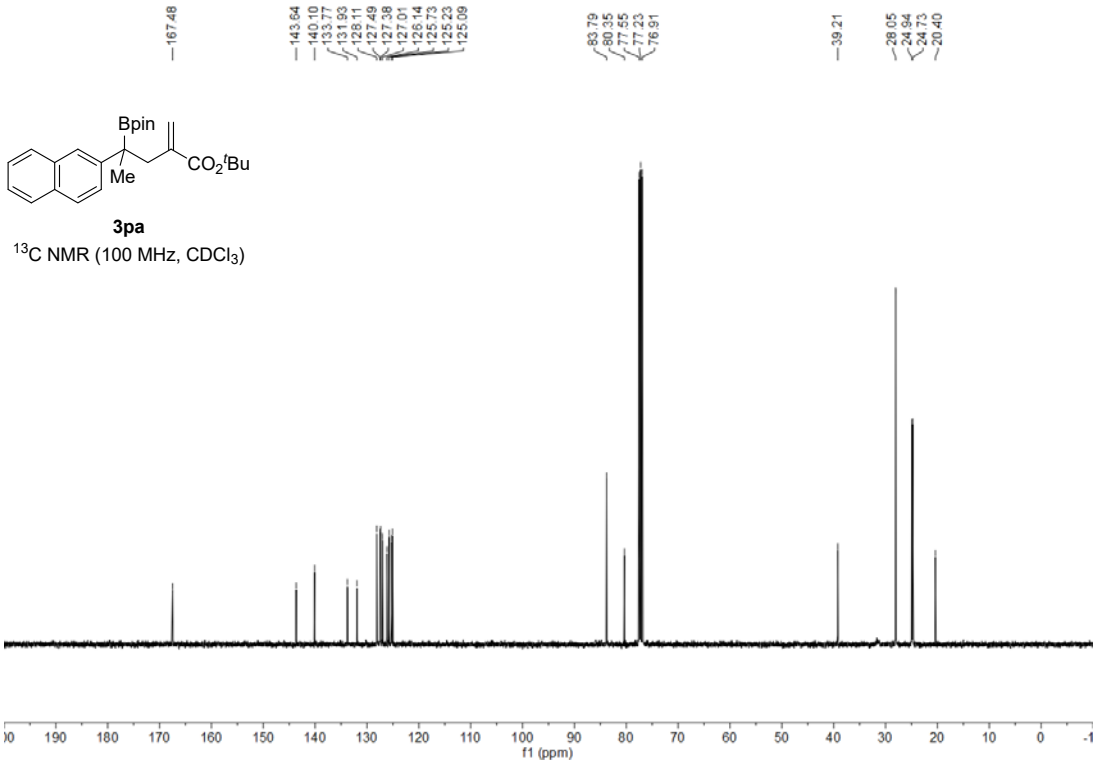
^{19}F NMR (376 MHz, $CDCl_3$)



3pa

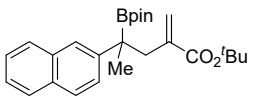
^{1}H NMR (400 MHz, $CDCl_3$)





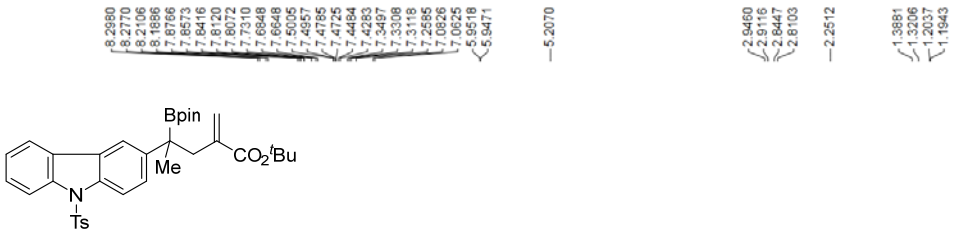
3pa

^{13}C NMR (100 MHz, $CDCl_3$)



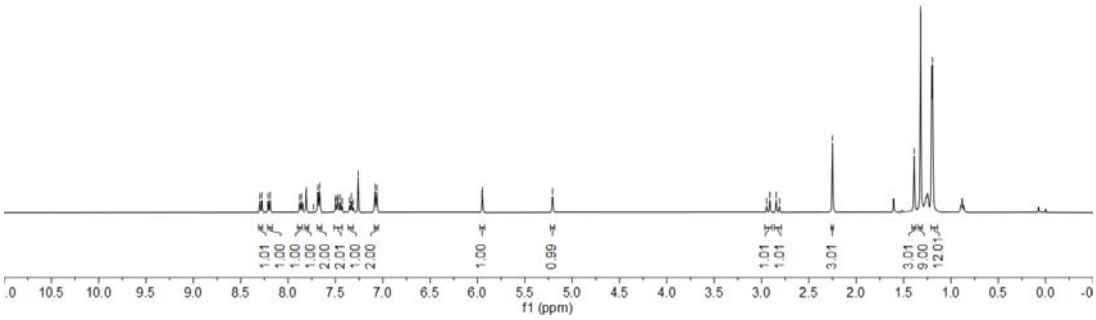
3pa

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



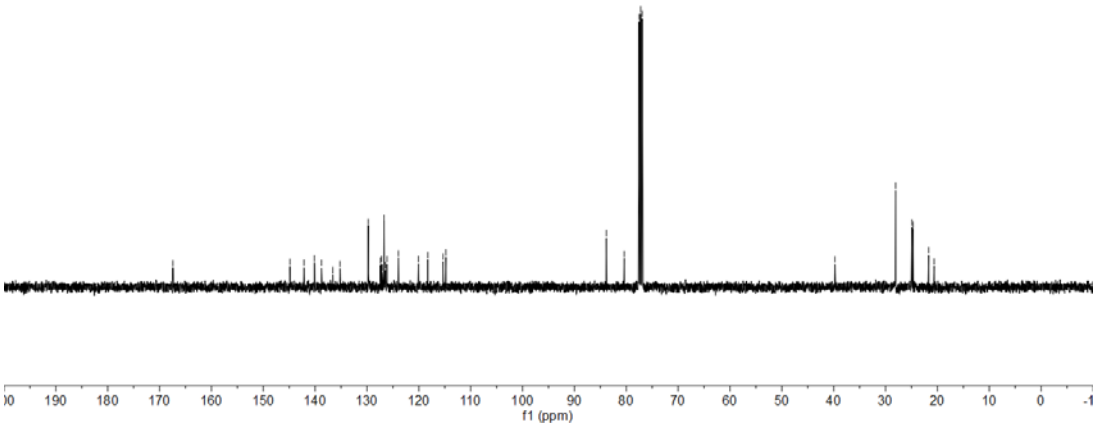
3qa

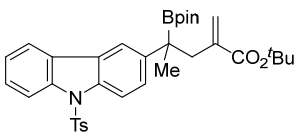
^{1}H NMR (400 MHz, $CDCl_3$)



3qa

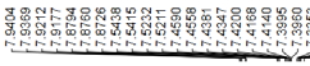
^{13}C NMR (100 MHz, $CDCl_3$)

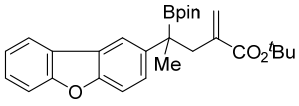




3qa

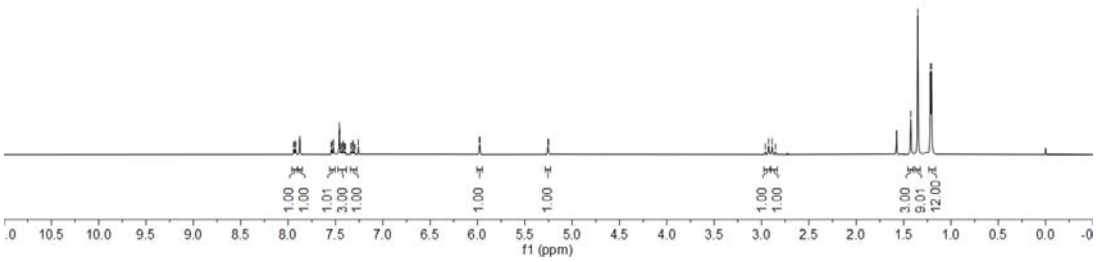
^{11}B NMR (128 MHz, $CDCl_3$)

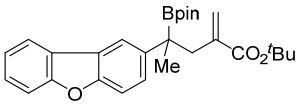




3ra

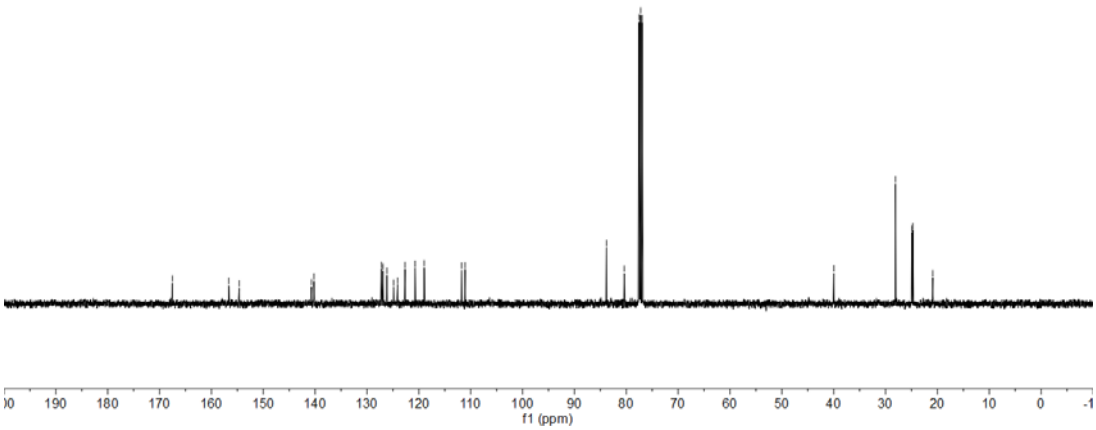
^{1}H NMR (400 MHz, $CDCl_3$)

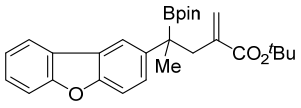




3ra

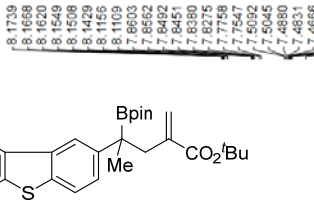
^{13}C NMR (100 MHz, $CDCl_3$)





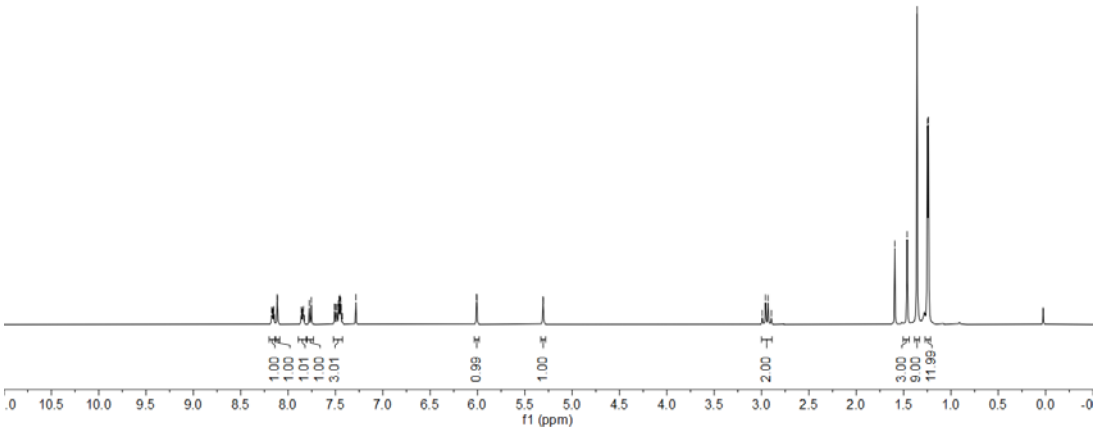
3ra

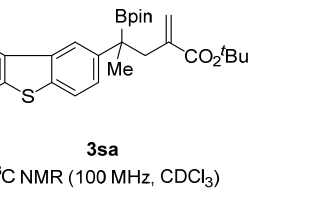
^{11}B NMR (128 MHz, $CDCl_3$)



3sa

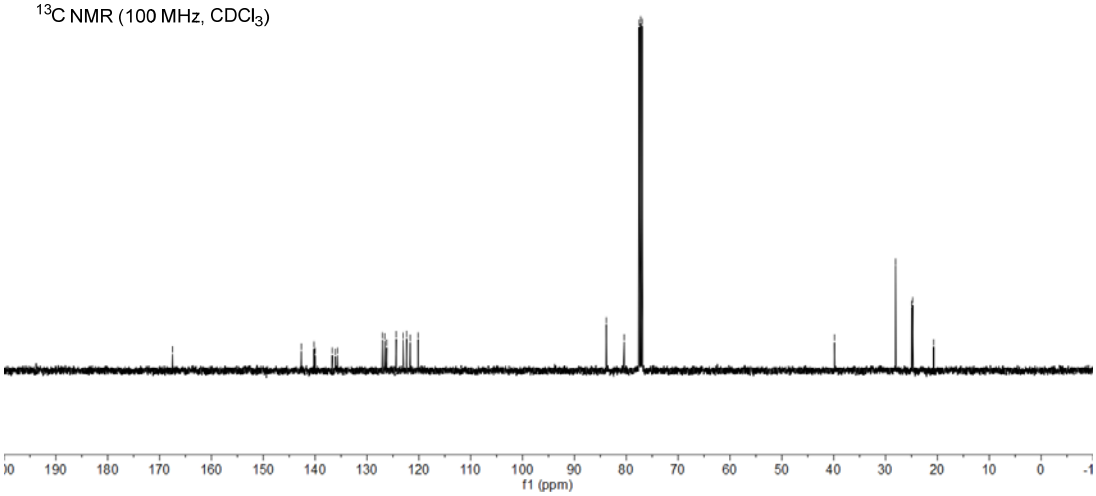
^{1}H NMR (400 MHz, $CDCl_3$)

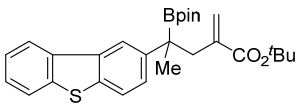




3sa

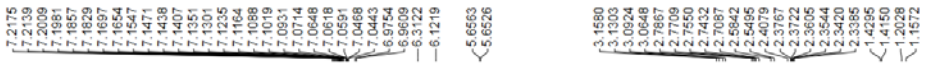
^{13}C NMR (100 MHz, $CDCl_3$)

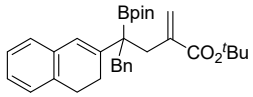




3sa

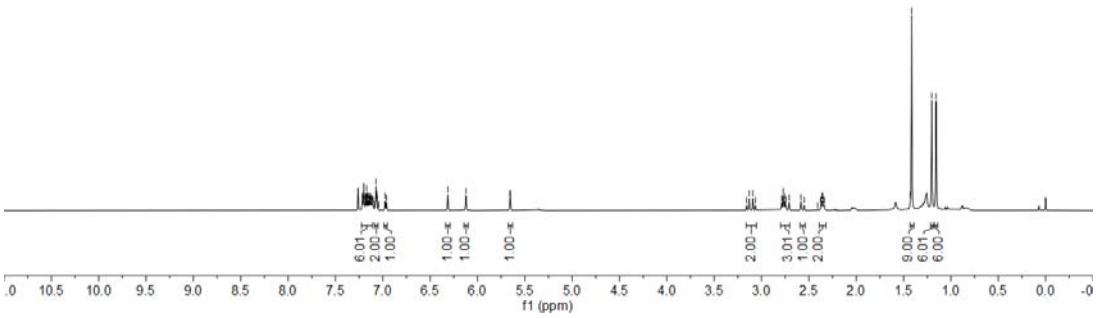
^{11}B NMR (128 MHz, $CDCl_3$)





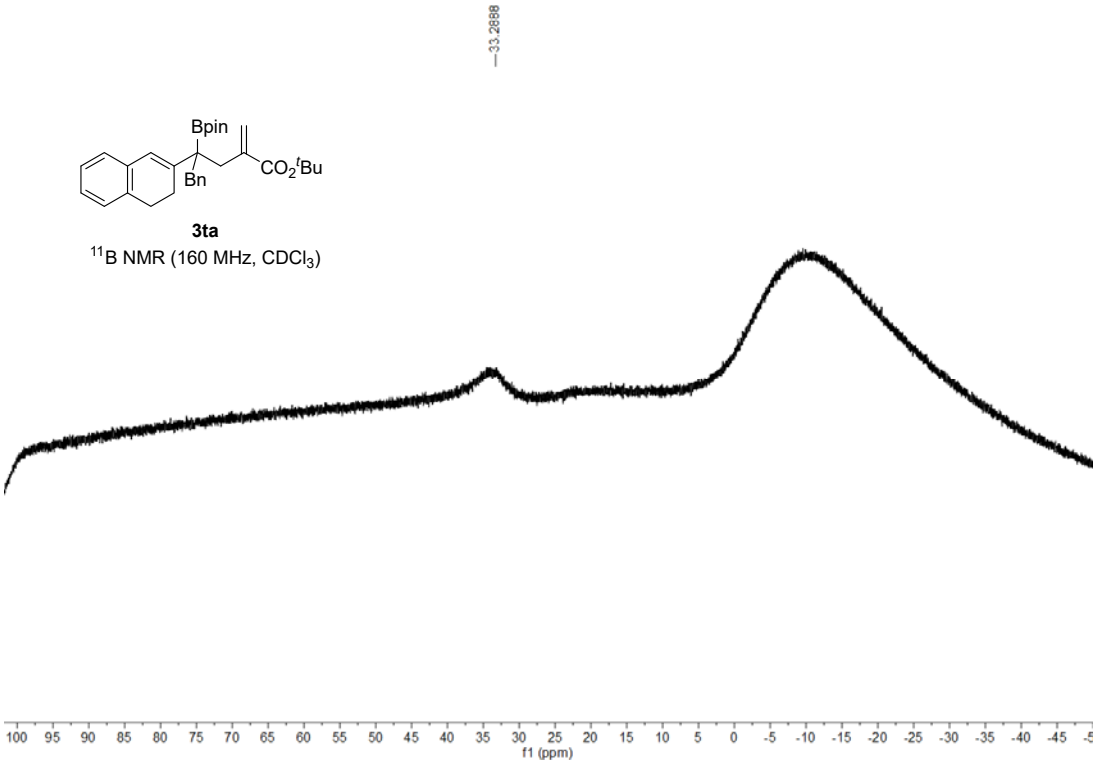
3ta

^{1}H NMR (500 MHz, $CDCl_3$)



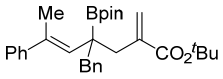
3ta

^{13}C NMR (125 MHz, $CDCl_3$)



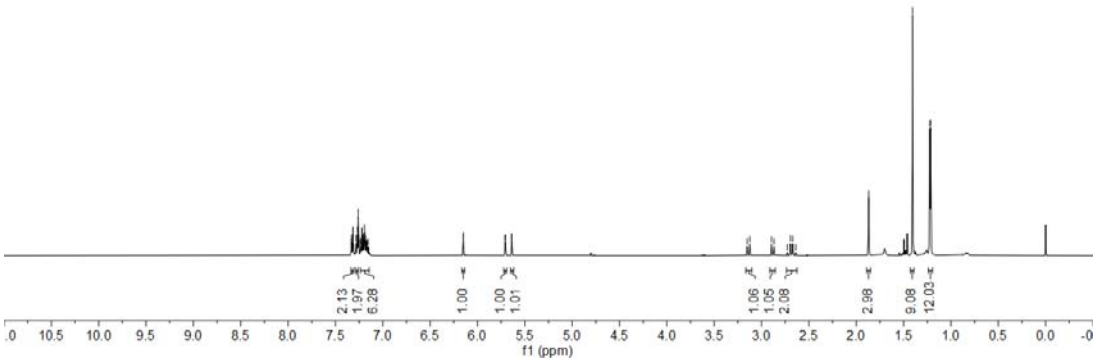
3ta

^{11}B NMR (160 MHz, $CDCl_3$)



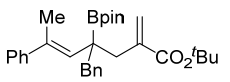
3ua

^{1}H NMR (500 MHz, $CDCl_3$)



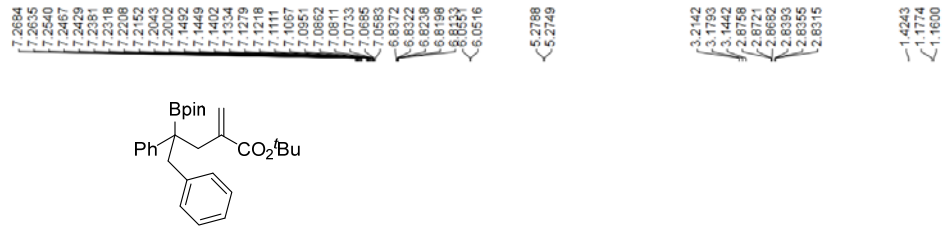
3ua

^{13}C NMR (125 MHz, $CDCl_3$)



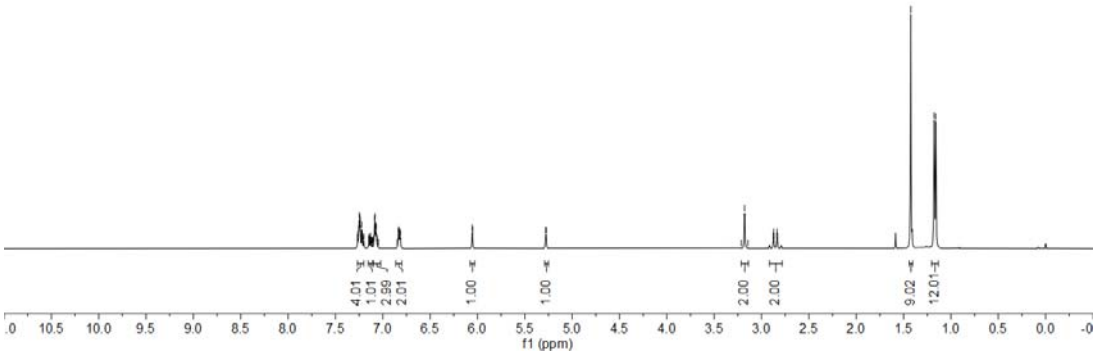
3ua

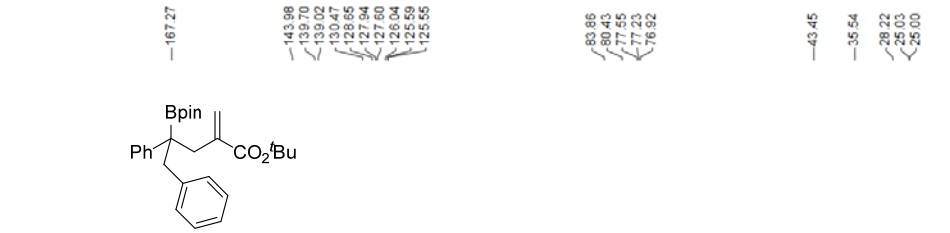
^{11}B NMR (160 MHz, $CDCl_3$)



3va

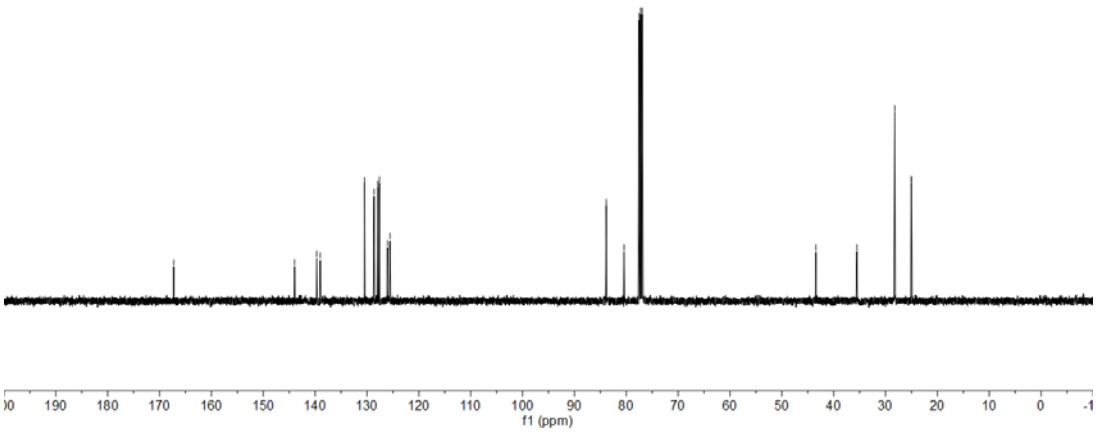
^{1}H NMR (400 MHz, $CDCl_3$)

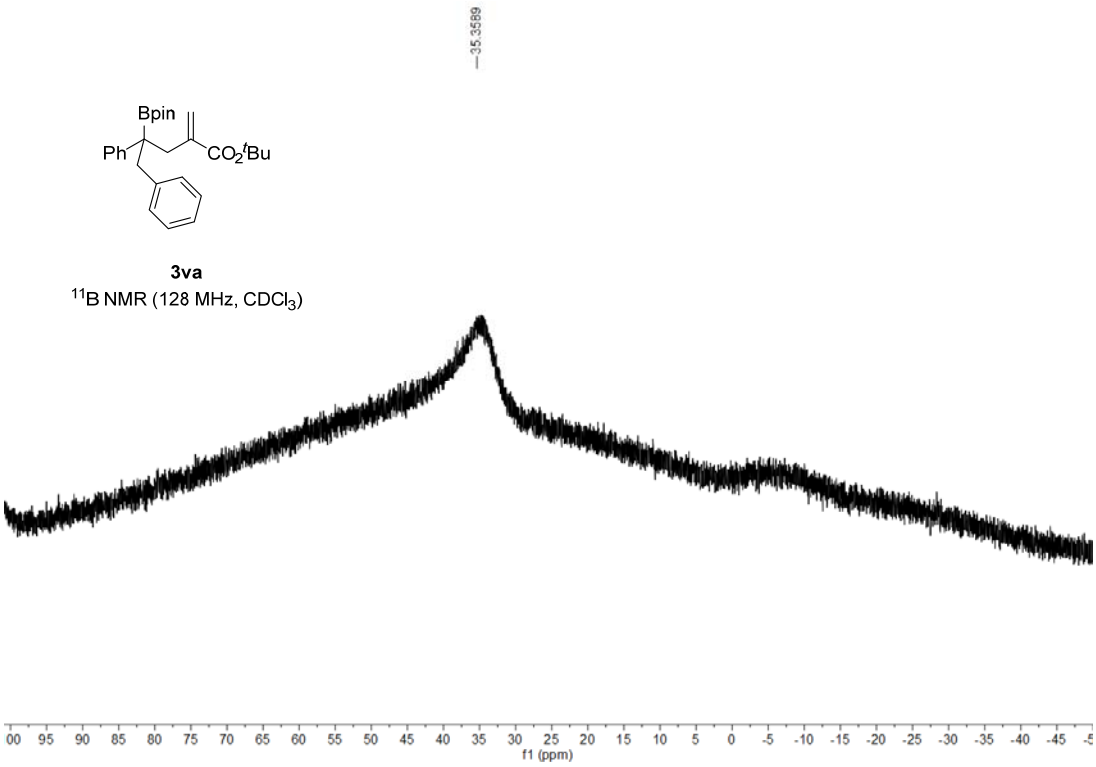




3va

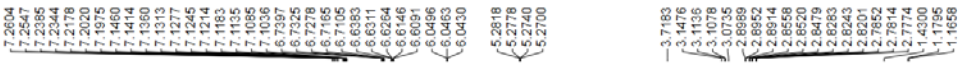
^{13}C NMR (100 MHz, $CDCl_3$)

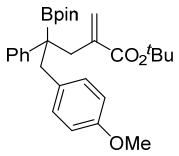




3va

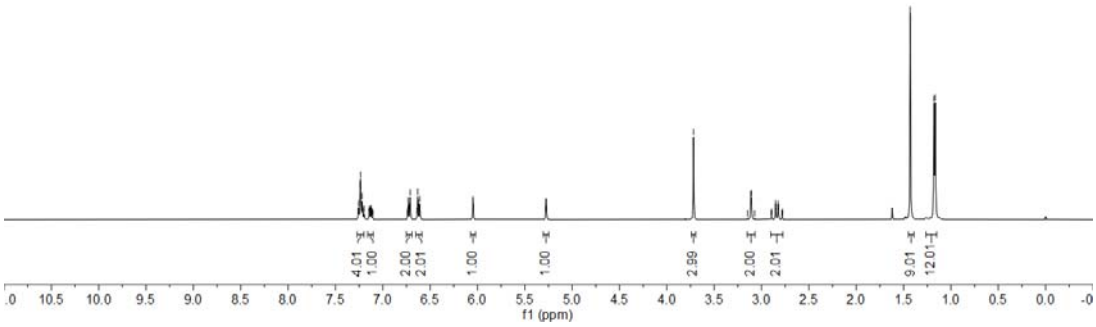
^{11}B NMR (128 MHz, $CDCl_3$)

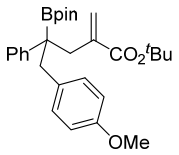




3wa

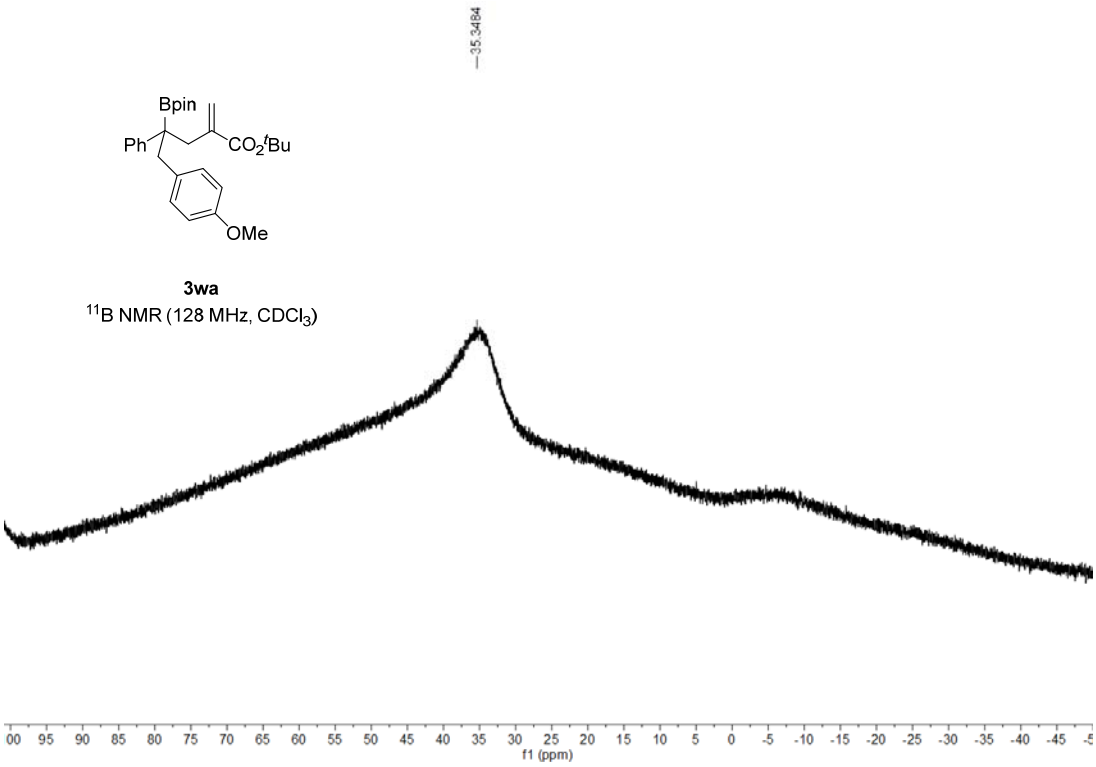
^{1}H NMR (400 MHz, $CDCl_3$)





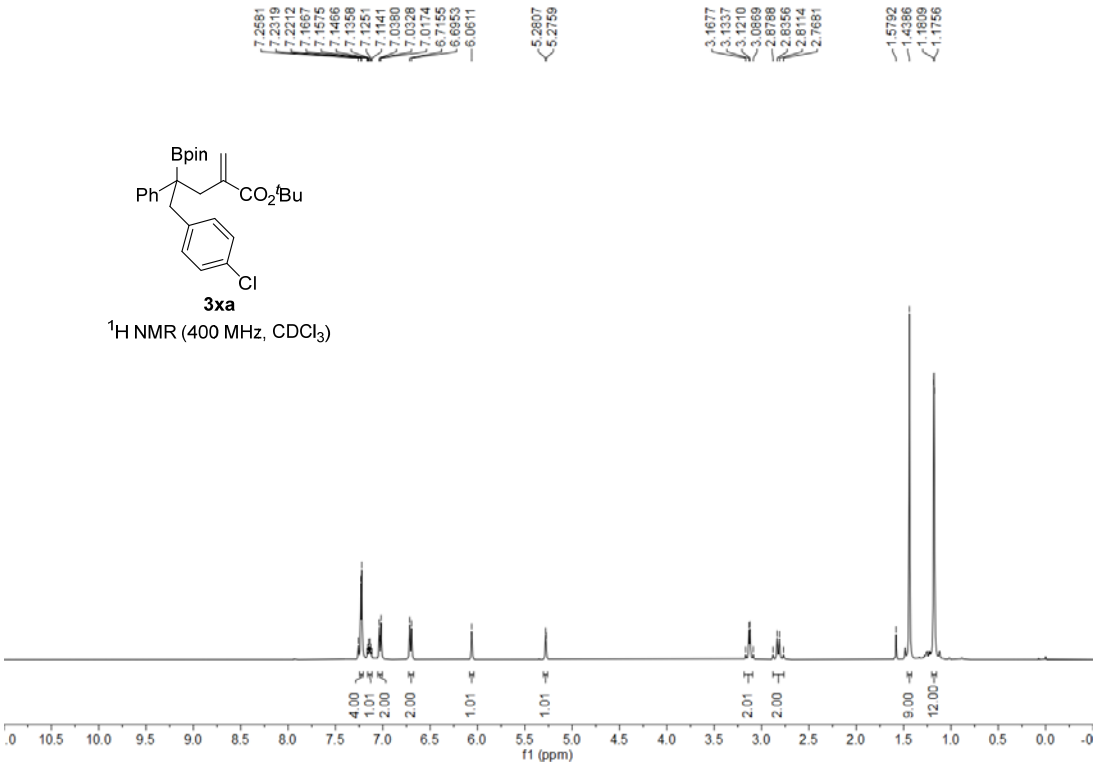
3wa

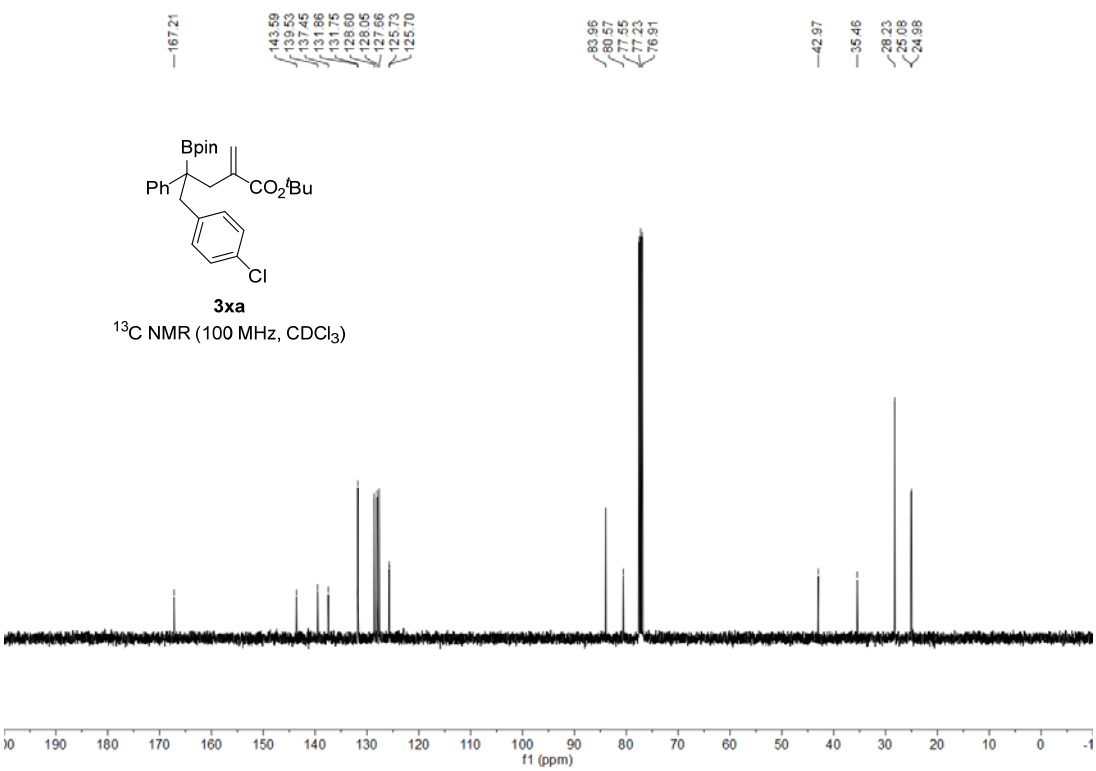
^{13}C NMR (100 MHz, $CDCl_3$)

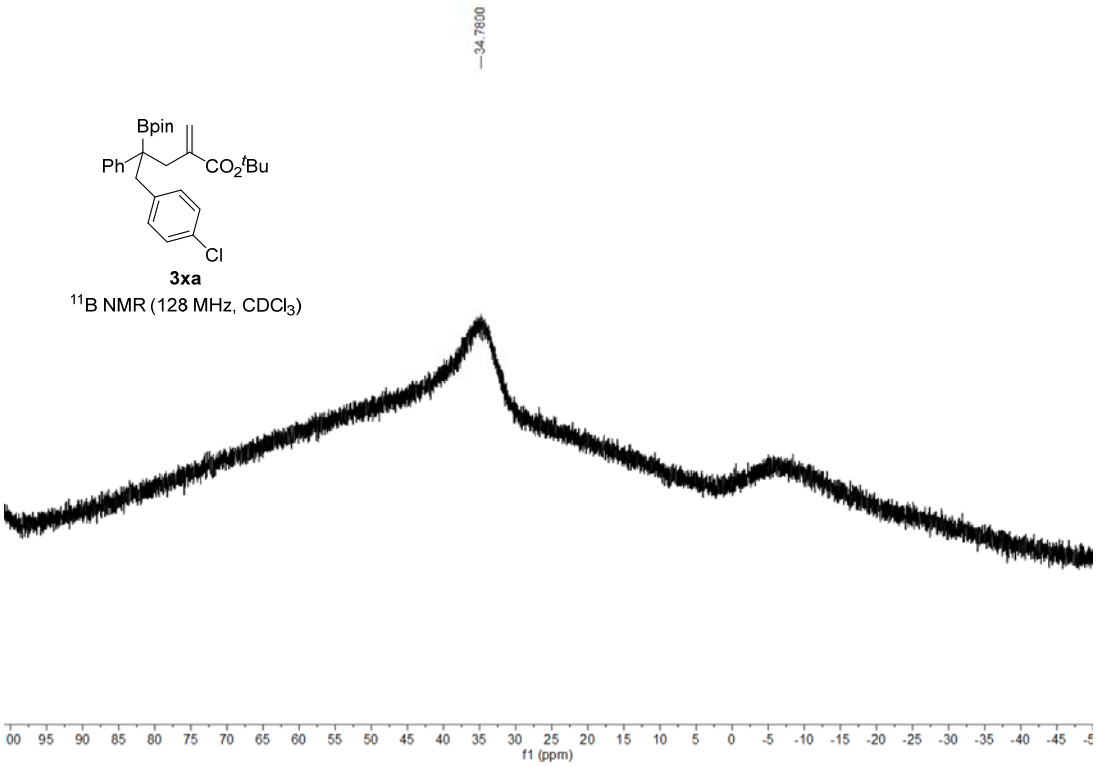


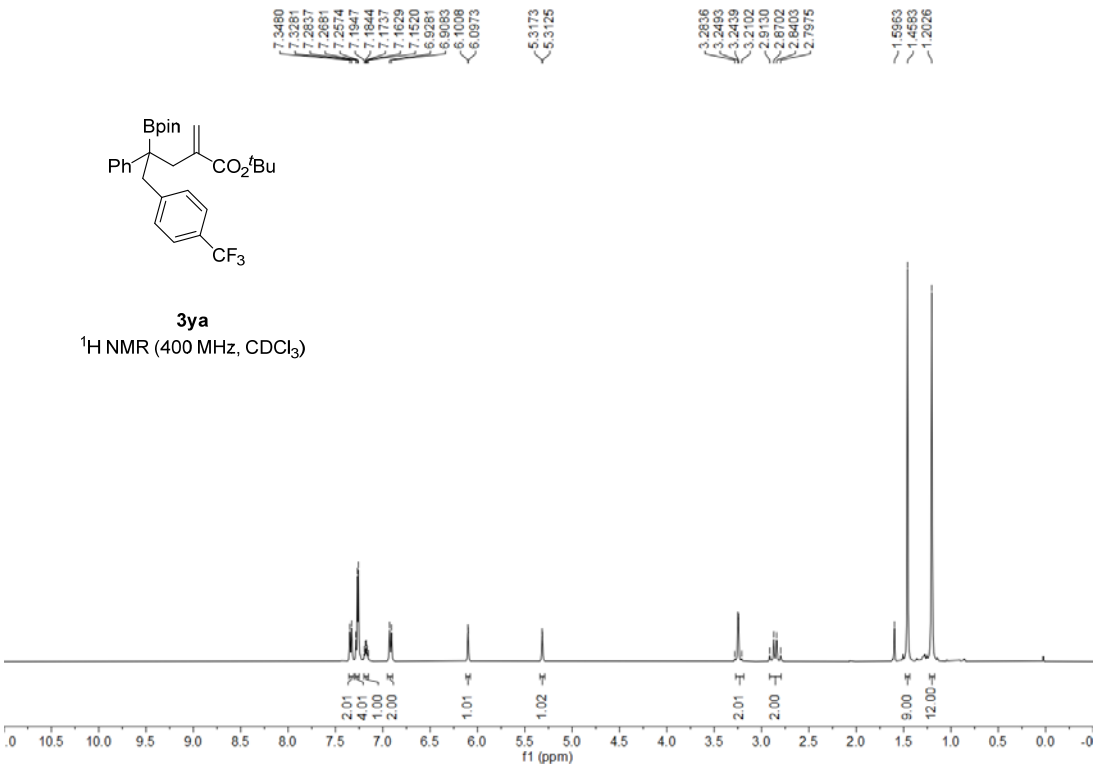
3wa

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


Bpin
Ph
CO2tBu
Cl
3xa
1H NMR (400 MHz, CDCl3)
f1 (ppm)

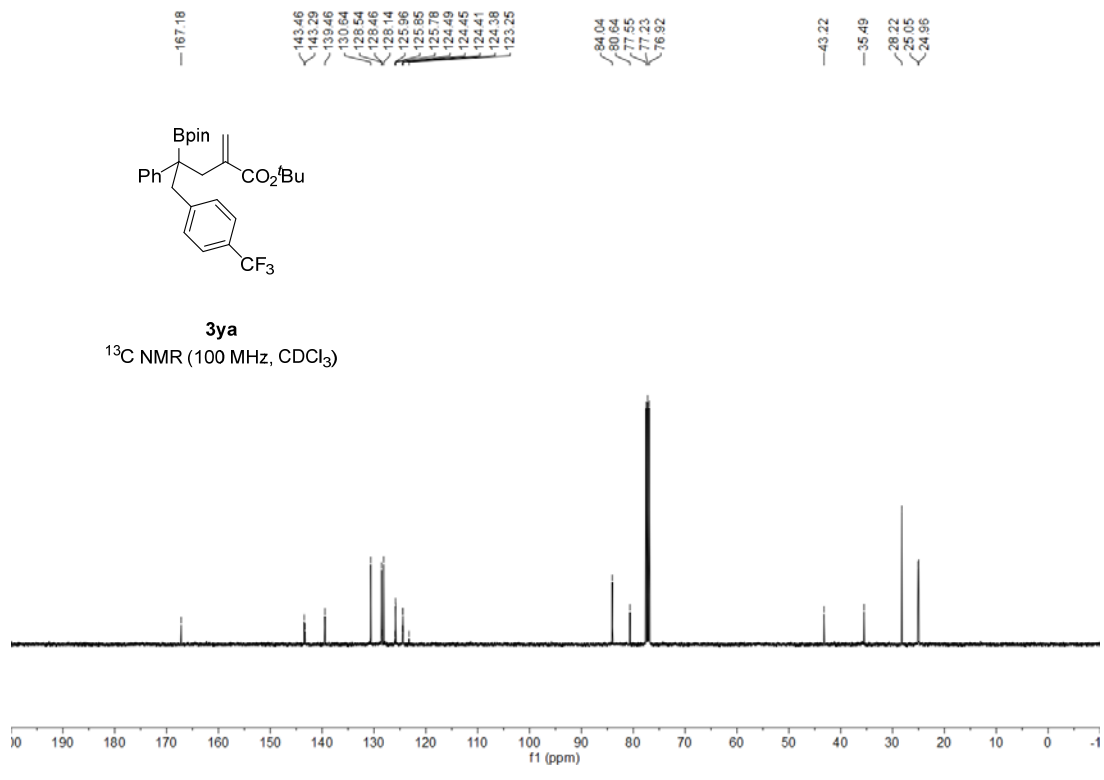

Bpin
Ph
CO2tBu
Cl
3xa
13C NMR (100 MHz, CDCl3)
f1 (ppm)


34.7800
Bpin
Ph
CO2tBu
Cl
3xa
11B NMR (128 MHz, CDCl3)
f1 (ppm)



3ya

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



3ya

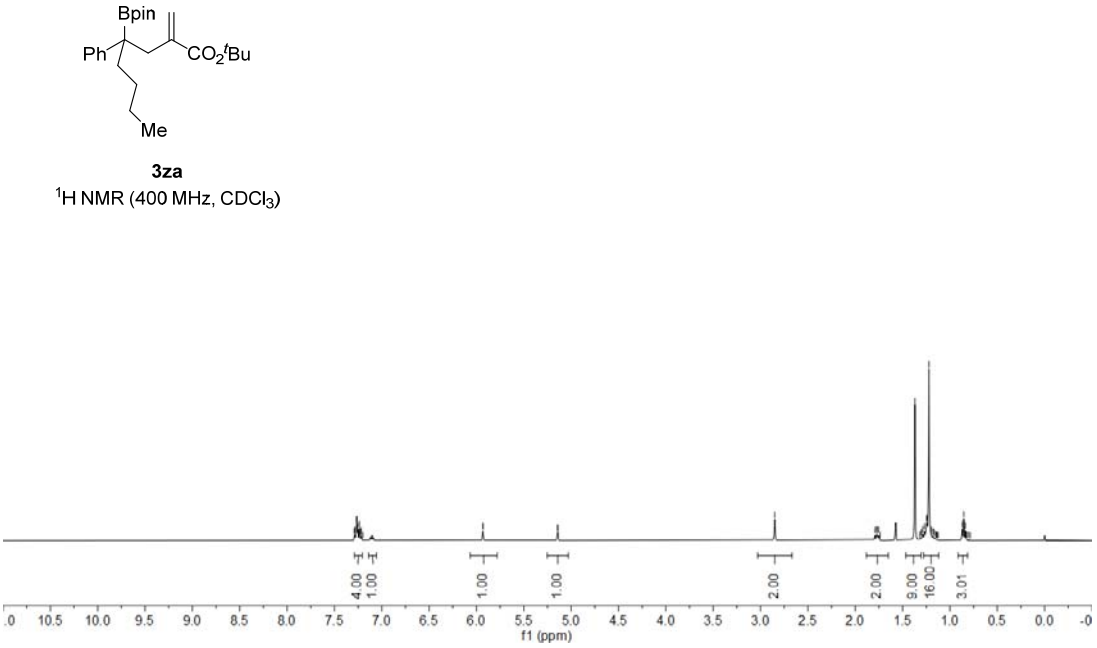
^{13}C NMR (100 MHz, $CDCl_3$)

3ya

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

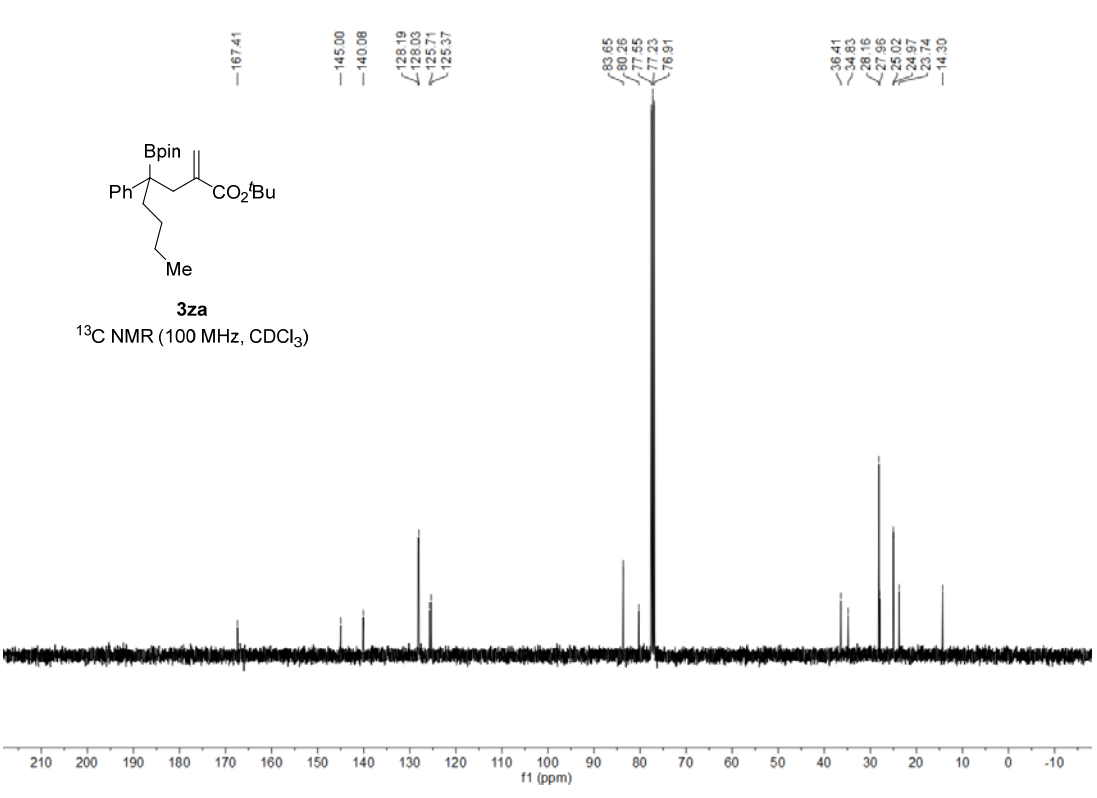
3ya

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



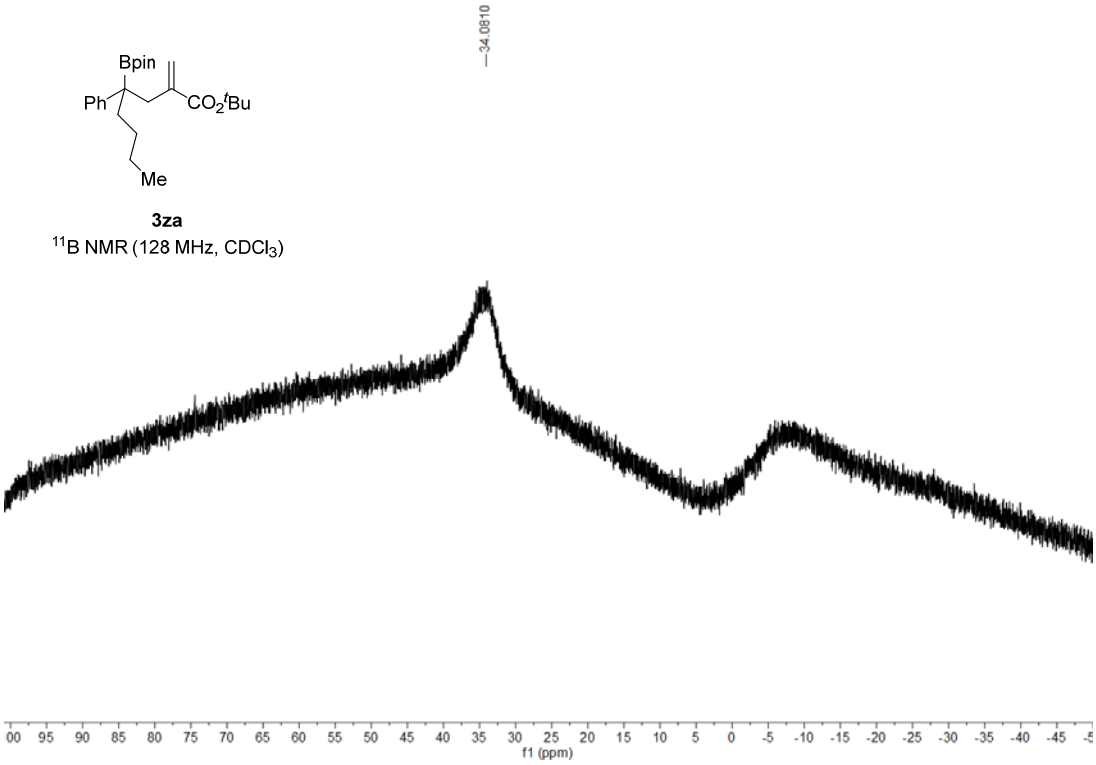
3za

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



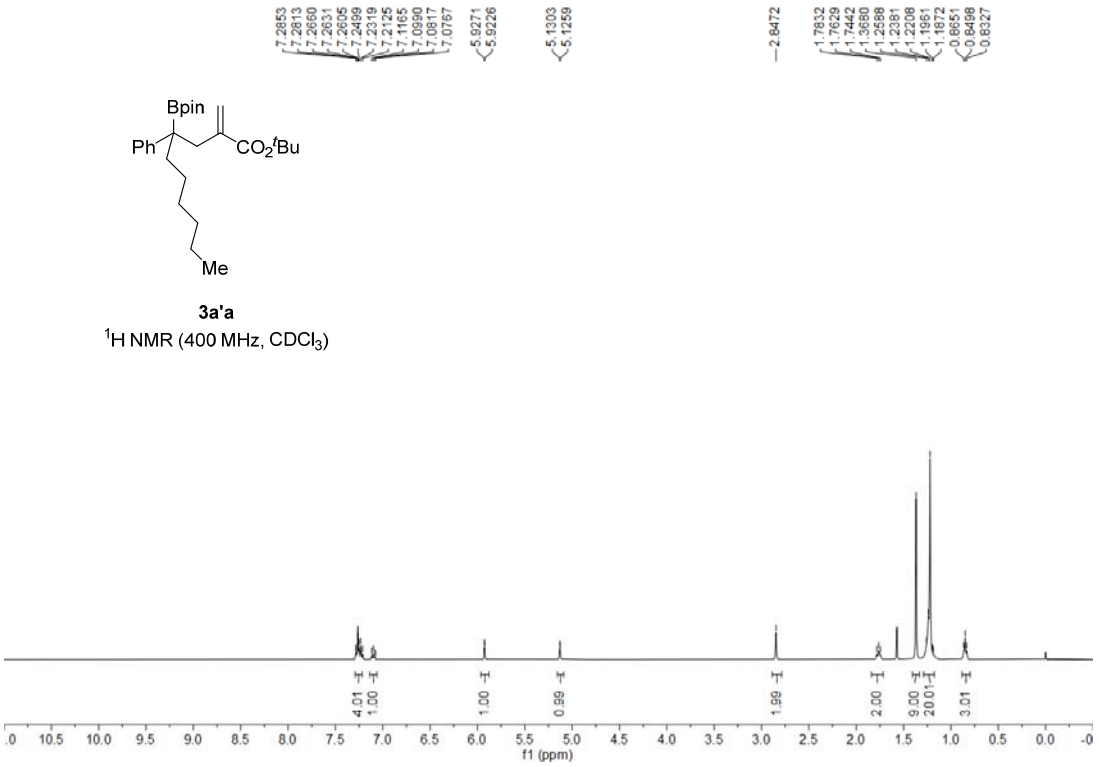
3za

^{13}C NMR (100 MHz, $CDCl_3$)



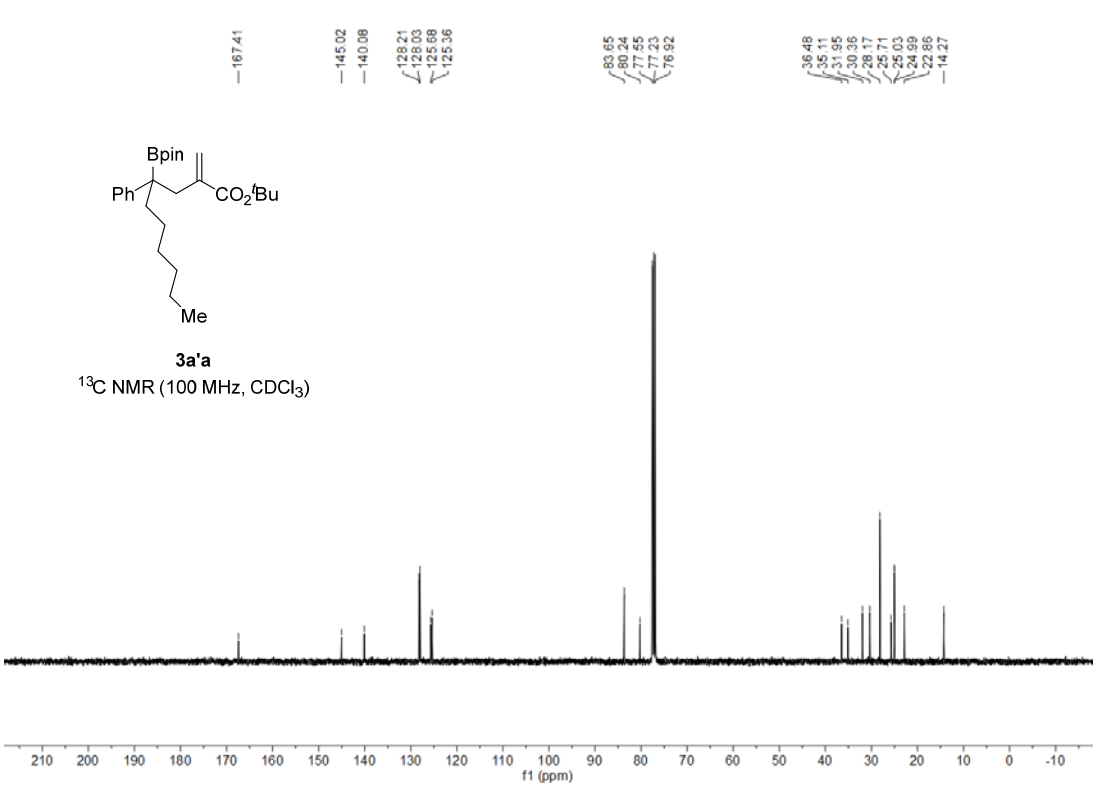
3za

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



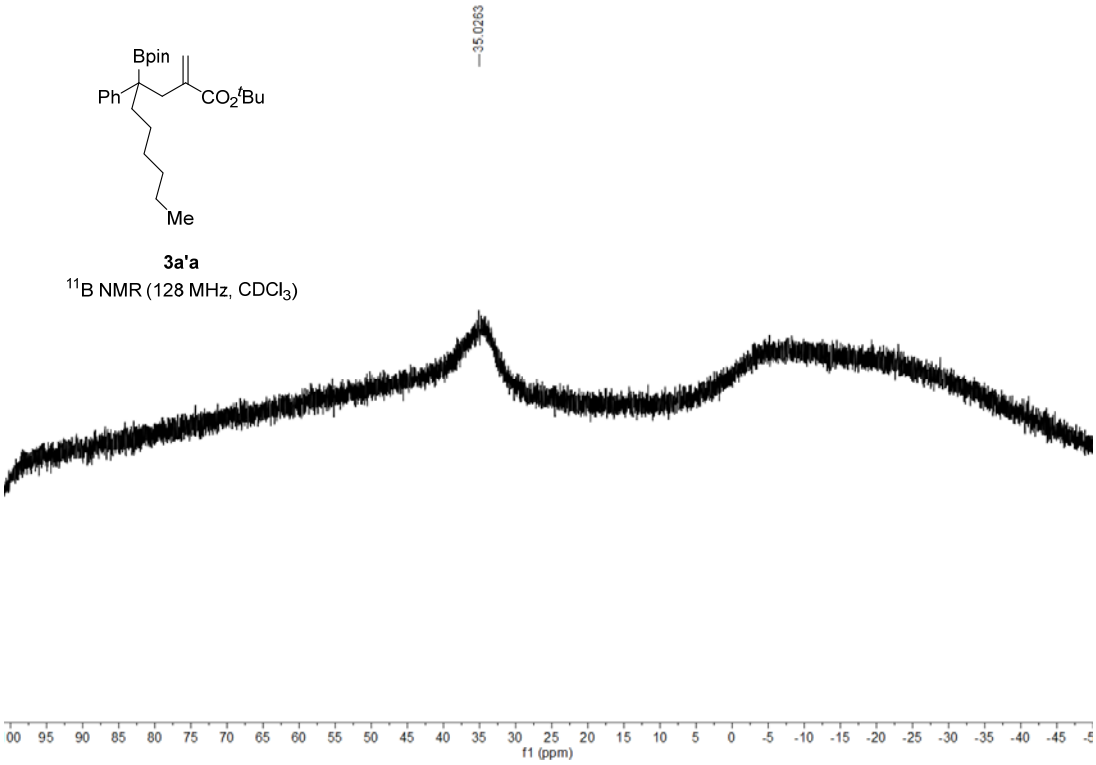
3a'a

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



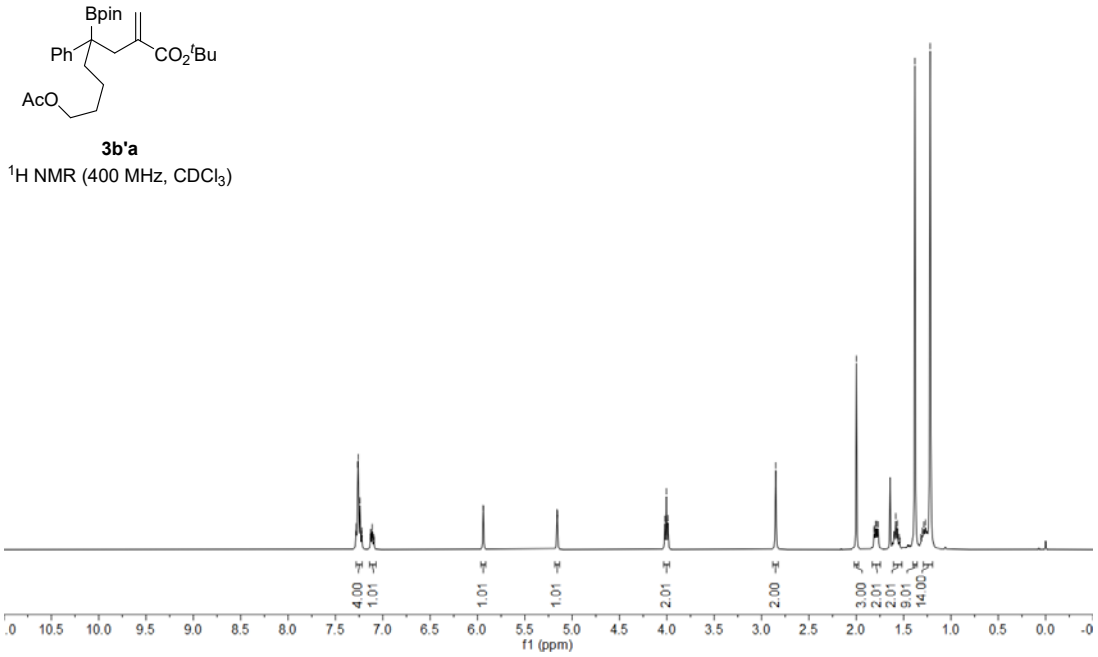
3a'a

^{13}C NMR (100 MHz, $CDCl_3$)



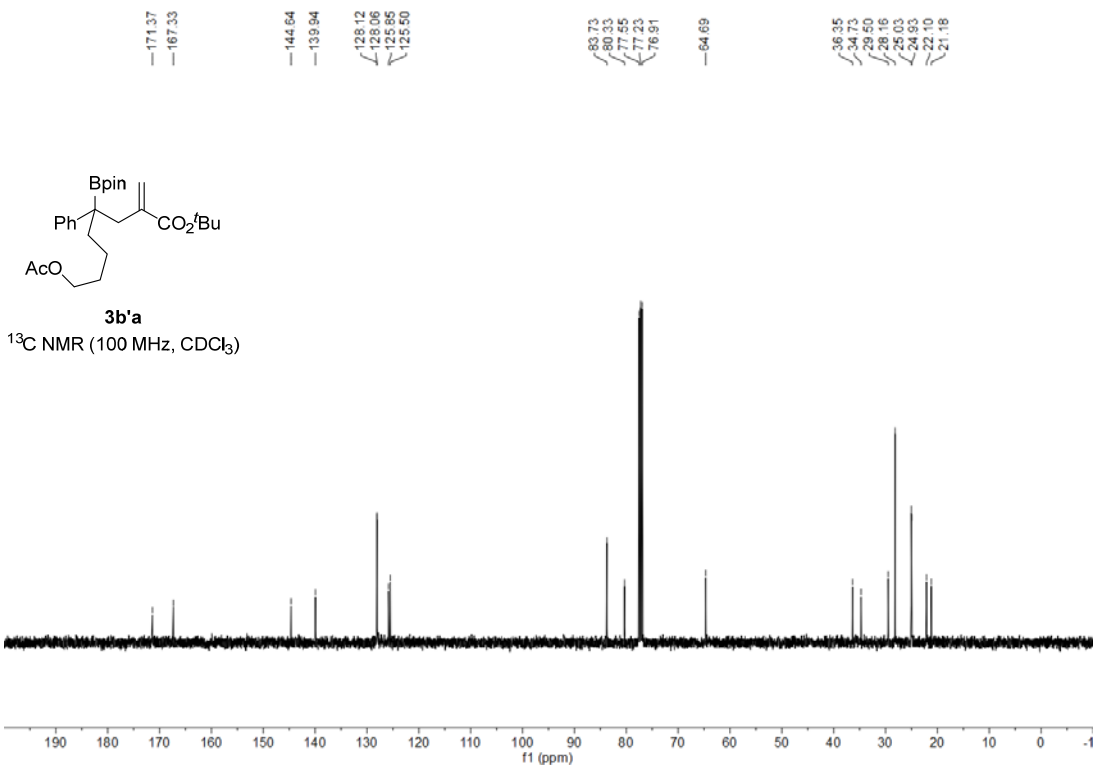
3a'a

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



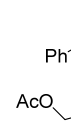
3b'a

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



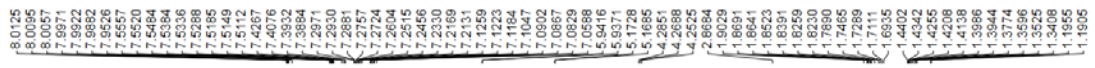
3b'a

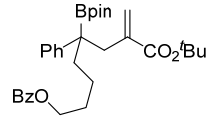
^{13}C NMR (100 MHz, $CDCl_3$)



3b'a

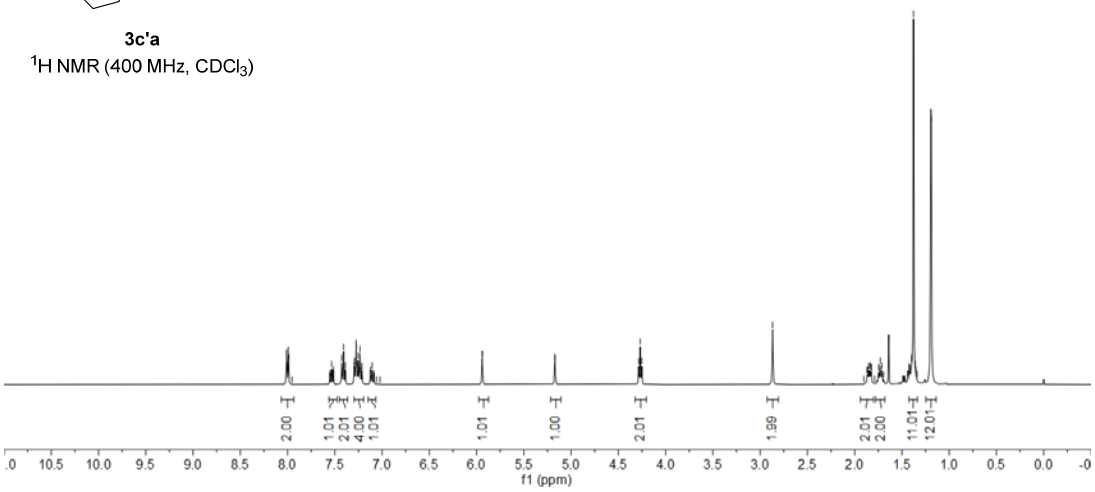
^{11}B NMR (128 MHz, $CDCl_3$)

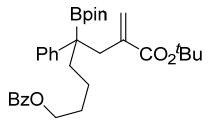




3c'a

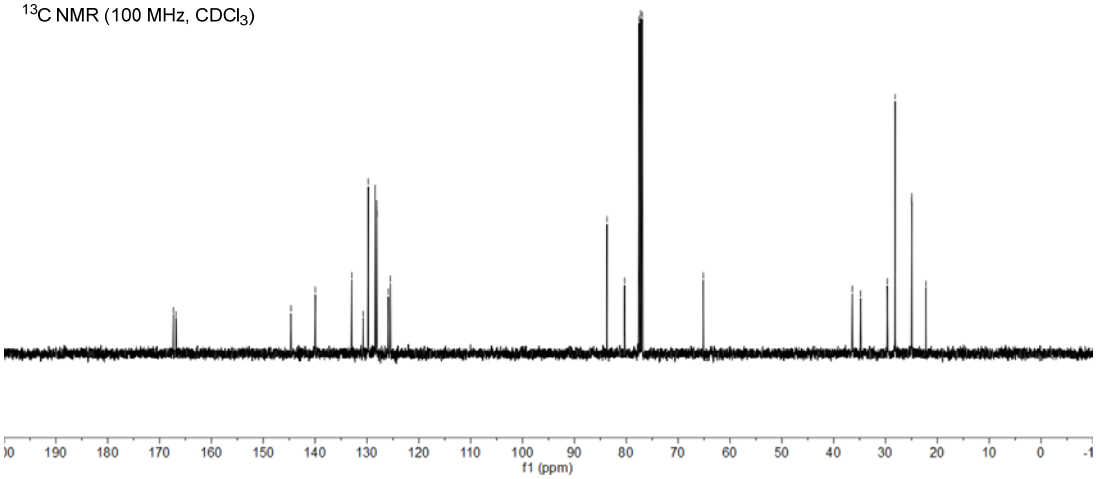
^{1}H NMR (400 MHz, $CDCl_3$)

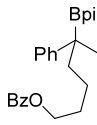




3c'a

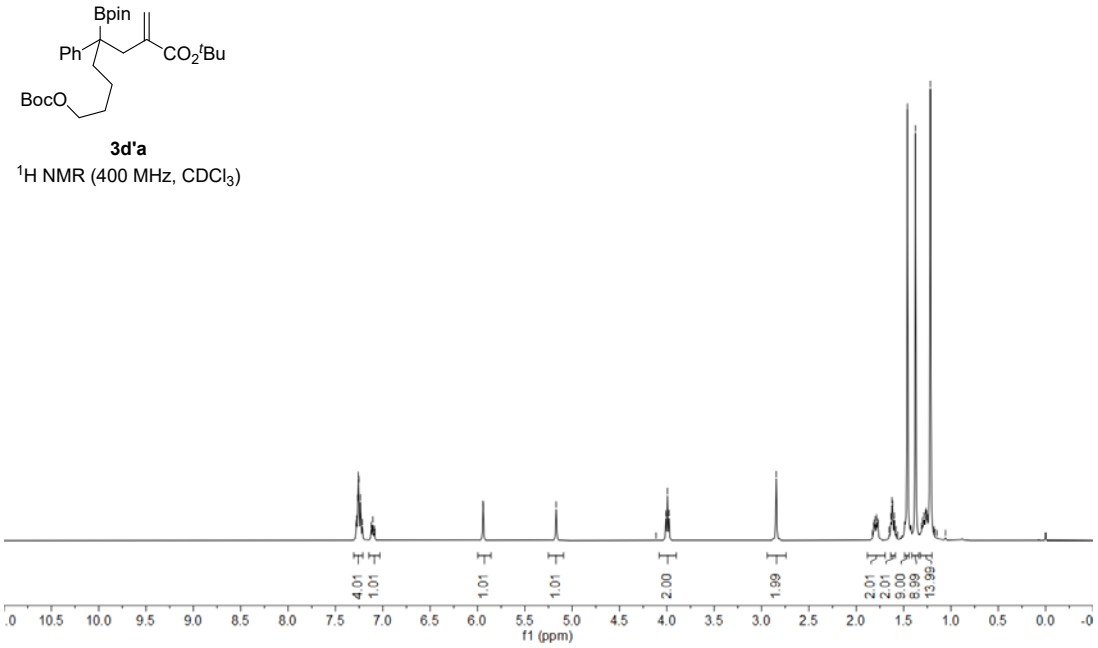
^{13}C NMR (100 MHz, $CDCl_3$)





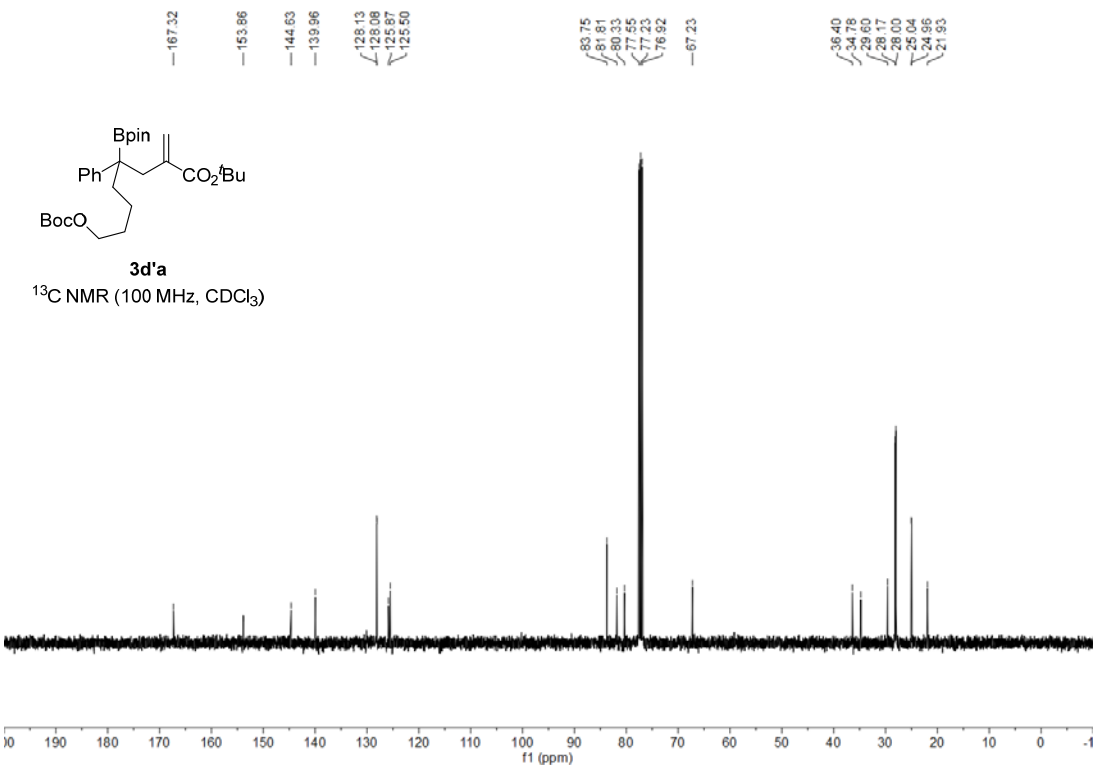
3c'a

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



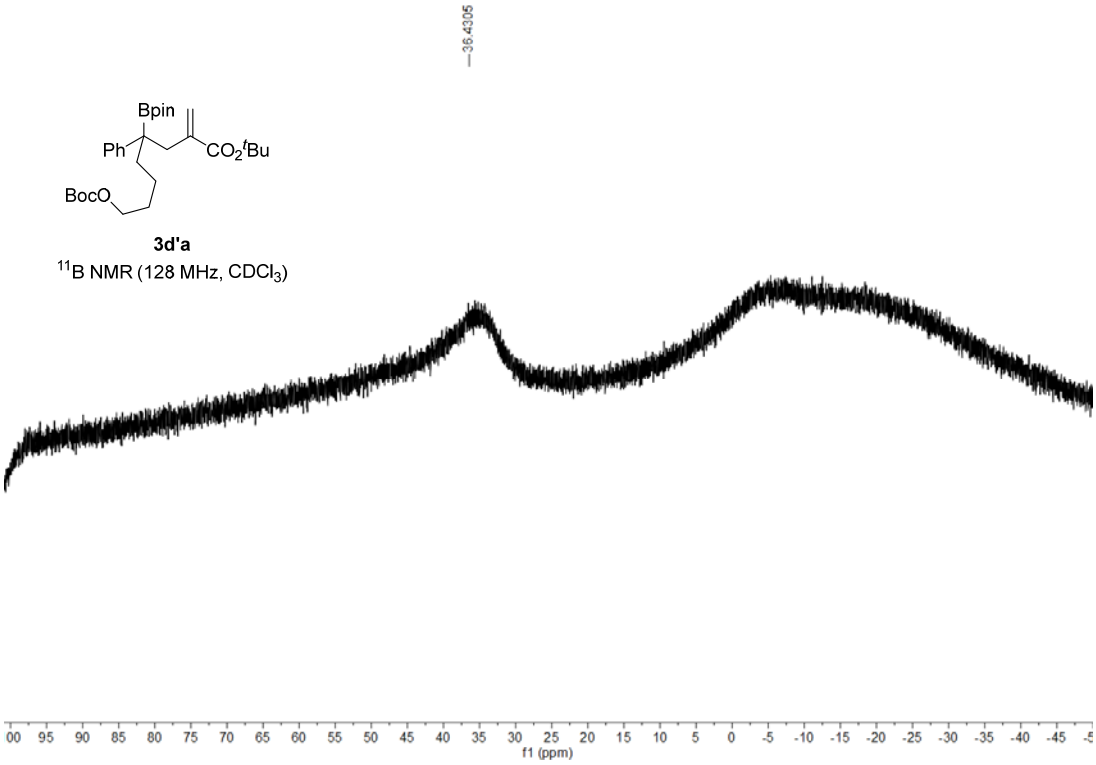
3d'a

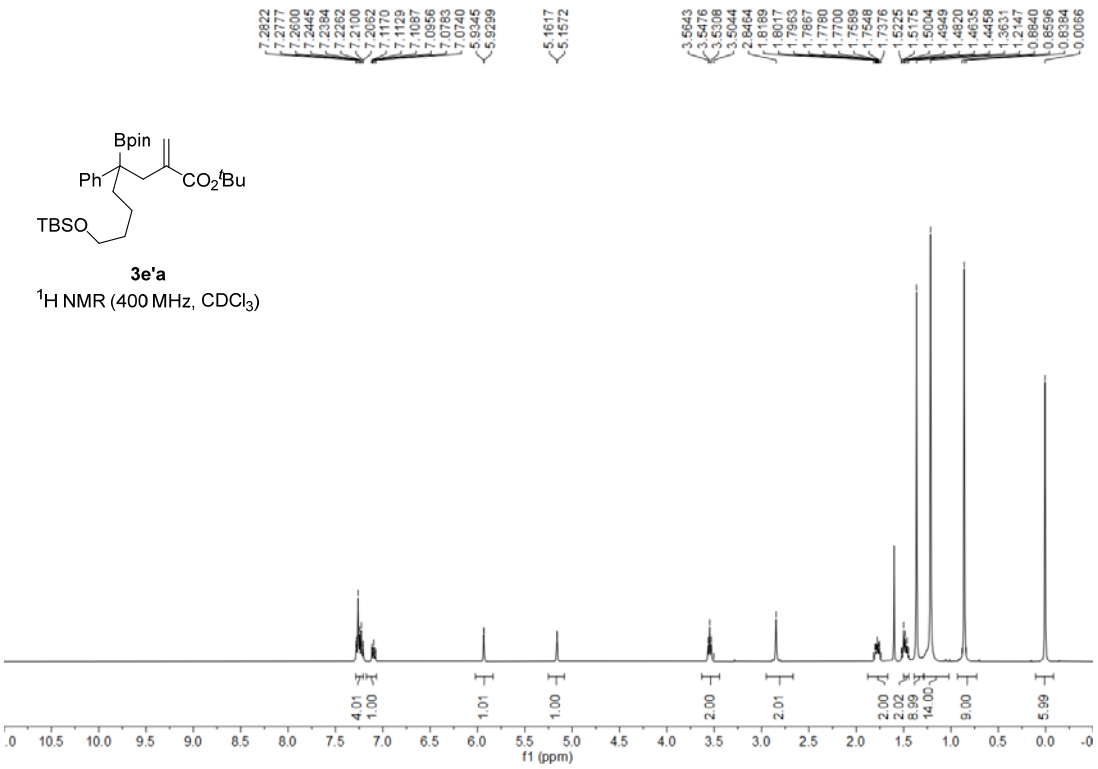
^{1}H NMR (400 MHz, $CDCl_3$)



3d'a

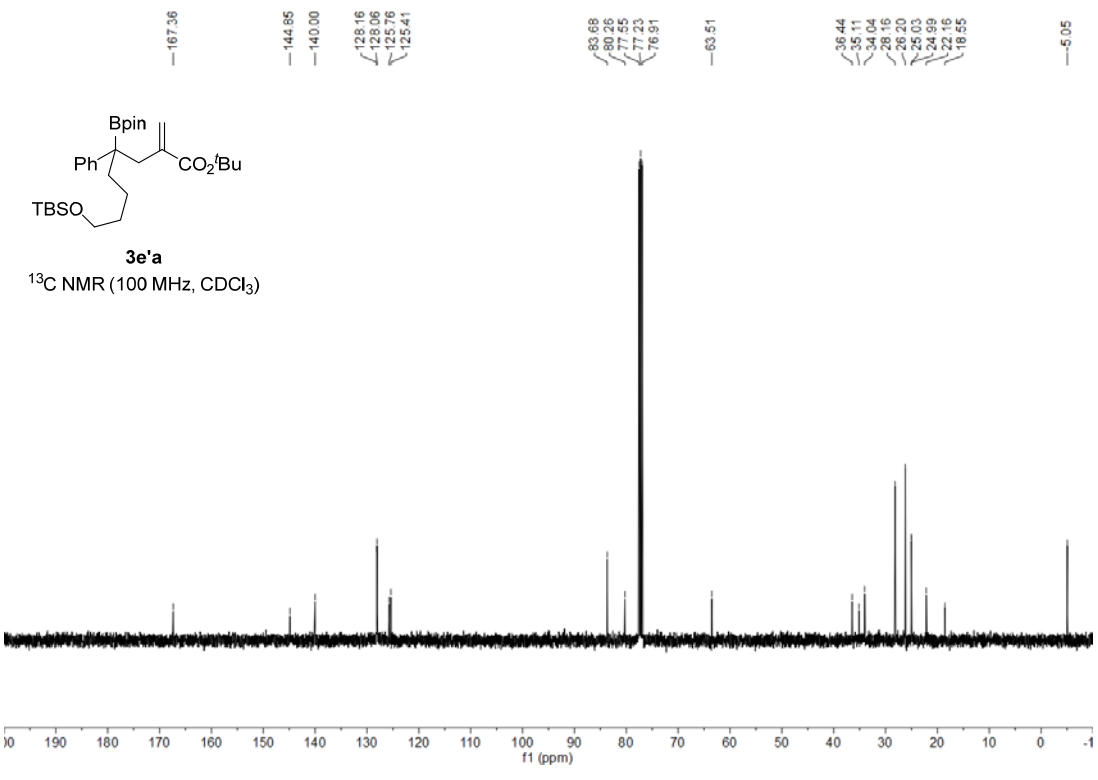
^{13}C NMR (100 MHz, $CDCl_3$)


36.4305
Bpin
Ph
CO2tBu
BocO
3d'a
11B NMR (128 MHz, CDCl3)
f1 (ppm)



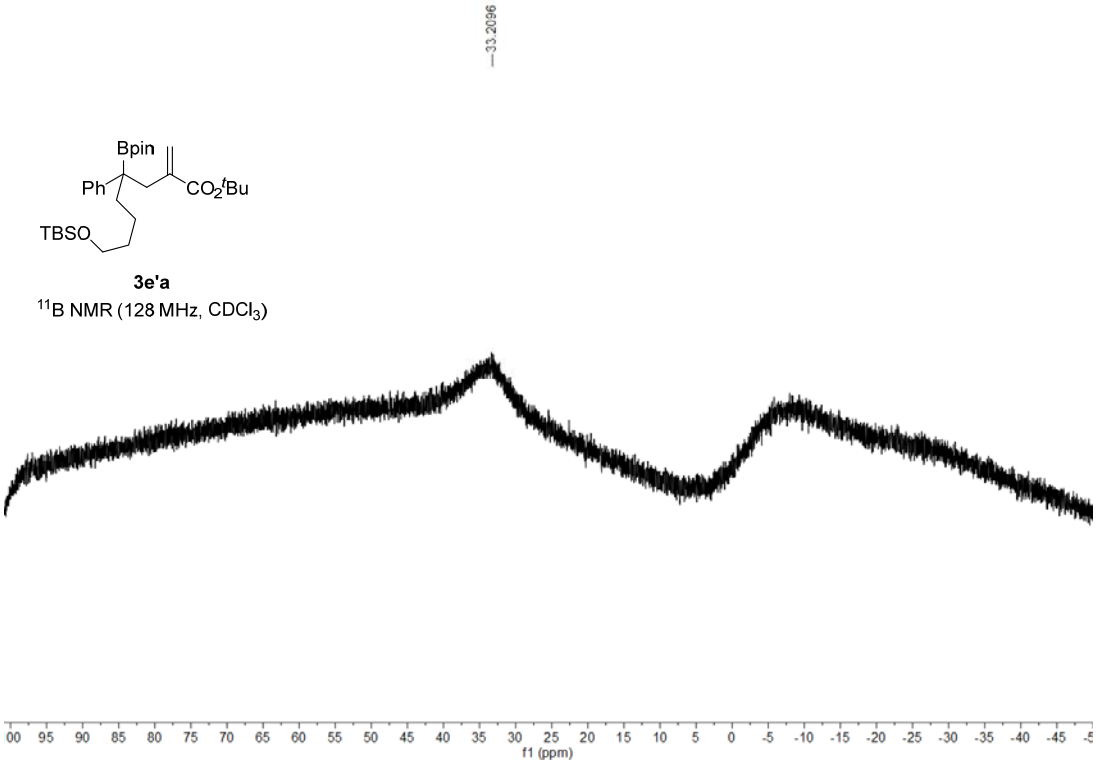
3e'a

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



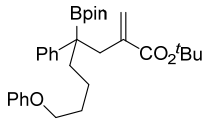
3e'a

^{13}C NMR (100 MHz, $CDCl_3$)



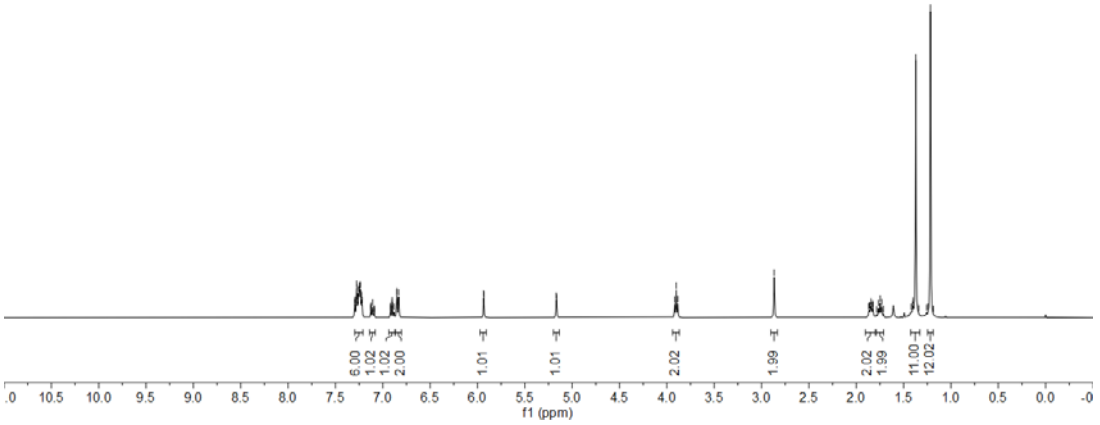
3e'a

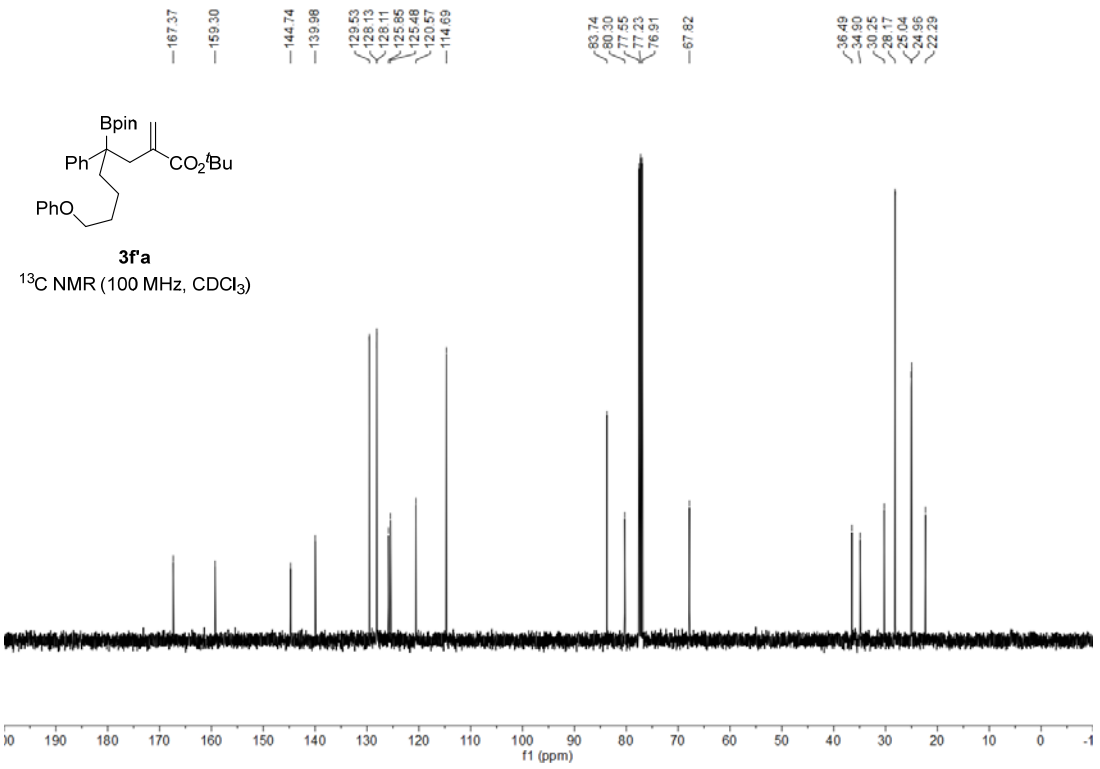
^{11}B NMR (128 MHz, $CDCl_3$)



3f'a

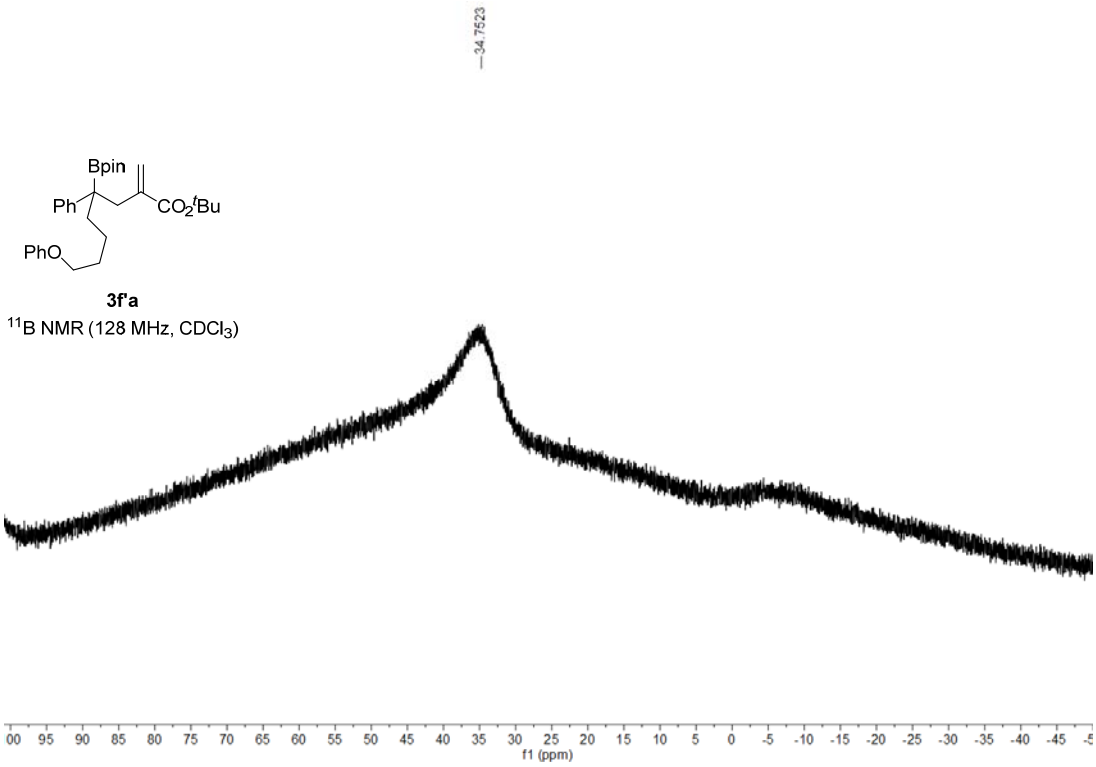
^{1}H NMR (400 MHz, $CDCl_3$)





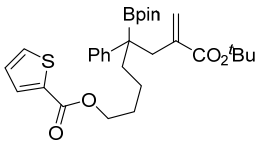
3f'a

^{13}C NMR (100 MHz, $CDCl_3$)



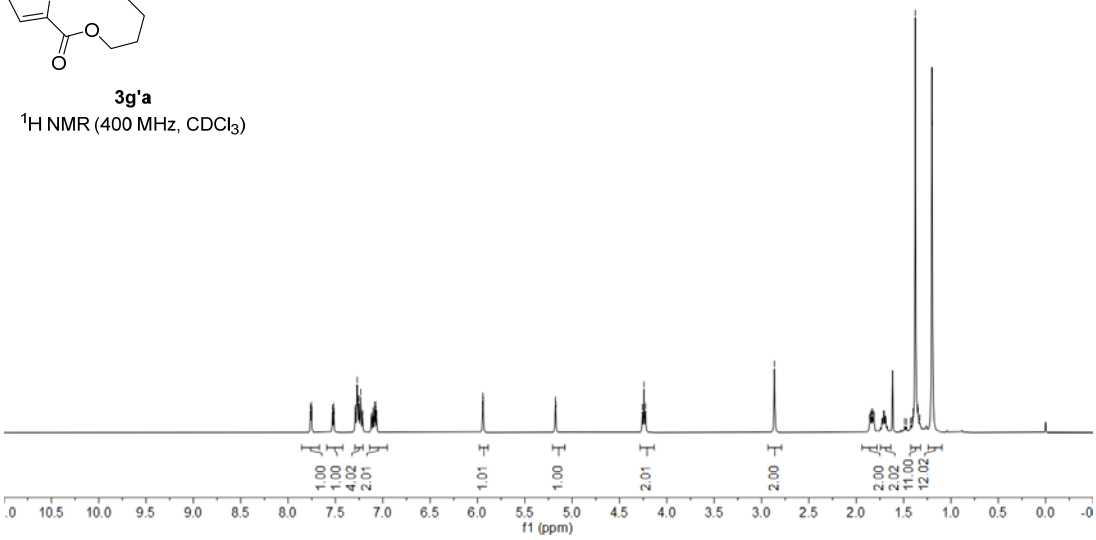
3f'a

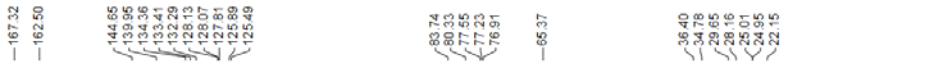
^{11}B NMR (128 MHz, $CDCl_3$)

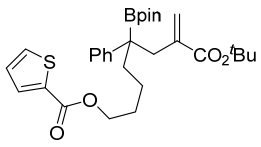


3g'a

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

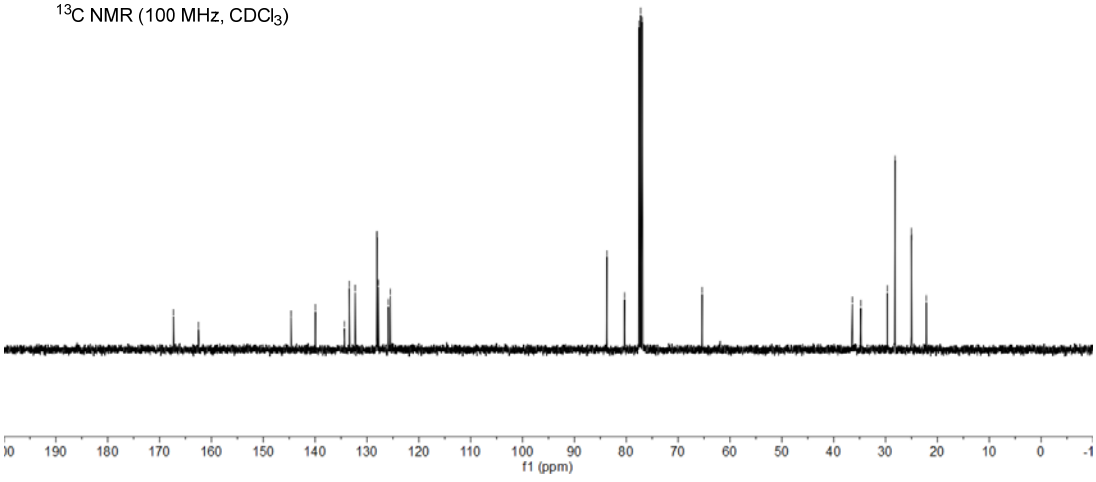


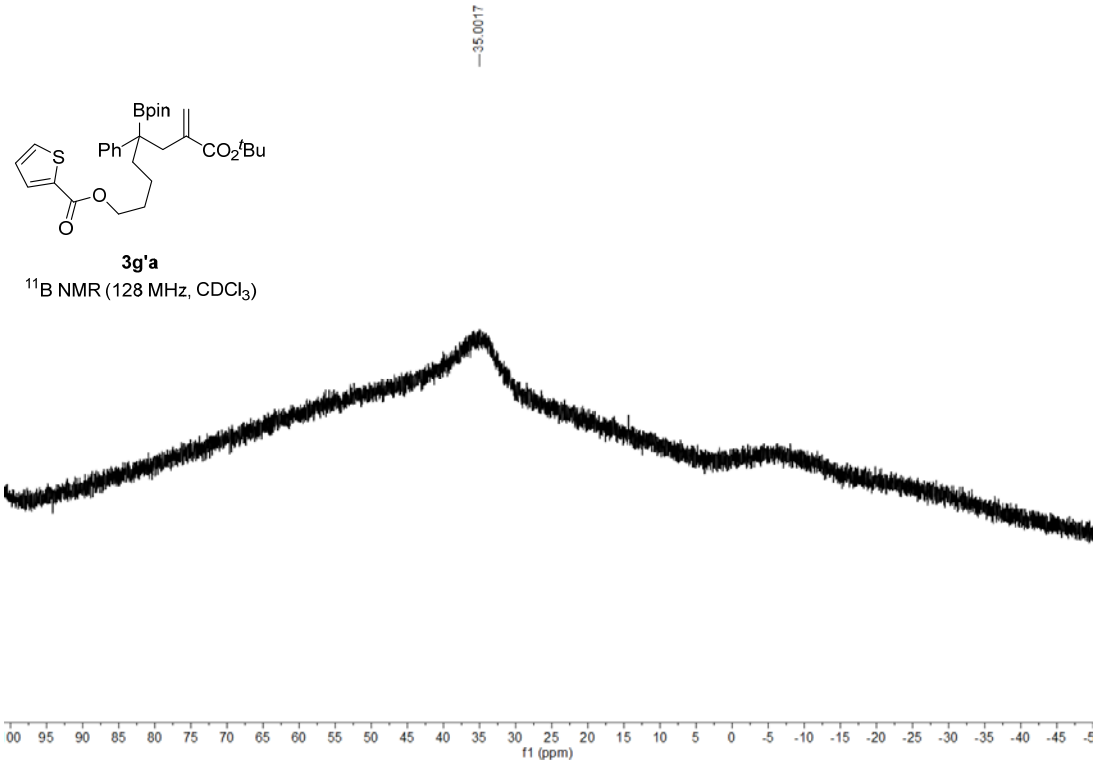




3g'a

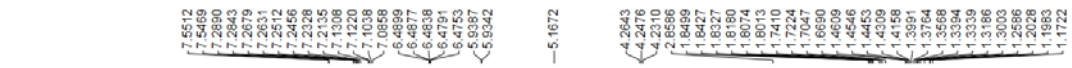
^{13}C NMR (100 MHz, $CDCl_3$)

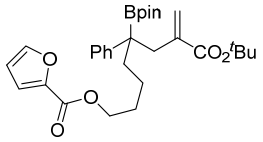




3g'a

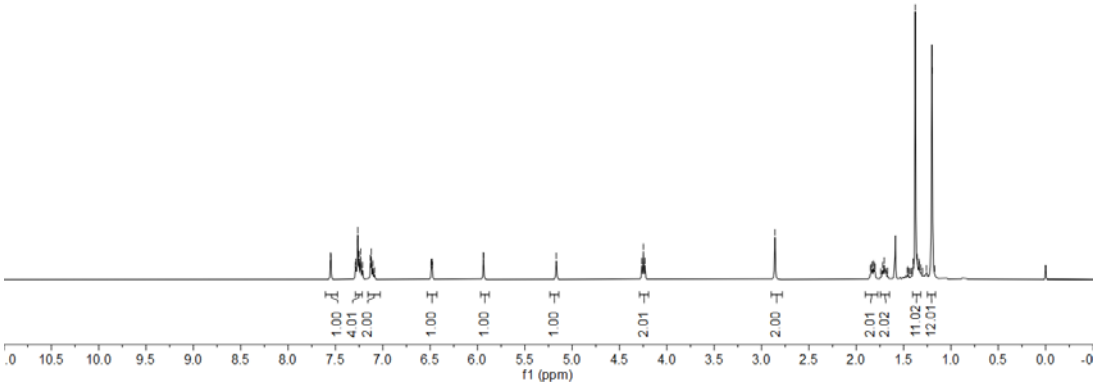
^{11}B NMR (128 MHz, $CDCl_3$)

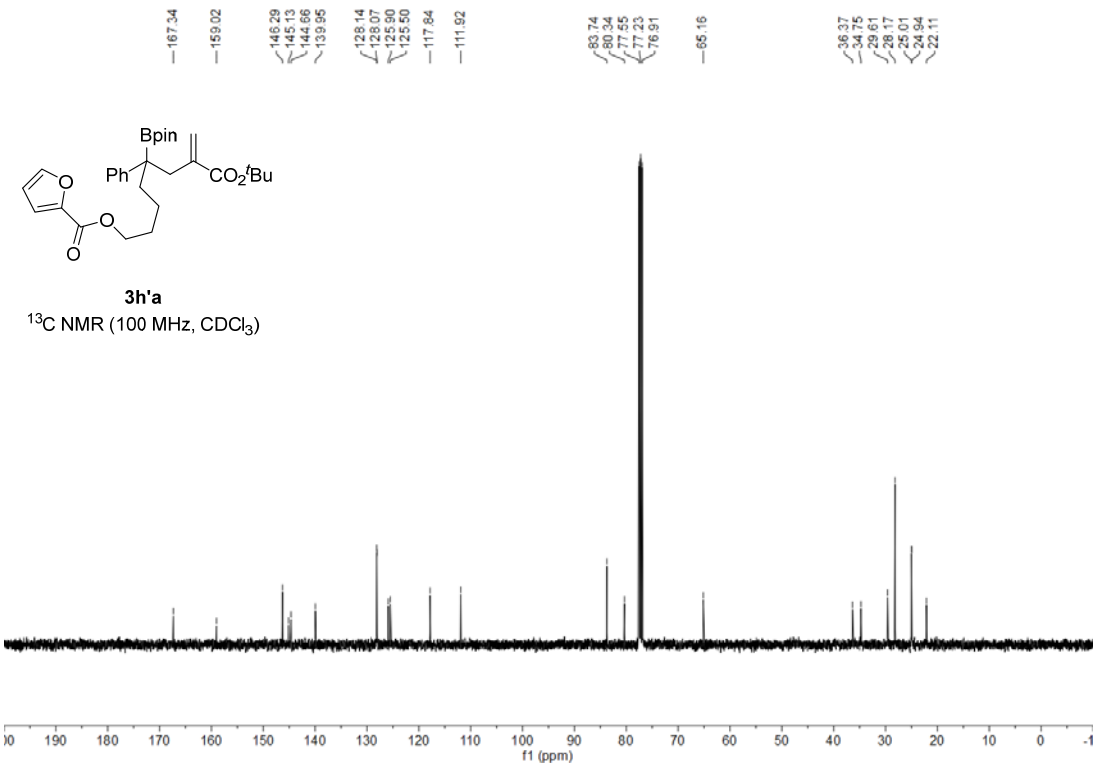




3h'a

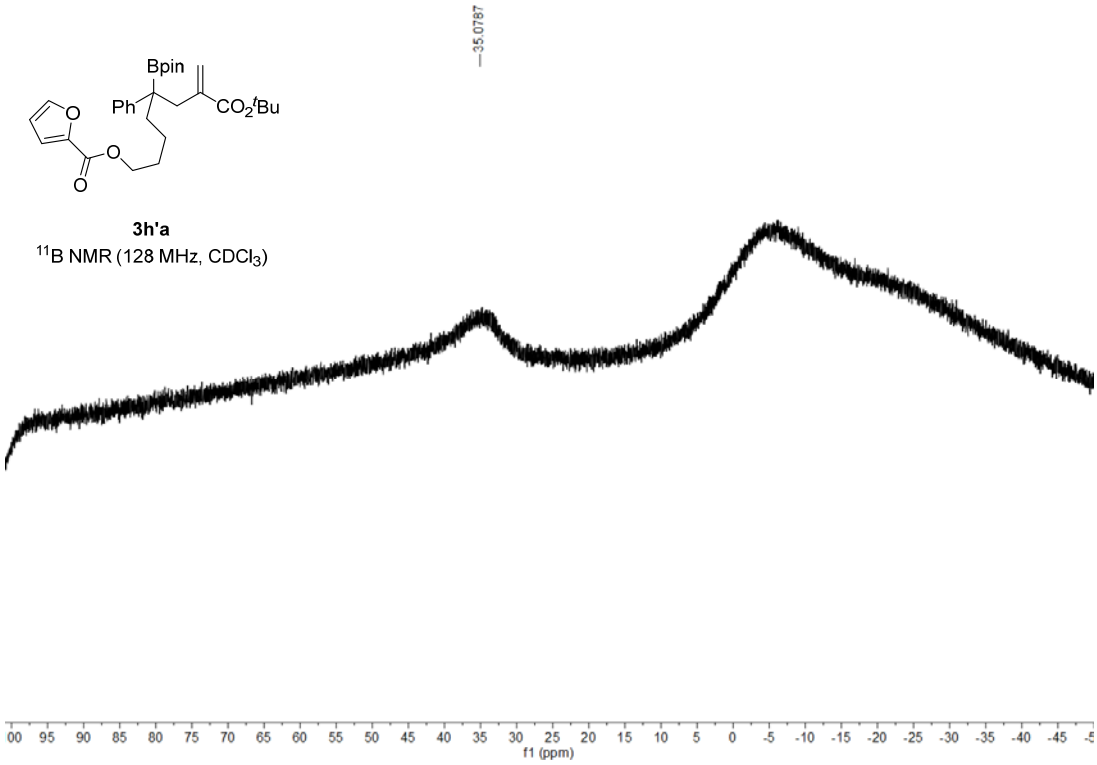
^{1}H NMR (400 MHz, $CDCl_3$)





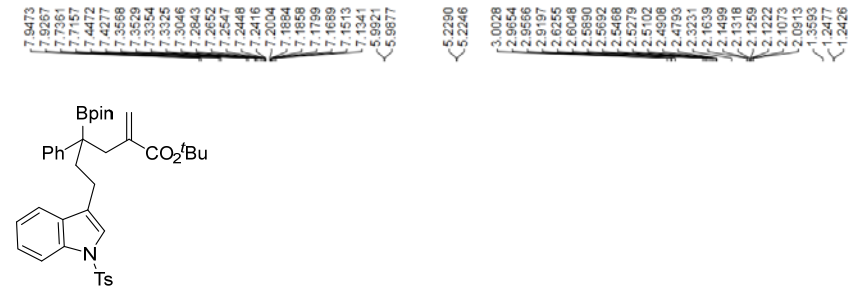
3h'a

^{13}C NMR (100 MHz, $CDCl_3$)



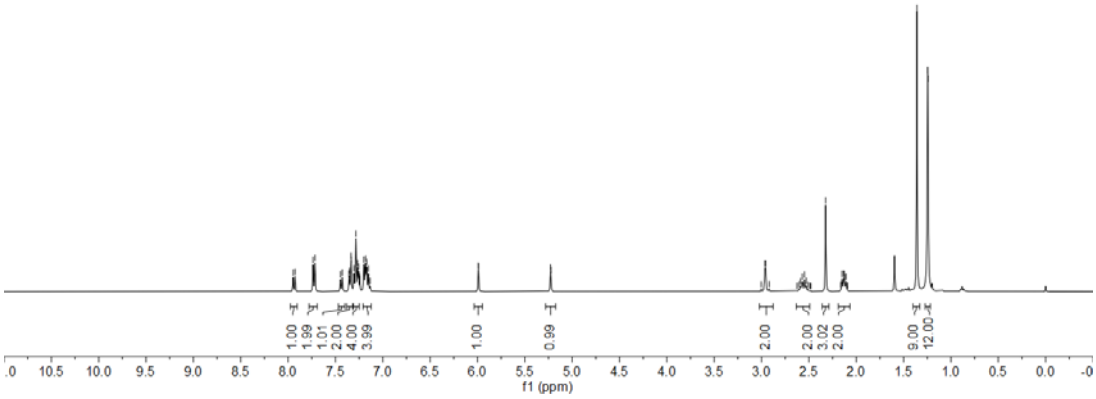
3h'a

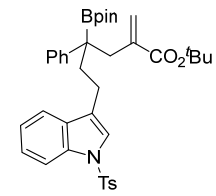
^{11}B NMR (128 MHz, $CDCl_3$)



3i'a

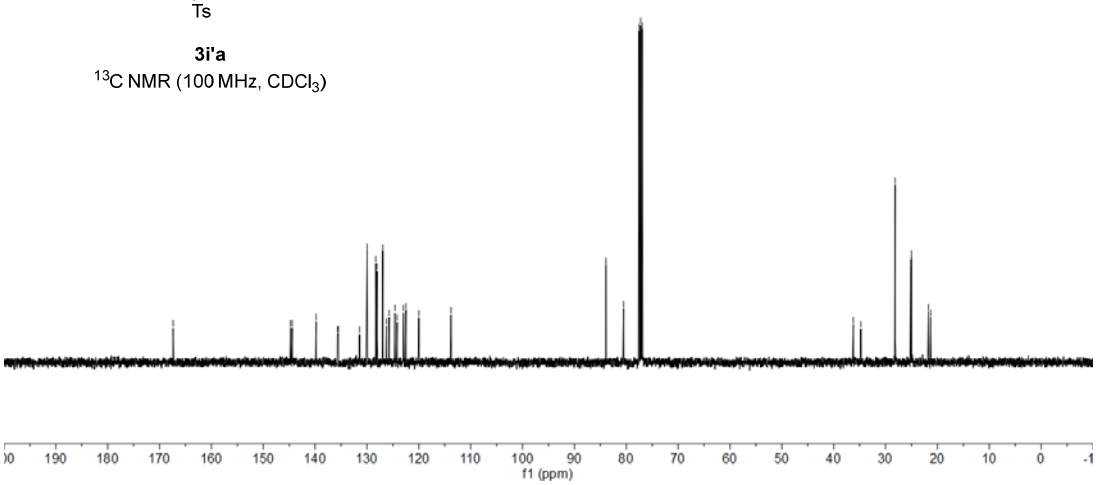
^{1}H NMR (400 MHz, $CDCl_3$)

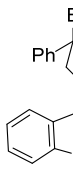




3i'a

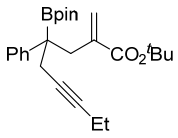
^{13}C NMR (100 MHz, $CDCl_3$)





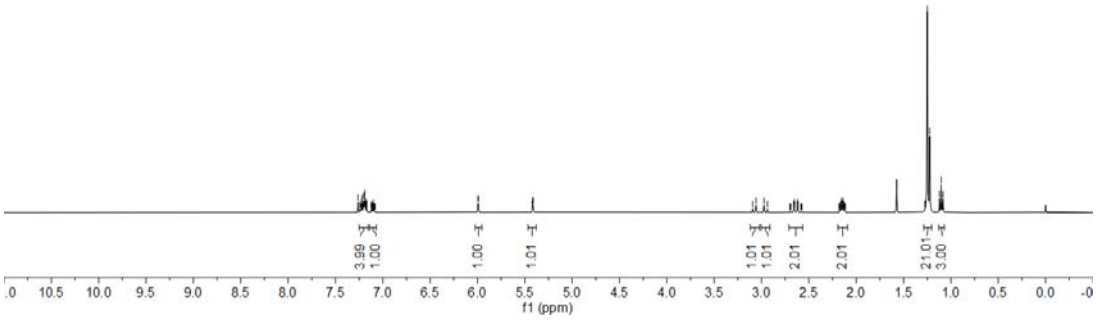
3i'a

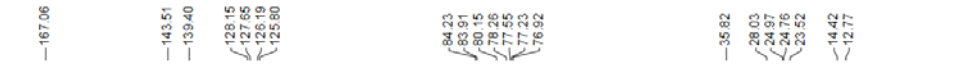
^{11}B NMR (128 MHz, $CDCl_3$)

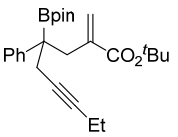


3j'a

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

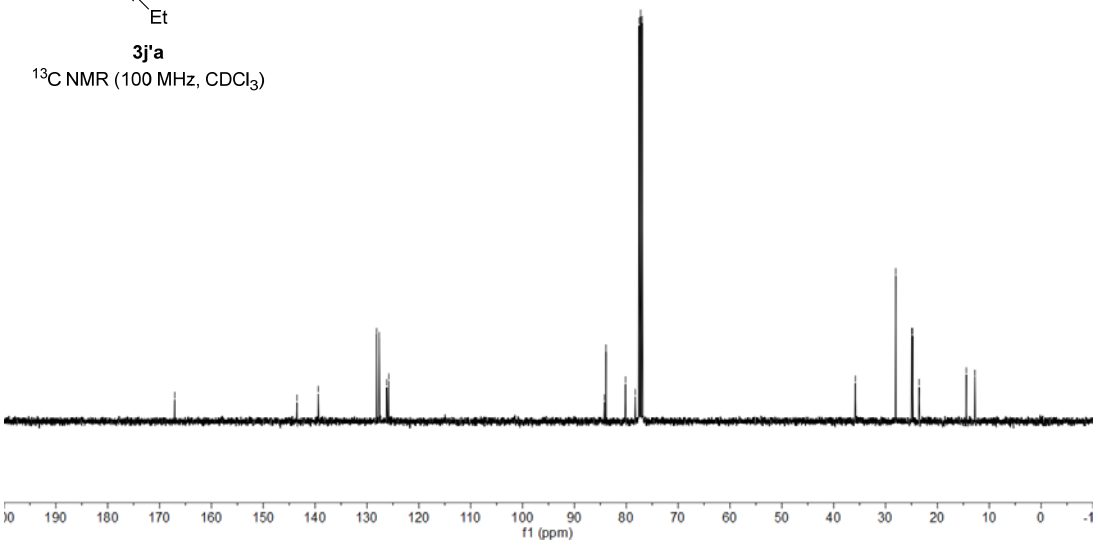


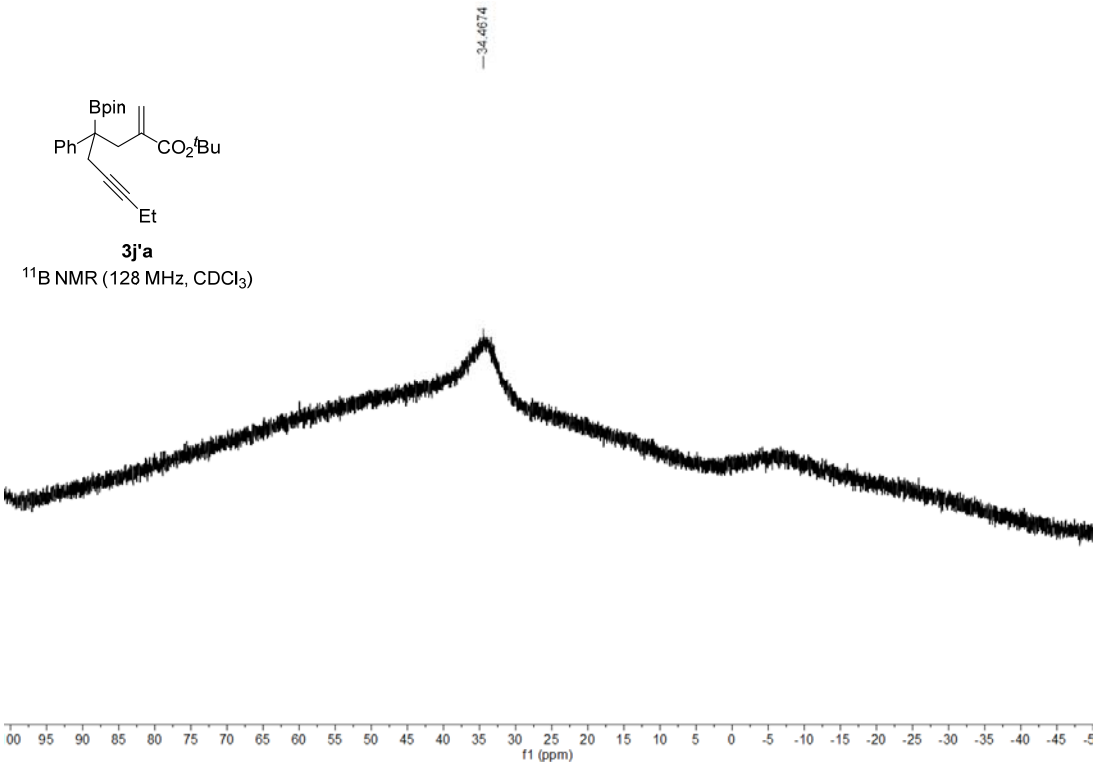




3j'a

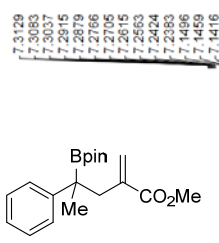
^{13}C NMR (100 MHz, $CDCl_3$)





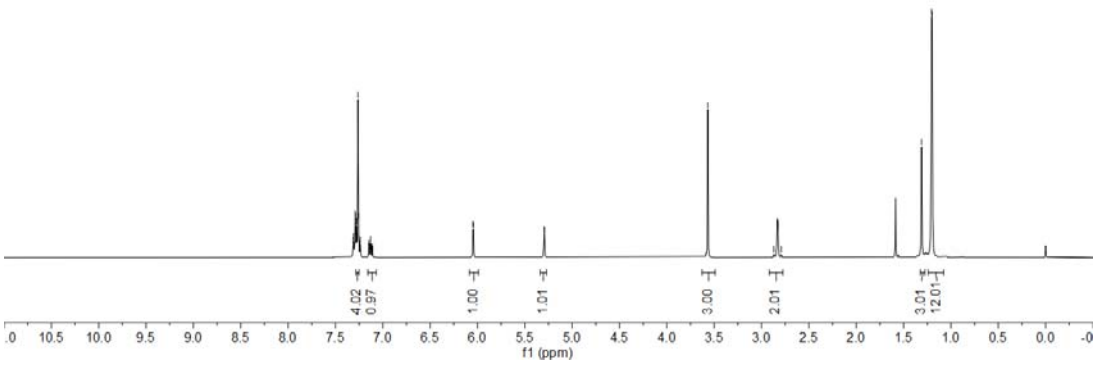
3j'a

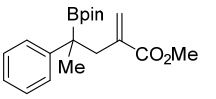
^{11}B NMR (128 MHz, $CDCl_3$)



3ab

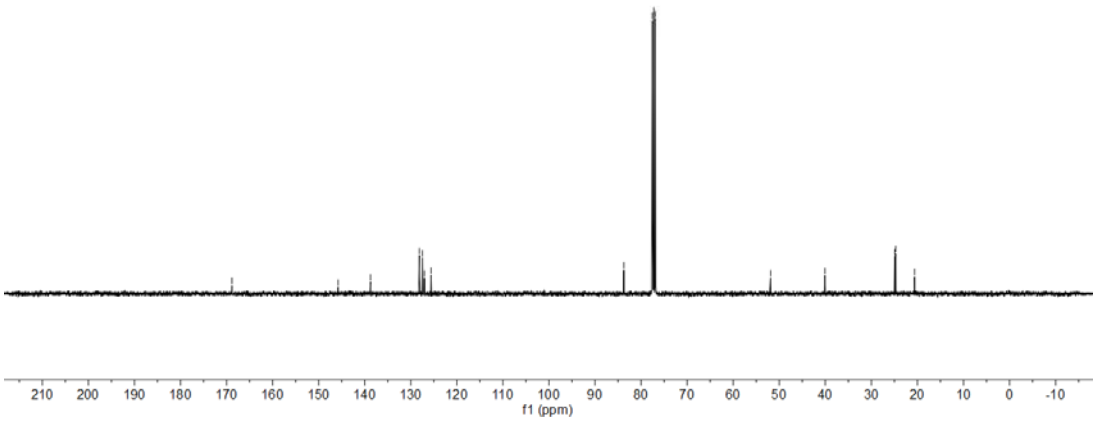
^{1}H NMR (400 MHz, $CDCl_3$)

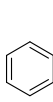




3ab

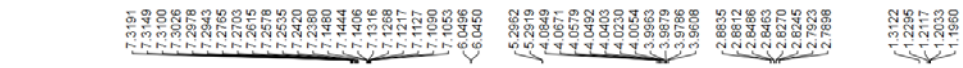
^{13}C NMR (100 MHz, $CDCl_3$)

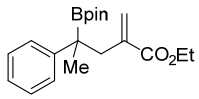




3ab

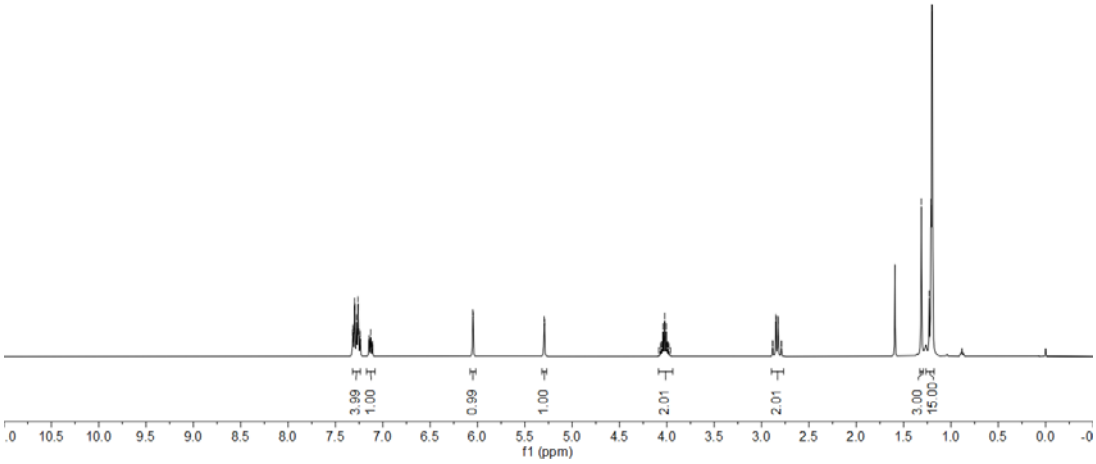
^{11}B NMR (128 MHz, $CDCl_3$)

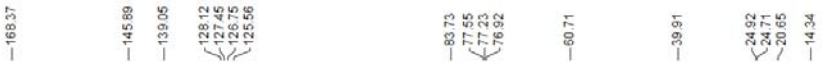


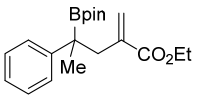


3ac

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

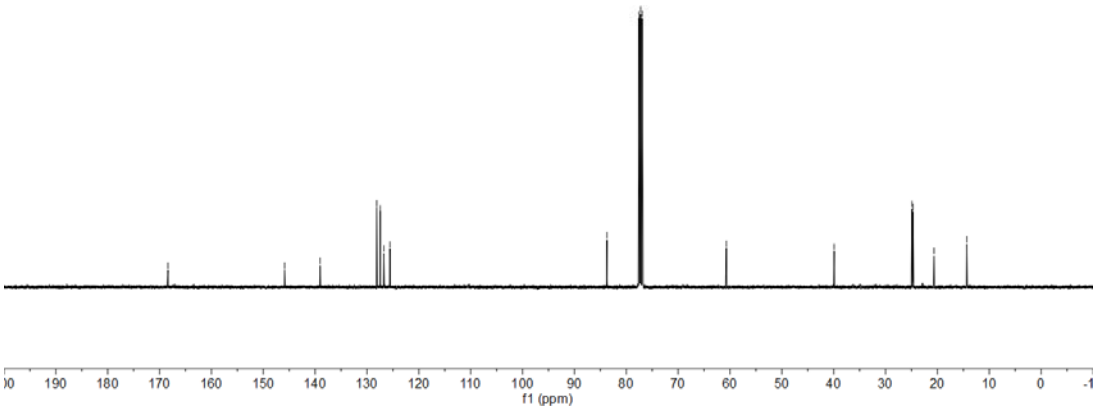


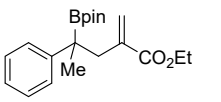




3ac

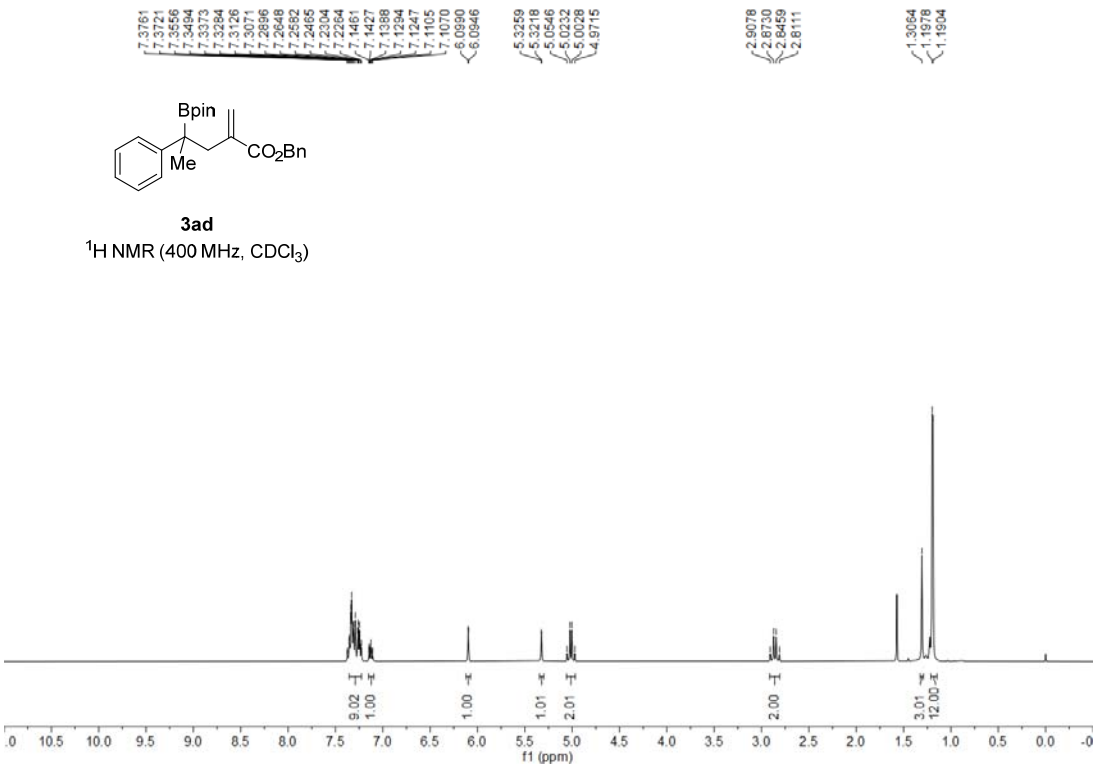
^{13}C NMR (100 MHz, $CDCl_3$)





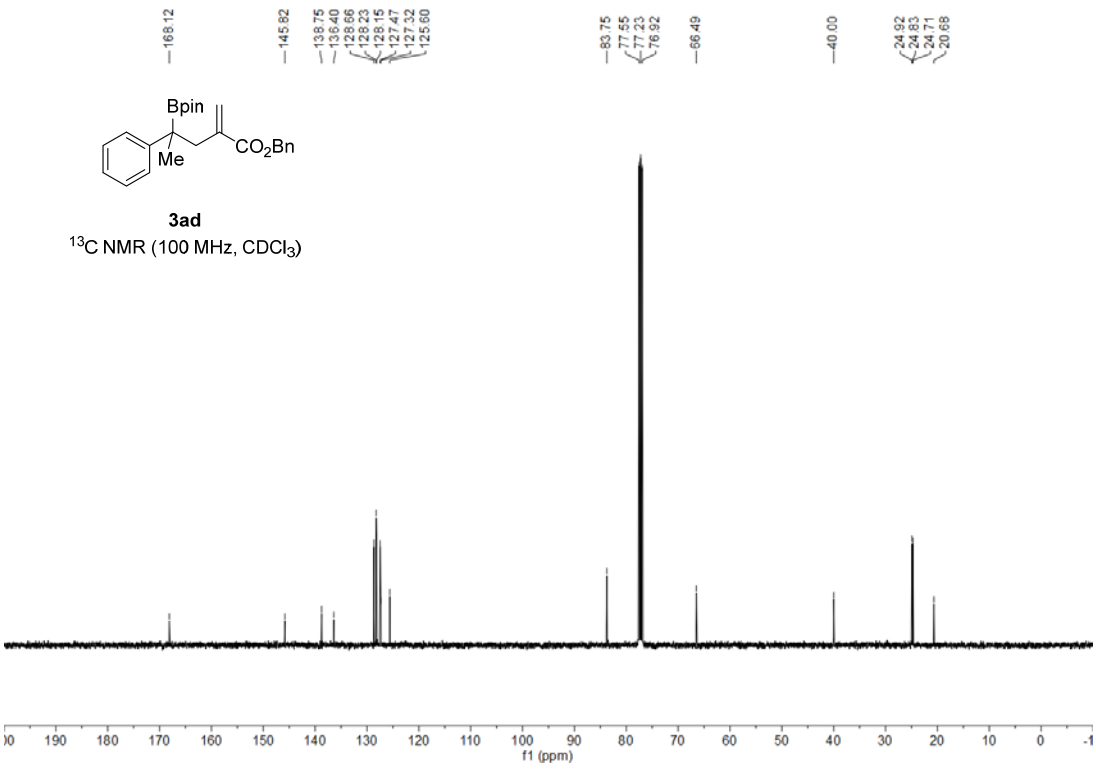
3ac

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



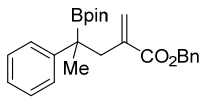
3ad

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



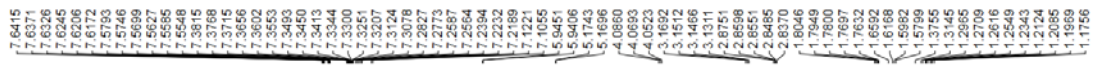
3ad

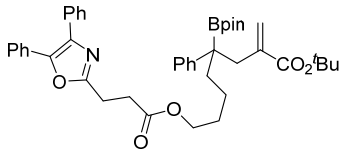
^{13}C NMR (100 MHz, $CDCl_3$)



3ad

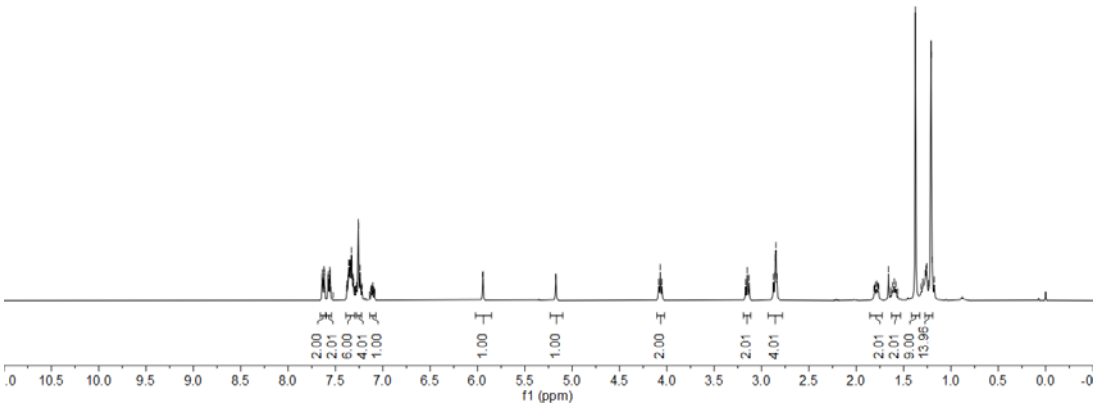
^{11}B NMR (128 MHz, $CDCl_3$)

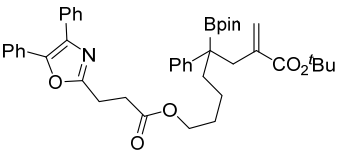




3k'a

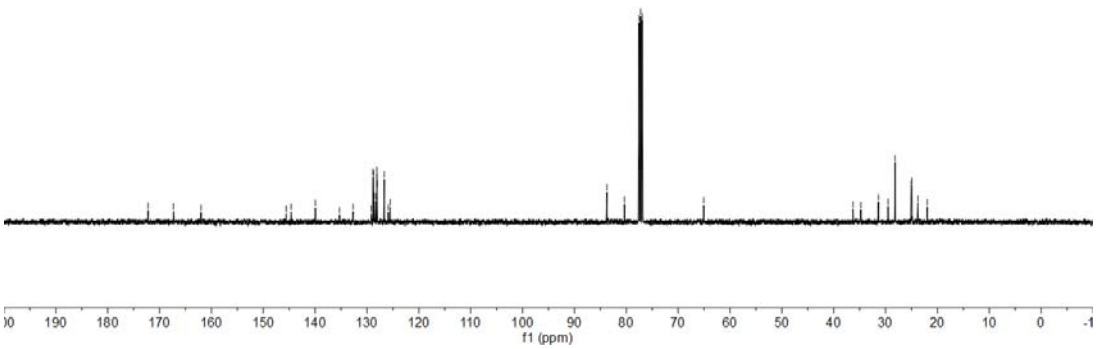
^{1}H NMR (400 MHz, $CDCl_3$)

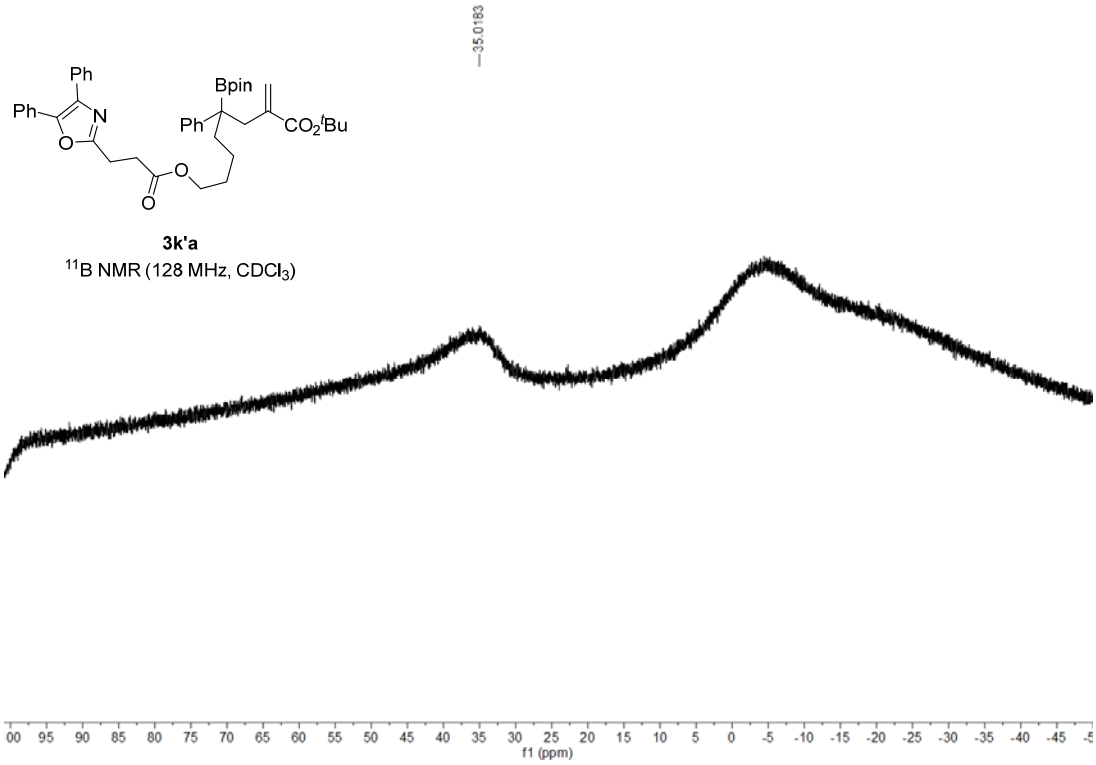




3k'a

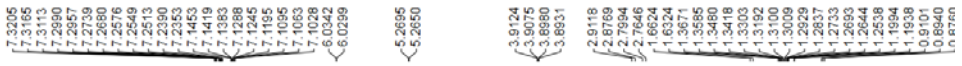
^{13}C NMR (100 MHz, $CDCl_3$)

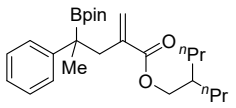




3k'a

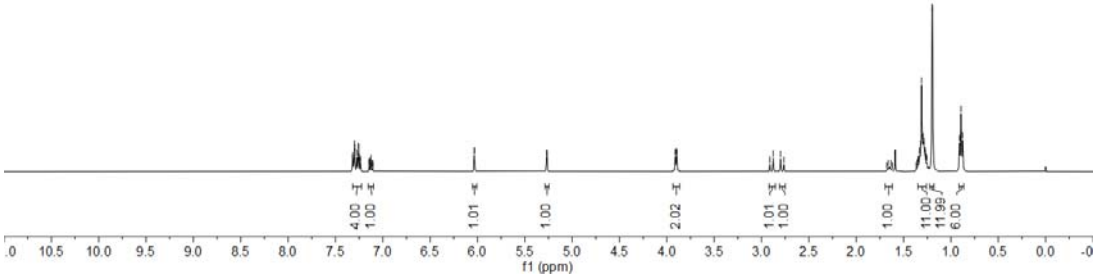
^{11}B NMR (128 MHz, $CDCl_3$)

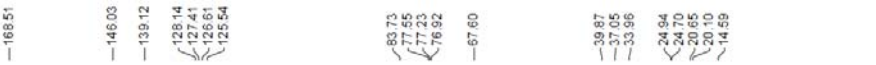


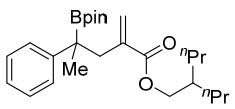


3af

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

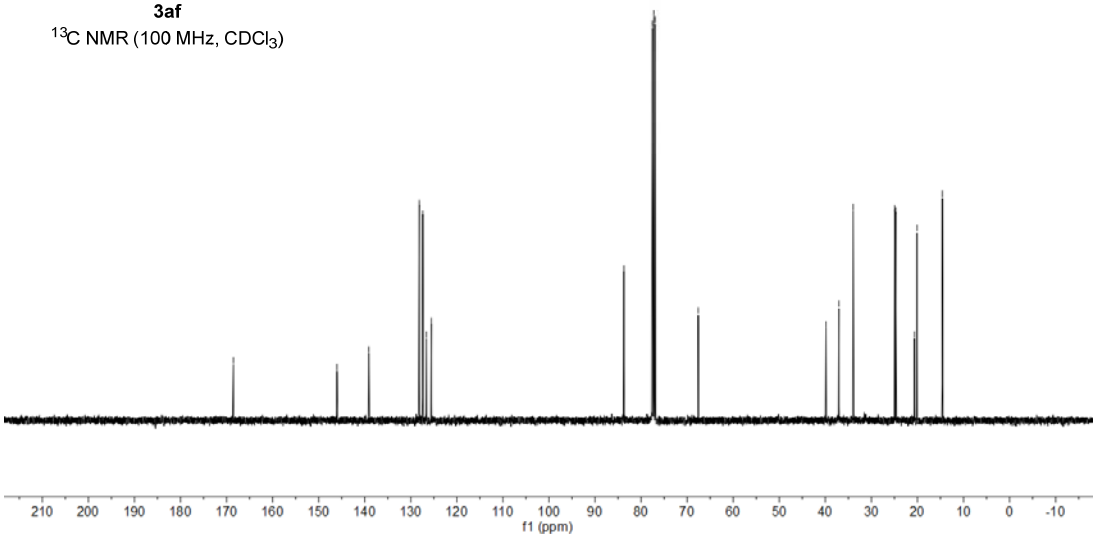


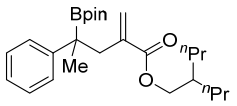




3af

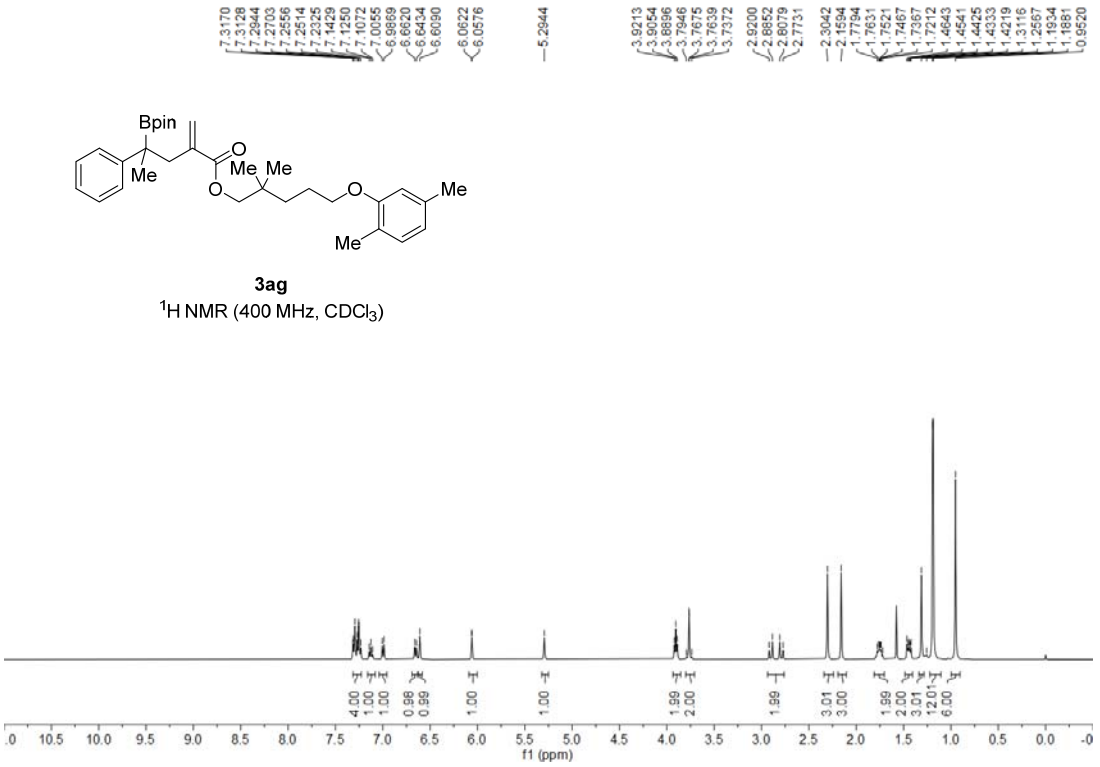
^{13}C NMR (100 MHz, $CDCl_3$)





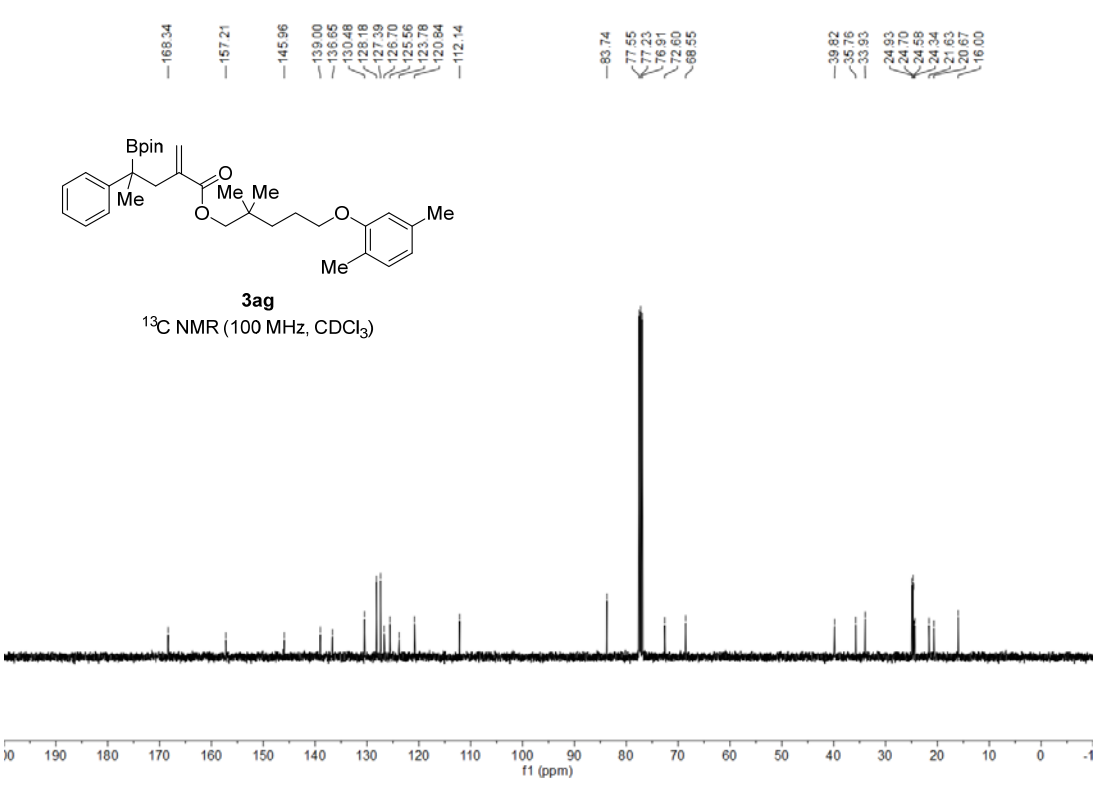
3af

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



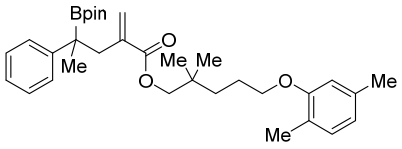
3ag

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



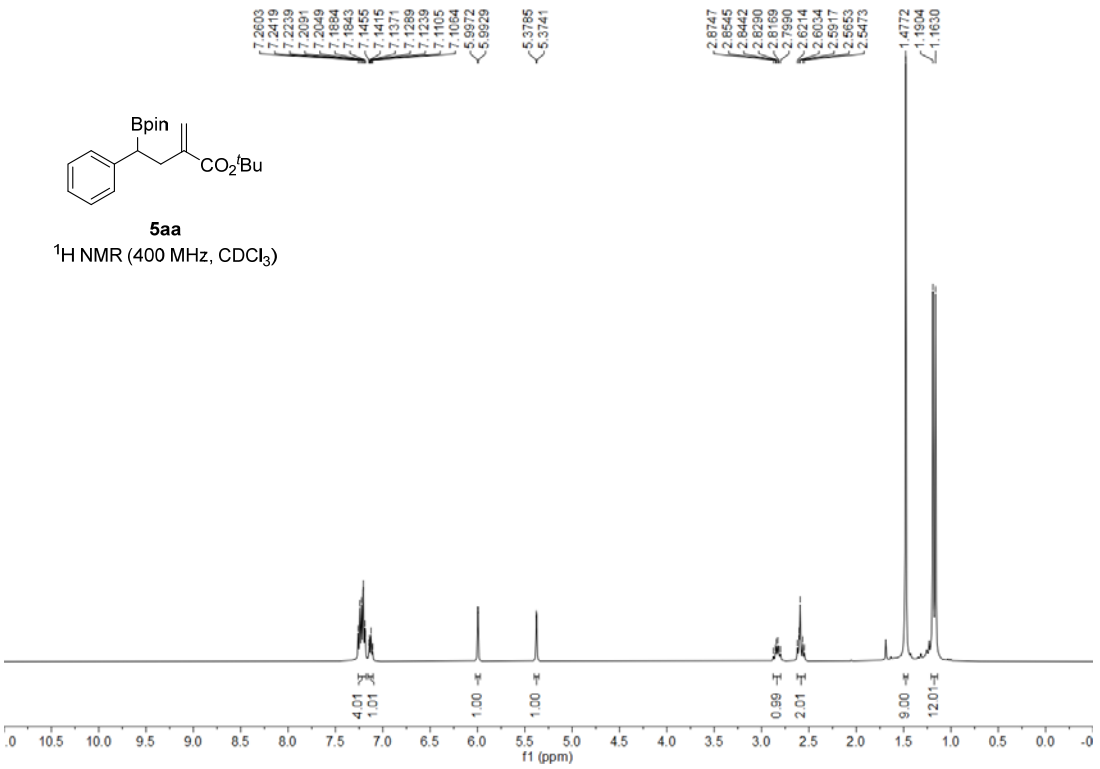
3ag

^{13}C NMR (100 MHz, $CDCl_3$)



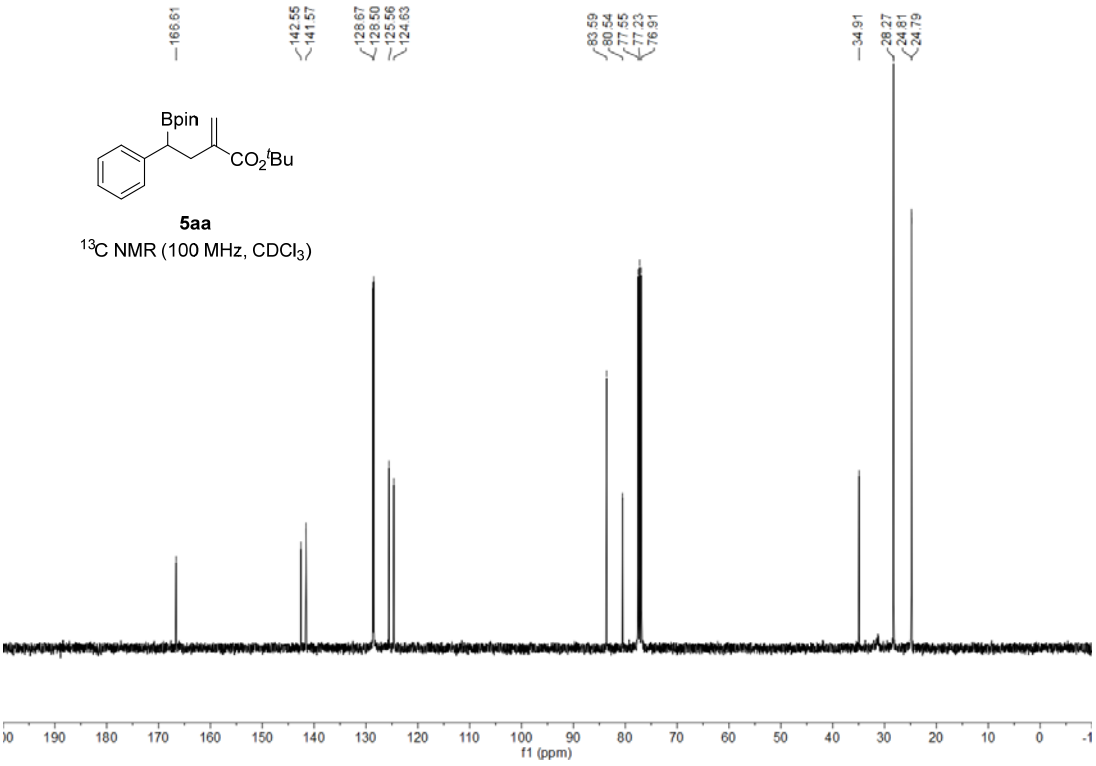
3ag

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



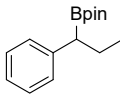
5aa

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



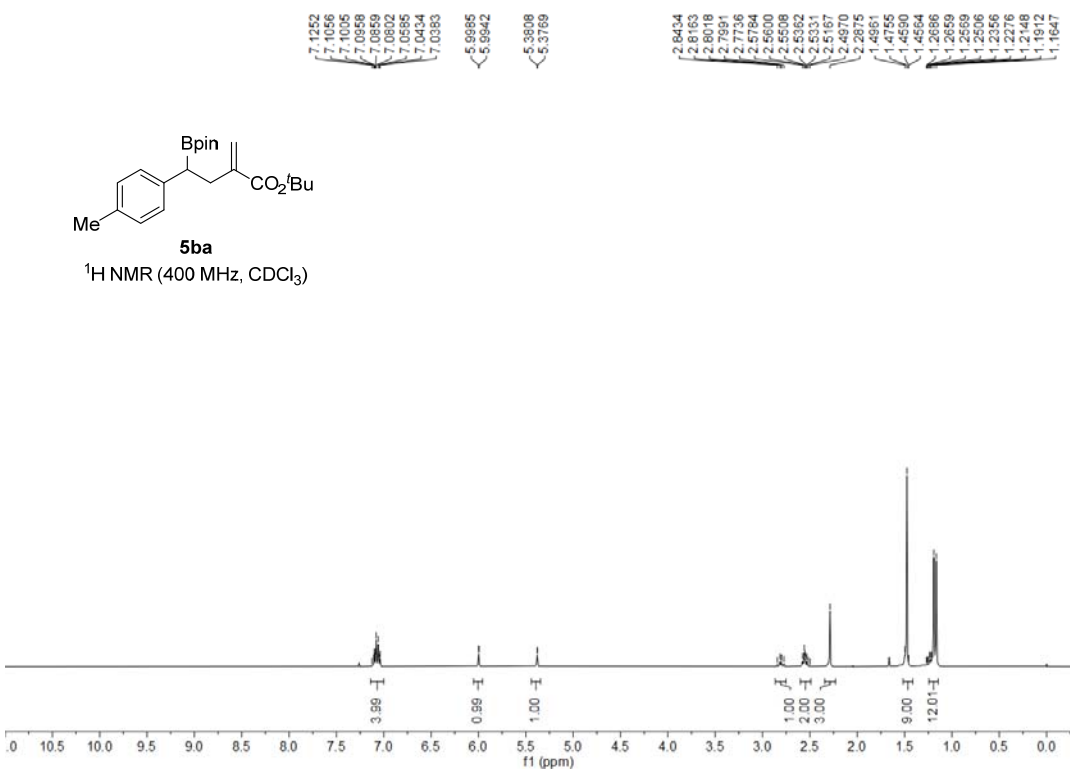
5aa

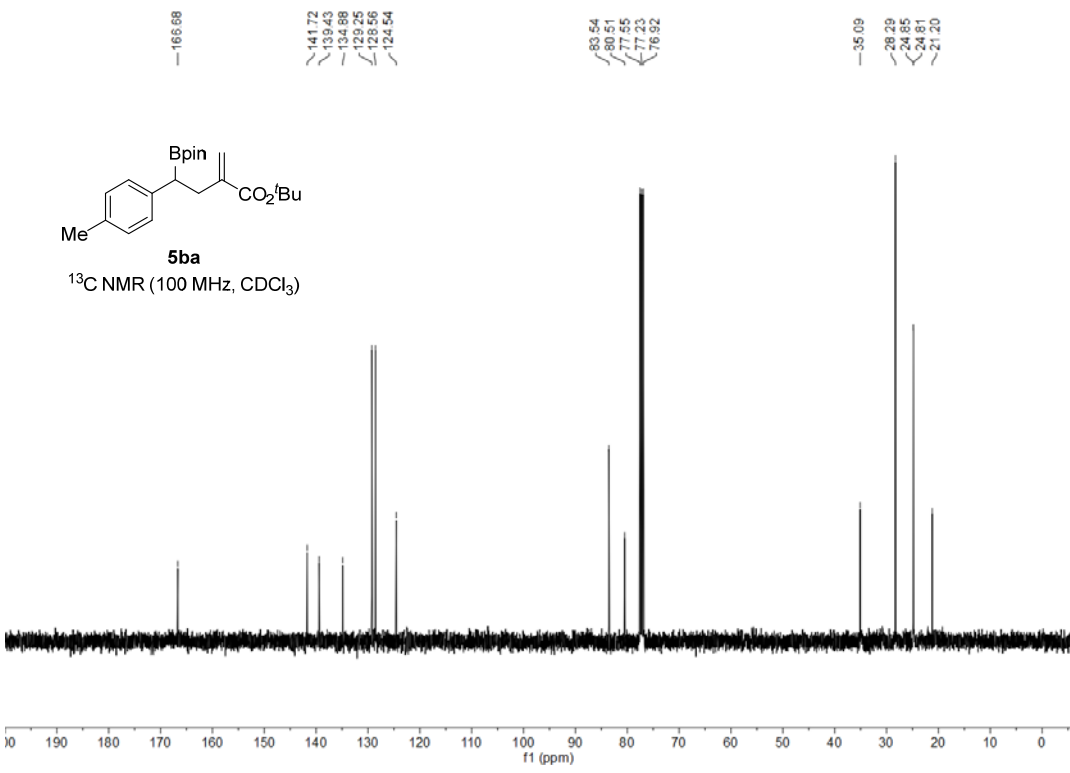
^{13}C NMR (100 MHz, $CDCl_3$)

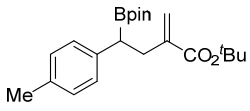


5aa

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

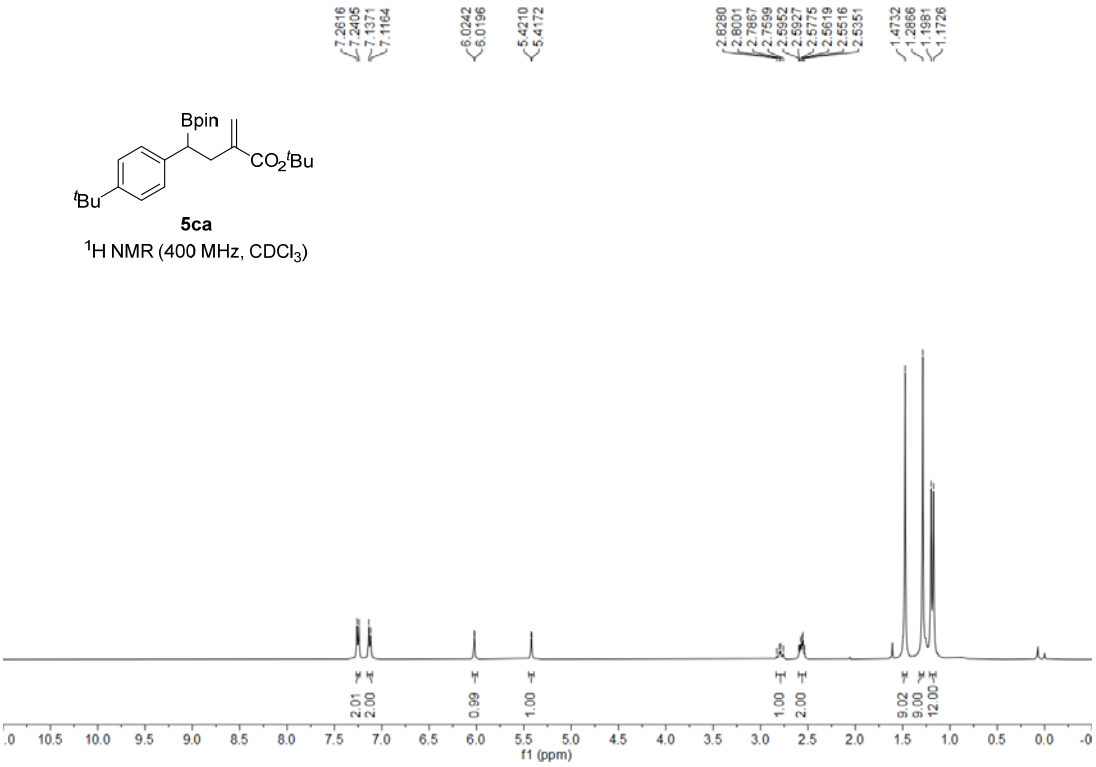

Bpin
CO2tBu
Me
5ba
1H NMR (400 MHz, CDCl3)
f1 (ppm)

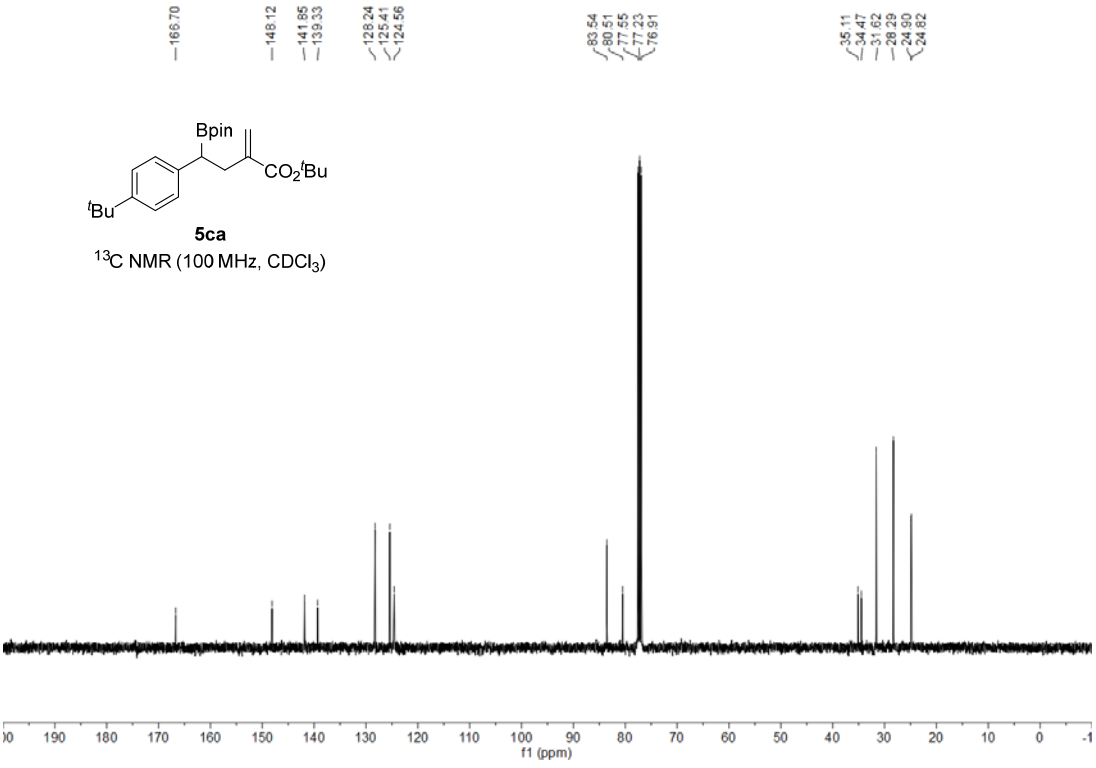

Bpin
CO2tBu
Me
5ba
13C NMR (100 MHz, CDCl3)
f1 (ppm)

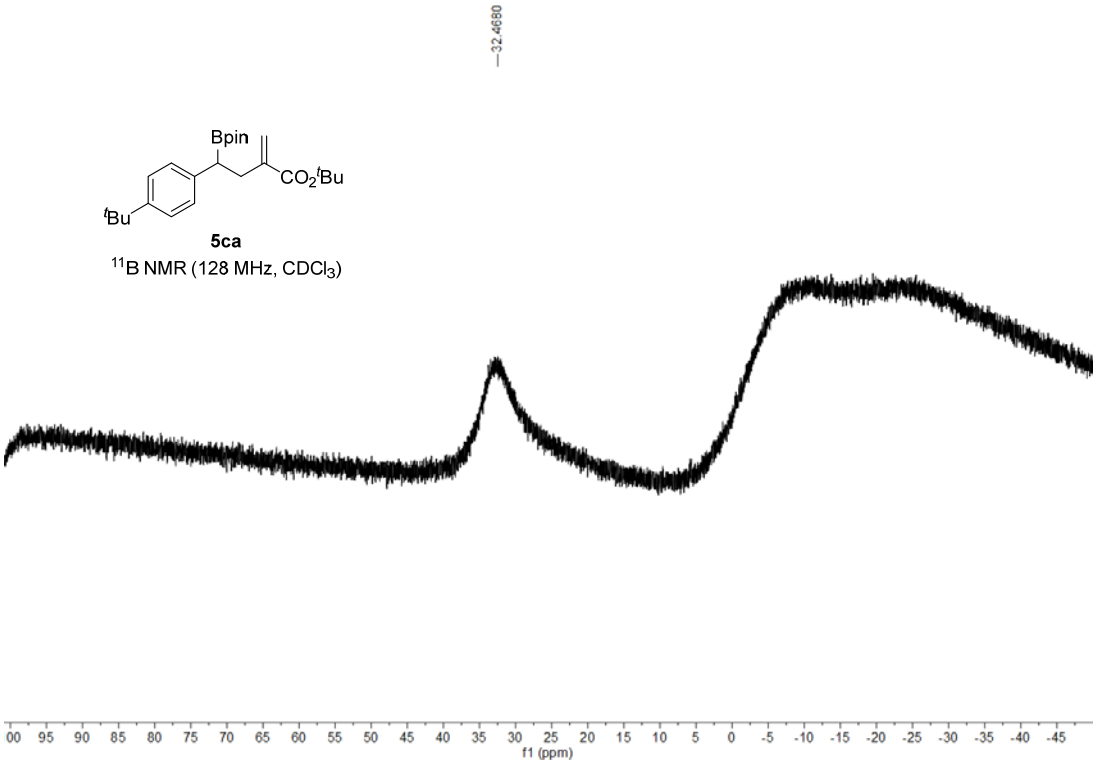


5ba

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

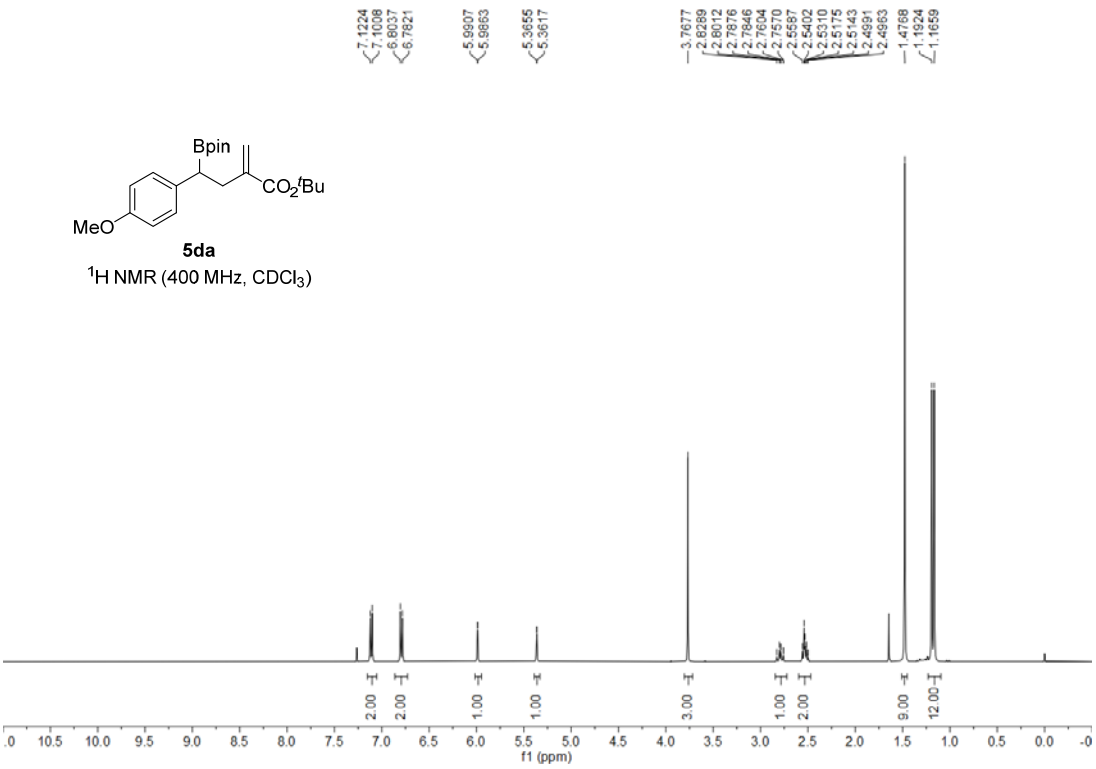

Bpin
CO2tBu
tBu
5ca
1H NMR (400 MHz, CDCl3)
f1 (ppm)

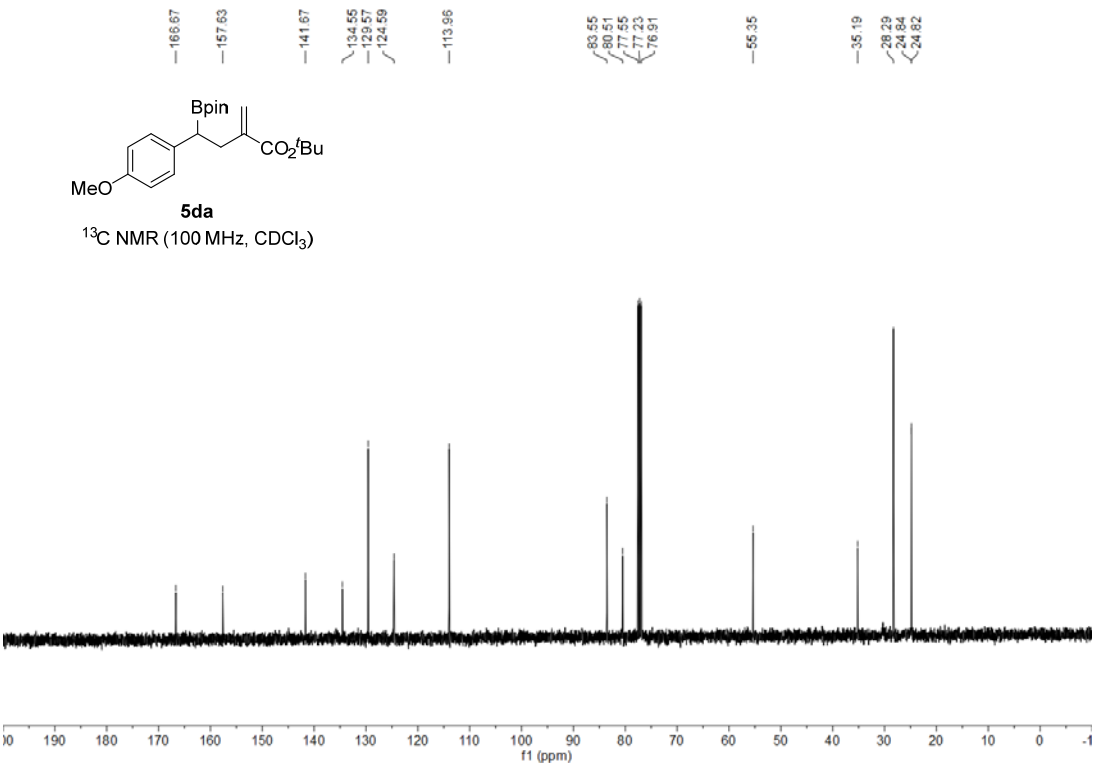

Bpin
CO2tBu
tBu
5ca
13C NMR (100 MHz, CDCl3)
f1 (ppm)

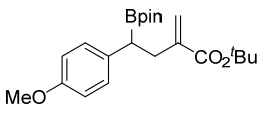


5ca

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

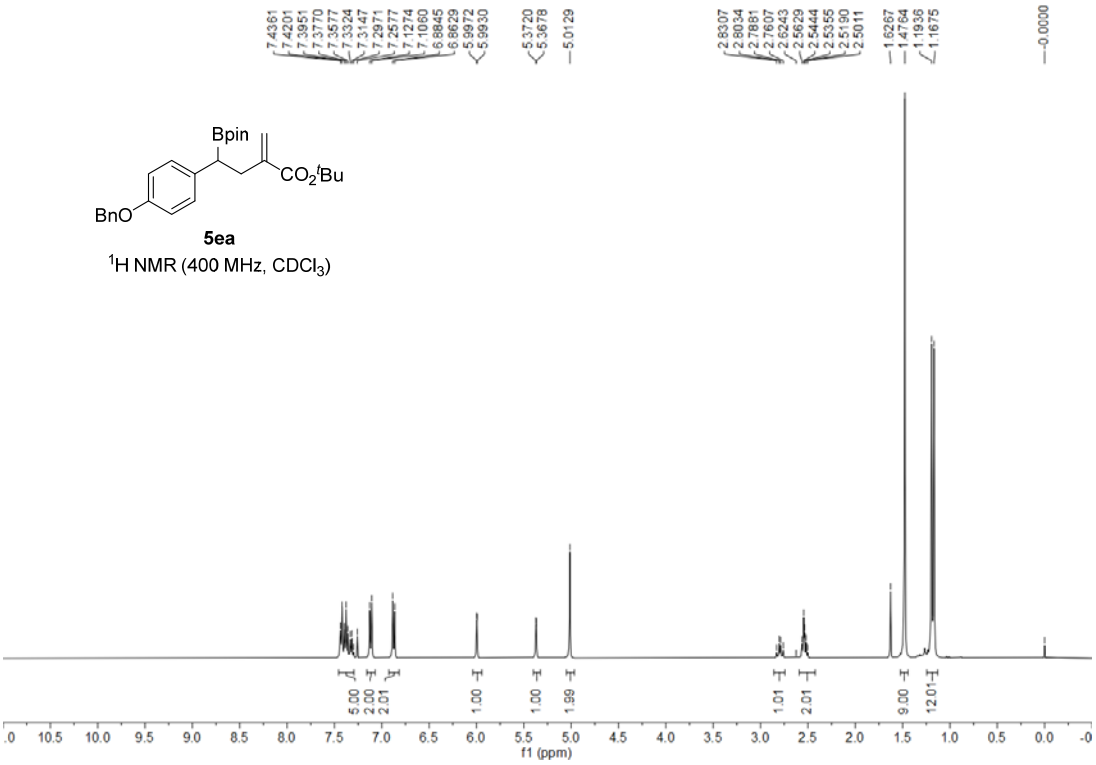

Bpin
CO2tBu
MeO
5da
1H NMR (400 MHz, CDCl3)
f1 (ppm)

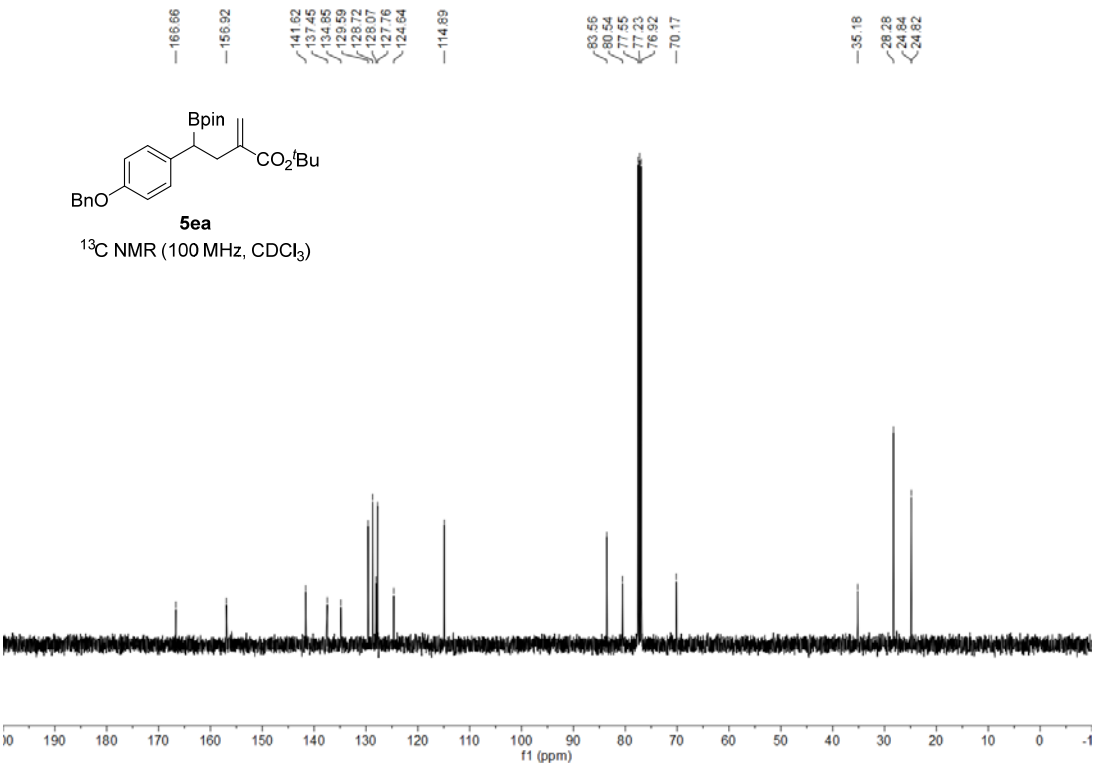

Bpin
CO2tBu
MeO
5da
13C NMR (100 MHz, CDCl3)
f1 (ppm)

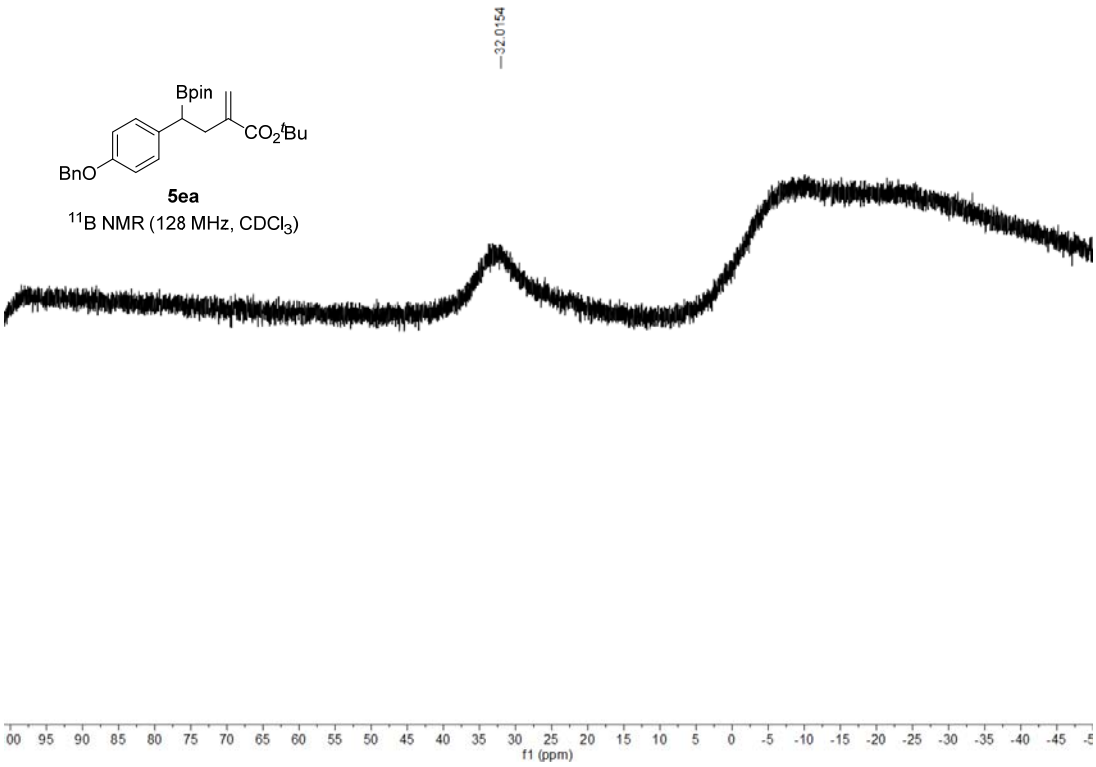


5da

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

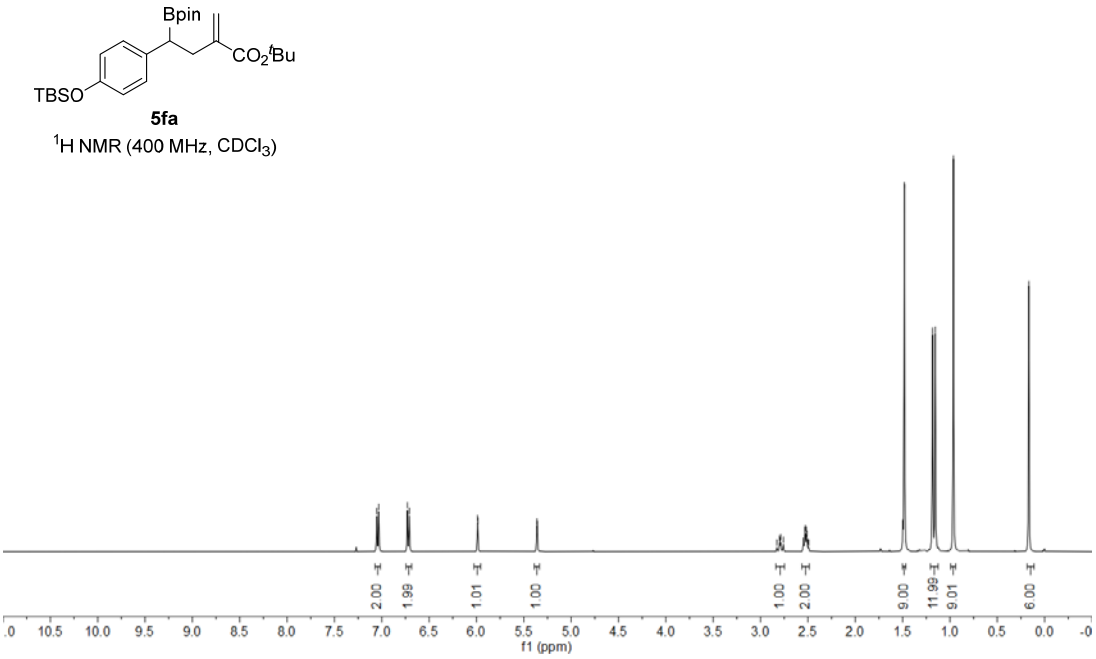

Bpin
CO2tBu
BnO
5ea
1H NMR (400 MHz, CDCl3)
f1 (ppm)

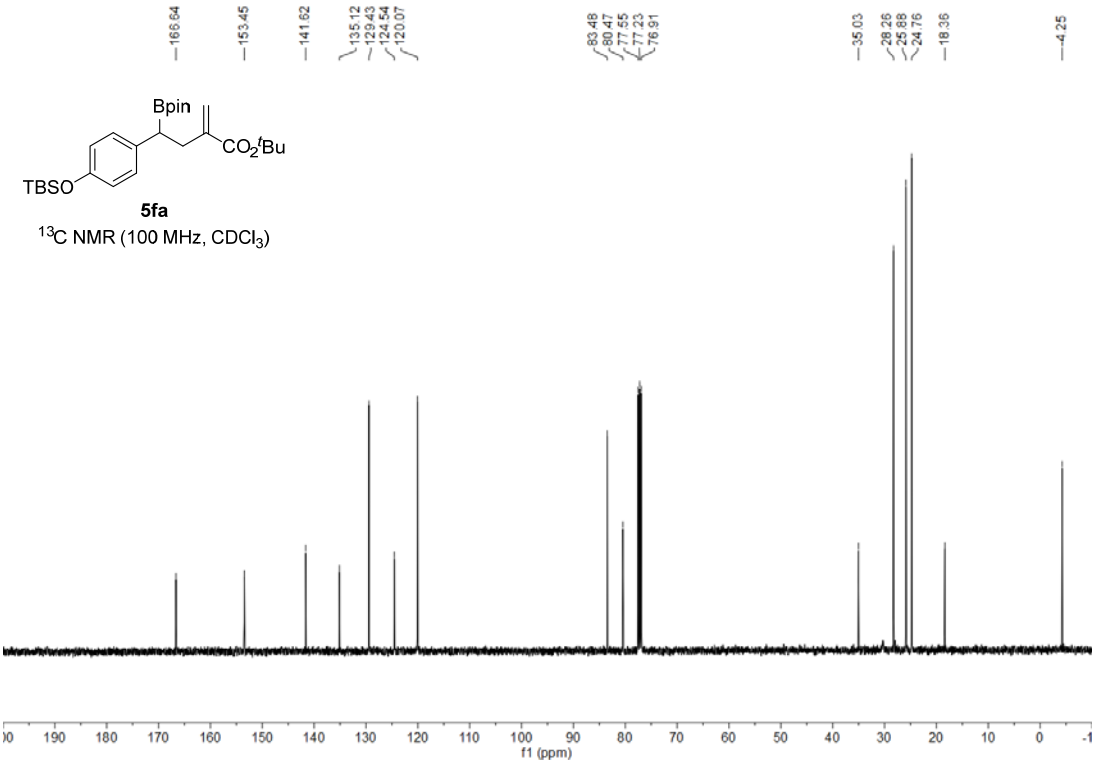

Bpin
CO2tBu
BnO
5ea
13C NMR (100 MHz, CDCl3)
f1 (ppm)

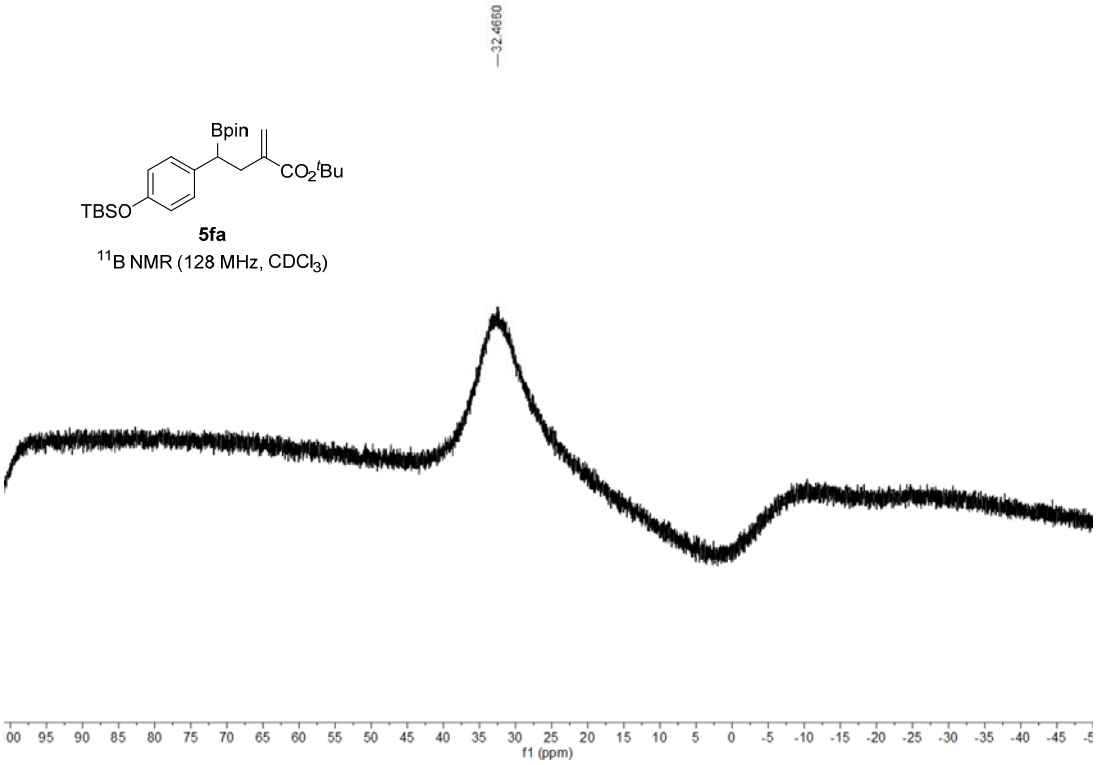


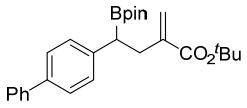
5ea

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


Bpin
CO2tBu
TBSO
5fa
1H NMR (400 MHz, CDCl3)
f1 (ppm)

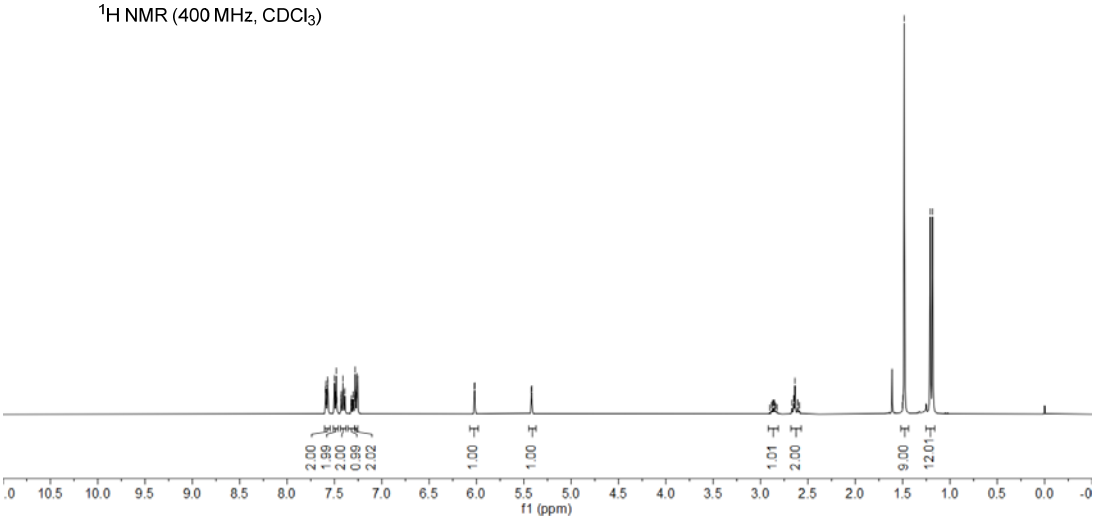

Bpin
CO2tBu
TBSO
5fa
13C NMR (100 MHz, CDCl3)
f1 (ppm)

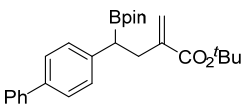

32.4660
Bpin
CO2tBu
TBSO
5fa
11B NMR (128 MHz, CDCl3)
f1 (ppm)



5ga

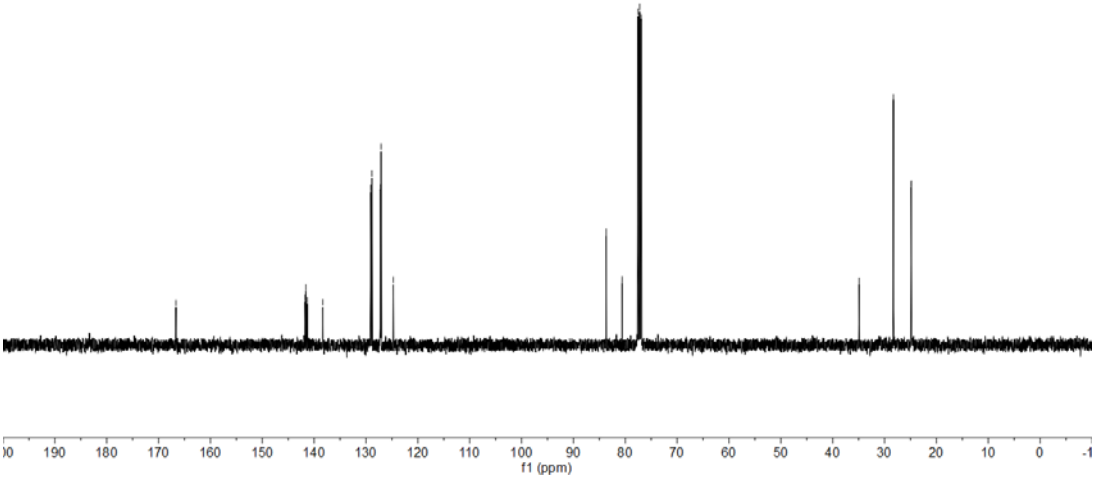
^{1}H NMR (400 MHz, $CDCl_3$)

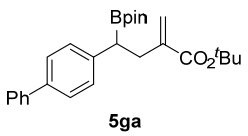




5ga

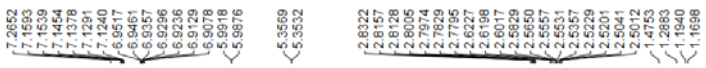
^{13}C NMR (100 MHz, $CDCl_3$)

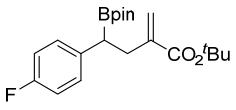




5ga

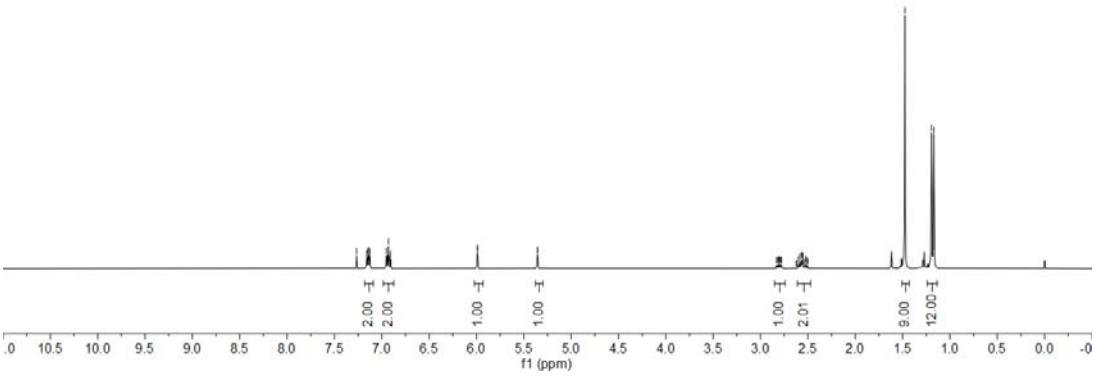
^{11}B NMR (128 MHz, $CDCl_3$)

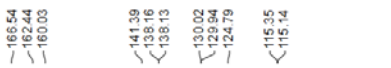


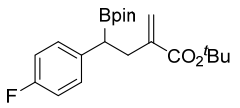


5ha

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

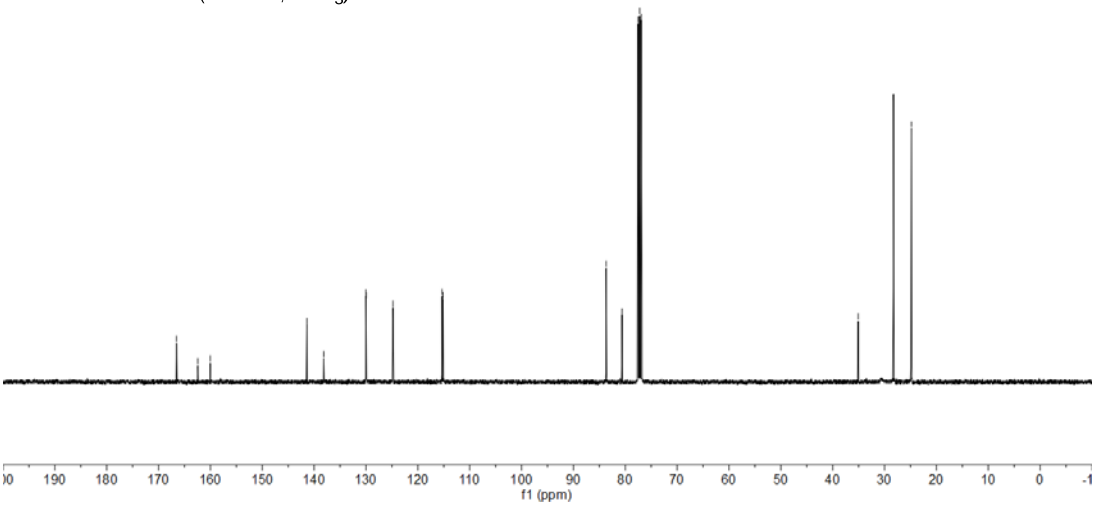


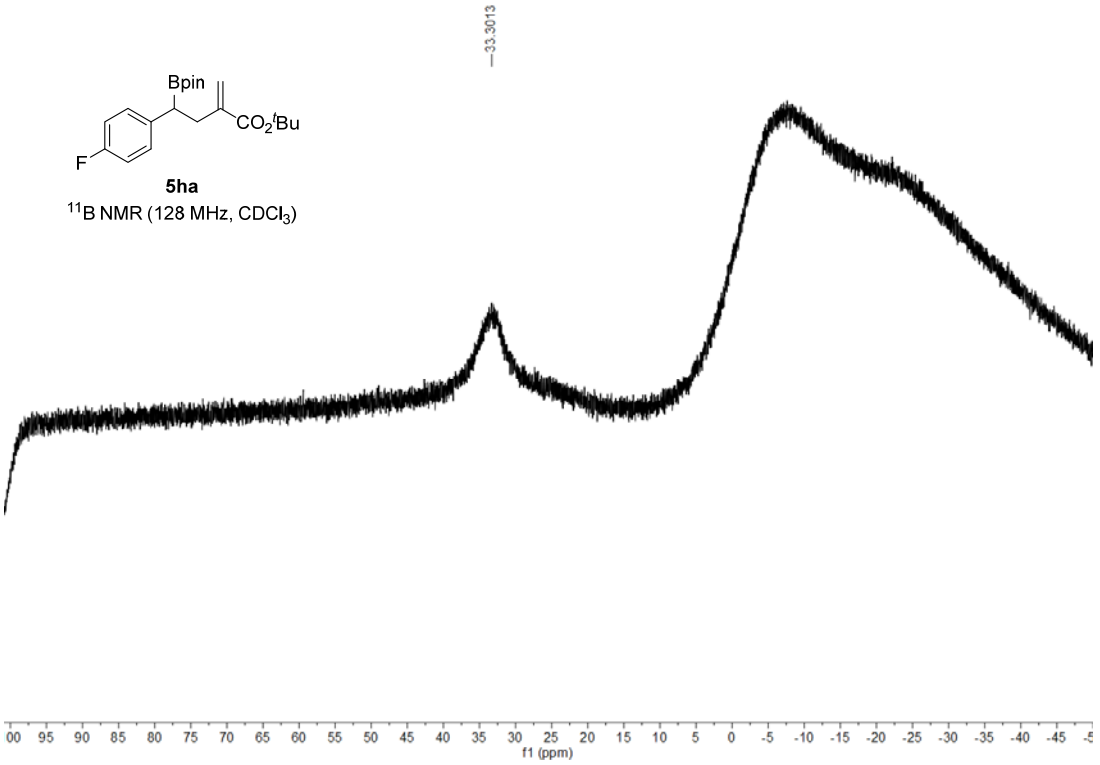


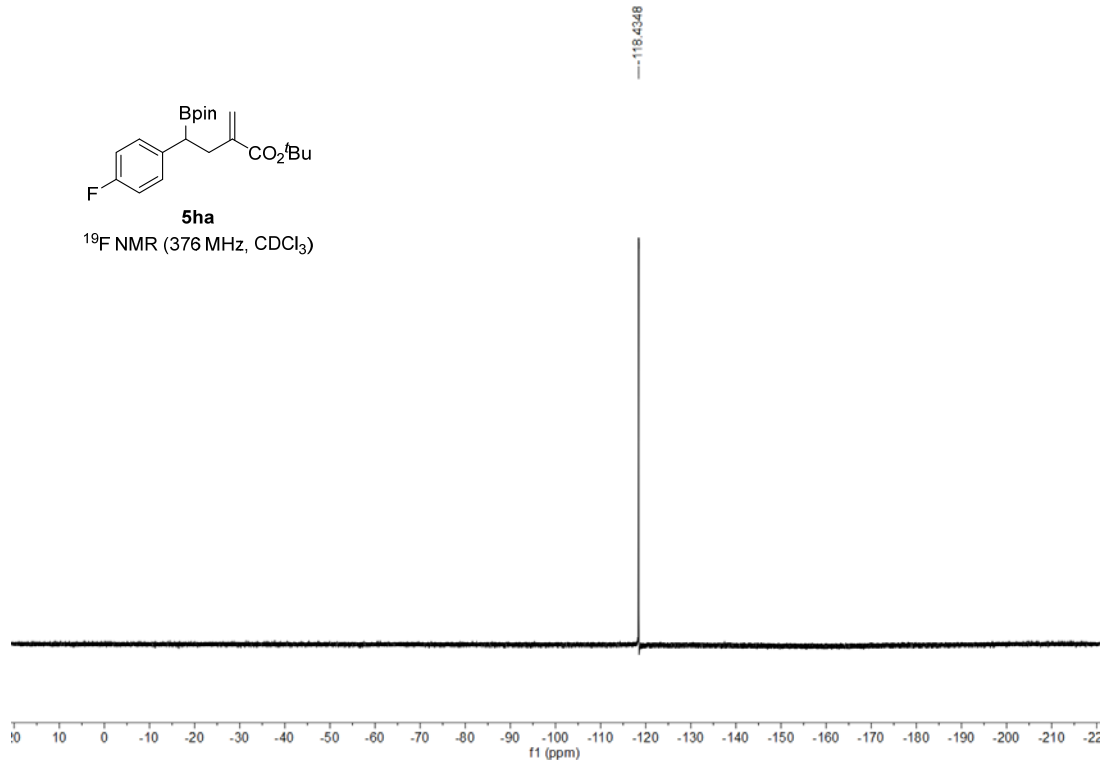


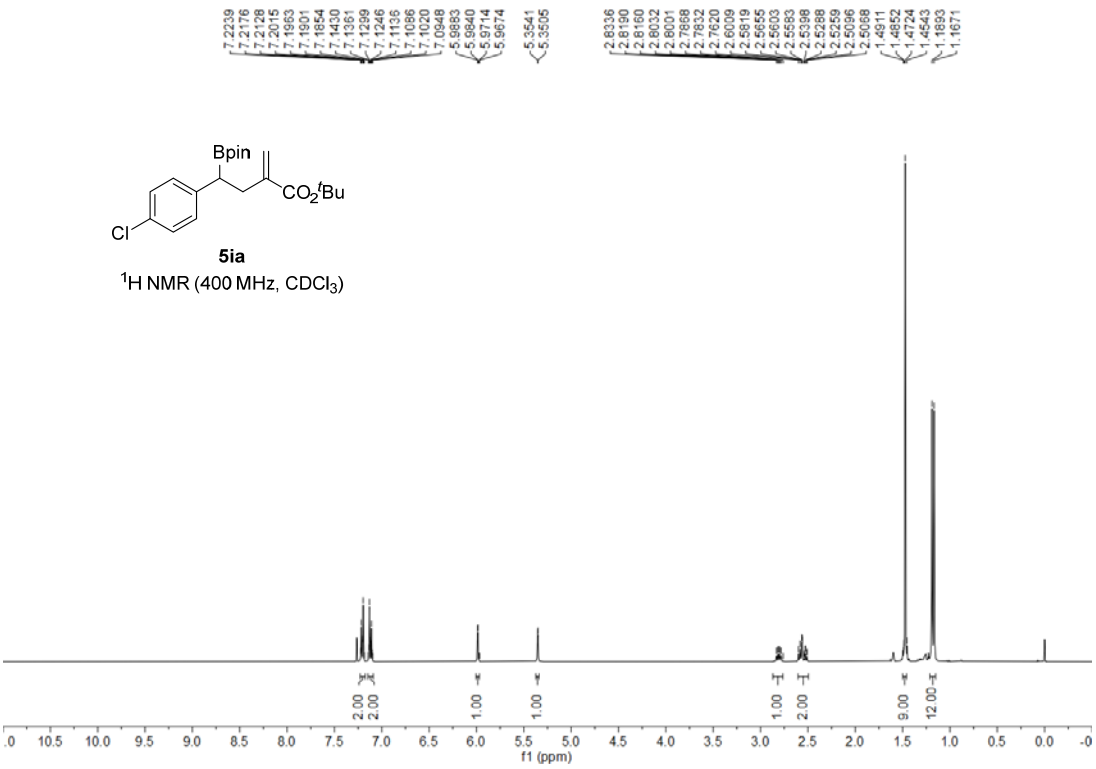
5ha

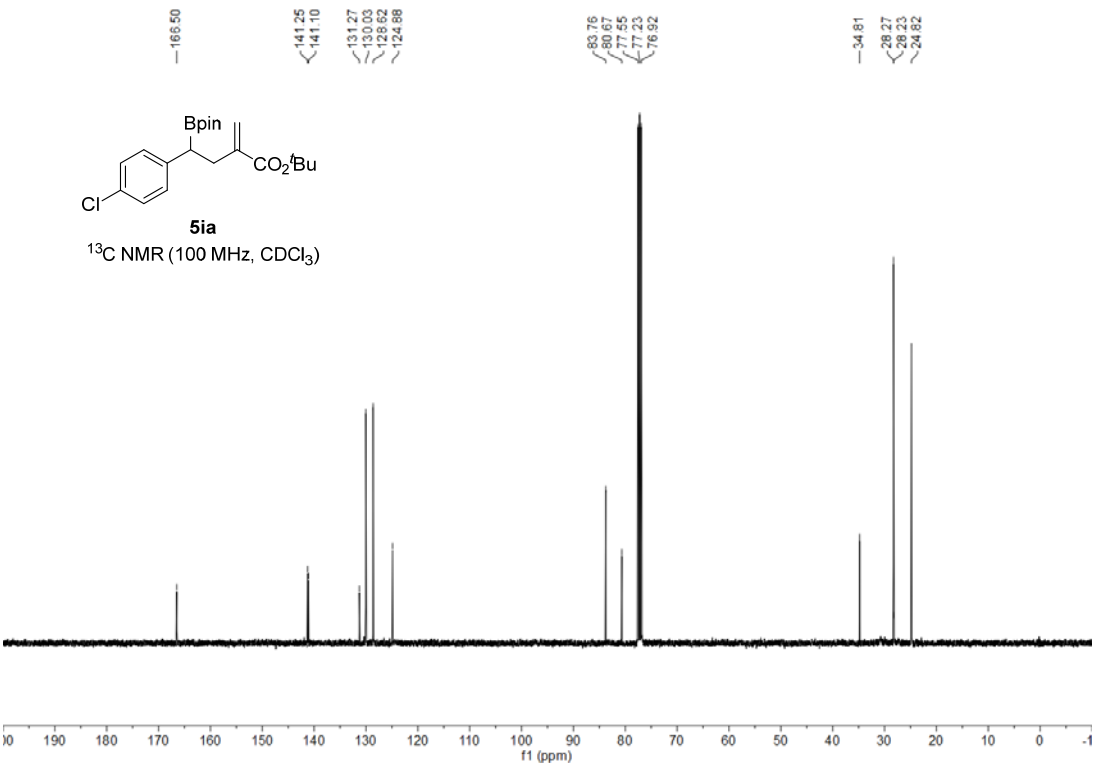
^{13}C NMR (100 MHz, $CDCl_3$)

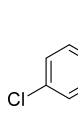



Bpin
CO2tBu
F
5ha
11B NMR (128 MHz, CDCl3)
33.3013
f1 (ppm)


Bpin
CO2tBu
F
5ha
19F NMR (376 MHz, CDCl3)
118.4348
f1 (ppm)

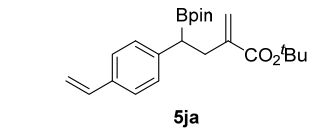

Bpin
CO2tBu
Cl
5ia
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Bpin
CO2tBu
Cl
5ia
13C NMR (100 MHz, CDCl3)
f1 (ppm)



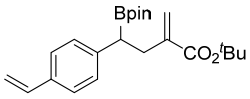
5ia

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



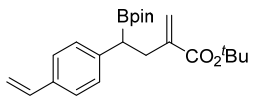
5ja

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



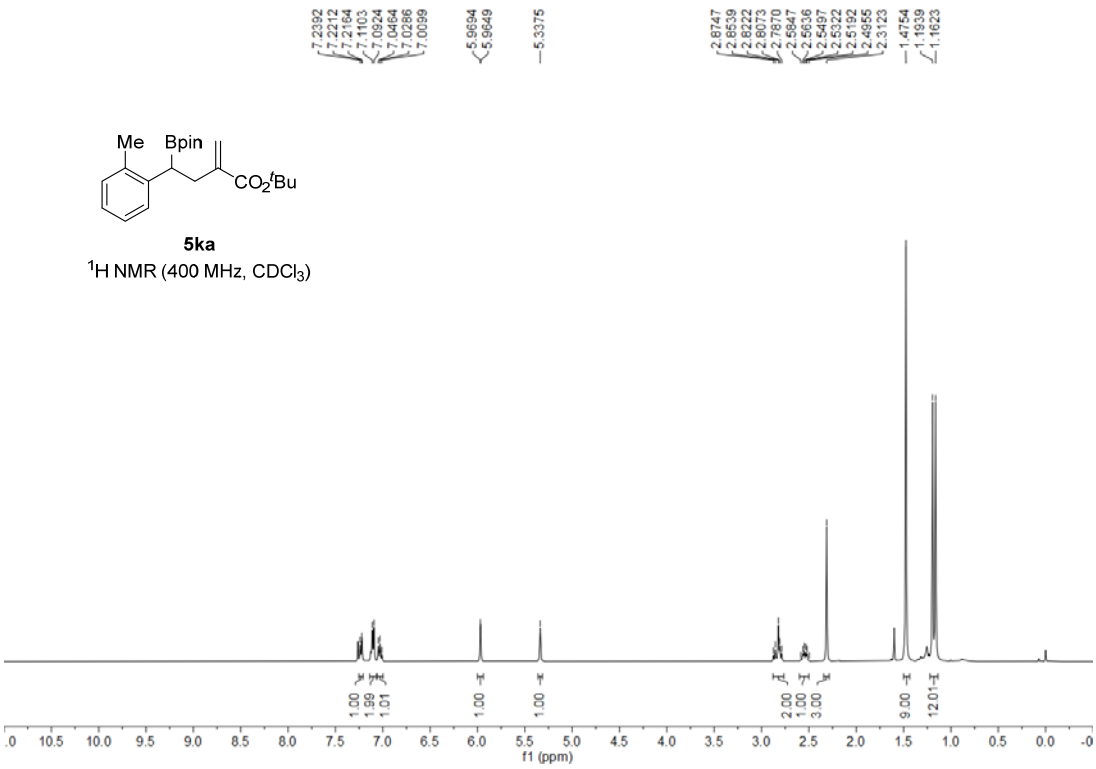
5ja

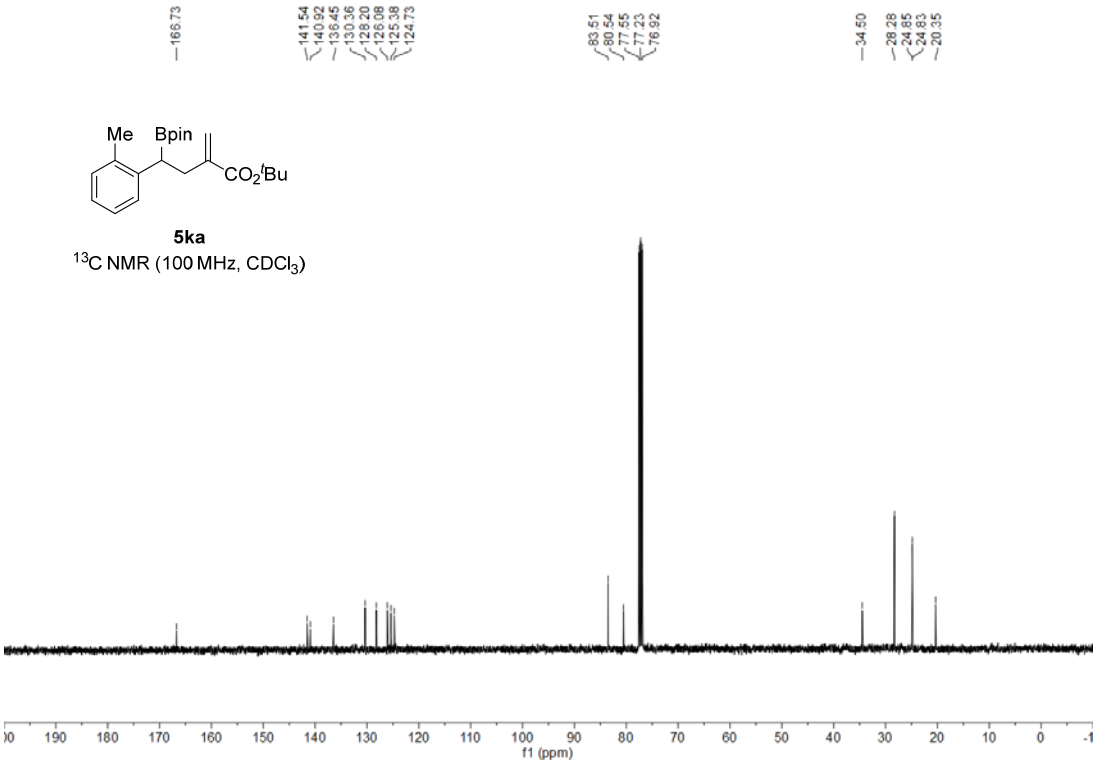
^{13}C NMR (100 MHz, $CDCl_3$)

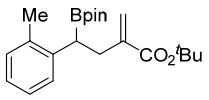


5ja

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

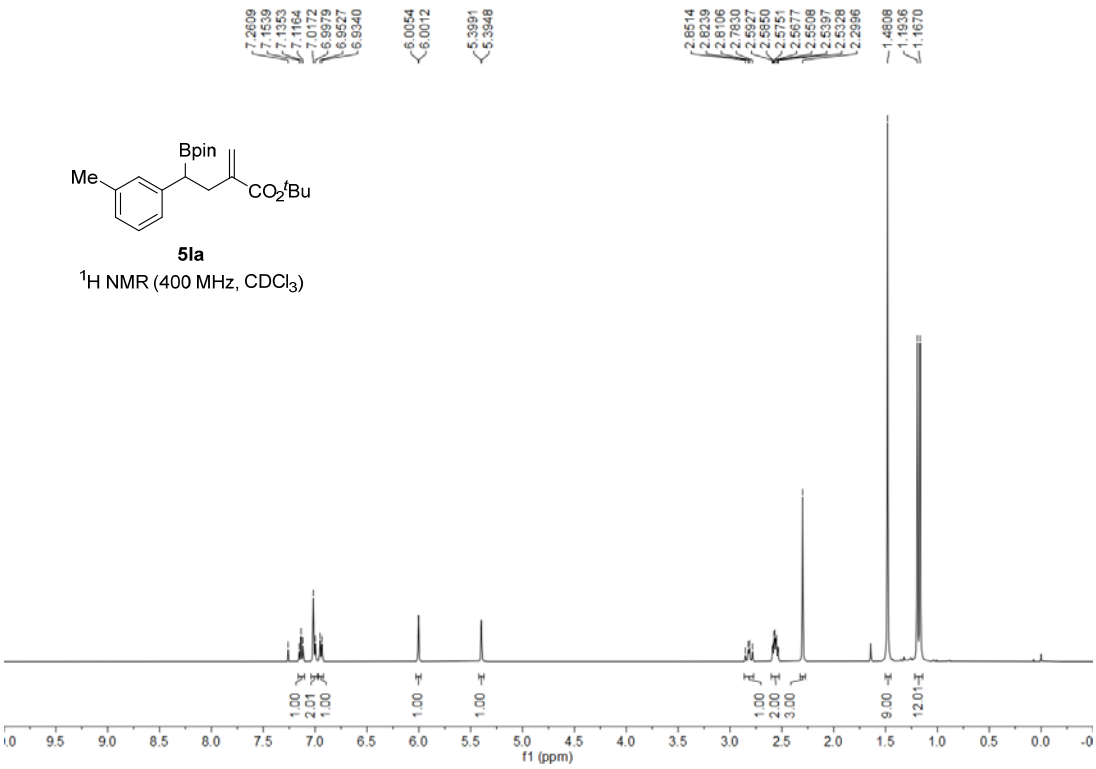

Me
Bpin
CO2tBu
5ka
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Me
Bpin
CO2tBu
5ka
13C NMR (100 MHz, CDCl3)
f1 (ppm)



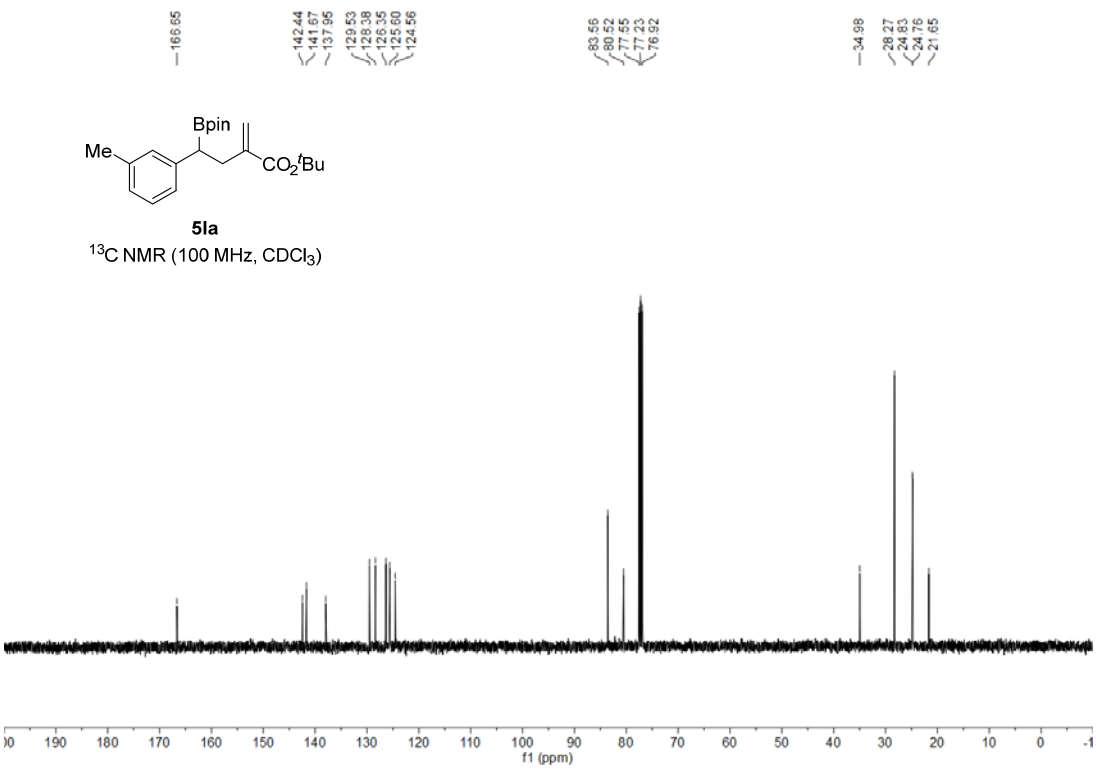
5ka

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



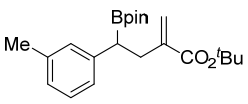
5la

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



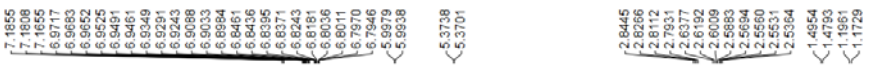
5la

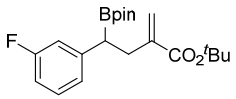
^{13}C NMR (100 MHz, $CDCl_3$)



5la

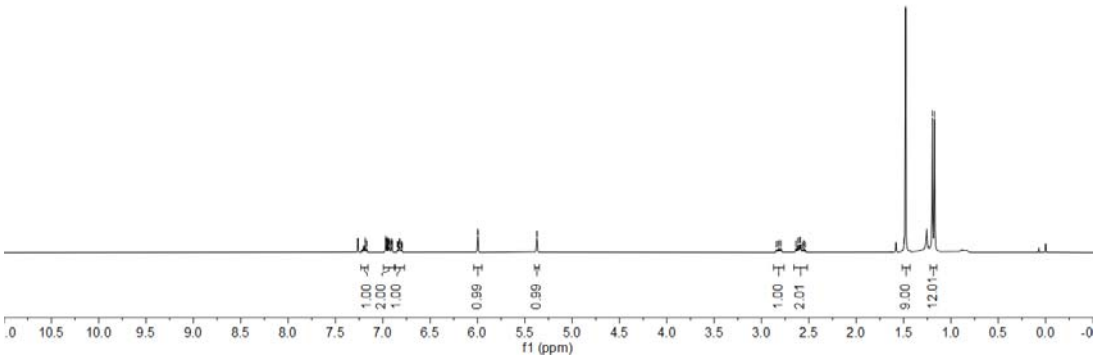
^{11}B NMR (128 MHz, $CDCl_3$)

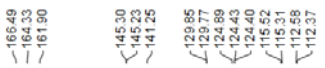


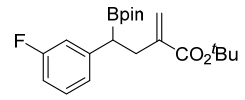


5ma

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

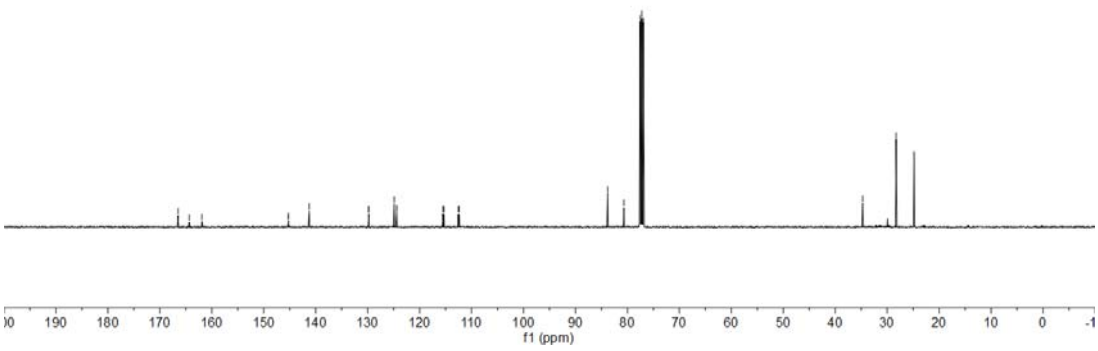


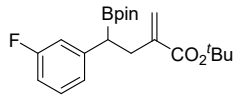




5ma

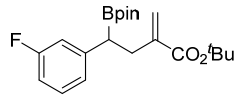
^{13}C NMR (100 MHz, $CDCl_3$)





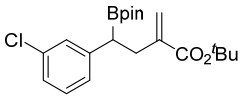
5ma

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



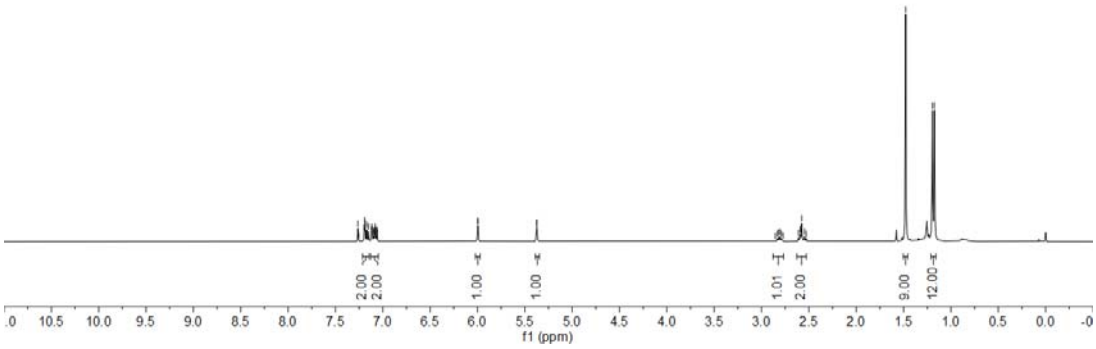
5ma

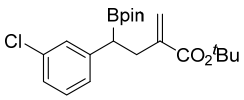
^{19}F NMR (376 MHz, $CDCl_3$)



5na

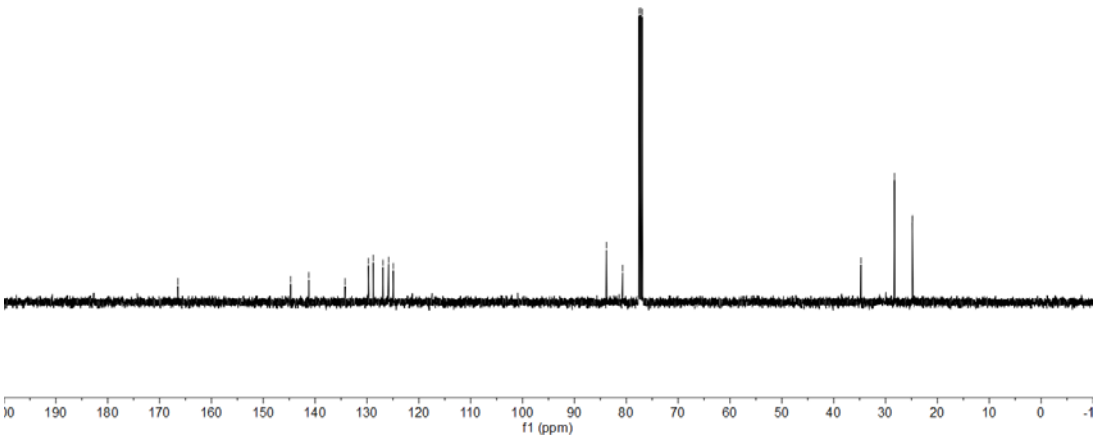
^{1}H NMR (400 MHz, $CDCl_3$)

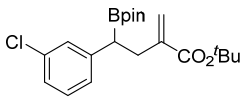




5na

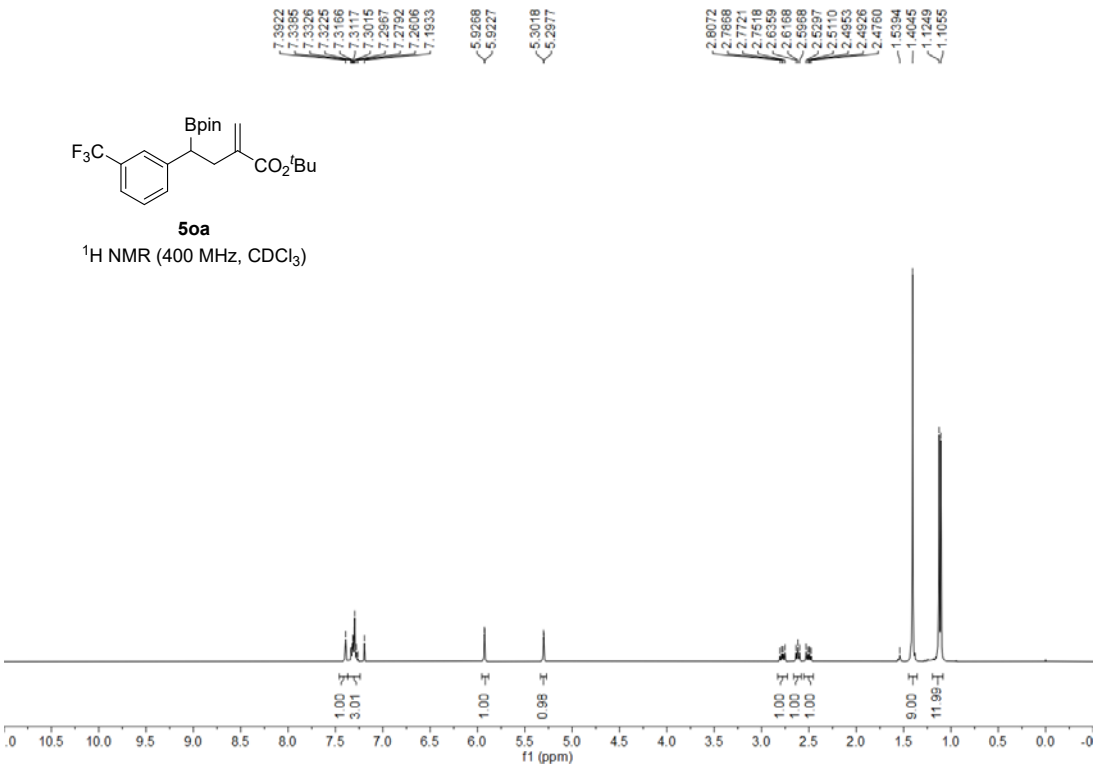
^{13}C NMR (100 MHz, $CDCl_3$)

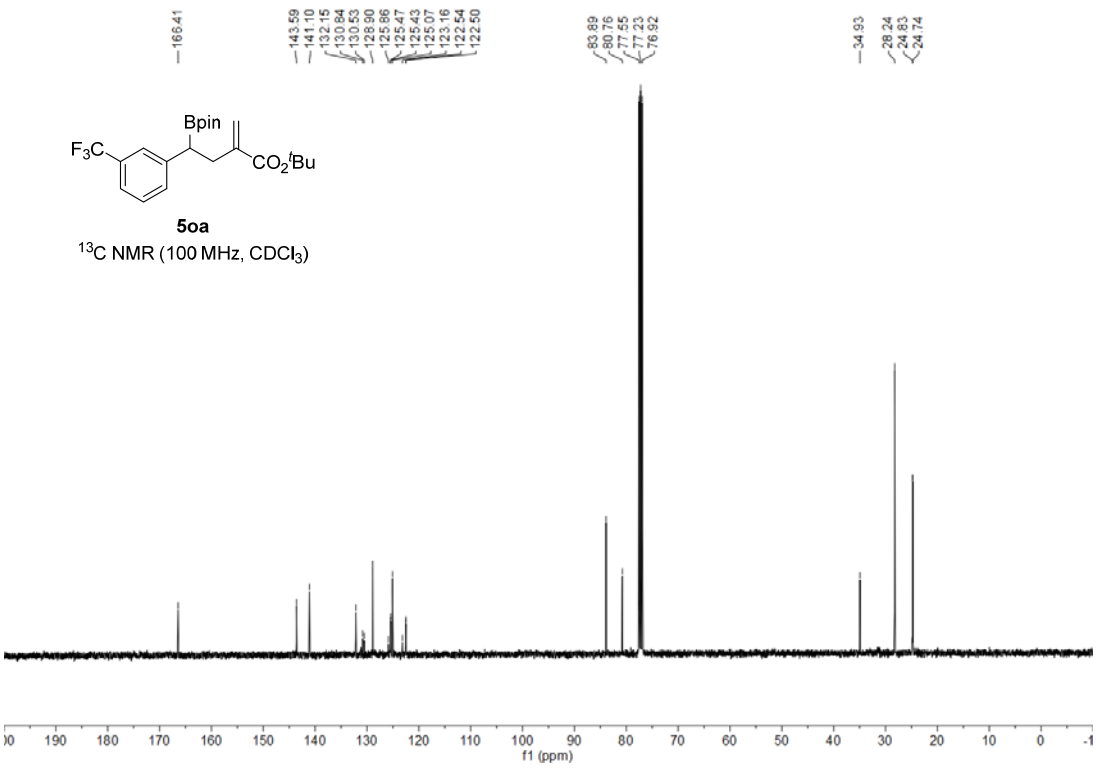


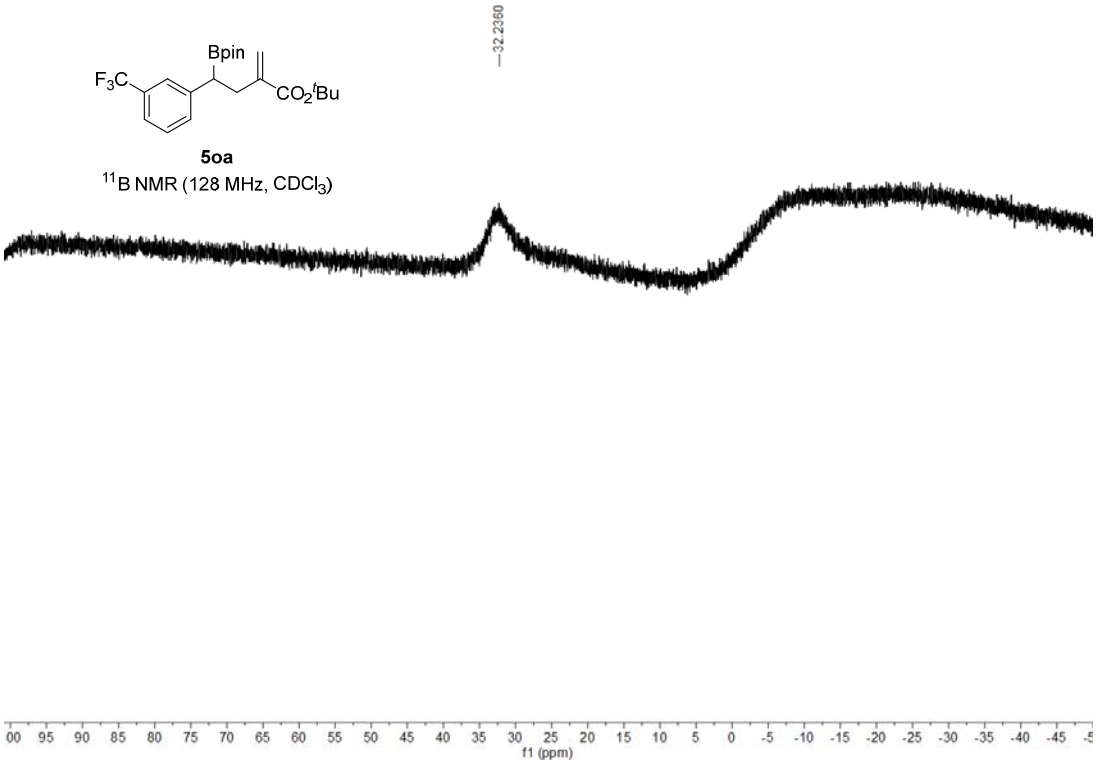


5na

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

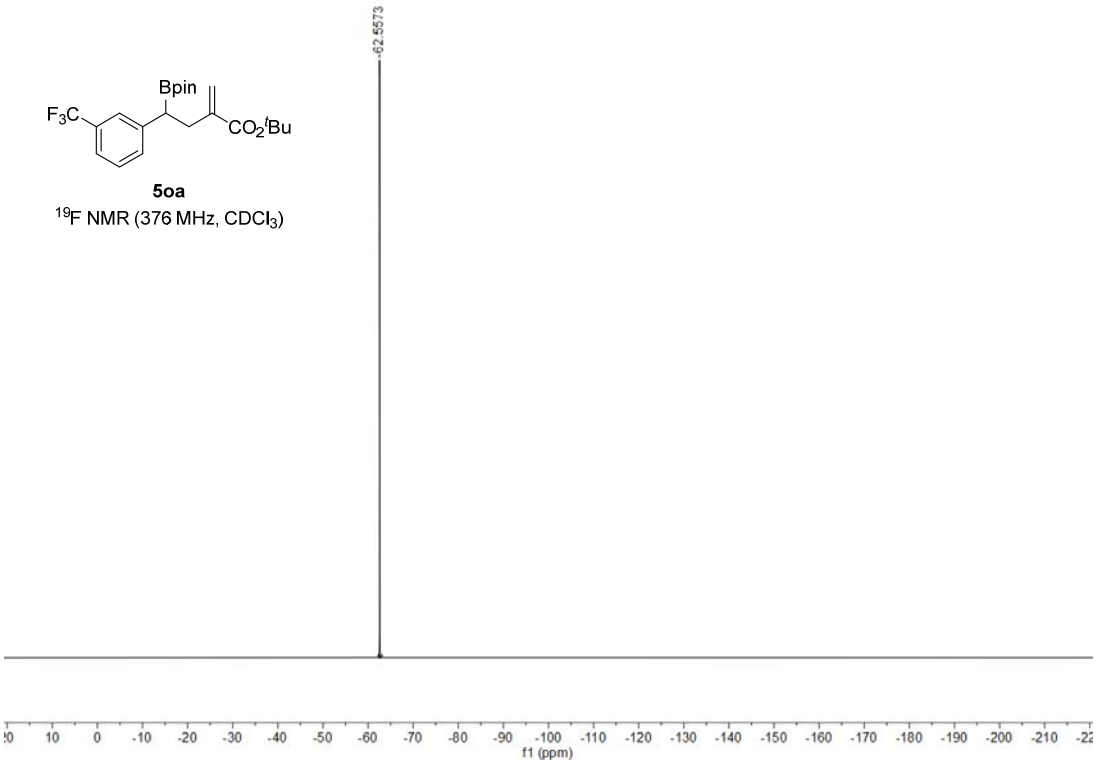

Bpin
F3C
CO2tBu
5oa
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Bpin
F3C
CO2tBu
5oa
13C NMR (100 MHz, CDCl3)
f1 (ppm)



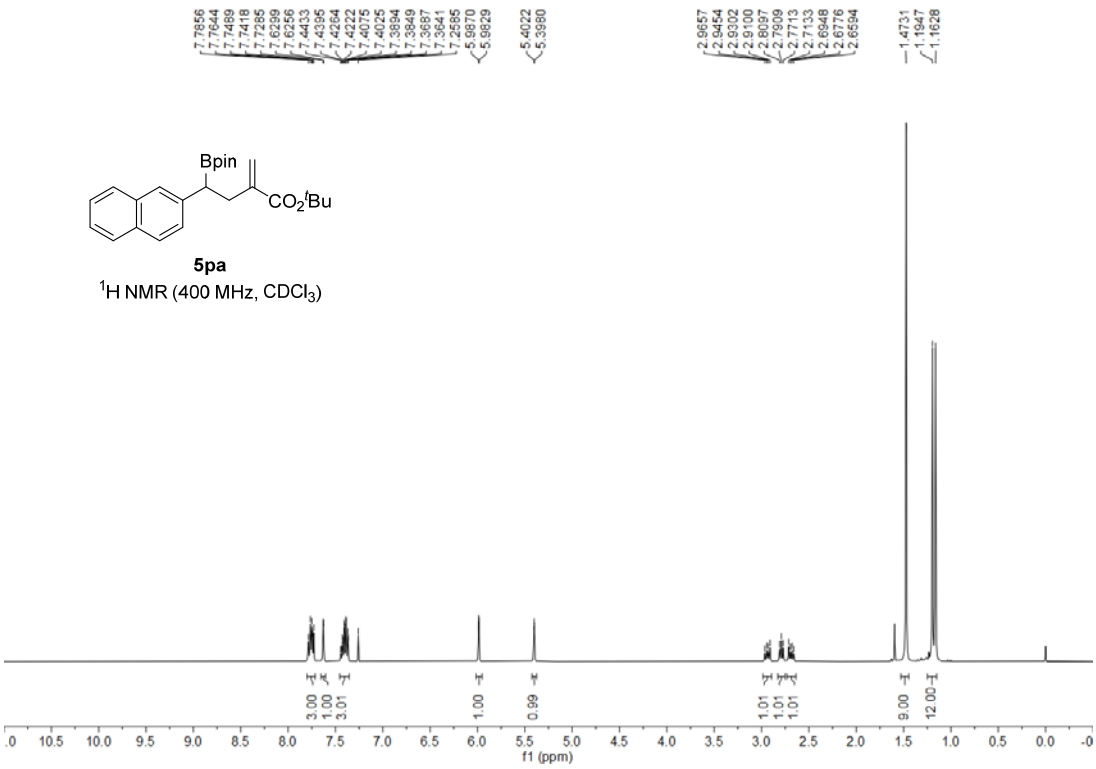
5oa

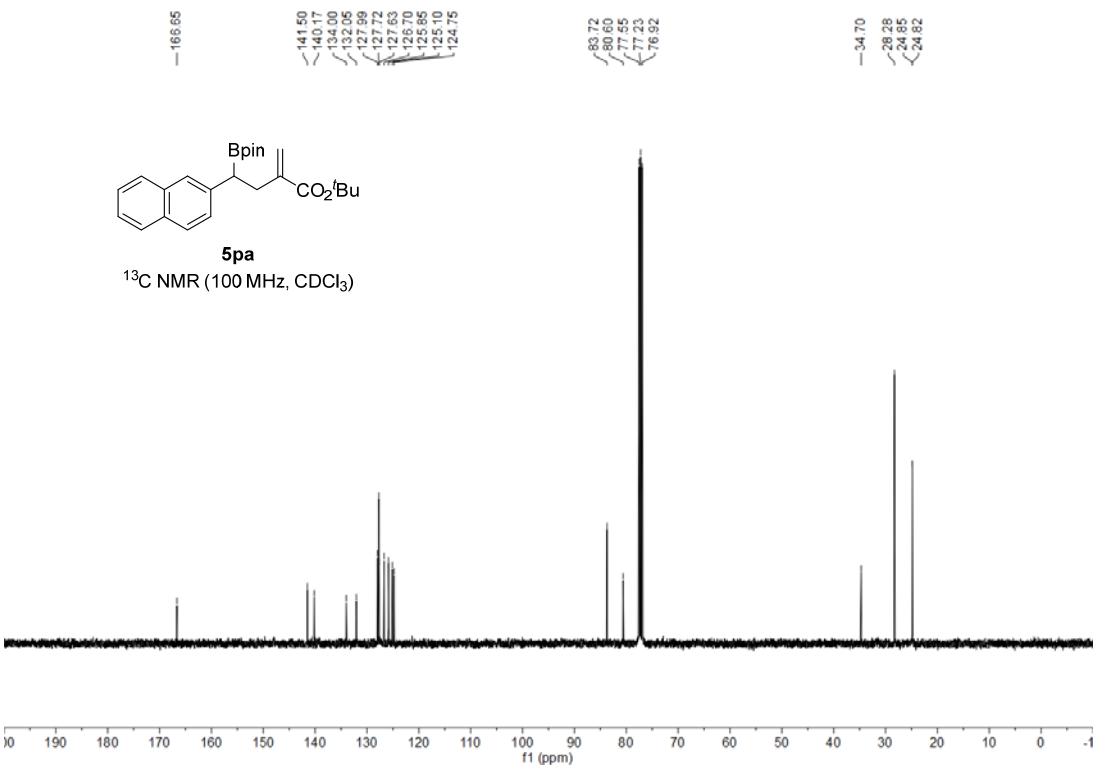
^{11}B NMR (128 MHz, $CDCl_3$)

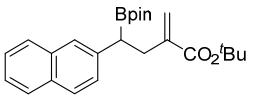


5oa

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

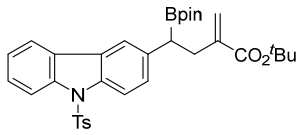

Bpin
CO2tBu
5pa
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Bpin
CO2tBu
5pa
13C NMR (100 MHz, CDCl3)
f1 (ppm)



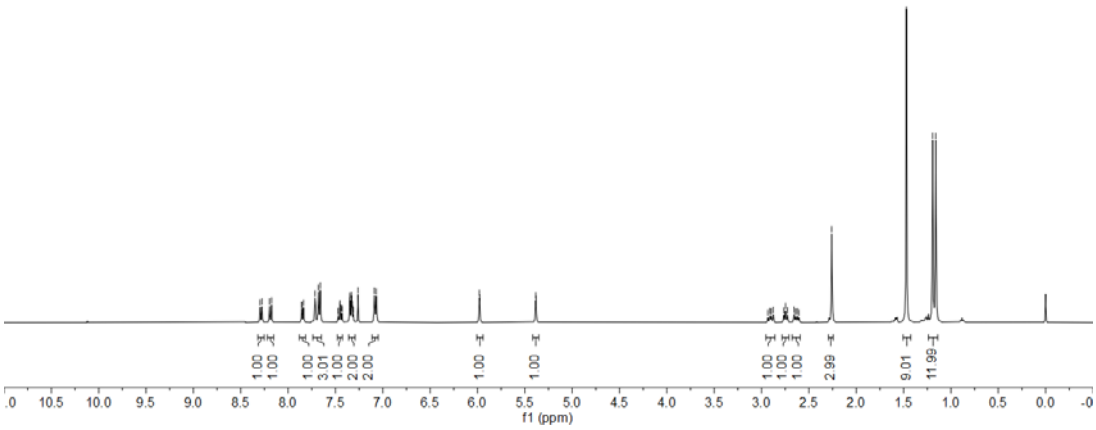
5pa

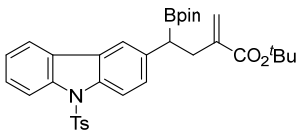
^{11}B NMR (128 MHz, $CDCl_3$)



5qa

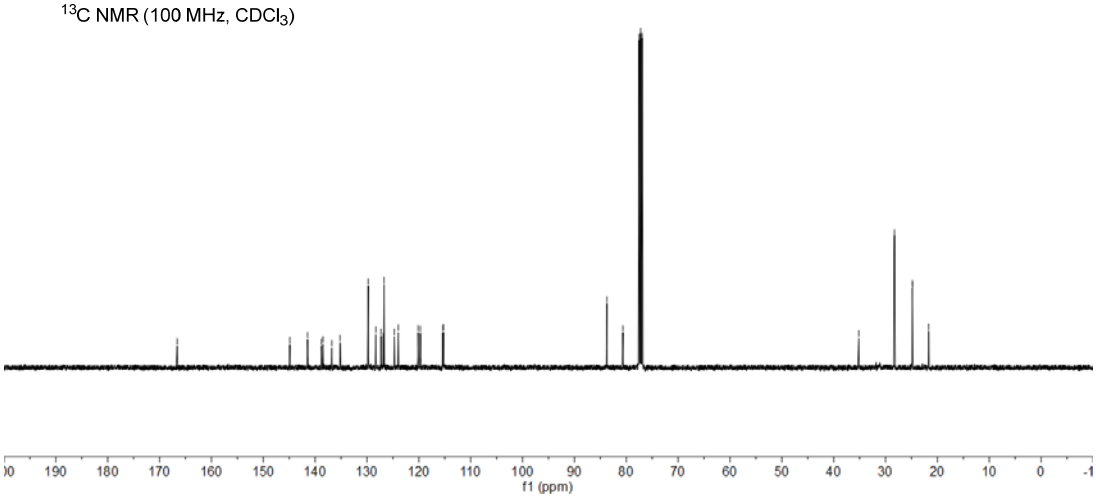
^{1}H NMR (400 MHz, $CDCl_3$)

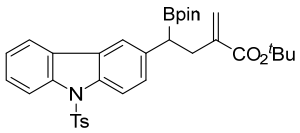




5qa

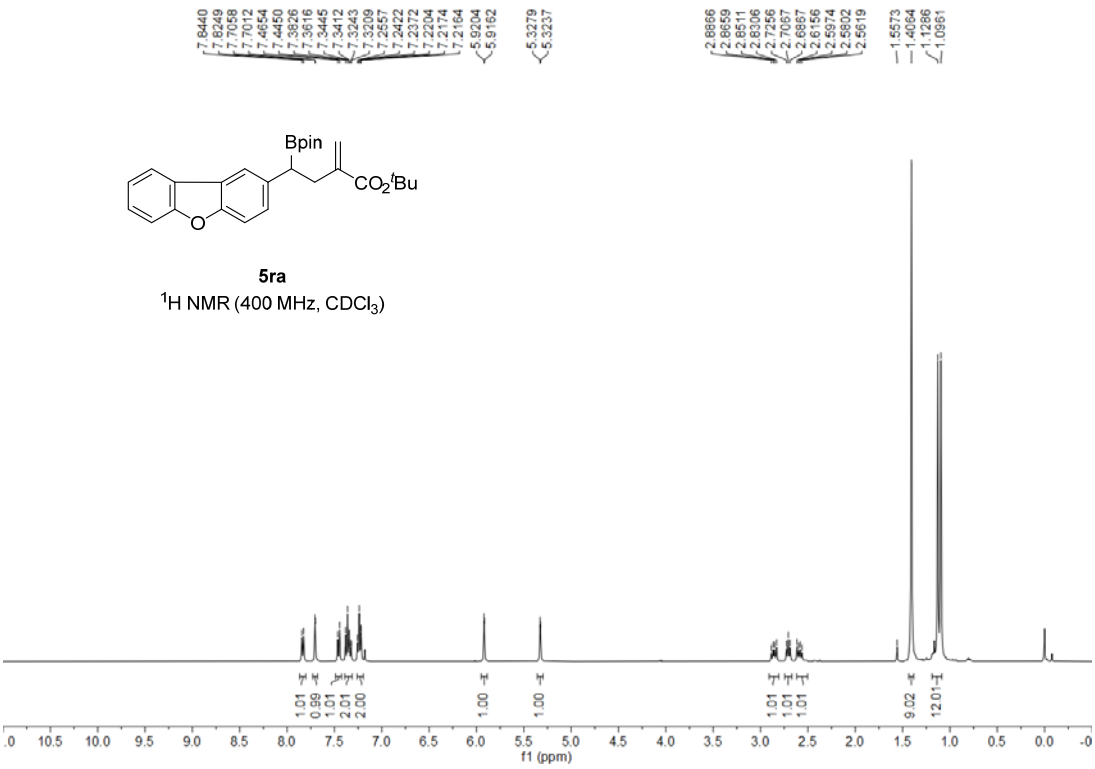
^{13}C NMR (100 MHz, $CDCl_3$)





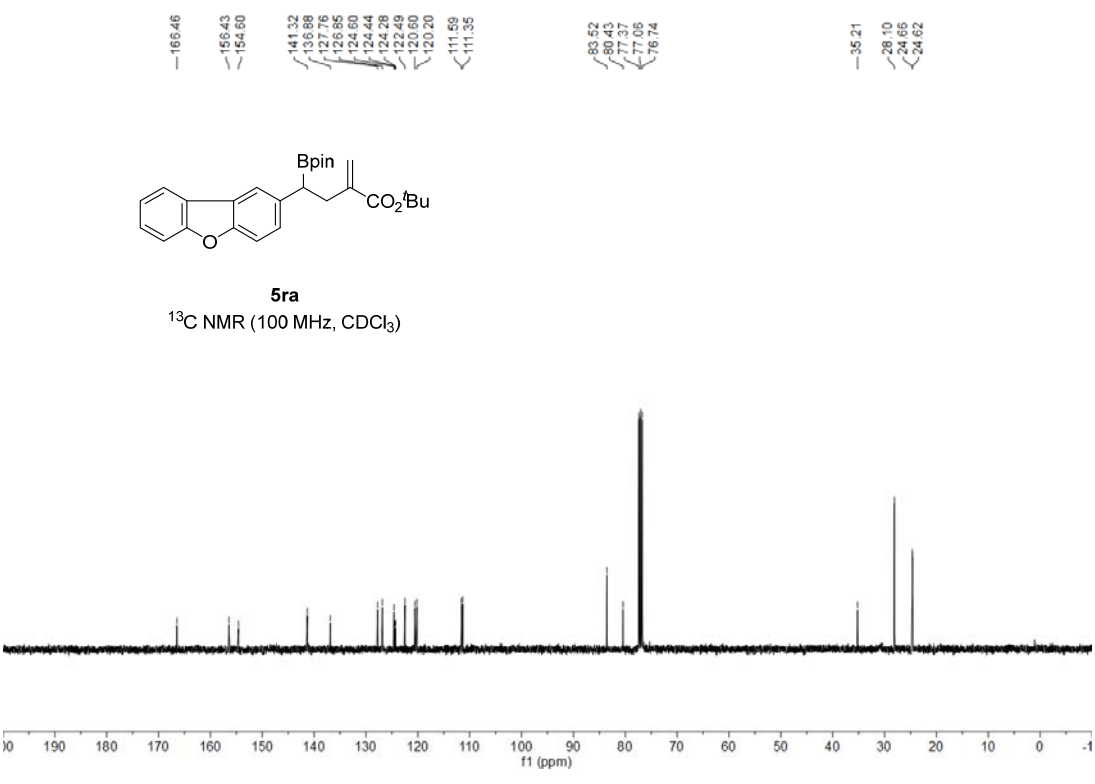
5qa

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



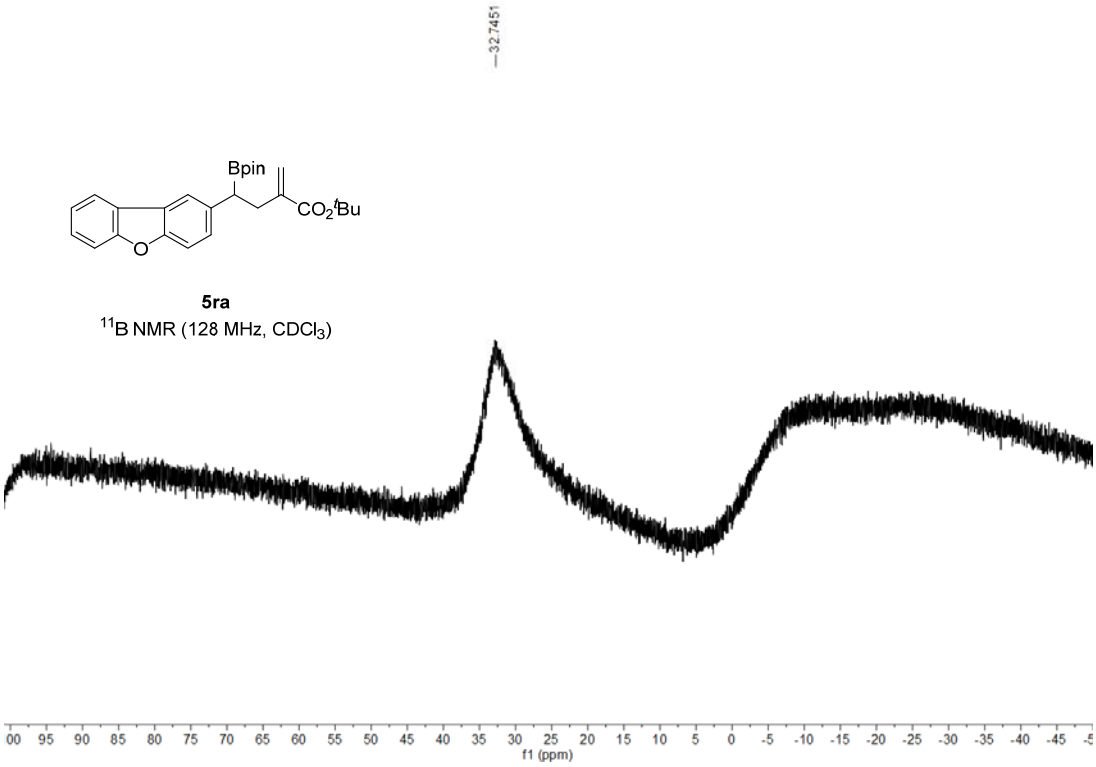
5ra

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



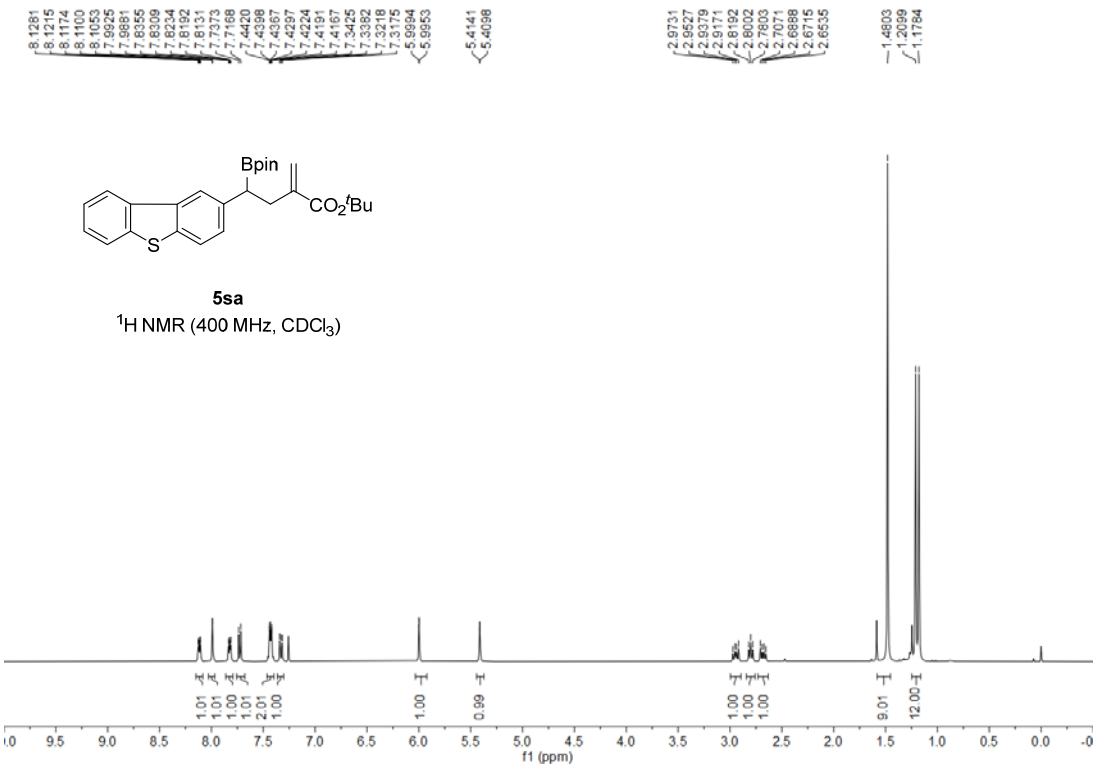
5ra

^{13}C NMR (100 MHz, $CDCl_3$)



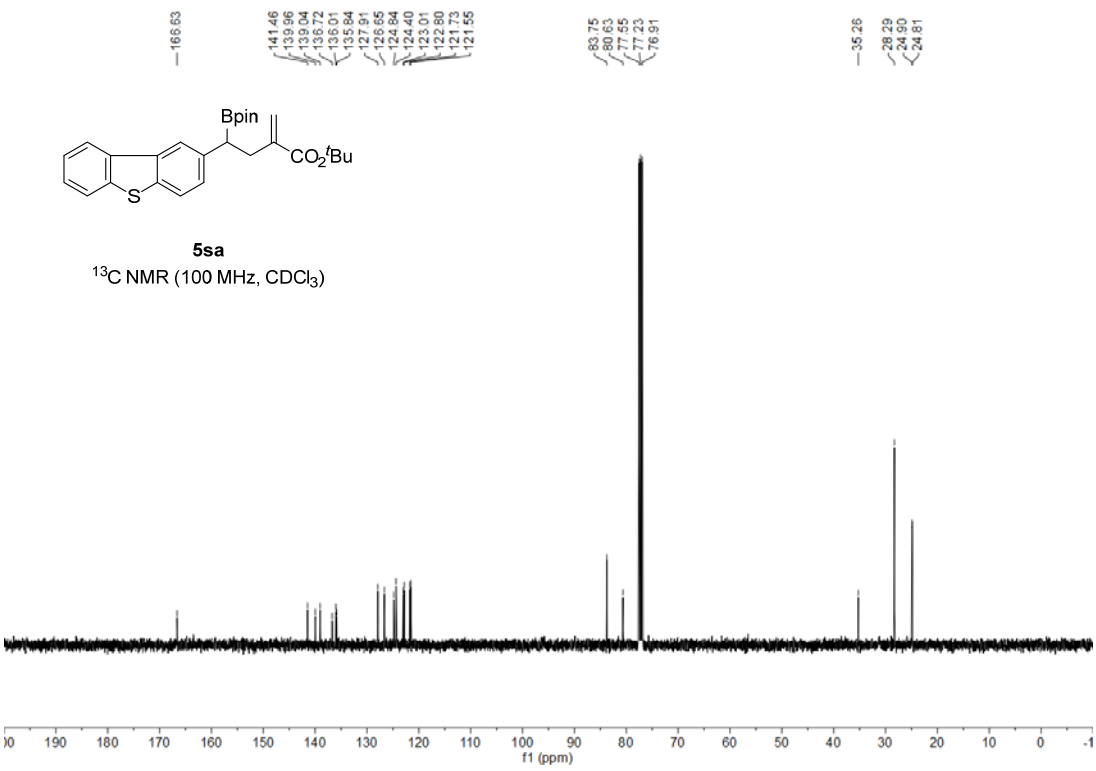
5ra

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



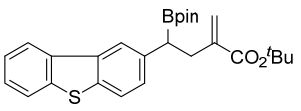
5sa

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



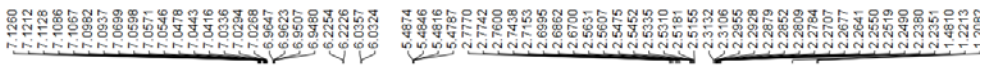
5sa

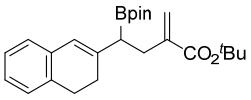
^{13}C NMR (100 MHz, $CDCl_3$)



5sa

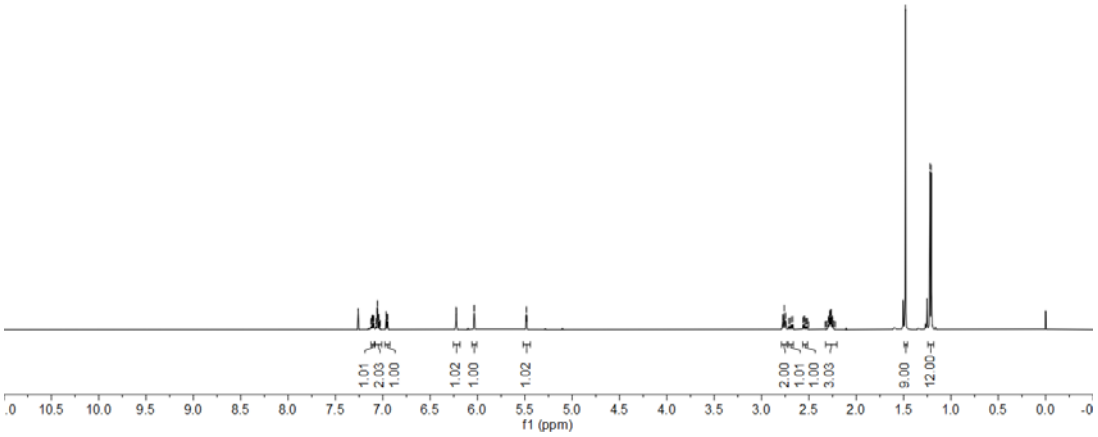
^{11}B NMR (128 MHz, $CDCl_3$)

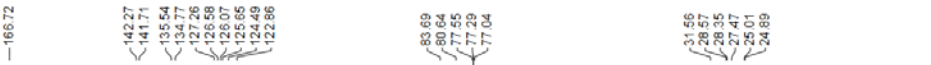


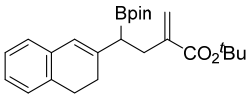


5ta

^{1}H NMR (500 MHz, $CDCl_3$)

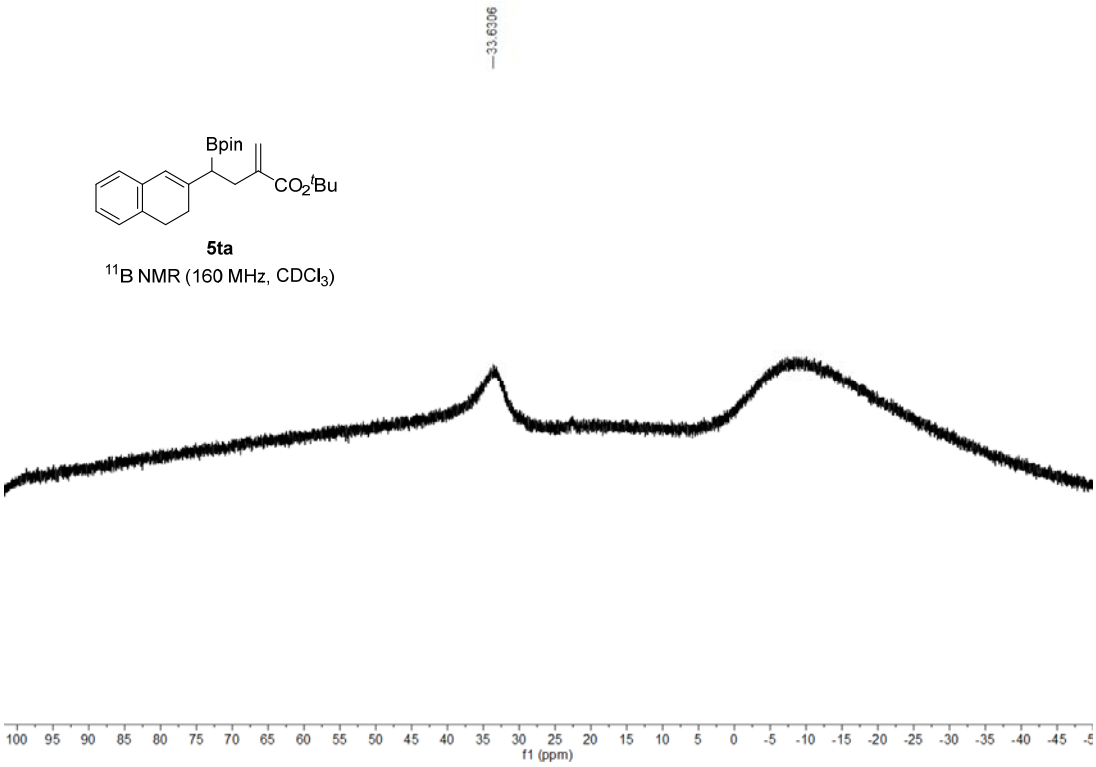






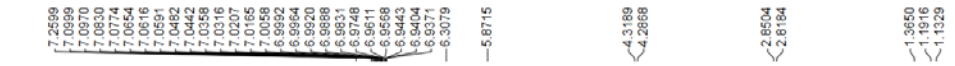
5ta

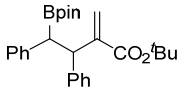
^{13}C NMR (125 MHz, $CDCl_3$)



5ta

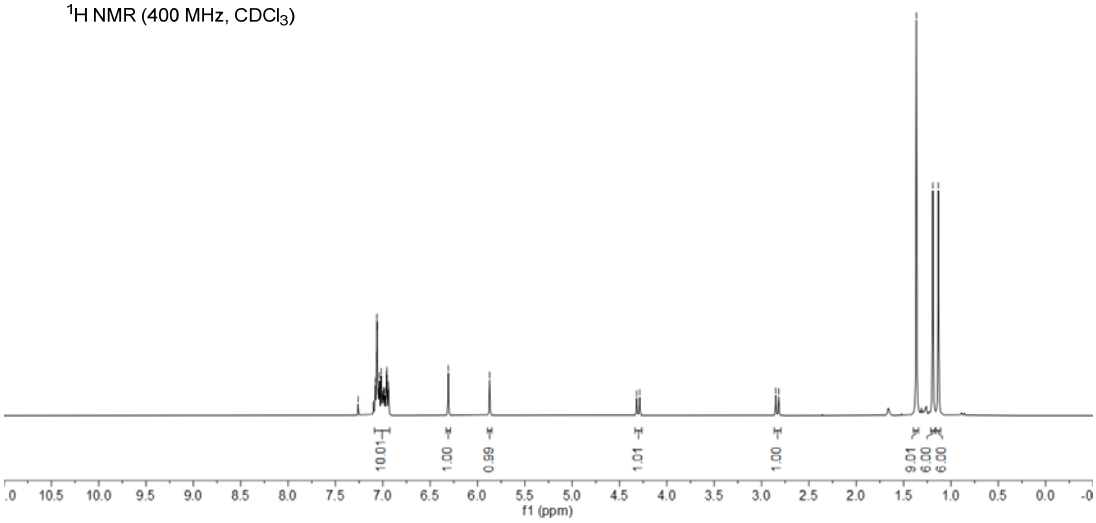
^{11}B NMR (160 MHz, $CDCl_3$)

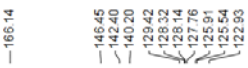


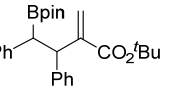


5ae major

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

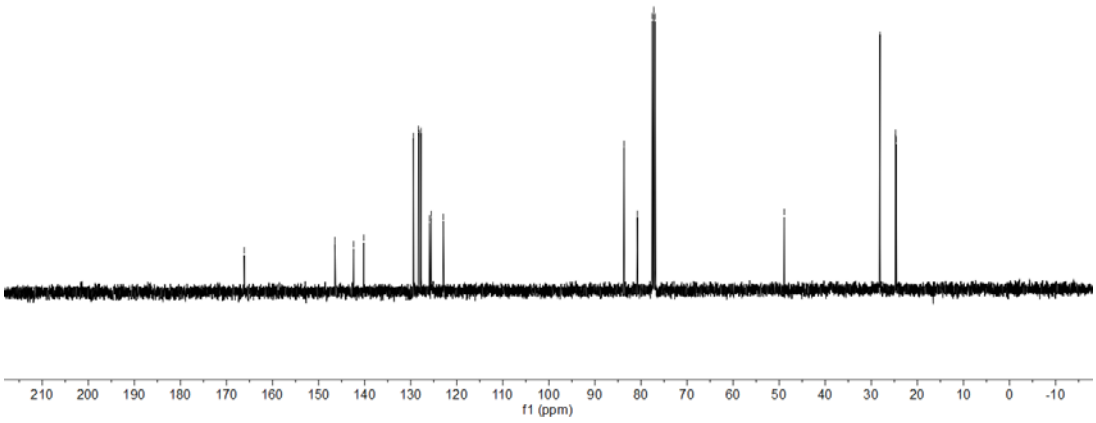


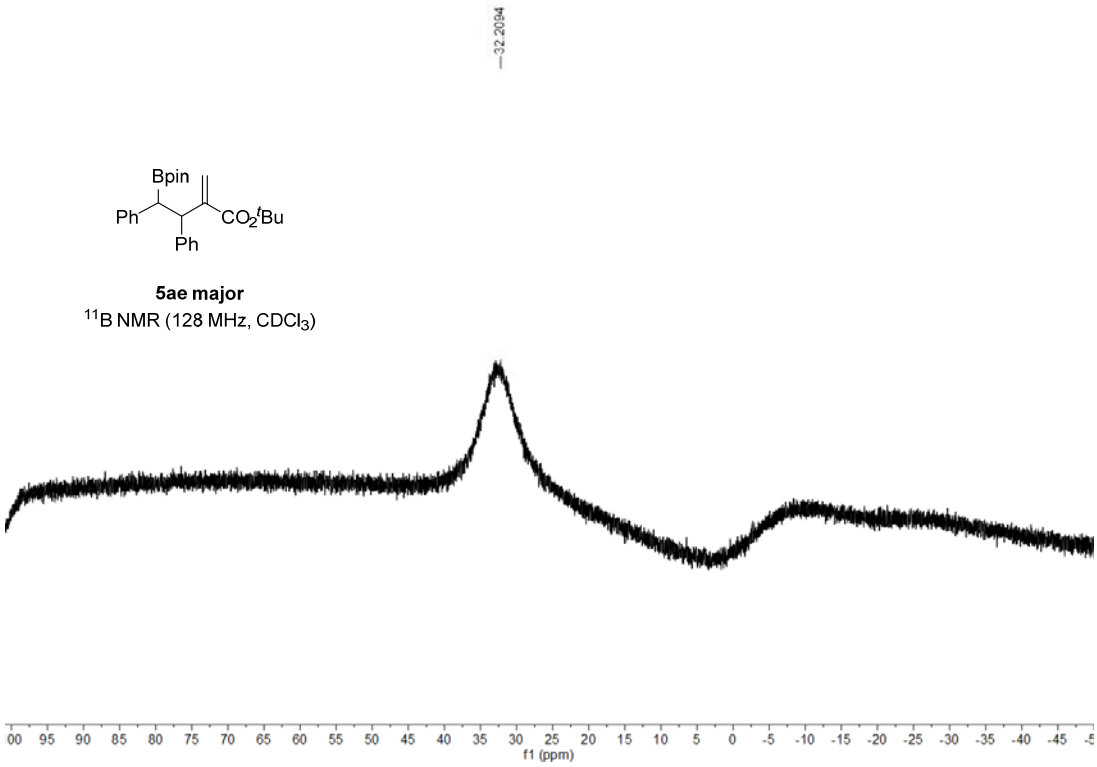




5ae major

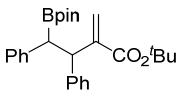
^{13}C NMR (100 MHz, $CDCl_3$)





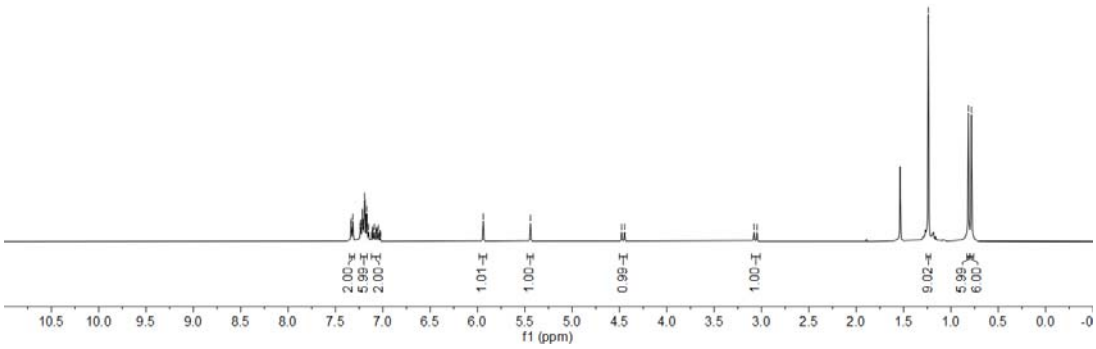
5ae major

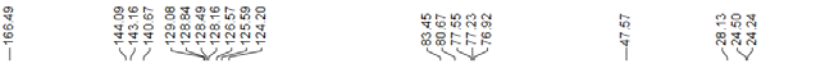
^{11}B NMR (128 MHz, $CDCl_3$)

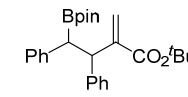


5ae minor

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

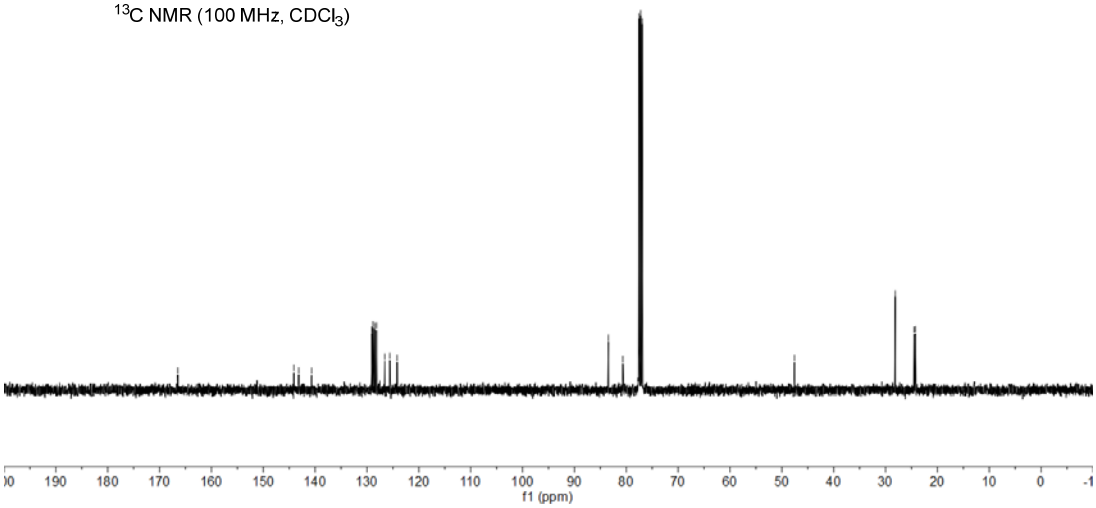


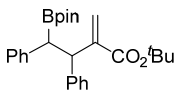




5ae minor

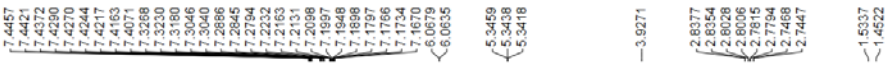
^{13}C NMR (100 MHz, $CDCl_3$)

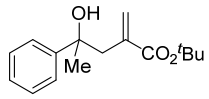




5ae minor

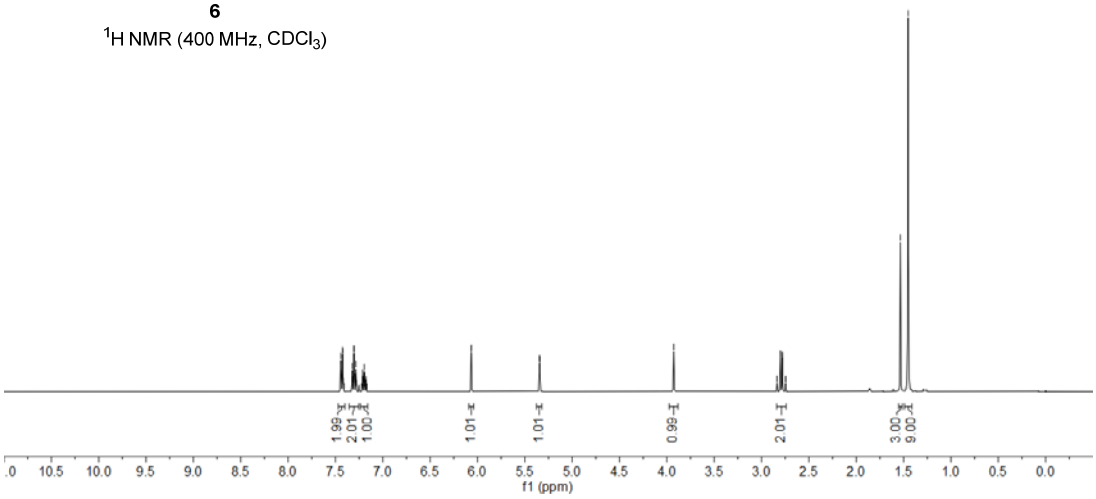
^{11}B NMR (128 MHz, $CDCl_3$)

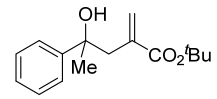




6

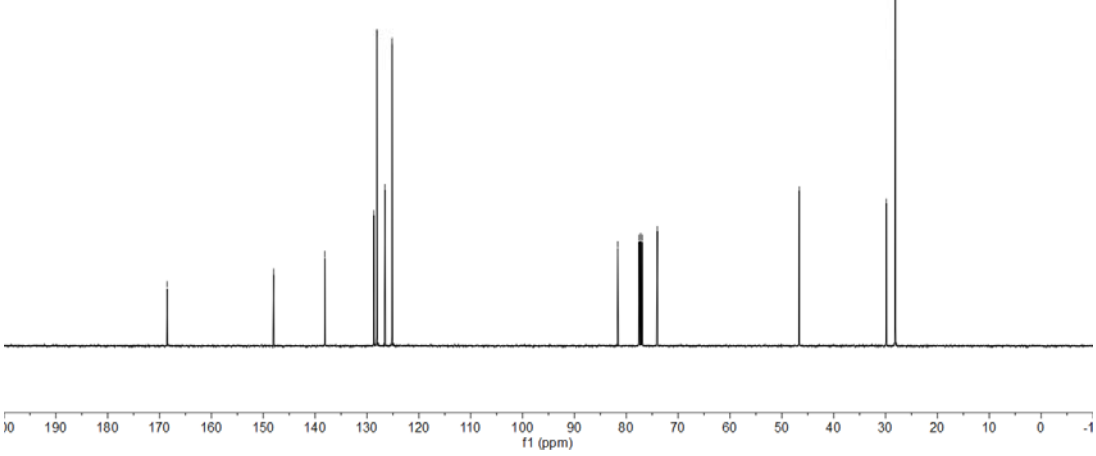
^{1}H NMR (400 MHz, $CDCl_3$)

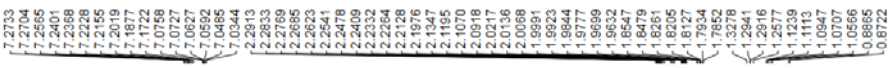


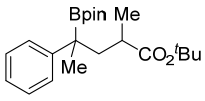


6

^{13}C NMR (100 MHz, $CDCl_3$)

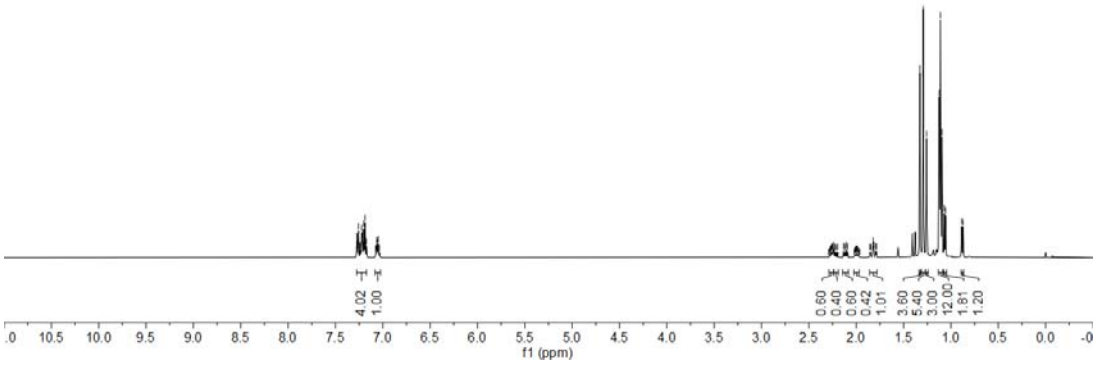


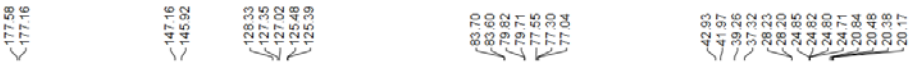


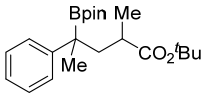


7

^{1}H NMR (500 MHz, $CDCl_3$)

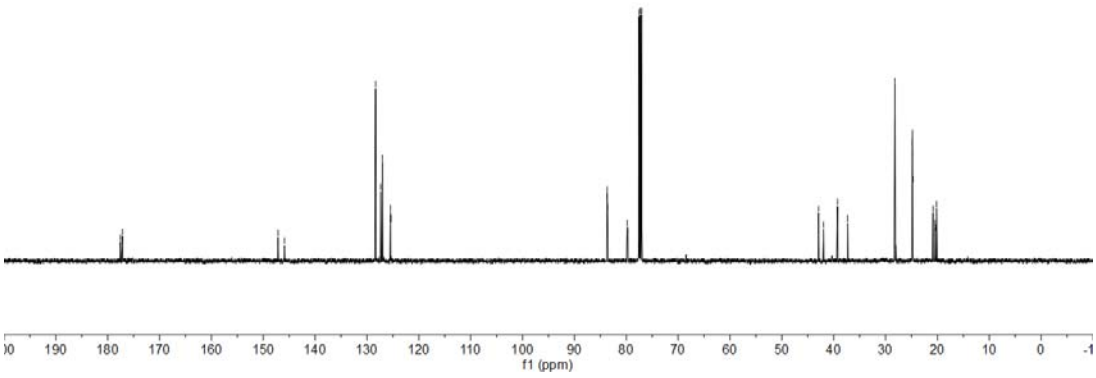


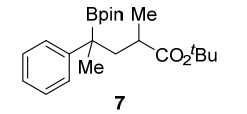




7

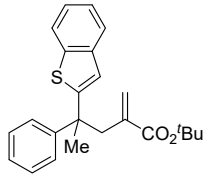
^{13}C NMR (125 MHz, $CDCl_3$)





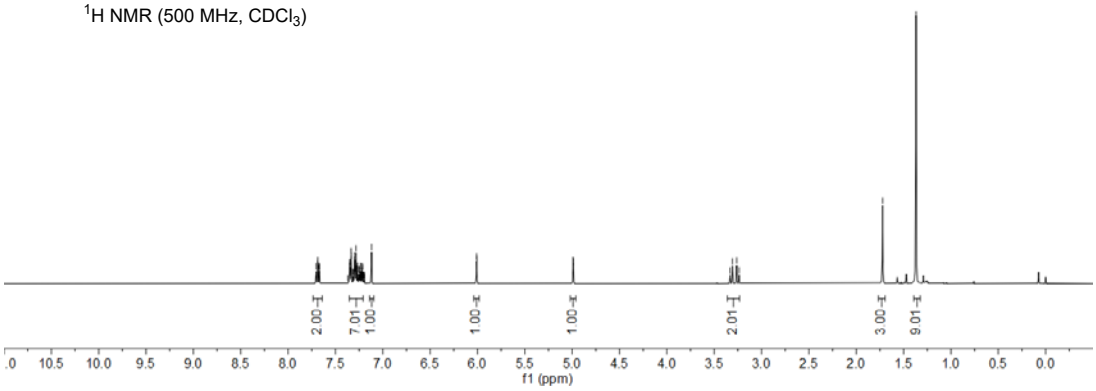
7

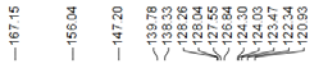
^{11}B NMR (160 MHz, $CDCl_3$)

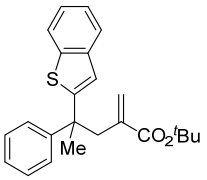


8

^{1}H NMR (500 MHz, $CDCl_3$)

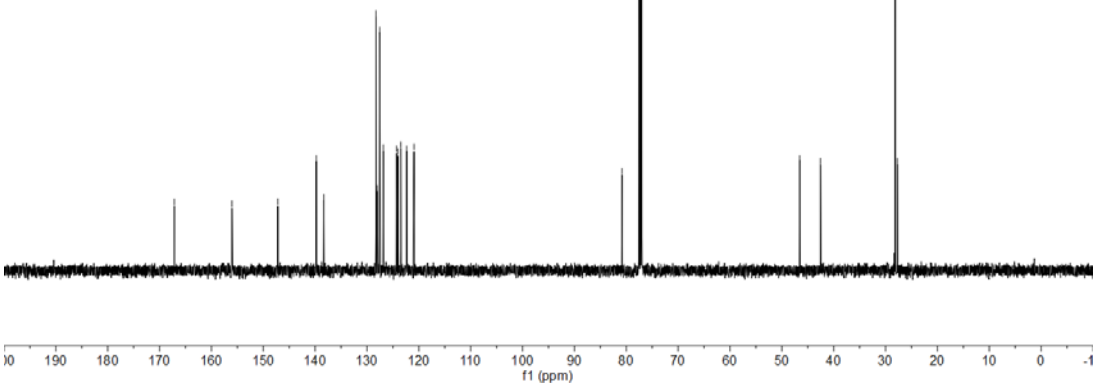


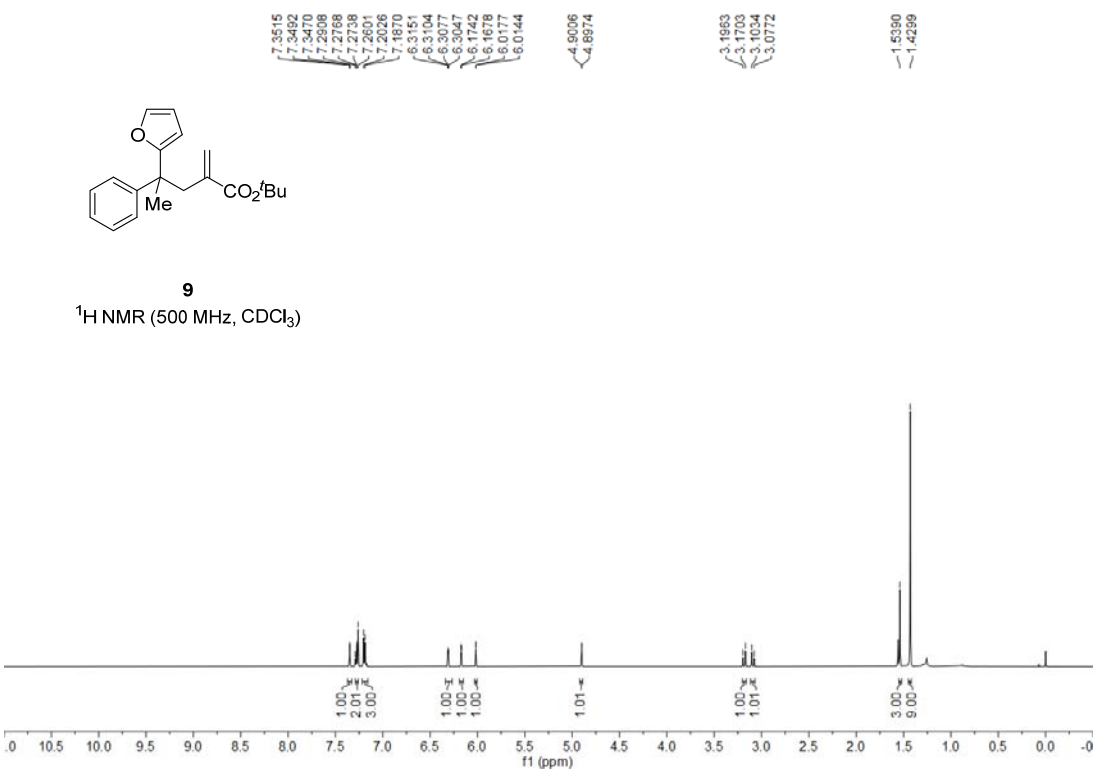




8

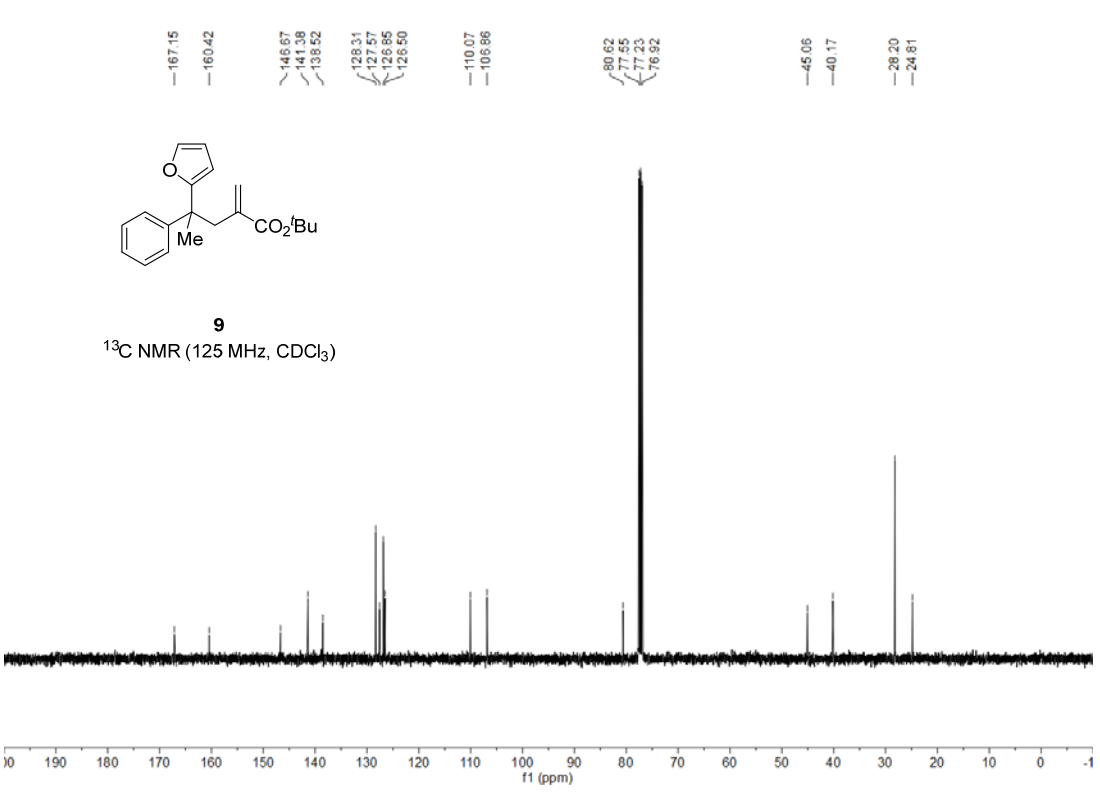
^{13}C NMR (125 MHz, $CDCl_3$)





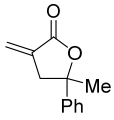
9

^{1}H NMR (500 MHz, $CDCl_3$)



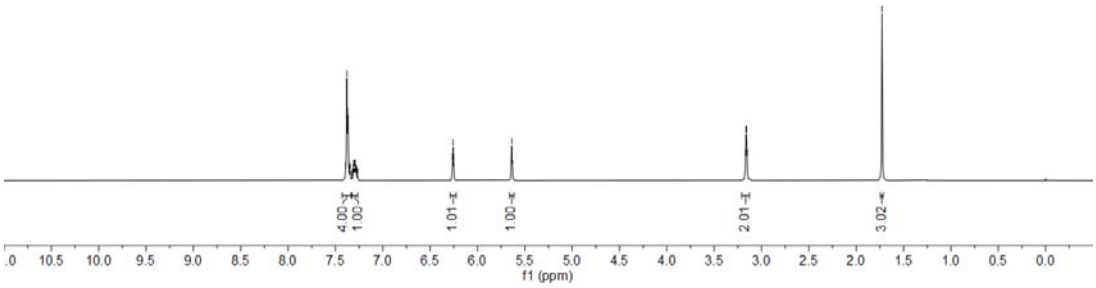
9

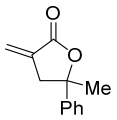
^{13}C NMR (125 MHz, $CDCl_3$)



10

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





10

^{13}C NMR (100 MHz, $CDCl_3$)