Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for:

Iron-Catalyzed Boration of Allylic Esters: An Efficient Approach to Allylic Boronates

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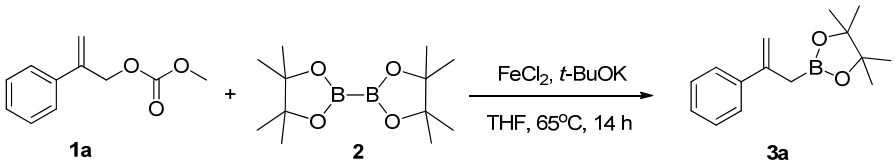


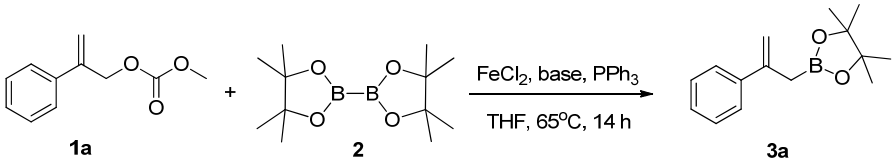
1a **2** **3a**

entry	*t*-BuOK	**2**	conv. (%)[b]	yield (%)[c]
1	0.6 eq	1.5 eq	57	39
2	1.0 eq	1.5 eq	78	45
3	1.2 eq	1.5 eq	80	29
4	1.5 eq	1.5 eq	92	22
5	3.0 eq	1.5 eq	100	0
6	1.0 eq	1 eq	79	26

[a] Reaction conditions: **1a** (0.3 mmol), **2**, $FeCl_2$ (0.03 mmol, 10 mol%) and *t*-BuOK in THF (4 mL) at 65 °C for 14 h. [b, c] Conversion and yield were determined by ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard.

Survey reaction conditions base on species of base

Table S2 Survey reaction conditions base on species of base[a]



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

entry	base	conv. (%)[b]	yield (%)[c]
1	*t*-BuOK	91	83
2	K_2CO_3	0	0
3	$KHCO_3$	0	0
4	KOH	15	14
5	NaOH	33	0
6	MeONa	3	3
7	*t*-BuONa	99	29
8	*t*-BuOLi	96	75

[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.45 mmol), $FeCl_2$ (0.03 mmol, 10 mol%), PPh_3 (0.06 mmol), base (0.3 mmol) in THF (4 mL) at 65 °C for 14 h. [b, c] Conversion and yield were determined by ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard.

General procedure for the synthesis of allylic carbonates

To a cooled (0 °C) mixture of allylic alcohol (**1k** and **1l**) [1] and *n*-BuLi (2.5 M) (2 eq.) in THF (0.5 M) was slowly added methyl chloroformate (1.5 eq.) over a period of 10 min. The resultant reaction mixture was allowed to stir for 3 h and then diluted with a solution of dilute HCl (3 M). The mixture was extracted with EtOAc (3 x mL) and the combined organic extracts were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–97 :

3) afforded the title compound. The synthesis of allylic carbonates (**1a-1j**, **1m-1o**) referred to the literature.[2]

1a, **1e**, **1g** in accordance with previously reported spectra.[3]

Characterization data of the new substrates

2-(4-Chlorophenyl)allyl methyl carbonate (1b)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.37 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 5.56 (s, 1H), 5.43 (s, 1H), 5.00 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 141.0, 136.2, 134.0, 128.7, 127.4, 116.5, 68.9, 54.9. HRMS (ESI): *m/z* calc. for $C_{11}H_{12}ClO_3$ $[M+H]^+$: 227.0475, found: 227.0469.

2-(Naphthalen-2-yl)allyl methyl carbonate (1c)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.96 – 7.75 (m, 4H), 7.62 (m, 1H), 7.55 – 7.41 (m, 2H), 5.74 (s, 1H), 5.54 (s, 1H), 5.18 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 141.9, 135.0, 133.3, 133.1, 128.4, 128.3, 127.6, 126.4, 126.3, 125.0, 124.1, 116.3, 69.2, 55.0. HRMS (ESI): *m/z* calc. for $C_{15}H_{15}O_3$ $[M+H]^+$: 243.1021, found: 243.1016.

2-(4-Bromophenyl)allyl methyl carbonate (1d)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.46 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 5.56 (s, 1H), 5.42 (s, 1H), 4.99 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 141.1, 136.6, 131.7, 127.7, 122.2, 116.6, 68.9, 55.0. HRMS (ESI): *m/z* calc. for $C_{11}H_{12}BrO_3$ $[M+H]^+$: 270.9970, found: 270.9966.

2-(2-Fluorophenyl)allyl methyl carbonate (1f)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.45 – 7.24 (m, 2H), 7.23 – 6.97 (m, 2H), 5.60 (s, 1H), 5.52 (s, 1H), 5.05 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, J = 248.1 Hz), 155.5, 138.9 (d, J = 1.4 Hz), 130.0 (d, J = 4.1 Hz), 129.7 (d, J = 8.4 Hz), 126.2 (d, J = 14.0 Hz), 124.3 (d, J = 3.5 Hz), 118.7 (d, J = 2.8 Hz), 115.9 (d, J = 22.6 Hz), 69.4 (d, J = 5.1 Hz), 54.8. HRMS (ESI): *m/z* calc. for $C_{11}H_{12}FO_3$ $[M+H]^+$: 211.0770, found: 211.0766.

2-(3-(Trifluoromethyl)phenyl)allyl methyl carbonate (1h)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.67 (s, 1H), 7.59 (m, 2H), 7.48 (m, 1H), 5.63 (s, 1H), 5.51 (s, 1H), 5.04 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 141.1, 138.6, 131.0 (q, J = 32.2 Hz), 129.34 (d, J = 1.1 Hz), 129.33, 124.9 (q, J = 3.7 Hz), 124.0 (q, J = 272.4 Hz), 122.9 (q, J = 3.8 Hz), 117.6, 68.8, 55.0. HRMS (ESI): *m/z* calc. for $C_{12}H_{12}F_3O_3$ $[M+H]^+$: 261.0739, found: 261.0737.

2-(2,5-Dimethylphenyl)allyl methyl carbonate (1i)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.17 – 6.79 (m, 3H), 5.50 (s, 1H), 5.13 (s, 1H), 4.83 (s, 2H), 3.81 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 143.7, 138.6, 135.1, 132.4, 130.2, 129.4, 128.5, 115.6, 69.9, 54.9, 20.9, 19.2. HRMS (ESI): *m/z* calc. for $C_{13}H_{17}O_3$ $[M+H]^+$: 221.1178, found: 221.1173.

2-(4-(*tert*-Butyl)phenyl)allyl methyl carbonate (1j)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.40 (s, 4H), 5.58 (s, 1H), 5.38 (s, 1H), 5.05 (s, 2H), 3.80 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 151.2, 141.6, 134.8, 125.6, 125.5, 115.0, 69.2, 54.9, 34.6, 31.3. HRMS (ESI): *m/z* calc. for $C_{15}H_{21}O_3$ $[M+H]^+$: 249.1491, found: 249.1485.

(3-(3-Chlorophenyl)-2-methylbut-3-en-2-yl) methyl carbonate (1k)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.44 – 7.00 (m, 4H), 5.45 (s, 1H), 5.16 (s, 1H), 3.70 (s, 3H), 1.65 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 151.5, 142.2, 133.7, 129.1, 128.7, 127.4, 126.8, 116.0, 83.2, 54.2, 27.4. HRMS (ESI): *m/z* calc. for $C_{13}H_{15}ClO_3Na$ $[M+Na]^+$: 277.0607, found: 277.0604.

(2-Methyl-3-phenylbut-3-en-2-yl) methyl carbonate (1l)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.69 – 6.99 (m, 5H), 5.43 (s, 1H), 5.15 (s, 1H), 3.68 (s, 3H), 1.66 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 152.7, 140.5, 128.6, 127.8, 127.2, 115.1, 83.6, 54.1, 27.5. HRMS (ESI): *m/z* calc. for $C_{13}H_{16}O_3Na$ $[M+Na]^+$: 243.0997, found: 243.0993.

(3-Phenylbut-3-en-2-yl) methyl carbonate (1m)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.55 – 7.28 (m, 5H), 5.66 (q, *J* = 6.4 Hz, 1H), 5.38 (s, 1H), 5.33 (s, 1H), 3.80 (s, 3H), 1.40 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 149.1, 139.1, 128.5, 127.9, 126.9, 113.4, 75.7, 54.7, 20.2. HRMS (ESI): *m/z* calc. for $C_{12}H_{15}O_3$ $[M+H]^+$: 207.1021, found: 207.1017.

(2-(4-Methoxyphenyl)undec-1-en-3-yl) methyl carbonate (1n)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.53 – 5.36 (m, 1H), 5.26 (s, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 1.74 – 1.54 (m, 2H), 1.21 (m, 12H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 155.4, 147.7, 131.7, 128.1, 113.8, 112.8, 80.0, 55.2, 54.7, 34.1, 31.8, 29.4, 29.23, 29.18, 25.4, 22.7, 14.1. HRMS (ESI): *m/z* calc. for $C_{20}H_{31}O_4$ $[M+H]^+$: 335.2222, found: 335.2218.

(3-(4-Methoxyphenyl)-1-phenylbut-3-en-2-yl) methyl carbonate (1o)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.34 – 7.11 (m, 5H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.73 (m, 1H), 5.31 (s, 1H), 5.27 (s, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.09 – 2.84 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 155.2, 147.0, 137.2, 131.5, 129.4, 128.32, 128.27, 126.6, 113.9, 113.4, 80.3, 55.3, 54.8, 40.5. HRMS (ESI): *m/z* calc. for $C_{19}H_{21}O_4$ $[M+H]^+$: 313.1440, found: 313.1436.

2-(3-Methoxyphenyl)allyl methyl carbonate (1p)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (98 : 2–96 : 4). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.27 (t, *J* = 8.0 Hz, 1H), 7.05 – 6.93 (m, 2H), 6.86 (dd, *J* = 8.2, 2.1 Hz, 1H), 5.57 (s, 1H), 5.41 (s, 1H), 5.02 (s, 2H), 3.82 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.7, 155.6, 142.0, 139.3, 129.5, 118.5, 115.9, 113.5, 111.9, 69.1, 55.2, 54.9. HRMS (ESI): *m/z* calc. for $C_{12}H_{15}O_4$ $[M+H]^+$: 223.0970, found: 223.0961.

Characterization data of allylic boronates

Note: The carbon attached to boron is not observed, or just a broad and low intensity signal around 10 ppm in ^{13}C NMR spectra.[4]

2-(2-Phenylallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Colorless oil (220 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) *δ* 7.47-7.45 (m, 2H), 7.30-7.26 (m, 2H), 7.23-7.20 (m, 1H), 5.36 (d, *J* = 1.3 Hz, 1H), 5.10 (d, *J* = 1.3 Hz, 1H), 2.16 (s, 2H), 1.16 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 144.4, 141.8, 128.1, 127.2, 125.9, 112.2, 83.4, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$) *δ* 33.27. These spectroscopic data correspond to reported data.[5]

2-(2-(4-Chlorophenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Pale yellow oil (192 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) *δ* 7.41 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 5.36 (s, 1H), 5.13 (s, 1H), 2.15 (s, 2H), 1.18 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 143.2, 140.2, 133.0, 128.1, 127.2, 112.8, 83.5, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$) *δ* 33.28. HRMS (EI): *m/z* calc. for $C_{15}H_{20}BClO_2$, 278.1245, found: 278.1251.

2-(2-(Naphthalen-2-yl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Pale yellow oil (215 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) *δ* 7.85-7.65 (m, 5H), 7.42-7.39 (m, 2H), 5.54 (s, 1H), 5.21 (s, 1H), 2.28 (s, 2H), 1.15 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 144.0, 138.8, 133.4, 132.8, 128.2, 127.6, 127.4, 126.0, 125.7, 124.6, 124.3, 112.8, 83.5, 24.7. ^{11}B NMR (128 MHz, $CDCl_3$) *δ* 33.21. HRMS (EI): *m/z* calc. for $C_{19}H_{23}BO_2$, 294.1791; found: 294.1797.

2-(2-(4-Bromophenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Colorless oil (122 mg, 38%); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) *δ* 7.44 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 5.38 (d, *J* = 0.9 Hz, 1H), 5.15 (d, *J* = 0.9 Hz, 1H), 2.16 (s, 2H), 1.20 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 143.3, 140.7, 131.1, 127.5, 121.1, 112.9, 83.5, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$) *δ* 33.15. HRMS (EI): *m/z* calc. for $C_{15}H_{20}BBrO_2$, 322.0740; found: 322.0751.

2-(2-(*p*-Tolyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Colorless oil (132 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) *δ* 7.37 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 5.34 (d, *J* = 1.2 Hz, 1H), 5.05 (d, *J* =

1.2 Hz, 1H), 2.33 (s, 3H), 2.14 (s, 2H), 1.18 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 136.9, 128.7, 125.7, 111.4, 100.0, 83.4, 24.6, 21.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.40. HRMS (ESI): *m/z* calc. for $C_{16}H_{24}BO_2$ $[M+H]^+$: 259.1869, found: 259.1868.

2-(2-(2-Fluorophenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Colorless oil (192 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.33-6.98 (m, 4H), 5.25 (s, 1H), 5.23 (s, 1H), 2.16 (s, 2H), 1.17 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (d, *J* = 246.3 Hz), 140.9, 133.7 (d, *J* = 19.6 Hz), 130.8 (d, *J* = 13.7 Hz), 129.8 (d, *J* = 4.4 Hz), 128.5 (d, *J* = 3.1 Hz), 123.7 (d, *J* = 3.5 Hz), 115.9 (d, *J* = 23.1 Hz), 83.3, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.77. HRMS (ESI): *m/z* calc. for $C_{15}H_{21}BFO_2$ $[M+H]^+$: 263.1619, found: 263.1617.

2-(2-(4-Fluorophenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Colorless oil (173 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.44-7.41 (m, 2H), 6.99-6.95 (m, 2H), 5.29 (d, *J* = 0.9 Hz, 1H), 5.07 (d, *J* = 0.9 Hz, 1H), 2.14 (s, 2H), 1.16 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.9 Hz), 143.3, 137.9 (d, *J* = 3.2 Hz), 127.5 (d, *J* = 7.9 Hz), 114.8 (d, *J* = 21.3 Hz), 112.1, 83.5, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.28. These spectroscopic data correspond to reported data.[5]

2-(2-(3-(Trifluoromethyl)phenyl)allyl)-4,4,5,5-tetramethyl -1,3,2-dioxaborolane (3h)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Colorless oil (200 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.73-7.41 (m, 4H), 5.43 (d, *J* = 0.9 Hz, 1H), 5.21 (d, *J* = 0.9 Hz, 1H), 2.19 (s, 2H), 1.18 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 142.6, 129.1, 128.5, 130.4 (q, *J* = 31.9 Hz), 124.3 (q, *J* = 272.3 Hz), 123.8 (q, *J* = 3.9 Hz), 122.7 (q, *J* = 3.9 Hz), 113.7, 83.6, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.18. HRMS (ESI): *m/z* calc. for $C_{16}H_{20}BF_3O_2Na$ $[M+Na]^+$: 335.1406, found: 335.1401.

2-(2-(2,5-Dimethylphenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Colorless oil (109 mg, 40%); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.09 – 6.97 (m, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 5.20 (s, 1H), 4.84 (s, 1H), 2.28 (s, 6H), 2.03 (s, 2H), 1.18 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 144.0, 134.4, 131.4, 129.9, 129.0, 127.3, 114.2, 83.3, 24.7, 20.9, 19.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.44. HRMS (ESI): *m/z* calc. for $C_{17}H_{26}BO_2$ $[M+H]^+$: 273.2026, found: 273.2022.

2-(2-(4-(*tert*-Butyl)phenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Colorless oil (195 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 5.35 (d, *J* = 1.2 Hz, 1H), 5.06 (d, *J* = 1.2 Hz, 1H), 2.15 (s, 2H), 1.31 (s, 9H), 1.18 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 144.1, 139.0, 125.5, 124.9, 111.5, 83.4, 34.5, 31.3, 24.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.20. HRMS (ESI): *m/z* calc. for $C_{19}H_{30}BO_2$ $[M+H]^+$: 301.2339, found: 301.2336.

2-(2-(3-Chlorophenyl)-3-methylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Pale yellow oil (251 mg, 82%); ^{1}H NMR (400 MHz,

$CDCl_3$, Me_4Si) δ 7.20-7.13 (m, 3H), 7.04 (d, J = 7.5 Hz, 1H), 1.95 (s, 2H), 1.78 (s, 3H), 1.56 (s, 3H), 1.17 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 133.4, 129.6, 129.1, 128.9, 127.3, 126.9, 125.7, 83.2, 24.7, 22.1, 20.7. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.90. HRMS (ESI): *m/z* calc. for $C_{17}H_{25}BClO_2$ $[M+H]^+$: 307.1636, found: 307.1639.

2-(3-Methyl-2-phenylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Pale yellow oil (171 mg, 63%); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.28-7.15 (m, 5H), 1.99 (s, 2H), 1.79 (s, 3H), 1.58 (s, 3H), 1.15 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 130.7, 128.7, 127.7, 126.3, 125.6, 83.1, 24.7, 22.1, 20.8. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.04. HRMS (ESI): *m/z* calc. for $C_{17}H_{26}BO_2$ $[M+H]^+$: 273.2026, found: 273.2030.

(*E/Z*)-2-(2-Phenylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56:44 mixture of regioisomers) (3m)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Pale yellow oil (243 mg, 94%); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.38 – 7.15 (m, 5H), 5.82 (q, J = 6.8 Hz, 1H × 0.56), 5.57 (q, J = 6.8 Hz, 1H × 0.44), 2.10 (s, 2H × 0.56), 2.03 (s, 2H × 0.44), , 1.78 (d, J = 6.8 Hz, 3H × 0.56), 1.58 (d, J = 6.8 Hz, 3H × 0.44), 1.16 (s, 12H × 0.56), 1.11 (s, 12H × 0.44); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 142.2, 137.6, 136.9, 128.4, 128.0, 127.8, 126.2, 125.9, 121.5, 121.4, 83.2, 83.1, 24.7, 24.6, 15.0, 14.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.13, 22.40. HRMS (EI): *m/z* calc. for $C_{16}H_{23}BO_2$, 258.1791; found: 258.1797.

(*E/Z*)-2-(2-(4-Methoxyphenyl)undec-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38:62 mixture of regioisomers) (3n)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Pale yellow oil (343 mg, 89%); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.4-7.1 (m, 2H), 6.82 (br, 2H), 5.66 (m, 1H × 0.38), 5.42 (m, 1H × 0.62), 3.79 (s, 3H), 2.14 (s, 2H × 0.38), 2.06 (s, 2H × 0.62), 1.99 (m, 2H), 1.28-1.14 (m, 24H), 0.87 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 158.0, 137.1, 136.0, 135.0, 134.9, 129.4, 127.5, 126.9, 126.5, 113.3, 113.1, 83.2, 83.1, 55.2, 55.1, 31.9, 30.2, 29.7, 29.6, 29.55, 29.48, 29.35, 29.30, 29.23, 29.22, 29.1, 24.7, 22.7, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.03, 22.61. HRMS (EI): *m/z* calc. for $C_{24}H_{39}BO_3$, 386.2992; found: 386.2989.

(*E/Z*)-2-(2-(4-Methoxyphenyl)-4-phenylbut-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25:75 mixture of regioisomers) (3o)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (99 : 1–97 : 3). Pale yellow oil (247 mg, 68%); ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.30 – 7.17 (m, 7H), 6.88 – 6.85 (m, 2H), 5.84 (t, J = 7.1 Hz, 1H × 0.25), 5.63 (t, J = 7.4 Hz, 1H × 0.75), 3.81 (s, 3H × 0.25), 3.80 (s, 3H × 0.75), 3.55 (d, J = 7.1 Hz, 2H × 0.25), 3.35 (d, J = 7.4 Hz, 2H × 0.75), 2.19 (s, 2H × 0.25), 2.07 (s, 2H × 0.75), 1.20 (s, 12H × 0.25), 1.16 (s, 12H × 0.75). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 158.2, 141.9, 141.5, 137.7, 134.4, 129.4, 128.6, 128.4, 128.3, 128.2, 127.1, 125.8, 125.6, 125.1, 124.5, 113.4, 113.3, 83.4, 83.2, 55.3, 55.2, 35.4, 35.3, 24.72, 24.69. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.03, 22.66. HRMS (EI): *m/z* calc. for $C_{23}H_{29}BO_3$, 364.2210; found: 364.2214.

2-(2-(3-Methoxyphenyl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p)

Title compound was isolated by flash chromatography on silica gel eluting with petroleum

ether/ethyl acetate (99 : 1–97 : 3). Pale yellow oil (233 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.21 (m, 1H), 7.04 (m, 2H), 6.79 (m, 1H), 5.37 (s, 1H), 5.11 (s, 1H), 3.81 (s, 3H), 2.15 (s, 2H), 1.18 (s, 12H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.27. ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 144.3, 143.4, 129.0, 118.5, 112.9, 112.4, 111.5, 83.4, 55.2, 24.6. HRMS(ESI): *m/z* calc. for $C_{16}H_{24}BO_3$ $[M+H]^+$: 275.1819, found: 275.1828.

References

1 T. Tomioka, R. Sankranti, T. Yamada and C. Clark, *Org. Lett*., 2013, **15**, 5099-5101.

2 S. M. Smith, G. L. Hoang, R. Pal, B. M. O. Khaled, L. S. W. Pelter, X. C. Zenga and J. M. Takacs, *Chem. Commun*., 2012, **48**, 12180-12182.

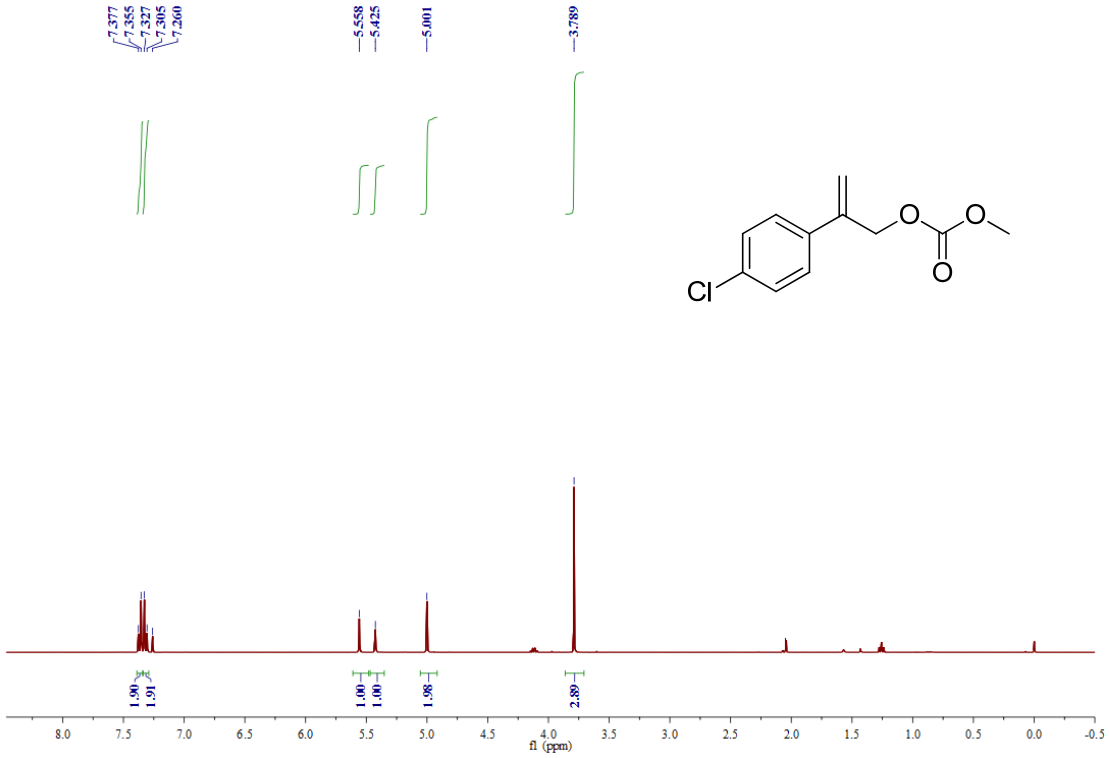
3 C. Zhao, Z. Tan, Z. Liang, W. Deng and H. Gong, *Synthesis*, 2014, **46**, 1901-1907.

4 (a) P. J. Unsworth, D. Leonori and V. K. Aggarwal, *Angew. Chem., Int. Ed.* 2014, **53**, 9846-9850; (b) K. Semba and Y. Nakao, *J. Am. Chem. Soc*. 2014, **136**, 7567-7570; (c) E. Yamamoto, K. Izumi, Y. Horita and H. Ito, *J. Am. Chem. Soc*. 2012, **134**, 19997-20000.

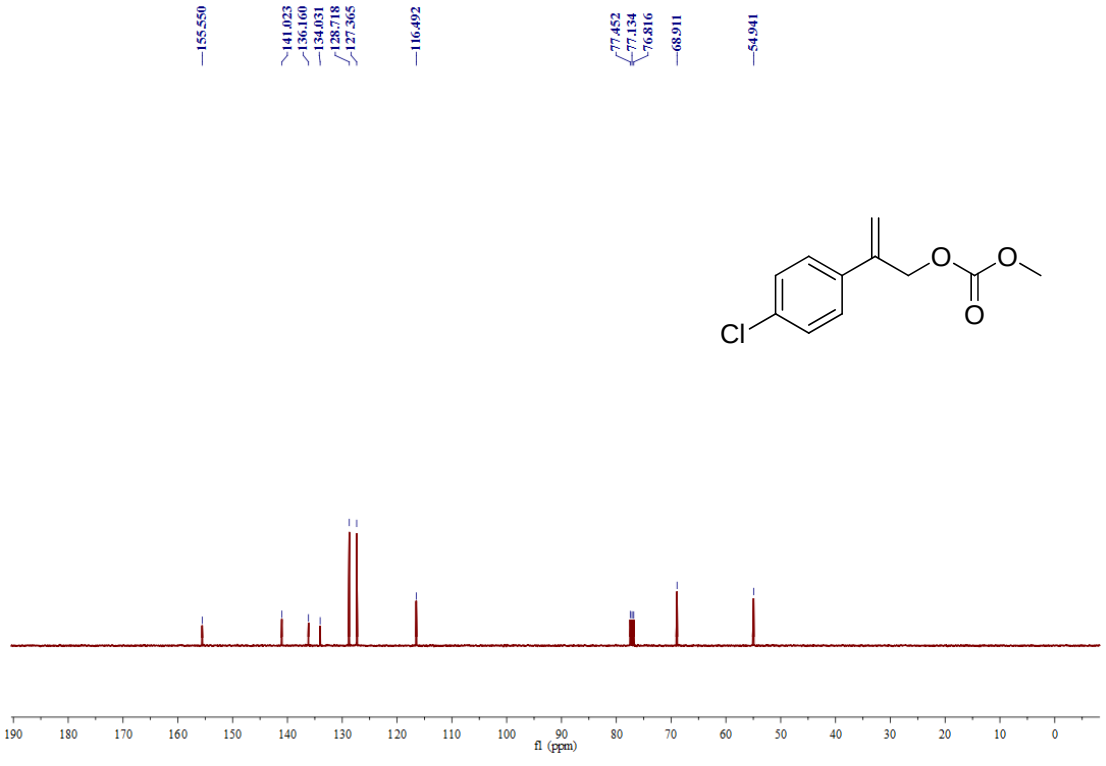
5 R. Corberan, N. W. Mszar and A. H. Hoveyda, *Angew. Chem., Int. Ed.*, 2011, **50**, 7079-7082.

NMR Spectra of new substrates

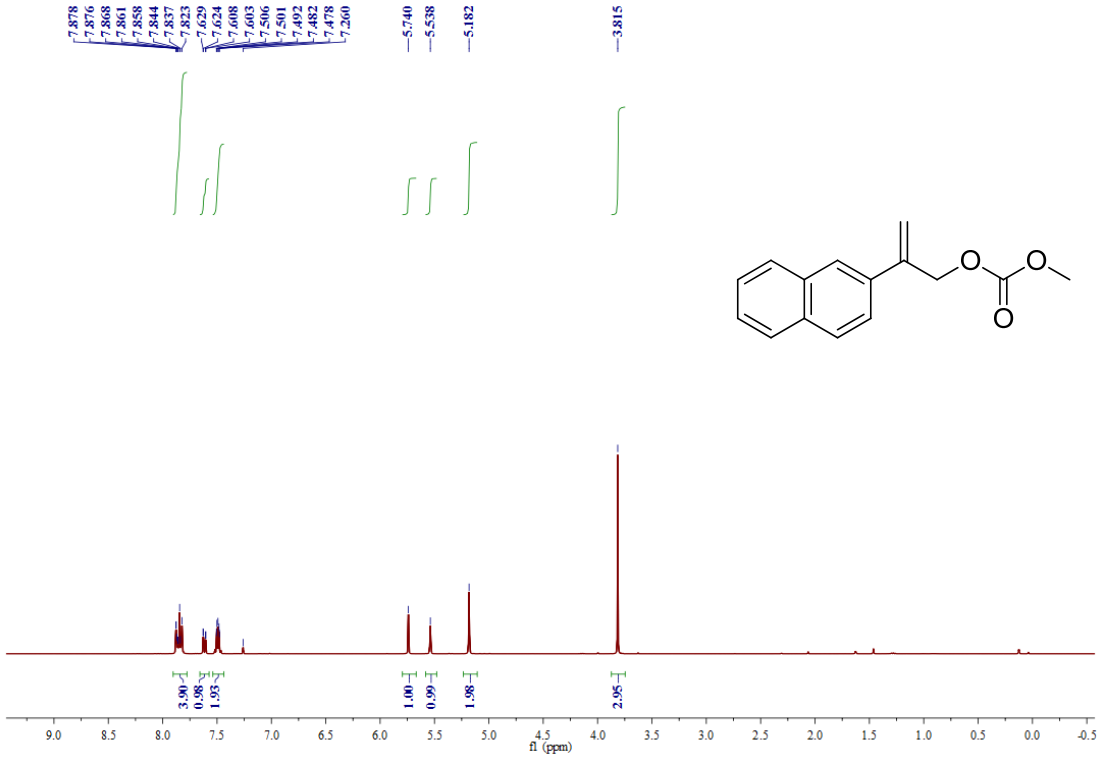
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1b)**



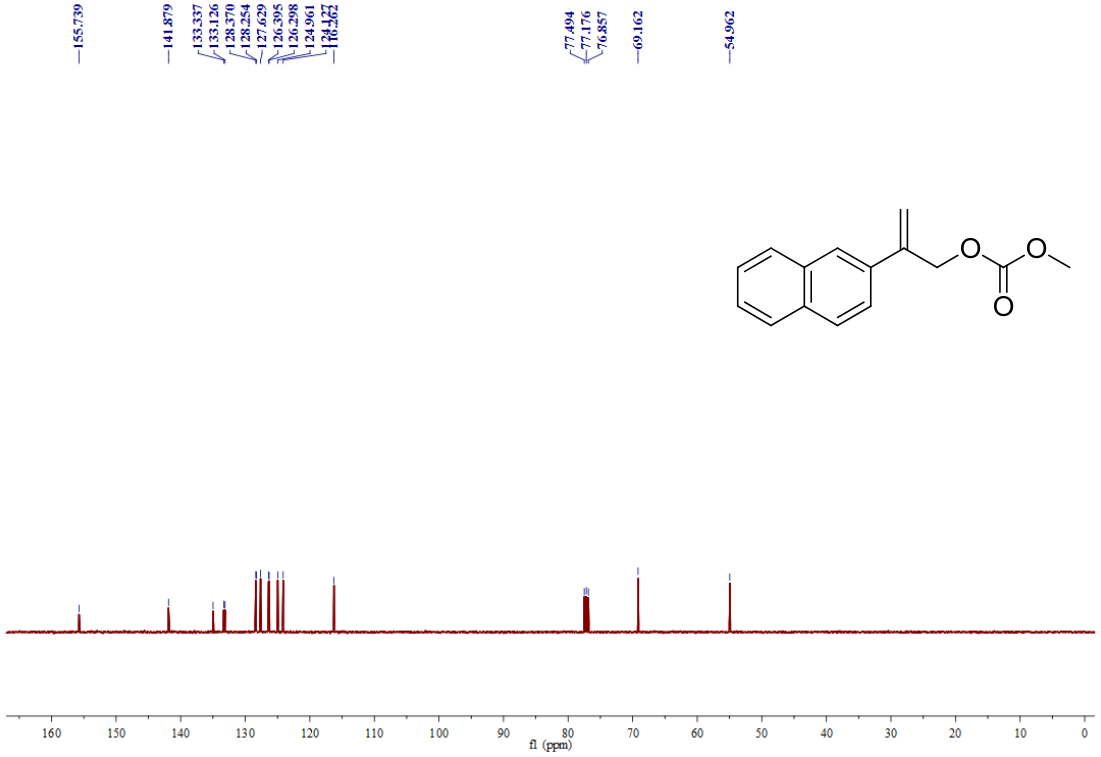
^{13}C NMR (101 MHz, $CDCl_3$) **(1b)**



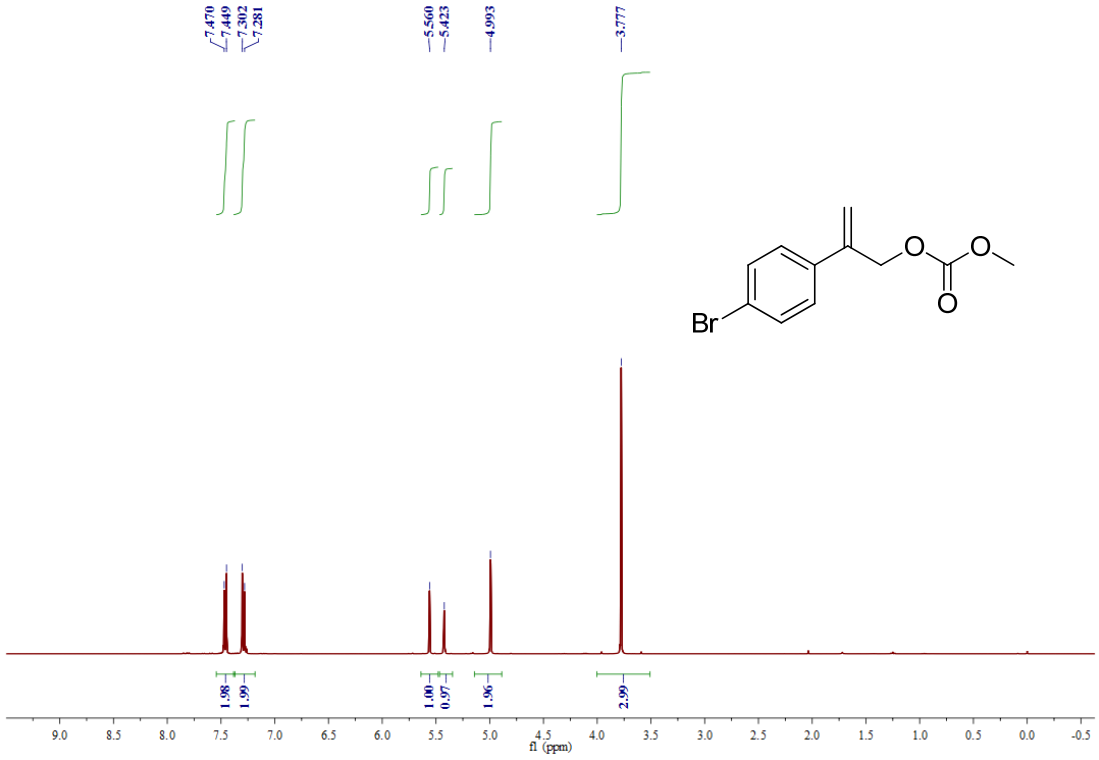
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1c)**



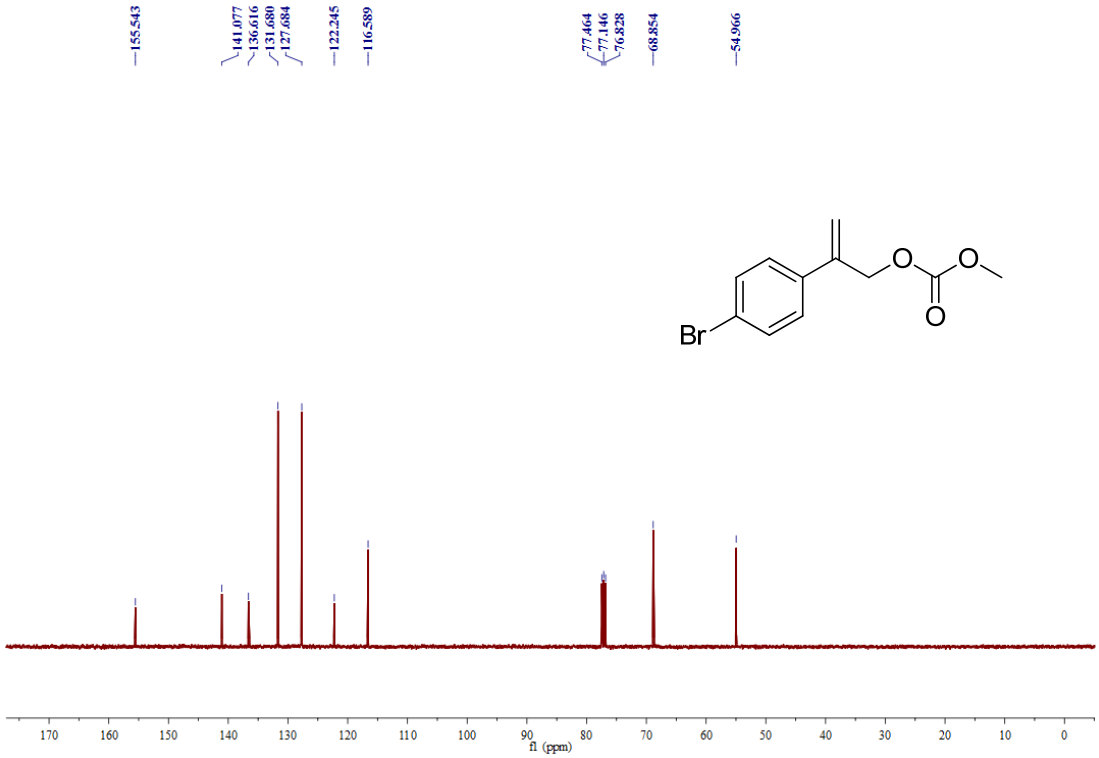
^{13}C NMR (101 MHz, $CDCl_3$) **(1c)**



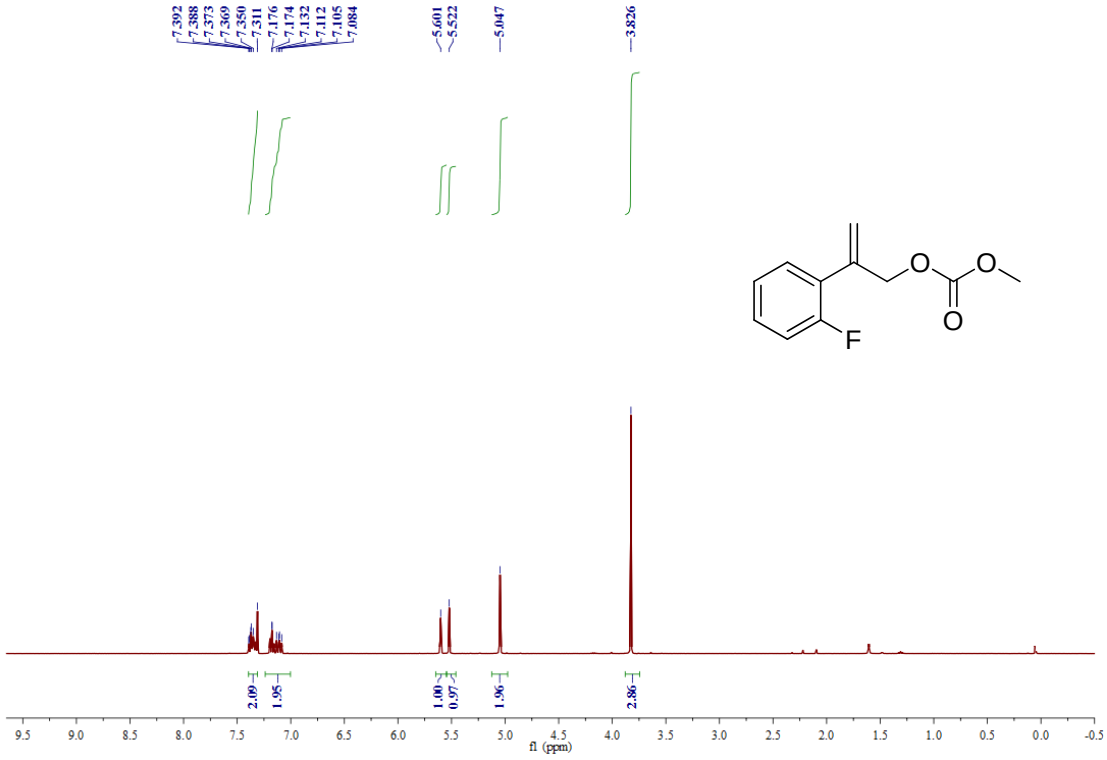
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1d)**



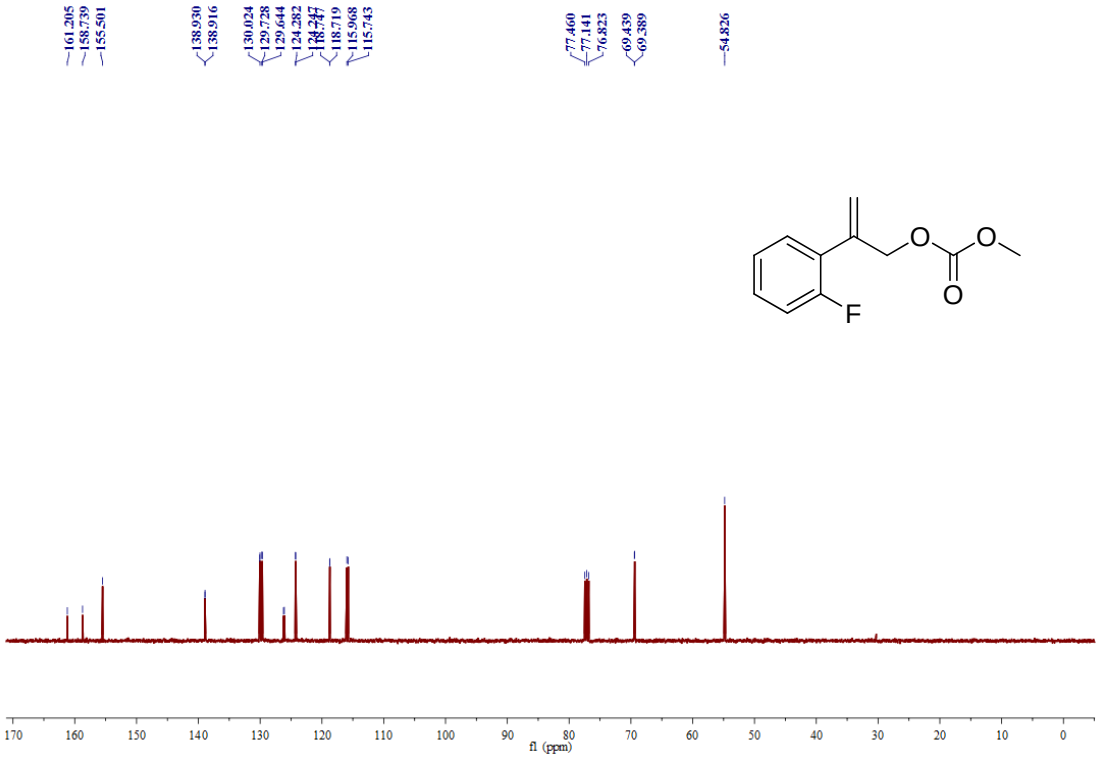
^{13}C NMR (101 MHz, $CDCl_3$) **(1d)**



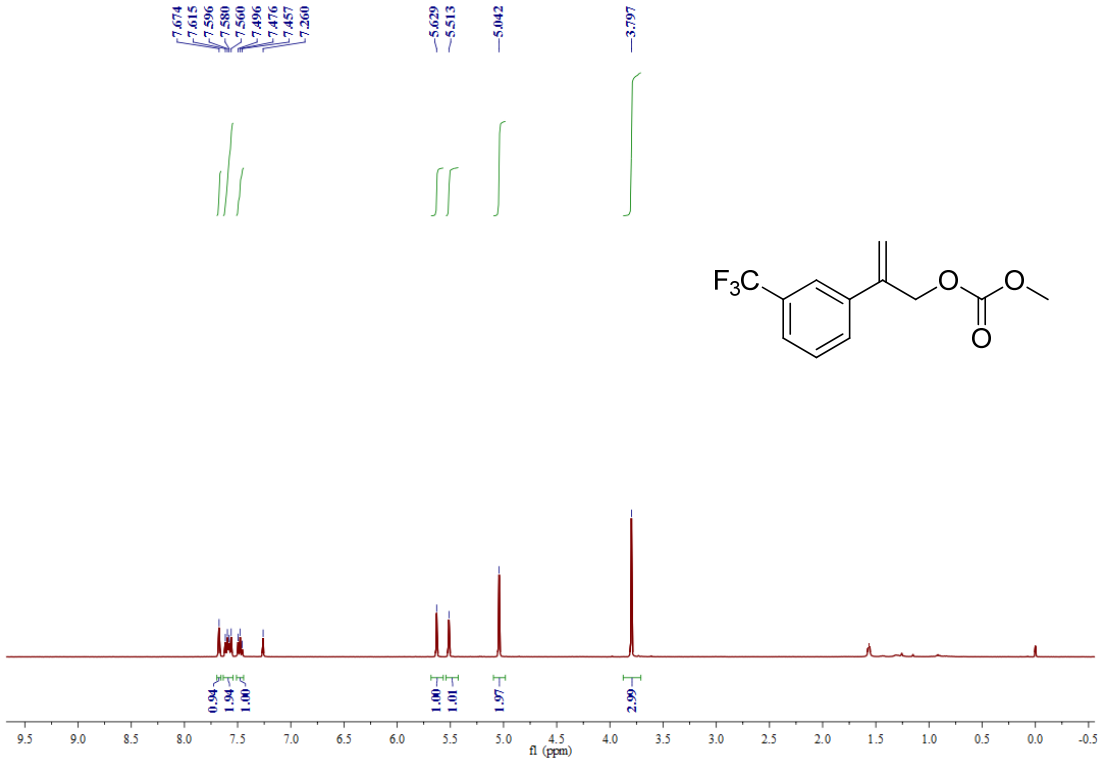
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1f)**



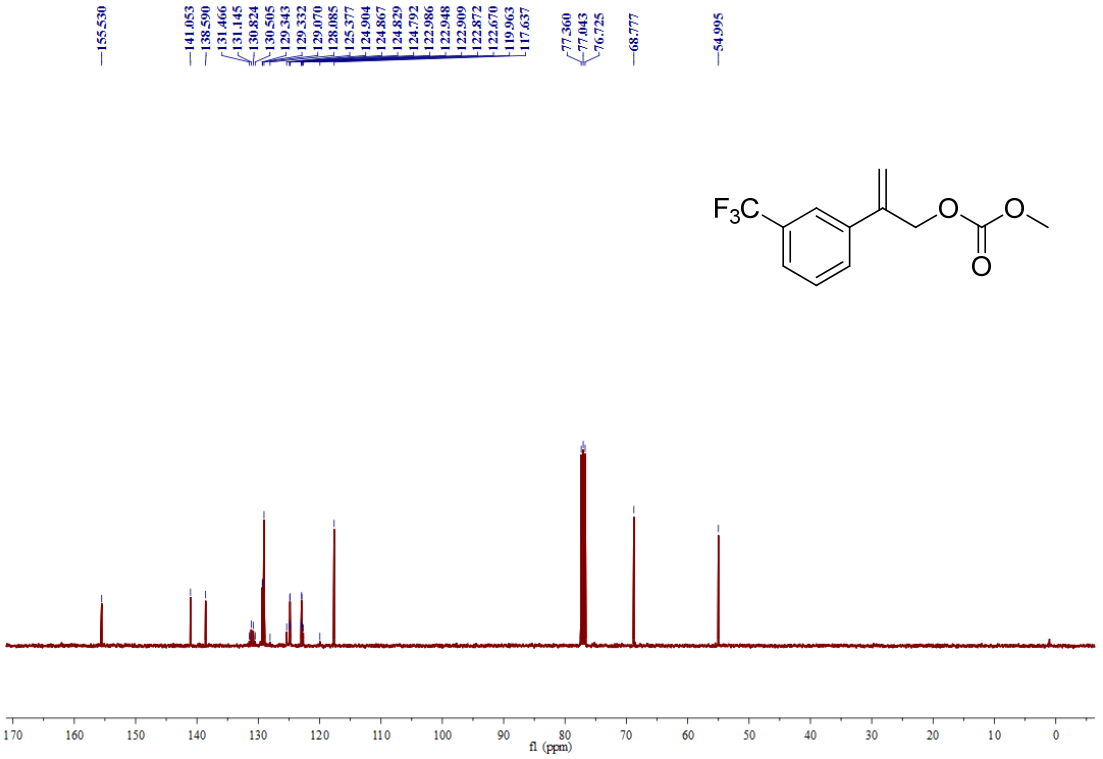
^{13}C NMR (101 MHz, $CDCl_3$) **(1f)**



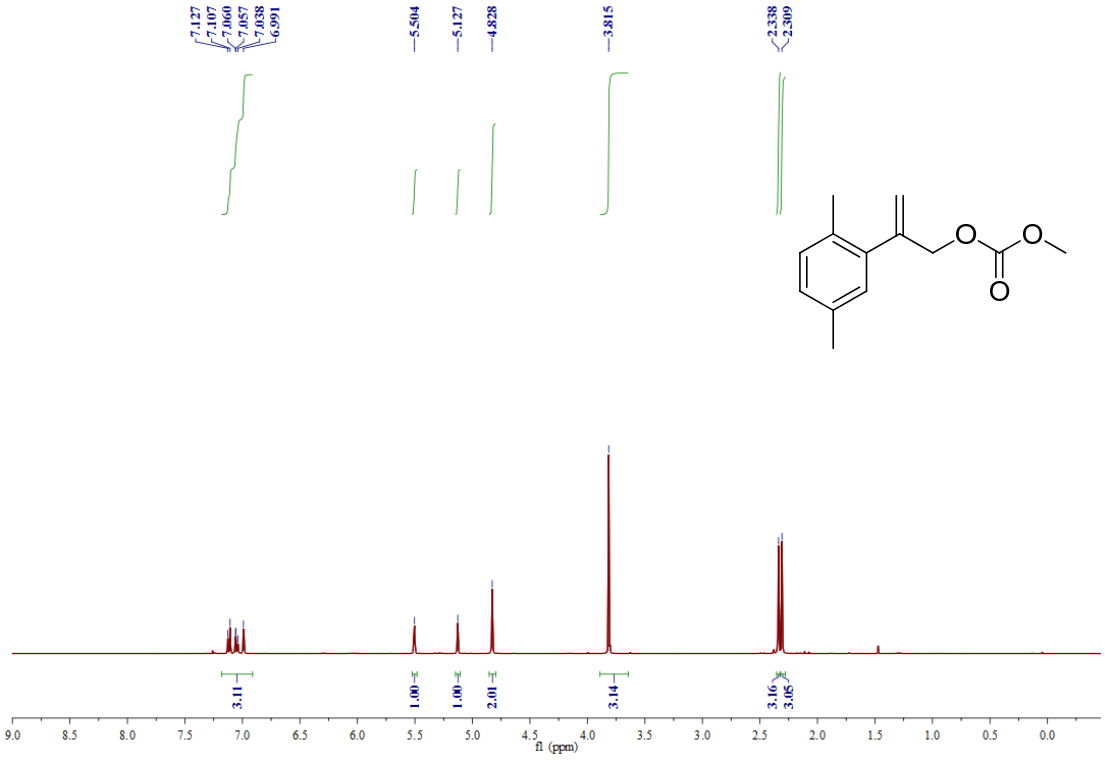
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1h)**



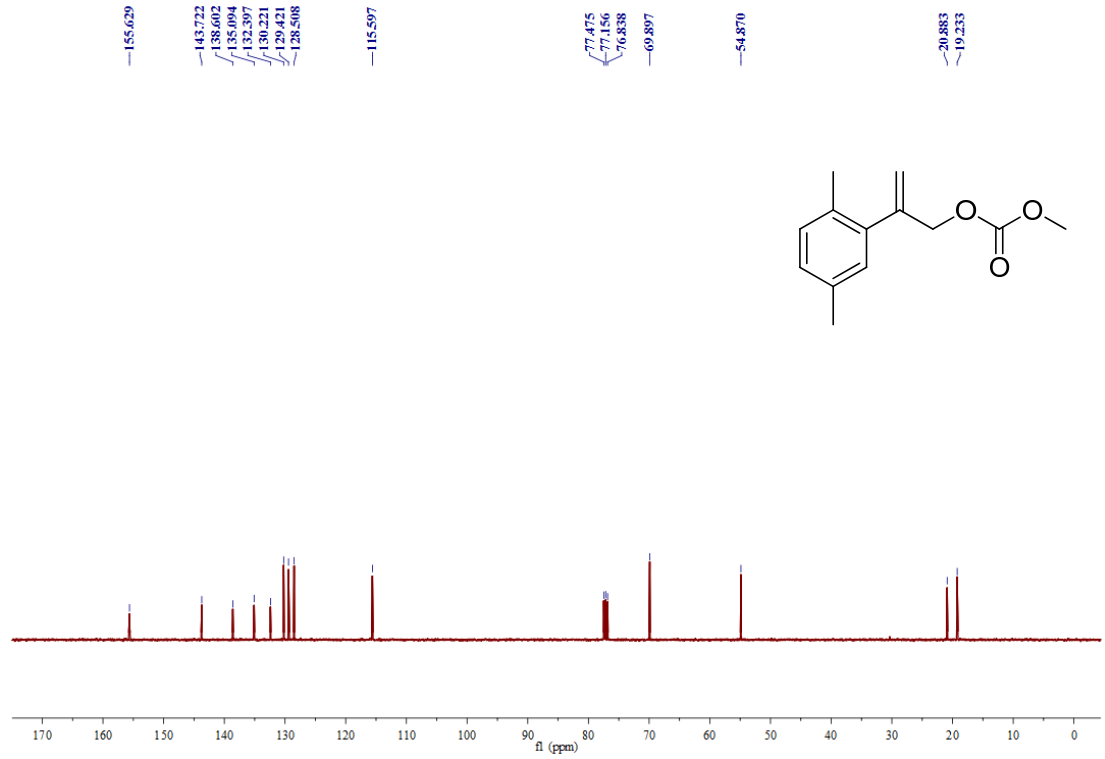
^{13}C NMR (101 MHz, $CDCl_3$) **(1h)**



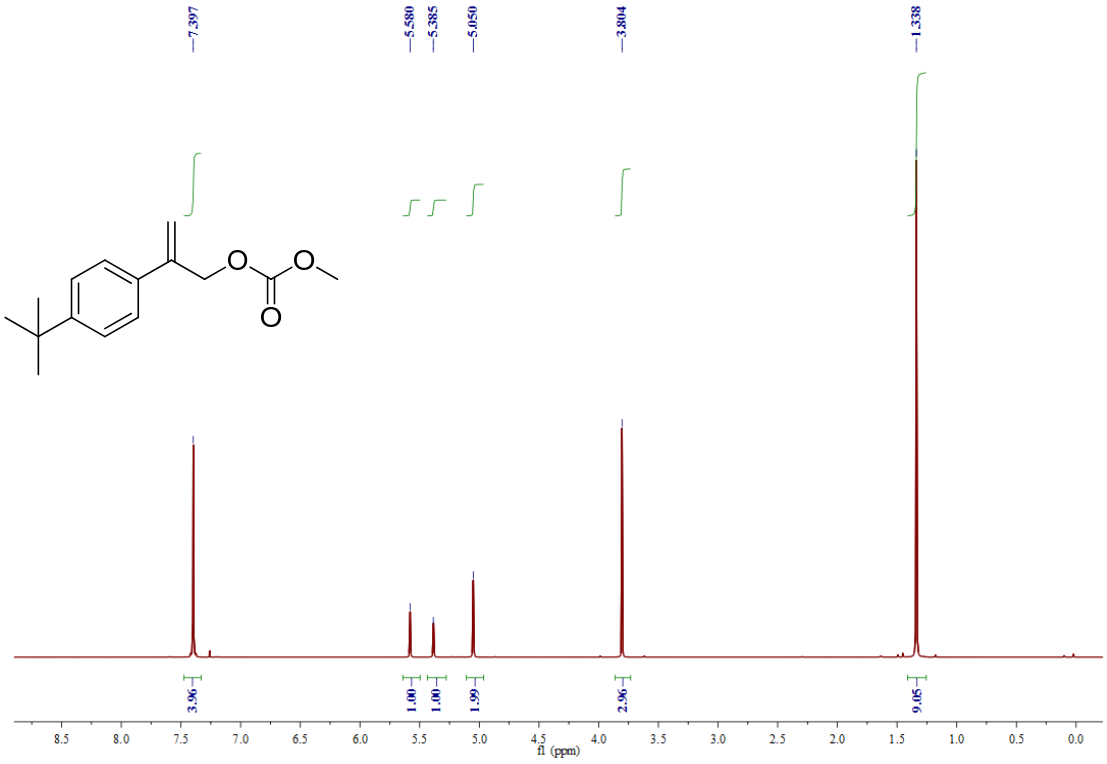
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1i)**



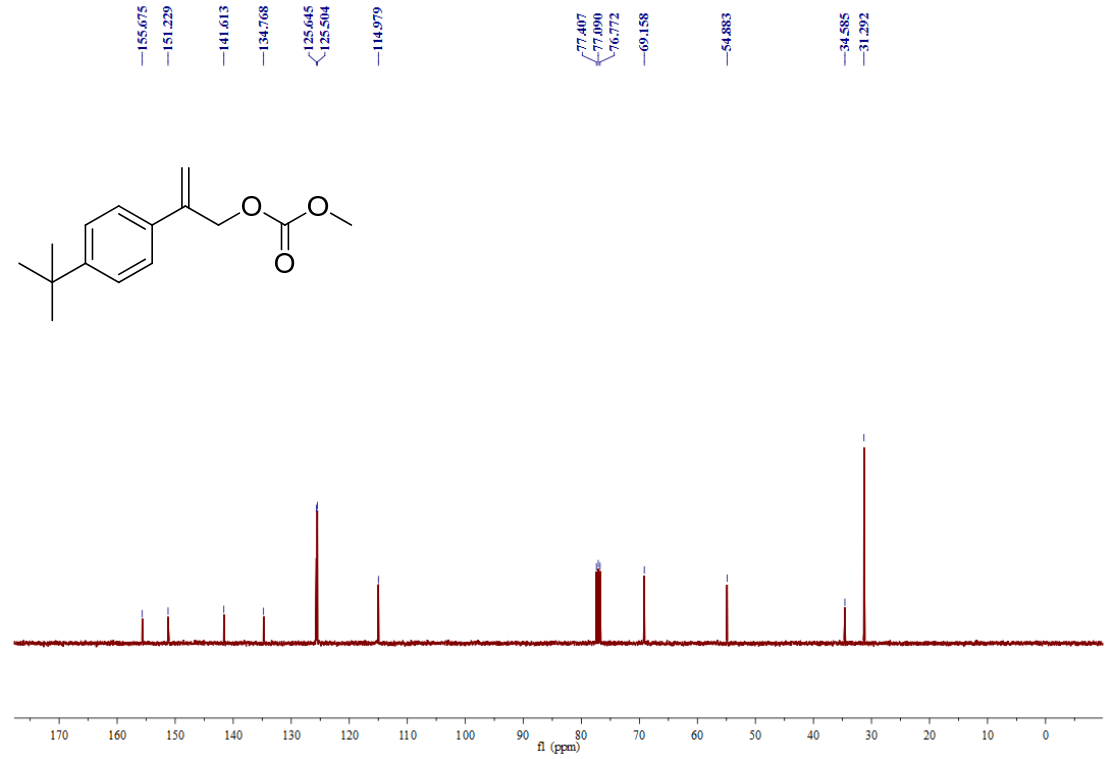
^{13}C NMR (101 MHz, $CDCl_3$) **(1i)**



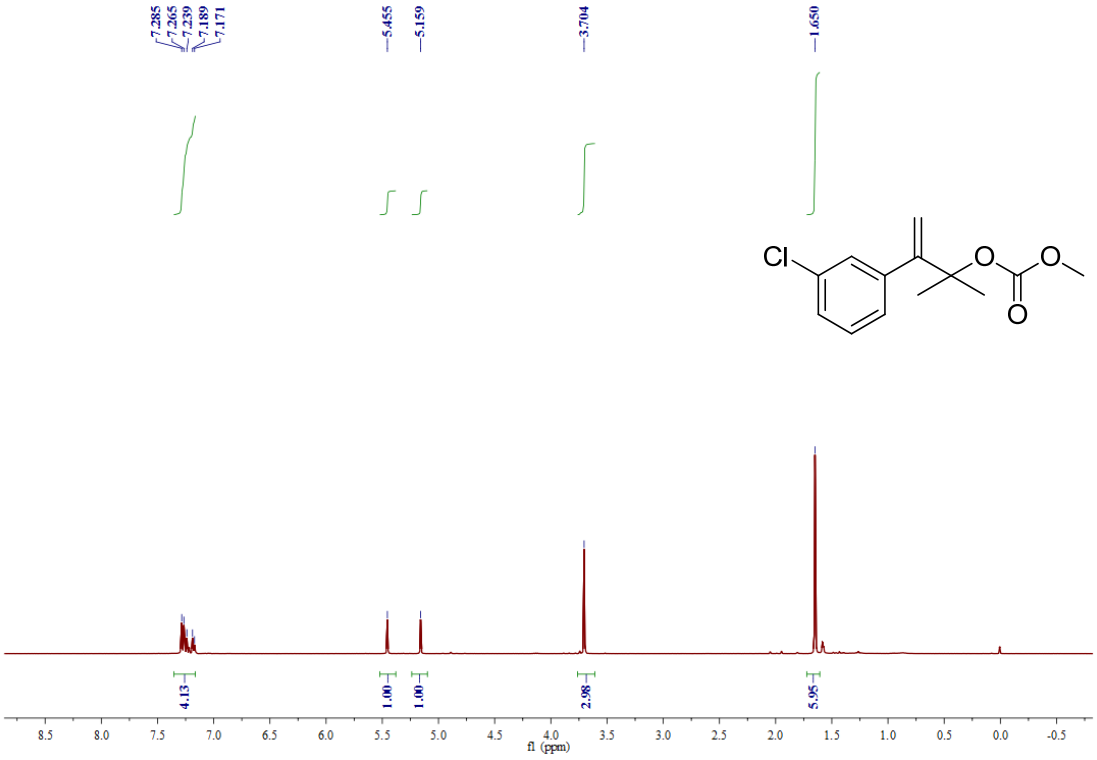
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1j)**



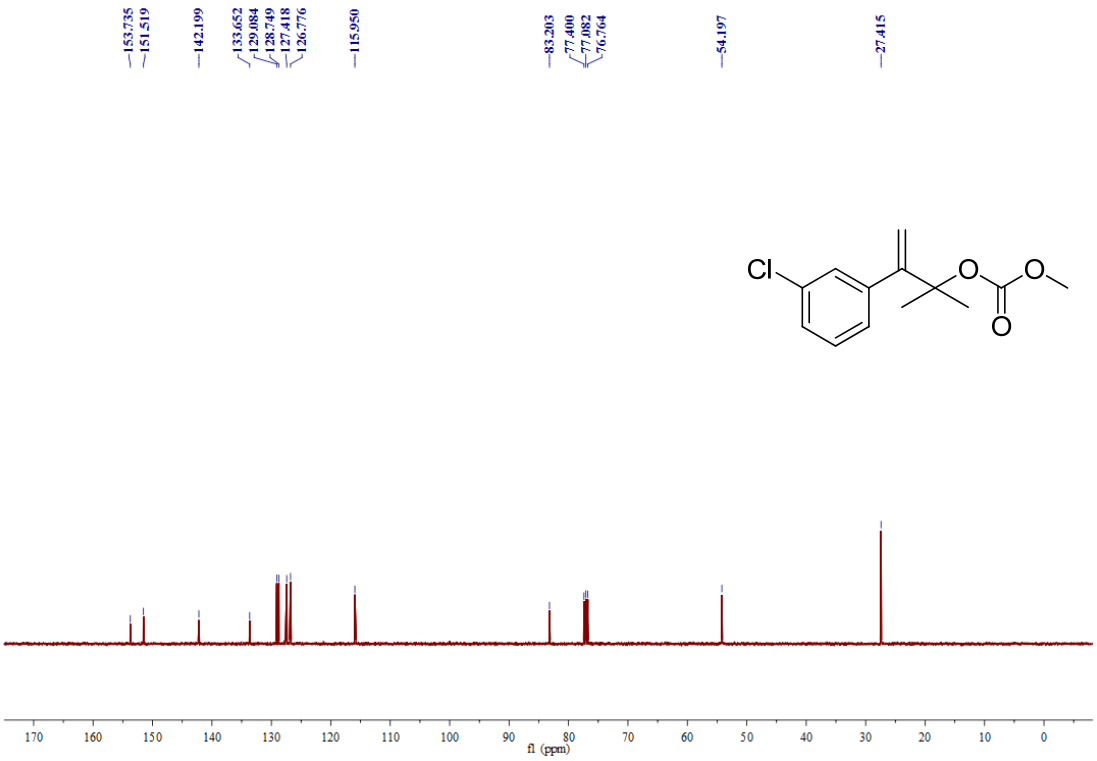
^{13}C NMR (101 MHz, $CDCl_3$) **(1j)**



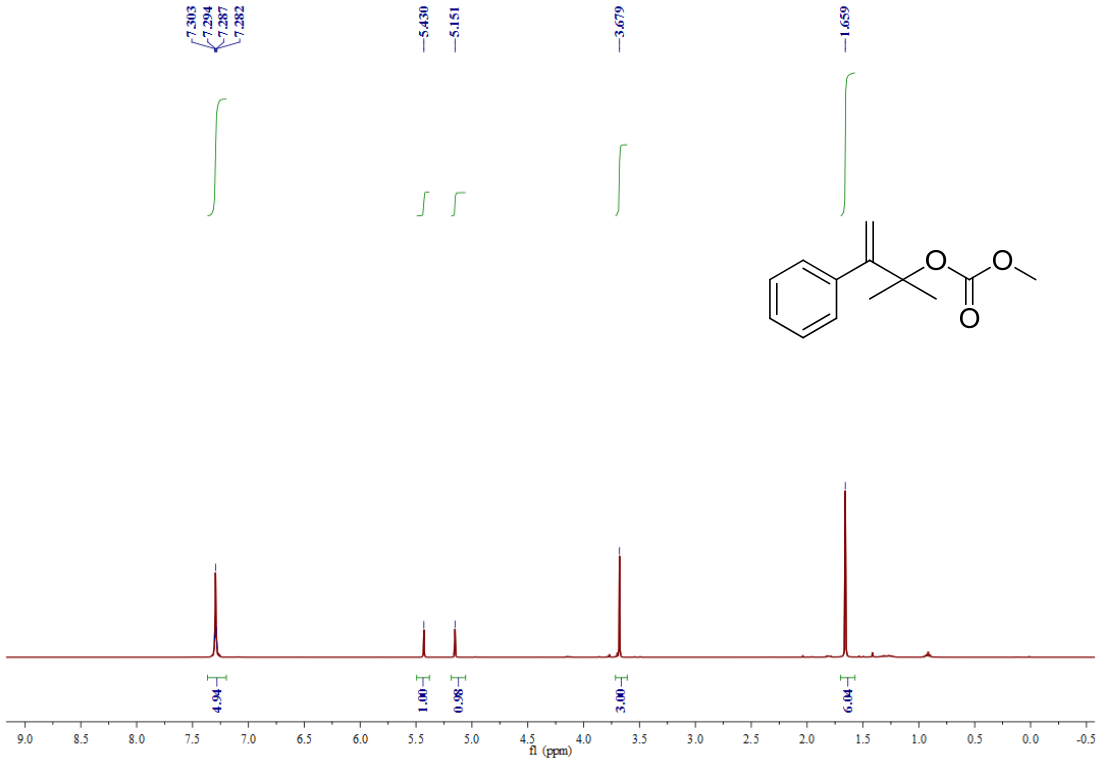
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1k)**



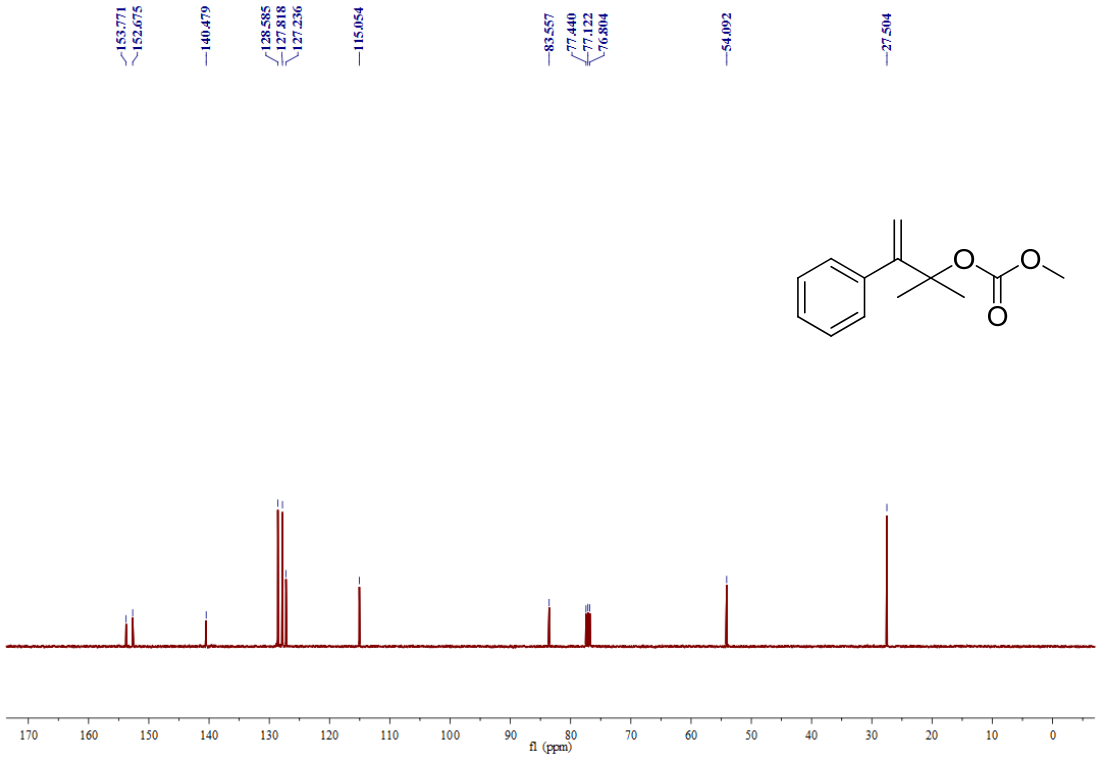
^{13}C NMR (101 MHz, $CDCl_3$) **(1k)**



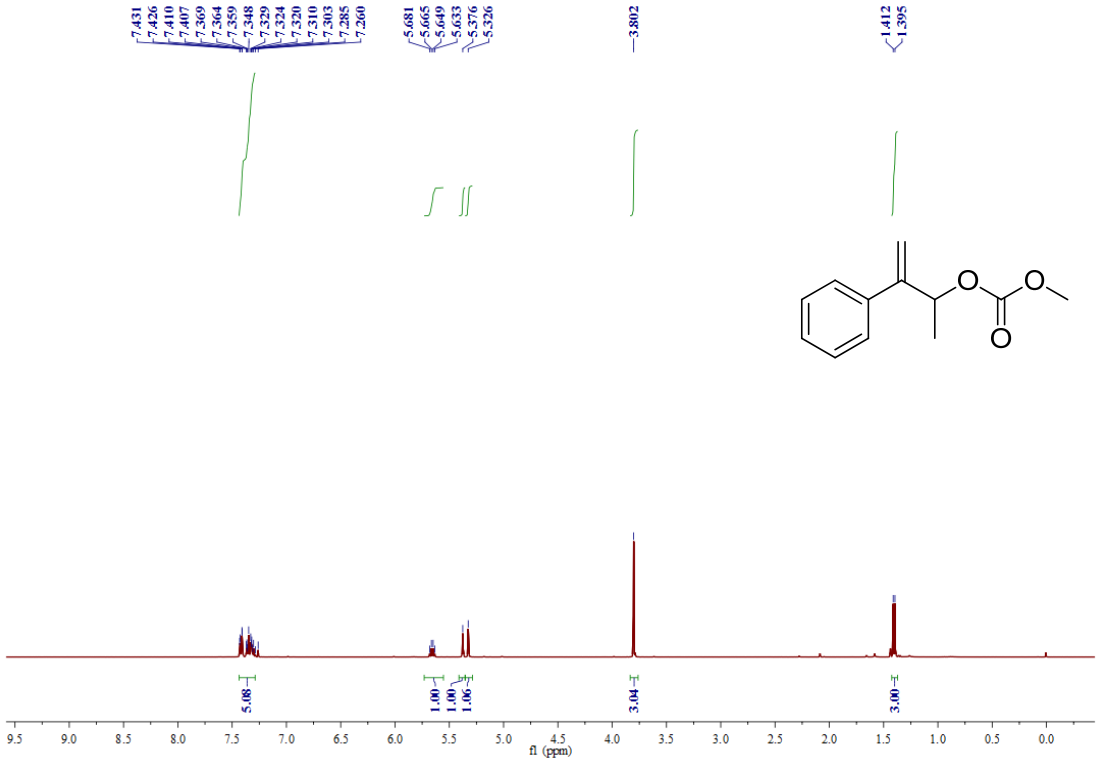
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1l)**



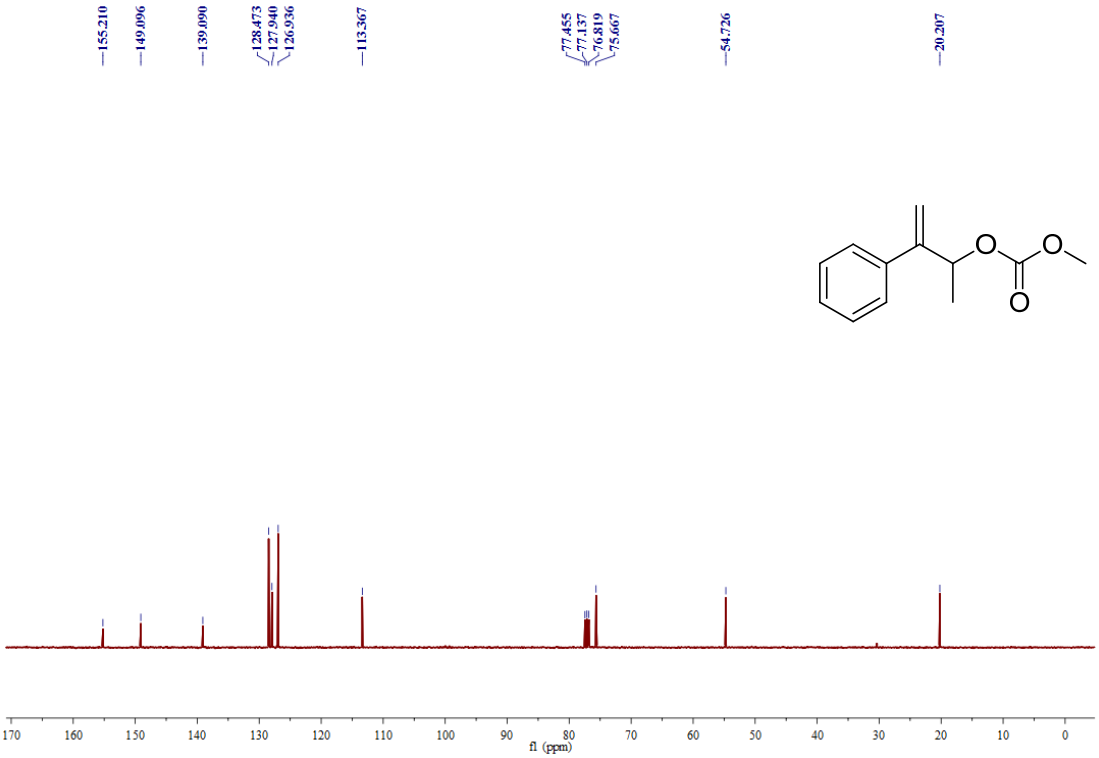
^{13}C NMR (101 MHz, $CDCl_3$) **(1l)**



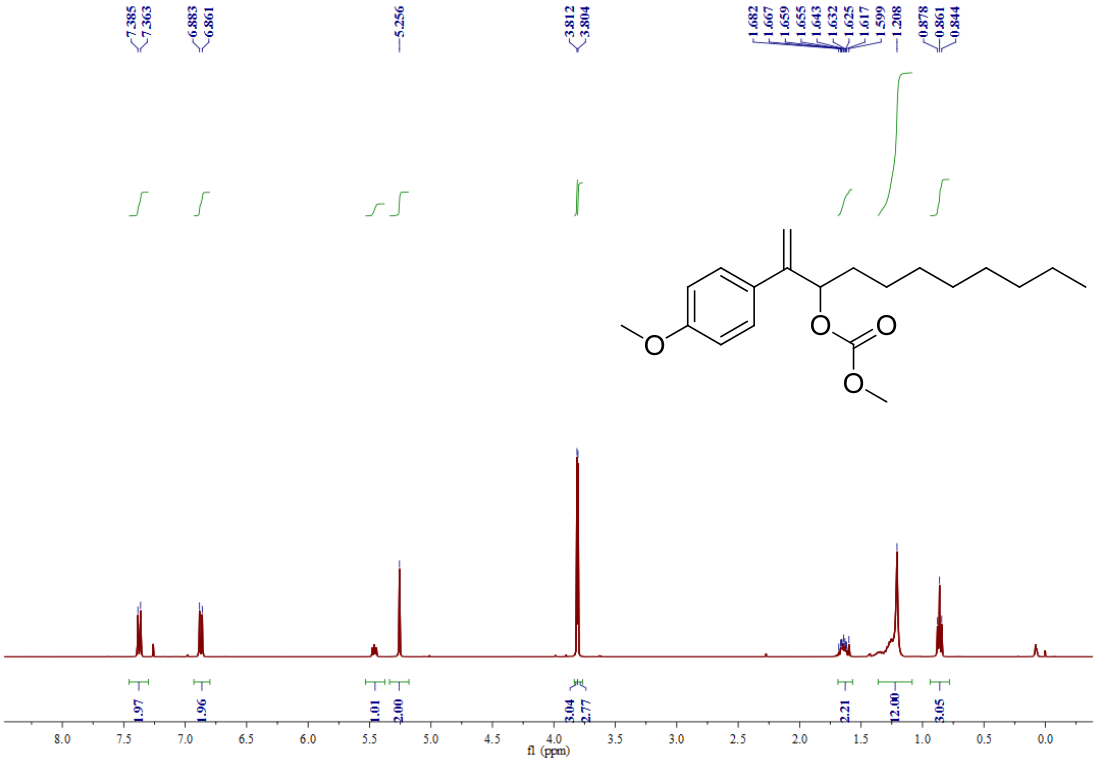
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1m)**



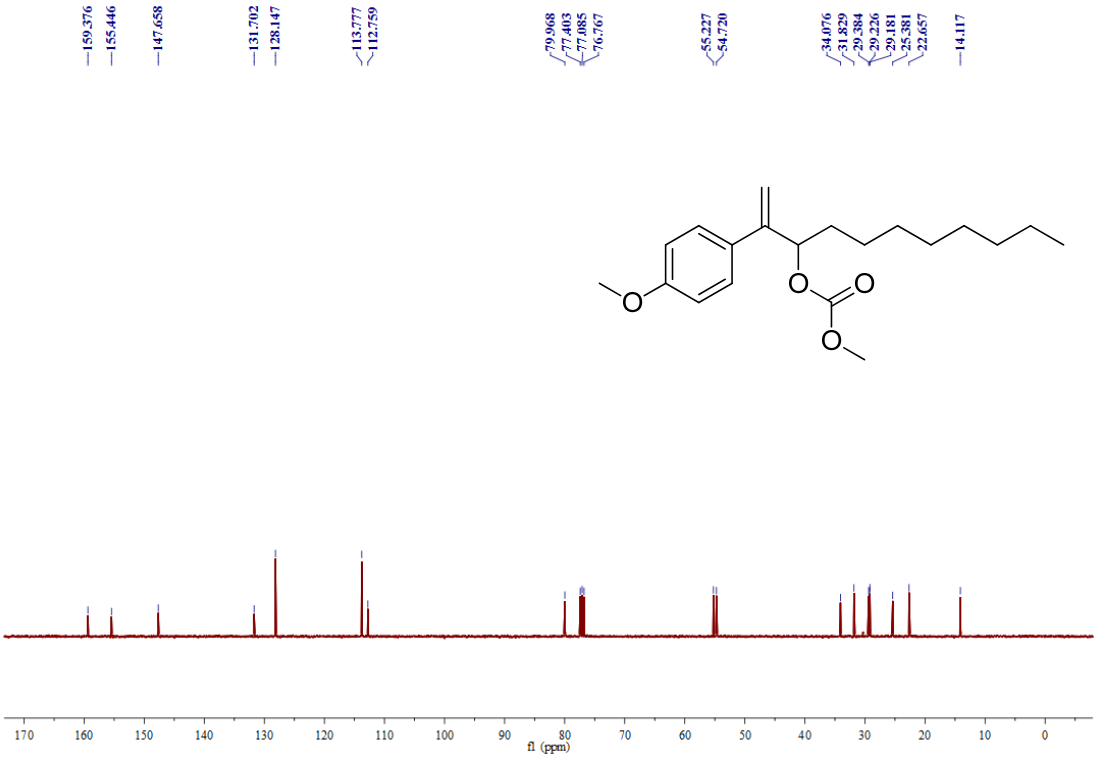
^{13}C NMR (101 MHz, $CDCl_3$) **(1m)**



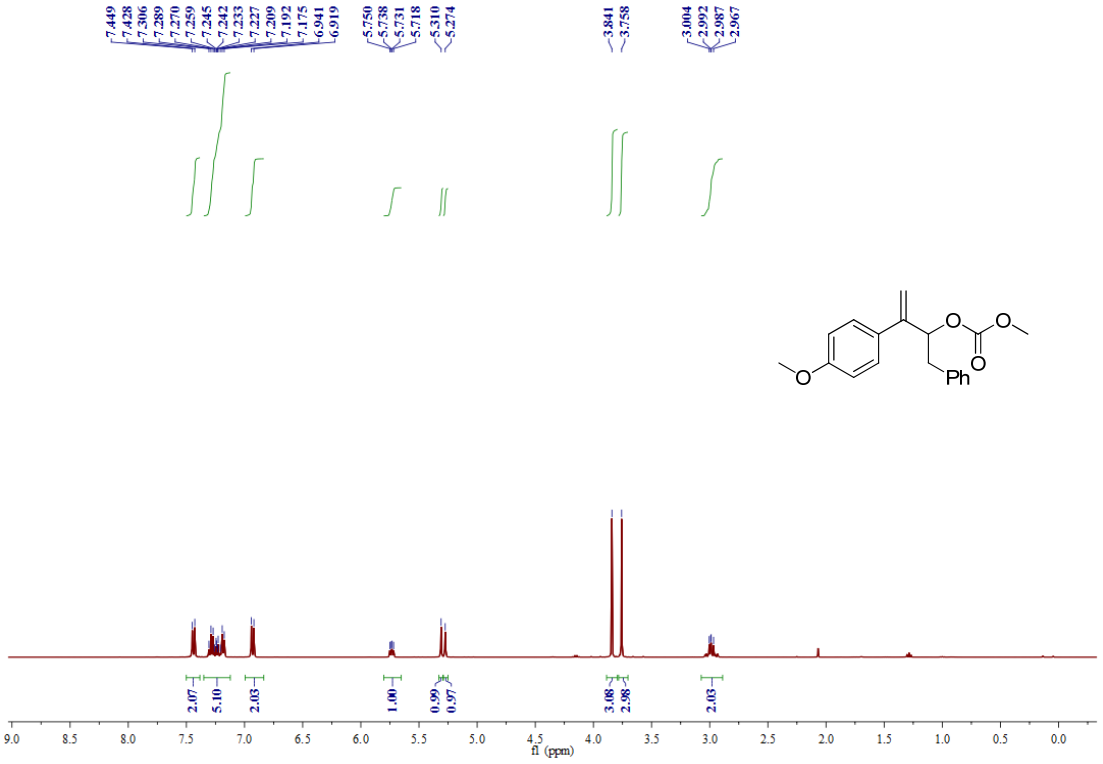
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1n)**



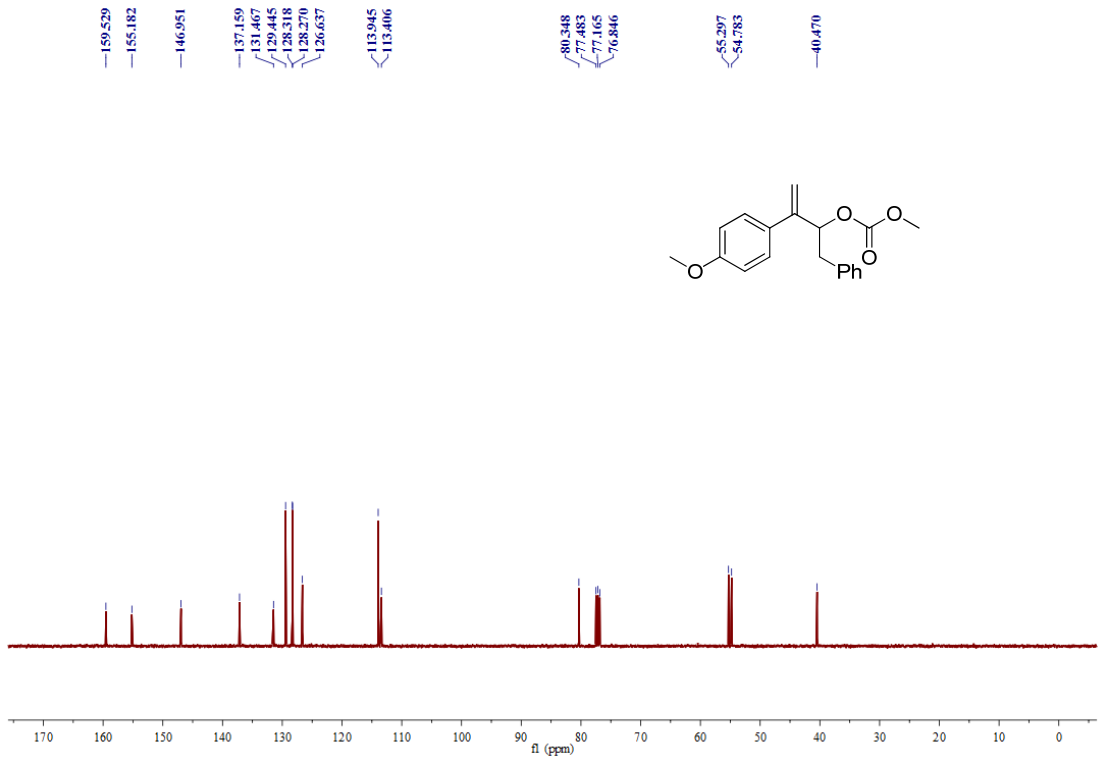
^{13}C NMR (101 MHz, $CDCl_3$) **(1n)**



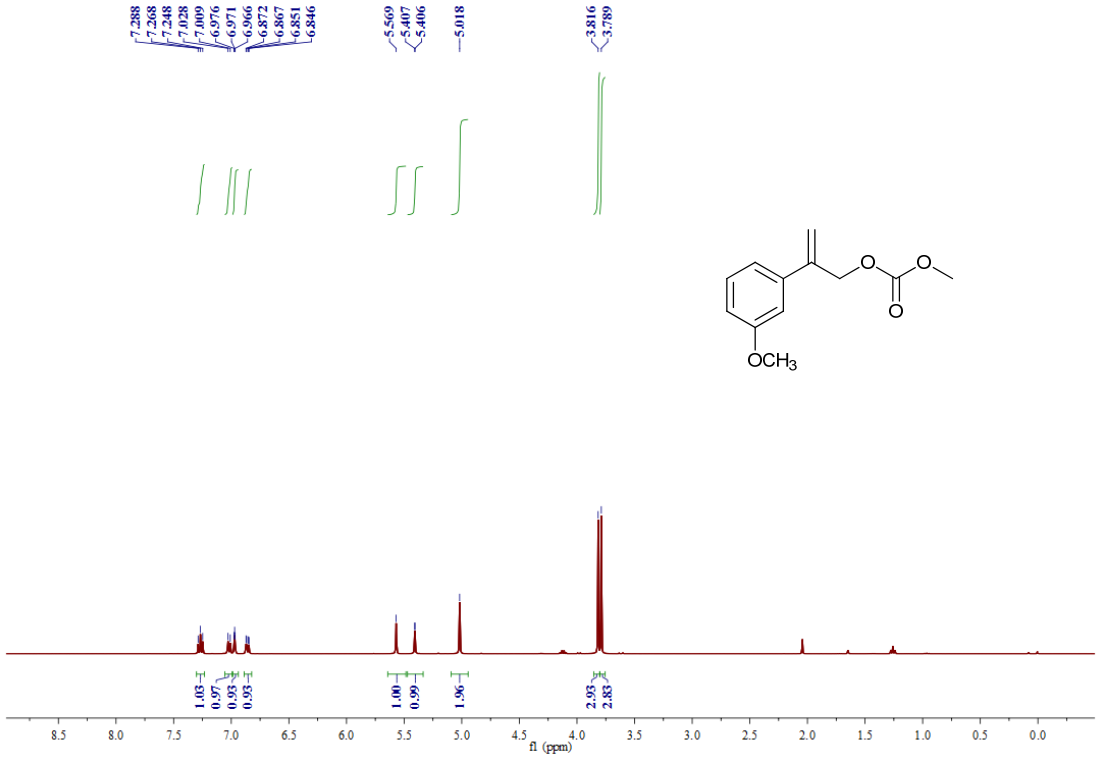
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1o)**



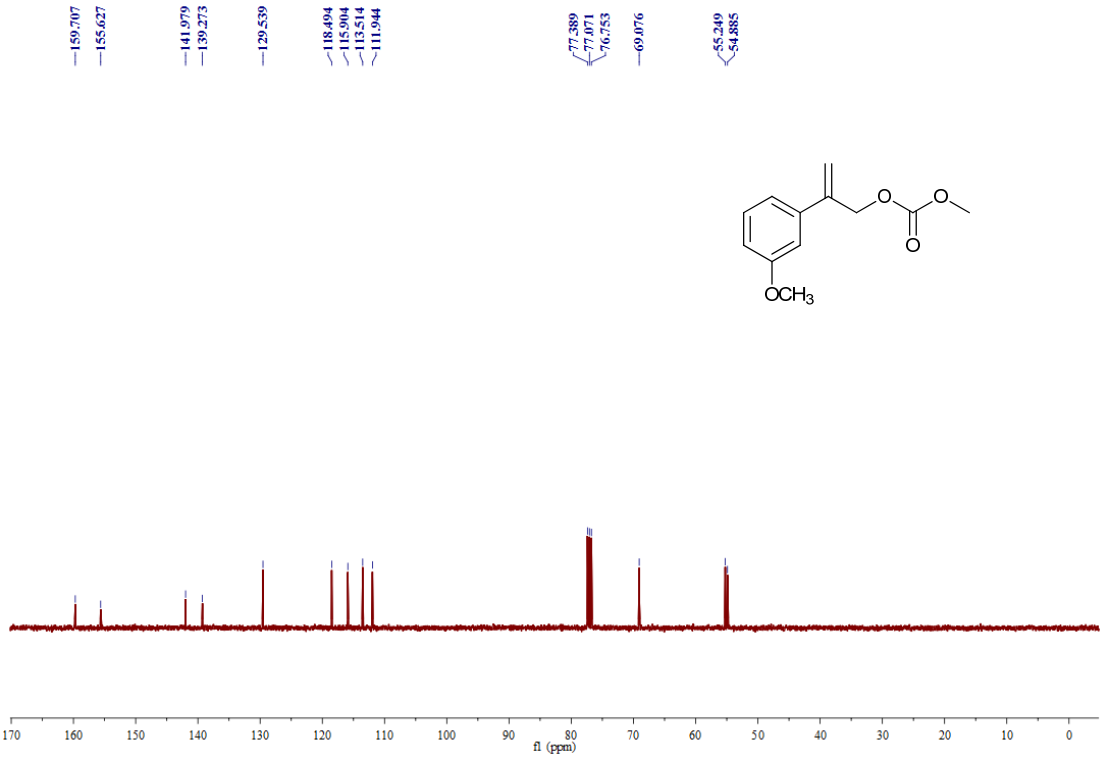
^{13}C NMR (101 MHz, $CDCl_3$) **(1o)**



^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(1p)**

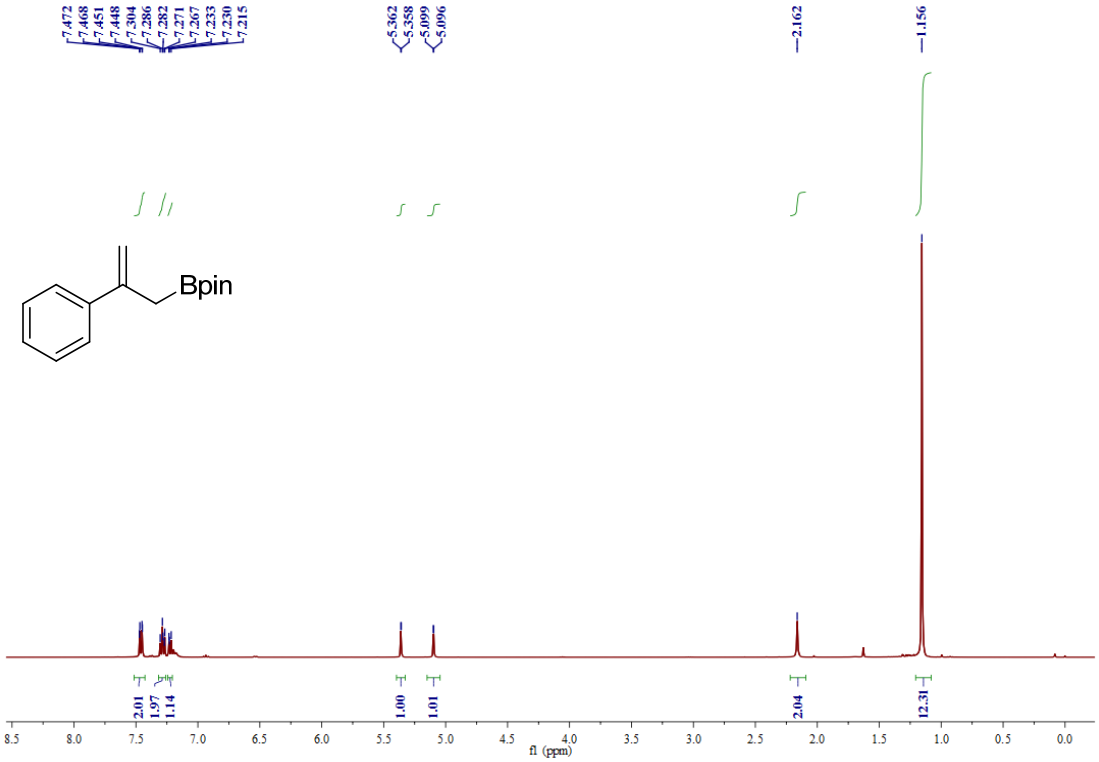


^{13}C NMR (101 MHz, $CDCl_3$) **(1p)**

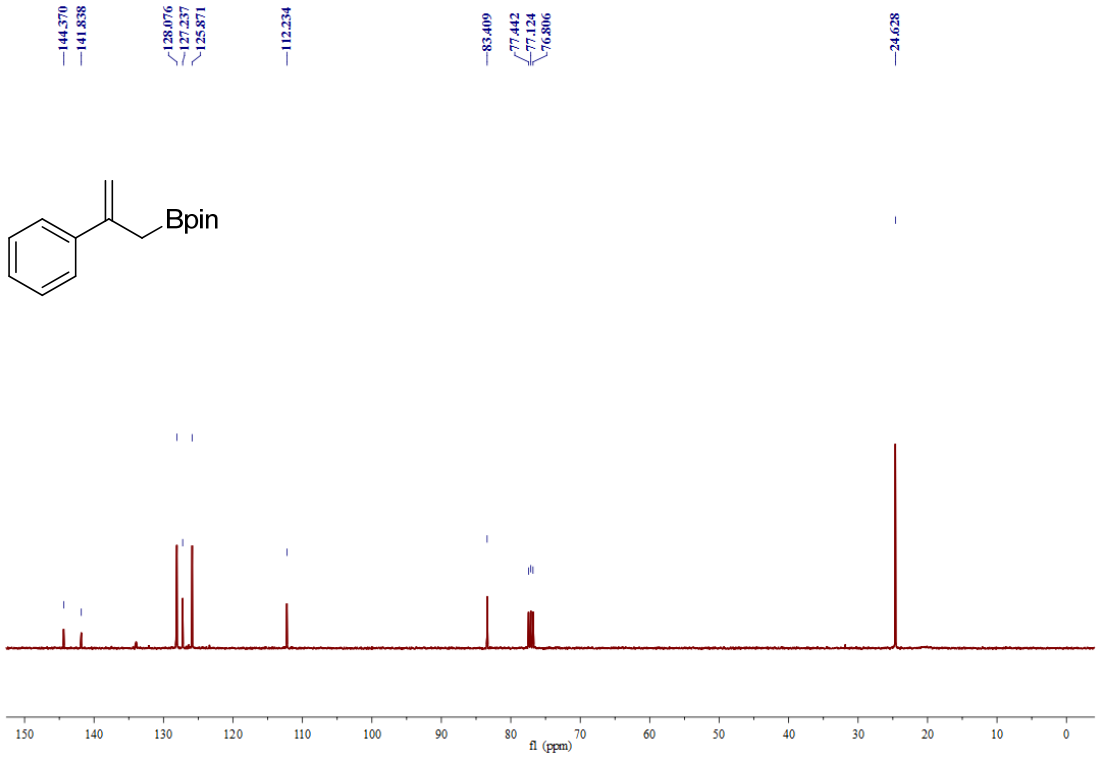


NMR Spectra of products

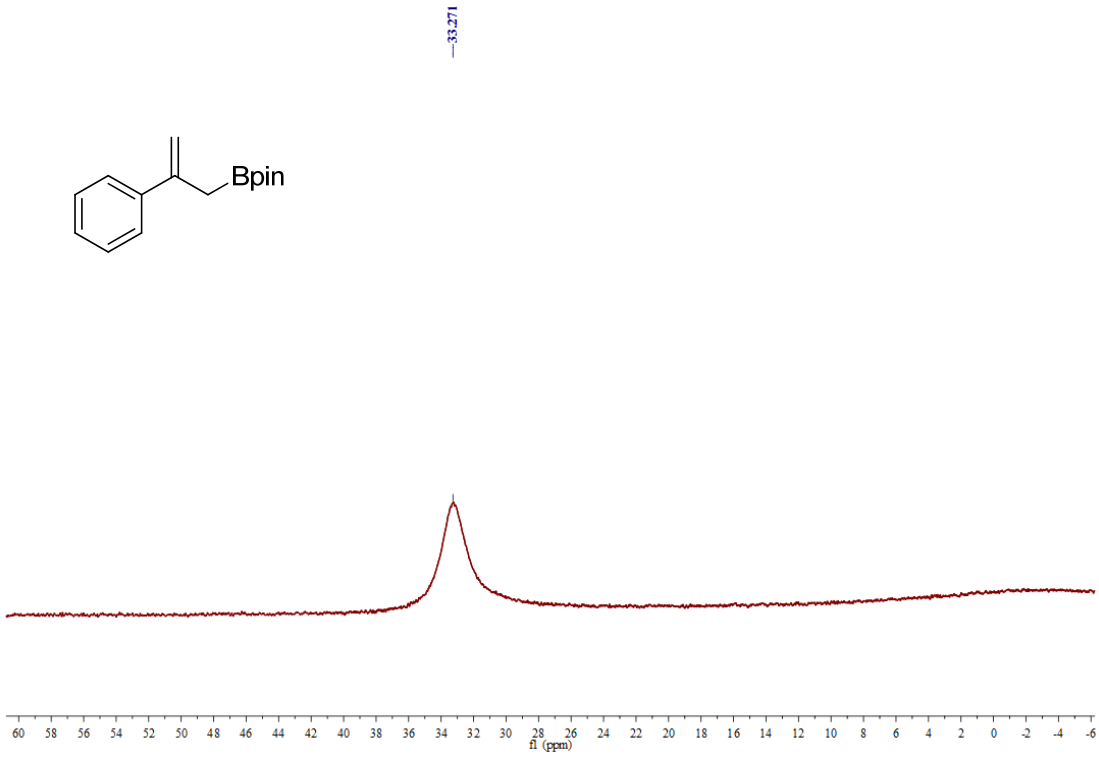
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3a)**



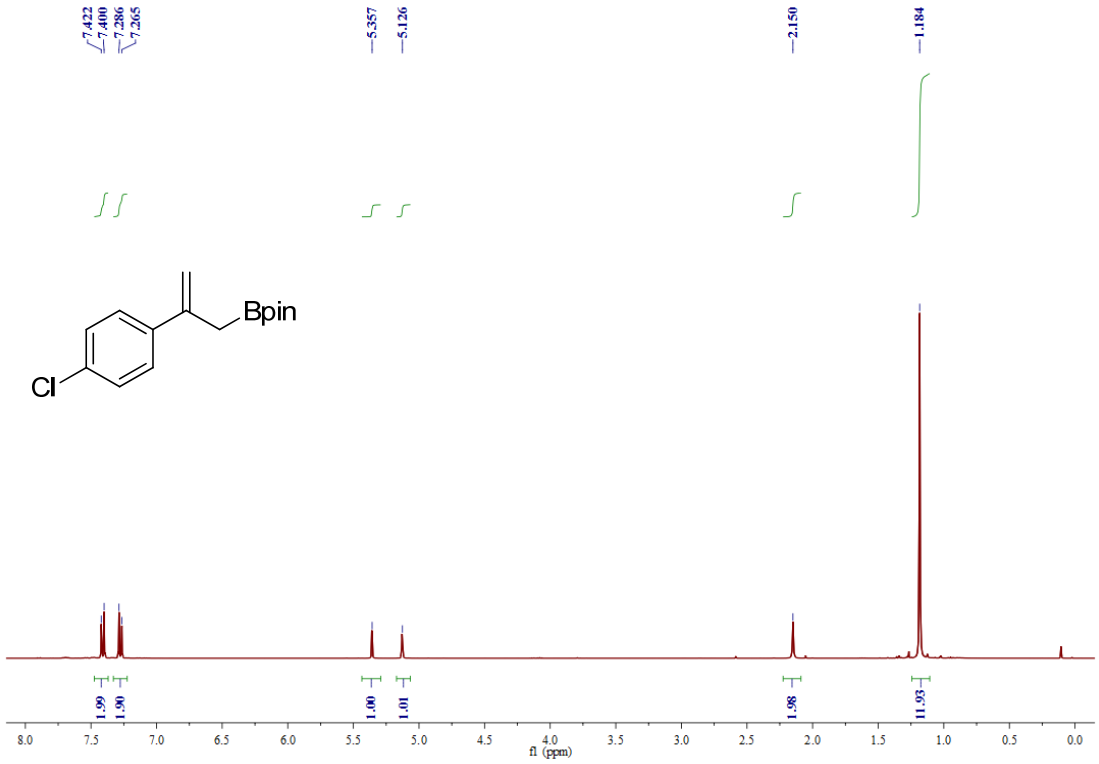
^{13}C NMR (101 MHz, $CDCl_3$) **(3a)**



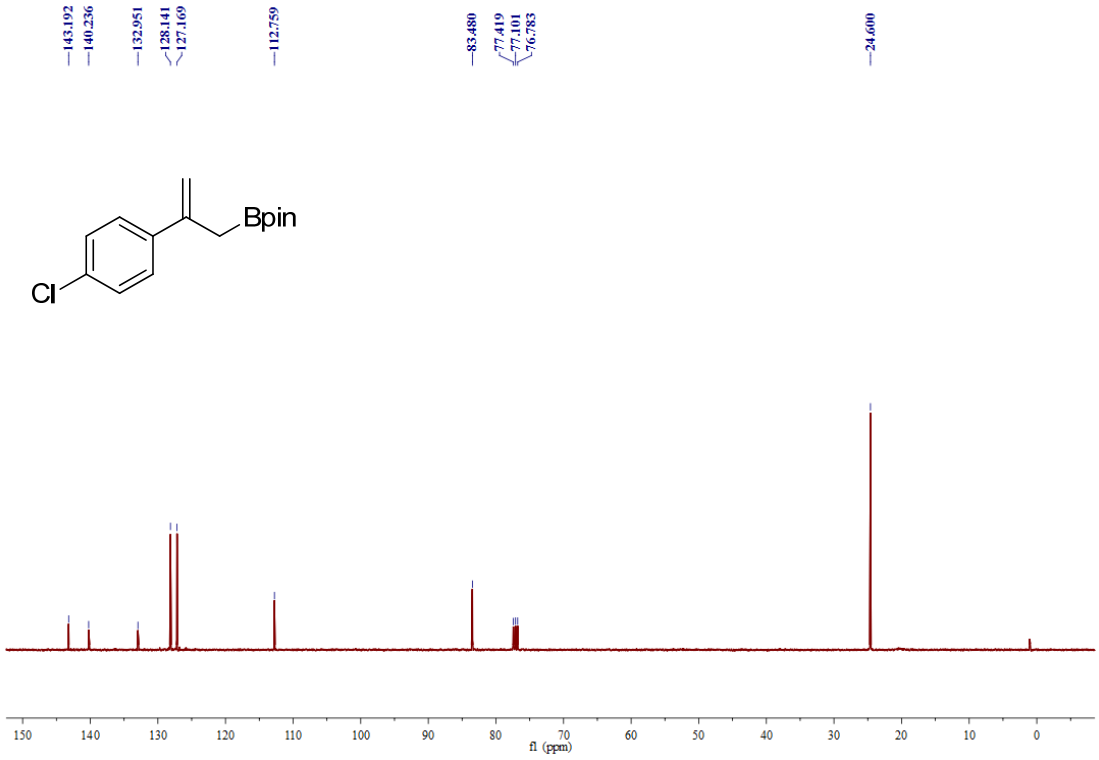
^{11}B NMR (128 MHz, $CDCl_3$) **(3a)**



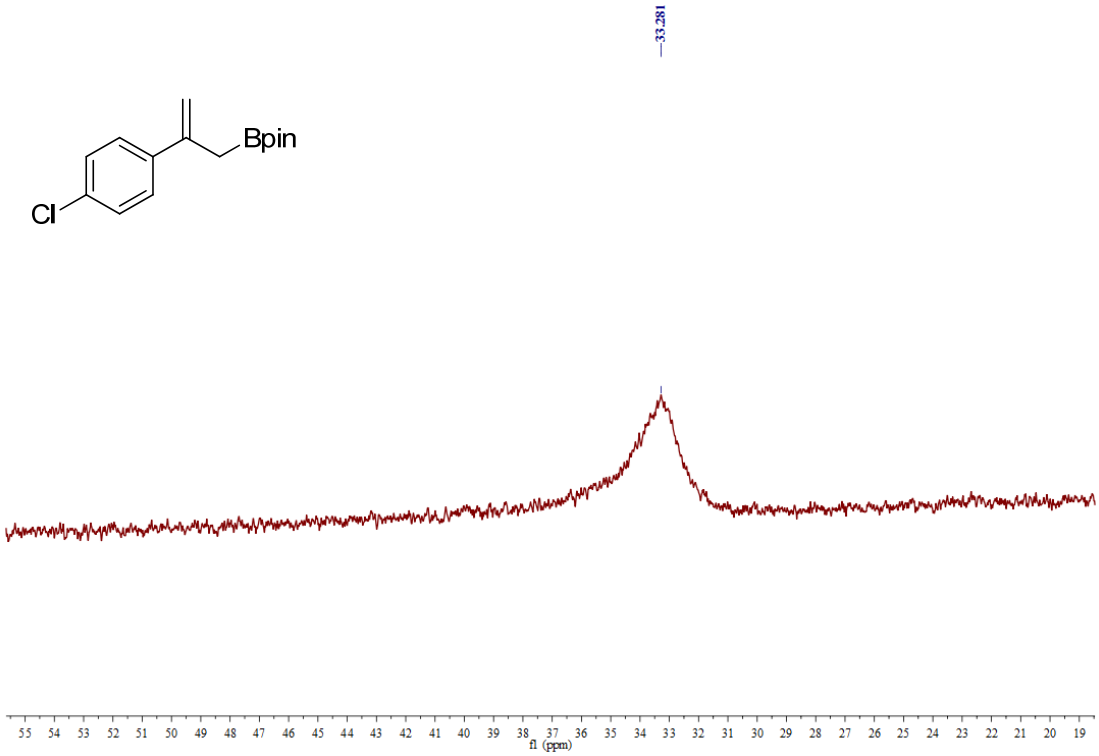
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3b)**



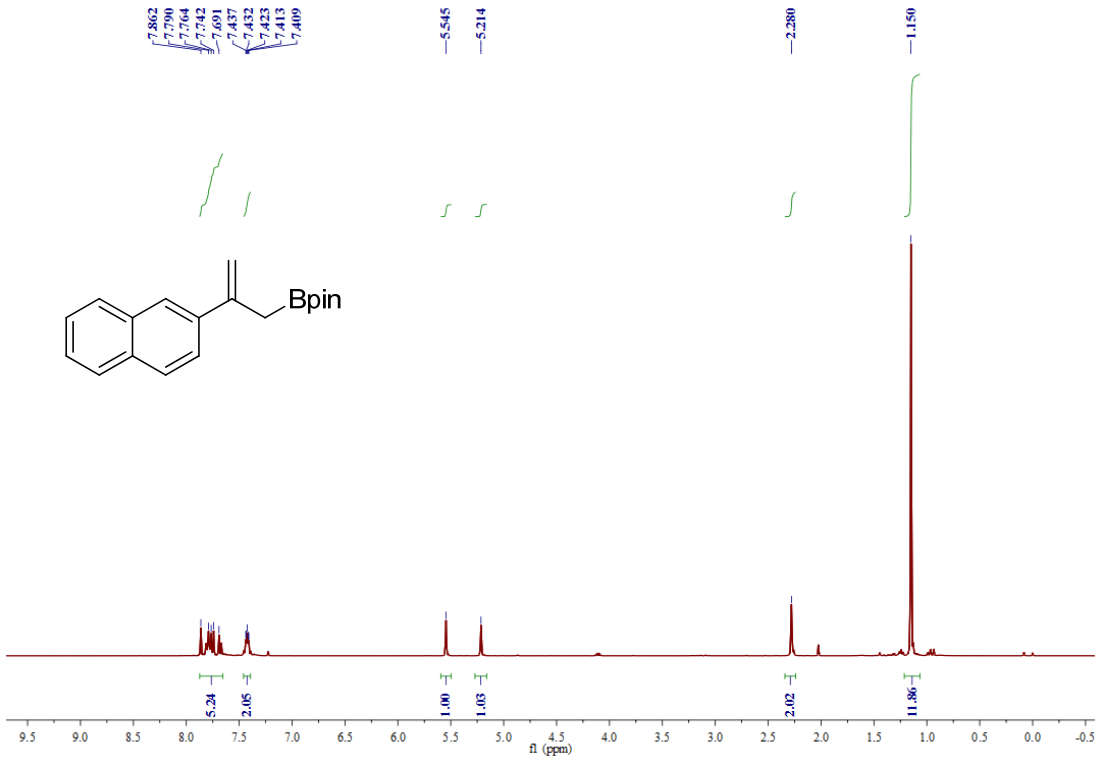
^{13}C NMR (101 MHz, $CDCl_3$) **(3b)**



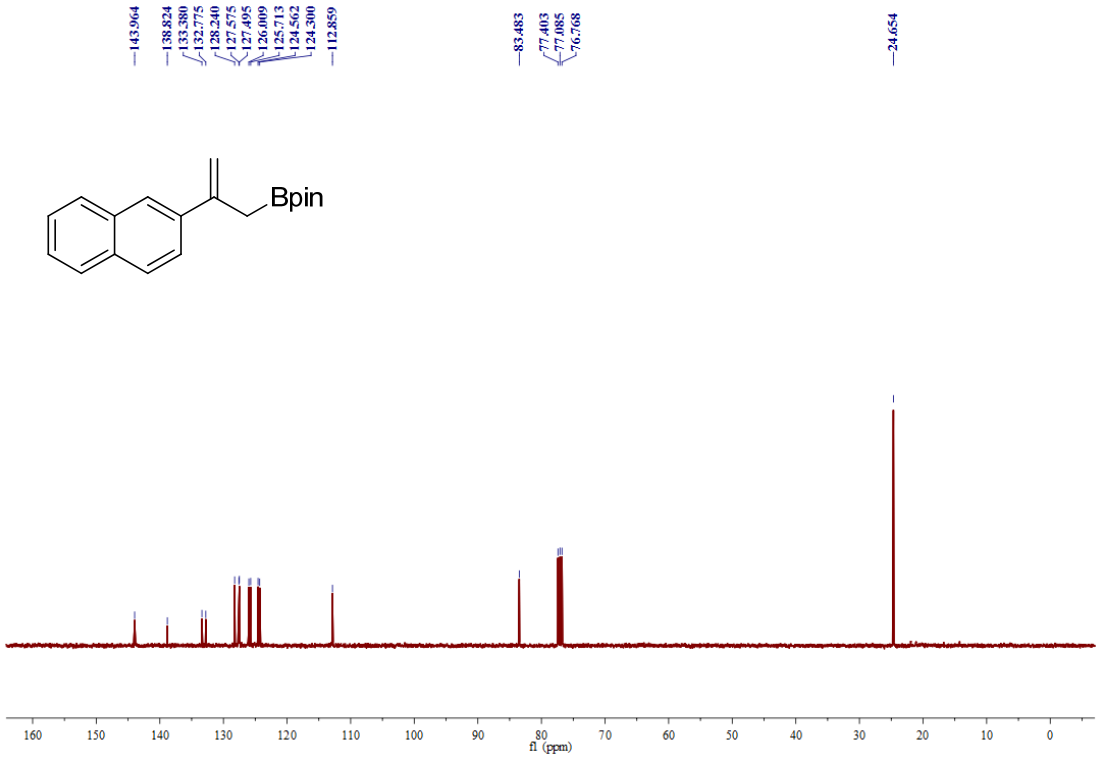
^{11}B NMR (128 MHz, $CDCl_3$) **(3b)**



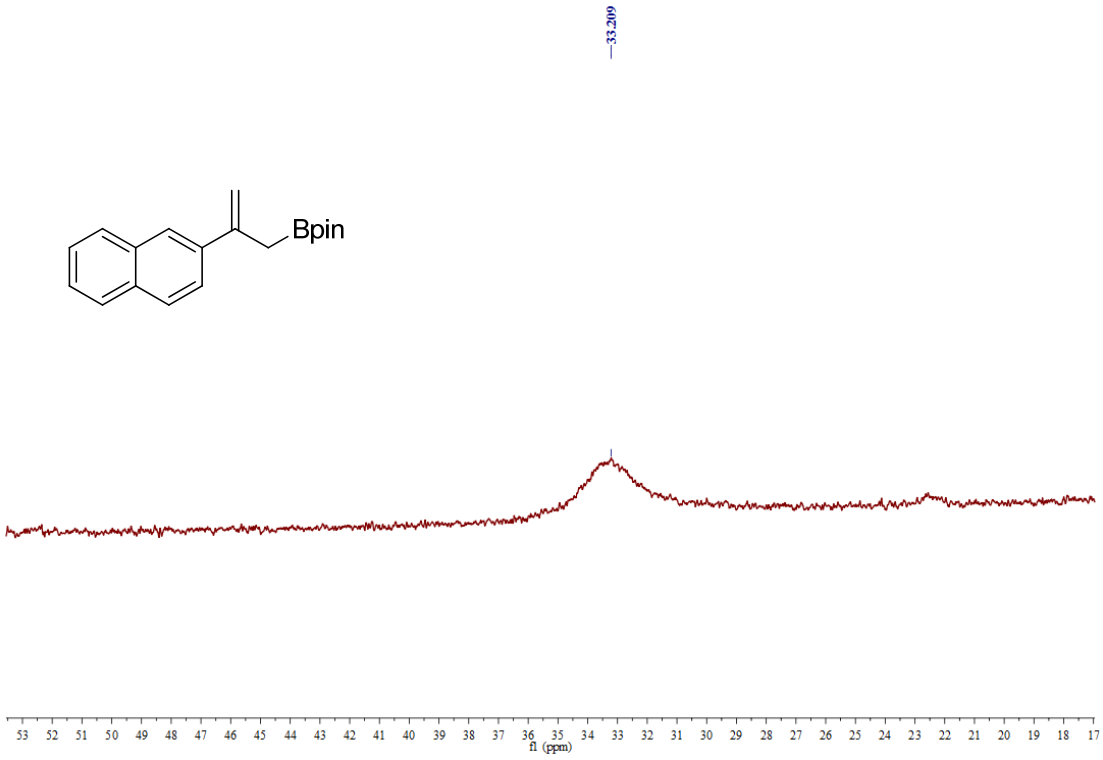
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3c)**



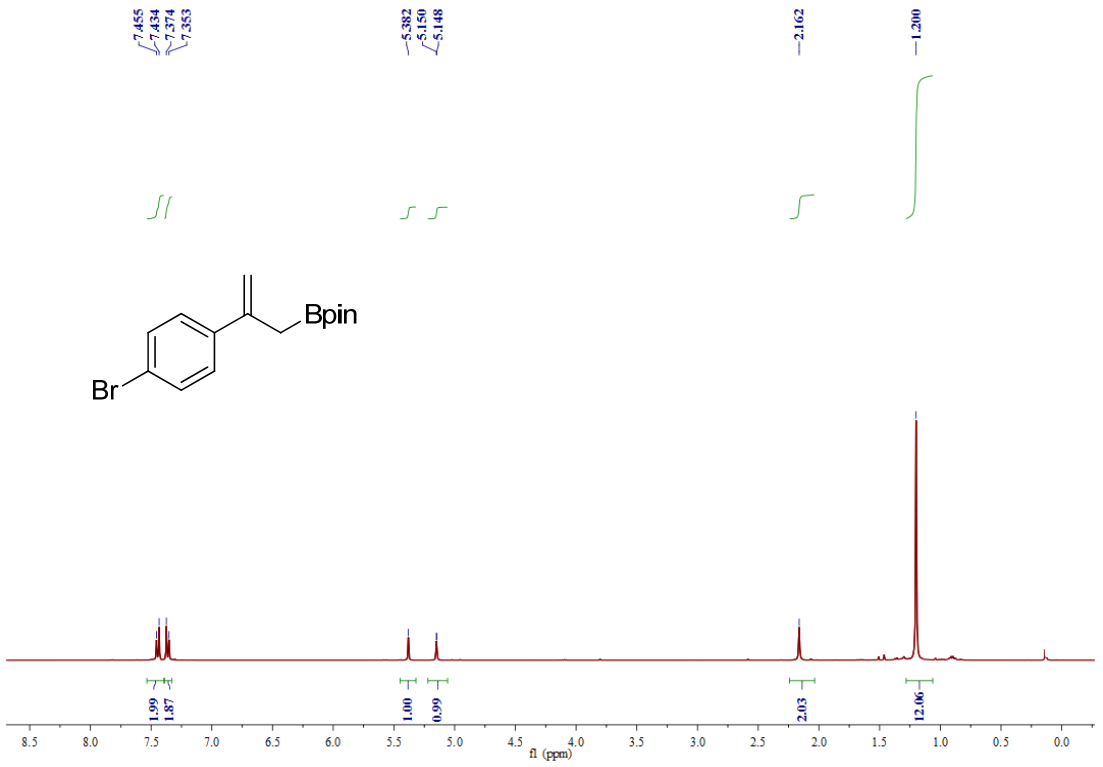
^{13}C NMR (101 MHz, $CDCl_3$) **(3c)**



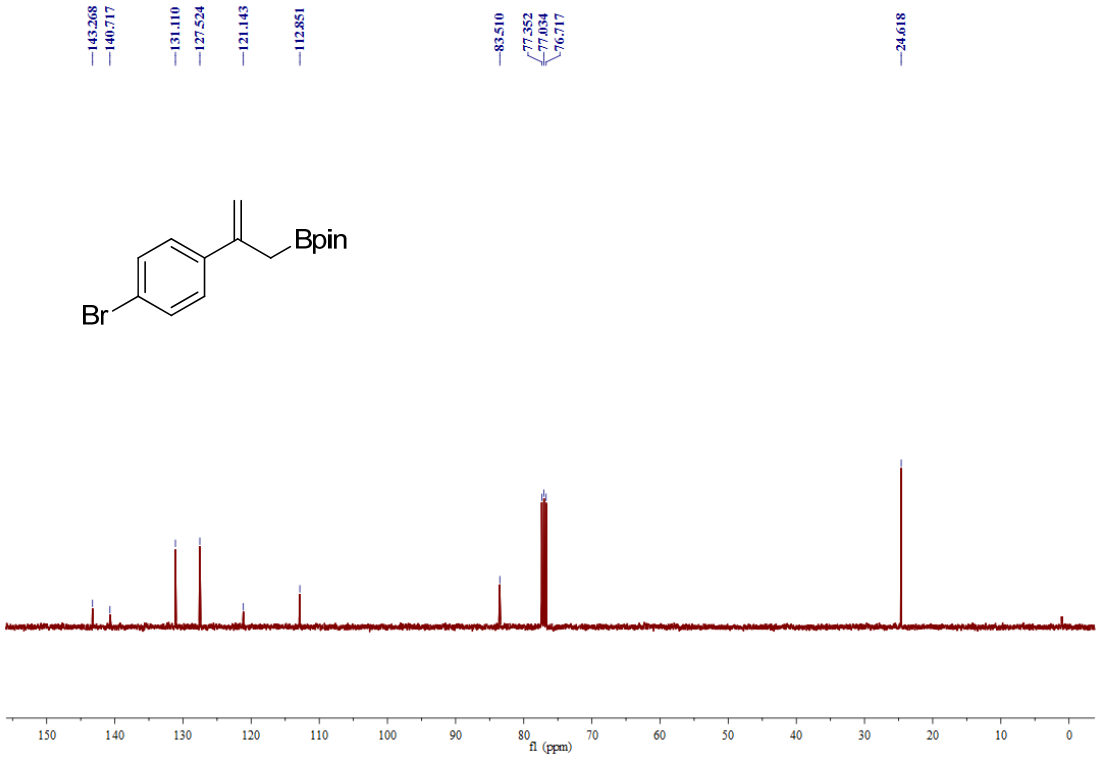
^{11}B NMR (128 MHz, $CDCl_3$) **(3c)**



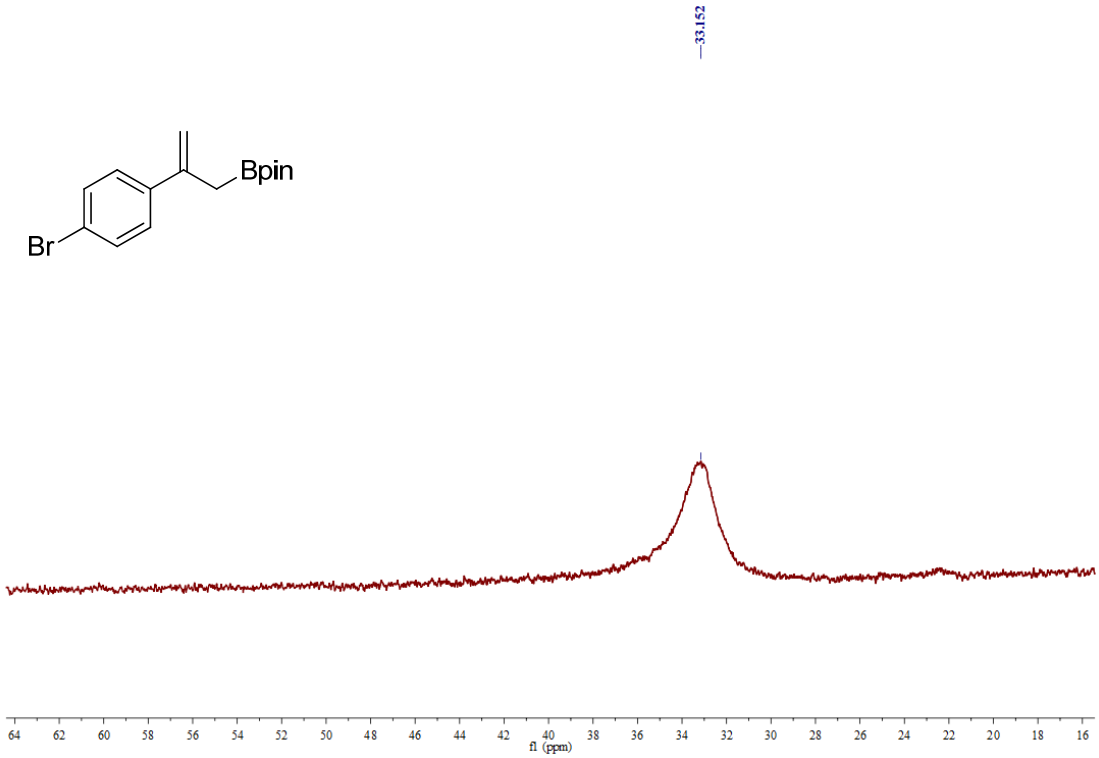
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3d)**



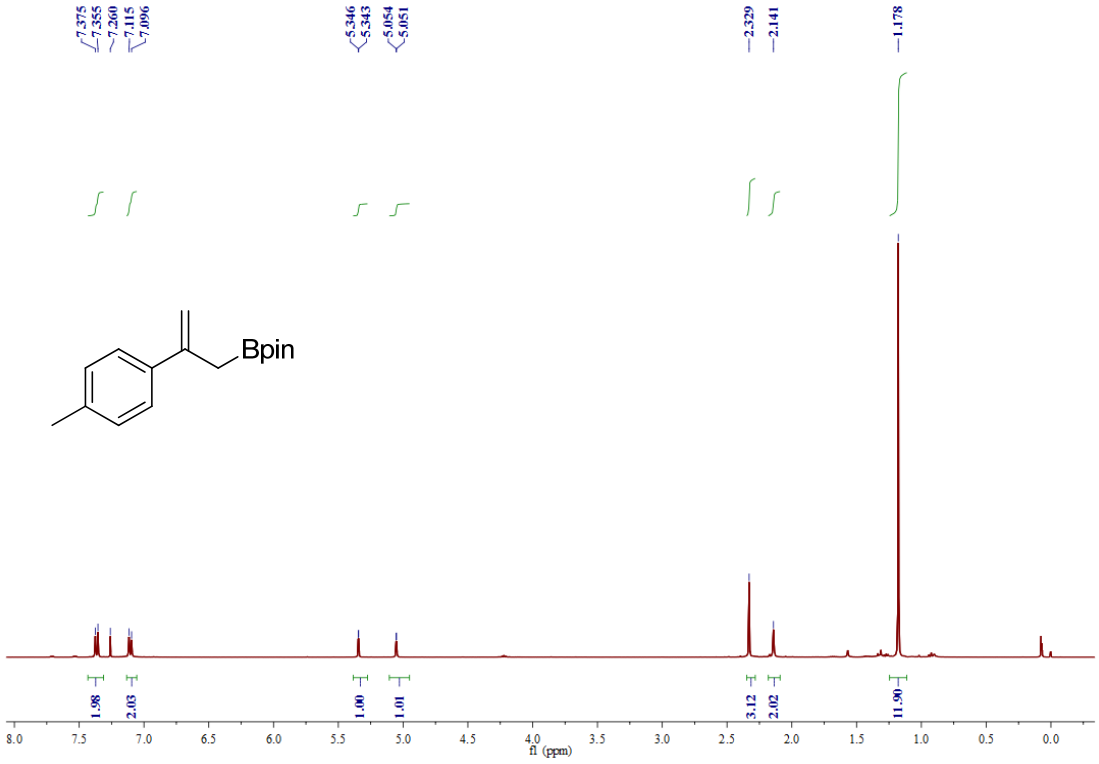
^{13}C NMR (101 MHz, $CDCl_3$) **(3d)**



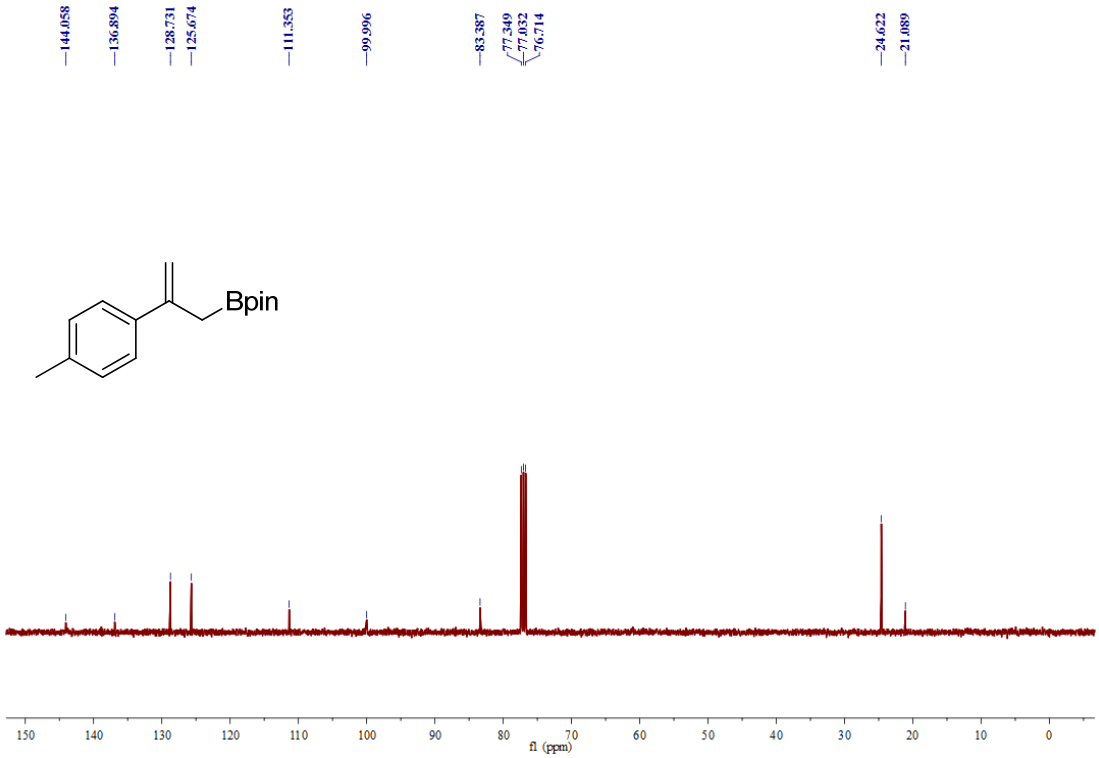
^{11}B NMR (128 MHz, $CDCl_3$) **(3d)**



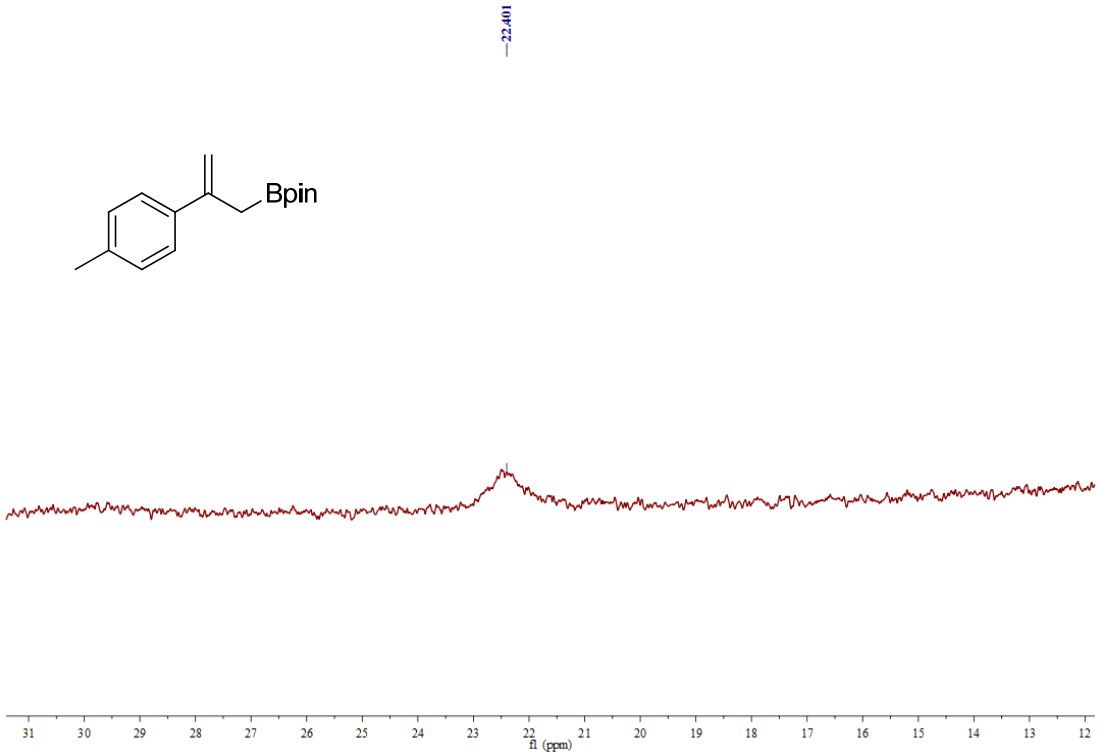
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3e)**



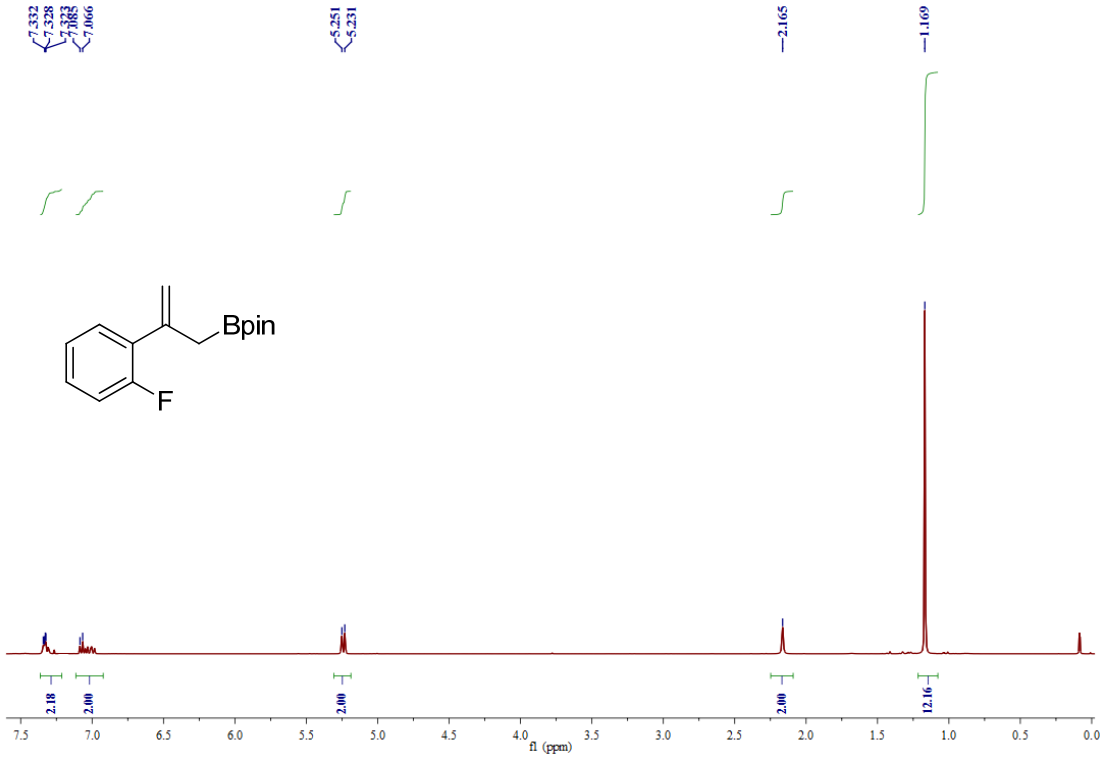
^{13}C NMR (101 MHz, $CDCl_3$) **(3e)**



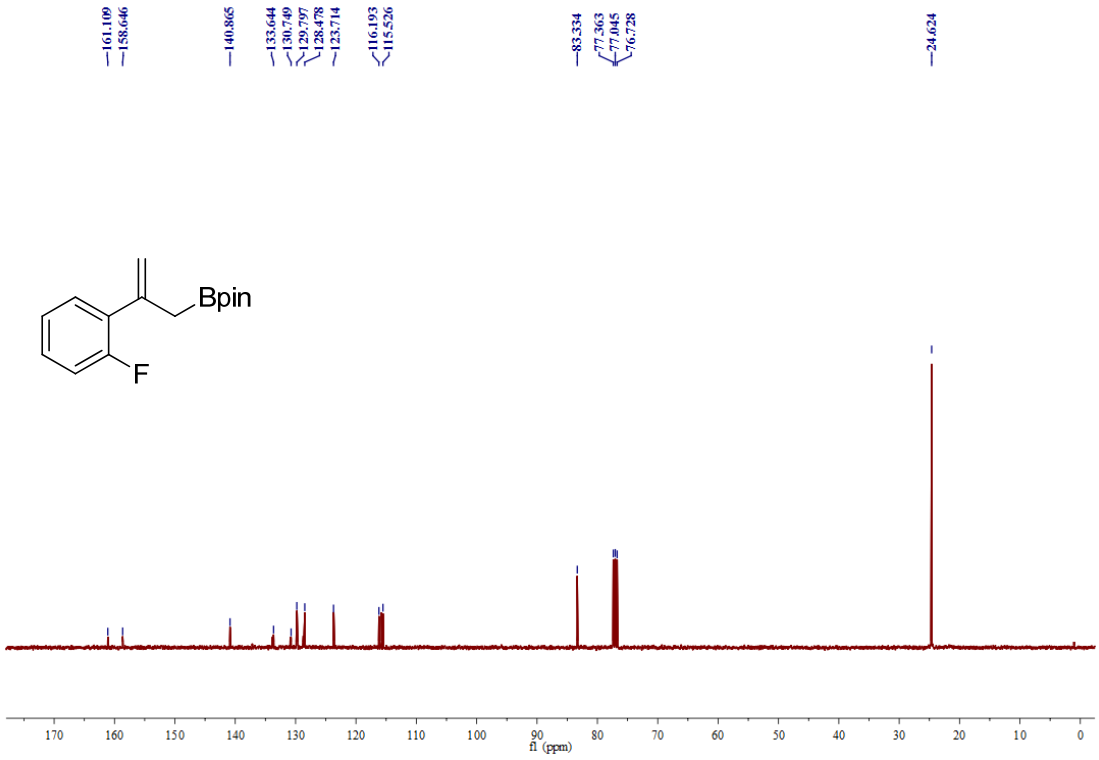
^{11}B NMR (128 MHz, $CDCl_3$) **(3e)**



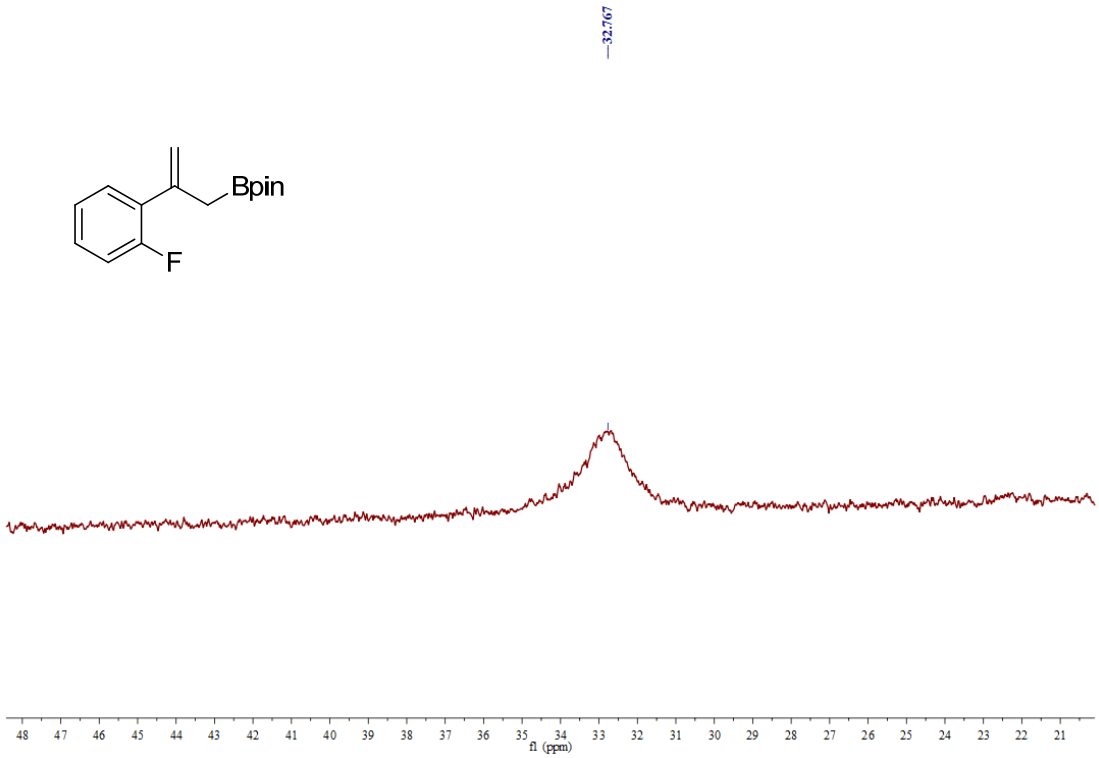
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3f)**



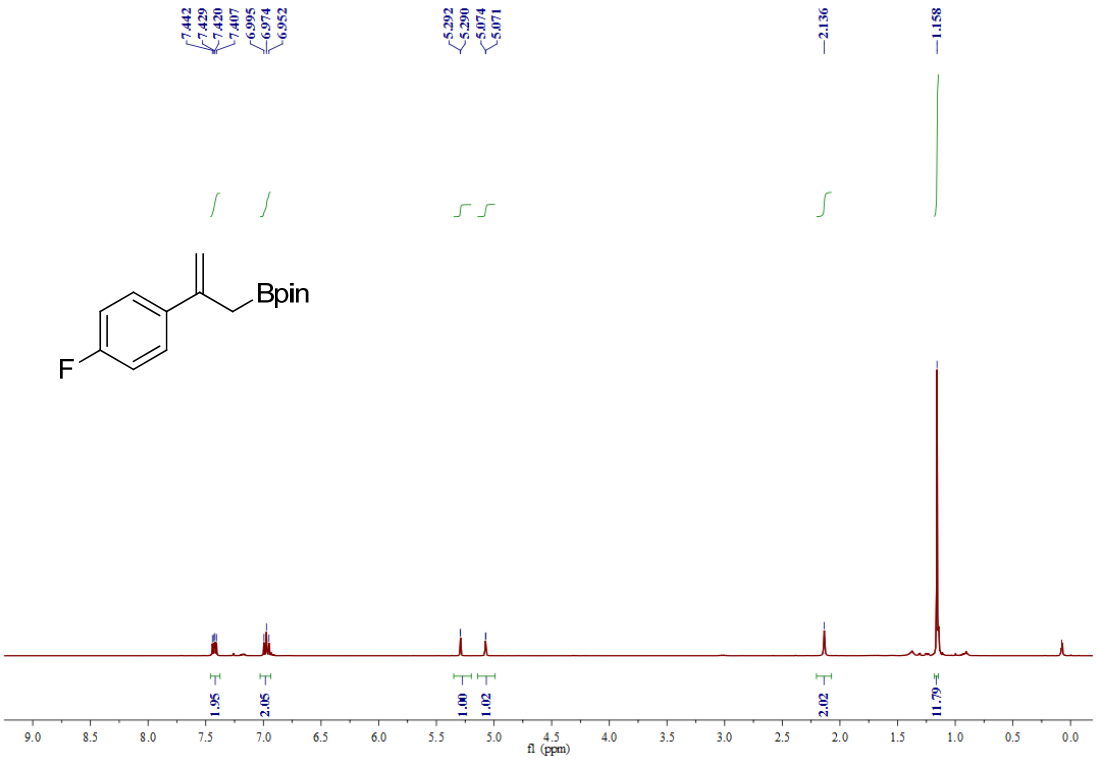
^{13}C NMR (101 MHz, $CDCl_3$) **(3f)**



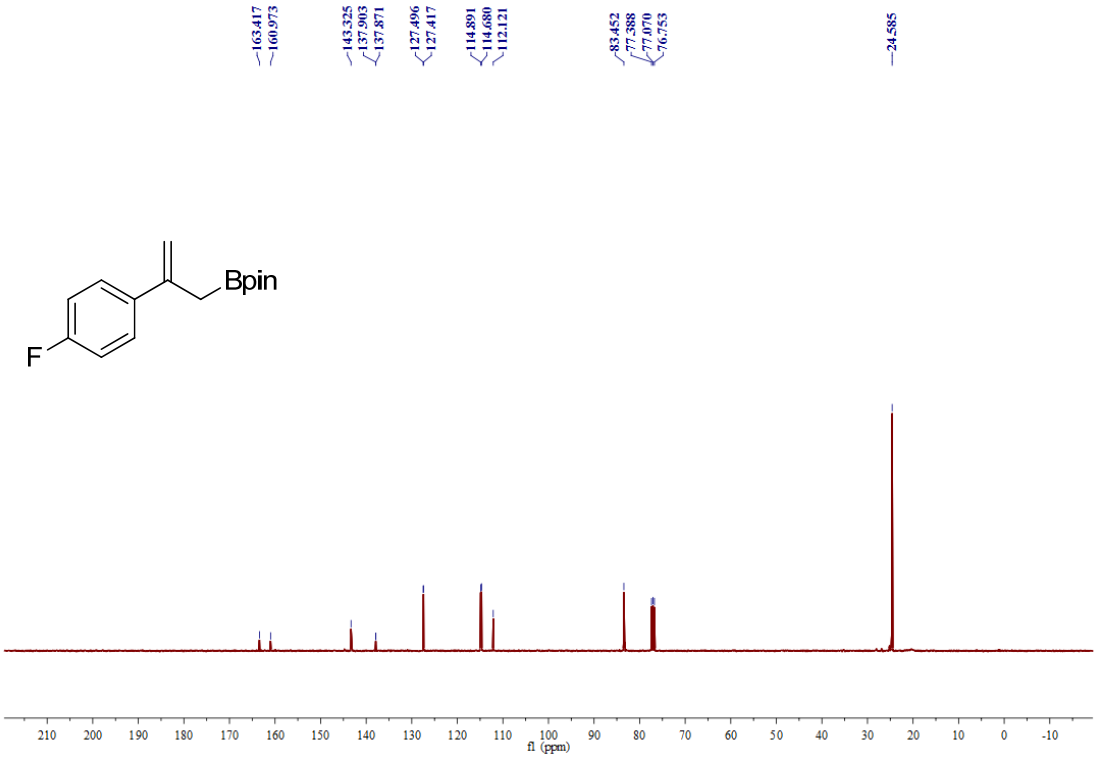
^{11}B NMR (128 MHz, $CDCl_3$) **(3f)**



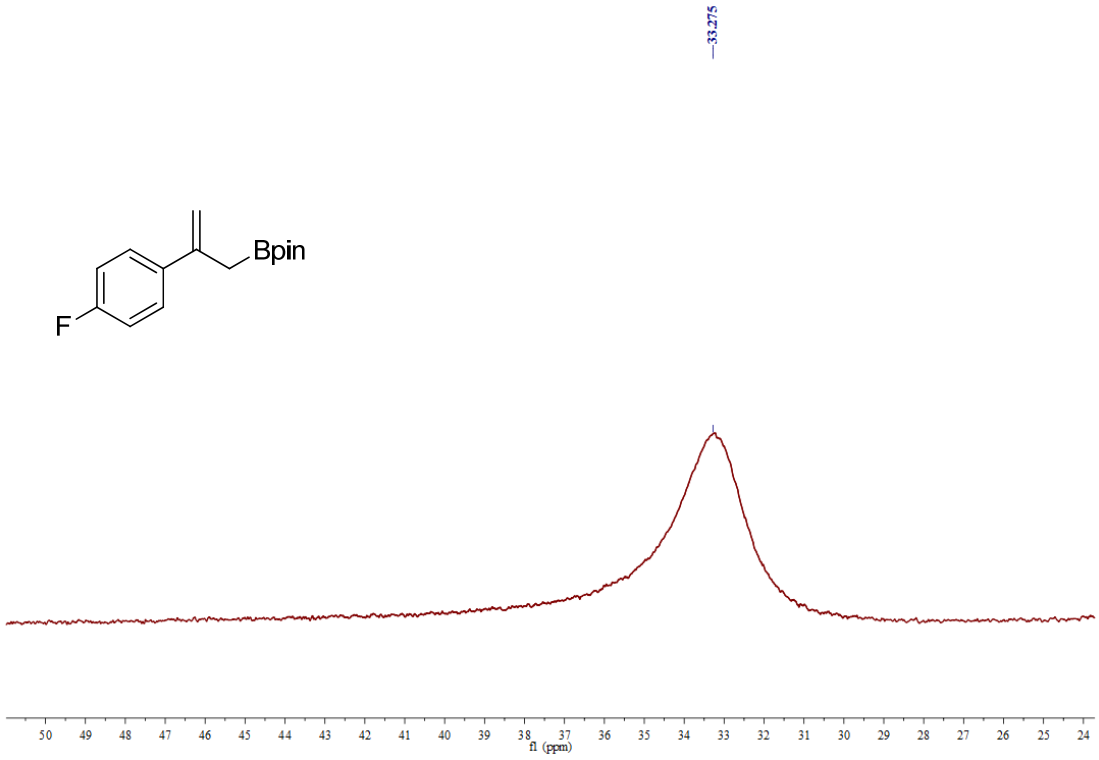
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3g)**



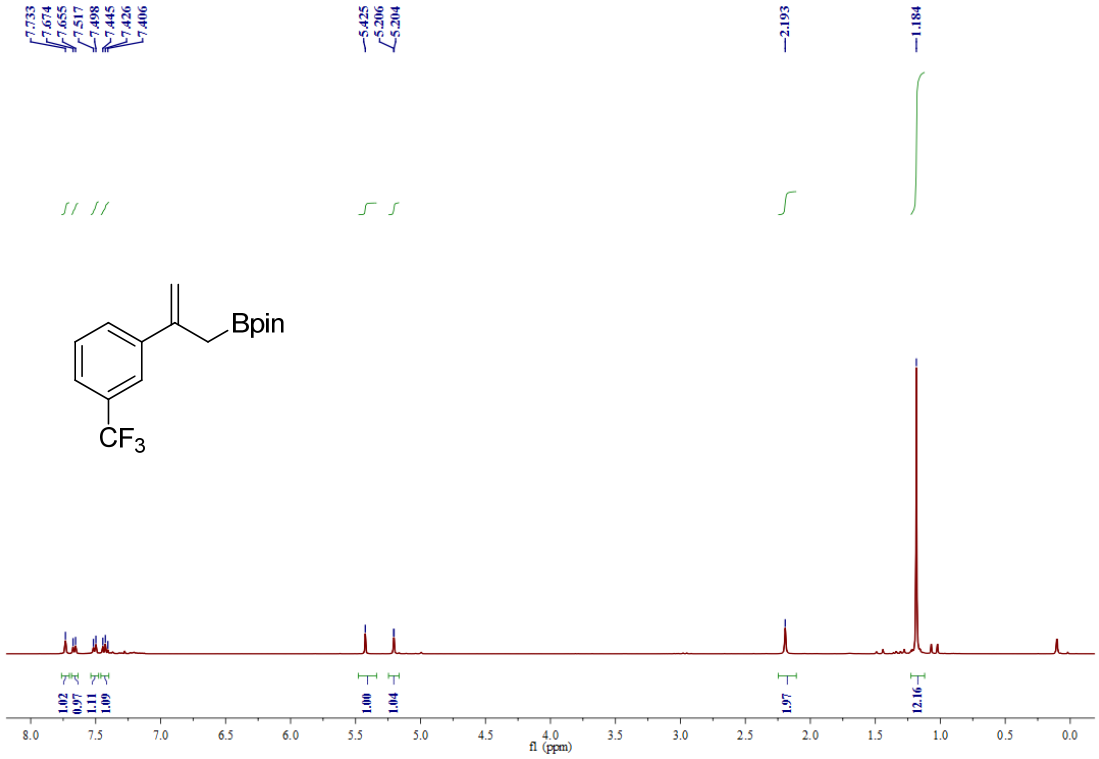
^{13}C NMR (101 MHz, $CDCl_3$) **(3g)**



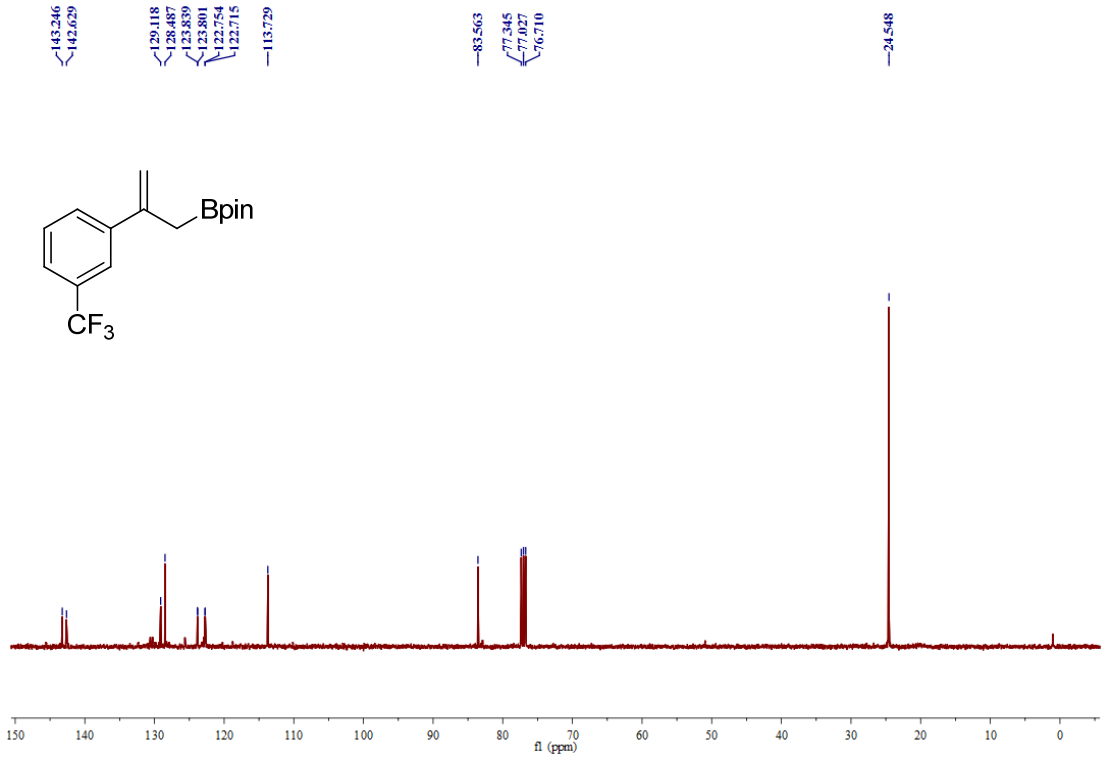
^{11}B NMR (128 MHz, $CDCl_3$) **(3g)**



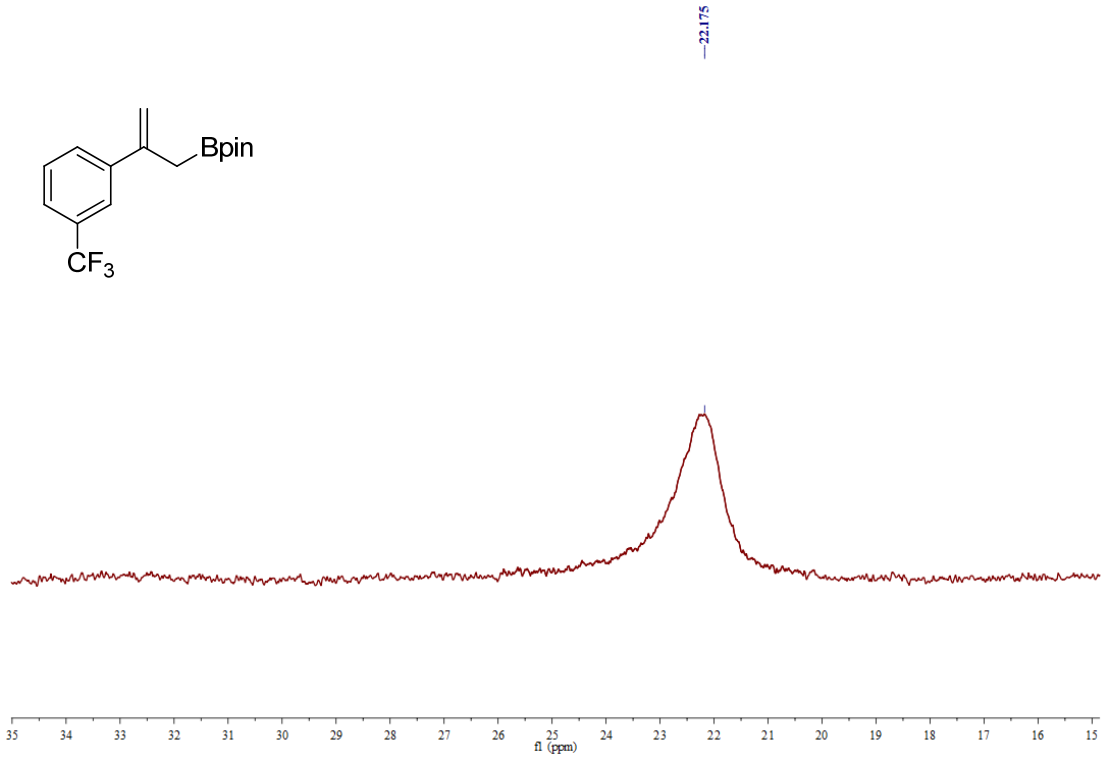
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3h)**



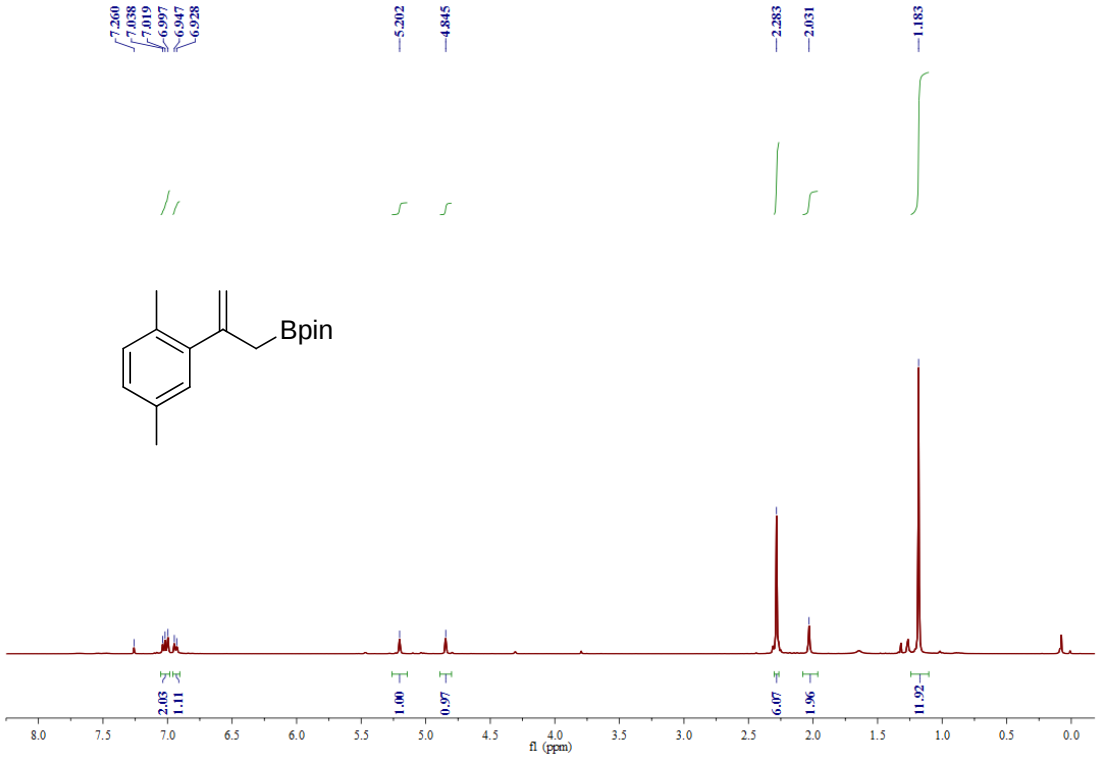
^{13}C NMR (101 MHz, $CDCl_3$) **(3h)**



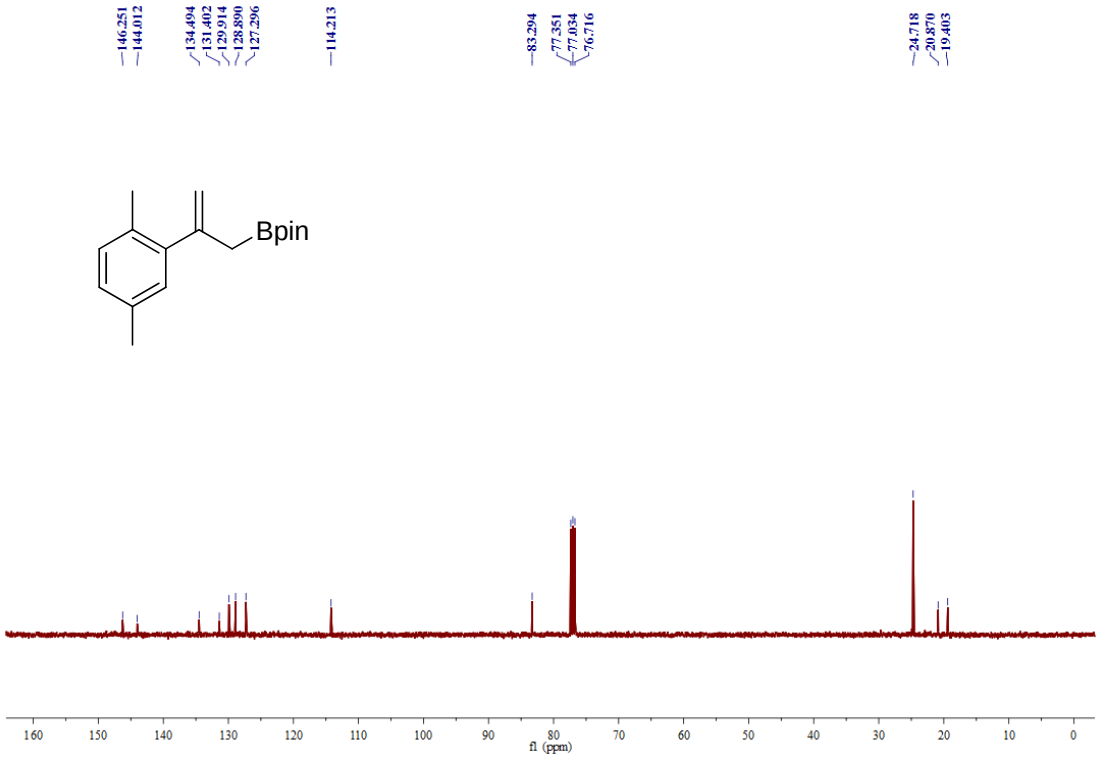
^{11}B NMR (128 MHz, $CDCl_3$) **(3h)**



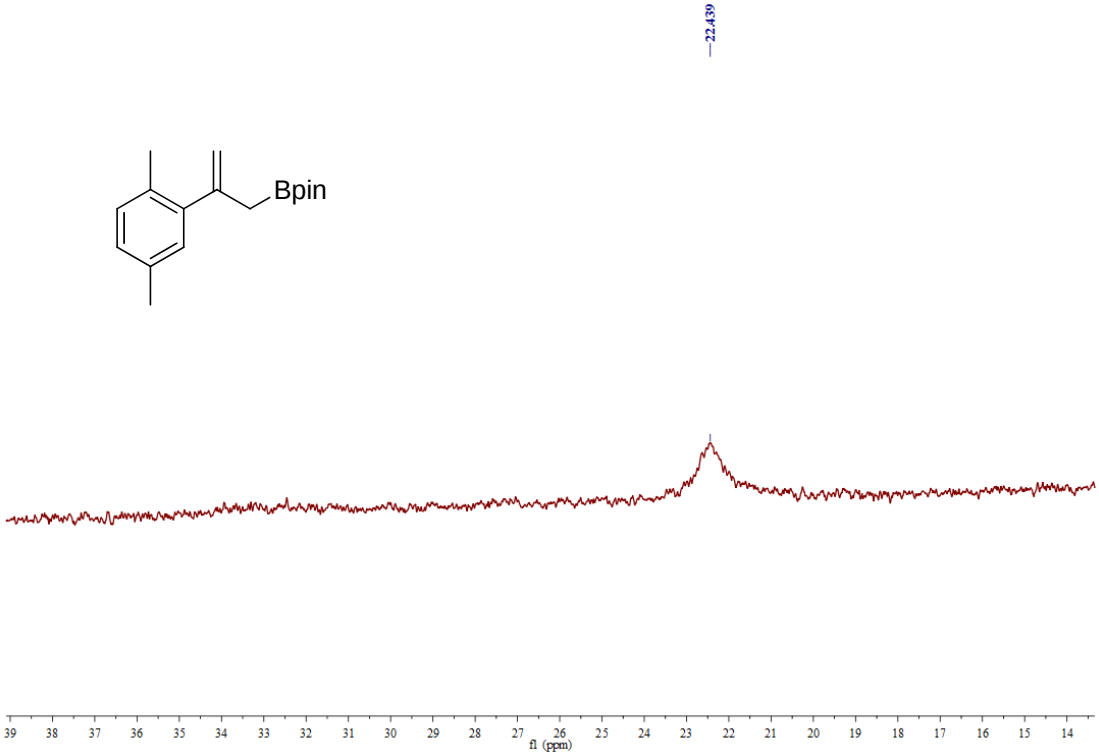
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3i)**



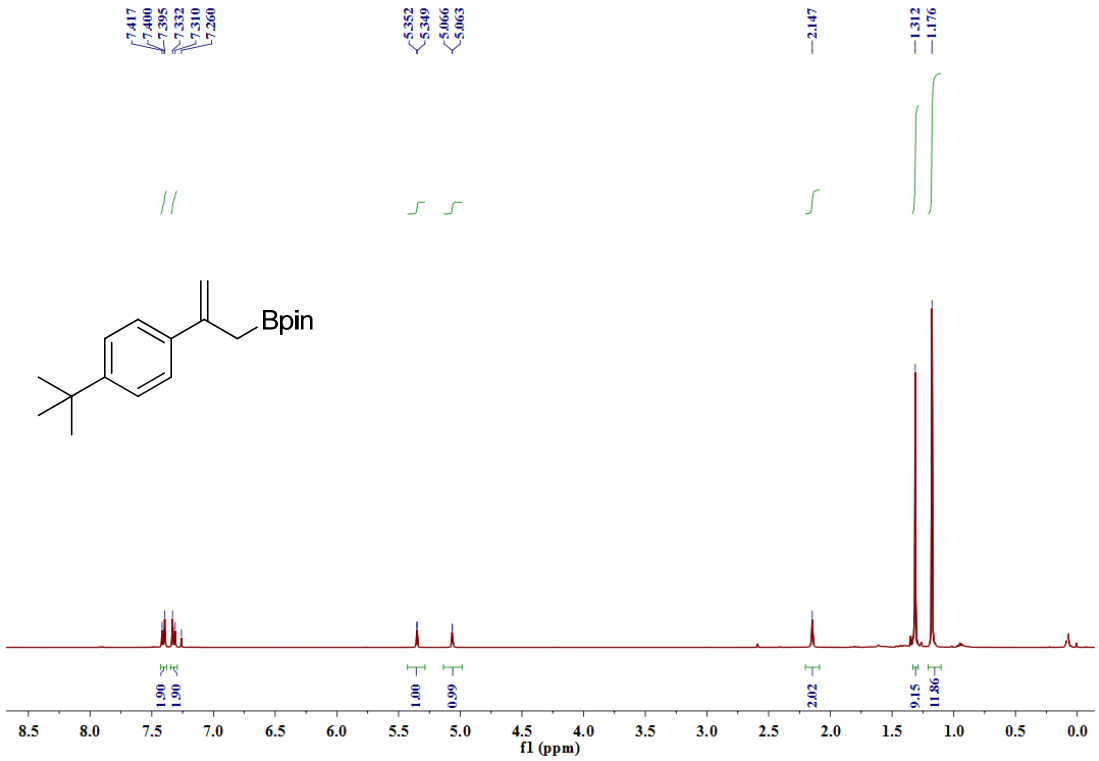
^{13}C NMR (101 MHz, $CDCl_3$) **(3i)**



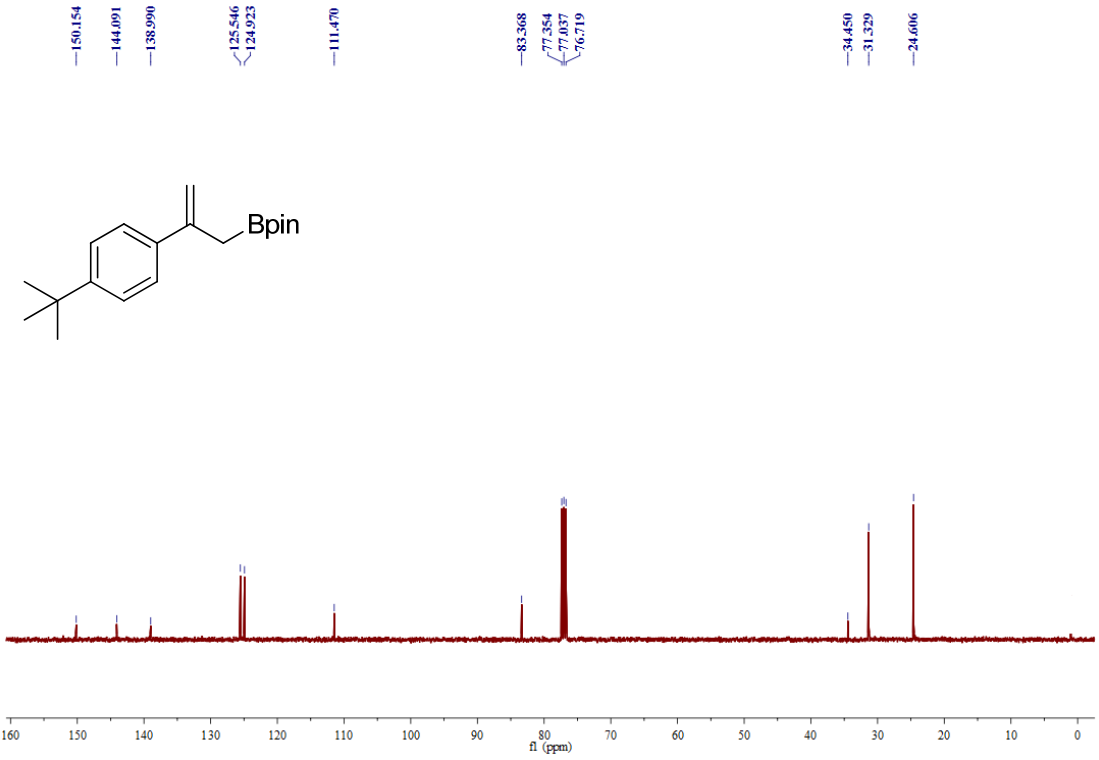
^{11}B NMR (128 MHz, $CDCl_3$) **(3i)**



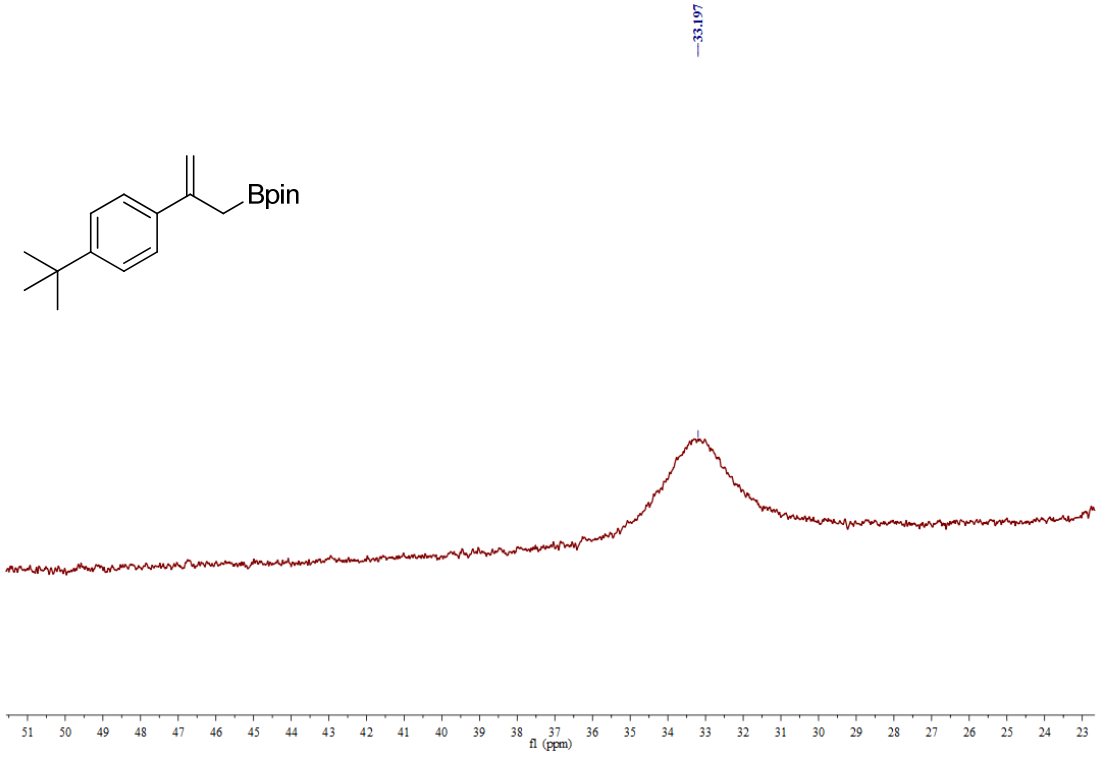
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3j)**



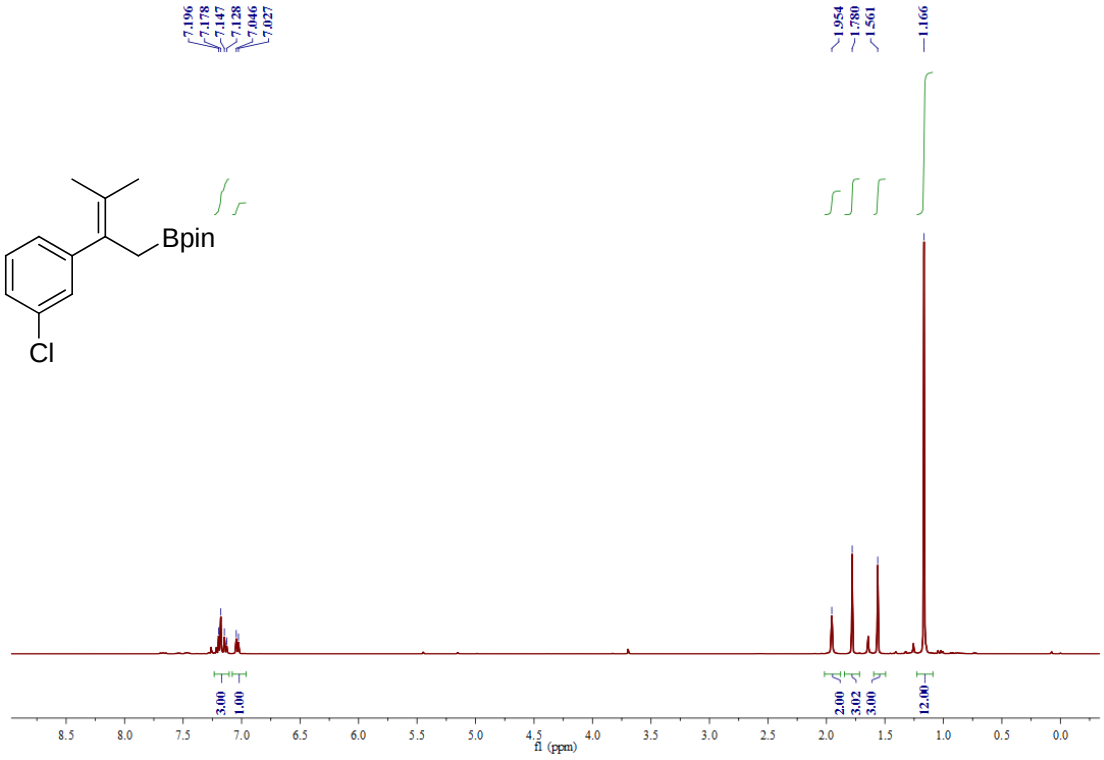
^{13}C NMR (101 MHz, $CDCl_3$) **(3j)**



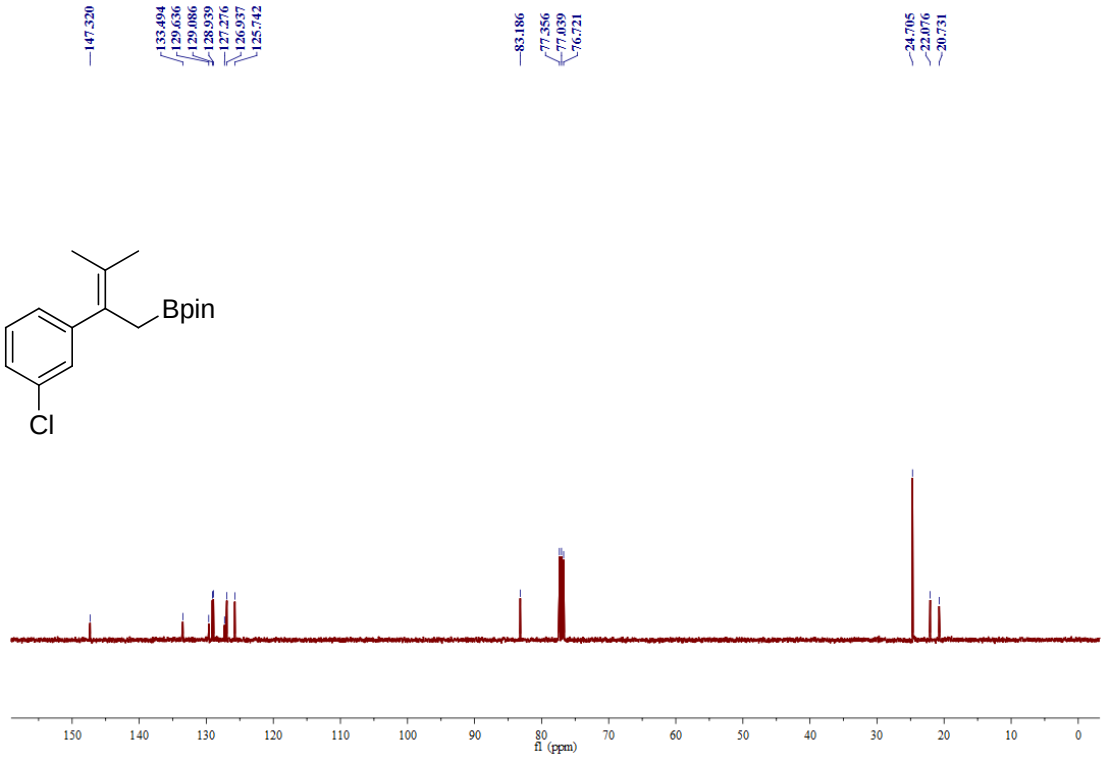
^{11}B NMR (128 MHz, $CDCl_3$) **(3j)**



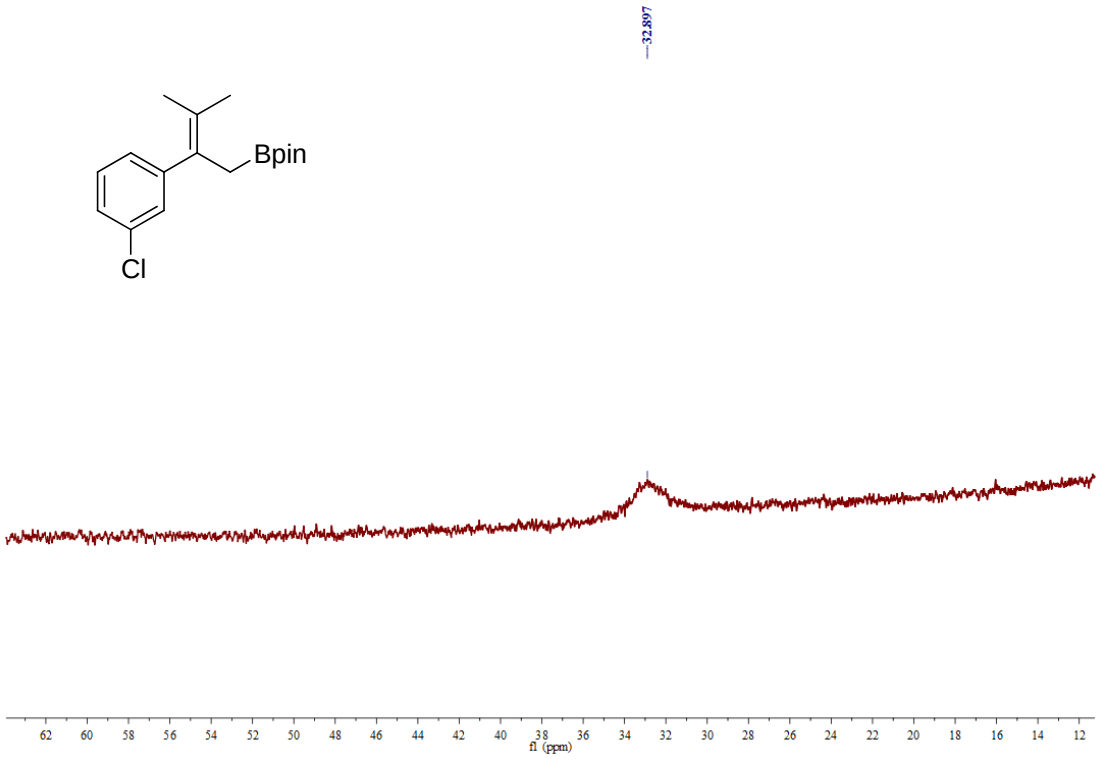
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3k)**



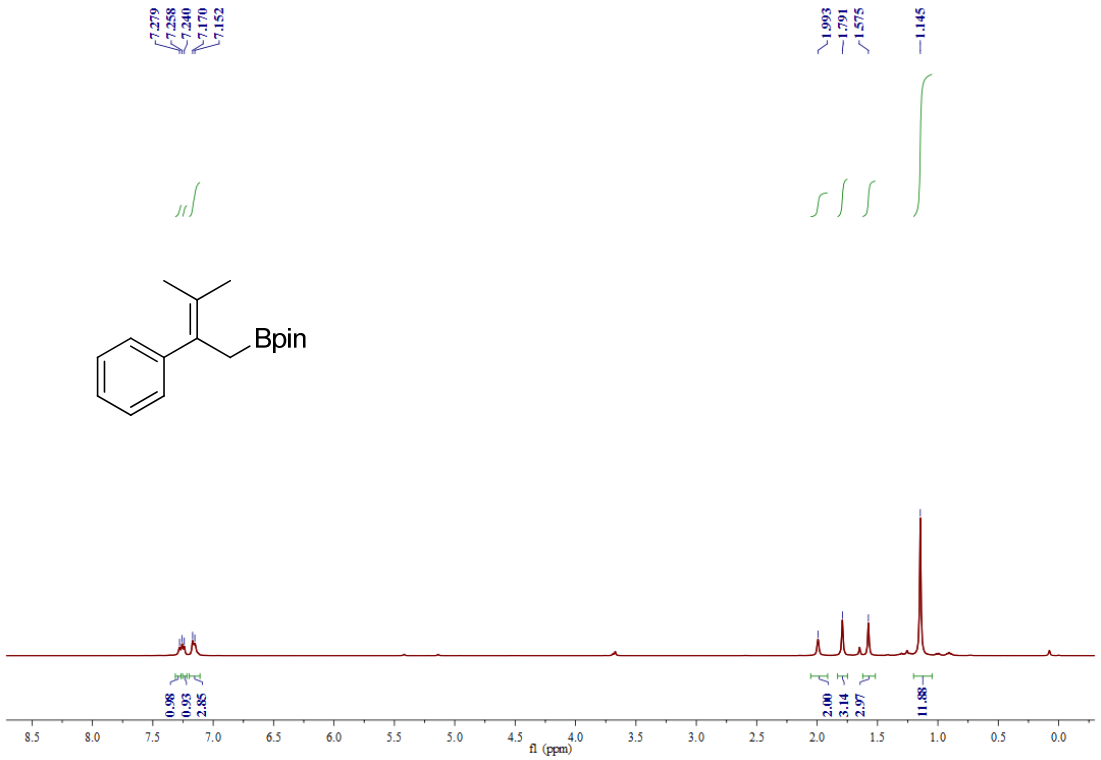
^{13}C NMR (101 MHz, $CDCl_3$) **(3k)**



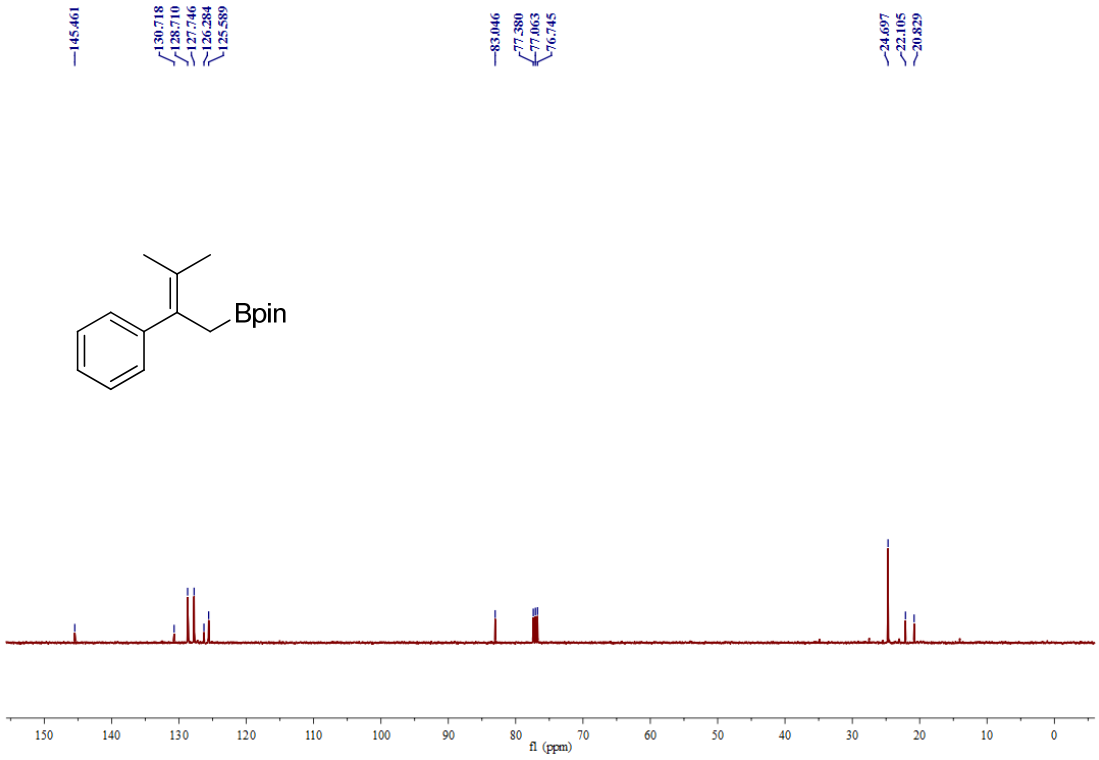
^{11}B NMR (128 MHz, $CDCl_3$) **(3k)**



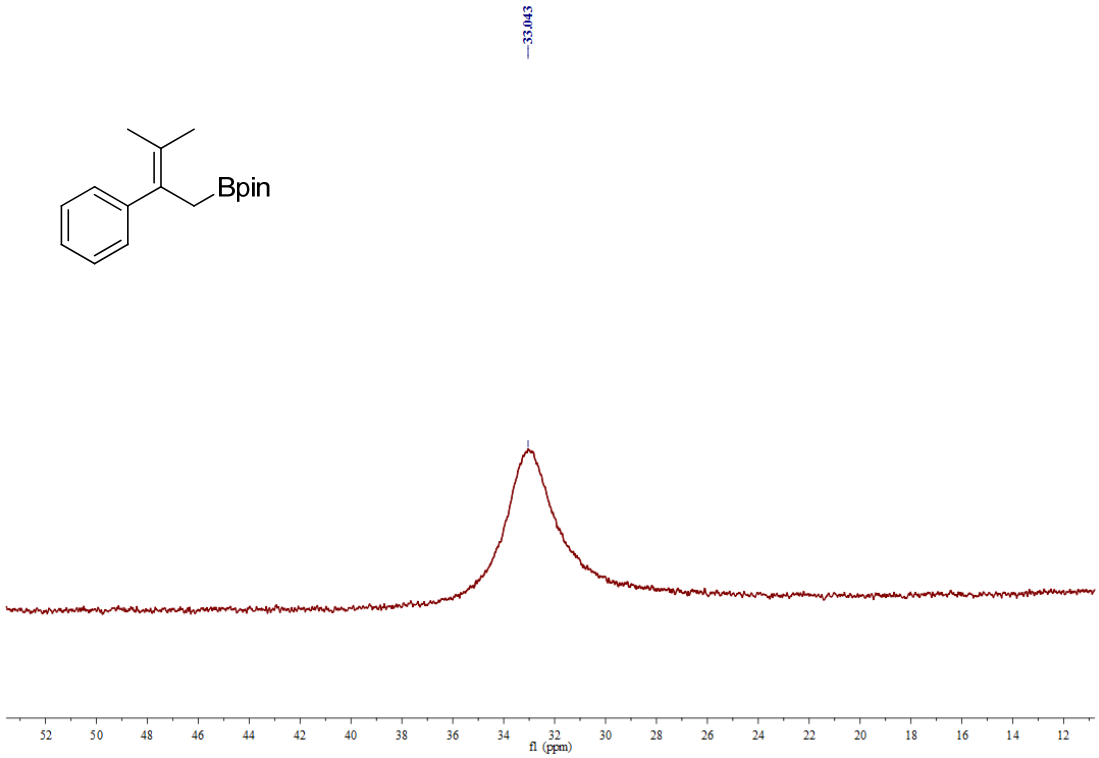
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3l)**



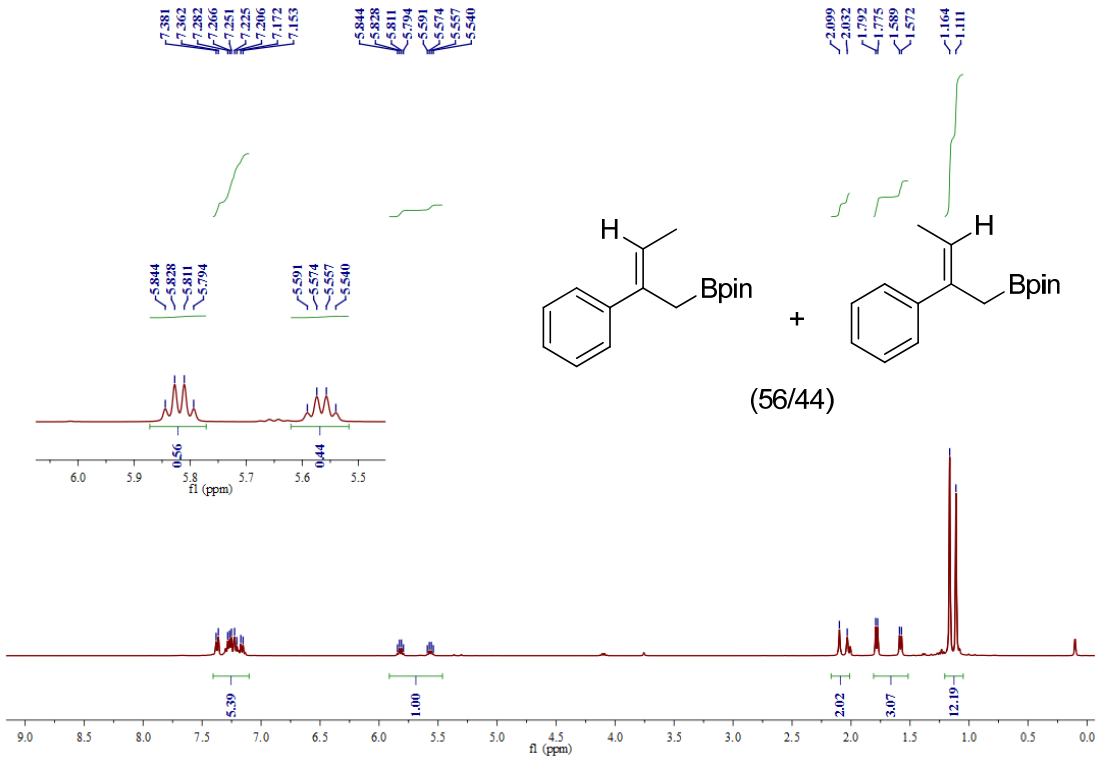
^{13}C NMR (101 MHz, $CDCl_3$) **(3l)**



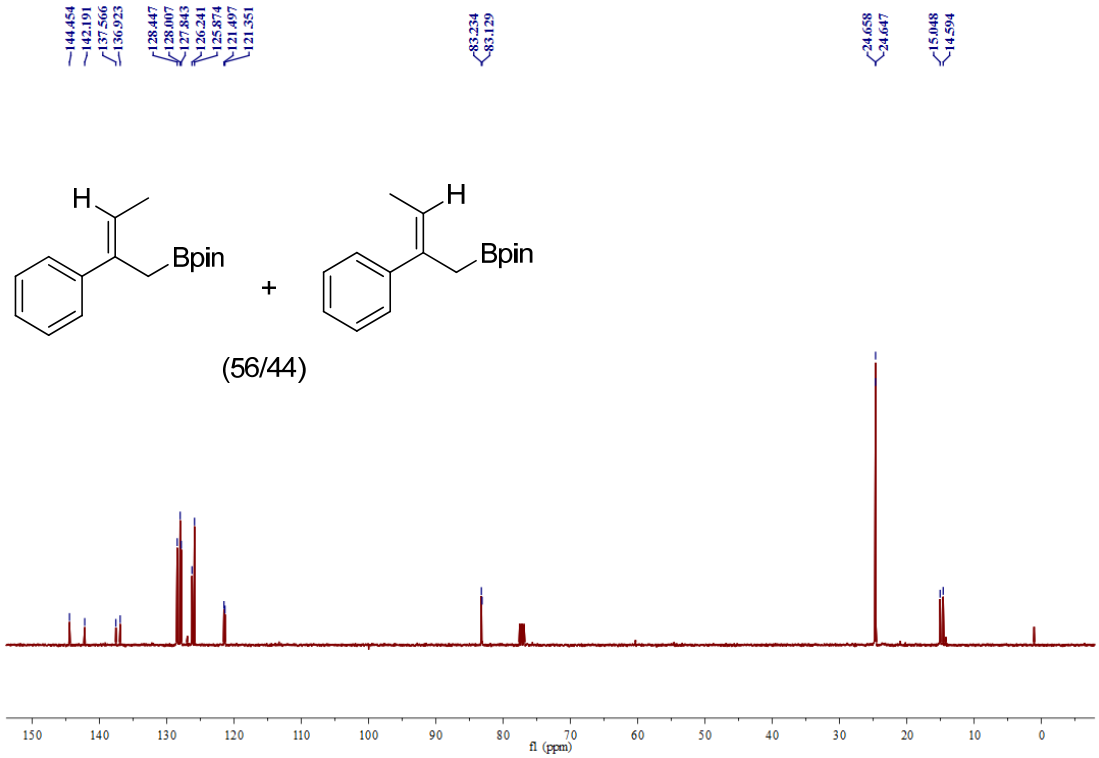
^{11}B NMR (128 MHz, $CDCl_3$) **(3l)**



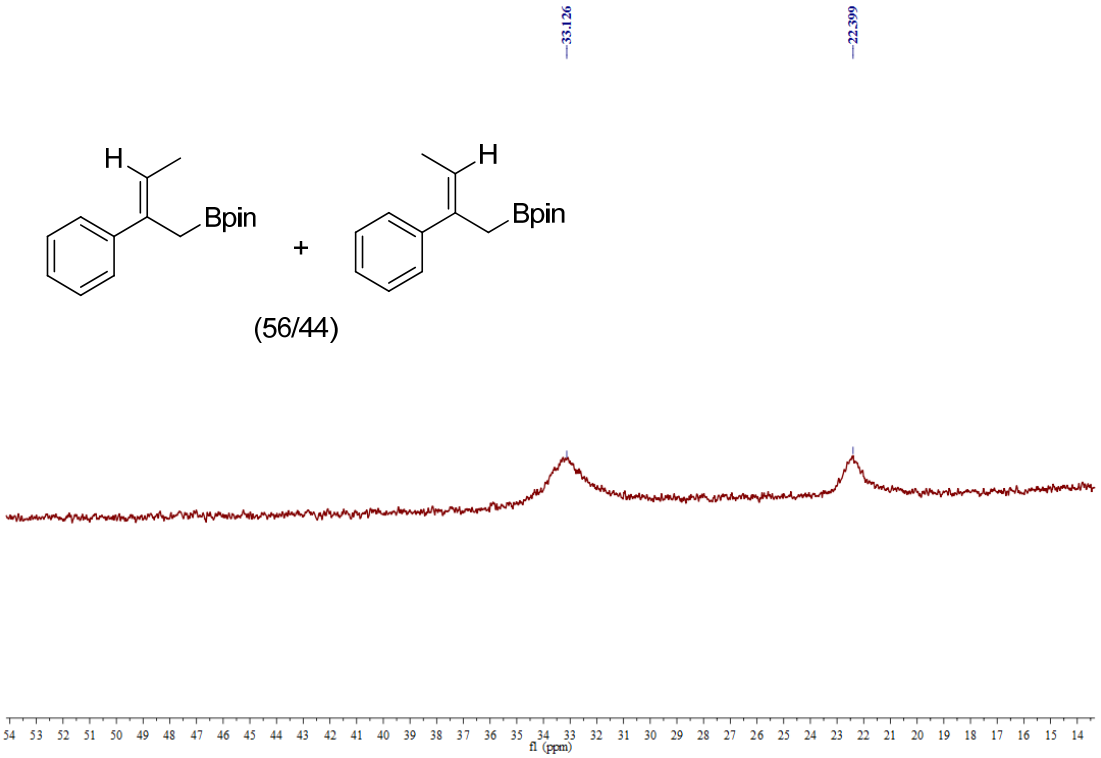
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3m)**



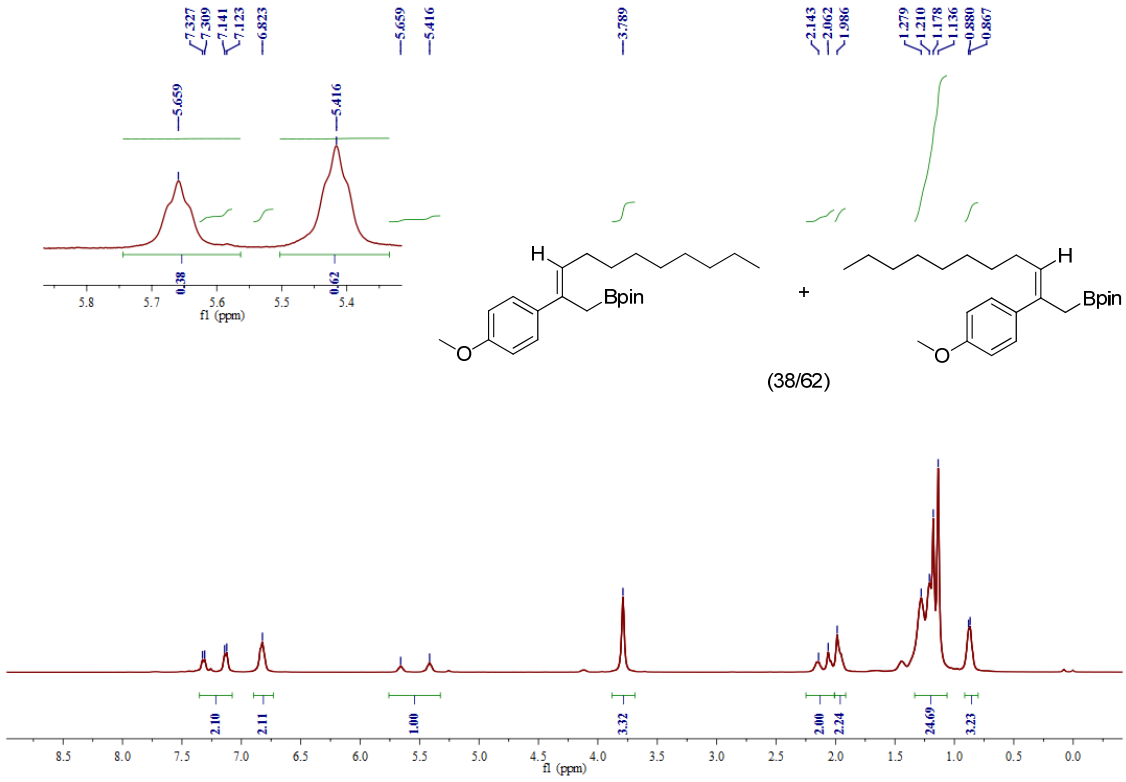
^{13}C NMR (101 MHz, $CDCl_3$) **(3m)**



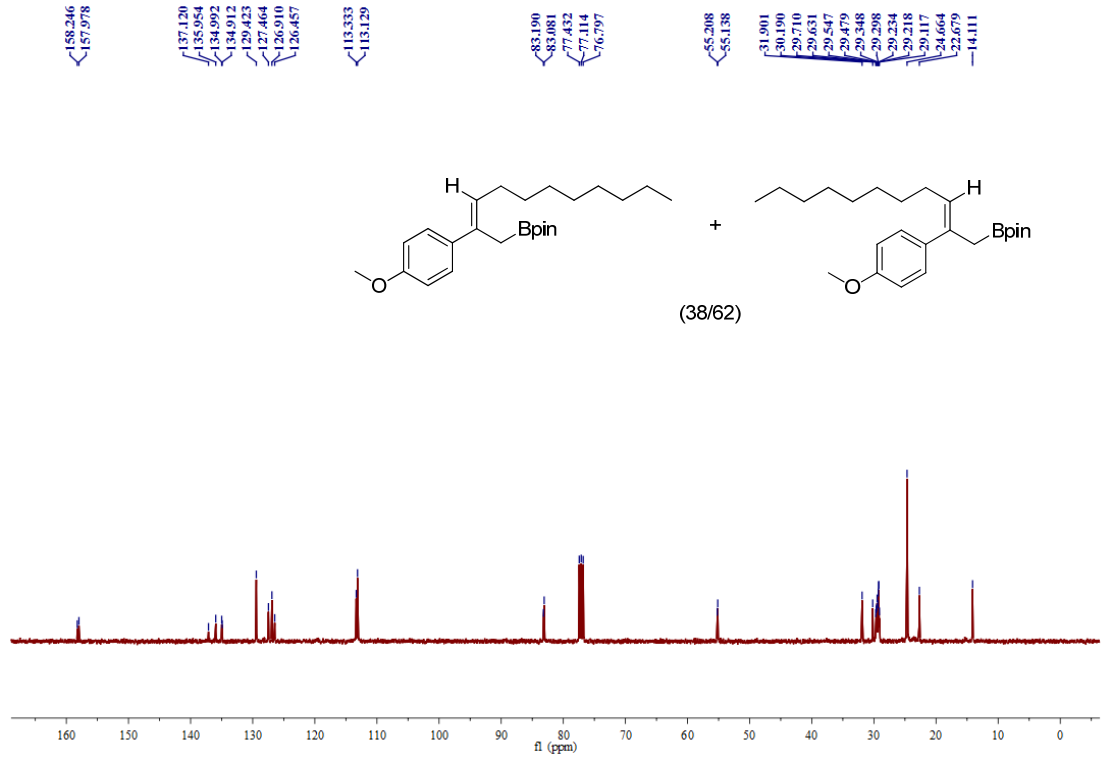
^{11}B NMR (128 MHz, $CDCl_3$) **(3m)**



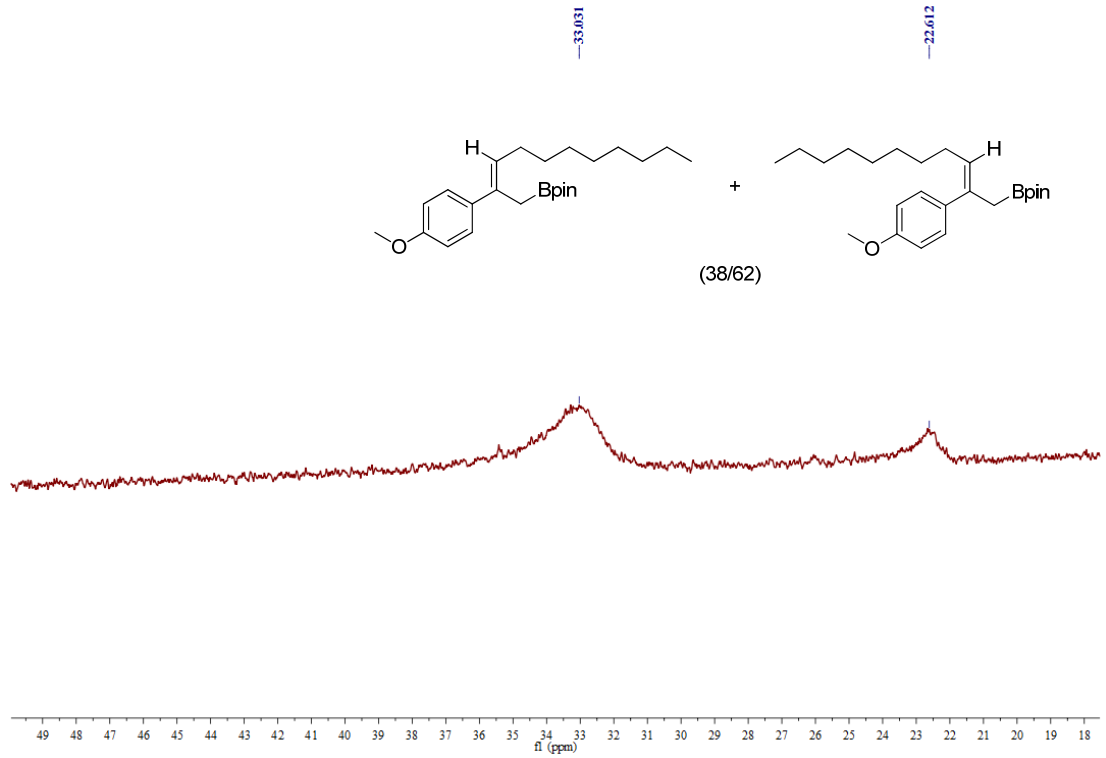
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3n)**



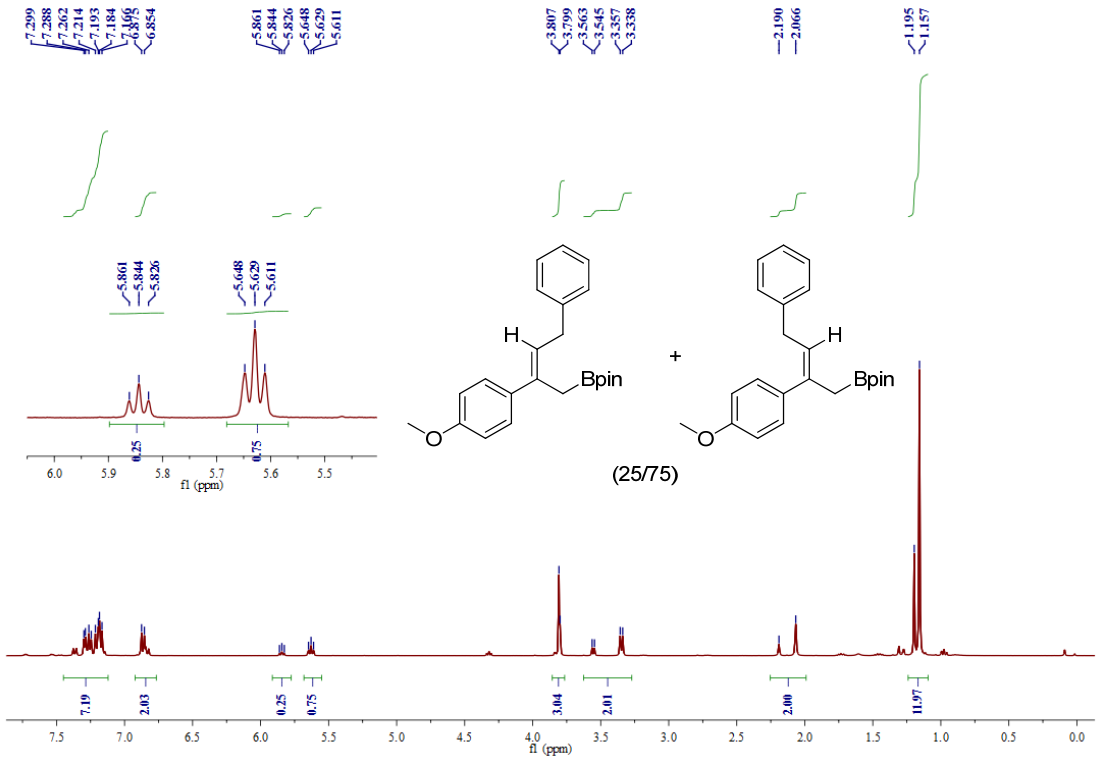
^{13}C NMR (101 MHz, $CDCl_3$) **(3n)**



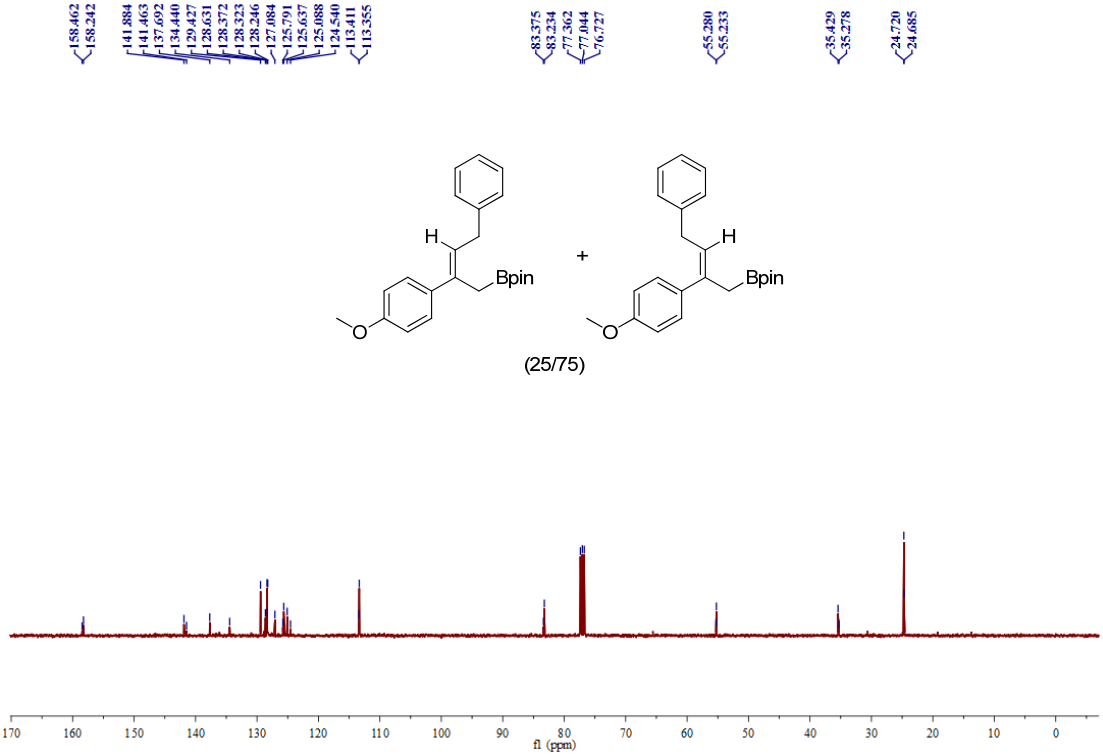
^{11}B NMR (128 MHz, $CDCl_3$) **(3n)**



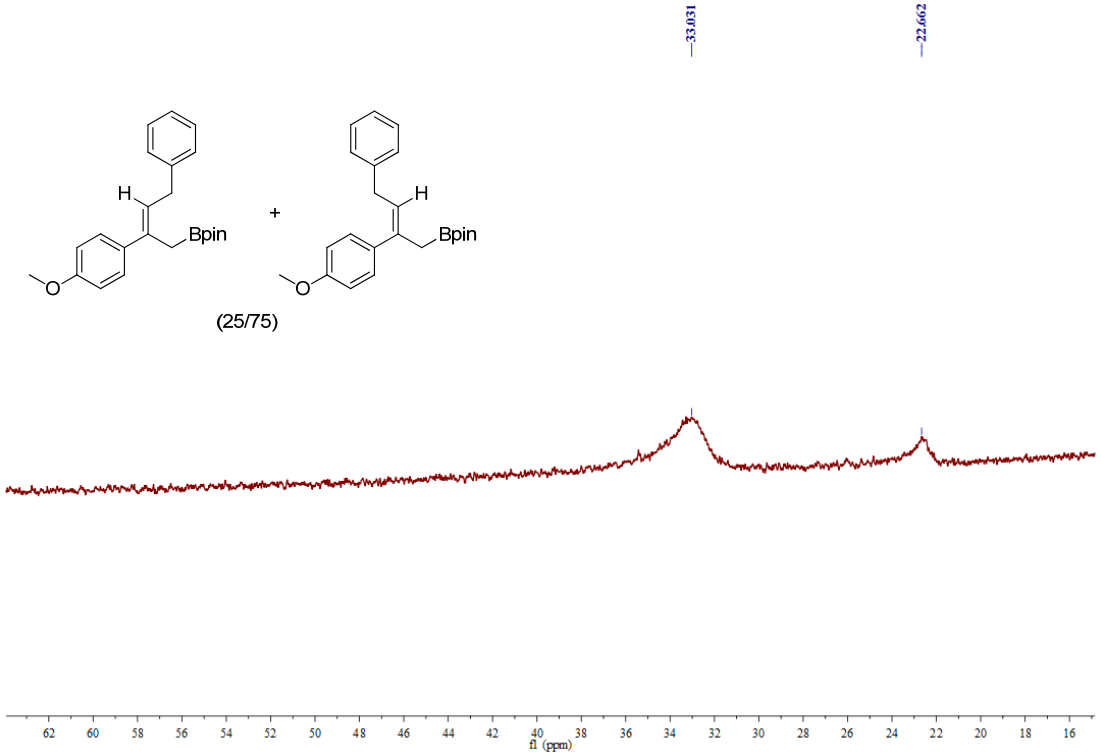
^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3o)**



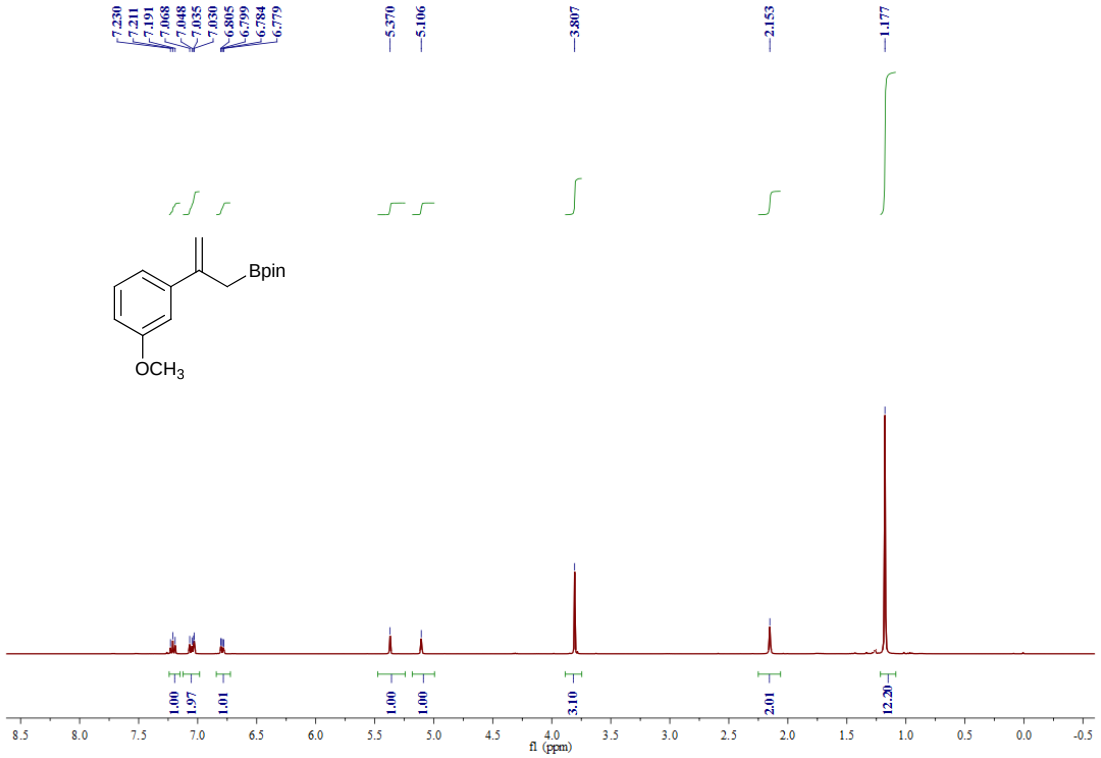
^{13}C NMR (101 MHz, $CDCl_3$) **(3o)**



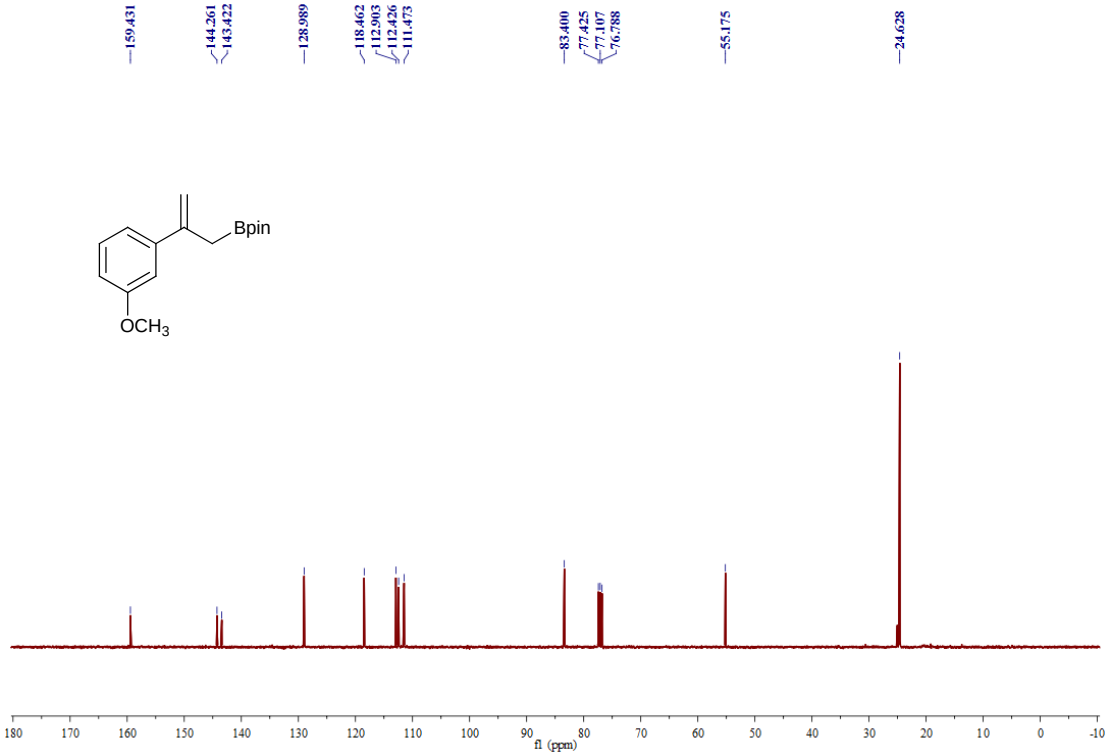
^{11}B NMR (128 MHz, $CDCl_3$) **(3o)**



^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) **(3p)**



^{13}C NMR (101 MHz, $CDCl_3$) **(3p)**



^{11}B NMR (128 MHz, $CDCl_3$) **(3p)**