# Electronic Supplementary Information for
# Photocatalytic Borylcyclopropanation of α-Boryl Styrenes

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**General Information:** Infrared spectra were recorded on a SHIMADZU IRAffinity-1 spectrometer. $^{1}$H NMR spectra were recorded on a JEOL JNM-ECA500II (500 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane (0.00 ppm) resonance as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), and coupling constants (Hz). $^{13}$C NMR spectra were recorded on a JEOL JNM-ECA500II (126 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance ($(CD_3)_2CO$: 29.84 ppm). $^{11}$B NMR spectra were recorded on a JEOL JNM-ECA500II (160 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from $BF_3 \cdot OEt_2$ resonance (0.0 ppm) as the external standard. $^{19}$F NMR spectra were recorded on a JEOL JNM-ECA500II (471 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from benzotrifluoride resonance (−64.0 ppm) as the external standard. The high resolution mass spectra were conducted on Thermo Fisher Scientific Exactive (ESI). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 $GF_{254}$, 0.25 mm). Flash column chromatography was conducted on silica gel 60 (Merck 1.09385.9929, 230–400 mesh).

Acetonitrile (MeCN) was supplied from Kanto Chemical Co., Inc. as “Dehydrated” and further purified by passing through neutral alumina under nitrogen atmosphere. 2-(Diiodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1**) was prepared according to the literature procedure.[1] Other simple chemicals were purchased and used as such.

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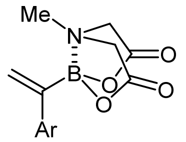
[1] G. Benoit, A. B. Charette, *J. Am. Chem. Soc.*, 2017, **139**, 1364.

**Experimental Section:**

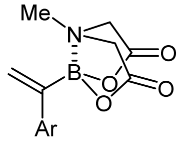
**Synthesis and Characterization of α-MIDA-boryl Styrenes:**

α-MIDA-boryl styrenes were prepared by following the literature procedures.[2]



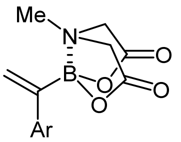
(Ar = 4-MeOC$_6$H$_4$)

**1-MIDA-boryl-1-(4-methoxyphenyl)ethene (2b)**: $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 7.34 (2H, d, *J* = 8.5 Hz), 6.87 (2H, d, *J* = 8.5 Hz), 5.65 (2H, br), 4.22 (2H, d, *J* = 17.3 Hz), 3.85 (2H, d, *J* = 17.3 Hz), 3.78 (3H, s), 2.81 (3H, s); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 169.0, 159.6, 137.5, 129.5, 126.9, 114.5, 62.7, 55.4, 47.6, one carbon atom was not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, (CD$_3$)$_2$CO) δ 9.76; IR (film) 2961, 1768, 1507, 1457, 1335, 1283, 1244, 1122, 1057, 1023, 1005, 965, 868 cm$^{-1}$; HRMS (ESI) Calcd for $C_{14}H_{16}O_5NBNa^+$ ([M+Na]$^+$) 312.1014. Found 312.1014.



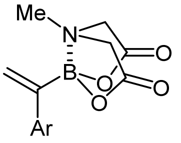
(Ar = 3-MeOC$_6$H$_4$)

**1-MIDA-boryl-1-(3-methoxyphenyl)ethene (2c)**: $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 7.22 (1H, t, *J* = 8.0 Hz), 6.99 (1H, t, *J* = 2.0 Hz), 6.96 (1H, d, *J* = 8.0 Hz), 6.81 (1H, dd, *J* = 8.0, 2.0 Hz), 5.74 (1H, brd, *J* = 3.5 Hz), 5.71 (1H, br), 4.23 (2H, d, *J* = 16.8 Hz), 3.84 (2H, d, *J* = 16.8 Hz), 3.77 (3H, s), 2.83 (3H, s); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 169.0, 160.5, 146.8, 130.2, 128.0, 120.7, 113.6, 113.2, 62.8, 55.3, 47.6, one carbon atom was not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, (CD$_3$)$_2$CO) δ 9.75; IR (film) 2959, 1766, 1595, 1573, 1485, 1336, 1285, 1229, 1024, 950, 892, 864 cm$^{-1}$; HRMS (ESI) Calcd for $C_{14}H_{16}O_5NBNa^+$ ([M+Na]$^+$) 312.1014. Found 312.1013.



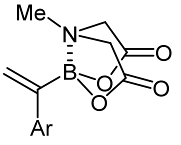
(Ar = 4-MeC$_6$H$_4$)

**1-MIDA-boryl-1-(4-methylphenyl)ethene (2d)**: $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 7.29 (2H, d, *J* = 8.8 Hz), 7.12 (2H, d, *J* = 8.8 Hz), 5.69 (1H, d, *J* = 3.0 Hz), 5.66 (1H, br), 4.22 (2H, d, *J* = 17.0 Hz), 3.84 (2H, d, *J* = 17.0 Hz), 2.84 (3H, s), 2.30 (3H, s); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 168.9, 142.5, 136.8, 129.8, 128.3, 127.4, 62.7, 47.6, 21.0, one carbon atom was not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, (CD$_3$)$_2$CO) δ 9.76; IR (film) 2970, 1738, 1459, 1334, 1283, 1243, 1121, 1038, 1002, 959, 908, 825 cm$^{-1}$; HRMS (ESI) Calcd for $C_{14}H_{16}O_4NBNa^+$ ([M+Na]$^+$) 296.1065. Found 296.1057.



(Ar = 4-$^t$BuC$_6$H$_4$)

**1-MIDA-boryl-1-(4-*tert*-butylphenyl)ethene (2f)**: $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 7.35 (4H, s), 5.72-5.65 (2H, m), 4.23 (2H, d, *J* = 17.0 Hz), 3.85 (2H, d, *J* = 17.0 Hz), 2.81 (3H, s), 1.30 (9H, s); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 169.0, 150.1, 142.4, 128.1, 127.6, 126.0, 62.7, 47.7, 34.9, 31.6, one carbon atom was not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, (CD$_3$)$_2$CO) δ 9.81; IR (film) 2978, 1766, 1294, 1005, 868 cm$^{-1}$; HRMS (ESI) Calcd for $C_{17}H_{22}O_4NBNa^+$ ([M+Na]$^+$) 338.1535. Found 338.1534.



(Ar = 4-ClC$_6$H$_4$)

**1-MIDA-boryl-1-(4-chlorophenyl)ethene (2g)**: $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 7.41 (2H, d, *J* = 8.5 Hz), 7.33 (2H, d, *J* = 8.5 Hz), 5.75 (1H, d, *J* = 3.0 Hz), 5.73 (1H, br), 4.25 (2H, d, *J* = 17.3 Hz), 3.92 (2H, d, *J* = 17.3 Hz), 2.84 (3H, s); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 168.9, 144.2, 132.9, 130.1, 129.2, 128.9, 62.7, 47.8, one carbon atom was not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, (CD$_3$)$_2$CO) δ 10.1; IR (film) 2958, 1769, 1485, 1455, 1335, 1292, 1261, 1054, 1011, 951, 869 cm$^{-1}$; HRMS (ESI) Calcd for $C_{13}H_{13}O_4NB^{35}ClNa^+$ ([M+Na]$^+$) 316.0518. Found 316.0517.

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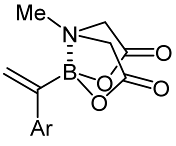
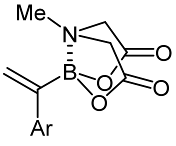
[2] E. M. Woerly, J. E. Miller, M. D. Burke, *Tetrahedron* 2013, **69**, 7732.



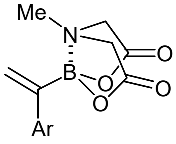
(Ar = 3-ClC$_6$H$_4$)

**1-MIDA-boryl-1-(3-chlorophenyl)ethene (2h)**: $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 7.43 (1H, br), 7.36 (1H, d, *J* = 7.5 Hz), 7.33 (1H, t, *J* = 7.5 Hz), 7.28 (1H, d, *J* = 7.5 Hz), 5.77 (1H, br), 5.75 (1H, br), 4.26 (2H, d, *J* = 17.5 Hz), 3.93 (2H, d, *J* = 17.5 Hz), 2.86 (3H, s); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 168.9, 147.5, 134.5, 130.8, 129.4, 128.3, 127.4, 127.0, 63.0, 47.8, one carbon atom was not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, (CD$_3$)$_2$CO) δ 9.51; IR (film) 3013, 1766, 1591, 1560, 1462, 1398, 1336, 1292, 1251, 1133, 1049, 1023, 950, 872 cm$^{-1}$; HRMS (ESI) Calcd for $C_{13}H_{13}O_4NB^{35}ClNa^+$ ([M+Na]$^+$) 316.0521. Found 316.0521.



(Ar = 2-naphthyl)

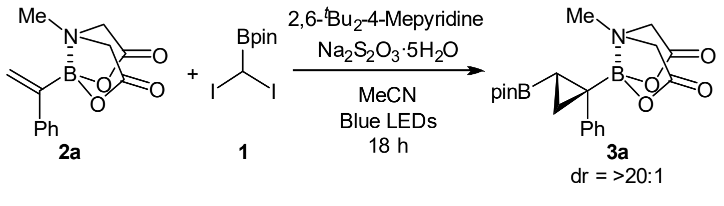
**1-MIDA-boryl-1-(2-naphthyl)ethene (2j)**: $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 7.90 (1H, s), 7.88 (1H, d, *J* = 8.0 Hz), 7.84 (2H, d, *J* = 8.0 Hz), 7.58 (1H, dd, *J* = 8.0, 1.5 Hz), 7.49 (1H, td, *J* = 8.0, 1.5 Hz), 7.46 (1H, td, *J* = 8.0, 1.5 Hz), 5.85 (1H, d, *J* = 3.0 Hz), 5.83 (1H, br), 4.25 (2H, d, *J* = 16.8 Hz), 3.89 (2H, d, *J* = 16.8 Hz), 2.87 (3H, s); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 169.0, 143.0, 134.5, 133.3, 128.9, 128.7, 128.6, 128.3, 127.3, 126.9, 126.7, 126.5, 62.8, 47.8, one carbon atom was not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, (CD$_3$)$_2$CO) δ 9.76; IR (film) 3016, 1762, 1336, 1286, 1248, 1050, 1023, 956, 895, 867 cm$^{-1}$; HRMS (ESI) Calcd for $C_{17}H_{16}O_4NBNa^+$ ([M+Na]$^+$) 332.1065. Found 332.1064.



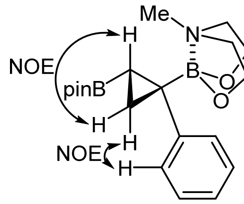
(Ar = 3,4-methylenedioxyphenyl)

**1-MIDA-boryl-1-(3,4-methylenedioxyphenyl)ethene (2k)**: $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 6.92 (1H, d, *J* = 1.5 Hz), 6.90 (1H, dd, *J* = 7.5, 1.5 Hz), 6.79 (1H, d, *J* = 7.5 Hz), 5.97 (2H, s), 5.66 (2H, s), 4.23 (2H, d, *J* = 16.8 Hz), 3.88 (2H, d, *J* = 16.8 Hz), 2.84 (3H, s); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 168.9, 148.5, 147.4, 139.4, 127.4, 121.6, 108.9, 101.9, 62.7, 47.7, one carbon atom was not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, (CD$_3$)$_2$CO) δ 9.62; IR (film) 2972, 1768, 1484, 1336, 1288, 1227, 1036, 950, 869 cm$^{-1}$; HRMS (ESI) Calcd for $C_{14}H_{14}NO_6BNa^+$ ([M+Na]$^+$) 326.0803. Found 326.0803.

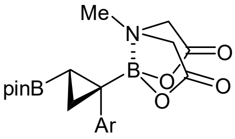
**Representative Procedure for Borylcyclopropanation of α-MIDA-boryl Styrenes 2 under Photoredox Conditions:**



In a flame and vacuum dried test tube, 1-MIDA-boryl-1-phenylethene **2a** (25.9 mg, 0.10 mmol), 2-(diiodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1**, 196.9 mg, 0.50 mmol), 4CzIPN (3.9 mg, 0.0050 mmol), 2,6-$^t$Bu$_2$-4-Me-pyridine (61.6 mg, 0.30 mmol), and $Na_2S_2O_3 \cdot 5H_2O$ (79.1 mg, 0.50 mmol) were placed under argon atmosphere. After addition of MeCN (5.0 mL), evacuation of the tube followed by backfill with argon was conducted three times. The test tube was then illuminated with blue LEDs (456 nm) for 18 h at room temperature with fans (Fans are employed to maintain the temperature below 40 °C.). The reaction was quenched by adding a water (5.0 mL) and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The diastereomeric ratio of the product was determined to be >20:1 by $^1$H NMR (500 MHz) analysis of the crude aliquot and relative stereochemistry of **3a** was determined by the NOE experiment. Purification of the crude residue was performed by column chromatography on silica gel twice (hexane/ethyl acetate = 1:1 to 0:1 as eluent for the first time, $CH_2Cl_2$/MeCN = 5:1 as eluent for the second time) to afford the diastereomerically pure product **3a** in 58% yield (23.2 mg, 0.058 mmol). **3a:** $^1$H NMR (500 MHz, $(CD_3)_2CO$) δ 7.42 (2H, d, $J$ = 7.7 Hz), 7.19 (2H, t, $J$ = 7.7 Hz), 7.11 (1H, t, $J$ = 7.7 Hz), 4.15 (1H, d, $J$ = 16.5 Hz), 3.97 (1H, d, $J$ = 16.5 Hz), 3.92 (1H, d, $J$ = 16.5 Hz), 3.09 (3H, s), 3.01 (1H, d, $J$ = 16.5 Hz), 1.35 (1H, dd, $J$ = 6.6, 3.0 Hz), 1.07 (1H, dd, $J$ = 8.9, 3.0 Hz), 1.01 (6H, s), 0.77 (6H, s), 0.51(1H, dd, $J$ = 8.9, 6.6 Hz); $^{13}$C NMR (126 MHz, $(CD_3)_2CO$) δ 168.9, 168.1, 144.2, 132.2, 128.5, 126.2, 83.1, 63.6, 63.1, 46.5, 25.3, 24.8, 13.5, two carbon atoms were not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, $(CD_3)_2CO$) δ 31.7, 11.0; IR (film) 2977, 1766, 1408, 1324, 1286, 1242, 1146, 1028, 1001, 865 cm$^{-1}$; HRMS (ESI) Calcd for $C_{20}H_{27}O_6NB_2Na^+$ ($[M+Na]^+$) 422.1917. Found 422.1915.

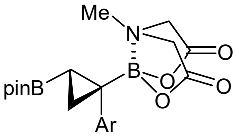


**3a**



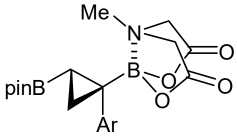
(Ar = 4-MeOC$_6$H$_4$)
dr = >20:1

**3b:** $^1$H NMR (500 MHz, $(CD_3)_2CO$) δ 7.31 (2H, d, $J$ = 9.3 Hz), 6.77 (2H, d, $J$ = 9.3 Hz), 4.13 (1H, d, $J$ = 17.3 Hz), 3.97 (1H, d, $J$ = 16.3 Hz), 3.91 (1H, d, $J$ = 17.3 Hz), 3.73 (3H, s), 3.09 (3H, s), 3.04 (1H, d, $J$ = 16.3 Hz), 1.30 (1H, dd, $J$ = 6.0, 3.0 Hz), 1.04-1.01 (1H, m), 1.03 (6H, s), 0.80 (6H, s), 0.45 (1H, dd, $J$ = 8.2, 6.0 Hz); $^{13}$C NMR (126 MHz, $(CD_3)_2CO$) δ 168.9, 168.1, 158.6, 135.8, 132.9, 114.0, 83.1, 63.6, 63.2, 55.5, 46.5, 25.3, 24.8, 13.6, two carbon atoms were not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, $(CD_3)_2CO$) δ 31.8, 11.0; IR (film) 2930, 1766, 1408, 1324, 1286, 1234, 1254, 1150, 1025, 993, 960, 864 cm$^{-1}$; HRMS (ESI) Calcd for $C_{21}H_{29}O_7NB_2Na^+$ ($[M+Na]^+$) 452.2022. Found 452.2018.



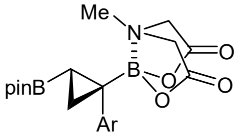
(Ar = 3-MeOC$_6$H$_4$)
dr = >20:1

**3c:** $^1$H NMR (500 MHz, $(CD_3)_2CO$) δ 7.10 (1H, t, $J$ = 8.0 Hz), 7.03 (1H, br), 6.96 (1H, d, $J$ = 8.0 Hz), 6.67 (1H, dd, $J$ = 8.0, 2.0 Hz), 4.16 (1H, d, $J$ = 17.3 Hz), 3.98 (1H, d, $J$ = 16.3 Hz), 3.93 (1H, d, $J$ = 17.3 Hz), 3.75 (3H, s), 3.11 (3H, s), 3.01 (1H, d, $J$ = 16.3 Hz), 1.36 (1H, dd, $J$ = 6.6, 3.1 Hz), 1.06 (1H, dd, $J$ = 8.5, 6.6 Hz), 1.02 (6H, s), 0.79 (6H, s), 0.51 (1H, dd, $J$ = 8.5, 6.6 Hz); $^{13}$C NMR (126 MHz, $(CD_3)_2CO$) δ 168.9, 168.2, 160.1, 145.7, 129.5, 123.9, 117.5, 112.6, 83.1, 63.7, 63.2, 55.2, 46.4, 25.3, 24.8, 13.6, two carbon atoms were not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, $(CD_3)_2CO$) δ 31.4, 11.0; IR (film) 2979, 1766, 1598, 1463, 1408, 1325, 1285, 1247, 1146, 1118, 1087, 1035, 962, 856 cm$^{-1}$; HRMS (ESI) Calcd for $C_{21}H_{29}O_7NB_2Na^+$ ($[M+Na]^+$) 452.2022. Found 452.2021.



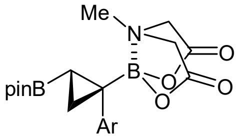
(Ar = 4-MeC$_6$H$_4$)
dr = >20:1

**3d:** $^1$H NMR (500 MHz, $(CD_3)_2CO$) δ 7.29 (2H, d, $J$ = 8.5 Hz), 7.01 (2H, d, $J$ = 8.5 Hz), 4.13 (1H, d, $J$ = 16.5 Hz), 3.96 (1H, d, $J$ = 16.0 Hz), 3.91 (1H, d, $J$ = 16.0 Hz), 3.09 (3H, s), 3.01 (1H, d, $J$ = 16.5 Hz), 2.24 (3H, s), 1.31 (1H, dd, $J$ = 6.5, 3.0 Hz), 1.04 (1H, dd, $J$ = 8.5, 3.0 Hz), 1.02 (6H, s), 0.78 (6H, s), 0.47 (1H, dd, $J$ = 8.5, 6.5 Hz); $^{13}$C NMR (126 MHz, $(CD_3)_2CO$) δ 168.9, 168.1, 141.0, 135.4, 132.0, 129.2, 83.1, 63.6, 63.2, 46.5, 25.3, 24.8, 21.0, 13.5, two carbon atoms were not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, $(CD_3)_2CO$) δ 31.4, 11.0; IR (film) 2954, 1766, 1409, 1325, 1286, 1251, 1144, 1113, 1032, 1001, 960 cm$^{-1}$; HRMS (ESI) Calcd for $C_{21}H_{29}O_6NB_2Na^+$ ($[M+Na]^+$) 436.2073. Found 436.2076.



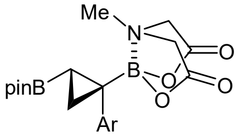
(Ar = 3-MeC$_6$H$_4$)
dr = >20:1

**3e:** $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 7.26 (1H, s), 7.18 (1H, d, *J* = 7.5 Hz), 7.08 (1H, t, *J* = 7.5 Hz), 6.92 (1H, d, *J* = 7.5 Hz), 4.14 (1H, d, *J* = 16.5 Hz), 3.95 (1H, d, *J* = 16.8 Hz), 3.90 (1H, d, *J* = 16.8 Hz), 3.10 (3H, s), 2.96 (1H, d, *J* = 16.5 Hz), 2.24 (3H, s), 1.33 (1H, dd, *J* = 6.0, 2.5 Hz), 1.05 (1H, dd, *J* = 8.4, 2.5 Hz), 1.01 (6H, s), 0.78 (6H, s), 0.49 (1H, dd, *J* = 8.4, 6.0 Hz); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 168.9, 168.1, 144.0, 137.7, 133.3, 128.9, 128.5, 126.8, 83.1, 63.6, 63.1, 46.4, 25.3, 24.8, 21.5, 13.5, two carbon atoms were not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, (CD$_3$)$_2$CO) δ 31.4, 11.0; IR (film) 2990, 1766, 1404, 1325, 1284, 1249, 1142, 1088, 1033, 959, 891 cm$^{-1}$; HRMS (ESI) Calcd for $C_{21}H_{29}O_6NB_2Na^+$ ([M+Na]$^+$) 436.2073. Found 436.2078.



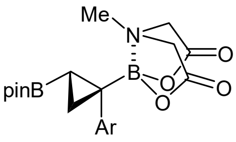
(Ar = 4-$^t$BuC$_6$H$_4$)
dr = >20:1

**3f:** $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 7.34 (2H, d, *J* = 8.5 Hz), 7.24 (2H, d, *J* = 8.5 Hz), 4.15 (1H, d, *J* = 17.8 Hz), 3.97 (1H, d, *J* = 16.5 Hz), 3.95 (1H, d, *J* = 17.8 Hz), 3.08 (3H, s), 3.01 (1H, d, *J* = 16.5 Hz), 1.35 (1H, dd, *J* = 6.3, 3.0 Hz), 1.26 (9H, s), 1.02 (1H, dd, *J* = 8.5, 3.0 Hz), 1.00 (6H, s), 0.74 (6H, s), 0.48 (1H, dd, *J* = 8.5, 6.3 Hz); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 168.9, 168.2, 148.8, 141.0, 131.7, 125.4, 83.1, 63.6, 63.1, 46.6, 34.8, 31.7, 25.4, 24.8, 13.2, two carbon atoms were not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, (CD$_3$)$_2$CO) δ 31.3, 11.1; IR (film) 2966, 1766, 1408, 1322, 1285, 1253, 1151, 992, 960, 867 cm$^{-1}$; HRMS (ESI) Calcd for $C_{24}H_{35}O_6NB_2Na^+$ ([M+Na]$^+$) 478.2543. Found 478.2538.



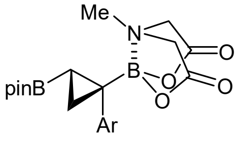
(Ar = 4-ClC$_6$H$_4$)
dr = >20:1

**3g:** $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 7.41 (2H, d, *J* = 7.8 Hz), 7.22 (2H, d, *J* = 7.8 Hz), 4.18 (1H, d, *J* = 16.8 Hz), 4.03 (1H, d, *J* = 16.3 Hz), 3.97 (1H, d, *J* = 16.8 Hz), 3.22 (1H, d, *J* = 16.3 Hz), 3.09 (3H, s), 1.33 (1H, br), 1.08 (1H, brd, *J* = 7.5 Hz), 1.03 (6H, s), 0.81 (6H, s), 0.53 (1H, dd, *J* = 7.5, 7.0 Hz); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 168.7, 168.2, 143.4, 133.8, 131.4, 128.5, 83.3, 63.7, 63.3, 46.8, 25.3, 24.8, 13.7, two carbon atoms were not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, (CD$_3$)$_2$CO) δ 31.4, 10.8; IR (film) 2973, 1766, 1408, 1330, 1292, 1244, 1148, 1037, 1010, 960, 866 cm$^{-1}$; HRMS (ESI) Calcd for $C_{20}H_{26}O_6NB_2{}^{35}ClNa^+$ ([M+Na]$^+$) 456.1527. Found 456.1525.



(Ar = 3-ClC$_6$H$_4$)
dr = >20:1

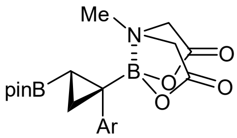
**3h:** $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 7.43 (1H, t, *J* = 2.0 Hz), 7.36 (1H, dt, *J* = 7.5, 2.0 Hz), 7.22 (1H, t, *J* = 7.5 Hz), 7.14 (1H, dd, *J* = 7.5, 2.0 Hz), 4.20 (1H, d, *J* = 16.5 Hz), 4.05 (1H, d, *J* = 17.0 Hz), 3.99 (1H, d, *J* = 16.5 Hz), 3.25 (1H, d, *J* = 17.0 Hz), 3.11 (3H, s), 1.35 (1H, dd, *J* = 6.5, 2.1 Hz), 1.09 (1H, dd, *J* = 8.5, 2.1 Hz), 1.04 (6H, s), 0.82 (6H, s), 0.55 (1H, dd, *J* = 8.5, 6.5 Hz); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 168.7, 168.1, 147.1, 133.9, 132.3, 130.5, 130.1, 126.2, 83.3, 63.7, 63.3, 46.9, 25.3, 24.9, 13.7, two carbon atoms were not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, (CD$_3$)$_2$CO) δ 31.3, 10.9; IR (film) 2979, 1765, 1560, 1457, 1408, 1328, 1284, 1241, 1144, 1121, 1090, 1034, 998, 960, 892, 868, 852 cm$^{-1}$; HRMS (ESI) Calcd for $C_{20}H_{26}O_6NB_2{}^{35}ClNa^+$ ([M+Na]$^+$) 456.1527. Found 456.1525.



(Ar = 4-FC$_6$H$_4$)
dr = >20:1

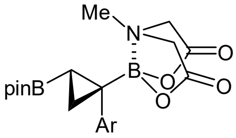
**3i:** $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 7.42 (2H, dd, $J_{H\text{-}F}$ = 5.5 Hz, $J_{H\text{-}H}$ = 8.6 Hz), 6.96 (2H, dd, $J_{H\text{-}F}$ = 8.6 Hz, $J_{H\text{-}H}$ = 8.6 Hz), 4.17 (1H, d, *J* = 17.3 Hz), 4.01 (1H, d, *J* = 16.0 Hz), 3.96 (1H, d, *J* = 17.3 Hz), 3.15 (1H, d, *J* = 16.0 Hz), 3.09 (3H, s), 1.33 (1H, dd, *J* = 6.0, 3.0 Hz), 1.08 (1H, dd, *J* = 8.5, 6.0 Hz), 1.03 (6H, s), 0.81 (6H, s), 0.51 (1H, dd, *J* = 8.5, 6.0 Hz); $^{13}$C

NMR (126 MHz, $(CD_3)_2CO$) δ 168.8, 168.1, 161.8 (d, $J_{C\text{-}F}$ = 232.3 Hz), 140.2, 133.7 (d, $J_{C\text{-}F}$ = 8.1 Hz), 115.1 (d, $J_{C\text{-}F}$ = 20.9 Hz), 83.2, 63.7, 63.2, 46.7, 25.3, 24.8, 13.7, two carbon atoms were not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, $(CD_3)_2CO$) δ 31.5, 10.8; $^{19}$F NMR (471 MHz, $(CD_3)_2CO$) δ –119.3; IR (film) 2965, 1766, 1409, 1327, 1287, 1241, 1142, 1035, 1008, 992, 960, 866 cm$^{-1}$; HRMS (ESI) Calcd for $C_{20}H_{26}O_6NB_2FNa^+$ ($[M+Na]^+$) 440.1822. Found 440.1821.



(Ar = 2-naphthyl)
dr = >20:1

**3j:** $^1$H NMR (500 MHz, $(CD_3)_2CO$) δ 7.87 (1H, s), 7.81 (1H, d, $J$ = 8.0 Hz), 7.78 (1H, d, $J$ = 8.0 Hz), 7.73 (1H, d, $J$ = 8.0 Hz), 7.61 (1H, dd, $J$ = 8.0, 1.5 Hz), 7.44 (1H, td, $J$ = 8.0, 1.5 Hz), 7.40 (1H, td, $J$ = 8.0, 1.5 Hz), 4.16 (1H, d, $J$ = 17.0 Hz), 3.95 (1H, d, $J$ = 17.0 Hz), 3.94 (1H, d, $J$ = 17.0 Hz), 3.16 (3H, s), 3.06 (1H, d, $J$ = 17.0 Hz), 1.49 (1H, dd, $J$ = 6.5, 3.1 Hz), 1.17 (1H, dd, $J$ = 8.5, 3.1 Hz), 0.94 (6H, s), 0.60 (1H, dd, $J$ = 8.5, 6.5 Hz), 0.59 (6H, s); $^{13}$C NMR (126 MHz, $(CD_3)_2CO$) δ 168.9, 168.1, 142.0, 134.3, 132.8, 131.0, 130.3, 128.3, 128.2, 127.9, 126.5, 125.9, 83.1, 63.7, 63.2, 46.7, 25.2, 24.8, 13.9, two carbon atoms were not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, $(CD_3)_2CO$) δ 31.4, 11.1; IR (film) 2979, 1766, 1407, 1325, 1248, 1150, 1085, 1027, 992, 963, 859 cm$^{-1}$; HRMS (ESI) Calcd for $C_{24}H_{29}O_6NB_2Na^+$ ($[M+Na]^+$) 472.2073. Found 472.2074.

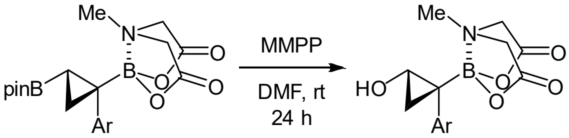


(Ar = 3,4-methylenedioxyphenyl)
dr = >20:1

**3k:** $^1$H NMR (500 MHz, $(CD_3)_2CO$) δ 6.91 (1H, d, $J$ = 1.5 Hz), 6.88 (1H, dd, $J$ = 8.0, 1.5 Hz), 6.69 (1H, d, $J$ = 8.0 Hz), 5.90 (1H, s), 5.89 (1H, s), 4.16 (1H, d, $J$ = 16.8 Hz), 4.01 (1H, d, $J$ = 16.5 Hz), 3.95 (1H, d, $J$ = 16.8 Hz), 3.22 (1H, d, $J$ = 16.5 Hz), 3.13 (3H, s), 1.29 (1H, dd, $J$ = 6.3, 3.0 Hz), 1.05 (6H, s), 1.03 (1H, dd, $J$ = 8.5, 3.0 Hz), 0.86 (6H, s), 0.46 (1H, dd, $J$ = 8.5, 6.3 Hz); $^{13}$C NMR (126 MHz, $(CD_3)_2CO$) δ 168.9, 168.2, 148.0, 146.3, 138.0, 124.8, 112.8, 108.3, 101.6, 83.2, 63.7, 63.2, 46.6, 25.4, 24.8, 14.0, two carbon atoms were not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, $(CD_3)_2CO$) δ 31.4, 11.0; IR (film) 2929, 1766, 1485, 1408, 1333, 1288, 1247, 1142, 1086, 1027, 991, 962 cm$^{-1}$; HRMS (ESI) Calcd for $C_{21}H_{27}O_6NB_2Na^+$ ($[M+Na]^+$) 466.1815. Found 466.1819.

**Derivatization Section:**

**Selective Oxidation of Pinacol-borate Moiety to Give MIDA-borylated Cyclopropanol:**



**3b** (Ar = 4-MeOC$_6$H$_4$)
dr = >20:1

**4** (Ar = 4-MeOC$_6$H$_4$)
91%, dr = >20:1

To a solution of **3b** (42.9 mg 0.1 mmol) in DMF (2.0 mL) was added magnesium monoperoxyphthalate hexahydrate (148.4 mg, 0.30 mmol) at room temperature. After being stirred for 24 h, the reaction mixture was diluted with a saturated aqueous solution of $Na_2SO_3$ at 0 °C. The aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The diastereomeric ratio of the product was determined to be >20:1 by $^1$H NMR (500 MHz) analysis of the crude aliquot. Purification of the crude residue was performed by column chromatography on silica gel (hexane/ethyl acetate = 1:2 to 0:1, then ethyl acetate/MeCN = 2:1 as eluent) to afford the diastereomerically pure product **4** in 91% yield (28.9 mg, 0.091 mmol). **4:** $^1$H NMR (500 MHz, $(CD_3)_2CO$) δ 7.31 (2H, d, *J* = 8.5 Hz), 6.80 (2H, d, *J* = 8.5 Hz), 4.09 (1H, d, *J* = 17.3 Hz), 3.95 (1H, d, *J* = 16.8 Hz), 3.85 (1H, d, *J* = 17.3 Hz), 3.75 (3H, s), 3.65-3.62 (2H, m), 3.12 (3H, s), 3.09 (1H, d, *J* = 16.8 Hz), 1.07 (1H, td, *J* = 5.0, 1.5 Hz), 1.00 (1H, dd, *J* = 5.0, 2.8 Hz); $^{13}$C NMR (126 MHz, $(CD_3)_2CO$) δ 169.0, 168.1, 158.5, 133.6, 132.9, 114.2, 63.2, 63.0, 55.3, 53.4, 46.2, 17.0, one carbon atom was not detected due to quadrupolar broadening; $^{11}$B NMR (160 MHz, $(CD_3)_2CO$) δ 10.5; IR (film) 3500, 3005, 2971, 1759, 1749, 1696, 1609, 1511, 1459, 1337, 1289, 1241, 1127, 1027, 989, 875 cm$^{-1}$; HRMS (ESI) Calcd for $C_{15}H_{18}O_6NBNa^+$ ($[M+Na]^+$) 342.1119. Found 342.1121.

**Electrochemical Analysis of 2-(Diiodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1):** Cyclic and square wave voltammetries were performed on an ALS/chi-617A electrochemical analyser. The voltammetric cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgNO$_3$ reference electrode. The measurements were carried out under N$_2$ using a solution of **1** with a concentration of 1.0 mM in MeCN containing Bu$_4$NClO$_4$ as a supporting electrolyte (0.10 M). The scan rate was 1500 mV/s at cyclic voltammetry analysis. Nitrogen was passed through the sample during measurements to avoid the deleterious influence of oxygen. The redox potentials were calibrated to the SCE scale with a ferrocene/ferrocenium ion couple (Fig. S1).

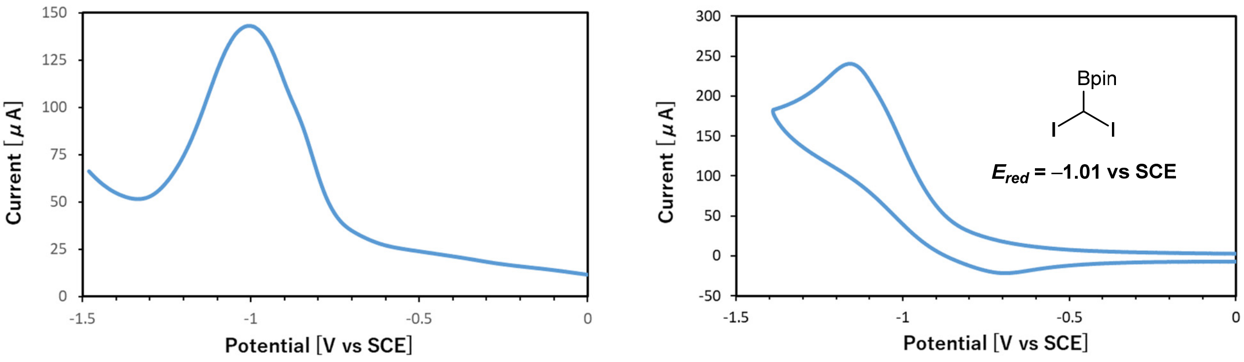


**Fig. S1.** Cyclic (left) and square wave (right) voltammograms of **1**

**UV-Visible Absorption Spectroscopy of 1:** UV-Visible absorption spectra was measured in MeCN (for spectrochemical analysis) on a Shimadzu UV-3510 spectrometer (Fig. S2).

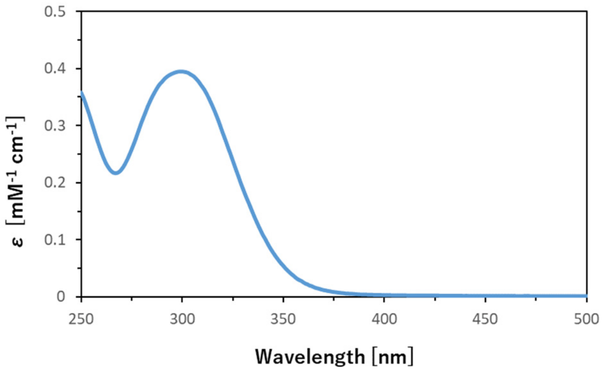
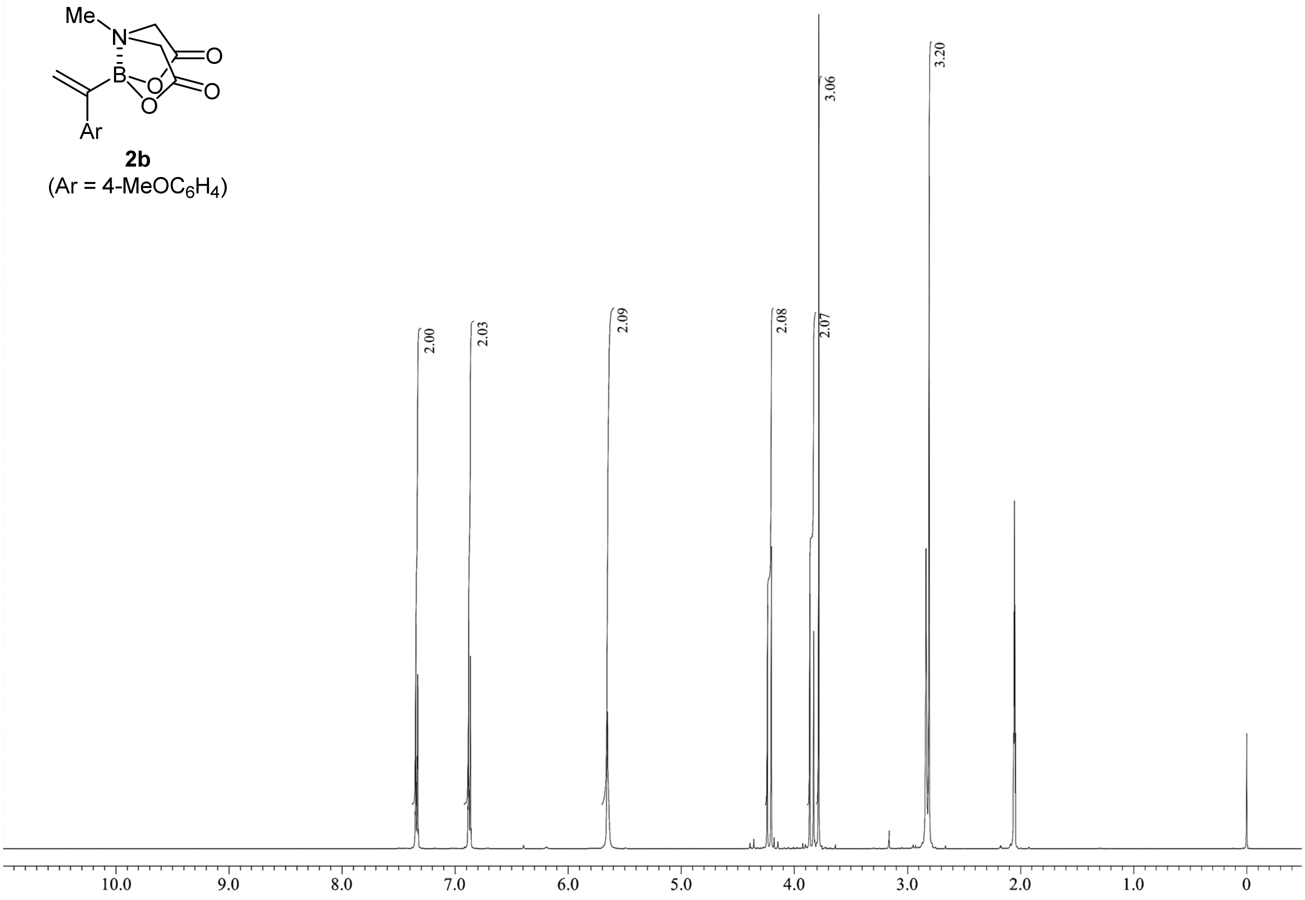
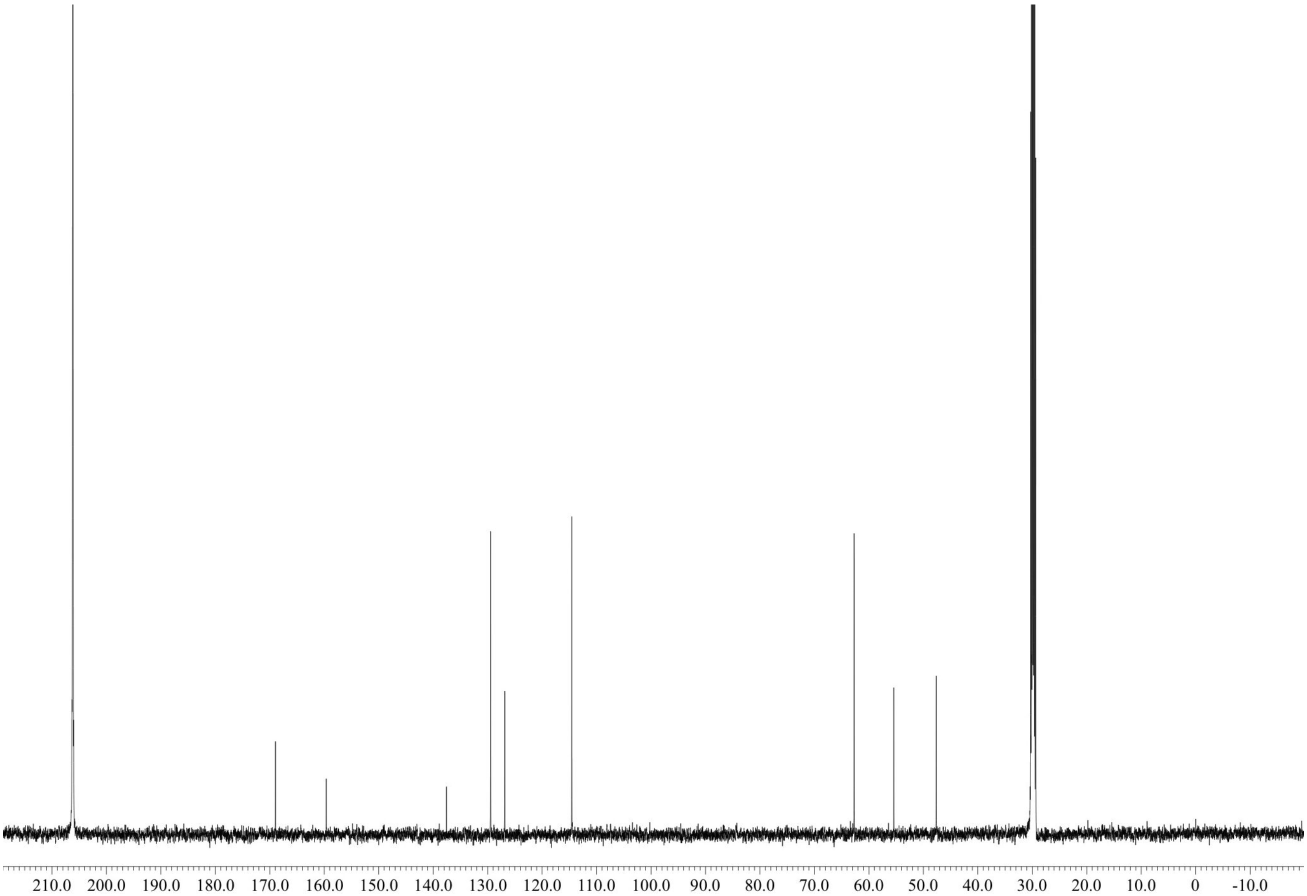
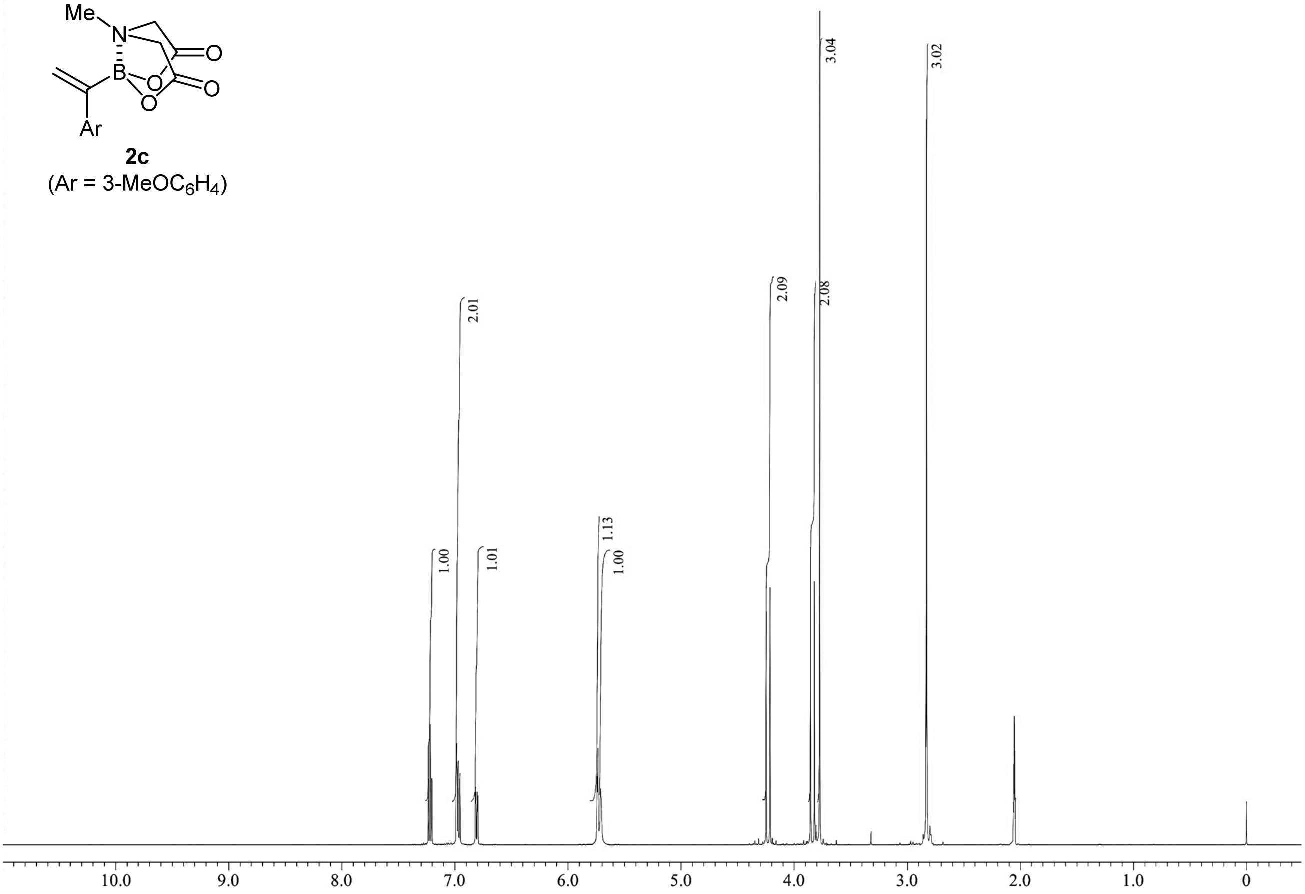


**Fig. S2.** UV-Vis absorption spectrum of **1**

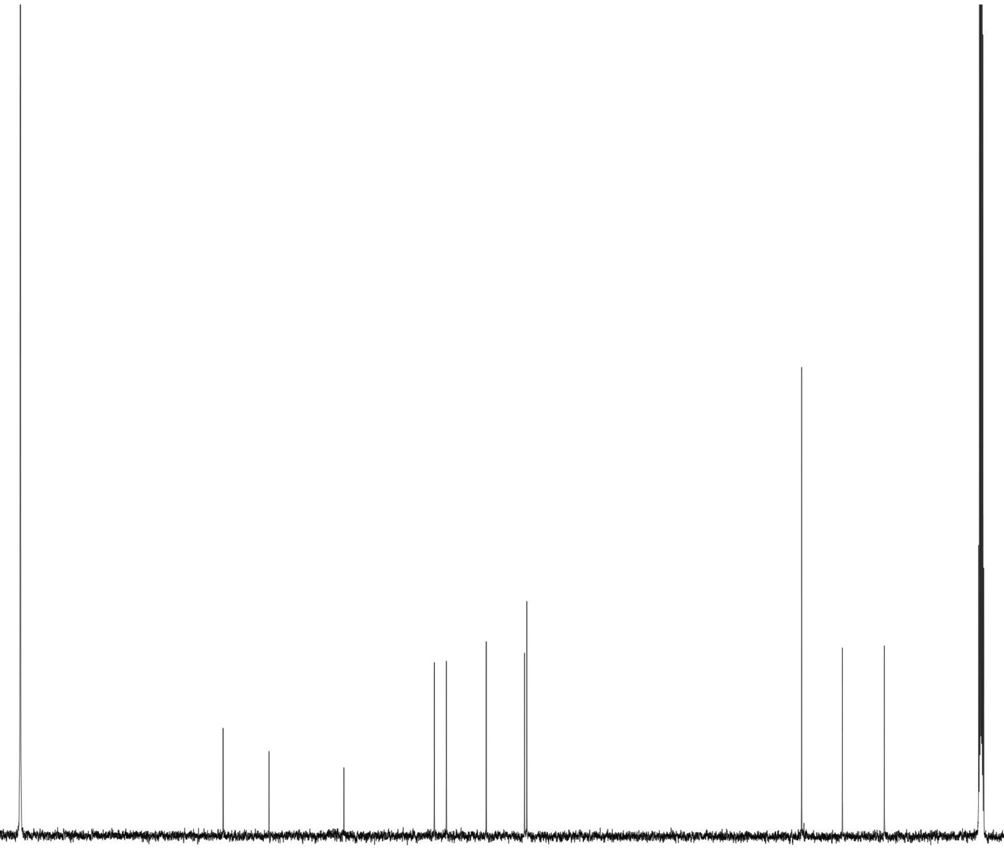
## Copies of $^1$H and $^{13}$C NMR Spectra:

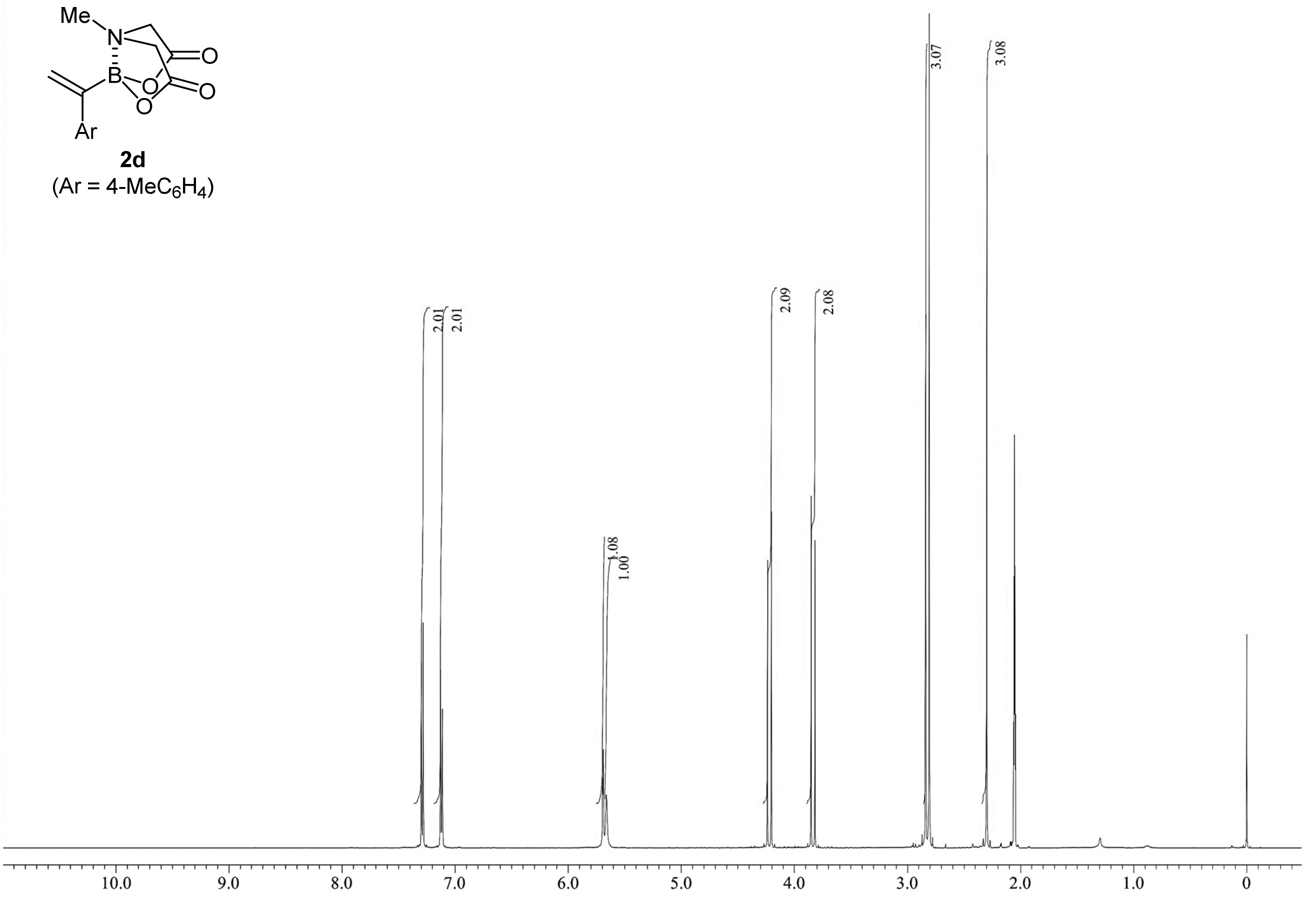

**2b**
(Ar = 4-MeOC$_6$H$_4$)





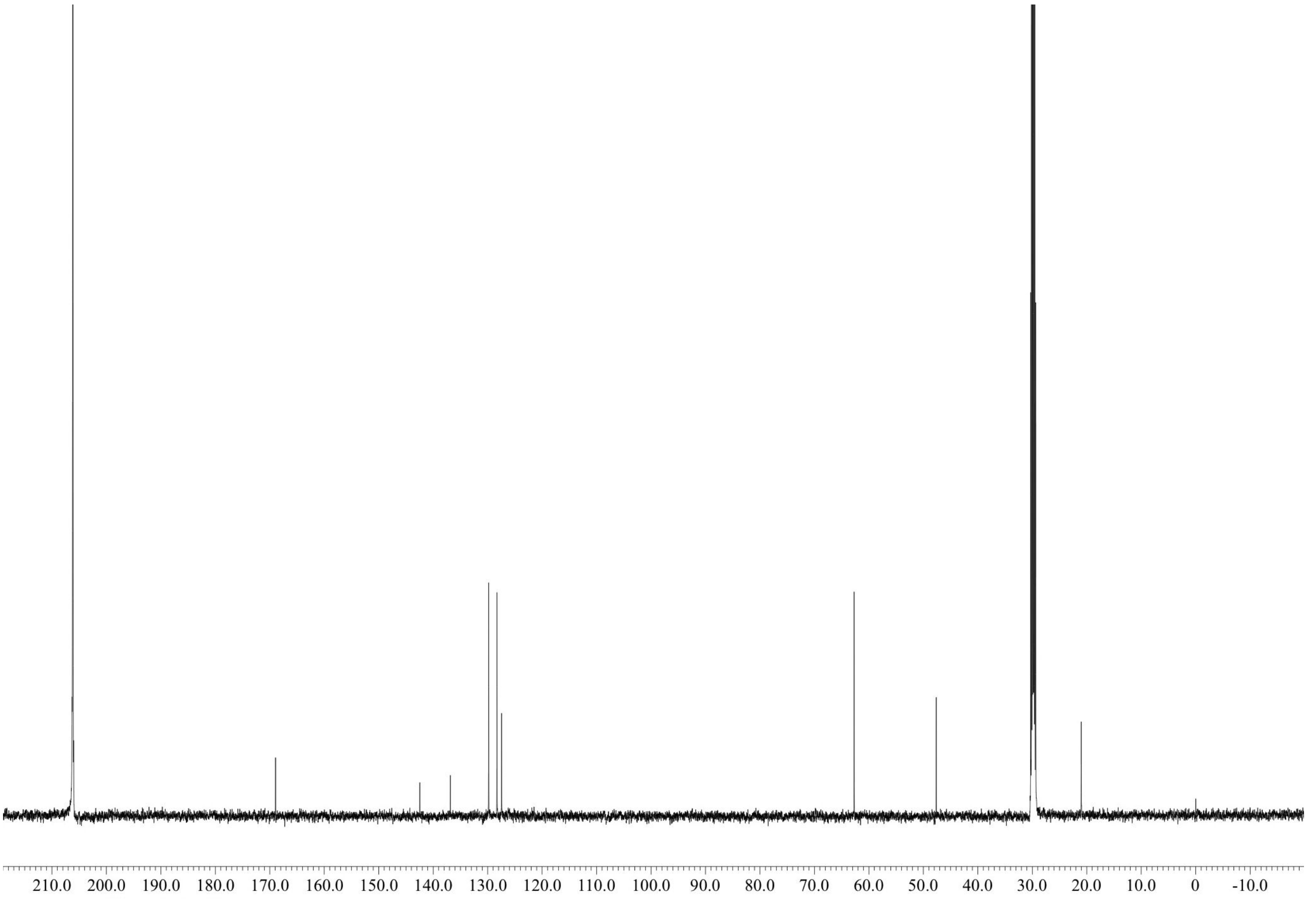
**2c**
(Ar = 3-MeOC$_6$H$_4$)

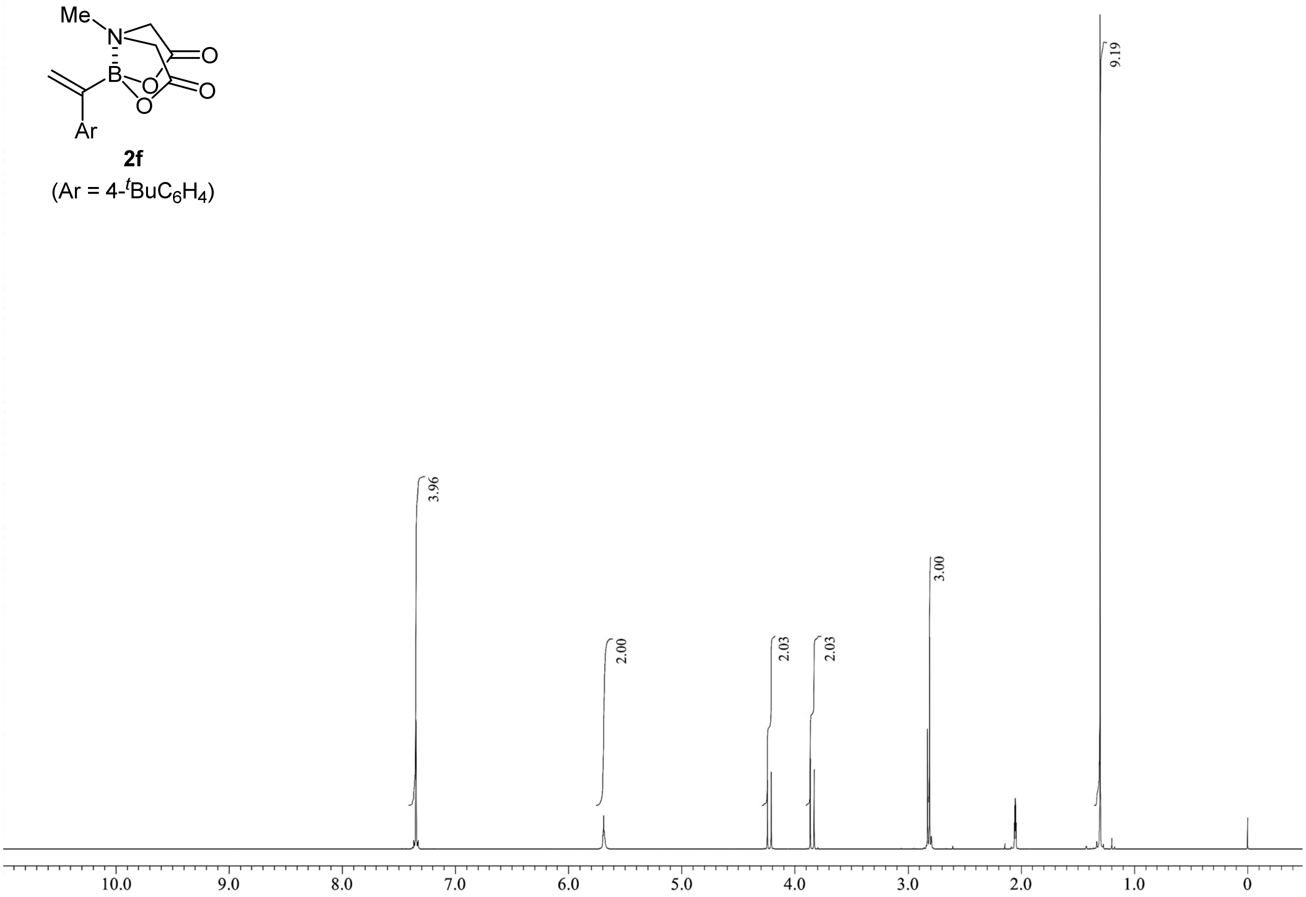




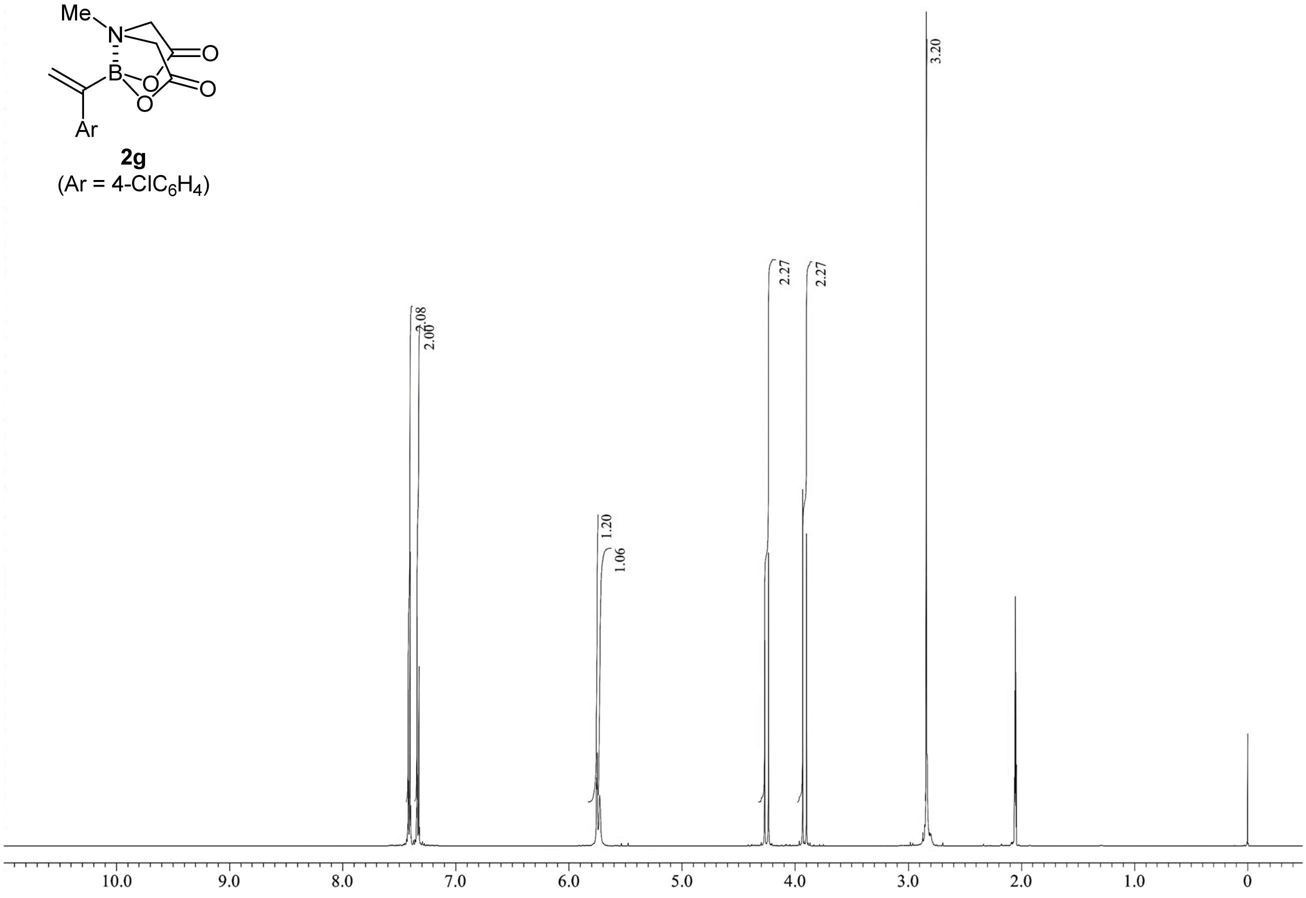
**2d**

(Ar = 4-MeC$_6$H$_4$)

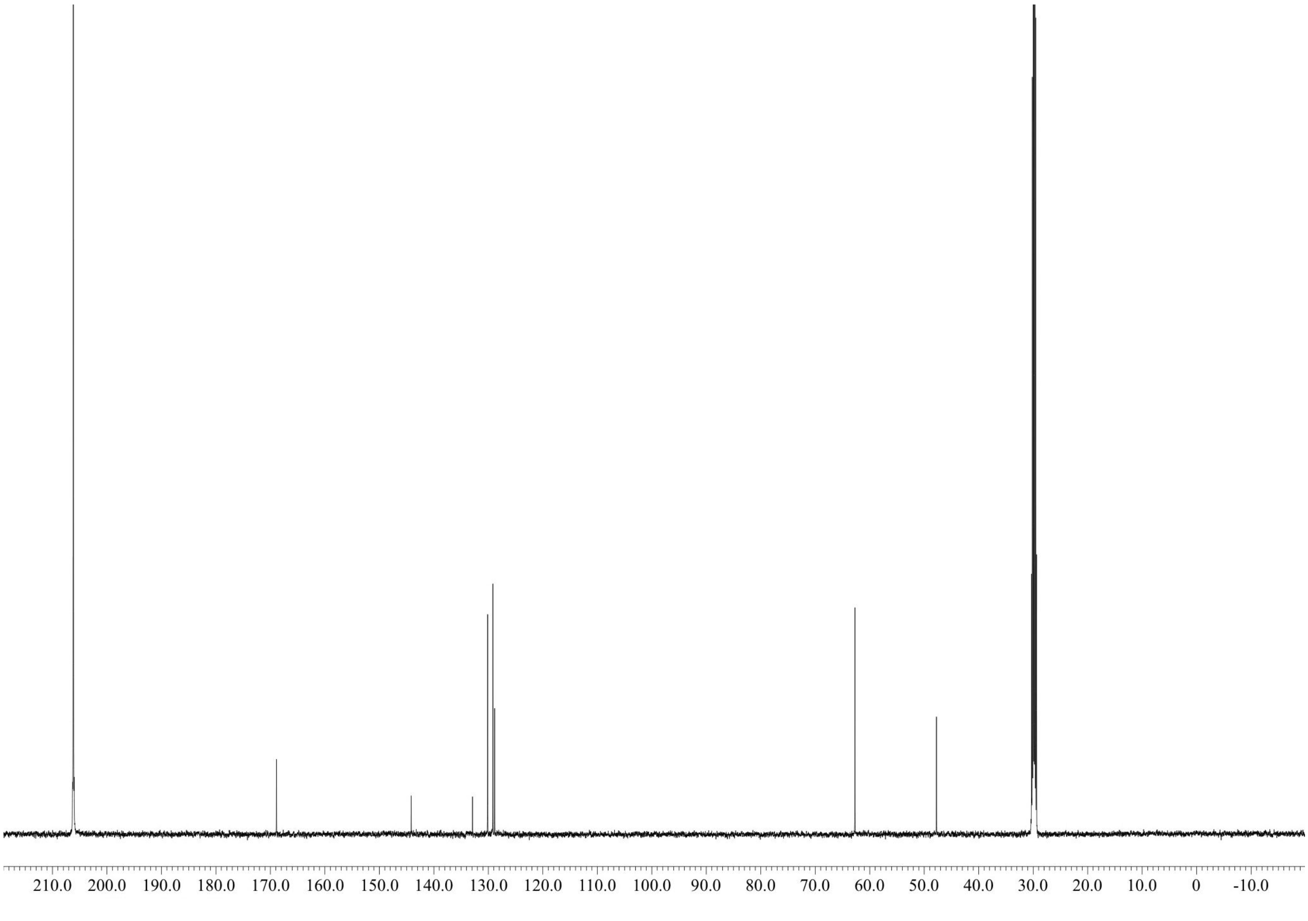


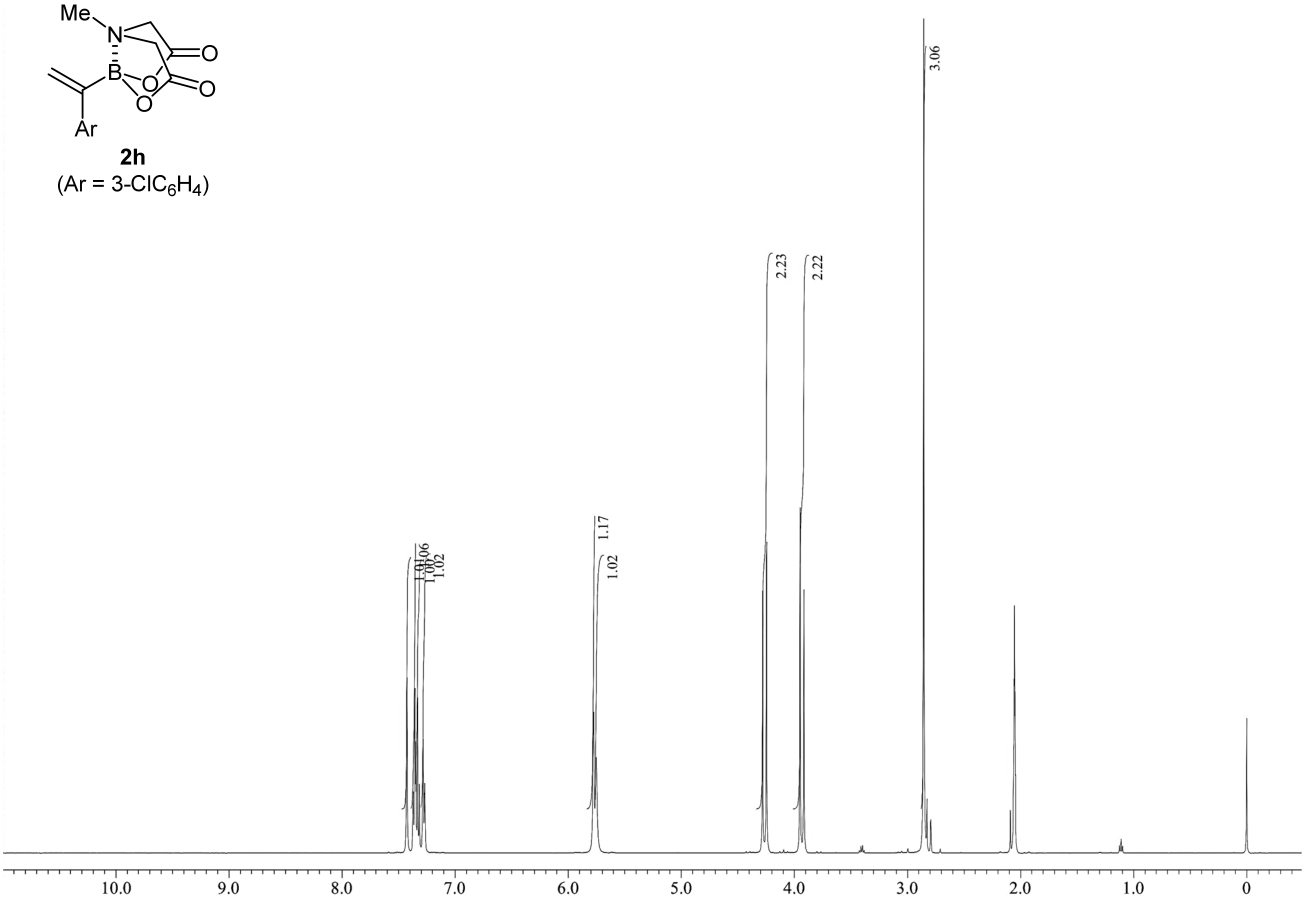


**2f**
(Ar = 4-$^t$BuC$_6$H$_4$)

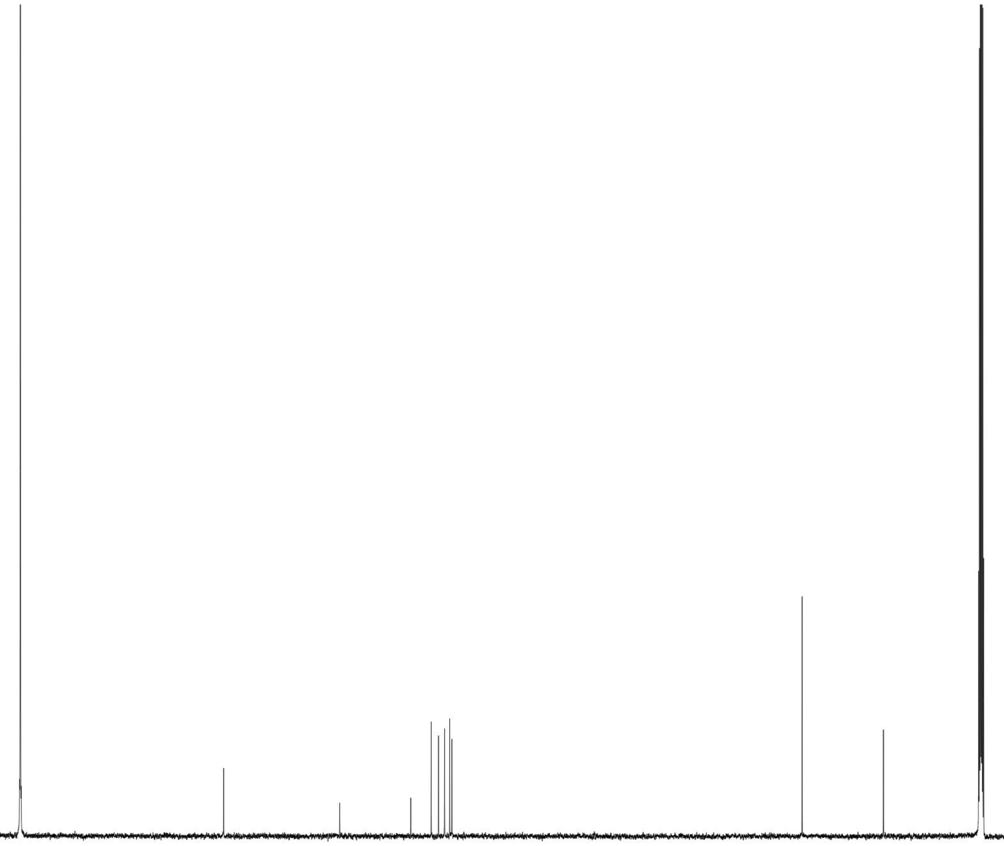


**2g**
(Ar = 4-ClC$_6$H$_4$)

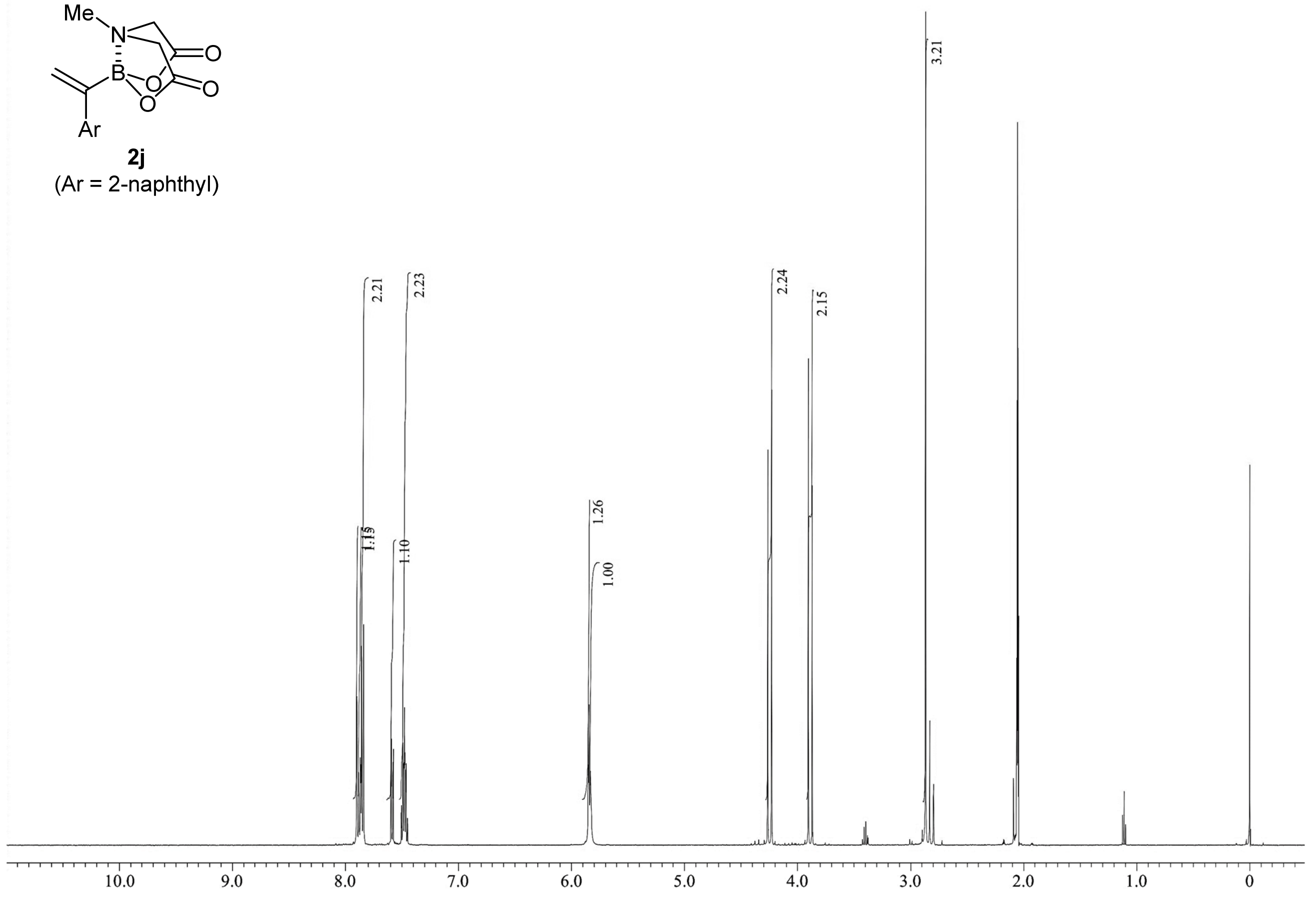


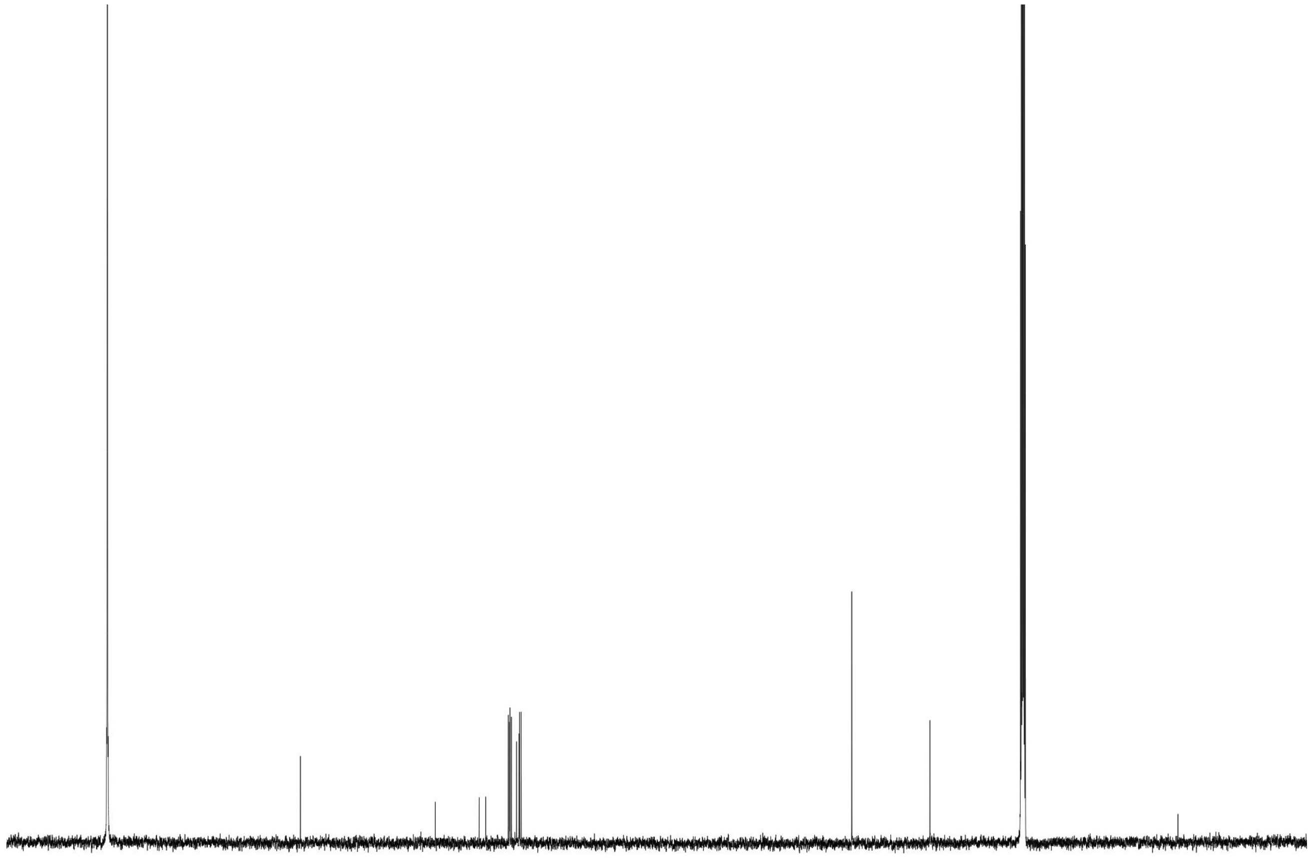


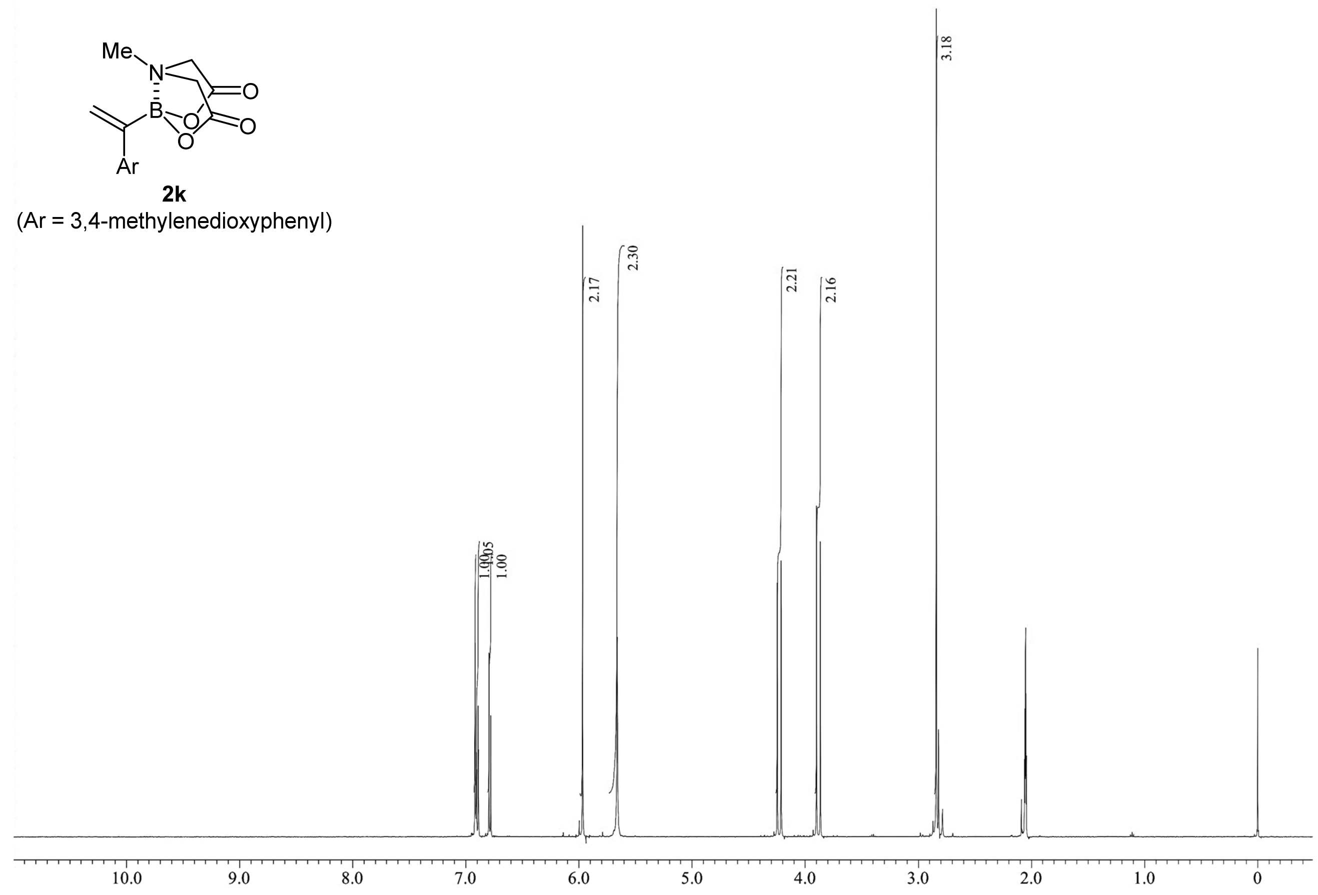
**2h**
(Ar = 3-Cl$C_6H_4$)



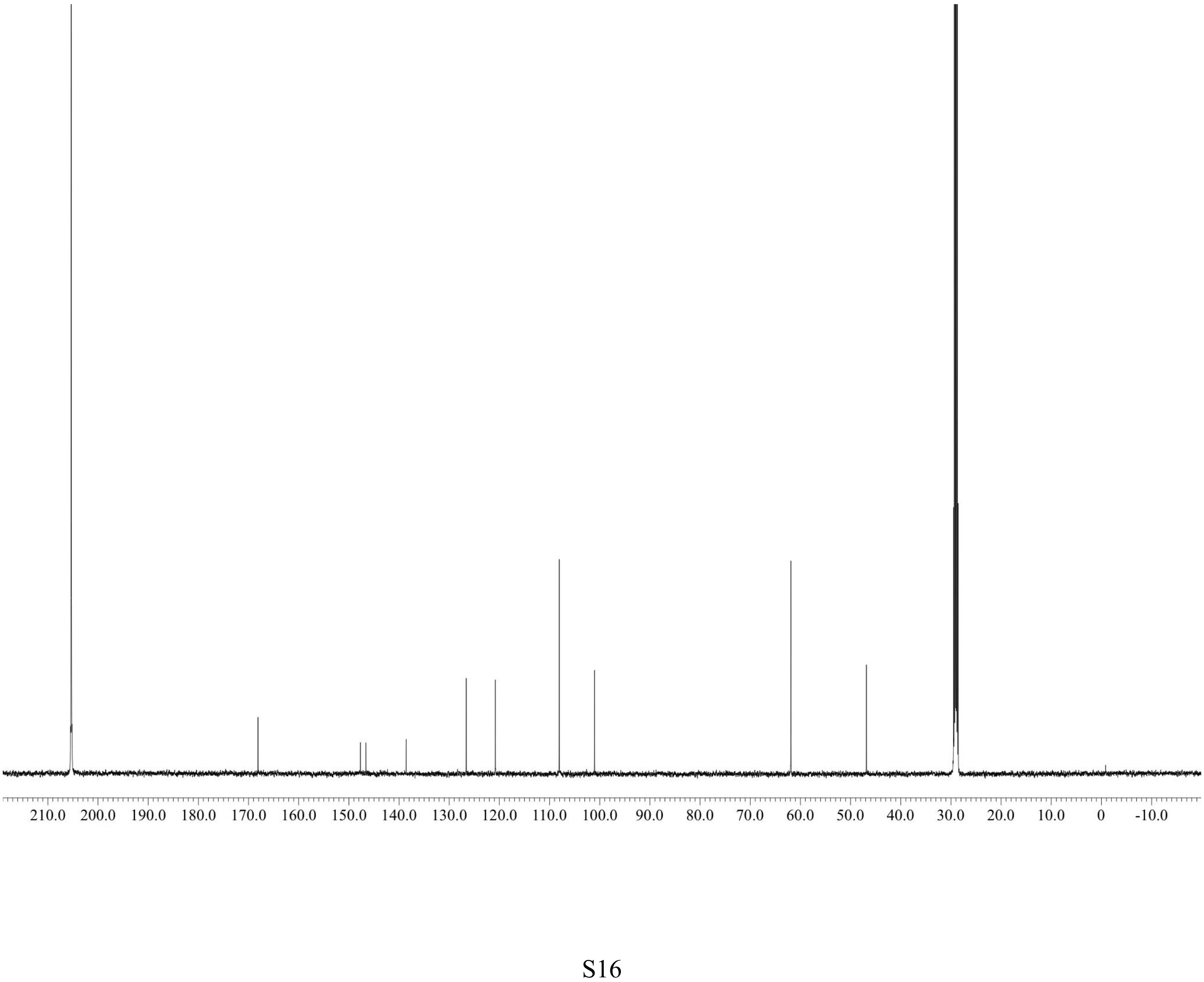
**2j**
(Ar = 2-naphthyl)

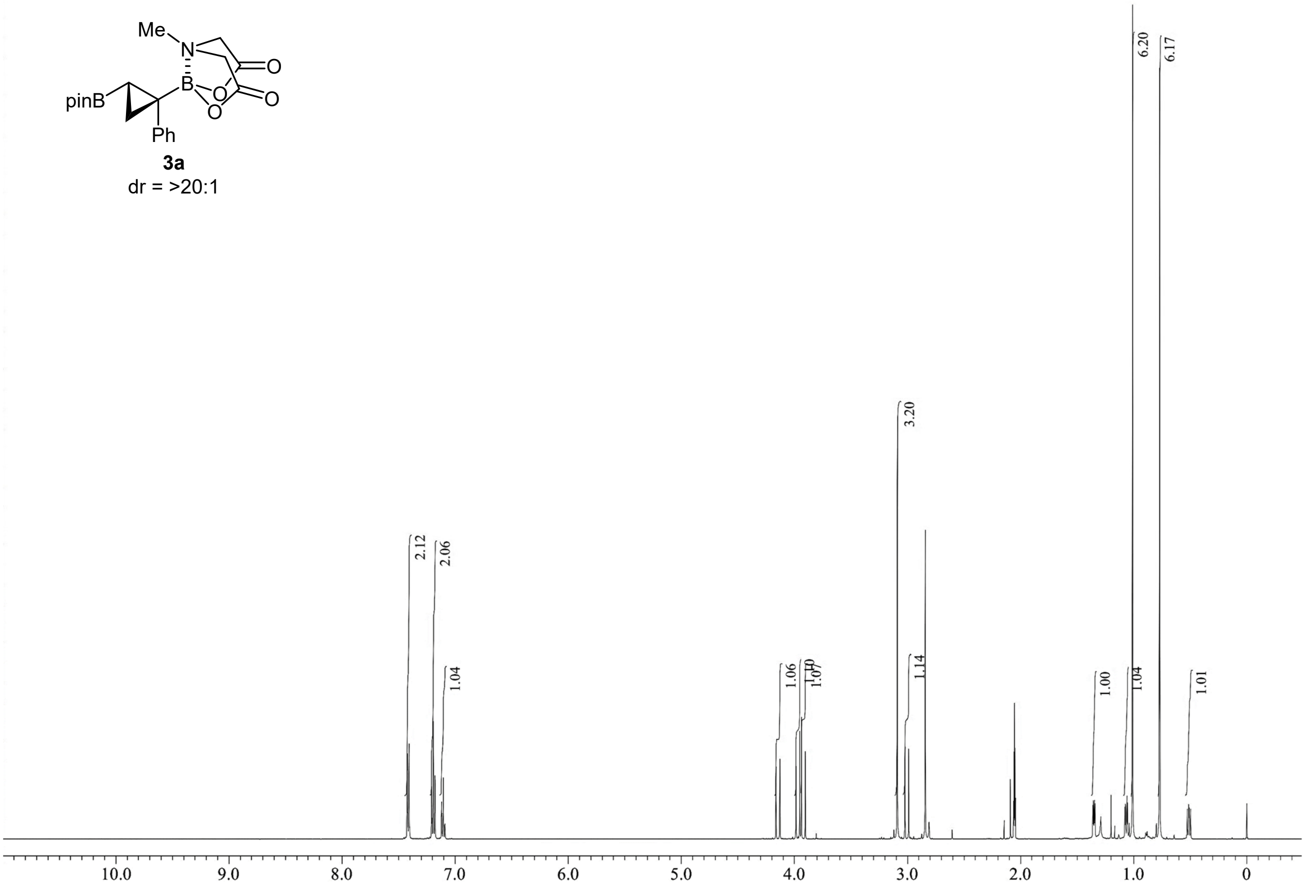






**2k**
(Ar = 3,4-methylenedioxyphenyl)




Me
N
O
pinB
B
O
O
O
Ph

**3a**
dr = >20:1

6.20
6.17
3.20
2.12
2.06
1.04
1.06
1.10
1.07
1.14
1.00
1.04
1.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
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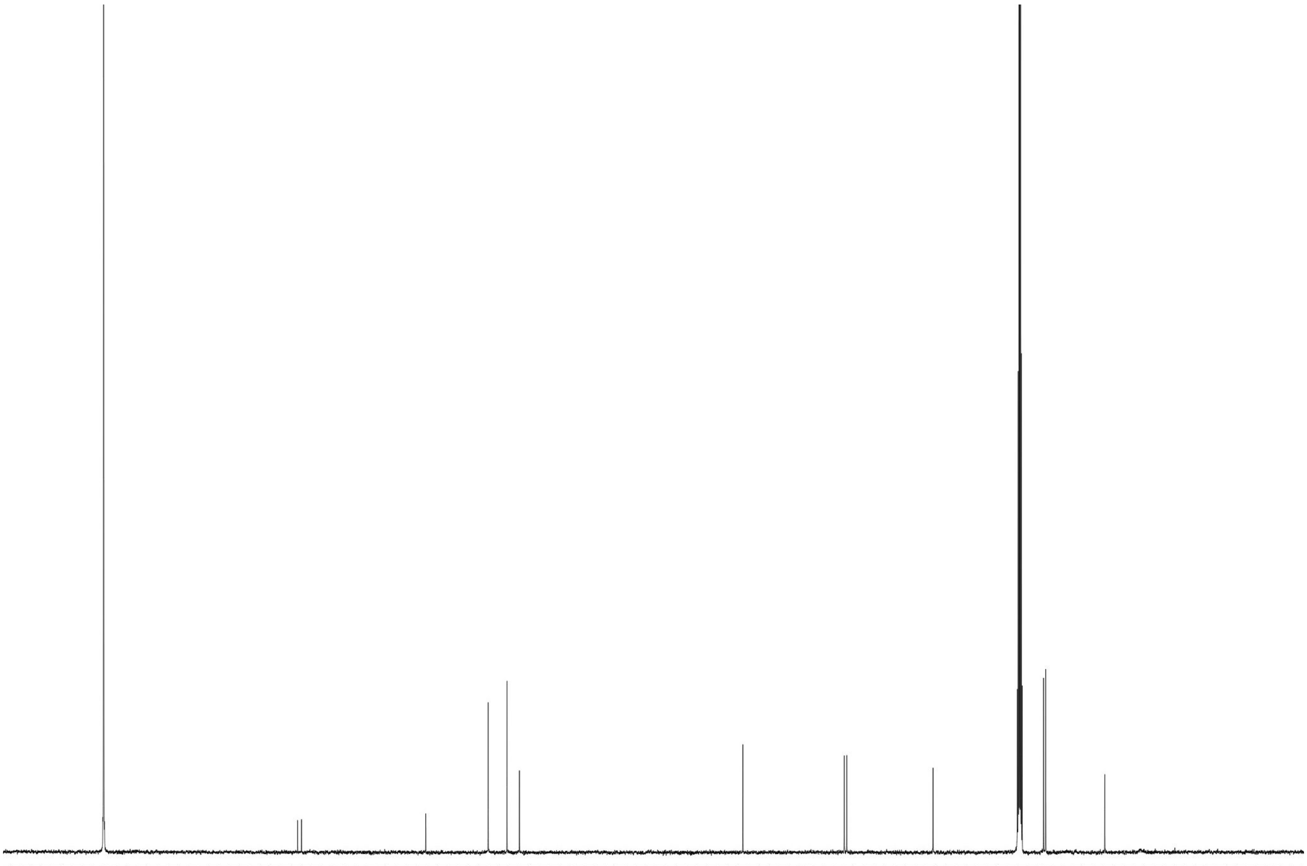
1.0
0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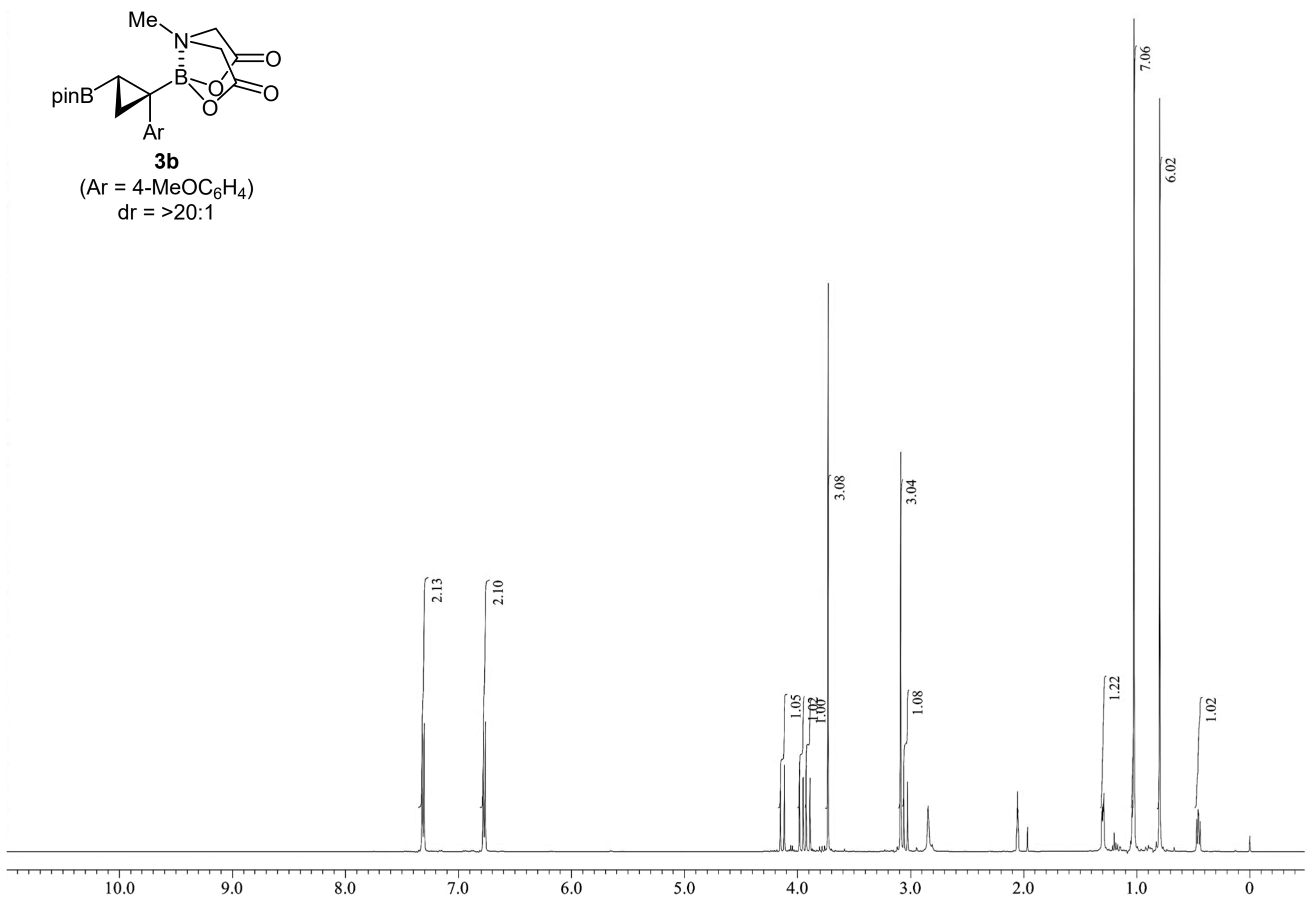
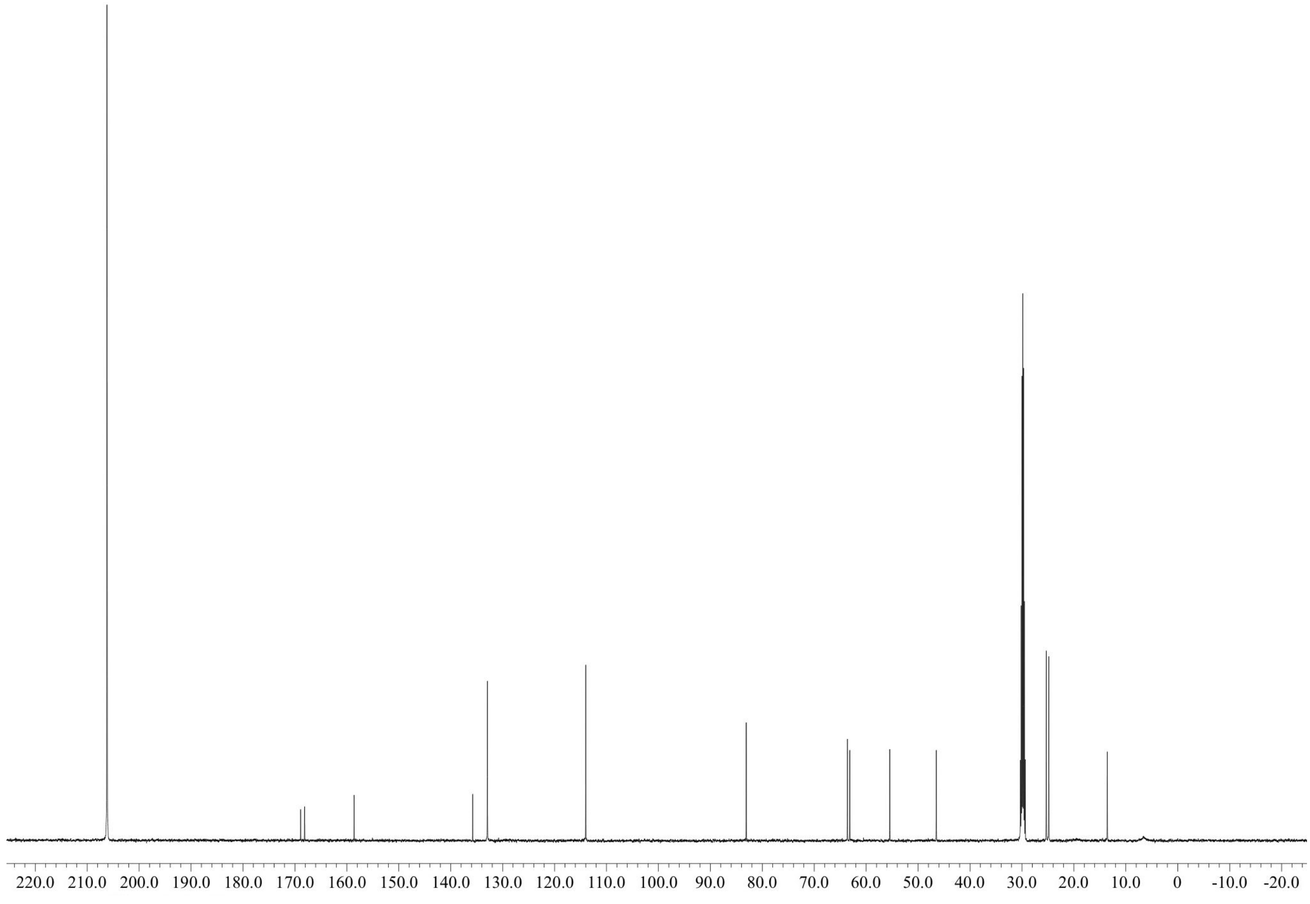
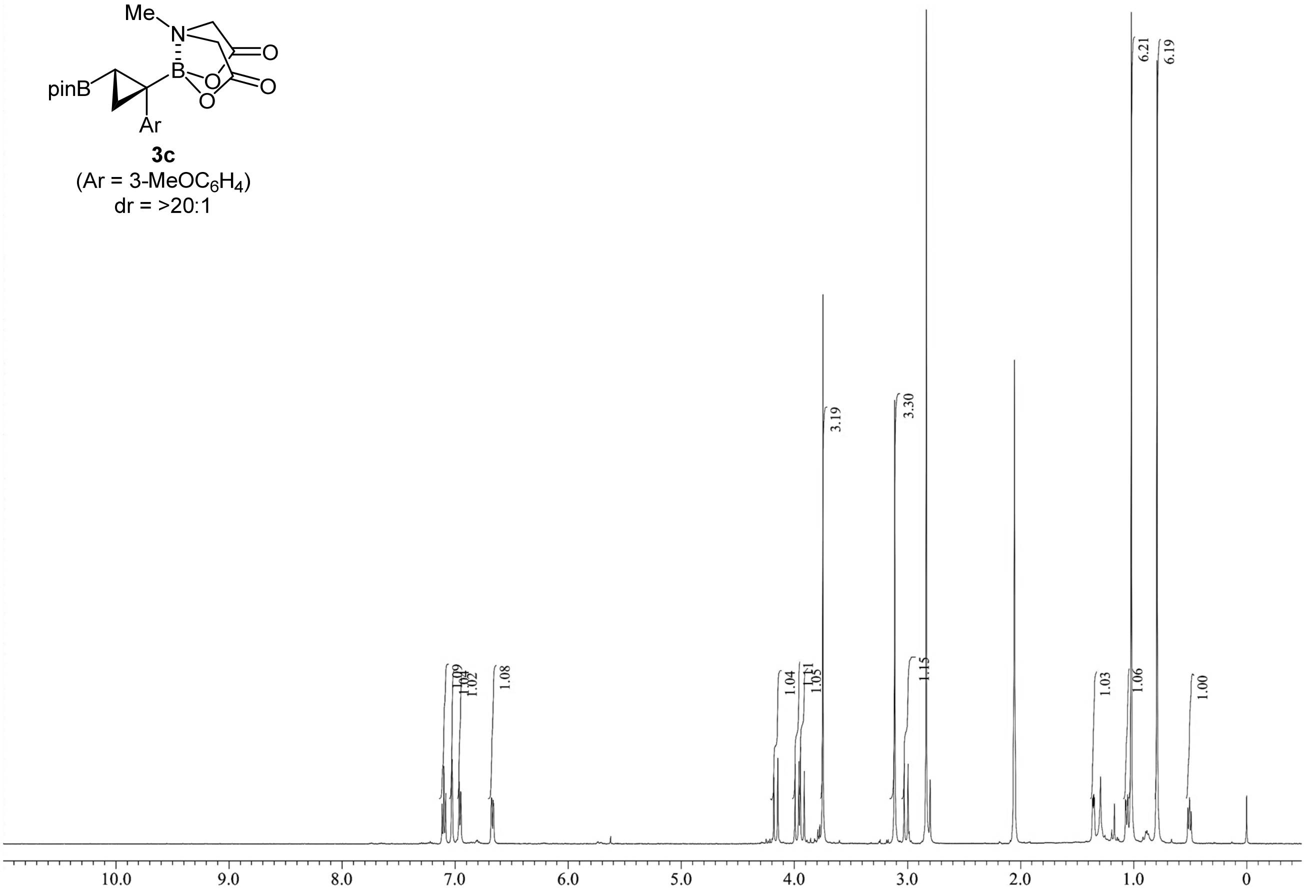
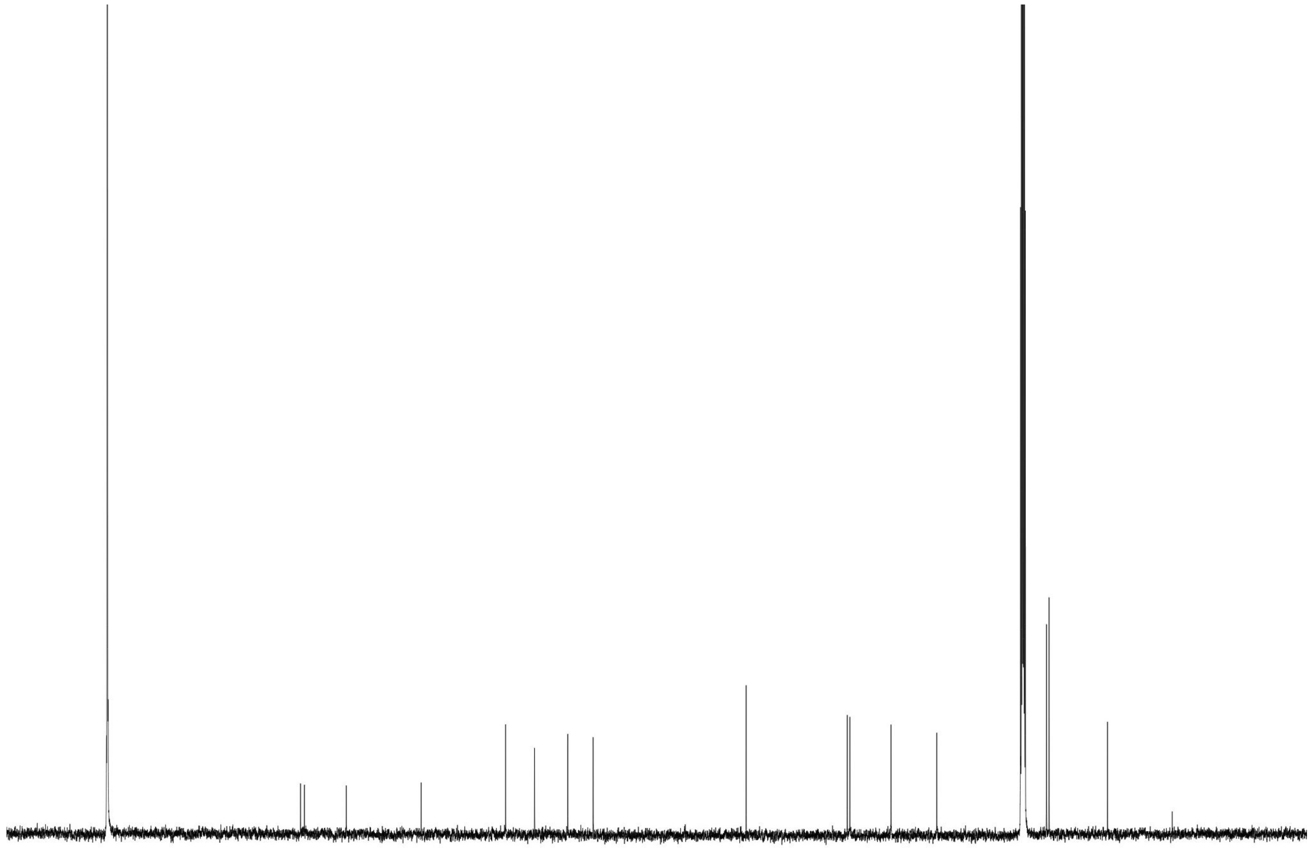


**3b**
(Ar = 4-MeOC$_6$H$_4$)
dr = >20:1

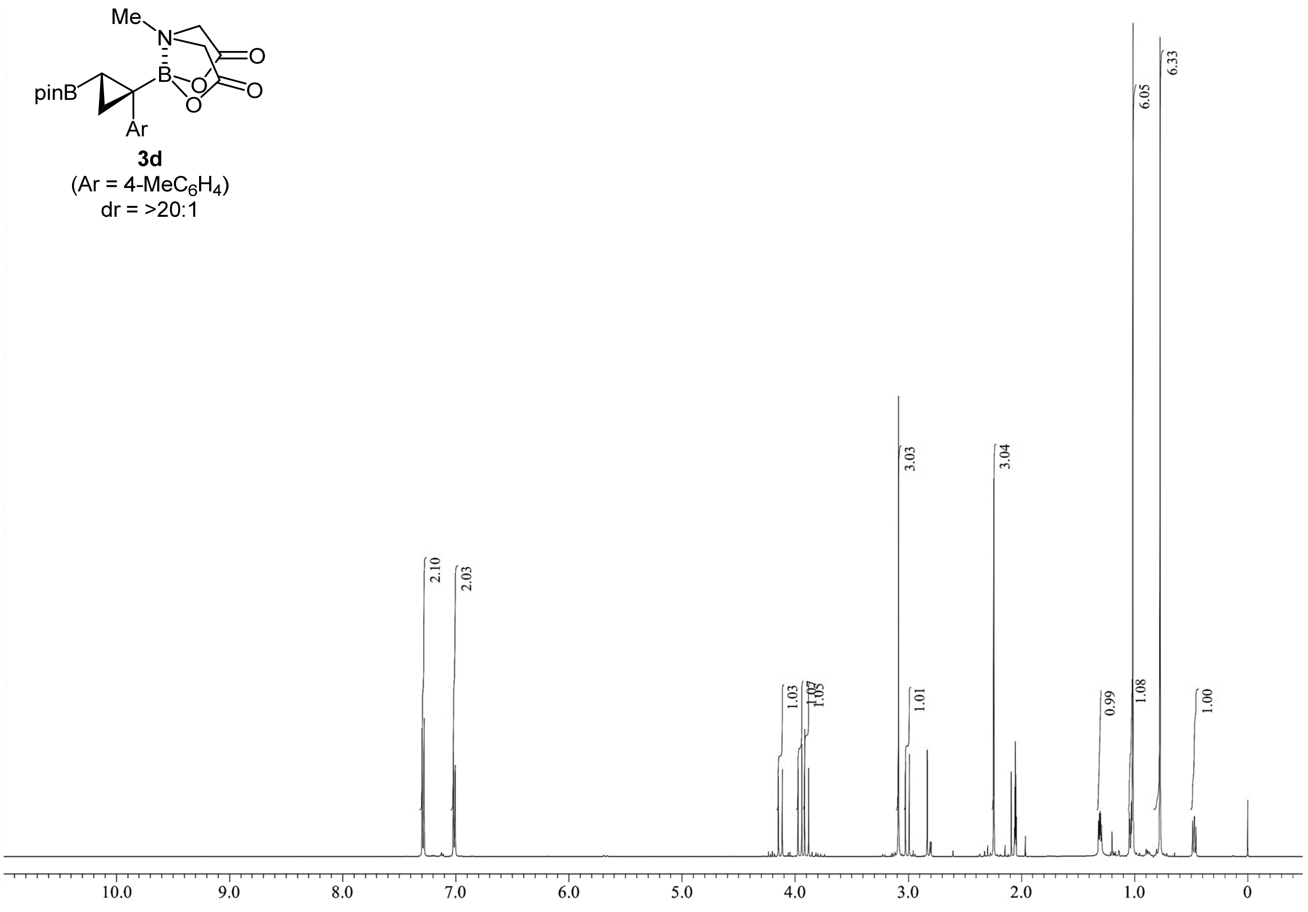


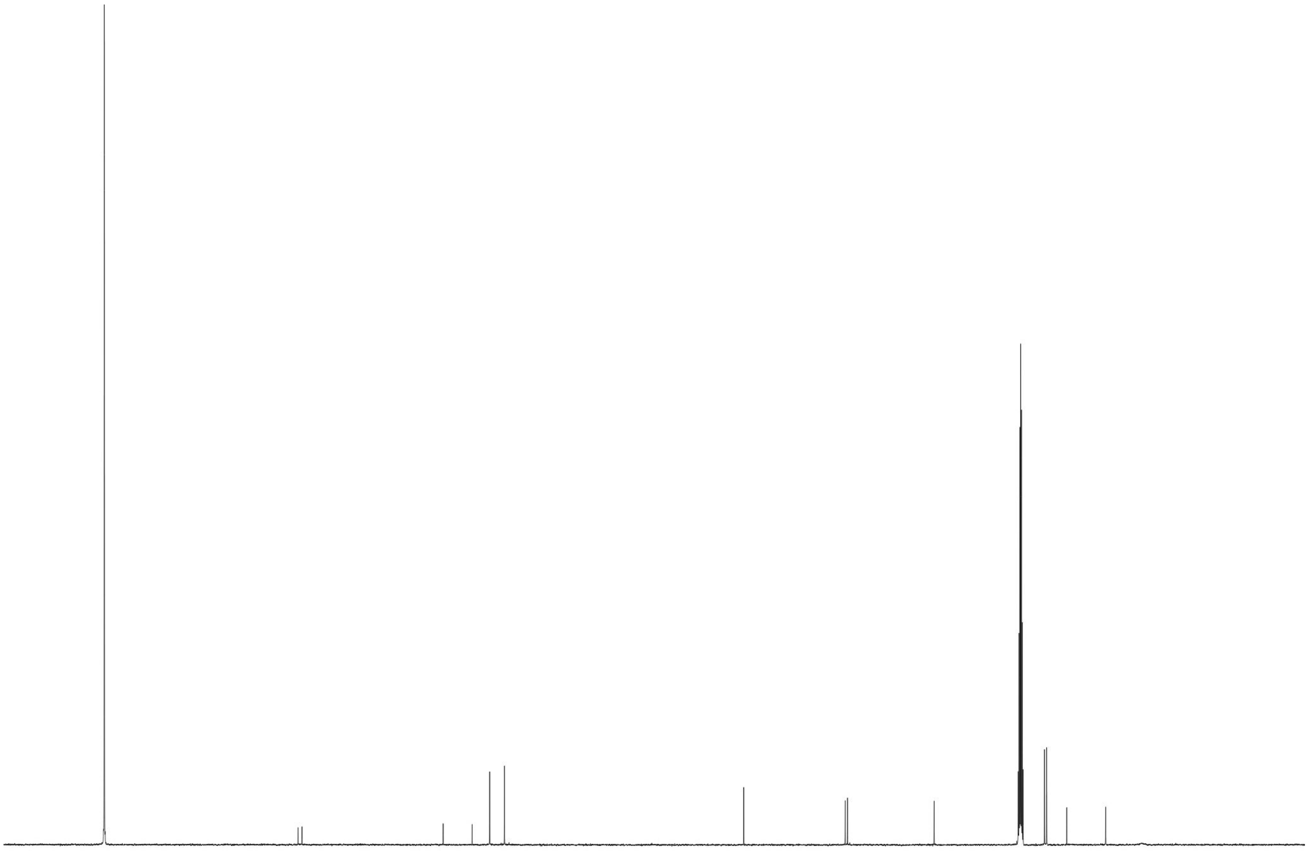


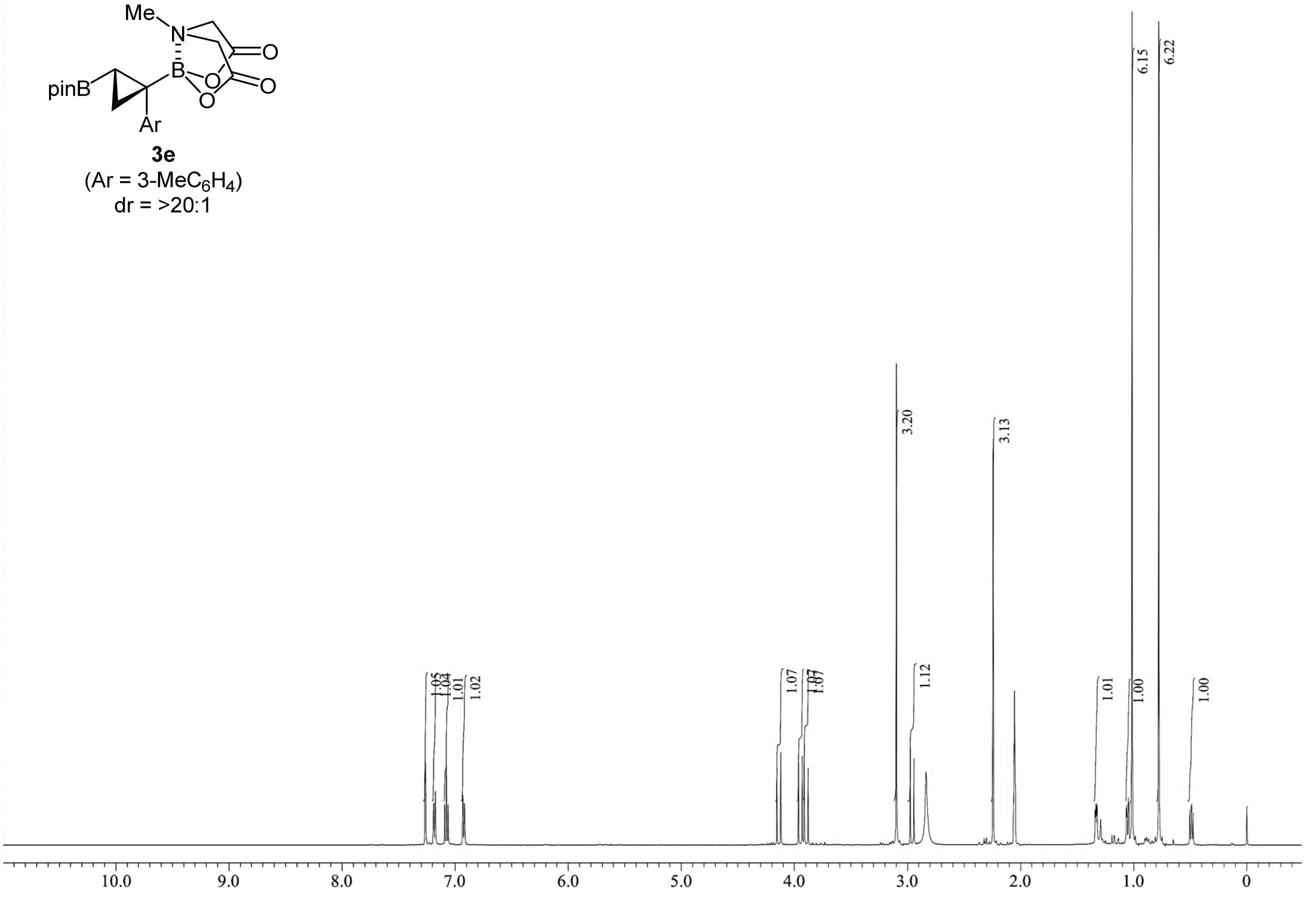
**3c**
(Ar = 3-MeOC$_6$H$_4$)
dr = >20:1



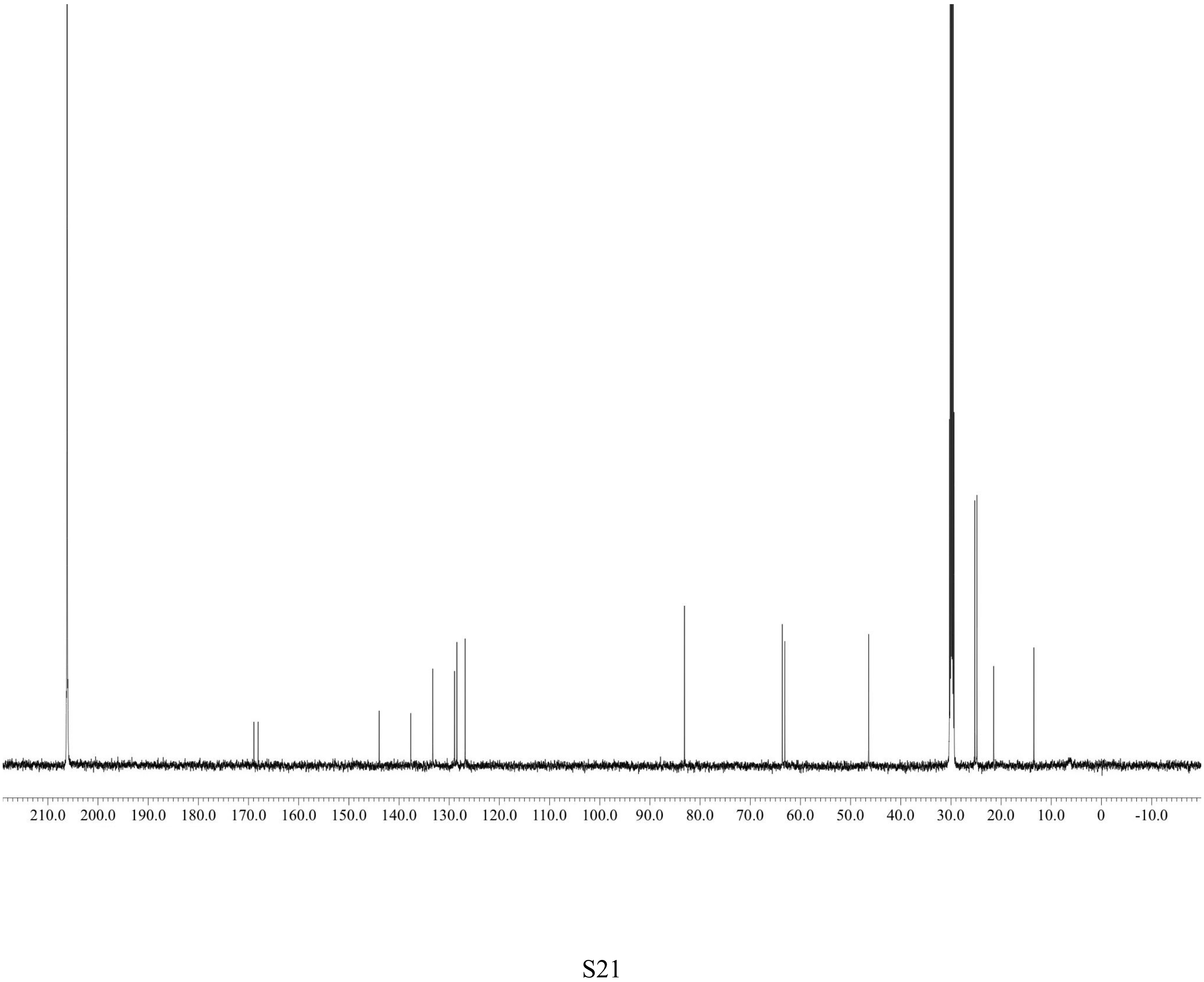
**3d**
(Ar = 4-Me$C_6H_4$)
dr = >20:1

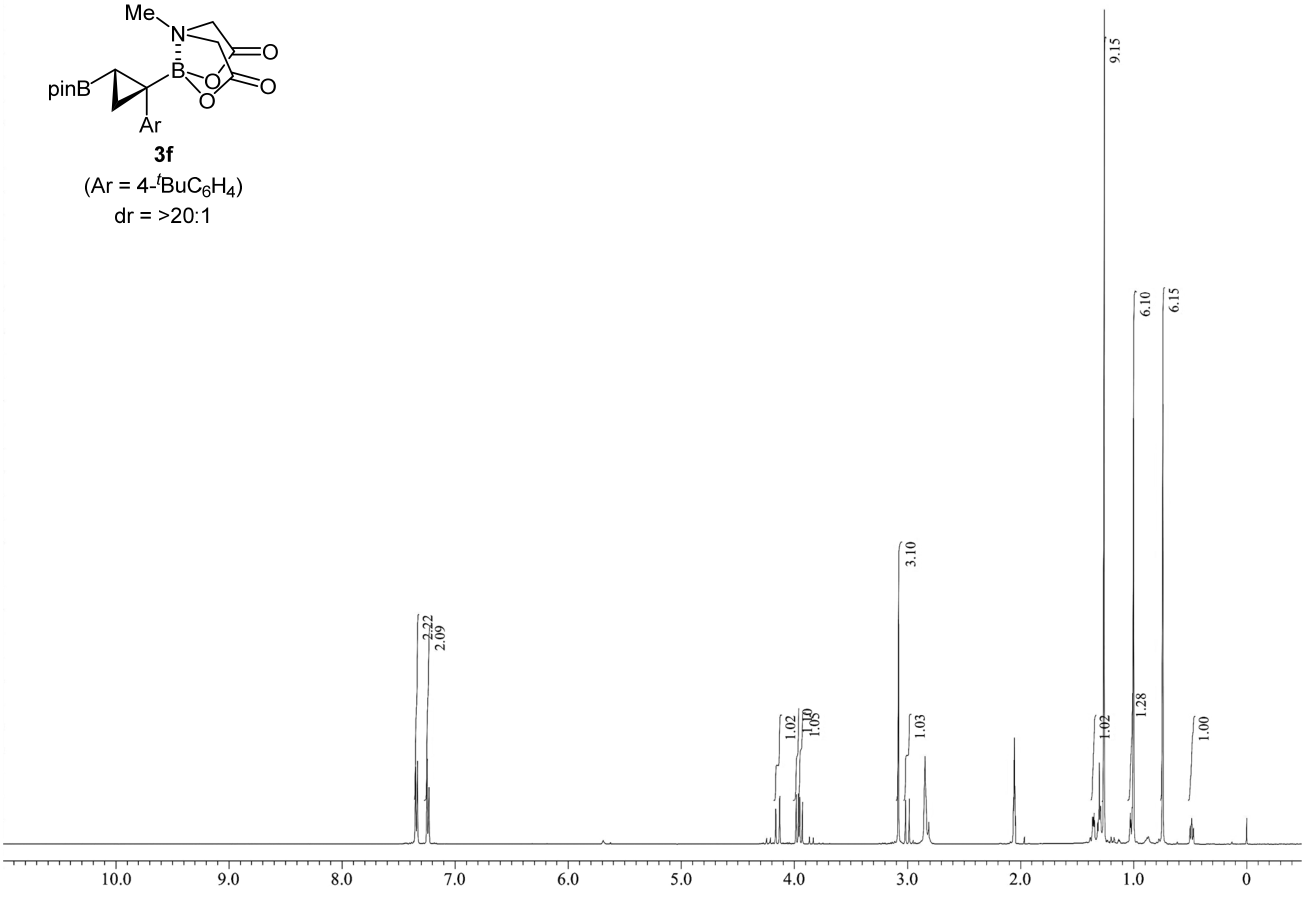






**3e**
(Ar = 3-MeC$_6$H$_4$)
dr = >20:1

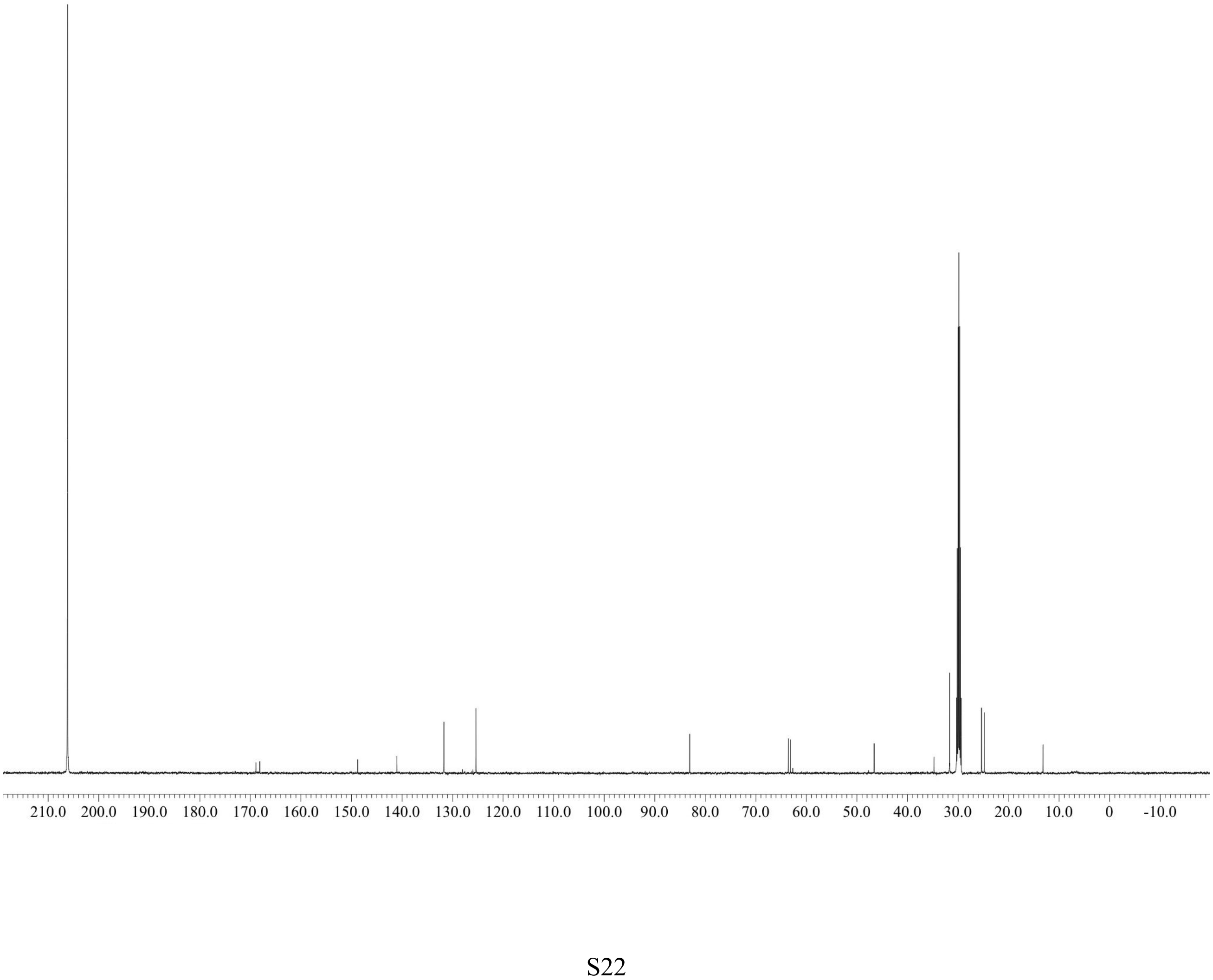


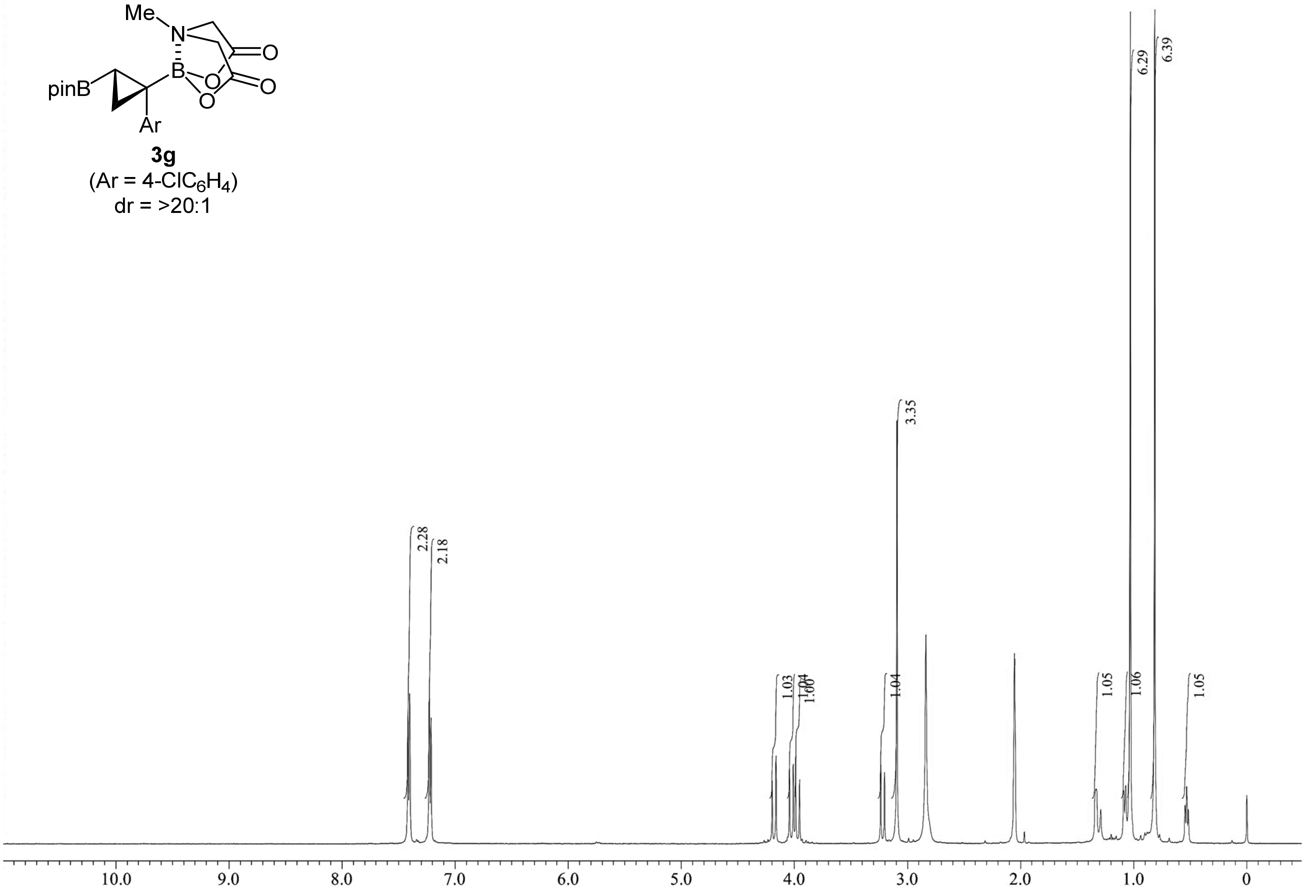


**3f**

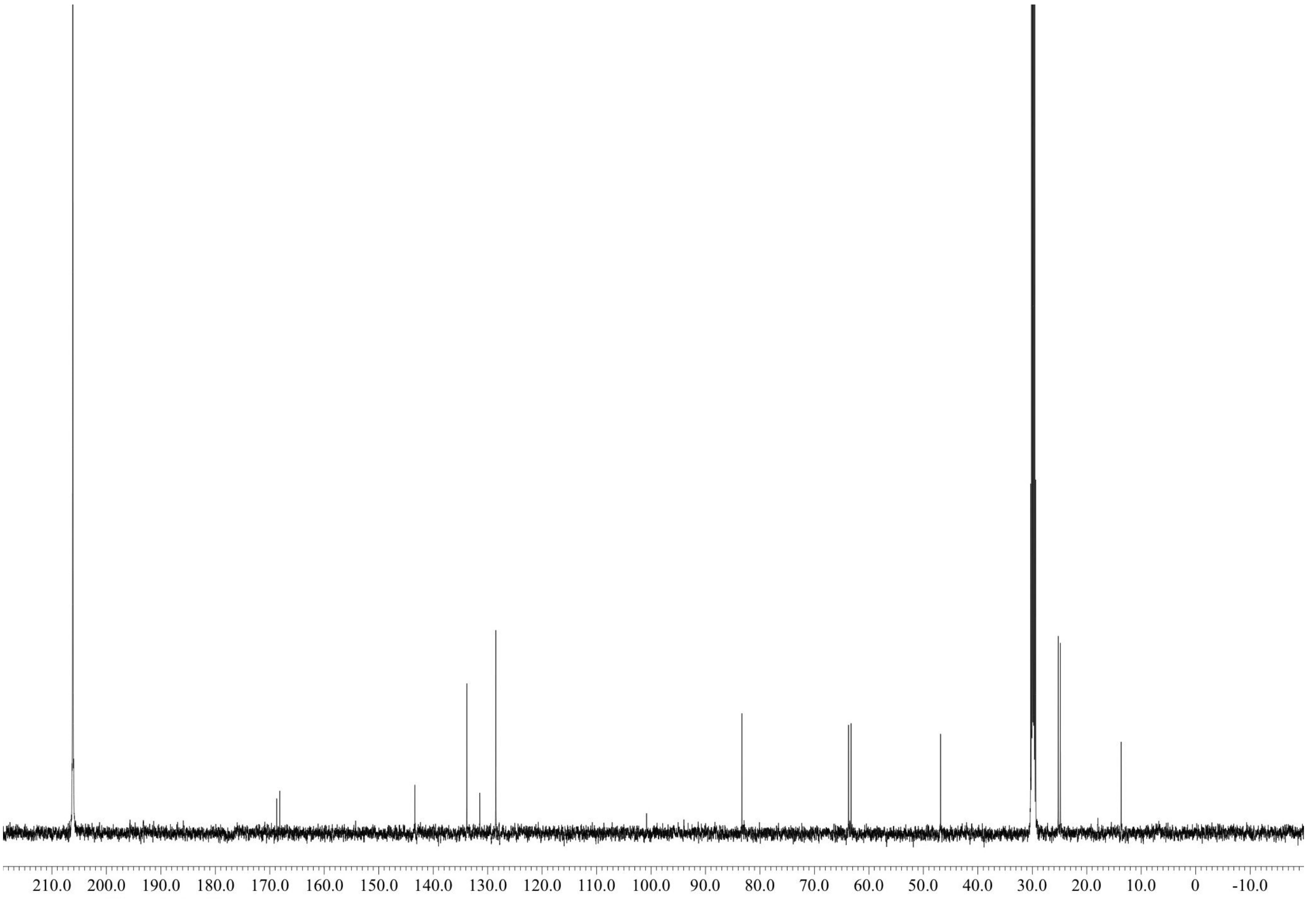
(Ar = 4-${}^{t}$BuC$_6$H$_4$)

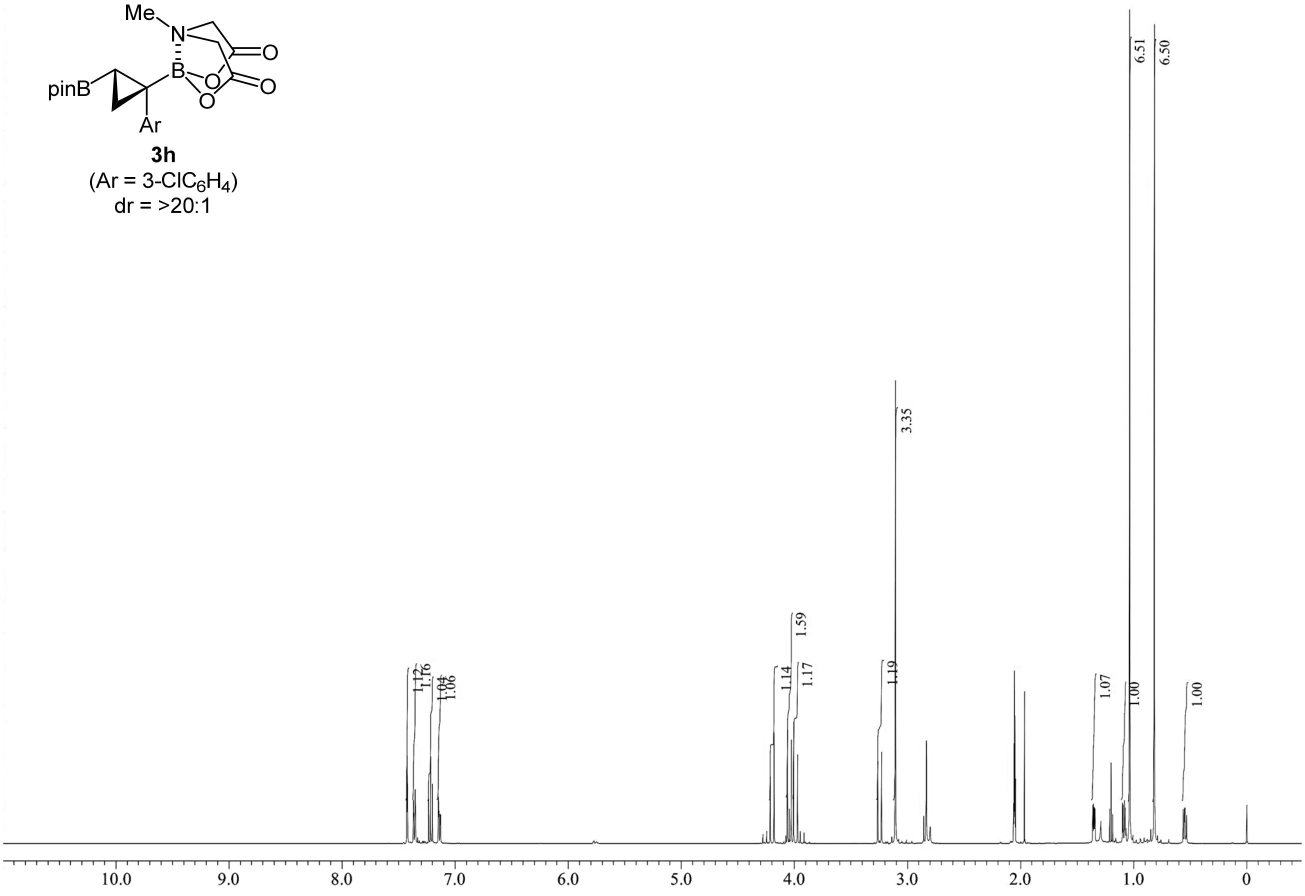
dr = >20:1



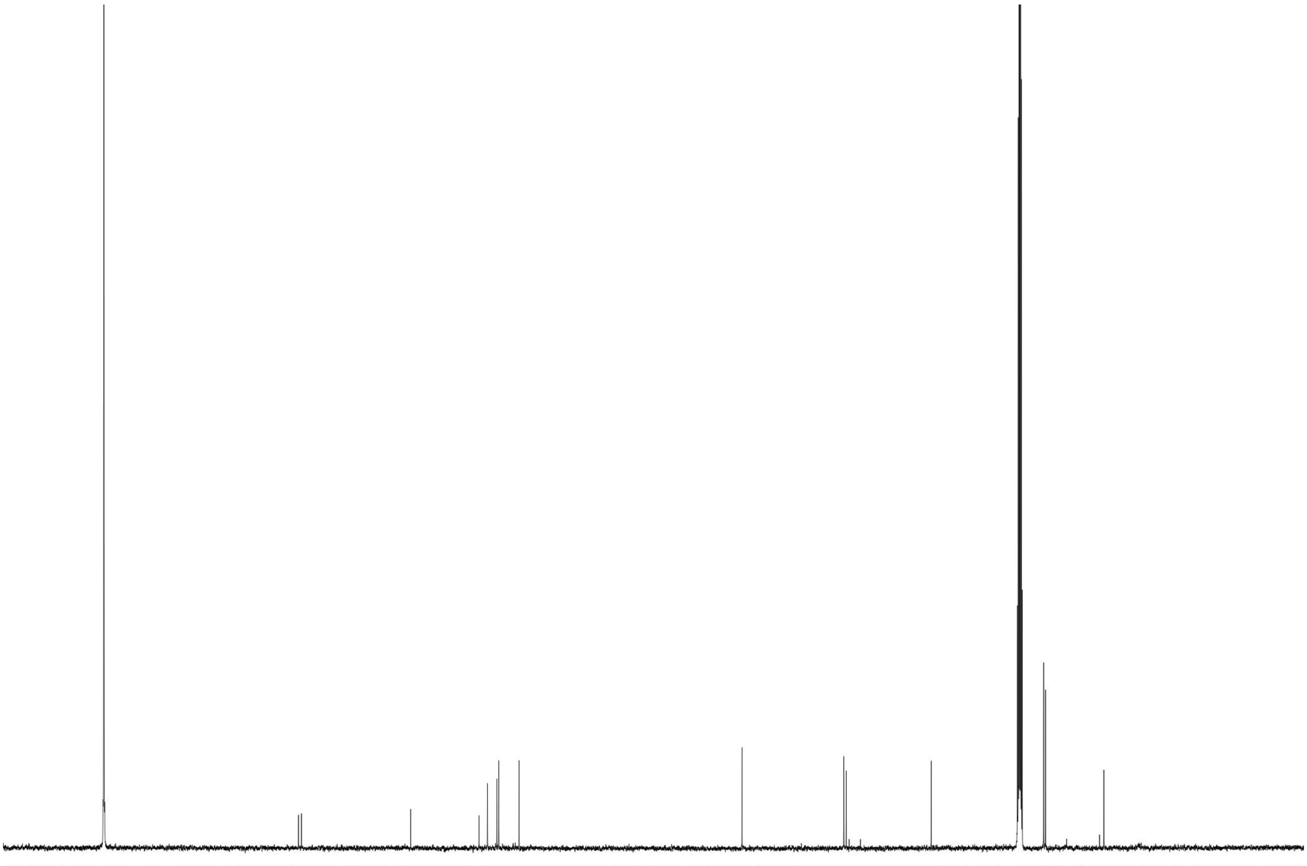


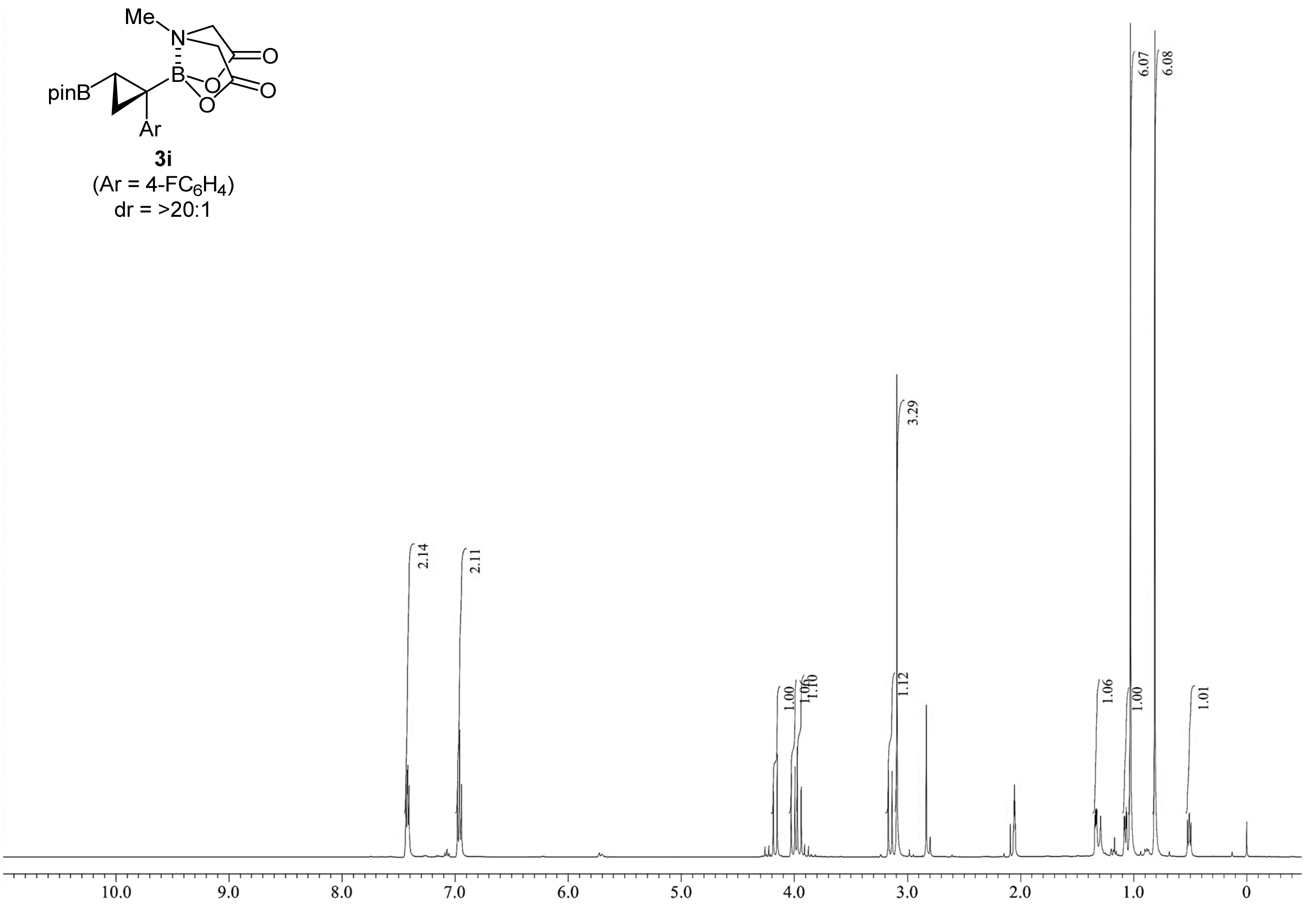
**3g**
(Ar = 4-ClC$_6$H$_4$)
dr = >20:1



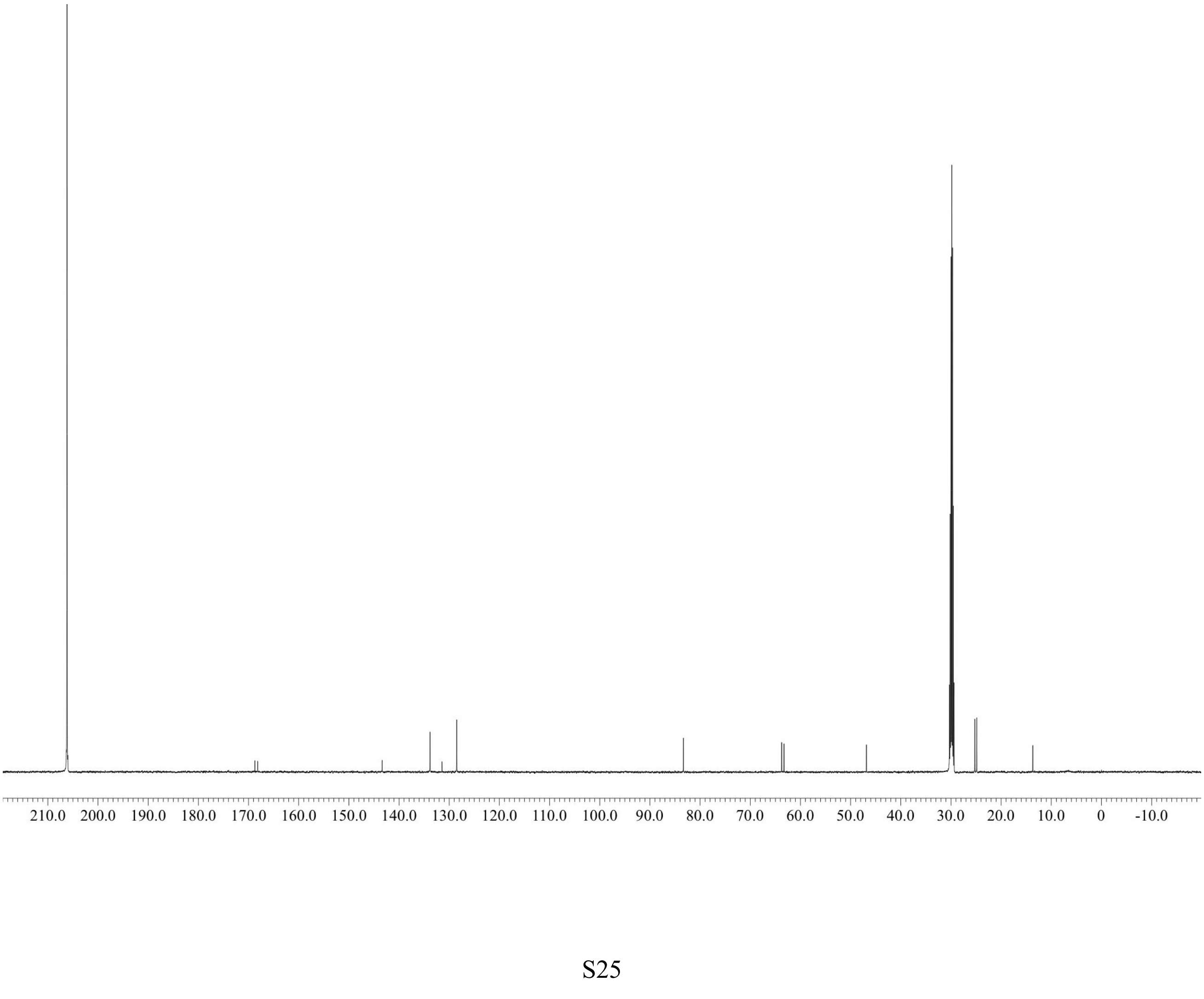


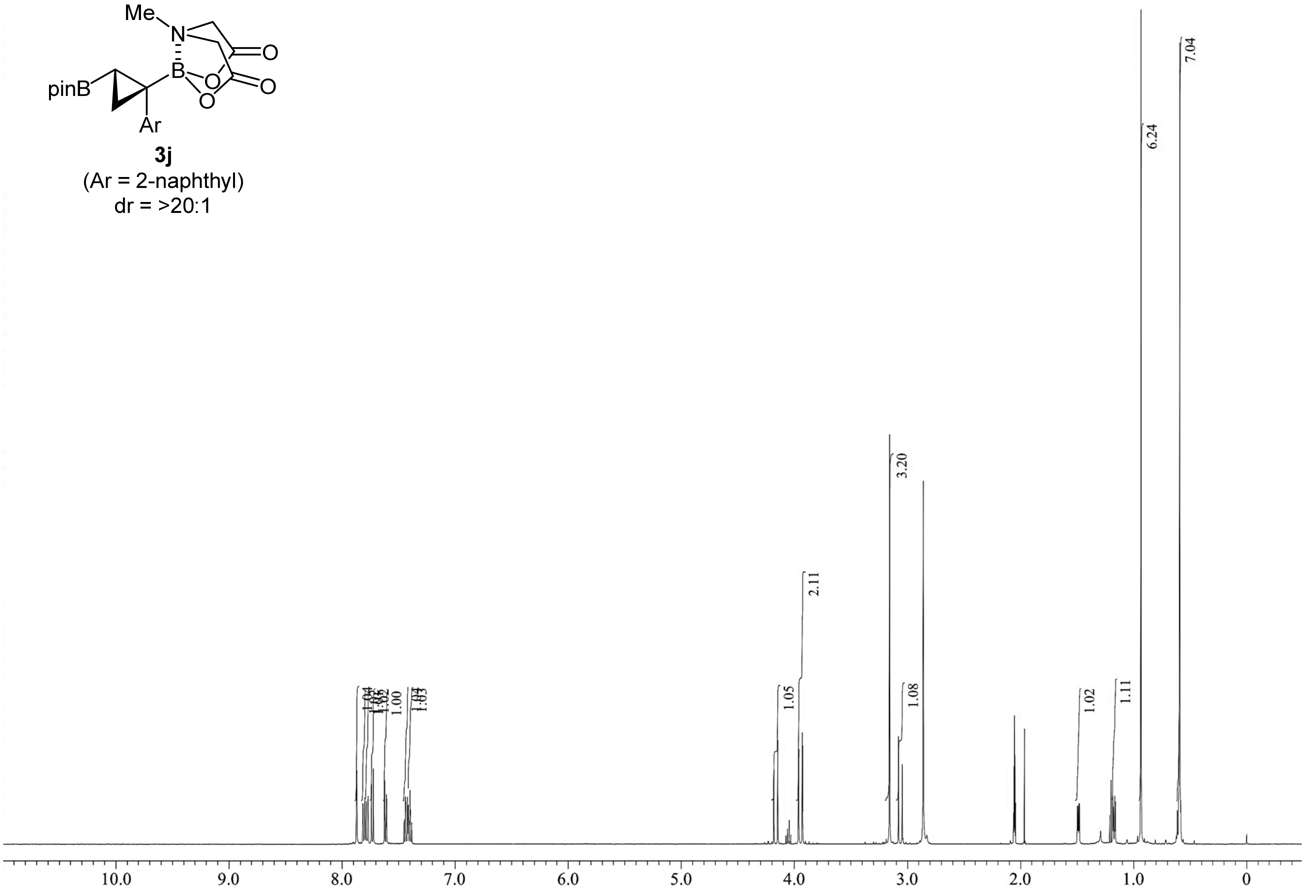
**3h**
(Ar = 3-ClC$_6$H$_4$)
dr = >20:1



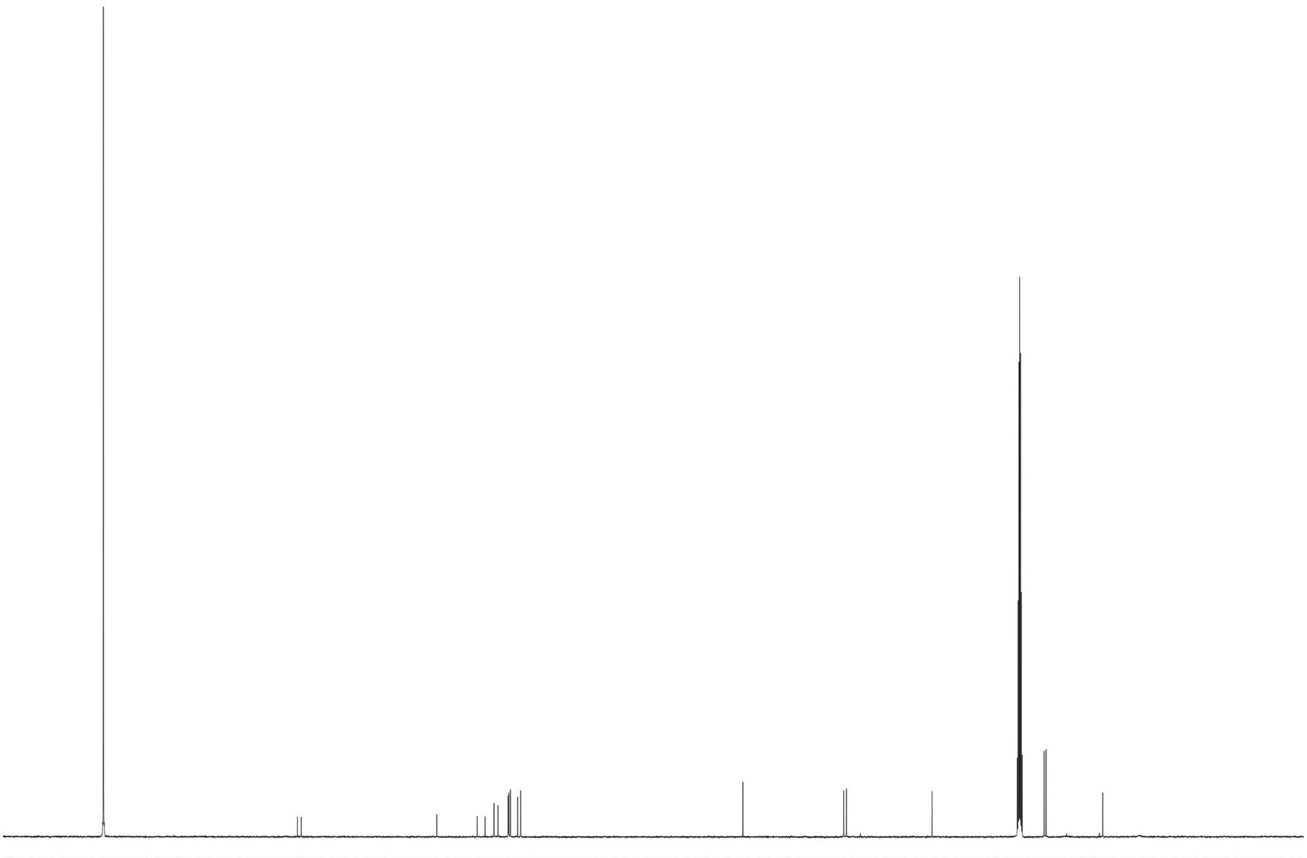


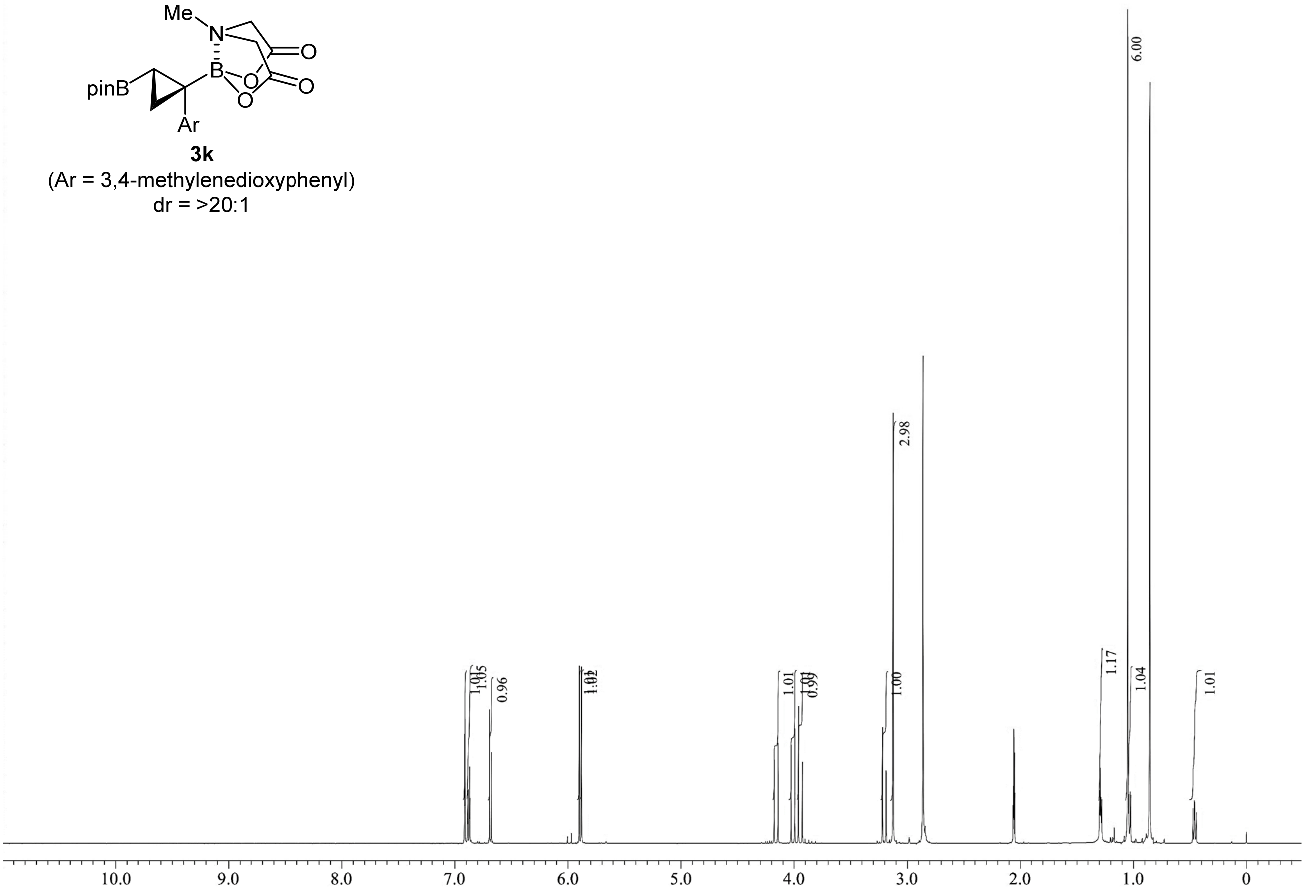
**3i**
(Ar = 4-FC$_6$H$_4$)
dr = >20:1



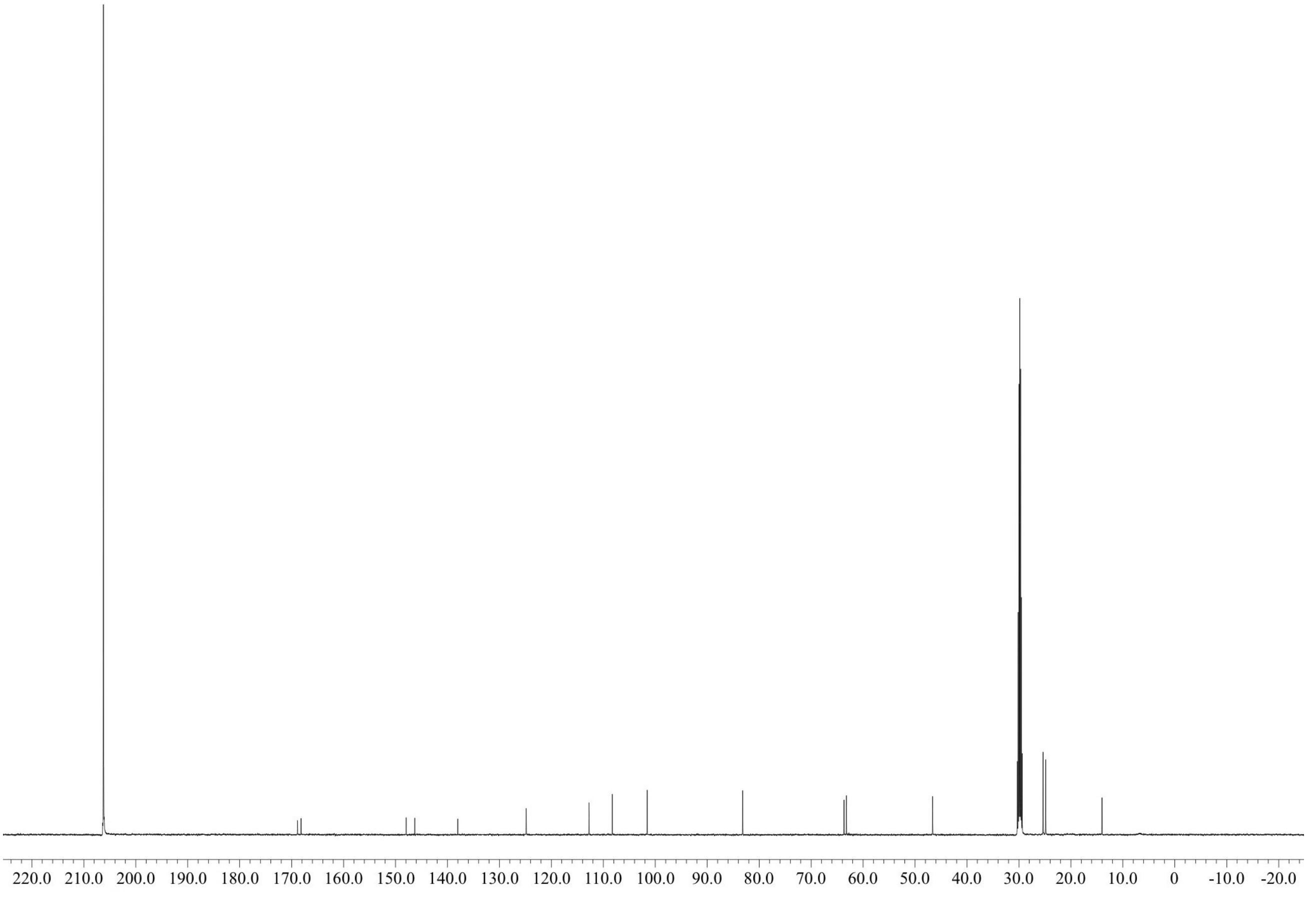


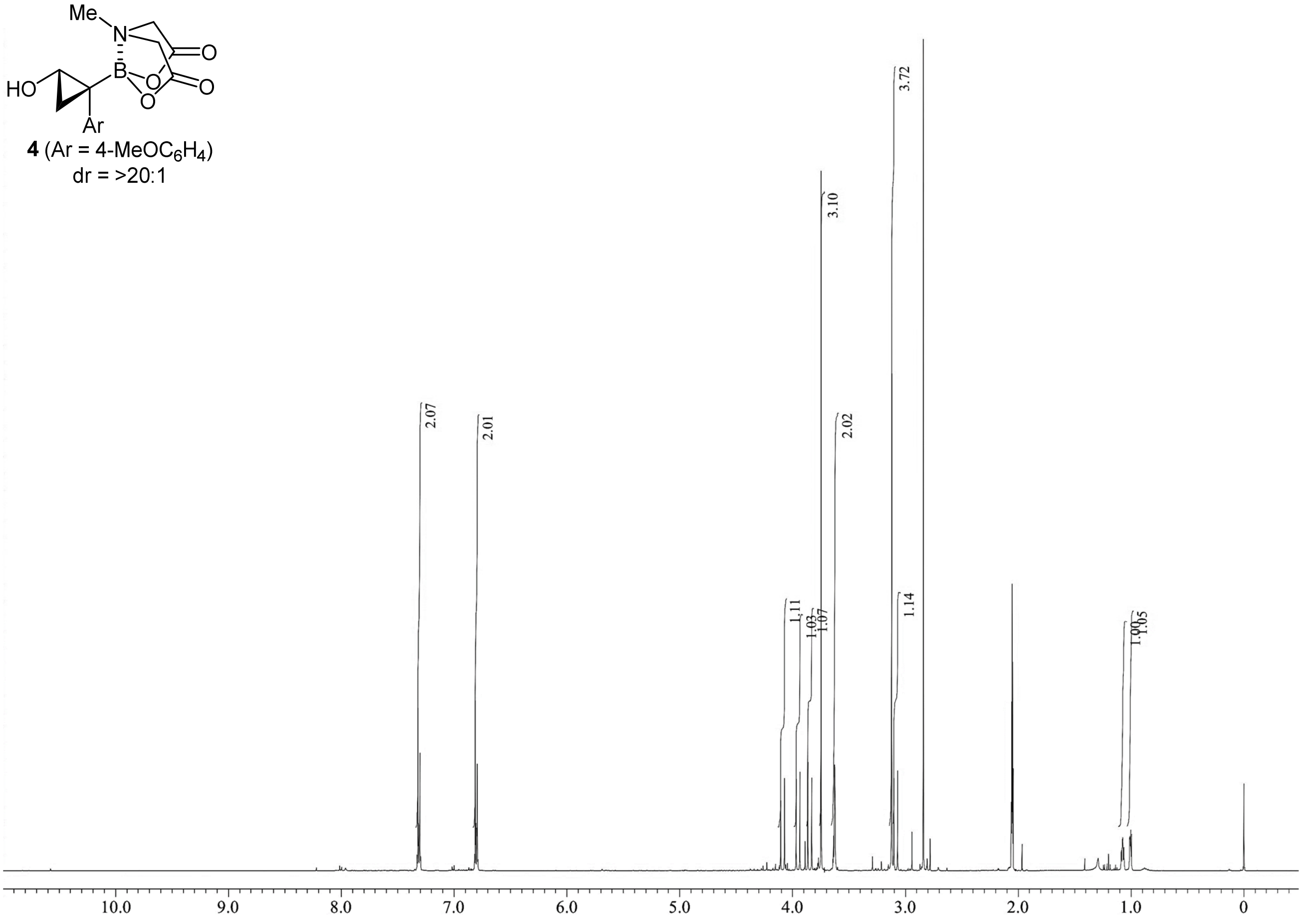
**3j**
(Ar = 2-naphthyl)
dr = >20:1





**3k**
(Ar = 3,4-methylenedioxyphenyl)
dr = >20:1





**4** (Ar = 4-MeOC$_6$H$_4$)
dr = >20:1