Electronic Supplementary Information

Main group metal-ligand cooperation of N-heterocyclic germylene:

An efficient catalyst for hydroboration of carbonyl compounds

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Table S1. Crystal data and structure refinement details for compound M

	M·0.5*n*hexane
CCDC	1502097
empirical formula	$C_{39}H_{53}GeN_2O$
formula weight	638.42
temp, K	100.01(10)
cryst syst	Triclinic
space group	*P*-1
a, Å	10.7269(6)
b, Å	11.2060(8)
c, Å	14.4819(9)
α, deg	86.134(5)
β, deg	88.938(5)
γ, deg	81.551(6)
V, Å^3	1717.92(19)
Z	2
D_{calcd}, g/cm^3	1.234
μ, mm^{-1}	1.441
F(000)	682.0
θ range, deg	4.00 – 72.16
index range	$-10 \le h \le 12$
	$-13 \le k \le 13$
	$-17 \le l \le 14$
reflns collected/unique	11983 / 6542 [R(int) = 0.0776]
data/restraints/param	6542/0/406
GOF on F^2	1.080
final R indices	R1 = 0.0618,
[I >2σ(I)]	wR2 = 0.1661
R indices (all data)	R1 = 0.0734,
	wR2 = 0.1970
largest diff peak/hole,e/Å^3	0.97/-1.49

General information

All manipulations were carried out on a Schlenk line or in an argon atmosphere glovebox. Solvents were dried by refluxing with sodium benzophenone under N_2, distilled, and stored over 3 Å sieves. *N*-Heterocyclic ylide-like germylene was prepared using literature methods.[S1] Unless otherwise stated, commercial reagents were used without further purification. IR spectra were recorded on a Nicolet 330 spectrometer. ^{1}H, ^{11}B and ^{13}C NMR spectra were recorded on a Bruker AV-500M or a Bruker AV-400M spectrometer. ^{1}H and ^{13}C NMR spectroscopic chemical shifts were given relative to residual solvent peaks. The diffraction data were collected on an Agilent SuperNova X-Ray single crystal diffractometer using Mo Kα (λ = 0.710 73 Å) micro-focus X-ray sources at 100 K. The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS-97 and SHELXL-97[S2] within OLEX2.[S3]

Reference

S1. M. Driess, S. Yao, M. Brym, C. van Wüllen, *Angew. Chem. Int. Ed.* **2006**, *45*, 4349-4352.

S2. G. M. Sheldrick, *Acta Crystallographica Section A* **2008**, *64*, 112-122.

S3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.

Experimental section

*Synthesis of **M***:

At -78 °C, a solution of PhCHO (0.106 g, 1 mmol) in toluene (10 mL) was added slowly to a solution of N-heterocyclic germylene **L** (0.489 g, 1 mmol) in toluene (25 mL). The mixture was stirred and slowly warmed to room temperature under nitrogen. After stirring for additional 4 h, the solvent was removed and the residues were extracted with ^{n}hexane (2 × 5 mL). The residual pale yellow crystalline solid was proved to be **M** (0.547 g, 92 %). The solution of **M** in ^{n}hexane was stored at -20 °C for additional 12 h, and yellow block crystals of **M** suitable for X-ray test were obtained. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.33-7.32 (m, 2H, Ar*H*), 6.99-6.96 (m, 3H, Ar*H*), 6.92-6.89 (m, 2H, Ar*H*), 6.79-6.71 (m, 4H, Ar*H*), 5.87 (s, 1H, GeOC*H*, 3.84, (s, 1H, γ-*H*), 3.65 (sept, *J* = 6.9 Hz, 1H, overlapped, C*H*Me$_2$), 3.62 (s, 1H, overlapped, NCC*H*$_2$), 3.27 (sept, *J* = 6.5 Hz, 1H, C*H*Me$_2$), 3.19 (sept, *J* = 6.9 Hz, 1H, overlapped, C*H*Me$_2$), 3.19 (s, 1H, overlapped, NCC*H*$_2$), 2.79 (sept, *J* = 6.7 Hz, 1H, C*H*Me$_2$), 1.15 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$), 1.12 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 1.08 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$), 1.06 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$), 0.98 (d, *J* = 6.7 Hz, 3H, CH*Me*$_2$), 0.94 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$), 0.87 (s, 6H, β-*Me*), 0.68 (d, *J* = 6.7 Hz, 3H, CH*Me*$_2$), 0.58 (d, *J* = 6.7 Hz, 3H, CH*Me*$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 182.77 (*C*=N), 149.61, 147.66, 147.24, 143.24, 140.59, 139.76, 139.50, 139.09, 127.451 126.01, 125.89, 125.05, 124.29, 124.00, 123.38, 123.03 (*Ar*), 79.35 (GeO*C*H), 78.19 (NC*C*H$_2$), 61.29 (γ-*C*H), 27.77, 27.68, 27.18, 27.04, 25.33, 25.28, 24.81 (CH*Me*$_2$), 24.38 (β-*Me*), 24.31, 24.00, 23.61, 23.39 (CH*Me*$_2$). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2724.1, 1625.7, 1601.4, 1536.5, 1467.6, 1380.5, 1364.3, 1319.7, 1301.5, 1252.9, 1224.5, 1169.8, 1052.3, 1026.0, 932.8, 906.5, 868.0, 793.0, 770.74, 754.5, 716.0, 703.9. HRMS (ESI): m/z calcd for $C_{13}H_{47}GeN_2O$: 596.4150 $[(M+H)]^+$; found: 596.4155

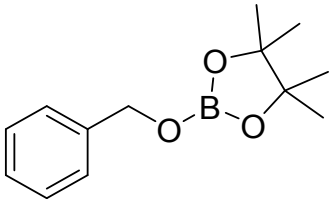
General Catalytic Procedures for the Hydroboration of Aldehydes and Ketones:

In an argon atmosphere glovebox, aldehyde or ketones (0.50 mmol), HBpin (0.52 mmol) were loaded in a dried NMR tube, N-heterocyclic germylene **L** (0.4 mL of 0.025M of **L** in C_6D_6, 0.01 mmol) was added in slowly in room temperature. The tube was sealed securely before being brought outside of the glove box, shaken and monitored by NMR spectroscopy. The products were isolated by removing volatiles under vacuum for more than 4 hours.

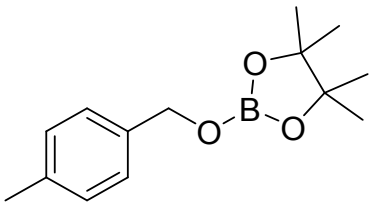
*Hydrolysis of the boronate ester **4j**:*

The crude product of **4j** was dissolved in 10 mL CH_2Cl_2 and washed with 1M HCl (3 × 5 mL). The aqueous phase was extract with CH_2Cl_2 (3 × 10 mL). The combined organic phase was dried with $MgSO_4$. After remove the solvent, and the residue was purified by silica gel column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the hydrolysis product **5j**.

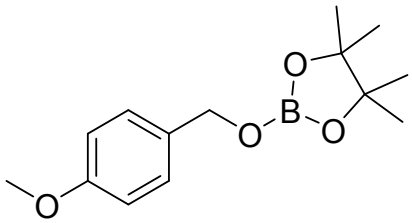
Spectral Data



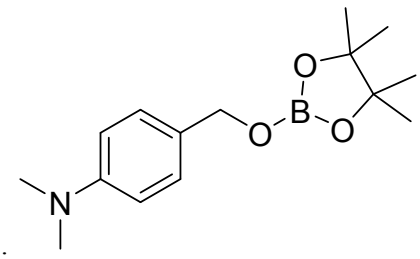
2a *(CAS 95843-98-4)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.28 (m, 2H, Ar*H*), 7.12 (m, 2H, Ar*H*), 7.04 (m, 1H, Ar*H*), 4.92 (s, 2H, OCH_2), 1.03 (s, 12H, CH_3). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 139.95, 128.52, 127.52, 126.97 (*Ar*), 82.72 (*C*$(CH_3)_2$), 66.86 (O*C*H_2), 24.63 (C(*C*$H_3)_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.77. HRMS (ESI): m/z calcd for $C_{13}H_{19}BNaO_3$: 257.1325 $[(M+Na)]^+$; found: 257.1328.



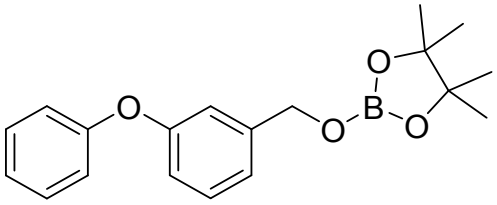
2b *(CAS 1143018-79-4)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 6.98 (d, *J* = 7.8 Hz, 2H, Ar*H*), 6.71 (d, *J* = 7.8 Hz, 2H, Ar*H*), 4.67 (s, 2H, OCH_2), 1.84 (s, 3H, ArCH_3), 0.80 (s, 12H, C(C$H_3)_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 137.08, 136.90, 129.22, 127.18 (*Ar*), 82.64 (*C*$(CH_3)_2$), 66.82 (O*C*H_2), 29.66 (C(*C*$H_3)_2$), 21.06 (Ar*C*H_3). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.74. HRMS (ESI): m/z calcd for $C_{14}H_{21}BNaO_3$: 271.1481 $[(M+Na)]^+$; found: 271.1487.



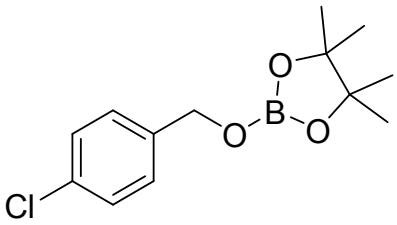
2c *(CAS 1143018-81-8)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 6.99 (d, *J* = 8.5 Hz, 2H, Ar*H*), 6.50 (d, *J* = 8.5 Hz, 2H, Ar*H*), 4.65 (s, 2H, OCH_2), 3.09 (s, 2H, OCH_3), 0.81 (s, 12H, C(C$H_3)_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 159.58, 132.04, 128.80, 114.01 (*Ar*), 82.66 (*C*$(CH_3)_2$), 66.68 (O*C*H_2), 54.77 (O*C*H_3), 24.64 (C(*C*$H_3)_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.66. HRMS (ESI): m/z calcd for $C_{14}H_{21}BNaO_4$: 287.1431 $[(M+Na)]^+$; found: 287.1439.



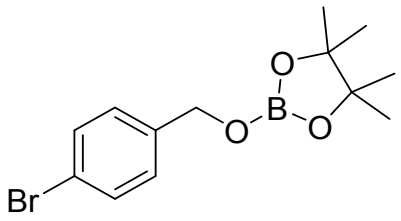
2d *(CAS 1644292-20-5)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.05 (d, *J* = 8.6 Hz, 2H, Ar*H*), 6.31 (d, *J* = 8.6 Hz, 2H, Ar*H*), 4.71 (s, 2H, OCH_2), 2.29 (s, 2H, N(CH_3)$_2$), 0.83 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 150.46, 128.86, 127.85, 112.66 (*Ar*), 82.48 (*C*(CH$_3$)$_2$), 67.12 (O*C*H$_2$), 40.26 (N(*C*H$_3$)$_2$), 24.72 (C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.71. HRMS (ESI): m/z calcd for $C_{15}H_{24}BNNaO_3$: 300.1747 [(M+Na)]$^+$; found: 300.1751.



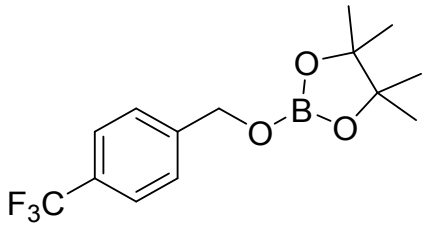
2e *(New Compound)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.11-7.01 (m, 5H, Ar*H*), 6.92-6.81 (m, 4H, Ar*H*), 4.83 (s, 2H, OCH_2), 1.02 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 157.86, 157.79, 142.13, 129.98, 123.31, 121.76, 119.17, 118.15, 117.55 (*Ar*), 82.79 (*C*(CH$_3$)$_2$), 66.45 (O*C*H$_2$), 24.62 (C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.78. HRMS (ESI): m/z calcd for $C_{19}H_{23}BNaO_4$: 349.1587 [(M+Na)]$^+$; found: 349.1590.



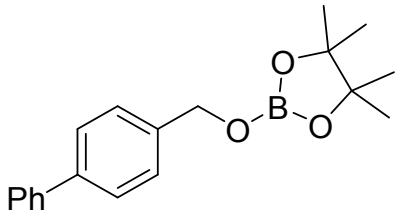
2f *(CAS 1143018-85-2)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 6.82 (d, *J* = 8.2 Hz, 2H, Ar*H*), 6.76 (d, *J* = 8.2 Hz, 2H, Ar*H*), 4.50 (s, 2H, OCH_2), 0.79 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ139.01, 133.87, 129.26, 128.97 (*Ar*), 83.48 (*C*(CH$_3$)$_2$), 66.63 (O*C*H$_2$), 25.23 (C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.66. HRMS (ESI): m/z calcd for $C_{13}H_{18}BClNaO_3$: 291.0935 [(M+Na)]$^+$; found: 291.0942.



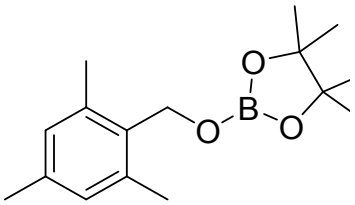
2g *(CAS 1566593-61-0)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 6.97 (d, *J* = 8.1 Hz, 2H, Ar*H*), 6.70 (d, *J* = 8.1 Hz, 2H, Ar*H*), 4.48 (s, 2H, OCH_2), 0.79 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 138.87, 131.60, 128.65, 121.39 (*Ar*), 82.83 (*C*(CH$_3$)$_2$), 66.03 (O*C*H$_2$), 24.64 (C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.65. HRMS (ESI): m/z calcd for $C_{13}H_{18}BBrNaO_3$: 335.0430 $[(M+Na)]^+$; found: 335.0439.



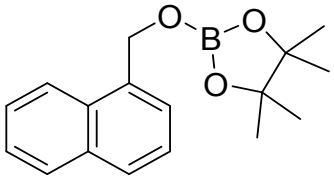
2h *(New Compound)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.08 (d, *J* = 8.1 Hz, 2H, Ar*H*), 6.88 (d, *J* = 8.1 Hz, 2H, Ar*H*), 4.54 (s, 2H, OCH_2), 0.81 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 143.92 (*Ar*), 129.53 (q, $J_{C\text{-}F}$ = 32.2 Hz, *Ar*), 126.86 (*Ar*), 125.39 (q, $J_{C\text{-}F}$ = 3.7 Hz, *Ar*), 124.94 (q, $J_{C\text{-}F}$ = 270.6 Hz, *C*F$_3$), 82.01 (*C*(CH$_3$)$_2$), 65.95 (O*C*H$_2$), 24.56 (C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.69. HRMS (ESI): m/z calcd for $C_{14}H_{18}BF_3NaO_3$: 325.1199 $[(M+Na)]^+$; found: 325.1198.



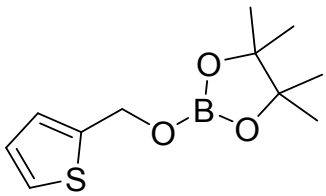
2i *(New Compound)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.42 (t, *J* = 6.7 Hz, 4H, Ar*H*), 7.35 (d, *J* = 7.9 Hz, 2H, Ar*H*), 7.21 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.13 (t, *J* = 7.3 Hz, 1H, Ar*H*), 4.99 (s, 2H, OCH_2), 1.06 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 141.31, 140.62, 138.98, 128.97, 128.19, 127.81, 127.52, 127.35 (*Ar*), 82.77 (*C*(CH$_3$)$_2$), 66.67 (O*C*H$_2$), 24.67 (C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.86. HRMS (ESI): m/z calcd for $C_{19}H_{23}BNaO_3$: 330.1638 $[(M+Na)]^+$; found: 330.1643.



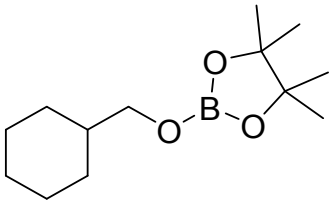
2j *(CAS 1373393-11-3)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 6.70 (s, 2H, Ar*H*), 4.98 (s, 2H, OCH_2), 2.34 (s, 6H, 2,6-Ar(CH_3)$_2$), 2.10 (s, 3H, 4-ArCH_3), 1.03 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 138.31, 137.94, 133.50, 129.89 (*Ar*), 83.11 (*C*(CH$_3$)$_2$), 62.05 (O*C*H$_2$), 25.26 (C(*C*H$_3$)$_2$), 21.63 (4-Ar*C*H$_3$), 20.19 (2,6-Ar(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.56. HRMS (ESI): m/z calcd for $C_{16}H_{25}BNaO_3$: 299.1794 [(M+Na)]$^+$; found: 299.1798.



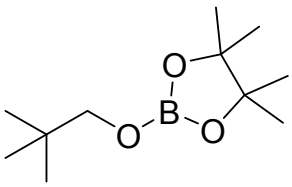
2k *(CAS 1937219-09-4)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.93-7.91 (m, 1H, Ar*H*), 7.62-7.61 (m, 2H, Ar*H*), 7.56-7.54 (m, 1H, Ar*H*), 7.24-7.21 (m, 3H, Ar*H*), 5.40 (s, 2H, OCH_2), 1.03 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 135.35, 134.07, 131.44, 128.82, 128.40, 126.26, 125.83, 125.60, 124.99, 123.77 (*Ar*), 82.76 (*C*(CH$_3$)$_2$), 65.26 (O*C*H$_2$), 24.65 (C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.79. HRMS (ESI): m/z calcd for $C_{17}H_{22}BNaO_3$: 307.1481 [(M+Na)]$^+$; found: 307.1473.



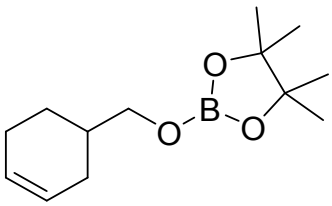
2l *(CAS 1811523-11-1)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 6.65-6.64 (m, 1H, Ar*H*), 6.58-6.57 (m, 1H, Ar*H*), 6.45-6.44 (m, 1H, Ar*H*), 4.74 (s, 2H, OCH_2), 0.80 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 142.64, 126.74, 126.06, 125.64 (*Ar*), 82.91 (*C*(CH$_3$)$_2$), 61.74 (O*C*H$_2$), 24.63 (C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.66. HRMS (ESI): m/z calcd for $C_{11}H_{17}BNaO_3S$: 263.0889 [(M+Na)]$^+$; found: 263.0889.



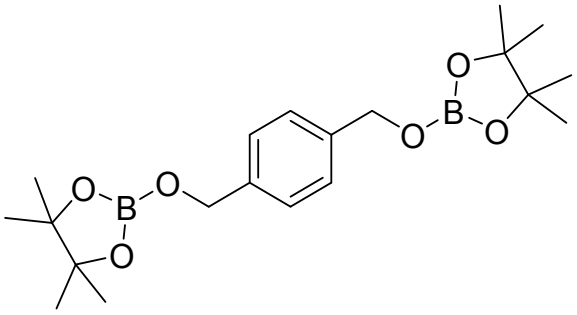
2m *(CAS 1566593-62-1)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 3.74 (d, *J* = 6.8 Hz, 2H, OCH_2), 1.71-1.58 (m, 4H, C_6H_{11}), 1.55-1.47 (m, 2H, C_6H_{11}), 1.15-1.01 (m, 3H, overlapped, C_6H_{11}), 1.07 (s, 12H, overlapped, C(CH_3)$_2$), 0.93-0.88 (m, 2H, C_6H_{11}). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 82.29 (*C*(CH$_3$)$_2$), 70.51 (O*C*H$_2$), 39.79, 29.67, 26.83, 26.11 (*C*$_6$H$_{11}$), 24.70 (C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.46. HRMS (ESI): m/z calcd for $C_{13}H_{25}BNaO_3$: 263.1794 [(M+Na)]$^+$; found: 263.1791.



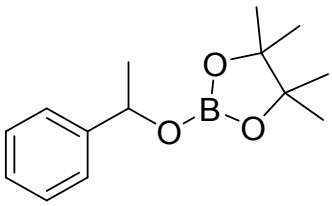
2n *(CAS 821008-74-6)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 3.37 (s, 2H, OCH_2), 0.86 (s, 12H, C(CH_3)$_2$), 0.66 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 82.33 (*C*(CH$_3$)$_2$), 74.99 (O*C*H$_2$), 32.47 (*C*(CH$_3$)$_3$), 26.18 (C(*C*H$_3$)$_3$), 24.68 (C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.46. HRMS (ESI): m/z calcd for $C_{11}H_{23}BNaO_3$: 237.1638 [(M+Na)]$^+$; found: 237.1639.



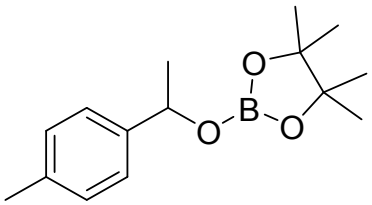
2o *(New Compound)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 5.39-5.34 (m, 2H, C*H*=C*H*), 3.58-3.52 (m, 2H, CH_2O), 1.80-1.45 (m, 6H, OCH_2), 1.04-0.96 (m, 1H, OCH$_2$C*H*), 0.83 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 127.12, 126.19 (*C*H=*C*H), 82.37 (*C*(CH$_3$)$_2$), 69.63 (O*C*H$_2$), 35.71 (OCH$_2$*C*H), 28.24, 25.47, 24.85 (*C*H$_2$), 24.69 (C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.48. HRMS (ESI): m/z calcd for $C_{13}H_{24}BO_3$: 239.1819 [(M+H)]$^+$; found: 239.1824.



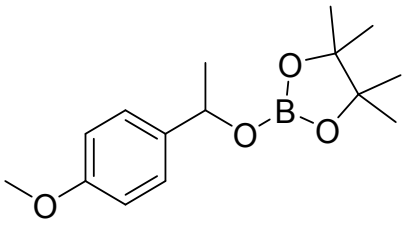
2p *(CAS 1373393-10-2)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.25 (s, *4*H, Ar*H*), 4.90 (s, 4H, OCH_2), 1.03 (s, 24H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 139.08, 127.06 (*Ar*), 82.68 (*C*(CH$_3$)$_2$), 66.70 (O*C*H$_2$), 24.64 (C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.74. HRMS (ESI): m/z calcd for $C_{20}H_{32}B_2NaO_6$: 413.2283 $[(M+H)]^+$; found: 413.2291.



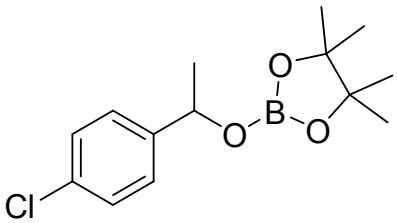
4a *(CAS 1143018-72-7)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.35 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.13 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.04 (t, *J* = 7.4 Hz, 1H, Ar*H*), 5.40 (q, *J* = 6.5 Hz, 1H, OC*H*), 1.44 (d, *J* = 6.5 Hz, 3H, OCHCH_3), 1.01 (d, *J* = 13.3 Hz, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 145.32, 128.48, 127.29, 125.63 (*Ar*), 82.49 (*C*(CH$_3$)$_2$), 72.89 (O*C*H), 25.73 (OCH*C*H$_3$), 24.58 (d, *J* = 10.1 Hz, C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.56. HRMS (ESI): m/z calcd for $C_{14}H_{21}BNaO_3$: 271.1481 $[(M+Na)]^+$; found: 271.1486.



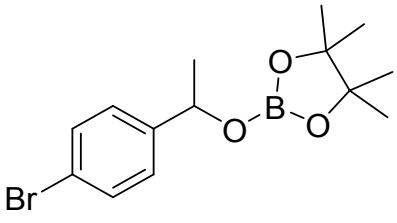
4b *(CAS 1416719-04-4)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.30 (d, *J* = 7.9 Hz, 2H, Ar*H*), 6.97 (d, *J* = 7.9 Hz, 2H, Ar*H*), 5.42 (q, *J* = 6.4 Hz, 1H, OC*H*), 2.09 (s, 3H, ArCH_3), 1.48 (d, *J* = 6.5 Hz, 3H, OCHCH_3), 1.02 (d, *J* = 11.5 Hz, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 142.47, 136.58, 29.16, 125.65 (*Ar*), 82.44 (*C*(CH$_3$)$_2$), 72.80 (O*C*H), 25.76 (OCH*C*H$_3$), 24.60 (d, *J* = 9.2 Hz, C(*C*H$_3$)$_2$), 21.01 (Ar*C*H$_3$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.53. HRMS (ESI): m/z calcd for $C_{15}H_{23}BNaO_3$: 285.1638 $[(M+Na)]^+$; found: 285.1635.



4c *(CAS 1566593-64-3)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.29 (d, *J* = 8.7 Hz, 2H, Ar*H*), 6.75 (d, *J* = 8.7 Hz, 2H, Ar*H*), 5.39 (q, *J* = 6.4 Hz, 1H, OC*H*), 3.30 (s, 3H, OCH_3), 1.47 (d, *J* = 6.5 Hz, 3H, OCHCH_3), 1.02 (d, *J* = 10.4 Hz, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 159.01, 137.11, 126.60, 113.62 (*Ar*), 82.11 (*C*(CH$_3$)$_2$), 72.26 (O*C*H), 54.41 (O*C*H$_3$), 25.37 (OCH*C*H$_3$), 24.29 (d, *J* = 11.0 Hz, C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.51. HRMS (ESI): m/z calcd for $C_{15}H_{23}BNaO_4$: 301.1587 $[(M+Na)]^+$; 301.1589.

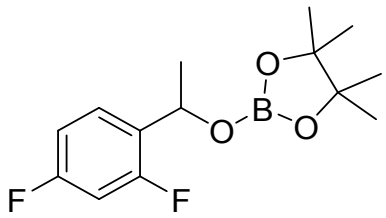


4d *(CAS 1416719-03-3)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.09-7.05 (m, 4H, Ar*H*), 5.24 (q, *J* = 6.5 Hz, 1H, OC*H*), 1.33 (d, *J* = 6.5 Hz, 3H, OCHCH_3), 1.00 (d, *J* = 13.7 Hz, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 143.74, 133.00, 128.61, 127.09 (*Ar*), 82.62 (*C*(CH$_3$)$_2$), 72.15 (O*C*H), 25.50 (OCH*C*H$_3$), 24.57 (d, *J* = 8.9 Hz, C(*C*H$_3$)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.46. HRMS (ESI): m/z calcd for $C_{14}H_{20}BClNaO_3$: 305.1092 $[(M+Na)]^+$; found: 305.1097.

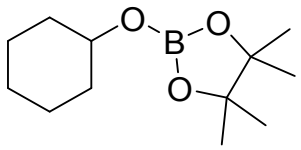


4e *(New Compound)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.23 (d, *J* = 8.4 Hz, 2H, Ar*H*), 6.99 (d, *J* = 8.4 Hz, 2H, Ar*H*), 5.21 (q, *J* = 6.4 Hz, 1H, OC*H*), 1.32 (d, *J* = 6.5 Hz, 3H, OCHCH_3), 1.00 (d, *J* = 13.9 Hz, 12H, C(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 144.22, 131.57, 127.43, 121.13 (*Ar*), 82.61 (*C*(CH$_3$)$_2$),

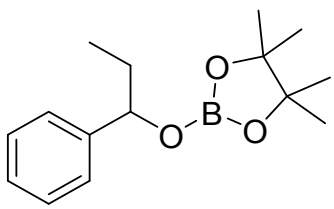
72.17 (O*C*H), 25.46 (OCH*C*H_3), 24.58 (d, J = 8.2 Hz, C(*C*H_3)$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.43. HRMS (ESI): m/z calcd for $C_{14}H_{20}BBrNaO_3$: 349.0587 [(M+Na)]$^+$; found: 349.0582.



4f *(New Compound)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.14 (q, J = 7.9 Hz, 1H, Ar*H*), 6.31 (td, J = 8.4, 1.8 Hz, 1H, Ar*H*), 6.22 (td, J = 10.9, 2.5 Hz, 1H, Ar*H*), 5.43 (q, J = 6.4 Hz, 1H, OC*H*), 1.15 (d, J = 6.5 Hz, 3H, OCHC*H*$_3$), 0.77 (d, J = 13.4 Hz, 12H, C(C*H*$_3$)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 162.36 (dd, $J_{C\text{-}F}$ = 247.1, 11.9 Hz, *Ar*), 159.48 (dd, $J_{C\text{-}F}$ = 247.9, 11.8 Hz, *Ar*), 128.41 (dd, $J_{C\text{-}F}$ = 13.8, 3.7 Hz, *Ar*), 128.01 (d, $J_{C\text{-}F}$ = 15.4 Hz, *Ar*), 111.38 (dd, $J_{C\text{-}F}$ = 21.0, 3.6 Hz, *Ar*), 103.50 (t, $J_{C\text{-}F}$ = 25.5 Hz, *Ar*), 82.76 (*C*(CH$_3$)$_2$), 66.58 (d, J = 4.2 Hz, O*C*H), 24.52 (d, J = 4.2 Hz, C(*C*H$_3$)$_2$) , 24.41 (OCH*C*H$_3$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.43. HRMS (ESI): m/z calcd for $C_{14}H_{19}BF_2NaO_3$: 307.1293 [(M+Na)]$^+$; found: 307.1296.

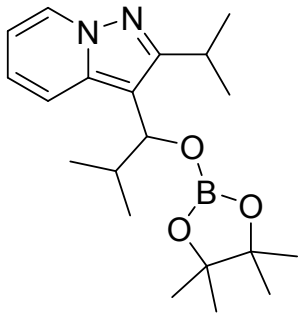


4g *(CAS 96649-78-4)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 4.17 (hept, J = 4.4 Hz, 1H, OC*H*), 1.87-1.85 (m, 2H, C*H*$_2$), 1.62-1.59 (m, 2H, C*H*$_2$), 1.48-1.41 (m, 2H, C*H*$_2$), 1.30-1.27 (m, 1H, C*H*$_2$), 1.16-1.01 (m, 3H, overlapped, C*H*$_2$), 1.07 (d, J = 13.4 Hz, 12H, overlapped, C(C*H*$_3$)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 82.15 (*C*(CH$_3$)$_2$), 72.64 (O*C*H), 34.72, 25.74 (*C*H$_2$), 24.69 (C(*C*H$_3$)$_2$) , 24.06 (*C*H$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.30. HRMS (ESI): m/z calcd for $C_{12}H_{23}BNaO_3$: 249.1638 [(M+Na)]$^+$; found: 249.1637.

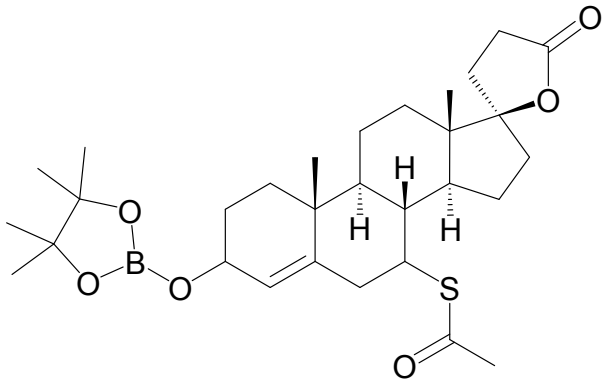


4h *(New Compound)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.34 (d, J = 7.6 Hz, 2H, Ar*H*), 7.14 (t, J = 7.6 Hz, 2H, Ar*H*), 7.05 (t, J = 7.4 Hz, 1H, Ar*H*), 5.19 (dd, J = 7.1, 5.8 Hz, 1H, OC*H*), 1.77 (m, 2H, OCHC*H*$_2$), 1.01 (d, J = 15.5 Hz, 12H, C(C*H*$_3$)$_2$), 0.87 (t, J = 7.4 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6, ppm):

δ 144.09, 128.38, 127.33, 126.21 (*Ar*), 82.47 (*C*(CH_3)$_2$), 78.09 (O*C*H), 32.48 (OCH*C*H_2), 24.56 (d, *J* = 7.6 Hz, C(*C*H_3)$_2$), 10.01 (CH_2*C*H_3). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.59. HRMS (ESI): m/z calcd for $C_{15}H_{23}BNaO_3$: 285.1638 $[(M+Na)]^+$; found: 285.1643.

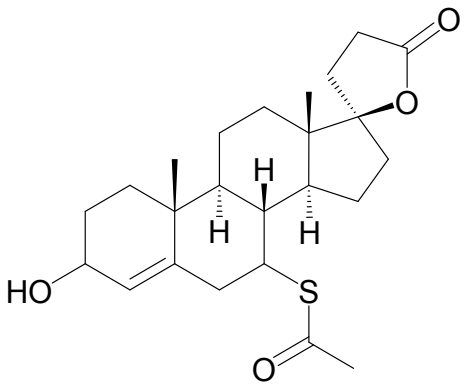


4i *(New Compound)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 8.12 (d, *J* = 6.9 Hz, 1H, Ar*H*), 7.63 (d, *J* = 8.9 Hz, 1H, Ar*H*), 6.53 (dd, *J* = 8.8, 6.8 Hz, 1H, Ar*H*), 6.02 (t, *J* = 6.8 Hz, 1H, Ar*H*), 5.24 (d, *J* = 8.3 Hz, 1H, O*CH*), 3.38 (hept, *J* = 6.9 Hz, 1H, ArC*H*Me_2), 2.30-2.23 (m, 1H, OCHC*H*Me_2), 1.58 (dd, *J* = 13.9, 6.9 Hz, 6H, ArCH(CH_3)$_2$), 1.17 (d, *J* = 6.6 Hz, 3H, OCHCH(CH_3)$_2$), 0.96 (d, *J* = 16.5 Hz, 12H, C(CH_3)$_2$), 0.79 (d, *J* = 6.8 Hz, 3H, OCHCH(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 158.80, 138.70, 128.46, 122.08, 118.50, 110.59, 108.80 (*Ar*), 82.37 (*C*(CH_3)$_2$), 75.90 (O*C*H), 35.57 (*C*HMe_2), 27.00 (*C*HMe_2), 24.54 (d, *J* = 25.7 Hz, C(*C*H_3)$_2$), 24.54, 23.74 (CH*Me*$_2$), 19.38 (d, *J* = 3.0 Hz, CH*Me*$_2$). ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.72. HRMS (ESI): m/z calcd for $C_{20}H_{31}BN2NaO_3$: 381.2325 $[(M+Na)]^+$; found: 381.2326.



4j *(New Compound)*: ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 5.30 (br, 1H), 4.66-4.62 (m, 1H), 3.68 (q, *J* = 3.0 Hz, 1H), 2.21-2.18 (m, 1H), 1.87 (dd, *J* = 14.1, 2.3 Hz, 1H), 1.77-1.71 (m, 4H), 1.64 (s, 3H), 1.50-1.40 (m, 2H), 1.30 (td, *J* = 11.0, 3.3 Hz, 1H), 1.23-1.18 (m, 2H), 1.12-1.06 (m, 1H), 0.96-0.87 (m, 5H), 0.82 (d, *J* = 4.7 Hz, 12H), 0.77-0.74 (m, 2H), 0.55 (s, 3H), 0.52 (s, 3H), 0.49-0.39 (m, 2H). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 193.46, 175.19, 142.12, 127.13, 94.53, 82.44, 70.39, 50.05, 46.26, 46.17, 45.55, 39.26,

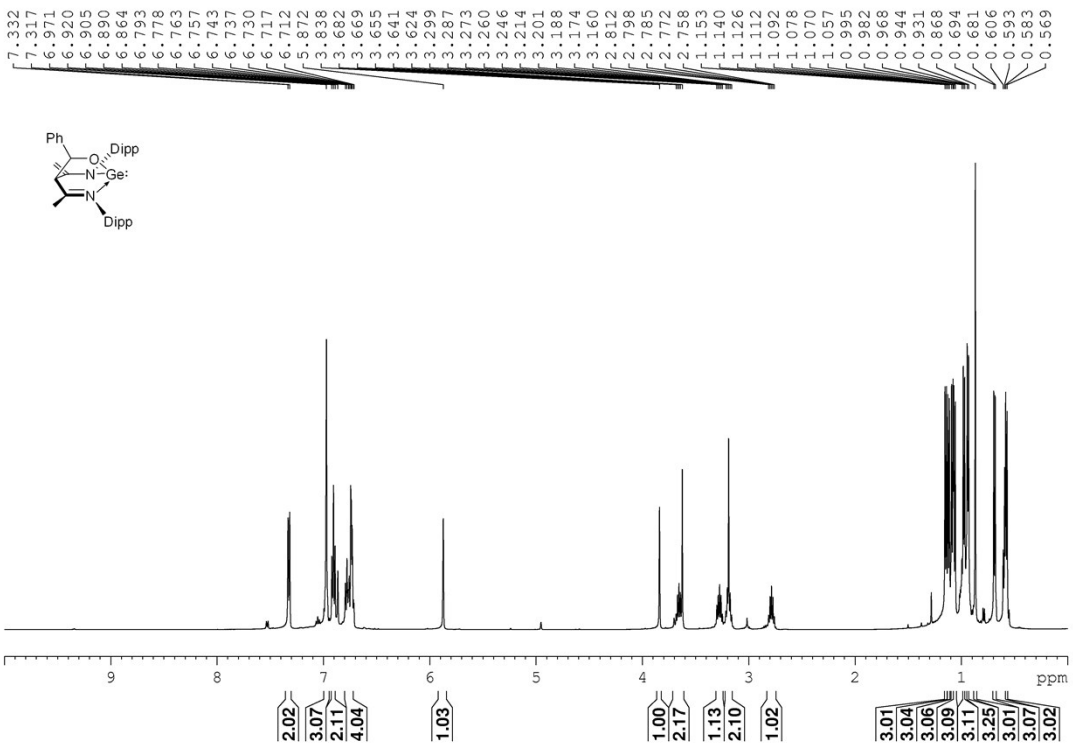
39.19, 37.37, 35.34, 35.33, 31.17, 31.05, 30.81, 29.19, 28.10, 24.65 (d, J = 10.2 Hz), 22.53, 20.42, 18.86, 14.63. ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 22.98. HRMS (ESI): m/z calcd for $C_{30}H_{45}BNaBrO_6S$: 567.2928 $[(M+Na)]^+$; found: 567.2935

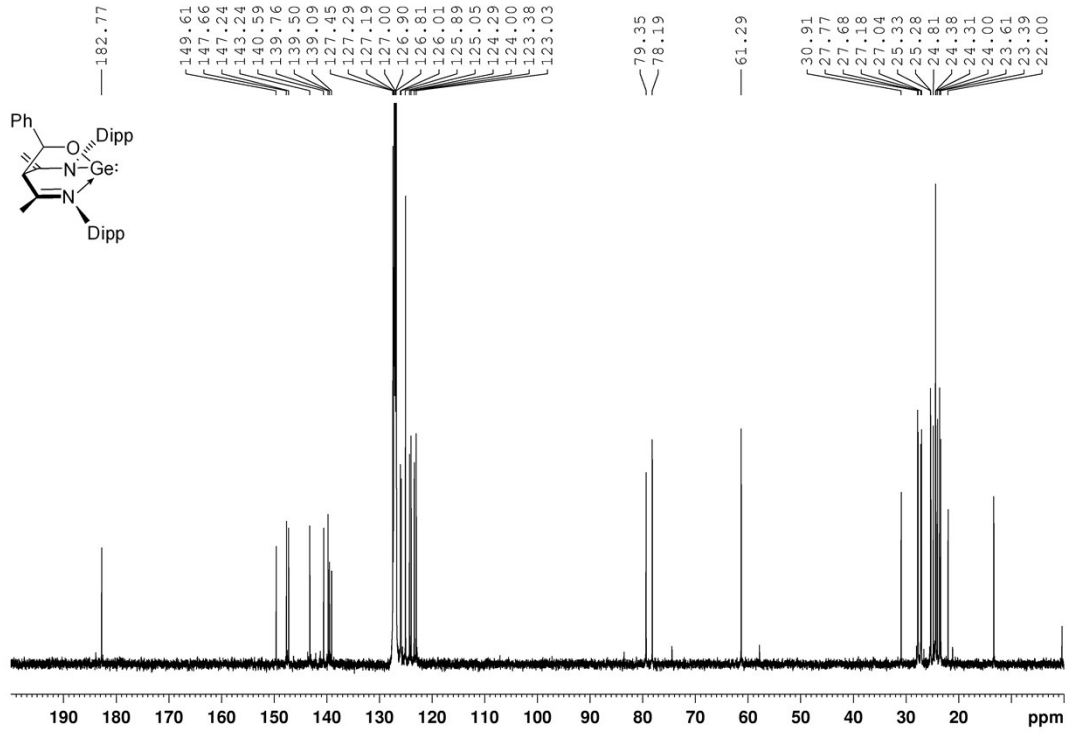


5j *(racemic)* (For reference, see: E. Jones-Mensah, L. A. Nickerson, J. L. Deobald, H. J. Knox, A. B. Ertel, J. Magolan *Tetrahedron,* **2016***, 72(26)*, 3748–3753): ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 5.31 (br, 1H), 4.24-4.21 (m, 1H), 3.93 (q, J = 2.8 Hz, 1H), 2.71-2.67 (m, 1H), 2.58-2.44 (m, 2H), 2.40-2.35 (m, 1H, overlapped), 2.34 (s, 3H, overlapped), 2.24-2.19 (m, 1H), 2.11 (dd, J = 14.2, 2.2 Hz, 1H), 1.96-1.91 (m, 3H), 1.79-1.73 (m, 3H), 1.61-1.35 (m, 8H), 1.30-1.24 (m, 4H), 1.00 (s, 3H), 0.96 (s, 3H), 0.82 (td, J = 11.7, 4.4 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 194.86, 176.74, 141.98, 127.71, 95.78, 67.49, 49.86, 46.04, 45.94, 45.47, 39.19, 39.14, 37.29, 35.25, 35.16, 31.26, 31.18, 31.12, 29.21, 29.06, 22.35, 20.28, 19.05, 14.50. HRMS (ESI): m/z calcd for $C_{24}H_{35}O_4S$: 419.2256 $[(M+H)]^+$; found: 419.2259.

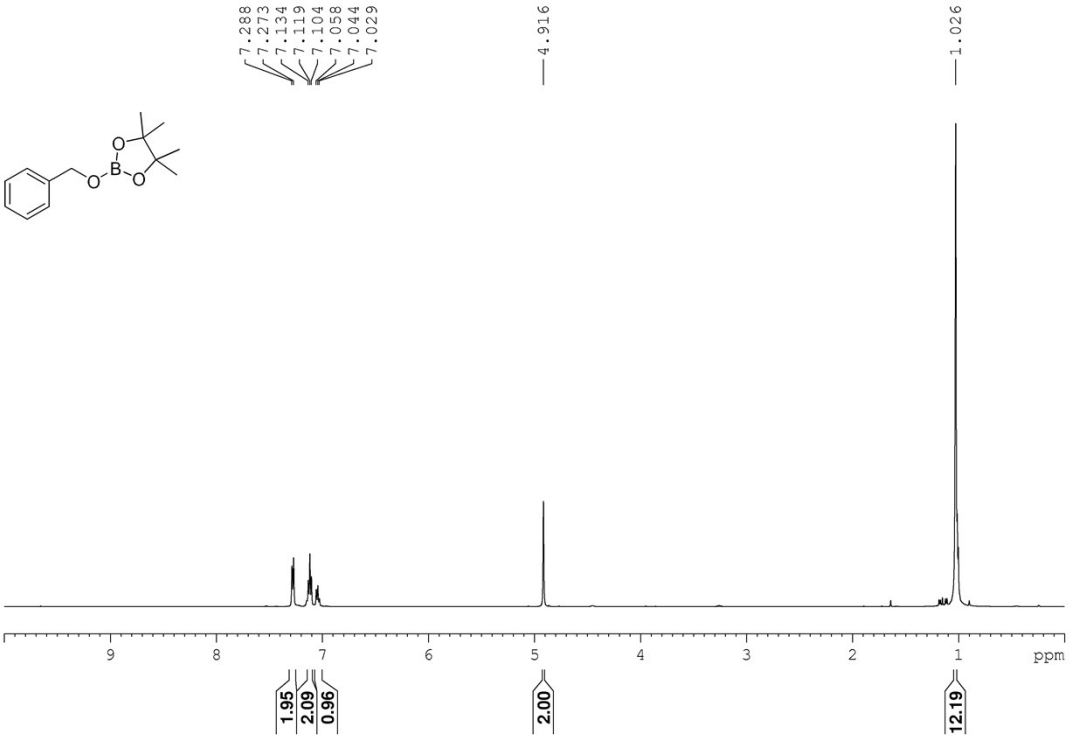
Spectra

Compound M:





2a: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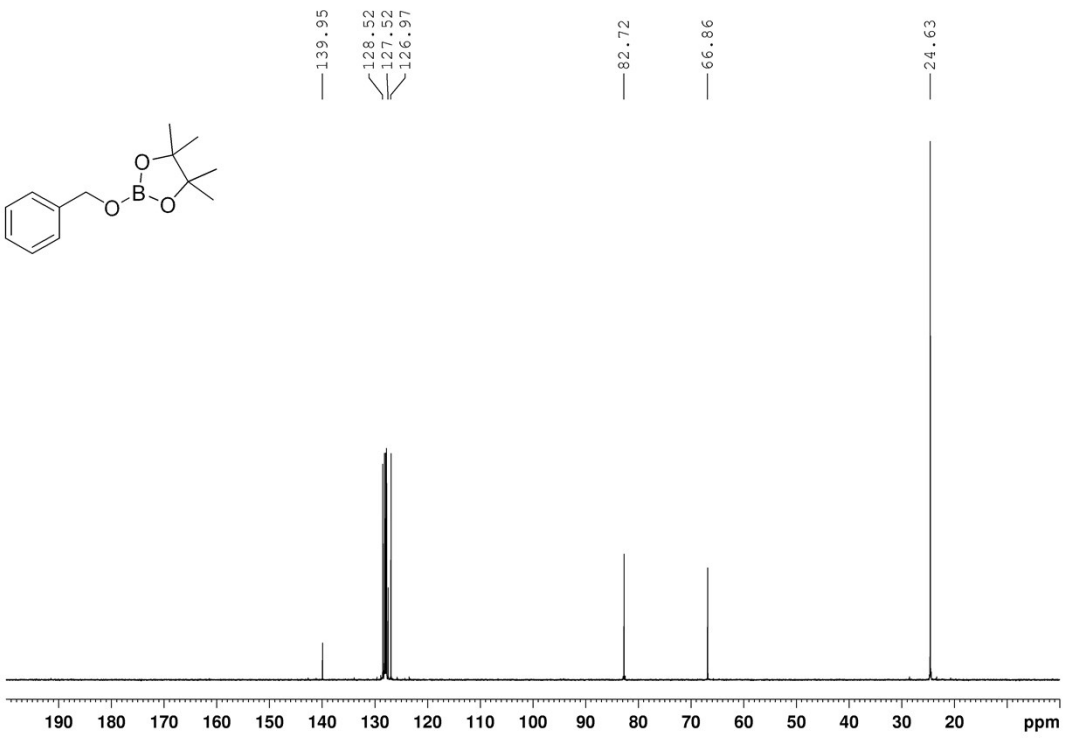
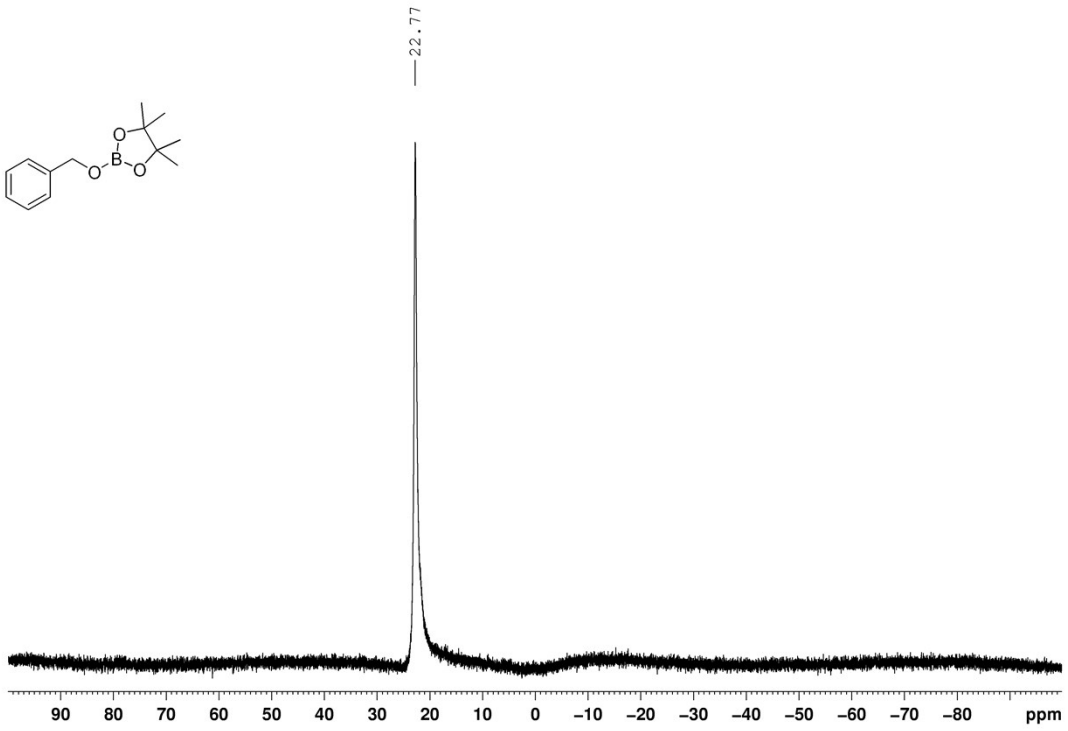
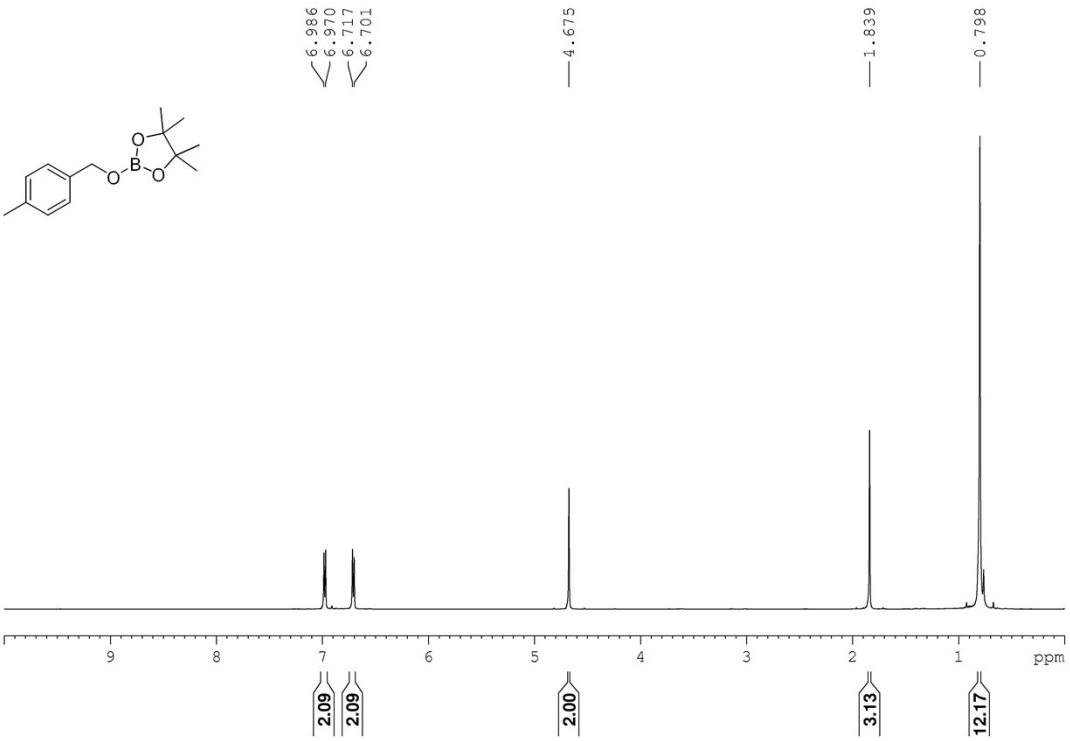
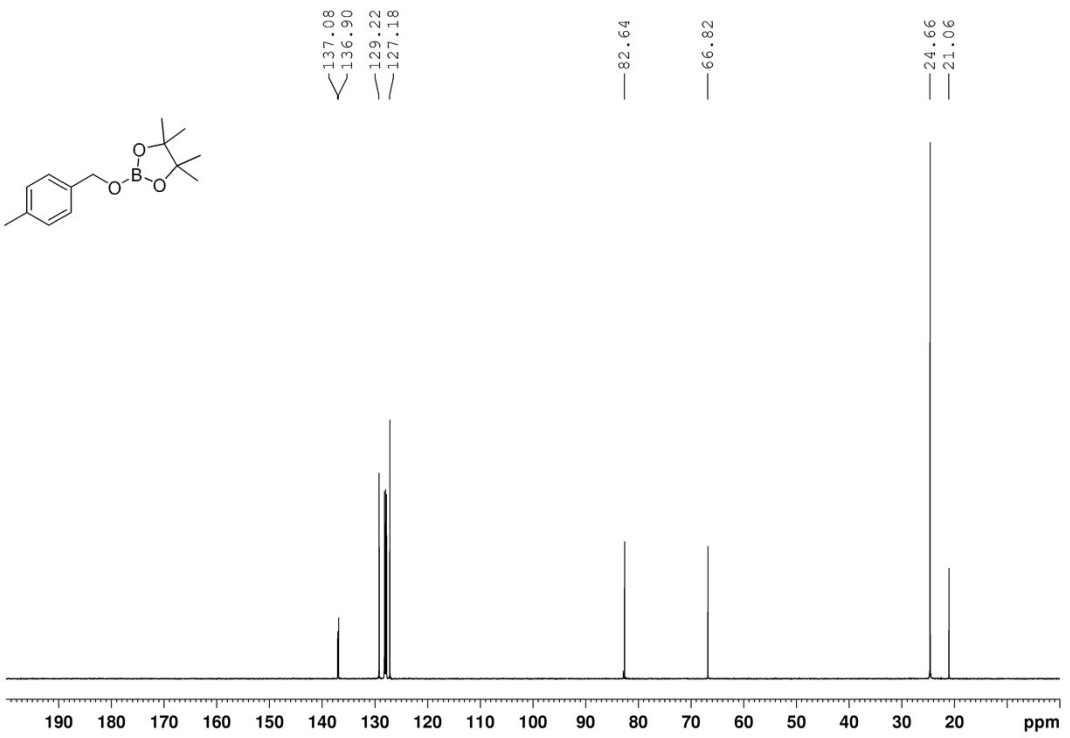
7.273
7.134
7.119
7.104
7.058
7.044
7.029
4.916
1.026
ppm
1.95
2.09
0.96
2.00
12.19


139.95
128.52
127.52
126.97
82.72
66.86
24.63
ppm


22.77
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

2b:


6.986
6.970
6.717
6.701
4.675
1.839
0.798
9
8
7
6
5
4
3
2
1
ppm
2.09
2.09
2.00
3.13
12.17


137.08
136.90
129.22
127.18
82.64
66.82
24.66
21.06
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160
150
140
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120
110
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80
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30
20
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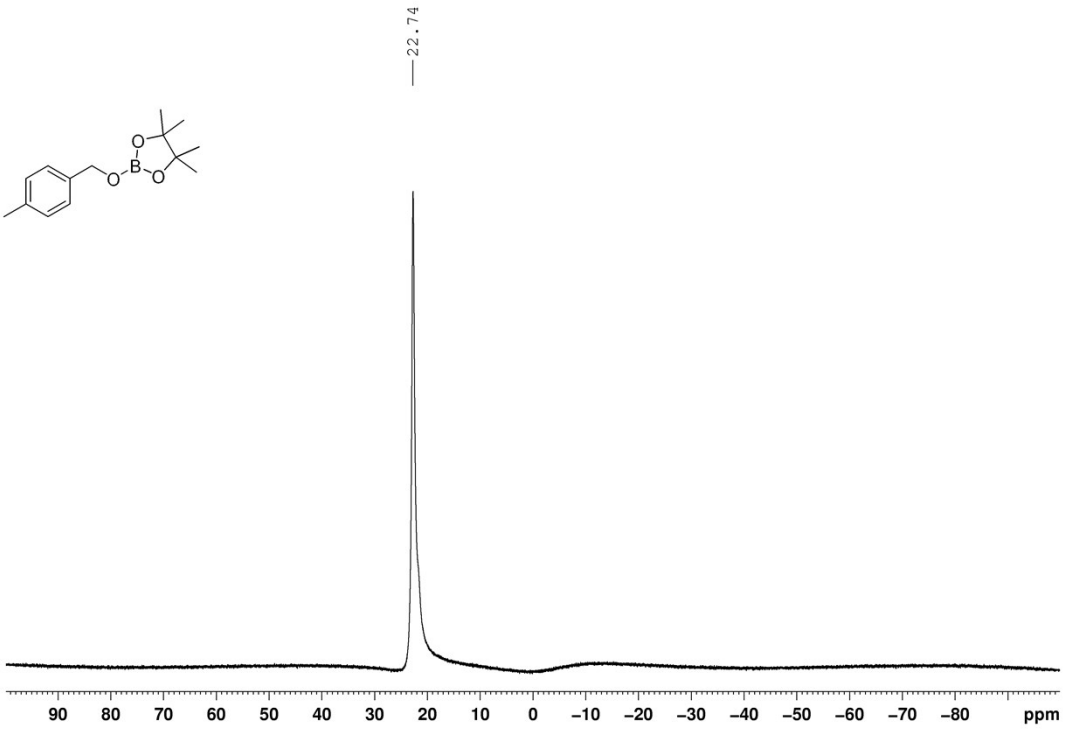
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O
B
O
O
90
80
70
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20
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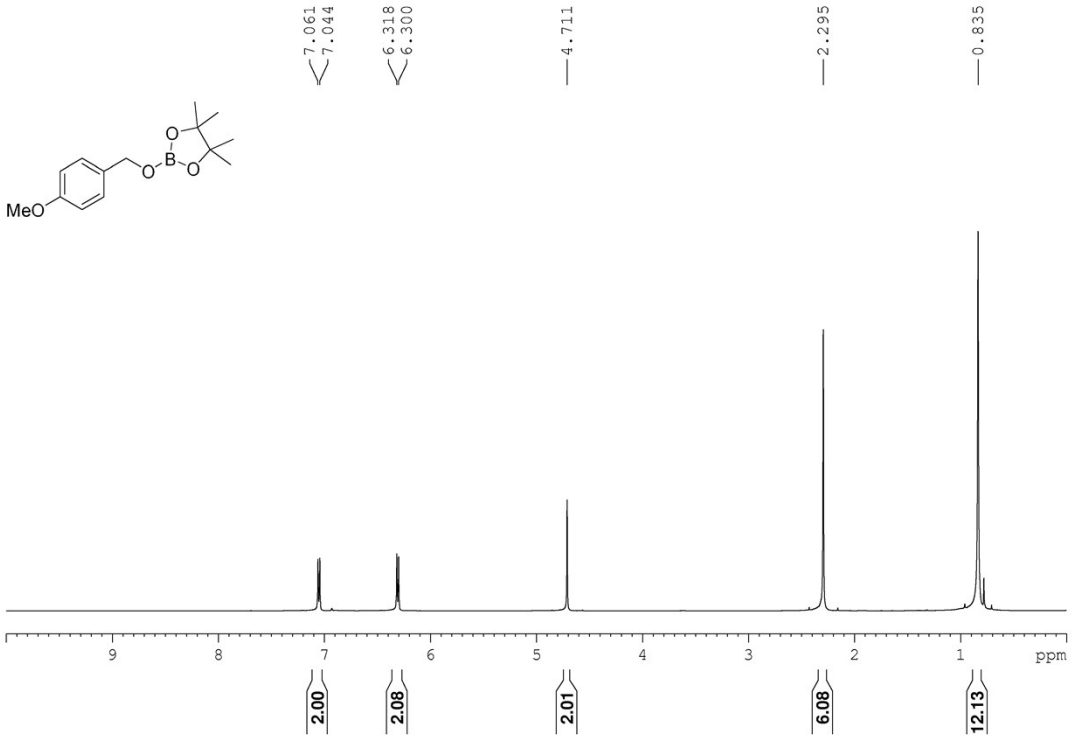
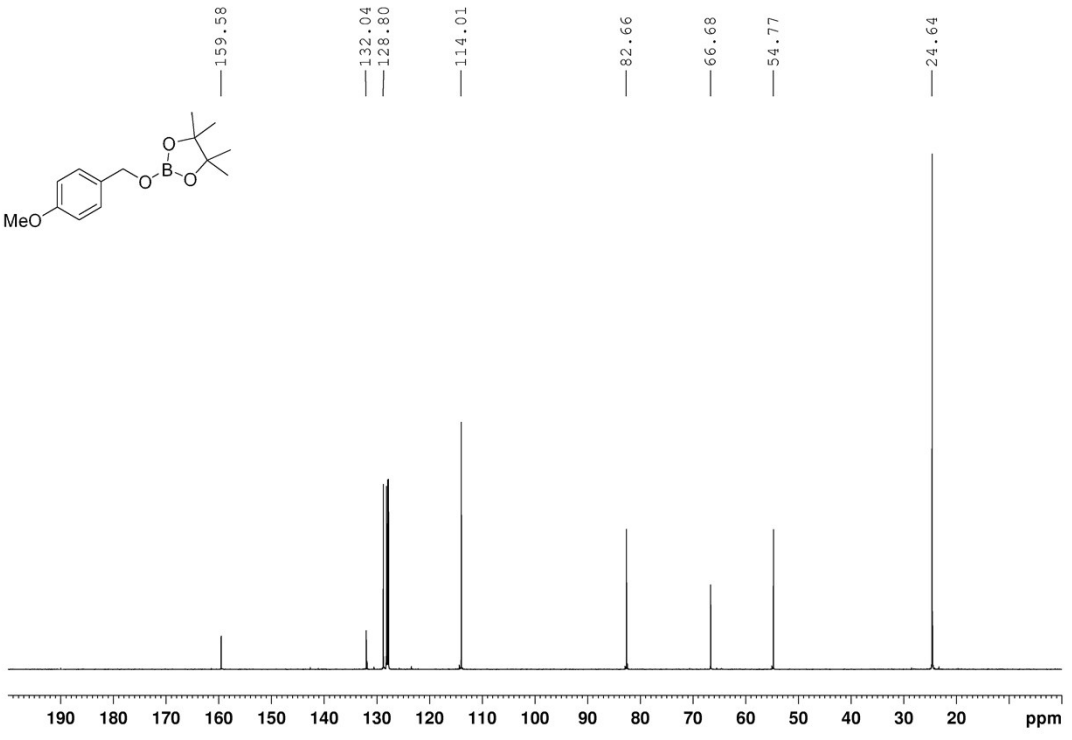
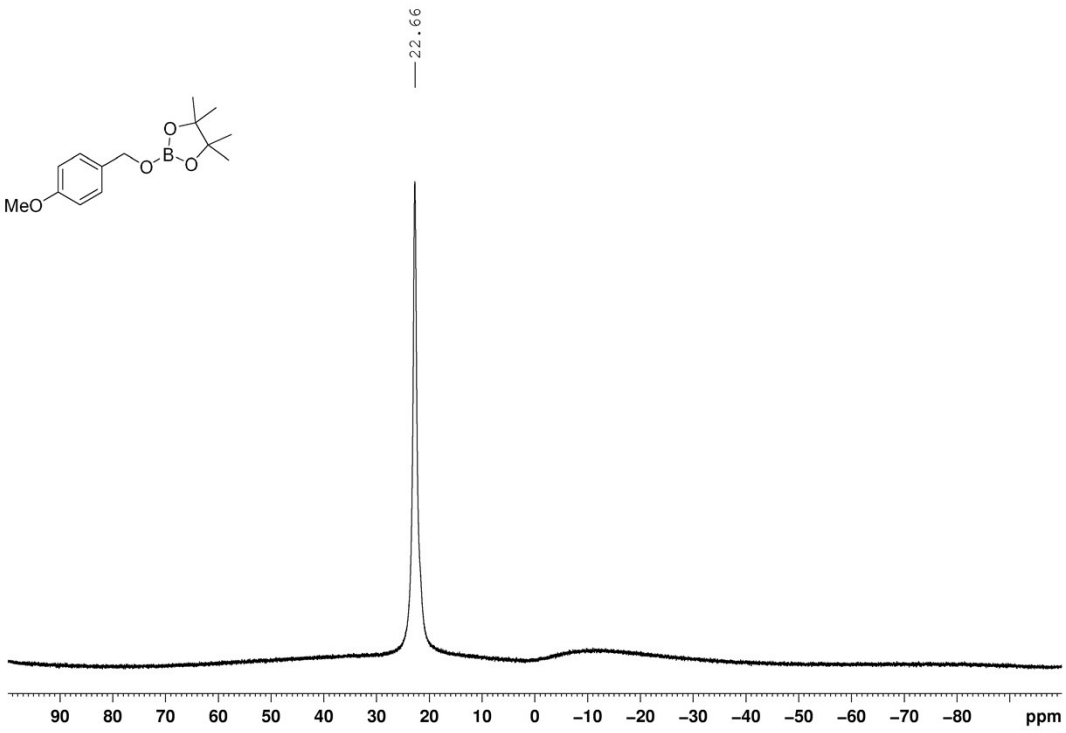
−70
−80
ppm

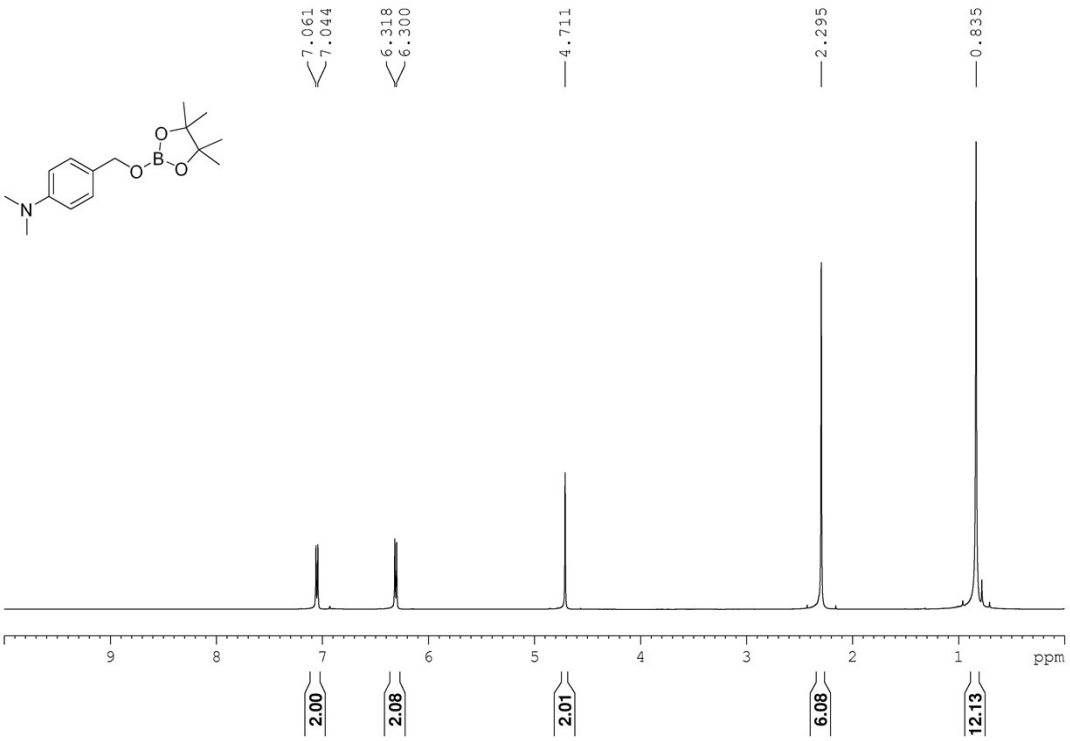
2c:

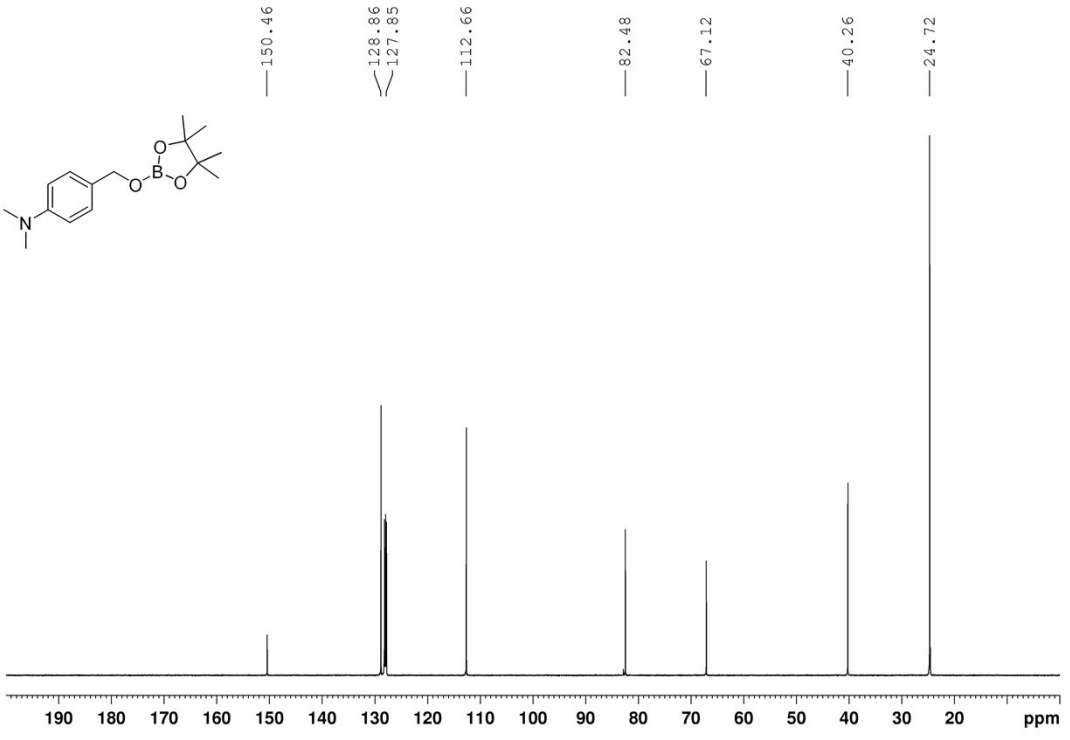

7.061
7.044
6.318
6.300
4.711
2.295
0.835
MeO
9
8
7
6
5
4
3
2
1
ppm
2.00
2.08
2.01
6.08
12.13


159.58
132.04
128.80
114.01
82.66
66.68
54.77
24.64
MeO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.66
MeO
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

2d:


7.061
7.044
6.318
6.300
4.711
2.295
0.835
9
8
7
6
5
4
3
2
1
ppm
2.00
2.08
2.01
6.08
12.13


150.46
128.86
127.85
112.66
82.48
67.12
40.26
24.72
190
180
170
160
150
140
130
120
110
100
90
80
70
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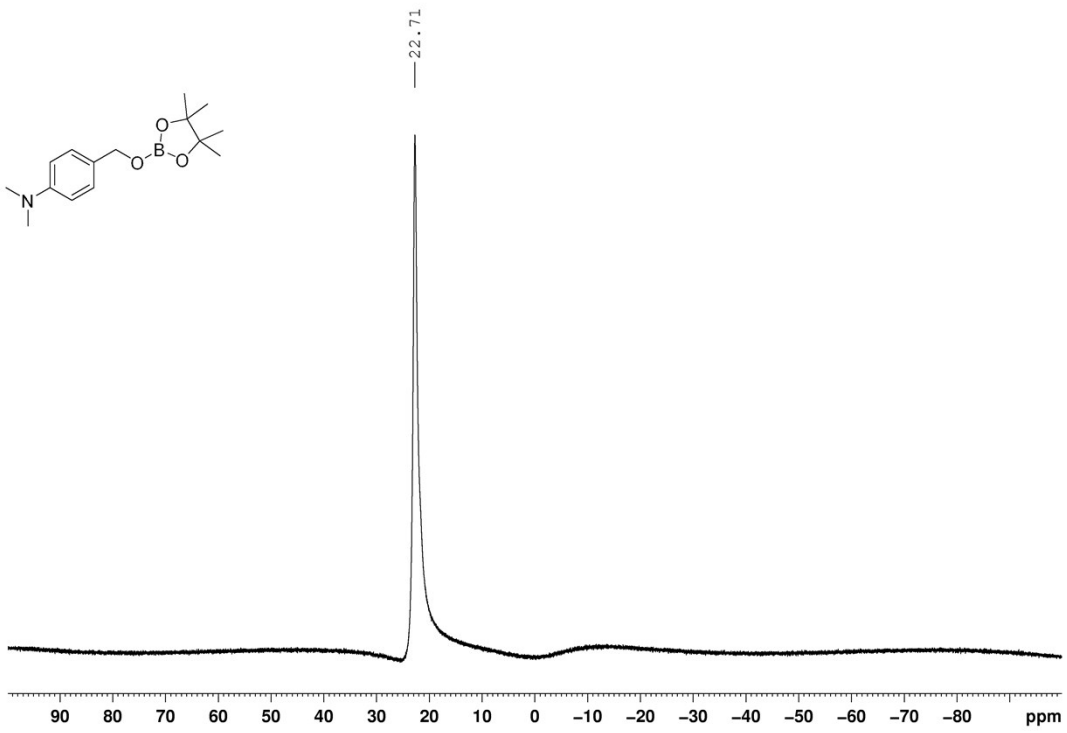
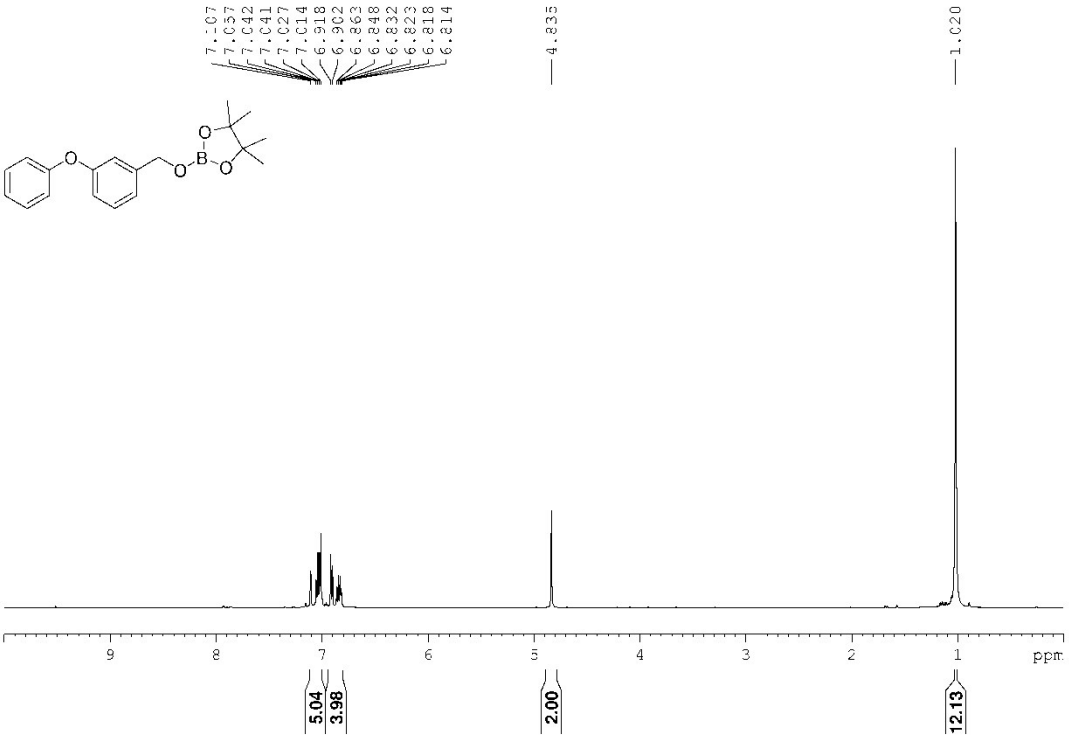
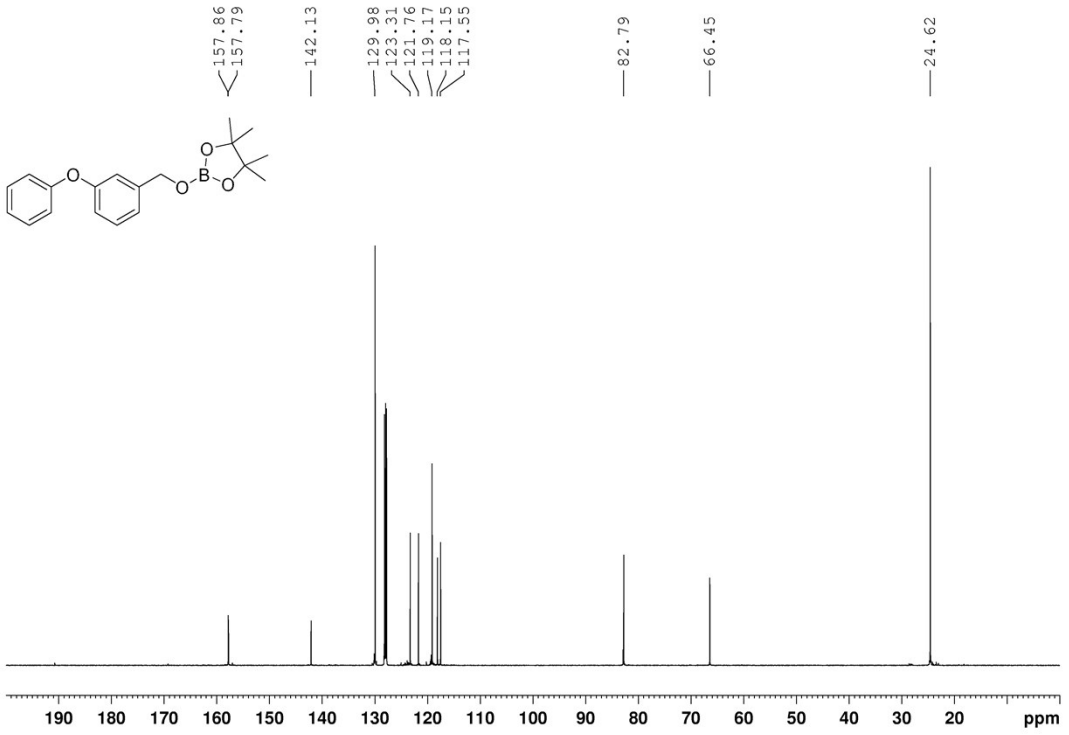
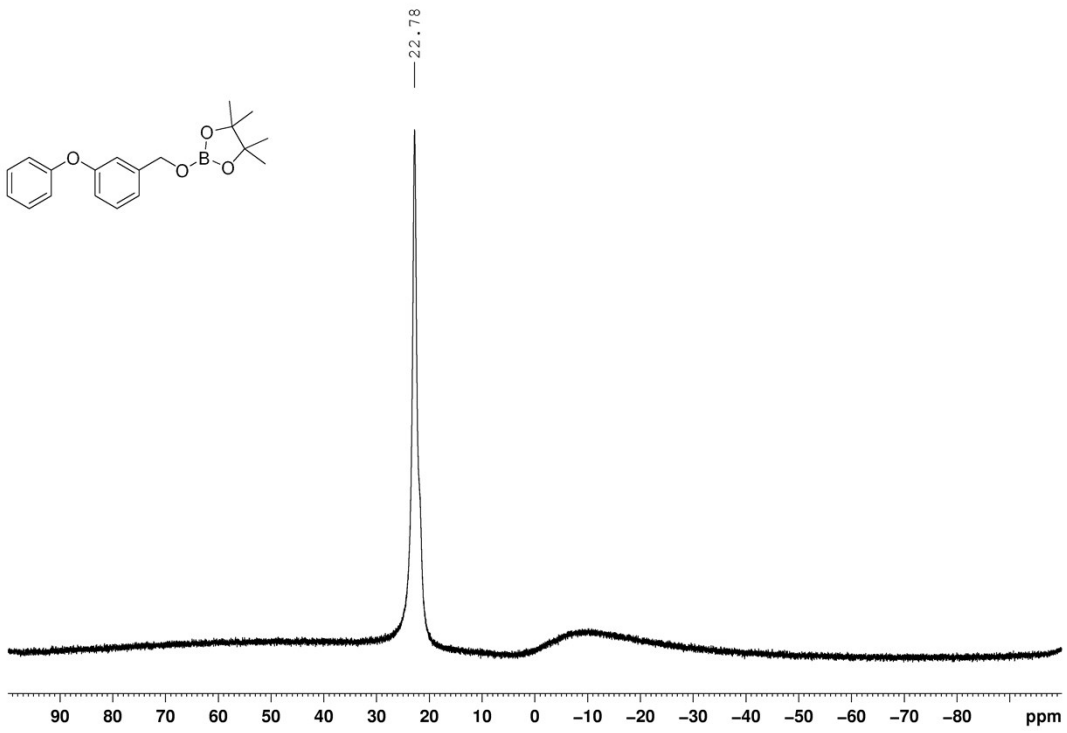
50
40
30
20
ppm


22.71
O
B
O
O
N
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

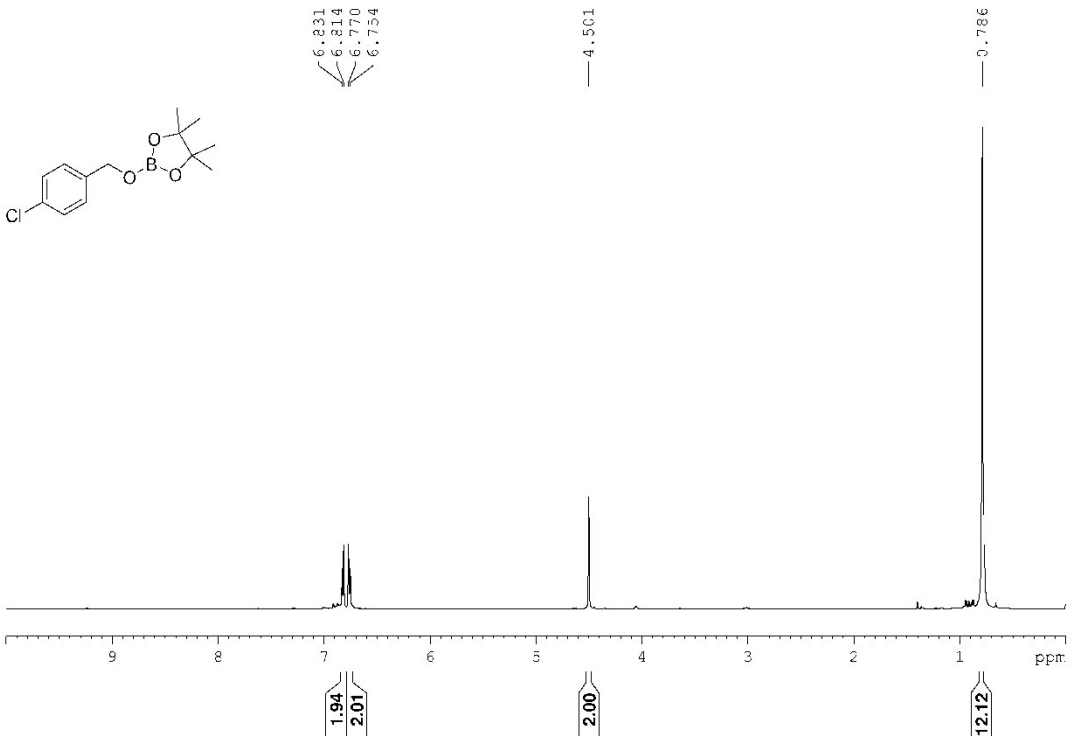
2e:

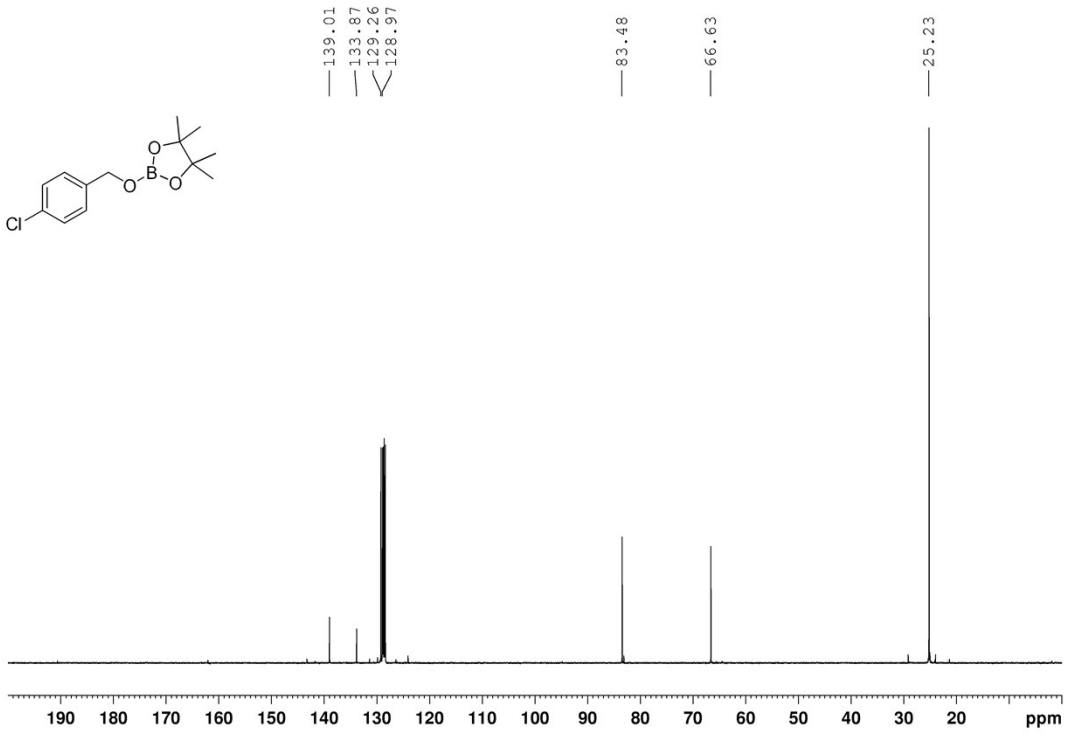

7.167
7.157
7.142
7.141
7.127
7.114
6.918
6.902
6.863
6.848
6.832
6.823
6.818
6.814
4.835
1.020
ppm
5.04
3.98
2.00
12.13

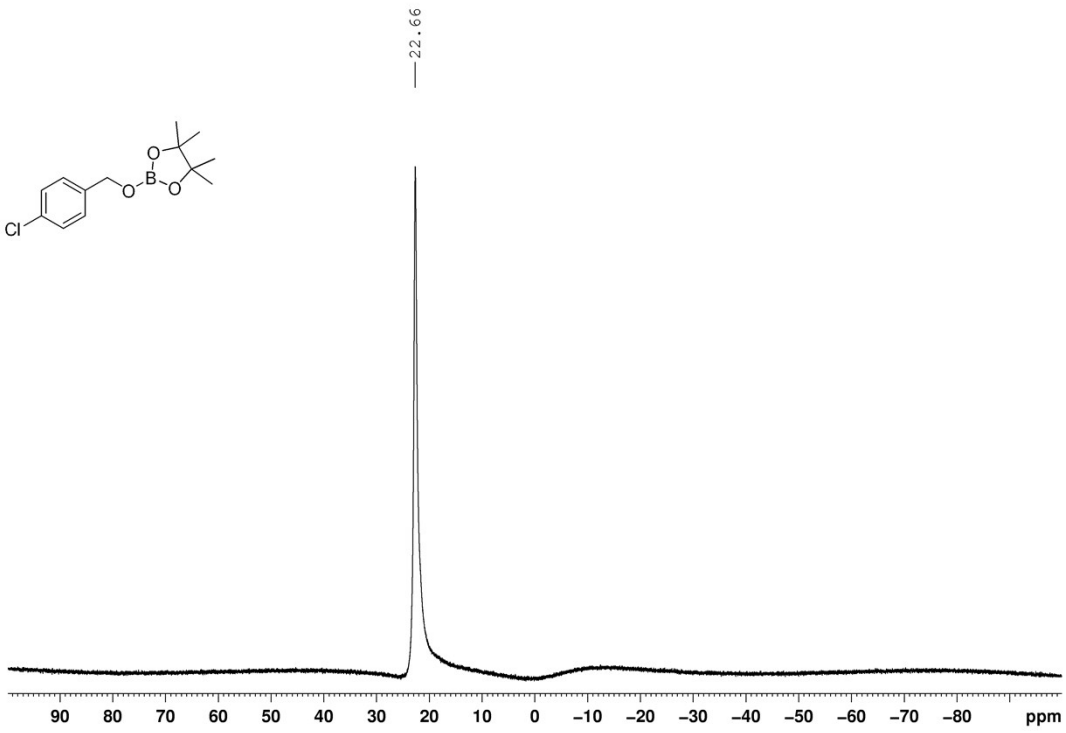

157.86
157.79
142.13
129.98
123.31
121.76
119.17
118.15
117.55
82.79
66.45
24.62
ppm


22.78
O
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

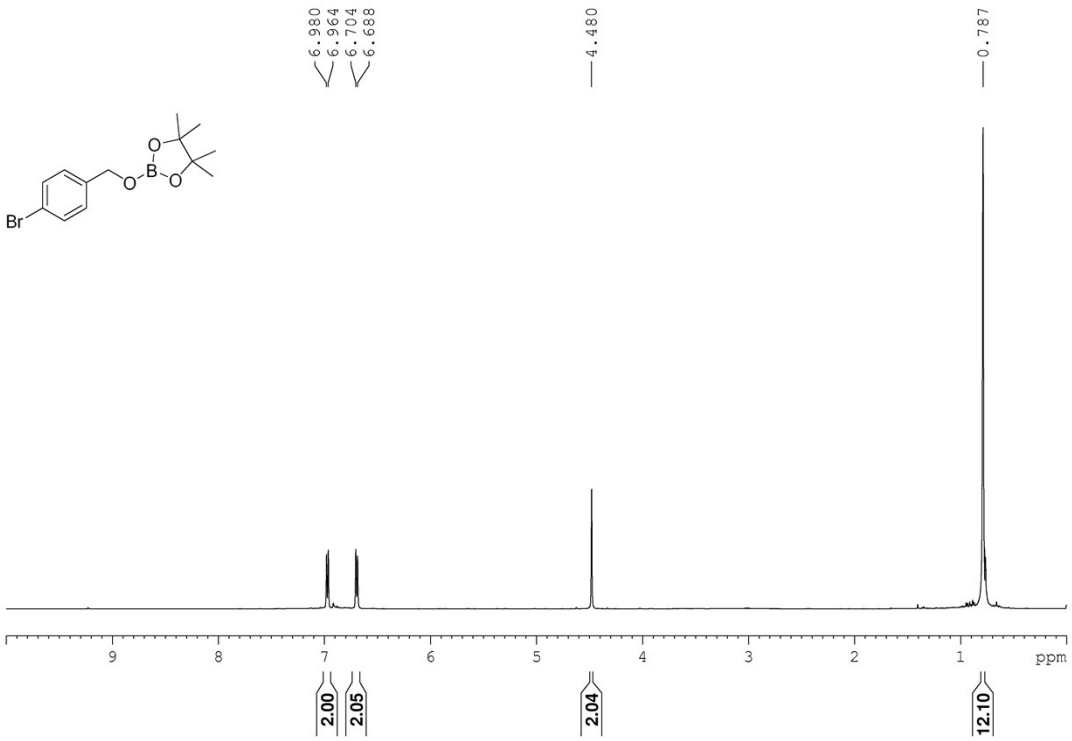
2f:

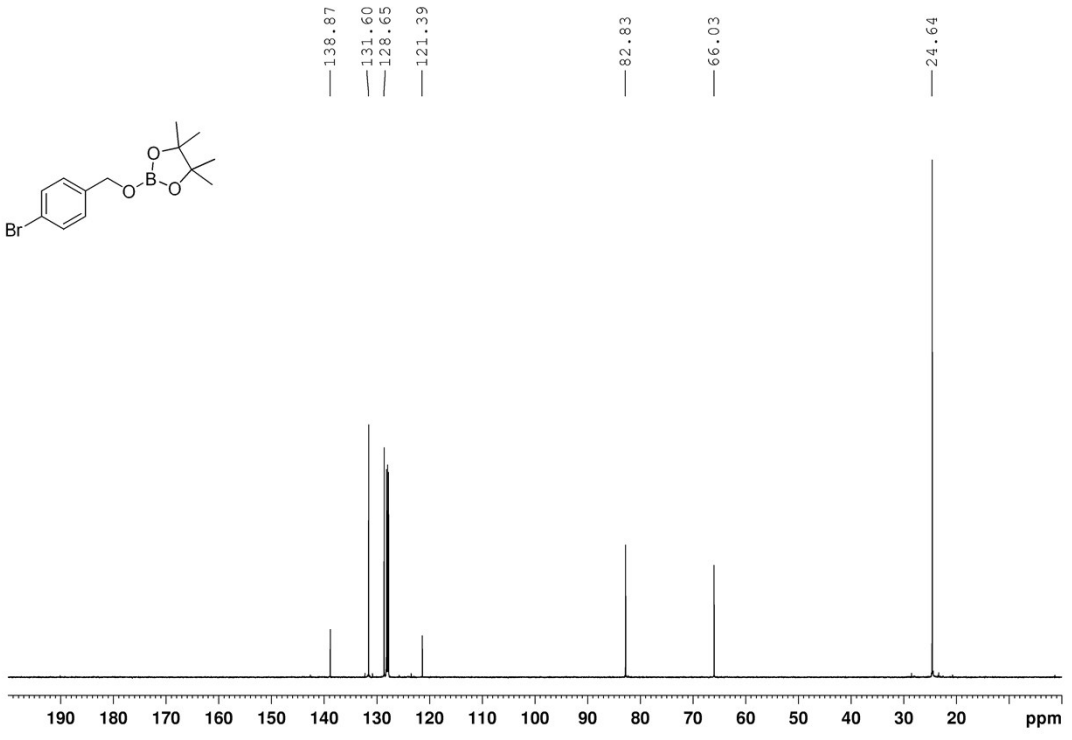

6.831
6.814
6.770
6.754
4.561
0.786
Cl
O
B
O
O
9
8
7
6
5
4
3
2
1
ppm
1.94
2.01
2.00
12.12

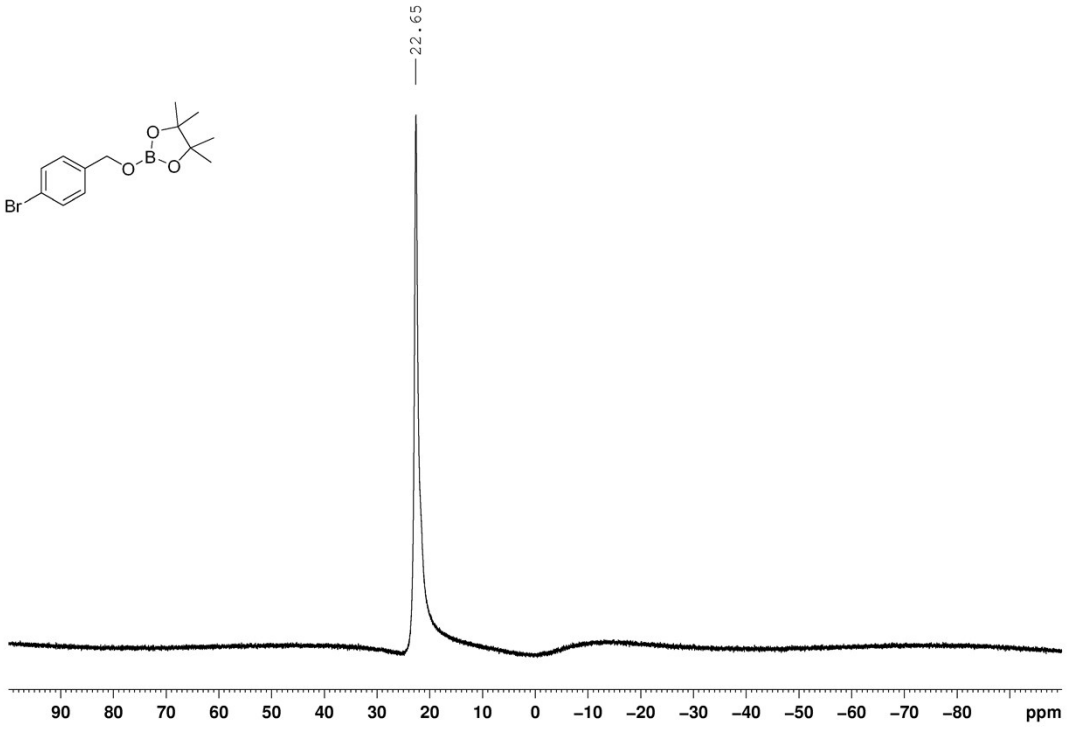

139.01
133.87
129.26
128.97
83.48
66.63
25.23
Cl
O
B
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.66
Cl
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

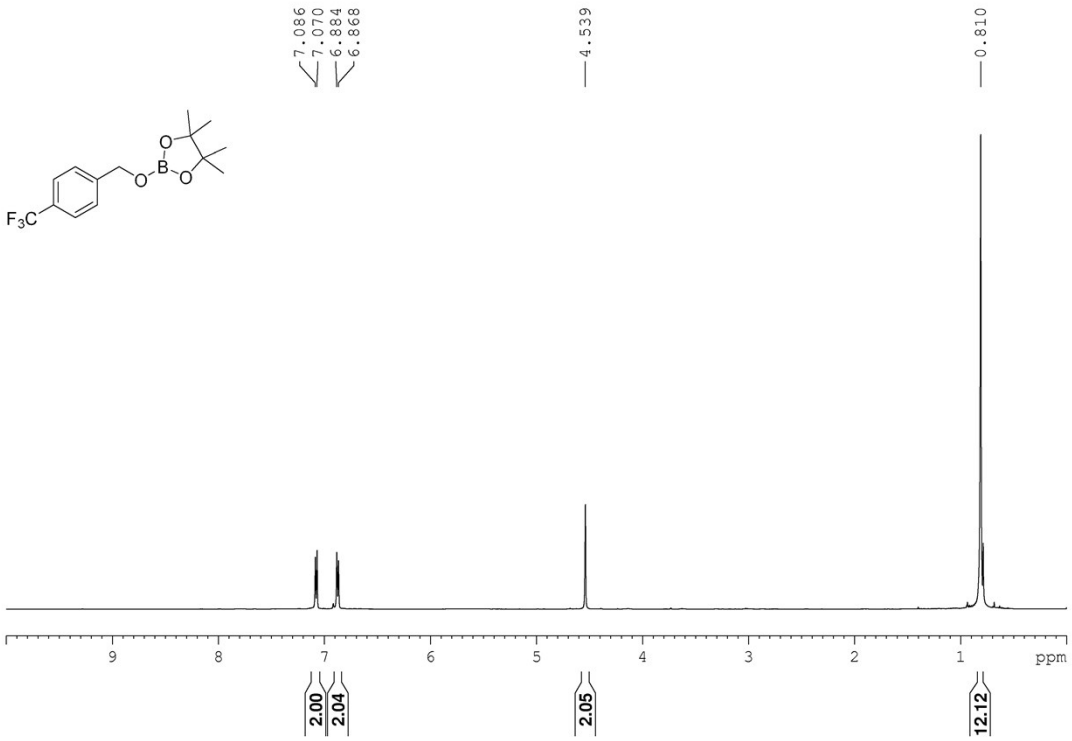
2g:

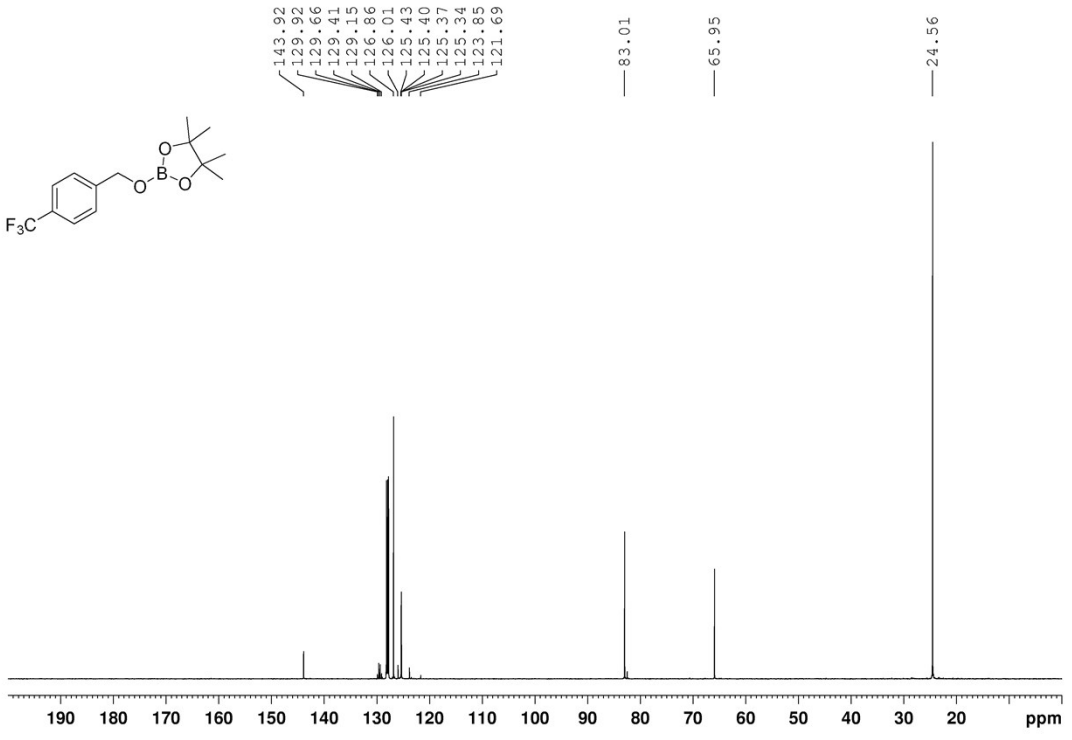

6.980
6.964
6.704
6.688
4.480
0.787
Br
9
8
7
6
5
4
3
2
1
ppm
2.00
2.05
2.04
12.10

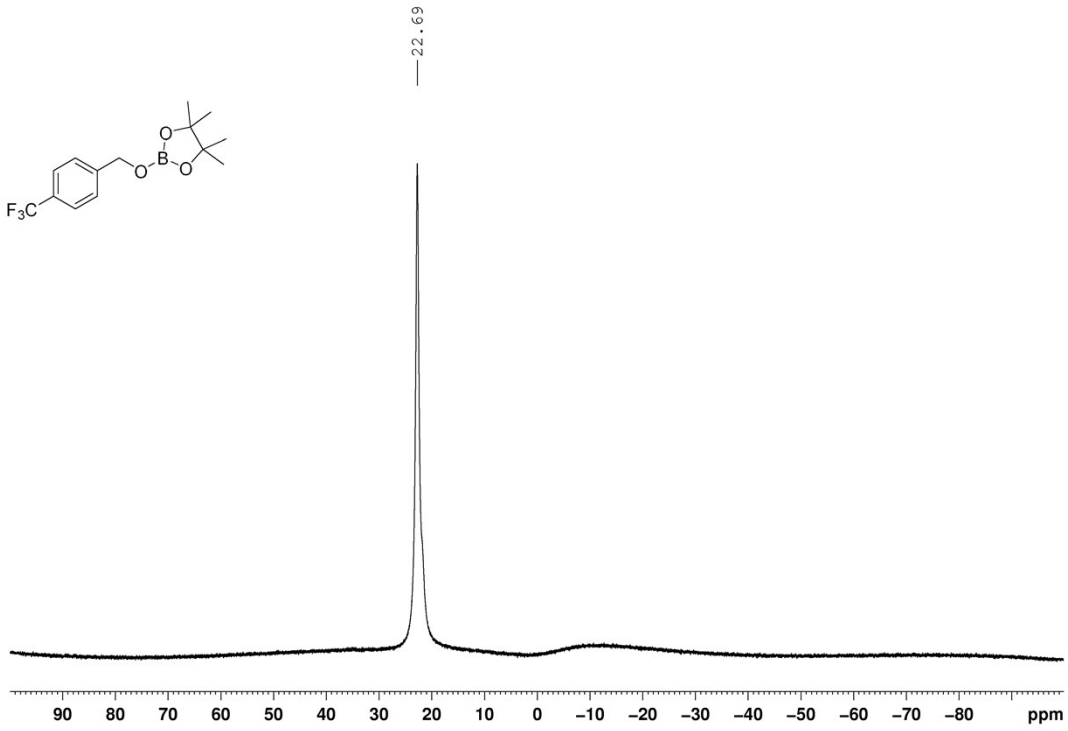

138.87
131.60
128.65
121.39
82.83
66.03
24.64
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.65
Br
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

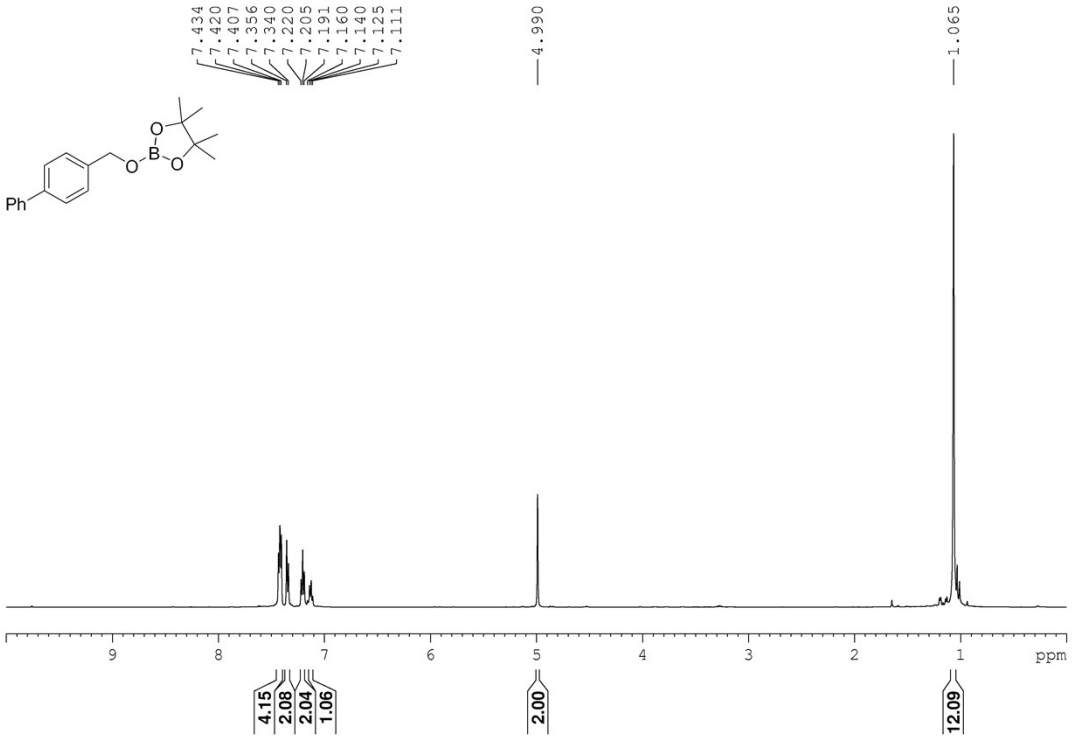
2h:

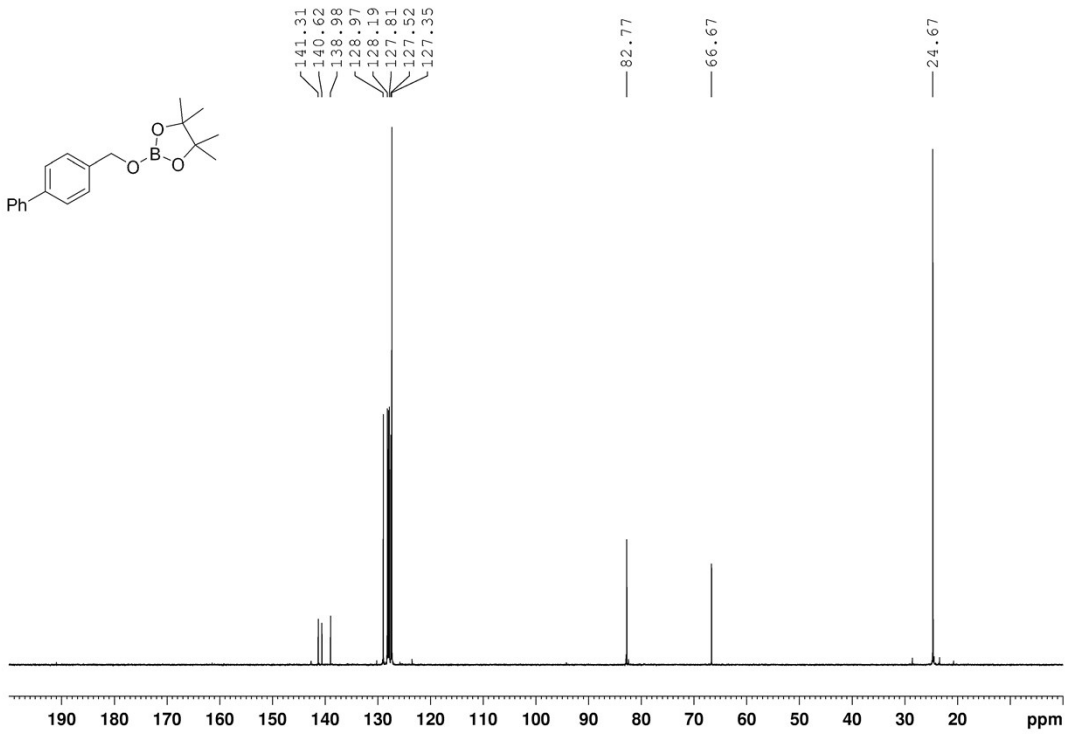

7.086
7.070
6.884
6.868
4.539
0.810
F3C
9
8
7
6
5
4
3
2
1
ppm
2.00
2.04
2.05
12.12

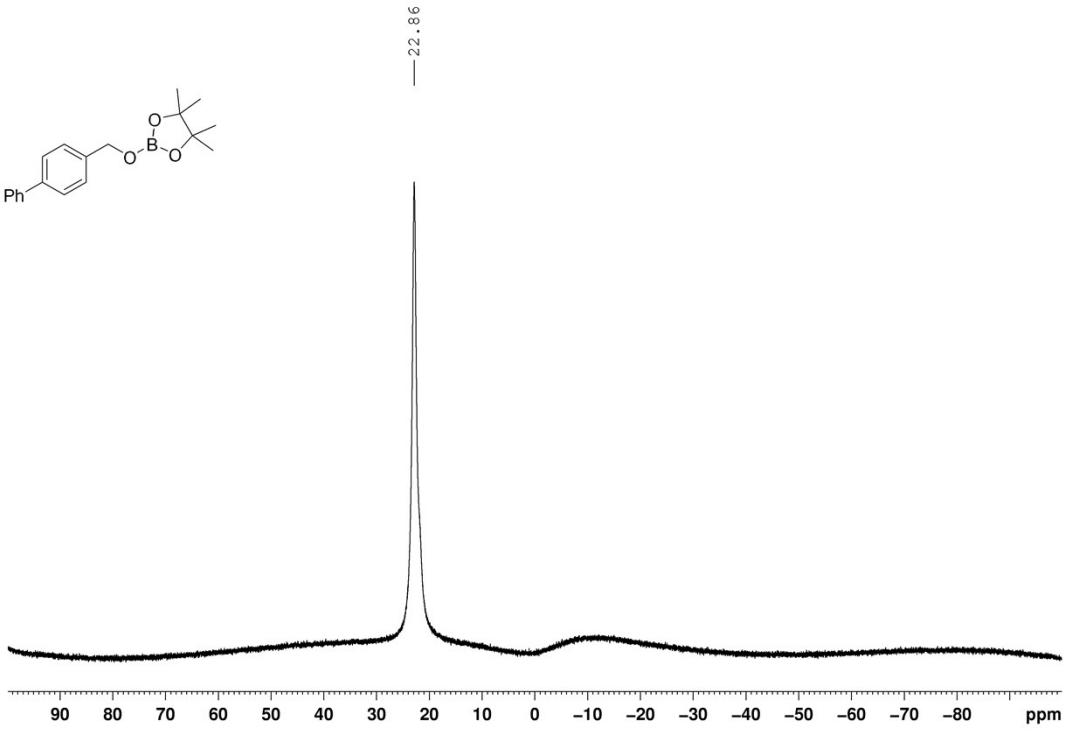

143.92
129.92
129.66
129.41
129.15
126.86
126.01
125.43
125.40
125.37
125.34
123.85
121.69
83.01
65.95
24.56
F3C
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.69
F3C
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

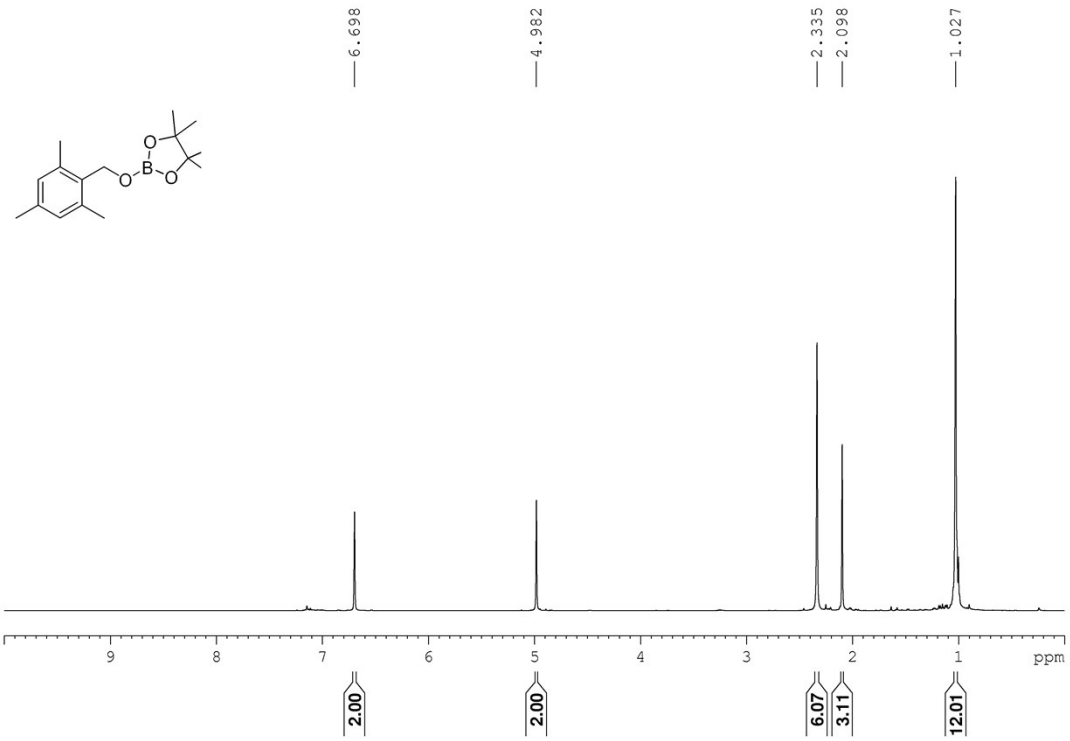
2i:

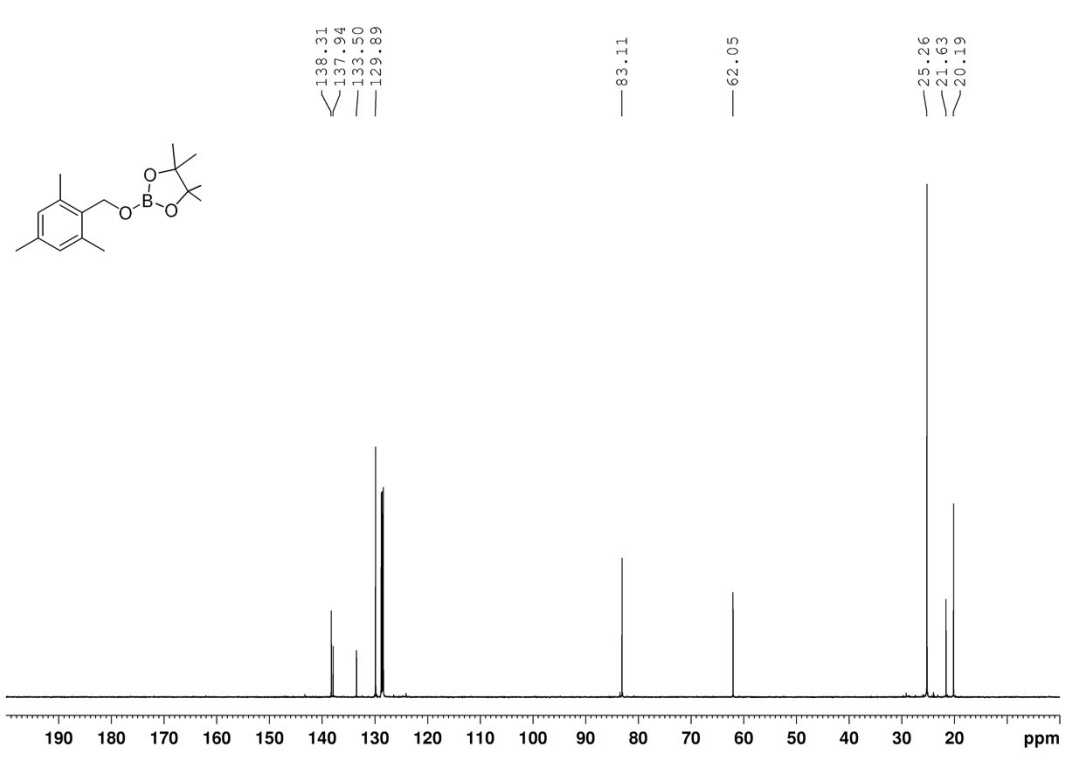

7.434
7.420
7.407
7.356
7.340
7.220
7.205
7.191
7.160
7.140
7.125
7.111
4.990
1.065
Ph
ppm
4.15
2.08
2.04
1.06
2.00
12.09

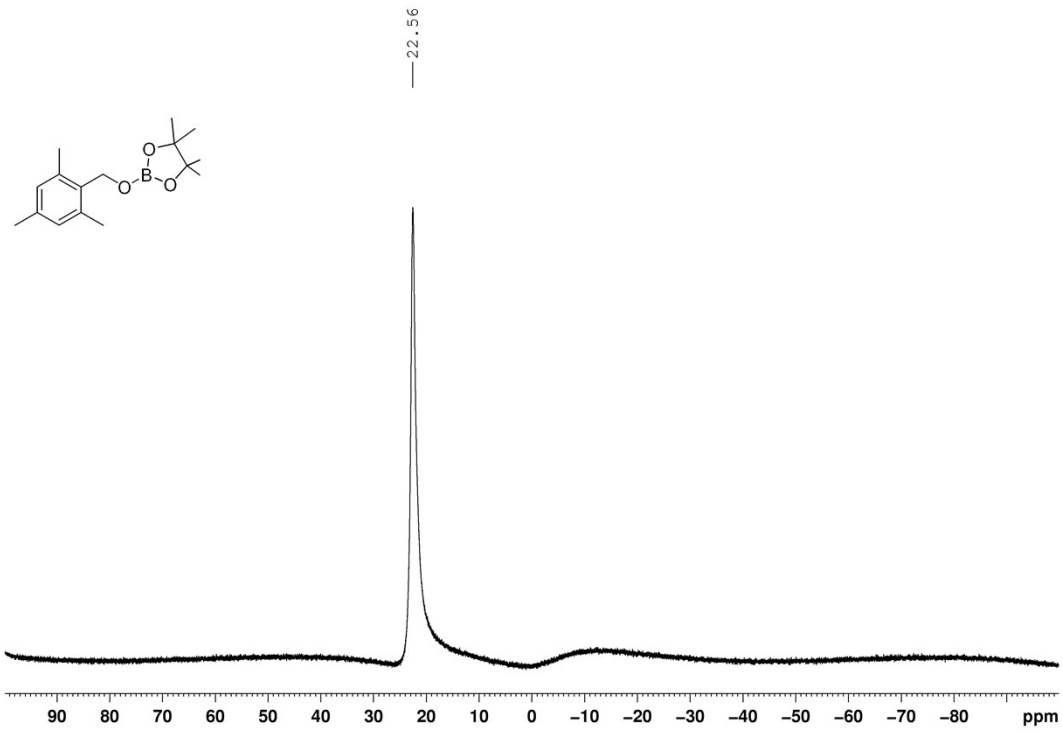

141.31
140.62
138.98
128.97
128.19
127.81
127.52
127.35
82.77
66.67
24.67
Ph
ppm


22.86
Ph
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

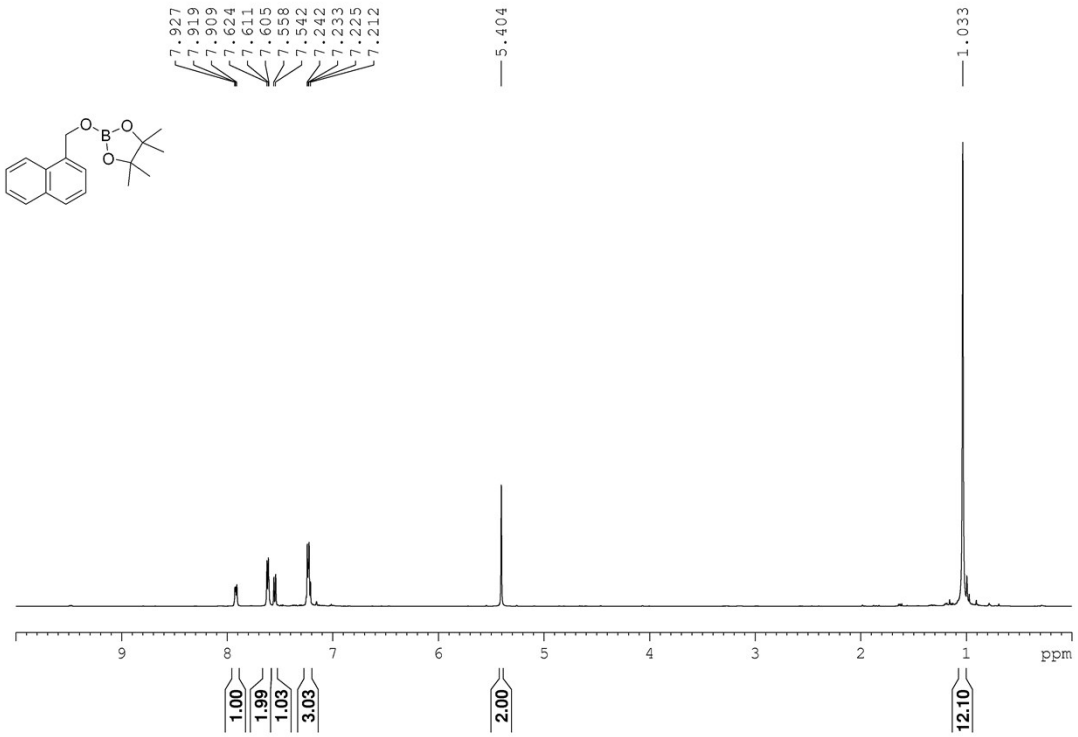
2j:

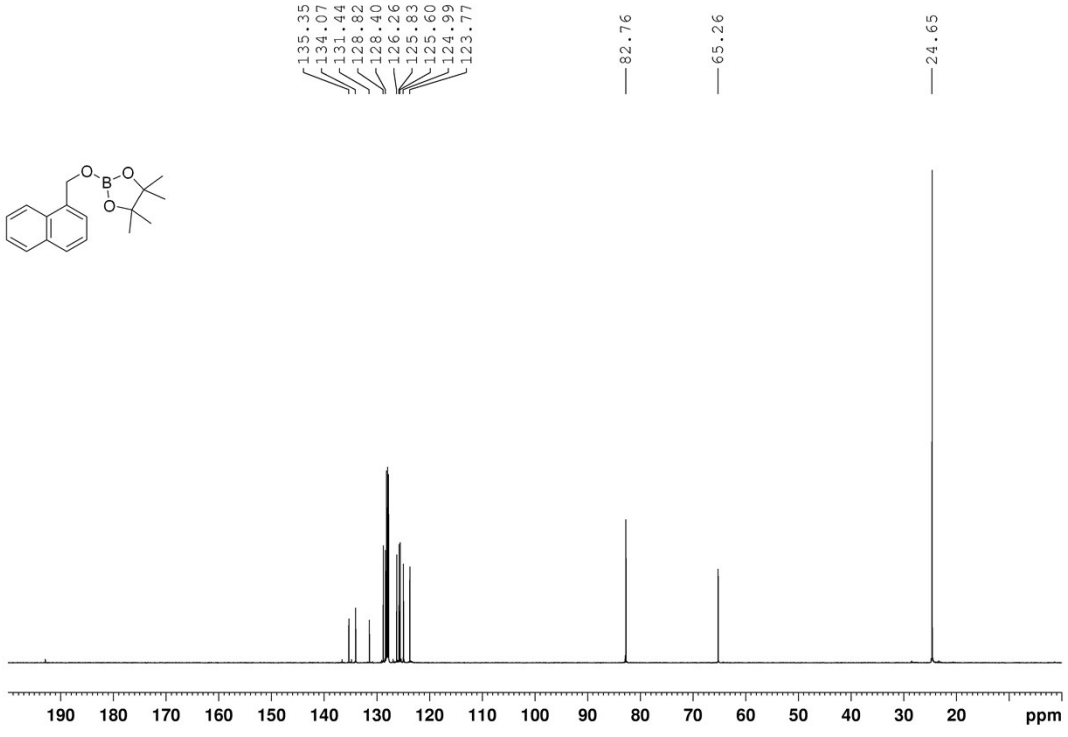

6.698
4.982
2.335
2.098
1.027
ppm
2.00
2.00
6.07
3.11
12.01

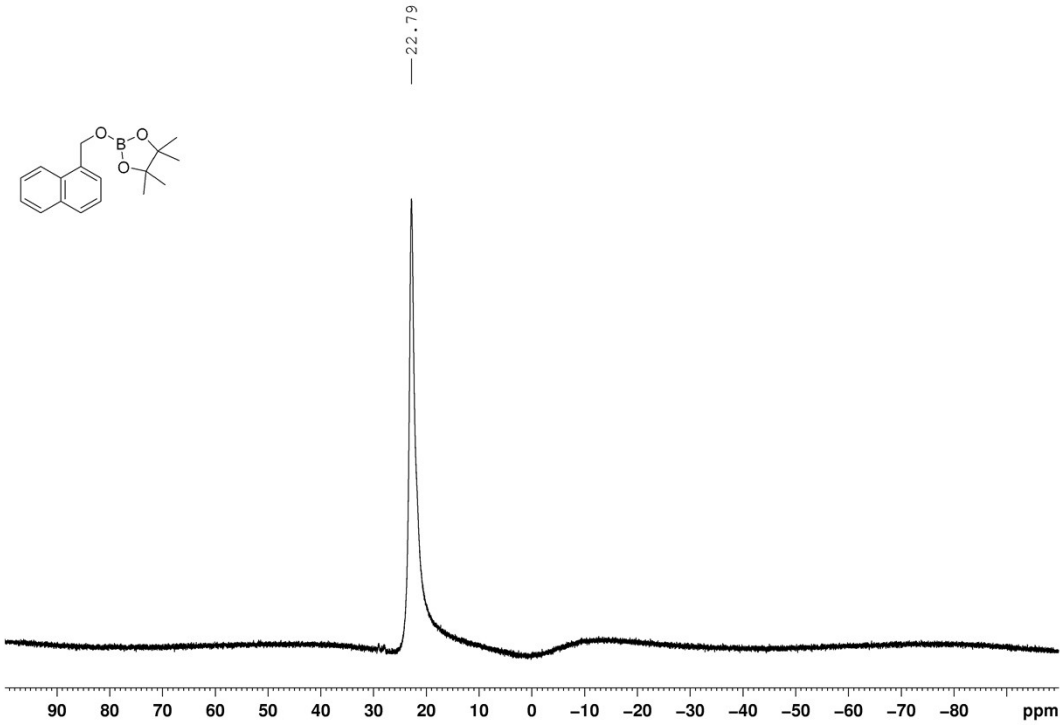

138.31
137.94
133.50
129.89
83.11
62.05
25.26
21.63
20.19
ppm


22.56
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

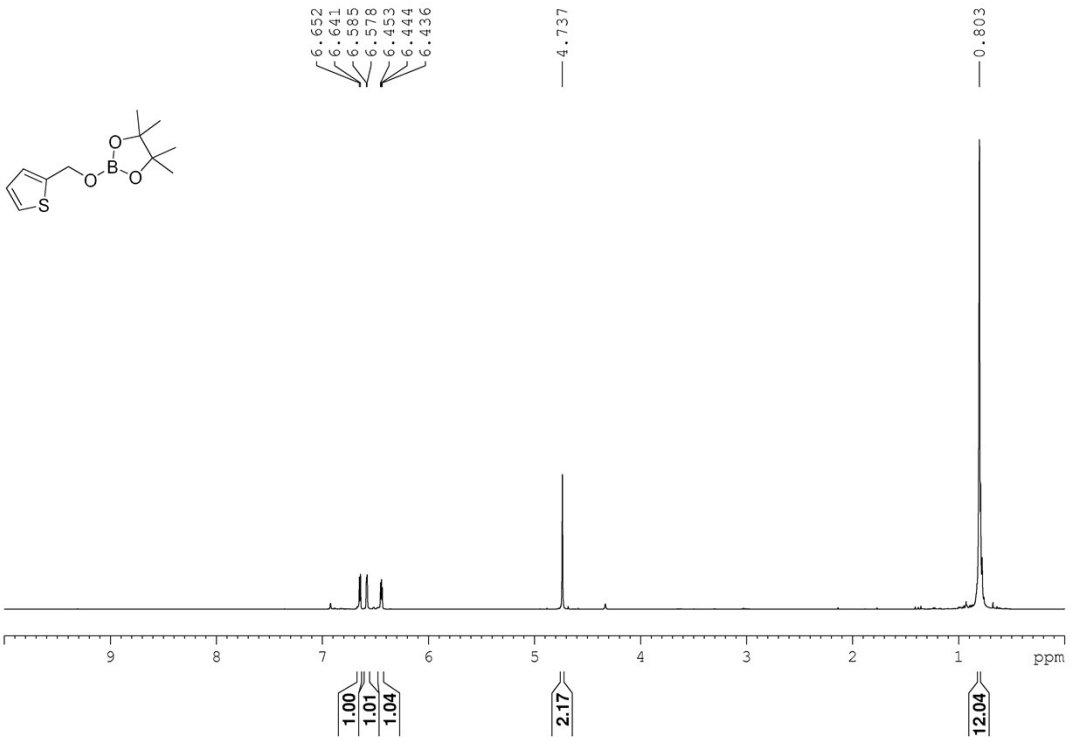
2k:

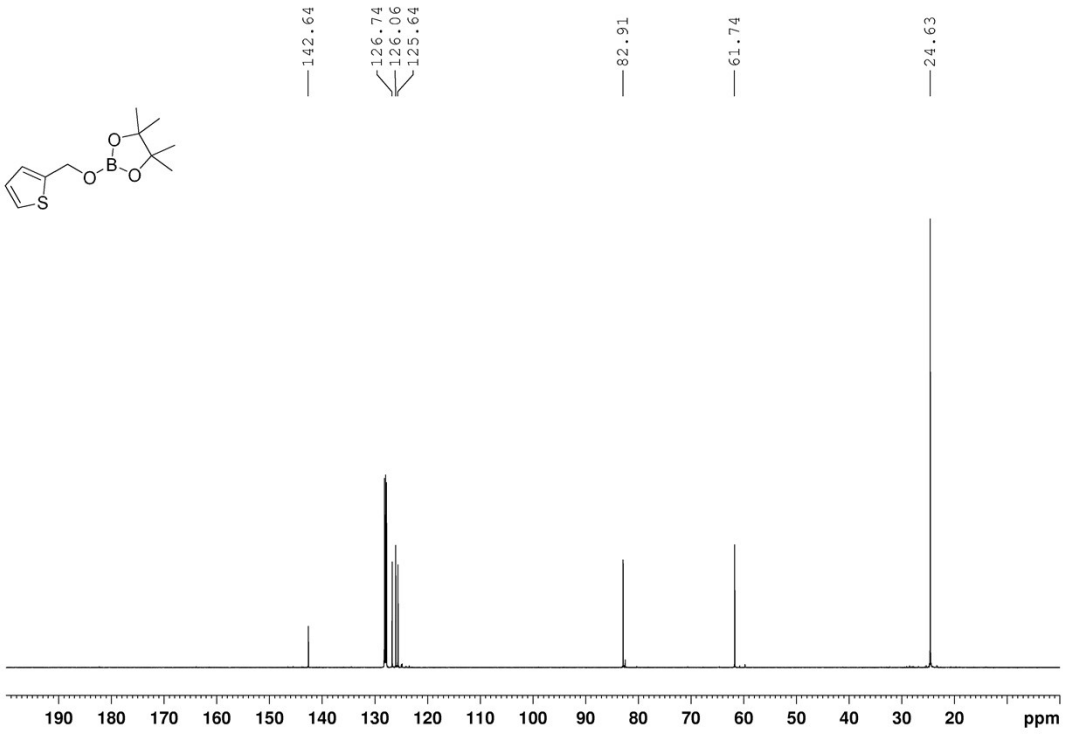

7.927
7.919
7.909
7.624
7.611
7.605
7.558
7.542
7.242
7.233
7.225
7.212
5.404
1.033
9
8
7
6
5
4
3
2
1
ppm
1.00
1.99
1.03
3.03
2.00
12.10

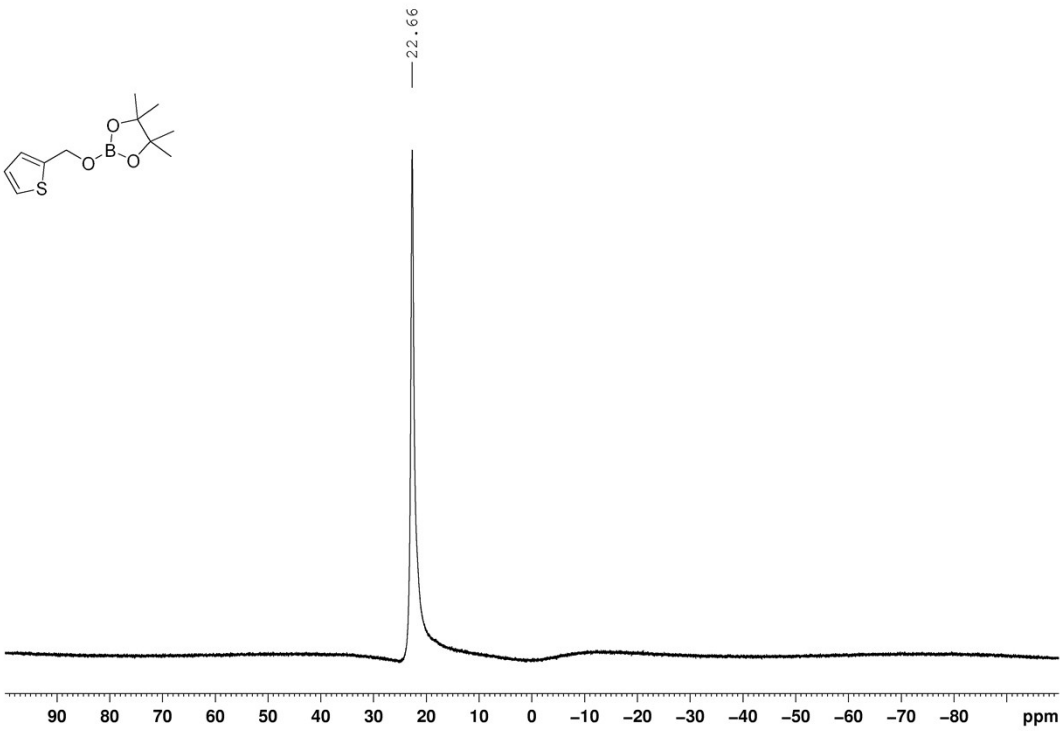

135.35
134.07
131.44
128.82
128.40
126.26
125.83
125.60
124.99
123.77
82.76
65.26
24.65
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.79
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

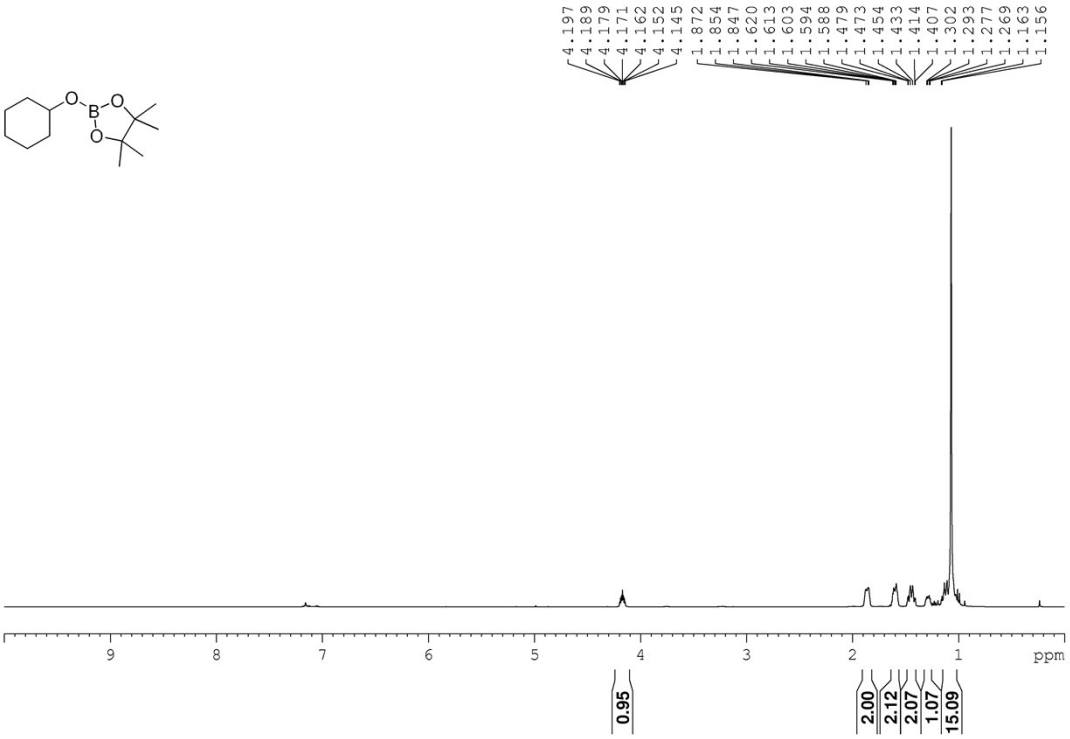
2l:

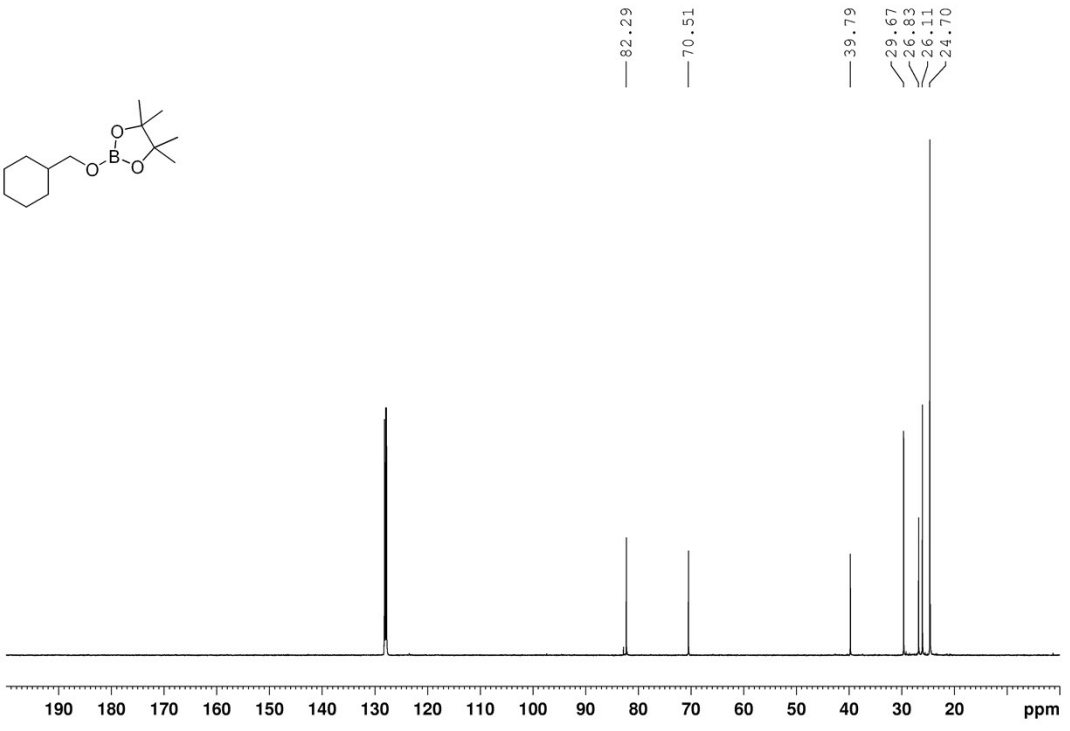

6.652
6.641
6.585
6.578
6.453
6.444
6.436
4.737
0.803
ppm
1.00
1.01
1.04
2.17
12.04

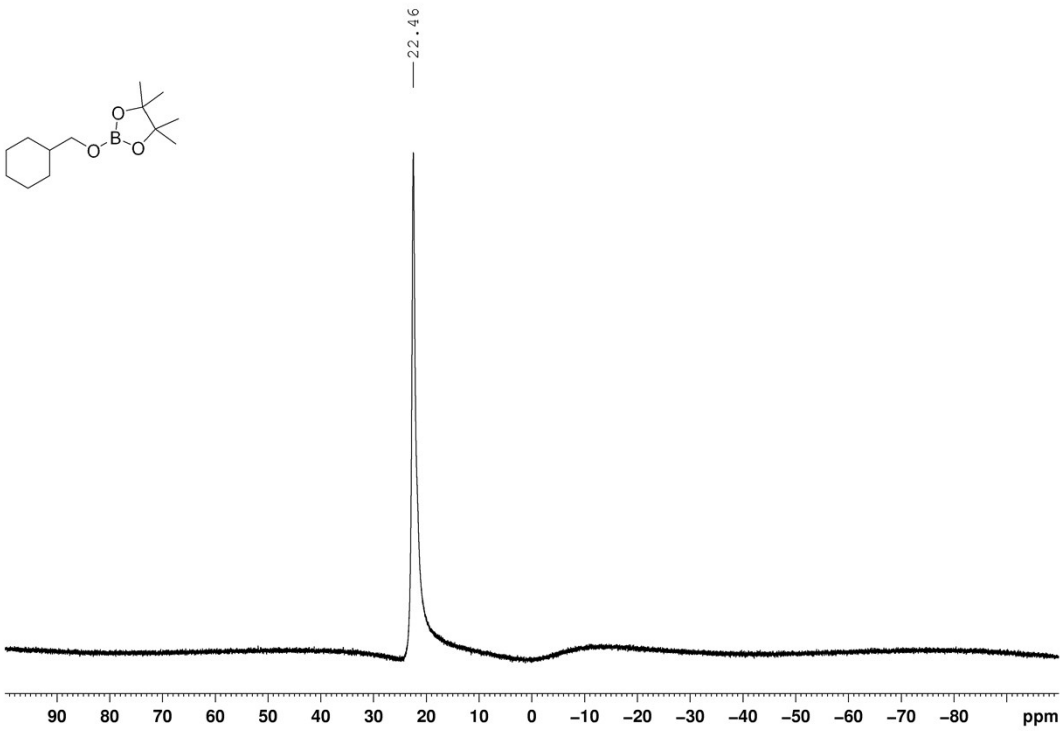

142.64
126.74
126.06
125.64
82.91
61.74
24.63
ppm


22.66
O
B
O
O
S
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

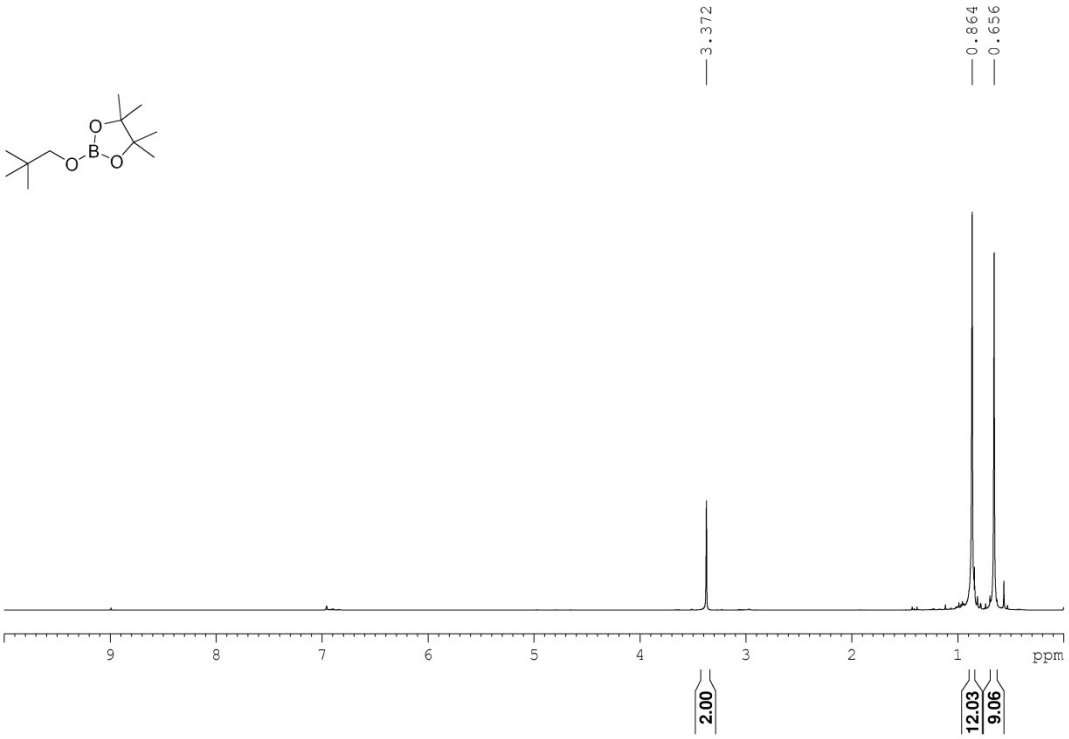
2m:

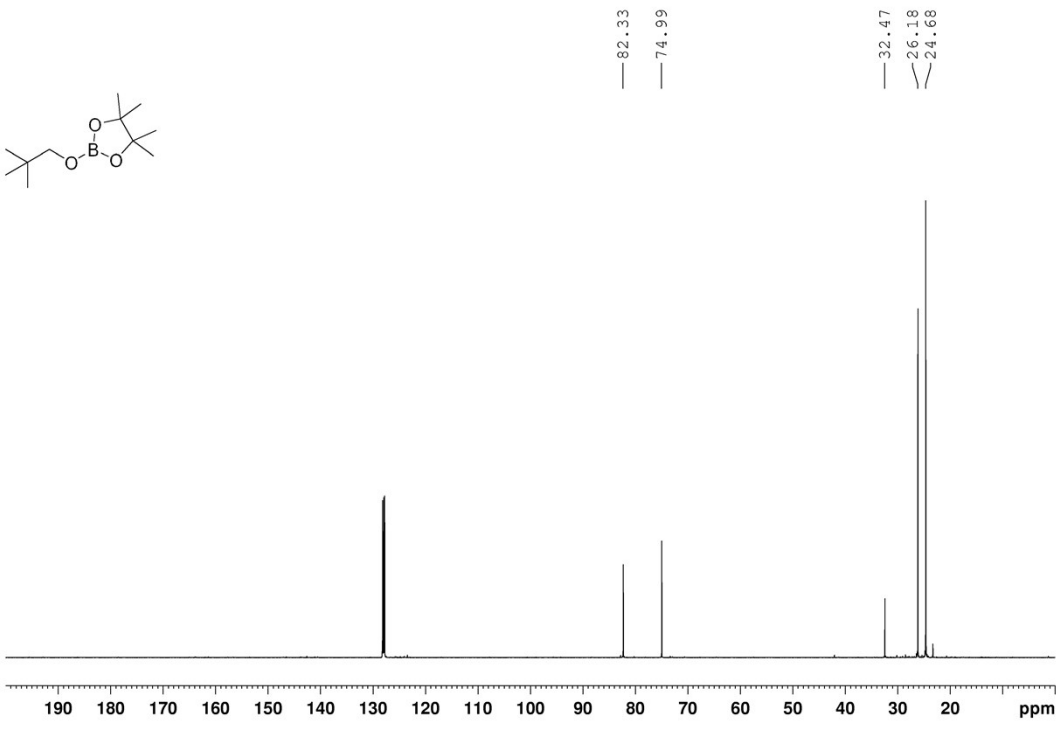

4.197
4.189
4.179
4.171
4.162
4.152
4.145
1.872
1.854
1.847
1.620
1.613
1.603
1.594
1.588
1.479
1.473
1.454
1.433
1.414
1.407
1.302
1.293
1.277
1.269
1.163
1.156
9
8
7
6
5
4
3
2
1
ppm
0.95
2.00
2.12
2.07
1.07
15.09

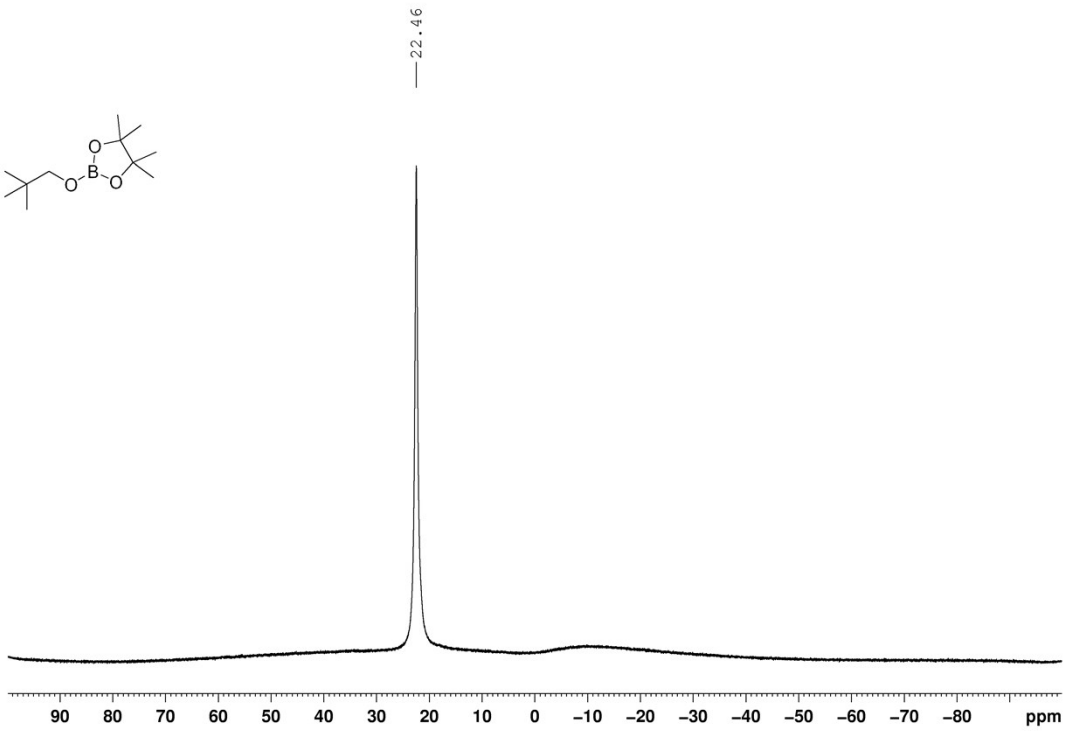

82.29
70.51
39.79
29.67
26.83
26.11
24.70
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.46
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

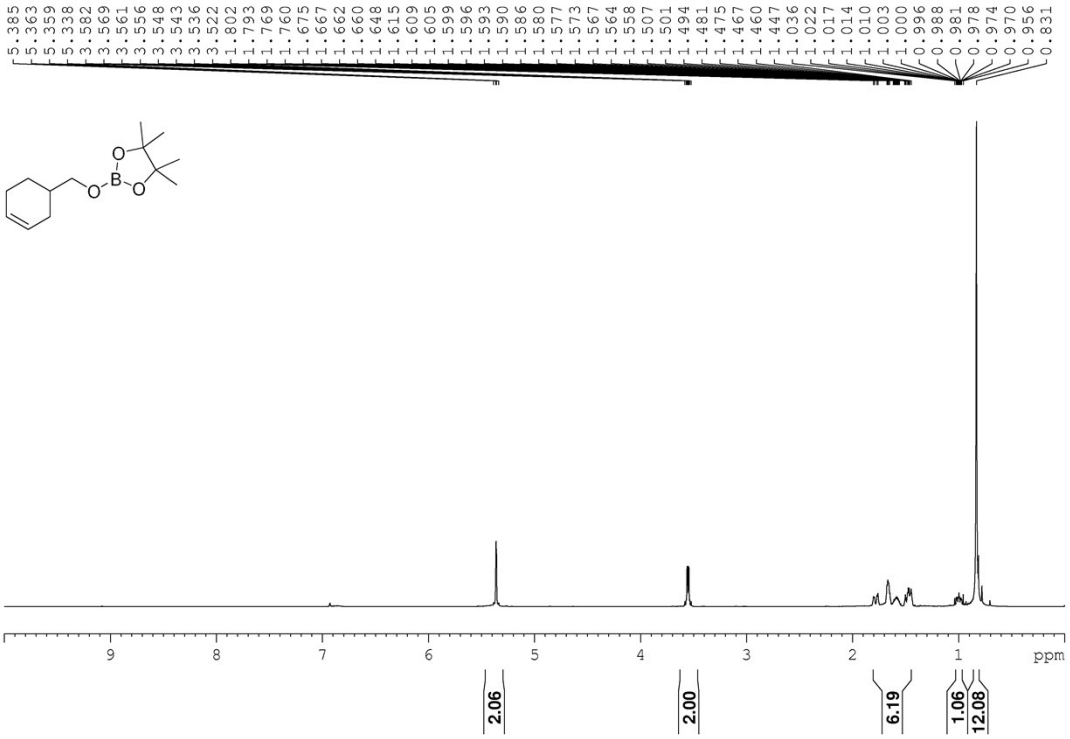
2n:

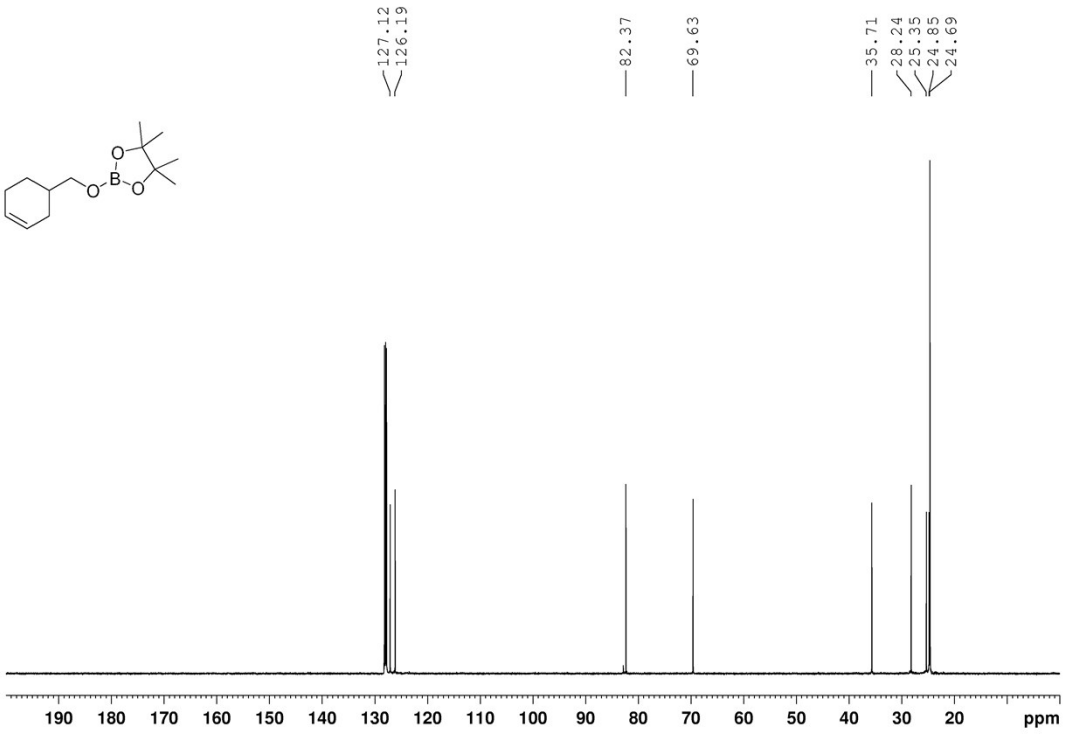

3.372
0.864
0.656
9
8
7
6
5
4
3
2
1
ppm
2.00
12.03
9.06

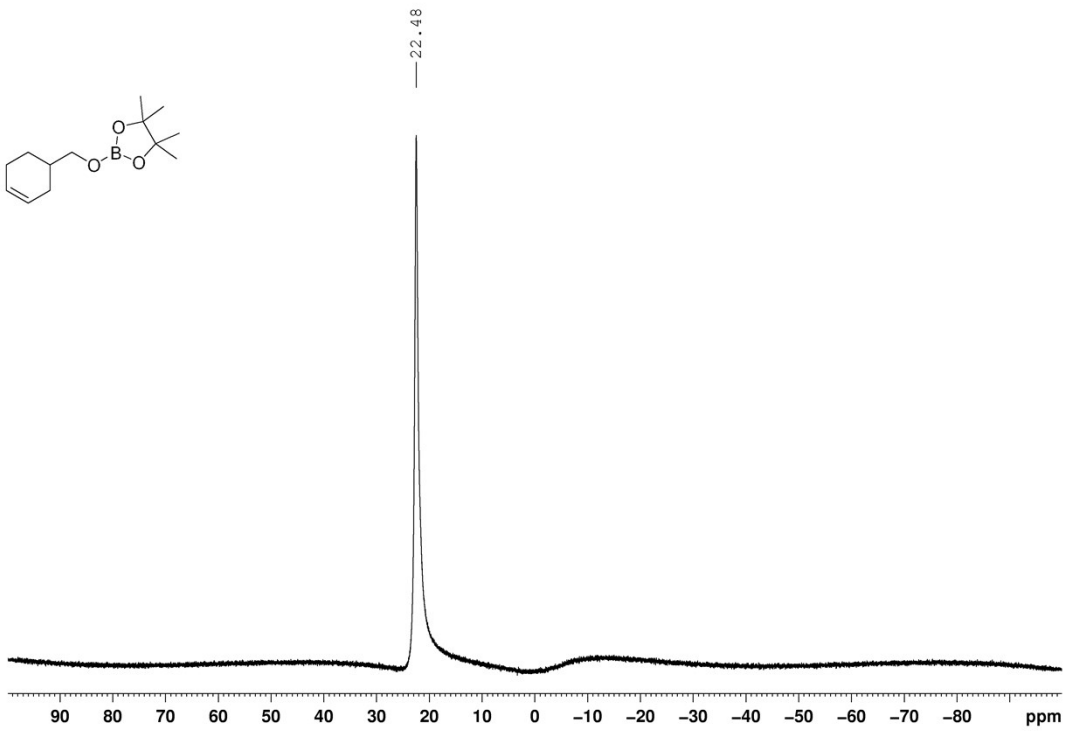

82.33
74.99
32.47
26.18
24.68
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.46
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

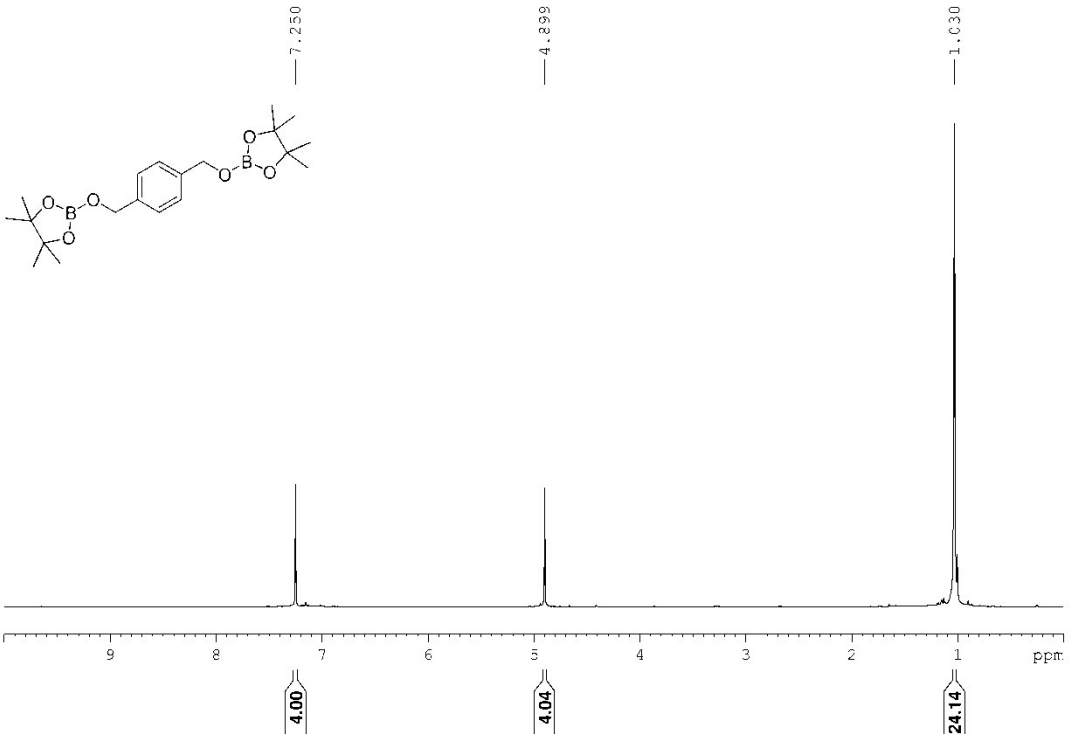
2o:

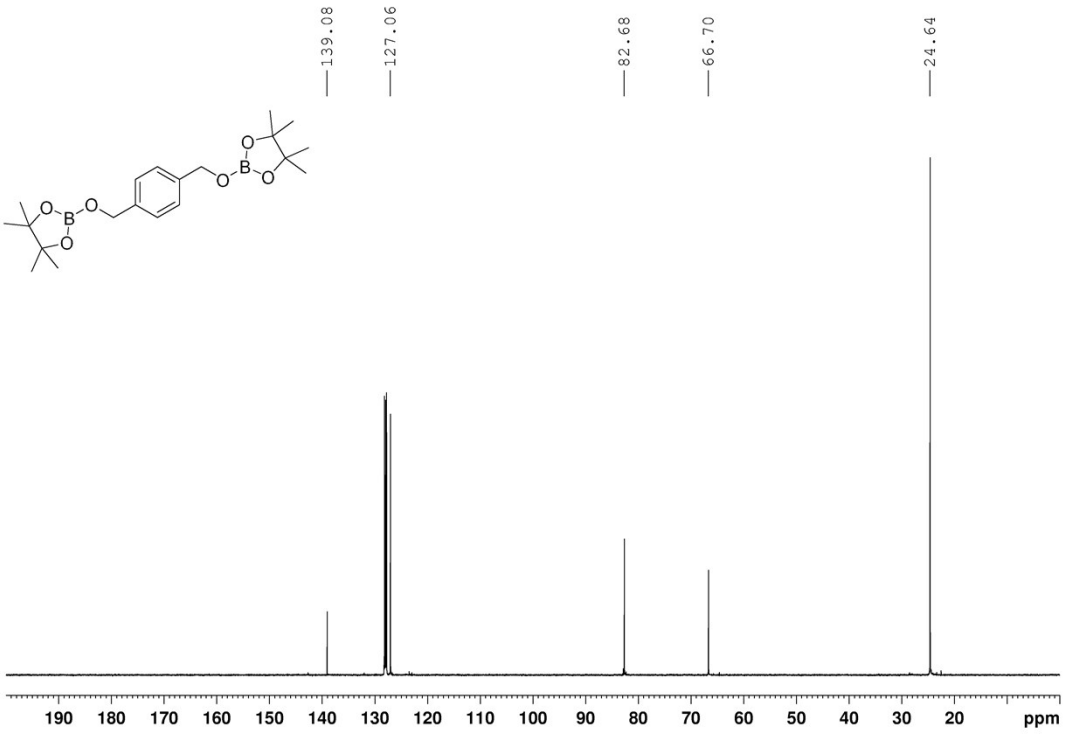

5.385
5.363
5.359
5.338
3.582
3.569
3.561
3.556
3.548
3.543
3.536
3.522
1.802
1.793
1.769
1.760
1.675
1.667
1.662
1.660
1.648
1.615
1.609
1.605
1.599
1.596
1.593
1.590
1.586
1.580
1.577
1.573
1.567
1.564
1.558
1.507
1.501
1.494
1.481
1.475
1.467
1.460
1.447
1.036
1.022
1.017
1.014
1.010
1.003
1.000
0.996
0.988
0.981
0.978
0.974
0.970
0.956
0.831
O
B
O
O
9
8
7
6
5
4
3
2
1
ppm
2.06
2.00
6.19
1.06
12.08

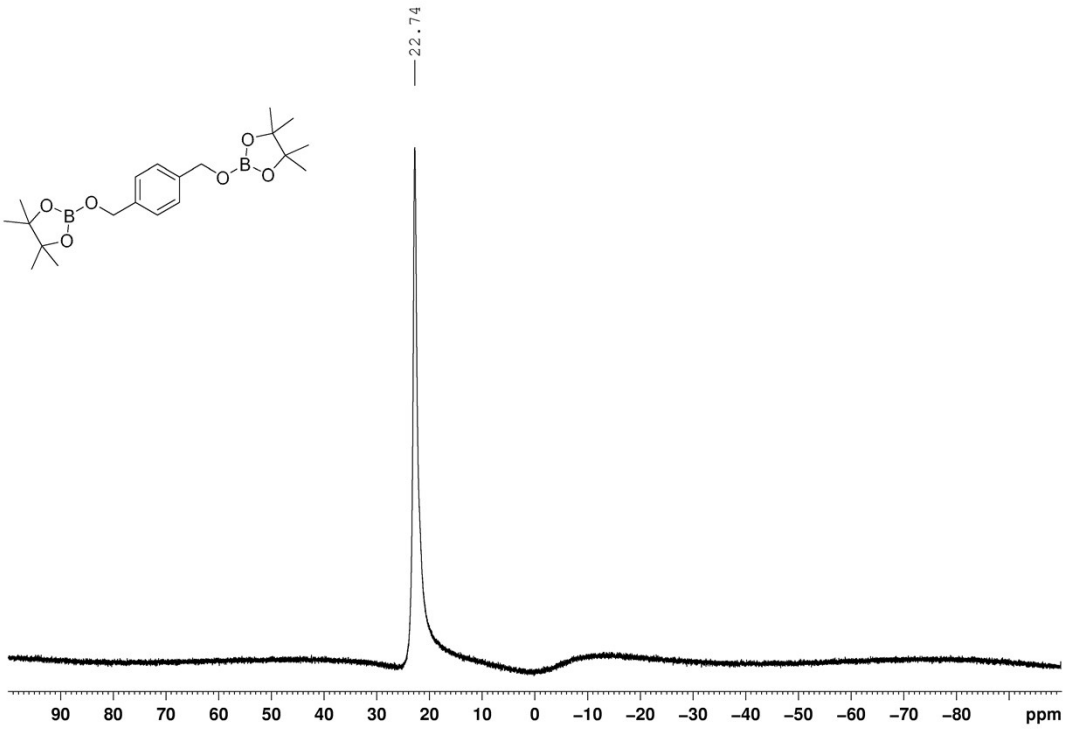

127.12
126.19
82.37
69.63
35.71
28.24
25.35
24.85
24.69
O
B
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.48
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

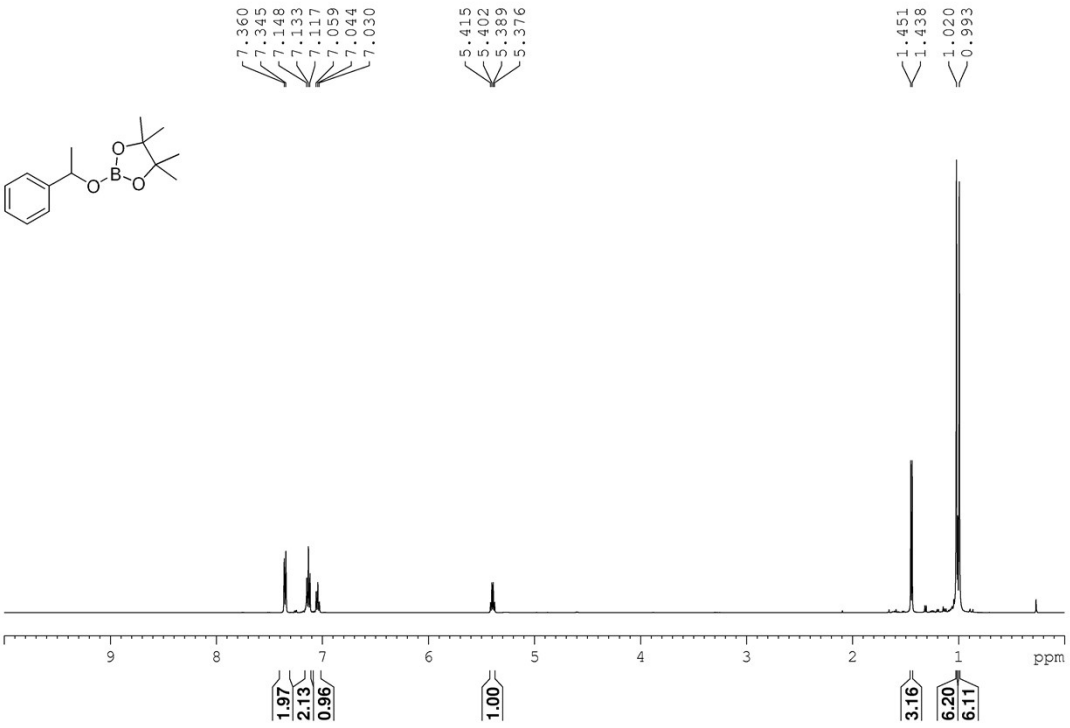
2p:

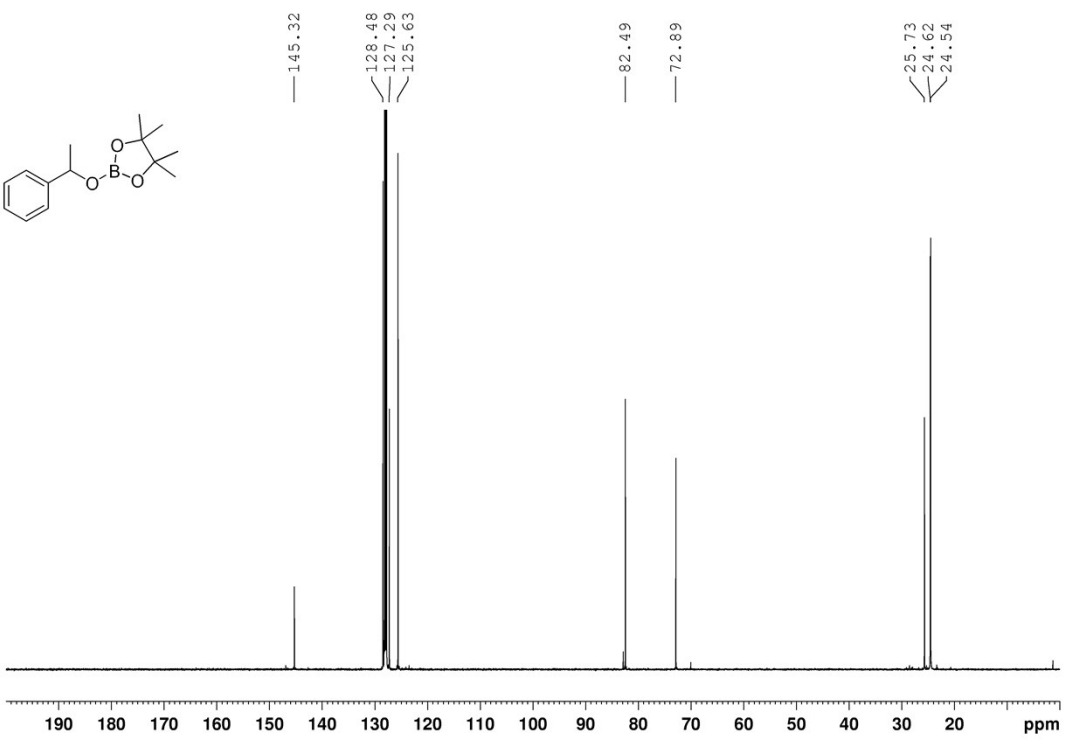

7.250
4.899
1.030
9
8
7
6
5
4
3
2
1
ppm
4.00
4.04
24.14

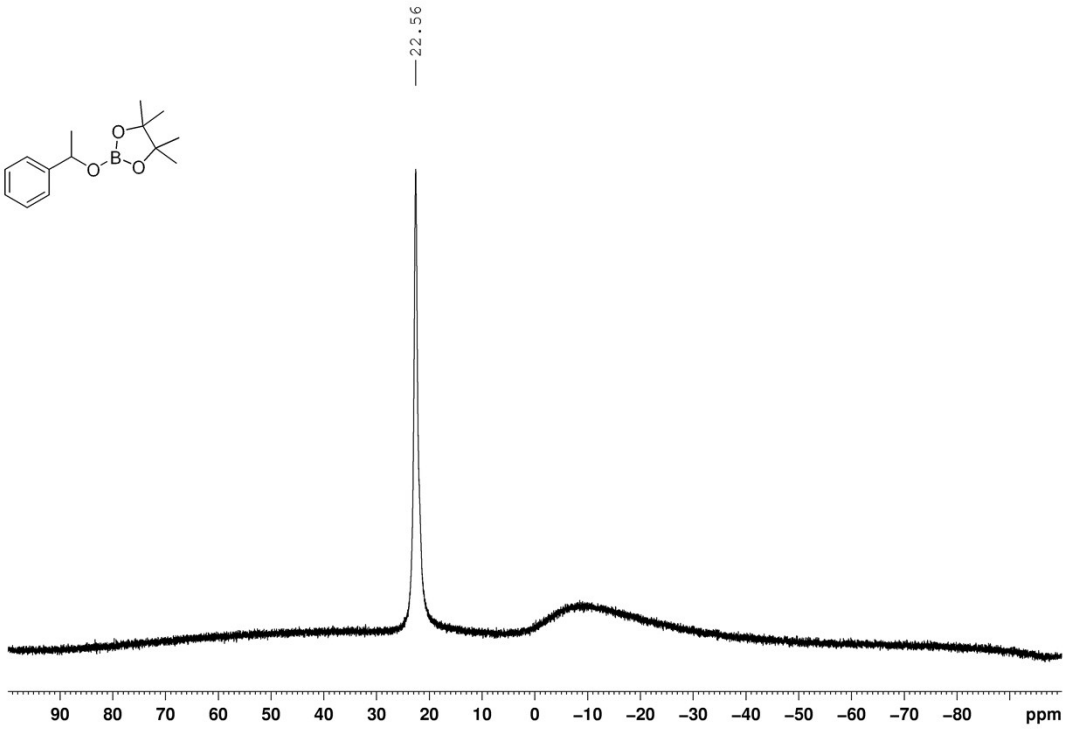

139.08
127.06
82.68
66.70
24.64
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.74
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

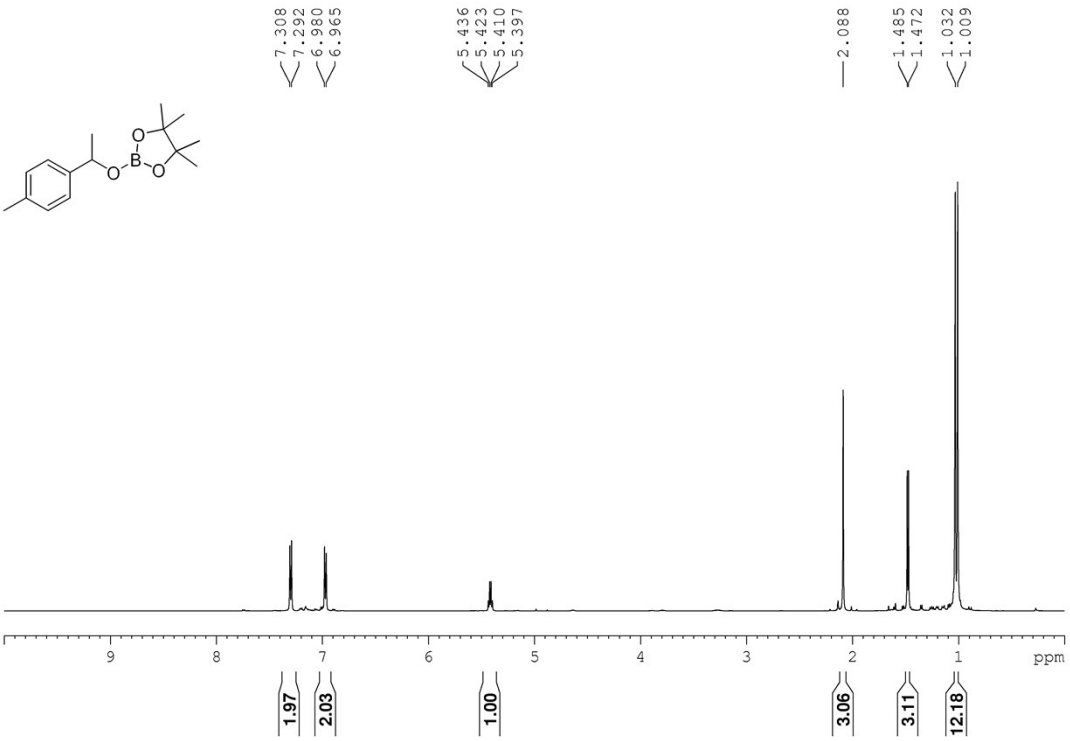
4a:

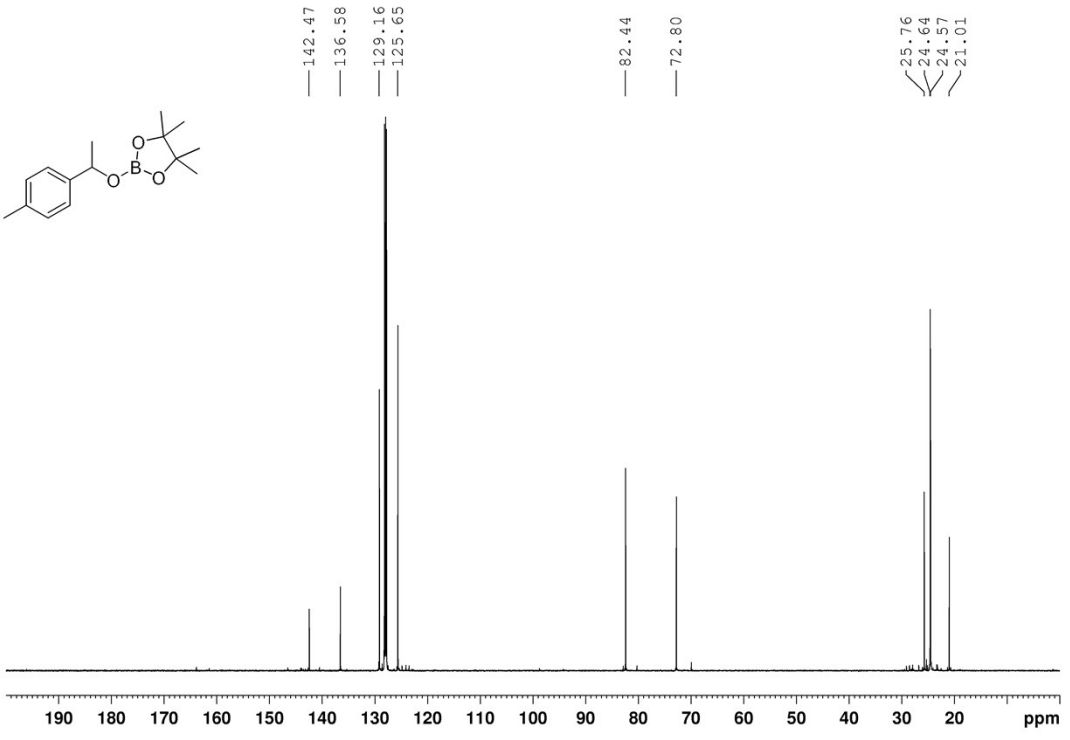

7.360
7.345
7.148
7.133
7.117
7.059
7.044
7.030
5.415
5.402
5.389
5.376
1.451
1.438
1.020
0.993
ppm
1.97
2.13
0.96
1.00
3.16
6.20
6.11

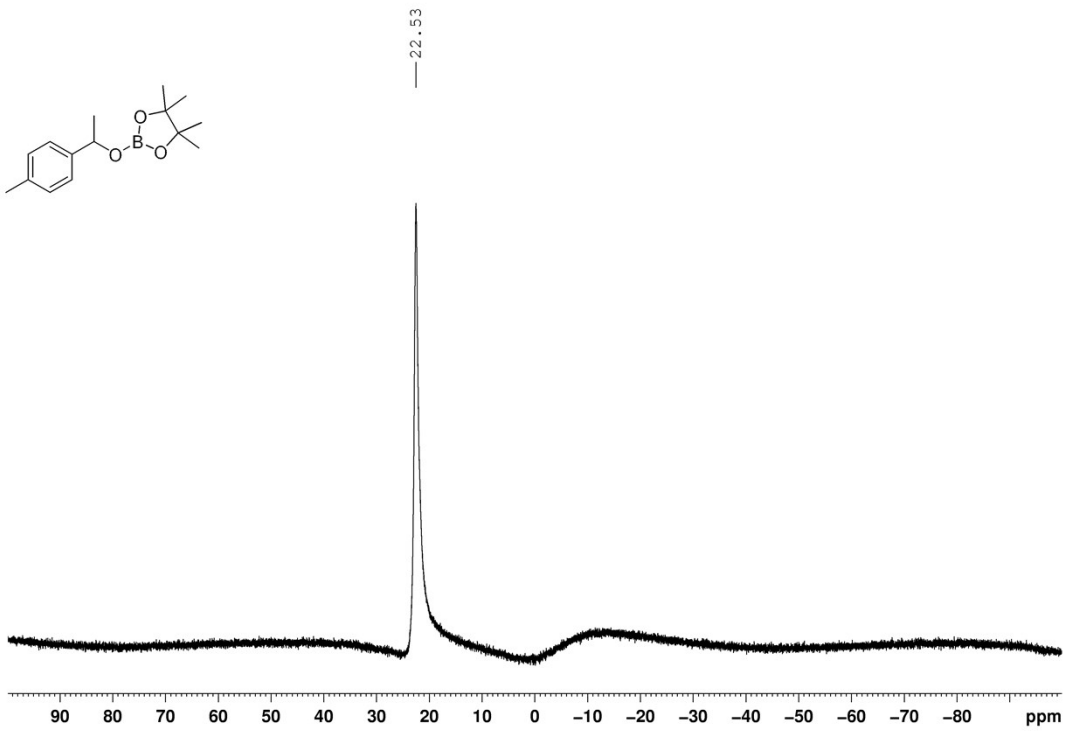

145.32
128.48
127.29
125.63
82.49
72.89
25.73
24.62
24.54
ppm


22.56
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

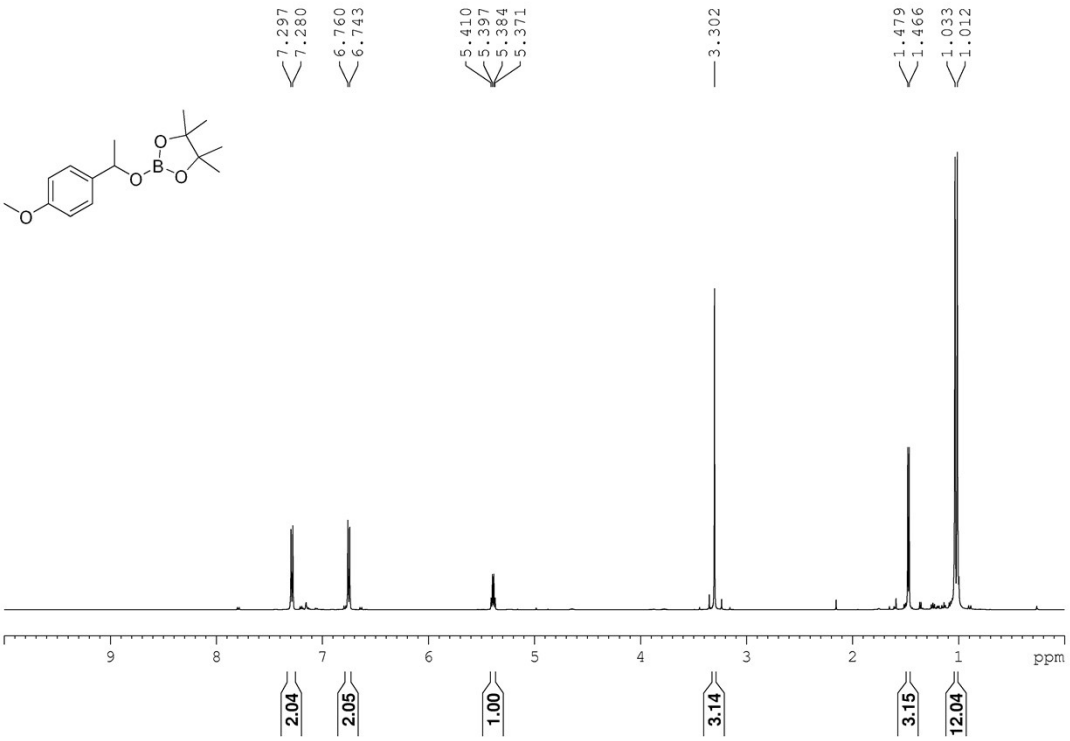
4b:

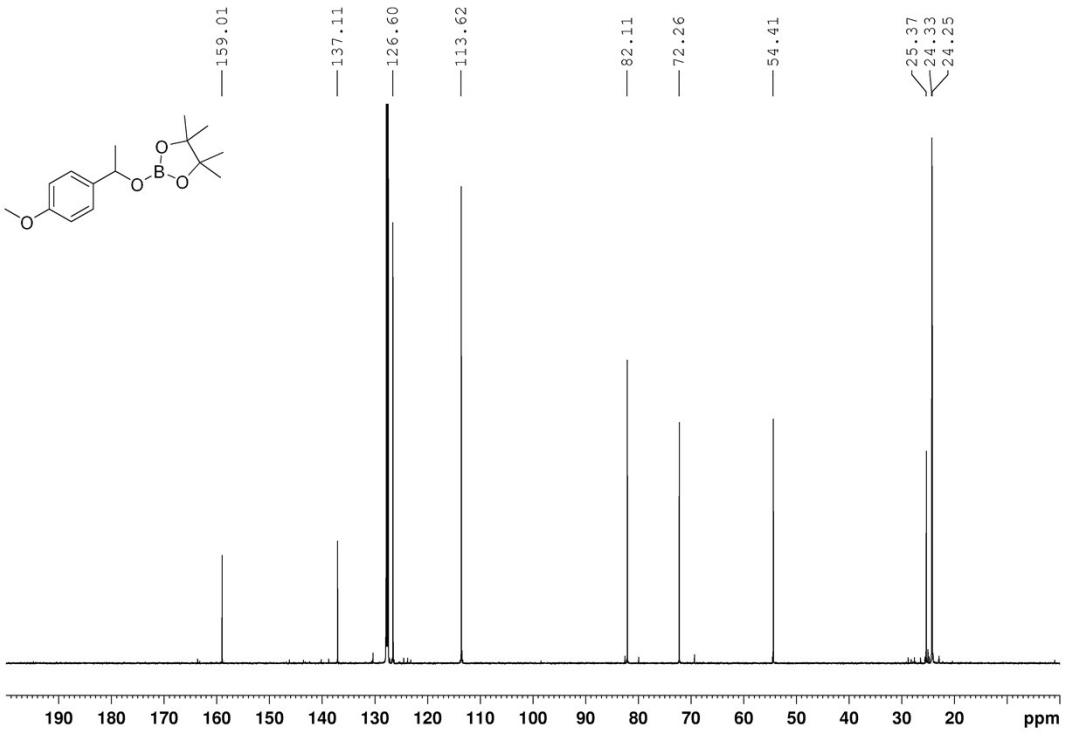

7.308
7.292
6.980
6.965
5.436
5.423
5.410
5.397
2.088
1.485
1.472
1.032
1.009
1.97
2.03
1.00
3.06
3.11
12.18
ppm

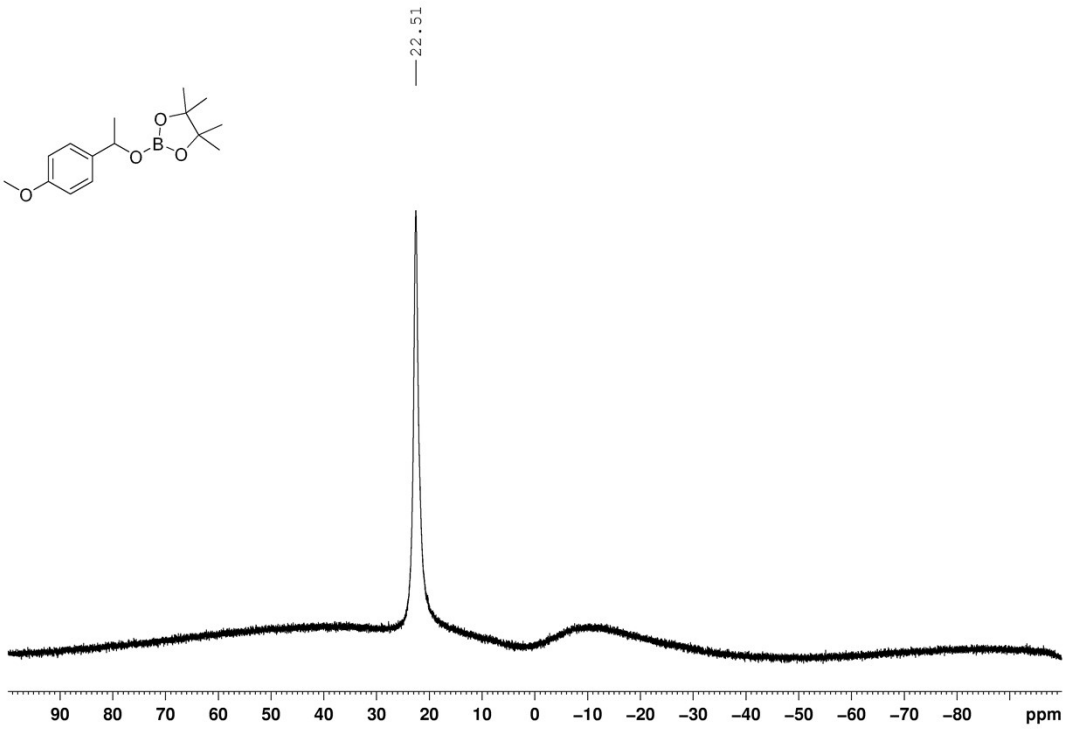

142.47
136.58
129.16
125.65
82.44
72.80
25.76
24.64
24.57
21.01
ppm


22.53
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

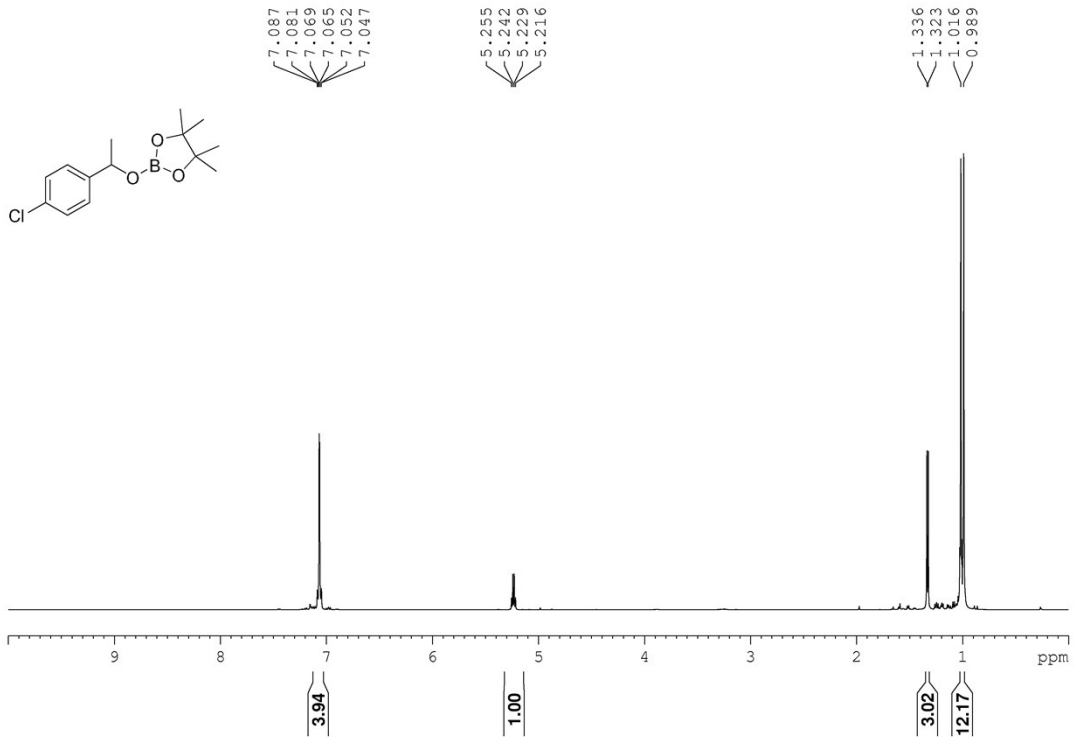
4c:

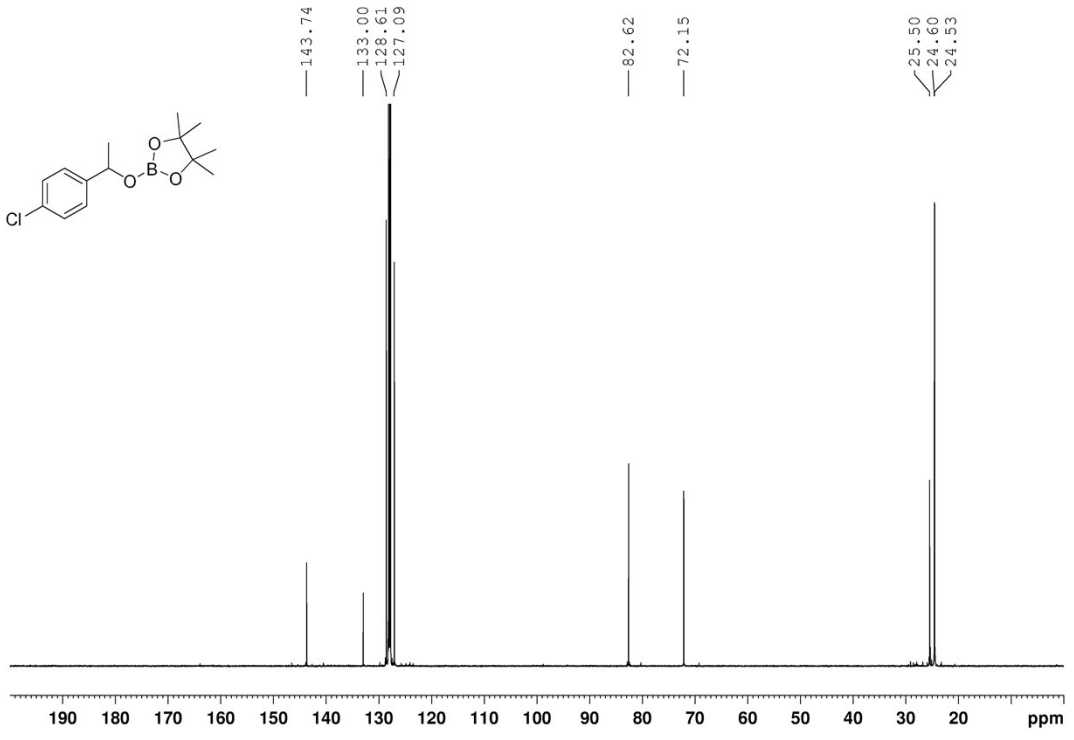

7.297
7.280
6.760
6.743
5.410
5.397
5.384
5.371
3.302
1.479
1.466
1.033
1.012
9
8
7
6
5
4
3
2
1
ppm
2.04
2.05
1.00
3.14
3.15
12.04

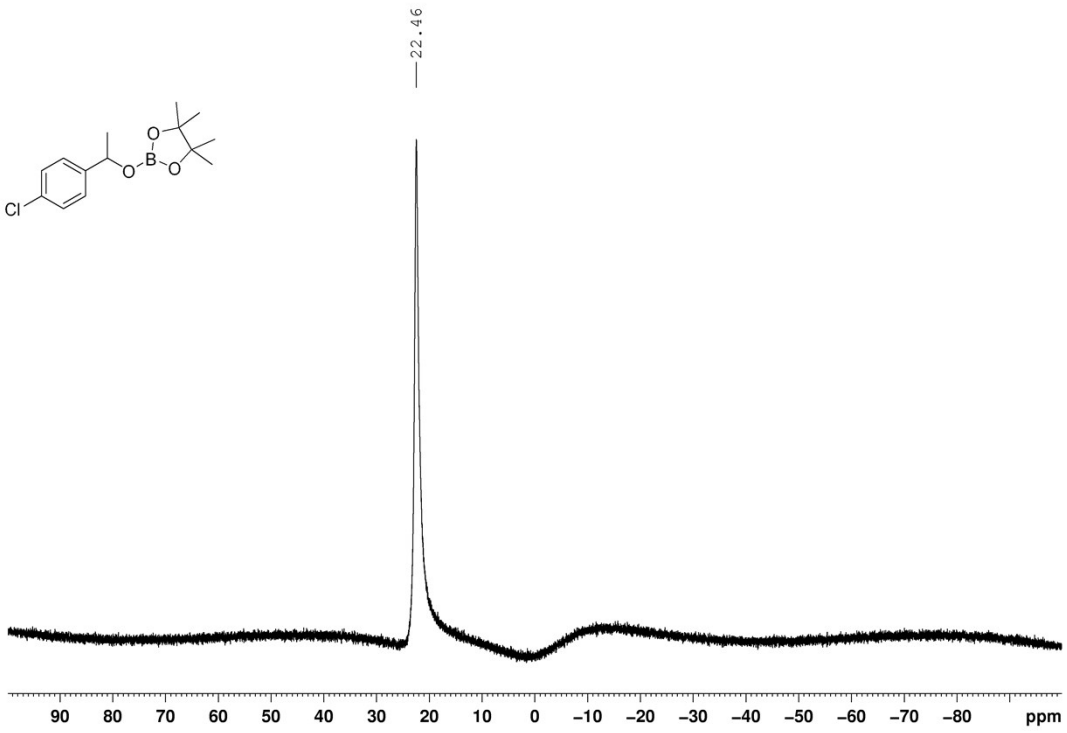

159.01
137.11
126.60
113.62
82.11
72.26
54.41
25.37
24.33
24.25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.51
O
B
O
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

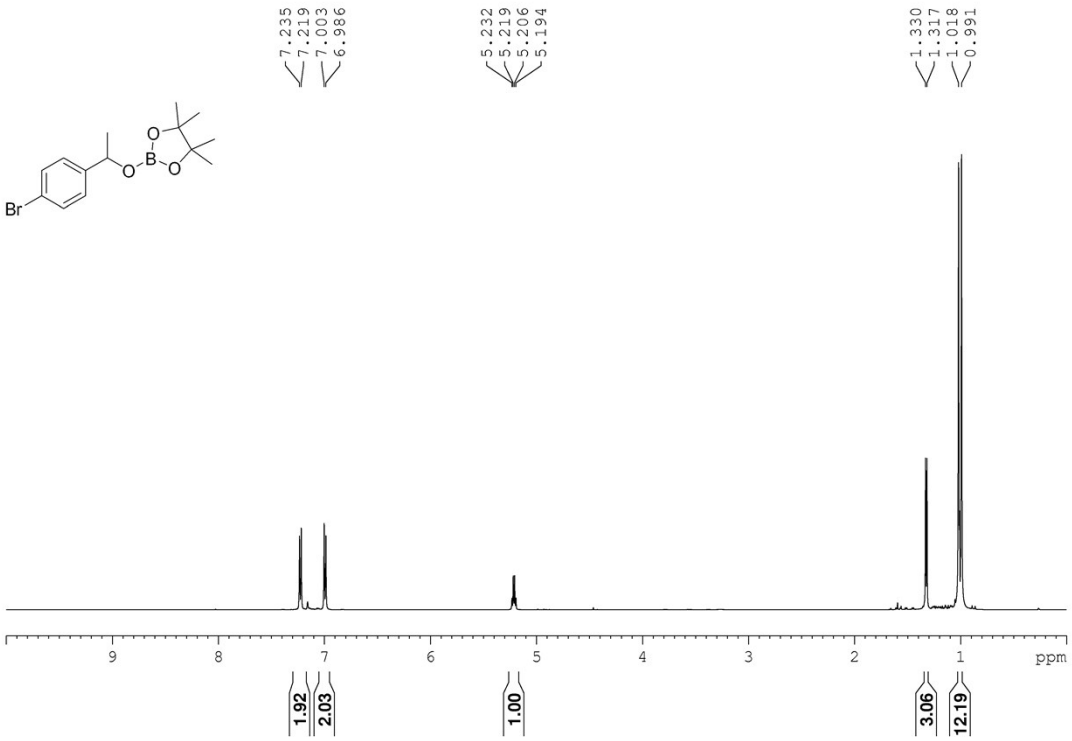
4d:

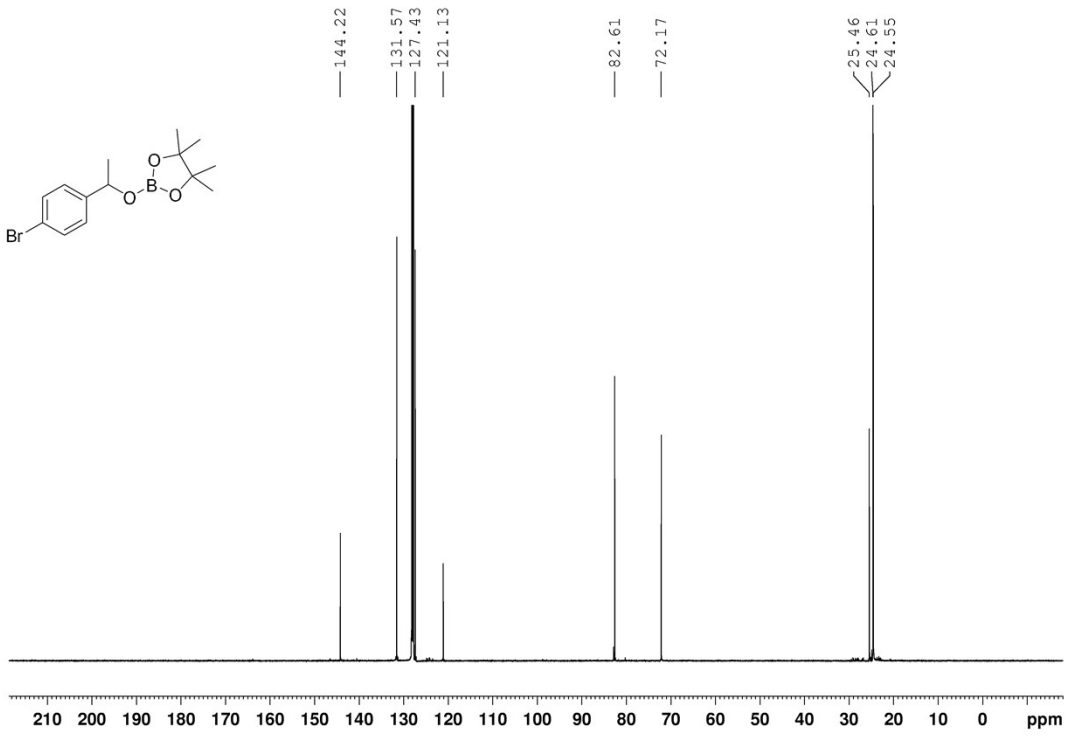

7.087
7.081
7.069
7.065
7.052
7.047
5.255
5.242
5.229
5.216
1.336
1.323
1.016
0.989
Cl
O
B
O
O
9
8
7
6
5
4
3
2
1
ppm
3.94
1.00
3.02
12.17

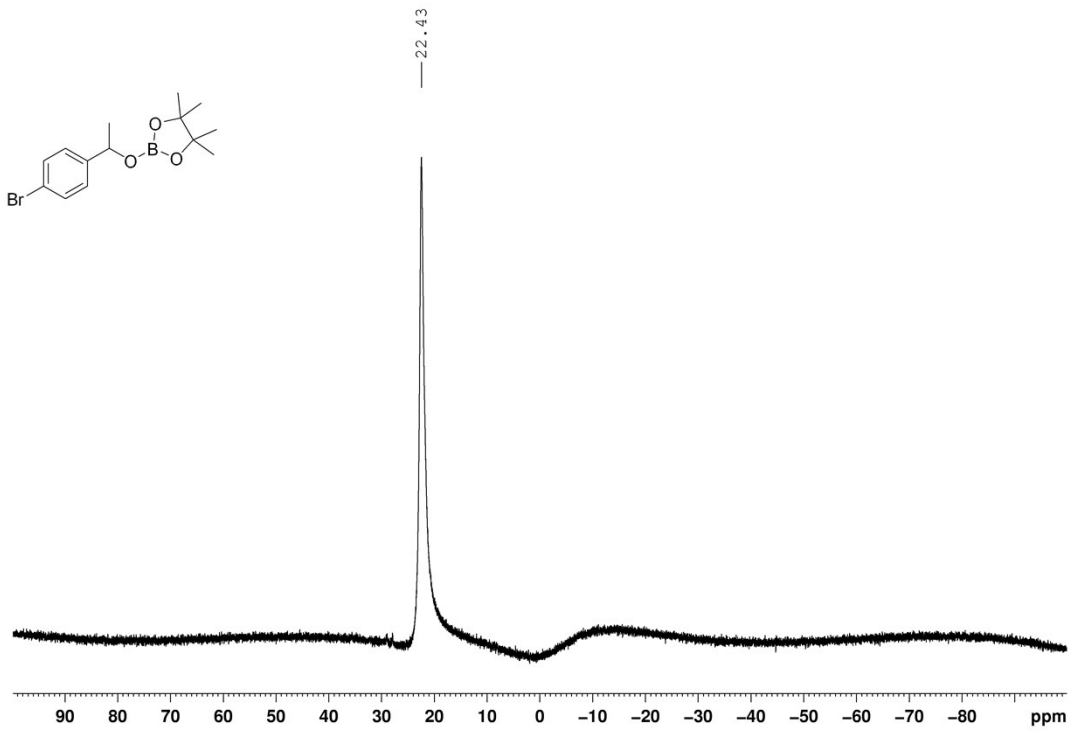

143.74
133.00
128.61
127.09
82.62
72.15
25.50
24.60
24.53
Cl
O
B
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.46
Cl
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

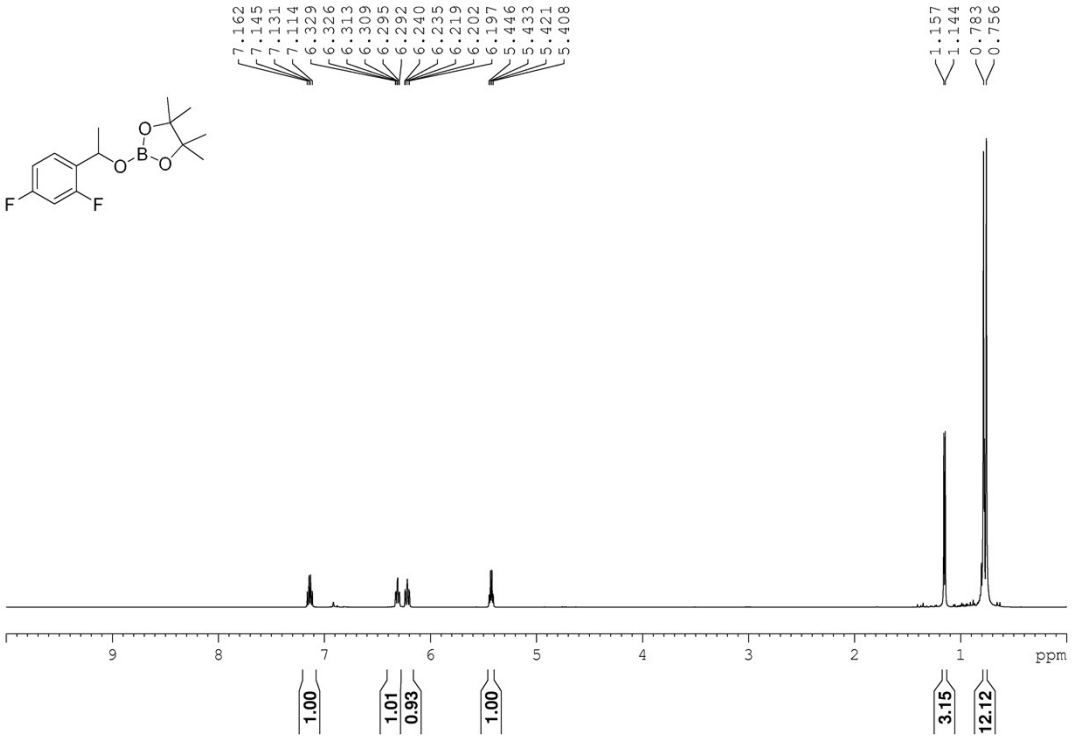
4e:

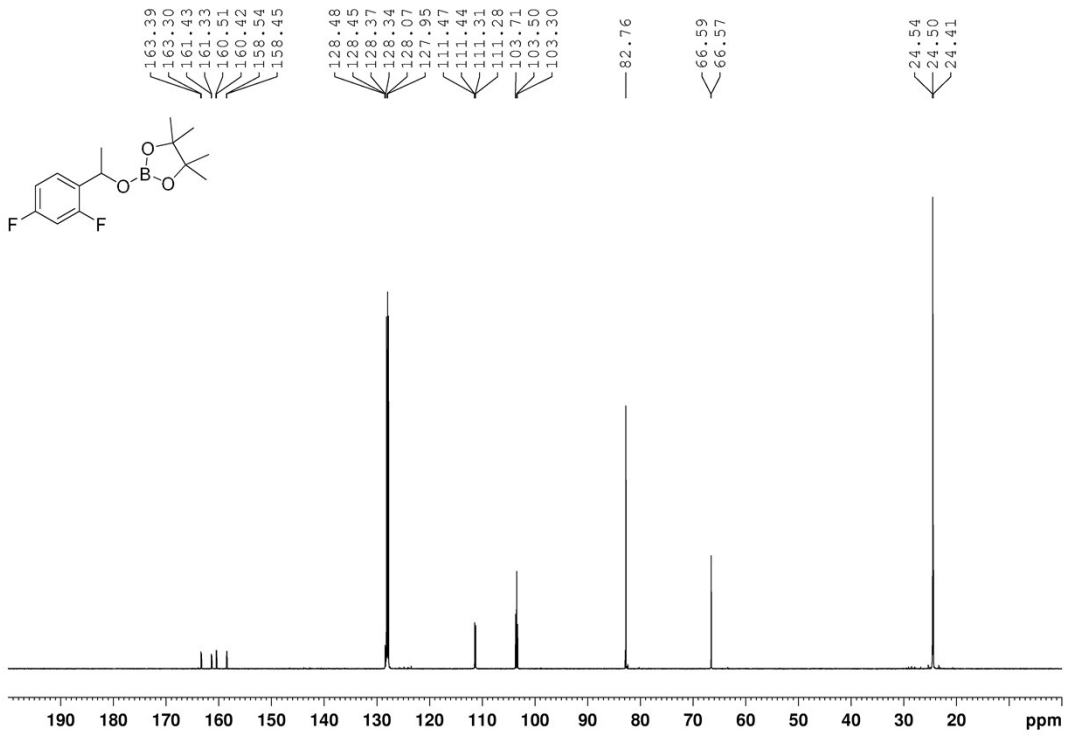

7.235
7.219
7.003
6.986
5.232
5.219
5.206
5.194
1.330
1.317
1.018
0.991
Br
ppm
1.92
2.03
1.00
3.06
12.19

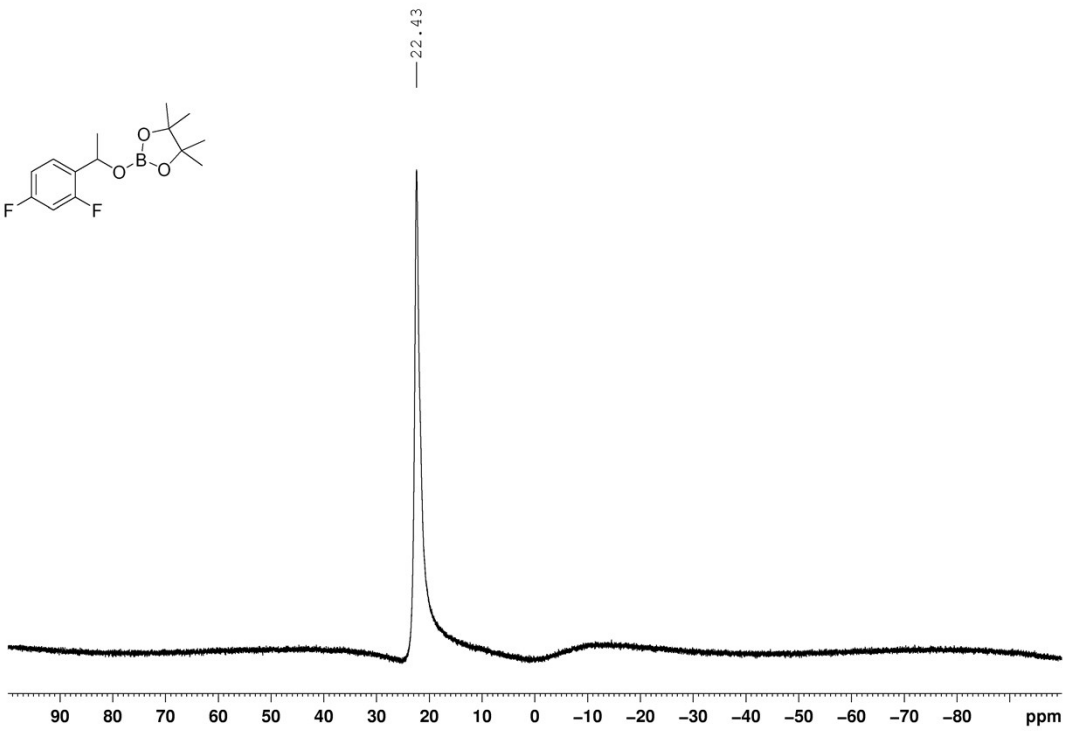

144.22
131.57
127.43
121.13
82.61
72.17
25.46
24.61
24.55
Br
ppm


22.43
Br
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

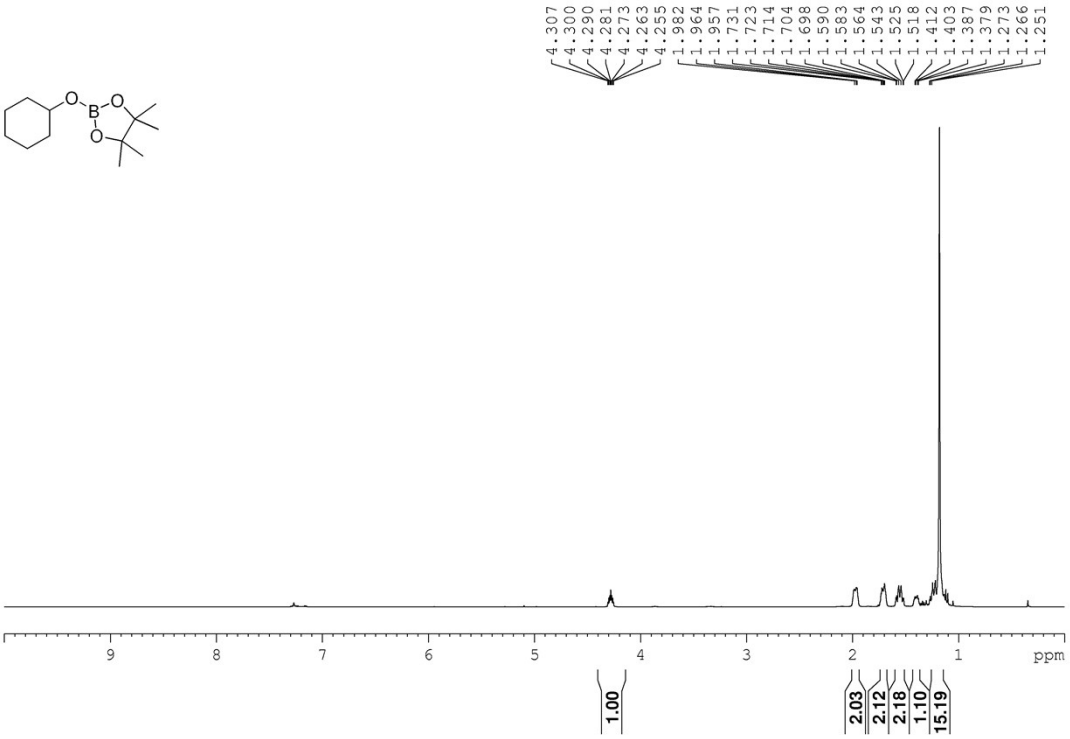
4f:

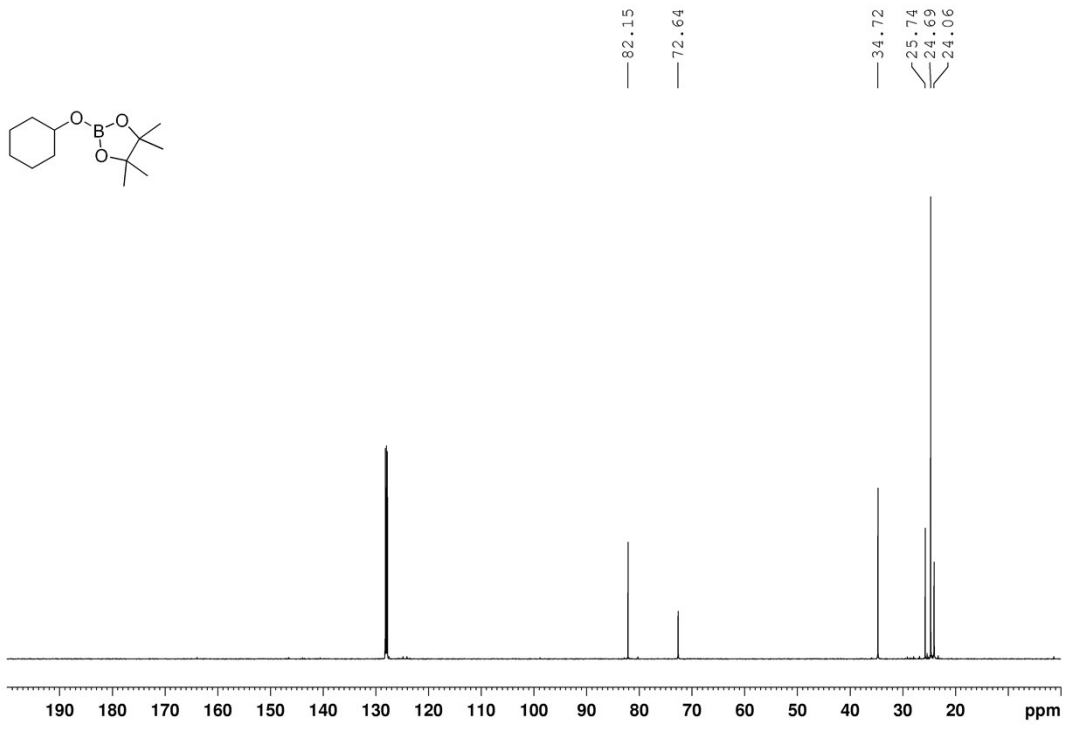

7.162
7.145
7.131
7.114
6.329
6.326
6.313
6.309
6.295
6.292
6.240
6.235
6.219
6.202
6.197
5.446
5.433
5.421
5.408
1.157
1.144
0.783
0.756
O
B
O
O
F
F
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
0.93
1.00
3.15
12.12

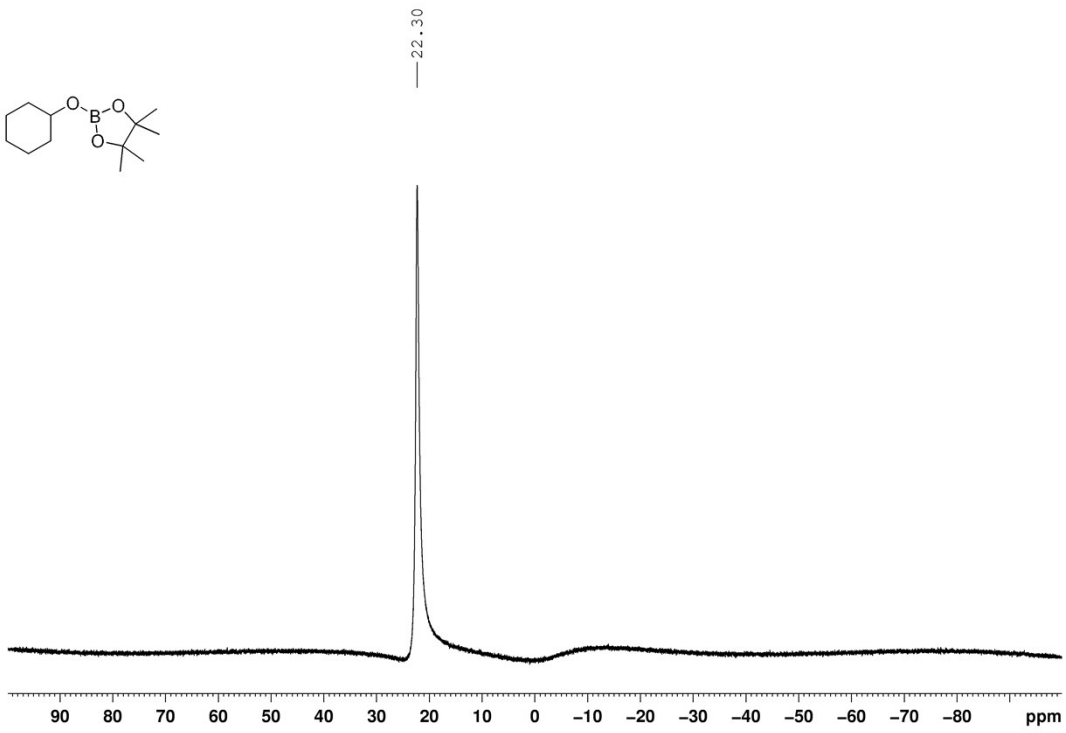

163.39
163.30
161.43
161.33
160.51
160.42
158.54
158.45
128.48
128.45
128.37
128.34
128.07
127.95
111.47
111.44
111.31
111.28
103.71
103.50
103.30
82.76
66.59
66.57
24.54
24.50
24.41
O
B
O
O
F
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.43
O
B
O
O
F
F
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

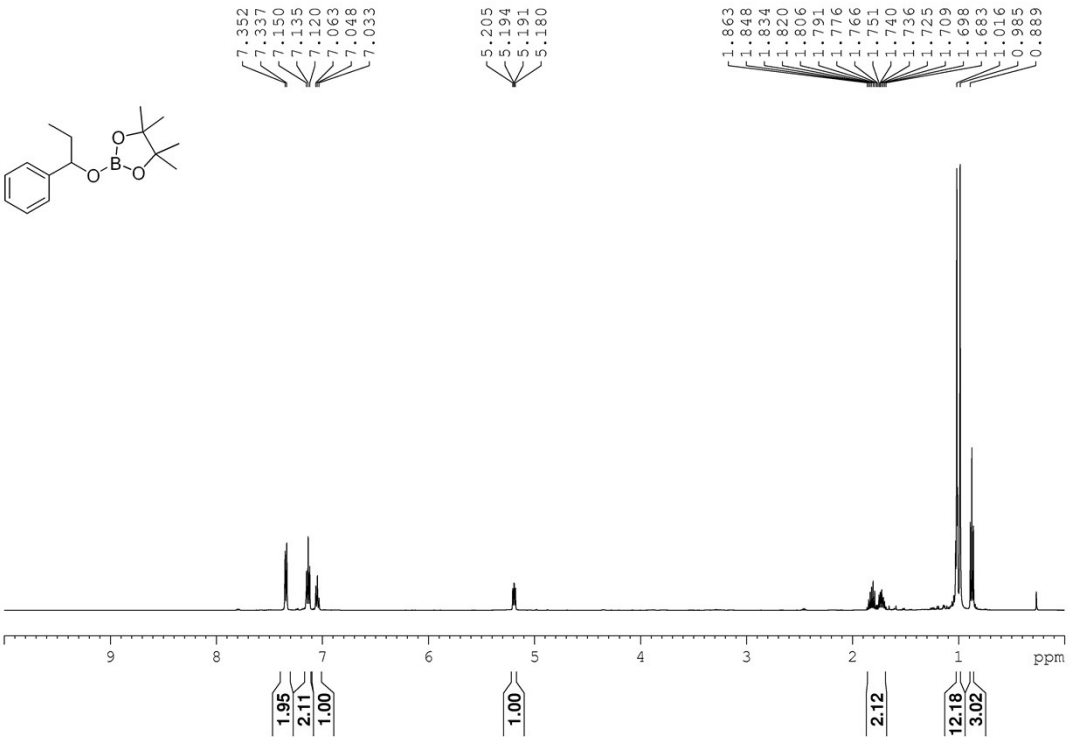
4g:

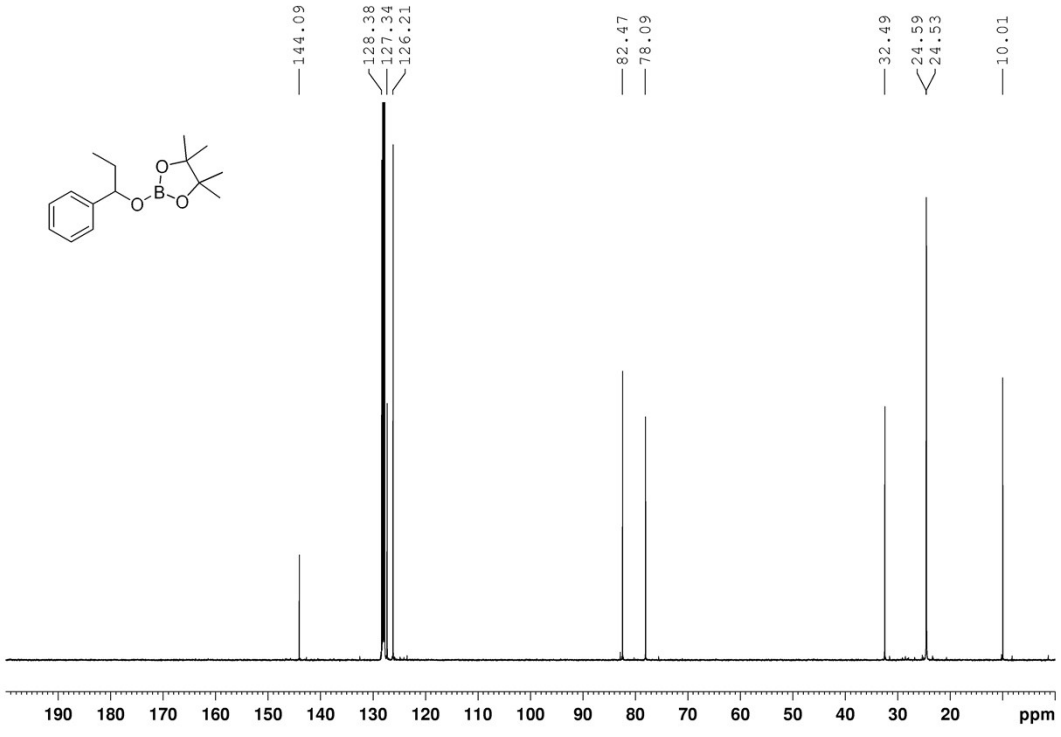

4.307
4.300
4.290
4.281
4.273
4.263
4.255
1.982
1.964
1.957
1.731
1.723
1.714
1.704
1.698
1.590
1.583
1.564
1.543
1.525
1.518
1.412
1.403
1.387
1.379
1.273
1.266
1.251
O
B
O
O
9
8
7
6
5
4
3
2
1
ppm
1.00
2.03
2.12
2.18
1.10
15.19

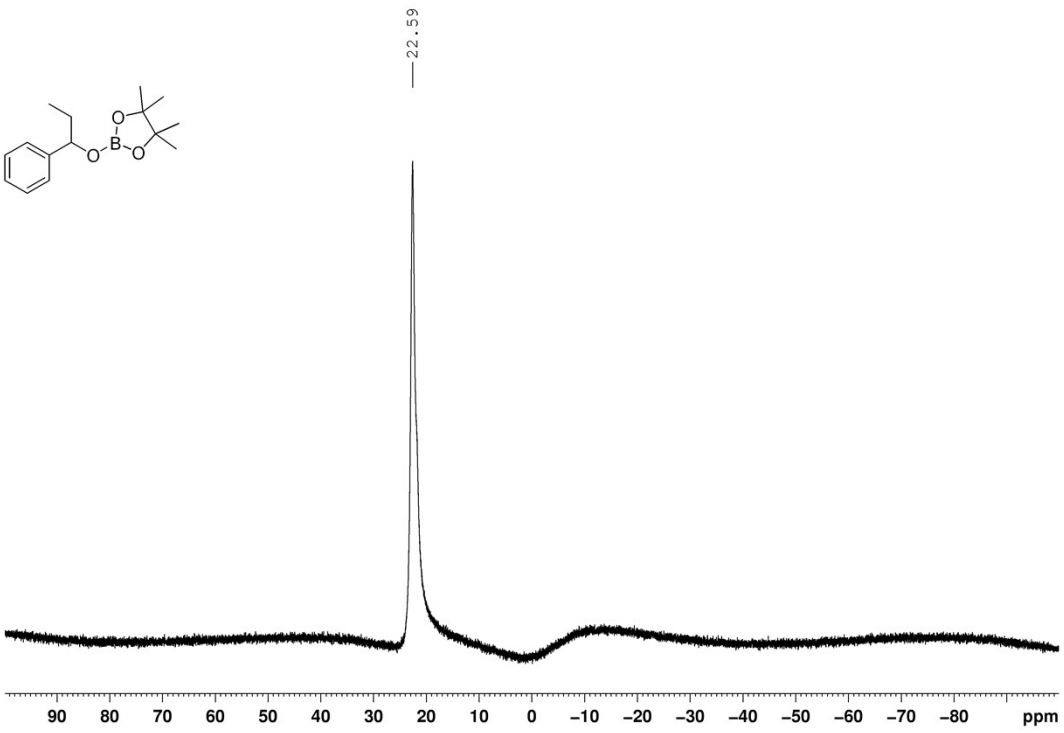

82.15
72.64
34.72
25.74
24.69
24.06
O
B
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


22.30
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

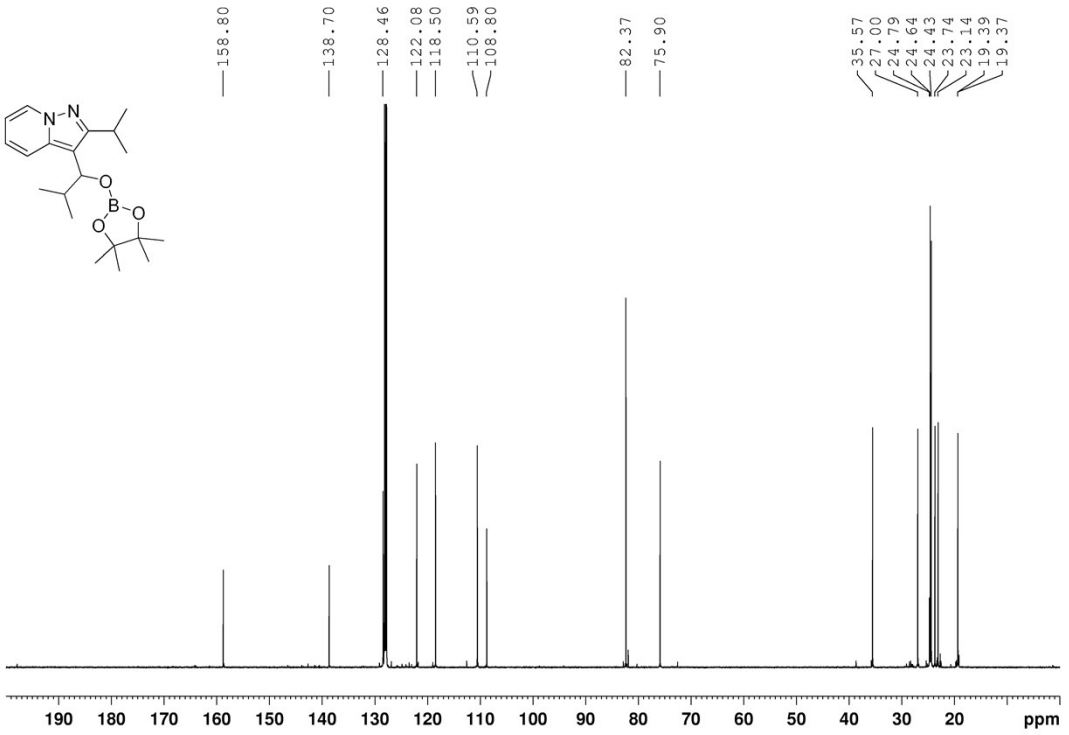
4h:

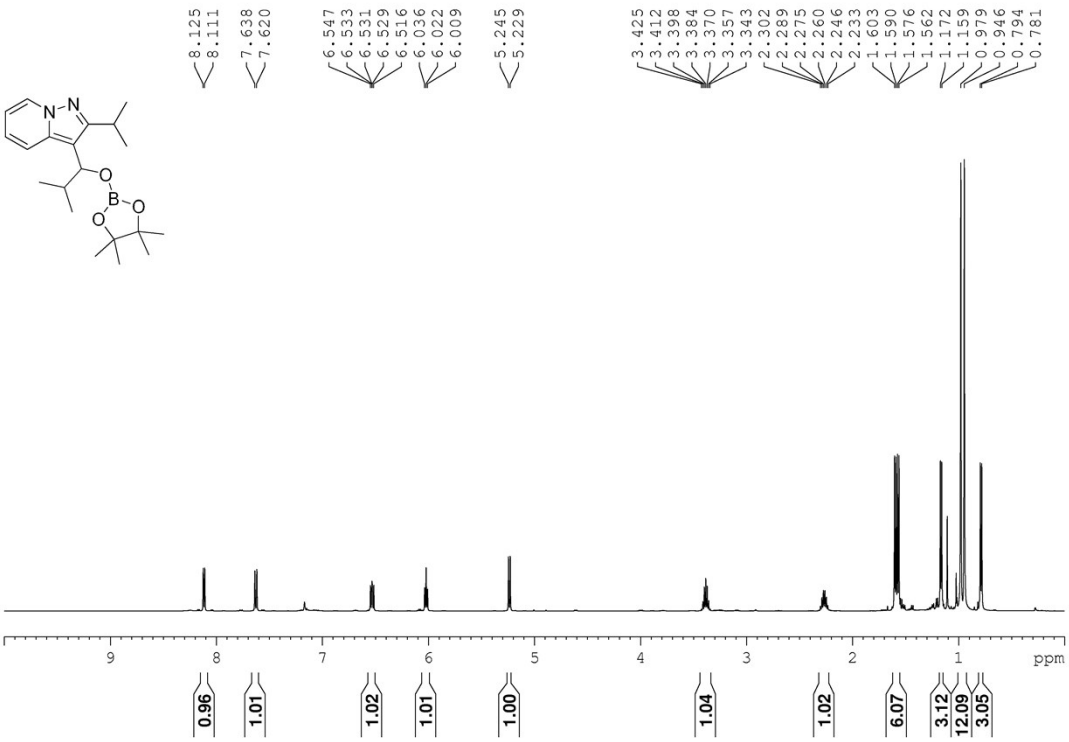

7.352
7.337
7.150
7.135
7.120
7.063
7.048
7.033
5.205
5.194
5.191
5.180
1.863
1.848
1.834
1.820
1.806
1.791
1.776
1.766
1.751
1.740
1.736
1.725
1.709
1.698
1.683
1.016
0.985
0.889
ppm
1.95
2.11
1.00
1.00
2.12
12.18
3.02

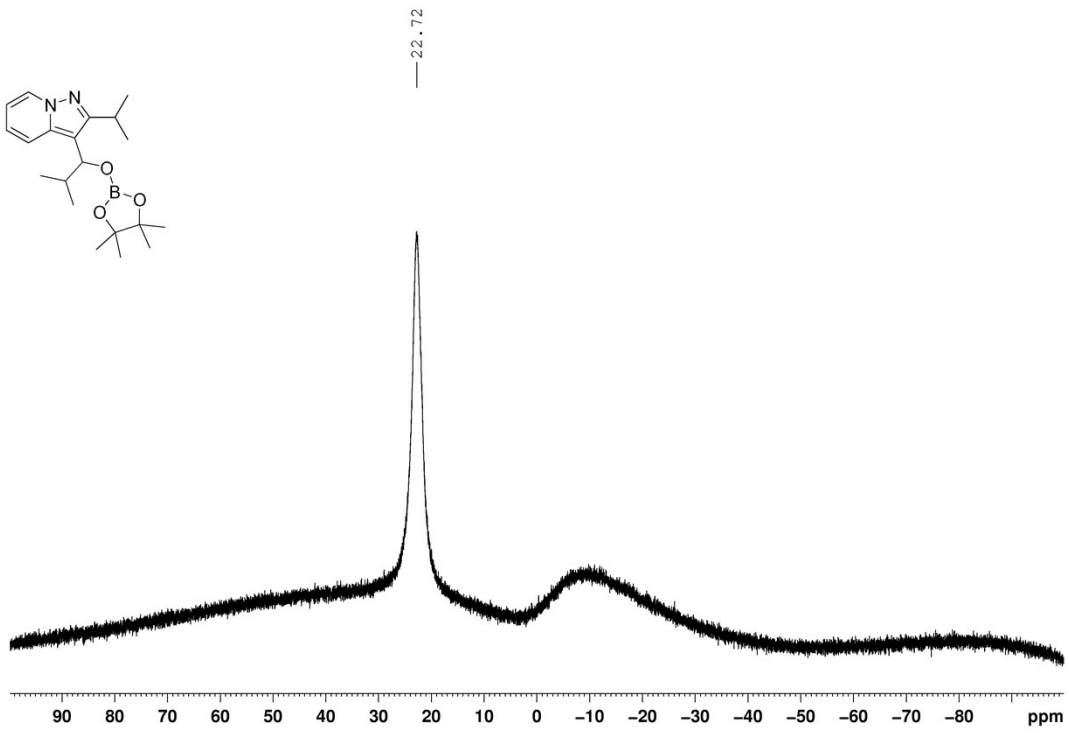

144.09
128.38
127.34
126.21
82.47
78.09
32.49
24.59
24.53
10.01
ppm


22.59
O
B
O
O
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

4i:


158.80
138.70
128.46
122.08
118.50
110.59
108.80
82.37
75.90
35.57
27.00
24.79
24.64
24.43
23.74
23.14
19.39
19.37
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.125
8.111
7.638
7.620
6.547
6.533
6.531
6.529
6.516
6.036
6.022
6.009
5.245
5.229
3.425
3.412
3.398
3.384
3.370
3.357
3.343
2.302
2.289
2.275
2.260
2.246
2.233
1.603
1.590
1.576
1.562
1.172
1.159
0.979
0.946
0.794
0.781
9 8 7 6 5 4 3 2 1 ppm
0.96
1.01
1.02
1.01
1.00
1.04
1.02
6.07
3.12
12.09
3.05


22.72
N
N
O
B
O
O
90
80
70
60
50
40
30
20
10
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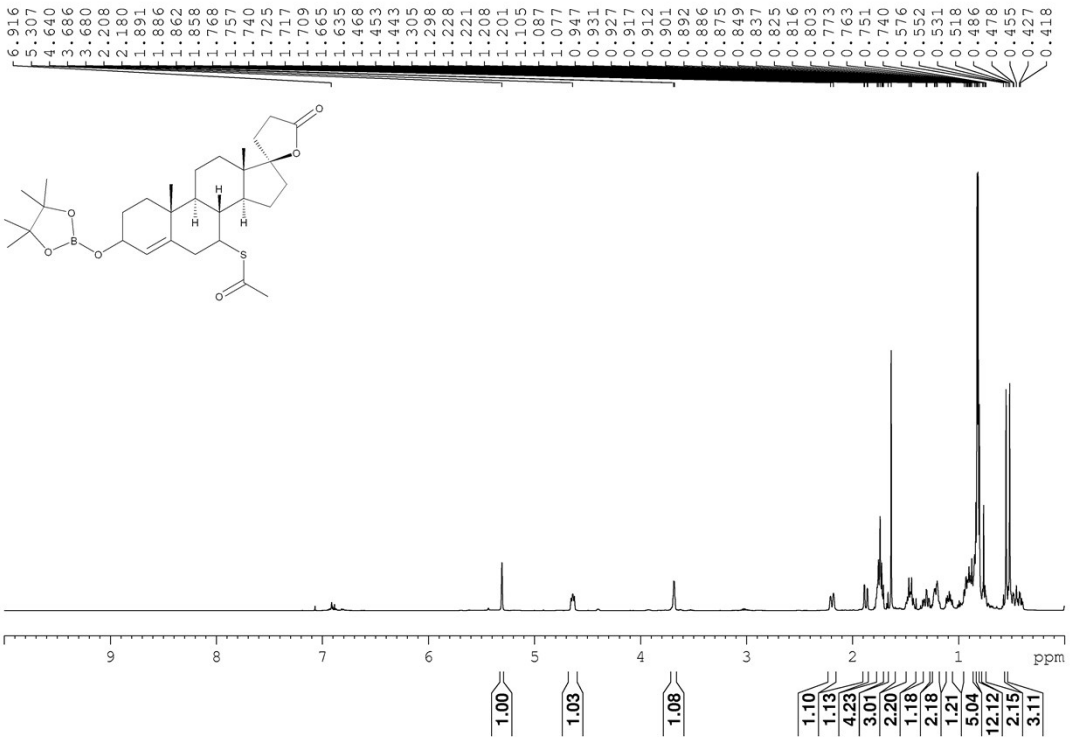
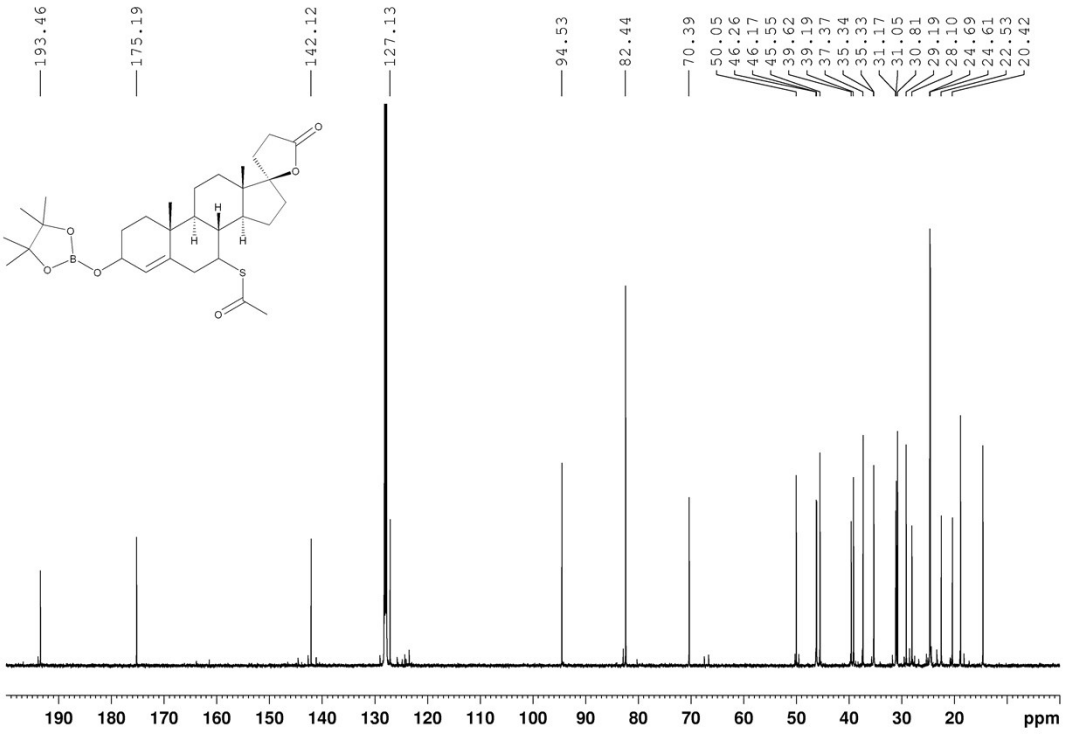
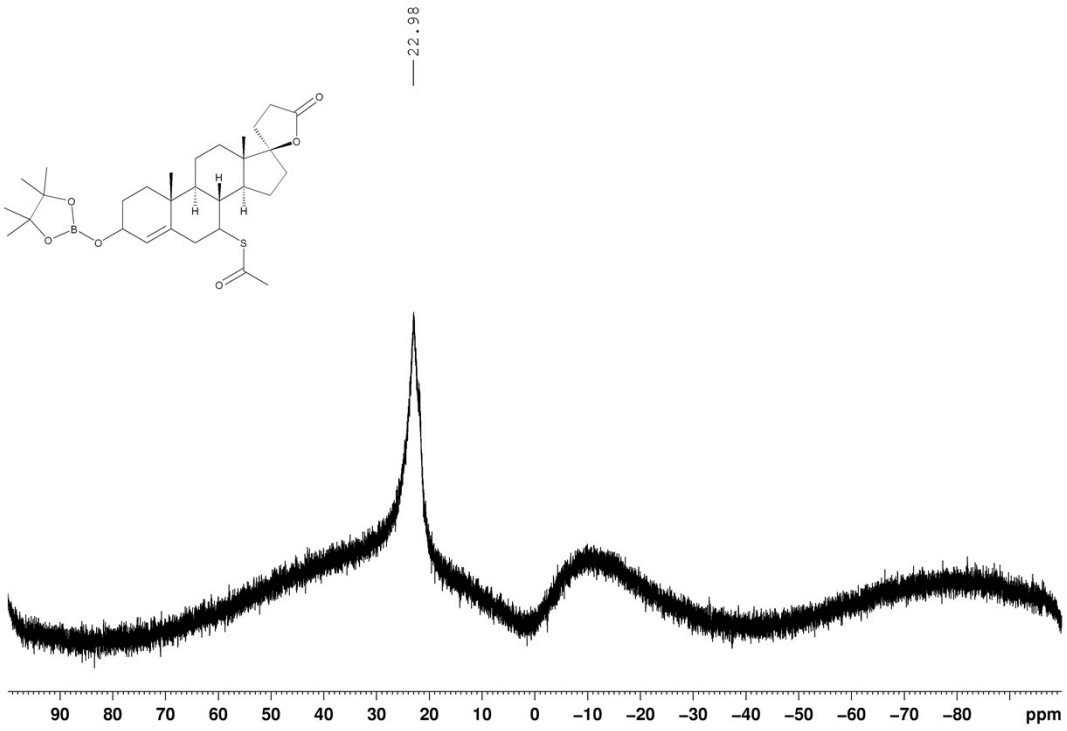
−10
−20
−30
−40
−50
−60
−70
−80
ppm

4j:


6.916
5.307
4.640
3.686
3.680
2.208
2.180
1.891
1.886
1.862
1.858
1.768
1.757
1.740
1.725
1.717
1.709
1.665
1.635
1.468
1.453
1.443
1.305
1.298
1.228
1.221
1.208
1.201
1.105
1.087
1.077
0.947
0.931
0.927
0.917
0.912
0.901
0.892
0.886
0.875
0.849
0.837
0.825
0.816
0.803
0.773
0.763
0.751
0.740
0.576
0.552
0.531
0.518
0.486
0.478
0.455
0.427
0.418
ppm
1.00
1.03
1.08
1.10
1.13
4.23
3.01
2.20
1.18
2.18
1.21
5.04
12.12
2.15
3.11


193.46
175.19
142.12
127.13
94.53
82.44
70.39
50.05
46.26
46.17
45.55
39.62
39.19
37.37
35.34
35.33
31.17
31.05
30.81
29.19
28.10
24.69
24.61
22.53
20.42
ppm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90
80
70
60
50
40
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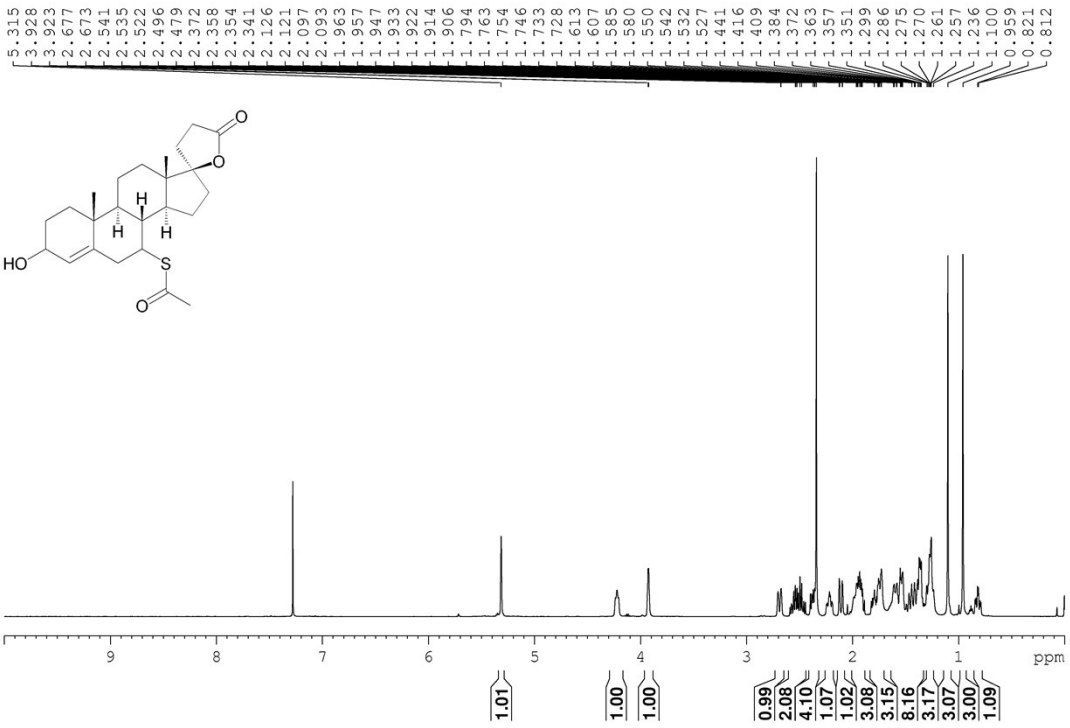
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

5j: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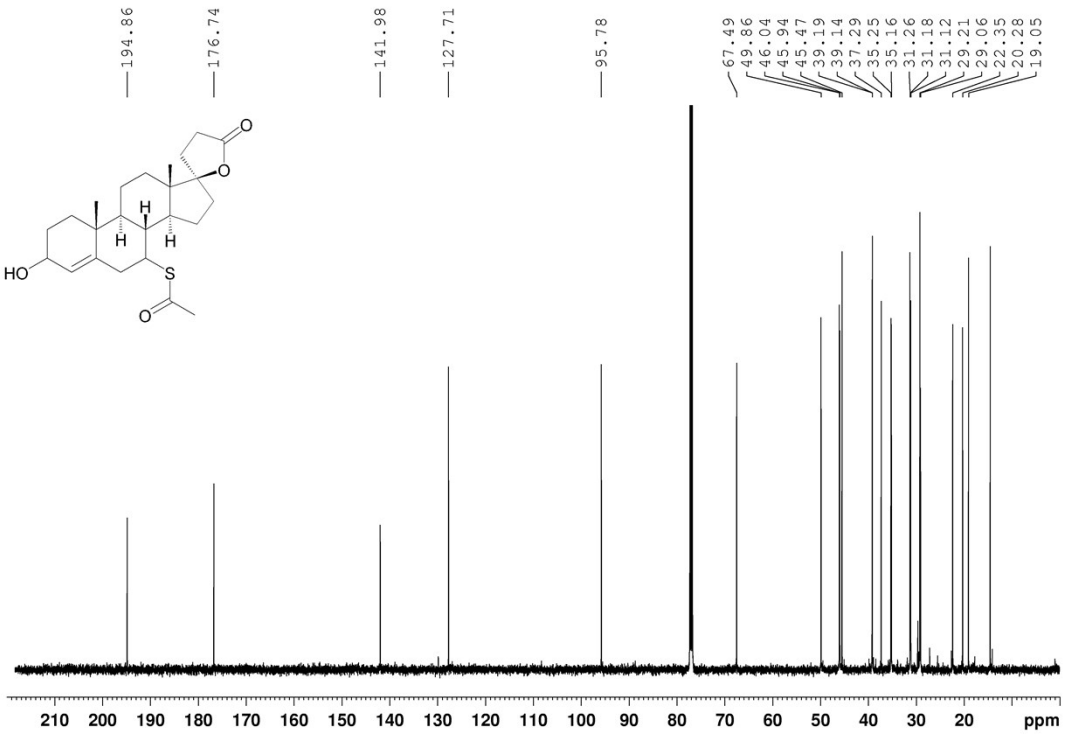
3.928
3.923
2.677
2.673
2.541
2.535
2.522
2.496
2.479
2.372
2.358
2.354
2.341
2.126
2.121
2.097
2.093
1.963
1.957
1.947
1.933
1.922
1.914
1.906
1.794
1.763
1.754
1.746
1.733
1.728
1.613
1.607
1.585
1.580
1.550
1.542
1.532
1.527
1.441
1.416
1.409
1.384
1.372
1.363
1.357
1.351
1.299
1.286
1.275
1.270
1.261
1.257
1.236
1.100
0.959
0.821
0.812
HO
O
O
H
H
H
S
O
9
8
7
6
5
4
3
2
1
ppm
1.01
1.00
1.00
0.99
2.08
4.10
1.07
1.02
3.08
3.15
8.16
3.17
3.07
3.00
1.09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176.74
141.98
127.71
95.78
67.49
49.86
46.04
45.94
45.47
39.19
39.14
37.29
35.25
35.16
31.26
31.18
31.12
29.21
29.06
22.35
20.28
19.05
HO
O
O
H
H
H
S
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm