Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supporting Information

An experimental and computational study for a Pd(II) catalysed hydroboration and reductive amination reaction of carbonyl compounds

Shreya Mahato, Parveen Rawal, Devadkar Ajitaro Kisan, Mayank Joshi, Angshuman Roy Choudhury, Bhaskar Biswas,* Puneet Gupta* and Tarun K. Panda*

Table TS1. Crystallographic data and refinement parameters of Pd complex **1**.

Crystal Parameters	**1**
CCDC No.	2116643
Empirical formula	$C_{20}H_{14}N_2O_2Pd$
Formula weight	420.73
T (K)	296
λ (Å)	0.71075
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 5.3533(4) Å, b = 16.8012(8) Å, c = 17.7277(12) Å, α = 90°, β = 90°, γ = 90°
V ($Å^3$)	1594.46(18)
Z, calculated density (mg/m^3)	4, 1.753
Absorption coefficient (mm^{-1})	1.180
F (000)	840
Theta range for data collection	2.598 to 32.763 deg
Limiting indices	$-7 \leq h \leq 6, -25 \leq k \leq 10, -25 \leq l \leq 23$,
Reflections collected/ unique	13717 /5493 [R(int) = 0.0923]
Completeness to theta	99.7%
Absorption correction	Multi-scan
Max. and min. transmission	0.899 and 0.745
Refinement method	Full-matrix least-squares on F2
Data/restrains/parameters	5358 / 0 / 226
Goodness-of-fit on F^2	0.971
Final R indices [I>=2σ (I)] R indices (all data)	R_1 = 0.0698, wR_2 = 0.1852

Largest diff. peak/hole (e Å^{-3})	-1.00 and 1.21

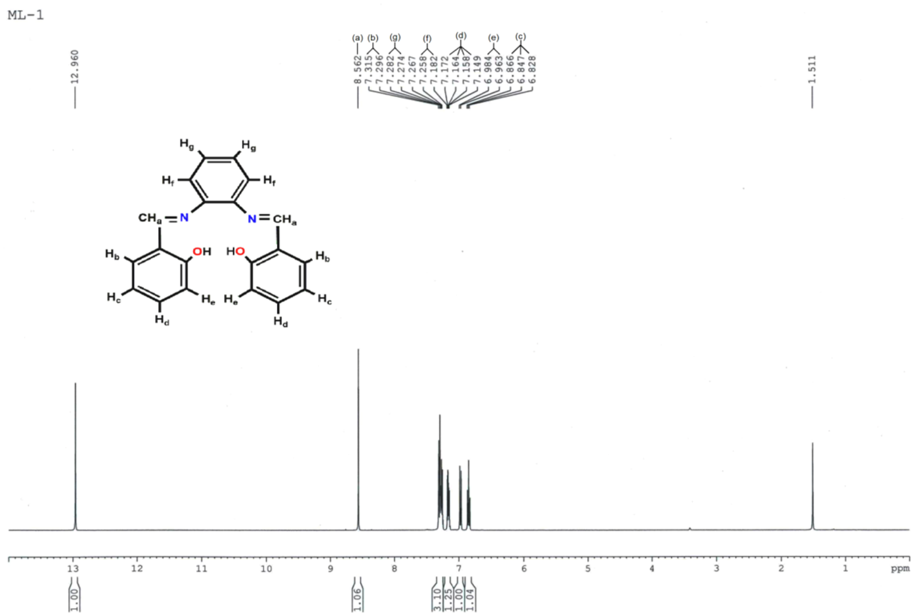


Fig. S1. ^{1}H NMR spectrum of the Schiff base ligand **H$_2$L** in CDCl$_3$.

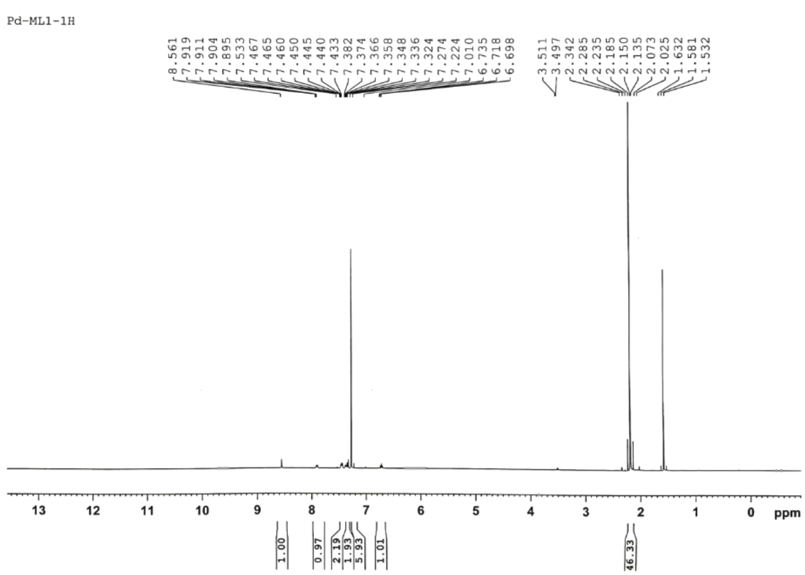


Fig. S2. ^{1}H NMR spectrum of the Palladium(II) complex **1** in $CDCl_3$.

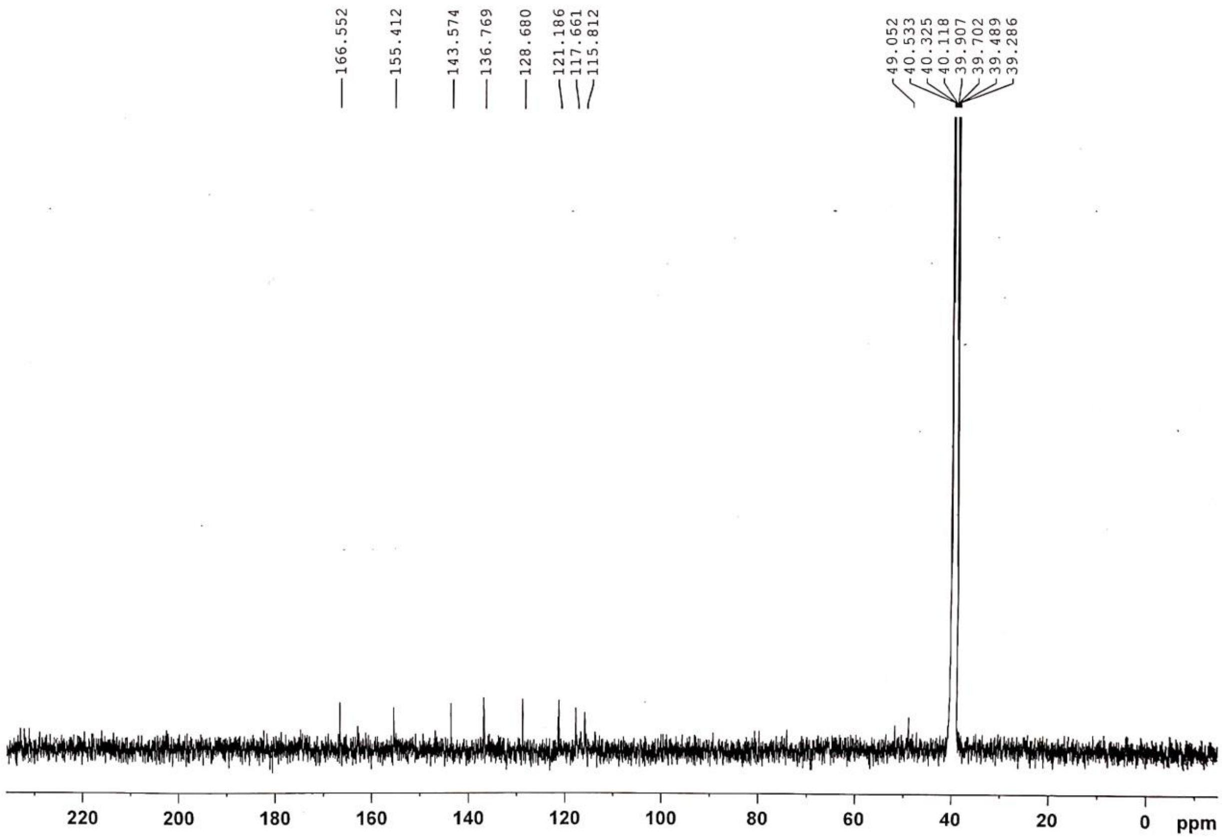


Fig. S3. $^{13}C\{^{1}H\}$ NMR spectrum of the Palladium(II) complex **1** in DMSO-d_6.

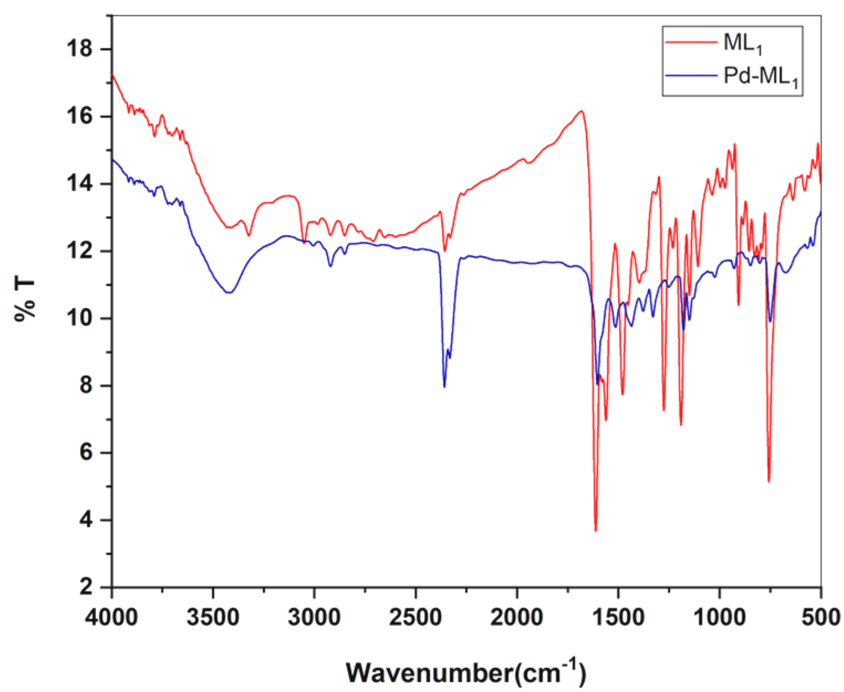


Fig S4. FT-IR spectra of the Schiff base and Pd(II) complex **1**.

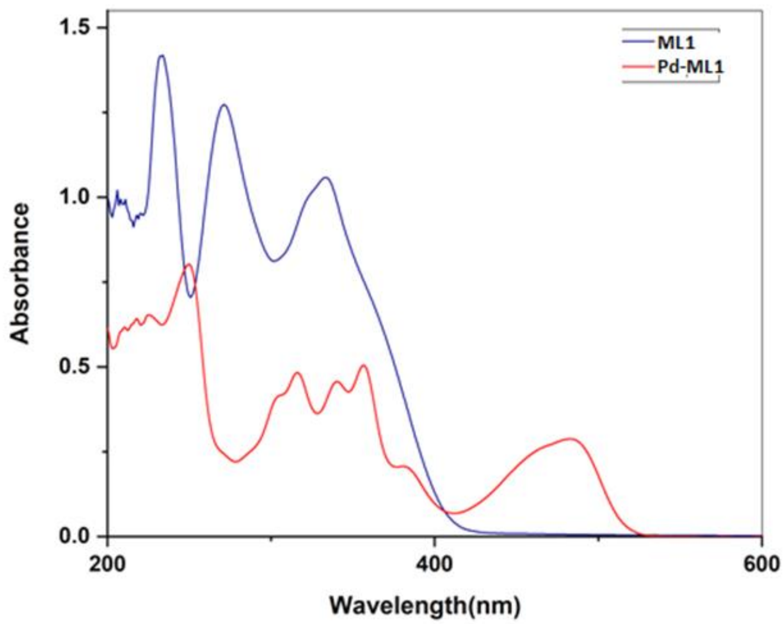
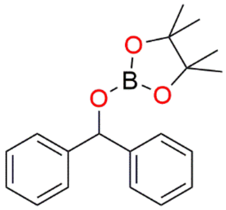


Fig S5. UV-Vis spectra of the Schiff base and Pd(II) complex **1** in MeCN medium.

A typical procedure for catalytic hydroboration of aldehydes and ketones (2a-5l).

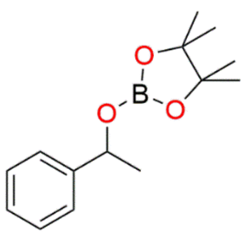
Hydroboration of aldehydes and ketones with HBpin was performed using the standard protocol. In the glove box, the Pd(II) catalyst **1** (1 mol %) was taken and the corresponding ketone or aldehyde (1.0 mmol) was added to a Schlenk tube followed by the addition of HBpin (1.0 mmol). The Schlenk tube was taken out and the reaction mixture was stirred in an oil bath at 60°C for 12 hours. The progress of the reaction was monitored using 1H NMR spectrum. The observation of a new CH_2 peak in the case of aldehyde and CH peak in the case of ketone indicated the conversion of the corresponding derivatives. The reaction was quenched by $CDCl_3$ and 1,3,5-trimethoxybenzene was introduced as internal standard. The products were characterised by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

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



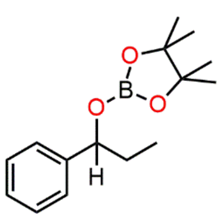
Yield: 96%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38 (m, 4H, Ar-H), 7.28 (m, 4H, Ar-H), 7.21 (m, 2H, Ar-H), 6.18 (s,1H, CH), 1.19 (s, 12H, Bpin-CH_3) ppm.^{11}B{^{1}H}NMR (128 MHz, $CDCl_3$): δ_B 22.30 ppm.^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ_C 143.2, 128.6, 128.3, 127.4, 126.6, 83.10, 78.0, 77.5, 76.8, 24.6 ppm. NMR data are in accordant with the literature.[15]

2-(1-phenylethoxy)4,4,5,5-tetramethyl-1,2,3-dioxaborolane (2b).



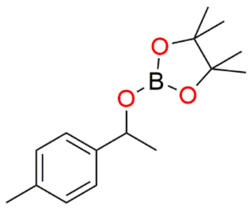
Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.36 (d, *J* = 4 Hz, 2H, Ar-H), 7.31 (d, *J* = 8 Hz, 2H, Ar-H), 7.26 -7.23 (t, 6Hz, 1H, Ar-H), 5.24 (q, *J* = 6.8 Hz, 1H), 1.49 (d, *J* = 4, 3H), 1.34 - 1.24 (s, 12H, Bpin-CH_3). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.26 ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 144.6, 133.2, 128.7, 128.3, 127.2, 125.4, 83.2, 82.8, 77.5, 76.8, 72.7, 25.5, 24.6, ppm. NMR data are in accordant with the literature.[15]

2-(1-phenylpropoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c).



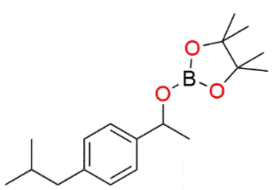
Yield: 99%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.26 (d, *J* = 4 Hz, 2H, Ar-H), 7.23 - 7.17 (m, 2H, Ar-H), 7.15 (m, 1H, 7.15), 4.92 (t, *J* = 8 Hz, 1H, CH), 1.71 (m, 2H, CH_2), 1.15 (s, 12H, Bpin-CH_3), 0.83 - 0.79 (t, J = 8 Hz, 3H, CH_3) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 22.43 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 143.5, 128.2, 127.2, 126.0, 83.2, 82.8, 77.8, 77.5, 76.8, 32.1, 24.8 – 24.5, 9.9, ppm. NMR data are in accordant with the literature.[16]

2-(1-(p-tolyl) ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d).



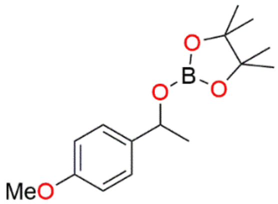
Yield: 98%. ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.26 - 7.24 (d, J = 8 Hz, 2H, Ar-H), 7.13 - 7.11 (d, J = 8 Hz, 2H, Ar-H), 5.22 (q, J = 6.7 Hz, 1H, CH), 2.32 (s, 3H, Me), 1.48 - 1.46 (d, J = 8 Hz, 3H, CH_3), 1.23 (s, 12H, Bpin-CH_3) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 22.34 ppm.$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 141.7, 136.7, 128.9, 125.3, 82.7, 77.5, 76.8, 72.5, 25.5, 24.6, 21.1, ppm. NMR data are in accordant with the literature.[15]

2-(1-(4-isobutylphenyl) ethoxy)-4,4,5,5, -tetramethyl-1,3,2-dioxaborolane (2e).



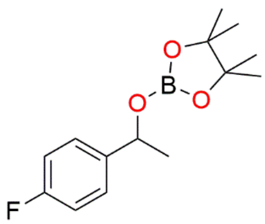
Yield 98%. ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.28 - 7.26 (d, J = 8.1 Hz, 2H, Ar-H), 7.10 - 7.08 (d, J = 8.0 Hz, 2H, Ar-H), 5.22 (q, J = 6.4 Hz, 5 H), 2.44 (d, J = 7.1 Hz, 2H), 1.83 (d, J = 8 Hz, 3H), 1.48 (m, 1H), 1.26 (s, 12H, Bpin-CH_3), 0.89 (d, J = 6.7 Hz, 6H) $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 22.28 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 141.9, 140.6, 129.4, 129.0, 128.4, 125.2, 82.8, 77.5, 76.8, 72.6, 45.2, 30.3, 25.5, 24.8 –24.4, 24.2, 22.5 ppm. Elemental analysis ($C_{18}H_{29}BO_3$) (304.2). Calcd C 71.06, H 9.61. Found C 70.95, H 9.53.

2-(1-(4-methoxyphenyl) ethoxy)-4,4,5,5, -tetramethyl-1,3,2-dioxaborolane (2f).



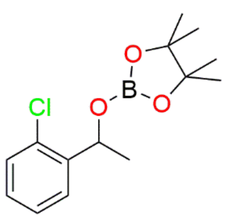
Yield 98%. [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.22 - 7.19 (d, *J* = 6 Hz, 2H, Ar-H), 6.78 - 6.75 (d, *J* = 6 Hz, 2H, Ar-H), 5.12 (q, *J* = 6.7 Hz, 1H, CH), 3.69 (s, 3H, OCH_3), 1.39 (d, *J* = 4 Hz, 3H, CH_3), 1.15 (s, 12H, Bpin-CH_3) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 23.23 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 158.8, 136.8, 126.7, 113.6, 82.7, 77.5, 76.8, 72.3, 25.4, 24.6 ppm. NMR data are in accordant with the literature.[15]

2-(1-(4-flourophenyl) ethoxy)-4,4,5,5, -tetramethyl-1,3,2-dioxaborolane (2g).



Yield 99%. [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.33 - 7.32 (d, *J* = 4 Hz, 2H, Ar-H), 7.02 - 6.99 (d, *J* = 6 Hz, 2H, Ar-H), 5.22 (q, *J* = 6.6 Hz,1H, CH), 1.48 - 1.46 (d, *J* = 4 Hz, 3H, CH_3), 1.24 (s, 12H, Bpin-CH_3) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 23.36 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 140.4, 129.9, 129.0, 127.1, 115.2, 115.0, 82.9, 77.5, 76.9, 72.1, 25.5, 24.7, 24.2 ppm. NMR data are in accordant with the literature.[15]

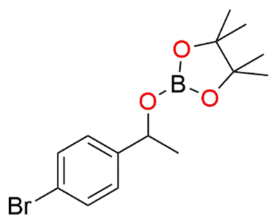
2-(1-(2-chlorophenyl) ethoxy)-4,4,5,5, -tetramethyl-1,3,2-dioxaborolane (2h).



Yield: 96%. [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.63 - 7.59 (m, 1H, Ar-H), 7.31 - 7.26 (d, *J* = 12 Hz, 2H, Ar-H), 7.19 - 7.15 (m, 1H, Ar-H), 5.59 (q, *J* = 6.6 Hz, 1H, CH), 1.48 - 1.47 (d, *J* = 4 Hz, 3H,

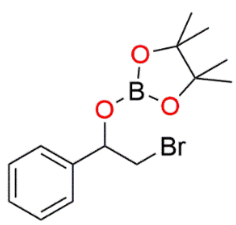
CH_3), 1.25 (s, 12H, Bpin-CH_3) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 23.30 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 142.3, 131.2, 129.2, 128.5, 128.2, 127.2, 126.7, 83.0, 77.5, 76.8, 69.6, 24.6, 24.0, ppm. NMR data are in accordant with the literature.[15]

2-(1-(4-bromophenyl) ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i).



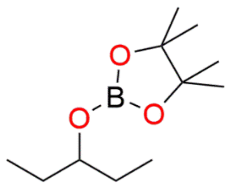
Yield: 99%. ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.44 - 7.42 (d, J = 8 Hz, 2H, Ar-H), 7.25 - 7.23 (d, J = 8 Hz, 2H, Ar-H), 5.20 (q, J = 6.6 Hz, 1H, CH), 1.46 - 1.45 (d, J = 4 Hz, 3H, CH_3), 1.24 (s, 12H, Bpin-CH_3) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 22.27 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 143.7, 132.0, 131.4, 130.0, 127.2, 121.0, 83.0, 77.5, 76.8, 72.1, 25.4, 24.6 ppm. NMR data are in accordant with the literature.[15]

2-(2-bromo-1-phenylethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j).



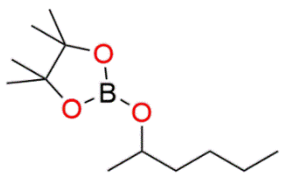
Yield: 98%. ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.39 - 7.30 (m, 5H, Ar-H), 5.30 (t, J = 8 Hz, 1H, Ar-H), 3.45 (d, J = 4 Hz, 2H, CH_2), 1.15 (s, 12H, Bpin-CH_3) ppm.$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 22.43 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 140.0, 134.0, 129.0, 128.5, 126.1, 83.2, 77.5, 76.84, 76.1, 38.0, 24.6 ppm. NMR data are in accordant with the literature.[16]

2-(pentan-3-yloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a).



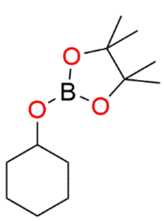
Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.81 (m, 1H, CH), 1.43 - 1.39 (m, 4H, CH_2), 1.18 (s, 12H, Bpin-CH_3), 0.84 - 0.80 (m, 6H, CH_3) ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.19 ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 83.1, 83.1, 82.4, 77.4, 77.2, 77.0, 76.7, 31.6, 29.1, 28.7, 24.5, 24.5, 24.5, 22.7, 14.1, 9.8 ppm. NMR data are in accordant with the literature.[17]

2-(hexan-2-yloxy)-4,4,5,5, -tetramethyl-1,3,2-dioxaborolane (3b).



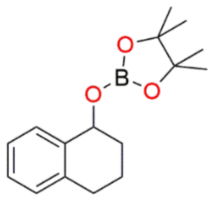
Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.07 (m, 1H, CH), 1.48 - 1.38 (m, 2H), 1.36 - 1.26 (m, 2H), 1.22 (m, J =7.4 Hz, 2H), 1.17 (s, 12H, Bpin-CH_3), 1.10 (d, J = 6.2 Hz, 3H), 0.81 (t, J = 6.7 Hz, 2H), ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.23 ppm.^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 82.5, 77.5, 76.9, 71.0, 38.0, 27.8, 24.6, 22.6, 14.1 ppm. NMR data are in accordant with the literature.[15]

2-(cyclohexyloxy)- 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c).



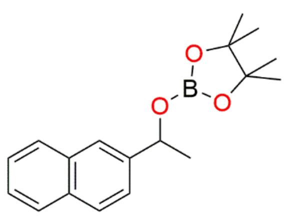
Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.02 - 3.97 (m, 1H, CH), 1.83 (m, 4H 2CH_2), 1.72 (m, 4H, 2CH_2), 1.37 - 1.29 (m, 2H, CH_2), 1.25 (s, 12H, Bpin-CH_3).^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.37 ppm.^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 82.5, 77.5, 76.9, 72.8, 34.4, 25.6, 24.7, 24.0, ppm. NMR data are in accordant with the literature.[18]

2-((1,2,3,4-tetrahydronaphthalen-1-yl) oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d).



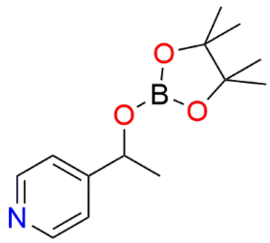
Yield: 97%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.32 - 7.30 (m, 1H, Ar-H), 7.09 - 7.07 (m, 2H, Ar-H), 7.00 - 6.97 (m, 1H, Ar-H), 5.13 - 5.11 (t, *J* = 4 Hz, 1H, CH), 2.76 - 2.70 (m, 1H, CH_2), 2.65 - 2.62 (m, 1H, CH_2), 1.89 - 1.87 (m, 1H, CH_2), 1.89 - 1.85 (m, 2H, CH_2), 1.70 - 1.67 (m, 2H, CH_2), 1.20 (s, 12H, Bpin-CH_3) ppm.^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.33 ppm.^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 137.5, 137.2, 128.9, 127.5, 125.9, 82.9, 77.5, 76.8, 70.5, 31.4, 29.1, 24.7, 18.7 ppm. NMR data are in accordant with the literature.[16]

2-(1-(naphthalen-2-yl) ethoxy)-4,4,5,5, -tetramethyl-1,3,2-dioxaborolane (3e).



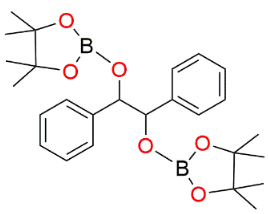
Yield: 97%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.83 - 7.77 (m, 4H, Ar-H), 7.49 - 7.42 (m, 3H, Ar-H), 5.41 (q, *J* = 6.4 Hz, 1H, CH), 1.57 - 1.56 (d, *J* = 6.4 Hz, 3H, CH_3), 1.21 (s, 12H, Bpin-CH_3) ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.34 ppm.^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 142.1, 133.3, 132.8, 128.0, 127.7, 126.0, 125.7, 123.8, 82.9, 77.5, 76.8, 72.7, 25.6, 24.6, ppm. NMR data are in accordant with the literature.[15]

4- (1-((4,4,5,5, -tetramethy-1,3,2-dioxaborolane-2-yl) oxy) ethyl) pyridine (3f).



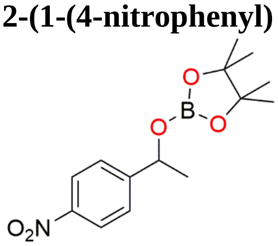
Yield: 93%.[1]H NMR (400 MHz, $CDCl_3$): δ_H 8.56 (s, 2H, Ar-H), 7.33(s, 2H, Ar-H), 5.25 - 5.21 (, q, J = 5.4 Hz, 1H CH), 1.48 (d, J = 4 Hz, 3H, CH_3), 1.25 (s, 12H, Bpin-CH_3) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 22.27 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 154.2, 149.4, 145.3, 129.8, 127.9, 127.0, 120.6, 83.2, 77.5, 76.8, 71.2, 24.9, 24.6, ppm. NMR data are in accordant with the literature.[22]

1,2-diphenyl-1,2-bis((4,4,5,5-tetramethyl-1,3,2-dioxborolan-2-2yl) oxy) ethane (3g).



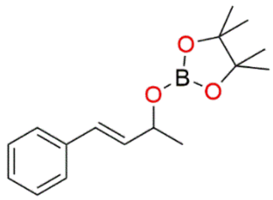
Yield: 92%.[1]H NMR (400 MHz, $CDCl_3$): δ_H 7.37 (d, J = 8.0 Hz, 4H, Ar-H), 7.30 - 7.24 (m, 6H, Ar-H), 5.09 (s, 1H, CH), 1.04 (s, 12H, Bpin-CH_3) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 22.27 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C139.8, 135.0, 133.1, 130.0, 129.1, 127.6, 82.7, 79.7, 77.5, 76.8, 24.8 – 24.4, ppm. NMR data are in accordant with the literature.[23]

2-(1-(4-nitrophenyl) ethoxy) 4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4a).



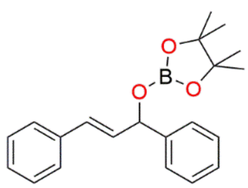
Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.18 (d, J = 8.8 Hz, 2H, Ar-H), 7.54 (d, J = 8.6 Hz, 2H, Ar-H), 5.34 (q, J = 6.5 Hz, 1H), 1.51 (d, J = 6.5 Hz, 3H), 1.24 (s, 12H, Bpin-CH_3) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$):δ_B 22.43 ppm.$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 152.0, 147.1, 126.2, 123.6, 83.2, 77.5, 76.9, 71.8, 25.3, 24.6 ppm. NMR data are in accordant with the literature.[15]

(E)- 2-((4-phenyl but-3-en-yl) -4,4,5,5-tetramethyl)-1,3,2-dioxaborolane (4b).



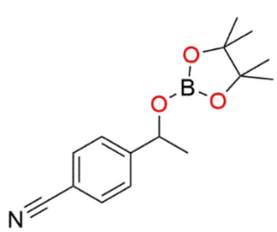
Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.37 - 7.35 (d, *J* = 4 Hz, 2H, Ar-H) 7.31 - 7.27 (d, *J* = 8 Hz, 2H, Ar-*H*), 7.25 - 7.21 (t, *J* = 8 Hz, 1H, Ar-H) 6.57 (d, *J* = 15.9 Hz, 1H,CH), 6.22 (dd, *J* = 15.9 1H, CH), 4.85 – 4.82 (m, 1H, CH), 1.37 (d, *J* = 6.4 Hz 3H, CH_3), 1.26 (s, 12H, Bpin-CH_3) ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.28 ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 143.6, 137.0, 132.1, 130.6, 129.0, 128.7 - 128.2, 127.5, 127.2, 126.5, 82.8, 77.4, 76.8, 71.2, 24.6, 23.2, ppm. NMR data are in accordant with the literature.[15]

(E)-2-((1,3-diphenylally) oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c).



Yield: 92%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.4 - 7.25 (m, 10H, Ar-H), 6.67 (d, *J* = 8 Hz, 1H, Ar-H), 6.32 (d, *J* = 8 Hz, 1H Ar-H), 5.74 (d, *J* = 4 Hz, 1H, CH), 1.24 (s, 12H, Bpin-CH_3) ppm. ^{11}B{1H} NMR (128 MHz, $CDCl_3$): δ_B 22.34 ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 142.1, 141.6, 137.0, 133.4, 131.0, 130.2, 129.0 – 128.6, 128.4, 127.0, 126.9, 126.7, 126.4, 83.3, 77.7, 77.4, 77.1, 40.8, 30.4, 24.9, ppm. NMR data are in accordant with the literature.[18]

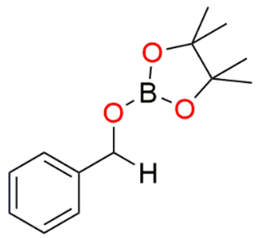
4-(1-(4,4,5,5, -tetramethyl-1,3,2-dioxaborolane-2-yl) oxy) ethyl) benzonitrile (4d).



Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.47 (d, *J* = 8.2 Hz, 2H, Ar-H), 5.27 (q, *J* = 6.6 Hz, 1H, CH), 1.49 (d, *J* = 6.5 Hz, 3H, CH_3), 1.25 (s, 12H, Bpin-CH_3)

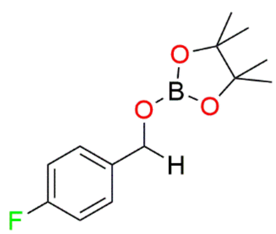
ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 22.34 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 149.9, 132.4, 132.2, 126.1, 119.0, 110.9, 83.1, 77.5, 76.8, 72.0, 25.3, 24.6, ppm. NMR data are in accordant with the literature.[15]

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



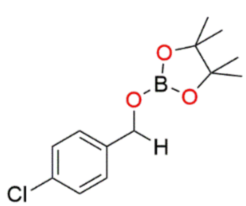
Yield: 99%.^1H NMR (400 MHz, $CDCl_3$): δ_H 7.34 - 7.31 (s, 5H, Ar-H), 4.93 (s, 2H, CH_2), 1.26 (s, 12H, Bpin-CH_3) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 22.36 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 139.2, 130.2, 129.1, 128.3, 127.4, 126.7, 83.0, 77.5, 76.8, 66.7, 24.6, ppm. NMR data are in accordant with the literature.[15]

2-((4-fluorobenzyl) oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b).



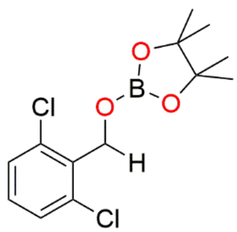
Yield: 95%.^1H NMR (400 MHz, $CDCl_3$): δ_H 7.23 - 7.22 (d, J = 8 Hz, 2H, Ar-H), 6.94 - 6.92 (d, J = 8 Hz, 2H, Ar-H), 4.79 (s, 2H, CH_2), 1.17 (s, 12H, Bpin-CH_3) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B 22.23 ppm. $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 135.0, 132.3, 128.7, 116.5, 116.3, 115.3, 115.1, 83.1, 77.5, 76.8, 66.1, 24.7, ppm. NMR data are in accordant with the literature.[15]

2-((4-chlorobenzyl) oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c).



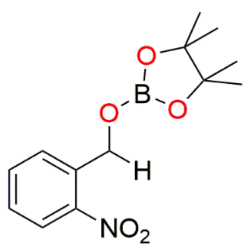
Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.28 (d, J = 4 Hz, 2H, Ar-H), 7.26 - 7.25 (d, J = 4 Hz, 2H, Ar-H), 4.88 (s, 2H, CH_2), 1.26 (s, 12H, Bpin-CH_3) ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ_B 22.34 ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 137.8, 133.1, 129.8, 129.1, 128.4, 83.2, 77.5, 76.8, 66.0, 24.6, ppm. NMR data are in accordant with the literature.[15]

2-((2,6-dichlorobenzyl) oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d).



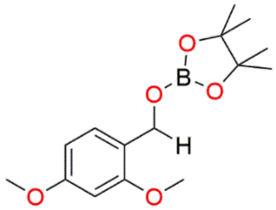
Yield: 98%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.29 - 7.27 (d, J = 8.2 Hz, 2H, Ar-H), 7.17 - 7.13 (m, 1H, Ar-H), 5.19 (s, 2H, CH_2), 1.27 (s, 12H, Bpin-CH_3) ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.35 ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ_C 136.6, 133.9, 130.0, 128.3, 83.1, 77.5, 76.8, 61.8, 24.6, ppm. NMR data are in accordant with the literature.[16]

2-((2-nitrobenzyl) oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e).



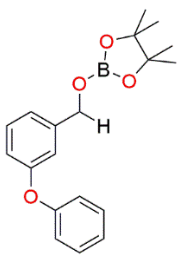
Yield: 99%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.10 - 8.12 (d, J = 7.9 Hz, 1H Ar-H), 7.86 - 7.84 (d, J = 7.5 Hz, 1H, Ar-H), 7.69 - 7.65 (t, J = 7.3 Hz, 1H, Ar-H), 7.46 - 7.442 (t, J = 7.5 Hz, 1H, Ar-H), 5.35 (s, 2H, CH_3), 1.28 (s, 12H, Bpin-CH_3), ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.30 ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 146.5, 136.1, 134.0, 127.8, 124.7, 83.3, 77.5, 76.8, 63.8, 24.6, ppm. NMR data are in accordant with the literature.[15]

2-((2,4 dimethoxybenzyl) oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5f).



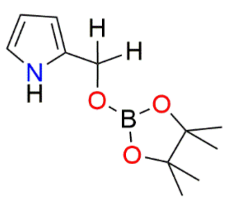
Yield: 99%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.27 (d, J = 8.1 Hz, 2H, Ar-H), 6.42 (s 1H, Ar-H), 4.89 (s, 2H, CH_2), 3.83 (s, 3H, CH_3), 3.74 (s, 3H, CH_3), 1.26 (s, 12H, Bpin-CH_3) ppm. $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ_B 22.35 ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 160.3, 157.9, 130.7, 130.1, 129.7, 128.8, 120.1, 103.6, 98.1, 82.7, 77.5, 76.8, 62.0, 55.6 - 55.2, 24.5, ppm. NMR data are in accordant with the literature.[16]

2-((3-phenoxybenzyl) oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5g).



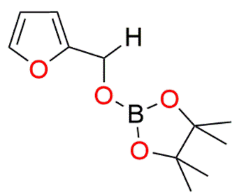
Yield: 98%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.33 - 7.26 (m, 3H, Ar-H), 7.10 – 7.06 (d, J = 8 Hz, 2H, Ar-H), 7.00 - 6.98 (m, 3H, Ar-H), 6.92 - 6.89 (s, 1H, Ar-H), 4.89 (s, 2H, CH_2), 1.24 (s, 12H, Bpin-CH_3) ppm. $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ_B 22.29 ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 157.3, 141.4, 129.8, 123.3, 121.6, 118.0, 118.0, 117.2, 83.1, 77.5, 76.8, 66.4, 24.7, ppm. NMR data are in accordant with the literature.[16]

2-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) oxy) methyl)-1H-pyrrole (5h).



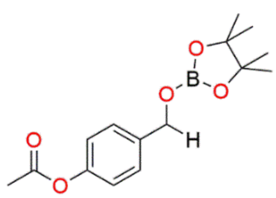
Yield: 99%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.74 (d, *J* = 6 Hz 1H, CH), 6.74 - 6.73 (m, 1H, CH), 6.11(d, *J* = 6.1 Hz 1H, CH), 4.84(s 2H, CH_2), 1.27 (s, 12H, Bpin-CH_3) ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.36 ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 129.4, 127.0, 118.4, 111.3, 108.1, 107.8, 107.0, 83.3, 77.5, 76.8, 59.9, 57.9, 24.7, ppm. NMR data are in accordant with the literature.[23]

2-(furan-2-ylmethoxy))-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5i).



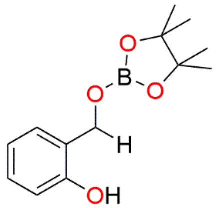
Yield: 97%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.37(d, *J* = 4 Hz 1H, CH), 6.33 - 6.32 (d, *J* = 4 Hz 1H, CH),6.31 (d, *J* = 4 Hz, 1H), 4.82 (s 2H CH_2), 1.26 (s, 12H, Bpin-CH_3) ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.27 ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 152.5, 142.5, 110.4, 108.4, 107.8, 83.2, 77.5, 76.8, 59.2, 57.4, 24.6, ppm. NMR data are in accordant with the literature.[15]

4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) oxy) methyl) phenyl acetate (5j).



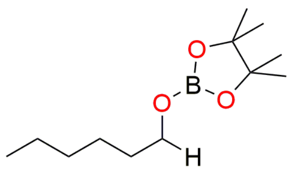
Yield: 96%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.36 - 7.34 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.05 - 7.03 (d, *J* = 8.6 Hz, 2H, Ar-H), 4.91 (s, 2H, CH_2), 2.27 (s, 3H, CH_3), 1.25 (s, 12H, Bpin-CH_3) ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.30 ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 169.6, 149.9, 136.9, 127.8, 121.4, 83.1, 77.5, 76.8, 66.1, 24.6, 21.1 ppm. NMR data are in accordant with the literature.[23]

4-((4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2-yl) oxy) methyl) phenol (5k).



Yield: 95%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.19 - 7.17 (d, J = 7.4 Hz, 2H, Ar-H), 6.90 - 6.88 (d, J = 7.4 Hz, 2H, Ar-H), 4.97 (s, 2H, CH_2), 1.26 (s, 12H, Bpin-CH_3) ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B 22.41 ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 138.1, 129.0, 128.8, 127.8, 121.4, 113.5, 83.2, 77.5, 76.8, 45.3, 25.8, 24.6, ppm. NMR data are in accordant with the literature.[16]

2-(hexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5l).



Yield: 97%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.85-3.82 (t, J = 6 Hz, 2H, CH_2),1.59 - 1.52 (m, 2H, CH_2), 1.32 - 1.29 (m, 6H, CH),1.27 (s, 12H, Bpin – CH_3), 0.90 – 0.86 (t, J = 8 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 83.1, 77.5, 65.0, 31.6, 25.3, 24.6, 22.7, 14.1, ppm. NMR data are in accordant with the literature.[15]

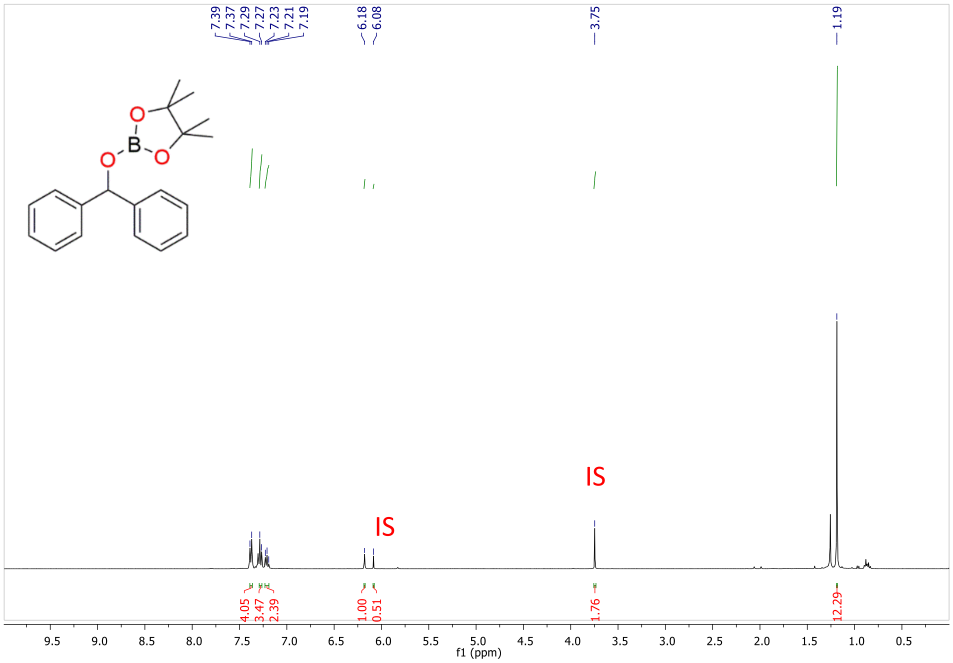


Figure S6. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2a**.

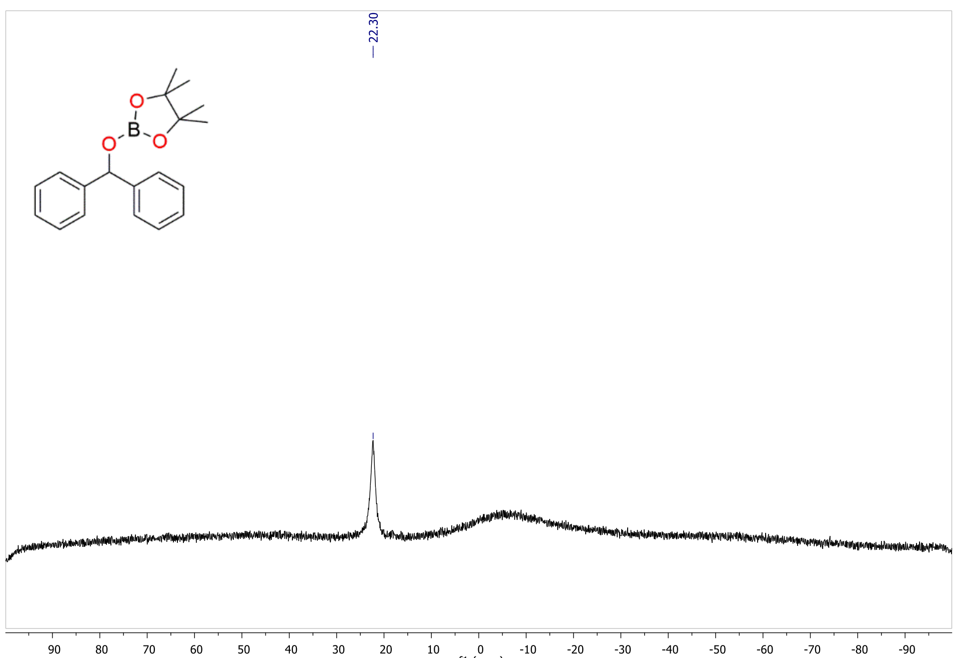


Figure S7. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **2a**.

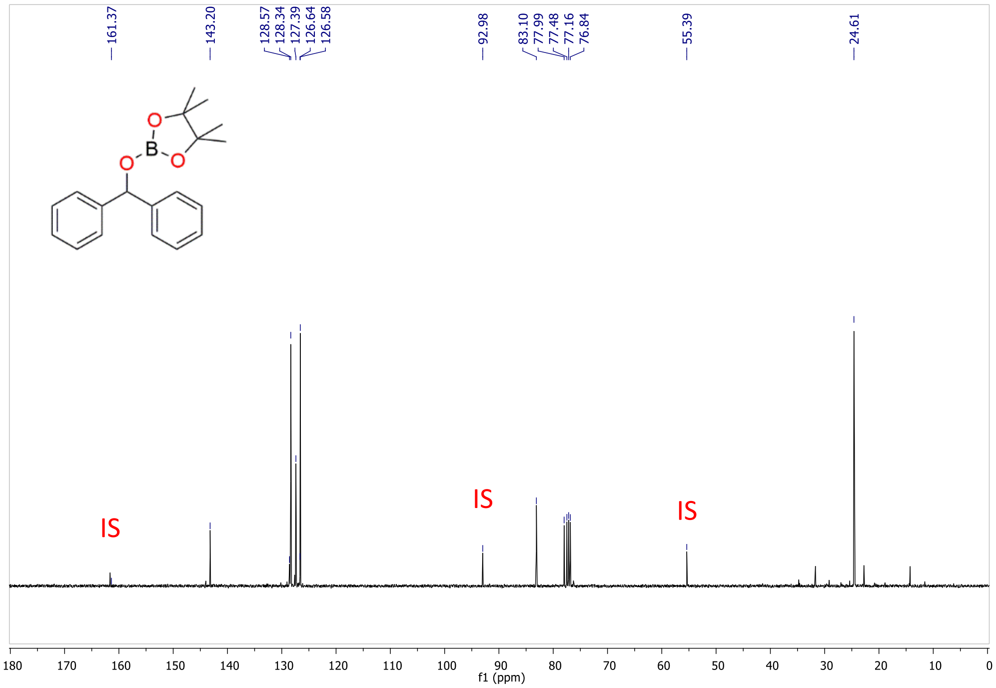


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **2a**.

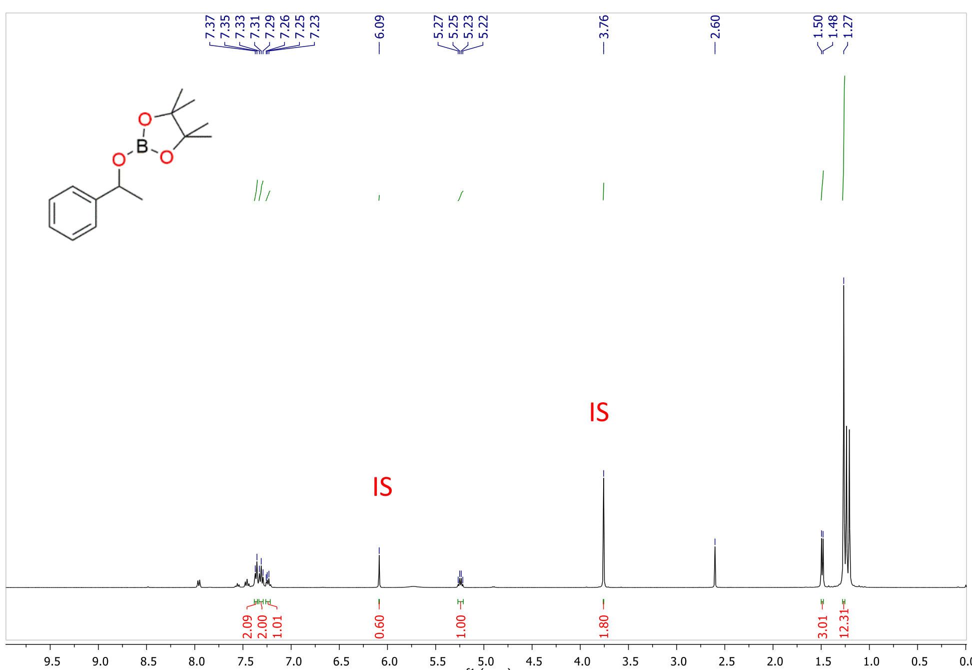


Figure S9. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2b**.

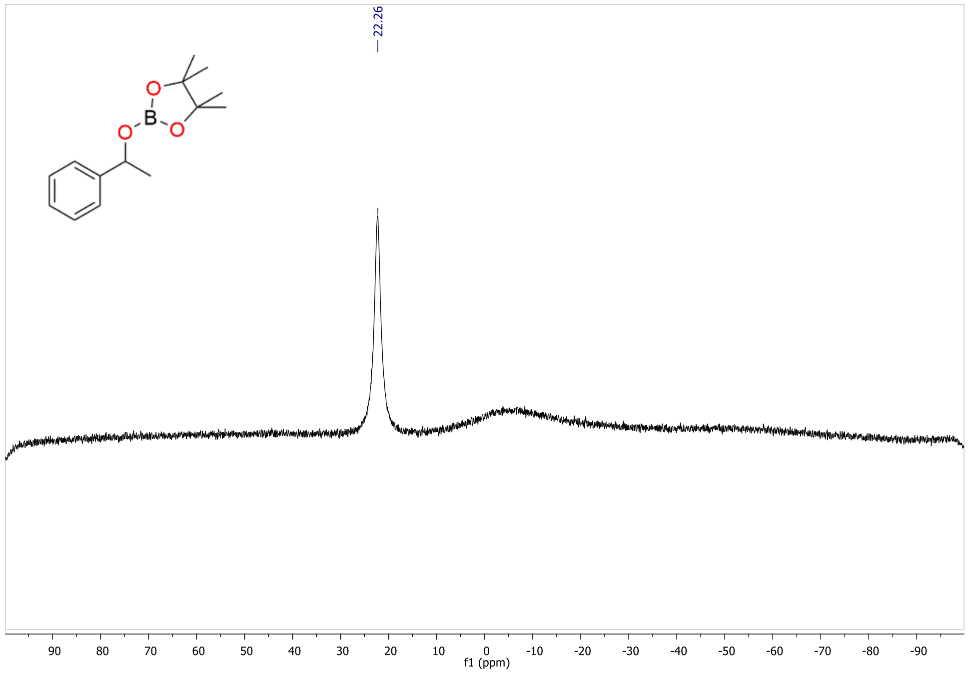


Figure S10. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **2b**.

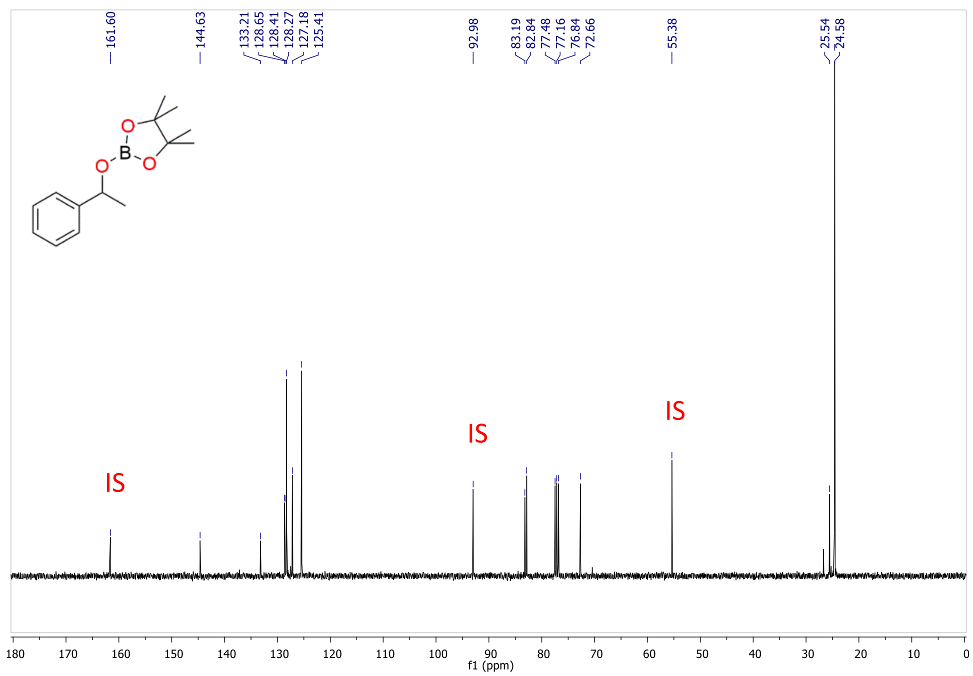


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **2b**.

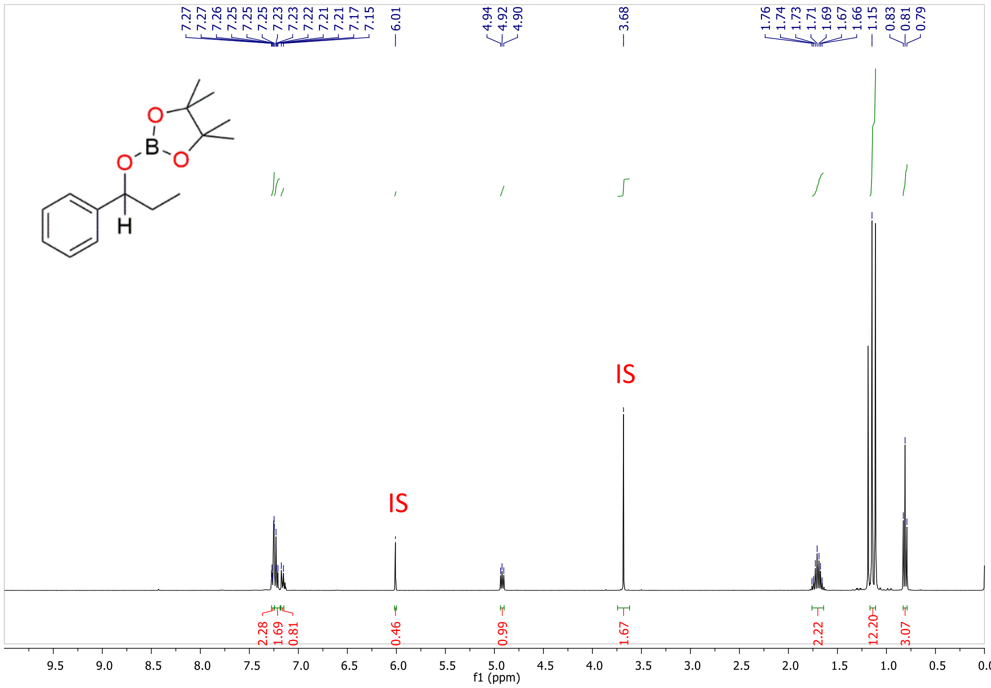


Figure S12. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2c**.

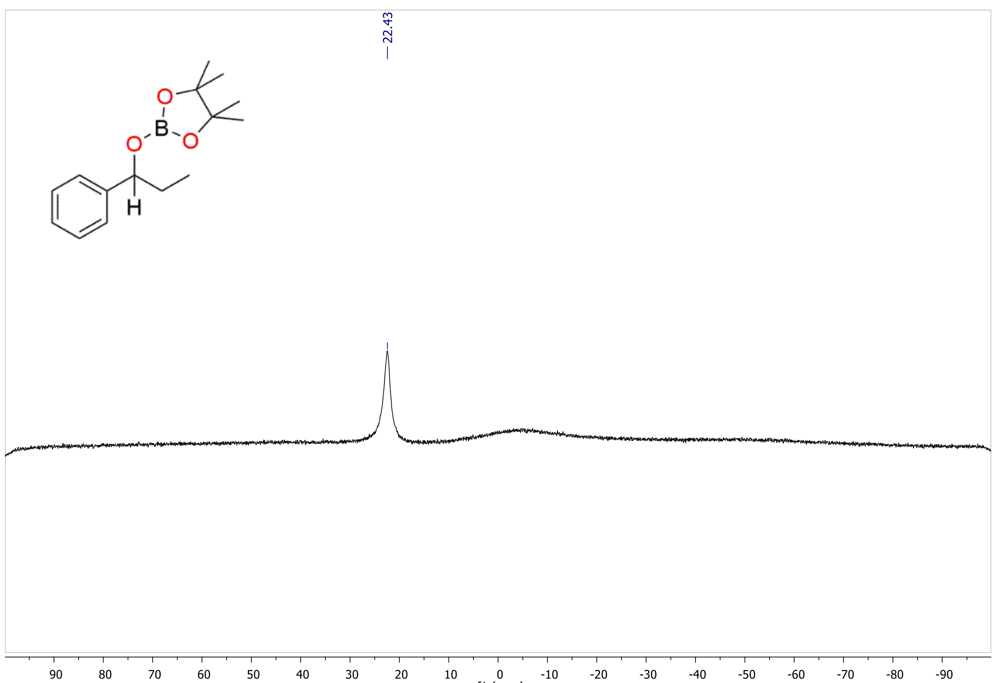


Figure S13. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **2c**.

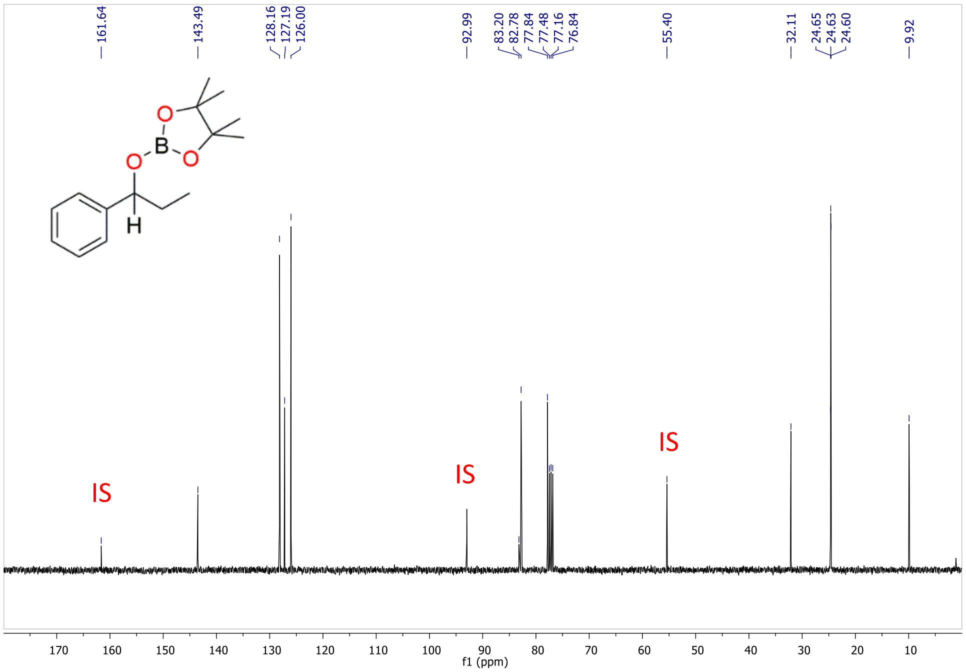


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **2c**.

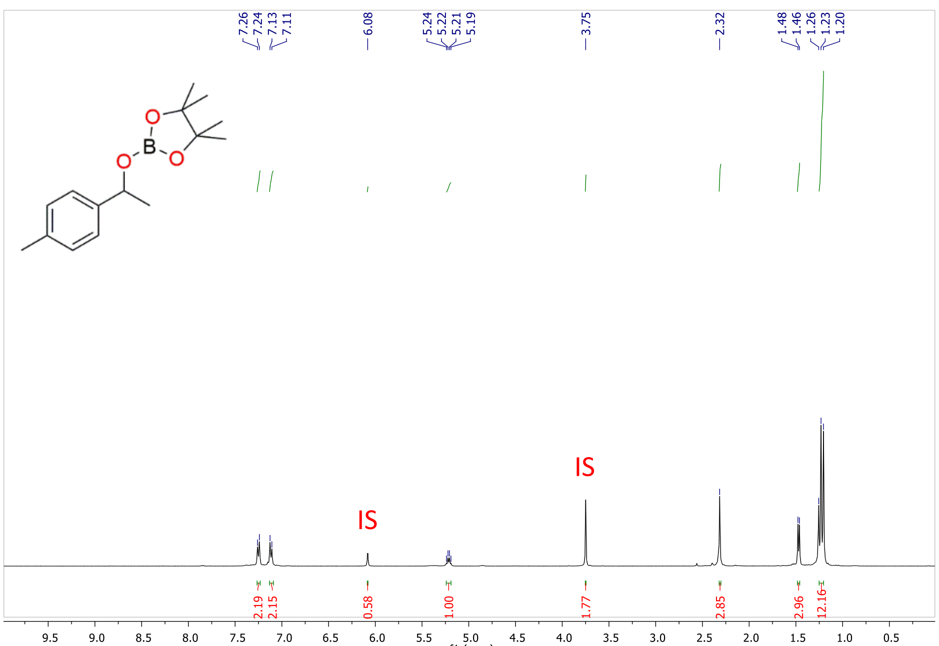


Figure S15. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2d**.

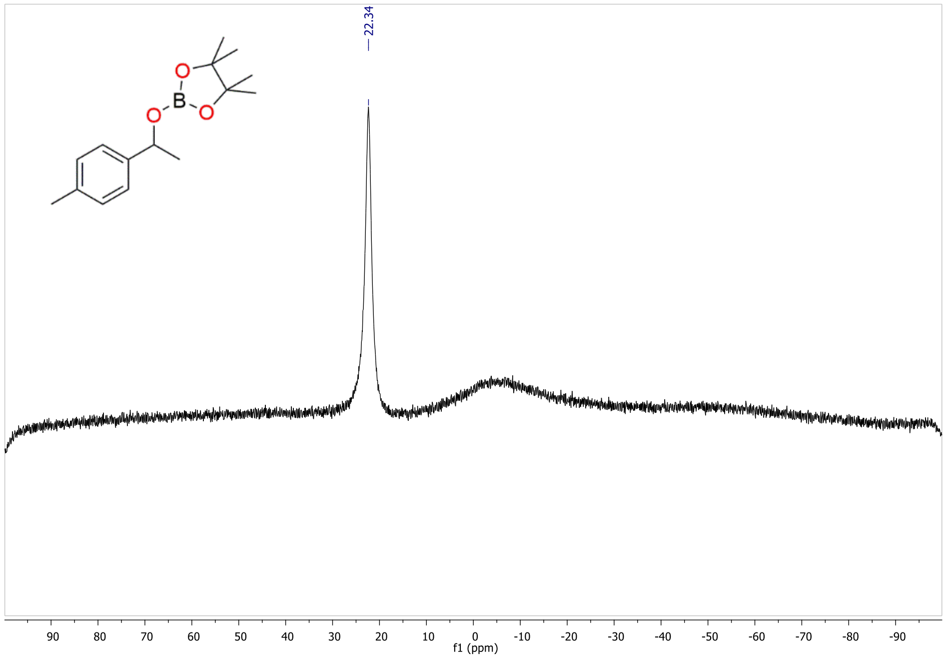


Figure S16. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **2d**.

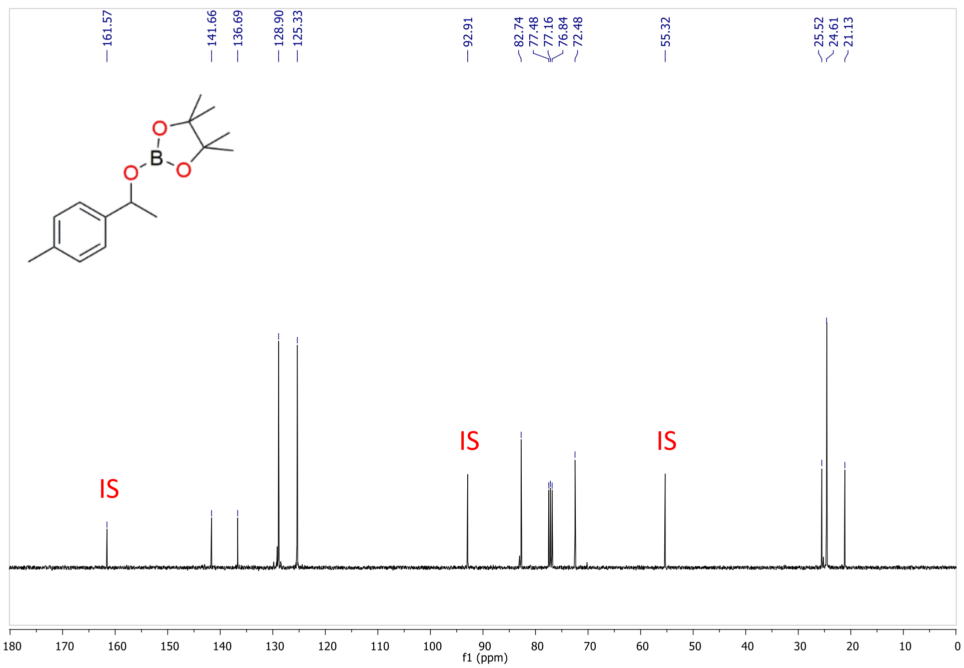


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **2d**.

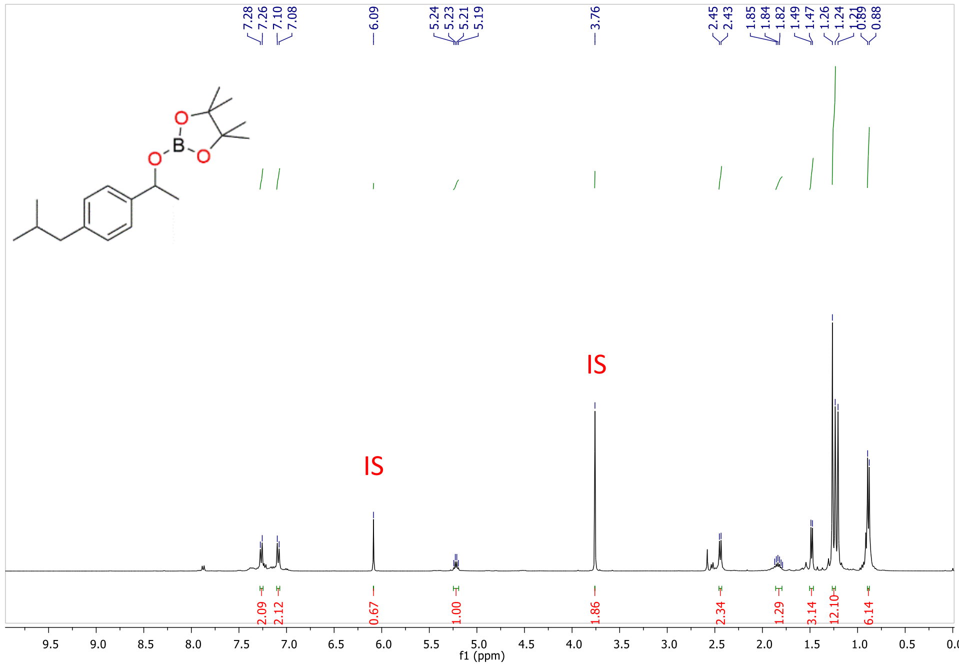


Figure S18. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2e**.

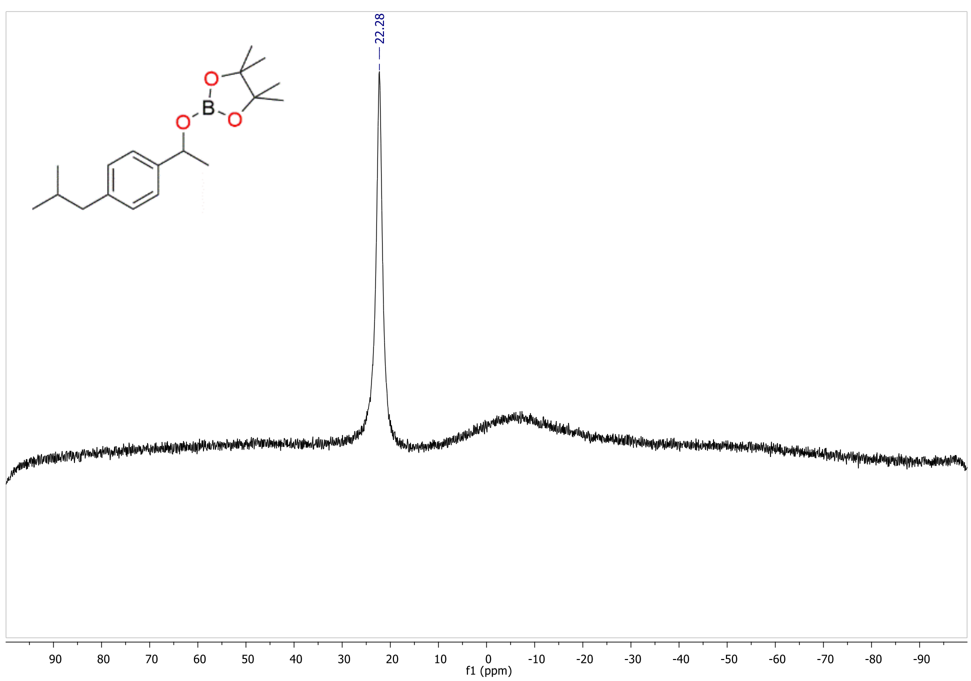


Figure S19. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **2e**.

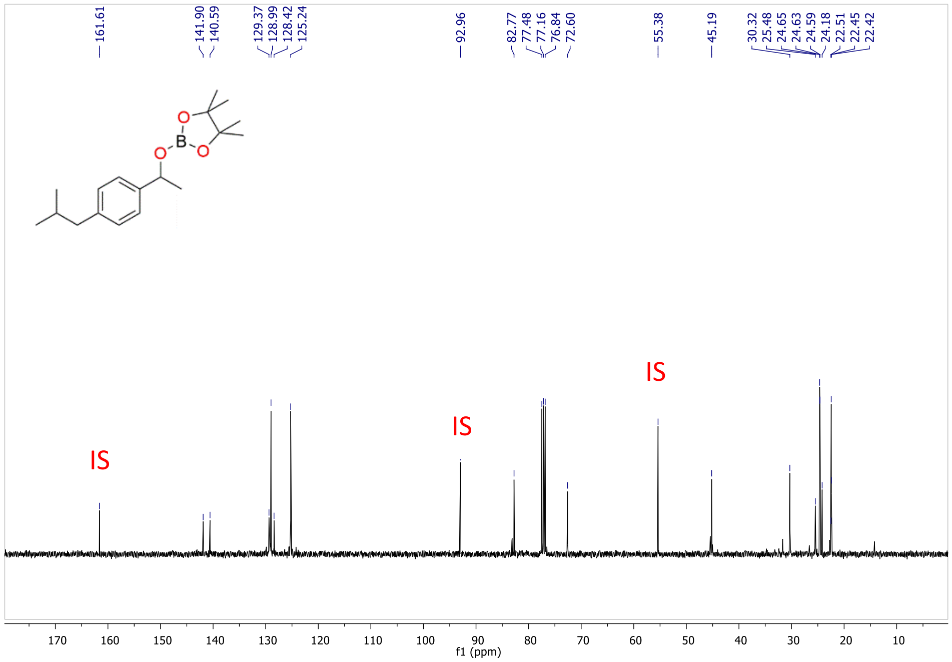


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **2e**.

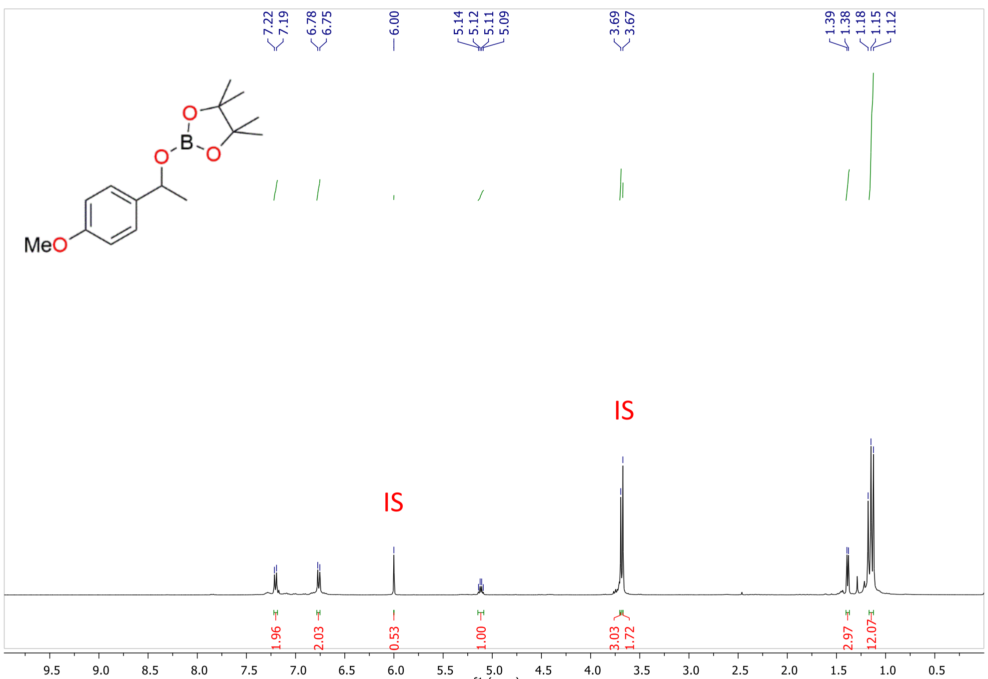


Figure S21. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2f**.

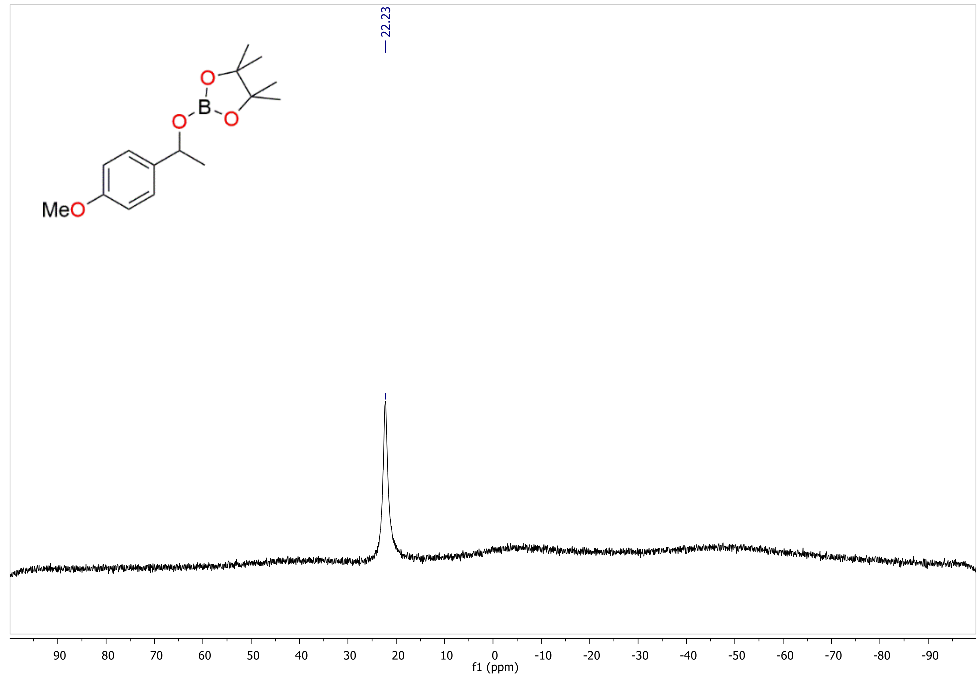


Figure S22. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of (**2f**).

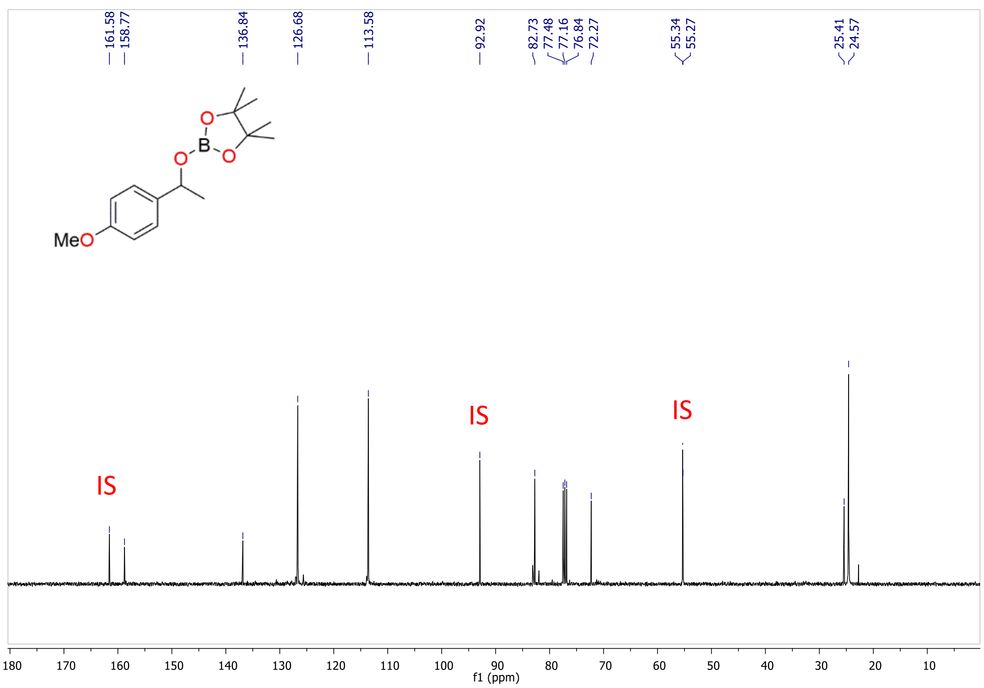


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **2f**.

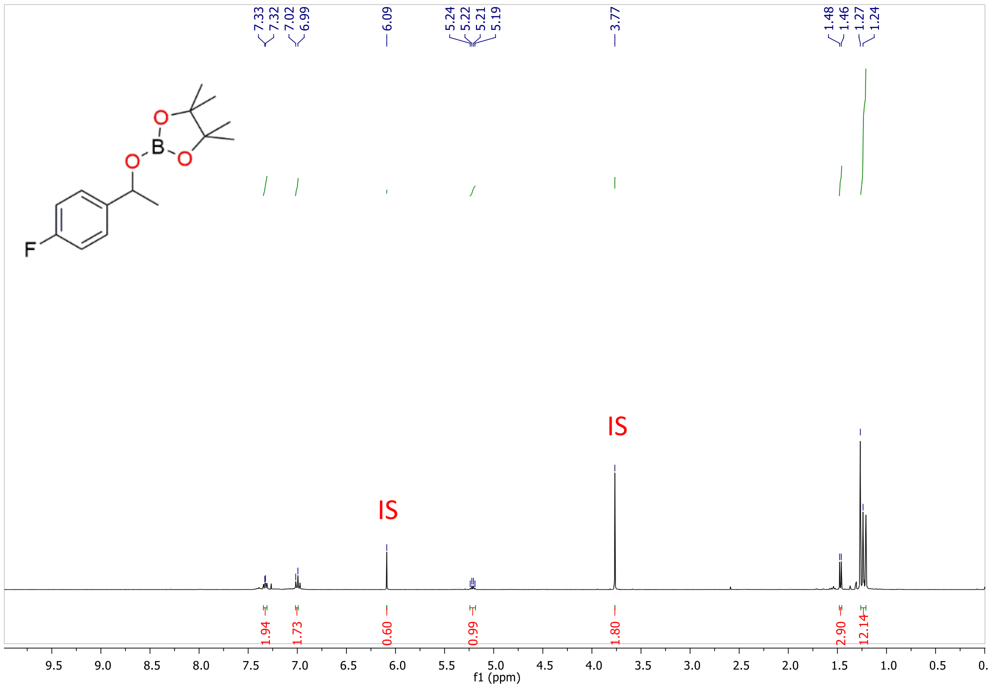


Figure S24. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2g**.

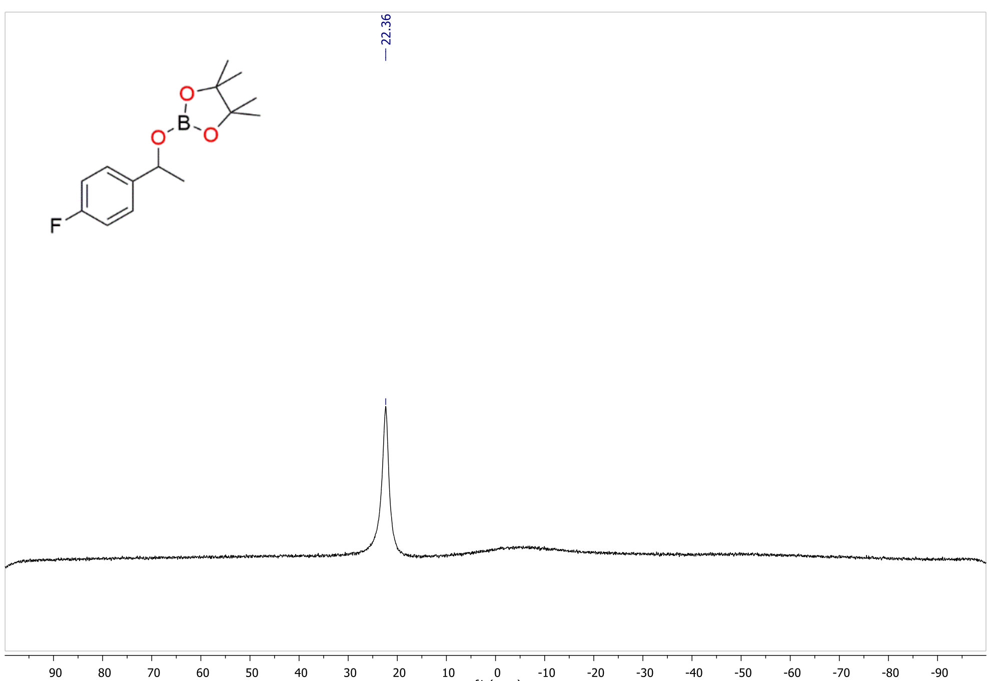


Figure S25. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **2g.**

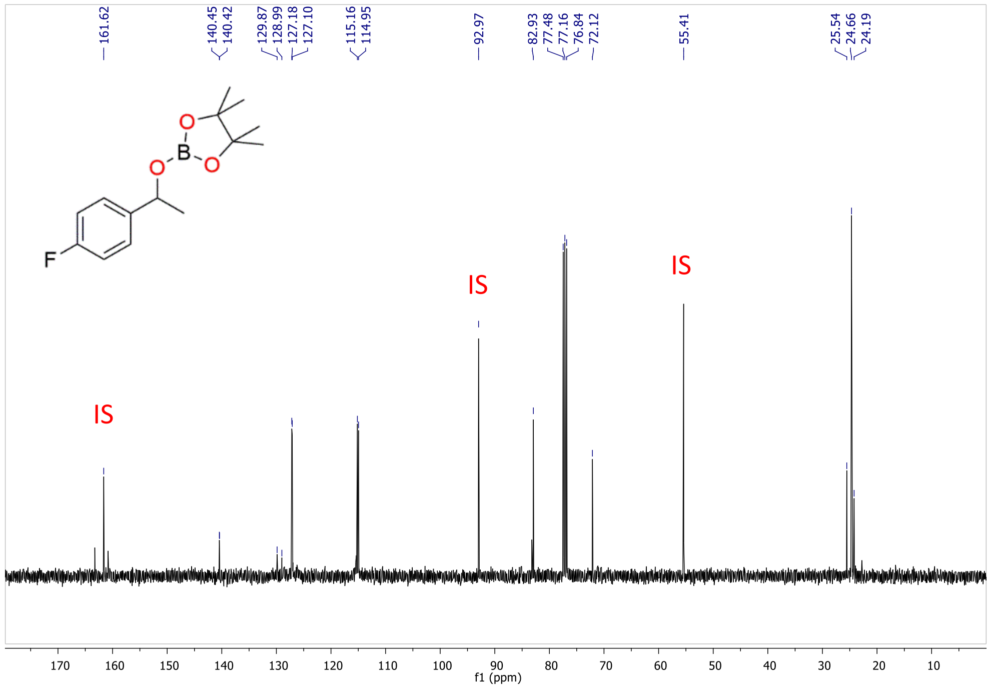


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **2g**.

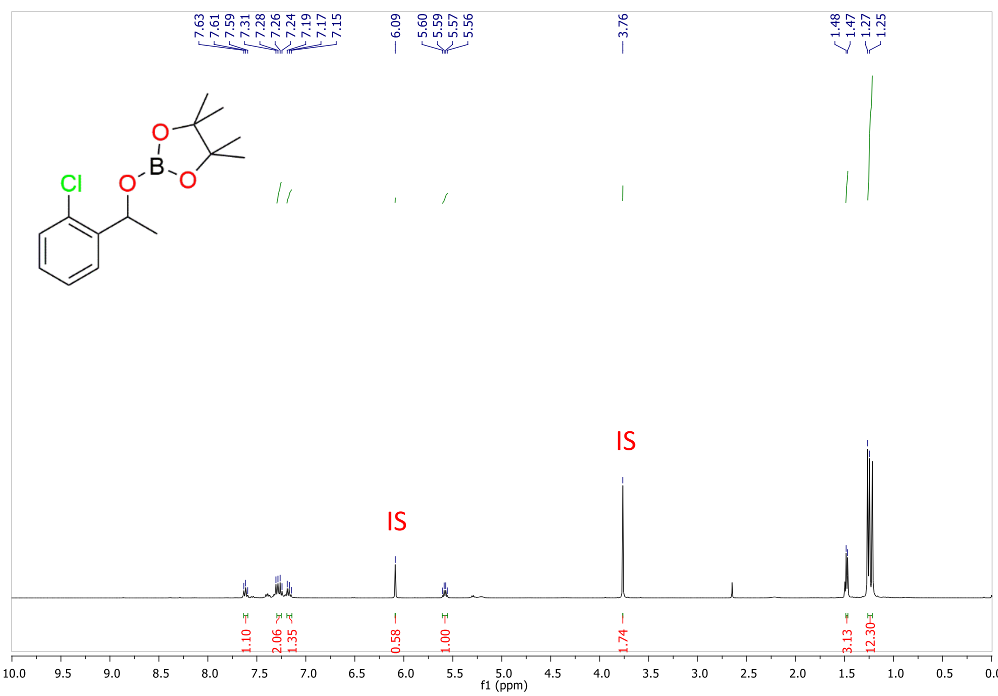


Figure S27. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2h**.

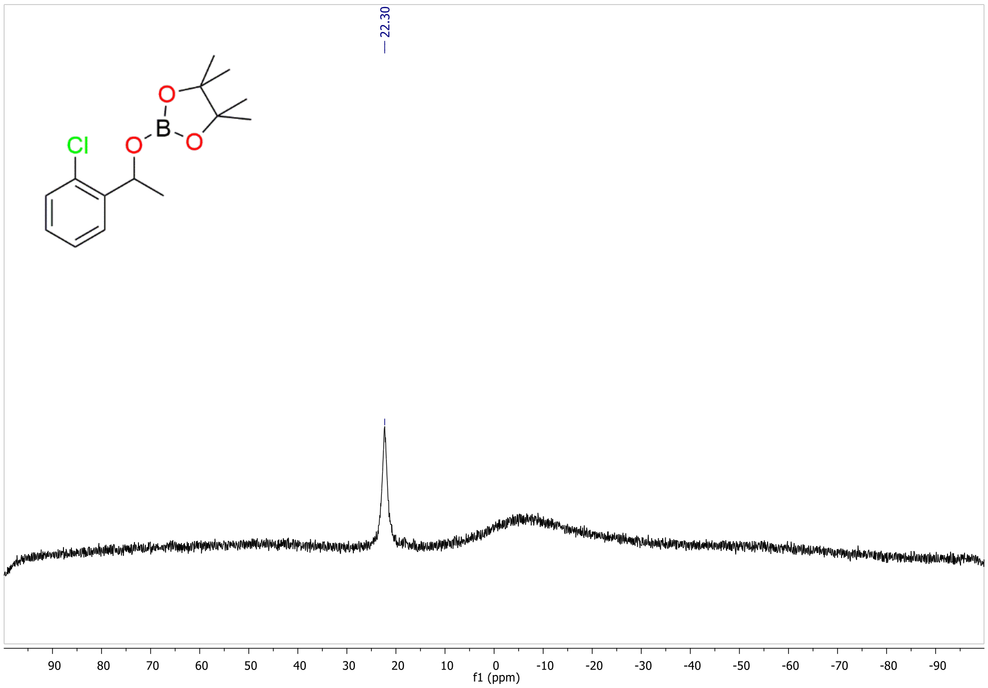


Figure S28. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **2h**.

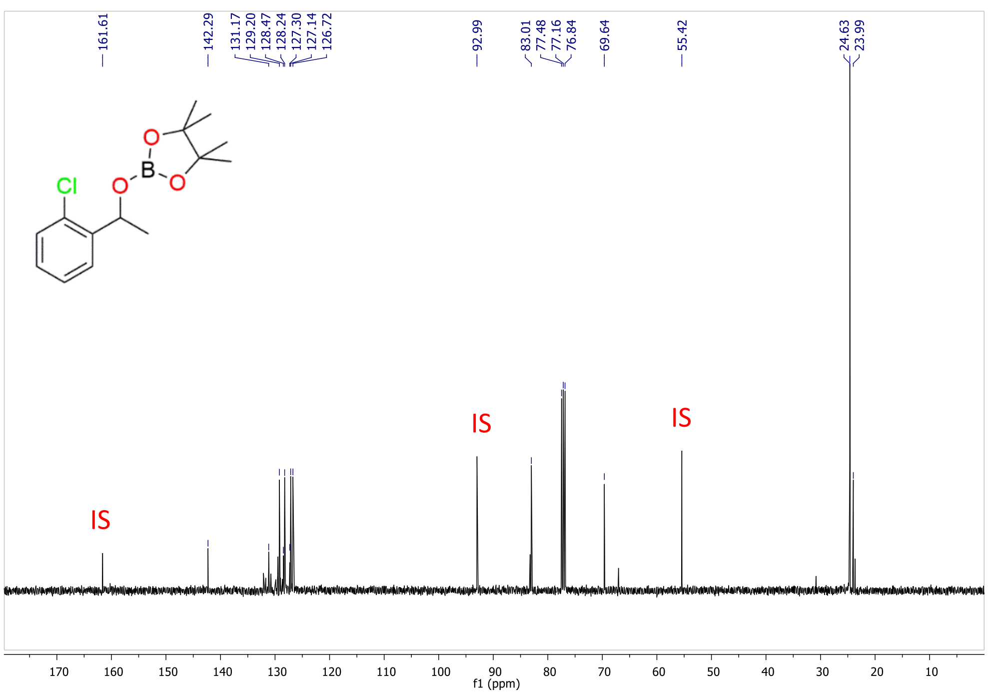


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **2h**.

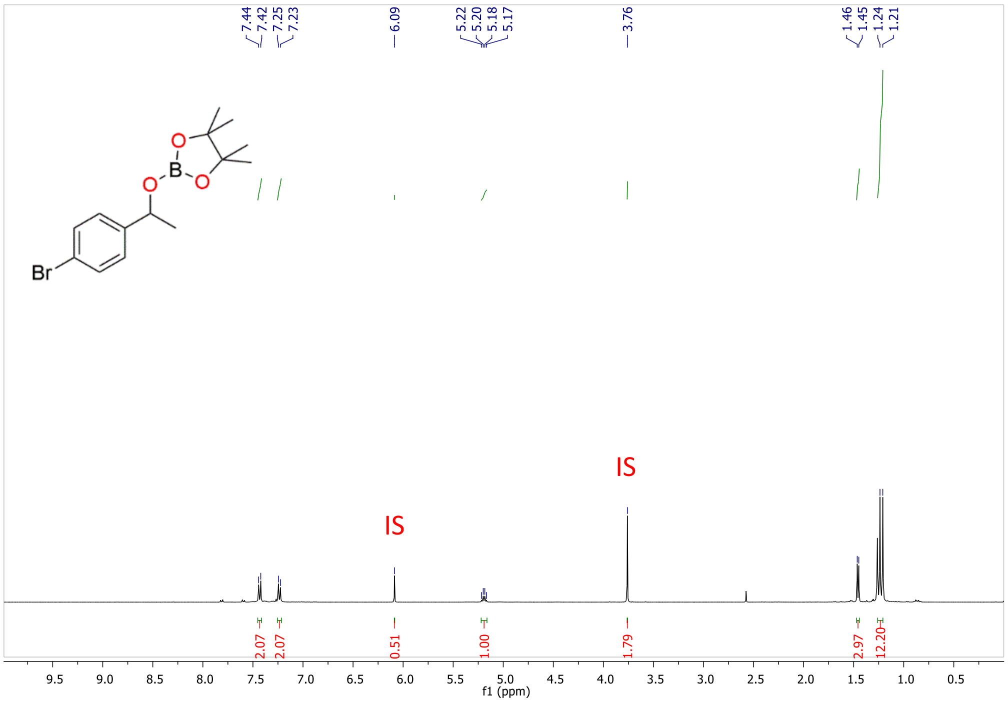


Figure S30. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2i**.

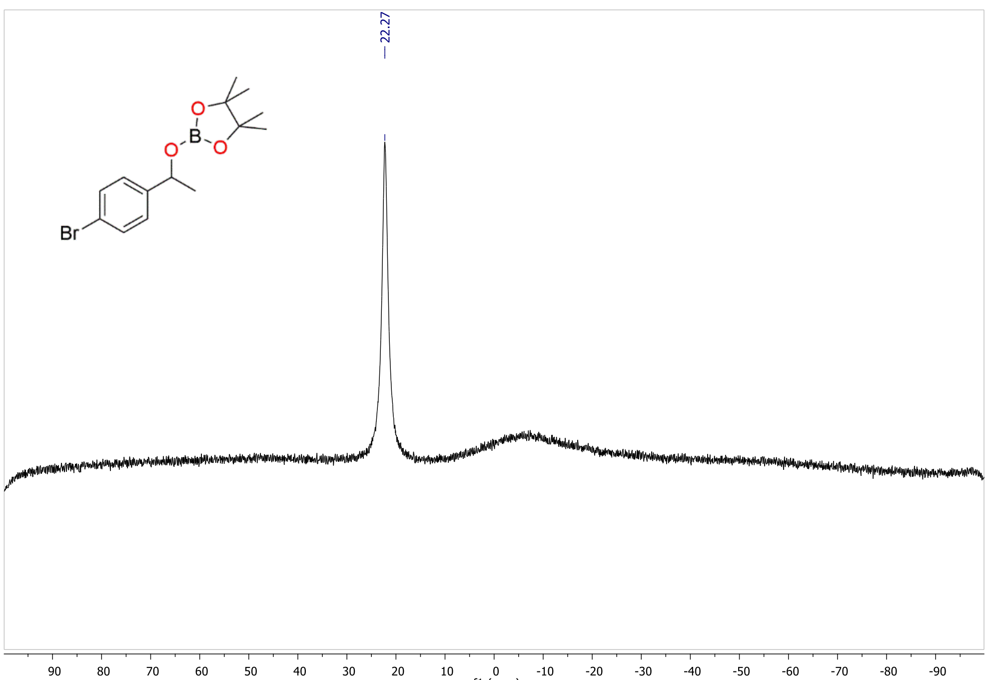


Figure S31. ^{11}B{^{1}H} NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **2i**.

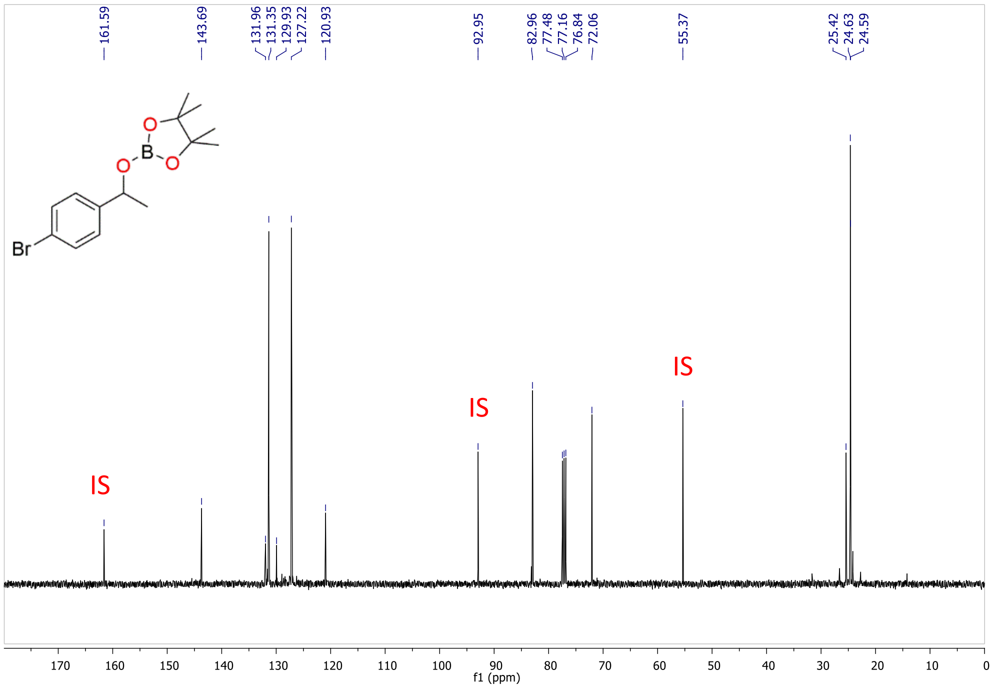


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **2i**.

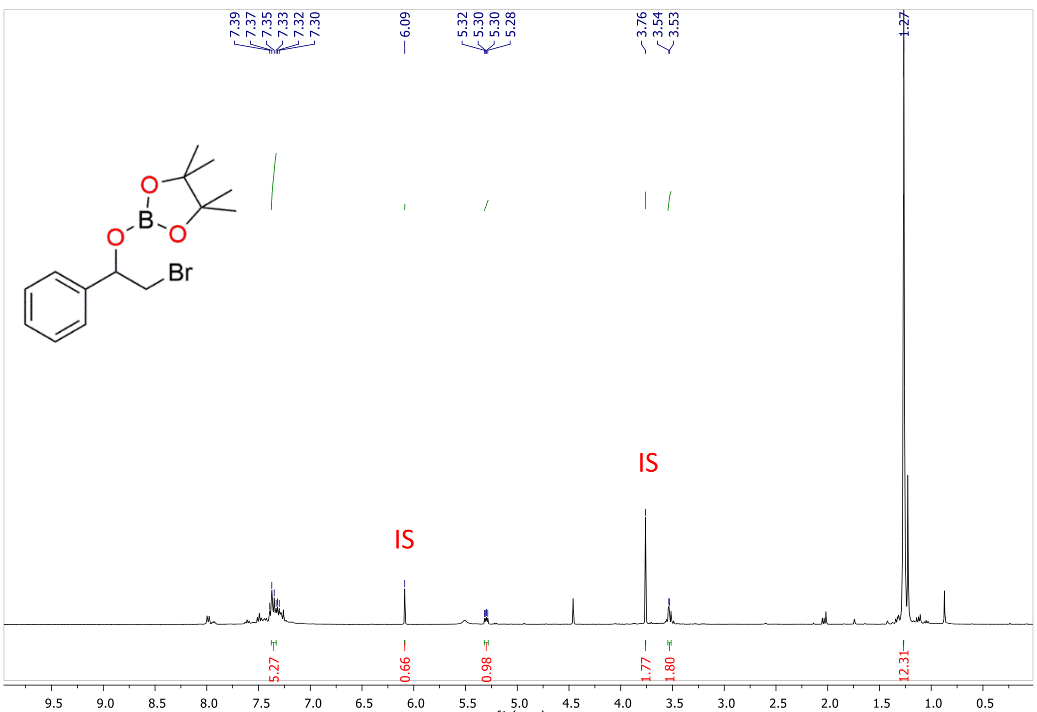


Figure S33. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2j**.

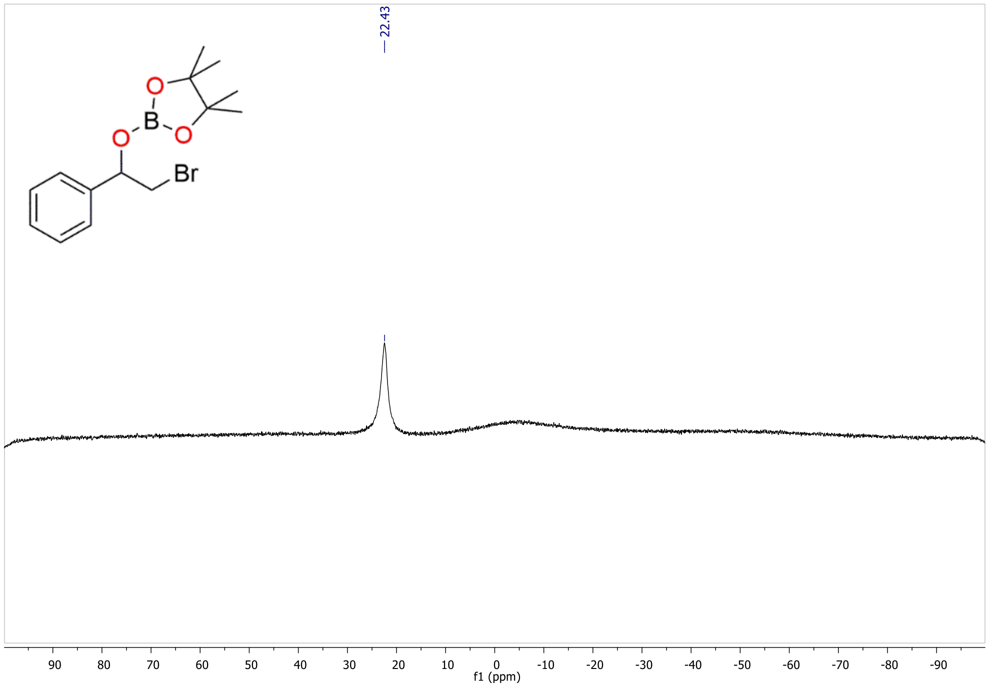


Figure S34. $^{11}B\{^1H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **2j**.

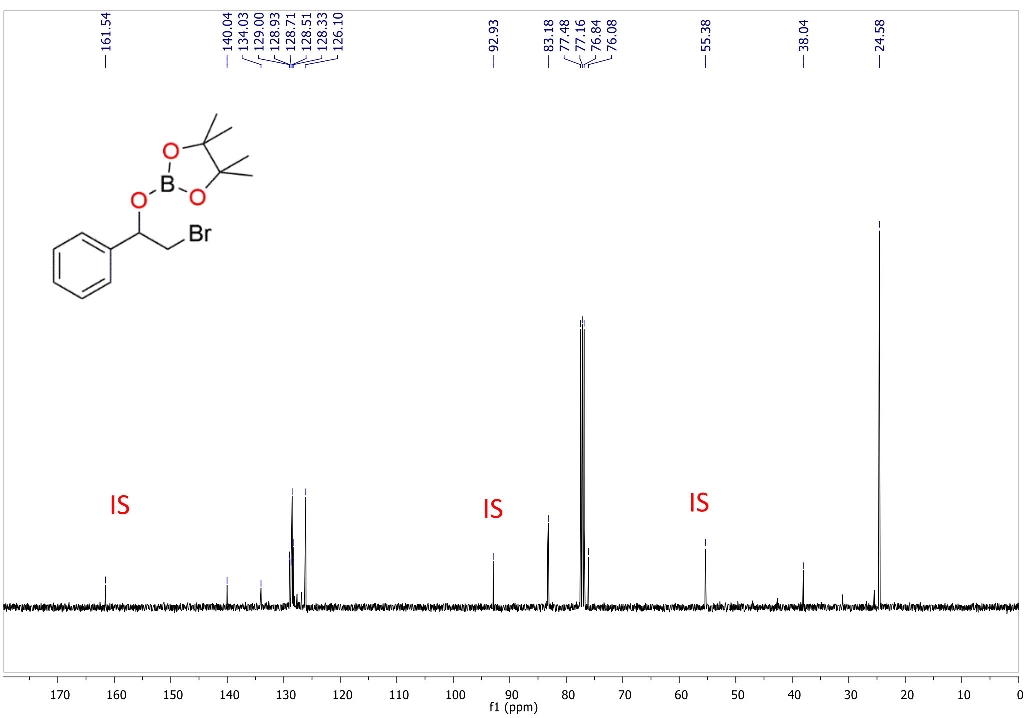


Figure S35. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **2j**.

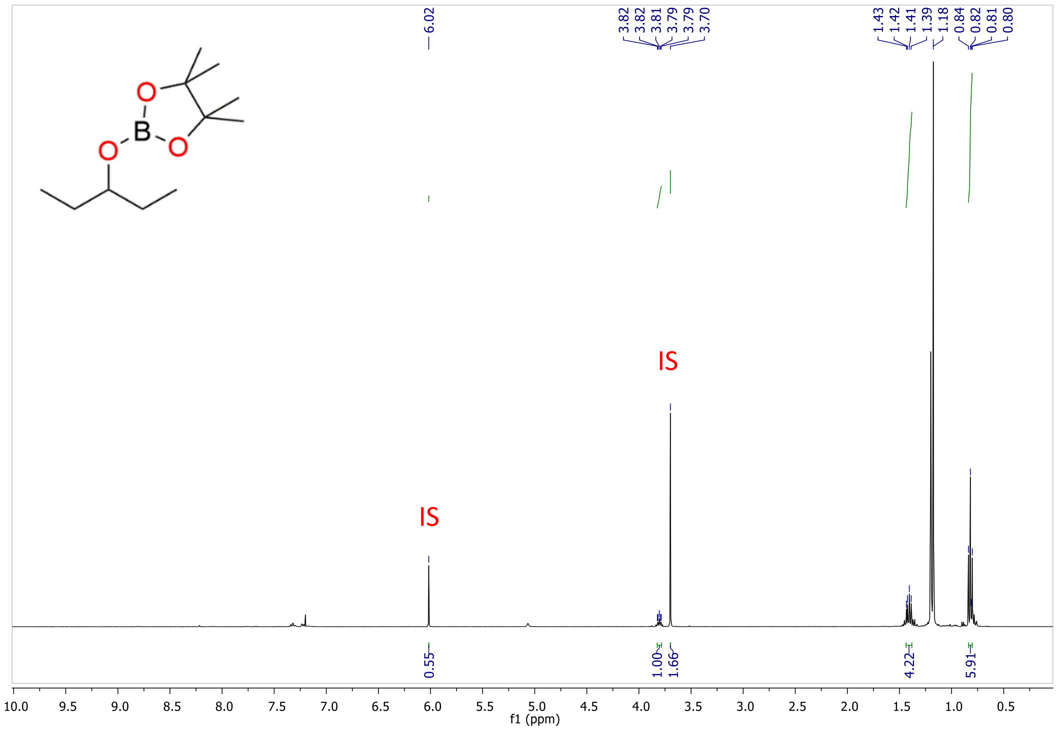


Figure S36. ^{1}H NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **3a**.

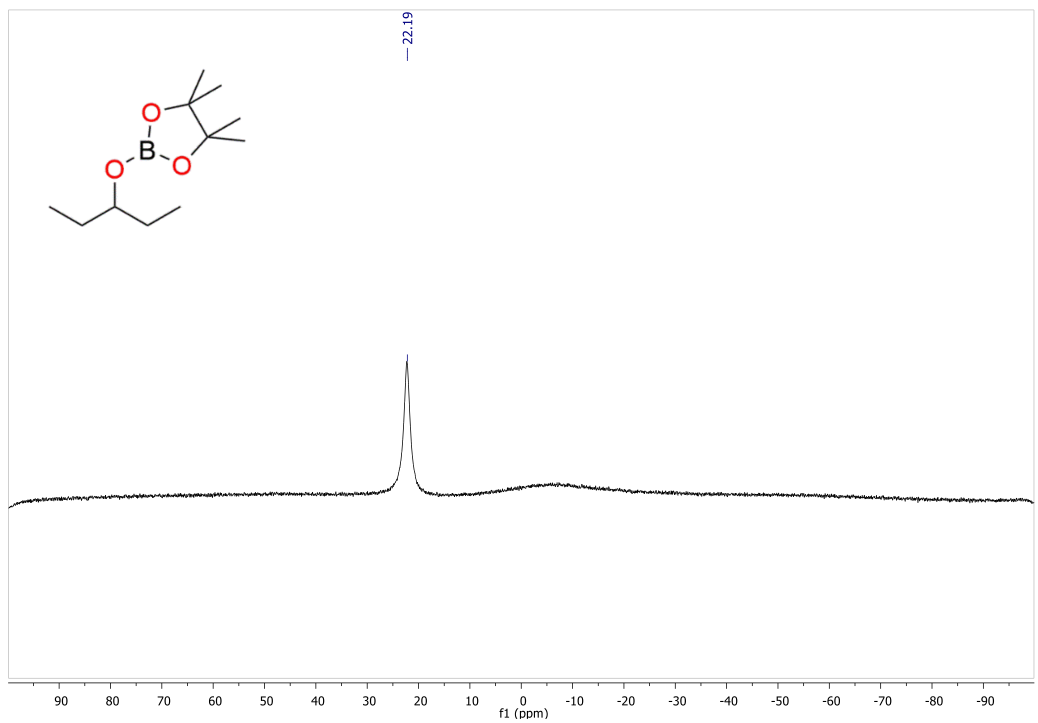


Figure S37. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **3a**.

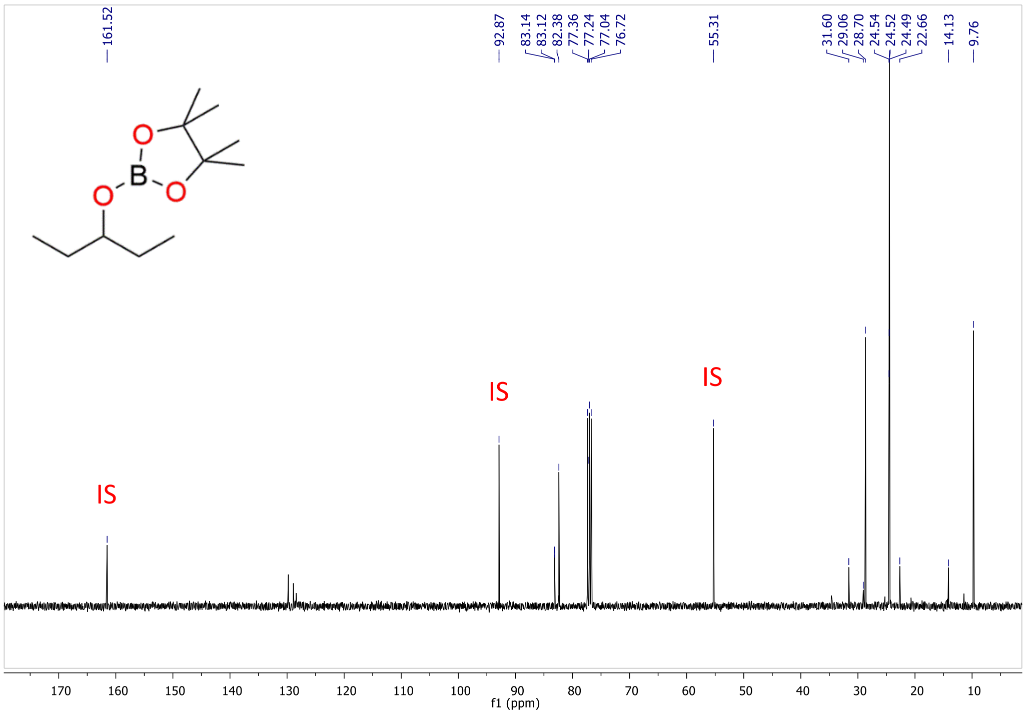


Figure FS 38. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **3a**.

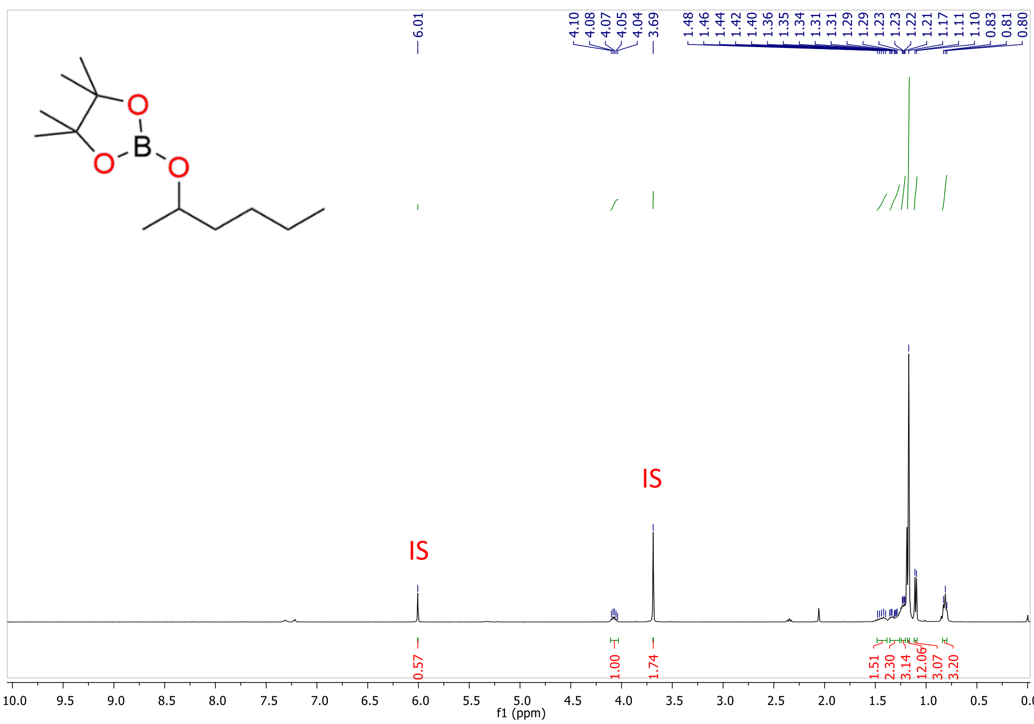


Figure FS 39. ^1H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of (**3b**).

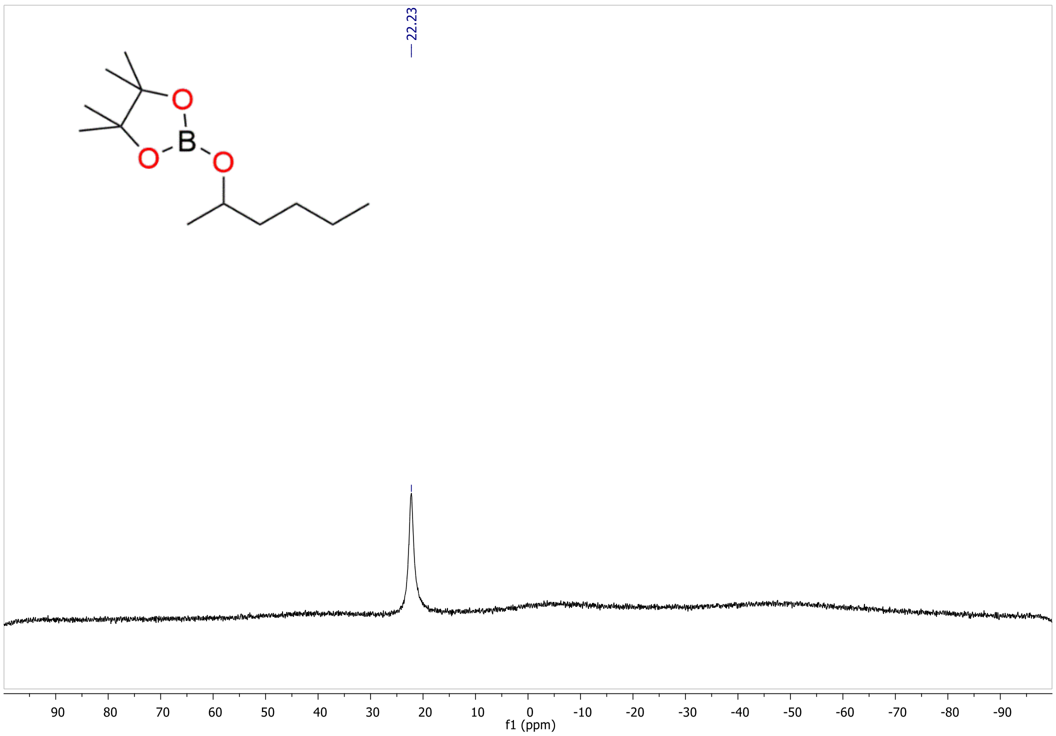


Figure S40. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of (**3b**).

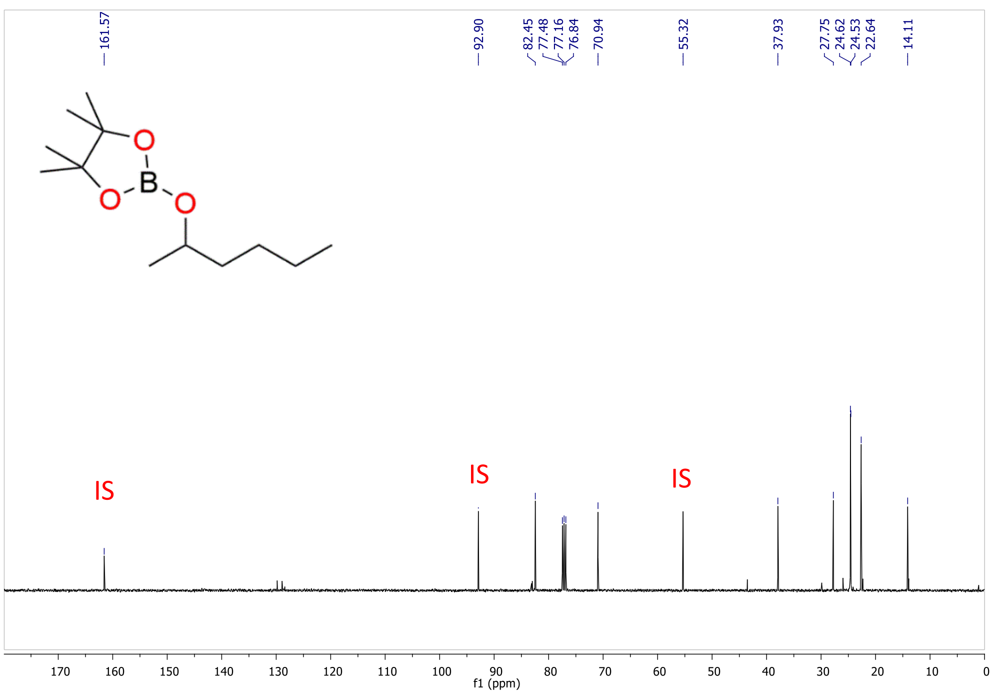


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **3b**.

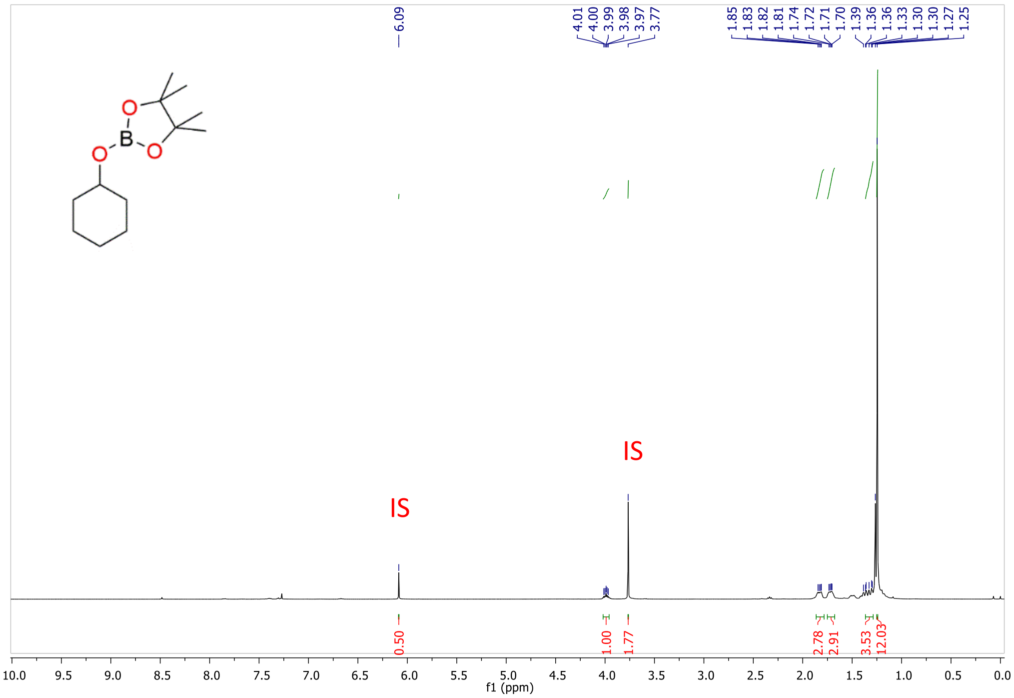


Figure S42. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **3c**.

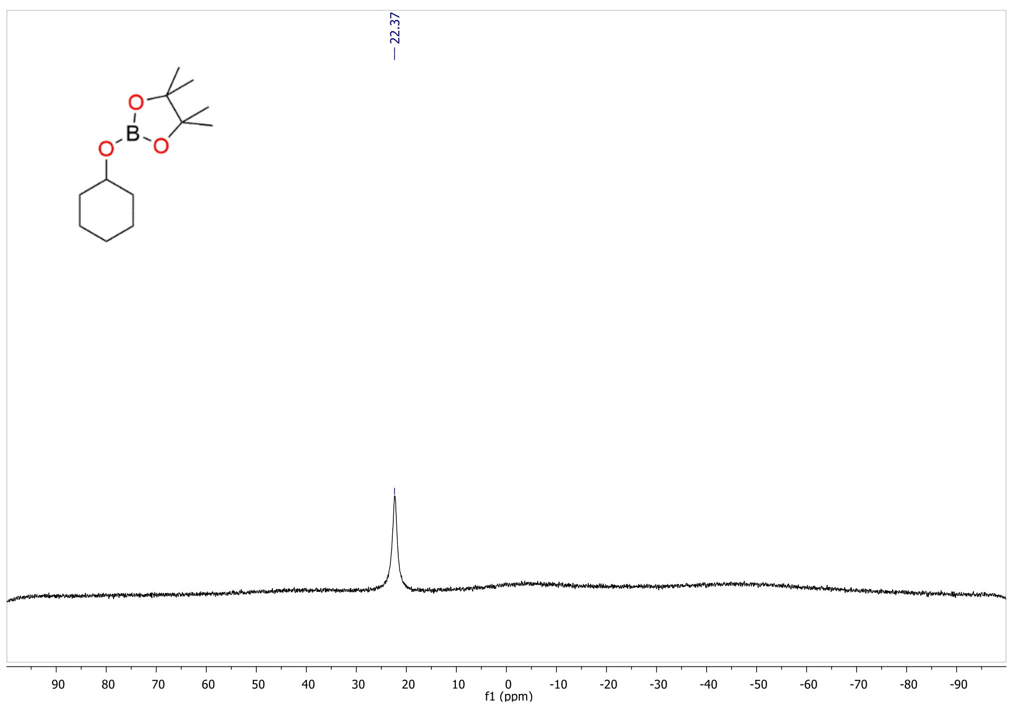


Figure S43. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **3c.**

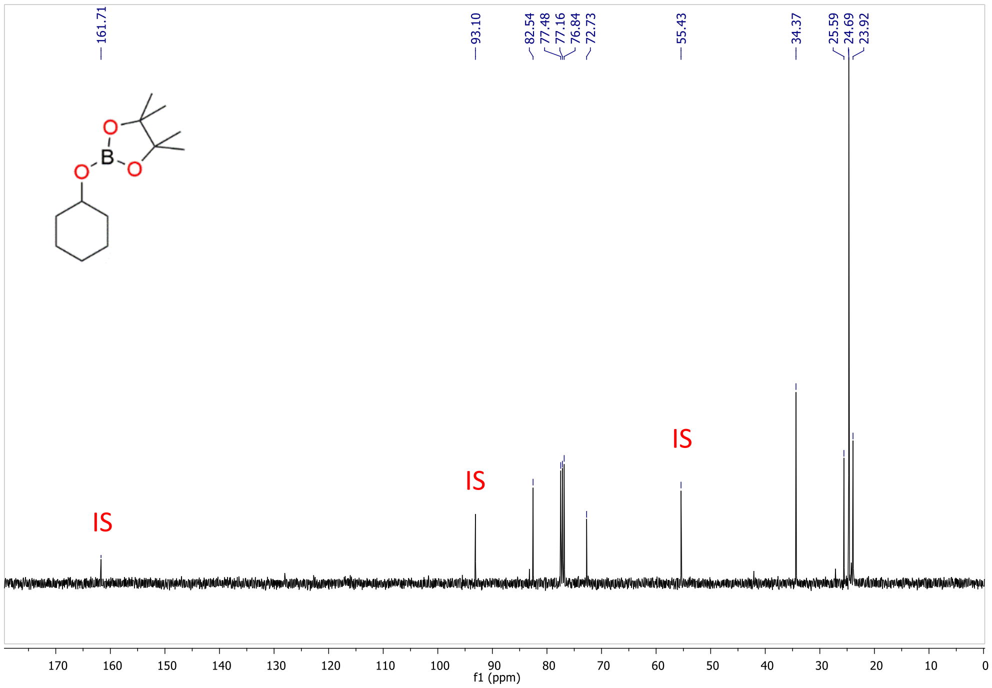


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **3c**.

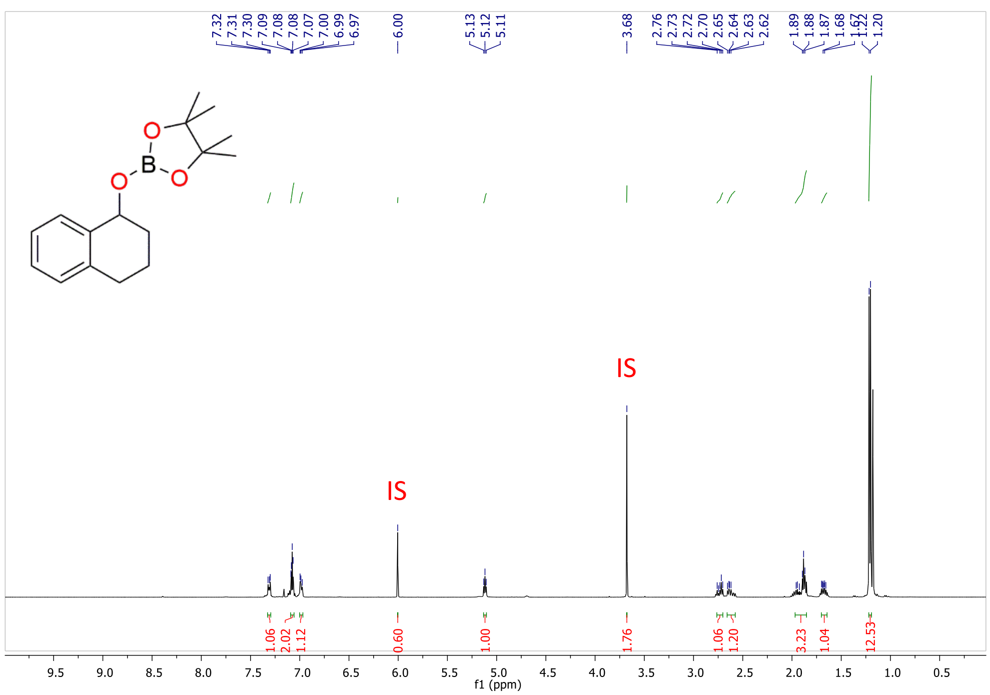


Figure S45. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **3d**.

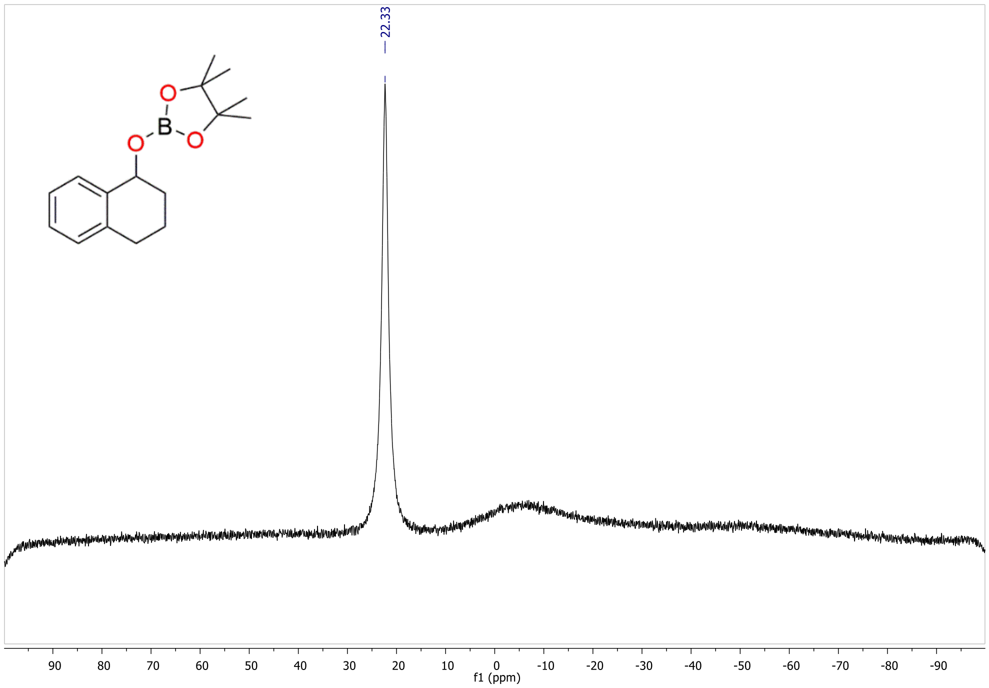


Figure S46. $^{11}B\{^1H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **3d**.

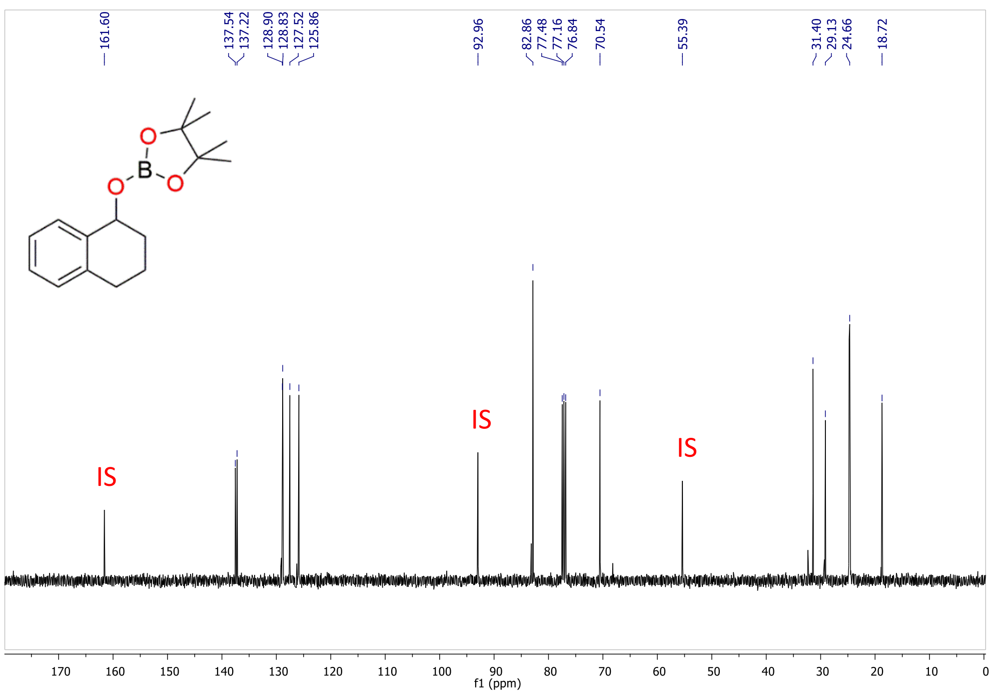


Figure S47. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, 25 °C, CDCl3) of **3d**.

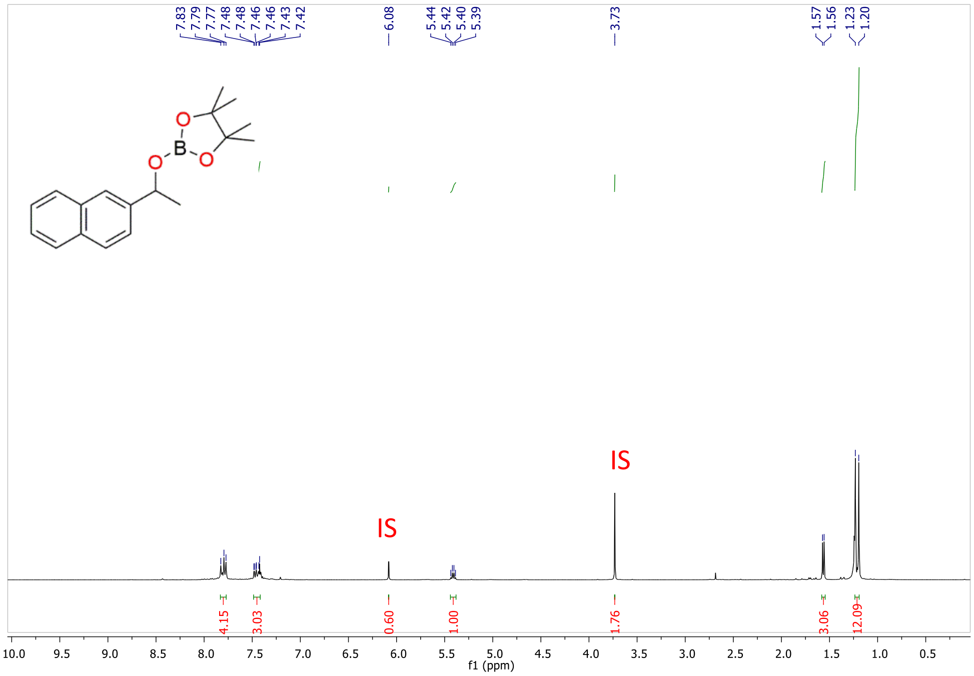


Figure S48. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **3e**.

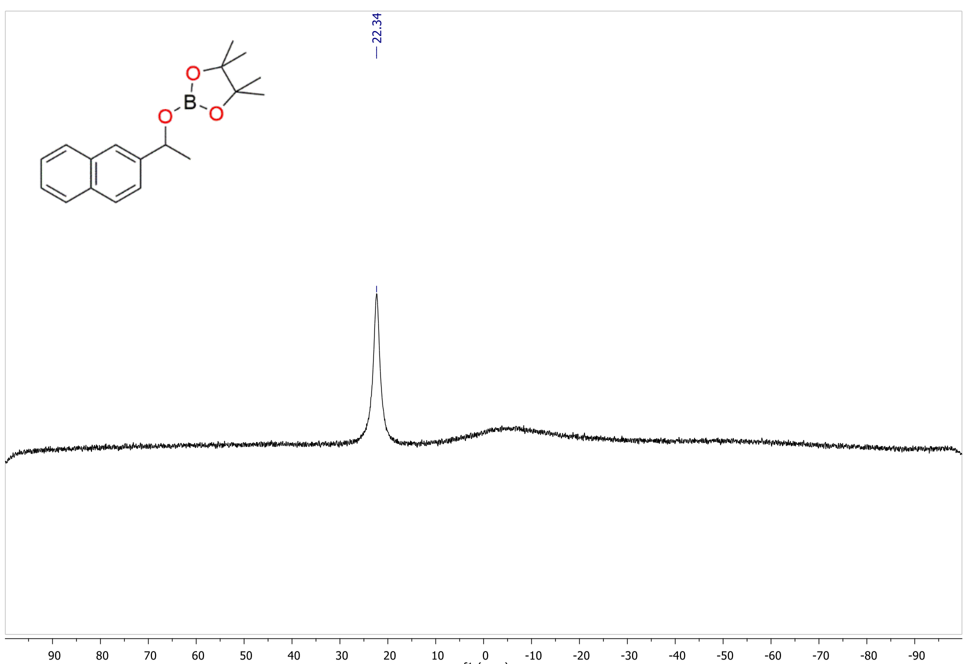


Figure S49. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **3e**.

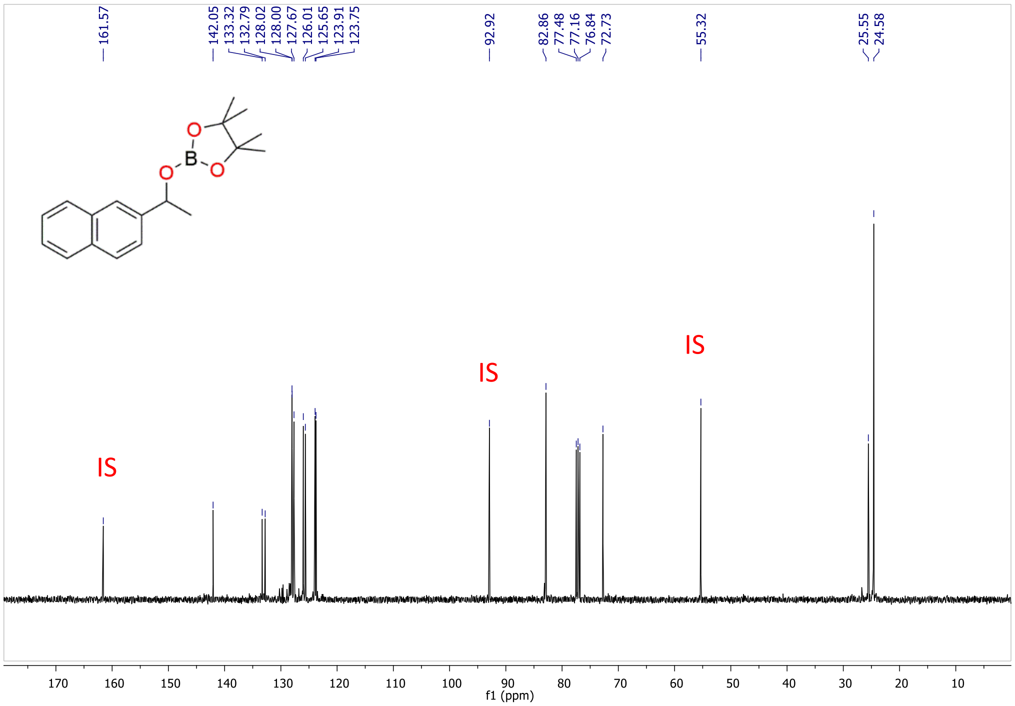


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **3e**.

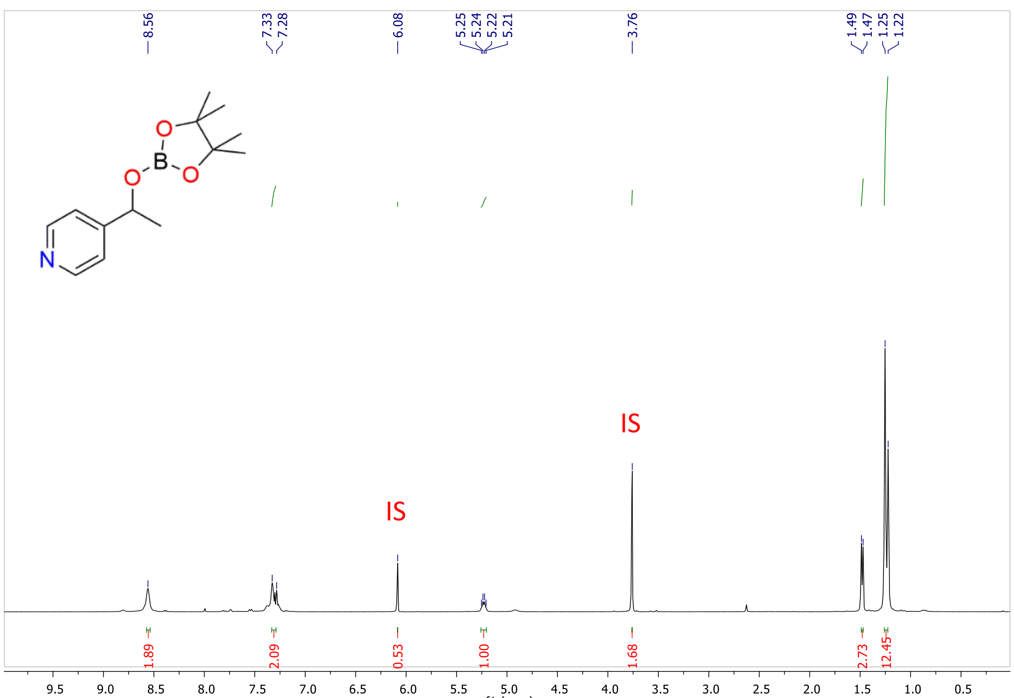


Figure S51. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **3f**.

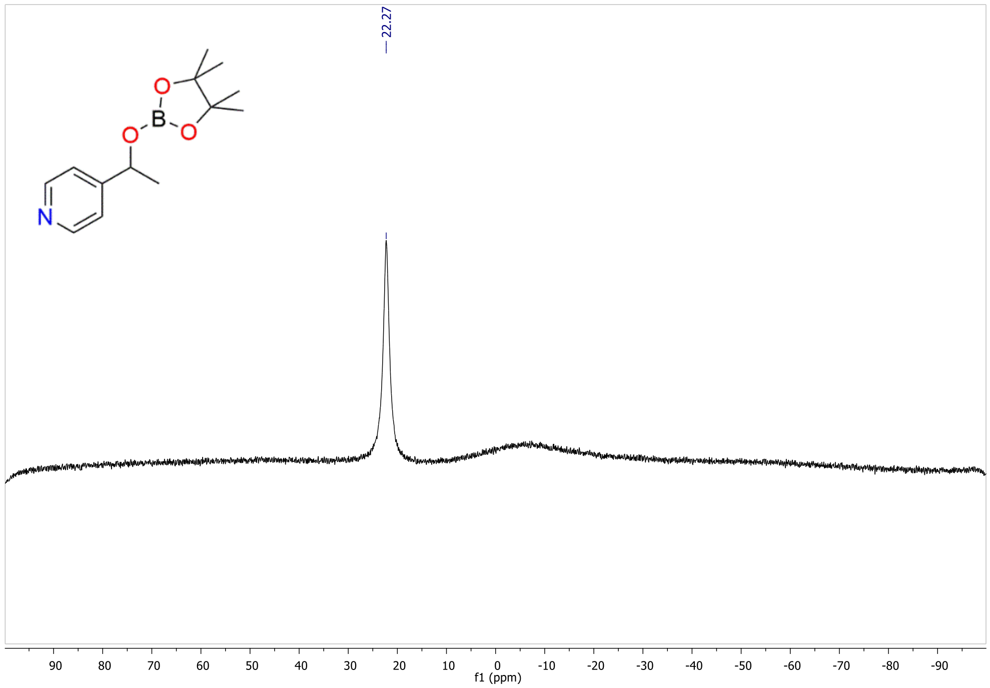


Figure S52. $^{11}B\{^1H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **3f**.

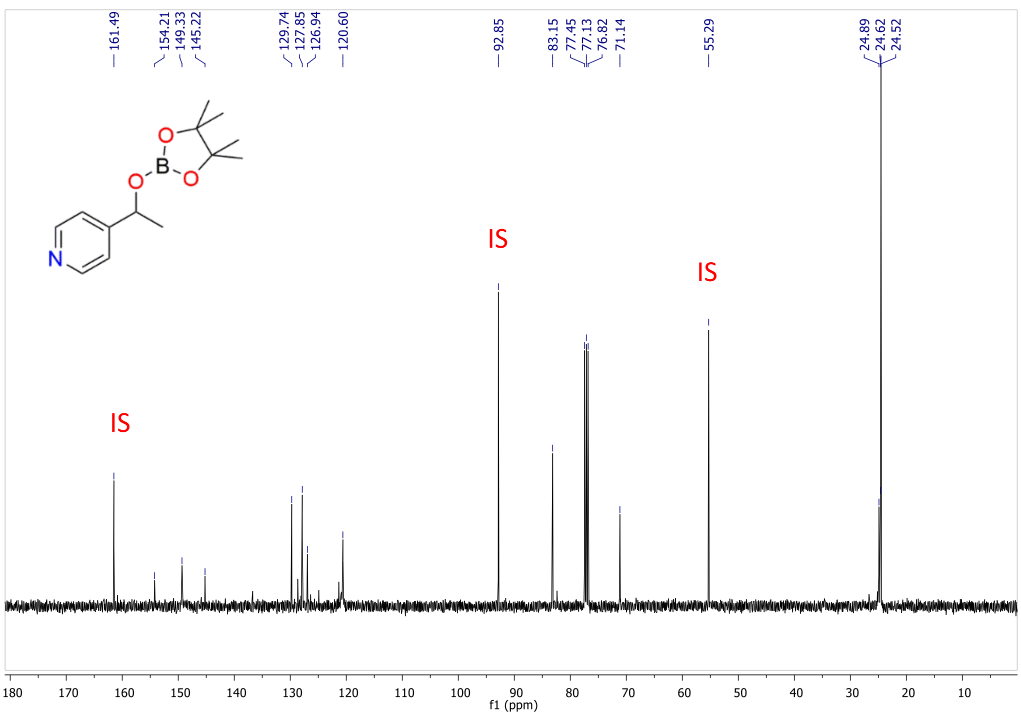


Figure S53. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **3f**.

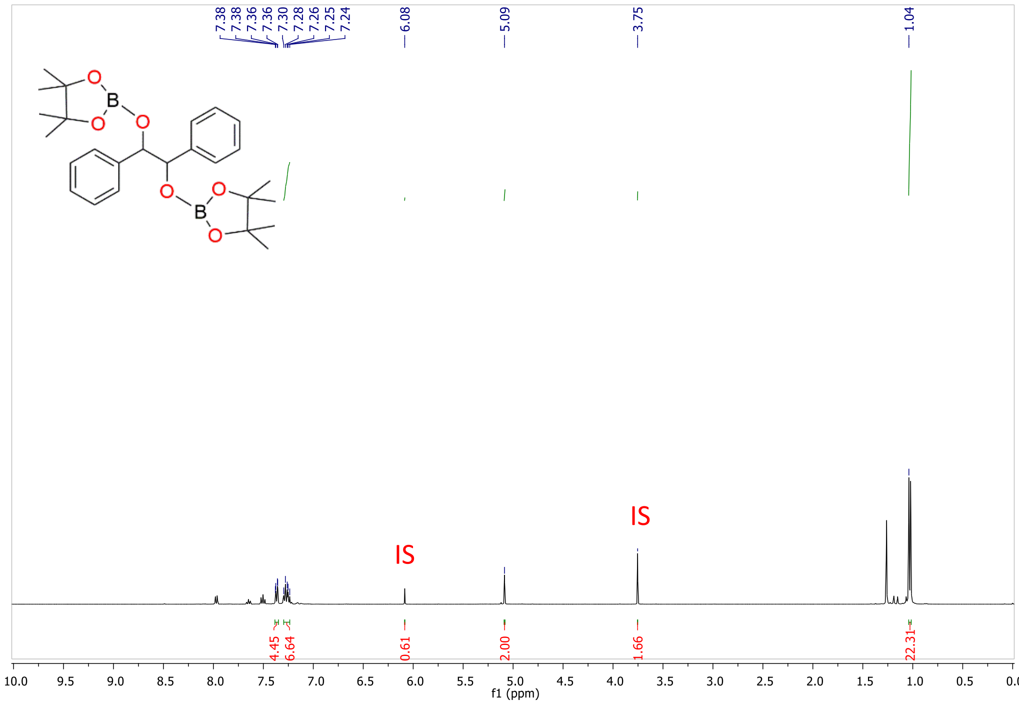


Figure S54. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **3g**.

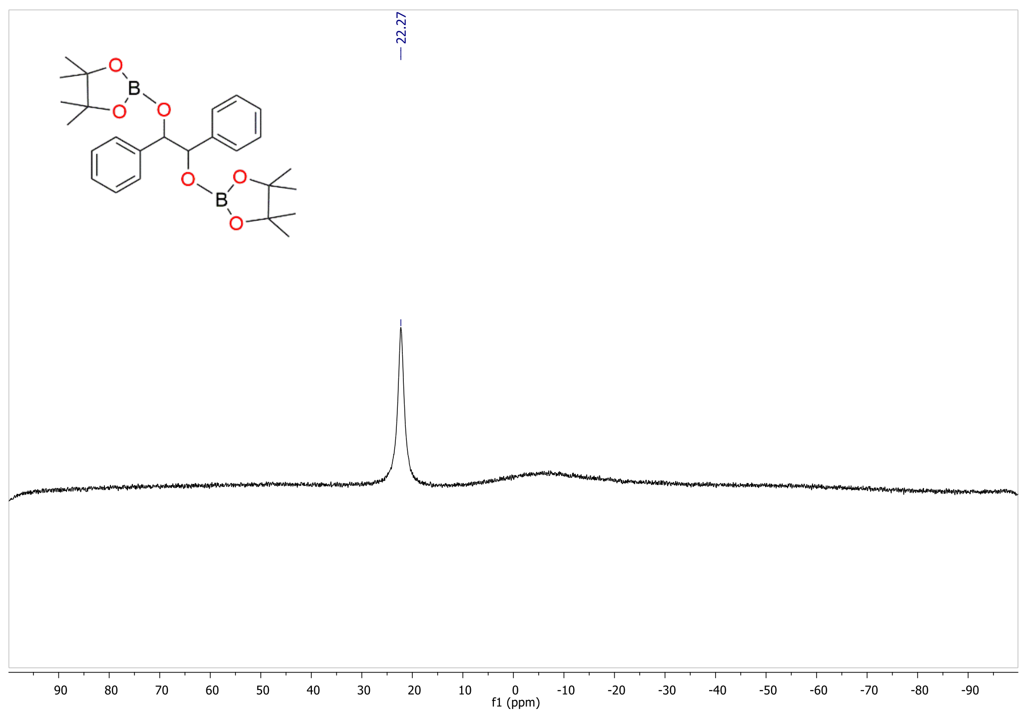


Figure S55. ^{11}B{^{1}H} NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **3g**.

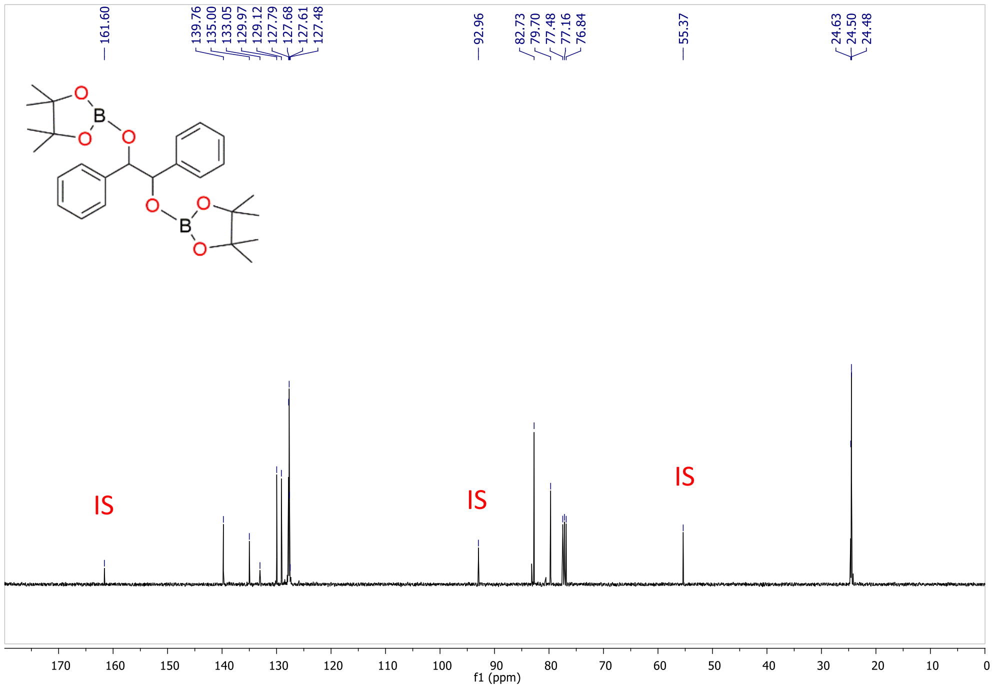


Figure S56. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **3g**.

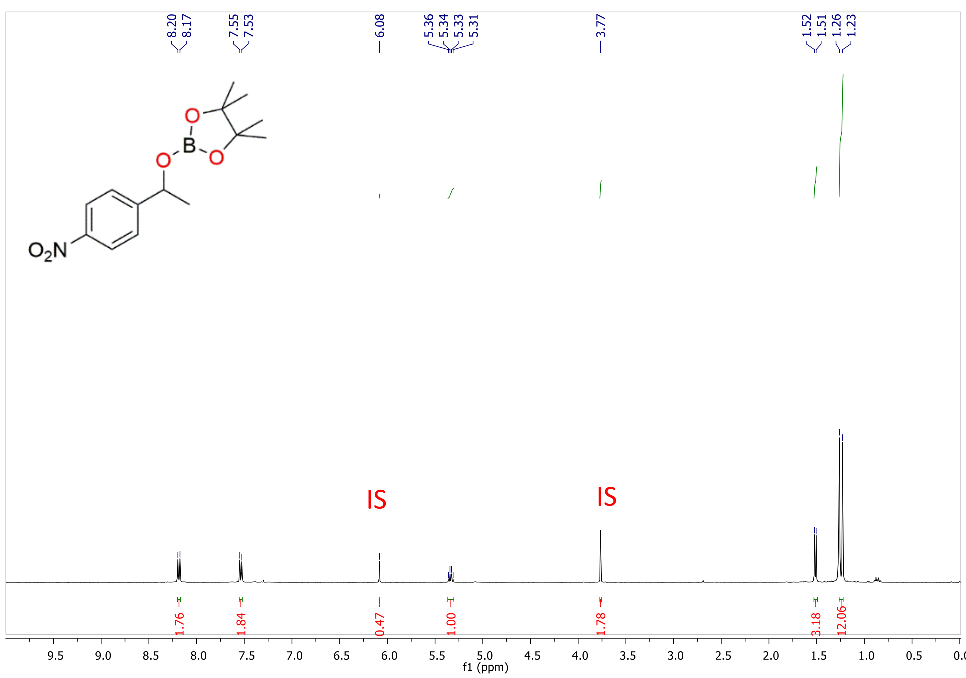


Figure S57. ^1H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **4a**.

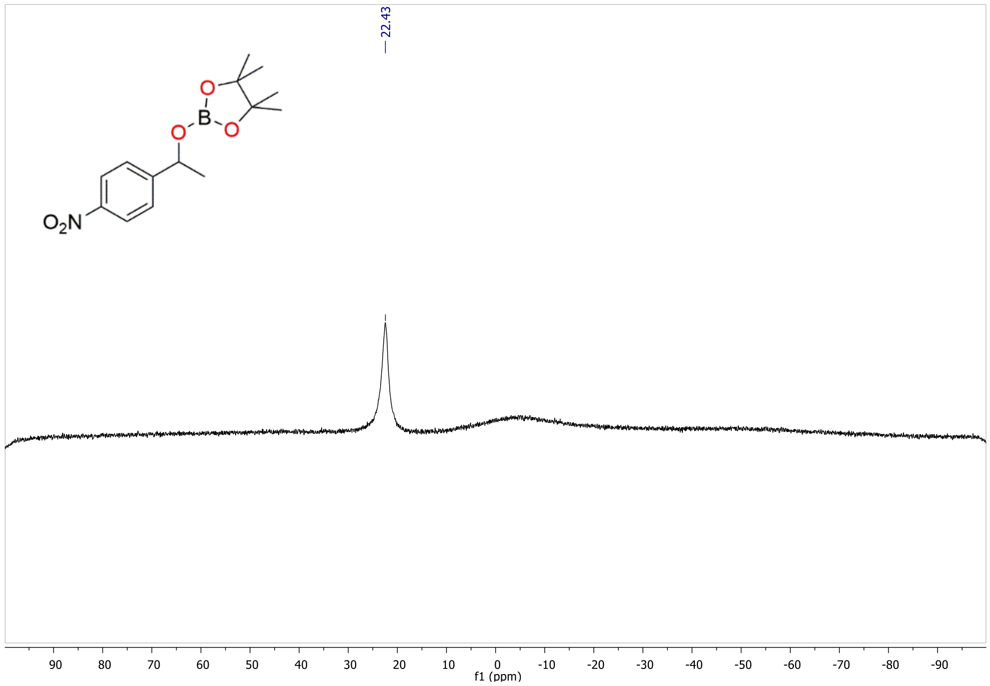


Figure S58. $^{11}B\{^1H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **4a**.

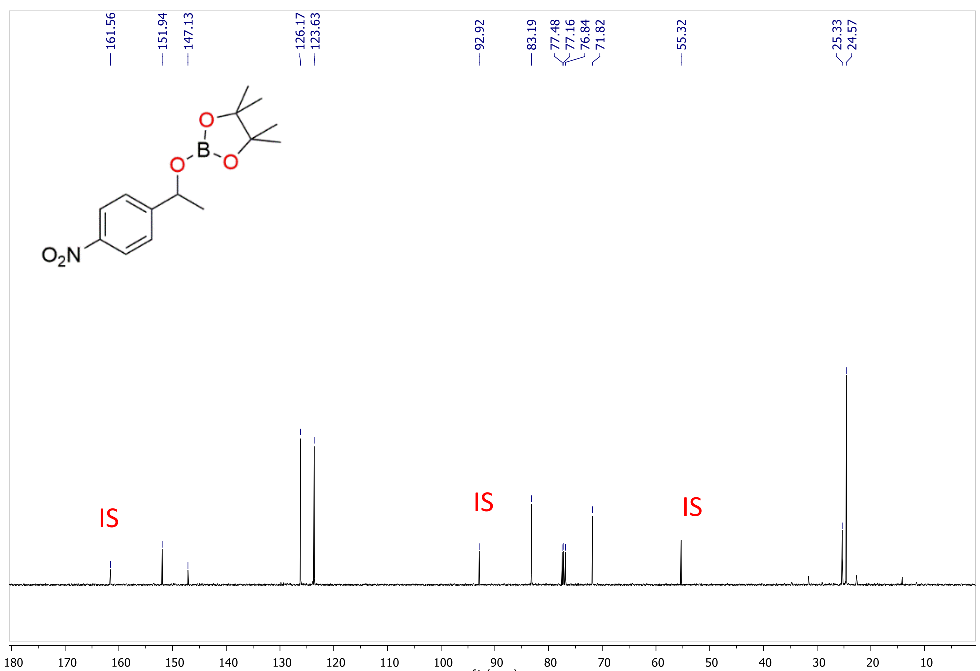


Figure S59. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **4a**.

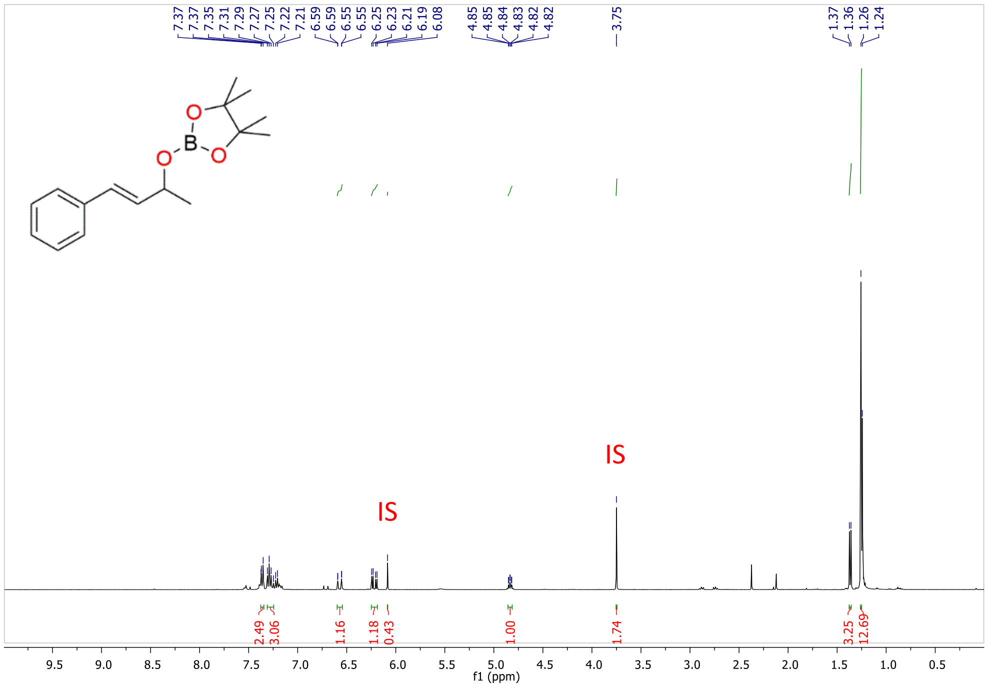


Figure S60. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **4b**.

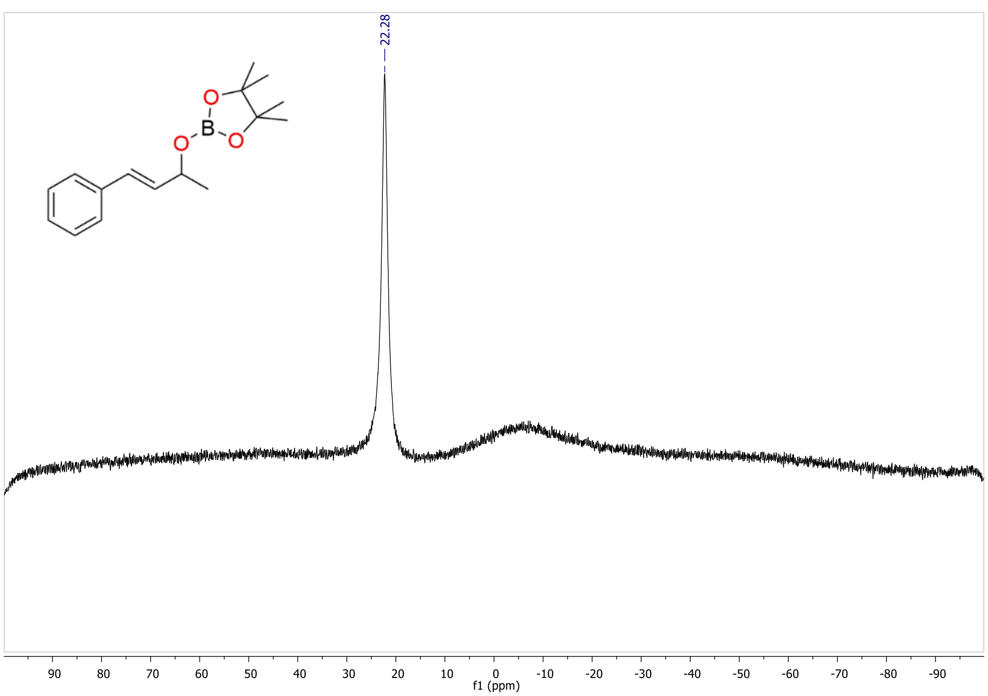


Figure S61. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **4b**.

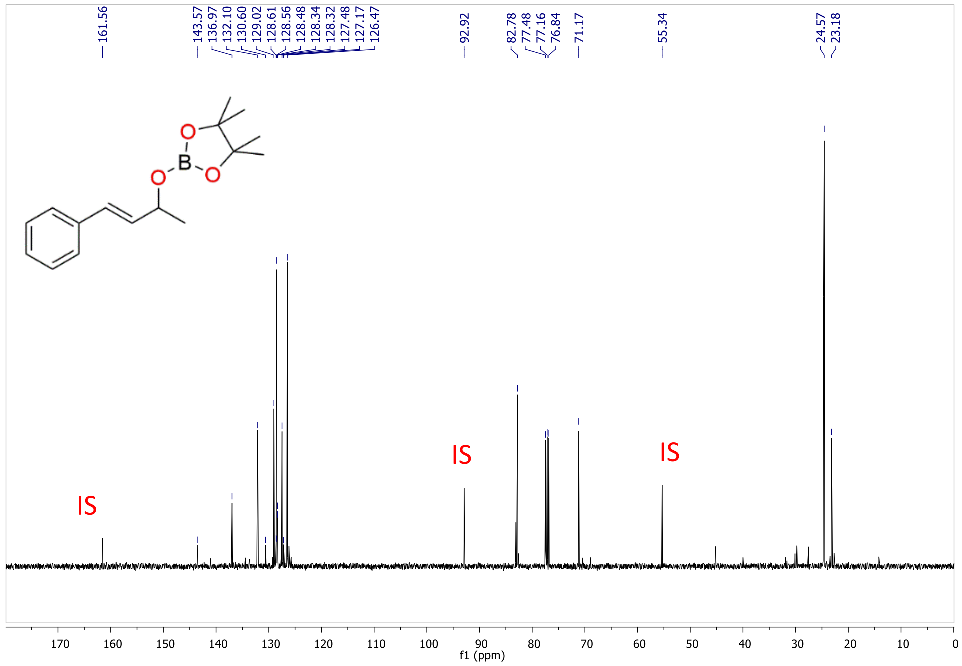


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **4b**.

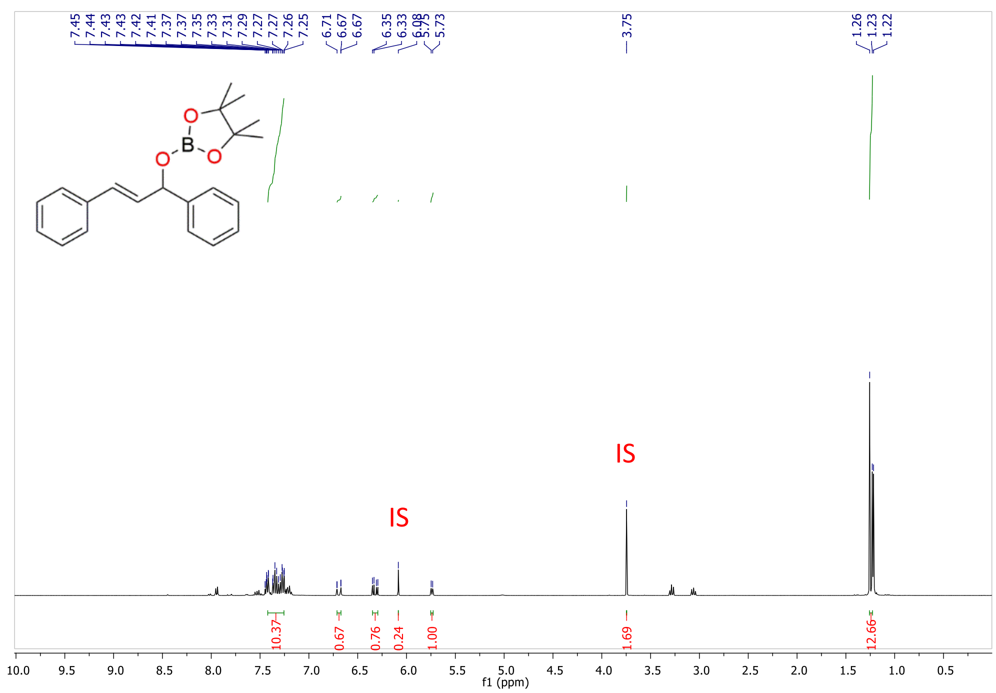


Figure S63. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **4c**.

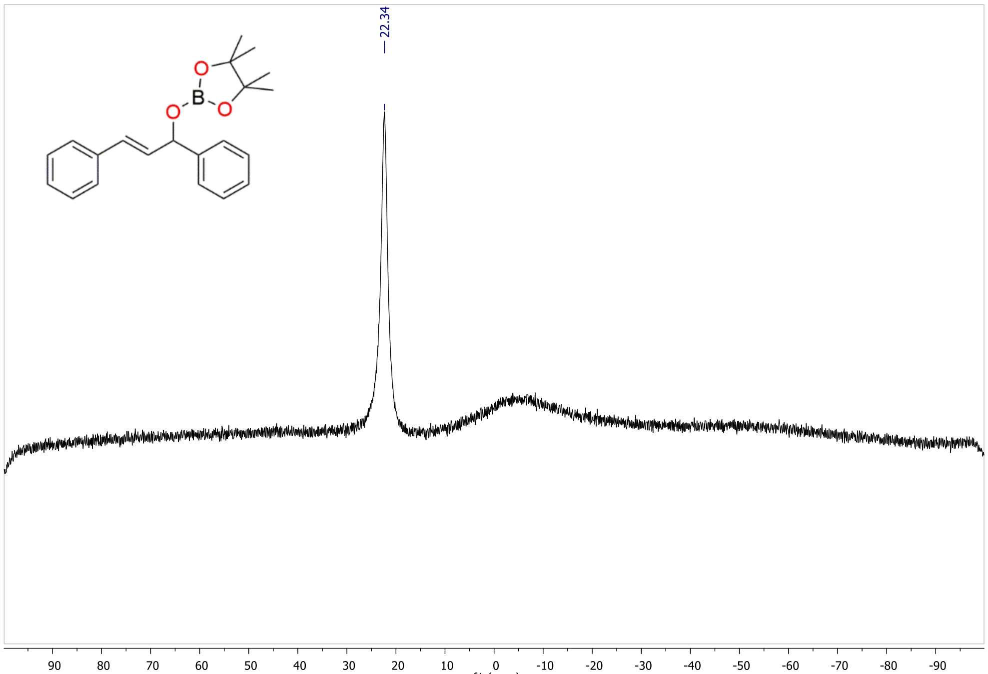


Figure S64. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **4c**.

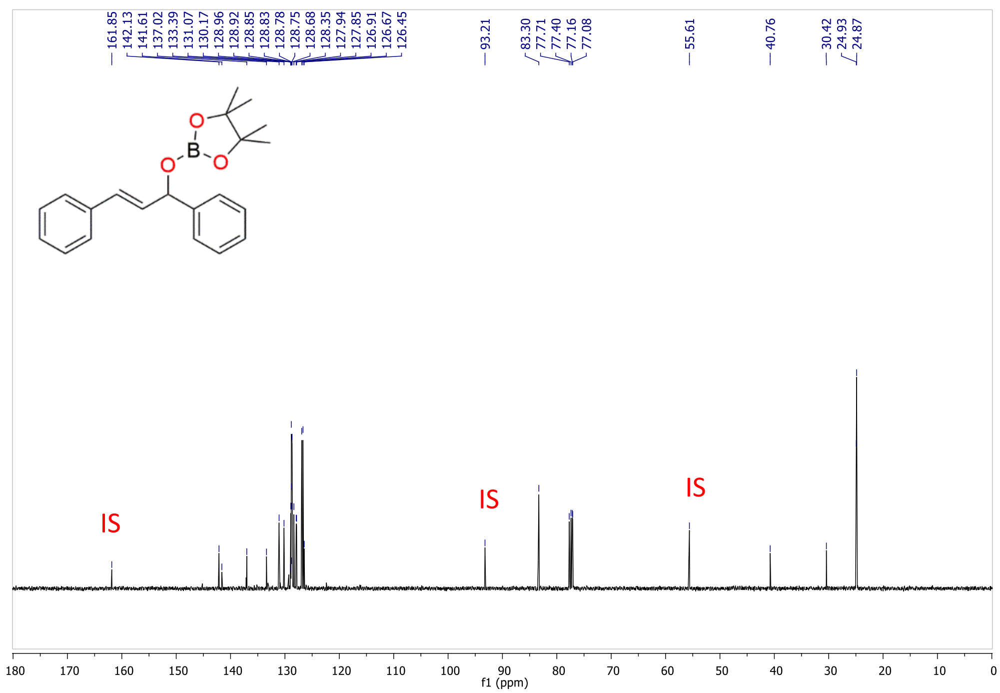


Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **4c**.

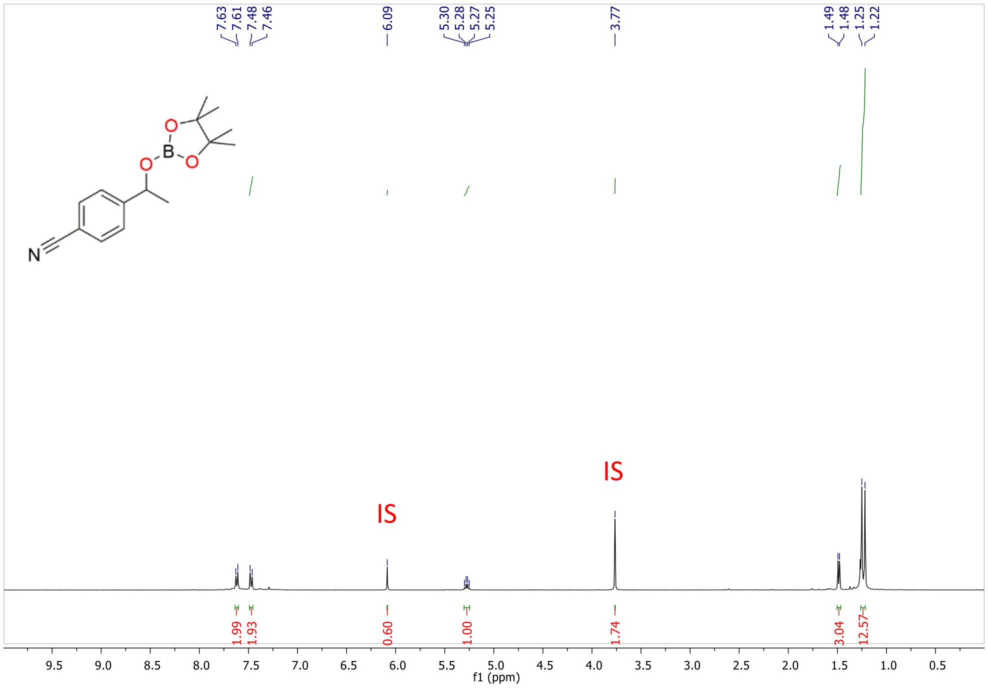


Figure S66. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **4d**.

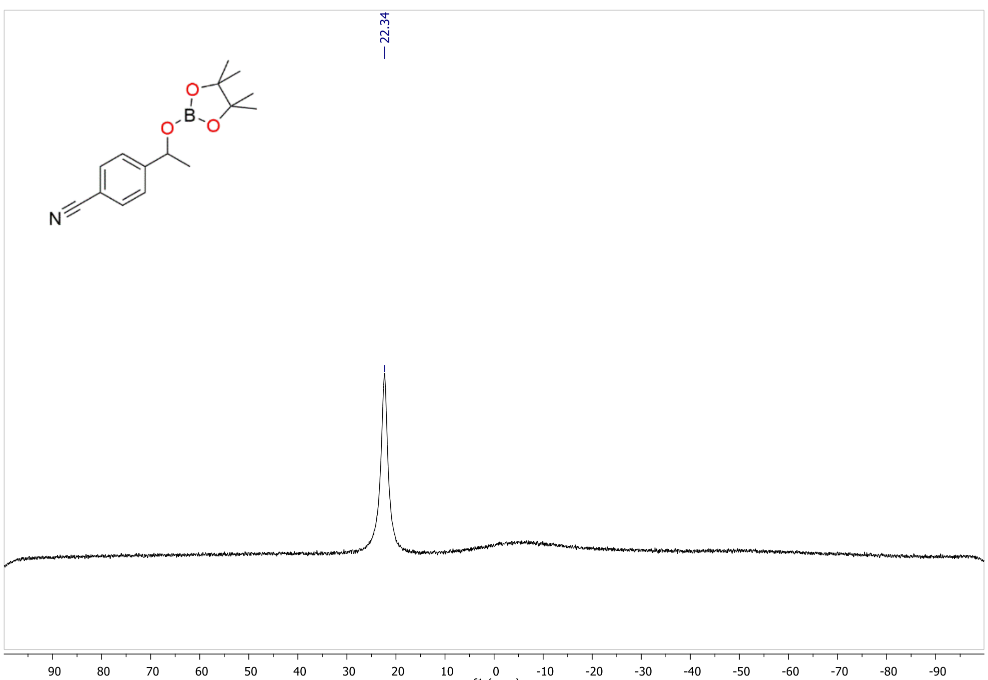


Figure S67. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **4d**.

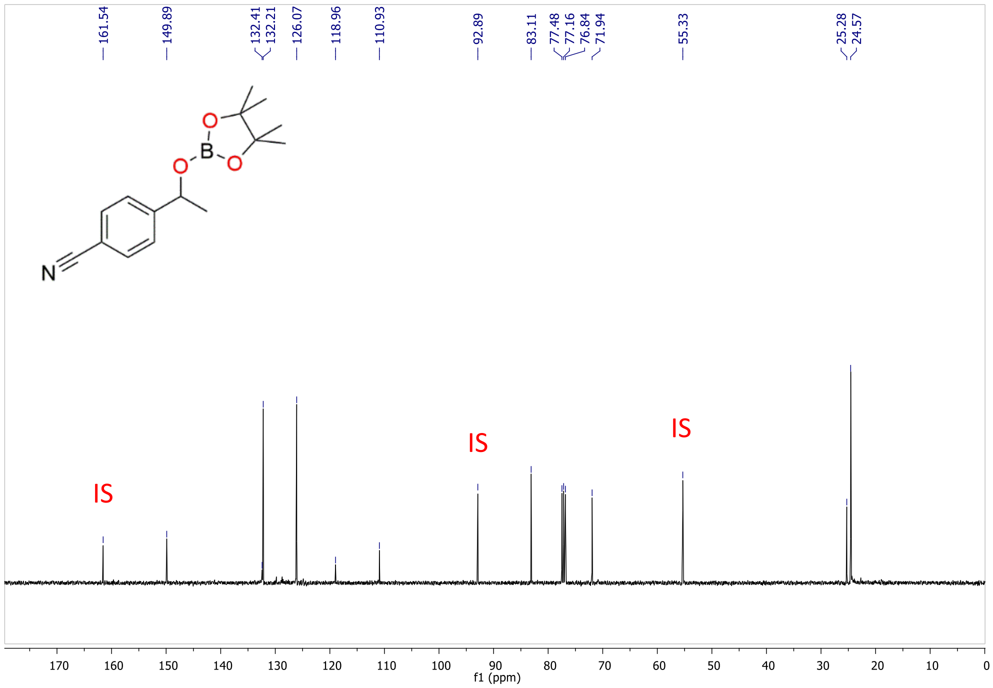


Figure S68. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **4d**.

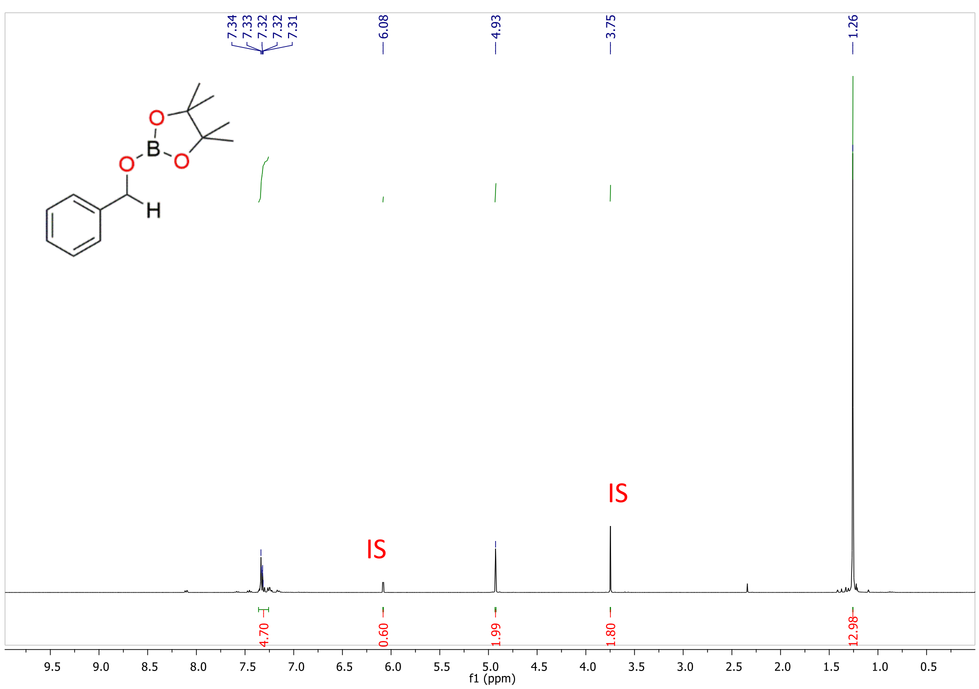


Figure S69. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of **5a**.

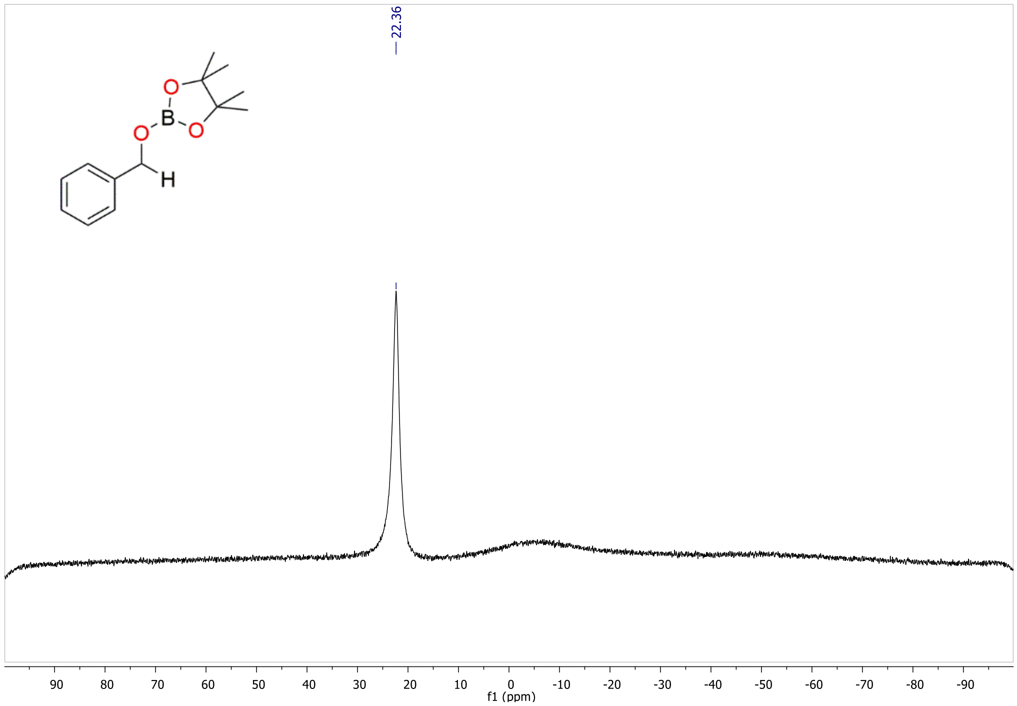


Figure 70. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **5a.**

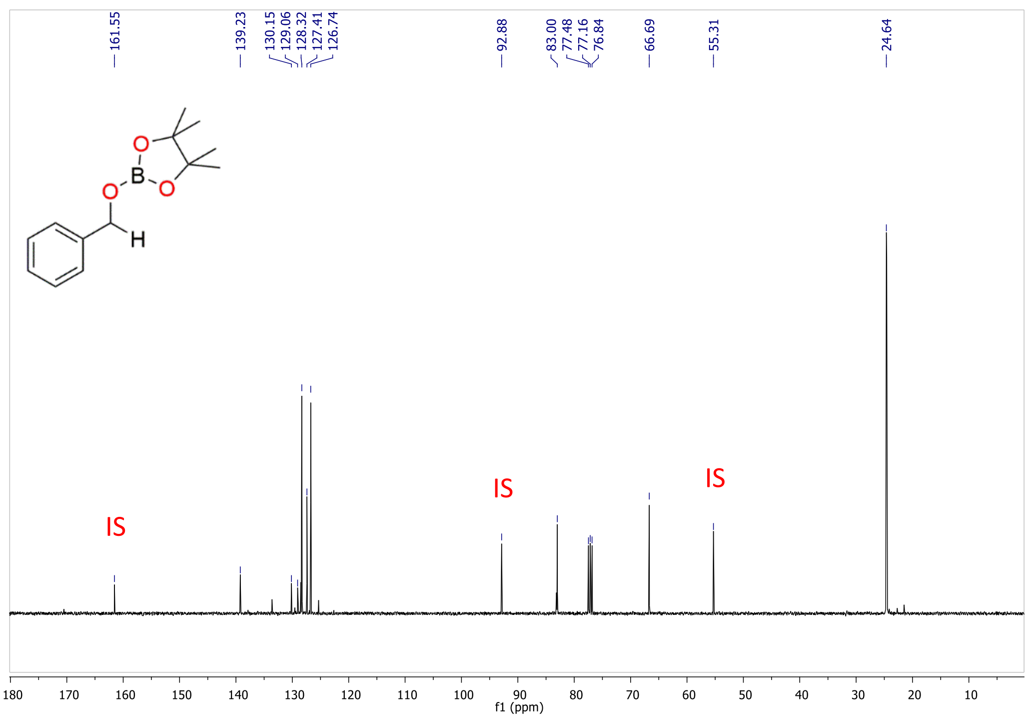


Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5a**.

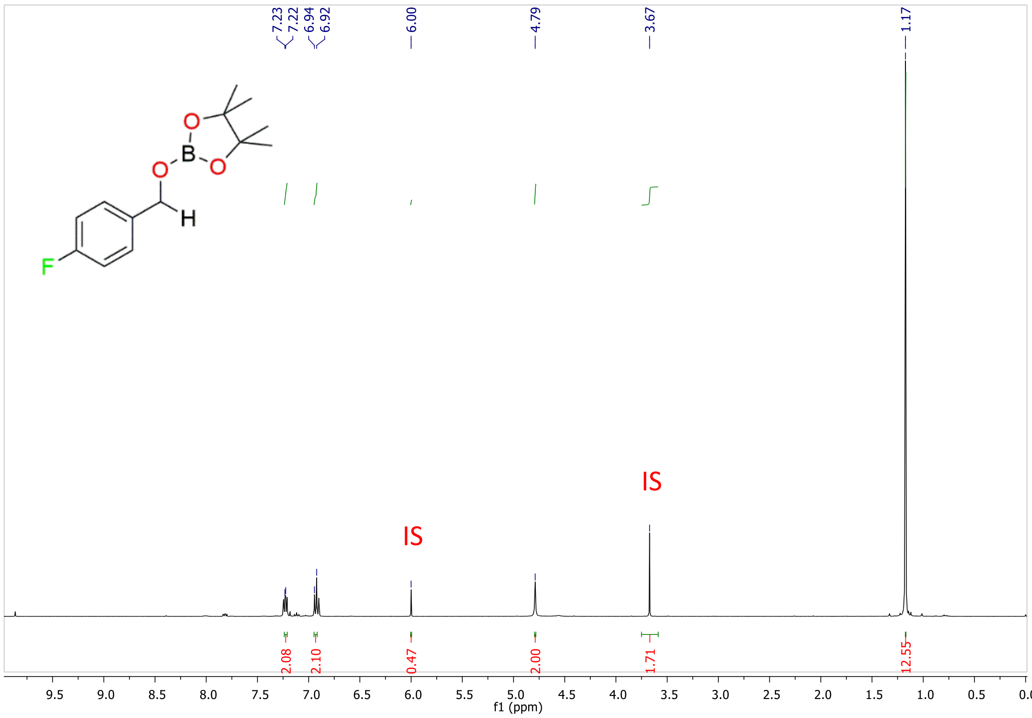


Figure S72. ^{1}H NMR spectrum (400 MHz, 25°C, CDCl3) of **5b**.

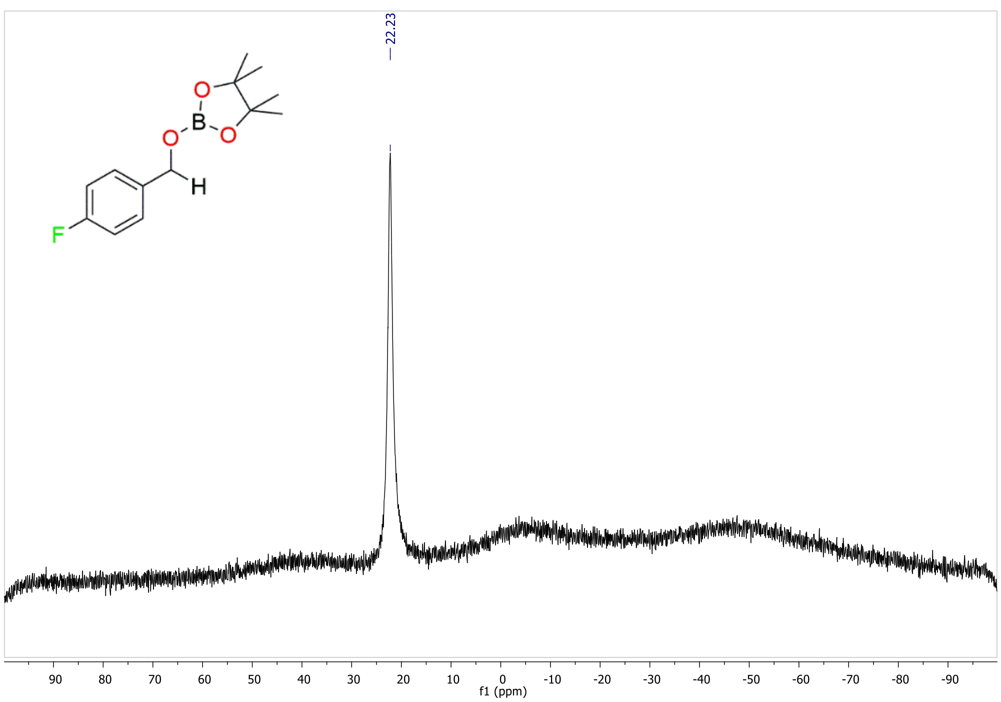


Figure 73. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **5b.**

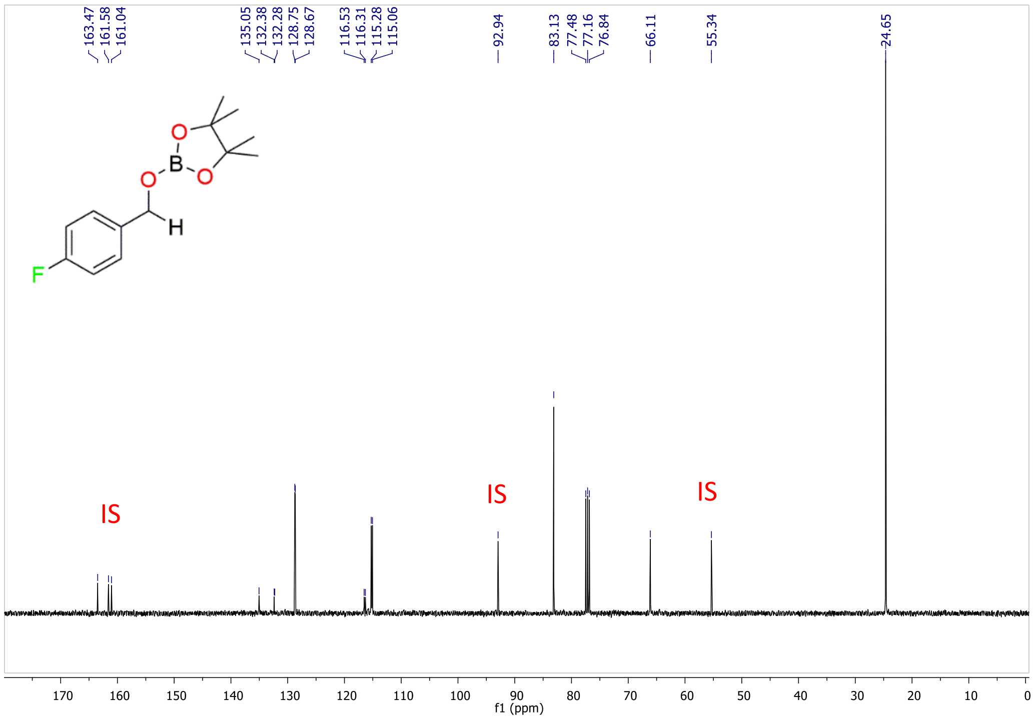


Figure S74. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5b**.

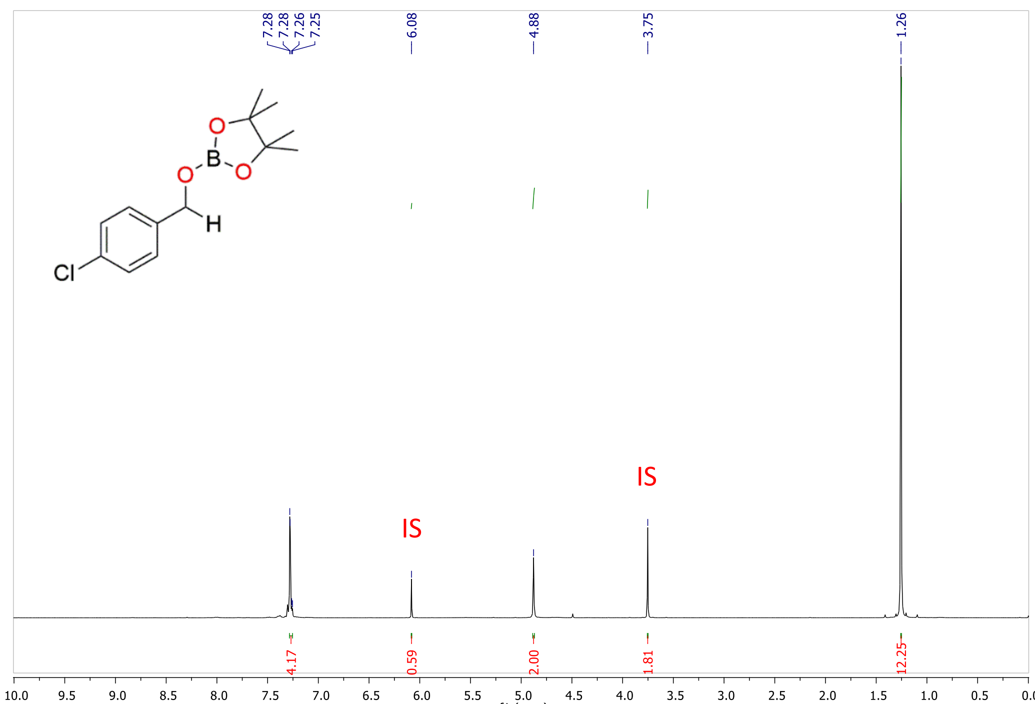


Figure S75. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **5c**.

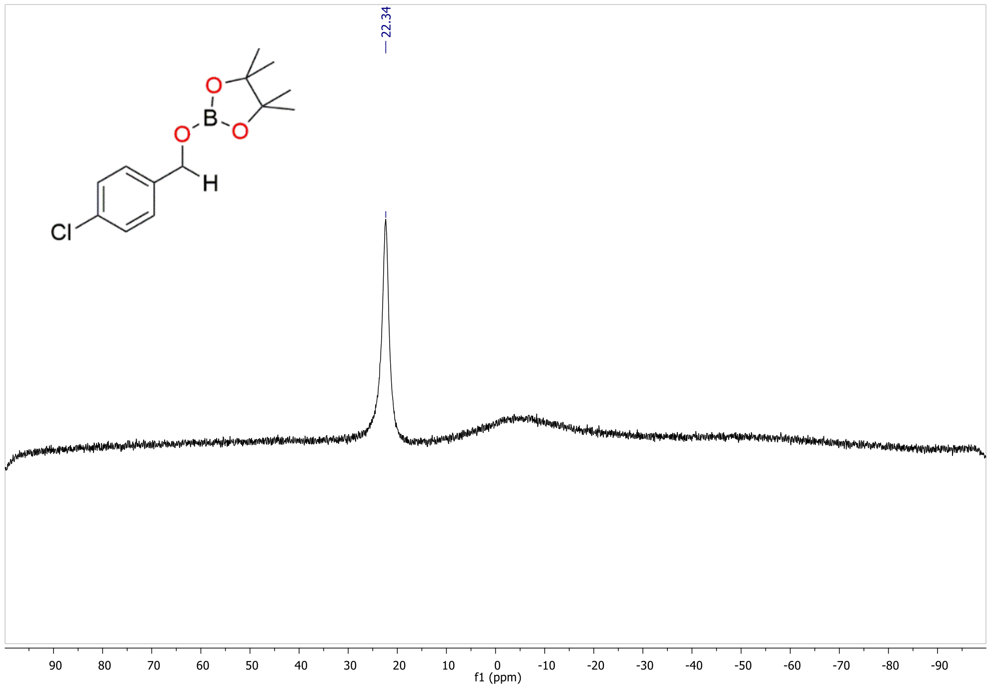


Figure S76. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **5c**.

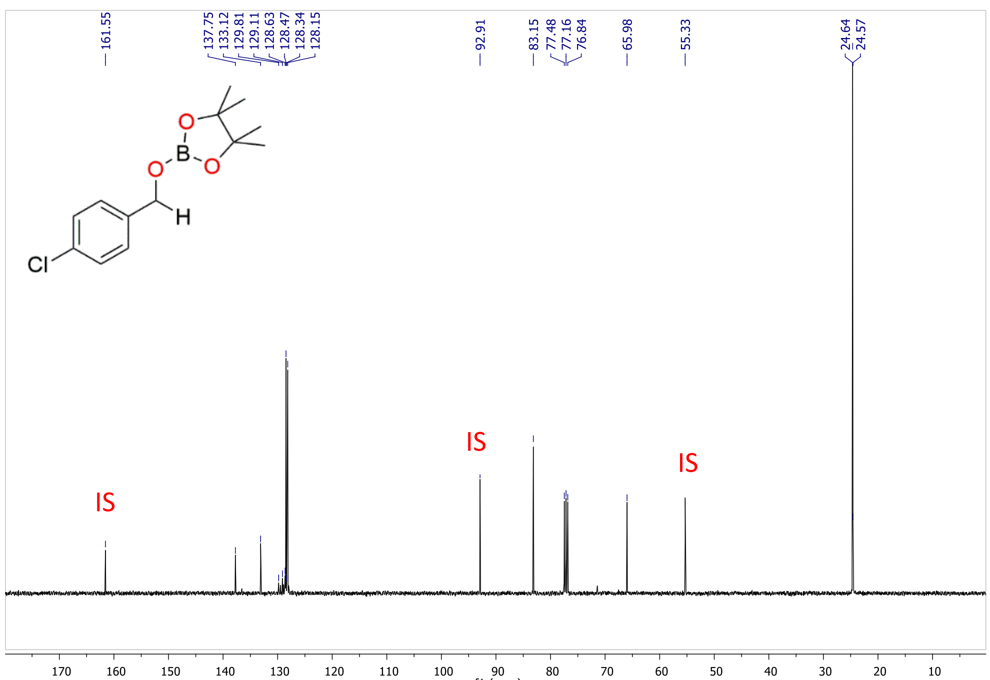


Figure S77. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5c**.

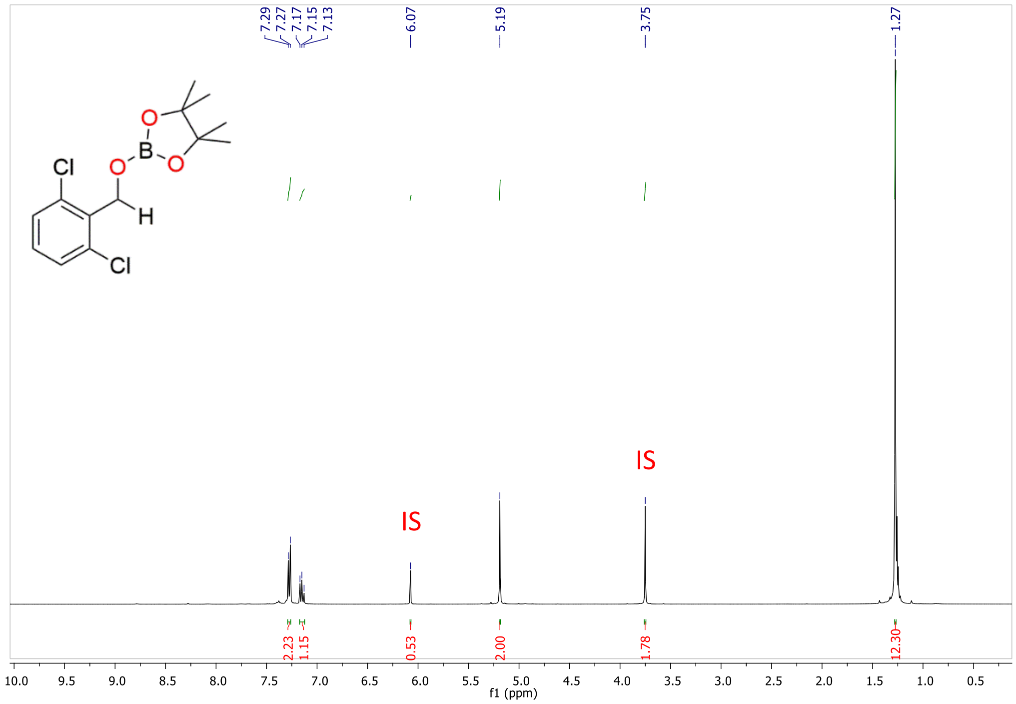


Figure S78. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of **5d**.

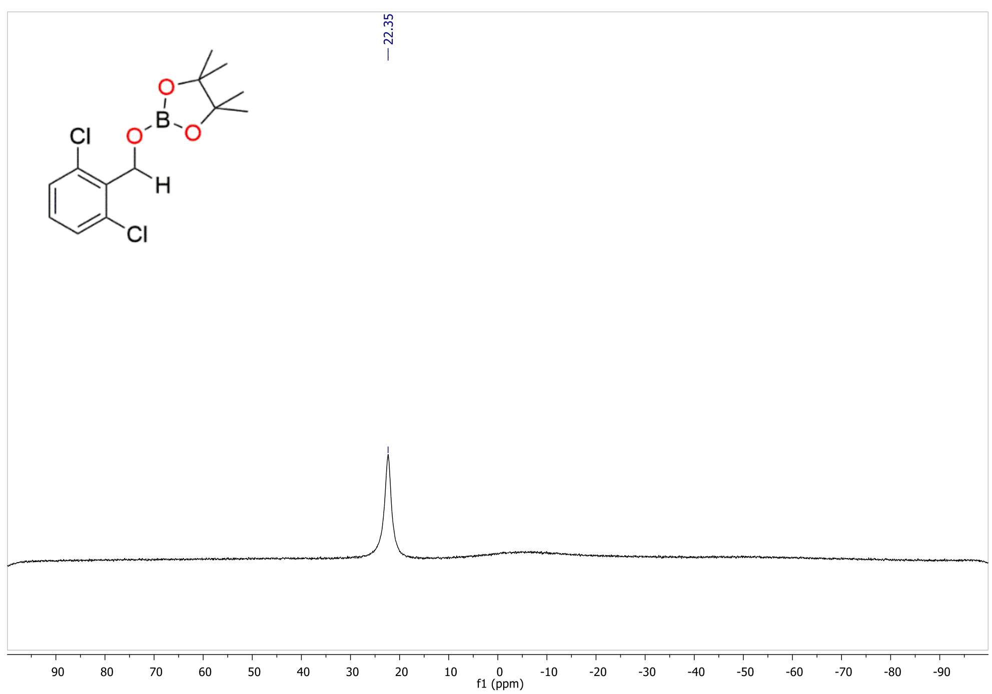


Figure S79. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **5d**.

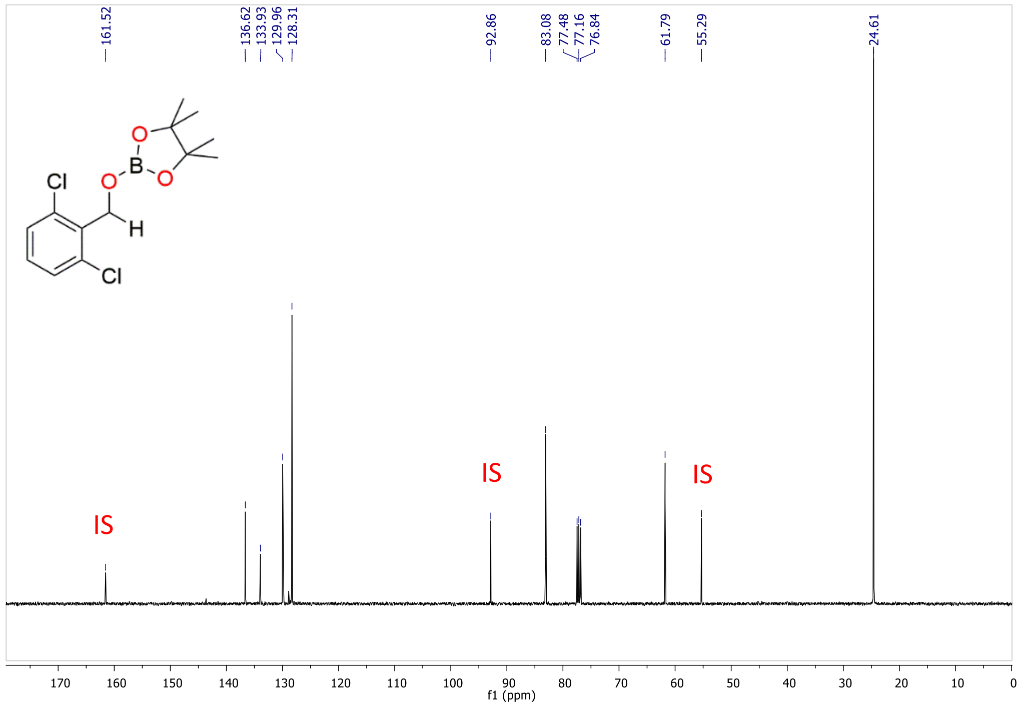


Figure S80. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5d**.

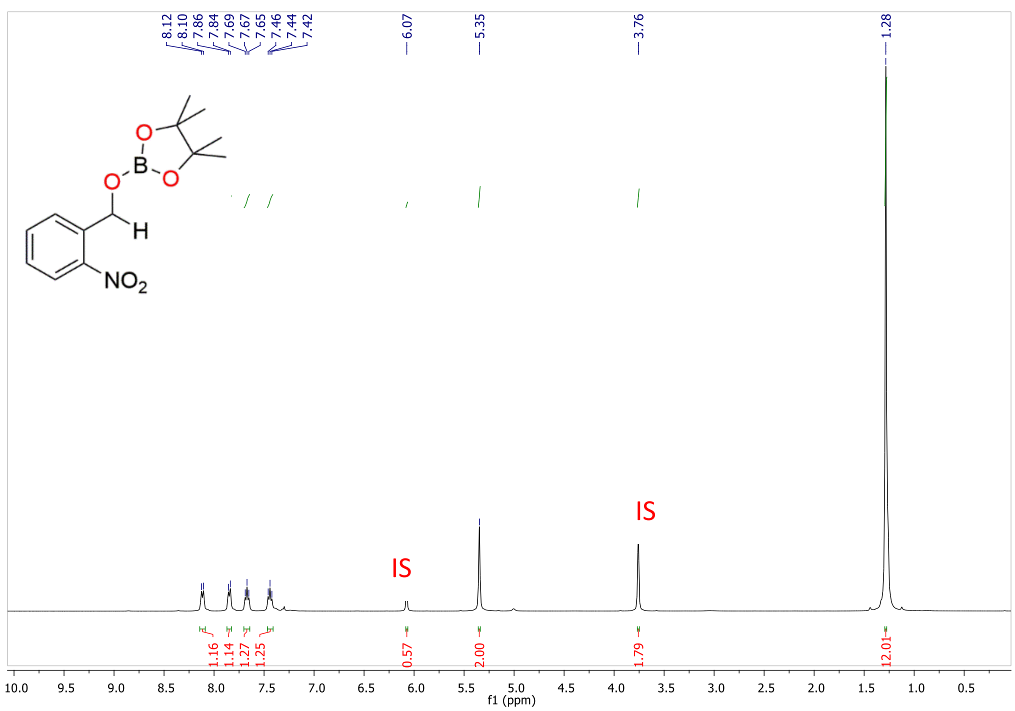


Figure S81. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of **5e**.

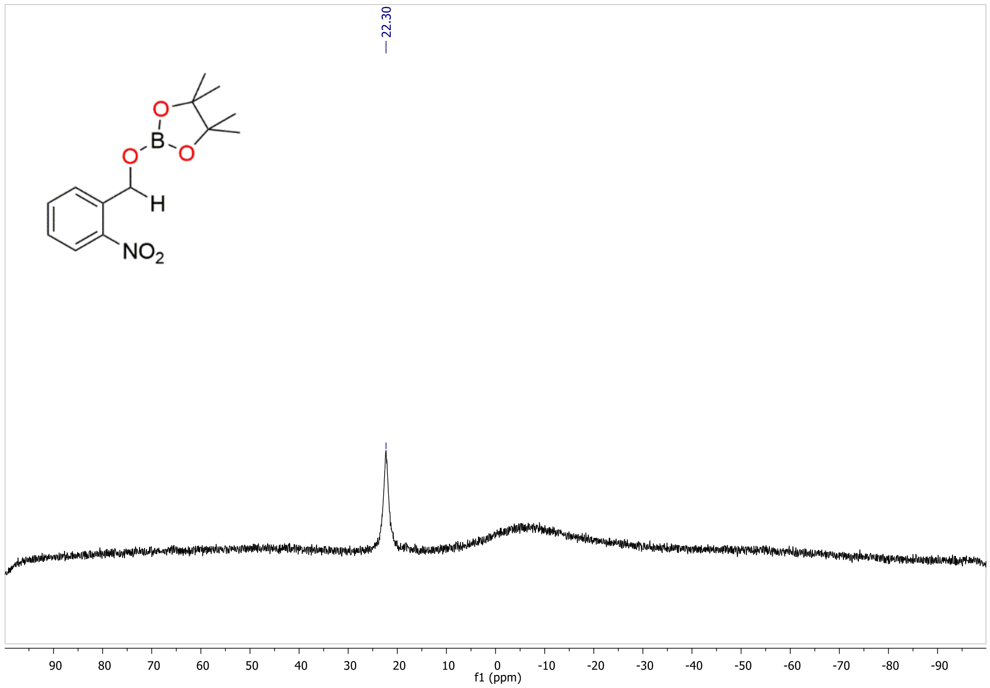


Figure S82. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **5e**.

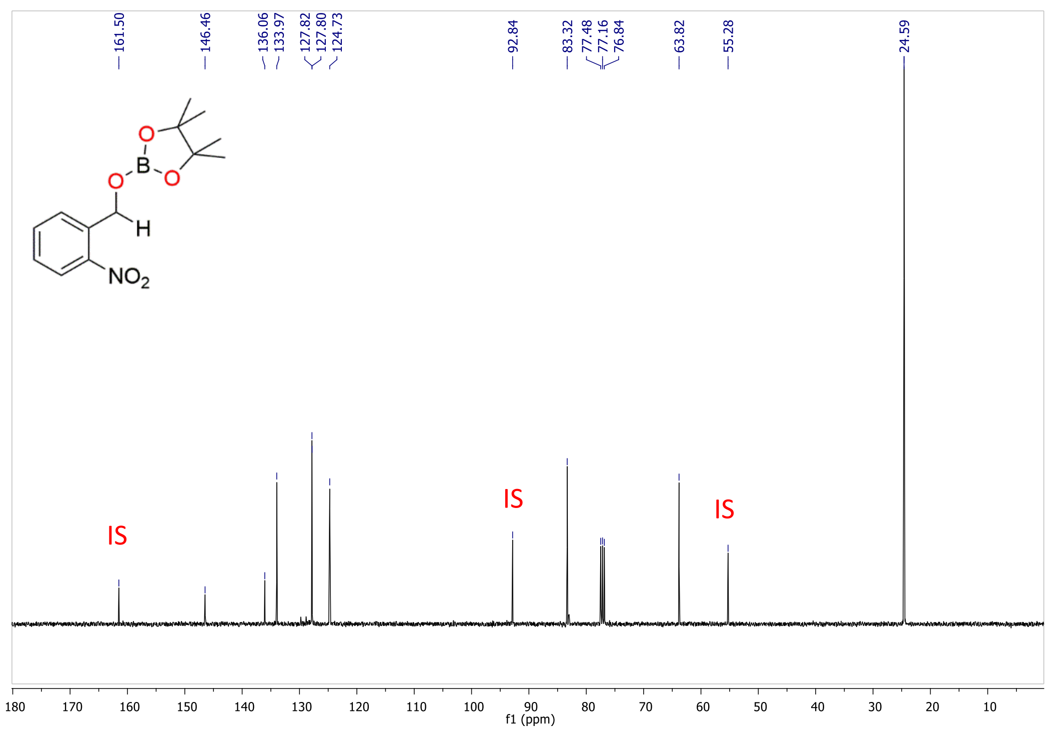


Figure S83. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5e**.

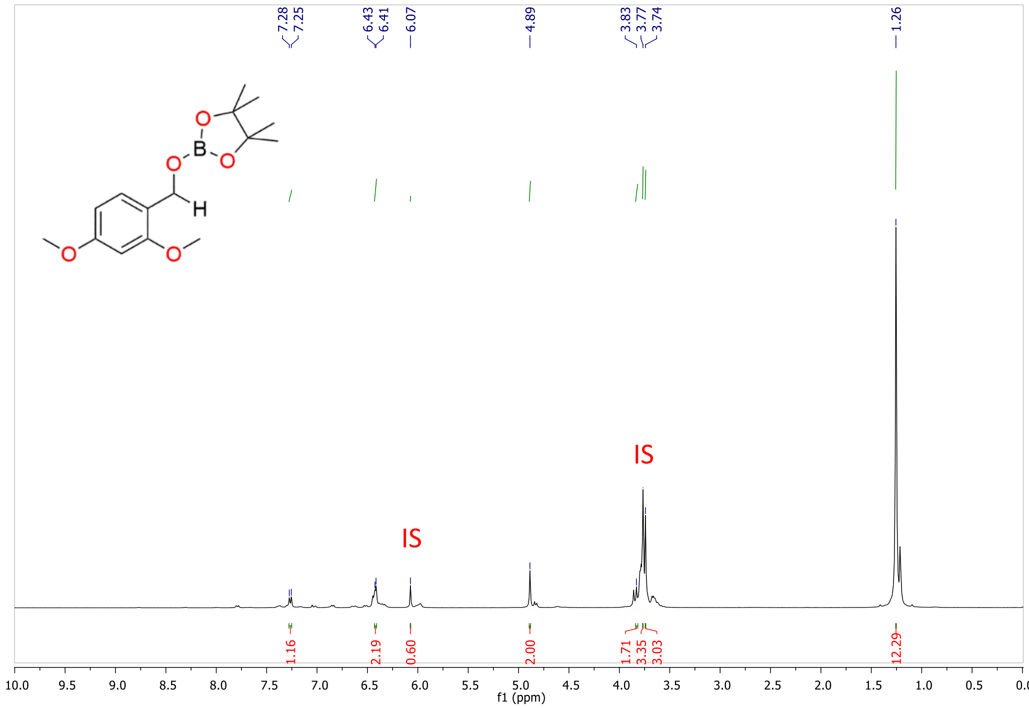


Figure S84. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **5f**.

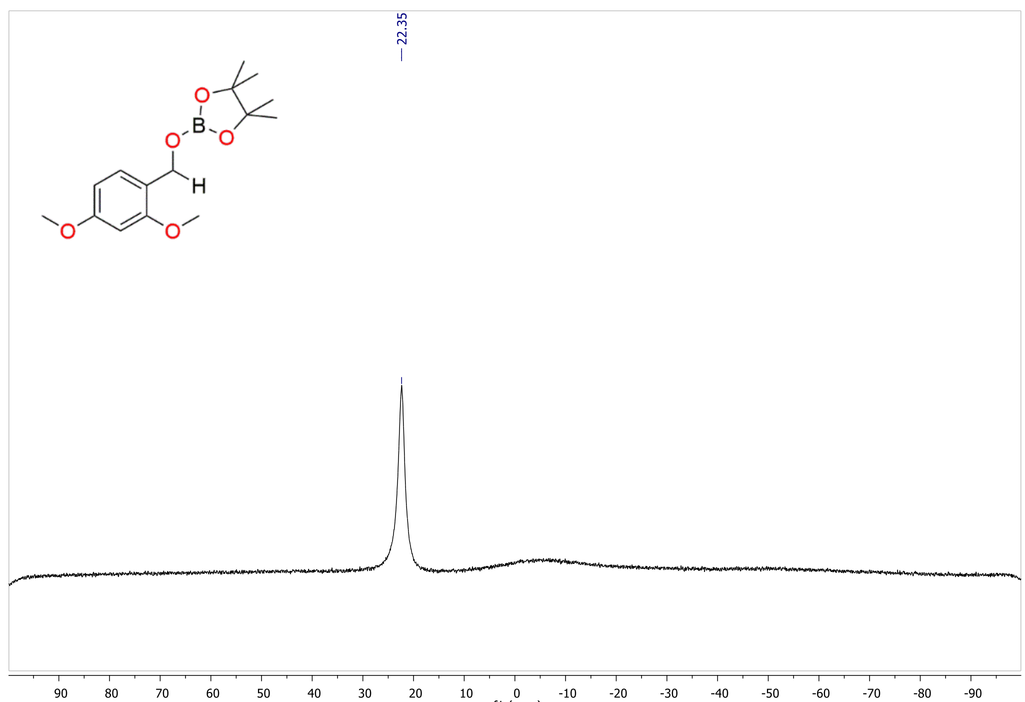


Figure 85. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **5f**.

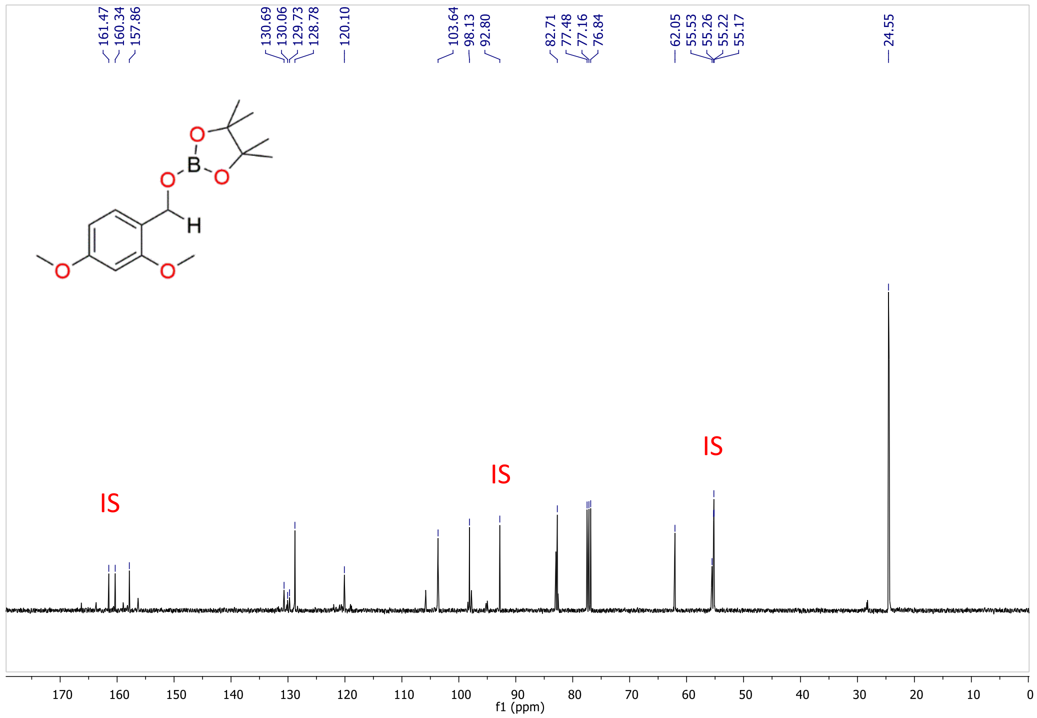


Figure S86. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5f**.

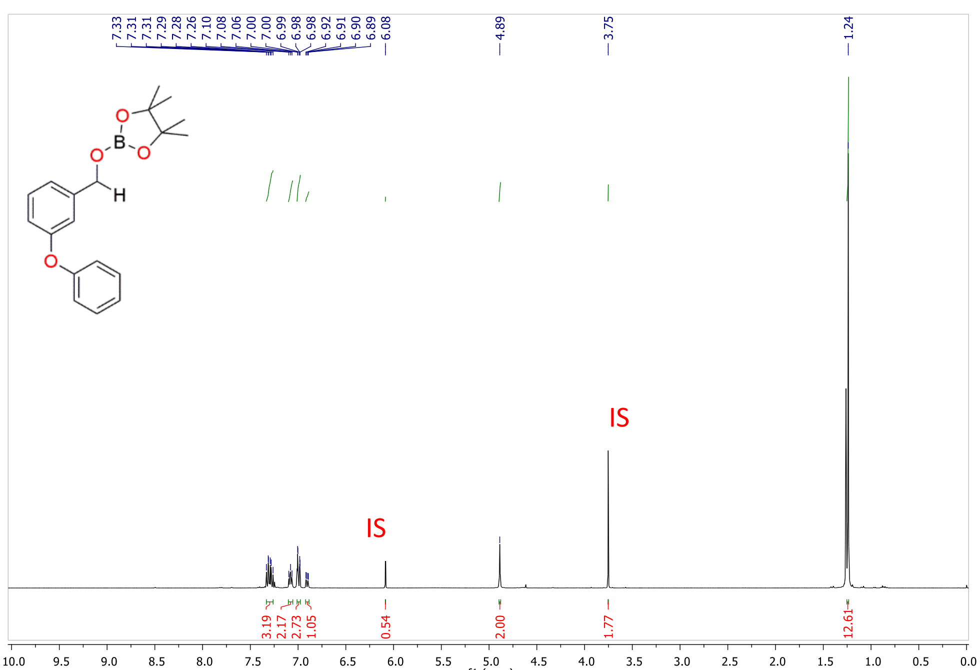


Figure S87. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of **5g**.

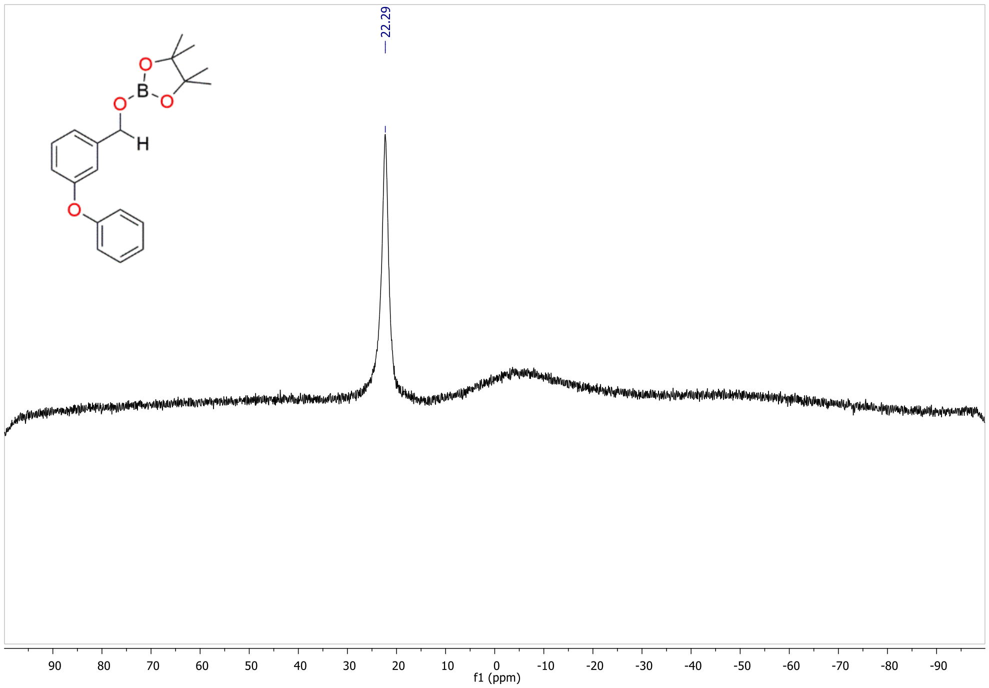


Figure S88. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **5g.**

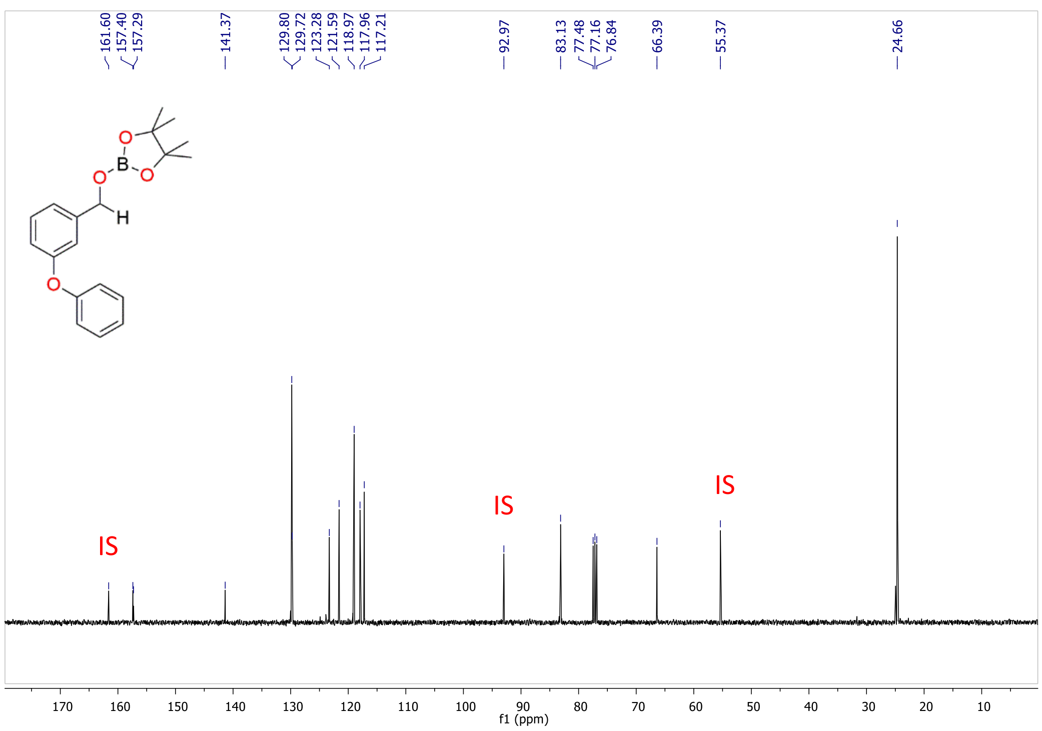


Figure S89. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5g**.

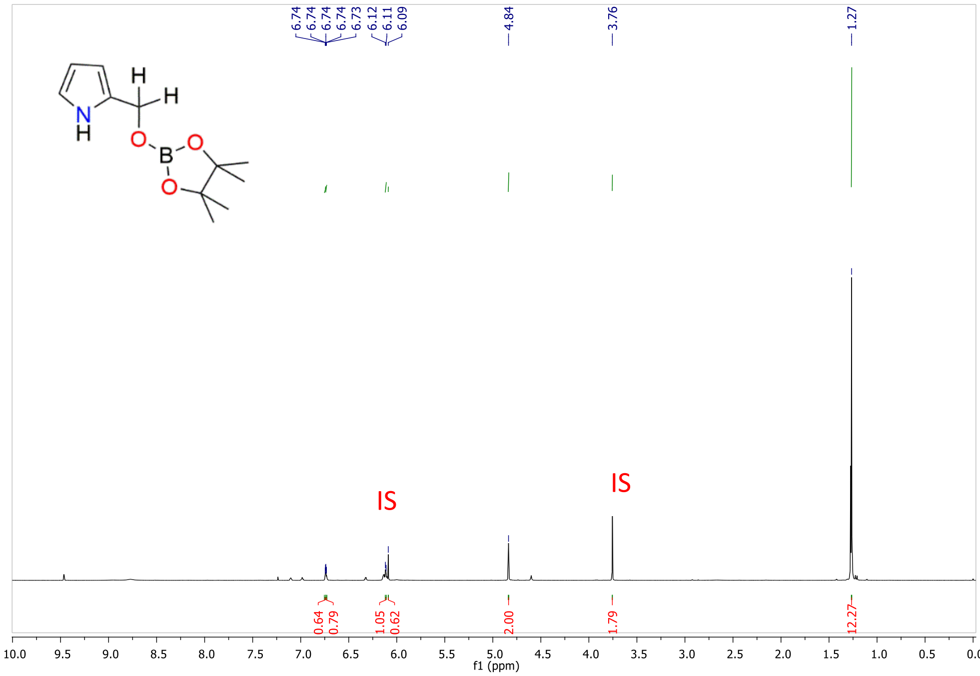


Figure S90. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of **5h**.

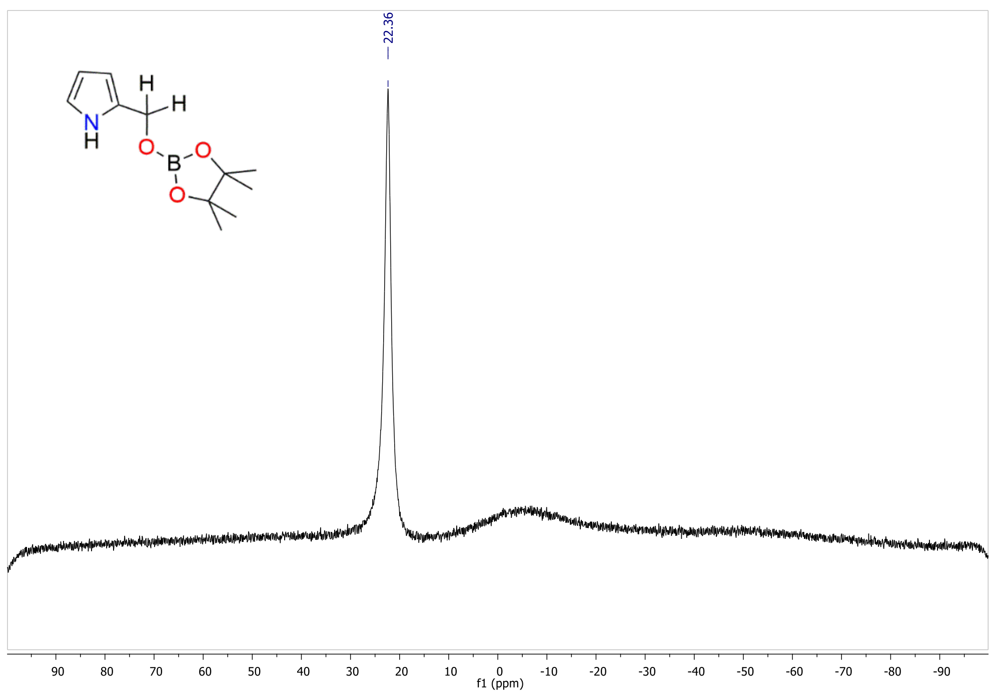


Figure S91. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **5h**.

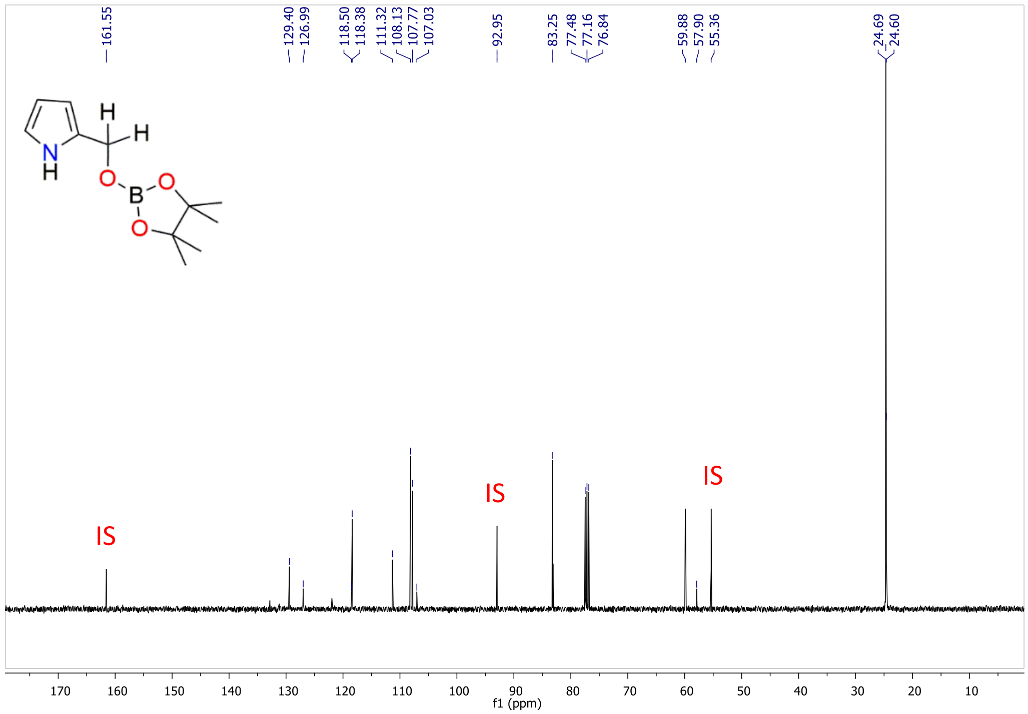


Figure S92. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5h**.

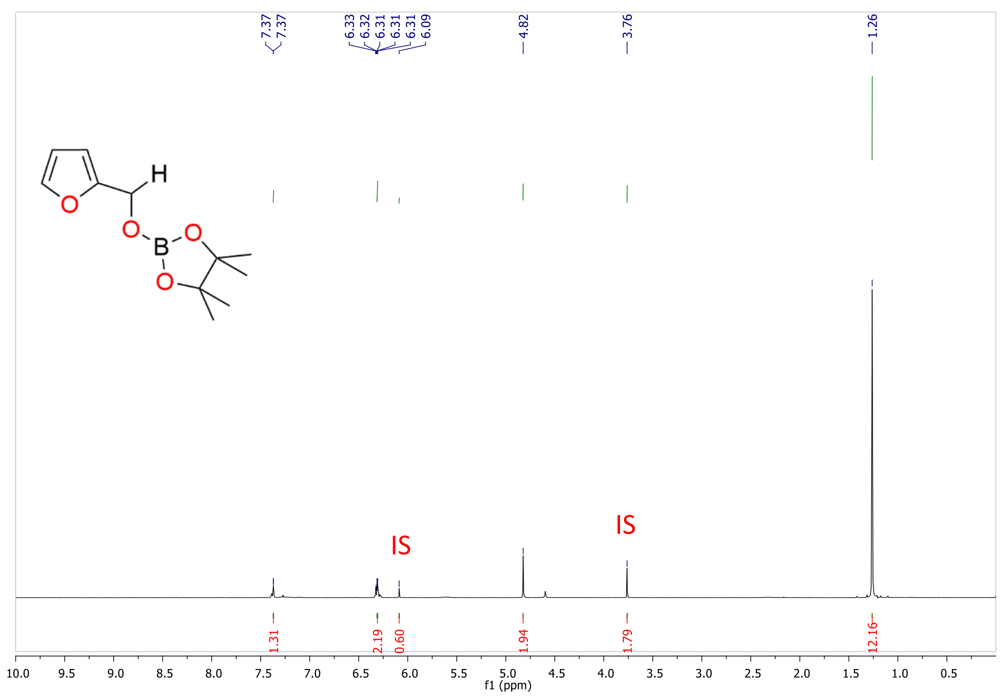


Figure S93. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **5i**.

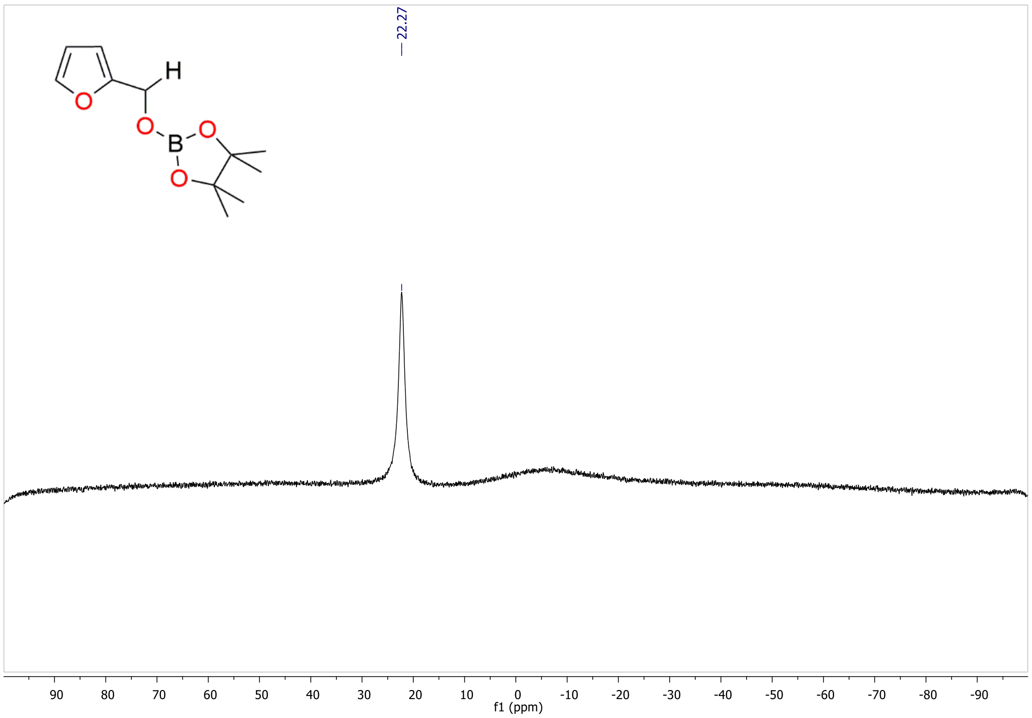


Figure S94. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5i**.

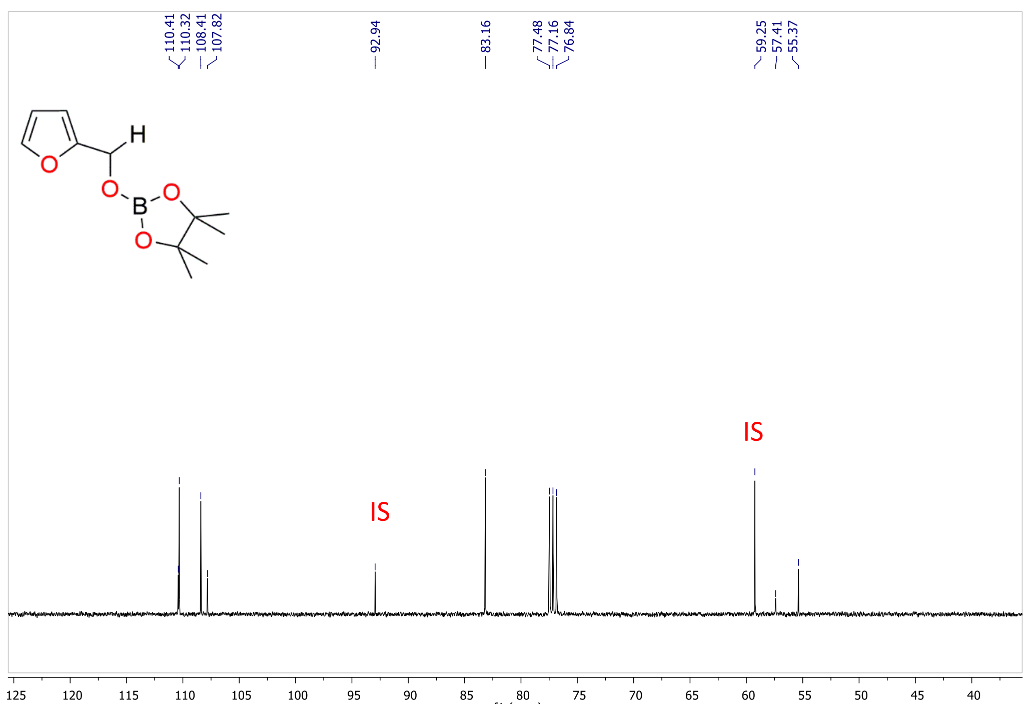


Figure S95. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5i**.

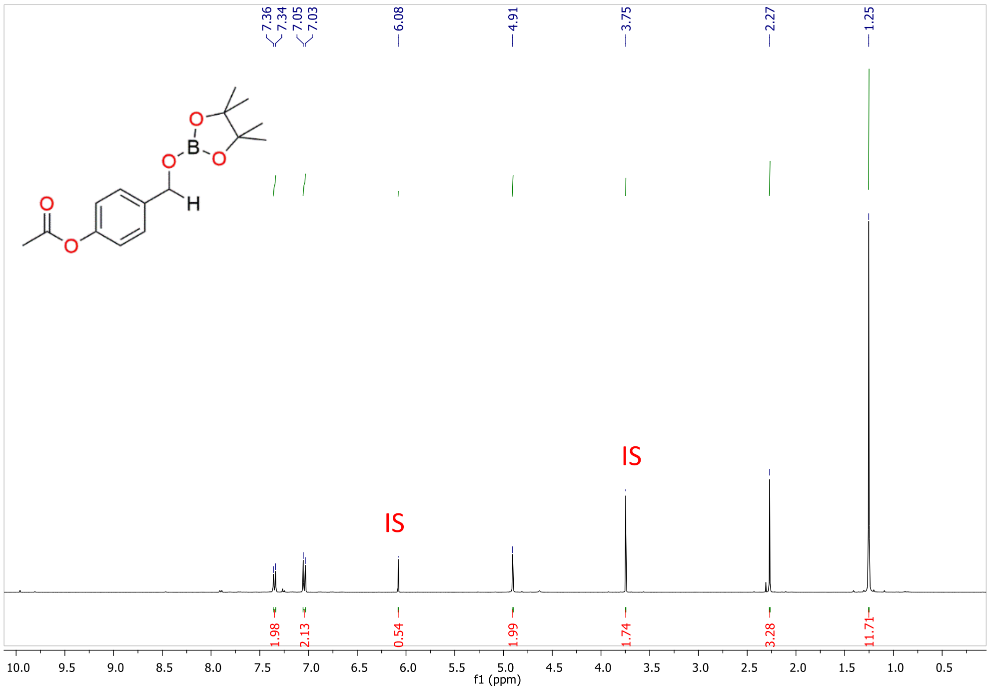


Figure S96. ^{1}H NMR spectrum (400 MHz, 25°C, CDCl3) of **5j**.

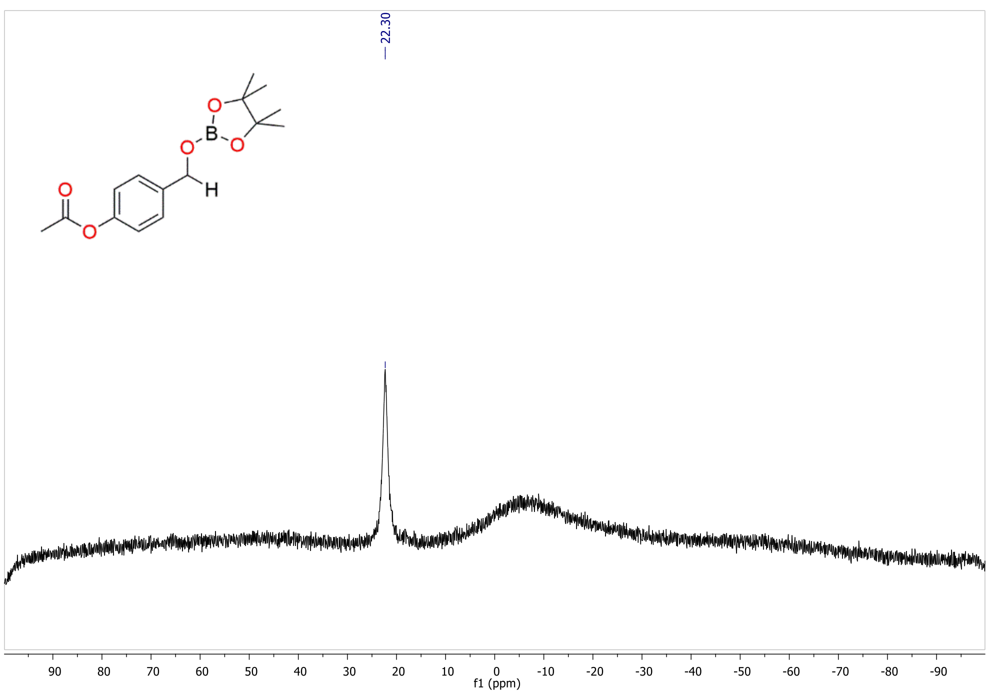


Figure S97. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **5j**.

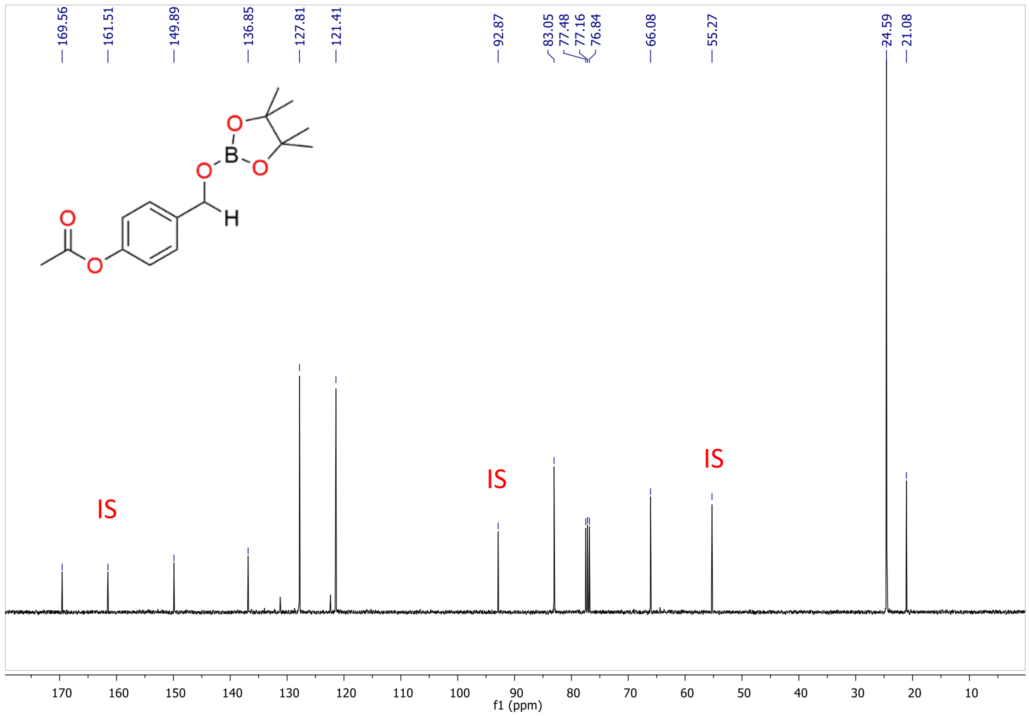


Figure S98. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5j**.

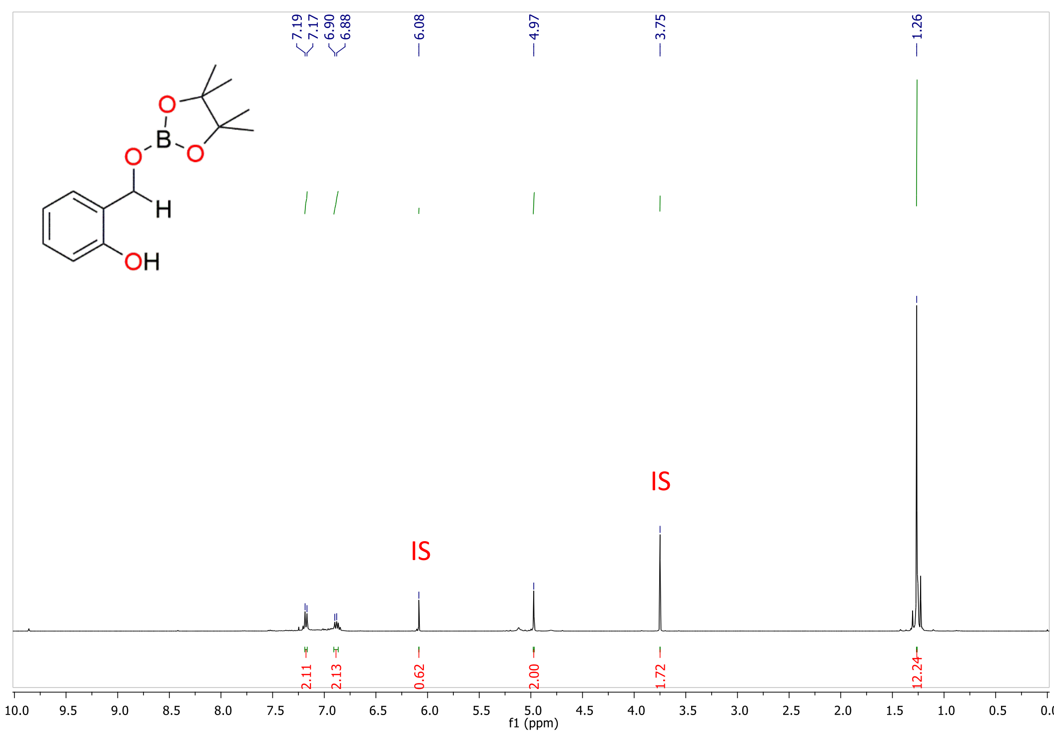


Figure S99. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of **5k**.

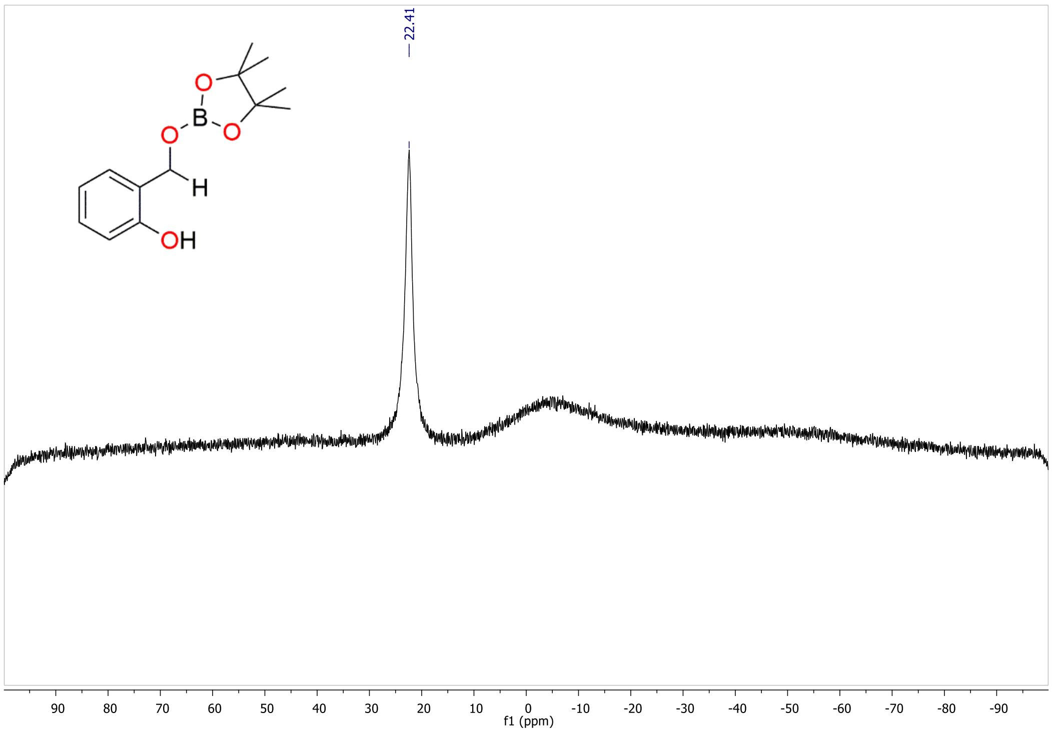


Figure S100. $^{11}B\{^{1}H\}$ NMR spectrum (128.4 MHz, 25 °C, $CDCl_3$) of **5k.**

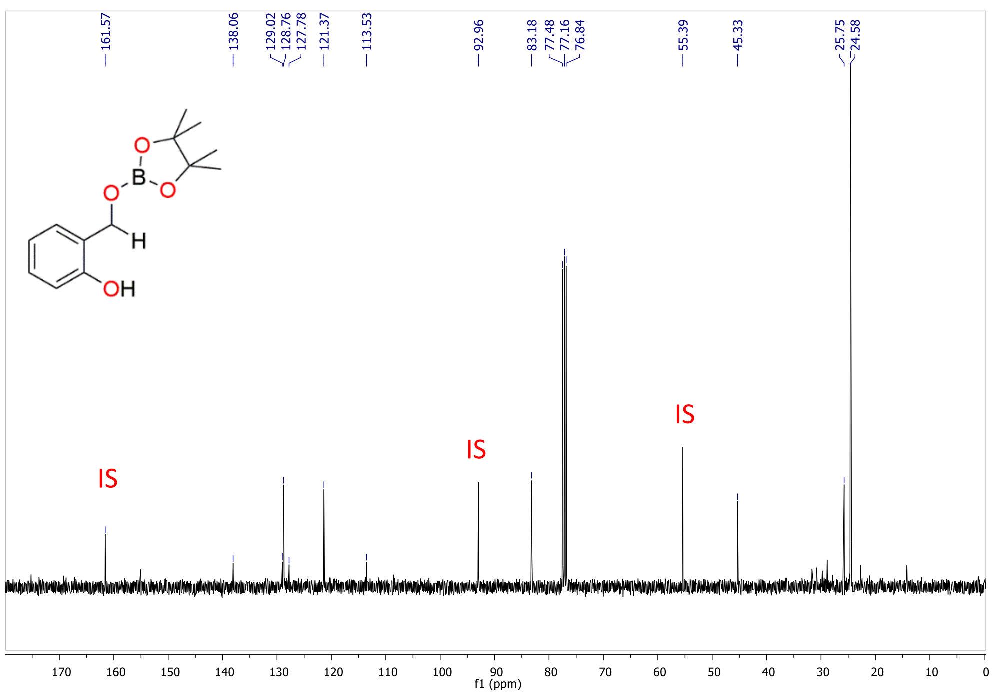


Figure S101. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5k**.

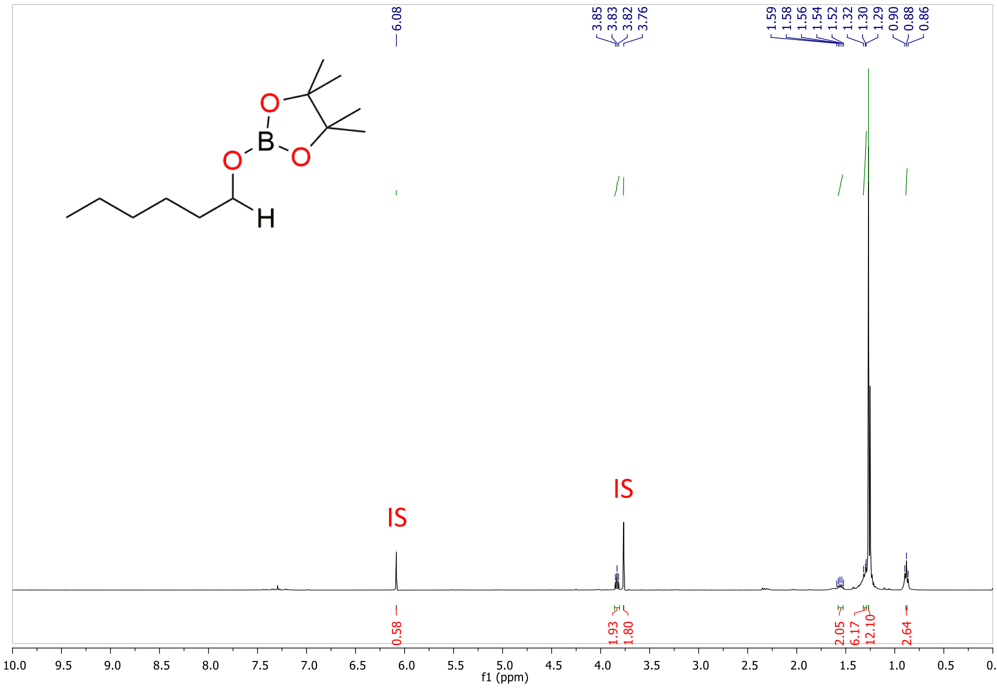


Figure S102. ^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **5l.**

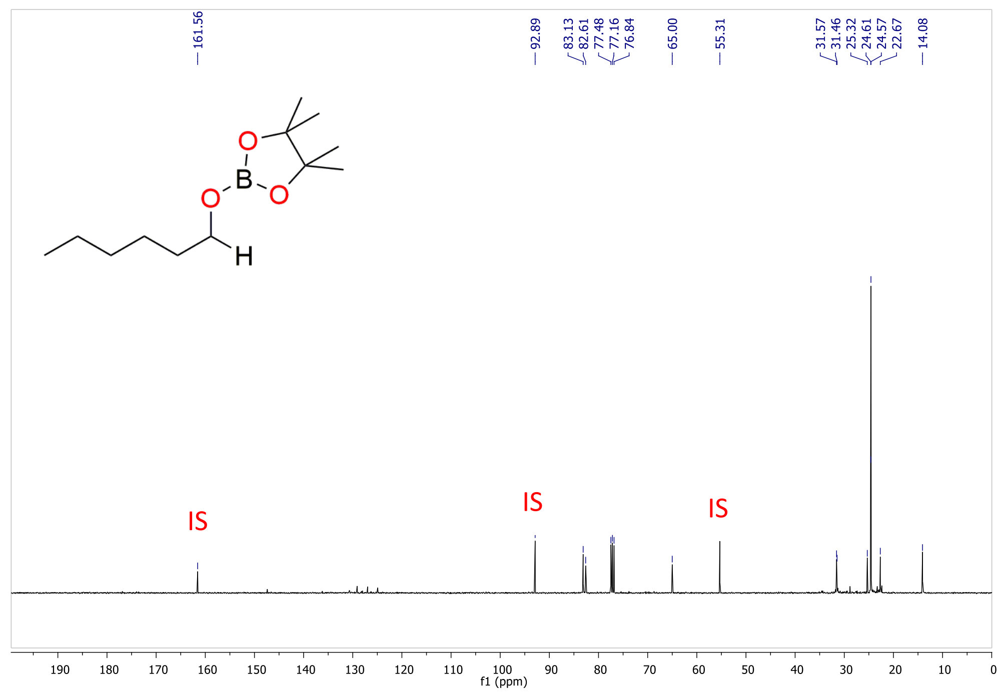


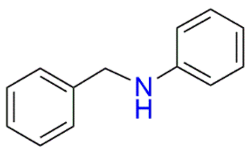
Figure S103. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **5l**.

The typical procedure for the Pd(II) complex 1 catalysed reductive amination of aldehydes with primary amines (6a-6j).

Hydroboration of aldimines with HBpin was performed using the standard protocol. The aldehyde (1 mmol) and amine (1 mmol) was taken in 25 mL Schlenk flask. The catalyst 1 (1 mol %) was then added and the reaction mixture was stirred for 3 hours at room temperature. HBpin (1.1 eq.) was added to it and the reaction mixture was heated at 60 ˚C for 12 hours. After the specified time, little amount of silica and methanol was added and the reaction mixture was further heated at 60 ˚C for 6 hours for further hydrolysis. The corresponding products were isolated and purified using column chromatography.

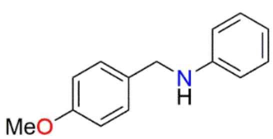
NMR data of Secondary amine:

N-benzyl aniline (6a).



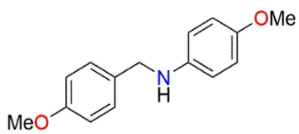
Yield: 90%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.35 (m, 4H, Ar-H), 7.25 (m, 1H, Ar-H), 7.17 (2H, m, Ar-H), 6.71 (t, J = 6.9 Hz, 1H, Ar-H), 6.63 (m, 2H, Ar-H), 4.32 (s, 2H, CH_2), 4.02 (s, 1H, NH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 148.2, 139.4, 129.3, 128.7, 127.5, 127.3, 117.6, 112.9, 77.4, 77.1, 76.7, 48.3, ppm. NMR data are in accordant with the literature.[12]

N-(4-methoxybenzyl) aniline (6b).



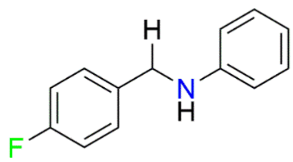
Yield: 86%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25 (d, J = 8.6 Hz, 2H, Ar-H), 7.17 - 7.13 (m, 2H, Ar-H), 6.87 - 6.83 (m, 2H, Ar-H), 6.69 (t, J = 7.3 Hz, 1H, Ar-H), 6.60 (dd, J = 8.5 Hz, 2H, Ar-H), 4.20 (s, 2H, CH_2), 3.93 (s, 1H, NH), 3.76 (s, 3H, OCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 158.9, 148.3, 131.5, 129.4, 128.9, 117.6, 114.1, 112.9, 77.5, 77.2, 76.9, 55.4, 47.8, ppm. NMR data are in accordant with the literature.[12]

4-methoxy- *N*-(4-methoxybenzyl) aniline (6c).



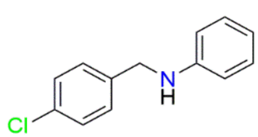
Yield: 88%.^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.21 (d, J = 8 Hz, 2H, Ar-H), 6.80 (d, J = 8 Hz, 2H, Ar-H), 6.70 (d, J = 8 Hz, 2H Ar-H), 6.52 (d, J = 6 Hz, 2H, Ar-H), 4.12 (s, 2H, CH_2), 3.72 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3) ppm.^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 158.8, 152.2, 142.5, 131.7, 128.9, 114.9, 114.1, 77.4, 77.1, 76.8, 55.8, 55.3, 48.7 ppm. NMR data are in accordant with the literature.[12]

***N*-(4-Fluorobenzyl) aniline (6d).**



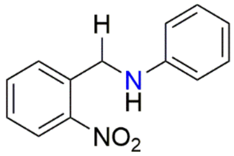
Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.24 (d, J = 3.3 Hz, 1H, Ar-H), 7.10 (dd, J = 6.9 Hz, 3H, Ar-H), 6.93 (t, J = 8.6 Hz, 2H, Ar-H), 6.64 (dd, J = 2.4, 1H, Ar-H), 6.53 (d, J = 7.6 Hz, 2H, Ar-H), 4.49 (s, 1H, NH), 4.20 (s, 2H, CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 162.2, 159.8, 147.8, 146.9, 134.0, 132.9, 128.2, 127.9, 127.2, 116.7, 116.2, 114.4, 111.7, 76.3, 76.0, 75.7, 52.5, 46.5, ppm. NMR data are in accordant with the literature.[12]

N-(4-Chlorobenzyl) aniline (6e).



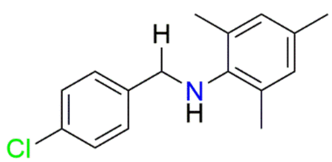
Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.23 (d, J = 4 Hz, 2H, Ar-H), 7.12 - 7.07 (m, 3H Ar-H), 6.65 (t, J = 7.3 Hz, 1H, Ar-H), 6.53 (d, J = 7.6 Hz, 3H, Ar-H), 4.23 (s, 2H, CH_2), 3.98 (s, 1H, NH) ppm.[13]C{[1]H} NMR (100 MHz, $CDCl_3$): δ_C 146.8, 136.9, 131.8, 128.3, 127.7, 116.7, 111.8, 76.3, 76.0, 75.7, 46.5, ppm. NMR data are in accordant with the literature.[12]

N-(2-Nitrorobenzyl) aniline (6f).



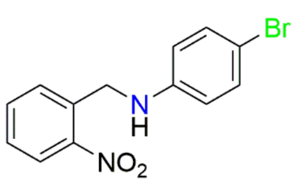
Yield: 90%. [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.98 (dd, *J* = 8.1 Hz, 1H, Ar-H), 7.58 (dd, *J* = 7.8 Hz, 1H, Ar-H), 7.47 (t, *J* = 6.9 Hz, 1H, Ar-H), 7.31 (d, *J* = 8.7, 1H, Ar-H), 7.08 – 7.04 (m, 2H, Ar-H), 6.62 (d, *J* = 6Hz, 1H, Ar-H), 6.49 - 6.45 (m, 2H, Ar-H), 4.63 (s 2H, CH_2), 4.27 (s, 1H, NH) ppm.[13]C{[1]H}NMR (100 MHz, $CDCl_3$): δ_C 148.2, 147.4, 135.7, 133.7, 129.8, 129.4, 128.0, 125.2, 118.0, 112.9, 77.4, 77.1, 76.8, 45.8, ppm. NMR data are in accordant with the literature.[10]

***N*-(4-Chlorobenzyl) trimethylaniline (6g).**



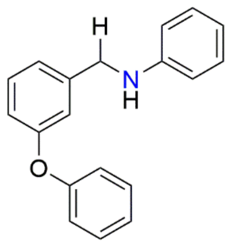
Yield: 84%. [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.09 (d, *J* = 8.4 Hz 1H, Ar-H), 6.96 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.76 (s, 2H, Ar-H), 6.70 (s, 1H, Ar-H), 4.09 (s, 1H, NH), 3.95 (s, 2H, CH_2), 2.15 (s, 6H, CH_3), 1.79 (s, 3H, CH_3) ppm.[13]C{[1]H} NMR (100 MHz, $CDCl_3$): δ_C 142.9, 139.0, 136.1, 133.0, 131.9, 130.9, 130.2, 129.4, 129.1, 128.7, 128.1, 77.4, 77.0, 76.7, 52.9, 52.3, 20.6, ppm. NMR data are in accordant with the literature.[12]

4-bromo-N-(2-nitrobenzyl) aniline (6h).



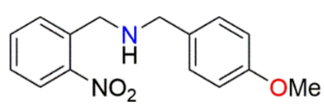
Yield: 88%. ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.99 (d, *J* = 4 Hz, 1H, Ar-H), 7.51 (d, *J* = 8 Hz, 2H, Ar-H), 7.35(d, *J* = 4.1 Hz, 1H, Ar-H),7.15 (d, *J* = 6 Hz, 2H, Ar-H), 6.36 (d, *J* = 6 Hz, 2H, Ar-H), 4.62 (s, 2H, CH$_2$), 4.32 (s, 1H, NH) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ_C 148.2, 146.4, 135.1, 133.8, 132.1, 129.7, 128.2, 125.4, 114.5, 109.7, 77.4, 77.0, 76.8, 45.8, ppm. NMR data are in accordant with the literature.[10]

N-(3-phenoxybenzyl) aniline (6i).



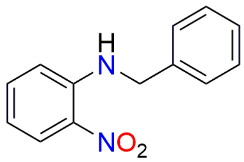
Yield: 90%. ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.24 - 7.19 (m, 3H, Ar-H), 7.09 - 7.01 (m, 4H, Ar-H), 6.92 (s, 3H, Ar-H), 6.81 (s, 1H, Ar-H), 6.64 (d, *J* = 6.6 Hz, 1H, Ar-H), 6.51 (s, 2H, Ar-H), 4.21 (s, 2H, CH$_2$), 3.95 (s, 1H, NH) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ_C 157.6, 157.1, 148.0, 141.7, 129.9, 129.3, 123.3, 122.2, 119.0, 117.9 – 117.4, 112.9, 77.4, 77.1, 76.8, 48.1 ppm. NMR data are in accordant with the literature.[21]

***N*-(4-methoxybenzyl)-1-(2-nitrophenyl) methenamine (6j).**



Yield: 88%. ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.94 (dd, *J* = 8.1 Hz, 1H, Ar-H), 7.59 (d, *J* = 8 Hz, 2H Ar-H), 7.44 - 7.37 (m, 1H, Ar-H), 7.27 - 7.24 (m, 2H, Ar-H), 6.87 (d, *J* = 8.7 Hz, 2H Ar-H), 4.04 (s, 2H, CH$_2$), 3.80 (s, 3H, OCH$_3$), 3.76 (s, 2H, CH$_2$), 1.86 (s 1H, NH) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ_C 158.7, 135.7, 133.1, 132.0, 131.3, 129.4, 128.7, 128.0, 124.8, 113.8, 77.4, 77.1, 76.7, 55.3, 52.9, 50.1, ppm. NMR data are in accordant with the literature.[21]

N-benzyl-2-nitroaniline (6k).



Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.43 (s 1H, NH), 8.19 - 8.17 (d, J = 4Hz ,2H, Ar-H), 7.36 - 7.34 (dd, J = 4 Hz, 3H, Ar-H), 6.81 - 6.79 (d, J = 2 Hz , 2H, Ar-H), 6.67 - 6.63 (d, J = 8 Hz, 2H, Ar-H), 4.54 - 4.53 (d, J = 2 Hz, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 145.3, 137.4, 136.3, 132.3, 129.0, 127.8, 127.1, 126.0, 115.8, 114.3,77.1, 47.1, ppm. NMR data are in accordant with the literature.[24]

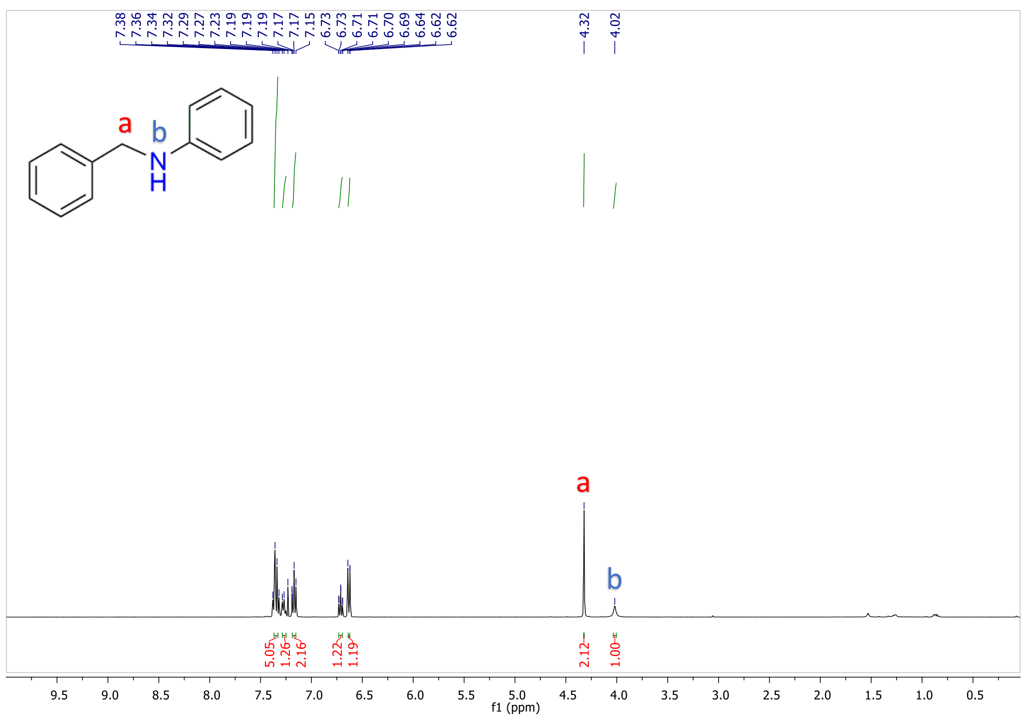


Figure S104. ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectrum of **6a**.

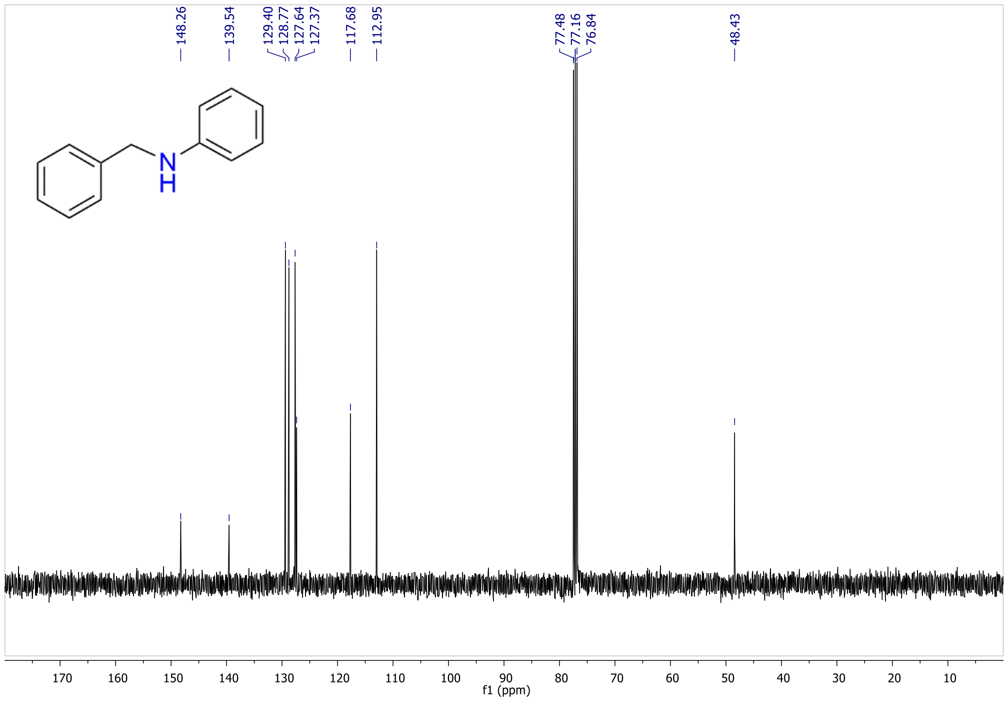


Figure S105. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 ˚C, $CDCl_3$) spectrum of **6a**.

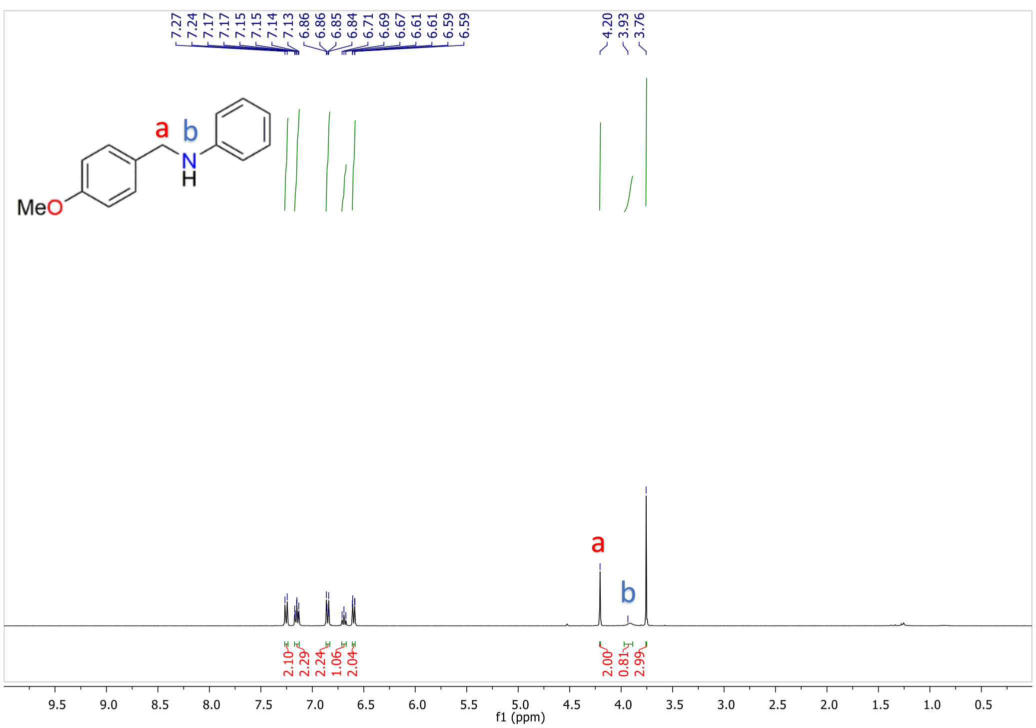


Figure S106. ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectrum of **6b.**

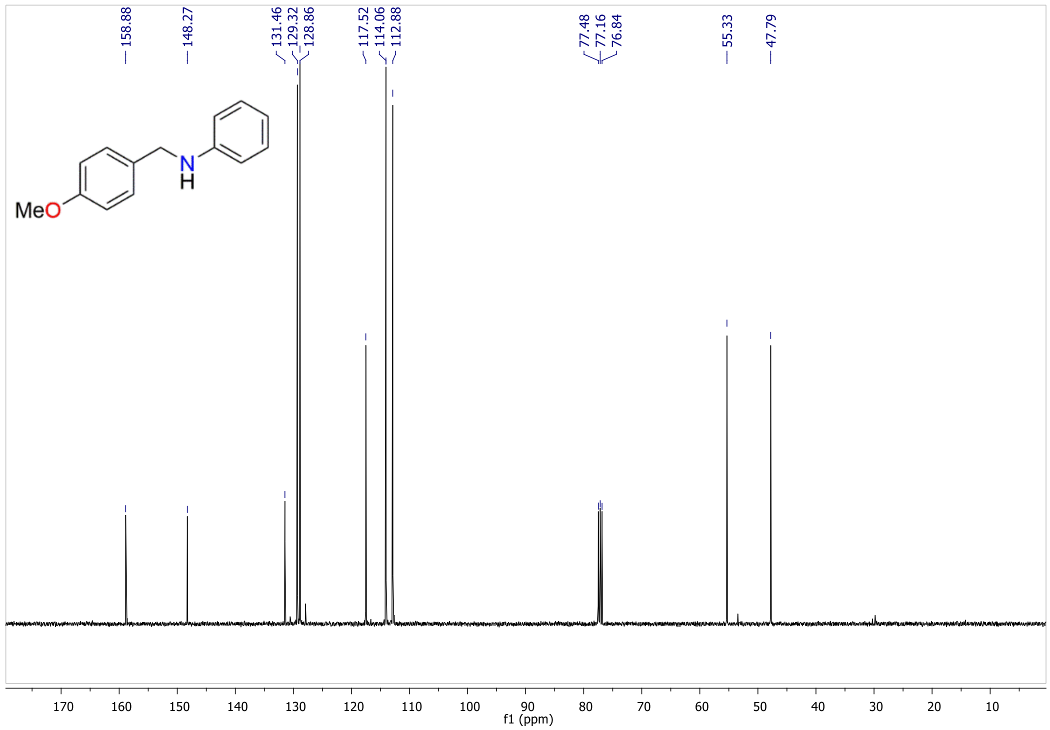


Figure S107. $^{13}C\{^1H\}$ NMR (100 MHz, 25 ˚C, $CDCl_3$) spectrum of **6b**.

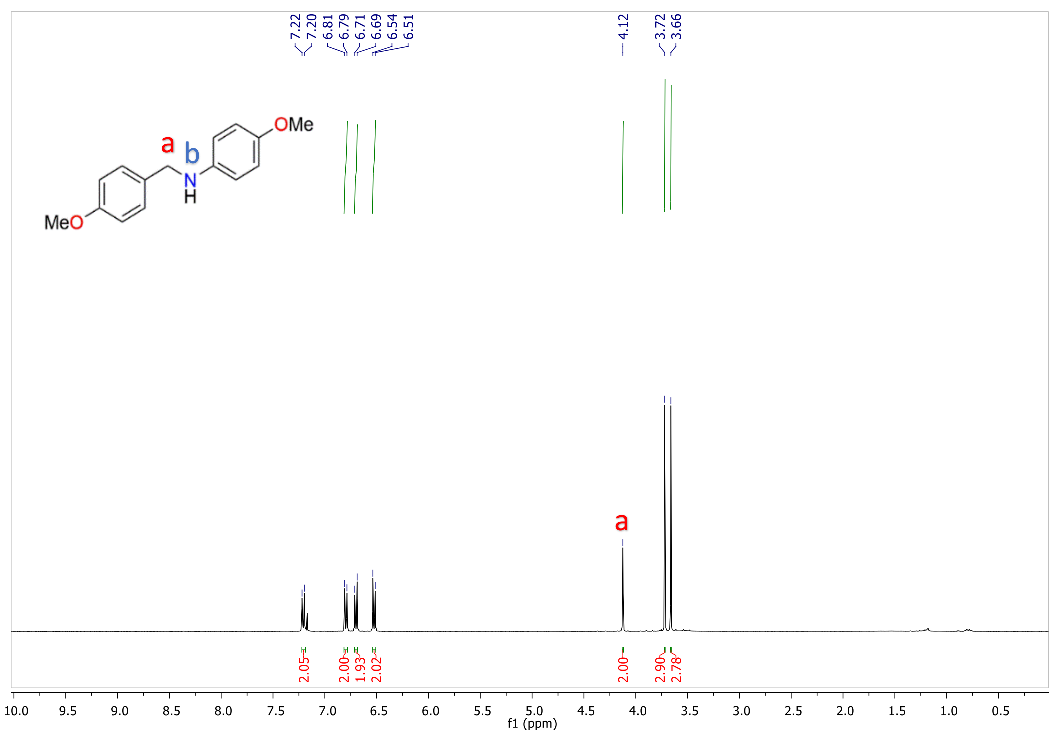


Figure S108. ^1H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectrum of **6c**.

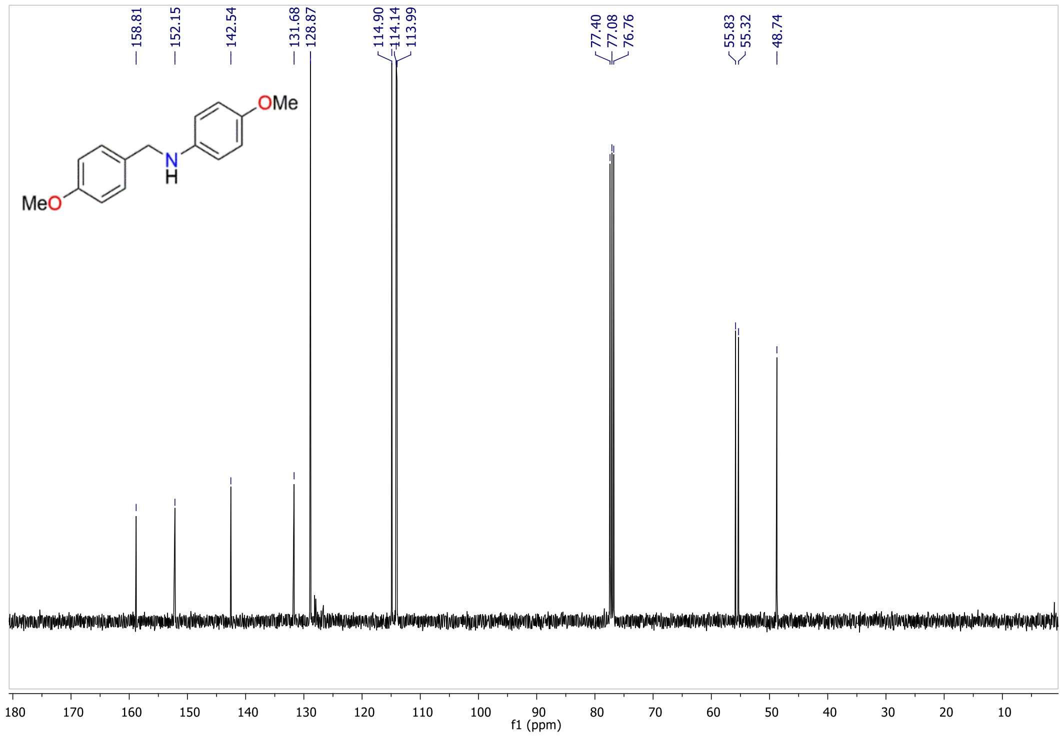


Figure S109. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 ˚C, $CDCl_3$) spectrum of **6c**.

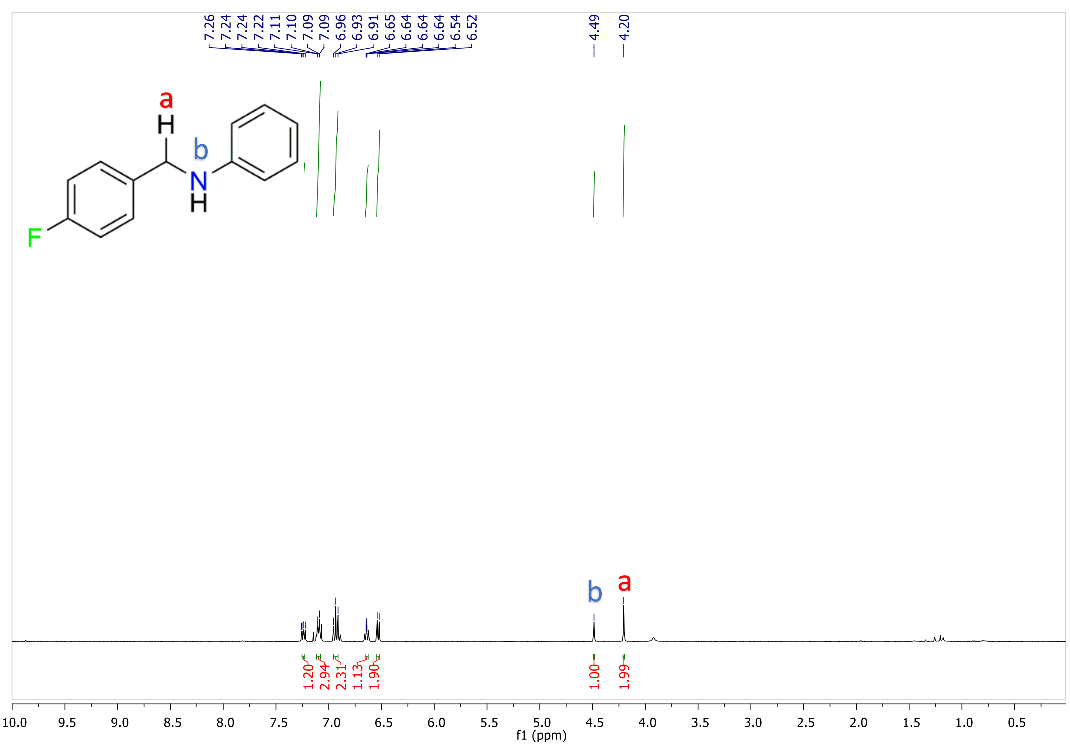


Figure S110. ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectrum of **6d**.

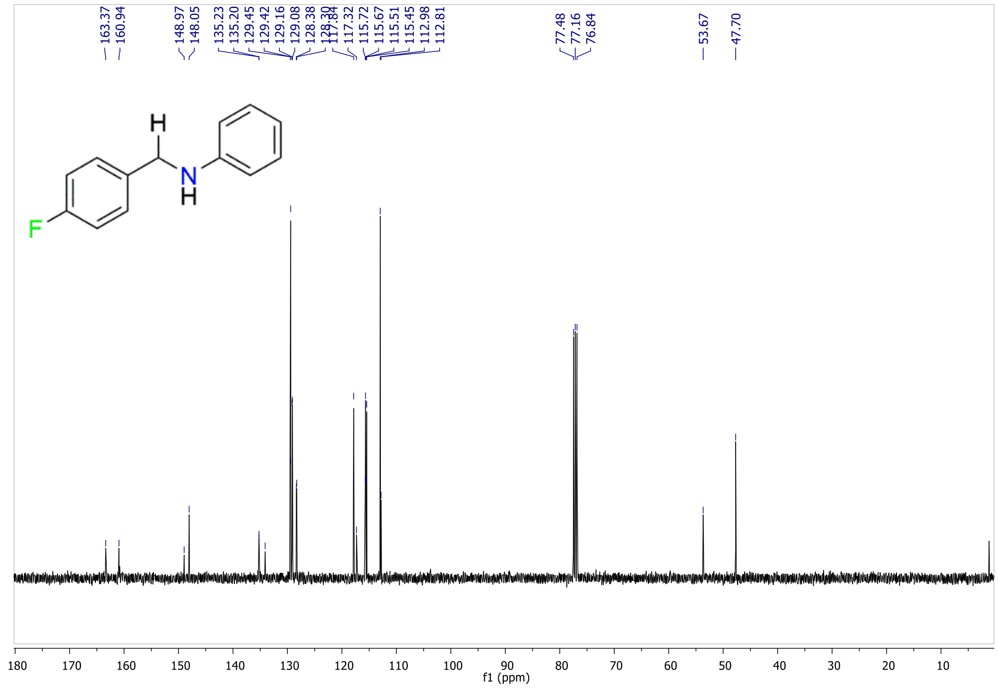


Figure S111. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 ˚C, $CDCl_3$) spectrum of **6d**.

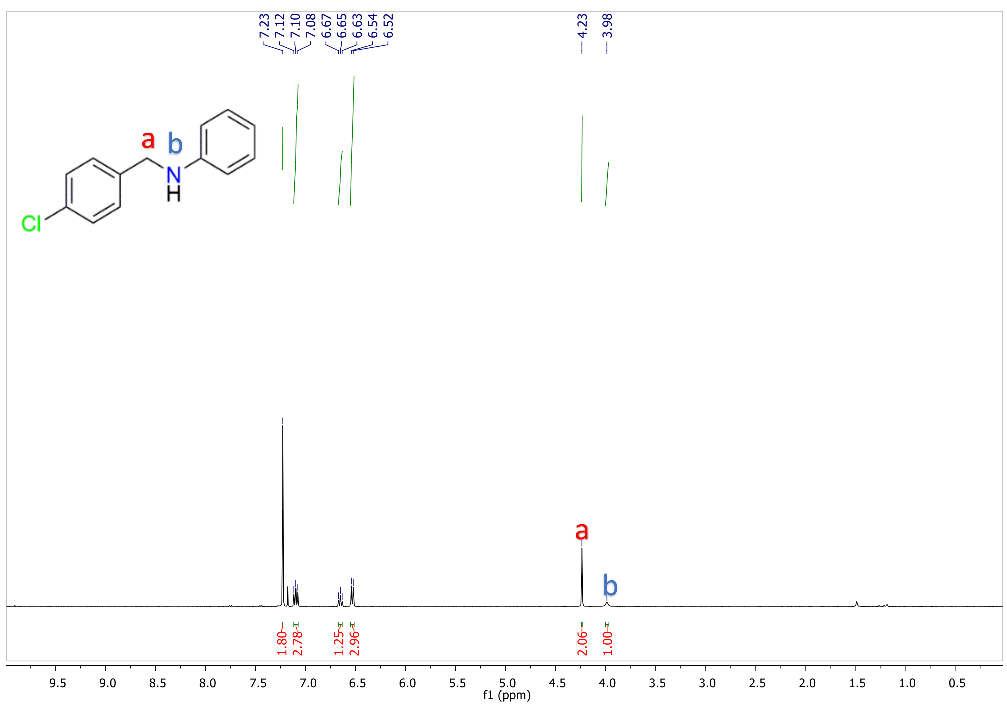


Figure S112. ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectrum of **6e**.

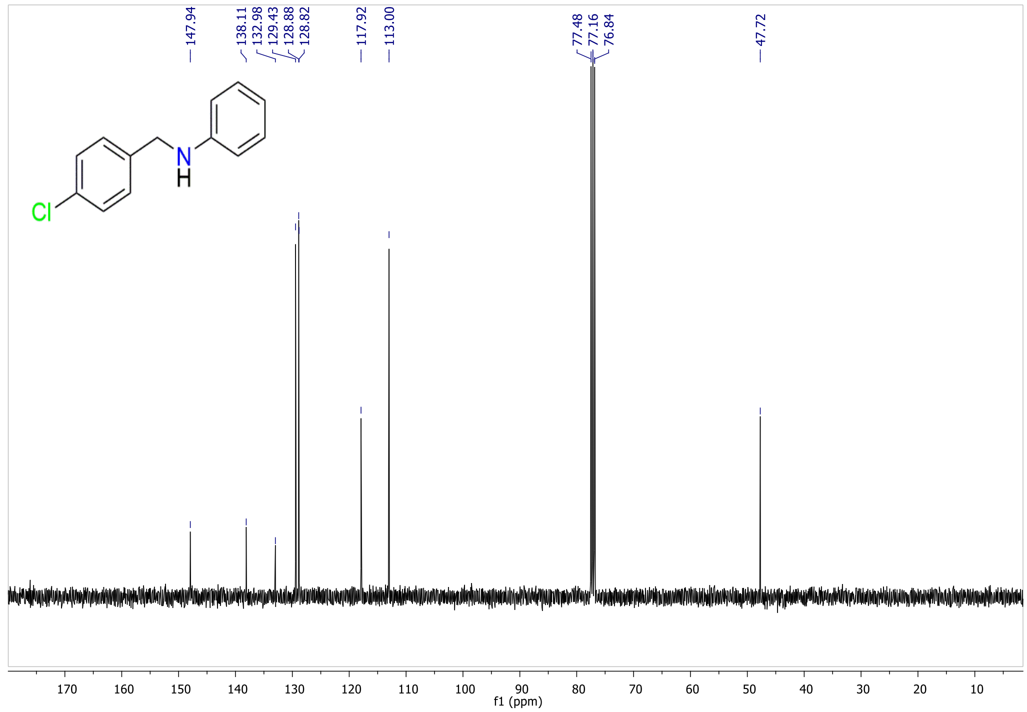


Figure S113. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 ˚C, $CDCl_3$) spectrum of **6e**.

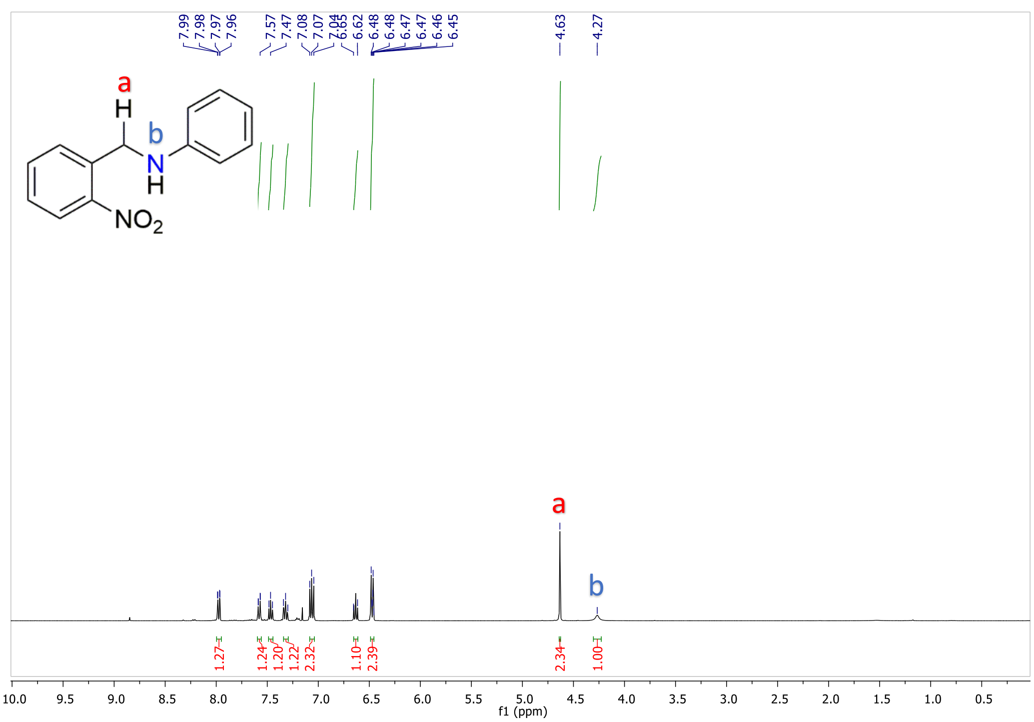


Figure S114. ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectrum of **6f**.

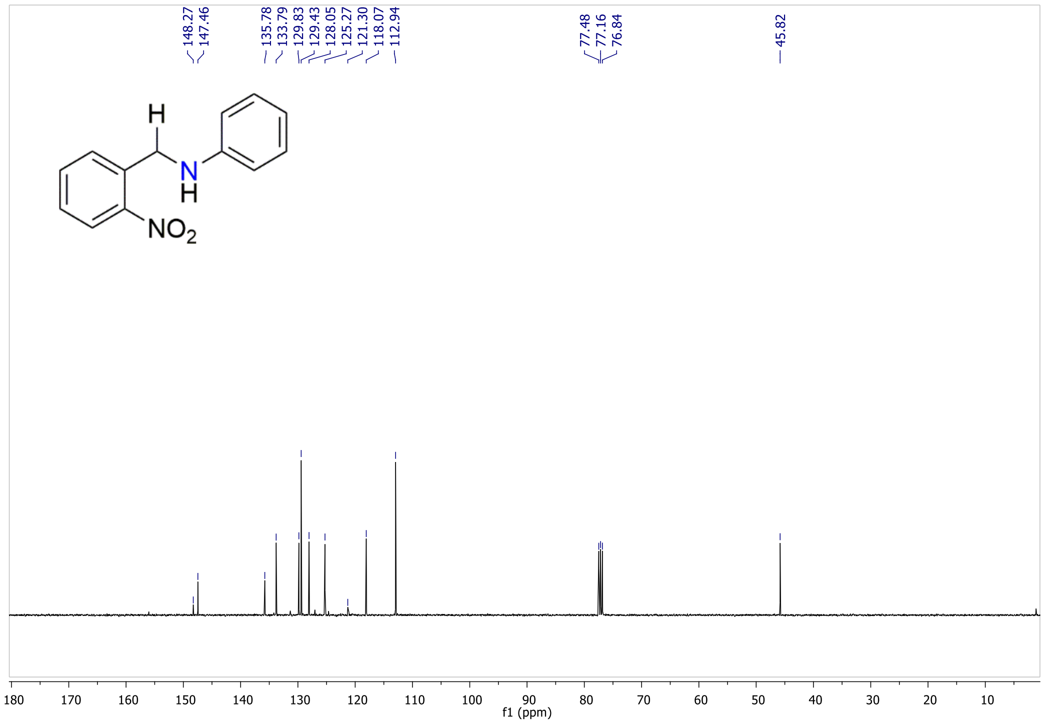


Figure S115. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 ˚C, $CDCl_3$) spectrum of **6f**.

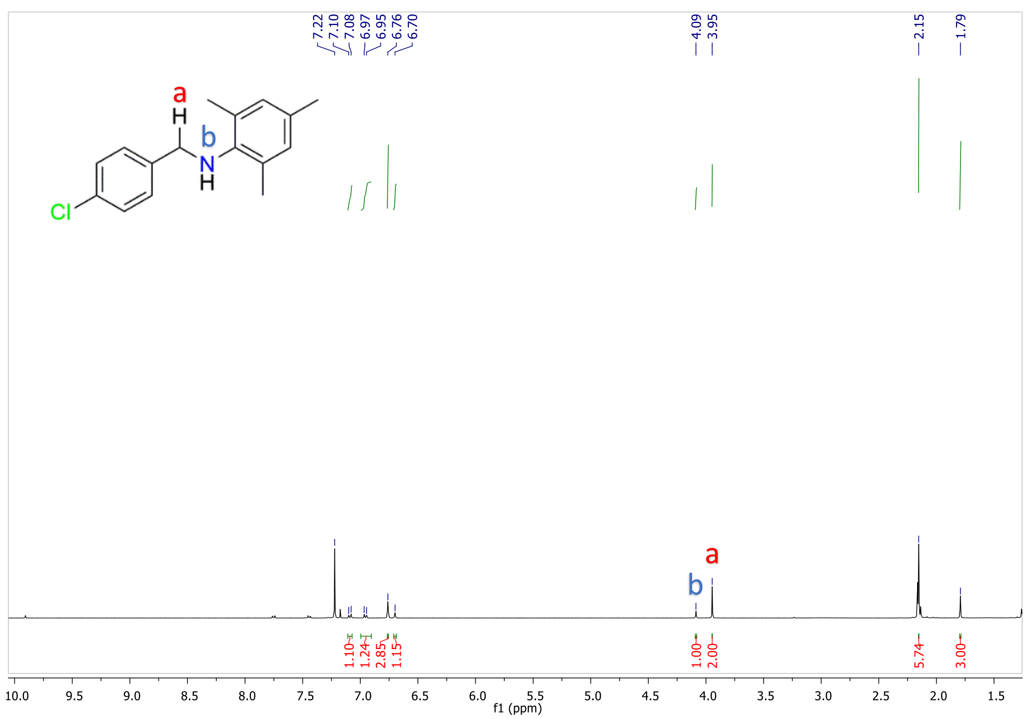


Figure S116. ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectrum of **6g**.

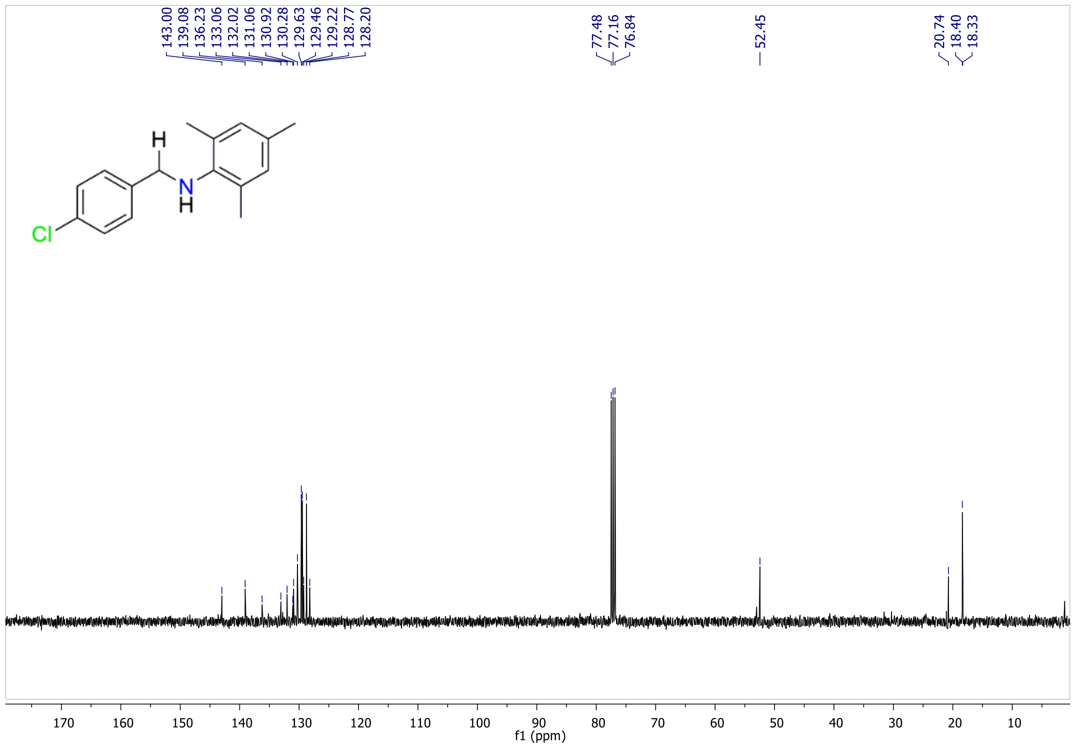


Figure S117. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 ˚C, $CDCl_3$) spectrum of **6g**.

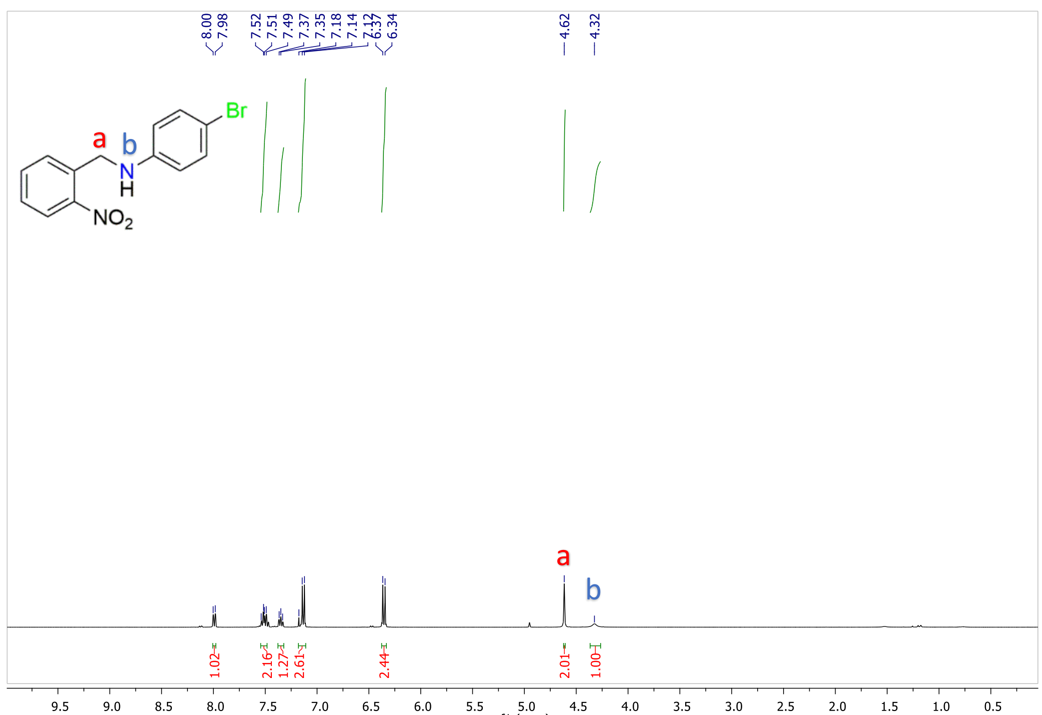


Figure S118. ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectrum of **6h**.

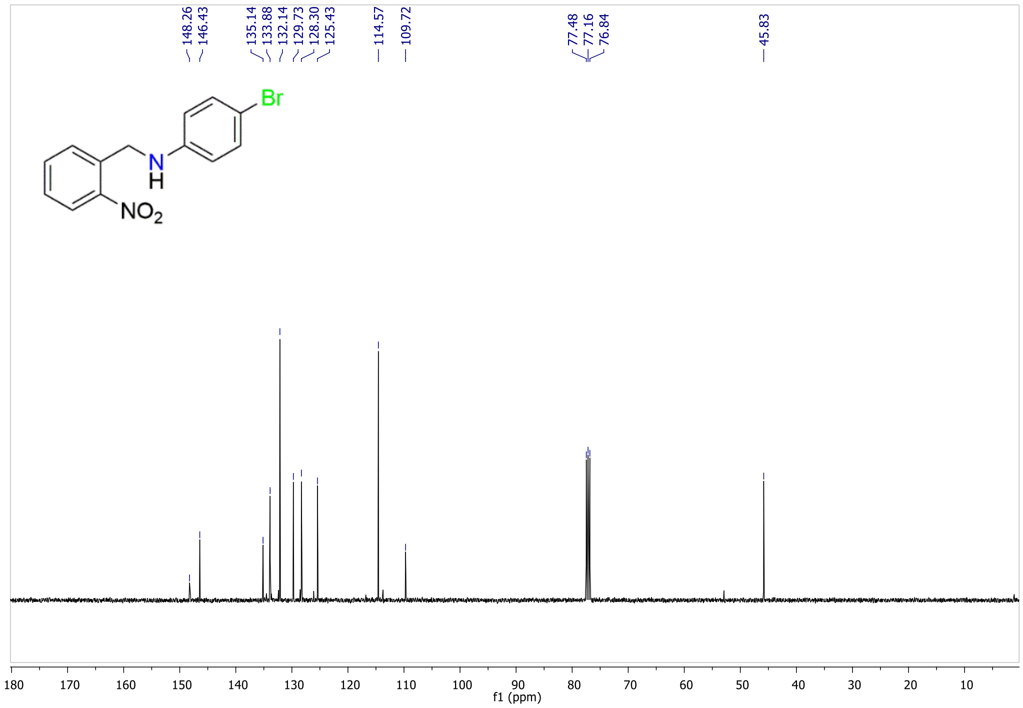


Figure S119. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 ˚C, $CDCl_3$) spectrum of **6h**.

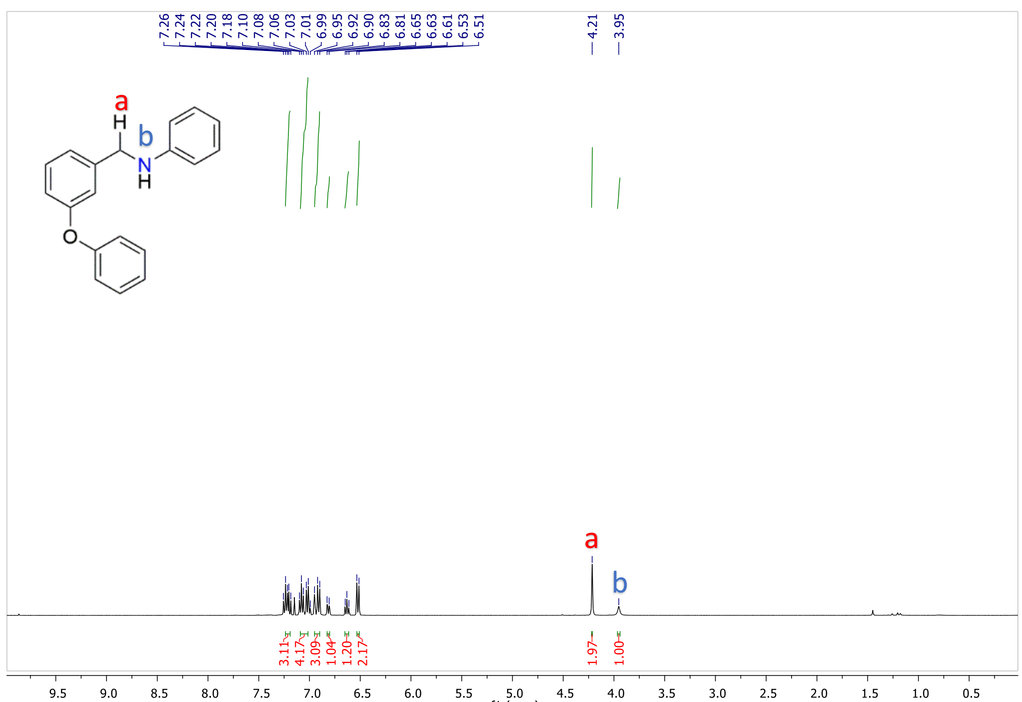


Figure S120. ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectrum of **6i**.

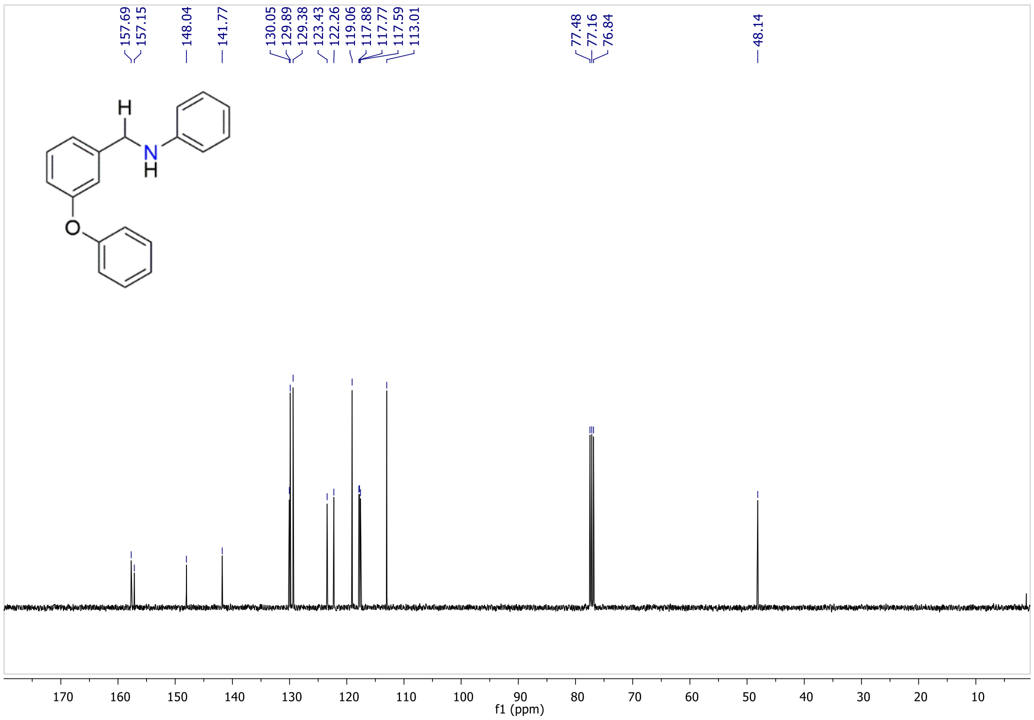


Figure S121. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 ˚C, $CDCl_3$) spectrum of **6i.**

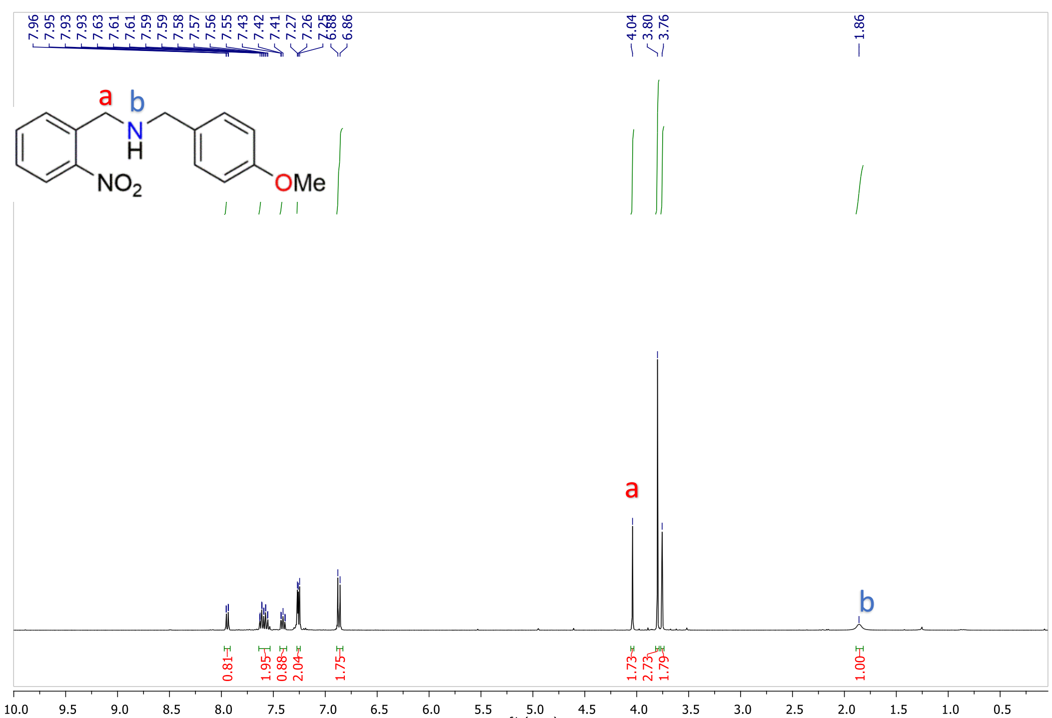


Figure S122. ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectrum of **6j**.

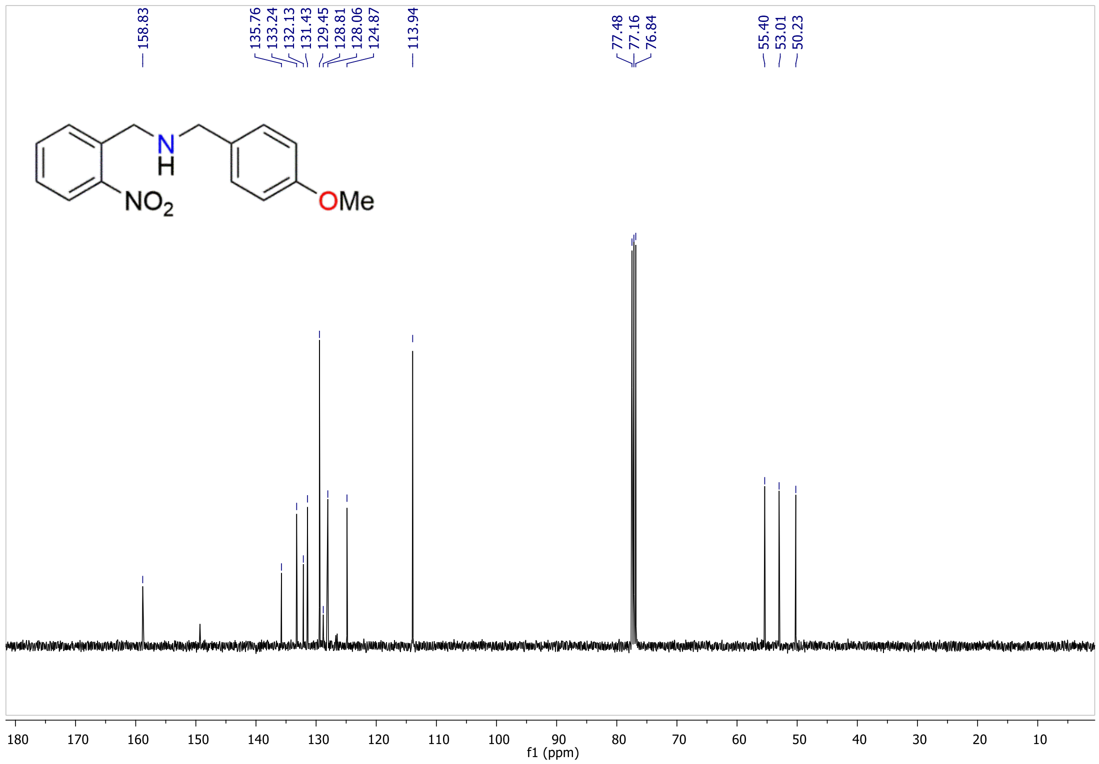


Figure S123. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 ˚C, $CDCl_3$) spectrum of **6j**.

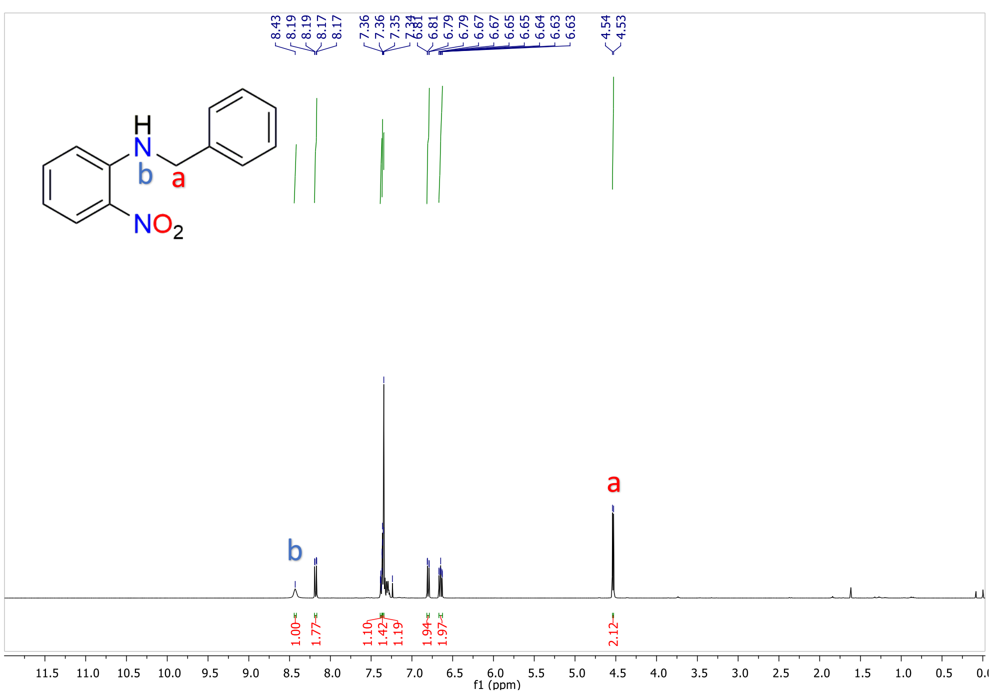


Figure S124. ^{1}H NMR (400 MHz, 25 ˚C, $CDCl_3$) spectrum of **6k**.

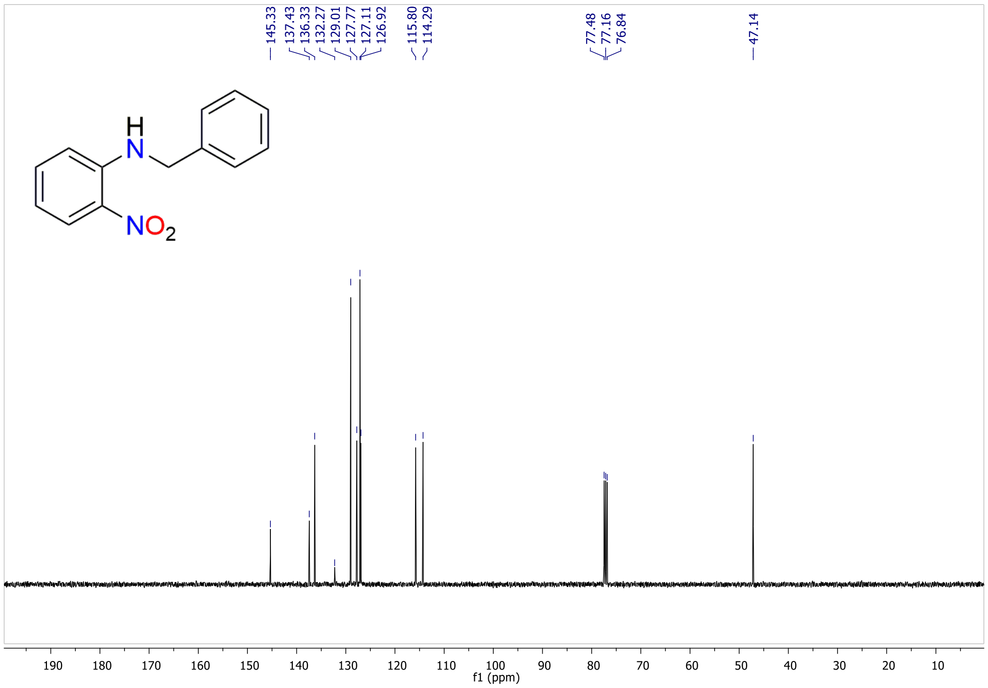


Figure S125. $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 ˚C, $CDCl_3$) spectrum of **6k**.

50. Computational Details

All calculations were carried out using the ORCA quantum chemical program package.[25] Geometries were optimized with the GGA (generalized gradient approximation) density functional BP86[26, 27] in conjunction with def2-SVP[28] basis sets. To accelerate the overall calculations, the RI[29, 30, 31] (resolution-of-identity) approximation was applied for the expensive integral calculations. Noncovalent interactions were accounted by using atom-pairwise dispersion corrections with Becke-Johnson (D3BJ) damping.[32] Subsequent numerical frequency calculations were undertaken for the optimized geometries to confirm that they correspond to stationary points. The minimum energy intermediates located in the calculations have only positive eigenvalues, whereas the transition states carry all positive eigenvalues except one as an imaginary mode. Gibbs free energies were calculated by single point calculations with BP86/def2-TZVP[28] method on the BP86/def2-SVP geometries.

51. Energy Table for Molecules Involved in the Hydride Transfer from HBpin to Pd in Figure 3

Total electronic energies and Gibbs free energies (333 K) of the molecules present in the hydride transfer in Figure 3. Employed DFT method: BP86-D3/def2-TZVP // BP86-D3/def2-SVP.

Molecule	E_{tot} [au]	G_{333} [au]	Imaginary Frequency
1	−1159.124601	−1158.891108	
B	−1571.190403	−1570.784181	
TS_{BC}	−1571.144426	−1570.737963	*i*149
C	−1571.177318	−1570.771877	
HBpin	−412.045185	−411.898881	

52. Energy Table for Molecules Involved in Path-1 in Figure 4

Total electronic energies and Gibbs free energies (333 K) of the molecules present in Path-1 in Figure 4. Employed DFT method: BP86-D3/def2-TZVP // BP86-D3/def2-SVP.

Molecule	E_{tot} [au]	G_{333} [au]	Imaginary Frequency
D	−1843.099083	−1842.566246	
TS_{DE}	−1843.054910	−1842.522038	*i*373
E	−1843.058177	−1842.522849	
$C_2H_5COC_2H_5$	−271.900012	−271.798484	

53. Energy Table for Structures Involved in Path-2 in Figure 4

Total electronic energies and Gibbs free energies (333 K) of the molecules present in Path-2 in Figure 4. Employed DFT method: BP86-D3/def2-TZVP // BP86-D3/def2-SVP.

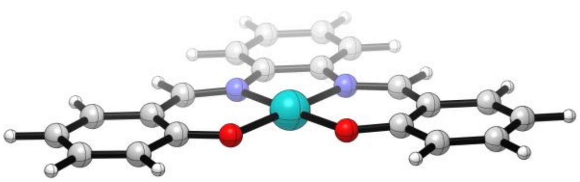
Molecule	E_{tot} [au]	G_{333} [au]	Imaginary Frequency
D’	−1843.097717	−1842.563515	
TS$_{D'E'}$	−1843.097442	−1842.562757	*i*24
E’	−1843.098258	−1842.562946	
TS$_{E'F'}$	−1843.078553	−1842.543658	*i*439
F’	−1843.160222	−1842.619786	

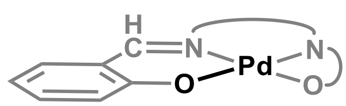
54. Cartesian Coordinates of the Optimized Structures

DFT optimization method: BP86-D3/def2-SVP

54.1. XYZ coordinates of the molecules involved in the hydride transfer from HBpin to Pd in Figure 3

1






```
C       -1.106670000      0.296206000     -1.008855000
C       -1.168550000     -1.025565000     -0.454854000
C       -1.649701000     -1.195882000      0.910929000
C       -2.038486000     -0.010422000      1.622230000
C       -1.962285000      1.245936000      1.042828000
C       -1.491526000      1.413806000     -0.289726000
C       -0.751757000     -2.093966000     -1.298506000
Pd      -1.274940000     -4.105879000      0.753413000
O       -1.756918000     -2.325890000      1.537614000
H       -0.738747000      0.405715000     -2.041640000
H       -2.399766000     -0.152031000      2.650511000
H       -2.272067000      2.128286000      1.624725000
H       -1.435135000      2.416217000     -0.738335000
H       -0.412535000     -1.797173000     -2.307282000
C        0.070036000     -6.788862000     -2.219772000
C       -0.336951000     -5.717785000     -1.396411000
C       -0.303894000     -4.385811000     -1.906913000
C        0.131702000     -4.160332000     -3.229949000
C        0.530752000     -5.233730000     -4.034283000
C        0.500652000     -6.548176000     -3.529123000
N       -0.792572000     -5.842594000     -0.063615000
N       -0.728474000     -3.382697000     -1.005406000
H        0.051973000     -7.818705000     -1.838402000
```

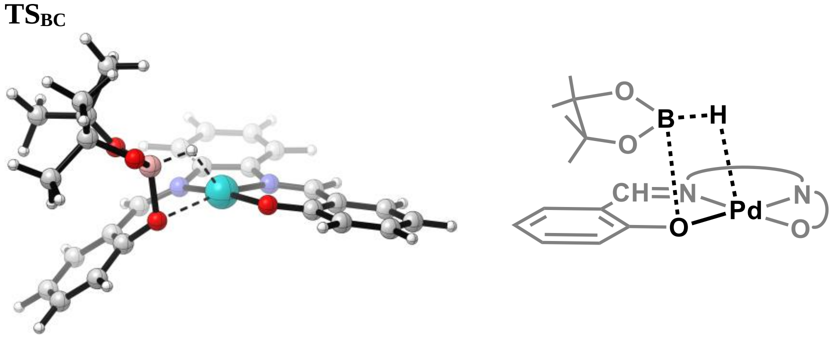
H	0.161031000	-3.142051000	-3.641799000
H	0.868444000	-5.043795000	-5.063551000
H	0.815803000	-7.390855000	-4.161627000
C	-1.353793000	-8.563995000	2.376310000
C	-1.336756000	-7.207724000	1.909653000
C	-1.772070000	-6.145548000	2.809156000
C	-2.194192000	-6.533917000	4.125510000
C	-2.193267000	-7.859416000	4.530714000
C	-1.769990000	-8.896963000	3.653050000
C	-0.888548000	-6.995827000	0.575133000
O	-1.809845000	-4.881685000	2.521961000
H	-1.020036000	-9.351418000	1.681267000
H	-2.519080000	-5.725444000	4.795883000
H	-2.526007000	-8.112402000	5.549658000
H	-1.773076000	-9.944905000	3.986677000
H	-0.591978000	-7.907991000	0.026407000

B

C	-1.732651000	-0.236791000	1.055980000
C	-1.413168000	-1.619550000	1.258512000
C	-1.146300000	-2.090669000	2.611897000
C	-1.195904000	-1.118277000	3.665995000
C	-1.508578000	0.209673000	3.420372000
C	-1.787176000	0.667095000	2.102508000
C	-1.375576000	-2.443330000	0.096388000
Pd	-0.859563000	-4.855363000	1.659251000
O	-0.875910000	-3.315421000	2.945486000
H	-1.942072000	0.098127000	0.027186000
H	-0.982229000	-1.483285000	4.680850000
H	-1.544233000	0.919558000	4.261988000
H	-2.040953000	1.721054000	1.919611000
H	-1.596369000	-1.931273000	-0.857231000
C	-0.992044000	-6.744760000	-2.107636000
C	-1.004057000	-5.904254000	-0.976445000
C	-1.126164000	-4.494980000	-1.148414000
C	-1.243594000	-3.958812000	-2.446998000
C	-1.245497000	-4.807160000	-3.559191000
C	-1.117551000	-6.199490000	-3.389952000
N	-0.911263000	-6.345297000	0.361646000
N	-1.127612000	-3.739334000	0.046708000
H	-0.875715000	-7.830904000	-1.989133000
H	-1.331171000	-2.873537000	-2.594946000
H	-1.337912000	-4.379133000	-4.568235000
H	-1.106129000	-6.863355000	-4.266812000
C	-1.097561000	-9.554408000	2.180267000
C	-0.947089000	-8.136227000	2.043098000
C	-0.735980000	-7.330508000	3.237910000
C	-0.648251000	-8.024735000	4.489748000
C	-0.797130000	-9.401026000	4.572898000
C	-1.031767000	-10.185953000	3.410789000
C	-1.016883000	-7.609966000	0.720283000
O	-0.641273000	-6.035102000	3.268241000
H	-1.271891000	-10.145168000	1.266282000
H	-0.475197000	-7.407795000	5.382927000
H	-0.735854000	-9.891436000	5.557552000

H	-1.156073000	-11.275741000	3.489837000
H	-1.195193000	-8.351061000	-0.079080000
O	-4.007746000	-6.491227000	0.097722000
B	-4.271736000	-5.503155000	-0.819315000
C	-4.884846000	-6.261139000	1.250452000
C	-5.281475000	-4.732407000	1.085603000
O	-5.074854000	-4.498700000	-0.347139000
H	-3.853108000	-5.526484000	-1.950773000
C	-6.737847000	-4.410003000	1.414169000
H	-7.438517000	-4.974357000	0.772554000
H	-6.961804000	-4.641038000	2.474822000
H	-6.922811000	-3.329663000	1.252935000
C	-4.341181000	-3.781791000	1.830109000
H	-4.487827000	-3.829510000	2.926394000
H	-3.281352000	-4.028362000	1.622016000
H	-4.528107000	-2.743356000	1.493670000
C	-6.070042000	-7.219668000	1.080933000
H	-6.640193000	-7.001775000	0.155591000
H	-5.684748000	-8.255616000	1.008270000
H	-6.765213000	-7.167100000	1.941899000
C	-4.117818000	-6.583220000	2.529050000
H	-4.745768000	-6.381802000	3.419922000
H	-3.834490000	-7.653451000	2.539755000
H	-3.190425000	-5.988952000	2.612010000

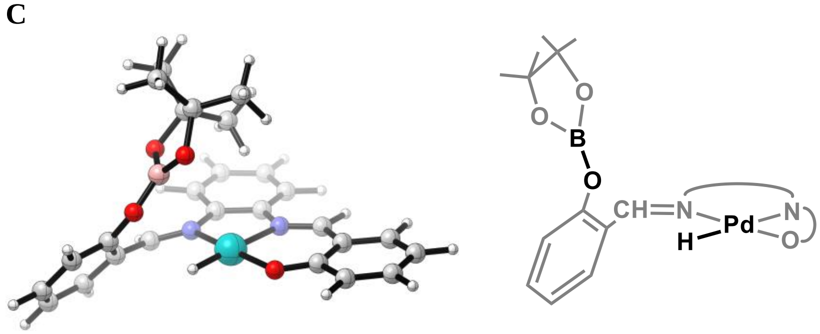
TS$_{BC}$



C	-0.060880000	0.279592000	-0.203097000
C	-0.608119000	-1.006195000	0.114031000
C	-1.368153000	-1.165341000	1.346461000
C	-1.521072000	-0.007009000	2.178276000
C	-0.962333000	1.214887000	1.834235000
C	-0.221234000	1.372802000	0.631071000
C	-0.403428000	-2.048523000	-0.836750000
Pd	-1.767463000	-4.024578000	0.845609000
O	-1.931728000	-2.262422000	1.756455000
H	0.501206000	0.381653000	-1.145337000
H	-2.099276000	-0.138521000	3.103841000
H	-1.100530000	2.077027000	2.505939000
H	0.211929000	2.347860000	0.367224000
H	0.113293000	-1.753786000	-1.768697000
C	-1.011448000	-6.620183000	-2.353587000
C	-1.016772000	-5.598681000	-1.386243000
C	-0.643197000	-4.272646000	-1.746648000
C	-0.215758000	-4.009731000	-3.063620000
C	-0.187781000	-5.041315000	-4.011803000
C	-0.596377000	-6.341666000	-3.663172000
N	-1.357911000	-5.781936000	-0.018823000
N	-0.774226000	-3.309296000	-0.720129000
H	-1.363963000	-7.626893000	-2.089502000
H	0.070792000	-2.992486000	-3.363692000
H	0.130794000	-4.820313000	-5.041175000
H	-0.610521000	-7.139337000	-4.420439000
C	-0.750818000	-8.588110000	2.304462000
C	-1.268406000	-7.308330000	1.952937000

C	-1.734374000	-6.444626000	3.002318000
C	-1.577471000	-6.853775000	4.344463000
C	-1.048841000	-8.110652000	4.656769000
C	-0.646351000	-8.994951000	3.633190000
C	-1.175377000	-6.947448000	0.562670000
O	-2.317804000	-5.269777000	2.750422000
H	-0.411318000	-9.256895000	1.497539000
H	-1.924833000	-6.162071000	5.124341000
H	-0.961445000	-8.416266000	5.711110000
H	-0.242865000	-9.987189000	3.880566000
H	-0.784643000	-7.752630000	-0.087373000
O	-3.995467000	-6.488622000	1.411977000
B	-3.768023000	-5.242243000	2.095527000
C	-5.351145000	-6.875596000	1.670168000
C	-5.617114000	-6.237637000	3.096471000
O	-4.795250000	-5.057049000	3.069658000
H	-3.668533000	-4.226778000	1.318881000
C	-7.068062000	-5.819178000	3.346291000
H	-7.393054000	-5.048237000	2.623539000
H	-7.754858000	-6.687872000	3.276477000
H	-7.160892000	-5.388514000	4.363614000
C	-5.134880000	-7.145095000	4.241551000
H	-5.809498000	-8.010295000	4.400543000
H	-4.113437000	-7.523282000	4.048839000
H	-5.104141000	-6.548707000	5.175093000
C	-6.243128000	-6.260300000	0.577296000
H	-6.212974000	-5.153822000	0.621671000
H	-5.855302000	-6.573355000	-0.412693000
H	-7.298415000	-6.589641000	0.659114000
C	-5.440478000	-8.401572000	1.624024000
H	-6.450955000	-8.754936000	1.914441000
H	-5.239748000	-8.757678000	0.592932000
H	-4.694264000	-8.867981000	2.293874000

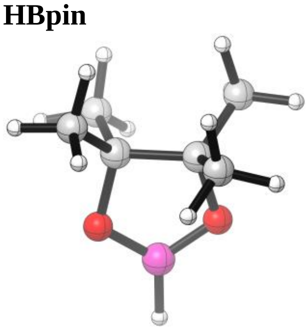
C



C	-1.864314000	0.037800000	-0.208777000
C	-1.598458000	-1.265039000	0.328087000
C	-1.318586000	-1.393219000	1.757084000
C	-1.333241000	-0.181552000	2.530683000
C	-1.599606000	1.055101000	1.964612000
C	-1.872039000	1.179123000	0.574268000
C	-1.624266000	-2.344516000	-0.608775000
Pd	-1.069143000	-4.319530000	1.592144000
O	-1.052333000	-2.486994000	2.406504000
H	-2.072880000	0.112200000	-1.289086000
H	-1.117869000	-0.290054000	3.603562000
H	-1.599163000	1.953500000	2.602379000
H	-2.084989000	2.162697000	0.131263000
H	-1.822410000	-2.048724000	-1.659445000
C	-1.509942000	-7.083376000	-1.595119000
C	-1.313685000	-5.973324000	-0.748214000
C	-1.495592000	-4.654432000	-1.266793000
C	-1.772775000	-4.493603000	-2.642861000
C	-1.912935000	-5.605466000	-3.480331000

C	-1.795323000	-6.905443000	-2.954992000
N	-1.033263000	-6.099445000	0.648501000
N	-1.442262000	-3.617606000	-0.327727000
H	-1.488876000	-8.099518000	-1.179321000
H	-1.902680000	-3.485175000	-3.059563000
H	-2.144146000	-5.458034000	-4.546118000
H	-1.949946000	-7.783107000	-3.599419000
C	0.698716000	-8.636291000	2.608094000
C	-0.379973000	-7.718062000	2.443097000
C	-1.179200000	-7.421941000	3.593239000
C	-0.812623000	-7.966286000	4.843944000
C	0.284775000	-8.818963000	4.977944000
C	1.047563000	-9.169365000	3.846579000
C	-0.568282000	-7.246740000	1.084047000
O	-2.278090000	-6.647494000	3.620886000
H	1.289337000	-8.899178000	1.716524000
H	-1.438696000	-7.697336000	5.706302000
H	0.538776000	-9.226238000	5.968103000
H	1.904974000	-9.852101000	3.936240000
H	-0.228409000	-7.968110000	0.315601000
O	-3.672172000	-7.048674000	1.638790000
B	-3.305909000	-6.333208000	2.756872000
C	-4.881615000	-6.405513000	1.113073000
C	-5.404821000	-5.575256000	2.365045000
O	-4.191801000	-5.353012000	3.133837000
H	-0.709137000	-4.870289000	2.996609000
C	-6.014579000	-4.218491000	2.019838000
H	-5.274901000	-3.560543000	1.528656000
H	-6.892649000	-4.338965000	1.353660000
H	-6.351734000	-3.717029000	2.947864000
C	-6.354183000	-6.381263000	3.262365000
H	-7.339792000	-6.539616000	2.782682000
H	-5.922191000	-7.369675000	3.515342000
H	-6.509583000	-5.827688000	4.208414000
C	-4.472745000	-5.505156000	-0.053450000
H	-3.762041000	-4.724666000	0.279011000
H	-3.980261000	-6.113688000	-0.834487000
H	-5.355268000	-5.014738000	-0.506497000
C	-5.826114000	-7.503081000	0.628713000
H	-6.790898000	-7.070142000	0.296262000
H	-5.371474000	-8.025919000	-0.236024000
H	-6.026478000	-8.252884000	1.416080000

HBpin

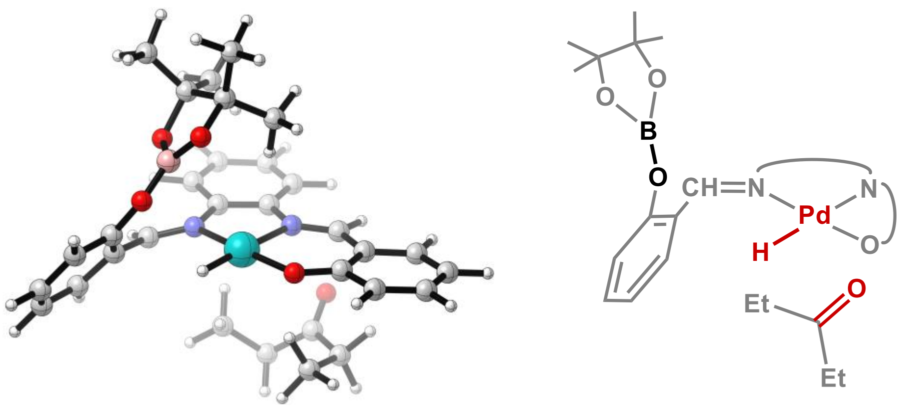


O	11.504277000	-0.950512000	28.775864000
B	11.106585000	0.123892000	29.531689000
C	11.161679000	-2.157405000	29.527614000
C	11.029354000	-1.612353000	31.011052000
O	10.701376000	-0.202227000	30.801605000
H	11.113994000	1.258133000	29.115536000
C	9.915136000	-2.254721000	31.834095000
H	8.924150000	-2.103203000	31.368687000
H	10.090734000	-3.343153000	31.951066000
H	9.889890000	-1.801264000	32.844141000

C	12.351785000	-1.643957000	31.789004000
H	12.639228000	-2.677092000	32.066157000
H	13.175322000	-1.193085000	31.201593000
H	12.234686000	-1.054073000	32.718743000
C	9.834851000	-2.671016000	28.952838000
H	9.019527000	-1.936743000	29.105705000
H	9.953763000	-2.827856000	27.863062000
H	9.535218000	-3.632691000	29.413583000
C	12.266837000	-3.190840000	29.321104000
H	12.084022000	-4.091794000	29.940527000
H	12.292544000	-3.504163000	28.258959000
H	13.261145000	-2.781723000	29.577593000

54.2. XYZ coordinates of the molecules involved in Path-1 in Figure 4

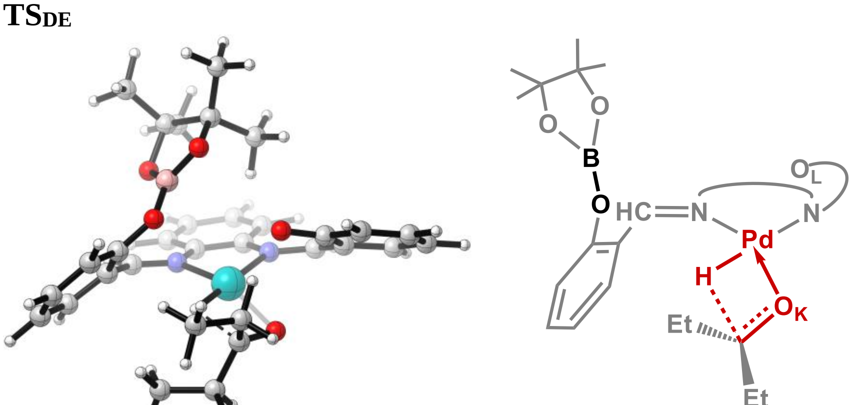
D



C	-1.365273000	-0.013981000	1.170381000
C	-1.350460000	-1.371196000	1.629313000
C	-1.479320000	-1.630674000	3.059894000
C	-1.646504000	-0.487424000	3.913012000
C	-1.660340000	0.808924000	3.420118000
C	-1.513273000	1.062245000	2.029564000
C	-1.195335000	-2.367791000	0.612940000
Pd	-1.216144000	-4.538684000	2.693513000
O	-1.439163000	-2.789611000	3.652026000
H	-1.251044000	0.157353000	0.087331000
H	-1.753193000	-0.695837000	4.987746000
H	-1.784188000	1.651805000	4.118693000
H	-1.520613000	2.091962000	1.643938000
H	-1.065189000	-1.978799000	-0.414513000
C	-0.953158000	-7.007878000	-0.745768000
C	-0.964614000	-5.976080000	0.214816000
C	-1.059606000	-4.617119000	-0.211236000
C	-1.067628000	-4.331286000	-1.593722000
C	-1.009412000	-5.363998000	-2.534442000
C	-0.961457000	-6.706428000	-2.113034000
N	-0.942698000	-6.221126000	1.621511000
N	-1.174400000	-3.666462000	0.809967000
H	-0.985080000	-8.056762000	-0.422542000
H	-1.122909000	-3.288948000	-1.932638000
H	-1.022359000	-5.122100000	-3.608033000
H	-0.958117000	-7.521747000	-2.851357000
C	0.406504000	-8.815829000	3.772615000
C	-0.658142000	-7.953961000	3.384469000
C	-1.746465000	-7.781405000	4.298061000
C	-1.676643000	-8.389762000	5.570303000
C	-0.588401000	-9.183914000	5.941185000
C	0.463464000	-9.411152000	5.031736000
C	-0.551806000	-7.396562000	2.047934000

O	-2.868211000	-7.072632000	4.068819000
H	1.222790000	-8.979720000	3.051531000
H	-2.520480000	-8.217825000	6.253524000
H	-0.566695000	-9.642025000	6.941483000
H	1.317036000	-10.047479000	5.307204000
H	-0.053835000	-8.059484000	1.314019000
O	-3.528722000	-7.302908000	1.710493000
B	-3.607965000	-6.723415000	2.958710000
C	-4.748500000	-6.911898000	0.999830000
C	-5.216486000	-5.618477000	1.796889000
O	-4.643506000	-5.835874000	3.117735000
H	-1.144929000	-5.216980000	4.089184000
C	-4.615690000	-4.318703000	1.250798000
H	-3.515116000	-4.394035000	1.164246000
H	-5.040560000	-4.052145000	0.263376000
H	-4.833399000	-3.498040000	1.961441000
C	-6.731356000	-5.484649000	1.943260000
H	-7.217000000	-5.408179000	0.949475000
H	-7.168202000	-6.342984000	2.485308000
H	-6.967536000	-4.564206000	2.512725000
C	-4.414519000	-6.658843000	-0.466428000
H	-3.608945000	-5.912193000	-0.584199000
H	-4.079301000	-7.597906000	-0.947788000
H	-5.312409000	-6.297697000	-1.007080000
C	-5.721657000	-8.089250000	1.136416000
H	-6.656367000	-7.919157000	0.567393000
H	-5.236106000	-9.002787000	0.741011000
H	-5.982131000	-8.272281000	2.197106000
O	1.565747000	-2.802252000	-0.535413000
C	2.232120000	-2.851394000	0.493550000
C	3.159422000	-4.038482000	0.756878000
H	3.732622000	-4.217494000	-0.177399000
H	3.883230000	-3.799439000	1.562740000
C	2.350367000	-5.298149000	1.113083000
H	1.663875000	-5.552555000	0.282129000
H	1.733168000	-5.144278000	2.022697000
H	3.021127000	-6.162316000	1.292244000
C	2.160410000	-1.758614000	1.549202000
H	3.133587000	-1.214255000	1.507186000
H	1.373722000	-1.045814000	1.234979000
C	1.917749000	-2.260040000	2.981212000
H	2.770898000	-2.853436000	3.368410000
H	1.007115000	-2.889269000	3.048158000
H	1.768089000	-1.401942000	3.664907000

TS$_{DE}$

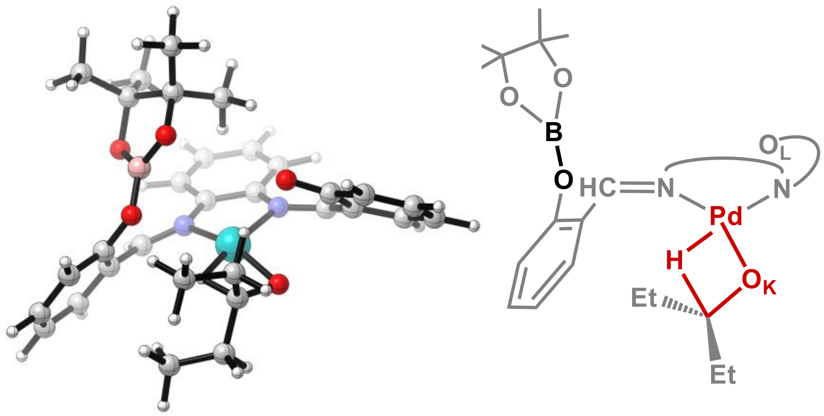


C	-1.662366000	0.058107000	-0.011047000
C	-1.583380000	-1.293796000	0.467837000
C	-1.704266000	-1.561330000	1.921995000
C	-1.851947000	-0.387599000	2.766952000

C	-1.897289000	0.892305000	2.252643000
C	-1.807645000	1.131575000	0.844423000
C	-1.480609000	-2.313096000	-0.503690000
Pd	-0.174948000	-4.343604000	1.315356000
O	-1.719014000	-2.720855000	2.425286000
H	-1.589747000	0.225379000	-1.099318000
H	-1.933255000	-0.577749000	3.848072000
H	-2.011450000	1.749973000	2.936000000
H	-1.856822000	2.158538000	0.453704000
H	-1.622171000	-1.988877000	-1.556210000
C	-1.438177000	-7.004941000	-1.727822000
C	-1.188372000	-5.941841000	-0.834610000
C	-1.506694000	-4.602567000	-1.226590000
C	-2.128680000	-4.389431000	-2.484671000
C	-2.362821000	-5.455453000	-3.354110000
C	-2.007982000	-6.768503000	-2.982110000
N	-0.690535000	-6.110303000	0.492645000
N	-1.248339000	-3.609322000	-0.291930000
H	-1.200975000	-8.037984000	-1.441944000
H	-2.438775000	-3.375898000	-2.772130000
H	-2.837118000	-5.267559000	-4.328998000
H	-2.198085000	-7.610417000	-3.663642000
C	0.840342000	-8.661865000	2.527495000
C	-0.130015000	-7.637452000	2.361809000
C	-0.712891000	-7.075514000	3.537334000
C	-0.262810000	-7.498195000	4.804585000
C	0.735416000	-8.469974000	4.934573000
C	1.289949000	-9.064154000	3.786663000
C	-0.497594000	-7.307391000	0.989881000
O	-1.687060000	-6.128868000	3.546444000
H	1.267376000	-9.120429000	1.622001000
H	-0.741292000	-7.048639000	5.685786000
H	1.067446000	-8.778351000	5.937177000
H	2.064900000	-9.839635000	3.876346000
H	-0.591735000	-8.177774000	0.316048000
O	-3.162106000	-6.877684000	1.743131000
B	-2.843342000	-6.046933000	2.794487000
C	-4.557106000	-6.597200000	1.402119000
C	-4.783493000	-5.158931000	2.040836000
O	-3.811475000	-5.140090000	3.128453000
H	0.678905000	-4.936783000	2.532292000
C	-4.414145000	-4.014860000	1.092561000
H	-3.389348000	-4.142349000	0.701589000
H	-5.125339000	-3.932240000	0.247580000
H	-4.418050000	-3.065750000	1.660436000
C	-6.173541000	-4.942793000	2.634003000
H	-6.952528000	-5.027274000	1.849786000
H	-6.394658000	-5.671582000	3.434889000
H	-6.231706000	-3.926435000	3.069742000
C	-4.703733000	-6.647230000	-0.115198000
H	-4.002215000	-5.958146000	-0.618388000
H	-4.492815000	-7.671658000	-0.480595000
H	-5.737351000	-6.381969000	-0.415546000
C	-5.396042000	-7.694157000	2.067137000
H	-6.468278000	-7.607408000	1.802719000
H	-5.030420000	-8.682443000	1.725277000
H	-5.302072000	-7.655587000	3.170522000
O	1.068988000	-2.736799000	1.840976000
C	1.470761000	-3.535274000	2.785342000
C	2.882499000	-4.139972000	2.648821000
H	3.245829000	-3.832852000	1.647467000
H	3.512514000	-3.609975000	3.398669000
C	3.023949000	-5.655540000	2.818891000
H	2.489273000	-6.187953000	2.006702000
H	2.603057000	-6.018149000	3.776465000
H	4.089516000	-5.960233000	2.782356000

C	0.923360000	-3.222087000	4.182135000
H	1.374086000	-2.232418000	4.424673000
H	-0.163914000	-3.037625000	4.057177000
C	1.207698000	-4.222028000	5.299003000
H	2.291737000	-4.344231000	5.498818000
H	0.793419000	-5.219727000	5.057902000
H	0.733649000	-3.887987000	6.243331000

E

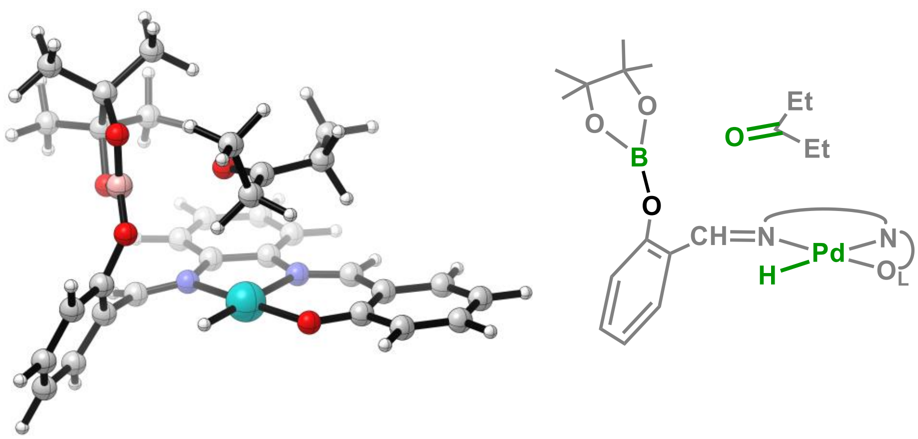


C	-0.796181000	0.214163000	-0.318523000
C	-1.156763000	-1.088442000	0.167473000
C	-1.649945000	-1.241622000	1.565157000
C	-1.635775000	-0.027909000	2.372947000
C	-1.245159000	1.190345000	1.861413000
C	-0.829558000	1.327660000	0.495556000
C	-1.095905000	-2.166057000	-0.733497000
Pd	-0.319872000	-4.253472000	1.249852000
O	-2.086280000	-2.326977000	2.025263000
H	-0.464040000	0.304361000	-1.366354000
H	-1.967987000	-0.137652000	3.415915000
H	-1.256161000	2.083613000	2.507750000
H	-0.534831000	2.313855000	0.107681000
H	-0.946604000	-1.914889000	-1.805917000
C	-1.898332000	-6.841236000	-1.742529000
C	-1.409767000	-5.799062000	-0.926232000
C	-1.571552000	-4.438145000	-1.334584000
C	-2.200723000	-4.168476000	-2.578318000
C	-2.631362000	-5.216829000	-3.394877000
C	-2.489887000	-6.557271000	-2.978315000
N	-0.816409000	-6.009734000	0.343178000
N	-1.187695000	-3.469816000	-0.427580000
H	-1.860879000	-7.878157000	-1.381024000
H	-2.386277000	-3.127114000	-2.875286000
H	-3.122344000	-4.988356000	-4.352794000
H	-2.880861000	-7.376044000	-3.599203000
C	1.131466000	-8.692229000	1.905905000
C	0.122967000	-7.688975000	1.925322000
C	-0.398351000	-7.304756000	3.197223000
C	0.122070000	-7.874787000	4.372936000
C	1.144883000	-8.829322000	4.320549000
C	1.652267000	-9.245961000	3.076036000
C	-0.326623000	-7.196082000	0.636120000
O	-1.366612000	-6.363104000	3.356853000
H	1.520264000	-9.014830000	0.927340000
H	-0.307804000	-7.551319000	5.331032000
H	1.537813000	-9.258670000	5.254001000
H	2.448434000	-10.002917000	3.021395000
H	-0.208185000	-7.914137000	-0.197930000
O	-3.084363000	-7.198173000	1.821788000
B	-2.606953000	-6.295945000	2.743209000

C	-4.515833000	-6.905268000	1.685656000
C	-4.606106000	-5.401285000	2.190088000
O	-3.481214000	-5.317229000	3.119454000
H	0.456616000	-4.665062000	2.752541000
C	-4.352295000	-4.380729000	1.079317000
H	-3.464139000	-4.652080000	0.480226000
H	-5.224826000	-4.294063000	0.402537000
H	-4.128047000	-3.399239000	1.535338000
C	-5.882417000	-5.062745000	2.955420000
H	-6.773859000	-5.204583000	2.312238000
H	-5.992993000	-5.684898000	3.862344000
H	-5.849780000	-4.001761000	3.270090000
C	-4.919983000	-7.102173000	0.228647000
H	-4.297247000	-6.494386000	-0.451585000
H	-4.804893000	-8.167553000	-0.054187000
H	-5.981946000	-6.820396000	0.081224000
C	-5.250407000	-7.896586000	2.594743000
H	-6.350039000	-7.796085000	2.505691000
H	-4.967798000	-8.928341000	2.305169000
H	-4.971476000	-7.749498000	3.657353000
O	0.735055000	-2.722725000	2.015749000
C	0.974661000	-3.548200000	3.059442000
C	2.458221000	-3.963147000	3.228469000
H	2.958456000	-3.685670000	2.278566000
H	2.888709000	-3.311362000	4.020859000
C	2.715234000	-5.438654000	3.545578000
H	2.340879000	-6.090971000	2.728722000
H	2.212442000	-5.763954000	4.476364000
H	3.799824000	-5.637105000	3.660441000
C	0.200693000	-3.132263000	4.325777000
H	0.647283000	-2.157289000	4.621818000
H	-0.835732000	-2.910084000	3.997184000
C	0.210190000	-4.108394000	5.500731000
H	1.232875000	-4.308167000	5.881182000
H	-0.253469000	-5.072916000	5.214874000
H	-0.380043000	-3.698925000	6.345015000

54.3. XYZ coordinates of the molecules involved in Path-2 in Figure 4

D’

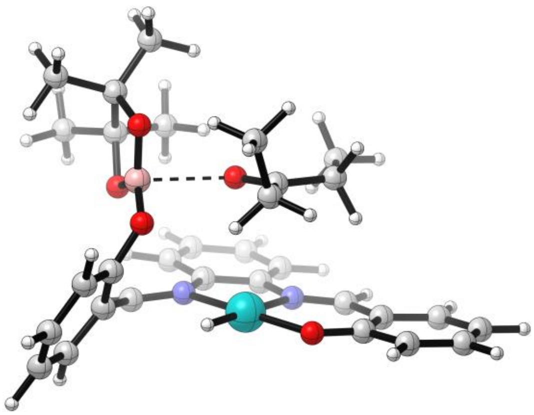


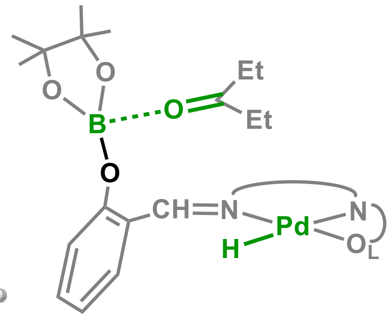
C	-1.396549000	-0.353200000	-0.951702000
C	-1.204963000	-1.546501000	-0.181163000
C	-0.722811000	-1.425958000	1.194187000
C	-0.484577000	-0.094512000	1.680952000
C	-0.691254000	1.029810000	0.896835000
C	-1.154761000	0.911336000	-0.441831000
C	-1.532971000	-2.774861000	-0.839989000
Pd	-0.867297000	-4.333816000	1.641814000

O	-0.488798000	-2.396452000	2.026916000
H	-1.759637000	-0.466784000	-1.986387000
H	-0.120651000	-0.015115000	2.715352000
H	-0.490035000	2.027391000	1.318766000
H	-1.317721000	1.806353000	-1.059142000
H	-1.864508000	-2.666046000	-1.892467000
C	-2.181025000	-7.572258000	-0.782827000
C	-1.759724000	-6.356377000	-0.210590000
C	-1.881278000	-5.147727000	-0.961800000
C	-2.391513000	-5.207713000	-2.278763000
C	-2.780261000	-6.428496000	-2.840651000
C	-2.675698000	-7.614882000	-2.092306000
N	-1.237523000	-6.248105000	1.117065000
N	-1.497969000	-3.972805000	-0.301221000
H	-2.157102000	-8.495201000	-0.189558000
H	-2.493619000	-4.286251000	-2.868436000
H	-3.181865000	-6.453592000	-3.864387000
H	-3.003780000	-8.573524000	-2.519952000
C	0.754393000	-8.035078000	3.443670000
C	-0.472766000	-7.387820000	3.161465000
C	-1.221068000	-6.843865000	4.243026000
C	-0.679225000	-6.874199000	5.542052000
C	0.568146000	-7.460880000	5.786544000
C	1.287068000	-8.059546000	4.736387000
C	-0.896679000	-7.329942000	1.764277000
O	-2.460475000	-6.299663000	4.116881000
H	1.316519000	-8.480708000	2.608177000
H	-1.275873000	-6.432907000	6.352733000
H	0.974016000	-7.467298000	6.809782000
H	2.260796000	-8.534141000	4.924173000
H	-0.858593000	-8.287586000	1.210597000
O	-3.549155000	-7.808367000	2.523191000
B	-3.576820000	-6.861186000	3.518700000
C	-4.927000000	-8.175562000	2.211164000
C	-5.788835000	-7.434314000	3.356236000
O	-4.812997000	-6.638842000	4.072951000
H	-0.350941000	-4.665665000	3.071298000
C	-6.859129000	-6.484541000	2.810067000
H	-6.411500000	-5.713322000	2.158539000
H	-7.631219000	-7.035628000	2.237854000
H	-7.358352000	-5.976123000	3.658457000
C	-6.415595000	-8.389853000	4.378276000
H	-7.191872000	-9.030946000	3.916337000
H	-5.654735000	-9.040776000	4.849038000
H	-6.890903000	-7.793719000	5.181549000
C	-5.236494000	-7.673820000	0.797760000
H	-5.025621000	-6.592561000	0.709398000
H	-4.596530000	-8.203122000	0.068292000
H	-6.291977000	-7.871290000	0.526774000
C	-5.002716000	-9.703526000	2.253413000
H	-6.030011000	-10.062097000	2.043213000
H	-4.330930000	-10.122991000	1.478290000
H	-4.682454000	-10.106172000	3.232171000
O	-4.085751000	-4.891261000	1.918686000
C	-3.968328000	-3.697317000	2.202161000
C	-3.511576000	-3.236291000	3.573029000
H	-2.710120000	-3.921069000	3.911714000
H	-3.082968000	-2.216719000	3.499976000
C	-4.688056000	-3.272028000	4.568401000
H	-5.076609000	-4.304040000	4.663087000
H	-5.519052000	-2.608151000	4.249800000
H	-4.354216000	-2.932708000	5.569356000
C	-4.358616000	-2.616377000	1.211325000
H	-5.044169000	-1.913801000	1.738713000
H	-3.442330000	-2.010997000	1.027715000
C	-4.961375000	-3.139354000	-0.087711000

H	-5.917924000	-3.667859000	0.098902000
H	-4.282277000	-3.868756000	-0.570823000
H	-5.155797000	-2.312443000	-0.798739000

TS$_{D'E'}$

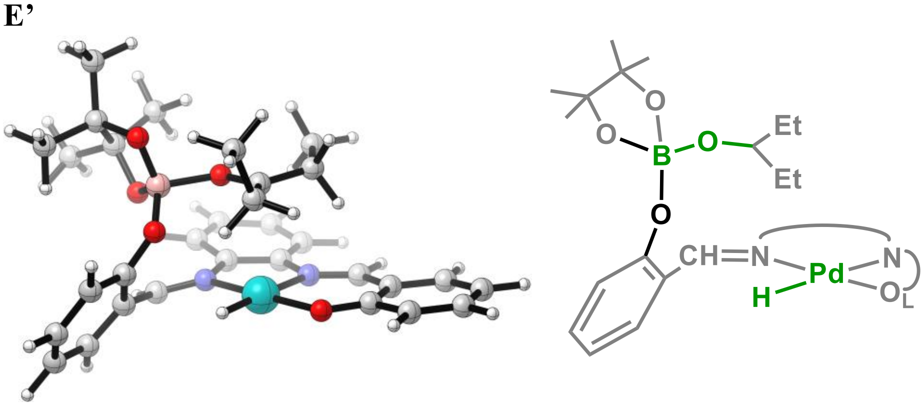




C	-1.377951000	-0.406805000	-1.030875000
C	-1.187935000	-1.587811000	-0.241274000
C	-0.691599000	-1.446292000	1.126970000
C	-0.436807000	-0.108426000	1.586957000
C	-0.641423000	1.003319000	0.784636000
C	-1.119969000	0.864621000	-0.546747000
C	-1.530138000	-2.825101000	-0.876157000
Pd	-0.857624000	-4.343490000	1.628377000
O	-0.459161000	-2.403247000	1.975712000
H	-1.752052000	-0.535979000	-2.059812000
H	-0.062042000	-0.013614000	2.616193000
H	-0.426758000	2.006467000	1.186224000
H	-1.281467000	1.749607000	-1.178753000
H	-1.874670000	-2.731103000	-1.925841000
C	-2.223857000	-7.615278000	-0.719891000
C	-1.775327000	-6.393113000	-0.181642000
C	-1.889822000	-5.198693000	-0.956336000
C	-2.411066000	-5.280855000	-2.267635000
C	-2.820628000	-6.508734000	-2.799035000
C	-2.729457000	-7.679601000	-2.024565000
N	-1.247007000	-6.263904000	1.138870000
N	-1.492531000	-4.014862000	-0.319721000
H	-2.217075000	-8.521049000	-0.100046000
H	-2.507252000	-4.371218000	-2.876443000
H	-3.230921000	-6.550644000	-3.818805000
H	-3.078694000	-8.641597000	-2.427250000
C	0.672725000	-8.035820000	3.556000000
C	-0.529775000	-7.372103000	3.213001000
C	-1.309110000	-6.786733000	4.251653000
C	-0.815745000	-6.794586000	5.570512000
C	0.410226000	-7.398138000	5.875078000
C	1.156183000	-8.037430000	4.868007000
C	-0.910201000	-7.336629000	1.804677000
O	-2.530348000	-6.225319000	4.062572000
H	1.256203000	-8.512575000	2.752862000
H	-1.433277000	-6.322771000	6.347665000
H	0.777919000	-7.386175000	6.912639000
H	2.112704000	-8.524982000	5.104966000
H	-0.858060000	-8.300636000	1.262775000
O	-3.567304000	-7.758744000	2.454124000
B	-3.634894000	-6.789134000	3.434879000
C	-4.938725000	-8.161721000	2.148340000
C	-5.738738000	-7.678097000	3.442753000
O	-4.884525000	-6.648506000	4.003630000
H	-0.343079000	-4.652999000	3.063887000

C	-7.104990000	-7.062092000	3.143019000
H	-7.007070000	-6.176161000	2.489692000
H	-7.774616000	-7.797166000	2.652509000
H	-7.582003000	-6.740227000	4.089711000
C	-5.866145000	-8.768695000	4.515764000
H	-6.559193000	-9.575882000	4.208046000
H	-4.880329000	-9.216147000	4.750956000
H	-6.255600000	-8.309549000	5.445077000
C	-5.370133000	-7.444911000	0.863844000
H	-5.304116000	-6.347709000	0.976431000
H	-4.688067000	-7.731024000	0.041746000
H	-6.398891000	-7.733478000	0.572322000
C	-4.943690000	-9.674396000	1.930119000
H	-5.975711000	-10.047185000	1.771772000
H	-4.355227000	-9.917832000	1.022900000
H	-4.498304000	-10.217576000	2.783622000
O	-4.050265000	-4.868759000	2.033968000
C	-3.919499000	-3.670165000	2.293812000
C	-3.447810000	-3.187984000	3.651379000
H	-2.599403000	-3.830774000	3.956754000
H	-3.076699000	-2.146982000	3.571606000
C	-4.587184000	-3.295339000	4.683239000
H	-4.937618000	-4.342188000	4.765244000
H	-5.453712000	-2.658136000	4.407416000
H	-4.234694000	-2.964434000	5.680680000
C	-4.306485000	-2.610829000	1.280249000
H	-4.979793000	-1.888491000	1.796727000
H	-3.385857000	-2.019266000	1.074643000
C	-4.924877000	-3.157546000	-0.001719000
H	-5.891719000	-3.660063000	0.202801000
H	-4.262035000	-3.913144000	-0.466968000
H	-5.105343000	-2.346506000	-0.734321000

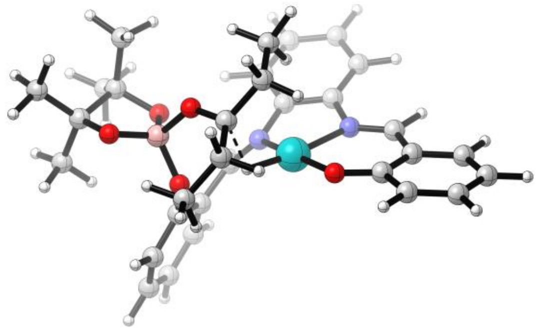
E’

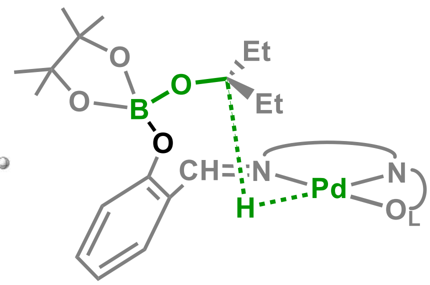


C	-1.114909000	-0.285583000	-1.120583000
C	-1.024303000	-1.467282000	-0.314690000
C	-0.658120000	-1.328820000	1.093340000
C	-0.420761000	0.004225000	1.573303000
C	-0.523366000	1.117139000	0.752734000
C	-0.876688000	0.982478000	-0.616942000
C	-1.327800000	-2.701358000	-0.979499000
Pd	-0.946830000	-4.218121000	1.589791000
O	-0.527338000	-2.288239000	1.964562000
H	-1.393083000	-0.410619000	-2.180151000
H	-0.140956000	0.095431000	2.632814000
H	-0.324723000	2.116894000	1.170578000
H	-0.958363000	1.867861000	-1.263622000
H	-1.574945000	-2.603132000	-2.056347000
C	-2.387479000	-7.417953000	-0.787702000
C	-1.821332000	-6.237253000	-0.263709000
C	-1.773042000	-5.063006000	-1.075101000

C	-2.187759000	-5.141374000	-2.423234000
C	-2.692209000	-6.338130000	-2.945464000
C	-2.807901000	-7.474051000	-2.122530000
N	-1.356500000	-6.131751000	1.077019000
N	-1.369368000	-3.888759000	-0.420394000
H	-2.542784000	-8.281255000	-0.128930000
H	-2.139216000	-4.249731000	-3.063643000
H	-3.026241000	-6.377186000	-3.992922000
H	-3.250671000	-8.401426000	-2.515097000
C	0.178688000	-8.267422000	3.565097000
C	-0.846006000	-7.372596000	3.161878000
C	-1.629681000	-6.719002000	4.166409000
C	-1.285843000	-6.913599000	5.523918000
C	-0.225235000	-7.747269000	5.891060000
C	0.509291000	-8.443068000	4.909978000
C	-1.088100000	-7.232649000	1.738102000
O	-2.682036000	-5.940966000	3.900348000
H	0.746523000	-8.799420000	2.785318000
H	-1.897951000	-6.397423000	6.277005000
H	0.018763000	-7.877193000	6.957030000
H	1.331440000	-9.114606000	5.197900000
H	-1.001186000	-8.167104000	1.149279000
O	-3.695191000	-7.387942000	2.216229000
B	-3.846173000	-6.259536000	3.077079000
C	-4.961416000	-8.074130000	2.169188000
C	-5.565350000	-7.721179000	3.587306000
O	-5.081937000	-6.380974000	3.793794000
H	-0.564476000	-4.536952000	3.062150000
C	-7.091586000	-7.715407000	3.645114000
H	-7.515068000	-6.964047000	2.953297000
H	-7.504892000	-8.711767000	3.386598000
H	-7.429701000	-7.462206000	4.669896000
C	-4.986772000	-8.614178000	4.698990000
H	-5.398527000	-9.642728000	4.668529000
H	-3.882234000	-8.671203000	4.626706000
H	-5.241654000	-8.165922000	5.679600000
C	-5.787869000	-7.489827000	1.011807000
H	-6.036003000	-6.428218000	1.198604000
H	-5.184226000	-7.534987000	0.083583000
H	-6.727792000	-8.053497000	0.847248000
C	-4.702665000	-9.562727000	1.937429000
H	-5.638484000	-10.147738000	2.040179000
H	-4.317938000	-9.727505000	0.909837000
H	-3.956037000	-9.956510000	2.651691000
O	-4.053459000	-4.953627000	2.133695000
C	-3.786652000	-3.733336000	2.320018000
C	-3.407303000	-3.157094000	3.655905000
H	-2.608012000	-3.777389000	4.096767000
H	-3.014125000	-2.134420000	3.500516000
C	-4.641110000	-3.157574000	4.588530000
H	-5.009439000	-4.189546000	4.748073000
H	-5.472305000	-2.550341000	4.173580000
H	-4.361697000	-2.723107000	5.568242000
C	-4.136013000	-2.778972000	1.211152000
H	-4.813841000	-2.018392000	1.665523000
H	-3.215771000	-2.200058000	0.975865000
C	-4.750572000	-3.415456000	-0.030203000
H	-5.740589000	-3.858647000	0.195201000
H	-4.110882000	-4.230107000	-0.419041000
H	-4.882349000	-2.660571000	-0.829403000

TS$_{E'F'}$

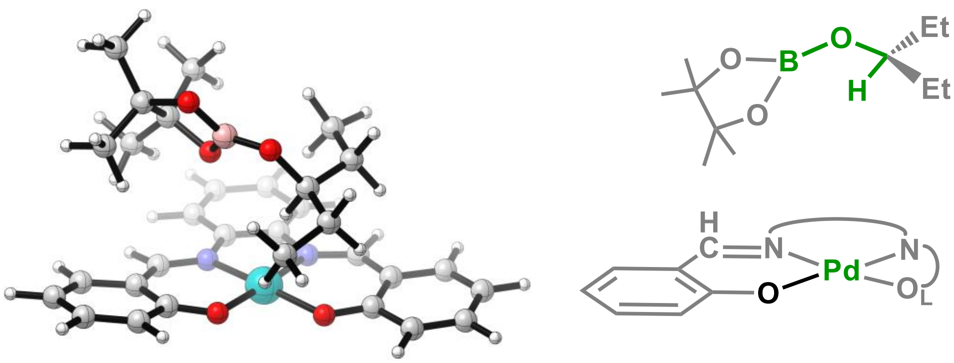




C	0.317845000	-0.439634000	-1.143567000
C	-0.382406000	-1.463767000	-0.428929000
C	-0.945818000	-1.147665000	0.878073000
C	-0.763341000	0.190553000	1.358797000
C	-0.062954000	1.145558000	0.635237000
C	0.490831000	0.837625000	-0.634977000
C	-0.544897000	-2.713449000	-1.112674000
Pd	-1.846023000	-3.918775000	1.304858000
O	-1.616544000	-1.956503000	1.655230000
H	0.725996000	-0.696832000	-2.134180000
H	-1.194270000	0.420087000	2.343679000
H	0.062983000	2.155793000	1.055829000
H	1.038413000	1.600511000	-1.206579000
H	-0.201342000	-2.727667000	-2.166719000
C	-2.451235000	-7.177568000	-1.202173000
C	-1.929000000	-6.034170000	-0.574704000
C	-1.448103000	-4.941015000	-1.352607000
C	-1.459830000	-5.043936000	-2.758151000
C	-1.952467000	-6.203407000	-3.376635000
C	-2.459390000	-7.263291000	-2.603755000
N	-1.852767000	-5.901493000	0.843442000
N	-1.078313000	-3.802869000	-0.611301000
H	-2.892092000	-7.968785000	-0.579787000
H	-1.113169000	-4.202771000	-3.375049000
H	-1.971050000	-6.264343000	-4.475470000
H	-2.887096000	-8.150817000	-3.093457000
C	-0.203298000	-8.127672000	3.224982000
C	-1.225884000	-7.186678000	2.915069000
C	-1.919169000	-6.550985000	3.992861000
C	-1.491637000	-6.795027000	5.320243000
C	-0.443181000	-7.678104000	5.589443000
C	0.199900000	-8.365687000	4.538376000
C	-1.466536000	-6.969042000	1.504893000
O	-2.958959000	-5.755143000	3.794683000
H	0.298787000	-8.649280000	2.394524000
H	-2.041402000	-6.290855000	6.127126000
H	-0.137775000	-7.858026000	6.631920000
H	1.008995000	-9.079859000	4.750671000
H	-1.168022000	-7.828306000	0.870101000
O	-4.132946000	-7.216458000	2.245413000
B	-4.271215000	-6.169294000	3.226249000
C	-5.225703000	-8.128763000	2.422772000
C	-5.537584000	-7.969979000	3.968120000
O	-5.246974000	-6.582554000	4.192819000
H	-2.607532000	-4.036902000	2.685367000
C	-6.991774000	-8.238219000	4.359552000
H	-7.680372000	-7.541666000	3.846711000
H	-7.288380000	-9.279110000	4.117006000
H	-7.116694000	-8.092489000	5.451713000
C	-4.593331000	-8.819112000	4.838554000
H	-4.848815000	-9.897915000	4.807563000
H	-3.538944000	-8.698182000	4.522046000

H	-4.672045000	-8.470789000	5.887516000
C	-6.394445000	-7.662469000	1.537762000
H	-6.753617000	-6.666156000	1.859642000
H	-6.035854000	-7.572503000	0.492937000
H	-7.245847000	-8.372742000	1.556791000
C	-4.767557000	-9.527017000	2.002939000
H	-5.542915000	-10.287662000	2.227095000
H	-4.577781000	-9.548949000	0.909827000
H	-3.830861000	-9.811548000	2.518536000
O	-4.764682000	-4.876661000	2.539212000
C	-4.324795000	-3.664707000	2.521012000
C	-4.195512000	-2.788823000	3.764822000
H	-3.489618000	-1.971893000	3.507876000
H	-5.201619000	-2.306993000	3.822667000
C	-3.869297000	-3.408448000	5.119748000
H	-2.821504000	-3.756605000	5.158435000
H	-4.519417000	-4.276355000	5.341985000
H	-4.015888000	-2.646221000	5.911962000
C	-4.743589000	-2.876021000	1.280467000
H	-5.730380000	-2.435026000	1.560921000
H	-4.055094000	-2.018207000	1.153120000
C	-4.905592000	-3.693235000	0.001457000
H	-5.553350000	-4.573306000	0.175196000
H	-3.927229000	-4.069224000	-0.355022000
H	-5.350088000	-3.074710000	-0.803393000

F’



C	-1.548582000	-0.575198000	-0.781755000
C	-1.306619000	-1.814716000	-0.102445000
C	-0.808595000	-1.782802000	1.267063000
C	-0.568681000	-0.492911000	1.848416000
C	-0.821384000	0.679106000	1.152344000
C	-1.321620000	0.649714000	-0.179137000
C	-1.578831000	-3.008187000	-0.831509000
Pd	-0.947078000	-4.712435000	1.451902000
O	-0.581254000	-2.820431000	2.011040000
H	-1.932614000	-0.619279000	-1.813253000
H	-0.185181000	-0.482025000	2.878236000
H	-0.633259000	1.647742000	1.641485000
H	-1.522499000	1.585725000	-0.719188000
H	-1.930928000	-2.859141000	-1.868131000
C	-1.851143000	-7.836345000	-1.236934000
C	-1.597114000	-6.642386000	-0.528473000
C	-1.753556000	-5.387725000	-1.188899000
C	-2.176234000	-5.357089000	-2.534338000
C	-2.434529000	-6.549718000	-3.220018000
C	-2.266621000	-7.789253000	-2.572910000
N	-1.214962000	-6.567108000	0.828215000
N	-1.460534000	-4.251159000	-0.401376000
H	-1.723230000	-8.811374000	-0.747851000
H	-2.305741000	-4.398509000	-3.054442000
H	-2.766401000	-6.512886000	-4.267659000

H	-2.463451000	-8.726853000	-3.112928000
C	-0.824621000	-8.901773000	3.660751000
C	-0.813237000	-7.625190000	3.009709000
C	-0.621255000	-6.425970000	3.812590000
C	-0.500562000	-6.597646000	5.232137000
C	-0.542323000	-7.852745000	5.819841000
C	-0.699632000	-9.027468000	5.033588000
C	-1.052036000	-7.620827000	1.604779000
O	-0.534548000	-5.217160000	3.348179000
H	-0.958675000	-9.800295000	3.036539000
H	-0.370464000	-5.684942000	5.830550000
H	-0.449523000	-7.939255000	6.914210000
H	-0.727221000	-10.017574000	5.510786000
H	-1.148151000	-8.615939000	1.135562000
O	-4.374356000	-6.198069000	2.135173000
B	-5.052294000	-5.455659000	3.102190000
C	-5.101728000	-7.458219000	2.039795000
C	-5.687194000	-7.598293000	3.497416000
O	-5.940670000	-6.212911000	3.849171000
H	-3.114686000	-3.951535000	2.302347000
C	-6.994968000	-8.379629000	3.593287000
H	-7.795336000	-7.900817000	2.999266000
H	-6.860776000	-9.421780000	3.239309000
H	-7.332413000	-8.417022000	4.647875000
C	-4.648059000	-8.141569000	4.491469000
H	-4.476326000	-9.228759000	4.363185000
H	-3.676392000	-7.618909000	4.384328000
H	-5.016832000	-7.966146000	5.521097000
C	-6.192294000	-7.270339000	0.975191000
H	-6.915786000	-6.489805000	1.282758000
H	-5.717263000	-6.947981000	0.028524000
H	-6.748063000	-8.209776000	0.785647000
C	-4.154064000	-8.575995000	1.627590000
H	-4.697051000	-9.540988000	1.571641000
H	-3.741119000	-8.358967000	0.623024000
H	-3.319854000	-8.682106000	2.340711000
O	-4.923369000	-4.127013000	3.329242000
C	-3.952927000	-3.302801000	2.655683000
C	-3.410298000	-2.308011000	3.682370000
H	-2.718631000	-1.617406000	3.157279000
H	-4.264555000	-1.691675000	4.041611000
C	-2.696193000	-2.978345000	4.857587000
H	-1.835987000	-3.579152000	4.501685000
H	-3.387402000	-3.651817000	5.403641000
H	-2.317207000	-2.223629000	5.576476000
C	-4.576212000	-2.612556000	1.438894000
H	-5.403612000	-1.955931000	1.787824000
H	-3.800388000	-1.937284000	1.018549000
C	-5.077184000	-3.566222000	0.352057000
H	-5.939105000	-4.165946000	0.705899000
H	-4.288121000	-4.283970000	0.049571000
H	-5.410065000	-3.011341000	-0.548796000

References

1. A. Harinath, J. Bhattacharjee, K. R. Gorantla, B. S. Mallik, T. K. Panda, *Eur. J. Org. Chem.* 2018, **24**, 3180-3192.
2. C. Erken, A. Kaithal, S. Sen, T. Weyhermüller, M. Hölscher, C. Werlé, W. Leitner, *Nat. Commun.* 2018, **9**, 4521-4529.
3. a) J. Lua, A. Zhanga, H. Songa, Q. Tongb, C.-H. Tunga, W. Wang, *Chin. Chem. Lett.* 2018, **29**, 949-953; b) C. K. Blasius, V. Vasilenko, L. H. Gade, *Angew. Chem.*, *Int. Ed*. 2018, **57**, 10231-10235; c) A. Baishya, S. Baruah, K. Geetharani, *Dalton Trans.* 2018, **47**, 9231-9236.
4. A. Y. Khalimon, P. Farha, L. G. Kuzmina, G. I. Nikonov, *Chem. Commun.* 2012, **48**, 455-457.
5. R. J. Newland, J. M. Lynam, S. M. Mansell, *Chem. Commun.* 2018, **54**, 5482-5485.
6. a) A. Kaithal, B. Chatterjee, C. Gunanathan, *Org. Lett.* 2015, **17**, 4790- 4793; b) J. B. Geri, N. K. Szymczak, *J. Am. Chem. Soc.* 2015, **137**, 12808- 12814.
7. P. K. Verma, A. S. Sethulekshmi, K. Geetharani, *Org. Lett.* 2018, **20**, 7840 - 7845.
8. H. Zeng, J. Wu, S. Li, C. Hui, A. Ta, S.-Y. Cheng, S. Zheng, G. Zhang, *Org. Lett.* 2019, **21**, 401-406.
9. H. Stachowiak, J. Kaźmierczak, K. Kuciński, G. Hreczycho, *Green Chem.* 2018, **20**, 1738-1742.
10. S. Yadav, S. Pahar, S. S. Sen, *Chem. Commun.* 2017, **53**, 4562-4564.
11. a) D. W. Stephan, G. Erker, *Angew Chem Int. Ed.* 2015, **54**, 6400; b) P. Eisenberger, A. M. Bailey, C. M. Crudden, *J. Am. Chem. Soc*. 2012, **134**, 17384.
12. D. Yan, X. Wu, J. Xiao, Z. Zhu, X. Xu, X. Bao, Y. Yao, Q. Shen, M. Xue, *Org. Chem. Front.* 2019, **6**, 648.
13. H. Elsen, C. Färber, G. Ballmann, S. Harder, *Angew Chem. Int. Ed.* 2018, **57**, 7156.
14. R. T. Baker, J. C. Calabrese, S. A. Westcott, *J. Organomet. Chem.* 1995, **498**, 109.
15. D. H. Ma, A. K. Jaladi, J. H. Lee, T. S. Kim, W. K. Shin, H. Hwang and D. K. An, *ACS Omega*, 2019, **4**, 15893.
16. G. S. Kumar, A. Harinath, R. Kawaria and T. K. Panda, *Eur. J. Inorg. Chem.*, 2020, ***2020***, 467.
17. M. W. Stanford, A. Bismuto and M. J. Cowley, *Chem. Eur. J.*, 2020, **26**, 9855.
18. N. Edugurala, Z. Wang, U. Chaudhary, N. Nelson, K. Kandel, T. Kobayashi, I. I. Slowing, M. Pruski and A. D. Sadow, *ACS Catal.*, 2015, **5**, 7399.
19. W. Wang, M. Luo, Weiwei Yao, Mengtao Ma, S. A. Pullarkat, L. Xu and P. H. Leung, *New J. Chem.* 2019, **43**, 10744.
20. T. Ghatak, K. Makarov, N. Fridman and M. S. Eisen, *Chem. Commun.* 2018, **54**, 11001.
21. I. Banerjee, S. Sagar, T. K. Panda, *Appl. Organomet. Chem.* 2020, **34**, 5765.
22. N. Antil, N. Akhtar, R. Newar, W. Begum, A. Kumar, M. Chauhan, and K. Manna *ACS Catal.* 2021, **11**, 10450−10459
23. A. Harinath, J. Bhattacharjee, H. P. Nayek, and T. K. Panda, *Dalton Transactions* 2018, **47**, 12613-12622

24. R. Arundhathi, D. C. Kumar, and B. Sreedhar, *J. Org. Chem. 2010,* ***19****, 3621–3630.*
25. F. Neese, *WIREs Comput. Mol. Sci.* 2012, **2**, 73–78.
26. J. P. Perdew, *Phys. Rev. B* 1986, **33**, 8822–8824.
27. A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098–3100.
28. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297–3305.
29. R. A. Kendall, H. A. Früchtl, Theor. Chem. Acc. 1997, **97**, 158–163.
30. K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, Chem. Phys. Lett. 1995, **240**, 283–290.
31. K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* 1997, **97**, 119–124.
32. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.