Supporting Information

Ruthenium-Catalyzed Selective Hydro*boronolysis* of Ethers

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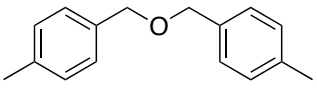
1. General methods

All catalytic reactions were performed under argon atmosphere. All stoichiometric reactions were performed in nitrogen atmosphere MBraun glove box. Chemicals were purchased from Acros, Sigma-Aldrich, Alfa-aesar, Himedia Chemicals and used without further purification. Dry solvents were prepared according to standard procedures. ^{1}H, ^{13}C spectra were recorded at Bruker AV-400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz). ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts were reported in ppm downfield from tetramethyl silane. Multiplicity is abbreviated as: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; dq, doublet of quartet; m, multiplate; br, broad. Assignment of spectra was done based on one dimensional (dept-135) NMR techniques. IR Spectra were recorded in Perkin-Elmer FT-IR Spectrometer. Mass spectra were recorded on Bruker micrOTOF-Q II Spectrometer.

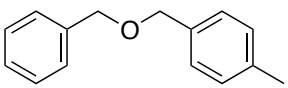
2. Standard procedure for the synthesis of ether derivatives

In an oven dried 100 mL RB flask, alcohol (10 mmol) was dissolved in 6 mL of DMF under argon atmosphere. This solution was transferred via cannula to another flask containing DMF (5 mL) solution of sodium hydride (20 mmol, 55% in mineral oil, pre-washed with dry hexane) under ice-cold condition and the solution was stirred for 30 minutes. To this solution, bromo compound (11 mmol) dissolved in 6 mL of DMF was slowly added under ice-cold condition and then the reaction mixture was warm to room temperature and stirred. Reaction progress was monitored by TLC. Upon completion, the reaction mixture was poured into ice-cold water and extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulphate and evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography.

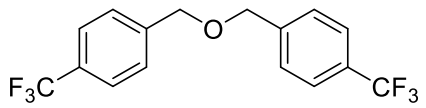
2.1 Spectral data of ether derivatives



4,4'-(Oxybis(methylene))bis(methylbenzene)[1]: ^{1}H NMR ($CDCl_3$): δ 7.29-7.31 (d, *J* = 8 Hz, 4H, ArC*H*), 7.19-7.21 (d, *J* = 8 Hz, 4H, ArC*H*), 4.54 (s, 4H, CH_2), 2.39 (s, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.37 (quat. *C*), 135.44 (quat. *C*), 129.18 (Ar*C*H), 128.01 (Ar*C*H), 71.90 (*C*H_2), 21.29 (*C*H_3).

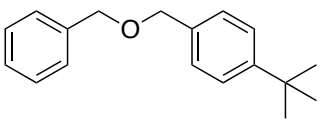


1-((Benzyloxy)methyl)-4-methylbenzene[2]: ^{1}H NMR ($CDCl_3$): δ 7.41-7.44 (m, 4H, ArC*H*), 7.34 (t, *J* = 8 Hz, 3H, ArC*H*), 7.22-7.25 (m, 2H, ArC*H*), 4.59-4.60 (m, 4H, CH_2), 2.42 (s, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.50 (quat-*C*), 137.40 (quat-*C*), 135.34 (quat-*C*), 129.18 (Ar*C*H), 128.48 (Ar*C*H), 128.00 (Ar*C*H), 127.87 (Ar*C*H), 127.67 (Ar*C*H), 72.08 (*C*H_2), 72.01 (*C*H_2), 21.28 (*C*H_3).

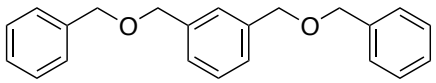


4,4'-Oxybis(methylene)bis(trifluromethyl)benzene[3]: ^{1}H NMR ($CDCl_3$): *δ* 7.67-7.65 (d, 2H, *J* = 8 Hz ArC*H*), 7.53-7.51 (d, 2H, *J* = 8 Hz ArC*H*), 4.67 (s. 4H. CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): *δ* 141.99 (Ar*C*H), 127.63 (Ar*C*H), 125.51 (Ar*C*H), 125.47 (Ar*C*H), 125.43 (Ar*C*H), 125.39 (Ar*C*H), 71.66 (*C*H_2).

1-((Benzyloxy)methyl)-4-(*tert*-butyl)benzene: ^{1}H NMR ($CDCl_3$): δ 7.37-7.46 (m, 9H, ArC*H*), 4.63 (s, 2H, CH_2), 4.60 (s, 2H, CH_2), 1.39 (s, 9H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 150.71 (quat. *C*), 138.54 (quat. *C*), 135.38 (quat. *C*), 128.49 (Ar*C*H), 127.88 (Ar*C*H), 127.77 (Ar*C*H), 127.68 (Ar*C*H), 125.44 (Ar*C*H), 72.17 (*C*H_2), 72.04 (*C*H_2), 34.64 (*C*H), 31.49 (*C*H_3).

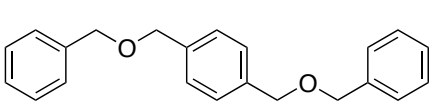


1,3-Bis((benzyloxy)methyl)benzene: ^{1}H NMR ($CDCl_3$): δ 7.36-7.43 (m, 14H, ArC*H*), 4.02 (s, 8H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$):

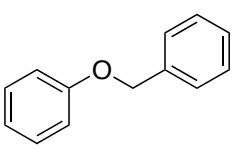


δ 138.49 (quat-*C*), 138.22 (quat-*C*), 128.61 (Ar*C*H), 128.49 (Ar*C*H), 127.91 (Ar*C*H), 127.75 (Ar*C*H), 127.26 (Ar*C*H), 127.20 (Ar*C*H), 72.26 (*C*H_2), 72.09 (*C*H_2).

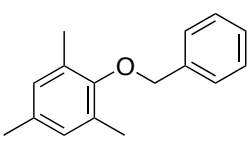
1,4-Bis((benzyloxy)methyl)benzene[4]**:** ^{1}H NMR ($CDCl_3$): δ 7.38 (s, 12H, ArC*H*), 7.30-7.37 (m, 2H, ArC*H*), 4.58 (d, *J* = 4 Hz, 8H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.39 (quat-*C*), 137.84 (quat-*C*), 128.54 (Ar*C*H), 128.03 (Ar*C*H), 127.92 (Ar*C*H), 127.77 (Ar*C*H), 72.20 (*C*H_2), 72.01 (*C*H_2).



(Benzyloxy)benzene[5]**:** ^{1}H NMR ($CDCl_3$): δ 7.45-7.47 (m, 2H, ArC*H*), 7.38-7.43 (m, 2H, ArC*H*), 7.29-7.34 (m, 3H, ArC*H*), 6.98-7.02 (m, 3H, ArC*H*), 5.09 (2, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 158.94 (quat-*C*), 137.23 (quat-*C*), 129.62 (Ar*C*H), 128.72 (Ar*C*H), 128.07 (Ar*C*H), 127.62 (Ar*C*H), 121.08 (Ar*C*H), 115.00 (Ar*C*H), 70.05 (*C*H_2).



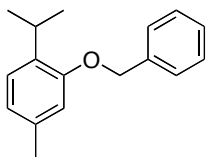
2-(Benzyloxy)-1,3-dimethylbenzene[6]**:** ^{1}H NMR ($CDCl_3$): δ 7.51-7.53 (d, *J* = 8 Hz, 2H, ArC*H*), 7.37-7.45 (m, 3H, ArC*H*), 6.97-7.07 (m, 3H, ArC*H*), 4.84 (s, 2H, CH_2), 2.34 (s, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.89 (quat. *C*), 135.87 (quat. *C*), 131.25 (Ar*C*H), 129.01 (Ar*C*H), 128.65 (Ar*C*H), 128.08 (quat. *C*), 127.90 (Ar*C*H), 124.12 (Ar*C*H), 74.05 (*C*H_2), 16.53 (*C*H_3).



2-(Benzyloxy)-1,3,5-trimethylbenzene[7]**:** ^{1}H NMR ($CDCl_3$): δ 7.51-7.52 (m, 2H, ArC*H*), 7.36-7.44 (m, 3H, ArC*H*), 4.81 (s, 2H, CH_2), 2.30 (s, 6H, CH_3), 2.28 (2, 3H, CH_3). ^{13}C{^{1}H} NMR

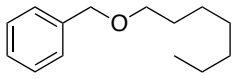
($CDCl_3$) δ 153.67 (quat. *C*), 137.97 (quat. *C*), 133.40 (quat. *C*), 130.84 (quat. *C*), 129.59 (Ar*C*H), 128.64 (Ar*C*H), 128.05 (Ar*C*H), 127.93 (Ar*C*H), 74.19 (*C*H_2), 20.83 (*C*H_3), 16.45 (*C*H_3).

2-(Benzyloxy)-1-isopropyl-4-methylbenzene[8]**:** ^{1}H NMR ($CDCl_3$): δ 7.38-7.52



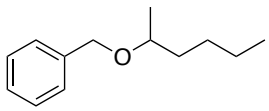
(m, 5H, ArC*H*), 7.18-7.21 (m, 1H, ArC*H*), 6.81-6.85 (m, 2H, ArC*H*), 5.13 (s, 2H, CH_2), 3.43-3.48 (m, 1H, C*H*), 2.39 (s, 3H, CH_3), 1.29-1.31 (m, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.97 (quat. *C*), 137.80 (quat. *C*), 136.45 (quat. *C*), 134.50, (quat. *C*) 128.63 (Ar*C*H), 127.80 (Ar*C*H), 127.24 (Ar*C*H), 126.09 (Ar*C*H), 121.58 (Ar*C*H), 112.81 (Ar*C*H), 70.06 (*C*H_2), 26.74 (*C*H), 22.96 (*C*H_3), 21.50 (*C*H_3).

((Heptyloxy)methyl)benzene[9]**:** ^{1}H NMR ($CDCl_3$): δ 7.35-7.36 (m, 4H, ArC*H*),



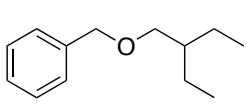
7.29-7.31 (m, 1H,ArC*H*), 4.52 (s, 2H, CH_2), 3.47-3,50 (t, *J* = 8 Hz, 2H, CH_2), 1.60-1.65 (q, *J* = 8 Hz, *J* = 4 Hz, 2H CH_2), 1.28-1.39 (m, 8H, CH_2), 0.88-0.92 (t, *J* = 8 Hz, 3H, CH_3) ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.88 (quat. *C*), 128.46 (Ar*C*H), 127.74 (Ar*C*H), 127.58 (Ar*C*H), 72.99 (*C*H_2), 70.67 (*C*H_2), 31.97 (*C*H_2), 29.93 (*C*H_2), 29.30 (*C*H_2), 26.30 (*C*H_2), 22.76 (*C*H_2), 14.22 (*C*H_3).

((Hexan-2-yloxy)methyl)benzene[10]**:** ^{1}H NMR ($CDCl_3$): δ 7.33-7.38 (m, 4H, ArC*H*),



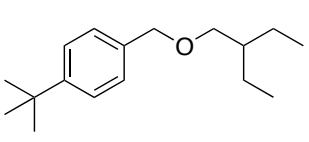
7.26-7.30 (m, 1H, ArC*H*), 4.47-4.60 (q, *J* = 28 Hz, 8 Hz, 2H, OCH_2), 3.50-3.55 (m, 1H, C*H*), 1.60-1.66 (m, 1H, C*H*), 1.28-1.49 (m ,5H, C*H*), 1.21 (d, 3H, *J* = 8 Hz, CH_3), 0.92 (t, 3H, *J* = 8 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 139.31 (quat. *C*), 128.38 (Ar*C*H), 127.70 (Ar*C*H), 127.42 (Ar*C*H), 75.04 (O*C*H_2), 70.38 (O*C*H_2), 36.49 (*C*H_2), 27.86 (*C*H_2), 22.90 (*C*H_3), 19.74 (*C*H_2), 14.19 (*C*H_3).

((2-Ethylbutoxy)methyl)benzene: ^{1}H NMR ($CDCl_3$): δ 7.28-2.37 (m, 5H, ArC*H*),



4.52 (s, 2H, OCH_2), 3.38-3.39 (d, *J* = 4 Hz, 2H, OCH_2), 1.35-1.52 (m, 5H, CH_2 & C*H*), 0.89-0.92 (s, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 139.06 (quat. *C*), 128.42 (Ar*C*H), 127.63 (Ar*C*H), 127.50 (Ar*C*H), 73.16 (O*C*H_2), 72.99 (O*C*H_2), 41.43 (*C*H_2), 23.55 (*C*H_2), 11.25 (*C*H_3).

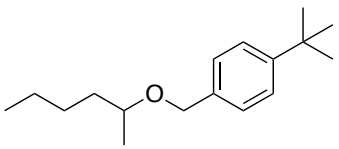
1-(*tert*-Butyl)-4-((2-ethylbutoxy)methyl)benzene: ^{1}H NMR ($CDCl_3$): δ 7.39-7.41



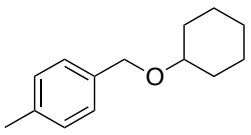
(m, 2H, ArC*H*), 7.30-7.36 (m, 2H, ArC*H*), 4.51 (s, 2H,

OCH_2), 3.39-3.41 (d, J = 8 Hz, 2H, OCH_2), 1.36 (s, 14H, CH, CH_2 & CH_3), 0.90-0.93 (t, J = 8 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 150.43 (quat. *C*), 136.03 (quat. *C*), 127.46 (Ar*C*H), 125.33 (Ar*C*H), 73.04 (O*C*H$_2$), 72.01 (O*C*H$_2$), 41.41 (*C*H$_2$), 34.63 (*C*H), 31.51 (*C*H$_3$), 23.55 (*C*H$_2$), 11.26 (*C*H$_3$).

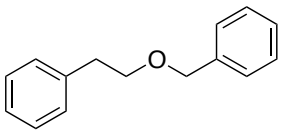
1-(*tert*-Butyl)-4-((hexan-2-yloxy)methyl)benzene: ^{1}H NMR ($CDCl_3$): δ 7.37 (d, 2H, J = 12 Hz, ArCH), 7.29 (d, J = 12 Hz, 2H, ArCH), 4.43-4.56 (q, J = 12 Hz, 8 Hz, 2H, OCH_2), 3.49-3.54 (m, 1H, CH), 1.60-1.64 (m, 1H, CH), 1.39-1.48 (m, 2H, CH_2) , 1.33 (s, 12H, CH_3), 1.20 (d, J = 8 Hz, 3H, CH_3), 0.91 (t, J = 8 Hz, 3H, CH_3).



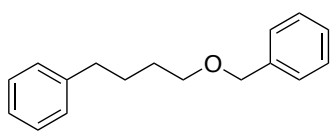
1-((Cyclohexyloxy)methyl)-4-methylbenzene[11]**:** ^{1}H NMR ($CDCl_3$): δ 7.20-7.31 (m, 2H, ArCH), 7.15-7.17 (m, 2H, ArCH), 4.53 (s, 2H, OCH_2), 3.34-3.39 (m, 1H, CH), 2.36 (s, 3H, CH_3), 1.95-1.98 (m, 2H, CH_2), 1.76-1.80 (m, 2H, CH_2), 1.55-1.65 (m, 2H, CH_2), 1.24-1.39 (m, 4H, CH_2).



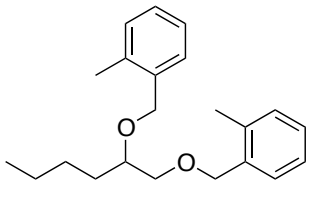
(**2-(Benzyloxy)ethyl)benzene**[12]**:** ^{1}H NMR ($CDCl_3$): δ 7.29-7.41 (m, 7H, ArCH), 7.23- 7.27 (m, 3H, ArCH), 4.57 (s, 2H, CH_2), 3.72-3.75 (m, 2H, CH_2), 2.96-2.99 (m, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 139.09 (quat-*C*), 138.53 (quat-*C*), 129.06 (Ar*C*H), 128.48 (Ar*C*H), 128.46 (Ar*C*H), 127.73 (Ar*C*H), 127.65 (Ar*C*H), 126.31 (Ar*C*H), 73.08 (*C*H$_2$), 71.38 (*C*H$_2$), 36.51 (*C*H$_2$).



(4-(Benzyloxy)butyl)benzene[13]**:** ^{1}H NMR ($CDCl_3$): δ 7.36-7.37 (m, 4H, ArCH), 7.28-7.32 (m, 3H, ArCH), 7.19-7.21 (m, 3H, ArCH), 4.52 (s, 2H, CH_2),3.50- 3.53 (m, 2H, CH_2), 2.66 (t, 2H, J = 8 Hz, CH_2), 1.68-1.77 (m, 4H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 142.57 (quat. *C*), 138.74 (quat. *C*), 128.55 (Ar*C*H), 128.47 (Ar*C*H), 128.38 (Ar*C*H), 127.75 (Ar*C*H), 127.61 (Ar*C*H), 125.80 (Ar*C*H), 73.02 (O*C*H$_2$), 70.33 (O*C*H$_2$), 35.84 (*C*H$_2$), 29.53 (*C*H$_2$), 28.19 (*C*H$_2$).

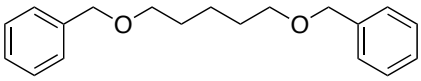


1,2-Bis((2-methylbenzyl)oxy)hexane: ^{1}H NMR ($CDCl_3$): δ 7.34-7.36 (m, 2H, ArCH), 7.17-7.22 (m, 6H, ArCH), 4.51-4.53 (s, 4H, OCH_2), 3.52-3.62 (m, 3H, CH & CH_2), 2.34 (s, 6H, CH_3), 1.28-1.46 (m, 6H, CH_2), 0.87- 0.92 (m, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 136.89 (quat. *C*), 136.67 (quat. *C*), 136.59 (quat. *C*), 136.40



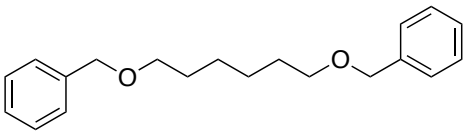
(quat. *C*), 130.39 (Ar*C*H), 130.23 (Ar*C*H), 130.19 (Ar*C*H), 128.82 (Ar*C*H), 128.49 (Ar*C*H), 127.77 (Ar*C*H), 127.70 (Ar*C*H), 125.79 (Ar*C*H), 78.29 (O*C*H_2), 74.82 (O*C*H_2), 73.20 (O*C*H), 71.84 (O*C*H_2), 70.36 (*C*H_2), 31.81 (*C*H_2), 27.69 (*C*H_2), 22.87 (*C*H_3), 18.86 (*C*H_3), 14.14 (*C*H_3).

1,5-Bis(benzyloxy)pentane[14]**:** ^{1}H NMR ($CDCl_3$): δ 7.30-7.37 (m, 10H, ArC*H*), 4.53



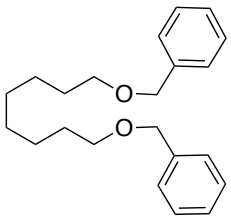
(s, 4H, OC*H*$_2$), 3.51-3.52 (m, 4H, OC*H*$_2$), 1.50-1.70 (m, 6H, C*H*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.77 (quat. *C*), 128.45 (Ar*C*H), 127.71 (Ar*C*H), 127.58 (Ar*C*H), 72.98 (O*C*H_2), 70.43 (O*C*H_2), 29.69 (*C*H_2), 22.97 (*C*H_2).

1,6-Bis(benzyloxy)hexane[15]**:** ^{1}H NMR ($CDCl_3$): δ 7.30-7.37 (m, 10H, ArC*H*), 4.53



(s, 4H, C*H*$_2$), 3.48-3.50 (t, *J* = 8 Hz, 4H, C*H*$_2$), 1.66-1.67 (m, 4H, C*H*$_2$), 1.42-1.44 (m, 4H, C*H*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.79 (quat. *C*), 128.45 (Ar*C*H), 127.72 (Ar*C*H), 127.57 (Ar*C*H), 72.96 (*C*H_2), 70.49 (*C*H_2), 29.83 (*C*H_2), 26.17 (*C*H_2).

1,8-Bis(benzyloxy)octane[16]**:** ^{1}H NMR ($CDCl_3$): δ 7.30-7.37 (m, 10H, ArC*H*), 4.53 (s,



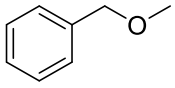
4H, C*H*$_2$), 3.47-3.51 (t, *J* = 8 Hz, 4H, C*H*$_2$), 1.63-1.66 (t, *J* = 8 Hz, 4H, C*H*$_2$), 1.35-1.39 (t, *J* = 8 Hz, 8H, C*H*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.83 (quat. *C*), 128.44 (Ar*C*H), 127.72 (Ar*C*H), 127.56 (Ar*C*H), 72.97 (*C*H_2), 70.60 (*C*H_2), 29.87 (*C*H_2), 29.52 (*C*H_2), 26.25 (*C*H_2).

3. Standard procedure for the synthesis of methyl ether derivatives

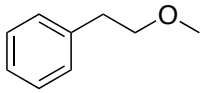
In an oven dried 100 mL RB flask, alcohol (10 mmol) was dissolved in 6 mL of THF under nitrogen atmosphere. This solution was transferred via cannula to another flask containing THF (5 mL) solution of sodium hydride (20 mmol, 55% in mineral oil, pre-washed with dry hexane) under ice-cold condition and the solution was stirred for 30 minutes. To this solution, methyliodide (11 mmol, 2M in hexane solution) was slowly added under ice-cold condition and then the reaction mixture was warm to room temperature and stirred. Progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was poured into ice-cold water and extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulphate and evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography.

3.1 Spectral Data of Methyl Ether Derivatives

(Methoxymethyl)benzene[17]: ^{1}H NMR ($CDCl_3$): δ 7.42-7.40 (m, 5H, ArC*H*), 4.52 (s. 2H. CH_2), 3.45 (s. 3H. CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.24 (Ar*C*H), 128.45 (Ar*C*H), 127.79 (Ar*C*H), 127.71 (Ar*C*H), 74.75 (*C*H$_2$), 58.13 (*C*H$_3$).

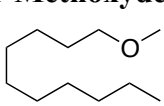


(2-Methoxyethyl)benzene[18]**:** ^{1}H NMR ($CDCl_3$): δ 7.24-7.26 (m, 2H, ArC*H*), 7.21-7.23 (m, 3H, ArC*H*), 3.61-3.64 (t, *J* = 8 Hz, 2H, OCH_2), 3.37 (s, 3H, OCH_3), 2.89-2.92 (t, *J* = 8 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.91 (quat. *C*), 128.96 (Ar*C*H), 128.57 (Ar*C*H), 126.63 (Ar*C*H), 64.99 (*C*H$_3$), 35.16 (*C*H$_2$), 21.02 (*C*H$_2$).



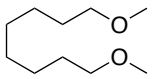
(4-Methoxybutyl)benzene[19]**:** ^{1}H NMR ($CDCl_3$): δ 7.27-7.31 (m, 2H, ArC*H*), 7.19-7.21 (m, 3H, ArC*H*), 3.39-3.42 (t, *J* = 8 Hz, 2H, OCH_2), 3.34 (s, 3H, OCH_3), 2.64-2.67 (t, *J* = 8 Hz, 2H, CH_2), 1.61-1.73 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.57 (quat. *C*), 128.54 (Ar*C*H), 128.39 (Ar*C*H), 125.82 (Ar*C*H), 72.81 (O*C*H$_3$), 58.69 (O*C*H$_2$), 35.86 (*C*H$_2$), 29.42 (*C*H$_2$), 28.12 (*C*H$_2$).

1-Methoxydecane[20]**:** ^{1}H NMR ($CDCl_3$): δ 3.34-3.37 (t, *J* = 8 Hz, 2H, OCH_2), 3.32 (s, 3H, OCH_3), 1.54-1.58 (m, 2H, CH_2), 1.26 (s, 14H, CH_2), 0.86-0.89



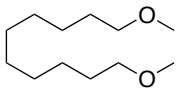
(t, J = 8 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 73.14 (OCH_3), 58.66 (OCH_2), 32.05 (CH_2), 29.80 (CH_2), 29.75 (CH_2), 29.71 (CH_2), 29.66 (CH_2), 29.47 (CH_2), 26.29 (CH_2), 22.82 (CH_2), 14.25 (CH_3).

1,8-Dimethoxyoctane[21]**:** ^1H NMR ($CDCl_3$): δ 3.33-3.36 (t, J = 8 Hz, 2H, OCH_2), 3.31



(s, 3H, OCH_3), 1.53-1.56 (m, 2H, CH_2), 1.30 (s, 12H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 73.07 (OCH_3), 58.65 (OCH_2), 29.74 (CH_2), 29.55 (CH_2), 26.20 (CH_2).

1,10-Dimethoxydecane[21]**:** ^1H NMR ($CDCl_3$): δ 3.33-3.36 (t, J = 8 Hz, 2H, OCH_2),



3.31 (s, 3H, OCH_3), 1.53-1.55 (m, 4H, CH_2), 1.27 (CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 73.09 (OCH_3), 58.64 (OCH_2), 29.76 (CH_2), 29.64 (CH_2), 29.60 (CH_2), 26.25 (CH_2).

4. Standard procedure and reaction optimization for the hydroboronolysis of dibenzyl ether

To an oven dried Schlenk tube containing a small stirrer bar, dibenzyl ether (1 mmol, 190.46 μL), pinacolborane (2 mmol, 290.20 μL), [Ru(*p*-cymene)Cl]$_2$Cl$_2$ (2 mol%, 12.24 mg) were charged inside the glove box. The reaction mixture was taken out from the glove box and immersed into the pre-heated oil bath of 135 °C. Progress of the reaction was monitored by ^{1}H NMR. The alkyl boronate ester products are highly moisture sensitive. All experimental procedures were carried out and NMR samples (in dry $CDCl_3$) were prepared under the nitrogen atmosphere glove box. The optimization table is shown in the manuscript which corresponds to table 1.

5. Standard procedure for the hydroboronolysis of ethers

Ether (1 mmol), pinacolborane (2 mmol), [Ru(*p*-cymene)Cl]$_2$Cl$_2$ (2.0 mol%) were charged in a 15 mL seal tube with a stirrer bar inside the glove box. The reaction mixture was taken out from the glove box and immersed into the pre-heated oil bath of 135 °C. Progress of the reaction was monitored either by GC or ^{1}H NMR using anisole or mesitylene as an internal standard. The alkyl boronate ester products are highly moisture sensitive. All experimental procedures were carried out and NMR samples (in dry CDCl3) were prepared under the nitrogen atmosphere glove box.

6. Standard procedure for catalytic hydroboronolysis of methyl ether Derivatives

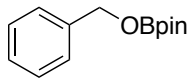
Methyl ether (1 mmol), pinacolborane (2 mmol), [Ru(*p*-cymene)Cl]$_2$Cl$_2$ (5.0 mol%) were charged in a 15 mL seal tube containing a stirrer bar inside glove box. Then the seal tube was taken out from the glove box and immersed into the pre-heated oil bath of 135 °C. Progress of the reaction was monitored by ^{1}H NMR analyses. These products are highly moisture sensitive. All experimental procedures were carried out and NMR samples (in dry $CDCl_3$) were prepared inside the nitrogen atmosphere glove box.

7. Isolation of representative ether boronolysis products

After reaction completion, reaction mixture was extracted with dry hexane (10 mL x 3) and the extracted solution was filtered through syringe filter (0.45 mm). The filtrate was dried under vacuum to get the pure boronate ester products for further analysis.

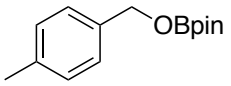
7.1 Spectral Data of Isolated Boronate Esters

2-(Benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[22]: ^{1}H NMR ($CDCl_3$): δ



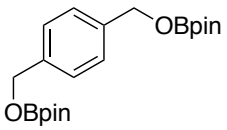
7.29-7.37 (m, 5H, ArC*H*), 4.96 (s, 2H, CH_2), 1.29 (s, 12H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 139.30 (quat. *C*), 128.37 (Ar*C*H), 127.45 (Ar*C*H), 126.80 (Ar*C*H), 83.06 (quat. *C*), 66.75 (*C*H_2), 21.29 (*C*H_3). ^{11}B NMR (tol-d8): 28.43 (O*B*).

4,4,5,5-Tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-



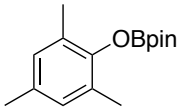
dioxaborolane[23]: ^{1}H NMR ($CDCl_3$): δ 7.26-7.28 (d, *J* = 8 Hz, 2H, ArC*H*), 7.16-7.18 (d, *J* = 8 Hz, 2H, ArC*H*), 4.92 (s, 2H, CH_2), 2.36 (s, 3H, CH_3), 1.29 (s, 12H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.12 (quat. *C*), 136.34 (quat. *C*), 129.07 (Ar*C*H), 126.95 (Ar*C*H), 83.02 (quat. *C*), 66.69 (*C*H_2), 24.74 (OBpin*C*H_3), 21.26 (*C*H_3).

1,4-Bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzene: ^{1}H NMR



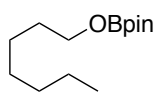
($CDCl_3$): δ 7.32 (s, 4H, ArC*H*), 4.92 (s, 4H, CH_2), 1.26 (s, 24H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.41 (quat. *C*), 126.73 (Ar*C*H), 82.98 (quat. *C*), 66.49 (OBpin*C*H_2), 24.65 (*C*H_3).

2-(Mesityloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[24]:



^{1}H NMR ($CDCl_3$): δ 6.81-6.83 (m, 2H, ArC*H*), 2.24 (s, 3H, CH_3), 2.20 (s, 6H, CH_3), 1.30 (s, 12H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.40 (quat. *C*), 132.61 (quat. *C*), 129.18 (Ar*C*H), 129.12 (quat. *C*), 128.04 (quat. *C*), 83.56 (quat. *C*), 24.99 (*C*H_3), 24.58 (OBpin*C*H_3), 20.78 (*C*H_3), 16.51 (*C*H_3).

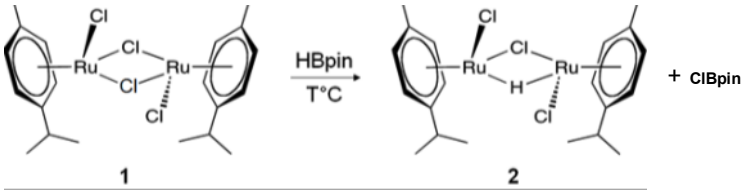
2-(Heptyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[25]: ^{1}H NMR



($CDCl_3$): δ

3.80-3.84 (t, J = 8 Hz, 2H, OBpinCH_2), 1.53-1.55 (d, J = 8 Hz, 2H, CH_2), 1.24-1.26 (overlapped-s, 18H, CH_2 & OBpinCH_3), 0.86 (bs, 5H, CH_2 & CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 83.24 (quat. *C*), 82.72 (quat. *C*), 65.13 (OBpin*C*H_2), 31.97 (*C*H_2), 31.60 (*C*H_2), 29.13 (*C*H_2), 25.69 (*C*H_2), 24.73 (*C*H_2), 22.75 (*C*H_2), 14.24 (*C*H_3).

8. Stoichiometric reaction of 1 with pinacolborane



1 (6.12 mg, 0.01 mmol), HBpin (3.19 µL, 0.022 mmol) and Tol-d8 (0.5 mL as a solvent) were charged in a Teflon tapped NMR tube under argon atmosphere. The NMR tube was heated at indicated temperature in Fig. S1. ^{1}H NMR of the reaction mixture of **1** and HBpin were measured at different time intervals, which confirmed the formation of Ru-hydride intermediate **2**.[26]

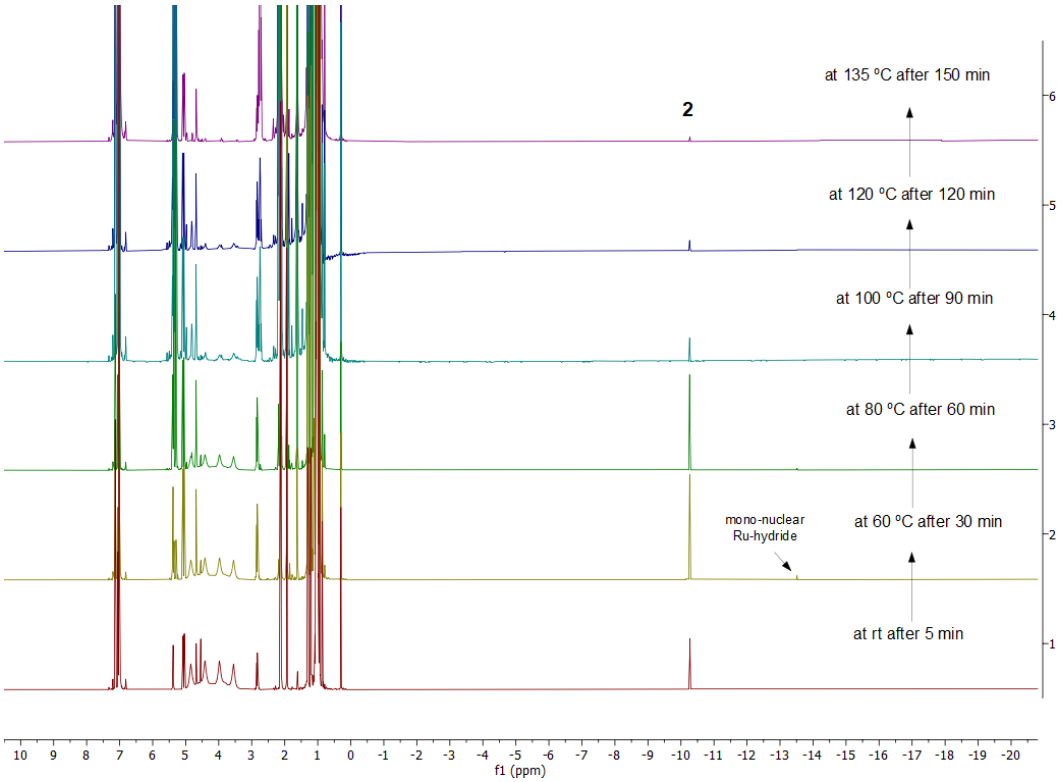


Figure S1: Superposed ^{1}H NMR (tol-d_8, 298 K) spectrum of Ru-hydride intermediate **2** at different temperatures and time intervals

9. Stoichiometric reaction of 1 with pinacolborane at 135 °C

1 (6.12 mg, 0.01 mmol), HBpin (3.19 µL, 0.022 mmol) and Tol-d8 (0.5 mL as a solvent) were charged in a Teflon tapped NMR tube under argon atmosphere. The NMR tube was heated at 135 °C in Fig. S2. ^{1}H NMR of the reaction mixture of **1** and HBpin were measured at different time intervals, which confirmed the formation of Ru-hydride intermediate **2**.

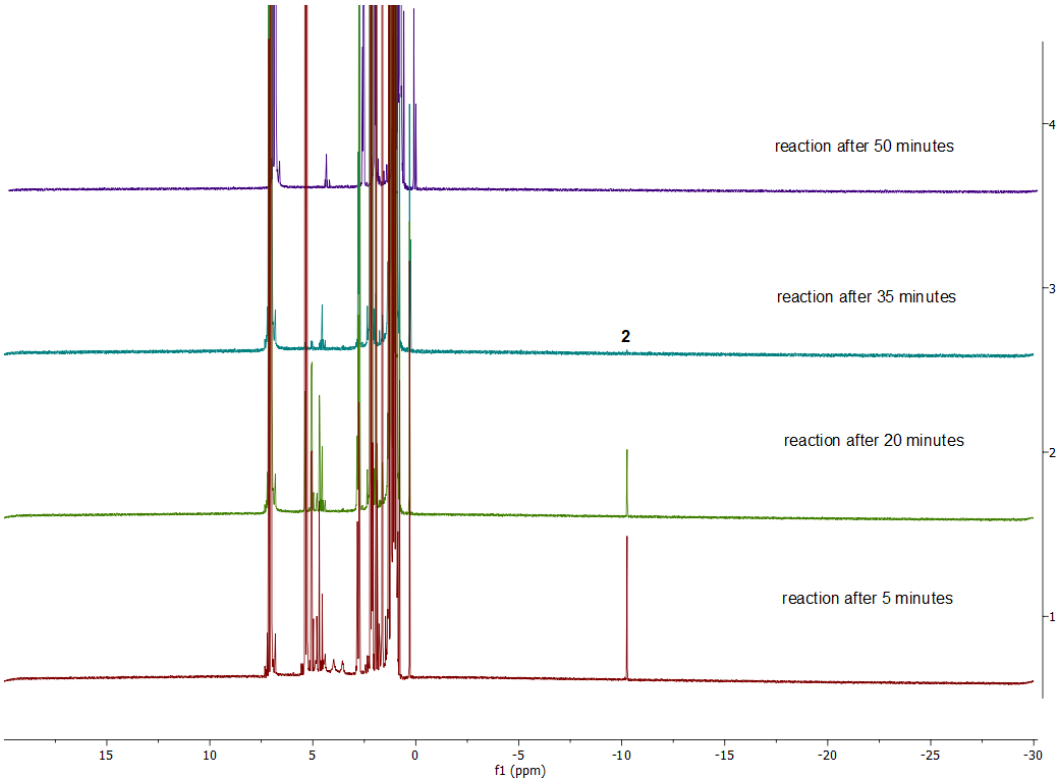
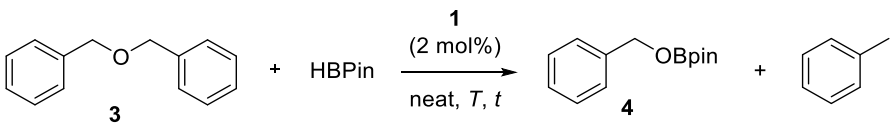


Figure S2: Superposed ^{1}H NMR (tol-d_8, 298 K) spectrum of Ru-hydride intermediate **2** at time intervals and 135 °C.

10. Reaction of dibenzyl ether with pinacolborane in the presence of 1 (time and temperature profile)



Dibenzyl ether (47.5 µL, 0.25 mmol), HBpin (76.2 µL, 0.53 mmol) and Tol-d8 (0.5 mL as a solvent) were charged in a Teflon tapped NMR tube under argon atmosphere. The NMR tube was heated at certain temperature. ^{1}H NMR of the reaction mixture were measured at different time intervals.

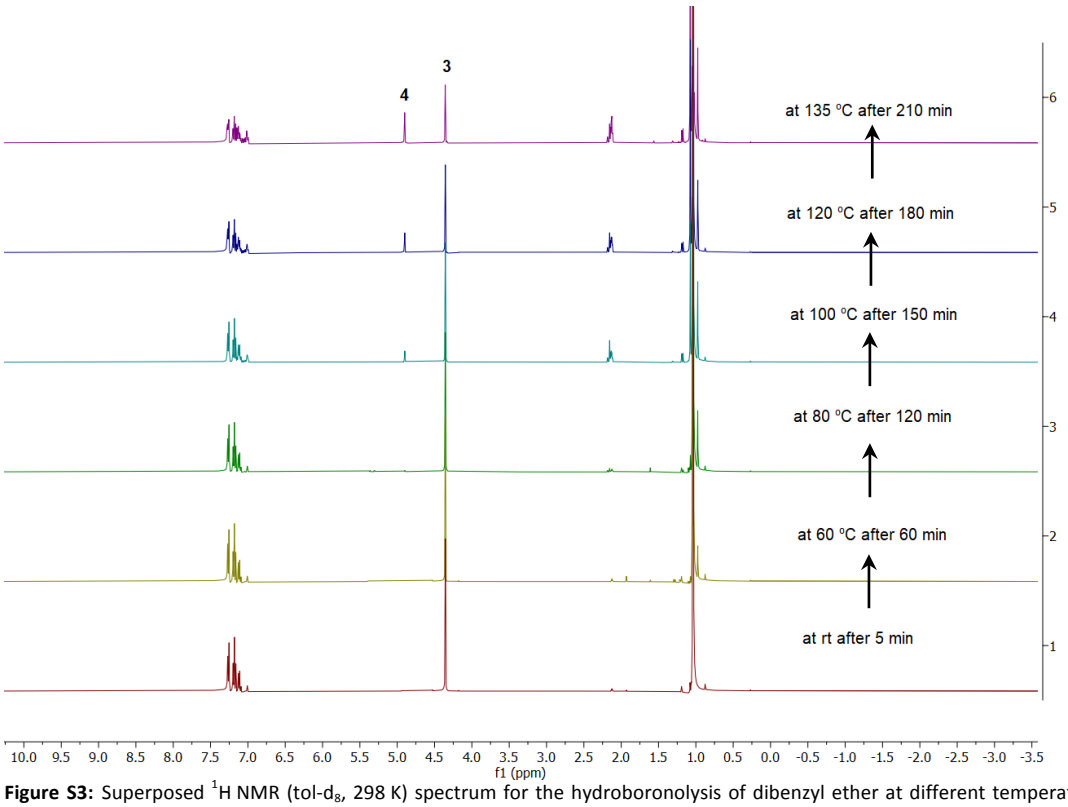


Figure S3: Superposed ^{1}H NMR (tol-d_8, 298 K) spectrum for the hydroboronolysis of dibenzyl ether at different temperatures and time intervals

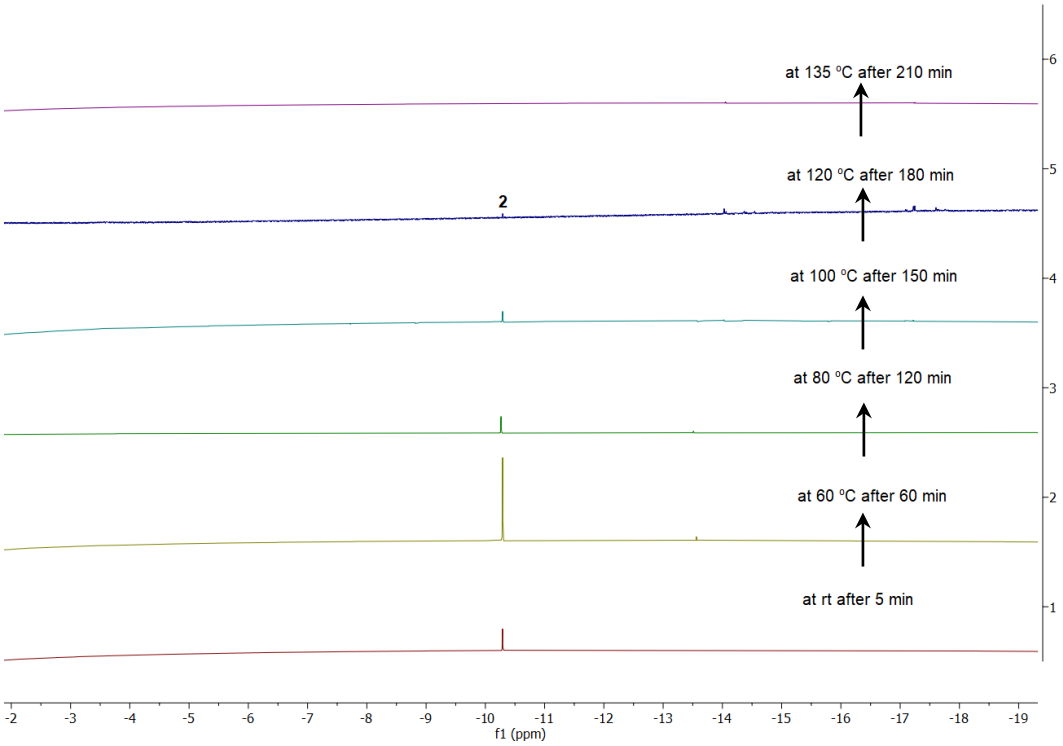
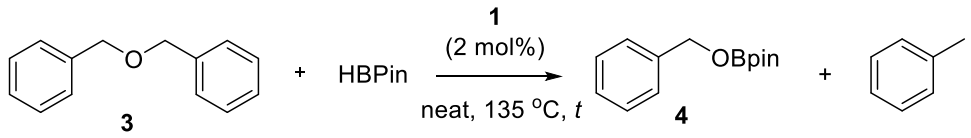


Figure S4: Superposed ^{1}H NMR (tol-d_8, 298 K) spectrum of Ru-hydride intermediate **2** for the above-mentioned reaction at different temperatures and time intervals.

11. Reaction of dibenzyl ether with pinacolborane in the presence of 1 at 135 °C (time and temperature profile)



Dibenzyl ether (47.5 µL, 0.25 mmol), HBpin (76.2 µL, 0.53 mmol) and Tol-d8 (0.5 mL as a solvent) were charged in a Teflon tapped NMR tube under argon atmosphere. The NMR tube was heated at 135 °C. ^{1}H NMR of the reaction mixture were measured at different time intervals.

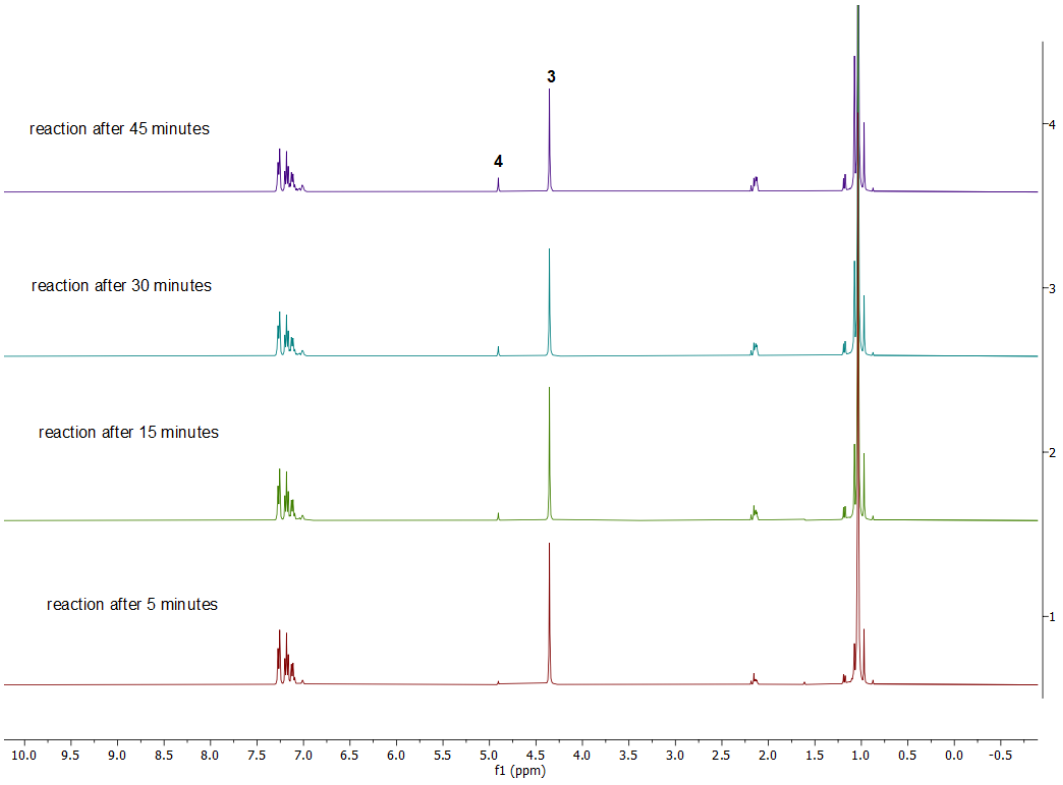


Figure S5: Superposed ^{1}H NMR (tol-d_8, 298 K) spectrum for the hydroboronolysis of dibenzyl ether at time intervals and 135 °C.

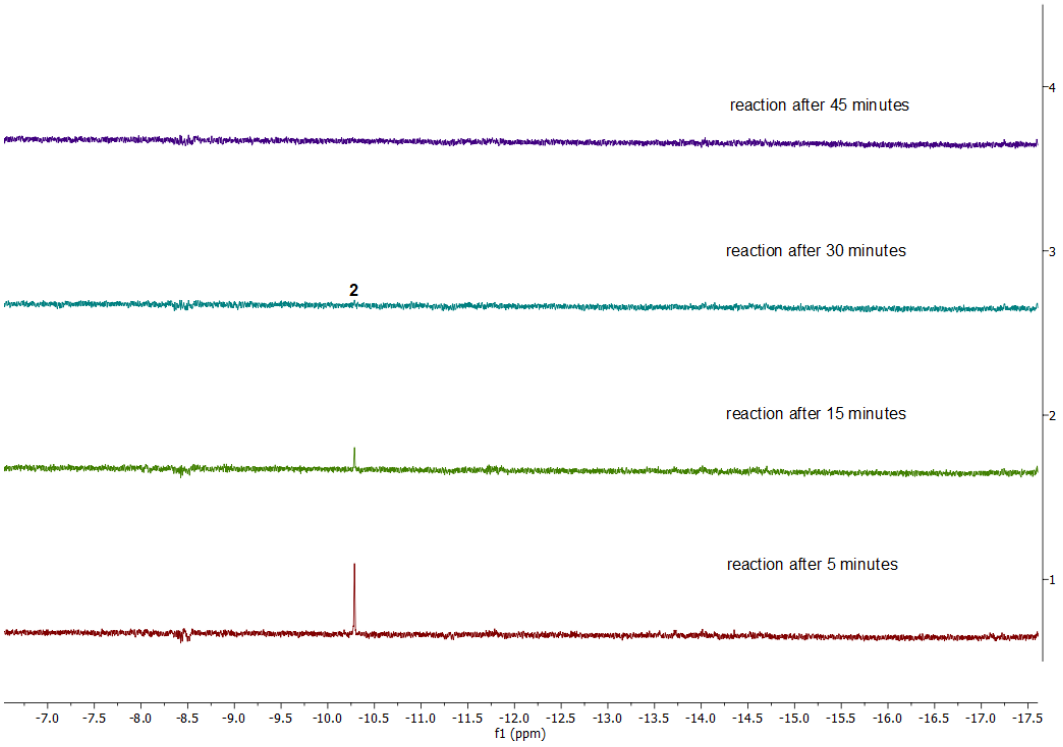


Figure S6: Superposed ^{1}H NMR (tol-d_8, 298 K) spectrum of Ru-hydride intermediate **2** for the above-mentioned reaction at 135 ^{o}C and time intervals.

12. Standard Procedure for poisoning experiments with DCT

To an oven dried Schlenk tube containing a small stirrer bar, dibenzyl ether (1 mmol, 190.46 µL), pinacolborane (2 mmol, 290.20 µL), [Ru(*p*-cymene)Cl]$_2$Cl$_2$ (0.02 mmol, 12.24 mg), DCT (dibenzo[a,e]cyclooctene, 8.17 mg, 2.0 equiv, w.r.t. catalyst) were charged under argon atmosphere in the glove box. The reaction mixture was taken out from the glove box and immersed into the pre-heated oil bath of 135 °C. The reaction was repeated at 15 min, 30 min, 1 h, 2 h, 6 h, 8 h and 18 h of time intervals. After completion of the reaction it was monitored by ^{1}H NMR analysis.

13. Standard Procedure for poisoning experiments with mercury

To an oven dried Schlenk tube containing a small stirrer bar, dibenzyl ether (1 mmol, 190.46 µl), pinacolborane (2 mmol, 290.20 µl), [Ru(*p*-cymene)Cl]$_2$Cl$_2$ (0.02 mmol, 12.24 mg), were charged under argon atmosphere in the glove box. The reaction mixture was taken out from the glove box and immersed into the pre-heated oil bath of 135 °C. After completion of reaction, it was cooled down. The formed black color precipitate of Ru(0) was again charged with fresh substrate i.e Dibenzyl ether (1 mmol, 190.46 µl), pinacolborane (2 mmol, 290.20 µl), Hg (100.29 mg, 0.5 mmol) was added to this evolved catalytic system in

the glove box and immersed into the pre-heated oil bath of 135 °C for 24 h. After completion of the reaction, it was monitored by ^{1}H NMR analysis.

14. Standard Procedure for poisoning experiments with 1,10-phenanthroline

To an oven dried Schlenk tube containing a small stirrer bar, dibenzyl ether (1 mmol, 190.46 µL), pinacolborane (2 mmol, 290.20 µL), [Ru(*p*-cymene)Cl]$_2$Cl$_2$ (0.02 mmol, 12.24 mg), were charged under argon atmosphere in the glove box. The reaction mixture was taken out from the glove box and immersed into the pre-heated oil bath of 135 °C. After completion of reaction, it was cooled down. The formed black color precipitate of Ru(0) was again charged with fresh substrate i.e dibenzyl ether (1 mmol, 190.46 µL), pinacolborane (2 mmol, 290.20 µL) and different concentration of poison 1,10-phenanthroline (0.0 equiv. |(no poison added), 0.50 equiv. (1.80 mg), 1.0 equiv. (3.60 mg), 2.0 (7.20 mg), 5.0 (18.20 mg) was added to this evolved catalytic system. The reaction mixture was taken out from the glove box and immersed into the pre-heated oil bath of 135 °C for 4 h. After completion of the reaction, it was monitored by ^{1}H NMR analysis.

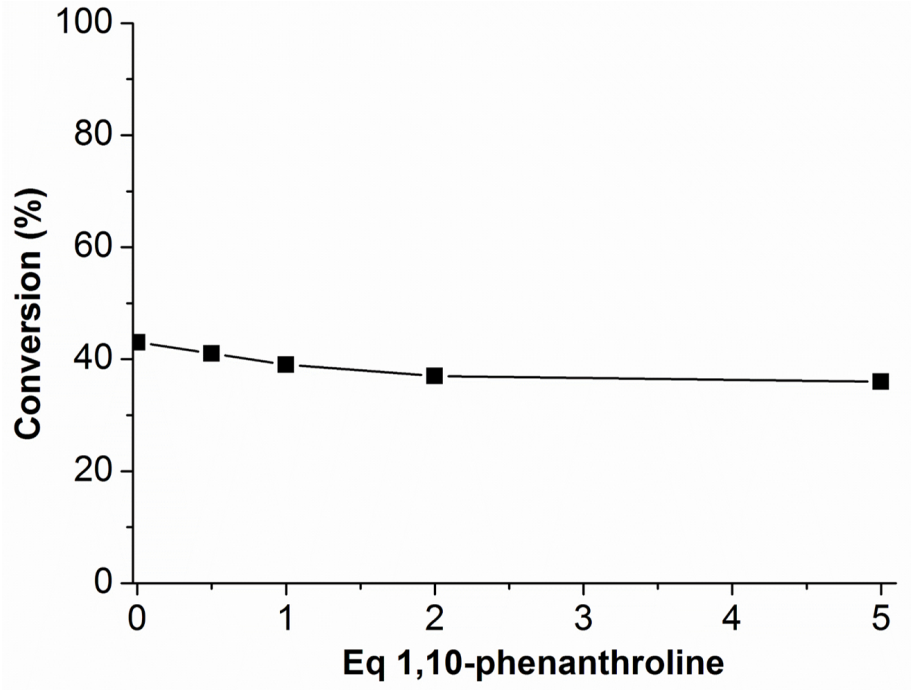
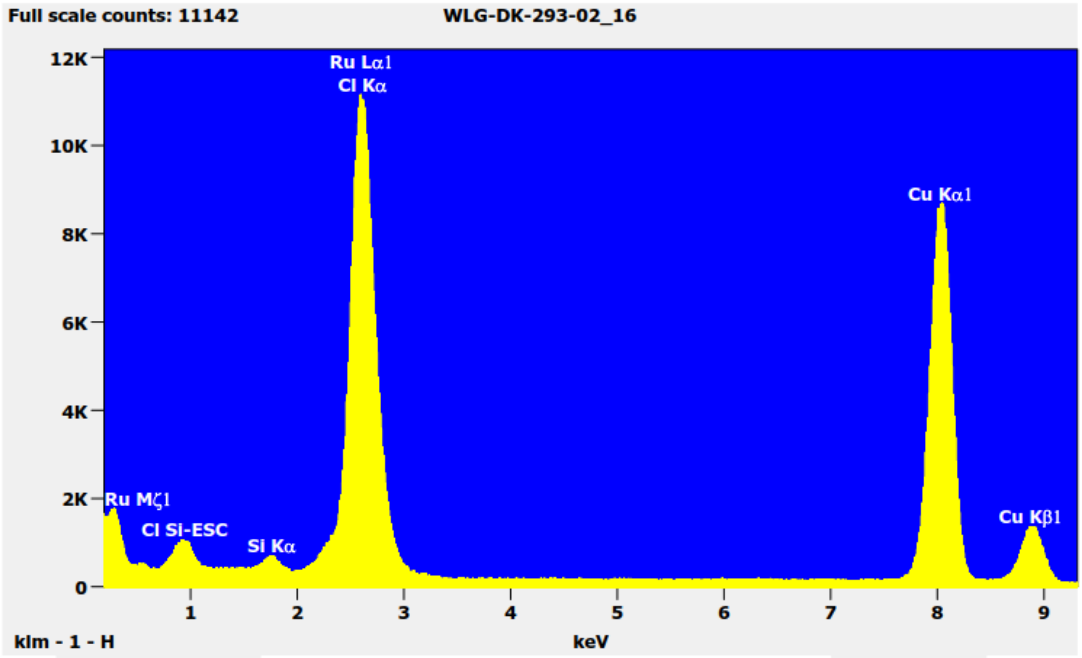


Figure S7: Catalytic hydroboronolysis of dibenzylether using recovered catalyst in the presence of different equivalents of 1,10-phenanthroline. (2 mol% "evolved" catalyst, 135 °C, neat, 4 h).



Quantitative Results for: WLG-DK-293-02_16

Element Line	Net Counts	Weight %	Weight % Error	Atom %
Si K	6387	1.3	± 0.1	3.7
Cl K	53423	10.6	± 0.6	24.5
Ru L	247372	88.2	± 1.7	71.7
Total		100.0		100.0

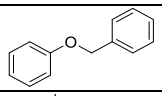
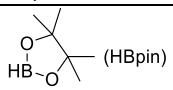
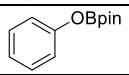
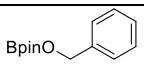
Figure S8: Characterization of the material obtained after catalysis by EDX analysis, confirming the formation of Ru NPs.

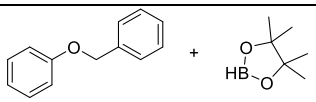
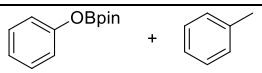
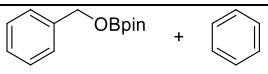
15. Computation study for the hydroboronolysis of (benzyloxy)benzene

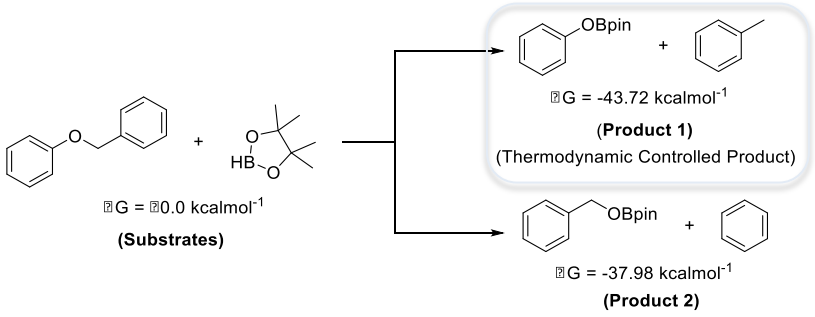
The stability of the all molecules was calculated with DFT methods using the program Gaussian[27] together with the PBE0 functional[28] and dispersion correction with Becke-Johnson damping by Grimme[29-30] and the def2-TZVP basis set[31]. The energies tabulated refer to the gas phase. Frequency calculations confirmed that all structures correspond to local minima.

15.1 Investigation of the product formation for the hydroboronolysis of (benzyloxy)benzene

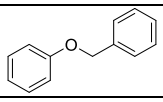
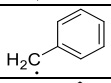
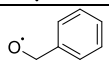
Table S1: Comparison of the relative stability of the substrate and product molecules.

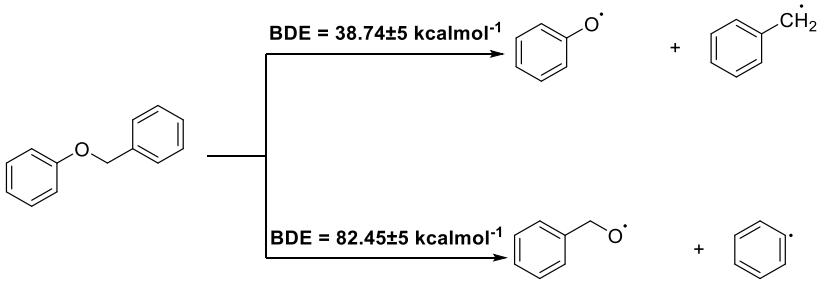
Compound	Electronic energy [Hartree]	Gibbs free energy [Hartree]
	-577.3725742	-577.1962012
	-411.5549372	-411.3973382
	-717.6560086	-717.4212946
	-271.3392651	-271.2419121
	-756.9337908	-756.6728158
	-232.0544958	-231.9812428

	ΔG relative to Substrates [kcalmol^{-1}]
	±0.0
	-43.72
	-37.98



15.2 Calculation of Bond dissociation energy for (benzyloxy)benzene

Compound	Electronic energy [Hartree]	Gibbs free energy [Hartree]
	-577.3725742	-577.1962012
	-306.5920548	-306.5298388
	-270.6897828	-270.6046218
	-345.8402719	-345.7552919
	-231.3691663	-231.3095103



15.3 Cartesian coordinates of computed compounds

(benzyloxy)benzene

C	3.48566100	-1.35697100	0.13995100
C	3.67375200	-0.24372400	-0.67044700
C	2.71269400	0.74683100	-0.73665800
C	1.54380800	0.63547500	0.01235800
C	1.34321200	-0.47726100	0.82141100
C	2.32014400	-1.46339300	0.87849700
H	4.23973900	-2.13287200	0.19016000
H	4.58053900	-0.14461700	-1.25629400
H	2.84655200	1.62288000	-1.35994400
H	0.42971500	-0.59761500	1.38748500
H	2.15461900	-2.32953100	1.50918600
O	0.66507700	1.66276200	-0.11406400
C	-0.50157600	1.64788100	0.67451500
H	-0.24994500	1.47462900	1.72792100
H	-0.89762800	2.66400800	0.59751700
C	-1.54431200	0.66179400	0.22003900
C	-1.58716800	0.21802800	-1.09527700
C	-2.50294300	0.20995800	1.11943400
C	-2.57580400	-0.66393600	-1.50388600
H	-0.83368500	0.55905800	-1.79523800
C	-3.49663600	-0.66560800	0.71023800
H	-2.46891500	0.54292100	2.15257000
C	-3.53456100	-1.10629000	-0.60450900
H	-2.59580200	-1.00929600	-2.53122600
H	-4.23772100	-1.01147100	1.42175500
H	-4.30570300	-1.79689200	-0.92538000

pinacolborane

C	0.77918900	-0.18583600	0.05237700
C	-0.77918300	-0.18584200	-0.05238000
B	-0.00000700	1.93179900	-0.00003000
H	-0.00005400	3.12154500	0.00002400
O	-1.06651000	1.18656300	-0.40240900
O	1.06650400	1.18658300	0.40232800

C	1.46504000	-0.45040900	-1.27802800
H	2.52992300	-0.23748100	-1.17283700
H	1.34933100	-1.49060100	-1.58782900
H	1.06582700	0.19405000	-2.06346900
C	1.34511300	-1.09314500	1.12198100
H	1.08229100	-2.13452200	0.92111600
H	2.43347400	-1.01350100	1.12904600
H	0.97838200	-0.82439700	2.11164200
C	-1.34512600	-1.09322000	-1.12191700
H	-1.08231200	-2.13459000	-0.92100000
H	-2.43348600	-1.01356800	-1.12895200
H	-0.97843000	-0.82454100	-2.11160700
C	-1.46501400	-0.45034300	1.27804500
H	-2.52988600	-0.23734600	1.17287900
H	-1.34936900	-1.49053600	1.58786300
H	-1.06572700	0.19410300	2.06346000

4,4,5,5-tetramethyl-2-phenoxy-1,3,2-dioxaborolane

C	3.18714500	-1.23803900	0.41184500
C	2.12112900	-0.52359700	-0.11781400
C	2.30886500	0.76890300	-0.58961600
C	3.56996200	1.34142000	-0.51549700
C	4.63961400	0.63831400	0.01714200
C	4.44139300	-0.65501400	0.47891500
H	3.01377500	-2.24801900	0.76298600
H	1.47361300	1.32038900	-0.99940800
H	3.71381800	2.35115600	-0.88302800
H	5.62125400	1.09362000	0.06970400
H	5.26942800	-1.21772300	0.89458500
O	0.92309600	-1.17339600	-0.18877000
C	-1.99827400	0.79936700	0.37109300
C	-2.55348400	-0.52419200	-0.24711700
B	-0.31200800	-0.61587800	-0.09696400
O	-1.42378500	-1.41037200	-0.14188700
O	-0.59211800	0.71645700	0.05550300
C	-2.55982300	2.06778000	-0.22997900
H	-3.64014200	2.11943400	-0.07583900

H	-2.10688100	2.93436900	0.25480900
H	-2.35590000	2.12910900	-1.29816500
C	-2.11035800	0.83612100	1.88602500
H	-1.52304400	1.67522400	2.26201000
H	-3.14518400	0.96643800	2.20731800
H	-1.72003200	-0.08026700	2.33317300
C	-2.88125100	-0.39127900	-1.72558900
H	-3.06107700	-1.38613600	-2.13563300
H	-3.77392400	0.21592500	-1.88591800
H	-2.05158500	0.05756200	-2.27565200
C	-3.72257600	-1.12855700	0.49778600
H	-4.57214200	-0.44154100	0.50358600
H	-4.03432200	-2.04919600	0.00167400
H	-3.45922100	-1.36982100	1.52668600

toluene

C	-1.19267600	1.19738500	0.00200800
C	0.19380800	1.19451300	-0.00895000
C	0.90871400	0.00024400	-0.01133200
C	0.19409000	-1.19435400	-0.00895200
C	-1.19225900	-1.19760800	0.00201100
C	-1.89194200	-0.00016000	0.00861700
H	-1.72917100	2.13955100	0.00145600
H	0.73316300	2.13637300	-0.01822200
H	0.73372600	-2.13607100	-0.01824100
H	-1.72854300	-2.13989600	0.00146800
H	-2.97572800	-0.00035300	0.01408900
C	2.40696100	0.00010600	0.00913200
H	2.78311100	-0.01337100	1.03698300
H	2.81171800	-0.87790200	-0.49780500
H	2.81155000	0.89091800	-0.47493800

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

C	3.26143300	0.48663500	1.50404800
C	2.46565200	-0.56741000	1.08428700
C	2.27309700	-0.80858700	-0.27233400
C	2.89052500	0.02167800	-1.19851400

C	3.69474100	1.07174000	-0.78107600
C	3.88038500	1.30846800	0.57249000
H	3.40076200	0.66719700	2.56398000
H	1.97494500	-1.20489500	1.81122400
H	2.72616500	-0.14617000	-2.25793500
H	4.16688400	1.71468200	-1.51526500
H	4.50175300	2.13348700	0.90128700
C	1.40627200	-1.94984700	-0.72769400
H	1.13053100	-1.80515400	-1.77666700
H	1.95071300	-2.89505300	-0.65077600
O	0.24822700	-2.09974100	0.07585300
C	-1.67734000	0.83165200	-0.47602400
C	-2.60389400	-0.02354700	0.44864000
O	-0.73237600	-0.14849000	-0.94482000
O	-1.70374900	-1.03662300	0.93497100
C	-3.18178000	0.72481700	1.62888700
H	-3.80568500	1.55548300	1.29025600
H	-3.80494600	0.05108800	2.21957800
H	-2.39699200	1.11617600	2.27482700
C	-0.88192500	1.87769600	0.28890500
H	-0.10795500	2.27869700	-0.36742100
H	-1.51664200	2.70020000	0.62358300
H	-0.38757300	1.43953700	1.15826800
C	-3.70701100	-0.73294500	-0.31979800
H	-4.17820900	-1.46466500	0.33823700
H	-4.47133500	-0.03332800	-0.66305000
H	-3.30561900	-1.26306700	-1.18583600
C	-2.36927400	1.45887600	-1.66477200
H	-3.15047000	2.14799200	-1.33525000
H	-1.64431900	2.02493800	-2.25242100
H	-2.81717300	0.70463800	-2.31055800
B	-0.69338900	-1.12766100	0.01672700

benzene

C	-0.85479900	1.09303700	0.00000100
C	-1.37399800	-0.19380500	0.00001100
C	-0.51921300	-1.28677800	-0.00000300

C	0.85484300	-1.09300300	0.00000100
C	1.37400500	0.19375000	0.00000600
C	0.51916200	1.28679900	-0.00000900
H	-1.52267200	1.94692200	-0.00001100
H	-2.44743800	-0.34514100	0.00000000
H	-0.92473600	-2.29212700	-0.00003100
H	1.52260000	-1.94697800	-0.00000200
H	2.44742600	0.34522700	0.00000600
H	0.92481700	2.29209400	-0.00000100

phenol radical

C	-1.08003000	-1.21818900	-0.00000500
C	0.28863200	-1.23242300	-0.00000100
C	1.04185400	-0.00000200	0.00004400
C	0.28863500	1.23241500	-0.00004300
C	-1.08002700	1.21819400	0.00002800
C	-1.77286400	0.00000200	-0.00000800
H	-1.63676100	-2.14827200	-0.00001800
H	0.85612100	-2.15553100	-0.00013900
H	0.85612900	2.15552200	-0.00015600
H	-1.63675400	2.14827900	0.00003100
H	-2.85663000	0.00000400	0.00005900
O	2.28758600	0.00000200	0.00001700

toluene radical

C	-1.12631600	1.20433500	0.00002200
C	0.25089400	1.20997800	-0.00010600
C	0.98714000	-0.00013100	0.00005800
C	0.25079600	-1.21009300	-0.00004800
C	-1.12642200	-1.20424000	-0.00003700
C	-1.82747200	0.00007300	0.00007200
H	-1.66806400	2.14343500	-0.00000600
H	0.79235500	2.14982700	-0.00023000
H	0.79211700	-2.15002300	-0.00017800
H	-1.66827200	-2.14328000	-0.00015500
H	-2.91085400	0.00010900	0.00010700
C	2.38701300	0.00001700	0.00032900

H	2.94469900	-0.92777600	-0.00052500
H	2.94422800	0.92807800	-0.00075500

benzylalcohol radical

C	0.48435500	0.23169100	0.00717700
C	-0.42718400	1.28174800	-0.00263700
C	-1.78962400	1.02942500	-0.00826400
C	-2.25211700	-0.27904000	-0.00485700
C	-1.34536100	-1.32863500	0.00397900
C	0.01839800	-1.07500600	0.01039800
H	-0.06864500	2.30723800	-0.00704200
H	-2.49239900	1.85469100	-0.01634600
H	-3.31727300	-0.47919700	-0.00993900
H	-1.70187200	-2.35243900	0.00560800
H	0.73524800	-1.88745800	0.01592500
C	1.96165900	0.52752500	0.01820400
H	2.22664900	1.23196400	-0.79672100
H	2.22884600	1.11905500	0.91991600
O	2.81108600	-0.51501300	-0.03192500

benzene radical

C	-1.20653300	0.62787100	-0.00000500
C	-1.21943400	-0.76700800	0.00002000
C	-0.00001300	-1.38784200	-0.00000900
C	1.21943500	-0.76700300	-0.00000600
C	1.20654700	0.62784300	0.00001500
C	-0.00000100	1.31486000	-0.00000400
H	-2.14422400	1.17334500	-0.00002400
H	-2.15249000	-1.31875200	-0.00001000
H	2.15245700	-1.31880500	-0.00002200
H	2.14421800	1.17335300	0.00000900
H	0.00003100	2.39853000	-0.00001700

16. NMR spectra of isolated ether products

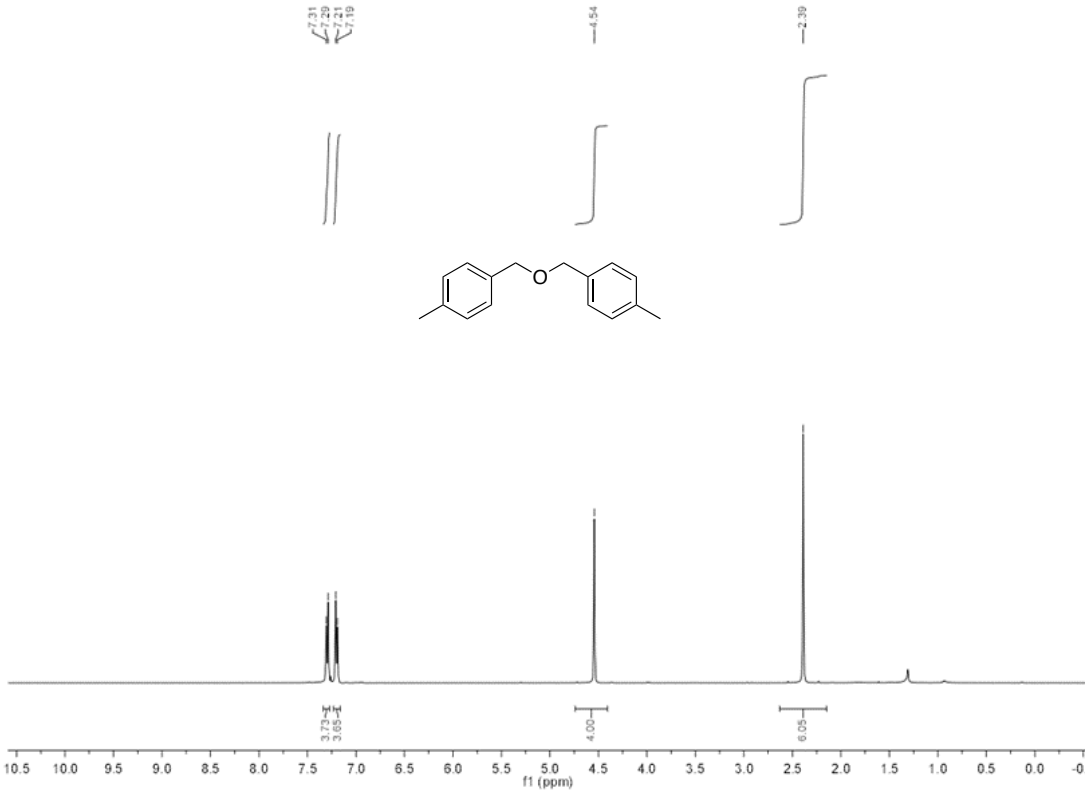


Figure S9: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 4,4'-(oxybis(methylene))bis(methylbenzene)

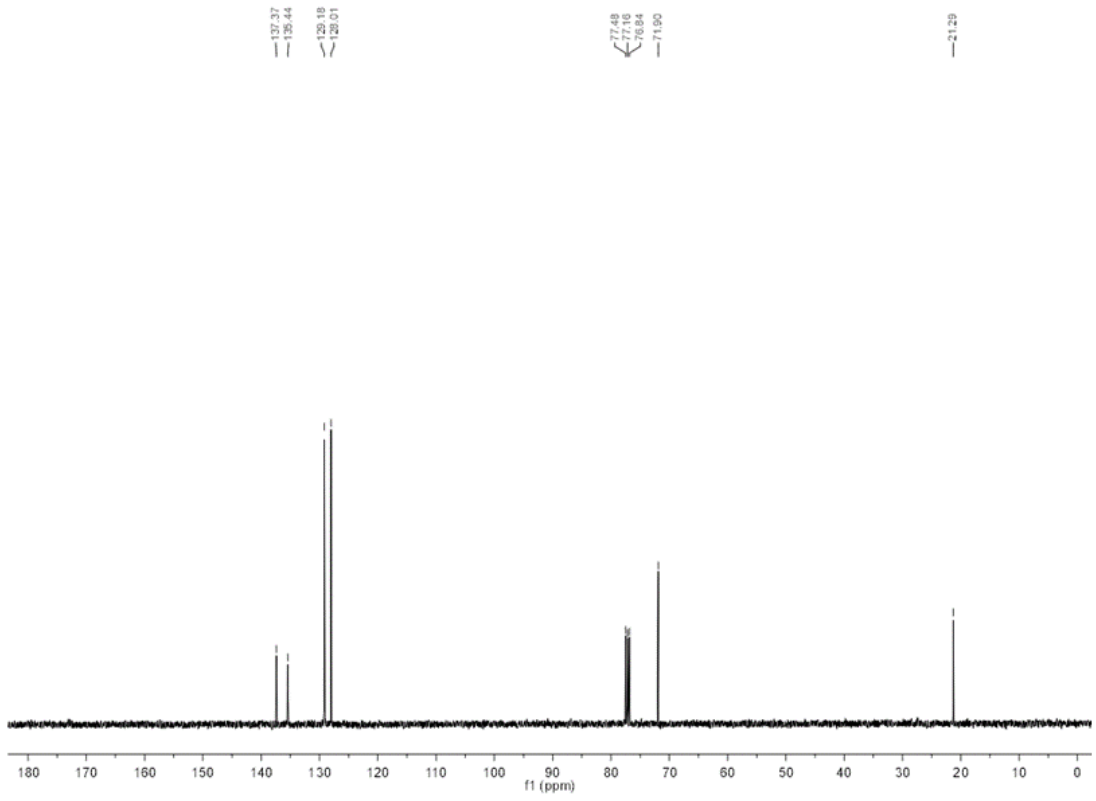


Figure S10: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 4,4'-(oxybis(methylene))bis(methylbenzene)

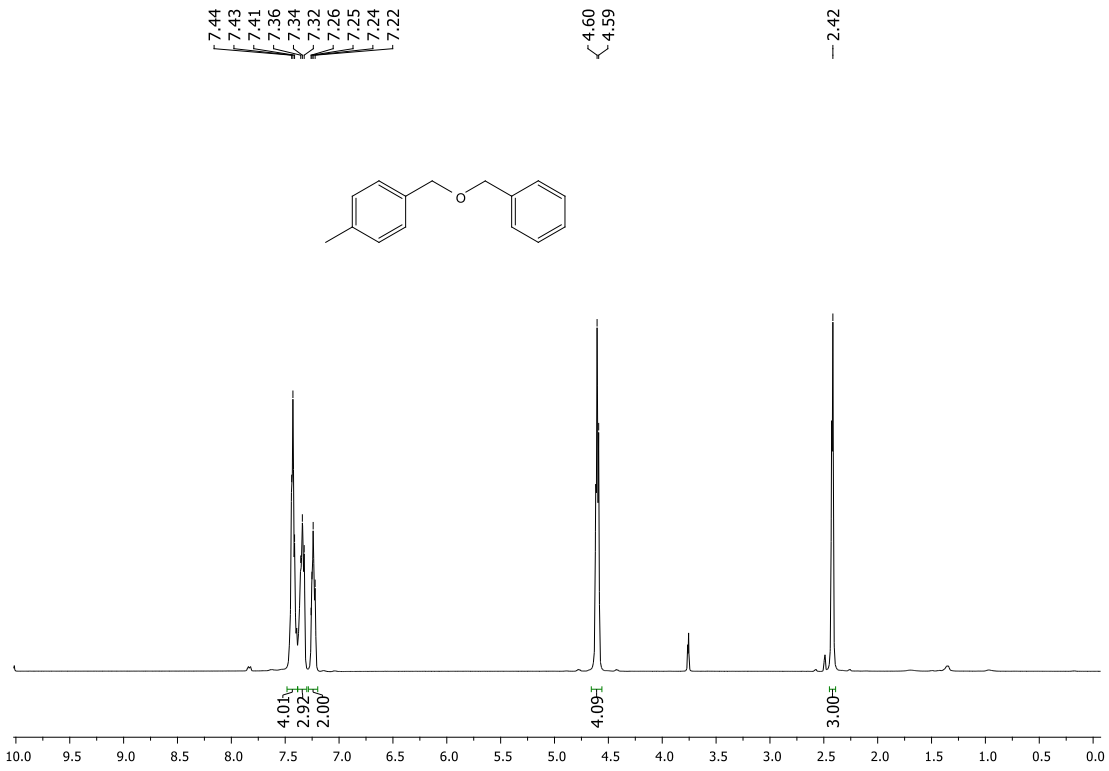


Figure S11: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1-((benzyloxy)methyl)-4-methylbenzene

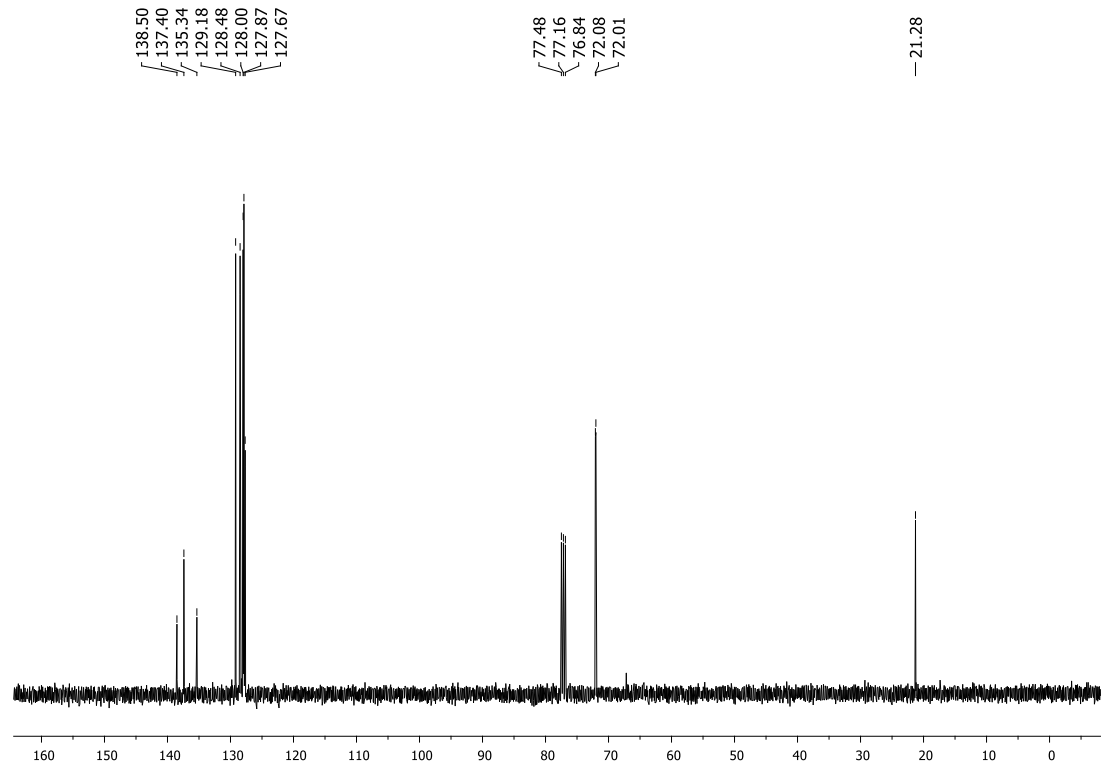


Figure S12: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 1-((benzyloxy)methyl)-4-methylbenzene

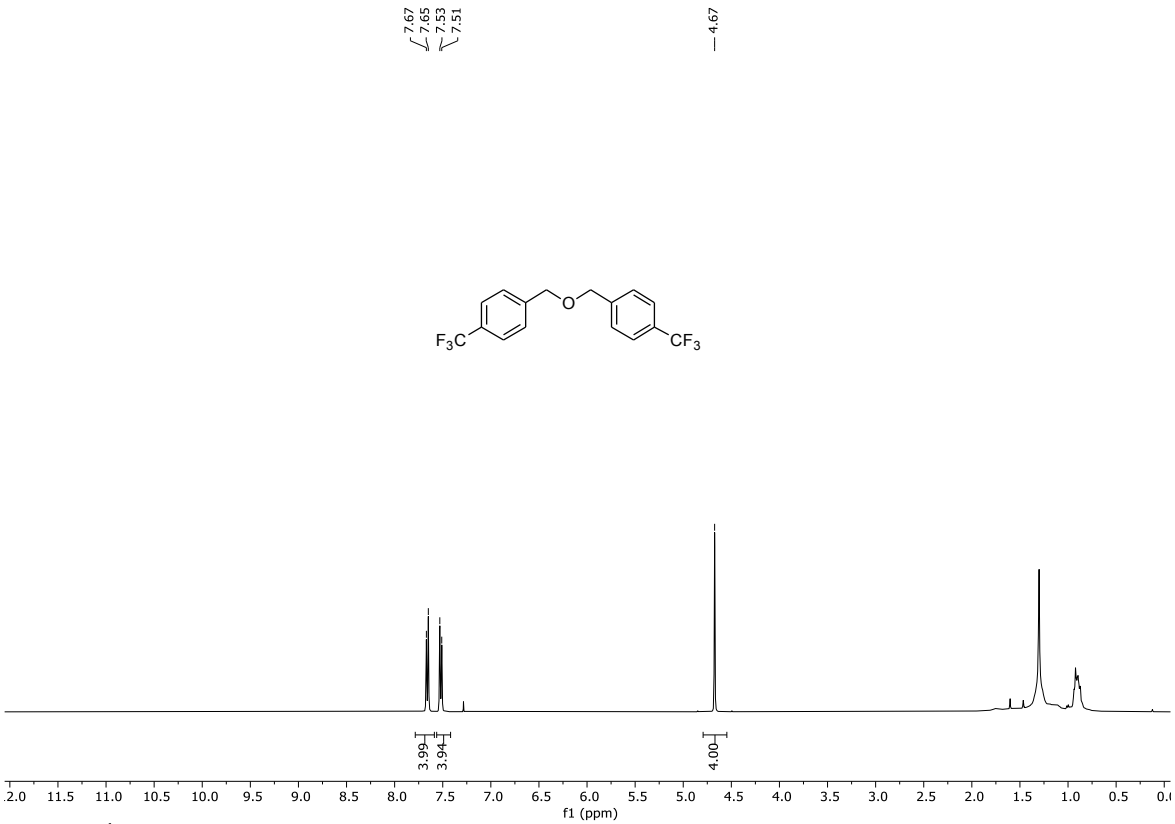


Figure S13: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 4,4'-(oxybis(methylene))bis((trifluoromethyl)benzene)

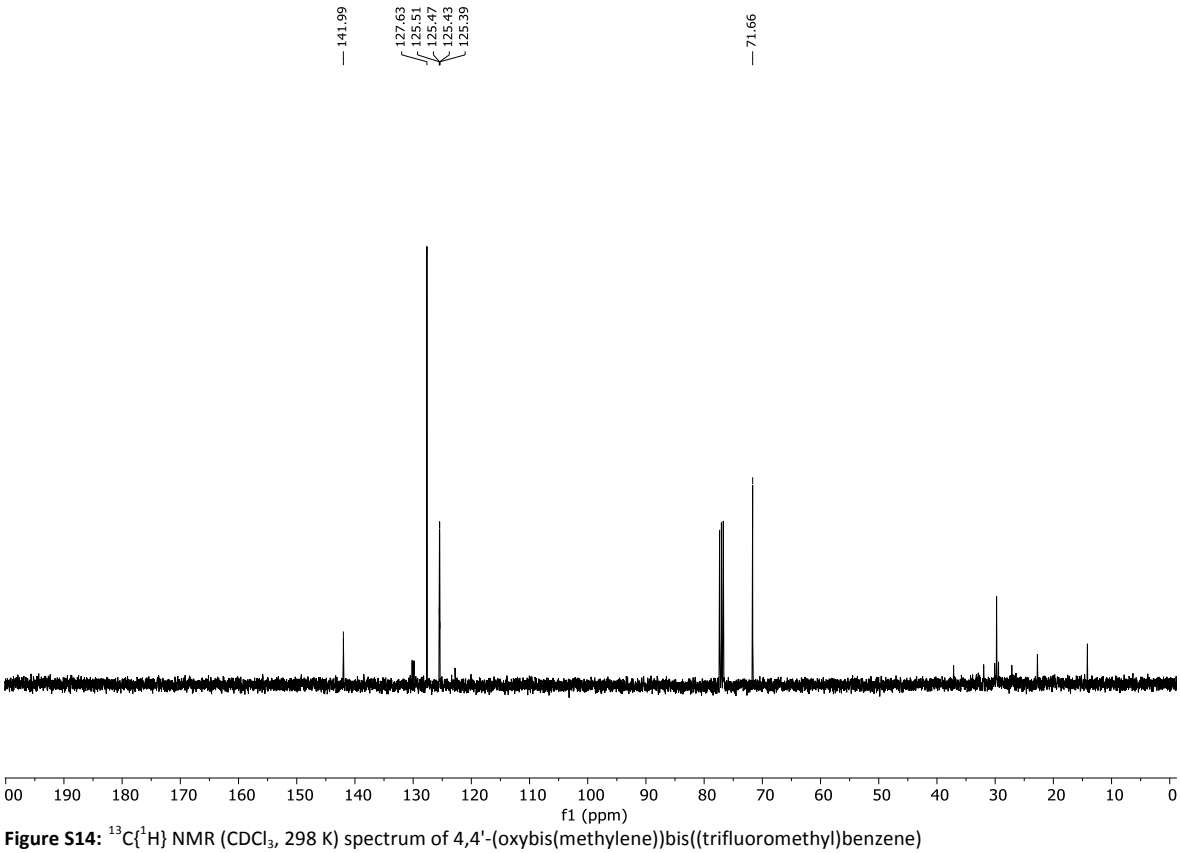


Figure S14: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 4,4'-(oxybis(methylene))bis((trifluoromethyl)benzene)

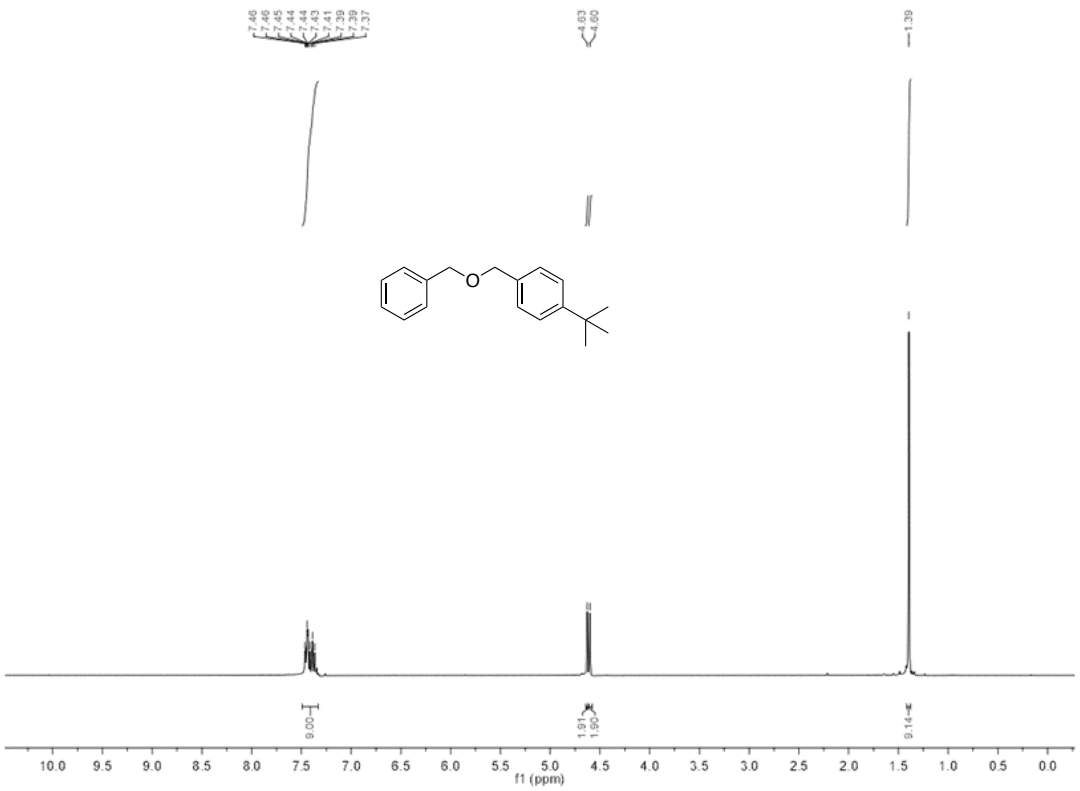


Figure S15: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1-((benzyloxy)methyl)-4-(*tert*-butyl)benzene

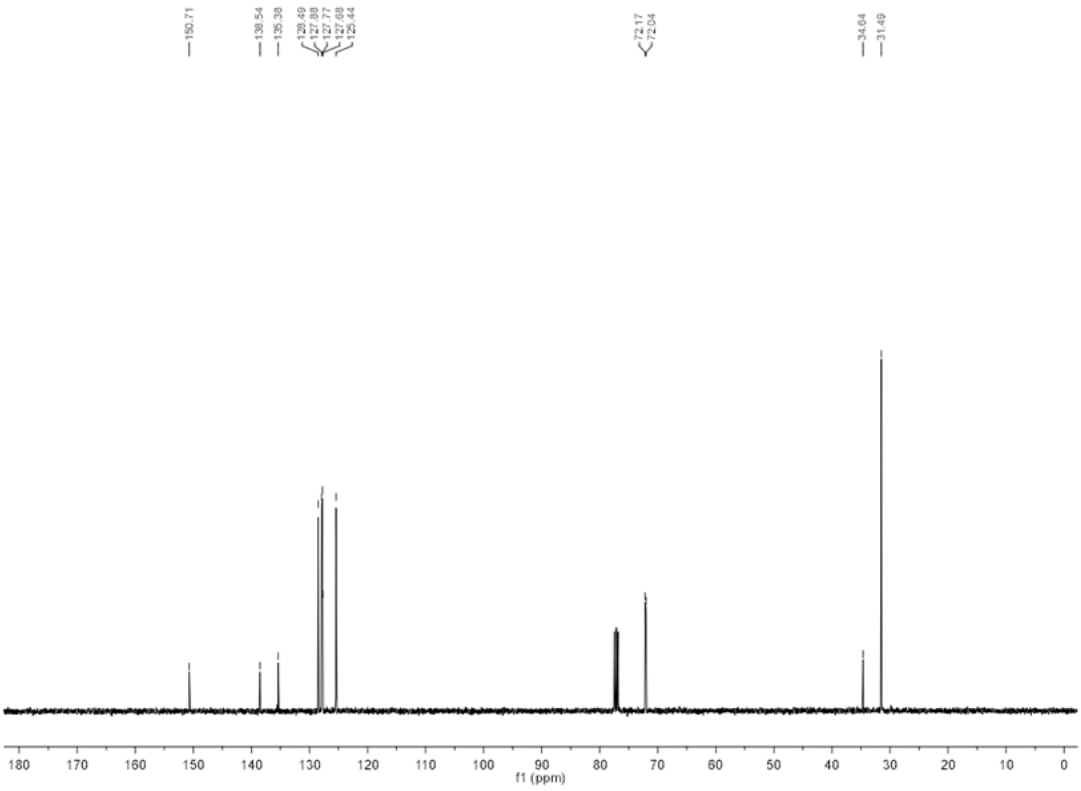


Figure S16: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 1-((benzyloxy)methyl)-4-(*tert*-butyl)benzene

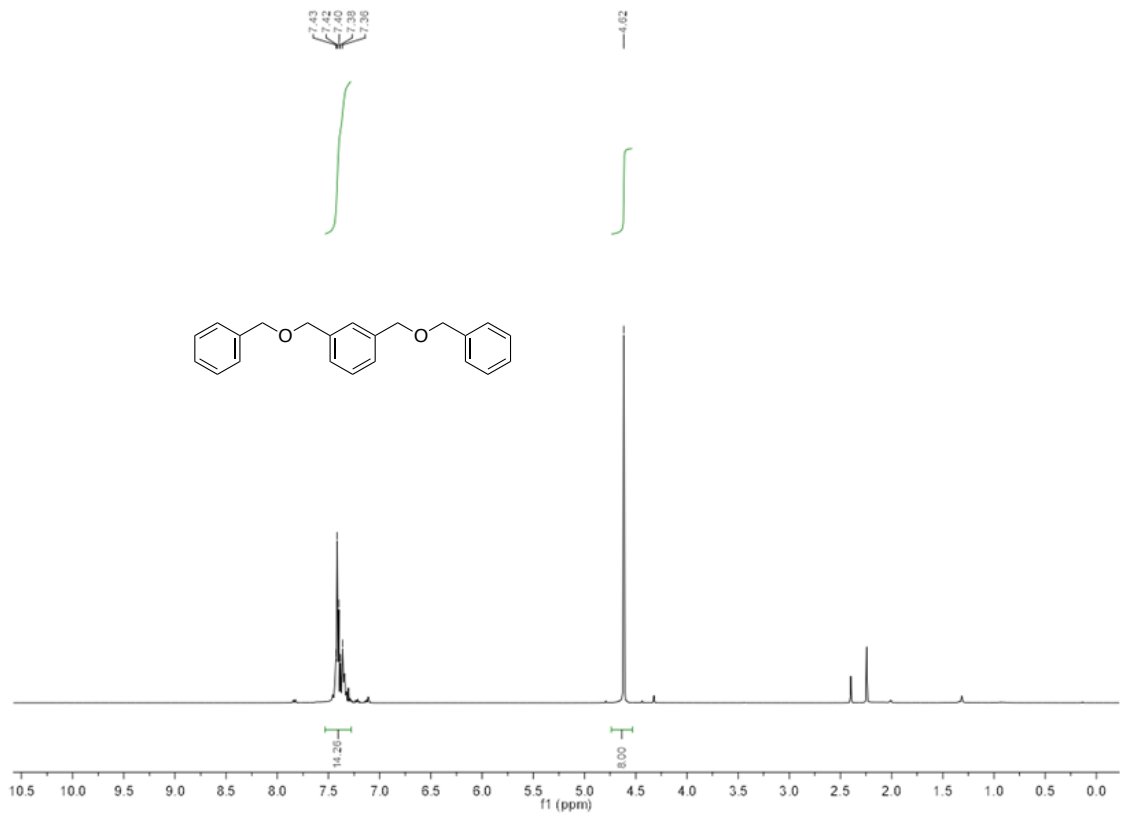


Figure S17: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1,3-bis((benzyloxy)methyl)benzene

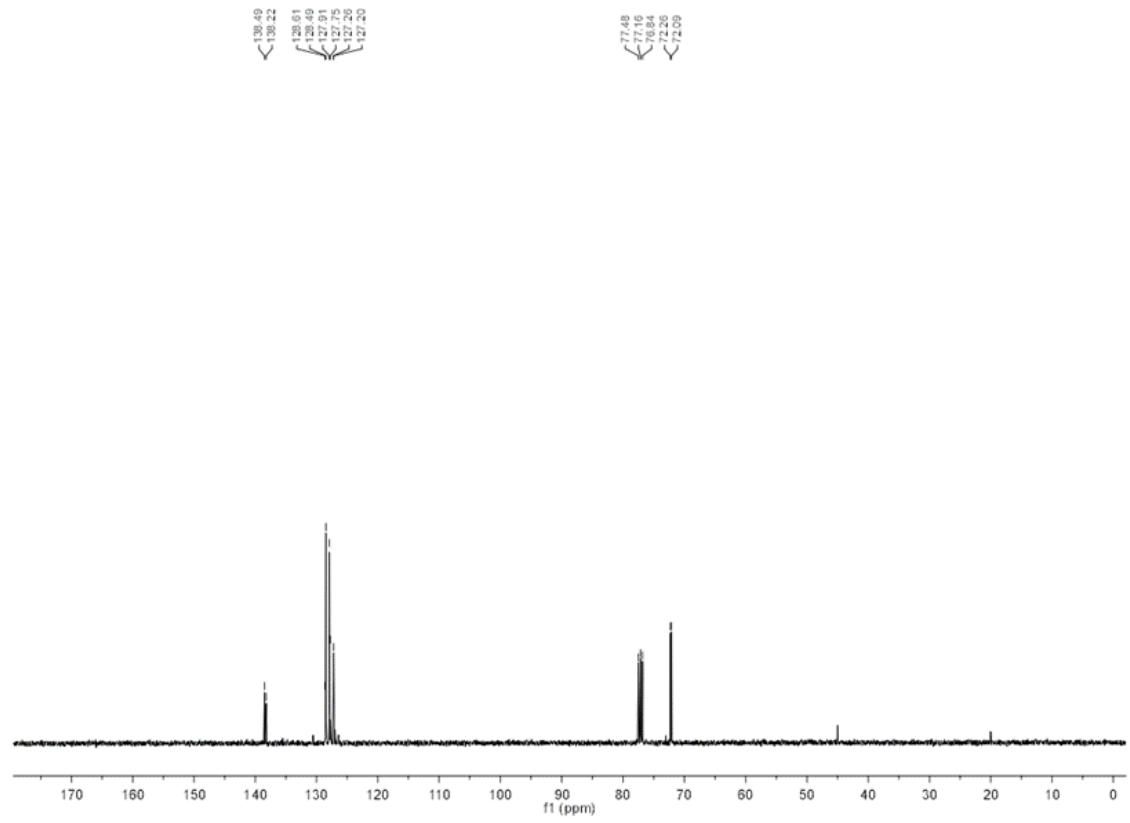


Figure S18: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 1,3-bis((benzyloxy)methyl)benzene

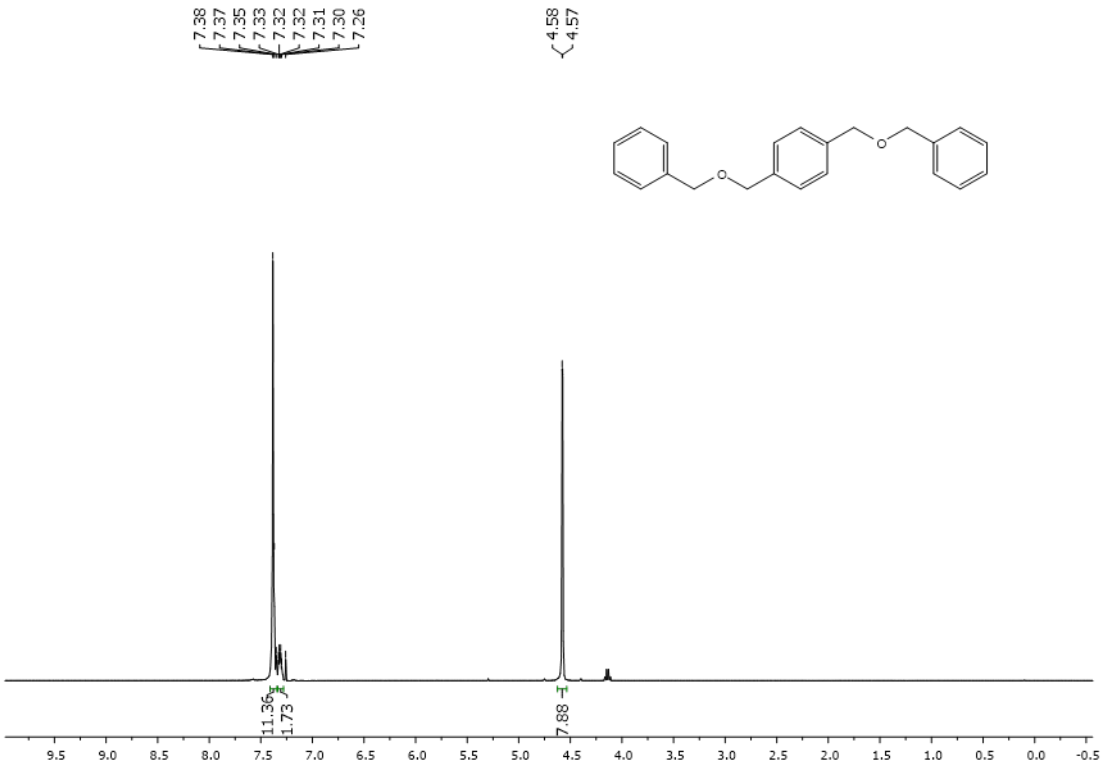


Figure S19: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1,4-bis((benzyloxy)methyl)benzene

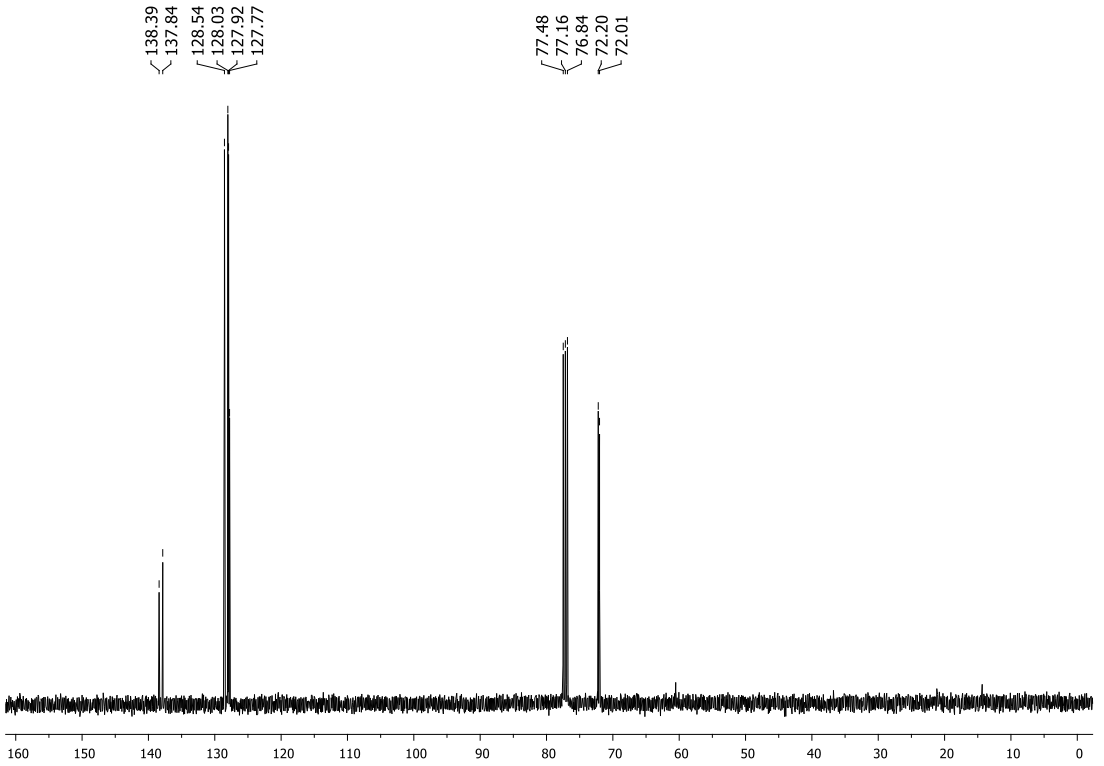


Figure S20: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 1,4-bis((benzyloxy)methyl)benzene

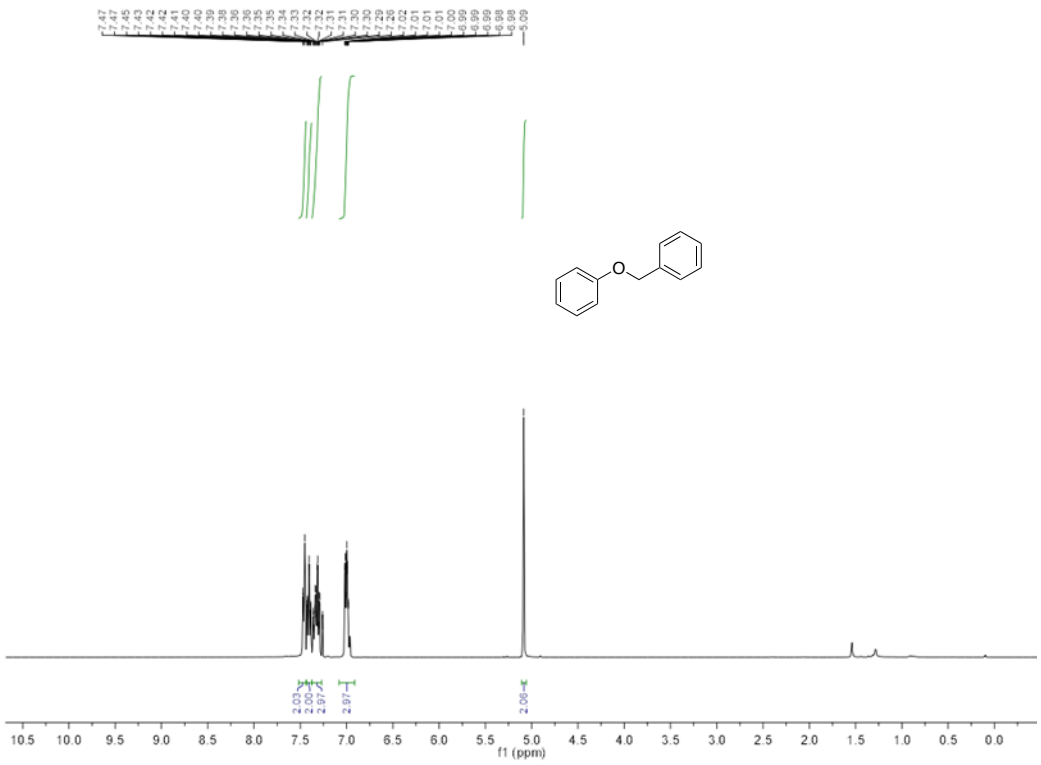


Figure S21: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of (benzyloxy)benzene

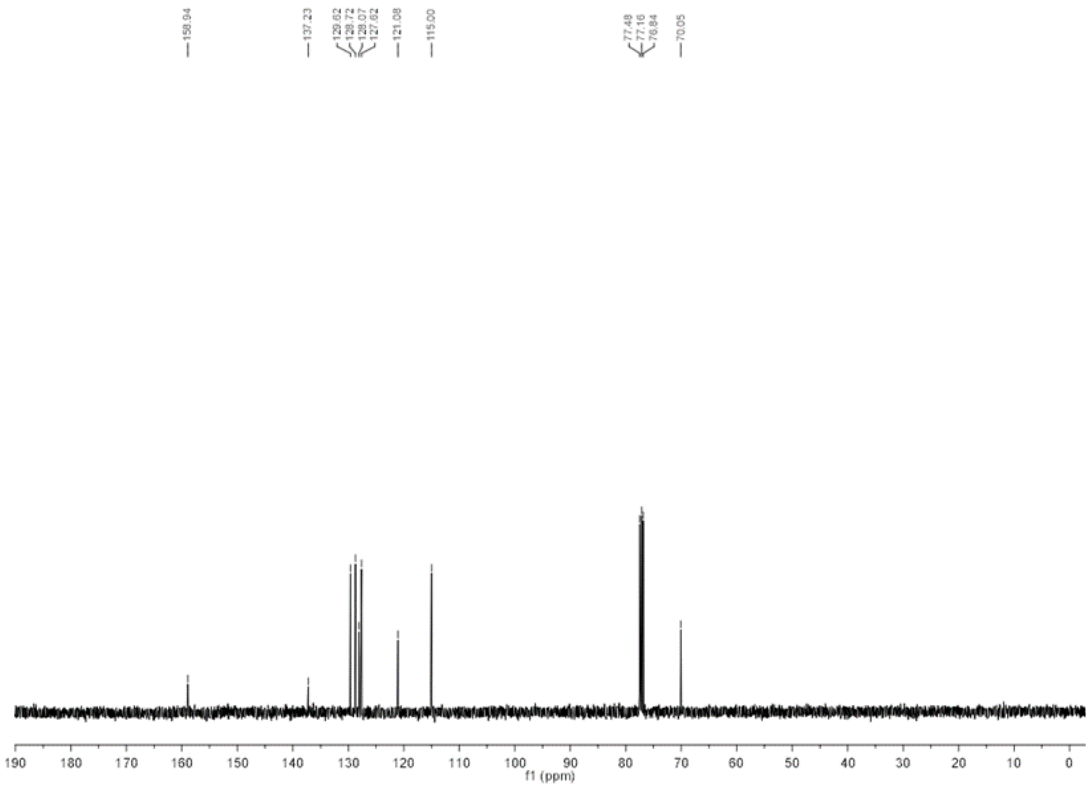


Figure S22: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of (benzyloxy)benzene

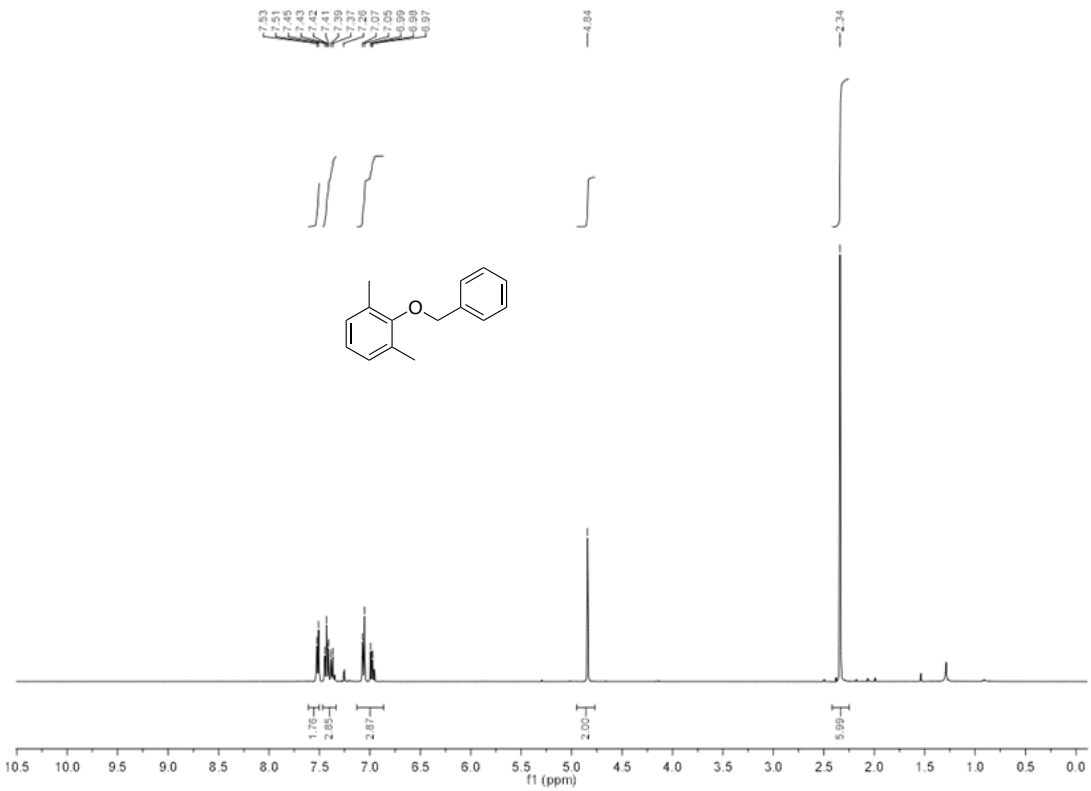


Figure S23: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 2-(benzyloxy)-1,3-dimethylbenzene

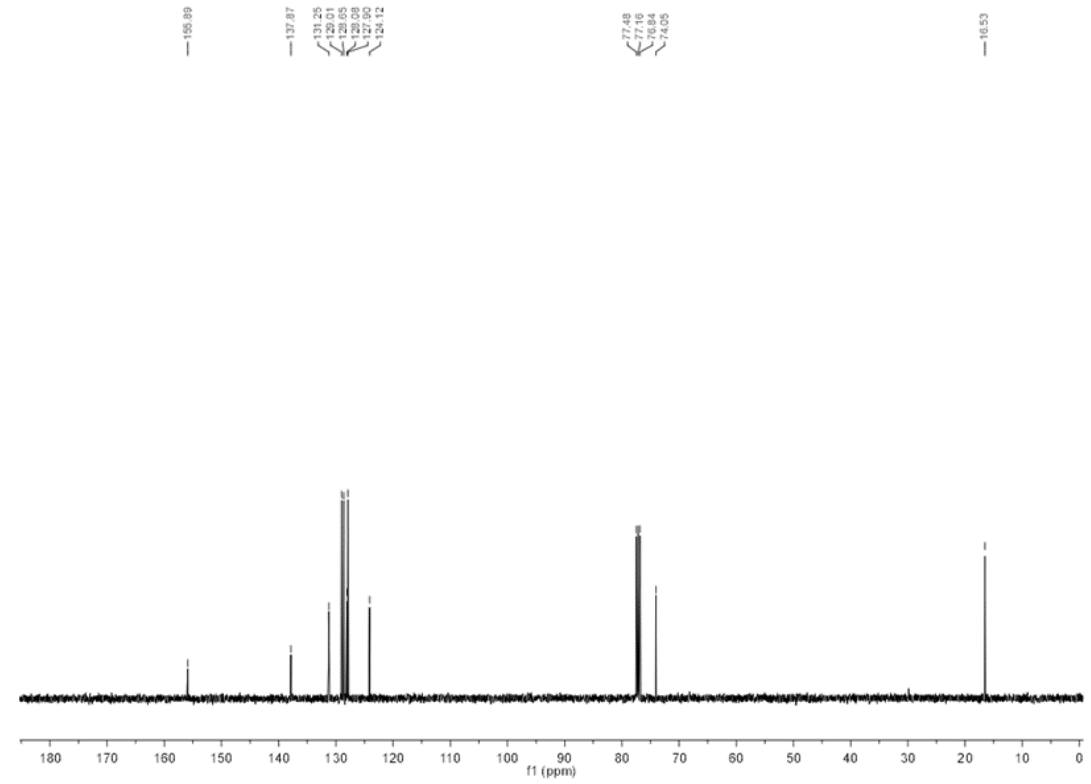


Figure S24: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 2-(benzyloxy)-1,3-dimethylbenzene

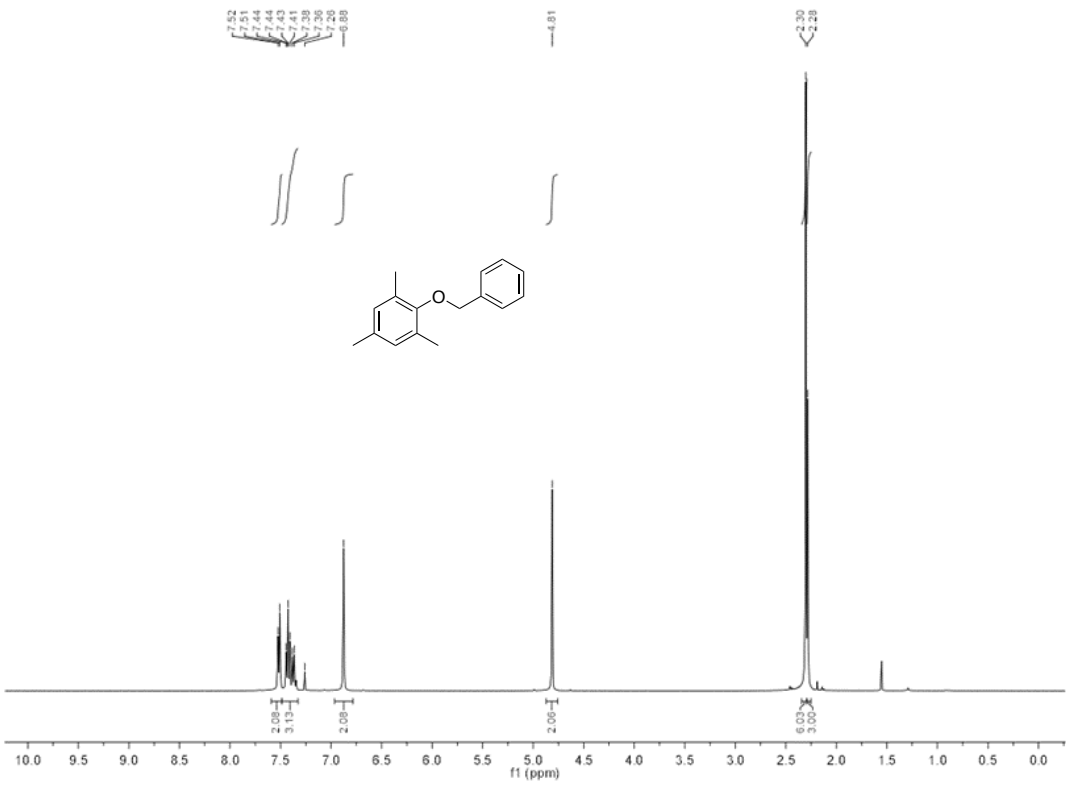


Figure S25: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 2-(benzyloxy)-1,3,5-trimethylbenzene

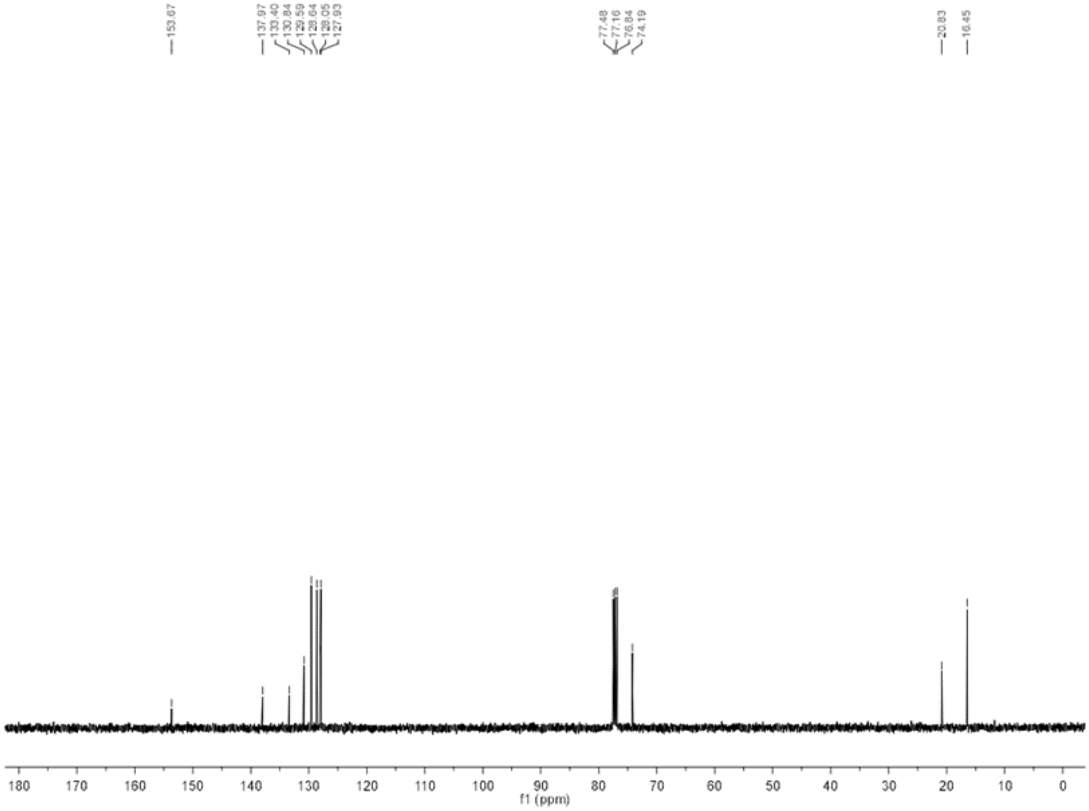


Figure S26: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 2-(benzyloxy)-1,3,5-trimethylbenzene

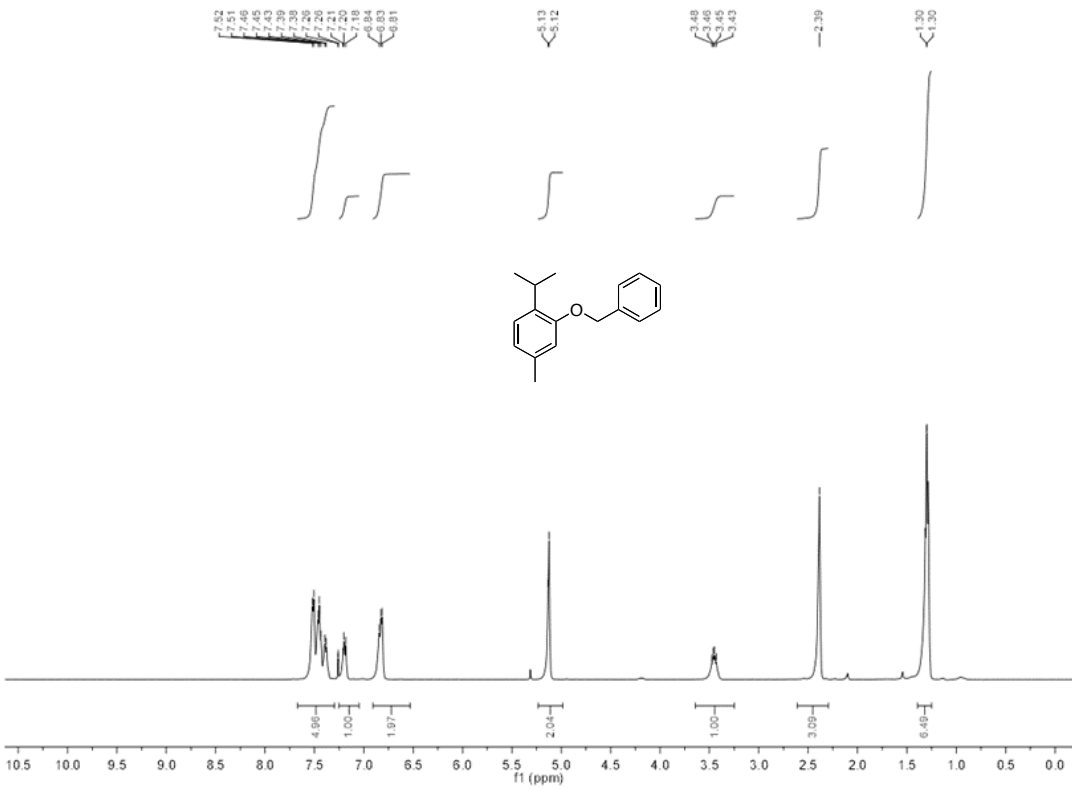


Figure S27: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 2-(benzyloxy)-1-isopropyl-4-methylbenzene

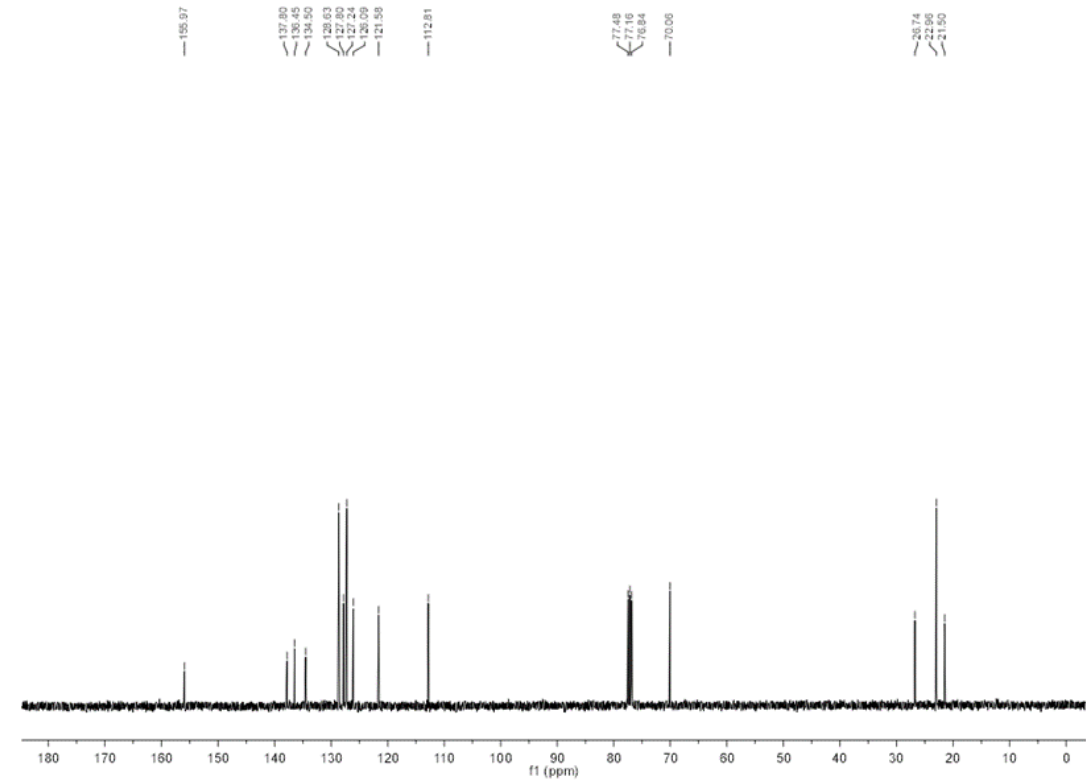


Figure S28: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 2-(benzyloxy)-1-isopropyl-4-methylbenzene

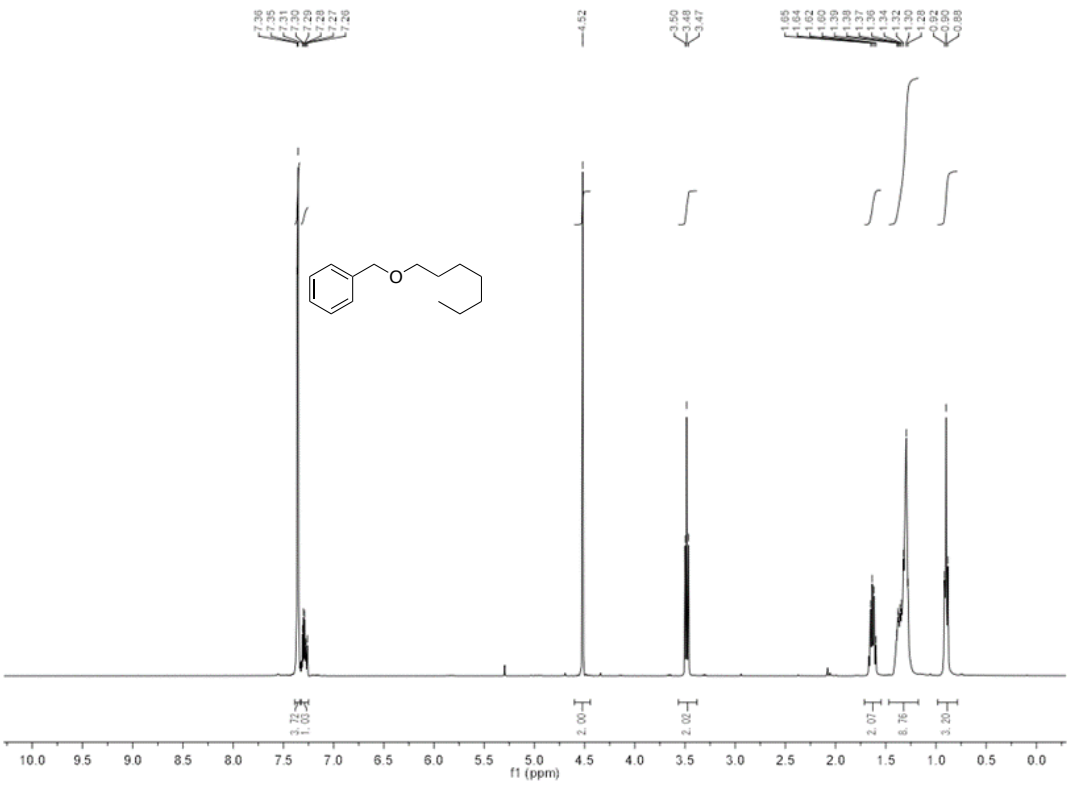


Figure S29: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of ((heptyloxy)methyl)benzene

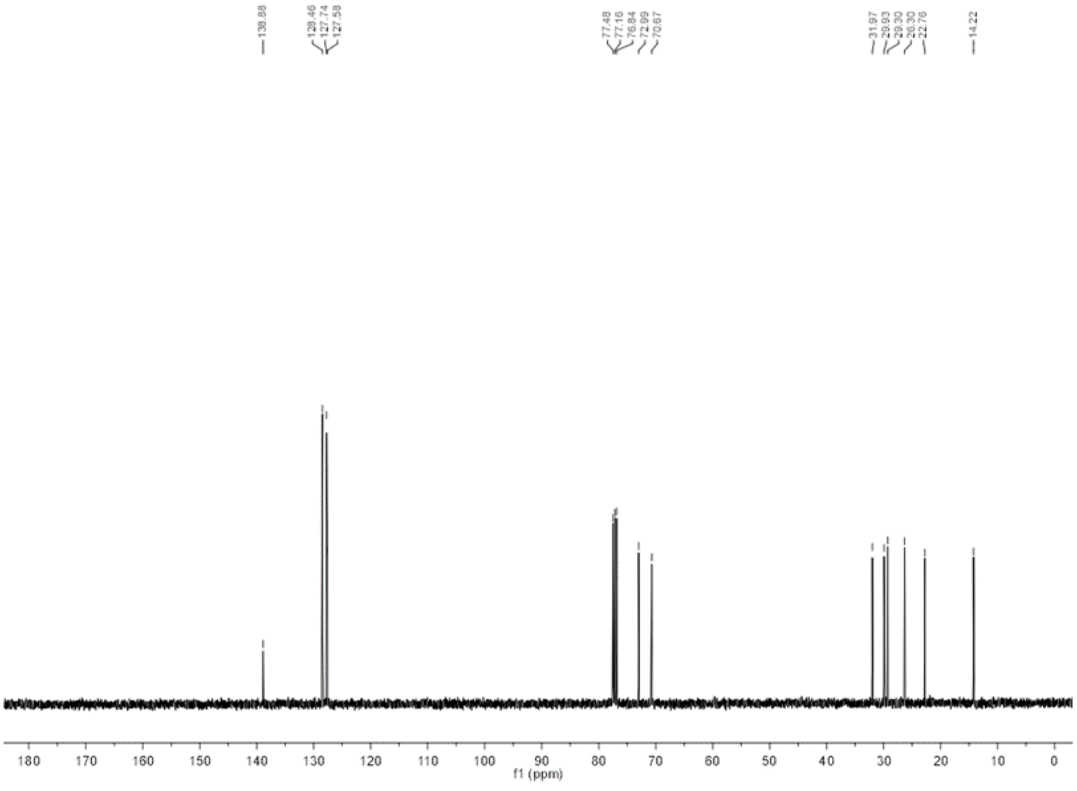


Figure S30: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of ((heptyloxy)methyl)benzene

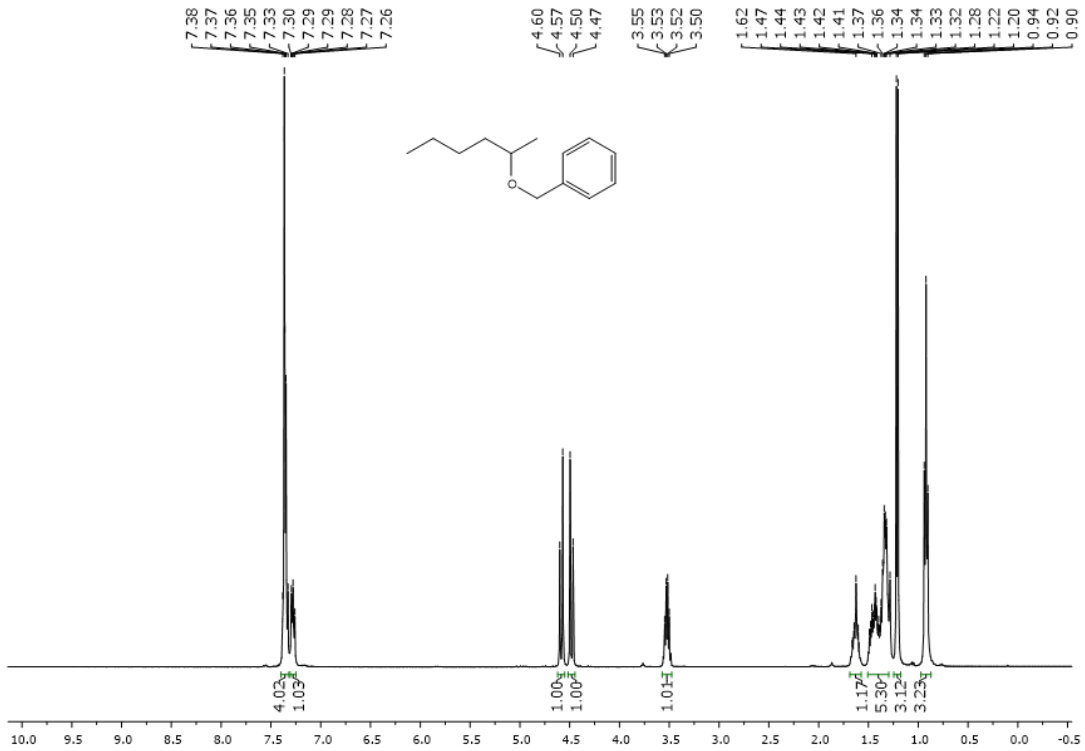


Figure S31: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of ((hexan-2-yloxy)methyl)benzene

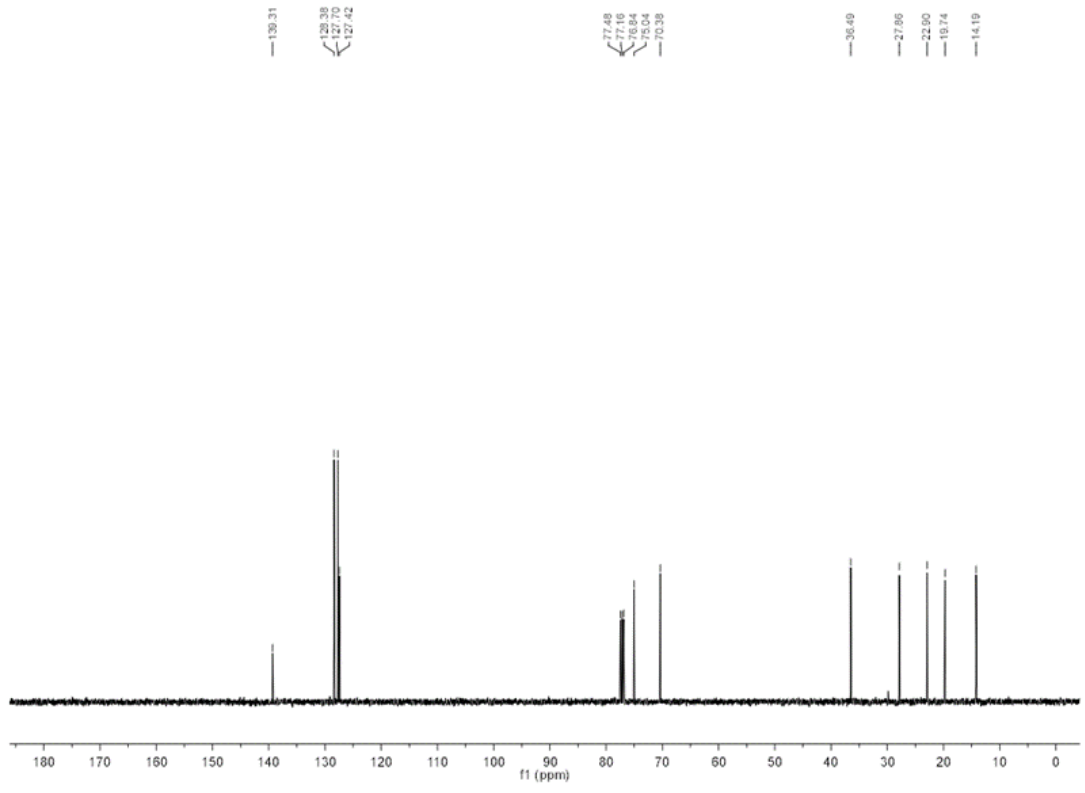


Figure S32: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of ((hexan-2-yloxy)methyl)benzene

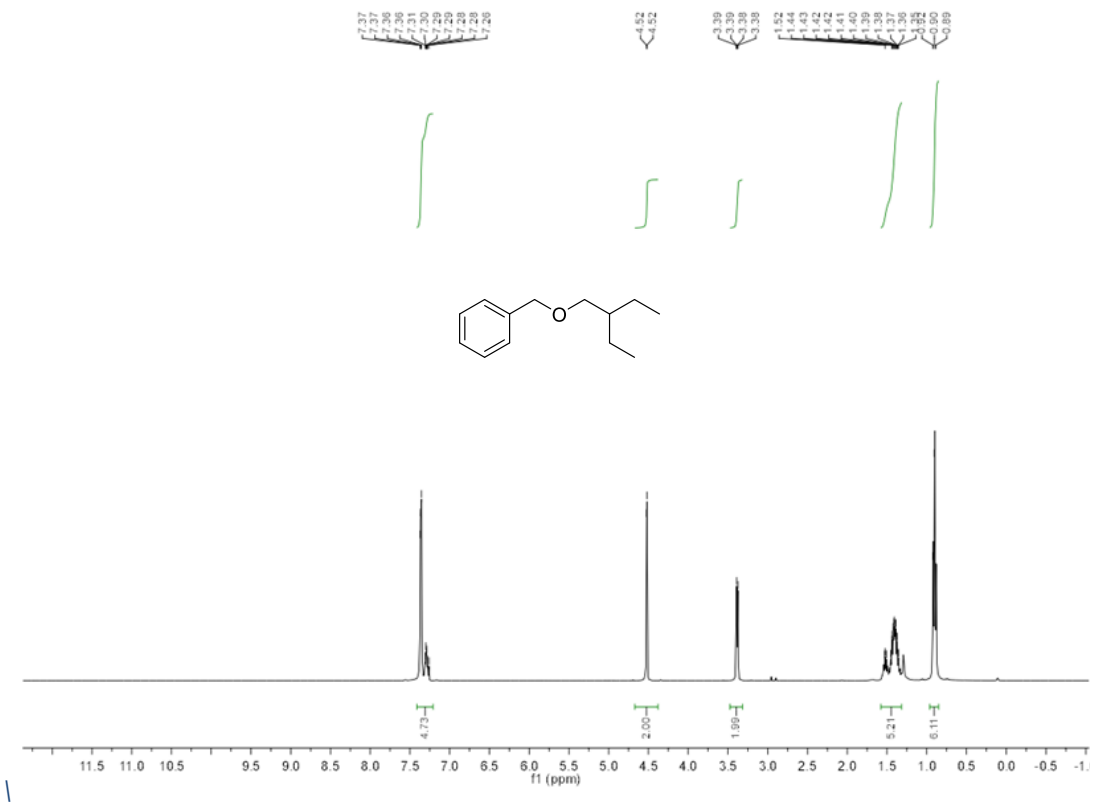


Figure S33: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of ((2-ethylbutoxy)methyl)benzene

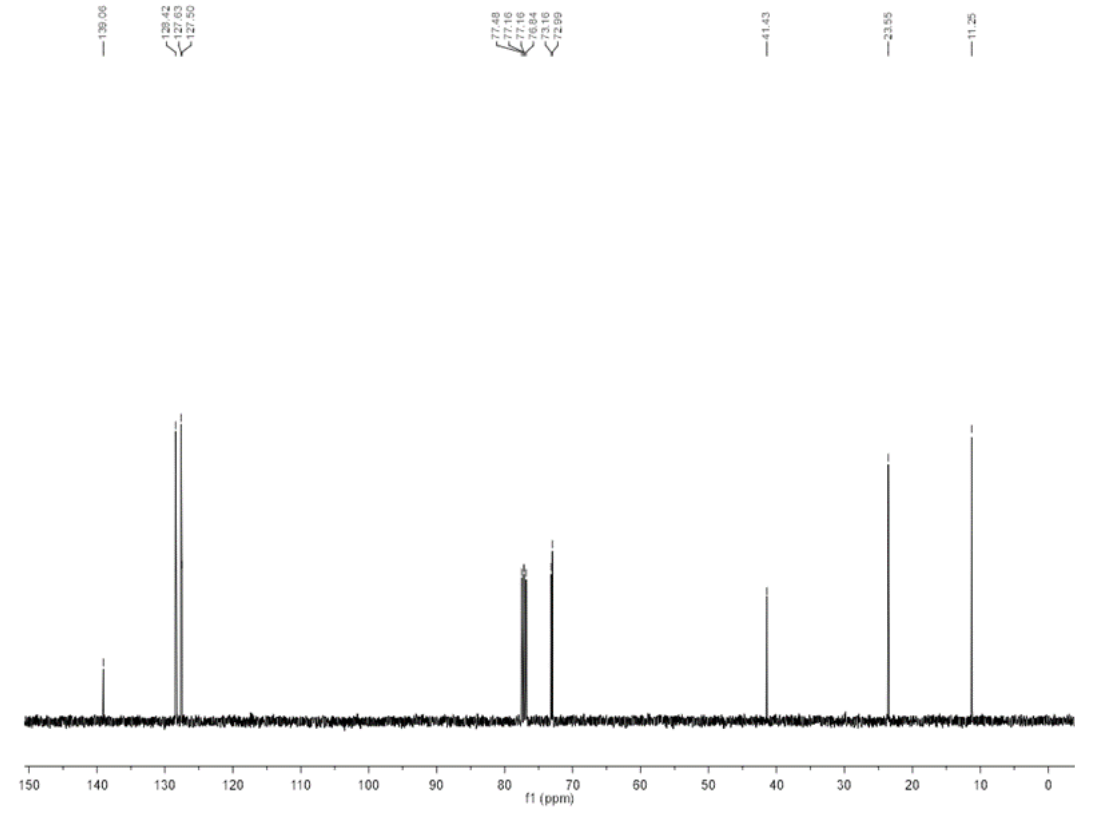


Figure S34: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of ((2-ethylbutoxy)methyl)benzene

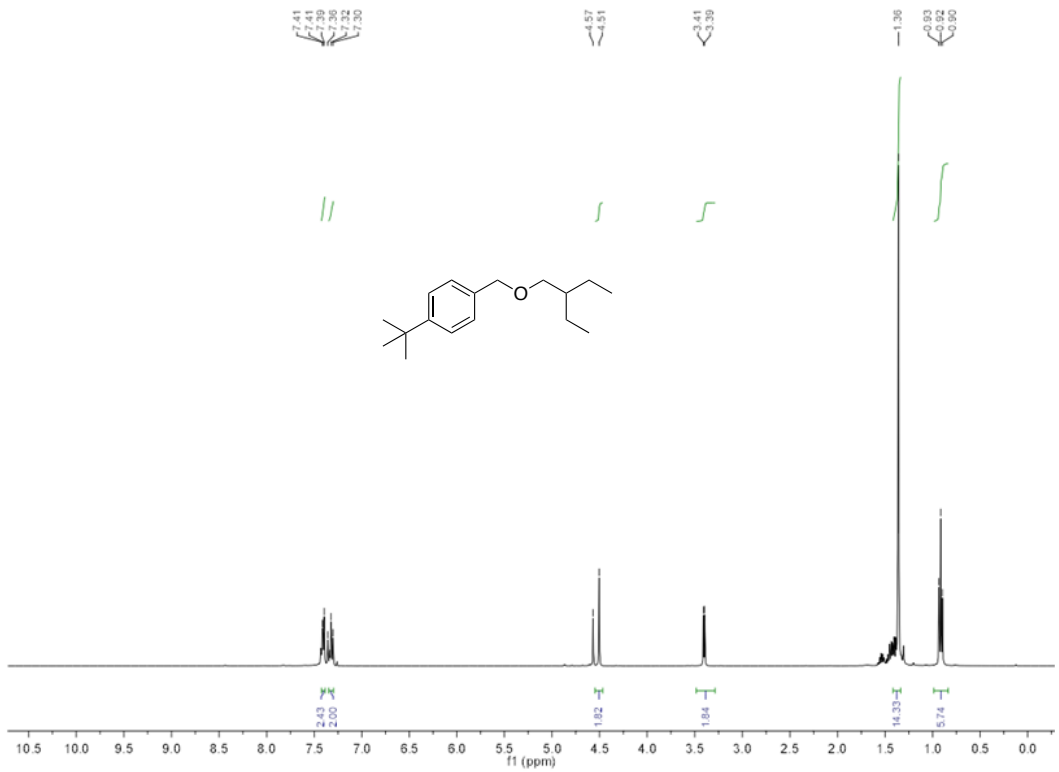


Figure S35: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1-(tert-butyl)-4-((2-ethylbutoxy)methyl)benzene

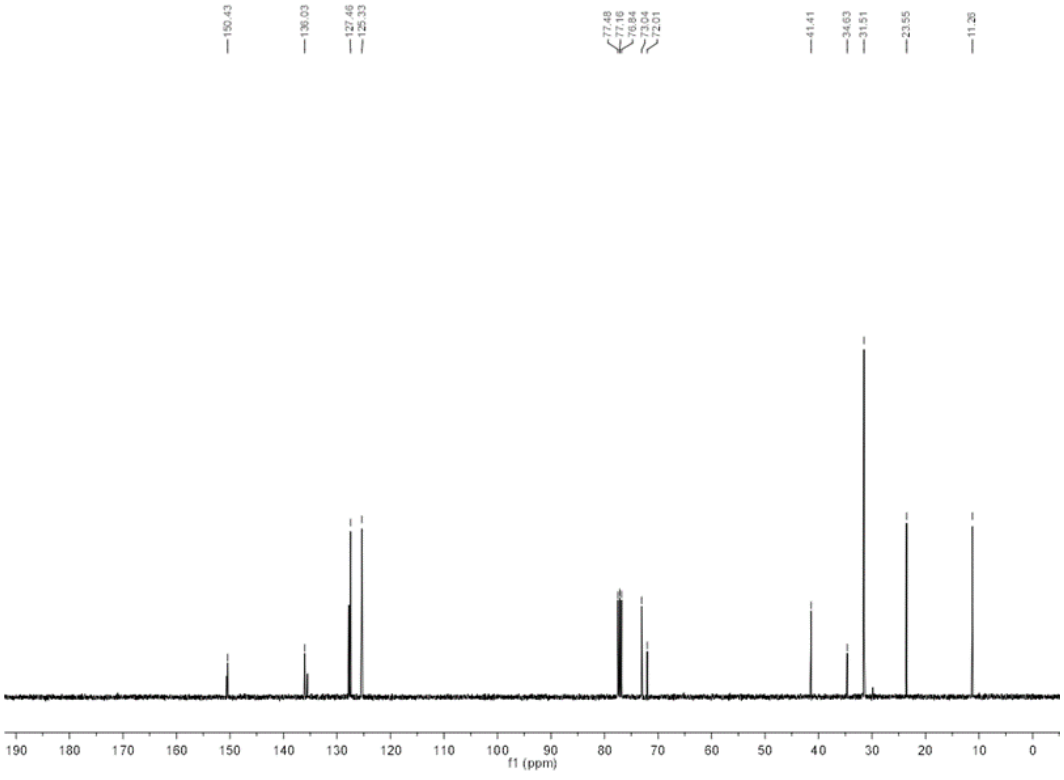


Figure S36: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 1-(*tert*-butyl)-4-((2-ethylbutoxy)methyl)benzene

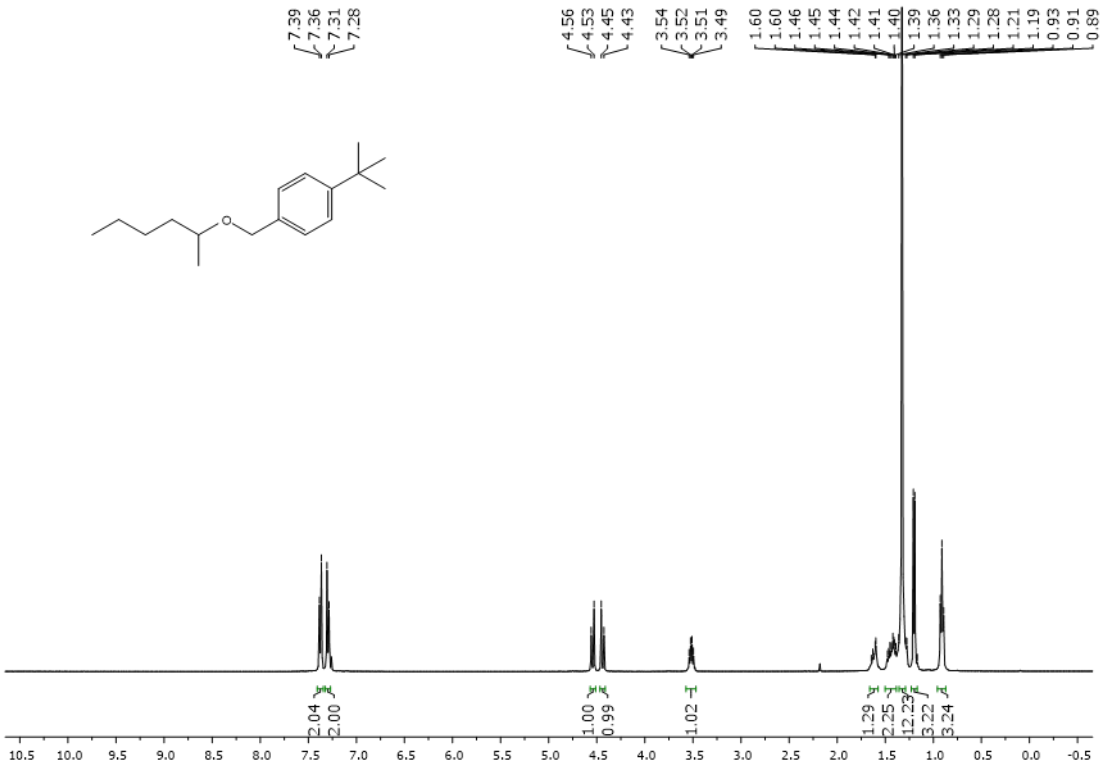


Figure S37: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1-(*tert*-butyl)-4-((hexan-2-yloxy)methyl)benzene

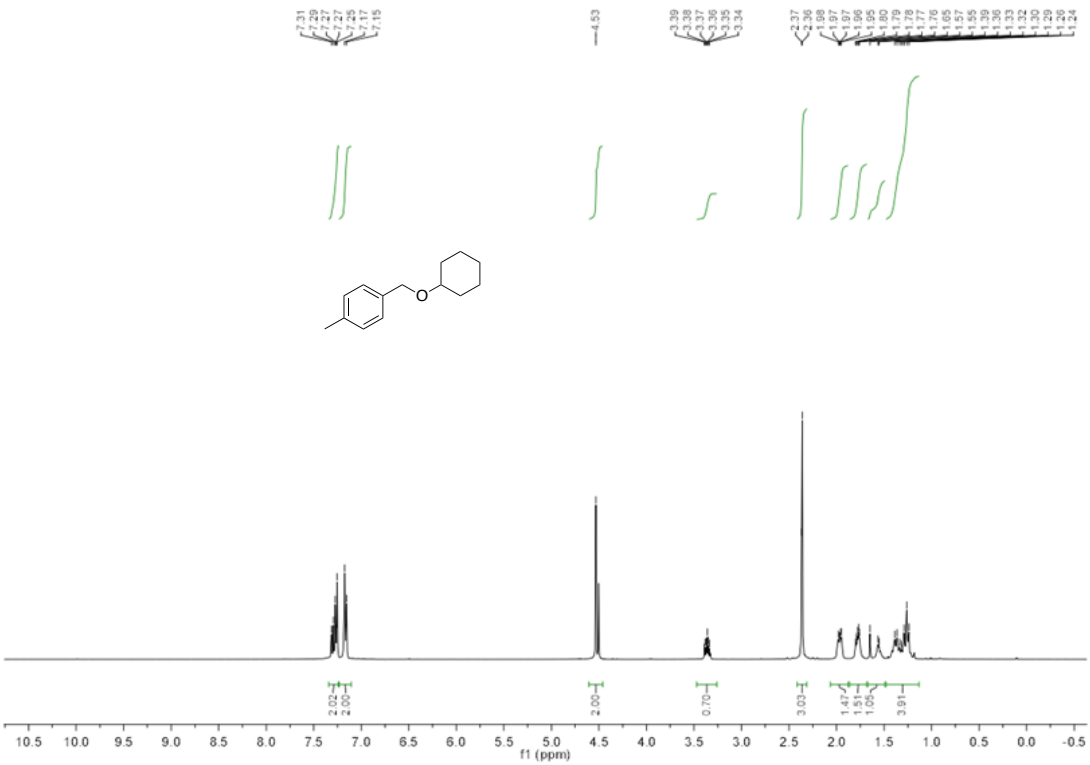


Figure S38: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1-((cyclohexyloxy)methyl)-4-methylbenzene

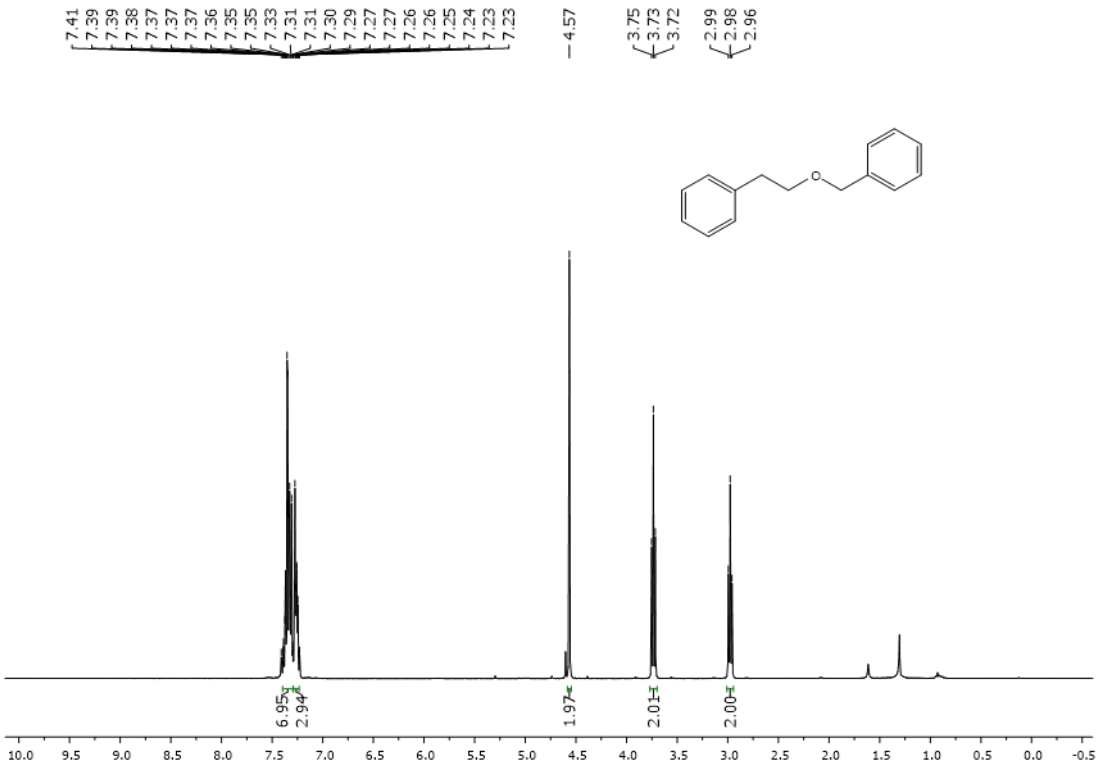


Figure S39: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of (2-(benzyloxy)ethyl)benzene

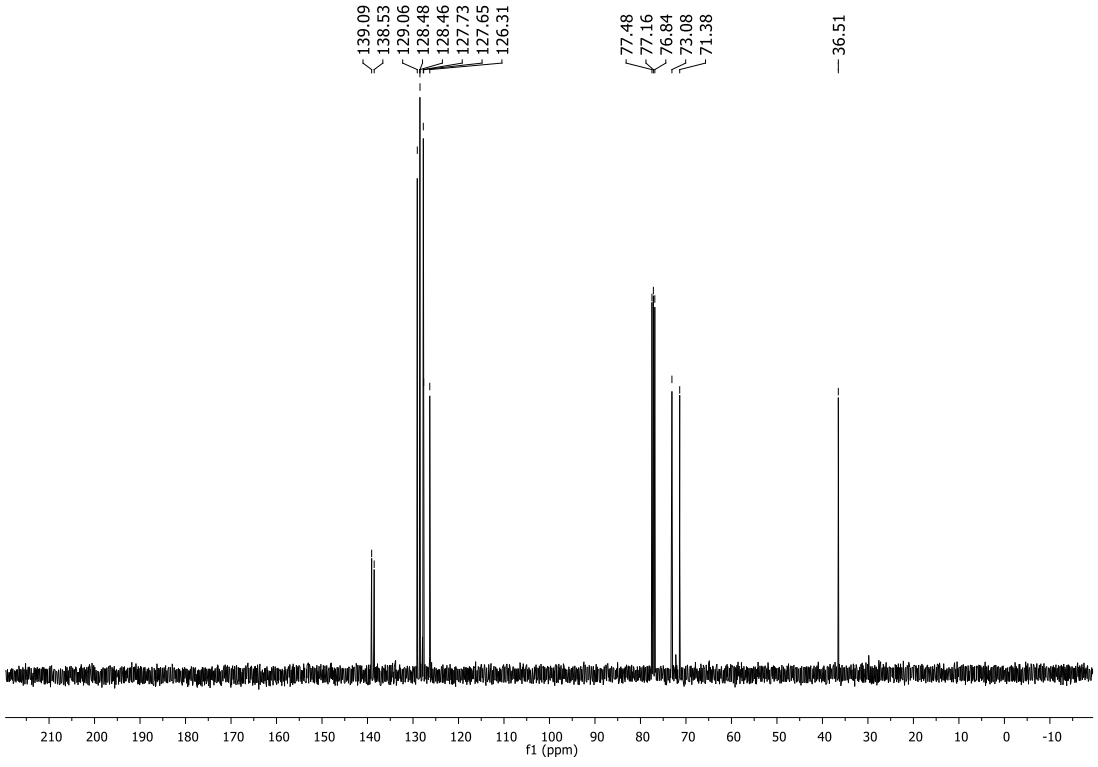


Figure S40: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of (2-(benzyloxy)ethyl)benzene

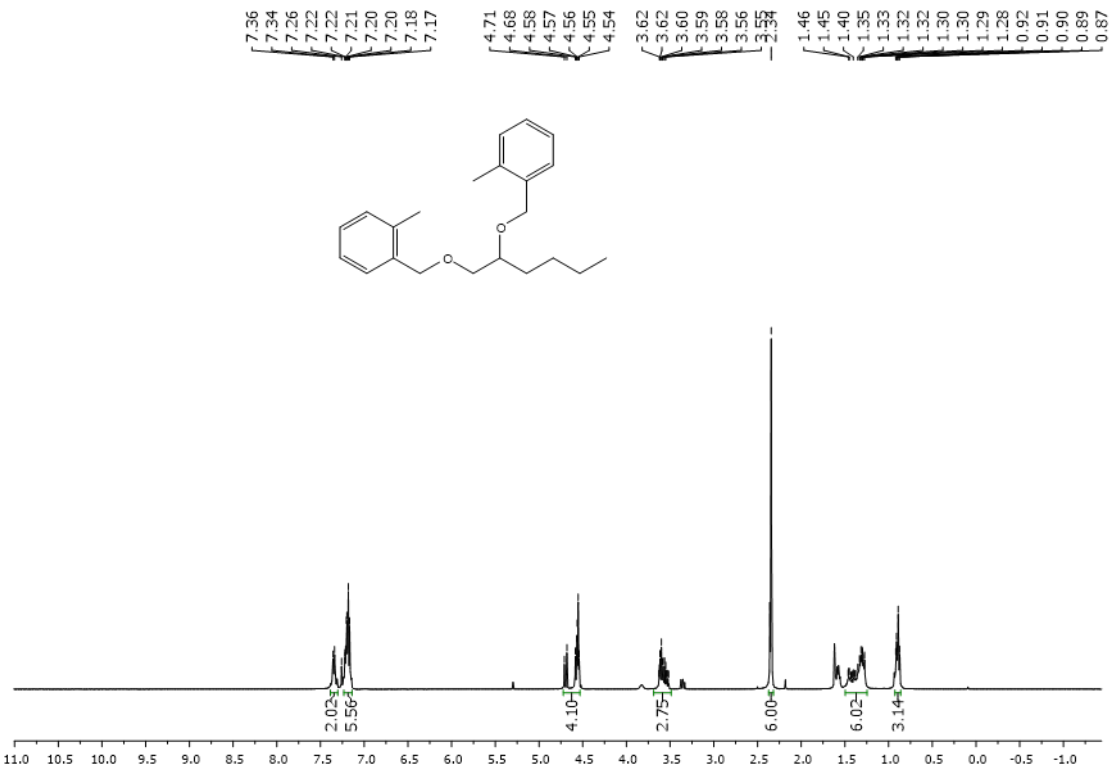


Figure S41: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1,2-bis((2-methylbenzyl)oxy)hexane

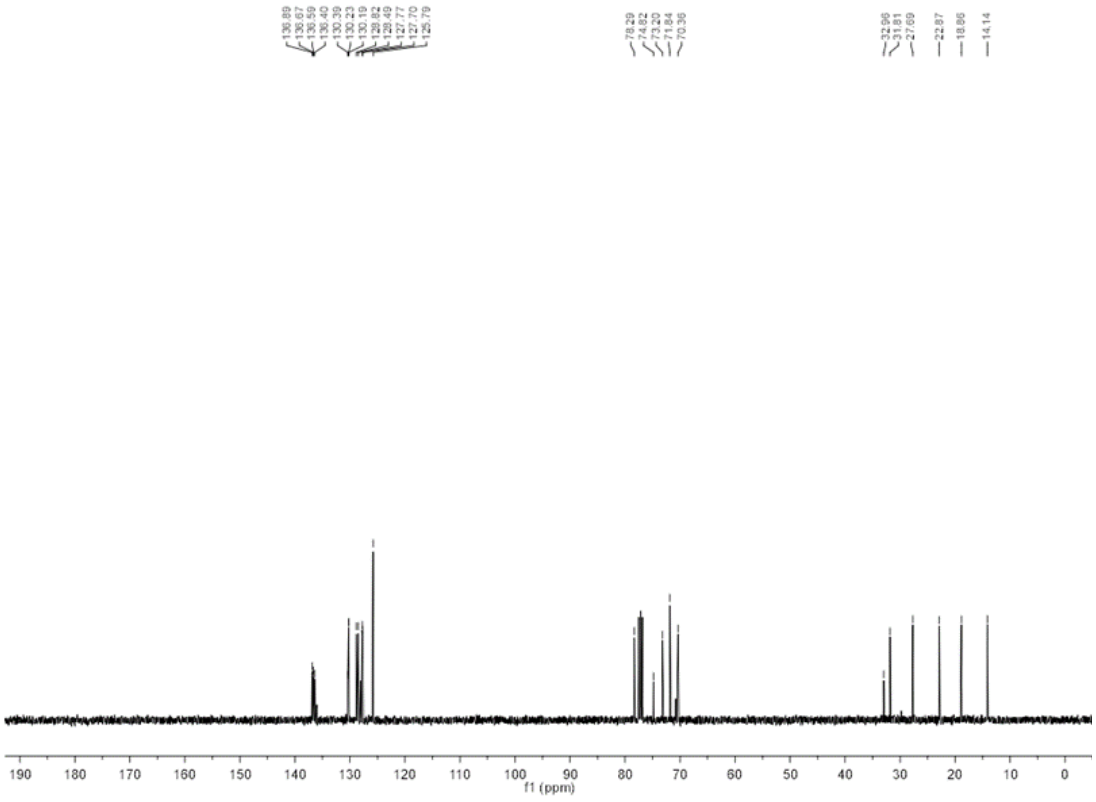


Figure S42: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 1,2-bis((2-methylbenzyl)oxy)hexane

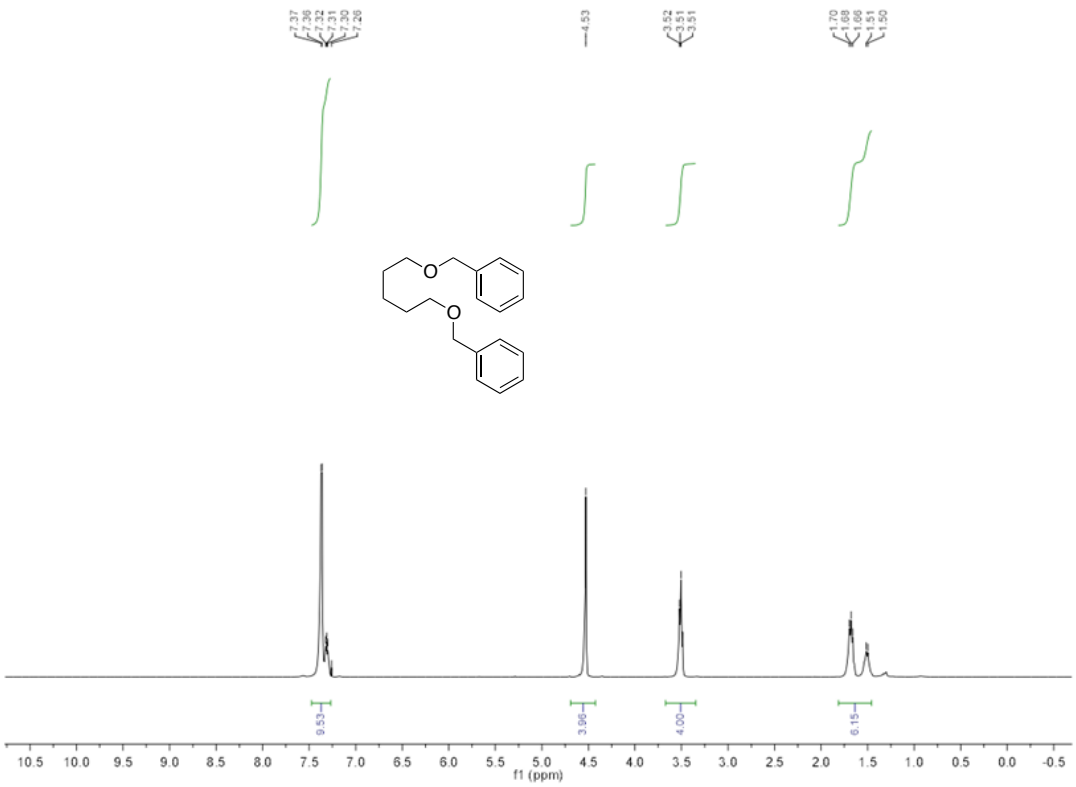


Figure S43: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1,5-bis(benzyloxy)pentane

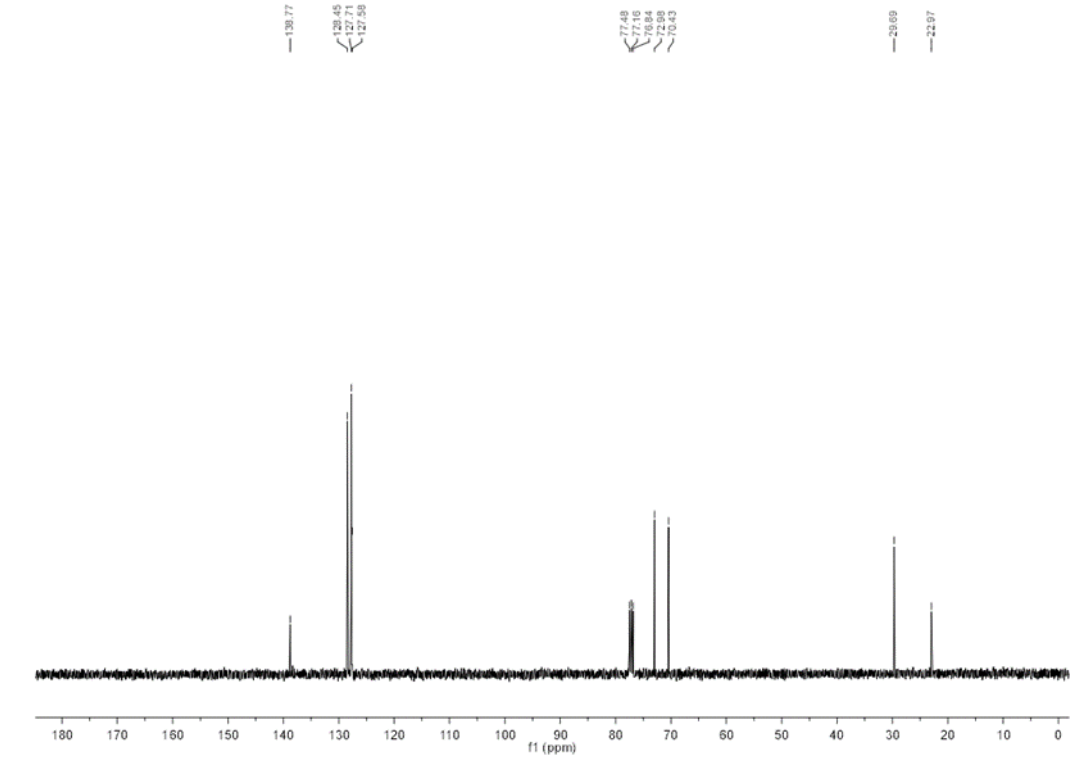


Figure S44: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 1,5-bis(benzyloxy)pentane

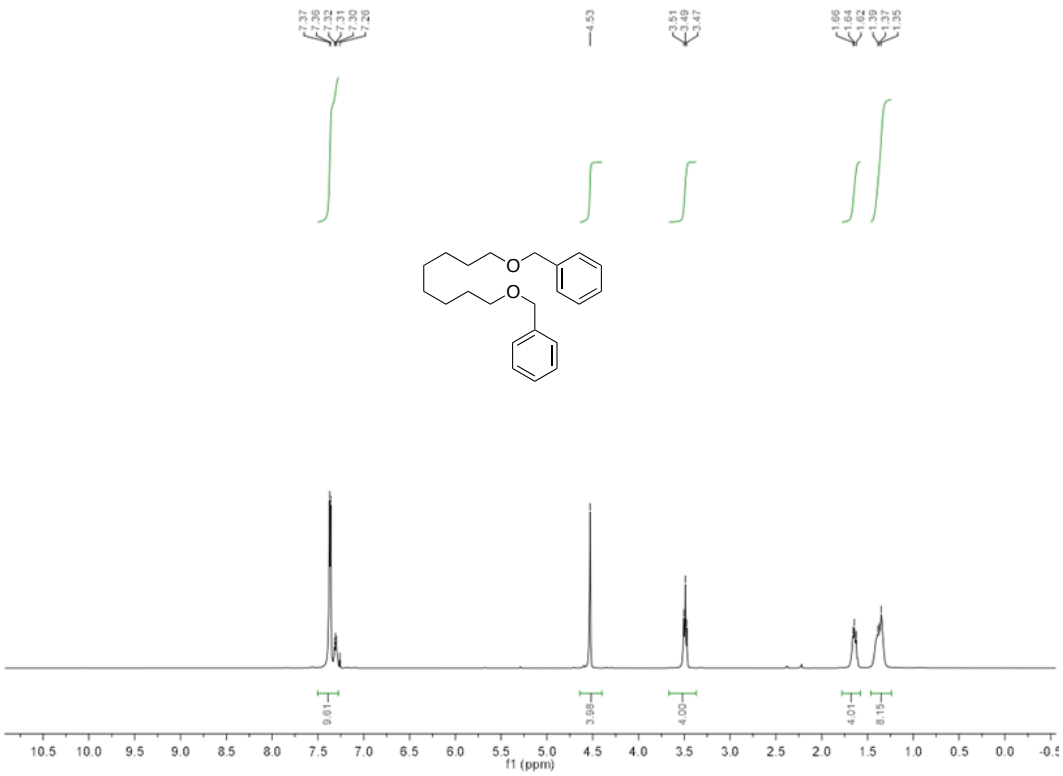


Figure S45: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1,8-bis(benzyloxy)octane

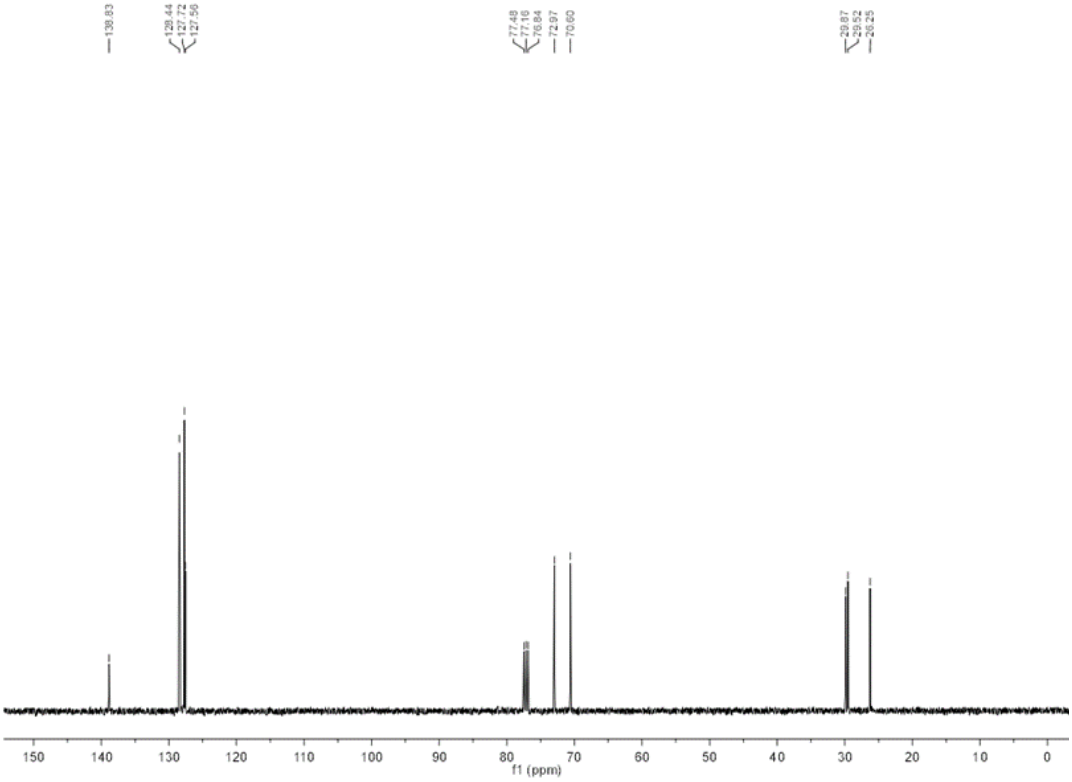


Figure S46: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 1,8-bis(benzyloxy)octane

17. NMR spectra of isolated methyl ether derivatives

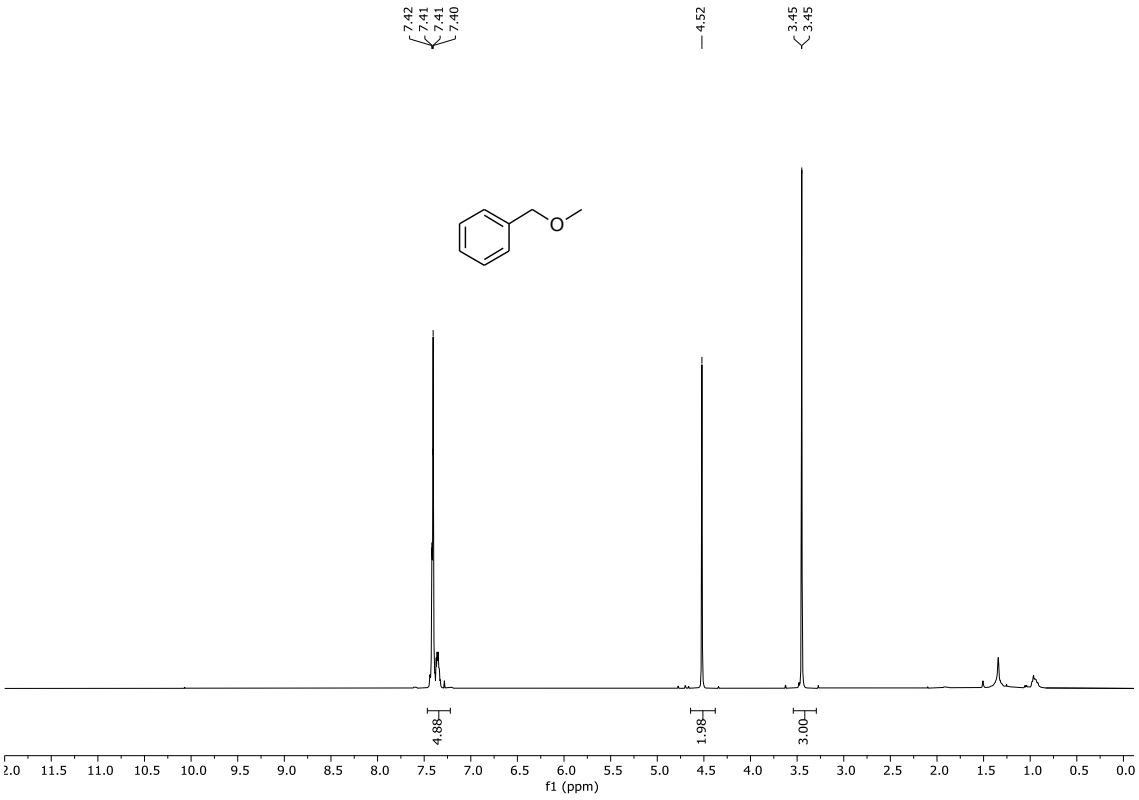


Figure S47: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of (methoxymethyl)benzene

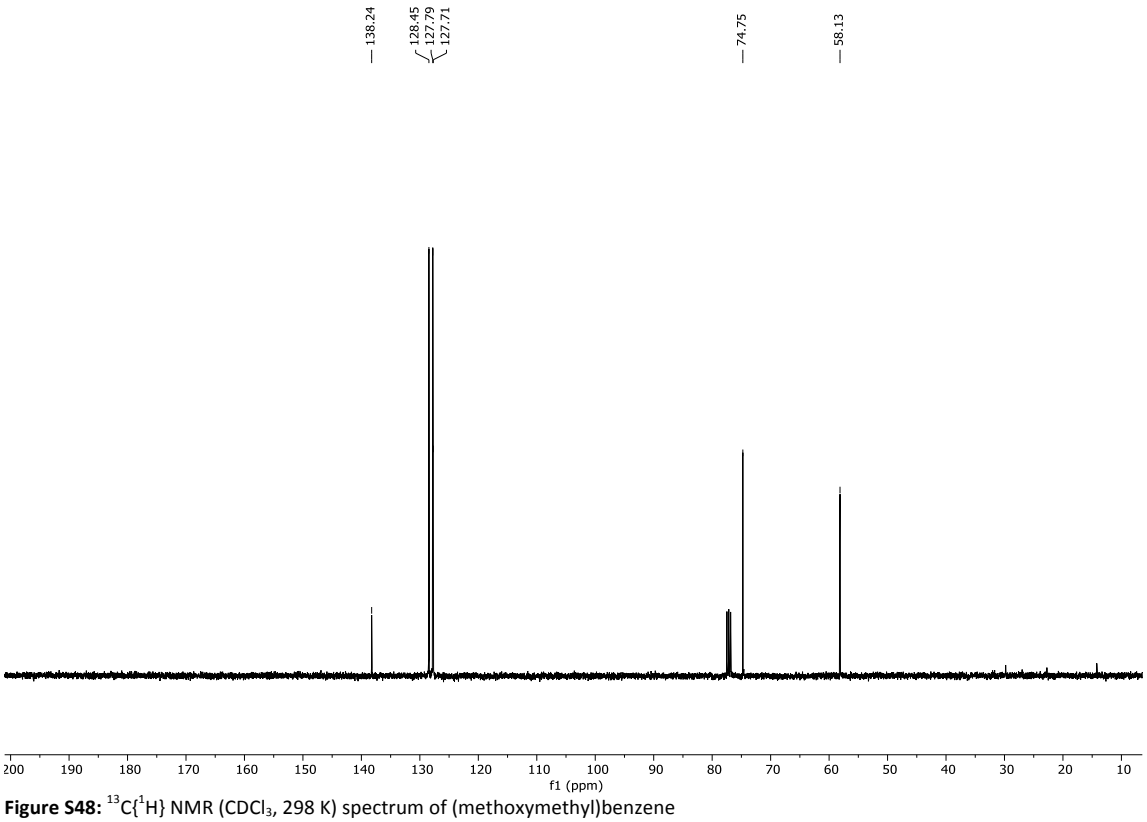


Figure S48: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of (methoxymethyl)benzene

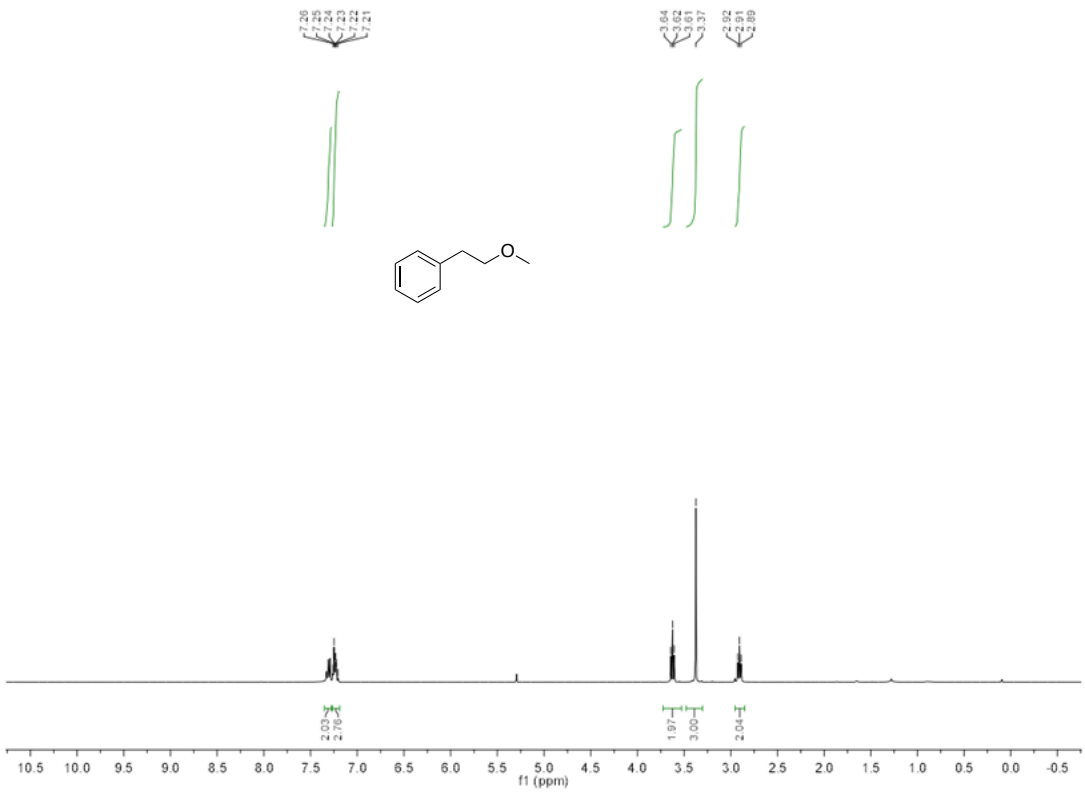


Figure S49: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of (2-methoxyethyl)benzene

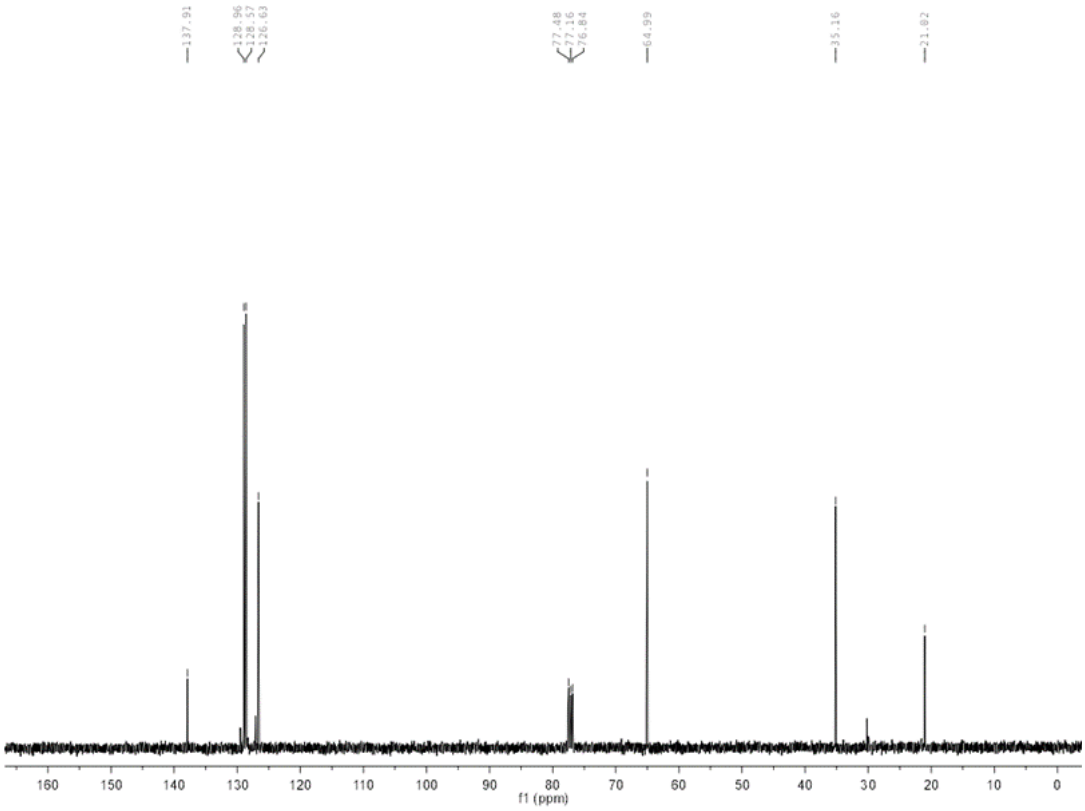


Figure S50: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of (2-methoxyethyl)benzene

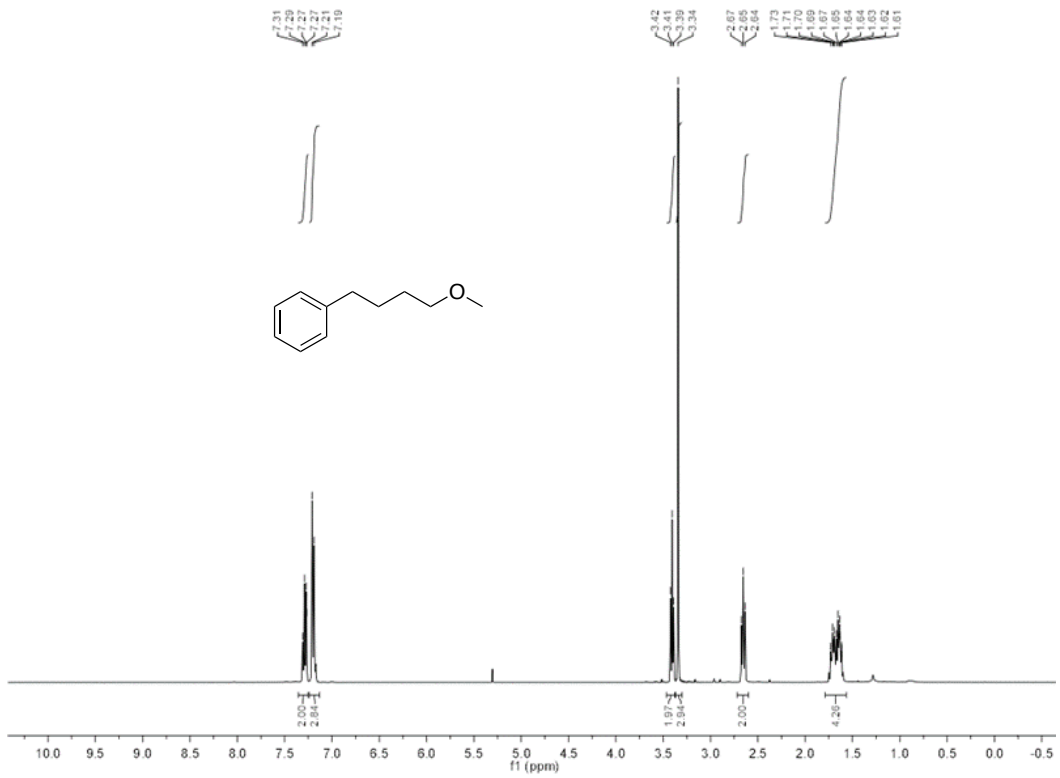


Figure S51: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of (4-methoxybutyl)benzene

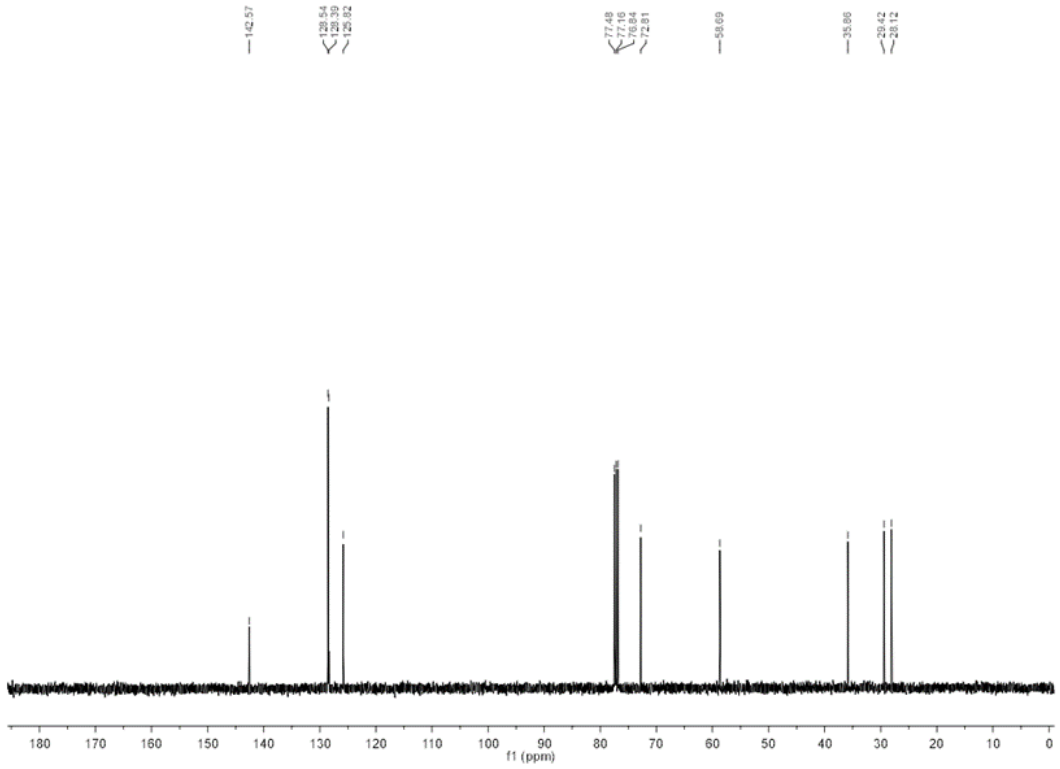


Figure S52: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of (4-methoxybutyl)benzene

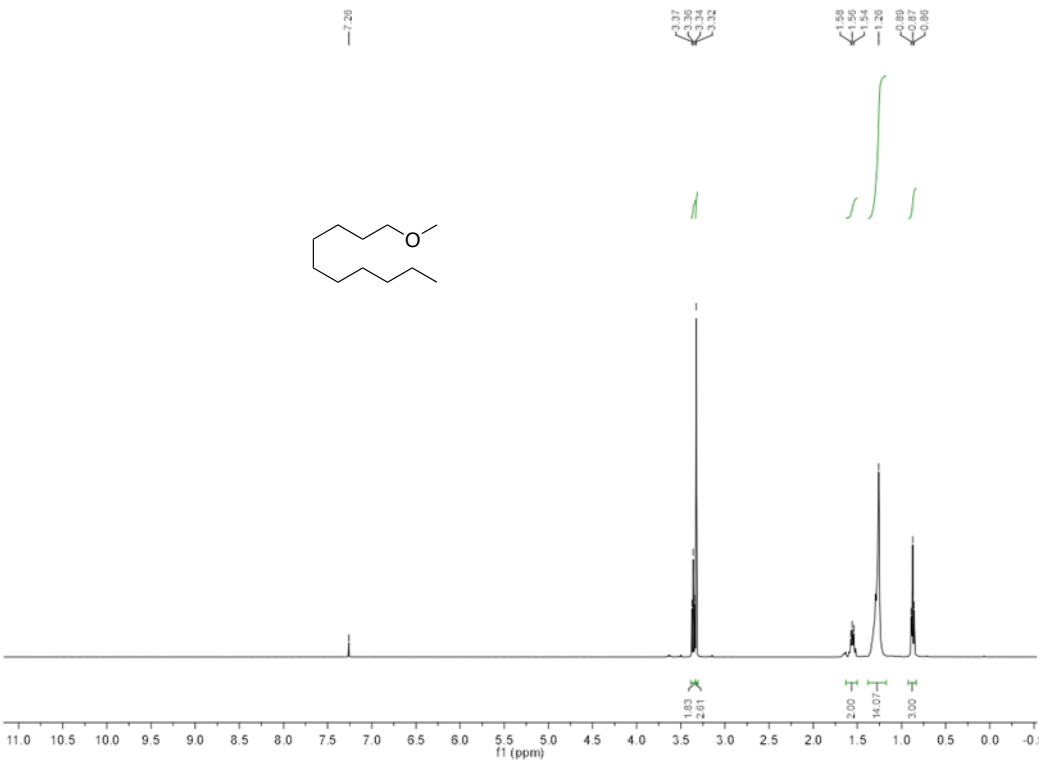


Figure S53: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1-methoxydecane

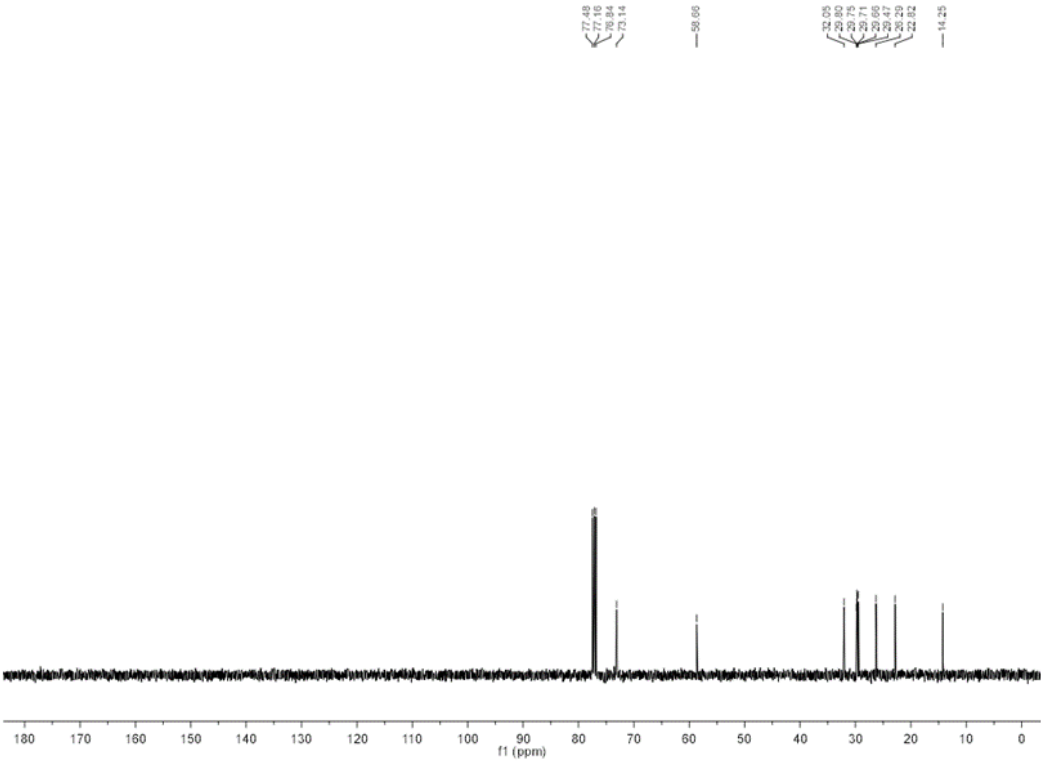


Figure S54: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 1-methoxydecane

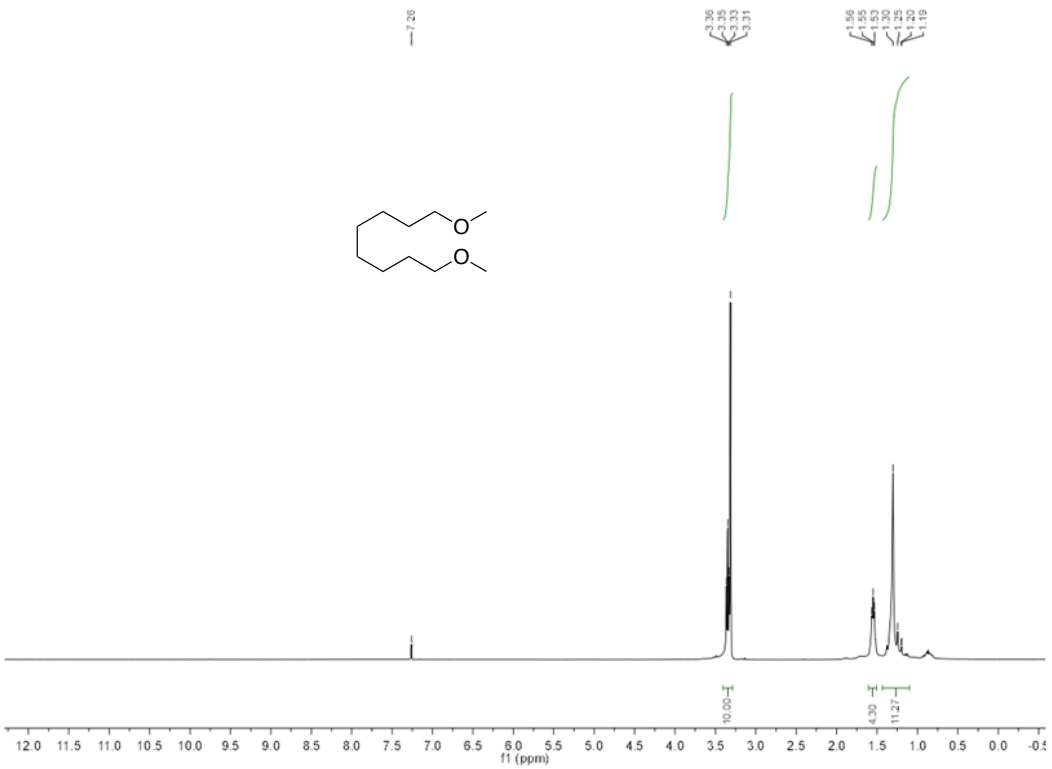


Figure S55: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1,8-dimethoxyoctane

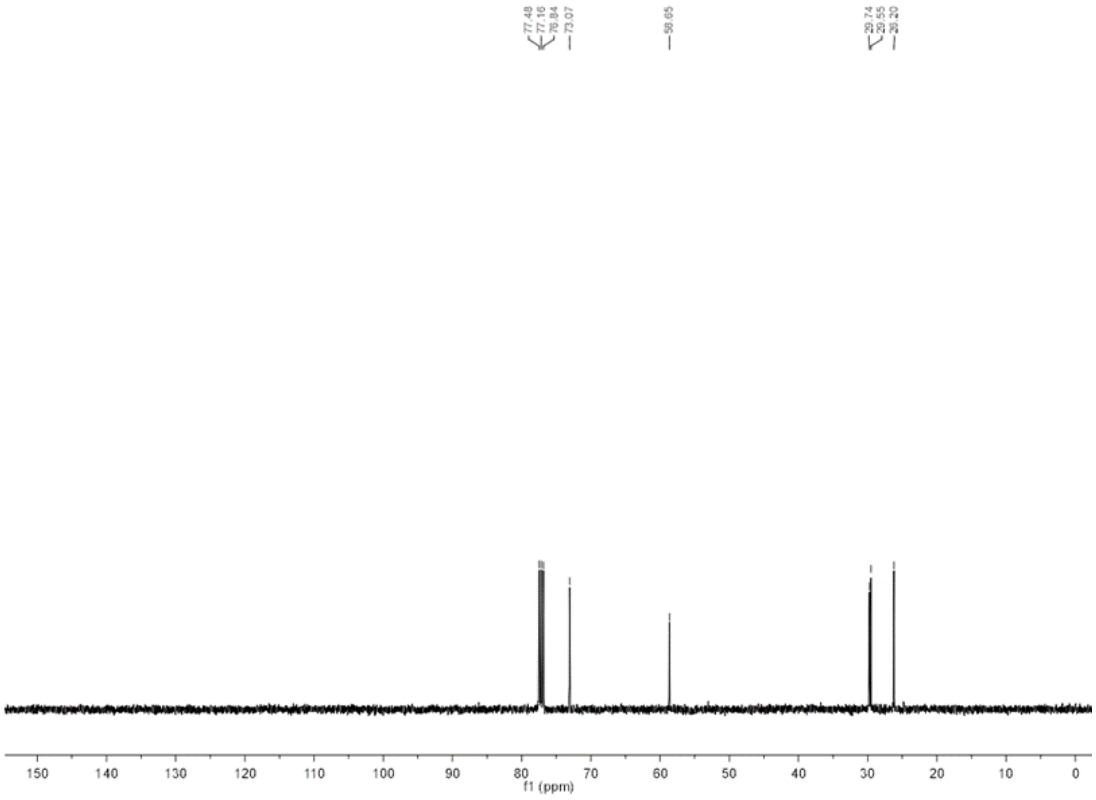


Figure S56: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 1,8-dimethoxyoctane

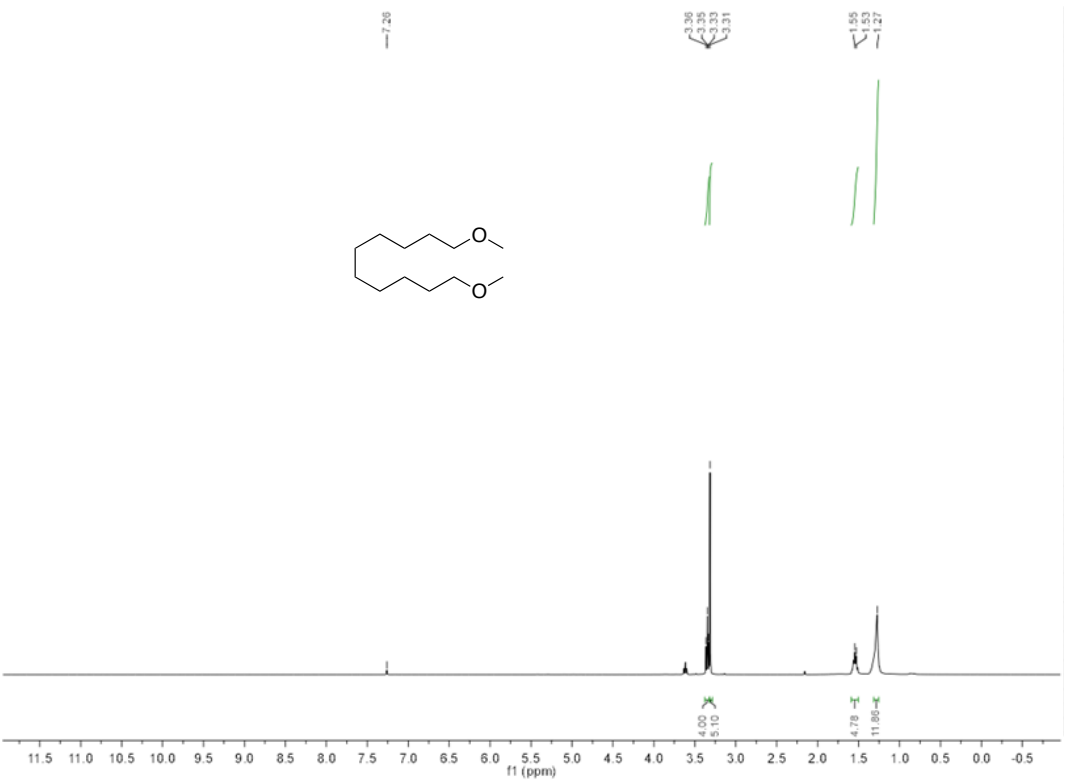


Figure S57: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1,10-dimethoxydecane

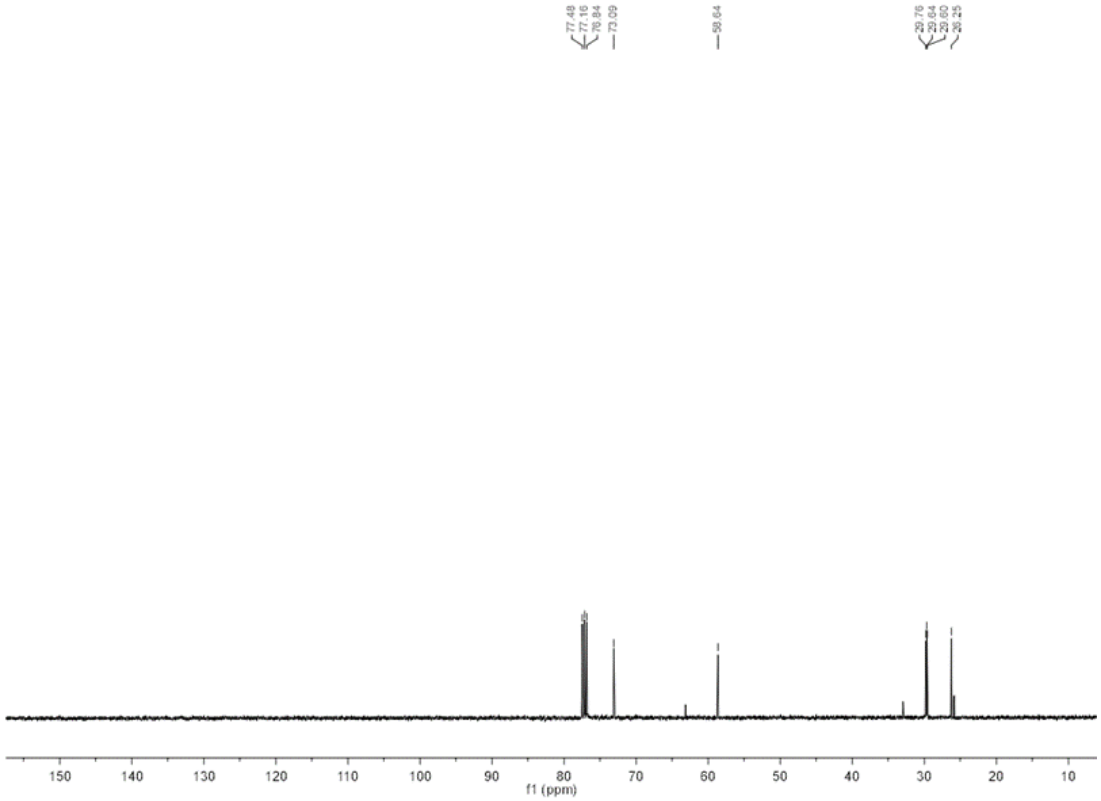


Figure S58: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 1,10-dimethoxydecane

18. ^{1}H NMR reaction mixture spectra for the hydrobonolysis of ethers

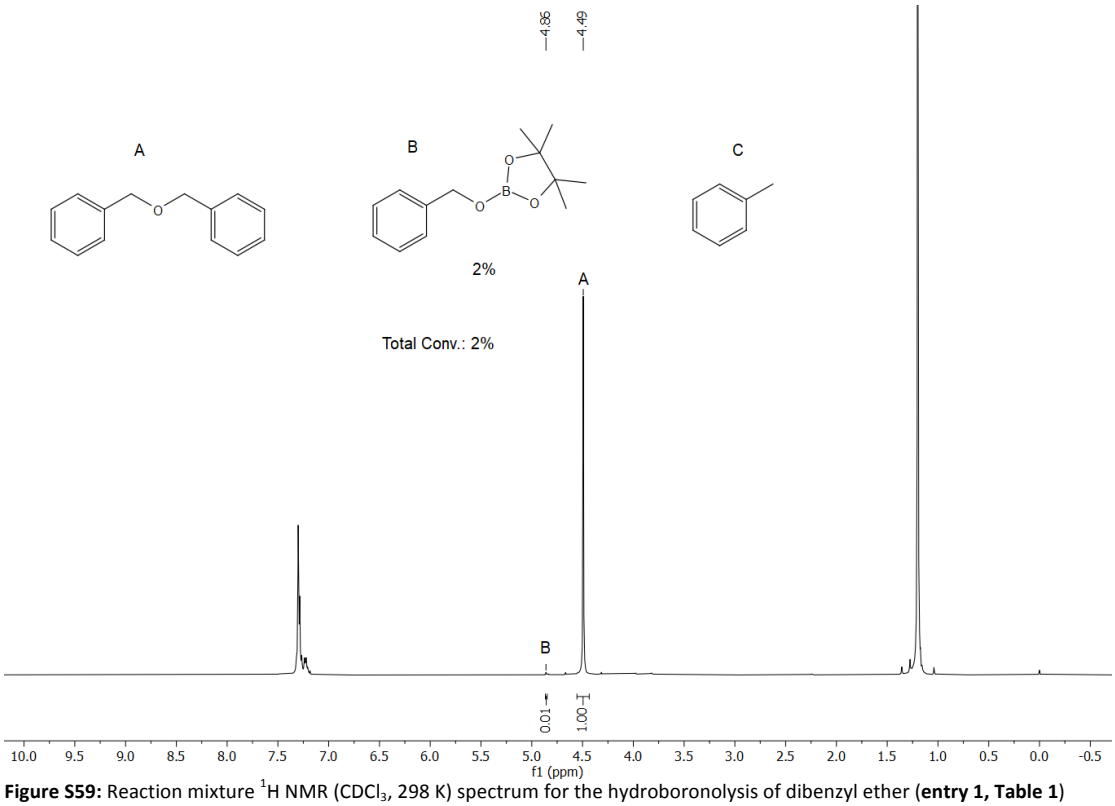


Figure S59: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of dibenzyl ether (**entry 1, Table 1**)

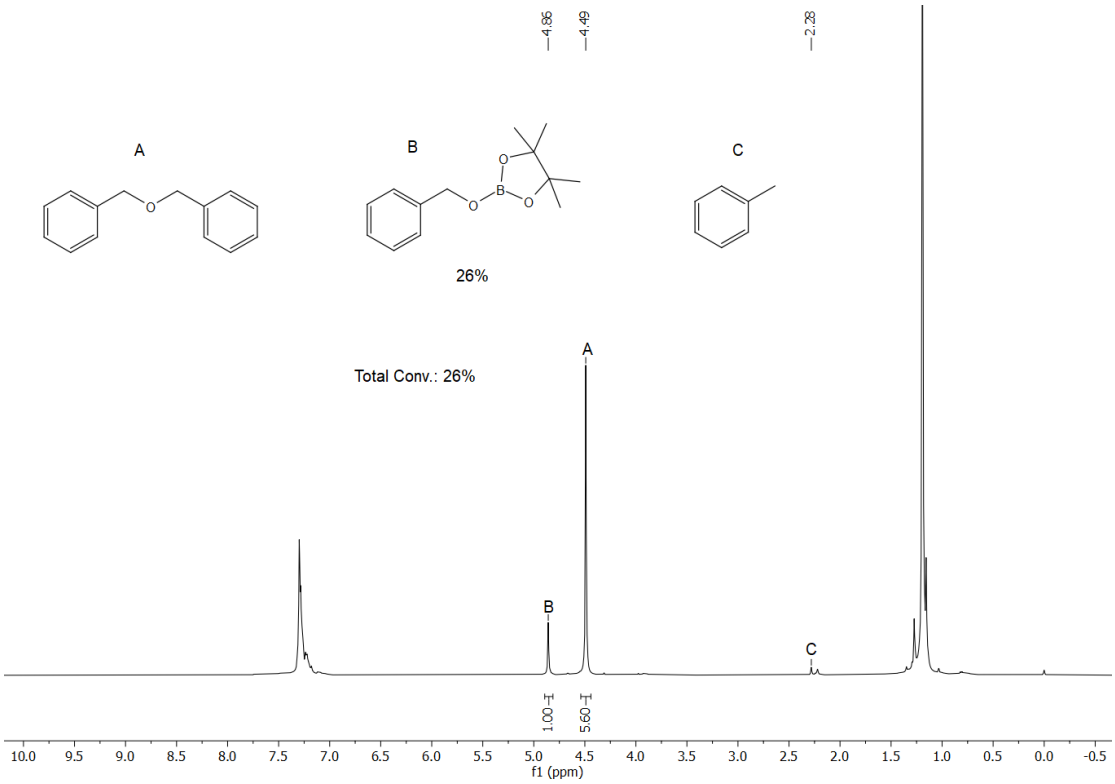


Figure S60: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of dibenzyl ether **(entry 2, Table 1)**

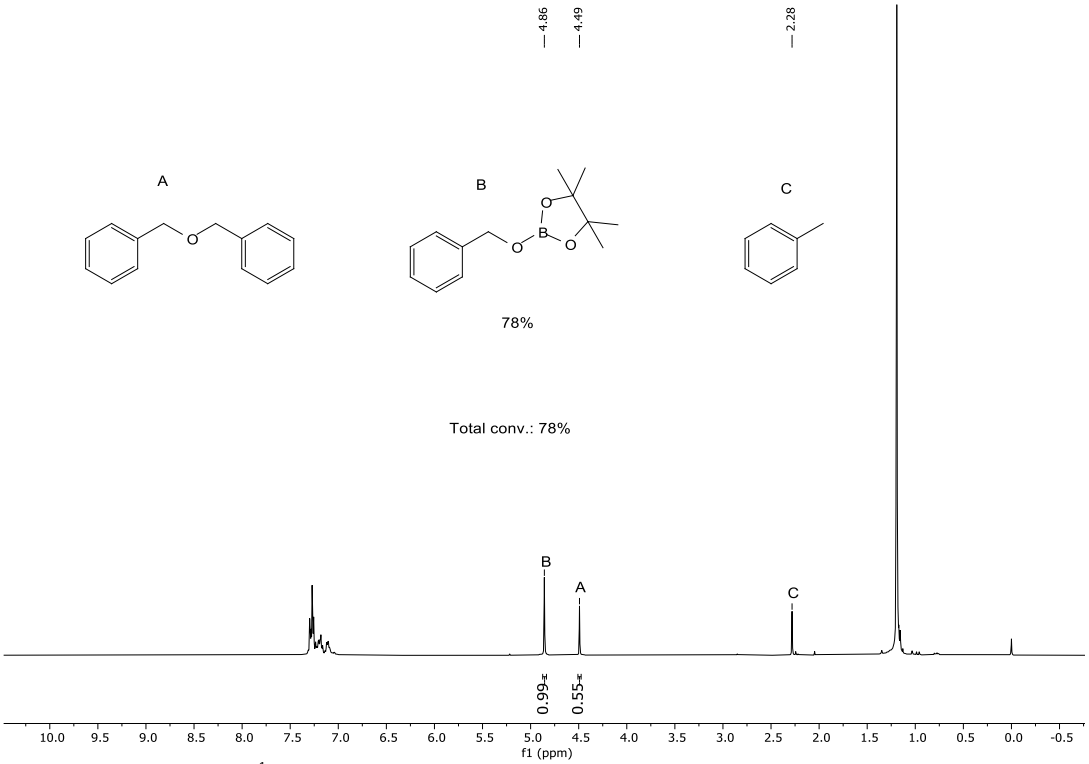


Figure S61: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of dibenzyl ether (**entry 3, Table 1**)

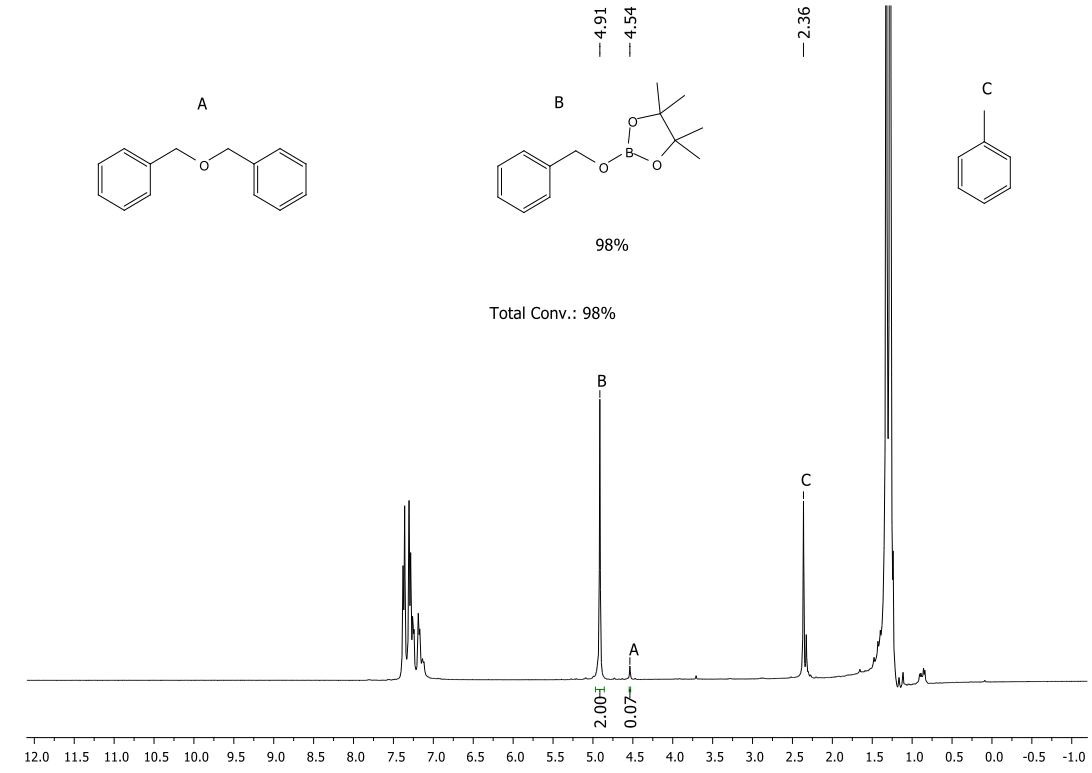


Figure S62: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of dibenzyl ether (2 mol% catalyst) (**entry 4, Table 1**) (**entry 1, Table 2**)[32]

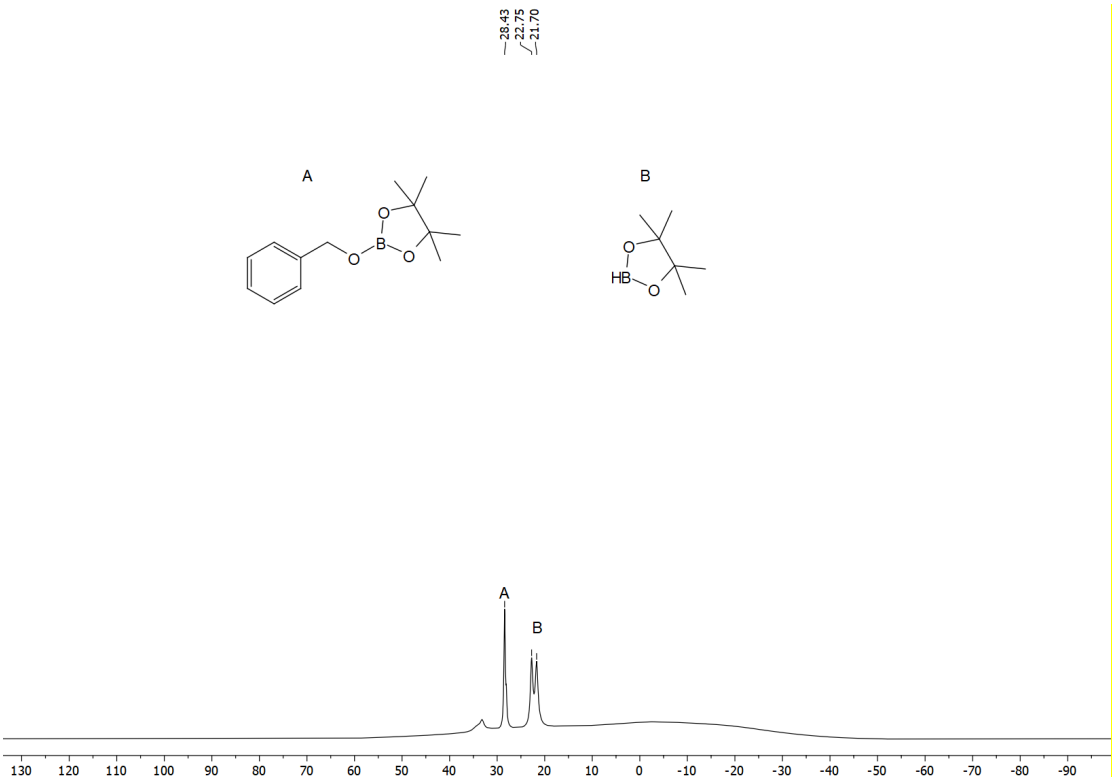


Figure S63: Reaction mixture ^{11}B (tol-d8, 298 K) spectrum for the hydroboronolysis of dibenzyl ether (2 mol% catalyst) **(entry 4, Table 1) (entry 1, Table 2)**[32]

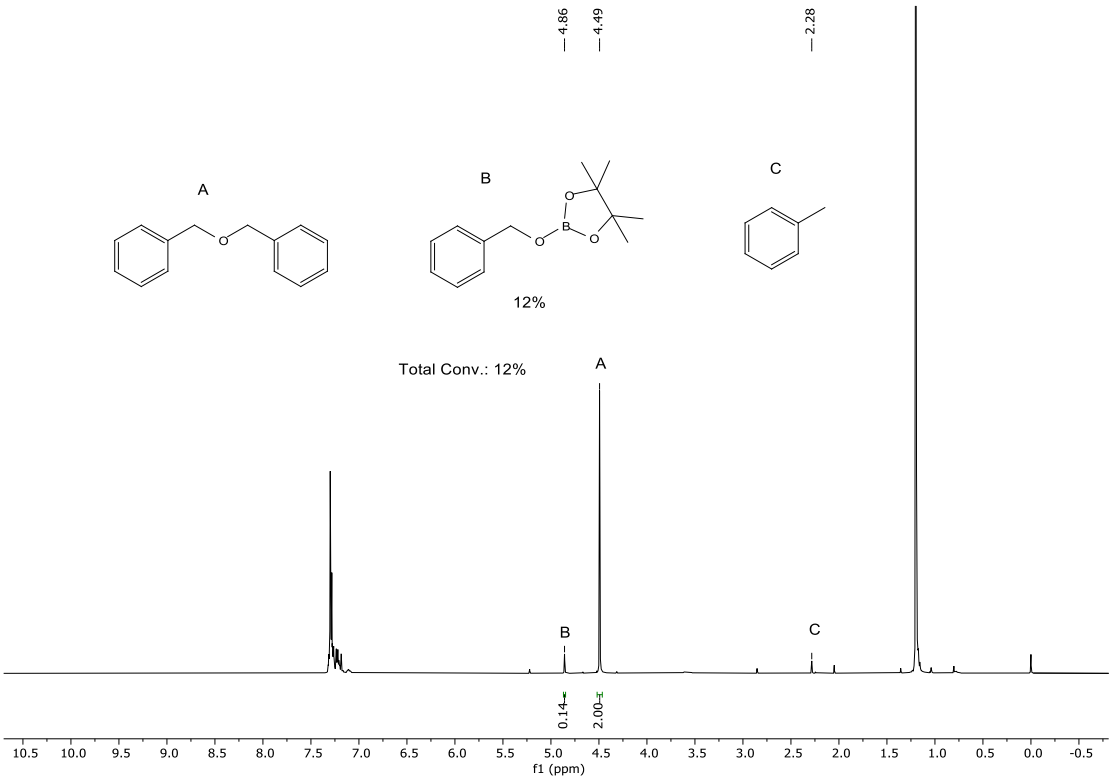


Figure S64: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of dibenzyl ether (**entry 5, Table 1**)

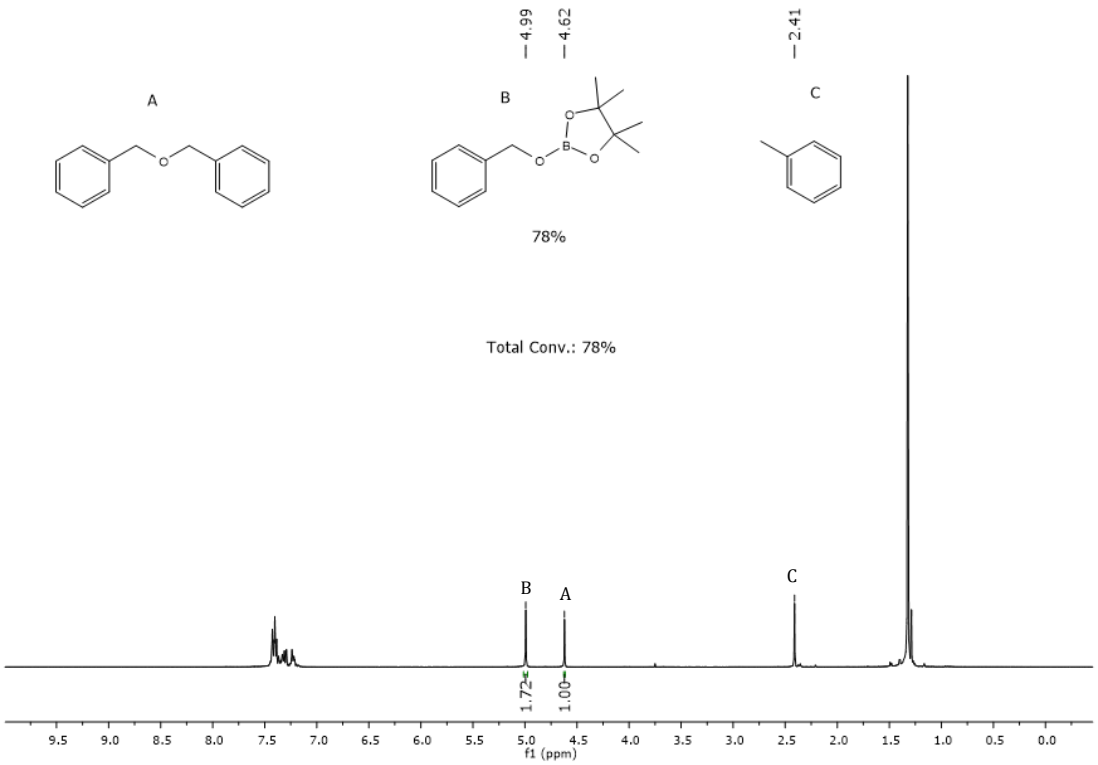


Figure S65: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of dibenzyl ether (**entry 6, Table 1**)

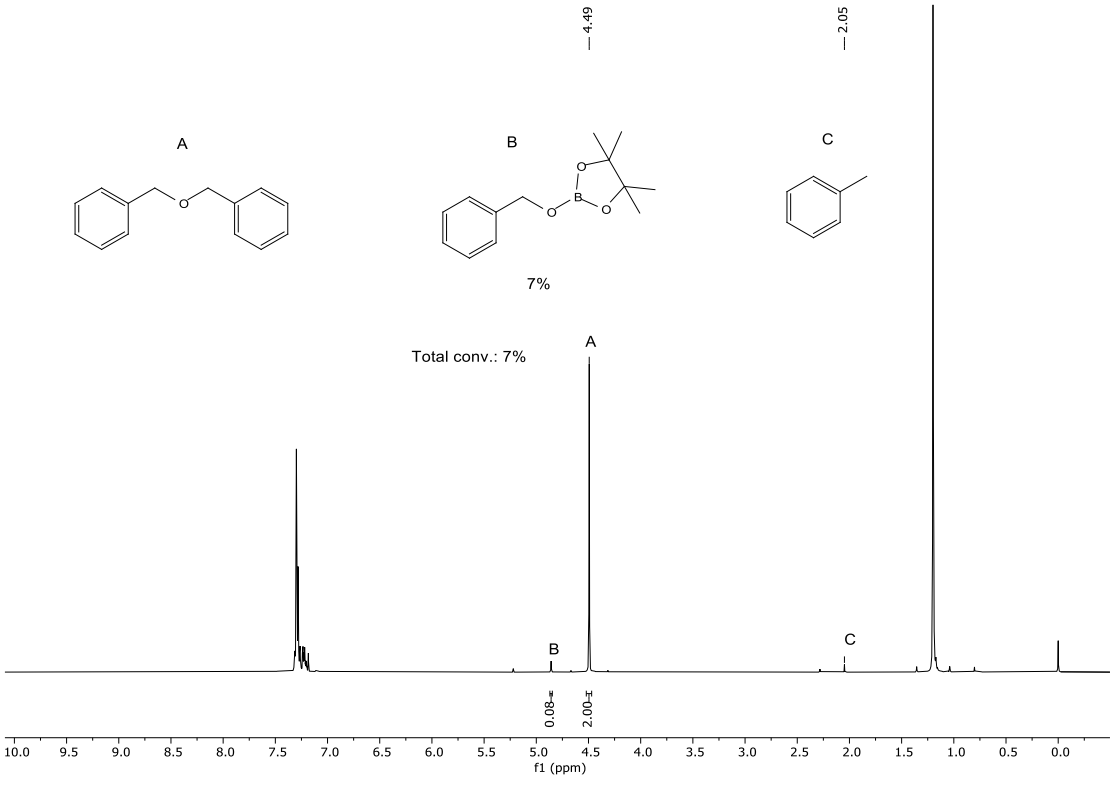


Figure S66*:* Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of dibenzyl ether (**entry 7, Table 1**)

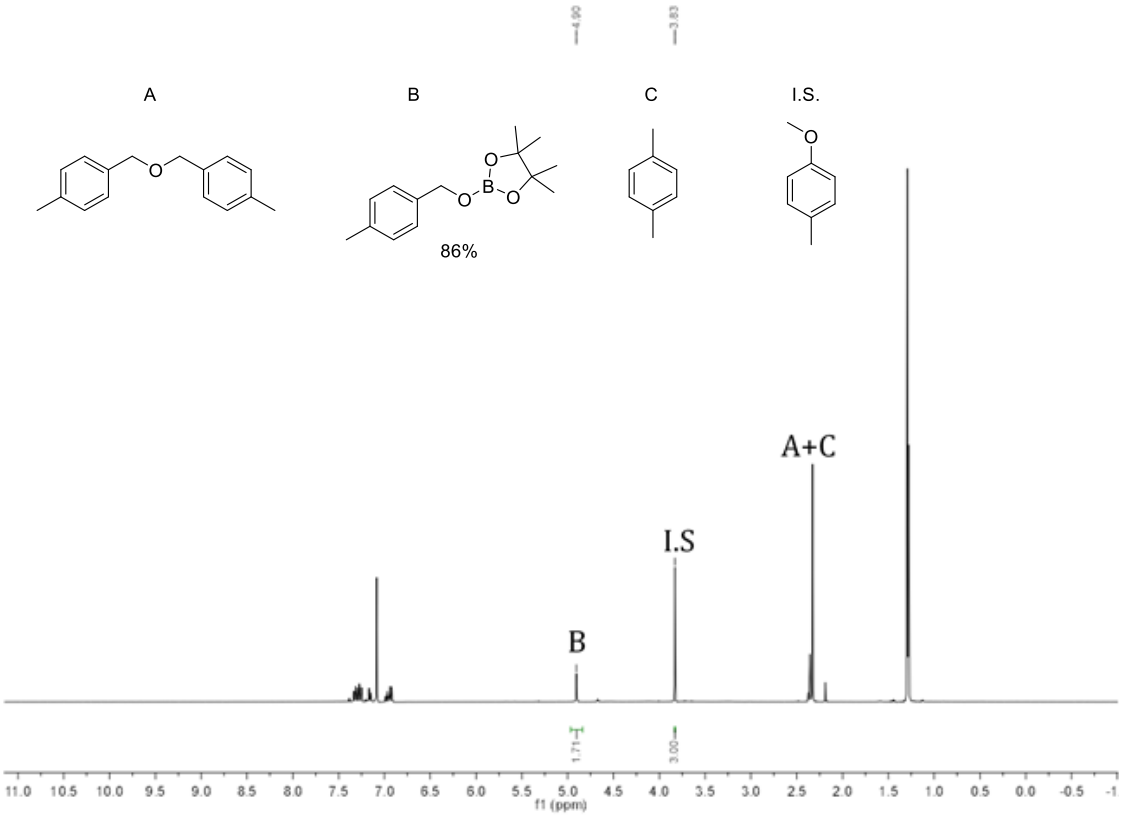


Figure S67: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 4,4'-(oxybis(methylene))bis(methylbenzene) **(entry 2, Table 2)**[33]

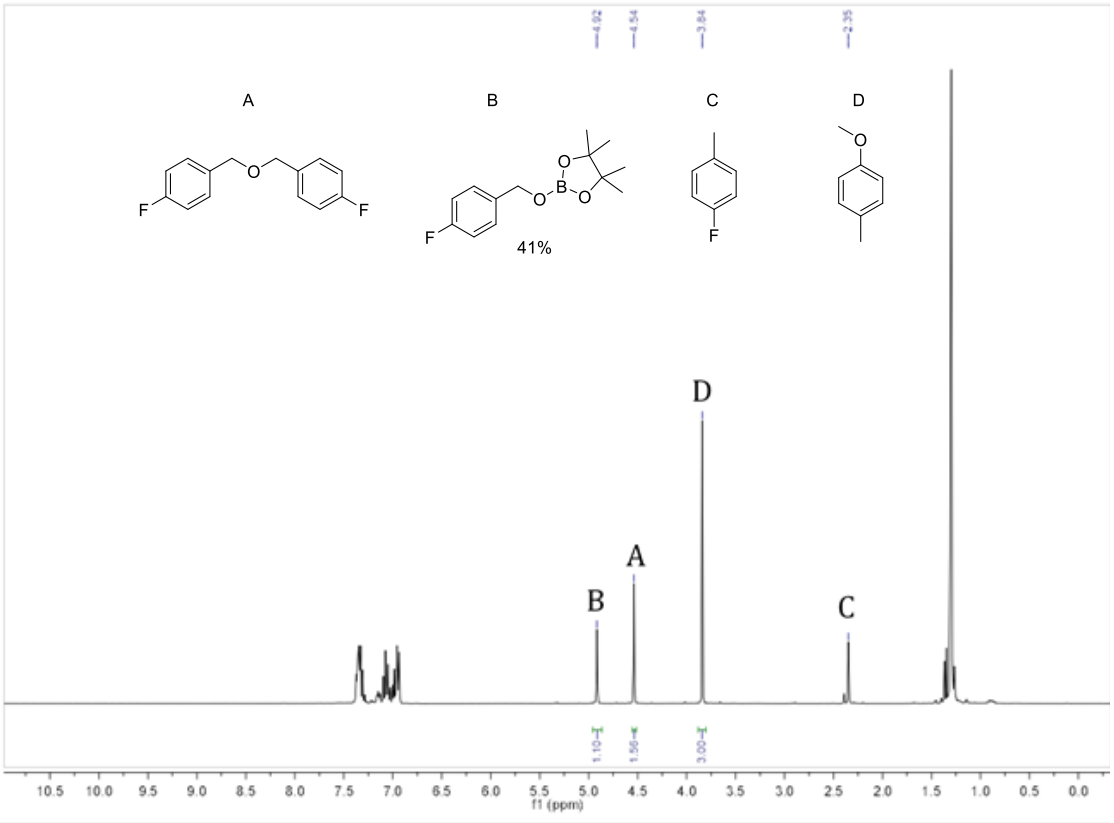


Figure S68: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 4,4'-(oxybis(methylene))bis(fluorobenzene) **(entry 3, Table 2)**[34]

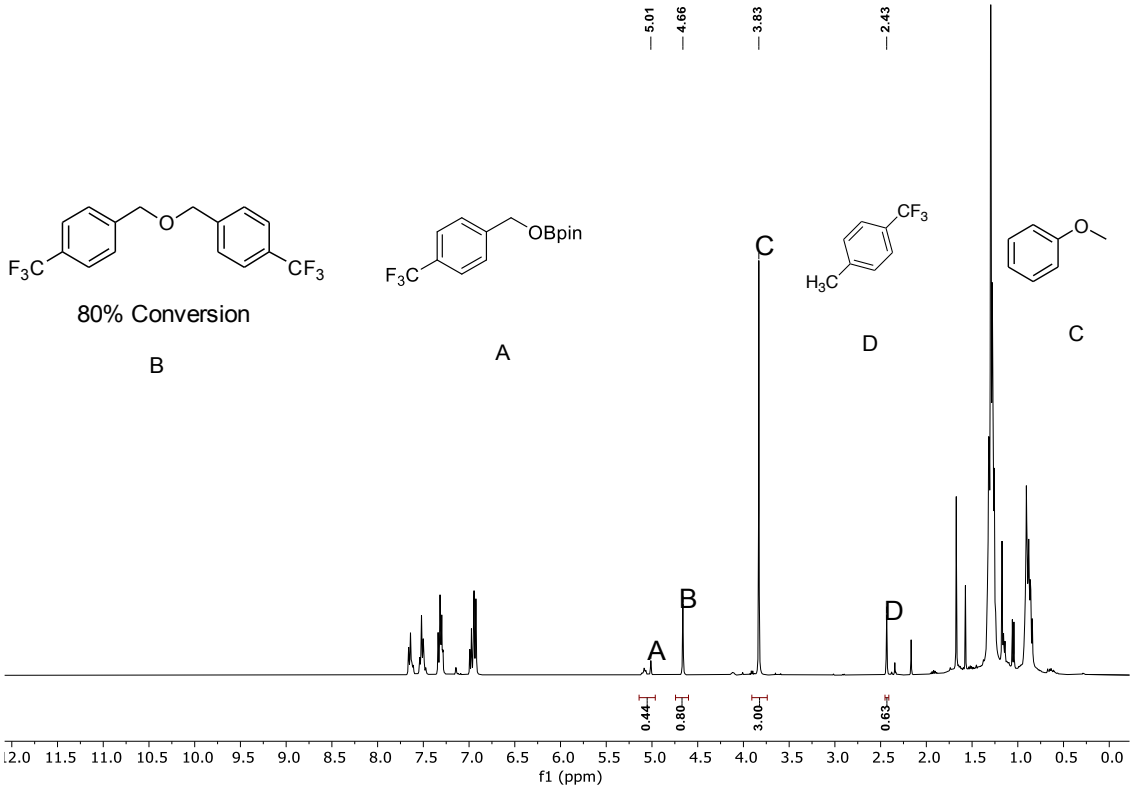


Figure S69: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 4,4'-(oxybis(methylene))bis((trifluoromethyl)benzene) **(entry 4, Table 2)**[35]

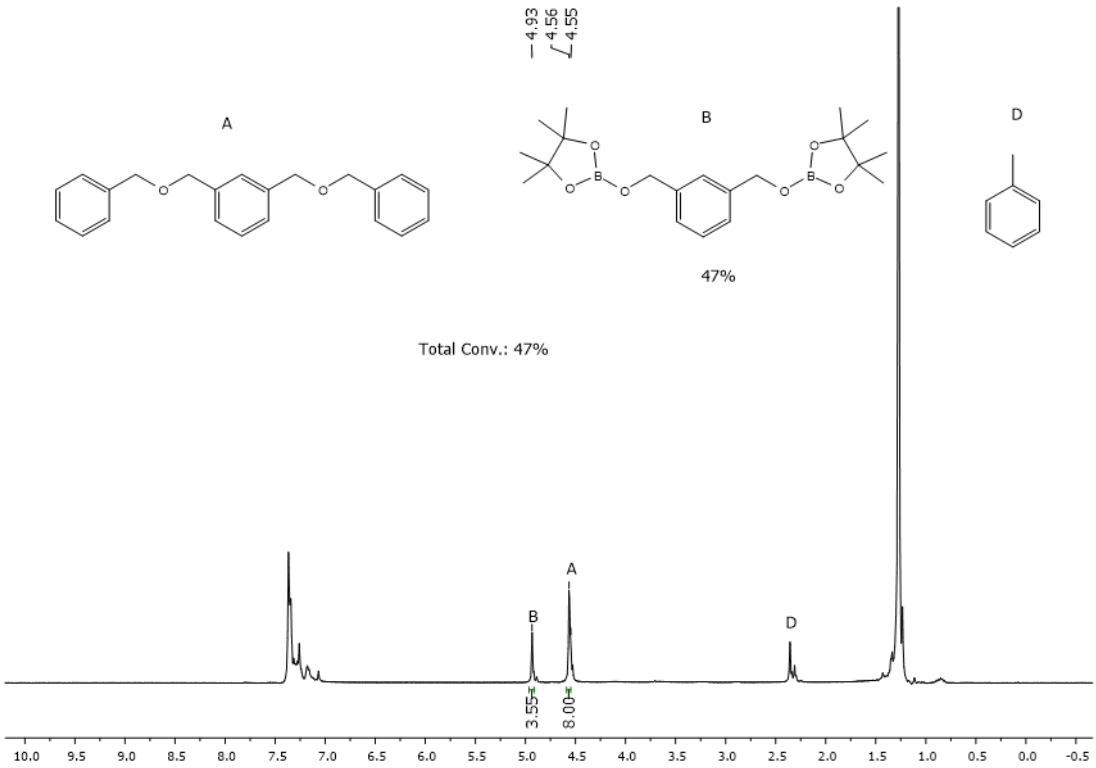


Figure S70: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1,3-bis((benzyloxy)methyl)benzene **(entry 5, Table 2).**[36]

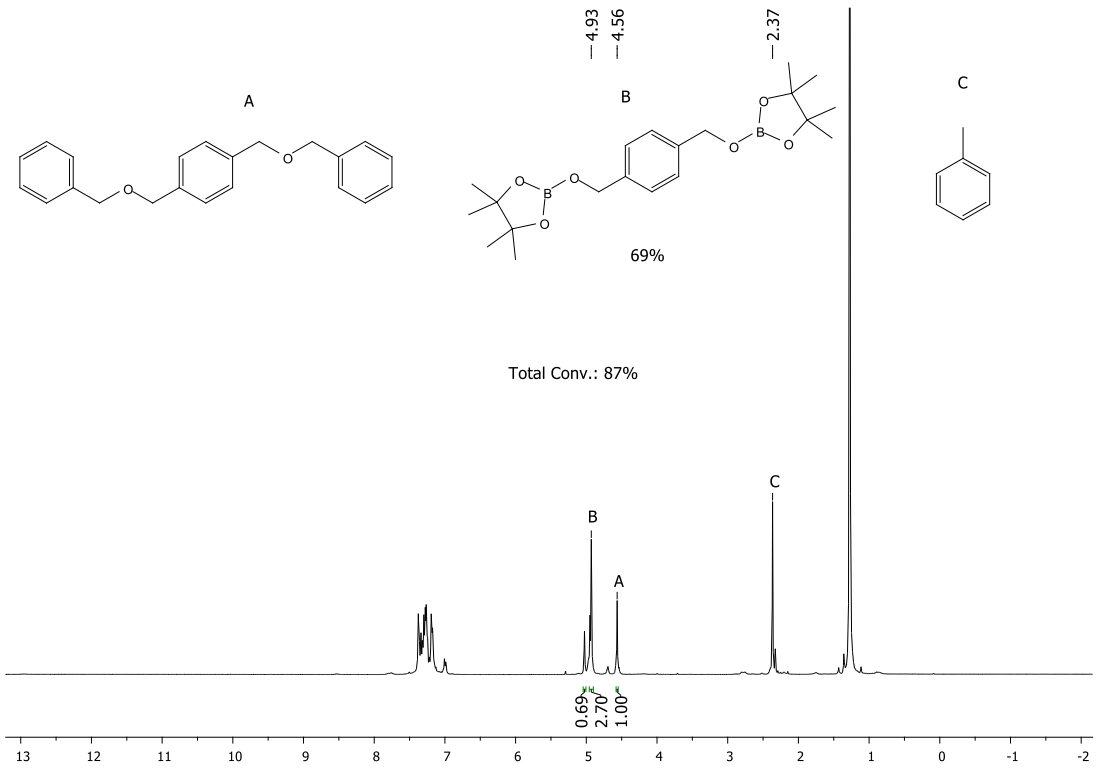


Figure S71: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1,4-bis((benzyloxy)methyl)benzene **(entry 6, Table 2)**.[37]

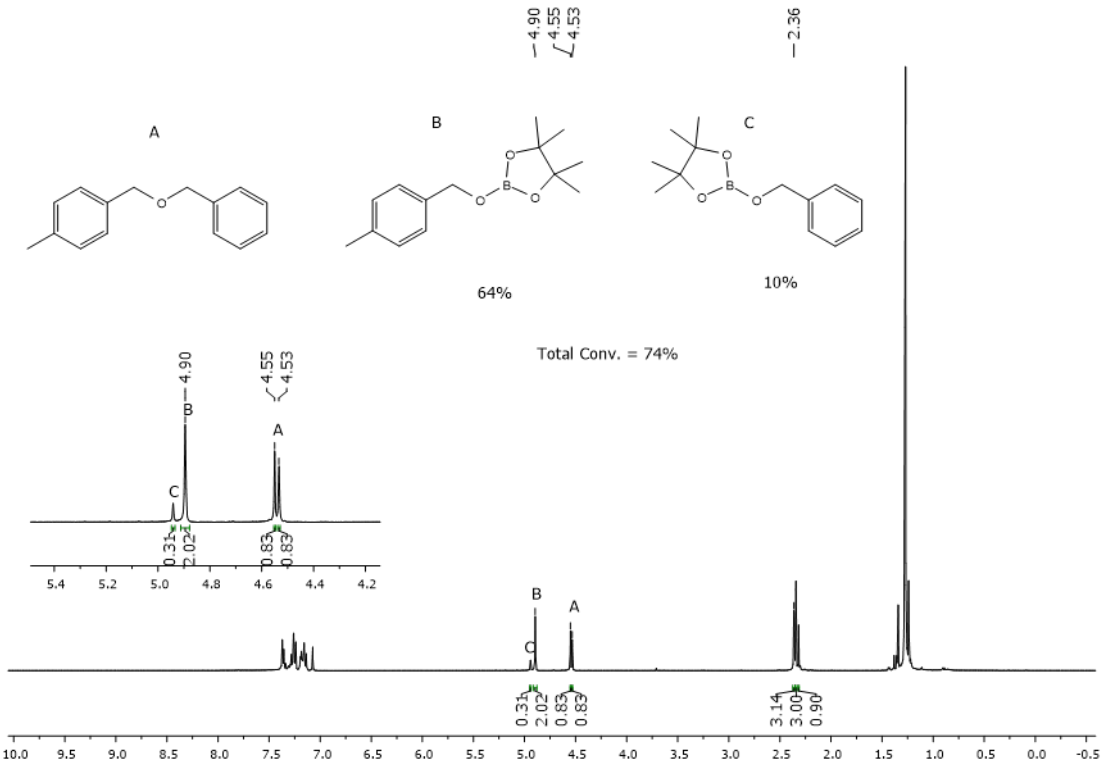


Figure S72: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1-((benzyloxy)methyl)-4-methylbenzene **(entry 7, Table 2)**

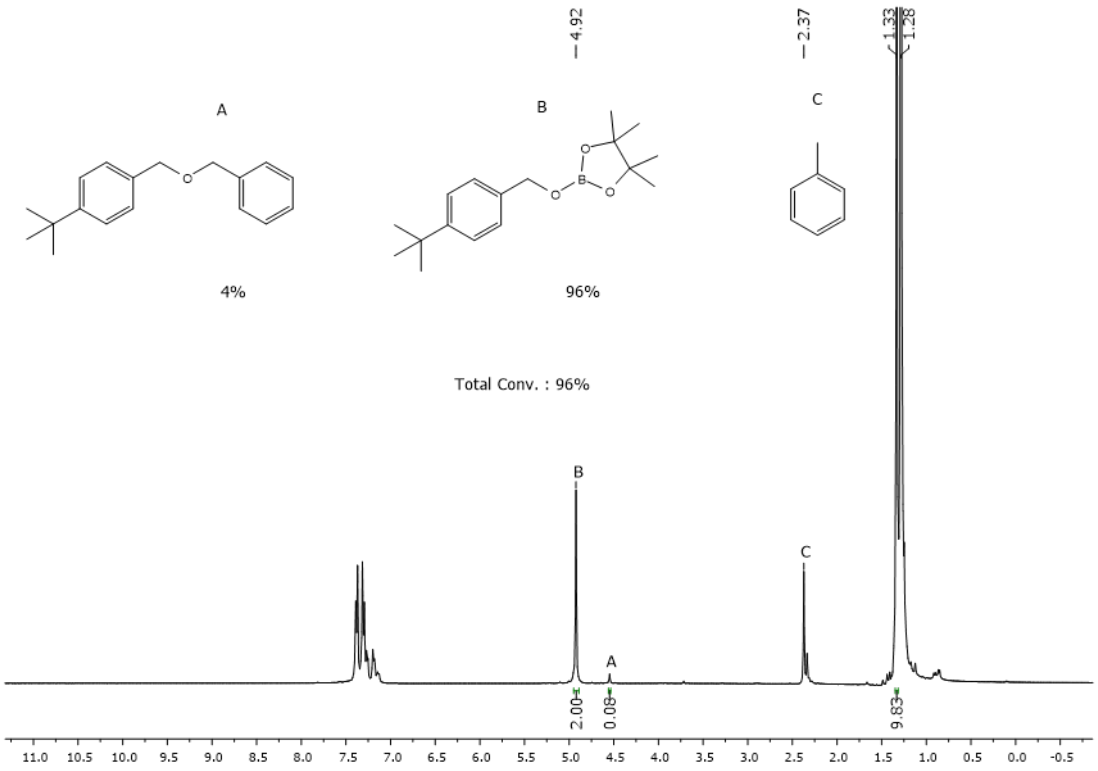


Figure S73: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1-((benzyloxy)methyl)-4-(tert-butyl)benzene **(entry 8, Table 2)**[38]

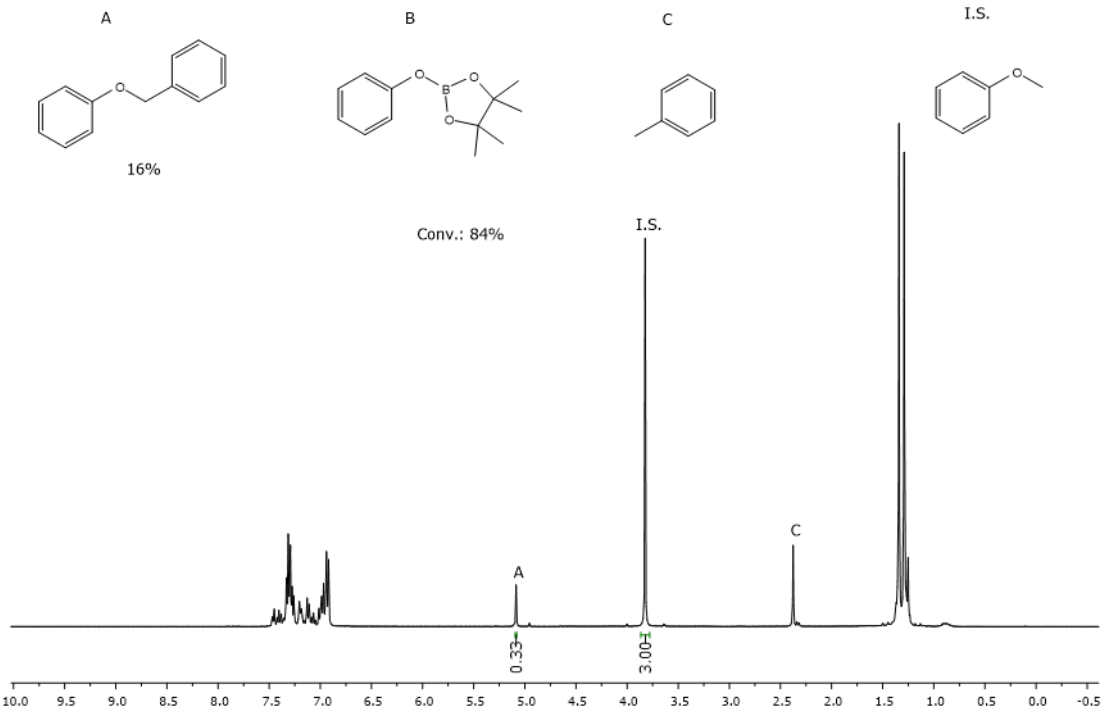


Figure S74: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of (benzyloxy)benzene **(entry 9, Table 2)**[39]

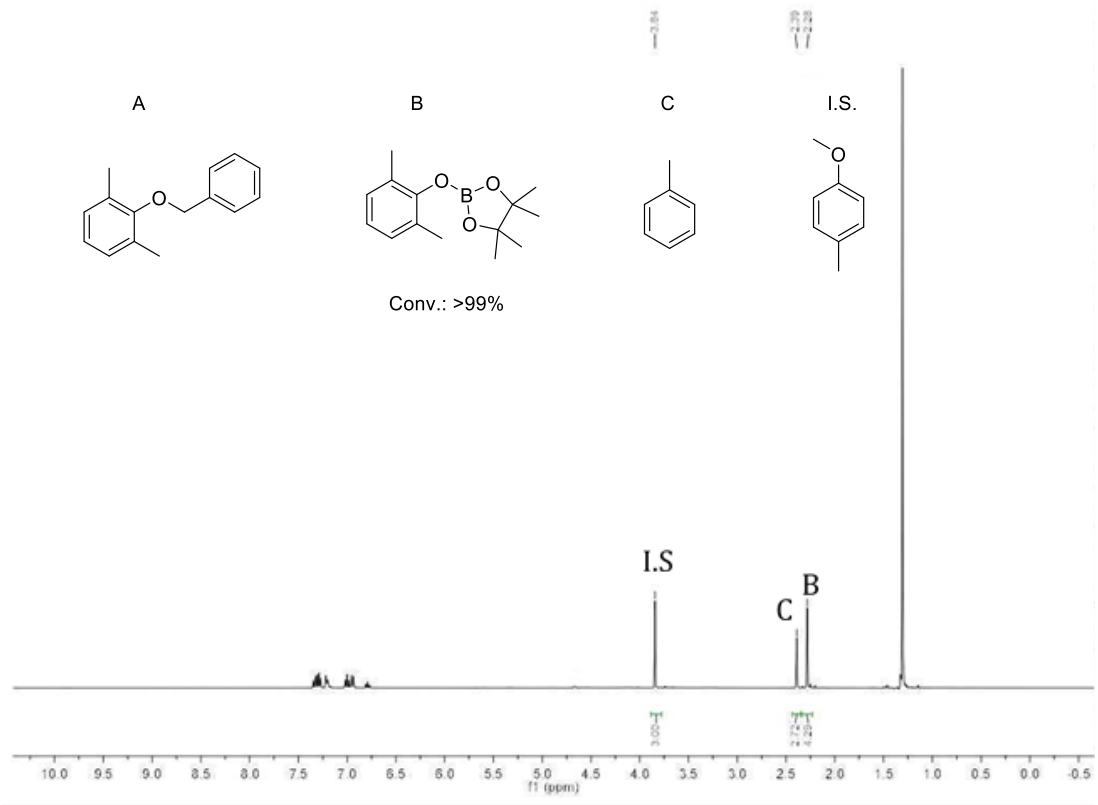


Figure S75: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 2-(benzyloxy)-1,3-dimethylbenzene **(entry 10, Table 2)**[40]

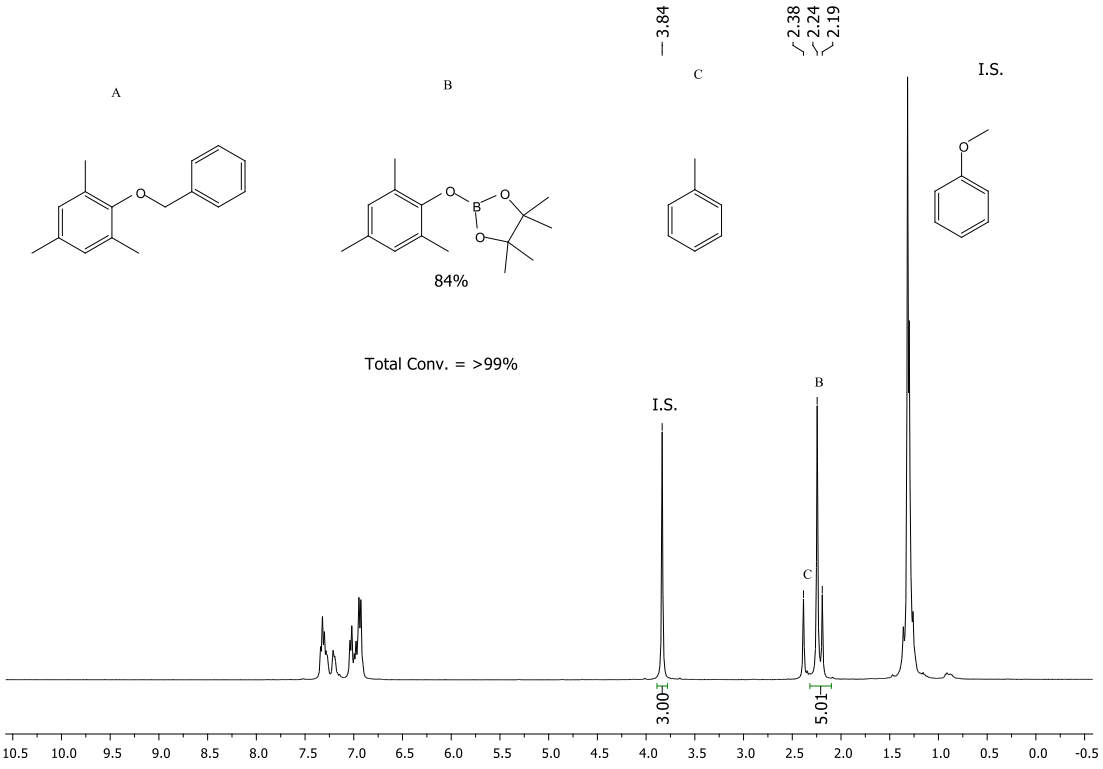


Figure S76: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 2-(benzyloxy)-1,3,5-trimethylbenzene **(entry 11, Table 2)**[24]

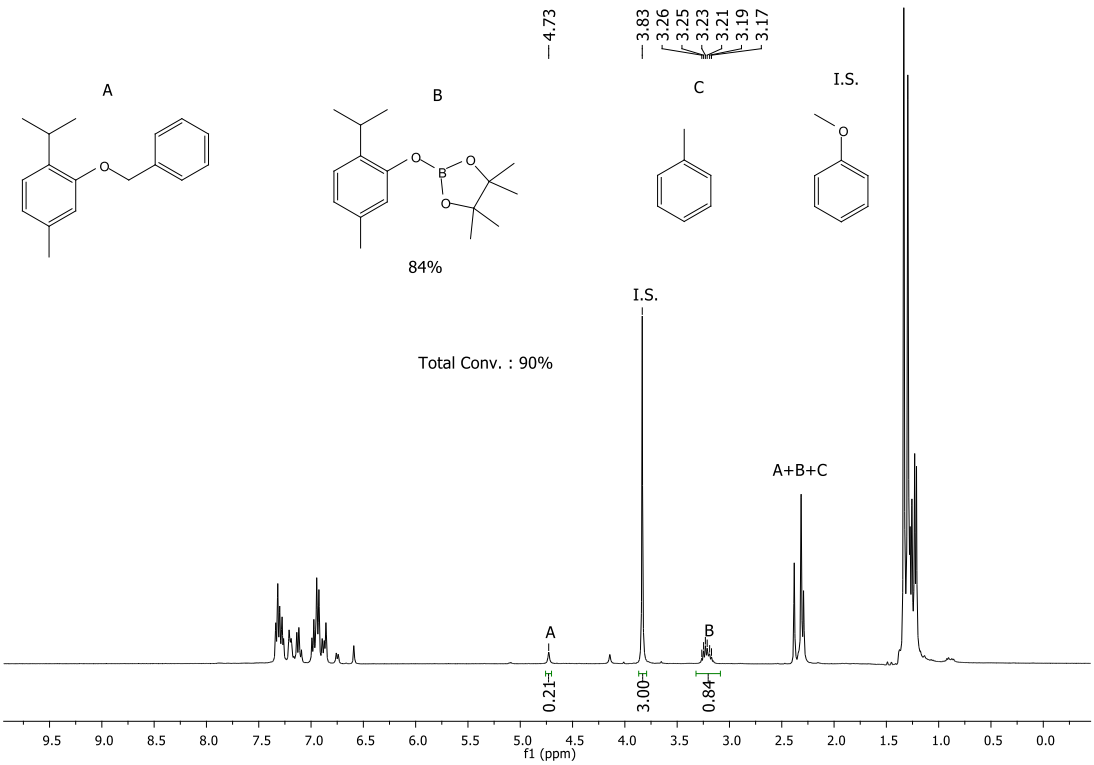


Figure S77: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 2-(benzyloxy)-1-isopropyl-4-methylbenzene **(entry 12, Table 2)**

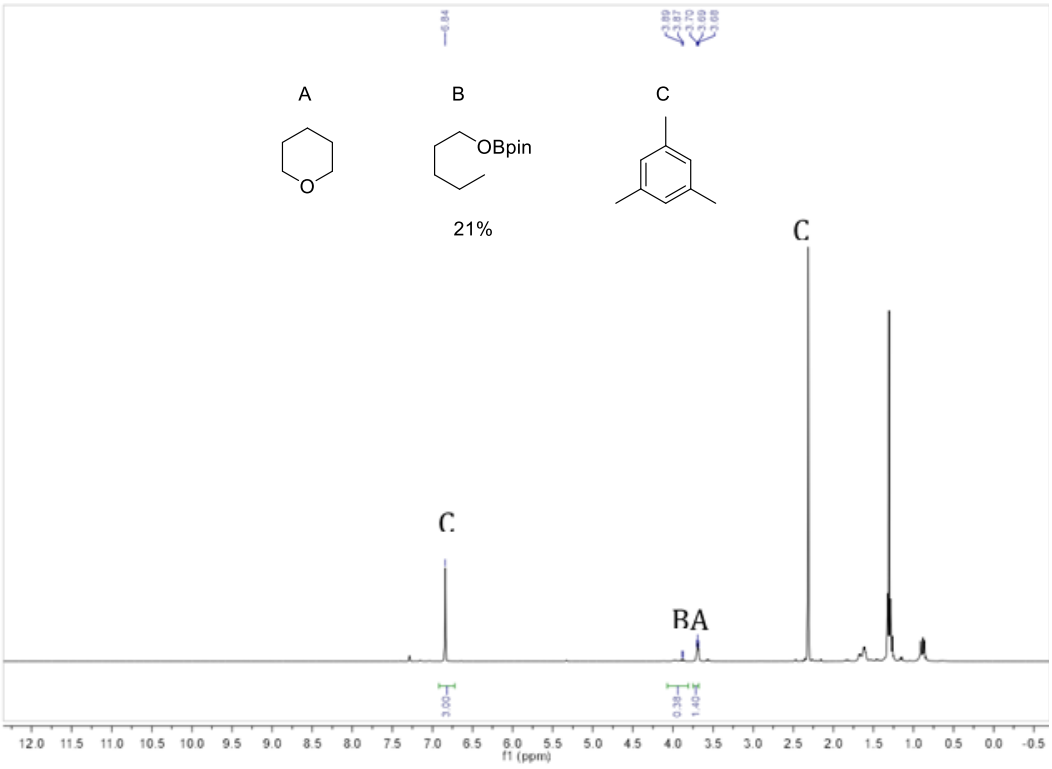


Figure S78: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of Tetrahydropyran **(entry 13, Table 2)**[41]

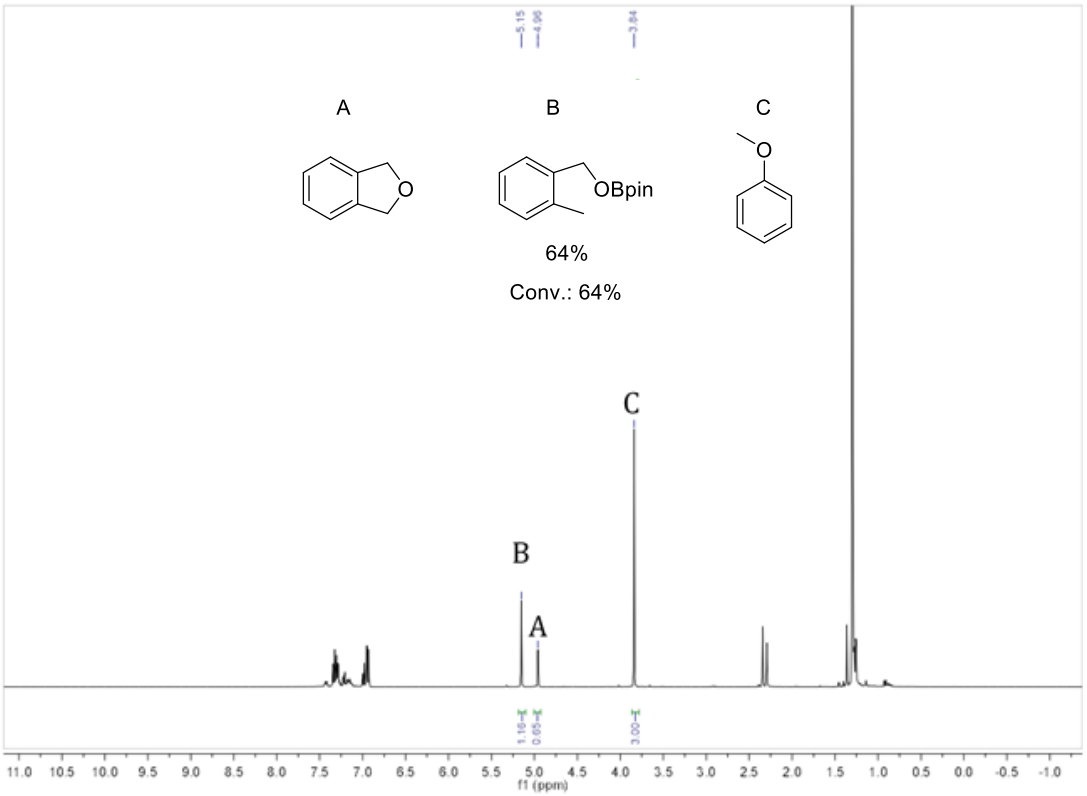


Figure S79: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of phthalan **(entry 15, Table 2)**[42]

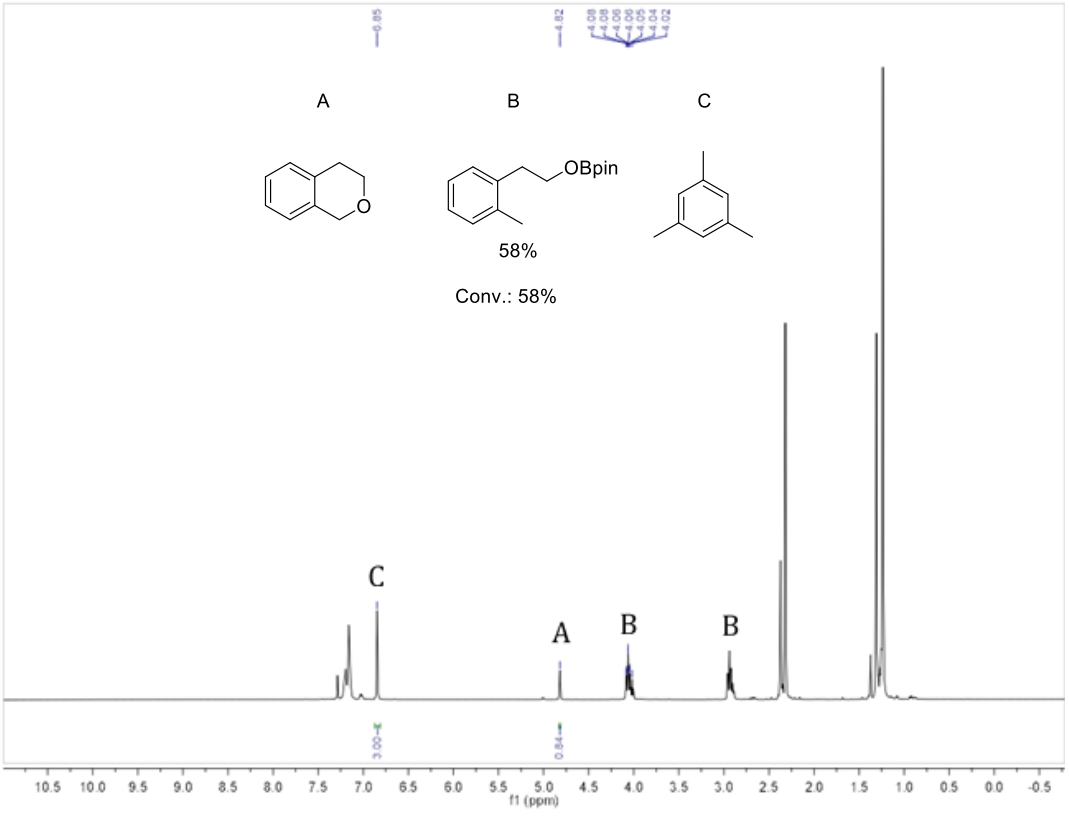


Figure S80: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of isochroman **(entry 16, Table 2)**[43]

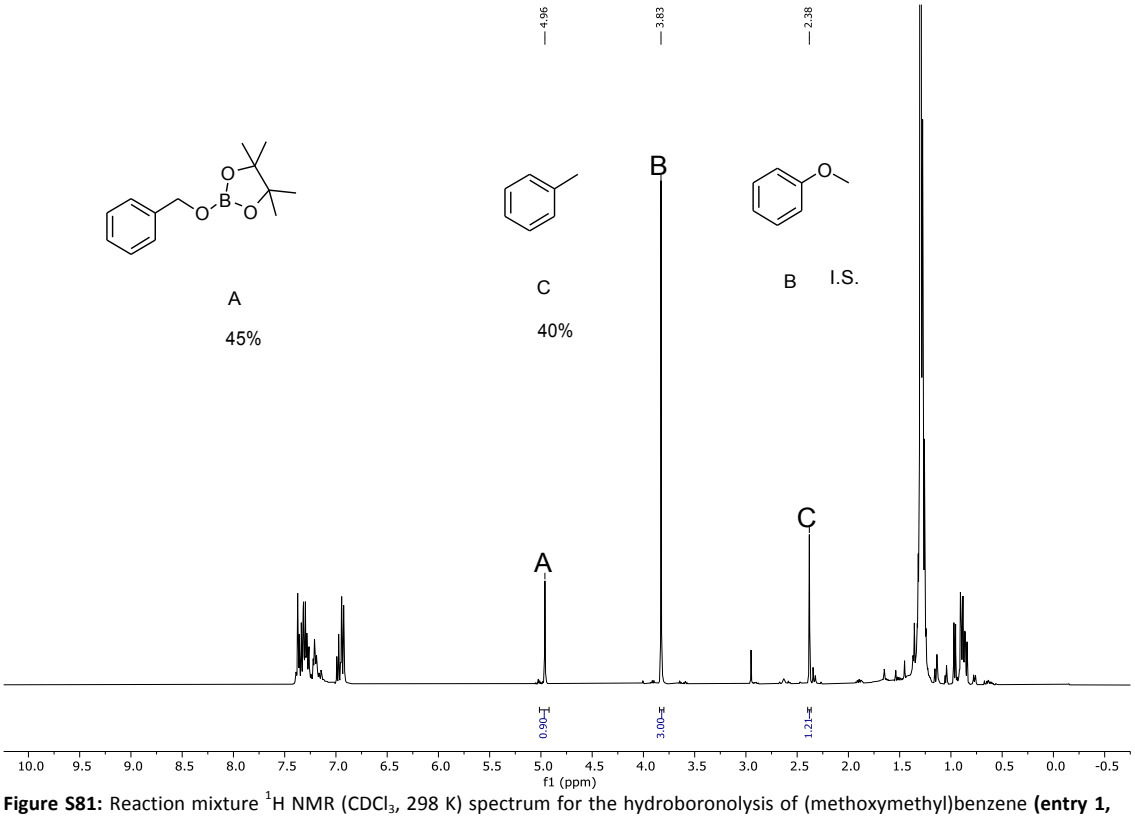


Figure S81: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of (methoxymethyl)benzene **(entry 1, Table 3)**

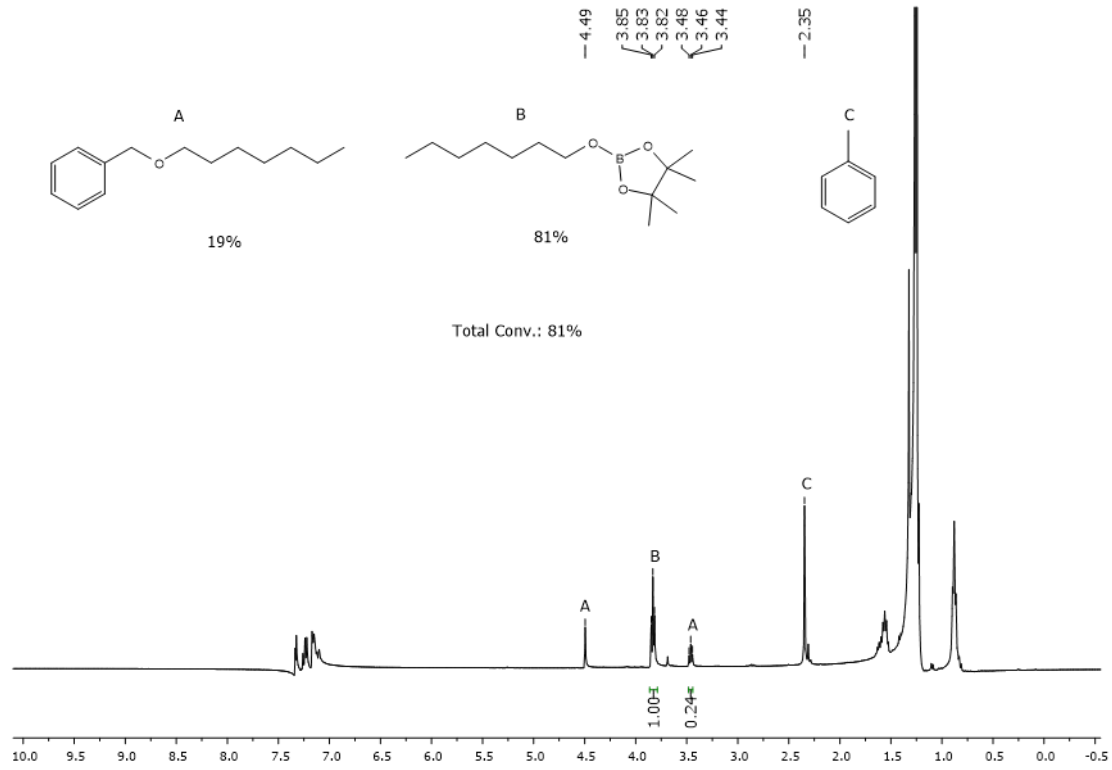


Figure S82: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of ((heptyloxy)methyl)benzene **(entry 2, Table 3)**[38]

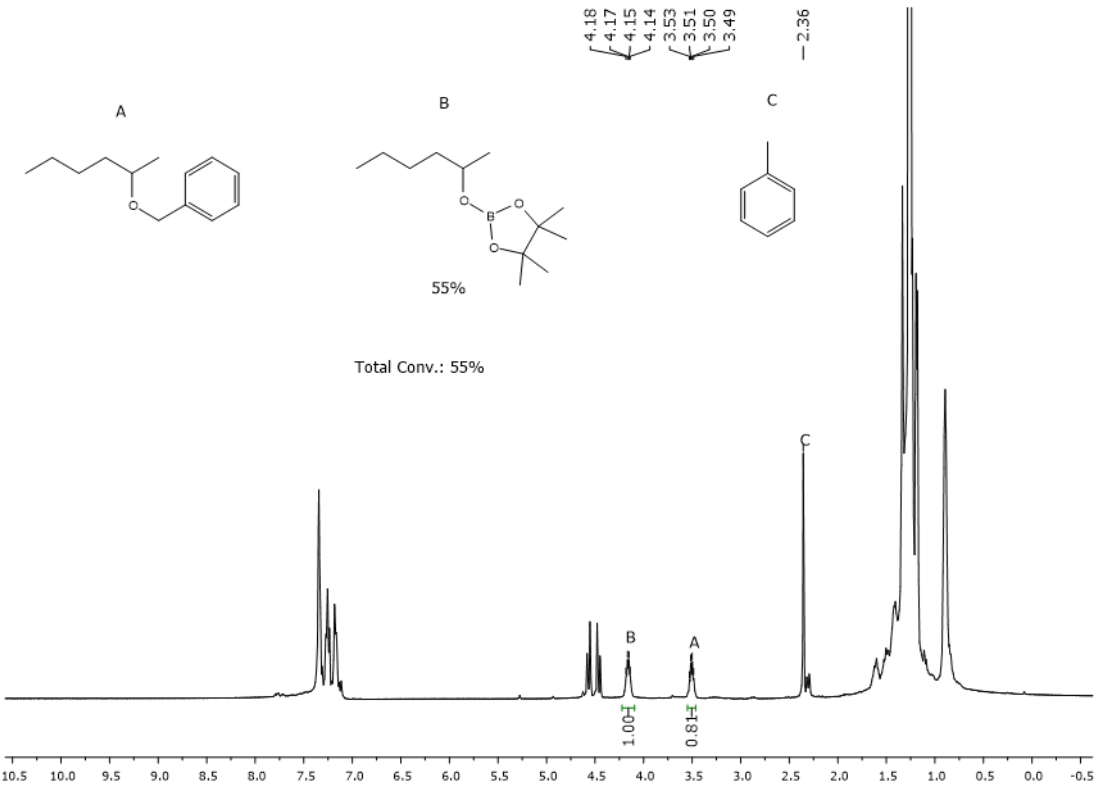


Figure S83: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of ((hexan-2-yloxy)methyl)benzene **(entry 3, Table 3)**

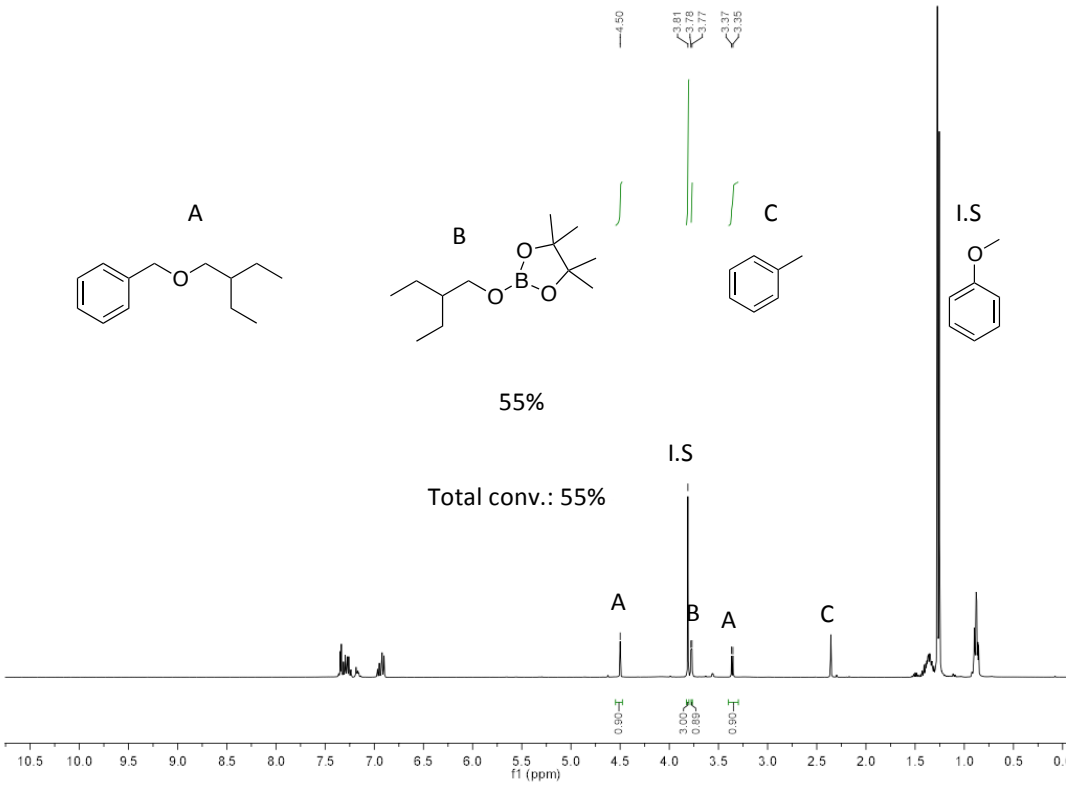


Figure S84: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of ((2-ethylbutoxy)methyl)benzene **(entry 4, Table 3)**

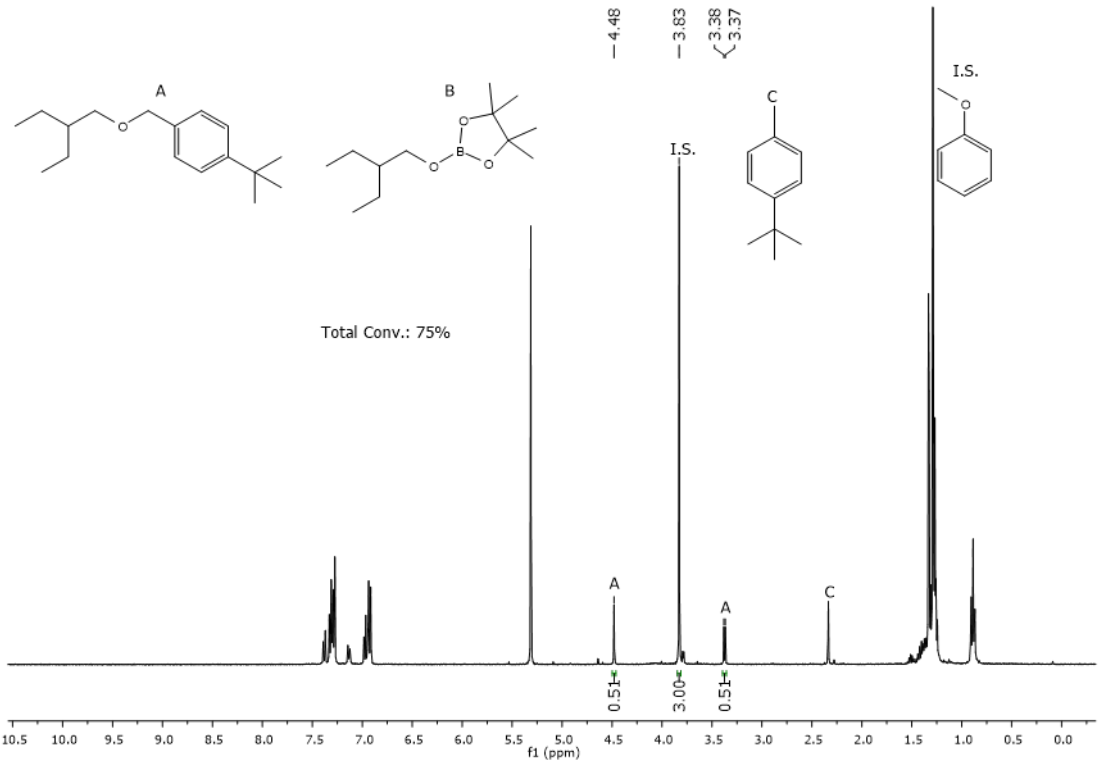


Figure S85: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1-(*tert*-butyl)-4-((2-ethylbutoxy)methyl)benzene **(entry 5, Table 3)**

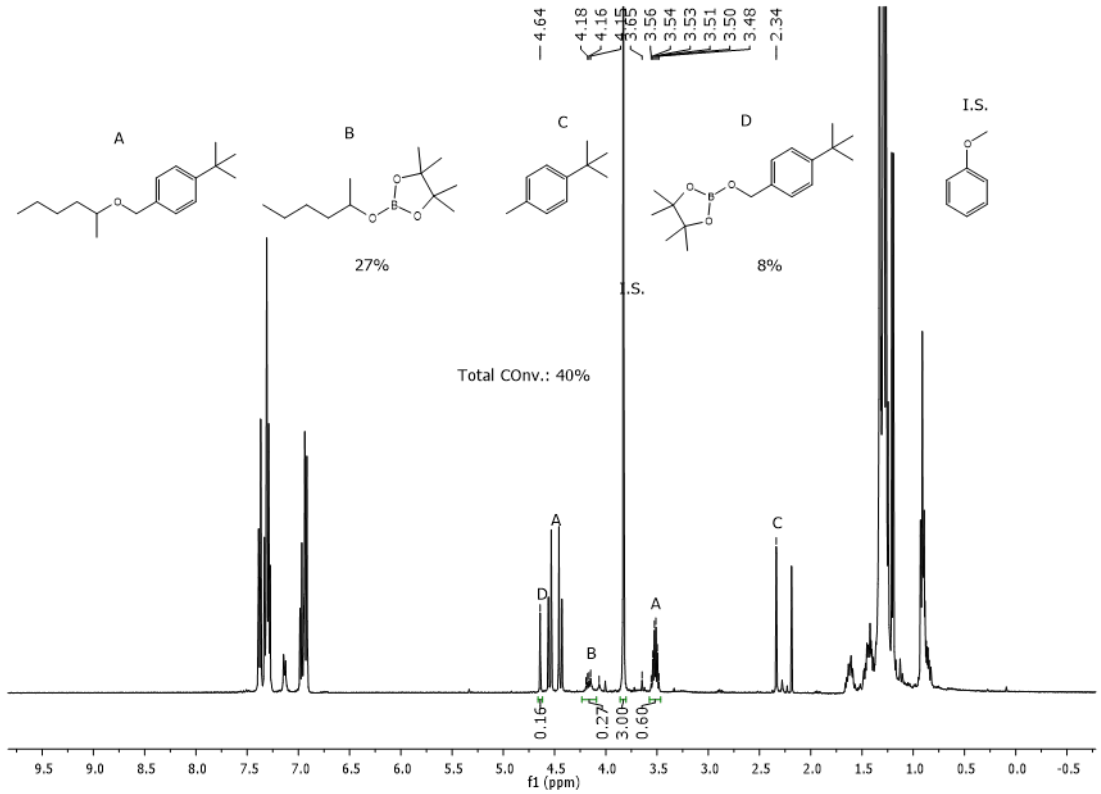


Figure S86: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1-(*tert*-butyl)-4-((hexan-2-yloxy)methyl)benzene **(entry 6, Table 3)**

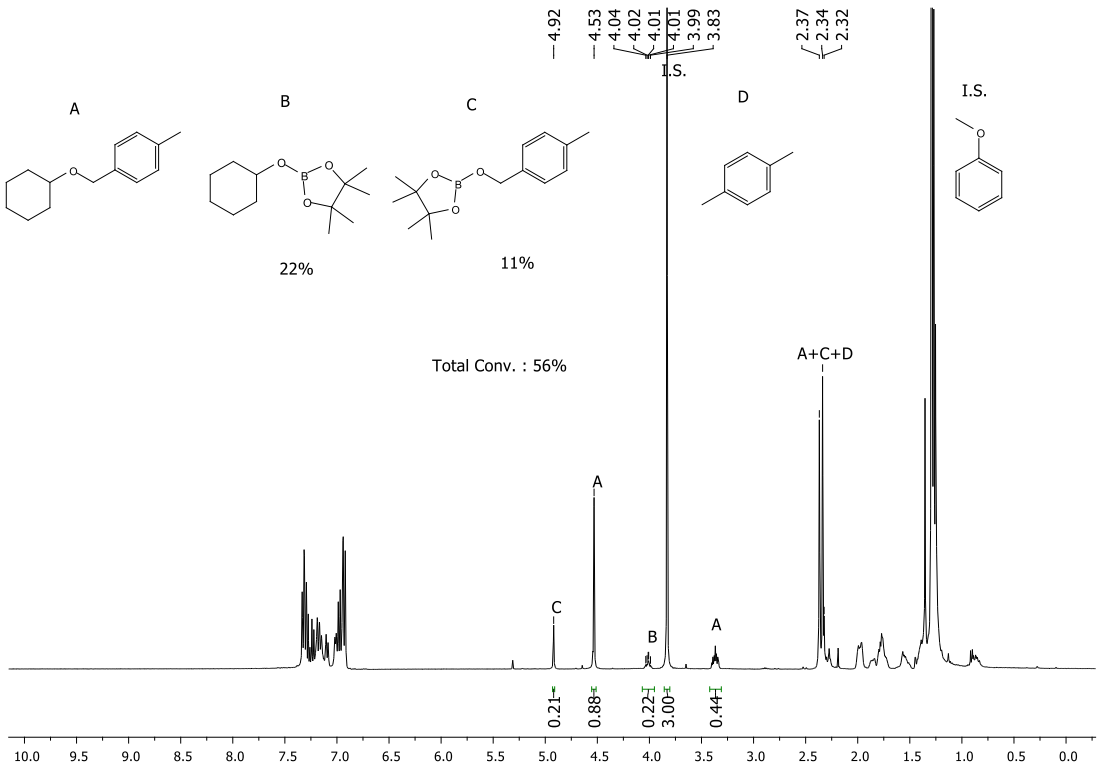


Figure S87: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1-((cyclohexyloxy)methyl)-4-methylbenzene **(entry 7, Table 3)**[33, 44]

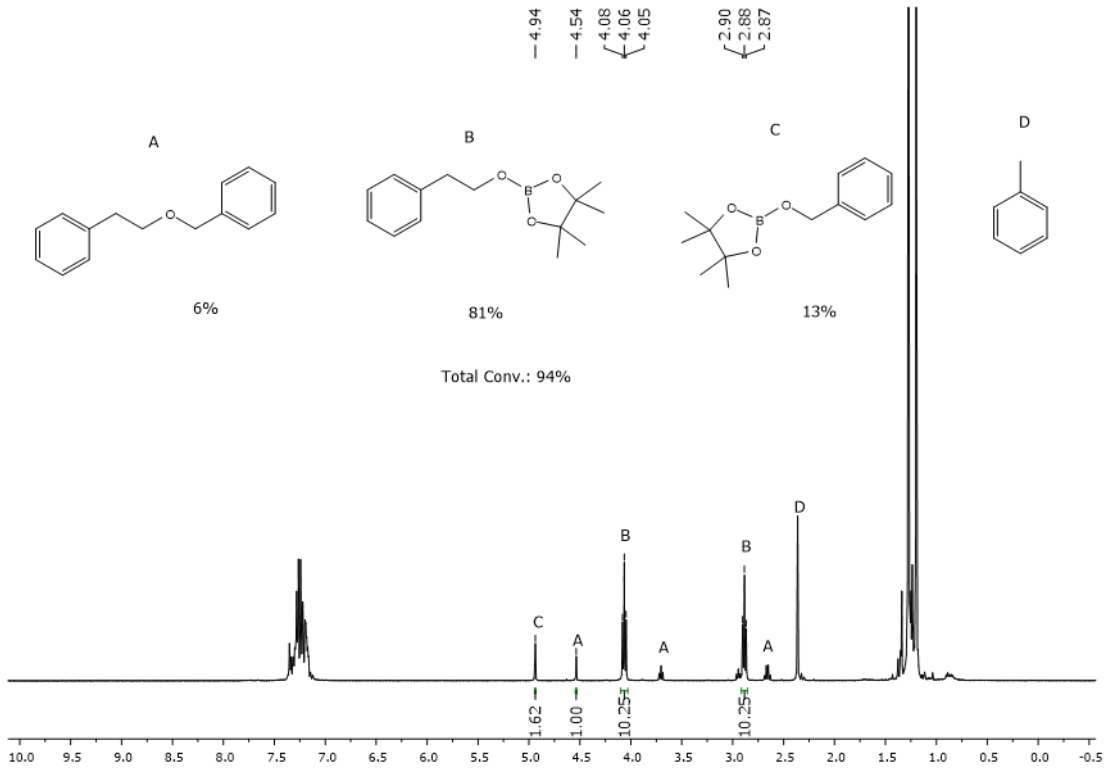


Figure S88: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of (2-(benzyloxy)ethyl)benzene **(entry 8, Table 3)**[45]

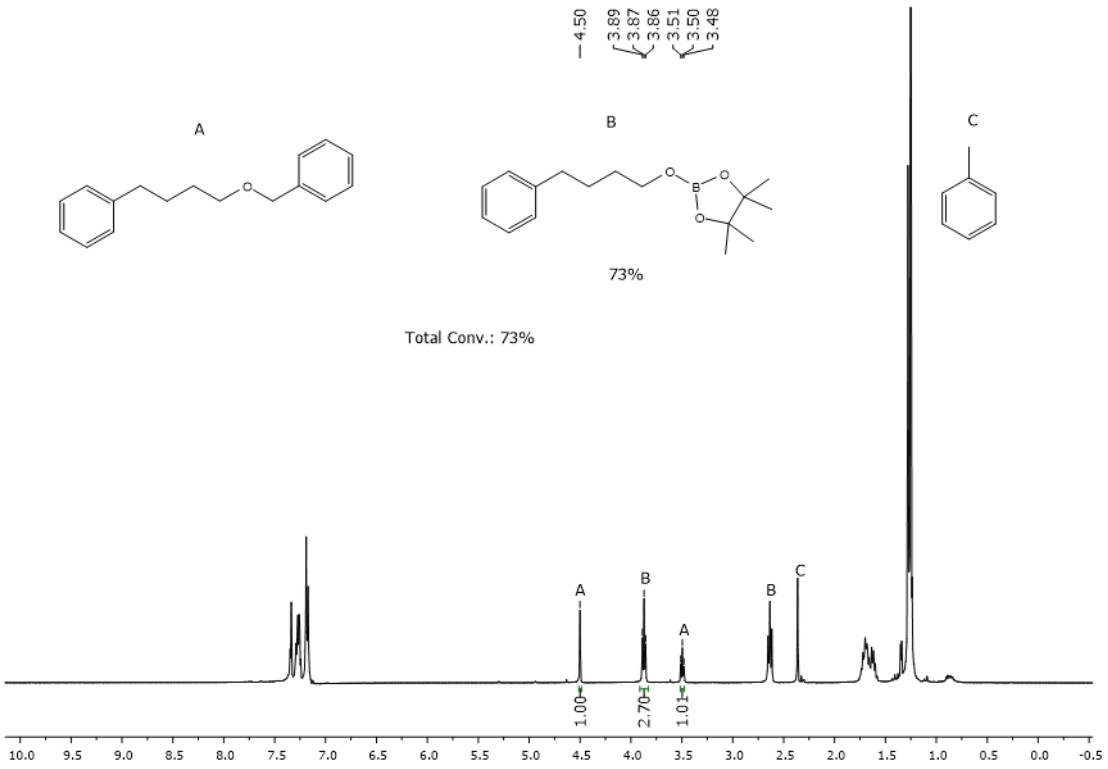


Figure S89: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of (4-(benzyloxy)butyl)benzene **(entry 9, Table 3)**[38]

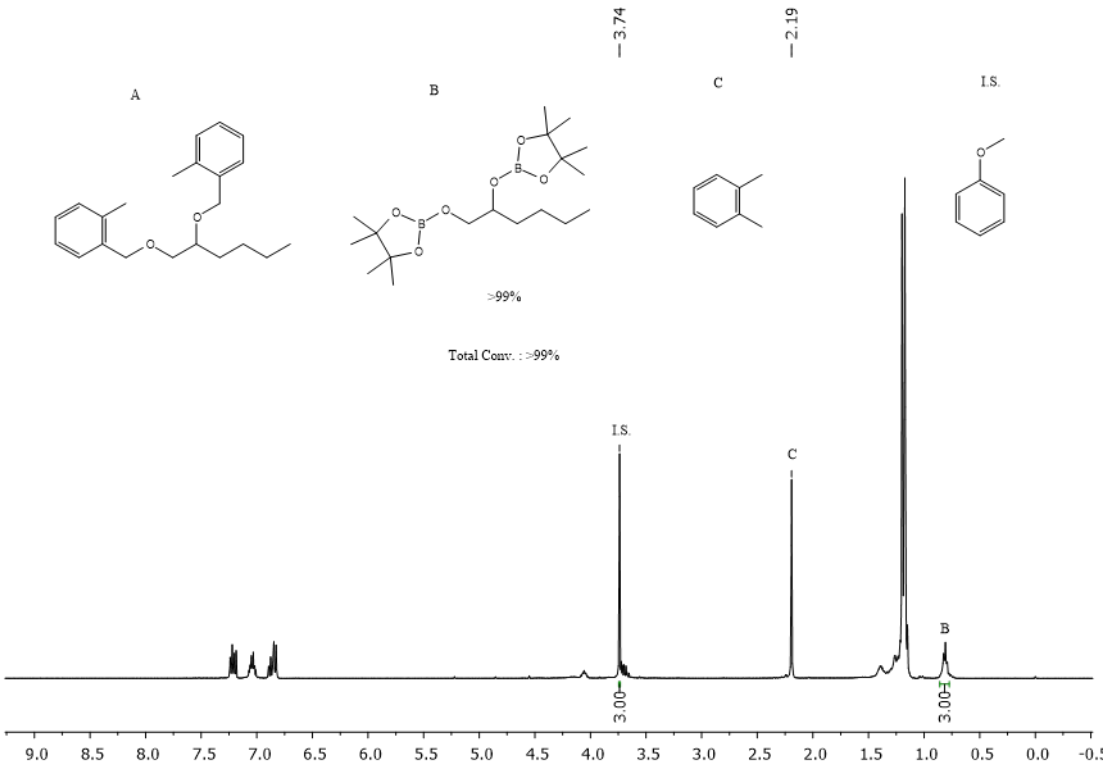


Figure S90: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1,2-bis((2-methylbenzyl)oxy)hexane **(entry 10, Table 3)**

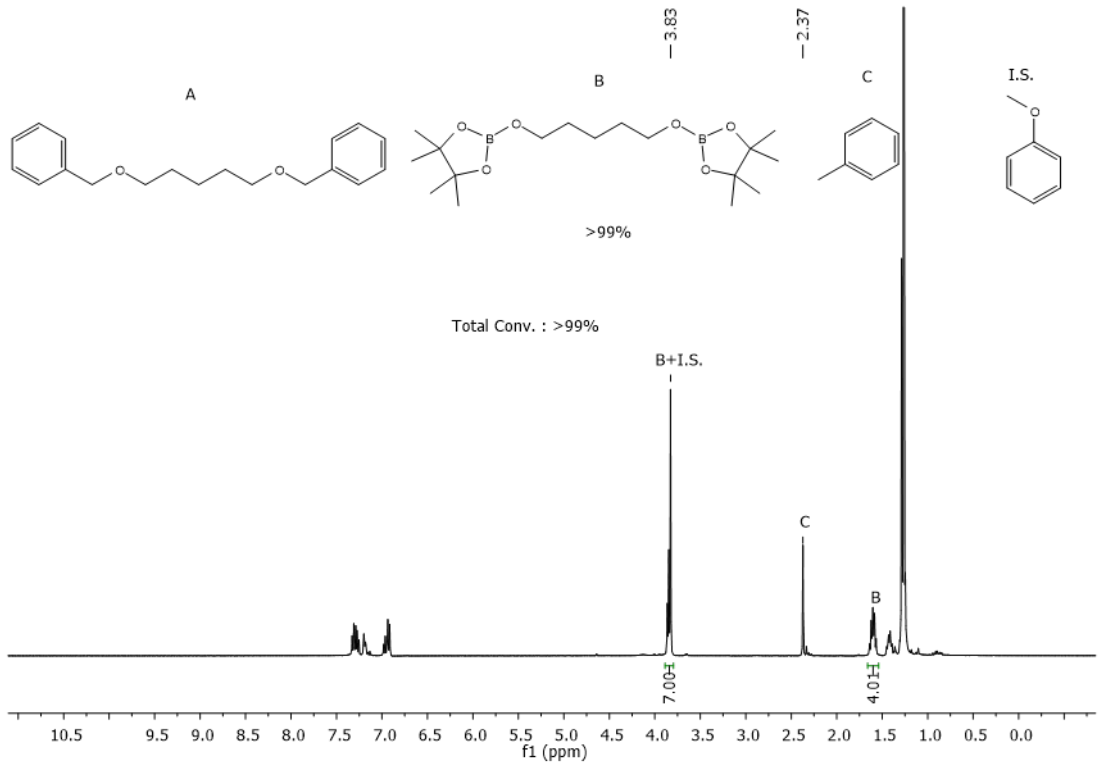


Figure S91: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of ((5-(benzyloxy)pentyl)oxy)benzene **(entry 11, Table 3)**[46]

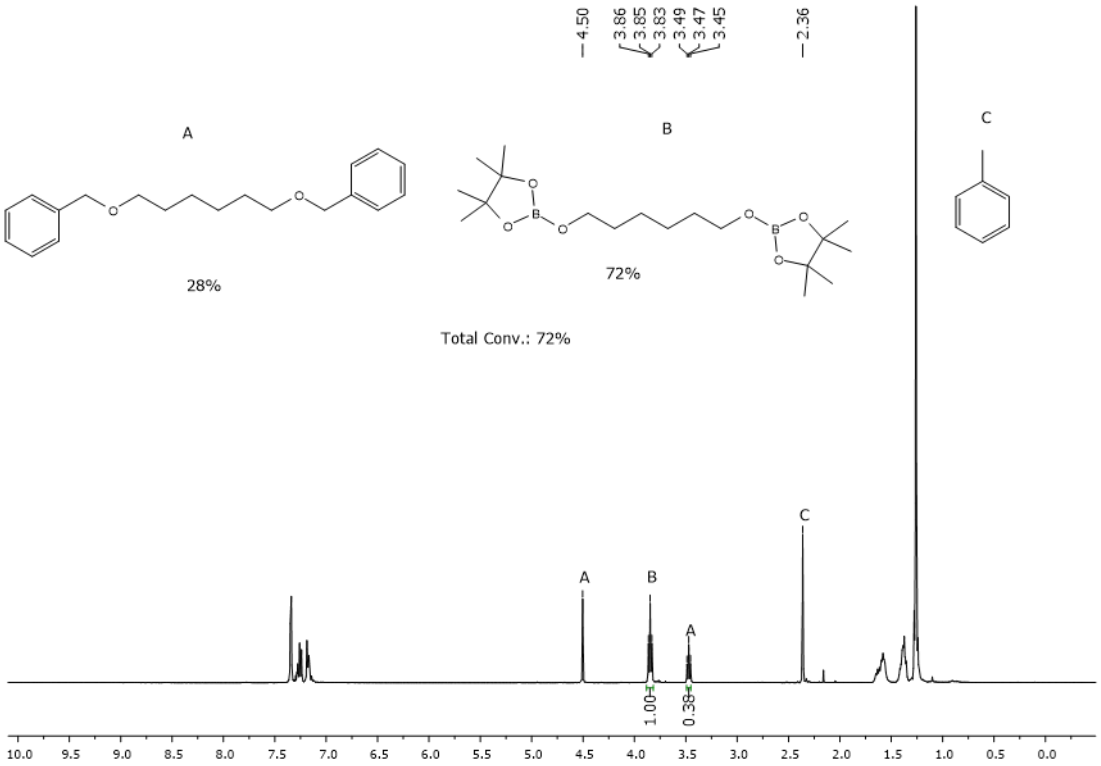


Figure S92: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1,6 bis(benzyloxy)hexane **(entry 12, Table 3)**[38]

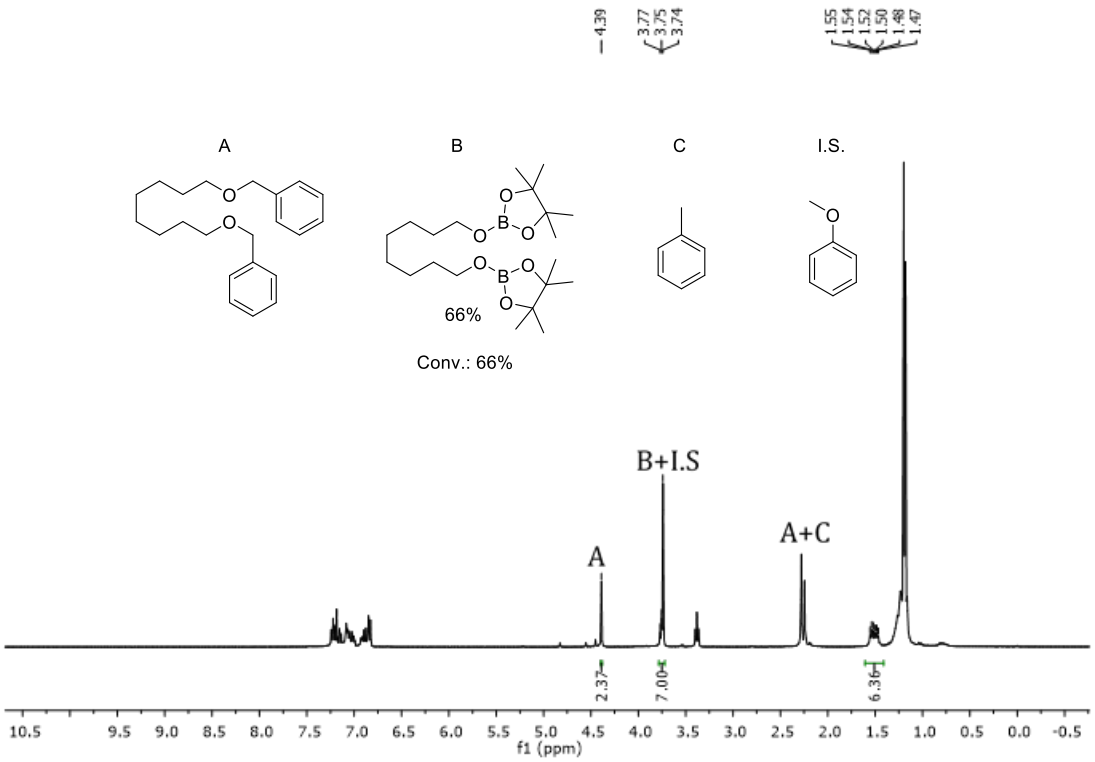


Figure S93: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1,8-bis((3-methylbenzyl)oxy)octane **(entry 13, Table 3)**

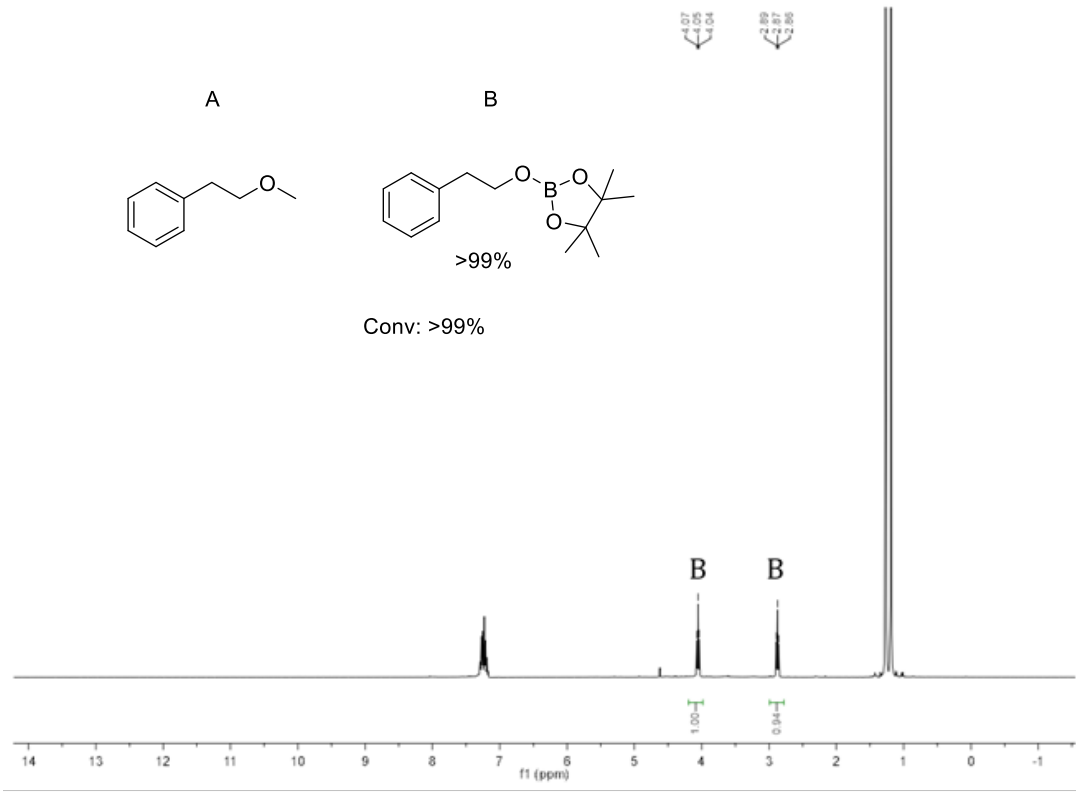


Figure S94: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of (2-methoxyethyl)benzene **(entry 1, Table 4)**[45]

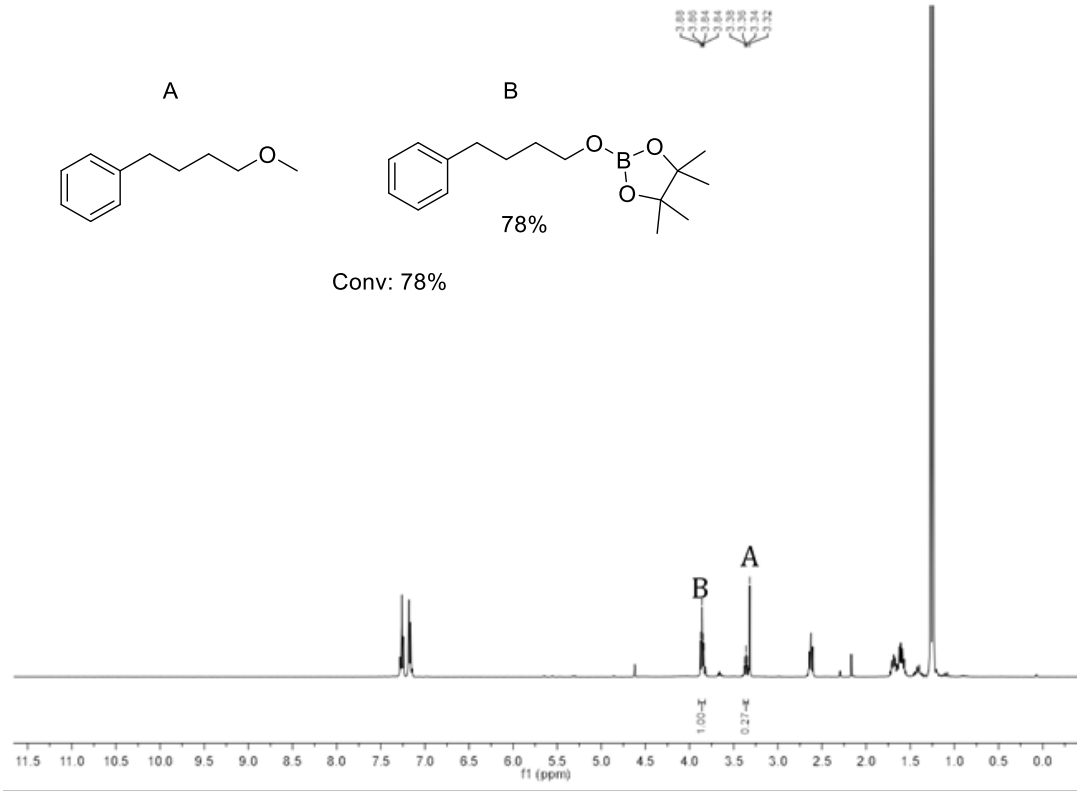


Figure S95: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of (4-methoxybutyl)benzene **(entry 2, Table 4)**[38]

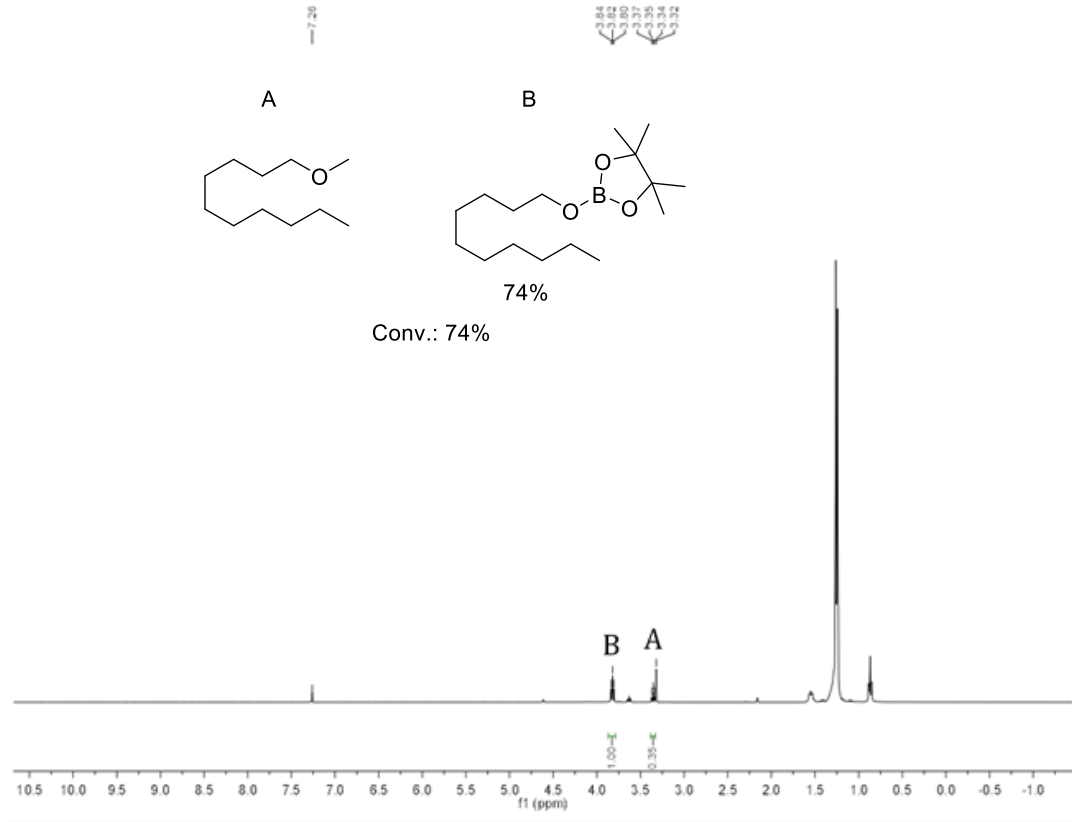


Figure S96: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1-methoxydecane **(entry 3, Table 4)**[36]

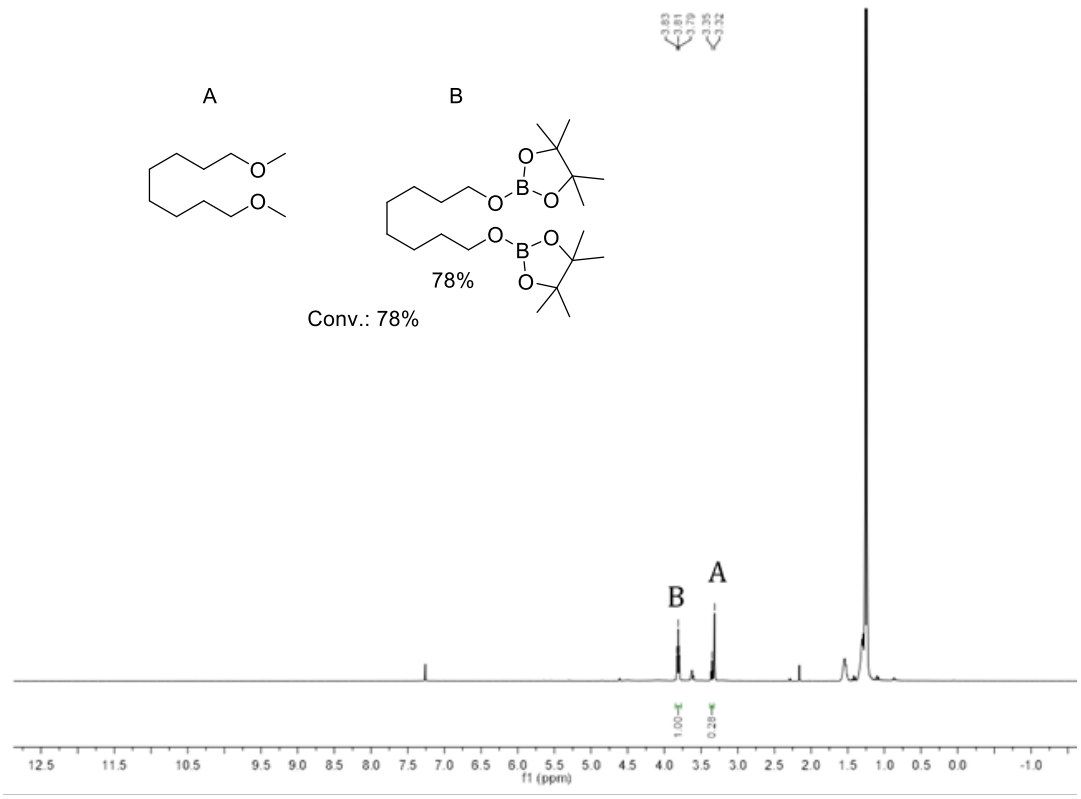


Figure S97: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1,8-dimethoxyoctane **(entry 4, Table 4)**

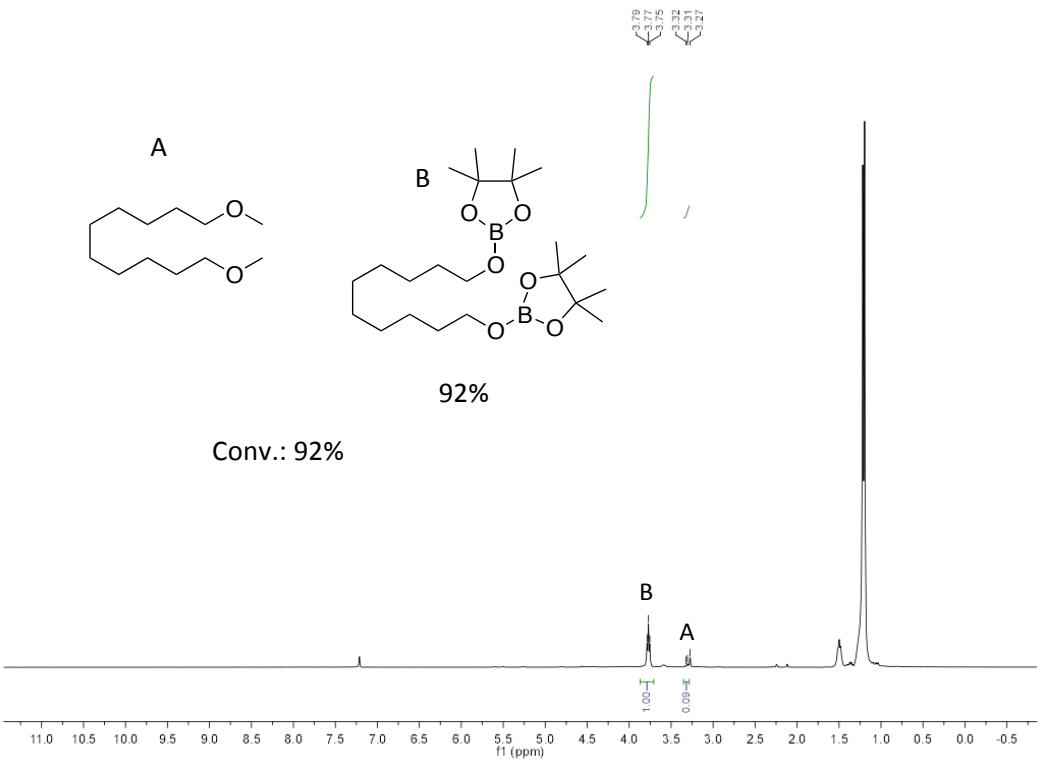


Figure S98: Reaction mixture ^{1}H NMR ($CDCl_3$, 298 K) spectrum for the hydroboronolysis of 1,10-dimethoxydecane **(entry 5, Table 4)**

19. Isolated NMR Spectra of Boronate Esters

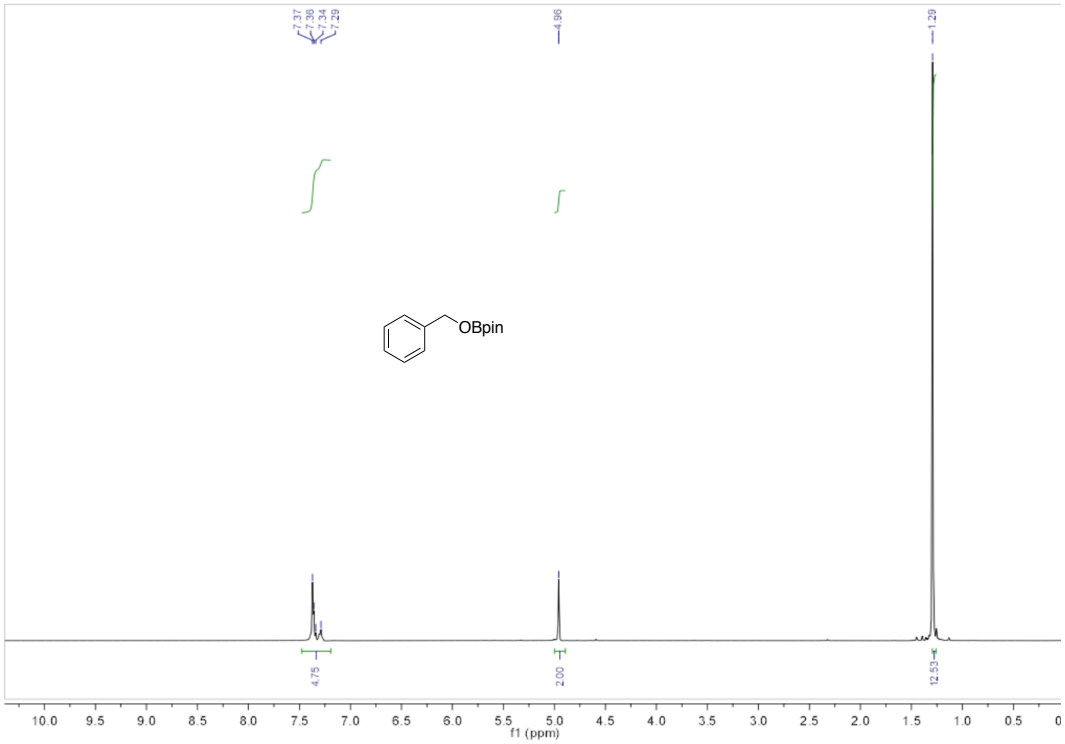


Figure S99: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

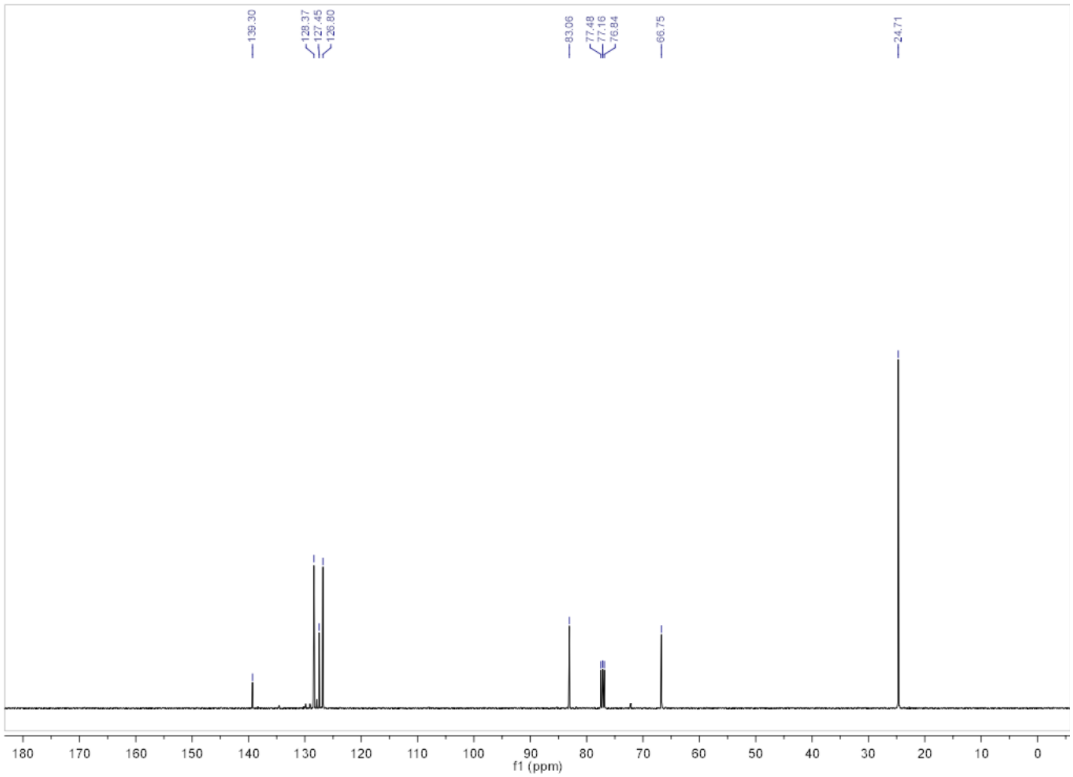


Figure S100: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

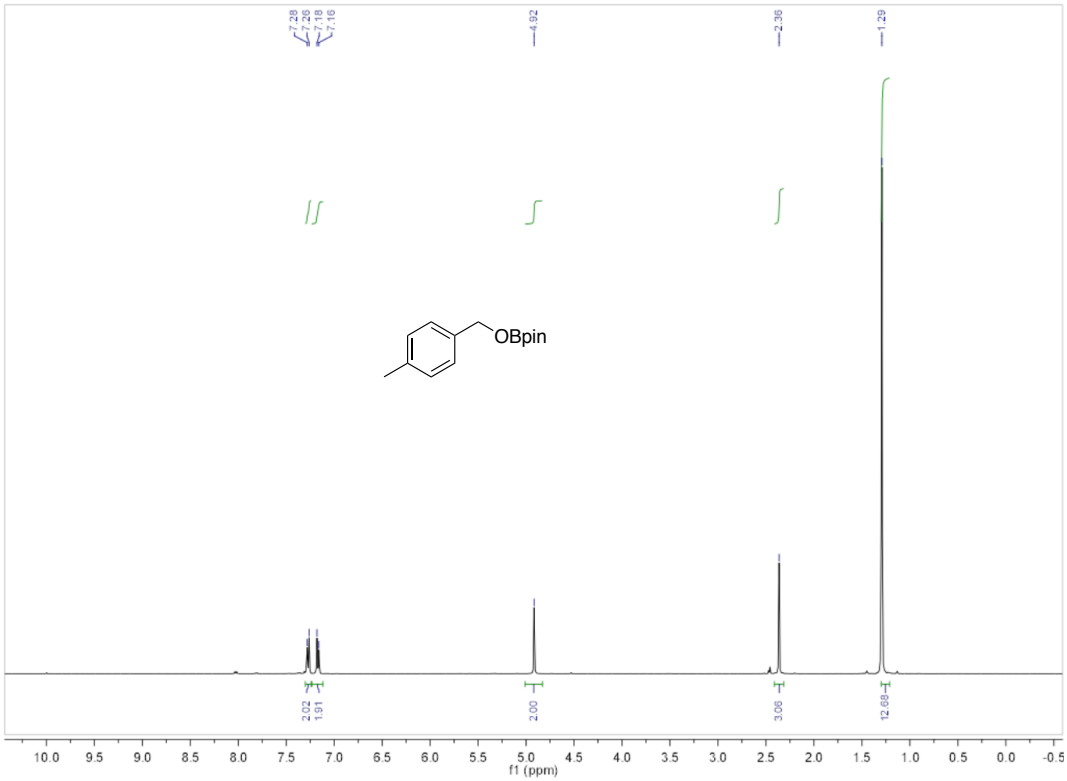


Figure S101: ^{1}H NMR spectrum ($CDCl_3$, 298 K) of 4,4,5,5-tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane

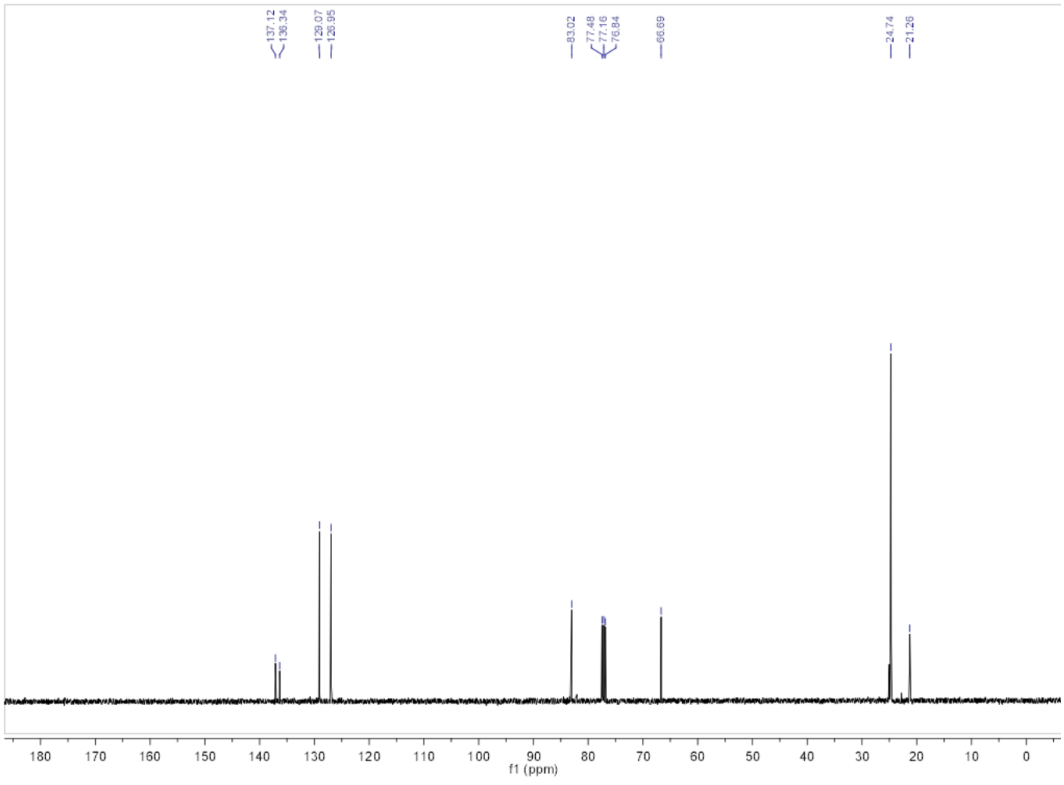


Figure S102: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 4,4,5,5-tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane

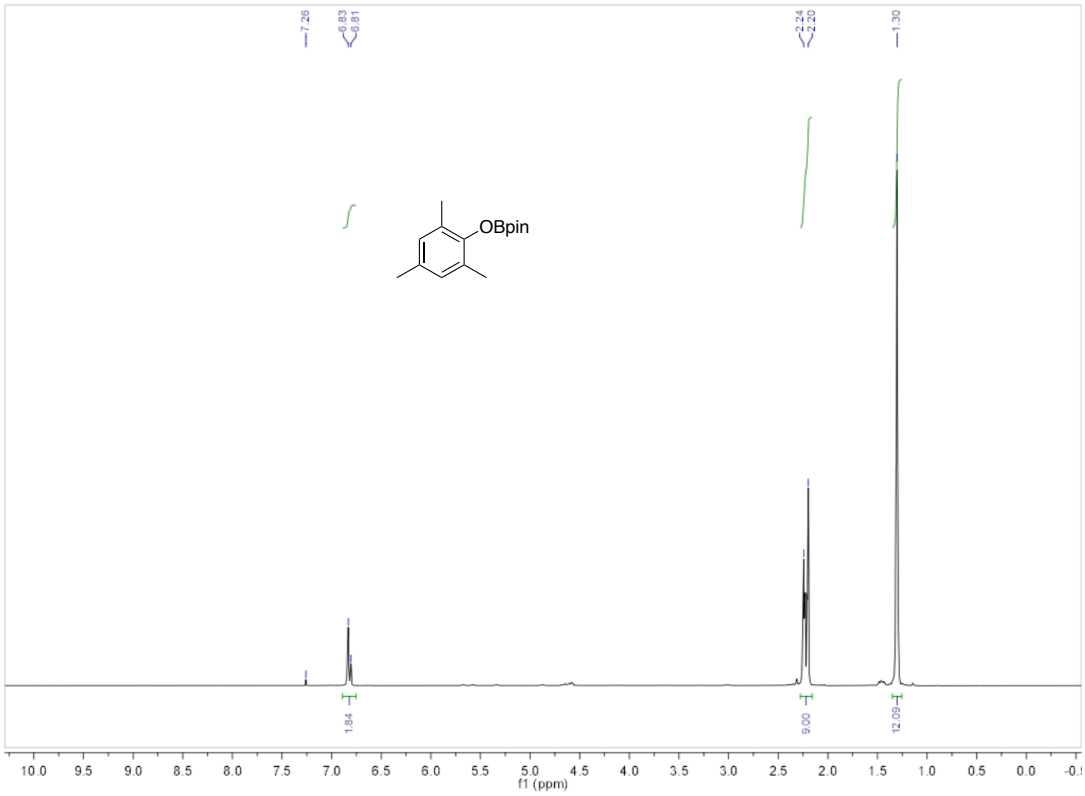


Figure S103: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 4,4,5,5-tetramethyl-2-((2,4,6-trimethylbenzyl)oxy)-1,3,2-dioxaborolane

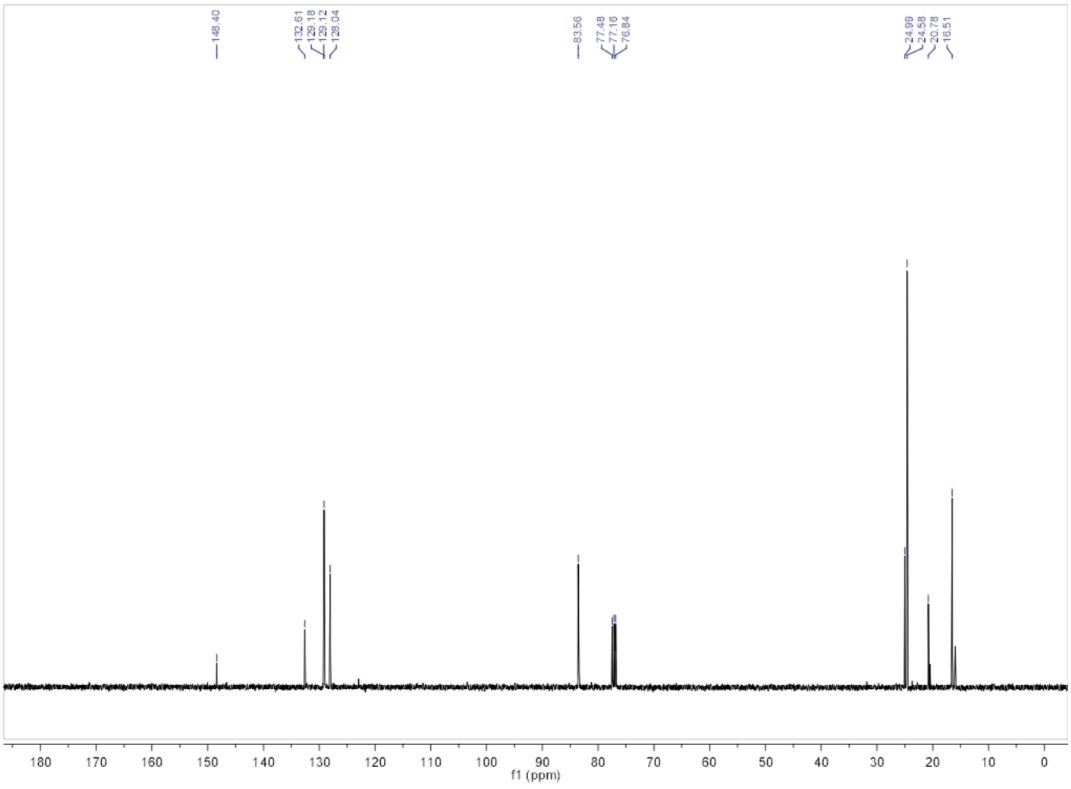


Figure S104: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 4,4,5,5-tetramethyl-2-((2,4,6-trimethylbenzyl)oxy)-1,3,2-dioxaborolane

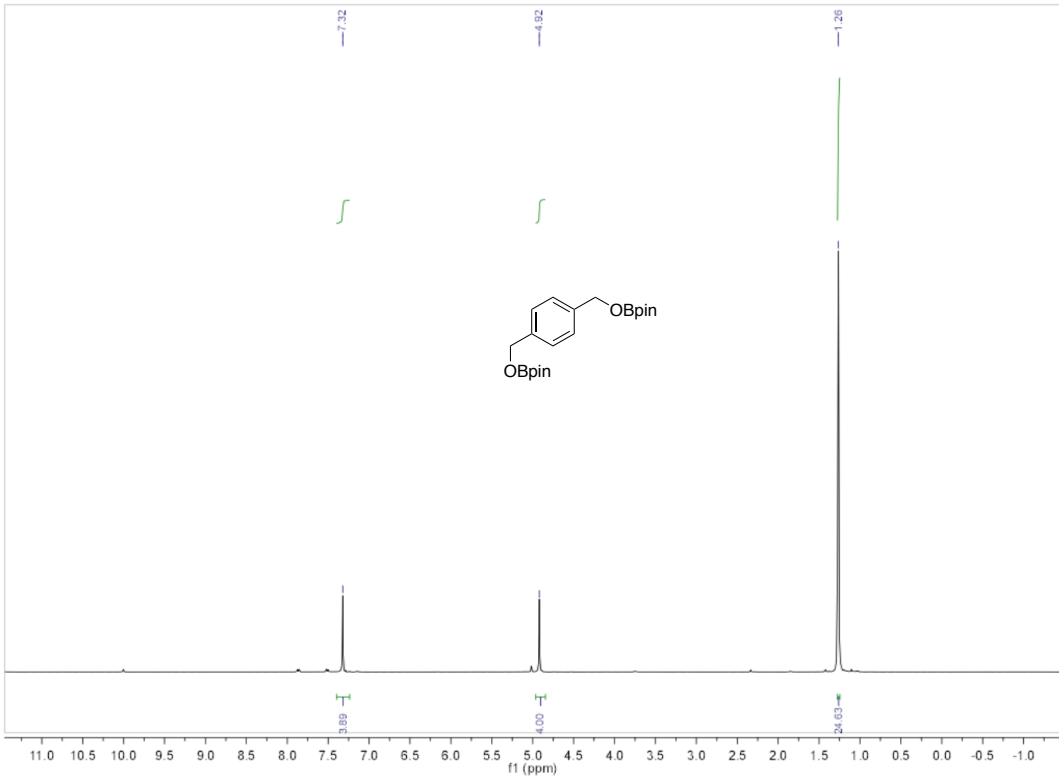


Figure S105: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 1,4-bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene

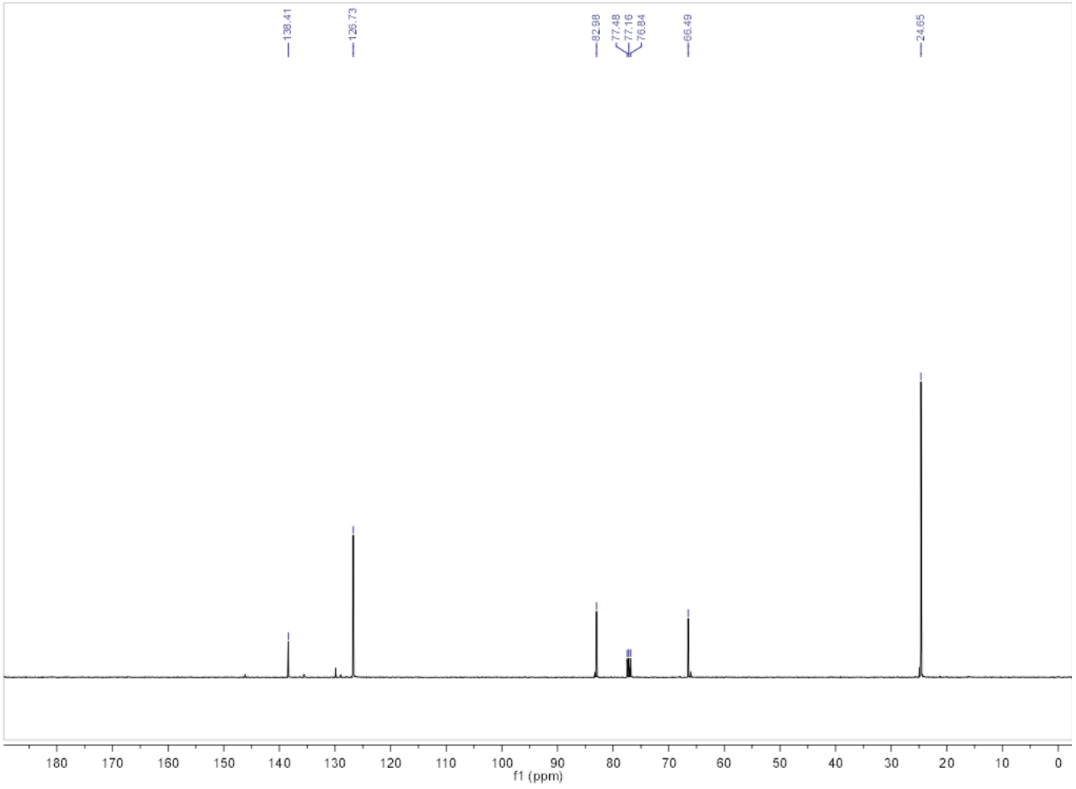


Figure S106: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 1,4-bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene

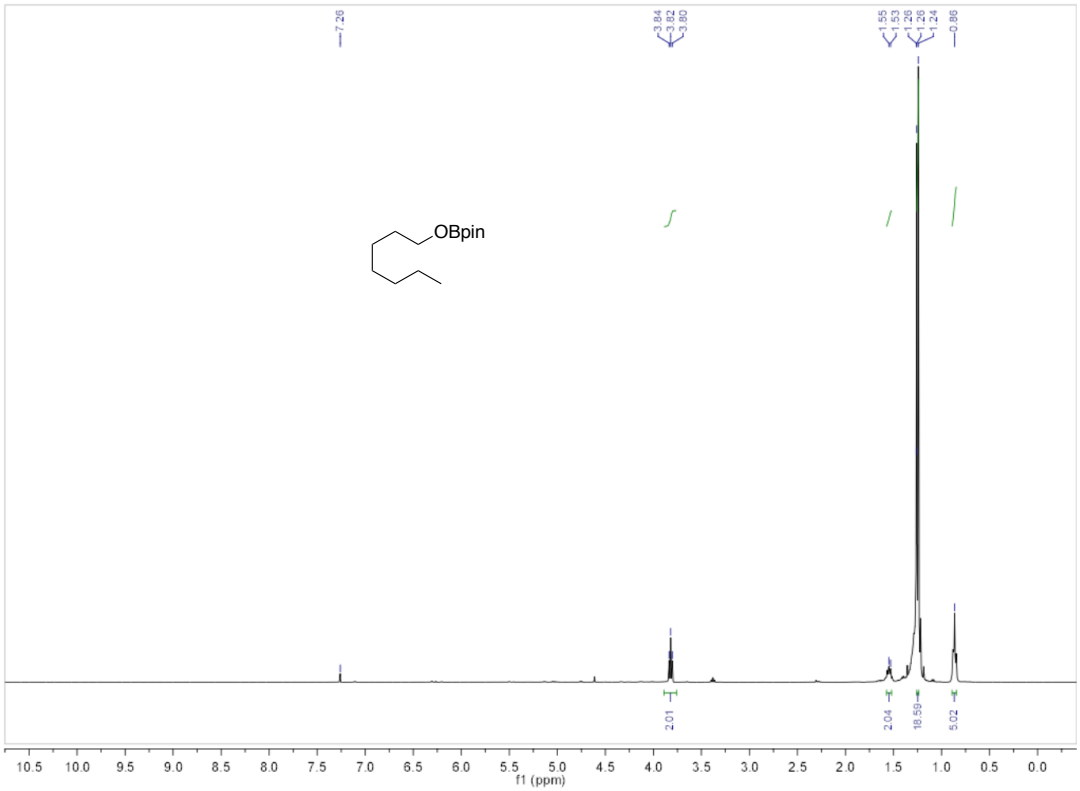


Figure S107: ^{1}H NMR ($CDCl_3$, 298 K) spectrum of 2-(heptyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

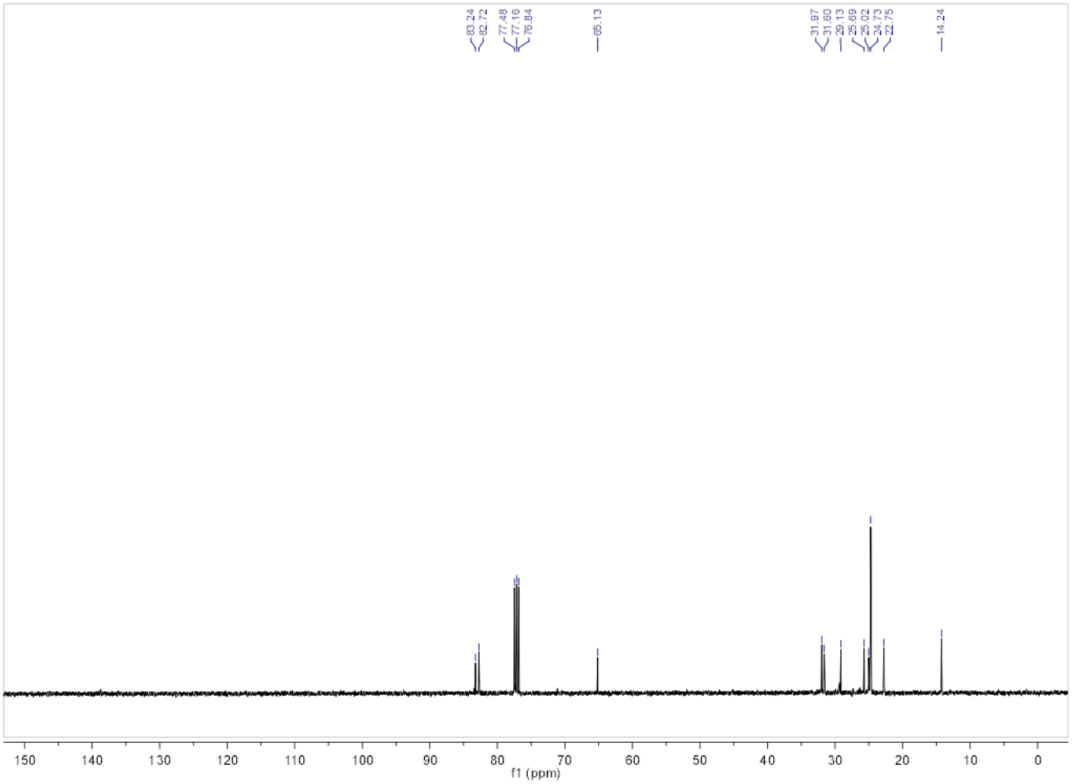


Figure S108: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K) spectrum of 2-(heptyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

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