Supporting Information

Hydroboration of Aldehydes and Ketones Under Mild Conditions Mediated by Iron Salen Complex

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1. General considerations

All manipulations were carried out under standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitrogen. Acetonitrile was dried over CaH_2 (reflux), distilled then freeze-pump-thaw degassed × 3 and stored under an inert atmosphere. Benzene, toluene and tetrahydrofuran (THF) were distilled from Na/benzophenone and stored over activated 3 Å molecular sieves. Dimethylformamide (DMF) was dried over three batches of activated 3 Å molecular sieves. Glassware was dried for 12 hours at 120°C prior to use. d_3-Acetonitirile, d_6-benzene and d_1-chloroform were purchased from Sigma Aldrich and used without further purification.

NMR spectra were obtained on Bruker or Agilent 300, 400 or 500 MHz instruments, all peaks are references against residual solvent peak or internal standard peak where stated with values quoted in ppm. Data were processed in MestReNova.

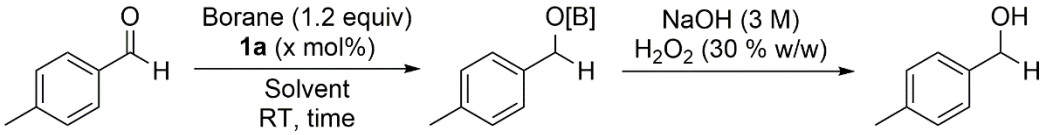
2. Materials

Chemicals were purchased from Sigma Aldrich and Alfa Aesar and used without further purification unless stated. Pinacolborane (HBpin) and catecholborane (HBcat) were purified by trap-to-trap distillation then freeze-pump-thaw degassed × 3 and stored under an inert atmosphere. Aldehydes and ketones were freeze-pump-thaw degassed × 3 prior to use where applicable, otherwise used without further purification. The synthesis of [Fe(salen)]$_2$-μ-oxo complexes **1a**[1], **1b**[2] and **1c**[3] were all prepared according to literature procedures.

3. Optimisation

3.1 Solvent and Borane source

μ-oxo-bis(*N*,*N*')-ethylenebis(salicylideniminato)iron(III) (**1a**) (1 mol%), 4-methylbenzaldehyde (30 μL, 0.25 mmol, 1 equiv) were dissolved in solvent of choice (1 mL). Borane (0.30 mmol, 1.2 equiv) was added and the reaction left to stir at room temperature for designated time. The reaction was diluted with addition of diethyl ether (10 mL) then quenched with NaOH (1 mL, 3 M) and H_2O_2 (1 mL, 30% w/w in H_2O). The mixture was extracted with diethyl ether (3 × 10 mL) and the organic layers were combined, dried over $MgSO_4$, filtered, and reduced *in vacuo* to leave the crude product *p*-tolylmethanol. Yield calculated by ^{1}H NMR spectroscopy in $CDCl_3$ referenced against 1,3,5-trimethoxybenzene (4.4 mg, 0.026 mmol, 0.1 equiv) as the internal standard.



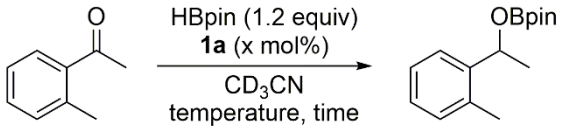
[B] = Bpin or Bcat

Exp	Solvent	1a / mol%	Borane	Time / h	Yield of alcohol / %
1	CH_2Cl_2	1	HBpin	1	99
2	THF	1	HBpin	1	>99
3	Toluene	1	HBpin	1	>99
4	Benzene	1	HBpin	1	>99
5	DMF	1	HBpin	1	97
6	Neat	1	HBpin	1	>99
7	**CH_3CN**	**1**	**HBpin**	**1**	**88**
8	Toluene	1	HBcat	1	83
9	Toluene	1	HBcat	100	93

High conversions in all solvents tested. CH_3CN continued for further optimisation due to greater solubility of **1a** and ease of characterisation in CD_3CN without overlap of residual solvent peak(s).

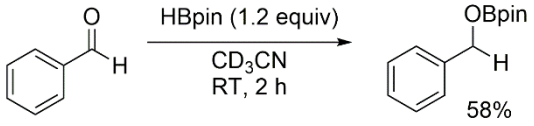
3.2 Temperature and Catalyst Loading

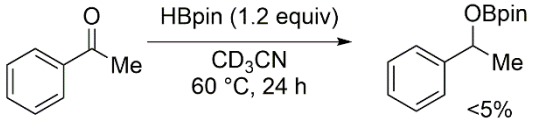
μ-oxo-bis(*N*,*N*')-ethylenebis(salicylideniminato)iron(III) (**1a**) (1 – 2 mol%), 2-methylacetophenone (33 μL, 0.25 mmol, 1 equiv) and 1,2-dichloroethane (20 μL, 1.26 M, CD_3CN, 1 equiv) were dissolved in CD_3CN (500 μL). HBpin (44 μL, 0.30 mmol, 1.2 equiv) was added and the reaction was left at the relevant temperature and monitored by ^{1}H and ^{11}B NMR spectroscopy at timed intervals. Yield calculated by ^{1}H NMR spectroscopy referenced against 1,2-dichloroethane as the internal standard.



Exp	1a / x mol%	Temperature	Yield of HB product			
			2 h	4 h	24 h	48 h
1	1	50	38	41	64	72
2	2	50	36	42	65	73
3	**1**	**60**	**53**	**60**	**78**	**83**
4	2	60	41	46	76	83

3.3 Control reactions

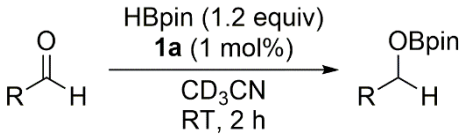




Benzaldehyde or acetophenone (0.25 mmol, 1 equiv) and 1,2-dichloroethane (20 µL, 0.25 mmol, 1 equiv) were dissolved in CD_3CN (400 µL). HBpin (44 µL, 0.30 mmol, 1.2 equiv) was added and the reaction left to react at room temperature for 2 h for benzaldehyde and at 60 °C for 24 h for acetophenone. Yield calculated by ^1H NMR spectroscopy in CD_3CN referenced against 1,2-dichloroethane as the internal standard.

4. General method for hydroboration with 1a

4.1 Aldehydes



μ-oxo-bis(*N*,*N*')-ethylenebis(salicylideniminato)iron(III) (**1a**) (100 μl, 0.025 M, CD_3CN, 0.01 equiv), aldehyde (0.25 mmol, 1 equiv) and 1,2-dichloroethane (20 μL, 0.25 mmol, 1 equiv) were dissolved in CD_3CN (400 μL). HBpin (44 μL, 0.30 mmol, 1.2 equiv) was added and the reaction left to react at room temperature for 2 h. Yield calculated by ^1H NMR spectroscopy in CD_3CN referenced against 1,2-dichloroethane as the internal standard.

4.1.1 *In-situ* NMR spectroscopy characterisation of HB of aldehydes.

2-(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2a**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 7.46 – 7.23 (m, 5H, Ar*H*), 4.87 (s, 2H, CH_2), 1.24 (s, 12H, C(CH_3)$_2$). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.5 (s). Data comparable to previous literature report.[4]

2-((4-methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 7.26 (d, $^3J_{HH}$ = 8.6 Hz, 2H, Ar*H*), 6.90 (d, $^3J_{HH}$ = 8.7 Hz, 2H, Ar*H*), 4.79 (s, 2H, CH_2), 3.77 (s, 3H, OCH_3), 1.24 (s, 12H, C(CH_3)$_2$). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.5 (s). Data comparable to previous literature report.[5]

4,4,5,5-tetramethyl-2-((4-(trifluoromethyl)benzyl)oxy)-1,3,2-dioxaborolane (**2c**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 7.66 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar*H*), 7.50 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 4.95 (s, 2H, CH_2), 1.24 (s, 12H, C(CH_3)$_2$). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.5 (s). Data comparable to previous literature report.[6]

2-((4-bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2d**). **^{1}H NMR (400 MHz, 298 K, CD_3CN) δ/ppm:** 7.50 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar*H*), 7.25 (d, $^3J_{HH}$ = 8.3 Hz, 2H, Ar*H*), 4.82 (s, 2H, CH_2), 1.23 (s, 12H, C(CH_3)$_2$). **^{11}B{^{1}H} NMR (128 MHz, 298 K, CD_3CN) δ/ppm:** 22.5 (s). Data comparable to previous literature report.[7]

2-((3-bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2e**). **^{1}H NMR (400 MHz, 298 K, CD_3CN) δ/ppm:** 7.50 (s, 1H, Ar*H*), 7.44 (d appt t, $^3J_{HH}$ = 7.0 Hz and J_{HH} = 2 Hz, 1H, Ar*H*), 7.33 – 6.22 (m, 2H, Ar*H*), 4.84 (s, 2H, CH_2), 1.23 (s, 12H, C(CH_3)$_2$). **^{11}B{^{1}H} NMR (128 MHz, 298 K, CD_3CN) δ/ppm:** 25.5 (s). Data comparable to previous literature report.[8]

4,4,5,5-tetramethyl-2-((4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)benzyl)oxy)-1,3,2-dioxaborolane (**2f**). **^{1}H NMR (400 MHz, 298 K, CD_3CN) δ/ppm:** 7.27 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar*H*), 7.04 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar*H*), 4.82 (s, 2H, CH_2), 1.29 (s, 12H, C(CH_3)$_2$), 1.24 (s, 12H, C(CH_3)$_2$). **^{13}C{^{1}H} NMR (101 MHz, 298 K, CD_3CN) δ/ppm:** 153.8 (s, ArO), 135.4 (s, ArC) 129.0 (s, Ar), 120.5 (s, Ar), 83.6 (s, *C*(CH$_3$)$_2$), 66.8 (s, *C*H$_2$), 24.8 (s, fC(*C*H$_3$)$_2$). **^{11}B{^{1}H} NMR (128 MHz, 298 K, CD_3CN) δ/ppm:** 22.4 (br s).

N,N-dimethyl-4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)aniline (**2g**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 7.18 (d, $^{3}J_{HH}$ = 6.6 Hz, 2H, Ar*H*), 6.72 (d, $^{3}J_{HH}$ = 6.8 Hz, 2H, Ar*H*), 4.49 (s, 2H, CH_2), 2.88 (s, 6H, N(CH_3)$_2$), 1.24 (s, 12H, C(CH_3)$_2$). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.4 (s). Data comparable to previous literature report.[5]

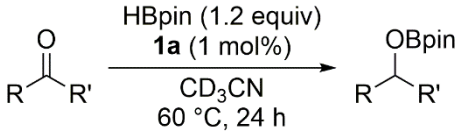
2-(cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2h**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 7.42 (2H, d, $^{3}J_{HH}$ = 7.0 Hz, Ar*H*), 7.33 (t, $^{3}J_{HH}$ = 7.0 Hz, 2H, Ar*H*), 7.29 – 7.17 (m, 1H, Ar*H*), 6.59 (d, $^{3}J_{HH}$ = 15.9 Hz, 1H, C*H*), 6.34 (dt, $^{3}J_{HH}$ = 15.7 and 4.7 Hz, 1H, C*H*) 4.48 (d, $^{3}J_{HH}$ = 4.2 Hz, 2H, CH_2), 1.24 (s, 12H, C(CH_3)$_2$). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.4 (s). Data comparable to previous literature report.[5]

4,4,5,5-tetramethyl-2-(pentyloxy)-1,3,2-dioxaborolane (**2i**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** OCH_2 peak obscured by 1,2-dichloroethane (ISTD), 1.51 (br s, 2H, CH_2), 1.28 (br s, 4H, CH_2), 1.20 (br s, 12H, C(CH_3)$_2$), 0.88 (br s, 3H, CH_3). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.2. Data comparable to previous literature report.[9]

2-(heptyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2j**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 3.76 (t, $^{3}J_{HH}$ = 6.5 Hz, 2H, OCH_2), 1.51 (appt t, J_{HH} = 5 Hz, 2H, CH_2), 1.28 (br , 8H, CH_2), 1.20 (s, 12H, C(CH_3)$_2$), 0.88 (t, $^{3}J_{HH}$ = 6.0 Hz, 3H, CH_3). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.2. Data comparable to previous literature report.[9]

4,4,5,5-tetramethyl-2-(naphthalen-2-ylmethoxy)-1,3,2-dioxaborolanee (**2k**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 8.01 – 7.70 (m, 4H, Ar*H*), 7.48 (br s, 3H, Ar*H*), 5.04 (s, 2H, CH_2), 1.25 (s, 12H, C(CH_3)$_2$). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.6 (s). Data comparable to previous literature report.[10]

4.2 Ketones



μ-oxo-bis(*N*,*N*')-ethylenebis(salicylideniminato)iron(III) (**1a**) (100 μl, 0.025 M, CD_3CN, 0.01 equiv), ketone (0.25 mmol, 1 equiv) and 1,2-dichloroethane (20 μL, 0.25 mmol, 1 equiv) were dissolved in CD_3CN (400 μL). HBpin (44 μL, 0.30 mmol, 1.2 equiv) was added and the reaction left to react at 60 °C for 24 h. Yield calculated by ^{1}H NMR spectroscopy in CD_3CN referenced against 1,2-dichloroethane as the internal standard.

4.2.1 *In-situ* NMR spectroscopy characterisation of HB of ketones.

4,4,5,5-tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (**3a**). **^{1}H NMR (400 MHz, 298 K, CD_3CN) δ/ppm:** 7.34 (appt d, J_{HH} = 4 Hz, 4H, Ar*H*), 7.30 – 7.23 (appt sext, J_{HH} = 4 Hz, 1H, Ar*H*), 5.20 (q, $^{3}J_{HH}$ = 6.2 Hz, 1H, C*H*), 1.24 (s, 12H, C(CH_3)$_2$), 1.20 (d, $^{3}J_{HH}$ = 12.5 Hz, 3H, CH_3). **^{11}B{^{1}H} NMR (128 MHz, 298 K, CD_3CN) δ/ppm:** 22.2 (s). Data comparable to previous literature report.[6]

2-(1-(4-methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**). **^{1}H NMR (400 MHz, 298 K, CD_3CN) δ/ppm:** 7.25 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 6.87 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 5.14 (q, $^{3}J_{HH}$ = 6.0 Hz, 1H, C*H*), 3.76 (s, 3H, OCH_3), 1.24 (s, 12H, C(CH_3)$_2$), 1.19 (d, $^{3}J_{HH}$ = 10.4 Hz, 3H, CH_3). **^{11}B{^{1}H} NMR (128 MHz, 298 K, CD_3CN) δ/ppm:** 22.2 (s). Data comparable to previous literature report.[6]

2-(1-(2-methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 7.39 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H, Ar*H*), 7.23 (appt t, J_{HH} = 7 Hz, 1H, Ar*H*), 6.96 (d, $^{3}J_{HH}$ = 7.4 Hz, 1H, Ar*H*), 6.92 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, Ar*H*), 5.48 (q, $^{3}J_{HH}$ = 6.0 Hz, 1H, C*H*), 3.81 (s, 3H, OCH_3), 1.24 (s, 12H, C(CH_3)$_2$), 1.19 (d, $^{3}J_{HH}$ = 8.8 Hz, 3H, CH_3). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.2 (s). Data comparable to previous literature report.[8]

4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)ethoxy)-1,3,2-dioxaborolane (**3d**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 7.65 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H, Ar*H*), 7.52 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H, Ar*H*), 5.27 (q, $^{3}J_{HH}$ = 6.3 Hz, 1H, C*H*), 1.23 (s, 12H, C(CH_3)$_2$), 1.19 (d, $^{3}J_{HH}$ = 10.3 Hz, 3H, CH_3). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.3 (s). Data comparable to previous literature report.[11]

2-(1-(4-bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 7.48 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ar*H*), 7.25 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ar*H*), 5.15 (q, $^{3}J_{HH}$ = 5.9 Hz, 1H, C*H*), 1.23 (s, 12H, C(CH_3)$_2$), 1.21 (d, $^{3}J_{HH}$ = 9.7 Hz, 3H, CH_3). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.2 (s). Data comparable to previous literature report.[7]

2-(1-(4-chlorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 7.32 (s, 4H, Ar*H*), 5.17 (q, $^{3}J_{HH}$ = 6.1 Hz, 1H, C*H*), 1.23 (s, 12H, C(CH_3)$_2$), 1.18 (d, $^{3}J_{HH}$ = 9.1 Hz, 3H, CH_3). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.3 (s). Data comparable to previous literature report.[7]

4,4,5,5-tetramethyl-2-(1-(p-tolyl)ethoxy)-1,3,2-dioxaborolane (**3g**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 7.22 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, Ar*H*), 7.15 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, Ar*H*), 5.16 (q, $^{3}J_{HH}$ = 6.1 Hz, 1H, C*H*), 2.31 (s, 3H,ArCH_3), 1.24 (s, 12H, C(CH_3)$_2$), 1.20 (d, $^{3}J_{HH}$ = 8.3 Hz, 3H, CH_3). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.3 (s). Data comparable to previous literature report.[7]

4-(1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)pyridine (**3h**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 11.44 (br s, 2H, Ar*H*), 8.22 (br s, 2H, Ar*H*), 4.89 (m, 1H, C*H*), 1.21 (s, 12H, C(CH_3)$_2$), 1.19 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, CH_3). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.3 (s). Data comparable to previous literature report.[12]

2-(cyclohexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 3.91 (br m, 1H, C*H*), 1.87 – 1.73 (br m, 4H, CH_2), 1.73 – 1.59 (br m, 4H, CH_2), 1.56 – 1.44 (br m, 2H, CH_2), 1.20 (s, 12H, C(CH_3)$_2$). **^{11}B{^{1}H} NMR (128 MHz, 298 K, CD_3CN) δ/ppm:** 22.0 (s). Data comparable to previous literature report.[5]

4,4,5,5-tetramethyl-2-((tetrahydro-2H-pyran-4-yl)oxy)-1,3,2-dioxaborolane (**3j**). **^{1}H NMR (500 MHz, 298 K, CD_3CN) δ/ppm:** 4.14 (tt, $^{3}J_{HH}$ = 8.6 and 4.1 Hz, 1H, C*H*), 3.83 (t, J_{HH} = 4.3 Hz, 2H, CH_2), 3.40 (td, $^{3}J_{HH}$ = 10.8 and 2.5 Hz, 2H, CH_2), 1.82 (dd, J_{HH} = 12.8 and 3.4 Hz, 2H, CH_2), 1.50 (dtd, J_{HH} = 13.2, 9.1 and 4.0 Hz, 2H, CH_2), 1.22 (s, 12H, C(CH_3)$_2$). **^{13}C{^{1}H} NMR (126 MHz, 298 K, CD_3CN) δ/ppm:** 83.5 (s,

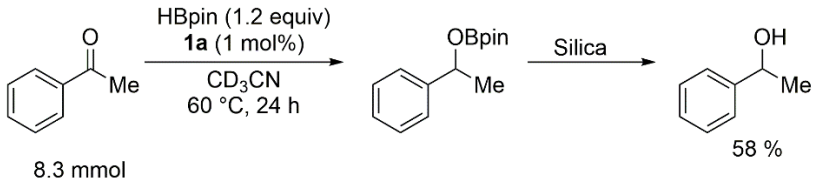
C(CH_3)$_2$), 70.1 (s, *C*H), 65.8 (s, *C*H_2), 35.1 (s, *C*H_2), 25.0 (s, *C*H_3). **^{11}B{^{1}H} NMR (160 MHz, 298 K, CD_3CN) δ/ppm:** 22.0 (s).

4,4,5,5-tetramethyl-2-((2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)oxy)-1,3,2-dioxaborolane (**3k**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 5.52 – 5.45 (br m, 1H, C=C*H*), 4.74 ─ 4.67 (m, 2H, C=C*H*$_2$), 4.63 – 4.54 (br m, 1H, C*H*), unable to unambiguously assign both CH_2 and one of the CH_3 peaks due to overlap with starting material, 1.64 (s, 3H, CH_3), 1.22 (s, 12H, C(C*H*$_3$)$_2$). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 21.2 (s). Data comparable to previous literature report.[13]

2-(benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3l**). **^{1}H NMR (400 MHz, 298 K, CD_3CN) δ/ppm:** 7.36 (t, $^3J_{HH}$ = 7.7, 4H, Ar*H*), 7.32 (t, $^3J_{HH}$ = 7.0, 4H, Ar*H*), 7.26 (t, $^3J_{HH}$ = 6.1 Hz, 2H, Ar*H*), 6.16 (s, 1H, C*H*), 1.18 (s, 12H, C(C*H*$_3$)$_2$). **^{11}B{^{1}H} NMR (128 MHz, 298 K, CD_3CN) δ/ppm:** 22.5 (s). Data comparable to previous literature report.[5]

2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3m**). **^{1}H NMR (300 MHz, 298 K, CD_3CN) δ/ppm:** 4.25 (hept, $^3J_{HH}$ = 6.4 Hz 1H, C*H*), 1.20 (s, 12H, C(C*H*$_3$)$_2$), 1.14 (d, $^3J_{HH}$ = 6.1 Hz, 6H, CH(C*H*$_3$)$_2$). **^{11}B{^{1}H} NMR (96 MHz, 298 K, CD_3CN) δ/ppm:** 25.0 (s). Data comparable to previous literature report.[14]

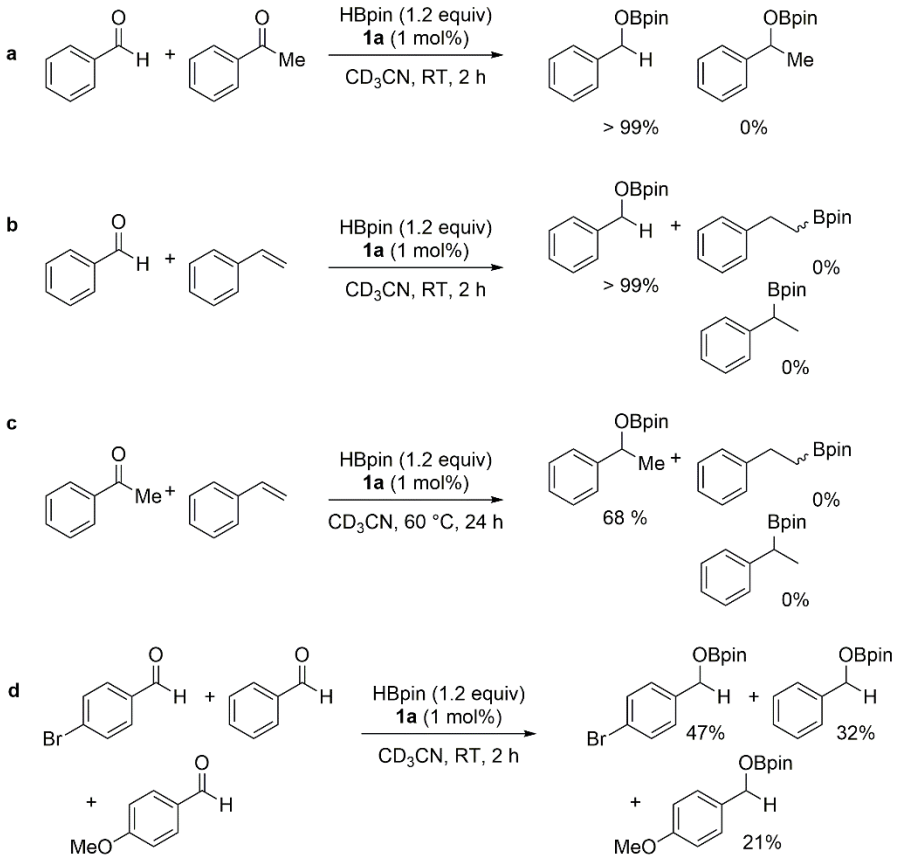
4.3 Large scale synthesis



μ-oxo-bis(*N*,*N*')-ethylenebis(salicylideniminato)iron(III) (**1a**) (55 mg, 0.083 mmol) and acetophenone (0.98 mL, 8.3 mmol) were dissolved in CH_3CN (4 mL). HBpin (1.45 mL, 10 mmol) was added and the reaction left to react at 60 °C for 24 h. Reaction vessel opened to air and all volatiles removed *in vacuo*. Residue redissolved in dichloromethane and filtered through a silica plug to remove Fe residue. The crude was purified by column chromatography (Petroleum ether/EtOAc 90:10) to give 1-phenyl ethan-1-ol as a colourless oil (0.59 g, 58%).

^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ/ppm: 7.26 – 7.16 (m, 4H, Ar*H*), 4.79 (qd, $^3J_{HH}$ = 6.4 Hz and $^3J_{HH}$ = 3.1 Hz, 1H, C*H*), 1.73 (dm $^3J_{HH}$ = 3.4 Hz, 1H, O*H*), 1.39 (d, $^3J_{HH}$ = 6.4 Hz, 3H, C*H*$_3$). Data comparable to previous literature report.[15]

5. Competition reactions

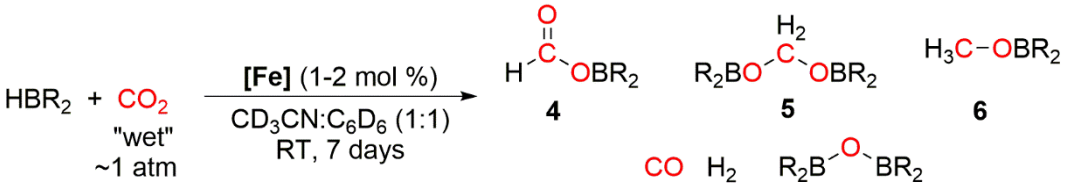


Reactions **a** and **b**: μ-oxo-bis(*N*,*N*')-ethylenebis(salicylideniminato)iron(III) (**1a**) (100 μl, 0.025 M, CD_3CN, 0.01 equiv), 1,2-dichloroethane (20 μL, 0.25 mmol, 1 equiv), benzaldehyde (0.25 mmol, 1 equiv) and acetophenone/styrene (0.25 mmol, 1 equiv) were dissolved in CD_3CN (500 μL). HBpin (44 μL, 0.30 mmol, 1.2 equiv) was added and the reaction monitored at room temperature for 2 h. Yield calculated by ^1H NMR spectroscopy in CD_3CN referenced against 1,2-dichloroethane as the internal standard.

Reaction **c:** μ-oxo-bis(*N*,*N*')-ethylenebis(salicylideniminato)iron(III) (**1a**) (100 μl, 0.025 M, CD_3CN, 0.01 equiv), 1,2-dichloroethane (20 μL, 0.25 mmol, 1 equiv), acetophenone (0.25 mmol, 1 equiv) and styrene (0.25 mmol, 1 equiv) were dissolved in CD_3CN (500 μL). HBpin (44 μL, 0.30 mmol, 1.2 equiv) was added and the reaction monitored at 60 °C for 24 h. Yield calculated by ^1H NMR spectroscopy in CD_3CN referenced against 1,2-dichloroethane as the internal standard.

Reaction **d**: μ-oxo-bis(*N*,*N*')-ethylenebis(salicylideniminato)iron(III) (**1a**) (100 μl, 0.025 M, CD_3CN, 0.01 equiv), 1,2-dichloroethane (20 μL, 0.25 mmol, 1 equiv), acetophenone (0.25 mmol, 1 equiv) 4-boromoacetophenone (0.25 mmol, 1 equiv) and 4-methoxyacetophenone (0.25 mmol, 1 equiv) were dissolved in CD_3CN (500 μL). HBpin (44 μL, 0.30 mmol, 1.2 equiv) was added and the reaction monitored at room temperature for 2 h. Yield calculated by ^1H NMR spectroscopy in CD_3CN referenced against 1,2-dichloroethane as the internal standard.

6. CO_2 reduction reaction



Room temperature: Fe salen catalyst (1 - 2 mol%) and 1,3,5-trimethoxybenzene (12.6 mg, 0.075 mmol) were dissolved in 1:1 CD_3CN:C_6D6 (600 µL). HBR_2 (0.30 mmol) was added and the reaction was freeze-pump-thawed × 3. CO_2 (1 atm) was added to the J.Young tube NMR and sealed up, agitated at room temperature and monitored by multinuclear NMR spectroscopy. Yield calculated by ^{1}H NMR spectroscopy referenced against 1,3,5-trimethoxybenzene as the internal standard. **NB**: The theoretical maximum CO_2 inserted into the reaction was calculated to be 0.08 mmol. After 7 days at room temperature the reaction was freeze-pump-thawed × 3 and CO_2 (1 atm) was inserted again into the reaction vessel, sealed, agitated at room temperature, and monitored by multinuclear NMR spectroscopy. No additional conversion was observed suggesting not all the CO_2 was originally consumed in the first iteration.

60 °C: Fe salen catalyst (1-2 mol%) and 1,3,5-trimethoxybenzene (2.1 mg, 12.5 µmol) were dissolved in 1:1 CD_3CN:C_6D6 (600 µL). HBR_2 (0.05 mmol) was added and the reaction was freeze-pump-thawed × 3. CO_2 (1 atm) was added to the J.Young tube NMR and sealed up, agitated at room temperature and monitored by multinuclear NMR spectroscopy. Yield calculated by ^{1}H NMR spectroscopy referenced against 1,3,5-trimethoxybenzene as the internal standard.

[Fe]	Temp	Borane	4	5	6	CO + H_2 + R_2BOBR_2
1a (1 mol%)	RT	HBpin	5%	1%	1%	8%
1a (1 mol%)	RT	HBcat	-	-	12%	44%
1a (1 mol%)	RT	9-BBN	6%	-	-	-
1b (1 mol%)	RT	HBpin	-	-	-	20%
1c (2 mol%)	RT	HBpin	8%	2%	7%	22%
1a (1 mol%)	60 °C	HBpin	9%	1%	-	~49%[1]
1a (1 mol%)	60 °C	HBcat	1%	-	9%	21%
1a (1 mol%)	60 °C	9-BBN	1%	-	-	YES[2]
1b (1 mol%)	60 °C	HBpin	1%	1%	-	~64%[1]
1c (2 mol%)	60 °C	HBpin	14%	1%	-	62%

[1] Formation of BOB estimated by ^{11}B NMR spectroscopy due to broadness of peaks in ^{1}H NMR spectroscopy

[2] Unable to quantify how much BOB (δ_B = 56.9 ppm) formed but observed in ^{11}B NMR spectroscopy. 9-BBN peak (δ_B = 57.9 ppm).

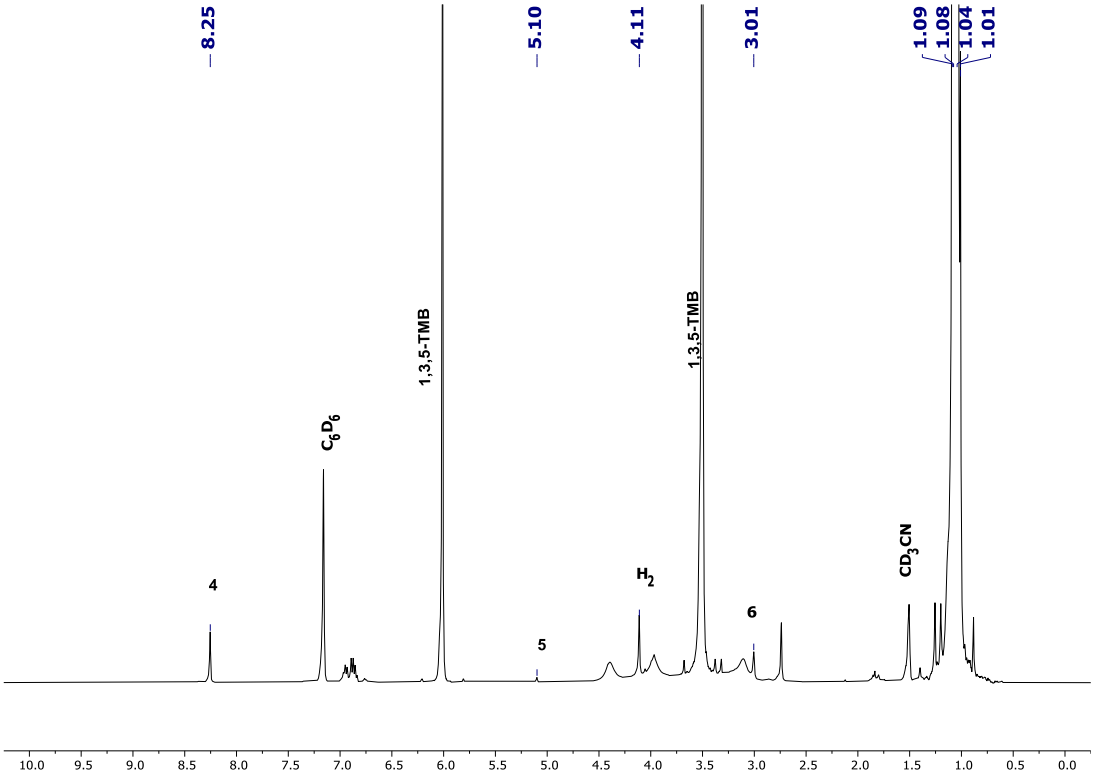


Figure S1. Representative ^{1}H NMR spectrum of product distribution from the reduction of CO_2 with HBpin (400 MHz, 1:1 CD_3CN:C_6D_6, 298 K)

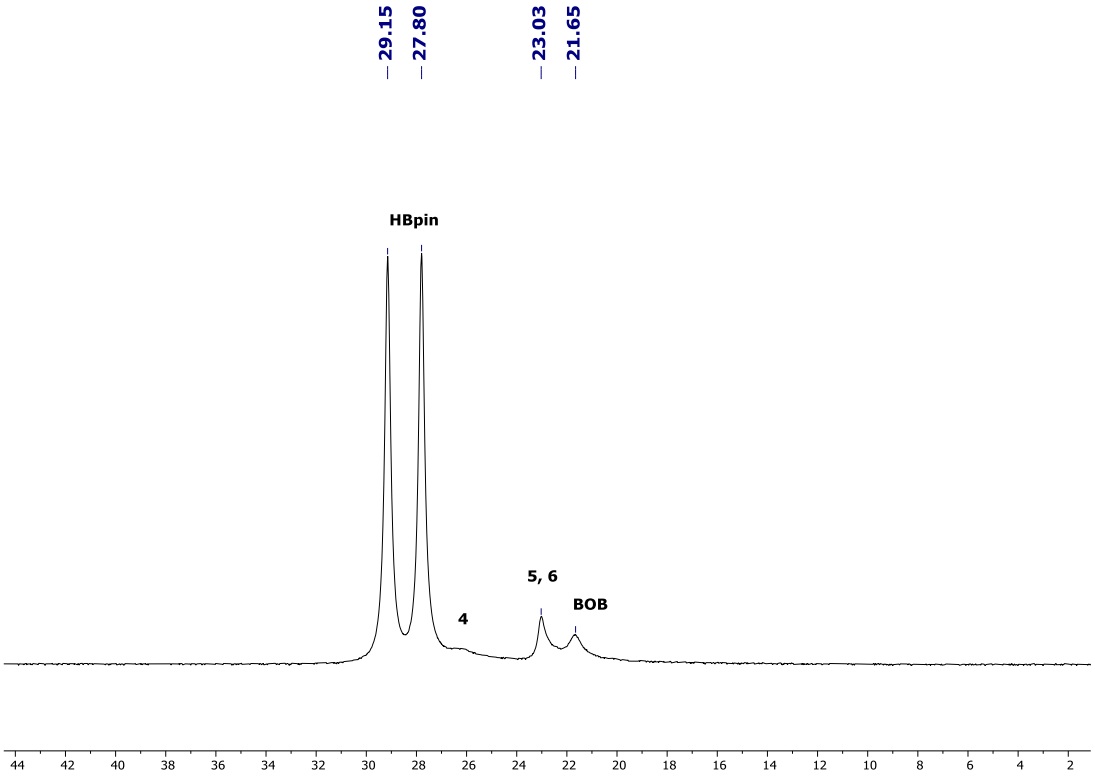


Figure S2. Representative ^{11}B NMR spectrum of product distribution from the reduction of CO_2 with HBpin (128 MHz, 1:1 CD_3CN:C_6D_6, 298 K)=

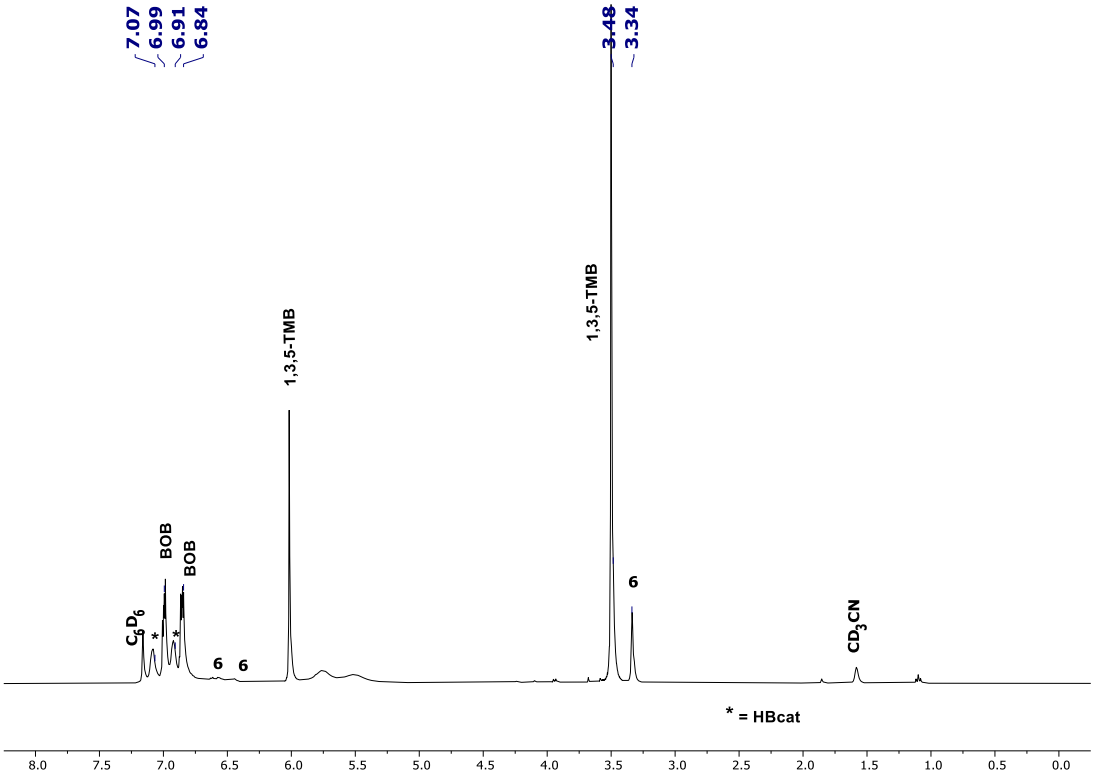


Figure S3. Representative ^{1}H NMR spectrum of product distribution from the reduction of CO_2 with HBcat (400 MHz, 1:1 CD_3CN:C_6D_6, 298 K)

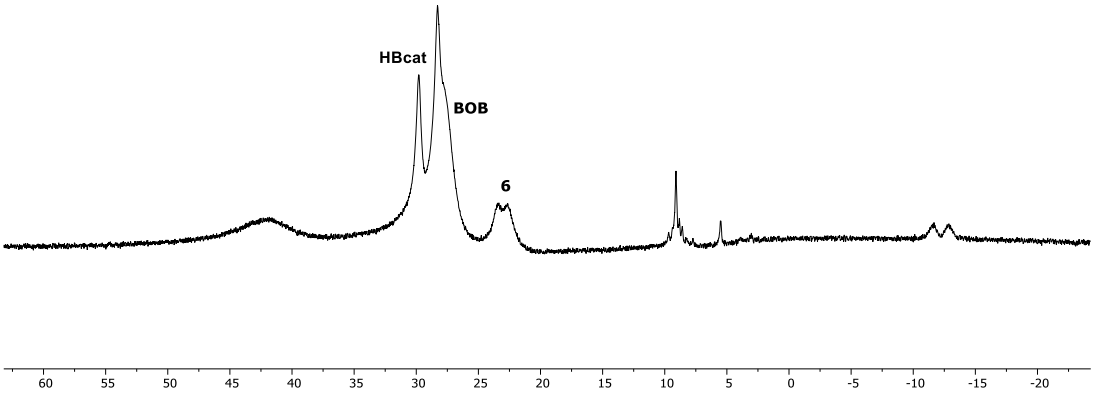


Figure S4. Representative ^{11}B NMR spectrum of product distribution from the reduction of CO_2 with HBcat (128 MHz, 1:1 CD_3CN:C_6D_6, 298 K)

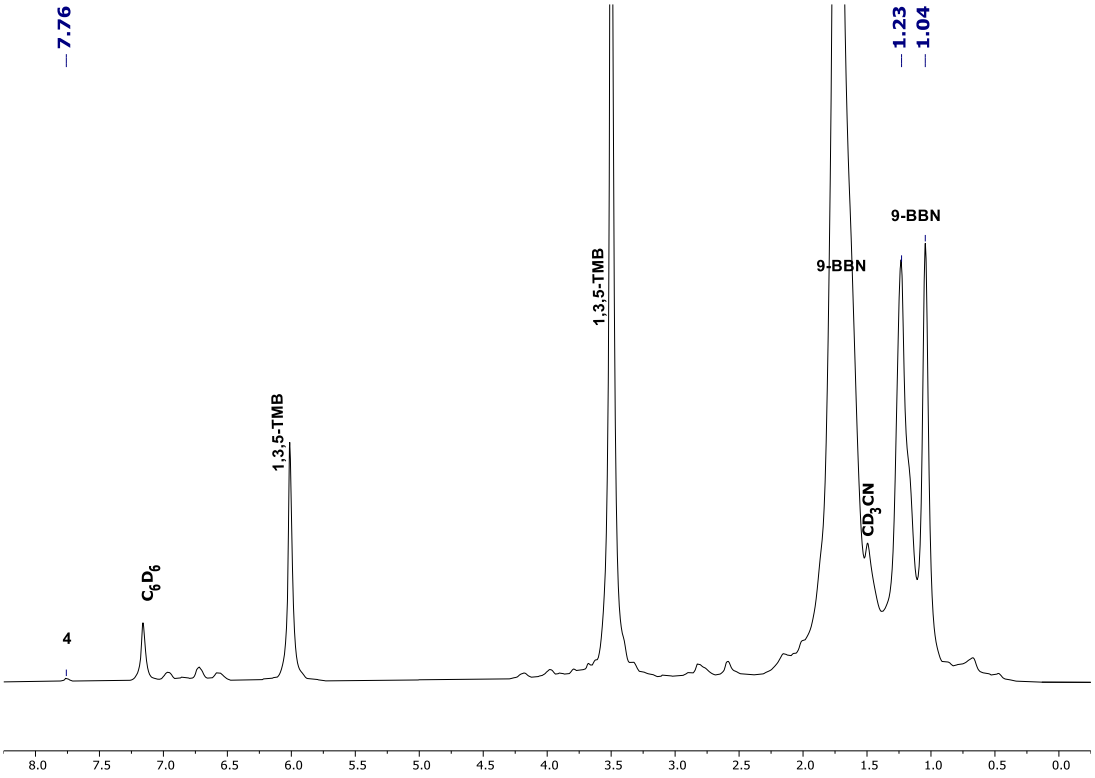


Figure S5. Representative ^{1}H NMR spectrum of product distribution from the reduction of CO_2 with 9-BBN (400 MHz, 1:1 CD_3CN:C_6D_6, 298 K)

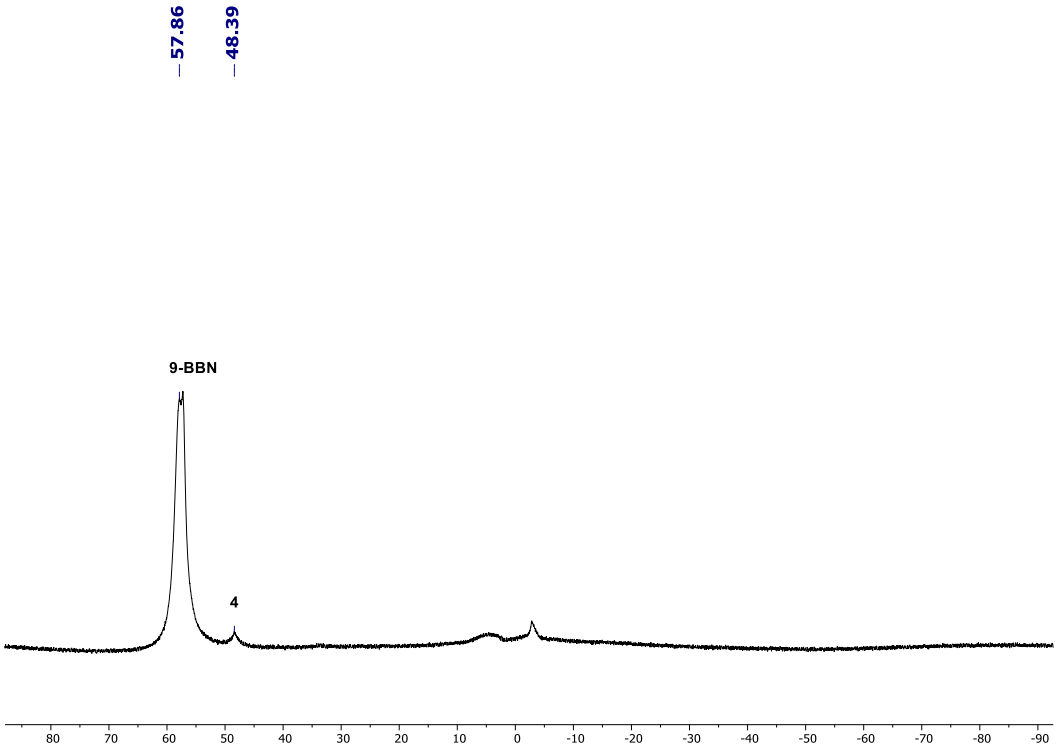
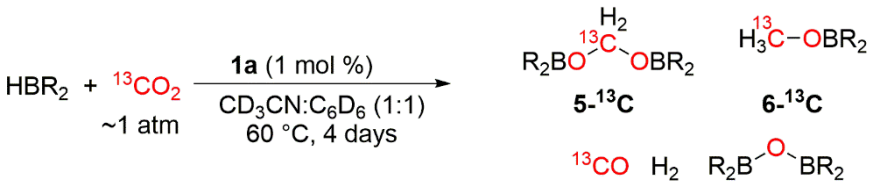


Figure S6. Representative ^{11}B NMR spectrum of product distribution from the reduction of CO_2 with 9-BBN (128 MHz, 1:1 CD_3CN:C_6D_6, 298 K)



1a (1 mol%) was dissolved in 1:1 $CD_3CN:C_6D6$ (600 µL). HBpin (0.05 mmol) was added and the reaction was freeze-pump-thawed × 3. $^{13}CO_2$ (1 atm) was added to the J.Young tube NMR and sealed up, heated to 60 °C for 4 days and monitored by multinuclear NMR spectroscopy. Unfortunately, no free ^{13}CO or any Fe–^{13}CO species could be observed in $^{13}C\{^1H\}$ NMR spectrum due to potentially small scale of the reaction, solubility of ^{13}CO in solvent and/or paramagnetic nature of any iron species generated in the reaction.

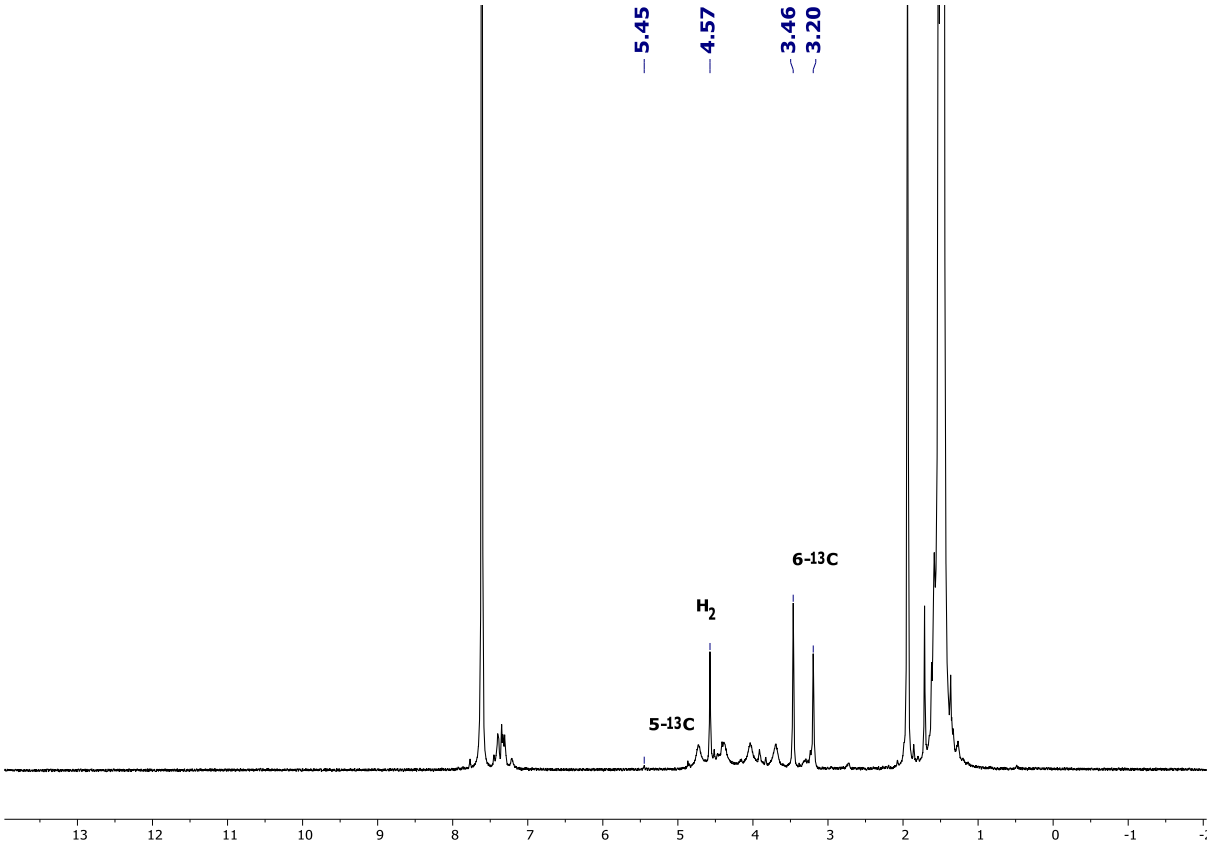


Figure S7. ^1H NMR spectrum of product distribution from the reduction of $^{13}CO_2$ with HBpin (500 MHz, 1:1 $CD_3CN:C_6D_6$, 298 K)

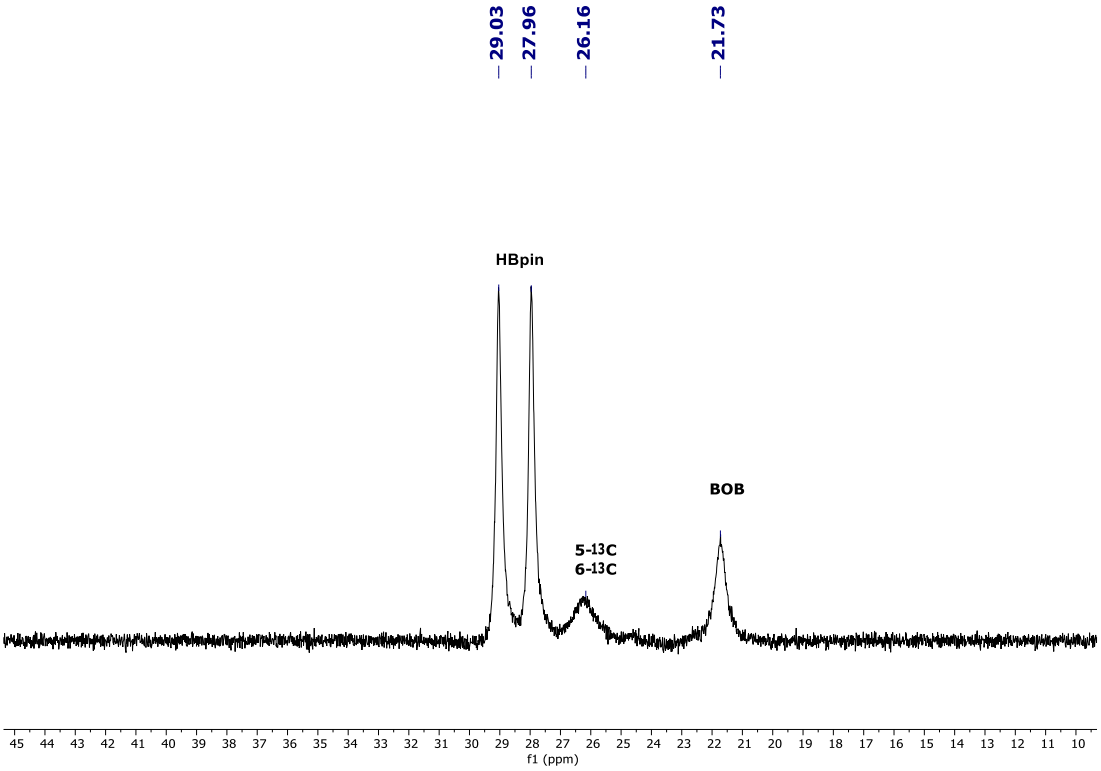


Figure S8. $^{11}B\{^{1}H\}$ NMR spectrum of product distribution from the reduction of $^{13}CO_2$ with HBpin (160 MHz, 1:1 CD_3CN:C_6D_6, 298 K)

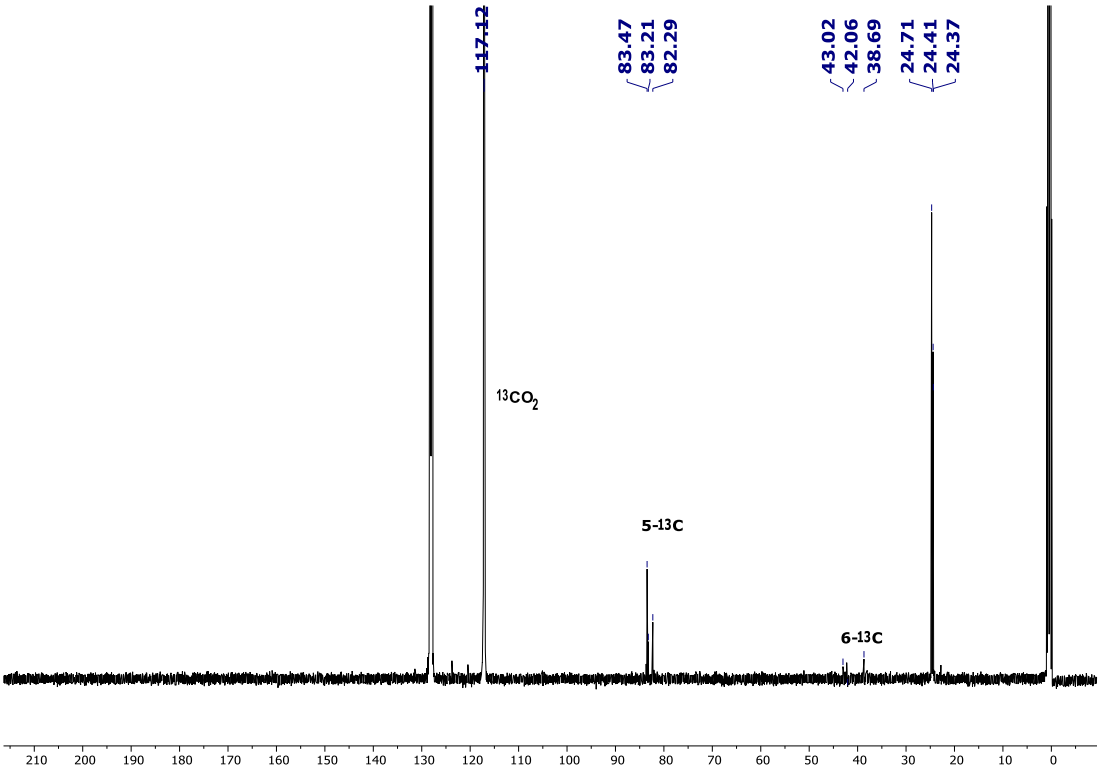
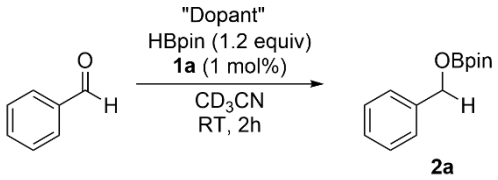


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of product distribution from the reduction of $^{13}CO_2$ with HBpin (126 MHz, 1:1 CD_3CN:C_6D_6, 298 K)

7. Homogeneity reactions



2a

Dopant	Spectroscopic Yield of 2a / %
None	92
PMe_3 (2 mol%)	58
PMe_3 (4 mol%)	36
Hg	82

8. Spectra of new compounds

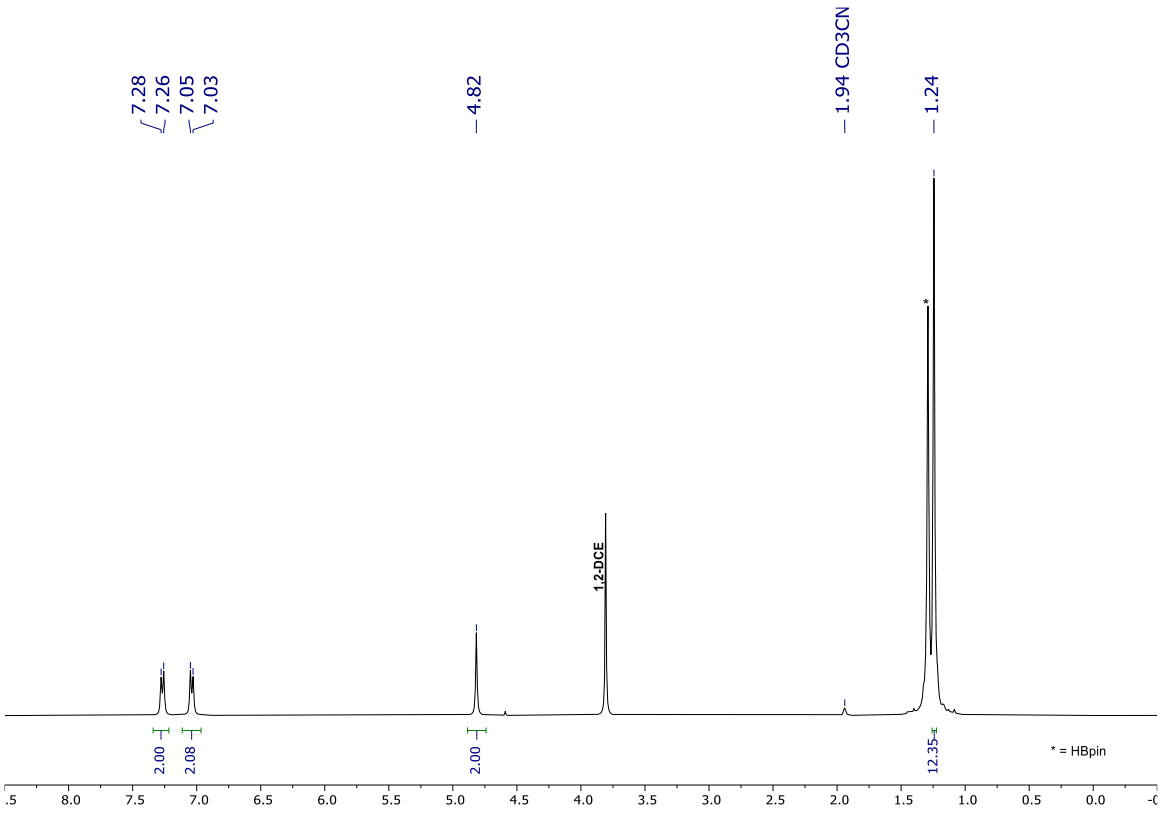


Figure S10. ^{1}H NMR spectrum of **2f** (400 MHz, CD_3CN, 298 K)

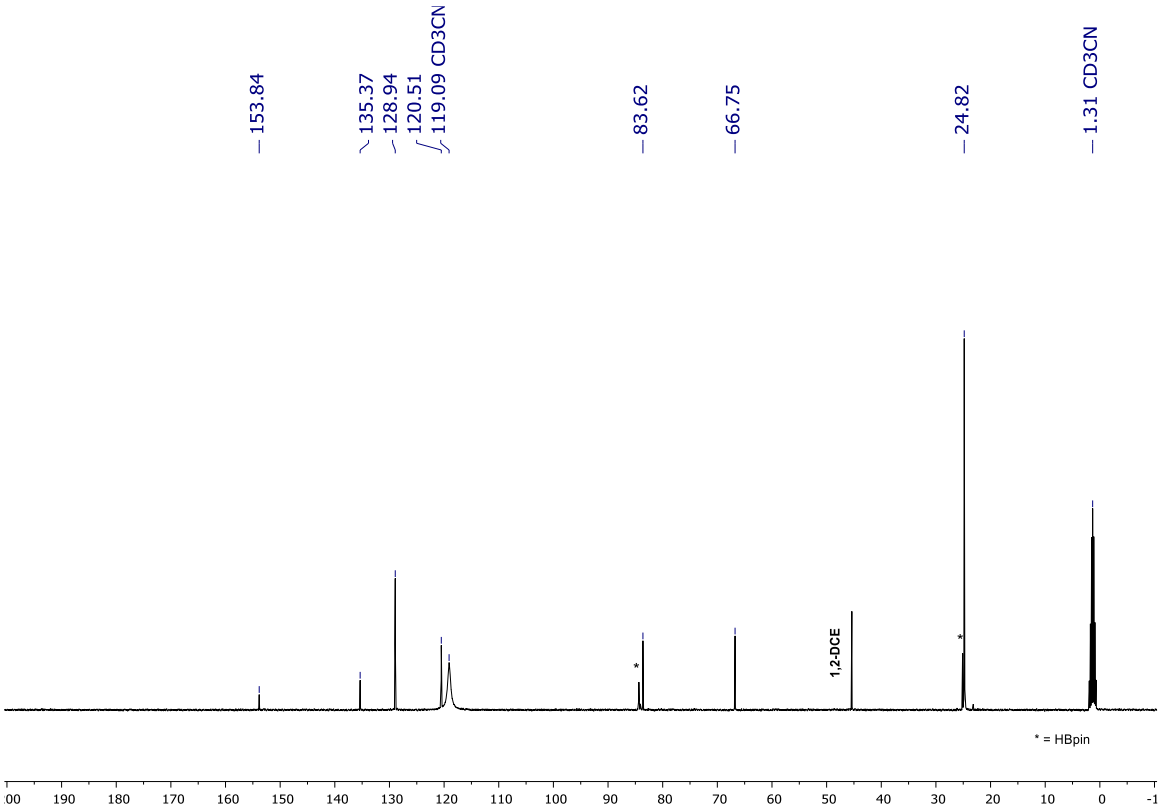


Figure S11. ^{13}C{^{1}H} NMR spectrum of **2f** (101 MHz, CD_3CN, 298 K)

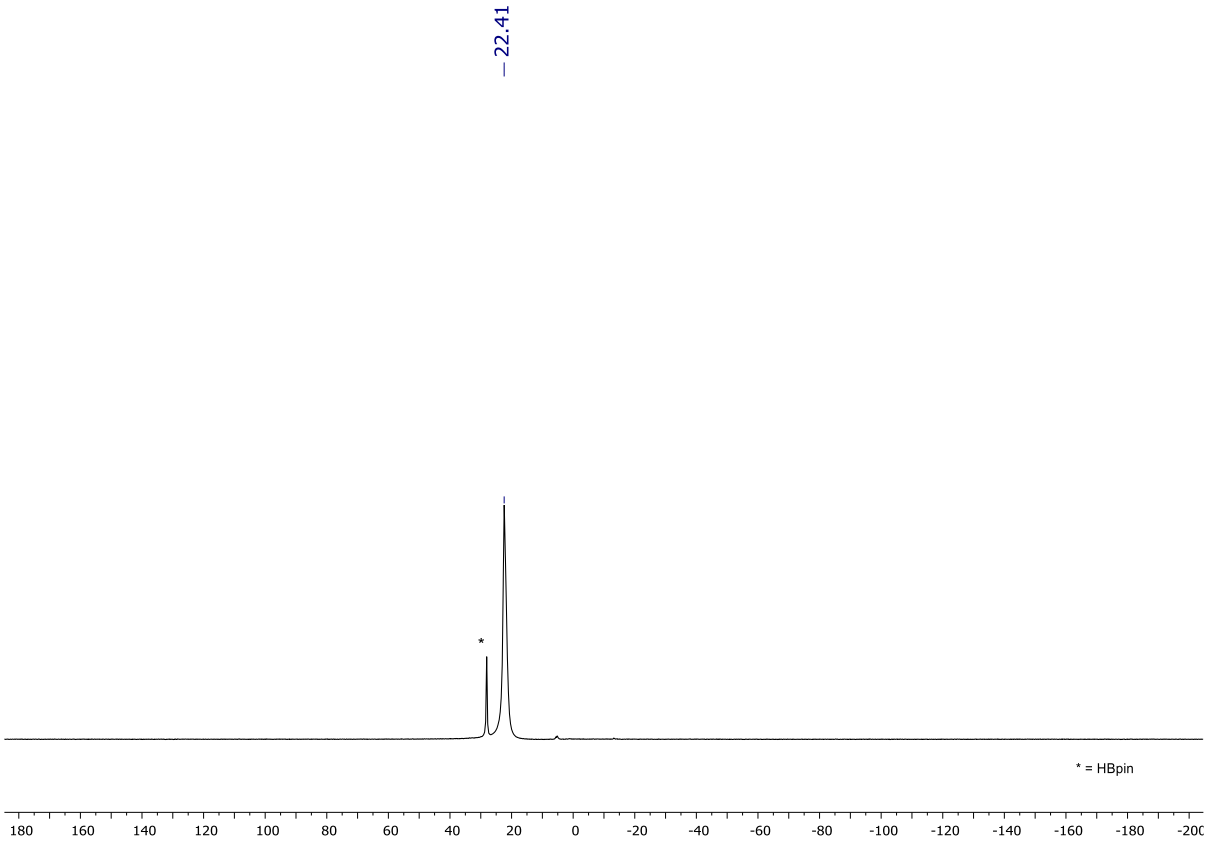


Figure S12. $^{11}B\{^{1}H\}$ NMR spectrum of **2f** (128 MHz, CD_3CN, 298 K)

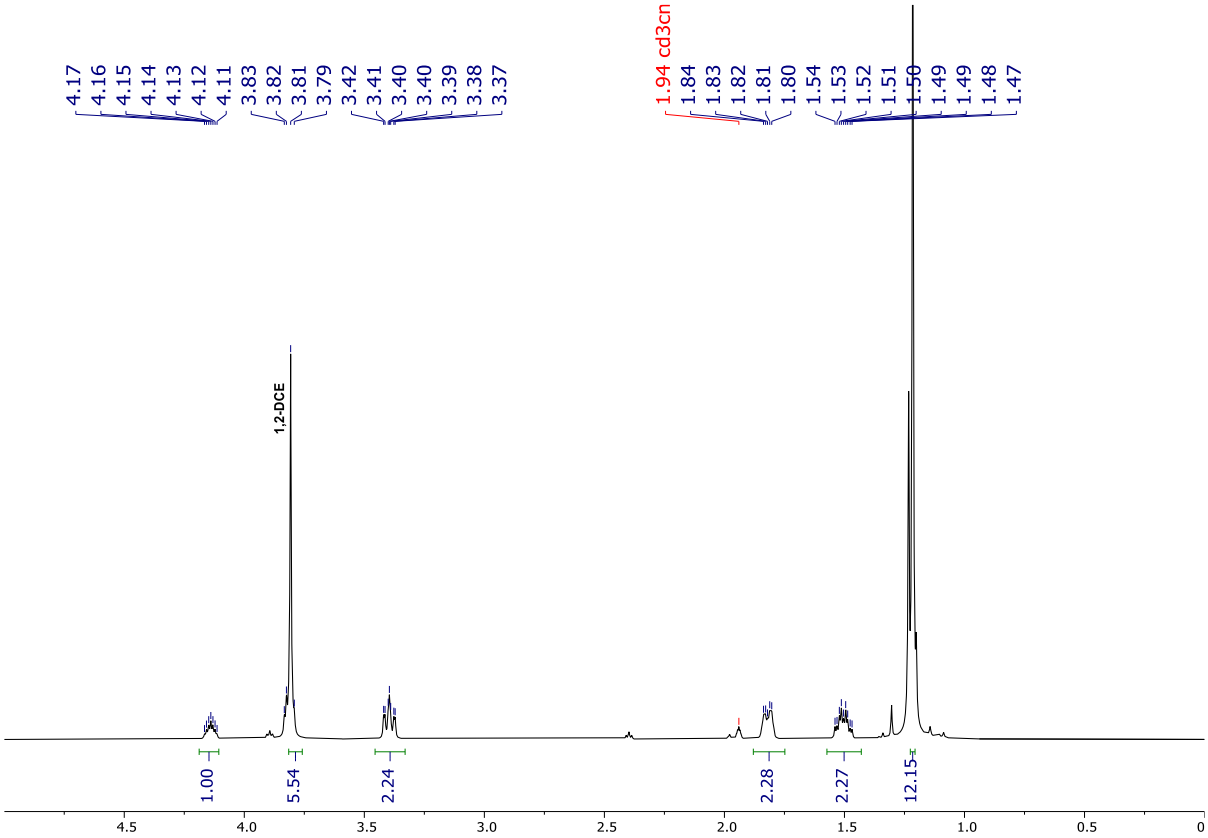


Figure S13. ^{1}H NMR spectrum of **3j** (500 MHz, CD_3CN, 298 K)

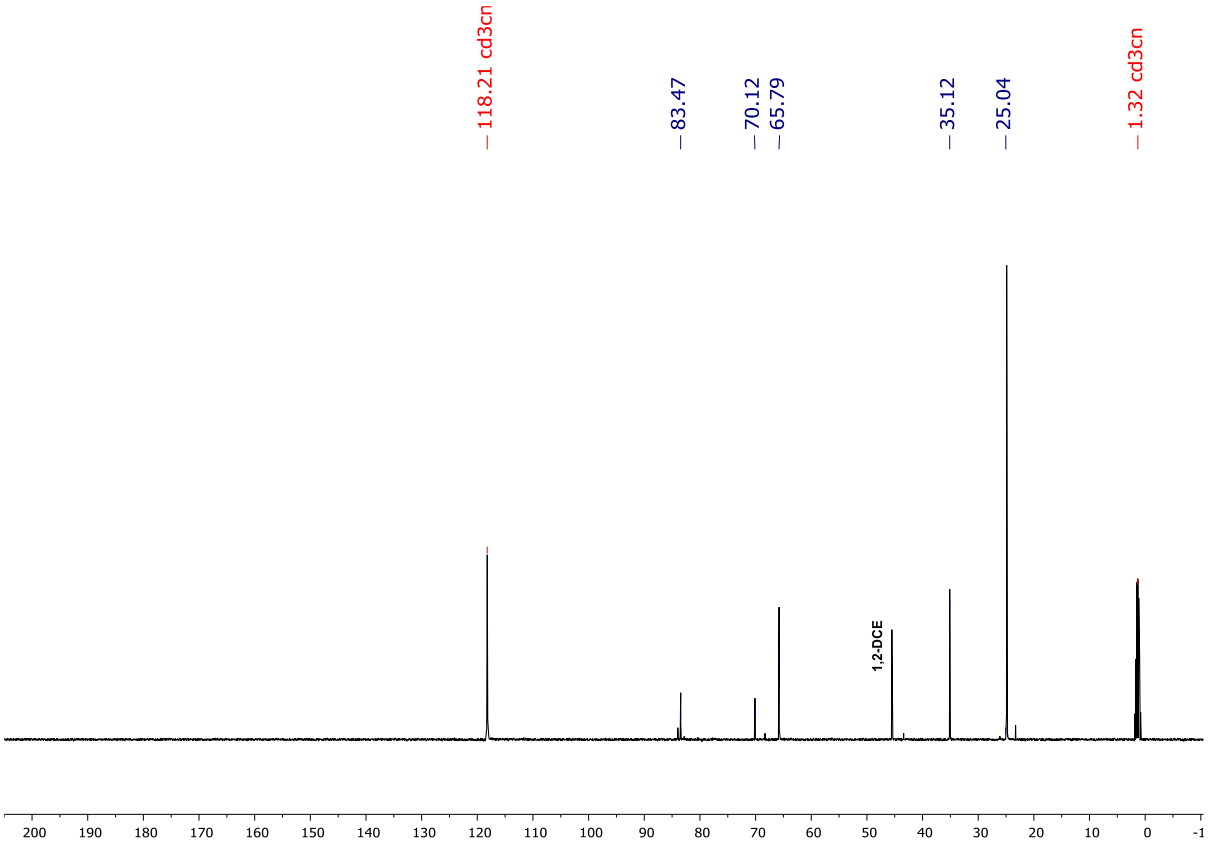


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **3j** (126 MHz, CD_3CN, 298 K)

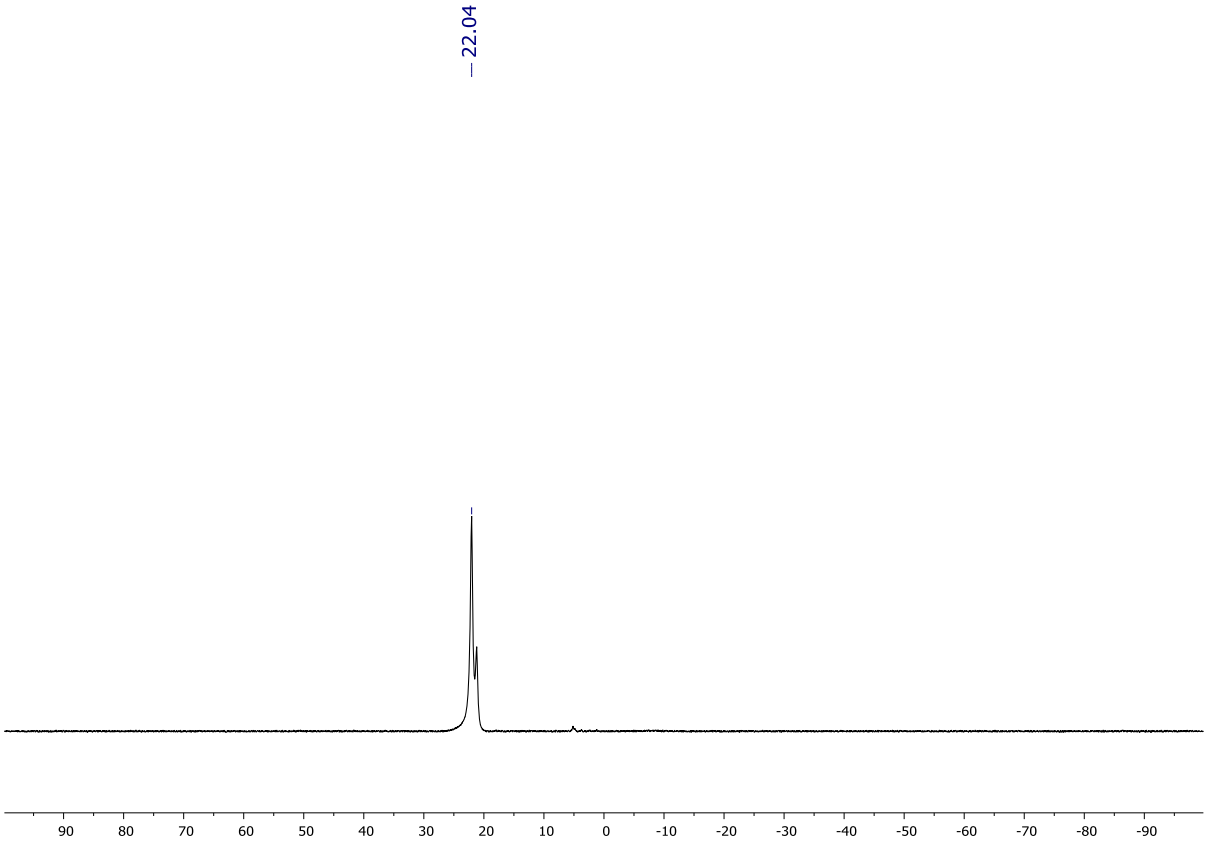
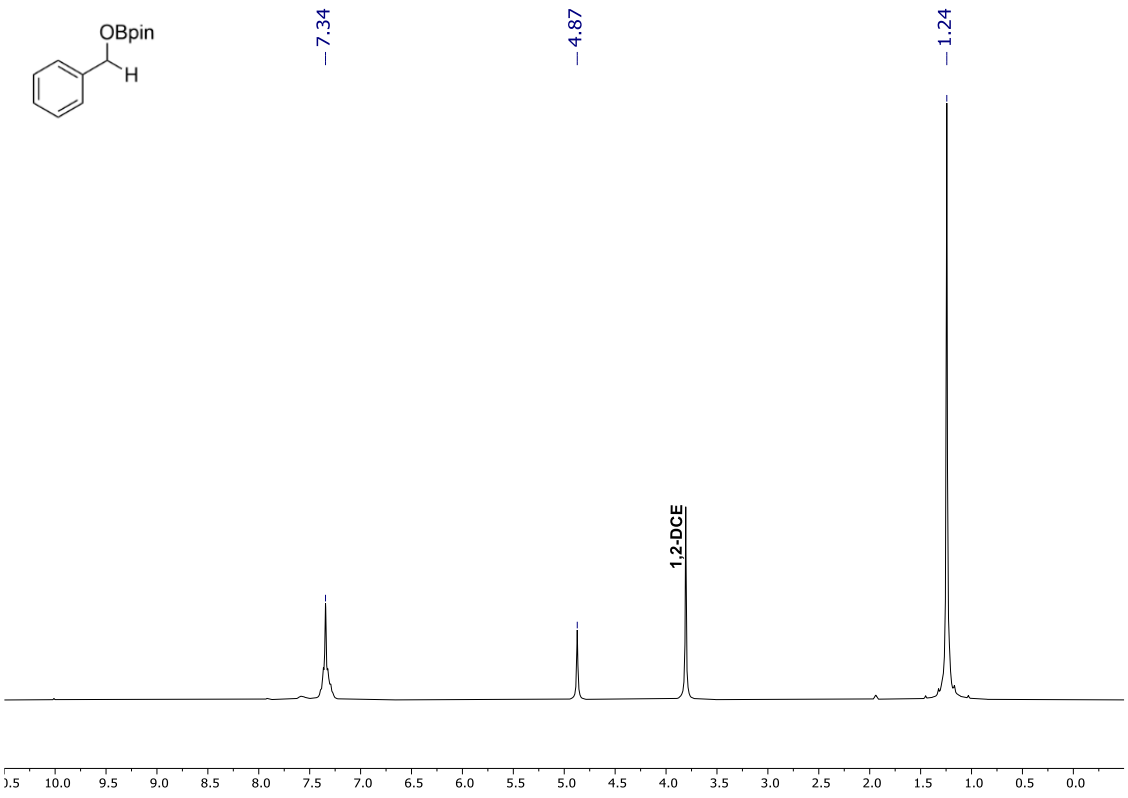
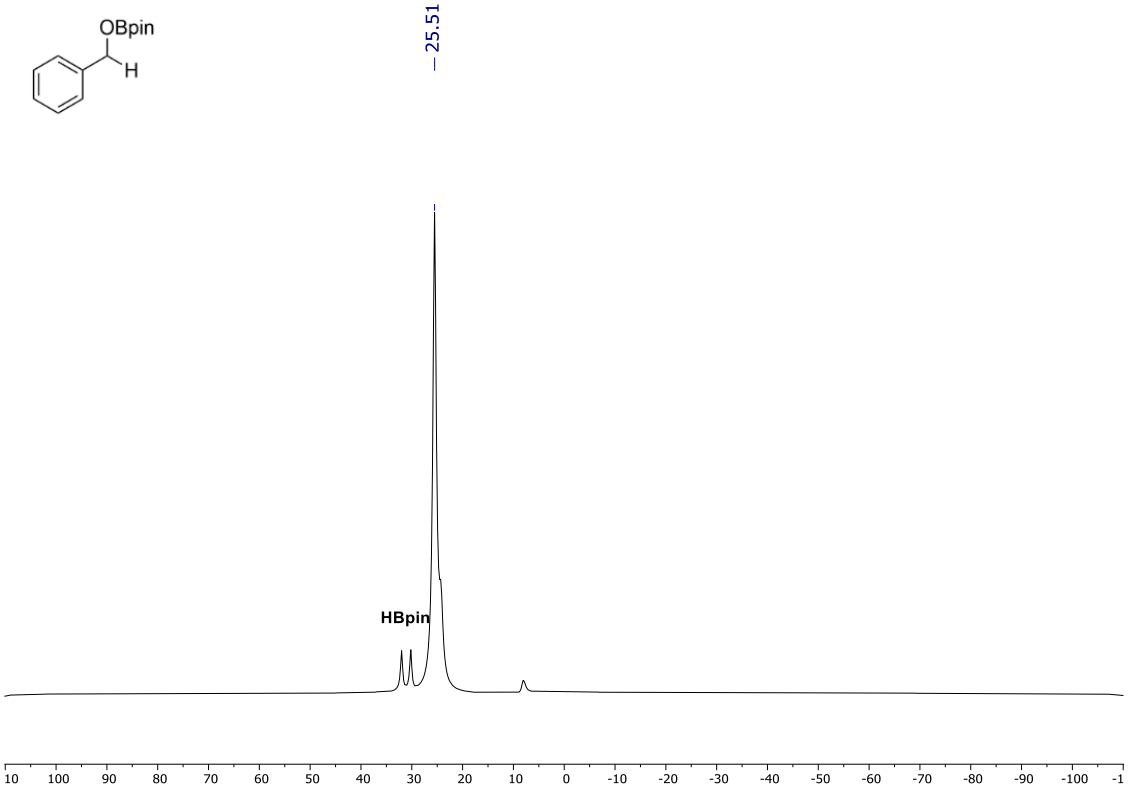
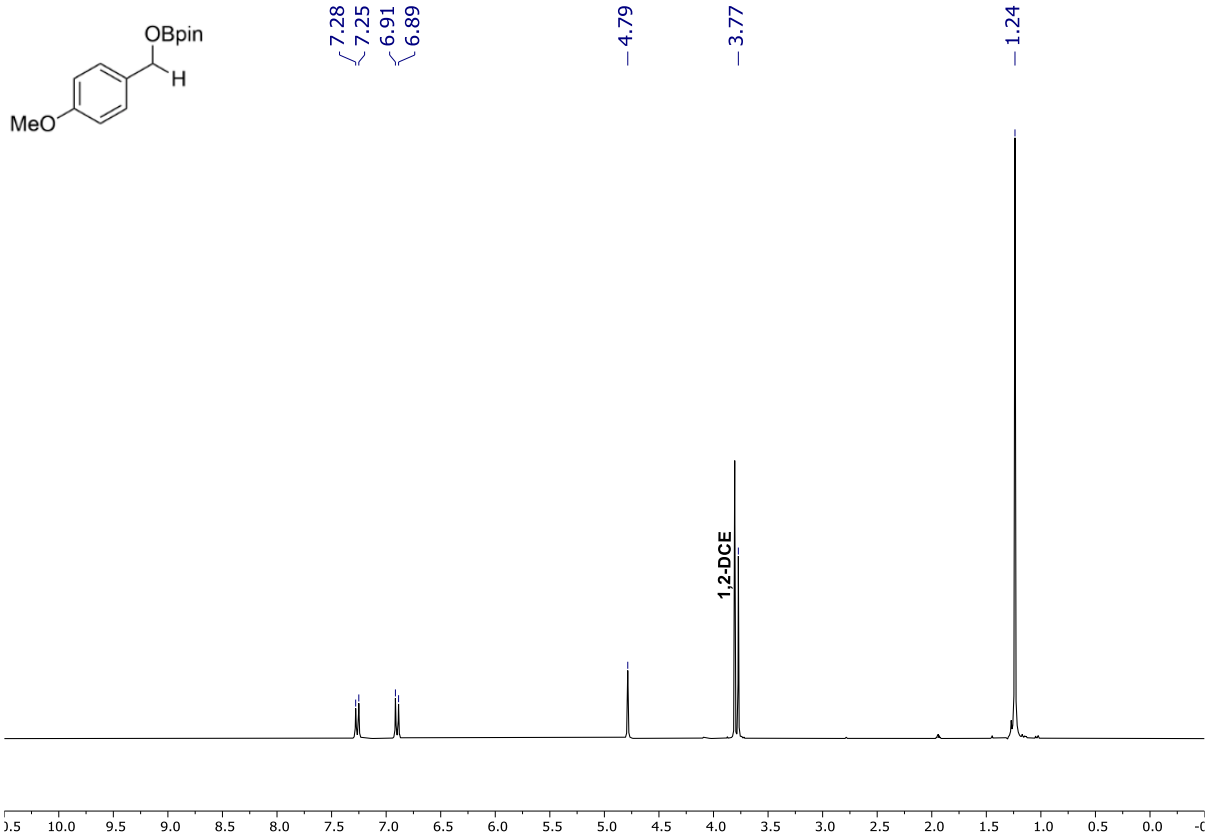


Figure S15. $^{11}B\{^{1}H\}$ NMR spectrum of **3j** (160 MHz, CD_3CN, 298 K)

9. Spectra of Known Compounds



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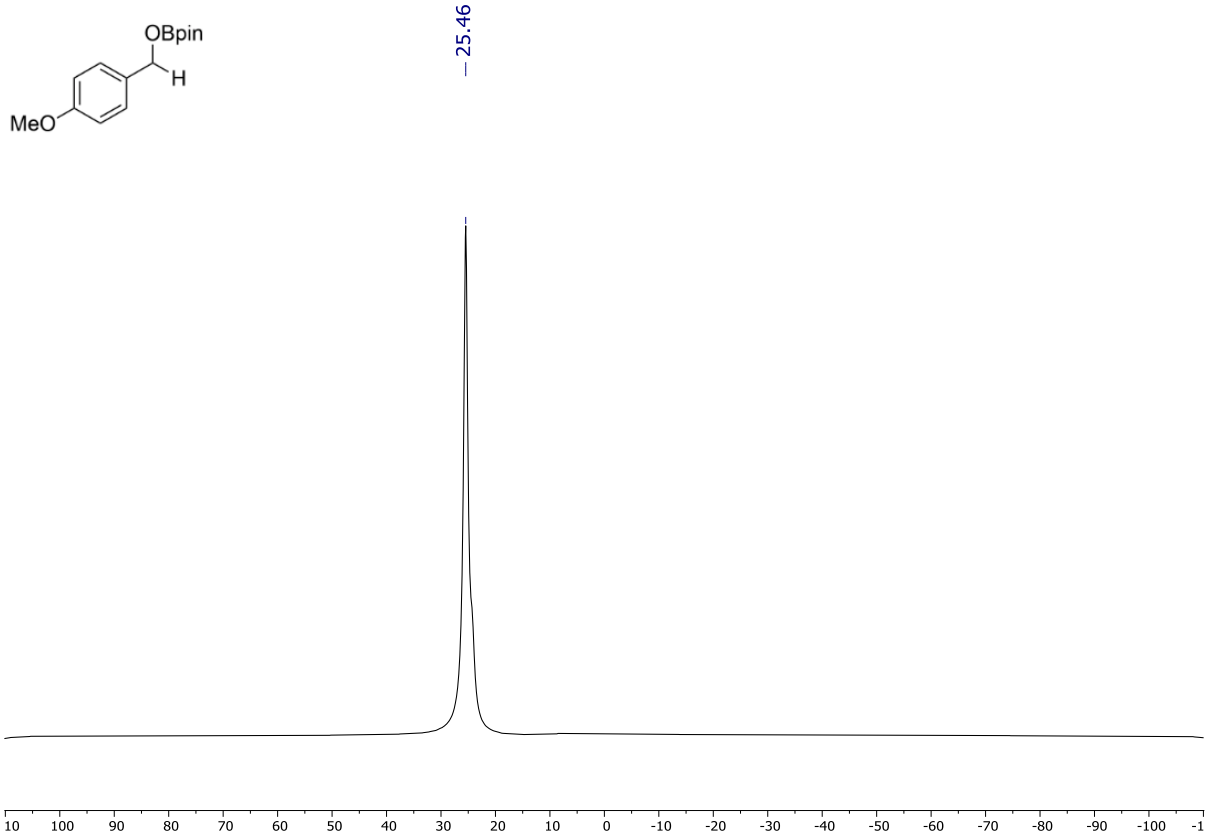
7.25
6.91
6.89
4.79
3.77
1.24
1,2-DCE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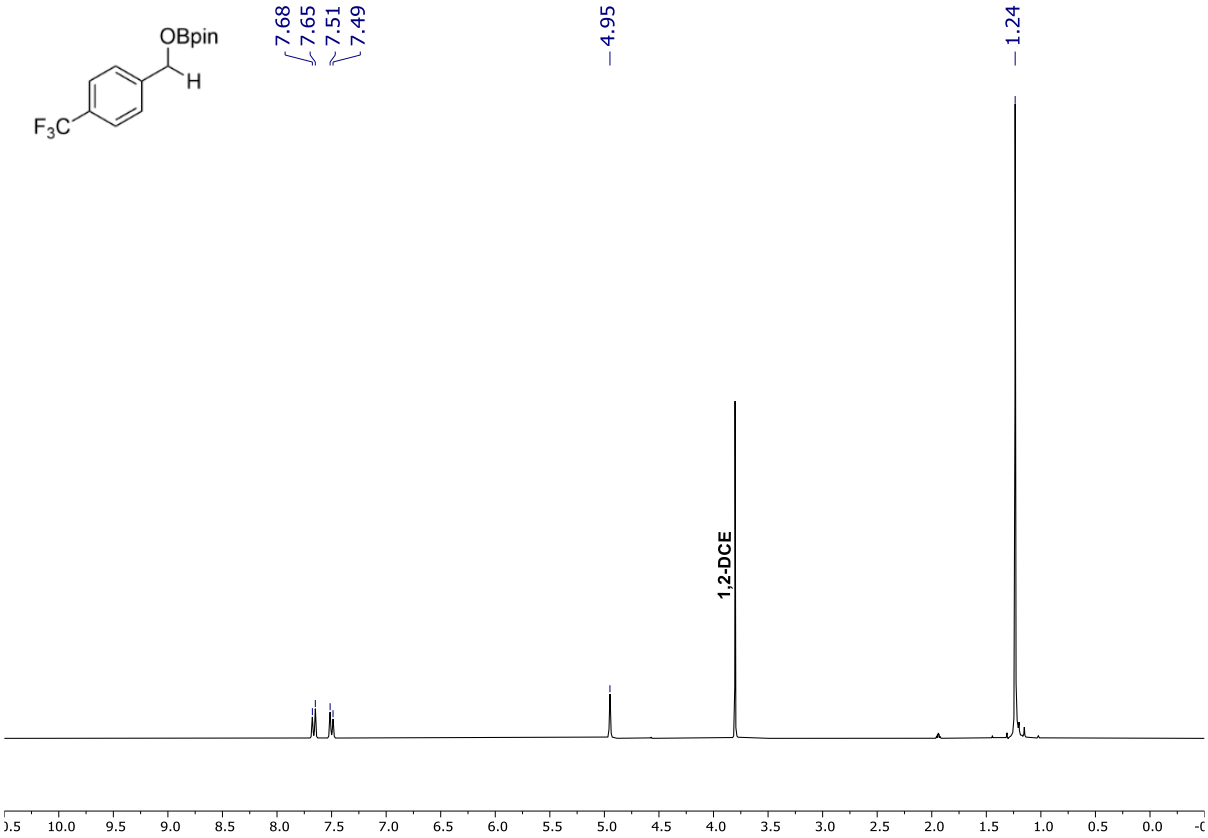
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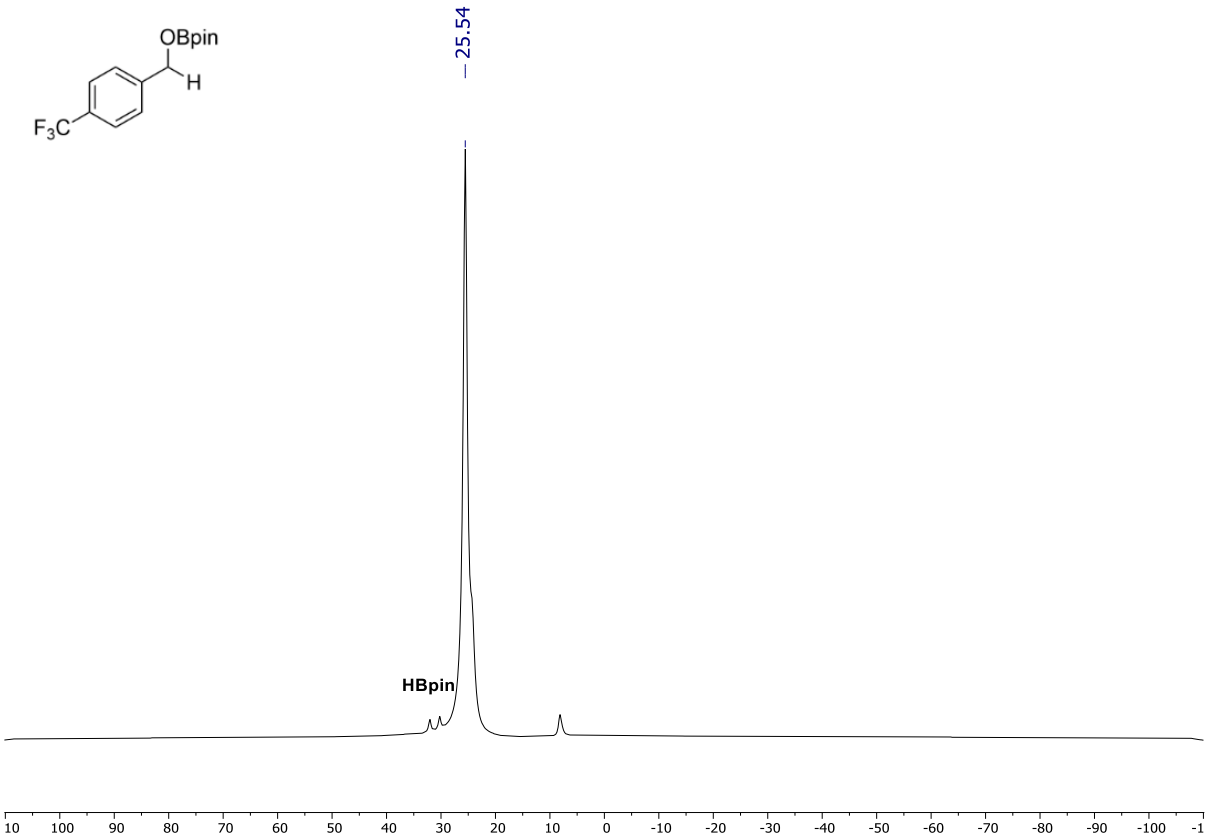
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F3C
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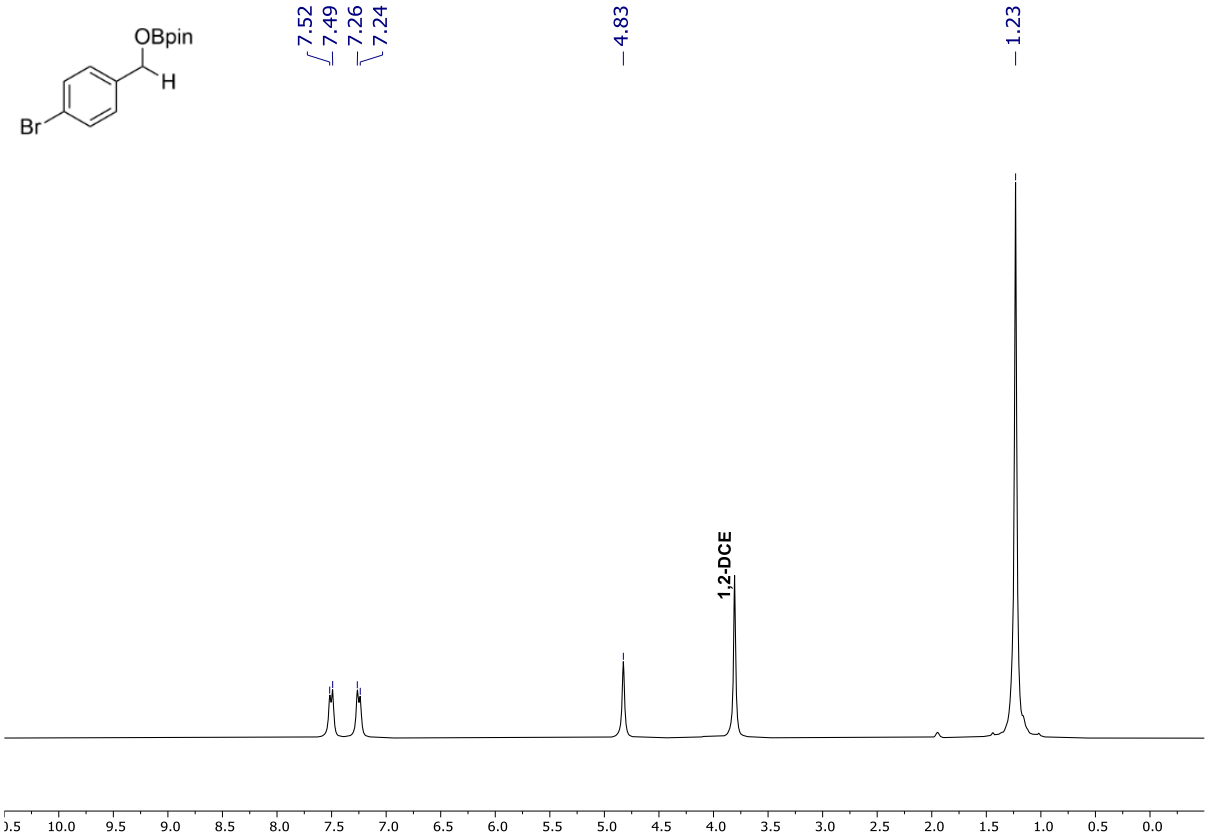
HBpin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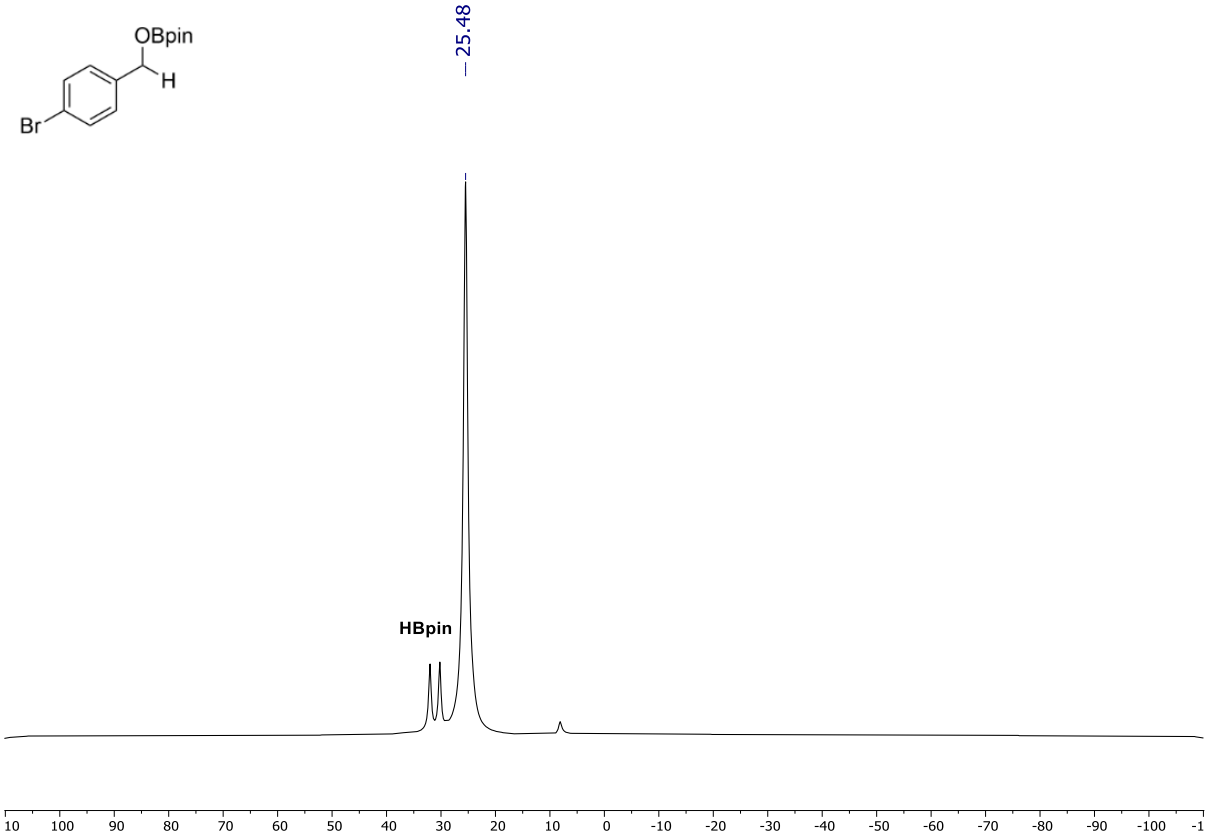
1.23
1,2-DCE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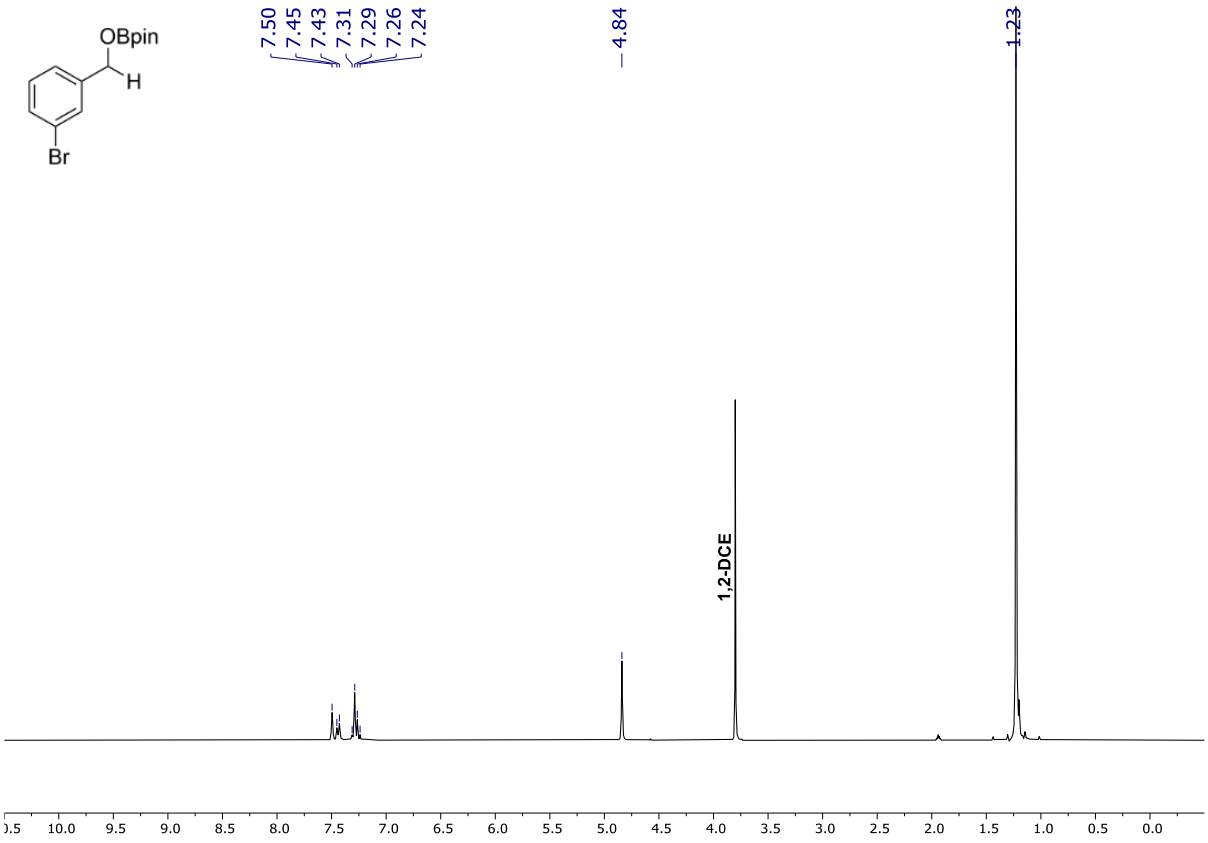
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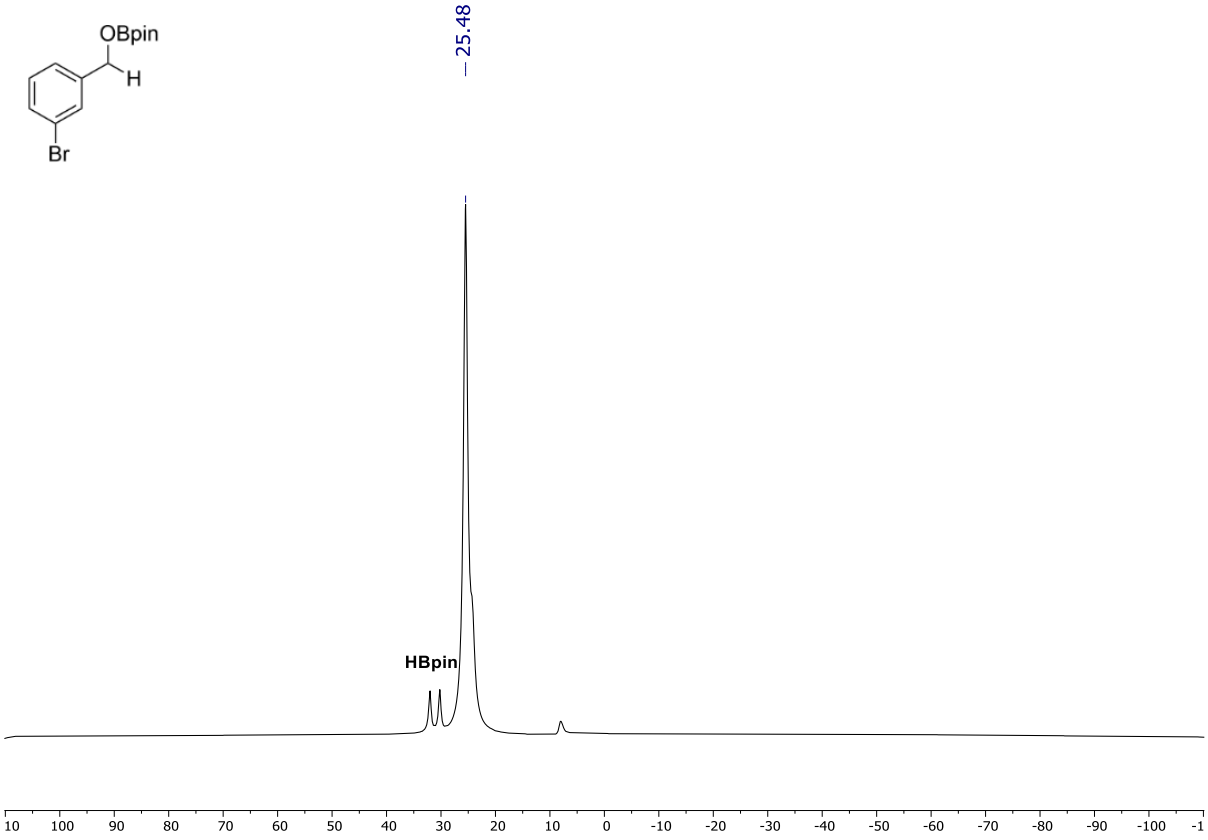
1.23
1,2-DCE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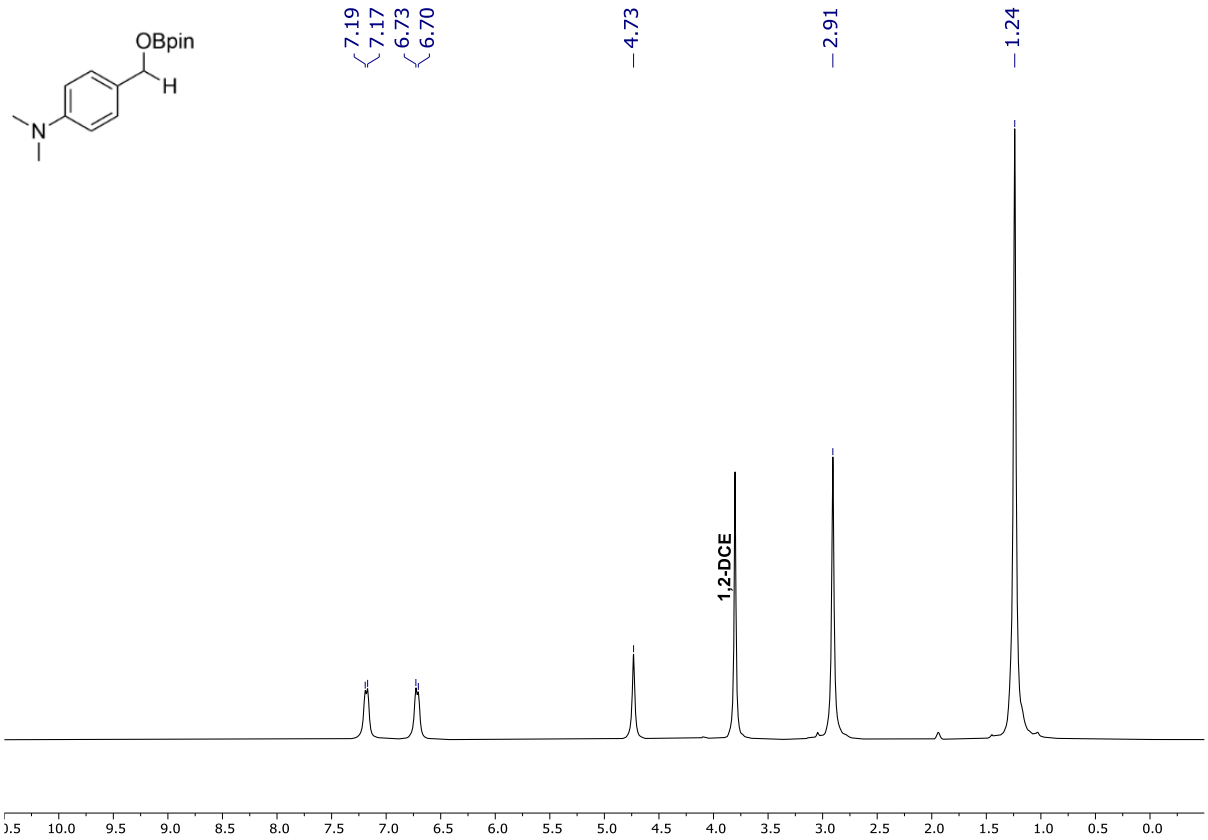
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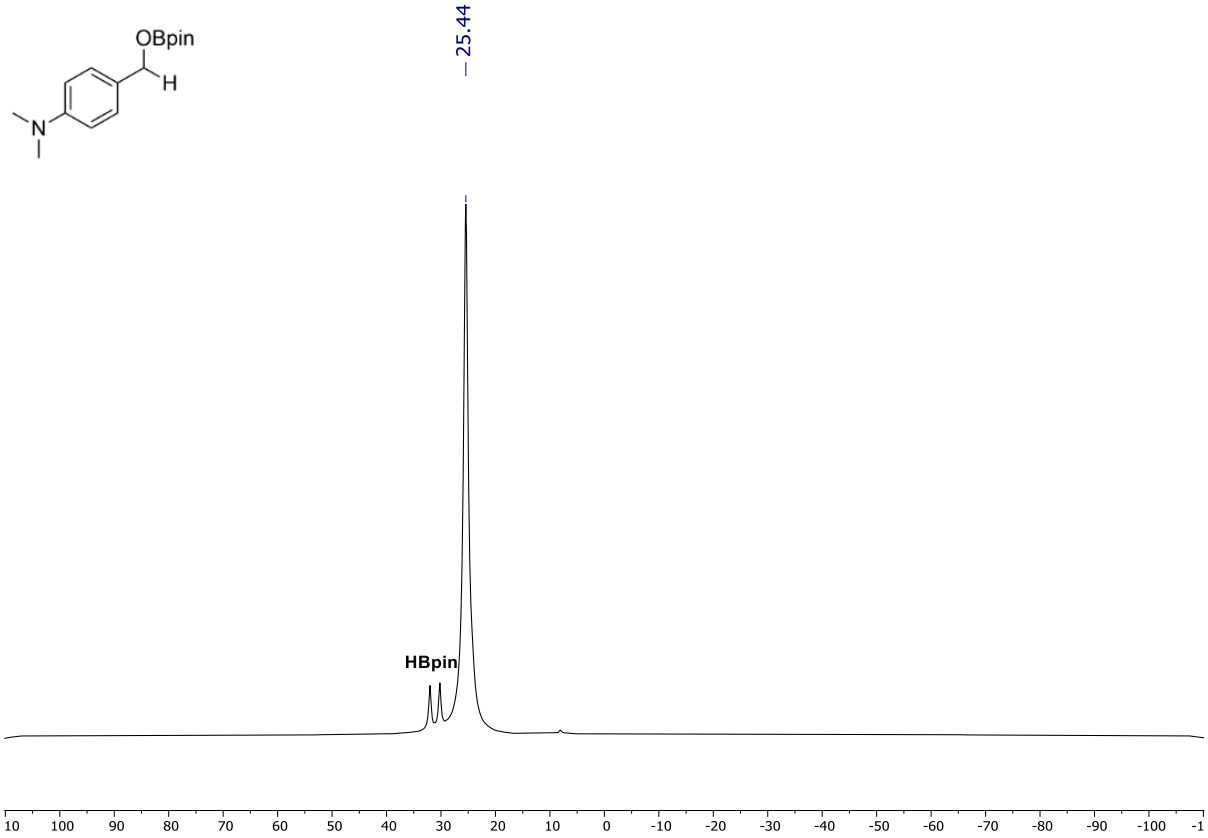
1,2-DCE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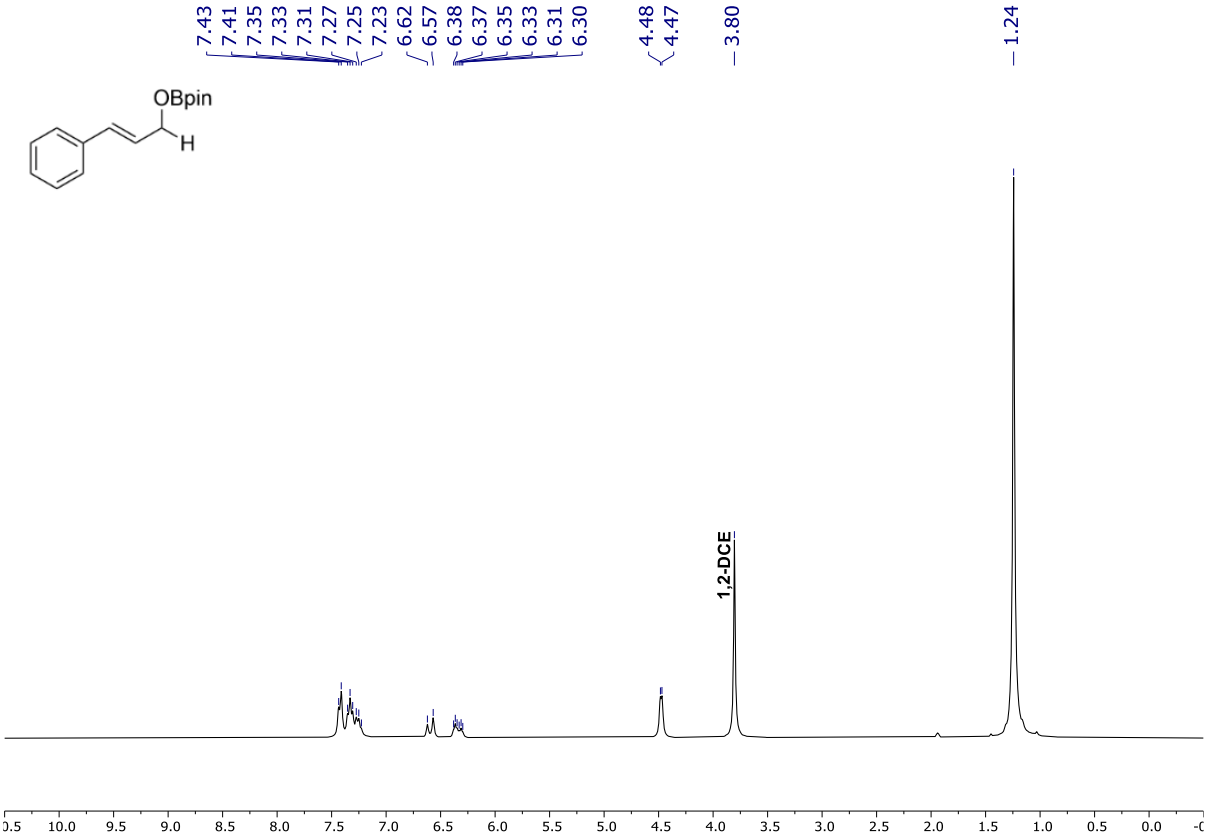
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3.80
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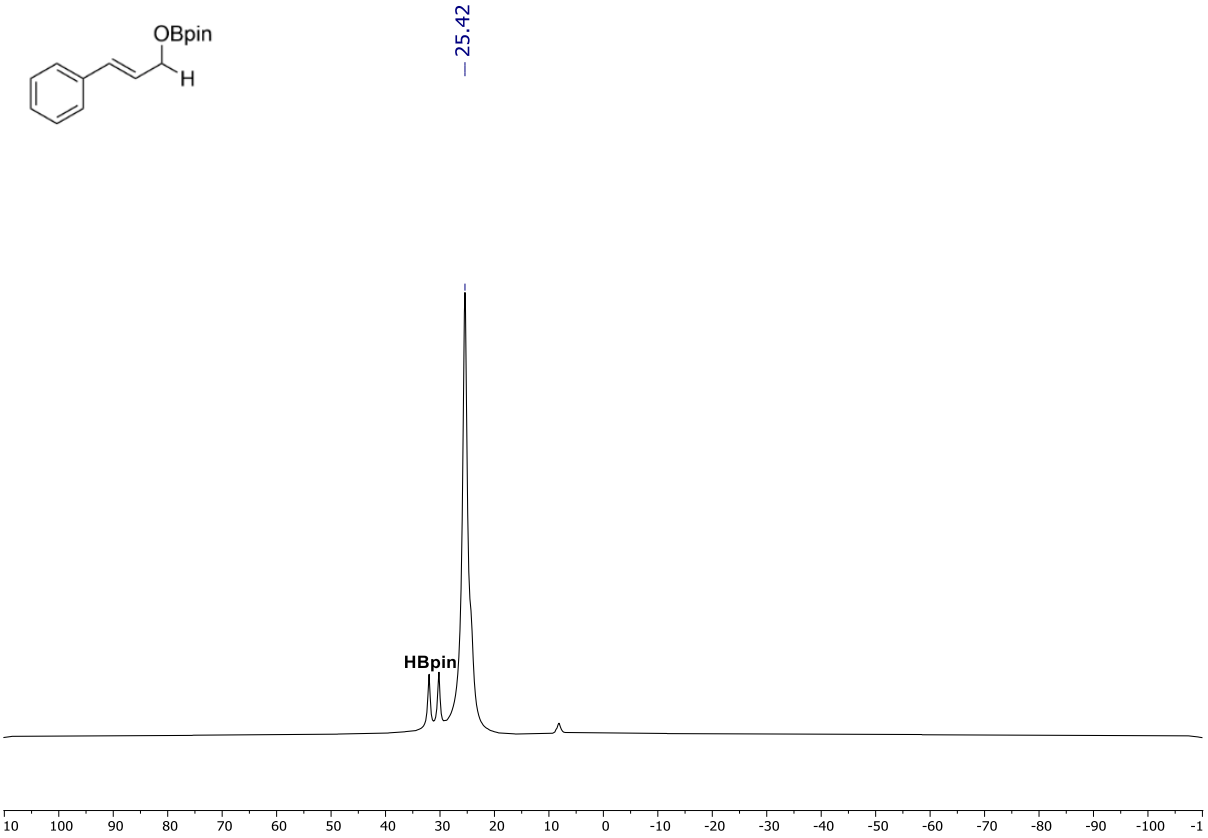
H
1,2-DCE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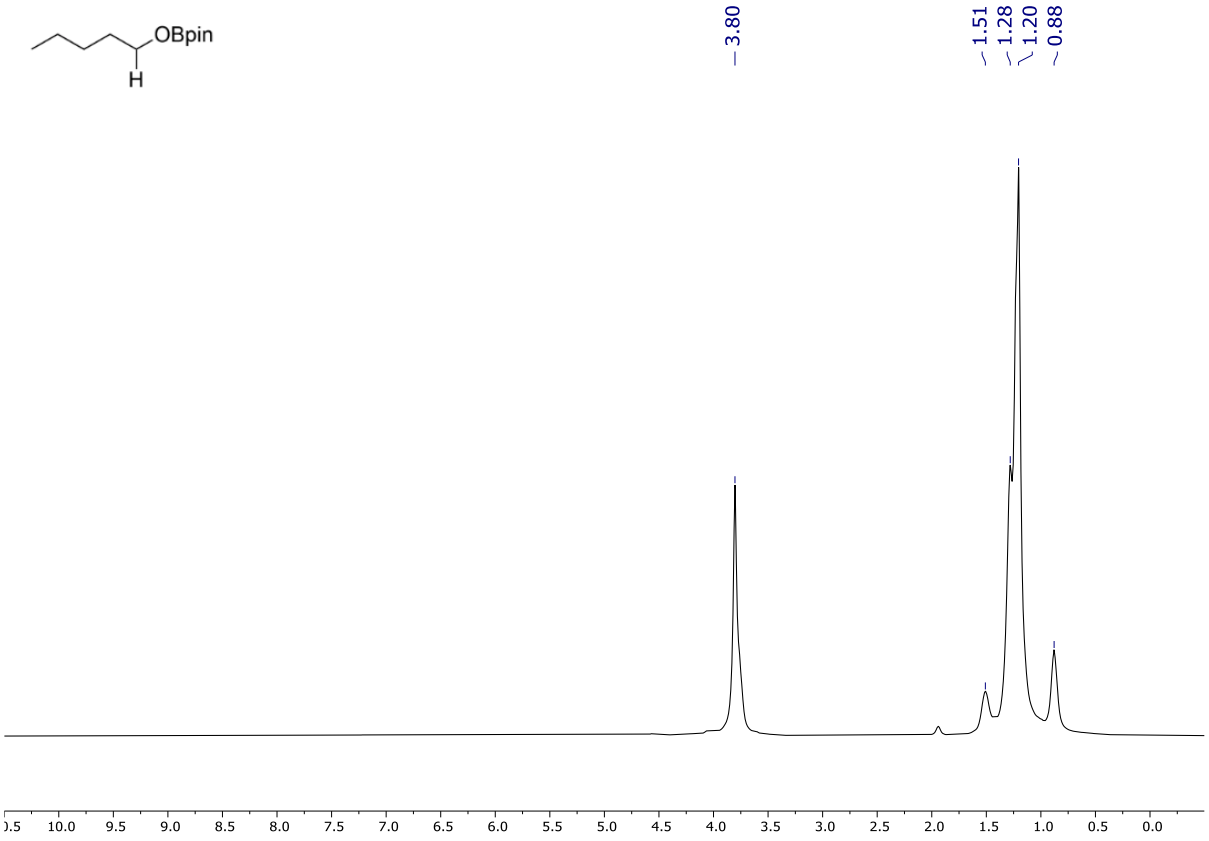
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9.5
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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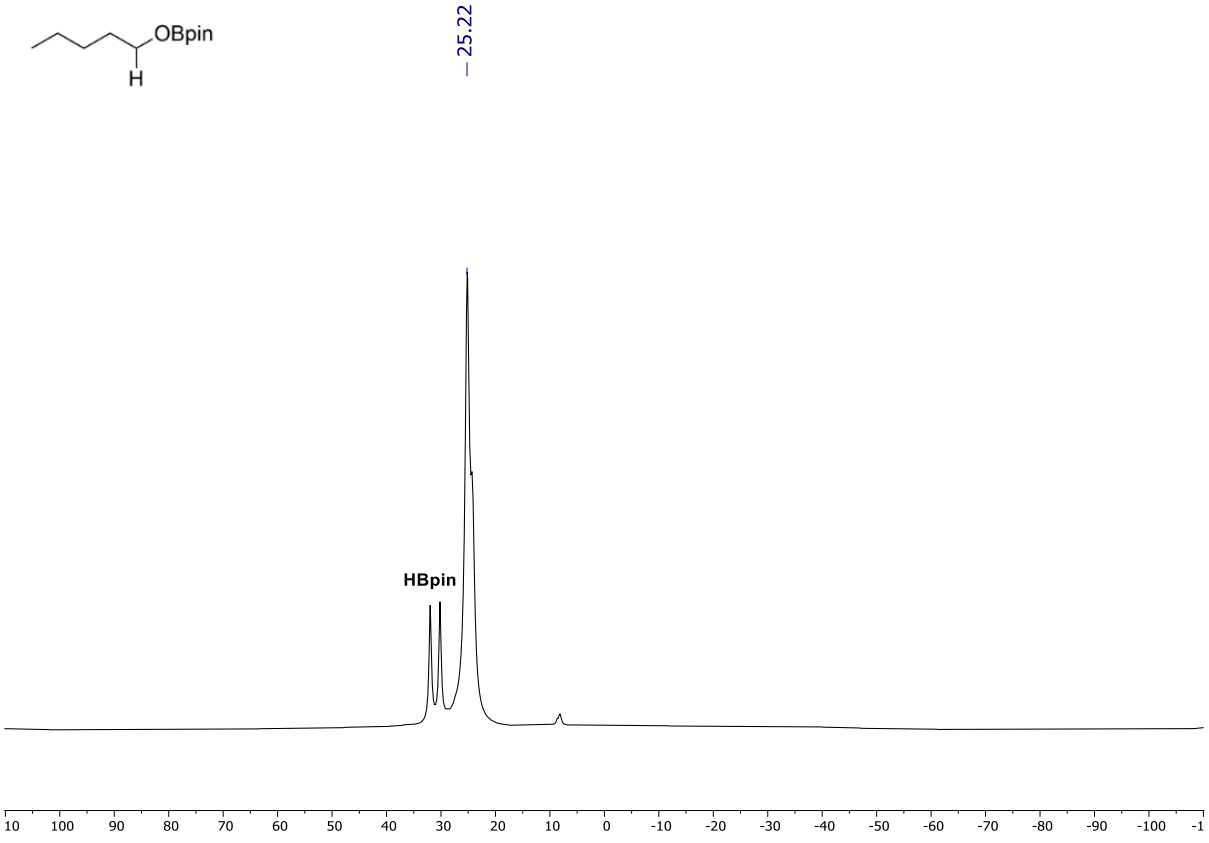
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HBpin
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100
90
80
70
60
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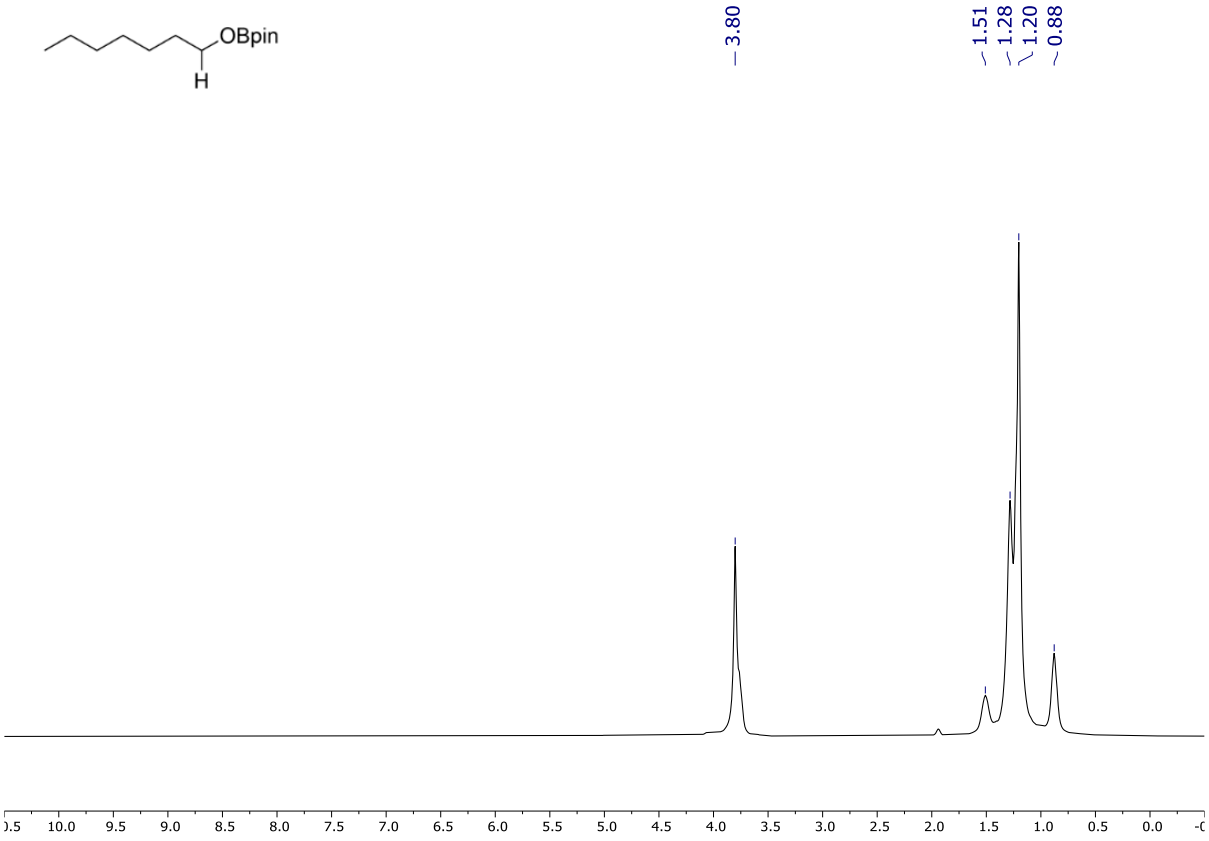
-50
-60
-70
-80
-90
-100
-1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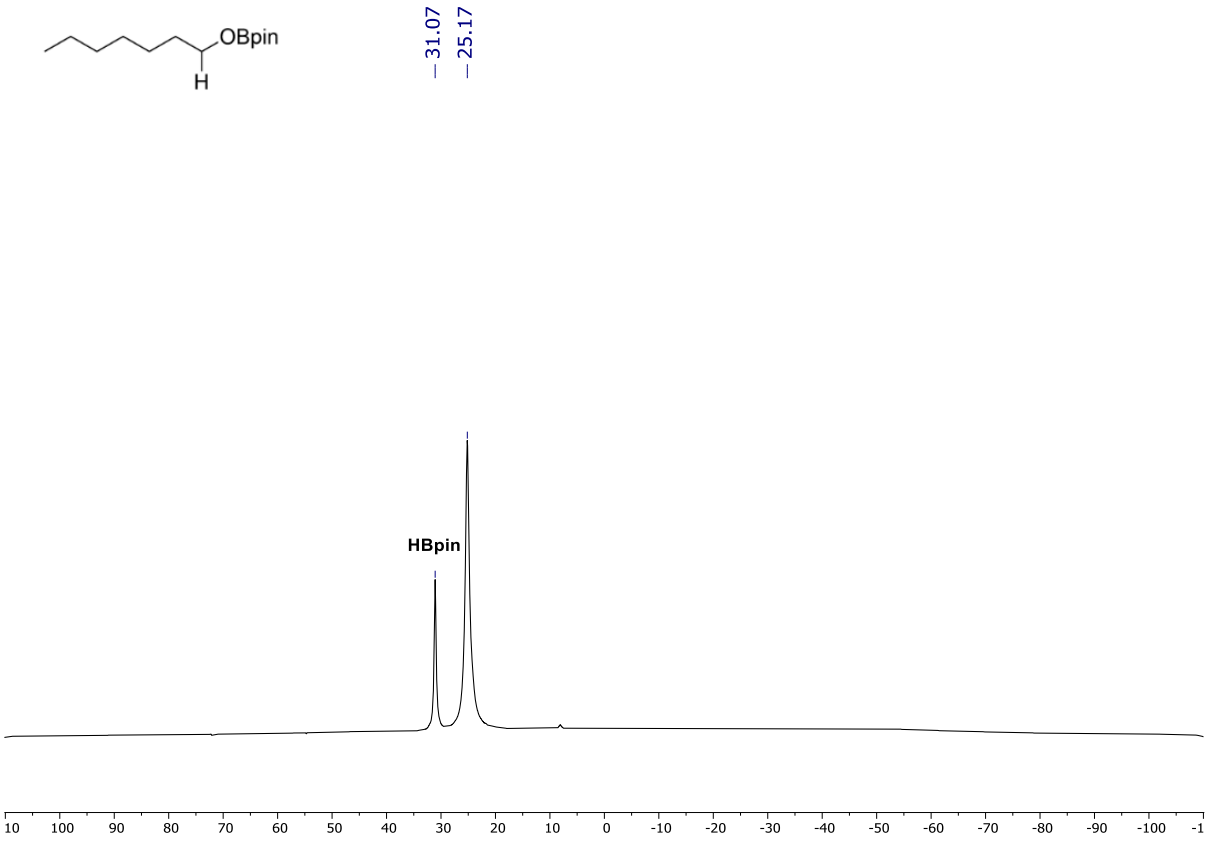
1.51
1.28
1.20
0.88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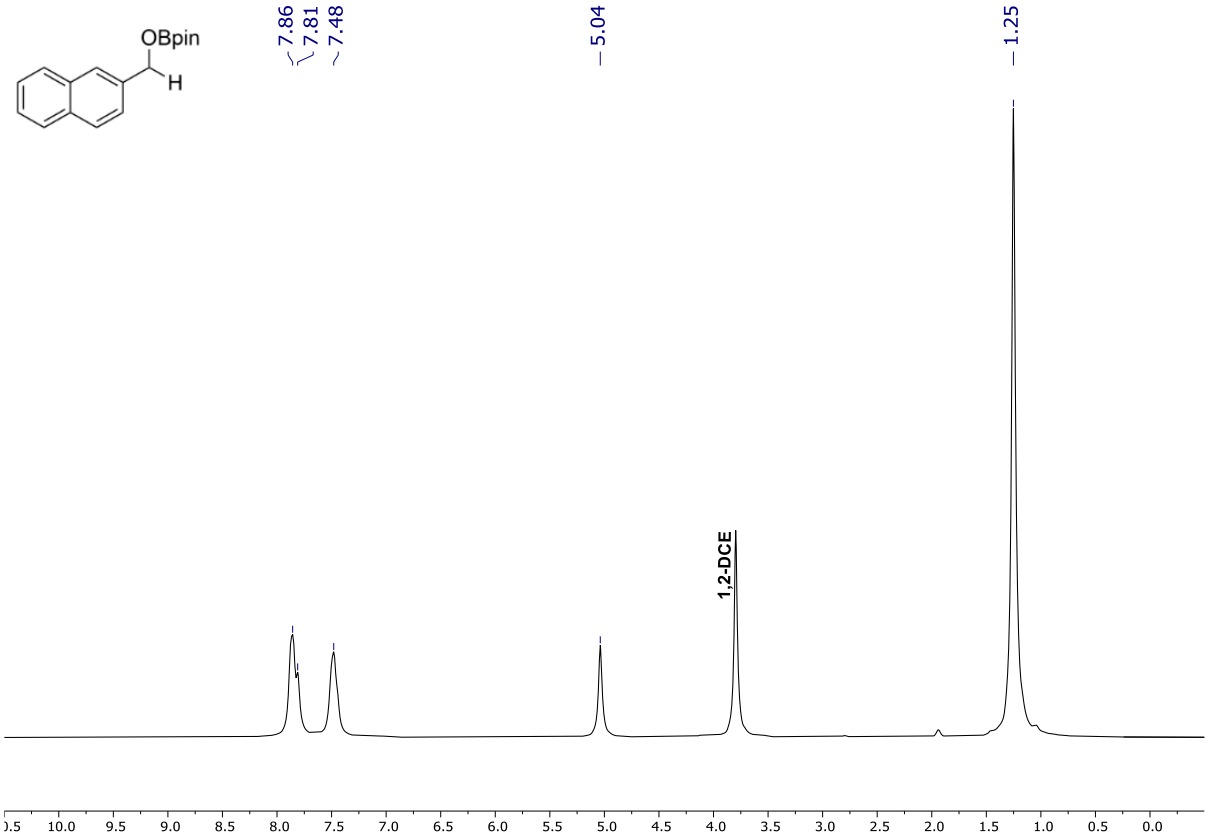
31.07
25.17
HBpin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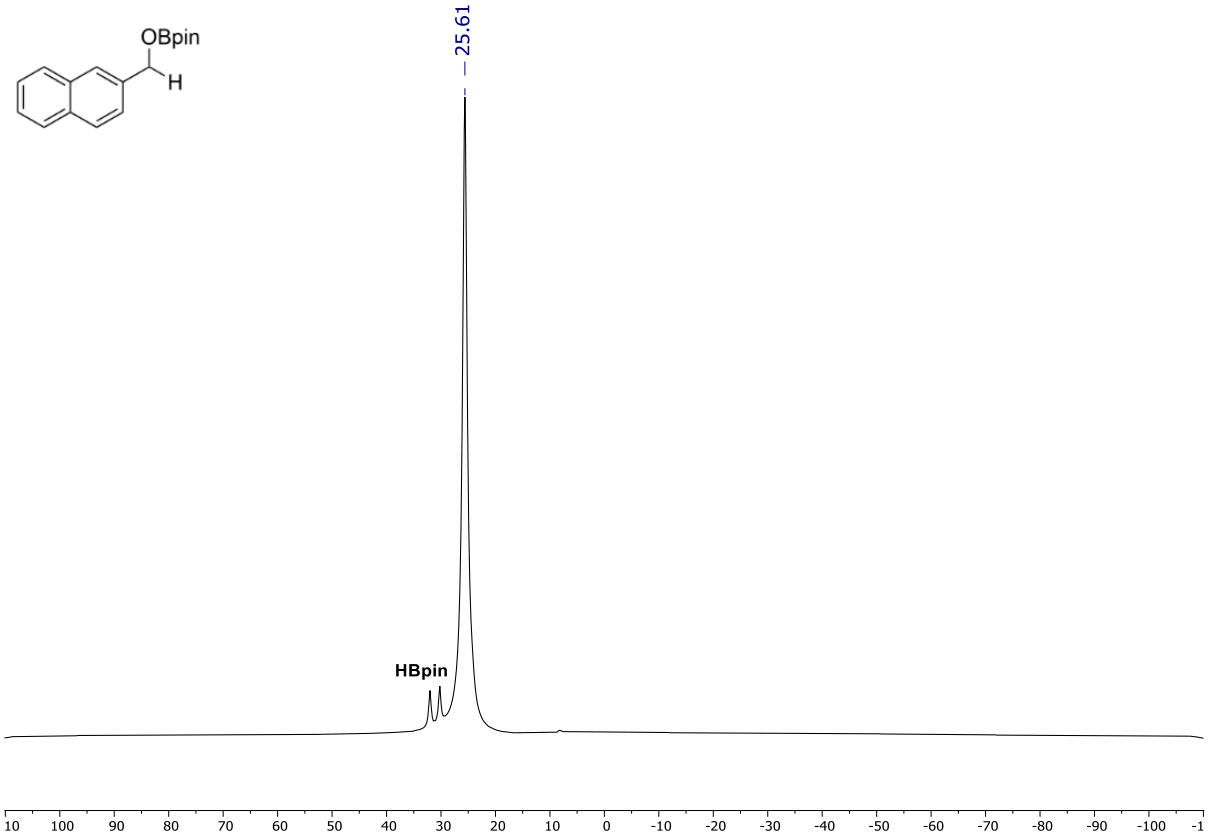
7.81
7.48
5.04
1.25
1,2-DCE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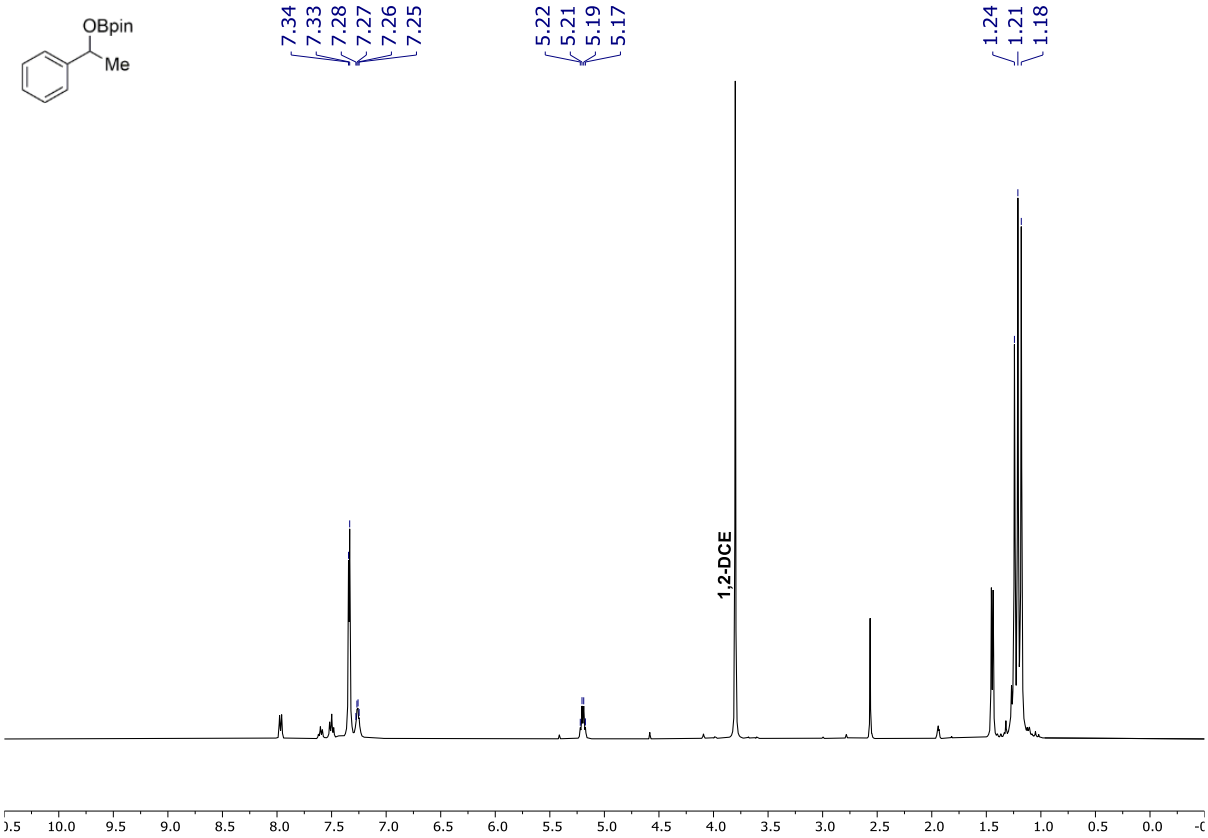
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Me
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7.33
7.28
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5.22
5.21
5.19
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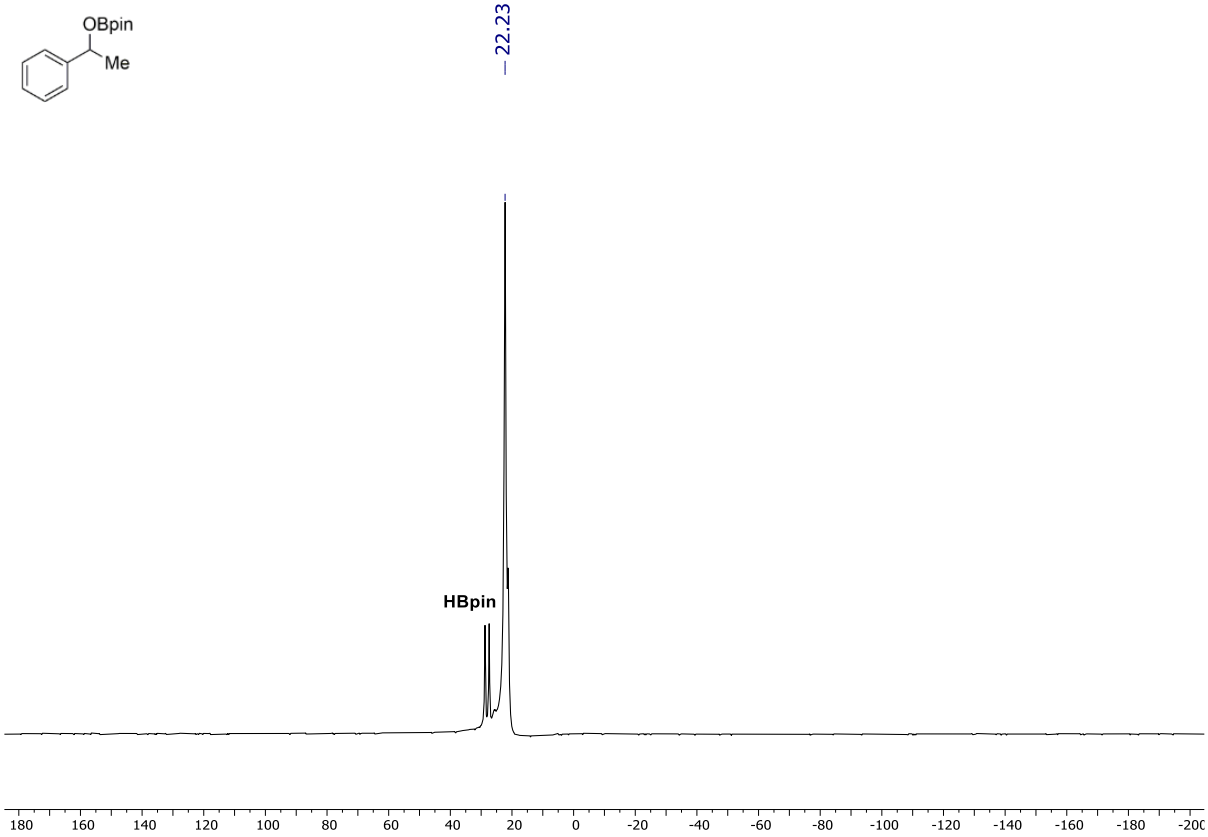
1.24
1.21
1.18
1,2-DCE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Me
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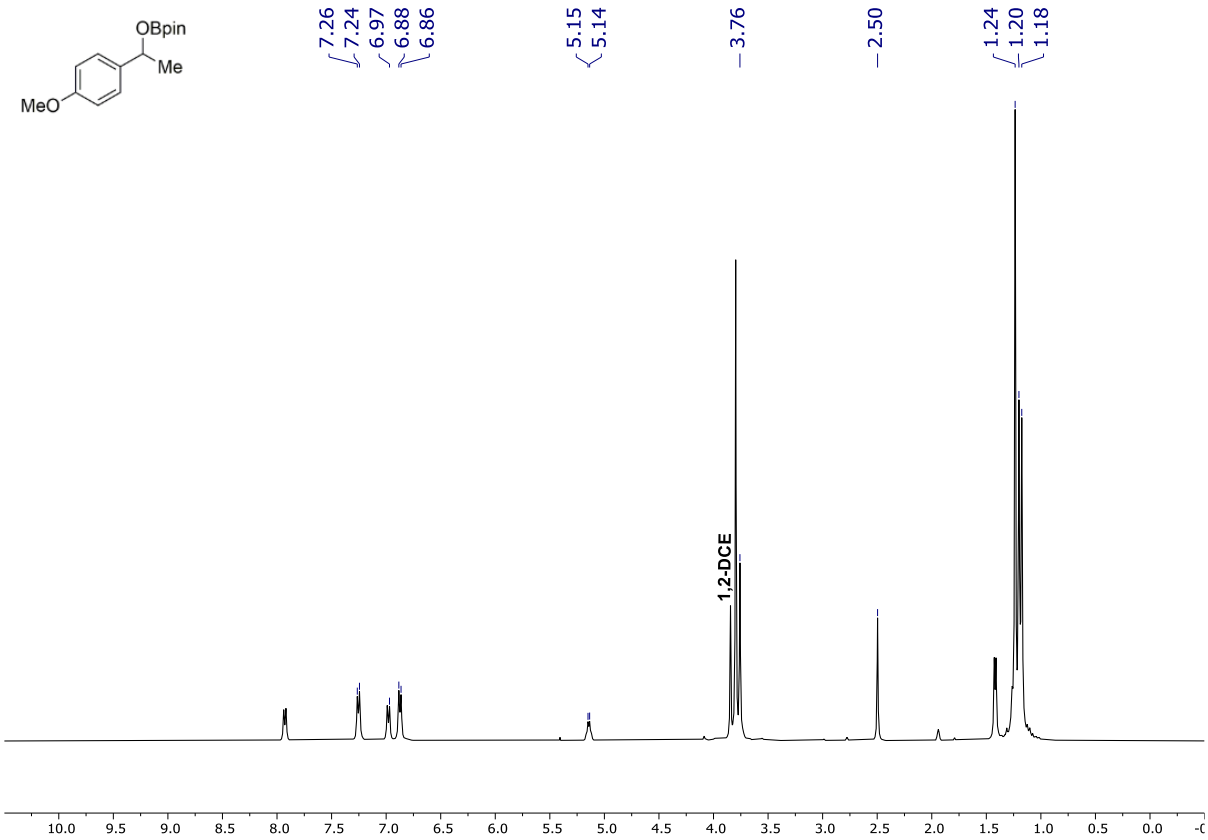
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Me
MeO
7.26
7.24
6.97
6.88
6.86
5.15
5.14
3.76
2.50
1.24
1.20
1.18
1,2-DCE
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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2.0
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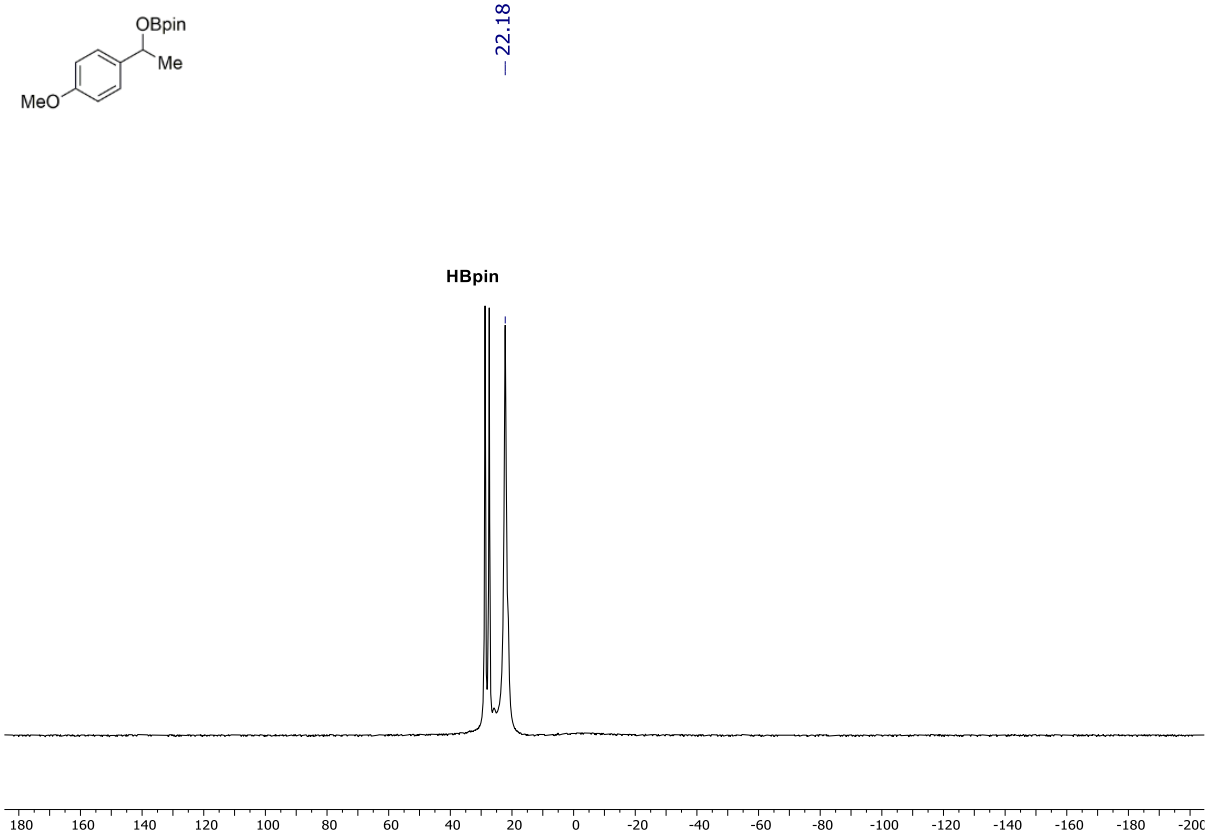
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Me
MeO
22.18
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-80
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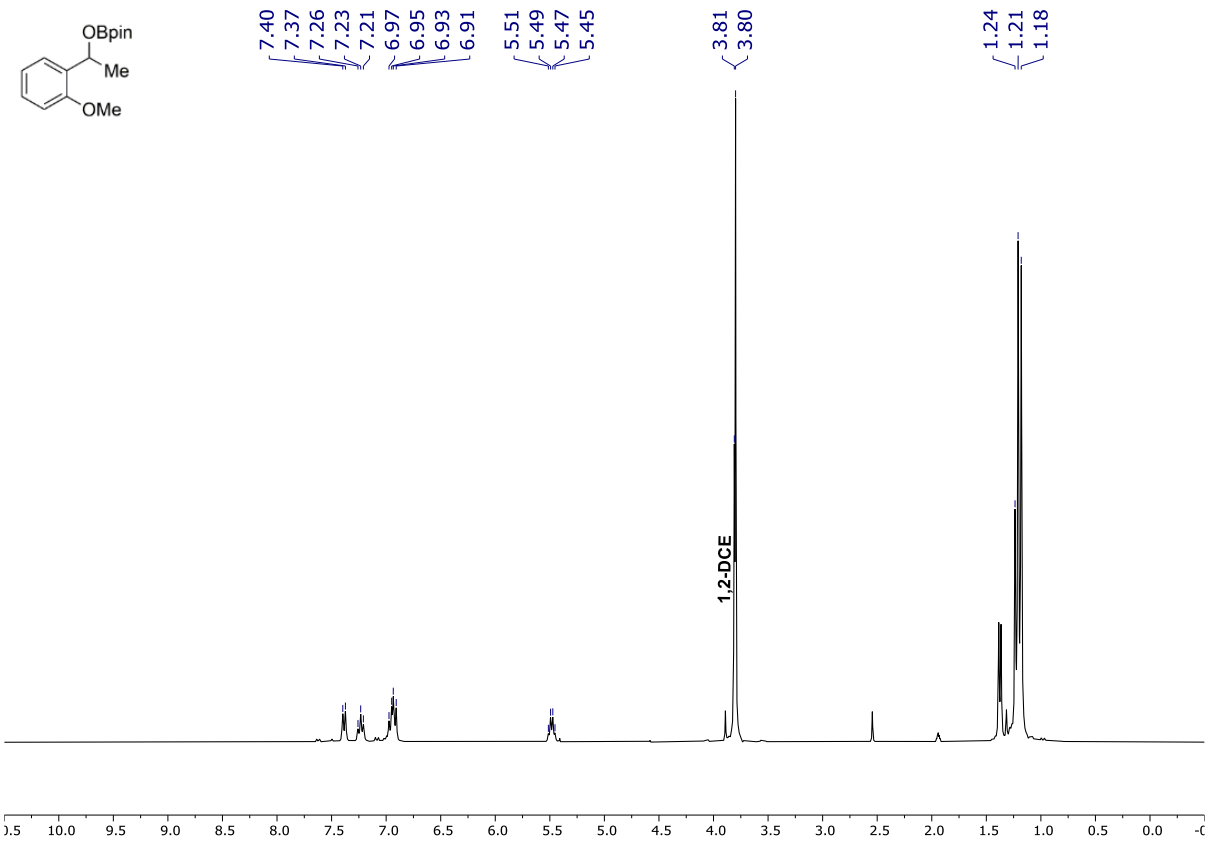
-160
-180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Me
OMe
7.40
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5.49
5.47
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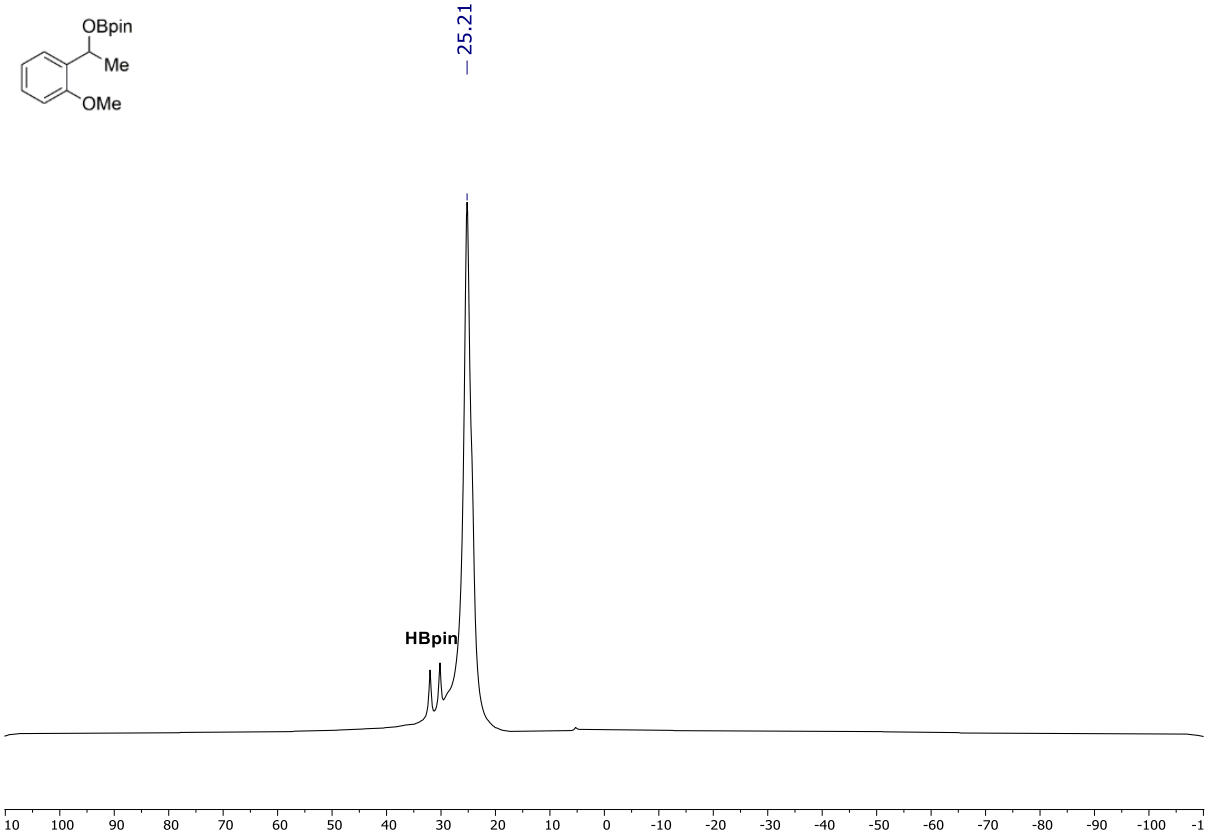
3.81
3.80
1.24
1.21
1.18
1,2-DCE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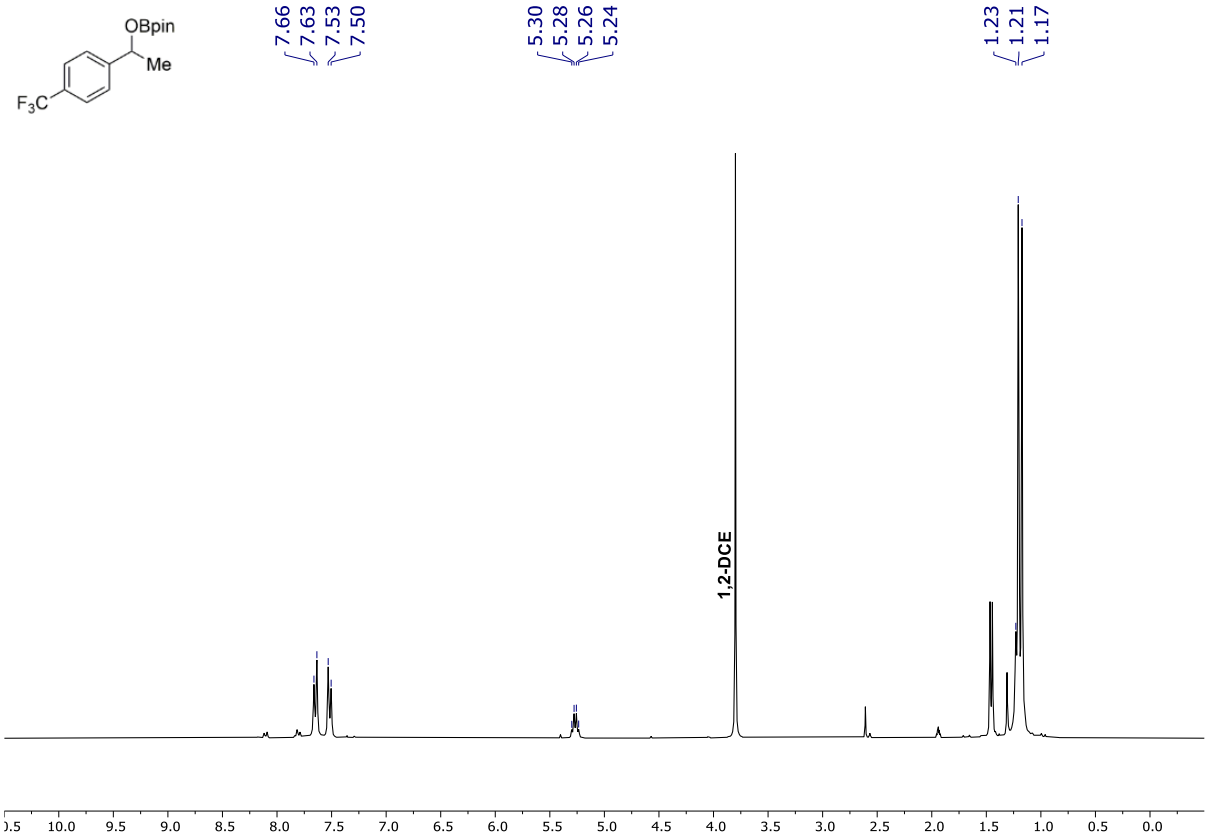
OMe
25.21
HBpin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Me
F3C
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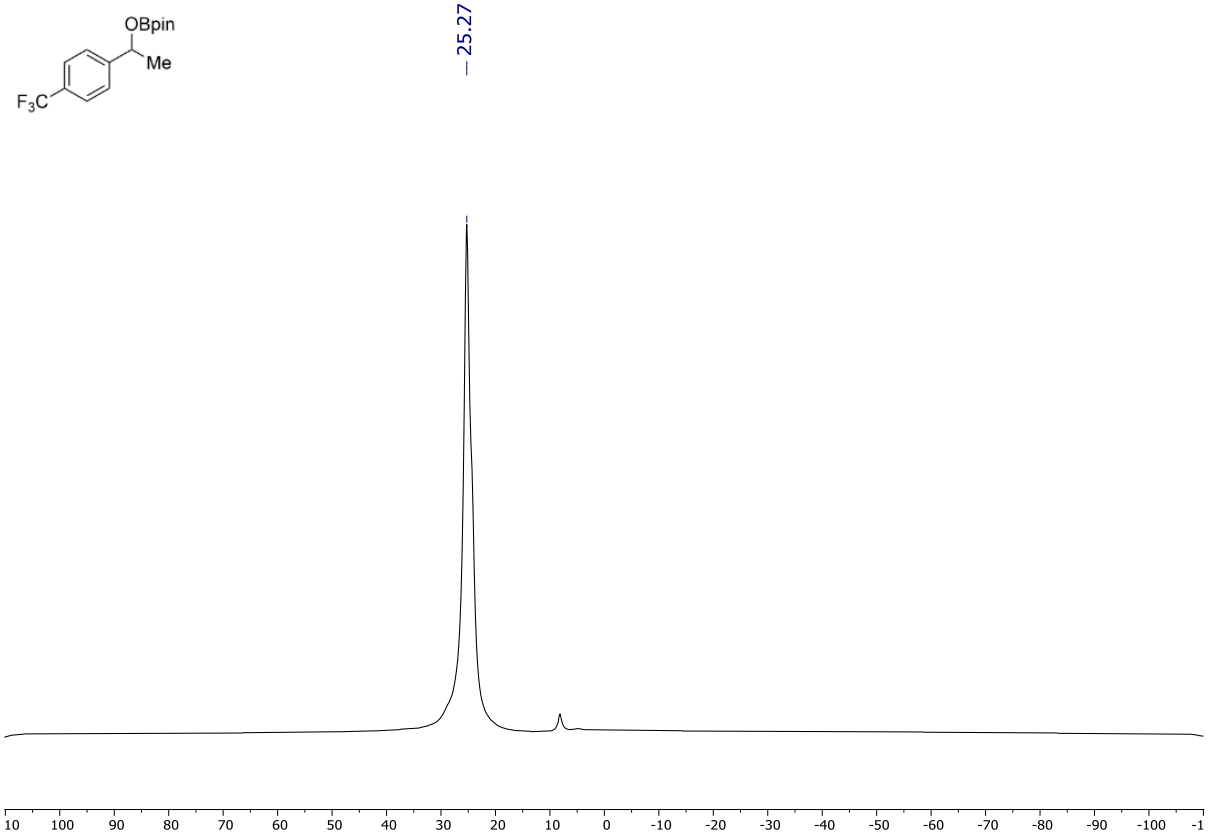
5.30
5.28
5.26
5.24
1.23
1.21
1.17
1,2-DCE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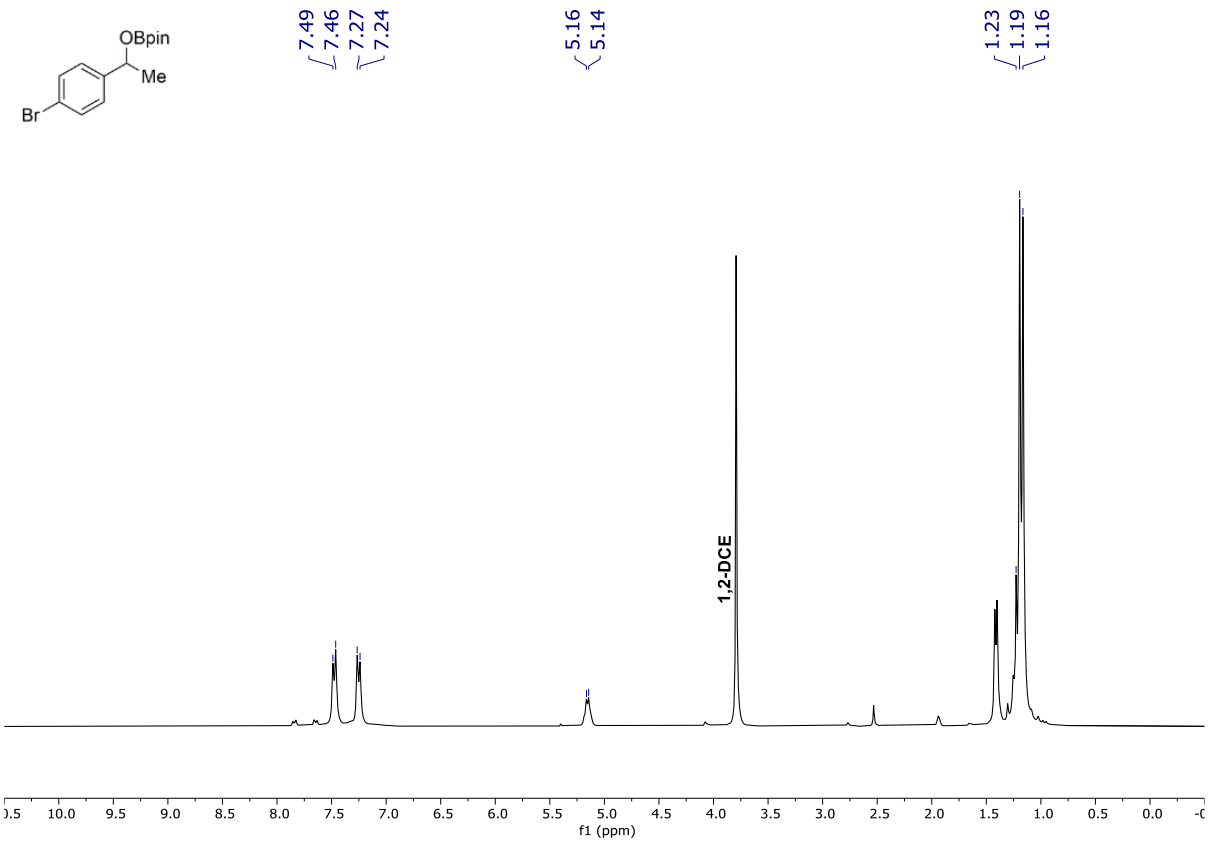
Me
F3C
25.27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Me
Br
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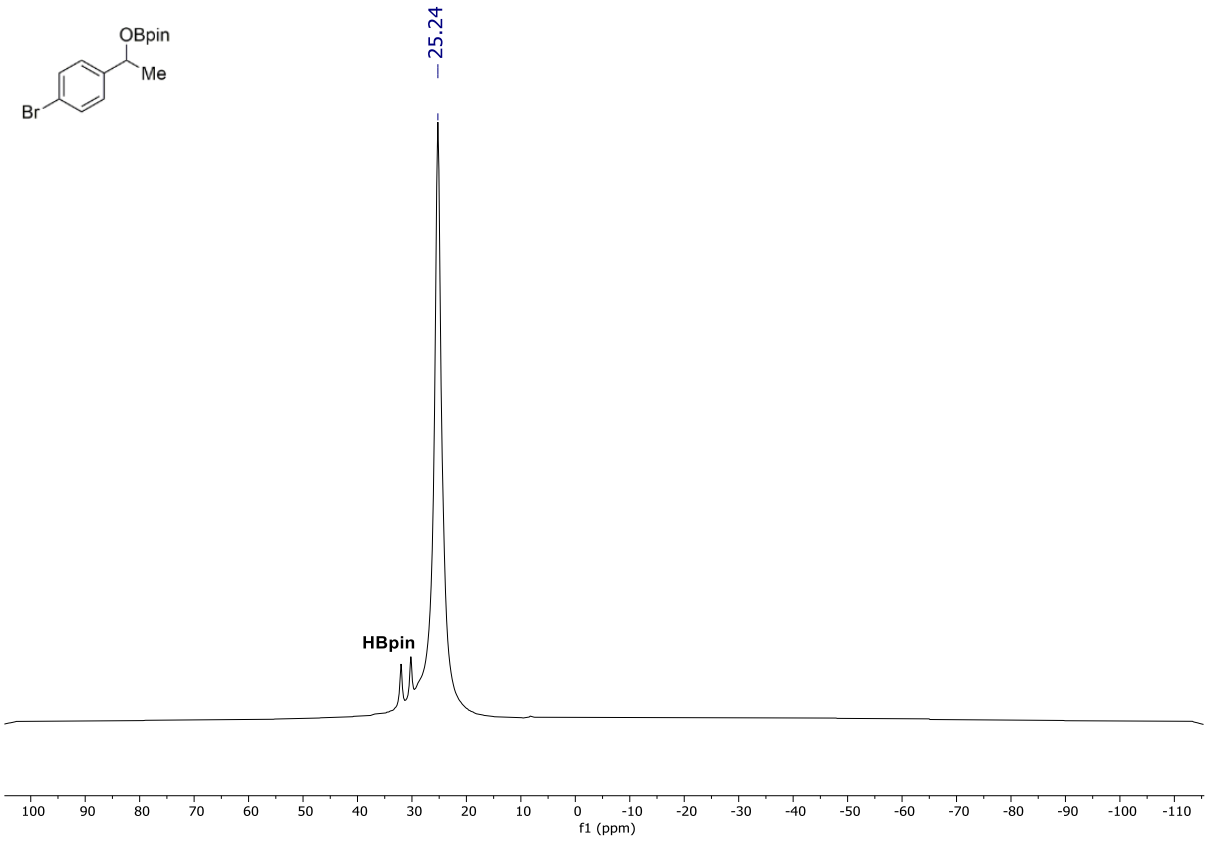
7.27
7.24
5.16
5.14
1.23
1.19
1.16
1,2-DCE
f1 (ppm)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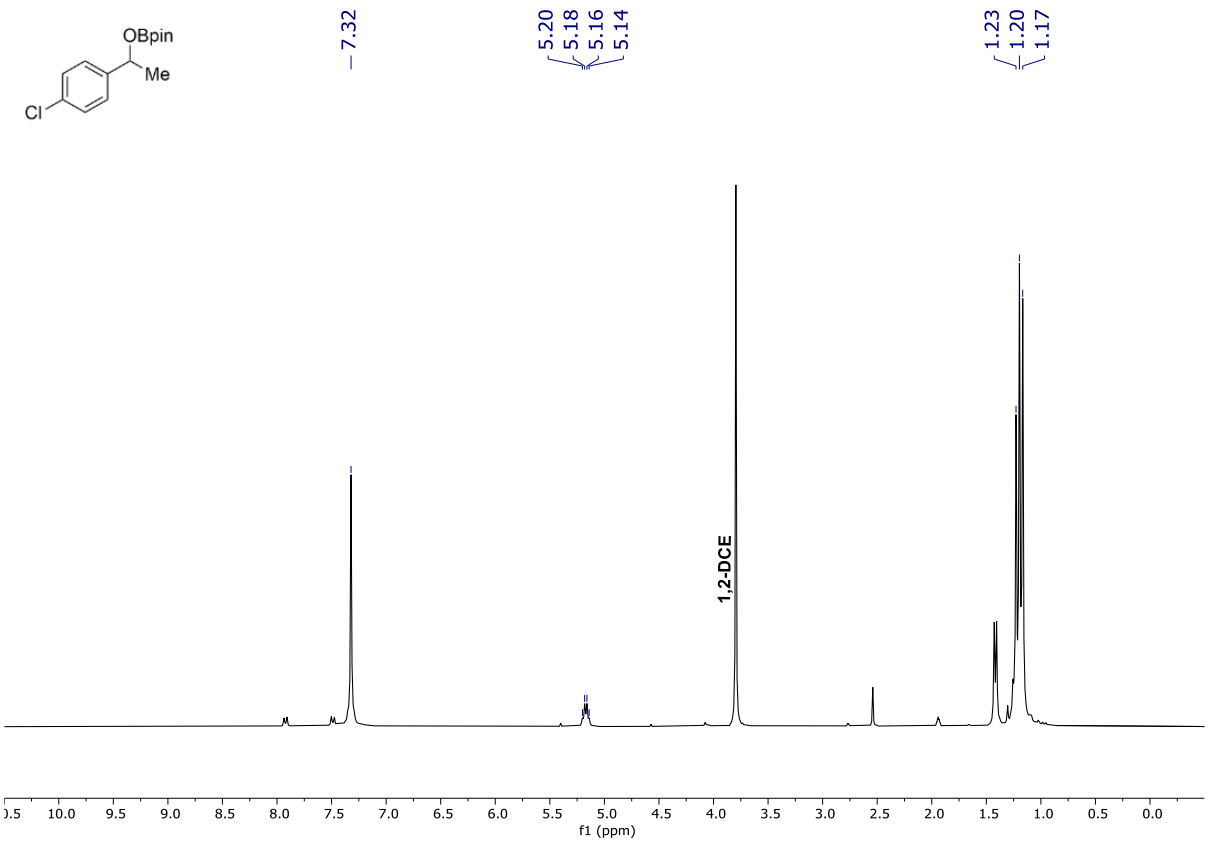
Me
Br
25.24
HBpin
f1 (ppm)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Me
Cl
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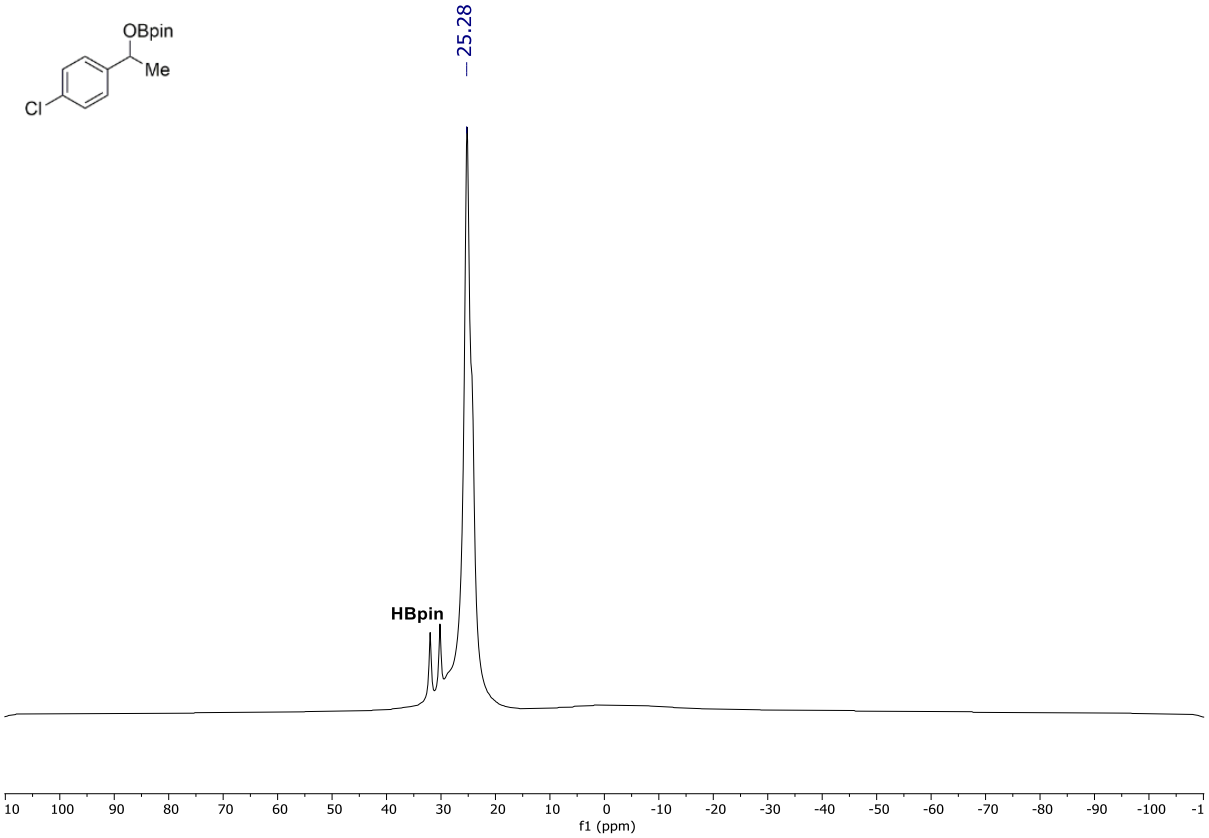
5.16
5.14
1.23
1.20
1.17
1,2-DCE
f1 (ppm)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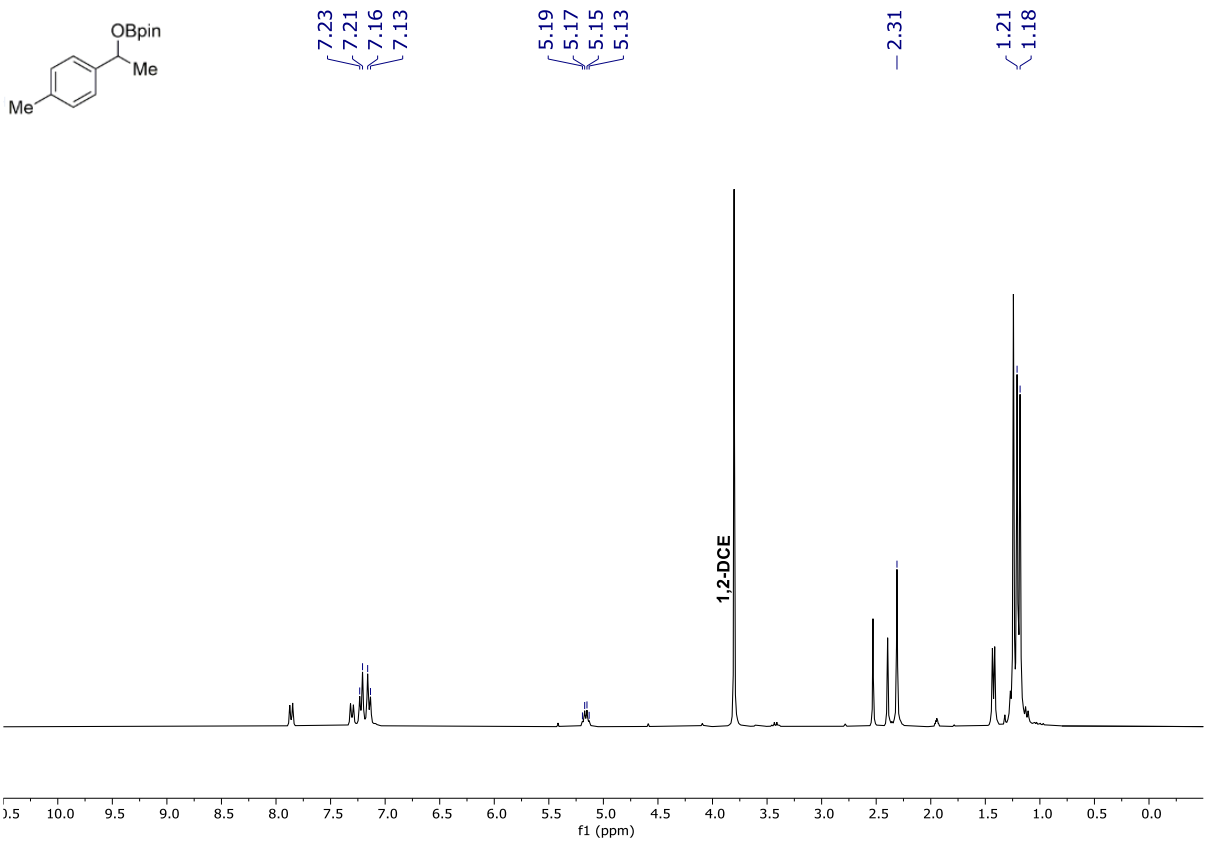
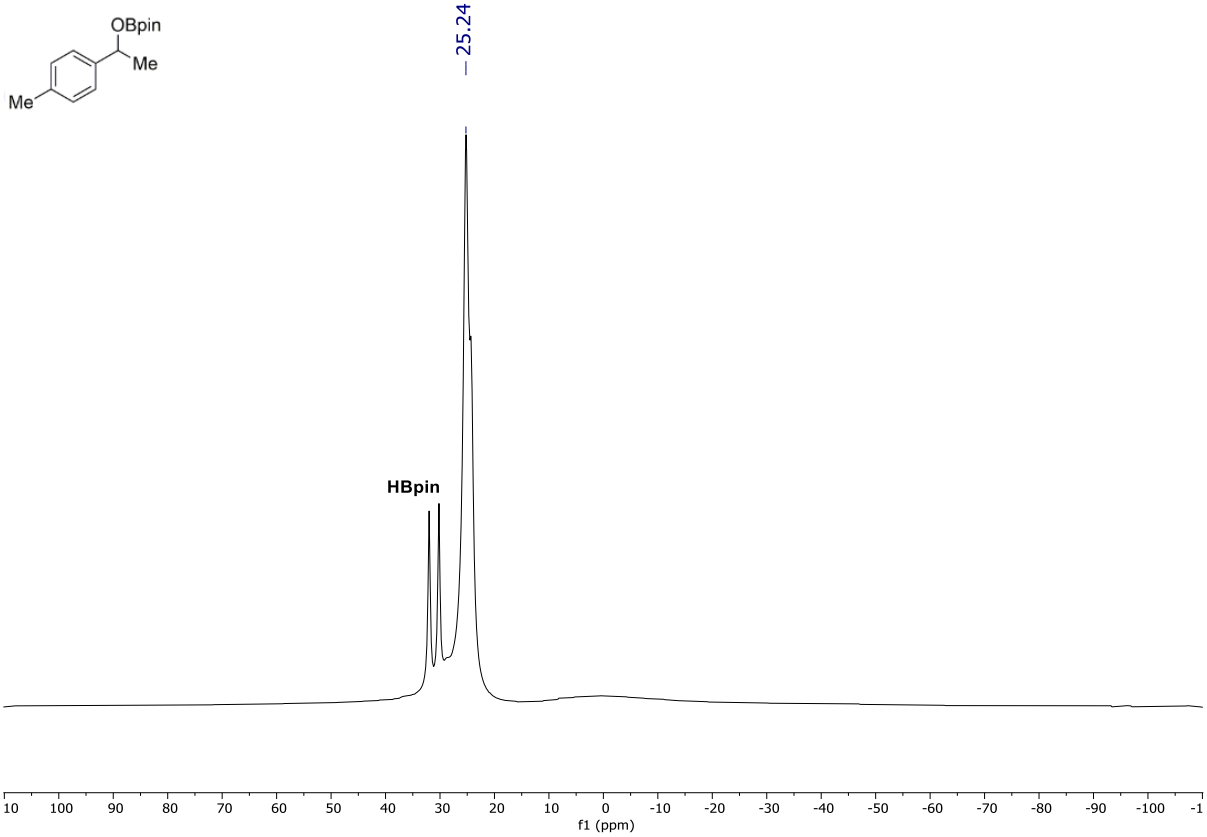
Me
Cl
25.28
HBpin
f1 (ppm)


OBpin
Me
Me
7.23
7.21
7.16
7.13
5.19
5.17
5.15
5.13
2.31
1.21
1.18
1,2-DCE
f1 (ppm)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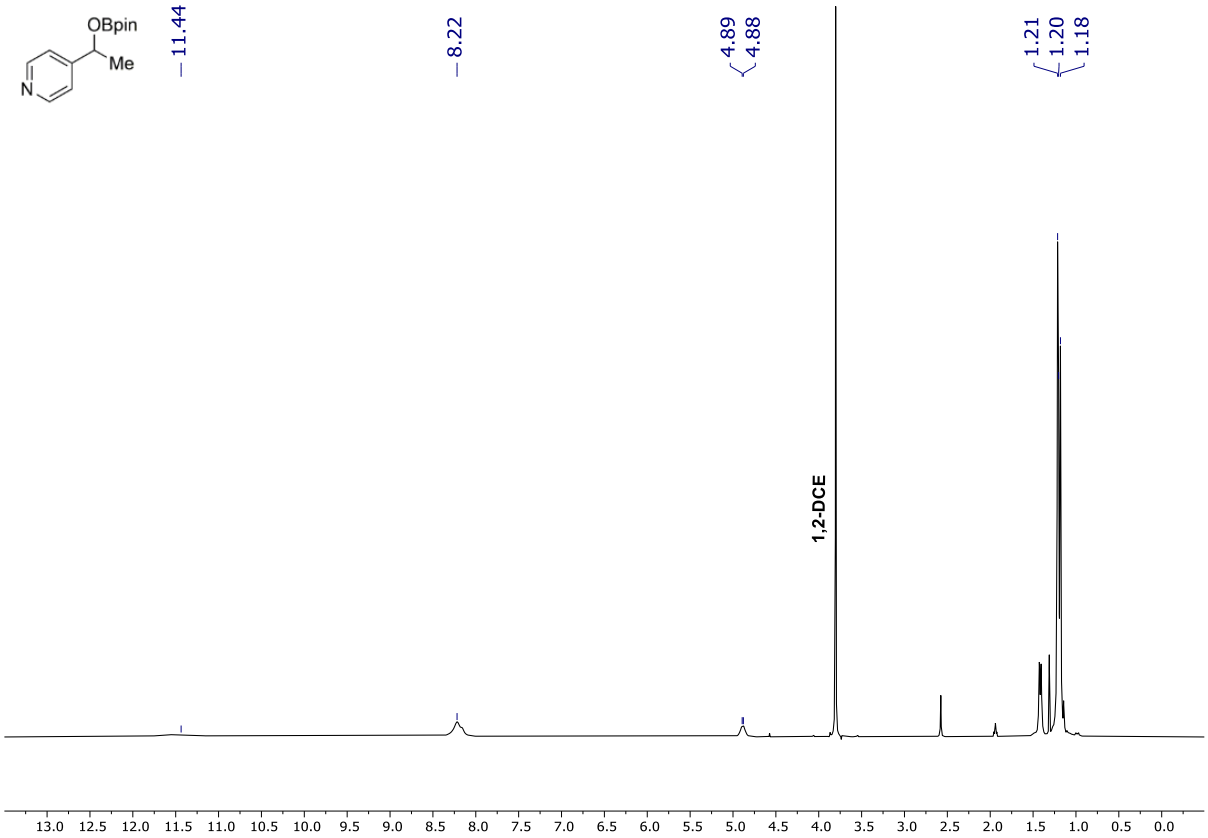
Me
Me
25.24
HBpin
f1 (ppm)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Me
N
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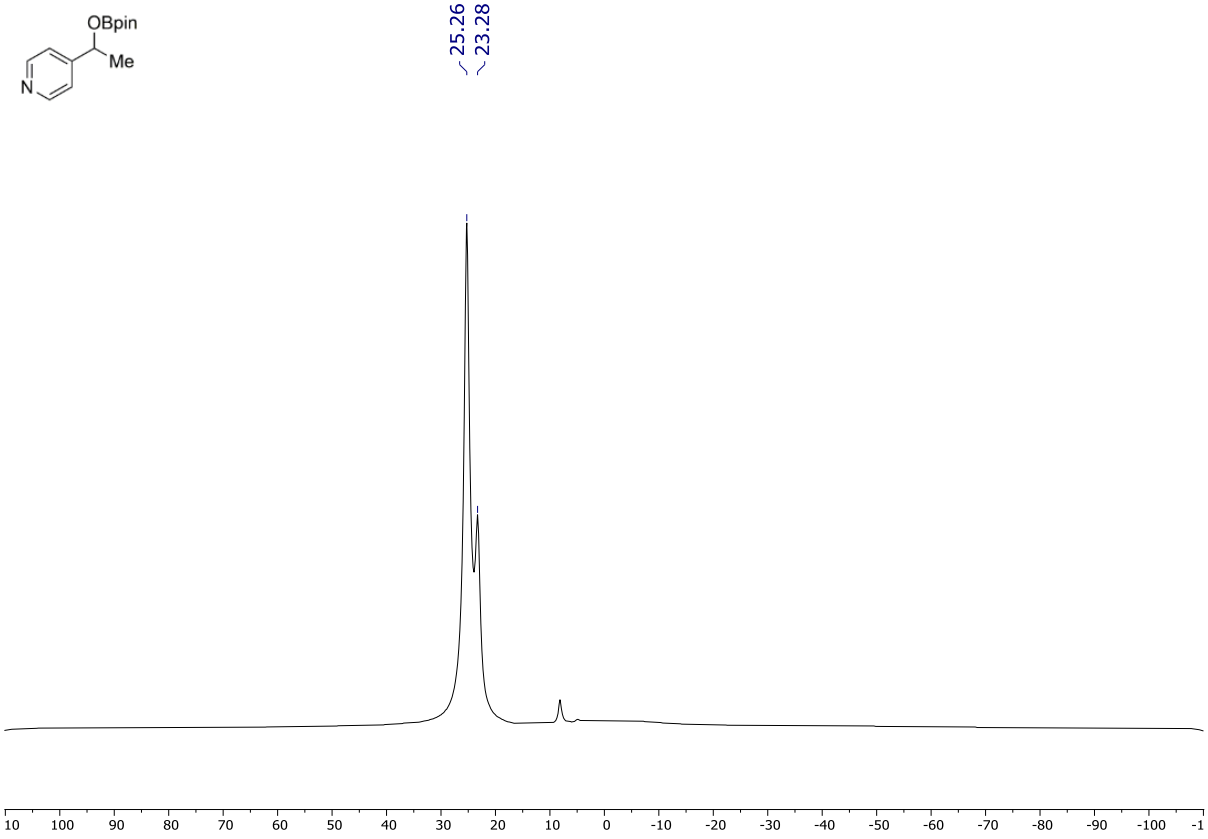
4.89
4.88
1,2-DCE
1.21
1.20
1.18
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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Me
N
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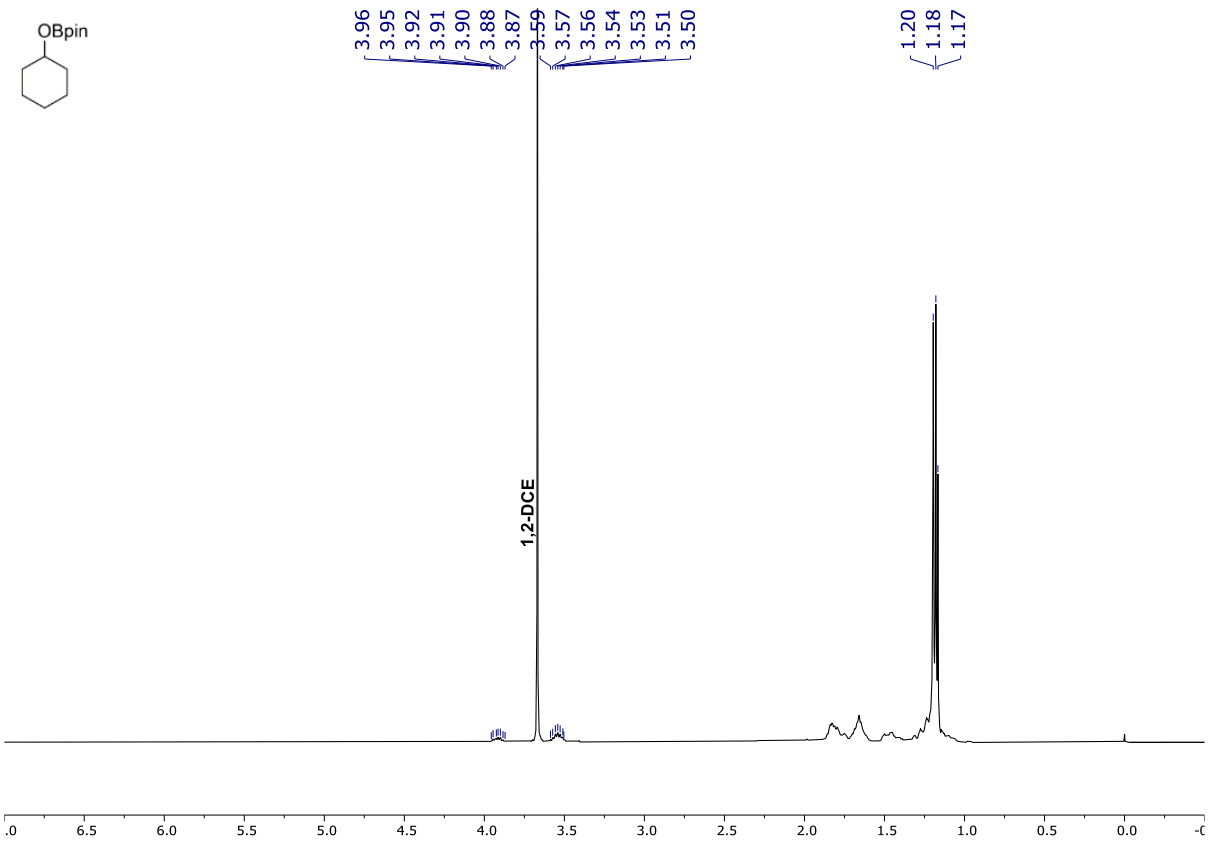
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3.54
3.53
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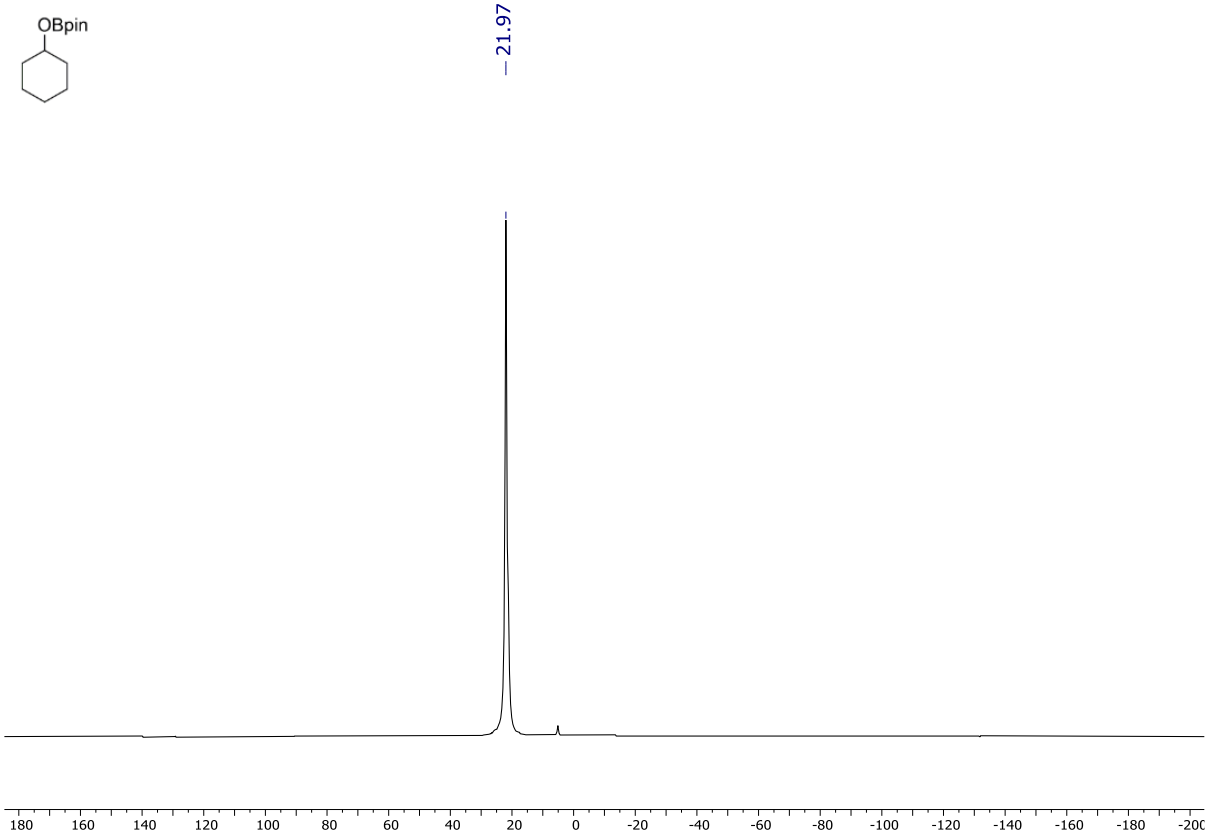
1.20
1.18
1.17
1,2-DCE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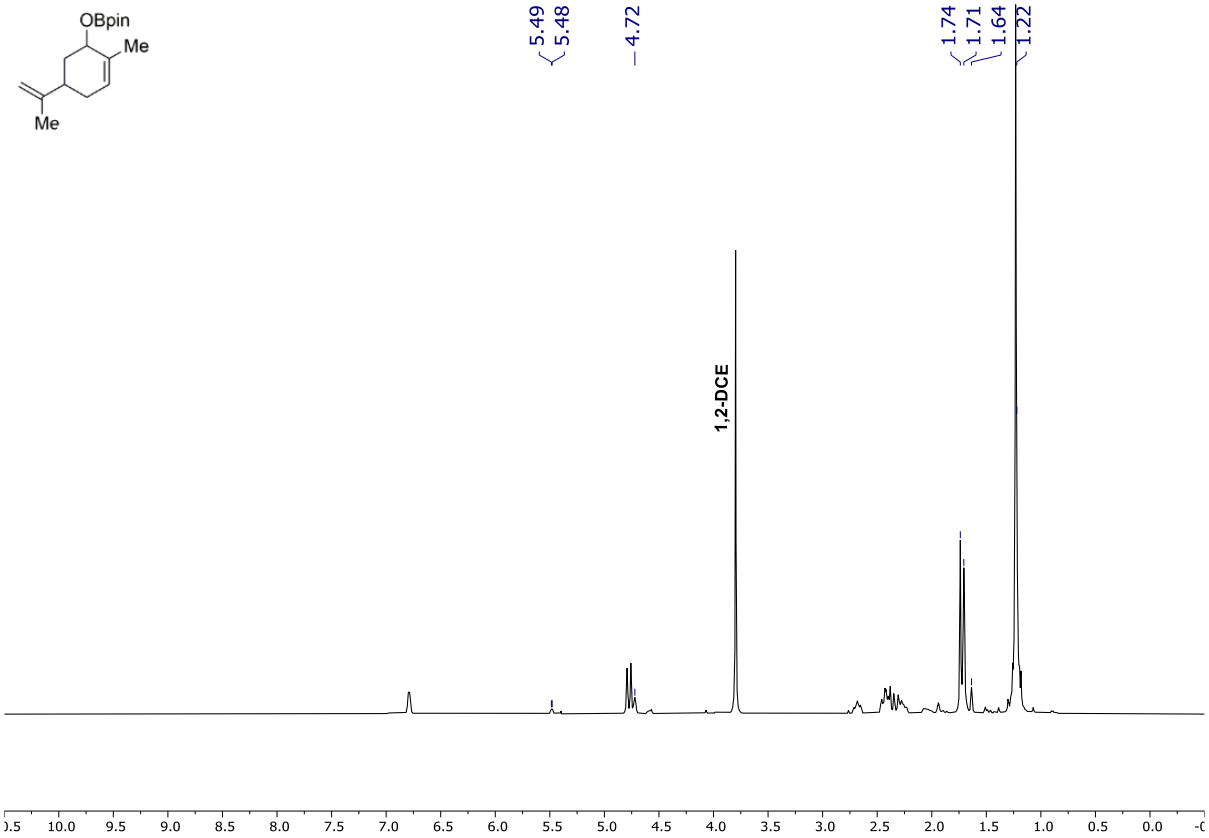
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Me
Me
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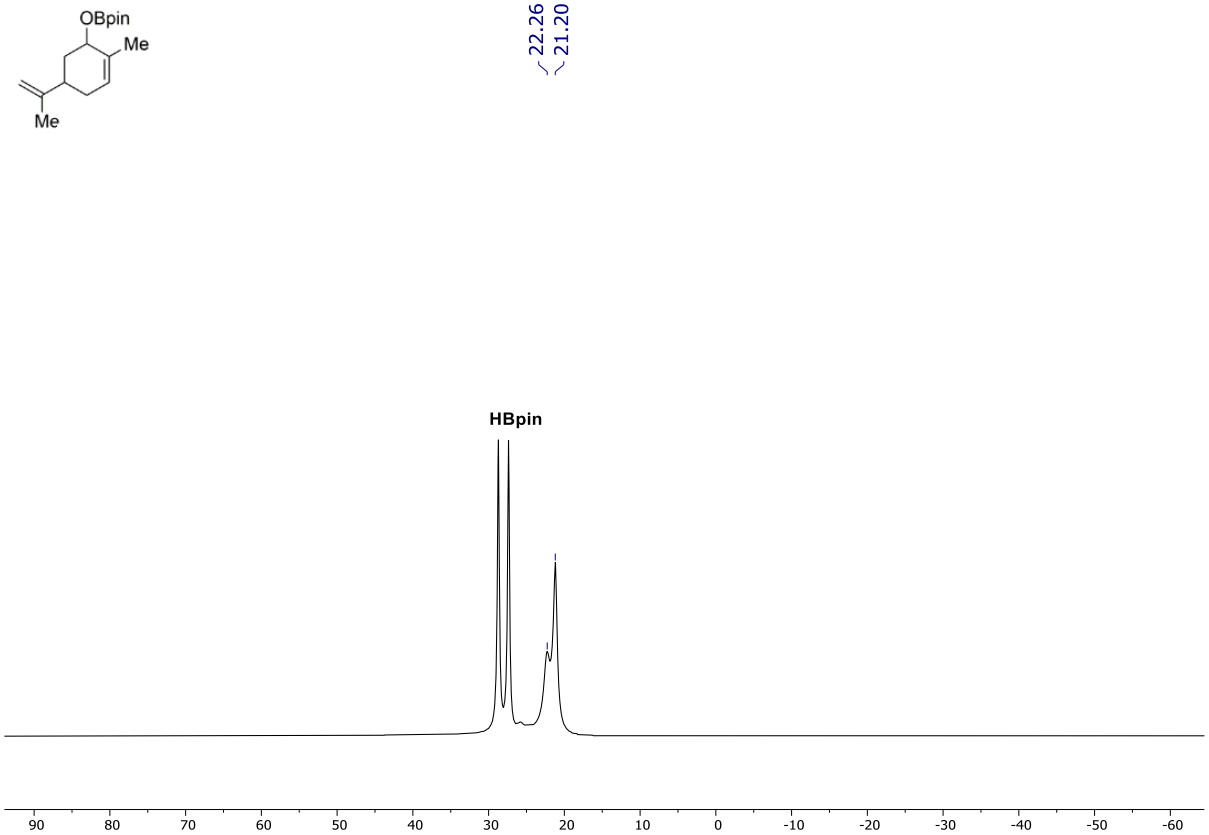
1.71
1.64
1.22
1,2-DCE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Me
Me
22.26
21.20
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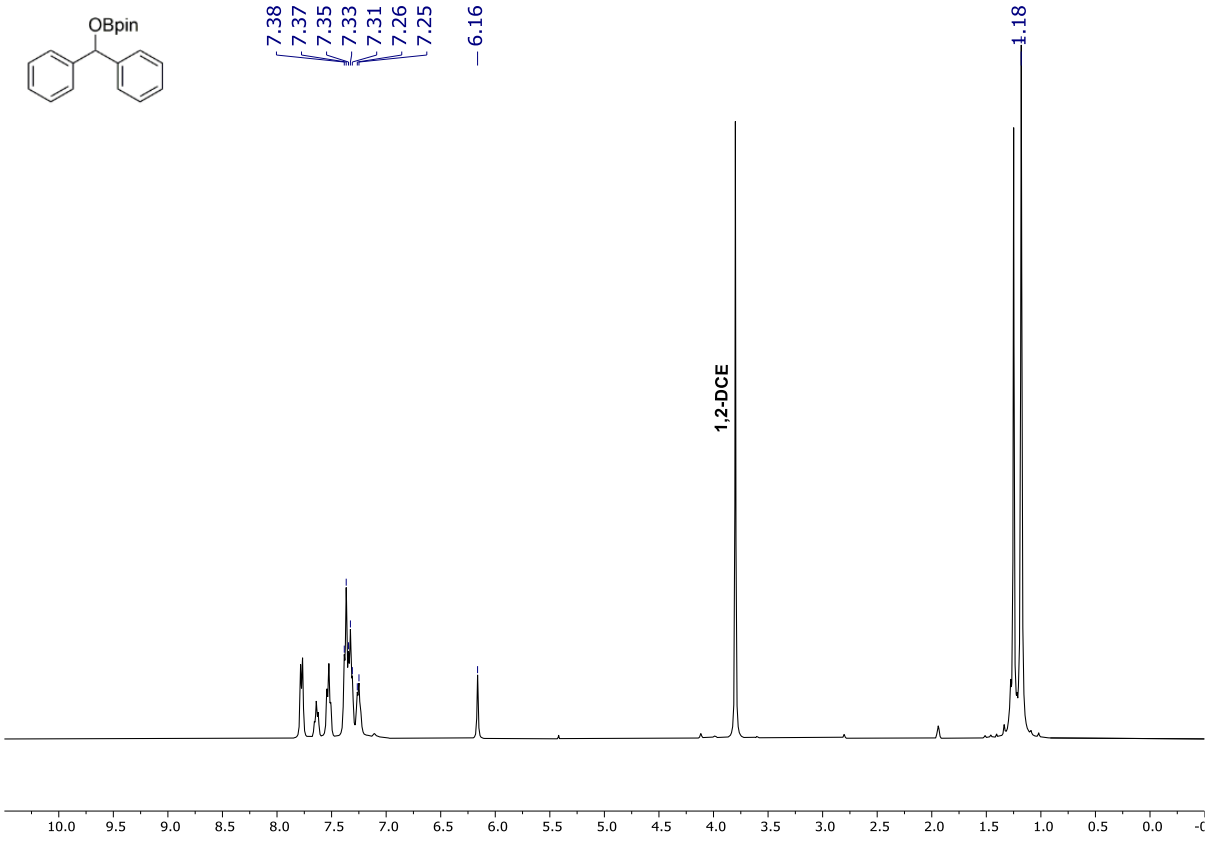
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7.33
7.31
7.26
7.25
6.16
1.18
1,2-DCE
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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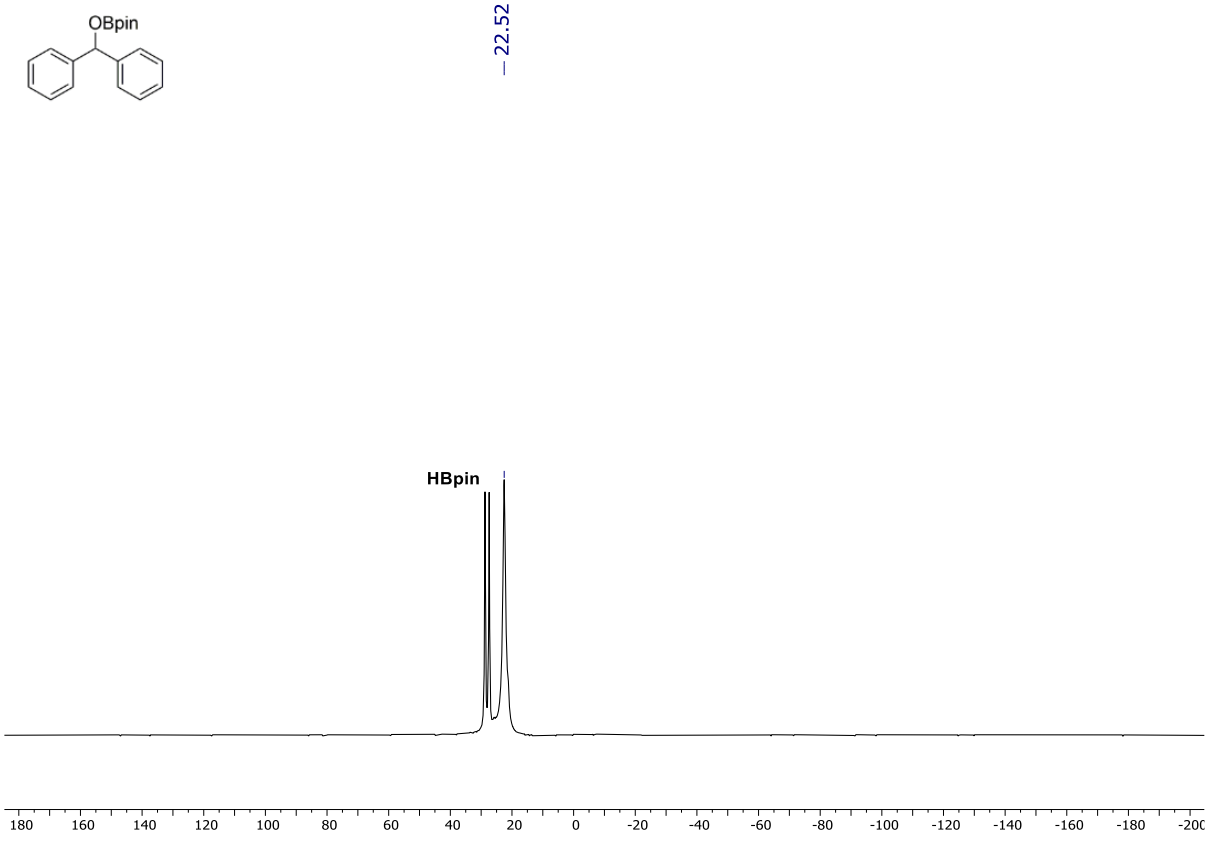
OBpin
22.52
HBpin
180
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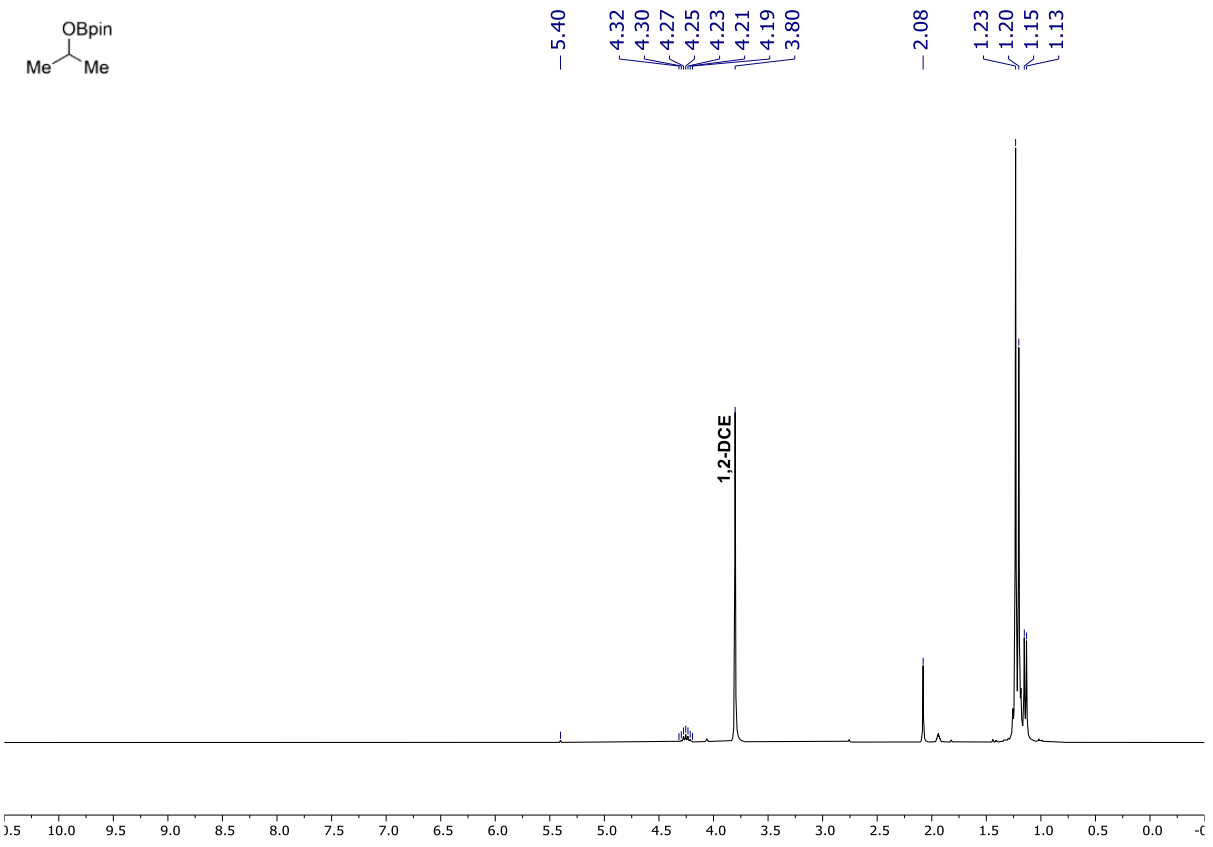
-140
-160
-180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Me
Me
5.40
4.32
4.30
4.27
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4.21
4.19
3.80
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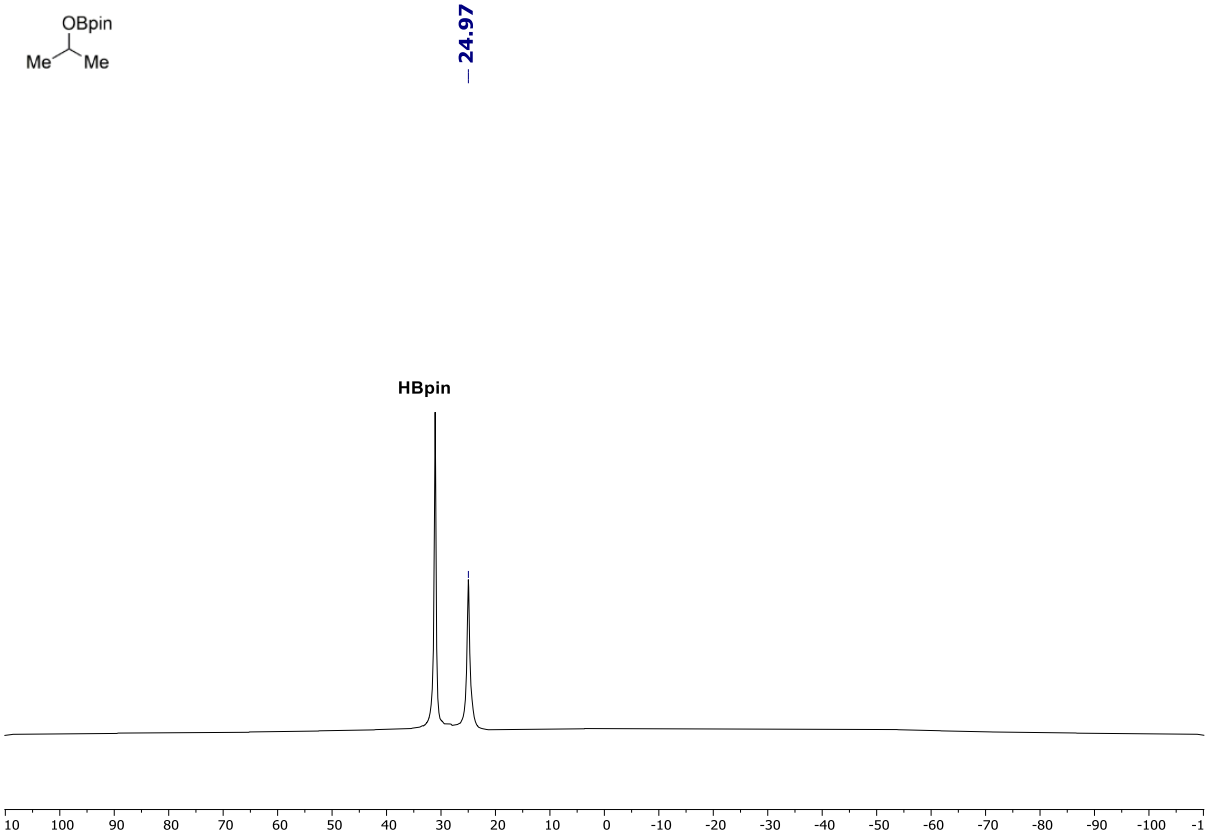
1.23
1.20
1.15
1.13
1,2-DCE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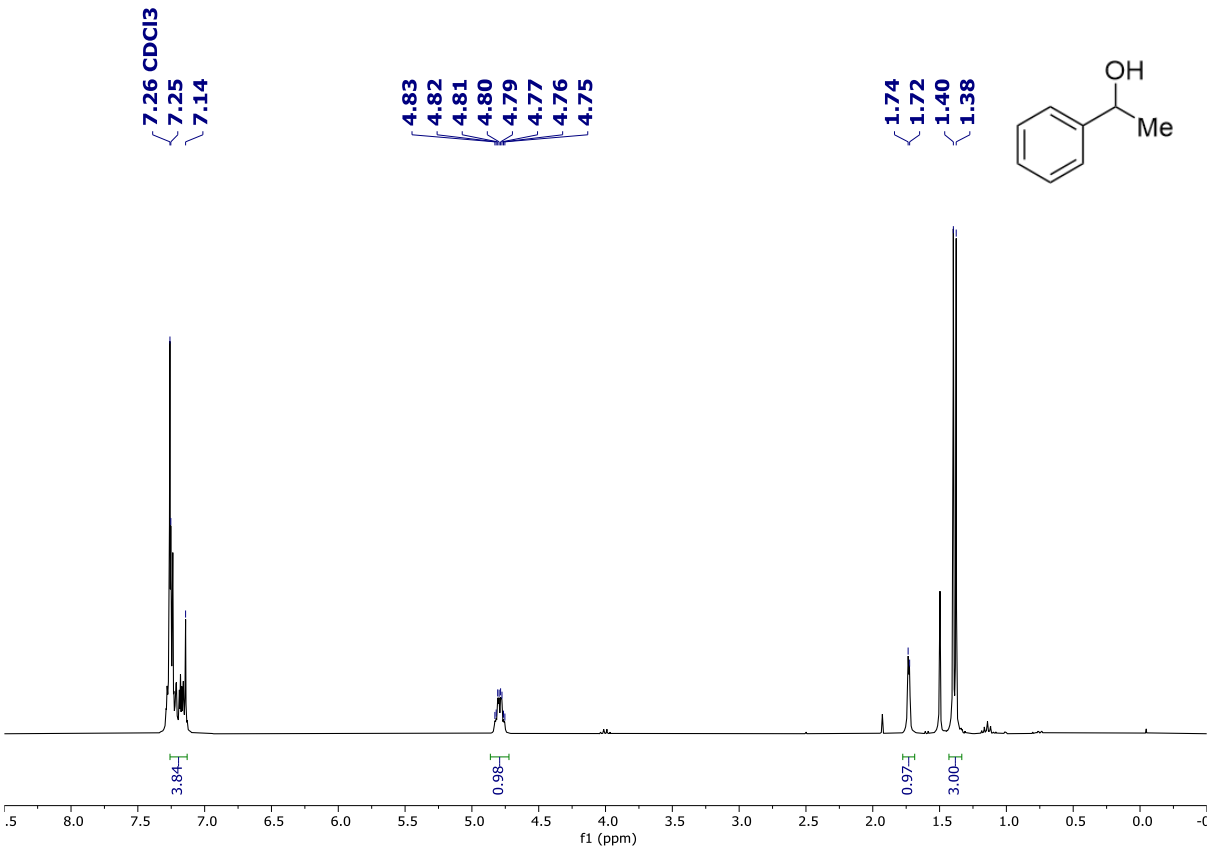
Me
Me
24.97
HBpin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7.14
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4.82
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4.80
4.79
4.77
4.76
4.75
1.74
1.72
1.40
1.38
OH
Me
3.84
0.98
0.97
3.00
f1 (ppm)

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