Supporting Information

Magnesium halide-catalyzed hydroboration of isocyanates and ketones

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Experimental

All air-sensitive manipulation were carried out using standard Schlenk-line or glove box techniques under an atmosphere of high-purity argon. ^{1}H, ^{11}B, ^{13}C and ^{19}F NMR spectra were recorded at 25 °C on Bruker Avance III 600 and 400 MHz spectrometer in deuterated solvents and were referenced to the resonances of the solvent used. All reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros Organics and Energy Chemical without further purification. Magnesium complex **1** was prepared by the literature procedure.[1]

General procedure A for product 2 catalyzed by $MgCl_2$

In a glove box, isocyanates (0.2 mmol) and HBpin (0.6 mmol) were added to a 10 mL flask, the catalyst $MgCl_2$ (1 mol%) was added to the mixture, respectively. The reaction mixture was stirred at 60 °C for required time. The progress of the reaction was monitored by ^{1}H NMR and ^{11}B NMR NMR spectroscopy. The representative products **2g**, **2i**, **2l** were added with MeOH to hydrolyze at 60 °C for 12 h, respectively. The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography to afford the pure amine products **2g', 2i', 2l'** in high isolated yields and characterized by ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectroscopy.

General procedure B for product 2 catalyzed by Magnesium complex 1

In a glove box, catalyst **1** (5 mol%) was added to a solution of isocyanates (0.2 mmol) and HBpin (0.6 mmol) in a J-Young NMR tube which was charged with C_6D_6 (0.5 mL), then heated at 60 °C for required time. The progress of the reaction was monitored by ^{1}H NMR and ^{11}B NMR spectroscopy.

Spectroscopic data of products 2. *N-isopropyl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (**2a**).*[2] ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.59 (sept, J = 6.6 Hz, 1H, C*H*CH$_3$), 2.47 (s, 3H, NC*H*$_3$), 1.20 (s, 12H, C(C*H*$_3$)$_2$), 1.04 (d, J = 6.6 Hz, 6H, CHC*H*$_3$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 23.75.

N-ethyl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine ***(2b)***.[2] ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.91 (q, *J* = 7.2 Hz, 2H, CH_2), 2.57 (s, 3H, NCH_3), 1.21 (s, 12H, $C(CH_3)_2$), 1.02 (t, *J* = 7.2 Hz, 3H, CH_2CH_3). ^{11}B NMR (193 MHz, $CDCl_3$): δ 23.83.

N,4,4,5,5-pentamethyl-N-propyl-1,3,2-dioxaborolan-2-amine ***(2c)***.[2] ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.84 (t, *J* = 7.2 Hz, 2H, NCH_2), 2.56 (s, 3H, NCH_3), 1.43 (m, 2H, CH_3CH_2), 1.20 (s, 12H, $C(CH_3)_2$), 0.83 (t, *J* = 7.2 Hz, 3H, CH_2CH_3). ^{11}B NMR (193 MHz, $CDCl_3$): δ 23.97.

N-butyl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine ***(2d)***.[3] ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.87 (t, *J* = 6.9 Hz, 2H, NCH_2), 2.55 (s, 3H, NCH_3), 1.42-1.37 (m, 4H, -C_2H_4-), 1.20 (s, 12H, $C(CH_3)_2$), 0.90 (t, *J* = 7.2 Hz, 3H, CH_2CH_3). ^{11}B NMR (193 MHz, $CDCl_3$): δ 23.94.

N-(tert-butyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine ***(2e)***.[2] ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.59 (s, 3H, NCH_3), 1.37 (s, 9H, $C(CH_3)_3$), 1.21 (s, 12H, $C(CH_3)_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 24.05.

N-cyclohexyl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine ***(2f)***.[2] ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.49 (s, 3H, NCH_3), 1.75-1.32 (m, 11H, C_6H_{11}), 1.20 (s, 12H, $C(CH_3)_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 23.89.

N,4,4,5,5-pentamethyl-N-(p-tolyl)-1,3,2-dioxaborolan-2-amine ***(2g)***.[3] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17-7.15 (m, 2H, Ar-*H*), 7.03 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 3.02 (s, 3H, NCH_3), 2.26 (s, 3H, Ar-CH_3), 1.26 (s, 12H, $C(CH_3)_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 24.14.

N-(4-methoxyphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine ***(2h)***.[3] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.19 (d, *J* = 9.6 Hz, 2H, Ar-*H*), 6.81 (d, *J* = 9.6 Hz, 2H, Ar-*H*), 3.76 (s, 3H, NCH_3), 3.02 (s, 3H, OCH_3), 1.27 (s, 12H, $C(CH_3)_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 24.01.

N-(4-chlorophenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine ***(2i)***.[3] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23-7.17 (m, 4H, Ar-*H*), 3.01 (s, 3H, NCH_3), 1.27 (s, 12H, $C(CH_3)_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 24.33.

4-(methyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)amino)benzonitrile ***(2j)***.[3] ^{1}H

NMR (600 MHz, $CDCl_3$): δ 7.50 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 7.39 (d, *J* = 8.4 Hz, Ar-*H*), 3.06 (s, 3H, NC*H₃*), 1.31 (s, 12H, C(C*H*$_3$)$_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 24.62.

N-mesityl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine ***(2k)***.[2] ^{1}H NMR (600 MHz, C_6D_6): δ 6.85 (s, 2H, Ar-*H*), 2.78 (s, 3H, NC*H*$_3$), 2.23 (s, 3H, Ar-C*H*$_3$), 2.19 (s, 6H, Ar-C*H*$_3$), 1.26 (d, 12H, C(C*H*$_3$)$_2$). ^{11}B NMR (193 MHz, C_6D_6): δ 23.73.

N-((3s,5s,7s)-adamantan-1-yl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine ***(2l)***.[2] ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.55 (s, 3H, NC*H*$_3$), 2.00 (m, 3H, Ad-*H*), 1.83 (d, *J* = 2.4 Hz, 6H, Ad-*H*), 1.59 (s, 6H, Ad-*H*), 1.14 (s, 12H, C(C*H*$_3$)$_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 24.02.

N-methyl-p-toluidine ***(2g')***.[4] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.02 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.56 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 2.83 (s, 3H, NC*H*$_3$), 2.26 (s, 3H, Ar-C*H*$_3$), ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 147.2, 129.7, 126.5, 112.6, 31.1, 20.4.

4-chloro-N-methylaniline ***(2i')***.[4] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.4, 2H, Ar-*H*), 6.52 (d, *J* = 8.4, 2H, Ar-*H*), 3.69 (s, 1H, N*H*), 2.81 (s, 3H, NC*H*$_3$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 147.9, 129.0, 121.8, 113.4, 30.8.

Adamantan-2-yl-(methyl)amine ***(2l')***.[4] ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.51 (s, 1H, N*H*), 3.60 (s, 3H, NC*H*$_3$), 2.07 (s, 3H, Ad-*H*), 1.92 (s, 6H, Ad-*H*), 1.66 (s, 6H, Ad-*H*). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 50.6, 41.9, 36.3, 29.5.

General procedure for product 3 catalyzed by MgI_2

In a glove box, ketones (0.5 mmol), HBpin (0.55 mmol) and the catalyst MgI_2 (0.1 mol%) were added to a 10 mL flask, respectively. The reaction mixture was stirred at 25 °C for the required time. The progress of the reaction was monitored by ^{1}H NMR, ^{11}B NMR, and ^{19}F NMR spectroscopy. The representative products **3a**, **3d**, **3q**, **3z**, **3ac**, **3af** were added with MeOH to hydrolyze at 60 °C for 12 h, respectively. The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography to afford the pure alcohol products **3a'**, **3d'**, **3q'**, **3z'**, **3ac'**, **3af'** in high isolated yields and characterized by ^{1}H NMR and ^{13}C{^{1}H} NMR spectroscopy.

Gram-scale reaction

In a glove box, acetophenone (10 mmol), HBpin (11 mmol) and the catalyst MgI_2 (0.1 mol%) were added to a 10 mL flask, respectively. The reaction mixture was stirred at 25 °C for 1 h. Subsequently, the reaction mixture was quenched with MeOH (2 mL) and stirred at 60 °C for 12 h. The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography to afford the pure alcohol product **3a'** (1.16 g, 95% yield).

Spectroscopic data of products 3. *4,4,5,5-tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (**3a**).*[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.30 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 7.22 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 5.24 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.49 (d, *J* = 6.6 Hz, 3H, CHC*H*$_3$), 1.23 (s, 6H, C(C*H*$_3$)$_2$), 1.20 (s, 6H, C(C*H*$_3$)$_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 22.16.

*4,4,5,5-tetramethyl-2-(1-(o-tolyl)ethoxy)-1,3,2-dioxaborolane (**3b**).*[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.18 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 7.13-7.07 (m, 2H, Ar-*H*), 5.43 (q, *J* = 6.0 Hz, 1H, OC*H*CH_3), 2.33 (s, 3H, Ar-C*H*$_3$), 1.45 (d, *J* = 6.0 Hz, 3H, CHC*H*$_3$), 1.22 (s, 6H, C(C*H*$_3$)$_2$), 1.18 (s, 6H, C(C*H*$_3$)$_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 22.14.

*4,4,5,5-tetramethyl-2-(1-(m-tolyl)ethoxy)-1,3,2-dioxaborolane (**3c**).*[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20-7.18 (m, 2H, Ar-*H*), 7.14 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.04 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 5.21 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 2.33 (s, 3H, Ar-C*H*$_3$), 1.48 (d, *J* = 6.6 Hz, 3H, CHC*H*$_3$), 1.23 (s, 6H, C(C*H*$_3$)$_2$), 1.21 (s, 6H, C(C*H*$_3$)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.11.

*4,4,5,5-tetramethyl-2-(1-(p-tolyl)ethoxy)-1,3,2-dioxaborolane (**3d**).*[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.11 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 5.21 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 2.31 (s, 3H, Ar-C*H*$_3$), 1.47 (d, *J* = 6.6 Hz, 3H, CHC*H*$_3$), 1.23 (s, 6H, C(C*H*$_3$)$_2$), 1.20 (s, 6H, C(C*H*$_3$)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.13.

*2-(1-(2-methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**).*[6] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H, Ar-*H*), 7.20 (dt, *J* = 8.4

Hz, 1.8 Hz, 1H, Ar-*H*), 6.95 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 6.82 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 5.58 (q, *J* = 6.6 Hz, 1H, OC*H*CH3), 3.80 (s, 3H, Ar-OC*H*3), 1.44 (d, *J* = 6.6 Hz, 3H, CHC*H*3), 1.24 (s, 6H, C(C*H*3)2), 1.22 (s, 6H, C(C*H*3)2). ^{11}B NMR (193 MHz, CDCl3): δ 22.17.

2-(1-(3-methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3f)***.[7] ^{1}H NMR (600 MHz, CDCl3): δ 7.21 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 6.94-6.92 (m, 2H, Ar-*H*), 6.78-6.76 (m, 1H, Ar-*H*), 5.22 (q, *J* = 6.6 Hz, 1H, OC*H*CH3), 3.78 (s, 3H, Ar-OC*H*3), 1.48 (d, *J* = 6.6 Hz, 3H, CHC*H*3), 1.24 (s, 6H, C(C*H*3)2), 1.21 (s, 6H, C(C*H*3)2). ^{11}B NMR (128 MHz, CDCl3): δ 22.13.

2-(1-(4-methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3g)***.[1] ^{1}H NMR (600 MHz, CDCl3): δ 7.28 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.84 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 5.20 (q, *J* = 6.0 Hz, 1H, OC*H*CH3), 3.77 (s, 3H, Ar-OC*H*3), 1.47 (d, *J* = 6.0 Hz, 3H, CHC*H*3), 1.23 (s, 6H, C(C*H*3)2), 1.20 (s, 6H, C(C*H*3)2). ^{11}B NMR (128 MHz, CDCl3): δ 22.16.

4,4,5,5-tetramethyl-2-(1-(4-(methylthio)phenyl)ethoxy)-1,3,2-dioxaborolane ***(3h)***.[8] ^{1}H NMR (400 MHz, CDCl3): δ 7.28 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.21 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 5.20 (q, *J* = 6.4 Hz, 1H, OC*H*CH3), 2.46 (s, 3H, Ar-SC*H*3), 1.47 (d, *J* = 6.4 Hz, 3H, CHC*H*3), 1.23 (s, 6H, C(C*H*3)2), 1.21 (s, 6H, C(C*H*3)2). ^{11}B NMR (128 MHz, CDCl3): δ 22.09.

N,N-dimethyl-4-(1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)aniline ***(3i)***.[9] ^{1}H NMR (600 MHz, CDCl3): δ 7.25 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.70 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 5.17 (q, *J* = 6.0 Hz, 1H, OC*H*CH3), 2.92 (s, 6H, N(C*H*3)2), 1.47 (d, *J* = 6.6 Hz, 3H, CHC*H*3), 1.24 (s, 6H, C(C*H*3)2), 1.21 (s, 6H, C(C*H*3)2). ^{11}B NMR (193 MHz, CDCl3): δ 22.37.

4,4,5,5-tetramethyl-2-(1-(4-(tert-butyl)phenyl)ethoxy)-1,3,2-dioxaborolane ***(3j)***.[10] ^{1}H NMR (600 MHz, CDCl3): δ 7.34 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.29 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 5.23 (q, *J* = 6.6 Hz, 1H, OC*H*CH3), 1.49 (d, *J* = 6.6 Hz, 3H, CHC*H*3), 1.30 (s, 9H, Ar-(C*H*3)3), 1.23 (s, 6H, C(C*H*3)2), 1.21 (s, 6H, C(C*H*3)2). ^{11}B NMR (128 MHz, CDCl3): δ 22.18.

4,4,5,5-tetramethyl-2-(1-((2,5-dimethyl)phenyl)ethoxy)-1,3,2-dioxaborolane ***(3k)***.[1] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (s, 1H, Ar-*H*), 6.98-6.93 (m, 2H, Ar-*H*), 5.40 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 2.30 (s, 3H, Ar-CH_3), 2.28 (s, 3H, Ar-CH_3), 1.44 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.23 (s, 6H, C(CH_3)$_2$), 1.20 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.10.

2-(1-(2-fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3l)***.[1] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55-7.53 (m, 1H, Ar-*H*), 7.22-7.18 (m, 1H, Ar-*H*), 7.13-7.10 (m, 1H, Ar-*H*), 6.99-6.96 (m, 1H, Ar-*H*), 5.55 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.49 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.24 (s, 6H, C(CH_3)$_2$), 1.21 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.13. ^{19}F NMR (565 MHz, $CDCl_3$): δ -119.60.

2-(1-(3-fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3m)***.[11] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28-7.24 (m, 1H, Ar-*H*), 7.12-7.08 (m, 2H, Ar-*H*), 6.93-6.90 (m, 1H, Ar-*H*), 5.23 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.47 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.24 (s, 6H, C(CH_3)$_2$), 1.21 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.11. ^{19}F NMR (565 MHz, $CDCl_3$): δ -113.39.

2-(1-(4-fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3n)***.[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.4 Hz, 5.4 Hz, 2H, Ar-*H*), 6.99 (t, *J* = 9.0 Hz, 2H, Ar-*H*), 5.22 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.47 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.24 (s, 6H, C(CH_3)$_2$), 1.21 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 22.11. ^{19}F NMR (565 MHz, $CDCl_3$): δ -115.91.

2-(1-(2-chlorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3o)***.[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H, Ar-*H*), 7.29-7.24 (m, 2H, Ar-*H*), 7.16 (dt, *J* = 7.8 Hz, 1.2 Hz, 1H, Ar-*H*), 5.58 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.48 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.24 (s, 6H, C(CH_3)$_2$), 1.21 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.13.

2-(1-(3-chlorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3p)***.[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (s, 1H, Ar-*H*), 7.25-7.19 (m, 3H, Ar-*H*), 5.20 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.47 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.24 (s, 6H, C(CH_3)$_2$), 1.21 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.12.

2-(1-(4-chlorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3q)***.[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30-7.26 (m, 4H, Ar-*H*), 5.21 (q, *J* = 6.0 Hz, 1H, OC*H*CH_3), 1.46 (d, *J* = 6.0 Hz, 3H, CHC*H*$_3$), 1.23 (s, 6H, C(C*H*$_3$)$_2$), 1.21 (s, 6H, C(C*H*$_3$)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.07.

2-(1-(2-bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3r)***.[11] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H, Ar-*H*), 7.47 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H, Ar-*H*), 7.31-7.28 (m, 1H, Ar-*H*), 7.08 (dt, *J* = 7.8 Hz, 1.8 Hz, 1H, Ar-*H*), 5.52 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.47 (d, *J* = 6.6 Hz, 3H, CHC*H*$_3$), 1.24 (s, 6H, C(C*H*$_3$)$_2$), 1.21 (s, 6H, C(C*H*$_3$)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.12.

2-(1-(3-bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3s)***.[12] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (s, 1H, Ar-*H*), 7.36 (dd, *J* = 7.8 Hz, 0.6 Hz, 1H, Ar-*H*), 7.26 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.17 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 5.19 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.47 (d, *J* = 6.6 Hz, 3H, CHC*H*$_3$), 1.24 (s, 6H, C(C*H*$_3$)$_2$), 1.21 (s, 6H, C(C*H*$_3$)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.10.

2-(1-(4-bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3t)***.[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.23 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 5.19 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.46 (d, *J* = 6.6 Hz, 3H, CHC*H*$_3$), 1.23 (s, 6H, C(C*H*$_3$)$_2$), 1.21 (s, 6H, C(C*H*$_3$)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.14.

4,4,5,5-tetramethyl-2-(1-(2-(trifluoromethyl)phenyl)ethoxy)-1,3,2-dioxaborolane ***(3u)***.[13] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.58-7.53 (m, 2H, Ar-*H*), 7.33 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 5.65 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.49 (d, *J* = 6.0 Hz, 3H, CHC*H*$_3$), 1.22 (s, 6H, C(C*H*$_3$)$_2$), 1.18 (s, 6H, C(C*H*$_3$)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.11. ^{19}F NMR (565 MHz, $CDCl_3$): δ -58.50.

4,4,5,5-tetramethyl-2-(1-(3-(trifluoromethyl)phenyl)ethoxy)-1,3,2-dioxaborolane ***(3v)***.[13] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (s, 1H, Ar-*H*), 7.54 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.50 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.43 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 5.29 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.51 (d, *J* = 6.6 Hz, 3H, CHC*H*$_3$), 1.25 (s, 6H, C(C*H*$_3$)$_2$), 1.22 (s, 6H, C(C*H*$_3$)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.14. ^{19}F NMR (565 MHz, $CDCl_3$): δ -62.60.

4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)ethoxy)-1,3,2-dioxaborolane ***(3w)***.[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.40 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 5.29 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.49 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.25 (s, 6H, C(CH_3)$_2$), 1.22 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 22.08. ^{19}F NMR (565 MHz, $CDCl_3$): δ -62.46.

4-(1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)benzonitrile ***(3x)***.[1] ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.54 (d, *J* = 9.0 Hz, 2H, Ar-*H*), 5.34 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.52 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.26 (s, 6H, C(CH_3)$_2$), 1.23 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 22.15.

4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)ethoxy)-1,3,2-dioxaborolane ***(3y)***.[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83-7.77 (m, 4H, Ar-*H*), 7.48-7.39 (m, 3H, Ar-*H*), 5.41 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.56 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.23 (s, 6H, C(CH_3)$_2$), 1.19 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.29.

2-(benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3z)***.[1] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.8 Hz, 4H, Ar-*H*), 7.27 (t, *J* = 7.2 Hz, 4H, Ar-*H*), 7.20 (t, *J* = 7.2 Hz, 2H, Ar-*H*), 6.18 (s, 1H, OC*H*), 1.18 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.50.

2-(1-(furan-2-yl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3aa)***.[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (d, *J* = 1.2 Hz, 1H, Ar-*H*), 6.29 (t, *J* = 2.4 Hz, 1H, Ar-*H*), 6.23 (d, *J* = 3.6 Hz, 1H, Ar-*H*), 5.24 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.54 (d, *J* = 6.6 Hz, 1H, CHCH_3), 1.25 (s, 6H, C(CH_3)$_2$), 1.25 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.20.

2-(1-(thiophene-3-yl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ***(3ab)***.[14] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 (dd, *J* = 5.4 Hz, 3.0 Hz, 1H, Ar-*H*), 7.18 (d, *J* = 3.0 Hz, 1H, Ar-*H*), 7.06 (dd, *J* = 5.4 Hz, 1.2 Hz, 1H, Ar-*H*), 5.32 (q, *J* = 6.0 Hz 1H, OC*H*CH_3), 1.51 (d, *J* = 6.0 Hz, 1H, CHCH_3), 1.24 (s, 6H, C(CH_3)$_2$), 1.23 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 22.17.

3-(1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)pyridine ***(3ac)***.[7] ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.60 (d, *J* = 1.8 Hz, 1H, Ar-*H*), 8.51 (dd, *J* = 4.8 Hz, 1.2 Hz, 1H, Ar-*H*), 7.73 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.26 (dd, *J* = 7.8 Hz, 4.8 Hz, 1H, Ar-*H*), 5.28 (q, *J* = 6.6 Hz, 1H, OC*H*CH_3), 1.52 (d, *J* = 6.6 Hz 1H, CHCH_3), 1.25 (s, 6H, C(CH_3)$_2$), 1.22 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 22.10.

*2-(cyclohexylmethoxy)pinacolborane (**3ad**).*[1] ^{1}H NMR (600 MHz, C_6D_6): δ 4.13-4.09 (m, 1H, OC*H*CH_3), 1.87-1.85 (m, 1H, Cy-*H*), 1.68-1.62 (m, 3H, Cy-*H*), 1.56-1.54 (m, 1H, Cy-*H*), 1.32-1.31 (m, 1H, Cy-*H*), 1.16 (d, *J* = 6.0 Hz, 3H, CHCH_3), 1.12-1.10 (m, 2H, Cy-*H*), 1.07 (s, 12H, C(CH_3)$_2$), 1.03-1.00 (m, 2H, Cy-*H*), 0.97-0.95 (m, 1H, Cy-*H*). ^{11}B NMR (193 MHz, C_6D_6): δ 21.95.

*2-(1-cinnamylethoxy)pinacolborane (**3ae**).*[15] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.29 (t, *J* = 7.2 Hz, 2H, Ar-*H*), 7.21 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 6.57 (d, *J* = 16.2 Hz, 1H, Ar-C*H*), 6.22 (dd, *J* = 15.6 Hz, 5.4 Hz, 1H, CHCH_2), 4.85-4.81 (m, 1H, OC*H*CH_3), 1.37 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.26 (s, 6H, C(CH_3)$_2$), 1.24 (s, 6H, C(CH_3)$_2$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.14.

*2-(1-hydrocinnamylethoxy)pinacolborane (**3af**).*[15] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26-7.24 (m, 2H, Ar-*H*), 7.18-7.15 (m, 3H, Ar-*H*), 4.21-4.18 (m, 1H, OC*H*CH_3), 2.75-2.59 (m, 2H, CH_2), 1.87-1.70 (m, 2H, CH_2), 1.26 (s, 6H, C(CH_3)$_2$), 1.25 (s, 6H, C(CH_3)$_2$), 1.22 (d, *J* = 6.0 Hz, 3H, CHCH_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.13.

*2-(tert-butyryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3ag**).*[17] ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.87 (q, *J* = 6.0 Hz, 1H, OC*H*CH_3), 1.26 (s, 6H, C(CH_3)$_2$), 1.25 (s, 6H, C(CH_3)$_2$), 1.11 (d, *J* = 6.0 Hz, 1H, CHCH_3), 0.87 (s, 9H, C(CH_3)$_3$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 21.95.

*2-(cyclohexyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3ah**).*[1] ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.01-3.97 (m, 1H, OC*H*), 1.85-1.82 (m, 2H, Cy-*H*), 1.74-1.70 (m, 2H, Cy-*H*), 1.50-1.48 (m, 1H, Cy-*H*), 1.38-1.30 (m, 5H, Cy-*H*), 1.28 (s, 12H, C(CH_3)$_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 21.81.

*2-(2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)pinacolborane (**3ai**).*[15] ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.47 (broad s, 1H, =C*H*), 4.71 (s, 2H, =CH_2), 4.64 (broad s, 1H, OC*H*), 2.30-2.25 (m, 1H, CH_2), 2.12-2.09 (m, 1H, CH_2), 2.05-2.02 (m, 1H, CH_2), 1.95-1.90 (m, 1H, CH_2), 1.72 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.60-1.54 (m, 1H, CH_2), 1.26

(s, 12H, $C(CH_3)_2$). ^{11}B NMR (193 MHz, $CDCl_3$): δ 22.36.

*1-Phenylethanol (**3a'**).*[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35-7.24 (m, 5H, Ar-*H*), 4.85 (q, *J* = 6.6 Hz, 1H, $CHCH_3$), 2.21 (s, 1H, CHO*H*), 1.46 (d, *J* = 6.6 Hz, 3H, $CHCH_3$). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 145.9, 128.5, 127.5, 125.4, 70.4, 25.2.

*1-(p-tolyl)ethan-1-ol (**3d'**).*[11] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.17 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 4.87 (q, *J* = 6.6 Hz, 1H, $CHCH_3$), 2.35 (s, 3H, Ar-CH_3), 1.70 (s, 1H, CHO*H*), 1.49 (d, *J* = 6.6 Hz, 3H, $CHCH_3$). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 142.9, 137.2, 129.2, 125.4, 70.3, 25.1, 21.1.

*1-(4-Chlorophenyl)ethanol (**3q'**).*[11] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32-7.29 (m, 4H, Ar-*H*), 4.87 (q, *J* = 6.6 Hz, 1H, $CHCH_3$), 1.89 (s, 1H, CHO*H*), 1.47 (d, *J* = 6.6 Hz, 3H, $CHCH_3$). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 144.3, 133.1, 128.6, 126.8, 69.8, 25.3.

*1,1-Diphenylmethanol (**3z'**).*[11] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41-7.29 (m, 10H, Ar-*H*), 5.81 (s, 1H, C*H*OH), 2.58 (s, 1H, CHO*H*). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 143.9, 128.5, 127.6, 126.6, 76.2.

*1-(3-Pyridyl)ethanol (**3ac'**).*[13] ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.43 (d, *J* = 1.8 Hz, 1H, Ar-*H*), 8.34 (dd, *J* = 4.8 Hz, 1.2 Hz, 1H, Ar-*H*), 7.72 (dt, *J* = 7.8 Hz, 1.8 Hz, 1H, Ar-*H*), 7.23 (dd, *J* = 7.8 Hz, 4.8 Hz, 1H, Ar-*H*), 4.89 (q, *J* = 6.6 Hz, 1H, $CHCH_3$), 1.47 (d, *J* = 6.6 Hz 1H, $CHCH_3$). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 148.0, 147.1, 141.8, 133.6, 123.6, 67.5, 25.2.

*1-phenyl-3-butanol (**3af'**).*[18] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28-7.26 (m, 2H, Ar-*H*), 7.20-7.16 (m, 3H, Ar-*H*), 3.82-3.79 (m, 1H, $CHCH_3$), 2.77-2.63 (m, 2H, CH_2), 1.82 (s, 1H, CHO*H*), 1.81-1.70 (m, 2H, CH_2), 1.21 (d, *J* = 6.0 Hz, 3H, $CHCH_3$). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 142.1, 128.4, 125.8, 67.5, 40.9, 32.2, 23.7.

NMR Spectra of products 2 and 3 (*: excessive HBpin; &: Bpin-O-Bpin)

Fig. S1 ^{1}H NMR (600 MHz, $CDCl_3$) of **2a**

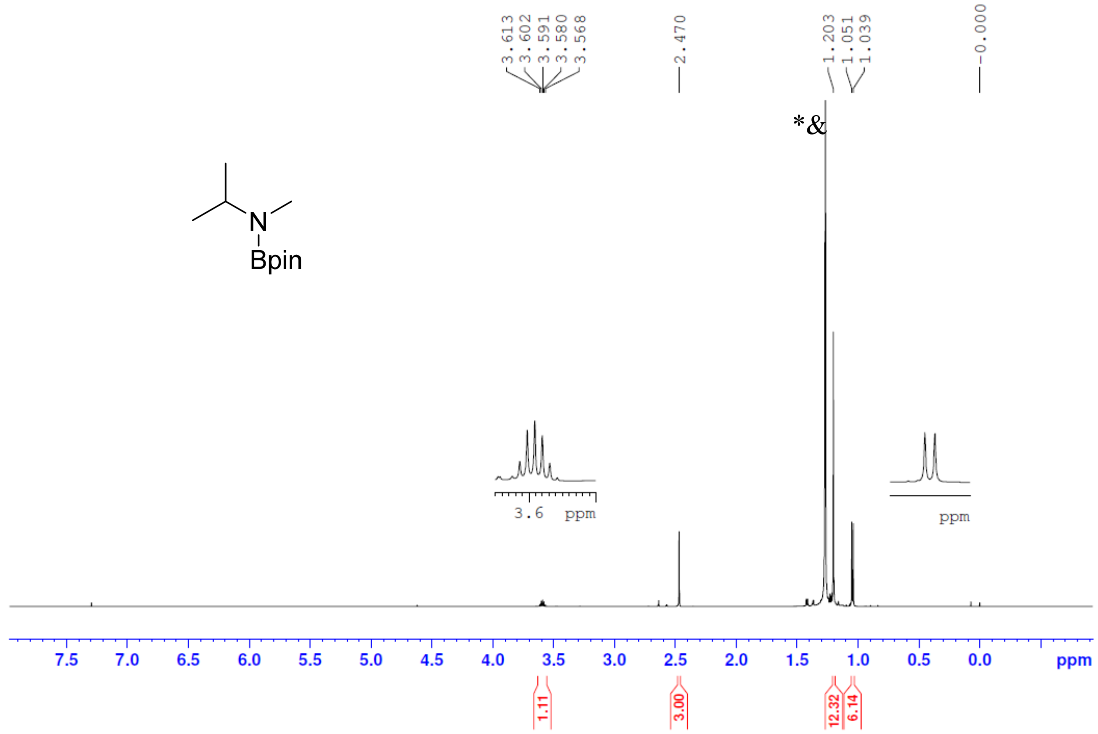


Fig. S2 ^{11}B NMR (193 MHz, $CDCl_3$) of **2a**

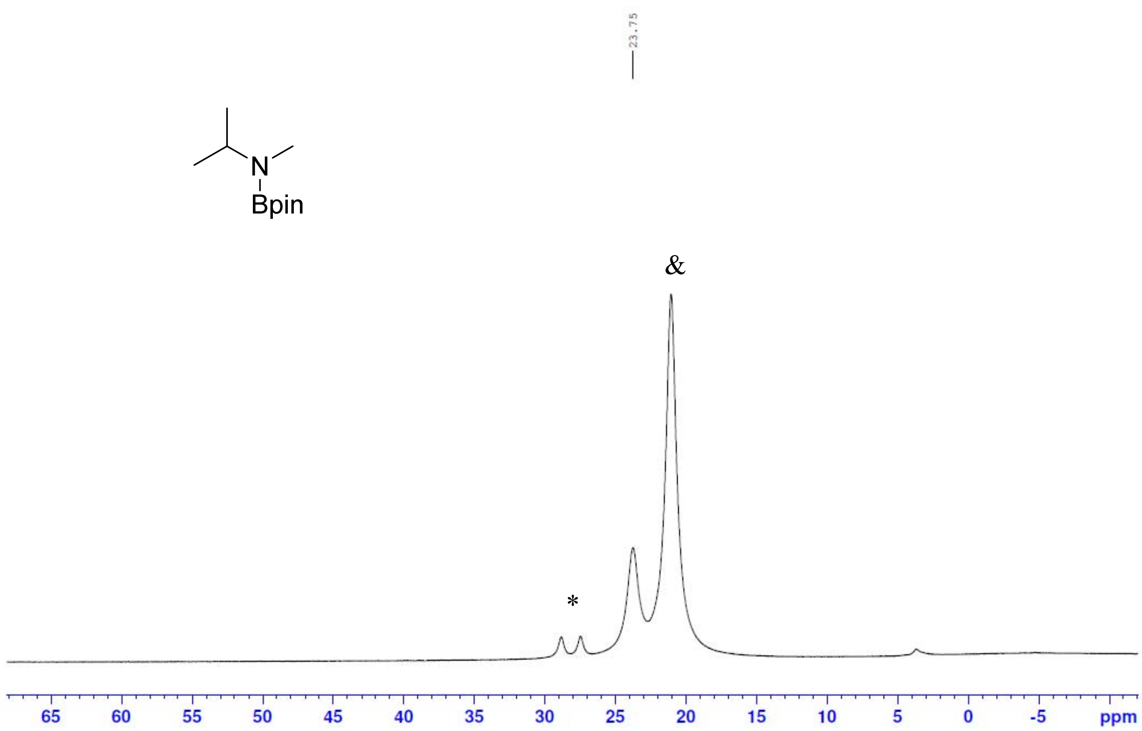


Fig. S3 ^{1}H NMR (600 MHz, $CDCl_3$) of **2b**

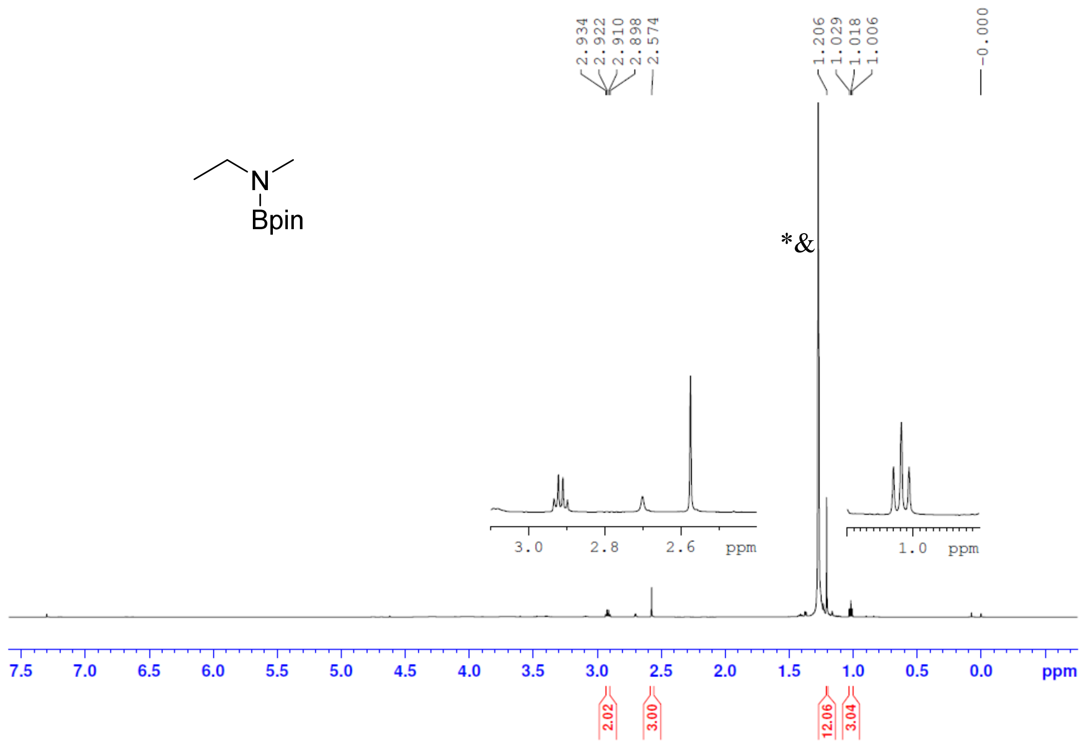


Fig. S4 ^{11}B NMR (193 MHz, $CDCl_3$) of **2b**

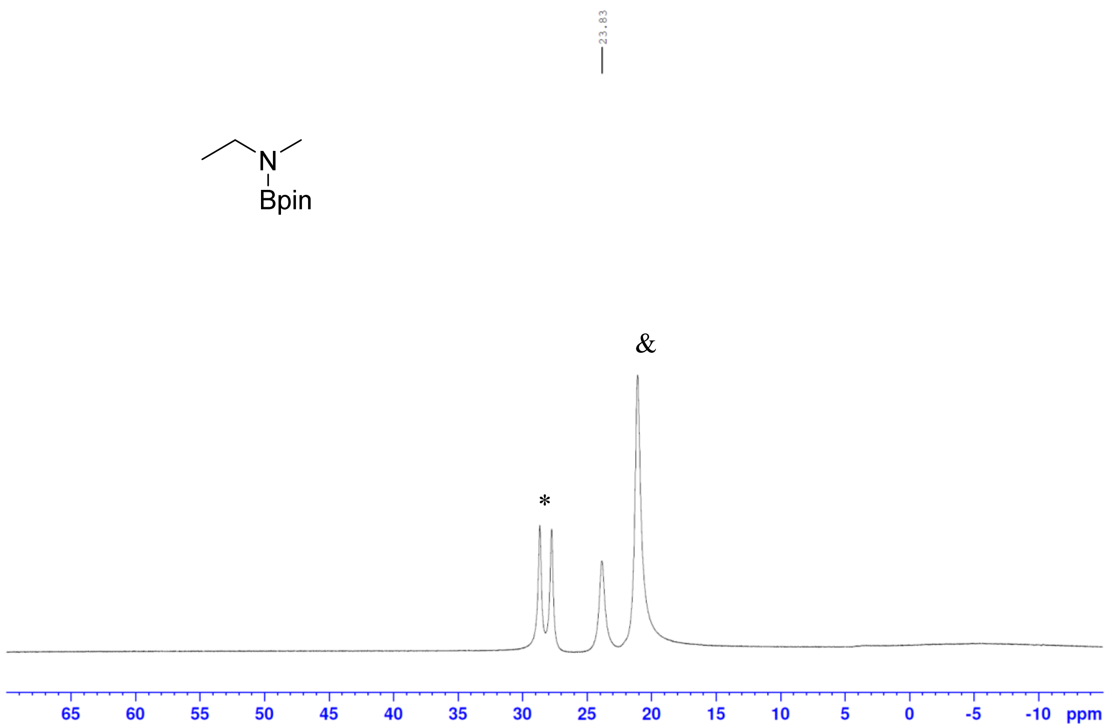


Fig. S5 ^{1}H NMR (600 MHz, $CDCl_3$) of **2c**

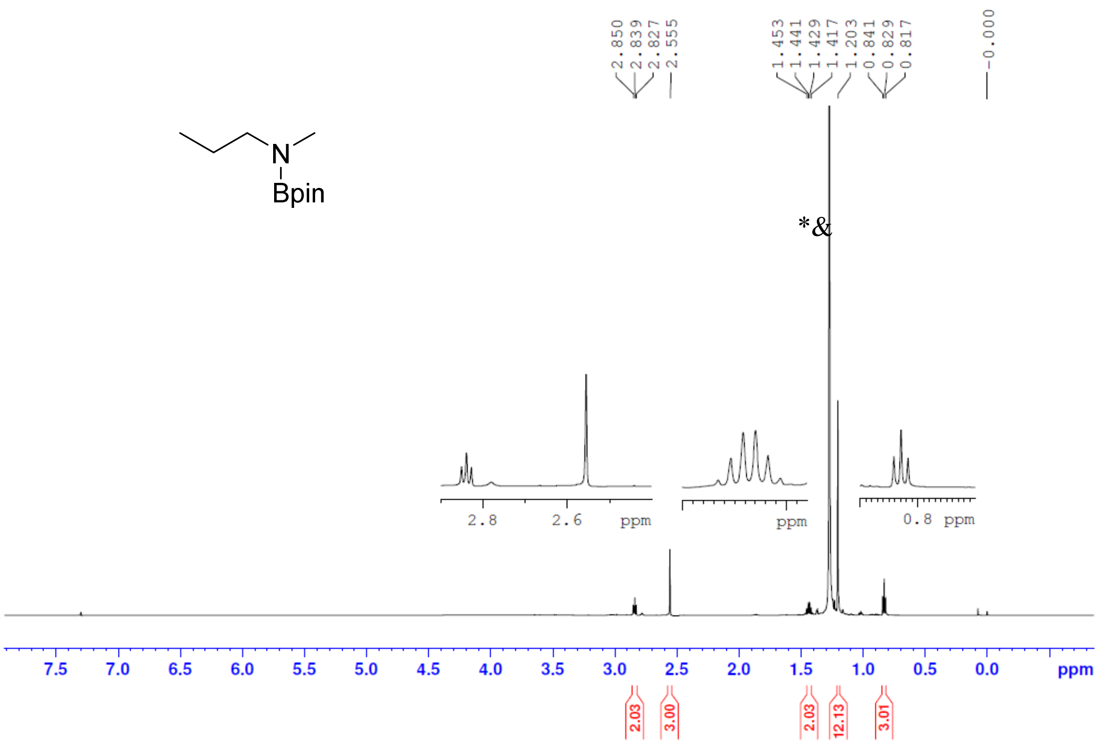


Fig. S6 ^{11}B NMR (193 MHz, $CDCl_3$) of **2c**

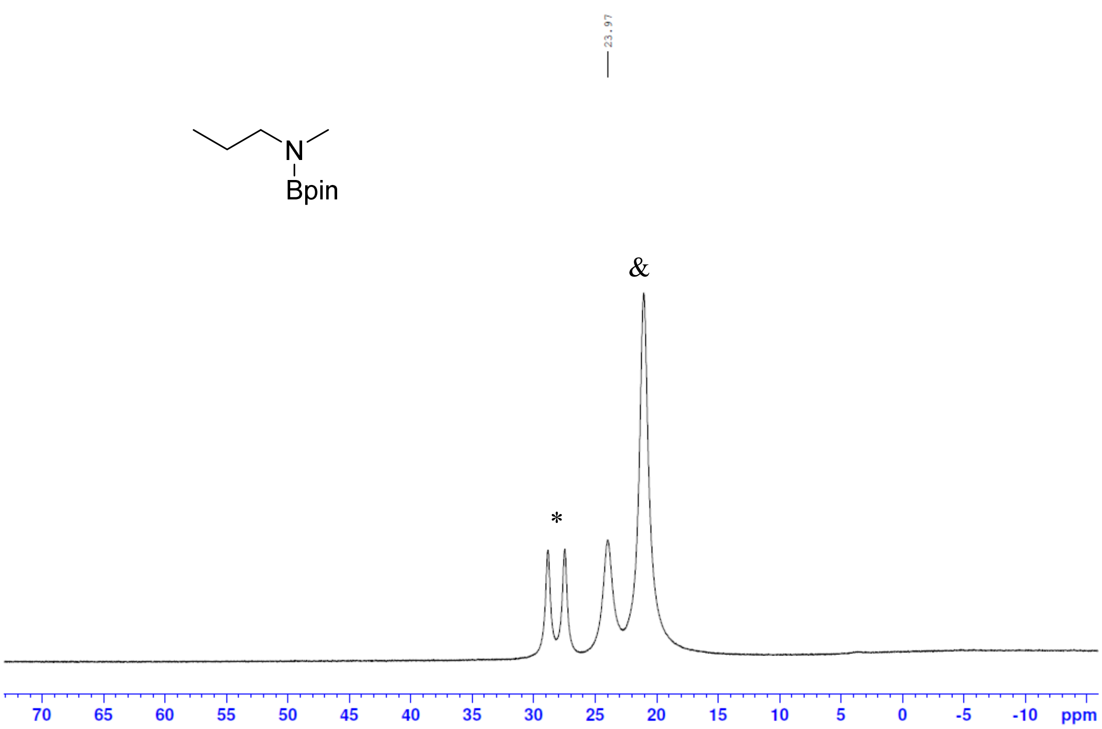


Fig. S7 ^{1}H NMR (600 MHz, $CDCl_3$) of **2d**

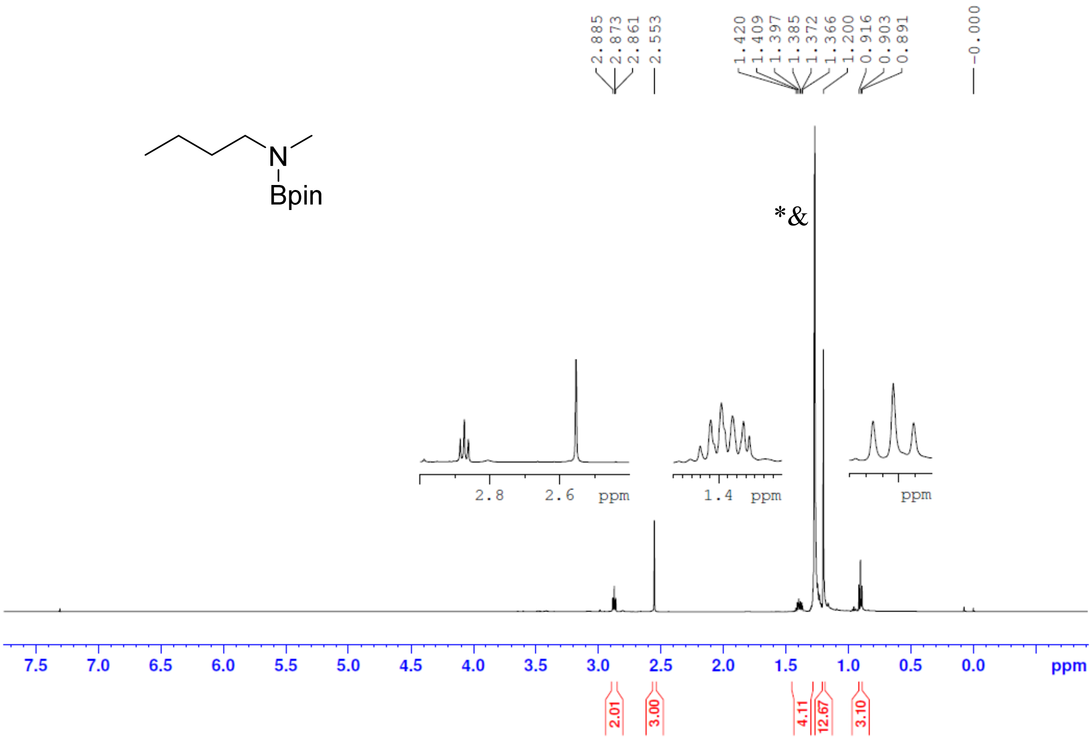


Fig. S8 ^{11}B NMR (193 MHz, $CDCl_3$) of **2d**

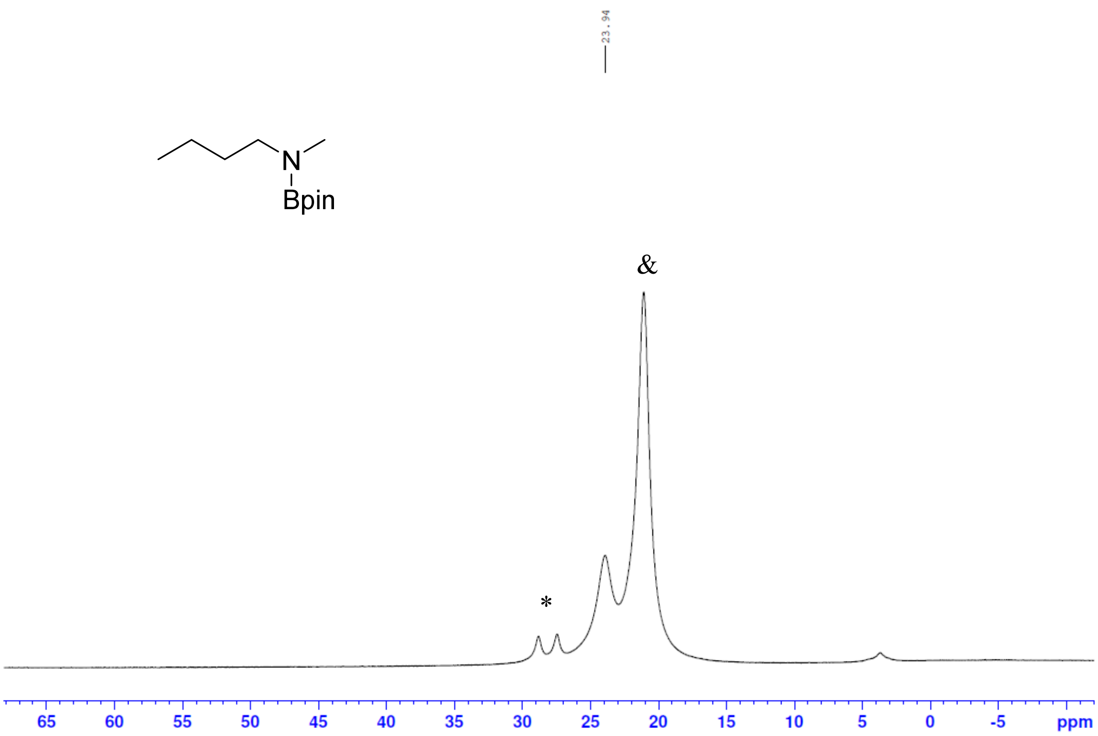


Fig. S9 ^{1}H NMR (600 MHz, $CDCl_3$) of **2e**

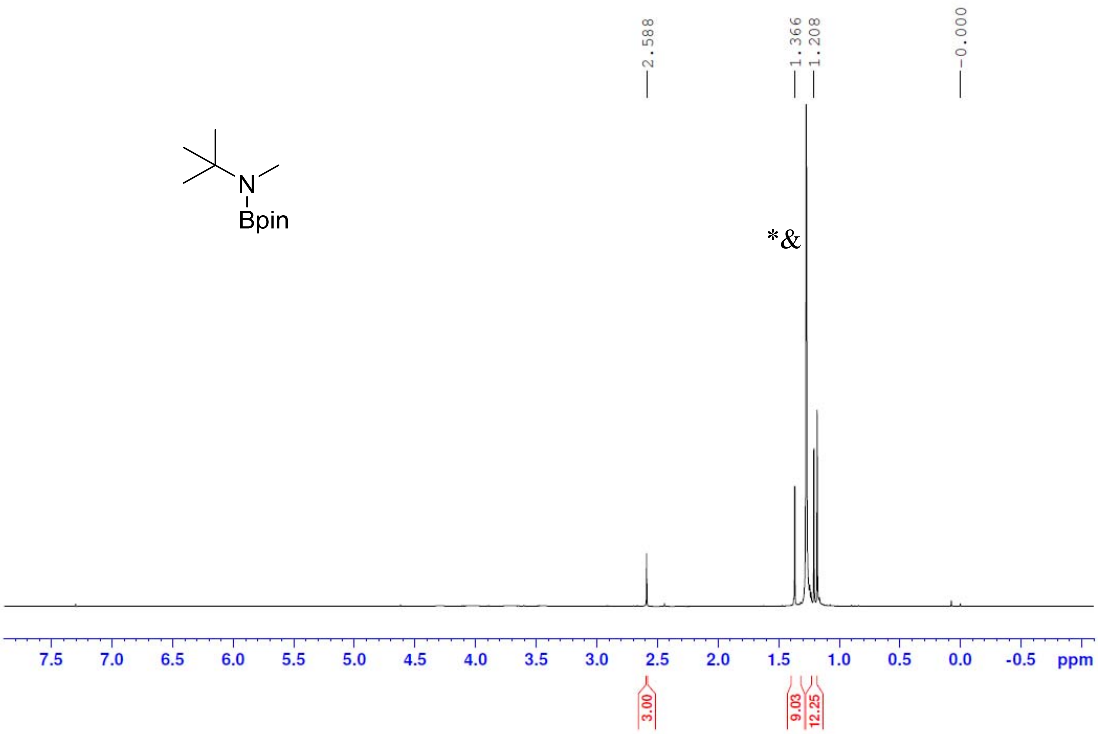


Fig. S10 ^{11}B NMR (193 MHz, $CDCl_3$) of **2e**

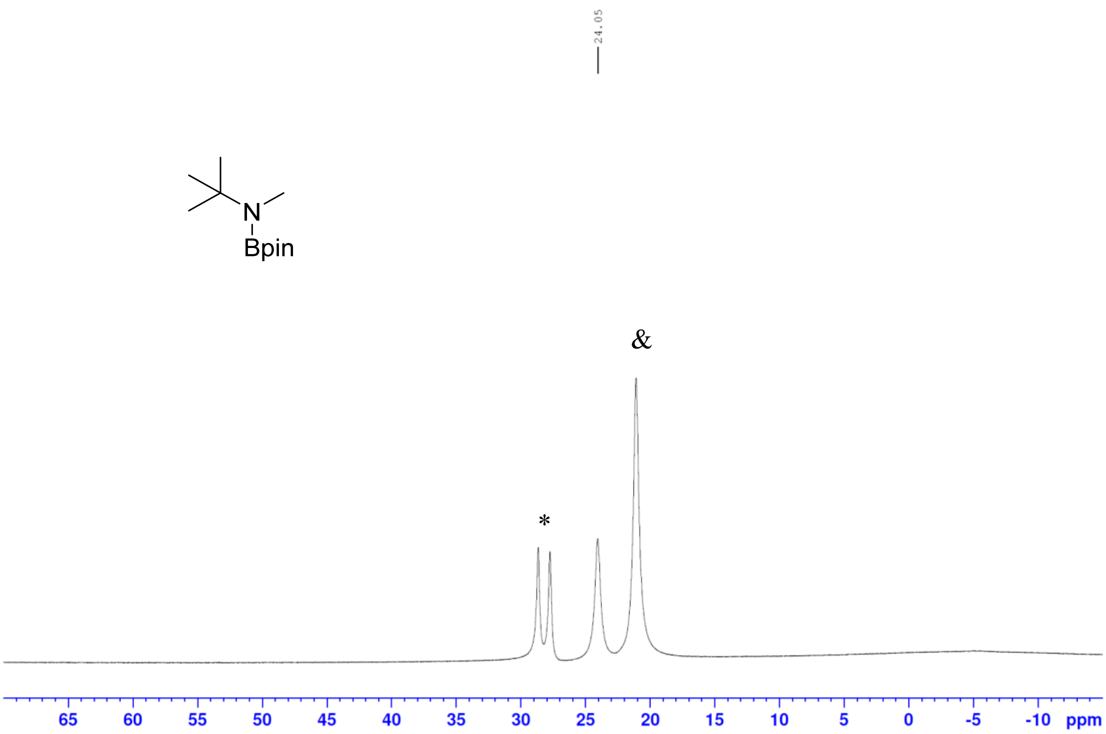


Fig. S11 ^{1}H NMR (600 MHz, $CDCl_3$) of **2f**

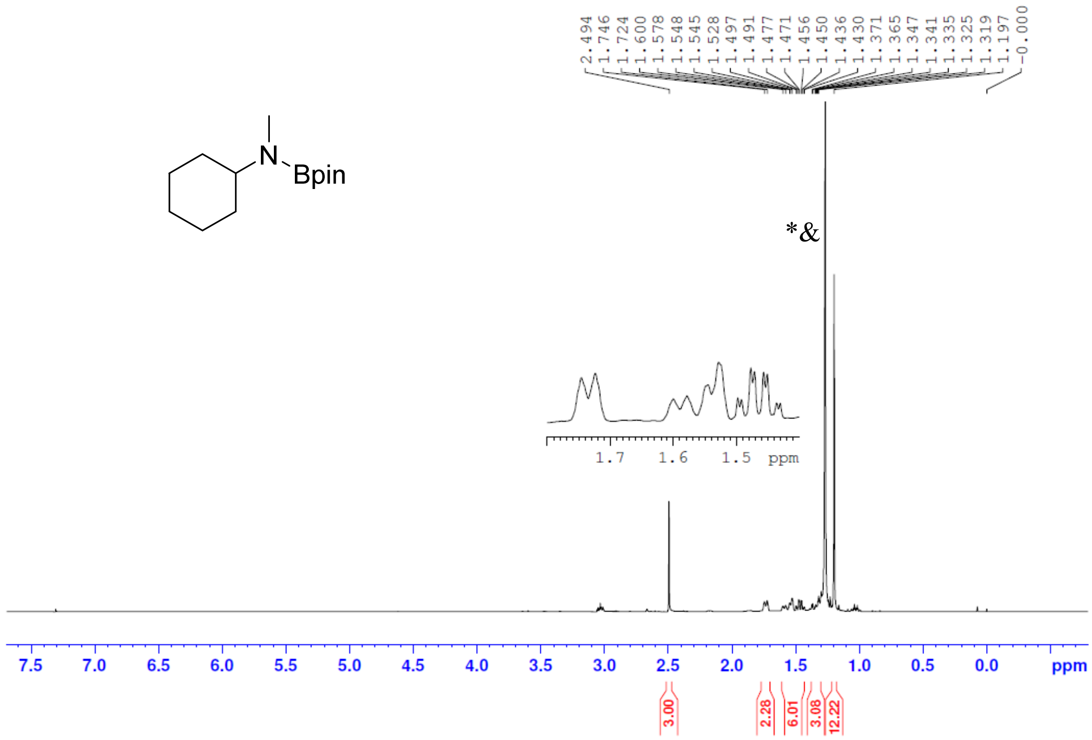


Fig. S12 ^{11}B NMR (193 MHz, $CDCl_3$) of **2f**

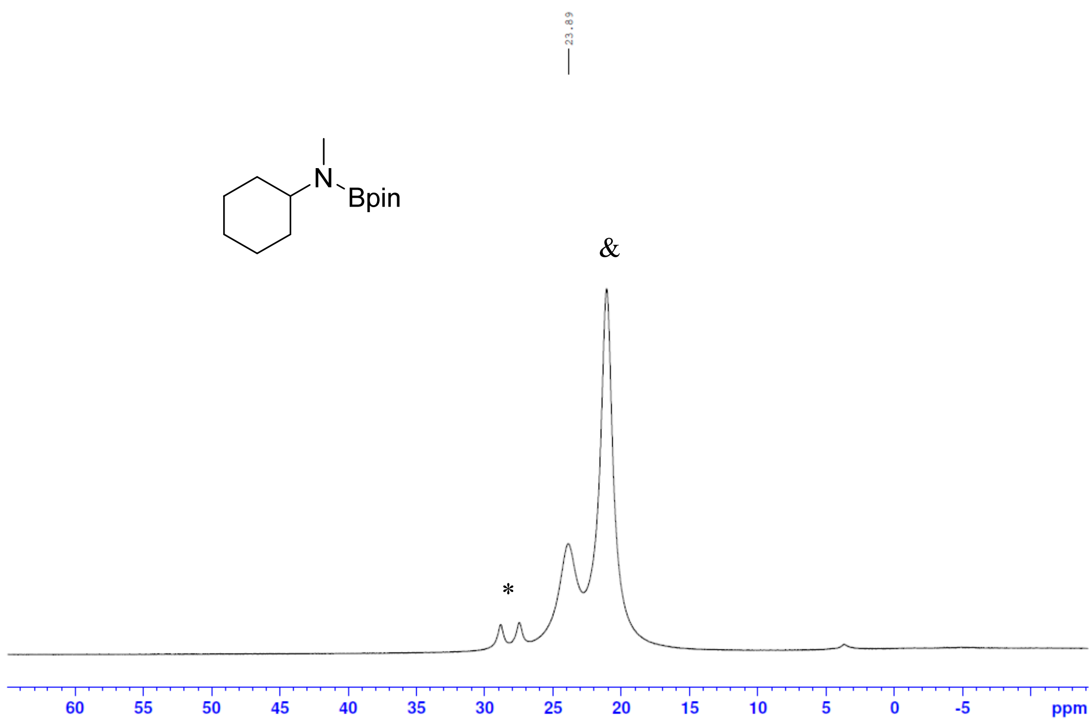


Fig. S13 ^{1}H NMR (600 MHz, $CDCl_3$) of **2g**

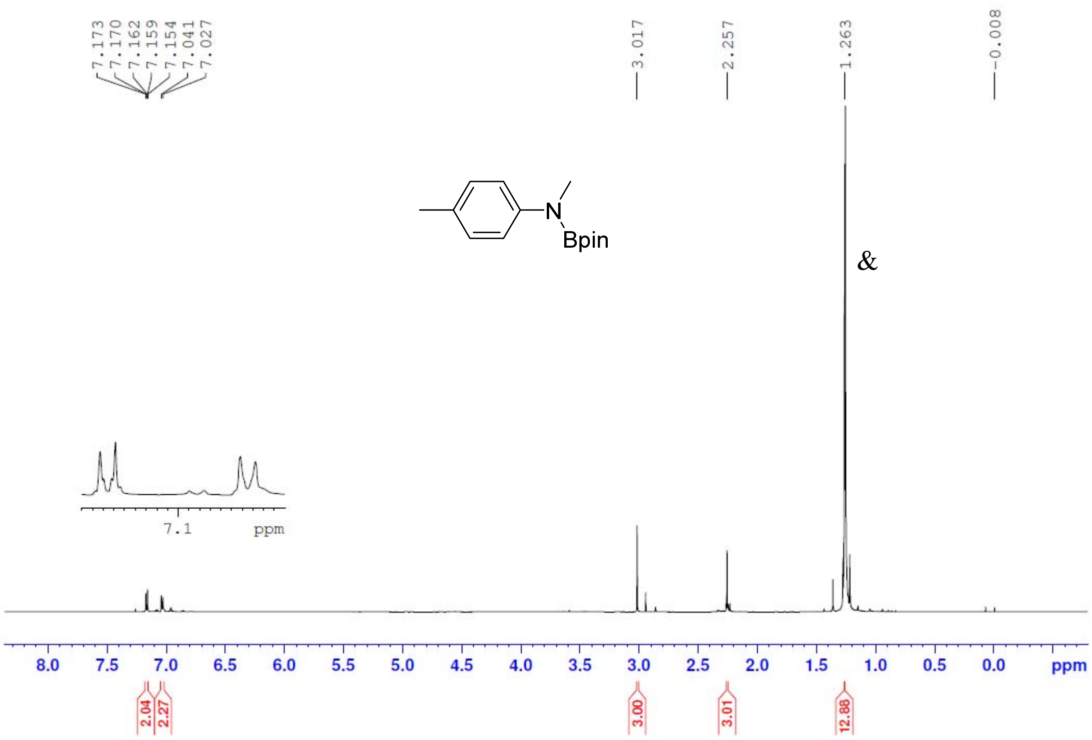


Fig. S14 ^{11}B NMR (193 MHz, $CDCl_3$) of **2g**

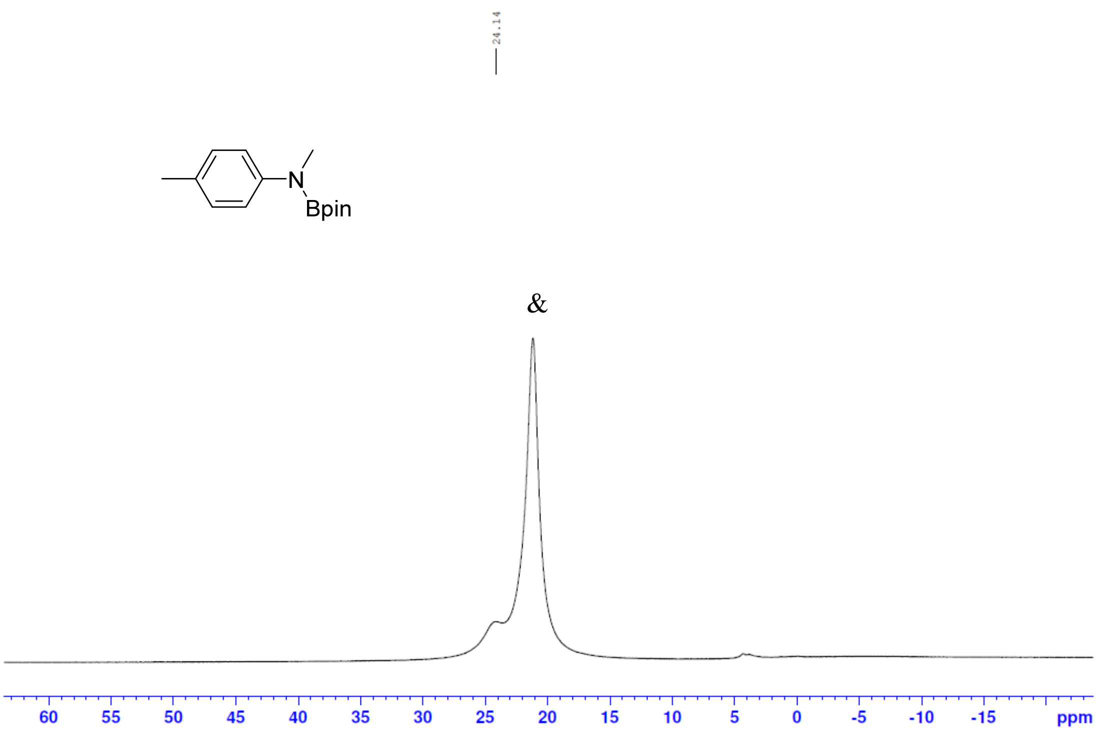


Fig. S15 ^{1}H NMR (600 MHz, $CDCl_3$) of **2h**

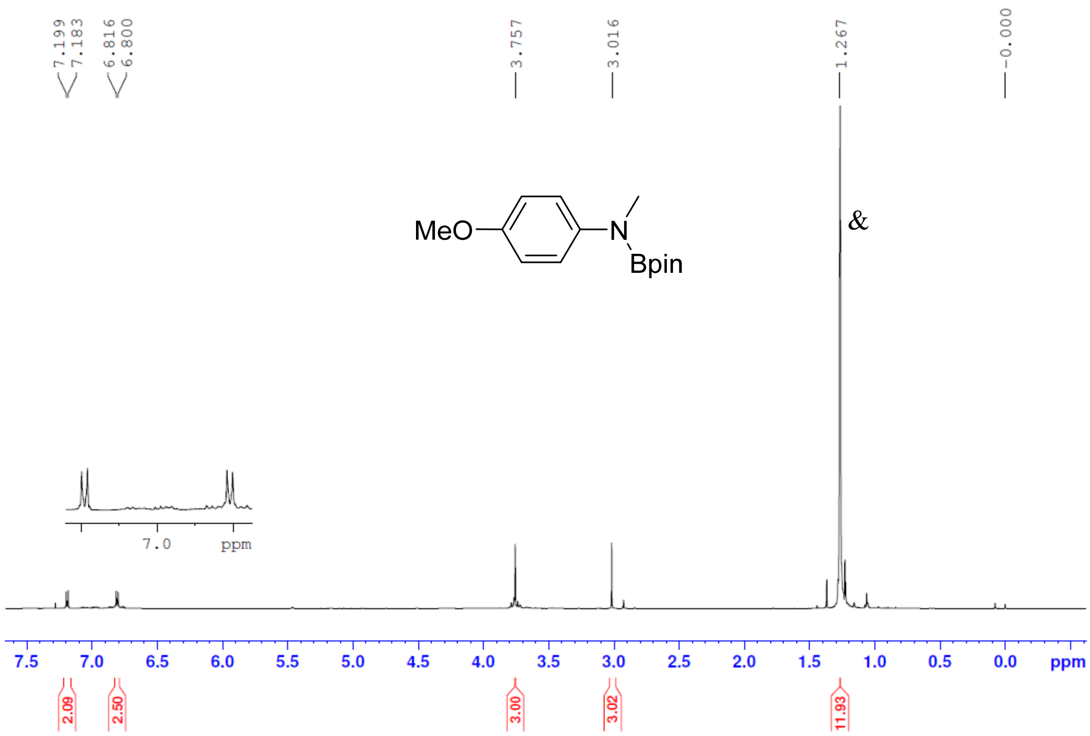


Fig. S16 ^{11}B NMR (193 MHz, $CDCl_3$) of **2h**

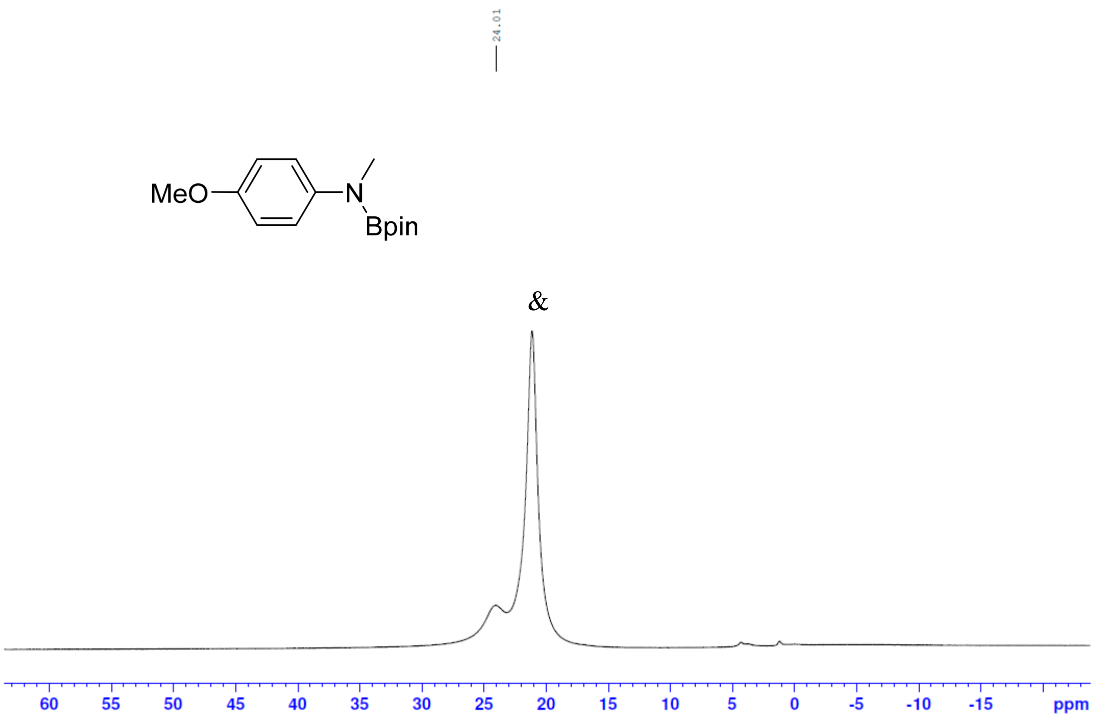


Fig. S17 ^{1}H NMR (600 MHz, $CDCl_3$) of **2i**

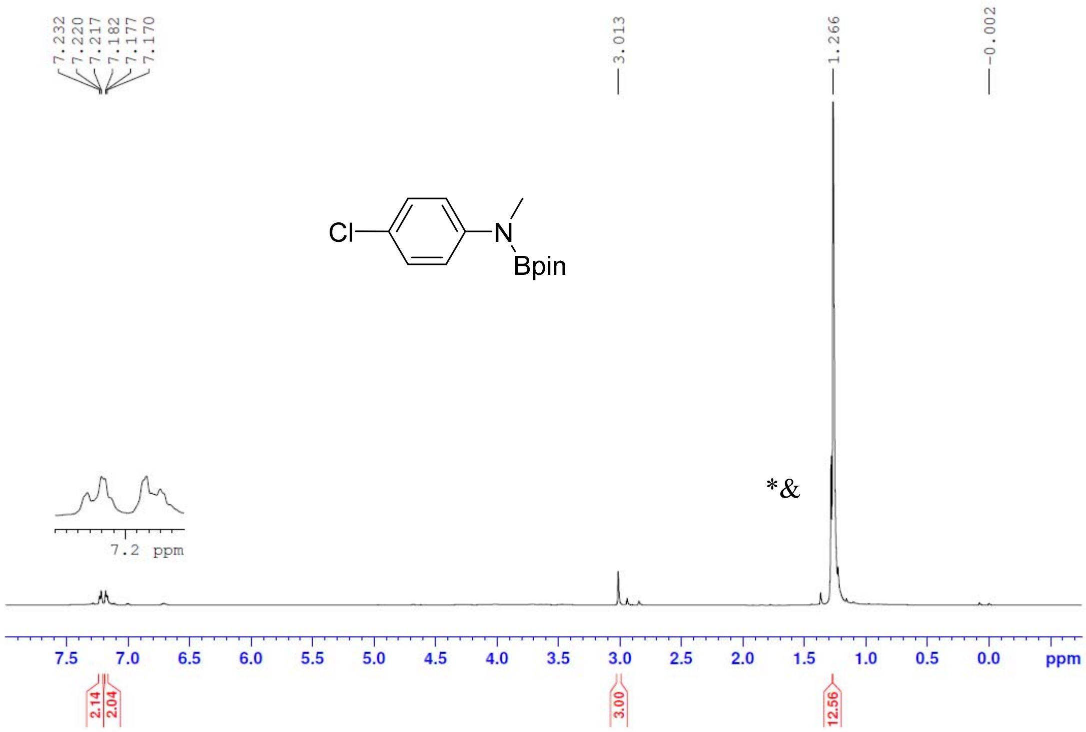


Fig. S18 ^{11}B NMR (193 MHz, $CDCl_3$) of **2i**

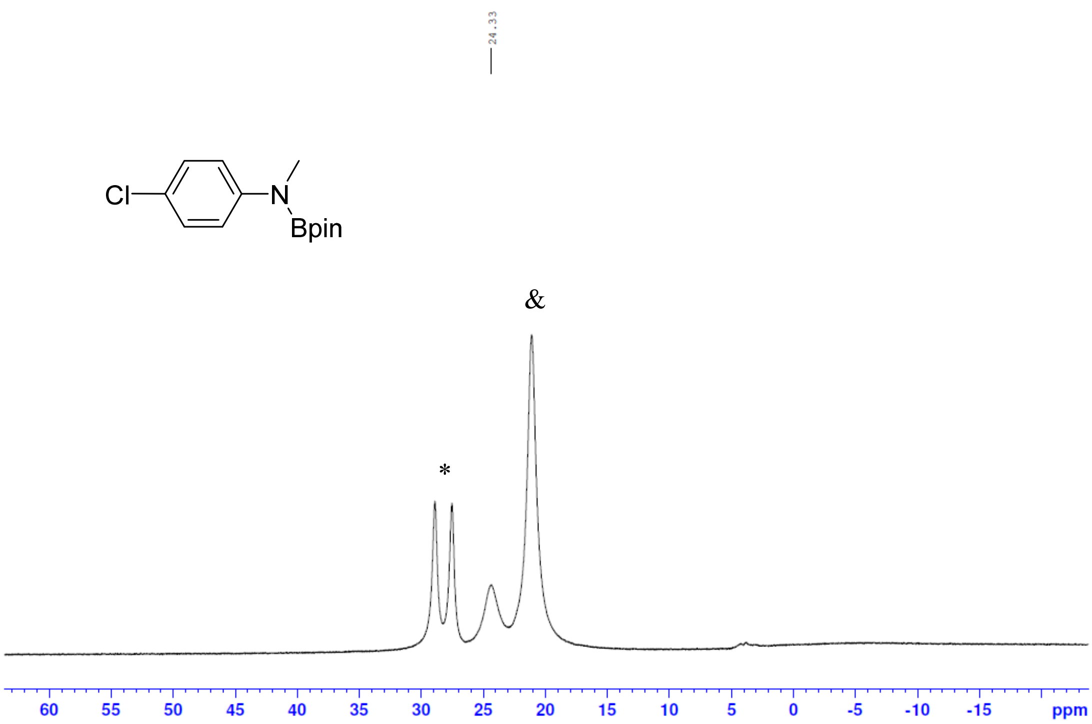


Fig. S19 ^{1}H NMR (600 MHz, $CDCl_3$) of **2j**

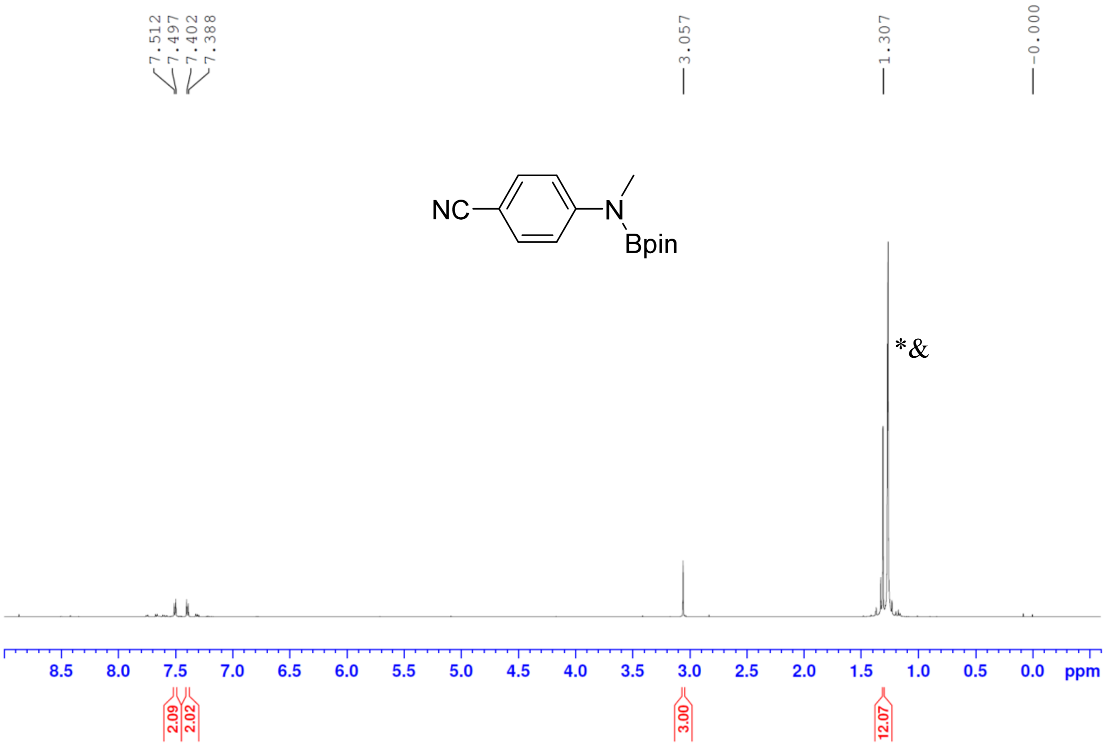


Fig. S20 ^{11}B NMR (193 MHz, $CDCl_3$) of **2j**

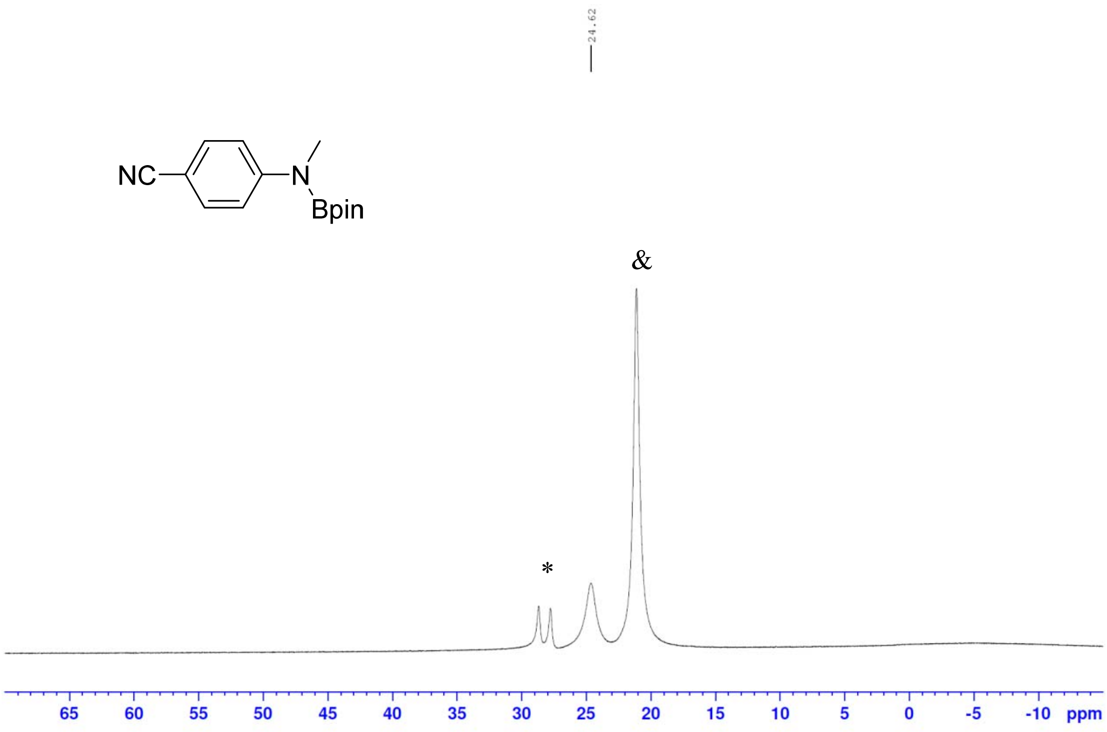


Fig. S21 ^{1}H NMR (600 MHz, CDCl$_3$) of **2k**

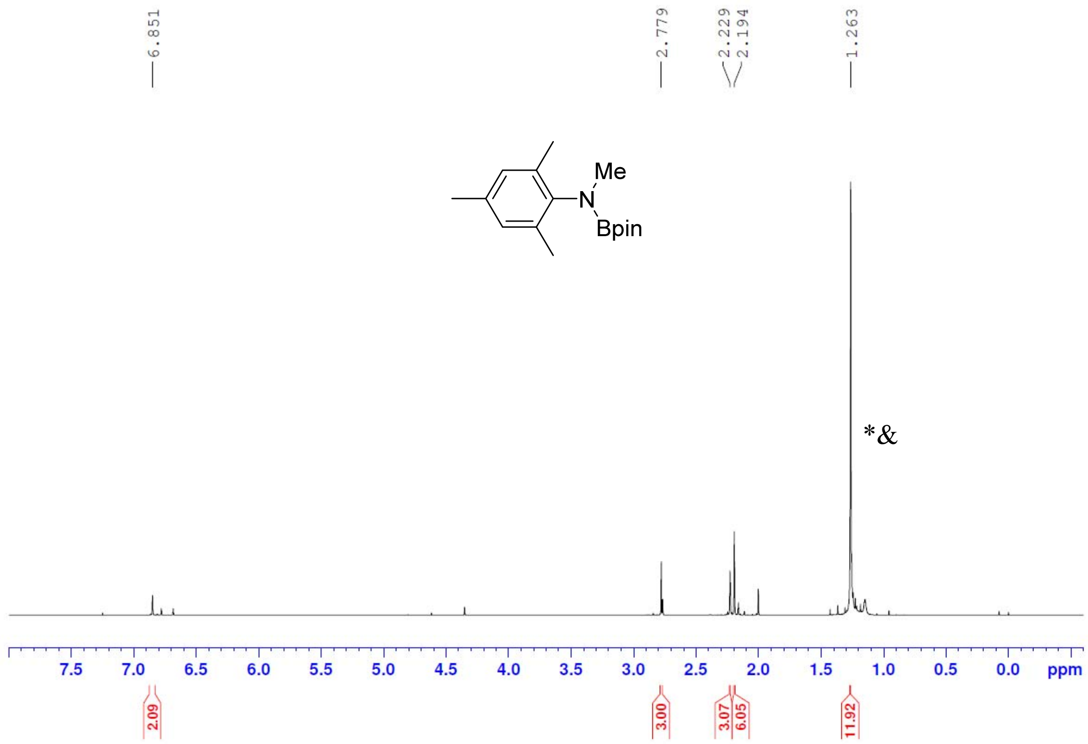


Fig. S22 ^{11}B NMR (193 MHz, CDCl$_3$) of **2k**

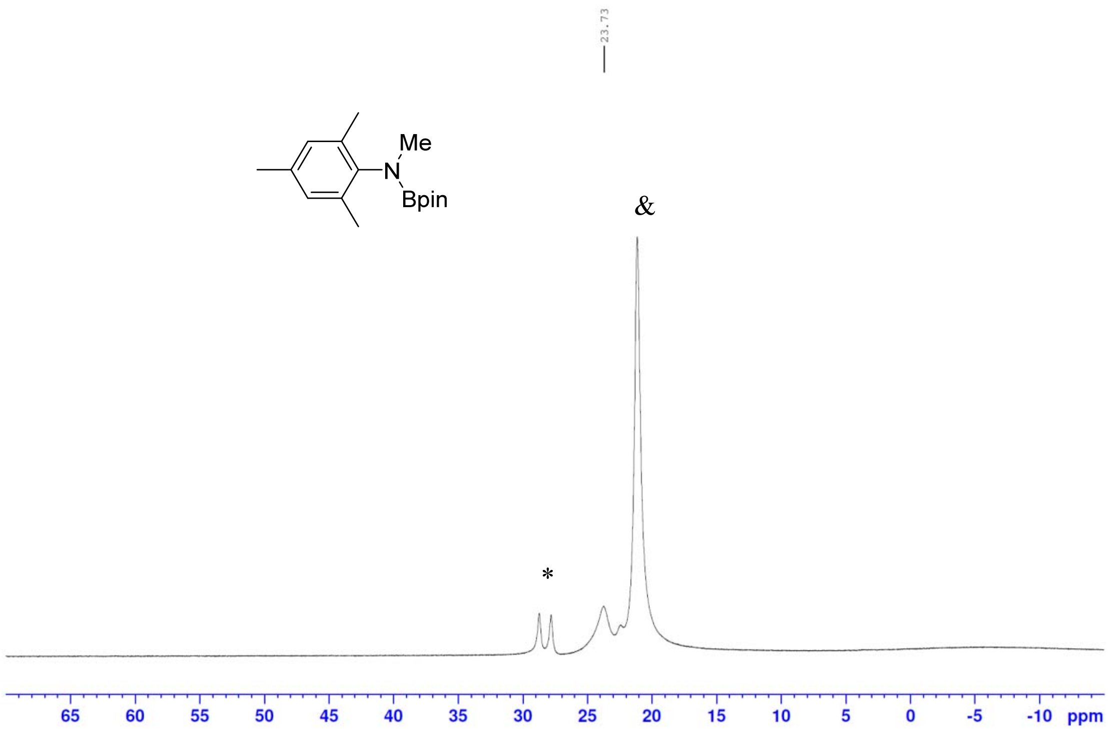


Fig. S23 ^{1}H NMR (600 MHz, $CDCl_3$) of **2l**

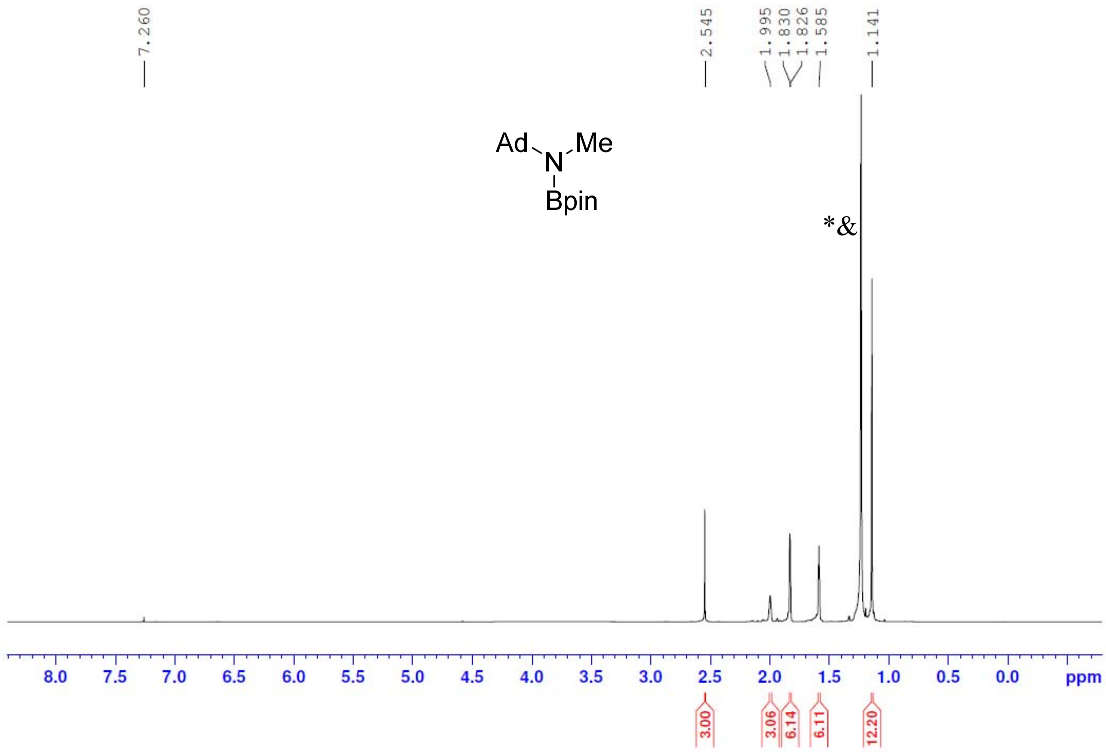


Fig. S24 ^{11}B NMR (193 MHz, $CDCl_3$) of **2l**

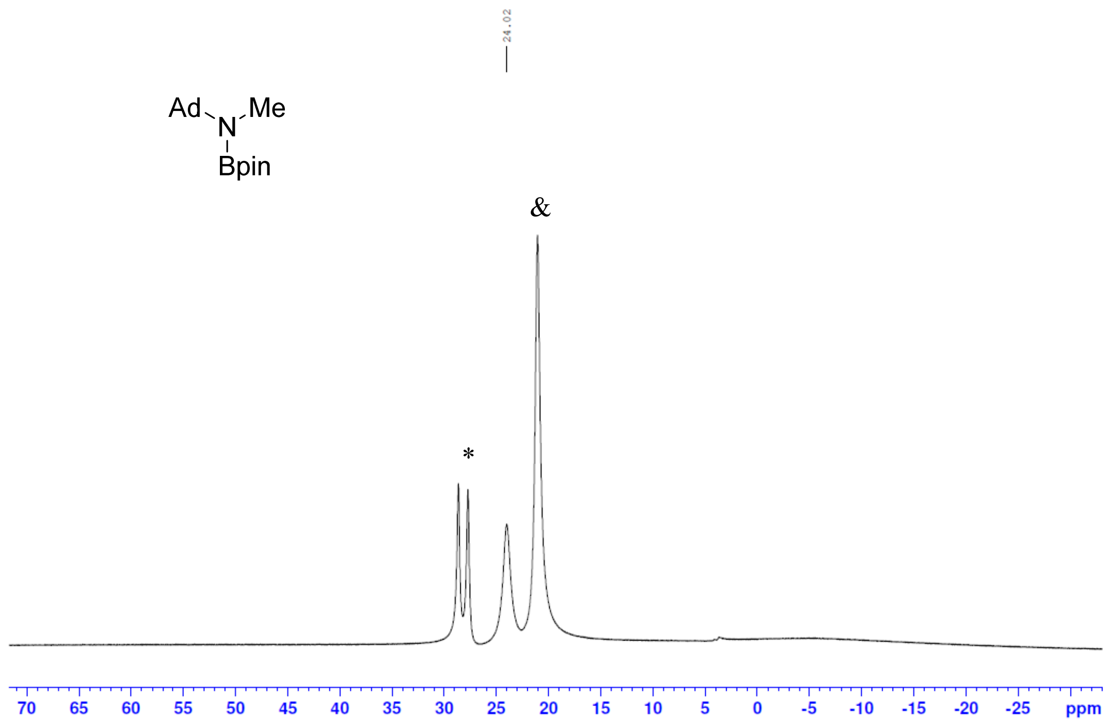


Fig. S25 ^{1}H NMR (600 MHz, $CDCl_3$) of **2g’**

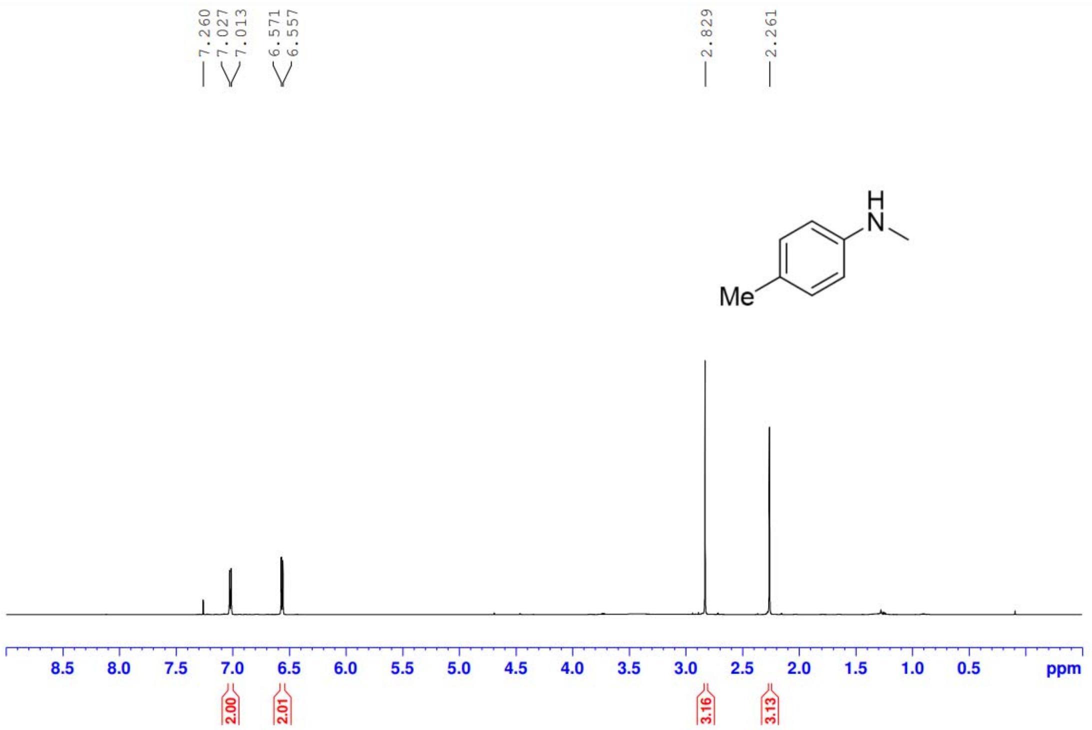


Fig. S26 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of **2g’**

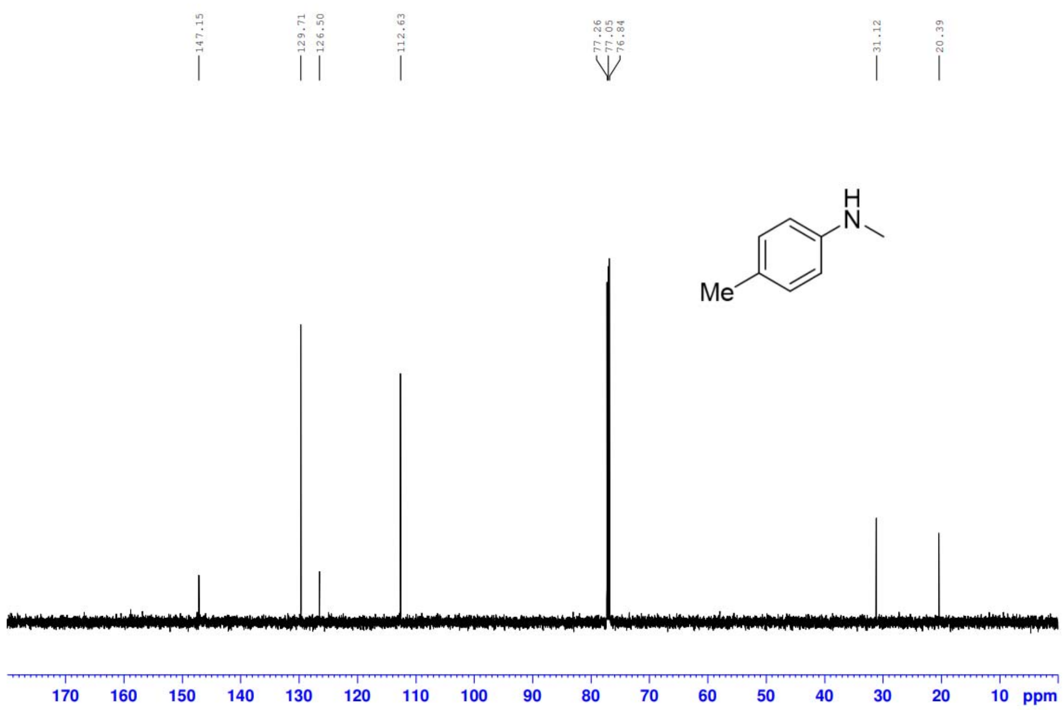


Fig. S27 ^{1}H NMR (600 MHz, $CDCl_3$) of **2i'**

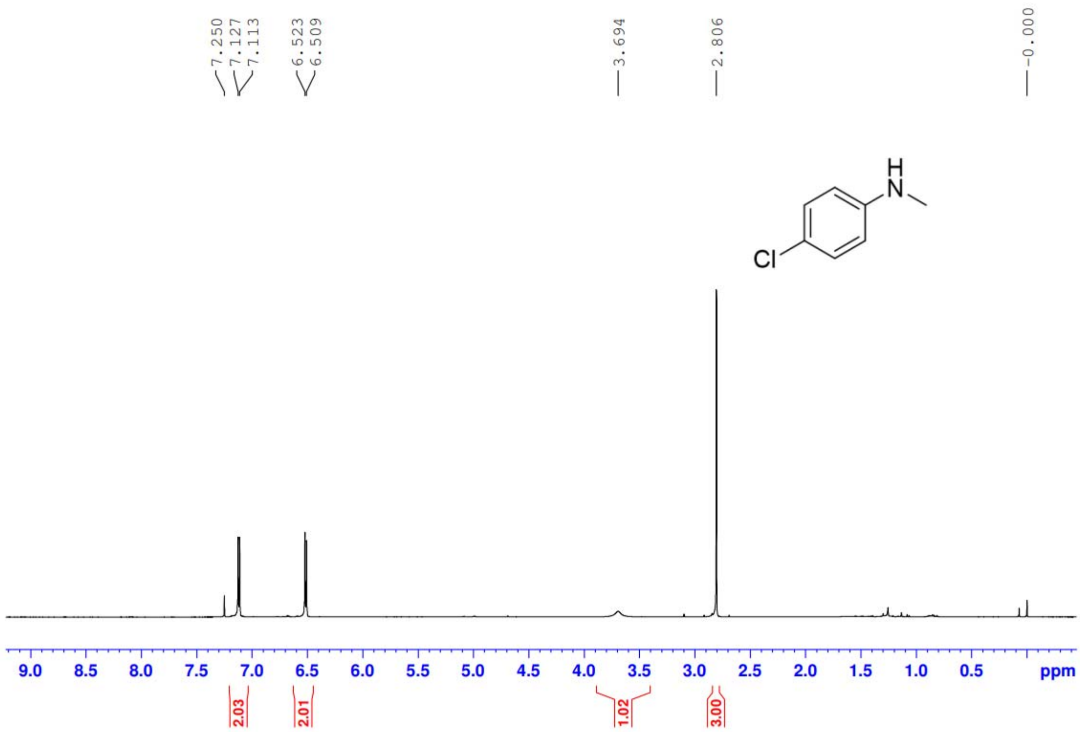


Fig. S28 $^{13}C\{^{1}H\}$ NMR (151 MHz, CDCl3) of **2i'**

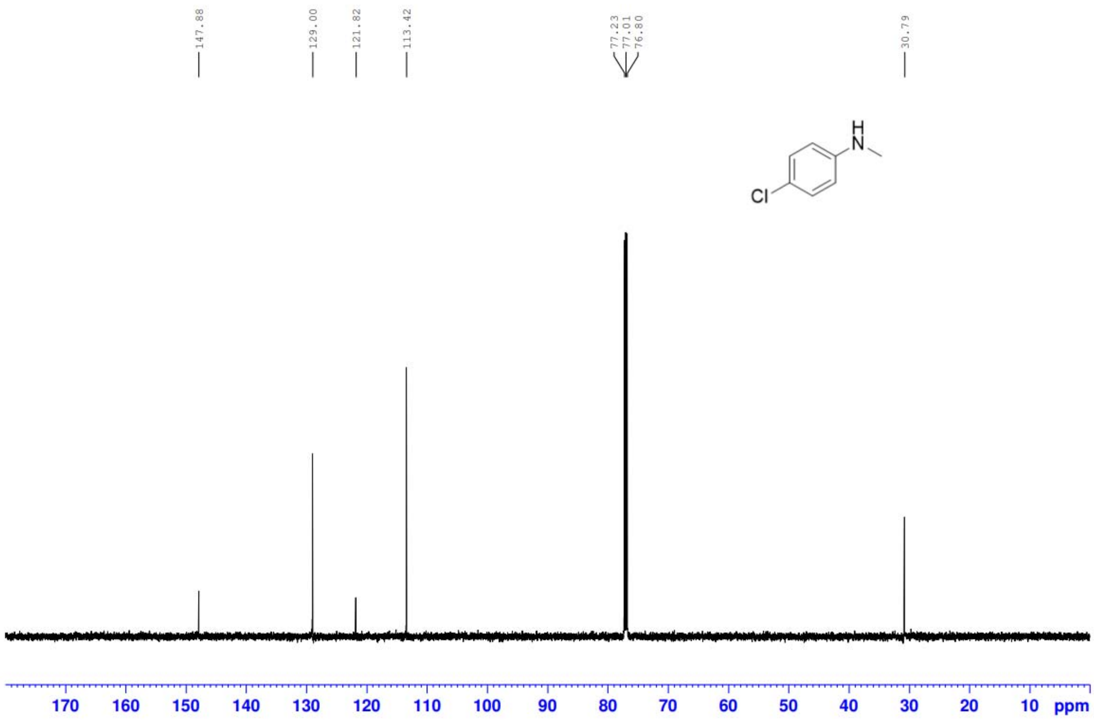


Fig. S29 ^{1}H NMR (600 MHz, $CDCl_3$) of **2l’**

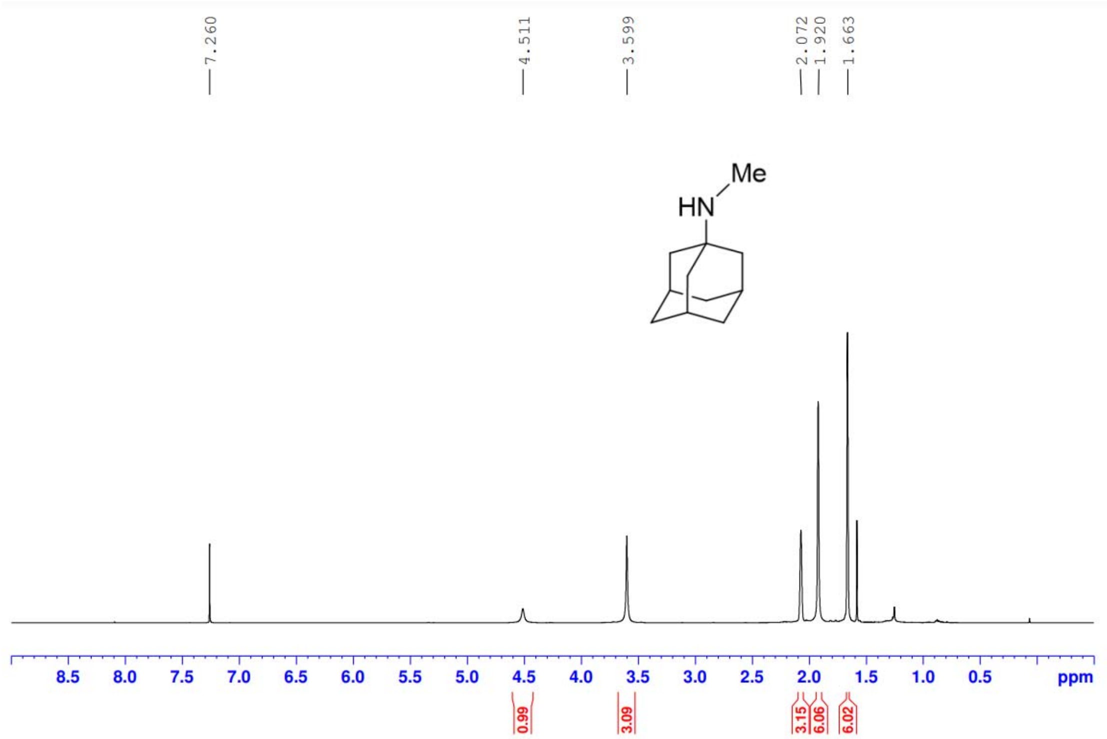


Fig. S30 $^{13}C\{^{1}H\}$ NMR (151 MHz, CDCl3) of **2l’**

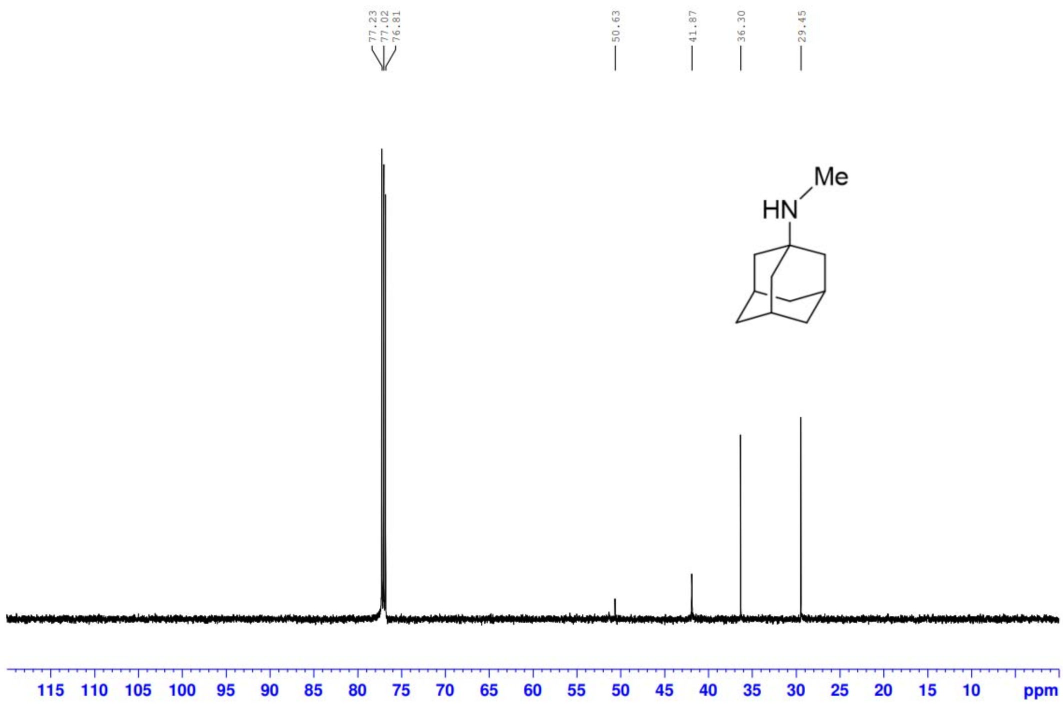


Fig. S31 ^{1}H NMR (600 MHz, $CDCl_3$) of **3a**

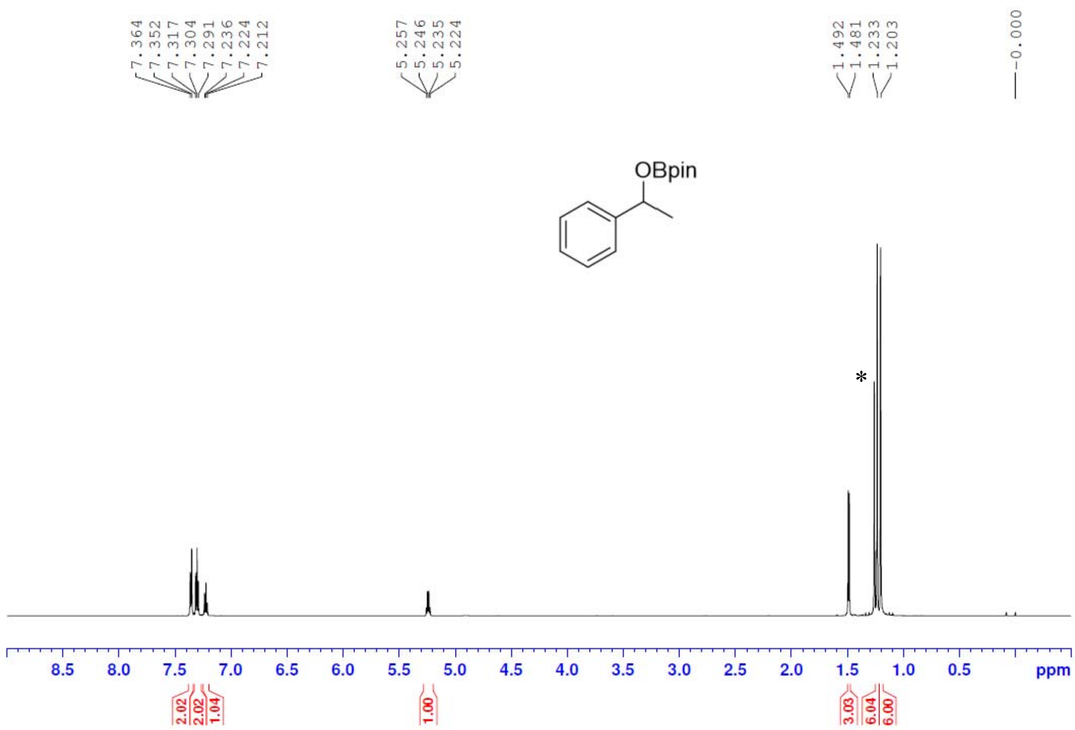


Fig. S32 ^{11}B NMR (128 MHz, $CDCl_3$) of **3a**

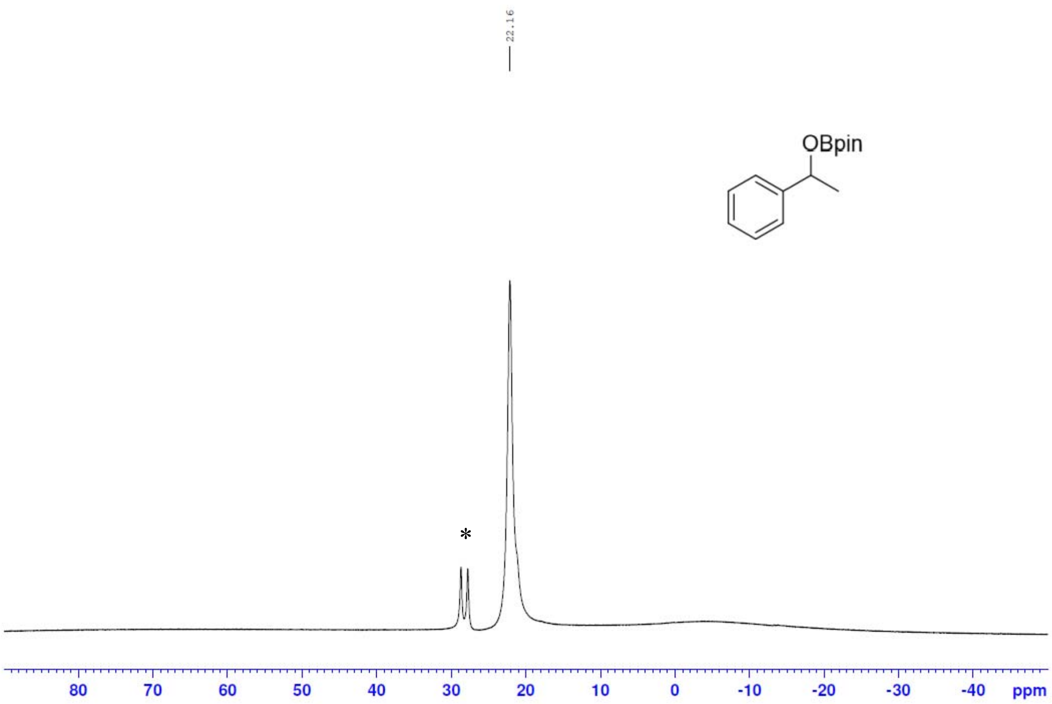


Fig. S33 ^{1}H NMR (600 MHz, $CDCl_3$) of **3b**

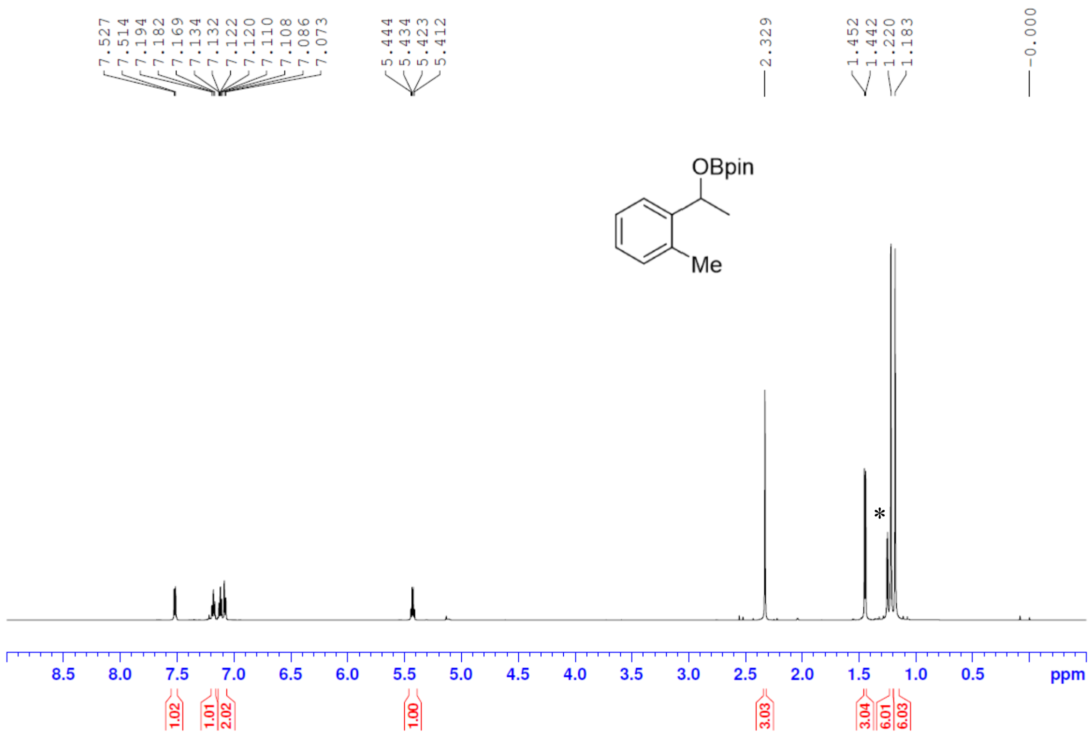


Fig. S34 ^{11}B NMR (193 MHz, $CDCl_3$) of **3b**

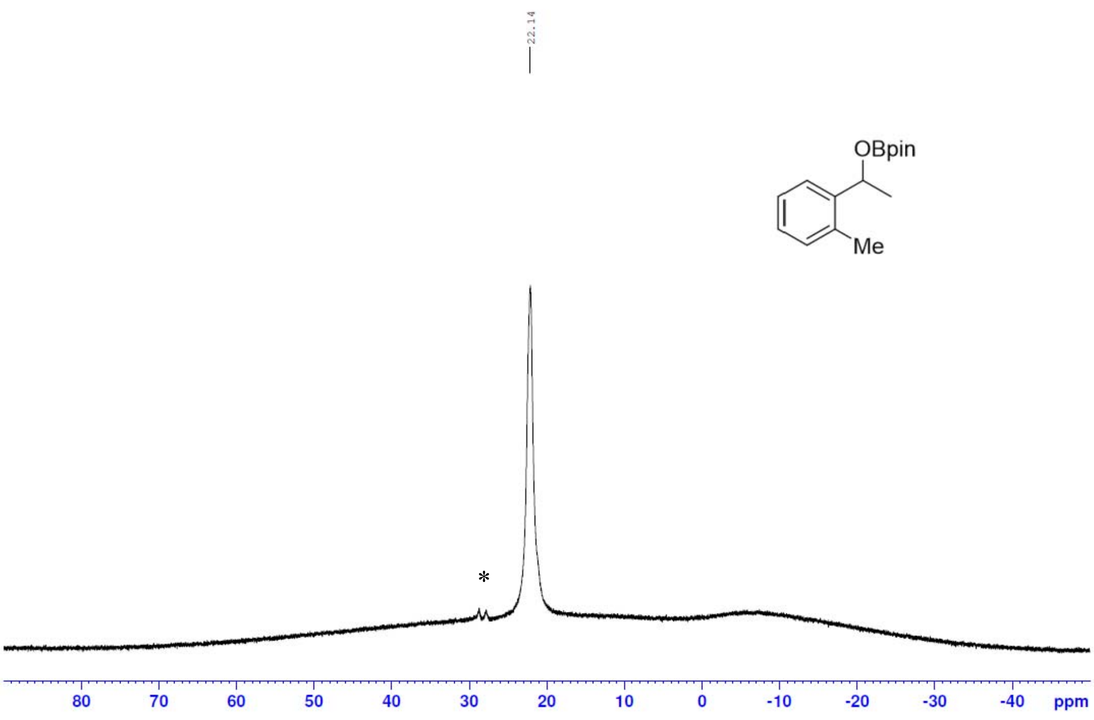


Fig. S35 ^{1}H NMR (600 MHz, $CDCl_3$) of **3c**

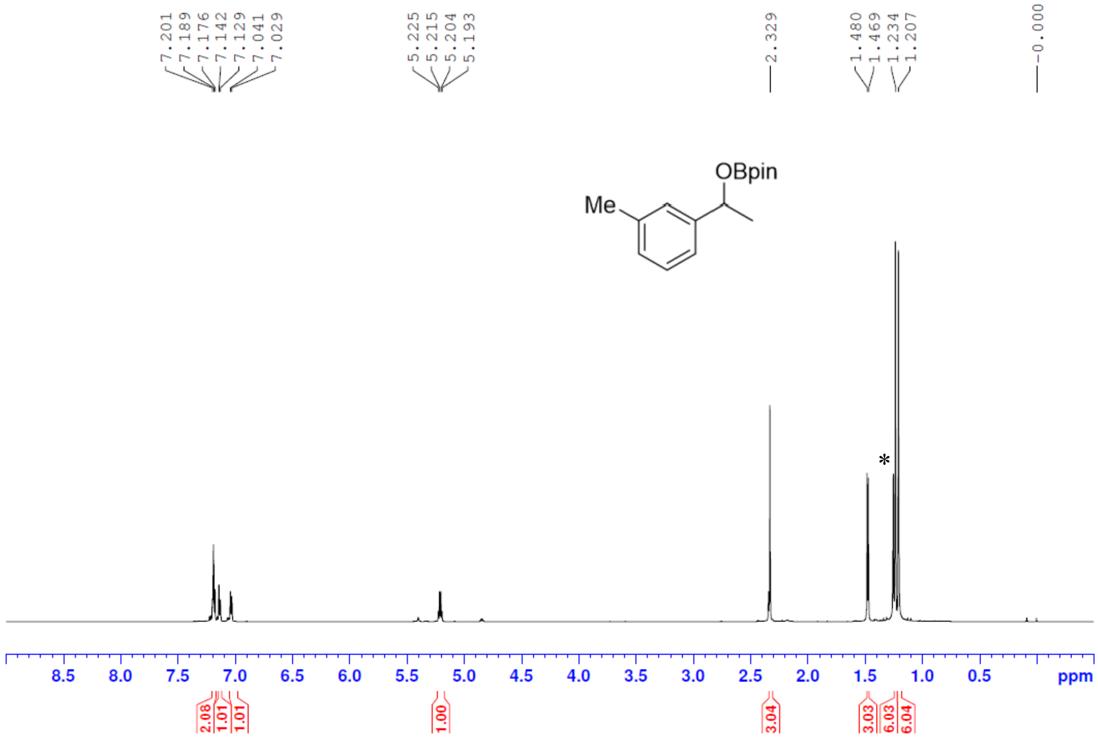


Fig. S36 ^{11}B NMR (128 MHz, $CDCl_3$) of **3c**

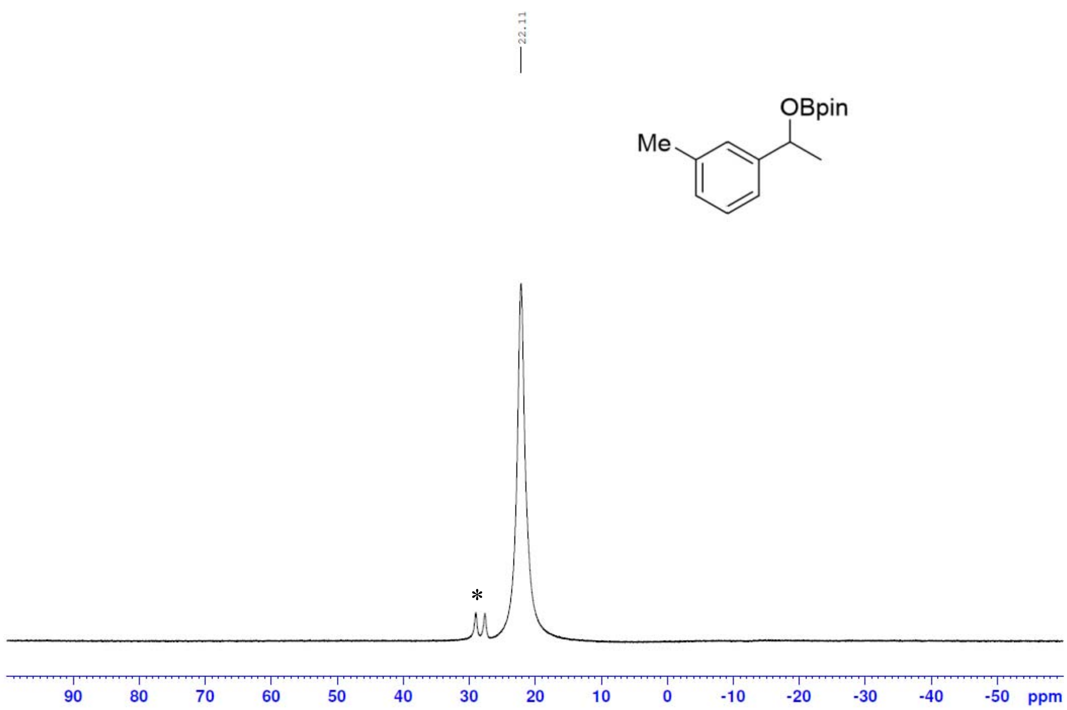


Fig. S37 ^{1}H NMR (600 MHz, $CDCl_3$) of **3d**

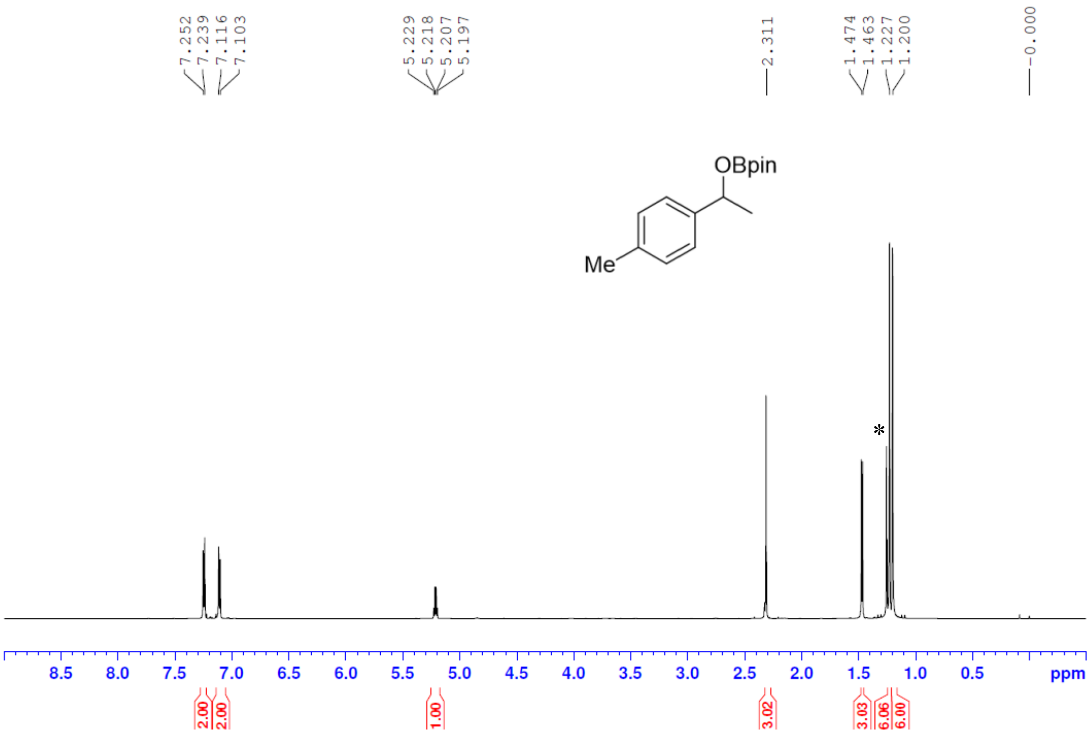


Fig. S38 ^{11}B NMR (128 MHz, $CDCl_3$) of **3d**

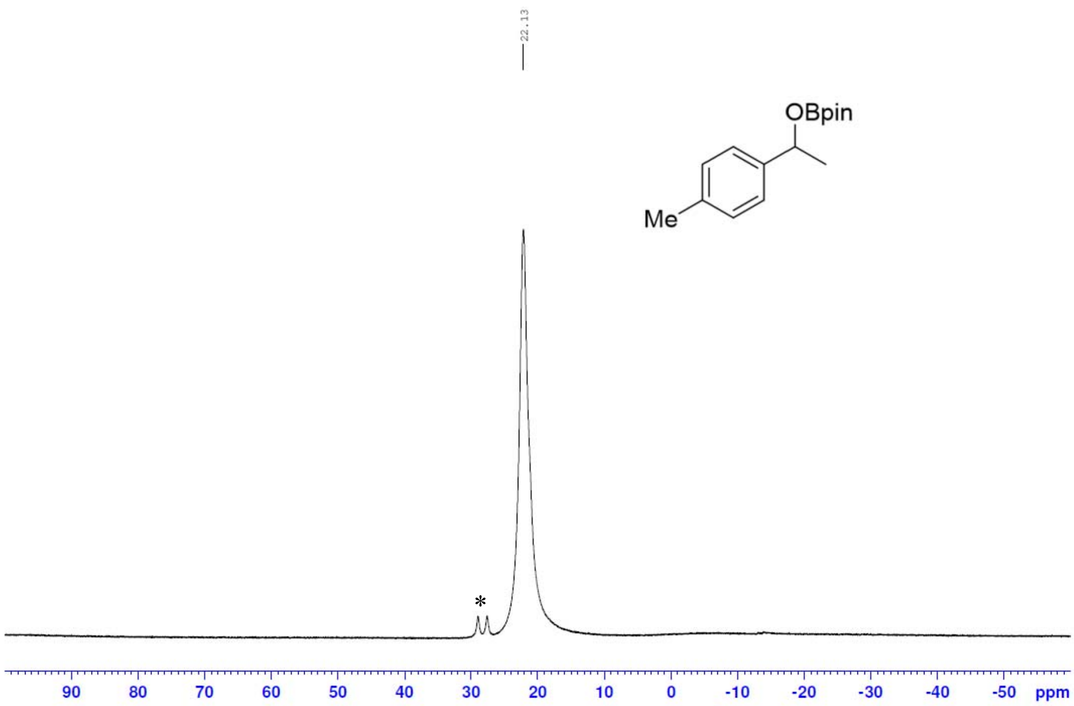


Fig. S39 ^{1}H NMR (600 MHz, $CDCl_3$) of **3e**

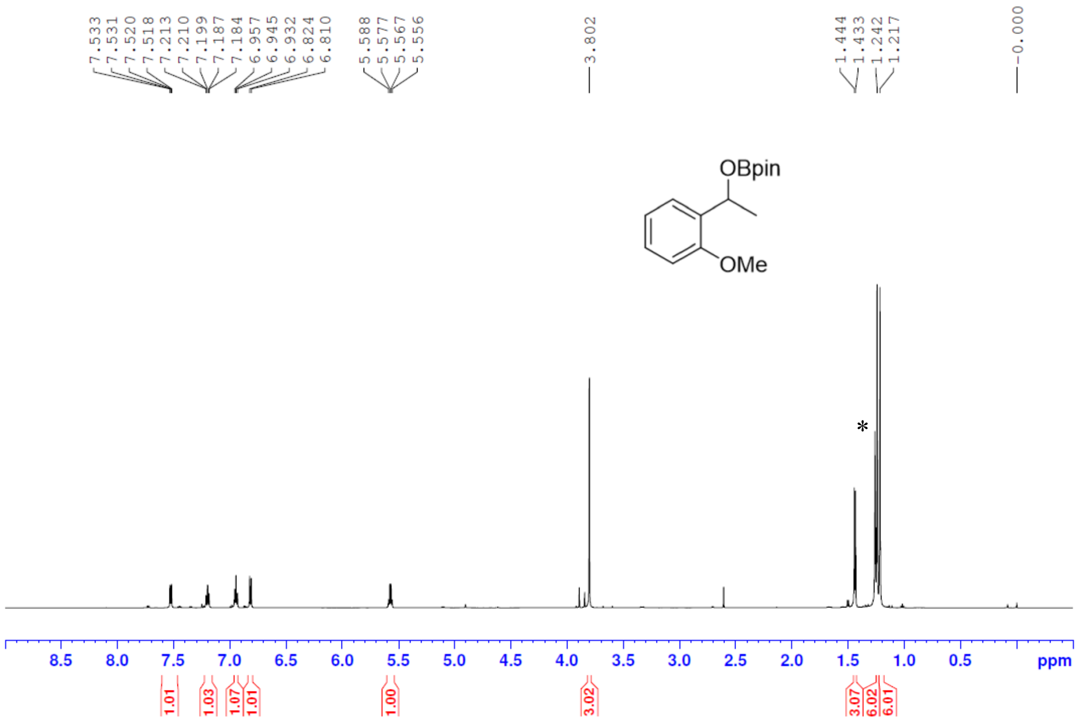


Fig. S40 ^{11}B NMR (193 MHz, $CDCl_3$) of **3e**

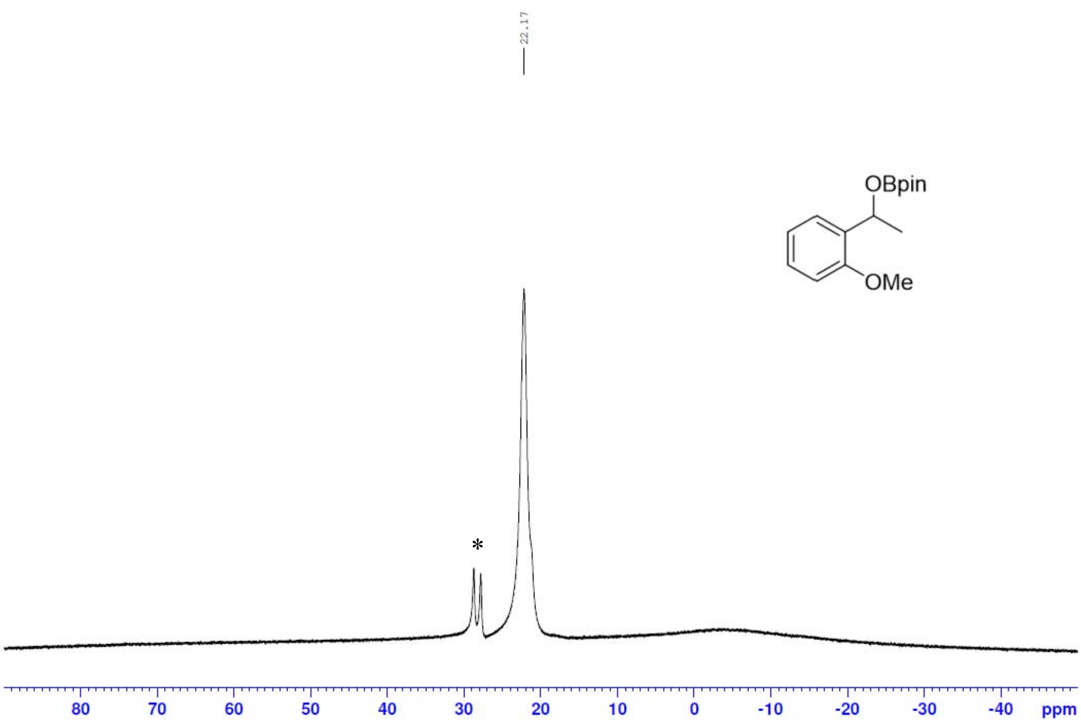


Fig. S41 ^{1}H NMR (600 MHz, $CDCl_3$) of **3f**

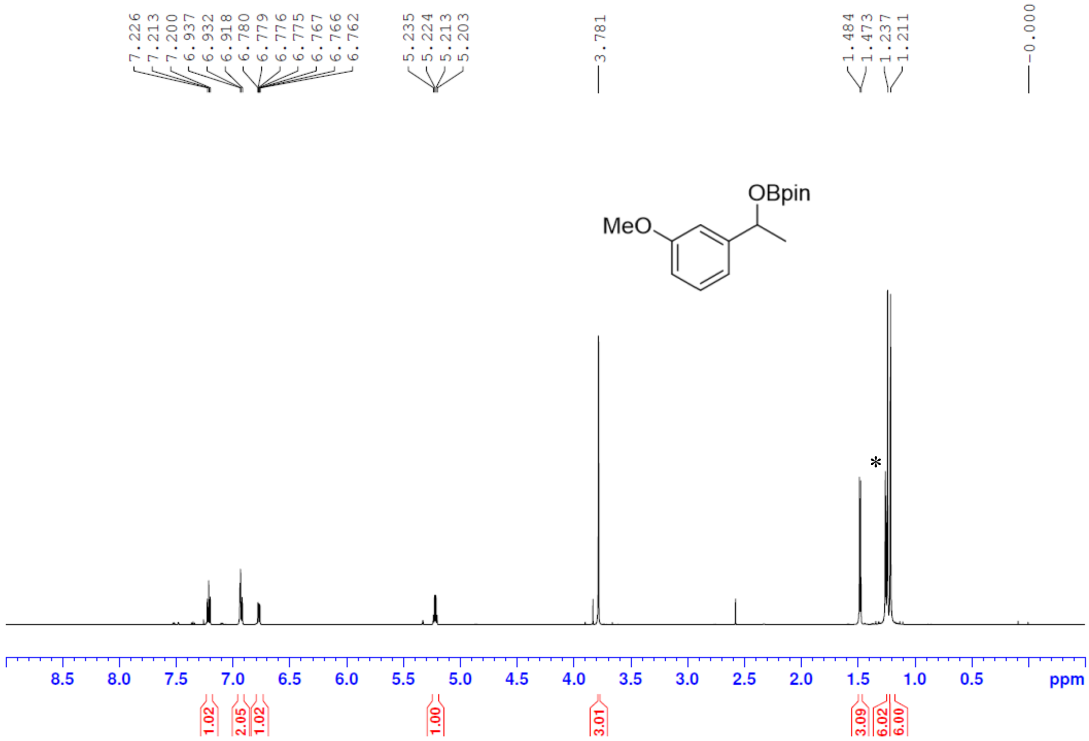


Fig. S42 ^{11}B NMR (128 MHz, $CDCl_3$) of **3f**

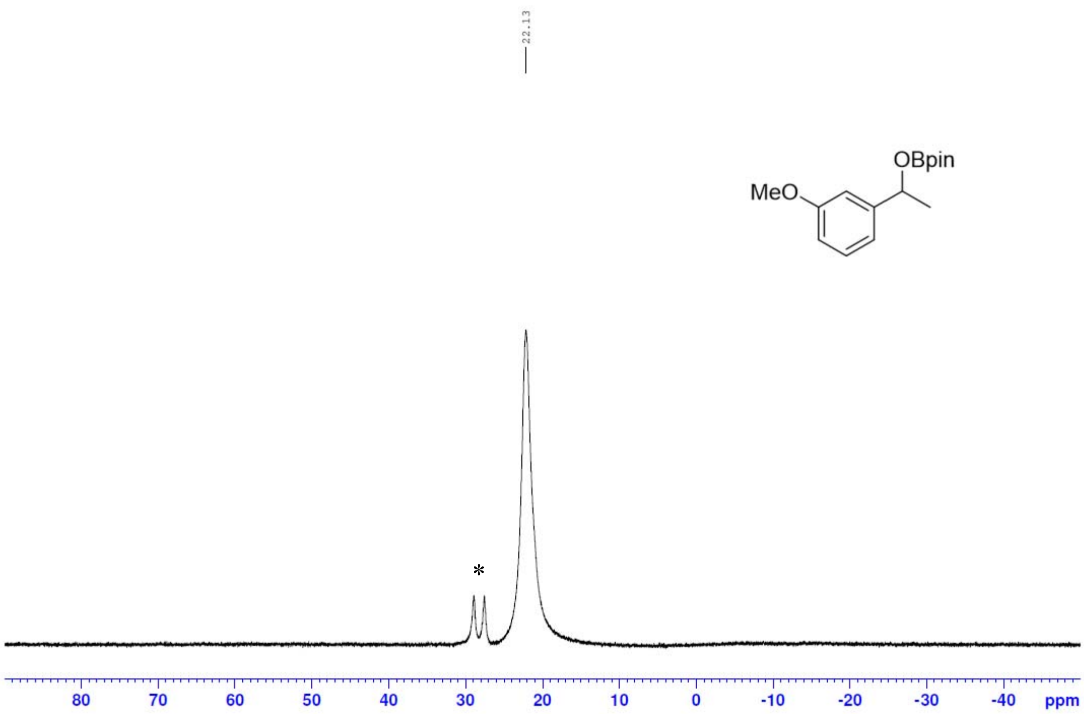


Fig. S43 ^{1}H NMR (600 MHz, $CDCl_3$) of **3g**

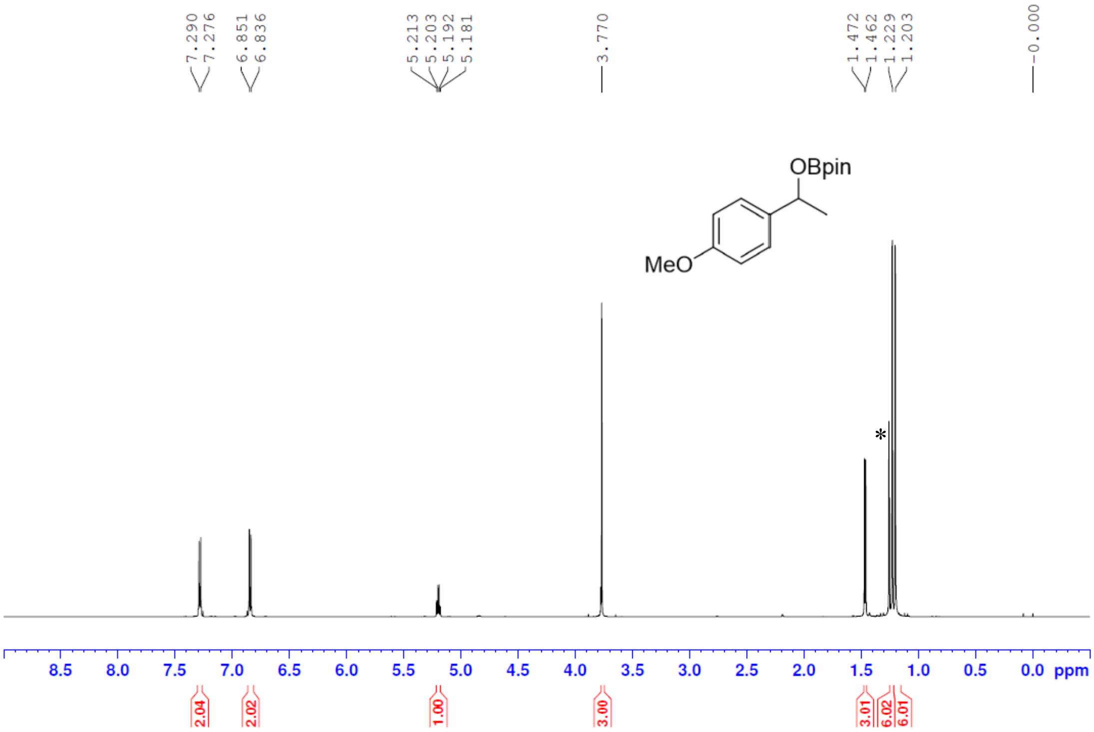


Fig. S44 ^{11}B NMR (128 MHz, $CDCl_3$) of **3g**

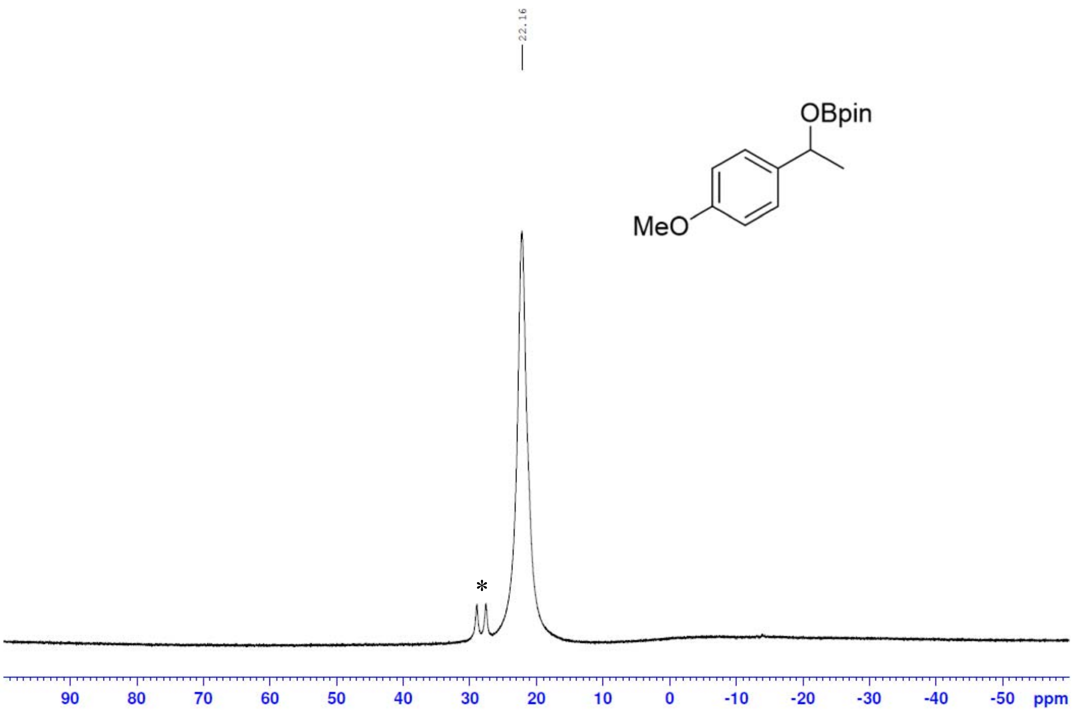


Fig. S45 ^{1}H NMR (400 MHz, $CDCl_3$) of **3h**

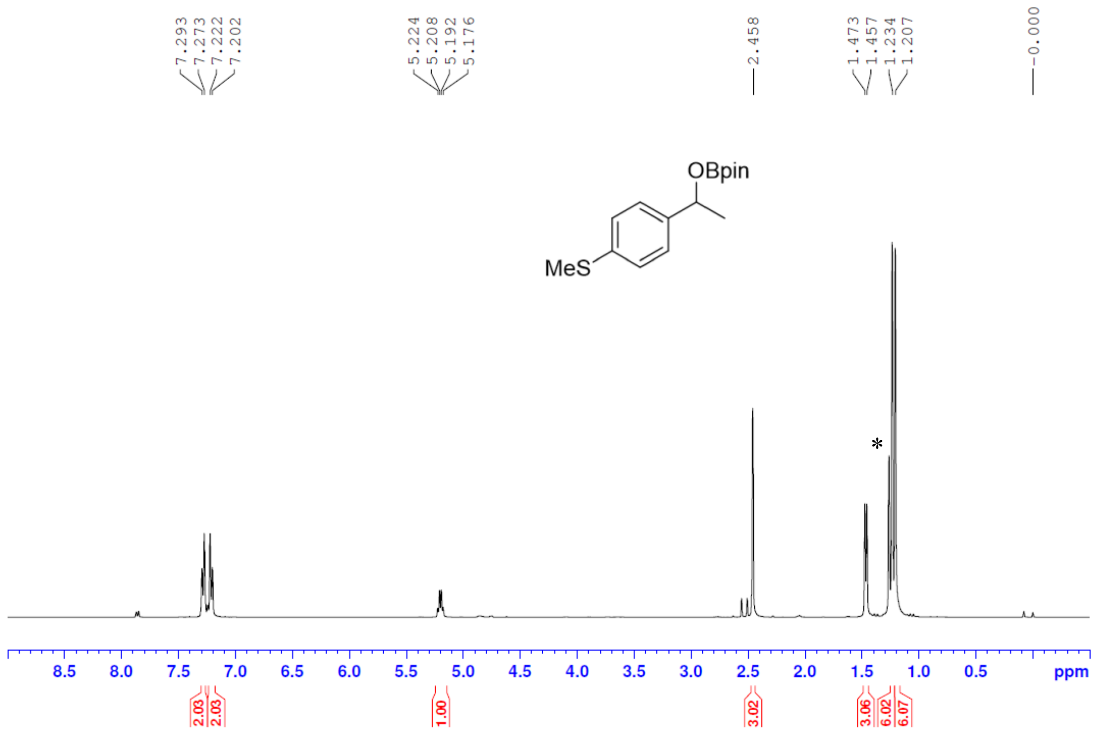


Fig. S46 ^{11}B NMR (128 MHz, $CDCl_3$) of **3h**

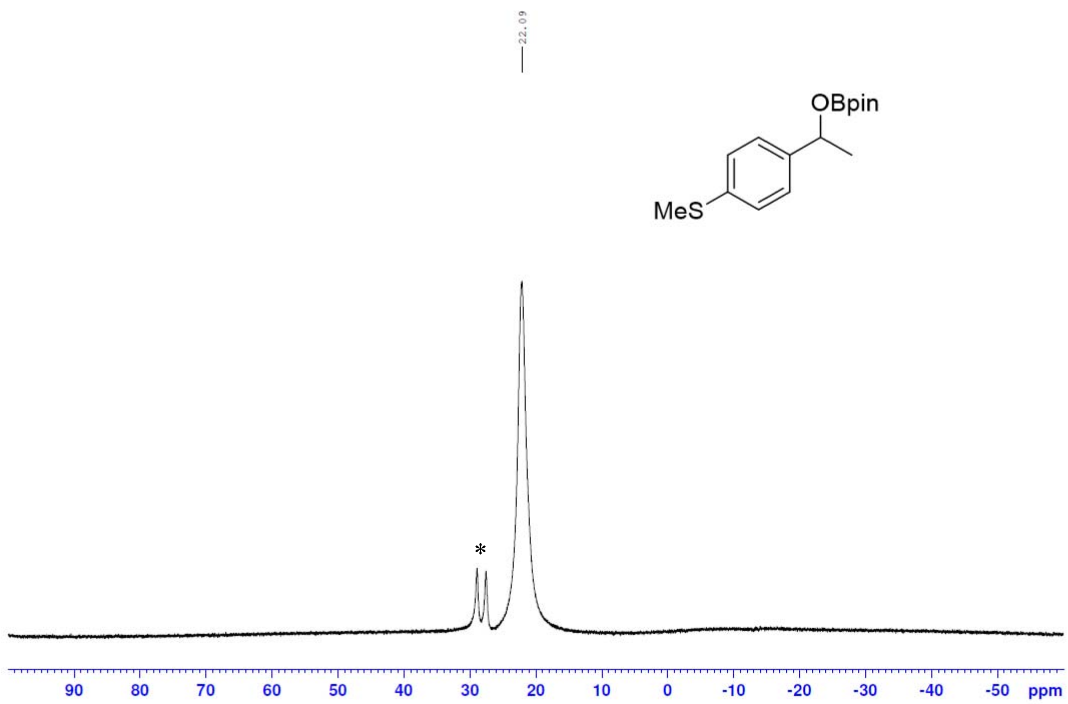


Fig. S47 ^{1}H NMR (600 MHz, $CDCl_3$) of **3i**

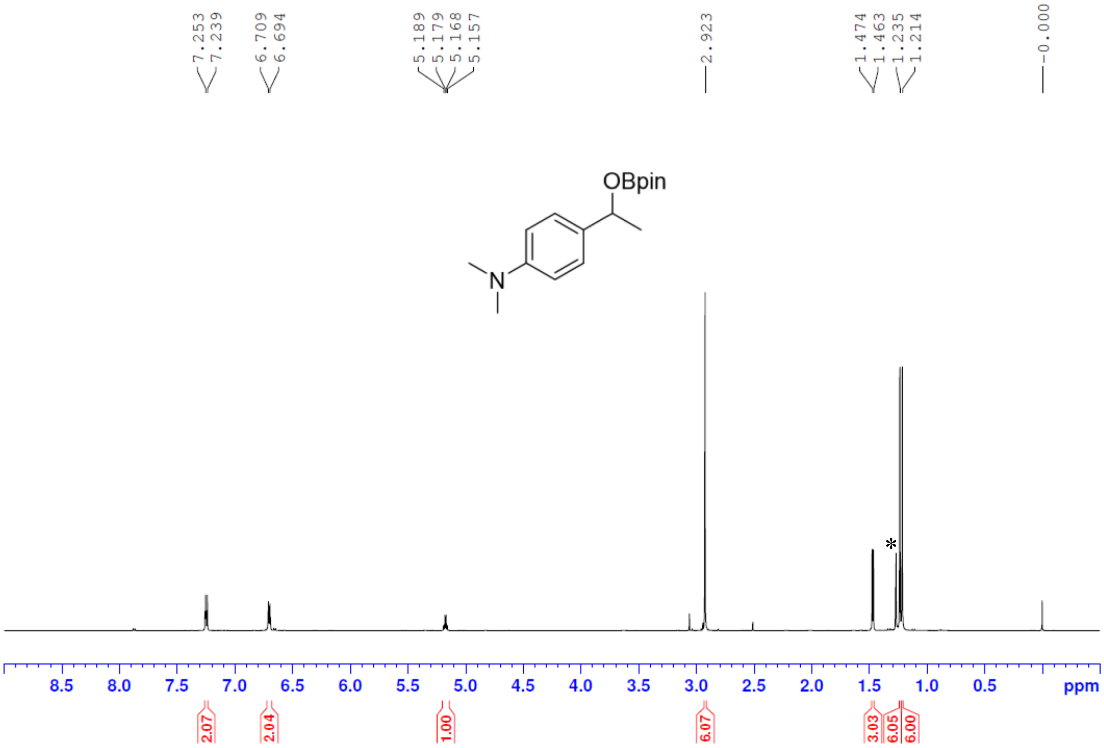


Fig. S48 ^{11}B NMR (193 MHz, $CDCl_3$) of **3i**

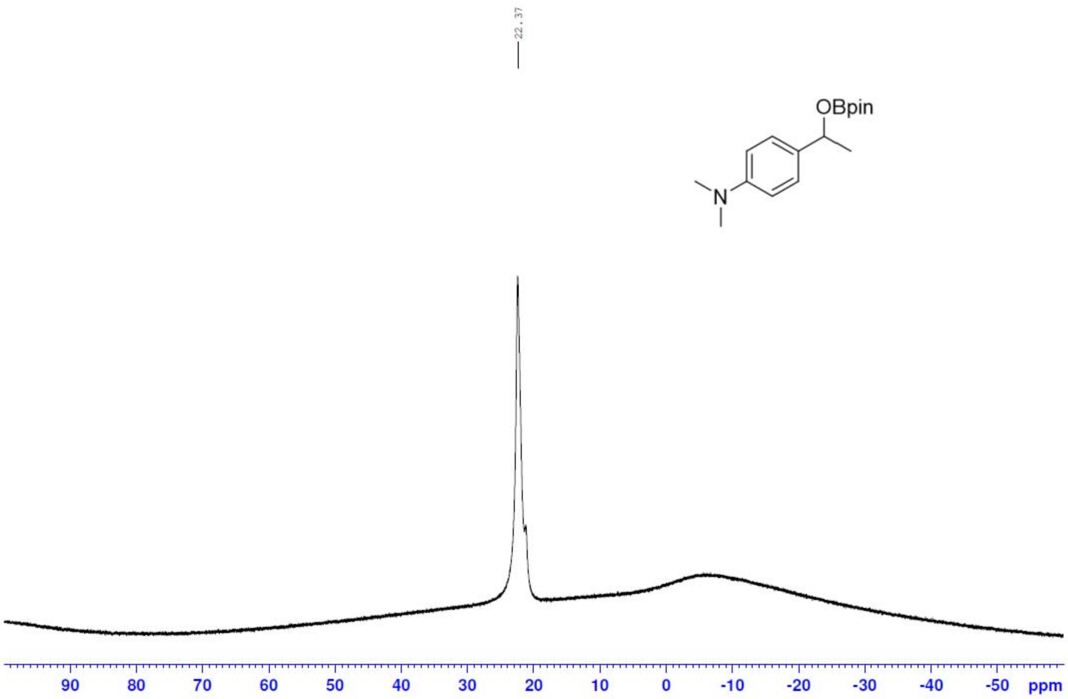


Fig. S49 ^{1}H NMR (600 MHz, $CDCl_3$) of **3j**

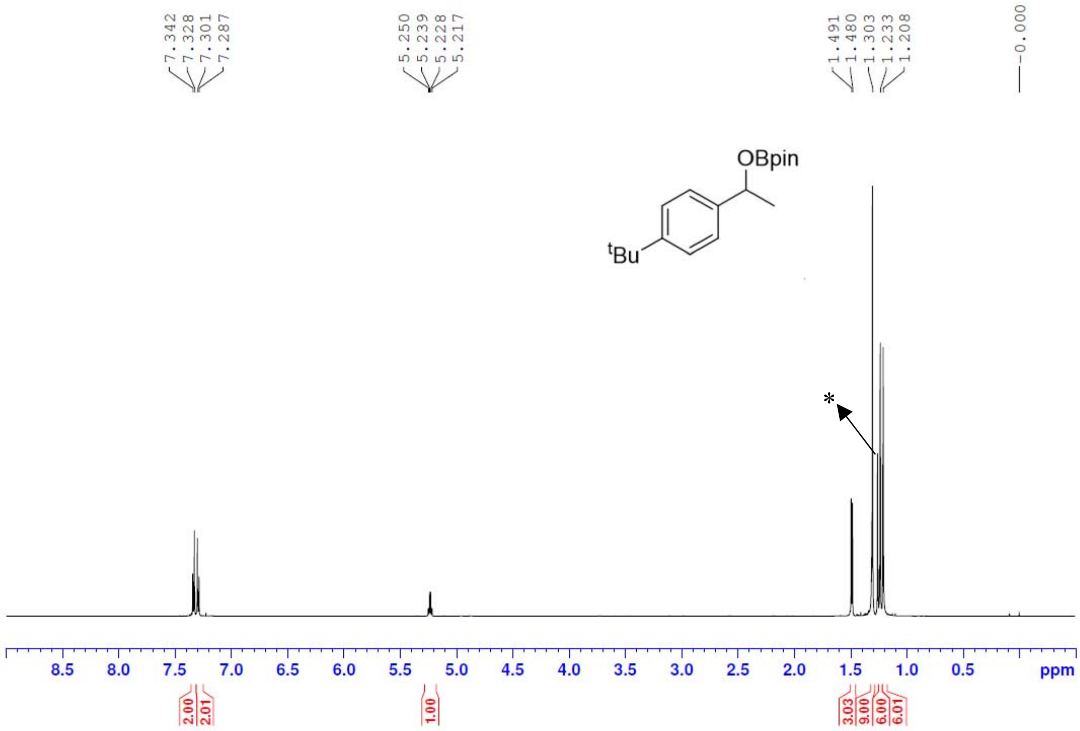


Fig. S50 ^{11}B NMR (128 MHz, $CDCl_3$) of **3j**

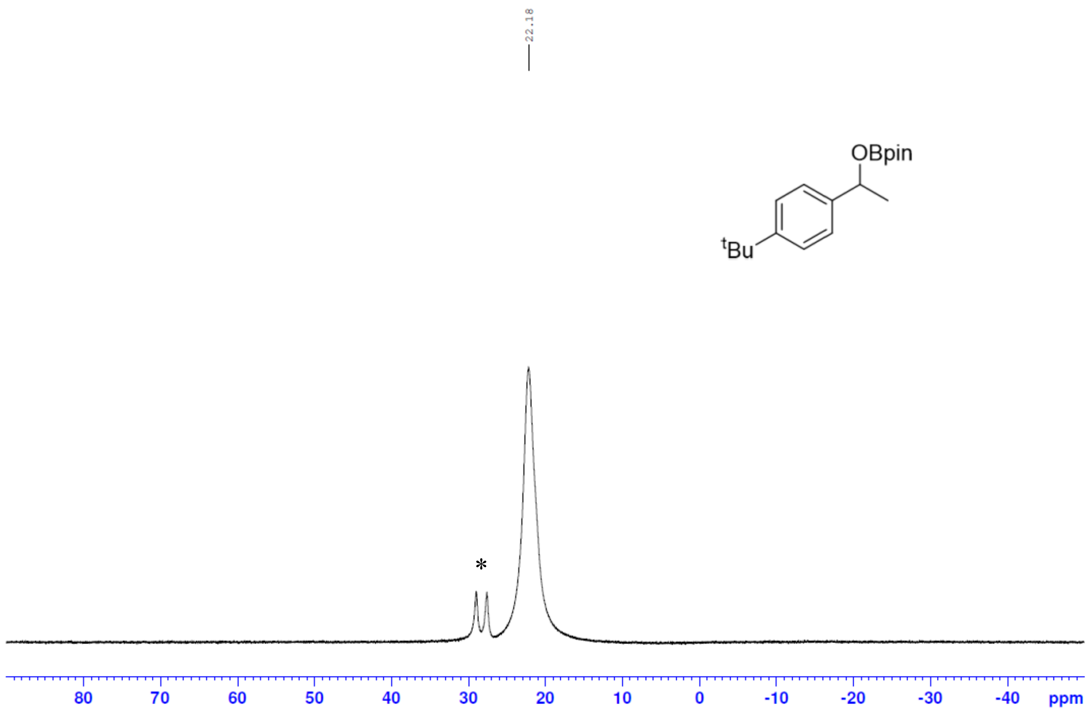


Fig. S51 ^{1}H NMR (600 MHz, $CDCl_3$) of **3k**

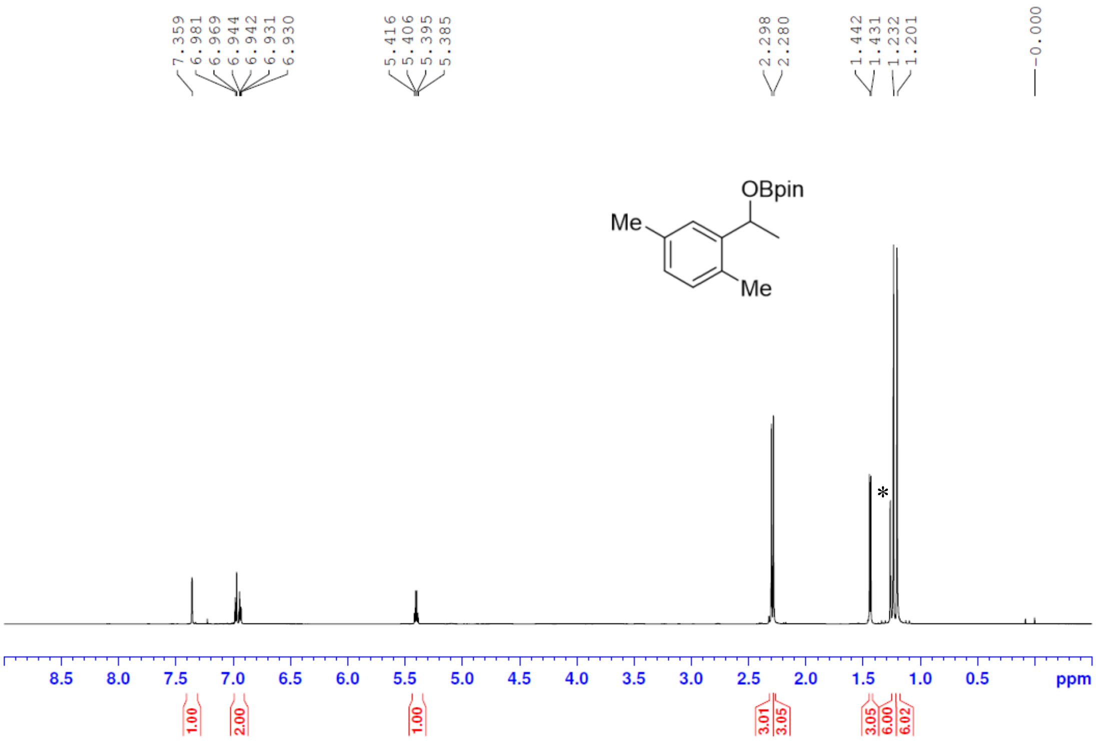


Fig. S52 ^{11}B NMR (128 MHz, $CDCl_3$) of **3k**

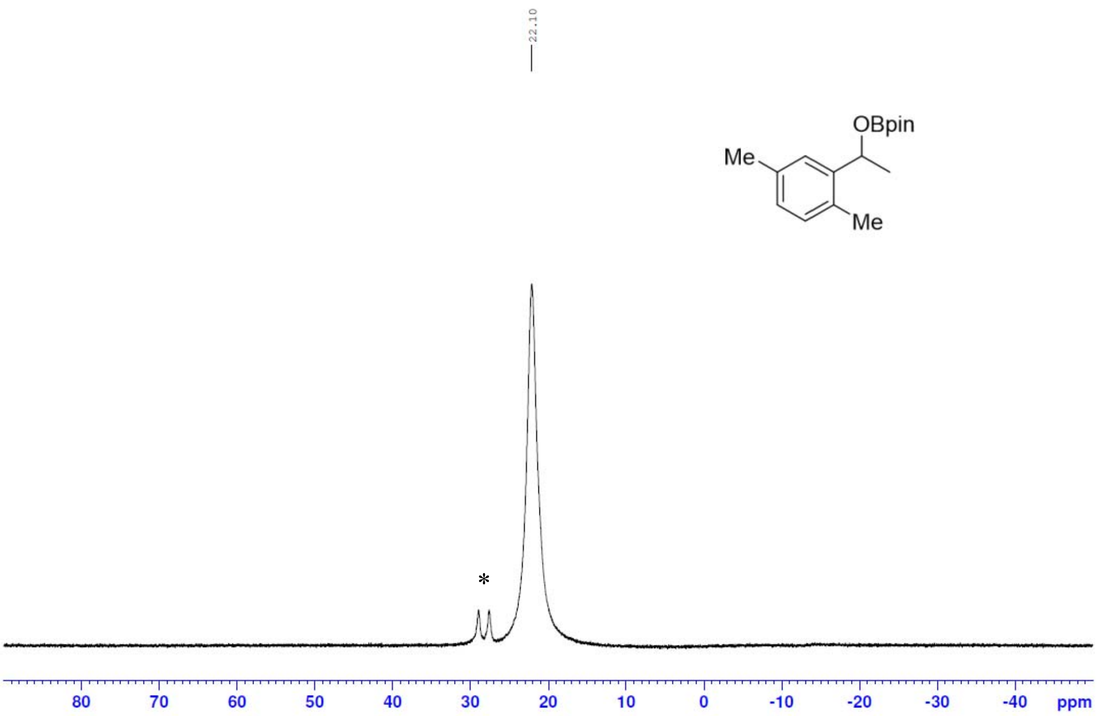


Fig. S53 ^{1}H NMR (600 MHz, $CDCl_3$) of **3l**

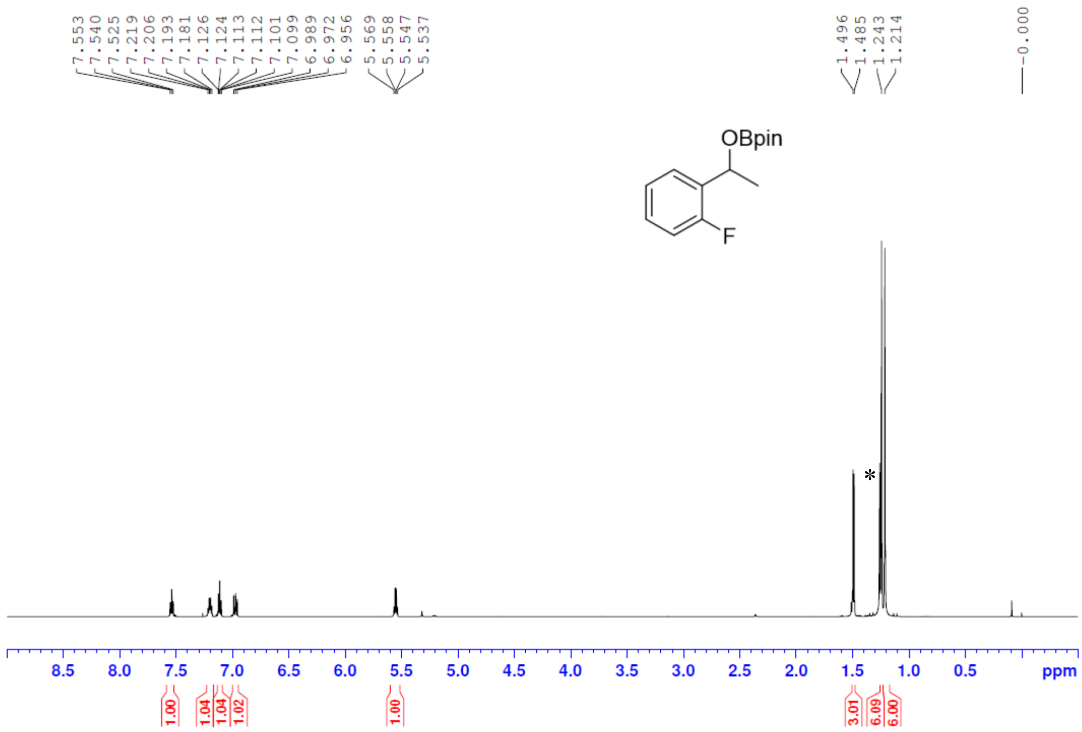


Fig. S54 ^{11}B NMR (128 MHz, $CDCl_3$) of **3l**

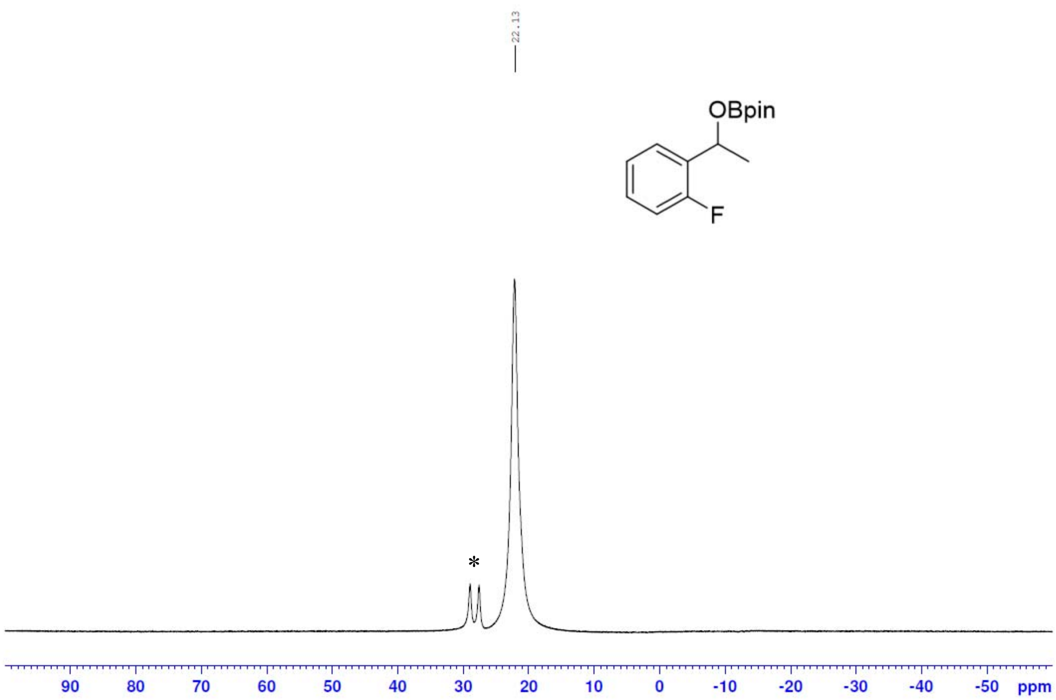


Fig. S55 ^{19}F NMR (565 MHz, $CDCl_3$) of **3l**

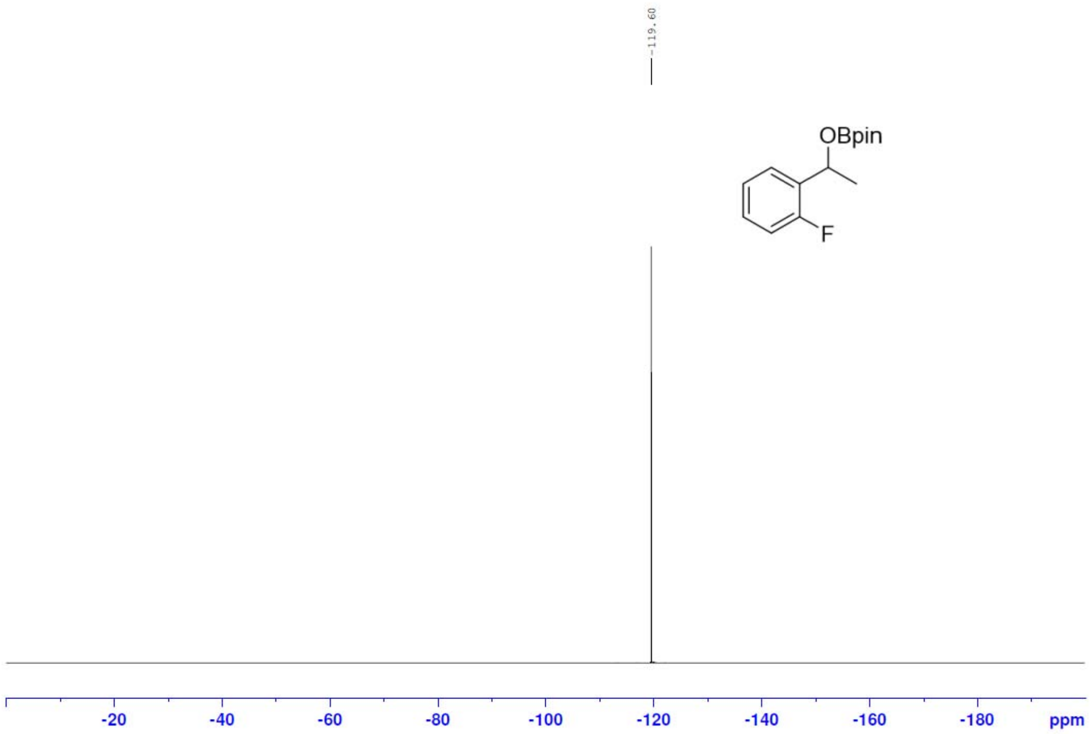


Fig. S56 ^{1}H NMR (600 MHz, $CDCl_3$) of **3m**

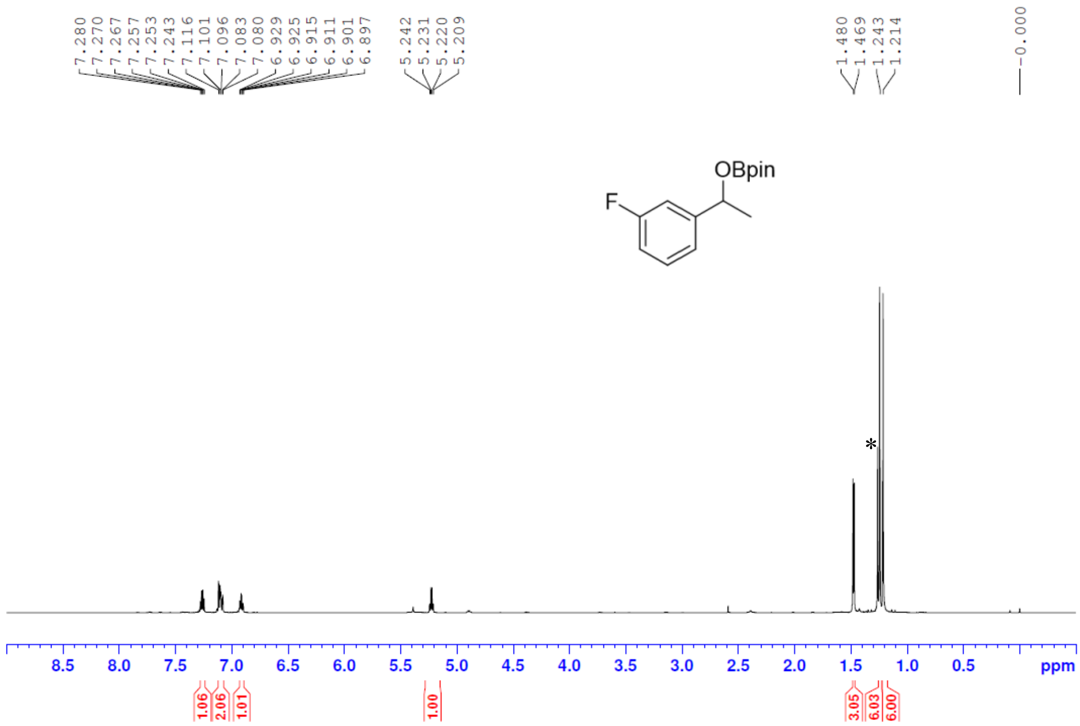


Fig. S57 ^{11}B NMR (128 MHz, $CDCl_3$) of **3m**

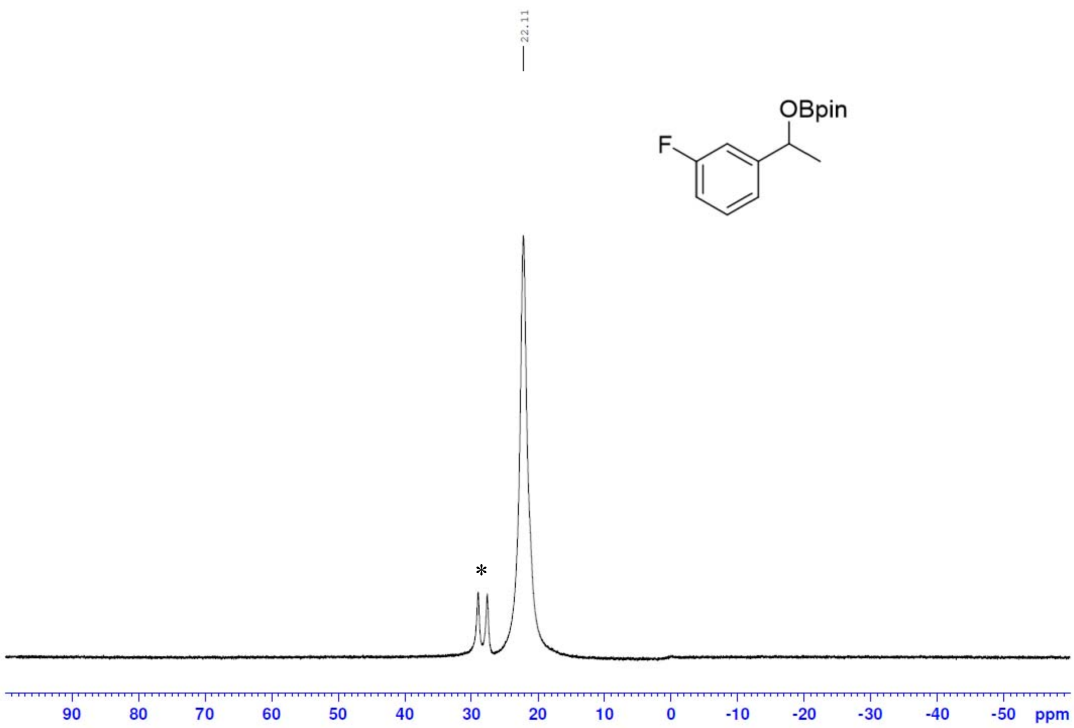


Fig. S58 ^{19}F NMR (565 MHz, $CDCl_3$) of **3m**

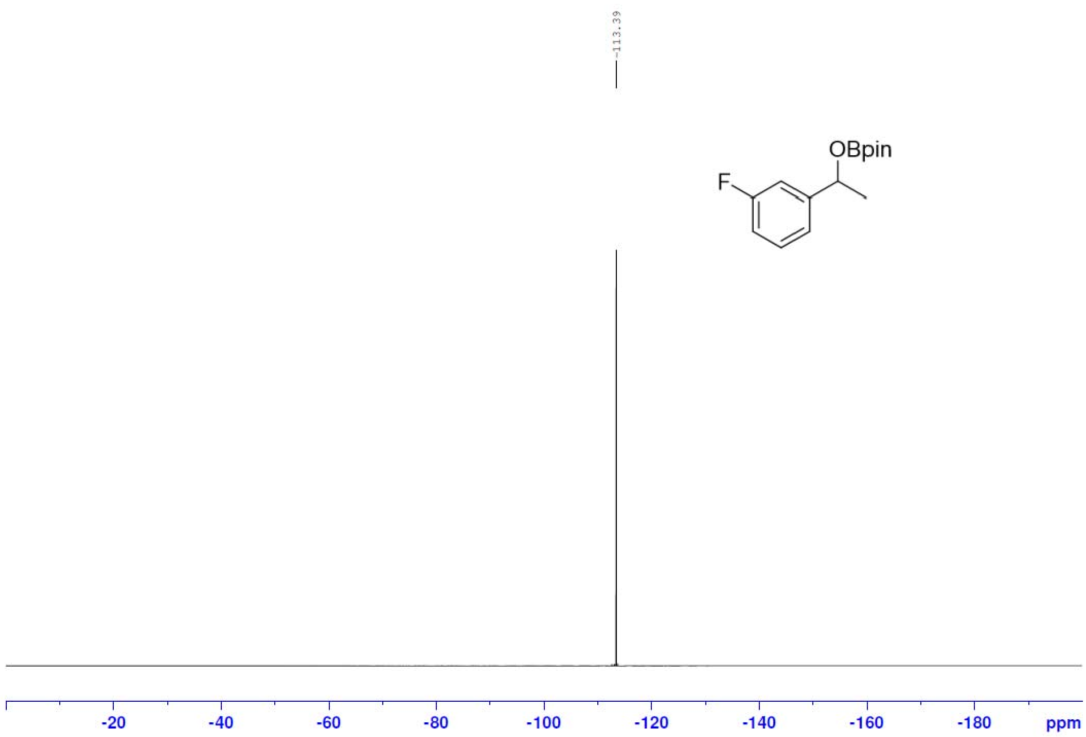


Fig. S59 ^{1}H NMR (600 MHz, $CDCl_3$) of **3n**

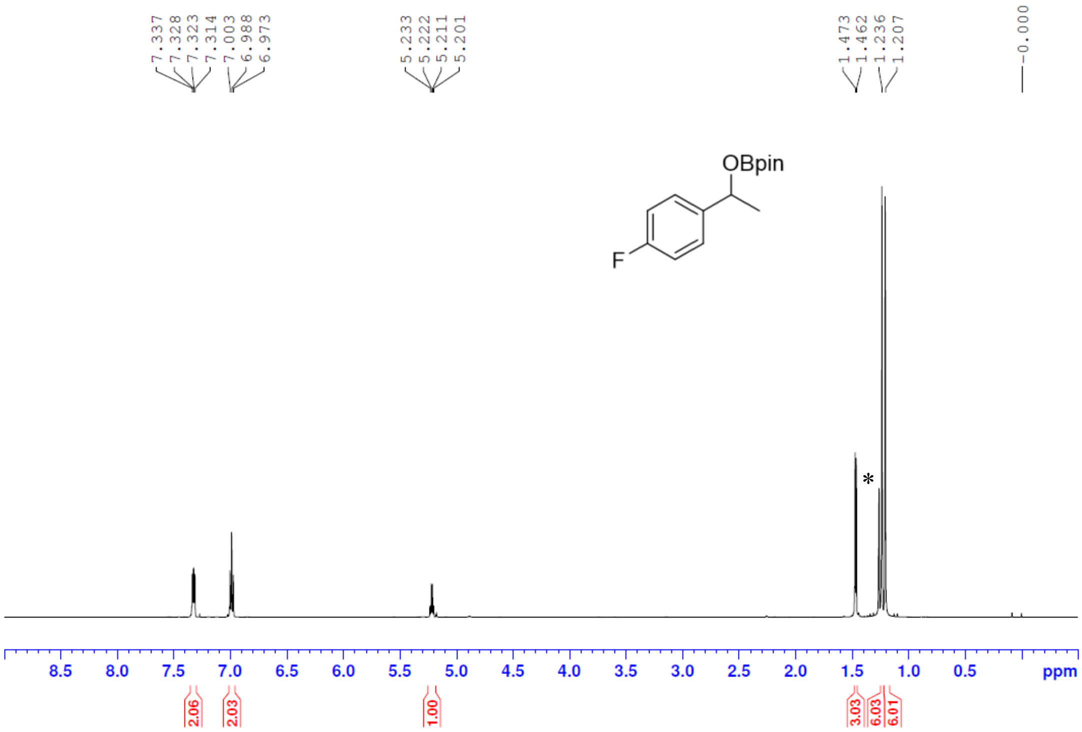


Fig. S60 ^{11}B NMR (193 MHz, $CDCl_3$) of **3n**

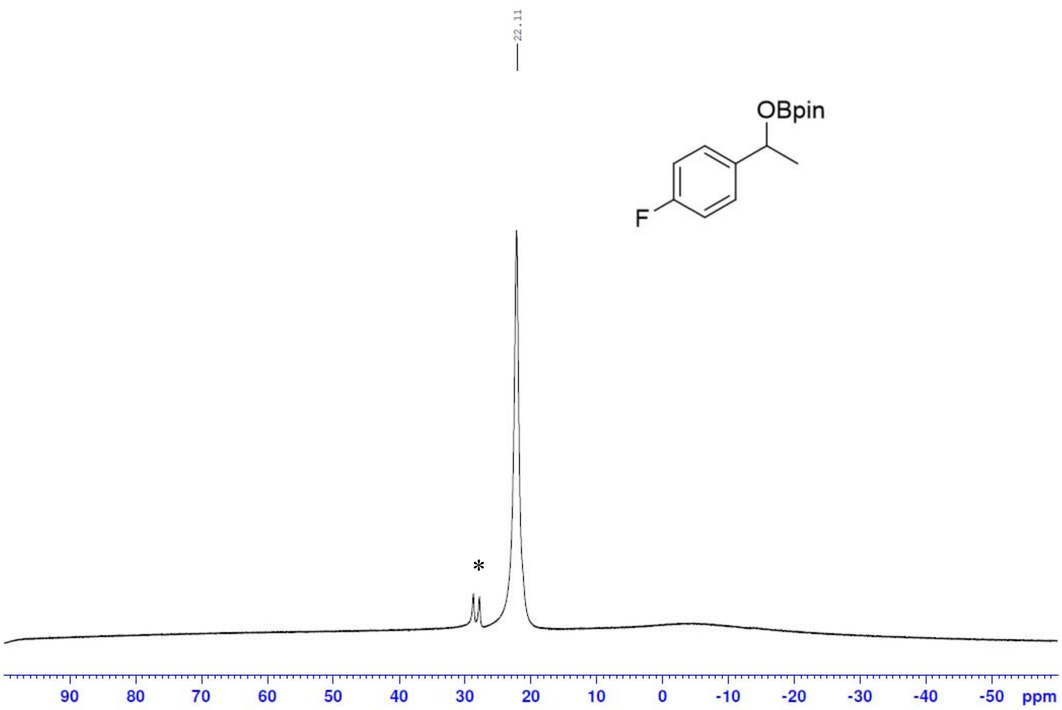


Fig. S61 ^{19}F NMR (565 MHz, $CDCl_3$) of **3n**

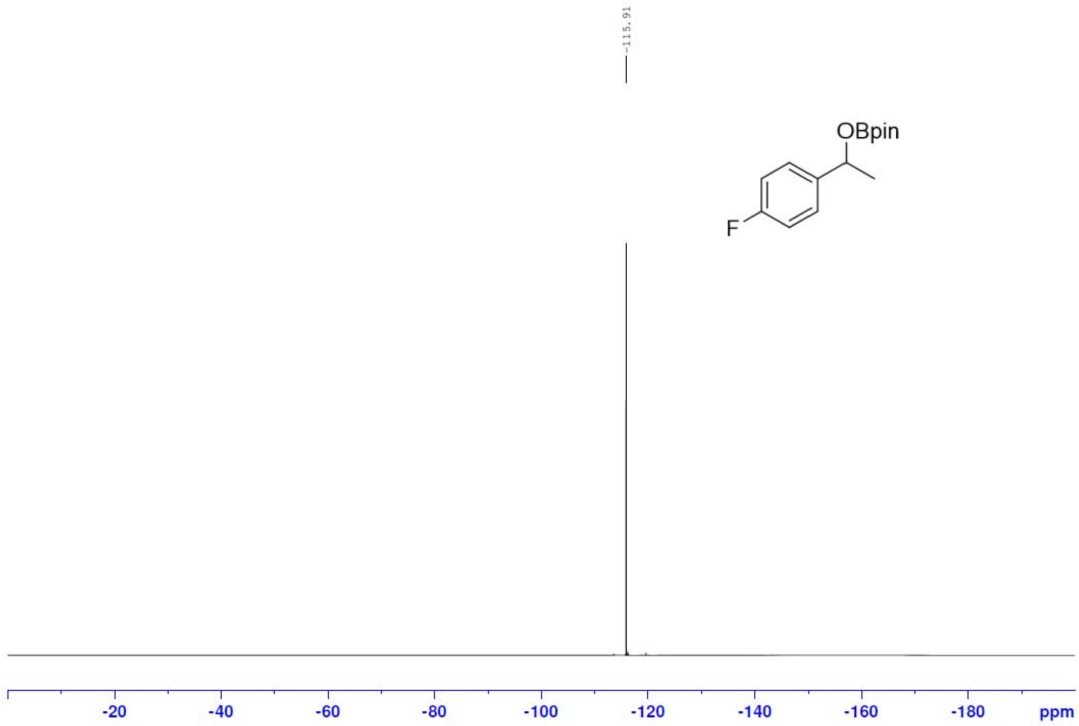


Fig. S62 ^{1}H NMR (600 MHz, $CDCl_3$) of **3o**

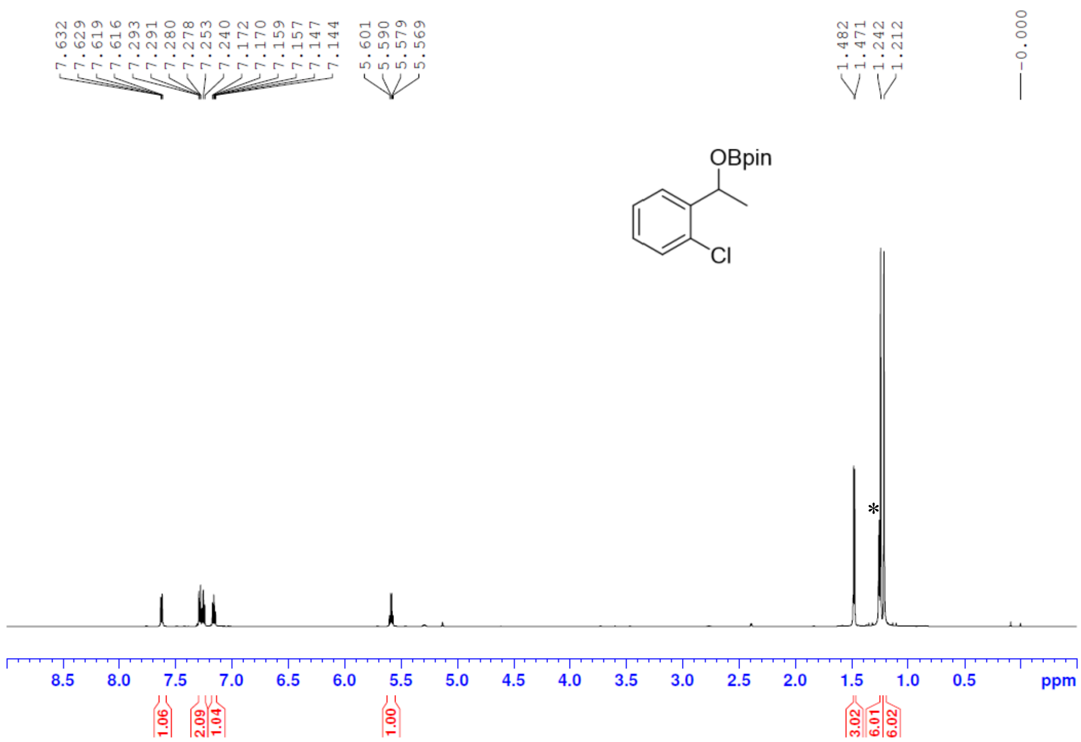


Fig. S63 ^{11}B NMR (128 MHz, $CDCl_3$) of **3o**

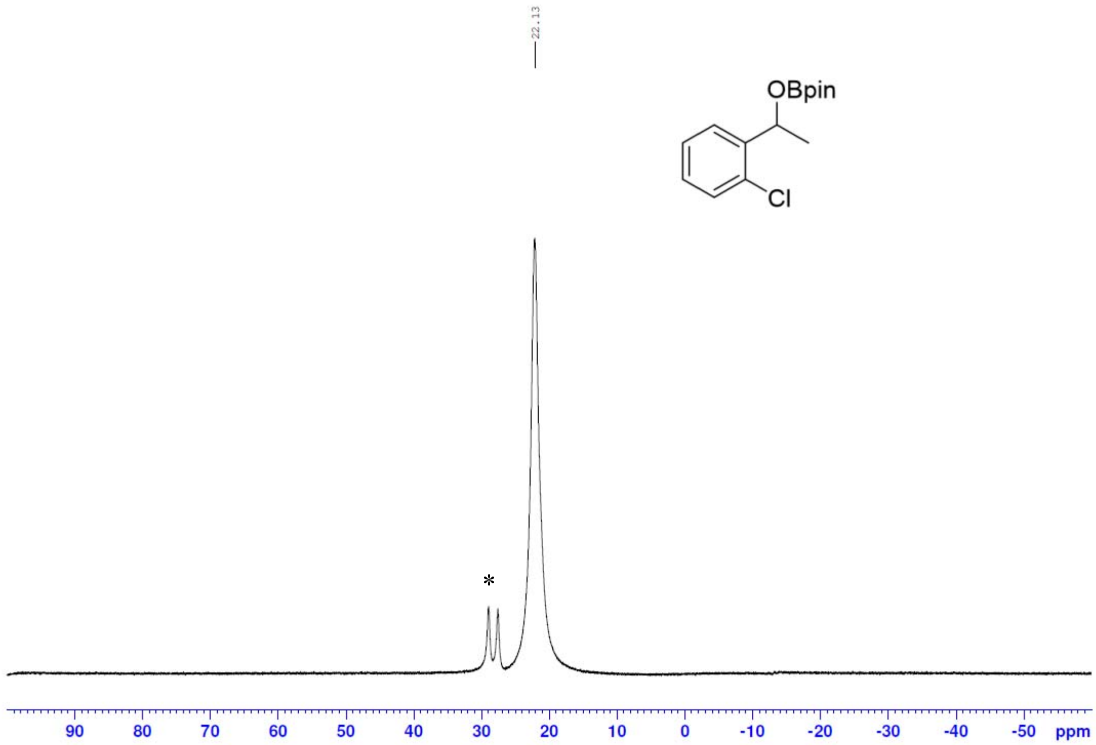


Fig. S64 ^{1}H NMR (600 MHz, $CDCl_3$) of **3p**

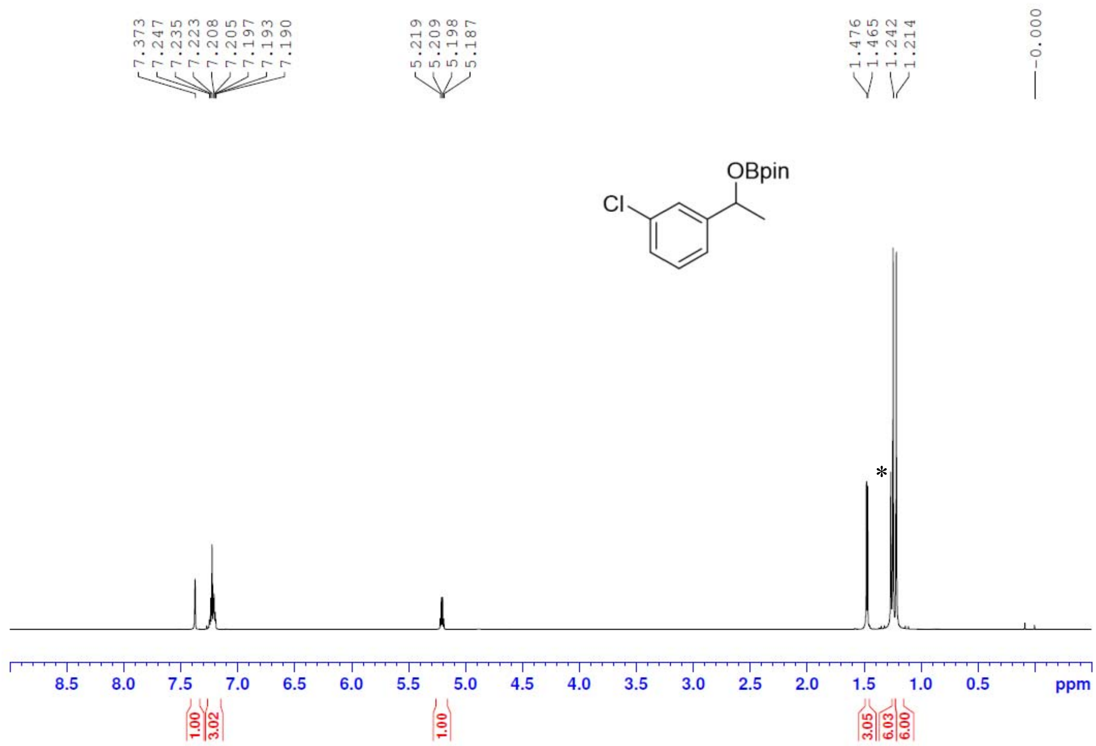


Fig. S65 ^{11}B NMR (128 MHz, $CDCl_3$) of **3p**

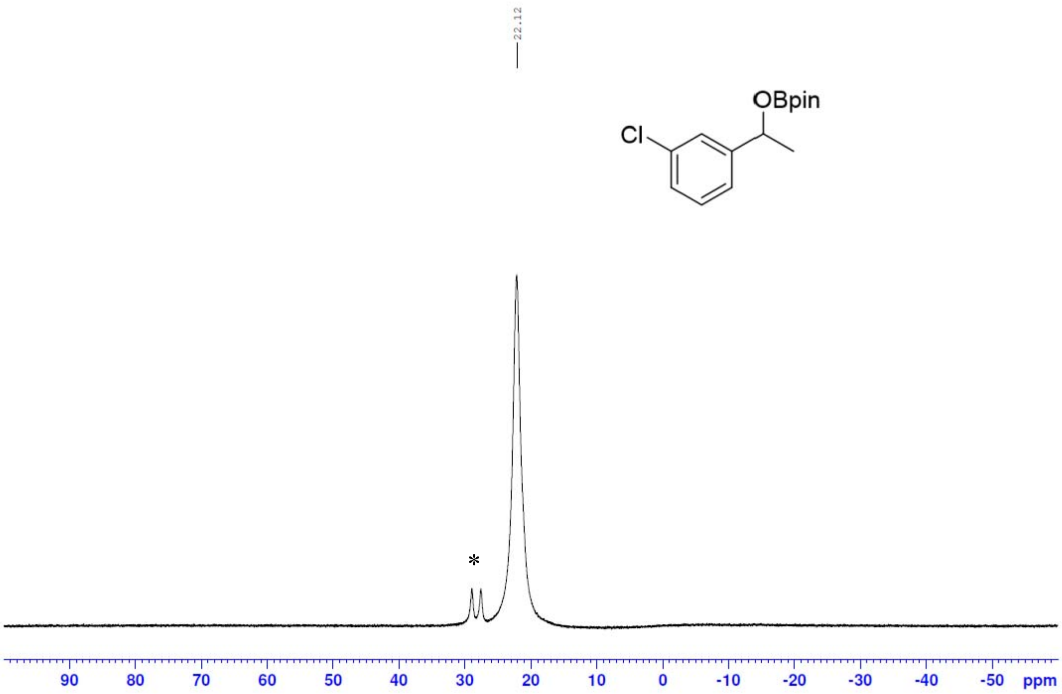


Fig. S66 ^{1}H NMR (600 MHz, $CDCl_3$) of **3q**

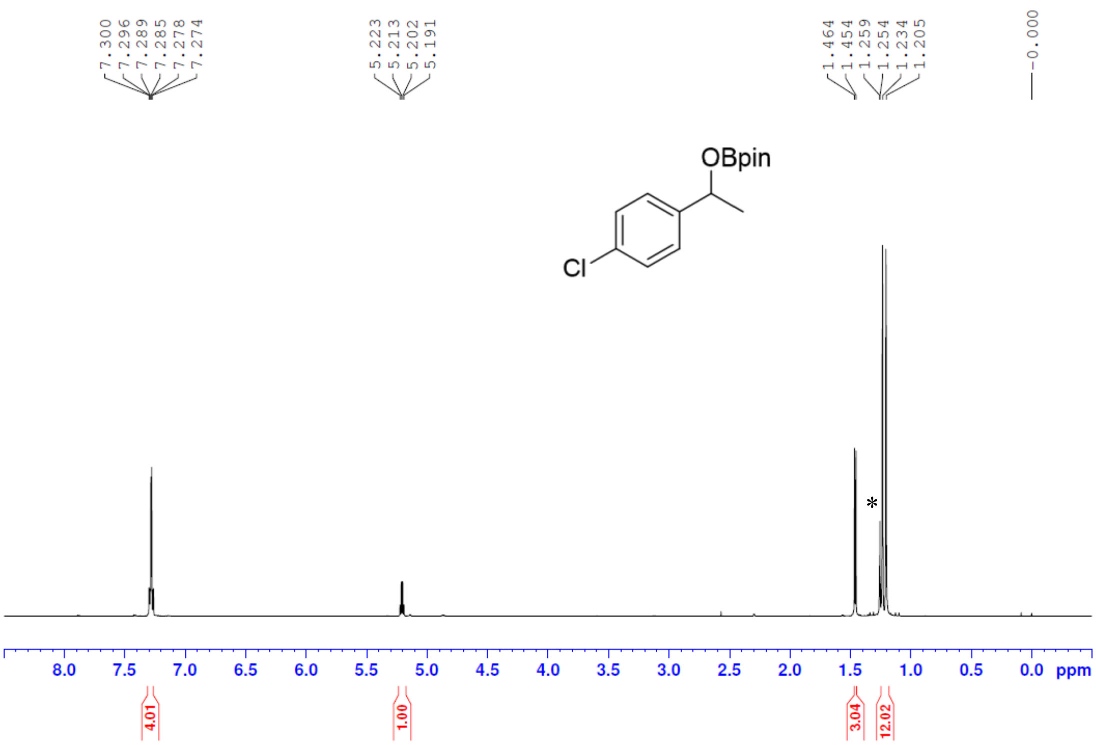


Fig. S67 ^{11}B NMR (128 MHz, $CDCl_3$) of **3q**

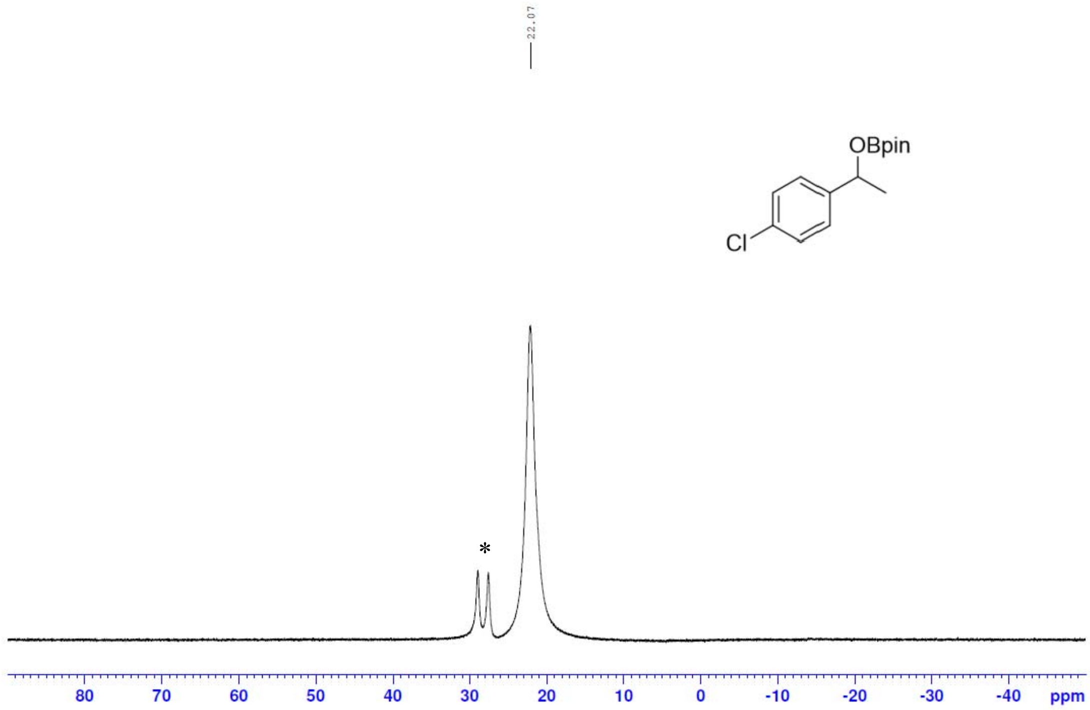


Fig. S68 ^{1}H NMR (600 MHz, $CDCl_3$) of **3r**

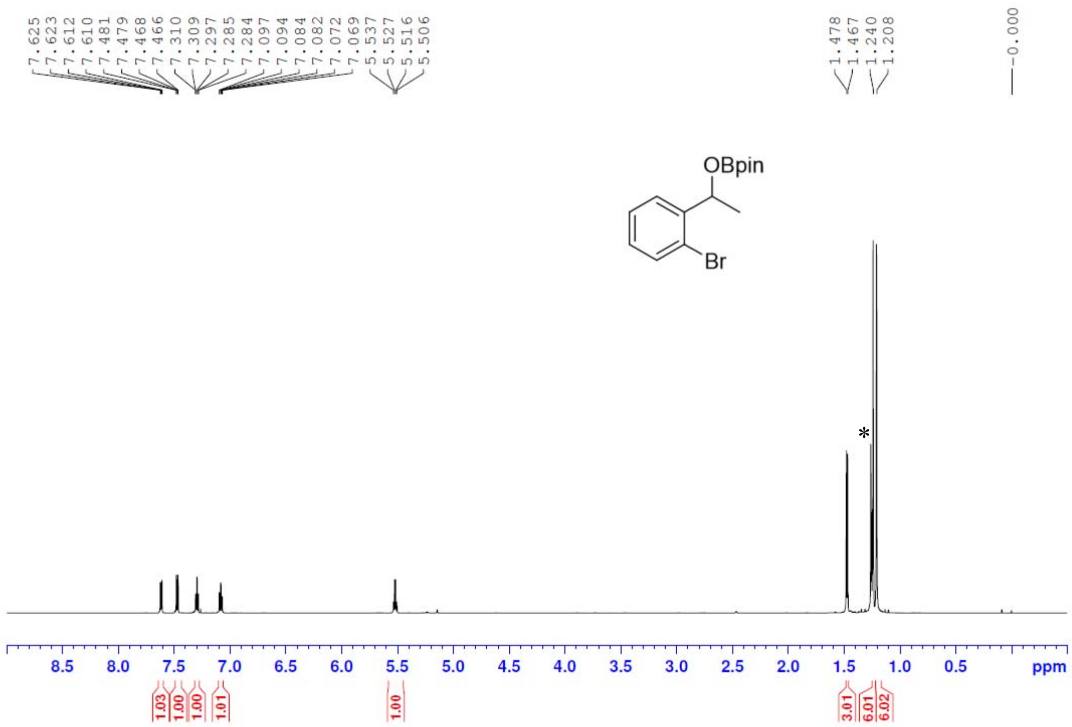


Fig. S69 ^{11}B NMR (128 MHz, $CDCl_3$) of **3r**

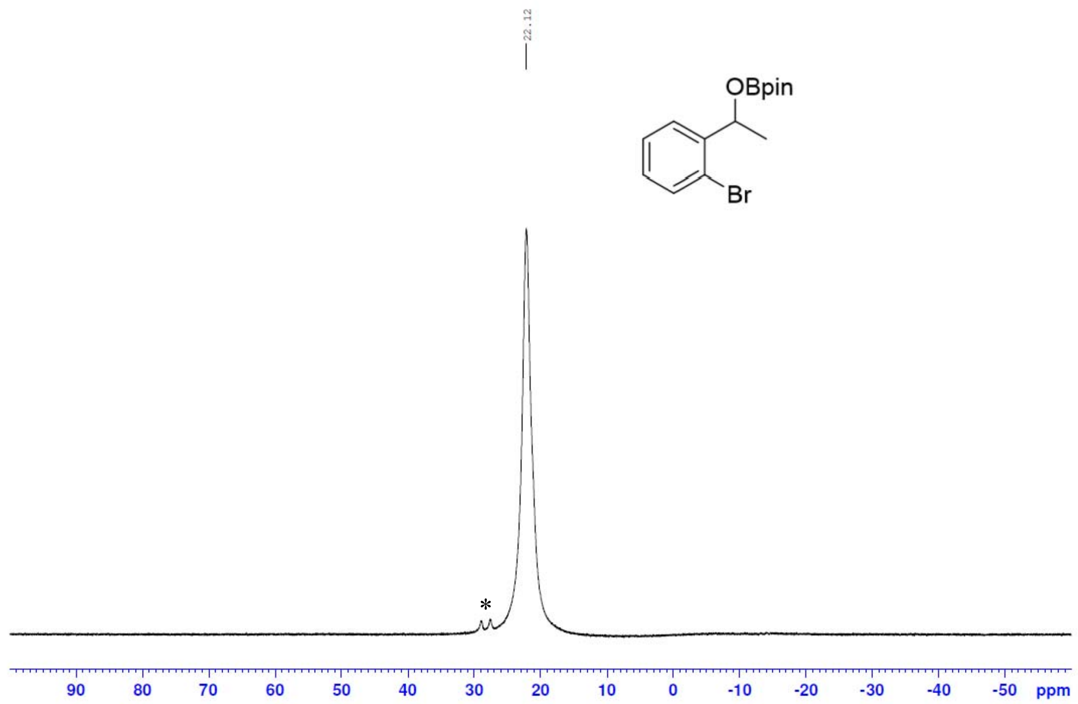


Fig. S70 ^{1}H NMR (600 MHz, $CDCl_3$) of **3s**

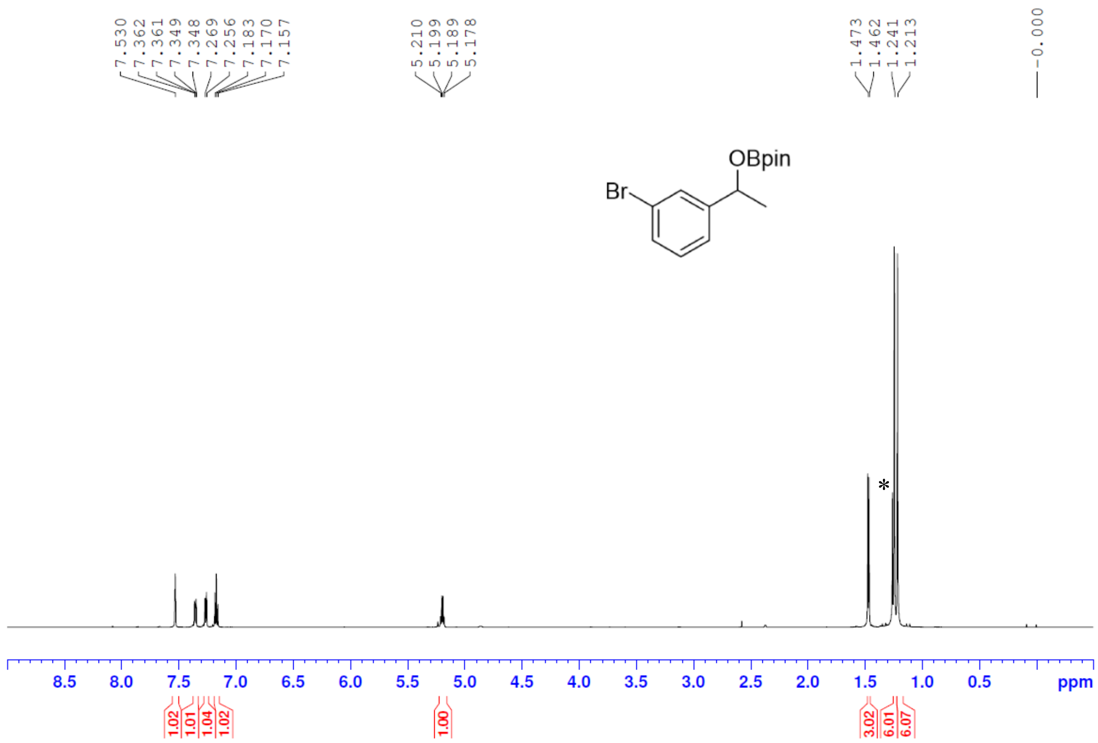


Fig. S71 ^{11}B NMR (128 MHz, $CDCl_3$) of **3s**

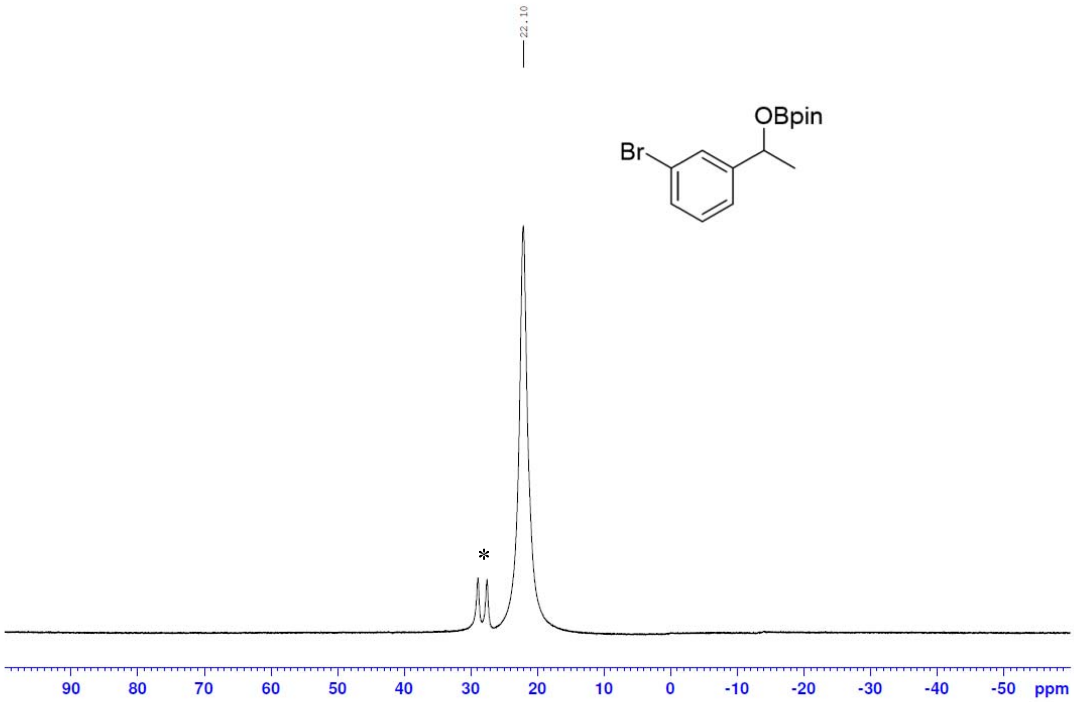


Fig. S72 ^{1}H NMR (600 MHz, $CDCl_3$) of **3t**

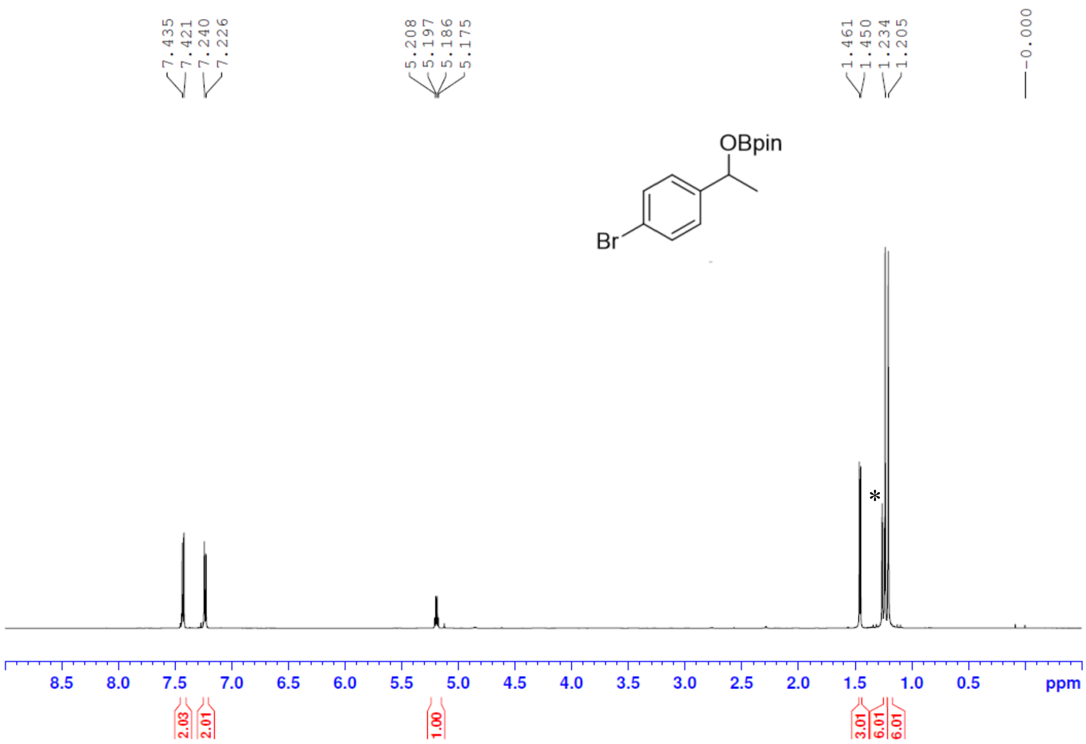


Fig. S73 ^{11}B NMR (128 MHz, $CDCl_3$) of **3t**

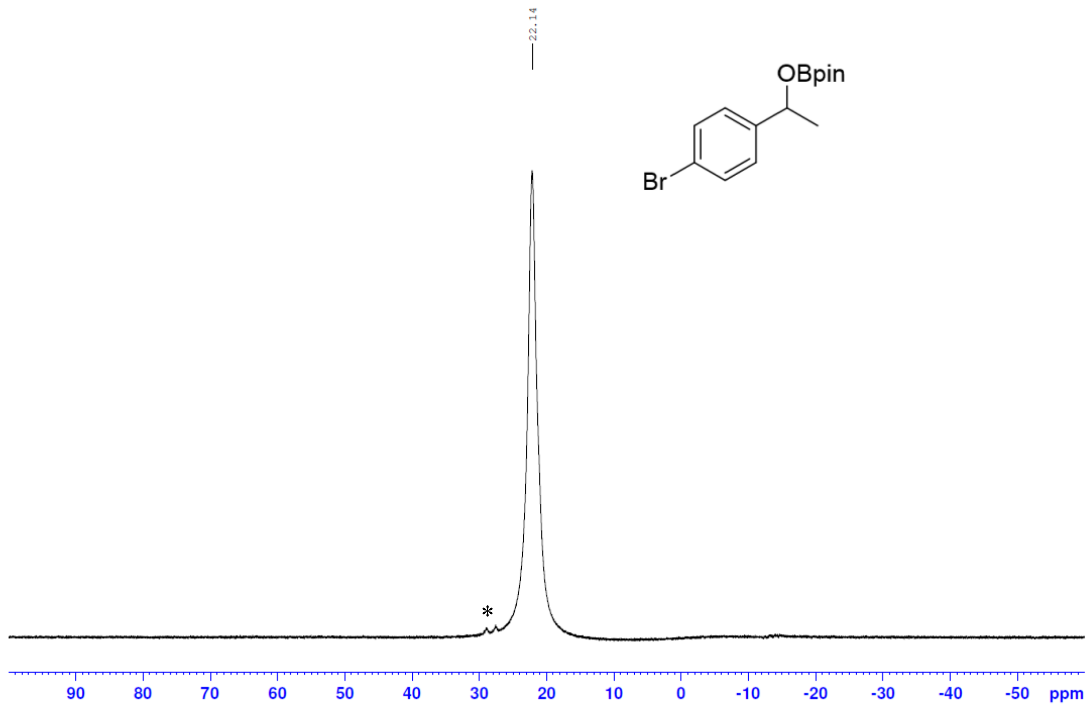


Fig. S74 ^{1}H NMR (600 MHz, $CDCl_3$) of **3u**

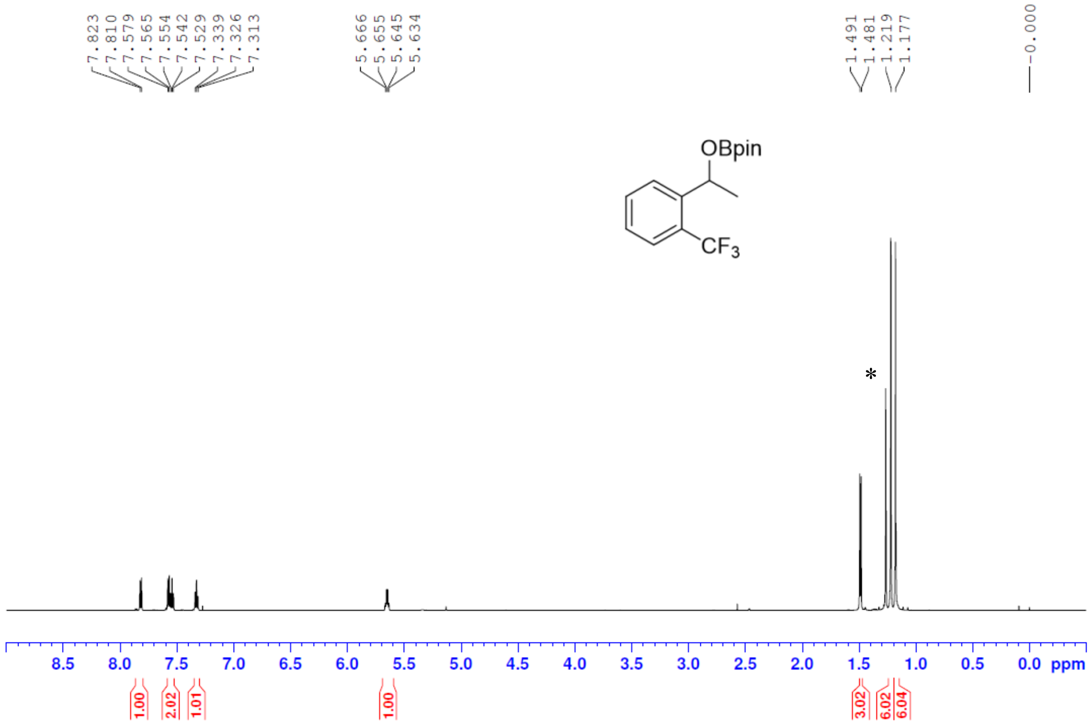


Fig. S75 ^{11}B NMR (128 MHz, $CDCl_3$) of **3u**

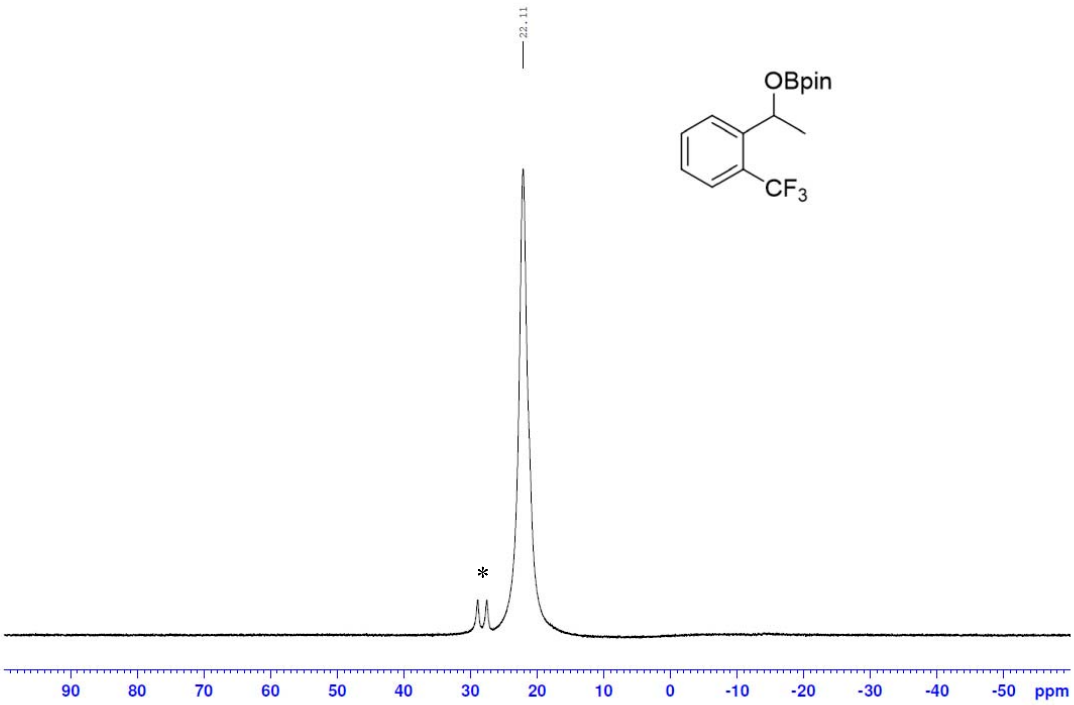


Fig. S76 ^{19}F NMR (565 MHz, $CDCl_3$) of **3u**

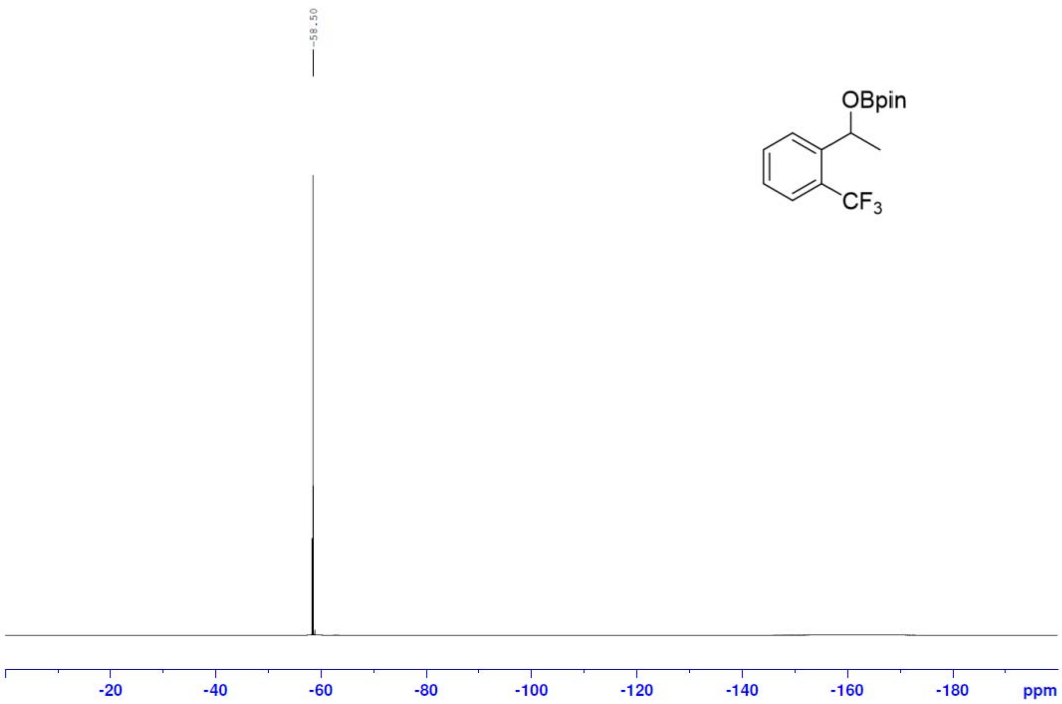


Fig. S77 ^{1}H NMR (600 MHz, $CDCl_3$) of **3v**

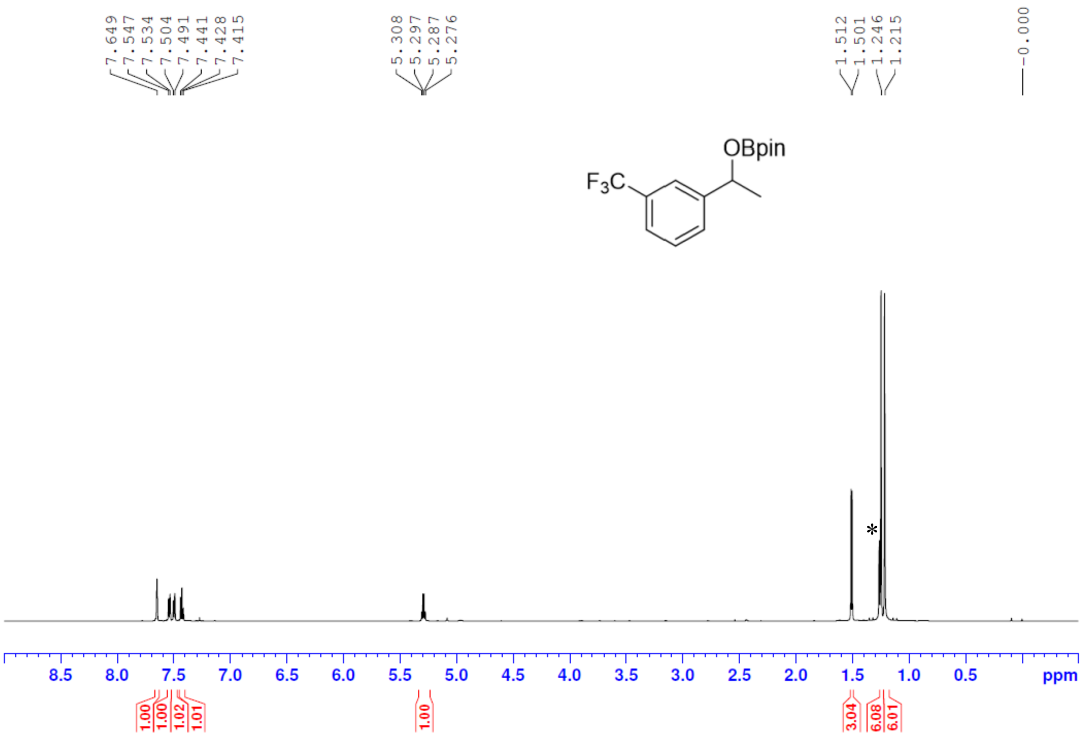


Fig. S78 ^{11}B NMR (128 MHz, $CDCl_3$) of **3v**

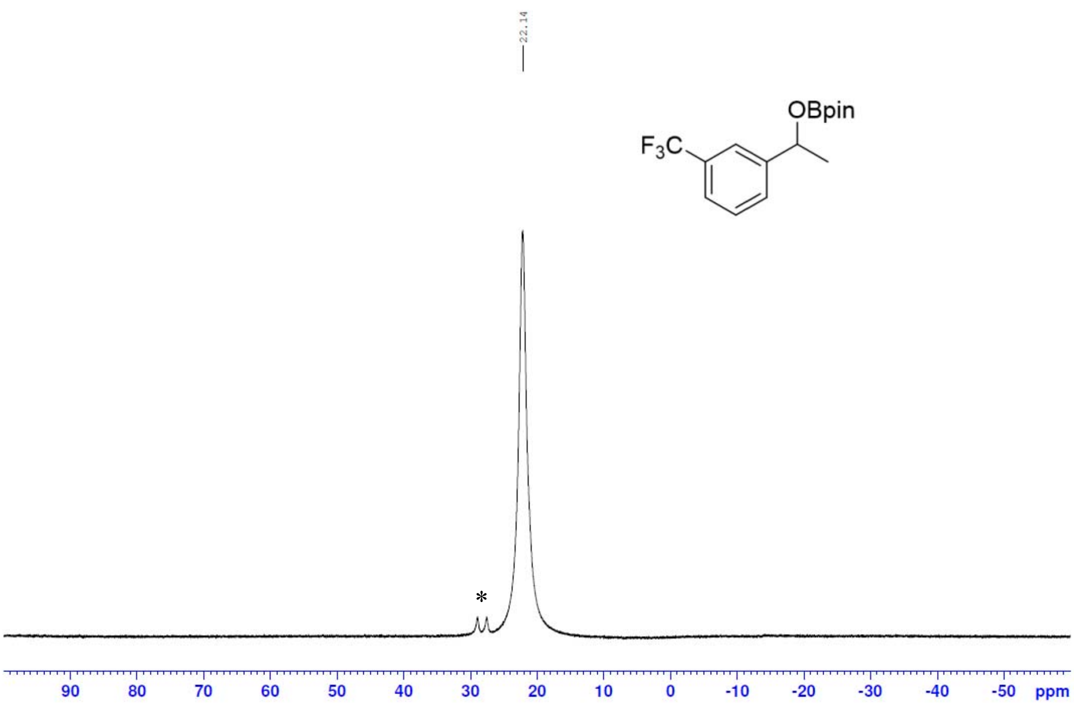


Fig. S79 ^{19}F NMR (565 MHz, $CDCl_3$) of **3v**

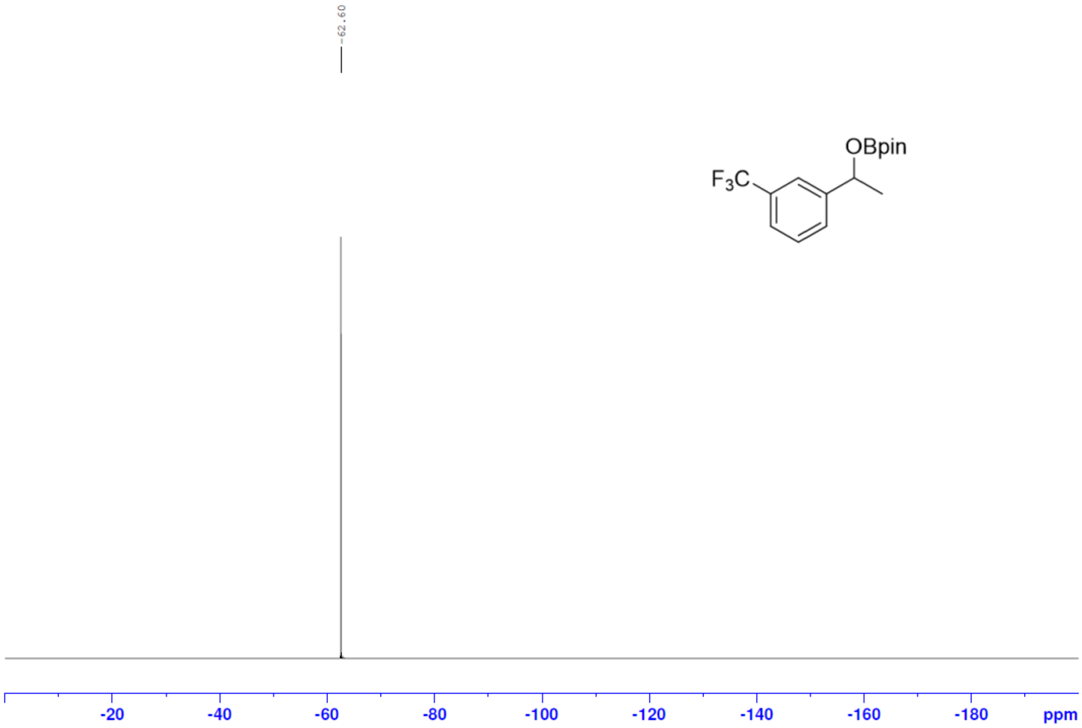


Fig. S80 ^{1}H NMR (600 MHz, $CDCl_3$) of **3w**

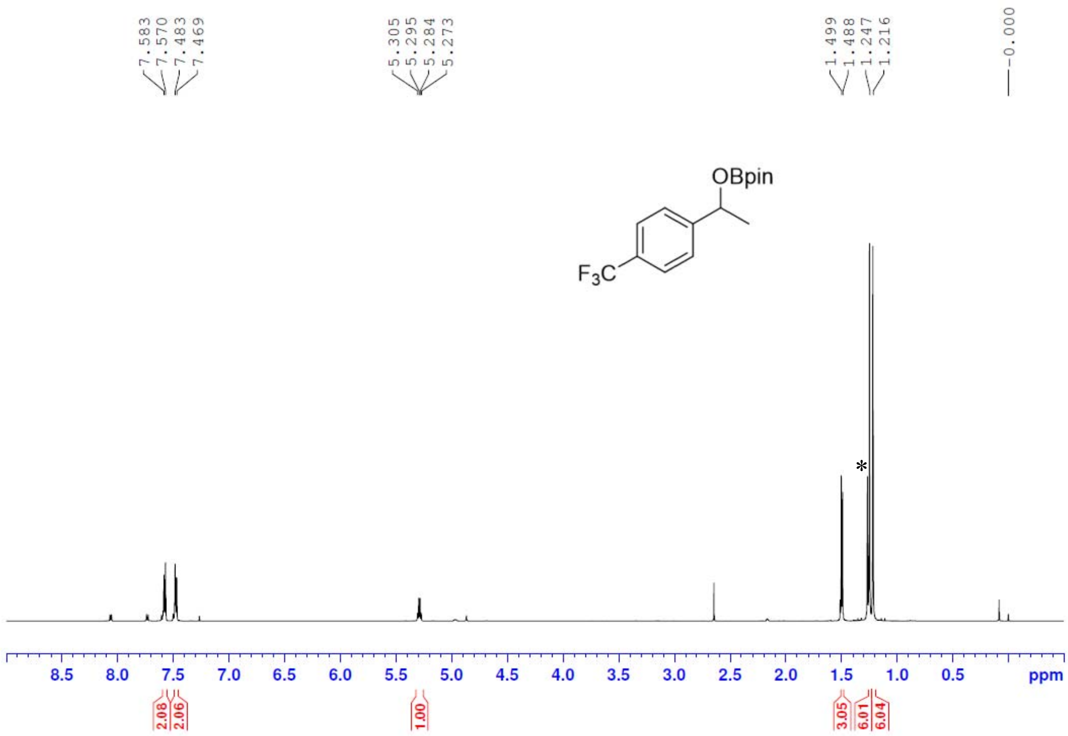


Fig. S81 ^{11}B NMR (193 MHz, $CDCl_3$) of **3w**

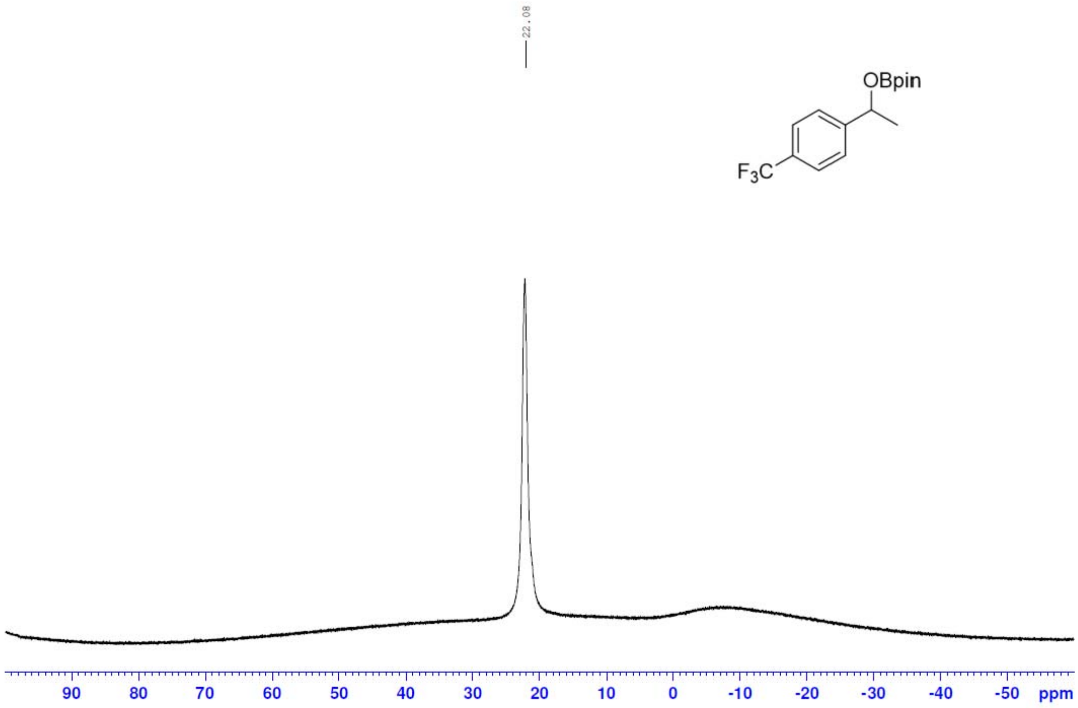


Fig. S82 ^{19}F NMR (565 MHz, $CDCl_3$) of **3w**

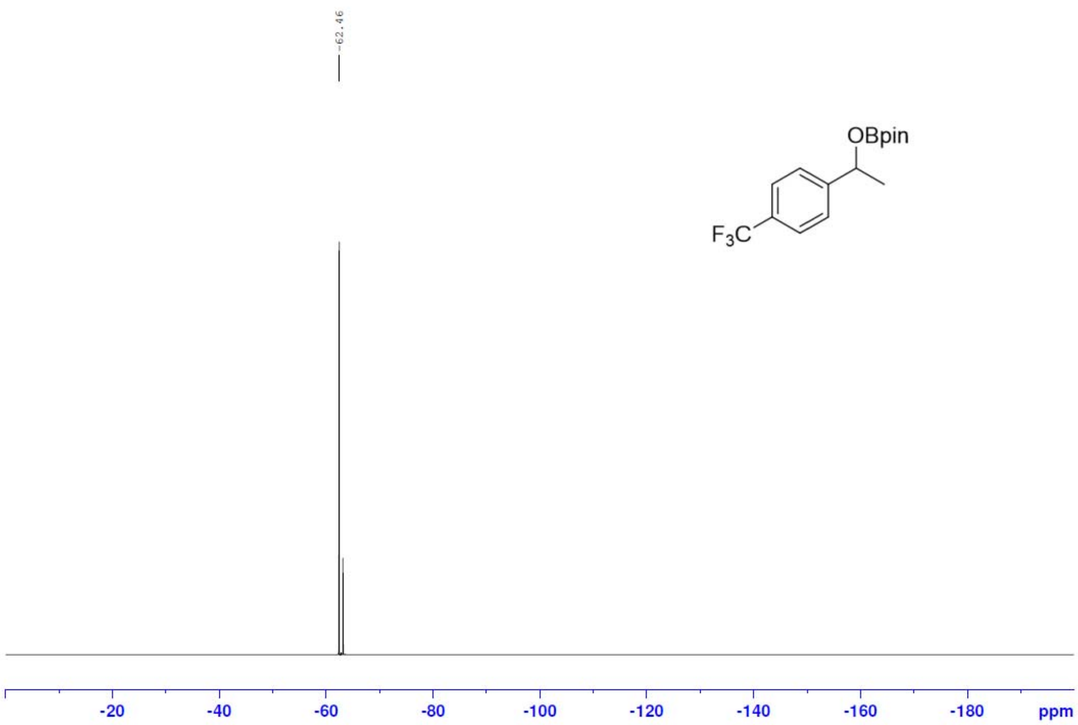


Fig. S83 ^{1}H NMR (600 MHz, CDCl$_3$) of **3x**

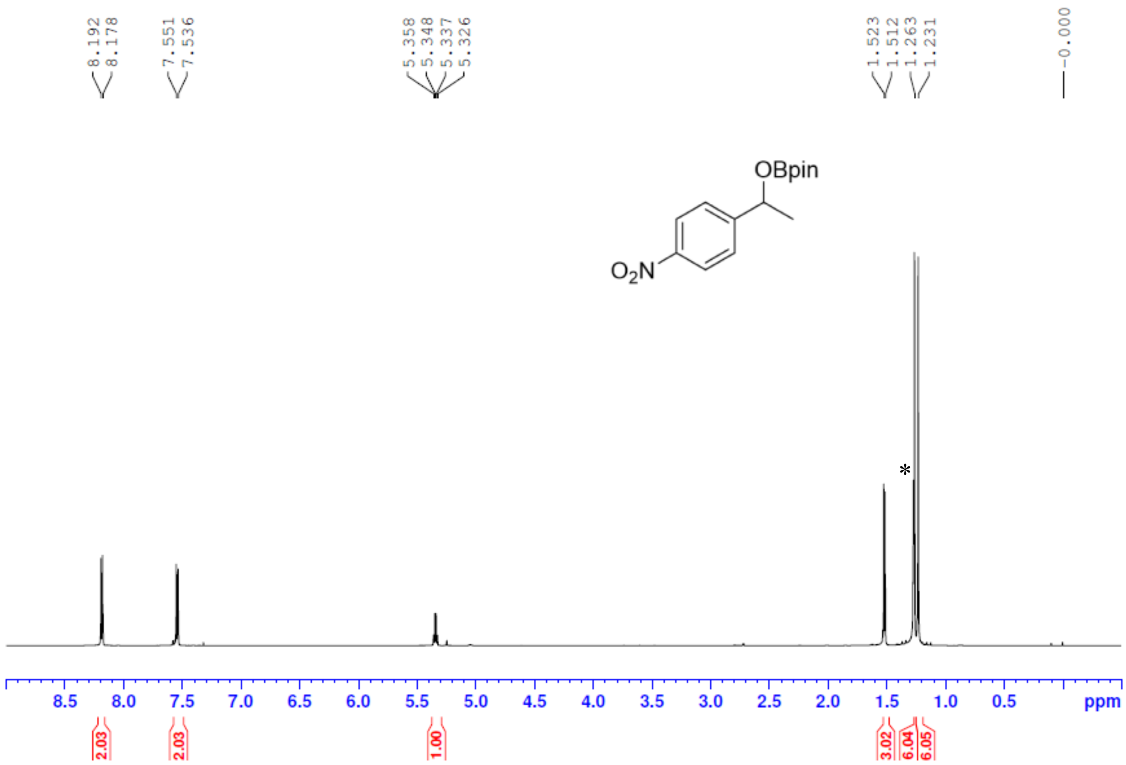


Fig. S84 ^{11}B NMR (193 MHz, CDCl$_3$) of **3x**

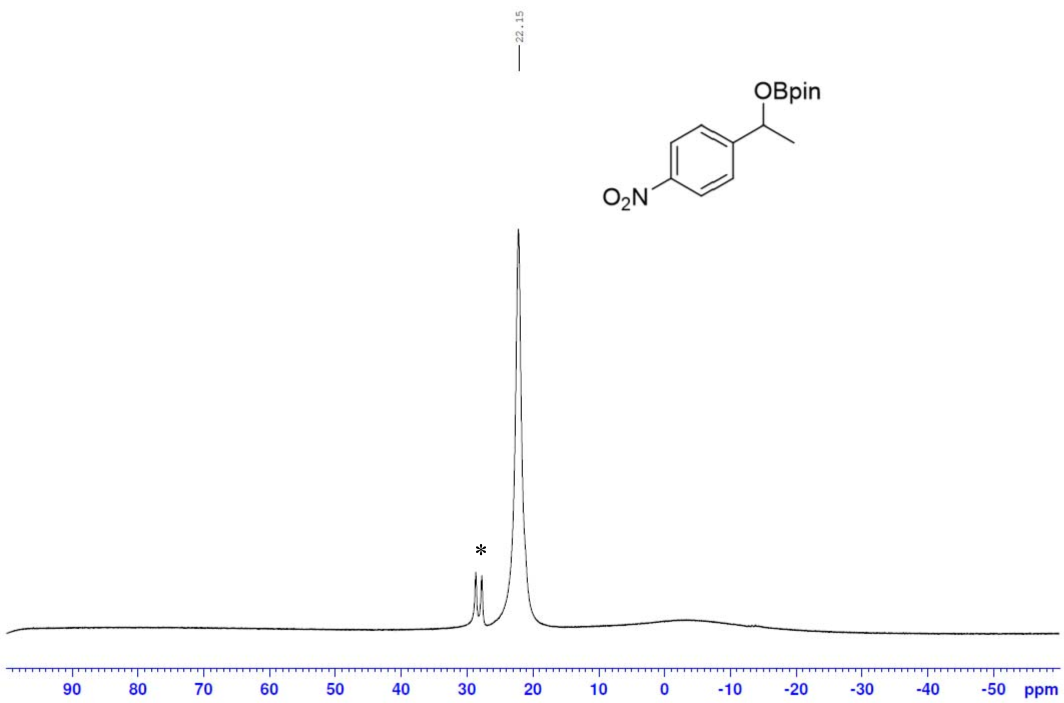


Fig. S85 ^{1}H NMR (600 MHz, $CDCl_3$) of **3y**

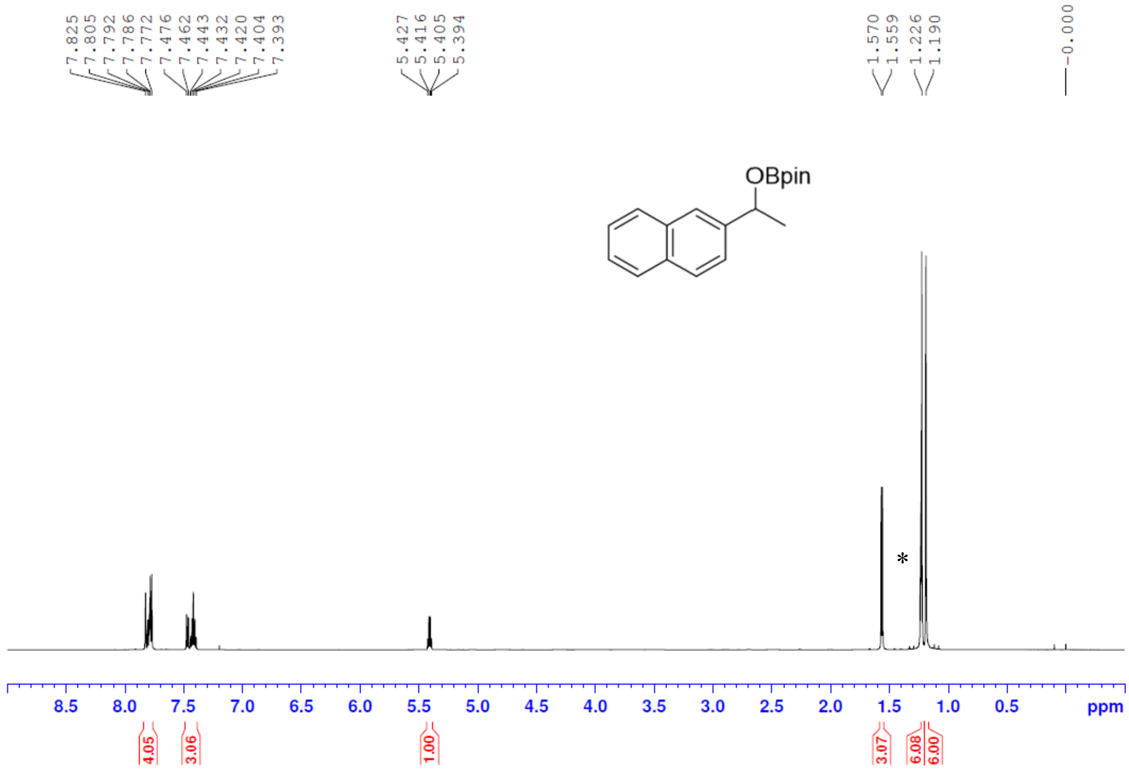


Fig. S86 ^{11}B NMR (128 MHz, $CDCl_3$) of **3y**

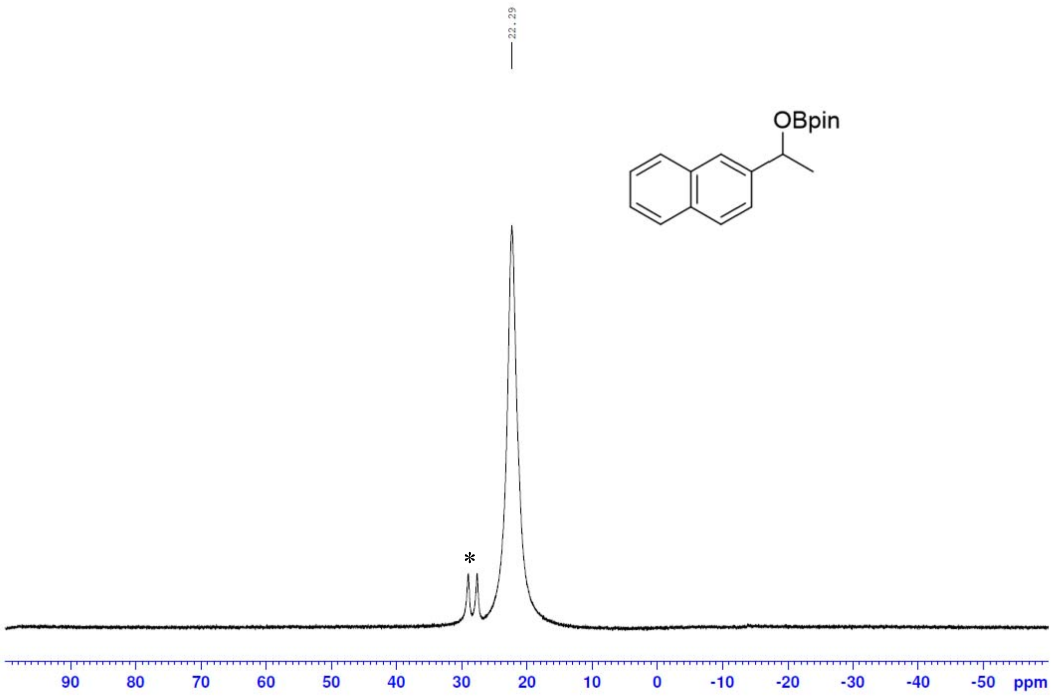


Fig. S87 ^{1}H NMR (600 MHz, $CDCl_3$) of **3z**

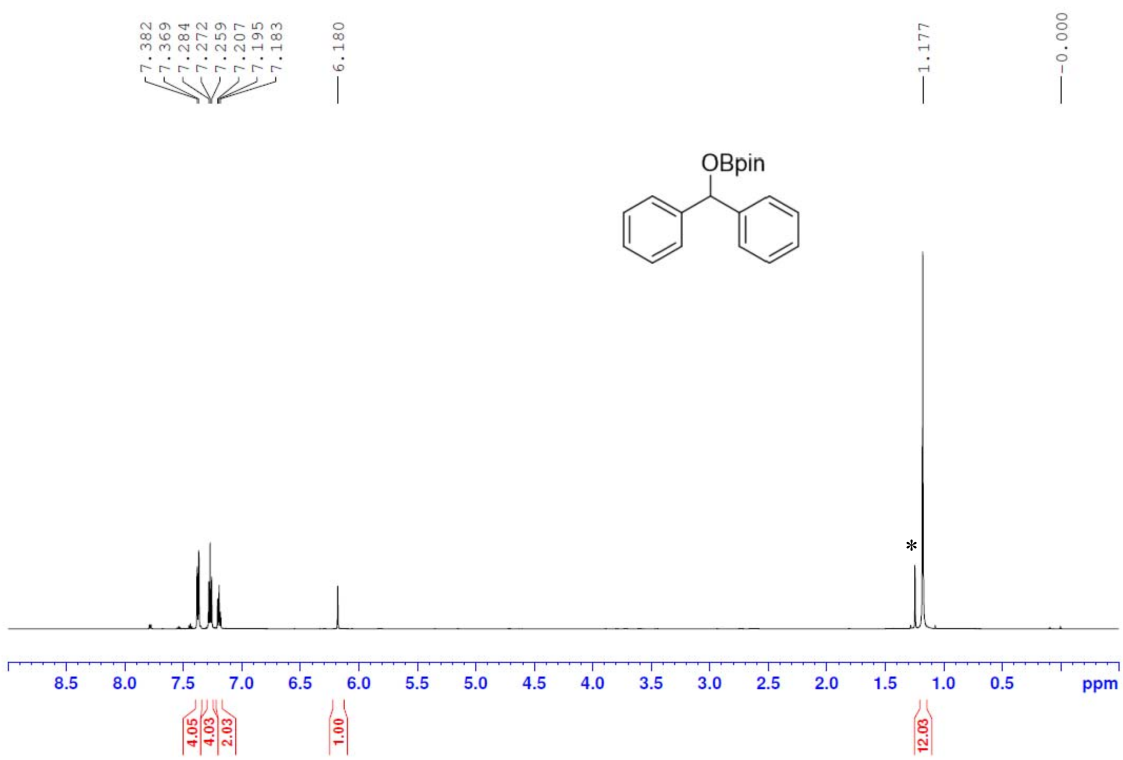


Fig. S88 ^{11}B NMR (128 MHz, $CDCl_3$) of **3z**

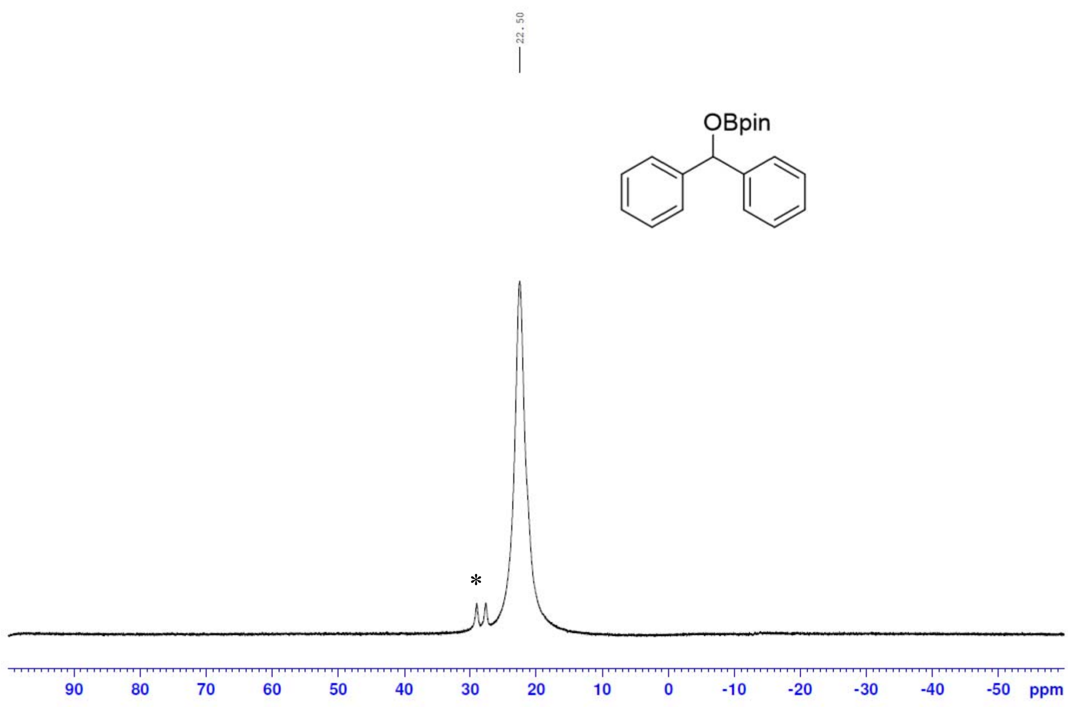


Fig. S89 ^{1}H NMR (600 MHz, $CDCl_3$) of **3aa**

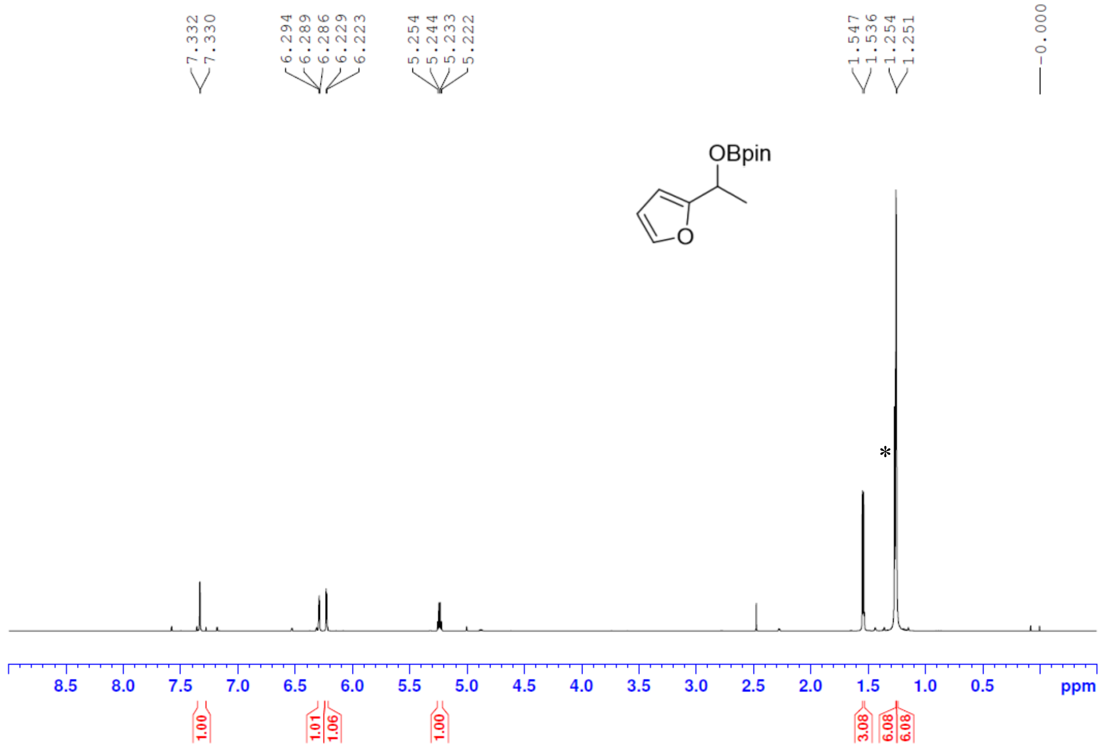


Fig. S90 ^{11}B NMR (128 MHz, $CDCl_3$) of **3aa**

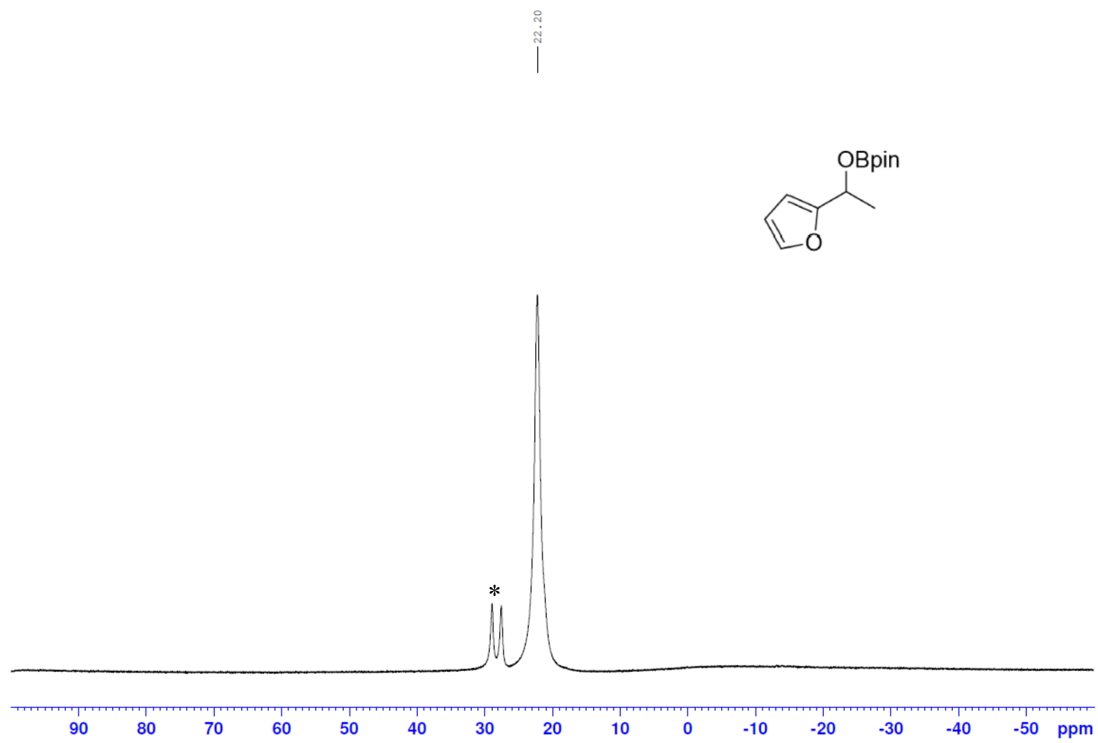


Fig. S91 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ab**

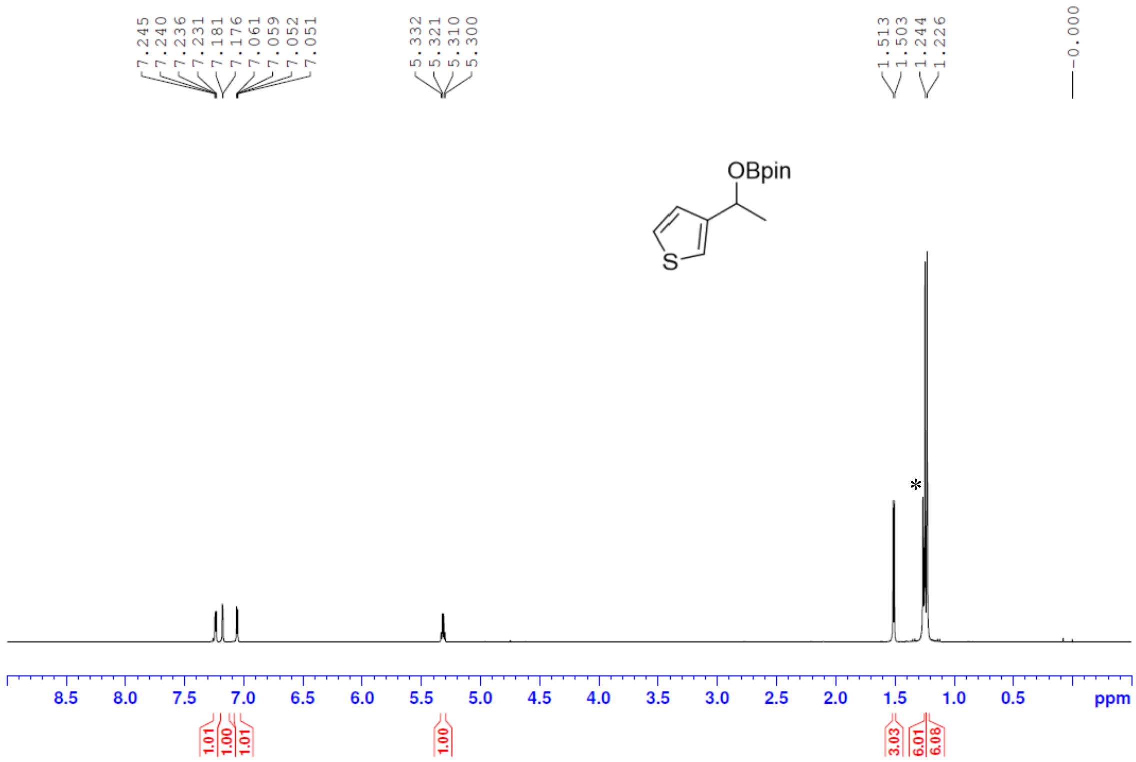


Fig. S92 ^{11}B NMR (193 MHz, $CDCl_3$) of **3ab**

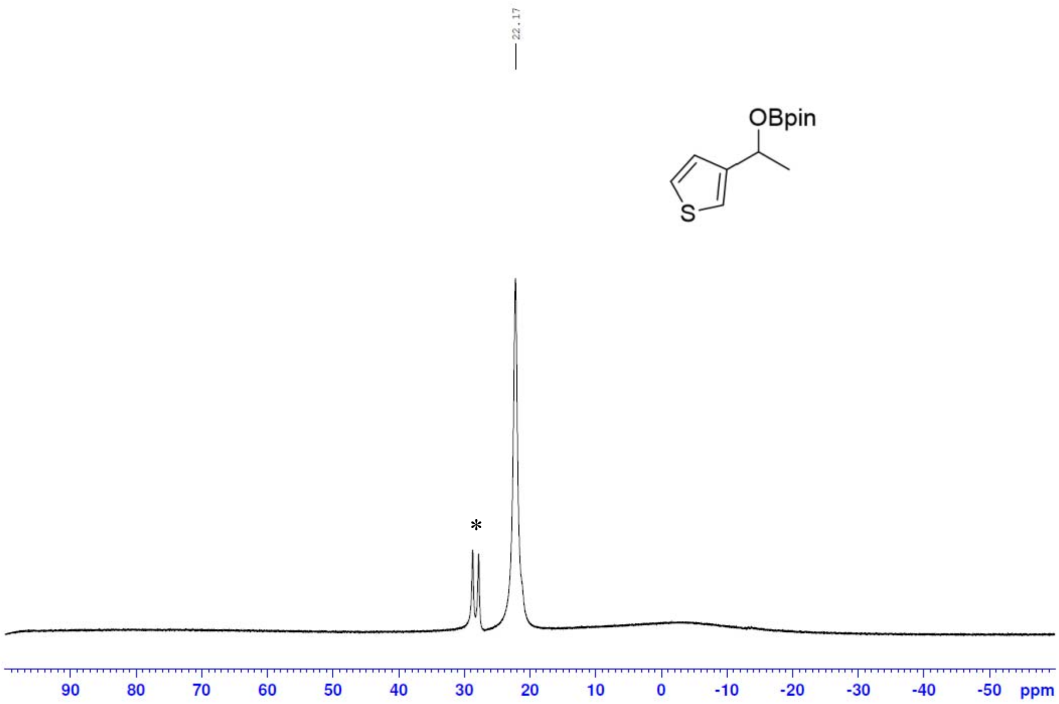


Fig. S93 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ac**

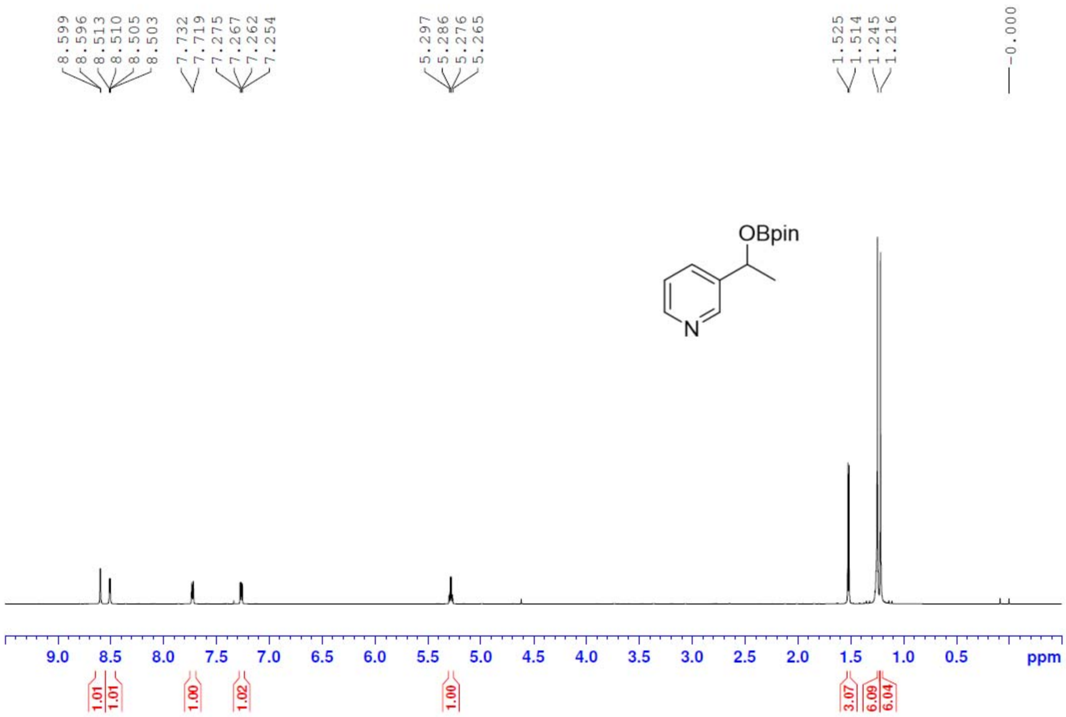


Fig. S94 ^{11}B NMR (193 MHz, $CDCl_3$) of **3ac**

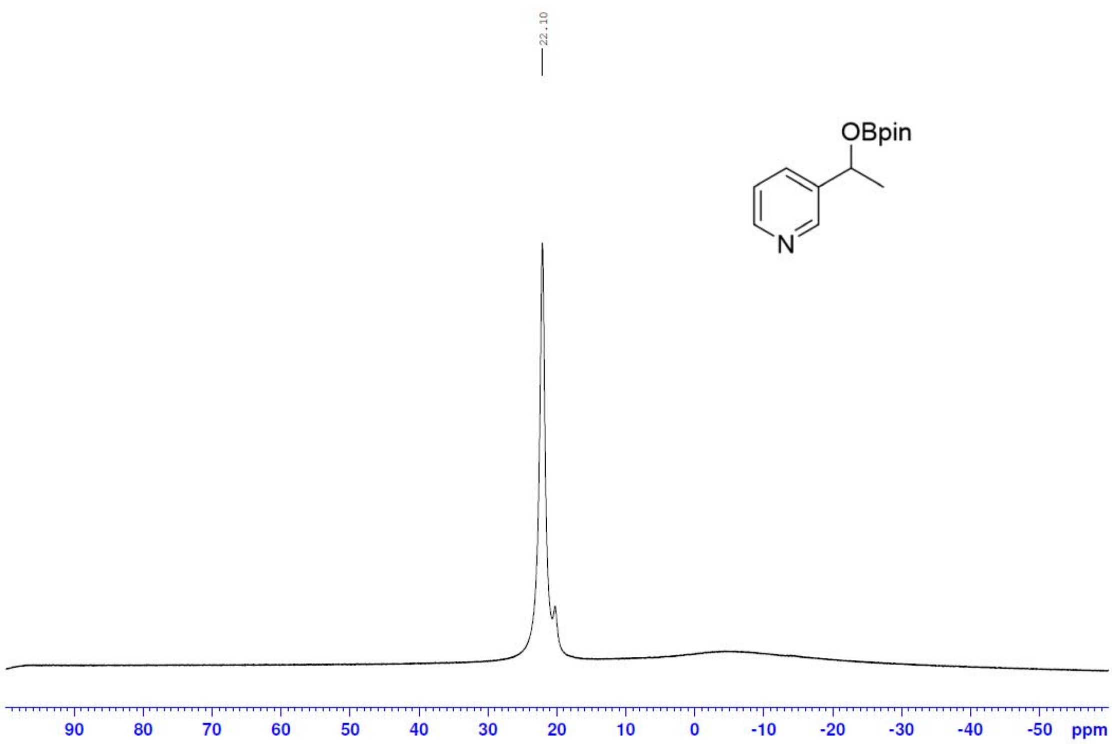


Fig. S95 ^{1}H NMR (600 MHz, C_6D_6) of **3ad**

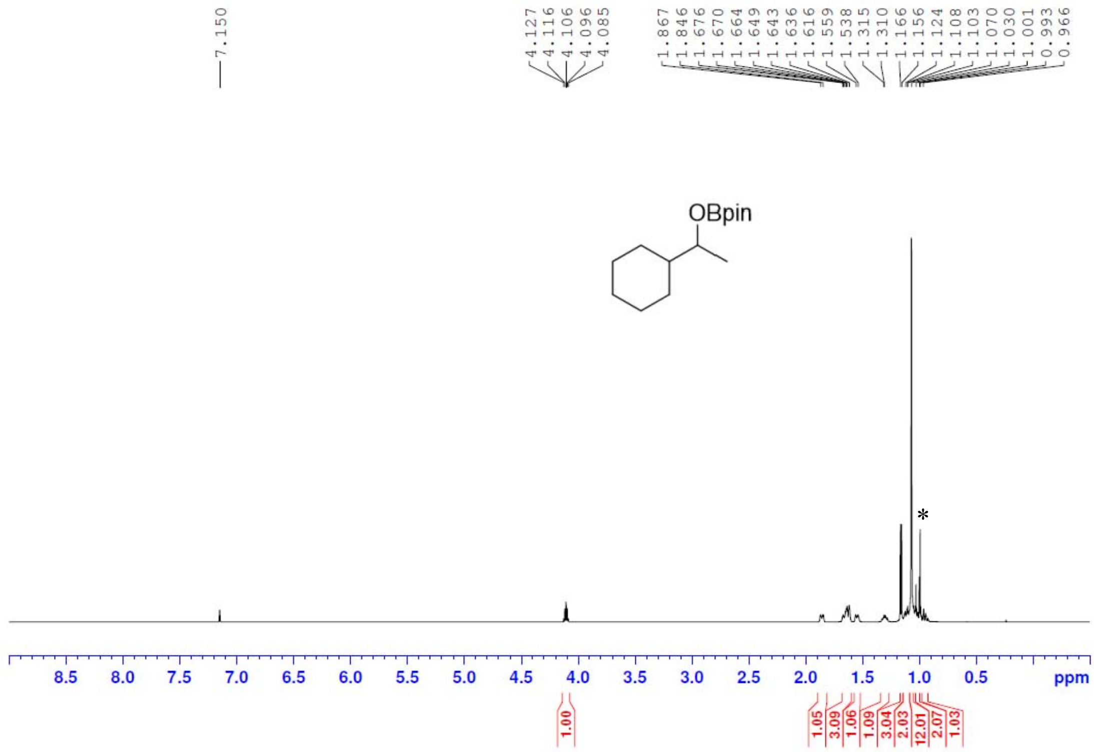


Fig. S96 ^{11}B NMR (193 MHz, C_6D_6) of **3ad**

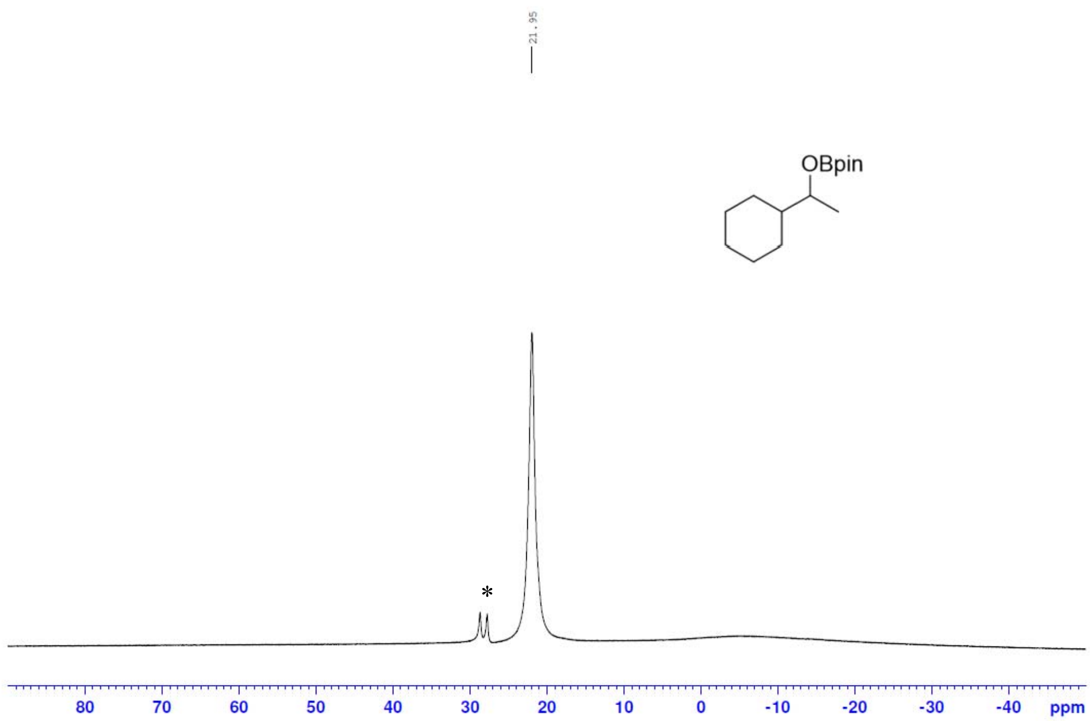


Fig. S97 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ae**

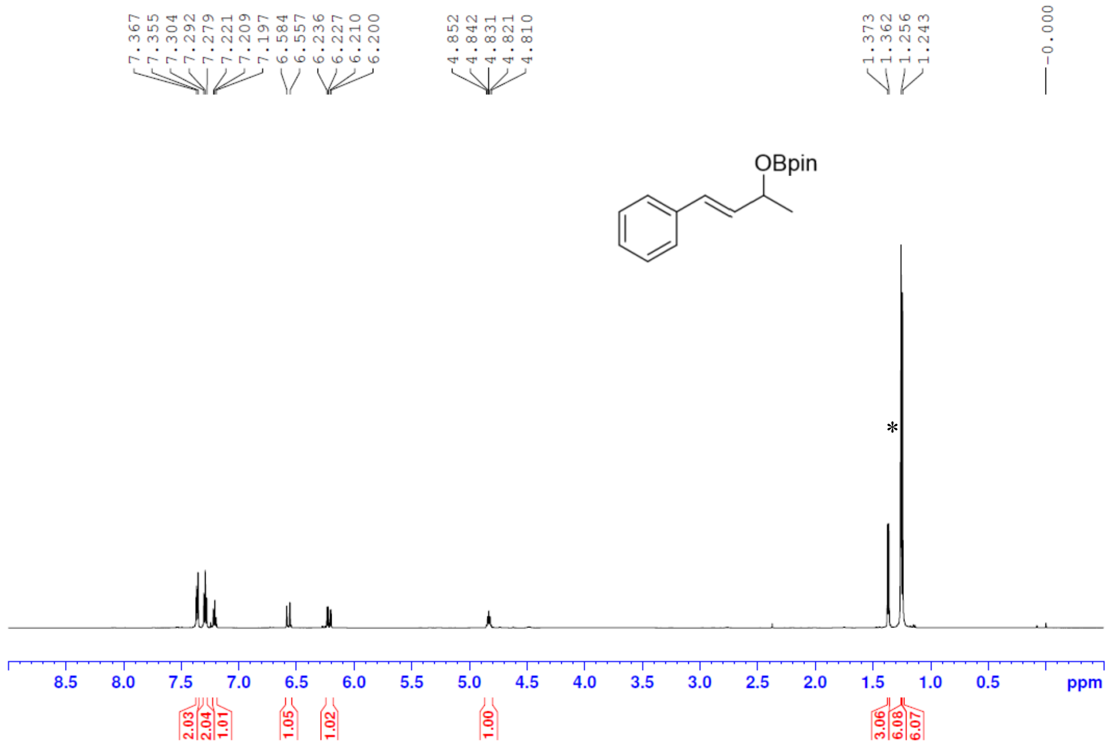


Fig. S98 ^{11}B NMR (128 MHz, $CDCl_3$) of **3ae**

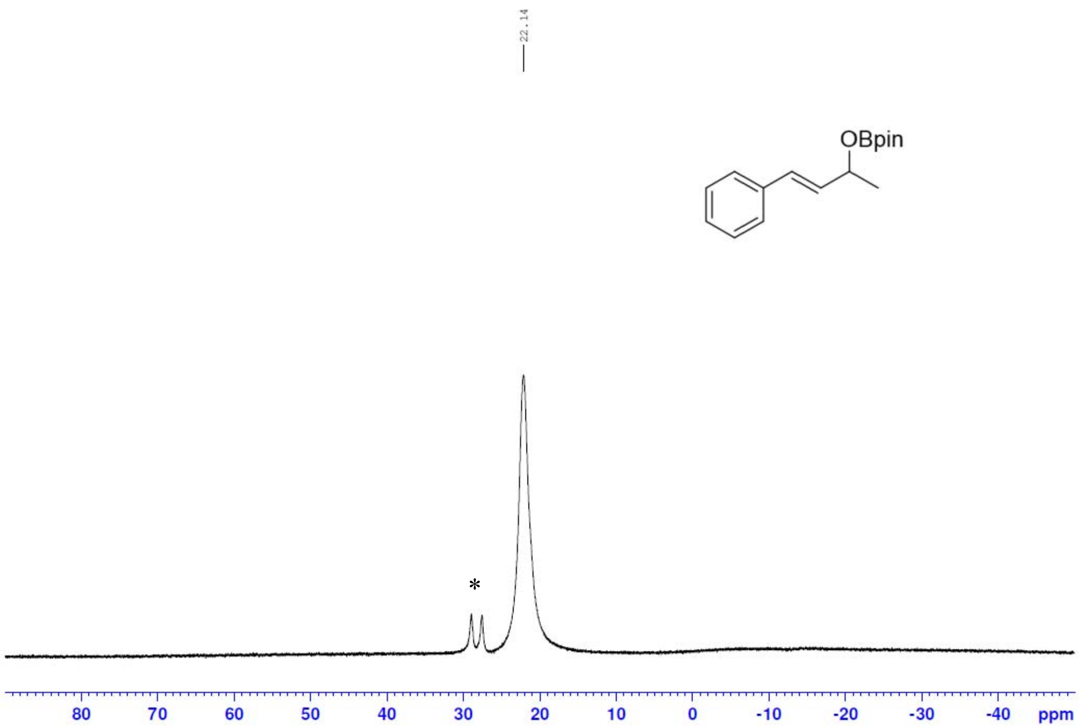


Fig. S99 ^{1}H NMR (600 MHz, $CDCl_3$) of **3af**

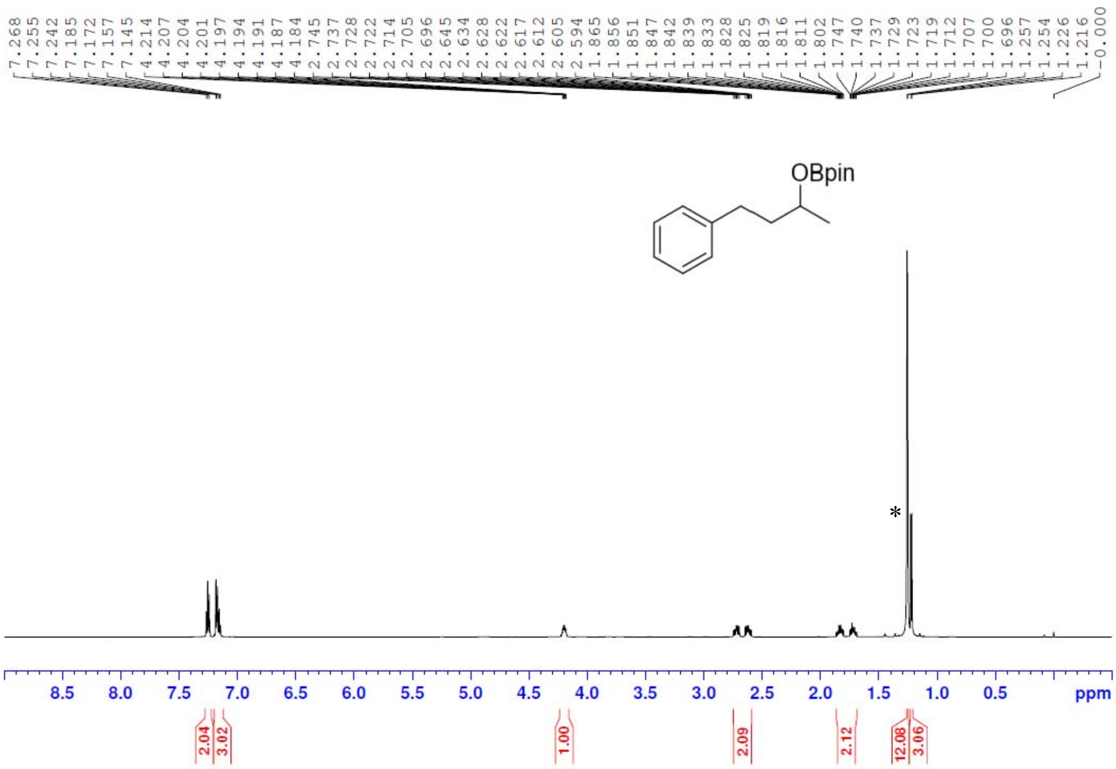


Fig. S100 ^{11}B NMR (128 MHz, $CDCl_3$) of **3af**

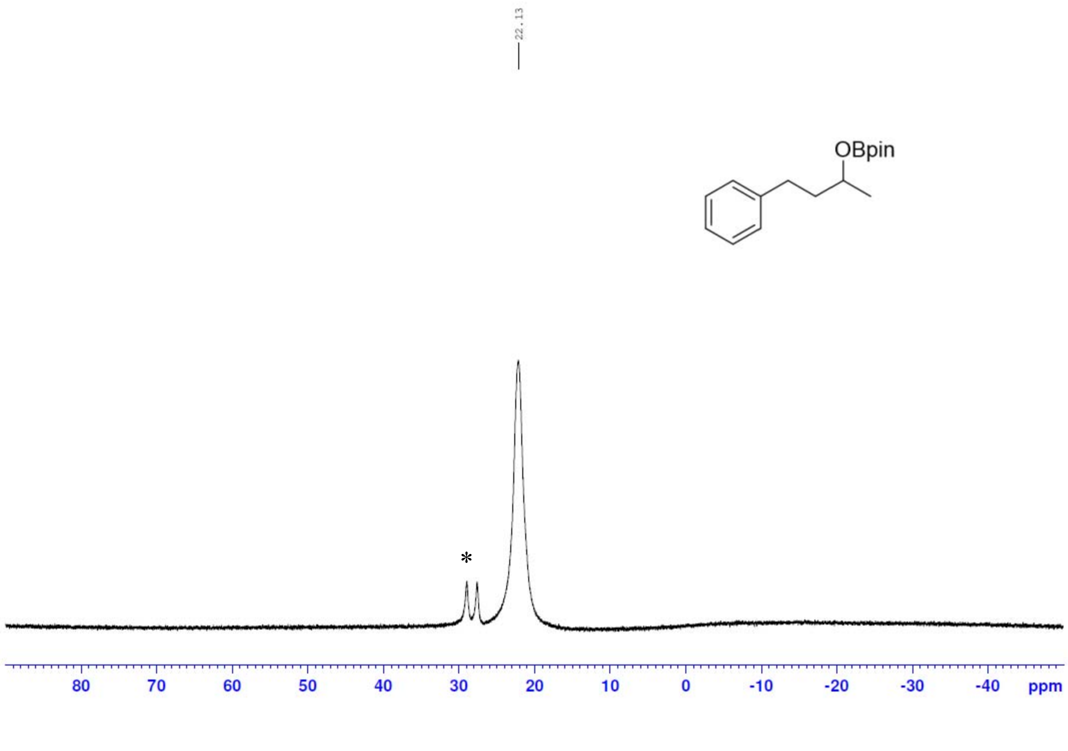


Fig. 101 ^{1}H NMR (600 MHz, CDCl$_3$) of **3ag**

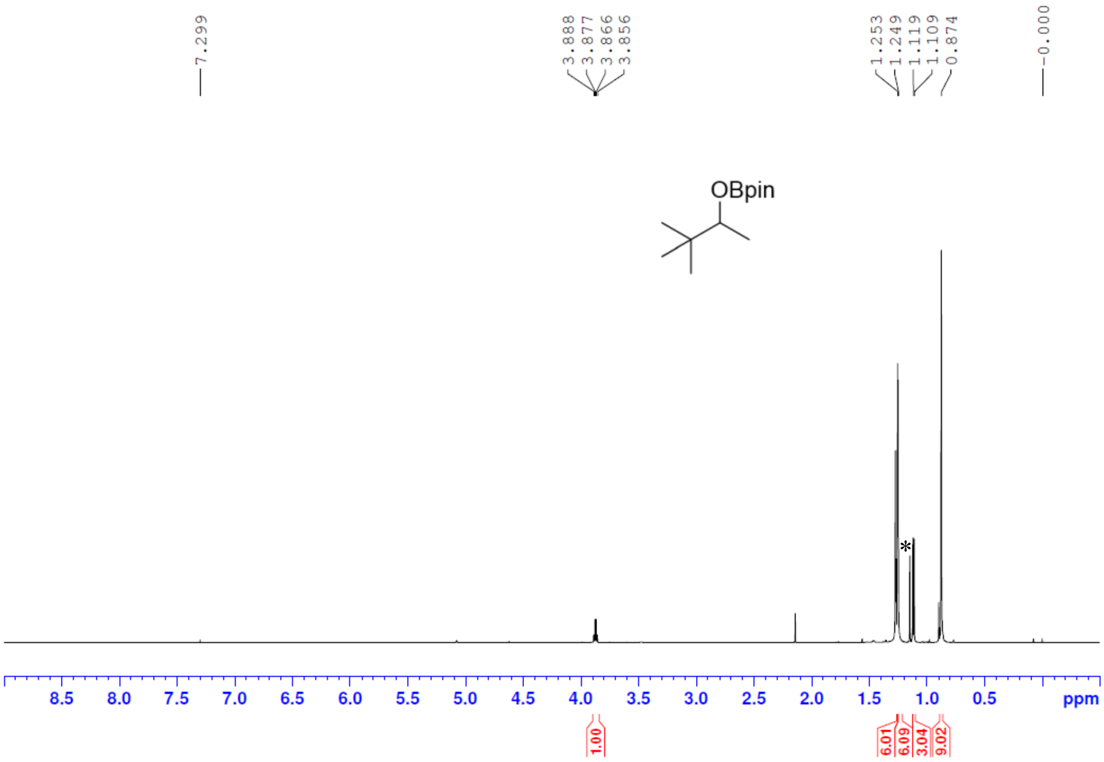


Fig. S102 ^{11}B NMR (193 MHz, CDCl$_3$) of **3ag**

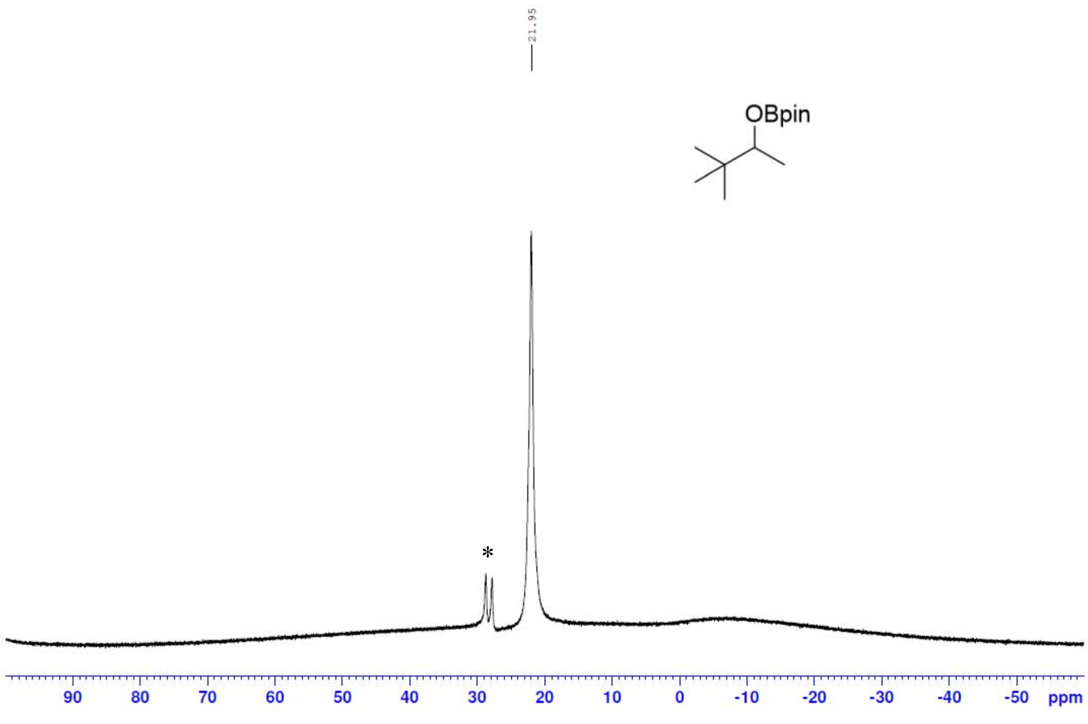


Fig. S103 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ah**

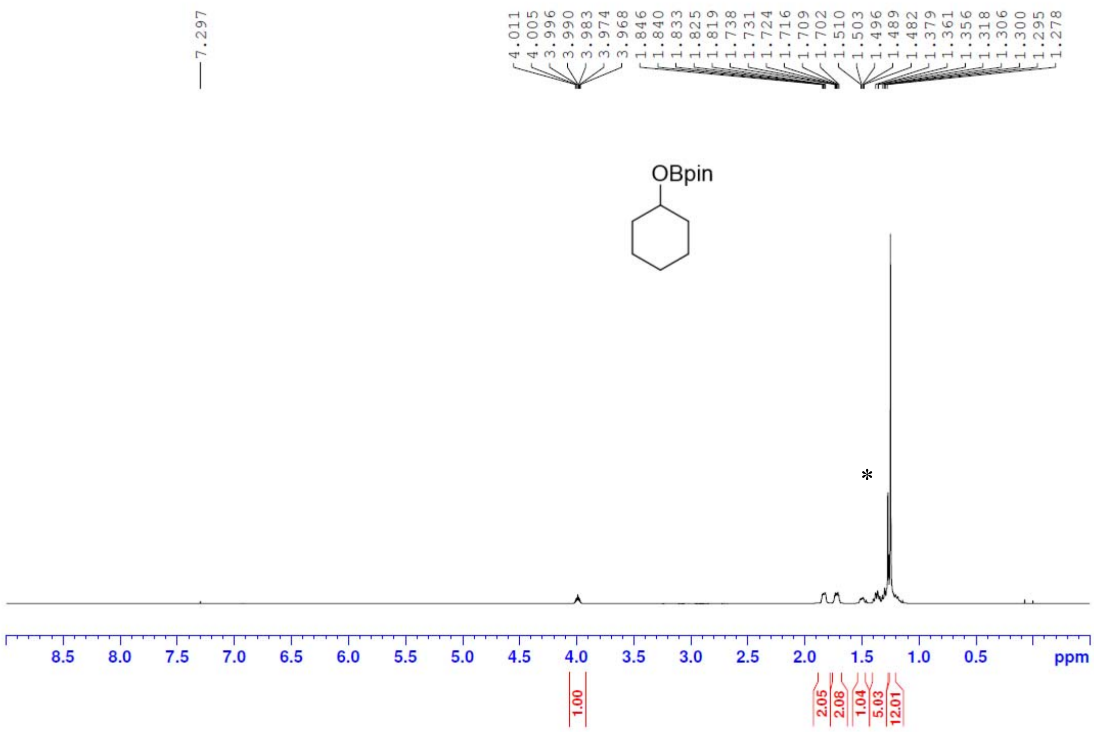


Fig. S104 ^{11}B NMR (193 MHz, $CDCl_3$) of **3ah**

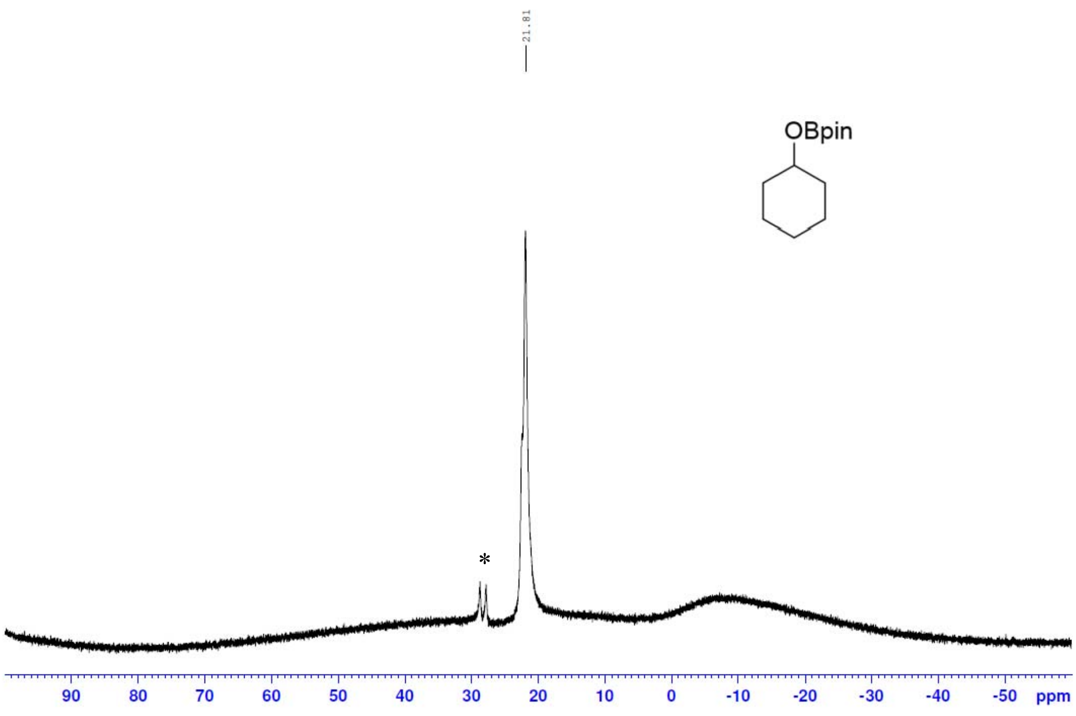


Fig. S105 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ai**

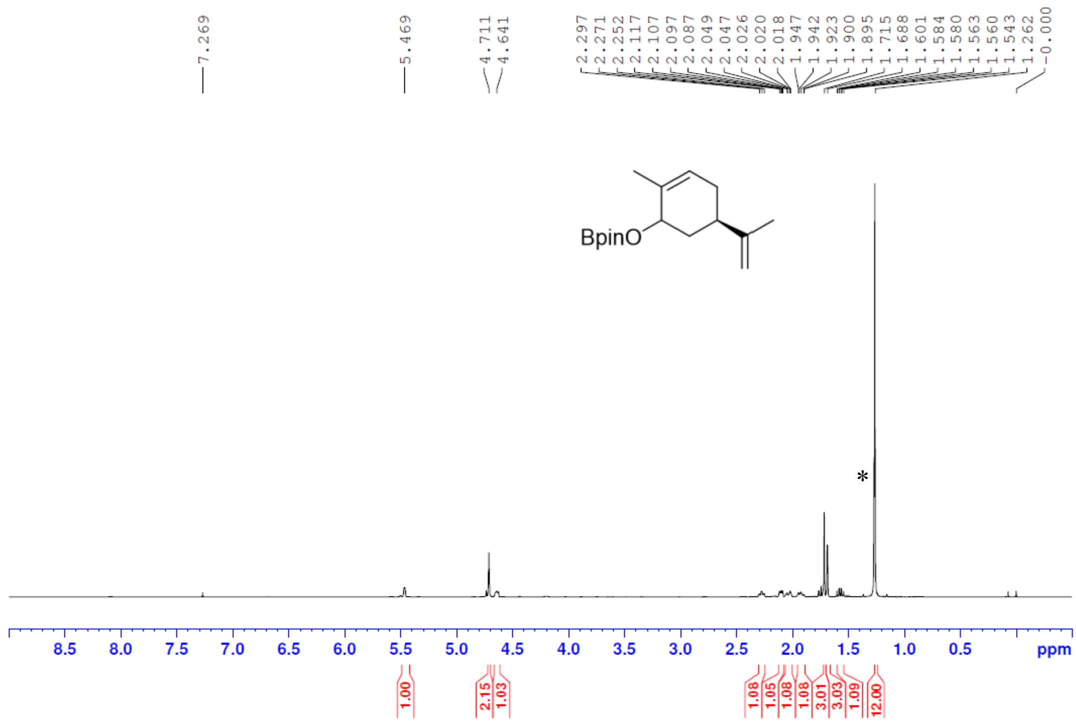


Fig. S106 ^{11}B NMR (193 MHz, $CDCl_3$) of **3ai**

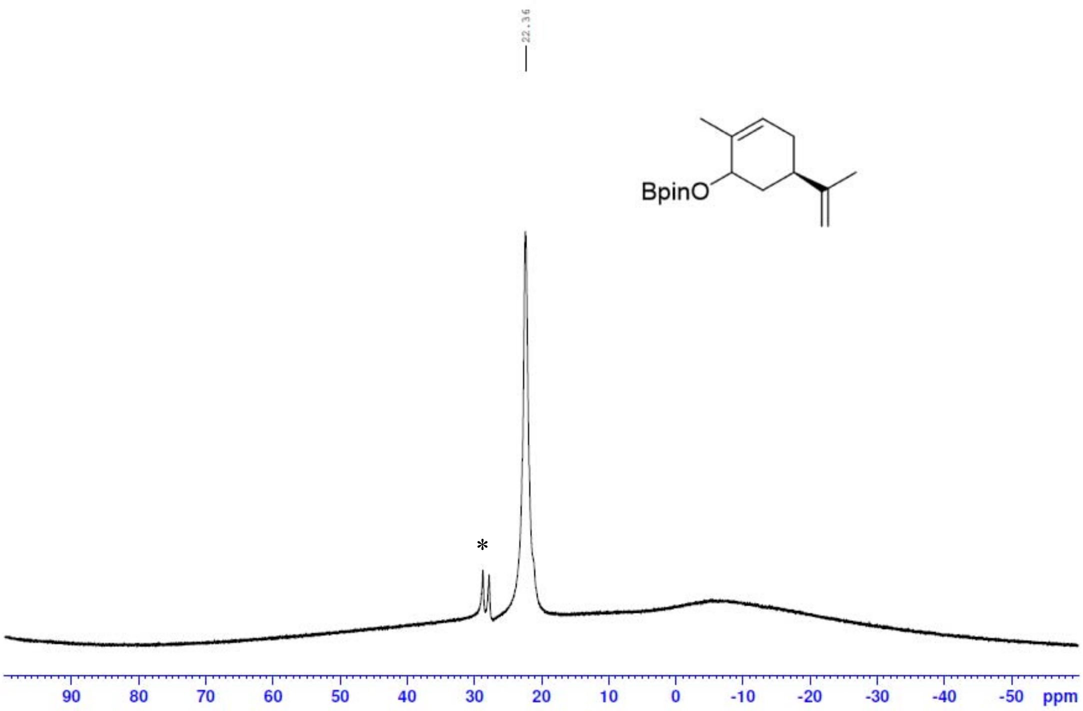


Fig. S107 ^{1}H NMR (600 MHz, $CDCl_3$) of **3a’**

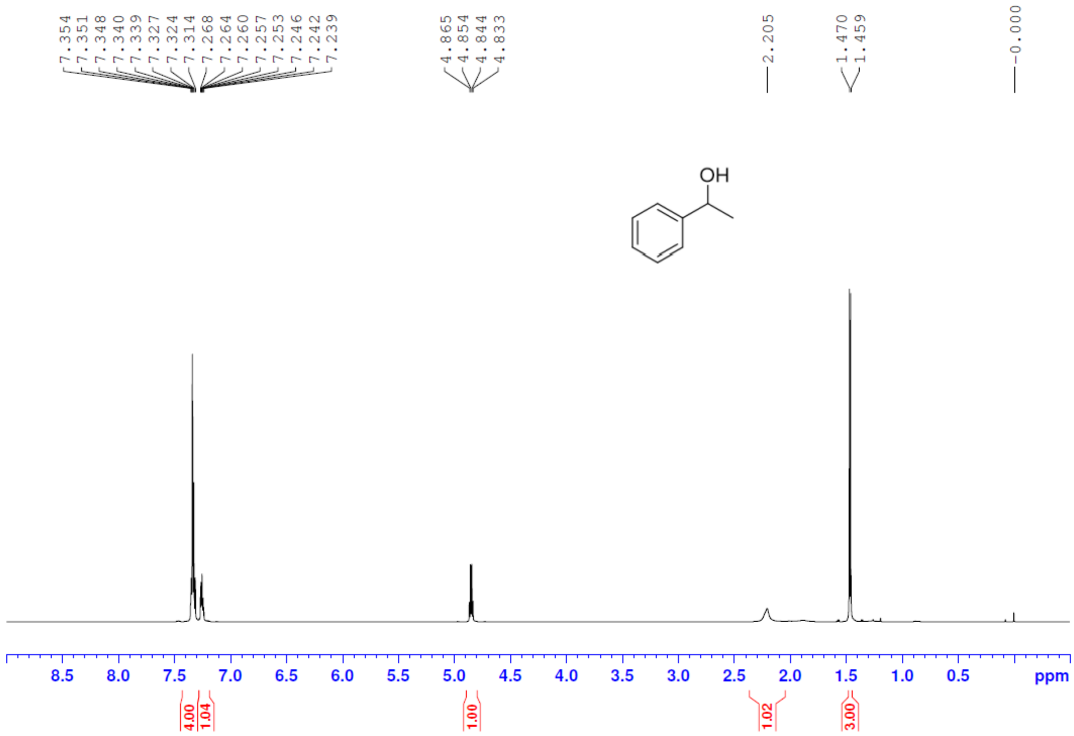


Fig. S108 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of **3a’**

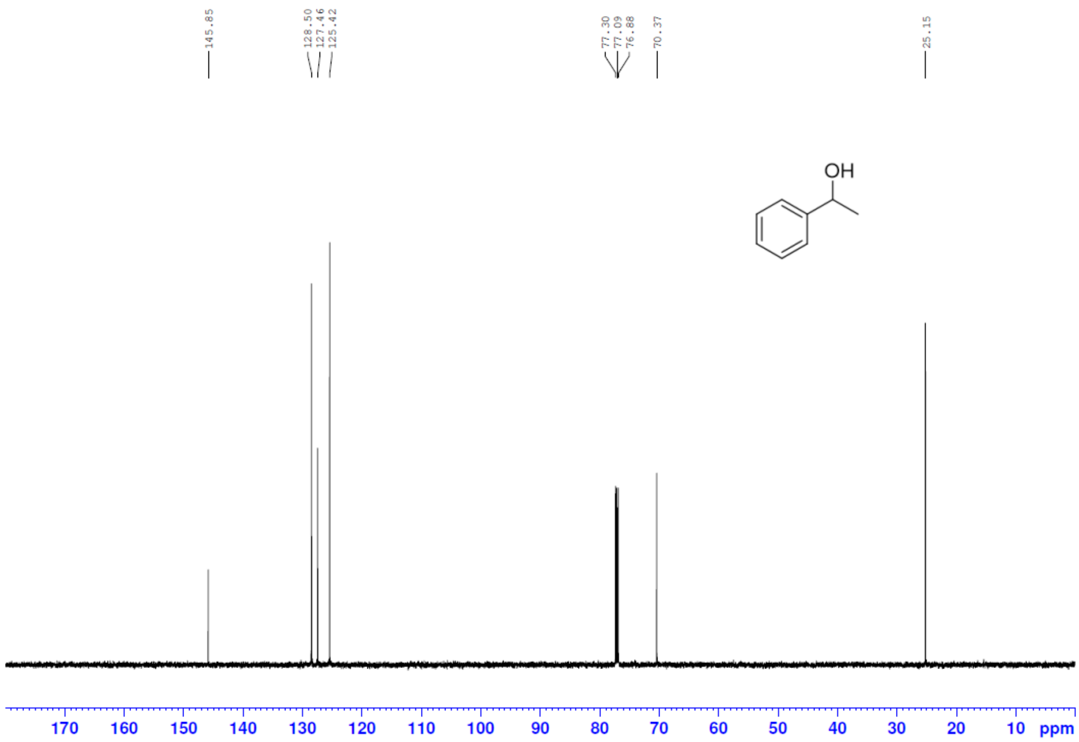


Fig. S109 ^{1}H NMR (600 MHz, $CDCl_3$) of **3d'**

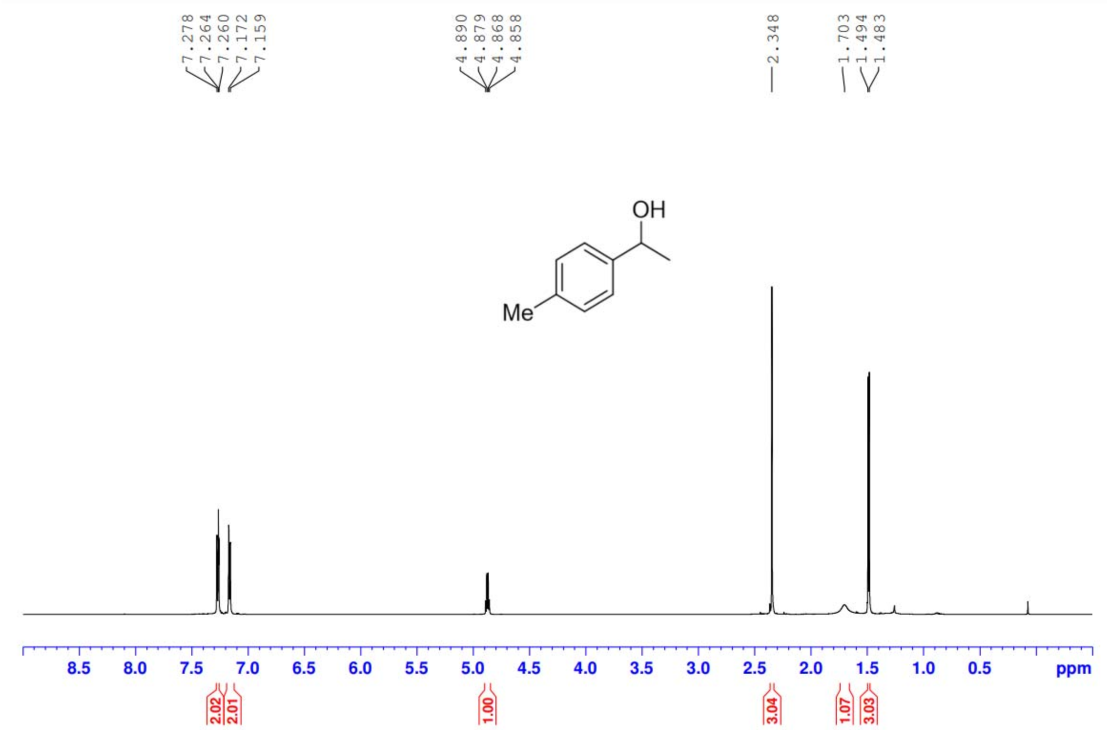


Fig. S110 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of **3d'**

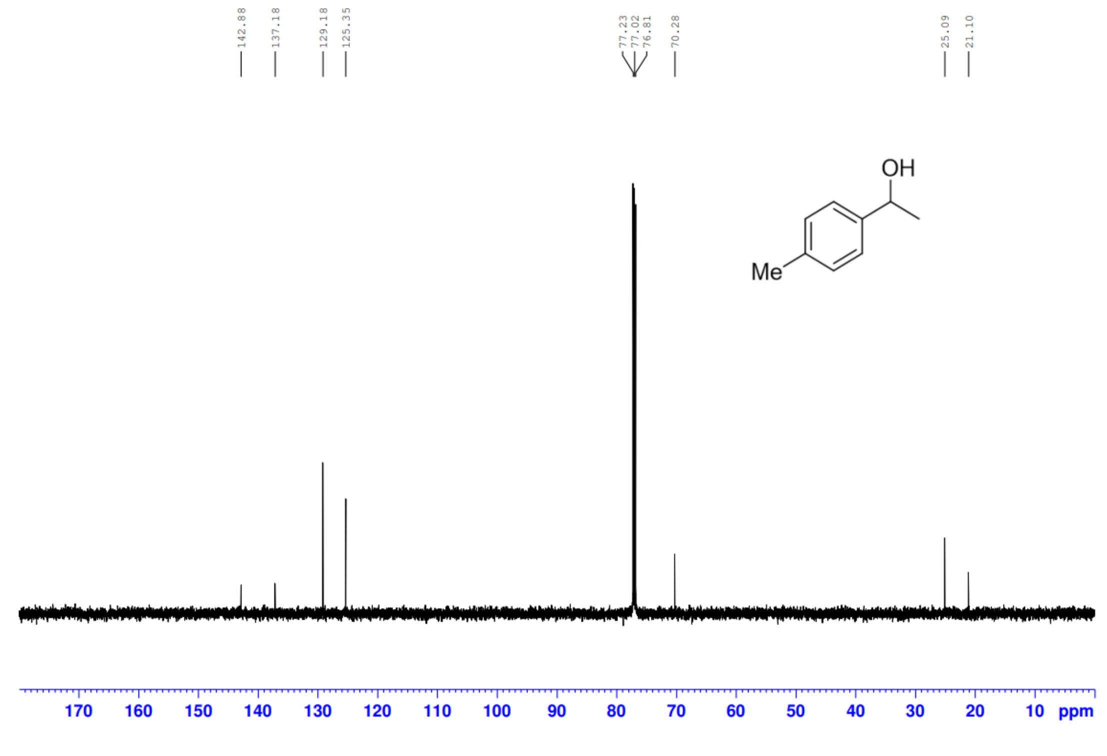


Fig. S111 ^{1}H NMR (600 MHz, $CDCl_3$) of **3q'**

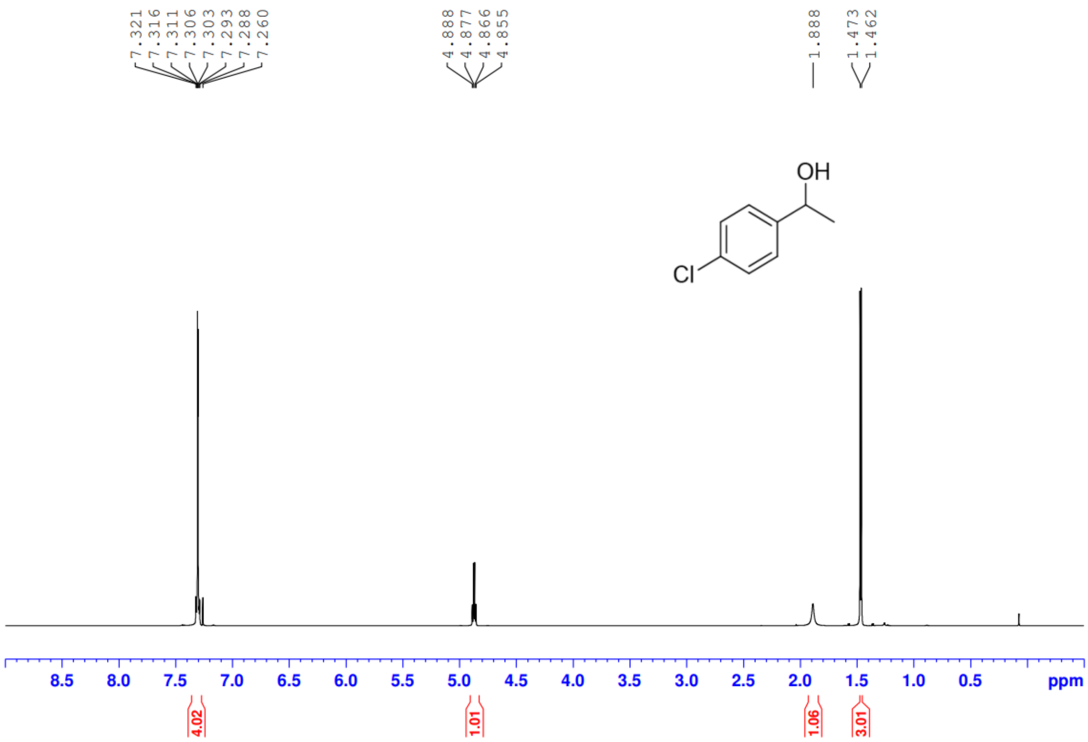


Fig. S112 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of **3q'**

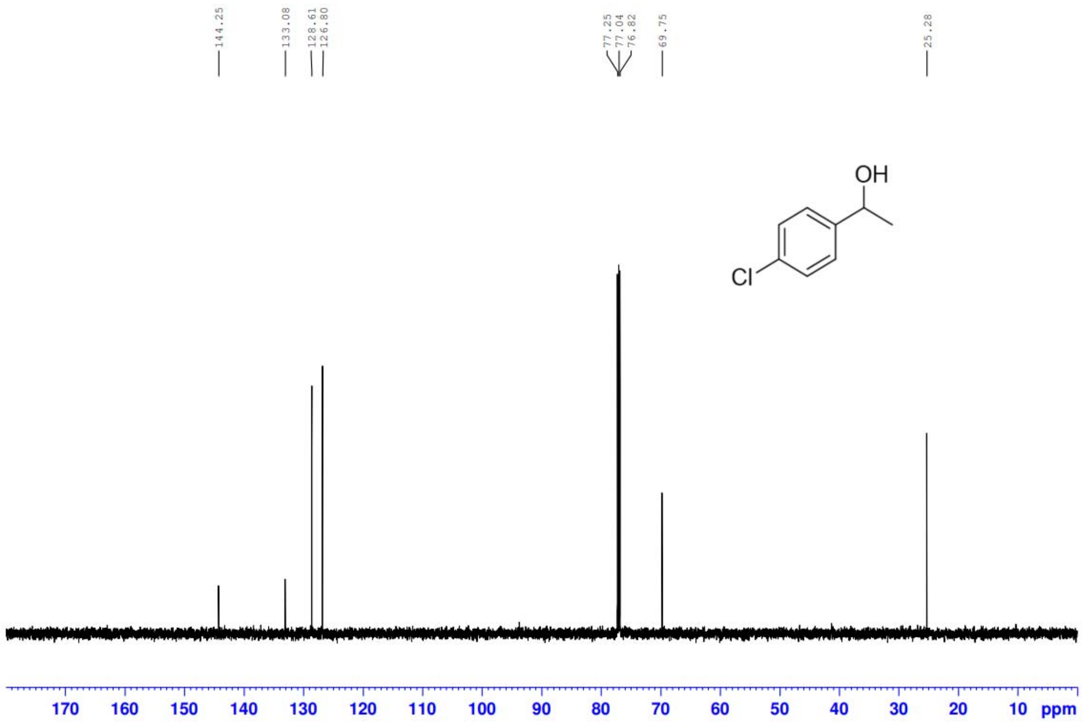


Fig. S113 ^{1}H NMR (600 MHz, $CDCl_3$) of **3z'**

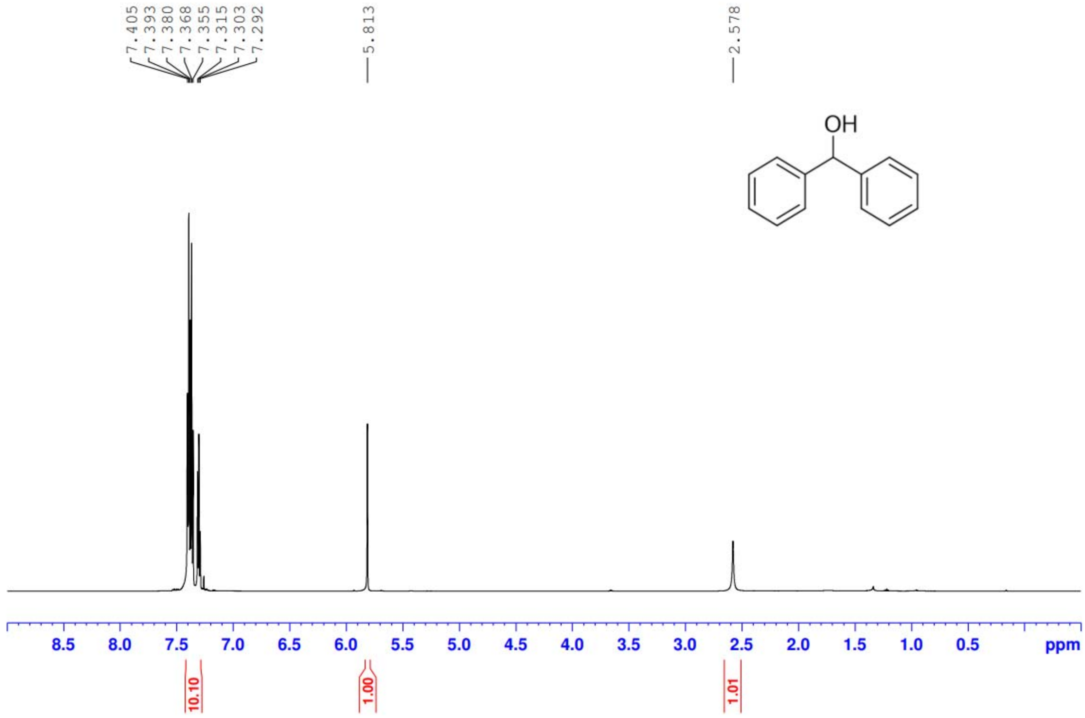


Fig. S114 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of **3z'**

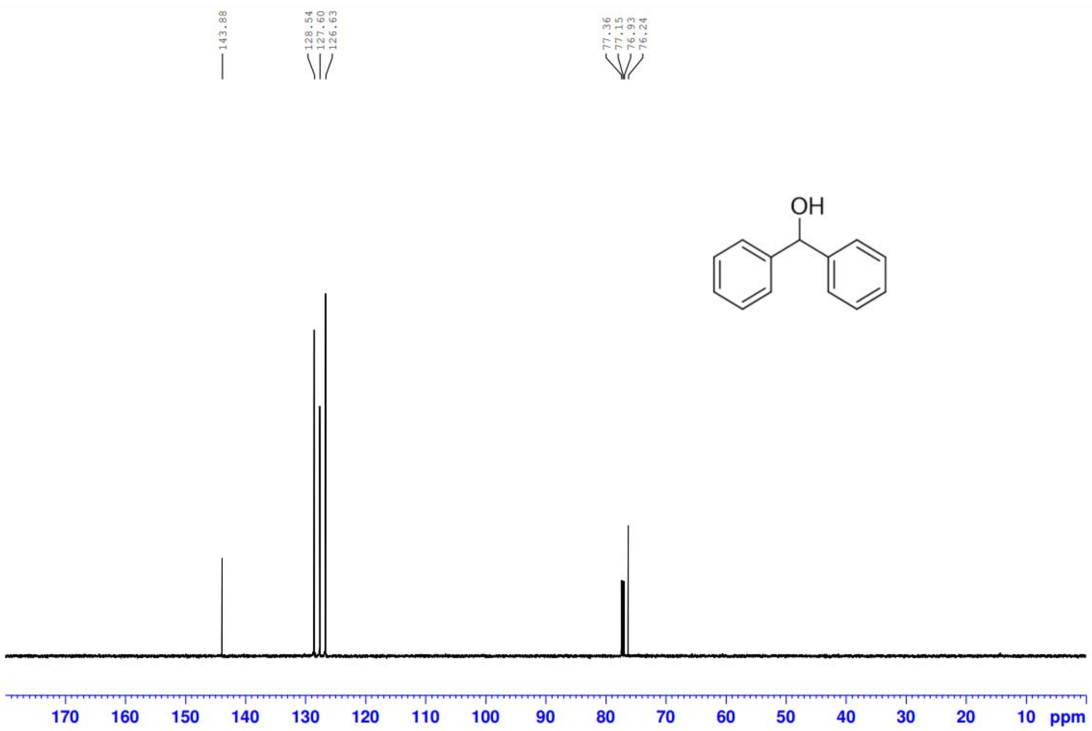


Fig. S115 ^{1}H NMR (600 MHz, $CDCl_3$) of **3ac'**

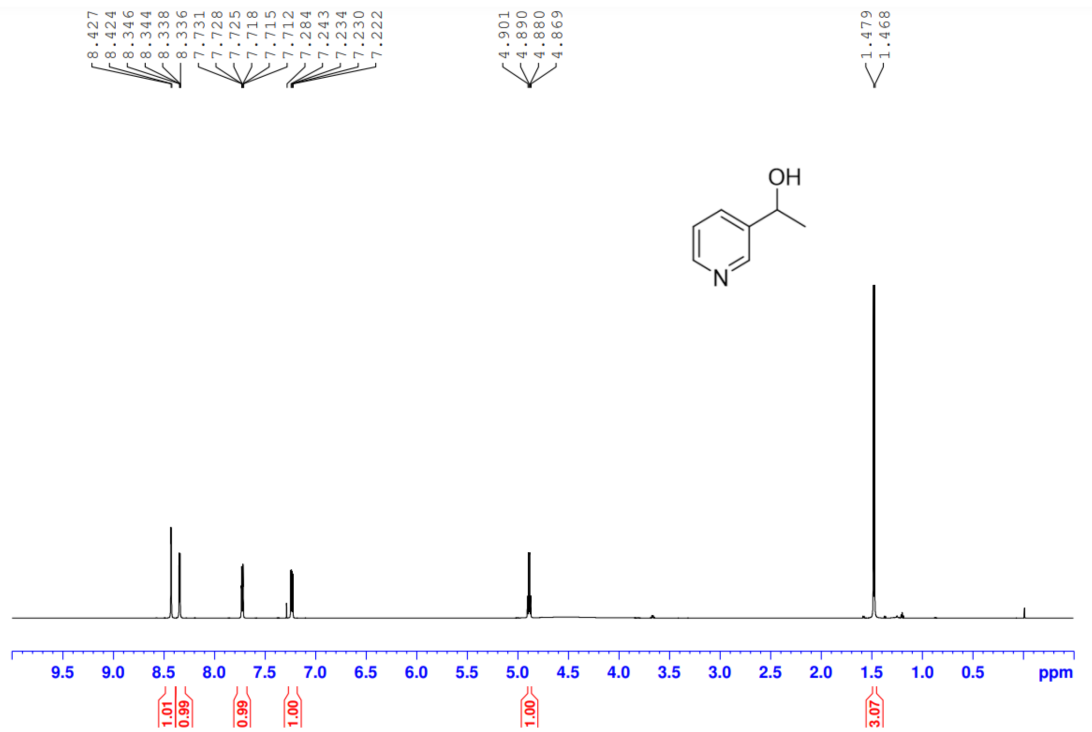


Fig. S116 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of **3ac'**

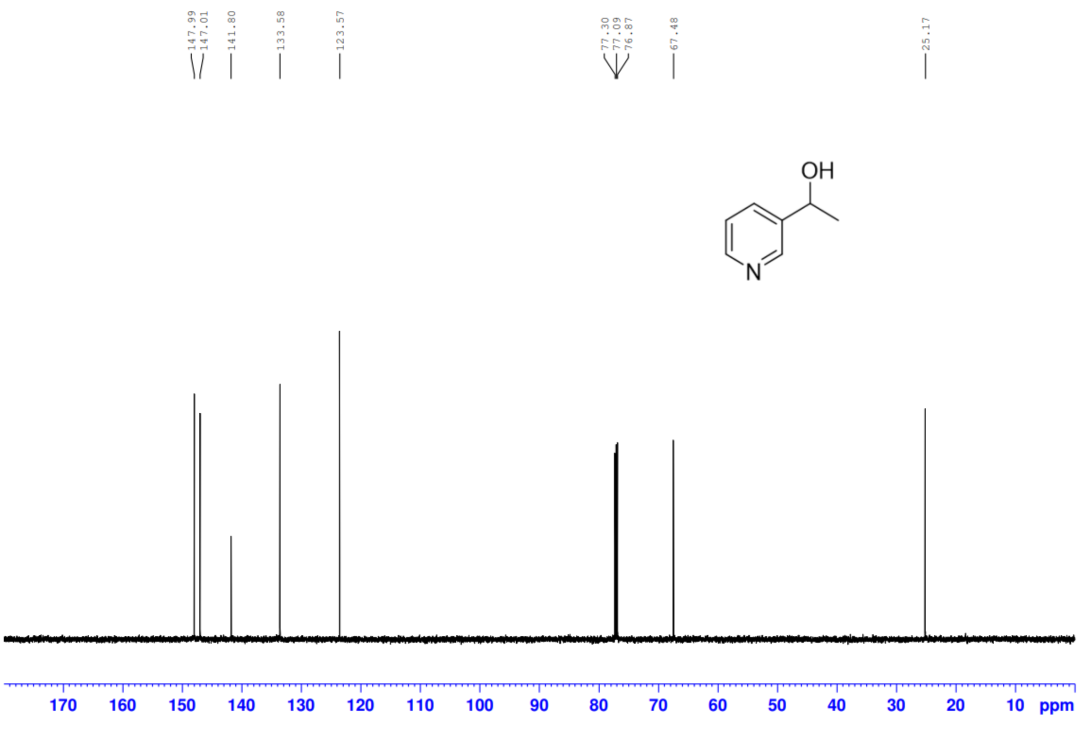


Fig. S117 ^{1}H NMR (600 MHz, $CDCl_3$) of **3af'**

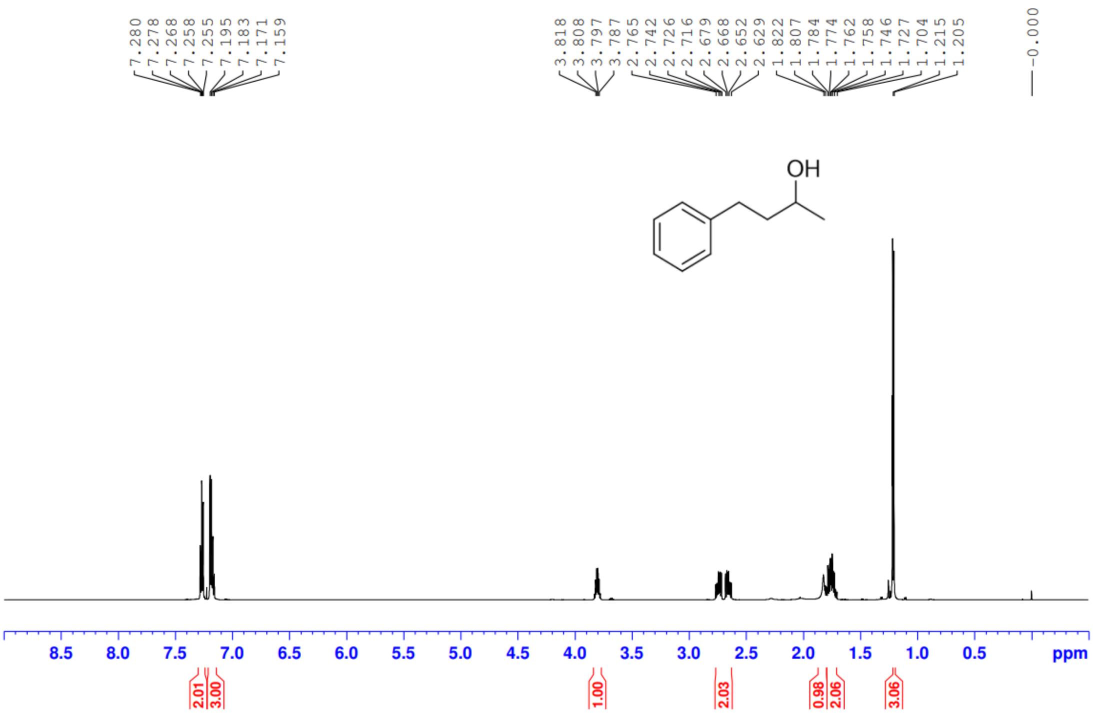
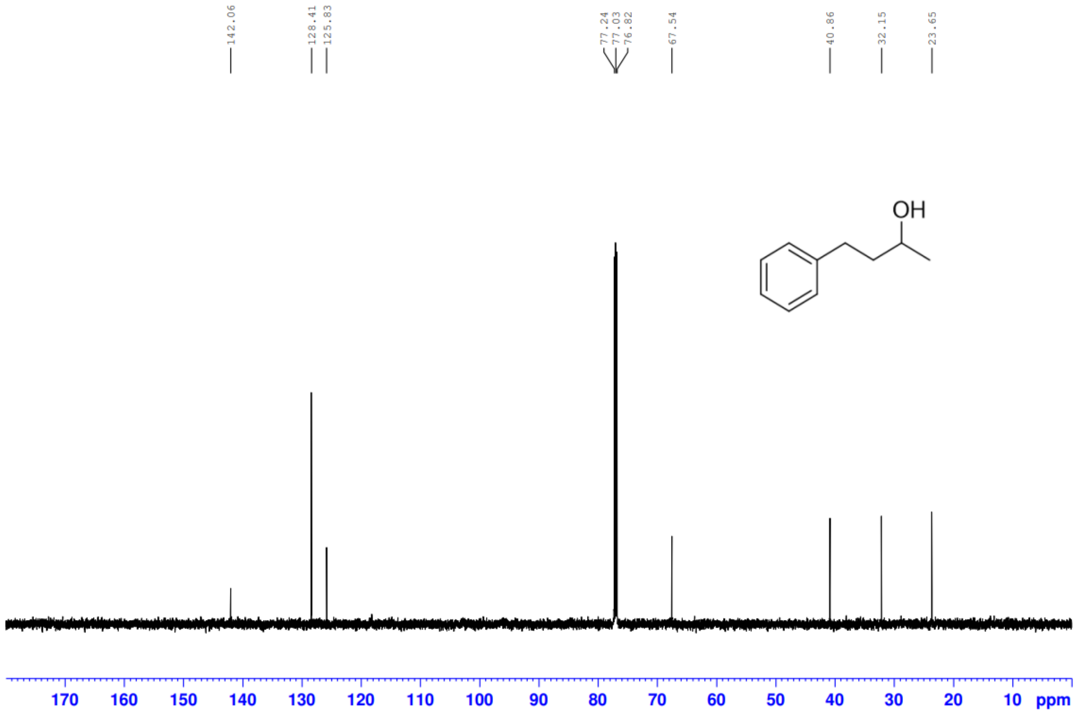


Fig. S118 $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of **3af'**



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