# Electronic Supporting Information for:

# Unlocking the Catalytic Potential of Tris(3,4,5-trifluorophenyl) Borane with Microwave Irradiation

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#### **GENERAL EXPERIMENTAL**

With the exception of the starting materials and column chromatography, all reactions and manipulations were carried out under an atmosphere of dry, O<sub>2</sub>-free nitrogen using standard double-manifold techniques with a rotary oil pump. A nitrogen-filled glove box (MBraun) was used to manipulate solids including the storage of starting materials, room temperature reactions, product recovery and sample preparation for analysis. Reagents were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, Acros, Fluorochem, TCI) and were used as received without purification. All solvents (Et<sub>2</sub>O, CHCl<sub>3</sub>, pentane) were dried by employing a solvent purification system MB SPS-800 and stored under a nitrogen atmosphere. Deuterated solvents were distilled and/or dried over molecular sieves before use. Microwave synthesis was carried out using a Biotage<sup>®</sup> Initiator+ Robot 60 Microwave Synthesizer. <sup>1</sup>H, {<sup>1</sup>H}<sup>13</sup>C, <sup>11</sup>B, and {<sup>1</sup>H}<sup>19</sup>F NMR spectra were recorded on a Bruker Avance II 400 spectrometer. Chemical shifts are expressed as parts per million (ppm,  $\delta$ ) downfield of tetramethylsilane (TMS) and are referenced to CDCl<sub>3</sub> (<sup>19</sup>F). The description of signals includes: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br. = broad. All coupling constants are absolute values and are expressed in Hertz (Hz). <sup>13</sup>C NMR were measured as <sup>1</sup>H decoupled. All spectra were analysed assuming a first order approximation.

#### General procedures.

#### General procedure a:

In accordance with the literature known procedure,<sup>[1]</sup> the required aldehyde (10 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and MgSO<sub>4</sub> was added. To this, the requisite amine (10 mmol) was added and the reaction was allowed to stir overnight. Subsequent filtration and removal of volatiles *in vacuo* left the pure imine.

#### **General procedure b**

In an NMR tube, pinacol borane (31.9 mg, 0.22 mmol) and the substrate (aldehyde/ketone/imine) (0.2 mmol) were combined in deuterated chloroform (0.7 mL). To this, tris(3,4,5-trifluorophenyl)borane (1.6 mg, 2 mol%, 0.004 mmol) was added, and the NMR tube sealed. The mixture was left at room temperature and conversion was monitored *via in situ* <sup>1</sup>H NMR spectroscopy using mesitylene (13.9  $\mu$ L, 0.1 mmol) as an internal standard until the desired boronate ester had been formed in >95% yield. A parallel reaction with the same amounts of reagents and catalyst, but without a mesitylene internal standard was also prepared and upon quantitative conversion the boronate ester was hydrolysed, either by passing the solution through a silica plug, or *via* washing with 1 M NaOH (3 x 10 mL), to isolate the desired alcohol or imine.

#### General procedure c

In an NMR tube, pinacol borane (31.9 mg, 0.22 mmol) and the substrate (aldehyde/ketone/imine) (0.2 mmol) were combined in deuterated chloroform (0.7 mL). To this, tris(3,4,5-trifluorophenyl)borane (1.6 mg, 2 mol%, 0.004 mmol) was added, and the NMR tube sealed. The mixture was heated to 70 °C and conversion was monitored *via in situ* <sup>1</sup>H NMR spectroscopy using mesitylene (13.9  $\mu$ L, 0.1 mmol) as an internal standard until the desired boronate ester had been formed in >95% yield. A parallel reaction with the same amounts of reagents and catalyst, but without a mesitylene internal standard was also prepared and upon quantitative conversion the boronate ester was hydrolysed, either by passing the solution through a silica plug, or *via* washing with 1 M NaOH (3 x 10 mL), to isolate the desired alcohol or imine.

#### General procedure d

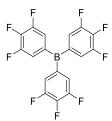
In a 2 mL microwave vial, pinacol borane (62.8 mg, 0.44 mmol), and the substrate (aldehyde/ketone/imine) (0.4 mmol) were combined in chloroform (2 mL). To this, tris(3,4,5-trifluorophenyl)borane (3.2 mg, 2 mol%, 0.008 mmol) was added, and the microwave vial sealed and placed into the microwave. The reaction was heated to 180 °C for 5 minutes, and the catalyst was removed by the addition of 1 M NaOH (5 mL) immediately after the microwave allowed the removal of the vial. The solution was washed with 1 M NaOH (3 x 5 mL), and the solvent was removed *in vacuo* to yield the desired product. For further purification, the desired alcohol/amine was isolated using flash column chromatography using a suitable eluent.

#### General procedure e

In a 2 mL microwave vial, pinacol borane (62.8 mg, 0.44 mmol), and the substrate (alkene/alkyne) (0.4 mmol) were combined in chloroform (2 mL). To this, tris(3,4,5-trifluorophenyl)borane (8.1 mg, 5 mol%, 0.02 mmol) was added, and the microwave vial sealed and placed into the microwave. The reaction was heated to 180 °C for 90 minutes, and the catalyst was removed by passing the solution through a silica plug. The solvent was subsequently removed *in vacuo* to yield the desired boronate ester. For further purification, the desired alcohol/amine was isolated using flash column chromatography using a suitable eluent.

#### Starting material synthesis:

# Tris(3,4,5-trifluorophenyl)borane B(3,4,5-Ar<sup>F</sup>)<sub>3</sub>



Mg turnings (3.053 g, 0.126 mol) were suspended in  $Et_2O$  and cooled to 0 °C. 1,2dibromoethane (0.1 mL, 1.17 mmol) and 1-bromo-3,4,5-fluorobenzene (15 mL, 0.126 mol) were added dropwise with vigorous stirring. After addition, the reaction mixture was allowed to warm to room temperature and stirred until all magnesium turnings were consumed. The solution was then cooled to 0 °C and added dropwise to a solution of

BF<sub>3</sub>•Et<sub>2</sub>O (5.184 mL, 0.042 mol) in Et<sub>2</sub>O, also at 0 °C. The solution was allowed to warm to room temperature and stirred for a further hour. All volatiles were removed *in vacuo*, and sublimation of the resultant solid (120 °C, 1 x 10<sup>-3</sup> mbar) resulted in oily yellow crystals. These yellow crystals were washed with pentane (3 x 5 mL), and sublimed again (120 °C, 1 x 10<sup>-3</sup> mbar) to afford tris(3,4,5-trifluorophenyl)borane as white crystals. Yield: 2.03 g, 5.02 mmol, 11.9%. Spectroscopic data agrees with literature values.<sup>[2]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 7.17 (m, 6H). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 65.0 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 151.5 (ddd, <sup>1</sup>J<sub>CF</sub> = 253.8 Hz, <sup>2</sup>J<sub>CF</sub> = 10.0 Hz, <sup>3</sup>J<sub>CF</sub> = 3.1 Hz, *m*C), 142.9 (dt, <sup>1</sup>J<sub>CF</sub> = 260.8 Hz, <sup>2</sup>J<sub>CF</sub> = 16.7 Hz, *p*C), 136.4 – 136.0, (m, C-B), 121.9 (dd, <sup>2</sup>J<sub>CF</sub> = 13.6, <sup>3</sup>J<sub>CF</sub> = 5.0 Hz, *o*C). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: -133.18 (d, <sup>3</sup>J<sub>HF</sub> = 20.0 Hz, *m*F), -152.39 (t, <sup>3</sup>J<sub>HF</sub> = 19.8 Hz, *p*F).

#### (Z)-N,1-diphenylmethanimine



Synthesised in accordance with general procedure **a** using benzaldehyde (1.02 mL, 10 mmol) and aniline (913  $\mu$ L, 10 mmol). Spectroscopic analyses agree with literature values.<sup>[3]</sup> Yield: 1.63 g, 9.0 mmol, 90%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 8.43 (s, 1H, CH), 7.90 – 7.80 (m, 2H, aryl), 7.55 – 7.31 (m, 5H, aryl), 7.28 – 7.05 (m, 3H, aryl).

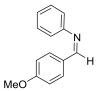
#### (Z)-N-phenyl-1-(p-tolyl)methanimine



Synthesised in accordance with general procedure **a** using 4-tolualdehyde (1.18 mL, 10 mmol) and aniline (913  $\mu$ L, 10 mmol). Spectroscopic analyses agree with literature values.<sup>[4]</sup> Yield: 1.79 g, 9.2 mmol, 92%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 8.42 (s, 1H, CH), 7.76 (d, <sup>3</sup>J<sub>HH</sub> = 8.9 Hz, 1H, aryl), 7.12 – 7.05 (m, 2H, aryl), 7.03 (dd, <sup>3</sup>J<sub>HH</sub> = 7.4, <sup>4</sup>J<sub>HH</sub> = 1.6 Hz, 1H, aryl), 6.99 (d,

<sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 1H, aryl), 6.96 – 6.87 (m, 4H, aryl), 2.26 (s, 3H, Me).

# (Z)-1-(4-methoxyphenyl)-N-phenylmethanimine



Synthesised in accordance with general procedure a using 4-anisaldehyde (1.22 mL, 10 mmol) and aniline (913  $\mu$ L, 10 mmol). Spectroscopic analyses agree with literature values.<sup>[4]</sup> Yield: 1.88 g, 8.9 mmol, 89%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 8.44 (s, 1H, CH), 7.91  $(d, {}^{3}J_{HH} = 8.9 \text{ Hz}, 2\text{H}, aryl), 7.50 - 7.41 (m, 2\text{H}, aryl), 7.30 - 7.23 (m, 3\text{H}, aryl), 7.04 (d, {}^{3}J_{HH} =$ 

8.8 Hz, 2H, aryl), 3.92 (s, 3H, OMe).

#### (Z)-1-(4-(trifluoromethyl)phenyl)-N-phenylmethanimine



Synthesised in accordance with general procedure a using 4-(trifluoromethyl)benzaldehyde (1.36 mL, 10 mmol) and aniline (913 µL, 10 mmol). Spectroscopic analyses agree with literature values.<sup>[5]</sup> Yield: 2.34 g, 9.4 mmol, 94%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 8.44 (s, 1H, CH), 7.95 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 2H, aryl), 7.66 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2H, aryl), 7.47 – 7.28

(m, 2H, aryl), 7.25 – 7.11 (m, 3H, aryl). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 62.81 (s, 3F, p-CF<sub>3</sub>)

#### (Z)-1-phenyl-N-(4-(trifluoromethyl)phenyl)methanimine



Synthesised in accordance with general procedure a using benzaldehyde (1.02 mL, 10 mmol) and 4-trifluoromethylaniline (1.26 mL, 10 mmol). Spectroscopic analyses agree with literature values.<sup>[4]</sup> Yield 2.32 g, 9.3 mmol, 93%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 8.43 (s, 1H, CH), 7.92 (dd, <sup>3</sup>Јнн = 7.8, <sup>4</sup>Јнн = 1.8 Hz, 2H, aryl), 7.65 (d, <sup>3</sup>Јнн = 8.3 Hz, 2H, aryl), 7.58 – 7.46 (m, 3H,

aryl), 7.26 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, aryl). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 62.00 (s, 3F, p-CF<sub>3</sub>)

#### (Z)-N-isopropyl-1-phenylmethanimine



Synthesised in accordance with general procedure a using benzaldehyde (1.02 mL, 10 mmol) and isopropylamine (859 µL, 10 mmol). Spectroscopic analyses agree with literature values.<sup>[4]</sup> Yield: 1.32 g, 9.0 mmol, 90%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 8.31 (s, 1H, CH), 7.79 – 7.68 (m, 2H, aryl), 7.51 – 7.35 (m, 3H, aryl), 3.54 (hept, <sup>3</sup>Јнн = 6.4 Hz, 1H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.27 (d, <sup>3</sup>Јнн = 6.3 Hz, 6H, CH(C<u>H<sub>3</sub>)<sub>2</sub>).</u>

# (Z)-N-butyl-1-phenylmethanimine

C<sub>4</sub>H<sub>9</sub> N Synthesised in accordance with general procedure a using benzaldehyde (1.02 mL, 10 mmol) and *n*-butylamine (988 µL, 10 mmol). Spectroscopic analyses agree with literature values.<sup>[4]</sup> Yield: 1.47 g, 9.1 mmol, 91%.  $^{1}$ H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 8.19 (s, 1H, CH), 7.93 – 7.56 (m, 2H, aryl), 7.36 – 7.29 (m, 3H, aryl), 3.54 (t, <sup>3</sup>J<sub>HH</sub> = 7.0, 2H, NCH<sub>2</sub>), 1.67 – 1.58 (m, 2H, CH<sub>2</sub>), 1.38 – 1.27 (m, 2H, CH<sub>2</sub>), 0.88 (t,  ${}^{3}J_{HH}$  = 7.4 Hz, 3H, CH<sub>3</sub>).

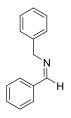
#### (Z)-N-cyclopentyl-1-phenylmethanimine



Synthesised in accordance with general procedure **a** using benzaldehyde (1.02 mL, 10 mmol) and cyclopentylamine (987  $\mu$ L, 10 mmol). Spectroscopic analyses agree with literature values.<sup>[4]</sup> Yield: 1.61 g, 9.3 mmol, 93%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 8.29 (s, 1H, CH), 7.73 (dd, <sup>3</sup>*J*<sub>HH</sub> = 6.7, <sup>4</sup>*J*<sub>HH</sub> = 3.0 Hz, 2H, aryl), 7.75 – 6.58 (m, 3H, aryl), 3.77 (p, <sup>3</sup>*J*<sub>HH</sub> = 6.3 Hz, 1H), 1.96 – 1.83 (m, 4H,

cyclopentyl H), 1.80 – 1.63 (m, 4H, cyclopentyl H).

### (Z)-N-benzyl-1-phenylmethanimine



Synthesised in accordance with general procedure **a** using benzaldehyde (1.02 mL, 10 mmol) and benzylamine (1.09 mL, 10 mmol). Spectroscopic analyses agree with literature values.<sup>[4]</sup> Yield: 1.72 g, 8.8 mmol, 88%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 8.30 (s, 1H, CH<sub>2</sub>), 7.71 (dd, <sup>3</sup>J<sub>HH</sub> = 6.8, <sup>4</sup>J<sub>HH</sub> = 2.9 Hz, 2H, aryl), 7.37 – 7.28 (m, 3H, aryl), 7.26 (d, <sup>2</sup>J<sub>HH</sub> = 4.4 Hz, 4H, aryl), 7.23 – 7.16 (m, 1H, aryl), 4.74 (s, 2H, CH<sub>2</sub>).

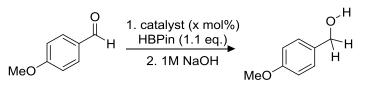
#### (E)-N,1-diphenylethan-1-imine



In accordance with the literature known procedure,<sup>[6]</sup> a flame dried Schlenk was charged with dry toluene, dry 3 Å molecular sieves, acetophenone (2 mL, 17.1 mmol), and aniline (3 mL, 32.9 mmol). The reaction was heated to reflux for 18 h and filtered to remove molecular sieves. The volatiles were removed *in vacuo*, and the product was purified by Kugelrohr distillation to yield

the pure imine. Spectroscopic analyses agree with literature values.<sup>[6]</sup> Yield: 1.17 g,, 5.9 mmol, 35%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm:  $\delta$  8.05 – 7.96 (m, 2H, aryl), 7.50 – 7.42 (m, 3H, aryl), 7.36 (t, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 2H), 7.10 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 1H, aryl), 6.81 (d, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 2H), 2.25 (s, 3H, Me).

# **Optimization of microwave reaction conditions**



Entry	Catalyst	Catalyst loading (mol%)	Time (min)	Conversion (%) <sup>[a]</sup>
1	No catalyst	-	5	11
2	B(3,4,5-Ar <sup>F</sup> ) <sub>3</sub>	0.5	1	40
3	B(3,4,5-Ar <sup>F</sup> ) <sub>3</sub>	0.5	3	60
4	B(3,4,5-Ar <sup>F</sup> ) <sub>3</sub>	0.5	5	73
5	B(3,4,5-Ar <sup>F</sup> ) <sub>3</sub>	1	1	70
6	B(3,4,5-Ar <sup>F</sup> ) <sub>3</sub>	1	3	80
7	B(3,4,5-Ar <sup>F</sup> ) <sub>3</sub>	1	5	90
8	B(3,4,5-Ar <sup>F</sup> ) <sub>3</sub>	2	1	80
9	B(3,4,5-Ar <sup>F</sup> ) <sub>3</sub>	2	3	93
10	B(3,4,5-Ar <sup>F</sup> )₃	2	5	>95
11	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	2	5	30

Anisaldehyde (0.4 mmol, 54.4 mg), HBPin (0.44 mmol, 63.8  $\mu$ L). Microwave reaction conditions - 180 °C, 20 bar. Pressure and temperature were measured by the microwave's in-built sensors <sup>[a]</sup>Conversion determined by <sup>1</sup>H NMR spectroscopy.

#### Synthesis of products

#### Phenylmethanol (2a)



In accordance with general procedure **b**, using benzaldehyde (21.2 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 2 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 20 mg, 185  $\mu$ mol, 93%.

In accordance with general procedure **c**, using benzaldehyde (21.2 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 0.5 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 19 mg, 175 µmol, 88%.

In accordance with general procedure **d**, using benzaldehyde (42.2 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 41 mg, 379 µmol, 95%.

Spectroscopic data agrees with literature values.<sup>[7] 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 7.65 – 6.96 (m, 5H, aryl), 4.55 (s, 2H, CH<sub>2</sub>), 2.17 (s, 1H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 140.9 (s), 128.6 (s), 127.7 (s), 127.1 (s), 65.3 (s).

#### p-Tolylmethanol (2b)



In accordance with general procedure **b**, using 4-methylbenzaldehyde (24.0 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 24 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 23 mg,

188 µmol, 94%.

In accordance with general procedure **c**, using 4-methylbenzaldehyde (24.0 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 0.5 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 23 mg, 188 µmol, 94%.

In accordance with general procedure **d**, using 4-methylbenzaldehyde (48.0 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 42 mg, 341 µmol, 85%.

Spectroscopic data agrees with literature values.<sup>[7]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 7.26 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 2H, aryl), 7.18 (d, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 2H, aryl), 4.64 (s, 2H, CH<sub>2</sub>), 2.36 (s, 3H, Me), 1.81 (s, 1H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 138.0 (s), 137.5 (s), 129.4 (s), 127.2 (s), 65.4 (s), 21.3 (s).

#### (4-Methoxyphenyl)methanol (2c)



In accordance with general procedure **b**, using 4-methoxybenzaldehyde (27.2 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 24 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 24 mg,

#### 174 µmol, 87%.

In accordance with general procedure **c**, using 4-methoxybenzaldehyde (27.2 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 0.5 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 27 mg, 196  $\mu$ mol, 98%.

In accordance with general procedure **d**, using 4-methoxybenzaldehyde (54.5 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 49 mg, 355 µmol, 88%.

Spectroscopic data agrees with literature values.<sup>[7]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 7.15 (d, <sup>3</sup>J<sub>HH</sub> = 8.8 Hz, 2H, aryl), 6.77 (d, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz, 2H, aryl), 4.44 (s, 2H, CH<sub>2</sub>), 3.68 (s, 3H, OMe), 2.41 (s, 1H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 159.1 (s), 133.2 (s), 128.7 (s), 113.9 (s), 64.8 (s), 55.3 (s).

#### (4-(Trifluoromethyl)phenyl)methanol (2d)



In accordance with general procedure **b**, using 4-(trifluoromethyl)benzaldehyde (34.8 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 16 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 33

mg, 187 µmol, 94%.

In accordance with general procedure **c**, using 4-(trifluoromethyl)benzaldehyde (34.8 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 0.5 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 33 mg, 187  $\mu$ mol, 94%.

In accordance with general procedure **d**, using 4-(trifluoromethyl)benzaldehyde (69.6 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 64 mg, 364 µmol, 91%.

Spectroscopic data agrees with literature values.<sup>[8]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 7.58 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H, aryl), 7.42 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2H, aryl), 4.69 (s, 2H, CH<sub>2</sub>), 2.76 (s, 1H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 144.8 (s), 129.8 (q, <sup>2</sup>J<sub>CF</sub> = 32.4 Hz), 126.9 (s), 125.5 (q, <sup>1</sup>J<sub>CF</sub> = 3.8 Hz), 64.4 (s). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: -62.51 (s, 3F, *p*-CF<sub>3</sub>).

#### (4-Nitrophenyl)methanol (2e)



In accordance with general procedure **b**, using 4-nitrobenzaldehyde (30.2 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 16 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a brown oil. Yield: 30 mg, 196

#### µmol, 98%.

In accordance with general procedure **c**, using 4-nitrobenzaldehyde (30.2 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 0.5 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a brown oil. Yield: 26 mg, 170  $\mu$ mol, 85%.

In accordance with general procedure **d**, using 4-nitrobenzaldehyde (60.4 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a brown oil. Yield: 57 mg, 372 µmol, 93%.

Spectroscopic data agrees with literature values.<sup>[7]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 8.18 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H, aryl), 7.51 (d, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2H, aryl), 4.82 (s, 2H, CH<sub>2</sub>), 2.30 (s, 1H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 148.4 (s), 147.3 (s), 127.1 (s), 123.8 (s), 64.1 (s).

#### 1-Phenylethanol (2f)

OH In accordance with general procedure b, using acetophenone (24.0 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 1 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 22 mg, 180 µmol, 90%. General procedures c and d were not required due to rapid reaction at room temperature. Spectroscopic data agrees with literature values.<sup>[9]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 7.38 – 7.32 (m, 4H, aryl), 7.28 – 7.24 (m, 1H, aryl), 4.88 (q, <sup>3</sup>J<sub>HH</sub> = 6.2 Hz, 1H, CH), 1.87 (s, 1H, OH), 1.49 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298K)

#### 1-(p-Tolyl)ethan-1-ol (2g)

298K) δ/ppm: 145.9 (s), 128.6 (s), 127.6 (s), 125.5 (s), 70.6 (s), 25.3 (s).



In accordance with general procedure **b**, using 4-methylacetophenone (26.8 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 1 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 26 mg,

191 µmol, 96%. General procedures **c** and **d** were not required due to rapid reaction at room temperature. Spectroscopic data agrees with literature values.<sup>[9] 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 7.19 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, aryl), 7.08 (d, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 2H, aryl), 4.79 (q, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 1H, CH), 2.27 (s, 3H, Me), 1.77 (s, 1H, OH), 1.41 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 142.9 (s), 137.2 (s), 129.2 (s), 125.4 (s), 70.3 (s), 25.1 (s), 21.1 (s).

#### 1-(4-trifluoromethyl)phenyl)ethan-1-ol (2h)



In accordance with general procedure **b**, using 4-(trifluoromethyl)acetophenone (37.6 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 2 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 34

#### mg, 179 μmol, 89%.

In accordance with general procedure **c**, using 4-(trifluoromethyl)acetophenone (37.6 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 0.5 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 33 mg, 174  $\mu$ mol, 87%.

In accordance with general procedure **d**, using 4-(trifluoromethyl)acetophenone (75.2 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed 71% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 48 mg, 253 µmol, 63%.

Spectroscopic data agrees with literature values.<sup>[8]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 7.61 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, aryl), 7.49 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, aryl), 4.97 (q, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 1H, CH), 1.90 (s, 1H, OH), 1.51 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 149.8 (s), 129.8 (q, <sup>2</sup>J<sub>CF</sub> = 32.3 Hz), 125.8 (s), 125.6 (q, <sup>1</sup>J<sub>CF</sub> = 3.7 Hz), 70.0 (s), 25.6 (s). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: -62.46 (s, 3F, *p*-CF<sub>3</sub>).

#### 1-(4-Nitrophenyl)ethan-1-ol (2i)

<sup>OH</sup> In accordance with general procedure **b**, using 4-nitroacetophenone (33.0 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 0.5 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a brown oil. Yield: 30 mg, 180 μmol, 90%. General procedures **c** and **d** were not required due to rapid reaction at room temperature. Spectroscopic data agrees with literature values.<sup>[9]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 8.18 (d, <sup>3</sup>J<sub>HH</sub> = 8.8 Hz, 2H, aryl), 7.53 (d, <sup>3</sup>J<sub>HH</sub> = 8.8 Hz, 2H, aryl), 5.02 (q, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 1H, CH), 1.51 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 153.2 (s), 147.3 (s), 126.2 (s), 123.9 (s), 69.6 (s), 25.6 (s).

#### **Diphenylmethanol (2j)**



In accordance with general procedure **b**, using benzophenone (36.4 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 156 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 31 mg,

#### 168 µmol, 85%.

In accordance with general procedure **c**, using benzophenone (36.4 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 30 h. Between 30 h and 72h there was no increase in conversion from 85%, and the title compound was isolated by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent. Yield: 26 mg, 141  $\mu$ mol, 71%.

In accordance with general procedure **d**, using benzophenone (72.8 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed 25%

conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 14 mg, 76  $\mu$ mol, 19%.

Spectroscopic data agrees with literature values.<sup>[10]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 7.34 – 7.22 (m, 8H, aryl), 7.21 – 7.15 (m, 2H, aryl), 5.75 (s, 1H, CH), 2.20 (s, 1H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 143.9 (s), 128.6 (s), 127.7 (s), 126.7 (s), 76.4 (s).

#### N-Benzylaniline (2k)



In accordance with general procedure **b**, using (*Z*)-*N*,1-diphenylmethanimine (36.2 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 24 h. The boronate ester was hydrolysed *via* a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 34 mg, 186  $\mu$ mol, 93%.

In accordance with general procedure **c**, using (*Z*)-*N*,1-diphenylmethanimine (36.2 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 1 h. The boronate ester was hydrolysed *via* a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 32 mg, 175  $\mu$ mol, 87%.

In accordance with general procedure **d**, using (*Z*)-*N*,1-diphenylmethanimine (72.4 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 68 mg, 371  $\mu$ mol, 93%.

Spectroscopic data agrees with literature values.<sup>[2]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 7.39 (q, <sup>3</sup>*J*<sub>HH</sub> = 8.2 Hz, 4H, aryl), 7.32 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.7 Hz, 1H, aryl), 7.22 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 2H, aryl), 6.76 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, 1H, aryl), 6.68 (d, <sup>3</sup>*J*<sub>HH</sub> = 9.4 Hz, 2H, aryl), 4.36 (s, 2H, CH<sub>2</sub>), 4.05 (s, 1H, NH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 148.3 (s), 139.6 (s), 129.4 (s), 128.8 (s), 127.6 (s), 127.3 (s), 117.7 (s), 113.0 (s), 48.4 (s).

#### *N*-(4-Methylbenzyl)aniline (2l)



In accordance with general procedure **b**, using (*Z*)-*N*-phenyl-1-(*p*-tolyl)methanimine (39.0 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 60 h. The boronate ester was hydrolysed *via* a basic workup (3 x 10 mL 1 M NaOH washings) through a silica plug to isolate the title compound as a colourless oil. Yield: 38 mg, 193  $\mu$ mol, 96%.

In accordance with general procedure **c**, using (*Z*)-*N*-phenyl-1-(*p*-tolyl)methanimine (39.0 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 4 h. The boronate ester was hydrolysed *via* a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 34 mg, 172  $\mu$ mol, 86%.

In accordance with general procedure **d**, using (*Z*)-*N*-phenyl-1-(*p*-tolyl)methanimine (78.0 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 61 mg, 309 µmol, 77%.

Spectroscopic data agrees with literature values.<sup>[11]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 7.29 – 7.24 (m, 2H, aryl), 7.22 – 7.11 (m, 4H, aryl), 6.71 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 1H, aryl), 6.66 – 6.62 (m, 2H, aryl), 4.29 (s, 2H, CH<sub>2</sub>), 3.98 (s, 1H, NH), 2.35 (s, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 148.3 (s), 137.0 (s), 136.5 (s), 129.4 (s), 129.4 (s), 127.7 (s), 117.6 (s), 112.9 (s), 48.2 (s), 21.3 (s).

#### *N*-(4-Methoxybenzyl)aniline (2m)



In accordance with general procedure **b**, using (Z)-1-(4-methoxyphenyl)-*N*-phenylmethanimine (42.2 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 36 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 39 mg, 183 μmol, 92%.

In accordance with general procedure **c**, using (*Z*)-1-(4-methoxyphenyl)-*N*-phenylmethanimine (42.2 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 4 h. The boronate ester was hydrolysed through a silica plug to isolate the title compound as a colourless oil. Yield: 40 mg, 188  $\mu$ mol, 94%.

In accordance with general procedure **d**, using (*Z*)-1-(4-methoxyphenyl)-*N*-phenylmethanimine (84.4 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 77 mg, 361  $\mu$ mol, 90%.

Spectroscopic data agrees with literature values.<sup>[12]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 7.31 (d, <sup>3</sup>J<sub>HH</sub> = 8.8 Hz, 2H, aryl), 7.24 – 7.15 (m, 2H, aryl), 6.90 (d, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz, 2H, aryl), 6.73 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 1H, aryl), 6.65 (d, <sup>3</sup>J<sub>HH</sub> = 9.7 Hz, 2H, aryl), 4.27 (s, 2H, CH<sub>2</sub>), 3.96 (s, 1H, NH), 3.82 (s, 3H, OMe). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 159.0 (s), 148.3 (s), 131.5 (s), 129.4 (s), 128.9 (s), 117.6 (s), 114.1 (s), 113.0 (s), 55.4 (s), 47.9 (s).

#### *N*-(4-Trifluoromethyl)benzyl)aniline (2n)



In accordance with general procedure **b**, using (Z)-1-(4-(trifluoromethyl)phenyl)-*N*-phenylmethanimine (49.8 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 8 h. The boronate ester was hydrolysed *via* a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 46 mg, 183 µmol, 92%.

In accordance with general procedure **c**, using (*Z*)-1-(4-(trifluoromethyl)phenyl)-*N*-phenylmethanimine (49.8 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 2 h. The boronate ester was hydrolysed *via* a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 41 mg, 163  $\mu$ mol, 82%.

In accordance with general procedure **d**, using (*Z*)-1-(4-(trifluoromethyl)phenyl)-*N*-phenylmethanimine (99.6 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 1 h. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 86 mg, 343  $\mu$ mol, 86%.

Spectroscopic data agrees with literature values.<sup>[12] 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 7.59 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, aryl), 7.49 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 2H, aryl), 7.23 - 7.08 (m, 2H, aryl), 6.91 - 6.64 (m, 1H, aryl), 6.61 (d, <sup>3</sup>J<sub>HH</sub> = 8.6

Hz, 2H, aryl), 4.42 (s, 2H, CH<sub>2</sub>), 4.16 (s, 1H, NH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 147.8 (s), 143.9 (s), 129.5 (s), 127.6 (s), 125.7 (q, <sup>1</sup>*J*<sub>CF</sub> = 3.8 Hz), 118.1 (s), 113.0 (s) 47.9 (s). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: -62.39 (s, 3F, *p*-CF<sub>3</sub>).

#### N-Benzyl-4-(trifluoromethyl)aniline (20)



In accordance with general procedure **b**, using (Z)-1-phenyl-N-(4-(trifluoromethyl)) phenyl)methanimine (49.8 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 8 h. The boronate ester was hydrolysed via a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 43 mg, 171 µmol, 86%.

In accordance with general procedure c, using (Z)-1-phenyl-N-(4-(trifluoromethyl)phenyl)methanimine (49.8 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 0.5 h. The boronate ester was hydrolysed via a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 43 mg, 171 µmol, 86%.

In accordance with general procedure d, using (Z)-1-phenyl-N-(4-(trifluoromethyl)phenyl)methanimine (99.6 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 90 mg, 358 µmol, 90%.

Spectroscopic data agrees with literature values.<sup>[12]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 7.83 (d, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 1H, aryl), 7.56 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 1H, aryl), 7.47 – 7.37 (m, 1H, aryl), 7.33 – 7.26 (m, 3H, aryl), 7.25 – 7.14 (m, 2H, aryl), 6.53 (d, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, 2H, aryl) 4.27 (s, 2H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 147.8 (s), 143.9 (s), 129.5 (s), 127.6 (s), 125.8 (s), 125.7 (q, <sup>2</sup>J<sub>CF</sub> = 3.8 Hz), 118.1 (s), 113.0 (s), 47.9 (s). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: -61.01 (s, 3F, *p*-CF<sub>3</sub>).

#### *N*-benzylpropan-2-amine (2p)



In accordance with general procedure **b**, using (Z)-*N*-isopropyl-1-phenylmethanimine (29.4 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 0.5 h. The boronate ester was hydrolysed via a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 26 mg, 174 µmol, 87%. General procedures c and d were not required due to rapid reaction at room temperature.

Spectroscopic data agrees with literature values.<sup>[13]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 7.27 (d, <sup>3</sup>J<sub>HH</sub> = 4.4 Hz, 4H, aryl), 7.21 – 7.16 (m, 1H, aryl), 3.73 (d, <sup>2</sup>/<sub>HH</sub> = 6.6 Hz, 2H, CH<sub>2</sub>), 2.86 – 2.74 (m, 1H, CH), 1.20 (s, 1H, NH), 1.05 (d, <sup>3</sup>J<sub>HH</sub> = 6.3 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 141.0 (s), 128.5 (s), 128.2 (s), 126.9 (s), 51.8 (s), 48.2 (s), 23.1 (s).

#### N-Benzylbutan-1-amine (2q)

 $C_{4}H_{9}$  NH H In accordance with general procedure **b**, using (*Z*)-*N*-butyl-1-phenylmethanimine (32.2 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 8 h. The boronate ester was hydrolysed *via* a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 30 mg, 184 µmol, 92%.

In accordance with general procedure **c**, using (*Z*)-*N*-butyl-1-phenylmethanimine (32.2 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 2 h. The boronate ester was hydrolysed *via* a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 31 mg, 190  $\mu$ mol, 95%.

In accordance with general procedure **d**, using (*Z*)-*N*-butyl-1-phenylmethanimine (64.4 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The title compound was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 61 mg, 374  $\mu$ mol, 94%.

Spectroscopic data agrees with literature values.<sup>[14]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 7.58 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 2H, aryl), 7.42 – 7.30 (m, 3H, aryl), 4.04 (s, 2H, CH<sub>2</sub>), 2.82 – 2.63 (m, 2H, CH<sub>2</sub>), 1.87 – 1.73 (m, 2H, CH<sub>2</sub>), 1.31 (h, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2H), 0.86 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 130.5 (s), 130.4 (s), 129.5 (s), 129.2 (s), 50.7 (s), 45.9 (s), 28.0 (s), 20.2 (s), 13.6 (s).

#### N-Benzylcyclopentanamine (2r)



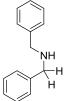
In accordance with general procedure **b**, using (*Z*)-*N*-cyclopentyl-1-phenylmethanimine (34.6 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 4 h. The boronate ester was hydrolysed *via* a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 31 mg, 177  $\mu$ mol, 89%.

In accordance with general procedure **c**, using (*Z*)-*N*-cyclopentyl-1-phenylmethanimine (34.6 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 0.5 h. The boronate ester was hydrolysed *via* a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 30 mg, 171 μmol, 86%.

In accordance with general procedure **d**, using (*Z*)-*N*-cyclopentyl-1-phenylmethanimine (69.2 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 62 mg, 354 µmol, 89%.

Spectroscopic data agrees with literature values.<sup>[14]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 7.54 (m, 2H, aryl), 7.46 – 7.28 (m, 3H, aryl), 3.93 (s, 2H, CH<sub>2</sub>), 3.20 (q, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz, 1H, CH), 1.96 (s, 1H, NH), 1.96 – 1.87 (m, 2H, cyclopentyl H), 1.88 – 1.72 (m, 4H, cyclopentyl H), 1.63 – 1.42 (m, 2H, cyclopentyl H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 132.0 (s), 130.3 (s), 129.1 (s), 57.7 (s), 50.2 (s), 30.1 (s), 24.0 (s).

#### Dibenzylamine (2s)



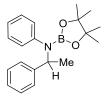
In accordance with general procedure **b**, using (*Z*)-*N*-benzyl-1-phenylmethanimine (39.0 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 156 h. The boronate ester was hydrolysed *via* a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 38 mg, 193 µmol, 96%.

In accordance with general procedure **c**, using (*Z*)-*N*-benzyl-1-phenylmethanimine (39.0 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 0.5 h. The boronate ester was hydrolysed *via* a basic workup (3 x 10 mL 1 M NaOH washings) to isolate the title compound as a colourless oil. Yield: 31 mg, 162 µmol, 89%.

In accordance with general procedure **d**, using (*Z*)-*N*-benzyl-1-phenylmethanimine (78.0 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 76 mg, 386 µmol, 96%.

Spectroscopic data agrees with literature values.<sup>[12] 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 7.29 – 7.21 (m, 8H, aryl), 7.20 – 7.12 (m, 2H, aryl), 3.72 (s, 4H, CH<sub>2</sub>), 1.78 (s, 1H, NH). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 140.4 (s), 128.5 (s), 128.3 (s), 127.1 (s), 53.3 (s).

# 4,4,5,5-Tetramethyl-N-phenyl-N-(1-phenylethyl)-1,3,2-dioxoborolan-2-amine (1t)



In accordance with general procedure **b**, using (*E*)-*N*,1-diphenylethan-1-imine (39.0 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 24 h. The boronate ester was purified *via* a basic workup (3 x 10 mL 1 M NaOH washings) but not hydrolysed to isolate the title compound as a colouless oil. Yield: 55 mg, 170  $\mu$ mol, 85%.

In accordance with general procedure **c**, using (*E*)-*N*,1-diphenylethan-1-imine (39.0 mg, 0.2 mmol) as the substrate gave the corresponding boronate ester after 0.5 h. The boronate ester was purified *via* a basic workup (3 x 10 mL 1 M NaOH washings) but not hydrolysed to isolate the title compound as a colourless oil. Yield: 57 mg, 176  $\mu$ mol, 88%.

In accordance with general procedure **d**, using (*E*)-*N*,1-diphenylethan-1-imine (78.0 mg, 0.4 mmol) as the substrate gave the corresponding boronate ester after 5 min. Crude <sup>1</sup>H NMR analysis of the hydrolysed material revealed >95% conversion. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (5:1) as the eluent to afford the title compound as a colourless oil. Yield: 104 mg, 322  $\mu$ mol, 80%.

Spectroscopic data agrees with literature values.<sup>[15]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 7.28 (dd, <sup>3</sup>J<sub>HH</sub> = 8.3, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, 2H, aryl), 7.22 (td, <sup>3</sup>J<sub>HH</sub> = 6.8, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 2H, aryl), 7.13 (tt, <sup>3</sup>J<sub>HH</sub> = 6.4, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz, 1H, aryl), 7.04 – 6.95 (m, 2H, aryl), 6.55 (tt, *J* = 7.4, 1.1 Hz, 1H, aryl), 6.47 – 6.38 (m, 2H, aryl), 4.39 (q, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 1H, CH), 1.42 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 3H, Me), 1.18 (s, 12H, pinacol). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 22.3 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 147.4 (s), 145.3 (s), 129.2 (s), 128.7 (s), 127.0 (s), 125.9 (s), 117.3 (s), 113.4 (s), 83.2 (s), 53.6 (s), 25.1 (s), 24.7 (s).

# 4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane (3a)



In accordance with general procedure **e**, using styrene (41.6 mg, 0.4 mmol) as the substrate gave the title compound. Crude conversion by NMR >95%. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford **3a** as a colourless oil. Yield: 84 mg, 362 µmol, 90%. Spectroscopic data agrees with literature

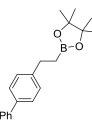
values.<sup>[16] 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 7.29 – 7.20 (m, 4H, aryl), 7.15 (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 1H, aryl), 2.81 – 2.67 (m, 2H, CH<sub>2</sub>), 1.22 (s, 12H, pinacol), 1.19 – 1.10 (m, 2H, CH<sub>2</sub>). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 33.9 (s). <sup>13</sup>C{<sup>1</sup>H} NMR *partial* (101 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 144.5 (s), 128.3 (s), 128.1 (s), 125.6 (s), 83.2 (s), 30.1 (s), 25.0 (s).

#### 4,4,5,5-Tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (3b)

In accordance with general procedure **e**, using 4-methylstyrene (47.2 mg, 0.4 mmol) as the substrate gave the title compound. Crude conversion by NMR >95%. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford **3b** as a colourless oil. Yield: 90 mg, 366  $\mu$ mol, 91%. Spectroscopic data agrees with literature values.<sup>[16]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 7.09 (q, <sup>3</sup>J<sub>HH</sub> = 8.1

Hz, 4H, aryl), 2.71 (m, 2H, CH<sub>2</sub>), 2.31 (s, 3H, CH<sub>3</sub>), 1.23 (s, 12H, pinacol), 1.12 (m, 2H, CH<sub>2</sub>). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 33.9 (s). <sup>13</sup>C{<sup>1</sup>H} NMR *partial* (101 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 141.5 (s), 135.0 (s), 129.0 (s), 128.0 (s), 83.2 (s), 29.7 (s), 25.0 (s), 21.1 (s).

# 4,4,5,5-Tetramethyl-2-2([1,1'-biphenyl]4-yl)ethyl)-1,3,2-dioxaborolane (3c)

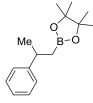


Me

In accordance with general procedure **e**, using 4-vinylbiphenyl (72.0 mg, 0.4 mmol) as the substrate gave the title compound. Crude conversion by NMR >95%. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford **3c** as a colourless oil. Yield: 115 mg, 372 µmol, 93%. Spectroscopic data agrees with literature values.<sup>[17]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 7.65 – 7.57 (m, 2H, aryl), 7.55

-7.49 (m, 2H, aryl), 7.48 -7.40 (m, 2H, aryl), 7.37 -7.29 (m, 3H, aryl), 3.02 -2.70 (m, 2H, CH<sub>2</sub>), 1.25 (s, 12H, pinacol), 1.20 (dd, <sup>3</sup>*J*<sub>HH</sub> = 8.8, 7.5 Hz, 2H, CH<sub>2</sub>). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 34.0 (s). <sup>13</sup>C{<sup>1</sup>H} NMR *partial* (101 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 143.7 (s), 141.4 (s), 138.6 (s), 128.8 (s), 128.6 (s), 127.1 (s), 127.1 (s), 127.0 (s), 83.3 (s), 77.2 (s), 29.8 (s), 25.0 (s).

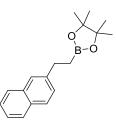
#### 4,4,5,5-Tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (3d)



In accordance with general procedure **e**, using alpha-methylstyrene (47.3 mg, 0.4 mmol) as the substrate gave the title compound. Crude conversion by NMR >95%. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford **3d** as a colourless oil. Yield: 88 mg, 357 µmol, 89%. Spectroscopic data agrees with literature values.<sup>[18]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 7.28 – 7.22 (m, 4H, aryl),

7.06 – 7.00 (m, 1H, aryl), 3.14 – 2.98 (m, 1H, CH), 1.28 (d,  ${}^{3}J_{HH}$  = 6.9 Hz, 3H, CH<sub>3</sub>), 1.16 (s, 12H, pinacol), 1.00 – 0.83 (m, 2H, CH<sub>2</sub>).  ${}^{11}B$  NMR (128 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 33.7 (s).  ${}^{13}C{}^{1}H$  NMR (101 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 149.4 (s), 128.3 (s), 126.8 (s), 125.8 (s), 83.1 (s), 36.0 (s), 25.1 (s), 24.9 (s), 24.8 (s).

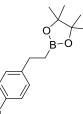
### 4.4.5.5-Tetramethyl-2-(2-(napthalen-2-yl)ethyl)-1,3,2-dioxaborolane (3e)



In accordance with general procedure **e**, using 2-vinylnapthalene (61.6 mg, 0.4 mmol) as the substrate gave the title compound. Crude conversion by NMR 84%. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford **3e** as a colourless oil. Yield: 80 mg, 284 µmol, 71%. Spectroscopic data agrees with literature values.<sup>[19]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 7.82 – 7.73

(m, 3H, aryl), 7.66 (s, 1H, aryl), 7.47 – 7.35 (m, 3H, aryl), 2.98 – 2.89 (m, 2H, CH<sub>2</sub>), 1.29 – 1.25 (m, 2H, CH<sub>2</sub>), 1.23 (s, 12H, pinacol).<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 34.0 (s). <sup>13</sup>C{<sup>1</sup>H} NMR *partial* (101 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 142.1 (s), 133.8 (s), 132.0 (s), 127.8 (s), 127.7 (s), 127.6 (s), 127.4 (s), 125.8 (s), 125.8 (s), 125.0 (s), 83.3 (s), 30.3 (s), 25.0 (s).

### 4,4,5,5-Tetramethyl-2-(4-(tert-butyl)phenethyl)-1,3,2-dioxaborolane (3f)

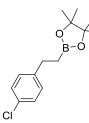


<sup>t</sup>Bı

In accordance with general procedure **e**, using 4-*tert* butylstyrene (64.1 mg, 0.4 mmol) as the substrate gave the title compound. Crude conversion by NMR 77%. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford **3f** as a colourless oil. Yield: 76 mg, 264 µmol, 66%. Spectroscopic data agrees with literature values.<sup>[17]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 7.29 (d, <sup>3</sup>J<sub>HH</sub> = 8.4

Hz, 2H, aryl), 7.15 (d,  ${}^{3}J_{HH}$  = 8.5 Hz, 2H, aryl), 2.84 – 2.63 (m, 2H, CH<sub>2</sub>), 1.30 (s, 9H,  ${}^{t}Bu$ ), 1.22 (s, 12H, pinacol), 1.14 (dd,  ${}^{3}J_{HH}$  = 9.0, 7.5 Hz, 2H, CH<sub>2</sub>).  ${}^{11}B$  NMR (128 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 34.0 (s).  ${}^{13}C{}^{1}H$  NMR *partial* (101 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 148.4 (s), 141.5 (s), 127.8 (s), 125.2 (s), 83.2 (s), 34.5 (s), 31.6 (s), 29.5 (s), 25.0 (s).

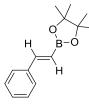
# 2-(4-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)



In accordance with general procedure **e**, using 4-chlorostyrene (55.2 mg, 0.4 mmol) as the substrate gave the title compound. Crude conversion by NMR 32%. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford **3g** as a colourless oil. Yield: 18 mg, 68 µmol, 17%. Spectroscopic data agrees with literature values.<sup>[20]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 7.22 (d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 2H, aryl),

7.14 (d,  ${}^{3}J_{HH}$  = 8.4 Hz, 2H, aryl), 2.71 (m, 2H, CH<sub>2</sub>), 1.21 (s, 12H, pinacol), 1.11 (m, 2H, CH<sub>2</sub>).  ${}^{11}B$  NMR (128 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 33.9 (s).  ${}^{13}C{}^{1}H$  NMR *partial* (101 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 143.0 (s), 131.3 (s), 129.5 (s), 128.4 (s), 83.3 (s), 29.5 (s), 25.0 (s).

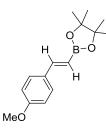
# (E)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (3h)



In accordance with general procedure **e**, using phenyl acetylene (40.8 mg, 0.4 mmol) as the substrate gave the title compound. Crude conversion by NMR >95%. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford **3h** as a colourless oil. Yield: 85 mg, 369 µmol, 92%. Spectroscopic data agrees with literature values.<sup>[4]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 7.41 (d, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2H, aryl),

7.33 (d,  ${}^{3}J_{HH}$  = 18.5 Hz, 1H, =CH), 7.29 – 7.19 (m, 3H, aryl), 6.10 (d,  ${}^{3}J_{HH}$  = 18.4 Hz, 1H, =CH), 1.24 (s, 12H, pinacol). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 30.2 (s). <sup>13</sup>C{<sup>1</sup>H} NMR *partial* (101 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 149.6 (s), 137.6 (s), 129.0 (s), 128.7 (s), 127.2 (s), 83.5 (s), 24.9 (s).

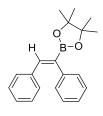
#### (E)-2-(4-Methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)



In accordance with general procedure **e**, using 4-ethynylanisole (52.8 mg, 0.4 mmol) as the substrate gave the title compound. Crude conversion by NMR 93%. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford **3i** as a colourless oil. Yield: 86 mg, 331 µmol, 83%. Spectroscopic data agrees with literature values.<sup>[21]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ /ppm: 7.43 (d, <sup>3</sup>J<sub>HH</sub> = 8.6 Hz, 2H, aryl), 7.36 (d, <sup>3</sup>J<sub>HH</sub> = 18.4 Hz, 1H, CH), 6.86 (d, <sup>3</sup>J<sub>HH</sub> = 8.8 Hz, 2H, aryl),

6.01 (d, <sup>3</sup>*J*<sub>HH</sub> = 18.4 Hz, 1H, CH), 3.80 (s, 3H, OMe), 1.31 (s, 12H, pinacol). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 30.3 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) δ/ppm: 160.4 (s), 149.2 (s), 130.5 (s), 128.5 (s), 114.0 (s), 83.3 (s), 77.4 (s), 55.3 (s), 24.9 (s).

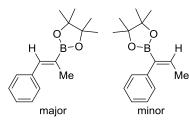
# (Z)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)



In accordance with general procedure **e**, using diphenylacetylene (71.2 mg, 0.4 mmol) as the substrate gave the title compound. Crude conversion by NMR 50%. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford **3j** as a colourless oil. Yield: 53 mg, 173  $\mu$ mol, 43%. Spectroscopic data agrees with literature values.<sup>[4]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$ /ppm: 7.29 (s, 1H, aryl), 7.24 – 7.14 (m,

3H, aryl), 7.14 – 7.08 (m, 2H, aryl, =CH), 7.06 – 7.02 (m, 3H, aryl), 7.01 – 6.95 (m, 2H, aryl), 1.24 (s, 12H, pinacol). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 30.6 (s). <sup>13</sup>C{<sup>1</sup>H} NMR *partial* (101 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 143.3 (s), 140.5 (s), 137.1 (s), 130.1 (s), 129.0 (s), 128.4 (s), 128.0 (s), 127.7 (s), 126.4 (s), 83.9 (s), 24.9 (s).

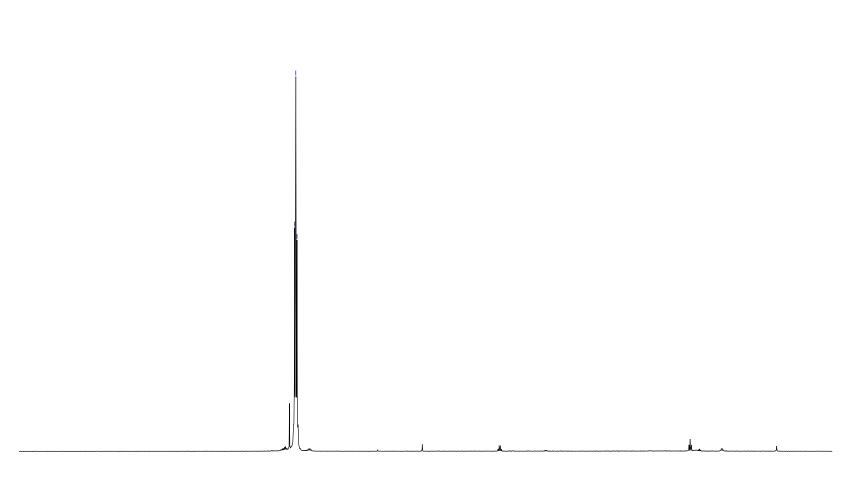
# (Z)-4,4,5,5-Tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane and (Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (3k)



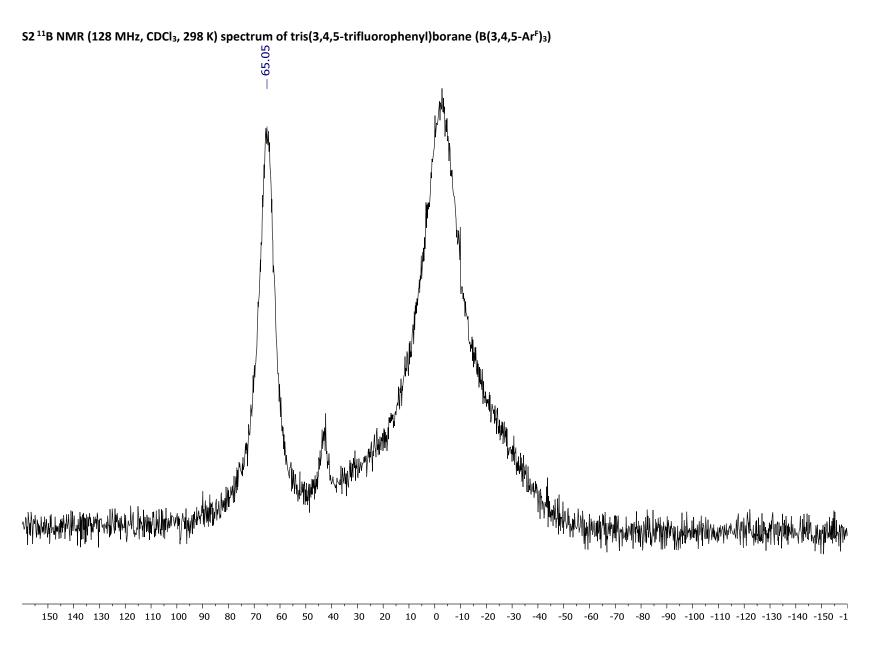
In accordance with general procedure **e**, using 1-phenyl-1-propyne (46.4 mg, 0.4 mmol) as the substrate gave the title compounds. Crude conversion by NMR >95%. The crude material was purified by flash-column chromatography using hexane/ethyl acetate (20:1) as the eluent to afford **3k** as a colourless oil. Yield: 84 mg, 344 µmol, 86%. Isolated as a mix of

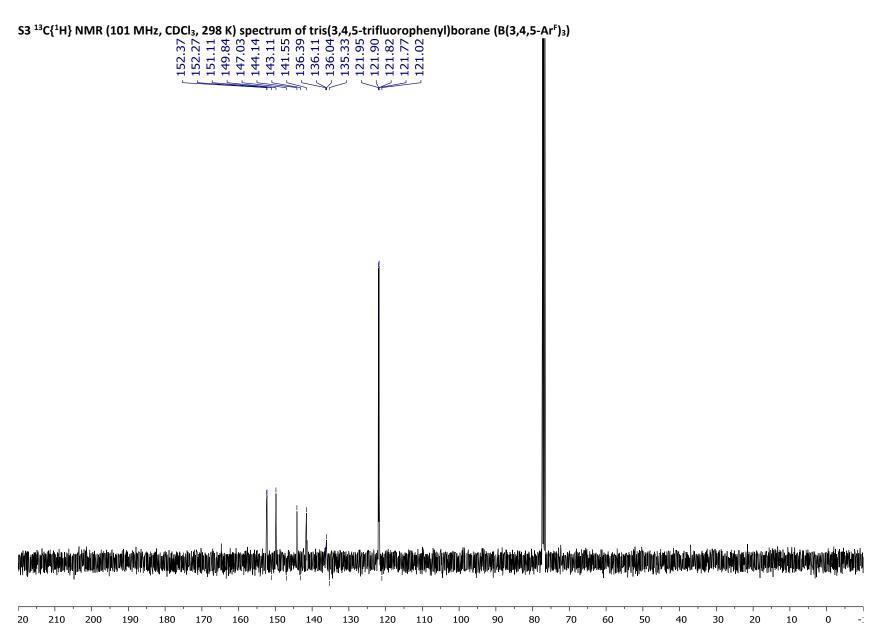
regioisomers (3:1 linear:branched). Spectroscopic data agrees with literature values.<sup>[21]</sup> Major isomer - <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 7.44 – 7.29 (m, 5H, aryl), 7.24 – 7.23 (m, 1H, CH), 1.99 (d, <sup>3</sup>*J*<sub>HH</sub> = 1.8 Hz, 3H, CH<sub>3</sub>), 1.32 (s, 12H, pinacol). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 30.7 (s). <sup>13</sup>C{<sup>1</sup>H} NMR *partial* (101 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 142.5 (s), 138.0 (s) 129.5 (s), 128.2 (s), 127.3 (s), 83.7 (s), 25.0 (s), 16.1 (s). Minor isomer - <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 7.22 – 7.13 (m, 5H, aryl), 6.72 (q, <sup>2</sup>*J*<sub>HH</sub> = 6.9 Hz, 1H, CH), 1.77 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz, 3H, CH<sub>3</sub>), 1.27 (s, 12H, pinacol). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 30.7 (s). <sup>13</sup>C{<sup>1</sup>H} NMR *partial* (101 MHz, CDCl<sub>3</sub>, 298K) δ/ppm: 142.9 (s), 139.9 (s), 129.2 (s), 127.9 (s), 126.0 (s), 83.6 (s), 24.9 (s), 16.1 (s).

Supporting information of starting materials S1<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of tris(3,4,5-trifluorophenyl)borane (B(3,4,5-Ar<sup>F</sup>)<sub>3</sub>)



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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	-0.5



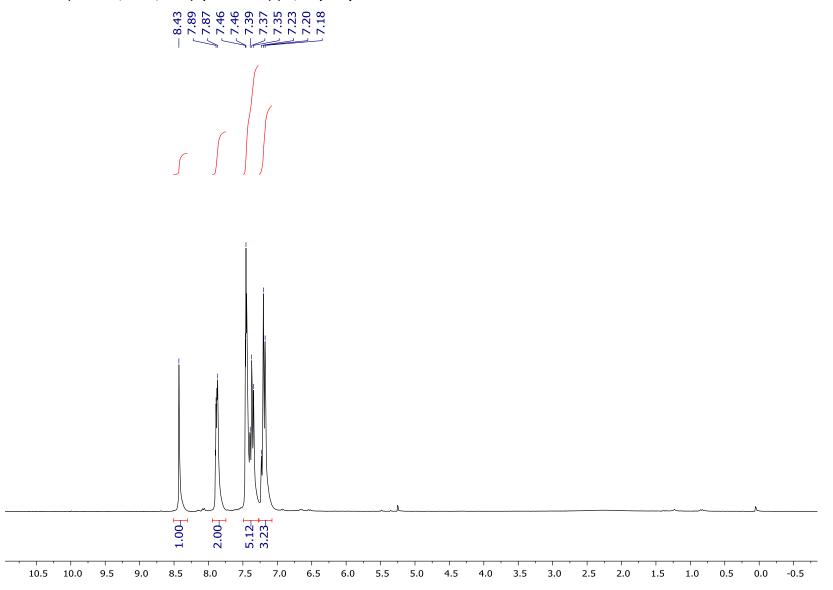


S4 <sup>19</sup> F NMR (376 MHz)	, CDCl <sub>3</sub> , 298K)	spectrum of tris	(3,4,5-trifluoro	phenyl)borane	(B(3,4,5-Ar <sup>F</sup> ) <sub>3</sub> )

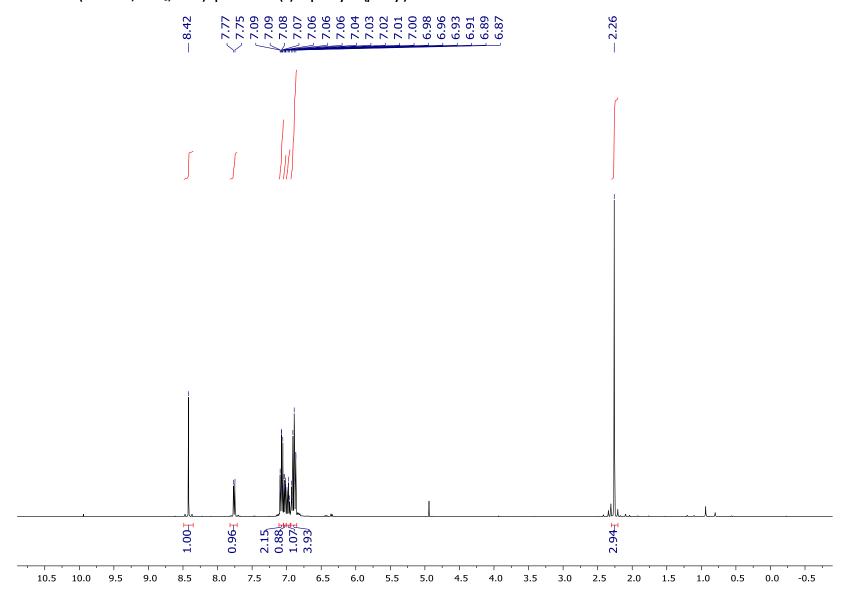
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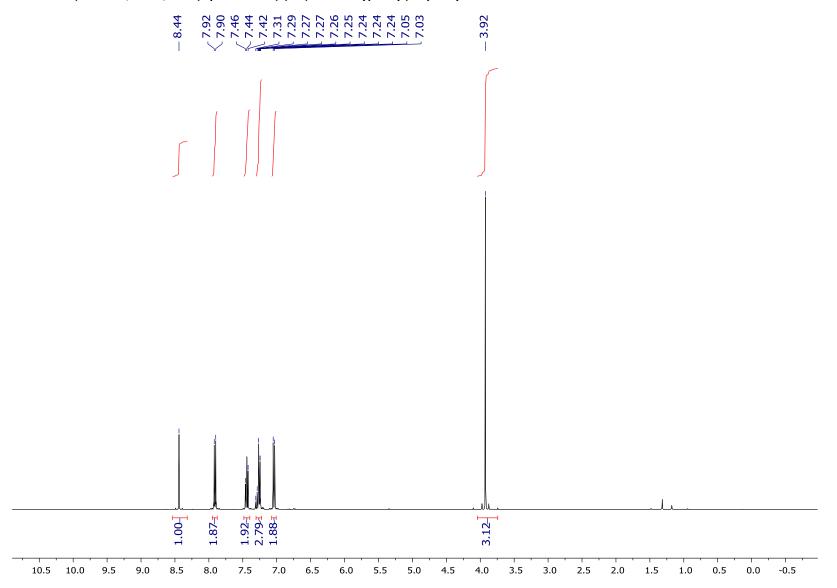
S5<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of (Z)-*N*,1-diphenylmethanimine



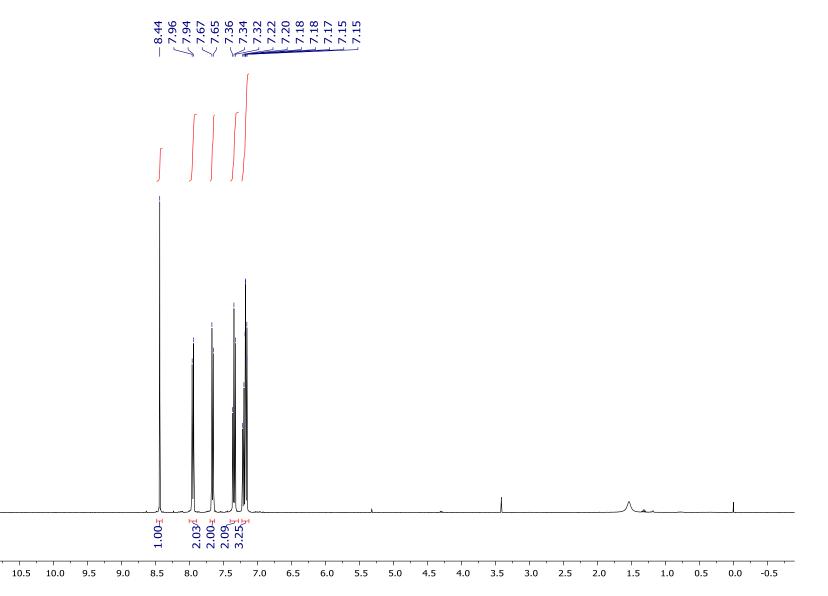
S6<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of (Z)-*N*-phenyl-1-(*p*-tolyl)methanimine



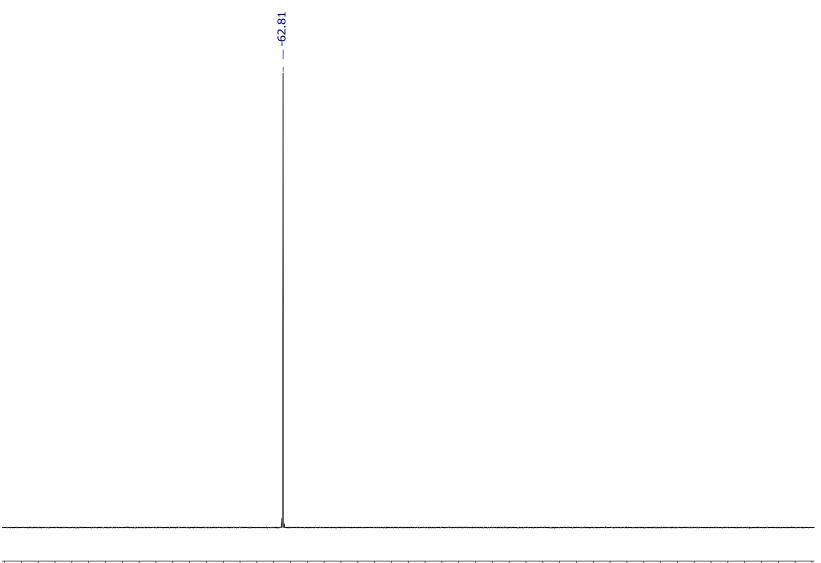
S7<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of (Z)-1-(4-methoxyphenyl)-*N*-phenylmethanimine



S8<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of (Z)-1-(4-(trifluoromethyl)phenyl)-*N*-phenylmethanimine

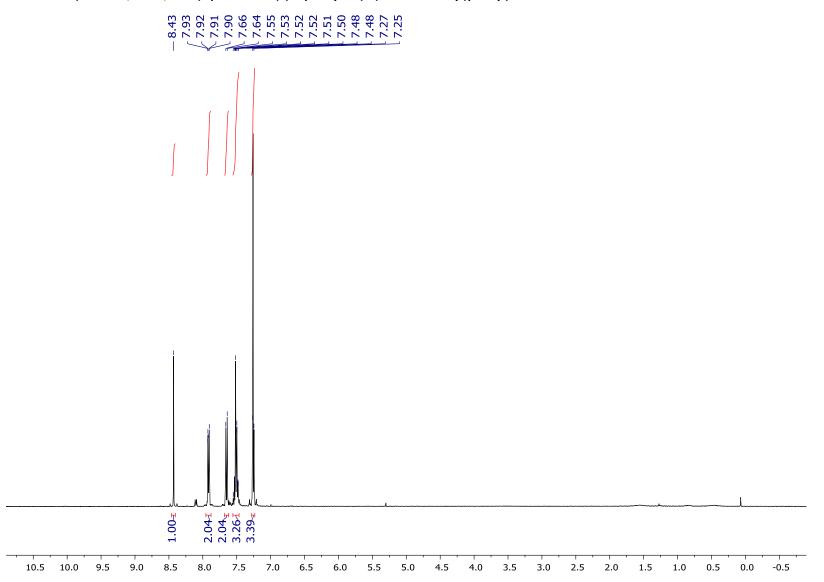


S9<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) spectrum of (Z)-1-(4-(trifluoromethyl)phenyl)-*N*-phenylmethanimine

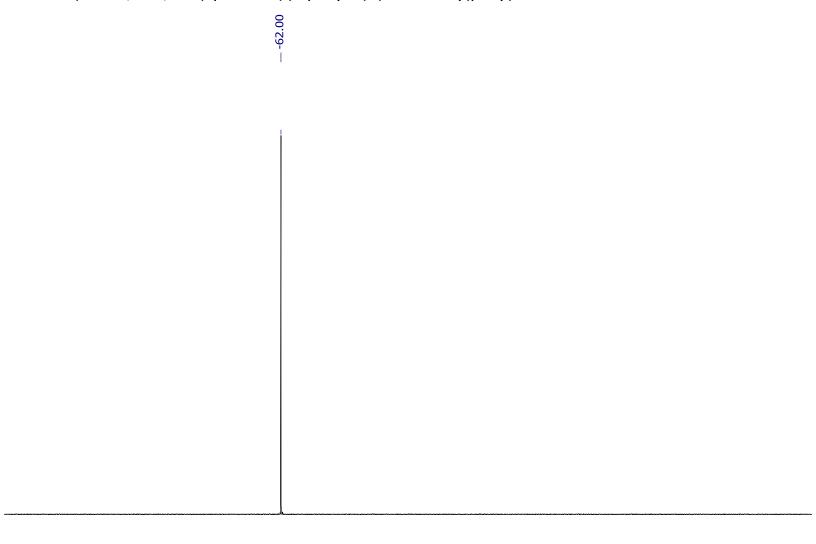


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20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200	-210	-2:

S10<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of (Z)-1-phenyl-N-(4-(trifluoromethyl)phenyl)methanimine

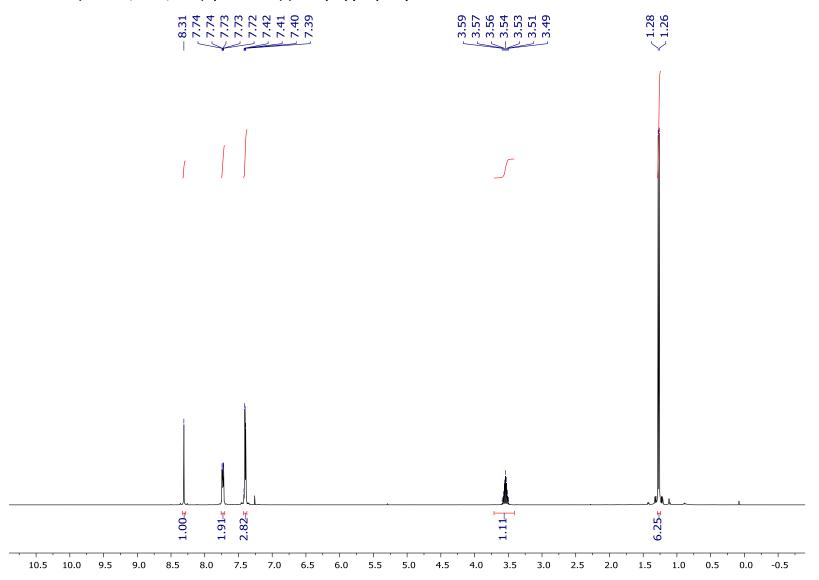


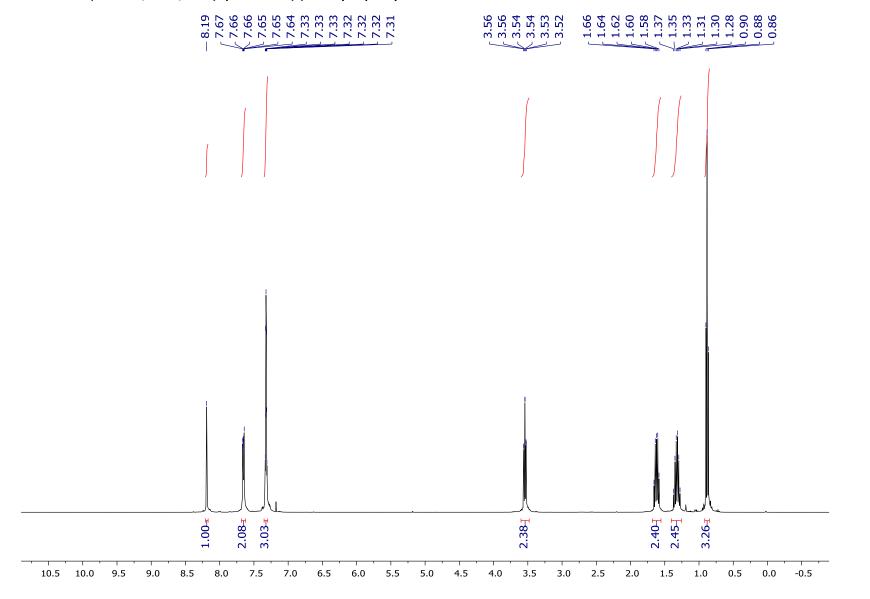
S11<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) spectrum of (Z)-1-phenyl-*N*-(4-(trifluoromethyl)phenyl)methanimine



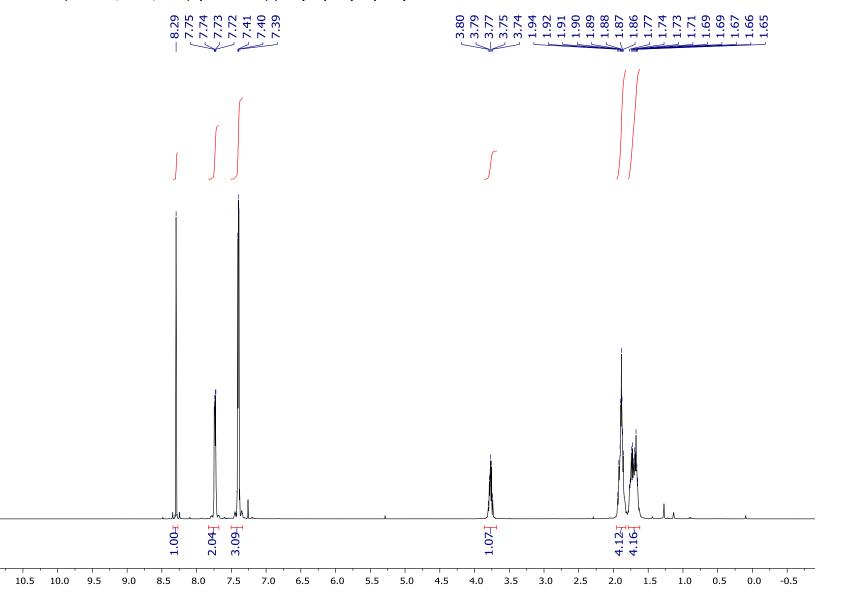
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20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200	-210	-22



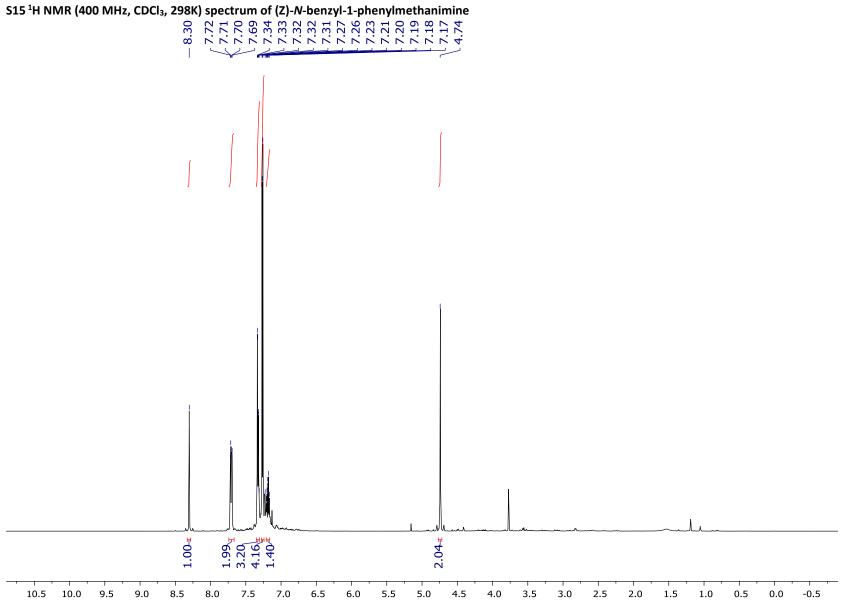




S13<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of (*Z*)-*N*-butyl-1-phenylmethanimine

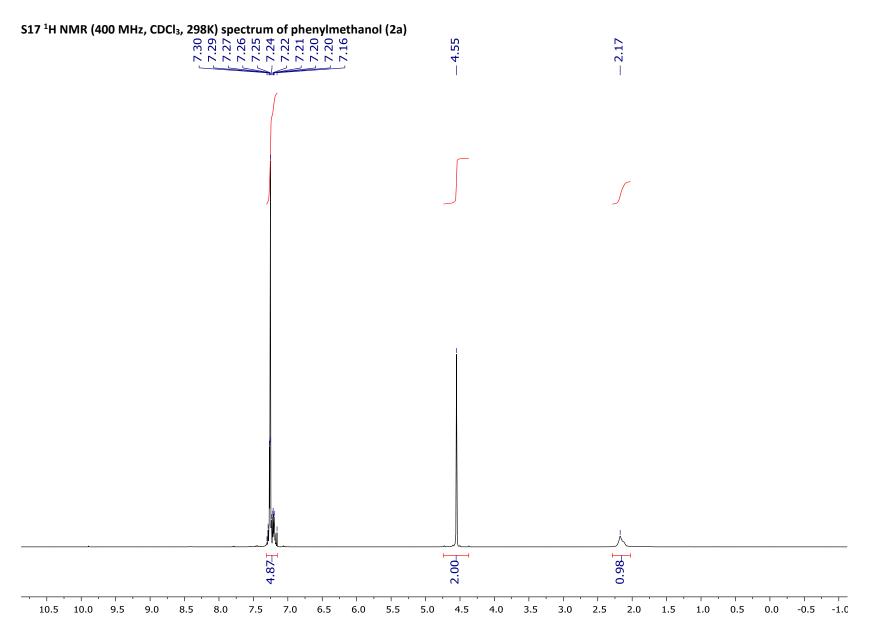


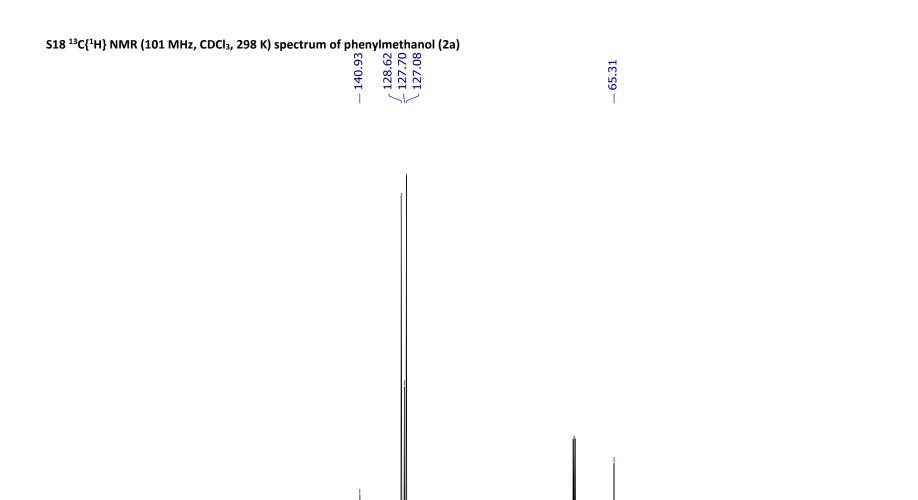
S14<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of (Z)-N-cyclopentyl-1-phenylmethanimine



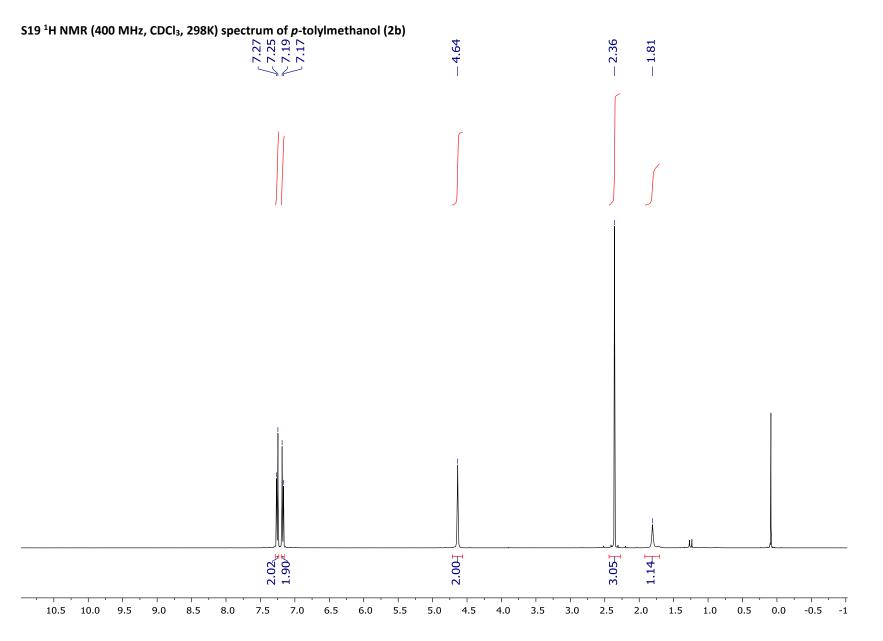
2.25 . . 2.05**∃** 3.19<mark>4</mark> 2.14∕<sup>1</sup> 1.07⁄<sup>±</sup> 1.97<sub>±</sub> 3.00₌ 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5

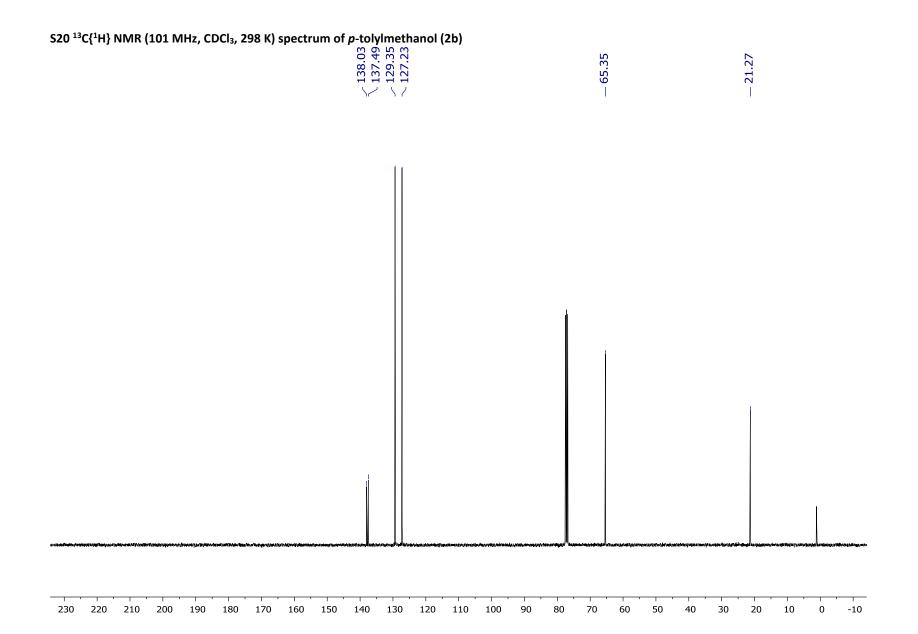
S16<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of (*E*)-*N*,1-diphenylethan-1-imine

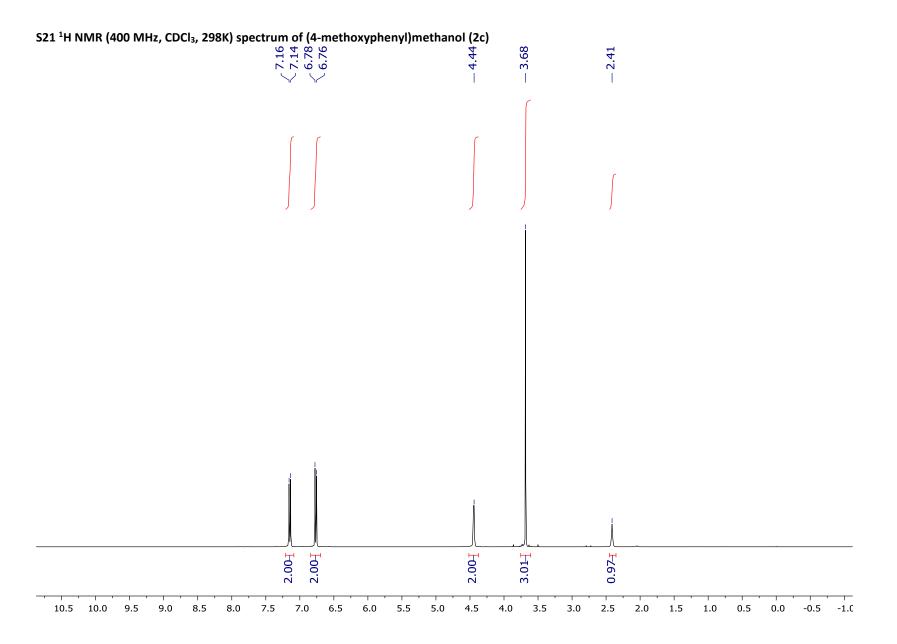


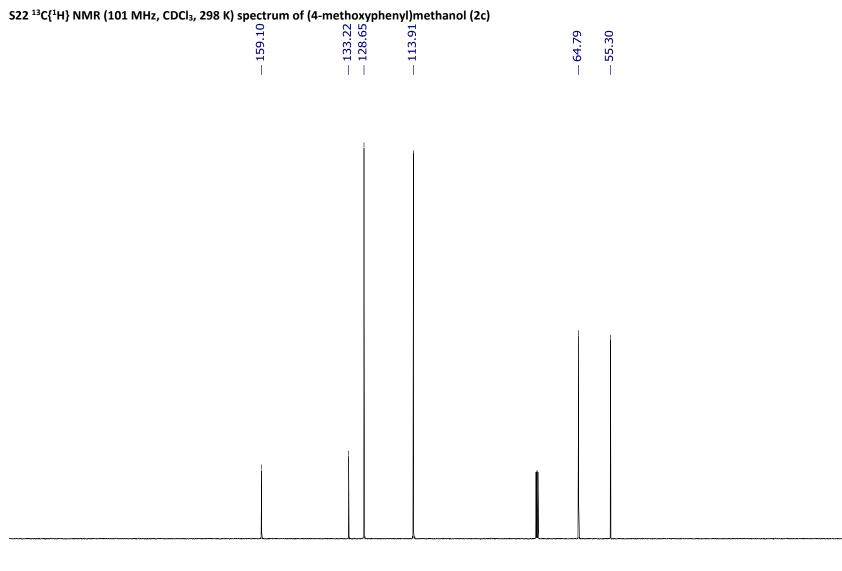


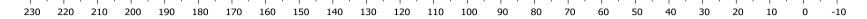
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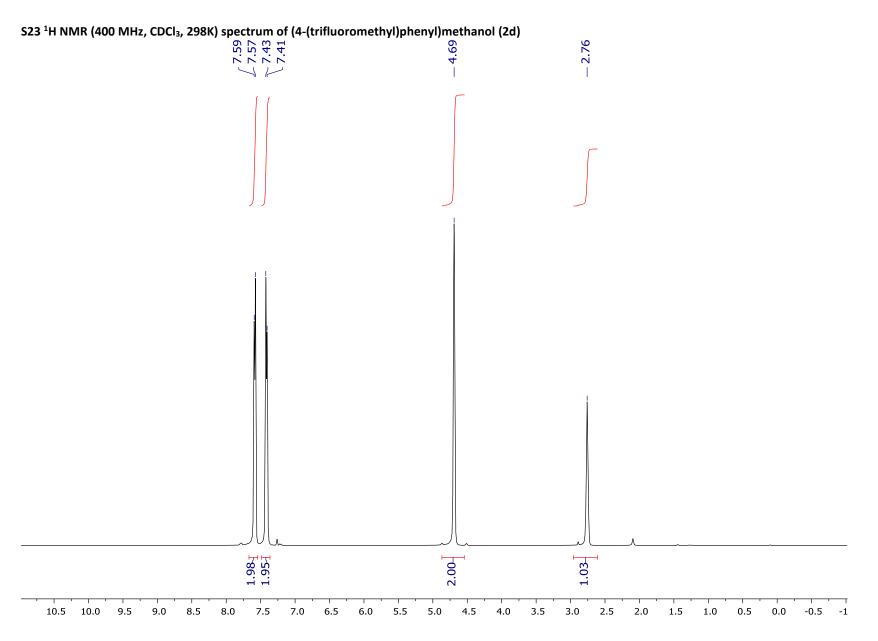






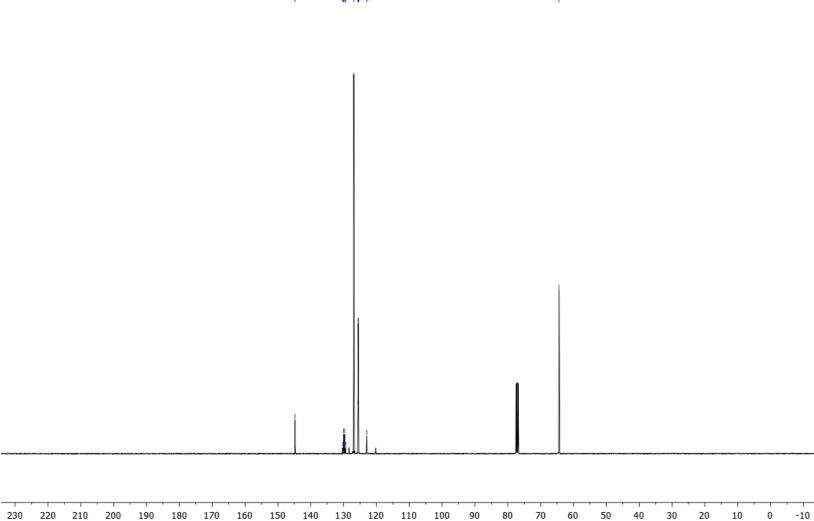






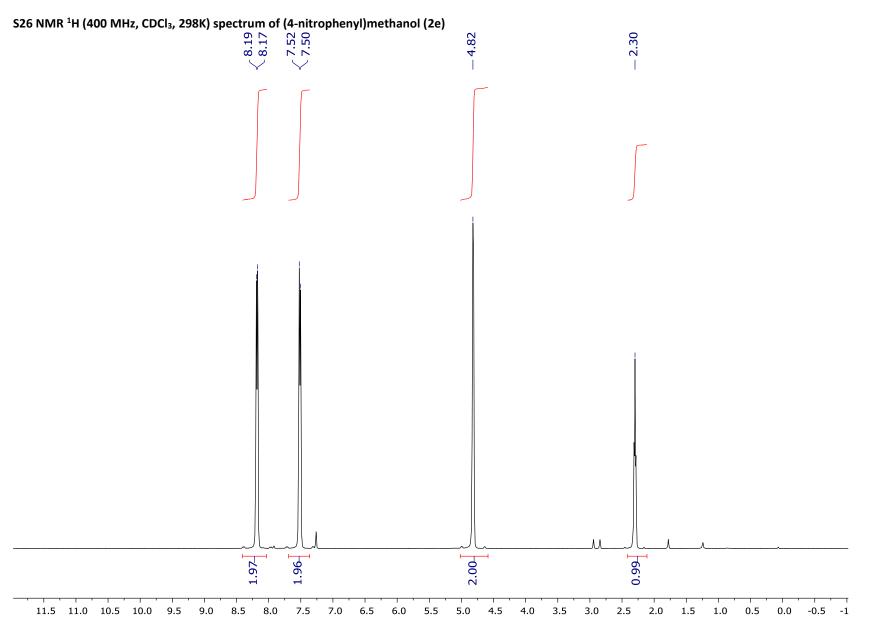
S24 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) spectrum of (4-(trifluoromethyl)phenyl)methanol (2d)

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S25 <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298K) spectrum of (4-(trifluoromethyl)phenyl)methanol (2d)

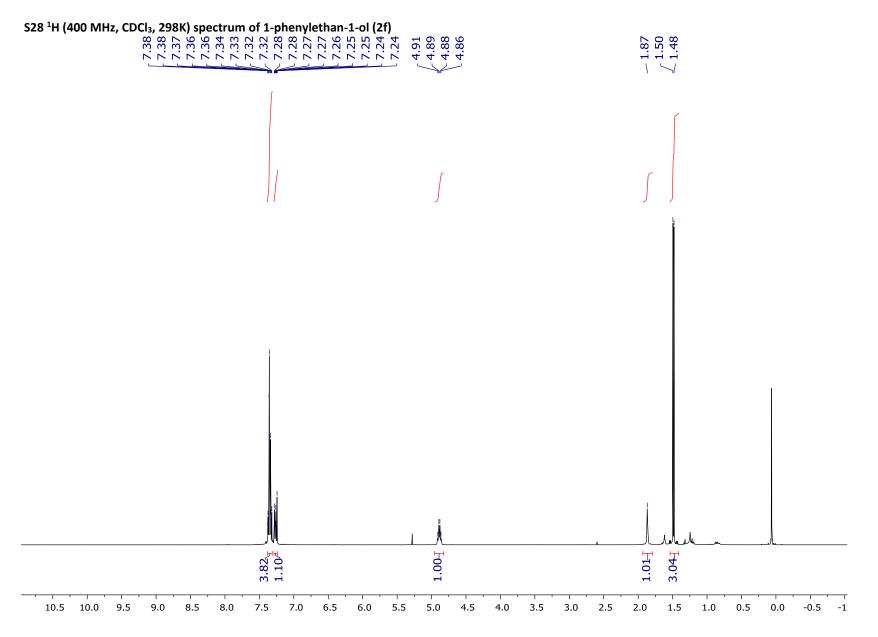
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10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200	-210	

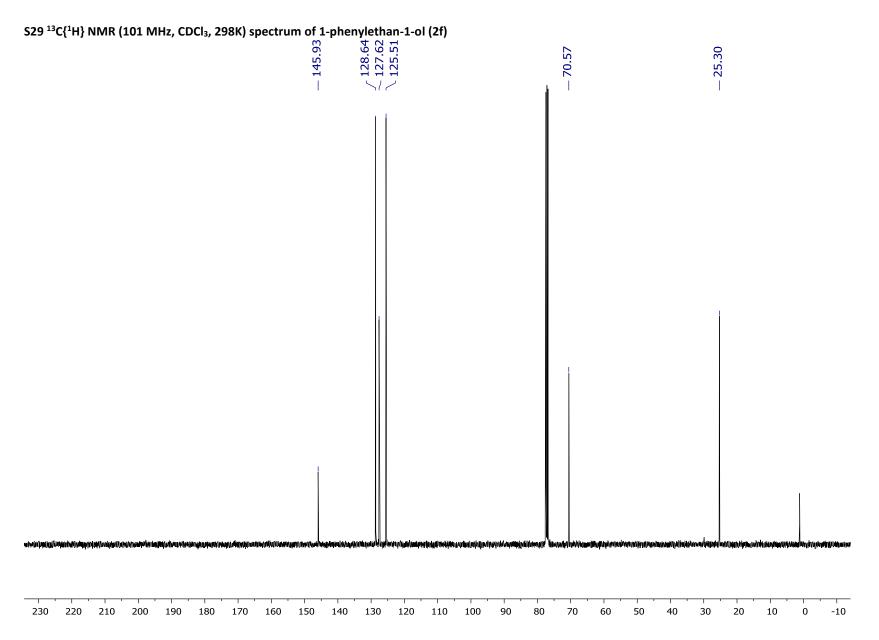


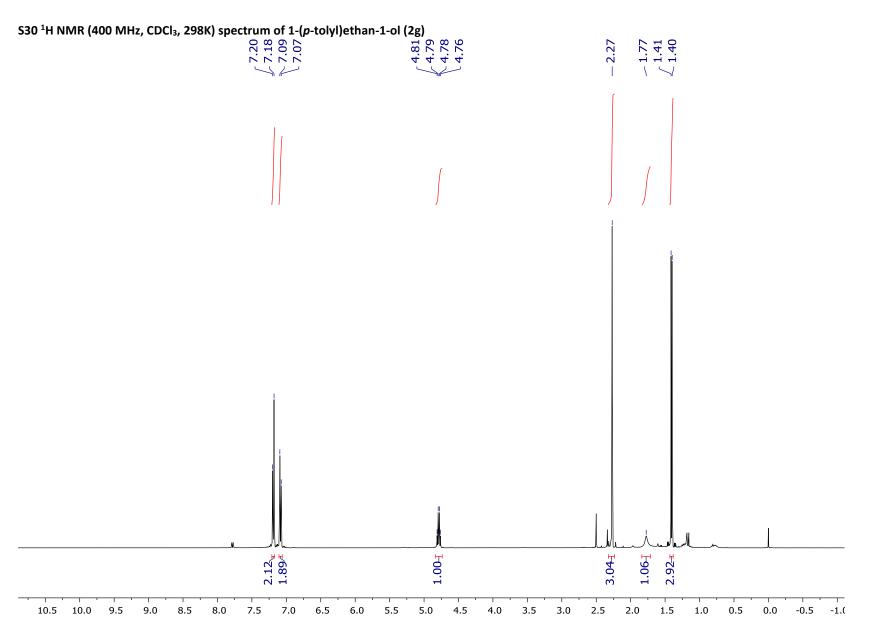
# S27 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) spectrum of (4-nitrophenyl)methanol (2e)

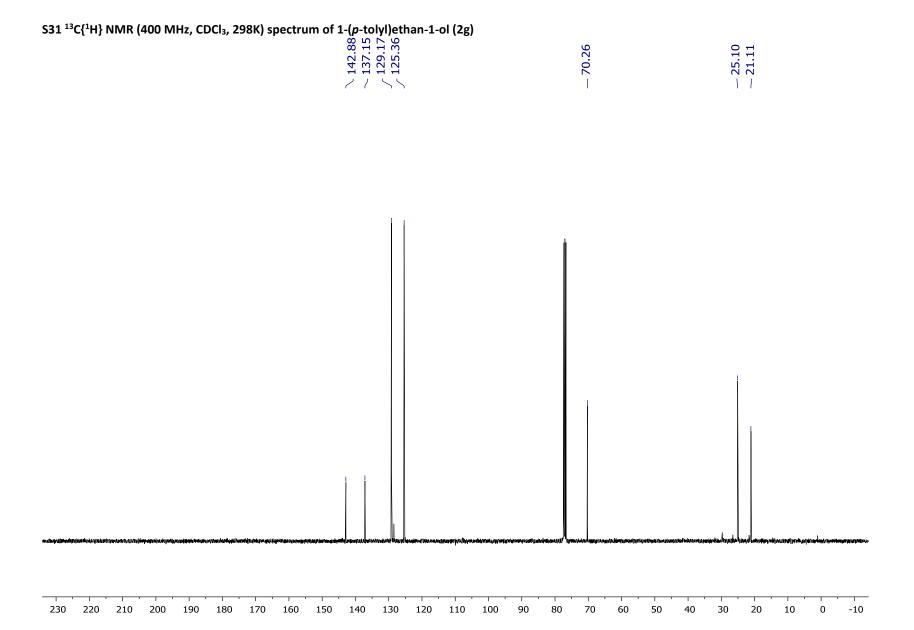
S27 <sup>13</sup> C{ <sup>1</sup> H} NMR (101 MHz, CDCl₃, 298 K) spectrun	H8.37 H7.32	23.81	- 64.06
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230	220	210	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	-10

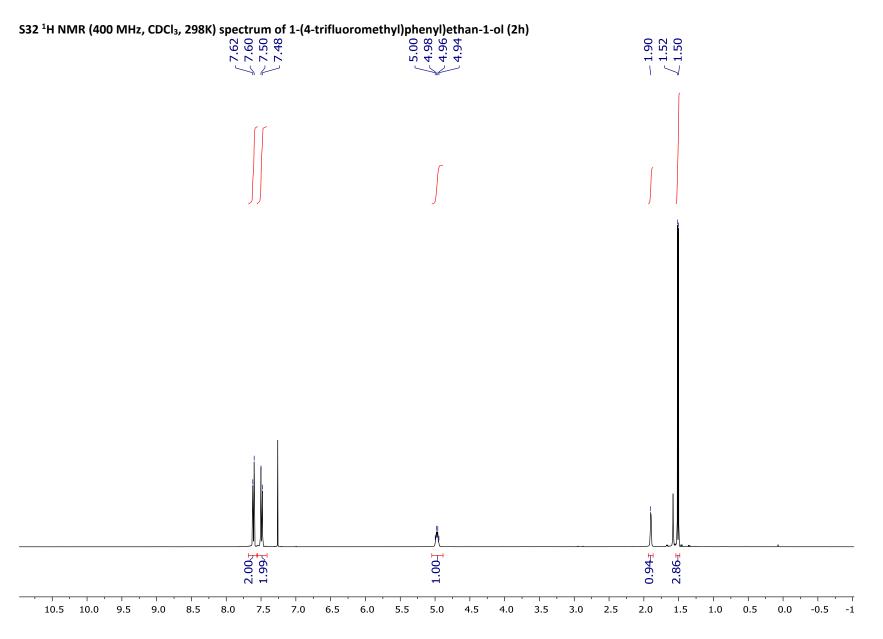


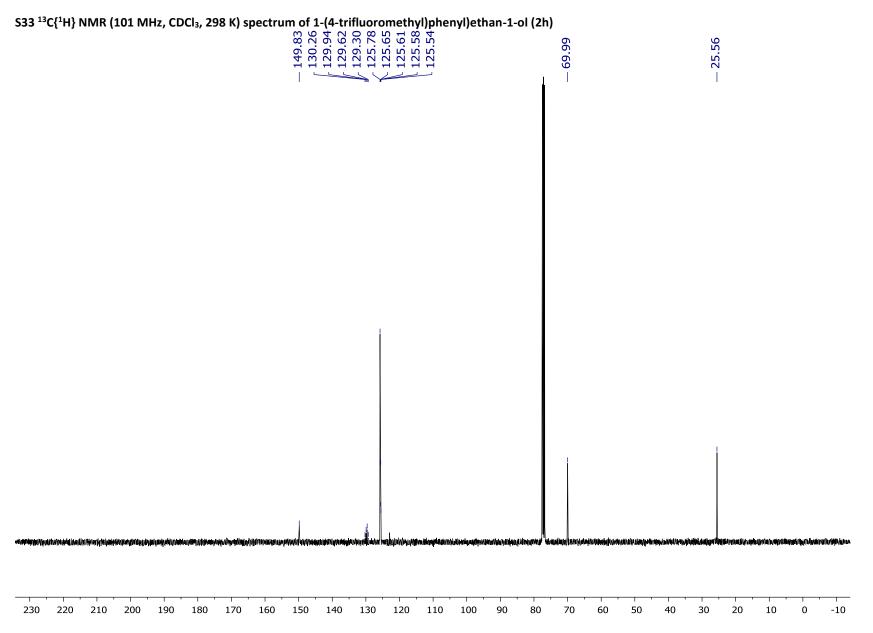






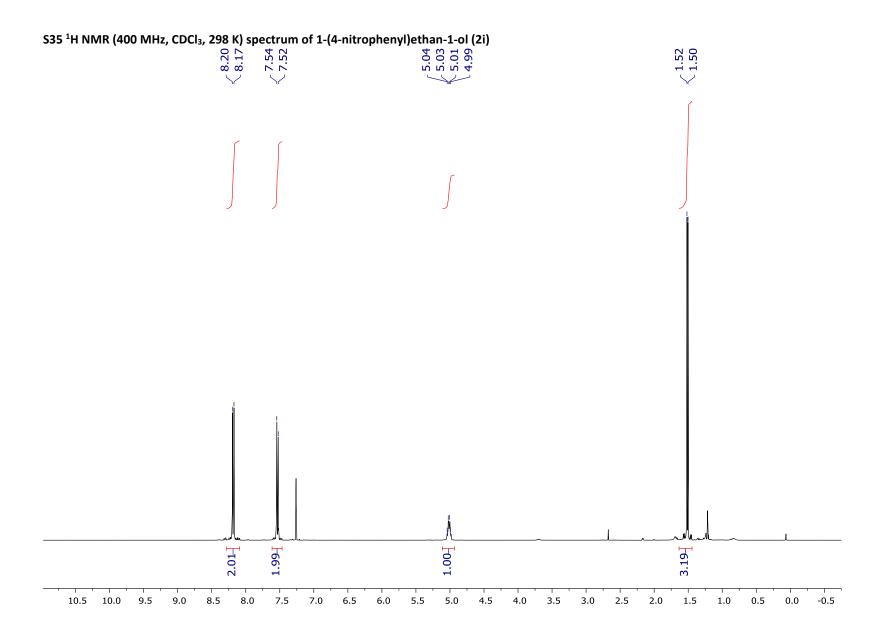


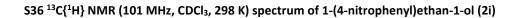


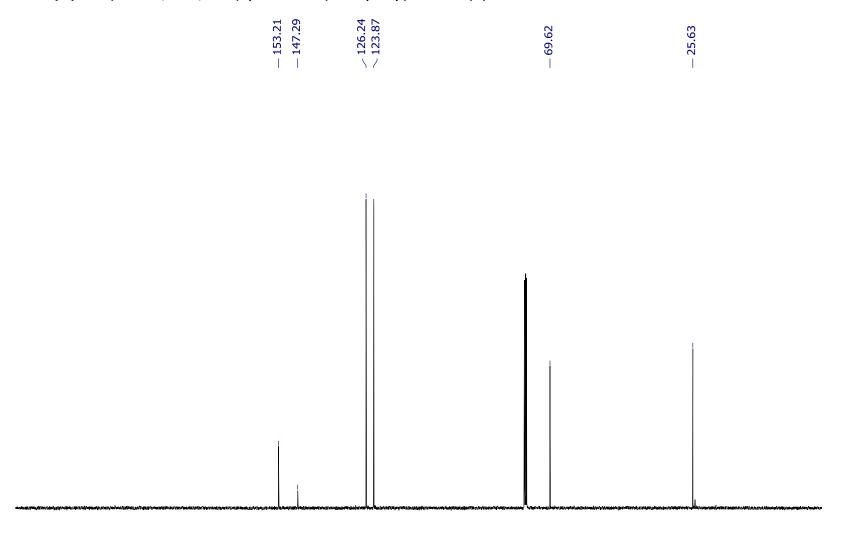


S34<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298K) spectrum of 1-(4-trifluoromethyl)phenyl)ethan-1-ol (2h) 

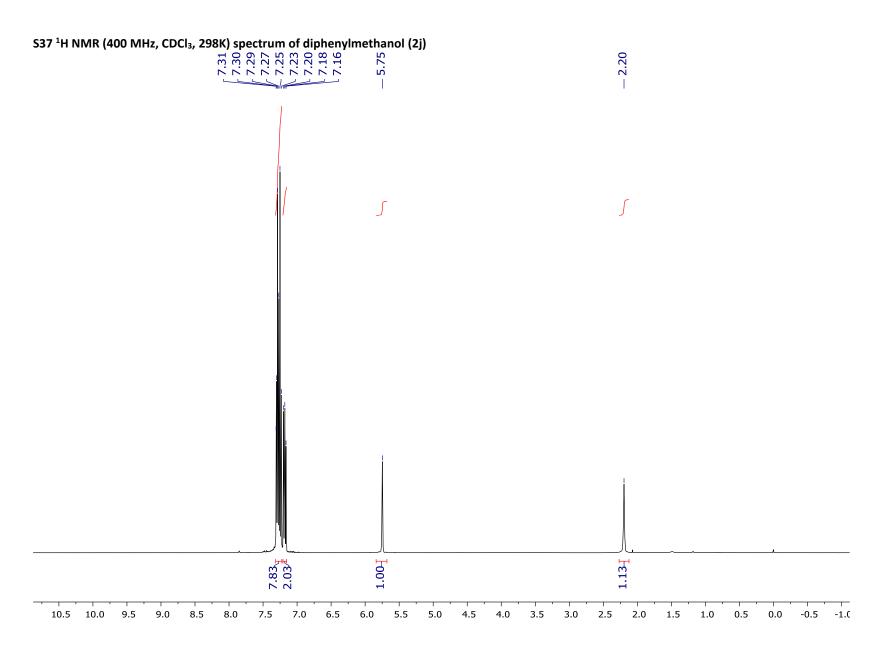
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10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200	-210

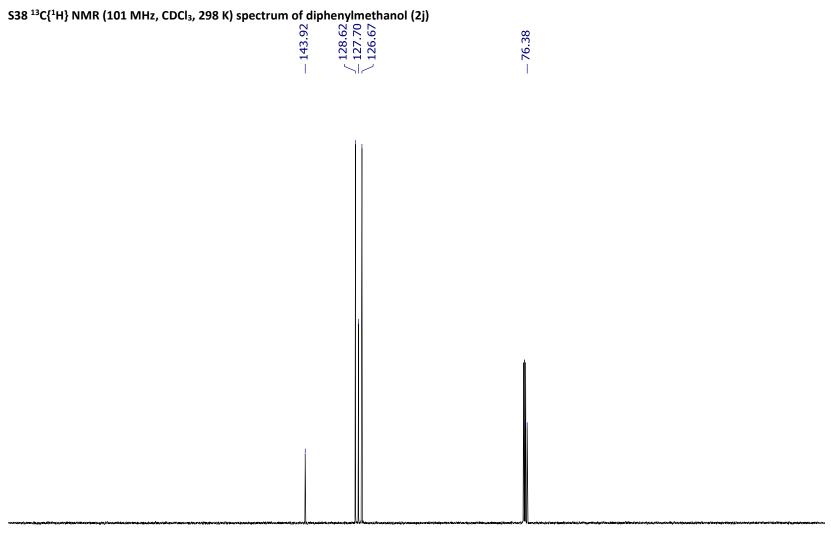




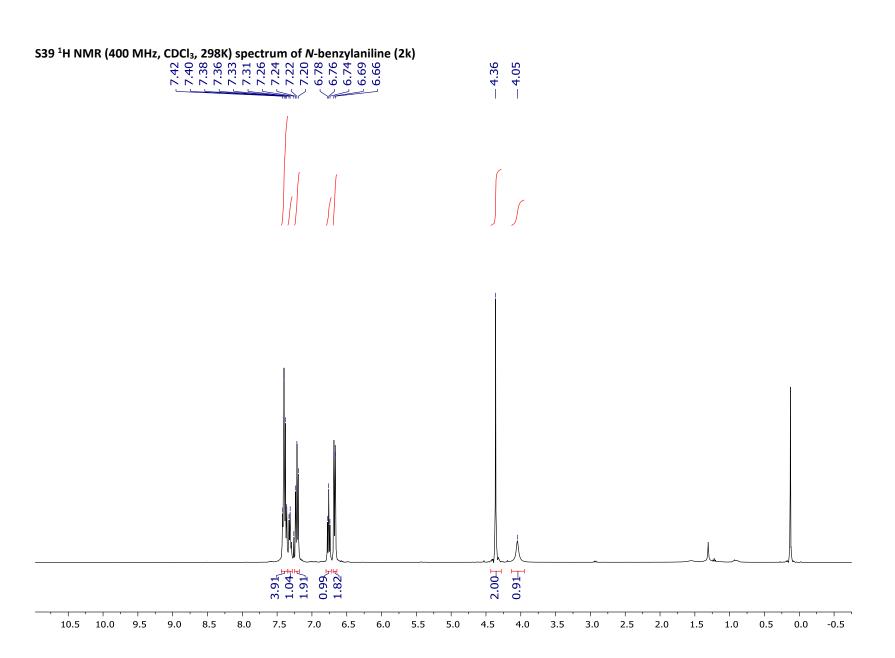


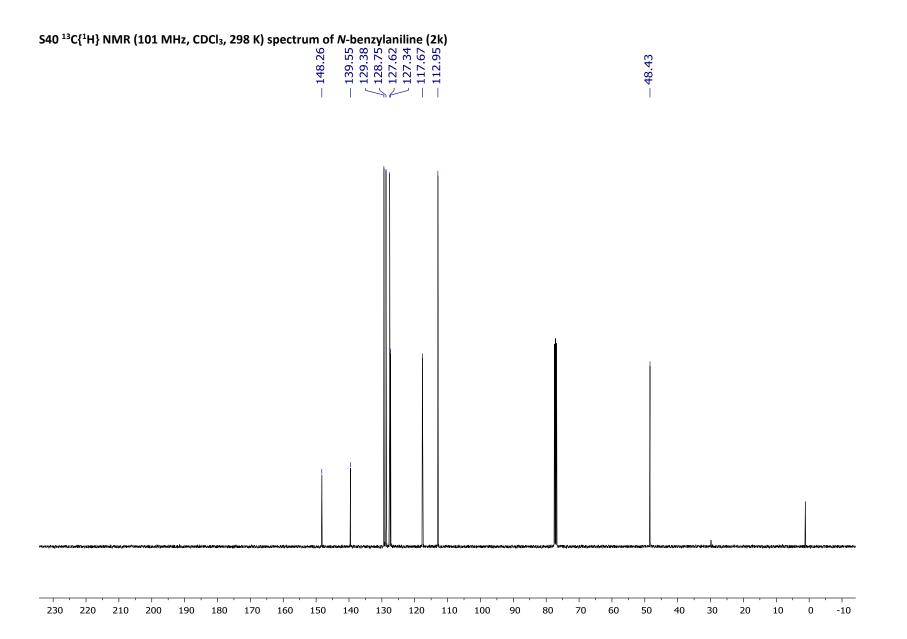
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230	220	210	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	-10

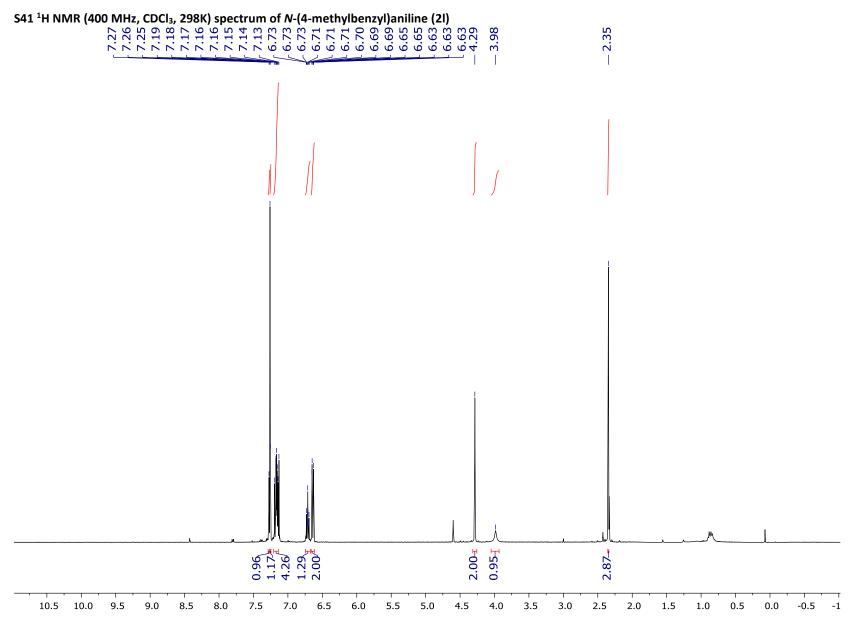


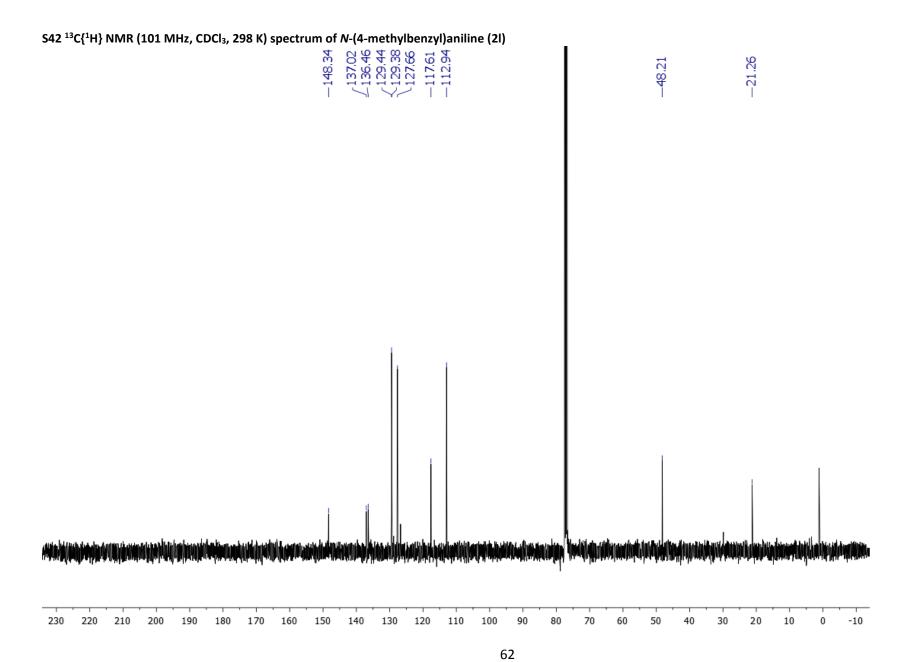


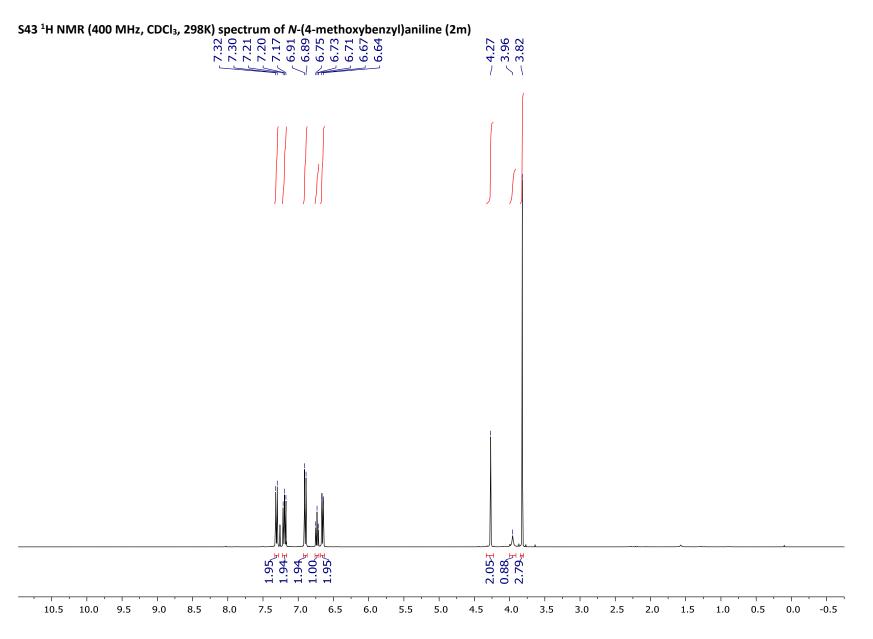
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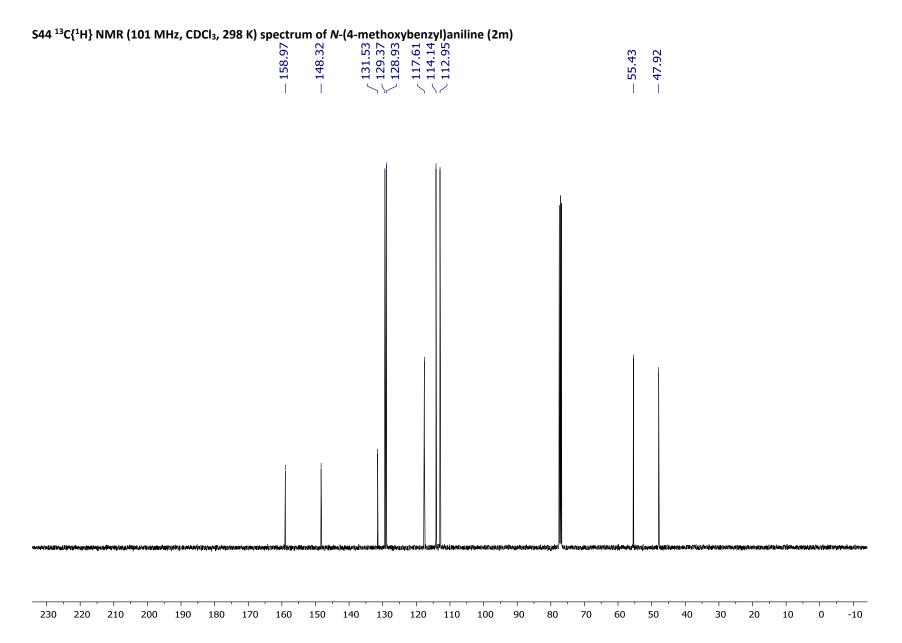


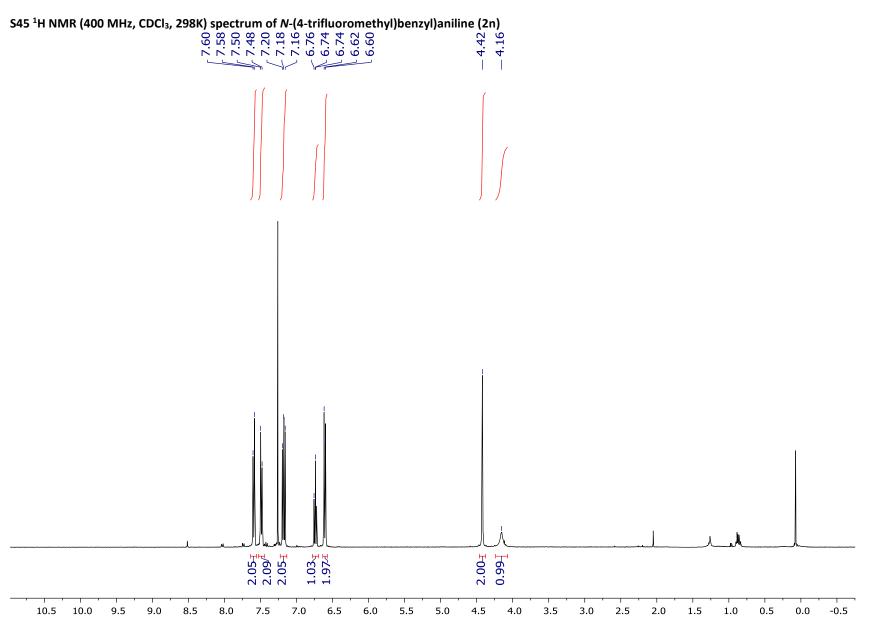


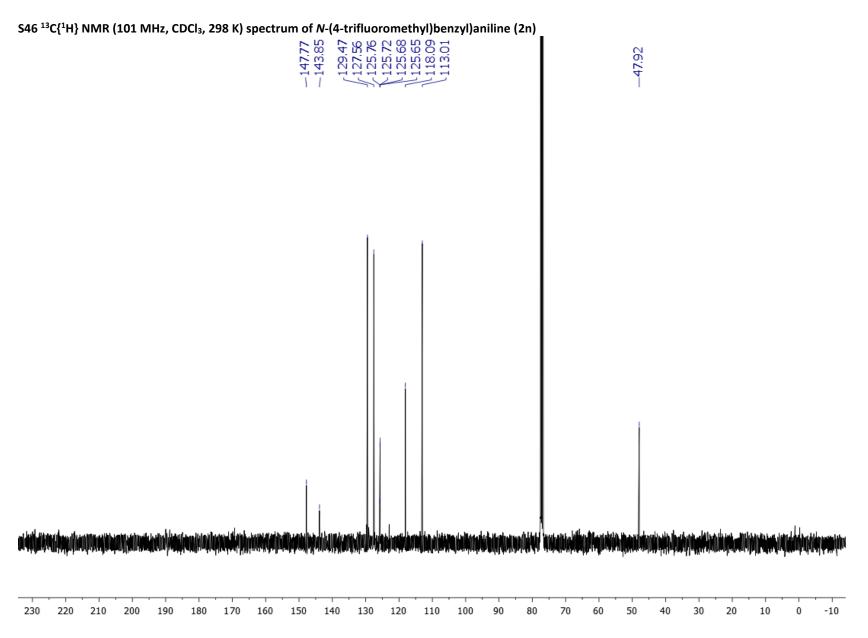






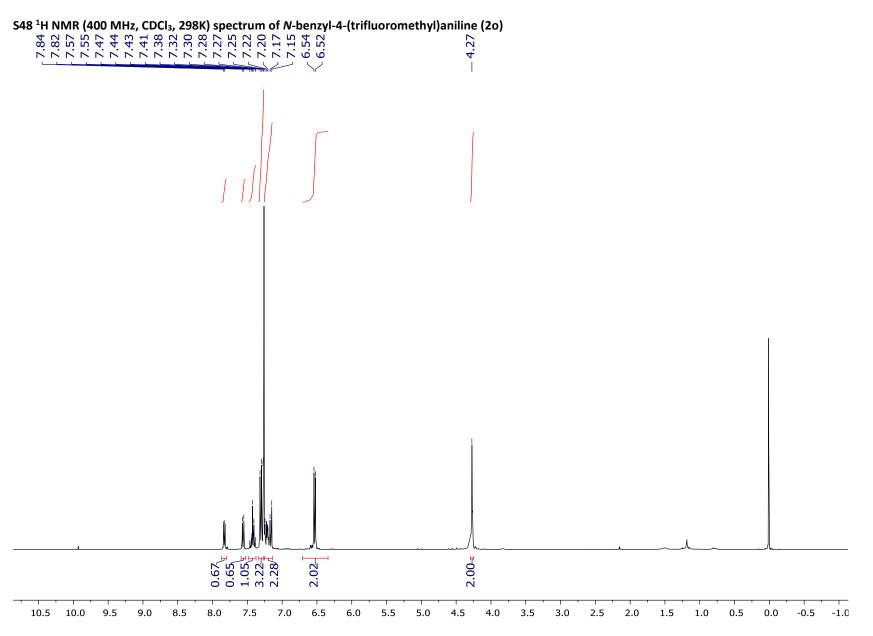


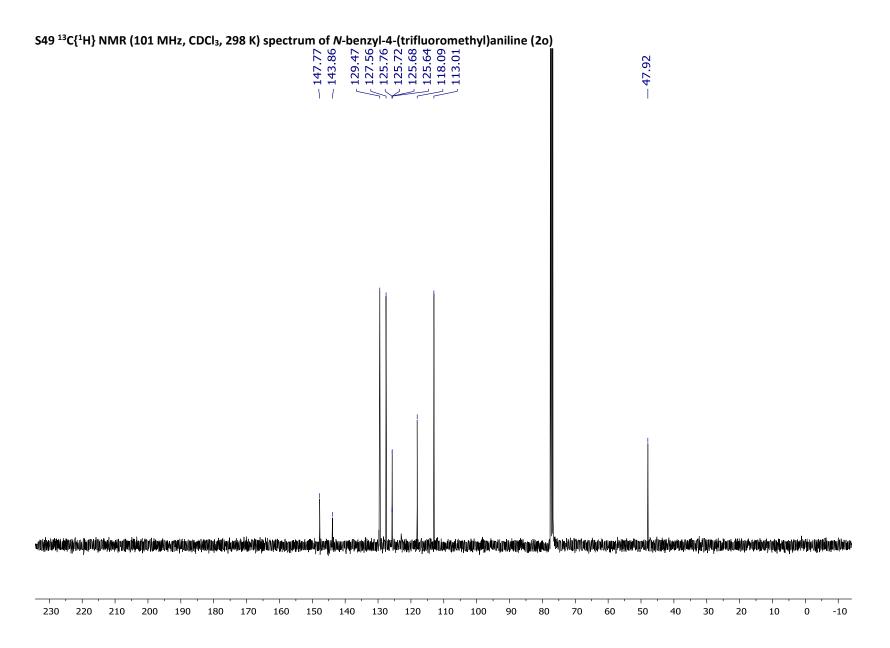




S47 <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298K) spectrum of *N*-(4-trifluoromethyl)benzyl)aniline (2n)

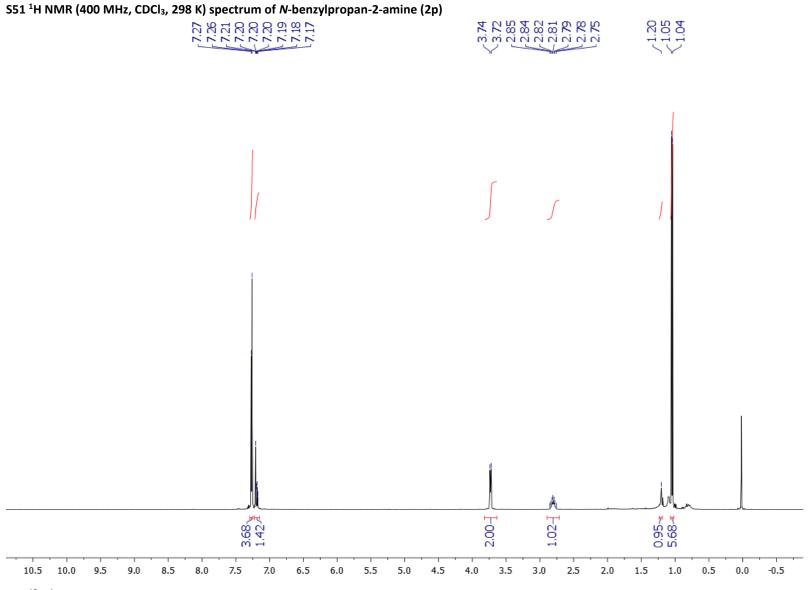
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10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200	-210	



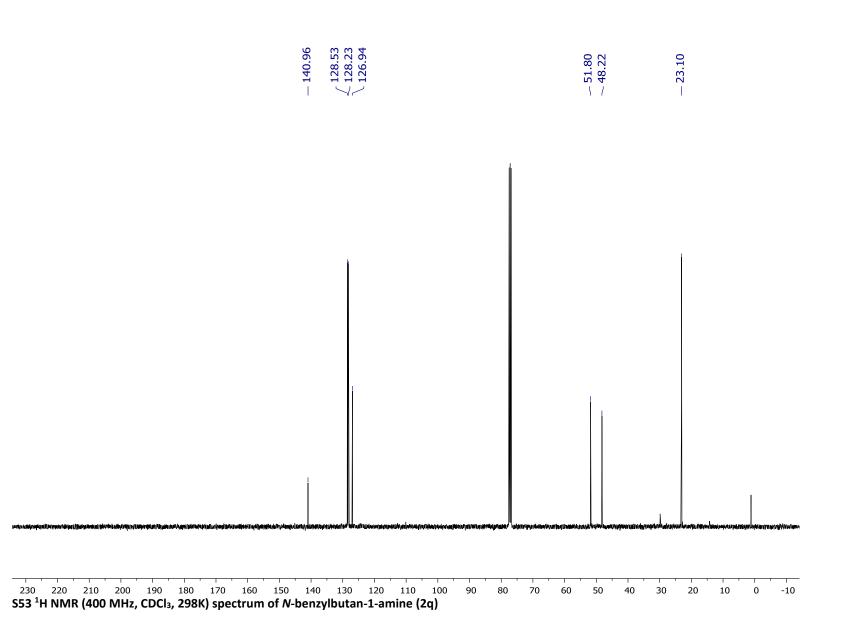


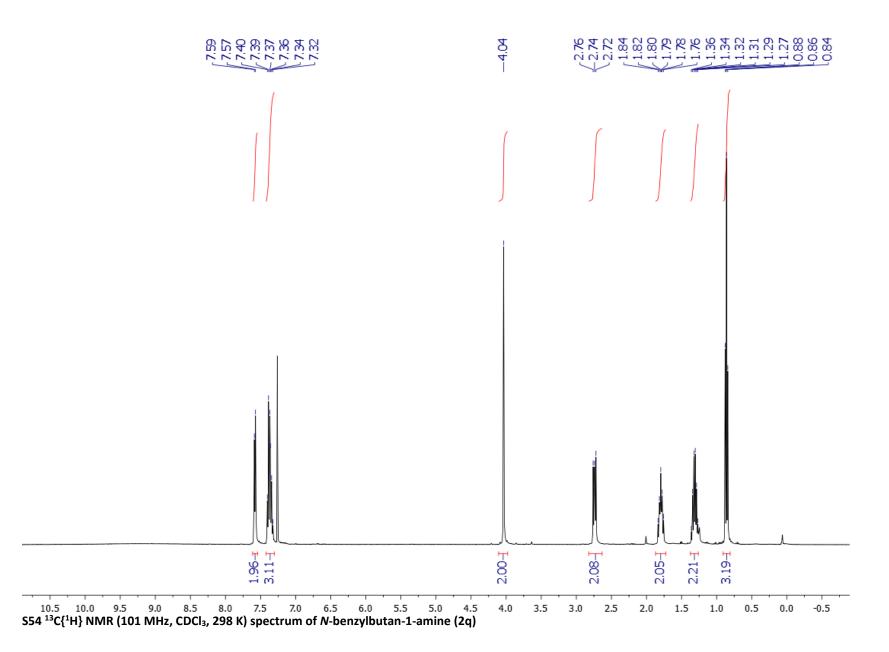
S50 <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298K) spectrum of *N*-benzyl-4-(trifluoromethyl)aniline (2o)

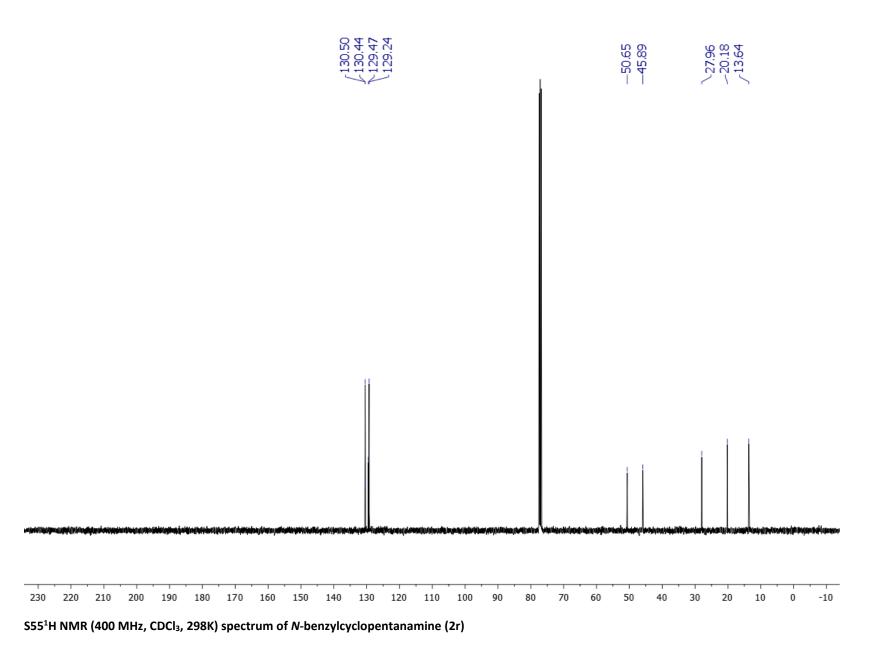
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10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-170	-180	-190	-200	-210

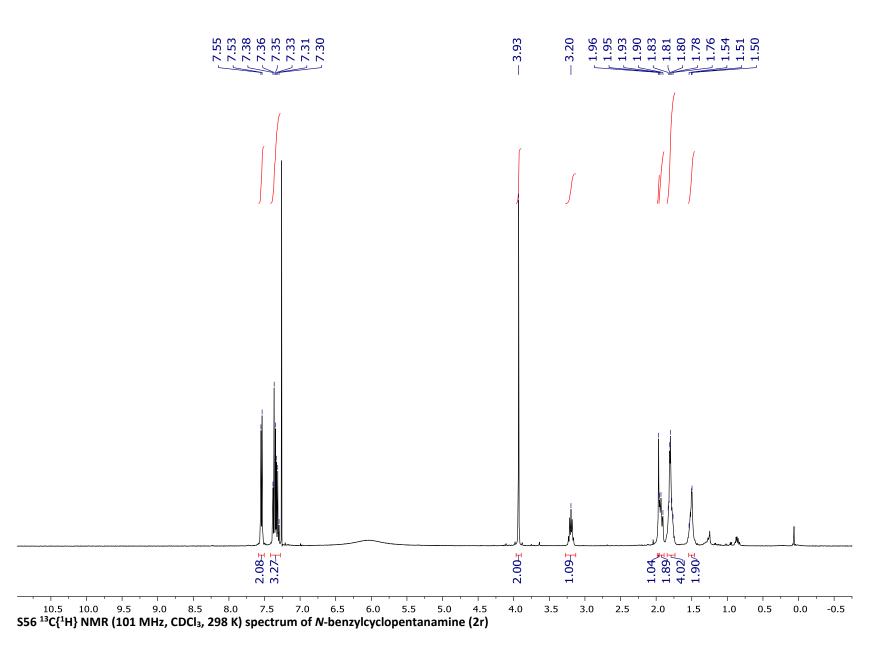


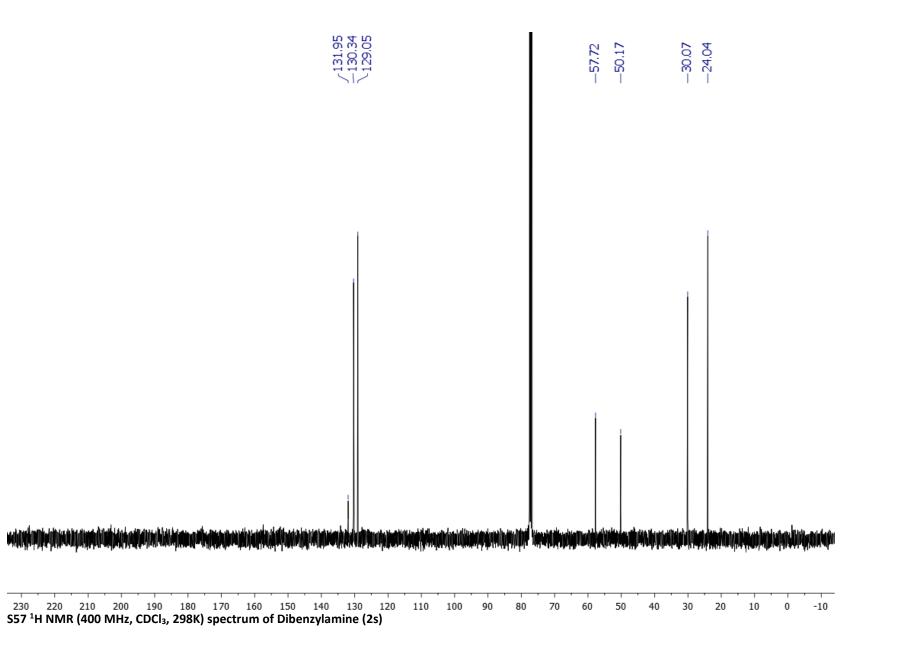
S52 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) spectrum of *N*-benzylpropan-2-amine 1H NMR (2p)

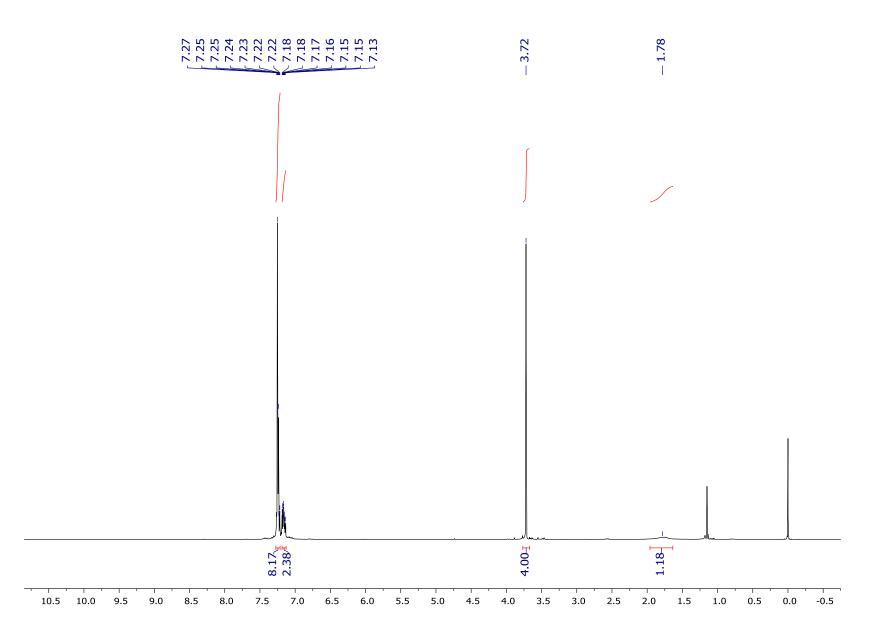


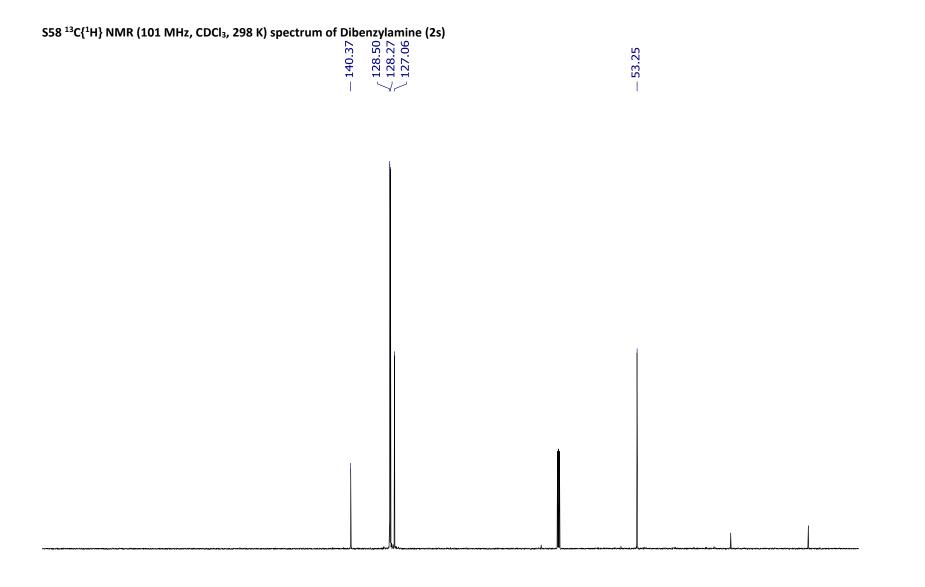




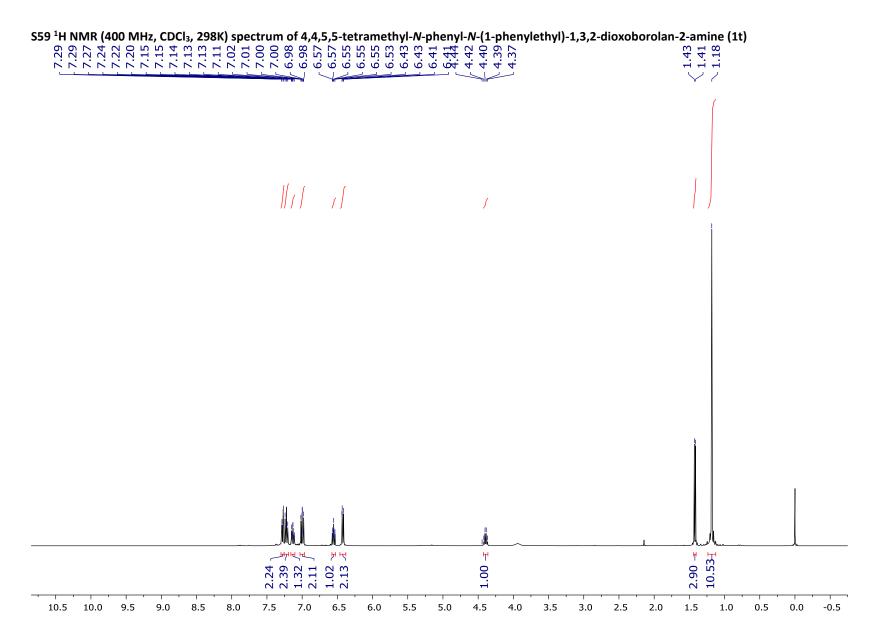


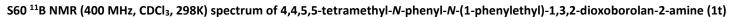


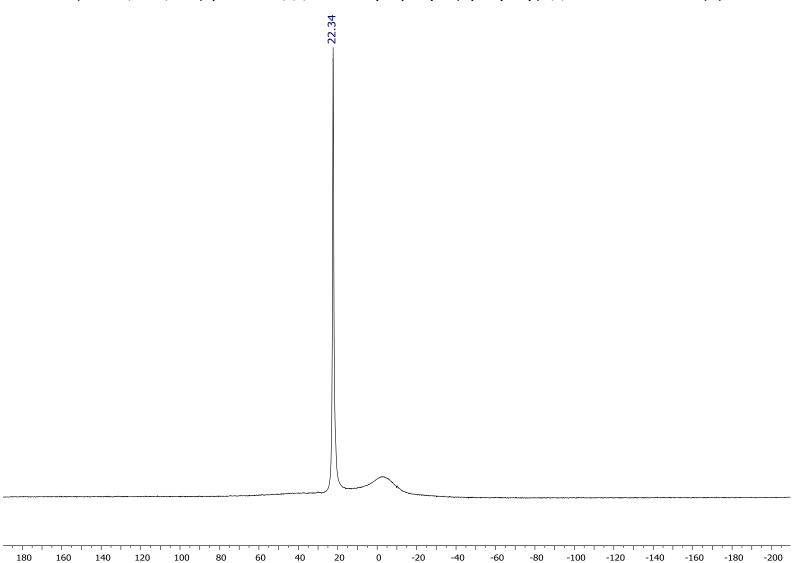


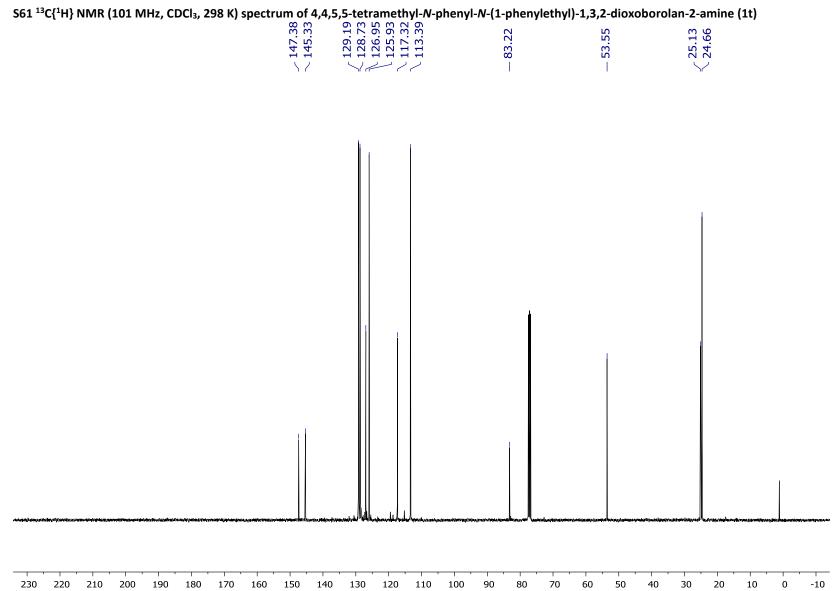


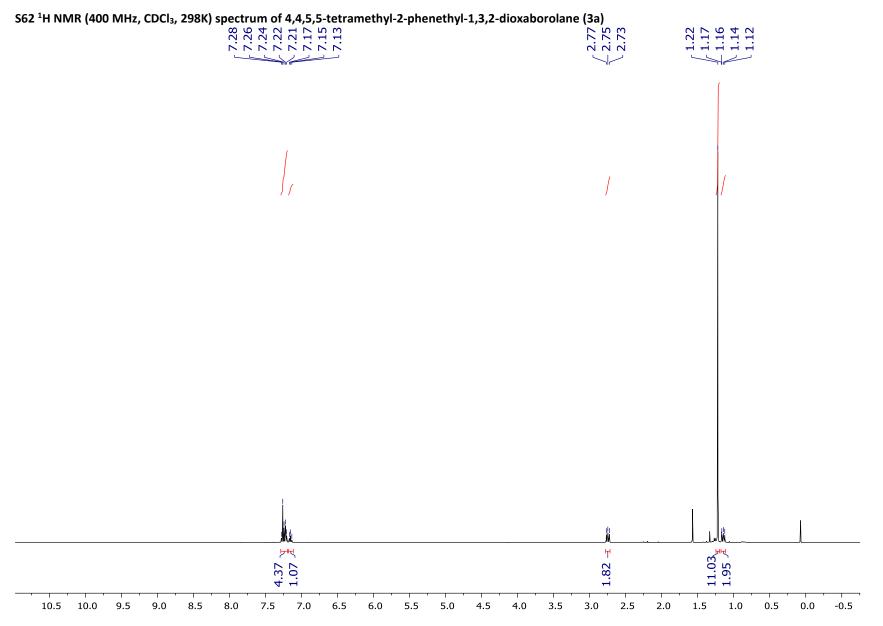
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230	220	210	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	-10

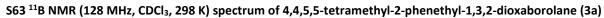


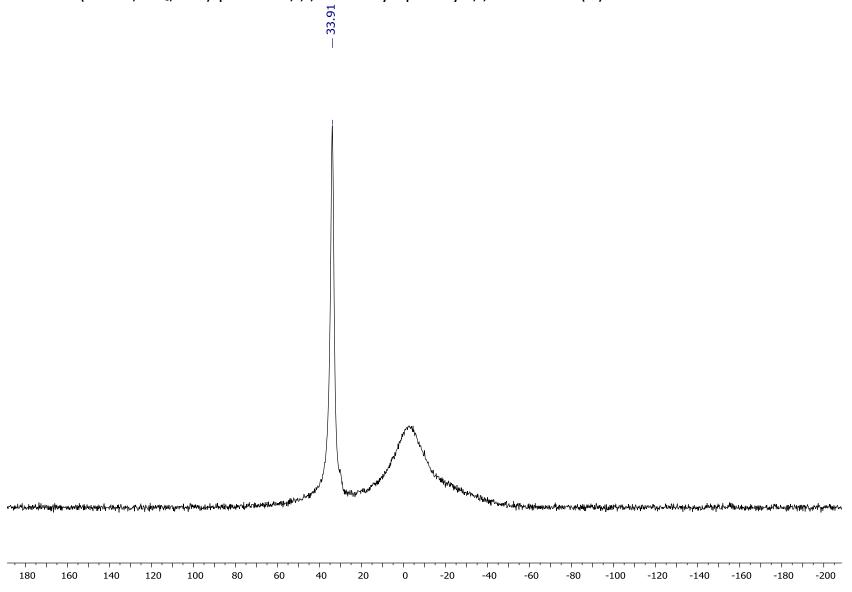




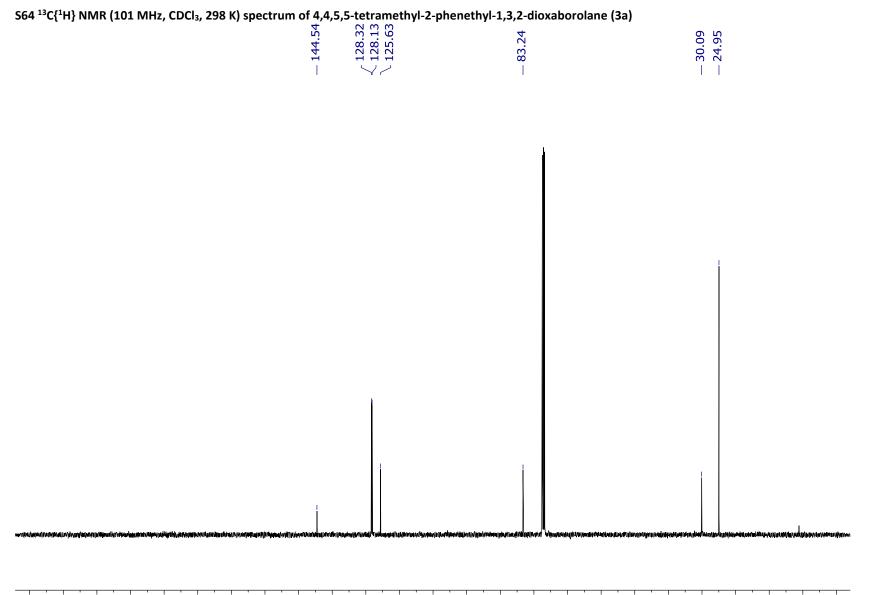




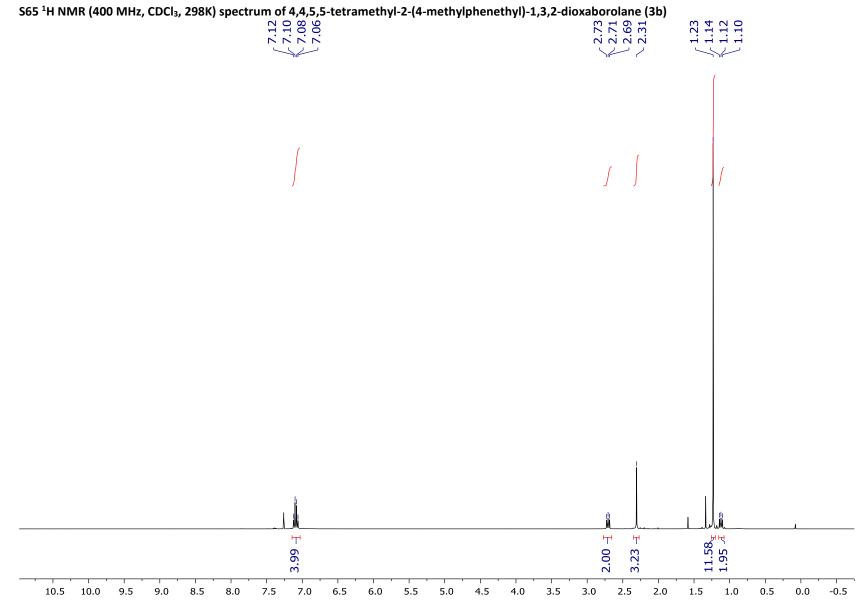




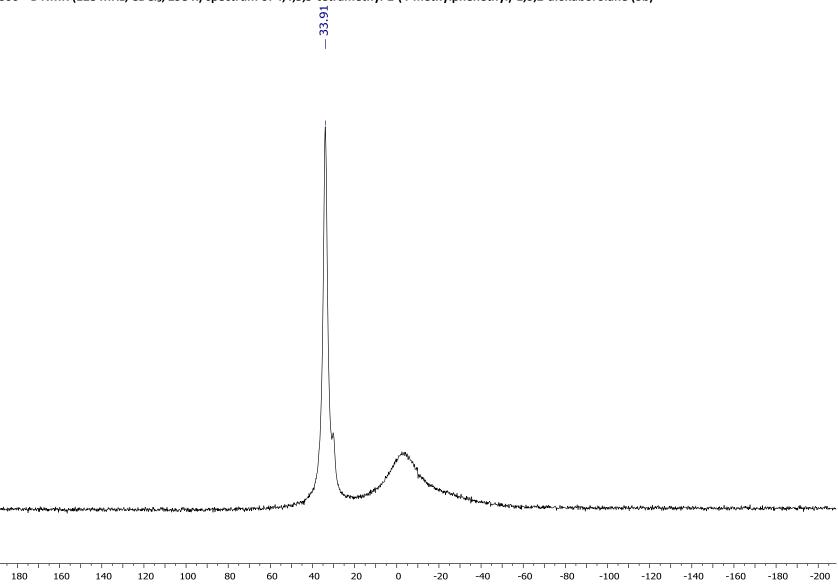
230 220 210 200 190 180 170 160 150 140 130 120 110 100

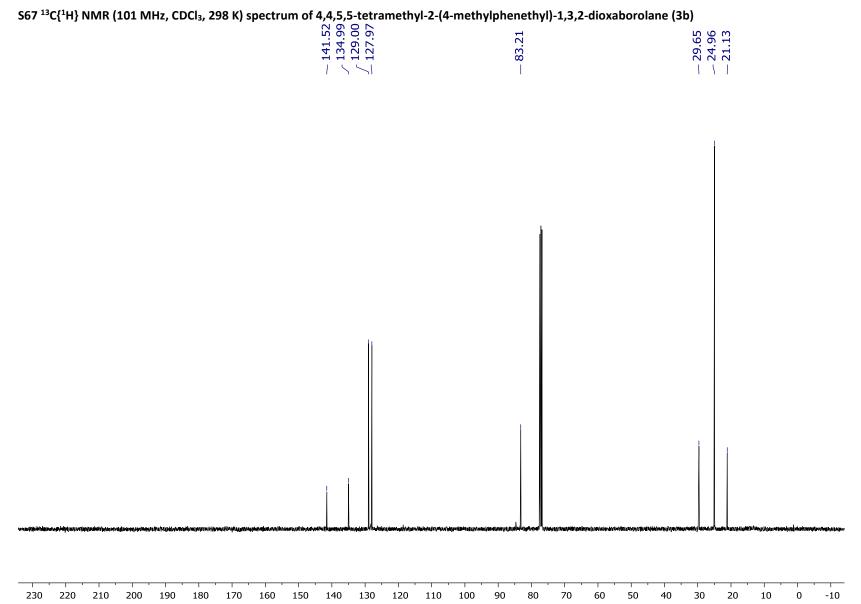


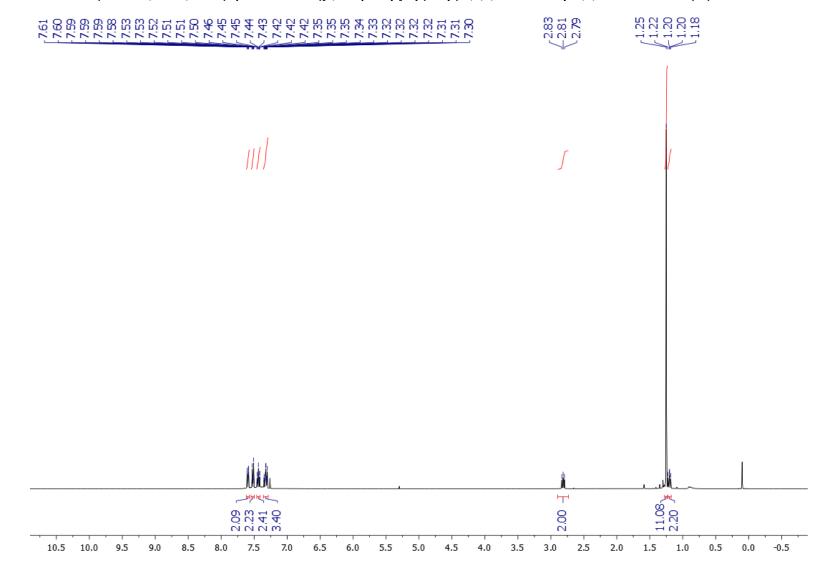
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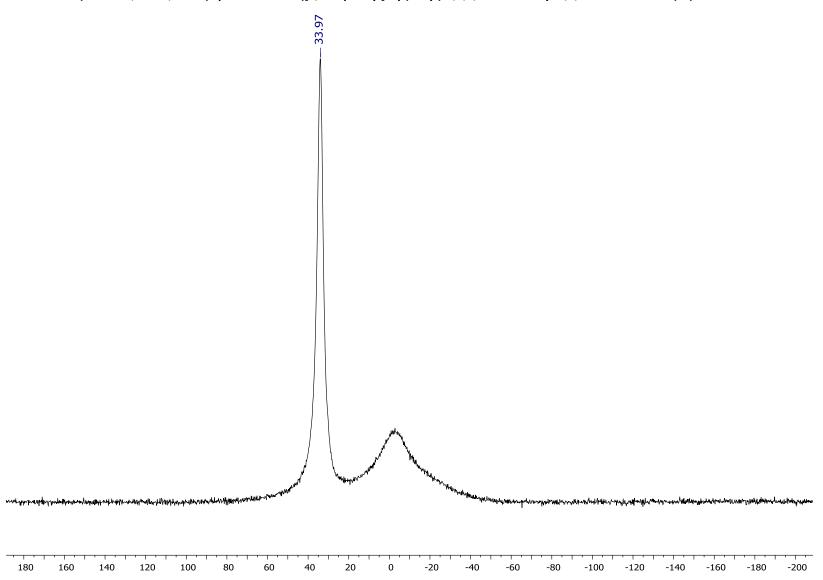




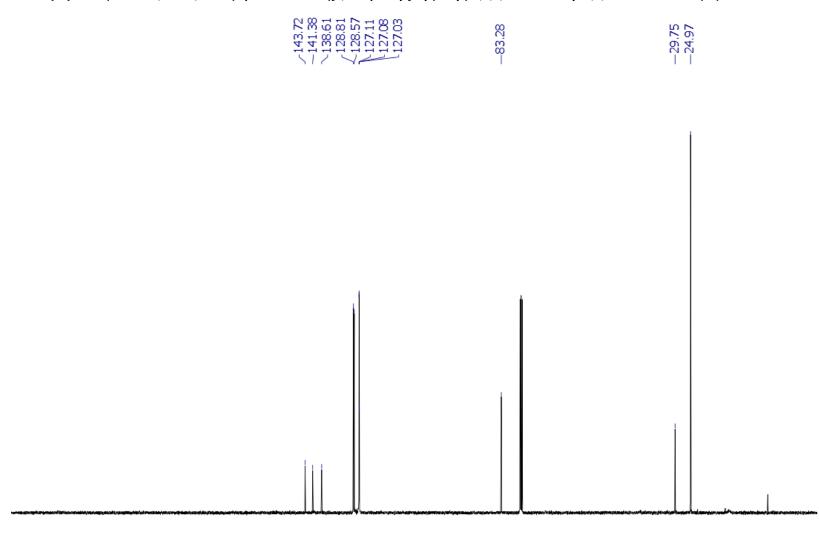


S68 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) spectrum of 2-2([1,1'-biphenyl]4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

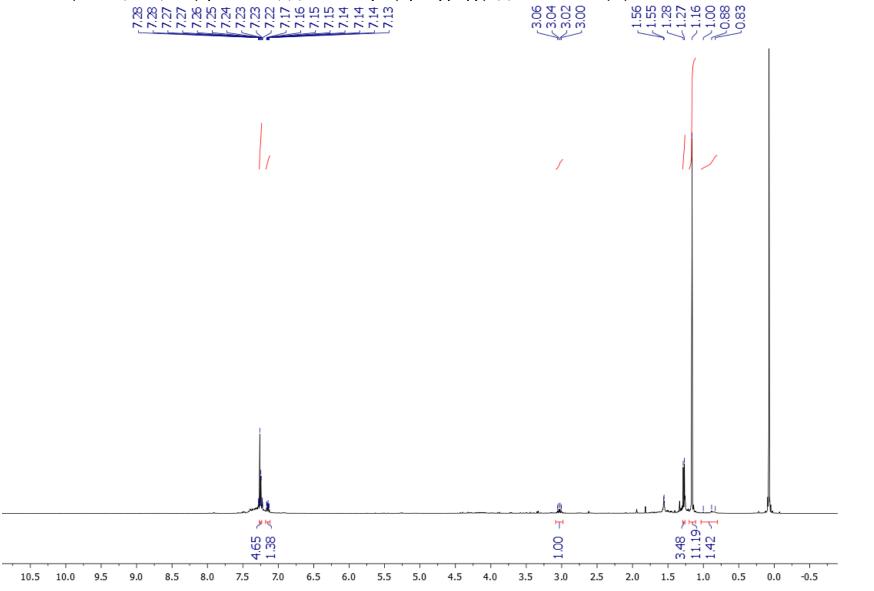




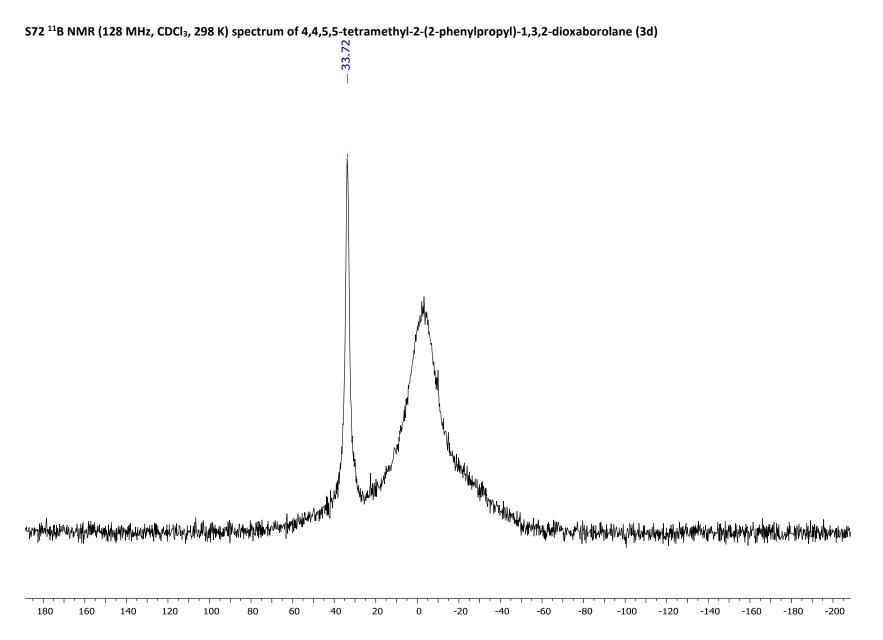
S70 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) spectrum of 2-2([1,1'-biphenyl]4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

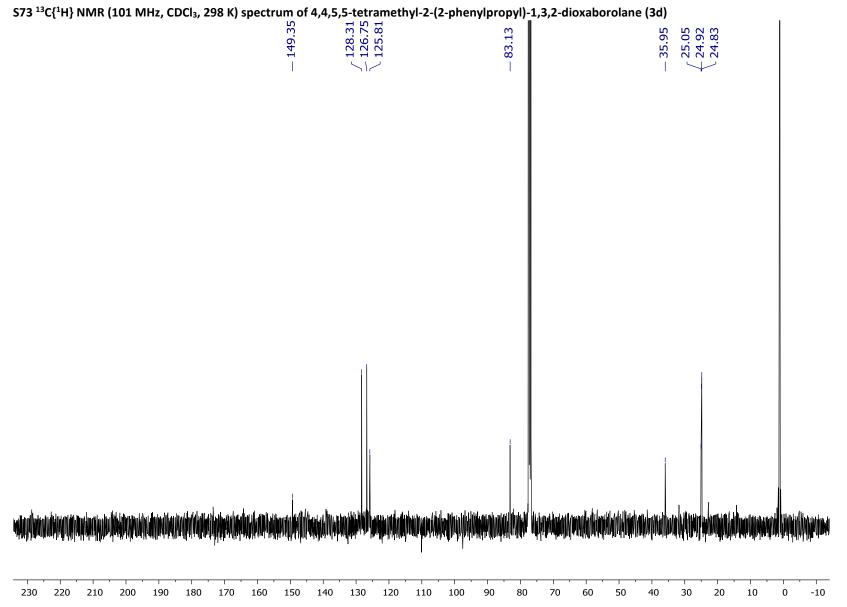


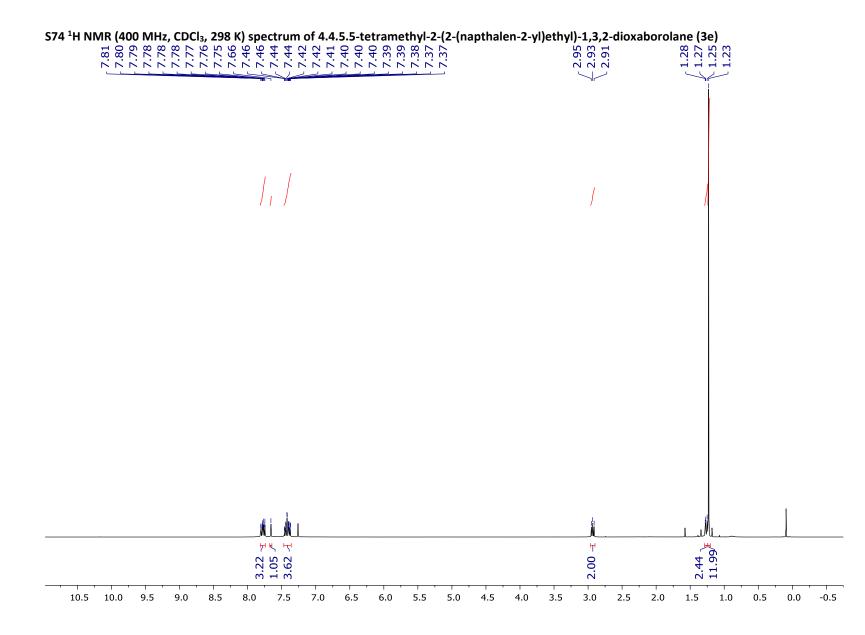
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230	220	210	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	-10

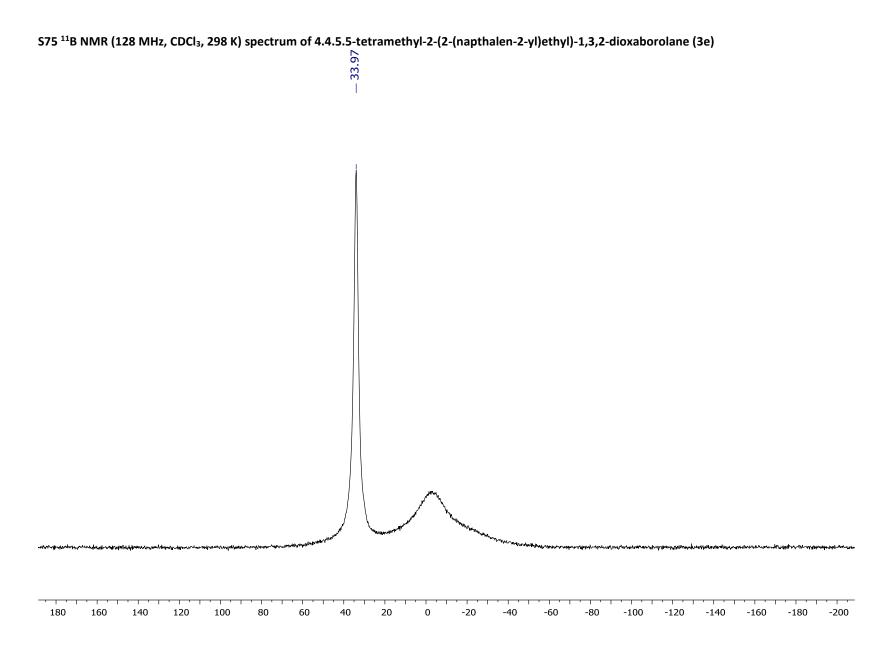


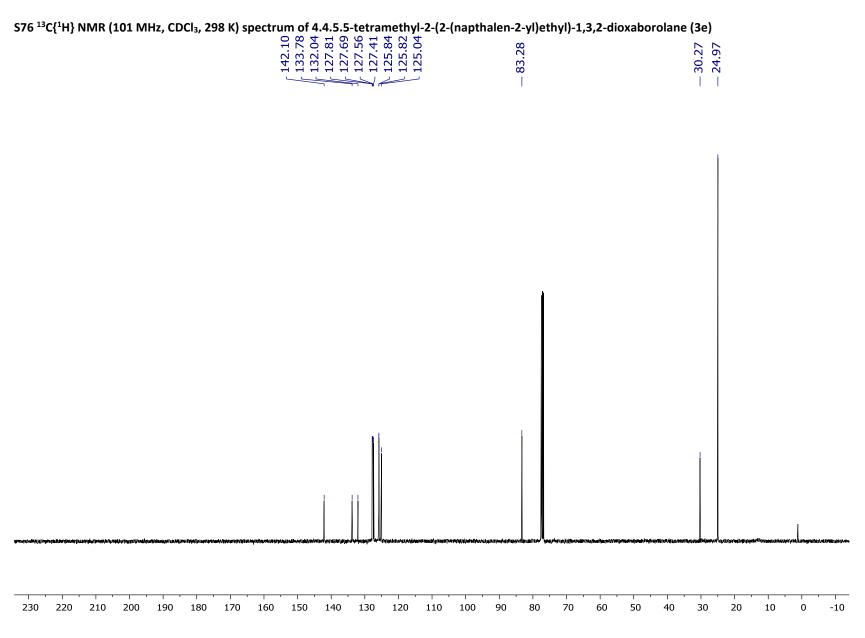
S71 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of 4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (3d)

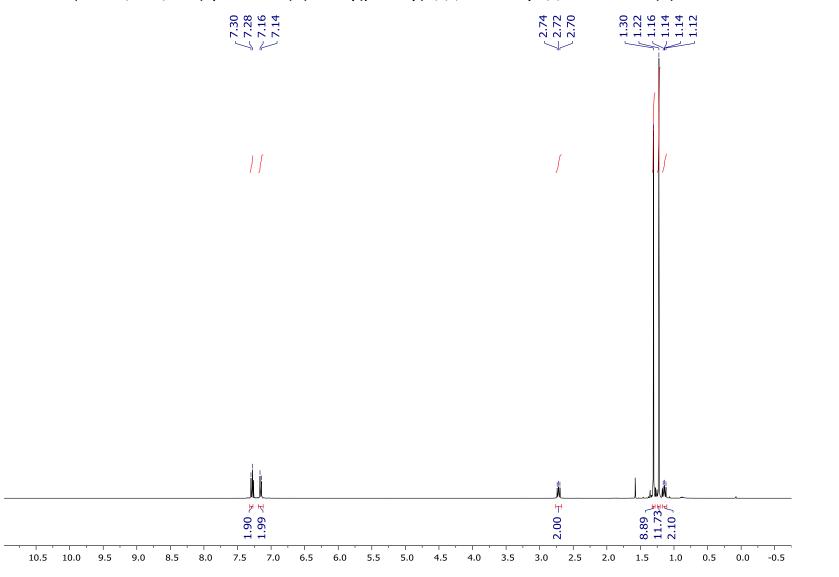






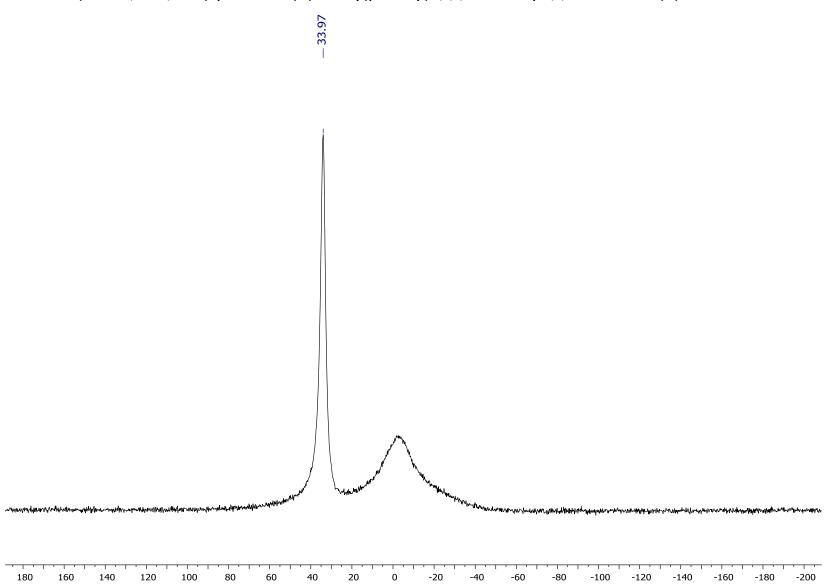


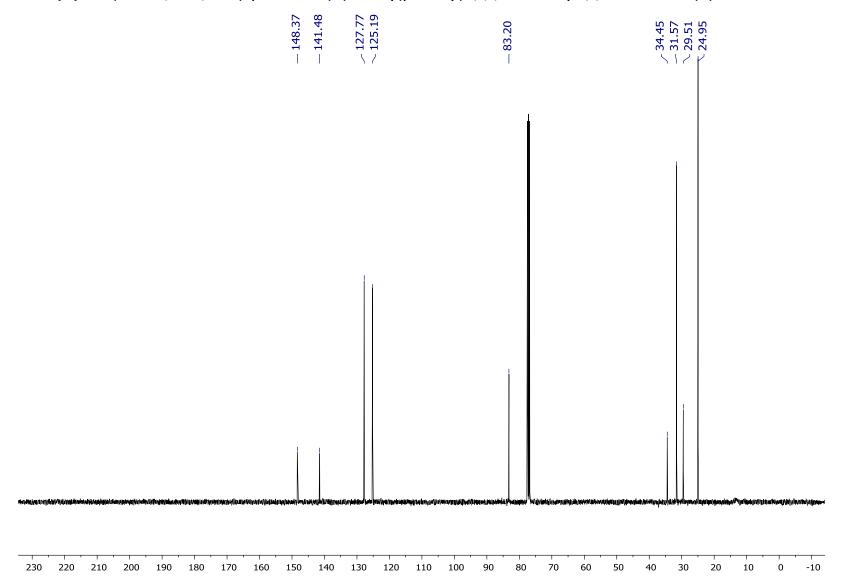




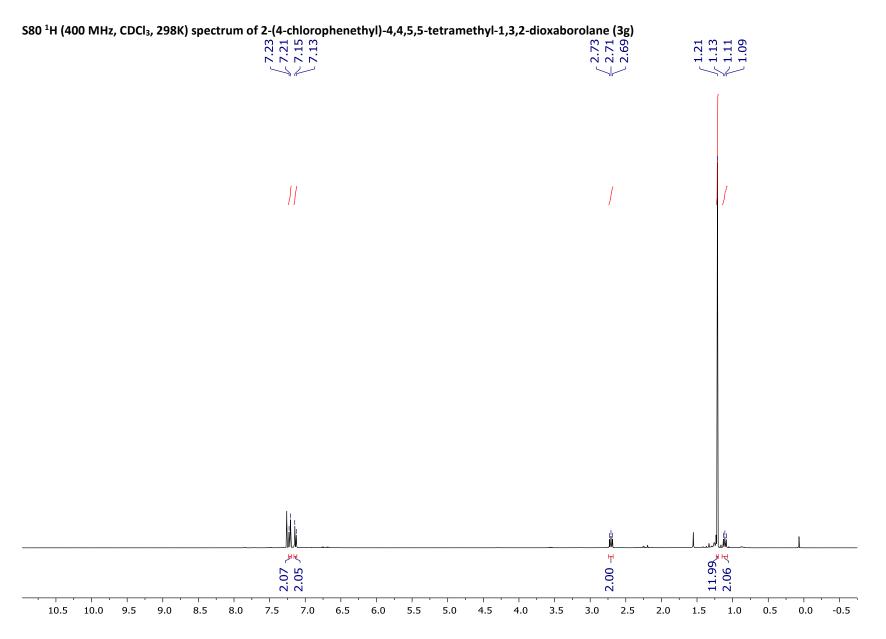
S77 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) spectrum of 2-(4-(*tert*-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)

S78 <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298 K) spectrum of 2-(4-(*tert*-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)

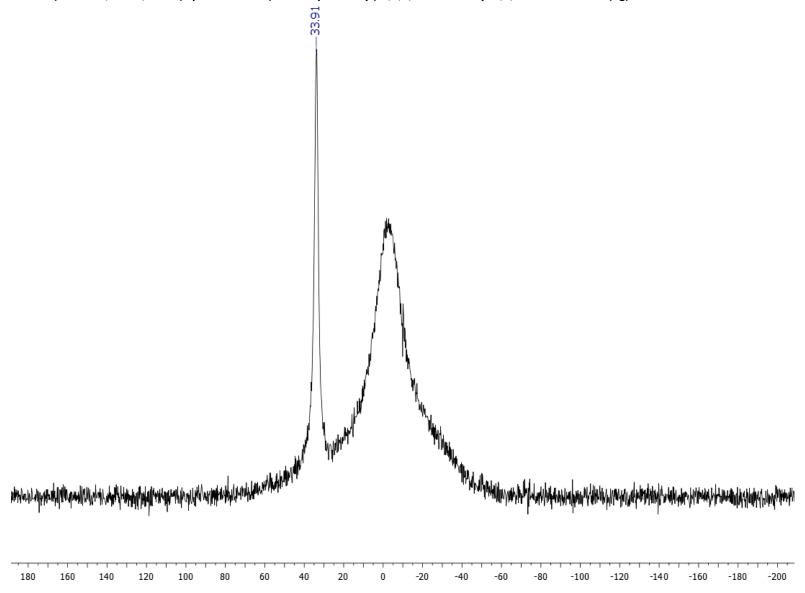


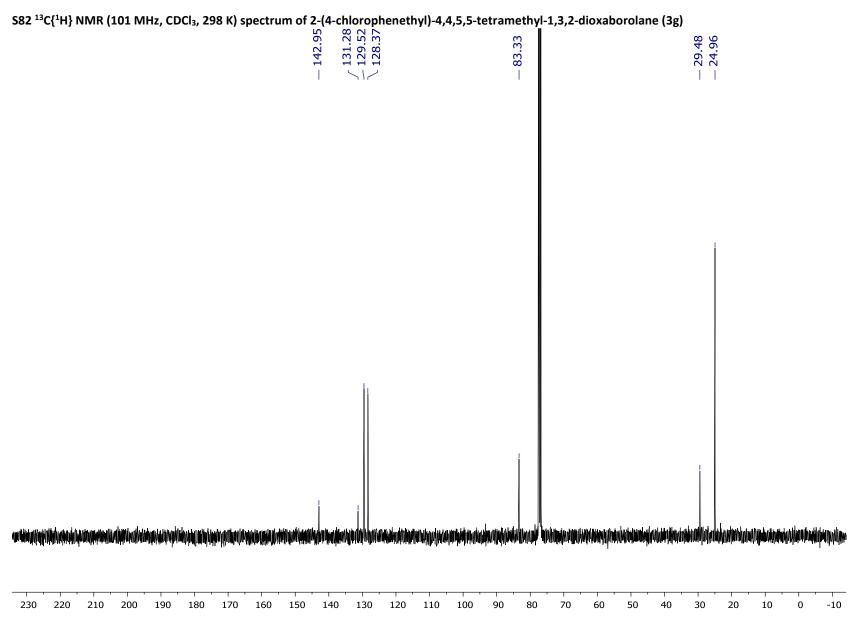


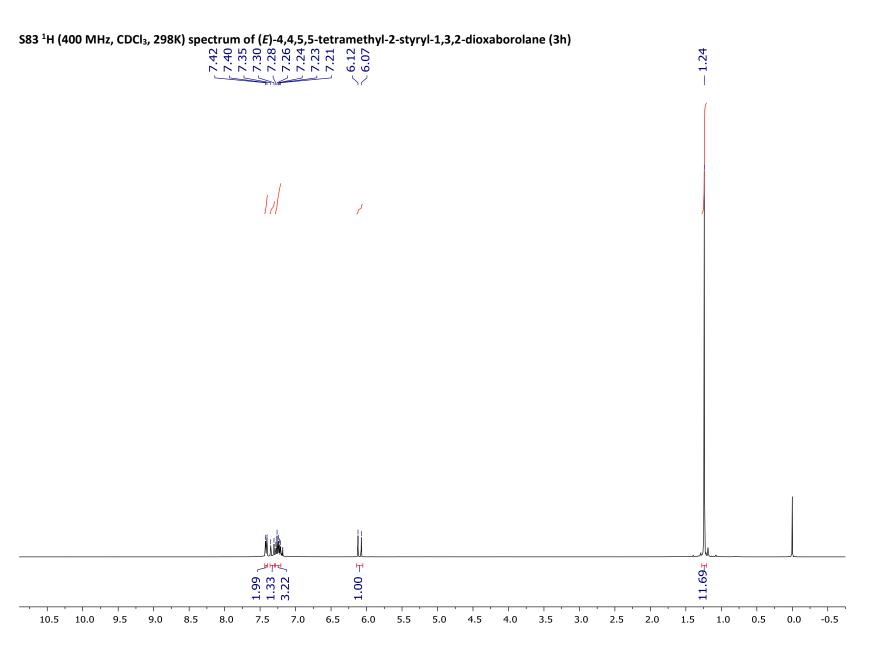
S79 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) spectrum of 2-(4-(*tert*-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)

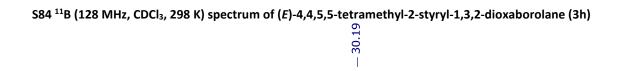




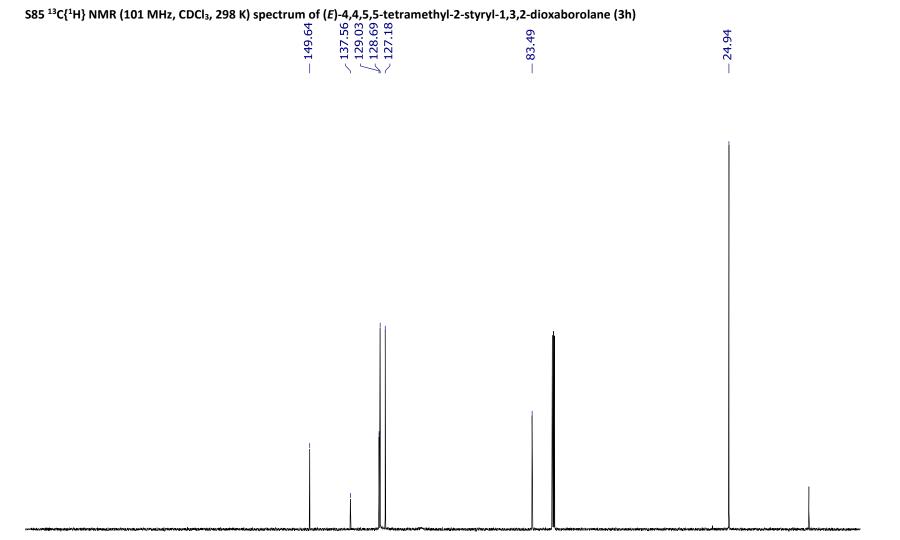


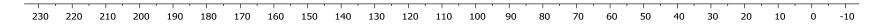


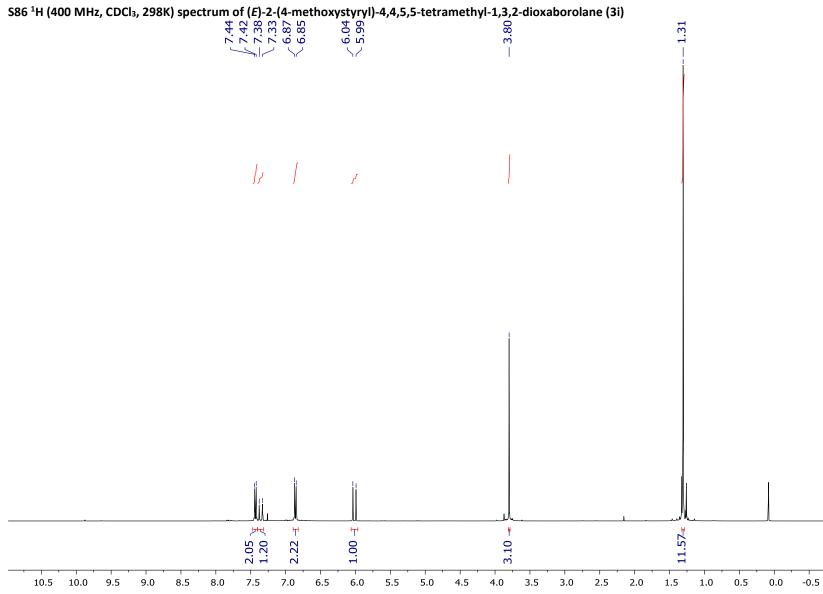




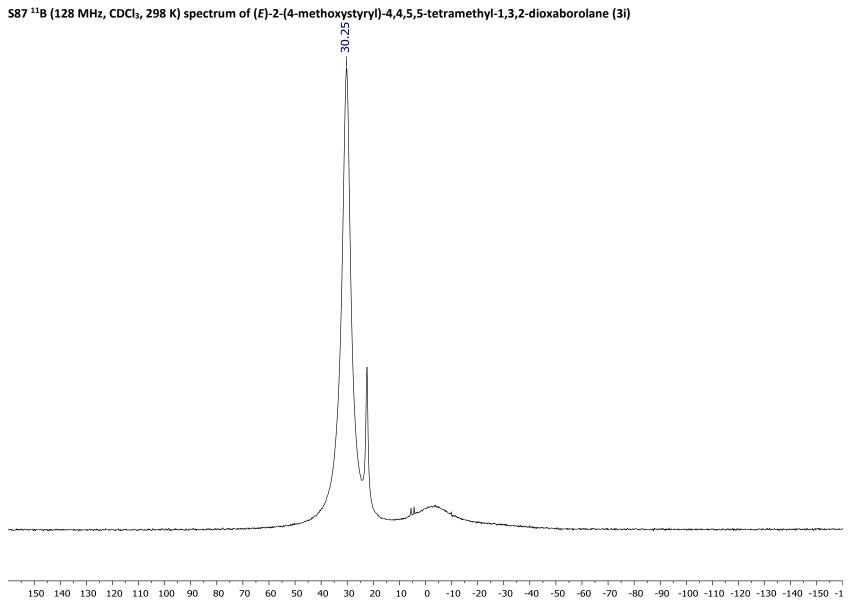




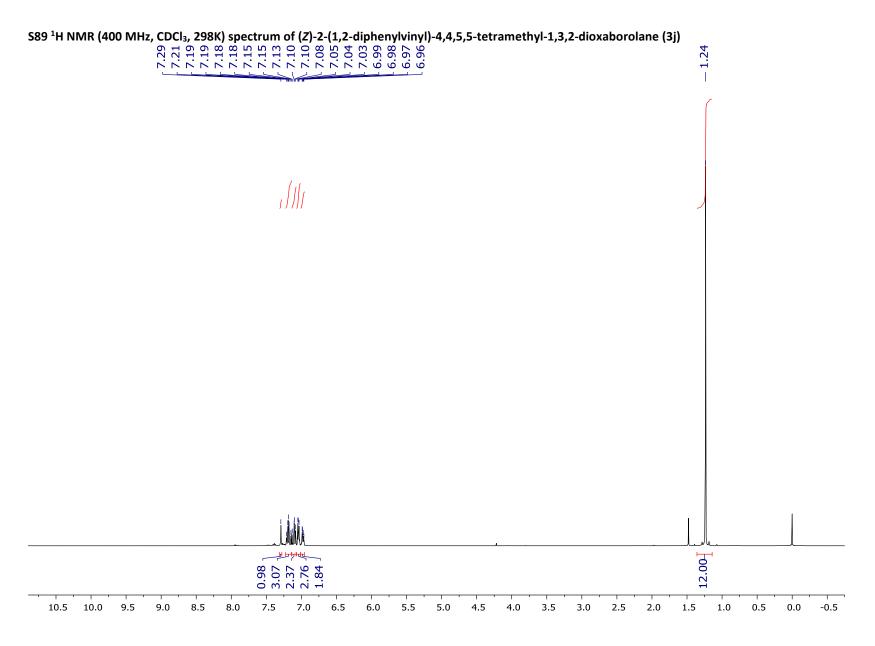


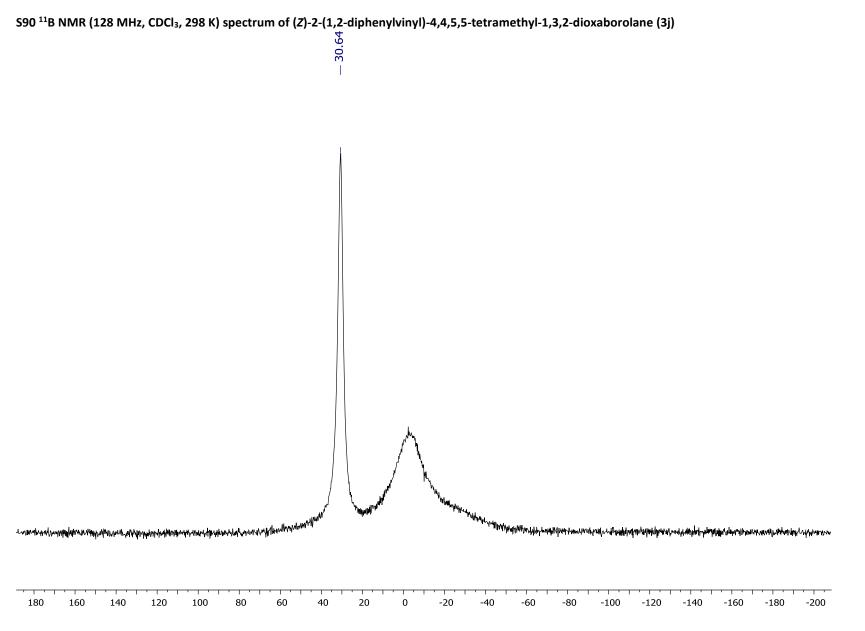


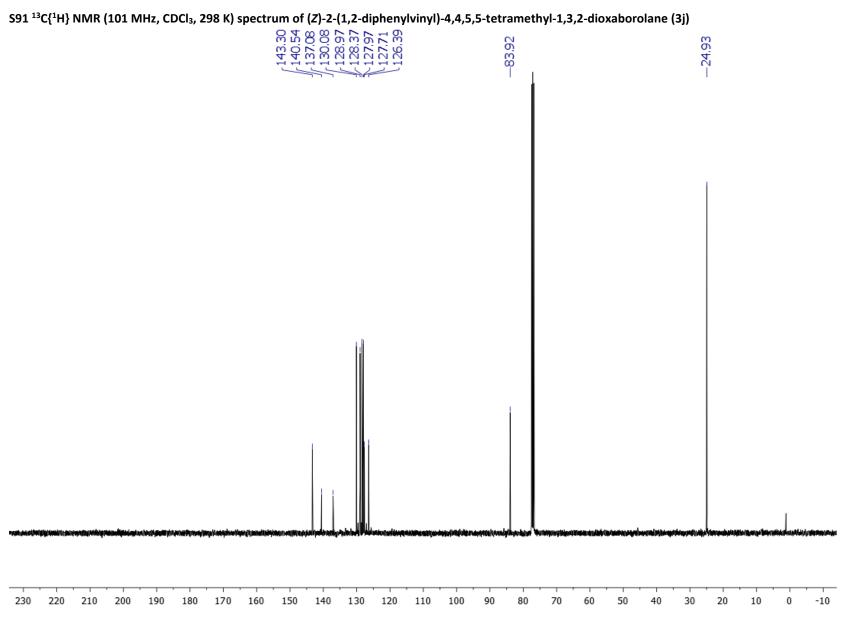




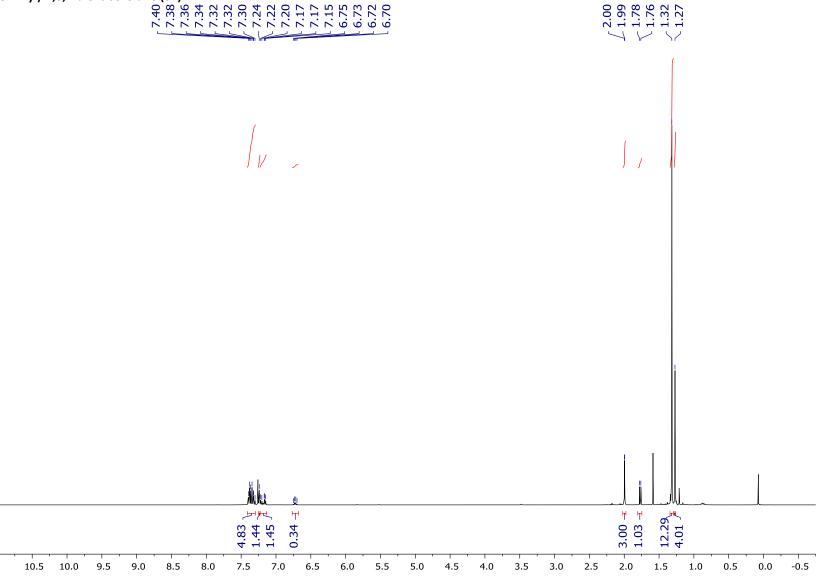
<sup>13</sup> C{ <sup>1</sup> H} NMR (101 MHz, CDCl₃, 298	· · · · · · · · · · · · · · · · · · ·	49.15	30.45	14.04	<b>,</b> ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	33.29 77.36		52.32 55.32		24.88 24.88			
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											L		
D 220 210 200 190 180 1	70 160	150	140 130	120 110	100	90 80	70	60 5	50 40	30	20	10	0



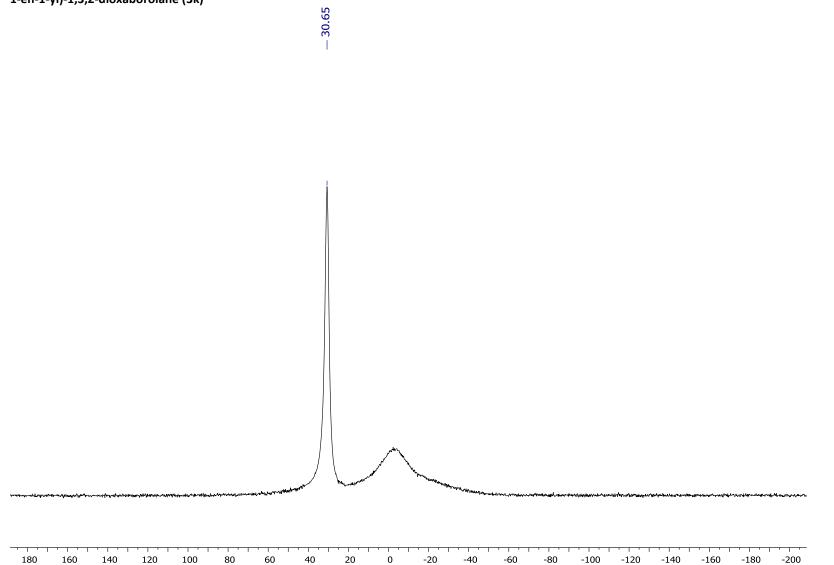




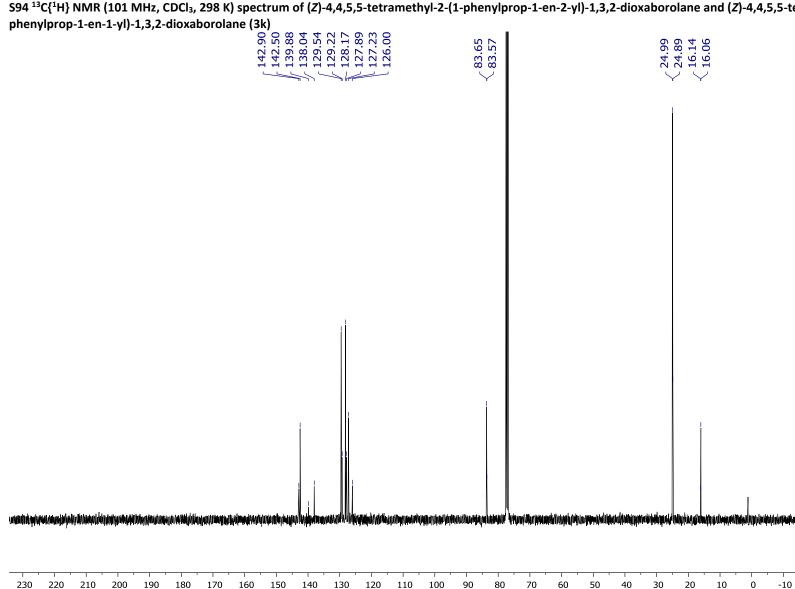
S92 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane and (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (3k)



S93 <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 298 K) spectrum of (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane and (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborol



S94 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 298 K) spectrum of (Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane and (Z)-4,4,5,5-tetramethyl-2-(1-



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