Convenient Synthesis of Stable Aldimine-Borane Complexes, Chiral δ -Amino Alcohols, and γ -Substituted GABA Analogs from Nitriles

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1. General Information

Unless otherwise noted, all manipulations were carried out under inert atmosphere in flame-dried glassware. Tetrahydrofuran (THF) was freshly distilled before use from sodium benzophenone ketyl; all other chemicals and solvents were purchased commercially and used without further purification, unless otherwise noted. (-)-*B*-allyldiisopinocampheylborane (**5**) was prepared according to Brown's procedure by the treatment of (-)-*B*-methoxydiisopinocampheylborane with allylmagnesium bromide.

The ^1H , ^{11}B , and ^{13}C nuclear magnetic resonance (NMR) spectra were plotted on Varian Gemini-300 spectrometer and Varian Inova-300 spectrometer with Nalorac-quad probes using CDCl_3 as solvent at room temperature. The NMR chemical shifts (δ) are reported in ppm. Flash chromatography was performed using standard grade silica gel (Sorbant Technologies, particle size: 40-63 μm , 230 X 400 mesh).

2. Experimental Procedures

General procedure for the synthesis of aromatic aldimine-triethylborane complexes (4a, 4b, 4c, 4d, and 4e):

(*E*)-1-phenylmethanimine triethylborane complex (**4a**): To a solution of benzonitrile **1a** (500mg, 4.85mmol) in diethyl ether (10 ml) lithium triethylborohydride (**2**; 1 M in THF; 4.85 mL, 4.85 mmol) was added at 0 °C and the solution was stirred for 2 h. Methanol (155 mg, 4.85 mmol) was added to the reaction mixture and stirred for 30 minutes. Next, the solvent was evaporated under reduced pressure and the residue was dissolved in dry pentane (5 mL) and filtered through a kramer filter. Benzaldimine-triethylborane complex was then precipitated out by cooling the solution slowly to -78 °C using an acetone-dry ice bath. Removal of the liquid using a double-ended needle, washing the solid with cold pentane, and drying in vacuum provided pure **4a** as white crystals (858 mg, 84% yield) at room temperature. ¹H NMR: (300 MHz, CDCl₃) δ 9.37 (d, *J*=21.5 Hz, 1H), 8.13 (d, *J*=21.5 Hz, 1H), 7.71-7.57 (m, 5H), 0.81 (t, *J*=7.6 Hz, 9H), 0.39 (q, *J*=7.7 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 164.3, 134.2, 129.9, 129.8, 127.9, 14.2, 9.8; ¹¹B NMR (64 MHz, CDCl₃) δ -2.5.

4b, **4c**, **4d**, and **4e** were prepared following the general procedure described for the preparation of **4a**.

(*E*)-*p*-tolylmethanimine triethylborane complex (**4b**): White crystals at room temperature. ^1H NMR: (300 MHz, CDCl_3) δ 9.27 (d, $J=21.4$ Hz, 1H), 8.09 (d, $J=21.4$ Hz, 1H), 7.58 (d, $J=8.0$ Hz, 2H), 7.41 (d, $J=8.0$ Hz, 2H), 2.51 (s, 3H), 0.85 (t, $J=7.7$ Hz, 9H), 0.44 (q, $J=7.7$ Hz, 6H); ^{13}C NMR: (75 MHz, CDCl_3) δ 163.9, 145.5, 130.5, 128.0, 127.2, 21.8, 14.5, 9.6; ^{11}B NMR: (64 MHz, CDCl_3) δ -2.5.

(*E*)-(4-methoxyphenyl)methanimine triethylborane complex (**4c**): Pale yellow oil at room temperature. ^1H NMR: (300 MHz, CDCl_3) δ 9.07(d, $J=21.3$ Hz, 1H), 7.99 (d, $J=21.3$ Hz, 1H), 7.62 (d, $J=8.8$ Hz, 2H), 7.05 (d, $J=8.8$ Hz, 2H), 3.90 (s, 3H), 0.78 (t, $J=7.7$ Hz, 9H), 0.35 (q, $J=7.7$ Hz, 6H); ^{13}C NMR: (75 MHz, CDCl_3) δ 163.1, 134.0, 130.1, 122.9, 115.2, 55.7, 14.4, 9.8; ^{11}B NMR: (64 MHz, CDCl_3) δ -3.0.

(*E*)-(4-nitrophenyl)methanimine triethylborane complex (**4d**): Yellow solid at room temperature. ^1H NMR: (300 MHz, CDCl_3) δ 9.05 (d, $J=20.5$ Hz, 1H), 8.4 (d, $J=20.5$ Hz, 1H), 8.13 (d, $J=8.7$ Hz, 2H), 7.60 (d, $J=8.6$ Hz, 2H), 0.78 (t, $J=7.7$ Hz, 9H), 0.35 (q, $J=7.7$ Hz, 6H); ^{13}C NMR: (75 MHz, CDCl_3) δ 162.9, 130.5, 130.1, 124.3, 123.0, 115.1, 14.4, 9.7; ^{11}B NMR: (64 MHz, CDCl_3) δ -1.5.

(*E*)-thiophen-2-ylmethanimine triethylborane complex (**4e**): Pale yellow oil at room temperature. ^1H NMR: (200 MHz, CDCl_3) δ 8.73 (d, $J=20.4$ Hz, 1H), 8.11 (d, $J=20.8$ Hz, 1H), 7.73 (d, $J=4.8$ Hz, 1H), 7.61 (d, $J=3.6$ Hz, 1H), 7.24 (t, $J=4.0$ Hz, 1H), 0.77 (t, $J=7.6$ Hz, 9H), 0.33 (q, $J=7.6$ Hz, 6H); ^{13}C NMR: (75 MHz, CDCl_3) δ 156.5, 135.9, 135.0, 133.8, 129.6, 15.6, 11.1; ^{11}B NMR: (64 MHz, CDCl_3) δ -2.4.

General procedure for the synthesis of aromatic C-deuterated aldimine-triethylborane complexes (C-deuterated 4a, C-deuterated 4b, C-deuterated 4c, and C-deuterated 4e) :

(*E*)-1-phenyl-C-deuterio-methanimine triethylborane complex (**C-deuterated 4a**) : To a solution of benzonitrile **1a** (500mg, 4.85mmol) in diethyl ether (10 ml) lithium triethylborodeuteride (**2**; 1 M in THF; 4.85 mL, 4.85 mmol) was added at 0 °C and the solution was stirred for 3 h. Methanol (155 mg, 4.85 mmol) was added to the reaction mixture and stirred for 30 minutes. Next, the solvent was evaporated under reduced pressure and the residue was dissolved in dry pentane (5 mL) and filtered through a kramer filter. C-deuterio-benzaldimine-triethylborane complex was then precipitated out by cooling the solution slowly to -78 °C using an acetone-dry ice bath. Removal of the liquid using a double-ended needle, washing the solid with cold pentane, and drying in vacuum provided pure **C-deuterated 4a** as yellow solid (898 mg, 4.27

mmol, 88% yield) at room temperature. ^1H NMR: (300 MHz, CDCl_3) δ 9.41 (s, 1H), 7.63-7.48 (m, 5H), 0.84 (t, $J=7.3$ Hz, 9H), 0.43 (q, $J=7.6$ Hz, 6H); ^{13}C NMR: (75 MHz, CDCl_3) δ 163.0 (t, $J=25.3$ Hz), 134.2, 130.2, 129.8, 127.9, 14.2, 9.7; ^{11}B NMR: (64 MHz, CDCl_3) δ -2.4.

C-deuterated 4b, **C-deuterated 4c**, and **C-deuterated 4e** were prepared following the general procedure described for the preparation of **C-deuterated 4a**.

(*E*)-*p*-tolyl-*C*-deuterio-methanimine triethylborane complex (**C-deuterated 4b**) :

Yellow oil at room temperature. ^1H NMR: (300 MHz, CDCl_3) δ 9.2 (s, 1H), 7.55 (d, $J=8.0$ Hz, 2H), 7.37 (d, $J=8.0$ Hz, 2H), 2.49 (s, 3H), 0.80 (t, $J=7.6$ Hz, 9H), 0.38 (q, $J=7.6$ Hz, 6H); ^{13}C NMR: (75 MHz, CDCl_3) δ 162.0 (t, $J=24.9$ Hz), 144.4, 130.5, 129.4, 128.0, 21.8, 14.4, 9.9; ^{11}B NMR: (64 MHz, CDCl_3) δ -2.7.

(*E*)-(4-methoxyphenyl)-*C*-deuterio-methanimine triethylborane

complex (**C-deuterated 4c**) : Pale yellow oil at room temperature. ^1H NMR: (300 MHz, CDCl_3) δ 8.96 (s, 1H), 7.59 (d, $J=8.8$ Hz, 2H), 7.03 (d, $J=8.8$ Hz, 2H), 3.90 (s, 3H), 0.75 (t, $J=7.6$ Hz, 9H), 0.32 (q, $J=7.8$ Hz, 6H); ^{13}C NMR: (300 MHz, CDCl_3) δ 162.8 (t, $J=25.1$ Hz), 134.0, 129.8, 122.9, 114.8, 55.6, 14.4, 9.8; ^{11}B NMR: (64 MHz, CDCl_3) δ -2.5.

(*E*)-thiophen-2-yl-*C*-deuterio-methanimine triethylborane complex

(*C*-deuterated **4e)** : Yellow solid at room temperature. ^1H NMR: (300 MHz, CDCl_3) δ 8.72 (s, 1H), 7.73 (d, $J=4.8$ Hz, 1H), 7.61 (d, $J=3.0$ Hz, 1H), 7.24 (t, $J=4.2$ Hz, 1H), 0.76 (t, $J=7.6$ Hz, 9H), 0.32 (q, $J=7.6$ Hz, 6H); ^{13}C NMR: (75 MHz, CDCl_3) δ 156.1 (t, $J=26.4$ Hz), 135.8, 134.9, 133.7, 129.6, 15.7, 11.1; ^{11}B NMR: (64 MHz, CDCl_3) δ -2.5.

General procedure for the synthesis of aromatic *N*-deuterated aldimine-triethylborane complex (*N*-deuterated **4a):**

(*E*)-1-phenyl-*N*-deuterio-methanimine triethylborane complex (*N*-

deuterated **4a**): To a solution of benzonitrile **1a** (500mg, 4.85mmol) in diethyl ether (10 ml) lithium triethylborohydride (**2**; 1 M in THF; 4.85 mL, 4.85 mmol) was added at 0 °C and the solution was stirred for 2 h. CD_3OD (175 mg, 4.85 mmol) was added to the reaction mixture and stirred for 30 minutes. Next, the solvent was evaporated under reduced pressure and the residue was dissolved in dry pentane (5 mL) and filtered through a kramer filter. *N*-deuterio-benzaldimine-triethylborane complex was then precipitated out by cooling the solution slowly to -78 °C using an acetone-dry ice bath. Removal of the liquid using a double-ended needle, washing the solid with cold pentane,

and drying in vacuum provided pure ***N*-deuterated 4a** as pale yellow solid (836 mg, 3.98 mmol, 82% yield) at room temperature. ^1H NMR: (300 MHz, CDCl_3) δ 8.22 (s, 1H), 7.78-7.67 (m, 5H), 0.95 (t, $J=7.6$ Hz, 9H), 0.53 (q, $J=7.4$ Hz, 6H); ^{13}C NMR: (75 MHz, CDCl_3) δ 164.2, 134.3, 130.2, 129.9, 128.0, 14.4, 9.9; ^{11}B NMR: (64 MHz, CDCl_3) δ -2.3.

General procedure for the synthesis of aromatic *C,N*-dideuterated aldimine-triethylborane complexe (*C,N*-dideuterated 4a) :

(*E*)-1-phenyl-*C,N*-dideuterio-methanimine triethylborane complex

(*C,N*-dideuterated 4a): To a solution of benzonitrile **1a** (500mg, 4.85mmol) in diethyl ether (10 ml) lithium triethylborodeuteride (1 M in THF; 4.85 mL, 4.85 mmol) was added at 0 °C and the solution was stirred for 2 h. CD_3OD (175 mg, 4.85 mmol) was added to the reaction mixture and stirred for 30 minutes. Next, the solvent was evaporated under reduced pressure and the residue was dissolved in dry pentane (5 mL) and filtered through a kramer filter. *C,N*-dideuterio-benzaldimine triethylborane complex was then precipitated out by cooling the solution slowly to -78 °C using an acetone-dry ice bath. Removal of the liquid using a double-ended needle, washing the solid with cold pentane, and drying in vacuum provided pure ***C,N*-dideuterated 4a** as pale white solid (815 mg, 3.88 mmol, 80% yield) at room temperature. ^1H NMR: (300 MHz, CDCl_3) δ 7.68-7.56 (m, 5H), 0.84 (t, $J=7.7$ Hz, 9H), 0.42 (q, $J=7.5$ Hz, 6H); ^{13}C NMR: (75 MHz, CDCl_3) δ 164.1 (t, $J=27.1$ Hz), 134.2, 129.9, 129.8, 127.9, 14.4, 9.9; ^{11}B NMR: (64 MHz, CDCl_3) δ -2.5.

Table 1. Aldimine-borane complexes

Entry	Aldimine-Borane Complex	%Yield
1	4a	84
2	4b	86
3	4c	90
4	4d	30 ^a
5	4e	82
6	C-deuterated 4a	88
7	N-deuterated 4a	82
8	C,N-dideuterated 4a	80
9	C-deuterated 4b	81
10	C-deuterated 4c	79
11	C-deuterated 4e	85

^aLow yield is due to the difficulty in isolation of the complex.

64% yield of the homoallylic amine (**7d**) by one-pot allylboration of 4-nitrobenzonitrile (**1d**) suggests the formation of **4d** in at least 64% yield.

General procedure for the preparation of homoallylic amines by one-pot allylboration of aromatic and fluoro-benzonitriles (7a-7e and 7h-7k) :

(*S*)-1-phenylbut-3-en-1-amine (**7a**): To a solution of benzonitrile **1a** (300mg, 2.9 mmol) in diethyl ether (5 ml) lithium triethylborohydride (**2**; 1 M in THF; 2.9 mL, 2.9 mmol) was added at 0 °C and the solution was stirred for 2 h. Methanol (92 mg, 2.9 mmol) was added to the reaction mixture and stirred for 30 minutes. The reaction mixture was cooled to -100 °C and slowly transferred to *via* canula to a stirring solution

of (-)-*B*-allyldiisopinocampheylborane (**5**, 1 M in diethyl ether; 3.48 mL, 3.48 mmol) pre-cooled to -100 °C and diluted with ether. After 6 h, the reaction mixture was slowly warmed to -78 °C and stirring was continued for 16 h more. Then the reaction mixture was oxidised very slowly with NaOH (3 M in H₂O; 1.2 mL) and H₂O₂ (30% in H₂O; 1.2 mL) and was left stirring overnight under positive N₂ pressure while it slowly warmed to room temperature. The product was then extracted with Et₂O (3x30 mL), the combined organic layer was washed with saturated brine solution and dried over anhy. Na₂SO₄. Next, the solvent was evaporated under reduced pressure, and the crude product was purified on silica gel (hexanes:ethyl acetate:triethylamine 84.5:15:0.5) to afford 336 mg (2.29 mmol, 79% yield) of **7a** with 92% ee as determined by ¹⁹F NMR after conversion to Mosher amide. ¹H NMR: (300 MHz, CDCl₃) δ 7.37-7.22 (m, 5H), 5.82-5.69 (m, 1H), 5.15-5.07 (m, 2H), 4.00 (t, *J*=8.0 Hz, 1H), 2.50-2.32 (m, 2H), 1.59 (br s, 2H); ¹³C NMR: (75 MHz, CDCl₃) δ 146.0, 135.7, 128.7, 127.3, 126.6, 118.1, 56.4, 45.3.

7b-7e and **7h-7k** were prepared following the general procedure described for the preparation of **7a**.

1:1 Et₂O - THF was used as solvent for the preparation of **7d**.

(*S*)-1-*p*-tolylbut-3-en-1-amine (**7b**): ¹H NMR: (300 MHz, CDCl₃) δ 7.26-7.14 (m, 4H), 5.83-5.69 (m, 1H), 5.15-5.06 (m, 2H), 3.97 (dd, *J*=7.8 Hz, *J*=5.5 Hz, 1H), 2.50-2.34 (m, 5H), 1.60 (br s, 2H); ¹³C NMR: (75 MHz, CDCl₃) δ 143.6, 135.7, 129.3, 129.1, 126.2, 117.5, 55.1, 44.3, 21.1.

(*S*)-1-(4-methoxyphenyl)but-3-en-1-amine (**7c**): ^1H NMR: (300 MHz, CDCl_3) δ 7.26 (d, $J=8.64$ Hz, 2H), 6.87 (d, $J=8.64$ Hz, 2H), 5.82-5.68 (m, 1H), 5.14-5.06 (m, 2H), 3.95 (dd, $J=7.6$ Hz, $J=5.5$ Hz, 1H), 3.80 (s, 3H), 2.48-2.28 (m, 2H), 1.55 (br s, 2H); ^{13}C NMR: (75 MHz, CDCl_3) δ 157.9, 138.7, 134.1, 126.9, 118.7, 113.5, 56.5, 55.2, 48.2.

(*S*)-1-(4-nitrophenyl)but-3-en-1-amine (**7d**): ^1H NMR: (300 MHz, CDCl_3) δ 8.26 (d, $J=8.7$ Hz, 2H), 7.61 (d, $J=8.7$ Hz, 2H), 5.86-5.72 (m, 1H), 5.21-5.17 (m, 2H), 4.21 (dd, $J=7.6$ Hz, $J=5.2$ Hz, 1H), 2.66-2.38 (m, 2H), 1.85 (br s, 2H); ^{13}C NMR: (75 MHz, CDCl_3) δ 153.1, 147.2, 134.2, 127.4, 123.7, 118.8, 54.9, 44.0.

(*S*)-1-(thiophen-2-yl)but-3-en-1-amine (**7e**): 7.19-7.16 (m, 1H), 6.96-6.92 (m, 2H), 5.89-5.68 (m, 1H), 5.18-5.09 (m, 2H), 4.27 (dd, $J=7.6$ Hz, $J=5.4$ Hz, 1H), 2.64-2.34 (m, 2H), 1.69 (br s, 2H); ^{13}C NMR: (75 MHz, CDCl_3) δ 150.8, 135.1, 126.9, 123.9, 123.1, 118.6, 52.3, 45.8.

(*S*)-1-(3-fluorophenyl)but-3-en-1-amine (**7h**) : ^1H NMR: (300 MHz, CDCl_3) δ 7.33-7.22 (m, 1H), 7.15-7.04 (m, 2H), 6.97-6.88 (m, 1H), 5.83-5.63 (m, 1H), 5.16-5.07 (m, 2H), 4.01 (dd, $J=7.6$ Hz, $J=5.4$ Hz, 1H), 2.57-2.26 (m, 2H), 1.66 (br s, 2H); ^{13}C NMR: (75 MHz, CDCl_3) δ 161.4, 148.2, 134.8, 129.9(d, $J_{\text{C-F}}=8.1$ Hz), 122.1, 118.2, 113.9 (d, $J_{\text{C-F}}=20.8$ Hz), 113.3(d, $J_{\text{C-F}}=21.3$ Hz), 54.9, 43.8.

(*S*)-1-(4-fluorophenyl)but-3-en-1-amine (**7i**) : ^1H NMR: (300 MHz, CDCl_3) δ 7.33-7.26 (m, 2H), 7.002 (t, $J=8.6$ Hz, 2H), 5.83-5.62 (m, 1H), 5.15-5.06 (m, 2H), 3.99 (dd, $J=7.5$ Hz, $J=5.7$ Hz, 1H), 2.47-2.25 (m, 2H), 1.61 (br s, 2H); ^{13}C NMR: (75 MHz, CDCl_3) δ 160.2, 141.6, 135.2, 127.8 (d, $J_{\text{C-F}}=8.5$ Hz), 117.8, 115.1(d, $J_{\text{C-F}}=21$ Hz), 54.7, 44.4.

(*S*)-1-(2,6-difluorophenyl)but-3-en-1-amine (**7j**) : ^1H NMR: (300 MHz, CDCl_3) δ 7.17-7.09 (m, 1H), 6.89-6.78 (m, 2H), 5.79-5.66 (m, 1H), 5.08-4.99 (m, 2H), 4.30 (t, $J=7.35$ Hz, 1H), 2.59-2.51 (m, 2H), 1.77 (br s, 2H); ^{13}C NMR: (75 MHz, CDCl_3) δ 159.5, 135.1, 128.3 (d, $J_{\text{C-F}}=10.4$ Hz), 117.6, 111.7 (d, $J_{\text{C-F}}=17.7$ Hz), 111.3 (d, $J_{\text{C-F}}=3.8$ Hz), 47.2, 42.1.

(*S*)-1-(3,4-difluorophenyl)but-3-en-1-amine (**7k**) : ^1H NMR: (300 MHz, CDCl_3) δ 7.22-7.05 (m, 3H), 5.79-5.65 (m, 1H), 5.14-5.08 (m, 2H), 3.98 (dd, $J=7.7$ Hz, $J=5.6$ Hz, 1H), 2.45-2.25 (m, 2H), 1.58 (br s, 2H); ^{13}C NMR: (75 MHz, CDCl_3) δ 152.1, 143.7, 134.7, 122.2, 118.2, 117.0 (d, $J_{\text{C-F}}=17.2$ Hz), 115.2 (d, $J_{\text{C-F}}=17.1$ Hz), 113.9, 54.5, 44.2.

(*S*)-1-deuterio-1-phenylbut-3-en-1-amine (γ -deuterated **7a**) : ^1H NMR: (300 MHz, CDCl_3) δ 7.42-7.29 (m, 5H), 5.90-5.76 (m, 1H), 5.23-5.14 (m, 2H), 2.58-2.39 (m, 2H), 1.74 (br s, 2H); ^{13}C NMR: (75 MHz, CDCl_3) δ 145.9, 135.5, 128.5, 127.1, 126.4, 117.7, 55.2 (t, $J=21.0$ Hz), 44.2.

General procedure for the preparation of homoallylic amines by one-pot allylboration of aliphatic nitriles (7f**, **7g**) :**

Lithium triethylborohydride (**2**; 1 M in THF; 2.3 mL, 2.3 mmol) was added to a solution of cyclohexanecarbonitrile **1f** (250 mg, 2.3 mmol) in THF (5 mL) and the reaction mixture was refluxed for 5h. Methanol (73 mg, 2.3 mmol) was added to the reaction mixture after cooling down to room temperature and stirred for 30

minutes. Then the reaction mixture was cooled to -78°C and slowly transferred to *via* canula to a stirring solution of (-)-*B*-allyldiisopinocampheylborane (**5**, 1 M in diethyl ether; 2.8 mL, 2.8 mmol) pre-cooled to -78°C and diluted with diethyl ether. After 16 h, the reaction mixture was oxidised very slowly with NaOH (3 M in H_2O ; 0.8 mL) and H_2O_2 (30% in H_2O ; 0.8 mL) and was left stirring overnight under positive N_2 pressure while it slowly warmed to room temperature. The product was then extracted with Et_2O (3x30 mL), the combined organic layer was washed with saturated brine solution and dried over anhy. Na_2SO_4 . Next, the solvent was evaporated under reduced pressure, and the material was purified on silica gel (hexanes:ethyl acetate:triethylamine 84.5:15:0.5) to afford 146 mg (0.96 mmol, 42% yield) of **7f** with 84% ee as determined by ^{19}F NMR after conversion to Mosher amide. ^1H NMR: (300 MHz, CDCl_3) δ 5.84-5.59 (m, 1H), 5.12-5.06 (m, 2H), 2.31-2.01 (m, 3H), 1.87-1.67 (m, 5H), 1.37 (br s, 2H), 1.35-0.97 (m, 6H); ^{13}C NMR: (75 MHz, CDCl_3) δ 134.5, 117.9, 55.2, 45.5, 42.1, 26.9, 26.8, 26.6

7g was prepared following the general procedure described for the preparation of **7f**.

(*S*)-2-methylhex-5-en-3-amine (**7g**) : ^1H NMR: (300 MHz, CDCl_3) δ 5.66-5.53 (m, 1H), 4.98-4.92 (m, 2H), 2.57-2.51 (m, 2H), 2.44 (q, $J=6.7$ Hz, 1H), 2.31 (br s, 2H), 2.37-2.19 (t, $J=8.3$ Hz, 1H), 1.04 (d, $J=6.1$ Hz, 6H); ^{13}C NMR: (75 MHz, CDCl_3) δ 136.4, 116.3, 76.7, 37.9, 32.2, 19.8.

General procedure for the one-pot preparation of δ -amino alcohols (9a, 9b, 9c, 9e) :

(*S*)-4-amino-4-phenylbutan-1-ol (**9a**) : To a solution of benzonitrile **1a** (300mg, 2.9 mmol) in diethyl ether (5 ml) lithium triethylborohydride (**2**; 1 M in THF; 2.9 mL, 2.9 mmol) was added at 0 °C and the solution was stirred for 2h. Methanol (92 mg, 2.9 mmol) was added to the reaction mixture and stirred for 30 minutes. The reaction mixture was cooled to -100 °C and slowly transferred to *via* canula to a stirring solution of (-)-*B*-allyldiisopinocampheylborane (**5**, 1 M in diethyl ether; 3.48 mL, 3.48 mmol) pre-cooled to -100 °C and diluted with ether. After 6 h, the reaction mixture was slowly warmed to -78 °C and stirring was continued for 16 h more. 10 M BH₃-SMe₂ (0.435 mL, 4.35 mmol) in 3 mL Et₂O was added to the reaction mixture and stirred for 48 h while slowly warming to room temperature. Then the reaction mixture was oxidised very slowly with NaOH (3 M in H₂O; 2.8 mL) and H₂O₂ (30% in H₂O; 2.8 mL) and was left stirring overnight under positive N₂ pressure. The product was then extracted with Et₂O (3x30 mL), the combined organic layer was washed with saturated brine solution and dried over anhy. Na₂SO₄. Next, the solvent was evaporated under reduced pressure, and the material was purified on silica gel (dichloromethane : methanol : triethylamine 94.5 : 4.5 : 0.5) to afford 359 mg (2.18 mmol, 75% yield) of **9a**. ¹H NMR: (300 MHz, CDCl₃) δ 7.34-7.20 (m, 5H), 3.86 (dd, *J*=7.3 Hz, *J*=5.4 Hz, 1H), 3.67-3.51 (m, 2H), 2.95 (br s, 2H), 1.86-1.69 (m, 2H), 1.65-1.57 (m, 2H); ¹³C NMR: (75 MHz, CDCl₃) δ 146.4, 128.6, 127.1, 126.0, 62.6, 56.2, 37.1, 30.6.

9b, **9c**, and **9e** were prepared following the general procedure described for the preparation of **9a**.

(*S*)-4-amino-4-p-tolylbutan-1-ol (**9b**): ^1H NMR:

(300 MHz, CDCl_3) δ 7.19-7.13 (m, 4H), 3.79 (m, 1H), 3.61-3.53 (m, 2H), 3.0 (br s, 2H), 2.32 (s, 3H), 1.81-1.72 (m, 2H), 1.62-1.56 (m, 2H); ^{13}C NMR: (75 MHz, CDCl_3) δ 143.5, 136.6, 129.1, 125.9, 62.4, 55.9, 36.9, 30.5, 21.1.

(*S*)-4-amino-4-(4-methoxyphenyl)butan-1-ol (**9c**):

^1H NMR: (300 MHz, CDCl_3) δ 7.20-7.14 (m, 2H), 6.85-6.79 (m, 2H), 3.84-3.76 (m, 4H), 3.60-3.53 (m, 2H), 3.18 (br s, 2H), 1.77-1.69 (m, 2H), 1.60-1.51 (m, 2H); ^{13}C NMR: (75 MHz, CDCl_3) δ 158.6, 138.3, 127.1, 113.9, 62.5, 55.3, 55.2, 36.9, 30.4.

(*S*)-4-amino-4-(thiophen-2-yl)butan-1-ol (**9e**): ^1H NMR:

(300 MHz, CDCl_3) δ 7.18-7.16 (m, 1H), 7.0-6.91 (m, 2H), 3.78 (t, $J=5.6$ Hz, 1H), 3.66-3.55 (m, 2H), 3.36 (br s, 2H), 1.98-1.74 (m, 2H), 1.69-1.61 (m, 2H); ^{13}C NMR: (75 MHz, CDCl_3) δ 126.9, 126.7, 123.7, 123.1, 62.4, 51.8, 37.4, 29.9.

Table 2. δ -Amino alcohols

Entry	δ -Amino Alcohol	%Yield
1	9a	75
2	9b	66
3	9c	71
4	9e	55

(*S*)-4-(tert-butoxycarbonylamino)-4-deuterio-4-phenylbutanoic acid (**γ -deuterated 10a**): ^1H NMR: (300 MHz, CDCl_3) δ 7.43-7.25 (5, 5H), 2.79-2.47 (m, 3H), 1.99-1.89 (m, 1H), 1.30 (s, 9H); ^{13}C NMR: (75 MHz, CDCl_3) δ 174.9, 149.6, 142.5, 128.8, 127.7, 125.1, 82.9, 61.3 (t, $J=22.7$ Hz), 31.3, 27.7.

3. ^1H , ^{13}C , and ^{11}B NMR Spectra

Figure 1: ^1H NMR spectrum of *(E)*-1-phenylmethanimine triethylborane complex (**4a**)

Figure 2: ^{13}C NMR spectrum of *(E)*-1-phenylmethanimine triethylborane complex (**4a**)

Figure 3: ^{11}B NMR spectrum of *(E)*-1-phenylmethanimine triethylborane complex (**4a**)

Figure 4: ^1H NMR spectrum of *(E)*-p-tolylmethanimine triethylborane complex (**4b**)

Figure 5: ^{13}C NMR spectrum of (E) -p-tolylmethanimine triethylborane complex (**4b**)

Figure 6: ^{11}B NMR spectrum of (E) -p-tolylmethanimine triethylborane complex (**4b**)

Figure 7: ¹H NMR spectrum of *(E)*-(4-methoxyphenyl)methanimine triethylborane complex (**4c**)

Figure 8: ¹³C NMR spectrum of *(E)*-(4-methoxyphenyl)methanimine triethylborane complex (**4c**)

Figure 9: ^{11}B NMR spectrum of *(E)*-(4-methoxyphenyl)methanimine triethylborane complex (**4c**)

Figure 10: ^1H NMR spectrum of *(E)*-(4-nitrophenyl)methanimine triethylborane complex (**4d**)

Figure 11: ¹³C NMR spectrum of (*E*)-(4-nitrophenyl)methanimine triethylborane complex (**4d**)

Figure 12: ¹¹B NMR spectrum of (*E*)-(4-nitrophenyl)methanimine triethylborane complex (**4d**)

Figure 13: ¹H NMR spectrum of (*E*)-thiophen-2-ylmethanimine triethylborane complex (4e)

Figure 14: ¹³C NMR spectrum of (*E*)-thiophen-2-ylmethanimine triethylborane complex (4e)

Figure 15: ¹¹B NMR spectrum of (*E*)-thiophen-2-ylmethanimine triethylborane complex (**4e**)

Figure 16: ¹H NMR spectrum of (*E*)-1-phenyl-*C*-deuterio-methanimine triethylborane complex (**C-deuterated 4a**)

Figure 17: ^{13}C NMR spectrum of (*E*)-1-phenyl-*C*-deuterio-methanimine triethylborane complex (**C-deuterated 4a**)

Figure 18: ^{11}B NMR spectrum of (*E*)-1-phenyl-*C*-deuterio-methanimine triethylborane complex (**C-deuterated 4a**)

Figure 19: ¹H NMR spectrum of (*E*)-p-tolyl-*C*-deuterio-methanimine triethylborane complex (**C-deuterated 4b**)

Figure 20: ¹³C NMR spectrum of (*E*)-p-tolyl-*C*-deuterio-methanimine triethylborane complex (**C-deuterated 4b**)

Figure 21: ^{11}B NMR spectrum of (E) -p-tolyl- C -deuterio-methanimine triethylborane complex (C -deuterated **4b**)

Figure 22 ^1H NMR spectrum of (E) -(4-methoxyphenyl)- C -deuterio-methanimine triethylborane complex (C -deuterated **4c**)

Figure 23: ¹³C NMR spectrum of (*E*)-(4-methoxyphenyl)-C-deuterio-methanimine triethylborane complex (**C-deuterated 4c**)

Figure 24: ¹¹B NMR spectrum of (*E*)-(4-methoxyphenyl)-C-deuterio-methanimine triethylborane complex (**C-deuterated 4c**)

Figure 25: ¹H NMR spectrum of (*E*)-thiophen-2-yl-*C*-deuterio-methanimine triethylborane complex (**C-deuterated 4e**)

Figure 26: ¹³C NMR spectrum of (*E*)-thiophen-2-yl-*C*-deuterio-methanimine triethylborane complex (**C-deuterated 4e**)

Figure 27: ^{11}B NMR spectrum of (*E*)-thiophen-2-yl-*C*-deuterio-methanimine triethylborane complex (**C-deuterated 4e**)

Figure 28: ^1H NMR spectrum of (*E*)-1-phenyl-*N*-deuterio-methanimine triethylborane complex (**N-deuterated 4a**)

Figure 29: ^{13}C NMR spectrum of (E) -1-phenyl- N -deuterio-methanimine triethylborane complex (N -deuterated **4a**)

Figure 30: ^{11}B NMR spectrum of (E) -1-phenyl- N -deuterio-methanimine triethylborane complex (N -deuterated **4a**)

Figure 31: ^1H NMR spectrum of (E) -1-phenyl- C,N -dideuterio-methanimine triethylborane complex (C,N -dideuterated **4a**)

Figure 32: ^{13}C NMR spectrum of (E) -1-phenyl- C,N -dideuterio-methanimine triethylborane complex (C,N -dideuterated **4a**)

Figure 33: ^{11}B NMR spectrum of (E) -1-phenyl- C,N -dideuterio-methanimine triethylborane complex (C,N -dideuterated 4a)

Figure 34: ^1H NMR spectrum of (S) -1-phenylbut-3-en-1-amine (7a)

Figure 35: ¹³C NMR spectrum of (S)-1-phenylbut-3-en-1-amine (**7a**)

Figure 36: ¹H NMR spectrum of (S)-1-p-tolylbut-3-en-1-amine (**7b**)

Figure 37: ¹³C NMR spectrum of (S)-1-*p*-tolylbut-3-en-1-amine (7b)

Figure 38: ¹H NMR spectrum of (S)-1-(4-methoxyphenyl)but-3-en-1-amine (7c)

Figure 39: ¹³C NMR spectrum of (S)-1-(4-methoxyphenyl)but-3-en-1-amine (7c)

Figure 40: ¹H NMR spectrum of (S)-1-(4-nitrophenyl)but-3-en-1-amine (7d)

Figure 41: ¹³C NMR spectrum of (S)-1-(4-nitrophenyl)but-3-en-1-amine (7d)

Figure 42: ¹H NMR spectrum of (S)-1-(thiophen-2-yl)but-3-en-1-amine (7e)

Figure 43: ¹³C NMR spectrum of (S)-1-(thiophen-2-yl)but-3-en-1-amine (**7e**)

Figure 44: ¹H NMR spectrum of (S)-1-cyclohexylbut-3-en-1-amine (**7f**)

Figure 45: ¹³C NMR spectrum of (S)-1-cyclohexylbut-3-en-1-amine (7f)

Figure 46: ¹H NMR spectrum of (S)-2-methylhex-5-en-3-amine (7g)

Figure 47: ^{13}C NMR spectrum of (S)-2-methylhex-5-en-3-amine (**7g**)

Figure 48: ^1H NMR spectrum of (S)-1-(3-fluorophenyl)but-3-en-1-amine (**7h**)

Figure 49: ¹³C NMR spectrum of (S)-1-(3-fluorophenyl)but-3-en-1-amine (7h)

Figure 50: ¹H NMR spectrum of (S)-1-(4-fluorophenyl)but-3-en-1-amine (7i)

Figure 51: ^{13}C NMR spectrum of (S)-1-(4-fluorophenyl)but-3-en-1-amine (7i)

Figure 52: ^1H NMR spectrum of (S)-1-(2,6-difluorophenyl)but-3-en-1-amine (7j)

Figure 53: ¹³C NMR spectrum of (S)-1-(2,6-difluorophenyl)but-3-en-1-amine (7j)

Figure 54: ¹H NMR spectrum of (S)-1-(3,4-difluorophenyl)but-3-en-1-amine (7k)

Figure 55: ¹³C NMR spectrum of (S)-1-(3,4-difluorophenyl)but-3-en-1-amine (**7k**)

Figure 56: ¹H NMR spectrum of (S)-1-deuterio-1-phenylbut-3-en-1-amine (γ -deuterated **7a**)

Figure 57: ¹³C NMR spectrum of (S)-1-deuterio-1-phenylbut-3-en-1-amine (γ-deuterated 7a)

Figure 58: ¹H NMR spectrum of (S)-4-amino-4-phenylbutan-1-ol (9a)

Figure 59: ^{13}C NMR spectrum of (S)-4-amino-4-phenylbutan-1-ol (**9a**)

Figure 60: ^1H NMR spectrum of (S)-4-amino-4-p-tolylbutan-1-ol (**9b**)

Figure 61: ^{13}C NMR spectrum of (S)-4-amino-4-*p*-tolylbutan-1-ol (**9b**)

Figure 62: ^1H NMR spectrum of (S)-4-amino-4-(4-methoxyphenyl)butan-1-ol (**9c**)

Figure 63: ¹³C NMR spectrum of (S)-4-amino-4-(4-methoxyphenyl)butan-1-ol (9c)

Figure 64: ¹H NMR spectrum of (S)-4-amino-4-(thiophen-2-yl)butan-1-ol (9e)

Figure 65: ¹³C NMR spectrum of (S)-4-amino-4-(thiophen-2-yl)butan-1-ol (9e)

Figure 66: ¹H NMR spectrum of (S)-4-(tert-butoxycarbonylamino)-4-deuterio-4-phenylbutanoic acid (γ-deuterated 10a)