Supporting Information

Asymmetric Allylboration as a Surrogate for the Enantioselective Synthesis of Allylic Amines and α -Amino Acids *via* Overman Rearrangement.

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Experimental Procedures and Spectral Data

Materials: All 'allyl'boration reactions and preparation of trichloroacetimidates were carried out under nitrogen atmosphere. Tetrahydrofuran was distilled from sodium benzophenone ketyl prior to use; other reagents were purchased from commercial sources and used without further purification. The NMR chemical shifts (δ) are reported in ppm.

I. Preparation of α,β -Unsaturated Aldehydes.

(2E)-3-phenylbut-2-enal (**4b**). To ethyl (2E)-3-phenylbut-2-enoate (1.0 mL, 5.4 mmol) diluted with THF (20 mL) and cooled to 0 °C was added LiAlH₄ (1 M in THF; 9 mL, 9 mmol) and the reaction was stirred at RT for 1 h. Excess LiAlH₄ was quenched with water; the product was extracted with Et₂O (3×30 mL) and dried with MgSO₄. After removal of the solvent under reduced pressure, the resulting alcohol was diluted with CH₂Cl₂ and Dess-Martin periodinane (2.8 g, 6.6 mmol) was added. After stirring at RT for 0.5 h, the solvent was removed; the residue was extracted with pentane (5×30 mL) and filtered through Celite. After evaporation of the solvent, the obtained product was purified on silica gel (flash; 96:4 hexanes:ethyl acetate) to afford 0.7 g (4.8 mmol, 89% yield) of **4b**. ¹H NMR (300 MHz, CDCl₃, δ): 2.57 (d, *J* = 0.72 Hz, 3H), 6.40 (dq, *J* = 1.24 Hz, 7.88 Hz, 1H), 7.40-7.55 (m, 5H), 10.19 (d, *J* = 7.83 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃, δ): 16.4, 126.3, 127.3, 128.8, 130.1, 140.6, 157.7, 191.3.

(2E)-3-phenyl-2-propylpropenal (**4c**). To ethyl 2-[(acetyloxy)(phenyl)methyl]acrylate (4.3 g, 13.3 mmol) diluted with THF (60 mL) and cooled to -78 °C was added ethylmagnesium bromide (3 M in Et₂O; 5 mL, 15 mmol) and the reaction was stirred for 0.5 h at -78 °C and 1 h at 0 °C, at which point LiAlH₄ (1 M in THF; 15 mL, 15 mmol) was added, followed by stirring at 0 °C for 1 h. Upon quenching with H₂O, the product was extracted with Et₂O (3×50 mL), washed with brine, dried over MgSO₄, and the solvent was removed under reduced pressure. To the obtained crude (2E)-3-phenyl-2-propylprop-2-en-1-ol diluted with CH₂Cl₂ (60 mL) was added Dess-Martin periodinane (6.6 g, 15.5 mmol) and the mixture was stirred for 0.5 h at RT. The solvent was removed; the resulting residue was extracted with pentane (5×50 mL) and filtered through Celite. After removal of the solvent, the obtained product was purified on silica gel (flash; 96:4 hexanes:ethyl acetate) to afford 1.1 g (6.1 mmol, 46% yield) of **4c**. ¹H NMR (300 MHz, CDCl₃, δ): 0.98 (t, *J* = 7.4 Hz, 3H), 1.49-1.57 (m, 2H), 2.48-2.54 (m, 2H), 7.19 (s, 1H), 7.37-7.50 (m, 5H), 9.53 (s, 1H); ¹³C NMR (75 MHz, CDCl₃, δ): 14.4, 21.7, 26.8, 128.8, 129.6, 129.7, 135.0, 143.2, 149.9, 195.7.

(2E)-4-(*tert*-butyldimethylsilyloxy)but-2-enal (**4d**). To (2Z)-but-2-ene-1,4-diol (10 mL, 121 mmol) diluted with DMF (120 mL) and cooled to 0 °C was added imidazole (8.2 g, 120 mmol) and *tert*-butyldimethylsilyl chloride (18.3 g, 121 mmol) and the mixture was stirred at 0 °C for 3 h. After addition of H₂O (50 mL), the product was extracted with pentane (5×100 mL), the solvent was evaporated and the product purified on silica gel (95:5 hexanes:ethyl acetate) to afford 18.8 g (93.4 mmol, 77%) of (2Z)-4-(*tert*-butyl-dimethylsilyloxy)-but-2-en-1-ol. ¹H NMR (300 MHz, CDCl₃, δ): 0.05 (s, 6H), 0.87 (s, 9H), 2.82 (br s, 1H), 4.18 (dd, *J* = 4.29 Hz, 23.22 Hz, 2H), 5.51-5.66 (m, 2H); ¹³C NMR (75 MHz, CDCl₃, δ): -5.2, 10.3, 25.9, 58.5, 59.5, 130.1, 131.0. The monoprotected alcohol (7.7 g, 37.8 mmol) was added rapidly to a stirring solution of pyridinium chlorochromate (39.9 g, 184 mmol) and sodium acetate (17.1 g, 202 mmol) in CH₂Cl₂ (300 mL). Note: oxidation under Dess-Martin or Swern conditions would afford the aldehyde with *Z* stereochemistry. After 3 h at RT the reaction was complete;

the crude material was filtered through silica gel (Et₂O eluent), evaporated, and purified on silica gel (97:3 hexanes:ethyl acetate) to give 6.0 g (30.2 mmol, 80%) of **4d**. ¹H NMR (300 MHz, CDCl₃, δ): 0.04 (d, *J* = 1.23 Hz, 6H), 0.87 (d, *J* = 1.23 Hz, 9H), 4.4 (s, 2H), 6.35 (dd, *J* = 3.54 Hz, 4.71 Hz, 1H), 6.81-6.87 (m, 1H), 9.55 (d, *J* = 9.21 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃, δ): -5.5, 18.3, 25.8, 62.2, 130.5, 156.5, 193.3.

(2*E*)-3-pentafluorophenylprop-2-enal (**4e**). Pentafluorobenzaldehyde (1.5 mL, 12.1 mmol) was added to a solution of (triphenylphosphoranyliden)acetaldehyde (3.6 g, 11.8 mmol) in toluene (120 mL) and the mixture was stirred for 1 h at 80 °C. The solvent was removed under reduced pressure and the product was purified on a short plug of silica gel (flash; 98:2 hexanes:ethyl acetate) to afford **4e** in 93% yield (2.4 g, 11.0 mmol) with a minor toluene contamination. ¹H NMR (300 MHz, CDCl₃, δ): 6.95 (dd, *J* = 7.41 Hz, 16.47 Hz, 1H), 7.46 (d, *J* = 16.56 Hz, 1H), 9.71 (d, *J* = 7.38 Hz, 1H); ¹⁹F NMR (282 MHz, CDCl₃, δ): -158.87—158.71 (m, 2F), -146.96 (t, *J* = 21.52 Hz, 1F), -136.41 (d, *J* = 12.87 Hz, 2F); ¹³C NMR (75 MHz, CDCl₃, δ): 135.2, 125.2-150.6 (m), 193.2.

(2*E*,4*R*)-5-(*tert*-butyldimethylsilyloxy)-4-methylpent-2-enal (**4f**). To methyl (2*S*)-3-hydroxy-2-methylpropanoate (3.0 mL, 27.1 mmol) in DMF (100 mL) cooled to 0 °C was added imidazole (1.8 g, 26.4 mmol) and *tert*-butyldimethylsilyl chloride (4.2 g, 27.8 mmol) and the mixture was stirred for 1 h at RT. The obtained product was extracted with pentane (4×50 mL), washed with water (4×20 mL), and concentrated under reduced pressure. The obtained residue was diluted with THF (100 mL), borane-dimethyl sulphide complex (12 mL, 120 mmol) was added, and the reaction was stirred for 24 h at RT. Excess of the borane was quenched with water, the product was extracted with Et₂O (3×100 mL), washed with brine, and solvent was evaporated. To the crude alcohol diluted with CH₂Cl₂ (100 mL) was added Dess-Martin periodinane (14.0 g, 33.0 mmol) and the reaction was stirred for 0.5 h at RT, then it was concentrated under reduced pressure. The product was extracted with pentane (3×100 mL), filtered through Celite, and the solvents were removed in vacuo. To the crude aldehyde diluted with toluene (60 mL) was added (triphenylphosphoranyliden)acetaldehyde (7.5 g, 26.6 mmol) and the reaction was stirred at 80 °C for 14 h. The crude material was purified on silica gel (9:1 hexanes:ethyl acetate) to afford 2.9 g (12.9 mmol, 48% yield) of **4f**. ¹H NMR (300 MHz, CDCl₃, δ): 0.10 (s, 3H), 0.13 (s, 3H), 0.94 (s, 9H), 1.16 (d, *J* = 6.60 Hz, 3H), 2.70 (qn, *J* = 6.52 Hz, 1H), 3.59-3.71 (m, 2H), 6.20 (dd, *J* = 7.95 Hz, 15.75 Hz, 1H), 6.91 (dd, *J* = 6.9 Hz, 15.9 Hz, 1H), 9.58 (d, *J* = 8.10 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃, δ): -5.1, 15.6, 18.6, 26.2, 39.9, 67.0, 132.6, 161.4, 194.5.

(2*E*,4*R*)-5-(4-methoxybenzyloxy)-4-methylpent-2-enal (**4g**). To methyl (2*S*)-3-hydroxy-2-methylpropanoate (3.0 mL, 27.1 mmol) in CH₂Cl₂ (20 mL) and cyclohexane (40 mL) cooled to 0 °C were added 4-methoxybenzyl 2,2,2-trichloroethanimidoate (15.5 g, 54.8 mmol) and pyridinium 4-toluene sulphonate (0.4 g, 1.6 mmol) and the mixture was stirred for 14 h at RT. The product was extracted with Et₂O (3×50 mL) and washed with brine. After the volatiles were removed under reduced pressure, the product was purified on silica gel (9:1 hexanes:ethyl acetate) to give the desired methyl (2*S*)-3-(4-methoxybenzyloxy)-2-methylpropanoate. To the obtained ether dissolved in THF (50 mL) and cooled to 0 °C was added LiAlH₄ (1.1 g, 29.0 mmol) and the reaction was stirred for 2 h at RT. After quenching with EtOAc and water, the product was extracted with Et₂O (3×50 mL), washed with brine, and concentrated under reduced pressure to furnish the desired (2*R*)-3-[(4-methoxybenzyl)oxy]-2-methylpropan-1-ol. To the crude alcohol diluted with CH₂Cl₂ (50 mL) was added Dess-Martin periodinane (14.0 g, 33.0 mmol) and the reaction was stirred for 0.5 h at RT, then it was concentrated under reduced pressure. The product was extracted with pentane (4×50 mL), filtered through Celite, concentrated under reduced pressure, and purified on silica gel (9:1 hexanes:ethyl acetate) to give (2*S*)-3-[(4-methoxybenzyl)oxy]-2-methylpropanal in 85% yield (4.7 g, 22.6 mmol) from the Roche ester.

^1H NMR (300 MHz, CDCl_3 , δ): 1.07 (d, J = 7.14 Hz, 3H), 2.55-2.61 (m, 1H), 3.54-3.60 (m, 2H), 3.73 (s, 3H), 4.40 (s, 2H), 6.84 (d, J = 8.49 Hz, 2H), 7.20 (d, J = 8.46 Hz, 2H), 9.65 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 10.7, 46.8, 55.1, 69.7, 72.9, 113.8, 114.3, 129.2, 130.1, 159.3, 203.8. The obtained aldehyde (0.7 g, 3.3 mmol) was added to a suspension of (triphenylphosphoranylidene)acetaldehyde (1.0 g, 3.3 mmol) in toluene (50 mL) and the mixture was heated for 24 h at 80 °C. Among several batches, the TLC analysis always showed only partial product formation, even if excess of the ylide was used, the reaction time was extended to 48 h, the reaction was done at 110 °C, or benzene was used as the solvent. Additionally, the product was highly unstable and was decomposing rapidly during purification. We believe that treatment of the sensitive aldehyde with the ylide caused partial racemisation of the material, which was later reflected in low diastereoselectivity of **5g** and **6g** (Table 1, Entry 7). **4g** was obtained in 28% yield (0.21 g, 0.9 mmol) from the aldehyde (23% from Roche ester). ^1H NMR (300 MHz, CDCl_3 , δ): 1.09 (d, J = 6.87 Hz, 1.2H), 1.12 (d, J = 6.84 Hz, 1.8H), 2.66 (qn, J = 6.71 Hz, 0.4H), 2.77 (qn, J = 6.65 Hz, 0.6H), 3.37-3.44 (m, 2H), 4.45 (s, 2H), 3.80 (s, 3H), 6.34-6.83 (m, 2H), 6.88 (d, J = 8.58 Hz, 2H), 7.25 (d, J = 8.58 Hz, 2H), 9.51 (d, J = 7.92 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 15.9, 37.2, 55.3, 72.9, 113.9, 129.3, 130.1, 132.2, 159.3, 160.9, 194.3.

II. Preparation of Homoallylic Alcohols.

(1*E*,3*S*)-1-phenylhexa-1,5-dien-3-ol (**5a**). To (–)-*B*-allyldiisopinocampheylborane (**1**; 1 M in pentane; 24 mL, 24 mmol) diluted with Et_2O (24 mL) and cooled to –100 °C was added cinnamaldehyde (2 mL, 15.8 mmol) diluted with Et_2O (5 mL) pre-cooled to –78 °C. The mixture was stirred for 4 h, while it was allowed to warm to –78 °C. To the reaction mixture at –78 °C was added 3 M aq. NaOH (9 mL) and (slowly!) 30% aq. H_2O_2 (6 mL), and the reaction was left stirring for 14 h under positive N_2 pressure while it slowly warmed to RT. The product was then extracted with Et_2O (3×50 mL), washed with brine, dried with MgSO_4 , and the solvent was removed under reduced pressure. Since TLC analysis showed the alcohol inseparable from isopinocampheol (Ipc-OH), the crude material was diluted with CH_2Cl_2 (100 mL) and cooled to 0 °C. Added were pyridine (3 mL, 37.2 mmol) and acetyl chloride (3 mL, 42.2 mmol), and the mixture was stirred for 1 h at 0 °C. The excess pyridine was quenched with 10% aq. HCl (30 mL); the product was extracted with CH_2Cl_2 (1×30 mL) and Et_2O (2×50 mL), washed with brine, and dried with MgSO_4 . Upon removal of the solvents, the material was purified on silica gel (200:1 hexanes:ethyl acetate) to afford pure (1*S*)-1-[(*E*)-2-phenylvinyl]but-3-enyl acetate. To the obtained acetate diluted with methyl alcohol (50 mL) and cooled to 0 °C was added K_2CO_3 (1.8 g, 13.0 mmol) and the reaction was stirred for 3 h at RT, when the mixture was quenched with brine, the product extracted with Et_2O , solvent removed under reduced pressure and the residue purified on silica gel (flash; 96:4 hexanes:ethyl acetate) to furnish the desired pure **5a** in 73% yield (2.0 g, 11.5 mmol) and 94% ee. ^1H NMR (300 MHz, CDCl_3 , δ): 2.45 (t, J = 6.74 Hz, 2H), 2.95 (br s, 1H), 4.37 (q, J = 5.91 Hz, 1H), 5.15-5.23 (m, 2H), 5.86-5.95 (m, 1H), 6.28 (dd, J = 6.39 Hz, 15.93 Hz, 1H), 6.63 (d, J = 15.99 Hz, 1H), 7.28-7.41 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 42.0, 71.9, 118.1, 126.6, 127.6, 128.7, 130.3, 131.9, 134.3, 136.9.

(4*S*,5*E*)-6-phenylhepta-1,5-dien-4-ol (**5b**). ^1H NMR (300 MHz, CDCl_3 , δ): 1.95 (br s, 1H), 2.13 (d, J = 1.32 Hz, 3H), 2.42 (t, J = 6.48 Hz, 2H), 4.63 (q, J = 7.05 Hz, 1H), 5.15-5.23 (m, 2H), 5.79-5.95 (m, 2H), 7.28-7.44 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 16.7, 42.4, 68.4, 118.5, 126.1, 127.6, 128.5, 130.2, 134.5, 137.6, 143.1.

(1*E*,3*S*)-1-phenyl-2-propylhexa-1,5-dien-3-ol (**5c**). ^1H NMR (300 MHz, CDCl_3 , δ): 0.94 (t, J = 7.28 Hz, 3H), 1.48-1.54 (m, 2H), 1.81 (br s, 1H), 2.09-2.14 (m, 1H), 2.32-2.43 (m, 3H), 4.28 (q, J = 4.05 Hz, 1H), 5.16-5.20 (m, 2H), 5.81-5.87 (m, 1H), 6.58 (s, 1H), 7.20-7.28 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 14.5, 22.4, 30.8, 40.8, 74.5, 118.2, 125.5, 126.4, 128.2, 128.6, 134.8, 137.7, 144.4.

(4*S*,5*E*)-7-(*tert*-butyldimethylsilyloxy)hepta-1,5-dien-4-ol (**5d**) was obtained after conversion to diol: To the obtained crude allylboration material dried thoroughly with Na₂SO₄, diluted with THF (50 mL) and cooled to 0 °C was added tetrabutylammonium fluoride (1 M in THF; 5 mL, 5 mmol) and the reaction was stirred for 2 h at RT. The product was extracted with Et₂O (3×50 mL) and washed with brine; after the solvent was removed under reduced pressure, the material was purified on silica gel (1:1 hexanes:ethyl acetate) to give 0.5 g (3.9 mmol, 70% from aldehyde) of (2*E*,4*S*)-hepta-2,6-diene-1,4-diol. ¹H NMR (300 MHz, CDCl₃, δ): 2.26 (t, *J* = 6.72 Hz, 2H), 3.46-3.66 (br m, 2H), 4.06 (d, *J* = 4.95 Hz, 2H), 4.13 (q, *J* = 4.03 Hz, 1H), 5.05-5.11 (m, 2H), 5.69-5.78 (m, 3H); ¹³C NMR (75 MHz, CDCl₃, δ): 41.7, 62.5, 71.2, 117.9, 130.0, 133.4, 134.3. To the obtained diol diluted with DMF (40 mL) and cooled to 0 °C was added imidazole (0.2 g, 2.9 mmol) and *tert*-butyldimethylsilyl chloride (0.6 g, 4.0 mmol) and the mixture was stirred at 0 °C for 1 h. After addition of H₂O (20 mL), the product was extracted with pentane (5×30 mL), the solvent was evaporated and the product purified on silica gel (flash; 98:2 hexanes:ethyl acetate) to afford **5d** (0.9 g, 3.8 mmol, 68% from aldehyde; 91% ee after conversion to cinnamyl ester). ¹H NMR (300 MHz, CDCl₃, δ): 0.05 (s, 6H), 0.89 (s, 9H), 1.93 (br s, 1H), 2.23-2.32 (m, 2H), 4.15-4.19 (m, 3H), 5.08-5.14 (m, 2H), 5.72-5.84 (m, 3H); ¹³C NMR (75 MHz, CDCl₃, δ): -4.9, 18.7, 26.2, 42.2, 63.4, 71.4, 118.4, 130.5, 132.2, 134.6.

(1*E*,3*S*)-1-pentafluorophenylphenylhexa-1,5-dien-3-ol (**5e**). ¹H NMR (300 MHz, CDCl₃, δ): 2.01 (br s, 1H), 2.32-2.51 (m, 2H), 4.38-4.41 (m, 1H), 5.18-5.23 (m, 2H), 5.77-5.90 (m, 1H), 6.57-6.58 (m, 2H); ¹⁹F NMR (282 MHz, CDCl₃, δ): -160.75–160.58 (m, 2F), -154.05 (t, *J* = 21.04 Hz, 1F), -140.57–140.49 (m, 2F); ¹³C NMR (75 MHz, CDCl₃, δ): 42.1, 71.7, 114.3, 119.5, 133.6, 141.0, 141.2, 141.3, 136.0-146.44 (m).

(4*S*,5*E*,7*R*)-8-(*tert*-Butyldimethylsilyloxy)-7-methyl-octa-1,5-dien-4-ol (**5f**) was obtained through conversion to (2*R*,3*E*,5*S*)-2-methyl-octa-3,7-diene-1,5-diol. ¹H NMR (300 MHz, CDCl₃, δ): 0.93 (d, *J* = 6.87 Hz, 1H), 0.97 (d, *J* = 6.81 Hz, 2H), 2.24-2.32 (m, 3H), 2.80 (br s, 2H), 3.31-3.50 (m, 2H), 4.06-4.13 (m, 1H), 5.06-5.11 (m, 2H), 5.45-5.55 (m, 2H), 5.70-5.84 (m, 1H); ¹³C NMR (75 MHz, CDCl₃, δ): 16.4, 16.7, 36.9.2, 39.8, 42.0, 42.1, 67.3, 71.8, 72.2, 118.0, 118.2, 133.3, 133.6, 134.1, 134.7, 134.8, 134.9 (see preparation of **5d**). ¹H NMR (300 MHz, CDCl₃, δ): 0.03 (s, 6H), 0.88 (s, 9H), 0.99 (d, *J* = 6.87 Hz, 3H), 1.70 (br s, 1H), 2.21-2.36 (m, 3H), 3.37-3.51 (m, 2H), 4.12 (q, *J* = 6.13 Hz, 1H), 5.10-5.16 (m, 2H), 5.47-5.65 (m, 2H), 5.74-5.88 (m, 1H); ¹³C NMR (75 MHz, CDCl₃, δ): -5.0, 16.8, 18.7, 26.3, 39.3, 42.4, 68.3, 72.2, 118.3, 132.2, 134.8, 134.9.

(4*S*,5*E*,7*S*)-8-(4-methoxybenzyloxy)-7-methylocta-1,5-dien-4-ol (**5g**) (dr 2:1). ¹H NMR (300 MHz, CDCl₃, δ): 0.99 (d, *J* = 6.78 Hz, 1.2H), 1.00 (d, *J* = 6.81 Hz, 1.8H), 1.91 (br s, 1H), 2.20-2.27 (m, 2H), 2.45 (qn, *J* = 6.61 Hz, 1H), 3.21-3.34 (m, 2H), 3.76 (s, 3H), 4.08 (q, *J* = 6.21 Hz, 1H), 4.40 (s, 2H), 5.01-5.12 (m, 2H), 5.46-5.84 (m, 3H), 6.84 (d, *J* = 8.73 Hz, 2H), 7.22 (d, *J* = 8.19 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃, δ): 36.7, 42.2, 42.3, 72.0, 72.9, 75.0, 75.1, 114.0, 114.2, 118.2, 118.2, 128.9, 129.5, 130.9, 132.2, 134.6, 134.7, 159.4.

(1*E*,3*R*,4*S*)-4-methyl-1-phenylhexa-1,5-dien-3-ol (**7a**). To potassium *tert*-butoxide (1 M in THF; 8 mL, 8 mmol) diluted with THF (8 mL) and cooled to -78 °C was added *trans*-butene (2 mL, 21 mmol) and butyllithium (2.5 M in hexanes; 3.2 mL, 8.0 mmol). The mixture was stirred for 0.1 h at -78 °C, followed by 0.3 h at -55 °C, and cooled again to -78 °C, when a solution of (-)-*B*-

methoxydiisopinocampheylborane (4.6 g, 14.5 mmol) in THF (5 mL) was added and the reaction was stirred for 1 h at -78°C . Subsequently, boron trifluoride diethyl etherate (1.0 mL, 7.9 mmol) was added and the mixture was stirred for 0.1 h, followed by addition of cinnamaldehyde (1.0 mL, 7.9 mmol) and stirring at -78°C for 5 h. Since oxidative workup with aq. NaOH (3 mL) and H_2O_2 (2.5 mL) afforded the desired alcohol inseparable from isopinocampheol, the pure **7** was obtained after conversion to acetate, purification, and removal of the acetyl group (see preparation of **6a**). ^1H NMR (300 MHz, CDCl_3 , δ): 1.08 (d, $J = 6.87$ Hz, 3H), 1.92 (br s, 1H), 2.35-2.42 (m, 1H), 4.07 (t, $J = 6.9$ Hz, 1H), 5.13-5.22 (m, 2H), 5.77-5.89 (m, 1H), 6.22 (dd, $J = 6.84$ Hz, 15.9 Hz, 1H), 6.62 (d, $J = 15.93$ Hz, 1H), 7.23-7.42 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 16.4, 45.0, 76.5, 117.0, 126.8, 128.0, 128.9, 130.3, 132.0, 137.0, 140.5.

MEM(1*E*,3*R*,4*R*)-4-[(2-methoxyethoxy)methoxy]-1-phenylhexa-1,5-dien-3-ol (**8a**). To 3-[(2-methoxyethoxy)methoxy]prop-1-ene (1.25 g, 8.4 mmol) diluted with THF (12 mL) and cooled to -78°C was added *sec*-butyllithium (1.4 M in cyclohexane; 6 mL, 8.4 mmol) and the mixture was stirred for 1 h at -78°C . Then, a solution of (–)-*B*-methoxydiisopinocampheylborane (4.5 g, 14.2 mmol) in THF (5 mL) was added and the mixture was stirred for 1 h. Subsequently, $\text{BF}_3\cdot\text{OEt}_2$ (2.6 mL, 20.5 mmol) was added and the reaction was stirred for 0.1 h, followed by cinnamaldehyde (1.0 mL, 7.9 mmol) and stirring for 5 h at -78°C . After the oxidative workup, the product was purified on silica gel (7:3 hexanes:ethyl acetate). ^1H NMR (300 MHz, CDCl_3 , δ): 3.21 (br s, 1H), 3.37 (s, 3H), 3.51-3.52 (m, 2H), 3.63-3.66 (m, 1H), 3.81-3.84 (m, 1H), 4.06 (t, $J = 7.14$ Hz, 1H), 4.26 (t, $J = 6.43$ Hz, 1H), 4.77 (dd, $J = 6.96$ Hz, 20.07 Hz, 2H), 5.36-5.32 (m, 2H), 5.81-5.75 (m, 1H), 6.20 (dd, $J = 6.02$ Hz, 15.98 Hz, 1H), 6.69 (d, $J = 15.93$ Hz, 1H), 7.29-7.38 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 59.2, 67.7, 71.9, 74.6, 81.6, 93.4, 120.0, 126.7, 127.8, 128.2, 128.7, 132.0, 134.6, 137.0.

MEM(3*R*,4*R*,5*E*)-3-[(2-methoxyethoxy)methoxy]-6-phenylhepta-1,5-dien-4-ol (**8b**). ^1H NMR (300 MHz, CDCl_3 , δ): 2.08 (s, 3H), 3.13 (br s, 1H), 3.37 (s, 3H), 3.52-3.55 (m, 2H), 3.67-3.72 (m, 1H), 3.82-3.87 (m, 1H), 4.04-4.12 (m, 1H), 4.47 (t, $J = 7.5$ Hz, 1H), 4.79 (dd, $J = 7$ Hz, 18.3 Hz, 2H), 5.25-5.35 (m, 2H), 5.66-5.74 (m, 2H), 7.24-7.39 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 17.2, 59.2, 67.9, 71.2, 72.0, 82.0, 93.7, 119.7, 126.2, 126.3, 127.6, 128.5, 134.6, 139.7, 143.3.

II. Preparation of Allylic Amides.

2,2,2-trichloro-*N*-[(1*S*,2*E*)-1-phenylhexa-2,5-dienyl]acetamide (**6a**). To **5a** (2.0 g, 11.5 mmol) diluted with THF (60 mL) and cooled to -42°C (acetonitrile - dry ice bath) was added sodium bis(trimethylsilyl)amide (1 M in THF; 1.2 mL, 1.2 mmol) and the reaction was stirred for 0.5 h, when trichloroacetonitrile (1.7 mL, 16.9 mmol) was added. The reaction was stirred for 0.1 h at -42°C , and allowed to warm to RT. The solvent was removed under reduced pressure and to the obtained crude material diluted with xylenes (50 mL) was added potassium carbonate (1.7 g, 12.3 mmol) and the reaction was stirred at reflux (150°C) for 14 h. The reaction mixture was filtered through Celite, concentrated under reduced pressure, and purified on silica gel (flash; hexane to 99:1 hexanes:ethyl acetate) to afford 3.2 g (10.0 mmol, 89% yield) of **6a** as an oily substance, which slowly crystallised upon standing. ^1H NMR (300 MHz, CDCl_3 , δ): 2.87 (t, $J = 5.89$ Hz, 2H), 5.03-5.09 (m, 2H), 5.55 (dd, $J = 5.49$ Hz, 7.68 Hz, 1H), 5.65-5.91 (m, 3H), 6.90 (d, $J = 6.48$ Hz, 1H), 7.26-7.42 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 36.2, 56.7, 116.1, 126.9, 128.2, 128.7, 129.0, 131.9, 135.8, 139.5, 160.6. MS (EI): 282/284 ($\text{M}-\text{Cl}$), 115 (C_9H_7^+); (CI): 318/320/322 ($\text{M}+\text{H}$), 157.

 2,2,2-trichloro-*N*-[(1*S*,2*E*)-1-methyl-1-phenylhexa-2,5-dienyl]acetamide (**6b**). ¹H NMR (300 MHz, CDCl₃, δ): 1.89 (s, 3H), 2.87 (t, *J* = 6.35 Hz, 2H), 5.03-5.09 (m, 2H), 5.58-5.68 (m, 1H), 5.78-5.97 (m, 2H), 6.96 (br s, 1H), 7.29-7.39 (m, 5H); ¹³C NMR (75 MHz, CDCl₃, δ): 26.4, 36.6, 61.2, 76.9, 93.6, 116.3, 125.7, 126.6, 127.9, 128.7, 129.3, 134.3, 136.4, 144.0, 160.1. MS (EI): 331/333, 170 (M–NH₂COCCL₃), 129 (C₁₀H₉⁺); (CI): 332/334/336 (M+H), 171 (M+H–NH₂C(=O)CCl₃).

 2,2,2-trichloro-*N*-[(1*S*,2*E*)-1-phenyl-2-propylhexa-2,5-dienyl]acetamide (**6c**). ¹H NMR (300 MHz, CDCl₃, δ): 0.92 (t, *J* = 7.28 Hz, 3H), 1.4-1.45 (m, 2H), 1.84-1.89 (m, 1H), 2.09-2.14 (m, 1H), 2.88 (t, *J* = 6.71 Hz, 2H), 4.99-5.04 (m, 2H), 5.43-5.47 (m, 2H), 5.78-5.83 (m, 1H), 6.91 (d, *J* = 7.2 Hz, 2H), 7.27-7.34 (m, 5H); ¹³C NMR (75 MHz, CDCl₃, δ): 14.4, 22.2, 31.7, 32.1, 59.8, 93.0, 115.5, 125.2, 127.7, 128.4, 129.1, 136.7, 138.9, 139.1, 160.8. MS (EI): 324/326 (M–HCl), 91 (C₇H₇⁺); (CI): 360/362/364 (M⁺), 199 (M–H₂NC(=O)CCl₃).

 2,2,2-trichloro-*N*-[(1*S*,2*E*)-1-(*tert*-butyldimethylsilanyloxymethyl)-hexa-2,5-dienyl]acetamide (**6d**). ¹H NMR (300 MHz, CDCl₃, δ): 0.07 (s, 6H), 0.89 (s, 9H), 2.81 (t, *J* = 6.32 Hz, 2H), 3.69 (dd, *J* = 3.55 Hz, 10.19 Hz, 1H), 3.80 (dd, *J* = 3.89 Hz, 10.07 Hz, 1H), 4.39-4.45 (m, 1H), 5.01-5.07 (m, 2H), 5.50 (dd, *J* = 6.87 Hz, 16.14 Hz, 1H), 5.70-5.87 (m, 2H), 7.16 (d, *J* = 6.75 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃, δ): –5.2, 18.5, 26.1, 36.6, 54.5, 64.9, 116.2, 127.3, 131.8, 136.3, 161.4. MS (EI): 328/330/332 (M–C₄H₉), 73 (SiC(CH₃)₃⁺); (CI): 386/388/390 (M+H).

 2,2,2-trichloro-*N*-[(1*S*,2*E*)-1-pentafluorophenylhexa-2,5-dienyl]acetamide (**6e**). ¹H NMR (300 MHz, CDCl₃, δ): 2.81-2.85 (m, 2H), 5.00-5.08 (m, 2H), 5.67-5.91 (m, 4H), 7.24 (d, *J* = 7.05 Hz, 1H); ¹⁹F NMR (282 MHz, CDCl₃, δ): –160.58–160.40 (m, 2F), –153.32 (t, *J* = 20.54 Hz, 1F), –140.16–140.05 (m, 2F); ¹³C NMR (75 MHz, CDCl₃, δ): 36.3, 48.6, 92.3, 117.0, 125.4, 134.7, 135.1, 126.58-146.81 (m), 161.3. MS (EI): 372/374 (M–Cl), 246 (M–H₂NC(=O)CCl₃); (CI): 408/410/412 (M+C₃H₃), 247 (M+H–H₂NC(=O)CCl₃).

 2,2,2-trichloro-*N*-[(1*R*,2*E*)-1-[(1*S*)-2-(*tert*-Butyldimethylsilanyloxy)-1-methylethyl]-hexa-2,5-dienyl]acetamide (**6f**). ¹H NMR (300 MHz, CDCl₃, δ): 0.08 (s, 3H), 0.09 (s, 3H), 0.86 (d, *J* = 7.11 Hz, 3H), 0.91 (s, 9H), 2.08-2.17 (m, 1H), 3.58 (d, *J* = 7.20 Hz, 2H), 3.58 (d, *J* = 7.20 Hz, 2H), 4.37-4.42 (m, 1H), 5.00-5.08 (m, 2H), 5.43 (dd, *J* = 6.6 Hz, 15.45 Hz, 1H), 5.69-5.87 (m, 2H), 8.09 (d, *J* = 7.83 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃, δ): –5.0, –4.9, 14.3, 19.1, 26.5, 36.7, 38.7, 57.3, 66.8, 93.5, 116.1, 125.3, 132.3, 136.5, 161.1. MS (EI): 218/220/222, 93; (CI): 414/416/418 (M+H).

 2,2,2-trichloro-*N*-[(1*R*,2*E*)-1-[(1*S*)-2-(4-methoxybenzyloxy)-1-methylethyl]-hexa-2,5-dienyl]acetamide (**6g**) (dr 2:1). ¹H NMR (300 MHz, CDCl₃, δ): 0.88 (d, *J* = 7.14

Hz, 1.8H), 1.13 (d, J = 7.14 Hz, 1.2H), 1.92-1.95 (m, 0.4H), 2.21-2.29 (m, 0.6H), 2.79 (q, J = 6.41 Hz, 2H), 3.44 (d, J = 7.41 Hz, 2H), 3.81 (s, 3H), 4.32-4.46 (m, 3H), 5.01-5.07 (m, 2H), 5.31-5.42 (m, 1H), 5.61-5.86 (m, 2H), 6.87 (d, J = 8.01 Hz, 2H), 7.23 (d, J = 8.43 Hz, 0.8H), 7.25 (d, J = 8.49 Hz, 1.2H), 8.18 (d, J = 6.99 Hz, 0.4H), 8.43 (d, J = 7.83 Hz, 0.6H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 14.5, 15.7, 36.4, 36.6, 36.8, 37.0, 55.6, 57.3, 57.3, 72.2, 73.1, 73.9, 93.3, 114.0, 114.1, 115.9, 116.0, 125.0, 129.1, 129.7, 129.8, 130.2, 130.4, 132.3, 136.6, 159.8, 159.9, 161.0, 161.9. MS (ESI): pos. 442/444/446 ($\text{M}+\text{Na}^+$).

2,2,2-trichloro-*N*-[(1*S*,2*E*,4*S*)-4-methyl-1-phenylhexa-2,5-dienyl]acetamide (**9a**). ^1H NMR (300 MHz, CDCl_3 , δ): 1.14 (d, J = 6.87 Hz, 3H), 2.89-3.00 (m, 1H), 4.99-5.05 (m, 2H), 5.53-5.85 (m, 4H), 6.90 (d, J = 6.81 Hz, 1H), 7.26-7.42 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 19.9, 40.2, 56.9, 93.0, 114.1, 126.8, 127.2, 128.4, 129.3, 138.1, 139.9, 142.1, 161.1. MS (EI): 296/298 ($\text{M}-\text{HCl}$), 91 (C_7H_7^+); (CI): 332/334 (M^+), 296 ($\text{M}+\text{H}-\text{HCl}$), 171 ($\text{M}+\text{H}-\text{NH}_2\text{C}(=\text{O})\text{CCl}_3$).

2,2,2-trichloro-*N*-[(1*S*,2*E*,4*R*)-4-[(2-methoxyethoxy)methoxy]-1-phenylhexa-2,5-dienyl]acetamide (**10a**). ^1H NMR (300 MHz, CDCl_3 , δ): 3.33 (s, 3H), 3.52-3.64 (m, 4H), 4.64 (t, J = 6.35 Hz, 1H), 4.76 (d, J = 2.61 Hz, 2H), 5.19-5.25 (m, 2H), 5.59 (t, J = 6.87 Hz, 1H), 5.67-5.76 (m, 2H), 5.95 (dd, J = 5.66 Hz, 15.56 Hz, 1H), 7.04 (d, J = 8.01 Hz, 1H), 7.27-7.33 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 56.4, 59.2, 67.3, 72.1, 76.8, 77.0, 93.1, 117.7, 127.3, 128.6, 129.3, 130.2, 132.3, 136.9, 139.2, 161.3. MS (ESI): pos. 444/446/448 ($\text{M}+\text{Na}^+$).

2,2,2-trichloro-*N*-[(1*S*,2*E*,4*R*)-4-[(2-methoxyethoxy)methoxy]-1-methyl-1-phenylhexa-2,5-dienyl]acetamide (**10b**). ^1H NMR (300 MHz, CDCl_3 , δ): 1.87 (s, 3H), 3.35 (s, 3H), 5.52-5.54 (m, 2H), 6.67-3.69 (m, 2H), 4.67 (t, J = 6.4 Hz, 1H), 4.74 (s, 2H), 5.19-5.31 (m, 2H), 5.60 (dd, J = 6.6 Hz, 15.8 Hz, 1H), 5.74-5.84 (m, 1H), 6.17 (d, J = 15.8 Hz, 1H), 6.99 (br s, 1H), 7.26-7.39 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 26.2, 59.2, 60.8, 67.2, 72.0, 76.6, 92.8, 93.4, 117.6, 125.5, 127.9, 129.0, 129.9, 135.3, 137.0, 143.5, 160.0.

IV. Preparation of α -Amino Acids.

(2*R*)-Amino(phenyl)acetic acid hydrochloride (**5a**). **Method A:** Ozone was passed for 3 h through **4a** (1.0 g, 3.1 mmol) dissolved in CH_2Cl_2 (500 mL) and cooled to -78°C . The mixture was quenched with Me_2S (2 mL), stirred for 0.5 h at -78°C , then for 1 h at RT; the solvents were removed under reduced pressure to give the desired aldehyde, which was purified on silica gel (95:5 hexanes:ethyl acetate) to give 0.7 g (2.5 mmol, 89%) of 2,2,2-trichloro-*N*-[(1*R*)-2-oxo-1-phenylethyl]acetamide. ^1H NMR (300 MHz, CDCl_3 , δ): 5.54 (d, J = 6.03 Hz, 1H), 7.26-7.48 (m, 5H), 7.98 (d, J = 6.81 Hz, 1H), 9.6 (d, J = 3.12 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 63.7, 90.7, 126.7, 128.5, 128.8, 130.2, 160.2, 191.9. To the obtained aldehyde diluted with 2-methylpropan-2-ol (30 mL) and 2-methylbut-2-ene (5 mL) was added sodium chlorite (1.8 g, 19.5 mmol), sodium phosphate monobasic (NaH_2PO_4) (1.9 g, 14.0 mmol), and water (15 mL). The mixture was stirred at RT for 0.5 h and the product was extracted with ethyl acetate (3×30 mL). The solvents were removed under reduced pressure

and the obtained acid was filtered through a short plug of silica gel using ether to give the *N*-protected amino acid. The solvent was removed under reduced pressure and the obtained acid was refluxed with concentrated aq. HCl (6 mL) for 1 h. Following the evaporation of HCl, the obtained solid was washed with Et₂O and dried to give **11a** in 72% yield (0.3 g, 1.8 mmol) from the aldehyde, 64% yield from **6a**. ¹H NMR (300 MHz, D₂O, δ): 5.02 (s, 1H), 7.36-7.39 (m, 5H); ¹³C NMR (75 MHz, D₂O, δ): 56.5, 128.0, 129.7, 130.3, 131.4, 170.8. α_D²⁰ = –82° (D₂O, c = 1.10).

(2R)-Amino(phenyl)acetic acid hydrochloride (11a). Method B: To **6a** (1.5 g, 4.7 mmol) dissolved in EtOH (50 mL) and water (10 mL) was added KOH (0.9 g, 16.0 mmol) and the mixture was stirred for 24 h at RT. The product was extracted with Et₂O (3×50 mL) and concentrated under reduced pressure to approximately 30 mL. To this mixture was added di-*tert*-butyl-dicarbonate (2.0 g, 9.2 mmol) and the reaction was stirred for 3 h at RT. The solvent was removed in vacuo and the product was purified on silica gel (8:2 hexane:ethyl acetate) to give 1.1 g (4.0 mmol, 88% yield) of *tert*-butyl (1*S*,2*E*)-1-phenylhexa-2,5-dienylcarbamate. ¹H NMR (300 MHz, CDCl₃, δ): 2.87 (t, *J* = 5.8 Hz, 2H), 5.04-5.10 (m, 2H), 5.55 (dd, *J* = 5.49 Hz, 7.71 Hz, 1H), 5.66-5.90 (m, 3H), 6.93 (d, *J* = 6.69 Hz, 1H), 7.31-7.41 (m, 5H); ¹³C NMR (75 MHz, CDCl₃, δ): 36.5, 57.0, 93.0, 116.4, 127.2, 128.4, 129.0, 129.3, 132.2, 136.0, 139.8, 161.1. The *N*-Boc protected diene (1.1 g, 4.0 mmol) was dissolved in CH₂Cl₂ (300 mL) and cooled to –78 °C. Ozone was passed for 3 h, followed by quenching with Me₂S (2 mL) and stirring for 0.5 h at –78 °C, then for 1 h at RT, followed by wash with H₂O (2×50 mL) and concentration under reduced pressure to give the desired aldehyde. To the crude aldehyde diluted with 2-methylpropan-2-ol (50 mL) and 2-methylbut-2-ene (6 mL) was added sodium chlorite (2.5 g, 27.1 mmol), sodium phosphate monobasic (NaH₂PO₄) (2.7 g, 19.9 mmol), and water (20 mL). The mixture was stirred at RT for 2 h and the product was extracted with ethyl acetate (3×50 mL). The solvents were removed under reduced pressure and the obtained acid was filtered through a short plug of silica gel (ether). The solvent was partially evaporated and the resulting material was treated with HCl (1 M in Et₂O; 10 mL, 10 mmol) for 0.5 h. The obtained solid was filtered and dried to afford pure **11a** in 83% yield (0.48 g, 2.6 mmol). NMR analysis showed the product to be identical with one obtained using Method A above. α_D²⁰ = –84° (D₂O, c = 1.06), –138° (2 M HCl, c = 0.7).

(2R)-2-amino-2-phenylpropanoic acid hydrochloride (11b). ¹H NMR (300 MHz, D₂O, δ): 2.00 (s, 3H), 7.48-7.53 (m, 5H); ¹³C NMR (75 MHz, D₂O, δ): 21.5, 69.1, 125.0, 127.0, 129.2, 129.4, 137.1, 175.8. α_D²⁰ = –77° (10% aq. HCl, c = 0.2).

(2R)-2-Amino-3-hydroxypropanoic acid hydrochloride (11d). ¹H NMR (200 MHz, D₂O, δ): 1.49 (br s, 1H), 2.27 (br s, 1H), 3.90-4.06 (m, 2H); ¹³C NMR (50 MHz, D₂O, δ): 55.6, 60.1, 178.4. α_D²⁰ = +9° (D₂O, c = 0.4).

(2R)-Amino(pentafluorophenyl)acetic acid hydrochloride (11e). ¹H NMR (300 MHz, D₂O, δ): 3.09 (br s, 1H); ¹⁹F NMR (282 MHz, D₂O, δ): –161.04–160.88 (m, 1F), –156.21 (q, *J* = 8.6 Hz, 1F), –151.13 (t, *J* = 20.7 Hz, 1F), –143.19 (q, *J* = 8.6 Hz, 1F), –141.28 (d, *J* = 15.8 Hz, 1F); ¹³C NMR (50 MHz, D₂O, δ): 42.4, 136.5, 178.5. α_D²⁰ = +36° (D₂O, c = 0.75).

NMR Spectra¹

I. NMR Spectra of α,β -Unsaturated Aldehydes

(2E)-3-phenyl-but-2-enal (4b)

(1) Unless noted otherwise, all spectra were taken using CDCl₃ as a solvent using Varian Gemini 300 instrument: (¹H NMR - 300 MHz, ¹⁹F NMR - 282 MHz, and ¹³C NMR - 75 MHz).

(2E)-3-phenyl-2-propyl-propenal (4c)

(2E)-4-(tert-butyltrimethylsilyloxy)but-2-enal (4d)

(2E)-3-pentafluorophenylprop-2-enal (4e)

(2E,4R)-5-(tert-butyldimethylsilyloxy)-4-methylpent-2-enal (4f)

(2*E*,4*R*)-5-(4-methoxybenzyloxy)-4-methylpent-2-enal (4g)

II. NMR Spectra of Homoallylic Alcohols

(1*E*,3*S*)-1-phenylhexa-1,5-dien-3-ol (5a)

(4*S*,5*E*)-6-phenylhepta-1,5-dien-4-ol (5b)

(1*E*,3*S*)-1-phenyl-2-propylhexa-1,5-dien-3-ol (5c)

(4*S*,5*E*)-7-(*tert*-butyldimethylsilyloxy)hepta-1,5-dien-4-ol (**5d**)

(1*E*,3*S*)-1-pentafluorophenylphenylhexa-1,5-dien-3-ol (5e)

(4*S*,5*E*,7*R*)-8-(*tert*-Butyldimethylsilyloxy)-7-methyl-octa-1,5-dien-4-ol (5f)

(4*S*,5*E*,7*S*)-8-(4-methoxybenzyloxy)-7-methylocta-1,5-dien-4-ol (**5g**)

(1E,3R,4S)-4-methyl-1-phenylhexa-1,5-dien-3-ol (7a)

(1*E*,3*R*,4*R*)-4-[(2-methoxyethoxy)methoxy]-1-phenylhexa-1,5-dien-3-ol (8a)

(3*R*,4*R*,5*E*)-3-[(2-methoxyethoxy)methoxy]-6-phenylhepta-1,5-dien-4-ol (8b)

IV. NMR Spectra of Allylic Amides

2,2,2-trichloro-*N*-[(1*S*,2*E*)-1-phenylhexa-2,5-dienyl]acetamide (**6a**)

2,2,2-trichloro-*N*-[(1*S*,2*E*)-1-methyl-1-phenylhexa-2,5-dienyl]acetamide (**6b**)

2,2,2-trichloro-*N*-[(1*S*,2*E*)-1-phenyl-2-propylhexa-2,5-dienyl]acetamide (**6c**)

2,2,2-trichloro-N-[(1*S*,2*E*)-1-(*tert*-butyldimethylsilanyloxymethyl)-hexa-2,5-dienyl]acetamide (**6d**)

2,2,2-trichloro-*N*-[(1*S*,2*E*)-1-pentafluorophenylhexa-2,5-dienyl]acetamide (**6e**)

2,2,2-trichloro-*N*-{(1*R*,2*E*)-1-[(1*S*)-2-(*tert*-butyldimethylsilyloxy)-1-methyl-ethyl]-hexa-2,5-dienyl}acetamide
(6f)

2,2,2-trichloro-*N*-{[(1*R*,2*E*)-1-[(1*S*)-2-(4-methoxybenzyloxy)-1-methylethyl]hexa-2,5-dienyl}acetamide (**6g**)

2,2,2-trichloro-*N*-[(1*S*,2*E*,4*S*)-4-methyl-1-phenylhexa-2,5-dienyl]acetamide (**9a**)

2,2,2-trichloro-*N*-{(1*S*,2*E*,4*R*)-4-[(2-methoxyethoxy)methoxy]-1-phenylhexa-2,5-dienyl}acetamide (10a)

2,2,2-trichloro-*N*-{(1*S*,2*E*,4*R*)-4-[(methoxyethoxy)methoxy]-1-methyl-1-phenylhexa-2,5-dienyl}acetamide
(10b)

V. NMR Spectra of α -Amino Acids

(2*R*)-Amino(phenyl)acetic acid hydrochloride (**11a**) (in D₂O)

(2R)-2-amino-2-phenylpropanoic acid hydrochloride (11b) (in D₂O)

(2R)-Amino(pentafluorophenyl)acetic acid hydrochloride (11d) (in D₂O)

(2R)-2-Amino-3-hydroxypropanoic acid hydrochloride (11e) (in D₂O)