Asymmetric Michael addition of α -hydroxyketones to nitroolefins catalyzed by chiral diamine

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Generalities: All reactions were carried out under a nitrogen atmosphere with oven dried glassware. All chemicals were obtained from Acros Organics or Fluka. All solvents were purchased from Acros Organics, Fluka or Biosolve Ltd. Silica gel (32-63 μm , Brunschwing) was used for air-flashed chromatography.

^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Brüker DRX-300, DRX-400 or DRX-500 Fourier Transform spectrometer. Chemical shifts are quoted in ppm relative to tetramethylsilane (0 ppm) for ^1H and ^{13}C spectra, and CFCl_3 (0 ppm) for ^{19}F spectra. The following abbreviations are used: s-singlet, bs-broad singlet, d-doublet, t-triplet, q-quartet, hept-heptet, m-multiplet. Coupling constants (J) are given in Hertz (Hz). Optical rotations were measured using a Perkin-Elmer 241 polarimeter, in a cell of 1 dm path length. The concentration c is expressed in mg/mL. Melting points are reported in degrees Celsius and are uncorrected

Addition of unmodified ketones to nitroolefine catalysed by diamine:

General Procedure 1: To a solution of pyrrolidine or chiral diamine **A2** (0.05 mmol, 15 mol%) in solvent (3 mL) was added at room temperature the ketone (3.35 mmol) and the nitroolefin (0.335 mmol). The evolution of the reaction was monitored by TLC until completion. The solution was then hydrolyzed with 1N HCl (2 mL). The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 3 mL). The combined organic phases were dried over MgSO_4 , filtered, concentrated and purified by flash column chromatography on silica gel using a mixture of cyclohexane and ethylacetate as eluent.

(7*S*,8*S*)-2,2-dimethyl-1,3-diazatricyclo[6.3.0.0^{3,7}]undecane (**A1**): A mixture of 2,2'-bipyrrolidine¹ (500 mg, 3.57 mmol) in acetone (15 mL) and molecular sieves 4Å (~ 0.5 g) was stirred overnight, then K_2CO_3 was added and the mixture was filtered. Removal of the solvent gives a pale yellow oil (623 mg, 97%). The crude product was used for the reduction step without further purification.

^1H NMR (400MHz, C_6D_6): δ = 3.27-3.21 (m, 2H), 2.86-2.76 (m, 4H), 1.80-1.67 (m, 6H), 1.36-1.29 (m, 2H), 1.26 (s, 6H).

^{13}C NMR (100.6 MHz, C_6D_6): δ = 79.86 (C_{quat}), 70.05 (2 CH), 46.97 (2 CH_2), 29.82 (2 CH_2), 27.10 (2 CH_2), 25.99 (2 CH_3).

(2*S*,2'*S*)-1-(1-Methylethyl)-2,2'-bipyrrolidine (**A2**): To a solution of aminal **A1** (456 mg, 2.5 mmol) in MeOH (10 mL) was added by portion at 0°C NaBH_4 (1.5 eq., 3.75 mmol, 142 mg) then acetic acid (4eq., 10.0 mmol, 0.60 g, 0.57 mL). The solution was stirred 3 hours at 0°C and then diluted with ether (20 mL) and hydrolyzed with NaOH_{aq} , 30% (5 mL) and water (10 mL). The solution was decanted, the aqueous phase was extracted two times with EtOAc. The combined organic phases were washed with brine, dried over K_2CO_3 , filtered and concentrated in vacuo. Purification by bulb to bulb distillation (70°C, 0.2 mmbar) gave a colourless oil (410 mg, 90%).

¹ Alexakis, A. ; Tomassini, A. ; Chouillet, C. ; Roland, S. ; Mangeney, P. ; Bernardinelli, G. *Angew. Chem. Int. Ed.* **2000**, 39, 4093.

$[\alpha]_D^{25} = -29.6$ ($c = 4.8$, CHCl_3)

^1H NMR (400 MHz, CDCl_3) : $\delta = 3.12$ (hept, 1H, $J = 6.6$), 3.02-2.96 (m, 1H), 2.86-2.71 (m, 4H), 2.63-2.57 (m, 1H), 2.04 (bs, 1H, NH), 1.78-1.59 (m, 6H), 1.53-1.47 (m, 1H), 1.34-1.26 (m, 1H), 1.09 (d, 3H, $J = 6.8$), 0.93 (d, 3H, $J = 6.3$).

^{13}C NMR (100.6 MHz, CDCl_3) : $\delta = 64.67$ (CH), 64.37 (CH), 51.09 (CH), 46.22 (CH_2), 46.09 (CH_2), 29.07 (CH_2), 28.10 (CH_2), 24.55 (2 CH_2), 22.61 (CH_3), 14.92 (CH_3).

IR (CHCl_3) : 3163, 2959, 2875, 2495, 1458, 1384, 1263, 1165, 1096, 1059 cm^{-1} .

MS (EI): 113 (13), 112 (100), 111 (1), 98 (4), 97 (1), 96 (2), 71 (2), 70 (38), 69 (1), 68 (2).

HRMS Calcd for $\text{C}_{11}\text{H}_{22}\text{N}_2$ 182.1783, found 182.1780.

(3*R**,4*S**)-3-Methoxy-5-nitro-4-phenylpentan-2-one (**A3**) : From α -methoxyacetone according to *General Procedure 1* to obtained two inseparable diastereoisomers, (*syn*, major) **A3** and (*anti*, minor) **A3** as a pale yellow oil. The enantiomeric excess was determined by GC (Hydrodex B-3P, 150°C isotherm).

(*Syn* adduct): ^1H NMR (400 MHz, CDCl_3) : $\delta = 7.35$ -7.20 (m, 5H), 4.93 (dd, 1H, $J = 8.4$, 12.9), 4.66 (dd, 1H, $J = 6.8$, 12.9), 3.93-3.80 (m, 2H), 3.45 (s, 3H), 1.77 (s, 3H).

^{13}C NMR (100.6 MHz, CDCl_3) : $\delta = 209.91$ (C=O), 134.45 (C_{quat}), 128.98 (2 CH), 128.84 (2 CH), 128.38 (CH), 86.77 (CH), 76.53 (CH_2), 59.80 (CH_3), 46.34 (CH), 26.61 (CH_3).

(*Anti* adduct): ^1H NMR (400 MHz, CDCl_3) : $\delta = 7.35$ -7.20 (m, 5H), 4.86 (dd, 1H, $J = 5.6$, 13.4), 4.72 (dd, 1H, $J = 8.6$, 13.2), 3.93-3.80 (m, 2H), 3.67 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (100.6 MHz, CDCl_3) : $\delta = 208.12$ (C=O), 135.35 (C_{quat}), 129.13 (2 CH), 128.49 (CH), 128.11 (2 CH), 88.16 (CH), 76.73 (CH_2), 58.82 (CH_3), 45.90 (CH), 26.23 (CH_3).

IR (CHCl_3) (isomers mixture): 3029, 3011, 2937, 2834, 1713, 1556, 1495, 1456, 1427, 1378, 1357, 1120, 1054, 909 cm^{-1} .

MS (EI) (isomers mixture): 194 (11), 148 (12), 147 (100), 117 (29), 115 (10), 104 (14), 91 (18), 77 (10).

(3*R**,4*S**)-3-Hydroxy-5-nitro-4-phenylpentan-2-one (**A4'**) : From α -hydroxyacetone according to *General Procedure 1* using pyrrolidine as achiral catalyst to obtained two inseparable diastereoisomers (*syn/anti* 75 :25), (*syn*) **A4'** and (*anti*) **A4** as a pale yellow oil. The enantiomers were separated by SFC (OJ column, 5% MeOH).

^1H NMR (400 MHz, CDCl_3) : $\delta = 7.41$ -7.23 (m, 5H), 5.03 (dd, 1H, $J = 7.8$, 13.4), 4.74 (dd, 1H, $J = 7.1$, 13.4), 4.54-4.52 (m, 1H), 4.03 (dt, 1H, 3.0, 7.6), 3.75 (d, 1H, $J = 4.8$), 2.17 (s, 3H).

^{13}C NMR (100.6 MHz, CDCl_3) : $\delta = 206.30$ (C=O), 133.81 (C_{quat}), 128.99 (2 CH), 128.69 (CH), 128.53 (2 CH), 77.00 (CH, CH_2), 45.72 (CH), 25.52 (CH_3).

(3*R*,4*R*)-3-Hydroxy-5-nitro-4-phenylpentan-2-one (**A4**) : From α -hydroxyacetone according to *General Procedure 1* using diamine **A2** to obtained two inseparable diastereoisomers, (*syn*) **A4'** and (*anti*) **A4** as a pale yellow oil. The enantiomeric excess was determined by SFC (OJ column, 5% MeOH).

^1H NMR (400 MHz, CDCl_3) : δ = 7.41-7.23 (m, 5H), 4.82 (dd, 1H, J = 76.3, 13.6), 4.66 (dd, 1H, J = 8.3, 13.6), 4.42-4.38 (m, 1H), 3.83 (dt, 1H, J = 7.6, 5.9), 3.76-3.74 (m, 1H), 2.06 (s, 3H).

^{13}C NMR (100.6 MHz, CDCl_3) : δ = 207.99 (C=O), 137.15 (C_{quat}), 129.36 (2 CH), 128.45 (CH), 128.03 (2 CH), 78.70 (CH), 76.06 (CH_2), 46.90 (CH), 26.51 (CH_3).

MS (EI) (isomers mixture): 180 (8), 134 (11), 133 (100), 105 (97), 104 (96), 103 (30), 91 (39), 79 (24), 78 (23), 77 (38), 74 (10), 55 (11), 51 (18).

(3*R*^{*},4*S*^{*})-3-Hydroxy-5-nitro-4-(4-methylphenyl)pentan-2-one (**A5'**) : From α -hydroxyacetone according to *General Procedure 1* using pyrrolidine as achiral catalyst to obtained two inseparable diastereoisomers (*syn/anti* 77 :23), (*syn*) **A5'** and (*anti*) **A5** as a pale yellow solid. The enantiomers were separated by SFC (AS-H column, 5% MeOH).

^1H NMR (400 MHz, CDCl_3) : δ = 7.13 (d, 2H, J = 8.1), 7.09 (d, 2H, J = 8.1), 5.01 (dd, 1H, J = 8.1, 13.4), 4.71 (dd, 1H, J = 7.1, 13.4), 4.52-4.51 (m, 1H), 4.00 (dt, 1H, J = 3.0, 7.6), 3.75-3.68 (m, 1H), 2.29 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100.6 MHz, CDCl_3) : δ = 206.36 (C=O), 138.49 (C_{quat}), 130.66 (C_{quat}), 129.68 (2 CH), 128.27 (2 CH), 77.09 (CH_2), 77.04 (CH), 45.41 (CH), 25.52 (CH_3), 21.07 (CH_3).

(3*R*,4*R*)-3-Hydroxy-5-nitro-4-(4-methylphenyl)pentan-2-one (**A5**) : From α -hydroxyacetone according to *General Procedure 1* using diamine **A2** to obtained two inseparable diastereoisomers, (*syn*) **A5'** and (*anti*) **A5** as a pale yellow solid. The enantiomeric excess was determined by SFC (AS-H column, 5% MeOH).

^1H NMR (400 MHz, CDCl_3) : δ = 7.24 (d, 2H, J = 8.1), 7.19 (d, 2H, J = 8.1), 4.81 (dd, 1H, J = 6.2, 13.4), 4.64 (dd, 1H, J = 8.5, 13.4), 4.37 (d, 1H, J = 5.6), 3.78 (dt, 1H, J = 8.6, 5.8), 3.75-3.68 (m, 1H), 2.35 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (100.6 MHz, CDCl_3) : δ = 208.13 (C=O), 138.37 (C_{quat}), 133.94 (C_{quat}), 130.02 (2 CH), 127.88 (2 CH), 78.76 (CH_2), 76.31 (CH), 46.72 (CH), 26.65 (CH_3), 21.11 (CH_3).

MS (EI) (isomers mixture): 237 (1), 190 (8), 164 (52), 148 (14), 147 (100), 119 (35), 118 (90), 117 (30), 115 (13), 105 (26), 99 (12), 97 (64), 91 (29), 87 (12), 86 (60), 85 (17), 84 (91), 77 (13), 74 (16), 71 (12), 57 (23), 47 (17).

HRMS Calcd 237.1001 for $\text{C}_{12}\text{H}_{15}\text{NO}_4$, found 237.1008.

(3*R**,4*S**)-3-Hydroxy-5-nitro-4-(4-methoxyphenyl)pentan-2-one (**A6'**) : From α -hydroxyacetone according to *General Procedure 1* using pyrrolidine as achiral catalyst to obtained two inseparable diastereoisomers (*syn/anti* 80 :20), (*syn*) **A6'** and (*anti*) **A6** as a pale yellow solid. The enantiomers were separated by SFC (AS-H column, 5% MeOH).

^1H NMR (400 MHz, CDCl_3) : δ = 7.16 (d, 2H, J = 8.6), 6.79 (d, 2H, J = 8.6), 4.97 (dd, 1H, J = 7.7, 13.4), 4.69 (dd, 1H, J = 7.5, 13.4), 4.50-4.48 (m, 1H), 3.97 (dt, 1H, 3.0, 7.6), 3.78-3.73 (m, $1\text{H}_{\text{syn}} + 2\text{H}_{\text{anti}}$), 3.74 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (100.6 MHz, CDCl_3) : δ = 206.55 (C=O), 159.63 (C_{quat}), 129.57 (2 CH), 125.65 (C_{quat}), 114.29 (2 CH), 77.26 (CH_2), 77.08 (CH), 55.16 (CH_3), 45.01 (CH), 25.48 (CH_3).

(3*R*,4*R*)-3-Hydroxy-5-nitro-4-(4-methoxyphenyl)pentan-2-one (**A6**) : From α -hydroxyacetone according to *General Procedure 1* using diamine **A2** to obtained two diastereoisomers inseparable by column chromatography, (*syn*) **A6'** and (*anti*) **A6** as a pale yellow solid. The enantiomeric excess was determined by SFC (AS-H column, 5% MeOH). A sample was crystallized in ether to give the isomer **A6** optically pure for analysis.

m.p. (ether) : 109-112°C.

$[\alpha]_D^{25} = -47.3$ (c = 8.6, CHCl_3).

^1H NMR (400 MHz, CDCl_3) : δ = 7.28 (d, 2H, J = 8.6), 6.91 (d, 2H, J = 8.6), 4.80 (dd, 1H, J = 6.0, 13.4), 4.63 (dd, 1H, J = 8.6, 13.4), 4.38-4.36 (m, 1H), 3.81 (s, 3H), 3.76 (dt, 1H, J = 8.6, 5.9), 3.68-3.67 (m, 1H), 2.01 (s, 3H).

^{13}C NMR (100.6 MHz, CDCl_3) : δ = 208.06 (C=O), 159.63 (C_{quat}), 129.13 (2 CH), 128.80 (C_{quat}), 114.71 (2 CH), 78.81 (CH_2), 76.48 (CH), 55.31 (CH_3), 46.42 (CH), 26.68 (CH_3).

MS (EI): 253 (3), 180 (18), 135 (16), 134 (100), 121 (8), 91 (7), 77 (5).

HRMS Calcd 253.0950 for $\text{C}_{12}\text{H}_{15}\text{NO}_5$, found 253.0953.

(3*R**,4*S**)-3-Hydroxy-5-nitro-4-[2-(trifluoromethyl)phenyl]pentan-2-one (**A7'**) : From α -hydroxyacetone according to *General Procedure 1* using pyrrolidine as achiral catalyst to obtained two inseparable diastereoisomers (*syn/anti* 74 :26), (*syn*) **A7'** and (*anti*) **A7** as a pale yellow oil. The enantiomers were separated by SFC (OD-H column, 5% MeOH).

^1H NMR (400 MHz, CDCl_3) : δ = 7.83 (d, 1H, J = 7.8), 7.71 (d, 1H, J = 7.3), 7.53-7.42 (m, $2\text{H}_{\text{syn}} + 1\text{H}_{\text{anti}}$), 5.09-5.03 (m, 1H), 4.71-4.67 (m, 1H), 4.58-4.50 (m, $2\text{H}_{\text{syn}} + 2\text{H}_{\text{anti}}$), 4.02-3.96 (m, 1H), 2.07 (s, 3H).

^{13}C NMR (100.6 MHz, CDCl_3) : δ = 206.85 (C=O), 133.43 (C_{quat}), 132.70 (CH), 129.80 (CH), 128.64 (CH), 128.29 (q, C_{quat} , $J_{\text{C-F}} = 29.6$), 126.77 (q, CH, $J_{\text{C-F}} = 5.8$), 124.13 (q, CF_3 , $J_{\text{C-F}} = 273.7$), 76.22 (CH), 75.58 (CH_2), 39.39 (CH), 25.25 (CH_3).

(3*R*,4*R*)-3-Hydroxy-5-nitro-4-[2-(trifluoromethyl)phenyl]pentan-2-one (**A7**) : From α -hydroxyacetone according to *General Procedure 1* using diamine **A2** to obtained two inseparable diastereoisomers, (*syn*) **A7'** and (*anti*) **A7** as a pale yellow oil. The enantiomeric excess was determined by SFC (OD-H column, 5% MeOH).

$[\alpha]_D^{25} = -32.0$ ($c = 33.2$, CHCl_3 , dr 95:5, 99% ee).

^1H NMR (400 MHz, CDCl_3) : $\delta = 7.77$ (d, 1H, $J = 7.8$), 7.75 (d, 1H, $J = 8.1$), 7.63 (t, 1H, $J = 7.6$), 7.53-7.42 (m, $1\text{H}_{\text{anti}} + 2\text{H}_{\text{syn}}$), 4.77 (dd, 1H, $J = 7.3, 13.9$), 4.61 (dd, 1H, $J = 6.3, 13.7$), 4.58-4.50 (m, $2\text{H}_{\text{anti}} + 2\text{H}_{\text{syn}}$), 4.37

(br s, 1H), 2.37 (s, 3H).

^{13}C NMR (100.6 MHz, CDCl_3) : $\delta = 206.96$ (C=O), 136.60 (C_{quat}), 132.77 (CH), 129.52 (CH), 128.01 (q, C_{quat} , $J_{\text{C-F}} = 29.9$), 128.27 (CH), 126.47 (q, CH, $J_{\text{C-F}} = 5.8$), 124.34 (q, CF_3 , $J_{\text{C-F}} = 273.7$), 78.31 (CH), 73.72 (CH_2), 40.10 (CH), 25.24 (CH_3).

IR (CHCl_3) 3459, 3029, 2979, 2928, 2874, 1717, 1608, 1559, 1456, 1380, 1363, 1314, 1167, 1118, 1038, 968, 909 cm^{-1} .

MS (EI) (isomers mixture): 201 (68), 182 (10), 181 (77), 173 (31), 172 (100), 171 (27), 169 (11), 159 (19), 153 (83), 151 (37), 140 (11), 133 (62), 127 (12), 103 (11), 97 (21), 77 (10), 75 (10), 73 (12), 61 (10), 57 (17), 55 (12).

(2*R*, 1'*R*, 2'*R*)-3,3,3-Trifluoro-2-methoxy-2-phenyl-propionic acid 1-acetyl-3-nitro-2-(2-trifluoromethyl-phenyl)-propyl ester (**A8**) : To a solution of alcohol (**A7**) (33 mg, 0.113 mmol) in dry CH_2Cl_2 (0.8 mL) was added (*R*)-Mosher's acid (0.170 mmol, 40 mg) then a solution of DCC (0.198 mmol, 41 mg) and DMAP (0.028 mmol, 3.5 mg) in dry CH_2Cl_2 (1.0 mL). The white mixture was stirred overnight at rt then directly purified by flash chromatography on silica gel (*c*-Hexane/EtOAc 9 :1) to give a colourless solid (55 mg, 96 %).

m.p. (ether): 129-132°C.

^1H NMR (400 MHz, CDCl_3) : $\delta = 7.71$ (d, 1H, $J = 7.8$), 7.55 (d, 1H, $J = 7.6$), 7.51-7.37 (m, 4H), 7.37 (t, 1H, $J = 7.8$), 7.10 (t, 1H, $J = 7.7$), 6.99 (d, 1H, $J = 7.8$), 5.27 (d, 1H, $J = 1.8$), 4.82-4.73 (m, 2H), 4.64 (dt, 1H, $J = 1.8, 6.9$), 3.77 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (75.5 MHz, CDCl_3) : $\delta = 200.82$ (C=O), 165.74 (C=O), 134-120 (15C), 80.29 (CH), 73.27 (CH_2), 56.13 (CH_3), 37.37 (CH), 26.90 (CH_3).

^{19}F NMR (282.4 MHz, CDCl_3) : $\delta = -58.05, -71.23$.

(2*S*, 1'*R*, 2'*R*)-3,3,3-Trifluoro-2-methoxy-2-phenyl-propionic acid 1-acetyl-3-nitro-2-(2-trifluoromethyl-phenyl)-propyl ester (**A9**) : To a solution of alcohol (**A7**) (30 mg, 0.103 mmol) in dry CH₂Cl₂ (0.8 mL) was added (*S*)-Mosher's acid (0.155 mmol, 36 mg) then a solution of DCC (0.180 mmol, 37 mg) and DMAP (0.026 mmol, 3.2 mg) in dry CH₂Cl₂ (1.0 mL). The white mixture was stirred overnight at rt then directly purified by flash chromatography on silica gel (*c*-Hexane/EtOAc 9 :1) to give a colourless solid (32 mg, 62 %).

m.p. (ether): 108-110°C.

¹H NMR (400 MHz, CDCl₃) : δ = 7.82-7.79 (m, 1H), 7.54-7.40 (m, 8H), 5.35 (d, 1H, J = 1.8), 5.27 (d, 1H, J = 1.8), 4.85 (dd, 1H, J = 8.4, 14.3), 4.77

(dd, 1H, J = 5.2, 14.3), 4.73-4.69 (m, 1H), 3.49 (s, 3H), 2.45 (s, 3H).

¹³C NMR (75.5 MHz, CDCl₃) : δ = 200.82 (C=O), 165.74 (C=O), 134-120 (15C), 80.29 (CH), 73.27 (CH₂), 56.13 (CH₃), 37.37 (CH), 26.90 (CH₃).

¹⁹F NMR (282.4 MHz, CDCl₃) : δ = -58.08, -71.02.

(3*R**, 4*S**)-3-Hydroxy-5-nitro-4-(thien-2-ylphenyl)pentan-2-one (**A10'**) : From α-hydroxy-acetone according to *General Procedure 1* using pyrrolidine as achiral catalyst to obtained two inseparable diastereoisomers (*syn/anti* 68 :32), (*syn*) **A10'** and (*anti*) **A10** as a brown oil. The enantiomers were separated by SFC (OJ column, 5% MeOH).

¹H NMR (400 MHz, CDCl₃) : δ = 7.22 (dd, 1H, J = 0.8, 5.0), 6.95 (dd, 1H, J = 1.3, 3.5), 6.92 (dd, 1H, J = 3.5, 5.0), 4.96 (dd, 1H, J = 7.7, 13.5), 4.67 (dd, 1H, J = 7.0, 13.5), 4.48-4.42 (m, 2H_{syn} + 1H_{anti}), 3.93-3.92 (m, 1H), 2.22 (s, 3H).

¹³C NMR (100.6 MHz, CDCl₃) : δ = 205.67 (C=O), 134.22 (C_{quat}), 127.37 (CH), 126.80 (CH), 126.47 (CH), 77.57 (CH₂), 76.34 (CH), 41.88 (CH), 25.24 (CH₃).

(3*R*, 4*R*)-3-Hydroxy-5-nitro-4-(thien-2-ylphenyl)pentan-2-one (**A10**) : From α-hydroxy-acetone according to *General Procedure 1* using diamine **A2** to obtained two inseparable diastereoisomers, (*syn*) **A10'** and (*anti*) **A10** as a brown oil. The enantiomeric excess was determined by SFC (OJ column, 5% MeOH).

¹H NMR (400 MHz, CDCl₃) : δ = 7.29 (dd, 1H, J = 1.0, 5.1), 7.05 (dd, 1H, J = 0.8, 3.6), 6.99 (dd, 1H, J = 3.6, 5.1), 4.75 (dd, 1H, J = 6.0, 13.5), 4.62 (dd, 1H, J = 8.1, 13.5), 4.48-4.42 (m, 1H_{anti} + 2H_{syn}), 4.21 (dt, 1H, J = 8.1, 5.4), 3.76-3.74 (m, 1H), 2.15 (s, 3H).

¹³C NMR (100.6 MHz, CDCl₃) : δ = 205.67 (C=O), 134.22 (C_{quat}), 127.37 (CH), 126.80 (CH), 126.47 (CH), 77.57 (CH₂), 76.34 (CH), 41.88 (CH), 25.24 (CH₃).

MS (EI) (isomers mixture): 211 (1), 182 (7), 156 (20), 139 (11), 112 (7), 111 (24), 110 (100), 109 (9), 97 (17).

1-Chloro-4-(2-nitro-vinyl)-benzene (A11): A mixture of 4-chlorobenzaldehyde (10 g, 71.1 mmol), nitromethane (26.4 mL, 0.49 mol) and ammonium acetate (13 g, 0.17 mol) in acetic acid (100 mL) was heated at 95°C during 5h30. The solution was then cooled to room temperature and kept overnight at this temperature. The crystals formed were filtered, washed with water (2*20 mL) and dried under vacuum to afford a yellow solid (4.16 g). The mixture of acetic acid and water gave new solid material after 3 hours. This solid was filtered, washed with water (2*20 mL) and dried under vacuum to afford a yellow solid (5.91 g). The two fractions were pure and were mixed together to give (10.07 g, 77%) of pure material.

¹H NMR (400 MHz, CDCl₃) : δ = 7.97 (d, 1H, J = 13.6), 7.57 (d, 1H, J = 13.6), 7.51-7.49 (m, 2H), 7.45-7.43 (m, 2H).

¹³C NMR (100.6 MHz, CDCl₃) : δ = 138.36 (C_{quat.}), 137.72 (CH), 137.44 (CH), 130.29 (2CH), 129.79 (2CH), 128.54 (C_{quat.}).

(3*R,4*S**)-4-(4-Chlorophenyl)-3-hydroxy-5-nitro-pentan-2-one (A12')**: From α-hydroxyacetone according to *General Procedure 1* using pyrrolidine as achiral catalyst to obtain two inseparable diastereoisomers (*syn/anti* 75 :25), (*syn*) **A12'** and (*anti*) **A12** as a colourless oil. The enantiomers were separated by SFC (AS-H column, 5% MeOH, 55°C).

¹H NMR (400 MHz, CDCl₃) : δ = 7.32-7.29 (m, 2H), 7.26-7.22 (m, 2H), 5.02 (dd, 1H, J = 7.6, 13.6), 4.75 (dd, 1H, J = 7.5, 13.6), 4.54 (dd, 1H, J = 3.0, 4.6), 4.05 (dt, 1H, J = 2.8, 7.6), 3.78 (d, 1H, J = 4.5), 2.21 (s, 3H).

¹³C NMR (100.6 MHz, CDCl₃) : δ = 205.93 (C=O), 134.79 (C_{quat.}), 132.28 (C_{quat.}), 129.83 (2 CH), 129.26 (2 CH), 76.97 (CH₂), 76.89 (CH), 45.12 (CH), 25.48 (CH₃).

(3*R*,4*R*)-4-(4-Chlorophenyl)-3-hydroxy-5-nitro-pentan-2-one (A12): From α-hydroxyacetone according to *General Procedure 1* using diamine **A2** to obtain two inseparable diastereoisomers, (*syn*) **A12'** and (*anti*) **A12** as a colourless oil. The enantiomers were separated by SFC (AS-H column, 5% MeOH, 55°C).

¹H NMR (400 MHz, CDCl₃) : δ = 7.41-7.32 (m, 4H), 4.77 (dd, 1H, J = 6.0, 13.6), 4.64 (dd, 1H, J = 8.6, 13.6), 4.39 (t, 1H, J = 4.8), 3.89 (ddd, 1H, J = 4.6, 6.0, 8.3), 3.79 (d, 1H, J = 4.8), 2.19 (s, 3H).

¹³C NMR (100.6 MHz, CDCl₃) : δ = 207.48 (C=O), 135.82 (C_{quat.}), 134.52 (C_{quat.}), 129.53 (2 CH), 129.47 (2 CH), 78.60 (CH), 75.66 (CH₂), 45.99

(CH), 26.32 (CH₃).

MS (EI) (isomers mixture): 260 (<1), 259 (<1), 258 (<1), 257 (<1), 169 (18), 165 (55), 141 (15), 140 (37), 139 (40), 138 (100), 132 (13), 125 (23), 103 (58), 102 (11), 77 (28), 75 (10), 74 (19), 51 (11).

1,3-Dichloro-2-(2-nitro-vinyl)-benzene (A13) : A mixture of 2,6-dichlorobenzaldehyde (2.5 g, 14.28 mmol), nitromethane (5.3 mL, 98.4 mmol) and ammonium acetate (2.64 g, 34.3 mmol) in acetic acid (25 mL) was heated at 95°C during 5h30. After cooling to rt, the orange solution was diluted with ether (40 mL) and water (40 mL). The mixture was decanted and extracted with ether (2*30 mL). The combined organic layers were washed with water (50 mL), dried over magnesium sulfate, filtered and concentrated to give an orange solid. The solid was purified by crystallization in a EtOAc/pentane mixture to give a yellow solid (1.26 g, 40%).

m.p. : 59-61°C

¹H NMR (400 MHz, CDCl₃) : δ = 8.27 (d, 1H, J = 13.9), 7.86 (d, 1H, J = 13.9), 7.44 (d, 2H, J = 8.1), 7.32 (dd, 1H, J = 7.5, 8.7).

¹³C NMR (100.6 MHz, CDCl₃) : δ = 142.99 (CH), 136.09 (2 C_{quat.}), 132.08 (CH), 131.63 (CH), 129.30 (2CH), 127.56 (C_{quat.}).

MS (EI) : 219 (31), 217 (48), 184(32), 182 (96), 174 (13), 173 (27), 172 (59), 171 (35), 170 (85), 159 (12), 154 (33), 152 (92), 138 (24), 137 (38), 136 (72), 135 (96), 123 (12), 109 (18), 101 (18), 100 (21), 99 (100), 98 (12), 89 (11), 85 (14), 75 (52), 74 (46), 73 (14), 68 (27), 63 (15), 62 (12), 51 (23), 50 (32).

(3*R,4*S**)-4-(2,6-Dichlorophenyl)-3-hydroxy-5-nitro-pentan-2-one (A14')**: From α-hydroxy-acetone according to *General Procedure 1* using pyrrolidine as achiral catalyst to obtained two inseparable diastereoisomers (*syn/anti* 54 :46), (*syn*) **A14'** and (*anti*) **A14** as a colourless oil. The enantiomers were separated by SFC (AS-H column, 5% MeOH, 30°C).

¹H NMR (500 MHz, CDCl₃) : δ = 7.42-7.39 (m, 1H), 7.34-7.32 (m, 1H), 7.21 (t, 1H, J = 8.0), 5.19-5.13 (m, 1H), 5.02-4.98 (m, 2H), 4.74-4.68 (m, 1H), 2.91 (d, 1H, J = 5.3), 2.32 (s, 3H).

¹³C NMR (125.8 MHz, CDCl₃) : δ = 208.67 (C=O), 137.80 (C_{quat.}), 134.87 (C_{quat.}), 131.74 (C_{quat.}), 130.30 (CH), 130.00 (CH), 129.19 (CH), 75.96 (CH), 74.44 (CH₂), 42.42 (CH), 26.32 (CH₃).

(3*R*,4*R*)-4-(2,6-Dichlorophenyl)-3-hydroxy-5-nitro-pentan-2-one (A14): From α-hydroxy-acetone according to *General Procedure 1* using diamine **A2** to obtained two inseparable diastereoisomers, (*syn*) **A14'** and (*anti*) **A14** as a colourless oil. The enantiomeric excess was determined by SFC (AS-H column, 5% MeOH, 30°C).

¹H NMR (400.1 MHz, CDCl₃) : δ = 7.41-7.38 (m, 2H), 7.25 (t, 1H, J = 8.0), 5.27 (dd, 1H, J = 6.1, 14.1), 5.04 (dd, 1H, J = 7.2, 14.1), 4.86 (dd, 1H, J = 6.6, 9.6), 4.69 (ddd, 1H, J = 6.3, 7.1, 9.6), 3.71 (d, 1H, J = 6.8), 1.85 (s, 3H).

¹³C NMR (100.6 MHz, CDCl₃) : δ = 207.69 (C=O), 137.19 (C_{quat.}), 134.84 (C_{quat.}), 132.09 (C_{quat.}), 130.53 (CH), 130.40 (CH), 129.50 (CH), 75.04 (CH), 74.88 (CH₂), 43.81 (CH), 26.73 (CH₃).

MS (EI) : 203 (55), 201 (84), 177 (12), 176 (10), 175 (66), 174 (33), 173 (100), 172 (37), 161 (11), 159 (17), 139 (26), 138 (17), 137 (70), 136 (10), 125 (10), 103 (15), 102 (46), 101 (52), 99 (11), 77 (14), 75 (27), 74 (15=), 73 (14), 63 (10), 51 (18).

1,2-Dichloro-4-(2-nitro-vinyl)-benzene (A15) : A mixture of 3,4-dichlorobenzaldehyde (2.5 g,

14.28 mmol), nitromethane (5.3 mL, 98.4 mmol) and ammonium acetate (2.64 g, 34.3 mmol) in acetic acid (25 mL) was heated at 95°C during 5h30. After cooling to rt, the orange solution was diluted with ether (40 mL) and water (40 mL). The mixture was decanted and extracted with ether (2*30 mL). The combined organic layers were washed with water (50 mL), dried over magnesium sulfate, filtered and concentrated to give a brown oil. The oil was purified by chromatography on silica gel (*c*-Hexane/EtOAc 8 :2) to give a orange solid (0.93 g, 30%).

m.p. : 83-85°C

¹H NMR (400 MHz, CDCl₃) : δ = 7.94 (d, 1H, J = 13.6), 7.68 (d, 1H, J = 2.0), 7.59 (d, 1H, J = 13.6), 7.58 (d, 1H, J = 8.3), 7.43 (dd, 1H, J = 2.0, 8.3).

¹³C NMR (100.6 MHz, CDCl₃) : δ = 138.30 (CH), 136.46 (CH), 136.42 (C_{quat.}), 133.99 (C_{quat.}), 131.50 (CH), 130.62 (CH), 130.02 (C_{quat.}), 127.94 (CH).

MS (EI) : 219 (43), 217 (67), 184 (13), 182 (31), 174 (15), 173 (19), 172 (62), 171 (15), 170 (91), 161 (23), 159 (35), 155 (10), 154 (14), 152 (15), 138 (36), 137 (28), 136 (100), 135 (60), 126 (17), 123 (18), 111 (14), 109 (29), 101 (24), 100 (15), 99 (67), 98 (12), 89 (14), 85 (15), 84 (10), 75 (49), 74 (44), 72 (15).

(3*R,4*S**)-4-(3,4-Dichlorophenyl)-3-hydroxy-5-nitro-pentan-2-one (A16')**: From α-hydroxyacetone according to *General Procedure 1* using pyrrolidine as achiral catalyst to obtained two inseparable diastereoisomers (*syn/anti* 74 :26), (*syn*) **A16'** and (*anti*) **A16** as a colourless oil. The enantiomers were separated by SFC (OJ column, 5% MeOH, 30°C).

¹H NMR (500 MHz, CDCl₃) : δ = 7.40 (d, 1H, J = 2.2), 7.38 (d, 1H, J = 8.2), 7.13 (dd, 1H, J = 2.2, 8.2), 4.98 (dd, 1H, J = 7.5, 13.7), 4.72 (dd, 1H, J = 7.6, 13.7), 4.51 (t, 1H, J = 3.2), 4.00 (dt, 1H, J = 2.9, 7.6), 3.78 (d, 1H, J = 4.2), 2.21 (s, 3H).

¹³C NMR (125.8 MHz, CDCl₃) : δ = 205.56 (C=O), 137.67 (C_{quat.}), 133.93 (C_{quat.}), 133.19 (C_{quat.}), 130.95 (CH), 130.37 (CH), 127.83 (CH), 76.74 (CH₂), 76.73 (CH), 44.80 (CH), 25.44 (CH₃).

(3*R*,4*R*)-4-(3,4-Dichlorophenyl)-3-hydroxy-5-nitro-pentan-2-one (A16): From α-hydroxyacetone according to *General Procedure 1* using diamine **A2** to obtained two inseparable diastereoisomers, (*syn*) **A16'** and (*anti*) **A16** as a colourless oil. The enantiomeric excess was determined by SFC (OJ column, 5% MeOH, 30°C).

¹H NMR (400.1 MHz, CDCl₃) : δ = 7.54 (d, 1H, J = 2.3), 7.47 (d, 1H, J = 8.4), 7.27 (dd, 1H, J = 2.3, 8.4), 4.67 (dd, 1H, J = 6.2, 13.9), 4.59 (dd, 1H, J = 8.3, 13.9), 4.38-4.34 (m, 1H), 3.89 (ddd, 1H, J = 3.6, 6.3, 8.1), 3.80-3.75 (m, 1H), 2.25 (s, 3H).

¹³C NMR (100.6 MHz, CDCl₃) : δ = 207.06 (C=O), 136.69 (C_{quat.}), 133.40 (C_{quat.}), 132.85 (C_{quat.}), 131.23 (CH), 130.16 (CH), 127.47 (CH), 78.42 (CH), 75.06 (CH₂), 45.34 (CH), 26.06 (CH₃).

MS (EI) : 292 (1), 203 (41), 202 (11), 201 (63), 188 (13), 176 (13), 175 (32), 174 (69), 172 (100), 168 (12), 16 (35), 161 (14), 159 (21), 139 (17), 138 (17), 137 (48), 125 (12), 111 (11), 103 (15), 102 (43), 101 (32), 99 (10), 77 (10), 75 (24), 74 (26), 73 (21), 55 (10), 51 (15).
 HRMS Calcd 291.00651 for $C_{11}H_{11}^{35}Cl_2NO_4$, found 291.00864.

2,4-Dichloro-1-(2-nitro-vinyl)-benzene (A17) : A mixture of 2,6-dichlorobenzaldehyde (2.5 g, 14.28 mmol), nitromethane (5.3 mL, 98.4 mmol) and ammonium acetate (2.64 g, 34.3 mmol) in acetic acid (25 mL) was heated at 95°C during 5h30. After cooling to rt, the orange solution was diluted with ether (40 mL) and water (40 mL). The mixture was decanted and extracted with ether (2*30 mL). The combined organic layers were washed with water (50 mL), dried over magnesium sulfate, filtered and concentrated to give a brown solid. The solid was purified by crystallization in a EtOAc/pentane mixture to give a yellow solid (1.3 g) which is not pure enough. This product was purified by chromatography on silica gel (*c*-Hexane/EtOAc 8 :2) to give a yellow solid (0.76 g, 24%)

m.p. : 115-117°C

1H NMR (400 MHz, $CDCl_3$) : δ = 8.35 (d, 1H, J = 13.6), 7.59 (d, 1H, J = 13.6), 7.54 (d, 1H, J = 8.3), 7.54 (d, 1H, J = 2.3), 7.35 (dd, 1H, J = 2.3, 8.3).

^{13}C NMR (100.6 MHz, $CDCl_3$) : δ = 139.06 (CH), 138.52 ($C_{quat.}$), 136.72 ($C_{quat.}$), 134.03 (CH), 130.73 (CH), 129.30 (CH), 128.07 (CH), 127.14 ($C_{quat.}$).

MS (EI) : 219 (27), 217 (42), 184 (33), 182 (100), 174 (11), 173 (18), 172 (53), 171 (21), 170 (80), 161 (12), 159 (18), 154 (34), 152 (99), 138 (25), 137 (33), 136 (73), 135 (83), 123 (15), 111 (10), 109 (20), 101 (19), 10 (20), 99 (93), 98 (14), 89 (10), 85 (14), 75 (53), 74 (49), 73 (15), 68 (16), 65 (15), 62 (13), 51 (23), 50 (35).

(3*R,4*S**)-4-(2,4-Dichlorophenyl)-3-hydroxy-5-nitro-pentan-2-one (A18')**: From α -hydroxy-acetone according to *General Procedure 1* using pyrrolidine as achiral catalyst to obtained two inseparable diastereoisomers (*syn/anti* 80 :20), (*syn*) **A18'** and (*anti*) **A18** as a colourless oil. The enantiomers were separated by SFC (AS-H column, 5% MeOH, 30°C).

1H NMR (500 MHz, $CDCl_3$) : δ = 7.52 (d, 1H, J = 8.5), 7.41 (d, 1H, J = 2.2), 7.21 (dd, 1H, J = 2.2, 8.5), 4.98 (dd, 1H, J = 8.5, 13.7), 4.75 (ddd, 1H, J = 3.2, 6.5, 8.4), 4.61 (dd, 1H, J = 6.5, 13.6), 4.58 (t, 1H, J = 3.8), 3.79 (d, 1H, J = 4.1), 2.23 (s, 3H).

^{13}C NMR (125.8 MHz, $CDCl_3$) : δ = 206.27 (C=O), 135.15 ($C_{quat.}$), 134.36 ($C_{quat.}$), 130.46 (CH), 129.94 (CH), 127.91 (CH), 76.17 (CH), 75.98 (CH_2),

39.79 (CH), 25.48 (CH_3).

(3*R*,4*R*)-4-(3,4-Dichlorophenyl)-3-hydroxy-5-nitro-pentan-2-one (**A18**): From α -hydroxyacetone according to *General Procedure 1* using diamine **A2** to obtained two inseparable diastereoisomers, (*syn*) **A18'** and (*anti*) **A18** as a colourless oil. The enantiomeric excess was determined by SFC (AS-H column, 5% MeOH, 30°C).

^1H NMR (400.1 MHz, CDCl_3): δ = 7.48 (d, 1H, J = 2.3), 7.45 (d, 1H, J = 8.6), 7.31 (dd, 1H, J = 2.2, 8.5), 4.70-4.58 (m, 3H), 4.37-4.33 (m, 1H), 3.82 (d, 1H, J = 4.0), 2.36 (s, 3H).

^{13}C NMR (100.6 MHz, CDCl_3): δ = 207.03 (C=O), 134.81 (C_{quat}), 134.25 (C_{quat}), 133.78 (C_{quat}), 129.98 (CH), 129.75 (CH), 128.10 (CH), 77.55

(CH), 73.16 (CH_2), 41.04 (CH), 25.45 (CH_3).

MS (EI): 292 (1), 203 (49), 202 (10), 201 (75), 188 (12), 176 (14), 175 (50), 174 (70), 173 (77), 172 (100), 166 (15), 161 (18), 159 (28), 139 (20), 138 (16), 137 (57), 136 (12), 125 (11), 111 (10), 103 (14), 102 (44), 101 (38), 99 (12), 77 (10), 75 (26), 74 (24), 73 (19), 51 (17).

HRMS Calcd 291.00651 for $\text{C}_{11}\text{H}_{11}^{35}\text{Cl}_2\text{NO}_4$, found 291.00262.

1-(2-Nitro-vinyl)-naphthalene (**A19**): A mixture of 1-naphthaldehyde (2.75 g, 17.6 mmol), nitromethane (6.5 mL, 121 mmol) and ammonium acetate (3.25 g, 42.2 mmol) in acetic acid (30 mL) was heated at 95°C during 5h30. After cooling to rt, the dark brown solution was diluted with ether (40 mL) and water (40 mL). The mixture was decanted and extracted by ether (2*30 mL). The combined organic layers were washed by water (50 mL), dried over magnesium sulfate, filtered and concentrated to give an

brown oil. The oil was purified by consecutive chromatography on silica gel (c-Hexane/EtOAc 8 :2) and crystallisation in a EtOAc/pentane mixture to give a yellow solid (0.62 g, 18%).

m.p.: 84-86°C

^1H NMR (400 MHz, CDCl_3): δ = 8.86 (d, 1H, J = 13.4), 8.16 (d, 1H, J = 8.1), 8.02 (d, 1H, J = 8.3), 7.94 (d, 1H, J = 7.9), 7.78 (d, 1H, J = 7.1), 7.67 (d, 1H, J = 13.4), 7.68-7.59 (m, 2H), 7.54 (t, 1H, J = 7.7)

^{13}C NMR (100.6 MHz, CDCl_3): δ = 138.57 (CH), 136.22 (CH), 133.82 (C_{quat}), 132.63 (CH), 131.63 (C_{quat}), 129.13 (CH), 127.81 (CH), 127.05 (C_{quat}), 126.86 (CH), 125.46 (CH), 123.05 (CH).

MS (EI): 199 (33), 153 (24), 152 (100), 151 (18), 141 (9), 127 (9), 115 (9), 76 (15).

(3*R**,4*S**)-4-(1-Naphthyl)-3-hydroxy-5-nitro-pentan-2-one (**A20'**): From α -hydroxyacetone according to *General Procedure 1* using pyrrolidine as achiral catalyst to obtained two inseparable diastereoisomers (*syn/anti* 76 :24), (*syn*) **A20'** and (*anti*) **A20** as a colourless oil. The enantiomers were separated by (AS-H column, 5% MeOH, 30°C).

^1H NMR (500 MHz, CDCl_3): δ = 8.18 (d, 1H, J = 8.5), 7.88 (d, 1H, J = 8.5), 7.80 (d, 1H, J = 8.2), 7.71 (d, 1H, J = 7.0), 7.62 (t, 1H, J = 7.4), 7.53 (t, 1H, J = 7.7), 7.39 (t, 1H, J = 7.7), 5.19-5.00 (m, 2H), 4.77-4.72 (m, 2H), 3.98 (bs, 1H), 1.96 (s, 3H).

^{13}C NMR (125.8 MHz, CDCl_3): δ = 206.75 (C=O), 134.08 (C_{quat}), 130.97 (C_{quat}), 130.20 (C_{quat}), 129.56 (CH), 129.17 (CH), 127.21 (CH), 126.03 (CH), 125.45 (CH), 121.71 (CH), 76.77 (CH), 76.57 (CH_2), 38.51 (CH), 25.52 (CH_3).

(3*R*,4*R*)-4-(1-Naphthyl)-3-hydroxy-5-nitro-pentan-2-one (**A20**): From α -hydroxy-acetone according to *General Procedure 1* using diamine **A2** to obtained two inseparable diastereoisomers, (*syn*) **A20'** and (*anti*) **A20** as a colourless oil. The enantiomeric excess was determined by SFC (AS-H column, 5% MeOH, 30°C).

¹H NMR (400.1 MHz, CDCl₃) : δ = 8.13 (d, 1H, J = 8.6), 7.93-7.91 (m, 1H), 7.86 (d, 1H, J = 8.4), 7.66-7.49 (m, 4H), 5.19-4.83 (m, 2H), 4.77-4.69 (m, 1H), 4.55-4.49 (m, 1H), 3.85 (d, 1H, J = 4.8), 2.12 (s, 3H).

¹³C NMR (100.6 MHz, CDCl₃) : δ = 207.99 (C=O), 134.19 (C_{quat}), 133.22 (C_{quat}), 130.90 (C_{quat}), 129.57 (CH), 129.05 (CH), 127.34 (CH), 126.27 (CH), 125.62 (CH), 121.89 (CH), 78.51 (CH), 75.11 (CH₂), 40 (broad signal, CH), 26.22 (CH₃).

EI (MS) : 274 (2), 273 (10), 200 (8), 183 (8), 155 (23), 154 (100), 153 (30), 152 (13), 141 (9).

HRMS Calcd 273.10011 for C₁₅H₁₅NO₄, found 273.10020.

(2*S*^{*},3*R*^{*})-3-Hydroxy-1-nitro-2-phenyl-heptan-4-one (**A21'**): From 1-hydroxypentan-2-one according to *General Procedure 1* using pyrrolidine as achiral catalyst in *i*PrOH to obtained two inseparable diastereoisomers (*syn/anti* 69 :31), (*syn*) **A21'** and (*anti*) **A21** as a colourless oil. The enantiomers were separated by (AS-H column, 3% MeOH, 30°C).

¹H NMR (400.1 MHz, CDCl₃) : δ = 7.30-7.23 (m, 5H), 5.04 (dd, 1H, J = 8.1, 13.4), 4.73 (dd, 1H, J = 6.9, 13.4), 4.51 (d, 1H, J = 2.5), 4.03 (dt, 1H, J = 3.2, 7.5), 3.77 (bs, 1H), 2.53-2.38 (m, 2H), 1.72-1.45 (m, 2H), 0.84 (t, 3H, J = 7.4).

¹³C NMR (100.6 MHz, CDCl₃) : δ = 208.64 (C=O), 133.89 (C_{quat}), 128.97 (2 CH), 128.66 (CH), 128.47 (2 CH), 77.06 (CH₂), 76.39 (CH), 45.99 (CH), 40.15 (CH₂), 16.82 (CH₂), 13.60 (CH₃).

(2*R*^{*},3*R*^{*})-3-Hydroxy-1-nitro-2-phenyl-heptan-4-one (**A21**): From 1-hydroxypentan-2-one according to *General Procedure 1* using diamine **A2** to obtained two inseparable diastereoisomers, (*syn*) **A21'** and (*anti*) **A21** as a colourless oil. The enantiomeric excess was determined by SFC (AS-H column, 5% MeOH, 30°C).

¹H NMR (400.1 MHz, CDCl₃) : δ = 7.41-7.35 (m, 5H), 4.80 (dd, 1H, J = 6.1, 13.4), 4.67 (dd, 1H, J = 8.6, 13.6), 4.38 (t, 1H, J = 4.8), 3.83 (dt, 1H, J = 8.3, 5.7), 3.68 (d, 1H, J = 5.3), 2.28 (t, 2H, J = 7.3), 1.63-1.54 (m, 2H), 0.85 (t, 3H, J = 7.3).

¹³C NMR (100.6 MHz, CDCl₃) : δ = 210.42 (C=O), 137.18 (C_{quat}), 129.37 (2 CH), 128.55 (CH), 128.05 (2 CH), 78.21 (CH), 76.17 (CH₂), 47.19 (CH), 41.28 (CH₂), 16.97 (CH₂), 13.60 (CH₃).

¹H Spectrum

7.1500

3.2608
3.2008
2.8517
2.8333
2.8277
2.8094
2.8062
2.7917
2.7772
2.7683
2.7670
2.7525

1.7992
1.7827
1.7809
1.7657
1.7619
1.7487
1.7297
1.7183
1.7158
1.7013
1.6969
1.6824
1.6672
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1.3439
1.3155
1.3042
1.2934
1.2846
1.2694
1.2549

*** Current Data Parameters ***
NAME : 00274
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.130000 MHz
Solvent C6D6

¹³C CPD-Spectrum

*** Current Data Parameters ***

NAME : 00274

EXPNO : 11

PROCNO : 1

*** Processing Parameters ***

SF : 100.6127786 MHz

Solvent C6D6

C13-DEPT-135 CH,CH3 up - CH2 down

*** Current Data Parameters ***

NAME : 00274

EXPNO : 12

PROCNO : 1

*** Processing Parameters ***

SF : 100.6127786 MHz

¹H Spectrum

*** Current Data Parameters ***

NAME : od279

EXPNO : 10

PROCNO : 1

*** Processing Parameters ***

SF : 400.1300177 MHz

7.2694

3.1782
3.0803
3.0210
2.9648
2.8612
2.7116
2.6346
2.5727
2.0398
1.7828
1.7538
1.5941
1.5265
1.5158
1.5107
1.4987
1.4880
1.4766
1.4716
1.3440
1.3396
1.3289
1.3163
1.3081
1.3043
1.2986
1.2954
1.2834
1.2784
1.2632
1.0972
1.0801
0.9343
0.9185

1.0000
1.0449
4.1323
1.0939
1.3104
6.4995
1.1285
1.2274
3.2219
3.0444

13C CPD-Spectrum

*** Current Data Parameters ***

NAME : 0a279

EXPNO : 11

PROCNO : 1

*** Processing Parameters ***

SF : 100.612786 MHz

Cl3-DEPT-135 CH,CH3 up - CH2 down

*** Current Data Parameters ***

NAME : 00279

EXPNO : 12

PROCNO : 1

*** Processing Parameters ***

SF : 100.612786 MHz

A3 : A3'
84 : 16

7.3506
7.2041

4.9584
4.9375
4.9262
4.9053
4.8832
4.8700
4.8504
4.8365
4.7431
4.7216
4.7102
4.6881
4.6831
4.6667
4.6515
4.6345

3.9305
3.8749
3.8642
3.7979
3.4450
3.3692

2.0339
1.7699

*** Current Data Parameters ***
NAME : aa554
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.130052 MHz

209.9051
208.1165

A3 : A3'
84 : 16

135.3534
134.4467
129.1304
128.9821
128.8420
128.4875
128.3804
128.1084

88.1579
86.7732

77.4099
77.0885
76.7753
76.5280

59.7961
58.8235

46.3364
45.8996

26.6125
26.2252

*** Current Data Parameters ***
NAME : 00554
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

129.1304
128.9821
128.8420
128.4875
128.3886
128.1084

88.1579
86.7732

76.7258
76.5280

59.7961
58.8235

46.3364
45.8996

26.6125
26.2252

*** Current Data Parameters ***
NAME : 00554
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

A4' : A4
79 : 21

- 7.4100
- 7.3367
- 7.3089
- 7.2344
- 5.0543
- 5.0347
- 5.0209
- 5.0013
- 4.8485
- 4.8327
- 4.8144
- 4.7986
- 4.7645
- 4.7468
- 4.7311
- 4.7127
- 4.6856
- 4.6648
- 4.6515
- 4.6307
- 4.5347
- 4.5265
- 4.5227
- 4.5151
- 4.4065
- 4.3933
- 4.3800
- 4.0549
- 4.0473
- 4.0359
- 4.0283
- 4.0170
- 4.0094
- 3.8591
- 3.8440
- 3.8389
- 3.8301
- 3.8250
- 3.8093
- 3.7600
- 3.7480
- 2.1747
- 2.0597

*** Current Data Parameters ***
NAME : 04593
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.130052 MHz

207.9929
206.2950

137.1502
133.8121
129.3612
128.9903
128.6936
128.5288
128.4463
128.0342

78.6957
77.4182
77.1050
76.9978
76.7835
76.0582

46.8969
45.7182

26.5136
25.5163

*** Current Data Parameters ***

NAME : 0a593
EXPNO : 11
PROCNO : 1

*** Processing Parameters ***

SF : 100.6127690 MHz

A4' : A4
79 : 21

A4' : A4
79 : 21

129.3612
128.9903
128.6936
128.4463
128.0342

78.6957
76.9978
76.0582

46.8969
45.7182

26.5136
25.5246

*** Current Data Parameters ***
NAME : oas93
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

A4 : A4'
80 : 20

7.4169
 7.2382
 5.0651
 5.0448
 5.0316
 5.0114
 4.8548
 4.8397
 4.8213
 4.8056
 4.7670
 4.7494
 4.7330
 4.7153
 4.6881
 4.6673
 4.6540
 4.6332
 4.5429
 4.5214
 4.3996
 4.0593
 4.0517
 4.0403
 4.0334
 4.0214
 4.0138
 3.8623
 3.8478
 3.8421
 3.8333
 3.8276
 3.8131
 3.7632
 3.7095
 2.1911
 2.0743

*** Current Data Parameters ***
 NAME : 00594
 EXPNO : 10
 PROCNO : 1
 *** Processing Parameters ***
 SF : 400.130052 MHz

207.9270

A4 : A4'
80 : 20

137.1420
129.3777
128.5617
128.0177

78.7040
77.3770
77.0555
76.7423
76.0582

46.9134

26.5054

*** Current Data Parameters ***
NAME : oa594
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

A4 : A4'
80 : 20

129.3777
128.5535
128.0177

78.7040
76.0582

46.9216

26.5136

*** Current Data Parameters ***
NAME : aa594
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

A5' : A5
77 : 23

7.2692
7.2546
7.2344
7.1984
7.1782
7.1429
7.1227
7.0999
7.0797

5.0347
5.0145
5.0013
4.9811
4.8384
4.8232
4.8049
4.7891
4.7405
4.7229
4.7071
4.6894
4.6679
4.6465
4.6338
4.6130
4.5094
4.3813
4.3674
4.0201
4.0126
4.0012
3.9936
3.9823
3.9747
3.8042
3.7897
3.7834
3.7745
3.7682
3.7531
3.7284
3.6754
2.3451
2.2946
2.1791
2.0440

*** Current Data Parameters ***
NAME : od615
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.130052 MHz

208.1248
206.3609

138.4855
138.3701
133.9440
130.6553
130.0206
129.6827
128.2732
127.8776

78.7617
77.4099
77.0885
77.0390
76.7753
76.3137

46.7155
45.4133

26.9175
26.6455
25.5246
21.1067
21.0737

A5' : A5
77 : 23

*** Current Data Parameters ***
NAME : oad15
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

130.0206
129.6827
128.2732
127.8776

78.7617
77.0885
77.0390
76.3137

46.7155
45.4133

26.6455
25.5246
21.1067
21.0737

A5' : A5
77 : 23

*** Current Data Parameters ***
NAME : oad15
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

7.2698
7.2546
7.2344
7.2003
7.1801
7.1429
7.1220
7.1012
7.0810

5.0366
5.0164
5.0032
4.9830
4.8397
4.8245
4.8062
4.7904
4.7399
4.7222
4.7064
4.6888
4.6679
4.6465
4.6338
4.6130
4.5145
4.5076
4.3819
4.3680
4.0195
4.0119
4.0006
3.9936
3.9816
3.9741
3.8036
3.7884
3.7827
3.7739
3.7676
3.7531
2.3470
2.2965
2.1822
2.0465

*** Current Data Parameters ***
NAME : od620
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.130052 MHz

A5 : A5'
84 : 16

208.1330
206.3609

A5 : A5'
84 : 16

138.3866
133.9357
130.0289
129.6909
128.2650
127.8694

78.7617
77.4017
77.0802
76.7670
76.3137

46.7238
45.4050

26.6538
25.5328
21.1149
21.0819

*** Current Data Parameters ***

NAME : 00620
EXPNO : 11
PROCNO : 1

*** Processing Parameters ***

SF : 100.6127690 MHz

130.0289
129.6909
128.2650
127.8694

78.7617
77.0802
77.0390
76.3137

46.7238
45.4133

26.6538
25.5328
21.1149

*** Current Data Parameters ***
NAME : 00620
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

- 7.2692
- 7.2471
- 7.1719
- 7.1505
- 6.8954
- 6.8739
- 6.8000
- 6.7786
- 4.9912
- 4.9722
- 4.9584
- 4.9388
- 4.8049
- 4.7898
- 4.7715
- 4.7563
- 4.7184
- 4.6995
- 4.6850
- 4.6667
- 4.6427
- 4.6212
- 4.6092
- 4.5877
- 4.4823
- 4.4741
- 4.4709
- 4.4634
- 4.3529
- 4.3390
- 4.3251
- 3.9936
- 3.9867
- 3.9747
- 3.9671
- 3.9557
- 3.9482
- 3.7752
- 3.7676
- 3.7562
- 3.7360
- 2.1443
- 2.0181

A6' : A6
80 : 20

*** Current Data Parameters ***
NAME : od616
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.130052 MHz

208.3061
206.5505

159.6270
159.5611

129.5673
129.1552
128.8007
125.6522

114.6405
114.2943

78.7699
77.4594
77.2616
77.1379
77.0802
76.8165
76.4785

55.2711
55.1639

46.3694
45.0094

26.9010
26.6785
25.4833

A6' : A6
80 : 20

*** Current Data Parameters ***
NAME : od616
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

A6' : A6
80 : 20

129.5673
129.1552

114.6405
114.2943

78.7699
77.2616
77.0802
76.4785

55.2711
55.1639

46.3776
45.0094

26.6785
25.4833

*** Current Data Parameters ***
NAME : oad16
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

7.8319
7.8123
7.7808
7.7612
7.7442
7.7240
7.7050
7.6867
7.6387
7.6204
7.6008
7.5169
7.5150
7.4986
7.4796
7.4626
7.4417
7.4222
7.4032
7.2700

5.0792
5.0691
5.0608
5.0495
5.0413
5.0299
5.0211
5.0122
4.7837
4.7654
4.7490
4.7306
4.6757
4.6214
4.6056
4.5873
4.5715
4.5570
4.5475
4.5368
4.5267
4.5191
4.4989
4.4888
4.3581
4.0058
3.9844
3.9768
3.9427
2.3542
2.0593

*** Current Data Parameters ***
NAME : od617
EXPNO : 13
PROCNO : 1
*** Processing Parameters ***
SF : 400.130000 MHz

A7' : A7
74 : 26

206.9642
206.8488

136.5996
133.4345
133.4180
132.7669
132.7010
129.7997
129.5194
128.7282
128.6375
128.4314
128.2748
128.2171
128.1677
128.1347
127.8710
127.8462
126.8572
126.7995
126.7418
126.6841
126.4945
126.4368
125.6950
125.4972
122.9750
122.7772
120.2551
120.0572

78.3099
77.3621
77.0406
76.7274
76.2246
75.5817
73.7190

40.0903
39.3980
39.3815

26.8861
25.2542
25.2377
25.0563

A7' : A7
74 : 26

*** Current Data Parameters ***
NAME : oa617
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

A7' : A7
74 : 26

132.7751
 132.7092
 129.7997
 129.5194
 128.6375
 128.2831
 126.8572
 126.7995
 126.7418
 126.6841
 126.5522
 126.4945
 126.4368
 126.3791

78.3099
 76.2164
 75.5817
 73.7190

40.1068
 40.0903
 39.3897
 39.3732
 25.2542
 25.2377
 25.0563

*** Current Data Parameters ***
 NAME : oa617
 EXPNO : 12
 PROCNO : 1
 *** Processing Parameters ***
 SF : 100.6127690 MHz

7.7812
7.7616
7.7471
7.7269
7.6410
7.6221
7.6031
7.4838
7.4649
7.4453

4.7822
4.7639
4.7475
4.7298
4.6187
4.6029
4.5840
4.5682
4.5543
4.5492
4.5360
4.5334
4.5202
4.5158
4.4987
4.4886
4.3579
3.9608

2.3533
2.0604

A7 : A7'
95 : 5

*** Current Data Parameters ***
NAME : od623
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.1300052 MHz

206.9873

136.6227
132.7983
129.8063
129.5343
128.6606
128.4711
128.4381
128.2980
128.1826
127.8859
127.5891
126.7567
126.5753
126.5176
126.4599
126.4022
125.7099
122.9899

78.3248
77.3770
77.0637
76.7423
73.7421

40.1299
40.1135

26.9010
25.0712

A7 : A7'
95 : 5

*** Current Data Parameters ***
NAME : oad23
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

132.7900
129.5343
128.3062
126.5753
126.5176
126.4599
126.4022

78.3248
73.7421

40.1299
40.1135

25.0712

A7 : A7'
95 : 5

*** Current Data Parameters ***
NAME : oad23
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

7.6943
7.6747
7.5282
7.5093
7.4771
7.4076
7.3874
7.3571
7.3376
7.3180
7.2700
7.0913
7.0724
7.0528
6.9739
6.9543

5.2383
5.2338

4.7938
4.7774
4.7578
4.7521
4.7414
4.7344
4.7180
4.6991
4.6315
4.6271
4.6138
4.6101
4.5968
4.5924
3.7381
3.7356

2.4148

*** Current Data Parameters ***
NAME : o0666
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.130052 MH

200.8246

165.7357

134.0423
132.5238
132.0631
129.8364
128.7700
128.5738
128.4714
127.0467
126.8590
126.7823
126.7055
126.0401

80.2872
77.4719
77.0453
76.6273
73.2746

56.1268

37.3667

*** Current Data Parameters ***
NAME : 00006
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 75.4677496

*** Current Data Parameter
NAME : oad64
EXPNO : 1.
PROCNO :
*** Processing Parameters :
SF : 75.46749

132.5408
129.8364
128.7786
128.5738
128.4714
127.0638
126.7823
126.7055

80.2957

73.2746

56.1268

37.3667

26.8989

— -58.0553

— -71.2274

*** Current Data Parameters ***

NAME	:	oa666
EXPNO	:	13
PROCNO	:	1

*** Processing Parameters ***

SF	:	282.4043460 MHz
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¹H Spectrum

7.7852
7.7751
7.7707
7.7618
7.5055
7.3742
7.2700

5.3197
5.3153

4.8462
4.8253
4.8108
4.7894
4.7616
4.7490
4.7262
4.7130
4.6965
4.6574

3.4572

2.4154

*** Current Data Parameters ***
NAME : oa665
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.1300180 MHz

200.3895

165.7443

134.2215
132.6091
131.3123
130.0241
128.8724
128.8212
128.6079
127.6780
127.0894
127.0126
126.9273

80.5687
77.4719
77.0453
76.6188
73.2404

55.4699

37.6056

*** Current Data Parameters ***
NAME : oa665
EXPNO : 11
PROCNO : 1

*** Processing Parameters ***
SF : 75.4677490 MHz

— -58.0845

— -71.0193

*** Current Data Parameters ***

NAME : oa665
EXPNO : 13
PROCNO : 1

*** Processing Parameters ***

SF : 282.4043460 MHz

A10' : A10
68 : 32

127.3666
127.3006
126.8720
126.7979
126.4599
125.9324

78.7452
77.5665
76.5857
76.3384

42.3224
41.8773

26.4477
25.2443

*** Current Data Parameters ***
NAME : oad18
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

207.5890
205.6686

138.8399
134.2242
127.3666
127.3006
126.8720
126.7979
126.4599
125.9324

78.7452
77.5665
77.4264
77.1050
76.7917
76.5857
76.3384

42.3224
41.8773

26.4477
25.2443

*** Current Data Parameters ***
NAME : oad18
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

A10' : A10
68 : 32

A10' : A10
68 : 32

127.3666
127.3006
126.8720
126.7979
126.4599
125.9324

78.7452
77.5665
76.5857
76.3384

42.3224
41.8773

26.4477
25.2443

*** Current Data Parameters ***
NAME : oad18
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

7.3070
7.3045
7.2944
7.2913
7.2698
7.2357
7.2338
7.2231
7.2212
7.0608
7.0589
7.0520
7.0501
7.0109
7.0021
6.9983
6.9895
6.9623
6.9585
6.9535
6.9503
6.9421
6.9333
6.9295
6.9206

A10 : A10'
78 : 22

4.9975
4.9779
4.9634
4.9438
4.7803
4.7658
4.7468
4.7317
4.7026
4.6856
4.6692
4.6521
4.6319
4.6180
4.5978
4.4836
4.4451
4.4331
4.2316
4.2178
4.2114
4.2045
4.1976
4.1843
3.9330
3.9229
3.7499
2.2340
2.1671

*** Current Data Parameters ***
NAME : oa624
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.130052 MHz

207.4736
205.5532

138.8316
134.1747
127.3501
127.3089
126.8803
126.7979
126.4764
125.9489

78.7617
77.3852
77.0637
76.7505
76.5692
76.3302

42.3471
41.8855

26.4312
25.2278

A10 : A10'
78 : 22

*** Current Data Parameters ***
NAME : 0a024
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

127.3501
127.3171
126.8885
126.8061
126.4764
125.9571

78.7617
77.5253
76.5692
76.3302

42.3471
41.8773

26.4312
25.2278

A10 : A10'
78 : 22

*** Current Data Parameters ***
NAME : oad24
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

A12' : A12
75 : 25

*** Current Data Parameters ***
NAME : oa639
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.130052 MHz

207.4819
205.9323

135.8150
134.7929
134.5209
132.2790
129.8310
129.5343
129.4684
129.2623

78.5968
77.4099
77.0967
76.9731
76.8907
76.7753
75.6626

45.9902
45.1248

26.3241
25.4833

A12' : A12
75 : 25

*** Current Data Parameters ***
NAME : 00639
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

129.8310
129.5343
129.4684
129.2623

78.5968
76.9731
76.8907
75.6626

45.9902
45.1248

26.3241
25.4833

*** Current Data Parameters ***
NAME : oac39
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

A12 : A12'
83 : 17

7.4055
7.3828
7.3695
7.3474
7.3102
7.2887
7.2837
7.2534
7.2477
7.2262

5.0442
5.0253
5.0108
4.9912
4.7904
4.7753
4.7563
4.7412
4.7222
4.6686
4.6477
4.6345
4.6130
4.5499
4.5398
4.5315
4.3990
4.3876
4.3756
4.0669
4.0593
4.0479
4.0403
4.0290
4.0214
3.9078
3.8958
3.8920
3.8863
3.8806
3.8749
3.8711
3.8598
3.7922
3.7802
2.2075
2.1816

*** Current Data Parameters ***
NAME : oad40
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.130052 MHz

207.5725
206.0312

135.8067
134.7682
134.5044
132.2955
129.8393
129.5261
129.4766
129.2541

78.5886
77.4264
77.1132
76.9648
76.8907
76.7917
75.6626

45.9820
45.1165

26.9422
26.3488
25.4916

A12 : A12'
83 : 17

*** Current Data Parameters ***
NAME : oac40
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

A12 : A12'

83 : 17

129.8475

129.5261

129.4766

129.2541

78.5886

76.9731

76.8907

75.6626

45.9820

45.1165

26.3488

25.4916

*** Current Data Parameters ***

NAME	:	oac40
EXPNO	:	12
PROCNO	:	1

*** Processing Parameters ***

SF	:	100.6127690 MHz
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7.4185
7.4055
7.3898
7.3368
7.3207
7.2700
7.2668
7.2508
7.2344
7.2252
7.2092
7.1931

5.3017
5.2925
5.2806
5.2645
5.2525
5.1854
5.1766
5.1671
5.1513
5.1416
5.1337
5.0669
5.0524
5.0391
5.0243
5.0168
5.0130
5.0092
5.0048
4.9878
4.9752
4.8793
4.8655
4.8598
4.8462
4.7381
4.7227
4.7088
4.6770
3.6943
3.6807
2.9176
2.9044
2.3238

2.0364
1.8586
1.4268

A14' : A14
54 : 46

*** Current Data Parameters ***
NAME : od676
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 500.130080 MHz

208.6743
207.5435

A14' : A14
54 : 46

137.8090
137.1900
134.8685
134.8128
132.0972
131.7423
130.4856
130.3329
130.2958
130.0027
129.4642
129.1897

77.2964
77.0405
76.7867
75.9593
74.9956
74.8223
74.4446

43.7973
42.4230

26.9054
26.6742
26.3234

*** Current Data Parameters ***

NAME : 00676
EXPNO : 11
PROCNO : 1

*** Processing Parameters ***
SF : 125.7577890 MHz

130.4877
130.3370
130.2978
130.0048
129.4662
129.1918

75.9593
74.9935
74.8223
74.4446

43.7952
42.4168

26.6804
26.3276

*** Current Data Parameters ***

NAME : oad76

EXPNO : 12

PROCNO : 1

*** Processing Parameters ***

SF : 125.7577890 MHz

A14' : A14
54 : 46

7.4127
7.4026
7.3925
7.3824
7.3325
7.3117
7.2700
7.2656
7.2460
7.2258
7.2226
7.2024
7.1822

5.2938
5.2787
5.2585
5.2433
5.1814
5.1776
5.1164
5.1114
5.0634
5.0451
5.0280
5.0103
4.9655
4.8809
4.8645
4.8569
4.8405
4.7218
4.7060
4.7041
4.6978
4.6883
4.6820
4.6801
4.6643
3.7223
3.7053
2.9919
2.9754
2.3182

A14 : A14'
84 : 16

*** Current Data Parameters ***
NAME : 00680
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.1300170 MHz

208.9243
207.6879

137.1914
134.8424
132.0894
131.8092
130.5316
130.3998
130.3173
130.0371
129.5013
129.2211

77.4346
77.1132
76.8000
75.9428
75.0361
74.8795
74.4757

43.8060
42.4295

26.7279
26.3570

A14 : A14'
84 : 16

*** Current Data Parameters ***
NAME : oa680
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

130.5316
130.3998
130.3173
130.0371
129.5013
129.2211

75.9428
75.0361
74.8795
74.4757

43.8060
42.4295

26.7279
26.3653

A14 : A14'
84 : 16

*** Current Data Parameters ***
NAME : oad80
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

7.5423
7.5379
7.4771
7.4604
7.4005
7.3961
7.3876
7.3712
7.2782
7.2738
7.2700
7.2615
7.2571
7.1405
7.1360
7.1238
7.1197

5.0042
4.9893
4.9770
4.9619
4.7429
4.7277
4.7154
4.7003
4.6950
4.6824
4.6669
4.6546
4.6155
4.5991
4.5878
4.5714
4.5210
4.5144
4.5081
4.3694
4.3628
4.3561
4.0202
4.0142
4.0050
3.9994
3.9899
3.9842
3.9095
3.9020
3.8972
3.8928
3.8900
3.8856
3.8805
3.8733
3.7872
3.7787
3.7633
2.2545
2.2094

A16' : A16
74 : 26

*** Current Data Parameters ***
NAME : od677
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 500.130080 MHz

206.9327
205.5646

137.6728
133.9317
133.3828
133.1888
132.8277
131.1975
130.9540
130.3659
130.1266
127.8340
127.4172

78.3963
77.2902
77.0364
76.7826
76.7351
75.0348

45.3222
44.8002

26.9074
25.9974
25.4444

A16' : A16
74 : 26

*** Current Data Parameters ***
NAME : od677
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 125.7577890 MHz

131.1975
130.9561
130.3659
130.1266
127.8340
127.4172

78.3963
76.7393
76.7310
75.0348

45.3202
44.8002

25.9995
25.4444

A16' : A16
74 : 26

*** Current Data Parameters ***
NAME : od677
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 125.7577890 MHz

7.5402
7.5345
7.4765
7.4556
7.3994
7.3944
7.3868
7.3660
7.2782
7.2725
7.2700
7.2574
7.2523
7.1412
7.1362
7.1210
7.1153

5.0078
4.9889
4.9737
4.9548
4.7477
4.7287
4.7136
4.6997
4.6947
4.6839
4.6650
4.6498
4.6189
4.5981
4.5842
4.5633
4.5210
4.5135
4.5059
4.3758
4.3424
4.0222
4.0153
4.0039
3.9964
3.9850
3.9774
3.9118
3.9029
3.8960
3.8916
3.8871
3.8821
3.8758
3.8669
3.8013
3.7482
2.2513
2.2077

A16 : A16'
88 : 12

*** Current Data Parameters ***
NAME : 00681
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.1300170 MHz

207.0615

137.6942
133.9687
133.4000
133.2021
132.8477
131.2322
130.9932
130.3998
130.1607
127.8941
127.4737

78.4237
77.4099
77.0885
76.7753
75.0609

45.3391
44.8198

26.9422
26.0603
25.4998

A16 : A16'
88 : 12

*** Current Data Parameters ***
NAME : 00681
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

C13-DEPT-135 CH,CH3 up - CH2 down

131.2322
130.1607
127.4737

78.4237
75.0609

45.3391

26.0603

A16 : A16'
88 : 12

*** Current Data Parameters ***
NAME : oa681
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

7.4554
7.4383
7.4138
7.4097
7.3892
7.3725
7.3343
7.3299
7.2495
7.2454
7.2328
7.2284
7.1956
7.1499
7.1455
7.1329
7.1285

4.9232
4.9062
4.8961
4.8791
4.6912
4.6849
4.6783
4.6723
4.6682
4.6616
4.6553
4.6222
4.6083
4.5967
4.5806
4.5670
4.5566
4.5437
4.5295
4.5163
4.5081
4.5012
4.2935
4.2830
4.2723
3.7315
3.7230
3.7160
3.7078
2.2902
2.1546

A18' : A18
80 : 20

*** Current Data Parameters ***

NAME : oad78
EXPNO : 10
PROCNO : 1

*** Processing Parameters ***

SF : 500.1300449 MHz

206.8894
206.2724135.1512
134.8025
134.3588
134.2082
133.7563
130.4588
130.4485
129.9429
129.7056
128.0672
127.912477.5234
77.2964
77.0426
76.7888
76.1656
75.9758
73.121941.0116
39.789926.9054
25.4774 **A18' : A18**
80 : 20

*** Current Data Parameters ***
NAME : oad78
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 125.7577890 MHz

130.4588
129.9429
129.7056
128.0692
127.9124

77.5234
76.1656
75.9758
73.1178

41.0074
39.7858

26.9054
25.4795

A18' : A18
80 : 20

*** Current Data Parameters ***
NAME : oad678
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 125.7577890 MHz

1H Spectrum

7.5289
7.5074
7.4828
7.4771
7.4588
7.4373
7.4032
7.3982
7.3205
7.3155
7.2997
7.2940
7.2700
7.2214
7.2157
7.1999
7.1942

4.9977
4.9769
4.9642
4.9434
4.7628
4.6965
4.6801
4.6643
4.6555
4.6391
4.6094
4.5842
4.5779
4.3708
4.3512
4.3291
3.8290
3.8189
3.8019

2.3561
2.2235

A18 : A18'
91 : 9

*** Current Data Parameters ***
NAME : 00682
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.1300170 MHz

207.0285

134.8094
134.2489
133.7791
130.5069
129.9794
129.7486
128.1002
127.9435

77.5500
77.4346
77.1132
76.7917
76.1983
76.0252
73.1569

41.0366
39.8250

26.9422
25.4504

A18 : A18'
91 : 9

*** Current Data Parameters ***
NAME : 00682
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

130.5069
129.9794
129.7486
128.1002
127.9435

77.5500
76.1983
76.0252
73.1569

41.0366
39.8250
38.3661

25.5328
25.4504

A18 : A18'
91 : 9

*** Current Data Parameters ***
NAME : 00682
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

ANDREY PROTON CDCl3

8.0580
8.0410
8.0097
7.9930
7.8017
7.7857
7.7585
7.7418
7.6816
7.6653
7.5830
7.5691
7.5023
7.4878
7.4727
7.4144
7.3996
7.3838
7.2848
7.2697
7.2543
7.1405

5.0593
5.0401
5.0149
4.9556
4.8708
4.7678
4.6417
4.5951
4.4053
3.8468
3.7214

1.9964
1.9220
1.8312

1.3150

*** Current Data Parameter:
NAME : oad75
EXPNO : 16
PROCNO : 1
*** Processing Parameters *
SF : 500.130071;

A20' : A20
76 : 24

207.8819
206.7511

134.1587
134.0823
133.2115
130.9685
130.8735
130.2008
129.5653
129.5178
129.1691
128.9999
127.2933
127.2129
126.2162
126.1440
126.0263
125.5703
125.4486
121.8168
121.7074

78.4788
77.3294
77.0756
76.8218
76.7682
76.5659
75.0699

38.4920

26.9219
26.1460
25.5145

A20' : A20
76 : 24

*** Current Data Parameters
NAME : o0679
EXPNO : 11
PROCNO : 1
*** Processing Parameters **
SF : 125.7577890

129.5653
129.5199
129.1691
128.9978
127.2933
127.2129
126.2162
126.1419
126.0263
125.5703
125.4486
121.8374
121.7115

78.4747
76.7661
76.5659
75.0699

26.9239
26.1480
25.5166

A20' : A20
76 : 24

*** Current Data Parameters **
NAME : od679
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 125.7577890 MHz

1H Spectrum

*** Current Data Parameters:
 NAME : 00683
 EXPNO : 1
 PROCNO : 1
 *** Processing Parameters *
 SF : 400.1300170

A20 : A20'
 78 : 22

207.9929
206.8555

A20 : A20'

78 : 22

134.1912
134.1170
133.2186
131.0097
130.9025
130.2267
129.6085
129.5673
129.2211
129.0480
127.3419
127.2677
126.2704
126.0808
125.6192
125.4956
125.3142
121.8854
121.7783

78.5061
77.4594
77.1462
76.8247
76.6187
75.1103

26.2169
25.5740

*** Current Data Parameters
NAME : 00683
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690

129.6085
129.5673
129.2211
129.0480
127.3419
127.2677
126.2704
126.0808
125.6192
125.5038
125.2648
121.8854
121.7701

78.5061
76.8000
76.6187
75.1103

26.2169
25.5823

A20 : A20'

78 : 22

*** Current Data Parameters
NAME : aa683
EXPNO : 12
PROCNO : 1
*** Processing Parameters **
SF : 100.6127690

¹H Spectrum

7.4108
7.3427
7.3048
7.2277

5.0659
5.0457
5.0325
5.0123
4.8235
4.8083
4.7894
4.7743
4.7572
4.7402
4.7237
4.7061
4.7010
4.6795
4.6676
4.6461
4.5192
4.5129
4.3841
4.3708
4.0545
4.0469
4.0349
4.0292
4.0172
4.0090
3.8512
3.8367
3.8297
3.8228
3.8158
3.8013
3.7742
3.6927

2.5323
2.3801
2.2911
2.2728
2.2545

1.7165
1.4501

0.8680
0.8623
0.8490
0.8440
0.8307
0.8251

A21' : A21
61 : 39

*** Current Data Parameters ***
NAME : od632a
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 400.130050 MHz

210.4244
208.6358

137.1420
133.8945
129.3365
128.9656
128.6606
128.5123
128.4711
128.0260

78.1765
77.3605
77.2451
77.0473
76.7258
76.3879
76.1406

47.1689
45.9820
41.2509
40.1382

26.9175

16.9278
16.8207
13.5979
13.5650

A21' : A21
61 : 39

*** Current Data Parameters ***
NAME : odc32a
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

Cl3-DEPT-135 CH,CH3 up - CH2 down

129.3365
128.9656
128.6606
128.5123
128.4711
128.0260

78.1765
77.0555
76.3879
76.1406

47.1689
45.9902
41.2509
40.1464

16.9278
16.8207
13.6062
13.5732

A21' : A21
61 : 39

*** Current Data Parameters ***
NAME : odc32a
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

A21 : A21'
92 : 8

7.4146
7.3458
7.2700

4.8235
4.8083
4.7900
4.7748
4.7016
4.6801
4.6675
4.6460
4.3916
4.3796
4.3676
3.8530
3.8385
3.8316
3.8246
3.8177
3.8032
3.6857
3.6725

2.2948
2.2765
2.2582

1.6332
1.6294
1.6142
1.6111
1.5959
1.5934
1.5770
1.5751
1.5593
1.5561
1.5410
0.8717
0.8534
0.8351

*** Current Data Parameters ***

NAME : 0d699

EXPNO : 10

PROCNO : 1

*** Processing Parameters ***

SF : 400.130052 MHz

A21 : A21'
92 : 8

*** Current Data Parameters ***
NAME : od699
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

129.3695
128.5452
128.0507

78.2094
76.1653

47.1936
41.2674

26.9505
16.9690
13.5979

A21 : A21'
92 : 8

*** Current Data Parameters ***
NAME : 0d699
EXPNO : 12
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz

150-55 hydrodexB-3P

```

=====
Injection Date   : 26.10.2002 11:28:20
Sample Name     : oa554
Acq. Operator   : Olivier A
Location        : Vial 1
Inj             : 1
Inj Volume      : 1 µl

Acq. Method     : D:\HPCHEM\3\METHODS\150-55.M
Last changed    : 26.10.2002 11:59:43 by Olivier A
                  (modified after loading)
Analysis Method : D:\HPCHEM\3\METHODS\120-140.M
Last changed    : 01.04.2003 09:32:35 by OA
                  (modified after loading)
=====

```

```

=====
Area Percent Report
=====

```

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	28.743	MM	0.2401	133.57086	9.27175	42.25157
2	29.242	MM	0.2286	133.50137	9.73178	42.22959
3	33.520	MM	0.3392	49.06008	2.41066	15.51884

Totals : 316.13231 21.41418

Results obtained with enhanced integrator!

```

=====
*** End of Report ***

```

150-35 hydrodex B-3P

```

=====
Injection Date   : 13.11.2002 09:18:14
Sample Name     : oa579 2j rt
Acq. Operator   : OLIVIER A
Location        : Vial 8
Inj             : 1
Inj Volume      : 1 µl

Acq. Method     : D:\HPCHEM\3\METHODS\150-35.M
Last changed    : 13.11.2002 09:58:59 by OLIVIER A
                  (modified after loading)

Analysis Method : D:\HPCHEM\3\METHODS\120-140.M
Last changed    : 01.04.2003 09:35:54 by OA
                  (modified after loading)
=====

```

```

=====
Area Percent Report
=====

```

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	28.697	MM	0.2485	49.37445	3.31134	12.78230
2	29.279	MM	0.2508	271.52267	18.04157	70.29312
3	33.536	MM	0.3567	65.37492	3.05421	16.92458

Totals : 386.27205 24.40711

Results obtained with enhanced integrator!

```

=====
*** End of Report ***

```

OJ 5-6-1-15% 200 Bars 2 ml/min 30 C

```
=====
Acq. Method      : OJ5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1002
Injection Date   : 21-11-02 12:53:32           Inj     :   -
Sample Name      : OA593                       Inj Volume: Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
(modified after loading)

CHIRALCEL OJ

=====
Area Percent Report
=====

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.069	MM	0.122	7100.02393	967.44574	38.7131
2	3.511	MM	0.139	7139.44434	858.56104	38.9281
3	4.047	MM	0.158	2051.38354	216.02374	11.1852
4	4.757	MM	0.181	2049.25024	188.81673	11.1736

Totals : 18340.10156 2230.84717

=====
*** End of Report ***

OJ 5%-5-1-20 200 Bars 2 ml/min 30 C

```
=====
Acq. Method   : OJ5-6.M                      Seq. Line :   -
Acq. Operator : OA                          Vial   : 1001
Injection Date: 16-01-03 10:22:27           Inj    :   -
Sample Name   : OA628                      Inj Volume: Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
(modified after loading)

CHIRALCEL OJ

LDAD1 B, Sig=220,15 Ref=450,40 of OA0\OA628.D

```
=====
Area Percent Report
=====
```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.284	MM	0.131	121.12409	15.40788	1.6359
2	3.768	MM	0.148	1130.73474	126.95428	15.2719
3	4.312	MM	0.171	75.13150	7.30880	1.0147
4	5.050	MM	0.215	6077.03418	471.98486	82.0774

Totals : 7404.02441 621.65582

```
=====
*** End of Report ***
=====
```

AS 5%-5-1-15 200 Bars 2 ml/min 30 C

```

=====
Acq. Method      : AS5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1002
Injection Date   : 18-12-02 15:47:16           Inj      :   -
Sample Name      : OA615                       Inj Volume: Unknown
=====

```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
(modified after loading)

CHIRALCEL OJ

```

=====
                          Area Percent Report
=====

```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	2.706	MM	0.114	15041.75684	2204.97900	33.8373
2	2.920	MM	0.120	15750.01074	2182.31274	35.4306
3	3.135	MM	0.097	6853.06104	1183.16150	15.4164
4	3.366	MM	0.105	6808.34668	1082.25220	15.3158

Totals : 44453.17578 6652.70557

```

=====
*** End of Report ***
=====

```


AS-H 5-6-1-15 200 Bars 2 ml/min 30 C

```

=====
Acq. Method      : AS5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1001
Injection Date   : 13-01-03 12:50:59           Inj     :   -
Sample Name      : OA620                       Inj Volume: Unknown
=====

```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
(modified after loading)

CHIRALCEL OJ

=====
Area Percent Report
=====

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	2.851	MM	0.079	850.47473	179.60358	14.6442
2	3.083	MM	0.077	107.08102	23.04129	1.8438
3	3.273	MM	0.080	58.77890	12.23355	1.0121
4	3.522	MM	0.102	4791.24170	779.38281	82.4999

Totals : 5807.57617 994.26123

=====
*** End of Report ***

AS 5%-5-1-15 200 Bars 2 ml/min 30 C

```
=====
Acq. Method      : AS5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1003
Injection Date   : 18-12-02 15:55:41           Inj    :   -
Sample Name      : OA616                      Inj Volume : Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
(modified after loading)

CHIRALCEL OJ

```
=====
                          Area Percent Report
=====
```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.194	MM	0.123	16773.61719	2273.08618	38.2056
2	3.479	MM	0.131	17163.18555	2186.42700	39.0929
3	3.944	MM	0.125	4971.50732	661.83899	11.3237
4	4.532	MM	0.143	4995.30225	582.21503	11.3779

Totals : 43903.61328 5703.56738

```
=====
*** End of Report ***
=====
```

AS-H 5-6-1-15 200 Bars 2 ml/min 30 C

```
=====
Acq. Method      : AS5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1002
Injection Date   : 13-01-03 13:19:30           Inj      :   -
Sample Name      : OA621                       Inj Volume: Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
(modified after loading)

CHIRALCEL OJ

=====
Area Percent Report
=====

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.400	MM	0.102	477.28400	77.90977	17.2953
2	3.676	MM	0.098	58.04630	9.88577	2.1034
3	4.122	MM	0.110	29.48444	4.48757	1.0684
4	4.744	MM	0.135	2194.80322	270.06702	79.5329

Totals : 2759.61792 362.35013

=====
*** End of Report ***

OD-H 5%-5-1-15 200 Bars 2 ml/min 30 C

```
=====
Acq. Method      : OD-H5-6.M                      Seq. Line :   -
Acq. Operator    : OA                            Vial   : 1004
Injection Date   : 18-12-02 15:25:57              Inj     :   -
Sample Name      : OA617                          Inj Volume: Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
(modified after loading)

CHIRALCEL OJ

```
=====
Area Percent Report
=====
```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	2.686	MM	0.128	12241.16602	1592.74866	70.3246
2	3.135	MM	0.082	2565.11572	519.03308	14.7364
3	3.661	MM	0.095	2600.37988	455.44998	14.9390

Totals : 17406.66211 2567.23169

```
=====
*** End of Report ***
=====
```

OD-H 5%-5-1-20 200 Bars 2 ml/min 30 C

```

=====
Acq. Method      : OD-H5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1001
Injection Date   : 16-01-03 09:31:57             Inj    :   -
Sample Name      : JC505                       Inj Volume: Unknown
=====

```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
(modified after loading)

CHIRALCEL OJ

```

=====
Area Percent Report
=====

```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	2.634	MM	0.080	161.05301	33.40682	5.2923
2	3.102	MM	0.070	20.96364	5.02146	0.6889
3	3.608	MM	0.090	2861.16479	532.51923	94.0189

Totals : 3043.18140 570.94751

```

=====
*** End of Report ***
=====

```

OJ 5%-5-1-15 200 Bars 2 ml/min 30 C

```

=====
Acq. Method      : OJ5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1005
Injection Date   : 18-12-02 11:15:59           Inj     :   -
Sample Name      : OA618                       Inj Volume : Unknown
=====

```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
(modified after loading)

CHIRALCEL OJ

=====
Area Percent Report
=====

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.472	MM	0.188	29453.14063	2605.61011	28.5241
2	3.674	MM	0.223	34702.95313	2595.50439	33.6083
3	4.749	MM	0.193	19479.93945	1680.86389	18.8655
4	5.241	MM	0.215	19620.98242	1519.39880	19.0021

Totals : 103257.01563 8401.37695

=====
*** End of Report ***

OJ 5%-5-1-20 200 Bars 2 ml/min 30 C

```

=====
Acq. Method      : OJ5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1001
Injection Date   : 16-01-03 10:00:55           Inj     :   -
Sample Name      : OA624                       Inj Volume: Unknown
=====

```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
(modified after loading)

CHIRALCEL OJ

```

=====
                          Area Percent Report
=====

```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.355	MM	0.123	150.83154	20.40633	2.5753
2	3.577	MM	0.137	1143.66455	139.29585	19.5270
3	4.577	MM	0.172	84.90497	8.24520	1.4497
4	5.036	MM	0.200	4477.43945	373.59998	76.4480

Totals : 5856.84033 541.54736

```

=====
*** End of Report ***
=====

```

AS-H 5%-6-2-20 200 Bars 2 ml/min 55 C

```

=====
Acq. Method      : AS5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1001
Injection Date   : 28-01-03 14:20:36           Inj     :   -
Sample Name      : OA639                      Inj Volume: Unknown
=====

```

```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
                  (modified after loading)

```

CHIRALCEL OJ

```

=====
Area Percent Report
=====

```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.460	MM	0.097	4154.57031	711.69910	37.5683
2	3.747	MM	0.104	4176.94287	671.19043	37.7707
3	4.078	MM	0.111	1370.17200	206.27356	12.3900
4	4.391	MM	0.117	1357.01306	193.21490	12.2710

Totals : 11058.69824 1782.37793

```

=====
*** End of Report ***
=====

```



```

=====
Acq. Method      : AS5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1001
Injection Date   : 30-01-03 14:23:08           Inj    :   -
Sample Name      : OA640                       Inj Volume: Unknown
  
```

```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
                  (modified after loading)
  
```

CHIRALCEL OJ

```

=====
                        Area Percent Report
=====
  
```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.755	MM	0.093	484.87799	86.89998	11.3754
2	4.047	MM	0.100	67.53957	11.29873	1.5845
3	4.352	MM	0.105	41.40655	6.57706	0.9714
4	4.656	MM	0.117	3668.69238	523.69562	86.0687

Totals : 4262.51660 628.47137

```

=====
*** End of Report ***
  
```

AS-H 5%-6-2-20 200 bars 2 ml/min 30 C

```
=====
Acq. Method      : AS5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1002
Injection Date   : 05-03-03 15:55:51           Inj      :   -
Sample Name      : OA677                       Inj Volume: Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OD-HSR.M
(modified after loading)

CHIRALCEL OD-H

```
=====
                          Area Percent Report
=====
```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	4.387	FF	0.133	1504.84302	173.83464	23.1986
2	5.242	FF	0.155	1467.90918	146.81865	22.6292
3	5.837	FF	0.177	1764.67859	153.83577	27.2042
4	6.398	FV	0.199	1749.36047	135.40509	26.9680

Totals : 6486.79102 609.89417

```
=====
*** End of Report ***
=====
```

AS-H 28-6-2-20 200 bars 2 ml/min 30 C

```

=====
Acq. Method   : AS5-6.M                      Seq. Line :   -
Acq. Operator : OA                          Vial   : 1001
Injection Date: 10-03-03 10:53:04           Inj    :   -
Sample Name   : OA680                       Inj Volume: Unknown
=====

```

Analysis Method : C:\BERGER\1\METHODS\OD-HSR.M
(modified after loading)

CHIRALCEL OD-H

```

=====
                          Area Percent Report
=====

```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	4.286	MM	0.190	2797.33423	244.80937	83.1210
2	5.111	MM	0.191	27.05843	2.36428	0.8040
3	5.576	MM	0.241	531.77557	36.83812	15.8014
4	6.143	MM	0.145	9.20869	1.05840	0.2736

Totals : 3365.37695 285.07019

```

=====
*** End of Report ***
=====

```

OJ 5%-6-2-20 200 bars 2 ml/min 30 C

```
=====
Acq. Method   : OJ5-6.M                      Seq. Line :   -
Acq. Operator : OA                          Vial   : 1001
Injection Date: 05-03-03 16:43:02           Inj    :   -
Sample Name   : OA676                      Inj Volume: Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OD-HSR.M
(modified after loading)

CHIRALCEL OD-H

```
=====
                          Area Percent Report
=====
```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	6.016	MM	0.239	3174.69653	221.64397	37.3538
2	6.732	MM	0.267	3161.54907	197.48557	37.1991
3	7.533	MM	0.301	1050.37122	58.17139	12.3588
4	8.993	MM	0.269	1112.37781	69.01104	13.0883

Totals : 8498.99414 546.31195

```
=====
*** End of Report ***
=====
```

OJ 2%-6-2-20 200 bars 2 ml/min 30 C

```
=====
Acq. Method      : OJ5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1001
Injection Date   : 10-03-03 11:17:58           Inj     :   -
Sample Name      : OA681                       Inj Volume: Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OD-HSR.M
(modified after loading)

CHIRALCEL OD-H

```
=====
                          Area Percent Report
=====
```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	6.107	MM	0.225	49.31103	3.64963	1.7236
2	6.831	MM	0.266	282.13165	17.68268	9.8616
3	7.694	MM	0.269	23.48489	1.45450	0.8209
4	9.067	MM	0.278	2505.97900	150.48453	87.5939

Totals : 2860.90649 173.27135

```
=====
*** End of Report ***
=====
```

AS-H 5%-6-2-20 200 bars 2 ml/min 30 C

```

=====
Acq. Method      : AS5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1003
Injection Date   : 05-03-03 16:06:08           Inj     :   -
Sample Name      : OA678                       Inj Volume: Unknown
=====

```

Analysis Method : C:\BERGER\1\METHODS\OD-HSR.M
(modified after loading)

CHIRALCEL OD-H

```

=====
                          Area Percent Report
=====

```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.205	FF	0.096	4120.65088	666.29816	39.3658
2	3.449	FF	0.105	4204.86523	618.87695	40.1703
3	3.862	FF	0.115	1044.82300	139.69499	9.9815
4	4.143	FV	0.145	1097.26221	114.03379	10.4825

Totals : 10467.60156 1538.90393

```

=====
*** End of Report ***
=====

```

AS-H 5%-6-2-20 200 bars 2 ml/min 30 C

```
=====
Acq. Method      : AS5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1001
Injection Date   : 12-03-03 11:11:43           Inj     :   -
Sample Name      : OA682                       Inj Volume: Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OD-HSR.M
(modified after loading)

CHIRALCEL OD-H

```
=====
Area Percent Report
=====
```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.343	MM	0.089	183.69049	34.22047	7.5254
2	3.620	MM	0.096	35.96706	6.25650	1.4735
3	4.019	MM	0.102	15.24545	2.48702	0.6246
4	4.326	MM	0.148	2206.03931	248.65190	90.3765

Totals : 2440.94238 291.61591

```
=====
*** End of Report ***
=====
```

AS-H 58-6-2-20 200 bars 2 ml/min 30 C

```
=====
Acq. Method      : AS5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1004
Injection Date   : 05-03-03 16:13:56           Inj     :   -
Sample Name      : OA679                       Inj Volume: Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OD-HSR.M
(modified after loading)

CHIRALCEL OD-H

=====
Area Percent Report
=====

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	4.537	MM	0.149	13564.68066	1521.54956	37.9827
2	5.104	MM	0.183	13938.88770	1268.61877	39.0305
3	5.648	MM	0.188	4128.71191	365.77744	11.5609
4	6.829	MM	0.228	4080.53564	298.91455	11.4260

Totals : 35712.81641 3454.86035

=====
*** End of Report ***

AS-H 5%-6-2-20 200 bars 2 ml/min 30 C

```
=====
Acq. Method      : AS5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1001
Injection Date   : 12-03-03 15:47:24           Inj      :   -
Sample Name      : OA683                       Inj Volume: Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OD-HSR.M
(modified after loading)

CHIRALCEL OD-H

```
=====
                          Area Percent Report
=====
```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	4.724	MM	0.133	1173.02490	146.89215	20.0829
2	5.400	MM	0.155	88.94884	9.55205	1.5229
3	5.841	MM	0.160	38.20756	3.99018	0.6541
4	7.116	MM	0.225	4540.72217	336.43054	77.7401

Totals : 5840.90332 496.86493

```
=====
*** End of Report ***
```

AS-H 3%-8-2-15 200 Bars 2 ml/min 30 C

```
=====
Acq. Method   : AS5-6.M                      Seq. Line :   -
Acq. Operator : OA                          Vial   : 1001
Injection Date: 21-01-03 16:54:48           Inj     :   -
Sample Name   : OA632                      Inj Volume: Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
(modified after loading)

CHIRALCEL OJ

```
=====
Area Percent Report
=====
```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.224	MM	0.093	1939.51965	347.64456	30.3760
2	3.660	MM	0.103	1976.39917	318.98764	30.9535
3	3.941	MM	0.107	1250.99670	194.56969	19.5926
4	4.314	MM	0.123	1218.13452	165.30045	19.0779

Totals : 6385.04980 1026.50232

```
=====
*** End of Report ***
=====
```

AS-H 3%-6-2-20

200 bars 2 ml/min 30C

```
=====
Acq. Method      : AS5-6.M                      Seq. Line :   -
Acq. Operator    : OA                          Vial   : 1001
Injection Date   : 28-03-03 09:50:10           Inj      :   -
Sample Name      : OA699                       Inj Volume: Unknown
=====
```

Analysis Method : C:\BERGER\1\METHODS\OJ1-4.M
(modified after loading)

CHIRALCEL OJ

```
=====
                          Area Percent Report
=====
```

Sorted by Signal

Multiplier : 1.000000

Signal 1: LDAD1 B, Sig=220,15 Ref=450,40

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.119	MM	0.112	49.10084	7.28802	6.8113
2	3.535	MM	0.108	6.11388	9.41303e-1	0.8481
3	3.786	MM	0.096	5.42196	9.42718e-1	0.7521
4	4.183	MM	0.140	660.23859	78.61249	91.5885

Totals : 720.87524 87.78453

```
=====
*** End of Report ***
=====
```

UV/Vis Spectra

CD Spectra

Table S1. Summary of crystal data, intensity measurement and structure refinement for **A8**.

Formula	C ₂₂ H ₁₉ NO ₆ F ₆
Mol. wt.	507.4
Diffractometer	Stoe IPDS
Crystal habit	hexagonal prism
Crystal dimensions	0.23 x 0.23 x 0.32 x 0.26
Crystal color	colorless
Temperature (K)	200
Crystal system	Orthorhombic
Space Group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	9.8059(4)
<i>b</i> (Å)	11.3493(7)
<i>c</i> (Å)	20.3434(11)
<i>V</i> (Å ³)	2264.0(2)
<i>Z</i>	4
D _c gr.cm ⁻³	1.489
μ(MoKα) mm ⁻¹	0.14
T min.,max	0.9669 , 0.9766
2θ range (°)	4.5 – 53.9
hkl rang	-12 , 12 ; -14 , 14 ; -26 , 25
No. measured reflc.	31770
No. unique refl.	4959
No. observed reflc.	3312
Criterion for observed	<i>F</i> _o > 4σ(<i>F</i> _o)
Refinement (on <i>F</i>)	Full-matrix
No. parameters	316
Weighting scheme	ω = 1 / [σ ² (<i>F</i> _o) + 0.00015 (<i>F</i> _o) ²]
Max. Δ/σ	0.00045
Max. and min. Δρ (e.Å ⁻³)	0.19 , -0.29
<i>S</i> ^{a)}	1.62(2)
<i>R</i> ^{b)} , ω <i>R</i> ^{c)}	0.030 , 0.031

$$a) S = [\sum \{((F_o - F_c) / \sigma(F_o))^2\} / (N_{ref} - N_{var})]^{1/2}$$

$$b) R = \sum ||F_o| - |F_c|| / \sum |F_o| ;$$

$$c) \omega R = [\sum (\omega |F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}$$

Ortep view of **A8** with atom numbering. Ellipsoids are represented with 40% probability.

Table S2. Atomic coordinates and displacement parameters ($\text{\AA}^2$) with e.s.d.'s in parenthesis for **A8**. (U_{eq} is the average of eigenvalues of U).

Non-Hydrogen Positional and Isotropic Displacement Parameters

	x/a	y/b	z/c	U_{eq}
O(1)	0.4144(3)	0.3874(3)	0.5595(1)	0.051(1)
O(2)	0.2050(3)	0.4145(2)	0.6412(1)	0.0322(8)
O(3)	0.3442(3)	0.5539(3)	0.6833(1)	0.0427(9)
O(4)	0.2783(3)	0.2653(2)	0.7364(1)	0.0387(9)
O(5)	0.1976(4)	0.2854(3)	0.4499(2)	0.065(1)
O(6)	0.2226(4)	0.1532(3)	0.5250(2)	0.081(2)
N(1)	0.1674(4)	0.2413(3)	0.5024(2)	0.047(1)
F(1)	0.0202(3)	0.6760(2)	0.4889(1)	0.0543(9)
F(2)	-0.0885(3)	0.5436(2)	0.4340(1)	0.0460(8)
F(3)	-0.1899(3)	0.7032(2)	0.4620(2)	0.067(1)
F(4)	0.3687(3)	0.5268(2)	0.8257(1)	0.0497(8)
F(5)	0.3861(3)	0.3428(2)	0.8500(1)	0.0570(9)
F(6)	0.5110(3)	0.4172(3)	0.7739(1)	0.0539(9)
C(1)	-0.0624(4)	0.4784(3)	0.5765(2)	0.032(1)
C(2)	-0.1445(4)	0.5655(3)	0.5470(2)	0.036(1)
C(3)	-0.2658(5)	0.6006(4)	0.5760(2)	0.047(2)
C(4)	-0.3088(5)	0.5506(4)	0.6344(2)	0.051(2)
C(5)	-0.2303(5)	0.4677(5)	0.6643(2)	0.050(2)
C(6)	-0.1076(4)	0.4313(4)	0.6361(2)	0.043(1)
C(7)	-0.1015(5)	0.6217(4)	0.4841(2)	0.043(1)
C(8)	0.0677(4)	0.4305(3)	0.5446(2)	0.031(1)
C(9)	0.0573(4)	0.2961(3)	0.5427(2)	0.037(1)
C(10)	0.1975(4)	0.4757(3)	0.5795(2)	0.032(1)
C(11)	0.3291(5)	0.4564(4)	0.5404(2)	0.036(1)
C(12)	0.3482(5)	0.5272(4)	0.4787(2)	0.052(2)
C(13)	0.2832(4)	0.4625(3)	0.6883(2)	0.032(1)
C(14)	0.2721(4)	0.3857(3)	0.7509(2)	0.033(1)
C(15)	0.3862(4)	0.4195(4)	0.8001(2)	0.040(1)
C(16)	0.3976(5)	0.2215(4)	0.7025(2)	0.049(1)
C(17)	0.1329(4)	0.4097(3)	0.7827(2)	0.033(1)
C(18)	0.0793(5)	0.5231(4)	0.7845(2)	0.041(1)
C(19)	-0.0467(5)	0.5437(4)	0.8133(2)	0.050(2)
C(20)	-0.1200(5)	0.4515(5)	0.8399(2)	0.056(2)
C(21)	-0.0666(5)	0.3392(5)	0.8385(2)	0.058(2)
C(22)	0.0596(5)	0.3170(4)	0.8105(2)	0.045(1)

Hydrogen Positional and Isotropic Displacement Parameters

	x/a	y/b	z/c	U
H(3)	-0.3217	0.6615	0.5550	0.050
H(4)	-0.3949	0.5756	0.6544	0.050
H(5)	-0.2604	0.4321	0.7059	0.050
H(6)	-0.0525	0.3715	0.6586	0.050
H(8)	0.0773	0.4614	0.4998	0.050
H(91)	0.0638	0.2656	0.5877	0.050
H(92)	-0.0311	0.2745	0.5239	0.050
H(10)	0.1904	0.5615	0.5844	0.050
H(121)	0.4256	0.5786	0.4838	0.050
H(122)	0.3637	0.4748	0.4423	0.050

H(123)	0.2671	0.5740	0.4702	0.050
H(161)	0.4218	0.2750	0.6669	0.050
H(162)	0.4743	0.2158	0.7337	0.050
H(163)	0.3776	0.1414	0.6842	0.050
H(18)	0.1309	0.5885	0.7655	0.050
H(19)	-0.0838	0.6239	0.8147	0.050
H(20)	-0.2099	0.4652	0.8596	0.050
H(21)	-0.1195	0.2741	0.8576	0.050
H(22)	0.0968	0.2367	0.8104	0.050

Atomic Anisotropic Displacement Parameters

	U11	U22	U33	U12	U13	U23
O(1)	.036(2)	.071(2)	.046(2)	.012(2)	.005(1)	-.008(2)
O(2)	.030(1)	.038(1)	.028(1)	-.003(1)	-.001(1)	-.001(1)
O(3)	.044(2)	.045(2)	.040(1)	-.014(1)	-.001(1)	-.000(1)
O(4)	.036(2)	.035(1)	.045(2)	.003(1)	.002(1)	-.002(1)
O(5)	.070(2)	.063(2)	.061(2)	-.001(2)	.022(2)	-.016(2)
O(6)	.073(3)	.057(2)	.113(3)	.029(2)	.013(2)	.001(2)
N(1)	.038(2)	.040(2)	.064(2)	.001(2)	.003(2)	-.012(2)
F(1)	.052(2)	.051(1)	.060(2)	-.017(1)	-.004(1)	.008(1)
F(2)	.050(2)	.051(1)	.037(1)	-.003(1)	-.006(1)	-.000(1)
F(3)	.069(2)	.055(2)	.077(2)	.018(2)	-.014(2)	.014(1)
F(4)	.049(2)	.056(1)	.044(1)	-.012(1)	-.003(1)	-.010(1)
F(5)	.059(2)	.068(2)	.044(1)	-.013(1)	-.018(1)	.014(1)
F(6)	.030(1)	.075(2)	.057(2)	-.005(1)	-.003(1)	-.003(1)
C(1)	.026(2)	.039(2)	.032(2)	-.000(2)	-.000(2)	-.008(2)
C(2)	.030(2)	.036(2)	.043(2)	.000(2)	-.004(2)	-.010(2)
C(3)	.032(2)	.047(3)	.062(3)	.007(2)	-.007(2)	-.013(2)
C(4)	.033(2)	.063(3)	.058(3)	.002(2)	.008(2)	-.020(2)
C(5)	.038(3)	.072(3)	.041(2)	-.007(3)	.010(2)	-.010(2)
C(6)	.035(2)	.060(3)	.035(2)	.001(2)	.000(2)	.001(2)
C(7)	.040(3)	.038(2)	.052(3)	.001(2)	-.012(2)	.001(2)
C(8)	.027(2)	.038(2)	.028(2)	.002(2)	.002(2)	-.000(2)
C(9)	.029(2)	.040(2)	.043(2)	-.001(2)	-.000(2)	-.008(2)
C(10)	.033(2)	.035(2)	.030(2)	-.000(2)	.003(2)	.000(2)
C(11)	.034(2)	.040(2)	.035(2)	-.004(2)	.001(2)	-.010(2)
C(12)	.052(3)	.052(3)	.051(3)	-.006(2)	.018(2)	-.001(2)
C(13)	.025(2)	.041(2)	.030(2)	.001(2)	.004(2)	-.005(2)
C(14)	.030(2)	.035(2)	.034(2)	-.002(2)	-.002(2)	.001(2)
C(15)	.036(2)	.048(2)	.034(2)	-.008(2)	-.001(2)	.003(2)
C(16)	.044(3)	.048(2)	.054(3)	.012(2)	.004(2)	-.004(2)
C(17)	.031(2)	.042(2)	.027(2)	-.002(2)	.001(2)	-.002(2)
C(18)	.041(3)	.045(2)	.036(2)	.001(2)	.005(2)	.001(2)
C(19)	.049(3)	.056(3)	.044(2)	.017(2)	.007(2)	-.003(2)
C(20)	.036(3)	.085(4)	.046(2)	.007(3)	.013(2)	.002(3)
C(21)	.044(3)	.071(3)	.059(3)	-.010(3)	.016(2)	.016(3)
C(22)	.041(3)	.050(3)	.045(2)	-.004(2)	.005(2)	.007(2)

Table S3. Bond lengths (Å), bond angles and torsional angles (°) for **A8**

Bond Distances (Angstroms)			
O1-C11	1.210(5)	O2-C10	1.437(4)
O2-C13	1.343(4)	O3-C13	1.201(5)
O4-C14	1.399(4)	O4-C16	1.446(5)
O5-N1	1.216(6)	O6-N1	1.226(6)
N1-C9	1.492(6)	F1-C7	1.347(5)
F2-C7	1.357(5)	F3-C7	1.345(5)
F4-C15	1.335(5)	F5-C15	1.338(5)
F6-C15	1.335(5)	C1-C2	1.409(6)
C1-C6	1.397(6)	C1-C8	1.531(5)
C2-C3	1.386(6)	C2-C7	1.491(6)
C3-C4	1.383(7)	C4-C5	1.359(7)
C5-C6	1.395(6)	C8-C9	1.528(5)
C8-C10	1.545(5)	C10-C11	1.531(6)
C11-C12	1.503(6)	C13-C14	1.547(5)
C14-C15	1.548(6)	C14-C17	1.534(6)
C17-C18	1.391(6)	C17-C22	1.395(6)
C18-C19	1.386(7)	C19-C20	1.380(7)
C20-C21	1.378(8)	C21-C22	1.385(7)
Bond Angles (degrees)			
C10-O2-C13	117.2(3)	C14-O4-C16	118.1(3)
O5-N1-O6	123.9(4)	O5-N1-C9	119.2(4)
O6-N1-C9	116.9(4)	C2-C1-C6	117.2(4)
C2-C1-C8	123.0(3)	C6-C1-C8	119.7(3)
C1-C2-C3	120.7(4)	C1-C2-C7	120.3(4)
C3-C2-C7	119.0(4)	C2-C3-C4	120.6(4)
C3-C4-C5	119.8(4)	C4-C5-C6	120.6(4)
C1-C6-C5	121.1(4)	F1-C7-F2	105.7(3)
F1-C7-F3	106.3(3)	F1-C7-C2	112.6(3)
F2-C7-F3	105.0(3)	F2-C7-C2	113.1(3)
F3-C7-C2	113.5(4)	C1-C8-C9	108.0(3)
C1-C8-C10	112.0(3)	C9-C8-C10	113.5(3)
N1-C9-C8	112.4(3)	O2-C10-C8	106.4(3)
O2-C10-C11	110.0(3)	C8-C10-C11	114.2(3)
O1-C11-C10	120.6(4)	O1-C11-C12	121.8(4)
C10-C11-C12	117.5(4)	O2-C13-O3	125.0(3)
O2-C13-C14	108.6(3)	O3-C13-C14	126.3(3)
O4-C14-C13	112.0(3)	O4-C14-C15	110.3(3)
O4-C14-C17	107.5(3)	C13-C14-C15	110.0(3)
C13-C14-C17	108.0(3)	C15-C14-C17	109.1(3)
F4-C15-F5	107.3(3)	F4-C15-F6	106.9(3)
F4-C15-C14	112.7(3)	F5-C15-F6	106.9(3)
F5-C15-C14	109.2(3)	F6-C15-C14	113.6(3)
C14-C17-C18	120.8(4)	C14-C17-C22	119.7(4)
C18-C17-C22	119.4(4)	C17-C18-C19	120.3(4)
C18-C19-C20	120.1(4)	C19-C20-C21	119.7(5)
C20-C21-C22	121.1(5)	C17-C22-C21	119.4(4)

Dihedral Angles (degrees)

C13-O2-C10-C8	-160.3(3)	C13-O2-C10-C11	75.6(4)
C10-O2-C13-O3	2.0(5)	C10-O2-C13-C14	177.8(3)
C16-O4-C14-C13	58.1(4)	C16-O4-C14-C15	-64.7(4)
C16-O4-C14-C17	176.5(3)	O5-N1-C9-C8	-43.0(5)
O6-N1-C9-C8	136.9(4)	C6-C1-C2-C3	-.9(6)
C6-C1-C2-C7	178.7(4)	C8-C1-C2-C3	176.0(4)
C8-C1-C2-C7	-4.3(6)	C2-C1-C6-C5	1.1(6)
C8-C1-C6-C5	-175.9(4)	C2-C1-C8-C9	-127.2(4)
C2-C1-C8-C10	107.1(4)	C6-C1-C8-C9	49.7(5)
C6-C1-C8-C10	-76.0(5)	C1-C2-C3-C4	-.2(6)
C7-C2-C3-C4	-179.9(4)	C1-C2-C7-F1	-59.0(5)
C1-C2-C7-F2	60.6(5)	C1-C2-C7-F3	-179.9(4)
C3-C2-C7-F1	120.6(4)	C3-C2-C7-F2	-119.7(4)
C3-C2-C7-F3	-.2(5)	C2-C3-C4-C5	1.3(7)
C3-C4-C5-C6	-1.1(7)	C4-C5-C6-C1	-.2(7)
C1-C8-C9-N1	170.2(3)	C10-C8-C9-N1	-65.0(4)
C1-C8-C10-O2	72.9(4)	C1-C8-C10-C11	-165.7(3)
C9-C8-C10-O2	-49.7(4)	C9-C8-C10-C11	71.7(4)
O2-C10-C11-O1	7.5(5)	O2-C10-C11-C12	-171.7(3)
C8-C10-C11-O1	-111.9(4)	C8-C10-C11-C12	68.8(5)
O2-C13-C14-O4	43.2(4)	O2-C13-C14-C15	166.1(3)
O2-C13-C14-C17	-75.0(4)	O3-C13-C14-O4	-141.1(4)
O3-C13-C14-C15	-18.2(5)	O3-C13-C14-C17	100.7(4)
O4-C14-C15-F4	-167.3(3)	O4-C14-C15-F5	-48.3(4)
O4-C14-C15-F6	70.9(4)	C13-C14-C15-F4	68.7(4)
C13-C14-C15-F5	-172.2(3)	C13-C14-C15-F6	-53.0(4)
C17-C14-C15-F4	-49.5(4)	C17-C14-C15-F5	69.6(4)
C17-C14-C15-F6	-171.2(3)	O4-C14-C17-C18	-160.4(3)
O4-C14-C17-C22	20.1(5)	C13-C14-C17-C18	-39.5(5)
C13-C14-C17-C22	141.0(4)	C15-C14-C17-C18	80.0(4)
C15-C14-C17-C22	-99.5(4)	C14-C17-C18-C19	179.9(4)
C22-C17-C18-C19	-.6(6)	C14-C17-C22-C21	-179.4(4)
C18-C17-C22-C21	1.0(6)	C17-C18-C19-C20	-.4(7)
C18-C19-C20-C21	.9(7)	C19-C20-C21-C22	-.4(7)
C20-C21-C22-C17	-.6(7)		