Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Acylative kinetic resolution of racemic methyl-substituted cyclic alkylamines with 2,5-dioxopyrrolidin-1-yl (*R*)-2-phenoxypropanoate

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Experimental

General: ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 500 spectrometer (500 and 126 MHz, respectively) with TMS as internal standard. The ^{13}C chemical shifts were referenced to the [D_6]DMSO or $CDCl_3$ solvent signals (δ_C 39.5 or 77.0 ppm, respectively). The signals in the ^{1}H and ^{13}C NMR spectra were assigned based on 2D ^{1}H-^{13}C HSQC and HMBC experiments. Melting points were obtained with an SMP3 apparatus (Barloworld Scientific, UK). Optical rotations were measured with a Perkin–Elmer M341 polarimeter. Elemental analysis was performed by using a Perkin–Elmer 2400 II analyser. Analytical TLC was performed with Sorbfil plates (Imid, Russia). Flash column chromatography was performed on silica gel (230–400 mesh, Alfa Aesar, UK). The high-resolution mass spectra of compounds **1e**, (*R,R*)-**3e,f** and (*S*)-**4b,d-f** were obtained with a Bruker maXis Impact HD mass spectrometer (ESI). GC analysis of amide **3a** was performed by using a Shimadzu GC-2010 instrument with a ZB-5 capillary column (30 m × 0.25 mm × 0.25 μm): $t_{(R^*,R^*)\text{-}\mathbf{3a}}$ = 23.00 min, $t_{(R^*,S^*)\text{-}\mathbf{3a}}$ = 23.16 min. Determination of diastereoisomeric composition of amide **3a** was carried out with a Knauer Smartline-1100 instrument using a Chiralpak AS-H column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 40:1 as an eluent. HPLC analysis of compounds **3b,c,e** and **4a-f** was carried out with a Knauer Smartline-1100 instrument using Chiralcel OD-H (**3b-e**, **4e,f**) or *S,S*-Whelk O1 (**4a-d**) columns (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH as an eluent. HPLC analysis of compounds **3d** and **3f** was carried out with an Agilent 1100 instrument using Kromasil 100-5 C18 and Phenomenex Luna C18(2) columns (250 × 4.6 mm), respectively; detection at 220 nm, 1 mL/min flow rate, MeCN/H_2O as an eluent. Racemic acyl chloride **1a** has been described earlier.[S1] Racemic hexahydro-2-methyl-1*H*-azepine (**2d**)[S2] and 1-methyl-1,2,3,4-tetrahydroisoquinoline (**2f**)[S3] were obtained according to described procedures. Other reagents are commercially available. The solvents were purified according to traditional methods and used freshly distilled.

Synthetic procedures and compound characterization

General procedure for the synthesis of active esters 1b-e: EDCI hydrochloride (1.21 g, 6.31 mmol) was added portion-wise to a solution of 2-phenoxypropanoic acid (1.02 g, 6.14 mmol), appropriate phenol or N-hydroxyimide (6.45 mmol), and DMAP (0.02 g, 0.16 mmol) in CH_2Cl_2 (20 mL) under stirring at 0 °C. The reaction mixture was stirred for 24 h at room temperature, then successively washed with 1 M HCl (3 × 10 mL), saturated aqueous NaCl solution (3 × 20 mL), 10% aqueous Na_2CO_3 (3 × 10 mL), and water (3 × 20 mL). Organic layer was separated, dried with Na_2SO_4 and evaporated to dryness under reduced pressure. Esters (*RS*)-**1b** and (*RS*)-**1c** were purified by flash column chromatography on silica gel (*n*-hexane/EtOAc, from 95:5 to 9:1). Compound (*RS*)-**1d** was used without purification (NMR purity >96%). Analytical samples of esters **1b-e** were obtained after recrystallization from *n*-hexane/$CHCl_3$, 5:1.

4-Nitrophenyl (*RS*)-2-phenoxypropanoate [(*RS*)-1b]. Yield 1.23 g (70%). Colourless viscous oil. ^{1}H NMR ($CDCl_3$): δ = 8.25 (d, *J* = 9.2 Hz, 2H, H-3'), 7.33 (dd, *J* = 8.7, 7.4 Hz, 2H, H*m*), 7.21 (d, *J* = 9.2 Hz, 2H, H-2'), 7.04 (tt, *J* = 7.4, 0.9 Hz, 1H, H*p*), 6.97 (dd, *J* = 8.7, 0.9 Hz, 2H, H*o*), 5.03 (q, *J* = 6.8 Hz, 1H, H-2), 1.81 (d, *J* = 6.8 Hz, 3H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 169.98 (C=O), 157.26 (C*i*), 154.86 (C-O), 145.56 (C-4'), 129.75 (2C*m*), 125.23 (2C-3'), 122.18 (2C-2'), 122.16 (C*p*), 115.14 (2C*o*), 72.51 (C-2), 18.45 (Me) ppm. $C_{15}H_{13}NO_5$ (287.27): calcd. C 62.72, H 4.56, N 4.88; found C 62.73, H 4.53, N 4.69.

2,3,4,5,6-Pentachlorophenyl (*RS*)-2-phenoxypropanoate [(*RS*)-1c]. Yield 1.63 g (64%). Colourless solid, m.p. 129–130 °C (*n*-hexane/$CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.31 (t, *J* = 8.0 Hz, 2H, H*m*), 7.03-7.00 (m, 3H, Ar), 5.14 (q, *J* = 6.8 Hz, 1H, H-2), 1.89 (d, *J* = 6.8 Hz, 3H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 168.15 (C=O), 157.15 (C*i*), 143.39 (C-O), 132.13 (C-4'), 131.91 (2C-3'), 129.61 (2C*m*), 127.51 (2C-2'), 122.19 (C*p*), 115.30 (2C*o*), 72.14 (C-2), 18.77 (Me) ppm. $C_{15}H_9Cl_5O_3$ (414.48): calcd. C 43.47, H 2.19, Cl 42.76; found C 43.72, H 2.33, Cl 42.54.

2,5-Dioxopyrrolidin-1-yl (*RS*)-2-phenoxypropanoate [(*RS*)-1d]. Yield 1.60 g (99%). Colourless solid, m.p. 79–81 °C (*n*-hexane/$CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.31 (t, *J* = 8.0 Hz, 2H, H*m*), 7.01 (t, *J* = 7.3 Hz, 1H, H*p*), 6.96 (d, *J* = 8.4 Hz, 2H, H*o*), 5.05 (q, *J* = 6.8 Hz, 1H, 2-H), 2.81 (s, 4H, CH_2CH_2), 1.81 (d, *J* = 6.8 Hz, 3H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 168.58 (C=O), 167.71 (C-2' and C-5'), 156.88 (C*i*), 129.68 (2C*m*), 122.28 (C*p*), 115.26 (2C*o*), 70.77 (C-2), 25.53 (C-3' and C-4'), 18.83 (Me) ppm. $C_{13}H_{13}NO_5$ (263.25): calcd. C 59.31, H 4.98, N 5.32; found C 59.14, H 4.81, N 5.36.

2,5-Dioxopyrrolidin-1-yl (*R*)-2-phenoxypropanoate [(*R*)-1d]. Yield 1.23 g (76%). Colourless viscous oil. $[\alpha]_D^{20}$ = +117 (*c* = 1.0, $CHCl_3$). NMR spectra are identical to those of compound (*RS*)-**1d**. $C_{13}H_{13}NO_5$ (263.25): calcd. C 59.31, H 4.98, N 5.32; found C 59.04, H 5.00, N 5.54.

2,7-Dioxoisoindol-1-yl (*RS*)-2-phenoxypropanoate [(*RS*)-1e]. Yield 1.24 g (65%). Colourless solid, m.p. 136–137 °C (*n*-hexane/$CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.90-7.86 (m, 2H, H-4', H-7'), 7.80-7.76 (m, 2H, H-5', H-6'), 7.34 (dd, *J* = 8.5, 7.5 Hz, 2H, H*m*), 7.04 (t, *J* = 7.5 Hz, 1H, H*p*), 7.01 (d, *J* = 8.0 Hz, 2H, H*o*), 5.12 (q, *J* = 6.9 Hz, 1H, H-2), 1.87 (d, *J* = 6.9 Hz, 3H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 168.67 (C=O), 161.54 (C-1', C-3'), 156.94 (C*i*), 134.84 (C-5', C-6'), 129.70 (2C*m*), 128.81 (C-3'a, C-7'a), 124.03 (C-4', C-7'), 122.31 (C*p*), 115.30 (2C*o*), 70.88 (C-2), 18.89 (Me) ppm. $C_{17}H_{13}NO_5$ (311.29): calcd. C 65.59, H 4.21, N 4.50; found C 65.32, H 3.99, N 4.58.

General procedure for the acylation of racemic amine 2a with racemic esters 1a-e: A solution of an appropriate acylating agent (0.5 mmol) in toluene (2.5 mL) was added to a solution of amine **2a** (49.6 mg, 0.5 mmol) in toluene (2.5 mL) at +20 °C. The reaction mixture was kept in a thermostat at +20 °C for 24 h, then successively washed with 6 M HCl (2 × 3 mL), saturated aqueous NaCl solution (4 × 3 mL), 5% aqueous $NaHCO_3$ solution (2 × 3 mL), and water (2 × 3 mL), dried with Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was analysed by GC.

(*R*,R)-2-Methyl-1-(2-phenoxypropanoyl)piperidine [(*R*,R**)-3a].** Yield 98 mg (79%), from ester (*RS*)-**1d**. Colourless oil. GC: $t_{(R,R)\text{-}\mathbf{3a}}$ = 23.00 min, $t_{(R,S)\text{-}\mathbf{3a}}$ = 23.16 min, (*R*,R**)/(*R*,S**) 93:7. ^{1}H NMR ([D$_6$]DMSO, 100 °C) (predominant diastereomer): δ = 7.24 (dd, *J* = 8.6, 7.4 Hz, 2H, H*m*), 6.91 (t, *J* = 7.4 Hz, 1H, H*p*), 6.85 (dd, *J* = 8.6, 0.9 Hz, 2H, H*o*), 5.07 (q, *J* = 6.6 Hz, 1H, H-2 propanoate), 4.54 (br. s, 1H, H-2'), 4.03 (br. d, *J* = 11.4 Hz, 1H, H_A-6'), 2.92 (m, 1H, H_B-6', overlapped with H_2O signal), 1.65-1.58 (m, 2H, H_A-4' and H_A-5'), 1.53-1.46 (m, 3H, H_A-3', H_B-3' and H_B-4'), 1.44 (d, *J* = 6.6 Hz, 3H, Me propanoate), 1.25 (tt, *J* = 13.1, 4.5 Hz, 1H, H_B-5'), 1.11 (d, *J* = 6.9 Hz, 3H, Me) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 °C): δ = 167.98 (C=O), 156.96 (C*i*), 128.77 (2C*m*), 120.41 (C*p*), 114.69 (2C*o*), 71.67 (C-2), 44.85 (br. s, C-2'), 37.60 (br. s, C-6'), 29.35 (C-3'), 24.93 (C-5'), 17.74 (C-4'), 17.09 (Me propanoate), 15.24 (br. s, Me) ppm. $C_{15}H_{21}NO_2$ (247.34): calcd. C 72.84, H 8.56, N 5.66; found C 72.68, H 8.81, N 5.65.

General procedure for the kinetic resolution of racemic amines 2a-f with ester (*R*)-1d: A solution of ester (*R*)-**1d** (131.6 mg, 0.5 mmol) in toluene (5 mL) was added to a solution of an appropriate amine **2a-f** (1.0 mmol) in toluene (5 mL) at –20 °C. The reaction mixture was kept in a thermostat at –20 °C for 24 h, then successively washed with 6 M HCl (2 × 4 mL), saturated aqueous NaCl solution (4 × 5 mL), 5% aqueous $NaHCO_3$ solution (2 × 5 mL), and water (2 × 5 mL), dried with Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was analysed by GC or HPLC, then purified by recrystallisation or flash column chromatography on silica gel to afford amides (*R*,*R*)-**3a-f**. Acidic aqueous solutions were separated and alkalised with NaOH to pH 11-12, then extracted with CH_2Cl_2 (2 × 4 mL).

Combined organic layers were separated, dried with Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was re-dissolved in CH_2Cl_2 (5 mL); NEt_3 (73 µL, 0.53 mmol) and benzoyl chloride (0.53 mmol) (for amines **2a,b**) or carbobenzoxy chloride (0.53 mmol) (for amines **2c-f**) were added at to the resulting solution room temperature. The reaction mixture was stirred at room temperature for 24 h, then successively washed with 1 M HCl (4 mL), saturated aqueous NaCl solution (3 × 5 mL), 5% aqueous Na_2CO_3 solution (2 × 5 mL), and water (2 × 5 mL), dried with Na_2SO_4 and evaporated to dryness under reduced pressure to afford crude compounds (*S*)-**4a-f**. The residue was purified by flash column chromatography and analysed by chiral HPLC.

(*R,R*)-2-Methyl-1-(2-phenoxypropanoyl)piperidine [(*R,R*)-3a]. Yield 82 mg (66%) after flash column chromatography (benzene/EtOAc, 95:5)). Colourless oil. GC: $t_{(R,R)\text{-}\mathbf{3a}}$ = 23.00 min, $t_{(R,S)\text{-}\mathbf{3a}}$ = 23.16 min; 94.8% *de*. NMR spectra are identical to those of compound (*R*,R**)-**3a**. $C_{15}H_{21}NO_2$ (247.34): calcd. C 72.84, H 8.56, N 5.66; found C 72.64, H 8.76, N 5.95.

(*S*)-1-Benzoyl-2-methylpiperidine [(*S*)-4a]. Yield 83 mg (41% relative to (*RS*)-**2a**, after flash column chromatography (benzene/EtOAc, 9:1). Colourless oil. $[\alpha]_D^{20}$ = +21 (*c* = 1.4, $CHCl_3$) [ref.[S4]: $[\alpha]_D^{20}$ = +32.9 (*c* = 0.8, $CHCl_3$)]. HPLC (*S,S*-Whelk O1, *n*-hexane/*i*PrOH, 5:1): $t_{(R)\text{-}\mathbf{4a}}$ = 31.6 min, $t_{(S)\text{-}\mathbf{4a}}$ = 33.2 min; 76.2% *ee*. ^{1}H NMR ($CDCl_3$) (conformers *A* and *B*, 1:1): δ = 7.40-7.35 (m, 5H, Ph), 5.33-3.35 (m, 2H, NCH_2), 2.99 (br. s, 1H, H-2), 1.91-1.37 (m, 6H, 3 × CH_2), 1.24 (br. d, *J* = 6.2 Hz, 3H, Me) ppm. ^{13}C NMR ($CDCl_3$) (conformers *A* and *B*): δ = 170.40 (C=O), 137.02 (C*i*), 129.07 (C*p*), 128.38 (2C*m*), 126.30 (br. s, 2C*o*), 49.98 and 44.38 (both br. s, C-2), 42.57 and 36.78 (both br. s, C-6), 30.36 (C-3), 25.99 (C-5), 18.83 (C-4), 16.08 (br. s, Me) ppm. $C_{13}H_{17}NO$

(203.29): calcd. C 76.81, H 8.43, N 6.89; found C 76.54, H 8.72, N 6.65.

(*R,R*)-3-Methyl-1-(2-phenoxypropanoyl)piperidine [(*R,R*)-3b]. Yield 92 mg (74%) after flash column chromatography (benzene/EtOAc, 95:5). Colourless oil. HPLC (Chiralcel OD-H, *n*-hexane/*i*PrOH, 40:1): $t_{(R,R)\text{-}\mathbf{3b}}$ = 12.5 min, $t_{(R,S)\text{-}\mathbf{3b}}$ = 14.4 min; 13.8% *de*. Diastereomerically pure amide (*R,R*)-**3b** (33 mg, 72% yield) was isolated from 80 mg of (*R,R*)/(*R,S*) mixture, 56.9:43.1, as a fast-eluting diastereomer using preparative HPLC (Shimadzu LC-20 Prominence instrument, Chiralcel OD-H column (250 × 20 mm, 5 µm), detection at 220 nm, 10 mL/min flow rate, *n*-hexane/*i*PrOH, 40:1). $[\alpha]_D^{20}$ = –56.0 (*c* = 0.5, $CHCl_3$). Analytical HPLC (Chiralcel OD-H, *n*-hexane/*i*PrOH, 40:1): $t_{(R,R)\text{-}\mathbf{3b}}$ = 13.1 min; >99% *de*. ^{1}H NMR ([D$_6$]DMSO, 100 °C): δ = 7.25 (dd, *J* = 8.7, 7.3 Hz, 2H, H*m*), 6.92 (tt, *J* = 7.3, 1.0 Hz, 1H, H*p*), 6.87 (dd, *J* = 8.7, 1.0 Hz, 2H, H*o*), 5.12 (q, *J* = 6.5 Hz, 1H, H-2 propanoate), 4.09-3.90 (m, 2H, H_2-6), 2.96-2.70 (br. m, 1H, H_A-2, partially overlapped with H_2O signal), 2.55 (br. s, 1H, H_B-2), 1.73 (dq, *J* = 13.0, 4.1 Hz, 1H, H_A-4), 1.62 (dqw, *J* = 13.4, 3.8 Hz, 1H, H_A-5), 1.48 (br. s, 1H, H-3), 1.43 (d, *J* = 6.5 Hz, 3H, Me propanoate), 1.30 (dtt, *J* = 13.4, 11.4, 4,1 Hz, 1H, H_B-5), 1.13 (dddd, *J* = 13.0, 11.4, 10.5, 3,8 Hz, 1H, 1H, 4-H_B), 0.81 (d, *J* = 6.6 Hz, 3H, Me) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 °C): δ = 167.85 (C=O), 156.86 (C*i*), 128.79 (2C*m*), 120.44 (C*p*), 114.73 (2C*o*), 71.33 (C-2), 49.9 (br. s, C-2'), 43.2 (br. s, C-6'), 31.83 (C-4'), 30.30 (br. s, C-3'), 24.18 (C-5'), 17.82 (Me), 16.91 (Me) ppm. $C_{15}H_{21}NO_2$ (247.34): calcd. C 72.84, H 8.56, N 5.66; found C 72.59, H 8.69, N 5.68.

(*S*)-1-Benzoyl-3-methylpiperidine [(*S*)-4b]. Yield 83 mg (41% relative to (*RS*)-**2b**, after flash column chromatography (benzene/EtOAc, 9:1)). Colourless oil. $[\alpha]_D^{20}$ = +6.8 (*c* = 1.1, MeOH) [ref.[S5]: $[\alpha]_D^{20}$ = +49.5 (*c* = 1.0, MeOH)]. HPLC (*S,S*-Whelk O1, *n*-hexane/*i*PrOH, 5:1): $t_{(R)\text{-}\mathbf{4b}}$ = 24.6 min, $t_{(S)\text{-}\mathbf{4b}}$ = 27.8 min; 13.6% *ee*. ^{1}H NMR ($CDCl_3$) (conformers *A* and *B*, 55:45): δ = 7.41-7.36 (m, 5H, Ph), 4.54 (m, 1H, H_A-6), 3.66 (d, *J* = 10.7 Hz, 0.55H, H_A-2 (*A*)), 3.59 (d, *J* = 11.2 Hz, 0.45H, H_A-2 (*B*)), 2.93 (br. t, *J* = 10.7 Hz, 0.55H, H_B-2 (*A*)), 2.81 (br. t, *J* = 11.5 Hz, 0.45H, H_B-6 (*B*)), 2.64 (br. t, *J* = 10.9 Hz, 0.45H, H_B-2 (*B*)), 2.44 (br. t, *J* = 11.1 Hz, 0.55H, H_B-6 (*A*)), 1.89-1.84 (m, 1H, H_A-4), 1.79-1.41 (m, 3H, H-3, H_2-5), 1.21-1.13 (m, 1H, H_B-4), 0.97 (br. d, *J* = 5.7 Hz, 1.65H, Me (*A*)), 0.79 (br. d, *J* = 5.5 Hz, 1.35H, Me (*B*)) ppm. ^{13}C NMR ($CDCl_3$) (conformers *A* and *B*, 55:45): δ = 170.25 (C=O), 136.54 (C*i*), 129.31 (C*p*), 128.37 (2C*m*), 126.78 (br. s, 2C*o*), 55.09 (br. s, C-2 (*B*)), 49.44 (br. s, C-6 (*A*)), 48.22 (br. s, C-2 (*A*)), 42.63 (br. s, C-6 (*B*)), 33.10 (C-4), 31.88 (br. s, C-3 (*B*)), 31.05 (br. s, C-3 (*A*)), 26.00 (br. s, C-5 (*A*)), 24.77 (br. s, C-5 (*B*)), 19.10 (br. s, Me (*A*)), 18.74 (br. s, Me (*B*)) ppm. HRMS (ESI): calcd. for $C_{13}H_{18}NO^+$ [M + H]$^+$ 204.1383; found 204.1385.

(*R,R*)-2-Methyl-1-(2-phenoxypropanoyl)pyrrolidine [(*R,R*)-3c]. Yield 51 mg (44%) after recrystallisation from *n*-hexane/EtOAc, 15:1. Colourless solid, m.p. 78–80 °C. HPLC (Chiralcel OD-H, *n*-hexane/*i*PrOH, 40:1): $t_{(R,R)\text{-}\mathbf{3c}}$ = 16.8 min, $t_{(R,S)\text{-}\mathbf{3c}}$ = 20.2 min; 29.2% *de*. ^{1}H NMR ([D$_6$]DMSO, 100 °C): δ = 7.25 (dd, *J* = 8.6, 7.4 Hz, 2H, H*m*), 6.92 (t, *J* = 7.4 Hz, 1H, H*p*), 6.87-6.85 (m, 2H, H*o*), 4.91 (br. q, *J* = 6.3 Hz, 1H, H-2 propanoate), 4.07 (br. s, 1H, H-2), 3.62-3.39 (m, 2H, H_2-5), 1.97-1.86 (m, 2H, H_2-4), 1.82-1.76 (m, 1H, H_A-3), 1.51 (m, 1H, H_B-3), 1.42 (d, *J* = 6.3 Hz, 1H, Me propanoate, *R,S*), 1.41 (d, *J* = 6.3 Hz, 2H, Me propanoate, *R,R*), 1.10 (d, *J* = 6.3 Hz, 2H, Me, *R,R*), 1.07 (br. m, 1H, Me, *R,S*) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 °C): δ = 167.79 (C=O, *R,S*), 167.70 (C=O, *R,R*), 156.94 (C*i*), 128.79 (2C*m*), 120.48 (C*p*, *R,R*), 120.43 (C*p*, *R,S*), 114.95 (C*o*, *R,R*), 114.81 (C*o*, *R,S*), 72.26 (C-2, *R,S*), 72.08 (C-2, *R,R*), 52.21 (C-2'), 44.96 (C-5'), 30.58 (br. s, CH_2), 23.33 (br. s, CH_2), 18.32 (br. s, Me), 16.36 (br. s, Me) ppm. $C_{14}H_{19}NO_2$ (233.31): calcd. C 72.07, H 8.21, N 6.00; found C 71.93, H 8.28, N 6.02.

Benzyl (*S*)-2-methylpyrrolidine-1-carboxylate [(*S*)-4c]. Yield 57 mg (26% relative to (*RS*)-**2c**, after flash column chromatography (*n*-hexane/EtOAc, 9:1)). Colourless oil. $[\alpha]_D^{20}$ = +5.3 (*c* = 1.04, $CHCl_3$) [ref.[S6]: $[\alpha]_D^{20}$ = −24.9 (*c* = 2.02, $CHCl_3$) for (*R*)-**4c**]. HPLC (*S,S*-Whelk O1, *n*-hexane/*i*PrOH, 10:1): $t_{(S)\text{-}\mathbf{4c}}$ = 19.5 min, $t_{(R)\text{-}\mathbf{4c}}$ = 22.8 min; 19.4% *ee*. ^{1}H NMR ($CDCl_3$) (conformers *A* and *B*, 1:1): δ = 7.44-7.28 (m, 5H, Ph), 5.18-5.09 (m, 2H, OCH_2), 3.97 (br. m, 1H, H-2), 3.45-3.36 (m, 2H, H_2-5), 2.04-1.53 (m, 4H, H_2-3 and H_2-4), 1.22 (br. d, *J* = 5.7 Hz, 1.5H, Me (*A*)), 1.16 (br. d, *J* = 5.7 Hz, 1.5H, Me (*B*)) ppm. ^{13}C NMR ($CDCl_3$) (conformers *A* and *B*): δ = 154.94 and 154.66 (C=O), 137.13 and 137.08 (C*i*), 128.37 (2C*m*), 127.74 (2C*o* and C*p*), 66.55 and 66.32 (OCH_2), 53.41 and 52.80 (C-2), 46.60 and 46.21 (C-5), 33.22 and 32.50 (C-3), 23.60 and 22.86 (C-4), 20.81 and 19.95 (Me) ppm. HRMS (ESI): calcd. for $C_{13}H_{18}NO_2^+$ [M + H]$^+$ 220.1332; found 220.1333.

(*R,R*)-2-Methyl-1-(2-phenoxypropanoyl)azepane [(*R,R*)-3d]. Yield 60 mg (46%) after flash column chromatography (benzene/EtOAc, 95:5). Colourless oil. HPLC (Kromasil 100-5 C18, MeCN/H_2O, 55:45): $t_{(R,S)\text{-}\mathbf{3d}}$ = 12.6 min, $t_{(R,R)\text{-}\mathbf{3d}}$ = 14.1 min; 82.9% *de*. ^{1}H NMR ([D$_6$]DMSO, 100 °C) (predominant diastereomer, conformers *A* and *B*, 55:45): δ = 7.25 (dd, *J* = 8.6, 7.4 Hz, 2H, H*m*), 6.93 (t, *J* = 7.4 Hz, 1H, H*p*), 6.91-6.87 (br. m, 2H, H*o*), 5.10 (br. m, 1H, H-2 propanoate), 4.29 (br. s, 0.45H, CH (*B*)), 4.11 (br. s, 0.55H, CH (*A*)), 3.84 (br. s, 0.55H, CH

(*A*)), 3.76 (br. s, 0.45H, CH (*B*)), 3.09 (br. s, 0.45H, CH (*B*)), 2.71 (br. s, 0.55H, CH (*A*)), 1.96 (br. s, 1H, CH), 1.75-1.56 (m, 3H, 3 CH), 1.44 (d, *J* = 6.4 Hz, 3H, Me propanoate), 1.42-1.12 (m, 4H, 4 CH), 1.04 (br. s, 3H, Me) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 °C) (predominant diastereomer, conformers *A* and *B*): δ = 169.03 (C=O (*A*)), 168.63 (C=O (*B*)), 156.94 (C*i*), 128.81 (2C*m*), 120.63 (C*p*), 115.19 (br. s, 2C*o*), 71.29 (C-2), 50.06 (br. s, C-2' (*A*)), 49.93 (C-2' (*B*)), 40.4 (br. s, C-7', overlapped with DMSO signal), 35.48 (*A*), 33.77 (*B*), 29.60 (*A*), 28.43 (*B*), 27.57 (*A*), 26.65 (*B*), 24.24 (*A*), 23.69 (*B*), 20.03 (*A*), 18.10 (*B*), 17.17 (Me) ppm. $C_{16}H_{23}NO_2$ (261.37): calcd. C 73.53, H 8.87, N 5.36; found C 73.23, H 8.89, N 5.41.

Benzyl (*S*)-2-methylazepane-1-carboxylate [(*S*)-4d]. Yield 82 mg (33% relative to (*RS*)-**2d**, after flash column chromatography (*n*-hexane/EtOAc, 9:1)). Yellowish oil. $[\alpha]_D^{20}$ = +33.5 (*c* = 1.05, $CHCl_3$) [ref.[S7]: $[\alpha]_D^{20}$ = –44.9 (*c* = 1.0, $CHCl_3$) for (*R*)-**4d**]. HPLC (*S,S*-Whelk O1, *n*-hexane/*i*PrOH, 10:1): $t_{(S)\text{-}\mathbf{4d}}$ = 13.5 min, $t_{(R)\text{-}\mathbf{4d}}$ = 17.3 min; 46.6% *ee*. ^{1}H NMR ($CDCl_3$) (conformers *A* and *B*, 55:45): δ = 7.36-7.28 (m, 5H, Ph), 5.18-5.12 (m, 2H, CH_2O), 4.18 (ddq, *J* = 9.3, 9.0, 6.5 Hz, 0.55H, H-2 (*A*)), 4.08 (ddq, *J* = 12.2, 6.5, 6.0 Hz, 0.45H, 2-H (*B*)), 3.83 (dm, *J* = 14.3, 0.45H, H$_A$-7 (*B*)), 3.3 (dm, *J* = 14.6, 0.55H, H$_A$-7 (*A*)), 2.78 (ddd, *J* = 14.6, 4.5, 1.5 Hz, 0.55H, H$_B$-7 (*A*)), 2.75 (ddd, *J* = 14.3, 4.6, 1.3 Hz, 0.45H, H$_B$-7 (*B*)), 2.04-1.92 (m, 1H, CH), 1.83-1.67 (m, 3H, 3 CH), 1.57-1.43 (m, 1H, CH), 1.31-1.17 (m, 3H, 3 CH), 1.08 (d, *J* = 6.5 Hz, 1.65H, Me (*A*)), 1.07 (d, *J* = 6.5 Hz, 1.35H, Me (*B*)) ppm. ^{13}C NMR ($CDCl_3$) (conformers *A* and *B*): δ = 156.11 (C=O (*A*)), 156.08 (C=O (*B*)), 137.28 (C*i*), 128.39 (2C*m*), 127.72 (C*p* (*A*)),127.70 (C*p* (*B*)), 127.58 (2C*o*), 66.69 (OCH_2 (*B*)), 66.63 (OCH_2 (*A*)), 51.72 (C-2 (*A*)), 51. 62 (C-2 (*B*)), 41.39 (C-7 (*B*)), 40.95 (C-7 (*A*)), 36.15 (C-3 (*B*)), 35.95 (C-3 (*A*)), 29.73 (C-6 (*B*)), 29.67 (C-6 (*A*)), 29.57 (C-5 (*A*)), 29.06 (C-5 (*B*)), 25.47 (C-4 (*B*)), 25.24 (C-4 (*A*)), 20.28 (Me (*B*)), 19.71 (Me (*A*)) ppm. HRMS (ESI): calcd. for $C_{15}H_{22}NO_2^+$ $[M + H]^+$ 248.1645; found 248.1643.

(*R,R*)-3-Methyl-4-(2-phenoxypropanoyl)morpholine [(*R,R*)-3e]. Yield 82 mg (66%) after flash column chromatography (benzene/EtOAc, 95:5). Colourless oil. HPLC (Chiralcel OD-H, *n*-hexane/*i*PrOH, 40:1): $t_{(R,R)\text{-}\mathbf{3e}}$ = 20.8 min, $t_{(R,S)\text{-}\mathbf{3e}}$ = 30.9 min; 79.2% *de*. ^{1}H NMR ([D$_6$]DMSO, 100 °C) (predominant diastereomer): δ = 7.26 (dd, *J* = 8.6, 7.4 Hz, 2H, H*m*), 6.93 (t, *J* = 7.4 Hz, 1H, H*p*), 6.87 (br. d, *J* = 8.6 Hz, 2H, H*o*), 5.09 (q, *J* = 6.5 Hz, 1H, H-2 propanoate), 4.29 (m, 1H, H-3), 3.88 (m, 1H, CH), 3.79-3.78 (m, 1H, CH), 3.58 (d, *J* = 11.5 Hz, 1H, H$_A$-2), 3.41 (dd, *J* = 11.5, 3.2 Hz, 1H, H$_B$-2), 3.28-3.22 (m, 2H, CH_2), 1.45 (d, *J* = 6.5 Hz, 3H, Me propanoate), 1.18 (d, *J* = 6.8 Hz, 3H, Me) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 °C): δ = 168.23 (C=O), 156.74 (C*i*), 128.85 (2C*m*), 120.61 (C*p*), 114.82 (2C*o*), 71.36 (C-2), 69.73 (C-2'), 65.76 (C-6'), 45.4 (br. s, C-3'), 38.3 (br. s, C-5'), 17.52 (Me propanoate), 16.95 (Me) ppm. HRMS (ESI): calcd. for $C_{14}H_{20}NO_3^+$ $[M + H]^+$ 250.1438; found 250.1436.

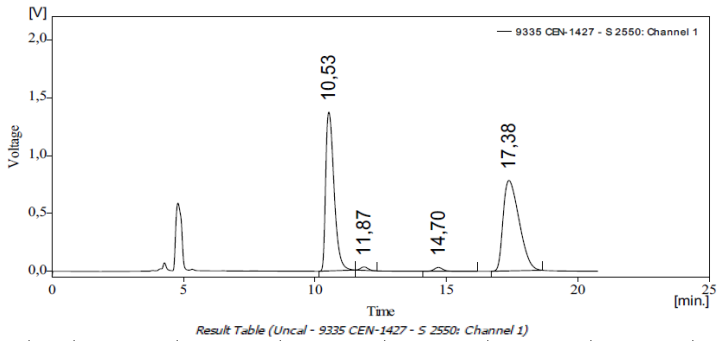
Benzyl (*S*)-3-methylmorpholine-4-carboxylate [(*S*)-4e]. Yield 59 mg (25% relative to (*RS*)-**2e**, after flash column chromatography (*n*-hexane/EtOAc, 9:1)). Yellowish oil. $[\alpha]_D^{20}$ = +37.6 (*c* = 1.05, $CHCl_3$) [ref.[S8]: $[\alpha]_D^{20}$ = –10.5 (*c* = 0.8, $CHCl_3$) for (*R*)-**4e** (52% *ee*)]. HPLC (Chiralcel OD-H, *n*-hexane/*i*PrOH/MeOH, 40:0.4:0.1): $t_{(R)\text{-}\mathbf{4e}}$ = 19.3 min, $t_{(S)\text{-}\mathbf{4e}}$ = 20.1 min; 53.2% *ee*. ^{1}H NMR ($CDCl_3$): δ = 7.38-7.30 (m, 5H, Ph), 5.16 (d, *J* = 12.4 Hz, 1H, OCH$_A$), 5.13 (d, *J* = 12.4 Hz, 1H, OCH$_B$), 4.14 (m, 1H, H-3), 3.85 (dd, *J* = 11.4, 3.5 Hz, 1H, H$_A$-2), 3.77 (dd, *J* = 13.2, 2.2 Hz, 1H, H$_A$-5), 3.65 (d, *J* = 11.6 Hz, 1H, H$_A$-6), 3.60 (dd, *J* = 11.4, 3.2 Hz, 1H, H$_B$-2), 3.44 (ddd, *J* = 12.4, 11.6, 3.1 Hz, 1H, H$_B$-6), 3.24 (ddd, *J* = 13.2, 12.4, 3.8 Hz, 1H, H$_B$-5), 1.28 (d, *J* = 6.9 Hz, 3H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 155.14 (C=O), 136.60 (C*i*), 128.48 (2C*m*), 128.02 (C*p*), 127.84 (2C*o*), 70.75 (C-2), 67.12 (OCH_2), 66.77 (C-6), 47.12 (C-3), 39.14 (C-5), 14.88 (Me) ppm. HRMS (ESI): calcd. for $C_{13}H_{18}NO_3^+$ $[M + H]^+$ 236.1281; found 236.1279.

(*R,R*)-1-Methyl-2-(2-phenoxypropanoyl)-1,2,3,4-tetrahydroisoquinoline [(*R,R*)-3f]. Yield 102 mg (69%) after flash column chromatography (benzene/EtOAc, 95:5). Colourless oil. HPLC (Phenomenex Luna C18(2), MeCN/H_2O, 48:52): $t_{(R,S)\text{-}\mathbf{3f}}$ = 28.2 min, $t_{(R,R)\text{-}\mathbf{3f}}$ = 29.9 min; 82.0% *de*. ^{1}H NMR ([D$_6$]DMSO, 100 °C) (predominant diastereomer): δ = 7.27-7.08 (m, 6H, Ar), 6.94-6.83 (m, 3H, Ar), 5.41 (q, *J* = 6.5 Hz, 1H, H-1'), 5.18 (q, *J* = 6.7 Hz, 1H, H-2 propanoate), 4.19 (br. s, 1H, H$_A$-3), 3.45 (br. s, H$_B$-3), 2.80-2.73 (m, 2H, H$_2$-4), 1.48 (d, *J* = 6.7 Hz, 3H, Me propanoate), 1.38 (br. d, *J* = 6.5 Hz, 3H, Me) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 °C) (predominant diastereomer): δ = 168.27 (C=O), 156.89 (C*i*), 137.63 (C-8'a), 132.87 (C-4'a), 128.83 (2C*m*), 127.97 (C-5'), 126.17 (C-7'), 125.72 (C-6'), 125.55 (C-8'), 120.58 (C*p*), 114.80 (2C*o*), 71.85 (C-2), 48.57 (br. s, C-1'), 47.89 (br. s, C-3'), 28.28 (br. s, C-4'), 21.05 (br. s, Me), 17.12 (Me propanoate) ppm. HRMS (ESI): calcd. for $C_{19}H_{22}NO_2^+$ $[M + H]^+$ 296.1645; found 296.1645.

Benzyl (*S*)-1-methyl-3,4-dihydroisoquinoline-2(1*H*)-carboxylate [(*S*)-4f]. Yield 107 mg (38% relative to (*RS*)-**2f**, after flash column chromatography (benzene/EtOAc, 95:5)). Colourless oil. $[\alpha]_D^{20}$ = +50.0 (*c* = 0.93, $CHCl_3$) [ref.[S8]: $[\alpha]_D^{20}$ = –40.6 (*c* = 1.9, $CHCl_3$) for (*R*)-**4f** (86% *ee*)]. HPLC (Chiralcel OD-H, *n*-hexane/*i*PrOH, 40:1): $t_{(S)\text{-}\mathbf{4f}}$ =

14.9 min, $t_{(R)\text{-}\mathbf{4f}}$ = 18.8 min; 55.0% *ee*. ^{1}H NMR ($CDCl_3$) (conformers *A* and *B*, 1:1): δ = 7.40-7.29 (m, 5H, Ar), 7.20-7.08 (m, 4H, Ar), 5.33-5.12 (m, 3H, H-1 and OCH_2), 4.26 (br. d, *J* = 11.6 Hz, 0.5H, H_A-3 (*A*)), 4.10 (br. d, *J* = 12.3 Hz, 0.5H, H_A-3 (*B*)), 3.38-3.32 (m, 0.5H, H_B-3 (*B*)), 3.28-3.22 (m, 0.5H, H_B-3 (*A*)), 2.99-2.87 (m, 1H, H_A-4), 2.77-2.72 (m, 1H, H_B-4), 1.48-1.45 (m, 3H, Me) ppm. ^{13}C NMR ($CDCl_3$) (conformers *A* and *B*): δ = 155.17 and 154.90 (C=O), 138.58 and 138.14 (C-8a), 136.85 (C*i*), 133.98 and 133.68 (C-4a), 128.95 and 128.69 (C-5), 128.48 (2C*m*), 127.95 (C*p*), 127.87 (br. s, 2C*o*), 126.91 and 126.78 (C-6), 126.38 (br. s, C-7), 126.27 and 126.20 (C-8), 67.13 and 66.99 (OCH_2), 50.54 and 50.47 (C-1), 37.95 and 37.45 (C-3), 28.97 and 28.80 (C-4), 22.39 and 21.92 (Me) ppm. HRMS (ESI): calcd. for $C_{18}H_{19}NNaO_2^+$ $[M + Na]^+$ 304.1308; found 304.1305.

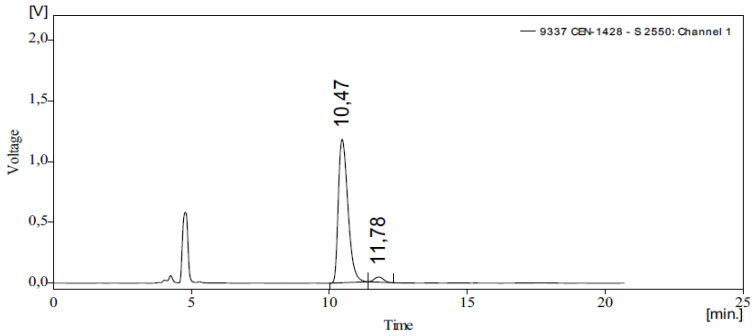
Determination of diastereoisomeric composition of amide 3a by chiral HPLC



Result Table (Uncal - 9335 CEN-1427 - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	10,533	30424,771	1372,029	47,0	61,9	0,37
2	11,867	586,362	29,474	0,9	1,3	0,33
3	14,700	763,227	32,912	1,2	1,5	0,37
4	17,383	32979,201	781,700	50,9	35,3	0,70
	Total	64753,560	2216,115	100,0	100,0	

HPLC of a diastereoisomeric mixture **3a** (Knauer Smartline-1100, Chiralpak AS-H column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 40:1):
$t_{(R,R)\text{-}\mathbf{3a}}$ = 10.5 min, $t_{(R,S)\text{-}\mathbf{3a}}$ = 11.9 min, $t_{(S,R)\text{-}\mathbf{3a}}$ = 14.7 min, $t_{(S,S)\text{-}\mathbf{3a}}$ = 17.4 min



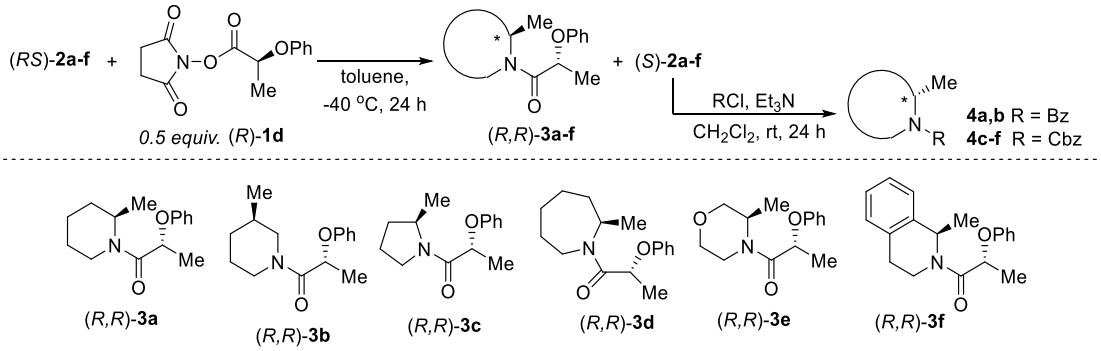
Result Table (Uncal - 9337 CEN-1428 - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	10,467	28512,545	1178,795	96,7	96,5	0,40
2	11,783	980,395	42,545	3,3	3,5	0,38
	Total	29492,940	1221,339	100,0	100,0	

HPLC of amide (*R,R*)-**3a** (Knauer Smartline-1100, Chiralpak AS-H column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 40:1):
$t_{(R,R)\text{-}\mathbf{3a}}$ = 10.5 min, $t_{(R,S)\text{-}\mathbf{3a}}$ = 11.8 min (93.4% *de*)

Stereochemical results

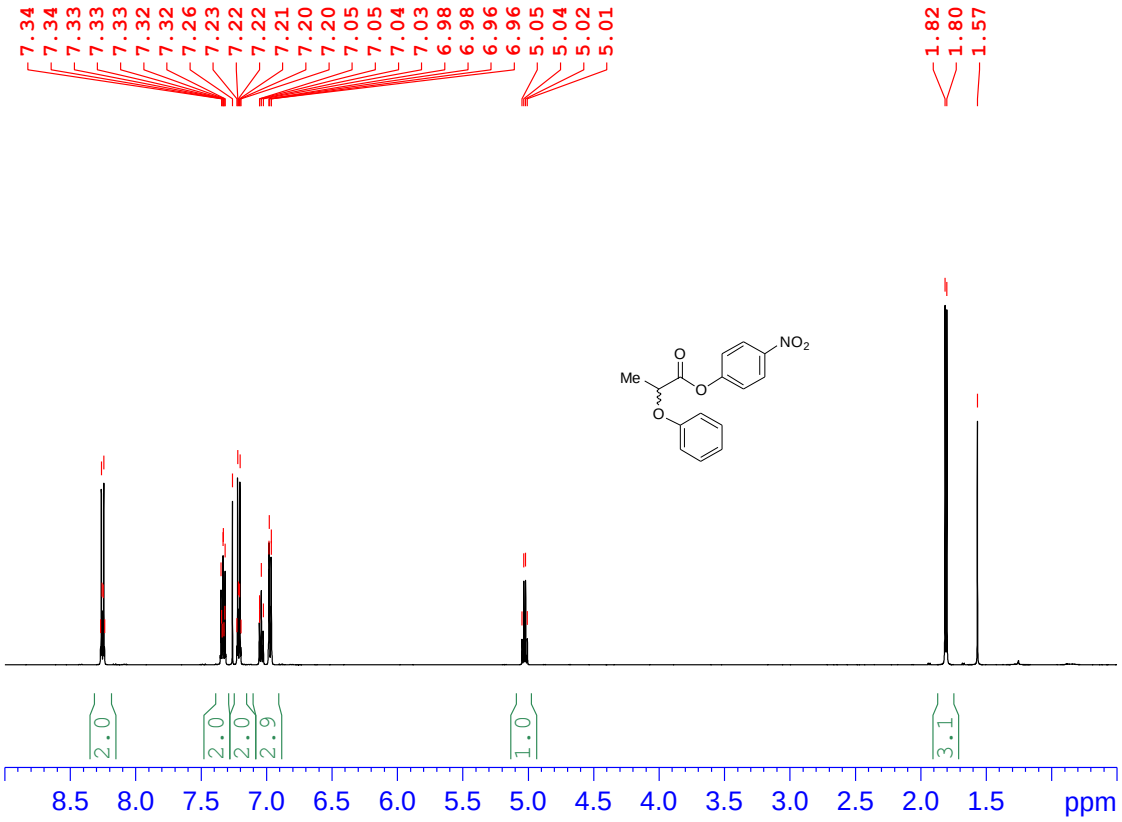
Table S1 Stereochemical results of KR of racemic amines (*RS*)-**2a-f** with enantiopure ester (*R*)-**1d** in toluene at –40 °C



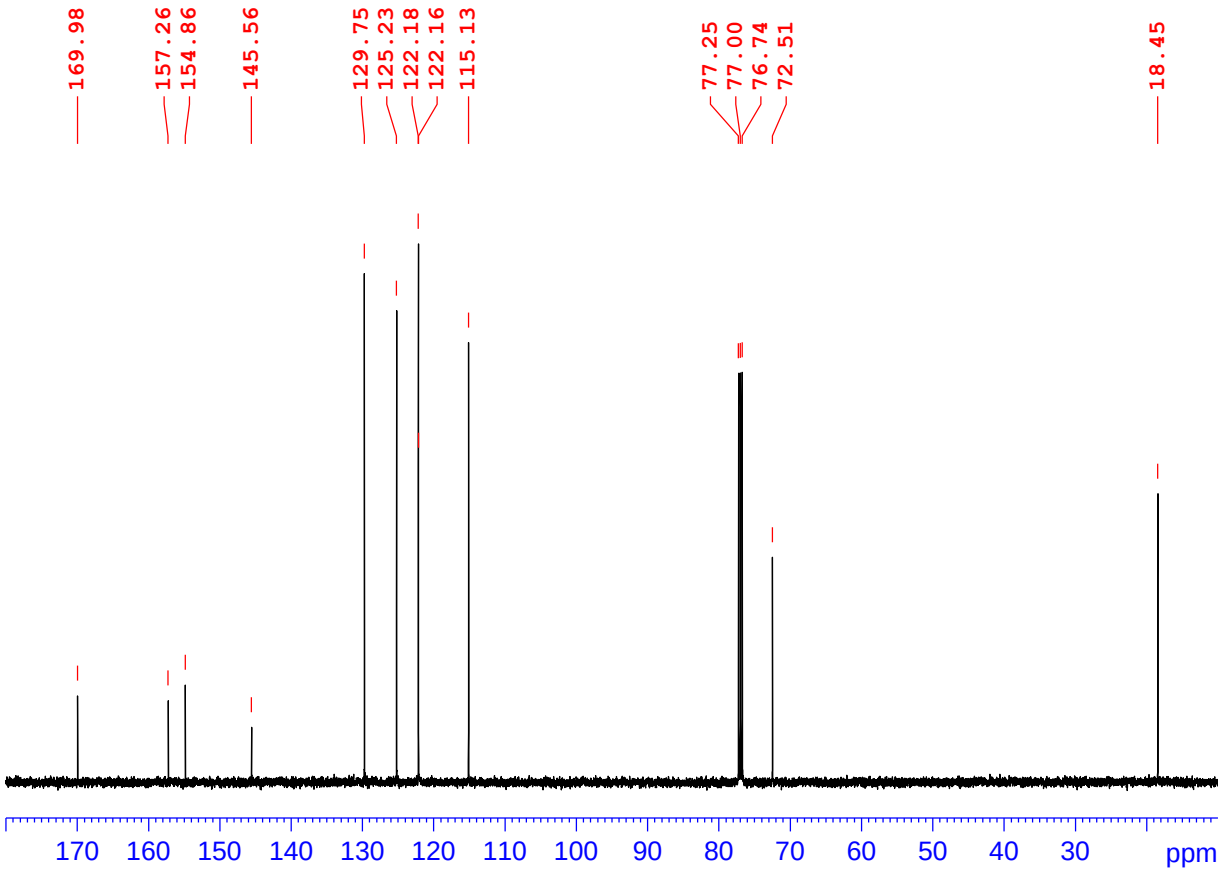
Racemic amine	(*R,R*)-Amide		Unreacted (*S*)-amine		Conversion	Selectivity factor
	de [%][a]	de_{AVG} [%]	*ee* [%][b]	ee_{AVG} [%]	*C* [%][c]	*s*[d]
(*RS*)-**2a**	**3a**, 94.4	**3a**, 93.7	**2a**, 73.8	**2a**, 75.4	44	73
	3a, 94.8		**2a**, 76.2			
	3a, 92.0		**2a**, 76.2			
(*RS*)-**2b**	**3b**, 16.0	**3b**, 15.7	**2b**, 15.2	**2b**, 15.4	49	1.6
	3b, 17.4		**2b**, 17.4			
	3b, 13.8		**2b**, 13.6			
(*RS*)-**2c**	**3c**, 29.2	**3c**, 28.8	**2c**, 19.4	**2c**, 20.2	41	2.2
	3c, 28.4		**2c**, 21.0			
(*RS*)-**2d**	**3d**, 83.0	**3d**, 83.0	**2d**, 49.6	**2d**, 48.1	37	17
	3d, 82.9		**2d**, 46.6			
(*RS*)-**2e**	**3e**, 77.8	**3e**, 78.5	**2e**, 57.8	**2e**, 55.5	41	14
	3e, 79.2		**2e**, 53.2			
(*RS*)-**2f**	**3f**, 82.4	**3f**, 82.2	**2f**, 55.4	**2f**, 55.2	40	18
	3f, 82.0		**2f**, 55.0			

[a] Determined by GC or chiral HPLC. [b] Determined by chiral HPLC after precolumn derivatization to compounds **4a-f**. [c] $C = [ee_{amine} / (ee_{amine} + de_{amide})] \times 100\%$.[S9] [d] $s = \ln[(1 - C) \times (1 - ee_{amine})] / \ln[(1 - C) \times (1 + ee_{amine})]$.[S9]

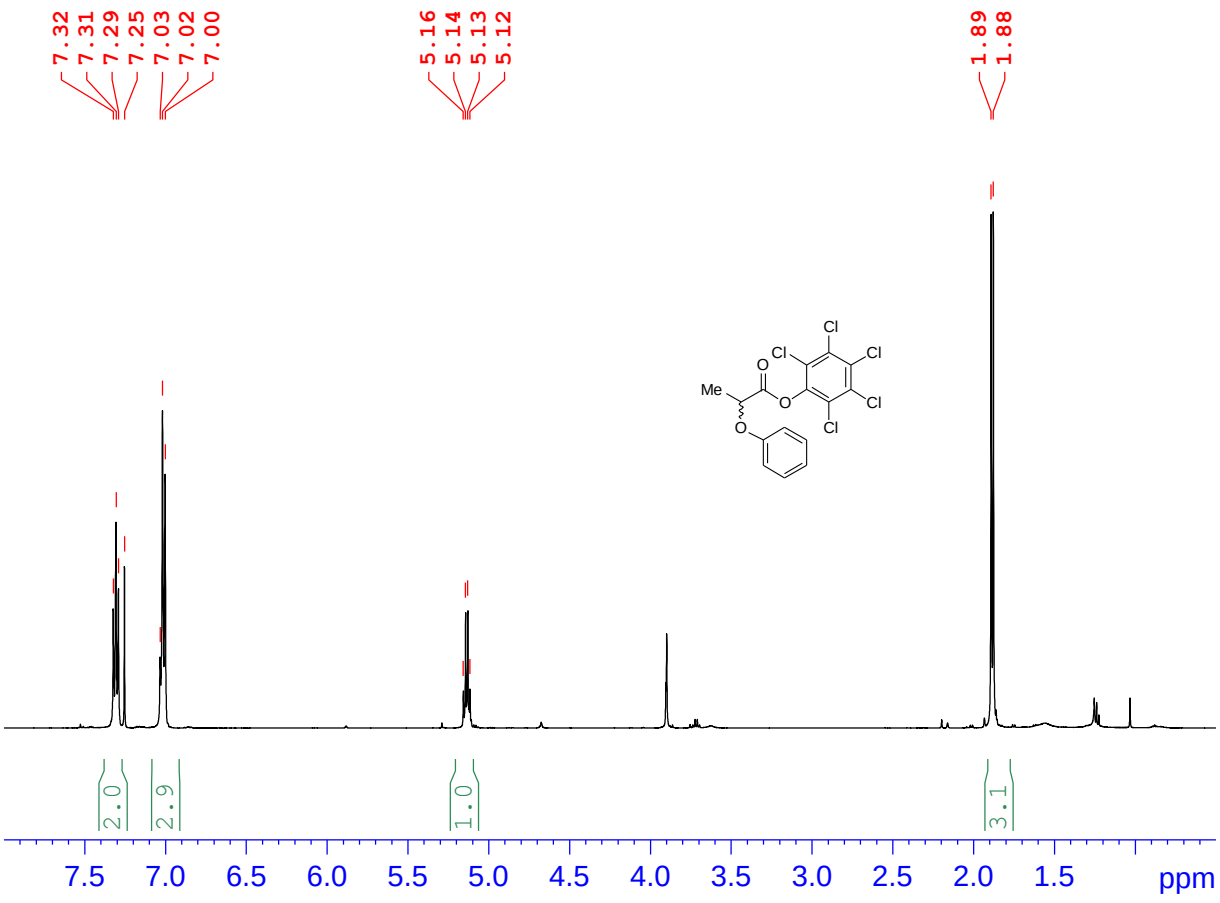
NMR spectra



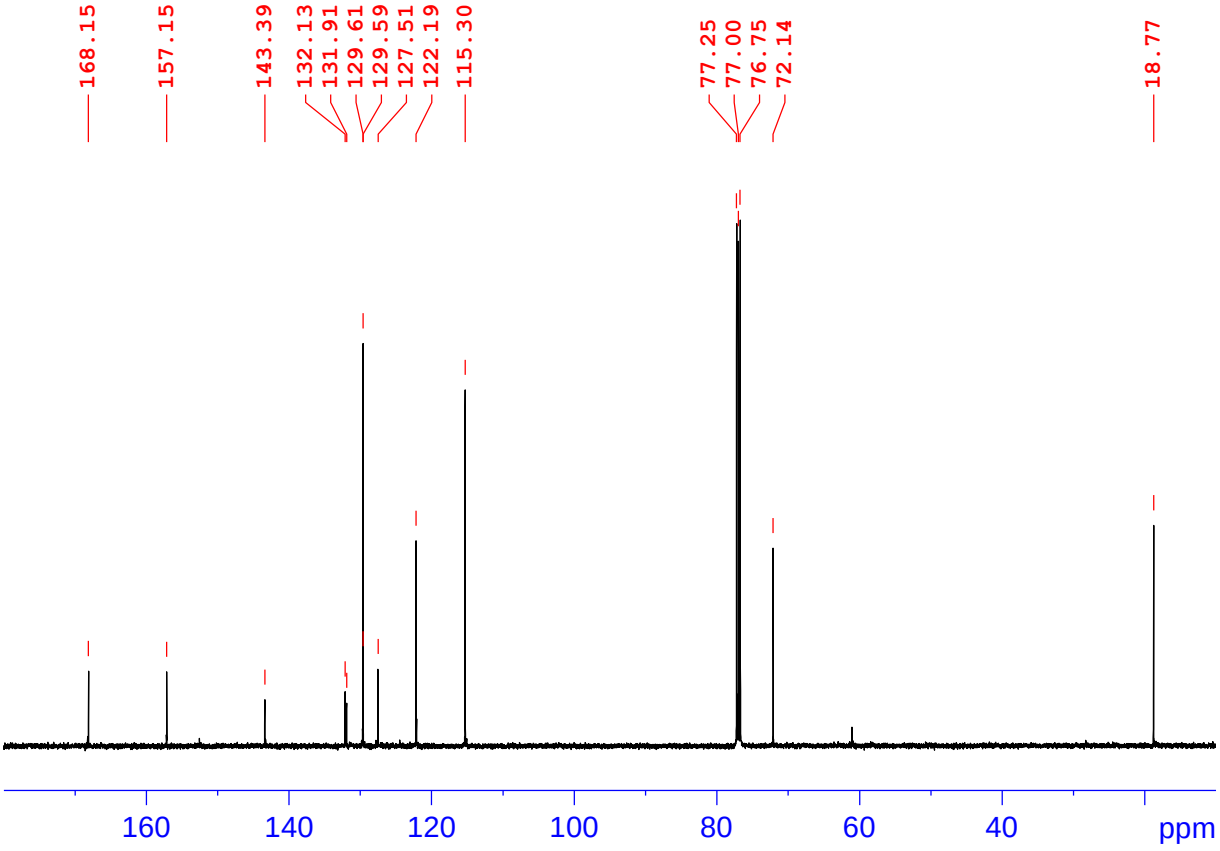
^{1}H NMR (500 MHz, $CDCl_3$) of ester (*RS*)-**1b**.



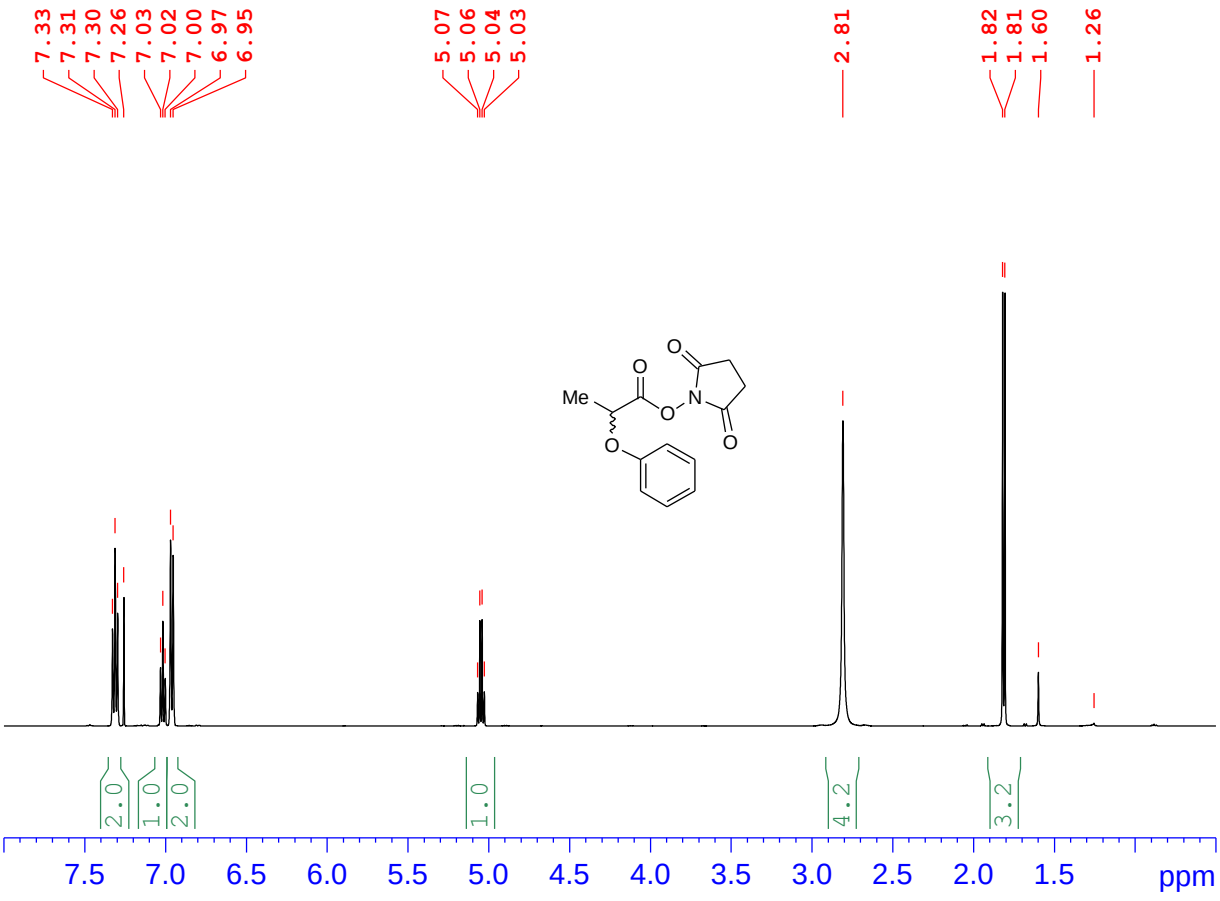
^{13}C NMR (126 MHz, $CDCl_3$) of ester (*RS*)-**1b**.



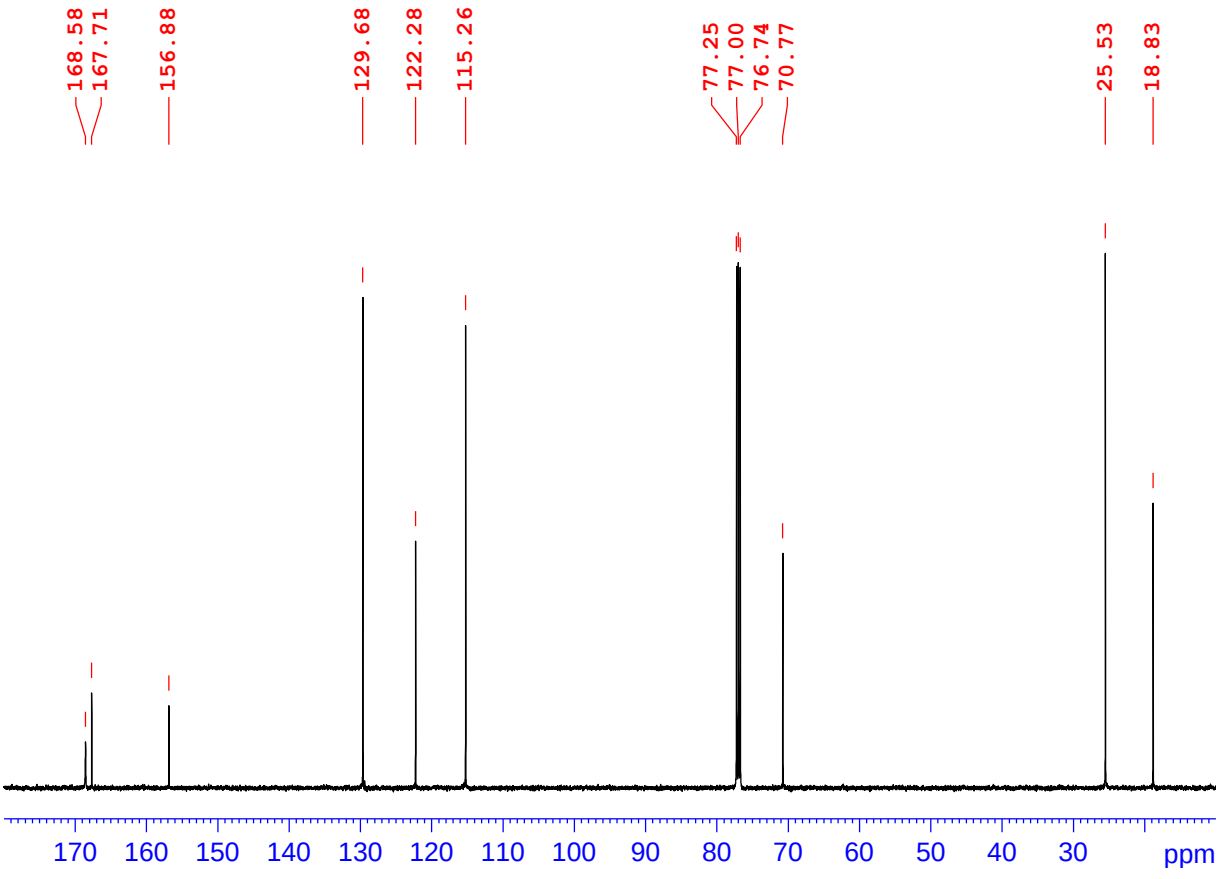
^{1}H NMR (500 MHz, $CDCl_3$) of ester (*RS*)-**1c**.



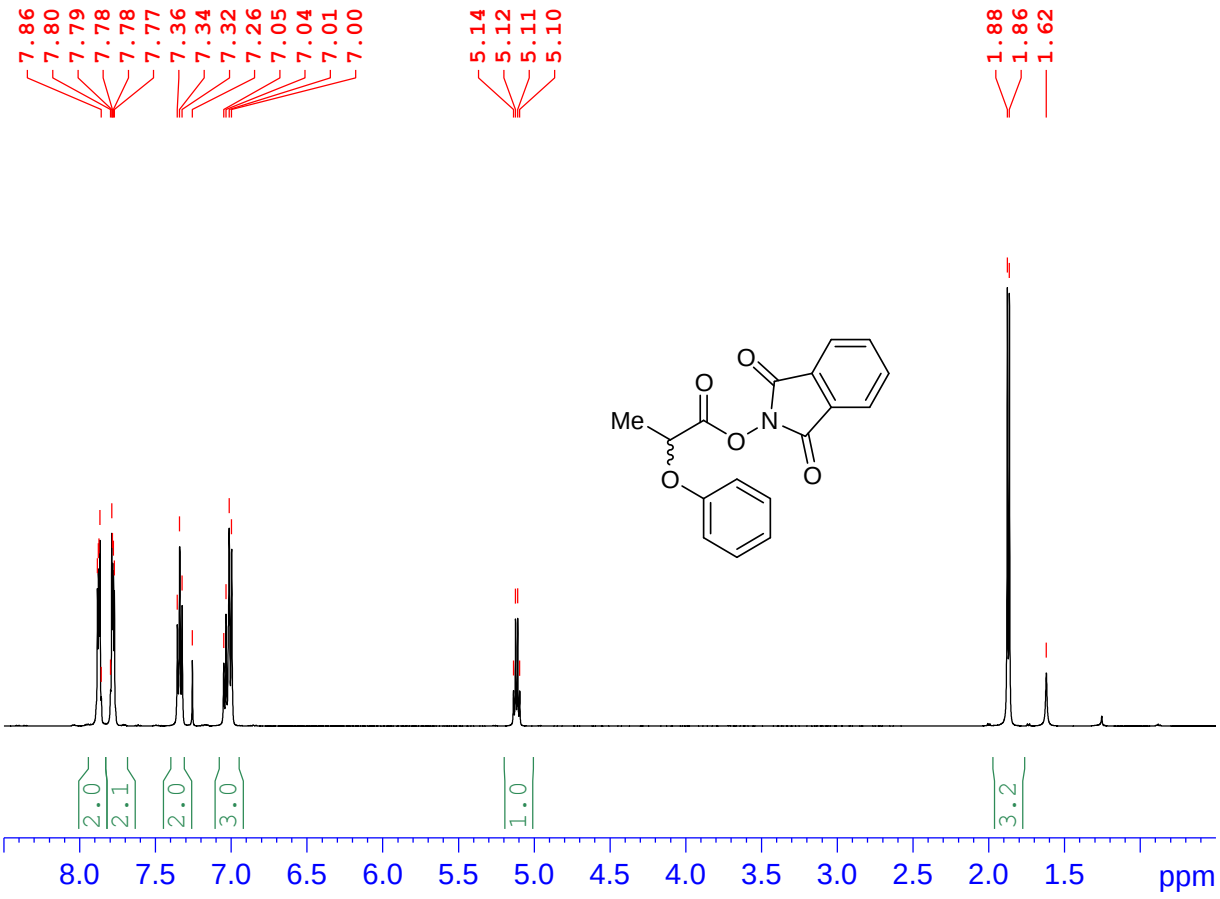
^{13}C NMR (126 MHz, $CDCl_3$) of ester (*RS*)-**1c**.



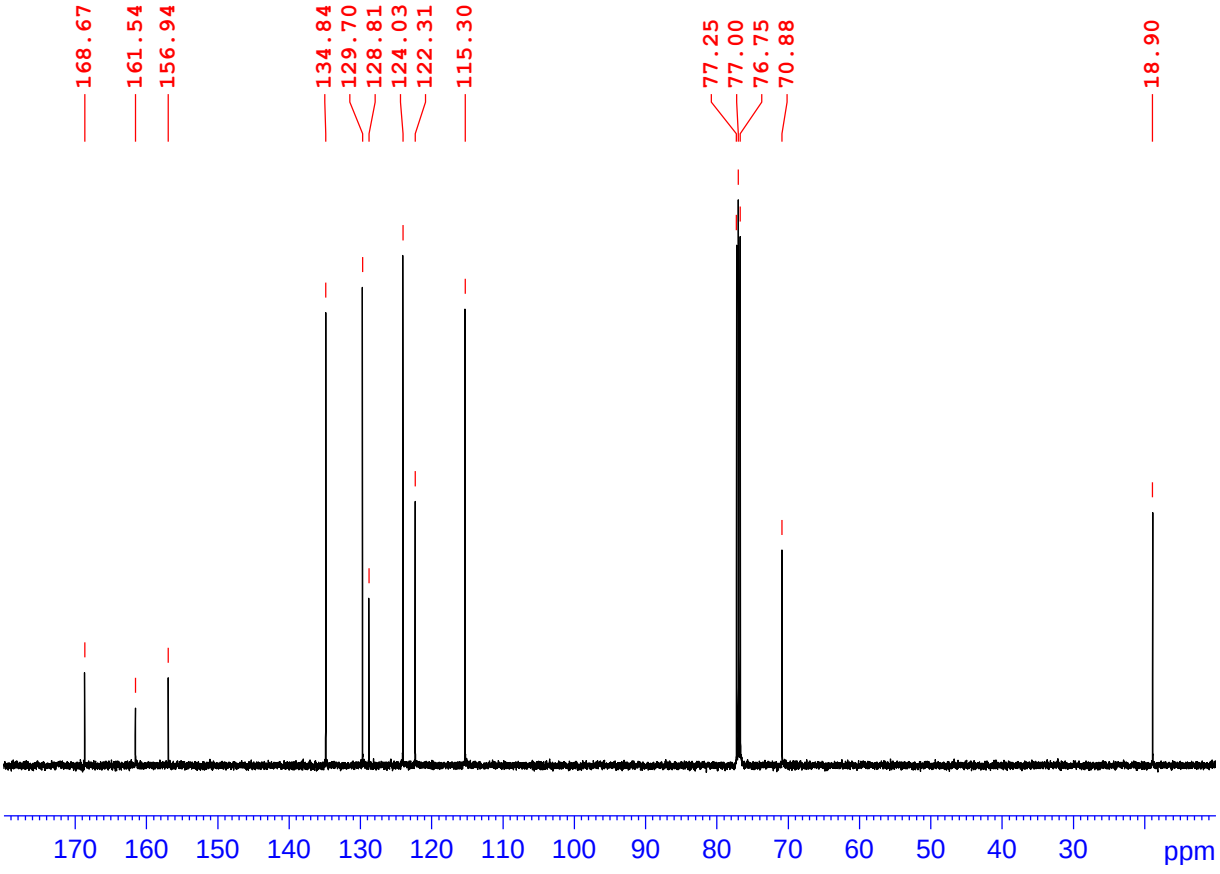
^{1}H NMR (500 MHz, $CDCl_3$) of ester (*RS*)-**1d**.



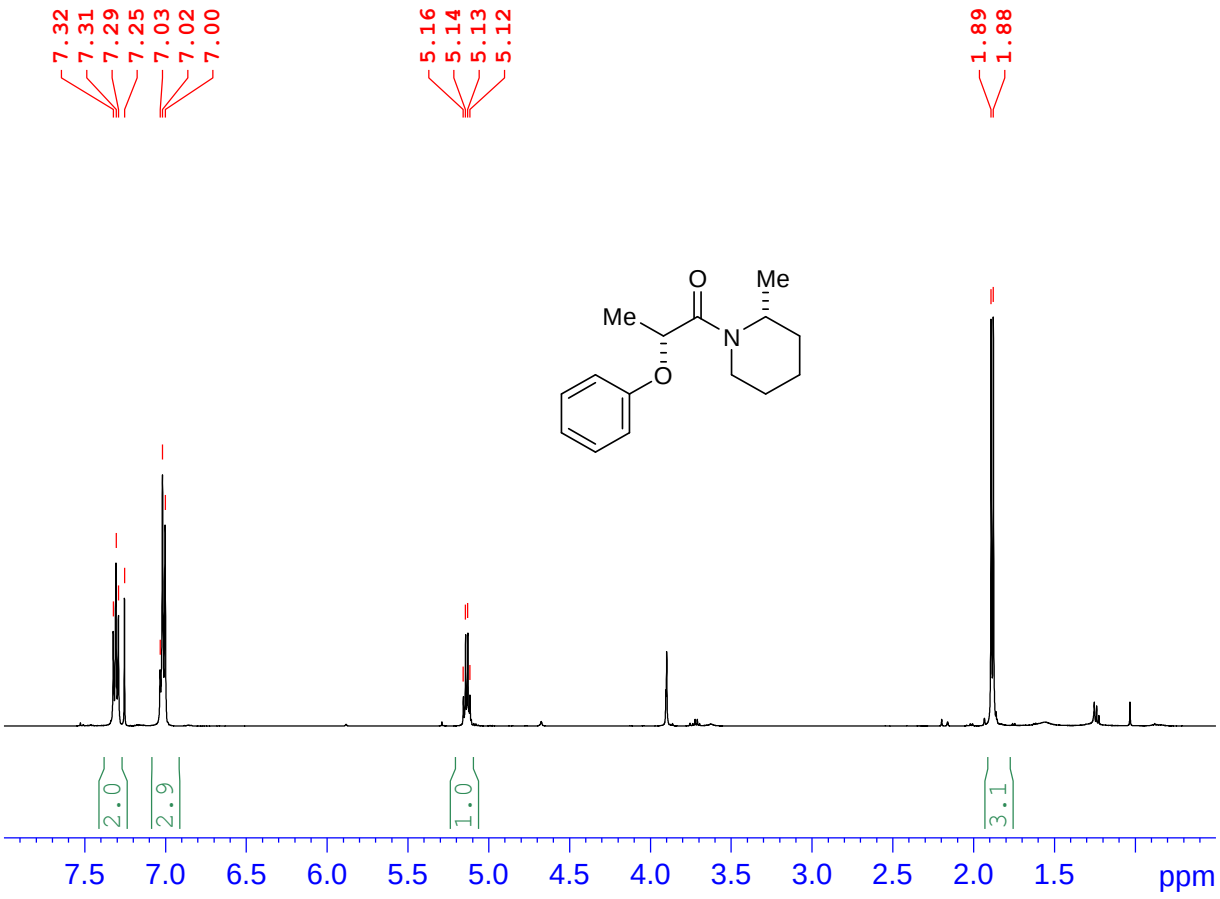
^{13}C NMR (126 MHz, $CDCl_3$) of ester (*RS*)-**1d**.



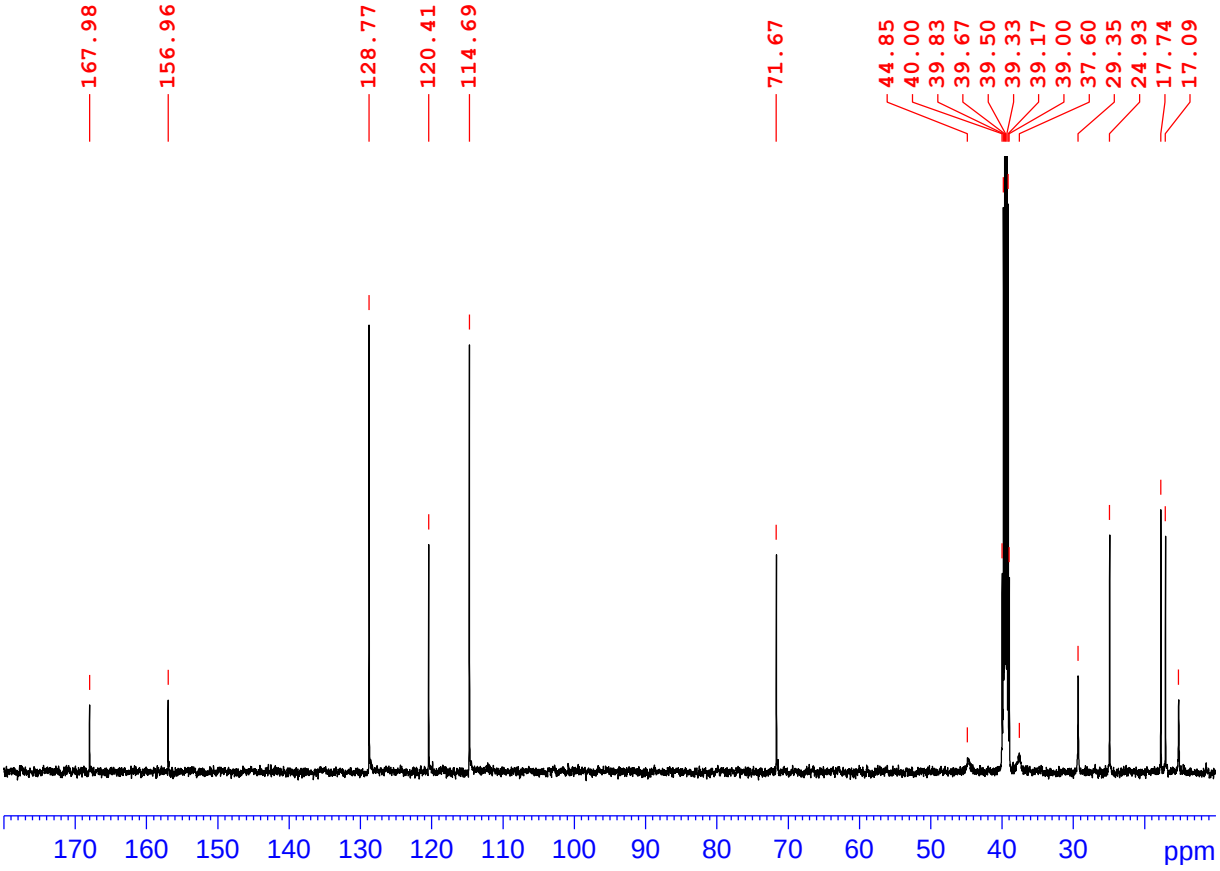
^{1}H NMR (500 MHz, $CDCl_3$) of ester (*RS*)-**1e**.



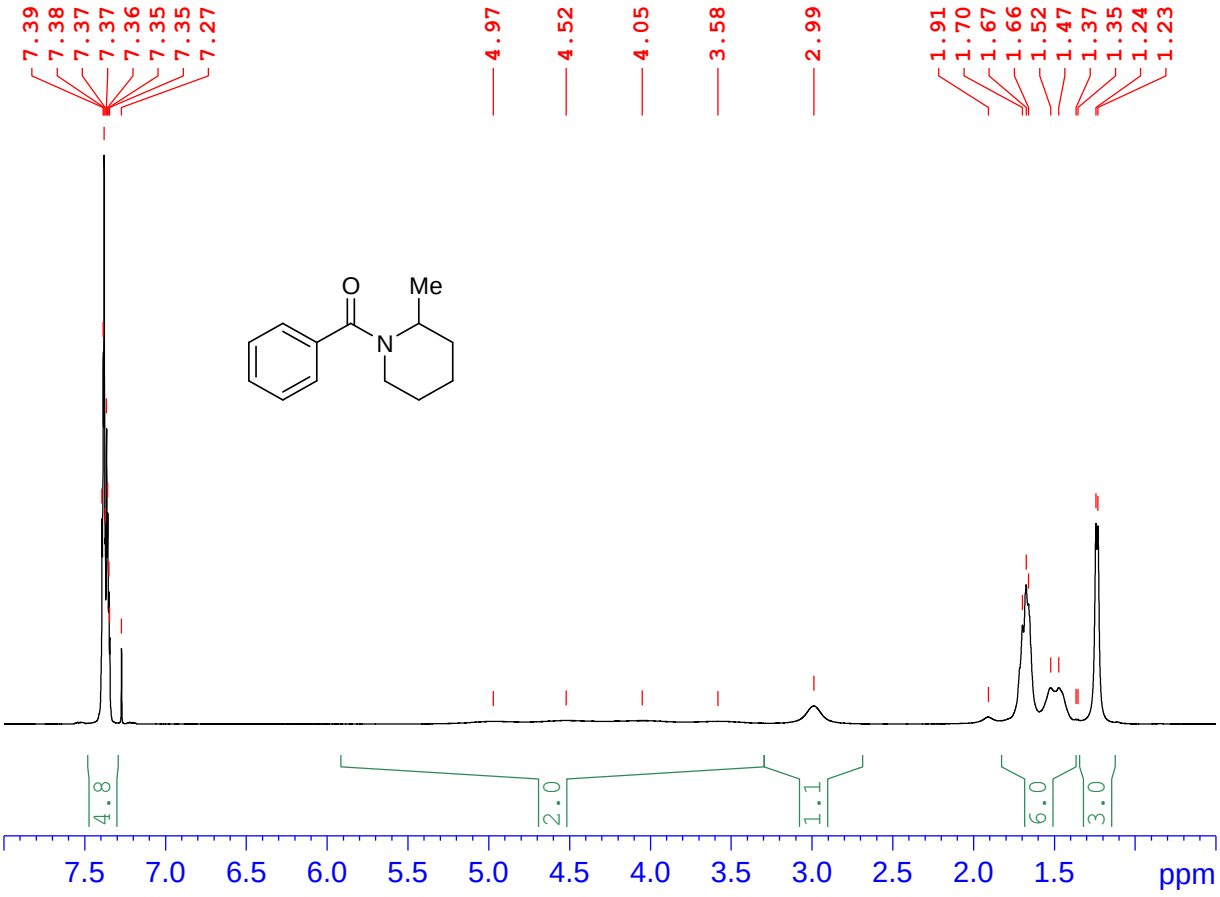
^{13}C NMR (126 MHz, $CDCl_3$) of ester (*RS*)-**1e**.



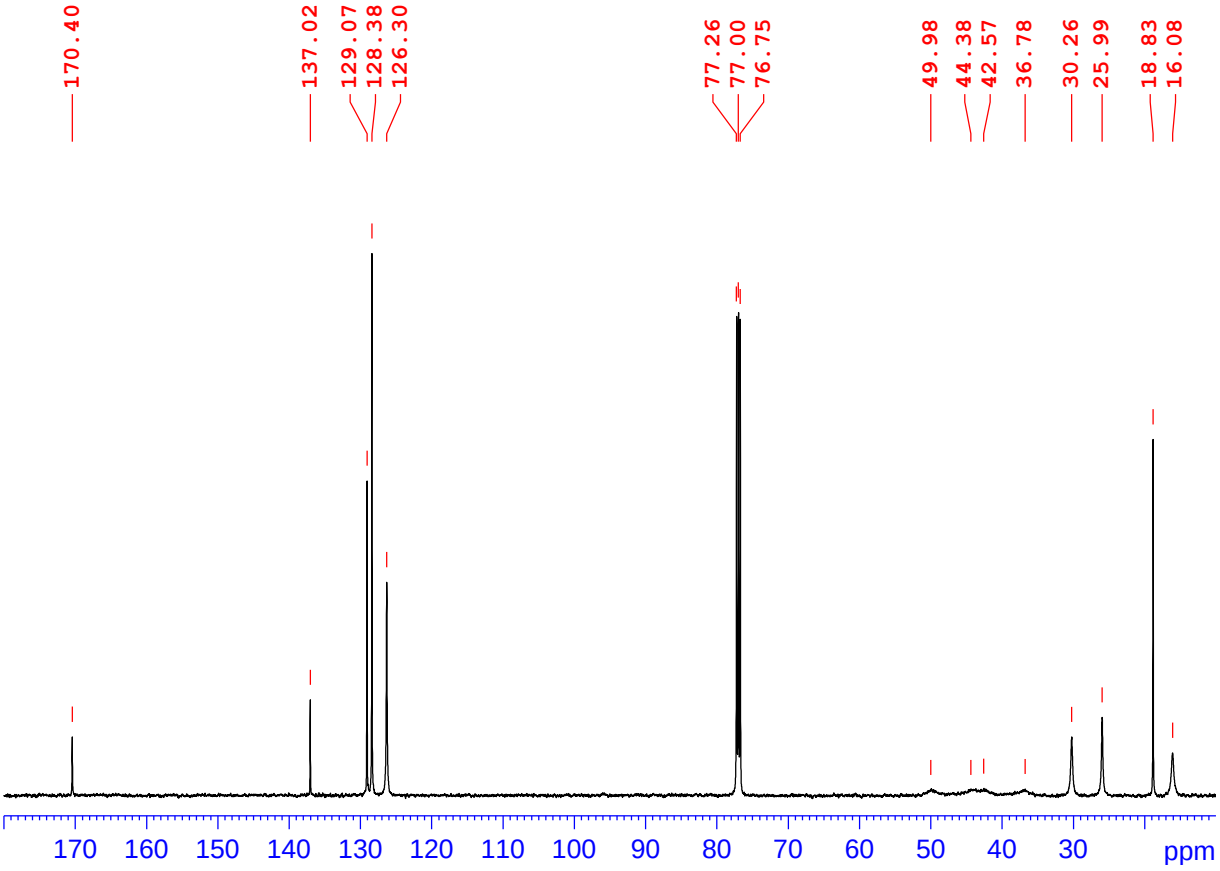
^{1}H NMR (500 MHz, [D_6]DMSO, 100 °C) of amide (*R,R*)-**3a**.



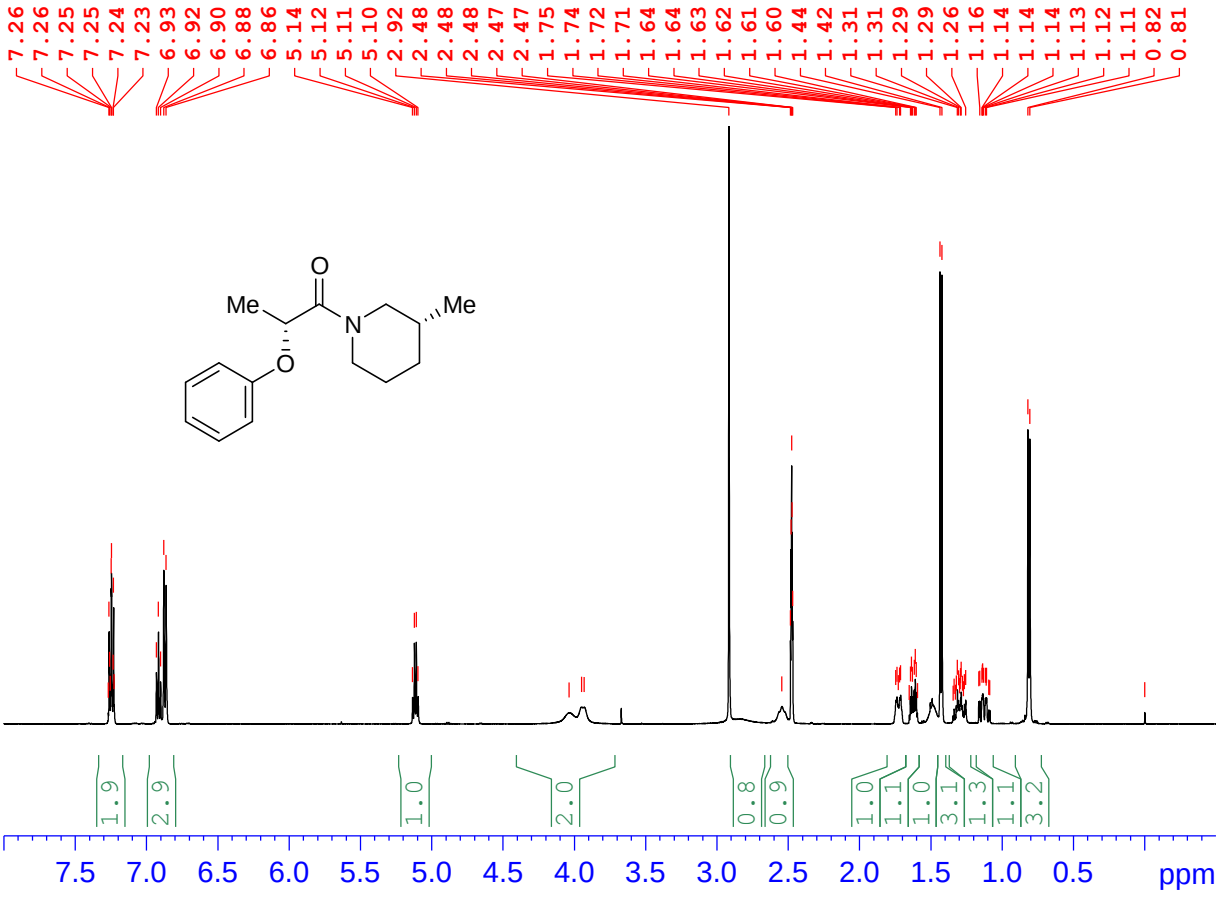
^{13}C NMR (126 MHz, [D_6]DMSO, 100 °C) of amide (*R,R*)-**3a**.



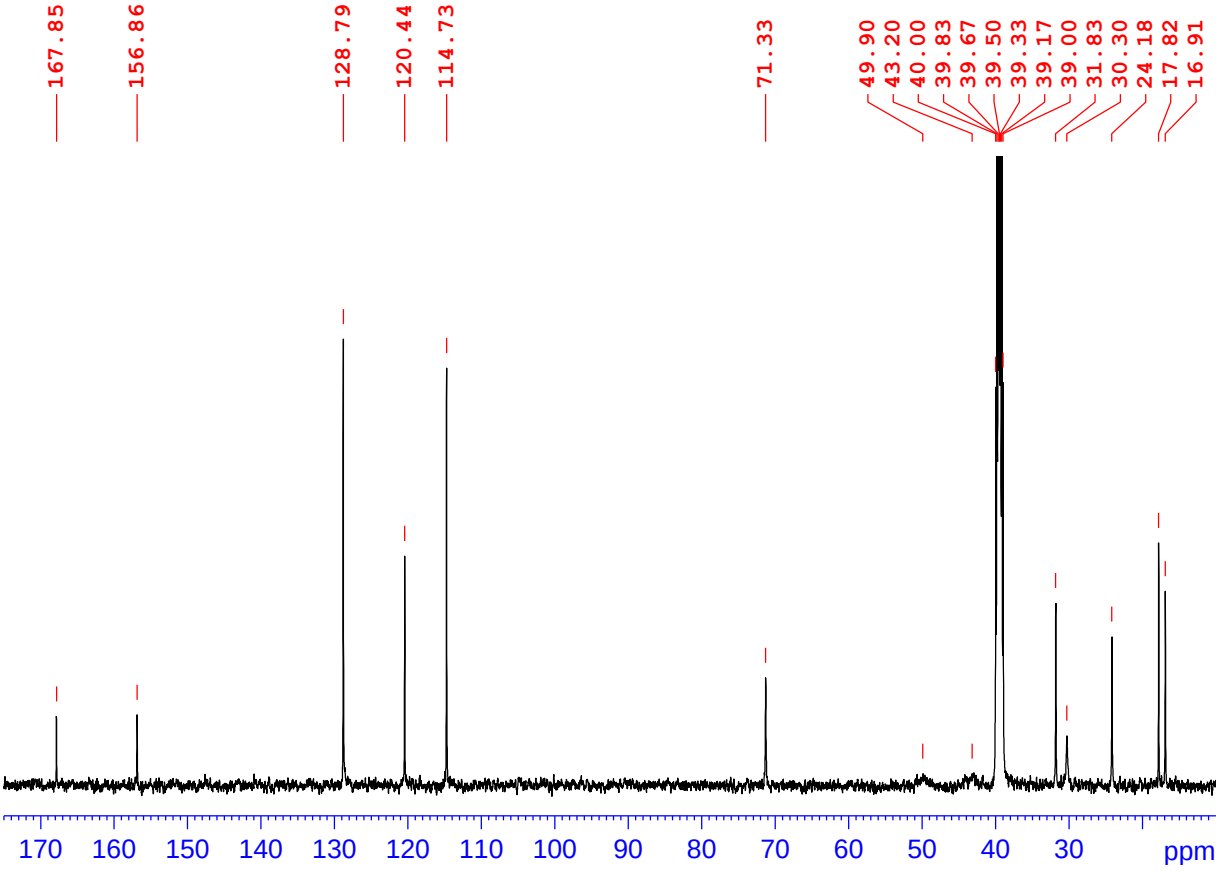
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4a**.



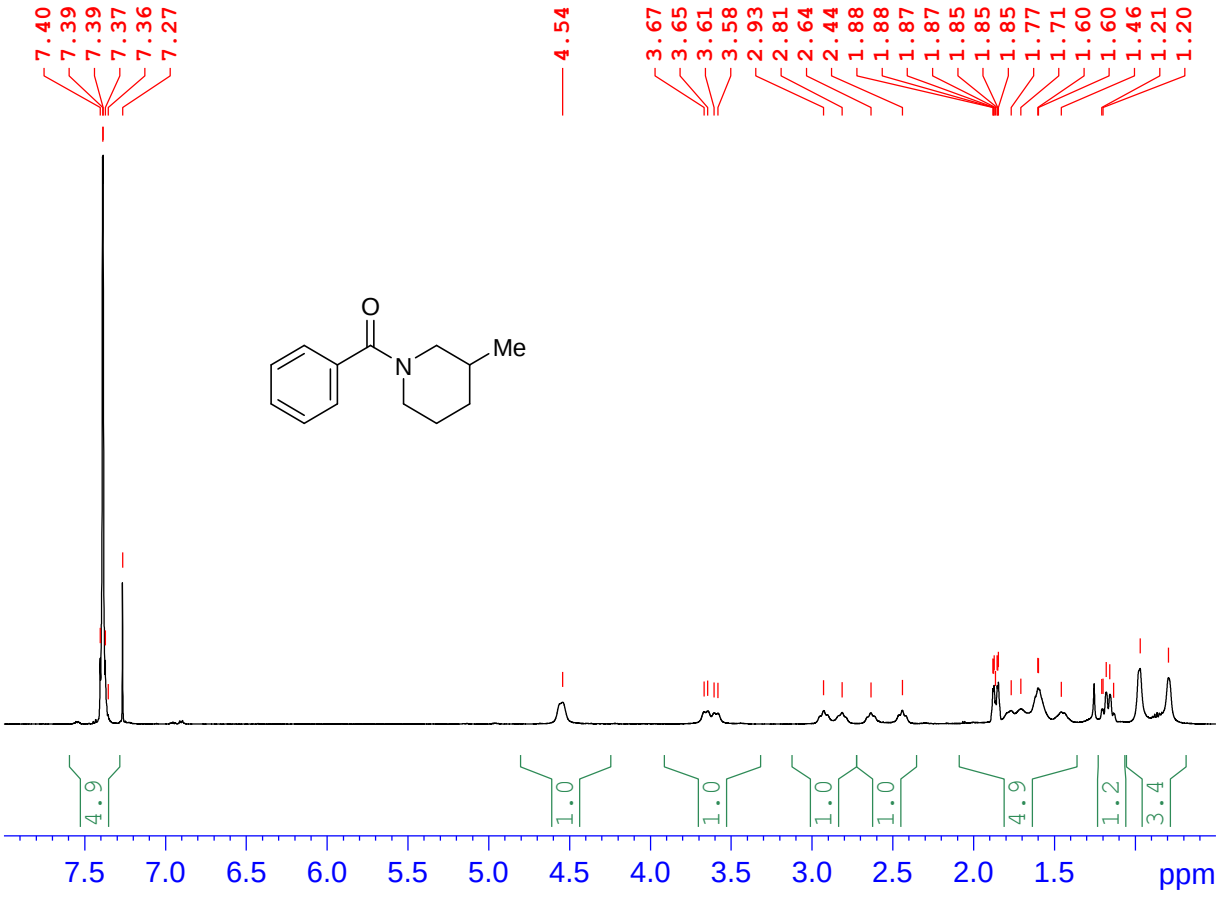
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4a**.



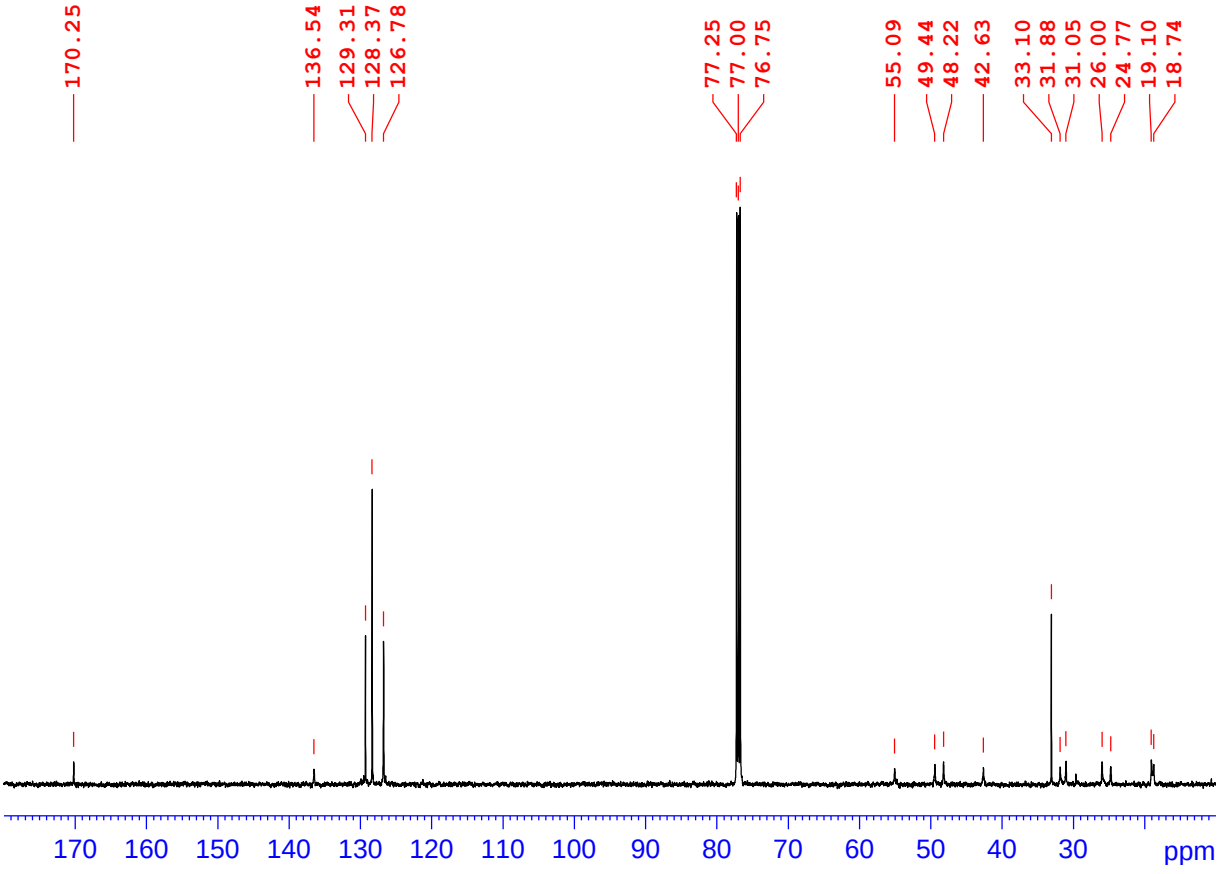
^{1}H NMR (500 MHz, [D$_6$]DMSO, 100 °C) of amide (*R,R*)-**3b**.



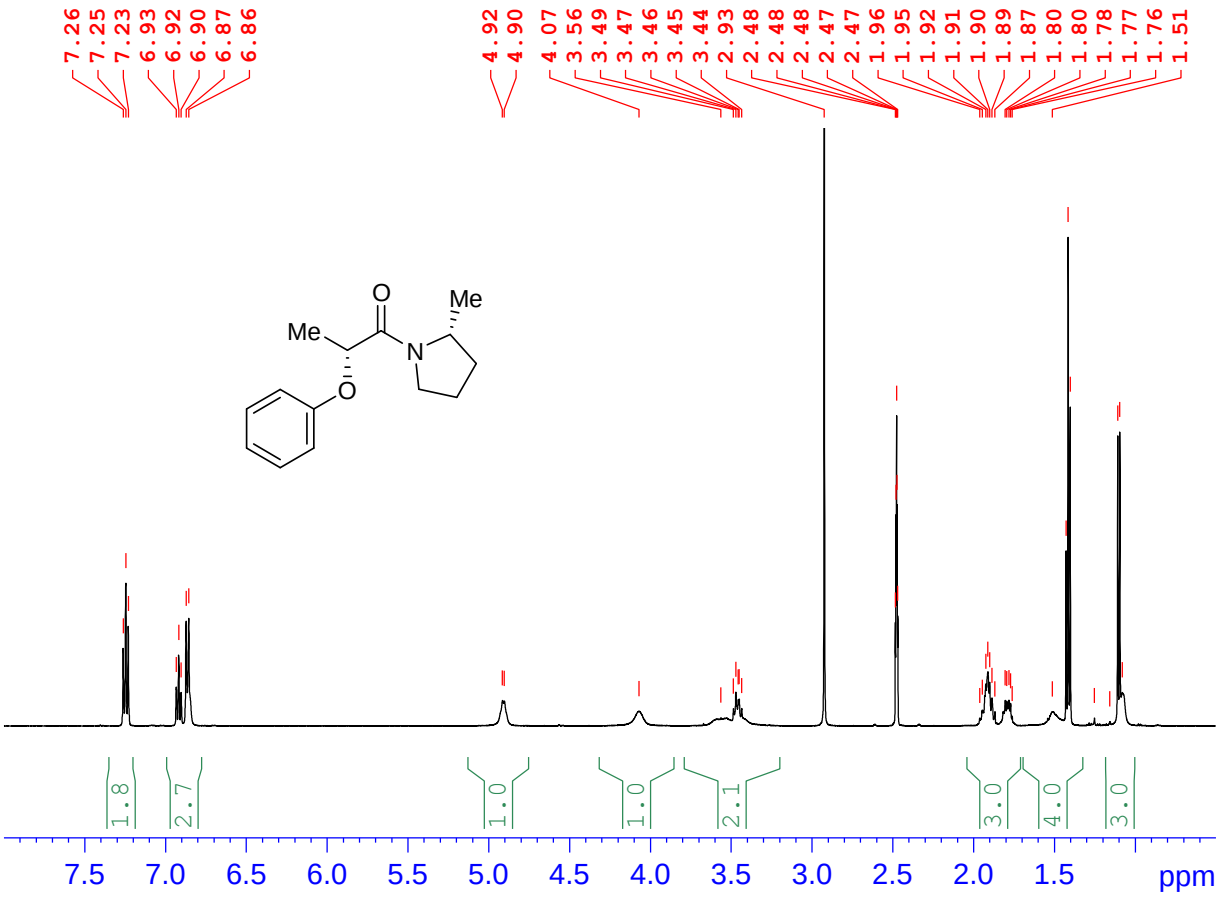
^{13}C NMR (126 MHz, [D$_6$]DMSO, 100 °C) of amide (*R,R*)-**3b**.



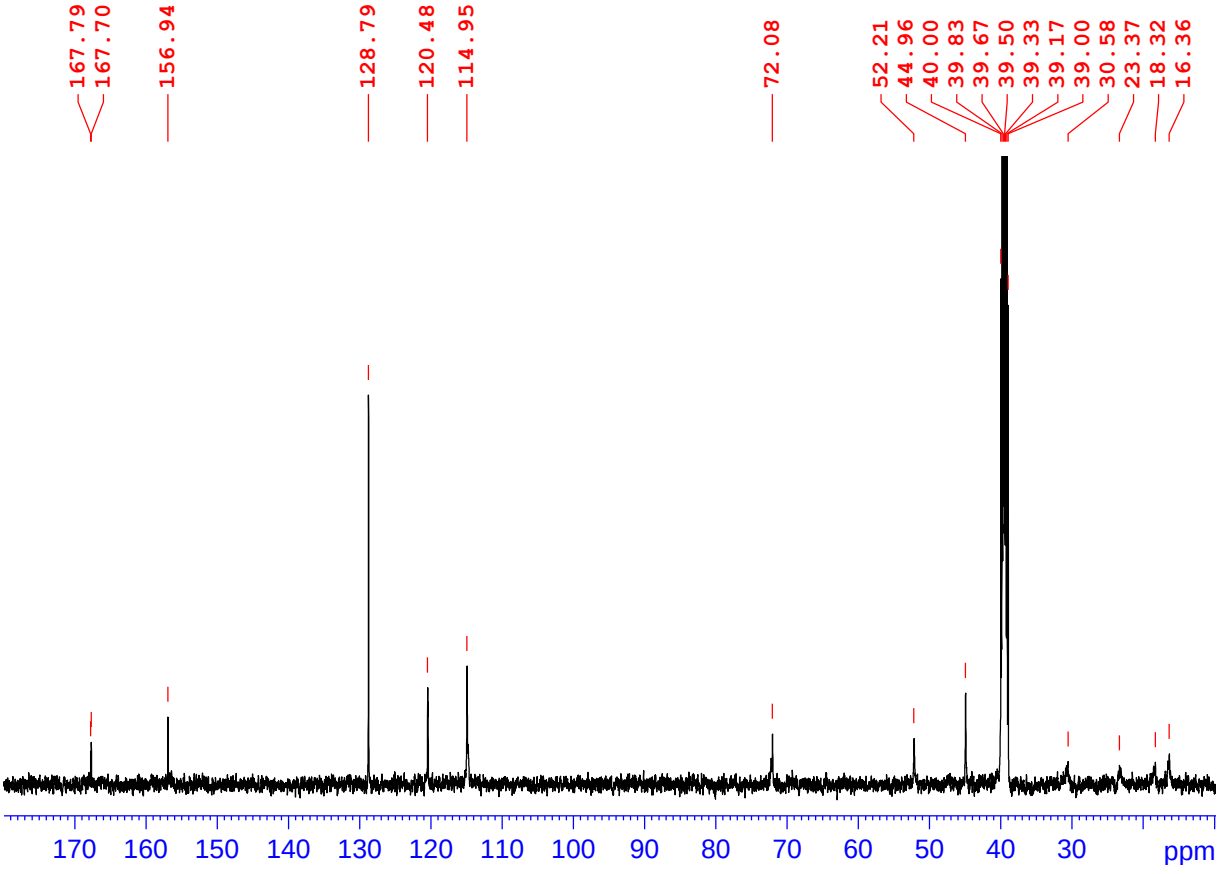
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4b**.



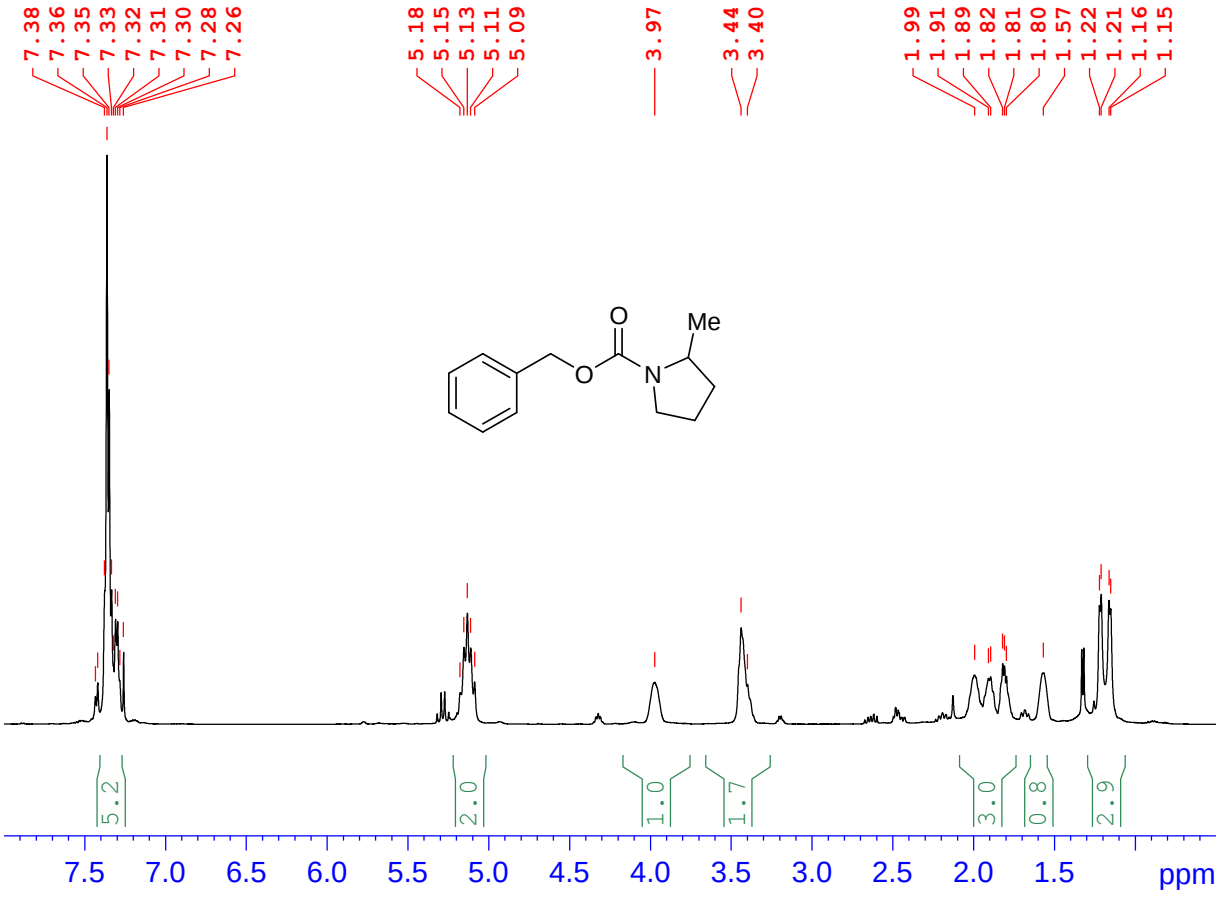
^{13}C NMR (500 MHz, $CDCl_3$) of compound **4b**.



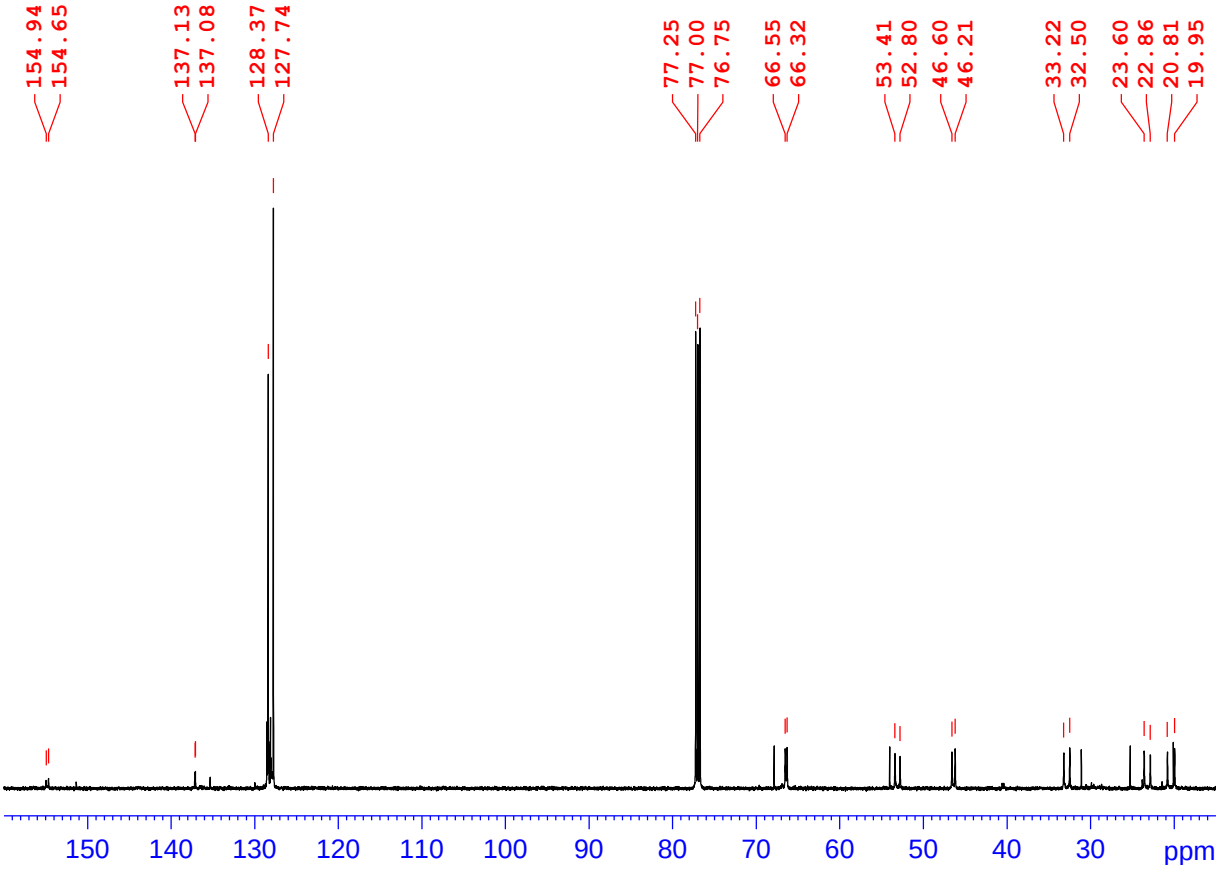
^{1}H NMR (500 MHz, [D_6]DMSO, 100 °C) of amide (*R,R*)-**3c**.



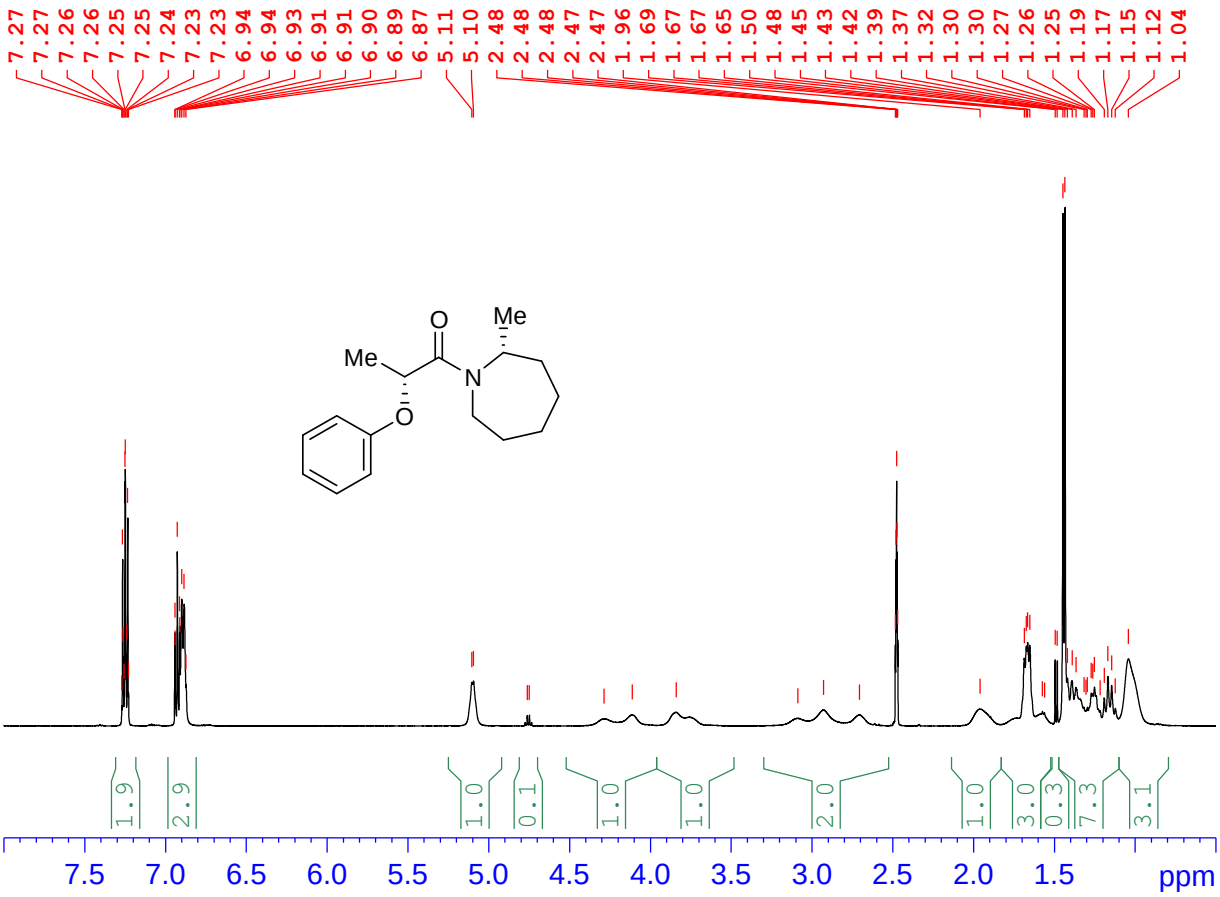
^{13}C NMR (126 MHz, [D_6]DMSO, 100 °C) of amide (*R,R*)-**3c**.



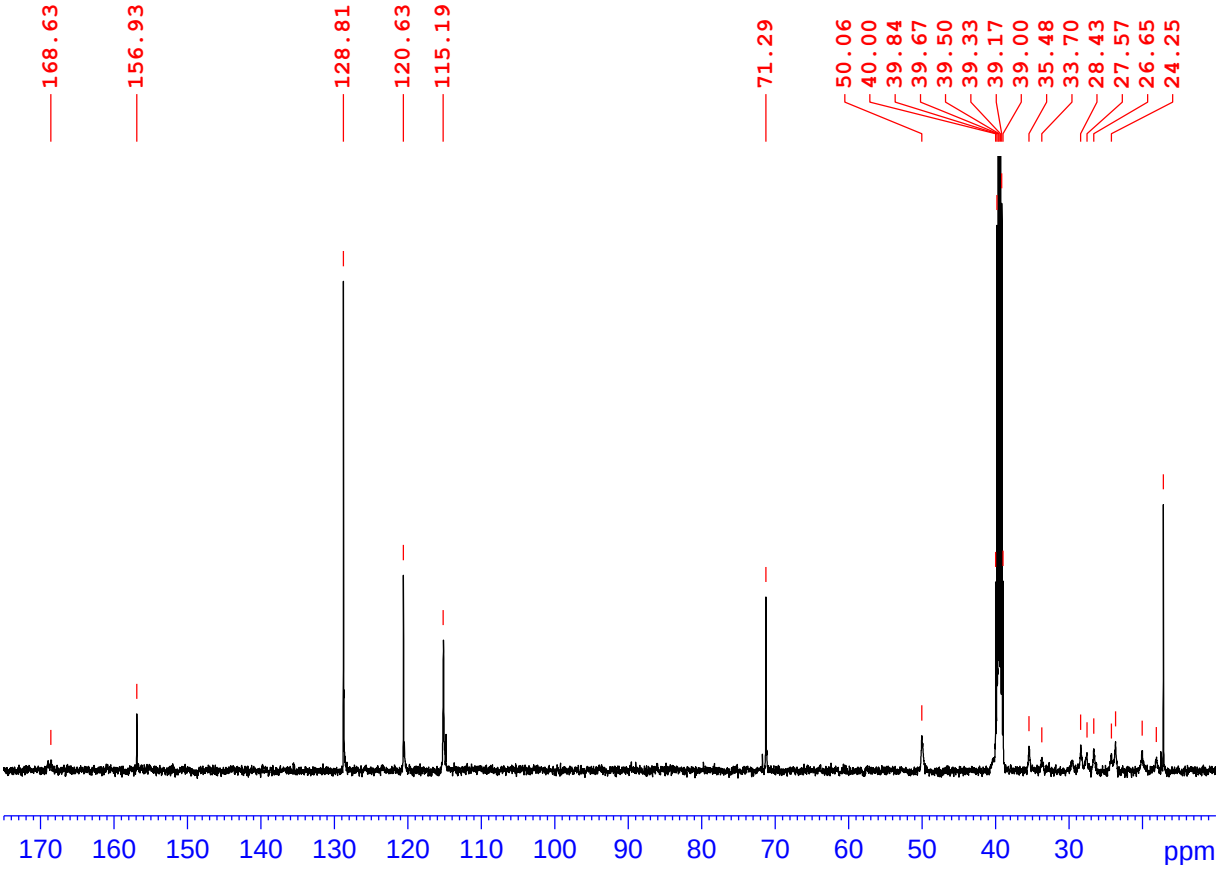
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4c**.



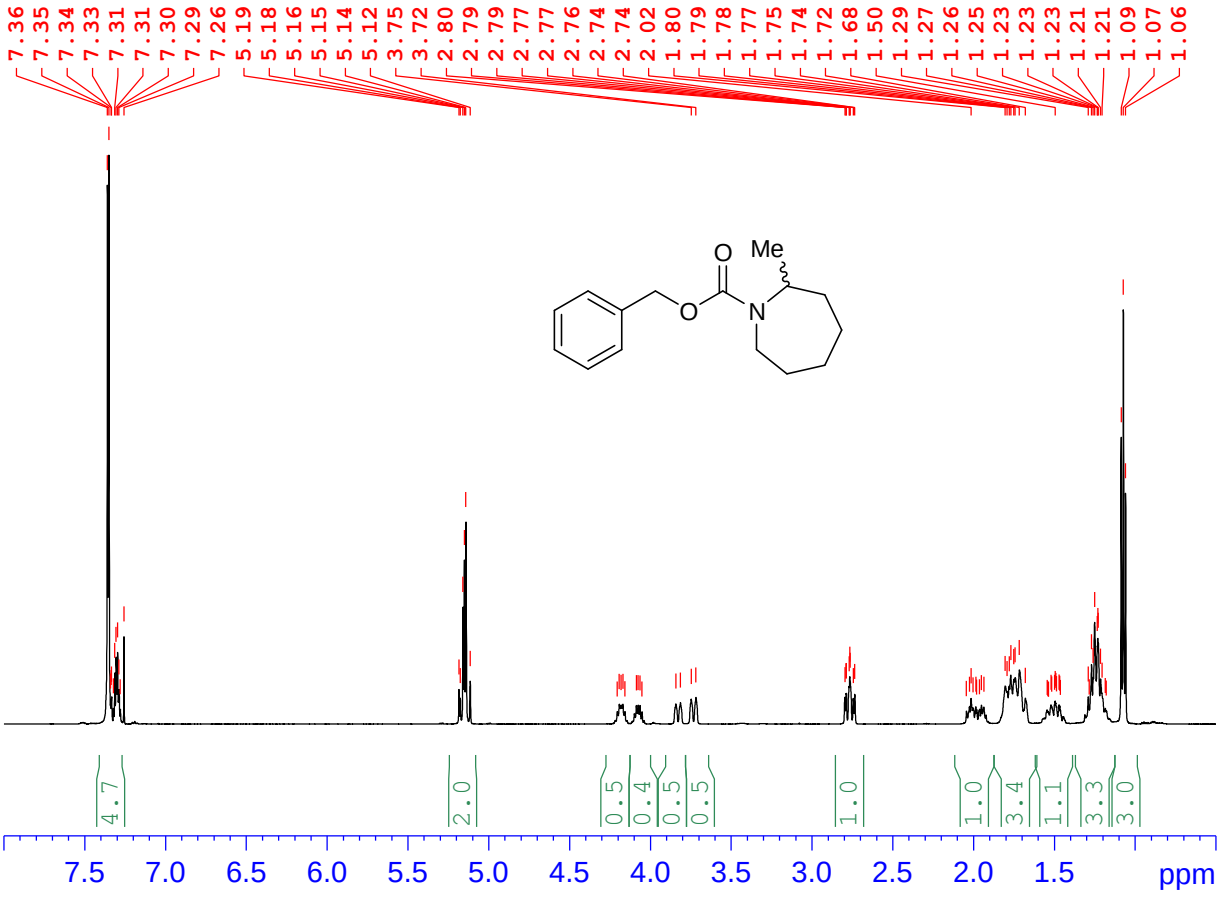
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4c**.



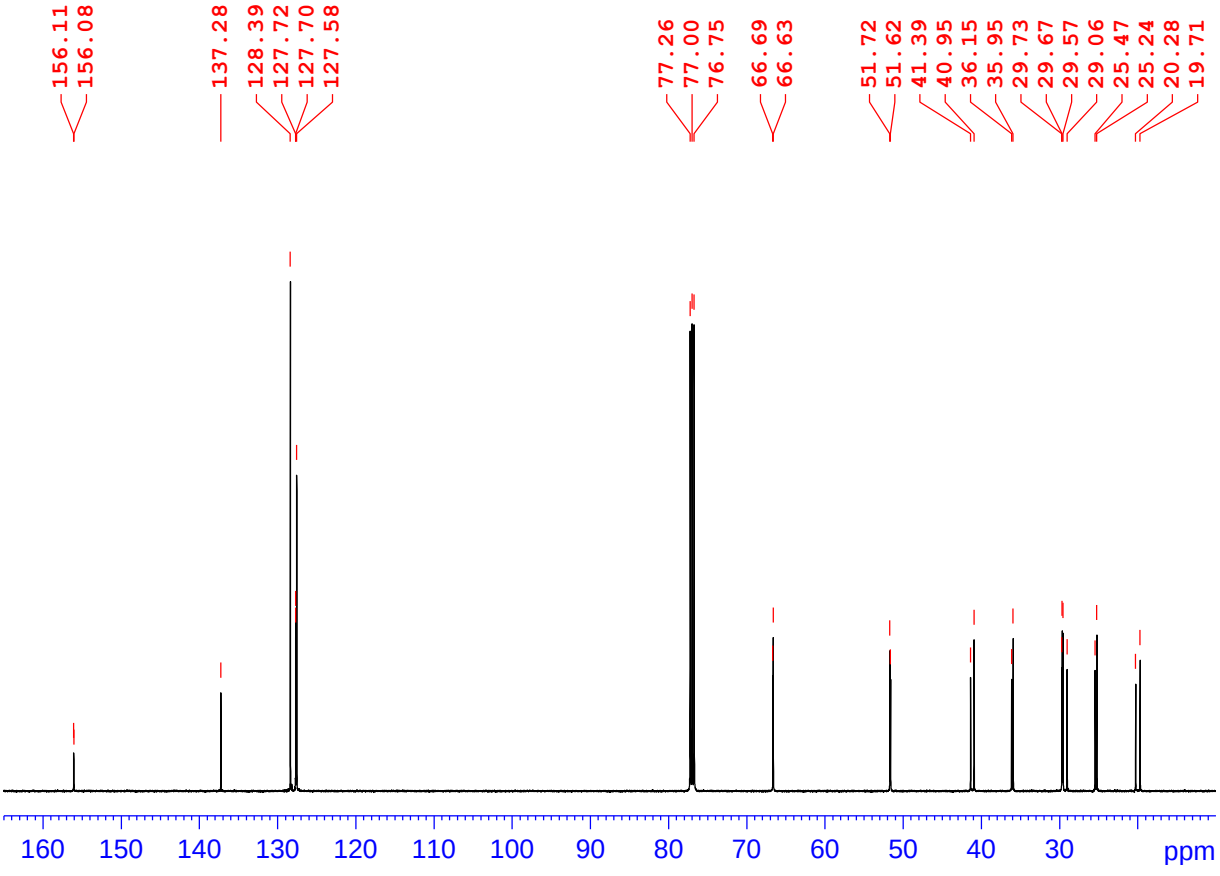
^{1}H NMR (500 MHz, [D$_6$]DMSO, 100 °C) of amide (*R,R*)-**3d**.



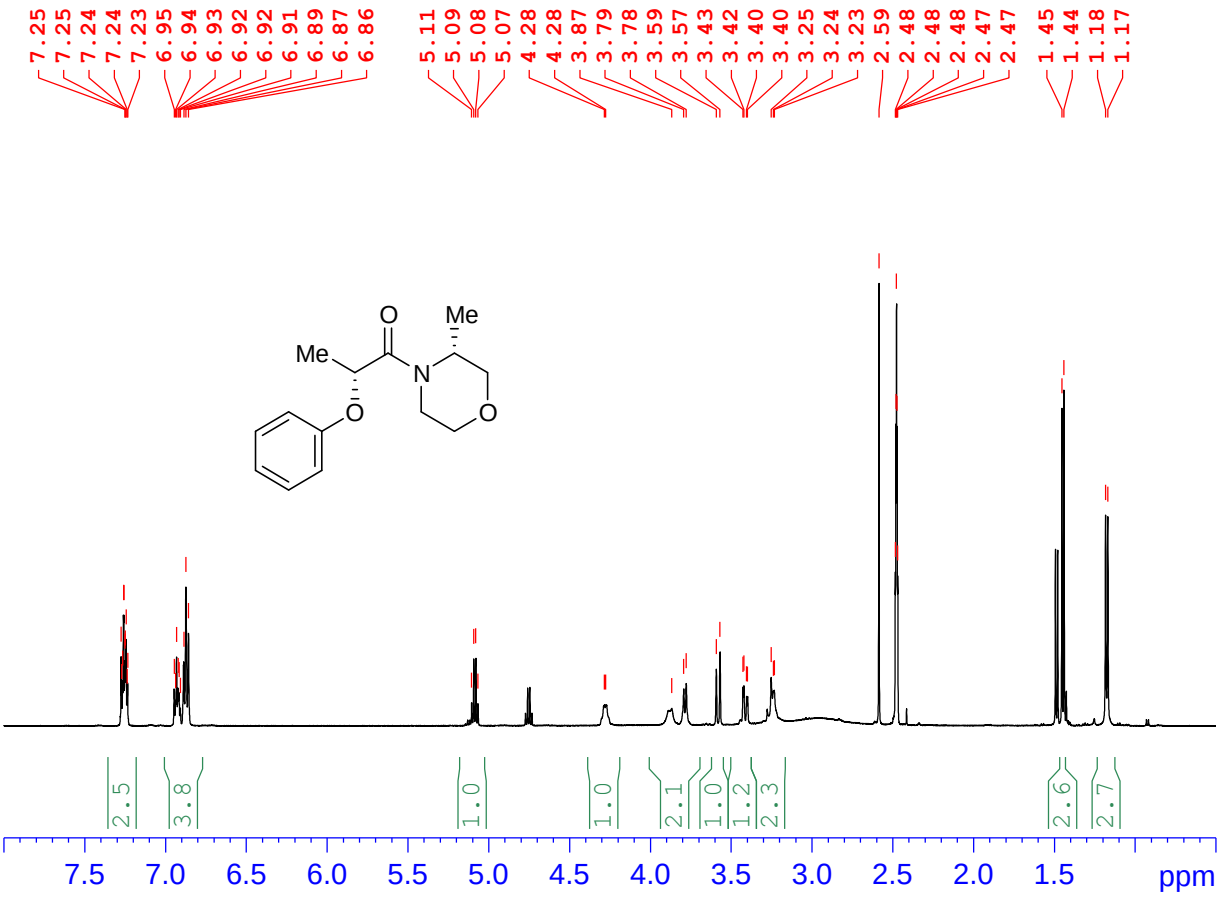
^{13}C NMR (126 MHz, [D$_6$]DMSO, 100 °C) of amide (*R,R*)-**3d**.



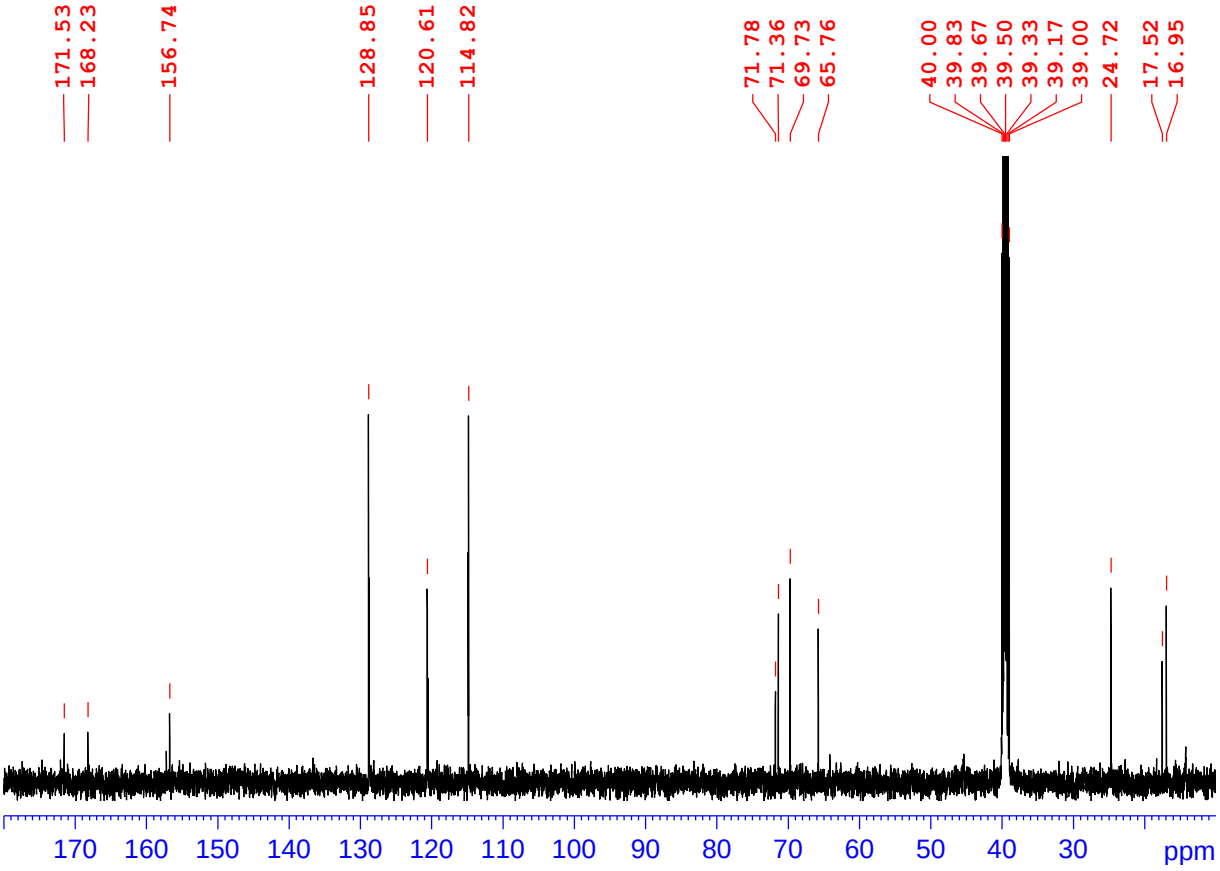
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4d**.



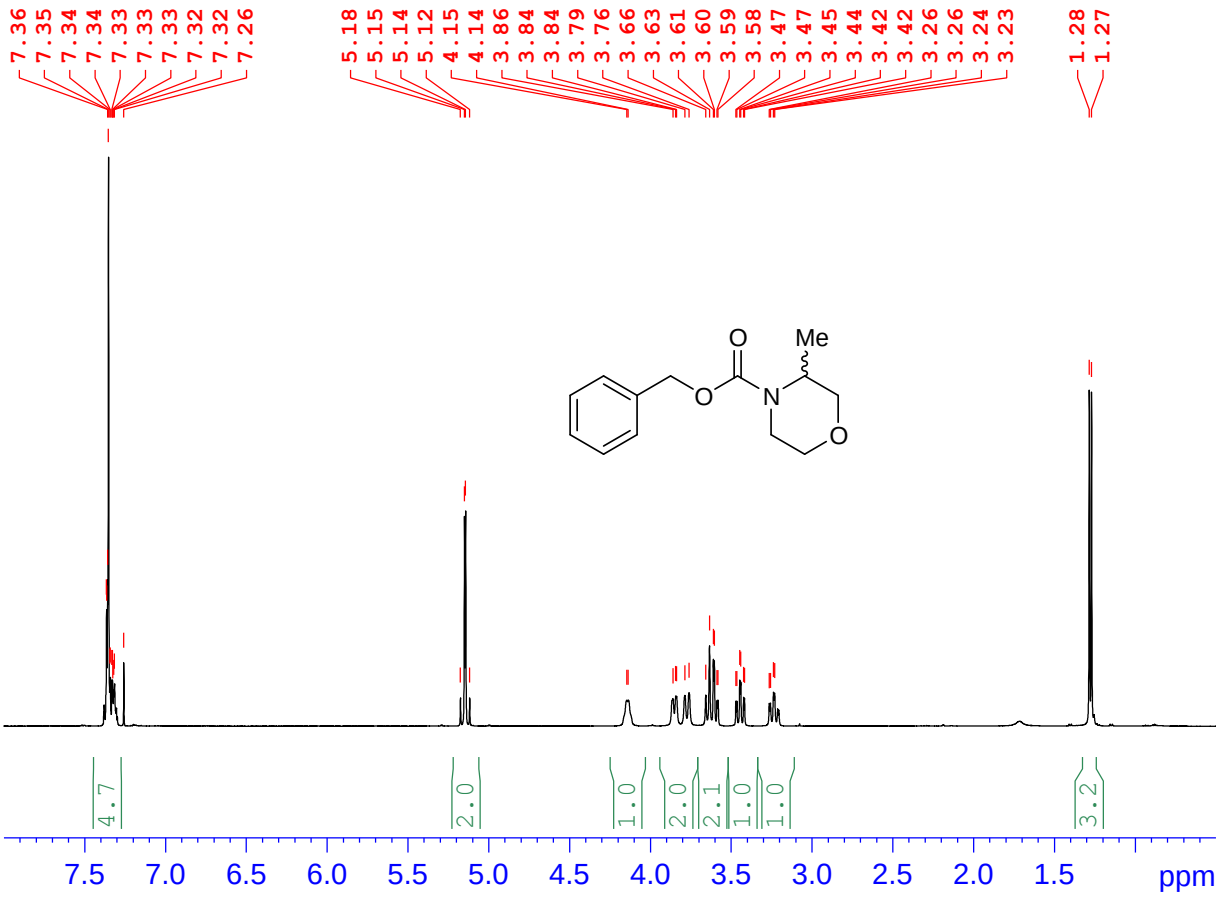
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4d**.



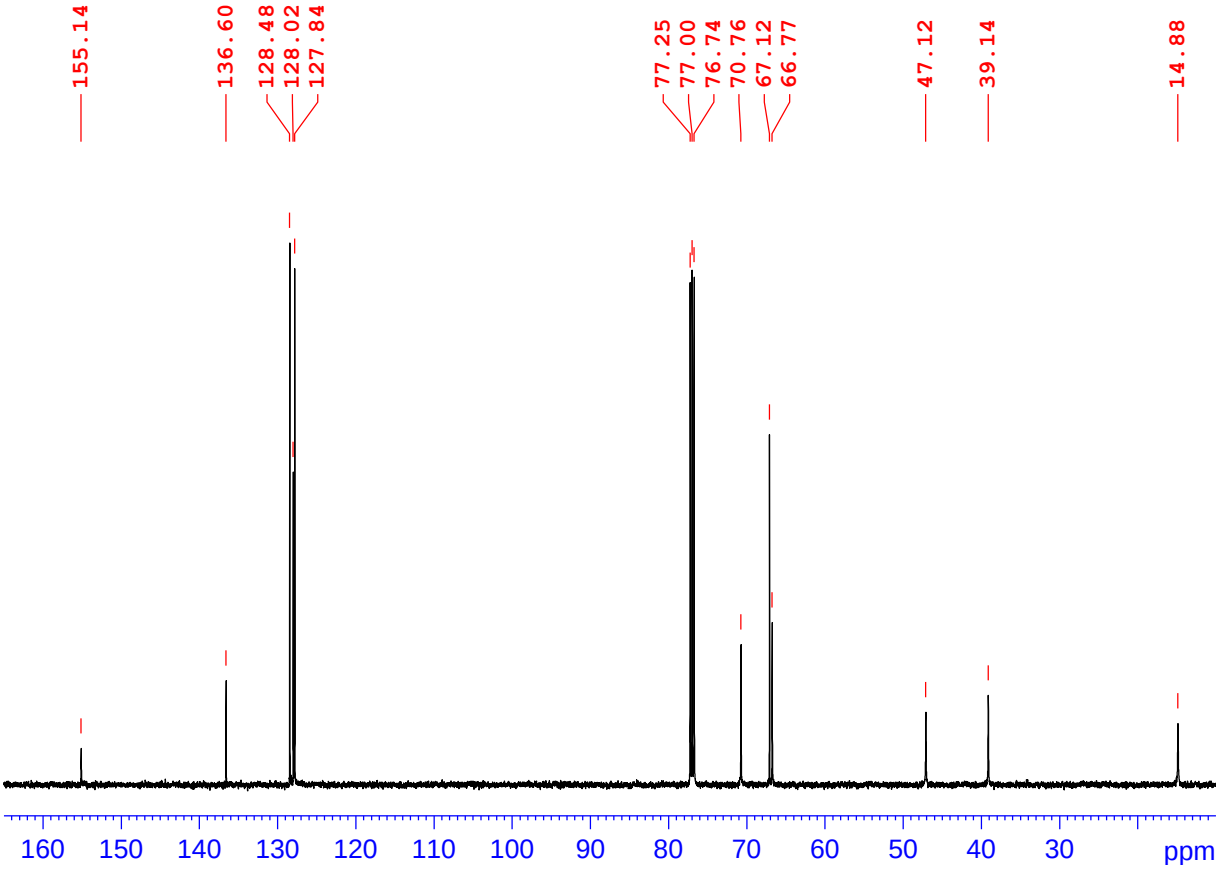
^{1}H NMR (500 MHz, [D$_6$]DMSO, 100 °C) of amide (*R,R*)-**3e**.



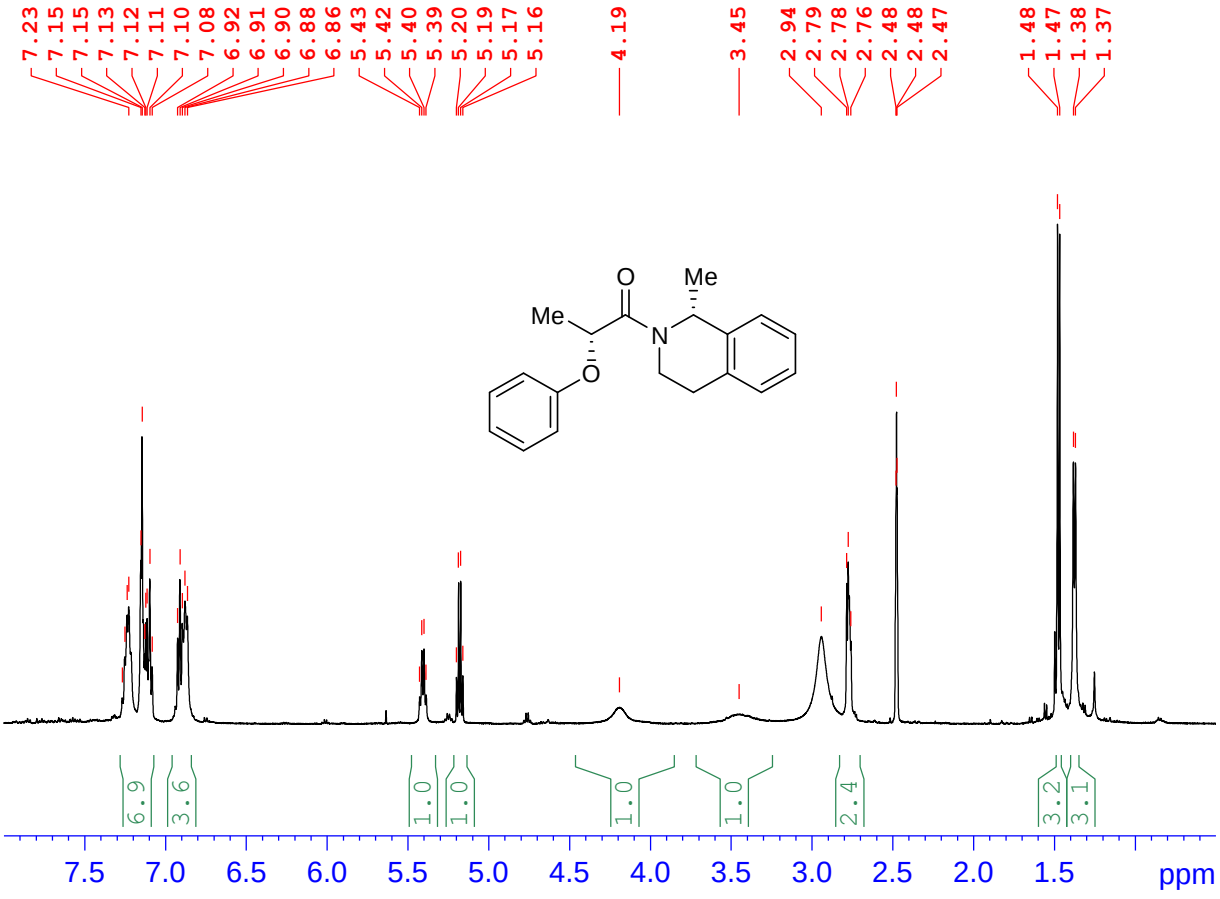
^{13}C NMR (126 MHz, [D$_6$]DMSO, 100 °C) of amide (*R,R*)-**3e**.



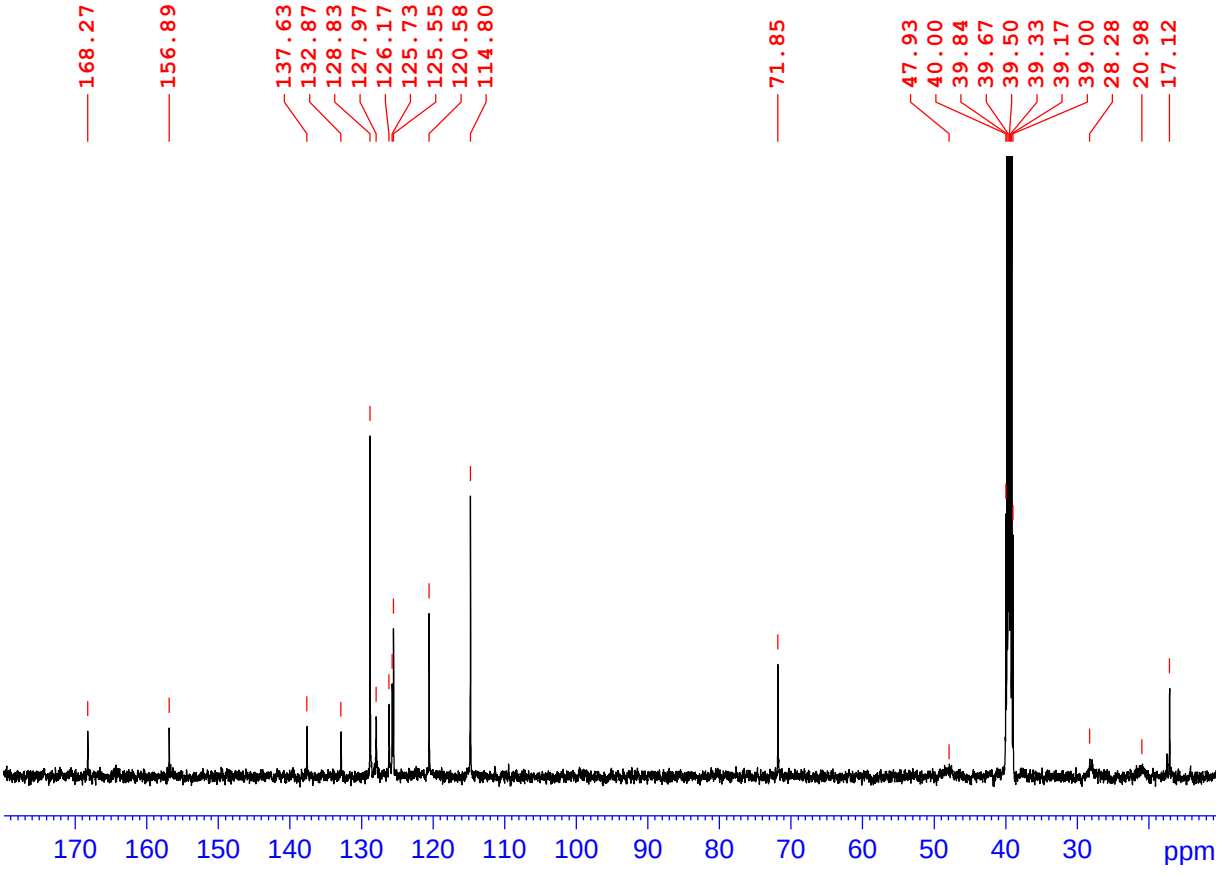
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4e**.



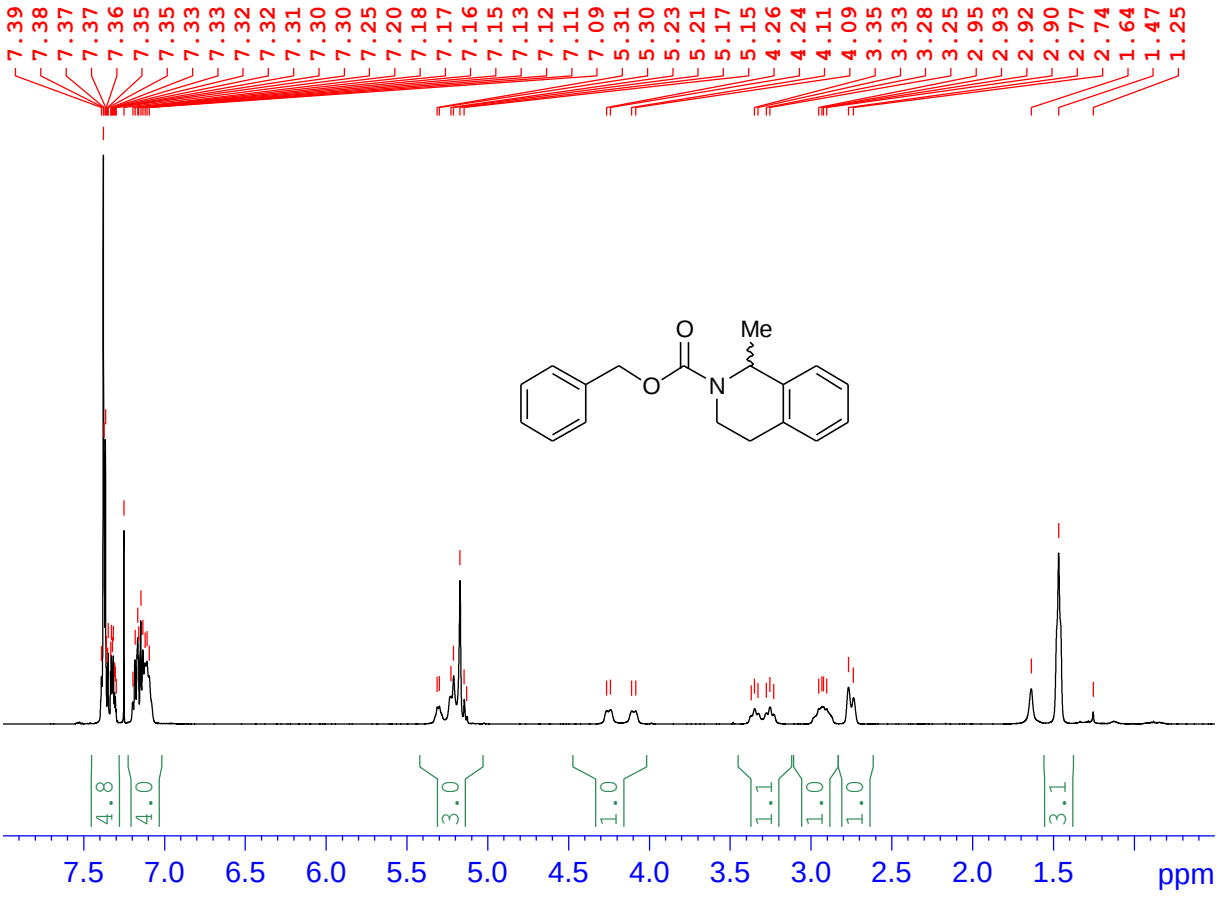
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4e**.



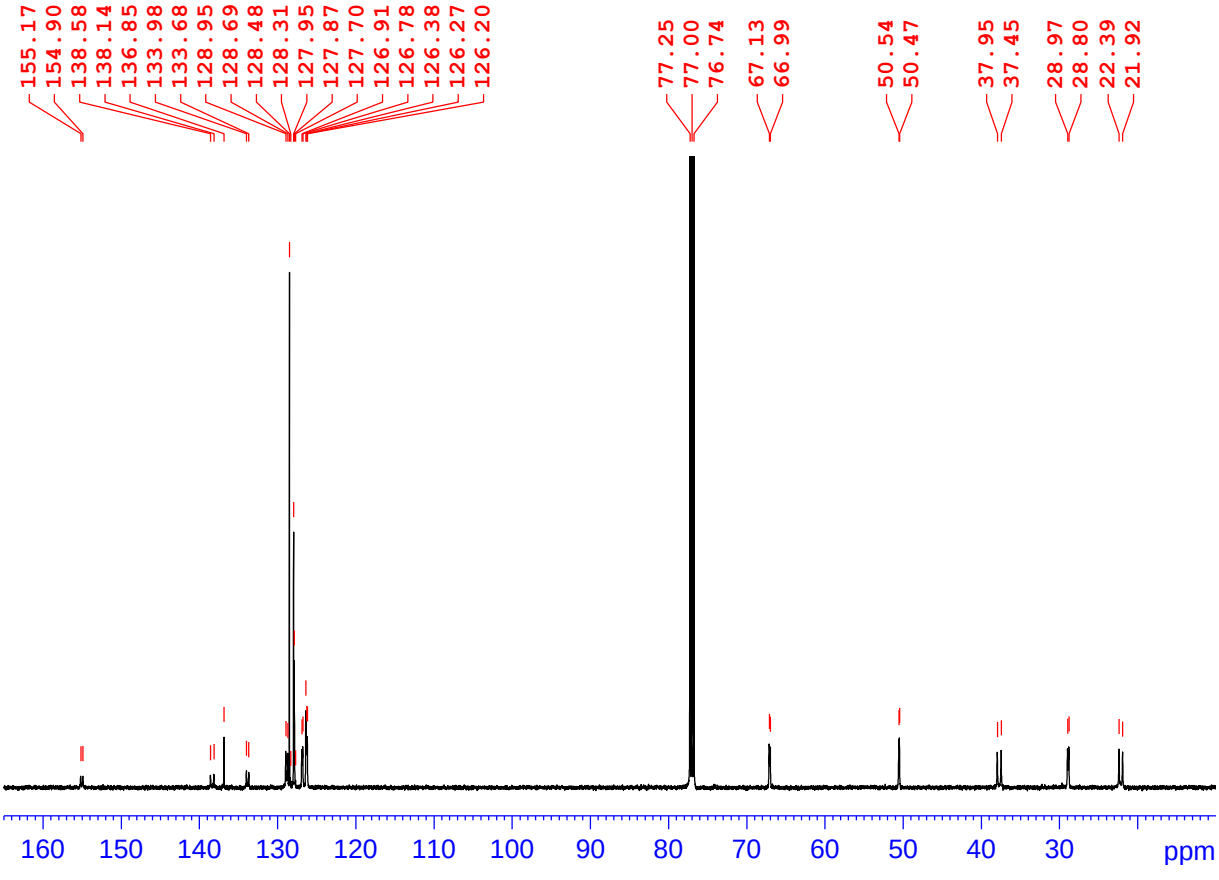
^{1}H NMR (500 MHz, [D_6]DMSO, 100 °C) of amide (*R,R*)-**3f**.



^{13}C NMR (126 MHz, [D_6]DMSO, 100 °C) of amide (*R,R*)-**3f**.

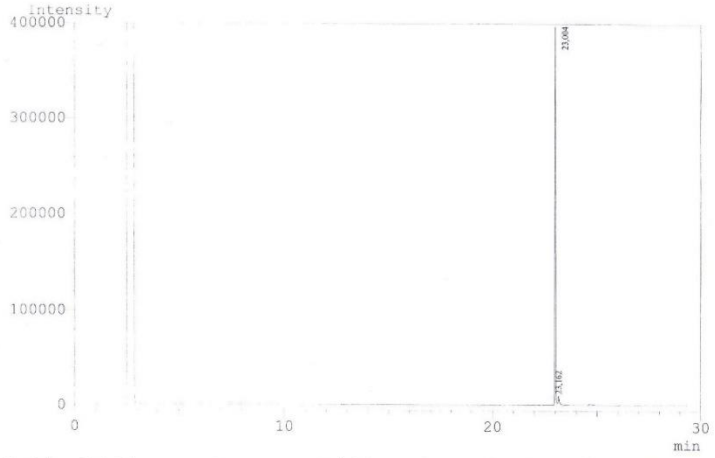


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4f**.



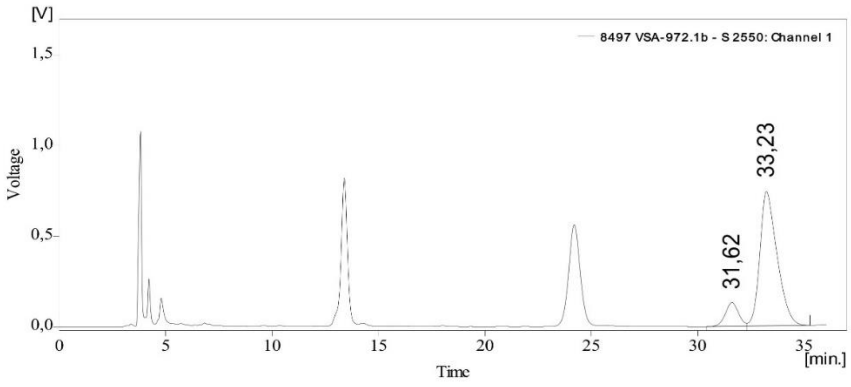
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4f**.

Selected GC and HPLC chromatograms



Peak#	Ret.Time	Area	Height	Площадь%	Высота%	Conc.
1	23,004	939199	393157	97,3922	98,0551	97,392
2	23,162	25148	7798	2,6078	1,9449	2,608
Сумма		964347	400955	100,0000	100,0000	100,000

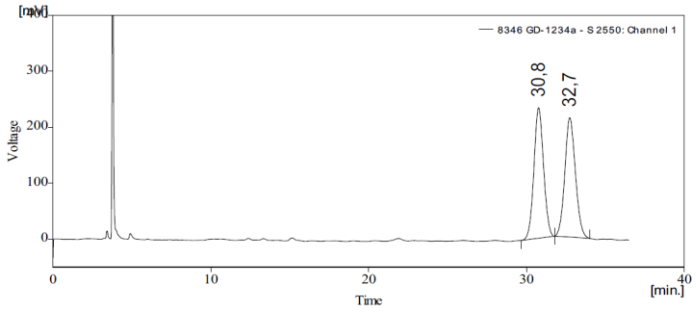
GC of compound (*R,R*)-**3a** (Shimadzu GC-2010, ZB-5 capillary column (30 m × 0.25 mm × 0.25 µm)): $t_{(R,R)\text{-}\mathbf{3a}}$ = 23.00 min, $t_{(R,S)\text{-}\mathbf{3a}}$ = 23.16 min (94.8% *de*)



Result Table (Uncal - 8497 VSA-972.1b - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	31,617	5637,047	130,764	11,9	15,0	0,67
2	33,233	41771,292	743,280	88,1	85,0	0,87
	Total	47408,339	874,044	100,0	100,0	

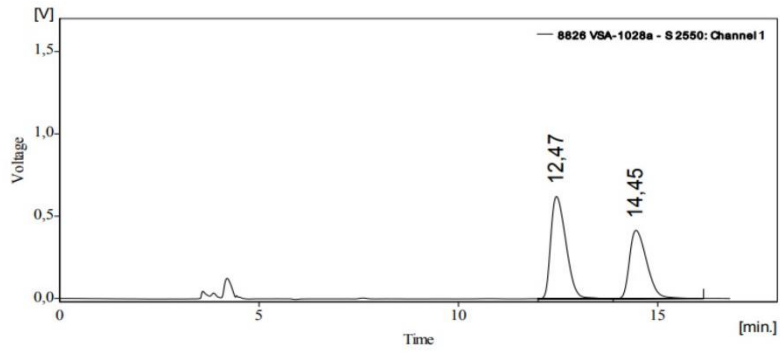
HPLC of compound (*S*)-**4a** (Knauer Smartline-1100, *S,S*-Whelk O1 column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 5:1): $t_{(R)\text{-}\mathbf{4a}}$ = 31.6 min, $t_{(S)\text{-}\mathbf{4a}}$ = 33.2 min (76.2% *ee*)



Result Table (Uncal - 8346 GD-1234a - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	30,767	9898,810	233,360	49,9	52,2	0,68
2	32,733	9937,382	213,385	50,1	47,8	0,72
	Total	19836,192	446,745	100,0	100,0	

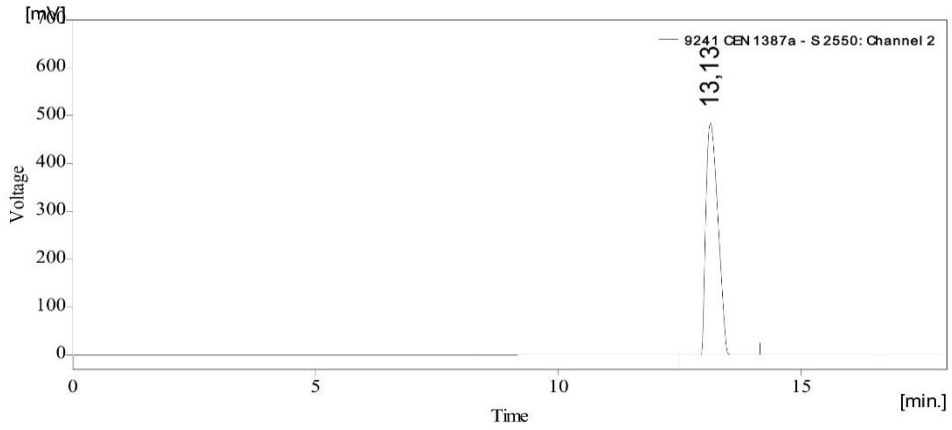
HPLC of compound (*RS*)-**4a** (Knauer Smartline-1100, *S,S*-Whelk O1 column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 5:1): $t_{(R)\text{-}\mathbf{4a}}$ = 30.8 min, $t_{(S)\text{-}\mathbf{4a}}$ = 32.7 min



Result Table (Uncal - 8826 VSA-1028a - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	12,467	16414,614	620,722	56,9	59,9	0,43
2	14,450	12413,546	414,797	43,1	40,1	0,48
	Total	28828,160	1035,519	100,0	100,0	

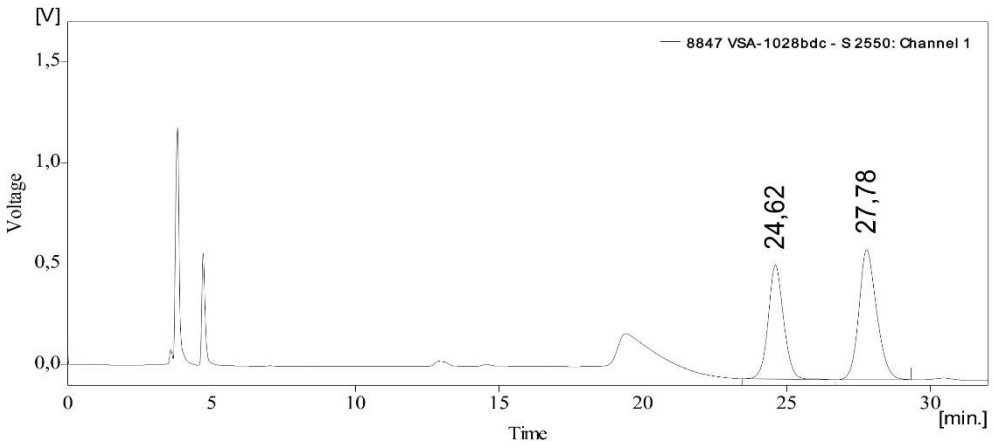
HPLC of compound (*R,R*)-**3b** (Knauer Smartline-1100, Chiralcel OD-H column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 40:1): $t_{(R,R)\text{-}\mathbf{3b}}$ = 12.5 min, $t_{(R,S)\text{-}\mathbf{3b}}$ = 14.4 min (13.8% *de*)



Result Table (Uncal - 9241 CEN 1387a - S 2550: Channel 2)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	13,133	8336,878	484,176	100,0	100,0	0,30
	Total	8336,878	484,176	100,0	100,0	

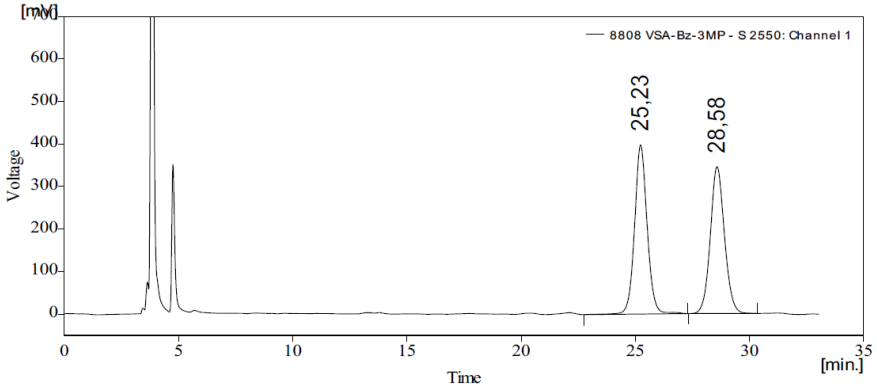
HPLC of compound (*R,R*)-**3b** (Knauer Smartline-1100, Chiralcel OD-H column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 40:1): $t_{(R,R)\text{-}\mathbf{3b}}$ = 13.1 min (>99% *de*)



Result Table (Uncal - 8847 VSA-1028bdc - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	24,617	21052,461	564,752	43,2	46,7	0,57
2	27,783	27658,739	644,406	56,8	53,3	0,67
	Total	48711,200	1209,158	100,0	100,0	

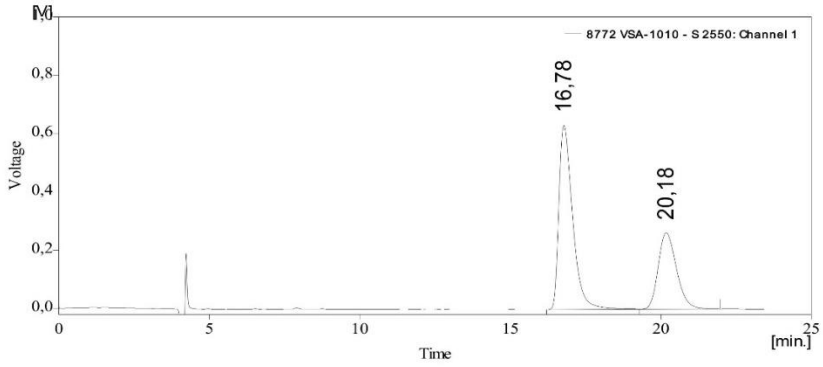
HPLC of compound (*S*)-**4b** (Knauer Smartline-1100, *S,S*-Whelk O1 column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 5:1): $t_{(R)\text{-}\mathbf{4b}}$ = 24.6 min, $t_{(S)\text{-}\mathbf{4b}}$ = 27.8 min (13.6% *ee*)



Result Table (Uncal - 8808 VSA-Bz-3MP - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	25,233	15289,863	398,055	50,6	53,5	0,58
2	28,583	14911,209	345,784	49,4	46,5	0,67
	Total	30201,072	743,838	100,0	100,0	

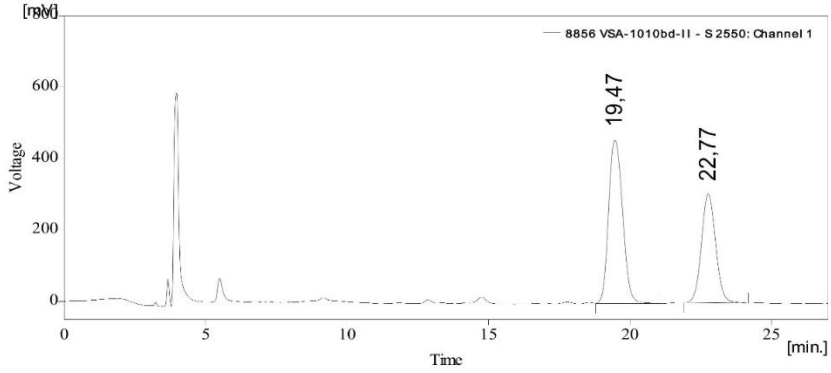
HPLC of compound (*RS*)-**4b** (Knauer Smartline-1100, *S,S*-Whelk O1 column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 5:1): $t_{(R)\text{-}\mathbf{4b}}$ = 25.2 min, $t_{(S)\text{-}\mathbf{4b}}$ = 28.6 min



Result Table (Uncal - 8772 VSA-1010 - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	16,783	20207,351	632,442	64,6	70,7	0,50
2	20,183	11085,685	262,202	35,4	29,3	0,67
	Total	31293,037	894,644	100,0	100,0	

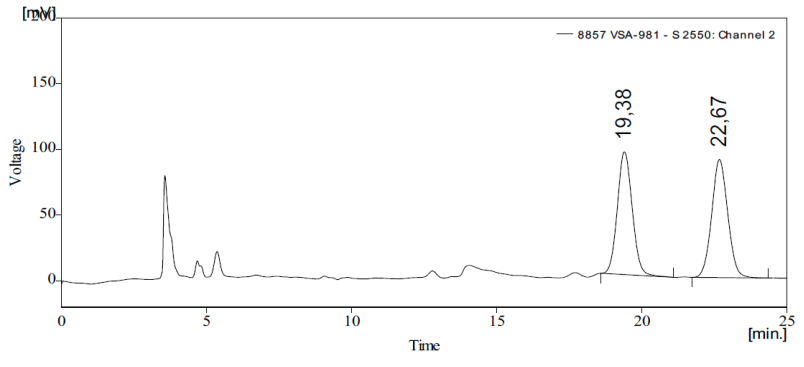
HPLC of compound (*R,R*)-**3c** (Knauer Smartline-1100, Chiralcel OD-H column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 40:1): $t_{(R,R)\text{-}\mathbf{3c}}$ = 16.8 min, $t_{(R,S)\text{-}\mathbf{3c}}$ = 20.2 min (29.2% *de*)



Result Table (Uncal - 8856 VSA-1010bd-II - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	19,467	15711,668	456,537	59,7	60,0	0,55
2	22,767	10606,020	304,671	40,3	40,0	0,55
	Total	26317,668	761,208	100,0	100,0	

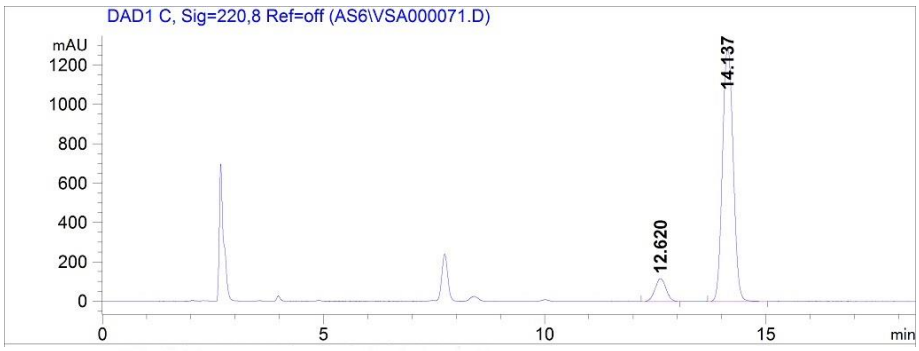
HPLC of compound (*S*)-**4c** (Knauer Smartline-1100, *S,S*-Whelk O1 column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 10:1): $t_{(S)\text{-}\mathbf{4c}}$ = 19.5 min, $t_{(R)\text{-}\mathbf{4c}}$ = 22.8 min (19.4% *ee*)



Result Table (Uncal - 8857 VSA-981 - S 2550: Channel 2)

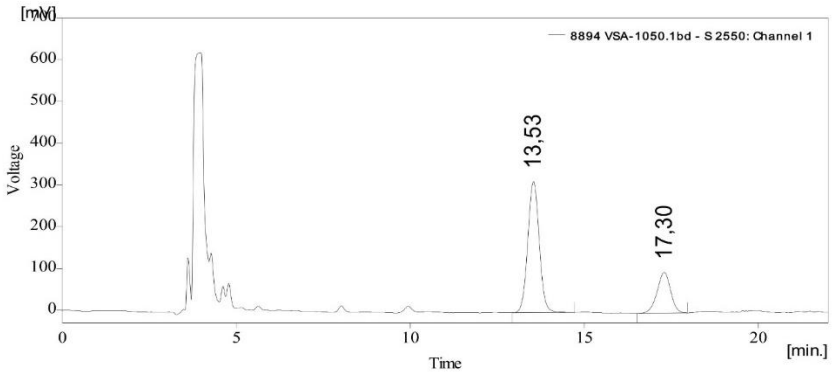
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	19,383	3329,883	93,340	49,1	50,9	0,57
2	22,667	3457,750	89,901	50,9	49,1	0,60
	Total	6787,633	183,241	100,0	100,0	

HPLC of compound (*RS*)-**4c** (Knauer Smartline-1100, *S,S*-Whelk O1 column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 10:1): $t_{(S)\text{-}\mathbf{4c}}$ = 19.4 min, $t_{(R)\text{-}\mathbf{4c}}$ = 22.7 min



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.620	BV	0.2692	2020.74329	116.02704	8.5366
2	14.137	BB	0.2667	2.16508e4	1284.08923	91.4634
Totals :				2.36716e4	1400.11627	

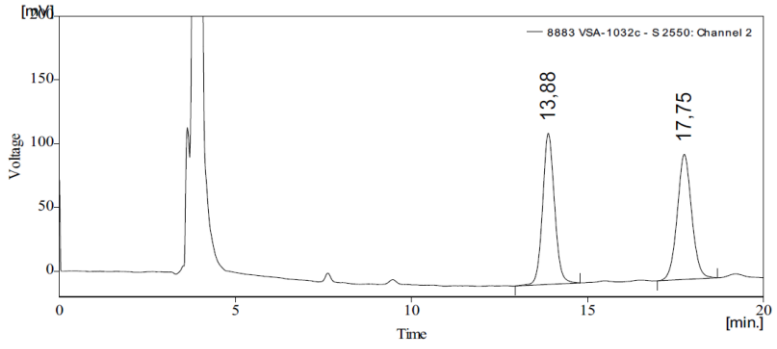
HPLC of compound (*R,R*)-**3d** (Agilent 1100, Kromasil 100-5 C18 column (250 × 4.6 mm), detection at 220 nm, 0.8 mL/min flow rate, MeCN/H_2O, 55:45): $t_{(R,S)\text{-}\mathbf{3d}}$ = 12.6 min, $t_{(R,R)\text{-}\mathbf{3d}}$ = 14.1 min (82.9% *de*)



Result Table (Uncal - 8894 VSA-1050.1bd - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	13,533	7229,460	314,262	73,3	76,3	0,37
2	17,300	2630,137	97,496	26,7	23,7	0,43
	Total	9859,597	411,759	100,0	100,0	

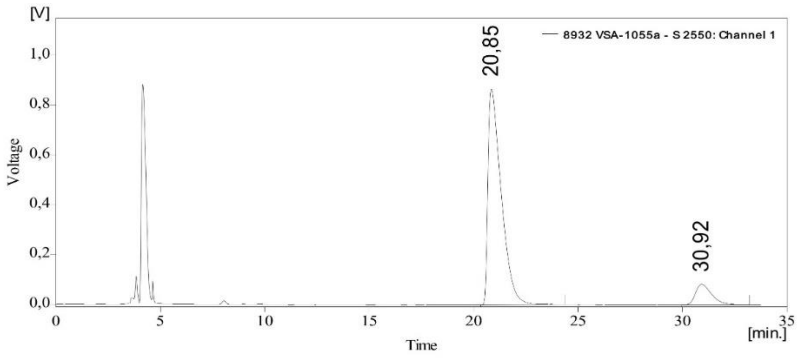
HPLC of compound (*S*)-**4d** (Knauer Smartline-1100, *S,S*-Whelk O1 column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 10:1): $t_{(S)\text{-}\mathbf{4d}}$ = 13.5 min, $t_{(R)\text{-}\mathbf{4d}}$ = 17.3 min (46.6% *ee*)



Result Table (Uncal - 8883 VSA-1032c - S 2550: Channel 2)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	13,883	2788,016	118,554	49,9	54,7	0,38
2	17,750	2799,685	98,153	50,1	45,3	0,45
	Total	5587,701	216,707	100,0	100,0	

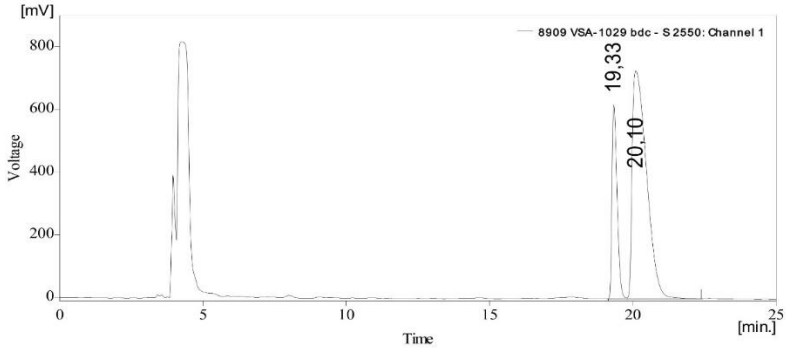
HPLC of compound (*RS*)-**4d** (Knauer Smartline-1100, *S,S*-Whelk O1 column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 10:1): $t_{(S)\text{-}\mathbf{4d}}$ = 13.9 min, $t_{(R)\text{-}\mathbf{4d}}$ = 17.8 min



Result Table (Uncal - 8932 VSA-1055a - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	20,850	38263,853	866,227	89,6	91,3	0,68
2	30,917	4449,195	82,171	10,4	8,7	0,83
	Total	42713,047	948,398	100,0	100,0	

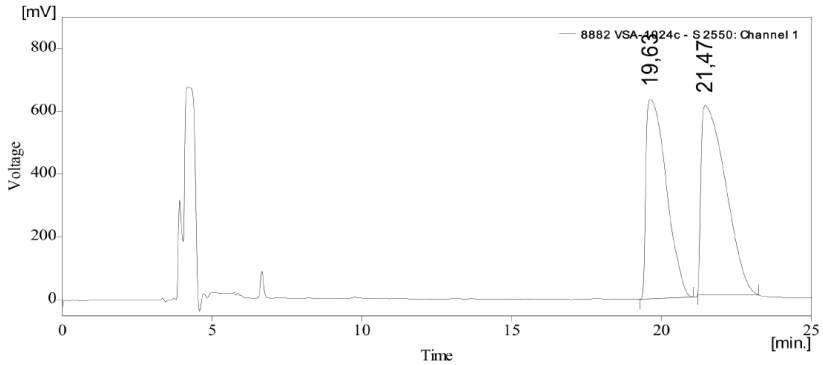
HPLC of compound (*R,R*)-**3e** (Knauer Smartline-1100, Chiralcel OD-H column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 40:1): $t_{(R,R)\text{-}\mathbf{3e}}$ = 20.8 min, $t_{(R,S)\text{-}\mathbf{3e}}$ = 30.9 min (79.2% *de*)



Result Table (Uncal - 8909 VSA-1029 bdc - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	19,333	7706,474	617,954	23,4	45,9	0,22
2	20,100	25277,951	727,551	76,6	54,1	0,57
	Total	32984,425	1345,505	100,0	100,0	

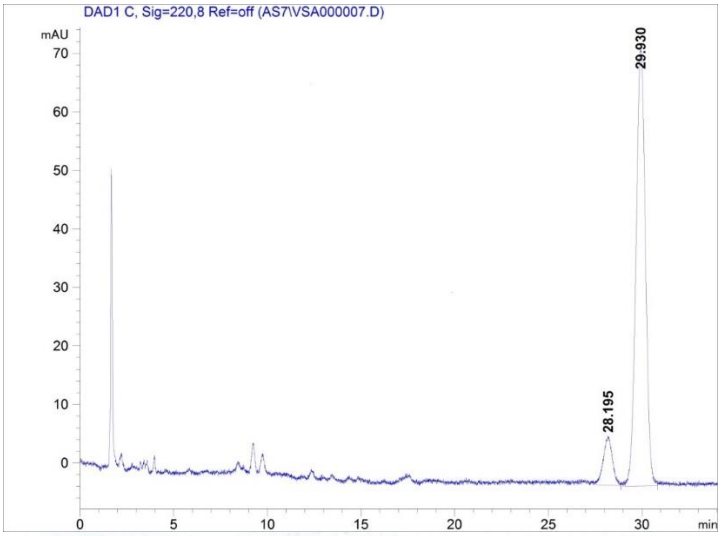
HPLC of compound (*S*)-**4e** (Knauer Smartline-1100, Chiralcel OD-H column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH/MeOH, 40:0.4:0.1): $t_{(R)\text{-}\mathbf{4e}}$ = 19.3 min, $t_{(S)\text{-}\mathbf{4e}}$ = 20.1 min (53.2% *ee*)



Result Table (Uncal - 8882 VSA-1024c - S 2550: Channel 1)

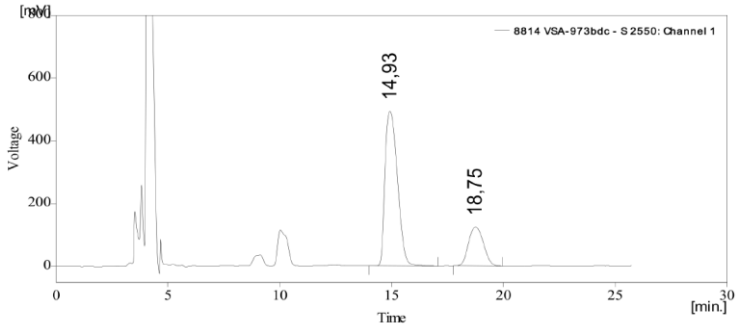
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	19,633	31108,577	634,243	48,4	51,3	0,77
2	21,467	33165,148	601,993	51,6	48,7	0,97
	Total	64273,543	1236,236	100,0	100,0	

HPLC of compound (*RS*)-**4e** (Knauer Smartline-1100, Chiralcel OD-H column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH/MeOH, 40:0.4:0.1): $t_{(R)\text{-}\mathbf{4e}}$ = 19.6 min, $t_{(S)\text{-}\mathbf{4e}}$ = 21.5 min



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.195	BB	0.4084	260.63734	8.22334	9.0220
2	29.930	VB	0.4418	2628.27129	74.58132	90.9780
Totals :				2888.90863	82.80466	

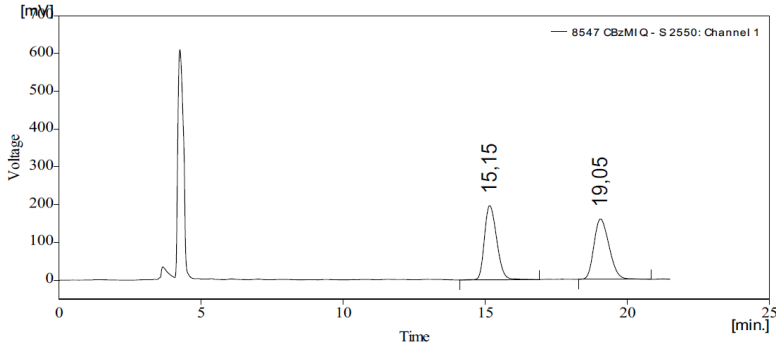
HPLC of compound (*R,R*)-**3f** (Agilent 1100, Phenomenex Luna C18(2) (250 × 4.6 mm), detection at 220 nm, 0.8 mL/min flow rate, MeCN/H_2O, 48:52): $t_{(R,S)\text{-}\mathbf{3f}}$ = 28.2 min, $t_{(R,R)\text{-}\mathbf{3d}}$ = 29.9 min (82.0% *de*)



Result Table (Uncal - 8814 VSA-973bdc - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	14,933	19252,164	491,896	77,5	79,9	0,63
2	18,750	5589,338	123,717	22,5	20,1	0,78
	Total	24841,502	615,613	100,0	100,0	

HPLC of compound (*S*)-**4f** (Knauer Smartline-1100, Chiralcel OD-H column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 40:1): $t_{(S)\text{-}\mathbf{4f}}$ = 14.9 min, $t_{(R)\text{-}\mathbf{4f}}$ = 18.8 min (55.0% *ee*)



Result Table (Uncal - 8547 CBzMIQ - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	15,150	5908,639	196,767	49,8	55,2	0,48
2	19,050	5944,443	159,915	50,2	44,8	0,60
	Total	11853,082	356,682	100,0	100,0	

HPLC of compound (*RS*)-**4f** (Knauer Smartline-1100, Chiralcel OD-H column (250 × 4.6 mm), detection at 220 nm, 1 mL/min flow rate, *n*-hexane/*i*PrOH, 40:1): $t_{(S)\text{-}\mathbf{4f}}$ = 15.2 min, $t_{(R)\text{-}\mathbf{4f}}$ = 19.0 min

Computational details

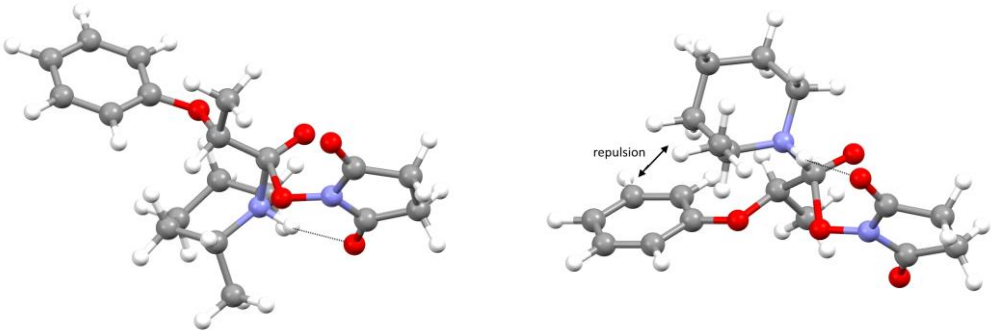
Graphic modelling and primary optimisation of the transition state (TS) geometry were performed by the Ammp and Mopac methods using the VEGA ZZ program set.[S10] All DFT calculations were performed using ORCA 4.0.1 program.[S11] The solvent effects were simulated using a conductive-type polarizable continuum model (CPCM solvation model[S12] in ORCA 4.0.1, CPCMC version). Corrections for dispersion effects were introduced according to the semiempirical scheme of pairwise Grimme correction (D3).[S13]

In order to determine the reaction mechanism, D3-corrected final single point energy (E_{FSP}) was calculated at the BLYP-D3/TZVP level of theory in CH_2Cl_2 with increasing N–C(O) bond length (from TS to reagents) and separately with increasing O–C(O) bond length (from TS to products) in the **1d**–**2a** system (Tables S2 and S3). The geometries and energies (E_{FSP}) of reagents, reagent complexes, TSs, and product complexes (only for **1d**–**2a**) were calculated using the hybrid B3LYP functional[S14] with the def2-SVP and def2-TZVP Ahlrich basis sets.[S15] At the first stage, TS search and Hessian calculations in gas phase were performed using B3LYP-D3-gCP/def2-SVP with changing length of the crucial N–CO bond. At every optimization step, single point energies E_{FSP} were calculated at the B3LYP-D3-gCP/def2-SVP level of theory using D3 and geometrical counterpoise (gCP) correction of basis set superposition error.[S16] Efficient numerical integration was performed with a integration grid (Grid 4). To speed up the calculation of the exchange integrals HF, the RIJCOSX[S11b, S17] approximation was used.

Subsequent optimization of the geometry of the ground and transition states (OptTS function), numerical calculation of vibration frequencies, and calculation of energy parameters of solvated structures were performed with the def2-TZVP basis set in a solvent (CPCMC-Solvent-B3LYP-D3-gCP/def2-TZVP//B3LYP-D3-gCP/def2-SVP general level of theory). We applied very tight convergence criteria when optimizing the geometry at this stage. The total thermal energy at 253 and 293 K was calculated as the sum of the total electronic energy, nonthermal energy of zero-point vibrations, and thermal corrections for oscillatory, rotational, and transfer motion. The entropy parameter corresponding to the symmetry number n = 1 was used, because all the reagents are chiral compounds.[S18]

The 3D structures of molecules as a result of the calculation were visualized using the ChemCraft software package.[S19] ChemCraft's animation of only one negative imaginary frequency has confirmed that the saddle points found in the optimization process are indeed transition states. All basic states of reagents, products, reagent complexes, and product complexes do not have negative imaginary frequencies.

Favoured ***Disfavoured***



TS-(*R*)-**1d**–(*R*)-**2a**-*ax* TS-(*R*)-**1d**–(*S*)-**2a**-*ax*

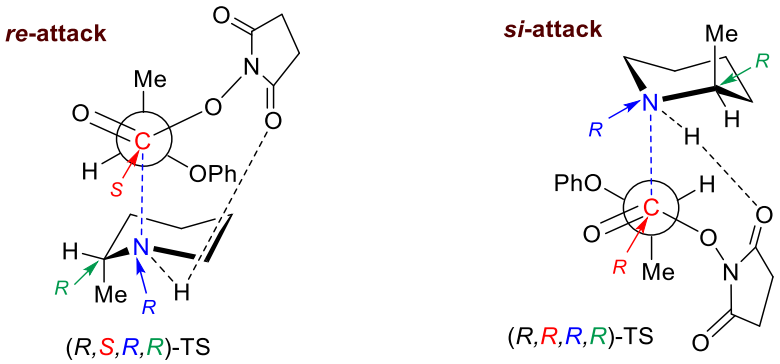
Stereoselection:

- Felkin-Ahn approach of N-heterocycle
- stabilisation *via* H-bonding between NH and O=C
- chiral center of amine is in the *trans*-position relative to carbonyl O atom
- axial N lone pair reacts
- non-covalent interactions between piperidine CH_2 and Ph of ester

Figure S1 Schematic representation of the TS-(*R*)-**1d**–(*R*)-**2a**-*ax* and TS-(*R*)-**1d**–(*S*)-**2a**-*ax* transition states and the most important factors determining the stereoselectivity of acylation of amine **2a** with ester (*R*)-**1d**.

Table S2 Relative total electronic energies (E_{rel}) of the most stable conformations, TS-(*R*)-**1d**–(*R*)-**2a** and TS-(*R*)-**1d**–(*S*)-**2a**, and the corresponding relative Gibbs free energies (G_{rel}) at 298.15 K in the gas phase at the B3LYP-D3-gCP/def2-SVP level of theory

TS-(*R*)-**1d**–(*R*)-**2a**



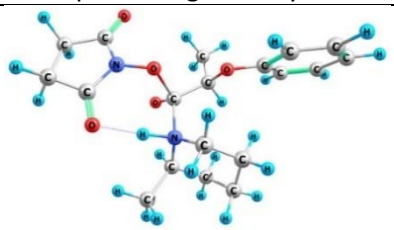
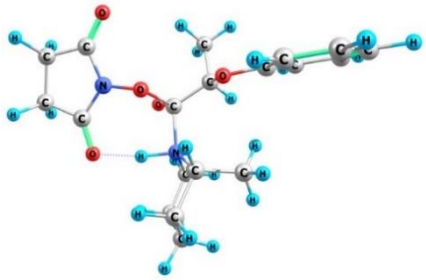
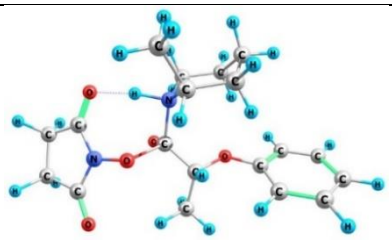
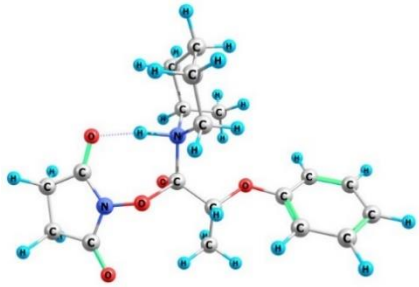
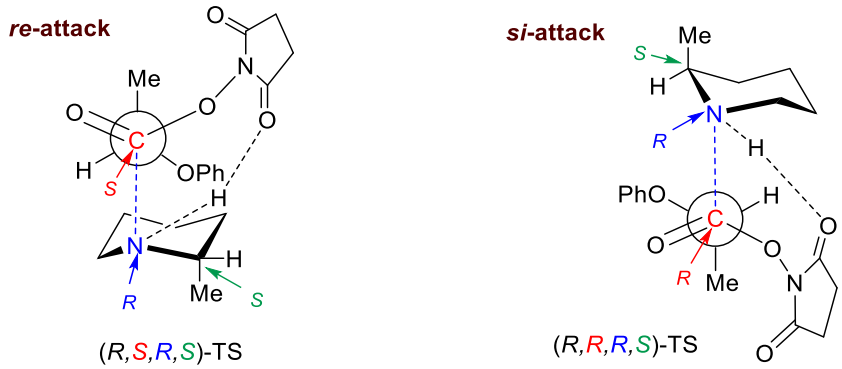
Configuration	DFT-optimized geometry	E_{rel}, kJ/mol	G_{rel}, kJ/mol
R,S,R,R-ax		12.56	11.89
R,S,S,R-eq		17.00	17.16
R,R,R,R-ax		0	0
R,R,S,R-eq		1.07	–1.09

Table S2 (*continued*)

TS-(*R*)-**1d**–(*S*)-**2a**



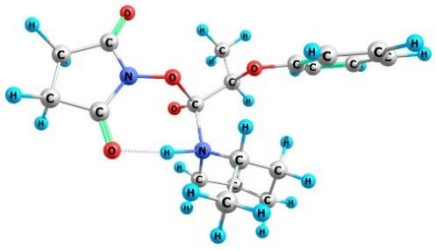
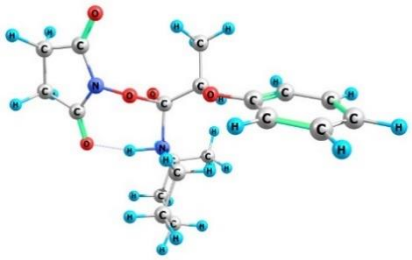
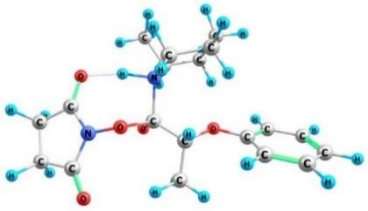
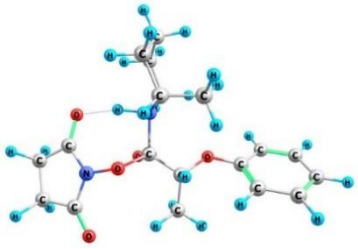
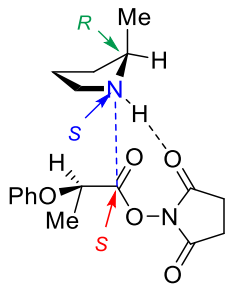
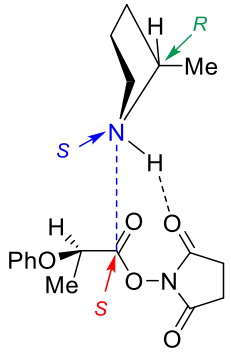
Configuration	DFT-optimized geometry	E_{rel}, kJ/mol	G_{rel}, kJ/mol
R,*S*,*S*,*S*-*ax*		19.23	16.39
R,*S*,*R*,*S*-*eq*		0	0
R,*R*,*S*,*S*-*ax*		6.36	5.34
R,*R*,*R*,*S*-*eq*		6.62	6.46

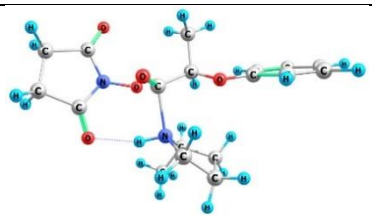
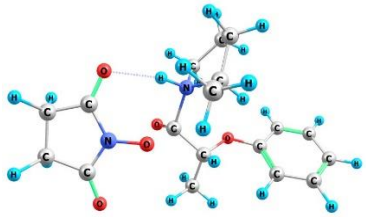
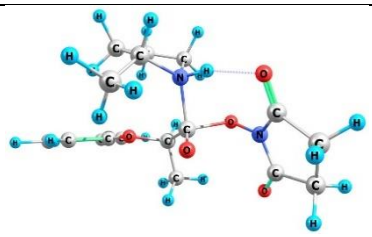
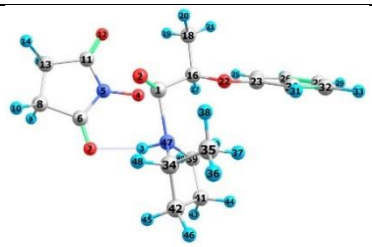
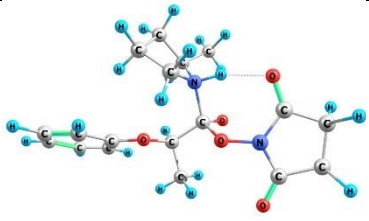
Table S3-1 Relative total electronic energies (E_{rel}) and relative Gibbs free energies (G_{rel}) of TS-(*R*)-**1d**–(*R*)-**2c** at 298.15 K in the gas phase at the B3LYP-D3-gCP/def2-SVP level of theory



TS-(*R*)-**1d**--(*R*)-**2c**-*ax*



TS-(*R*)-**1d**--(*R*)-**2c**-*eq*

Configuration	Amine attack	DFT-optimized geometry	E_{rel}, kJ/mol	G_{rel}, kJ/mol	% in the Maxwell-Boltzmann distribution over *G*
R,R,R,R-ax	*si*		0	0	13
R,R,R,R-eq	*si*		–3.98	0.31	13
R,R,S,R-ax	*si*		8.42	13.07	12
R,R,S,R-eq	*si*		4.10	7.61	13
R,S,R,R-ax	*re*		6.38	9.09	13

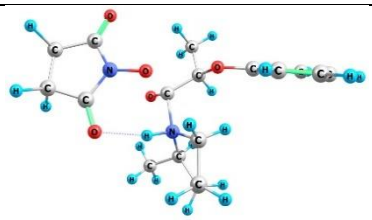
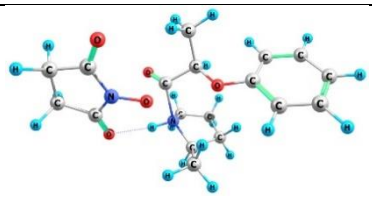
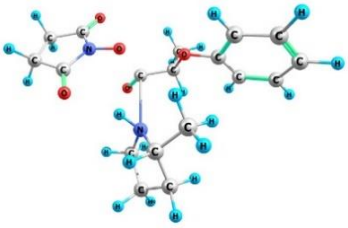
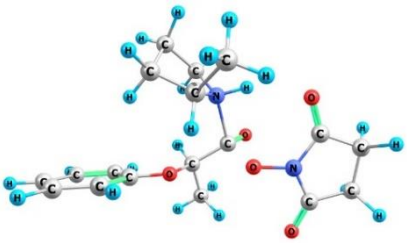
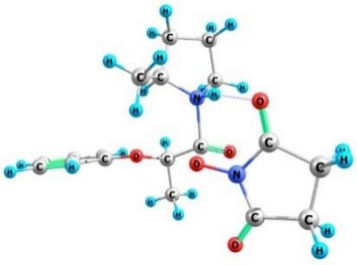
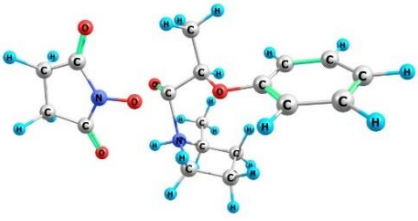
R,S,R,R-eq	*re*		15.46	16.80	12
R,S,S,R-ax	*re*		23.11	25.73	12
R,S,S,R-eq	*re*		35.25	17.99	12

Table S3-2 Relative total electronic energies (E_{rel}) of TS-(*R*)-**1d**–(*S*)-**2c** at 298.15 K in the gas phase at the B3LYP-D3-gCP/def2-SVP and CPCMC-CH_2Cl_2-B3LYP-D3-gCP/def2-TZVP//B3LYP-D3-gCP/def2-SVP levels of theory

Configuration	Amine attack	DFT-optimized geometry	E_{rel}, kJ/mol (def2-SVP)	E_{rel}, kJ/mol (def2- TZVP)	% in the Maxwell-Boltzmann distribution over *G*
R,S,S,S-ax	*re*		0	0	15
R,S,S,S-eq	*re*		8.51	-	14
R,S,R,S-ax	*re*		8.59	-	14

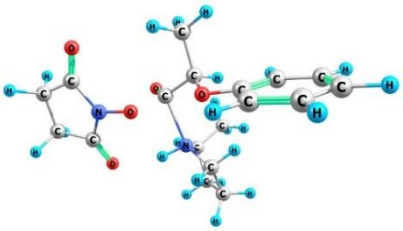
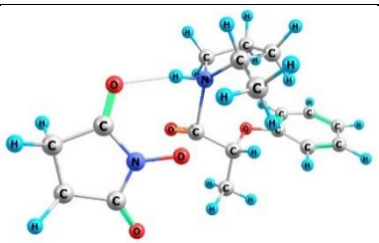
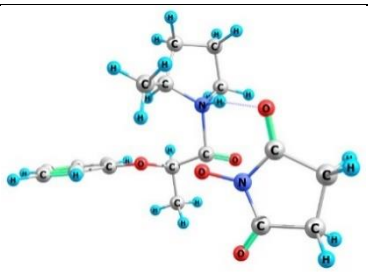
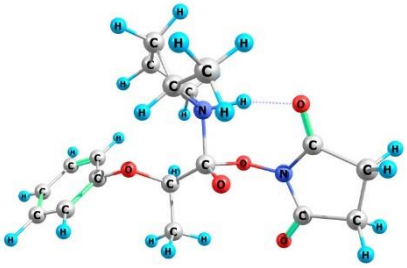
R,S,R,S-eq	*re*		4.56	9.89	14
R,R,R,S-ax	*si*		3.02	-	14
R,R,R,S-eq	*si*		8.30	10.78	14
R,R,S,S-eq	*si*		0.71	1.05	15
R,R,S,S-ax	transformed to *R,R,S,S-eq* during optimization				

Table S4 Calculated parameters for reagents **1d** and **2a**, reagent complexes (**RCs**), transition states (**TSs**), and product complexes (**PCs**) at 293 and 253 K in CH_2Cl_2 at the CPCMC-CH_2Cl_2-B3LYP-D3-gCP/def2-TZVP//B3LYP-D3-gCP/def2-SVP level of theory (amide (*R*,*R*)-**3a** predominates in the reaction product; a model with axial lone electron pair at N atom of amine **2a** was used)

Structure	E_{FSP}, au (absolute energy)	Relative energies					
		H, kJ/mol		*G*, kJ/mol		$\Delta G^{\#} = (G_{TS} - G_{RC})$, kJ/mol	
		293 K	253 K	293 K	253 K	293 K	253 K
Reagents	−1225.11797982	0	0	0	0		
(*R*,*R*)-**RC**	−1225.13101149	−24.52	−25.39	26.82	19.12		
(*R*,*R*)-**TS**	−1225.12184009	0.58	0.16	62.21	53.59	35.39	34.47
(*R*,*R*)-**PC**	−1225.14688399	−65.80	−66.43	−7.35	−15.80		
(*R*,*R*)-**3a** + SuOH	−1225.14245242	−58.41	−58.82	−59.91	−59.61		
(*R*,*S*)-**RC**	−1225.12946470	−23.92	−24.48	29.50	21.54		
(*R*,*S*)-**TS**	−1225.11718826	11.36	10.35	71.77	63.27	42.27	41.73
(*R*,*S*)-**PC**	−1225.15520091	−86.17	−87.08	−32.70	−40.68		
(*R*,*S*)-**3a** + SuOH	−1225.14349455	−61.55	−61.98	−62.64	−62.32		
						$\Delta\Delta G^{\#}$ = 6.88 kJ/mol[a]	$\Delta\Delta G^{\#}$ = 7.26 kJ/mol[b]

[a] Experimental $\Delta\Delta G^{\#}_{293}$ = 6.90 kJ/mol. [b] Experimental $\Delta\Delta G^{\#}_{253}$ = 7.29 kJ/mol

Table S5-1 Calculated parameters for reagent complexes (**RCs**) and transition states (**TSs**) for reaction of reagents **1d** and **2c** at 293 and 253 K in CH_2Cl_2 at the CPCMC-CH_2Cl_2-B3LYP-D3-gCP/def2-TZVP//B3LYP-D3-gCP/def2-SVP level of theory (amide (*R*,*R*)-**3d** predominates in the reaction product; a model with axial lone electron pair at N atom of amine **2d** was used)

Structure	E_{FSP}, au (absolute energy)	Relative energies					
		H, kJ/mol		*G*, kJ/mol		$\Delta G^{\#} = (G_{TS} - G_{RC})$, kJ/mol	
		293 K	253 K	293 K	253 K	293 K	253 K
Reagents	−1185.809531412	0	0	0	0		
(*R*,*R*)-**RC**	−1185.82353409	−30.10	−30.69	24.17	16.26		
(*R*,*R*)-**TS**	−1185.81835826	−14.64	−15.08	43.62	35.42	19.45	19.16
(*R*,*S*)-**RC**	−1185.82140198	−24.48	−25.03	31.25	23.08		
(*R*,*S*)-**TS**	−1185.81668056	−12.05	−12.15	52.61	43.68	21.36	20.60
						$\Delta\Delta G^{\#}$ = 1.91 kJ/mol	$\Delta\Delta G^{\#}_{253}$ =1.44 kJ/mol

Table S5-2 Calculated parameters for reagent complexes (**RCs**) and transition states (**TSs**) for reaction of reagents **1d** and **2c** at 233 in toluene at the CPCMC-Solvent-B3LYP-D3-gCP/def2-TZVP//B3LYP-D3-gCP/def2-SVP level of theory (amide (*R*,*R*)-**3d** predominates in the reaction product; a model with axial lone electron pair at N atom of amine **2d** was used)

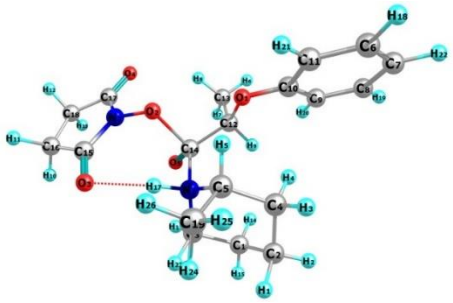
Structure	E_{FSP}, au (absolute energy)	Relative energies		
		H, kJ/mol	*G*, kJ/mol	$\Delta G^{\#} = (G_{TS} - G_{RC})$, kJ/mol
Reagents	−1185.79866461	0	0	
(*R*,*R*)-**RC**	−1185.81465952	−36.25	3.81	
(*R*,*R*)-**TS**	−1185.80871950	−19.64	27.84	24.03
(*R*,*S*)-**RC**	−1185.81263965	−33.32	8.24	
(*R*,*S*)-**TS**	−1185.80565837	−10.29	33.33	25.09
				$\Delta\Delta G^{\#}$ = 1.06 kJ/mol[a]

[a] Experimental $\Delta\Delta G^{\#}_{233}$ = 1.53 kJ/mol.

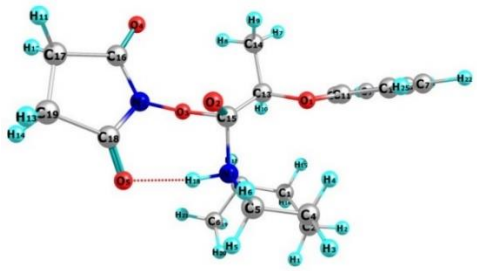
Table S6-1 Important geometry parameters of transition states in the reactions of ester (*R*)-**1d** with (*R*)- and (*S*)-enantiomers of amines **2a** and **2c**

Amine	Configuration of TS	Bond length, Å			Bond angle, deg.		
		N–C(O)	O–C(O)	NH···ON	N–C=O	O–C=O	N–C(O)–O
2a	TS-(*R*)-**1d**–(*S*)-**2a**	1.765	1.784	2.242	109.7	112.6	92.5
	TS-(*R*)-**1d**–(*R*)-**2a**	1.640	1.803	2.269	112.5	110.9	92.7
2c	TS-(*R*)-**1d**–(*S*)-**2c**	1.867	1.515	2.106	106.2	117.4	95.9
	TS-(*R*)-**1d**–(*R*)-**2c**	1.916	1.511	1.936	106.9	117.9	94.4

Table S6-2 Important geometry parameters of transition states in the reactions of ester (*R*)-**1d** with (*R*)- and (*S*)-enantiomers of amine **2a**



TS-(*R*)-**1d**–(*S*)-**2a**



TS-(*R*)-**1d**–(*R*)-**2a**

Configuration of TS	Dihedral angles, deg.				
TS-(*R*)-**1d**–(*S*)-**2a**	N1-C14-C12-O1	O1-C13-C14-O2	C*5-N1-C14-O5	C13-C12-C14-N1	N2-O2-C14-N1
	−55.6	42.7	167.6	−178.6	92.6
TS-(*R*)-**1d**–(*R*)-**2a**	N1–C15–C13-O1	O1–C13–C15–O2	C*3–N1–C15–O2	C14–C13–C15–N1	N2–O3–C15–N1
	−74.0	−170.7	178.9	167.3	105.3

Table S7-1 Dependence of D3-corrected final single point energy (E_{FSP}) on the N–CO bond length in (*R*)-**1d**–(*R*)-**2a** system (scanning "from TS to reagents") at the CPCMC-CH_2Cl_2-B3LYP-D3/def2-TZVP level of theory

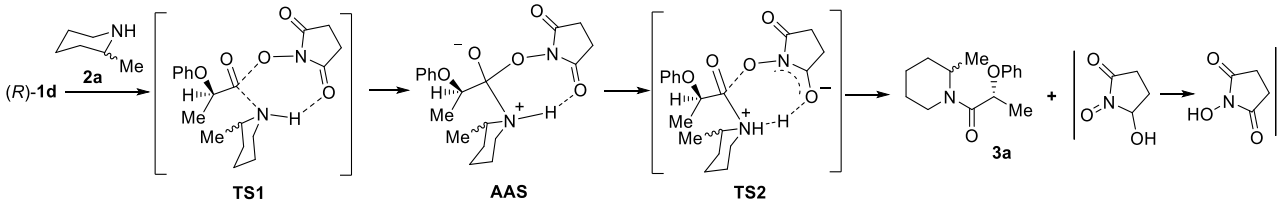
N–CO bond length Å	E_{FSP}, Hartree
1.6400	−1225.1590683
1.7053	−1225.1593357
1.7705	−1225.1596705
1.8358	−1225.1596903
1.9010	−1225.1597437
1.9663	−1225.1601722
2.0316	−1225.1608191
2.0968	−1225.1614237
2.1933	−1225.1618141
2.2867	−1225.1629472
2.3800	−1225.1639306
2.4733	−1225.1648976
2.5667	−1225.1657655
2.6600	−1225.1664394
2.7533	−1225.1667160
2.8467	−1225.1668916
2.9400	−1225.1664418
3.0333	−1225.1666570

Table S7-2 Dependence of D3-corrected final single point energy (E_{FSP}) on the O–CO bond length in (*R*)-**1d**–(*R*)-**2a** system (scanning "from TS to products") at the CPCMC-CH_2Cl_2-B3LYP-D3/def2-TZVP level of theory

O–CO bond length, Å	E_{FSP}, Hartree
1.803	−1225.1590683
2.000	−1225.160804
3.123	−1225.1822408
3.311	−1225.182144

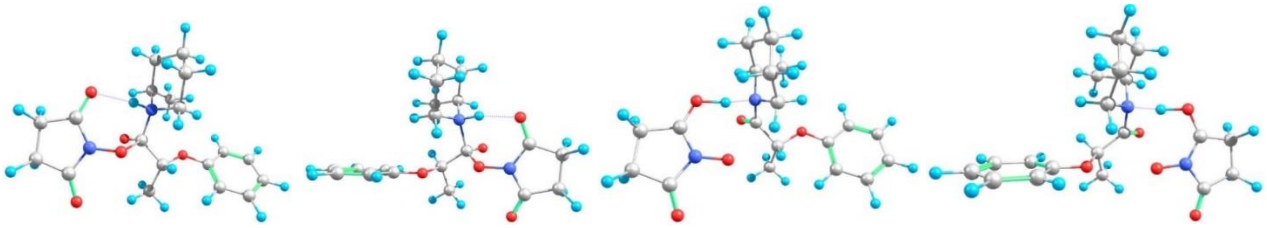
Simulation of the acylation reaction of amine 2a with ester (*R*)-1d proceeding by a plausible two-step mechanism *via* acyl ammonium salt

We performed the simulation of the acylation of amine **2a** with activated ester (*R*)-**1d** at the CPCMC-CH_2Cl_2-B3LYP-D3-gCP/def2-TZVP//B3LYP-D3-gCP/def2-SVP level of theory in accordance with a plausible two-step pathway involving the formation of an acyl ammonium salt (**AAS**) (Scheme S1). The formation of **AAS** proceeds through the **TS1** transition state followed by transformation of **AAS** into the reaction products through the **TS2** deprotonation transition state. This mechanism was calculated for structures with an equatorial lone electron pair at the amine nitrogen atom and the *trans*-position of proton at the amine N atom and the methyl group at the amine chiral center. The methyl group at the amine chiral center precisely in this conformation minimally interferes the deprotonation of the amine N atom from the carbonyl oxygen atom of the succinimide group in the (*R*,*S*,*R*,*S*)- and (*R*,*R*,*S*,*R*)-TSs.



Scheme S1 Plausible two-step pathway for acylation of amine **2a** with ester (*R*)-**1d**

Structures (*R*,*S*)-**AAS**, (*R*,*R*)-**AAS**, as well as (*R*,*S*)-**TS2** and (*R*,*R*)-**TS2** according to the results of DFT calculations at the CPCMC-CH_2Cl_2-B3LYP-D3-gCP/def2-TZVP//B3LYP-D3-gCP/def2-SVP level of theory are shown in Figure S2; calculated reaction coordinate, in Figure S3.



(*R*,*R*,*S*,*R*)-**AAS** (*R*,*S*,*R*,*S*)-**AAS** (*R*,*R*,*S*,*R*)-**TS2** (*R*,*S*,*R*,*S*)-**TS2**

Figure S2 Structures (*R*,*S*)-**AAS**, (*R*,*R*)-**AAS**, (*R*,*S*)-**TS2**, and (*R*,*R*)-**TS2** in the acylation of amine **2a** with ester (*R*)-**1d** *via* two-stage mechanism (CPCMC-CH_2Cl_2-B3LYP-D3-gCP/def2-TZVP//B3LYP-D3-gCP/def2-SVP level of theory).

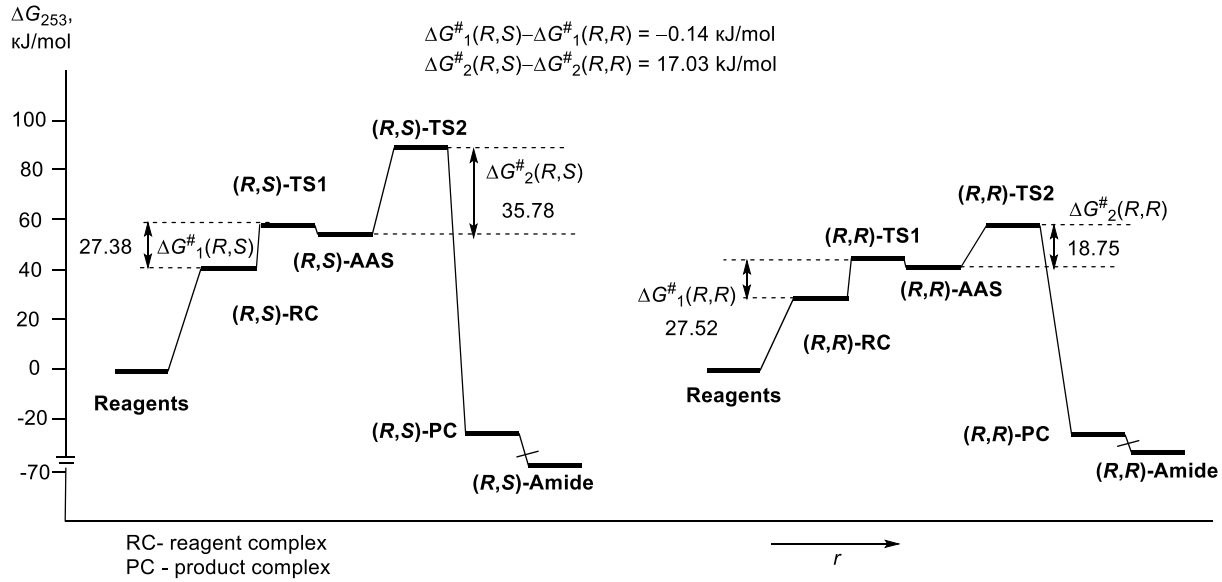


Figure S3 Reaction coordinate (*r*) for the acylation of amine **2a** with ester (*R*)-**1d** in CH_2Cl_2 at –20 °C *via* a two-step pathway.

The calculated value of $\Delta\Delta G^{\#}_1$ for the first step is –0.14 kJ/mol ((*R,S*)-amide predominates), which qualitatively and quantitatively disagrees with the experimentally observed value (6.9 kJ/mol) derived from the experimental selectivity factor *s* (*R,R*)-amide predominates); the calculated value of $\Delta\Delta G^{\#}_2$ for the proton transfer reaction (17.03 kJ/mol, (*R,R*)-amide predominates) is significantly higher than the experimentally observed one (see Figure S3). Since the calculated values of $\Delta\Delta G^{\#}_1$ and $\Delta\Delta G^{\#}_2$ do not agree with the experimental data (see Table S8), it can be assumed that the two-stage mechanism of acylation of aliphatic amines with activated ester (*R*)-**1d** involving the formation of a zwitterionic intermediate does not take place or is realized to an insignificant extent.

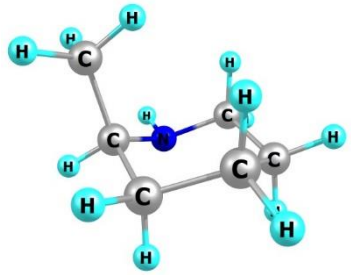
Table S8 Calculated Gibbs free energies ($\Delta G^{\#}_{R,R}$) for the fast-reacting (*R*)-enantiomer of amines **2a,c** and the differences in the Gibbs free energies of activation for enantiomers of amines **2a,c** ($\Delta\Delta G^{\#}_{253}$) with equatorial and axial conformation of the lone electron pair at the CPCMC-CH_2Cl_2-B3LYP-D3-gCP/def2-TZVP//B3LYP-D3-gCP/def2-SVP and CPCMC-Toluene-B3LYP-D3-gCP/def2-TZVP//B3LYP-D3-gCP/def2-SVP levels of theory in comparison with experimental values for the reactions of ester (*R*)-**1d** with amines **2a,c** at 253 K.

Amine	Calculated				Experimental	
	Conformation of N lone electron pair	$\Delta G^{\#}_{R,R}$, kJ/mol	$\Delta\Delta G^{\#}_{253}$, kJ/mol	s_{calc}	s_{exp}	$\Delta\Delta G^{\#}_{253}$, kJ/mol[a]
2a	*axial*	34.47	7.26	31.6	32 (CH_2Cl_2, –20 °C)	7.29
	equatorial	27.52	0.14 (*R,S*) predominates	1.08		
2c	*axial* (toluene)	24.03	1.06	1.73	2.2 (toluene, –40 °C)	1.53[b]
	axial (CH_2Cl_2)	19.16	1.44	1.98		
	equatorial (CH_2Cl_2)	30.05	4.95	10.5		

[a] $\Delta\Delta G^{\#}_{exp} = -RT\ln s$. [b] $\Delta\Delta G^{\#}_{233}$

Cartesian coordinates of reagents, products, reagent complexes (RCs), transitions states (TSs), product complexes (PCs) at the CPCMC-CH_2Cl_2-B3LYP-D3-gCP/def2-TZVP//B3LYP-D3-gCP/def2-SVP level of theory; *E*t is the total thermal energy, *H* and *G* are enthalpies and Gibbs free energies at 293 or 253 K (absolute energies, Hartree). The other solvents and temperatures are specially indicated.

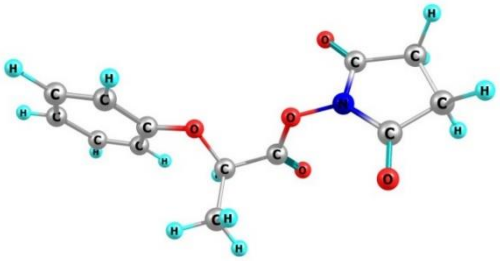
Amine **2a** Me-*ax*, :N-*ax*



E_{FSP}= −291.14536375
Et_{293} = −290.952743, H_{293}= −290.951315
G_{293}= −290.989169
Et_{253} = −290.954354, H_{253}= −290.953552
G_{253}= −290.984213
Imaginary frequency = 0

C	1.136329	−0.833754	−1.230042000
C	0.465492000	−1.981913000	−0.467067000
H	0.301686	−2.832529	−1.137594
H	1.127956	−2.338481	0.327200
C	0.212035	−0.204478	−2.282931
C	-0.874263	−1.525863	0.119958
H	-1.396337	−2.363133	0.592809
H	-0.693733	−0.773827	0.896718
C	-1.759157	−0.912211	−0.962723
H	-2.072940	−1.706632	−1.659265
H	-2.669734	−0.500447	−0.518279
N	-1.052981	0.185854	−1.633225
C	0.033380	−1.092816	−3.523112
H	1.421288	−0.054092	−0.515820
H	2.054476	−1.180208	−1.713385
H	0.679555	0.726755	−2.620611
H	-1.665238	0.613787	−2.319345
H	1.000457	−1.284403	−3.997419
H	-0.417396	−2.058201	−3.282769
H	-0.608621	−0.594733	−4.255689

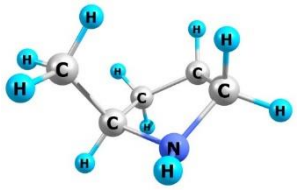
Ester **1d**



E_{FSP}= −933.97261607
Et_{293} = −933.711355, H_{293}= −933.710427
G_{293}= −933.769423
Et_{253} = −933.714998, H_{253}= −933.714197
G_{253}= −933.761989
Imaginary frequency = 0

C	−4.053044	5.850957	−0.228993
C	−4.300250	6.309744	1.059711
C	−4.284385	5.406378	2.120627
C	−4.022617	4.062289	1.893856
C	−3.765664	3.612313	0.599437
C	−3.783240	4.506217	−0.470135
O	−3.450194	2.277241	0.487417
C	−3.765590	1.598227	−0.722180
H	−3.550847	2.214885	−1.594398
C	−5.226775	1.144504	−0.728857
H	−5.412354	0.449971	0.091596
H	−5.868328	2.018376	−0.604114
H	−5.470422	0.657053	−1.674379
C	−2.865157	0.388842	−0.869169
O	−2.468549	−0.090768	0.363797
N	−1.714920	−1.237708	0.289368
C	−2.297003	−2.493668	0.137544
C	−1.154498	−3.482009	0.158376
H	−1.360617	−4.244073	0.909893
H	−1.117726	−3.974056	−0.815137
O	−3.480227	−2.683104	0.011800
C	−0.333222	−1.209718	0.462073
C	0.109985	−2.655589	0.451403
H	0.893010	−2.781882	−0.295870
H	0.541058	−2.884599	1.427817
O	0.318123	−0.204898	0.596631
O	−2.580831	−0.132294	−1.905183
H	−4.060190	6.542484	−1.063016
H	−4.483820	5.748536	3.129035
H	−4.011977	3.346367	2.706333
H	−3.577008	4.183815	−1.480980
H	−4.508350	7.357651	1.236259

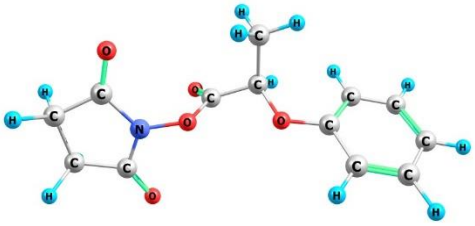
Amine **2c**, Me-*ax*, :N-*ax*



E_{FSP}= −251.83691534
Et_{293} = −251.674174, H_{293}= −251.673246
G_{293}= −251.709069
Et_{253} = −251.675524, H_{253}= −251.674722
G_{253}= −251.704331
Imaginary frequency = 0

C	1.060360	−0.136028	−2.852829
C	−0.317325	0.565314	−2.811690
C	1.297668	−0.637087	−1.403420
H	1.637058	−1.673799	−1.362919
H	2.054741	−0.023219	−0.912234
C	−0.054940	−0.452112	−0.697308
H	0.088627	−0.223349	0.363280
N	−0.584812	0.743713	−1.375754
H	1.845750	0.556298	−3.159441
H	1.059203	−0.957266	−3.571162
H	−0.314745	1.533469	−3.317607
H	−1.574624	0.869914	−1.192105
H	−1.072643	−0.058787	−3.307929
C	−0.959458	−1.684961	−0.814943
H	−1.112013	−1.975130	−1.858904
H	−0.519657	−2.538800	−0.291146
H	−1.939018	−1.483946	−0.371239

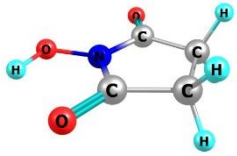
Ester **1d** in toluene at 233 K



E_{FSP}= −933.96379236
Et_{233} = −933.707522, H_{233}= −933.706784
G_{233}= −933.748536
Imaginary frequency = 0

C	−4.603575	5.763614	−0.173059
C	−4.458331	6.318376	1.090530
C	−3.986364	5.521881	2.132682
C	−3.655971	4.194386	1.910501
C	−3.795958	3.646314	0.634564
C	−4.279046	4.429528	−0.411944
O	−3.420876	2.332731	0.520854
C	−3.569836	1.679933	−0.731398
H	−3.292375	2.344179	−1.551516
C	−4.987465	1.130557	−0.913646
H	−5.208355	0.404911	−0.130174
H	−5.705330	1.948518	−0.848339
H	−5.087738	0.643707	−1.885347
C	−2.584526	0.530026	−0.805541
O	−2.468281	−0.096735	0.423152
N	−1.752622	−1.266251	0.359802
C	−2.373858	−2.465872	0.024000
C	−1.301620	−3.529514	0.134669
H	−1.605416	−4.240238	0.904843
H	−1.245241	−4.069970	−0.810335
O	−3.533076	−2.570260	−0.281390
C	−0.387958	−1.321722	0.638157
C	−0.002772	−2.780257	0.488664
H	0.753020	−2.852473	−0.294687
H	0.454856	−3.118542	1.418864
O	0.294816	−0.377107	0.928880
O	−2.038027	0.150591	−1.795027
H	−4.975144	6.365993	−0.993255
H	−3.873022	5.938999	3.126022
H	−3.284714	3.563829	2.708440
H	−4.413053	4.027821	−1.405701
H	−4.717773	7.354533	1.267298

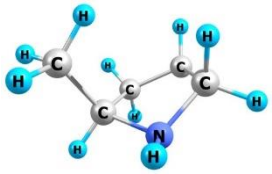
N-Hydroxysuccinimide



E_{FSP}= −435.81534699
Et_{293} = −435.713609, H_{293}= −435.712682
G_{293}= −435.751358
Et_{253} = −435.715139, H_{253}= −435.714339
G_{253}= −435.746243
Imaginary frequency = 0

O	2.953702	−0.068657	3.455796
N	4.115305	−0.760629	3.228048
C	5.288467	−0.478550	3.902397
C	6.315638	−1.460897	3.372878
O	5.412286	0.386284	4.737963
C	4.153213	−1.822496	2.353875
C	5.569637	−2.338665	2.352249
O	3.166944	−2.191105	1.747195
H	2.315717	−0.501064	2.853018
H	6.717019	−2.034142	4.209947
H	7.137115	−0.898441	2.926921
H	5.565676	−3.395583	2.624260
H	5.974520	−2.250259	1.342544

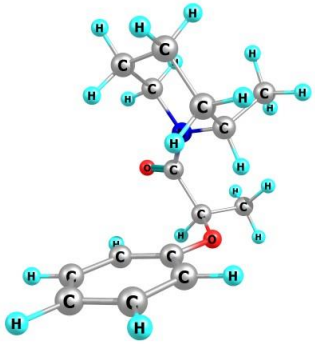
Amine **2c**, Me-*ax*, :N-*ax* in toluene at 233 K



E^{FSP} = −251.83487225
Et_{233} = −251.673892, H_{233}= −251.673154
G_{233}= −251.698993
Imaginary frequency = 0

C	1.060715	−0.134978	−2.853192
C	−0.317805	0.564849	−2.813367
C	1.296172	−0.637979	−1.404220
H	1.635735	−1.674726	−1.364532
H	2.052285	−0.024592	−0.911732
C	−0.056945	−0.452543	−0.698669
H	0.087366	−0.220075	0.361073
N	-0.584858	0.739486	−1.379565
H	1.845500	0.559135	−3.156638
H	1.063388	−0.954505	−3.573572
H	−0.314523	1.534576	−3.316231
H	−1.570457	0.882303	−1.189117
H	−1.070751	−0.058858	−3.315500
C	−0.959547	−1.687824	−0.812076
H	−1.114997	−1.979538	−1.855155
H	−0.518485	−2.541269	−0.288705
H	−1.938618	−1.489238	−0.366154

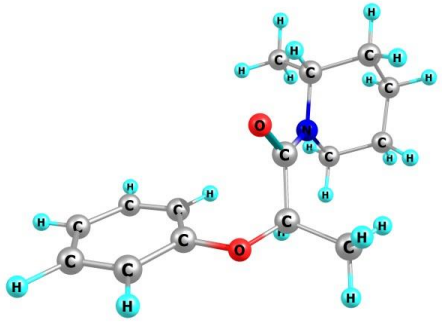
Amide (*R,S*)-**3a**



E_{FSP}= −789.32814756
Et_{293} = −788.973932, H_{293}= −788.973004
G_{293}= −789.031091
Et_{253} = −788.977821, H_{253}= −788.977019
G_{253}= −789.023696
Imaginary frequency = 0

C	1.314282	3.618212	−0.909747
C	−0.164410	3.243172	−1.018786
H	−0.650054	3.881105	−1.764692
H	−0.276749	2.213615	−1.368969
C	1.483213	5.022665	−0.329076
C	−0.840769	3.406158	0.342090
H	−1.911836	3.194947	0.275308
H	−0.412319	2.683005	1.042255
C	−0.648815	4.811857	0.934744
H	−0.999181	4.786370	1.958691
N	0.794743	5.134013	0.963692
C	−0.020347	0.947754	3.904776
C	1.339837	0.642769	3.865001
C	2.266242	1.677232	3.823369
C	1.854133	3.008256	3.810133
C	0.492095	3.301302	3.842182
C	−0.445429	2.267906	3.896225
O	−0.021671	4.569804	3.821256
C	0.821071	5.661461	3.433101
C	−0.007393	6.934362	3.540140
H	−0.324826	7.085844	4.573620
H	0.597385	7.787867	3.228034
H	−0.894176	6.886063	2.908330
H	1.664235	5.725598	4.123548
C	1.487704	5.548458	2.042991
O	2.669635	5.907899	1.984915
H	1.827147	2.905247	−0.254897
H	1.804996	3.574667	−1.885782
H	2.529141	5.266892	−0.167492
H	−0.755304	0.152161	3.934908
H	3.326614	1.456136	3.796252
H	2.594120	3.794017	3.764094
H	−1.499403	2.516732	3.915898
H	1.670832	−0.388288	3.865264
H	1.070411	5.768503	−1.015755
C	−1.438472	5.897662	0.198570
H	−1.213945	5.932843	−0.868383
H	−2.507949	5.705795	0.313735
H	−1.220550	6.880619	0.621427

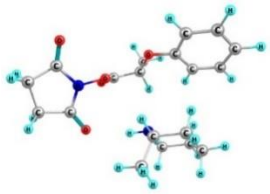
Amide (*R,R*)-**3a**



E_{FSP}= −789.327105427
Et_{293} = −788.972735, H_{293}= −788.971807
G_{293}= −789.030053
Et_{253} = −788.976515, H_{253}= −788.975814
G_{253}= −789.022666
Imaginary frequency = 0

C	−2.701532	−0.404379	1.904230
C	−2.782554	0.567574	3.083294
H	−3.751816	0.466732	3.582645
H	−2.022055	0.315817	3.826996
C	−3.667160	−0.035188	0.769675
C	−2.598366	2.012988	2.611647
H	−2.790291	2.712618	3.429918
H	−1.564515	2.167644	2.284446
C	−3.541496	2.348590	1.456674
H	−4.575448	2.346213	1.815094
H	−3.341152	3.347753	1.084871
N	−3.424995	1.368565	0.371623
C	−5.141318	−0.264232	1.110509
C	−5.007924	3.357999	−5.410555
C	−6.243179	3.226428	−4.775790
C	−6.283283	3.114947	−3.391475
C	−5.111612	3.128745	−2.636259
C	−3.880722	3.255388	−3.279778
C	−3.833799	3.373331	−4.671832
O	−2.673837	3.284246	−2.643581
C	−2.613403	3.081698	−1.236738
C	−1.165985	3.336601	−0.833225
H	−0.885150	4.361899	−1.080580
H	−1.025591	3.180086	0.236766
H	−0.510201	2.650322	−1.371968
H	−3.276764	3.800120	−0.753621
C	−3.006100	1.630438	−0.887635
O	−2.886793	0.761168	−1.749359
H	−1.684876	−0.398104	1.495610
H	−2.910105	−1.426115	2.233565
H	−3.418733	−0.634299	−0.102569
H	−5.300230	−1.314722	1.367564
H	−5.477756	0.336002	1.956789
H	−5.768723	−0.019291	0.250588
H	−4.958124	3.450144	−6.489206
H	−7.233418	3.007227	−2.881759
H	−5.177532	3.027155	−1.562287
H	−2.869466	3.474154	−5.155044
H	−7.157736	3.210155	−5.355096

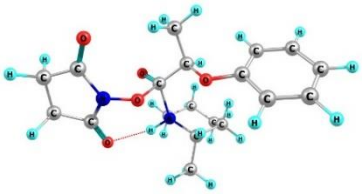
(*R*)-**1d**-(*S*)-**2a RC**



E_{FSP}=−1225.12946499 Et_{293} = −1224.672282,
H_{293}= −1224.671355 G_{293}= −1224.774735
Et_{253} = −1224.677874,
H_{253}= −1224.677073 G_{253}= −1224.737996
Imaginary frequency = 0

C	0.549921	0.568876	−2.750508
C	0.866082	−0.696845	−1.956259
H	0.331039	−1.546164	−2.393800
H	1.931078	−0.936393	−2.016898
C	−0.923966	0.923916	−2.628735
C	0.460762	−0.496547	−0.495007
H	0.630909	−1.405511	0.086493
H	1.107684	0.263391	−0.055356
C	−1.006428	−0.084095	−0.325646
H	−1.165287	0.274014	0.686495
N	−1.346969	1.085184	−1.210065
C	1.663892	0.026088	3.824522
C	2.993072	0.366507	3.580381
C	3.278288	1.330829	2.623439
C	2.259152	1.950396	1.905059
C	0.931771	1.588408	2.139355
C	0.638192	0.631013	3.115093
O	−0.138985	2.080356	1.456503
C	0.077597	2.902530	0.315006
C	0.211999	4.366433	0.713272
H	0.998573	4.476899	1.460988
H	0.460783	4.972628	−0.157672
H	−0.730584	4.721913	1.128121
H	0.973255	2.558942	−0.213087
C	−1.059141	2.748206	−0.694227
O	−2.495613	2.752734	0.363688
N	−3.433489	3.459697	−0.277497
C	−4.216338	2.904989	−1.262203
C	−5.164919	3.973053	−1.758116
H	−5.120626	4.011757	−2.847196
H	−6.181777	3.687049	−1.478151
O	−4.135762	1.748540	−1.637964
C	−3.589538	4.842149	−0.123241
C	−4.696476	5.265902	−1.071896
H	−5.479379	5.773462	−0.506573
H	−4.275187	5.986675	−1.774983
O	−2.951347	5.535359	0.623677
O	−1.174519	3.492563	−1.636245
H	1.156939	1.404067	−2.384562
H	0.794976	0.444467	−3.808753
H	−1.158441	1.864294	−3.123377
H	−2.373169	1.166343	−1.216354
H	1.423826	−0.719920	4.572463
H	4.303947	1.621250	2.427627
H	2.512353	2.707247	1.177783
H	−0.397759	0.371525	3.295394
H	3.791551	−0.109402	4.134709
H	−1.544101	0.145505	−3.079043
C	−1.987456	−1.228783	−0.576003
H	−1.924565	−1.625614	−1.591297
H	−1.768359	−2.047376	0.112662
H	−3.013223	−0.899815	−0.395127

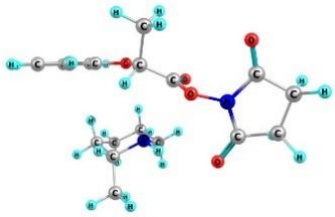
(*R*)-**1d**-(*S*)-**2a TS**



E_{FSP}=−1225.11718826 Et_{293} = −1224.658846,
H_{293}= −1224.657918 G_{293}= −1224.731255
Et_{253} = −1224.664419,
H_{253}= −1224.663617 G_{253}= −1224.722103
Imaginary frequency = 1

C	0.549921	0.568876	−2.750508
C	0.866082	−0.696845	−1.956259
H	0.331039	−1.546164	−2.393800
H	1.931078	−0.936393	−2.016898
C	−0.923966	0.923916	−2.628735
C	0.460762	−0.496547	−0.495007
H	0.630909	−1.405511	0.086493
H	1.107684	0.263391	−0.055356
C	−1.006428	−0.084095	−0.325646
H	−1.165287	0.274014	0.686495
N	−1.346969	1.085184	−1.210065
C	1.663892	0.026088	3.824522
C	2.993072	0.366507	3.580381
C	3.278288	1.330829	2.623439
C	2.259152	1.950396	1.905059
C	0.931771	1.588408	2.139355
C	0.638192	0.631013	3.115093
O	−0.138985	2.080356	1.456503
C	0.077597	2.902530	0.315006
C	0.211999	4.366433	0.713272
H	0.998573	4.476899	1.460988
H	0.460783	4.972628	−0.157672
H	−0.730584	4.721913	1.128121
H	0.973255	2.558942	−0.213087
C	−1.059141	2.748206	−0.694227
O	−2.495613	2.752734	0.363688
N	−3.433489	3.459697	−0.277497
C	−4.216338	2.904989	−1.262203
C	−5.164919	3.973053	−1.758116
H	−5.120626	4.011757	−2.847196
H	−6.181777	3.687049	−1.478151
O	−4.135762	1.748540	−1.637964
C	−3.589538	4.842149	−0.123241
C	−4.696476	5.265902	−1.071896
H	−5.479379	5.773462	−0.506573
H	−4.275187	5.986675	−1.774983
O	−2.951347	5.535359	0.623677
O	−1.174519	3.492563	−1.636245
H	1.156939	1.404067	−2.384562
H	0.794976	0.444467	−3.808753
H	−1.158441	1.864294	−3.123377
H	−2.373169	1.166343	−1.216354
H	1.423826	−0.719920	4.572463
H	4.303947	1.621250	2.427627
H	2.512353	2.707247	1.177783
H	−0.397759	0.371525	3.295394
H	3.791551	−0.109402	4.134709
H	−1.544101	0.145505	−3.079043
C	−1.987456	−1.228783	−0.576003
H	−1.924565	−1.625614	−1.591297
H	−1.768359	−2.047376	0.112662
H	−3.013223	−0.899815	−0.395127

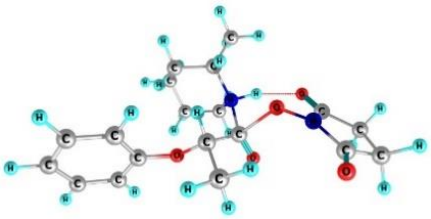
(*R*)-**1d**-(*R*)-**2a RC**



E_{FSP}=−1225.13101149 Et_{293} = −1224.6725094,
H_{293}= −1224.671581 G_{293}= −1224.748377
Et_{253} = −1224.678225,
H_{253}= −1224.677423 G_{253}= −1224.738920
Imaginary frequency = 0

C	1.078290	−1.272461	−0.590340
C	−0.089749	−2.134834	−0.097370
H	−0.207932	−3.014662	−0.740165
H	0.127423	−2.510568	0.907217
C	0.787970	−0.601748	−1.941606
C	−1.395187	−1.333775	−0.106134
H	−2.239190	−1.971111	0.174290
H	−1.339881	−0.519445	0.622855
C	−1.636095	−0.733958	−1.487020
H	−1.823546	−1.546337	−2.208673
H	−2.528383	−0.106193	−1.479146
N	−0.500976	0.109112	−1.872127
C	0.867990	−1.582109	−3.123156
C	2.090697	0.509680	3.184909
C	3.343772	0.871735	2.691637
C	3.420865	1.699122	1.578567
C	2.268069	2.168130	0.950271
C	1.021255	1.791721	1.446428
C	0.935248	0.965910	2.569595
O	−0.176000	2.162172	0.906703
C	−0.197561	2.929011	−0.284001
C	−0.102536	4.429734	0.011489
H	0.840322	4.648233	0.513084
H	−0.151992	5.003050	−0.914414
H	−0.924489	4.734119	0.661036
H	0.585580	2.609817	−0.972309
C	−1.526992	2.636374	−0.943173
O	−2.528996	2.230227	−0.447491
O	−1.452935	3.078580	−2.269979
N	−2.673369	3.134891	−2.890869
C	−3.550338	4.193799	−2.664375
O	−3.350000	5.077869	−1.870507
C	−4.713556	3.976187	−3.602097
H	−5.647810	4.087572	−3.053415
H	−4.674356	4.757321	−4.365107
C	−3.105588	2.161350	−3.785222
O	−2.466162	1.193375	−4.115421
C	−4.499044	2.574895	−4.200818
H	−5.190122	1.841870	−3.779163
H	−4.587586	2.535310	−5.286308
H	1.279186	−0.491686	0.146395
H	1.988522	−1.874223	−0.671742
H	1.552719	0.167191	−2.101311
H	−0.700305	0.528884	−2.774052
H	1.880461	−1.984266	−3.226458
H	0.186429	−2.426187	−3.001027
H	0.606914	−1.070126	−4.054511
H	2.012251	−0.136889	4.050714
H	4.386434	1.995462	1.185427
H	2.363430	2.812237	0.087859
H	−0.044100	0.680766	2.933624
H	4.245351	0.511894	3.171402

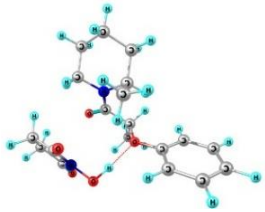
(*R*)-**1d**-(*R*)-**2a TS**



E_{FSP}=−1225.1218409 Et_{293} = −1224.662948,
H_{293}= −1224.662020 G_{293}= −1224.734896
Et_{253} = −1224.668489,
H_{253}= −1224.667687 G_{253}= −1224.725789
Imaginary frequency = 1

C	1.147819	−0.828911	−1.225621
C	0.471902	−1.987692	−0.490467
H	0.285746	−2.818534	−1.178329
H	1.141093	−2.367144	0.285284
C	0.249621	−0.171359	−2.277632
C	−0.843857	−1.518932	0.131418
H	−1.379349	−2.355387	0.588095
H	−0.645025	−0.792512	0.919697
C	−1.762289	−0.901276	−0.910856
H	−2.091395	−1.659680	−1.623207
H	−2.648124	−0.454738	−0.464054
N	−1.116987	0.186920	−1.724033
C	0.066730	−1.036906	−3.524656
C	1.905806	1.087260	3.832440
C	3.189659	1.400616	3.388088
C	3.374453	1.780818	2.064699
C	2.296827	1.853692	1.184255
C	1.016612	1.535744	1.636840
C	0.824226	1.149793	2.965470
O	−0.104172	1.524618	0.854555
C	−0.139221	2.261319	−0.381201
C	−0.287540	3.746716	−0.106351
H	0.575853	4.103783	0.458017
H	−0.360599	4.298596	−1.041264
H	−1.190846	3.926295	0.478278
H	0.758719	2.067673	−0.965815
C	−1.358677	1.687979	−1.108367
O	−2.500169	1.852570	−0.719270
O	−1.104834	2.477028	−2.709613
N	−2.302925	2.861845	−3.173163
C	−2.760427	4.180152	−3.138576
O	−2.137521	5.116125	−2.693870
C	−4.135359	4.193789	−3.769429
H	−4.836134	4.648299	−3.068676
H	−4.104308	4.821495	−4.661673
C	−3.223649	1.965833	−3.667216
O	−3.037288	0.759517	−3.733051
C	−4.454373	2.726351	−4.083328
H	−5.304356	2.343982	−3.516137
H	−4.650988	2.539580	−5.140482
H	1.471318	−0.088812	−0.494505
H	2.049930	−1.171650	−1.738173
H	0.687520	0.773402	−2.594091
H	−1.724283	0.378001	−2.551114
H	1.046247	−1.244881	−3.959312
H	−0.410945	−1.992146	−3.300309
H	−0.535022	−0.517049	−4.272466
H	1.743971	0.790514	4.862032
H	4.365165	2.027821	1.701906
H	2.470681	2.158748	0.162107
H	−0.176687	0.906535	3.300531
H	4.031848	1.349143	4.066581

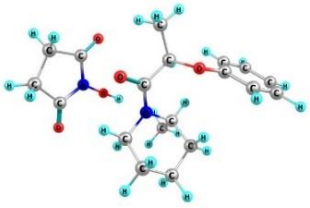
(*R*)-**1d**-(*S*)-**2a PC**



E_{FSP}=−1225.15520091 Et_{293} = −1224.695992,
H_{293}= −1224.695064 G_{293}= −1224.771047
Et_{253} = −1224.701718,
H_{253}= −1224.700917 G_{253}= −1224.761697
Imaginary frequency = 0

C	−0.551221	0.447128	−3.783367
C	0.130584	−0.808129	−3.237200
H	−0.631302	−1.544664	−2.961692
H	0.752928	−1.273699	−4.005819
C	−1.334974	1.162556	−2.686296
C	0.985015	−0.451191	−2.018945
H	1.429722	−1.346588	−1.575981
H	1.809615	0.194570	−2.338882
C	0.190847	0.285071	−0.926395
H	0.911288	0.647975	−0.199637
N	−0.486898	1.454335	−1.523474
C	0.321457	0.270122	4.242838
C	1.691360	0.421153	4.447373
C	2.422694	1.222125	3.579397
C	1.804087	1.866820	2.508331
C	0.437349	1.698510	2.309338
C	−0.307393	0.900226	3.178207
O	−0.269594	2.274762	1.275215
C	0.418781	2.974764	0.209977
C	0.545724	4.445310	0.547636
H	1.142785	4.567762	1.452591
H	1.040816	4.972995	−0.268505
H	-0.434424	4.894915	0.704725
H	1.406442	2.533442	0.074062
C	−0.412665	2.722561	−1.065461
O	−2.851356	3.172039	1.756463
N	−3.349338	3.382111	0.497722
C	−3.864949	2.352539	−0.276152
C	−4.391229	2.985851	−1.544111
H	−3.879179	2.540113	−2.395405
H	−5.452819	2.749133	−1.633671
O	−3.863517	1.185802	0.043691
C	−3.477841	4.658217	−0.040525
C	−4.116581	4.490019	−1.400521
H	−5.020002	5.098615	−1.450317
H	−3.412842	4.863007	−2.144384
O	−3.132935	5.674760	0.513196
O	−0.982084	3.669552	−1.611397
H	0.200071	1.133091	−4.189253
H	−1.238066	0.198084	−4.596839
H	−1.732143	2.107323	−3.044783
H	−1.920634	2.871873	1.633514
H	−0.263689	−0.348548	4.912329
H	3.485773	1.363339	3.733818
H	2.396208	2.493833	1.857702
H	−1.369070	0.772040	3.009094
H	2.179652	−0.077538	5.275014
H	−2.174957	0.543540	−2.354312
C	−0.792482	−0.629088	−0.191308
H	−1.458563	−1.155456	−0.876630
H	−0.229739	−1.374799	0.375590
H	−1.406477	−0.053594	0.500330

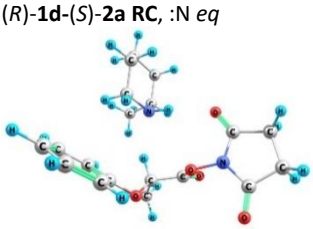
(*R*)-**1d**-(*R*)-**2a PC**



E_{FSP}=−1225.146883997 Et_{293} = −1224.688232,
H_{293}= −1224.687305 G_{293}= −1224.761391
Et_{253} = −1224.693851,
H_{253}= −1224.693049 G_{253}= −1224.752204
Imaginary frequency = 0

C	0.474099	−1.158503	−0.112864
C	−0.476735	−2.259816	−0.580611
H	−0.106366	−2.710426	−1.507189
H	−0.511408	−3.060043	0.163065
C	0.503416	0.038742	−1.075455
C	−1.874602	−1.682226	−0.807648
H	−2.547901	−2.433653	−1.228870
H	−2.299642	−1.359850	0.149613
C	−1.832319	−0.483174	−1.753425
H	−1.536367	−0.807403	−2.753025
H	−2.807634	−0.013685	−1.826575
N	−0.878258	0.542113	−1.286043
C	1.187761	−0.271034	−2.406993
C	2.782764	0.669528	3.091417
C	3.875257	1.289653	2.485171
C	3.654053	2.206321	1.464543
C	2.361351	2.496305	1.028233
C	1.278618	1.843827	1.618038
C	1.493224	0.941079	2.662094
O	−0.028285	1.995736	1.240753
C	−0.377293	2.622977	−0.010007
C	−0.964525	3.993547	0.252743
H	−0.213391	4.619852	0.738109
H	−1.265979	4.459947	−0.685069
H	−1.837910	3.916233	0.900278
H	0.501079	2.717482	−0.647124
C	−1.380906	1.665188	−0.686089
O	−2.577478	1.939321	−0.697722
O	−0.989218	1.889259	−4.225835
N	−2.278653	2.252128	−3.933941
C	−2.588621	3.485745	−3.373461
O	−1.768353	4.311319	−3.050855
C	−4.094015	3.540988	−3.271906
H	−4.362451	3.708414	−2.228718
H	−4.449772	4.392919	−3.853110
C	−3.360272	1.448257	−4.265785
O	−3.270916	0.367541	−4.797362
C	−4.596348	2.192065	−3.816442
H	−5.096375	1.592375	−3.053988
H	−5.277624	2.288225	−4.662017
H	0.152535	−0.796563	0.866958
H	1.491551	−1.540315	0.003737
H	1.081743	0.822851	−0.602582
H	−0.651819	1.460214	−3.417627
H	2.191709	−0.656221	−2.216632
H	0.653681	−1.016034	−2.996949
H	1.293631	0.635885	−3.007909
H	2.936444	−0.040661	3.894914
H	4.490700	2.708308	0.993162
H	2.221398	3.220299	0.237576
H	0.638766	0.449659	3.109967
H	4.882055	1.062322	2.813445

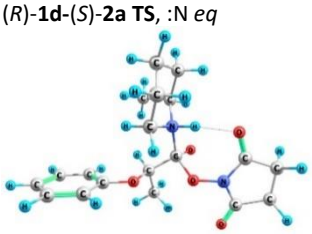
(*R*)-**1d**-(*S*)-**2a RC**, :N *eq*



E_{FSP}=−1225.12831946 Et_{293} = −1224.671028,
H_{293}= −1224.67010047 G_{293}= −1224.745575
Et_{253} = −1224.676607,
H_{253}= −1224.675806 G_{253}= −1224.736297
Imaginary frequency = 0

C	−1.184216	−2.093961	−1.358697
H	1.761385	−0.869993	−1.446925
O	−0.988581	−3.199256	−0.951785
C	−1.281473	−1.659472	−2.809470
H	−0.247509	−1.356400	−3.039411
C	−1.737818	−2.792273	−3.709828
H	−1.109930	−3.670502	−3.558276
H	−2.774456	−3.061154	−3.496796
H	−1.658206	−2.480045	−4.751806
O	−2.151669	−0.530805	−2.897148
C	−1.654257	0.627217	−3.445194
C	−0.853786	0.630044	−4.584177
H	−0.574431	−0.300455	−5.059807
C	−0.408058	1.839121	−5.106158
H	0.223205	1.836949	−5.986744
C	−0.766407	3.041598	−4.504760
H	−0.415938	3.980883	−4.914761
C	−2.020856	1.824183	−2.836358
H	−2.639386	1.794720	−1.948232
C	−1.578330	3.027699	−3.372559
H	−1.864099	3.958143	−2.896103
C	2.194180	0.584373	−2.806097
C	2.879879	−1.789374	−2.890268
C	4.310774	−1.393742	−2.469395
C	4.653607	0.050643	−2.856713
C	3.586654	1.024925	−2.346409
H	2.116835	0.698065	−3.891576
H	4.395181	−1.502461	−1.381412
H	5.031871	−2.088725	−2.911793
H	5.636285	0.318719	−2.456700
H	4.726055	0.138450	−3.947142
H	3.611651	1.056607	−1.249827
H	3.792596	2.039028	−2.706388
N	1.872110	−0.803353	−2.454995
H	1.419353	1.224963	−2.377930
H	2.622018	−2.721961	−2.378676
C	2.770785	−2.053635	−4.394310
H	3.459676	−2.849485	−4.688211
H	1.756017	−2.365405	−4.654102
H	3.016586	−1.170027	−4.987936
O	−1.258968	−0.982526	−0.526642
N	−1.051603	−1.281366	0.795678
C	0.223506	−1.325415	1.343369
O	1.242974	−1.175926	0.713419
C	−2.111352	−1.499537	1.673410
O	−3.273117	−1.506631	1.352518
C	0.033772	−1.589326	2.819167
H	0.577776	−2.496747	3.083379
H	0.475665	−0.762827	3.376787
C	−1.484942	−1.715099	3.031690
H	−1.783193	−2.699671	3.394588
H	−1.884723	−0.972036	3.722249

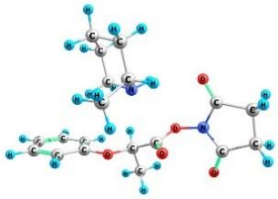
(*R*)-**1d**-(*S*)-**2a TS**, :N *eq*



E_{FSP}=−1225.121050623 Et_{293} = −1224.662689,
H_{293}= −1224.661762 G_{293}= −1224.734988
Et_{253} = −1224.66824682,
H_{253}= −1224.667446 G_{253}= −1224.725867
Imaginary frequency = 1

C	0.069103	−1.634696	−1.690422
H	1.784759	−0.961487	−0.704068
O	0.171753	−2.810255	−1.407310
C	−0.825100	−1.159796	−2.840704
H	−0.314215	−1.479118	−3.753175
C	−2.205326	−1.794473	−2.756170
H	−2.134816	−2.876809	−2.869539
H	−2.659557	−1.564908	−1.792078
H	−2.836734	−1.395338	−3.552318
O	−0.926270	0.260409	−2.823380
C	−1.052038	0.958482	−3.981902
C	−1.193323	0.393468	−5.249903
H	−1.252361	−0.677285	−5.382487
C	−1.280307	1.223477	−6.365623
H	−1.391902	0.773130	−7.344785
C	−1.237392	2.604591	−6.236707
H	−1.309078	3.240066	−7.109864
C	−1.022728	2.350713	−3.846086
H	−0.933789	2.770105	−2.851602
C	−1.113162	3.162219	−4.965325
H	−1.088579	4.238824	−4.844140
C	1.761241	0.552771	−2.057834
C	2.669136	−1.759412	−2.357770
C	4.049170	−1.264467	−1.896616
C	4.271157	0.222560	−2.192346
C	3.130806	1.061596	−1.614108
H	1.615005	0.686871	−3.128534
H	4.139460	−1.439185	−0.819204
H	4.817371	−1.873611	−2.380108
H	5.225360	0.544659	−1.767248
H	4.338877	0.390015	−3.272631
H	3.175421	1.037683	−0.519579
H	3.227414	2.107363	−1.920055
N	1.621038	−0.892036	−1.722406
H	0.961044	1.073928	−1.542995
H	2.484536	−2.750562	−1.943344
C	2.539782	−1.840093	−3.874607
H	3.323142	−2.497266	−4.257241
H	1.582734	−2.271459	−4.167541
H	2.652232	−0.874684	−4.369778
O	−0.476266	−0.652442	−0.386739
N	−0.452825	−1.374130	0.743845
C	0.705112	−1.650462	1.425753
O	1.820168	−1.294325	1.080918
C	−1.608029	−1.936266	1.303537
O	−2.709843	−1.860621	0.832304
C	0.344248	−2.455900	2.653429
H	0.866373	−3.413158	2.603986
H	0.707358	−1.931996	3.539290
C	−1.183907	−2.600853	2.603047
H	−1.525288	−3.636582	2.599787
H	−1.687869	−2.092516	3.427115

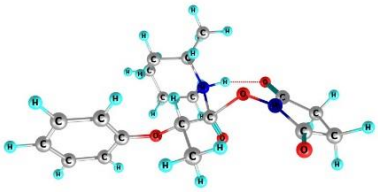
(*R*)-**1d**-(*R*)-**2a RC**, :N *eq*



E_{FSP}=−1225.13054710 Et_{293} = −1224.672322,
H_{293}= −1224.671394 G_{293}= −1224.748397
Et_{253} = −1224.6780369,
H_{253}= −1224.677236 G_{253}= −1224.738939
Imaginary frequency = 0

C	2.776292	3.926080	−1.897617
O	1.618071	3.675041	−1.782856
H	4.243296	1.818340	−0.513652
O	3.623042	3.215615	−2.768070
N	2.943474	2.313353	−3.542590
C	2.928109	0.951173	−3.266852
O	3.488351	0.428324	−2.334292
C	2.094305	0.317317	−4.358829
H	2.703796	−0.421584	−4.880117
H	1.260334	−0.207342	−3.890102
C	2.236880	2.723266	−4.670249
O	2.157555	3.869326	−5.036921
C	1.641436	1.471113	−5.269896
H	0.557238	1.588041	−5.304377
H	2.002930	1.370567	−6.294295
C	3.538672	5.138723	−1.405592
H	4.563383	4.826252	−1.205005
C	3.496125	6.217761	−2.492503
H	3.952675	5.850196	−3.411804
H	2.461677	6.497748	−2.698475
H	4.041034	7.099572	−2.155624
O	2.902175	5.576368	−0.216309
C	3.618002	6.301962	0.694120
C	4.940142	6.713284	0.525215
H	5.489955	6.494649	−0.378565
C	5.571846	7.426667	1.542171
H	6.599426	7.740057	1.400040
C	4.902930	7.740603	2.718310
H	5.403572	8.294104	3.502563
C	2.935737	6.624596	1.870134
H	1.910015	6.297363	1.984483
C	3.575549	7.340987	2.870518
H	3.035106	7.586225	3.777088
C	2.741629	1.731253	0.855562
C	1.807056	2.708928	1.570051
H	0.977151	2.166249	2.030888
H	2.317858	3.265508	2.358642
H	1.407478	3.431376	0.858531
C	4.863343	2.974581	1.054220
H	4.430983	3.781683	1.652347
C	5.463368	1.912806	1.981214
C	4.357799	1.189774	2.755449
C	3.296218	0.640309	1.794570
H	6.021125	1.185186	1.377413
H	6.176481	2.380137	2.668780
H	4.782072	0.376499	3.352273
H	3.893865	1.886994	3.462768
H	3.750373	−0.143764	1.176924
H	2.476619	0.174915	2.352427
N	3.824857	2.452893	0.160564
H	2.161795	1.239787	0.068635
H	5.644130	3.428038	0.437169

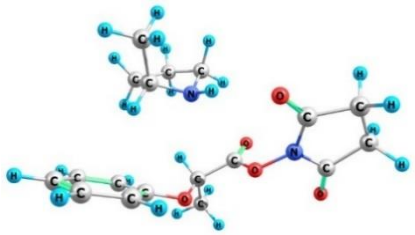
(*R*)-**1d**-(*R*)-**2a TS**, :N *eq*



E_{FSP}=−1225.12377347 Et_{293} = −1224.666338,
H_{293}= −1224.664411 G_{293}= −1224.737573
Et_{253} = −1224.670886,
H_{253}= −1224.670085 G_{253}= −1224.728459
Imaginary frequency = 1

C	1.147819	−0.828911	−1.225621
C	0.471902	−1.987692	−0.490467
H	0.285746	−2.818534	−1.178329
H	1.141093	−2.367144	0.285284
C	0.249621	−0.171359	−2.277632
C	−0.843857	−1.518932	0.131418
H	−1.379349	−2.355387	0.588095
H	−0.645025	−0.792512	0.919697
C	−1.762289	−0.901276	−0.910856
H	−2.091395	−1.659680	−1.623207
H	−2.648124	−0.454738	−0.464054
N	−1.116987	0.186920	−1.724033
C	0.066730	−1.036906	−3.524656
C	1.905806	1.087260	3.832440
C	3.189659	1.400616	3.388088
C	3.374453	1.780818	2.064699
C	2.296827	1.853692	1.184255
C	1.016612	1.535744	1.636840
C	0.824226	1.149793	2.965470
O	−0.104172	1.524618	0.854555
C	−0.139221	2.261319	−0.381201
C	−0.287540	3.746716	−0.106351
H	0.575853	4.103783	0.458017
H	−0.360599	4.298596	−1.041264
H	−1.190846	3.926295	0.478278
H	0.758719	2.067673	−0.965815
C	−1.358677	1.687979	−1.108367
O	−2.500169	1.852570	−0.719270
O	−1.104834	2.477028	−2.709613
N	−2.302925	2.861845	−3.173163
C	−2.760427	4.180152	−3.138576
O	−2.137521	5.116125	−2.693870
C	−4.135359	4.193789	−3.769429
H	−4.836134	4.648299	−3.068676
H	−4.104308	4.821495	−4.661673
C	−3.223649	1.965833	−3.667216
O	−3.037288	0.759517	−3.733051
C	−4.454373	2.726351	−4.083328
H	−5.304356	2.343982	−3.516137
H	−4.650988	2.539580	−5.140482
H	1.471318	−0.088812	−0.494505
H	2.049930	−1.171650	−1.738173
H	0.687520	0.773402	−2.594091
H	−1.724283	0.300078	−2.551114
H	1.046247	−1.244881	−3.959312
H	−0.410945	−1.992146	−3.300309
H	−0.535022	−0.517049	−4.272466
H	1.743971	0.790514	4.862032
H	4.365165	2.027821	1.701906
H	2.470681	2.158748	0.162107
H	−0.176687	0.906535	3.300531
H	4.031848	1.349143	4.066581

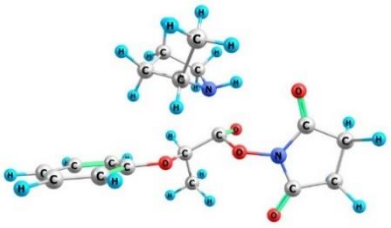
(*R*)-**1d**-(*S*)-**2c RC**



E_{FSP}=−1185.82140198 Et_{293} = −1185.393926,
H_{293}= −1185.392998 G_{293}= −1185.466590
Et_{253} = −1185.399255,
H_{253}= −1185.398454 G_{253}= −1185.457529
Imaginary frequency = 0

C	0.715121	0.327746	−2.751504
C	−0.733984	0.788710	−2.512203
C	1.105873	−0.437588	−1.458540
H	1.411397	−1.466411	−1.658970
H	1.939380	0.058850	−0.959545
C	−0.144679	−0.387737	−0.558493
H	0.139497	−0.227172	0.482925
N	−0.840015	0.813471	−1.050546
C	0.599440	0.046697	3.506318
C	1.889444	−0.337657	3.146209
C	2.597258	0.429944	2.228104
C	2.030320	1.570514	1.664945
C	0.736235	1.939987	2.024280
C	0.019385	1.176360	2.944724
O	0.106611	3.057916	1.543355
C	0.404096	3.511312	0.229022
C	1.212614	4.805645	0.270619
H	2.157565	4.620225	0.782916
H	1.421621	5.154779	−0.741456
H	0.664495	5.579514	0.811143
H	0.932046	2.738527	−0.329336
C	−0.884636	3.721074	−0.551369
O	−1.996425	3.627121	0.271310
N	−3.189757	3.829195	−0.378799
C	−4.077694	2.778605	−0.576003
C	−5.329450	3.390506	−1.161571
H	−5.504850	2.947681	−2.142926
H	−6.173624	3.128752	−0.522775
O	−3.843241	1.624177	−0.312325
C	−3.671716	5.104584	−0.671913
C	−5.066742	4.903867	−1.222201
H	−5.760149	5.480220	−0.608707
H	−5.105962	5.304935	−2.235689
O	−3.054271	6.123588	−0.492920
O	−0.946532	4.007765	−1.709294
H	1.368518	1.190578	−2.895713
H	0.796380	−0.294839	−3.643688
H	−0.937873	1.779806	−2.921923
H	−1.803403	0.855422	−0.733970
H	0.032873	−0.546509	4.214154
H	3.599643	0.139300	1.936368
H	2.601113	2.158439	0.958671
H	−0.988938	1.476417	3.200686
H	2.337454	−1.223443	3.579087
H	−1.439758	0.087526	−2.979756
C	−0.990733	−1.665870	−0.636428
H	−1.292246	−1.893182	−1.663407
H	−0.428403	−2.522423	−0.253037
H	−1.896986	−1.560953	−0.032248

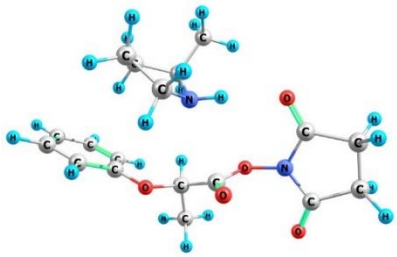
(*R*)-**1d**-(*S*)-**2c TS**



E_{FSP}=−1185.81668056 Et_{293} = −1185.389191,
H_{293}= −1185.388263 G_{293}= −1185.458453
Et_{253} = −1185.394348,
H_{253}= −1185.393547 G_{253}= −1185.449683
Imaginary frequency = 1

C	−0.851791	−0.208440	−3.332290
C	−1.674448	0.886093	−2.634453
C	0.325728	−0.458399	−2.381142
H	0.758922	−1.453684	−2.486990
H	1.121170	0.264061	−2.563559
C	−0.281578	−0.243064	−0.992963
H	0.459300	0.056013	−0.257153
N	−1.215013	0.912542	−1.209778
C	4.696795	0.347034	−1.073587
C	5.118442	0.802729	−2.321972
C	4.344345	1.736694	−2.998197
C	3.156630	2.218537	−2.450011
C	2.733280	1.742201	−1.209599
C	3.517227	0.815413	−0.516376
O	1.567984	2.092773	−0.594200
C	0.626713	2.935745	−1.258305
C	0.966790	4.407996	−1.052271
H	1.983758	4.608970	−1.392721
H	0.278596	5.031269	−1.622577
H	0.879914	4.668232	0.002870
H	0.598697	2.695812	−2.324173
C	−0.779160	2.658865	−0.714199
O	−0.635351	2.371843	0.766089
N	−1.658966	2.922277	1.465429
C	−2.878820	2.295405	1.615549
C	−3.748867	3.214065	2.439978
H	−4.665001	3.415021	1.883343
H	−4.024908	2.701464	3.362981
O	−3.150065	1.204821	1.155604
C	−1.558717	4.183469	2.045245
C	−2.899351	4.472885	2.682834
H	−2.753648	4.706989	3.738022
H	−3.316046	5.359154	2.200664
O	−0.566135	4.870440	2.017239
O	−1.721694	3.357038	−1.062803
H	−0.524947	0.106139	−4.323759
H	−1.449236	−1.113825	−3.449249
H	−1.502359	1.873654	−3.062360
H	−2.002208	0.837245	−0.565958
H	5.291590	−0.376814	−0.529037
H	4.664798	2.108593	−3.964333
H	2.576433	2.945141	−3.000128
H	3.174705	0.461963	0.448339
H	6.036685	0.431293	−2.759665
H	−2.745249	0.692322	−2.675752
C	−1.046842	−1.462090	−0.481798
H	−1.815356	−1.785062	−1.188213
H	−0.352832	−2.291699	−0.330294
H	−1.531203	−1.241354	0.472411

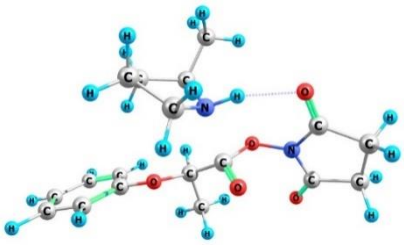
(*R*)-**1d**-(*R*)-**2c RC**



E_{FSP}=−1185.82353409 Et_{293} = −1185.396066,
H_{293}= −1185.395138 G_{293}= −1185.469288
Et_{253} = −1185.401408,
H_{253}= −1185.400607 G_{253}= −1185.460128
Imaginary frequency = 0

C	−0.035616	−1.405915	0.665605
C	−0.240403	−0.556303	−0.595585
C	−1.437258	−1.967907	0.957312
H	−1.594521	−2.900579	0.410842
H	−1.585016	−2.180034	2.017695
C	−2.398150	−0.876206	0.445358
H	−3.224694	−1.315631	−0.122287
H	−2.836160	−0.307484	1.270692
N	−1.579060	0.023876	−0.393293
C	−0.132196	−1.368604	−1.891986
C	−0.259210	−0.064532	4.460155
C	1.102089	0.204047	4.322008
C	1.514421	1.161831	3.403303
C	0.588806	1.847484	2.620688
C	−0.769466	1.559211	2.754069
C	−1.192321	0.607795	3.685082
O	−1.759531	2.164893	2.031419
C	−1.401552	2.896062	0.871507
C	−1.248834	4.386008	1.182051
H	−0.467304	4.523900	1.929737
H	−0.974645	4.939483	0.283090
H	−2.185074	4.784171	1.577752
H	−0.491978	2.491117	0.430498
C	−2.504824	2.686823	−0.146271
O	−3.651125	2.417779	0.025849
O	−1.974517	3.007491	−1.400268
N	−2.903264	3.063927	−2.407884
C	−3.539421	4.261312	−2.736954
O	−3.443425	5.277745	−2.097184
C	−4.292925	3.991048	−4.019138
H	−5.332526	4.297546	−3.906404
H	−3.841619	4.610459	−4.797168
C	−3.130446	1.997049	−3.266266
O	−2.620897	0.907382	−3.162832
C	−4.114330	2.490423	−4.297705
H	−5.041542	1.928612	−4.168007
H	−3.723203	2.271382	−5.291552
H	0.299809	−0.774340	1.489992
H	0.710440	−2.188410	0.514397
H	0.497464	0.254304	−0.637388
H	−2.021274	0.217801	−1.282689
H	0.888321	−1.734668	−2.043499
H	−0.804555	−2.231460	−1.874487
H	−0.405324	−0.748668	−2.750082
H	−0.597209	−0.807527	5.172432
H	2.566896	1.392998	3.288291
H	0.941735	2.593548	1.923500
H	−2.250310	0.396212	3.776987
H	1.828882	−0.323816	4.926171

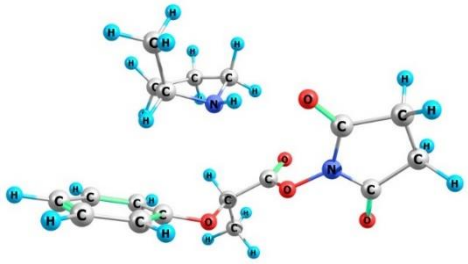
(*R*)-**1d**-(*R*)-**2c TS**



E_{FSP}=−1185.81835826 Et_{293} = −1185.390178,
H_{293}= −1185.3892504 G_{293}= −1185.461877
Et_{253} = −1185.3954663,
H_{253}= −1185.3946651 G_{253}= −1185.452829
Imaginary frequency = 1

C	−0.063672	−1.213637	0.280368
C	−0.343283	−0.384944	−0.977706
C	−1.395370	−1.931379	0.552530
H	−1.448967	−2.859927	−0.018813
H	−1.525936	−2.184304	1.605491
C	−2.472566	−0.947020	0.067779
H	−3.262601	−1.446863	−0.492399
H	−2.932850	−0.395067	0.884364
N	−1.768629	0.029320	−0.815306
C	−0.148210	−1.155562	−2.284078
C	−0.433673	0.607866	5.165654
C	0.879580	1.074081	5.206675
C	1.422879	1.668076	4.074327
C	0.675974	1.805787	2.905034
C	−0.639005	1.343274	2.877660
C	−1.189200	0.740858	4.011319
O	−1.464151	1.396628	1.793861
C	−1.159787	2.243157	0.686477
C	−1.316823	3.716682	1.046545
H	−0.624581	3.988595	1.843353
H	−1.110385	4.338631	0.175724
H	−2.336650	3.907143	1.385917
H	−0.151012	2.044712	0.319988
C	−2.185767	1.848137	−0.381045
O	−3.390157	1.904443	−0.211715
O	−1.624657	2.405222	−1.668724
N	−2.619289	2.782800	−2.514297
C	−3.040260	4.108813	−2.605494
O	−2.539029	5.028420	−2.006642
C	−4.195794	4.129073	−3.577602
H	−5.076405	4.492083	−3.044096
H	−3.976181	4.832921	−4.380867
C	−3.326804	1.886751	−3.290855
O	−3.125915	0.688919	−3.323568
C	−4.350992	2.679264	−4.061264
H	−5.337245	2.260571	−3.856515
H	−4.149407	2.560419	−5.127480
H	0.196287	−0.557502	1.111029
H	0.766478	−1.904699	0.130724
H	0.273777	0.513744	−1.013749
H	−2.216796	0.069835	−1.730506
H	0.900152	−1.441207	−2.398587
H	−0.755139	−2.064218	−2.308866
H	−0.428710	−0.534494	−3.137909
H	−0.876145	0.142858	6.038753
H	2.440700	2.039479	4.093205
H	1.123684	2.276778	2.041237
H	−2.212553	0.389307	3.967322
H	1.468222	0.977806	6.110298

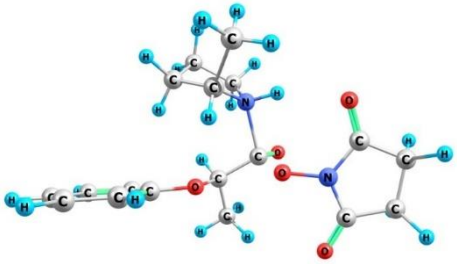
(*R*)-**1d**-(*S*)-**2c RC**, toluene, 233 K



E_{FSP}=−1185.81263965 Et_{233} = −1185.393969,
H_{233}= −1185.392631 G_{233}= −1185.444391
Imaginary frequency = 0

C	0.716027	0.266087	−2.736098
C	−0.715615	0.773240	−2.478297
C	1.108180	−0.492580	−1.439738
H	1.404458	−1.525574	−1.632695
H	1.948471	0.000705	−0.949290
C	−0.134506	−0.420878	−0.531494
H	0.159795	−0.269582	0.508450
N	−0.807572	0.794680	−1.015970
C	0.655535	0.048340	3.502831
C	1.938927	−0.327907	3.112613
C	2.618796	0.444065	2.178393
C	2.030540	1.579574	1.627670
C	0.741900	1.940565	2.014926
C	0.054523	1.172668	2.954303
O	0.088355	3.048020	1.546599
C	0.375022	3.523632	0.239048
C	1.172927	4.824270	0.298581
H	2.121153	4.640324	0.805730
H	1.372866	5.193700	-0.708069
H	0.619600	5.582951	0.854777
H	0.903208	2.761971	−0.334998
C	−0.917351	3.737010	−0.534938
O	−2.029244	3.624381	0.289280
N	−3.219326	3.846454	−0.357913
C	−4.057916	2.795350	−0.703817
C	−5.319313	3.427271	−1.253755
H	−5.486671	3.048313	−2.262494
H	−6.159227	3.104167	−0.636917
O	−3.795186	1.626493	−0.571464
C	−3.704599	5.133212	−0.602719
C	−5.084265	4.945383	−1.204037
H	−5.803711	5.470418	−0.574542
H	−5.102497	5.414590	−2.188204
O	−3.108829	6.148374	−0.361355
O	−0.985075	4.029088	−1.689706
H	1.392444	1.105679	−2.907757
H	0.762028	−0.372096	−3.619809
H	−0.891853	1.772290	−2.881574
H	−1.768392	0.857730	−0.695956
H	0.110623	−0.547899	4.224905
H	3.616295	0.160366	1.863811
H	2.581143	2.170094	0.907939
H	−0.948939	1.467557	3.233537
H	2.403340	−1.210039	3.535230
H	−1.449353	0.098666	−2.942147
C	−1.005898	−1.682126	−0.605014
H	−1.319941	−1.903365	−1.629578
H	−0.458674	−2.550141	−0.225471
H	−1.905887	−1.559521	0.004775

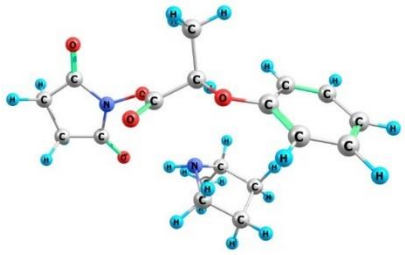
(*R*)-**1d**-(*S*)-**2c TS**, toluene, 233 K



E_{FSP}=−1185.80565837 Et_{233} = −1185.384595,
H_{233}= −1185.383857 G_{233}= −1185.434836
Imaginary frequency = 1

C	−0.886171	−0.397104	−3.180979
C	−1.209206	1.024062	−2.731497
C	0.246586	−0.778650	−2.223725
H	0.421643	−1.853763	−2.169006
H	1.180002	−0.304914	−2.537185
C	−0.211455	−0.206005	−0.871669
H	0.626759	0.149104	−0.284156
N	−1.041473	1.005001	−1.248959
C	4.584638	0.192271	−1.547398
C	4.976580	0.818164	−2.730098
C	4.262537	1.920386	−3.180595
C	3.153980	2.393824	−2.480881
C	2.756492	1.750198	−1.308336
C	3.484682	0.652487	−0.839815
O	1.666616	2.097856	−0.566419
C	0.730001	3.037844	−1.097607
C	1.091821	4.465209	−0.701128
H	2.128900	4.671646	−0.973773
H	0.444399	5.171354	−1.220895
H	0.966499	4.604965	0.372353
H	0.712090	2.938183	−2.183615
C	−0.695936	2.706166	−0.631299
O	−0.639301	2.363112	0.839073
N	−1.735563	2.854526	1.475600
C	−2.953781	2.204338	1.467264
C	−3.919200	3.068836	2.247291
H	−4.833244	3.192408	1.666895
H	−4.178884	2.544933	3.169873
O	−3.167547	1.136480	0.935692
C	−1.744782	4.128326	2.045656
C	−3.166182	4.382107	2.508075
H	−3.169598	4.700719	3.550606
H	−3.556238	5.208148	1.910014
O	−0.786773	4.852862	2.124304
O	−1.627208	3.405551	−1.010399
H	−0.597232	−0.445343	−4.231928
H	−1.750434	−1.050388	−3.035431
H	−0.476093	1.715889	−3.147894
H	−1.949051	0.923264	−0.793288
H	5.135651	−0.663331	−1.175590
H	4.565805	2.427485	−4.088997
H	2.625714	3.261276	−2.849315
H	3.164404	0.168388	0.074149
H	5.830893	0.453101	−3.286003
H	−2.198909	1.388446	−2.995861
C	−1.031333	−1.186676	−0.043555
H	−1.935651	−1.501363	−0.572175
H	−0.431802	−2.075085	0.166738
H	−1.334932	−0.738512	0.902619

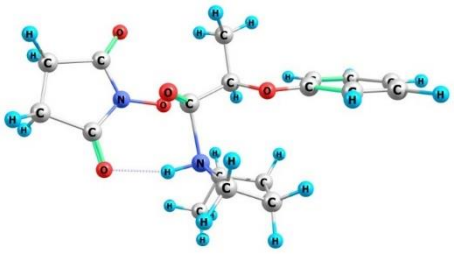
(*R*)-**1d**-(*R*)-**2c RC**, toluene, 233 K



E_{FSP}=−1185.814659518 Et_{233} = −1185.394483,
H_{233}= −1185.393745 G_{233}= −1185.446079
Imaginary frequency = 0

C	−0.059524	−1.434190	0.679043
C	−0.198224	−0.555929	−0.573237
C	−1.482531	−1.967281	0.904599
H	−1.650879	−2.859324	0.296266
H	−1.670076	−2.239543	1.944916
C	−2.385853	−0.815019	0.429836
H	−3.256393	−1.187648	−0.117849
H	−2.761827	−0.230430	1.273900
N	−1.536961	0.043024	−0.424218
C	−0.044424	−1.340655	−1.881022
C	−0.283170	−0.056094	4.469312
C	1.080469	0.198974	4.331403
C	1.501991	1.144882	3.405706
C	0.583684	1.831176	2.615397
C	−0.777480	1.556696	2.748004
C	−1.208856	0.616802	3.687036
O	−1.761547	2.160477	2.019009
C	−1.400543	2.894772	0.863797
C	−1.253623	4.384267	1.178875
H	−0.468960	4.524320	1.923061
H	−0.991400	4.943740	0.279867
H	−2.189826	4.774474	1.581940
H	−0.488761	2.492271	0.424776
C	−2.495825	2.683191	−0.162468
O	−3.639200	2.401243	−0.007814
O	−1.953021	3.023126	−1.412664
N	−2.878413	3.069729	−2.420601
C	−3.564162	4.248564	−2.719737
O	−3.482118	5.265292	−2.083725
C	−4.356932	3.957233	−3.976773
H	−5.404193	4.206938	−3.805699
H	−3.981531	4.612703	−4.765007
C	−3.097940	1.998455	−3.273975
O	−2.561199	0.922128	−3.191844
C	−4.117616	2.470008	−4.285425
H	−5.016716	1.863711	−4.160444
H	−3.727029	2.285129	−5.286754
H	0.258890	−0.826563	1.528013
H	0.674792	−2.230082	0.540809
H	0.555743	0.241242	−0.564209
H	−1.956204	0.205887	−1.330376
H	0.977264	−1.715358	−1.997925
H	−0.726562	−2.195200	−1.912633
H	−0.274442	−0.699661	−2.736165
H	−0.628698	−0.788885	5.188303
H	2.556630	1.366218	3.291179
H	0.943975	2.568081	1.912412
H	−2.269192	0.418187	3.778951
H	1.801541	−0.329452	4.941707

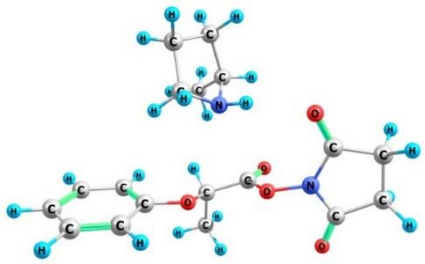
(*R*)-**1d**-(*S*)-**2c TS**, toluene, 233 K



E_{FSP}=−1185.808719504 Et_{233} = −1185.388162,
H_{233}= −1185.387428 G_{233}= −1185.436925
Imaginary frequency = 1

C	0.010533	−0.971628	0.323430
C	−0.366802	−0.318870	−1.010179
C	−1.288340	−1.636630	0.821289
H	−1.301885	−2.698613	0.571729
H	−1.384986	−1.555200	1.903250
C	−2.435560	−0.908566	0.094003
H	−3.036153	−1.598246	−0.501312
H	−3.103932	−0.368497	0.760883
N	−1.790752	0.079396	−0.813779
C	−0.236244	−1.256877	−2.207839
C	−0.384010	0.319591	5.039882
C	0.914425	0.824356	5.088901
C	1.390984	1.565649	4.016205
C	0.593748	1.810656	2.899680
C	−0.701836	1.296260	2.856830
C	−1.187166	0.552094	3.935874
O	−1.563433	1.427431	1.811831
C	−1.240668	2.264499	0.699804
C	−1.443526	3.735373	1.038224
H	−0.789079	4.029168	1.859372
H	−1.224076	4.355540	0.169236
H	−2.479889	3.900351	1.337188
H	−0.215078	2.081322	0.372637
C	−2.212281	1.829711	−0.402882
O	−3.422417	1.902055	−0.297964
O	−1.581832	2.404665	−1.689961
N	−2.550651	2.793679	−2.553896
C	−2.968682	4.123389	−2.640400
O	−2.464548	5.041998	−2.048109
C	−4.132495	4.146925	−3.607764
H	−5.007707	4.510900	−3.066200
H	−3.919329	4.853802	−4.410153
C	−3.270608	1.900965	−3.319164
O	−3.084401	0.700785	−3.350300
C	−4.293616	2.697578	−4.091598
H	−5.280049	2.280203	−3.884996
H	−4.096228	2.575786	−5.158431
H	0.352839	−0.218756	1.031232
H	0.823010	−1.688148	0.197585
H	0.211334	0.584371	−1.207672
H	−2.265349	0.098213	−1.719152
H	0.812188	−1.519991	−2.367168
H	−0.797270	−2.181557	−2.048061
H	−0.611856	−0.777536	−3.114670
H	−0.776770	−0.258794	5.867702
H	2.395410	1.971326	4.041950
H	0.992336	2.396966	2.084559
H	−2.196844	0.163998	3.884855
H	1.542672	0.640539	5.951072

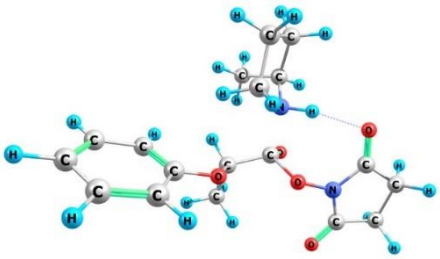
(*R*)-**1d**-(*S*)-**2c RC**, :N *eq*



E_{FSP}=−1185.82161744 Et_{293} = −1185.393229,
H_{293}= −1185.392301 G_{293}= −1185.468491
Et_{253} = −1185.398688,
H_{253}= −1185.397887 G_{253}= −1185.459145
Imaginary frequency = 0

C	−0.546188	−1.780724	−2.972033
H	1.452324	−1.293108	−0.956285
O	−0.520439	−2.974072	−2.929291
C	−0.080451	−0.948292	−4.148063
H	0.918295	−1.320201	−4.371028
C	−1.028783	−1.176925	−5.326098
H	−1.038722	−2.233208	−5.598578
H	−2.039732	−0.858585	−5.064837
H	−0.686818	−0.599017	−6.185007
O	−0.045307	0.421864	−3.776794
C	0.690836	1.295010	−4.530630
C	1.640073	0.923629	−5.483421
H	1.847647	−0.113724	−5.703402
C	2.338845	1.913197	−6.174127
H	3.072328	1.616982	−6.914556
C	2.102707	3.259641	−5.927097
H	2.646231	4.019704	−6.473911
C	0.451334	2.646568	−4.275733
H	−0.291062	2.913536	−3.534145
C	1.153353	3.619808	−4.970276
H	0.950496	4.664444	−4.764946
C	2.813176	−0.057903	−1.853229
C	2.915037	−2.420834	−1.819241
C	4.109100	−1.941237	−0.968141
C	4.213415	−0.433581	−1.288023
H	2.902302	0.303164	−2.880402
H	3.871582	−2.089646	0.089096
H	5.033359	−2.482278	−1.182396
H	4.465419	0.149689	−0.400649
H	4.989650	−0.239192	−2.031454
N	1.985068	−1.277539	−1.819076
H	2.322169	0.730168	−1.280616
H	2.409918	−3.273706	−1.359215
C	3.324543	−2.796763	−3.244175
H	4.034207	−3.628397	−3.236576
H	2.452479	−3.099535	−3.827116
H	3.804633	−1.956289	−3.753957
O	−1.170574	−1.004832	−2.000254
N	−1.783273	−1.756984	−1.028446
C	−1.179146	−2.037412	0.189186
O	−0.057000	−1.714106	0.496513
C	−3.080604	−2.240817	−1.197119
O	−3.734529	−2.092739	−2.198093
C	−2.201940	−2.798645	0.999862
H	−1.768092	−3.754153	1.296846
H	−2.408749	−2.230561	1.908188
C	−3.434586	−2.945620	0.092063
H	−3.677467	−3.983896	−0.138486
H	−4.327960	−2.477582	0.507856

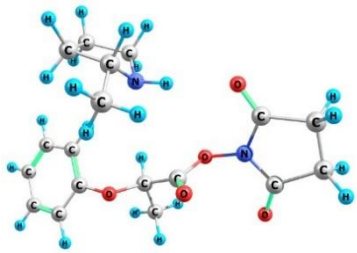
(*R*)-**1d**-(*S*)-**2c TS**, :N *eq*



E_{FSP}=−1185.81291339 Et_{293} = −1185.384262,
H_{293}= −1185.383334 G_{293}= −1185.454712
Et_{253} = −1185.389531,
H_{253}= −1185.388729 G_{253}= −1185.445812
Imaginary frequency = 1

C	0.107041	−1.717554	−2.725020
H	1.248673	−1.432460	−0.867538
O	−0.095992	−2.924707	−2.737573
C	0.241127	−0.921377	−4.030768
H	1.205447	−1.210069	−4.447851
C	−0.871821	−1.269051	−5.006658
H	−0.846262	−2.332694	−5.245195
H	−1.842228	−1.023562	−4.572320
H	−0.736267	−0.699739	−5.928221
O	0.222838	0.477	−3.740949
C	0.842570	1.359954	−4.576948
C	1.735641	1.013968	−5.592232
H	1.970097	−0.016974	−5.815313
C	2.339964	2.021478	−6.344677
H	3.031446	1.743705	−7.131318
C	2.063531	3.360472	−6.101808
H	2.535258	4.133062	−6.695614
C	0.558406	2.706032	−4.331568
H	−0.139976	2.953271	−3.541861
C	1.164268	3.696232	−5.088854
H	0.928620	4.734535	−4.886342
C	2.447963	−0.144585	−1.912690
C	2.648282	−2.523239	−1.866177
C	3.772009	−1.984622	−0.969864
C	3.813568	−0.464498	−1.259879
H	2.571255	0.118561	−2.959260
H	3.514068	−2.164237	0.076609
H	4.723109	−2.477651	−1.171254
H	3.965769	0.109095	−0.345749
H	4.621734	−0.209165	−1.945984
N	1.656683	−1.403236	−1.807001
H	1.899039	0.658549	−1.426625
H	2.169125	−3.403469	−1.440969
C	3.108783	−2.825621	−3.287653
H	3.839034	−3.636771	−3.257482
H	2.276971	−3.146463	−3.913714
H	3.595720	−1.964683	−3.752251
O	−0.798112	−0.881740	−1.808223
N	−1.504846	−1.666843	−0.955516
C	−0.985402	−2.128500	0.235253
O	0.158472	−1.941792	0.608598
C	−2.808792	−2.081626	−1.230707
O	−3.409735	−1.828050	−2.245671
C	−2.086214	−2.875155	0.946899
H	−1.733375	−3.876376	1.196398
H	−2.301575	−2.356991	1.883461
C	−3.276291	−2.866149	−0.024472
H	−3.570396	−3.864169	−0.352528
H	−4.160128	−2.376795	0.387769

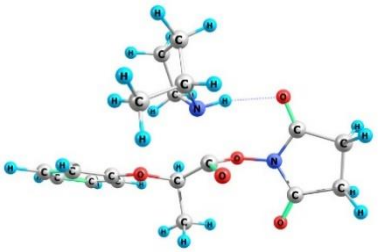
(*R*)-**1d**-(*R*)-**2c RC**, :N *eq*



E_{FSP}=−1185.82201923 Et_{293} = −1185.394973,
H_{293}= −1185.394045 G_{293}= −1185.468832
Et_{253} = −1185.400313,
H_{253}= −1185. 399951 G_{253}= −1185.459670
Imaginary frequency = 0

O	1.126512	3.897456	−1.879845
H	3.842363	1.905256	−0.655785
O	3.157760	3.658805	−2.883078
N	2.582145	2.739315	−3.721456
C	2.651230	1.373622	−3.479483
O	3.162571	0.872997	−2.507265
C	1.974762	0.709472	−4.657323
H	2.682132	0.024121	−5.125134
H	1.136396	0.121018	−4.281802
C	1.952260	3.130000	−4.902204
O	1.809289	4.277464	−5.241571
C	1.534607	1.851106	−5.590778
H	0.456800	1.878655	−5.755957
H	2.022350	1.810950	−6.565914
C	2.979548	5.390501	−1.319818
H	3.989231	5.045358	−1.086520
C	3.029846	6.593578	−2.265186
H	3.563549	6.338722	−3.181554
H	2.018735	6.918234	−2.517387
H	3.554469	7.411684	−1.770172
O	2.277567	5.704590	−0.120157
C	3.046969	6.368152	0.821227
C	4.127947	5.731630	1.426369
H	4.362053	4.709607	1.153338
C	4.880044	6.421062	2.371460
H	5.723997	5.931414	2.842894
C	4.547366	7.727866	2.721904
H	5.138502	8.261349	3.456034
C	2.699411	7.668185	1.167434
H	1.854999	8.138874	0.679446
C	3.452808	8.345878	2.122636
H	3.182359	9.359013	2.395894
C	3.248412	1.724206	1.316959
C	1.826889	2.265618	1.293869
H	1.245600	1.842799	2.117935
H	1.827654	3.354456	1.386564
H	1.321038	2.007469	0.360043
C	5.466923	1.942617	0.607002
H	6.179257	2.569946	0.066197
C	5.519070	2.154904	2.132922
C	4.042158	2.072168	2.588687
H	6.145180	1.402301	2.613301
H	5.945667	3.129997	2.375952
H	3.884450	1.330671	3.373304
H	3.705981	3.035873	2.979277
N	4.086371	2.295551	0.250152
H	3.206029	0.624375	1.227045
H	5.699984	0.893114	0.366481

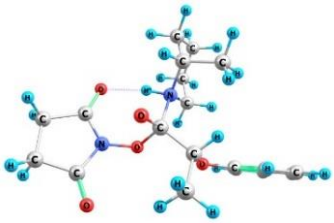
(*R*)-**1d**-(*R*)-**2c TS**, :N *eq*



E_{FSP}=−1185.81392148 Et_{293} = −1185.385569,
H_{293}= −1185.384642 G_{293}= −1185.457262
Et_{253} = −1185.39085991,
H_{253}= −1185. 390059 G_{253}= −1185.448225
Imaginary frequency = 1

C	2.718545	3.721063	−1.444999
O	1.539546	3.476398	−1.590850
H	3.565138	1.763220	−0.801217
O	3.684396	3.243671	−2.544885
N	3.080287	2.444728	−3.458641
C	2.945716	1.082817	−3.280630
O	3.303807	0.484274	−2.285324
C	2.289428	0.532228	−4.523544
H	2.949197	−0.213489	−4.969105
H	1.366270	0.028278	−4.233500
C	2.568851	2.940785	−4.656107
O	2.576966	4.105771	−4.972244
C	2.053985	1.748905	−5.432007
H	1.002408	1.912852	−5.670570
H	2.603258	1.686013	−6.372688
C	3.311863	5.096973	−1.107458
H	4.399347	5.015138	−1.148078
C	2.798515	6.120613	−2.113432
H	3.099062	5.841334	−3.123036
H	1.708986	6.157498	−2.065820
H	3.196802	7.108753	−1.881360
O	2.893602	5.434979	0.212028
C	3.574462	6.386345	0.914954
C	4.719239	7.044603	0.463981
H	5.136713	6.840765	−0.511140
C	5.332485	7.993676	1.280469
H	6.218787	8.500608	0.917500
C	4.820705	8.296181	2.535445
H	5.302938	9.036284	3.161500
C	3.054231	6.686932	2.177370
H	2.161592	6.172928	2.510256
C	3.673435	7.636505	2.976357
H	3.254348	7.867984	3.948670
C	2.416956	1.958089	0.850341
C	1.732506	3.016544	1.700651
H	1.058012	2.514305	2.398658
H	2.449825	3.599663	2.280900
H	1.156668	3.703836	1.084424
C	4.678957	2.743450	0.601805
H	4.752341	3.787441	0.898476
C	4.629474	1.812124	1.837591
C	3.312108	1.024202	1.678738
H	5.493546	1.148771	1.877998
H	4.624746	2.405588	2.753072
H	3.490205	0.098600	1.125682
H	2.855782	0.761220	2.634256
N	3.399116	2.515687	−0.130072
H	1.668772	1.409459	0.278394
H	5.505265	2.514869	−0.069469

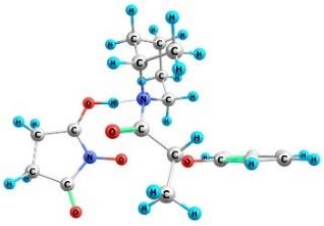
(*R*)-**1d**-(*S*)-**2a AAS**, :N *eq*



E_{FSP}=−1225.12243888 Et_{293} = −1224.662637,
H_{293}= −1224.6617095 G_{293}= −1224.735876
Et_{253} = −1224.668272,
H_{253}= −1224.667471 G_{253}= −1224.726641
Imaginary frequency = 0

C	2.479600	1.428872	−1.377994
H	2.524459	0.167538	0.257575
O	2.774300	0.583649	−2.226964
C	2.713509	2.915910	−1.700639
H	3.794546	3.054503	−1.680374
C	2.170905	3.253275	−3.082648
H	2.667690	2.643378	−3.836423
H	1.099406	3.055338	−3.124854
H	2.356207	4.305717	−3.307273
O	2.119801	3.747457	−0.699820
C	2.746370	4.896573	−0.314972
C	3.823676	5.478721	−0.983933
H	4.220051	5.045560	−1.890816
C	4.395424	6.647062	−0.482688
H	5.230622	7.090651	−1.011977
C	3.900523	7.248036	0.667633
H	4.351664	8.154831	1.051061
C	2.238939	5.502313	0.838519
H	1.401259	5.039296	1.345134
C	2.814268	6.667906	1.322368
H	2.413285	7.126104	2.218823
C	2.910984	1.865456	1.303936
C	4.525851	0.457174	0.003751
C	4.806380	−0.355159	1.274228
C	4.616944	0.469622	2.550462
C	3.216867	1.084738	2.580913
H	3.545652	2.743932	1.216516
H	4.131043	−1.217410	1.294447
H	5.823144	−0.749867	1.211408
H	4.773238	−0.164849	3.426182
H	5.368614	1.264289	2.599375
H	2.469407	0.292076	2.699984
H	3.098783	1.761937	3.430643
N	3.121390	0.994965	0.107286
H	1.876054	2.192355	1.282826
H	4.495544	−0.217581	−0.850442
C	5.563628	1.541516	−0.263455
H	6.555376	1.090508	−0.191252
H	5.462471	1.954875	−1.266805
H	5.522365	2.361488	0.453149
O	0.932081	1.374756	−0.898937
N	0.332188	0.257160	−1.361493
C	0.561369	−0.994551	−0.834431
O	1.332035	−1.227391	0.081727
C	−0.522302	0.273309	−2.462601
O	−0.786312	1.257487	−3.110050
C	−0.290999	−1.977502	−1.593558
H	0.362217	−2.729383	−2.038648
H	−0.956387	−2.484493	−0.892894
C	−1.034411	−1.138097	−2.639805
H	−0.840036	−1.457402	−3.664227
H	−2.114945	−1.135385	−2.482785

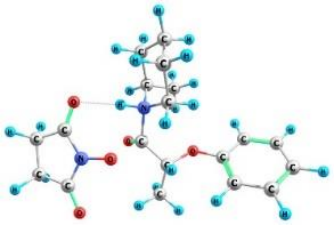
(*R*)-**1d**-(*S*)-**2a TS2**, :N *eq*



E_{FSP}=−1225.1040819 Et_{293} = −1224.649804,
H_{293}= −1224.648876 G_{293}= −1224.722134
Et_{253} = −1224.655363,
H_{253}= −1224.654562 G_{253}= −1224.713015
Imaginary frequency = 1

C	2.975112	1.551571	−1.426594
H	2.210096	0.077337	0.002551
O	2.993275	0.741075	−2.324504
C	3.004525	3.052181	−1.764128
H	4.067288	3.302404	−1.647659
C	2.569805	3.309921	−3.197034
H	3.175704	2.735482	−3.895852
H	1.524112	3.023196	−3.318241
H	2.685656	4.371105	−3.425827
O	2.239033	3.843113	−0.862747
C	2.764590	5.001012	−0.361881
C	3.865898	5.667479	−0.898203
H	4.370659	5.298009	−1.779397
C	4.314603	6.842496	−0.298634
H	5.169511	7.355017	−0.723620
C	3.674862	7.363300	0.819323
H	4.033777	8.275307	1.279808
C	2.110727	5.524557	0.756451
H	1.255419	4.994513	1.156316
C	2.564703	6.698705	1.339517
H	2.051949	7.093657	2.208496
C	3.065288	1.981117	1.074887
C	4.517153	0.258848	−0.038720
C	4.585957	−0.512594	1.280138
C	4.443798	0.398348	2.499393
C	3.149082	1.203241	2.386756
H	3.822575	2.769147	1.053707
H	3.790115	−1.262260	1.292997
H	5.534283	−1.055590	1.302399
H	4.445149	−0.202615	3.412308
H	5.297528	1.080915	2.566410
H	2.290699	0.526059	2.458246
H	3.057002	1.920221	3.206794
N	3.229557	1.064121	−0.083551
H	2.090861	2.444589	0.973767
H	4.429246	−0.456808	−0.853943
C	5.748398	1.130211	−0.282452
H	6.644376	0.514987	−0.173602
H	5.751047	1.544454	−1.293084
H	5.826676	1.956014	0.425689
O	0.517050	1.568651	−0.928949
N	0.093438	0.388197	−1.338
C	0.583338	−0.763768	−0.849307
O	1.558699	−0.836640	−0.028524
C	−0.951785	0.167546	−2.245742
O	−1.525751	1.061141	−2.812864
C	−0.135241	−1.944186	−1.402077
H	0.575285	−2.601796	−1.907546
H	−0.596350	−2.513013	−0.590921
C	−1.162418	−1.322381	−2.357070
H	−1.008930	−1.628394	−3.393373
H	−2.192690	−1.557937	−2.084680

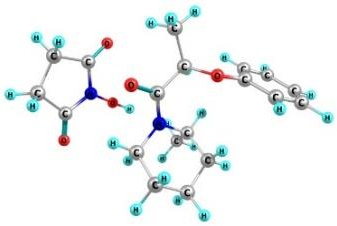
(*R*)-**1d**-(*R*)-**2a AAS**, :N *eq*



E_{FSP}= −1225.12614072 Et_{293} = −1224.666381,
H_{293}= −1224.665453 G_{293}= −1224.739739
Et_{253} = −1224.672036,
H_{253}= −1224. 671234 G_{253}= −1224.730490
Imaginary frequency = 0

C	2.553020	3.577795	−0.945989
O	1.487788	3.266312	−1.424792
H	3.431671	1.792610	−0.526622
O	3.992324	3.083289	−2.231137
N	3.403411	2.313109	−3.142477
C	3.059023	1.006902	−2.889887
O	3.266548	0.449137	−1.818484
C	2.405608	0.436459	−4.121984
H	3.006900	-0.395919	−4.492302
H	1.425206	0.040591	−3.852016
C	2.989623	2.773145	−4.388529
O	3.151887	3.907384	−4.783649
C	2.337952	1.612511	−5.107822
H	1.315956	1.892219	−5.369368
H	2.876058	1.421716	−6.037695
C	3.052541	5.020293	−0.823924
H	4.139838	5.023344	−0.815785
C	2.516565	5.868116	−1.960554
H	2.887463	5.486486	−2.911348
H	1.426333	5.836751	−1.964203
H	2.841822	6.901800	−1.835048
O	2.558020	5.490642	0.441044
C	3.282126	6.406125	1.153066
C	4.384194	7.101612	0.655967
H	4.730728	6.957594	−0.357356
C	5.046833	8.011721	1.477968
H	5.900897	8.548376	1.082394
C	4.621259	8.241098	2.780047
H	5.141742	8.951320	3.409876
C	2.847451	6.632694	2.461578
H	1.989945	6.083818	2.830219
C	3.512033	7.548627	3.264595
H	3.160778	7.723504	4.274802
C	2.028586	1.917615	0.963094
C	1.356955	2.916403	1.891219
H	0.561754	2.393566	2.426787
H	2.039680	3.332664	2.632269
H	0.912546	3.739240	1.334116
C	4.323567	2.973829	0.895243
H	4.018987	3.751635	1.591214
C	4.916888	1.773897	1.626525
C	3.877205	1.080159	2.508136
C	2.642063	0.710649	1.682674
H	5.313932	1.065911	0.890706
H	5.763221	2.125307	2.220851
H	4.307303	0.180985	2.955598
H	3.595060	1.739372	3.334627
H	2.914858	−0.040163	0.934415
H	1.868652	0.265356	2.312965
N	3.121510	2.550556	0.109266
H	1.298254	1.567680	0.236351
H	5.039748	3.388216	0.189932

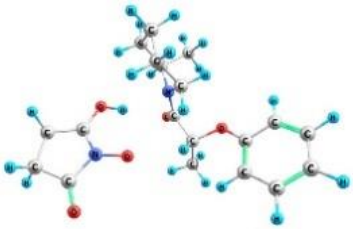
(*R*)-**1d**-(*R*)-**2a TS2**, :N *eq*



E_{FSP}= −1225.11363032 Et_{293} = −1224.660532,
H_{293}= −1224.659604 G_{293}= −1224.732443
Et_{253} = −1224.666083,
H_{253}= −1224. 664207 G_{253}= −1224.723349
Imaginary frequency = 0

C	2.194582	3.801230	−0.622563
O	1.066748	3.630977	−1.011470
H	2.901974	1.833228	−1.006671
O	3.983757	3.325699	−2.597144
N	3.675572	2.340868	−3.402129
C	3.095332	1.204834	−3.010361
O	2.757525	0.967321	−1.809039
C	2.907592	0.254993	−4.145597
H	3.467683	−0.662191	−3.948953
H	1.853475	−0.016625	−4.234554
C	3.935423	2.340242	−4.799553
O	4.466574	3.260958	−5.369869
C	3.437348	1.031370	−5.360520
H	2.660696	1.233168	−6.100365
H	4.256821	0.525061	−5.872061
C	2.889011	5.165739	−0.698610
H	3.937344	5.032065	−0.951186
C	2.214523	6.082427	−1.696530
H	2.356232	5.677595	−2.699704
H	1.147443	6.160803	−1.486725
H	2.658327	7.077129	−1.654920
O	2.765197	5.645950	0.653004
C	3.659797	6.558690	1.141254
C	4.663089	7.171380	0.391546
H	4.795323	6.953349	−0.658434
C	5.509897	8.093188	1.007087
H	6.282427	8.569667	0.415611
C	5.365935	8.411015	2.351730
H	6.026159	9.130695	2.818727
C	3.509782	6.871900	2.494455
H	2.726016	6.383228	3.059650
C	4.357379	7.793257	3.091352
H	4.225057	8.033515	4.139760
C	2.002665	2.002197	1.048281
C	1.669240	2.918032	2.223610
H	1.011346	2.379361	2.908670
H	2.556297	3.224220	2.778951
H	1.151140	3.817685	1.891717
C	4.281043	2.921329	0.473287
H	4.294995	3.632989	1.300197
C	4.925115	1.604635	0.888445
C	4.109503	0.893462	1.965748
C	2.672764	0.694056	1.478987
H	5.024727	0.957464	0.011290
H	5.934988	1.826078	1.243299
H	4.556889	−0.073759	2.207522
H	4.125531	1.485747	2.886086
H	2.669343	−0.002125	0.635842
H	2.053992	0.245133	2.259551
N	2.877497	2.698272	0.018495
H	1.083958	1.764960	0.514569
H	4.823083	3.343409	−0.367045

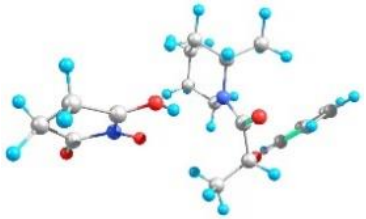
(*R*)-**1d**-(*R*)-**2a PC**, :N *eq*



E_{FSP}= −1225.12082053 Et_{293} = −1224.663241,
H_{293}= −1224.662313 G_{293}= −1224.737256
Et_{253} = −1224.668836,
H_{253}= −1224.668031 G_{253}= −1224.727992
Imaginary frequency = 0

C	1.830953	3.894061	−0.163011
O	0.653131	3.735473	−0.464735
H	2.748748	1.957575	−1.489933
O	3.892935	3.439448	−2.647243
N	3.842305	2.427179	−3.461224
C	3.221477	1.300681	−3.181480
O	2.618592	1.142773	−2.039023
C	3.291110	0.285220	−4.254314
H	3.759544	−0.627548	−3.878653
H	2.287647	0.023966	−4.598430
C	4.419580	2.371453	−4.781807
O	5.002440	3.296828	−5.273704
C	4.129261	0.996381	−5.333248
H	3.599990	1.094241	−6.281509
H	5.075443	0.489168	−5.529765
C	2.533915	5.231508	−0.455558
H	3.482261	5.035354	−0.956096
C	1.671080	6.143103	−1.304538
H	1.446314	5.654800	−2.254133
H	0.732007	6.363943	−0.796919
H	2.192228	7.078028	−1.511780
O	2.769745	5.781233	0.855397
C	3.798109	6.653994	1.066183
C	4.567940	7.233460	0.057864
H	4.389229	7.010642	−0.983718
C	5.581041	8.129097	0.399551
H	6.170650	8.577580	−0.390917
C	5.835951	8.451316	1.726254
H	6.622909	9.150181	1.979812
C	4.055653	6.966616	2.404510
H	3.450607	6.500460	3.172918
C	5.066267	7.861068	2.728648
H	5.258198	8.098573	3.768749
C	1.780286	1.871498	1.187053
C	1.339407	2.393693	2.559256
H	0.706581	1.650898	3.049929
H	2.188993	2.601617	3.212230
H	0.760438	3.313181	2.451511
C	3.939924	3.130789	0.925808
H	3.932476	3.586202	1.920855
C	4.721320	1.822473	0.956517
C	4.003698	0.755822	1.779063
C	2.574344	0.564840	1.270667
H	4.869674	1.464576	−0.067904
H	5.710156	2.033644	1.372581
H	4.542096	−0.193349	1.719009
H	3.996602	1.052553	2.833372
H	2.607199	0.108778	0.277926
H	2.022288	−0.124012	1.915481
N	2.556868	2.917104	0.464319
H	0.890542	1.693997	0.586717
H	4.434003	3.823710	0.252182

(*R*)-**1d**-(*S*)-**2a PC**, :N *eq*



E_{FSP}= −1225.11444827 Et_{293} = −1224.661100,
H_{293}= −1224.660173 G_{293}= −1224.732573
Et_{253} = −1224.666677
H_{253}= −1224.66576 G_{253}= −1224.723532
Imaginary frequency = 0

C	3.339450	2.551386	−1.536233
H	2.036202	0.368796	−1.257375
O	4.085837	2.144059	−2.418809
C	2.425354	3.767979	−1.896811
H	2.932803	4.203200	−2.780623
C	1.014530	3.326935	−2.308441
H	1.082489	2.647653	−3.176712
H	0.478451	2.791629	−1.505586
H	0.423762	4.210333	−2.609498
O	2.291971	4.775347	−0.891538
C	3.391118	5.441653	−0.423940
C	4.702710	5.254616	−0.898814
H	4.922032	4.562872	−1.717032
C	5.758837	5.964616	−0.304965
H	6.777789	5.797600	−0.676901
C	5.528139	6.867752	0.737457
H	6.360357	7.414521	1.195896
C	3.152387	6.363539	0.616346
H	2.124457	6.507194	0.969344
C	4.213544	7.066825	1.189750
H	4.010981	7.774537	2.003466
C	2.520419	2.487952	0.859316
C	4.405928	1.014635	0.042357
C	3.966183	−0.056156	1.065332
C	3.261136	0.529275	2.298227
C	2.079911	1.397226	1.845533
H	3.157837	3.231071	1.382913
H	3.281539	−0.764327	0.561436
H	4.857196	−0.643285	1.360244
H	2.913958	−0.287152	2.960241
H	3.973773	1.130683	2.898781
H	1.305220	0.774912	1.359376
H	1.595124	1.892984	2.708637
N	3.261217	1.924214	−0.298200
H	1.637611	3.027379	0.493331
H	4.671975	0.504435	−0.897425
C	5.644231	1.814812	0.495714
H	6.483367	1.123482	0.696384
H	5.968795	2.513233	−0.293122
H	5.466957	2.401208	1.415140
O	−0.135053	0.518541	−0.525776
N	−0.097511	−0.626712	−1.096853
C	0.968205	−1.140156	−1.700724
O	2.102980	−0.485172	−1.767751
C	−1.229935	−1.563265	−1.175051
O	−2.310513	−1.325987	−0.723827
C	0.762566	−2.514841	−2.248867
H	0.979943	−2.549686	−3.334732
H	1.461571	−3.228600	−1.770127
C	−0.719975	−2.801586	−1.909468
H	−1.341521	−2.975996	−2.806594
H	−0.851594	−3.684901	−1.258237

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