Supporting Information

Enantioselective Synthesis of Anti-β-Substituted γδ-Unsaturated Amino Acids: A Highly Selective Assymmetric Thio-Clasien Rearrangement
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General Information
All starting materials and reagents were purchased from Sigma-Aldrich and used without further purification unless otherwise noted. Dried THF was obtained from distillation over sodium and benzophenone. Dried methylene chloride was obtained from distillation over CaH2. 1H and 13C NMR spectra were acquired on a Varian Unity300 (300 MHz and 75 MHz, respectively), Bruker DRX500 (500 MHz and 125 MHz, respectively) or Varian Inova 600 (600 MHz and 150 MHz, respectively) spectrometers; CDCl3 or TMS is used as internal standard for reporting chemical shift values. IR spectra were recorded on a Nicolet Impact 410 IR spectrometer. HPLC analysis was obtained with a Chiralpak AD RH column (150 × 4.6 mm) on an HP 1100 HPLC machine or Shimadzu SCL-10A HPLC machine. Mass spectra were obtained from Mass Spectrometry Facility, Department of Chemistry, University of Arizona. Flash column chromatography was performed using silica gel 60 from the EM Science as the packing material. TLC was performed with plates (Silica Gel 60 F254) purchased from the EMD Chemicals and were visualized by UV and KMnO4 stain.

Experimental Section

Benzyl 2-((2S,5S)-2,5-diphenylpyrrolidin-1-yl)-2-oxoethylcarbamate (2). Nα-Cbz-Glycine (915 mg, 4.38 mmol) and HOAT (596 mg, 4.38 mmol) were dissolved in dry DCM (30 mL) in a 250-mL flask under argon atmosphere. Diisopropylcarbodiimide (DIC) (681 μL, 4.38 mmol) was added and the mixture was stirred for 15 min at room temperature before (2S,5S)-2,5-diphenylpyrrolidine (1) (630 mg, 3.44 mmol) dissolved in dry DCM (70 mL) was added. Then the reaction was quenched by the addition of a saturated ammonium chloride solution (5 mL) after 24 h. The organic layer was separated and washed with a saturated ammonium chloride solution (50 mL × 2), a saturated sodium bicarbonate solution (50 mL × 2), brine (50 mL × 1) and dried over anhydrous MgSO4. The solution was filtered and concentrated, then purified by flash column chromatography (Hexane:EtOAc = 4:1–2:1) to give 2 as a colorless oil (1051 mg, 90%). \( R_f = 0.33 \) (Hexane:EtOAc = 2:1), \([\alpha]_{D}^{23.3} +115.0 \) (c 0.73, MeOH), HRMS (FAB) calcd for C26H27N2O3 (MH+)
415.2022, found 415.2009. $^{1}$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.44-1.78 (m, 1H), 1.80-1.84 (m, 1H), 2.39-2.47 (m 1H), 2.54-2.61 (m, 1H), 3.43 (dd, 1H, $J$ = 3.6, 17.4 Hz), 4.11 (dd, 1H, $J$ = 5.4, 17.4 Hz), 5.02 (s, 2H), 5.26 (d, 1H, $J$ = 8.4 Hz), 5.51 (d, 1H, $J$ = 8.4 Hz), 5.55 (br, 1H), 7.17−7.39 (m, 15H); 13C (125 MHz, CDCl$_3$) $\delta$ 30.24, 33.01, 43.84, 61.85, 62.49, 66.66, 125.13, 125.14, 126.98, 127.76, 127.84, 128.92, 129.11, 136.44, 142.19, 142.43, 156.01, 167.58. IR (NaCl): 1722.04, 1652.99, 1495.92, 1450.86, 1425.98, 1249.50.

Benzyl-2-((2S,5S)-2,5-diphenylpyrrolidin-1-yl)-2-thioxoethylcarbamate (3). Compound 2 (1051 mg, 2.54 mmol) was dissolved in toluene (100 mL) with Lawesson reagent (1230 mg, 3.04 mmol) and sodium bicarbonate (2347 mg, 27.94 mmol). The reaction was stirred and refluxed at 120 °C for 3 h. Then the reaction was cooled to room temperature, and washed with a saturated ammonium chloride solution (50 mL × 2), brine (50 mL × 1) and dried over anhydrous MgSO$_4$. The solution was filtered and concentrated, then purified by flash column chromatography (Hexane:EioAc = 16:1−8:1) to give 3 as a colorless oil (1089 mg, 100%). $R_f$ = 0.40 (Hexane:EioAc = 3:1), [$\alpha$]$^{24}_{D}$ +24.9 (c 0.77, MeOH), HRMS (FAB) calcd for C$_{26}$H$_{27}$N$_2$O$_2$S (MH$^+$) 431.1793, found 431.1799. $^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.74−1.8 (m, 2H), 2.40-2.65 (m, 2H), 3.53 (dd, 1H, $J$ = 3.6, 17.7 Hz), 4.22 (dd, 1H, $J$ = 6.0, 17.4 Hz), 4.98 (s, 2H), 5.55 (d, 1H, $J$ = 8.1 Hz), 5.96 (d, 1H, $J$ = 7.8 Hz), 6.06 (br, 1H), 7.03−7.32 (m, 15H); 13C (125 MHz, CDCl$_3$) $\delta$ 30.00, 32.975, 49.49, 65.79, 66.68, 68.71, 125.06, 125.44, 126.87, 127.87, 127.94, 128.39, 128.55, 129.26, 136.40, 140.61, 140.98, 155.77, 197.36. IR (NaCl): 1416.99, 1495.35, 1448.57, 1257.42, 1211.84.

General procedure for the preparation of compounds 5. LDA was prepared in a 50 mL flask at 0 °C under argon atmosphere by mixing diisopropylamine (147 µL, 1.05 mmol) with n-butyl lithium (1.6 M in hexane, 0.67 mL, 1.05mmmol) in dry THF (10 mL) for 15 min. Then the LDA solution was transferred into a 100-mL flask which had compound 3 (150 mg, 0.35 mmol) dissolved in dry THF (20 mL) at -78 °C. The mixture was stirred for 30 min at -78 °C before HMPA (188 µL, 1.05 mmol) was added, and another 5 min before the allylic bromide (0.70 mmol) was added, respectively. The reaction was allowed to warm up slowly to room temperature (or other temperatures found in Table 1) over a period of 4 h. Then the reaction was quenched by the addition of a saturated sodium bicarbonate solution (5 mL). THF was removed under reduced pressure; the residue was extracted twice with hexanes and diethyl ether. The combined organic layers were pooled and washed with a saturated sodium bicarbonate solution (10 mL × 1), a saturated ammonium chloride solution (10 mL × 1) and dried over anhydrous MgSO$_4$. The dry solution was concentrated under reduced pressure, and the crude product was purified by flash column chromatography to afford compounds 5.
General procedure for HPLC analysis of ratio of diastereomers of thio-Claisen rearrangement. The ratio of diastereomeric thioamides from thio-Claisen rearrangement was determined by oxidizing the rearrangement product with mCPBA followed by HPLC analysis. A portion of the thio-Claisen rearrangement product (10 mg) was dissolved in DCM (2 mL) and cooled to -78 °C. mCPBA (10 mg) was added and the suspension was allowed to warm up to room temperature in 1 h. The reaction was diluted with ether and hexanes and washed with 1 N NaOH, brine, and dried with anhydrous MgSO₄. After the solvent was removed in vacuo, the residue was dissolved in MeOH and subjected to HPLC analysis.

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\text{Ph} \quad \text{S} \quad \text{R}_1 \quad \text{R}_2 \quad \text{R}_3 \quad \text{NHCbz} \quad 5 \quad \text{major} \quad \text{mCPBA} \quad 7 \quad \text{major} \\
\text{Ph} \quad \text{S} \quad \text{R}_3 \quad \text{R}_2 \quad \text{R}_1 \quad \text{NHCbz} \quad 6 \quad \text{minor} \\
\text{Ph} \quad \text{O} \quad \text{R}_3 \quad \text{R}_2 \quad \text{R}_1 \quad \text{NHCbz} \quad 8 \quad \text{minor} \quad 5a
\]

Benzyll-(R)-1-((2R,5R)-2,5-diphenylpyrrolidin-1-yl)-1-thioxopent-4-en-2-ylcarbamate (5a). Compound 3 (230 mg, 0.53 mmol), diisopropylamine (236 μL, 1.68 mmol), n-butyl lithium (1.6 M in hexane, 1.05 mL, 1.68 mmol), HMPA (300 μL, 1.68 mmol) and allyl bromide (71 μL, 0.84 mmol) were reacted and worked up as described above. Product 5a: yellow oil, 203 mg, yield 82.0%, \( R_f = 0.45 \) (Hexane:EtOAc 3:1), [\( \alpha \)] \( ^{23.4} \) D +8.3831 (c 0.83, MeOH), HRMS (FAB) calcd for C\(_{29}\)H\(_{31}\)N\(_2\)O\(_2\)S (MH\(^+\)) 471.2106, found 471.2100. \( ^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 1.80 (dd, 1H, \( J = 6.6, 12.6 \) Hz), 1.97 (dd, 1H, \( J = 6.6, 12.6 \) Hz), 2.41-2.50 (m, 2H), 2.55-2.63 (m, 1H), 2.65-2.75 (m, 1H), 4.64-4.72 (m, 1H), 4.82 (dd, \( J = 12.6, 15.6 \) Hz), 5.08-5.15 (m, 2H), 5.63 (d, 1H, \( J = 7.8 \) Hz), 5.72-5.80 (m, 1H), 5.84 (d, 1H, \( J = 9.0 \) Hz), 6.01 (d, 1H, \( J = 8.4 \) Hz), 7.02–7.38 (m, 15H); \( ^{13}\)C (150 MHz, CDCl\(_3\)) \( \delta \) 29.93, 33.17, 42.14, 57.02, 66.21, 66.53, 68.36, 118.89, 125.24, 125.70, 126.98, 127.76, 127.82, 127.88, 128.28, 128.42, 128.49, 128.49, 128.94, 132.87, 136.62, 140.97, 141.14, 153.99, 202.66. IR (NaCl): 1721.39, 1494.53, 1439.82, 1343.57, 1304.64, 1208.99, 1045.57, 1028.48.

HPLC analysis: de>99%. Chiralpak AD-RH column (CH\(_3\)CN/H\(_2\)O: 60/40, 0.5 mL/min, 254 nm); retention times of the only diastereomer observed: 21.4 min (7a).
Benzyl-(R)-1-((2R,5R)-2,5-diphenylpyrrolidin-1-yl)-3,3-dimethyl-1-thioxopent-4-en-2-ylcarbamate (5b). Compound 3 (150.2 mg, 0.35 mmol), diisopropylamine (147 μL, 1.05 mmol), n-butyl lithium (1.6 M in hexane, 0.67 mL, 1.05 mmol), HMPA (188 μL, 1.05 mmol) and 3,3-dimethylallyl bromide (83 μL, 0.70 mmol) were reacted and worked up as described above. Product 5b: yellow oil, 112.5 mg, yield 66.0%, \( R_f = 0.50 \) (Hexane:EtOAc = 3:1), \([\alpha]_{24.3}^D +11.4 \) (c 0.55, MeOH), HRMS (FAB) calcd for C\(_{31}\)H\(_{35}\)N\(_2\)O\(_2\)S (MH\(^+\)) 499.2419, found 499.2407. \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 1.03 (s, 3H), 1.05 (s, 3H), 1.72-1.81 (m, 1H), 1.94-1.98 (m, 1H), 2.37-2.47 (m, 1H), 2.75-2.85 (m, 1H), 4.56 (d, 1H, J = 9.0 Hz), 4.75 (s, 1H), 5.06-5.16 (m, 2H), 5.73 (d, 1H, J = 7.8 Hz), 5.84 (d, 1H, J = 9.0 Hz), 5.86-5.95 (m, 1H), 7.01-7.38 (m, 15H); \(^{13}\)C (150 MHz, CDCl\(_3\)) δ 23.12, 25.02, 29.87, 33.57, 43.61, 62.98, 66.22, 67.55, 68.97, 113.05, 125.19, 126.50, 127.01, 127.60, 127.86, 128.29, 128.33, 128.89, 136.79, 141.75, 142.08, 144.89, 154.11, 202.03. IR (NaCl): 2972.67, 1727.89, 1494.66, 1454.54, 1423.77, 1362.14, 1333.58, 1212.91, 1028.71.

HPLC analysis: \( \text{de}>99\% \). Chiralpak AD-RH column (CH\(_3\)CN/H\(_2\)O/MeOH: 0.7 mL/min, 254 nm); retention times of the only diastereomer observed: 23.0 min (7b).

Benzyl-(R)-1-((2R,5R)-2,5-diphenylpyrrolidin-1-yl)-4-methyl-1-thioxopent-4-en-2-ylcarbamate (5c). Compound 3 (152.1 mg, 0.35 mmol), diisopropylamine (147 μL, 1.05 mmol), n-butyl lithium (1.6 M in hexane, 0.67 mL, 1.05 mmol), HMPA (188 μL, 1.05 mmol) and 3-bromo-2-methylpropene (72 μL, 0.70 mmol) were reacted and worked up as described above. Product 5c: yellow oil, 120.5 mg, yield 73.5%, \( R_f = 0.50 \) (Hexane:EtOAc = 3:1), \([\alpha]_{24.3}^D +1.6 \) (c 1.01, MeOH), HRMS (FAB) calcd for C\(_{30}\)H\(_{33}\)N\(_2\)O\(_2\)S (MH\(^+\)) 485.2263, found 485.2259. \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 1.76-1.82 (m, 1H), 1.83 (s, 1H), 1.93-1.99 (m, 1H), 2.26-2.33 (m, 1H), 2.38-2.53 (m, 2H), 2.65-2.74 (m, 1H), 4.72-4.87 (m, 4H), 5.56 (d, 1H, J = 8.4 Hz), 5.76 (d, 1H, J = 9.0 Hz), 6.02 (d, 1H, J = 9.0 Hz), 6.98-7.40 (m, 15H); \(^{13}\)C (150 MHz, CDCl\(_3\)) δ 22.64, 29.93, 33.19, 46.78, 55.90, 66.10, 66.47, 68.38, 114.78, 125.09, 125.55, 126.95, 127.76, 127.80, 128.28, 128.46, 129.07, 136.73, 140.53, 140.80, 141.22, 154.09, 203.58. IR (NaCl): 2926.311, 1723.86, 1495.17, 1436.63, 1375.99, 1209.53, 1065.20, 1028.04, 902.29.

HPLC analysis: \( \text{de} > 99\% \). Chiralpak AD-RH column (CH\(_3\)CN/H\(_2\)O/MeOH: 0.7 mL/min, 254 nm); retention times of the diastereomeric mixture: 15.6 min (7c).
Benzyl-(2R,3R)-1-((2R,5R)-2,5-diphenylpyrrolidin-1-yl)-3-methyl-1-thioxopent-4-en-2-ylcarbamate (5d). Compound 3 (146.9 mg, 0.34 mmol), diisopropylamine (147 μL, 1.05 mmol), n-butyl lithium (1.6 M in hexane, 0.67 mL, 1.05 mmol), HMPA (188 μL, 1.05 mmol) and crotyl bromide (70 μL, 0.68 mmol) were reacted and worked up as described above. Product 5d: yellow oil, 127 mg, yield 77.8%, \( R_f = 0.55 \) (Hexane:EtOAc = 3:1), [α]^{24,3}D +3.6 (c 1.41, MeOH), HRMS (FAB) calcd for \( C_{30}H_{33}N_2O_2S \) (MH+) 485.2263, found 485.2278. \(^1\)H NMR (600 MHz, CDCl₃) \( \delta \) 1.06 (d, 3H, \( J = 6.6 \) Hz), 1.72-1.82 (m, 1H), 1.93-2.02 (m, 1H), 2.36-2.54 (m, 1H), 2.60-2.74 (m, 1H), 2.74-2.82 (m, 1H), 4.46-4.54 (m, 1H), 4.76 (dd, 2H, \( J = 12.6, 40.8 \) Hz), 4.87-4.98 (m, 1H), 5.64 (d, 1H, \( J = 9.0 \) Hz), 5.65-5.74 (m, 1H), 6.01 (d, 1H, \( J = 9.0 \) Hz), 7.02-7.34 (m, 15H); \(^{13}\)C (125 MHz, CDCl₃) \( \delta \) 17.22, 29.80, 33.43, 45.37, 61.00, 66.17, 66.72, 68.68, 116.12, 125.33, 125.91, 127.03, 127.64, 127.69, 127.70, 128.26, 128.43, 128.88, 136.74, 138.46, 141.22, 141.56, 154.29, 202.71. IR (NaCl): 2924.41, 1724.87, 1495.02, 1429.84, 1304.28, 1210.64, 1028.64.

HPLC analysis: de>99%, anti/syn>99:1. Chiralpak AD-RH column (CH₃CN/H₂O/MeOH: 30/60/10, 0.7 mL/min, 254 nm); retention times of the only diastereomer observed: 21.5 min (7d).

Benzyl-(2R,3R)-1-((2R,5R)-2,5-diphenylpyrrolidin-1-yl)-3-ethyl-1-thioxopent-4-en-2-ylcarbamate (5e). Compound 3 (150.2 mg, 0.35 mmol), diisopropylamine (147 μL, 1.05 mmol), n-butyl lithium (1.6 M in hexane, 0.67 mL, 1.05 mmol), HMPA (188 μL, 1.05 mmol) and 1-bromo-2-pentene (82 μL, 0.70 mmol) were reacted and worked up as described above. Product 5e: yellow oil, 131.5 mg, yield 76.1%, \( R_f = 0.50 \) (Hexane:EtOAc = 3:1), [α]^{24,3}D +1.8 (c 1.29, MeOH), HRMS (FAB) calcd for \( C_{31}H_{35}N_2O_2S \) (MH+) 499.2419, found 499.2407. \(^1\)H NMR (600 MHz, CDCl₃) \( \delta \) 0.92 (t, 3H, \( J = 7.2 \) Hz), 1.30-1.36 (m, 1H), 1.44-1.54 (m, 1H), 1.74-1.82 (m, 1H), 1.90-2.02 (m, 1H), 2.35-2.42 (m, 1H), 2.40-2.49 (m, 1H), 2.72-2.79 (m, 1H), 4.62 (dd, 1H, \( J = 6.0, 9.6 \) Hz), 4.78 (dd, 2H, \( J = 12.6, 26.4 \) Hz), 4.86-4.98 (m, 2H), 5.54 (ddd, 1H, \( J = 8.4, 9.6, 18.0 \) Hz), 5.69, (d, 1H, \( J = 7.8 \) Hz), 5.73 (d, 1H, \( J = 9.0 \) Hz), 6.01 (d, 1H, \( J = 9.0 \) Hz), 7.01-7.35 (m, 15H); \(^{13}\)C (125 MHz, CDCl₃) \( \delta \) 11.96, 24.24, 29.80, 33.43, 45.37, 61.00, 66.17, 66.72, 68.68, 116.12, 125.33, 125.91, 127.03, 127.64, 127.69, 127.70, 128.26, 128.43, 128.88, 136.74, 138.46, 141.22, 141.56, 154.29, 202.71. IR (NaCl): 2924.41, 1724.87, 1495.02, 1429.84, 1304.28, 1210.64, 1028.64.
HPLC analysis: de>78%, anti/syn>99:1. Chiralpak AD-RH column (CH₃CN/H₂O/MeOH: 30/60/10 to 90/0/10 in 40 min, 0.7 mL/min, 254 nm); retention times of the diastereomeric mixture: 15.3 min (7e), 19.5 min (8e).

**Benzyl (2R,3S)-1-((2R,5R)-2,5-diphenylpyrrolidin-1-yl)-3-phenyl-1-thioxopent-4-en-2-ylcarbamate (5f).** Compound 3 (240 mg, 0.56 mmol), diisopropylamine (236 μL, 1.68 mmol), n-butyl lithium (1.6 M in hexane, 1.05 mL, 1.68 mmol), HMPA (300 μL, 1.68 mmol) and cinnamyl bromide (108 μL, 0.73 mmol) were reacted and worked up as described above. Product 5e: yellow oil, 131.5 mg, yield 76.1%, Rᶠ = 0.50 (Hexane:EtOAc = 3:1), [α]^{23.0}_D +82.4 (c 0.44, MeOH), HRMS (FAB) calcd for C₃₅H₃₅N₂O₂S (MH⁺) 547.2419, found 547.2405. 1H NMR (600 MHz, CDCl₃) δ 1.57 (dd, 1H, J = 6.0, 12.0 Hz), 1.73 (dd, 1H, J = 5.4, 12.6 Hz), 2.18-2.27 (m, 1H), 2.29-2.37 (m, 1H), 3.82-3.91 (m, 1H), 6.66 (d, 1H, J = 12.6 Hz), 4.78 (d, 1H, J = 12.0 Hz), 4.89 (d, 1H, J = 10.8 Hz), 4.92-5.05 (m, 2H), 5.40 (d, 1H, J = 7.8 Hz), 5.50-5.60 (m, 1H), 5.83 (d, 1H, J = 9.0Hz), 5.92-6.03 (m, 1H), 6.24 (d, 1H, J = 7.2 Hz), 7.00-7.46 (m, 20H); 13C (125 MHz, CDCl₃) δ 29.99, 32.70, 59.72, 60.29, 66.13, 67.17, 68.71, 117.19, 125.21, 125.38, 126.33, 126.35, 127.09, 127.52, 127.82, 128.04, 128.14, 128.17, 128.26, 128.37, 128.66, 128.74, 128.79, 128.83, 129.05, 138.05, 140.55, 141.07, 141.29, 153.81, 201.99. IR (NaCl): 2924.78, 1716.65, 1493.88, 1441.54, 1304.51, 1209.64, 1131.80, 1028.18.

HPLC analysis: de>78%, anti/syn>73:1. Chiralpak AD-RH column (CH₃CN/H₂O/MeOH: 30/60/10 to 90/0/10 in 40 min, 0.7 mL/min, 254 nm); retention times of the diastereomeric mixture: 16.4 min (8e), 22.1 min (7e), 32.7 min (syn).

**General procedure for the preparation of compounds 10.** Compound 5 (0.15 mmol) was dissolved in a minimal amount of dry DCM under argon atmosphere and then 2,6-di-tert-butylpyridine (24 μL, 0.11 mmol) and MeOTf (50 μL, 0.45 mmol) were added. The reaction was stirred at room temperature overnight. Then dry THF (5 mL) was added and the reaction was cooled to -78 °C before LiBHEt₃ (1.0 M in THF, 0.45 mL, 0.45 mmol) was added. The reaction was stirred at -78 °C for 1 h. Upon completion of the addition, dry tert-butyl alcohol (1 mL) was added to the solution. The reaction was warmed up to 0 °C, followed by the addition of 2-methyl-2-butene (113 μL, 1.05 mmol), and a solution of sodium chlorite (34 mg, 0.3 mmol) in water (0.2 mL) and AcOH (1 mL). The mixture was allowed to warm up to room temperature with stirring. When the reaction was complete as indicated by TLC, the volatiles were removed under reduced pressure and the residue was dissolved in hexanes and diethyl ether (10 mL). The organic layer was extracted with 1 M LiOH (4 mL × 3). The combined aqueous layers were washed with CHCl₃ (3 mL × 3) and acidified to pH 1 with 6 M HCl. Then DCM (4 mL × 3) was used to extract the product. The combined organic layers were dried over anhydrous MgSO₄, concentrated under reduced pressure at room temperature to give the crude product.
Purification of the crude product by flash column chromatography (Hexane: EtOAc:AcOH = 75:25:2) afforded 10 as a colorless oil.

(2R,3R)-2-(benzyloxycarbonylamino)-3-ethylpent-4-enoic acid (10e). Compound 5e (56.6 mg, 0.114 mmol), 2,6-di-tert-butylpyridine (20 μL, 0.09 mmol), MeOTf (38 μL, 0.34 mmol), LiBHEt3 (1.0 M in THF, 0.34 mL, 0.34 mmol), 2-methyl-2-butene (86 μL, 0.80 mmol) and sodium chlorite (25.5 mg, 0.23 mmol) in water (0.15 mL) were reacted and worked up as described above. Product 7e: colorless oil, 13.5 mg, yield: 44%, \( R_f = 0.70 \) (EtOAc:Hexanes:AcOH = 25:25:1), \( [\alpha]^{24.1}_{D} +9.6 \) (c 0.16, MeOH), HRMS (FAB) calcd for C_{15}H_{20}NO_{4} (MH+) 278.1392, found 278.1389. \(^1\)H NMR (600 MHz, CDCl₃) δ 0.94 (t, 3H, \( J = 7.8 \) Hz), 1.38-1.47 (m, 1H), 1.52-1.60 (m, 1H), 2.54 (br, 1H), 4.50 (br, 1H), 5.08-5.18 (m, 4H), 5.50-5.59 (m, 1H), 7.28-7.37 (m, 5H); \(^13\)C (150 MHz, CDCl₃) δ 11.67, 23.55, 29.70, 47.52, 67.25, 118.88, 128.15, 128.55, 135.82, 156.38, 175.58. IR (NaCl): 2925.48, 1716.99, 1521.15. HPLC analysis: ee>87%, Chiralpak AD-RH column (CH₃CN/H₂O/MeOH: 35/55/10 to 45/45/10 in 35 min, 0.5 mL/min, 254 nm); retention times of the racemic mixture: 21.7 min and 24.7 min (10e).
The $^1$H and $^{13}$C NMR spectra for compounds 2, 3, 5, and 10. Note: rotamers were observed in NMR spectra of 5, 10.