Supporting Information

Efficient Radical Oxygenation of α-Iodocarboxylic Acid Derivatives

Nobuhiro Kihara, Cyril Ollivier and Philippe Renaud*

Université de Fribourg, Institut de Chimie Organique, Pérolles, CH-1700 Fribourg, Switzerland

General techniques. THF was freshly distilled from K under N_2; Et_2O from sodium–benzophenone; CH_2Cl_2, 1,2-dichloroethane and Et_3N from CaH_2 under N_2. Et_3B soln. (1M) in 1,2-dichloroethane was prepared from commercial Et_3B (95%, *Aldrich*). Other reagents were obtained from commercial sources and used as received. Flash column chromatography (FC) and filtration: *Baker* silica gel (0.063-0.200 mm); AcOEt, Et_2O and hexane as eluents. Thin-layer chromatography (TLC): *Baker* silica gel 25 UV_{254} analytical plates; detection either with UV, or by spraying or dipping in a soln. of $KMnO_4$ (3 g), K_2CO_3 (20 g), NaOH 5% (3 ml) in H_2O (300 ml) and subsequent heating. M.p.: not corrected; *Reichert Thermovar Kofler* hot stage apparatus. IR spectroscopy: *Perkin–Elmer 16PC*. FT–IR spectroscopy: *Mattson Unicam 5000*. NMR spectroscopy: *Varian Gemini 200* (^{1}H = 200 MHz, ^{13}C = 50.3 MHz), *Bruker AM 360* (^{1}H = 360 MHz), *Bruker avance DRX 500* (^{1}H = 500.13 MHz, ^{13}C = 125.8 MHz); chemical shift δ in ppm relative to tetramethylsilane (= 0 ppm) or $CHCl_3$ for ^{1}H, (= 7.26 ppm) and $CDCl_3$ for ^{13}C, (= 77.0 ppm). MS: *Vacuum Generators Micromass VG 70/70E* and *DS 11-250*; CI (CH_4), EI (70 eV); m/z (%). High resolution mass spectra (HRMS) were recorded on a FTICR mass spectrometer *Bruker 4.7T BioApex II*. Elementary analysis: Ecole d'Ingénieurs de Fribourg, *CH*-1705 Fribourg (Switzerland) and Ilse Beetz, Microanalytisches Laboratorium, *D*-8640 Kronach (Germany).

Preparation of iodides

General procedure 1. Iodination of lithium ester enolates.[1] Under N_2 atmosphere, *n*-BuLi (2.5M/hexane, 2.4 ml, 6.0 mmol) was added to a soln. of diisopropylamine (0.92 ml, 6.5 mmol) in THF (40 ml) at –78 °C. After 30 min, a soln. of ester (5 mmol) in THF (10 ml) was slowly added and the resulting mixture was stirred at the same temperature for 1.5 h. Then, the solution was transferred dropwise into a soln. of I_2 (1.9 g, 7.5 mmol) in THF (45 ml) at –78 °C, *via* cannula. The reaction was kept at –78 °C for 0.5 h, then at 0 °C for 0.5 h. The reaction mixture was diluted in AcOEt (150 ml), washed with 2N HCl (40 ml),

10% $Na_2S_2O_3$ (40 ml), brine and dried over $MgSO_4$. After concentration in vacuo, the crude product was purified by FC (hexane/AcOEt).

2-Iodo-*N*-methyl-*N*-phenylpropanamide (4a). To a soln. of *N*-methylaniline (11.81 g, 110.2 mmol), Et_3N (13.36 g, 132.1 mmol) and DMAP (= 4-(dimethylamino)pyridine) (669 mg, 5.48 mmol) in CH_2Cl_2 (100 ml), was added over 50 min at 0 °C a soln. of 2-bromopropionyl bromide (23.08 g, 106.9 mmol) in CH_2Cl_2 (40 ml). The reaction mixture was stirred at r.t. for 1 h. A soln. of HCl (2N, 50 ml) was added, the organic layer was separated and evaporated in vacuo to give a crude orange oil containing white crystals of hydrochlorides. Hexane (100 ml) and Et_2O (100 ml) were added and the suspension was washed with H_2O (4 × 10 ml) and brine (10 ml). The organic layer was dried over $MgSO_4$, and evaporated in vacuo to give a crude oil that was distilled under reduced pressure (b.p. 91–95 °C/0.6 mbar) to afford **1** (22.41g, 87%) as a yellow oil. A soln. of **1** (5.25 g, 21.7 mmol) and NaI (32.69 g, 218.1 mmol) in acetone (100 ml) was heated under reflux for 15 h. The reaction mixture was concentrated and the resulting oil was dissolved in Et_2O (100 ml) and washed with H_2O (50 ml). The organic layer was separated and washed with H_2O (20 ml), 10% $Na_2S_2O_3$ (20 ml), brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by FC (hexane/AcOEt 4:1) to afford **4a** (5.83 g, 93%) as a yellow oil that crystallized during storage in refrigerator. M.p. 45–47°C. IR (KBr) 3057, 2918, 1647, 1591, 1495, 1445, 1416, 1317, 1271, 1115, 1084, 771, 696 cm^{-1}. ^1H NMR (360 MHz) 7.47–7.37 (*m*, 3H), 7.31–7.29 (*m*, 2H), 4.32 (*q*, J = 6.7, 1H), 3.26 (*s*, 3H), 1.89 (*d*, J = 6.7, 3H). ^{13}C NMR (50 MHz) 171.0, 143.1, 129.9, 128.3, 126.8, 38.2, 23.8, 14.6. MS (CI^+, CH_4) *m/z* (%) 290 (MH^+, 100), 191 (10), 163 (MH^+–I, 65), 162 (M–I, 49), 134 (4), 107 (6). Anal. Calcd for $C_{10}H_{12}INO$ (289.12): C, 41.54; H, 4.18. Found: C, 41.36; H, 4.17.

Phenyl 2-iodopropanoate (4b). To a soln. of DCC (2.29 g, 11.11 mmol) in Et_2O (30 ml) was added 2-bromopropionic acid (0.9 ml, 10 mmol) at r.t. A soln. of phenol (953 mg, 10.13 mmol) and DMAP (70 mg, 0.57 mmol) in Et_2O (5 ml) was cannuled to the white resulting suspension. An exothermic reaction occured, and the mixture was allowed to stand at r.t. for 1.5 h with continuous stirring. Hexane (100 ml) was added, and the precipitate was filtered though *Celite*. The filtrate was concentrated in vacuo and the crude product was purified by FC (hexane/AcOEt 19:1) to give phenyl 2-bromopropionate (1.92 g, 84%) as a colorless oil. A suspension of the bromide (1.81 g, 7.93 mmol) and KI (13.79 g, 83.1 mmol) in acetone (60 ml) was heated under reflux overnight in the dark. After evaporation of acetone, AcOEt (60 ml) was added and the organic layer was successively washed with H_2O (100 ml), sat. Na_2SO_3 (50 ml), brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was purified by FC (hexane/AcOEt 19:1) to afford **4b** (2.06 g, 94%) as a pale yellow oil. IR (Neat) 3065,

2988, 2924, 1755, 1591, 1493, 1445, 1333, 1234, 1196, 1117, 1034, 918, 754, 692 cm^{-1}. ^1H NMR (360 MHz) 7.40–7.37 (*m*, 2H), 7.27–7.23 (*m*, 1H), 7.13–7.1 (*m*, 2H), 4.71 (*q*, J = 7.0, 1H), 2.07 (*d*, J = 7.0, 3H). ^{13}C NMR (50 MHz) 170.4, 150.5, 129.4, 126.1, 120.9, 23.0, 12.5. MS (CI^+, CH_4) *m/z* (%) 277 (MH^+, 69), 183 (MH^+–PhOH, 46), 151 (MH^+–I, 18), 135 (22), 123 (65), 95 (100), 57 (10). Anal. Calcd for $C_9H_9IO_2$ (276.07): C, 39.16; H, 3.29. Found: C, 38.90; H, 3.27.

3-Iodo-5-methyldihydro-2(3*H*)-furanone (4c). Prepared according to the general procedure 1 from γ-valerolactone (300 mg, 3.0 mmol). FC (hexane/Et_2O 50:50) gave **4c** (474 mg, 70%) as a 81:19 mixture of two isomers (^1H NMR).

Compound **4c**–major (less polar): Pale yellow oil. ^1H NMR (500 MHz) 4.83–4.76 (*m*, 1H), 4.57 (*dd*, J = 6.9, 1.1, 1H), 2.48 (*ddd*, J = 14.7, 4.9, 1.1, 1H), 2.21 (*ddd*, J = 14.7, 9.5, 6.9, 1H), 1.51 (*d*, J = 6.2, 3H). ^{13}C NMR (125 MHz) 174.4, 76.2, 42.6, 19.4, 12.0.

Compound **4c**–minor (more polar): Pale yelow oil. ^1H NMR (500 MHz) 4.77–4.71 (*m*, 1H), 4.72 (*t*, J = J = 8.9, 1H), 3.03 (*ddd*, J = 13.9, 8.9, 6.5, 1H), 2.32 (*ddd*, J = 13.9, 8.7, 7.5, 1H), 1.55 (*d*, J = 6.3, 3H). ^{13}C NMR (125 MHz) 174.2, 77.1, 41.8, 20.6, 8.7.

Mixture of isomers of **4c**: IR (Neat) 2980, 2932, 1776, 1445, 1387, 1338, 1294, 1180, 1072, 945 cm^{-1}. MS (CI^+, CH_4) *m/z* (%) 227 (MH^+, 81), 182 (M–CO_2, 4), 129 (7), 128 (13), 100 (MH^+–I, 100), 83 (8), 73 (4), 55 (38). Anal. Calcd for $C_5H_7IO_2$ (226.01): C, 26.57; H, 3.12. Found: C, 26.59; H, 3.20.

Ethyl 2-iodo-3-methoxy-2-methylpropanoate (4d). To a soln. of ethyl methacrylate (817 mg, 7.16 mmol) in MeOH (55 ml), was successively added $AgNO_3$ (1.46 g, 8.59 mmol) and I_2 (2.18 g, 8.59 mmol) at r.t. The mixture was stirred 3.5 h in the dark, then the solution was filtered and concentrated under reduced pressure. The crude mixture was dissolved in Et_2O (30 ml), washed successively with H_2O (10 ml), 10% $Na_2S_2O_3$ (10 ml), brine, dried over $MgSO_4$, and concentrated in vacuo to afford a 47:53 mixture of two regioisomers (^1H NMR). The crude oil was purified by FC (hexane/Et_2O 95:5) and gave the less polar isomer **4d** (798 mg, 41%) as a pale yellow oil. IR (Neat) 2984, 2932, 2828, 1730, 1448, 1383, 1300, 1230, 1103, 1065, 1024, 957, 868 cm^{-1}.^1H NMR (360 MHz) 4.24 (*q*, J = 7.0, 2H), 3.91 (*d*, J_{AB} = 9.4, A part of AB system, 1H), 3.69 (*d*, J_{AB} = 9.4, B part of AB system, 1H), 3.40 (*s*, 3H) , 2.09 (*s*, 3H), 1.29 (*t*, J = 7, 3H). ^{13}C NMR (50 MHz) 171.8, 80.3, 61.9, 59.3, 37.1, 27.7, 13.7. MS (CI^+, CH_4) *m/z* (%) 273 (MH^+, 28), 183 (M–MeO, 100), 213 (19), 185 (19), 157 (49), 145 (M–I, 45), 117 (14), 89 (60), 58 (18). Anal. Calcd for $C_7H_{13}IO_3$ (272.08): C, 30.90; H, 4.82. Found: C, 30.80; H, 4.86.

3-Iodo-3-methyl-3,4-dihydrocoumarin (4e). Prepared in two steps from 3,4-dihydrocoumarin according the procedure of Hoshino and al. Physical and spectral data were in accordance with literature data:[2] ^{1}H NMR (360 MHz) 7.36–7.31 (*m*, 2H), 7.18–7.09 (*m*, 3H), 3.19 (*d*, J_{AB} = 17.4, A part of AB system, 1H), 2.95 (*d*, J_{AB} = 17.4, B part of AB system, 1H), 2.38 (*s*, 3H).

***S*-Phenyl 2-iodopropanethioate (4f).** To a soln. of thiophenol (11.05 g, 100.3 mmol) in CH_2Cl_2 (60 ml) at 0 °C were successively added 2-bromopropionyl chloride (17.15 g, 100.0 mmol) in CH_2Cl_2 (10 ml), DMAP (649 mg, 5.31 mmol) in CH_2Cl_2 (5 ml) and Et_3N (14.22 ml, 102 mmol) dropwise. After complete addition, the temperature was raised to r.t., H_2O (100ml) was added, the organic layer was separated, and washed with sat. NH_4Cl (50 ml), brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by distillation and the b.p. 75–78 °C/0.1 mbar fraction was collected as a pale yellow oil. FC (hexane/AcOEt 19:1) gave the *S*-phenyl 2-bromopropanethioate (9.83 g, 40%) as pale yellow oil. A suspension of the bromide (1.29 g, 5.28 mmol) and NaI (11.97 g, 79.9 mmol) in acetone (50 ml) was heated under reflux for 15 h. The reaction mixture was evaporated and the resulting oil was dissolved in Et_2O (100 ml) and washed with H_2O (50 ml). The organic layer was separated and washed with H_2O (20 ml), 10% $Na_2S_2O_3$ (30 ml), brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by FC (hexane/AcOEt 90:10) to afford **4f** (1.36 g, 84%) as a yellow oil. Physical and spectral data were in accordance with literature data:[3] ^{1}H NMR (200 MHz) 7.42 (*s*, 5H), 4.79 (*q*, J = 7.2, 1H), 2.02 (*d*, J = 7.2, 3H).

2-Iodo-*N*-methyl-*N*-phenyl-4-pentenamide (12).[4] To a soln. of *N*-methyl-*N*-phenyl-4-pentenamide (626 mg, 3.3 mmol), prepared from 4-pentanoic acid (1.0 g, 10 mmol) and *N*-methylaniline (5.35 g, 50 mmol) according the procedure reported by Moeller and al.,[5] in CH_2Cl_2 (20 ml) was added I_2 (1.26g, 4.9 mmol) and sym.-collidine (0.65 ml, 4.95 mmol) at r.t. After 21 h, the reaction mixture was diluted with CH_2Cl_2 (20 ml), and washed with 2N HCl (20 ml), 10% $Na_2S_2O_3$ (20 ml), brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by FC (hexane/AcOEt 90:10) to afford **12** (820 g, 79%) as a yellow oil. IR (Neat) 3063, 2926, 1661, 1595, 1494, 1431, 1385, 1267, 1115, 924, 773, 700 cm^{-1}. ^{1}H NMR (360 MHz) 7.47–7.39 (m, 3H), 7.29–7.26 (m, 2H), 5.68–5.56 (m, 1H), 5.12 (s, 1H), 5.10–5.07 (*m*, 1H), 4.12 (*dd*, J = 9.0, 6.4, 1H), 3.26 (*s*, 3H), 2.96–2.87 (*m*, 1H), 2.68–2.60 (*m*, 1H). ^{13}C NMR (50 MHz) 169.8, 143.0, 135.1, 129.9, 128.4, 127.1, 118.3, 40.8, 38.1, 19.8. MS (CI^+, CH_4) *m/z* (%) 316 (MH^+, 92), 217 (12), 189 (MH^+–I, 100), 146 (23), 134 (14), 107 (21), 91 (5), 55 (4). Anal. Calcd for $C_{12}H_{14}INO$ (315.15): C, 45.73; H, 4.48. Found: C, 45.51; H, 4.51.

(4*S*)-3-(2-Iodopropanoyl)-4-isopropyl-1,3-oxazolidin-2-one (16). Prepared according to the general procedure 1 from (4*S*)-4-isopropyl-3-propionyl-1,3-oxazolidin-2-one (375 mg, 2 mmol). FC (hexane/AcOEt gradient 90:10 to 80:20) gave **16** (441 mg, 70%) as a 74:26 mixture of two isomers (^{1}H NMR).

Compound **16**–major (more polar): Yellow oil. IR (Neat) 2967, 1773, 1699, 1389, 1371, 1246, 1207, 1065, 698 cm^{-1}. ^{1}H NMR (500 MHz) 5.91 (*q*, J = 6.9, 1H), 4.50 (*dt*, J_{AX} = 8.4, J_{BX} = 3.6, X part of ABX system, 1H), 4.30 (*t*, J_{AB} = J_{AX} = 9.1, A part of ABX system, 1H), 4.25 (*dd*, J_{AB} = 9.1, J_{BX} = 3.4, B part of ABX system, 1H), 2.44–2.37 (*m*, 1H), 1.98 (*d*, J = 6.9, 3H), 1.00 (*d*, J = 6.9, 3H), 0.95 (*d*, J = 6.9, 3H). ^{13}C NMR (125 MHz) 171.5, 153.0, 63.3, 58.2, 27.8, 22.1, 17.9, 15.1, 13.6.

Compound **16**–minor (less polar): Pale yellow solid. M.p. 60–61 °C. IR (KBr) 2967, 1778, 1697, 1369, 1246, 1203 cm^{-1}. ^{1}H NMR (500 MHz) 5.88 (*q*, J = 6.9, 1H), 4.41 (*ddd*, J_{AX} = 8.2, J = 3.9, J_{BX} = 2.5, X part of ABX system, 1H), 4.35 (*t*, J_{AB} = J_{AX} = 8.9, A part of ABX system, 1H), 4.24 (*dd*, J_{AB} = 8.9, J_{BX} = 2.5, B part of ABX system, 1H), 2.43–2.37 (*m*, 1H), 2.00 (*d*, J = 6.9, 3H), 0.94 (*d*, J = 6.9, 3H), 0.88 (*d*, J = 6.9, 3H).^{13}C NMR (125 MHz) 171.7, 153.6, 63.8, 59.6, 28.9, 22.9, 18.3, 14.9, 13.7.

Mixture of isomers of **16**: MS (CI$^+$, CH_4) *m/z* (%) 312 (MH^+, 71), 184 (M–I, 73), 158 (34), 143 (9), 130 (100), 86 (7), 57 (15). Anal. Calcd for $C_9H_{14}INO_3$ (311.12): C, 34.75; H, 4.54; N, 4.50. Found: C, 34.96; H, 4.66; N, 4.40.

4-(2-iodopropanoyl)-10,10-dimethyl-3λ^6-thia-4-azatricyclo[5.2.1.0^{1,5}]decane-3,3-dione (18). Prepared according to the general procedure 1 from 10,10-dimethyl-4-propionyl-3λ^6-thia-4-azatricyclo[5.2.1.0^{1,5}]decane-3,3-dione[6] (432 mg, 1.59 mmol). FC (hexane/CH_2Cl_2 80:20) gave **18** (502 mg, 79%) as a 91:9 mixture of two isomers (^{1}H NMR). Physical and spectral data were in accordance with literature data.[7]

Compound **18**–major: ^{1}H NMR (360 MHz) 5.12 (*q*, J = 6.7, 1H), 3.96 (*dd*, J = 7.3, 5.2, 1H), 3.51 (*d*, J_{AB} = 13.7, A part of AB system, 1H), 3.43 (*d*, J_{AB}= 13.7, B part of AB system, 1H), 2.11–2.04 (*m*, 2H), 1.96 (*d*, J = 6.7, 3H), 1.96–1.91(*m*, 3H), 1.45–1.33 (*m*, 2H), 1.21 (*s*, 3H), 0.98 (*s*, 3H).

Radical hydroxylations

General procedure 2. The iodide (0.5 mmol) was placed in a two-necked flask under an oxygen atmosphere. After introduction of CH_2Cl_2 (0.5 ml), the soln. was cooled at –50 °C (acetone bath refrigerated with a cold finger), and a 1M soln. of Et_3B in 1,2–dichloroethane

(1.0 ml, 1.0 mmol) was added over 5 h using a syringe pump under magnetic stirring. The needle used for the addition of Et_3B was placed into the reaction mixture to avoid oxidation of Et_3B before the reaction takes place. At the end of the addition, MeOH (0.5 ml) was added followed by Me_2S (0.2 ml). After stirring for 15 min, the soln. was filtered through silica gel (Et_2O). The filtrate was concentrated and the crude alcohol was purified by FC.

2-Hydroxy-*N*-methyl-*N*-phenylpropanamide (5a). Prepared according to the general procedure 2 from **4a** (145 mg, 0.5 mmol). FC (hexane/AcOEt gradient 80:20 to 70:30) gave **5a** (63 mg, 70%). Physical and spectral data were in accordance with literature data:[8] ^{1}H NMR (200 MHz) 7.2–7.6 (*m*, 5H), 4.26 (*dq*, J = 8.1, 5.7, 1H), 3.52 (*d*, J = 8.1, 1H), 3.37 (*s*, 3H), 1.11 (*d*, J = 5.7, 3H).

Phenyl 2-hydroxypropanoate (5b). Prepared according to the general procedure 2 from **4b** (146 mg, 0.5 mmol). FC (hexane/AcOEt gradient 90:10 to 80:20) gave **5b** (61 mg, 69%) as a colorless oil. IR (Neat) 3426, 2986, 1761, 1591, 1493, 1198, 1117 cm^{-1}. ^{1}H NMR (360 MHz) 7.42–7.28 (*m*, 2H), 7.26–7.20 (*m*, 1H), 7.11–7.09 (*m*, 2H), 4.55 (*q*, J = 7.0, 1H), 3.60 (*br*, 1H), 1.60 (*d*, J = 7.0, 3H).^{13}C NMR (50 MHz) 174.3, 150.3, 129.6, 126.3, 121.2, 67.0, 20.4. MS (EI, 70eV) *m/z* (%) 167 (M^+, 23), 145 (32), 138 (55), 121 (10), 95 (100), 65 (6). Anal. Calcd for $C_9H_{10}O_3$ (166.18): C, 65.05; H, 6.07. Found: C, 64.54; H, 6.15. HRMS (CI, isobutane) for $C_9H_{11}O_3$ ($[M+H]^+$): calculated 167.0708; found 167.0701.

3-Hydroxy-5-methyldihydro-2(3*H*)-furanone (5c). Prepared according to the general procedure 2 from **4c** (113 mg, 0.5 mmol). FC (hexane/AcOEt 65:35) gave **5c** (71 mg, 69%) as a 50:50 mixture of two isomers (^{1}H NMR).

Compound **5c** (less polar): Colorless oil. ^{1}H NMR (500 MHz) 4.85–4.78 (*m*, 1H), 4.56 (*dd*, J = 7.7, 7.7, 1H), 3.42 (*br*, 1H), 2.39 (*ddd*, J = 13.1, 7.5, 7.5, 1H), 2.21 (*ddd*, J = 13.1, 8.0, 4.0, 1H), 1.41 (*d*, J = 6.4, 3H). ^{13}C NMR (125 MHz) 177.6, 75.1, 67.5, 37.1, 21.3.

Compound **5c** (more polar): Colorless oil. ^{1}H NMR (500 MHz) 4.55 (*dd*, J = 11.1, 8.3, 1H), 4.55–4.49 (*m*, 1H), 3.17 (*br*, 1H), 2.73 (*ddd*, J = 12.4, 8.3, 5.0, 1H), 1.87 (*ddd*, J = 12.4, 10.6, 10.6, 1H), 1.47 (*d*, J = 6.1, 3H). ^{13}C NMR (125 MHz) 177.5, 73.6, 69.0, 38.7, 20.8.

Mixture of isomers of **5c**: IR (Neat) 3433, 2984, 2938, 1769, 1448, 1389, 1331, 1202, 1128, 1047, 999, 949 cm^{-1}. MS (CI^+, CH_4) *m/z* (relative intensity) 117 (MH^+, 100), 101 (75), 99 (MH^+–H_2O, 76), 89 (65), 71 (75), 57 (22). HRMS (CI, isobutane) for $C_5H_9O_3$ ($[M+H]^+$): calculated 117.0551; found 117.0547.

Ethyl 2-hydroxy-3-methoxy-2-methylpropanoate (5d). Prepared according to the general procedure 2 from **4d** (136 mg, 0.5 mmol). FC (hexane/AcOEt 70:30) gave **5d** (66 mg, 81%) as a colorless oil. IR (Neat) 3504, 2983, 2936, 2824, 1736, 1458, 1381, 1297, 1233, 1144, 1114, 1021, 981, 911, 866 cm^{-1}. ^1H NMR (360 MHz) 4.25 (*dq*, J = 7.0, 1.8, 2H), 3.64 (*d*, J_{AB} = 9.4, A part of AB system, 1H), 3.38 (*d*, J_{AB}= 9.4, B part of AB system, 1H), 3.37 (*s*, 3H) , 1.35 (*s*, 3H), 1.30 (*t*, J = 7.0, 3H). ^{13}C NMR (50 MHz) 175.0, 78.5, 74.8, 61.8, 59.5, 21.8, 14.2. MS (EI, 70eV) *m/z* (%) 163 (M^++1, 16), 145 (M^+–H_2O, 2), 117 (67), 89 (100), 71 (80), 57 (98). HRMS (CI, isobutane) for $C_7H_{15}O_4$ ($[M+H]^+$): calculated 162.0970; found 162.0963.

3-Hydroxy-3-methyl-3,4-dihydrocoumarin (5e). Prepared according to the general procedure 2 from **4e** (144 mg, 0.5 mmol) in CH_2Cl_2 (0.25M) at rt. FC (hexane/AcOEt 75:25) gave **5e** (73 mg, 82%) as a white solid. M.p. 54–57 °C. IR (KBr) 3426, 1768, 1652, 1489, 1458, 1233, 1121, 1072, 916, 758 cm^{-1}. ^1H NMR (360 MHz) 7.30–7.05 (m, 4H), 3.37 (s, 1H), 3.27 (d, J_{AB} = 15.5, A part of AB system, 1H), 3.0 (d, J_{AB} = 15.5, B part of AB system, 1H), 1.41(s, 3H). ^{13}C NMR (50 MHz) 173.5, 150.8, 128.9, 128.6, 124.9, 121.6, 116.5, 69.4, 37.9, 25.2. MS (CI^+, CH_4) *m/z* (%) 179 (MH^+, 67), 161 (MH^+–H_2O, 100), 151 (56), 133 (14), 117 (5), 107 (18), 89 (25), 75 (100), 61 (86). Anal. Calcd for $C_{10}H_{10}O_3$ (178.19): C, 67.41; H, 5.66. Found: C, 67.02; H, 5.89.

***S*-Phenyl 2-hydroxypropanothiate (5f).** Prepared according to the general procedure 2 from **4f** (151 mg, 0.5 mmol). FC (CH_2Cl_2/AcOEt 97:3) gave **5f** (73 mg, 82%). Physical and spectral data were in accordance with literature data:[9] ^1H NMR (200 MHz) 7.41 (*s*, 5H), 4.49 (*dq*, J = 6.7, 5.8, 1H), 2.71 (*d*, J = 5.8, 1H), 1.54 (*d*, J = 6.7, 3H).

2-Hydroxy-*N*-methyl-*N*-phenyl-4-pentenamide (13). Prepared according to the general procedure 2 from **12** (158 mg, 0.5 mmol). FC (hexane/AcOEt gradient 80:20 to 75:25) gave **13** (71 mg, 69%) as a white waxy solid. M.p. 39 °C. IR (KBr) 3430, 3065, 2957, 1651, 1595, 1497, 1367, 1294, 1118, 1078, 914, 773, 702, 567 cm^{-1}. ^1H NMR (360 MHz) 7.47–7.36 (*m*, 3H), 7.26–7.21 (*m*, 2H), 5.70–5.59 (*m*, 1H), 5.01 (*d*, J = 9.4, 1H), 4.93 (*d*, J = 17.1, 1H), 4.27–4.22 (*m*, 1H), 3.45 (*d*, J = 8.2, 1H), 3.32 (*s*, 3H), 2.22–2.15 (*m*, 1H), 2.05–1.97 (*m*, 1H). ^{13}C NMR (50 MHz) 173.9, 142.2, 133.1, 130.1, 128.4, 127.5, 117.8, 68.1, 38.9, 38.1. MS (CI^+, CH_4) *m/z* (%) 206 (MH^+, 100), 188 (MH^+–H_2O, 17), 164 (53), 134 (15), 108 (28), 99 (25), 71 (5), 55 (3). Anal. Calcd for $C_{12}H_{15}NO_2$ (205.26): C, 70.22; H, 7.37. Found: C, 70.22; H, 7.59.

(4*S*)-3-(2-Hydroxypropanoyl)-4-isopropyl-1,3-oxazolidin-2-one (17). Prepared according to the general procedure 2 from **16** (152 mg, 0.5 mmol). FC (hexane/AcOEt 70:30) gave **17** (87 mg, 88%) as a 60:40 mixture of two isomers (^1H NMR).

Compound **17**–major (less polar): Colorless oil. ^{1}H NMR (500 MHz) 5.05 (*dq*, J = 7.3, 6.7, 1H), 4.44 (*dt*, J_{AX} = 8.1, J_{BX} = 2.9, X part of ABX system, 1H), 4.35 (*t*, J_{AB} = J_{AX} = 9.1, A part of ABX system, 1H), 4.30 (*dd*, J_{AB} = 9.1, J_{BX} = 2.8, B part of ABX system,1H), 3.73 (*d*, J = 7.5, 1H), 2.45–2.39 (*m*, 1H), 1.42 (*d*, J = 6.5, 3H), 0.94 (*d*, J = 7.0, 3H), 0.90 (*d*, J = 7.0, 3H). ^{13}C NMR (125 MHz) 174.9, 154.1, 67.1, 64.2, 58.9, 28.2, 19.7, 17.9, 14.5.

Compound **17**–minor (more polar): Colorless oil. ^{1}H NMR (500 MHz) 5.18 (*dq*, J = 8.3, 6.7, 1H), 4.51 (*dt*, J_{AX} = 8.5, J_{BX} = 3.5, X part of ABX system, 1H), 4.37 (*t*, J_{AB} = J_{AX} = 9.1, A part of ABX system, 1H), 4.27 (*dd*, J_{AB} = 9.1, J_{BX} = 3.4, B part of ABX system, 1H), 3.30 (*d*, J = 8.3, 1H), 2.42–2.31 (*m*, 1H), 1.48 (*d*, J = 6.7, 3H), 0.94 (*d*, J = 7.0, 3H), 0.89 (*d*, J = 7.0, 3H). ^{13}C NMR (125 MHz) 176.2, 153.4, 67.2, 64.3, 58.3, 28.4, 21.4, 17.7, 14.8.

Mixture of isomers of **17**: IR (Neat) 3476, 2967, 1783, 1705, 1391, 1304, 1252, 1207, 1124, 1042, 775, 712 cm^{-1}. MS (CI^+, CH_4) *m/z* (%) 202 (MH^+, 85), 184 (MH^+–H_2O, 100), 158 (12), 130 (81), 116 (6), 99 (3), 86 (20), 73 (28), 61 (59). Anal. Calcd for $C_9H_{15}NO_4$ (201.22): C, 53.72; H, 7.51; N, 6.96. Found: C, 53.47; H, 7.76; N, 6.40.

4-(2-Hydroxypropanoyl)-10,10-dimethyl-3λ^6-thia-4-azatricyclo[5.2.1.0^{1,5}]decane-3.3-dione(19). Prepared according to the general procedure 2 from **18** (198 mg, 0.5 mmol). FC (hexane/AcOEt 70:30) gave **19** (141 mg, 98%) as a 60:40 mixture of two isomers (^{1}H NMR).

Compound **19**–major (less polar): Colorless oil. ^{1}H NMR (500 MHz) 4.73 (*dq*, J = 7.0, 6.4, 1H), 3.89 (*dd*, J = 7.9, 5.0, 1H), 3.53 (*d*, J_{AB} = 13.8, A part of AB system, 1H), 3.47 (*d*, J_{AB} = 13.8, B part of AB system, 1H), 3.21 (*d*, J = 7.1, 1H), 2.22–2.17 (*m*, 1H), 2.08 (*dd*, J = 14.0, 7.9, 1H), 1.96–1.87 (*m*, 3H), 1.42 (*d*, J = 6.4, 3H), 1.47–1.34 (*m*, 2H), 1.15 (*s*, 3H), 0.98 (*s*, 3H). ^{13}C NMR (125 MHz) 172.9, 67.1, 65.1, 52.7, 49.1, 47.8, 44.3, 37.9, 32.6, 26.4, 20.6, 19.8, 18.7.

Compound **19**–minor (more polar): Colorless crystals. M.p. 174–175 °C. ^{1}H NMR (500 MHz) 4.82 (*dq*, J = 7.7, 6.8, 1H), 3.93 (*dd*, J = 7.7, 4.9, 1H), 3.48 (*d*, J_{AB} = 13.8, A part of AB system, 1H), 3.46 (*d*, J_{AB} = 13.8, B part of AB system, 1H), 3.05 (*d*, J = 7.7, 1H), 2.1 (*dd*, J = 13.9, 7.7, 1H), 2.06–2.01 (*m*, 1H), 1.97–1.87 (*m*, 3H), 1.45 (*d*, J = 6.8, 3H), 1.47–1.34 (*m*, 2H), 1.13 (*s*, 3H), 0.98 (*s*, 3H). ^{13}C NMR (125 MHz) 175.7, 67.5, 64.9, 52.8, 48.9, 47.8, 44.5, 38.0, 32.7, 26.4, 22.2, 20.6, 19.8.

Mixture of isomers of **19**: IR (KBr) 3532, 2992, 2965, 2886, 1692, 1331, 1281, 1136, 1111, 1065, 775, 536 cm^{-1}. MS (CI^+, CH_4) m/z (%) 288 (MH^+, 100), 244 (10), 216 (96), 179 (14), 135 (47), 119 (6), 109 (9), 73 (26), 63 (4). Anal. Calcd for $C_{13}H_{21}NO_4S$ (287.37): C, 54.33; H, 7.37; N, 4.87. Found: C, 54.35; H, 7.59; N, 4.75.

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