Supporting Information

**Highly Diastereoselective Synthesis of β -Carboxy- γ -lactams and their ethyl esters
via Sc(OTf)₃-catalyzed imino Mukaiyama-aldol Type Reaction of 2,5-
Bis(trimethylsilyloxy)furan with Imines**

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General remarks.

^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded in CDCl_3 using TMS as an internal standard. IR spectra were recorded on an FT-IR spectrometer. EI-MS were obtained at 70 eV. All new compounds were characterized by HR-TOF-MS and elemental analyses. Column chromatography and preparative TLC were carried out on silica gel.

General Procedure for the reaction of 2,5-bis(trimethylsilyloxy)furan (1**) with imines using $\text{Sc}(\text{OTf})_3$ as a catalyst.** To a 50 mL round-bottomed flask charged with $\text{Sc}(\text{OTf})_3$ (49 mg, 0.05 mmol) was added a solution of imine (1 mmol) in THF (1 mL) at room temperature. The mixture was further stirred at room temperature under an Argon atmosphere for 30 min. The mixture was brought to $-78\text{ }^\circ\text{C}$ (dry ice-acetone) and a solution of 2,5-bis(trimethylsilyloxy)furan (**1**) (0.244 g, 1 mmol) in THF (2 mL) was added dropwise. The resulting mixture was slowly warmed up to room temperature and was stirred overnight. After 16 h, saturated aqueous NH_4Cl (2 mL) was added and the mixture was stirred at room temperature for 1 h before it was extracted with EtOAc (3x30 mL). The combined organic layers were washed with water (3x30 mL), brine (30 mL) and dried over anhydrous Na_2SO_4 . Removal of solvents (aspirator then *vacuo*) yielded a crude γ -lactamcarboxylic acid whose diastereomeric ratio was determined by ^1H NMR integration. The crude material was purified by crystallization to yield the acid derivative or conversion to ethyl ester

derivative (SOCl₂, EtOH, -78 °C to rt) before chromatographic purification when the crystallization of the firstly formed acid was found difficult.

General Procedure A for ethyl ester formation: Thionyl chloride (0.2 mL, 3 mmol) was added dropwise to a stirred -78 °C dry EtOH (20 mL). To this mixture, was added a solution of a crude γ -lactamcarboxylic acid in dry EtOH (5 mL). The reaction mixture was allowed to warm to room temperature under an Argon atmosphere. After 5 h, EtOH was removed (aspirator). The residue was quenched by slow addition of saturated aqueous Na₂CO₃ at 0 °C. The aqueous layer was extracted with EtOAc (3x20 mL). The combined organic layers were washed with H₂O (25 mL), brine (25 mL), dried (Na₂SO₄), filtered and concentrated. The residue was purified by preparative thin-layer chromatography.

Reaction of 2,5-bis(trimethylsilyloxy)furan (1) with imines using Sc(OTf)₃ as a catalyst:

Preparation of benzyl-2-(4-methoxyphenyl)-5-oxopyrrolidine-3-carboxylic acid (3b). Imine **2b** (0.225 g, 1 mmol) was employed to produce a crude product **3b**, which consisted of a 99:1 mixture of *trans*:*cis*-isomers. A single isomer (*trans*) of **3b** was obtained after crystallization from *i*PrOH (0.234 g, 72%, m.p. = 160-161 °C).

¹H NMR (300 MHz, CDCl₃): δ 7.30-7.20 (m, 3H), 7.10-6.95 (m, 4H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.04 (d, *J* = 14.7 Hz, 1H), 4.58 (d, *J* = 5.9 Hz, 1H), 3.82 (s, 3H), 3.47 (d, *J* = 14.7 Hz, 1H), 3.15-3.05 (m, 1H), 3.00-2.75 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 175.9, 173.1, 159.8, 135.4, 130.3, 128.6, 128.4, 128.3, 127.6, 114.5, 63.2, 55.3, 45.9, 44.4, 33.6. IR (KBr): $\nu_{\max}$ 3448, 1731, 1649 cm⁻¹. MS: *m/z* (%) relative intensity 326 ([M+1]⁺, 6), 325 ([M]⁺, 25), 235 (7), 234 (45), 225 (36), 147 (35), 146

(40), 119 (40), 118 (100), 104 (30), 91 (60), 77 (18), 65 (16). HRMS (ESI-TOF) calcd for $C_{19}H_{19}NO_4Na$ $[M+Na]^+$: 348.1212; found: 348.1208.

Preparation of ethyl 1-benzyl-2-(3-methoxyphenyl)-5-oxopyrrolidine-3-carboxylate (3c). Imine **2c** (0.225 g, 1 mmol) was employed to produce a crude γ -lactamcarboxylic acid, which consisted of a 99:1 mixture of *trans*:*cis*-isomers. The ethyl ester derivative was prepared according to the General Procedure A. A crude residue was purified by preparative thin-layer chromatography (SiO_2 , 20% EtOAc in hexanes, triple runs) to give a pure *trans*-isomer of **3c** (0.261 g, 74%, a yellow oil).

1H NMR (300 MHz, $CDCl_3$): δ 7.30-7.10 (m, 4H), 7.00-6.95 (m, 2H), 6.85-6.55 (m, 3H), 5.01 (d, $J = 14.7$ Hz), 4.50 (d, $J = 5.4$ Hz, 1H), 4.01 (q, $J = 7.1$ Hz, 2H), 3.70 (s, 3H), 3.47 (d, $J = 14.7$ Hz), 3.15-2.90 (m, 1H), 2.85-2.65 (m, 2H), 1.08 (t, $J = 7.1$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.8, 172.1, 160.1, 140.6, 135.6, 130.1, 128.5, 128.3, 127.5, 119.0, 113.8, 112.3, 63.5, 61.3, 55.2, 45.8, 44.4, 33.5, 13.9. IR (neat): ν_{max} 1732, 1695 cm^{-1} . MS: m/z (%) relative intensity 354 $[M+1]^+$, 3), 353 ($[M]^+$, 13), 263 (15), 262 (100), 147 (14), 146 (10), 119 (9), 118 (33), 104 (12), 91 (42), 77 (9), 65 (10). HRMS (ESI-TOF) calcd for $C_{21}H_{23}NO_4Na$ $[M+Na]^+$: 376.1525; found: 376.1514.

Preparation of ethyl 1-benzyl-2-(3,4-dimethoxyphenyl)-5-oxopyrrolidine-3-carboxylate (3d). Imine **2d** (0.255 g, 1 mmol) was employed to produce a crude γ -lactamcarboxylic acid, which consisted of a 90:10 mixture of *trans*:*cis*-isomers. The ethyl ester derivative was prepared according to the General Procedure A. A crude residue was purified by preparative thin-layer chromatography (SiO_2 , 20% EtOAc in

hexanes, triple runs) to give a mixture of *trans*:*cis*-isomers (90:10) of **3d** (0.248 g, 65%, as a yellow oil).

^1H NMR (300 MHz, CDCl_3 , *trans*-isomers marked *): δ 7.40-6.40 (m, 16H, ArH of *trans*- and *cis*-isomers), 5.12 (d, $J = 14.7$ Hz, 1H), 5.04* (d, $J = 14.7$ Hz, 1H), 4.64 (d, $J_{\text{cis}} = 9.3$ Hz, 1H), 4.55* (d, $J_{\text{trans}} = 6.0$ Hz, 1H), 4.10 (q, $J = 7.1$ Hz, 2H), 3.90-3.30 (m, 3H), 3.90* (s, 3H), 3.88 (s, 3H), 3.82 (s, 6H, OCH_3 of *trans*- and *cis*-isomers), 3.55* (d, $J = 14.7$ Hz, 1H), 3.48 (d, $J = 14.7$ Hz, 1H), 3.22 (dd, $J = 17.3, 10.1$ Hz, 1H), 2.62 (dd, $J = 17.3, 9.4$ Hz, 1H), 3.10-3.00* (m, 1H), 2.95-2.70* (m, 2H), 1.17* (t, $J = 7.1$ Hz, 3H), 0.91 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , *trans*-isomers marked *): δ 173.0, 172.7*, 172.2*, 170.0, 149.5*, 149.2, 149.1*, 149.0, 136.0, 135.7*, 131.1*, 128.6, 128.5*, 128.4 (*trans*- and *cis*-isomers), 128.0, 127.7, 127.6*, 120.2*, 119.6, 111.2*, 110.9, 110.4, 109.5*, 63.6*, 62.2, 61.3*, 60.8, 55.9*, 55.8, 46.2*, 44.5*, 44.4, 42.9, 33.8*, 32.0, 14.0*, 13.8. IR (CHCl_3): ν_{max} 1731, 1683 cm^{-1} . MS: m/z (%) relative intensity 384 ($[\text{M}+1]^+$, 7), 383 ($[\text{M}]^+$, 24), 293 (16), 146 (13), 145 (6), 119 (7), 118 (17), 91 (40), 77 (6), 65 (9). HRMS (ESI-TOF) calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 406.1630; found: 406.1624.

Preparation of ethyl 1-benzyl-5-oxo-2-*p*-tolylpyrrolidine-3-carboxylate (3e). Imine **2e** (0.209 g, 1 mmol) was employed to produce a crude γ -lactamcarboxylic acid, which consisted of a 99:1 mixture of *trans*:*cis*-isomers. The ethyl ester derivative was prepared according to the General Procedure A. A crude residue was purified by preparative thin-layer chromatography (SiO_2 , 20% EtOAc in hexanes, triple runs) to give a pure *trans*-isomer of **3e** (0.235 g, 70%, a yellow oil).

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^1H NMR (300 MHz, CDCl_3): δ 7.35-6.95 (m, 9H), 5.10 (d, $J = 14.7$ Hz, 1H), 4.56 (d, $J = 5.6$ Hz, 1H), 4.09 (q, $J = 7.1$ Hz, 2H), 3.70 (s, 3H), 3.47 (d, $J = 14.7$ Hz, 1H), 3.05-2.95 (m, 1H), 2.90-2.75 (m, 2H), 2.37 (s, 3H), 1.16 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 172.7, 172.2, 138.4, 135.9, 135.7, 129.7, 128.5, 128.4, 127.5, 126.8, 63.3, 61.3, 46.1, 44.3, 33.6, 22.1, 14.0. IR (neat): ν_{max} 1733, 1694 cm^{-1} . MS: m/z (%) relative intensity 338 ($[\text{M}+1]^+$, 3), 337 ($[\text{M}]^+$, 5), 247 (16), 246 (100), 146 (16), 145 (7), 131 (13), 119 (10), 118 (37), 117 (7), 91 (52), 77 (4), 65 (13). HRMS (ESI-TOF) calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 360.1576; found: 360.1568.

Preparation of 1-benzyl-2-(4-chlorophenyl)-5-oxopyrrolidine-3-carboxylic acid (3f). Imine **2f** (0.230 g, 1 mmol) was employed to produce a crude product **3f**, which consisted of a 99:1 mixture of *trans*:*cis*-isomers. A single isomer (*trans*) of **3f** was obtained after crystallization from *i*PrOH to give a white solid of *trans*-**2f** (0.292 g, 89%, m.p. = 194-195 $^{\circ}\text{C}$).

^1H NMR (300 MHz, CDCl_3): δ 7.36 (d, $J = 8.45$ Hz, 3H), 7.30-7.20 (m, 5H), 7.10 (d, $J = 8.45$ Hz), 7.00-6.90 (m, 2H), 5.09 (d, $J = 14.7$ Hz, 1H), 4.59 (d, $J = 5.9$ Hz), 3.48 (d, $J = 14.7$ Hz, 1H), 3.10-3.00 (m, 1H), 3.00-2.75 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 175.2, 172.8, 137.2, 135.1, 134.6, 129.4, 128.7, 128.4, 127.8, 62.9, 45.6, 44.6, 33.4. IR (KBr): ν_{max} 3447, 1728, 1650 cm^{-1} . MS: m/z (%) relative intensity,

330 ($[M+1]^+$, 10), 329 ($[M]^+$, 26), 239 (9), 238 (100), 147 (41), 146 (70), 119 (31), 118 (79), 104 (61), 91 (53), 77 (15), 65 (19). HRMS (ESI-TOF) calcd for $C_{18}H_{16}NO_3Na$ $[M+Na]^+$: 352.0716; found: 352.0717.

Preparation of ethyl 1-benzyl-2-(4-nitrophenyl)-5-oxopyrrolidine-3-carboxylate (3g). Imine **2g** (0.240 g, 1 mmol) was employed to produce a crude γ -lactamcarboxylic acid, which consisted of a 99:1 mixture of *trans*:*cis*-isomers. The ethyl ester derivative was prepared according to the General Procedure A. A crude residue was purified by preparative thin-layer chromatography (SiO_2 , 20% EtOAc in hexanes, triple runs) to give a pure *trans*-isomer of **3g** (0.232 g, 63%, a yellow oil).

1H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 7.25-7.15 (m, 5H), 7.00-6.85 (m, 2H), 5.07 (d, J = 14.7 Hz, 1H), 4.64 (d, J = 5.8 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.45 (d, J = 14.7 Hz), 3.00-2.90 (m, 1H), 2.85-2.70 (m, 2H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 171.4, 148.0, 146.5, 135.0, 128.8, 128.4, 128.0, 127.9, 124.4, 62.9, 61.7, 45.9, 44.9, 33.3, 14.0. IR ($CHCl_3$): ν_{max} 1732, 1683 cm^{-1} . MS: m/z (%) relative intensity 369 ($[M+1]^+$, 2), 368 ($[M]^+$, 8), 278 (14), 277 (100), 147 (11), 146 (19), 119 (10), 118 (32), 104 (20), 91 (36), 77 (8), 65 (10), 55 (2). HRMS (ESI-TOF) calcd for $C_{20}H_{20}N_2O_5Na$ $[M+Na]^+$: 391.1270; found: 391.1270.

Preparation of 1-benzyl-2-(furan-3-yl)-5-oxopyrrolidine-3-carboxylic acid (3h). Imine **2h** (0.285 g, 1 mmol) was employed to produce a crude product **3h**, which consisted of a 99:1 mixture of *trans*:*cis*-isomers. The mixture was purified by Sephadex LH20 to give a pure *trans*-isomer of **3h** (0.214 g, 75%, a brownish oil).

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^1H NMR (300 MHz, CDCl_3): δ 7.29 (s, 1H), 7.20-6.95 (m, 5H), 6.24 (d, J = 3.0 Hz, 1H), 6.17 (d, J = 3.0 Hz, 1H), 4.86 (d, J = 14.9 Hz, 1H), 4.71 (d, J = 5.1 Hz, 1H), 3.52 (d, J = 14.9 Hz, 1H), 3.10-2.85 (m, 1H), 2.85-2.75 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 175.1, 173.1, 149.9, 143.4, 135.3, 128.5, 128.1, 127.6, 110.4, 110.1, 57.1, 44.7, 41.9, 33.5. IR (CHCl_3): ν_{max} 3670, 1717 1686 cm^{-1} . MS: m/z (%) relative intensity 285 $[\text{M}]^+$ (4), 204 (100), 164 (33), 147 (10), 146 (17), 119 (9), 118 (41), 105 (11), 91 (42), 77 (21), 65 (15). HRMS (ESI-TOF) calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 308.0899; found: 308.0900.

Preparation of ethyl 2-(4-methoxyphenyl)-5-oxo-1-phenylpyrrolidine-3-carboxylate (3j). Imine **2j** (0.215 g, 1 mmol) was employed to produce a crude γ -lactamcarboxylic acid, which consisted of an 80:20 mixture of *trans*:*cis*-isomers. The ethyl ester derivative was prepared according to the General Procedure A. A crude residue was purified by preparative thin-layer chromatography (SiO_2 , 20% EtOAc in hexanes, triple runs). The higher R_f was *trans*-**3j** (0.198 g, 59%, a pale yellow oil) and the lower R_f was *cis*-**3j** (39 mg, 11% yield, a pale yellow oil).

trans-**3j**: ^1H NMR (300 MHz, CDCl_3): δ 7.27 (d, J = 7.8 Hz, 2H), 7.16 (t, J = 7.3 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 6.99 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 8.6 Hz, 2H), 5.39 (d, J_{trans} = 4.9 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.66 (s, 3H), 2.75-3.10 (m, 3H),

1.19 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 172.2, 172.0, 159.3, 137.4, 131.5, 128.6, 127.4, 125.3, 122.9, 114.3, 65.4, 61.5, 55.1, 46.7, 34.4, 14.1. IR (neat): ν_{max} 1732 (C=O of ester), 1704 (C=O of amide) cm^{-1} . MS: m/z (%) relative intensity 340 ($[\text{M}+1]^+$, 24), 339 ($[\text{M}]^+$, 55), 210 (100), 91 (43), 77 (65). HRMS (ESI-TOF) calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_4$ $[\text{M}+1]^+$: 340.1549; found: 340.1549.

cis-**3j**: ^1H NMR (300 MHz, CDCl_3): δ 7.35 (d, $J = 8.0$ Hz, 2H), 7.15 (m, 2H), 7.05 (t, $J = 8.7$ Hz, 3H), 6.74 (d, $J = 8.7$ Hz, 2H), 5.38 (d, $J_{\text{cis}} = 8.8$ Hz, 1H), 3.90-3.60 (m, 3H), 3.68 (s, 3H), 3.28 (dd, $J = 17.5, 10.9$ Hz, 1H), 2.67 (dd, $J = 17.5, 8.9$ Hz, 1H), 0.97 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 172.6, 169.6, 159.6, 137.8, 128.7, 128.2, 128.0, 125.2, 122.2, 113.9, 64.7, 61.0, 55.1, 43.7, 32.9, 13.8. IR (CHCl_3): ν_{max} 1732 (C=O of ester), 1697 (C=O of amide) cm^{-1} . MS: m/z (%) relative intensity 340 ($[\text{M}+1]^+$, 20), 339 ($[\text{M}]^+$, 100), 266 (61), 210 (90), 91 (16), 77 (22). HRMS (ESI-TOF) calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 362.1368; found: 362.1368.

Preparation of ethyl 2-(3,4-dimethoxyphenyl)-5-oxo-1-phenylpyrrolidine-3-carboxylate (3k). Imine **2k** (0.245 g, 1 mmol) was employed to produce a crude γ -lactamcarboxylic acid, which consisted of an 80:20 mixture of *trans*:*cis*-isomers. The ethyl ester derivative was prepared according to the General Procedure A. A crude residue was purified by preparative thin-layer chromatography (SiO_2 , 20% EtOAc in hexanes, triple runs). The higher R_f was *trans*-**3k** (0.185 g, 50%, a pale yellow solid, m.p. = 136-137 $^\circ\text{C}$) and the lower R_f was *cis*-**3k** (40 mg, 10% yield, a yellow oil).

trans-**3k**: ^1H NMR (300 MHz, CDCl_3): δ 7.29 (d, $J = 8.4$ Hz, 2H), 7.20-6.90 (m, 4H), 6.80-6.50 (m, 2H), 5.39 (d, $J_{\text{trans}} = 5.0$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 2.78-3.08 (m, 3H), 1.21 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 177.3, 172.0, 149.4, 148.8, 137.5, 132.0, 128.7, 125.5, 122.9, 118.7, 111.3,

108.9, 66.0, 61.6, 55.9, 55.8, 46.7, 34.5, 14.1. IR (CHCl₃): $\nu_{\max}$ 1731 (C=O of ester), 1695 (C=O of amide) cm⁻¹. MS: m/z (%) relative intensity 371 ([M+2]⁺, 6), 370 ([M+1]⁺, 24), 369 ([M]⁺, 100), 240 (57), 91 (12), 77 (22). HRMS (ESI-TOF) calcd for C₂₁H₂₃O₅NNa [M+Na]⁺: 392.1474; found: 392.1477.

cis-**3k**: ¹H NMR (300 MHz, CDCl₃): δ 7.41 (d, J = 8.1 Hz, 2H), 7.26 (t, J = 6.7 Hz, 2H), 7.09 (t, J = 7.4 Hz, 1H), 6.70 (s, 2H), 6.67 (s, 1H), 5.43 (d, J_{cis} = 8.8 Hz, 1H), 3.75-3.95 (m, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 3.31 (dd, J = 17.3, 10.0 Hz, 1H), 2.72 (dd, J = 17.3, 8.9 Hz, 1H), 1.03 (t, J = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 172.7, 169.7, 149.2, 149.1, 137.9, 128.8, 128.6, 125.4, 122.3, 119.6, 111.1, 110.1, 65.0, 55.9, 55.8, 43.8, 33.1, 29.7, 13.8. IR (CHCl₃): $\nu_{\max}$ 1731 (C=O of ester), 1696 (C=O of amide) cm⁻¹. MS: m/z (%) relative intensity 371 ([M+2]⁺, 7), 370 ([M+1]⁺, 37), 369 ([M]⁺, 100), 91 (12), 77 (30). HRMS (ESI-TOF) calcd. for C₂₁H₂₃O₅NNa [M+Na]⁺: 392.1474; found: 392.1477.

Preparation of ethyl 2-(4-chlorophenyl)-5-oxo-1-phenylpyrrolidine-3-carboxylate (3l). Imine **2l** (0.220 g, 1 mmol) was employed to produce a crude γ -lactamcarboxylic acid, which consisted of a 90:10 mixture of *trans*:*cis*-isomers. The ethyl ester derivative was prepared according to the General Procedure A. A crude residue was purified by preparative thin-layer chromatography (SiO₂, 20% EtOAc in hexanes, triple runs). The higher R_f was *trans*-**3l** (0.190 g, 55%, a pale yellow solid, m.p. = 117-119 °C) and the lower R_f was *cis*-**3l** (33 mg, 10%, a yellow oil).

3l

trans-**3l**: ¹H NMR (300 MHz, CDCl₃): δ 7.27 (m, 2H), 7.20-7.05 (m, 6H), 7.01 (m, 1H), 5.44 (d, J_{trans} = 4.8 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.00-2.70 (m, 3H), 1.20 (t, J = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 171.8, 138.2, 137.1, 134.0, 129.2, 128.8, 127.7, 125.6, 122.7, 65.0, 61.7, 46.4, 34.3, 14.1. IR (neat): $\nu_{\max}$ 1731

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(C=O of ester), 1714 (C=O of amide) cm^{-1} . MS: m/z (%) relative intensity 344 ($[\text{M}+1]^+$, 16), 343 ($[\text{M}]^+$, 68), 270 (83), 242 (100), 240 (23), 216 (59), 91 (9), 77 (81), 55 (12). Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{ClNO}_3$: C, 66.38; H, 5.28; N, 4.07. Found: C, 66.17; H, 4.92; N, 4.00.

cis-**3l**: ^1H NMR (300 MHz, CDCl_3): δ 7.32 (m, 2H), 7.21-7.16 (m, 4H), 7.16-6.95 (m, 3H), 5.41 (d, $J_{cis} = 8.8$ Hz, 1H), 3.90-3.60 (m, 3H), 3.22 (dd, $J = 17.3$ and 10.5 Hz, 1H), 2.67 (dd, $J = 17.3$ and 9.3 Hz, 1H), 0.96 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 172.4, 169.4, 137.4, 134.8, 134.5, 128.6, 128.4, 125.5, 122.1, 64.4, 61.2, 43.4, 32.8, 13.7. IR (CHCl_3): ν_{max} 1732 (C=O of ester), 1698 (C=O of amide) cm^{-1} . MS: m/z (%) relative intensity 344 ($[\text{M}+1]^+$, 21), 343 ($[\text{M}]^+$, 93), 270 (90), 242 (100), 216 (71), 91 (9), 77 (53), 50 (12). HRMS (ESI-TOF) calcd. for $\text{C}_{19}\text{H}_{19}\text{ClNO}_3$ $[\text{M}+1]^+$: 344.1503 ; found; 344.1502.

¹H NMR Spectrum of 3a (300 MHz, CDCl₃)

¹³C NMR Spectrum of 3a (75 MHz, CDCl₃)

¹H NMR Spectrum of 3b (300 MHz, CDCl₃) ¹³C NMR Spectrum of 3b (75 MHz, CDCl₃)

S14

¹H NMR Spectrum of 3c (300 MHz, CDCl₃)

¹³C NMR Spectrum of 3c (75 MHz, CDCl₃)

¹H NMR Spectrum of 3d (300 MHz, CDCl₃)

^{13}C NMR Spectrum of 3d (75 MHz, CDCl_3)

S16

¹H NMR Spectrum of 3e (300 MHz, CDCl₃)

¹³C NMR Spectrum of 3e (75 MHz, CDCl₃)

S17

¹H NMR Spectrum of 3f (300 MHz, CDCl₃)

S18

¹H NMR Spectrum of 3g (300 MHz, CDCl₃)

¹³C NMR Spectrum of 3g (75 MHz, CDCl₃)

S19

¹H NMR Spectrum of 3h (300 MHz, CDCl₃)

¹³C NMR Spectrum of 3h (75 MHz, CDCl₃)

¹H NMR Spectrum of *trans*-3i (300 MHz, CDCl₃) ¹³C NMR Spectrum of *trans*-3i (75 MHz, CDCl₃)

¹H NMR Spectrum of *cis*-3i (75 MHz, CDCl₃)

¹³C NMR Spectrum of *cis*-3i (75 MHz, CDCl₃)

¹H NMR Spectrum of *cis*-3j (300 MHz, CDCl₃) ¹³C NMR Spectrum of *cis*-3j (75 MHz, CDCl₃)

¹H NMR Spectrum of *trans*-3k (300 MHz, CDCl₃) ¹³C NMR Spectrum of *trans*-3k (75 MHz, CDCl₃)

¹H NMR Spectrum of *cis*-3k (300 MHz, CDCl₃)

^{13}C NMR Spectrum of *cis*-3k (75 MHz, CDCl_3)

¹H NMR Spectrum of *trans*-3l (300 MHz, CDCl₃)

^{13}C NMR Spectrum of *trans*-3l (75 MHz, CDCl_3)

¹H NMR Spectrum of *cis*-3l (300 MHz, CDCl₃)

^{13}C NMR Spectrum of *cis*-31 (75 MHz, CDCl_3)