Intermolecular Radical Addition and Addition/Cyclization Reactions of Alkoxyamines onto Nonactivated Alkenes

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Supporting Information

General. ^1H - and ^{13}C -NMR spectra: recorded on a Bruker ARX 500, ARX 400, ARX 300, ARX 200 or a AC 200. Chemical shifts δ in ppm rel. to SiMe_4 as internal standard. TLC: Merck silica gel 60 F₂₅₄ plates; detection with UV or dipping into a soln. of KMnO_4 (1.5 g in 333 mL 1M NaOH) or a soln. of $\text{Ce}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (10 g), phosphormolybdic acid hydrate (25 g), conc. H_2SO_4 (60 mL), and H_2O (940 mL), followed by heating. FC: Merck or Fluka silica gel 60 (40 – 63 μm); at *ca.* 0.4 bar. GC: Hewlett Packard 5890 chromatograph using Hewlett Packard HP-5, Macherey-Nagel Optima δ - μ 3, or Supelco γ -DEX 120 columns. Melting points: Büchi 510 apparatus; uncorrected. I.R. spectra: recorded on a Perkin Elmer 782 or Bruker IFS-200 spectrophotometer. MS: Recorded on a VG Tribid, Varian CH7 (EI); IonSpec Ultima, Finnigan MAT TSQ 700 or a Finnigan MAT 95S (ESI) in m/z (% of basis peak). Solvents were purified by standard methods. Compounds sensitive to air and moisture were handled under argon using Schlenk techniques.

(2,2,6,6-Tetramethylpiperidine-1-yloxy)dimethylmalonate (10)

A soln. of diisopropylamine (2.16 mL, 15.36 mmol) in 1,2-dimethoxyethane (60 mL) was treated with BuLi (15.36 mmol) at $-60\text{ }^\circ\text{C}$; a white precipitate was formed. After stirring for 30 min. at $-60\text{ }^\circ\text{C}$, dimethyl malonate (1.6 mL, 13.96 mmol) was added dropwise. The precipitate disappeared. After stirring for another 30 min., 2,2,6,6-tetramethylpiperidin-1-oxyl radical (TEMPO) (2.40 g, 15.36 mmol) and subsequently anhydrous CuCl_2 (2.06 g, 15.36 mmol) were added. The reaction mixture turned brown. After stirring for 3 h at $0\text{ }^\circ\text{C}$, the reaction mixture was treated with a sat. NH_4Cl soln. and extracted with diethyl ether. The organic layer was washed with brine and dried (MgSO_4). Evaporation of the solvents *in vacuo* and purification of the crude product by FC (*t*-butylmethylether/pentane = 1:4) afforded the

alkoxyamine **10** (3.53 g, 88%) as colorless crystals. M.p. 81-82 °C. I.R. (film): 2963s, 1769s, 1745s, 1262s, 1093s, 1020s, 797s. ¹H-NMR (200 MHz, CDCl₃): 4.90 (s, 2 H, CH₂); 3.72 (s, 6 H, CH₃); 1.59-1.0 (m, br. 6 H, CH₂); 1.20 (s, br. 6 H, CH₃); 0.99 (s, br. 6 H, CH₃). ¹³C-NMR (75 MHz, CDCl₃): 167.6, 86.4, 60.3, 52.5, 40.1, 32.5, 20.1, 16.9; MS (ESI): 326 (70 [M+K]⁺), 310 (100 [M+Na]⁺), 288 (45 [M+H]⁺). HRMS (ESI) calcd for C₁₄H₂₅NNaO₅ ([M+Na]⁺): 310.1630. Found: 310.1629.

(2,2,6,6-Tetramethylpiperidine-1-yloxy)di-tert-butylmalonate (11)

Diisopropylamine (2.07 mL, 14.88 mmol) in 1,2-dimethoxyethane was deprotonated with BuLi (14.88 mmol, 1.7 M in hexanes) at 0 °C; a white precipitate was formed. After stirring for 30 min. at 0 °C, di-tert-butyl malonate (3.0 mL, 13.39 mmol) was added dropwise. The precipitate disappeared. After stirring for another 30 min., TEMPO (2.33 g, 14.88 mmol) and subsequently anhydrous CuCl₂ (2.00 g, 14.88 mmol) were added. The reaction mixture turned brown. After stirring for 1 h at 0 °C and 18 h at rt, the reaction mixture was treated with a sat. NH₄Cl soln. and was extracted with diethyl ether. The organic layer was washed with brine and dried (MgSO₄). Evaporation of the solvents *in vacuo* and purification of the crude product by FC (ether/pentane = 1:20) afforded the alkoxyamine **11** (4.20 g, 84%) as colorless crystals. M.p. 97-99 °C. I.R. (film): 2980s, 2938s, 1758s, 1734s, 1473m, 1371m, 1230m, 1132m cm⁻¹. ¹H-NMR (200 MHz, CDCl₃): 4.69 (s, 1 H, CH); 1.63–1.23 (m, 6 H, CH₂); 1.46 (m, 18 H, CH₃); 1.19 (s, 6 H, CH₃); 1.09 (s, 6 H, CH₃). ¹³C-NMR (75 MHz, CDCl₃): 166.6 (C), 87.6 (CH), 82.1 (C), 60.2 (C), 40.1 (CH₂), 32.6 (CH₃), 27.9 (CH₃), 20.1 (CH₃), 17.0 (CH₂). MS (ESI): 410 (13, [M+K]⁺), 394 (100, [M+Na]⁺), 372 (42, [M+H]⁺), 316 (18), 260 (55). HRMS (ESI) calcd for C₂₀H₃₇NNaO₅ ([M+Na]⁺): 394.2569. Found: 394.2566.

Addition products 12, 14, 15, 17, 19, 21, 34 and 38: General Procedure 1 (GP 1)

Alkoxyamine **10** and the alkene (5 equiv.) were dissolved in 1,2-dichloroethane (DCE) (1 M solution) under an argon atmosphere. The soln. was heated to 135 °C in a sealed tube (5 mL) for 3 d. The reaction mixture was then allowed to cool to rt and diethyl ether was added. Removal of the solvents and purification by FC afforded the product.

Addition products 13, 16, 18, 20, 35 and 39: General Procedure 2 (GP 2)

Alkoxyamine **11** and the alkene (5 equiv.) were dissolved in *tert*-butanol (*t*-BuOH) (1 M solution) under an argon atmosphere. The soln. was heated to 135 °C in a sealed tube (5 mL) for 5 d. The reaction mixture was then allowed to cool to rt and diethyl ether was added.

Removal of the solvents and purification by FC afforded the product.

Cyclization Products 26 – 33: General Procedure (GP 3)

A solution of the alkoxyamine (**10** or **11**) and the diene (**22-25**) in *t*-BuOH (0.08 mL) or DCE (0.09 mL) was heated for 48 h at 135°C (sealed tube). Removal of the solvent and purification by flash-chromatography (FC) afforded the desired product.

2-[2-(2,2,6,6-Tetramethylpiperidine-1-yloxy)octyl]dimethylmalonate (**12**)

According to GP 1, with **10** (100 mg, 0.348 mmol) and 1-octene (195 mg, 1.74 mmol) in DCE (0.35 mL). FC (ether/pentane = 1:20) afforded **12** (91 mg, 66%). I.R. (film): 3462_w, 2929_s, 2871_m, 1756_s, 1739_s, 1436_m, 1360_m, 1241_m, 1154_w cm⁻¹. ¹H-NMR (200 MHz, CDCl₃): 3.78–3.71 (*m*, 2 H, 2x CH); 3.73 (*s*, 3 H, CH₃); 3.72 (*s*, 3 H, CH₃); 2.17–2.09 (*m*, 2 H, CH₂); 2.07–2.03 (*m*, 1 H, CH₂); 1.50–1.42 (*m*, 5 H); 1.41–1.26 (*m*, 10 H); 1.08–1.04 (*m*, 12 H); 0.90–0.84 (*m*, 3 H). ¹³C-NMR (50 MHz, CDCl₃): 170.0 (C), 169.9 (C), 78.9 (CH), 59.9 (C), 59.0 (C), 52.3 (CH₃), 52.2 (CH₃), 48.5 (CH), 40.2 (CH₂), 40.0 (CH₂), 34.0 (2x CH₃), 32.9 (CH₂), 32.6 (CH₂), 31.7 (CH₂), 29.3 (CH₂), 25.7 (CH₂), 22.4 (CH₂), 20.4 (CH₃), 20.2 (CH₃), 17.1 (CH₂), 13.9 (CH₃). MS (ESI): 438 (5, [M+K]⁺), 422 (21, [M+Na]⁺), 400 (100, [M+H]⁺), 276 (11), 158 (8), 126 (42). HRMS (ESI) calcd for C₂₂H₄₂NO₅ ([M+H]⁺): 400.3063. Found: 400.3058.

2-[2-(2,2,6,6-Tetramethylpiperidin-1-yloxy)octyl]*tert*-butylmethylmalonate

According to GP 1, with **10** (100 mg, 0.348 mmol) and 1-octene (195 mg, 1.74 mmol) in *t*-BuOH (0.35 mL). FC (ether/pentane = 1:25) afforded the transesterification product (55 mg, 36%) besides **12** (49 mg, 35%). I.R. (film): 3447_w, 2930_s, 2871_m, 1751_s, 1734_s, 1457_m, 1369_m, 1257_m, 1146_s cm⁻¹. ¹H-NMR (200 MHz, CDCl₃): 3.80–3.60 (*m*, 2 H, 2x CH); 3.72 (*s*, 3 H, CH₃ isomer A); 3.71 (*s*, 3 H, CH₃ isomer B); 2.13–1.96 (*m*, 3 H, CH₂); 1.52–1.38 (*m*, 5 H, CH₂); 1.47 (*s*, 9 H, CH₃); 1.35–1.17 (*m*, 10 H, CH₂); 1.13–1.02 (*m*, 12 H, CH₃); 0.90–0.84 (*m*, 3 H). ¹³C-NMR (50 MHz, CDCl₃): 170.8 (C, isomer A), 170.6 (C, isomer B), 169.0 (C, isomer A), 168.7 (C, isomer B), 81.7 (CH, isomer A), 81.6 (CH, isomer B), 79.0 (CH, isomer A), 78.9 (CH, isomer B), 60.1 (C), 59.2 (C), 52.2 (CH isomer A), 52.1 (CH isomer B), 50.0 (CH₃ isomer A), 49.7 (CH₃ isomer B), 40.4 (CH₂), 40.2 (CH₂), 34.2 (CH₃), 34.1 (CH₃), 33.2 (CH₂ isomer A), 32.9 (CH₂ isomer B), 32.8 (CH₂ isomer A), 32.7 (CH₂ isomer B), 31.9 (CH₂), 29.6 (CH₂), 27.9 (CH₃), 26.0 (CH₂ isomer A), 25.8 (CH₂ isomer B), 20.4 (CH₃), 20.2 (CH₃), 17.3 (CH₂), 14.1 (CH₃). MS (ESI): 480 (3, [M+K]⁺), 464 (13, [M+Na]⁺), 442 (100, [M+H]⁺), 386

(87), 342 (10), 126 (25). HRMS (ESI) calcd for $C_{25}H_{48}NO_5$ ($[M+H]^+$): 442.3533. Found: 442.3532.

2-[2-(2,2,6,6-Tetramethylpiperidin-1-yloxy)octyl]di-*tert*-butylmalonate (13)

According to GP 2, with **11** (100 mg, 0.27 mmol) and 1-octene (151 mg, 1.35 mmol) in *t*-BuOH (0.27 mL). FC (ether/pentane = 1:50) afforded **13** (94 mg, 72%) besides unreacted starting material (19 mg, 19%). I.R. (film): 3411*w*, 2976*s*, 2930*s*, 1729*s*, 1457*w*, 1368*m*, 1256*m*, 1136*m* cm^{-1} . 1H -NMR (200 MHz, $CDCl_3$): 3.79–3.67 (*m*, 1 H, CH); 3.54 (*t*, $J = 7.5$ Hz, 1 H, CH); 2.02 (*dxd*, $J_1 = 8.3$ Hz, $J_2 = 6.5$ Hz, 2 H, CH_2); 1.57–1.38 (*m*, 6 H); 1.46 (*s*, 18 H, $C(CH_3)_3$); 1.37–1.17 (*m*, 10 H); 1.16–1.04 (*m*, 12 H); 0.91–0.84 (*m*, 3 H). ^{13}C -NMR (50 MHz, $CDCl_3$): 169.4 (C), 169.1 (C), 81.3 (C), 81.0 (C), 78.8 (CH), 60.2 (C), 59.3 (C), 51.0 (CH), 40.4 (CH_2), 40.2 (CH_2), 34.2 (CH_3), 34.1 (CH_3), 33.0 (CH_2), 32.9 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 27.9 (CH_3), 25.9 (CH_2), 22.7 (CH_2), 20.6 (2x CH_3), 17.4 (CH_2), 14.1 (CH_3). MS (ESI): 506 (7, $[M+Na]^+$), 484 (100, $[M+H]^+$), 428 (22), 372 (12), 195 (5). HRMS (ESI) calcd for $C_{28}H_{54}NO_5$ ($[M+H]^+$): 484.4002. Found: 400.4002.

2-[4-Phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)butyl]dimethylmalonate (14)

According to GP 1, with **10** (100 mg, 0.348 mmol) and 4-phenyl-1-butene (230 mg, 1.74 mmol) in DCE (0.35 mL). FC (ether/pentane = 1:20 to 1:10) afforded **14** (71 mg, 49%). I.R. (film): 3465*w*, 3062*w*, 2932*m*, 1738*s*, 1618*w*, 1496*w*, 1436*s*, 1360*m*, 1243*s*, 1153*s* cm^{-1} . 1H -NMR (200 MHz, $CDCl_3$): 7.28–7.13 (*m*, 5 H, CH); 3.78–3.70 (*m*, 2 H, CH); 3.74 (*s*, 3 H, CH_3); 3.73 (*s*, 3 H, CH_3); 2.70–2.34 (*m*, 2 H, CH_2); 2.23 (*dxd*, $J_1 = 7.2$ Hz, $J_2 = 5.5$ Hz, 2 H, CH_2); 1.65–1.25 (*m*, 8 H, CH_2); 1.10 (*s*, 3 H, CH_3); 1.04 (*s*, 3 H, CH_3); 1.03 (*s*, 3 H, CH_3); 0.98 (*s*, 3 H, CH_3). ^{13}C -NMR (50 MHz, $CDCl_3$): 170.1 (C), 170.0 (C), 142.1 (CH), 128.3 (CH), 128.2 (CH), 125.6 (CH), 78.3 (CH), 60.1 (C), 59.3 (C), 52.5 (CH_3), 52.4 (CH_3), 48.6 (CH), 40.3 (CH_2), 40.1 (CH_2), 34.3 (CH_2), 33.9 (2x CH_3), 33.0 (CH_2), 32.1 (CH_2), 20.5 (CH_3), 20.4 (CH_3), 17.3 (CH_2). MS (ESI): 458 (11, $[M+K]^+$), 442 (88, $[M+Na]^+$), 420 (83, $[M+H]^+$), 285 (62). HRMS (ESI) calcd for $C_{24}H_{38}NO_5$ ($[M+H]^+$): 420.2750. Found: 420.2743.

2-[2-Butoxy-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethyl]dimethylmalonate (15)

According to GP 1, with **10** (100 mg, 0.348 mmol), butyl vinyl ether (174 mg, 1.74 mmol) and KOH (2 mg) in DCE (0.35 mL). FC (ether/pentane = 1:20) afforded **15** (105 mg, 78%). I.R. (film): 3471*w*, 2933*s*, 2872*m*, 1740*s*, 1463*m*, 1362*m*, 1260*s*, 1242*m*, 1155*w* cm^{-1} . 1H -NMR (500 MHz, $CDCl_3$): 4.79 (*dxd*, $J_1 = 6.0$ Hz, $J_2 = 3.9$ Hz, 1 H, CH); 3.83 (*dxt*, $J_1 = 9.2$

Hz, $J_2 = 6.6$ Hz, 1 H, OCH₂); 3.72 (*s*, 3 H, CO₂CH₃); 3.71 (*s*, 3 H, CO₂CH₃); 3.65 (*dxd*, $J_1 = 6.4$ Hz, $J_2 = 3.6$ Hz, 1 H, CH); 3.41 (*dxt*, $J_1 = 9.2$ Hz, $J_2 = 6.9$ Hz, 1 H, CH₂); 2.29–2.18 (*m*, 2 H, CH₂); 1.60–1.27 (*m*, 10 H); 1.18 (*s*, 3 H); 1.06 (*t*, $J = 17.6$ Hz, 9 H); 0.89 (*t*, $J = 7.55$ Hz, 3 H, CH₃). ¹³C-NMR (125 MHz, CDCl₃): 170.0 (C), 169.9 (C), 104.7 (CH), 70.3 (CH₂), 60.6 (C), 59.3 (C), 52.4 (CH₃), 52.3 (CH₃), 47.1 (CH), 40.4 (CH₂), 40.1 (CH₂), 33.6 (CH₃), 33.2 (CH₃), 32.8 (CH₂), 31.9 (CH₂), 20.4 (CH₃), 20.0 (CH₃), 19.2 (CH₂), 17.2 (CH₂), 13.9 (CH₃). MS (ESI): 410 (100, [M+Na]⁺), 388 (92, [M+H]⁺), 158 (97). HRMS (ESI) calcd for C₂₀H₃₈NO₆ ([M+H]⁺): 388.2699. Found: 388.2702.

2-[2-Butoxy-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethyl]di-*tert*-butylmalonate (16)

According to GP 2, with **11** (100 mg, 0.27 mmol), butyl vinyl ether (134 mg, 1.35 mmol) and KOH (2 mg) in *t*-BuOH (0.27 mL). FC (ether/pentane = 1:50) afforded **16** (88 mg, 69%). I.R. (film): 3475*w*, 2977*s*, 2933*s*, 2873*m*, 1745*m*, 1729*m*, 1457*w*, 1368*m*, 1138*w* cm⁻¹. ¹H-NMR (200 MHz, CDCl₃): 4.78 (*dxd*, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 1 H, CH); 3.90 (*dxt*, $J_1 = 9.2$ Hz, $J_2 = 6.8$ Hz, 1 H, OCH₂); 3.48 (*dxt*, $J_1 = 9.3$ Hz, $J_2 = 6.8$ Hz, 1 H, OCH₂); 3.38 (*dxd*, $J_1 = 9.3$ Hz, $J_2 = 5.5$ Hz, 1 H, CH); 2.26–1.98 (*m*, 2 H, CH₂); 1.60–1.25 (*m*, 10 H); 1.45 (*s*, 18 H, C(CH₃)₃); 1.21 (*s*, 3 H); 1.09 (*t*, $J = 6.8$ Hz, 9 H); 0.91 (*t*, $J = 7.0$ Hz, 3 H, CH₃). ¹³C-NMR (50 MHz, CDCl₃): 168.3 (2x C), 105.0 (CH), 81.3 (C), 81.2 (C), 70.7 (CH₂), 60.5 (C), 59.3 (C), 50.0 (CH), 40.4 (CH₂), 40.2 (CH₂), 33.9 (CH₃), 33.2 (CH₃), 32.8 (CH₂), 31.9 (CH₂), 27.9 (CH₃), 27.8 (CH₃), 20.5 (CH₃), 20.0 (CH₃), 19.2 (CH₂), 17.3 (CH₂), 14.0 (CH₃). MS (ESI): 494 (17, [M+Na]⁺), 472 (100, [M+H]⁺), 394 (3), 227 (7), 158 (11). HRMS (ESI) calcd for C₂₆H₅₀NO₆ ([M+H]⁺): 472.3638. Found: 472.3625.

2-[5-Methoxycarbonyloxy-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)pentyl]dimethylmalonate (17)

According to GP 1, with **10** (100 mg, 0.348 mmol) and methyl-4-pentenylcarbonate (250 mg, 1.74 mmol) in DCE (0.35 mL). FC (ether/pentane = 1:3) afforded **17** (63 mg, 42%). I.R. (film): 3449*w*, 2977*s*, 2933*s*, 1749*s*, 1444*m*, 1369*m*, 1268*s*, 1139*s* cm⁻¹. ¹H-NMR (200 MHz, CDCl₃): 4.13 (*dxt*, $J_1 = 6.8$ Hz, $J_2 = 2.0$ Hz, 2 H, CH₂); 3.80–3.66 (*m*, 2 H, CH); 3.76 (*s*, 3 H, CO₂CH₃); 3.73 (*s*, 3 H, CO₂CH₃); 3.72 (*s*, 3 H, CO₂CH₃); 2.27–1.99 (*m*, 3 H, CH₂); 1.74–1.59 (*m*, 3 H, CH₂); 1.49–1.25 (*m*, 6 H, CH₂); 1.07–1.02 (*m*, 12 H, CH₃). ¹³C-NMR (50 MHz, CDCl₃): 170.0 (C), 169.9 (C), 155.8 (C), 78.5 (CH), 68.1 (CH₂), 60.6 (C), 59.3 (C), 54.6 (CH₃), 52.4 (CH₃), 52.3 (CH₃), 48.6 (CH), 40.3 (CH₂), 40.2 (CH₂), 34.1 (2x CH₃), 32.9 (CH₂), 29.0 (CH₂), 25.2 (CH₂), 20.6 (CH₃), 20.4 (CH₃), 17.3 (CH₂). MS (ESI): 454 (15, [M+Na]⁺),

432 (23, [M+H]⁺), 126 (100). HRMS (ESI) calcd for C₂₁H₃₈NO₈ ([M+H]⁺): 432.2597. Found: 432.2589.

2-[5-Methoxycarbonyloxy-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)pentyl]di-*tert*-butylmalonate (18)

According to GP 2, with **11** (100 mg, 0.27 mmol) and methyl-4-pentenylcarbonate (195 mg, 1.35 mmol) in *t*-BuOH (0.27 mL). FC (ether/pentane = 1:12) afforded **18** (53 mg, 38%). I.R. (film): 3449_w, 2977_s, 2933_s, 1749_s, 1444_m, 1367_m, 1268_s, 1139_s cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): 4.18–4.11 (*m*, 2 H, CH₂); 3.80–3.77 (*m*, 1 H, CH); 3.76 (*s*, 3 H, CH₃); 3.50 (*dxd*, *J*₁ = 8.9 Hz, *J*₂ = 5.8 Hz, 1 H, CH); 2.14–1.93 (*m*, 3 H, CH₂); 1.76–1.63 (*m*, 3 H, CH₂); 1.60–1.24 (*m*, 6 H, CH₂); 1.45 (*s*, 18 H, CH₃), 1.10–1.06 (*m*, 12 H, CH₃). ¹³C-NMR (100 MHz, CDCl₃): 169.1 (C), 168.9 (C), 155.8 (C), 81.4 (C), 81.2 (C), 78.3 (CH), 68.6 (CH₂), 60.0 (C), 59.4 (C), 54.6 (CH₃), 50.8 (CH), 40.3 (CH₂), 40.2 (CH₂), 34.2 (CH₃), 34.1 (CH₃), 32.7 (CH₂), 29.1 (CH₂), 27.9 (CH₃), 25.2 (CH₂), 20.6 (2x CH₃), 17.3 (CH₂). MS (ESI): 538 (13, [M+Na]⁺), 516 (65, [M+H]⁺), 460 (47), 404 (89), 126 (100). HRMS (ESI) calcd for C₂₇H₅₀NO₈ ([M+H]⁺): 516.3536. Found: 516.3515.

2-[5-(*tert*-Butyldimethylsilanyloxy)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)pentyl]dimethylmalonate (19)

According to GP 1, with **10** (100 mg, 0.348 mmol) and *tert*-butyldimethylpent-4-enyloxysilane (349 mg, 1.74 mmol) in DCE (0.35 mL). FC (ether/pentane = 1:15) afforded **19** (119 mg, 70%). I.R. (film): 3471_w, 2953_s, 2931_s, 2857_m, 1757_s, 1740_s, 1436_w, 1361_w, 1255_m, 1099_m, 836_m cm⁻¹. ¹H-NMR (200 MHz, CDCl₃): 3.82–3.70 (*m*, 2 H, 2x CH); 3.75 (*s*, 3 H, CO₂CH₃); 3.74 (*s*, 3 H, CO₂CH₃); 3.61 (*t*, *J* = 5.1 Hz, 2 H, CH₂OSi); 1.56–1.17 (*m*, 10 H); 1.09–1.04 (*m*, 12 H); 0.89 (*s*, 9 H, C(CH₃)₃); 0.04 (*s*, 6 H, Si(CH₃)₂). ¹³C-NMR (50 MHz, CDCl₃): 169.9 (C), 169.8 (C), 78.8 (CH), 62.9 (CH₂), 59.9 (C), 59.0 (C), 52.2 (CH₃), 52.1 (CH₃), 48.4 (CH), 40.1 (CH₂), 39.9 (CH₂), 33.8 (2x CH₃), 32.9 (CH₂), 29.0 (C), 28.8 (CH₂), 25.7 (CH₃), 20.3 (CH₃), 20.2 (CH₃), 18.0 (CH₂), 17.1 (CH₂), -5.5 (2x CH₃). MS (ESI): 523 (7, [M+K]⁺), 510 (42, [M+Na]⁺), 488 (100, [M+H]⁺), 364 (26), 353 (63), 158 (85). HRMS (ESI) calcd for C₂₅H₅₀NO₆Si ([M+H]⁺): 488.3407. Found: 488.3381.

2-[5-(*tert*-Butyldimethylsilyloxy)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)pentyl]di-*tert*-butylmalonate (20)

According to GP 2, with **11** (100 mg, 0.27 mmol) and *tert*-butyldimethylpent-4-enyloxysilane (270 mg, 1.35 mmol) in *t*-BuOH (0.27 mL). FC (ether/pentane = 1:20) afforded **20** (85 mg, 55%). I.R. (film): 3447*w*, 2931*s*, 2858*s*, 2143*w*, 1729*s*, 1473*m*, 1368*m*, 1255*s*, 1138*s* cm⁻¹. ¹H-NMR (200 MHz, CDCl₃): 3.78–3.73 (*m*, 1 H, CH); 3.65–3.57 (*m*, 2 H, CH₂); 3.54 (*dxd*, *J*₁ = 8.7 Hz, *J*₂ = 6.4 Hz, 1 H, CH); 2.05–2.01 (*m*, 2 H, CH₂); 1.59–1.41 (*m*, 8 H, CH₂); 1.45 (*s*, 9 H, CH₃); 1.44 (*s*, 9 H, CH₃); 1.33–1.19 (*m*, 2 H, CH₂); 1.09 (*s*, 6 H, CH₃); 1.06 (*s*, 6 H, CH₃); 0.90 (*s*, 9 H, CH₃); 0.04 (*s*, 6 H, CH₃). ¹³C-NMR (50 MHz, CDCl₃): 169.3 (C), 169.0 (C), 81.2 (C), 81.0 (C), 78.8 (CH), 63.2 (CH₂), 60.0 (C), 59.2 (C), 50.9 (CH), 40.2 (2x CH₂), 34.1 (2x CH₃), 32.9 (CH₂), 29.3 (C), 29.1 (CH₂), 27.9 (CH₃), 26.0 (CH₃), 20.6 (2x CH₃), 18.3 (CH₂), 17.3 (CH₂), -5.3 (2x CH₃). MS (ESI): 572 (100, [M+H]⁺), 516 (77), 460 (84), 126 (67). HRMS (ESI) calcd for C₃₁H₆₂NO₆Si ([M+H]⁺): 572.4346. Found: 572.4318.

2-[2-(2,2,6,6-Tetramethylpiperidine-1-yloxy)cyclohexyl]dimethylmalonate (21)

According to GP 1, with **10** (100 mg, 0.348 mmol) and cyclohexene (143 mg, 1.74 mmol) in DCE (0.35 mL). FC (ether/pentane = 1:20) afforded *trans*-**21** (50 mg, 39%) and *cis*-**21** (24 mg, 19%). *trans*-**21**: I.R. (film): 3466*w*, 2932*s*, 2870*m*, 1737*s*, 1452*m*, 1435*m*, 1360*m*, 1241*m*, 1137*w* cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): 3.89 (*dxt*, *J*₁ = 10.9 Hz, *J*₂ = 4.1 Hz, 1 H, CH); 3.81 (*d*, *J* = 10.5 Hz, 1 H, CH); 3.73 (*s*, 3 H, CH₃); 3.72 (*s*, 3 H, CH₃); 2.98 (*dxd*, *J*₁ = 10.5 Hz, *J*₂ = 4.1 Hz, 1 H, CH₂); 2.11 (*dxd*, *J*₁ = 13.0 Hz, *J*₂ = 3.8 Hz, 1 H, CH₂); 1.78–1.75 (*m*, 1 H, CH₂); 1.64–0.91 (*m*, 24 H). ¹³C-NMR (100 MHz, CDCl₃): 169.7 (C), 169.0 (C), 82.4 (CH), 60.2 (C), 58.5 (C), 52.4 (CH₃), 52.3 (CH₃), 51.2 (CH), 40.5 (CH₂), 40.2 (CH₂), 38.6 (CH), 34.9 (CH₃), 34.2 (CH₃), 28.7 (CH₂), 27.5 (CH₂), 24.6 (CH₂), 21.2 (CH₂), 20.5 (CH₃), 20.3 (CH₃), 17.3 (CH₂). MS (ESI): 408 (61, [M+K]⁺), 392 (100, [M+Na]⁺), 370 (27, [M+H]⁺), 167 (17), 142 (18), 126 (51). HRMS (ESI) calcd for C₂₀H₃₆NO₅ ([M+H]⁺): 370.2593. Found: 370.2612. *cis*-**21**: I.R. (film): 3466*w*, 2932*s*, 2869*m*, 1738*s*, 1683*m*, 1434*m*, 1376*m*, 1235*m*, 1134*w* cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): 4.03 (*d*, *J* = 5.1 Hz, 1 H, CH); 3.73 (*s*, 3 H, CH₃); 3.72 (*s*, 3 H, CH₃); 3.73–3.67 (*m*, 1 H, CH); 2.64–2.43 (*m*, 1 H, CH); 2.20–2.12 (*m*, 1 H, CH₂); 1.74–1.61 (*m*, 3 H), 1.52–1.33 (*m*, 6 H), 1.31–1.13 (*m*, 4 H), 1.12–1.01 (*m*, 12 H). ¹³C-NMR (100 MHz, CDCl₃): 170.1 (C), 169.4 (C), 81.4 (CH), 60.6 (C), 58.6 (C), 52.1 (CH₃), 52.0 (CH₃), 51.8 (CH), 43.7 (CH), 40.7 (CH₂), 40.1 (CH₂), 34.3 (CH₃), 33.9 (CH₃), 31.3 (CH₂), 27.5 (CH₂), 25.9 (CH₂), 24.6 (CH₂), 20.7 (CH₃), 20.2 (CH₃), 17.3 (CH₂). MS (ESI): 408 (39, [M+K]⁺), 392 (67, [M+Na]⁺), 370 (100, [M+H]⁺), 167 (17), 142 (18), 126 (83).

HRMS (ESI) calcd for $C_{20}H_{36}NO_5$ ($[M+H]^+$): 370.2593. Found: 370.2580.

3-(2,2-Bismethoxycarbonyl-ethyl)-4-(2,2,6,6-tetramethylpiperidin-1-yloxymethyl)-cyclopentane-1,1-dicarboxylic acid dimethyl ester (26)

According to GP 3 with **10** (100 mg, 0.35 mmol) and **22** (221 mg, 1.04 mmol) in DCE (0.09 mL) and purification by FC (SiO_2 , pentane/*t*-butylmethylether = 4:1) afforded **26** (107 mg, 68%) as *cis:trans* mixture of diastereoisomers. I.R. (film): 3469w, 2954s, 1735s, 1643w, 1436s, 1260s cm^{-1} . 1H -NMR (300 MHz, $CDCl_3$): *both diastereomeres*: 3.76-3.35 (*m*, 1 H); 3.67; 3.66; 3.65; 3.64 (*s*, 12 H, CH_3O); 3.53 (*dd*, $J_1 = 7.3$ Hz, $J_2 = 9.3$, 1 H, H_2CON); 3.43 (*dd*, $J_1 = 7.0$ Hz, $J_2 = 8.3$, 1 H, H_2CON); 2.49-1.67 (*m*, 8 H); 1.51-0.99 (*m*, 18 H, TEMPO). ^{13}C -NMR (75 MHz, $CDCl_3$): *both diastereomeres*: 173.0, 172.7, 169.8, 169.6, 59.8, 52.7, 52.5, 50.5, 44.8, 40.8, 39.7, 39.0, 38.5, 33.2, 33.0, 29.2, 20.1, 17.1; EI-MS: 484 (4) $[M^+ - Me]$, 343 (12) $[M^+ - TEMPO]$, 311 (29), 278 (100), 139 (80). EI-HRMS: calcd for $C_{24}H_{38}NO_9$ ($[M^+ - Me]$): 484.2547. Found: 484.2551.

3-(2,2-Bis-*tert*-butoxycarbonyl-ethyl)-4-(2,2,6,6-tetramethyl-piperidin-1-yloxymethyl)-cyclopentane-1,1-dicarboxylic acid dimethyl ester (27)

According to GP 3 with **11** (100 mg, 0.27 mmol) and **22** (171 mg, 0.81 mmol) in *t*-BuOH and purification by FC (SiO_2 , pentane/*t*-butylmethylether = 20:1, *t*-butylmethylether) afforded **27** (63 mg, 40 %) as a 2.2:1 *cis:trans* mixture of diastereoisomers and the corresponding telomer **27** (*n* = 2) (22 mg, 10%). I. R. (film): 2976s, 2933s, 1735s, 1456w, 1436w, 1393w, 1369m, 1256s, 1164s, 1138s, 1036w, 994w, 956w, 849w cm^{-1} . 1H -NMR (300 MHz, $CDCl_3$): *both diastereoisomers*: 3.68-3.18 (*m*, 3 H); 3.61 (*s*, 12 H, CH_3O); 2.44-0.78 (*m*, 14 H); 1.35 (*s*, 18 H, $C(CH_3)_3$); 1.04 (*s*, 6H, $CH_3(TEMPO)$); 0.98 (*s*, 6H, $CH_3(TEMPO)$). ^{13}C -NMR (75 MHz, $CDCl_3$): *both diastereoisomers*: 173.0, 172.9, 172.8, 168.91, 168.86, 168.6, 81.3, 81.2, 76.6, 59.82, 59.77, 52.8, 45.1, 40.6, 40.2, 40.0, 39.8, 38.9, 38.8, 37.7, 37.1, 33.2, 33.1, 29.0, 28.1, 27.9, 20.2, 17.1. MS (ESI): 584 (100, $[M+H]^+$), HRMS (ESI): calcd for $C_{31}H_{54}NO_9$ ($[M+H]^+$): 584.3799. Found: 584.3783; corresponding telomer **30** (*n*=2): MS (ESI): 833 (14, $[M+K]^+$), 818 (17, $[M+Na]^+$), 796 (100, $[M+H]^+$). HRMS (ESI): calcd for $C_{42}H_{70}NO_{13}$ ($[M+H]^+$): 796.4847. Found: 796.4820.

2-[4-(2,2,6,6-Tetramethyl-piperidin-1-yloxymethyl)-tetrahydro-furan-3-ylmethyl]dimethylmalonate (28)

According to GP 3 with **10** (154 mg, 0.54 mmol) and **23** (636 mg, 3.23 mmol) in DCE (0.18 mL) and purification by FC (SiO₂, pentane/*t*-butylmethylether = 7:1, pentane/*t*-butylmethylether = 4:1) afforded **28** (69 mg, 33%) as a 1.8:1 *cis:trans* mixture of diastereoisomers. I.R. (film): 3472_w, 2932_s, 1738_s, 1437_m, 1244_m, 1154_m, 1048_w, 771_m cm⁻¹. ¹H-NMR (300 MHz, CDCl₃): *both diastereoisomers*: 3.96 - 3.56 (*m*, 5 H, CH₂ON, CH(CO₂Me)₂, CH₂O); 3.73 (*s*, 6 H, OCH₃); 3.45 - 3.36 (*m*, 2 H, CH₂O); 2.54-1.86 (*br m*, 4 H, CH, CH₂); 1.62 - 1.08 (*m*, 18 H, TEMPO). ¹³C-NMR (75 MHz, CDCl₃): *both diastereoisomers*: 169.9, 169.8, 75.3, 73.5, 72.0, 71.6, 71.2, 60.2, 52.9, 51.1, 50.9, 45.2, 41.3, 40.9, 40.1, 40.0, 39.6, 33.5, 32.9, 28.3, 27.4, 20.4, 17.4. MS (ESI): 408 (100, [M+Na]⁺), 386 (35, [M+H]⁺), 126 (75). HRMS (ESI): calcd for C₂₀H₃₅NNaO₆ ([M+Na]⁺): 408.2362. Found: 408.2365.

2-[4-(2,2,6,6-Tetramethyl-piperidin-1-yloxymethyl)-tetrahydro-furan-3-ylmethyl]di-*tert*-butylmalonate (29)

According to GP 3 with **11** (100 mg, 0.27 mmol) and **23** (159 mg, 0.81 mmol) in *t*-BuOH and purification by FC (SiO₂, pentane/*t*-butylmethylether = 15:1, pentane/*t*-butylmethylether = 5:1, *t*-butylmethylether) afforded **29** (47 mg, 37%) as a 1.7:1 *cis:trans* mixture of diastereoisomers and the corresponding telomer **29** (n=2) (18 mg, 12%). I.R. (film): 2977_s, 2932_s, 2872_s, 1729_s, 1471_w, 1456_w, 1392_w, 1369_m, 1256_m, 1141_s, 1058_w, 994_w, 957_w, 925_w, 847_w. ¹H-NMR (200 MHz, CDCl₃): *both diastereoisomers*: 3.90-3.08 (*m*, 7 H); 2.44-0.88 (*m*, 10 H); 1.39 (*s*, 18 H, C(CH₃)₃); 1.09 (*s*, 6 H, CH₃ (TEMPO)); 1.02 (*s*, 6 H, CH₃ (TEMPO)). ¹³C-NMR (75 MHz, CDCl₃): *both diastereoisomers*: 168.6, 168.5, 168.4, 81.5, 77.9, 74.9, 73.1, 71.8, 71.3, 71.0, 59.8, 53.0, 52.8, 45.0, 40.9, 40.5, 39.65, 39.61, 39.1, 33.1, 32.0, 28.0, 27.9, 27.7, 26.6, 20.1, 17.0. MS (ESI): 492 (95, [M+Na]⁺), 470 (100, [M+H]⁺), HRMS (ESI): calcd for C₂₆H₄₈NO₆ ([M+H]⁺): 469.3403. Found: 469.3403; corresponding telomer **29** (n=2): MS (ESI): 568 (100, [M+H]⁺), HRMS (ESI): calcd for C₃₂H₅₈NO₇ ([M+H]⁺): 568.4213. Found: 568.4228.

2-[4-(2,2,6,6-Tetramethyl-piperidin-1-yloxymethyl)-1-(toluene-4-sulfonyl)-pyrrolidin-3-ylmethyl]dimethylmalonate (30)

According to GP 3 with **10** (68 mg, 0.24 mmol) and **24** (371 mg, 0.71 mmol) in DCE (0.08 mL) and purification by FC (SiO₂, pentane/*t*-butylmethylether = 2:1) afforded **30** (63 mg,

49%) as a 1.3:1 *cis:trans* mixture of diastereoisomers. I.R. (film): 3465*w*, 2930*s*, 1736*s*, 1598*w*, 1437*m*, 1346*m*, 1163*s*, 816*m*, 665*m* cm. ¹H-NMR (300 MHz): both diastereoisomers: 7.72-7.69 (*m*, 2 H, aryl-H); 7.33-7.30 (*m*, 2 H, aryl-H); 3.72, 3.71 (2 *s*, 6 H, CH₃O); 3.83-3.59 (*m*, 2 H, CH₂ON); 3.51-2.88 (*m*, 8 H, CH₂, CH); 2.43 (*s*, 3 H, PhCH₃); 1.80-1.00 (*br m*, 18 H, TEMPO). ¹³C-NMR (75 MHz): both diastereoisomers: 128.9, 126.8, 126.6, 73.7, 51.8, 50.2, 49.6, 39.4, 38.8, 37.5, 32.2, 28.9, 27.0, 26.5, 20.7, 19.2, 16.2. MS (ESI): 561 (100, [M+Na⁺], 539 (25, [M+H]⁺). HRMS (ESI) calcd for C₂₇H₄₂N₂NaO₇S ([M+Na⁺]): 561.2610. Found: 561.2608.

2-[4-(2,2,6,6-Tetramethylpiperidin-1-yloxymethyl)-1-(toluene-4-sulfonyl)-pyrrolidin-3-ylmethyl]di-*tert*-butylmalonate (31)

According to GP 3 with **11** (100 mg, 0.27 mmol) and **24** (406 mg, 0.81 mmol) in *t*-BuOH and purification by FC (SiO₂, pentane/*t*-butylmethylether = 4:1, *t*-butylmethylether) afforded **31** (70 mg, 42%) as a 1.5:1 *cis:trans* mixture of diastereoisomers and the corresponding telomer **31** (n=2) (55 mg, 23%). I.R. (film): 3448*w*, 2976*s*, 2932*s*, 1727*s*, 1598*m*, 1472*s*, 1455*s*, 1393*s*, 1347*s*, 1256*s*, 1094*s*, 1043*s*, 848*m*, 816*s*, 706*m*, 664*s*, 588*s*, 549*s*. ¹H-NMR (300 MHz, CDCl₃): *both diastereomeres*: 7.63 (*d*, *J* = 12.4 Hz, 2H, H (aromat)); 7.24 (*d*, *J* = 12.4 Hz, 2 H, H (aromat)); 3.75-2.80 (*m*, 7H); 2.36; 2.34 (2 *s*, 3 H, CH₃ (tol)); 2.09-0.62 (*m*, 10 H); 1.38; 1.36; 1.353; 1.347 (4 *s*, 18 H, C(CH₃)₃); 0.99; 0.97; 0.94 (3 *br s*, 12 H, 4 CH₃ (TEMPO)). ¹³C-NMR (75 MHz, CDCl₃): *both diastereomeres*: 168.6, 168.3, 143.7, 143.5, 134.6, 134.0, 133.3, 129.9, 127.7, 127.4, 81.9, 77.7, 74.9, 60.0, 53.2, 52.8, 51.6, 50.9, 49.6, 44.1, 40.5, 39.3, 38.8, 34.3, 33.3, 31.8, 28.3, 28.1, 27.3, 27.2, 23.7, 21.7, 20.4, 17.3; MS (ESI): 623 (100, [M+H]⁺), 523 (80). HRMS (ESI): calcd for C₃₃H₅₅N₂O₇S ([M+H]⁺): 623.3730. found: 623.3724; corresponding telomer **31** (n = 2): MS (ESI): 896 (17, [M+Na]⁺), 874 (100, [M+H]⁺). HRMS (ESI): calcd for C₄₆H₇₂N₃O₉S₂ ([M+H]⁺): 874.4710. Found: 874.4727.

2-[8,8-Dimethyl-3-(2,2,6,6-tetramethyl-piperidin-1-yloxymethyl)-7,9-dioxa-spiro [4.5] dec-2-ylmethyl]dimethylmalonate (32)

According to GP 3 with **10** (77 mg, 0.27 mmol) and **25** (158 mg, 0.81 mmol) in dichloroethane (0.08 mL) and purification by FC (SiO₂, pentane/*t*-butylmethylether = 4:1) afforded **32** (45 mg, 36%) as a 2.3:1 *cis:trans* mixture of diastereoisomers. I. R. (film): 2934*s*, 2866*s*, 1737*s*, 1437*s*, 1372*s*, 1261*s*, 1199*s*, 1154*s*, 1080*m*, 1030*m*, 931*w*, 831*m*, 804*w*, 733*m*, 520*w* cm⁻¹. ¹H-NMR (200 MHz, CDCl₃): *both diastereomeres*: 3.79 -3.50 (*m*, 7 H); 3.70;

3.692; 3.687; 3.682 (4 s, 6H, OCH₃); 2.26-0.77 (m, 14 H); 1.40; 1.37; 1.36; 1.35 (4 s, 6 H, CH₃-C-O); 1.10; 1.05; 1.02 (3 bs, 12 H, CH₃ (TEMPO)). ¹³C-NMR (75 MHz, CDCl₃): *both diastereomeres*: 170.0, 169.7, 97.7, 97.6, 78.8, 77.4, 71.0, 70.0, 69.5, 69.2, 59.8, 59.7, 52.4, 52.3, 50.8, 50.7, 44.5, 40.9, 40.5, 40.4, 40.2, 39.72, 39.69, 38.6, 38.4, 37.0, 36.1, 34.1, 33.2, 33.1, 30.0, 25.3, 24.5, 23.1, 22.2, 20.2, 17.1. MS (ESI): 506 (74, [M+Na⁺], 484 (100, [M+H⁺])). HRMS (ESI): calcd for C₂₆H₄₆NO₇ ([M+H⁺]): 484.327. Found: 484.329.

2-[8,8-Dimethyl-3-(2,2,6,6-tetramethyl-piperidin-1-yloxymethyl)-7,9-dioxa-spiro[4.5]dec-2-ylmethyl]di-*tert*-butylmalonate (33)

According to GP 3 with **11** (100 mg, 0.27 mmol) and **25** (158 mg, 0.81 mmol) in *t*-BuOH and purification by FC (SiO₂, pentane/*t*-butylmethylether = 10:1, pentane/*t*-butylmethyl-ether = 5:1, pentane/*t*-butylmethylether = 3:1) afforded **33** (52 mg, 34%) as a 2.1:1 *cis:trans* mixture of diastereoisomers and the corresponding telomer **33** (n = 2) (24 mg, 12%). I.R. (film): 2977s, 2933s, 2868m, 1728s, 1454m, 1369s, 1256m, 1199m, 1156s, 1081w, 1032w, 919w, 848w, 832w, 734m cm⁻¹; ¹H-NMR (200 MHz, CDCl₃): *both diastereomeres*: 3.78-2.75 (m, 7 H); 2.24-0.79 (m, 14 H); 1.43; 1.404; 1.402; 1.394; 1.387; 1.38; 1.36; 1.34 (8 s, 24 H, CH₃-C_q-O, C(CH₃)₃); 1.02; 1.03; 1.05 (3 br s, 12 H, CH₃ (TEMPO)). ¹³C-NMR (75 MHz, CDCl₃): *both diastereomeres*: 168.7, 168.6, 168.5, 97.25, 97.20, 80.8, 80.7, 79.5, 78.9, 78.8, 76.6, 76.2, 70.9, 70.8, 70.7, 69.8, 69.3, 69.2, 68.9, 59.4, 52.6, 52.5, 44.3, 43.7, 40.9, 40.6, 40.22, 40.16, 40.1, 40.0, 39.9, 39.6, 39.5, 38.3, 38.2, 37.2, 36.77, 35.9, 34.7, 34.5, 34.1, 33.2, 32.8, 32.7, 29.7, 29.3, 29.0, 27.7, 27.6, 27.42, 27.38, 25.8, 24.9, 24.5, 24.4, 22.6, 22.4, 22.0, 20.0, 16.7, 15.4. MS (ESI): 568 (100, [M+H⁺]), 468 (56). HRMS (ESI): calcd for C₃₂H₅₇NO₇ ([M+H⁺]): 568.4213. Found: 468.4233; corresponding telomer **33** (n=2): MS (ESI): 786 (16, [M+Na⁺]), 764 (24, [M+H⁺])). HRMS (ESI): calcd for C₄₄H₇₈NO₉ ([M+H⁺]): 764.5677. Found: 764.5656.

2-(2-Methylennonyl)dimethylmalonate (34)

According to GP 1, with **10** (100 mg, 0.348 mmol) and 2-methyl-1-nonene (244 mg, 1.74 mmol) in DCE (0.35 mL). FC (ether/pentane = 1:20) afforded **34** (35 mg, 37%). I.R. (film): 3468w, 3319w, 3267w, 2928m, 2856m, 1739s, 1647w, 1436m, 1222s, 1149s cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): *exo*-methylene: 4.75 (d, *J* = 21.4 Hz, 2 H, CH₂); 3.72 (s, 6 H, CH₃); 3.61 (t, *J* = 7.9 Hz, 1 H, CH); 2.62 (d, *J* = 7.9 Hz, 2 H, CH₂); 2.00 (t, *J* = 7.3 Hz, 2 H, CH₂); 1.46–1.38 (m, 2 H, CH₂); 1.34–1.19 (m, 8 H, CH₂); 0.87 (t, *J* = 6.3 Hz, 3 H, CH₃); β,γ-unsaturated (mixture of *E*- and *Z*-isomer): 5.44 (d, *J* = 9.4 Hz, 1 H, CH); 4.29 (d, *J* = 9.6 Hz, 1 H, CH,

minor isomer); 4.27 (*d*, $J = 9.4$ Hz, 1 H, CH, major isomer); 3.71 (*s*, 6 H, CH₃); 2.04 (*t*, $J = 7.5$ Hz, 2 H, CH₂); 1.61 (*s*, 3 H, CH₃, minor isomer); 1.60 (*s*, 3 H, CH₃, major isomer); 1.46–1.38 (*m*, 2 H, CH₂); 1.34–1.19 (*m*, 8 H, CH₂); 0.87 (*t*, $J = 6.3$ Hz, 3 H, CH₃); γ,δ -unsaturated (mixture of E- and Z-isomer): 5.19 (*t*, $J = 7.9$ Hz, 1 H, CH); 3.70 (*s*, 6 H, CH₃); 3.54 (*t*, $J = 5.4$ Hz, 1 H, CH, major isomer); 3.53 (*t*, $J = 7.9$ Hz, 1 H, CH, minor isomer); 2.65 (*d*, $J = 7.9$ Hz, 1 H, CH₂, minor isomer); 2.57 (*d*, $J = 7.9$ Hz, 1 H, CH₂, major isomer); 1.93 (*q*, $J = 6.8$ Hz, 2 H, CH₂); 1.76 (*s*, 3 H, CH₃, minor isomer); 1.67 (*s*, 3 H, CH₃, major isomer); 1.46–1.38 (*m*, 2 H, CH₂); 1.34–1.19 (*m*, 6 H, CH₂); 0.87 (*t*, $J = 6.3$ Hz, 3 H, CH₃). ¹³C-NMR (100 MHz, CDCl₃): *exo*-methylene: 169.5 (C), 145.8 (C), 110.9 (CH₂), 52.6 (CH₃), 52.4 (CH₃), 50.4 (CH), 35.9 (CH₂), 34.8 (CH₂), 31.8 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 27.6 (CH₂), 22.6 (CH₂), 14.1 (CH₃). MS (ESI): 309 (14, [M+K]⁺), 293 (100, [M+Na]⁺), 271 (8, [M+H]⁺), 207 (14), 158 (15), 126 (32). HRMS (ESI) calcd for C₁₅H₂₆O₄Na ([M+Na]⁺): 293.1729. Found: 293.1722.

2-(2-Methylennonyl)di-*tert*-butylmalonate (35)

According to GP 2, with **11** (100 mg, 0.27 mmol) and 2-methyl-1-nonene (189 mg, 1.35 mmol) in *t*-BuOH (0.27 mL). FC (ether/pentane = 1:50) afforded **35** (53 mg, 56%). I.R. (film): 3442*m*, 3931*s*, 2873*m*, 1731*s*, 1458*m*, 1369*m*, 1256*w*, 1140*m*, cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): *exo*-methylene: 4.75 (*d*, $J = 9.0$ Hz, 2 H, CH₂); 3.36 (*t*, $J = 7.7$ Hz, 1 H, CH); 2.51 (*d*, $J = 7.7$ Hz, 2 H, CH₂); 2.01 (*t*, $J = 8.0$ Hz, 2 H, CH₂); 1.51–1.37 (*m*, 2 H, CH₂); 1.44 (*s*, 18 H, CH₃); 1.33–1.21 (*m*, 8 H, CH₂); 0.88–0.85 (*m*, 3 H, CH₃); β,γ -unsaturated (mixture of E- and Z-isomer): 5.41 (*dxd*, $J_1 = 9.2$ Hz, $J_2 = 1.3$ Hz, 1 H, CH); 4.04 (*d*, $J = 9.6$ Hz, 1 H, CH, minor isomer); 4.02 (*d*, $J = 9.2$ Hz, 1 H, CH, major isomer); 2.04 (*t*, $J = 6.8$ Hz, 2 H, CH₂); 1.65 (*d*, $J = 1.0$ Hz, 3 H, CH₃, major isomer); 1.60 (*d*, $J = 0.6$ Hz, 3 H, CH₃, minor isomer); 1.51–1.37 (*m*, 2 H, CH₂); 1.45 (*s*, 18 H, CH₃); 1.33–1.21 (*m*, 8 H, CH₂); 0.88–0.85 (*m*, 3 H, CH₃); γ,δ -unsaturated (mixture of E- and Z-isomer): 5.19 (*dxd*, $J_1 = 6.4$ Hz, $J_2 = 5.8$ Hz, 1 H, CH); 3.33 (*t*, $J = 7.7$ Hz, 1 H, CH, major isomer); 3.31 (*t*, $J = 7.7$ Hz, 1 H, CH, minor isomer); 2.55 (*d*, $J = 7.9$ Hz, 2 H, CH₂, minor isomer); 2.47 (*d*, $J = 7.9$ Hz, 2 H, CH₂, major isomer); 1.94 (*q*, $J = 6.4$ Hz, 2 H, CH₂); 1.75 (*d*, $J = 1.3$ Hz, 3 H, CH₃, major isomer); 1.68 (*d*, $J = 0.8$ Hz, 3 H, CH₃, minor isomer); 1.51–1.37 (*m*, 2 H, CH₂); 1.43 (*s*, 18 H, CH₃); 1.33–1.21 (*m*, 6 H, CH₂); 0.88–0.85 (*m*, 6 H, CH₃). ¹³C-NMR (100 MHz, CDCl₃): *exo*-methylene: 168.6 (C), 168.5 (C), 146.2 (C), 110.6 (CH₂), 81.3 (C), 81.1 (C), 52.4 (CH), 35.9 (CH₂), 34.7 (CH₂), 31.8 (CH₂), 29.6 (CH₂), 29.2 (CH₂), 27.9 (CH₃), 27.6 (CH₂), 22.6 (CH₂), 14.1 (CH₃). MS (ESI): 393 (16, [M+K]⁺), 377 (100, [M+Na]⁺), 321 (43), 265 (28), 243 (45), 126 (22). HRMS

(ESI) calcd for $C_{21}H_{38}NaO_4$ ($[M+Na]^+$): 377.2668. Found: 377.2663.

3-(2,2-Bis-methoxycarbonyl-ethyl)-4-isopropenyl-cyclopentane-1,1-dicarboxylic acid dimethyl ester (37)

A solution of **10** (100 mg, 0.35 mmol) and **36** (504 mg, 2.10 mmol) in DCE (0.16 mL) was heated for 72 h at 135°C (sealed tube). Removal of the solvent and purification by FC (SiO₂, pentane/*t*-butylmethylether = 4:1) provided **37** (55 mg, 42%) as a 2.4:1 *cis:trans* mixture of diastereoisomers. I.R. (film): 3470_w, 2955_s, 1735_s, 1647_w, 1436_s, 1375_w, 1257_s, 1198_s, 1153_s, 1058_m, 915_w, 734_w. ¹H-NMR (200 MHz, CDCl₃): *both diastereomeres*: 3.85-3.36 (*m*, 2 H); 3.72; 3.70; 3.694; 3.688; 3.67 (*s*, 12 H, OCH₃), 3.43-3.36 (*m*, 1 H, CH-COOMe); 2.61-0.83 (*m*, 6 H); 1.70 (*s*, 3 H, CH₃-C_{sp2}). ¹³C-NMR (75 MHz, CDCl₃): *both diastereomeres*: 172.9, 172.7, 172.3, 169.8, 169.6, 169.5, 144.0, 143.4, 112.8, 111.7, 58.3, 58.0, 55.1, 53.5, 52.8, 52.7, 52.5, 52.4, 52.2, 51.3, 50.4, 49.8, 49.3, 44.6, 44.3, 39.9, 39.6, 39.4, 39.3, 37.85, 37.77, 35.6, 35.4, 33.2, 33.0, 32.6, 31.0, 29.2, 28.3, 26.1, 22.9, 20.2, 20.1, 18.6, 17.0, 15.1. MS (EI): 371 (34 $[M+H]^+$), 339 (70), 307 (86), 278 (85), 238 (100), 178 (85). HRMS (EI): calcd for C₁₈H₂₆O₈ ($[M+H]^+$): 371.1706. found: 371.1696.

2-(4-Isopropenylcyclohex-1-enylmethyl)dimethylmalonate (38)

According to GP 1, with **10** (100 mg, 0.348 mmol) and (1S)-(-)-(β)-pinene (237 mg, 1.74 mmol) in DCE (0.35 mL). FC (ether/pentane = 1:20 to 1:10) afforded **38** (51 mg, 55%). I.R. (film): 3462_w, 3081_w, 2953_s, 2921_s, 2840_m, 1739_s, 1644_m, 1436_s, 1346_m, 1234_s, 1153_m cm⁻¹. ¹H-NMR (200 MHz, CDCl₃): 5.46 (*s br*, 1 H, CH); 4.69-4.67 (*m*, 2 H, CH₂); 3.72 (*s*, 6 H, CH₃); 3.57 (*t*, *J* = 7.8 Hz, 1 H, CH); 2.55 (*d*, *J* = 7.8 Hz, 2 H, CH₂); 2.11-1.77 (*m*, 5 H); 1.71 (*s*, 3 H, CH₃); 1.53-1.07 (*m*, 2 H). ¹³C-NMR (50 MHz, CDCl₃): 169.6 (2x C), 149.7 (C), 133.3 (C), 123.3 (CH), 108.6 (CH₂), 52.4 (CH), 50.4 (2x CH₃), 40.7 (CH), 36.5 (CH₂), 30.6 (CH₂), 28.3 (CH₂), 27.6 (CH₂), 20.7 (CH₃). MS (ESI): 289 (100, $[M+Na]^+$), 235 (9), 135 (27). HRMS (ESI) calcd for C₁₅H₂₂NaO₄ ($[M+Na]^+$): 289.1416. Found: 289.1404.

2-(4-Isopropenylcyclohex-1-enylmethyl)di-*tert*-butylmalonate (39)

According to GP 2, with **11** (50 mg, 0.13 mmol) and (1S)-(-)-(β)-pinene (91 mg, 0.67 mmol) in *t*-BuOH (0.13 mL). FC (ether/pentane = 1:50) afforded **39** (34 mg, 75%). I.R. (film): 3476_w, 2978_s, 2931_s, 2838_m, 1730_s, 1644_w, 1456_m, 1249_s, 1136_s cm⁻¹. ¹H-NMR (300 MHz, CDCl₃): 5.46 (*m*, 1 H, CH); 4.69-4.67 (*m*, 2 H, CH₂); 3.33 (*t*, *J* = 7.3 Hz, 1 H, CH); 2.44 (*d*, *J* = 7.3 Hz, 2 H, CH₂); 2.14-1.62 (*m*, 5 H); 1.71 (*s*, 3 H, CH₃); 1.43 (*s*, 18 H, CH₃); 1.25-0.78

(*m*, 2 H). ^{13}C -NMR (75 MHz, CDCl_3): 168.7 (2x C), 149.9 (C), 133.8 (C), 123.0 (CH), 108.5 (CH₂), 81.2 (3x CH₃), 52.4 (CH), 41.0 (CH), 36.5 (CH₂), 30.7 (CH₂), 28.4 (CH₂), 27.9 (CH₂), 20.8 (CH₃). MS (ESI): 373 (100, $[\text{M}+\text{Na}]^+$), 317 (22), 261 (19), 158 (37). HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{34}\text{NaO}_4$ ($[\text{M}+\text{Na}]^+$): 373.2355. Found: 373.2338.

2-Hexyl-2-oxotetrahydrofuran-3-carboxylic acid methylester (40)

To the alkoxyamine **12** (150 mg, 0.375 mmol) dissolved in THF (1.2 mL) was added activated Zn dust (294 mg, 4.50 mmol), water (1.2 mL) and conc. acetic acid (3.7 mL). The mixture was heated to 85 °C for 6 h. After cooling to 0 °C, the reaction mixture was treated with 1 N NaOH, then extracted with ether. Drying over MgSO_4 and removal of the solvents provided the crude product which was purified by FC (SiO_2 , ether/pentane = 1:3) to afford the product **40** (62 mg, 73%, dr = 1:1) as a colorless oil. I.R. (film): 3468_w, 2932_s, 2859_m, 1780_s, 1742_s, 1456_w, 1437_w, 1355_m, 1263_m, 1165_m cm^{-1} . ^1H -NMR (400 MHz, CDCl_3): Isomer A: 4.63 (*d*×*q*, $J_1 = 7.2$ Hz, $J_2 = 5.6$ Hz, 1 H, CH); 3.76 (*s*, 3 H, CH₃); 3.58 (*d*×*d*, $J_1 = 9.6$ Hz, $J_2 = 4.9$ Hz, 1 H, CH); 2.70–2.64 (*m*, 1 H, CH₂); 2.11–2.03 (*m*, 1 H, CH₂); 1.83–1.53 (*m*, 2 H, CH₂); 1.48–1.19 (*m*, 8 H, CH₂); 0.85 (*t*, $J = 6.5$ Hz, 3 H, CH₃). Isomer B: 4.45–4.38 (*m*, 1 H, CH); 3.78 (*s*, 3 H, CH₃); 3.61 (*d*×*d*, $J_1 = 11.4$ Hz, $J_2 = 9.4$ Hz, 1 H, CH); 2.56–2.49 (*m*, 1 H, CH₂); 2.33–2.24 (*m*, 1 H, CH₂); 1.83–1.53 (*m*, 2 H, CH₂); 1.48–1.19 (*m*, 8 H, CH₂); 0.85 (*t*, $J = 6.5$ Hz, 3 H, CH₃). ^{13}C -NMR (50 MHz, CDCl_3): Isomer A: 171.6 (C), 168.2 (C), 80.3 (CH), 53.0 (CH₃), 46.7 (CH₂), 35.4 (CH₂), 31.9 (CH₂), 31.5 (CH₂), 28.8 (CH₂), 25.1 (CH₂), 22.4 (CH₂), 13.9 (CH₃). Isomer B: 171.7 (C), 168.3 (C), 79.6 (CH), 52.0 (CH₃), 47.2 (CH₂), 35.2 (CH₂), 32.1 (CH₂), 31.5 (CH₂), 28.8 (CH₂), 25.1 (CH₂), 22.4 (CH₂), 13.9 (CH₃). MS (EI): 228 (5.5, $[\text{M}]^+$), 159 (19), 143 (100), 111 (94), 87 (54). HRMS (EI) calcd for $\text{C}_{12}\text{H}_{20}\text{O}_4$ ($[\text{M}]^+$): 228.1362. Found: 228.1359.