Chemo-, Regio- and *E*/*Z*-Diastereoselective Synthesis of 2-Alkylidenetetrahydrofurans by Sequential Reactions of Ambident Dianions and Monoanions

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Supplementary Material

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General. All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For the ^{1}H and ^{13}C NMR spectra (^{1}H NMR: 200, 300 MHz, ^{13}C NMR: 50, 75 MHz) the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained using the electron ionization (70 eV), the chemical ionization (CI, H_2O) or the electrospray ionization technique (ESI). For preparative scale chromatography silica gel (60-200 mesh) was used. Melting points are uncorrected

Representative Experimental Procedure for the Alkylation of 1,3-Dicarbonyl Dianions: LDA was prepared by addition of *n*BuLi (25.10 mL, 40.00 mmol, 15% in *n*-hexane) to a solution of diisopropylamine (5.60 mL, 40.00 mmol) in THF (100 mL). To this solution was added *tert*-butylacetoacetate (3.30 mL, 20.00 mmol) at 0 °C. The deep yellow clear solution was stirred at 0 °C for 1 h. To this solution was added 1-iodo-3-methylbutane (4.492 g, 22.00 mmol) at –78 °C. The temperature was allowed to rise to ambient during 14 h and the solution was stirred at room temperature for 2 h. To the solution was added hydrochloric acid (200 mL, 10%) and the mixture was extracted with diethylether (4 x 250 mL). The organic layers were dried over Na_2SO_4, filtered and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) to give **2g** (4.495 g, 98%) as a yellow oil.

2a: Starting with *tert*-butylacetoacetate (8.20 mL, 50.00 mmol), diisopropylamine (17.60 mL, 125.00 mmol), *n*BuLi (78.50 mL, 125.00 mmol, 15% in *n*-hexane), and 1-iodopropane (9.35 g, 55.00 mmol) in THF (250 mL), **2a** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 20:1) as a yellow oil (9.003 g, 90%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.91 (t, J = 7.2 Hz, 3 H), 1.33 (sextet, J = 5.6 Hz, 2 H), 1.47 (s, 9 H), 1.58 (quint, J = 7.4 Hz, 2 H), 2.53 (t, J = 7.4 Hz, 2 H), 3.34 (s, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 13.4, 21.7, 25.1, 27.5, 42.1, 50.1, 81.1, 166.1, 202.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2964 (s), 2935 (s), 2873

(m), 1740 (s), 1715 (s), 1642 (m), 1460 (m), 1413 (m), 1369 (m), 1319 (s), 1255 (s), 1150 (s), 1075 (w), 955 (w), 842 (w). MS (EI, 70 eV): *m/z* (%) = 200 (M^+, 2), 144 (100), 127 (95). The exact molecular mass *m/z* = 200.1412 ± 2 mD [M^+] for $C_{11}H_{20}O_3$ was confirmed by HRMS (EI, 70 eV).

2b: Starting with *tert*-butylacetoacetate (1.64 mL, 10.00 mmol), diisopropylamine (3.52 mL, 25.00 mmol), *n*BuLi (15.70 mL, 25.00 mmol, 15% in *n*-hexane), and 1-iodohexane (1.62 mL, 11.00 mmol) in THF (150 mL), **2b** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 20:1) as a yellow oil (1.726 g, 71%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.27 (m, 6 H), 1.45 (m, 2 H), 1.47 (s, 9 H), 1.59 (m, 2 H), 2.52 (t, *J* = 4.4 Hz, 2 H), 3.33 (s, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.0, 22.5, 23.4, 27.9, 28.9, 29.0, 31.6, 42.8, 50.6, 81.7, 166.5, 203.4. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2958 (s), 2930 (s), 2872 (m), 2858 (s), 1741 (s), 1737 (s), 1718 (s), 1644 (w), 1458 (m), 1411 (w), 1394 (w), 1369 (s), 1318 (m), 1252 (s), 1150 (s). MS (EI, 70 eV): *m/z* (%) = 242 (M^+, 3), 186 (100), 169 (98). Anal. calcd. for $C_{14}H_{26}O_3$ (242.358): C 69.38, H 10.81; found: C 69.00, H 10.82.

2c: Starting with *tert*-butylacetoacetate (1.63 mL, 10.00 mmol), diisopropylamine (2.81 mL, 20 mmol), *n*BuLi (12.60 mL, 20.00 mmol, 15% in *n*-hexane), and 1-iodoheptane (1.80 mL, 11.00 mmol) in THF (100 mL), **2c** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 20:1) as a yellow oil (1.968 g, 77%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.75-0.88 (t, *J* = 7.2 Hz, 3 H), 1.10-1.30 (m, 10 H), 1.40 (s, 9 H), 1.45-1.60 (m, 2 H), 2.45 (t, *J* = 5.0 Hz, 2 H), 3.25 (s, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.0, 22.6, 23.4, 27.9, 29.0, 29.1, 29.3, 31.7, 42.9, 50.6, 81.8, 166.5, 203.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2957 (m), 2929 (s), 2872 (w), 2857 (m), 1739 (s), 1717 (s), 1644 (w), 1458 (w), 1412 (w), 1394 (w), 1369 (m), 1318 (w), 1252 (m), 1149 (s). MS (EI, 70 eV): *m/z* (%) = 256 (M^+, 9), 200 (100),

183 (36). The exact molecular mass *m/z* = 256.2038 ± 2 mD [M^+] for $C_{15}H_{28}O_3$ was confirmed by HRMS (EI, 70 eV).

2d: Starting with *tert*-butylacetoacetate (1.63 mL, 10 mmol), diisopropylamine (2.81 mL, 20 mmol), *n*BuLi (12.60 mL, 20.00 mmol, 15% in *n*-hexane), and 1-iodooctane (2.00 mL, 11.00 mmol) in THF (100 mL), **2d** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 20:1) as a yellow oil (2.348 g, 87%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.88 (t, *J* = 6.0 Hz, 3 H), 1.20-1.40 (m, 12 H), 1.47 (s, 9 H), 1.49-1.59 (m, 2 H), 2.52 (t, *J* = 8.0 Hz, 2 H), 3.34 (s, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.1, 22.6, 23.4, 27.9, 29.0, 29.2, 29.33, 29.34, 31.8, 42.9, 50.6, 81.8, 166.5, 203.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2959 (s), 2928 (s), 2856 (m), 1739 (s), 1718 (s), 1644 (w), 1457 (w), 1412 (w), 1394 (w), 1369 (m), 1317 (w), 1254 (m), 1179 (m), 1149 (s), 1110 (w), 1080 (w), 1046 (w), 840 (w). MS (EI, 70 eV): *m/z* (%) = 270 (M^+, 9), 214 (100), 197 (57). The exact molecular mass *m/z* = 270.2195 ± 2 mD [M^+] for $C_{16}H_{30}O_3$ was confirmed by HRMS (EI, 70 eV).

2e: Starting with *tert*-butylacetoacetate (1.63 mL, 10.00 mmol), diisopropylamine (2.81 mL, 20.00 mmol), *n*BuLi (12.60 mL, 20.00 mmol, 15% in *n*-hexane), and 1-iododecane (2.950 g, 11.00 mmol) in THF (100 mL), **2e** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 20:1) as a yellow oil (1.797 g, 60%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.91 (t, *J* = 6.0 Hz, 3 H), 1.20-1.40 (m, 16 H), 1.50 (s, 9 H), 1.52-1.65 (m, 2 H), 2.55 (t, *J* = 7.0 Hz, 2 H), 3.37 (s, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.1, 22.7, 23.5, 27.9, 29.0, 29.3, 29.4, 29.4, 29.6, 31.8, 42.9, 50.7, 81.8, 166.5, 203.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2956 (m), 2926 (s), 2855 (m), 1739 (m), 1717 (s), 1644 (w), 1466 (w), 1458 (w), 1411 (w), 1394 (w), 1369 (m), 1317 (w), 1251 (m), 1149 (s). MS (EI, 70 eV): *m/z* (%) = 298 (M^+, 8), 242

(100), 225 (51). The exact molecular mass *m/z* = 298.2508 ± 2 mD [M^+] for $C_{18}H_{34}O_3$ was confirmed by HRMS (EI, 70 eV).

2f: Starting with *tert*-butylacetoacetate (1.63 mL, 10.00 mmol), diisopropylamine (2.81 mL, 20.00 mmol), *n*BuLi (12.60 mL, 20.00 mmol, 15% in *n*-hexane), and 1-iodo-2-methylpropane (1.28 mL, 11.00 mmol) in THF (100 mL), **2f** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 20:1) as a yellow oil (0.940 g, 44%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.75-0.85 (d, *J* = 6.0 Hz, 6 H), 1.40 (s, 9 H), 1.40-1.60 (m, 2 + 1 H), 2.45 (t, *J* = 7.0 Hz, 2 H), 3.25 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.3, 26.5, 26.9, 31.2, 39.9, 49.6, 80.6, 165.5, 202.4. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2961 (s), 2933 (m), 2873 (w), 1739 (s), 1718 (s), 1644 (w), 1467 (m), 1457 (m), 1417 (m), 1390 (w), 1370 (m), 1318 (w), 1260 (s), 1178 (m), 1150 (s), 1093 (w), 1080 (m), 1022 (w), 803 (w). MS (EI, 70 eV): *m/z* (%) = 214 (M^+, 100), 198 (18), 171 (34), 158 (19), 141 (64).

2g: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.86-0.89 (d, *J* = 9.0 Hz, 6 H), 1.13-1.19 (m, 2 H), 1.48 (s, 9 H), 1.56-1.63 (m, 3 H), 2.50 (t, *J* = 7.4 Hz, 2 H), 3.34 (s, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 21.3, 22.4, 27.8, 27.9, 38.2, 43.1, 50.6, 81.8, 166.5, 203.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3005 (w), 2957 (s), 2935 (s), 2905 (m), 2872 (m), 1739 (s), 1715 (s), 1643 (m), 1469 (m), 1459 (m), 1411 (m), 1394 (m), 1386 (w), 1369 (s), 1319 (s), 1252 (s), 1149 (s), 1111 (w), 1074 (w), 950 (w), 843 (w). MS (EI, 70 eV): *m/z* (%) = 228 (M^+, 5), 183 (15), 171 (15), 155 (100). Anal. calcd. for $C_{13}H_{24}O_3$ (228.331): C 68.38, H 10.59; found: C 68.19, H 10.91.

2h: Starting with *tert*-butylacetoacetate (1.63 mL, 10.00 mmol), diisopropylamine (2.81 mL, 20.00 mmol), *n*BuLi (12.60 mL, 20.00 mmol, 15% in *n*-hexane), and benzylbromide (1.31 g, 11.00 mmol) in THF (100 mL), **2h** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 20:1) as a yellow oil (1.409 g, 57%). ^{1}H NMR ($CDCl_3$, 200

MHz): δ = 1.35 (s, 9 H), 2.79 (t, *J* = 7.0 Hz, 2 H), 2.80 (t, *J* = 7.0 Hz, 2 H), 3.24 (s, 2 H), 7.10-7.16 (m, 5 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 27.9, 29.4, 44.4, 50.7, 81.9, 126.1, 128.3, 128.5, 140.6, 166.3, 166.3. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2978 (m), 2930 (m), 1738 (s), 1714 (s), 1643 (w), 1453 (w), 1405 (w), 1368 (m), 1320 (m), 1256 (m), 1151 (s), 1078 (w), 749 (w), 701 (w). MS (EI, 70 eV): *m/z* (%) = 248 (M^+, 3), 191 (21), 175 (100). The exact molecular mass *m/z* = 248.1412 ± 2 mD [M^+] for $C_{15}H_{20}O_3$ was confirmed by HRMS (EI, 70 eV).

2i: Starting with methyl acetoacetate (2.20 mL, 20.00 mmol), diisopropylamine (5.62 mL, 40.00 mmol), *n*BuLi (25.20 mL, 40.00 mmol, 15% in *n*-hexane), and 1-chloro-3-iodopropane (5.315 g, 26.00 mmol) in THF (150 mL), **2i** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 1:1) as a yellow oil (2.976 g, 77%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.73-1.82 (m, 4 H), 2.60 (t, *J* = 6.8 Hz, 2 H), 3.46 (s, 2 H), 3.54 (t, *J* = 6.2 Hz, 2 H), 3.75 (s, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.4, 31.4, 41.7, 44.4, 48.7, 52.1, 167.4, 201.9. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2956 (m), 1751 (s), 1719 (s), 1650 (w), 1629 (w), 1438 (s), 1409 (m), 1362 (w), 1320 (s), 1265 (s), 1199 (m), 1180 (m), 1166 (m), 1091 (w), 1058 (w), 1050 (w), 1005 (w), 649 (w). MS (EI, 70 eV): *m/z* (%) = 192 (M^+, 17), 161 (18), 156 (100), 125 (35). The exact molecular mass *m/z* = 192.0553 ± 2 mD [M^+] for $C_8H_{13}O_3Cl$ was confirmed by HRMS (EI, 70 eV).

2j: Starting with *tert*-butylacetoacetate (4.10 mL, 25.00 mmol), diisopropylamine (8.80 mL, 62.50 mmol), *n*BuLi (39.30 mL, 62.50 mmol, 15% in *n*-hexane), and 1-chloro-6-iodohexane (7.062 g, 27.50 mmol) in THF (150 mL), **2j** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 30:1) as a yellow oil (5.564 g, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.27-1.36 (m, 4 H), 1.40-1.45 (m, 2 H), 1.47 (s, 9 H), 1.60 (t, *J* = 7.5 Hz, 2 H), 1.76 (quint, *J* = 6.9 Hz, 2 H), 2.53 (t, *J* = 7.35 Hz, 2 H), 3.34 (s, 2 H), 3.52 (t, *J* = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 23.5, 26.9, 28.2, 28.9, 29.1, 32.7, 43.0, 45.3, 50.9,

82.1, 166.7, 203.6. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2979 (m), 2935 (s), 2859 (m), 1737 (s), 1718 (s), 1642 (w), 1457 (m), 1432 (w), 1411 (w), 1394 (w), 1369 (s), 1315 (m), 1252 (s), 1150 (s), 1074 (w), 1065 (w), 840 (w), 728 (w), 650 (w). MS (EI, 70 eV): *m/z* (%) = 276 (M^+, 3), 220 (82), 203 (100). The exact molecular mass *m/z* = 276.1492 ± 2 mD [M^+] for $C_{14}H_{25}O_3Cl$ was confirmed by HRMS (EI, 70 eV).

Representative Experimental Procedure of the Cyclization of 1,3-Dicarbonyl Dianions with 1-Bromo-2-chloroethane: LDA was prepared by addition of *n*BuLi (13.75 mL, 21.90 mmol, 15% in *n*-hexane) to a solution of diisopropylamine (3.08 mL, 21.90 mmol) in THF (100 mL). To this solution was added **2g** (2.000 g, 8.76 mmol) at 0 °C. The solution was stirred at 0 °C for 1 h. To this solution was added 1-bromo-2-chloroethane (0.80 mL, 9.64 mmol) at –78 °C. The temperature was allowed to rise to ambient during 14 h and the solution was refluxed for 2 h. To the solution was added hydrochloric acid (150 mL, 10%) and the mixture was extracted with diethylether (4 x 250 mL). The organic layers were dried over Na_2SO_4, filtered and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc = 100:1 → 1:1) to give **3g** (1.068 g, 48%) as a yellow oil.

3a: Starting with **2a** (1.000 g, 5.00 mmol), diisopropylamine (1.80 mL, 12.50 mmol), *n*BuLi (7.90 mL, 12.50 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.46 mL, 5.50 mmol) in THF (70 mL), **3a** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 10:1) as a yellow oil (0.551 g, 49%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.90-0.97 (t, *J* = 7.0 Hz, 3 H), 1.28-1.45 (m, 2 H), 1.47 (s, 9 H), 1.51-1.70 (m, 3 H), 2.09-2.26 (m, 1 H), 2.68-2.84 (m, 1 H), 4.21-4.33 (dq, 1 H), 4.41-4.52 (m, 1 H), 4.78 (s, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 13.9, 20.7, 28.3, 29.4, 34.6, 43.6, 72.2, 78.9, 89.1, 165.9, 175.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2963 (s), 2932 (s), 2874 (w), 1710 (s), 1687 (m), 1648 (s), 1465 (w), 1456

(w), 1392 (w), 1365 (m), 1328 (w), 1304 (w), 1285 (w), 1253 (w), 1248 (w), 1234 (w), 1215 (m), 1170 (s), 1142 (s), 1029 (s), 965 (w), 805 (w). MS (EI, 70 eV): *m/z* (%) = 226 (M^+, 4), 184 (83), 169 (3), 153 (100). The exact molecular mass *m/z* = 226.1569 ± 2 mD [M^+] for $C_{13}H_{22}O_3$ was confirmed by HRMS (EI, 70 eV). Anal. calcd. for $C_{13}H_{22}O_3$ (226.315): C 68.99, H 9.80; found: C 68.84, H 10.15.

3b: Starting with **2b** (0.485 g, 2.00 mmol), diisopropylamine (0.70 mL, 5.00 mmol), *n*BuLi (3.14 mL, 5.00 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.18 mL, 2.20 mmol) in THF (20 mL), **3b** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 5:1) as a yellow oil (0.353 g, 66%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.86-0.91 (t, *J* = 7.0 Hz, 3 H), 1.26-1.45 (m, 8 H), 1.47 (s, 9 H), 1.63-1.73 (m, 3 H), 2.10-2.24 (m, 1 H), 2.66-2.74 (m, 1 H), 4.26-4.34 (m, 1 H), 4.45-4.49 (m, 1 H), 4.78 (s, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.0, 22.5, 27.4, 28.2, 29.0, 29.3, 31.5, 32.4, 43.8, 72.2, 78.9, 89.1, 165.9, 175.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2961 (s), 2929 (s), 2859 (m), 1710 (s), 1689 (m), 1646 (s), 1458 (m), 1393 (m), 1327 (w), 1306 (w), 1288 (w), 1251 (w), 1216 (m), 1163 (s), 1031 (s), 965 (w), 806 (w). MS (EI, 70 eV): *m/z* (%) = 268 (M^+, 7), 211 (51), 195 (100), 167 (5). The exact molecular mass *m/z* = 268.2038 ± 2 mD [M^+] for $C_{16}H_{28}O_3$ was confirmed by HRMS (EI, 70 eV).

3c: Starting with **2c** (1.000 g, 3.90 mmol), diisopropylamine (1.40 mL, 9.80 mmol), *n*BuLi (6.20 mL, 9.80 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.36 mL, 4.30 mmol) in THF (70 mL), **3c** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 5:1) as a yellow oil (0.559 g, 53%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.90 (t, *J* = 7.0 Hz, 3 H), 1.24-1.45 (m, 10 H), 1.47 (s, 9 H), 1.65-1.72 (m, 3 H), 2.17-2.19 (m, 1 H), 2.71-2.77 (m, 1 H), 4.24-4.32 (dq, 1 H), 4.44-4.51 (m, 1 H), 4.78 (s, 1 H). ^{13}C NMR ($CDCl_3$,

50 MHz): δ = 14.0, 22.6, 27.5, 28.3, 29.0, 29.4, 29.5, 31.7, 32.4, 43.8, 72.2, 78.9, 89.1, 165.9, 175.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2959 (w), 2928 (s), 2857 (w), 1699 (s), 1640 (s), 1366 (w), 1151 (m), 1108 (s), 1047 (w), 1027 (m). MS (EI, 70 eV): *m/z* (%) = 282 (M^+, 13), 225 (75), 209 (100). The exact molecular mass *m/z* = 282.2195 ± 2 mD [M^+] for $C_{17}H_{30}O_3$ was confirmed by HRMS (EI, 70 eV).

3d: Starting with **2d** (1.000 g, 3.70 mmol), diisopropylamine (1.31 mL, 9.30 mmol), *n*BuLi (5.84 mL, 9.30 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.34 mL, 4.10 mmol) in THF (70 mL), **3d** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 5:1) as a yellow oil (0.468 g, 43%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.89 (t, *J* = 7.0 Hz, 3 H), 1.28-1.45 (m, 12 H), 1.47 (s, 9 H), 1.60-1.75 (m, 3 H), 2.12-2.23 (m, 1 H), 2.73-2.75 (m, 1 H), 4.24-4.32 (dq, 1 H), 4.44-4.51 (m, 1 H), 4.78 (s, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.0, 22.6, 27.4, 28.3, 29.2, 29.3, 29.4, 29.4, 31.8, 32.4, 43.8, 72.2, 78.9, 89.1, 165.9, 175.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2960 (m), 2928 (s), 2857 (m), 1710 (s), 1689 (m), 1647 (s), 1459 (w), 1392 (w), 1366 (w), 1215 (m), 1162 (s), 1139 (s), 1030 (s). MS (EI, 70 eV): *m/z* (%) = 296 (M^+, 10), 239 (74), 223 (100). The exact molecular mass *m/z* = 296.2351 ± 2 mD [M^+] for $C_{18}H_{32}O_3$ was confirmed by HRMS (EI, 70 eV).

3e: Starting with **2e** (1.000 g, 3.40 mmol), diisopropylamine (1.18 mL, 8.40 mmol), *n*BuLi (5.28 mL, 8.40 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.31 mL, 3.70 mmol) in THF (70 mL), **3e** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 5:1) as a yellow oil (0.454 g, 41%). Upon standing this compound rearranges to a mixture of *E*/*Z* isomers. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 7.0 Hz, 3 H), 1.27-1.46 (m, 16 H), 1.47 (s, 9 H), 1.65-1.75 (m, 3 H), 2.12-2.23 (m, 1 H), 2.72-2.77 (m, 1 H), 4.24-4.32 (dq, 1 H), 4.44-4.78 (m, 1 H), 4.79 (s, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ =

14.1, 22.6, 27.5, 28.3, 28.5, 29.3, 29.4, 29.5, 29.6, 29.8, 31.8, 32.4, 43.8, 72.1, 78.9, 89.1, 166.0, 175.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2970 (s), 2854 (s), 1711 (s), 1642 (s), 1460 (m), 1393 (m), 1366 (m), 1327 (w), 1304 (w), 1250 (w), 1215 (s), 1169 (s), 1136 (s), 1031 (s), 967 (m), 804 (m). MS (EI, 70 eV): *m/z* (%) = 324 (M^+, 11), 267 (100), 251 (96). The exact molecular mass *m/z* = 324.2664 ± 2 mD [M^+] for $C_{20}H_{36}O_3$ was confirmed by HRMS (EI, 70 eV).

3f: Starting with **2f** (0.300 g, 1.40 mmol), diisopropylamine (0.50 mL, 3.50 mmol), *n*BuLi (2.20 mL, 3.50 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.13 mL, 1.54 mmol) in THF (20 mL), **3f** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 5:1) as a yellow oil (0.150 g, 45%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.90-0.98 (2 x d, *J* = 6.0 Hz, 6 H), 1.34-1.45 (m, 1 H), 1.47 (s, 9 H), 1.60-1.69 (m, 3 H), 2.20 (m, 1 H), 2.75-2.87 (m, 1 H), 4.24-4.32 (m, 1 H), 4.45-4.49 (m, 1 H), 4.78 (s, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 21.2, 26.2, 28.3, 29.6, 41.8, 41.8, 72.2, 79.0, 89.1, 165.9, 175.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2959 (s), 2931 (s), 2872 (m), 1710 (s), 1690 (s), 1646 (s), 1469 (w), 1391 (w), 1367 (m), 1332 (w), 1322 (w), 1290 (w), 1257 (w), 1216 (m), 1171 (s), 1145 (s), 1031 (s), 969 (w), 804 (w). MS (EI, 70 eV): *m/z* (%) = 240 (M^+, 1), 184 (100), 167 (94). The exact molecular mass *m/z* = 240.1725 ± 2 mD [M^+] for $C_{14}H_{24}O_3$ was confirmed by HRMS (EI, 70 eV).

3g: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88-0.92 (2 x d, *J* = 6.0 Hz, 6 H), 1.19-1.29 (m, 2 H), 1.48 (s, 9 H, O*t*Bu), 1.64-1.74 (m, 2 H), 2.12-2.23 (m, 1 H), 2.70-2.74 (m, 1 H), 3.48-4.11 (dq, *J* = 7.2 Hz, 1 H), 4.23-4.32 (dq, 1 H), 4.44-4.51 (m, 1 H), 4.79 (s, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 22.2, 22.6, 27.9, 28.3, 29.4, 30.2, 36.6, 44.0, 72.2, 78.9, 89.1, 165.9, 175.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2958 (s), 2932 (s), 2905 (m), 2871 (m), 1710 (s), 1687 (m), 1647 (s), 1469 (w), 1455 (w), 1390 (m), 1366 (m), 1328 (w), 1303 (w), 1282 (w), 1247 (w), 1214

(s), 1168 (s), 1143 (s), 1030 (s), 966 (w), 805 (w). MS (EI, 70 eV): *m/z* (%) = 254 (M^+, 14), 197 (52), 181 (100). Anal. calcd. for $C_{15}H_{26}O_3$ (254.369): C 70.82, H 10.30; found C 70.41, H 9.93.

3h: Starting with **2h** (0.200 g, 0.81 mmol), diisopropylamine (0.28 mL, 2.00 mmol), *n*BuLi (1.26 mL, 2.00 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.07 mL, 0.89 mmol) in THF (20 mL), **3h** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 5:1) as a yellow oil (0.089 g, 40%). Upon standing at room temperature this compound slowly rearranged to a mixture of *E*/*Z* isomers. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.49 (s, 9 H), 1.71-1.81 (m, 1 H), 1.93-2.02 (m, 1 H), 2.55-2.63 (dt, 1 H), 3.03-3.10 (dd, 2 H), 4.21-4.29 (dq, 1 H), 4.39-4.46 (m, 1 H), 4.90 (s, 1 H), 7.17-7.31 (m, 5 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 28.4, 29.2, 37.4, 42.6, 69.6, 78.9, 91.3, 126.4, 128.4, 129.2, 139.6, 167.4, 178.6). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2977 (m), 2927 (w), 1702 (s), 1643 (s), 1606 (w), 1454 (w), 1395 (w), 1367 (w), 1327 (w), 1291 (w), 1252 (w), 1218 (s), 1162 (s), 1137 (s), 1032 (s), 969 (w), 802 (m), 746 (m), 705 (w). MS (EI, 70 eV): *m/z* (%) = 274 (M^+, 3), 217 (8), 201 (100). The exact molecular mass *m/z* = 274.1569 ± 2 mD [M^+] for $C_{17}H_{22}O_3$ was confirmed by HRMS (EI, 70 eV).

3i: Starting with **2i** (1.000 g, 5.20 mmol), diisopropylamine (1.83 mL, 13.00 mmol), *n*BuLi (8.17 mL, 13.00 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.47 mL, 5.70 mmol) in THF (20 mL), **3i** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 10:1) as a yellow oil (0.460 g, 44%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.58-1.68 (m, 2 H), 1.73-1.86 (m, 1 H), 1.88-2.01 (m, 2 H), 2.10-2.21 (m, 1 H), 3.50-3.65 (m, 2 H), 3.66 (s, 3 H), 3.92-4.11 (m, 1 H), 4.12-4.23 (m, 1 H), 4.26 (t, *J* = 4.2 Hz, 1 H), 5.20 (s, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 28.6, 29.3, 31.1, 40.7, 44.5, 50.5, 69.9, 88.9, 168.2, 180.1.

IR (neat, cm^{-1}): $\tilde{\nu}$ = 2954 (m), 2907 (w), 1704 (s), 1642 (s), 1436 (m), 1379 (m), 1351 (m), 1307 (w), 1243 (w), 1188 (w), 1151 (w), 1118 (s), 1045 (m), 995 (w), 979 (w), 827 (w, C–Cl). MS (EI, 70 eV): *m/z* (%) = 218 (M^+, 45), 187 (100), 182 (7). Anal. calcd. for $C_{10}H_{15}O_3Cl$ (218.680): C 54.93, H 6.91; found: C 54.97, H 7.28.

3j: Starting with **2j** (0.500 g, 1.81 mmol), diisopropylamine (0.63 mL, 4.52 mmol), *n*BuLi (2.84 mL, 4.52 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.17 mL, 1.99 mmol) in THF (20 mL), **3j** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 1:1) as a yellow oil (0.498 g, 91%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.31-1.45 (m, 6 H), 1.47 (s, 9 H), 1.63-1.82 (m, 4 H), 2.13-2.23 (m, 1 H), 2.73-2.77 (m, 1 H), 3.53 (t, *J* = 6.6 Hz, 2 H), 3.59-4.16 (m, 1 H), 4.26-4.32 (dq, 1 H), 4.44-4.51 (m, 1 H), 4.79 (s, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 26.6, 27.2, 28.2, 28.6, 29.3, 32.2, 32.4, 43.7, 44.9, 72.1, 78.9, 89.1, 165.8, 174.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2977 (m), 2934 (s), 2860 (m), 1709 (s), 1689 (m), 1645 (s), 1455 (w), 1393 (w), 1366 (m), 1327 (w), 1309 (w), 1288 (w), 1251 (w), 1216 (s), 1148 (s), 1030 (s), 966 (w), 807 (w). MS (EI, 70 eV): *m/z* (%) = 302 (M^+, 100), 249 (81). Anal. calcd. for $C_{16}H_{27}O_3Cl$ (302.840): C 63.46, H 8.99; found: C 63.96, H 8.65.

3k: Starting with methyl 4-methoxyacetoacetate (0.731g, 5.00 mmol), diisopropylamine (1.80 mL, 12.50 mmol), *n*BuLi (7.90 mL, 12.50 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (0.46 mL, 5.50 mmol) in THF (70 mL), **3k** was isolated after chromatography (silica gel, *n*-hexane/EtOAc = 30:1 → 10:1) as a yellow oil (0.422 g, 49%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.02 (m, 1 H), 2.20-2.25 (dt, J_1 = 2.6 Hz, J_2 = 3.2 Hz, 1 H), 3.45 (s, 3 H), 3.70 (s, 3 H), 4.29-4.33 (dd, J_1 = 3.3 Hz, J_2 = 3.9 Hz, 2 H), 5.16 (dd, *J* = 4.8 Hz, 1 H), 5.43 (s, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 31.1, 50.8, 57.3, 70.3, 76.6, 92.5, 167.8, 172.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2989 (w), 2951 (m), 2911 (w), 2832 (w), 1711 (s), 1655 (s), 1438 (m), 1380 (w),

1350 (m), 1304 (w), 1191 (m), 1161 (m), 1119 (s), 1046 (m), 975 (m), 834 (m). MS (EI, 70 eV): *m/z* (%) = 172 (M^+, 9), 157 (15), 142 (100). The exact molecular mass *m/z* = 172.0736 ± 2 mD [M^+] for $C_8H_{12}O_4$ was confirmed by HRMS (EI, 70 eV).

3l: Starting with benzoylacetone (2.500 g, 15.40 mmol), diisopropylamine (7.03 mL, 50.00 mmol), *n*BuLi (31.40 mL, 50.00 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (2.40 mL, 17.00 mmol) in THF (100 mL), **3l** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 1:1) as a yellow oil (2.367 g, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.16 (quint, *J* = 7.2 Hz, 2 H), 3.29 (t, *J* = 7.8 Hz, 2 H), 4.30 (t, *J* = 7.2 Hz, 2 H), 6.55 (s, 1 H), 7.40-7.52 (m, 3 H), 7.86-7.92 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 23.5, 31.2, 71.7, 94.9, 127.4, 128.1, 131.5, 139.6, 179.0, 189.9. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2985 (w), 2900 (w), 1656 (s), 1599 (s), 1588 (s), 1570 (s), 1447 (w), 1388 (m), 1363 (w), 1269 (w), 1283 (w), 1166 (s), 1054 (w), 1016 (m), 967 (s), 929 (m), 885 (w), 786 (w), 704 (s), 655 (w). MS (EI, 70 eV): *m/z* (%) = 188 (M^+, 23), 77 (75), 70 (100). Anal. calcd. for $C_{12}H_{12}O_2$ (188.226): C 76.57, H 6.43; found: C 76.31, H 5.95.

3r:[13a] Starting with 2-acetyl-γ-butyrolactone (2.70 mL, 25.00 mmol), diisopropylamine (8.80 mL, 62.50 mmol), *n*BuLi (39.30 mL, 62.50 mmol, 15% in *n*-hexane), and 1-bromo-2-chloroethane (2.30 mL, 27.50 mmol) in THF (200 mL), **3r** was isolated without further purification as a white solid (2.236 g, 58%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.08-2.18 (dquint, 2 H), 2.85-2.92 (dt, 2 H), 3.09-3.16 (dt, 2 H), 4.28-4.37 (dt, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 23.8, 24.8, 28.7, 64.9, 72.2, 92.7, 169.2, 172.8. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2985 (m), 2951 (w), 2920 (m), 1729 (s), 1678 (s), 1480 (w), 1454 (w), 1375 (m), 1307 (w), 1299 (w), 1259 (s), 1211 (m), 1174 (s), 1080 (m), 1031 (s), 990 (m), 958 (w), 931 (m), 856 (w), 768

(w), 750 (m), 692 (w). MS (EI, 70 eV): *m/z* (%) = 154 (M^+, 100). Anal. calcd. for $C_8H_{10}O_3$ (154.165): C 62.23, H 6.54, found: C 62.60, H 6.37.

Representative Experimental Procedure for the Alkylation of 2-Alkylidenetetrahydrofurans: LDA was prepared by addition of *n*BuLi (1.36 mL, 2.17 mmol, 15% in *n*-hexane) to a solution of diisopropylamine (0.31 mL, 2.17 mmol) in THF (17 mL) at 0 °C. To this solution was added HMPA (0.34 mL, 1.92 mmol) at 0 °C and stirred for 20 min at this temperature. To the solution was added **3m** (0.200 g, 1.28 mmol) at –78 °C and the solution was stirred for 1 h. To the solution was added 1-iodohexane (0.21 mL, 1.41 mmol) at –78 °C and the temperature was allowed to rise to ambient during 14 h. The solution was stirred at room temperature for 5 h. To the solution was added hydrochloric acid (20 mL, 1 M) and the mixture was extracted with diethylether (4 x 50 mL). The organic layers were dried over Na_2SO_4, filtered and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) to give **4a** (0.175 g, 57%) as a colorless oil.

4a: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3), 1.28 (t, *J* = 4.1 Hz, 3 H), 1.30-1.40 (m, 8 H), 2.06 (quint, *J* = 7.5 Hz, 2 H), 2.26 (t, *J* = 7.8 Hz, 2 H), 3.06 (t, *J* = 7.8 Hz, 2 H), 4.14 (t, *J* = 7.2 Hz, 2 H), 4.19 (q, *J* = 4.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 14.4, 22.6, 24.4, 26.0, 28.4, 29.2, 30.9, 31.7, 59.2, 71.1, 103.0, 169.2, 170.3. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2957 (s), 2928 (s), 2858 (m), 1697 (s), 1635 (s), 1459 (w), 1372 (w), 1315 (w), 1294 (m), 1252 (w), 1175 (m), 1109 (s), 1055 (m). MS (EI, 70 eV): *m/z* (%) = 240 (M^+, 96), 211 (36), 195 (100), 156 (40). The exact molecular mass *m/z* = 240.1725 ± 2 mD [M^+] for $C_{14}H_{24}O_3$ was confirmed by HRMS (EI, 70 eV). Anal. calcd. for $C_{14}H_{24}O_3$ (240.34): C 69.97, H 10.07; found: C 69.56, H 9.95.

4b: Starting with **3m** (0.200 g, 1.28 mmol), diisopropylamine (0.31 mL, 2.17 mmol), *n*BuLi (1.36 mL, 2.17 mmol, 15% in *n*-hexane), HMPA (0.34 mL, 1.92 mmol), and 1-iodoheptane (0.23 mL, 1.41 mmol) in THF (17 mL), **4b** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a colorless oil (0.159 g, 49%). An unknown impurity could not be separated. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.26 (t, *J* = 2.3 Hz, 3 H), 1.30-1.40 (m, 10 H), 2.06 (quint, *J* = 7.5 Hz, 2 H), 2.26 (t, *J* = 7.8 Hz, 2 H), 3.06 (t, *J* = 7.7 Hz, 2 H), 4.14 (t, *J* = 7.2 Hz, 2 H), 4.22 (q, *J* = 3.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.0, 14.4, 22.6, 24.4, 26.0, 28.9, 29.2, 29.5, 30.9, 31.7, 59.2, 71.1, 103.0, 169.2, 170.4. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2955 (s), 2928 (s), 2857 (m), 1746 (m), 1714 (m), 1697 (s), 1634 (s), 1461 (w), 1371 (w), 1313 (m), 1277 (w), 1236 (m), 1173 (m), 1112 (s), 1057 (m), 1034 (w). MS (EI, 70 eV): *m/z* (%) = 254 (M^+, 100), 225 (51), 209 (85), 181 (10), 156 (45). The exact molecular mass *m/z* = 254.1882 ± 2 mD [M^+] for $C_{15}H_{26}O_3$ was confirmed by HRMS (EI, 70 eV).

4c: Starting with **3m** (0.200 g, 1.28 mmol), diisopropylamine (0.31 mL, 2.17 mmol), *n*BuLi (1.36 mL, 2.17 mmol, 15% in *n*-hexane), HMPA (0.34 mL, 1.92 mmol), and 1-iodooctane (0.26 mL, 1.41 mmol) in THF (17 mL), **4c** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a colorless oil (0.176 g, 51%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.27 (t, *J* = 6.9 Hz, 3 H), 1.30-1.40 (m, 12 H), 2.06 (quint, *J* = 7.4 Hz, 2 H), 2.29 (t, *J* = 7.4 Hz, 2 H), 3.06 (t, *J* = 7.8 Hz, 2 H), 4.09 (t, *J* = 6.5 Hz, 2 H), 4.20 (q, *J* = 6.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 14.4, 22.7, 24.4, 26.0, 29.2, 29.3, 29.5, 29.5, 31.0, 31.9, 59.3, 71.2, 103.0, 169.3, 170.4. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2957 (s), 2925 (s), 2871 (w), 2855 (m), 1699 (s), 1635 (s), 1463 (w), 1373 (w), 1319 (m), 1294 (m), 1269 (m), 1234 (w), 1195 (w), 1180 (w), 1169 (m), 1114 (s), 1105 (s), 1063 (s), 1029 (w), 987 (w). MS (EI, 70 eV): *m/z* (%) = 268 (M^+,100), 223 (63), 211 (53), 156 (53).

The exact molecular mass *m/z* = 268.2038 ± 2 mD [M^+] for $C_{16}H_{28}O_3$ was confirmed by HRMS (EI, 70 eV).

4d: Starting with **3m** (0.200 g, 1.28 mmol), diisopropylamine (0.31 mL, 2.17 mmol), *n*BuLi (1.36 mL, 2.17 mmol, 15% in *n*-hexane), HMPA (0.34 mL, 1.92 mmol), and 1-iododecane (0.378 g, 1.41 mmol) in THF (17 mL), **4d** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a colorless oil (0.183 g, 48%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.26 (t, *J* = 3.2 Hz, 3 H), 1.30 - 1.40 (m, 16 H), 2.06 (quint, *J* = 7.4 Hz, 2 H), 2.29 (t, *J* = 7.5 Hz, 2 H), 3.06 (t, *J* = 7.6 Hz, 2 H), 4.09 (t, *J* = 6.5 Hz, 2 H), 4.21 (q, *J* = 6.8 Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 14.1, 14.4, 22.6, 24.4, 26.0, 29.2, 29.3, 29.4, 29.5, 29.6, 29.6, 30.9, 31.9, 59.2, 71.1, 103.1, 169.3, 170.4. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2927 (s), 2855 (m), 1697 (s), 1635 (s), 1460 (w), 1372 (w), 1314 (w), 1298 (w), 1254 (w), 1240 (w), 1172 (m), 1112 (s), 1075 (m), 1052 (m). MS (EI, 70 eV): *m/z* (%) = 296 (M^+, 100), 267 (8), 251 (71), 156 (41). The exact molecular mass *m/z* = 296.2351 ± 2 mD [M^+] for $C_{18}H_{32}O_3$ was confirmed by HRMS (EI, 70 eV).

4e: Starting with **3n** (0.200 g, 1.09 mmol), diisopropylamine (0.26 mL, 1.85 mmol), *n*BuLi (1.16 mL, 1.85 mmol, 15% in *n*-hexane), HMPA (0.29 mL, 1.63 mmol), and 1-iodoethane (0.186 g, 1.19 mmol) in THF (17 mL), **4e** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a yellow oil (0.119 g, 51%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.98 (t, *J* = 7.4 Hz, 3 H), 1.48 (s, 9 H), 2.05 (quint, *J* = 7.2 Hz, 2 H), 2.28 (q, *J* = 7.5 Hz, 2 H), 3.01 (t, *J* = 7.6 Hz, 2 H), 4.18 (t, *J* = 7.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 13.8, 19.7, 24.5, 28.4, 30.9, 71.0, 78.9, 105.9, 168.5, 169.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2971 (m), 2933 (w), 1691 (s), 1636 (s), 1456 (w), 1370 (w), 1319 (w), 1256 (m), 1181 (m), 1100 (s), 1033 (w). MS (EI, 70 eV): *m/z* (%) = 212 (M^+, 8), 156 (52), 141 (100).

4f: Starting with **3n** (0.200 g, 1.09 mmol), diisopropylamine (0.26 mL, 1.85 mmol), *n*BuLi (1.16 mL, 1.85 mmol, 15% in *n*-hexane), HMPA (0.29 mL, 1.63 mmol), and 1-iodopropane (0.202 g, 1.19 mmol) in THF (17 mL), **4f** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a yellow oil (0.110 g, 45%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 7.3 Hz, 3 H), 1.37 (sextet, *J* = 6.0 Hz, 2 H), 1.48 (s, 9 H), 2.04 (quint, *J* = 7.3 Hz, 2 H), 2.24 (t, *J* = 7.6 Hz, 2 H), 3.02 (t, *J* = 7.6 Hz, 2 H), 4.17 (t, *J* = 7.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.0, 22.4, 24.5, 28.4, 30.9, 70.9, 78.8, 104.3, 168.6, 169.3. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2965 (s), 2932 (s), 2898 (m), 2873 (m), 1692 (s), 1635 (s), 1457 (m), 1370 (s), 1319 (s), 1252 (w), 1233 (m), 1181 (s), 1107 (s), 1038 (s), 988 (w), 855 (w), 801 (w). MS (EI, 70 eV): *m/z* (%) = 226 (M^+, 26), 170 (100), 152 (82). The exact molecular mass *m/z* = 226.1569 ± 2 mD [M^+] for $C_{13}H_{22}O_3$ was confirmed by HRMS (EI, 70 eV).

4g: Starting with **3n** (0.200 g, 1.09 mmol), diisopropylamine (0.18 mL, 1.31 mmol), *n*BuLi (0.82 mL, 1.31 mmol, 15% in *n*-hexane), HMPA (0.29 mL, 1.63 mmol), and 1-iodoheptane (0.20 mL, 1.19 mmol) in THF (17 mL), **4g** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a yellow oil (0.281 g, 91%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.88 (t, *J* = 7.0 Hz, 3 H), 1.27-1.47 (m, 10 H), 1.48 (s, 9 H), 2.04 (quint, *J* = 7.0 Hz, 2 H), 2.50 (t, *J* = 7.0 Hz, 2 H), 3.02 (t, *J* = 7.0 Hz, 2 H), 4.17 (t, *J* = 7.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.1, 22.7, 24.5, 26.4, 28.4, 29.2, 29.3, 29.6, 30.9, 31.9, 70.9, 78.9, 104.5, 168.7, 169.7. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2962 (s), 2927 (s), 2857 (s), 1693 (s), 1636 (s), 1457 (m), 1369 (m), 1320 (m), 1256 (m), 1170 (s), 1110 (s), 1055 (s), 991 (m), 859 (w), 800 (m). MS (EI, 70 eV): *m/z* (%) = 282 (M^+, 38), 225 (57), 209 (10). The exact

molecular mass *m/z* = 282.2195± 2 mD [M^+] for $C_{17}H_{30}O_3$ was confirmed by HRMS (EI, 70 eV).

4h: Starting with **3n** (0.200 g, 1.09 mmol), diisopropylamine (0.26 mL, 1.85 mmol), *n*BuLi (1.16 mL, 1.85 mmol, 15% in *n*-hexane), HMPA (0.29 mL, 1.63 mmol), and 1-iodo-2-methylpropane (0.14 mL, 1.19 mmol) in THF (17 mL), **4h** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a colorless oil (0.105 g, 40%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.86 (d, *J* = 6.6 Hz, 6 H), 1.47 (s, 9 H), 1.73 (m, *J* = 6.9 Hz, 1 H), 2.04 (quint, *J* = 7.5 Hz, 2 H), 2.16 (d, *J* = 6.9 Hz, 2 H), 3.04 (t, *J* = 7.6 Hz, 2 H), 4.15 (t, *J* = 7.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 22.5, 24.5, 24.5, 28.4, 30.9, 35.1, 70.8, 78.8, 103.6, 168.9, 169.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2957 (s), 2930 (s), 2897 (m), 2869 (m), 1728 (w), 1695 (s), 1637 (s), 1457 (m), 1390 (m), 1366 (s), 1341 (w), 1318 (m), 1307 (m), 1255 (w), 1233 (m), 1181 (s), 1151 (w), 1111 (s), 1045 (s), 1018 (w), 994 (m), 854 (w), 821 (w), 805 (w). MS (EI, 70 eV): *m/z* (%) = 240 (M^+,32), 197 (7), 184 (100), 167 (91). The exact molecular mass *m/z* = 240.1725 ± 2 mD [M^+] for $C_{14}H_{24}O_3$ was confirmed by HRMS (EI, 70 eV).

4i: Starting with **3n** (0.200 g, 1.09 mmol), diisopropylamine (0.26 mL, 1.85 mmol), *n*BuLi (1.16 mL, 1.85 mmol, 15% in *n*-hexane), HMPA (0.29 mL, 1.63 mmol), and allylbromide (0.10 mL, 1.19 mmol) in THF (17 mL), **4i** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a colorless oil (0.102 g, 42%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.47 (s, 9 H), 2.06 (quint, *J* = 7.3 Hz, 2 H), 3.04 (m, 4 H), 4.19 (t, *J* = 6.9 Hz, 2 H), 4.89-4.93 (m, 1 H), 4.98-5.04 (m, 1 H), 5.81 (m). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 24.4, 28.4, 30.7, 31.0, 71.2, 79.1, 101.8, 113.7, 137.2, 168.1, 170.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3077 (w), 2977 (m), 2930 (w), 1695 (s), 1638 (s), 1631 (s), 1477 (w), 1367 (m), 1320 (m), 1228 (w), 1214

(w), 1180 (s), 1151 (w), 1115 (s), 1067 (m), 1048 (s), 993 (w). MS (EI, 70 eV): *m/z* (%) = 224 (M^+, 16), 168 (100), 150 (29). The exact molecular mass *m/z* = 224.1412 ± 2 mD [M^+] for $C_{13}H_{20}O_3$ was confirmed by HRMS (EI, 70 eV).

4j: Starting with **3n** (0.200 g, 1.09 mmol), diisopropylamine (0.26 mL, 1.85 mmol), *n*BuLi (1.16 mL, 1.85 mmol, 15% in *n*-hexane), HMPA (0.29 mL, 1.63 mmol), and benzylbromide (0.14 mL, 1.19 mmol) in THF (17 mL), **4j** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a colorless oil (0.135 g, 45%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.41 (s, 9 H), 2.08 (quint, *J* = 7.3 Hz, 2 H), 3.09 (t, *J* = 7.5 Hz, 2 H), 3.63 (s, 2 H), 4.22 (t, *J* = 6.9 Hz, 2 H), 7.10-7.36 (m, 5 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 24.5, 28.3, 30.9, 32.1, 71.2, 79.2, 103.4, 125.3, 127.8, 128.4, 142.2, 168.2, 170.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3084 (w), 3062 (w), 3028 (w), 3001 (w), 2977 (s), 2931 (m), 2902 (m), 1738 (m), 1715 (m), 1694 (s), 1635 (s), 1604 (w), 1494 (m), 1454 (m), 1430 (w), 1391 (m), 1367 (s), 1322 (s), 1254 (w), 1166 (s), 1154 (s), 1105 (s), 1077 (s), 1052 (s), 998 (m), 962 (w), 933 (w), 854 (m), 744 (m), 700 (s). MS (EI, 70 eV): *m/z* (%) = 274 (M^+, 10), 218 (99), 200 (83), 172 (100). The exact molecular mass *m/z* = 274.1569 ± 2 mD [M^+] for $C_{17}H_{22}O_3$ was confirmed by HRMS (EI, 70 eV).

4k: Starting with **3n** (0.200 g, 1.09 mmol), diisopropylamine (0.20 mL, 1.42 mmol), *n*BuLi (0.89 mL, 1.42 mmol, 15% in *n*-hexane), HMPA (0.29 mL, 1.63 mmol), and 1-chloro-6-iodohexane (0.323 g, 1.31 mmol) in THF (17 mL), **4k** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a yellow oil (0.132 g, 40%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.26-1.46 (m, 6 H), 1.48 (s, 9 H), 1.77 (quint, *J* = 7.7 Hz, 2 H), 2.04 (quint, *J* = 7.6 Hz, 2 H), 2.26 (t, *J* = 6.7 Hz, 2 H), 3.02 (t, *J* = 7.7 Hz, 2 H), 3.52 (t, *J* = 6.6 Hz, 2 H), 4.17 (t, *J* = 7.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 24.5, 26.2, 26.8, 28.4, 28.8,

29.0, 30.9, 32.7, 45.2, 70.9, 78.9, 104.2, 168.5, 169.4. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2974 (s), 2931 (s), 2859 (m), 1692 (s), 1635 (s), 1455 (m), 1369 (s), 1273 (m), 1249 (m), 1178 (s), 1130 (s), 1109 (s), 1042 (s), 991 (w), 858 (w). MS (EI, 70 eV): *m/z* (%) = 302 (M^+, 35), 246 (100), 229 (81). Anal. calcd. for $C_{16}H_{27}O_3Cl$ (302.92): C 63.44, H 8.98; found: C 63.44, H 9.68; the exact molecular mass *m/z* = 302.1649 ± 2 mD [M^+] for $C_{16}H_{27}O_3Cl$ was confirmed by HRMS (EI, 70 eV).

4l: Starting with **3n** (0.200 g, 1.09 mmol), diisopropylamine (0.18 mL, 1.31 mmol), *n*BuLi (0.82 mL, 1.31 mmol, 15% in *n*-hexane), HMPA (0.29 mL, 1.63 mmol), and methyl bromoacetate (0.182 g, 1.19 mmol) in THF (17 mL), **4l** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 10:1) as a yellow oil (0.048 g, 25%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.46 (s, 9 H), 2.10 (quint, *J* = 7.0 Hz, 2 H), 3.11-3.12 (dd, 2 H), 3.33 (s, 2 H), 3.67 (s, 3 H), 4.22 (t, *J* = 7.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 24.4, 28.3, 30.9, 37.4, 71.6, 79.6, 97.5, 167.4, 171.7, 172.9. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2977 (m), 2955 (w), 2932 (w), 2850 (w), 1743 (s), 1705 (s), 1687 (m), 1644 (m), 1456 (w), 1436 (m), 1416 (w), 1392 (w), 1368 (m), 1352 (w), 1324 (m), 1258 (m), 1165 (s), 1115 (s), 1059 (s), 1015 (w), 991 (w). MS (EI, 70 eV): *m/z* (%) = 256 (M^+, 11), 200 (30), 182 (100), 169 (21), 154 (84), 123 (42). The exact molecular mass *m/z* = 256.1311 ± 2 mD [M^+] for $C_{13}H_{20}O_5$ was confirmed by HRMS (EI, 70 eV).

4m: Starting with **3n** (0.200 g, 1.09 mmol), diisopropylamine (0.18 mL, 1.31 mmol), *n*BuLi (0.82 mL, 1.31 mmol, 15% in *n*-hexane), HMPA (0.29 mL, 1.63 mmol), and methyl bromoacetate (0.182 g, 1.19 mmol) in THF (17 mL), **4m** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 10:1) as a yellow oil (0.061 g, 32%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.46 (s, 9 H), 1.87-2.08 (dd, 1 H), 2.18-2.32 (m, 1 H), 2.35-2.48 (dd,

2 H), 2.82-2.98 (dd, 1 H), 3.71 (s, 3 H), 3.88-4.35 (m, 2 H), 5.22 (s, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 28.1, 29.2, 35.5, 37.5, 51.6, 69.3, 79.1, 92.0, 166.9, 171.9, 176.5. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2978 (s), 2934 (w), 2908 (w), 1740 (s), 1696 (s), 1641 (s), 1455 (w), 1448 (w), 1438 (w), 1368 (m), 1352 (w), 1307 (w), 1258 (m), 1196 (m), 1169 (s), 1152 (s), 1114 (s), 1045 (m), 1026(m). MS (EI, 70 eV): *m/z* (%) = 256 (M^+, 13), 200 (97), 183 (100). The exact molecular mass *m/z* = 256.1311 ± 2 mD [M^+] for $C_{13}H_{20}O_5$ was confirmed by HRMS (EI, 70 eV).

4n: Starting with **3o** (0.300 g, 2.11 mmol), diisopropylamine (0.39 mL, 2.74 mmol), *n*BuLi (1.72 mL, 2.74 mmol, 15% in *n*-hexane), HMPA (0.56 mL, 3.17 mmol), and 1-iodo-3-methylbutane (0.474 g , 2.32 mmol) in THF (30 mL), **4n** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 30:1) as a yellow oil (0.355 g, 79%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.90 (d, *J* = 10.4 Hz, 6 H), 1.21-1.29 (m, 2 H), 1.50 (m, 1 H), 2.06 (quint, *J* = 7.3 Hz, 2 H), 2.29 (t, *J* = 8.0 Hz, 2 H), 3.05 (t, *J* = 7.8 Hz, 2 H), 3.69 (s, 3 H), 4.20 (t, *J* = 7.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 22.5, 24.0, 24.4, 28.0, 31.0, 38.4, 50.7, 71.2, 102.9, 169.7, 170.6. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2957 (s), 2873 (m), 1738 (s), 1632 (s), 1461 (m), 1441 (m), 1375 (m), 1320 (m), 1282 (s), 1261 (s), 1214 (s), 1178 (s), 1122 (s), 1054 (s), 987 (w). MS (EI, 70 eV): *m/z* (%) = 212 (M+, 100), 181 (76). The exact molecular mass *m/z* = 212.1412 ± 2 mD [M^+] for $C_{12}H_{20}O_3$ was confirmed by HRMS (EI, 70 eV).

4o: Starting with **3o** (0.200 g, 1.41 mmol), diisopropylamine (0.50 mL, 3.52 mmol), *n*BuLi (2.21 mL, 3.52 mmol, 15% in *n*-hexane), HMPA (0.59 mL, 3.38 mmol), and benzylbromide (0.40 mL, 3.38 mmol) in THF (17 mL), **4o** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a yellow oil (0.174 g, 38%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.02-2.18 (quint, *J* = 8.0 Hz, 2 H), 3.09-3.17 (t, *J* = 8.0 Hz, 2 H), 3.66

(s, 3 H), 3.67 (s, 2 H), 4.21-4.29 (t, J = 8.0 Hz, 2 H), 7.23-7.26 (m, 5 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 24.3, 31.1, 31.7, 50.9, 71.6, 101.7, 125.5, 128.0, 128.3, 141.8, 169.3, 171.9. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3082 (w), 3061 (w), 3027 (w), 2988 (w), 2948 (m), 2900 (w), 2848 (w), 1746 (w), 1703 (s), 1633 (s), 1493 (w), 1436 (m), 1374 (w), 1317 (m), 1177 (s), 1106 (s), 1073 (s), 1058 (s), 982 (m), 763 (w), 746 (w), 702 (m). MS (EI, 70 eV): *m/z* (%) = 232 (M^+, 100), 201 (52), 173 (83). The exact molecular mass *m/z* = 232.1099 ± 2 mD [M^+] for $C_{14}H_{16}O_3$ was confirmed by HRMS (EI, 70 eV).

4p: Starting with **3o** (0.200 g, 1.41 mmol), diisopropylamine (0.50 mL, 3.52 mmol), *n*BuLi (2.21 mL, 3.52 mmol, 15% in *n*-hexane), HMPA (0.59 mL, 3.38 mmol), and benzylbromide (0.40 mL, 3.38 mmol) in THF (17 mL), **4p** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a yellow oil (0.195 g, 43%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.95-1.97 (m, 2 H), 2.55-2.60 (m, 1 H), 3.12-3.25 (dd, 2 H), 3.70 (s, 2 H), 3.72 (s, 3 H), 3.90-4.10 (m, 1 H), 4.22-4.32 (m, 1 H), 7.22-7.36 (m, 10 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 27.8, 37.3, 43.4, 50.8, 70.0, 101.8, 126.4, 127.5, 128.0, 128.3, 128.5, 129.2, 139.5, 139.8, 168.5, 180.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3082 (w), 3062 (w), 3028 (m, CH), 2982 (m), 2950 (m), 2908 (m), 1738 (m), 1702 (s), 1640 (s), 1445 (m), 1350 (w), 1309 (w), 1278 (w), 1244 (w), 1176 (s), 1120 (s), 1085 (m), 1055 (s), 994 (w), 747 (m), 701 (s). MS (EI, 70 eV): *m/z* (%) = 322 (M^+, 100), 291 (16), 263 (35), 231 (31). The exact molecular mass *m/z* = 322.1569 ± 2 mD [M^+] for $C_{21}H_{22}O_3$ was confirmed by HRMS (EI, 70 eV).

4q: Starting with **3o** (0.400 g, 2.81 mmol), diisopropylamine (0.51 mL, 3.66 mmol), *n*BuLi (2.3 mL, 3.66 mmol, 15% in *n*-hexane), HMPA (0.74 mL, 4.22 mmol), and 1-chloro-3-iodopropane (0.704 g , 3.38 mmol) in THF (30 mL), **4q** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 30:1) as a yellow oil (0.254 g, 41%). ^{1}H NMR

($CDCl_3$, 300 MHz): δ = 1.89 (quint, *J* = 7.2 Hz, 2 H), 2.08 (quint, *J* = 7.5 Hz, 2 H), 2.43 (t, *J* = 7.4 Hz, 2 H), 3.07 (t, *J* = 7.1 Hz, 2 H), 3.51 (t, *J* = 7.0 Hz, 2 H), 3.69 (s, 3 H), 4.23 (t, *J* = 7.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 23.7, 24.3, 31.1, 32.3, 45.0, 50.9, 71.5, 100.9, 169.3, 171.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2987 (m), 2951 (s), 2900 (m), 1704 (s), 1699 (s), 1633 (s), 1435 (s), 1374 (m), 1322 (s), 1308 (s), 1270 (s), 1236 (w), 1200 (m), 1182 (s), 1148 (s), 1109 (s), 1079 (s), 1053 (m), 1030 (w), 1008 (w), 980 (m), 903 (w), 779 (m, C–Cl). MS (EI, 70 eV): *m/z* (%) = 218 (M^+, 100), 178 (85), 183 (8). Anal. calcd. for $C_{10}H_{15}O_3Cl$ (218.68): C 54.93, H 6.91; found: C 55.23, H 6.62.

4r: Starting with **3o** (0.300 g, 2.11 mmol), diisopropylamine (0.45 mL, 3.17 mmol), *n*BuLi (2.00 mL, 3.17 mmol, 15% in *n*-hexane), HMPA (0.56 mL, 3.17 mmol), and 1-chloro-5-iodopentane (0.556 g, 2.32 mmol) in THF (17 mL), **4r** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 75:1) as a yellow oil (0.233 g, 45%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.39-1.49 (m, 4 H), 1.78 (t, *J* = 7.4 Hz), 2.07 (quint, *J* = 7.2 Hz, 2 H), 2.31 (t, *J* = 7.2 Hz, 2 H), 3.06 (t, *J* = 7.8 Hz, 2 H), 3.53 (t, *J* = 6.8 Hz, 2H), 3.69 (s, 3 H), 4.21 (t, *J* = 6.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 24.4, 25.7, 26.6, 28.3, 31.0, 32.5, 45.2, 50.8, 71.3, 102.3, 169.61, 171.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2985 (w), 2948 (s), 2861 (m), 1736 (m), 1702 (s), 1631 (s), 1436 (m), 1374 (w), 1350 (w), 1321 (m), 1306 (m), 1278 (w), 1237 (w), 1182 (m), 1133 (m), 1110 (s), 1090 (m), 1044 (m), 1011 (w), 980 (m), 935 (w). MS (EI, 70 eV): *m/z* (%) = 246 (M^+, 46), 215 (56), 211 (100). The exact molecular mass *m/z* = 246.1023 ± 2 mD [M^+] for $C_{12}H_{19}O_3Cl$ was confirmed by HRMS (EI, 70 eV).

4s: Starting with **3p** (0.200 g, 1.28 mmol), diisopropylamine (0.31 mL, 2.18 mmol), *n*BuLi (1.37 mL, 2.18 mmol, 15% in *n*-hexane), HMPA (0.34 mL, 1.92 mmol), and 1-iodohexane (0.38 mL, 2.56 mmol) in THF (17 mL), **4s** was isolated after chromatography

(silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a yellow oil (0.128 g, 42%, *E*/*Z* = 2:1). The NMR data of the major isomer are listed. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.19 (d, *J* = 8.1 Hz, 3 H), 1.27 (m, 7 H), 1.78 (m, 2 H), 2.17 (m, 1 H), 2.27 (t, *J* = 7.4 Hz, 1 H), 2.59 (t, *J* = 9.0 Hz, 1 H), 3.69 (s, 3 H), 3.73 (m, 1 H), 4.21 (m, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.1, 18.0, 22.7, 26.1, 29.3, 29.7, 31.6, 32.3, 36.4, 50.7, 69.2, 102.2, 169.2, 175.4. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2956 (s), 2928 (s), 2872 (m), 2858 (m), 1736 (m), 1702 (s), 1632 (s), 1459 (w), 1434 (w), 1376 (w), 1323 (w), 1289 (w), 1259 (w), 1247 (w), 1215 (w), 1180 (s), 1115 (s), 1078 (m), 1047 (m), 996 (w). MS (EI, 70 eV): *m/z* (%) = 240 (M^+, 100), 226 (21), 209 (49). The exact molecular mass *m/z* = 240.1725 ± 2 mD [M^+] for $C_{14}H_{24}O_3$ was confirmed by HRMS (EI, 70 eV).

4t: Starting with **3q** (0.200 g, 1.09 mmol), diisopropylamine (0.26 mL, 1.85 mmol), *n*BuLi (1.16 mL, 1.85 mmol, 15% in *n*-hexane), HMPA (0.29 mL, 1.63 mmol), and 1-iodopropane (0.371 g, 2.18 mmol) in THF (17 mL), **4t** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a yellow oil (0.093 g, 38%, *E*/*Z* = 2:1). The NMR data of the major isomer are listed. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.90 (dt, 3 H, CH_3), 0.99 (t, *J* = 7.6 Hz, 3 H), 1.13 (m, 1 H), 1.28 (t, *J* = 4.4 Hz, 3 H), 1.40 (m, 1 H), 1.74 (m, 2 H), 1.96 (m, 2 H), 2.27 (t, *J* = 8.6 Hz, 1 H), 2.59 (t, *J* = 9.4 Hz, 1 H), 3.53 (m, 1 H), 4.14 (m, 3 H), 4.26 (dt, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 12.5, 13.9, 14.4, 22.4, 28.2, 28.5, 35.9, 43.4, 59.3, 69.3, 102.5, 168.8, 174.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2963 (s), 2935 (s), 2911 (m), 2904 (w), 2874 (m), 1730 (m), 1698 (s), 1629 (s), 1463 (m), 1373 (w), 1317 (w), 1296 (m), 1262 (m), 1215 (m), 1187 (m), 1171 (w), 1140 (m), 1107 (s), 1043 (s), 1031 (m), 1021 (s), 805 (m). MS (EI, 70 eV): *m/z* (%) = 226 (M^+, 45), 197 (100), 181 (20). Anal. calcd. for $C_{13}H_{22}O_3$ (226.315): C 68.99, H 9.80; found: C 69.24, H 10.47.

4u: Starting with **3b** (0.075 g, 0.28 mmol), diisopropylamine (0.08 mL, 0.56 mmol), *n*BuLi (0.35 mL, 0.56 mmol, 15% in *n*-hexane), HMPA (0.07 mL, 0.42 mmol), and 1-iododecane (0.113 g, 0.42 mmol) in THF (10 mL), **4v** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a yellow oil (0.105 g, 92%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.0 Hz, 6 H), 1.20 – 1.45 (m, 26 H), 1.48 (s, 9 H), 1.89 – 1.95 (dd, *J* = 6.0 Hz, 1 H), 2.00 – 2.13 (m, 1 H), 2.23 (t, *J* = 7.5 Hz, 2 H), 3.55 – 3.61 (m, 1 H), 4.05 – 4.15 (m, 1 H), 4.22 (dt, *J* = 5.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 14.1, 22.6, 22.7, 26.7, 27.9, 27.9, 28.4, 28.9, 29.4, 29.4, 29.6, 29.7, 31.8, 31.9, 32.4, 41.5, 68.9, 78.8, 104.2, 168.1, 173.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2958 (s), 2926 (s), 2856 (m), 1695 (s), 1632 (m), 1461 (w), 1176 (w), 1158 (w), 1111 (s), 1076 (w), 1047 (w), 1026 (w). MS (EI, 70 eV): *m/z* (%) = 408 (M^+, 14), 352 (100), 335 (21).

4v: Starting with **3k** (0.110 g, 0.64 mmol), diisopropylamine (0.18 mL, 1.28 mmol), *n*BuLi (0.80 mL, 1.28 mmol, 15% in *n*-hexane), HMPA (0.17 mL, 0.96 mmol), and 1-iodohexane (0.14 ml, 0.96 mmol) in THF (15 mL), **4v** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 10:1) as a dark yellow oil (0.122 g, 74%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.25 – 1.31 (m, 6 H), 1.36 – 1.42 (m, 2 H), 1.93 – 2.05 (m, 1 H), 2.17 – 2.23 (m, 1 H), 2.32 (t, *J* = 7.8 Hz, 2 H), 3.40 (s, 3 H), 3.72 (s, 3 H), 4.22 – 4.30 (m, 2 H), 5.11 (d, *J* = 4.5 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 14.3, 22.9, 26.6, 29.2, 29.5, 31.4, 31.9, 51.3, 57.3, 69.9, 77.9, 106.9, 167.3, 169.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2958 (s), 2929 (s), 2858 (w), 1707 (s), 1644 (s), 1462 (w), 1438 (w), 1260 (m), 1174 (m), 1116 (s), 1099 (s), 1020 (m), 803 (w). MS (EI, 70 eV): *m/z* (%) = 256 (M^+, 50), 241 (12), 225 (30), 209 (100), 197 (13), 165 (12).

4w: Starting with **3f** (0.300 g, 1.18 mmol), diisopropylamine (0.33 mL, 2.36 mmol), *n*BuLi (1.48 mL, 2.36 mmol, 15% in *n*-hexane), HMPA (0.31 mL, 1.77 mmol), and 1-iodohexane (0.26 ml, 1.77 mmol) in THF (20 mL), **4w** was isolated by chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 50:1) as a yellow oil. The starting material could not be completely removed (**4w**/**3f** = 3.3:1). The mixture amounts to 0.386 g which corresponds to 0.296 g of product and a 74% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.87 – 0.91 (m, 9 H), 1.23 – 1.37 (m, 12 H), 1.48 (s, 9 H), 1.43 – 1.63 (m, 2 H), 1.88 – 1.97 (m, *J* = 6.3 Hz, 1 H), 2.01 - 2.14 (m, 1 H), 2.24 (t, *J* = 7.8 Hz, 1 H), 3.51 – 3.61 (m, *J* = 4.5 Hz, 1 H),4.05 – 4.14 (m, 1 H), 4.24 (tt, *J* = 9.0, 1.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 22.4, 26.6, 28.4, 28.6, 28.9, 29.3, 29.9, 30.3, 31.8, 37.1, 41.6, 68.9, 78.8, 104.2, 168.1, 173.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2959 (s), 2928 (s), 2869 (m), 1696 (s), 1638 (s), 1461 (w), 1385 (w), 1369 (w), 1253 (m), 1172 (m), 1109 (s), 1049 (m), 1019 (m). MS (EI, 70 eV): *m/z* (%) = 338 (M^+, 17), 282 (100), 265 (23).

4x: Starting with **3r** (0.300 g, 1.95 mmol), diisopropylamine (0.68 mL, 4.87 mmol), *n*BuLi (3.06 mL, 4.87 mmol, 15% in *n*-hexane), HMPA (0.51 mL, 2.92 mmol), and benzylbromide (0.35 mL, 2.92 mmol) in THF (20 mL), **4x** was isolated after chromatography (silica gel, *n*-hexane → *n*-hexane/EtOAc = 1:1) as a white solid (0.172 g, 36%, *E*/*Z* = 2:1). The NMR data of the major isomer are listed. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.04-2.11 (m, 2 H), 2.87-2.94 (m, 2 H), 3.15-3.18 (d, *J* = 7.8 Hz, 2 H), 3.25-3.56 (m, 1 H), 4.02-4.11 (m, 2 H), 4.22-4.40 (m, 2 H), 7.07-7.26 (m, 5 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 25.5, 34.5, 39.1, 45.8, 65.3, 71.1, 94.6, 125.9, 182.3, 129.2, 140.9, 172.1, 172.6. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3060 (w), 3029 (w), 2972 (w), 2911 (w), 2862 (w), 1732 (s), 1665 (s), 1496 (w), 1453 (w), 1373 (w), 1256 (s), 1235 (w), 1220 (w), 1196 (w), 1187 (w), 1070 (w), 1051 (m), 1013 (m), 755 (w),

702 (m). MS (EI, 70 eV): *m/z* (%) = 244 (M^+, 100). The exact molecular mass *m/z* = 244.1099 ± 2 mD [M^+] for $C_{14}H_{24}O_3$ was confirmed by HRMS (EI, 70 eV).

Please note that the structures attached to the spectra are always drawn as the *E*-configured isomers. The true configurations for all individual compounds you will find in Tables 1 and 2 of the manuscript.