Conjugate Addition of Mixed Organozinc Compounds and Functionalized Organozinc Cuprates to Nitroolefins

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Supporting Information

General remarks:

^1H NMR and ^{13}C NMR spectra were recorded on a Gemini 200 (Varian) spectrometer (^1H : 200 MHz, ^{13}C : 50 MHz), Gemini 2000 (Varian) spectrometer (^1H : 200 MHz, ^{13}C : 50 MHz, ^{31}P : 81 MHz) or on an AC 250-P (Bruker) spectrometer (^1H : 250 MHz, ^{13}C : 63 MHz). NMR spectra were recorded using solutions in deuterated chloroform (CDCl_3), with TMS as the internal standard, and shift values are reported in parts per million (ppm). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were collected on a FT/IR-410 (Jasco) spectrometer from the neat oil film (sodium chloride plates) or from a solid in potassium bromide pellet. Peaks are reported in cm^{-1} with following abbreviations for signal intensity: s, strong; m, medium; w, weak; br., broad. Mass spectra were recorded on GCMS-QP5050A (Shimadzu) gas chromatograph/mass spectrometer using a HP-5MS (25 m, 0.25 mm ID, 0.33 μm , Hewlett Packard) column. Isobutane was used as reagent gas for CI measurements. Elemental analyses were performed on CHNS-932 (Leco) apparatus. Capillary gas chromatography was performed on a GC-17A (Shimadzu) gas chromatograph using a HP-5MS (25 m, 0.25 mm ID, 0.33 μm , Hewlett Packard) column. Analytical TLC was performed on silica gel plates 60 F₂₅₄ (Merck); compounds were visualized by illumination with UV light, staining with iodine or dipping the plates in a cerium sulfate-ammonium molybdate solution, followed by heating. Flash column chromatography was carried out with silica gel 60 (40-63 μm) from Merck. Melting points were measured on Melting Point B-540 (Büchi) apparatus and are uncorrected.

All reactions were performed under an inert atmosphere (argon or nitrogen). Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl immediately prior to use. Petrol ether (PE, 30-60 °C boiling point fraction) and ethyl acetate (EtOAc) were used for flash chromatography and were distilled over CaCl_2 . The following compounds were commercially available and used without further purification: diethylzinc (Fluka), zinc powder (-100 mesh, 99.998 % purity, Aldrich); copper(II) triflate (Aldrich), trimethylsilylmethylolithium solution (1 M in pentane; Fluka), trimethylsilyl bromide (Acros). Anhydrous LiCl (Aldrich) was dried with a heatgun at 0.01 mbar before use.

Trimethylsilyl chloride, dibromoethane and 1-methyl-2-pyrrolidone (NMP) were distilled prior to use.

General experimental procedure for conjugate addition of alkyl(trimethylsilylmethyl)zinc compounds to nitroolefins:

1,2-Dibromoethane (0.07 mL, 0.8 mmol) was added dropwise to a stirred mixture of zinc dust (0.52 g, 8.0 mmol) in THF (2.5 mL) at RT under argon, whilst heating with a heat gun to boil the solvent gently. After ca. 1 min the reaction mixture foams and the heating is interrupted. After 1-3 min, this heating-cooling procedure is repeated two more times. Upon complete addition the mixture was cooled to RT and then trimethylsilyl chloride (0.07 mL, 0.55 mmol) was added dropwise over 5 min, again with gentle heating. After complete addition, the mixture was stirred at RT for further 5 min. THF solutions (1.5 mL) of the appropriate iodo derivative (2.0 mmol) and of dodecane (ca. 0.4 mL) as internal standard for GC analysis were added dropwise over 5 min, and then the reaction was stirred at 50 °C for 2-4 h. The zinc insertion reaction was monitored by GC analysis. When the reaction was complete, the reaction mixture was cooled to RT and the excess zinc dust allowed to settle for 15 min. The pale grey solution was transferred to a flame dried flask that contained a solution of copper salt (0.05 mmol, 5 mol % referring to nitroolefin) in THF (2.0 mL) cooled to -40 °C. A solution of trimethylsilylmethyl lithium (1 M in pentane, 2.0 mL, 2.0 mmol,) was added dropwise to the zinc iodide solution. and then stirred at -40 °C for 1 h. NMP (0.33 mL, 3.4 mmol), trimethylsilyl bromide (0.35 mL, 2.7 mmol) and then nitroolefin (1.1 mmol) in THF (1.5 mL) were subsequently added dropwise at -40 °C. The reaction was allowed to warm up to -30 °C, stirred at this temperature for 3 h and finally allowed to warm up slowly to RT overnight. The reaction mixture was poured into saturated ammonium chloride solution (10 mL) and stirred at RT for 10 min. The resulting solution was extracted with diethyl ether (3×30 mL). The combined extracts were washed with brine (30 mL), dried (MgSO₄) and concentrated *in vacuo*. The crude residue was purified by column chromatography.

(1-Cyclohexyl-2-nitroethyl)-benzene (4a)

White crystals

Melting point:

64-65 °C

Molecular weight:

233.31 (C₁₄H₁₉NO₂)

Yield:

174 mg (70 %)

¹H-NMR (200 MHz, CDCl₃):

δ=0.77-1.88 (11H, m); 3.27 (1H, ddd, *J*=9.9 Hz, 8.0 Hz, 5.9 Hz); 4.62 (1H, dd, *J*=12.3 Hz, 9.9 Hz); 4.80 (1H, dd, *J*=12.3 Hz, 5.9 Hz); 7.06-7.43 (5H, m)

¹³C-NMR (50 MHz, CDCl₃):

δ=26.5, 31.0, 31.4, 41.3, 50.7, 79.3, 127.9, 128.7, 129.1, 139.3

MS: EI: m/z=186 (24 %); 105 (17 %); 104 (100 %); 91 (23 %); 83 (20 %); 55 (50 %); 41 (24 %)

IR (KBr): $\tilde{\nu}$ =2915 (s), 2852 (s), 1548 (s), 1442 (s), 1380 (s), 755 (s), 700 (s)

R_f: 0.37 (PE + 5 % Et₂O)

Elemental analysis (%): Calcd.: C 72.07; H 8.21; N 6.00
Found: C 72.32; H 7.91; N 5.98

(E)-(2-Cyclohexylethenyl)-benzene (5a)

Colourless oil

Molecular weight: 186.30 (C₁₄H₁₈)

Yield: 50 mg (28 %)

¹H-NMR (200 MHz, CDCl₃): δ =1.08-1.95 (10H, m); 2.18 (1H, m); 6.22 (1H, dd, *J*=6.6 Hz, 16.1 Hz); 6.40 (1H, d, *J*=16.1 Hz); 7.14-7.47 (5H, m)

¹³C-NMR (50 MHz, CDCl₃): δ =26.6, 26.7, 33.5, 41.7, 126.5, 127.2, 127.8, 129.0, 137.3, 138.6

MS: EI: m/z=186 (24 %); 129 (27 %); 128 (23 %); 117 (10 %); 115 (23 %); 105 (11 %); 104 (100 %); 91 (20 %)

IR (neat): $\tilde{\nu}$ =3025 (s), 2924 (s), 2850 (s), 1492 (m), 1446 (s), 963 (s), 742 (s), 692 (s)

R_f: 0.60 (PE)

1-Nitro-2-phenylnonane (4b)

Light yellow oil

Molecular weight: 249.36 (C₁₅H₂₃NO₂)

Yield: 64 % (106 mg)

¹H-NMR (250 MHz, CDCl₃): δ =0.86 (3H, m); 1.11-1.35 (10H, m); 1.60-1.73 (2H, m); 3.44 (1H, m); 4.47-4.61 (2H, m); 7.13-7.41 (5H, m)

¹³C-NMR (63 MHz, CDCl₃): δ=14.0, 22.6, 26.9, 29.0, 29.3, 31.7, 33.1, 44.4, 81.1, 127.5, 127.6, 128.8, 128.9, 129.0, 139.6

MS: CI: m/z=273 (13 %); 272 (69 %); 219 (11 %); 218 (16 %); 217 (21 %); 216 (100 %); 214 (35 %); 203 (16 %); 189 (28 %)

IR (neat): $\tilde{\nu}$ =2927 (s), 2856 (m), 1554 (s), 1454 (w), 1376 (m), 1056 (w), 763 (w), 701 (m)

R_f: 0.33 (PE + 2 % Et₂O)

(*E*)-1-Phenyl-1-nonene (5b)

Colourless oil

Molecular weight: 202.34 (C₁₅H₂₂)

Yield: 43 % (176 mg)

¹H-NMR (250 MHz, CDCl₃): δ=0.89 (3H, t, *J*=7.0 Hz); 1.17-1.36 (8H, m); 1.32-1.57 (2H, m); 2.21-2.27 (2H, m); 6.22 (1H, dt, *J*=15.8 Hz, 6.6 Hz); 6.38 (1H, d, *J*=15.8 Hz); 7.12-7.40 (5H, m)

¹³C-NMR (63 MHz, CDCl₃): δ=14.1, 22.7, 29.2, 29.4, 29.7, 31.9, 33.1, 125.9, 126.7, 128.5, 129.7, 131.3, 138.0

MS: CI: m/z=246 (2 %); 245 (14 %); 204 (15 %); 203 (100 %); 202 (43 %); 201 (19 %); 190 (12 %); 189 (81 %); 175 (7 %); 141 (9 %); 133 (13 %); 119 (14 %); 117 (19 %); 105 (26 %)

IR (neat): $\tilde{\nu}$ =2954 (m), 2923 (s), 2854 (m), 1461 (w), 964 (w)

R_f: 0.60 (PE)

Elemental analysis (%): Calcd.: C 89.04; H 10.96

Found: C 88.97; H 11.15

2-Phenyl-1-nitrohexane (4c)

Light yellow oil

Molecular weight: 207.27 (C₁₂H₁₇NO₂)

Yield: 180 mg (72 %)

¹H-NMR (200 MHz, CDCl₃): δ=0.84 (3H, t, *J*=6.6 Hz); 1.05-1.41 (4H, m); 1.60-1.79 (2H, m); 3.44 (1H, m); 4.55 (2H, m); 7.13-7.41 (5H, m)

¹³C-NMR (50 MHz, CDCl₃): δ=14.2, 22.8, 29.4, 33.1, 44.8, 81.5, 128.0, 128.0, 129.4, 140.1
 MS: EI: m/z=160 (17 %); 119 (10 %); 118 (100 %); 117 (14 %); 105 (11 %); 104 (23 %); 91 (55 %)
 IR (neat): $\tilde{\nu}$ =2960 (m), 2931 (m), 2859 (m), 1552 (s), 1454 (m), 1378 (m), 763 (m), 700 (s)
 R_f: 0.47 (PE:EtOAc / 15:1)
 Elemental analysis (%): Calcd.: C 69.54; H 8.27; N 6.76
 Found: C 69.59; H 8.17; N 6.79

2-Cyclohexyl-1,1-dimethoxy-3-nitropropane (4d)

Light yellow oil
 Molecular weight: 231.29 (C₁₁H₂₁NO₄)
 Yield: 64 mg (45 %)
¹H-NMR (200 MHz, CDCl₃): δ=0.82-1.84 (11H, m); 2.53 (1H, m); 3.34 (3H, s); 3.36 (3H, s); 4.29 (1H, dd, *J*=13.5 Hz, 5.6 Hz); 4.35 (1H, d, *J*=4.8 Hz); 4.51 (1H, dd, *J*=13.5 Hz, 6.4 Hz)
¹³C-NMR (50 MHz, CDCl₃): δ=26.7, 26.8, 26.9, 30.0, 31.1, 37.6, 45.8, 54.8, 56.0, 74.3, 105.4
 MS: EI: m/z=153 (5 %); 75 (100 %); 71 (10 %); 55 (9 %); 47 (11 %); 41 (13 %)
 IR (neat): $\tilde{\nu}$ =2927 (s), 2852 (s), 1554 (s), 1448 (m), 1380 (m), 1205 (m), 1130 (m), 1068 (s), 966 (m), 732 (m)
 R_f: 0.35 (PE:EtOAc / 15:1)
 Elemental analysis (%): Calcd.: C 57.12; H 9.15; N 6.06
 Found: C 57.18; H 9.04; N 6.03

1,1-Dimethoxy-2-(nitromethyl)nonane (4e)

Colourless oil

Molecular weight: 247.34 (C₁₂H₂₅NO₄)

Yield: 72 % (120 mg)

¹H-NMR (250 MHz, CDCl₃): δ=0.88 (3H, t, *J*=6.6 Hz); 1.19-1.41 (10H, m); 1.57 (2H, m); 2.53 (1H, m); 3.39 (3H, s); 3.40 (3H, s); 4.28 (1H, d, *J*=4.9 Hz); 4.29 (1H, dd, *J*=12.9 Hz, 6.6 Hz); 4.54 (1H, dd, *J*=12.8 Hz, 5.8 Hz)

¹³C-NMR (63 MHz, CDCl₃): δ=14.1, 22.6, 26.7, 27.7, 29.1, 29.6, 31.8, 40.9, 54.9, 56.1, 75.6, 105.8

MS: CI: *m/z*=216 (32 %); 214 (54 %); 182 (26 %); 170 (11 %); 169 (100 %)

IR (neat): $\tilde{\nu}$ =2929 (s); 2858 (s); 1554 (s); 1466 (m); 1381 (s); 1190 (m); 1117 (s); 1072 (s); 970 (w); 723 (w)

R_f: 0.23 (PE + 5 % Et₂O)

Elemental analysis (%): Calcd.: C 58.27; H 10.19; N 5.66

Found: C 58.54; H 10.28; N 5.61

Methyl 2-(Nitromethyl)nonanoate (4f)

Colourless oil

Molecular weight: 231.29 (C₁₁H₂₁NO₄)

Yield: 46 % (80 mg)

¹H-NMR (250 MHz, CDCl₃): δ=0.88 (3H, t, *J*=6.9 Hz); 1.14-1.48 (9H, m); 1.46-1.78 (3H, m); 3.20 (1H, m); 3.75 (3H, s); 4.41 (1H, dd, *J*=14.2, 4.9); 4.73 (1H, dd, *J*=14.2, 9.2)

¹³C-NMR (63 MHz, CDCl₃): δ=14.0, 22.6, 26.6, 28.9, 29.2, 29.3, 31.7, 43.0, 52.3, 75.2, 172.8

MS: CI: *m/z*=255 (5 %); 254 (34 %); 233 (4 %); 232 (29 %); 200 (65 %); 198 (59 %); 196 (16 %); 186 (16 %); 185 (100 %); 173 (28 %); 142 (82 %); 141 (11 %); 140 (34 %)

IR (neat): $\tilde{\nu}$ =2959 (w), 2926 (m), 2856 (m), 1739 (s), 1559 (s), 1438 (m), 1379 (s), 1251 (w), 1203 (w), 1174 (w)

R_f: 0.35 (PE:EtOAc / 10:1)

Elemental analysis (%): Calcd.: C 57.12; H 9.15; N 6.06

Found: C 57.82; H 9.09; N 5.72

Methyl 2-Cyclohexyl-3-nitropropanoate (4g)

Colourless oil

Molecular weight: 215.25 (C₁₀H₁₇NO₄)

Yield: 69 % (453 mg)

¹H-NMR (250 MHz, CDCl₃): δ=0.97-1.36 (5H, m); 1.59-1.84 (6H, m); 3.11 (1H, m); 3.74 (3H, s); 4.44 (1H, dd, *J*=14.6 Hz, 4.0 Hz); 4.79 (1H, dd, *J*=14.6 Hz, 10.5 Hz)

¹³C-NMR (63 MHz, CDCl₃): δ=25.9, 26.1, 26.2, 30.4, 30.5, 38.5, 48.7, 52.2, 73.9, 172.4

MS: CI: *m/z*=215 (19 %); 183 (53 %); 181 (55 %); 179 (19 %); 168 (79 %); 156 (69 %); 125 (100 %); 123 (68 %); 121 (39 %); 111 (17 %); 109 (17 %)

IR (neat): $\tilde{\nu}$ =2931 (s), 2854 (m), 1735 (s), 1558 (s), 1438 (m), 1376 (m), 1253 (w), 1203 (m), 1172 (w), 1041 (w)

R_f: 0.45 (PE:EtOAc / 10:1)

Methyl 2-(Nitromethyl)octanoate (4h)

Colourless oil

Molecular weight: 217.26 (C₁₀H₁₉NO₄)

Yield: 56 % (131 mg)

¹H-NMR (250 MHz, CDCl₃): δ=0.88 (3H, t, *J*=6.9 Hz); 1.17-1.42 (8H, m); 1.46-1.79 (2H, m); 3.19 (1H, m); 3.75 (3H, s); 4.42 (1H, dd, *J*=14.3 Hz, 4.9 Hz); 4.74 (1H, dd, *J*=14.3 Hz, 9.5 Hz)

¹³C-NMR (50 MHz, CDCl₃): δ=14.0, 22.5, 26.6, 28.9, 29.3, 31.5, 42.9, 52.4, 75.2, 172.8

MS: CI: *m/z*=241 (1 %); 240 (13 %); 219 (13 %); 218 (100 %); 186 (23 %); 184 (14 %); 173 (11 %); 172 (10 %); 171 (36 %); 139 (7 %); 128 (5 %)

IR (neat): $\tilde{\nu}$ =2954 (m), 2931 (m), 2858 (m), 1739 (s), 1558 (s), 1438 (m), 1380 (m), 1253 (w), 1203 (m), 1176 (m), 1049 (w)

R_f: 0.35 (PE:EtOAc / 10:1)

Elemental analysis (%): Calcd.: C 55.28; H 8.81; N 6.45

Found: C 55.07; H 8.95; N 6.76

General experimental procedure for conjugate addition of transmetallated functionalized diorganozinc compounds to nitroolefins:

A mixture of an iodo derivative (4.7 mmol) and neat diethylzinc (2.95 g, 23.9 mmol) was stirred at 50 °C for 14 h (reaction monitoring by GC of hydrolyzed reaction aliquots). The ethyl iodide formed, and excess diethylzinc were removed *in vacuo* (35 °C, 1 h, ca. 0.01 mbar). The resulting oil was dissolved in dry THF (4 mL) and added to a THF solution (5 mL) of copper(I) cyanide (211 mg, 2.4 mmol) and lithium chloride (199 mg, 4.7 mmol) at -20 °C. The resulting light-green solution was cooled to -78 °C, and trimethylsilyl chloride (598 mg, 5.5 mmol) followed by a solution of nitroolefin (2.3 mmol) in THF (1.5 mL) was added dropwise. The reaction mixture was slowly allowed to warm up to -10 °C overnight. Then ether was added (20 mL) and the mixture was quenched with saturated ammonium chloride solution (10 mL). The aqueous layer was extracted with ether (2×10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO₄), and filtered. The solvent was evaporated, and the residual oil was purified by flash chromatography to afford the product.

6-Nitro-5-phenylhexanenitrile (9a)

Colourless oil

Molecular weight: 218.25 (C₁₂H₁₄N₂O₂)

Yield: 67 % (196 mg)

¹H-NMR (250 MHz, CDCl₃): δ=1.38-1.71 (2H, m); 1.72-1.98 (2H, m); 2.29 (2H, t, *J*=7.0 Hz); 3.48 (1H, m); 4.57 (2H, d, *J*=7.6 Hz); 7.07-7.52 (5H, m)

¹³C-NMR (63 MHz, CDCl₃): δ=17.0, 23.0, 31.9, 43.8, 80.6, 119.3, 127.5, 128.2, 129.3, 138.1

MS: EI: *m/z*=184 (19 %); 158 (10 %); 132 (30 %); 130 (42 %); 118 (44 %); 117 (54 %); 116 (91 %); 115 (24 %); 104 (31 %); 103 (36 %); 91 (100 %); 90 (21 %); 89 (49 %); 78 (28 %); 77 (39 %); 65 (24 %); 51 (24 %); 41 (22 %); 39 (27 %)

IR (neat): $\tilde{\nu}$ =2937 (w), 2246 (w), 1550 (s), 1454 (w), 1430 (w), 1380 (m), 1043 (w), 763 (w), 701 (w)

R_f: 0.77 (PE:EtOAc / 3:1)

Elemental analysis (%): Calcd.: C 66.04; H 6.47; N 12.84

Found: C 66.12; H 6.23; N 12.79

Methyl 5-Cyano-2-(nitromethyl)pentanoate (9b)

Colourless oil

Molecular weight: 200.19 (C₈H₁₂N₂O₄)

Yield: 66 % (310 mg)

¹H-NMR (250 MHz, CDCl₃): δ=1.56-1.94 (4H, m); 2.41 (2H, t, *J*=6.6 Hz); 3.23 (1H, m); 4.46 (1H, dd, *J*=14.3 Hz, 5.2 Hz); 4.76 (1H, dd, *J*=14.3 Hz, 8.6 Hz)

¹³C-NMR (63 MHz, CDCl₃): δ=17.0, 22.9, 28.2, 42.3, 52.7, 75.1, 118.6, 171.7

MS: CI: *m/z*=202 (10 %); 201 (100 %); 169 (41 %); 154 (11 %); 122 (27 %)

IR (neat): $\tilde{\nu}$ =2956 (s), 2246 (m), 1735 (s), 1560 (s), 1436 (s), 1380 (s), 1207 (s), 1058 (m), 970 (m), 736 (w)

R_f: 0.48 (PE:EtOAc / 2:1)

Elemental analysis (%): Calcd.: C 48.00; H 6.04; N 14.00

Found: C 48.17; H 5.98; N 13.88

1-Methyl 6-Ethyl 2-(Nitromethyl)hexanedioate (9c)

Colourless oil

Molecular weight: 247.25 (C₁₀H₁₇NO₆)

Yield: 53 % (150 mg)

¹H-NMR (250 MHz, CDCl₃): δ=1.26 (3H, t, *J*=7.1 Hz); 1.56-1.80 (4H, m); 2.34 (2H, t, *J*=6.9 Hz); 3.23 (1H, m); 3.76 (3H, s); 4.13 (2H, q, *J*=7.1 Hz); 4.46 (1H, dd, *J*=14.3 Hz, 4.9 Hz); 4.76 (1H, dd, *J*=14.3 Hz, 9.2 Hz)

¹³C-NMR (63 MHz, CDCl₃): δ=14.2, 22.0, 28.6, 33.6, 42.7, 52.5, 60.6, 75.0, 172.4, 172.8

MS: CI: *m/z*=249 (15 %); 248 (100 %); 214 (8 %); 203 (6 %); 202 (9 %); 201 (37 %); 169 (6 %); 155 (8 %)

IR (neat): $\tilde{\nu}$ =2958 (m), 1735 (s), 1558 (s), 1438 (w), 1378 (m), 1203 (m), 1180 (m), 1031 (m)

R_f: 0.16 (PE:EtOAc / 6:1)

Elemental analysis (%): Calcd.: C 48.58; H 6.93; N 5.67

Found: C 48.56; H 6.84; N 5.67

General experimental procedure for conjugate addition of dimyrtanzylzinc (10) to nitroolefins:

Trimethylsilyl chloride (0.19 mL, 1.53 mmol) was added dropwise at $-30\text{ }^{\circ}\text{C}$ to a solution of nitroolefin (1.53 mmol) and copper(II) triflate (29 mg, 0.08 mmol, 5 mol % referring to nitroolefin) in THF (5 mL). The mixture was stirred for 10 min, and a solution of dimyrtanzylzinc¹ **10** (ca. 3.5 mmol, ca. 1 M solution in THF) was added dropwise. The mixture was stirred for 4 h at $-30\text{ }^{\circ}\text{C}$, diluted with THF (10 mL) and aqueous HCl solution (10 %, 5 mL) was added and stirring was continued for 15 min. The mixture was poured into a mixture containing ether (100 mL) and saturated aqueous NH_4Cl (50 mL), stirred for 20 min and filtered over Celite[®]. The layers were separated. The aqueous layer was washed with ether (2×30 mL). The combined organic layers were washed with brine (30 mL), dried (MgSO_4) and filtered. The solvent was evaporated, and the residual oil was purified by flash chromatography to afford the product.

(1*S*,2*S*,5*S*)-6,6-Dimethyl-2-(3'-nitro-2'-phenylpropyl)bicyclo[3.1.1]heptane (12a)

Colourless oil (mixture of diastereomers 1:1)

Molecular weight: 287.40 ($\text{C}_{18}\text{H}_{25}\text{NO}_2$)

Yield: 74 % (325 mg)

¹H-NMR (500 MHz, CDCl_3): δ =0.98 (6H, s); 1.13 (3H, s); 1.20 (3H, s); 1.36 (1H, m); 1.53 (1H, m); 1.64-1.98 (18H, m); 2.22 (1H, m); 2.29 (1H, m); 3.47-3.57 (2H, m); 4.45-4.57 (4H, m); 7.15-7.21 (4H, m); 7.23-7.29 (2H, m); 7.30-7.36 (4H, m)

¹³C-NMR (126 MHz, CDCl_3): δ =21.3, 22.8; 23.2, 23.4; 26.2, 26.3; 28.0, 28.1; 33.3, 33.6; 37.6, 38.0; 38.6, 38.7; 40.4, 40.7; 41.2, 41.3; 42.3, 42.4; 44.7, 47.3; 81.1, 81.4; 127.5, 127.7, 128.9, 139.2, 139.7

MS: CI: m/z =309 (18 %); 255 (18 %); 254 (20 %); 253 (100 %); 131 (10 %); 110 (11 %)

IR (neat): $\tilde{\nu}$ =2910 (s), 1552 (s), 1495 (w), 1468 (w), 1454 (w), 1378 (m), 762 (m), 700 (m)

R_f: Both diastereomers: 0.71 (PE:EtOAc / 10:1)

Elemental analysis (%): Calcd.: C 75.22; H 8.77; N 4.84

Found: C 75.32; H 9.19; N 4.84

Ethyl 3-((1'S,2'S,5,5'S)-6',6'-Dimethylbicyclo[3.3.1]hept-2'-yl)-2-(nitromethyl)propanoate (12b)

Colourless oil (mixture of diastereomers 1:1)

Molecular weight: 269.34 (C₁₄H₂₃NO₄).

Yield: 89 % (368 mg)

¹H-NMR (250 MHz, CDCl₃): δ=0.99 (2 signals, 6H, s); 1.19 (6H, s); 1.39-1.50 (2H, m); 1.54-1.63 (2H, m); 1.63-2.09 (16H, m); 2.30-2.41 (2H, m); 3.18-3.29 (2H, m); 3.74 (3H, s), 3.75 (3H, s); 4.40 (1H, dd, *J*=14.3 Hz, 10.4 Hz), 4.41 (1H, dd, *J*=14.3 Hz, 10.1 Hz); 4.70 (1H, dd, *J*=14.4 Hz, 2.5 Hz), (1H, dd, *J*=14.4 Hz, 2.5 Hz)

¹³C-NMR (126 MHz, CDCl₃): δ=22.0, 22.1; 23.2; 26.2; 28.0; 33.4, 33.5; 36.8, 37.1; 38.5, 38.5; 38.6, 38.6; 41.2, 41.2; 41.4, 41.5; 45.8, 46.2; 52.4, 52.5; 75.2, 75.7; 173.1, 173.2

MS: EI: *m/z*=234 (4 %); 82 (34 %); 81 (33 %); 79 (32 %); 69 (100 %); 67 (87 %); 55 (91 %); 41 (94 %); 18 (61 %); 15 (37 %)

R_f: Both diastereomers: 0.28 (PE:Et₂O / 10:1)

IR (neat): $\tilde{\nu}$ =2912 (s, br.), 1736 (s), 1558 (s), 1439 (m), 1379 (m), 1248 (m), 1203 (m), 1174 (m)

Elemental analysis (%): Calcd.: C 62.43; H 8.61; N 5.20

Found: C 62.47; H 8.70; N 5.34

Experimental procedure for conjugate addition of bis[2-(ethoxycarbonyl)ethyl]zinc (11) to nitrostyrene:

Ethyl 4-Phenyl-5-nitropentanoate (13)

305 mg of anhydrous zinc chloride (ca. 2.24 mmol) were heated to the melting point *in vacuo* (ca. 0.01 mbar). The residue was weighed (285 mg, 2.09 mmol), ether (9 mL) was added, and the mixture was sonicated until dissolution of the salt. 1-Ethoxy-1-(trimethylsilyloxy)cyclopropane² (0.91 g, 5.22 mmol) was added, and the mixture was stirred for 4 h at RT. About 6-7 mL of ether were removed under reduced pressure, and the residual solution was diluted with 8 mL of hexane. The supernatant liquid was separated, and the solvent was removed *in vacuo* to give bis[2-(ethoxycarbonyl)ethyl]zinc **11** as an oil. Ether (3 mL) was added, and the mixture was added dropwise at -40 °C to a solution of nitrostyrene (155 mg, 1.04 mmol) and copper(II) triflate (8 mg, 0.02 mmol, 2 mol % referring to nitroolefin) in ether (5 mL). The reaction mixture was

allowed to warm up to 0 °C overnight. It was diluted with ether (20 mL) and quenched by addition of a saturated aqueous NH₄Cl solution (20 mL). The aqueous layer was extracted with ether (3×30 mL). The combined organic layers were washed with brine (20 mL), dried (MgSO₄), and filtered. The solvent was evaporated, and the residual oil was purified by flash chromatography (pure PE) to afford the product.

Colourless oil

Molecular weight: 251.28 (C₁₃H₁₇NO₄)

Yield: 65 % (170 mg)

¹H-NMR (250 MHz, CDCl₃): δ=1.21 (3H, t, *J*=7.2 Hz); 1.88-2.24 (4H, m); 3.49 (1H, m); 4.08 (2H, q, *J*=7.2 Hz); 4.51-4.64 (2H, m); 7.12-7.43 (5H, m)

¹³C-NMR (63 MHz, CDCl₃): δ=14.2, 28.1, 31.7, 43.7, 60.6, 80.6, 127.6, 128.0, 129.1, 138.3, 172.5

MS: CI: *m/z*=252 (10 %); 219 (14 %); 218 (100 %); 172 (11 %)

IR (neat): $\tilde{\nu}$ =2981 (w), 1731 (s), 1552 (s), 1454 (m), 1378 (m), 1182 (m), 1159 (m), 1037 (m), 765 (w), 701 (m)

R_f: 0.35 (PE:EtOAc / 7:1)

Elemental analysis (%): Calcd.: C 62.14; H 6.82; N 5.57

Found: C 62.19; H 6.89; N 5.60

(1) For synthesis of dimyrtanylzinc, see: (a) Langer, F.; Devasagayaraj, A.; Chavant, P.-Y.; Knochel, P. *Synlett* **1994**, 410. (b) The Practical Approach in Chemistry Series, Knochel, P.; Jones, P.; Langer, F.; *Organozinc reagents : a practical approach*; Knochel, P.; Jones, P.; Eds.; Oxford: University Press; 1999, P. 167-168.

(2) For synthesis of 1-ethoxy-(1-trimethylsilyloxy)cyclopropane, see: Rühlmann, K.; *Synthesis* **1971**, 5, 236-253.