



Supporting Information

for

Diastereo- and enantioselective preparation of cyclopropanol derivatives

Marwan Simaan and Ilan Marek

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Experimental part

Unless stated otherwise, all glasswares were flame dried under vacuum, and cooled under argon prior to use. All reactions were carried out under positive pressure of argon. Thin-layer chromatography (TLC) was performed using Merck[®] silica gel 60 F254 plates. Column chromatography was performed using Bio-Lab silica gel 60A (0.040–0.063mm). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker[®] spectrometers DPX200, AV300 or AVIII400, AV500 and AV600 using CDCl₃ (unless otherwise specified) as solvent. Chemical shifts are reported in parts per million (ppm) with respect to the residual solvent signal CDCl₃ (¹H NMR: δ = 7.24 ppm; ¹³C NMR: δ = 77.16 ppm). Peak multiplicities are reported as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, m = multiplet. app = apparent, “bs” stands for broad singlet and “ABsyst” for AB system. HPLC chromatograms were recorded using Agilent[®] 1100 Series line with CHIRAL PAK[®] AD-H, CHIRALCEL[®] IA, CHIRALCEL[®] OD, CHIRALCEL[®] OC-H and CHIRAL PAK[®] AZ-H. [α]_D data were recorded using SCHMIDT and HAENSCH[®] Unipol L1000. Melting points were performed using Stuart Scientific SMP10 series. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F₂₅₄ pre-coated plates (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with anisaldehyde, phosphomolybdic acid, or potassium permanganate. Column chromatography was performed using Fluka silica gel 60 Å (40–63mm, 230–400 mesh). High-resolution mass spectra (HRMS) were obtained by the mass spectrometry facility at the Technion.

Reagents and materials

All solvents were purified and dried prior to use, dichloromethane was distilled from CaH₂, Ether and THF were dried from Pure-Solv[®] Purification System (Innovative Technology[®]). Copper cyanide, rhodium acetate dimer, rhodium proline dimer, Cu(MeCN)₄PF₆, (*R,S*)-JOSIPHOS), butyllithium (1.6 M in hexane), *tert* butyl hydroperoxide (5.5 M in nonane), chloroform-D were purchased from Aldrich or Tzamal Dchem. Copper cyanide, all alkyl Grignard reagents were prepared from the corresponding alkyl bromides. All cyclopropene carboxylates were prepared according to the know procedure [1-4]. All unfunctionalized cyclopropenes were prepared according to literature reports and were consistent with literature data [1,4-13].

General procedure for the preparation of cyclopropenyl methyl ethers (3a–d)

To a flame dried 3-necked round bottom flask equipped with a Teflon coated stirring bar, under argon atmosphere is added a suspension of NaH (1.5 equiv) in Et₂O (3 mL/mmol) at 0 °C. Then substituted cyclopropanol **2** (1 equiv) was added dropwise over a period of 2 min and the reaction mixture was allowed to stir at this temperature for an additional hour before introducing MeI (1.2 equiv). The reaction mixture was warmed to room temperature and stirred overnight. After that the reaction was completed (determined by TLC analysis of hydrolyzed aliquots), the reaction mixture was cooled in an ice bath and water was added. The reaction was extracted with Et₂O and dried over MgSO₄ to afford the final cyclopropenyl methyl ether **3a–d** as clear oil.

1-(Methoxymethyl)-2-propylcycloprop-2-en-1-yl) benzene (3a)

R_f = 0.6 (Hex/EtOAc = 90:10). Yield 70%. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 0.89 (t, *J* = 7.2 Hz, 3H), 1.49-1.54 (m, 2 H), 2.39 (t, *J* = 7.2 Hz, 2H), 3.29 (s, 3H), 3.67 (d_{AB syst}, *J* = 10.2 Hz, 1H), 3.80 (d_{AB syst}, *J* = 10.2 Hz, 1H), 6.68 (s, 1H), 7.05-7.21 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 14.0, 20.8, 27.0, 29.1, 58.5, 80.4, 102.4, 124.8, 125.1, 126.3, 128.0, 146.8. HRMS (ESI) calcd. for C₁₄H₁₉O [M⁺H]⁺: 203.1436; found: 203.1414.

(2-Butyl-1-(methoxymethyl)cycloprop-2-en-1-yl)benzene (3b)

R_f = 0.7 (Hex/EtOAc = 90:10). Yield 70%. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 0.82 (t, *J* = 7.6 Hz, 3H), 1.27-1.33 (m, 2H), 1.49 (m, 2H), 2.39-2.44 (m, 2H), 3.30 (s, 3H), 3.70 (d_{AB syst}, *J* = 10.4

Hz, 1H), 3.81 (d_{AB syst}, *J* = 10 Hz, 1H), 6.67 (s, 1H), 7.05-7.13 (m, 1H), 7.13-7.21 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 13.9, 22.5, 24.7, 29.2, 29.5, 58.6, 80.4, 102.3, 125.0, 125.1, 126.3, 128.0, 146.8. HRMS (ESI) calcd. for C₁₅H₂₁O [M⁺H]⁺: 217.1592; found: 217.1580.

(R)-(2-Cyclohexyl-1-(methoxymethyl)cycloprop-2-en-1-yl)benzene (3c)

R_f = 0.7 (Hex/EtOAc = 90:10). Yield 75%. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 1.14-1.27 (m, 5H), 1.50-1.53 (m, 1H), 1.53-1.59 (m, 2H), 1.60-1.77 (m, 2H), 2.44-2.47 (bs, 1 H), 3.29 (s, 3H), 3.57 (d_{AB syst}, *J* = 10Hz, 1H), 3.90 (d_{AB syst}, *J* = 10Hz, 1H), 6.63 (s, 1H), 7.02-7.06 (m, 1H), 7.14-7.16 (m, 4H) ¹³C NMR (100 MHz, CDCl₃): δ = 25.6, 25.6, 26.1, 29.5, 31.1, 31.1, 34.8, 58.5, 80.6, 100.7, 125.0, 126.3, 128.0, 128.7, 147.1; HRMS (ESI) calcd. for C₁₇H₂₃O [M⁺H]⁺: 243.1749; found: 243.1729.

The enantiomerically enriched form was obtained with similar spectral data, [α]_D: (CHCl₃, c = 2): 36.79°. *er* 93:7. The enantiomeric ratio assigned to the title compound was based on the enantiomeric ratio found for compound (R)-(2-cyclohexyl-1-phenylcycloprop-2-en-1-yl)methanol.

1-Hexyl-3-(methoxymethyl)-3-methylcycloprop-1-ene (3d)

R_f = 0.65 (Hex/EtOAc = 90:10). Yield 66%. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 0.82 (t, *J* = 7.2 Hz, 3H), 1.05 (s, 3H), 1.21-1.30 (m, 6H), 1.30-1.48 (m, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 3.23 (s, 5H), 6.64 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 14.2, 22.1, 22.6, 22.7, 25.8, 27.5, 29.1, 31.8, 58.4, 82.9, 108.4, 131.8. HRMS (ESI) calcd. for C₁₂H₂₃O [M+H]⁺: 183.1749; found: 183.1728.

General procedure for the carbocupration reaction of 3a,c with RCuCNLi

To a suspension of CuCN (1.5 equiv) in 8 ml of Et₂O was added alkylolithium dropwise at -35 °C (2 equiv.). The resulting mixture (pale yellow in case of MeLi and PhLi and dark brown in case of *n*-BuLi and *n*-HexLi) was allowed to stir for 30 min. Cyclopropene **3a-d** (1 equiv in 2 mL/mmol of Et₂O) was added at that temperature and the reaction mixture was stirred until TLC shows complete consumption of the starting material (eluent hexane/EtOAc 9:1 ca. 30 min). The reaction was then quenched with an aqueous solution of NH₄Cl/NH₄OH (2:1). The aqueous layer was extracted twice with EtOAc and the combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude mixtures were then purified by flash chromatography using pentane/diethyl ether as eluent.

1-(Methoxymethyl)-2-methyl-2-propylcyclopropylbenzene (4a)

R_f = 0.6 (Hex/EtOAc = 90:10). Yield 67%. Colorless oil, ¹H NMR (400 MHz, CDCl₃): δ = 0.36-0.47 (m, 1H), 0.70 (t, *J* = 7.2 Hz, 3H), 1.11 (m, 1H), 1.17-1.20 (m, 4H), 1.25-1.45 (m, 1H), 3.20 (s, 3H), 3.60 (m, 2H), 7.14-7.16 (m, 1H), 7.19-7.30 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 15.0, 17.9, 20.0, 24.2, 27.3, 32.2, 44.5, 59.9, 83.1, 125.6, 128.5, 130.1, 144.3 HRMS (ESI) calcd. for C₁₅H₂₃O [M⁺H]⁺: 219.1799; found: 219.1764.

2-Butyl-1-((methoxymethyl)-2-propylcyclopropyl)benzene (4b)

R_f = 0.6 (Hex/EtOAc = 90:10). Yield 72%. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 0.35-0.45 (m, 1H), 0.58 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H), 1.01-1.03 (m, 1H), 1.20-1.22 (m, 3H), 1.30-1.33 (m, 3H), 1.44-1.50 (m, 2H), 1.55-1.59 (m, 2H), 3.23 (s, 3H), 3.74 (bs, 2H), 7.12-7.30 (m, 5H), ¹³C NMR (100 MHz, CDCl₃): δ = 14.1, 14.7, 18.4, 21.0, 27.5, 31.2, 39.2, 41.6, 60.0, 82.9, 126.2, 127.8, 129.6, 144.1 . HRMS (ESI) calcd. for C₁₈H₂₉O [M⁺H]⁺: 261.2218; found: 261.2210.

(1-(Methoxymethyl)-2-propylcyclopropane-1,2-diyl)dibenzene (4c)

R_f = 0.54 (Hex/EtOAc = 90:10). Yield 62%. Colorless oil, ¹H NMR (400 MHz, CDCl₃): δ = 0.39 (m, 1H), 0.44-0.46 (m, 1H), 0.65 (t, *J* = 7.2 Hz, 3H), 1.01-1.03 (m, 1H), 1.12-1.15 (m, 2H), 1.30-1.35 (m,

1H), 3.02 (s, 3H), 3.25 (d_{AB syst}, *J* = 10.0 Hz, 1H), 3.70 (d_{AB syst}, *J* = 10.0 Hz, 1H), 3.94, 7.25-7.33 (m, 2H), 7.35-7.42 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ = 14.7, 18.1, 23.3, 28.5, 32.9, 42.3, 60.1, 82.7, 126.6, 126.8, 128.4, 128.6, 130.1, 139.5, 141.3. HRMS (ESI) calcd. for C₂₀H₂₅O [M+H]⁺: 281.1905; found: 281.1920.

(2-Cyclohexyl-1-(methoxymethyl)-2-methylcyclopropyl)benzene (4d)

R_f = 0.6 (Hex/EtOAc = 90:10). Yield 62%. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 0.060-0.115 (m, 1H), 0.56-0.60 (m, 1H), 0.90-0.95 (m, 3H), 1.01 (m, 1H), 1.05 (s, 3H), 1.08-1.11 (m, 2H), 1.45-1.48 (m, 2H), 1.52-1.58 (m, 2H), 3.20 (s, 3H), 3.70 (d_{AB syst}, *J* = 10Hz, 1H), 3.81 (d_{AB syst}, *J* = 10Hz, 1H), 7.15-7.18 (m, 1H), 7.21-7.24 (m, 2H), 7.27-7.29 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 7.6, 26.7, 26.8, 26.9, 28.3, 29.5, 35.5, 40.0, 42.0, 61.0, 75.5, 128.3, 129.0, 129.5, 141.8. HRMS (ESI) calcd. for C₁₈H₂₇O [M+H]⁺: 259.2061; found: 259.2062.

(2-Butyl-2-cyclohexyl-1-(methoxymethyl)cyclopropyl)benzene (4e)

R_f = 0.6 (Hex/EtOAc = 90:10). Yield 60%. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 0.03-0.04 (m, 1H), 0.42-0.44 (m, 1H), 1.01 (t, *J* = 7.2Hz, 3H), 1.05-1.06 (m, 3H), 1.08-1.10 (m, 1H) 1.13-1.16 (m, 2H), 1.38-1.51 (m, 5H), 1.55-1.62 (m, 5H), 3.11 (s, 3H), 3.77 (d_{AB syst}, *J* = 9.2Hz, 1H), 3.85 (d_{AB syst}, *J* = 9.2Hz, 1H), 7.15-7.19 (m, 1H), 7.25-7.30 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 14.6, 23.2, 24.5, 26.8, 27.1, 27.5, 30.8, 31.2, 32.2, 40.5, 41.5, 44.8, 61.9, 78.2, 127.3, 128.8, 131.0, 141.6. HRMS (ESI) calcd. for C₂₁H₃₃O [M+H]⁺: 301.2531; found: 301.2540.

General procedure for the combined carbocupration/oxidation sequence

The reaction was performed on a 1 mmol scale. To a suspension of CuCN (2 equiv) in 8 mL of Et₂O was added alkyllithium dropwise at -35 °C (2 equiv./2mmol). The resulting mixture (pale yellow in case of MeLi and PhLi and dark brown in case of *n*-BuLi and *n*-HexLi) was allowed to stir for 30 min. Cyclopropene **6** (1 equiv/1 mmol in 2 mL of Et₂O) was added at that temperature and the reaction mixture was stirred until TLC shows complete consumption of the starting material (eluent hexane/EtOAc 9:1 ca. 30 min). The oxenoid was prepared in a different flask by slowly adding *n*-BuLi (1.2 equiv) to a solution of *tert*-butyl hydroperoxide (2 equiv) in THF (5 mL/2 mmol) at -80 °C. After 30 min at -80 °C, the resulting *t*-BuOOLi was transferred to the organocopper dropwise at -78 °C via a cannula. The mixture (orange to brown) was stirred at this temperature until disappearance of the cyclopropylcopper species (followed by TLC, eluent hexane/EtOAc 9:1, ca. 30 min). The reaction was then quenched with an aqueous solution of NH₄Cl/NH₄OH (2:1). The aqueous layer was extracted twice with Et₂O and the combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. Crude mixtures were then purified by flash chromatography using pentane/diethyl ether as eluent.

2,3-Dimethyl-2-phenylcyclopropan-1-ol (7a)

R_f = 0.25 (Hex/EtOAc = 90:10). Yield 65%. Colorless oil, ¹H (300 MHz, CDCl₃): δ = 0.90 (d, *J* = 6.2 Hz, 3H), 1.05-1.09 (m, 1H), 1.35 (s, 3H), 3.72 (d, *J* = 6.2 Hz, 1H), 7.20-7.30 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ = 15.1, 25.3, 32.3, 58.2, 125.6, 126.0, 128.2, 128.3, 150.4; HRMS (ESI) calcd. for C₁₄H₂₀O [M+H]⁺: 205.1592; found: 205.1594.

3-Butyl-2-methyl-2-phenylcyclopropan-1-ol (7b)

R_f = 0.2 (Hex/EtOAc = 90:10). Yield 62%. Colorless oil ¹H NMR (300 MHz, CDCl₃): δ = 0.85 (t, *J* = 7.2Hz, 3H), 0.97 (dt, *J*₁ = 7.1Hz, *J*₂ = 6.8Hz, 1H), 1.20-1.26 (m, 4H), 1.31-1.41 (m, 4H), 1.41-1.47 (m, 2H), 2.01 (bs, 1H), 3.53 (d, *J* = 7.2 Hz, 1H), 7.03-7.21 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ = 13.4, 14.3, 21.9, 22.9, 27.2, 28.7, 32.3, 57.9, 125.7, 127.2, 128.5, 147.9. HRMS (ESI) calcd. for C₁₄H₂₁O [M+H]⁺: 205.1592; found: 205.1963.

3-Hexyl-2-methyl-2-phenylcyclopropan-1-ol (7c)

R_f = 0.2 (Hex/EtOAc = 90:10). Yield 60%. Colorless oil, ¹H NMR (300 MHz, CDCl₃): δ = 0.844 (t, *J* = 6.7 Hz, 3H), 0.94 (dt, *J*₁ = 7.1 Hz, *J*₂ = 6.6 Hz, 1H), 1.27-1.41 (m, 9H), 1.41-1.44 (m, 4H), 1.81 (bs, 1H), 3.54 (d, *J* = 7.2 Hz, 1H), 7.07-7.19 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ = 13.5, 14.3, 22.3, 22.8, 27.3, 28.8, 29.5, 30.0, 32.0, 58.0, 125.7, 127.2, 128.5, 148.0. HRMS (ESI) calcd. for C₁₆H₂₅O [M⁺H]⁺: 233.1905; found: 233.1902.

2-Methyl-2,3-diphenylcyclopropan-1-ol (7d)

R_f = 0.2 (Hex/EtOAc = 90:10). Yield 49%. Colorless oil, ¹H (400 MHz, CDCl₃): δ = 1.23 (s, 3H), 1.83 (bs, 1H), 2.32 (d, *J* = 8 Hz, 1H), 3.92 (d, *J* = 8 Hz, 1H), 7.14-7.24 (m, 2H), 7.25-7.33 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ = 15.7, 30.3, 32.2, 59.3, 126.2, 126.5, 127.4, 128.6, 128.7, 130.9, 135.6, 147.

3-Hexyl-2-methyl-2-(*p*-tolyl)cyclopropan-1-ol (7e)

R_f = 0.3 (Hex/EtOAc = 90:10). Yield 56%. Colorless oil, ¹H (300 MHz, CDCl₃): δ = 0.84 (t, *J* = 6.8 Hz, 3H), 0.94- 0.95 (m, 1H), 1.25-1.30 (m, 8H), 1.34-1.43 (m, 4H), 1.72 (bs, 1H), 2.23 (s, 3H), 2.53 (d, *J* = 5.4 Hz, 1H), 7-7.12 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ = 13.6, 14.3, 21.1, 22.3, 22.8, 27, 28.6, 29.5, 30, 32, 57.9, 127.1, 129.2, 135.3, 145.

3-Isopropyl-2-methyl-2-(*p*-tolyl)cyclopropan-1-ol (7f)

R_f = 0.25 (Hex/EtOAc = 90:10). Yield 53 %. Colorless oil, ¹H NMR (300 MHz, CDCl₃): δ = 0.78 (dd, *J*₁ = 7.2 Hz, *J*₂ = 3.5 Hz, 1H), 1.02 (d, *J* = 6.5 Hz, 3H), 1.09 (d, *J* = 6.5 Hz, 3H), 1.37 (s, 3H), 1.71 (bs, 1H), 1.72-1.80 (m, 1H), 2.30 (s, 3H), 3.59 (d, *J* = 9 Hz, 1H), 7.09 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ = 13.9, 21.1, 22.8, 23.0, 23.1, 27.4, 36.5 58.0, 127.3, 129.2, 135.3, 145.1 HRMS (ESI) calcd. for C₁₄H₂₁O [M⁺H]⁺: 205.1587; found: 205.1580

3-(*tert*-Butyl)-2-methyl-2-(*p*-tolyl)cyclopropan-1-ol (7g)

R_f = 0.3 (Hex/EtOAc = 90:10). Yield 50%. Colorless oil, ¹H (300 MHz, CDCl₃): δ = 0.68 (d, *J* = 9 Hz, 1H), 1.10 (s, 9H), 1.44 (s, 3H), 1.89 (bs, 1H), 2.21 (s, 3H), 3.64 (d, *J* = 9 Hz, 1H), 6.98-7.07 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 15.5, 21.1, 28.7, 31.6, 32.4, 38.9, 59.5, 127.5, 129.2, 135.2, 147.

2-Methyl-3-phenyl-2-(*p*-tolyl)cyclopropan-1-ol (7h)

R_f = 0.2 (Hex/EtOAc = 90:10). Yield 57%. Colorless oil, ¹H (300 MHz, CDCl₃): δ = 1.31 (s, 3H), 1.98 (bs, 1H), 2.37-2.41 (m, 4H), 3.99 (d, *J* = 6 Hz, 1H), 7.16- 7.19 (m, 2H), 7.28-7.30 (m, 3H), 7.37-7.41 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ = 15.8, 21.1, 29.9, 32.1, 59.3, 126.5, 127.3, 128.6, 129.4, 130.9, 135.7, 135.8, 144.1. HRMS (ESI) calcd. for C₁₇H₁₈O [M+H]⁺: 239.1436; found: 239.1445.

2-Butyl-2,3-dimethyl-3-phenylcyclopropan-1-ol (7i)

R_f = 0.25 (Hex/EtOAc = 90:10). Yield 65%. Colorless oil, ¹H (400 MHz, CDCl₃): δ = 0.76 (t, *J* = 7.2 Hz, 3H), 0.76-0.93 (m, 1H), 1.11-1.20 (m, 5H), 1.20-1.40 (m, 6H), 1.40-1.43 (m, 2H), 3.12 (s, 1H), 7.14-7.17 (m, 3H), 7.19-7.27 (m, 2H) ; ¹³C NMR (100 MHz, CDCl₃): δ = 14.3, 17.5, 23.4, 24.5, 27.9, 29.4, 32.2, 32.5, 65.3, 126.1, 128.7, 130.6, 142.2.

2,3-Dimethyl-2,3-diphenylcyclopropan-1-ol (7j)

R_f = 0.20 (Hex/EtOAc = 90:10). Yield 56%. Colorless oil, ¹H (300 MHz, CDCl₃): δ = 0.84 (s, 3H), 1.08 (s, 3H), 2.14 (bs, 1H), 3.73 (s, 1H), 7.09-7.13 (m, 2H), 7.14-7.28 (m, 8H); ¹³C NMR (75 MHz, CDCl₃): δ = 20.4, 26.7, 33.4, 35.4, 63.1, 126.2, 126.3, 128.6, 128.8, 129.1, 130.5, 140.8, 144; HRMS (ESI) calcd. for C₁₇H₁₉O [M+H]⁺: 239.1428; found: 239.1433.

2,3-Dimethyl-2-phenyl-3-propylcyclopropan-1-ol (7k)

R_f = 0.25 (Hex/EtOAc = 90:10). Yield 70%. Colorless oil, ¹H (400 MHz, CDCl₃): δ = 0.42-0.43 (m, 1H), 0.61 (t, *J* = 7.2 Hz, 3H), 0.97-0.98 (m, 1H), 1.06 (s, 3H), 1.17-1.24 (m, 5H), 2.10 (bs, 1H), 3.47 (s, 1H), 7.07-7.20 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 11.2, 14.3, 16.7, 19.7, 27.9, 33.3, 38.7, 60.9, 125.8, 128.3, 128.9, 145.2; HRMS (ESI) calcd. for C₁₄H₂₁O [M+H]⁺: 205.1592; found: 205.1596.

2-Butyl-3-methyl-3-phenyl-2-propylcyclopropan-1-ol (7l)

R_f = 0.3 (Hex/EtOAc = 90:10). Yield 70%. Colorless oil, ¹H (400 MHz, CDCl₃): δ = 0.05-0.07 (m, 1H), 0.63 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H), 1.18-0.134 (m, 9H), 1.44-1.46 (m, 3H), 2.08 (bs, 1H), 3.44 (s, 1H), 7.06-7.20 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 14.3, 14.3, 17.1, 19.6, 23.5, 23.8, 28.6, 31.6, 33.9, 35.5, 62.1, 125.8, 128.3, 129.1, 145.3; HRMS (ESI) calcd. for C₁₇H₂₇O [M+H]⁺: 247.2062; found: 247.2102.

2-Butyl-2-hexyl-3-methyl-3-phenylcyclopropan-1-ol (7m)

R_f = 0.3 (Hex/EtOAc = 90:10). Yield 60%. Colorless oil, ¹H (400 MHz, CDCl₃): δ = 0.90-0.12 (m, 1H), 0.72 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.91-1.31 (m, 8H), 1.31-1.45 (m, 3H), 2.18 (bs, 1H), 3.44 (s, 1H), 7.06-7.19 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 14.1, 14.3, 17.1, 22.7, 23.5, 23.8, 26.4, 28.7, 29.6, 31.7, 32, 33.3, 34.1, 62, 125.7, 128.3, 129.1, 145.3. HRMS (ESI) calcd. for C₂₀H₃₂O [M+H]⁺: 288.2453; found: 288.2450.

2-Hexyl-2,3-dimethyl-3-phenylcyclopropan-1-ol (7n)

R_f = 0.3 (Hex/EtOAc = 90:10). Yield 68%. Colorless oil, ¹H (400 MHz, CDCl₃): δ = 0.44-0.48 (m, 1H), 0.72 (t, *J* = 7.2 Hz, 3H), 0.96-1.11 (m, 12H), 1.11-1.24 (m, 4H), 2.20 (bs, 1H), 3.46 (s, 1H), 7.06-7.08 (m, 1H), 7.12-7.19 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 11.2, 14.1, 16.6, 22.6, 26.4, 27.9, 29.5, 31.8, 33.4, 36.5, 60.7, 125.7, 128.2, 128.9, 145.1; HRMS (ESI) calcd. for C₁₇H₂₆O [M+H]⁺: 247.2062; found: 247.2100.

2-Butyl-3-methyl-2-propyl-3-(*p*-tolyl)cyclopropan-1-ol (7o)

R_f = 0.3 (Hex/EtOAc = 90:10). Yield 52%. Colorless oil, ¹H (300 MHz, CDCl₃): δ = 0.65 (t, *J* = 6 Hz, 3H), 0.92 (t, *J* = 6 Hz, 3H), 1.19-1.36 (m, 10H), 1.44-1.45 (m, 3H), 1.82 (bs, 1H), 2.24 (s, 3H), 3.42 (s, 1H), 7.01 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ = 14.4, 17.2, 19.6, 21.2, 23.5, 23.7, 28.6, 31.4, 33.5, 35.4, 62.2, 129.1, 135.2, 142.2; HRMS (ESI) calcd. for C₁₈H₂₉O [M+H]⁺: 261.2218; found: 261.2210.

2-Hexyl-3-methyl-2-propyl-3-(*p*-tolyl)cyclopropan-1-ol (7p)

R_f = 0.3 (Hex/EtOAc = 90:10). Yield 47%. Colorless oil, ¹H (300 MHz, CDCl₃): δ = 0.05-0.09 (m, 1H), 0.65 (t, *J* = 7 Hz, 3H), 0.84 (t, *J* = 7 Hz, 3H), 1.18-1.27 (m, 13H), 1.41-1.48 (m, 3H), 1.97 (bs, 1H), 2.23 (s, 3H), 3.42 (s, 1H), 7.00 (s, 4H); ¹³C NMR (75 MHz, CDCl₃): δ = 14.3, 14.4, 17.2, 19.6, 21.2, 22.9, 24, 26.4, 30.2, 31.5, 32.1, 33.5, 35.4, 62.2, 128.9, 129.1, 135.2, 142.2. C₂₀H₃₃O [M+H]⁺: 289.2531; found: 289.2529.

2-Butyl-3-(4-chlorophenyl)-3-methyl-2-propylcyclopropan-1-ol (7q)

R_f = 0.25 (Hex/EtOAc = 90:10). Yield 51%. Colorless oil, ¹H (600 MHz, CDCl₃): δ = 0.12 (m, 1H), 0.96 (t, *J* = 6 Hz, 3H), 1.26 (t, *J* = 6 Hz, 3H), 1.29-1.41 (m, 9H), 1.51-1.53 (m, 3H), 1.97 (bs, 1H), 3.49 (s, 1H), 7.12-7.13 (d, *J* = 6 Hz, 2H), 7.23-7.25 (d, *J* = 6 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 14.3, 14.4, 16.9, 23.5, 23.7, 28.6, 31.7, 33.4, 35.5, 62.1, 128.5, 130.5, 131.4, 143.8. HRMS (ESI) calcd. for C₁₇H₂₆ClO [M]: 280.1570; found: 280.1598.

2-(4-Chlorophenyl)-3-hexyl-2-methyl-3-propylcyclopropan-1-ol (7r)

R_f = 0.25 (Hex/EtOAc = 90:10). Yield 48%. Colorless oil, ¹H (300 MHz, CDCl₃): δ = 0.05-0.12 (m, 1H), 0.70 (t, *J* = 6Hz, 3H), 0.89 (t, *J* = 6Hz, 3H), 1.22-1.33 (m, 14H), 1.48-1.49 (m, 3H), 1.72 (bs, 1H), 3.46 (s, 1H); 7.09 (d_{AB sys}, *J* = 6Hz, 2H), 7.21 (d_{AB sys}, *J* = 6Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ = 14.3, 14.4, 17, 19.6, 22.9, 24, 26.4, 30.2, 31.8, 32, 33.4, 35.5, 62.1, 128.6, 130.5, 131.4, 143.8. HRMS (ESI) calcd. for C₁₉H₃₀ClO [M]: 309.1985; found: 309.1974.

References

1. Delaye P-O.; Didier D.; Marek, I. *Angew. Chem. Int. Ed.*, **2013**, 52, 5333.
2. Li, C.; Zeng, Y.; Wang, J. *Tetrahedron Lett.* **2009**, 50, 2956.
3. Tarwade, V.; Liu, X.; Yan, N.; Fox, J. M. *J. Am. Chem. Soc.* **2009**, 131, 5382.
4. Uehara, M.; Suematsu, H.; Katsuki, T. *J. Am. Chem. Soc.* **2011**, 133, 170.
5. Phan, D. H. T.; Kou, K. G. M.; Dong, V. M. *J. Am. Chem. Soc.*, **2010**, 132, 16354.
6. Kremer, K.; Leong, P.; Lautens, M. *Org. Lett.* **2011**, 13, 819.
7. Sherrill, W.M.; Kim, R.; Rubina, M. *Tetrahedron*, **2008**, 64, 8610.
8. Smith, M. A.; Richey, H. G. Jr, *Organometallics*, **2007**, 26, 609.
9. Chen, W.; Tao, H.; Huang, W.; Wang, G.; Li, S.; Cheng, X.; Li, G. *Chem. Eur. J.* **2016**, 22, 9546.
10. Fort, D. A.; Woltering, T. J.; Nettekoven, M.; Knust, H.; Bach, T. *Chem. Commun.*, **2013**, 49, 2989.
11. Pratsch, G.; Overman, L. E. *J. Org. Chem.*, **2015**, 80, 11388.
12. Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.*, **2002**, 124, 11566.