[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín*

Instituto Universitario de Bio-Orgánica “Antonio González”, Universidad de La Laguna

C/Astrofísico Francisco Sánchez, 2, 38206 La Laguna, Tenerife, Spain
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Preparation of (4S)-Tridec-7-yn-4-ol (6a) Following a Classical Route. To a solution of epoxide \[^{3} \] (1.0 g, 8.6 mmol) in dry THF (43 mL) was slowly added Red-Al\(^{\circledast} \) (5.6 mL, 3.4 M solution in toluene, 18.9 mmol) at 0 °C under argon. The reaction mixture was stirred for 2.5 h, after which time TLC showed no remaining epoxide. Then water (4 mL) and HCl (5% w/v in water) (6 mL) were sequentially added, and the mixture was stirred until clear phases were reached (0.5 h). The phases were separated and the aqueous phase extracted with Et\(_2\)O. The combined organic phases were washed with saturated aqueous NaHCO\(_3\) and brine, dried (MgSO\(_4\)), filtered, concentrated, and purified to afford the corresponding 1,3-diol as a colorless oil.

To a stirred solution of the 1,3-diol obtained alcohol in dry CH\(_2\)Cl\(_2\) (40 mL) under argon were added imidazole (0.9 g, 12.9 mmol) and tert-butylchlorodimethylsilane (1.3 g, 8.6 mmol) at 0 °C. The reaction was allowed to warm to room temperature and stirred overnight. Then it was poured into H\(_2\)O and extracted with CH\(_2\)Cl\(_2\). The combined organic phases were washed with brine, dried, filtered and concentrated. The crude obtained was purified by flash chromatography affording (3S)-1-(tert-butyl-dimethyl-silanyloxy)-hexan-3-ol (1.46 g, 73% yield) as a colorless oil: [\( \alpha \)]\(_{D}^{25} \) = −5.8 (c=1.2 in CHCl\(_3\)); \(^{1} \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) = 0.07 (s, 6H), 0.90 (s, 9H), 1.30 – 1.51 (m, 4H), 1.63 (dd, \( J = 10.8, 5.7 \) Hz, 2H), 3.76 – 3.81 (m, 1H), 3.84–3.93 (m, 1H); \(^{13} \)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 14.1 (q), 18.1 (s), 18.7 (t), 25.8 (t), 38.4 (t), 36.7 (t), 62.8 (t), 71.8 (d); IR (film) \( \nu_{\text{max}} \) (cm\(^{-1}\)) 3422, 2859, 1464, 1255, 1091; MS \( m / z \) (relative intensity) (FAB) 233 (M + 1\(^{+}\)) (3), 232 (M\(^{+}\)) (4), 231(M – 1\(^{+}\)) (2), 217 (M – CH\(_3\))\(^{+}\) (2), 175 (M – Bu\(–t\))\(^{+}\) (6), 117 (100). Anal. Calcd for C\(_{12}\)H\(_{28}\)O\(_2\)Si: C, 62.01; H, 12.14. Found: C, 62.33; H, 12.42.

To a solution of the above silyl ether derivative (1 g, 4.31 mmol) in dry CH\(_2\)Cl\(_2\) (45 mL) under argon were added imidazole (889 mg, 12.9 mmol) and tert-butylchlorodiphenylsilane (1.37 mL, 5.17 mmol) at 0 °C. The reaction was allowed to warm to room temperature and stirred overnight. Then the mixture was diluted with CH\(_2\)Cl\(_2\) and poured into water and extracted with CH\(_2\)Cl\(_2\). The

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combined organic phases were washed with saturated aqueous NaCl, dried (MgSO₄), filtered and concentrated to afford the silyl ether that was used in the next step without further purification.

To a solution of the crude obtained in CH₂CN (39 mL) was added HF (4 mL) (HF:CH₂CN, 1:9) and the mixture was stirred for 10 min. Then it was diluted with CH₂Cl₂, poured into water and extracted with CH₂Cl₂. The combined organic phases were washed with saturated aqueous NaCl, dried (MgSO₄), filtered and concentrated. The crude obtained was purified by flash chromatography affording (3S)-3-(tert-Butyl-diphenyl-silanyloxy)-hexan-1-ol (1.24 g, 81% yield overall) as a colorless oil: 

\[ \alpha_{D}^{25} = +17.2 \text{ (c 2.0 in CHCl₃)} \]

\(^1\)H NMR (400 MHz, CDCl₃) δ = 0.69 (t, J = 7.4 Hz, 3H), 1.09 (s, 9H), 1.11–1.19 (m, 2H), 1.39–1.51 (m, 2H), 1.62–1.68 (m, 1H), 1.79–1.85 (m, 2H), 3.65 (dd, J = 11.0, 5.5 Hz, 1H), 3.76–3.82 (m, 1H), 3.95 (ddd, J = 11.6, 11.6, 5.4 Hz, 1H);

\(^{13}\)C NMR (75 MHz, CDCl₃) δ = 13.9 (q), 18.2 (t), 19.3 (s), 27.0 (q), 37.7 (t), 38.5 (t), 59.8 (t), 72.1 (d), 127.5 (d), 127.6 (d), 129.6 (d), 129.7 (d), 133.9 (s), 134.2 (s), 135.9 (d); IR (film) \( \gamma_{max} \) (cm\(^{-1}\)) 3072, 2959, 2859, 1472, 1428, 1111; MS m / z (relative intensity) 299 (M – Bu-t) (20), 271 (5), 221 (27), 199 (100). HMRS calcld for C₁₈H₂₃O₂Si (M – Bu-t) 299.146734, found 299.146544.

To a solution of the former alcohol (500 mg, 1.40 mmol) in dry CH₂Cl₂ (14 mL) and Et₃N (0.39 mL, 2.8 mmol) was added MeSO₂Cl (0.16 mL, 2.1 mmol) at 0 °C. The solution was allowed to warm to room temperature and stirred for 20 min. The reaction mixture was quenched with brine and extracted with CH₂Cl₂. The organic layer was washed with brine, dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was used in the next step without further purification.

To a solution of LiBr (184 mg, 2.1 mmol) in dry DMF (14 mL) was added the crude mesylate obtained above at 0 °C under argon. The mixture was allowed to warm to room temperature and was stirred overnight, after which time TLC showed no remaining starting material. The mixture was cooled at 0 °C and diluted with Et₂O. The combined organic phases were washed with saturated aqueous NaCl, dried (MgSO₄), filtered and concentrated. The residue obtained was purified by column chromatography to furnish pure (1S)-[1-(2-bromo-ethyl)-butoxy]-tert-butyl-diphenyl-silane (463 mg, 79% yield overall) as a colorless oil: \( \alpha_{D}^{25} = +9.9 \) (c 2.0 in CHCl₃); 

\(^1\)H NMR (400 MHz, CDCl₃) δ = 0.69 (t, J = 7.2 Hz, 3H), 0.99 (s, 9H), 1.16–1.26 (m, 2H), 1.37–1.53 (m, 2H), 1.98–2.02 (m, 1H), 3.42 (t, J = 7.3 Hz, 2H), 3.87 (t, J = 5.4 Hz, 1H), 7.35–7.43 (m, 6H), 7.67–7.70 (m, 4H); \(^{13}\)C NMR (75 MHz, CDCl₃) δ = 13.8 (q), 18.0 (t), 19.4 (s), 27.0 (q), 30.0 (t), 38.7 (t), 39.7 (t), 71.1 (d), 127.5 (d), 127.6 (d), 129.5 (d), 129.6 (d), 134.0 (s), 134.3 (s), 135.9 (d); IR (film) \( \gamma_{max} \) (cm\(^{-1}\)) 2959, 2932, 2859, 1472, 1428, 1111, 1059; MS m / z (relative intensity) 419

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(M)\(\gamma\)0.1, 362 (M – Bu-t) (6), 338 (M – HBr)\(\gamma\)1(1), 335 (25), 263 (100). Anal. Calcd for C_{22}H_{31}BrOSi: C, 62.99; H, 7.45. Found: C, 63.12; H, 7.76.

To a solution of 1-heptyne (0.13 mL, 0.99 mmol) in dry THF (5.5 mL) at \(-78^\circ\)C under argon was slowly added \(n\)-BuLi (0.48 mL, 1.9 M in hexane, 0.92 mmol). Then HMPA (1.5 mL) was added and stirred for 30 min. After which time a solution of the above bromide derivative (300 mg, 0.71 mmol) in dry THF was slowly added. The reaction mixture was stirred for 1 h, after which time TLC showed no remaining starting material. Then Et_{2}O and a saturated aqueous NH_{4}Cl were added. The combined organic phases were washed with saturated aqueous NaCl, dried (MgSO_{4}), filtered and concentrated.

To a stirred solution of the crude obtained in dry THF (4 mL) under argon was added \(n\)-TBAF 1 M in THF (1 mL, 1 mmol) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was poured into H_{2}O and extracted with ether. The combined organic solutions were washed with brine and dried. The resulting solution was concentrated and purified by column chromatography, yielding the bis-homopropargylic alcohol 6a (174.1 mg, 73% yield overall) as a colorless oil: \([\alpha]_{D}^{25}=+5.4\) (c=2.36 in CHCl_{3}); \(^{1}H\) NMR (400 MHz, CDCl_{3}) \(\delta=0.87-0.96\) (m, 6H), 1.31-1.62 (m, 12H), 2.12 (dd, J = 4.7, 2.4 Hz, 2H), 2.28 (dd, J = 4.4, 2.1 Hz, 2H), 3.75 (m, 1H); \(^{13}C\) NMR (75MHz, CDCl_{3}) \(\delta=13.9\) (q), 14.0 (q), 15.4 (t), 18.7 (t), 18.8 (t), 22.2 (t), 28.7 (t), 31.0 (t), 36.2 (t), 39.5 (t), 71.0 (d), 79.6 (s), 81.1 (s); IR (film) \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3422, 2932, 2861, 1645, MS \(m/z\) (relative intensity) 196 (M)\(^{+}\) (1), 178 (M – H_{2}O)\(^{+}\) (3), 167 (M – C_{2}H_{5})\(^{+}\) (4), 153 (100). Anal. Calcd for C_{13}H_{24}O: C, 79.53; H, 12.32. Found: C, 79.54; H, 12.42.

Preparation of (4S)-11-(\textit{tert}-Butyl-dimethyl-silanyloxy)-undec-7-yn-4-ol (6c). The same general procedure used to prepare 6b was applied to 4 (\(R^{1}=\textit{n}-C_{3}H_{7}\)) using the lithium salt from \(\textit{tert}\)-butyl-dimethyl-pent-4-ynyloxy-silane,\(^{[2]}\) yielding 6c in 68% yield from 5c as a colorless oil: \([\alpha]_{D}^{25}=+5.3\) (c=0.65 in CHCl_{3}); \(^{1}H\) NMR (400 MHz, CDCl_{3}) \(\delta=0.10\) (s, 6H), 0.90 (m, 12H), 1.2-1.72 (m, 8H), 2.20-2.29 (m, 24H), 3.68 (t, J = 5.9 Hz, 3H), 3.74 (br s, 1H); \(^{13}C\) NMR (75 MHz, CDCl_{3}) \(\delta=14.0\) (q), 15.1 (t), 15.4 (t), 18.3 (s), 18.8 (t), 25.6 (q), 25.9 (q), 32.0 (t), 36.2 (t), 39.5 (t), 61.7 (t), 70.9 (d), 79.8 (s), 80.5 (s); IR (film) \(\nu_{\text{max}}\) (cm\(^{-1}\)) 3420, 2957, 2932, 2861, 1645, 1457; MS \(m/z\) (relative intensity) 268 (M – 2CH_{3})\(^{+}\) (0.4), 241 (M – Bu-t)\(^{+}\) (9), 225 (21), 213 (13), 171 (2), 75 (100). Anal. Calcd for C_{13}H_{34}O_{2}Si: C, 76.39; H, 11.48. Found: C, 76.36; H, 11.30.

Preparation of (8S)-Undec-4-yn-1,8-diol (6g). The same general procedure used to prepare 6b was applied to 4 (\(R^{1}=\textit{n}-C_{3}H_{7}\)) using the lithium salt from 2-pent-4-ynyloxy-2H-3,4,5,6-tetrahydro-

pyran,[3] yielding 6g in 40% yield from 5d as a colorless oil: \[[\alpha]^{25}_D = +6.9 (c=1.99 \text{ in CHCl}_3)\]; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 0.93 \text{ (t, } J = 6.9 \text{ Hz, 3H)}, 0.95–1.56 \text{ (m, 4H)}, 1.59–1.82 \text{ (m, 4H)}, 3.74 \text{ (t, } J = 5.1 \text{ Hz, 2H)}, 3.74 \text{ (m, 1H)}; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta =14.0 \text{ (q), 15.3 (t), 15.4 (t), 18.8 (t), 31.5 (t), 36.1 (t), 39.5 (t), 62.0 (t), 71.0 (d), 80.1 (s), 80.5 (s);} \text{IR (film) } \nu_{\text{max}} \text{ (cm}^{-1} \text{) 3420, 2955, 2932, 2873, 1717, 1057; MS } m/z \text{ (relative intensity) 139 (M} – [(\text{CH}_3)_2\text{OH})]^{+}(30), 123 (87), 97 (100). \text{ Anal. Calcd for C}_{11}\text{H}_{20}\text{O}_2: C, 71.70; H, 10.94. \text{ Found: C, 71.53; H, 11.21.}

Preparation of Benzoic Acid (8S)-8-Hydroxy-undec-4-ynyl ester (6e). To a solution of the alcohol 5g (200 mg, 0.69 mmol) in dry CH\(_2\)Cl\(_2\) (4 mL) were sequentially added Et\(_3\)N (0.29 ml, 2.07 mmol) and benzyl chloride (89 \(\mu\)L, 0.76 mmol) at 0 \(^\circ\)C under argon. The reaction mixture was allowed to warm to room temperature and stirred for 1 h, whereupon it was quenched with brine and extracted with CH\(_2\)Cl\(_2\). The organic layer was washed with brine, dried (MgSO\(_4\)), filtered and concentrated. The resulting residue (secondary alcohol 5e) was used without any further purification.

The same procedure used to prepare 6b from 5b was applied to 5e yielding 6e in 77% yield as a colorless oil: \[[\alpha]^{25}_D = +8.1 (c=1.87 \text{ in CHCl}_3)\]; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 0.92 \text{ (t, } J = 6.9 \text{ Hz, 3H)}, 1.34–1.45 \text{ (m, 4H)}, 1.59–1.69 \text{ (m, 2H)}, 1.93–1.98 \text{ (m, 2H)}, 2.31 \text{ (m, 4H)}, 3.74 \text{ (m, 1H)}; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta =14.0 \text{ (q), 15.3 (t), 15.6 (t), 18.8 (t), 28.2 (t), 36.1 (t), 39.5 (t), 63.7 (t), 71.0 (d), 79.3 (s), 80.7 (s), 128.3 (d), 129.6 (d), 130.3 (s), 132.9 (d), 166.6 (s); IR (film) } \nu_{\text{max}} \text{ (cm}^{-1} \text{) 3421, 1718, 1647, 1274; MS } m/z \text{ (relative intensity) 289 (M} + 1)^+ (0.4), 271 (M–OH)^+ (0.6), 225 (M–C}_6\text{H}_5^+ (0.3), 211 (3), 199 (3), 183 (M–OBz)^+ (2), 105 (100). \text{ Anal. Calcd for C}_{18}\text{H}_{24}\text{O}_3: C, 74.97; H, 8.39. \text{ Found: C, 74.95; H, 8.55.}

Preparation of (4S)-9-(tert-Butyl-diphenyl-silanyloxy)-non-7-yn-4-ol (6f). The same general procedure used to prepare 6b was applied to 4 (\(R^1=n\text{-C}_3\text{H}_7\)) using the lithium salt from \(\text{tert-Butyl-diphenyl-prop-2-ynyl-silane,}[4]\) yielding 6f in 69% yield from 5f as a colorless oil: \[[\alpha]^{25}_D = +5.1 (c=1.93 \text{ in CHCl}_3)\]; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 0.92 \text{ (t, } J = 6.5 \text{ Hz, 3H)}, 1.06 \text{ (s, 9H)}, 1.35 – 1.47 \text{ (m, 3H)}, 1.55–1.66 \text{ (m, 3H)}, 2.25 – 2.31 \text{ (m, 2H)}, 3.68 \text{ (m, 1H)}, 4.10 \text{ (m, 1H)}, 4.31 \text{ (br s, 2H), 7.34 \text{ (m, 6H), 7.70–7.73 \text{ (m, 4H)}; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta =14.1 \text{ (q), 15.3 (t), 18.8 (t), 19.0 (s), 26.5 (q), 35.7 (t), 39.5 (t), 52.9 (t), 70.6 (d), 85.3 (s), 85.5 (s), 127.6 (d), 129.6 (d), 133.4 (s),}


134.8 (d), 135.6 (s); IR (film) \( \gamma_{\text{max}} \) (cm\(^{-1}\)) 3421, 2931, 1731, 1463, 1189; MS m / z (relative
intensity) 337 (M – Bu-t)\( \delta \), 319 (2), 289 (4), 229 (12), 199 (100). Anal. Calcd for C\(_{25}\)H\(_{34}\)O\(_2\)Si:
C, 76.09; H, 8.68. Found: C, 76.08; H, 8.68.

**Preparation of (1R,3R)-5-[3-(tert-Butyl-diphenyl-silanyloxymethyl)-2,2,3-trimethyl-
cyclopentyl]-pent-4-yn-1-ol (2).** The same procedure used to obtain \( 6b \) was applied to 3-
benzyloxy-propan-1-ol using the lithium salt from (1R,3R)-tert-butyl-(3-ethynyl-1,2,2-trimethyl-
cyclopentylmethoxy)-diphenyl-silane (1),\(^5\) yielding 2 in 83% yield from 1 as a colorless oil: \( \alpha\)\( ^{25}\)\_D = +15.3 (c = 2.10 in CHCl\(_3\)); \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) = 0.89 (s, 3H), 1.00 (s, 3H), 1.03 (s, 3H), 1.06 (s, 9H), 1.49 - 1.53 (m, 4H), 1.71 - 1.92 (m, 2H), 1.93 (d, \( J = 8.7 \) Hz, 1H), 2.30 (m, 2H), 2.67 (t, \( J = 9.3 \) Hz, 2H), 3.68 (d, \( J = 9.9 \) Hz, 1H), 3.58 (d, \( J = 9.9 \) Hz, 2H), 4.09 - 4.16 (m, 2H), 7.34 - 7.45 (m, 6H), 7.65 - 7.69 (m, 4H); \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 15.6 (t), 19.3 (q), 19.5 (q), 21.9 (q), 23.4 (q), 26.9 (q), 28.3 (t), 31.7 (t), 33.8 (t), 41.3 (d), 45.7 (s), 47.6 (s), 62.1 (t), 70.1 (t), 81.7 (s), 82.5 (s), 127.5 (d), 127.6 (d), 129.5 (d), 133.7 (s), 133.8 (s), 135.7 (d), 135.8 (d); IR (film) \( \gamma_{\text{max}} \) (cm\(^{-1}\)) 3360, 2959, 2858, 1427, 1111, 1073; MS m / z (relative intensity) 462 (M)\( \delta \), 405 (M – Bu-t)\( \delta \), 377 (3), 327 (7), 235 (7), 229 (3), 199 (100). Anal. Calcd for C\(_{30}\)H\(_{42}\)O\(_2\)Si: C, 77.87; H, 9.15. Found: C, 77.73; H, 9.23.

**Preparation of (4S,6S)-4-Hept-1-ynyl-6-tridecyl-[1,3]dioxane (11), formic acid (1S)-1-tridecyl-
dec-4-ynyl ester (12) and (10S)-tricos-6-yn-10-ol (13).** To a solution of ((2S,3S)-3-
tridecyloxiran-2-yl)methanol\(^6\) (1.0 g, 3.90 mmol) in dry THF (20 mL) was slowly added Red-Al\(^\circ\) (2.52 mL, 3.4 M solution in toluene, 8.6 mmol) at 0 °C under argon. The reaction mixture was stirred for 2.5 h, after which time TLC showed no remaining epoxide. Then water and HCl (5% w/v in water) were sequentially added, and the mixture was stirred until clear phases were reached (0.5 h). The phases were separated and the aqueous phase extracted with Et\(_2\)O. The combined organic phases were washed with saturated aqueous NaHCO\(_3\) and brine, dried (MgSO\(_4\)), filtered, concentrated to afford the corresponding 1,3-diol that was used without any further purification. To a solution of the crude 1,3-diol in dry CH\(_2\)Cl\(_2\) (40 mL) under argon were added imidazole (804 mg, 11.7 mmol) and tert-butylchlorodiphenylsilane (1.24 mL, 4.67 mmol) at 0 °C. The reaction was allowed to warm to room temperature and stirred overnight. Then the mixture was diluted with

\[ \text{[5]} \quad \text{I was obtained by coupling of the suitable lithium acetylide and aldehyde. For the acetylide preparation, see: J. M. Betancort, Aplicaciones de los complejos alquino-hexacarbonildicobalto en síntesis orgánica asimétrica, Doctoral Disertation, Universidad de La Laguna, 1998. For the aldehyde used, see: H.-J. Gutke, K. Oesterreich, D. Spitzner, N. A. Braun, Tetrahedron 2001, 57, 997.} \]

\[ \text{[6]} \quad \text{T. Martín, C. M. Rodríguez, V. S. Martín, J. Org. Chem. 1994, 61, 6450.} \]
CH$_2$Cl$_2$ and was poured into water and extracted with CH$_2$Cl$_2$. The combined organic phases were washed with saturated aqueous NaCl, dried (MgSO$_4$), filtered and concentrated to afford the alcohol (3S)-1-(tert-butyl-diphenyl-silanyloxy)-hexadecan-3-ol (1.33 g, 69% overall yield) as a colorless oil: $[\alpha]_{D}^{25} = -2.9$ ($c$=17.0 in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 0.88$ (t, $J = 6.9$ Hz, 3H), 1.03 (s, 9H), 1.26–1.43 (m, 1H), 1.28–1.46 (m, 1H), 1.46–1.56 (m, 1H), 1.66–1.69 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta = 14.1$ (q), 19.0 (s), 22.7 (t), 25.6 (t), 26.8 (q), 29.4 (t), 29.7 (t), 31.9 (d), 37.6 (t), 38.5 (t), 63.5 (t), 71.7 (d), 127.8 (d), 129.8 (d), 133.1 (s), 133.2 (s), 135.6 (d); IR (film) $\nu_{\text{max}}$ (cm$^{-1}$) 3420, 2927, 2855, 1466, 1112; MS $m/z$ (relative intensity) 497 (M + 1)$^+$ (15), 496 (M)$^+$ (30), 439 (M – Bu-t)$^+$ (28), 419 (M – C$_6$H$_5$)$^+$ (40), 199 (100). HRMS calc'd for C$_{32}$H$_{52}$O$_2$Si(M)$^+$ 496.373660, found 496.373507.

To a solution of (3S)-1-(tert-butyl-diphenyl-silanyloxy)-hexadecan-3-ol (1.0 g, 2.02 mmol) in dry i-Pr$_2$NEt (7 mL) was slowly added MOMCl (0.45 mL, 6.06 mmol) at 0 °C under argon. The reaction mixture was allowed to warm to room temperature and stirred for 1 h, after which time TLC showed no remaining starting material. Then Et$_2$O and HCl (5% w/v in water) were sequentially added, and the mixture was stirred until clear phases were reached (0.5 h). The phases were separated and the aqueous phase extracted with Et$_2$O. The combined organic phases were washed with saturated aqueous NaHCO$_3$ and brine, dried (MgSO$_4$), filtered and concentrated. The residue obtained was used without any further purification.

To a solution of the crude alcohol obtained above in dry THF (20 mL) was slowly added TBAF (3.03 mL of a solution 1 M in THF, 3.03 mmol) at 0 °C under argon. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Then water and Et$_2$O were sequentially added, the phases were separated and the aqueous phase extracted with Et$_2$O. The combined organic phases were washed with saturated aqueous NaHCO$_3$ and brine, dried (MgSO$_4$), filtered, and concentrated. Flash column chromatography yielded (3S)-3-methoxymethoxy-hexadecan-1-ol (493 mg, 81% yield overall) as a colorless oil: $[\alpha]_{D}^{25} = +29.5$ ($c$=4.0 in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 0.88$ (t, $J = 7.0$ Hz, 3H), 1.25 (br s, 21H), 1.48–1.70 (m, 4H), 1.78–1.82 (m, 1H), 3.41 (s, 3H), 3.67–3.84 (m, 3H), 4.67 (dd, $J = 13.8$, 6.7 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta = 22.6$ (t), 25.2 (t), 29.3 (t), 29.5 (t), 29.6 (t), 29.7 (t), 31.9 (t), 34.6 (t), 36.6 (t), 55.7 (q), 59.8 (t), 76.5 (d), 95.8 (t); IR (film) $\nu_{\text{max}}$ (cm$^{-1}$) 3280, 2927, 2854, 1467, 1151, 1038; MS $m/z$ (relative intensity) (FAB) 303 (M + 1)$^+$ (23), 302 (M)$^+$ (3), 301 (M – 1)$^+$ (7), 283 (M – CH$_3$)$^+$ (11), 271 (M – OCH$_3$)$^+$ (100). Anal. Calcd for C$_{18}$H$_{38}$O$_3$: C, 71.47; H, 12.66. Found: C, 71.63; H, 12.96.
The same procedure used to obtain 6b was applied to (3S)-3-methoxymethoxy-hexadecan-1-ol (200 mg, 0.66 mmol) using the lithium salt from 1-heptyne, yielding the mixture of 11:12:13 that were separated by a flash column chromatography yielding the products in a ratio 1:0.8:0.7 (81.7 mg of 11, 65.3 mg of 12, 52.7 mg of 13; 85% overall yield).

**4S,6S)-4-Hept-1-ynyl-6-tridecyl-[1,3]dioxane (11):** colorless oil, \([\alpha]_D^{25} = -4.9 (c=1.1 \text{ in CHCl}_3); \)

1H NMR (400 MHz, CDCl\(_3\)) \(\delta = 0.85 (t, J = 7.0 \text{ Hz, 3H}), 0.91 (t, J = 7.0 \text{ Hz, 3H}), 1.25 (br s, 28H), 1.44–1.55 (m, 1H), 1.70–1.75 (m, 1H), 2.18–2.23 (t, J = 5.6 \text{ Hz, 2H}), 3.52 (m, 1H), 4.31 (t, J = 7.6 Hz, 1H), 4.67 (d, J = 6.6 \text{ Hz, 1H}), 5.06 (d, J = 6.6 \text{ Hz, 1H}); \)

13C NMR (75 MHz, CDCl\(_3\)) \(\delta = 13.9 (q), 18.0 (t), 18.6 (t), 22.1 (t), 28.2 (t), 31.0 (t), 37.7 (t), 38.6 (t), 67.1 (d), 76.0 (d), 78.0 (s), 86.3 (s), 93.3 (t); IR (film) \(\nu_{\text{max}} (\text{cm}^{-1}) 2926, 2855, 1261, 1031; \)

MS \(m/z (\text{relative intensity}) 364 (M)^+ (6), 363 (M – 1)^+ (13), 349 (M – \text{CH}_3)^+ (10), 341 (38), 199 (32), 123 (100). \)


**Formic Acid (1S)-1-Tridecyl-dec-4-ynyl ester (12):** colorless oil, \([\alpha]_D^{25} = +8.6 (c=5.9 \text{ in CHCl}_3); \)

1H NMR (400 MHz, CDCl\(_3\)) \(\delta = 0.85 (t, J = 6.9 \text{ Hz, 3H}), 0.91 (t, J = 6.9 \text{ Hz, 3H}), 1.25 (br s, 26H), 1.38–1.47 (m, 2H), 1.49–1.51 (m, 2H), 1.76 (dd, J = 13.5, 6.6 Hz, 2H), 2.09–2.17 (m, 2H), 2.17–2.21 (m, 2H), 5.04–5.08 (m, 1H), 8.07 (s, 1H); \)

13C NMR (75 MHz, CDCl\(_3\)) \(\delta = 13.9 (q), 14.1 (q), 18.7 (t), 22.2 (t), 22.7 (t), 25.1 (t), 28.7 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.6 (t), 31.0 (t), 31.9 (t), 33.3 (t), 33.9 (t), 73.6 (d), 78.6 (s), 81.0 (s), 160.9 (s); IR (film) \(\nu_{\text{max}} (\text{cm}^{-1}) 2926, 2855, 1261, 1031; \)

MS \(m/z (\text{relative intensity}) 364 (M)^+ (0.5), 349 (M – \text{CH}_3)^+ (0.7), 320 (M – \text{OCHO})^+ (0.5), 227 (16), 199 (17), 149 (25), 55 (100). \)

HMRS calcd for C\(_{24}\)H\(_{44}\)O\(_2\): M\(^+\) 364.334131, found 364.334654.

**10S)-Tricos-6-yn-10-ol (13):** white solid, \([\alpha]_D^{25} = +1.6 (c=5.7 \text{ in CHCl}_3); \)

1H NMR (400 MHz, CDCl\(_3\)) \(\delta = 0.85 (t, J = 6.8 \text{ Hz, 3H}), 0.87 (t, J = 6.8 \text{ Hz, 3H}), 1.24 (br s, 26H), 1.38–1.47 (m, 2H), 1.49–1.51 (m, 2H), 1.76 (dd, J = 13.5, 6.6 Hz, 2H), 2.09–2.17 (m, 2H), 2.17–2.21 (m, 2H), 5.04–5.08 (m, 1H), 8.07 (s, 1H); \)

13C NMR (75 MHz, CDCl\(_3\)) \(\delta = 13.9 (q), 14.1 (q), 18.7 (t), 22.2 (t), 22.7 (t), 25.1 (t), 28.7 (t), 29.3 (t), 29.6 (t), 31.0 (t), 31.9 (t), 33.3 (t), 33.9 (t), 73.6 (d), 78.6 (s), 81.0 (s); IR (film) \(\nu_{\text{max}} (\text{cm}^{-1}) 3421, 2926, 2854, 1465; \)

MS \(m/z (\text{relative intensity}) 336 (M)^+ (3), 321 (M – \text{CH}_3)^+ (0.4), 319 (M – \text{OH})^+ (0.5), 154 (100). \)

HMRS calcd for C\(_{23}\)H\(_{44}\)O(M)^+ 336.339216, found 336.339360.

**Preparation of (3S)-3-(Benzyloxy)-hexadecan-1-ol (4, \(R^1=n\)-C\(_{13}\)H\(_{27}\)):** The same procedure used to obtain 4 (\(R^1=n\)-C\(_{3}\)H\(_{7}\)) from the epoxide 3 was applied to the (2S, 3S)-(3-tridecyl-oxiranyl)-methanol\(^6\) on a 5 g (19.5 mmol) scale, yielding 4 (\(R^1=n\)-C\(_{13}\)H\(_{27}\)) (4.96 g, 73% overall yield from
epoxide) as a colorless oil: \([\alpha]_D^{25} = +0.5 (c=170.0 \text{ in CHCl}_3)\); \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta = 0.89\) (t, \(J = 6.8 \text{ Hz}, 3\text{H})\), 1.26 (br s, 22H), 1.50–1.54 (m, 1H), 1.57 - 1.65 (m, 1H), 1.69 - 1.82 (m, 2H), 3.59 - 3.65 (m, 1H), 3.65 - 3.83 (m, 2H), 4.48 (d, \(J = 11.4 \text{ Hz}, 1\text{H})\), 4.59 (d, \(J = 11.4 \text{ Hz}, 1\text{H})\), 7.26–7.35 (m, 5H); \(^{13}\text{C NMR (75 MHz, CDCl}_3\) \(\delta = 13.9 \text{ (q)}, 22.7 \text{ (t)}, 25.1 \text{ (t)}, 29.3 \text{ (t)}, 29.6 \text{ (t)}, 29.8 \text{ (t)}, 31.9 \text{ (t)}, 33.4 \text{ (t)}, 35.9 \text{ (t)}, 60.7 \text{ (t)}, 70.7 \text{ (t)}, 78.6 \text{ (d)}, 127.7 \text{ (d)}, 127.8 \text{ (d)}, 128.4 \text{ (d)}, 138.4 \text{ (s)}\); IR (film) \(\gamma_{\text{max}} \text{ (cm}^{-1}\) 3448, 2929, 2867, 1466, 1093; MS \(m / z\) (relative intensity) 348 (M\(^+\) (2), 347 (M – 1\(^+\) (1), 331 (M – OH\(^+\) (1), 222 (5), 147 (11), 123 (34), 91 (100). HMRS calcd for \(\text{C}_{23}\text{H}_{44}\text{O}_2\) (M)\(^+\) 348.302831, found 348.302049.

**Preparation of Ketones 14.** To obtain the ketones 14b, 14c, 14d and 14e were used commercially available pentylmagnesium bromide, phenylmagnesium bromide, isopropylmagnesium chloride and tert-butylmagnesium chloride respectively, using the procedure to obtain 14a.

**(8S)-8-Benzylxy-heneicosan-6-one (14b):** colorless oil, \([\alpha]_D^{25} = +1.9 (c=0.6 \text{ in CHCl}_3)\); \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta = 0.87 \text{ (t, } J = 6.6 \text{ Hz, 6H}), 1.26 \text{ (br s, 28H), 1.37 - 1.58 (m, 4H), 2.45 (dd, } J = 15.8, 4.8 \text{ Hz, 2H), 2.73 (dd, } J = 15.7, 7.5 \text{ Hz, 1H), 3.91–3.95 (m, 1H), 4.49 (d, } J = 4.7 \text{ Hz, 2H), 7.28–7.45 (m, 5H); \(^{13}\text{C NMR (75 MHz, CDCl}_3\) \(\delta = 13.9 \text{ (q), 14.1 (q), 22.6 (t), 25.1 (t), 29.3 (t), 29.5 (t), 29.6 (t), 31.9 (t), 34.3 (t), 48.6 (t), 71.8 (t), 75.6 (d), 127.6 (d), 127.8 (d), 128.3 (d), 138.4 (s), 207.7 (s); IR (film) \(\gamma_{\text{max}} \text{ (cm}^{-1}\) 2929, 2854, 1714, 1466, 1067; MS \(m / z\) (relative intensity) 417 (M\(^+\) (100), 345 (M – C\(_5\)H\(_{11}\))\(^+\) (35). Anal. Calcd for \(\text{C}_{28}\text{H}_{48}\text{O}_2\): C, 80.71; H, 11.61. Found: C, 80.93; H, 11.72.

**(3S)-3-Benzylxy-1-phenyl-hexadecan-1-one (14c):** colorless oil, \([\alpha]_D^{25} = +6.6 (c=1.7 \text{ in CHCl}_3)\); \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta = 0.88 \text{ (t, } J = 6.9 \text{ Hz, 3H}), 1.26 \text{ (br s, 21H), 1.37–1.45 (m, 1H), 1.54–1.68 (m, 2H), 2.98 (dd, } J = 16.0, 5.3 \text{ Hz, 1H), 3.37 (dd, } J = 16.0, 6.8 \text{ Hz, 1H), 4.09 – 4.16 (m, 1H), 4.53 (s, 2H), 7.27 (br s, 5H), 7.40–7.50 (m, 2H), 7.53–7.58 (m, 1H), 7.96 (d, } J = 7.3 \text{ Hz, 2H); \(^{13}\text{C NMR (75 MHz, CDCl}_3\) \(\delta = 14.1 \text{ (q), 22.7 (t), 25.3 (t), 29.6 (t), 31.9 (t), 34.9 (t), 43.9 (t), 71.8 (t), 76.1 (d), 127.4 (d), 127.8 (d), 128.2 (d), 128.5 (d), 133.0 (d), 137.4 (s), 138.6 (s), 199.1 (s); IR (film) \(\gamma_{\text{max}} \text{ (cm}^{-1}\) 2929, 2854, 1449, 1069; MS \(m / z\) (relative intensity) 422 (M\(^+\) (0.1), 421 (M – 1\(^+\) (0.2), 345 (M – C\(_6\)H\(_5\))\(^+\) (0.2), 314 (7), 120 (11), 105 (100). HMRS calcd for \(\text{C}_{29}\text{H}_{42}\text{O}_2\) (M\(^+\) 422.318481, found 422.318716.

**(5S)-5-Benzylxy-2-methyl-octadecan-3-one (14d):** colorless oil, \([\alpha]_D^{25} = +8.2 (c=1.3 \text{ in CHCl}_3)\); \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta = 0.88 \text{ (t, } J = 6.9 \text{ Hz, 3H), 1.04 (d, } J = 15.9 \text{ Hz, 6H), 1.26 (br s, 21H), 1.38–1.62 (m, 3H), 2.50 (dd, } J = 17.3, 4.9 \text{ Hz, 1H), 2.80 (dd, } J = 16.1, 7.3 \text{ Hz, 1H),

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3.92–3.98 (m, 1H), 4.49 (d, J = 1.7 Hz, 2H), 7.23 – 7.34 (m, 5H); 13C NMR (75 MHz, CDCl3) δ = 14.0 (q), 17.8 (q), 17.9 (q), 22.6 (t), 25.2 (t), 29.3 (t), 29.5 (t), 29.6 (t), 31.9 (t), 34.6 (t), 41.7 (d), 45.5 (t), 71.8 (t), 75.8 (d), 127.4 (d), 127.7 (d), 128.2 (d), 138.2 (s), 138.7 (s), 213.4 (s); IR (film) νmax (cm⁻¹) 2929, 1687, 1450; MS m/z (relative intensity) 388 (M⁺ (1), 387 (M – 1)⁺ (2), 373 (M – CH₃)⁺ (1), 328 (13), 311 (M – C₆H₅)⁺ (1), 237 (43), 105 (100). HMRS calc for C₂₆H₄₃O₂ (M – 1)⁺ 387.326306, found 387.325623.

(5S)-5-Benzylxy-2,2-dimethyl-octadecan-3-one (14e): colorless oil, [α]D²⁵ = +10.3 (c=0.9 in CHCl₃); 1H NMR (400 MHz, CDCl₃) δ = 0.88 (t, J = 6.9 Hz, 3H), 1.13 (s, 9H), 1.26 (br s, 22H), 1.39–1.59 (m, 2H), 2.49 (dd, J = 16.9, 5.3 Hz, 1H), 2.88 (dd, J = 16.9, 6.9 Hz, 1H), 3.98–4.02 (m, 1H), 4.49 (br s, 2H), 7.22–7.34 (m, 5H); 13C NMR (75 MHz, CDCl₃) δ = 14.1 (q), 22.7 (t), 25.3 (t), 26.1 (q), 29.3 (t), 29.6 (t), 29.6 (t), 31.9 (t), 34.7 (t), 41.9 (d), 44.3 (s), 72.0 (t), 75.8 (d), 127.4 (d), 127.8 (d), 128.2 (d), 138.2 (s), 214.5 (s); IR (film) νmax (cm⁻¹) 2932, 1688, 1451, 1072; MS m/z (relative intensity) 345 (M – Bu – t)⁺ (1), 330 (M – CH₃)⁺ (2), 295 (M – OBr)⁺ (6), 237 (100). Anal. Calcd for C₂₇H₄₆O₂: C, 80.54; H, 11.51. Found: C, 80.66; H, 11.74.

Preparation of 17. The same procedure used to obtain 17a was applied to ketones 14b (300 mg, 0.72 mmol), 14c (300 mg, 0.71 mmol), 14d (300 mg, 0.77 mmol) and 14e (300 mg, 0.75 mmol) yielding the alcohols 17b (239 mg, 82% overall yield), 17c (247 mg, 84% overall yield), 17d (208 mg, 72% overall yield), and 17e (207 mg, 70% overall yield), respectively.

(4S,6R)-6-Pentyltridec-7-yn-4-ol (17b): colorless oil, [α]D²⁵ = –2.7 (c=1.54 in CHCl₃); 1H NMR (400 MHz, CDCl₃) δ = 0.87 (m, 6H), 1.25–1.56 (m, 40H), 2.16 (m, 2H), 2.38 (m, 1H), 2.60 (br s, 1H), 3.76 (m, 1H); 13C NMR (75 MHz, CDCl₃) δ = 13.9 (q), 14.0 (q), 14.1 (q), 18.6 (t), 22.1 (t), 22.6 (t), 25.4 (t), 26.7 (t), 28.7 (t), 29.3 (t), 29.6 (t), 29.6 (d), 31.0 (t), 31.5 (t), 31.6 (t), 31.9 (t), 35.9 (7), 37.4 (t), 43.0 (t), 71.6 (d), 83.1 (s), 83.4 (s); IR (film) νmax (cm⁻¹) 3359, 2929, 2856, 1465; MS m/z (relative intensity) 407 (M + 1)⁺ (2), 406 (M⁺ (6), 349 (M – C₄H₉)⁺ (8), 335 (M – C₅H₁₁)⁺ (19), 321 (M – C₆ H₁₂)⁺ (9), 223 (100). Anal. Calcd for C₂₈H₅₆O: C, 82.68; H, 13.38. Found: C, 82.42; H, 13.69.

(4S,6S)-6-Phenyltridec-7-yn-4-ol (17c): colorless oil, [α]D²⁵ = +2.4 (c=0.87 in CHCl₃); 1H NMR (400 MHz, CDCl₃) δ = 0.88 (t, J = 6.3 Hz, 3H), 0.90 (t, J = 6.7 Hz, 3H), 1.25 - 1.48 (m, 28H), 1.52 (t, J = 6.8 Hz, 2H), 1.88 (m, 2H), 2.21 (t, J = 6.7 Hz, 2H), 3.69 (m, 1H), 3.76 (m, 1H); 13C NMR (75 MHz, CDCl₃) δ = 14.0 (q), 14.1 (q), 18.8 (t), 22.2 (q), 22.7 (t), 25.4 (t), 28.6 (t), 28.7 (t), 29.3 (t), 29.6 (t), 31.1 (t), 31.9 (t), 35.5 (d), 37.5 (t), 46.2 (t), 70.7 (d), 81.9 (s), 84.2 (s), 126.7 (d), 127.4 (s), 128.5 (d), 142.4 (s); IR (film) νmax (cm⁻¹) 3360, 2925, 2855, 1714, 1465; MS m/z (relative
intensity) 413 (M + 1)$^+$ (16), 412 (M)$^+$ (11), 395 (M – OH)$^+$ (7), 341 (M – C$_5$H$_{11}$)$^+$ (7), 335 (M – C$_6$H$_5$)$^+$ (8), 316 (100). Anal. Calcd for C$_{30}$H$_{48}$O: C, 84.40; H, 11.72. Found: C, 84.35; H, 12.08.

(4S,6S)-6-Isopropyltridec-7-yn-4-ol (17d): colorless oil, [α]$^D_{25}$ = −12.9 (c=1.01 in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.86 (t, $J = 3.6$ Hz, 3H), 0.87 (t, $J = 3.7$ Hz, 3H), 0.92 (d, $J = 6.7$ Hz, 3H), 0.96 (t, $J = 6.8$ Hz, 2H), 1.25 (br s, H), 1.32 - 1.67 (m, 2H), 2.16 (t, $J = 7.0$ Hz, 1H), 2.31 (m, 1H), 2.71 (br s, 1H), 3.76 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 14.0 (q), 14.1 (q), 18.2 (q), 18.7 (t), 21.0 (d), 22.2 (t), 22.7 (t), 25.5 (t), 28.8 (t), 29.4 (t), 29.7 (t), 29.8 (t), 31.1 (t), 32.0 (t), 32.2 (d), 36.9 (d), 37.4 (t), 40.5 (t), 72.0 (d), 81.6 (s), 84.3 (s); IR (film) $\nu_{max}$ (cm$^{-1}$) 3368, 2929, 2856, 1729, 1465, 1367; MS $m/z$ (relative intensity) 379 (M + 1)$^+$ (29), 378 (M)$^+$ (30), 361 (22), 335 (20), 55 (100). Anal. Calcd for C$_{26}$H$_{50}$O: C, 82.47; H, 13.31. Found: C, 82.70; H, 13.43.

(4S,6S)-6-tert-Butyltridec-7-yn-4-ol (17e): colorless oil, [α]$^D_{25}$ = −18.3 (c=3.49 in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.86 (t, $J = 3.1$ Hz, 3H), 0.87 (t, $J = 3.1$ Hz, 3H), 0.95 (s, 6H), 1.25 (br s, 26H), 1.35-1.55 (m, 4H), 2.17 (m, 2H), 2.91 (br s, 1H), 3.75 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 13.9 (q), 14.0 (q), 18.6 (t), 22.1 (t), 22.7 (t), 25.4 (t), 27.3 (t), 28.7 (t), 29.3 (t), 29.6 (t), 29.7 (t), 31.1 (t), 31.9 (t), 33.6 (s), 37.2 (t), 41.9 (d), 72.5 (d), 82.2 (s), 84.6 (s); IR (film) $\nu_{max}$ (cm$^{-1}$) 3358, 2929, 2855, 1743, 1465, 1174; MS $m/z$ (relative intensity) 393 (M + 1)$^+$ (23), 392 (M)$^+$ (23), 391 (M – 1)$^+$ (56), 375 (M – OH)$^+$ (60), 335 (M – Bu-t)$^+$ (18), 321 (M – C$_5$H$_{11}$)$^+$ (23), 307 (16), 277 (100). Anal. Calcd for C$_{27}$H$_{52}$O: C, 82.58; H, 13.35. Found: C, 82.78; H, 13.48.

(4S,6R)-6-tert-Butyltridec-7-yn-4-ol (18e): colorless oil, [α]$^D_{25}$ = +11.9 (c=2.01 in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.87 (t, $J = 6.8$ Hz, 3H), 0.89 (t, $J = 6.9$ Hz, 3H), 0.95 (s, 6H), 1.25 (br s, 26H), 1.35-1.55 (m, 4H), 2.17 (m, 1H), 2.34 (m, 1H), 3.88 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 14.0 (q), 14.1 (q), 18.7 (t), 22.2 (t), 22.7 (t), 25.9 (t), 27.5 (t), 28.9 (t), 29.3 (t), 29.6 (t), 29.7 (t), 31.1 (t), 31.9 (t), 33.2 (s), 37.1 (t), 37.9 (t), 39.6 (d), 70.5 (d), 81.6 (s), 83.3 (s); IR (film) $\nu_{max}$ (cm$^{-1}$) 3360, 2929, 2855, 1743, 1465, 1174; MS $m/z$ (relative intensity) 393 (M + 1)$^+$ (25), 392 (M)$^+$ (24), 391 (M – 1)$^+$ (55), 375 (M – OH)$^+$ (61), 335 (M – Bu-t)$^+$ (20), 321 (M – C$_5$H$_{11}$)$^+$ (21), 307 (16), 277 (100). Anal. Calcd for C$_{27}$H$_{52}$O: C, 82.58; H, 13.35. Found: C, 82.58; H, 13.41.

**Preparation of 19.** The same procedure used to obtain 17a was applied to 17b (200 mg, 0.49 mmol), 17c (200 mg, 0.48 mmol) and 17d (200 mg, 0.53 mmol), yielding 19b (187.2 mg, 85% overall yield), 19c (190.6 mg, 87% overall yield) and 19d (190.3 mg, 85% overall yield).
(1S,3R,4Z)-Acetic Acid 3-Pentyl-1-tridecyl-dec-4-enyl Ester (19b): colorless oil, $[\alpha]^2_{D} = -0.2$ ($c=4.1$ in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ = 0.88–0.88 (m, 9H), 1.25 (br s, 35H), 1.46–1.58 (m, 5H), 2.00 (s, 3H), 2.32 (m, 1H), 4.10–4.13 (m, 1H), 4.85–4.89 (m, 1H), 5.08 (t, $J = 10.3$ Hz, 1H), 5.31–5.40 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 14.0 (q), 21.3 (q), 22.5 (t), 22.6 (t), 25.1 (t), 26.7 (t), 27.7 (t), 29.3 (t), 29.5 (t), 29.6 (t), 31.6 (t), 31.9 (t), 34.0 (q), 35.7 (t), 40.2 (t), 73.1 (d), 129.7 (d), 134.0 (d), 170.6 (s); IR (film) $\gamma_{\text{max}}$ (cm$^{-1}$) 2956, 2855, 1740, 1465, 1375, 1242, 1021; MS $m/z$ (relative intensity) 391 (M – OAc)$^+$ (17), 390 (55), 319 (64), 180 (100). Anal. Calcd for C$_{30}$H$_{58}$O$_2$: C, 79.93; H, 12.97. Found: C, 80.08; H, 13.31.

(1S,3R,4Z)-Acetic Acid 3-Phenyl-1-tridecyl-dec-4-enyl ester (19c): colorless oil, $[\alpha]^2_{D} = -48.7$ ($c=8.1$ in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ = 0.86 (t, $J = 6.9$ Hz, 3H), 0.88 (t, $J = 6.9$ Hz, 3H), 1.25 (br s, 30H), 1.49–1.54 (m, 2H), 1.90 (t, $J = 7.0$ Hz, 2H), 2.00 (s, 3H), 2.15–2.22 (m, 1H), 3.59–3.67 (m, 1H), 7.15–7.21 (m, 3H), 7.25–7.29 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 14.0 (q), 14.1 (q), 21.2 (q), 22.5 (t), 25.0 (t), 27.5 (t), 29.2 (t), 29.3 (t), 29.5 (t), 29.6 (t), 31.6 (t), 31.9 (t), 34.1 (q), 34.6 (t), 40.3 (d), 41.4 (t), 72.9 (d), 126.1 (d), 127.2 (d), 127.3 (d), 127.5 (d), 127.6 (d), 128.5 (d), 129.8 (d), 132.5 (d), 144.9 (s), 170.5 (s); IR (film) $\gamma_{\text{max}}$ (cm$^{-1}$) 2929, 2855, 1739, 1455, 1374, 1241; MS $m/z$ (relative intensity) 397 (M – OAc)$^+$ (1), 379 (M – C$_6$H$_5$)$^+$ (2), 385 (M – C$_5$H$_{11}$)$^+$ (1), 117 (100). Anal. Calcd for C$_{31}$H$_{52}$O$_2$: C, 81.52; H, 11.48. Found: C, 81.75; H, 11.80.

(1S,3R,4Z)-Acetic Acid 3-Isopropyl-1-tridecyl-dec-4-enyl ester (19d): colorless oil, $[\alpha]^2_{D} = +13.3$ ($c=0.1$ in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ = 0.79–0.89 (m, 12H), 1.25 (br s, 32H), 2.00 (s, 3H), 2.15–2.22 (m, 1H), 4.80–4.85 (m, 1H), 5.16 (t, $J = 10.4$ Hz, 1H), 5.38–5.47 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 14.0 (q), 19.5 (q), 20.5 (q), 21.0 (q), 22.6 (t), 25.1 (t), 29.3 (t), 29.5 (t), 29.6 (t), 31.7 (t), 31.9 (t), 32.8 (d), 34.3 (t), 37.2 (q), 39.9 (d), 78.1 (d), 131.2 (d), 131.4 (d); IR (film) $\gamma_{\text{max}}$ (cm$^{-1}$) 2939, 2855, 1739, 1455, 1374, 1241; MS $m/z$ (relative intensity) 423 (M)$^+$ (22), 422 (M)$^+$ (5), 421 (M – 1)$^+$ (13), 391 (18), 363 (M – OAc)$^+$ (100). HMRS calcd for C$_{28}$H$_{54}$O$_2$: M$^+$ 422.412381, found 422.412436.

**Preparation of 20.** The same procedure used to obtain 20a was applied to 19b (100 mg, 0.22 mmol) yielding 20b (52.79 mg, 71% overall yield) and to 19c (100 mg, 0.24 mmol) yielding 20c (46.87 mg, 63% overall yield).

(3R,5S)-3-Pentyl-5-tridecyl-dihydro-furan-2-one (20b): white solid; m.p. 53°C; $[\alpha]^2_{D} = -16.7$ ($c=1.32$ in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 0.87 (m, 6H), 1.24–1.55 (br s, 30H), 1.58–1.60
(m, 1H), 1.70–1.72 (m, 1H), 1.88–1.92 (m, 1H), 2.40–2.44 (m, 1H), 4.28–4.35 (m, 1H); 13C NMR (75 MHz, CDCl$_3$) δ = 13.9 (q), 14.0 (q), 22.3 (t), 22.6 (t), 25.2 (t), 26.9 (t), 29.2 (t), 29.4 (t), 29.5 (t), 30.2 (t), 31.4 (t), 31.8 (t), 35.2 (d), 35.5 (t), 40.9 (d), 78.8 (d), 179.0 (s); IR (film) γ$_{\text{max}}$ (cm$^{-1}$) 3440, 2921, 2851, 1640; MS m/z (relative intensity) 339 (M + 1)$^+$ (30), 338 (M)$^+$ (10), 289 (11), 137 (100). Anal. Calcd for C$_{22}$H$_{42}$O$_2$: C, 78.05; H, 12.50. Found: C, 78.09; H, 12.63.

(3R,5S)-3-Pentyl-5-tridecyl-dihydro-furan-2-one (20c): white solid; m.p. 41 °C; [α]$^D_{25}$ = –8.7 (c= 0.32 in CHCl$_3$); 1H NMR (400 MHz, CDCl$_3$) δ = 0.86 (t, J = 5.3 Hz, 3H), 0.89 (d, J = 5.1 Hz, 3H), 1.02 (d, J = 5.1 Hz, 3H), 1.25 (br s, 20H), 1.55–1.64 (m, 4H), 2.22 (m, 2H), 2.57 (m, 1H), 4.30 (m, 1H); 13C NMR (75 MHz, CDCl$_3$) δ = 14.1 (q), 18.2 (q), 20.7 (q), 22.7 (t), 24.8 (t), 27.4 (d), 29.1 (t), 29.3 (t), 29.4 (t), 29.5 (t), 30.4 (t), 31.9 (t), 35.6 (t), 47.1 (d), 78.4 (d), 178.1 (s); IR (film) γ$_{\text{max}}$ (cm$^{-1}$) 3428, 2922, 2852, 1748, 1644, 1468; MS m/z (relative intensity) 311 (M + 1)$^+$ (5), 310 (M)$^+$ (13), 268 (14), 250 (13), 206 (10), 127 (100). Anal. Calcd for C$_{20}$H$_{38}$O$_2$: C, 77.36; H, 12.33. Found: C, 77.67; H, 12.42.

Preparation of (3S,5S)-3-Phenyl-5-tridecyl-dihydro-furan-2-one (20d). To a stirred solution of 4-methylmorpholine N-oxide (74 mg, 0.63 mmol) in H$_2$O (40 mL) at rt, were added OsO$_4$ (0.1 mg, 0.34 µmol) and the alkene 19d (100 mg, 0.21 mmol) in THF:acetone (1:1) (2 mL). The mixture was vigorously stirred overnight. Then it was diluted with AcOEt and washed with a saturated solution of NaHSO$_3$, the aqueous phase was extracted with AcOEt and the combined organic phase was washed with H$_2$O and dried over MgSO$_4$, filtered and concentrated. Flash column chromatography yielded the corresponding diol that was used without any further purification. The 1,2-diol obtained was dissolved in a mixture dioxane/water (3:1) (2 mL) and were sequentially added NaIO$_4$ (180 mg, 0.84 mmol), Na$_2$CO$_3$ (15.2 mg, 0.11 mmol) and KMnO$_4$ (6.6 mg, 0.04 mmol). The mixture was vigorously stirred for 30 min, after which time was diluted with AcOEt and washed with an aqueous solution of HCl (5% weight/volume in water) and a saturated aqueous solution of NaCl. The combined organic layers were dried (MgSO$_4$), filtered and concentrated giving an acid derivative that was suitable for use without further purification. The residue was dissolved in Et$_2$O (1 mL) and a solution of NaOH (30% weight/volume in water, saturated with NaCl) (1 mL) was added and vigorously stirred for 1 h at room temperature. After this time HCl concentrated was added until getting a pH=2. The mixture was diluted with Et$_2$O and a saturated aqueous of NaCl was added and extracted with Et$_2$O. The combined organic phases were washed with saturated aqueous NaCl, dried (MgSO$_4$), filtered and concentrated to afford the lactone 20d (46.2 mg, 64% yield) as a white solid; m.p. 68 °C; [α]$^D_{25}$ = –6.1 (c=1.39 in CHCl$_3$); 1H
NMR (400 MHz, CDCl₃) δ = 0.92 (m, 3H), 1.31 (br s, 24H), 1.41–1.56 (m, 1H), 1.69–1.75 (m, 1H), 2.08 (dd, J = 9.5, 8.0 Hz, 1H), 2.75 (m, 1H), 3.88–3.94 (m, 1H), 4.50–4.55 (m, 1H), 7.30 – 7.33 (m, 3H), 7.33–7.42 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ = 13.9 (q), 14.0 (q), 22.3 (t), 22.6 (t), 25.2 (t), 26.9 (t), 29.2 (t), 29.4 (t), 29.5 (t), 30.2 (t), 31.4 (t), 31.8 (t), 35.2 (d), 35.5 (t), 40.9 (d), 78.8 (d), 179.0 (s); IR (film) γ max (cm⁻¹) 3425, 2922, 2851, 1754, 1644; MS m/z (relative intensity) 345 (M⁺ + 1)⁺ (7), 344 (M⁺)⁺ (6), 306 (12), 289 (19), 154 (100). Anal. Calcd for C₂₃H₃₆O₂: C, 80.16; H, 10.53. Found: C, 80.15; H, 10.74.

Preparation of (25,4S)-4-Benzylxy-methyl-2-phenyl-1,3-dioxane (24). To a suspension of NaH (459 mg, 11.5 mmol, 60% in mineral oil) in dry THF (50 mL), at 0°C were sequentially and slowly added a solution of the alcohol 23[7] (1 g, 5.2 mmol) in THF (25 mL), a catalytic amount of n-Bu₄NI, and benzyl bromide (1.28 mL, 10.7 mmol). The reaction mixture was stirred at room temperature for 24 h. Then, the mixture was diluted with Et₂O, washed with brine, dried, concentrated and purified by flash column chromatography yielding 24 (1.3 g, 91% yield) as a colorless oil: [α]D₂⁵⁺ = −2.2 (c=3.1 in CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 1.59 (d, J = 13.2 Hz, 1H), 1.90 (dddd, δ = 12.5, 12.5, 12.5, 5.1 Hz, 1H), 3.54 (dd, δ = 10.1, 4.7 Hz, 1H), 3.67 (dd, δ = 10.2, 5.9 Hz, 1H), 3.99 (dddd, δ = 12.0, 12.0, 2.4 Hz, 1H ), 4.09–4.16 (m, 1H), 4.30 (dd, δ = 11.4, 4.9 Hz, 1H), 4.60 (d, δ = 2.9 Hz, 2H), 5.55 (s, 1H), 7.27–7.41 (m, 8H), 7.49–7.54 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ = 28.0 (t), 66.6 (t), 72.8 (t), 73.3 (t), 76.2 (d), 101.0 (d), 126.0 (d), 126.4 (d), 127.5 (d), 127.6 (d), 127.7 (d), 128.0 (d), 128.2 (d), 128.3 (d), 128.6 (d), 128.8 (d), 138.1 (s), 138.5 (s); IR (film) γ max (cm⁻¹) 3500, 3031, 2857, 1956, 1716, 1454, 1362, 1106, 1027; MS m/z (relative intensity) (FAB) 285 (M⁺ + 1)⁺ (9), 284 (M⁺)⁺ (4), 283 (M – 1)⁺ (8), 107 (10), 91 (100). HMRS calcd for C₁₈H₂₀O₃ (M)⁺ 284.141245, found 284.141043.

Preparation of (3S)-3,4-bis-benzylxy-butan-1-ol (25). To a solution of 24 (1 g, 3.5 mmol), sodium cyanoborohydride (1.39 g, 21.0 mmol) and powdered 4-Å molecular sieves in dry CH₃CN (400 mL) was added a solution of TMSCl (27 mL, 21 mmol) in dry CH₃CN (140 mL), under argon at 0 ºC. The reaction mixture was stirred at room temperature for 5 h. Then, the mixture was filtered through a pad of Celite and the filter was poured into an aqueous solution of NaHCO₃ cooled with ice. The mixture was extracted with CH₂Cl₂, washed with brine, dried (MgSO₄), concentrated and purified by flash column chromatography yielding 25 (870.8 mg, 87% yield) as a colorless oil: [α]D₂⁵⁺ =+8.0 (c=4.2 in CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 1.83 (dd, δ = 11.4, 5.8 Hz, 3H), 1.90 (ddd, δ = 12.5, 12.5, 5.1 Hz, 1H), 3.94 (dd, δ = 10.2, 5.9 Hz, 1H), 3.99 (dddd, δ = 12.0, 12.0, 2.4 Hz, 1H ), 4.09–4.16 (m, 1H), 4.30 (dd, δ = 11.4, 4.9 Hz, 1H), 4.60 (d, δ = 2.9 Hz, 2H), 5.55 (s, 1H), 7.27–7.41 (m, 8H), 7.49–7.54 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ = 28.0 (t), 66.6 (t), 72.8 (t), 73.3 (t), 76.2 (d), 101.0 (d), 126.0 (d), 126.4 (d), 127.5 (d), 127.6 (d), 127.7 (d), 128.0 (d), 128.2 (d), 128.3 (d), 128.6 (d), 128.8 (d), 138.1 (s), 138.5 (s); IR (film) γ max (cm⁻¹) 3500, 3031, 2857, 1956, 1716, 1454, 1362, 1106, 1027; MS m/z (relative intensity) (FAB) 285 (M⁺ + 1)⁺ (9), 284 (M⁺)⁺ (4), 283 (M – 1)⁺ (8), 107 (10), 91 (100). HMRS calcd for C₁₈H₂₀O₃ (M)⁺ 284.141245, found 284.141043.

Hz, 2H), 3.60 (t, J = 5.0 Hz, 2H), 3.74 (d, J = 5.5 Hz, 2H), 3.79–3.87 (m, 1H), 4.57 (br s, 2H), 4.58 (d, J = 11.6 Hz, 1H), 4.73 (d, J = 11.6 Hz, 1H), 7.34 (br s, 10H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 34.6 (t), 60.2 (t), 72.1 (t), 72.4 (t), 73.5 (t), 76.6 (d), 127.7 (d), 127.8 (d), 127.9 (d), 128.5 (d), 138.0 (s), 138.3 (s); IR (film) $\nu_{max}$ (cm$^{-1}$) 3071, 2931, 2858, 1427, 1111; MS m/z (relative intensity) 385 (M$^+$ – 1)$^+$ (10), 269 (M – OH)$^+$ (5), 179 (M – OBn)$^+$ (5), 91 (100). Anal. Calcd for C$_{18}$H$_{22}$O$_3$: C, 75.50; H, 7.74. Found: C, 75.63; H, 8.08.

Preparation of (2$^S$)-1,2-bis-benzyloxy-nonan-4-one (26). The same procedure used above to obtain the ketone 14b from the alcohol 4 ($R^1$=n-C$_{13}$H$_{27}$) was applied to 25 (700 mg, 2.45 mmol) yielding the ketone 26 (623.8 mg, 72% overall yield) as a colorless oil: $[\alpha]_D^{25}$ = −14.9 (c=0.8 in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.87 (t, J = 7.0 Hz, 3H), 1.22–1.30 (m, 4H), 1.51–1.59 (m, 2H), 2.39 (t, J = 9.8 Hz, 2H), 2.63 (dd, J = 16.3, 5.0 Hz, 1H), 2.75 (dd, J = 16.3, 7.4 Hz, 1H), 3.52–3.58 (m, 2H), 4.11–4.18 (m, 1H), 4.53 (br s, 2H), 4.55 (d, J = 11.5 Hz, 1H), 4.64 (d, J = 11.5 Hz, 1H), 7.30 (br s, 10H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 13.9 (q), 22.4 (t), 23.2 (t), 31.3 (t), 43.9 (t), 45.2 (t), 71.7 (t), 72.4 (t), 73.3 (t), 74.5 (d), 127.6 (d), 127.8 (d), 128.3 (d), 138.1 (s), 138.4 (s), 209.3 (s); IR (film) $\nu_{max}$ (cm$^{-1}$) 2956, 1720, 1453, 1273; MS m/z (relative intensity) (FAB) 355 (M$^+$ + 1)$^+$ (14), 354 (M)$^+$ (9), 353 (M – 1)$^+$ (16), 322 (100), 277 (M – C$_6$H$_5$)$^+$ (16). Anal. Calcd for C$_{23}$H$_{30}$O$_3$: C, 77.93; H, 8.53. Found: C, 78.09; H, 8.80.

Preparation of (2$^R$,4$^R$)-1-benzyloxy-4-pentyl-5-undecin-2-ol (28). The same procedure used above to obtain 17b from the ketone 14b was applied to 26 (500 mg, 1.41 mmol) yielding the alcohol 28 (379 mg, 78% yield from 27) as a colorless oil: $[\alpha]_D^{25}$ = −9.3 (c=0.41 in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.89 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 7.0 Hz, 3H), 1.26–1.50 (m, 12H), 1.64 (m, 2H), 2.12 (m, 2H), 2.38 (m, 1H), 2.73 (br s, 1H), 3.41 (dd, J = 9.5, 6.8 Hz, 1H), 3.53 (dd, J = 9.5, 3.7 Hz, 1H), 4.03 (m, 1H), 4.57 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 14.0 (q), 14.1 (q), 18.7 (t), 22.2 (t), 22.6 (t), 26.8 (t), 28.7 (d), 31.0 (t), 31.6 (t), 35.5 (t), 39.0 (t), 69.6 (d), 73.3 (t), 74.0 (t), 82.5 (s), 83.1 (s), 127.7 (d), 128.4 (d), 138.1 (s); IR (film) $\nu_{max}$ (cm$^{-1}$) 3450, 2956, 2858, 1455, 1101; MS m/z (relative intensity) 345 (M + 1)$^+$ (6), 344 (M)$^+$ (6), 343 (M – 1)$^+$ (9), 307 (18), 289 (17), 154 (100). Anal. Calcd for C$_{23}$H$_{36}$O$_2$: C, 80.18; H, 10.53. Found: C, 80.33; H, 10.67.

Preparation of 1-Benzyloxy-8-(2-propenyl-penta-2,4-dienyloxy)-oct-4-yne-3,6-diol (30). To a solution of (ClCO)$_2$ (1.1 mL, 12.0 mmol) in dry CH$_2$Cl$_2$ (20 mL), was slowly added DMSO (1.1 mL, 15.1 mmol) under argon at −78°C. The mixture was stirred for 10 min, and then alcohol 29 (1 g, 6.0 mmol) in dry CH$_2$Cl$_2$ (4 mL) was added and stirred for 1 h. After which time, Et$_3$N (4.2 mL, 30 mmol) was added and allowed to warm to room temperature and stirred for 30 min. The mixture
was diluted with CH₂Cl₂ and poured into a saturated aqueous solution of NH₄Cl. The phases were separated and the aqueous phase extracted with CH₂Cl₂. The combined organic phases were washed with brine, dried (MgSO₄), filtered and concentrated. The aldehyde obtained was used in the next step without further purification.

To a solution of acetylene (4.33 mL, 0.6 M in THF, 2.6 mmol) in dry THF (17 mL), n-BuLi was slowly added (15.1 mL of a solution 1.9 M in hexanes, 8.37 mmol) under argon at 0 °C generating the di-lithium salt. The mixture was allowed to warm to 10 °C and stirred for 30 min. After which time was cooled at −78 °C and the aldehyde obtained above was dropwise added in dry THF (1.8 mL). The reaction mixture was stirred for 1 h, after which time TLC showed not remaining starting material. The mixture was diluted with Et₂O and a saturated aqueous solution of NH₄Cl was added. The phases were separated and the aqueous phase extracted with Et₂O. The combined organic phases were washed with brine, dried (MgSO₄), filtered and concentrated. The crude obtained was purified by flash chromatography affording the diol (0.7 g, 66% overall yield) as a colorless oil:

\[ \delta = 1.93−2.06 \text{ (m, 4H)}, 3.62−3.67 \text{ (m, 2H)}, 3.77−3.84 \text{ (m, 2H)}, 4.62 \text{ (s, 4H)}, 4.64 \text{ (t, } J = 5.4 \text{ Hz, 2H)}, 7.27−7.39 \text{ (m, 10H)}; \]

\[ \delta = 36.8 \text{ (t), 61.1 (d), 67.5 (t), 73.3 (t), 85.4 (s), 127.7 (d), 128.4 (d), 137.9 (s)}; \]

IR (film) \[ \gamma_{\text{max}} \text{ (cm}^{-1}) 3398, 2865, 1454, 1100, 1027; \]

MS \[ m/z \text{ (relative intensity) (FAB) 355 (M} + 1)^+ (10), 354 (M)^+ (8), 91 (100). \]

HMRS calcd for C₂₂H₂₆O₄ (M)\(^+\) 354.183110, found 354.182474.

Preparation of Hexacarbonyl-[\(\mu_2-\eta^2\)-(2-(benzyloxy)ethyl)-3,4-dydehydro-2,5,6,7-tetrahydro-oxe-pyne]-3-dicobalt (Co-Co) (34). The same procedure used above to obtain 6b from 4 (R\(^1\)=n-C\(_3\)H\(_7\)) was applied to the diol (500 mg, 1.42 mmol) using in this case 2.5 equiv. of BF\(_3\)-OEt\(_2\) (0.45 mL, 2.48 mmol), yielding 34 (593 mg, 81% overall yield) as a colorless oil:

\[ \delta = 1.81−1.88 \text{ (m, 2H)}, 1.91−2.02 \text{ (m, 1H)}, 2.14−2.22 \text{ (m, 1H)}, 2.77−2.89 \text{ (m, 1H)}, 3.26 \text{ (d, } J = 16.1 \text{ Hz, 1H)}, 3.47 \text{ (t, } J = 12.4 \text{ Hz, 1H)}, 3.64−3.39 \text{ (m, 2H)}, 4.31 \text{ (d, } J = 11.0 \text{ Hz, 1H)}, 4.52 \text{ (d, } J = 12.0 \text{ Hz, 2H)}, 4.56 \text{ (d, } J = 12.0 \text{ Hz, 2H)}, 4.59−4.64 \text{ (m, 1H)}, 7.31−7.40 \text{ (m, 5H)}; \]

\[ \delta = 30.1 \text{ (t), 33.5 (t), 37.7 (t), 66.7 (t), 73.0 (t), 73.8 (t), 79.6 (d), 127.5 (d), 127.7 (d), 128.3 (d), 138.5 (s); IR (film) } \gamma_{\text{max}} \text{ (cm}^{-1}) 2860, 2790, 2173, 2060, 1153; \]

MS \[ m/z \text{ (relative intensity) (FAB) 516 (M}^+ \text{) (12), 460 (M} − 2\text{CO})^+ \text{) (4), 432 (M} − 3\text{CO})^+ \text{) (24), 376 (M} − 5\text{CO})^+ \text{) (23), 348 (M} − 6\text{CO})^+ \text{) (5), 154 (100). } \]

Anal. Calcd for C\(_{21}\)H\(_{18}\)Co\(_2\)O\(_8\): C, 48.86; H, 3.51. Found: C, 48.89; H, 3.87. Preparation of 2-Oxepan-2-yl-ethanol (35). A mixture of cobalt complex 34 (100 mg, 0.19 mmol) and tributyltin hydride (0.32 mL, 1.14 mmol) in benzene (4 mL) was degassed and then
heated to 80 °C with stirring. After 5 h the reaction mixture was cooled to room temperature and concentrated in vacuum. The residue was purified by silica gel column chromatography to afford a regioisomeric mixture of 7-(2-benzyloxy-ethyl)-2,3,4,7-tetrahydro-oxepine and 2-(2-benzyloxy-ethyl)-2,3,6,7-tetrahydro-oxepine (33 mg, 75% yield) as a colorless oil: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 1.77–1.89 \text{ (m, 3H)}\), 2.16–2.48 (m, 3H), 3.38 (t, \(J = 11.2 \text{ Hz, 0.5H})\), 3.57–3.65 (m, 3H), 4.00–4.03 (m, 1H), 4.23 (br s, 0.5H), 4.51 (br s, 2H), 5.55 (d, \(J = 11.1 \text{ Hz, 0.5H})\), 5.78–5.80 (m, 1.5H), 7.28–7.33 (m, 5H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 26.0 \text{ (t)}, 26.9 \text{ (t)}, 29.1 \text{ (t)}, 32.5 \text{ (t)}, 36.5 \text{ (t)}, 37.0 \text{ (t)}, 37.8 \text{ (t)}, 66.9 \text{ (t)}, 67.2 \text{ (t)}, 69.9 \text{ (t)}, 71.4 \text{ (t)}, 72.9 \text{ (t)}, 73.0 \text{ (t)}, 72.9 \text{ (t)}, 130.6 \text{ (d)}, 132.0 \text{ (d)}, 134.5 \text{ (d)}, 138.7 \text{ (s)}\); IR (film) \(\gamma_{\text{max}} \text{ (cm}^{-1}\) 3351, 1431, 1052; MS \(m/z \) (relative intensity) (FAB) 232 (M\(^+\)) (28), 231 (M\(^+\) - 1) \(\text{+} \) (68), 229 (100). HMRS calcd for C\(_{15}\)H\(_{20}\)O\(_2\) (M\(^+\)) 232.146330, found 232.144175.

To a solution of the above mixture (25.0 mg, 0.11 mmol) in MeOH (8 mL) was added Pd/C (5% Pd) (1.3 mg, 5% w/w). The resulting suspension was vigorously stirred under an atmosphere of H\(_2\) (ca. 1 atmosphere) for 1 h at room temperature. After removal of the catalysts by filtration through a small pad of Celite, the filtrate was concentrated and purified by column chromatography yielding \(\text{35} \) (11.5 mg, 75% overall yield from \(\text{34}\)) as a colorless oil: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 1.51–1.79 \text{ (m, 10H)}, 3.51–3.64 \text{ (m, 2H)}, 3.77 \text{ (t, J = 5.8 Hz, 2H)}, 3.84–3.92 \text{ (m, 1H)}\); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 25.6 \text{ (t)}, 26.7 \text{ (t)}, 30.7 \text{ (t)}, 36.3 \text{ (t)}, 38.3 \text{ (t)}, 61.7 \text{ (t)}, 68.7 \text{ (t)}, 80.3 \text{ (d)}\); IR (film) \(\gamma_{\text{max}} \text{ (cm}^{-1}\) 3390, 2929, 2857, 1714, 1453, 1371, 1053; MS \(m/z \) (relative intensity) (FAB) 144 (M\(^+\)) (13), 143 (M\(^+\) - 1) \(\text{+} \) (13), 133 (100), 127 (M – OH) \(\text{+} \) (16). HMRS calcd for C\(_8\)H\(_{16}\)O\(_2\) (M\(^+\)) 144.115030, found 144.115997.

**Preparation of 8-Benzylxy-oct-4-yne-1,6-diol (36).** The same procedure used above to obtain \(\text{6b} \) from \(\text{5b} \) was applied to \(\text{30} \) (100 mg, 0.28 mmol) using only one equivalent of BF\(_3\)-OEt\(_2\) (36 \(\mu L\), 0.28 mmol) yielding \(\text{36} \) (9 mg, 13% overall yield) as a colorless oil: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 1.74 \text{ (ddd, J = 13.0, 6.4, 6.4 Hz, 2H)}, 1.94–2.05 \text{ (m, 2H)}, 2.24 \text{ (br s, 2H)}, 3.32 \text{ (ddd, J = 6.9, 6.9, 1.8 Hz, 2H)}, 3.63–3.65 \text{ (m, 1H)}, 3.72 \text{ (t, J = 6.1 Hz, 2H)}, 3.78–3.82 \text{ (m, 1H)}, 4.52 \text{ (br s, 2H)}, 4.56–4.60 \text{ (m, 1H)}, 7.28–7.38 \text{ (m, 5H)}\); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 15.2 \text{ (t)}, 31.1 \text{ (t)}, 37.3 \text{ (t)}, 61.0 \text{ (d)}, 61.3 \text{ (t)}, 67.5 \text{ (t)}, 73.2 \text{ (t)}, 81.3 \text{ (s)}, 84.7 \text{ (s)}, 127.7 \text{ (d)}, 128.4 \text{ (d)}, 137.9 \text{ (s)}\); IR (film) \(\gamma_{\text{max}} \text{ (cm}^{-1}\) 3382, 2928, 2869, 1366, 1075; MS \(m/z \) (relative intensity) (FAB) 249 (M + 1) \(\text{+} \) (17), 248 (M\(^+\)) (1), 229 (10), 138 (41), 91 (100). HMRS calcd for C\(_{15}\)H\(_{20}\)O\(_3\) (M\(^+\)) 248.141245, found 248.141380.

**Preparation of 5-Benzylxy-pent-1-yn-3-ol (37).** The same oxidation procedure (Swern oxidation) used above to obtain the corresponding aldehyde from the alcohol \(\text{29} \) was newly applied...
on a 500 mg (6.57 mmol) scale. The aldehyde obtained was used in the next step without further purification.

To a solution of trimethylsilylacetylene (1.9 mL, 13.1 mmol) in dry THF (100 mL) under argon was added dropwise 0.9 equiv of n-BuLi (6.2 mL, 11.7 mmol, 1.9 M in n-hexane) at –78°C. The reaction was allowed to warm to –20 °C and stirred for 15 min, after which time was added the aldehyde in dry THF (20 mL) at –78 °C. The reaction mixture was stirred for 1 h, after which time TLC showed complete conversion. The reaction was poured into NH₄Cl saturated aqueous solution and ether and the aqueous phase extracted with ether. The combined organic solutions were dried over MgSO₄ and concentrated and the crude was used without purification.

To a stirred solution of the alkene in dry THF (30 mL) under argon was added n-TBAF 1 M in THF (7.9 mL, 7.9 mmol) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was poured into H₂O and extracted with ether. The combined organic solutions were washed with brine and dried. The resulting solution was concentrated and purified by column chromatography, yielding the alcohol 37 (786 mg, 63% overall yield) as a colorless oil:

1H NMR (400 MHz, CDCl₃) δ = 1.94–2.00 (m, 1H), 2.07–2.12 (m, 1H), 2.45 (d, J = 2.0 Hz, 1H), 3.68 (ddd, J = 10.0, 4.7, 4.7 Hz, 1H), 3.86 (ddd, J = 9.3, 9.3, 4.0 Hz, 1H), 4.53 (br s, 2H), 4.60–4.64 (m, 1H), 7.27–7.38 (m, 5H); 13C NMR (75 MHz, CDCl₃) δ = 36.8 (t), 60.7 (d), 67.3 (t), 73.0 (d), 73.3 (t), 84.5 (s), 127.5 (d), 127.7 (d), 127.8 (d), 128.5 (d), 137.9 (s); IR (film) ?max (cm⁻¹) 3396, 3288, 3031, 2928, 2867, 1454, 1366, 1094, 1028; MS m/z (relative intensity) (FAB) 191 (M + 1)+ (21), 190 (M)+ (5), 189 (M – 1)+ (30), 173 (M – OH)+ (41), 91 (100). HMRS calcd for C₁₂H₁₄O₂ (M) 190.099380, found 190.098979.

Preparation of 1,10-bis-Benzylxy-deca-4,6-diyne-3,8-diol (38). To a solution of alcohol 37 (200 mg, 1.05 mmol) in dry MeOH (7.5 mL), were added pyridine (5.4 mL) and Cu(OAc)₂ (293 mg, 1.47 mmol) under argon at room temperature. The mixture was refluxed and stirred for 4 h, after which time TLC showed not remaining starting material and was cooled to room temperature. The mixture was diluted with Et₂O and poured into water. The phases were separated and the aqueous phase extracted with Et₂O. The combined organic phases were washed with brine, dried (MgSO₄), filtered and concentrated. The residue obtained was purified by column chromatography, yielding 38 (174.6 mg, 88% yield) as a colorless oil: 1H NMR (400 MHz, CDCl₃) δ = 1.90–2.00 (m, 2H), 2.07–2.17 (m, 2H), 3.68 (ddd, J = 10.0, 5.0, 5.0 Hz, 2H), 3.86 (ddd, J = 9.3, 9.3, 3.9 Hz, 2H), 4.53 (d, J = 1.7 Hz, 4H), 4.67 (d, J = 4.6 Hz, 4H), 7.27–7.40 (m, 10H); 13C NMR (75 MHz, CDCl₃) δ = 36.4 (t), 61.9 (d), 67.5 (t), 69.0 (s), 79.4 (t), 79.7 (s), 127.7 (d), 127.8 (d), 128.5 (d), 137.6 (s); IR (film) ?max (cm⁻¹) 3351, 2957, 1431, 1057; MS m/z (relative intensity) (FAB) 377 (M – 1)+ (18),
361 (M – OH)

Preparation of Deca-4,6-diyne-1,10-diol (40). The same procedure (complexation with Co\(_2\)(CO)\(_8\), addition of BF\(_3\)-OEt\(_2\) and demetalation with CAN) used above to obtain 6b from 4 (R\(^1\)=n-C\(_3\)H\(_7\)) was applied to 38 (100 mg, 0.26 mmol) using in this case 2.3 equiv. of Co\(_2\)(CO)\(_8\) (204 mg, 0.60 mmol) and 2.5 equiv. of BF\(_3\)-OEt\(_2\) (82 µL, 0.65 mmol) yielding 40 (32.4 mg, 63% overall yield) as a white solid: m.p. 45 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 1.76 (t, J = 6.4 \text{ Hz}, 4H), 1.81 (\text{br s}, 2H), 2.37 (t, J = 6.9 \text{ Hz}, 4H), 3.73 (t, J = 6.1 \text{ Hz}, 4H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 15.7 \text{ (t)}, 30.9 \text{ (t)}, 61.4 \text{ (t)}, 65.9 \text{ (s)}, 76.8 \text{ (s)}; \text{IR (film) } \gamma_{\text{max}} \text{ (cm}^{-1}) 3334, 2950, 1428, 1057, 928; \text{MS } m/z \text{ (relative intensity) (FAB) 167 (M+1)}^+ (7), 166 (M)^+ (11), 165 (M – 1)^+ (5), 149 (M – CH\(_2\)OH)^+ (7), 135 (M – CH\(_2\)OH)^+ (6), 154 (100). Anal. Calcd for C\(_{10}\)H\(_{14}\)O\(_2\): C, 72.26; H, 8.49. Found: C, 72.57; H, 8.81.

Preparation of (3R,4R)-3,4-bis(Benzyloxy)-hexane-1,6-diol (42). To a stirred solution of (E)-3-hexen-1,5-diol (41) in dry i-Pr\(_2\)NEt (13 mL) was added MOMCl (1.7 mL, 22.8 mmol) at 0 °C. The reaction was allowed to warm to room temperature and vigorously stirred for 30 min, after which time TLC analysis showed the end of the reaction. The mixture was diluted with Et\(_2\)O and 5% HCl were added and the aqueous phase extracted with Et\(_2\)O. The combined organic phases were washed with saturated aqueous NaHCO\(_3\) solution, brine, dried (MgSO\(_4\)), filtered and concentrated. The residue obtained was used without further purification. A suspension of AD-Mix-β (5.3 g, 1.4g/mmol of starting olefin) and CH\(_3\)SO\(_2\)NH\(_2\) (370 mg, 3.88 mmol) in t-BuOH:H\(_2\)O (1:1, 38 mL) was vigorously stirred at room temperature for 10 min and additional 10 min at 0 °C. The crude olefin previously obtained was added dropwise and the mixture stirred for 12 h at 0 °C. After which time, a saturated aqueous Na\(_2\)S\(_2\)O\(_3\) solution was added and the aqueous phase extracted with EtOAc. The combined organic phases were washed with brine, dried (MgSO\(_4\)), filtered and concentrated. The residue obtained was purified by column chromatography, yielding (3R,4R)-1,6-bis(methoxymethoxy)-hexane-3,4-diol (735.5 mg, 83% yield from 41) as slightly yellow oil: [α]\(^{25}\)_D = +13.7 (c= 0.9 in CHCl\(_3\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 1.77 \text{ dd, } J = 5.7 \text{ Hz, 4H}), 3.08 (\text{br s}, 2H), 3.33 (s, 6H), 3.61–3.69 (m, 2H), 3.69–3.76 (m, 4H), 4.59 (s, 4H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 33.7 \text{ (t)}, 55.3 \text{ (q), 65.4 (t), 72.6 (d), 96.5 (t); } \text{IR (film) } \gamma_{\text{max}} \text{ (cm}^{-1}) 3444, 2931, 2886, 1386, 1108, 1047; \text{MS } m/z \text{ (relative intensity) (FAB) 239 (M + 1)}^+ (18), 238 (M)^+ (1), 207 (M – CH\(_3\)O)^+ (6), 154 (100). Anal. Calcd for C\(_{10}\)H\(_{22}\)O\(_6\): C, 50.41; H, 9.31. Found: C, 50.54; H, 9.39.
To a suspension of NaH (259 mg, 6.47 mmol, 60% in mineral oil) in dry THF (30 mL) cooled at 0 °C and under argon, was dropwise added the previously obtained diol and the mixture stirred for 30 min. After which time, benzyl bromide (0.73 mL, 6.17 mmol) and a catalytic amount of TBAI was dropwise added. After 12 h at rt, the mixture was diluted with Et₂O and saturated aqueous NH₄Cl solution. The aqueous phase extracted with Et₂O, the combined organic phases were washed with brine, dried (MgSO₄), filtered and concentrated. The residue obtained purified by column chromatography, yielding (3R,4R)-1,6-bis(methoxymethoxy)-3,4-bis(benzyloxy)-hexane (1.09 g, 89% yield) as slightly yellow oil: [α]D²⁵ = +24.5 (c = 3.4 in CHCl₃); 1.77–1.78 (m, 2H), 1.95–2.03 (m, 2H), 3.32 (s, 6H), 3.58–3.67 (m, 4H), 3.69–3.77 (m, 2H), 4.53–4.74 (m, 8H), 7.33 (br s, 10H); ¹³C NMR (75 MHz, CDCl₃) δ = 30.2 (t), 55.2 (q), 64.6 (t), 72.7 (t), 76.6 (d), 96.4 (t), 127.6 (d), 127.9 (d), 128.3 (d), 128.7 (d), 129.7 (d), 138.6 (s); IR (film) νmax (cm⁻¹) 2930, 2882, 1720, 1453, 1384, 1274, 1109; MS m/z (relative intensity) (FAB) 419 (M + 1)⁺ (27), 418 (M)⁺ (16), 417 (M − 1)⁺ (27), 387 (M − CH₃O)⁺ (27), 311 (M − OBn)⁺ (16), 265 (100). HMRS calcd for C₂₄H₃₄O₆ (M)⁺ 418.235539, found 418.235664.

To a solution of (3R,4R)-1,6-bis(methoxymethoxy)-3,4-bis(benzyloxy)-hexane (1 g, 2.39 mmol) in MeOH (12 mL) at 0 °C was added a catalytic amount of concentrated HCl. The reaction mixture was vigorously stirred for 1 h, after which time TLC analysis showed the end of the reaction. Et₃N was added until pH ~ 7.0, the solvent was evaporated and the residue purified by column chromatography, yielding 42 (734 mg, 93% yield) as colorless oil: [α]D²⁵ = +32.1 (c = 2.6 in CHCl₃); 1.77–1.81 (m, 2H), 1.86–1.99 (m, 2H), 2.26 (br s, 2H), 3.66–3.75 (m, 4H), 3.76–3.82 (m, 2H), 4.55 (d, J = 11.5 Hz, 2H), 7.33 (s, 10H); ¹³C NMR (75 MHz, CDCl₃) δ = 32.4 (t), 60.1 (t), 72.6 (t), 77.7 (d), 127.9 (d), 128.0 (d), 128.5 (d), 138.1 (s); IR (film) νmax (cm⁻¹) 3382, 2879, 1716, 1359, 1062; MS m/z (relative intensity) (FAB) 331 (M + 1)⁺ (19), 330 (M)⁺ (2), 239 (M − 1)⁺ (5), 311 (M − H₂O)⁺ (3), 253 (M − C₆H₅)⁺ (5), 91 (100). HMRS calcd for C₂₀H₂₆O₄ (M)⁺ 330.183110, found 330.184165.

Preparation of (5S,6S)-5,6-bis(Benzyloxy)-1,9-decadiyne-3,8-diol (44). To a solution of the diol 42 (1.5 g, 4.54 mmol) in dry CH₂Cl₂ (25 mL) under argon were added 3,4-dihydro-2H-pyran (0.62 mL, 6.82 mmol) and a catalytic amount of PPTS at 0 °C. The reaction was allowed to warm to room temperature and stirred for 6 h. The mixture was poured into ice-water and extracted with CH₂Cl₂. The combined organic phases were washed with saturated aqueous NaCl, dried (MgSO₄), filtered and concentrated to afford the corresponding protected primary alcohol that was used in the next step without further purification.

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The same procedure used above to obtain 37 from 29 (steps 1 and 2) was applied to the previous alcohol. The residue obtained was acetylated (see preparation of 19a) and the THP group cleaved with catalytic HCl in MeOH at 0 °C, yielding the alcohol 43 (1.12 g, 53% overall yield).

The same sequence of reactions (Swern oxidation and addition of lithium trimethylsilylacetylide) used above was applied to the alcohol 43 (1 g, 2.14 mmol) to afford the corresponding propargylic alcohol, which was hydrolyzed with sodium methoxide as followed.

To a suspension of NaH (219 mg, 5.48 mmol, 60% in mineral oil) in dry CH₂Cl₂ (20 mL) cooled at a 0 °C and under argon, was dropwise added dry MeOH. After a few minutes, was added the acetylated crude obtained previously in dry CH₂Cl₂ (5 mL). After 30 min a saturated aqueous solution of NaCl was added. The phases were separated and the aqueous phase extracted with CH₂Cl₂. The combined organic phases were washed with brine, dried (MgSO₄), filtered and concentrated. The residue obtained was purified by column chromatography, yielding 44 (638.8 mg, 79% yield from 43) as a colorless oil:

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta = 1.89–2.11 (m, 4H), 2.47 (br s, 2H), 2.76 (br s, 1H), 2.95 (br s, 1H), 3.04 (br s, 1H), 3.79–3.99 (m, 1H), 4.13–4.17 (m, 1H), 4.48–4.70 (m, 6H), 7.33 (br s, 10H); } ^{13}C \text{NMR (75 MHz, CDCl}_3 \delta = 37.2 (t), 60.6 (d), 72.4 (t), 73.3 (s), 76.1 (d), 84.4 (s), 128.1 (d), 128.2 (d), 128.5 (d), 137.4 (s); } \text{IR (film)} \gamma_{\text{max}} (\text{cm}^{-1}) 3401, 3289, 2932, 1714, 1272, 1271; MS m/z (relative intensity) (FAB) 379 (M+1)\(^+\) (35), 378 (M)\(^+\) (5), 377 (M–1)\(^+\) (5), 271 (M–OBn)\(^+\) (13), 154 (100). \text{HMRS calcd for C}_{24}H_{26}O_4 (M)\(^+\) 378.183110, found 378.184573. \]

Preparation of the Mixture (2R,3S,5R and 5S)-3-Benzylxy-2-but-3-ynyl-5-ethynyl-tetrahydro-furan (45). The same procedure used above to obtain 40 from 38 was applied to 44 (150 mg, 0.40 mmol) yielding the diastereoisomeric mixture 45 (150 mg, 84% overall yield) as a colorless oil.

Diastereoisomer 1: \[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta = 1.64–1.97 (m, 3H), 2.13–2.18 (m, 1H), 2.28–2.33 (m, 2H), 2.45 (br s, 2H), 4.11 (br s, 1H), 4.20 (br s, 1H), 4.41 (d, J = 12.0 Hz, 1H), 4.59 (d, J = 12.0 Hz, 1H), 4.77–4.82 (m, 1H), 7.26–7.46 (m, 5H); } ^{13}C \text{NMR (75 MHz, CDCl}_3 \delta = 15.4 (t), 27.9 (t), 39.5 (t), 66.1 (d), 68.5 (s), 71.2 (t), 73.0 (s), 78.8 (d), 80.6 (d), 83.7 (s), 84.0 (s), 127.5 (d), 127.7 (d), 128.4 (d), 128.8 (d), 137.9 (s); } \text{IR (film)} \gamma_{\text{max}} (\text{cm}^{-1}) 3290, 2941, 2939, 2869, 1722, 1452, 1273, 1060; MS m/z (relative intensity) (FAB) 255 (M+1)\(^+\) (33), 254 (M)\(^+\) (20), 253 (M–1)\(^+\) (47), 204 (43), 164 (100). \text{HMRS calcd for C}_{17}H_{18}O_2 (M)\(^+\) 254.130680, found 254.130887. \]

Diastereoisomer 2: \[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta = 1.90–1.94 (m, 2H), 1.95–2.05 (m, 1H), 2.26–2.39 (m, 3H), 2.48 (br s, 2H), 3.90 (ddd, J = 9.4, 4.5, 4.5 Hz, 1H), 4.03–4.08 (m, 1H), 4.41 (d,}
Transfer of Chirality During the Nicholas Reaction in \(\gamma\)-Benzyloxy Propargylic Alcohols

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\[ J = 12.0 \text{ Hz, 1H}, 4.55 \text{ (ddd, } J = 7.0, 7.0, 2.0 \text{ Hz, 1H}), 4.63 \text{ (d, } J = 12.0 \text{ Hz, 1H}), 7.26 - 7.40 \text{ (m, 5H)}; \text{ IR (film) } \nu_{\text{max}} \text{ (cm}^{-1}) \text{ 3291, 2940, 2870, 1722, 1452, 1273, 1059}; \text{ MS } m/z \text{ (relative intensity) (FAB) 255 (M + 1)^+ (30), 254 (M)^+ (17), 253 (M – 1)^+ (39), 164 (100). HMRS calcd for C}_{17}\text{H}_{18}\text{O}_2 (M)^+ 254.130680, \text{ found 254.130687.} \]

Preparation of (2S,3R)-3-Benzyloxy-hexane-1,2-diol (49). The diol \(\text{49}\) (10 g, 42.0 mmol) was protected as benzylidene derivative applying the same procedure used in the synthesis of the alcohol \(\text{4} (R^1=\text{-}n\text{-C}_3\text{H}_7)\). The product obtained was hydrolyzed with sodium methoxide (see preparation of \(\text{44}\) ) and the secondary hydroxyl group protected as benzyl ether (see preparation of \(\text{44}\) ) to afford a crude which was dissolved in MeOH (100 mL) and added a catalytic amount of CSA at 0 °C yielding the diol \(\text{49} \) (7.24 g, 77% overall yield) as a colorless oil:

\[ [\alpha]_{D}^{25} = –0.66 \text{ (c= 7.7 in CHCl}_3\text{);} ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta = 0.93 \text{ (t, } J = 6.9 \text{ Hz, 3H), 1.35 – 1.66 \text{ (m, 4H), 2.65 \text{ (br s, 2H), 3.53 – 3.57 \text{ (m, 1H), 3.67 – 3.79 \text{ (m, 4H), 4.56 \text{ (d, } J = 11.3 \text{ Hz, 2H), 4.62 (d, } J = 11.3 \text{ Hz, 2H), 7.26 – 7.43 \text{ (m, 5H)}; ^13\text{C NMR (75 MHz, CDCl}_3\text{)} \delta = 14.2 \text{ (q), 18.7 (t), 32.7 (t), 63.3 (t), 72.7 (d), 72.7 (t), 81.1 (d), 127.8 (d), 127.9 (d), 128.3 (d), 128.5 (d), 129.7 (d), 138.2 (s); IR (film) } \nu_{\text{max}} \text{ (cm}^{-1}) \text{ 3401, 2934, 2873, 1715, 1454, 1275, 1071}; \text{ MS } m/z \text{ (relative intensity) (FAB) 225 (M + 1)^+ (10), 224 (M)^+ (8), 223 (M – 1)^+ (21), 207 (M – OH)^+ (30), 206 (M – H}_2\text{O})^+ (11), 91 (100). HMRS calcd for C}_{13}\text{H}_{20}\text{O}_3 (M) 224.141245, \text{ found 224.141659.} \]

Preparation of (2S,3R)-2,3-bis(Benzyloxy)hexan-1-ol (50). The same procedure used above to obtain \(\text{44}\) from the corresponding 1,3-diol was applied to the diol \(\text{49} \) (200 mg, 0.89 mmol) yielding the alcohol \(\text{50} \) (187 mg, 67% overall yield) as a colorless oil:

\[ [\alpha]_{D}^{25} = –4.9 \text{ (c= 0.6 in CHCl}_3\text{);} ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta = 0.91 \text{ (t, } J = 7.1 \text{ Hz, 3H), 1.26 – 1.60 \text{ (m, 4H), 2.31 \text{ (br s, 1H), 3.51 (dd, } J = 9.1, 4.5 \text{ Hz, 1H), 3.62 – 3.68 \text{ (m, 1H), 3.80 \text{ (br s, 2H), 4.58 \text{ (d, } J = 11.3 \text{ Hz, 1H), 4.64 \text{ (br s, 2H), 4.68 (d, } J = 11.3 \text{ Hz, 1H), 7.26 – 7.43 \text{ (m, 10H); ^13\text{C NMR (75 MHz, CDCl}_3\text{)} \delta = 14.2 \text{ (q), 18.6 (t), 33.5 (t), 61.5 (t), 72.1 (d), 72.8 (t), 79.4 (d), 80.9 (d), 127.7 (d), 127.8 (d), 127.9 (d), 128.4 (d), 128.5 (d), 138.4 (s); IR (film) } \nu_{\text{max}} \text{ (cm}^{-1}) \text{ 3423, 2361, 1650, 1276}; \text{ MS } m/z \text{ (relative intensity) (FAB) 315 (M + 1)^+ (10), 314 (M)^+ (5), 313 (M – 1)^+ (21), 207 (M – OH)^+ (30), 206 (M – H}_2\text{O})^+ (11), 91 (100). HMRS calcd for C}_{20}\text{H}_{26}\text{O}_3 (M)^+ 224.141245, \text{ found 224.141659.} \]

Preparation of (4R,5S)-5-Benzxyloxy-tridec-7-yn-4-ol (52). The same procedure used above to obtain \(\text{6b}\) from \(\text{4 (R^1=\text{-}n\text{-C}_3\text{H}_7)}\) was applied to the alcohol \(\text{50} \) (200 mg, 0.89 mmol) using the lithium salt of 1-heptyne yielding the alcohol \(\text{52} \) (see Table 4) as a colorless oil:

\[ [\alpha]_{D}^{25} = +1.7 \text{ (c=0.5 in CHCl}_3\text{);} ^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta = 088 \text{ (t, } J = 7.1 \text{ Hz, 3H), 0.90 (t, } J = 7.0 \text{ Hz, 3H), 1.25 – 1.47 \text{ (m, 5H), 1.48 – 1.69 \text{ (m, 5H), 2.15 (t, } J = 6.9 \text{ Hz, 2H), 2.43 – 2.51 \text{ (m, 2H), 3.49 – 3.57 (m,} \]

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1H), 3.81–3.85 (m, 1H), 4.59 (d, J = 11.6 Hz, 1H), 4.74 (d, J = 11.5 Hz, 1H), 7.27–7.37 (m, 5H);
13C NMR (75 MHz, CDCl3) δ = 13.9 (t), 14.0 (t), 18.7 (t), 19.1 (t), 22.2 (t), 28.6 (t), 29.7 (t), 31.0 (t), 34.0 (t), 72.2 (t), 75.9 (s), 79.0 (d), 80.9 (d), 82.5 (s), 127.9 (d), 128.4 (d), 129.7 (d), 138.3 (s);
IR (film) υmax (cm⁻¹) 3315, 3423, 2930, 2870, 2361, 1456, 1276, 1127, 1069; MS m/z (relative intensity) (FAB) 302 (M⁺) (7), 285 (M − OH)⁺ (13), 225 (M − C₆H₅⁺) (8), 154 (100). Anal. Calcd for C₂₀H₃₀O₂: C, 79.42; H, 10.00. Found: C, 79.74; H, 10.31.

Preparation of (2R,3S)-2,3-bis-Benzylxy-hexan-1-ol (53). To a solution of the commercial available trans-2-hexen-1-ol (1 g, 9.98 mmol) in dry CH₂Cl₂ (55 mL) under argon were added 3,4-dihydro-2H-pyran (1.36 mL, 14.9 mmol) and a catalytic amount of PPTS at 0 °C. The reaction was allowed to warm to room temperature and stirred for 4 h. The mixture was poured into ice-water and extracted with CH₂Cl₂. The combined organic phases were washed with saturated aqueous NaCl, dried (MgSO₄), filtered and concentrated to afford the corresponding protected alcohol that was used in the next step without further purification.

A mixture of t-BuOH:H₂O (1:1, 38 mL), AD-Mix-β (5.3 g, 1.4 g/mmol of starting alkene) and CH₃SO₂NH₂ (370 mg, 3.88 mmol) at room temperature was vigorously stirred for 10 min. Then was cooled at 0 °C and was stirred for additional 10 min and the crude alkene was dropwise added. The reaction mixture was stirred for 12 h at 0°C after which time a saturated aqueous solution of Na₂S₂O₃ was added. The phases were separated and the aqueous phase extracted with AcOEt. The combined organic phases were washed with brine, dried (MgSO₄), filtered and concentrated to afford the corresponding diol that was used in the next step without further purification. The hydroxyls group were protected as benzyl ethers and the THP group cleaved with HCl (see preparation of 44) yielding the alcohol 53 (1.85 g, 59% overall yield) as a colorless oil: [α]D²⁵ = +0.8 (c=2.5 in CHCl₃); 1H NMR (400 MHz, CDCl₃) δ = 0.89 (t, J = 7.1 Hz, 3H), 1.32–1.63 (m, 4H), 2.09 (br s, 1H), 3.55–3.67 (m, 3H), 3.76–3.81 (m, 1H), 4.58 (d, J = 8.4 Hz, 2H), 4.67 (d, J = 8.7 Hz, 2H), 7.28–7.38 (m, 10H); 13C NMR (75 MHz, CDCl₃) δ = 14.2 (q), 19.1 (t), 32.2 (t), 61.8 (t), 72.8 (t), 72.9 (t), 79.6 (d), 80.1 (d), 127.8 (d), 128.0 (d), 128.1 (d), 128.4 (d), 128.7 (d), 128.8 (d), 128.9 (d), 138.4 (s); IR (film) υmax (cm⁻¹) 3428, 2957, 2872, 1716, 1454, 1275, 1096; MS m/z (relative intensity) (FAB) 315 (M + 1)⁺ (55), 314 (M)⁺ (16), 313 (M − 1)⁺ (48), 297 (M − OH)⁺ (17), 207 (M − OBn)⁺ (25), 91 (100). Anal. Calcd for C₂₀H₂₆O₃: C, 76.40; H, 8.33. Found: C, 76.59; H, 8.68.

Preparation of (2S,3R)-3-Benzylxy-2-methoxy-hexan-1-ol (56). The same procedure used above to protect the hydroxyl group as tetrahydropyranylo ether (see preparation of 44) was applied
to the diol 49 (300 mg, 1.34 mmol) to afford the corresponding protected primary alcohol that was used in the next step without further purification.

To a suspension of NaH (80.4 mg, 2.01 mmol) in dry THF (10 mL) was added the alcohol previously obtained under argon at 0 °C and stirred for 10 min. MeI (0.15 mL, 2.41 mmol) was dropwise added and after 1 h TLC showed the end of the reaction, the mixture was diluted with Et₂O and a saturated aqueous solution of NH₄Cl was added. The phases were separated and the aqueous phase extracted with Et₂O. The combined organic phases were washed with brine, dried (MgSO₄), filtered and concentrated. The same procedure for cleaving the THP group (see preparation of 44) was applied to the crude obtained, to afford a residue that was purified by column chromatography, yielding 56 (207 mg, 65% overall yield) as a colorless oil: \( [\alpha]_{D}^{25} = -5.3 \) (c=1.8 in CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) \( \delta = 0.93 \) (t, \( J = 7.2 \) Hz, 3H), 1.49–1.54 (m, 2H), 3.24 (dd, \( J = 9.2, 4.6 \) Hz, 1H), 3.45 (s, 3H), 3.61 (m, 1H), 3.78 (d, \( J = 3.4 \) Hz, 2H), 4.58 (d, \( J = 11.3 \) Hz, 1H), 4.68 (d, \( J = 11.3 \) Hz, 1H), 7.29–7.34 (m, 5H); \(^1^3^C\) NMR (75 MHz, CDCl₃) \( \delta = 13.9 \) (q), 18.8 (t), 32.4 (t), 58.3 (q), 60.7 (t), 72.5 (d), 72.8 (t), 83.0 (d), 128.4 (d), 129.7 (d), 130.0 (d), 130.1 (d), 133.1 (d), 166.3 (s); IR (film) \( \tilde{\nu}_{\text{max}} \) (cm⁻¹) 3438, 2959, 2874, 1715, 1452, 1273, 1112; MS \( m/z \) (relative intensity) (FAB) 239 (M⁺) (11), 238 (M) (17), 237 (M – 1)⁺ (18), 221 (M – OH)⁺ (35), 207 (M – OCH₃)⁺ (21), 176 (100). HMRS calcd for C₁₄H₂₂O₃ (M⁺) 238.156895, found 238.156978.

**Preparation of (2R,3R)-3-Benzylxy-hexane-1,2-diol (58).** The same procedure used above to protect the hydroxyl group as mesylate (see preparation of bromide derivative in the synthesis of 6) was applied to the diol 49 (1 g, 4.46 mmol) to afford the corresponding dimesylate derivative, which was used in the next step without further purification.

To a solution of the previous crude in dry benzene (20 mL) was added KOAc (2.21 g, 22.3 mmol) at room temperature and stirred for 5 min, after which time was added 18-crown-6 (5.93 g, 22.0 mmol) and the mixture was refluxed overnight. The water was added and extracted with EtOAc. The combined organic phases were washed with brine, dried (MgSO₄), filtered and concentrated. The diacetate was hydrolyzed applying the same procedure used to obtain 44, yielding 58 (829 mg, 83% overall yield) as a colorless oil: \( [\alpha]_{D}^{25} = -10.8 \) (c=7.4 in CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) \( \delta = 0.93 \) (t, \( J = 5.1 \) Hz, 3H), 1.37–1.47 (m, 2H), 1.54–1.68 (m, 2H), 3.46–3.49 (m, 1H), 3.59–3.71 (m, 2H), 4.48 (d, \( J = 11.1 \) Hz, 1H), 4.62 (d, \( J = 11.1 \) Hz, 1H), 7.31 (br s, 5H); \(^1^3^C\) NMR (75 MHz, CDCl₃) = 13.9 (q), 18.5 (t), 32.4 (t), 64.0 (t), 71.3 (t), 72.8 (d), 79.6 (d), 127.8 (d), 128.4 (d), 128.5 (d), 129.7 (d), 138.0 (s); IR (film) \( \tilde{\nu}_{\text{max}} \) (cm⁻¹) 3417, 2959, 2873, 1714, 1453, 1273, 1071; MS \( m/z \)
(relative intensity) (FAB) 225 (M + 1)$^+$ (11), 224 (M)$^+$ (5), 223 (M − 1)$^+$ (18), 207 (M − OH)$^+$ (7), 154 (100). HMRS calcd for C$_{13}$H$_{20}$O$_3$ (M)$^+$ 224.141245, found 224.140842.

**Preparation of (2R,3R)-3-Benzylxy-2-methoxy-hexan-1-ol (59).** The same procedure used above to obtain 56 from 49 was applied to the diol 58 (200 mg, 0.89 mmol), yielding the alcohol 59 (138 mg, 65% overall yield) as a colorless oil: $[\alpha]_{D}^{25} = +7.3$ ($c$ = 1.0 in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.91 (t, $J$ = 6.4 Hz, 3H), 1.25−1.57 (m, 4H), 3.36−3.40 (m, 1H), 3.46 (s, 3H), 3.58−3.69 (m, 2H), 3.75−3.81 (m, 2H), 4.60 (d, $J$ = 4.0 Hz, 2H), 7.29−7.42 (br s, 5H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 14.2 (q), 19.1 (t), 32.1 (t), 35.7 (q), 58.7 (q), 61.6 (t), 72.8 (t), 79.1 (d), 82.0 (d), 127.7 (d), 128.0 (d), 128.4 (d), 129.7 (d), 138.4 (s); IR (film) $\gamma_{\text{max}}$ (cm$^{-1}$) 3438, 2959, 2873, 1716, 1452, 1273, 1097; MS m/z (relative intensity) (FAB) 344 (M)$^+$ (11), 343 (M − 1)$^+$ (15), 327 (M − OH)$^+$ (12), 312 (M − OCH$_3$)$^+$ (12), 121 (100). HMRS calcd for C$_{21}$H$_{28}$O$_4$ (M)$^+$ 344.198760, found 344.198142.

**Preparation of (2S,3R)-3-Benzylxy-2-(4-methoxy-benzyloxy)-hexan-1-ol (57).** The same procedure used above to obtain 50 from the diol 49 was repeated on 300 mg scale (1.34 mmol) using in this case 4-methoxybenzyl bromide for protecting the secondary hydroxyl group, yielding 57 (290 mg, 63% overall yield) as a colorless oil: $[\alpha]_{D}^{25} = -5.5$ ($c$ = 1.8 in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.90 (t, $J$ = 7.2 Hz, 3H), 1.33−1.64 (m, 4H), 3.49 (dd, $J$ = 9.0, 4.6 Hz, 1H), 3.62−3.65 (m, 1H), 3.76−3.77 (m, 1H), 3.80 (s, 3H), 4.53 (br s, 2H), 4.57 (d, $J$ = 11.3 Hz, 1H), 4.66 (d, $J$ = 11.3 Hz, 1H), 6.88 (d, $J$ = 8.5 Hz, 2H), 7.26−7.34 (m, 7H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 14.2 (q), 18.6 (t), 35.5 (t), 55.3 (q), 61.5 (t), 71.8 (t), 72.8 (t), 79.3 (d), 80.5 (d), 113.9 (d), 127.6 (d), 127.9 (d), 128.4 (d), 129.5 (d), 131.8 (d), 138.4 (s), 159.3 (s); IR (film) $\gamma_{\text{max}}$ (cm$^{-1}$) 3440, 2958, 2872, 1716, 1452, 1273, 1097; MS m/z (relative intensity) (FAB) 344 (M)$^+$ (11), 343 (M − 1)$^+$ (15), 327 (M − OH)$^+$ (12), 312 (M − OCH$_3$)$^+$ (12), 121 (100). HMRS calcd for C$_{21}$H$_{28}$O$_4$ (M)$^+$ 344.198760, found 344.198142.

**Preparation of (2R,3R)-3-Benzylxy-2-(4-methoxy-benzyloxy)-hexan-1-ol (60).** The same procedure used above to obtain 56 from the diol 49 was applied on 58 (300 mg, 1.34 mmol), yielding 60 (295 mg, 64% overall yield) as a colorless oil: $[\alpha]_{D}^{25} = +4.6$ ($c$ = 2.3 in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.89 (t, $J$ = 7.1 Hz, 3H), 1.25−1.31 (m, 1H), 1.42−1.48 (m, 2H), 1.55−1.60 (m, 1H), 3.45−3.65 (m, 3H), 3.74−3.76 (m, 1H), 3.80 (s, 3H), 4.52−4.63 (m, 4H), 6.87 (d, $J$ = 8.4 Hz, 2H), 7.24 (d, $J$ = 6.4 Hz, 2H), 7.32 (br s, 5H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 14.1 (q), 18.9 (t), 32.2 (t), 55.3 (q), 61.8 (t), 72.5 (t), 72.8 (t), 79.3 (d), 113.8 (d), 127.7 (d), 128.0 (d), 128.4 (d), 129.5 (d), 130.5 (d), 138.4 (s), 159.3 (s); IR (film) $\gamma_{\text{max}}$ (cm$^{-1}$) 3444, 2958, 2872, 1714, 1613, 1513.
1463, 1250, 1090; MS m/z (relative intensity) (FAB) 344 (M)+ (7), 343 (M – 1)+ (27), 253 (24), 135 (100). HMRS calcd for C_{21}H_{28}O_{4} (M)+ 344.198760, found 344.198360.

**Preparation of (2E,4R)-4-Benzyl氧-hept-2-eneoic acid Methyl Ester (61).** To a solution of the diol 49 (2 g, 8.92 mmol) in THF:H_{2}O (5:1, 89 mL), was added NaIO_{4} (7.53 g, 36.7 mmol) at room temperature. After 1 h, the mixture was diluted with Et_{2}O and water. The organic layer was washed with brine, dried (MgSO_{4}), filtered and concentrated yielding the corresponding aldehyde that was employed in the next step without further purification.

To a suspension of NaH (517 mg, 12.8 mmol, 60% in mineral oil) in dry C_{6}H_{6} (80 mL) under argon was added dropwise TMPA (2.28 mL, 14.2 mmol) in dry C_{6}H_{6} (25 mL). After 20 min was added the aldehyde obtained above in dry C_{6}H_{6} (25 mL). After 5 min TLC showed the end of the reaction and an aqueous saturated solution of NH_{4}Cl was added. The combined organic phases were washed with brine, dried (MgSO_{4}), filtered and concentrated. The crude obtained was purified by flash chromatography affording the ester 61 (1.97 g, 89% overall yield) as a colorless oil: [α]_{D}^{25} = +20.4 (c=1.8 in CHCl_{3}); \(^{1}\)H NMR (400 MHz, CDCl_{3}) δ = 0.88 (t, J = 7.1 Hz, 3H), 1.37–1.54 (m, 4H), 3.75 (s, 3H), 3.92–3.96 (m, 1H), 4.36 (d, J = 11.8 Hz, 1H), 4.58 (d, J = 11.8 Hz, 1H), 6.02 (d, J = 15.8 Hz, 1H), 6.88 (dd, J = 15.8, 6.5 Hz, 1H), 7.36 (br s, 5H); \(^{13}\)C NMR (75 MHz, CDCl_{3}) δ = 13.9 (q), 18.4 (t), 37.0 (t), 51.6 (q), 71.0 (t), 77.8 (d), 121.5 (d), 127.6 (d), 127.7 (d), 128.4 (d), 129.6 (d), 138.1 (s), 148.8 (d), 166.7 (s); IR (film) \(\nu_{\text{max}}\) (cm\(^{-1}\)) 2959, 2874, 1731, 1436, 1272; MS m/z (relative intensity) (FAB) 248 (M)+ (12), 233 (M – CH_{3})+ (16), 154 (100). Anal. Calcd for C_{15}H_{20}O_{3}: C, 72.55; H, 8.12. Found: C, 72.78; H, 8.25.

**Preparation of (2E,4R)-4-Benzyl氧-hept-2-en-1-ol (62).** To a suspension of LiAlH_{4} (227 mg, 5.80 mmol) in dry Et_{2}O (40 mL) was added slowly AlCl_{3} (255 mg, 1.88 mmol) under argon at 0 °C. The mixture was stirred for 15 min and the ester 61 (1.8 g, 7.26 mmol) dissolved Et_{2}O (10 mL). The reaction was allowed to warm to room temperature and stirred for 5 h after which time TLC showed not remaining starting material. The mixture was diluted with Et_{2}O and cooled at 0 °C in a ice bath, water (3 mL) was slowly added and vigorously stirred for 30 min. MgSO_{4} was added and the mixture was filtered through a pad of Celite and the solvent remove under vacuum. The residue obtained was purified by flash chromatography affording 62 (1.14 g, 89% overall yield) as a colorless oil: [α]_{D}^{25} = +14.5 (c=0.8 in CHCl_{3}); \(^{1}\)H NMR (400 MHz, CDCl_{3}) δ = 0.89 (t, J = 7.0 Hz, 3H), 1.29–1.61 (m, 4H), 3.77–3.81 (m, 1H), 4.18 (d, J = 5.2 Hz, 2H), 4.31 (d, J = 11.9 Hz, 1H), 4.57 (d, J = 11.9 Hz, 1H), 5.63 (dd, J = 15.6, 7.7 Hz, 1H), 5.80 (ddd, 10.6, 10.6, 5.4 Hz, 1H), 7.28 (br s, 5H); \(^{13}\)C NMR (75 MHz, CDCl_{3}) δ = 14.2 (q), 18.6 (t), 37.8 (t), 63.0 (t), 63.0 (t), 70.0 (t), 138.1 (s), 148.8 (d), 166.7 (s);
79.2 (d), 127.4 (d), 127.7 (d), 127.8 (d), 128.3 (d), 129.6 (d), 131.6 (d), 132.5 (s); IR (film) $\nu_{\text{max}}$ (cm$^{-1}$) 3412, 2958, 2872, 1716, 1454, 1274, 1096; MS $m/z$ (relative intensity) (FAB) 221 (M + 1)$^+$ (28), 220 (M)$^+$ (23), 219 (M − 1)$^+$ (35), 203 (M − OH)$^+$ (25), 165 (100). HMRS calcld for C$_{14}$H$_{20}$O$_2$ (M)$^+$ 220.146330, found 220.146646.

Preparation of [3-[(1R)-(2-Propenyl-penta-2,4-dienyloxy)-butyl]-(2S,3S)-oxiranyl]-methanol (63). To a solution of 62 (500 mg, 2.27 mmol) in dry CH$_2$Cl$_2$ (11 mL) containing activated 4 Å molecular sieves were added sequentially Ti(OPr-i)$_4$ (0.80 mL, 2.72 mmol) and (R,R)-(−)-DET (0.65 mL, 3.18 mmol) under argon. After 20 min TBHP (1.28 mL, 3.2 M in isooctane, 4.10 mmol) was added. The mixture was stirred for 3 h, after which time TLC showed not remaining allylic alcohol. An aqueous solution of 15% tartaric acid (30 mL) was added and vigorously stirred until clear the organic phase. The phases were separated and the aqueous phase extracted with CH$_2$Cl$_2$. The combined organic phases were washed with brine, dried (MgSO$_4$), filtered and concentrated. The residue obtained was dissolved in Et$_2$O and an aqueous solution of 15% de NaOH (30 mL) previously cooled at 0 °C was added. The mixture was stirred for 5 min and the phases were separated and the aqueous phase extracted with Et$_2$O. The combined organic phases were washed with brine, dried (MgSO$_4$), filtered and concentrated. The residue was purified by flash chromatography affording 63 (460 mg, 86% yield) as a colorless oil: $\left[\alpha\right]_{D}^{25} = +14.1$ (c=1.1 in CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.90 (t, $J = 6.8$ Hz, 3H), 1.25−1.39 (m, 2H), 1.44−1.70 (m, 2H), 2.94−2.95 (br s, 1H), 3.07 (dd, $J = 6.9$, 2.1 Hz, 1H), 3.10−3.20 (m, 1H), 3.64 (dd, $J = 12.6$, 4.1 Hz, 1H), 3.94 (dd, $J = 12.5$, 2.2 Hz, 1H), 4.57 (d, $J = 12.0$ Hz, 1H), 4.80 (d, $J = 12.0$ Hz, 1H), 7.28 (br s, 5H); $^{13}$C NMR (75 MHz, CDCl$_3$) 14.0 (q), 18.7 (t), 34.5 (t), 54.7 (d), 58.4 (d), 61.3 (t), 71.7 (t), 79.2 (d), 127.5 (d), 127.6 (d), 127.8 (d), 128.3 (d), 128.4 (d), 138.5 (s); IR (film) $\nu_{\text{max}}$ (cm$^{-1}$) 3417, 2960, 2874, 1720, 1276, 1071; MS $m/z$ (relative intensity) (FAB) 236 (M)$^+$ (11), 235 (M − 1)$^+$ (21), 219 (M − OH)$^+$ (14), 206 (100). HMRS calcld for C$_{14}$H$_{20}$O$_3$ (M)$^+$ 236.141245, found 236.141788.

Preparation of (2R,3S,4R)-3-Methyl-4-(benzyloxy)-heptane-1,2-diol (64). To a solution of epoxide 63 (400 mg, 1.69 mmol) in dry CH$_2$Cl$_2$ (3 mL) was dropwise added Me$_3$Al (2.54 mL, 5.07 mmol) under argon at 0 °C. The mixture was vigorously stirred for 1 h, after which time TLC showed not remaining epoxide and was diluted with CH$_2$Cl$_2$ and water (1 mL) and NaF (2.2 g) were added. The phases were separated and the aqueous phase extracted with CH$_2$Cl$_2$. The combined organic phases were washed with brine, dried (MgSO$_4$), filtered and concentrated. The residue was purified by flash chromatography affording the diol 64 (358 mg, 84% yield) as a colorless oil:
Preparation of (2R,3R)-3-Methyl-4-(benzyloxy)-heptane-1,2-diol (66). The same procedure used above to obtain 63 from 62 was applied again to 62 (500 mg, 2.27 mmol) using in this case (S,S)-(−)-DET, yielding 65 (445 mg, 83% yield) as a colorless oil: $[\alpha]_{D}^{25} = +24.0 \, (c=1.4 \text{ in CHCl}_3)$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 0.91 \, (t, \, J = 7.2 \text{ Hz}, \, 3\text{H}), \, 1.25–1.52 \, (m, \, 2\text{H}), \, 1.55–1.64 \, (m, \, 2\text{H}), \, 1.89 \, (br \, s, \, 1\text{H}), \, 2.94 \, (d, \, J = 3.3 \text{ Hz}, \, 1\text{H}), \, 3.11 \, (br \, s, \, 1\text{H}), \, 3.33 \, (dd, \, J = 11.1, \, 5.4 \text{ Hz}, \, 1\text{H}), \, 3.56 \, (dd, \, J = 12.6, \, 4.1 \text{ Hz}, \, 1\text{H}), \, 3.83 \, (dd, \, J = 12.6, \, 2.1 \text{ Hz}, \, 1\text{H}), \, 4.53 \, (d, \, J = 11.8 \text{ Hz}, \, 1\text{H}), \, 4.61 \, (d, \, J = 11.8 \text{ Hz}, \, 1\text{H}), \, 7.32 \, (br \, s, \, 5\text{H});$ $^{13}$C NMR (75MHz, CDCl$_3$) $\delta = 0.91 \, 14.0 \, (q), \, 18.3 \, (t), \, 34.9 \, (t), \, 56.9 \, (d), \, 57.1 \, (d), \, 61.4 \, (t), \, 72.5 \, (t), \, 77.4 \, (d), \, 127.5 \, (d), \, 127.6 \, (d), \, 128.4 \, (d), \, 138.6 \, (s);$ IR (film) $\gamma_{\text{max}} \,(\text{cm}^{-1}) \, 3417, \, 2960, \, 2874, \, 1714, \, 1453, \, 1276; \, MS \, m/z \,(\text{relative intensity}) \, (\text{FAB}) \, 235 \, (M – 1)^{\dagger} \, (5), \, 219 \, (M – \text{OH})^{\dagger} \, (4), \, 165 \, (11), \, 159 \, (M – \text{C}_8\text{H}_3)^{\dagger} \, (3), \, 154 \, (100). \, \text{HMRS \, calcd \, for \, C}_{14}\text{H}_{19}\text{O}_3 \, (M – 1)^{\dagger} \, 235.133420, \, \text{found} \, 235.133803.$

Preparation of (2S,3R,4R)-3-Methyl-4-(benzyloxy)-heptane-1,2-diol (66). The same procedure used above to obtain 64 from 63 was applied to 63 (400 mg, 1.69 mmol) yielding 67 (353 mg, 83% yield) as a colorless oil: $[\alpha]_{D}^{25} = +5.5 \, (c=1.3 \text{ in CHCl}_3)$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 0.83–0.94 \, (m, \, 6\text{H}), \, 1.22–1.28 \, (m, \, 2\text{H}), \, 1.43–1.61 \, (m, \, 2\text{H}), \, 1.79 \, (br \, s, \, 1\text{H}), \, 3.42 \, (br \, s, \, 1\text{H}), \, 3.56–3.61 \, (m, \, 1\text{H}), \, 3.80 \, (br \, s, \, 3\text{H}), \, 4.66 \, (d, \, J = 10.9 \text{ Hz}, \, 2\text{H}), \, 7.33 \, (br \, s, \, 5\text{H});$ $^{13}$C NMR (75MHz, CDCl$_3$) $\delta = 14.1 \, (q), \, 16.6 \, (q), \, 20.3 \, (t), \, 34.5 \, (t), \, 34.8 \, (d), \, 63.3 \, (t), \, 71.8 \, (d), \, 74.7 \, (t), \, 83.1 \, (d), \, 127.8 \, (d), \, 127.9 \, (d), \, 128.5 \, (d), \, 138.3 \, (s);$ IR (film) $\gamma_{\text{max}} \,(\text{cm}^{-1}) \, 3416, \, 2933, \, 2873, \, 1722, \, 1453, \, 1274; \, MS \, m/z \,(\text{relative intensity}) \, (\text{FAB}) \, 253 \, (M + 1)^{\dagger} \, (23), \, 252 \, (M)^{\dagger} \, (13), \, 251 \, (M – 1)^{\dagger} \, (10), \, 238 \, (13), \, 175 \, (M – \text{C}_8\text{H}_3)^{\dagger} \, (20), \, 154 \, (100). \, \text{HMRS \, calcd \, for \, C}_{15}\text{H}_{24}\text{O}_3 \, (M)^{\dagger} \, 252.172545, \, \text{found} \, 252.172917.$

General Procedure for the Preparation of the bis-Homopropargylic Alcohols 74b, 74c, 74d, 74e, 74f and 74g. The same procedure used to obtain 6 from 4 was applied to the alcohols 67 and 68 yielding the alcohols 73 and 74 respectively. This procedure also was applied to the alcohols 69 and 70 (obtained from 57 and 60) after the cleavage of 4-methoxybenzyl group made as follow: to a stirred solution of the corresponding addition products in 10:1 aqueous (0.1 M) was added CAN (2

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equiv) at 0 °C. After being stirred at 0 °C for 20 min, the reaction was quenched with saturated NaHCO₃. The mixture was diluted with CH₂Cl₂, extracted and washed with brine. The combined organic extracts were dried, filtered and concentrated giving the corresponding propargylic alcohol that was used in the next step without further purification) yielding 75 and 76 respectively. In a similar manner the application of the propargylic reductive protocol was applied to 71 and 72 yielding 77 and 78. The results obtained at different temperatures are showed in Table 2.

(4R,5S)-5-Methoxy-tridec-7-yn-4-ol (73): colorless oil, [α]D²⁵ = +1.4 (c=0.1 in CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 0.89 (t, J = 7.0 Hz, 3H), 0.94 (t, J = 7.0 Hz, 3H), 1.27-1.36 (m, 5H), 1.43-1.53 (m, 5H), 2.10-2.16 (m, 2H), 2.41-2.49 (m, 2H), 3.11 (dd, J = 11.2, 5.0 Hz, 1H), 3.47 (s, 3H), 3.65-3.70 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ = 13.9 (q), 14.0 (q), 18.7 (t), 18.9 (t), 20.0 (t), 22.2 (t), 28.6 (t), 31.0 (t), 37.2 (t), 58.1 (q), 75.9 (s), 77.4 (s), 81.6 (d), 85.9 (d); IR (film) γ max (cm⁻¹) 3444, 2969, 2872, 1642, 1260, 1106; MS m/z (relative intensity) 226 (M)+ (10), 209 (M – OH)+ (39), 154 (100). HMRS calcd for C₁₄H₂₆O₂ (M)+ 226.193280, found 226.192871.

(4R,5R)-5-Methoxy-tridec-7-yn-4-ol (74): colorless oil, [α]D²⁵ = – 21.7 (c=0.2 in CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 0.89 (t, J = 7.0 Hz, 3H), 0.95 (t, J = 7.0 Hz, 3H), 1.28-1.37 (m, 5H), 1.43-1.52 (m, 5H), 2.12 - 2.17 (m, 2H), 2.41-2.48 (m, 2H), 3.12 (dd, J = 11.2, 5.0 Hz, 1H), 3.46 (s, 3H), 3.65 - 3.69 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ = 13.9 (q), 14.0 (q), 18.7 (t), 18.9 (t), 20.0 (t), 22.2 (t), 28.6 (t), 31.0 (t), 35.4 (t), 58.1 (q), 72.2 (d), 75.9 (s), 77.4 (s), 82.6 (d); IR (film) γ max (cm⁻¹) 3444, 2969, 1643, 1260, 1097; MS m/z (relative intensity) 227 (M+1)+ (9), 226 (M)+ (9), 211 (M – CH₃)+ (11), 209 (M – OH)+ (25), 136 (100). HMRS calcd for C₁₄H₂₆O₂ (M)+ 226.193011.

(4R,5S)-Tridec-7-yne-4,5-diol (75): colorless oil, [α]D²⁵ = –11.6 (c=0.2 in CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 0.89 (t, J = 7.0 Hz, 3H), 0.96 (t, J = 7.0 Hz, 3H), 1.28–1.37 (m, 5H), 1.43-1.53 (m, 5H), 2.12 - 2.17 (m, 2H), 2.41-2.48 (m, 2H), 3.12 (dd, J = 11.2, 5.0 Hz, 1H), 3.46 (s, 3H), 3.65 - 3.69 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ = 13.9 (q), 14.0 (q), 18.7 (t), 18.9 (t), 20.0 (t), 22.2 (t), 28.6 (t), 31.0 (t), 35.4 (t), 58.1 (q), 72.2 (d), 75.9 (s), 77.4 (s), 82.6 (d); IR (film) γ max (cm⁻¹) 3315, 2959, 2359, 1261, 1089; MS m/z (relative intensity) 212 (M)+ (16), 197 (M – CH₃)+ (11), 195 (M – OH)+ (13), 194 (M – H₂O)+ (11), 136 (100). Anal. Calcd for C₁₃H₂₄O₂: C, 73.54; H, 11.39. Found: C, 73.80; H, 11.53.

(4R,5R)-Tridec-7-yne-4,5-diol (76): colorless oil, [α]D²⁵ = +11.4 (c=0.6 in CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ = 0.88 (t, J = 6.8 Hz, 3H), 0.92 (t, J = 6.8 Hz, 3H), 1.23–1.30 (m, 5H), 1.32–1.49 (m, 5H), 2.11–2.16 (m, 2H), 2.42–2.46 (m, 3H), 3.50–3.55 (m, 1H), 3.55–3.60 (m, 1H); ¹³C NMR
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(75 MHz, CDCl\(_3\)) \( \delta = 13.9 \) (q), 14.0 (q), 18.7 (t), 18.8 (t), 22.1 (t), 24.4 (t), 28.6 (t), 31.0 (t), 35.6 (t), 72.4 (d), 72.9 (d), 75.6 (s), 83.4 (s); IR (film) \( \gamma_{\text{max}} \) (cm\(^{-1}\)) 3316, 2930, 2871, 1456, 1127, 1068; MS m/z (relative intensity) 213 (M + 1\(^+\)) (24), 212 (M\(^+\)) (5), 195 (M – OH)\(^+\) (22), 139 (25), 55 (100). HMRS calcd for C\(_{13}\)H\(_{24}\)O\(_2\) (M\(^+\)) 212.177630, found 212.177817.

\((4R,5S)-5\)-Methyl-tridec-7-yn-4-ol (78): colorless oil, \([\alpha]^{25}_D = −3.4\) (c=0.7 in CHCl\(_3\)); \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 0.89\) (t, \( J = 7.0\) Hz, 6H), 0.99 (d, \( J = 6.7\) Hz, 3H), 1.28–1.37 (m, 5H), 1.43–1.57 (m, 5H), 1.64–1.71 (m, 2H), 2.11–2.22 (m, 2H), 2.23–2.25 (m, 1H), 3.49–3.54 (m, 1H); \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta = 13.9\) (q), 14.1 (q), 16.1 (q), 18.7 (t), 19.0 (t), 21.9 (t), 22.2 (t), 28.7 (t), 31.1 (t), 36.4 (t), 38.3 (d), 75.0 (d), 78.5 (s), 82.0 (s); IR (film) \( \gamma_{\text{max}} \) (cm\(^{-1}\)) 3390, 2991, 2872, 1727, 1463, 1286, 1122; MS m/z (relative intensity) 211 (M\(^+\)) (9), 210 (M\(^+\)) (8), 209 (M – 1\(^+\)) (10), 195 (M – CH\(_3\))\(^+\) (6), 192 (M – H\(_2\)O)\(^+\) (7), 154 (100). HMRS calcd for C\(_{14}\)H\(_{26}\)O (M\(^+\)) 210.198366, found 210.198001.

\((4R,5R)-5\)-Methyl-tridec-7-yn-4-ol (77): colorless oil, \([\alpha]^{25}_D = +14.0\) (c=0.5 in CHCl\(_3\)); \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 0.87–0.99\) (m, 9H), 1.30–1.48 (m, 10H), 1.65–1.70 (m, 2H), 2.12–2.19 (m, 2H), 2.19–2.28 (m, 1H), 3.69–3.74 (m, 1H); \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta = 13.3\) (q), 13.9 (q), 14.0 (q), 18.7 (t), 19.3 (t), 22.2 (t), 23.4 (t), 28.7 (t), 31.0 (t), 36.7 (t), 37.7 (d), 74.0 (d), 78.4 (s), 84.8 (s); IR (film) \( \gamma_{\text{max}} \) (cm\(^{-1}\)) 3410, 2931, 2872, 1726, 1462, 1277; MS m/z (relative intensity) 211 (M + 1\(^+\)) (9), 210 (M\(^+\)) (8), 209 (M – 1\(^+\)) (17), 193 (M – OH)\(^+\) (15), 166 (13), 154 (100). HMRS calcd for C\(_{14}\)H\(_{26}\)O (M\(^+\)) 210.198366, found 210.198530.

Preparation of But-3-enoic Acid Benzylamide (79). To a solution of commercial benzylamine (5.1 mL, 46.7 mmol) in dry CH\(_2\)Cl\(_2\) (200 mL) were sequentially added vinylacetic acid (5.9 mL, 70.0 mmol), DCC (19.2 g, 93.3 mmol) and DMAP (8.7 g, 70.0 mmol). The mixture was vigorously stirred for 2 h, after which time TLC showed not remaining amine and was diluted with CH\(_2\)Cl\(_2\) and water was added. The phases were separated and the aqueous phase extracted with CH\(_2\)Cl\(_2\). The combined organic phases were washed with an aqueous solution of HCl (5%) and brine, dried (MgSO\(_4\)), filtered and concentrated. The residue was purified by flash chromatography affording the amide 79 (7.2 g, 89% yield) as a colorless oil: \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 3.02\) (d, \( J = 7.1\) Hz, 2H), 4.43 (d, \( J = 10.2\) Hz, 2H), 5.17 (d, \( J = 5.7\) Hz, 1H), 5.23 (br s, 1H), 5.80–5.99 (m, 1H), 6.11 (br s, 1H), 7.23–7.34 (m, 5H); \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta = 41.3\) (t), 43.4 (t), 118.9 (t), 127.2 (d), 127.5 (d), 128.5 (d), 131.5 (d), 138.4 (s), 171.0 (s); IR (film) \( \gamma_{\text{max}} \) (cm\(^{-1}\)) 3307, 2925, 1651, 1454, 1343, 1080; MS m/z (relative intensity) (FAB) 176 (M + 1\(^+\)) (100), 175 (M\(^+\)) (95), 174 (M – 1\(^+\)) (5). HMRS calcd for C\(_{11}\)H\(_{13}\)NO (M\(^+\)) 175.099714, found 175.100101.
Preparation of Benzyl-but-3-enyl-amine (80). The same procedure used above to obtain 62 from 61 was applied to 79 (1 g, 5.7 mmol) at 50°C, yielding the amine 80 (837 mg, 91% yield) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ = 2.28 (dd, J = 13.6, 6.8 Hz, 2H), 2.69 (t, J = 6.8 Hz, 2H), 3.79 (s, 2H), 5.02 (dd, J = 13.5, 1.4 Hz, 2H), 5.72–5.86 (m, 1H), 7.21–7.35 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ = 34.3 (t), 48.3 (t), 53.9 (t), 116.3 (t), 126.8 (d), 126.9 (d), 128.1 (d), 128.3 (d), 128.4 (d), 136.5 (d), 140.4 (s); IR (film) γ max (cm⁻¹) 3063, 3027, 2919, 2814, 1639, 1454, 1119, 913; MS m/z (relative intensity) (FAB) 162 (M+1)⁺ (6), 161 (M)⁺ (5), 160 (M – 1)⁺ (10), 134 (M – CH₂CH)⁺ (6), 154 (100). HMRS calcd for C₁₁H₁₅N (M)⁺ 161.120450, found 161.120946.

Preparation of Benzyl-(3,4-dihydroxy-butyl)-carbamic Acid tert-Butyl Ester (81). To a solution of the amine 80 (500 mg, 3.1 mmol) and DMAP (454 mg, 3.7 mmol) in dry MeCN (10 mL) was added (Boc)₂O (828 mg, 3.7 mmol) at room temperature. The mixture was stirred for 2 h, after which time TLC showed not remaining starting material. The solvent was removed under vacuum and the residue was used in the next step without further purification.

The same procedure used to obtain the diols 64 and 65 respectively was applied to the diol 81 (736 mg, 81% overall yield) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ = 1.45 (br s, 9H), 3.05 (m, 1H), 3.27 (br s, 2H), 3.51 (m, 1H), 3.67 (m, 2H), 4.22–4.27 (m, 1H), 7.21–7.35 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ = 28.4 (q), 31.6 (t), 42.8 (t), 50.6 (t), 66.3 (t), 68.5 (d), 80.7 (s), 127.3 (d), 128.5 (d), 138.0 (s), 157.1 (s); IR (film) γ max (cm⁻¹) 3360, 2358, 1667, 1416, 1247, 1167; MS m/z (relative intensity) (FAB) 295 (M)⁺ (24), 278 (M – OH)⁺ (19), 239 (6), 154 (100). Anal. Calcd for C₁₆H₂₅NO₄: C, 65.06; H, 8.53. Found: C, 65.37; H, 8.68.

Preparation of 3-Benzyl-6-hept-1-ynyl-[1,3]oxazinan-2-one (82). The same procedure used to obtain the alcohol 71 and 72 from the diols 64 and 65 respectively was applied to the diol 81 (700 mg, 2.4 mmol), yielding 82 (488 mg, 85% yield) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ = 0.88 (t, J = 5.2 Hz, 9H), 1.24–1.31 (m, 4H), 1.47 (t, J = 5.3 Hz, 2H), 1.95–2.00 (m, 1H), 2.17 (ddd, J = 5.2, 5.2, 1.0 Hz, 3H), 3.14–3.17 (m, 1H), 3.44–3.47 (m, 1H), 4.48 (d, J = 11.2 Hz, 1H), 4.67 (d, J = 11.2 Hz, 1H), 5.03 (br s, 1H), 7.25–7.34 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ = 13.9 (q), 18.5 (t), 22.1 (t), 27.7 (t), 27.9 (t), 31.0 (t), 42.2 (t), 52.7 (t), 66.9 (d), 75.6 (s), 88.6 (s), 127.7 (d), 127.9 (d), 128.6 (d), 136.4 (s), 153.4 (s); IR (film) γ max (cm⁻¹) 2932, 2860, 1694, 1451, 1359, 1260, 1116; MS m/z (relative intensity) (FAB) 286 (M + 1)⁺ (100), 285 (M )⁺ (18), 164 (12), 124 (12). HMRS calcd for C₁₈H₂₃NO₂ (M)⁺ 285.172879, found 285.172514.

Preparation of 1-Benzylamino-dec-4-yn-3-ol (83). To a solution of the propargylic alcohol 82 (200 mg, 0.56 mmol) in dry CH₂Cl₂ (6 mL) was slowly added TFA (86 µL, 1.12 mmol) at 0°C.
The mixture was vigorously stirred for 1 h, after which time TLC showed not remaining starting material. Et₃N was added until getting a pH = 10. The solvent was removed under vacuum and the residue was purified by flash chromatography affording the aminoalcohol **83** (132 mg, 91% yield) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ = 0.84 (t, J = 5.1 Hz, 3H), 1.23 (br s, 4H), 1.32–1.37 (m, 4H), 2.05 (t, J = 6.7 Hz, 2H), 2.18 (br s, 1H), 3.07 (d, J = 6.5 Hz, 2H), 3.16 (br s, 1H), 4.09–4.21 (m, 2H), 7.36 (br s, 3H), 7.60 (br s, 2H); ¹³C NMR (75 MHz, CDCl₃) 13.9 (q), 18.6 (t), 22.1 (t), 28.2 (t), 31.0 (t), 33.6 (t), 43.9 (t), 51.2 (t), 60.6 (d), 79.4 (s), 86.4 (s), 129.1 (d), 129.4 (d), 130.3 (s), 130.6 (d); IR (film) ³ν max (cm⁻¹) 3356, 2933, 2359, 1460, 1030; MS m/z (relative intensity) (FAB) 260 (M⁺ + 1)⁺ (31), 259 (M)⁺ (33), 242 (M – OH)⁺ (31), 85 (100). HMRS calcd for C₁₇H₂₅NO (M)⁺ 259.193615, found 259.194563.

**Preparation of Dec-4-ynylamine (84).** The same procedure used to obtain **6** from **5** was applied to **83** (100 mg, 0.39 mmol) at 50°C, yielding the amine **84** (45 mg, 77% overall yield) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ = 0.89 (t, J = 6.8 Hz, 3H), 1.25 (br s, 4H), 1.47–1.49 (m, 2H), 1.68–1.78 (m, 2H), 2.09–2.13 (m, 2H), 2.14–2.26 (m, 2H), 2.93 (d, J = 6.4 Hz, 2H), 4.08 (br s, 2H); ¹³C NMR (CDCl₃) 13.9 (q), 16.2 (t), 18.6 (t), 22.1 (t), 28.7 (t), 30.6 (t), 31.0 (t), 40.1 (t), 78.5 (s), 81.2 (s); IR (film) ³ν max (cm⁻¹) 2960, 2859, 1643, 1556, 1405, 1333; MS m/z (relative intensity) (FAB) 154 (M + 1)⁺ (28), 153 (M)⁺ (28), 137 (M – NH₂)⁺ (38), 81 (52), 54 (100). HMRS calcd for C₁₀H₁₉N (M)⁺ 153.151750, found 153.152646.

**Preparation of (3S)-3-Benzyl(D,D)oxy-hexadecan-1-ol (86).** To a solution of **3** (R¹=n-C₁₃H₂₇)⁶ (500 mg, 1.95 mmol) in dry THF (10 mL) was slowly added Red-Al® (13 mL, 3.4 M solution in toluene, 3.8 mmol) at 0 °C under argon. The reaction mixture was stirred for 2.5 h, after which time TLC showed no remaining epoxide. Then water and HCl (5% w/v in water) were sequentially added, and the mixture was stirred until clear phases were reached (0.5 h). The phases were separated and the aqueous phase extracted with Et₂O. The combined organic phases were washed with saturated aqueous NaHCO₃ and brine, dried (MgSO₄), filtered and concentrated to afford the corresponding diol that was suitable for use without further purification.

To a solution of the crude diol in dry CH₂Cl₂ (10 mL) under argon were added 3,4-dihydro-2H-pyran (0.27 mL, 2.93 mmol) and a catalytic amount of PPTS at 0 °C. The reaction was allowed to warm to room temperature and stirred for 6 h. The mixture was poured into ice-water and extracted with CH₂Cl₂. The combined organic phases were washed with saturated aqueous NaCl, dried (MgSO₄), filtered and concentrated to afford the corresponding protected alcohol.

To a suspension of NaH (172 mg, 4.3 mmol, 60% in mineral oil) in dry THF (20 mL), at 0 °C were sequentially and slowly added a solution of the alcohol obtained above in THF (10 mL), a catalytic
amount of \(n\)-Bu₄NI, and benzyl\((D,D)\)bromide (0.48 mL, 4.0 mmol). The reaction mixture was stirred at room temperature for 24 h. Then, the mixture was diluted with Et₂O, washed with brine, dried and concentrated to afford a residue containing the corresponding benzyl ether. This residue was dissolved in CH₂OH (20 mL) and a catalytic amount of HCl was added at 0 °C. The mixture was stirred vigorously for 1 h, after which time TLC showed no remaining starting material. Then Et₃N was added until getting a pH ≈ 7, the mixture was concentrated and purified by flash column chromatography yielding \(86\) (383 mg, 56% overall yield) as a colorless oil: \([\alpha]_{D}^{25} = +14.9 \) (c 0.7 in CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) \(\delta = 0.88 \) (t, \(J = 6.9\) Hz, 3H), 1.26 (br s, 20H), 1.55–1.71 (m, 4H), 1.72–1.87 (m, 2H), 3.59–3.71 (m, 1H), 3.73–3.82 (m, 2H), 7.28–7.38 (m, 5H); \(^{13}\)C NMR (75 MHz, CDCl₃) \(\delta = 14.1 \) (q), 22.6 (t), 25.1 (q), 29.3 (t), 29.6 (t), 29.8 (t), 31.9 (t), 33.4 (t), 35.9 (t), 60.8 (t), 78.5 (d), 127.7 (d), 127.9 (t), 128.4 (t), 138.3 (s); IR (film) \(\nu_{\text{max}} \) (cm\(^{-1}\)) 3320, 2925, 2853, 1466, 1068; MS \(m/z\) (relative intensity) (FAB) \(348\) (M\(^+\)) (2), \(347\) (M – 1\(^+\)) (1), \(331\) (M – OH\(^+\)) (1), \(222\) (5), \(147\) (11), \(123\) (34), \(91\) (100). HMRS calcd for C\(_{23}\)H\(_{38}\)D\(_2\)O\(_2\) (M\(^+\)) 350.315384, found 350.315765.

**Preparation of (4S)-4-benzyl\((D,D)\)oxy-heptadecan-2-one (87)**. The same procedure used to obtain \(14a\) from the alcohol \(4\) (\(R^1=\text{n-C}_{13}\)H\(_{27}\)) was applied to \(86\) (350 mg, 1.0 mmol) yielding \(87\) (225 mg, 62% overall yield) as a colorless oil: \([\alpha]_{D}^{25} = +11.1 \) (c=0.5 in CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) \(\delta = 0.86 \) (t, \(J = 6.6\) Hz, 3H), 1.26 (br s, 20H), 1.43–1.48 (m, 4H), 2.09 (s, 3H), 2.49 (dd, \(J = 15.7, 4.7\) Hz, 2H), 2.74 (dd, \(J = 15.7, 7.5\) Hz, 1H), 3.87–3.93 (m, 1H), 7.26–7.33 (m, 5H); \(^{13}\)C NMR (75 MHz, CDCl₃) \(\delta = 14.1 \) (q), 22.6 (t), 25.1 (q), 29.3 (t), 29.5 (t), 29.6 (t), 31.1 (q), 31.9 (t), 34.3 (t), 48.6 (t), 65.5 (t), 75.6 (d), 127.6 (d), 127.8 (d), 128.3 (d), 138.4 (s), 207.8 (s); IR (film) \(\nu_{\text{max}} \) (cm\(^{-1}\)) 2930, 2853, 1714, 1466, 1063; MS \(m/z\) (relative intensity) (FAB) \(348\) (M\(^+\)) (2), \(347\) (M – 1\(^+\)) (1), \(331\) (M – OH\(^+\)) (1), \(222\) (5), \(147\) (11), \(123\) (34), \(91\) (100). Anal. Calcd for C\(_{24}\)H\(_{38}\)D\(_2\)O\(_2\): C, 79.50; H, 11.67. Found: C, 79.62; H, 11.88.

**Preparation of (8R,10S)-8-D-8-methyl-tricos-6-yn-10-ol (91)**. The same procedure used to obtain \(17a\) from the ketone \(14a\) was applied to \(87\) (200 mg, 0.57 mmol) yielding \(91\) (88 mg, 44% overall yield) as a colorless oil: \([\alpha]_{D}^{25} = -16.1 \) (c=2.16 in CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) \(\delta = 0.86 \) (t, \(J = 6.7\) Hz, 3H), 0.86 (t, \(J = 6.9\) Hz, 3H), 1.15 (s, 3H), 1.25 (br s, 30H), 1.43–1.50 (m, 2H), 1.52 (d, \(J = 5.9\) Hz, 2H), 2.13 (t, \(J = 7.0\) Hz, 1H), 2.49 (br s, 1H), 3.75 (m, 1H); \(^{13}\)C NMR (75 MHz, CDCl₃) \(\delta = 14.0 \) (q), 14.2 (q), 18.7 (t), 21.9 (q), 22.2 (t), 22.7 (t), 23.4 (s), 23.7 (s), 24.0 (s), 25.5 (t), 28.8 (t), 29.4 (t), 29.7 (t), 31.1 (t), 32.0 (t), 37.6 (t), 44.6 (t), 71.49 (d), 82.2 (s), 84.6 (s); IR (film) \(\nu_{\text{max}} \) (cm\(^{-1}\)) 3335, 2939, 2856, 1465, 1094; MS \(m/z\) (relative intensity) 352 (M + 1\(^+\)) (21), 351 (M\(^+\))

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Preparation of (10S,8S)-8-D-tricos-6-yn-10-ol (92). The same procedure used to obtain 6 from 4 (R1=n-C3H7) was applied to 88 on a 100 mg (0.28 mmol) scale using the lithium salt of 1-heptyne, yielding 92 (43.4 mg, 46% overall yield) as a colorless oil: [α]D25 = +1.5 (c=2.52 in CHCl3); 1H NMR (400 MHz, CDCl3) δ = 0.86 (m, 6H), 1.25 (br s, 26H), 1.36–1.64 (m, 4H), 2.12 (m, 2H), 2.28 (m, 1H), 3.72 (m, 1H); 13C NMR (75 MHz, CDCl3) δ = 14.0 (q), 14.1 (q), 14.9 (s), 15.2 (s), 15.4 (s), 18.7 (t), 22.2 (t), 22.7 (t), 25.6 (t), 28.8 (t), 29.3 (t), 29.7 (t), 31.1 (t), 31.9 (t), 36.1 (t), 37.4 (t), 71.4 (d), 79.6 (s), 81.2 (s); IR (film) νmax (cm⁻¹) 3379, 2935, 2860, 1640, 1465, 1084; MS m/z (relative intensity) 338 (M + 1)+ (45), 337 (M)+ (17), 336 (M – 1)+ (100). Anal. Calcd for C23H43DO: C, 81.83; H, 13.43. Found: C, 81.95; H, 13.62.
[1,3]-Transfer of Chirality During the Nicholas Reaction in \( \gamma \)-Benzyloxy Propargylic Alcohols

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\[ \text{H} \quad \text{OH} \]

\[ \text{OTBDPS} \]

\[^{\text{1}}\text{H RMN (CDCl}_3\text{)}\]

\[^{\text{13}}\text{C RMN (CDCl}_3\text{)}\]
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$\text{H RMN (CDCl}_3\text{)}$

$\text{C RMN (CDCl}_3\text{)}$

$\text{H RMN (CDCl}_3\text{)}$

$\text{C RMN (CDCl}_3\text{)}$
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$\text{H} \text{RMN (CDCl}_3\text{)}$

$\text{C} \text{RMN (CDCl}_3\text{)}$
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\( n\text{-C}_3\text{H}_7 \)

\( \text{OH} \)

\( \text{OTBS} \)

\( \text{6c} \)

\( \text{H} \)

RMN (CDCl\(_3\))

\( ^{1}\text{H} \text{RMN (CDCl}_3\))

RMN (CDCl\(_3\))

\( ^{13}\text{C} \text{RMN (CDCl}_3\))
$\text{1H RMN (CDCl}_3\text{)}$

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David D. Díaz, Miguel A. Ramírez and Víctor S. Martín
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[ \text{H RMN (CDCl}_3) \]

\[ \text{C RMN (CDCl}_3) \]
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzyl peroxypropargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

1H RMN (CDCl₃)

13C RMN (CDCl₃)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{1}\text{H RMN (CDCl}_3\text{)}$
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in $\gamma$-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^1$H RMN (CDCl$_3$)

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylöxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[ n-C_3H_7\overbrace{\text{OTBDPS}}^{\text{Br}} \]

$^1$H RMN (CDCl$_3$)

$^{13}$C RMN (CDCl$_3$)

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

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[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{1}$H RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in \( \gamma \)-Benzylxy Propargylic Alcohols

\( ^{13}C \) RMN (CDCl\(_3\))
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

$^{1}$H RMN (CDCl$_3$)

$^{1}$H RMN (CDCl$_3$)
NOE experiment (CDCl₃)

NOE experiment (CDCl₃)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[ \text{\textsuperscript{1}H RMN (CDCl}_3\text{)} \]
[1,3]-Transfer of Chirality During the Nicholas Reaction in \( \gamma \)-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\( ^{13}C \) RMN (CDCl\(_3\))

\( ^{1}H \) RMN (CDCl\(_3\))
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxoy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[
\text{Intermediate for 14}
\]

$^{1}H$ RMN (CDCl$_3$)

\[
\begin{align*}
\text{ppm} & \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \\
\end{align*}
\]

\[
\begin{align*}
\text{ppm} & \quad 20 \quad 40 \quad 60 \quad 80 \quad 100 \quad 120 \quad 140 \quad 160 \\
\end{align*}
\]
[1,3]-Transfer of Chirality During the Nicholas Reaction in $\gamma$-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$\text{H RMN (CDCl}_3\text{)}$

$\text{H RMN (CDCl}_3\text{)}$
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

$\text{H RMN (CDCl}_3\text{)}$

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín
[1,3]-Transfer of Chirality During the Nicholas Reaction in \( \gamma \)-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[ ^1H \text{RMN (CDCl}_3) \]
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{1}H$ RMN (CDCl$_3$)

$^{13}C$ RMN (CDCl$_3$)
Transfer of Chirality During the Nicholas Reaction in γ-Benzzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^1$H RMN (CDCl$_3$)

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxoy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{1}H$ RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{13}$C RMN (CDCl$_3$)
1H RMN (CDCl$_3$)

13C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in Γ-Benzzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{1}H$ RMN (CDCl$_3$)

$^{13}C$ RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$\text{H} \quad \text{Bu-t}$

$\text{n-C}_{13}\text{H}_{27}$

$\text{17e}$

$\text{C}_{17}\text{H}_{33}$

$\text{1H RMN (CDCl}_3\text{)}$
[1,3]-Transfer of Chirality During the Nicholas Reaction in $\gamma$-Benzyloxy Propargylic Alcohols

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Diaz, Miguel A. Ramirez and Victor S. Martin

$\textsuperscript{1}H$ RMN (CDCl$_3$)

$\textsuperscript{1}H$ RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$1^1$H RMN (CDCl$_3$)

$1^3$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in \(\gamma\)-Benzyloxy Propargylic Alcohols

\[
\begin{align*}
\text{AcO} & \quad \text{H} & \quad \text{H} & \quad \text{Ph} \\
n\text{C}_{13}\text{H}_{27} & \quad \text{H} & \quad \text{H} & \quad \text{C}_{3}\text{H}_{11} \cdot n
\end{align*}
\]

\(1^1\text{H} \text{ RMN (CDCl}_3\text{)}\)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{1}H$ RMN (CDCl$_3$)

$^{13}C$ RMN (CDCl$_3$)
EXPERIMENTO NOE (CDCl₃)
1H RMN (CDCl₃)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{13}$C RMN (CDCl$_3$)

NOE EXPERIMENT (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín
[1,3]-Transfer of Chirality During the Nicholas Reaction in \( \gamma \)-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[ \text{RMN (CDCl}_3\text{)} \]

\[ \text{RMN (CDCl}_3\text{)} \]
NOE EXPERIMENT (CDCl₃)

COSY (CDCl₃)
[1,3]-Transfer of Chirality During the Nicholas Reaction in $\gamma$-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

HSQC (CDCl$_3$)
Transfer of Chirality During the Nicholas Reaction in γ-Benzylloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^1$H RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in \( \gamma \)-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\( ^{13}\text{C} \text{RMN (CDCl}_3\text{)} \)

\[ \text{ppm} \quad 200 \quad 180 \quad 160 \quad 140 \quad 120 \quad 100 \quad 80 \quad 60 \quad 40 \quad 20 \]
NOE EXPERIMENT (CDCl₃)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^1$H RMN (CDCl$_3$)

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

NOE EXPERIMENT (CDCl₃)
Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín
[1.3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$\text{H RMN (CDCl}_3\text{)}$

$\text{C RMN (CDCl}_3\text{)}$

$\text{OBn}$

$\text{BnO}$

$\text{OH}$

$25$

$\text{H RMN (CDCl}_3\text{)}$

$\text{C RMN (CDCl}_3\text{)}$
[1,3]-Transfer of Chirality During the Nicholas Reaction in \(\gamma\)-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[ \text{\(\gamma\)-Benzylxy Propargylic Alcohol} \]

\[ \text{\(\text{H RMN (CDCl}_3\text{)}\)} \]
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

\[ ^{13}C\text{ RMN (CDCl}_3\text{)} \]

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín
[1,3]-Transfer of Chirality During the Nicholas Reaction in \( \gamma \)-Benzyloxy Propargylic Alcohols

\[
\begin{align*}
\text{HO} & \quad \text{H} & \quad \text{H} & \quad \text{C}_5\text{H}_{11-n} \\
\text{BnO} & \quad \text{28} & \quad \text{C}_5\text{H}_{11-n}
\end{align*}
\]

\(^1\text{H} \text{RMN (CDCl}_3\text{)}

\[^{13}\text{C} \text{RMN (CDCl}_3\text{)}

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$\text{OBn OH}$

$\text{OBn}$

$\text{30}$

$\text{OBn OH}$

$\text{30}$

$\text{OBn}$

$\text{OBn OH}$

$\text{30}$

$\text{OBn}$

$\text{OBn OH}$

$\text{30}$

$\text{OBn}$

$\text{1H RMN (CDCl}_3\text{)}$

$\text{13C RMN (CDCl}_3\text{)}$
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxoy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{1}H$ RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^1$H RMN (CDCl$_3$)

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

COSY (CDCl₃)

HSQC (CDCl₃)
[1,3]-Transfer of Chirality During the Nicholas Reaction in \( \gamma \)-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[ \text{H} \text{RMB} (\text{CDCl}_{3}) \]
$^{13}$C RMN (CDCl$_3$)

$^1$H RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxoy Propargylic Alcohols

$^13$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

$\text{OBn OH}$

$^{1}H$ RMN (CDCl₃)

$^{13}C$ RMN (CDCl₃)
[1,3]-Transfer of Chirality During the Nicholas Reaction in \(\gamma\)-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[ \text{OBn OH} \quad \equiv \quad \text{OH OBn} \]

1H RMN (CDCl₃)

13C RMN (CDCl₃)
$[^1]H$ RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in \(\gamma\)-Benzyloxy Propargylic Alcohols

\[1^3\text{C RMN (CDCl}_3\text{)}\]

David D. Diaz, Miguel A. Ramírez and Víctor S. Martín
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxoy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[ \text{intermediate for 42} \]

\[ ^1\text{H RMN (CDCl}_3) \]

\[ ^{13}\text{C RMN (CDCl}_3) \]
Transfer of Chirality During the Nicholas Reaction in \(\gamma\)-Benzylxoy Propargylic Alcohols

\[
\text{intermediate for 42}
\]

\[\begin{array}{c}
\text{OBn} \\
\text{MOMO} \\
\text{OMOM} \\
\text{OBn}
\end{array}\]

\(\text{\textsuperscript{1}H RMN (CDCl}_3\text{)}\)

\(\text{\textsuperscript{13}C RMN (CDCl}_3\text{)}\)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

^1H RMN (CDCl₃)

David D. Diaz, Miguel A. Ramírez and Victor S. Martín
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[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxox Propargylic Alcohols

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[\text{OBn} \quad 45\]

$^1$H RMN (CDCl$_3$)

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in \( \gamma \)-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\( \text{\^{1}H RMN (CDCl}_3\text{)} \)

\( \text{\^{13}C RMN (CDCl}_3\text{)} \)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^1$H RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{1}H$ RMN (CDCl$_3$)

$^{13}C$ RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{1}H$ RMN (CDCl$_3$)

$^{13}C$ RMN (CDCl$_3$)
$^1$H RMN (CDCl$_3$)
(1,3)-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^1{\text{C}}$ RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[ n-C_3H_7 \overset{OBn}{\longrightarrow} CO_2Me \]

\( ^1H \text{ RMN (CDCl}_3\text{)} \)

\( ^{13}C \text{ RMN (CDCl}_3\text{)} \)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylolxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[ n\text{-C}_3\text{H}_7\underset{\text{OBn}}{\overset{\text{OH}}{\xrightarrow{\text{Me}}} \text{64}} \]

\[ ^1\text{H} \text{RMN} (\text{CDCl}_3) \]

\[ ^{13}\text{C} \text{RMN} (\text{CDCl}_3) \]
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxoy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$\text{^1H RMN (CDCl}_3\text{)}$
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$\text{H RMN (CDCl}_3\text{)}$

$\text{C RMN (CDCl}_3\text{)}$
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

1H RMN (CDCl₃)

13C RMN (CDCl₃)
[1,3]-Transfer of Chirality During the Nicholas Reaction in \(\gamma\)-Benzyloxy Propargylic Alcohols

\[
\begin{align*}
\text{n-C}_3\text{H}_7 & \quad \text{OH} \\
\text{OH} & \quad \text{C}_5\text{H}_{11} \quad \text{n}
\end{align*}
\]

\(^1\text{H} \text{RMN (CDCl}_3\text{)}\)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

$^{13}$C RMN (CDCl$_3$)
[1.3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxoy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^1$H RMN (CDCl$_3$)

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzyloxy Propargylic Alcohols

$\text{OH}$

$\text{n-C}_3\text{H}_7$  $\text{Me}$  $\text{C}_9\text{H}_{11-n}$

$\text{Me}$  $\text{n-C}_7\text{H}_7$

$77$

$\text{H RMN (CDCl}_3\text{)}$

$\text{C RMN (CDCl}_3\text{)}$

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[
\begin{align*}
\text{1H RMN (CDCl}_3) & \\
\end{align*}
\]
[1,3]-Transfer of Chirality During the Nicholas Reaction in \( \gamma \)-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\( ^{13} \text{C RMN (CDCl}_3 \)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^1$H RMN (CDCl$_3$)

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzyloxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^1$H RMN (CDCl$_3$)

$^{13}$C RMN (CDCl$_3$)
Transfer of Chirality During the Nicholas Reaction in γ-Benzylpropargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxoy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^1$H RMN (CDCl$_3$)

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

COSY (CDCl₃)

HSQC (CDCl₃)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$\text{H N}$

OH

Ph

\begin{align}
\text{C}_8\text{H}_{11-n} & \\
83 & \\
\end{align}

$^{1}H \text{ RMN (CDCl}_3)$

$^{13}C \text{ RMN (CDCl}_3)$

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

**1H RMN (CDCl₃)**
Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

$^{13}$C RMN (CDCl$_3$)

$^1$H RMN (CDCl$_3$)

David D. Diaz, Miguel A. Ramirez and Victor S. Martin
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxoy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in γ-Benzylxy Propargylic Alcohols

$^1$H RMN (CDCl$_3$)

$^{13}$C RMN (CDCl$_3$)
[1,3]-Transfer of Chirality During the Nicholas Reaction in β-Benzylxy Propargylic Alcohols

David D. Díaz, Miguel A. Ramírez and Víctor S. Martín

\[ \text{HO} \quad \text{H} \quad \text{D} \quad \text{H} \]
\[ \text{n-C}_{13}\text{H}_{27} \quad \text{C}_{5}\text{H}_{11}\cdot \text{n} \]

$^1$H RMN (CDCl$_3$)

$^{13}$C RMN (CDCl$_3$)
Transfer of Chirality During the Nicholas Reaction in \(\gamma\)-Benzyl oxy Propargylic Alcohols

David D. Diaz, Miguel A. Ramírez and Víctor S. Martín