Supporting Information
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Rhodium Carbenoid Mediated C-H Activation of a Tertiary Methyl Group. An Enantiospecific Approach to the Angular Triquinanes Norsilphiperfolane and Norcameroonanes.

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Supplementary Material

Experimental Procedures:

2-[(1S,2S,5S)-1,5-Dimethylbicyclo[3.3.0]octane-spiro[7.2'-1,3-dioxolan-2-yl]propene (16): To a magnetically stirred solution of the diquinane\(^{scj}\) 9 (120 mg, 0.63 mmol) in dry benzene (5 mL) was added ethylene glycol (0.07 mL, 1.26 mmol) and a catalytic amount of \(p\)-TSA and the resultant reaction mixture was refluxed for 2 h using a Dean–Stark water separator. Saturated NaHCO\(_3\) solution (5 mL) was added to the reaction mixture and extracted with ether (3 x 4 mL). The ether extract was washed with brine (5 mL) and dried (Na\(_2\)SO\(_4\)). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexane (1:19) as an eluent furnished the ketal 16 (135 mg, 92%) as colorless oil. \([\alpha]_{D}^{22}\) : +2.3 (c 2.2, CHCl\(_3\)); IR (neat): \(\nu_{\text{max}}/\text{cm}^{-1}\) 3082, 2955, 2873, 1641, 1461, 1448, 1377, 1330, 1159, 1114, 1090, 1020, 984, 946, 888; \(^1\)H NMR (400 MHz, CDCl\(_3\)+CCl\(_4\)): \(\delta\) 4.78 (1 H, s) and 4.66 (1 H, s) [C=CH\(_2\)], 3.95-3.70 (4 H, m, OCH\(_2\)CH\(_2\)O), 2.66 (1 H, dd, \(J\) 11.1 and 7.3 Hz), 2.13 (1 H, d, \(J\) 13.9 Hz), 1.92 (1 H, d, \(J\) 13.8 Hz), 1.73 (3 H, s olefinic CH\(_3\)), 1.80-1.40 (6 H, m), 0.99 (3 H, s) and 0.73 (3 H, s) [2 x tert-CH\(_3\)]; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)+CCl\(_4\)): \(\delta\) 146.0 (C, C=CH\(_2\)), 116.8 (C, C-7), 111.1 (CH\(_2\), C=CH\(_2\)), 63.9 (CH\(_2\)) and 63.6 (CH\(_2\)) [OCH\(_2\)CH\(_2\)O], 55.6 (CH, C-2), 51.3 (CH\(_2\)), 50.8 (C), 50.0 (C), 49.6 (CH\(_2\)), 39.3 (CH\(_2\)), 27.7 (CH\(_2\)), 24.9 (CH\(_3\)) and 23.7 (CH\(_3\)) [2 x tert. CH\(_3\)], 19.0 (CH\(_3\), olefinic CH\(_3\)); HRMS: \(m/z\) Calcd. for C\(_{13}\)H\(_{24}\)O\(_2\)Na (M+Na): 259.1310; Found: 259.1312.

1-[(1S,2R,5S)-1,5-Dimethylbicyclo[3.3.0]octane-spiro[7.2'-1,3-dioxolan-2-yl]ethanone (17): Dry ozone gas in oxygen was passed through a cold (-70 °C) solution of the ketal 16 (137 mg, 0.58 mmol) and a catalytic amount of NaHCO\(_3\) in 1:4 MeOH and CH\(_2\)Cl\(_2\) (10 mL) for 5 min (until blue color appeared). Excess ozone was flushed off with oxygen. Dimethyl sulphide (0.20 mL, 2.9 mmol) was added to the reaction mixture and stirred for 4 h at RT. Excess of Me\(_2\)S was evaporated on hot water bath. Water (5 mL) was added to the reaction mixture and extracted with CH\(_2\)Cl\(_2\) (3 x 5 mL). The combined CH\(_2\)Cl\(_2\) extract was washed with brine (5 mL) and dried (Na\(_2\)SO\(_4\)). Evaporation of the solvent and purification of the
residue on a silica gel column using ethyl acetate–hexane (1:4) as an eluent furnished the ketone 17 (120 mg, 87%) as colorless oil. \([\alpha]_{D}^{29}: -69.6 (c 2.1, \text{CHCl}_3)\); IR (neat): \(\nu_{\text{max}}/\text{cm}^{-1}\) 2959, 2879, 1708 (C=O), 1452, 1354, 1331, 1238, 1161, 1114, 1091, 1070, 1040, 1019, 946, 894, 820, 727; \(^1\)H NMR (400 MHz, CDCl\(_3\)+CCl\(_4\)): \(\delta\) 3.95-3.65 (4 H, m, OCH\(_2\)CH\(_2\)O), 3.15 (1 H, dd, \(J\) 9.2 and 8.0 Hz), 2.24 (1 H, d, \(J\) 14.4 Hz), 2.09 (3 H, s, CH\(_3\)C=O), 2.10-1.45 (7 H, m), 0.94 (3 H, s) and 0.74 (3 H, s) [2 x tert-CH\(_3\)]; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 209.9 (C, C=O), 116.3 (C, C-7), 64.0 (CH\(_2\)) and 63.7 (CH\(_2\)) [OCH\(_2\)CH\(_2\)O], 61.0 (CH, C-2), 52.1 (C), 51.4 (C), 50.7 (CH\(_2\)), 49.6 (CH\(_2\), C-4), 37.8 (CH\(_2\)), 31.3 (CH\(_3\), CH\(_3\)C=O), 24.4 (CH\(_2\), C-3), 23.4 (CH\(_3\)), 18.5 (CH\(_3\)); HRMS: \(m/z\) Calcd. for C\(_{14}\)H\(_{22}\)O\(_3\)Na (M+Na): 261.1467; Found: 261.1465.

Ethyl 3-[(1S,2R,5S)-1,5-dimethylbicyclo[3.3.0]octane-spiro[7.2']-1,3-dioxolan-2-yl]-3-oxopropanoate (18): To a cold (-70 °C) magnetically stirred solution of hexamethyl-disilazane (0.34 mL, 1.6 mmol) in anhydrous THF (1 mL) was added a 2.5 \(M\) solution of \(n\)-butyllithium in hexane (0.51 mL, 1.28 mmol) dropwise over a period of 10 min. The temperature of the solution was brought to -50 °C and stirred for 20 min and recooled to -70 °C. To the LHMDS thus formed, was added a solution of the ketone 17 (76 mg, 0.32 mmol) in dry THF (2 mL) drop wise and stirred at the same temperature for 1 h. Ethyl chloroformate (0.09 mL, 0.96 mmol) was added in one portion. The reaction mixture was stirred for 5 h at RT. Water (5 mL) was added to the reaction mixture and extracted with ether (3 x 5 mL). The ether extract was washed with brine (5 mL) and dried (Na\(_2\)SO\(_4\)). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexane (1:19) as eluent furnished the ketoester 18 (87 mg, 88%) as colorless oil. \([\alpha]_{D}^{24}: -78.3 (c 4.3, \text{CHCl}_3)\); IR (neat): \(\nu_{\text{max}}/\text{cm}^{-1}\) 2959, 2877, 1746 (OC=O), 1713 (C=O), 1621, 1470, 1451, 1433, 1332, 1235, 1155, 1089, 1019, 949; \(^1\)H NMR (400 MHz, CDCl\(_3\)+CCl\(_4\)): (peaks due to keto form) \(\delta\) 4.18 (2 H, q, \(J\) 7.2 Hz, OCH\(_2\)CH\(_3\)), 4.00-3.70 (4 H, m, OCH\(_2\)CH\(_2\)O), 3.42 (2 H, s), 3.26 (1 H, dd, \(J\) 9.6 and 7.5 Hz), 2.21 (1 H, d, \(J\) 13.0 Hz), 2.20-1.50 (7 H, m), 1.26 (3 H, t, \(J\) 7.1 Hz, OCH\(_2\)CH\(_3\)), 0.99 (3 H, s) and 0.83 (3 H, s) [2 x tert-CH\(_3\)]; (selected peaks due to enol form) \(\delta\) 12.14 (1 H, s, enolic-OH), 4.94 (1 H, s, H-2), 2.90 (1 H, dd, \(J\) 10.6 and 7.1 Hz), 1.00 (3 H, s) and 0.84 (3 H, s) [2 x tert. CH\(_3\)]; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)+CCl\(_4\)): (peaks due to keto form): \(\delta\) 204.2 (C, C=O), 172.6 (C, OC=O), 116.1 (C, OC=O), 64.0 (CH\(_2\)) and 63.9 (CH\(_2\)) [OCH\(_2\)CH\(_2\)O], 61.1 (CH\(_2\), OCH\(_2\)CH\(_3\)), 60.5 (CH), 51.4 (C), 50.7 (CH\(_2\)), 50.5 (CH\(_2\)), 49.9 (C), 49.6 (CH\(_2\)), 38.0 (CH\(_2\)), 24.8 (CH\(_2\)), 23.5 (CH\(_3\)) and 18.8 (CH\(_3\)) [2 x tert-CH\(_3\)], 14.1 (CH\(_3\), OCH\(_2\)CH\(_3\)); (peaks due to enol form): \(\delta\) 179.9 (C, O-C=CH), 167.0 (C, OC=O), 116.3 (C, O-
C-O), 89.3 (CH, O-C=CH), 63.9 (CH2) and 63.7 (CH2) [OCH2CH2O], 59.8 (CH), 53.5 (C), 52.5 (C), 51.3 (CH2), 50.0 (CH2), 49.0 (CH2), 38.8 (CH2), 25.1 (CH2), 24.3 (CH3) and 18.5 (CH3) [2x tert-CH3], 14.2 (CH3, OCH2CH3); HRMS: m/z Calcd. for C17H26O5Na (M+Na): 333.1678; Found: 333.1681.

Ethyl 2-diazo-3-[(1S,2R,5S)-1,5-dimethylbicyclo[3.3.0]octane-spiro[7.2']-1,3-dioxolan-2-yl]-3-oxopropanoate (19): To a magnetically stirred solution of the β-keto ester 18 (110 mg, 0.35 mmol) in acetonitrile (0.5 mL) were added tosyl azide (69 mg, 0.35 mmol) and triethylamine (0.06 mL, 0.42 mmol) and stirred at RT for 4 h. Solvent was evaporated under reduced pressure and the residue was purified on a silica gel column using ethyl acetate-hexane (1:9) as an eluent to furnish the α-diazo-β-keto ester 19 (98 mg, 82%) as colorless oil. [α]D25 : -50.9 (c 3.0, CHCl3); IR (neat): ʋmax/cm⁻¹ 2960, 2878, 2136 (N=N), 1715 (OC=O), 1652 (C=O), 1470, 1455, 1378, 1334, 1301, 1206, 1116, 1092, 1043, 1020; 1H NMR (400 MHz, CDCl3 + CDCl4): δ 4.29 (2 H, q, J 7.1 Hz, OCH2CH3), 4.02 (1 H, dd, J 7.8 and 7.1 Hz), 3.95-3.75 (4 H, m, OCH2CH2O), 2.21 (1 H, d, J 14.2 Hz), 2.15-2.06 (1 H, m), 1.98 (1 H, d, J 14.1 Hz), 1.92 (1 H, d, J 14.9 Hz), 1.90-1.66 (4 H, m), 1.32 (3 H, t, J 7.1 Hz, OCH2CH3), 1.01 (3 H, s) and 0.91 (3 H, s) [2 x tert-CH3]; 13C NMR (100 MHz, CDCl3 + CDCl4): δ 195.0 (C, C=O), 161.3 (C, OC=O), 116.4 (C, O-C-O), 64.1 (C, C=N2), 64.0 (CH2) and 63.8 (CH2) [OCH2CH2O], 61.2 (CH2, OCH2CH3), 56.4 (CH), 53.6 (C), 52.3 (CH2), 51.2 (C), 49.9 (CH2), 39.9 (CH2), 26.7 (CH2), 23.1 (CH3), 19.9 (CH3), 14.4 (CH3, OCH2CH3); HRMS: m/z Calcd. for C17H24N2O5Na (M+Na): 359.1583; Found: 359.1579.

(1S,5R,8S)-8-methyltricyclo[6.3.0.01,5]undecane-4,10-dione (21): To a magnetically stirred refluxing suspension of Rh2(OAc)4 (3 mg) in dry CH2Cl2 (4 mL) was added a solution of the α-diazo-β-keto ester (60 mg, 0.18 mmol) in dry CH2Cl2 (14 mL) over a period of 30 min and refluxed for 2 h. Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexane (1:19) as an eluent furnished an epimeric mixture of the triquinane ester 20 (48 mg, 87%) along with its enol form as an oil.

A solution of the keto ester 20 (46 mg, 0.15 mmol) and LiCl (25 mg, 0.6 mmol) in DMSO (0.5 mL) and water (0.01 mL) was placed in a Carius tube and heated to 180 °C for 1.5 h. The reaction mixture was cooled to RT, diluted with ether (3 mL), washed with water (2 mL), 1N HCl (2 mL) and brine (3 mL), and dried (NaSO4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexane (1:4) as an eluent furnished the diketone 21 (23 mg, 82%) as a white solid. MP: 147-149 °C; [α]D25 : 62.6 (c 2.5, CHCl3); IR (neat): ʋmax/cm⁻¹ 2961, 2875, 1736 (C=O), 1405, 1272, 1227, 1178, 735; 1H NMR
(400 MHz, CDCl₃+CCl₄): δ 2.61 (1 H, d, J 18.7 Hz), 2.50-2.27 (4 H, m), 2.24 (2 H, s), 2.20-1.95 (2 H, m), 1.94-1.55 (4 H, m), 1.14 (3 H, s, tert. CH₃); ¹³C NMR (100 MHz, CDCl₃+CCl₄): 220.7 (C, C=O), 217.0 (C, C=O), 58.7 (CH, C-5), 57.3 (C, C-1), 51.2 (CH₂), 50.2 (C, C-8), 50.1 (CH₂), 39.8 (CH₂), 37.7 (CH₂), 29.2 (CH₂), 26.7 (CH₂), 21.5 (CH₃, tert. CH₃); HRMS: m/z Calcd. for C₁₂H₁₆O₂Na (M+Na): 215.1060; Found: 215.1048.

(1S,5S,8S)-4,10-Bismethylene-8-methyltricyclo[6.3.0.0³,⁸]dodecane (22): To a freshly prepared ¹AmOK [from potassium (57 mg, 1.46 mmol) and ¹AmOH (4 mL) followed by evaporation of ¹AmOH under vacuum] in dry THF (2 mL) was added methyltriphenylphosphonium bromide (555 mg, 1.56 mmol) and the resulting yellow solution was stirred for 1.5 h at RT. The solution was allowed to settle for 30 min. The dark yellow solution of methylenetriphenylphosphorane was added to a magnetically stirred solution of the diketone 21 (10 mg, 0.05 mmol) in dry THF (1 mL) at RT and stirred for 3 h. Water (2 mL) was added to the reaction mixture and extracted with ether (3 x 5 mL). The combined ether extract was washed with brine (5 mL) and dried (Na₂SO₄). Evaporation of the solvent and purification of the residue on a silica gel column using hexane as an eluent furnished the diene 22 (7 mg, 71%) as oil. [α]_D: -35.7 (c 1.0, CHCl₃); IR (neat): ν_max/cm⁻¹ 3072, 2947, 2862, 1654, 1464, 1456, 1375, 1210, 879; ¹H NMR (400 MHz, CDCl₃): δ 4.82 (1 H, s), 4.76 (1 H, s), 4.75 (1 H, s) and 4.72 (1 H, s) [2 x C=CH₂], 2.51 (1 H, d, J 8.8 Hz), 2.40 (1 H, d, J 15.4 Hz), 2.37-2.29 (2 H, m), 2.25 and 2.18 (2 H, 2 x d, J 16.4 Hz), 2.10-1.88 (1 H, m), 1.68 (1 H, td, J 12.4 and 8.4 Hz), 1.65-1.35 (5 H, m), 1.00 (3 H, s, tert. CH₃); ¹³C NMR (100 MHz, CDCl₃): 159.0 (C, C-4) and 151.4 (C, C-10), 105.1 (CH₂) and 104.4 (CH₂) [2 x C=CH₂], 62.9 (C, C-1), 56.2 (CH, C-5), 51.3 (C, C-8), 47.5 (CH₂), 46.2 (CH₂), 39.9 (CH₂), 35.2 (CH₂), 33.5 (CH₂), 31.6 (CH₂), 23.3 (CH₃); HRMS: m/z Calcd. for C₁₄H₂₆Na (M+Na): 211.1463; Found: 211.1475.