Supporting Information

Polycyclic High density Cage Compounds via Olefin Metathesis

Sambasivarao Kotha*, Usha Nandan Chaurasia

Department of Chemistry, Indian Institute of Technology-Bombay, Powai, India

Fax: 022-25727152; Phone: +91(22)-2572 7160, E-mail: srk@chem.iitb.ac.in

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General Information

The reactions were carried under nitrogen atmosphere and moisture-sensitive materials were transferred by using syringe. The reaction was monitored by TLC (thin-layer chromatography) with suitable solvent system mixture of EtOAc and petroleum ether. Column chromatography was done by 100-200 mesh silica gel in all cases. Photochemical reaction was carried out with 125W high-pressure mercury vapour lamp and Pyrex vessel. The coupling constants (J) are given in hertz (Hz) and chemical shifts are denoted in parts per million (ppm) downfield from internal standard, tetramethylsilane (TMS). The abbreviations, s, d, t, q, m, dd and dt refer to singlet, doublet, triplet, quartet, multiplet, doublet of doublets, and doublet of triplets, respectively. All IR samples were recorded with chloroform as solvents on a Nicolet Impact-400 FTIR spectrometer. Nuclear magnetic resonance (NMR) spectra (¹H, ¹³C, and DEPT 135) were recorded on 400 and 500 MHz spectrometers (Bruker) with a CDCl₃ solvent and chemical shifts (d ppm) are reported relative to the internal standard such as TMS. The coupling constants (J) are given in hertz (Hz) and chemical shifts are denoted in parts per million (ppm) downfield from internal standard, tetramethylsilane (TMS). The abbreviations, s, d, t, q, m, dd and dt refer to singlet, doublet, triplet, quartet, multiplet, doublet of doublets, and doublet of triplets. Mass spectra (HRMS) have been recorded under positive ion electrospray ionization (ESI, Q-TOF) mode. X-ray crystal analysis was performed on diffractometer equipped with graphite
monochromated Mo Ka radiation and structure was solved by direct methods shelxl-97 and refined by full-matrix least-squares against F [2] using shelxl-97 software.

**Experimental Section**

**General Procedure for cross-metathesis**

To a solution of dry DCM \( \text{toulene} \) was dissolved olefine (15, 14, 28 and 33) (1 equi.) and degassed with nitrogen. Then Grubbs-II catalyst \( \text{N-tolyl Grubbs catalyst} \) (10 mol%) was added and the reaction mixture was slightly warmed. Then other olefinic partner (allyl trimethyl silane, triisopropyl silane, methyl vinyl ketone and cis,1,4 diacetoxy-2-butene) (4 equi.) was added to the reaction mixture and was refluxed under nitrogen. At the conclusion of the reaction (TLC monitoring), the reaction mixture was cooled to rt and the solvent was removed. Then reaction mixture was subjected to silica gel column chromatography to furnish corresponding mono and di cross-metathesis products.

**Compound 16: Yield** 53 mg (40%), \( R_f = 0.4 \) (3% EtOAc-petroleum ether), **Appearance** White solid, **Mp** 106-108 °C. \( ^1H \text{NMR} \) (500 MHz, CDCl\(_3\)): \( \delta \) 5.89-5.83 (m, 1H), 5.57-5.50 (m, 1H), 5.33 (d, \( J = 15.16 \text{ Hz} \)), 1H), 5.13 (dd, \( J_1 = 16.53 \text{ Hz} \), \( J_2 = 0.83 \text{ Hz} \)), 1H), 5.02 (d, \( J = 10.93 \text{ Hz} \)), 1H), 2.77-2.70 (m, 2H), 2.52-2.47 (m, 2H), 2.36 (s, 2H), 2.20 (s, 2H), 1.51 (d, \( J = 10.75 \text{ Hz} \)), 1H), 1.44-1.42 (m, 2H), 1.05 (d, \( J = 10.93 \text{ Hz} \)), 1H), -0.01 (s, 9H) ppm. \( ^{13}\text{C NMR} \) (125 MHz, CDCl\(_3\)): \( \delta \) 143.2, 133.6, 125.5, 112.7, 77.0, 77.0, 51.5, 51.2, 44.9, 44.7, 41.7, 41.5, 40.3, 40.1, 34.0, 22.7, -1.7 ppm. **HRMS** (ESI, Q-ToF) m/z: [M+Na]\(^+\) calcd for \( C_{28}H_{32}NaO_Si \): 339.1755; found: 339.1751 IR (neat): \( \nu_{\text{max}} \) 3672, 2979, 1477, 1248, 1216, 815, 668 cm\(^{-1}\).

**Compound 17: Yield** 28 mg (20%), \( R_f = 0.5 \) (3% EtOAc-petroleum ether), **Appearance** white solid, **Mp** 103-105 °C. \( ^1H \text{NMR} \) (500 MHz, CDCl\(_3\)): \( \delta \) 5.57-5.51 (m, 2H), 5.34 (d, \( J = 14.41 \text{ Hz} \)), 2H), 2.7 (d, \( J = 4.56 \text{ Hz} \)), 2.45 (s, 2H), 2.36 (s, 2H), 2.18 (s, 2H), 1.56 (d, \( J = 10.04 \text{ Hz} \)), 1H), 1.43 (t, \( J_1 = 7.04 \text{ Hz} \)), 4H), 1.03 (d, \( J = 10.60 \text{ Hz} \)), 1H), -0.009 (s, 18H) ppm. \( ^{13}\text{C NMR} \) (125 MHz, CDCl\(_3\)): \( \delta \) 133.9, 125.3, 77.2, 51.5, 45.1, 41.9, 40.1, 34.0, 22.7, 1.0 ppm. **HRMS** (ESI, Q-ToF) m/z: [M+K]\(^+\) calcd for \( C_{23}H_{38}K_2O_Si_2 \): 441.2043; found: 441.2042. **IR** (neat): \( \nu_{\text{max}} \) 3735, 2960, 1217, 854, 769 cm\(^{-1}\).

**Compound 18:** Yield 52 mg (45%), \( R_f = 0.5 \) (15 % EtOAc-petroleum ether), **Appearance** colourless liquid. \( ^1H \text{NMR} \) (500 MHz, CDCl\(_3\)): \( \delta \) 6.75 (d, \( J = 19.10 \text{ Hz} \)), 1H), 6.30-5.83 (m, 3H), 5.1 (m, 1H), 2.79-2.58 (m, 4H), 2.52-2.50 (t, \( J = 8.79 \text{ Hz} \)), 1H), 2.42-2.35 (m, 3H), 2.25 (s, 3H), 1.57 (d, \( J = 15.4 \text{ Hz} \)), 2H) ppm. \( ^{13}\text{C NMR} \) (500 MHz, CDCl\(_3\)): \( \delta \) 199.3, 151.0, 142.6, 128.4, 113.6, 77.5, 77.1, 51.8, 51.2, 44.2, 41.8, 41.3, 40.6, 40.4, 40.0, 34.1, 27.6 ppm. **HRMS** (ESI, Q-ToF) m/z: [M+H]\(^+\) calcd for \( C_{17}H_{20}O_3 \): 273.1484; found: 273.1483. **IR** (neat): \( \nu_{\text{max}} \) 3456, 2953, 2502, 2323, 1711, 1361, 1259, 977, 673 cm\(^{-1}\).
Compound 19: Yield 40 mg (30%), Rf = 0.2 (40% EtOAc-petroleum ether), Appearance colourless liquid. $^1$H NMR (500 MHz, CDCl₃): δ 6.71 (d, J = 16.6 Hz, 2H), 6.18 (d, J = 15.46 Hz, 2H), 2.75 (s, 2H), 2.65 (s, 2H), 2.38 (s, 2H), 2.33 (s, 2H), 2.25 (s, 6H), 1.56 (d, J = 14.18 Hz, 2H) ppm. $^{13}$C NMR (500 MHz, CDCl₃): δ 199.3, 150.4, 128.6, 77.3, 51.7, 43.9, 41.7, 40.2, 34.2, 27.6 ppm. HRMS (ESI, Q-ToF) m/z: [M+K]+ calcd for C₁₉H₁₂₂KO₄: 353.1148; found: 353.1150. IR (neat): ν max 3707, 2971, 2865, 1675, 977, 776, 666 cm⁻¹.

Compound 20: Yield 57 mg (45%), Rf = 0.5 (15% EtOAc-petroleum ether), Appearance colourless liquid. $^1$H NMR (500 MHz, CDCl₃): δ 5.89-5.83 (m, 1 H), 5.79-5.76 (d, J = 15. 13 Hz, 1 H), 5.71-5.66 (m, 1H), 5.14 (dd, J₁ = 16.57 Hz, J₂ = 8.82 Hz, 1H), 5.05 (dd, J₁ = 10 Hz, J₂ = 1.38 Hz, 1H), 4.54 (d, J = 6.43 Hz, 2H), 2.74 (s, 2H), 2.54 (s, 2H), 2.38 (d, J = 8.16 Hz, 2H), 2.23 (s, 2H), 2.06 (s, 3H), 1.53 (d, J = 10.88 Hz, 1H), 1.08 (d, J = 10.13 Hz, 1H) ppm. $^{13}$C NMR (500 MHz, CDCl₃): δ 170.8, 142.8, 139.4, 122.6, 113.1, 77.3, 64.8, 51.5, 51.2, 44.5, 44.4, 41.8, 41.4, 40.2, 40.1, 34.0, 21.0 ppm. HRMS (ESI, Q-ToF) m/z: [M+Na]+ calcd for C₁₉H₁₂O₆Na: 311.1257; found: 311.1254. IR (neat): ν max 3198, 2972, 1738, 1455, 1240, 1147, 1067, 755, 666 cm⁻¹.

Compound 21: Yield 39 mg (25%), Rf = 0.3 (30% EtOAc-petroleum ether), Appearance colourless liquid. $^1$H NMR (500 MHz, CDCl₃): δ 5.79-5.76 (d, J = 16.24 Hz, 2H), 5.70-5.65 (m, 2H), 4.55-4.54 (d, J = 5.49 Hz, 4H), 2.71 (s, 2H), 2.55 (s, 2H), 2.35 (s, 2H), 2.24 (s, 2H), 2.05 (s, 6H), 1.53 (d, J = 11.15 Hz, 1H), 1.09 (d, J = 10.92 Hz, 1H) ppm. $^{13}$C NMR (125 MHz, CDCl₃): δ 170.8, 139.3, 122.8, 77.2, 64.7, 51.4, 44.4, 41.7, 40.1, 34.0, 20.9. HRMS (ESI, Q-ToF) m/z: [M+H]+ calcd for C₂₁H₂₀O₆: 397.1623; found: 397.1622. IR (neat): ν max 3851, 2980, 1736, 1218, 768, 667 cm⁻¹.

Compound 22: Yield 41 mg (40%), Rf = 0.5 (2% EtOAc-petroleum ether), Appearance white solid, Mp 104-106 °C. $^1$H NMR (500 MHz, CDCl₃): δ 5.90-5.83 (m, 1H), 5.70-5.62 (m, 1H), 5.39 (d, J = 15. 29 Hz, 1H), 5.14 (dd, J₁ = 16.11 Hz, J₂ = 1.35 Hz, 1H), 5.03 (dd, J₁ = 9.68 Hz, J₂ = 1.31 Hz, 1H), 2.72 (s, 2H), 2.49 (d, J = 3.54 Hz, 2H), 2.36 (d, J = 10.11 Hz, 2H), 2.49 (d, J = 3.54 Hz, 2H), 1.56 (d, J = 8.21 Hz, 2H), 1.52 (d, J = 10.57 Hz, 1H), 1.04 (s, 18 H) ppm. $^{13}$C NMR (125 MHz, CDCl₃): δ 143.4, 133.7, 126.5, 112.6, 77.3, 77.0, 51.5, 51.3, 44.8, 44.6, 42.0, 41.6, 40.2, 40.1, 34.0, 18.7, 15.5, 11.0 ppm. HRMS (ESI, Q-ToF) m/z: [M+K]+ calcd for C₂₁H₂₀OKOSi: 439.2425; found: 439.2429. IR (neat): ν max 3851, 3173, 2961, 2864, 1465, 1215, 1066, 883, 759, 667 cm⁻¹.

Compound 23: Yield 53 mg (40%), Rf = 0.7 (2% EtOAc-petroleum ether), Appearance white solid, Mp 110-112 °C. $^1$H NMR (500 MHz, CDCl₃): δ 6.00-5.93 (m, 1H), 5.53-5.29 (m, 2H), 5.12-5.05 (t, J = 19.01 Hz, 2H), 2.54 (s, 2H), 2.45 (s, 2H), 2.39 (s, 2H), 2.21-2.16 (m, 4H), 2.10 (d, J = 6.77 Hz, 2H), 2.06-2.03 (m, 1H), 1.48 (t, J = 7.05 Hz, 2H), 1.09 (d, J = 9.99 Hz, 1H), - 0.012 (s, 9 H) ppm. $^{13}$C NMR (125 MHz, CDCl₃): δ 134.1, 122.4, 121.1, 117.5, 77.8, 77.1, 49.4, 49.3, 44.3, 44.0, 43.1, 43.0, 43.0, 42.6, 42.6, 36.8,
34.0, 23.1, 18.7, -1.9 ppm. **HRMS** (ESI, Q-ToF) m/z: [M+H]⁺ calcd for C\textsubscript{21}H\textsubscript{33}O\textsubscript{2}Si: 345.2244; found: 345.2244. **IR** (neat): ν\textsubscript{max} 3762, 2979, 1477, 1248, 1216, 815, 660 cm\textsuperscript{-1}.

**Compound 24**: Yield 52 mg (45%), \( R_f = 0.5 \) (15 % EtOAc- petroleum ether), **Appearance** colourless liquid. $^1$H NMR (500 MHz, CDCl\textsubscript{3}): δ 7.0-6.98 (m, 1H), 6.06 (d, J = 16.57 Hz, 1H), 5.89 (m, 1H), 5.20 (d, J = 9.82 Hz, 1H), 5.15 (d, J = 17.4 Hz, 1H), 2.57 (d, J = 2.55 Hz, 2H), 2.50-2.46 (m, 3H), 2.42 (s, 1H), 2.36-2.32 (m, 2H), 2.26 (s, 3H), 2.17 (d, J = 6.92 Hz, 3H), 2.14-2.12 (m, 1H), 1.54 (d, J = 11.54 Hz, 1H), 1.11 (d, J = 10.61 Hz, 1H) ppm. $^{13}$C NMR (125 MHz, CDCl\textsubscript{3}): δ 199.0, 145.1, 133.6, 132.7, 119.8, 77.4, 77.4, 49.8, 49.4, 44.2, 44.1, 40.2, 42.9, 42.5, 39.9, 39.8, 33.9, 26.5 ppm. **HRMS** (ESI, Q-ToF) m/z: [M+Na]⁺ calcd for C\textsubscript{19}H\textsubscript{22}NaO\textsubscript{3}: 323.1615; found: 323.1618. **IR** (neat): ν\textsubscript{max} 3744, 2974, 1667, 1363, 1216, 757, 668 cm\textsuperscript{-1}.

**Compound 25**: Yield 39 mg (30%), \( R_f = 0.2 \) (40% EtOAc-petroleum ether), **Appearance** colourless liquid. $^1$H NMR (500 MHz, CDCl\textsubscript{3}): δ 6.94-6.88 (m, 2H), 6.10 (d, J = 13.10 Hz, 2H), 2.57 (s, 2H), 2.52 (s, 2H), 2.38 (s, 2H), 2.35 (d, J = 4.93 Hz, 2H), 2.30 (s, 1H), 2.27 (s, 6H), 2.17 (s, 2H), 1.56 (d, J = 10.81 Hz, 1H), 1.25 (s, 1H), 1.14 (d, J = 11.48 Hz, 1H) ppm. $^{13}$C NMR (125 MHz, CDCl\textsubscript{3}): δ 199.0, 144.1, 133.7, 77.7, 49.5, 44.1, 43.1, 42.9, 39.9, 33.9, 26.8 ppm. **HRMS** (ESI, Q-ToF) m/z: [M+Na]⁺ calcd for C\textsubscript{23}H\textsubscript{24}NaO\textsubscript{4}: 365.1723; found: 365.1723. **IR** (neat): ν\textsubscript{max} 3613, 2982, 1742, 1374, 1244, 1047, 847, 608 cm\textsuperscript{-1}.

**Compound 26**: Yield 56 mg (45%), \( R_f = 0.5 \) (15% EtOAc-petroleum ether), **Appearance** colourless liquid. $^1$H NMR (400 MHz, CDCl\textsubscript{3}): δ 5.92-5.80 (m, 2H), 5.66-5.56 (m, 1H), 5.11-5.04 (m, 2H), 4.58-4.47 (m, 2H), 2.52 (s, 2H), 2.43 (s, 2H), 2.37-2.34 (d, J = 13.51 Hz, 2H), 2.18-2.13 (m,4 H), 2.10-2.08 (m, 2H), 2.03-2.02 (d, J = 4.92 Hz, 3H), 1.52-1.50 (d, J = 11.35 Hz, 1H), 1.09-1.07 (d, J = 10.69 Hz,1H) ppm. $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}): δ 170.9, 133.5, 131.3, 126.8, 118.1, 77.5, 77.3, 65.2, 60.6, 49.2, 49.1, 44.1, 42.8, 42.7, 42.4, 39.9, 39.9, 39.8, 37.3, 21.0 ppm. **HRMS** (ESI, Q-ToF) m/z: [M+Na]⁺ calcd for C\textsubscript{20}H\textsubscript{26}NaO\textsubscript{4}: 353.1727; found: 353.1723. **IR** (neat): ν\textsubscript{max} 3748, 2973, 1738, 1239, 1155, 758 cm\textsuperscript{-1}.

**Compound 27**: Yield 38 mg (25%), \( R_f = 0.4 \) (20% EtOAc- petroleum ether), **Appearance** colourless liquid. $^1$H NMR (400 MHz, CDCl\textsubscript{3}): δ 5.88-5.78 (m, 2H), 5.61-5.56 (m, 2H), 4.57-4.49 (m, 4H), 2.52 (s, 2H), 2.42 (s, 2H), 2.36 (s, 2H), 2.24(s, 2H), 2.05 (s, 6H), 1.52 (d, J = 10.98 Hz, 1H), 1.08 (d, J = 10.20 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}): δ 170.8, 139.3, 122.8, 77.2, 64.7, 51.4, 44.4, 41.7, 40.1, 34.0, 20.9 ppm. **HRMS** (ESI, Q-ToF) m/z: [M+K]⁺ calcd for C\textsubscript{23}H\textsubscript{30}KO\textsubscript{6}: 441.1676; found: 441.1674. **IR** (neat): ν\textsubscript{max} 3745, 2960, 1739, 1235, 1026, 755, 607 cm\textsuperscript{-1}.

**Compound 29**: Yield 34 mg (30%), \( R_f = 0.5 \) (15% EtOAc-petroleum ether), **Appearance** colourless liquid. $^1$H NMR (500 MHz, CDCl\textsubscript{3}): δ 6.81-6.74 (m, 1H), 6.13 (d, J = 15.47 Hz, 1H), 5.83-5.75 (m, 1H), 3.74-3.66 (m, 2H), 3.58-3.49 (m, 2H), 3.44-3.36 (m, 2H), 2.99 (s, 3H), 2.17 (d, J = 6.92 Hz, 3H), 2.14-2.12 (m, 1H), 1.54 (d, J = 11.54 Hz, 1H), 1.11 (d, J = 10.61 Hz, 1H) ppm. **HRMS** (ESI, Q-ToF) m/z: [M+Na]⁺ calcd for C\textsubscript{21}H\textsubscript{23}O\textsubscript{2}Si: 345.2244; found: 345.2244. **IR** (neat): ν\textsubscript{max} 3762, 2979, 1477, 1248, 1216, 815, 660 cm\textsuperscript{-1}.
5.10 (dd, J₁ = 15.34 Hz, J₂ = 1.63 Hz, 1H), 5.05 (dd, J₁ = 9.37 Hz, J₂ = 0.99 Hz, 1H), 2.70 (dd, J₁ = 6.36 Hz, J₂ = 1.35 Hz, 2H), 2.60 (d, J = 2.28 Hz, 2H), 2.56-2.50 (m, 6H), 2.37 (d, J = 19.34 Hz, 2H), 2.25 (s, 3H), 1.86 (d, J = 10.23 Hz, 1H), 1.50 (d, J = 10.83 Hz, 1H) ppm. \(^\text{13C NMR}\) (125 MHz, CDCl₃): δ 198.6, 143.9, 134.2, 133.4, 117.2, 95.5, 94.4, 58.7, 58.6, 48.0, 47.9, 44.5, 44.4, 43.5, 41.8, 41.6, 37.4, 36.0, 26.9 ppm.

HRMS (ESI, Q-ToF) m/z: [M+H]⁺ calcd for C₁₉H₂₃O₂: 283.1692; found: 283.1693. IR (neat): ν max 2961, 2180, 1675, 1361, 1255, 1180, 982, 758, 537 cm⁻¹.

**Compound 30: Yield** 39 mg (30%), \( R_f = 0.3 \) (35% EtOAc-petroleum ether), **Appearance** colourless liquid. \(^\text{1H NMR}\) (500 MHz, CDCl₃): δ 6.79-6.73 (m, 2H), 6.12 (d, J = 15.29 Hz, 2H), 2.70 (dd, J₁ = 6.44 Hz, J₂ = 0.89 Hz, 4H), 2.69 (s, 2H), 2.54-2.51 (m, 4H), 2.37 (s, 2H), 2.24 (s, 6H), 1.87 (d, J = 10.65 Hz, 1H), 1.52 (d, J = 10.59 Hz, 1H) ppm. \(^\text{13C NMR}\) (125 MHz, CDCl₃): δ 198.5, 143.5, 133.4, 94.7, 58.6, 48.0, 44.3, 41.6, 35.8, 26.9 ppm. HRMS (ESI, Q-ToF) m/z: [M+H]^+ calcd for C₂₃H₂₅O₃: 325.1797; found: 325.1798. IR (neat): ν max 2961, 2180, 1675, 1361, 1255, 1180, 982, 758, 537 cm⁻¹.

**Compound 31: Yield** 32.46 mg (25%), \( R_f = 0.5 \) (12 % EtOAc-petroleum ether), **Appearance** colourless liquid. \(^\text{1H NMR}\) (500 MHz, CDCl₃): δ 5.77 (m, 2H), 5.64 (m, 1H), 5.11-5.07 (m, 1H), 5.05-5.02 (m, 1H), 4.51 (d, J = 6.20 Hz, 2H), 2.55 (m, 6H), 2.49 (m, 4H), 2.35 (d, J = 17.28 Hz, 2H), 2.04 (s, 3H), 1.83 (d, J = 10.52 Hz, 1H), 1.48 (d, J = 10.52 Hz, 1H) ppm. \(^\text{13C NMR}\) (125 MHz, CDCl₃): δ 170.8, 134.4, 131.8, 126.4, 117.1, 95.3, 95.0, 64.9, 58.6, 47.8, 47.8, 44.5, 44.5, 43.4, 41.8, 37.5, 35.9, 21.0 ppm. HRMS (ESI, Q-ToF) m/z: [M+Na]^+ calcd for C₂₀H₂₃NaO₃: 335.1618; found: 335.1618. IR (neat): ν max 3532, 2960, 2252, 1739, 1366, 1231, 1025, 606 cm⁻¹.

**Compound 32: Yield** 47.9 mg (30%), \( R_f = 0.3 \) (25% EtOAc-petroleum ether), **Appearance** colourless liquid. \(^\text{1H NMR}\) (500 MHz, CDCl₃): δ 5.78-5.72 (m, 2H), 5.68-5.62 (m, 2H), 4.52 (d, J = 6.68 Hz, 4H), 2.55 (d, J = 7.92 Hz, 4H), 2.49 (t, J = 2.63 Hz, 2H), 2.47 (s, 2H), 2.34 (s, 2H), 2.05 (s, 6H), 1.84 (d, J = 11.37 Hz, 1H), 1.48 (d, J = 9.63 Hz, 1H) ppm. \(^\text{13C NMR}\) (125 MHz, CDCl₃): δ 170.8, 131.7, 126.5, 95.1, 64.9, 58.5, 47.8, 44.5, 43.4, 41.7, 35.8, 21.0 ppm. HRMS (ESI, Q-ToF) m/z: [M+Na]^+ calcd for C₂₂H₂₆NaO₅: 407.1825; found: 407.1829. IR (neat): ν max 3851, 3023, 2968, 1735, 1365, 1234, 973, 757, 66 cm⁻¹.

**Compound 34: Yield** 56 mg (55%), \( R_f = 0.5 \) (15 % EtOAc-petroleum ether), **Appearance** colourless liquid. \(^\text{1H NMR}\) (500 MHz, CDCl₃): δ 7.10 (d, J = 16.27 Hz, 1H), 6.25-6.18 (m, 2H), 5.27 (dd, J₁ = 16.19 Hz, J₂ = 1.34 Hz, 1H), 5.18 (dd, J₁ = 9.70 Hz, J₂ = 1.10 Hz, 1H), 2.74 (d, J = 12.14 Hz, 6H), 2.51 (d, J = 18.61 Hz, 2H), 2.26 (s, 3H), 1.96 (d, J = 10.40 Hz, 1H), 1.59 (d, J = 10.14 Hz, 1H) ppm. \(^\text{13C NMR}\) (125 MHz, CDCl₃): δ 198.4, 144.3, 135.7, 128.6, 115.1, 96.5, 95.1, 60.0, 59.1, 50.4, 49.5, 44.8, 44.3, 43.6, 42.0, 41.8, 27.2 ppm. HRMS (ESI, Q-ToF) m/z: [M+H]^+ calcd for C₁₃H₁₄O₂: 255.1369; found: 255.1368. IR (neat): ν max 3850, 2970, 1677, 1258, 982 cm⁻¹.
Compound 35: Yield 51 mg (45%), Rf = 0.5 (10 % EtOAc-petroleum ether), Appearance colourless liquid. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 6.18 (m, 2H), 5.79 (m, 2H), 5.24 (d, \(J = 19.28\) Hz, 1H), 5.15 (d, \(J = 10.88\) Hz, 1H), 4.58 (d, \(J = 5.47\) Hz, 2H), 2.69 (d, \(J = 8.01\) Hz, 6H), 2.50 (s, 2H), 2.05 (s, 3H), 1.93 (d, \(J = 10.51\) Hz, 1H), 1.57 (d, \(J = 8.45\) Hz, 1H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 170.7, 136.2, 132.5, 124.0, 114.7, 96.1, 95.2, 64.5, 59.2, 59.1, 49.5, 49.3, 44.5, 43.5, 41.8, 41.8, 20.9 ppm. HRMS (ESI, Q-ToF) m/z: [M+H]\(^+\) calcd for C\(_{17}\)H\(_{18}\)O\(_3\): 271.1328; found: 271.1328 [M+H]\(^+\). IR (neat): \(v_{\text{max}}\) 2970, 1737, 1217, 758 cm\(^{-1}\).
\(^{1}\text{H} \text{ and } {^{13}}\text{C} \text{NMR (500 MHz, CDCl}_3\text{) of compound 16}
$^1$H and $^{13}$CNMR (500 MHz, CDCl$_3$) of compound 17
$^1$H and $^{13}$CNMR (500 MHz, CDCl$_3$) of compound 18
$^1$H and $^{13}$CNMR (500 MHz, CDCl$_3$) of compound 19
\(^1\)H and \(^{13}\)CNMR (500 MHz, CDCl\(_3\)) of compound 20
$^1$H and $^{13}$CNMR (500 MHz, CDCl$_3$) of compound 21
\(^1\text{H}\) and \(^{13}\text{C}\)NMR \((500\text{ MHz, CDCl}_3)\) of compound 22
$^1$H and $^{13}$CNMR (500 MHz, CDCl$_3$) of compound 23
$^1$H and $^{13}$C NMR (500 MHz, CDCl$_3$) of compound 24
$^1$H and $^{13}$CNMR (500 MHz, CDCl$_3$) of compound 25
$^1$H and $^{13}$C-NMR (400 MHz, CDCl$_3$) of compound 26
$^1$H and $^{13}$CNMR (400 MHz, CDCl$_3$) of compound 27
$^1$H and $^{13}$CNMR (500 MHz, CDCl$_3$) of compound 29

![NMR spectra of compound 29]
$^1$H and $^{13}$CNMR (500 MHz, CDCl$_3$) of compound 30
$^1$H and $^{13}$CNMR (500 MHz, CDCl$_3$) of compound 32
$^1$H and $^{13}$C NMR (500 MHz, CDCl$_3$) of compound 34

[Diagram of compound 34 with NMR peaks labeled]
$^1$H and $^{13}$CNMR (500 MHz, CDCl$_3$) of compound 35
1. X-ray data and refinement parameter for compound

\((2S,3S,3aS,5R,6R,7R)-2-((E)-3-(trimethylsilyl)prop-1-en-1-yl)-7-vinyloctahydro-1H-3,5,1-(epiethane[1,1,2]triyl)cyclobuta[cd]pentalene-2,7-diol\)

**CCDC Number = 2176337**

![Chemical structure image](image.png)

**Table S1. X-ray crystallographic data and refinement parameters for 16 (CCDC NO 2176337)**

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<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<td>Temperature</td>
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<td>Space group</td>
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<td>Unit cell dimensions</td>
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<tr>
<td></td>
<td>( b = 10.7960 \text{ Å} ) ( \beta = 96.625(11) )</td>
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<tr>
<td></td>
<td>( c = 13.3158(18) \text{ Å} ) ( \gamma = 93.042(10) )</td>
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<tr>
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<td>Absorption correction</td>
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<tr>
<td>Max. and Min. transmission</td>
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</tbody>
</table>
F (000) 344.0

Crystal size 0.116 × 0.11 × 0.05 mm³

Index ranges -7 ≤ h ≤ 7, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15

Theta range for data collection 3.156 to 49.998 °

Reflections collected 31086

Diffraction radiation wavelength 0.71073

Independent reflections 3085 [Rint = 0.1056, Rσ = 0.0573]

Refinement method Full-matrix least-squares on F²

Data/restraints/parameters 3085/0/204

Goodness-of-fit on F² 1.116

Final R indices [I≥2σ (I)] R₁ = 0.0476, wR₂ = 0.1248

R indices (all data) R₁ = 0.0689, wR₂ = 0.1461

Largest diff. peak and hole 0.28/-0.33 e Å³