Supporting Information

Polycyclic High density Cage Compounds via Olefin Metathesis

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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 (^{1}H, ^{13}C, 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\ toulene was dissolved olefine (**15, 14, 28 and 33**) (1 equi.) and degassed with nitrogen. Then Grubbs-II catalyst\ *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%), $\mathbf{R}_f$ =0.4 (3% EtOAc-petroleum ether), **Appearance** White solid, **Mp** 106-108 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.89-5.83 (m, 1H), 5.57-5.50 (m, 1H), 5.33 (d, J = 15.16 Hz,1H), 5.13 (dd, J_1 = 16.53 Hz, J_2 = 0.83 Hz, 1H), 5.02 (d, J = 10.93 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 Hz, 1H), 1.44-1.42 (m, 2H), 1.05 (d, J = 10.93 Hz, 1H), -0.01 (s, 9H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 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 $C_{19}H_{28}NaO_2Si$: 339.1755; found: 339.1751 **IR** (neat): ν_{max} 3672, 2979, 1477, 1248, 1216, 815, 668 cm^{-1}.

Compound 17: Yield 28 mg (20%), $\mathbf{R}_f$ = 0.5 (3% EtOAc-petroleum ether), **Appearance** white solid, **Mp** 103-105 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.57-5.51 (m, 2H), 5.34 (d, J = 14.41 Hz, 2H), 2.7 (d, J = 4.56 Hz, 2H), 2.45 (s, 2H), 2.36 (s, 2H), 2.18 (s, 2 H), 1.56 (d, J = 10.04 Hz, 1H), 1.43 (t, J_1 = 7.04 Hz, 4H), 1.03 (d, J = 10.60 Hz, 1H), -0.009 (s, 18H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 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 $C_{23}H_{38}KO_2Si_2$: 441.2043; found: 441.2042. **IR** (neat): ν_{max} 3735, 2960, 1217, 854, 769 cm^{-1}.

Compound 18: Yield 52 mg (45%), $\mathbf{R}_f$ = 0.5 (15 % EtOAc-petroleum ether), **Appearance** colourless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.75 (d, J = 19.10 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 Hz, 1H), 2.42-2.35 (m, 3H), 2.25 (s, 3H), 1.57 (d, J = 15.4 Hz, 2H) ppm. **^{13}C NMR** (500 MHz, $CDCl_3$): δ 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): ν_{max} 3456, 2953, 2502, 2323, 1711, 1361, 1259, 977, 673 cm-^{1}.

Compound 19: Yield 40 mg (30%), R_f = 0.2 (40% EtOAc-petroleum ether), **Appearance** colourless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): 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, $CDCl_3$): 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 $C_{19}H_{22}KO_4$:353.1148; found: 353.1150. **IR** (neat): ν_{max} 3707, 2971, 2865, 1675, 977, 756, 666 cm^{-1}.

Compound 20: Yield 57 mg (45%), R_f = 0.5 (15% EtOAc-petroleum ether), **Appearance** colourless liquid. **^{1}HNMR** (500 MHz, $CDCl_3$): 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, J_1= 16.57 Hz, J_2 = 8.82 Hz, 1H), 5.05 (dd, J_1= 10 Hz, J_2 = 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, $CDCl_3$): 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 $C_{17}H_{20}ONaO_4$: 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%), R_f = 0.3 (30% EtOAc-petroleum ether), **Appearance** colourless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): 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, $CDCl_3$): 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 $C_{21}H_{26}O_6$: 397.1623; found: 397.1622. **IR** (neat): ν_{max} 3851, 2980, 1736, 1218, 768, 667 cm^{-1}.

Compound 22: Yield 41mg (40%), R_f = 0.5 (2% EtOAc-petroleum ether), **Appearance** white solid, **Mp** 104-106 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.90-5.83 (m, 1H), 5.70-5.62 (m, 1 H), 5.39 (d, J = 15. 29 Hz, 1H), 5.14 (dd, J_1 = 16.11 Hz, J_2 = 1.35 Hz, 1H), 5.03 (dd, J_1 = 9.68 Hz, J_2 = 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, $CDCl_3$): 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 $C_{25}H_4OKO_2Si$: 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%), R_f = 0.7 (2% EtOAc-petroleum ether), **Appearance** white solid, **Mp** 110-112 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): 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, 2 H), 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, $CDCl_3$): 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 $C_{21}H_{33}O_2Si$: 345.2244; found: 345.2244. **IR** (neat): ν_{max} 3672, 2979, 1477, 1248, 1216, 815, 660 cm^{-1}.

Compound 24: Yield 52 mg (45%), R_f = 0.5 (15 % EtOAc- petroleum ether), **Appearance** colourless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): 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, $CDCl_3$): δ 199.0, 145.1, 133.6, 132.7, 119.8, 77.4, 77.4, 49.8, 49.4, 44.2, 44.1, 44.0, 43.2, 42.9, 42.5, 39.9, 39.8, 33.9, 26.5 ppm. **HRMS** (ESI, Q-ToF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{24}NaO_3$: 323.1615; found: 323.1618 . **IR** (neat): ν_{max} 3744, 2974, 1667, 1363, 1216, 757, 668 cm^{-1}.

Compound 25: Yield 39 mg (30%), R_f = 0.2 (40% EtOAc-petroleum ether), **Appearance** colourless liquid.**^{1}H NMR** (500 MHz, $CDCl_3$): 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, $CDCl_3$): 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 $C_{21}H_{26}NaO_4$: 365.1723; found: 365.1723. **IR** (neat): ν_{max} 3613, 2982, 1742, 1374, 1244, 1047, 847, 608 cm^{-1}.

Compound 26: Yield 56 mg (45%), R_f = 0.5 (15% EtOAc-petroleum ether), **Appearance** colourless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.92-5.80 (m, 2 H), 5.66-5.56 (m, 1 H), 5.11-5.04 (m, 2 H), 4.58-4.47 (m, 2H), 2.52 (s, 2 H), 2.43 (s, 2 H), 2.37-2.34 (d, *J* = 13.51 Hz, 2 H), 2.18-2.13 (m,4 H), 2.10- 2.08 (m, 2 H), 2.03-2.02 (d, *J* = 4.92 Hz, 3H), 1.52-1.50 (d, *J* = 11.35 Hz, 1 H), 1.09-1.07 (d, *J* = 10.69 Hz,1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): 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 $C_{20}H_{26}NaO_4$: 353.1727; found: 353.1723. **IR** (neat): ν_{max} 3748, 2973, 1738, 1239, 1155, 758 cm^{-1}.

Compound 27: Yield 38 mg (25%), R_f = 0.4 (20% EtOAc- petroleum ether), **Appearance** colourless liquid .**^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.88-5.78 (m, 2 H), 5.61-5.56 (m, 2 H), 4.57-4.49 (m, 4H), 2.52 (s, 2 H), 2.42 (s, 2 H), 2.36 (s, 2 H), 2.24(s, 2H), 2.05 (s, 6H), 1.52 (d, *J* = 10.98 Hz, 1 H), 1.08 (d, *J* = 10.20 Hz, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): 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 $C_{23}H_{30}KO_6$: 441.1676; found: 441.1674 . **IR** (neat): ν_{max} 3745, 2960, 1739, 1235, 1026, 755, 607 cm^{-1}.

Compound 29: Yield 34 mg (30%), R_f = 0.5 (15% EtOAc-petroleum ether), **Appearance** colourless liquid **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.81-6.74 (m, 1H), 6.13 (d, *J* = 15.47 Hz, 1H), 5.83-5.75 (m, 1H),

5.10 (dd, J_1 = 15.34 Hz, J_2 = 1.63 Hz, 1H), 5.05 (dd, J_1 = 9.37 Hz, J_2 = 0.99 Hz, 1H), 2.70 (dd, J_1 = 6.36 Hz , J_2 = 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. **^{13}C NMR** (125 MHz, $CDCl_3$): 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 $C_{19}H_{23}O_2$: 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. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.79-6.73 (m, 2H), 6.12 (d, J = 15.29 Hz, 2H), 2.70 (dd, J_1 = 6.44 Hz, J_2 = 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. **^{13}C NMR** (125 MHz, $CDCl_3$): 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 $C_{21}H_{25}O_3$: 325.1797; found: 325.1798. **IR** (neat): ν_{max} 2961, 2180, 1675, 1361, 1255, 1180, 982, 758, 537 cm^{-1}.

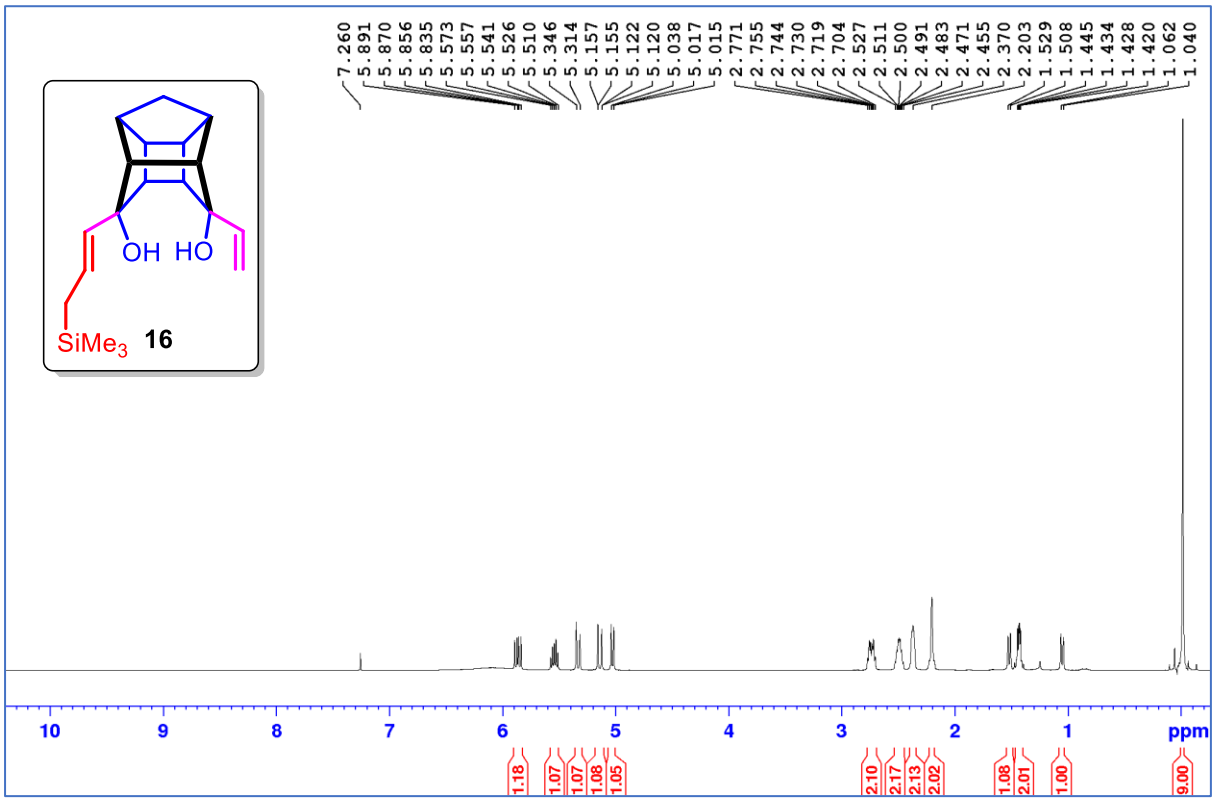
Compound 31: Yield 32.46 mg (25%), R_f = 0.5 (12 % EtOAc-petroleum ether), **Appearance** colourless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.77 (m, 2H), 5.64 (m, 1H), 5.11-5.07 (m, 1H), 5.05-5.02 (m, 1H), 4.51 (d, J = 6.20 Hz, 2H), 2.55 (m, 6H), 2.49 (m, 4H), 2.35 (d, J = 17.28 Hz, 2H), 2.04 (s, 3H), 1.83 (d, J= 10.52 Hz, 1H), 1.48 (d, J = 10.52 Hz, 1H) ppm.**^{13}C NMR** (125 MHz, $CDCl_3$): 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, 41.7, 37.5, 35.9, 21.0 ppm. **HRMS** (ESI, Q-ToF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{24}NaO_3$: 335.1618; found: 335.1618. **IR** (neat): ν_{max}3532, 2960, 2252, 1739, 1366, 1231, 1025, 606 cm-^{1}.

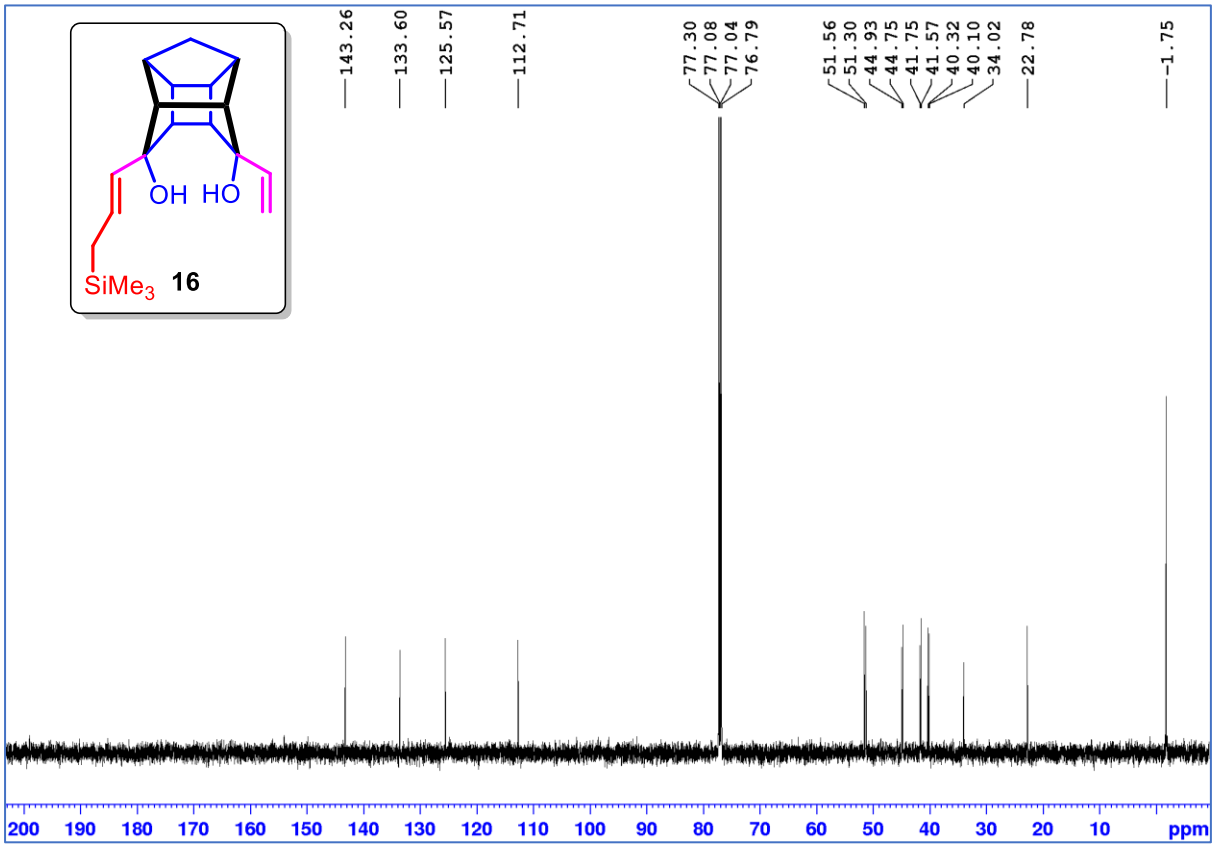
Compound 32: Yield 47.9 mg (30%), R_f = 0.3 (25% EtOAc-petroleum ether), **Appearance** colourless liquid.**^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.78-5.72 (m, 2H), 5.68-5.62 (m, 2H), 4.52 (d, J = 6.68 Hz, 4H), 2.55 (d, J = 7.92 Hz, 4H), 2.49 (t, J = 2.63 Hz, 2H), 2.47 (s, 2H), 2.34 (s, 2H), 2.05 (s, 6H), 1.84 (d, J = 11.37 Hz, 1H), 1.48 (d, J = 9.63 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): 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 $C_{23}H_{28}NaO_5$: 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. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.10 (d, J = 16.27 Hz, 1H), 6.25-6.18 (m, 2H), 5.27 (dd, J_1 = 16.19 Hz, J_2 = 1.34 Hz, 1H), 5.18 (dd, J_1 = 9.70 Hz, J_2 = 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. **^{13}C NMR** (125 MHz, $CDCl_3$): 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 $C_{17}H_{18}O_2$: 255.1369; found: 255.1368. **IR** (neat): ν_{max} 3850, 2970, 1677, 1258, 982 cm^{-1}.

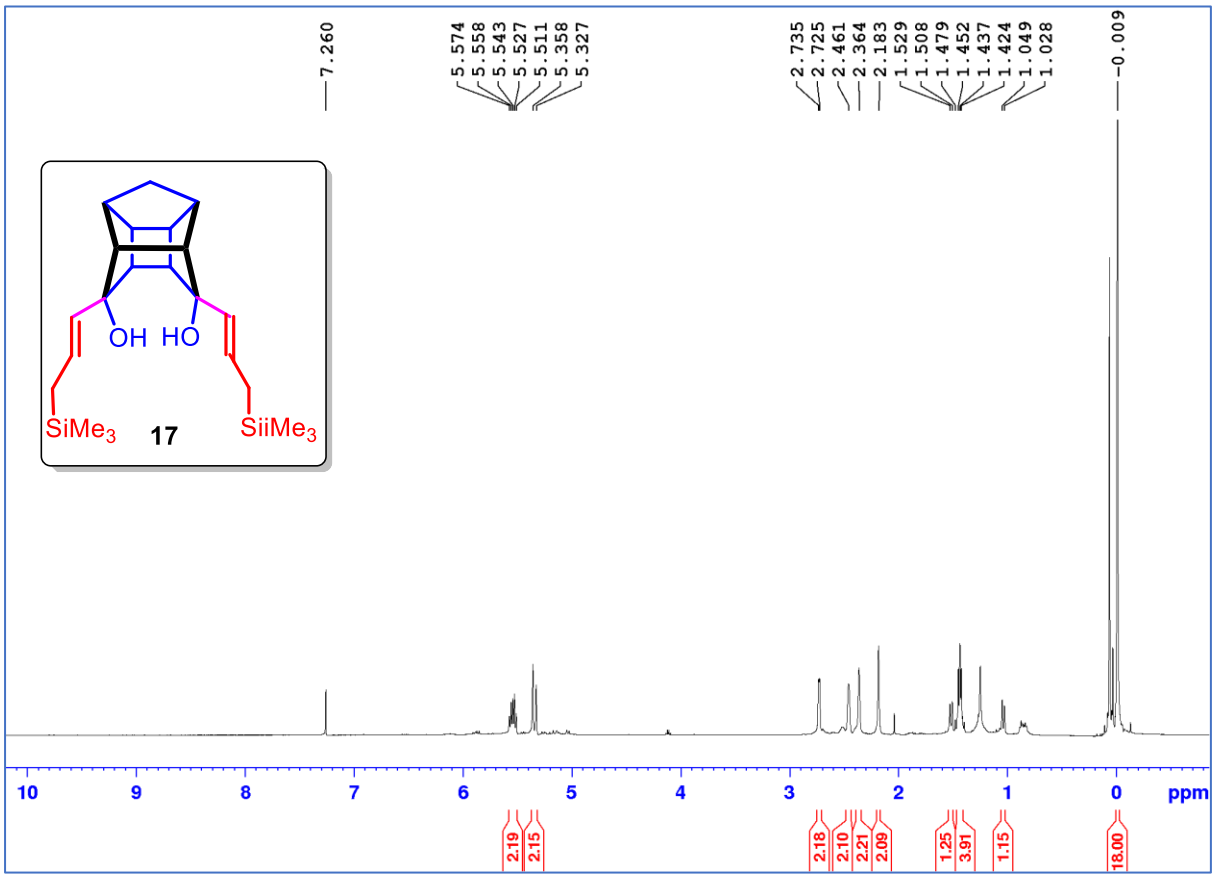
Compound 35: Yield 51 mg (45%), $\mathbf{R_f}$ = 0.5 (10 % EtOAc-petroleum ether), **Appearance** colourless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.18 (m, 2H), 5.79 (m, 2H), 5.24 (d, *J* = 19.28Hz, 1H), 5.15 (d, *J* = 10.88 Hz, 1H), 4.58 (d, *J* = 5.47 Hz, 2H), 2.69 (d, *J* = 8.01 Hz, 6H), 2.50 (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, $CDCl_3$): δ 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): ν_{max} 2970, 1737, 1217, 758 cm^{-1}.

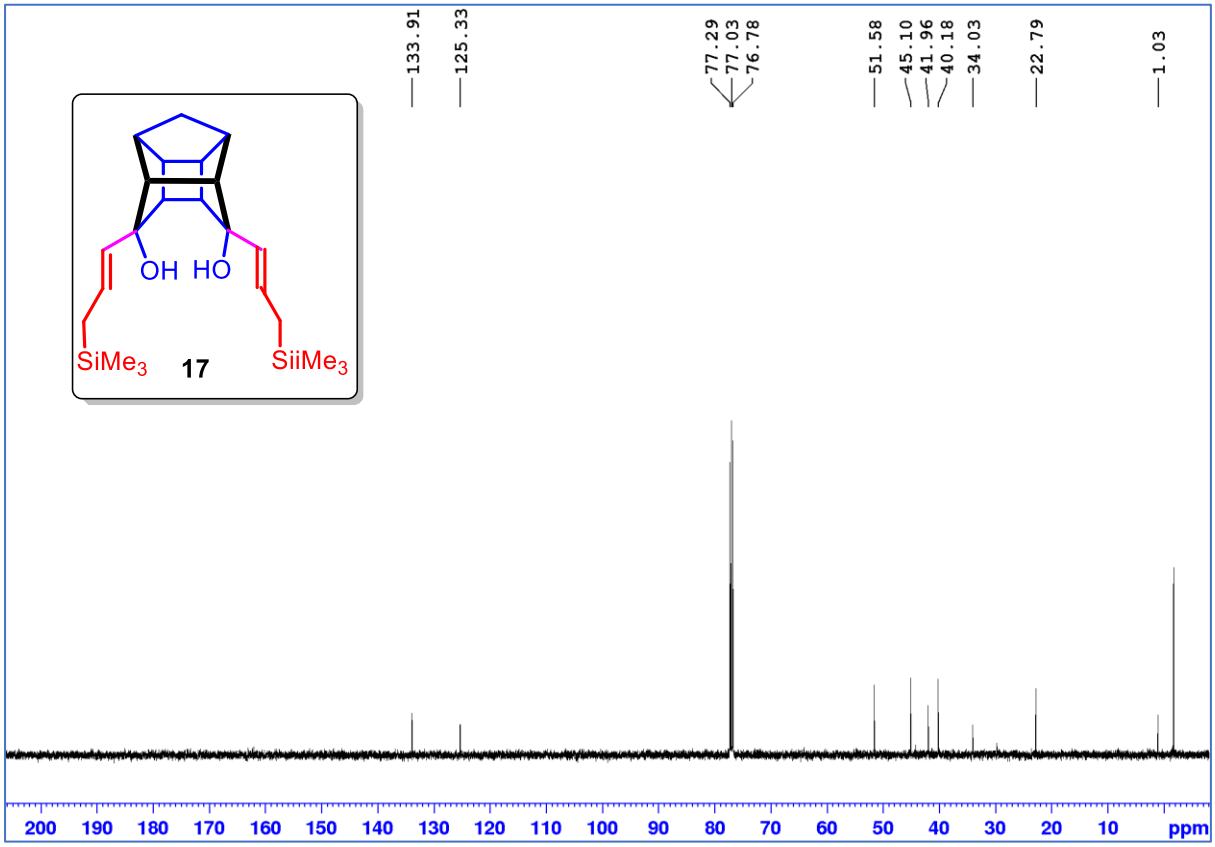
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 16



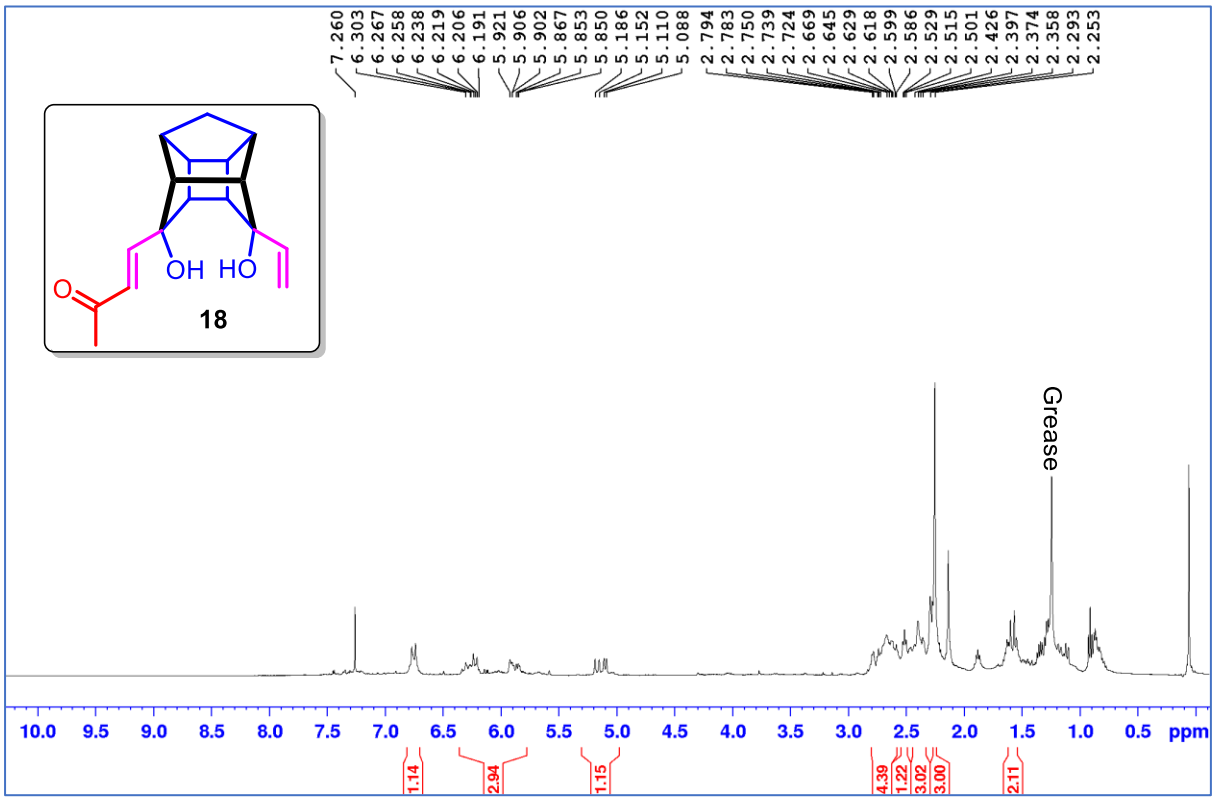


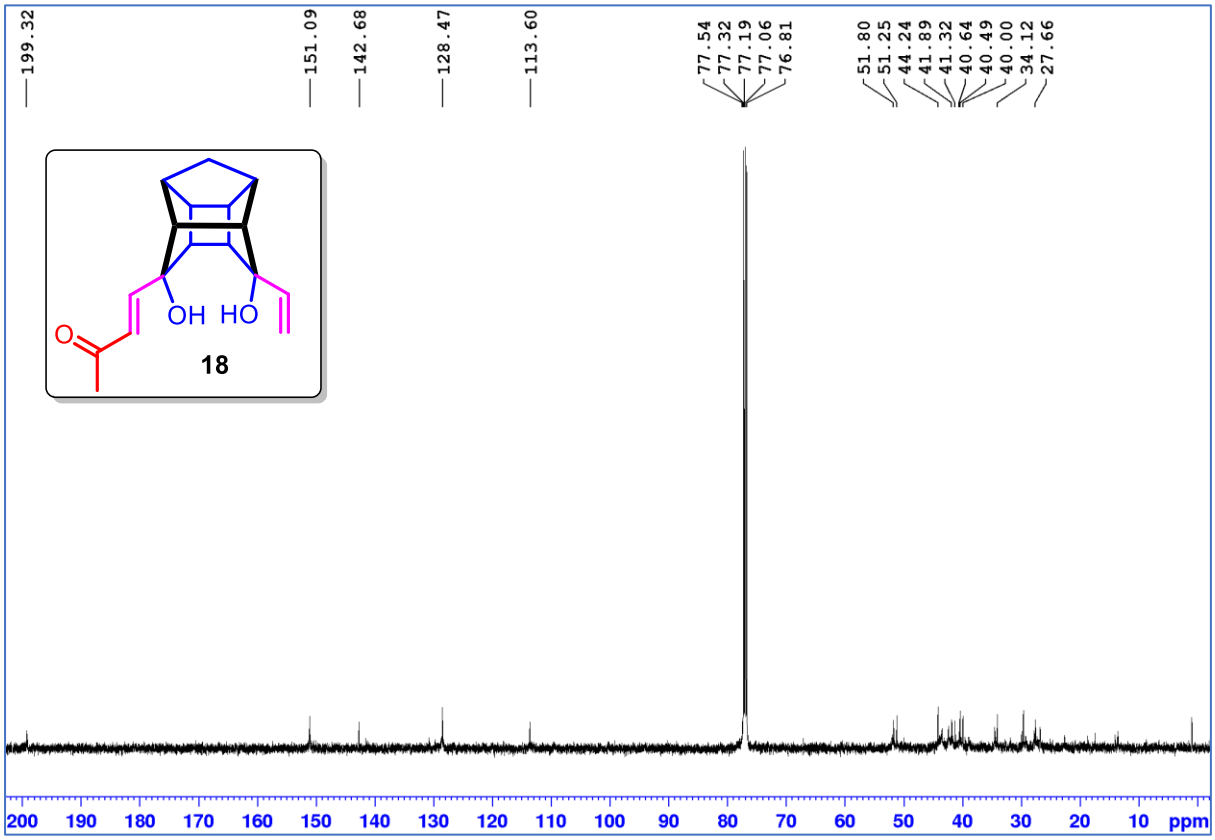
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 17



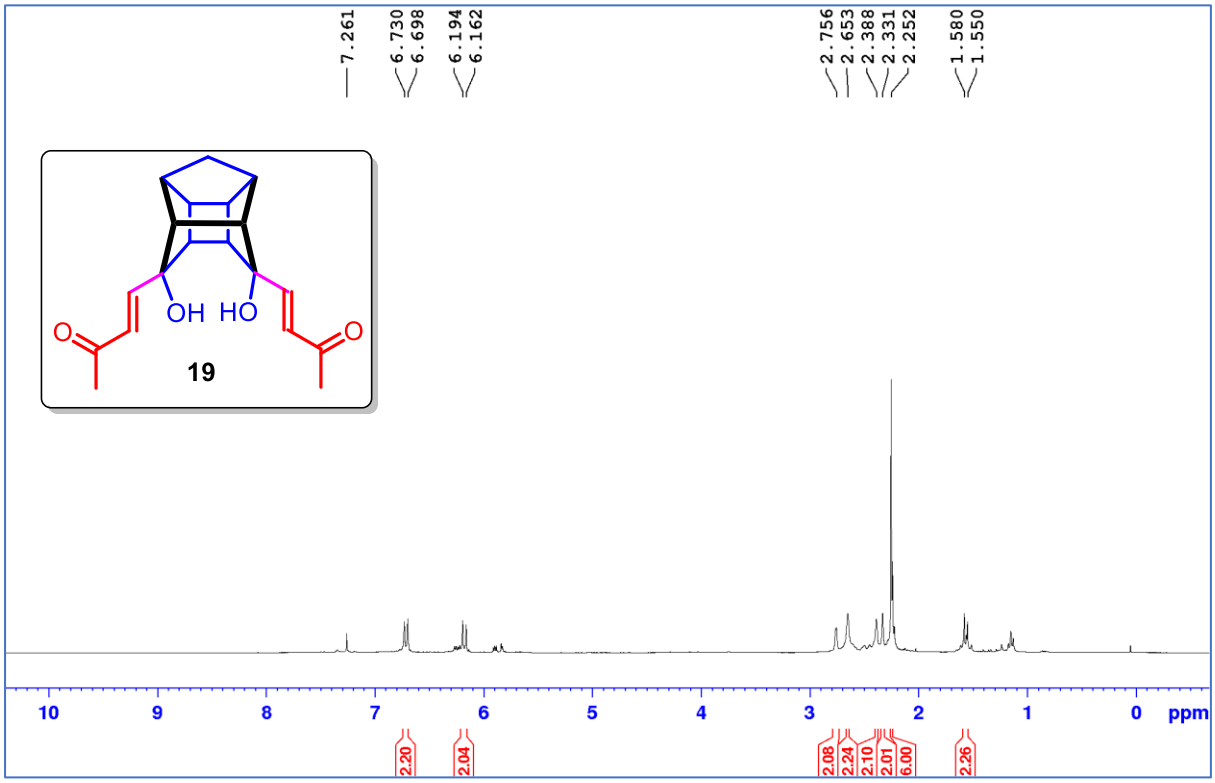


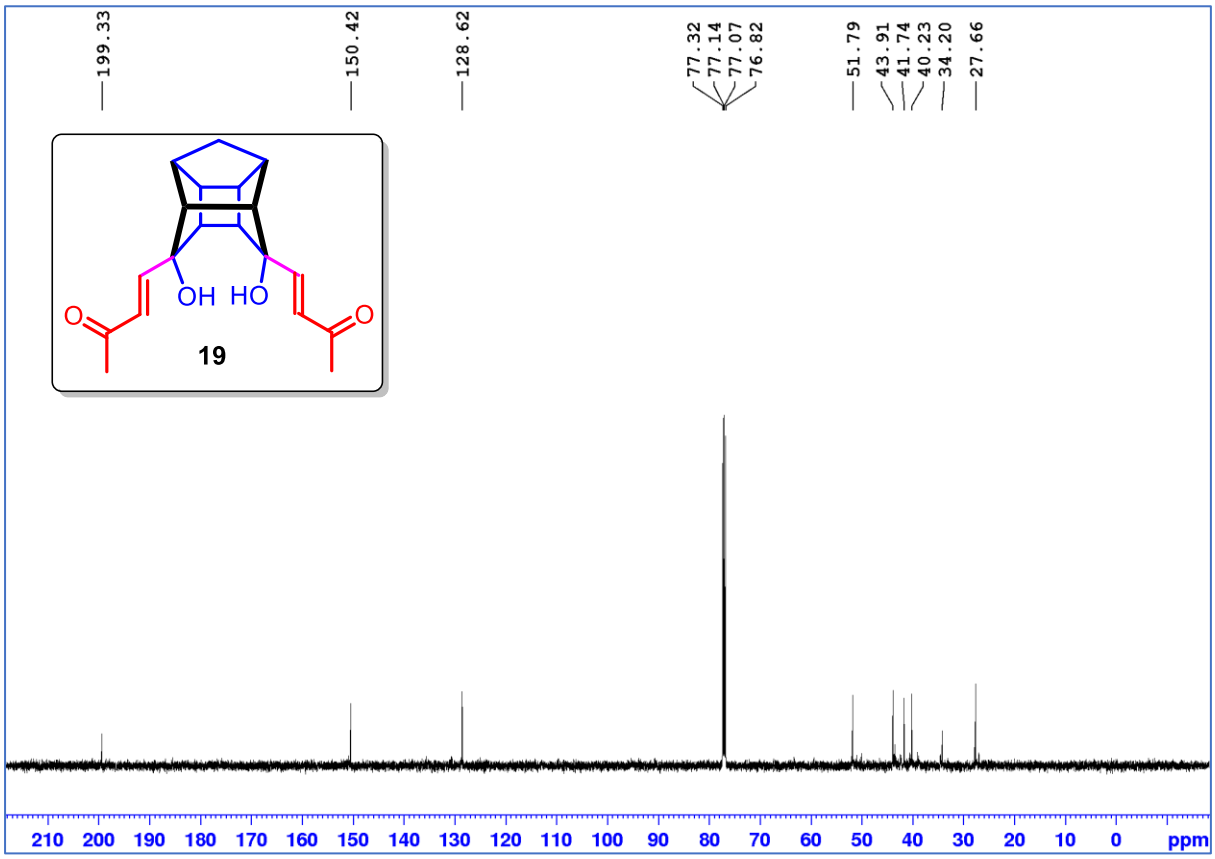
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 18



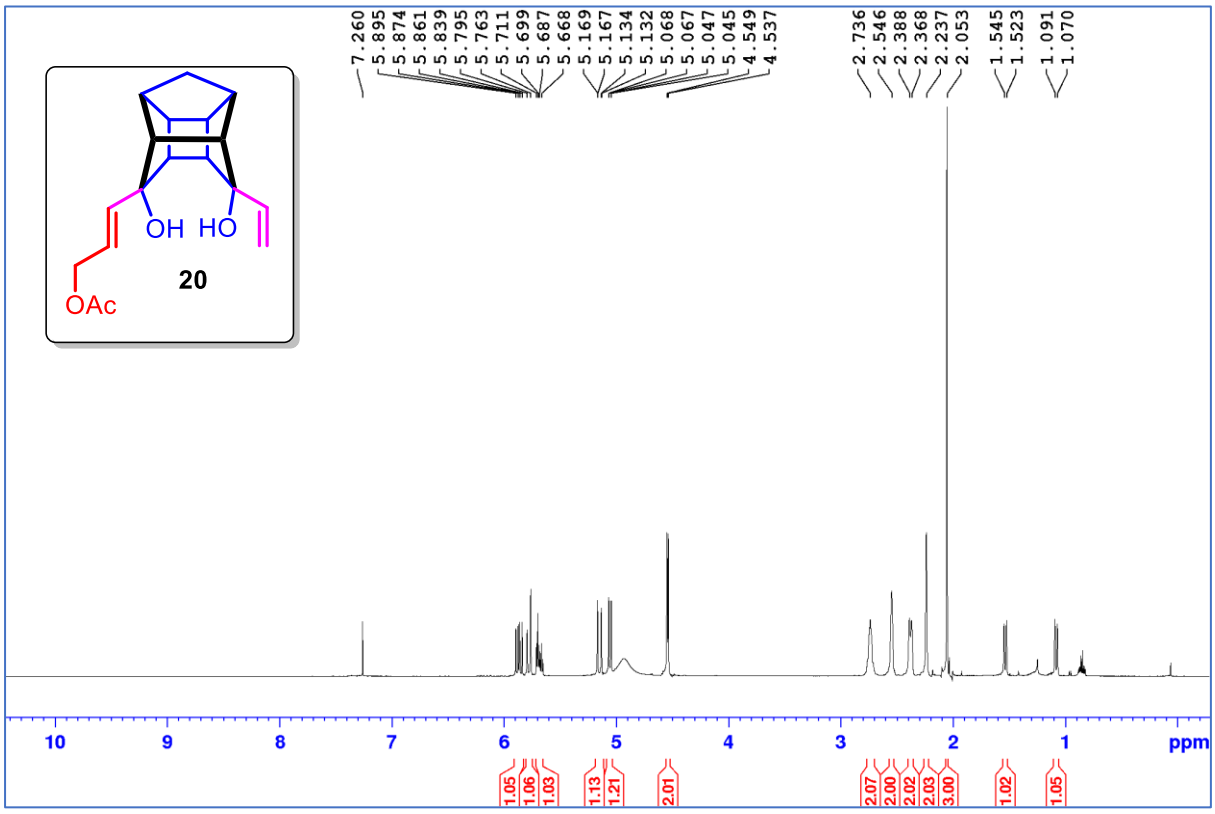


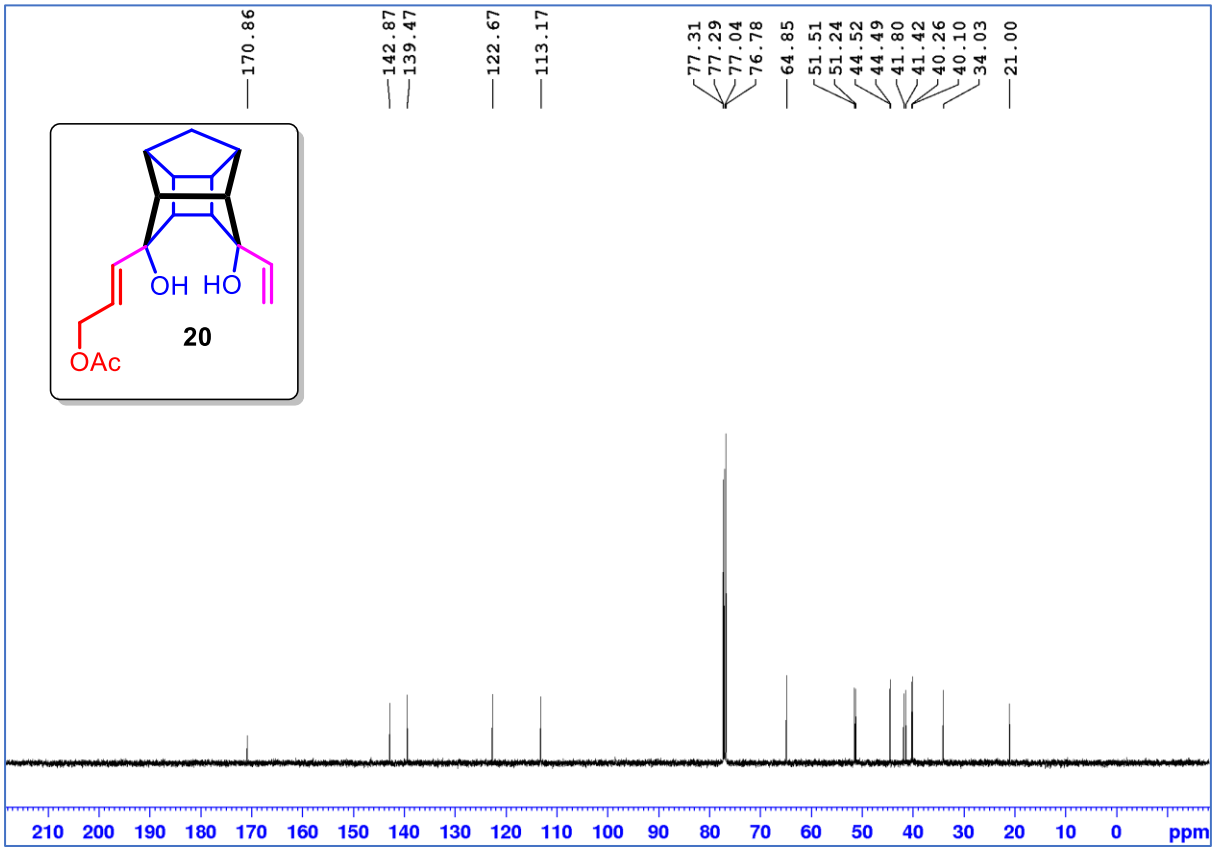
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 19



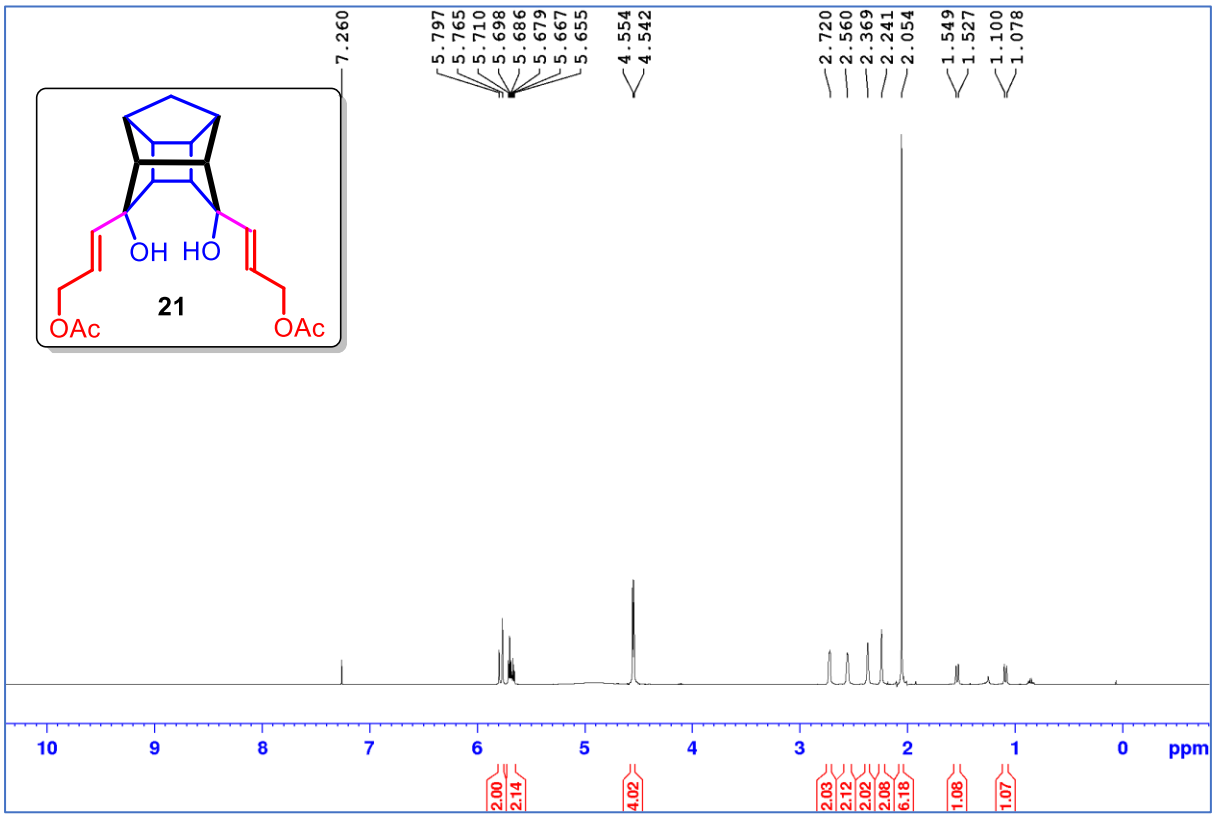


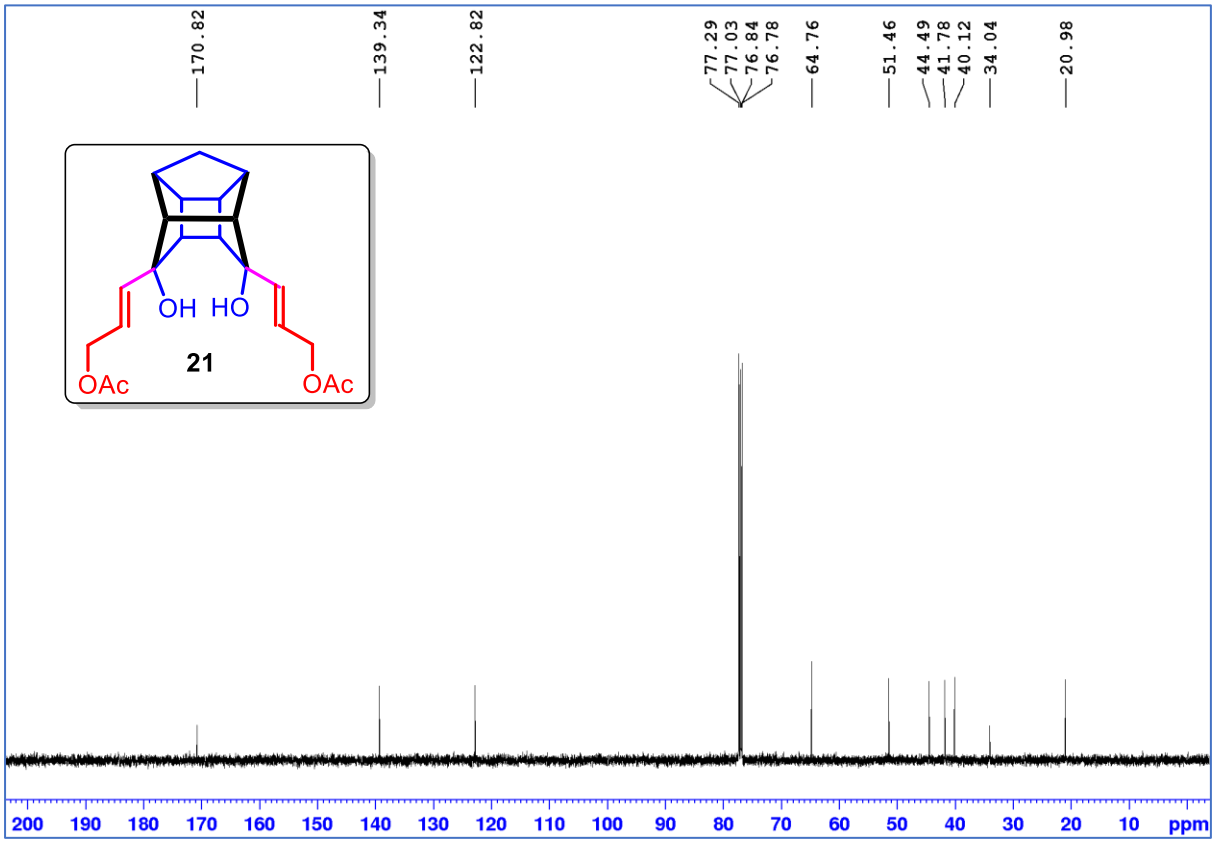
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 20



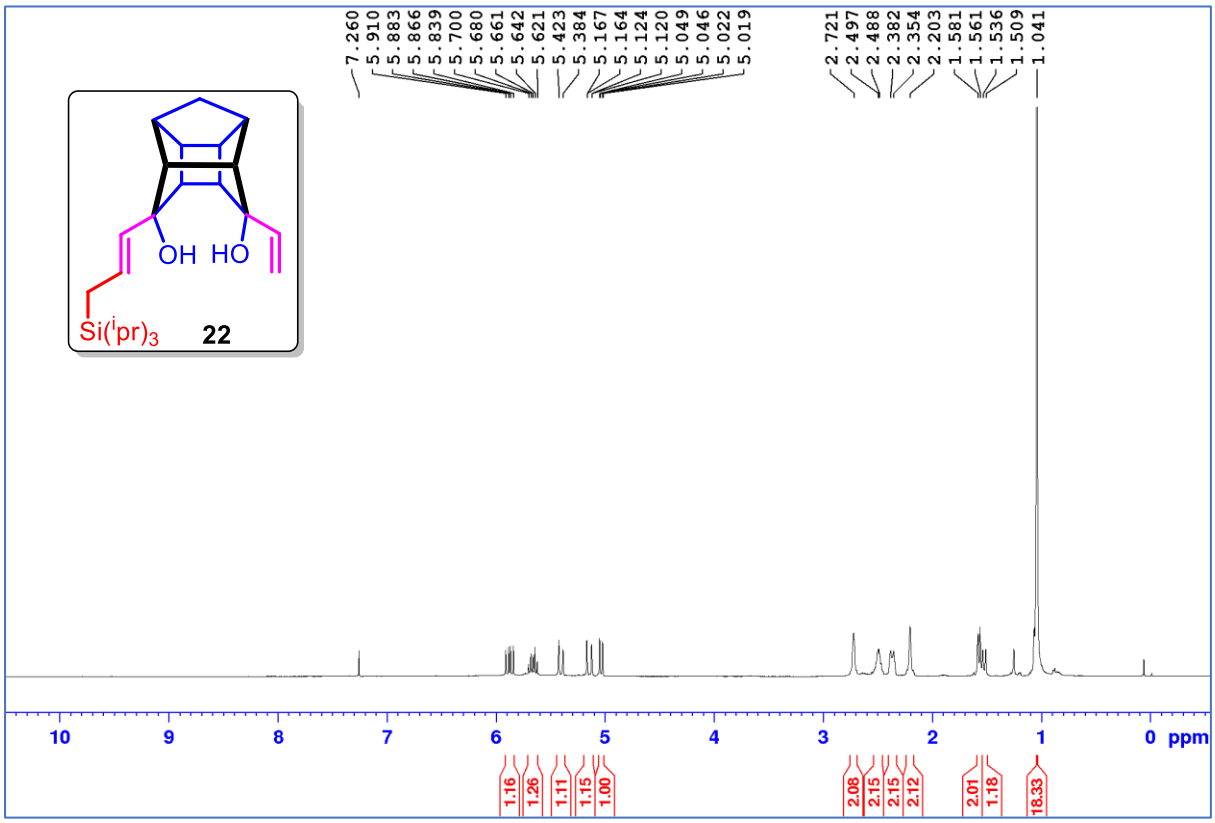


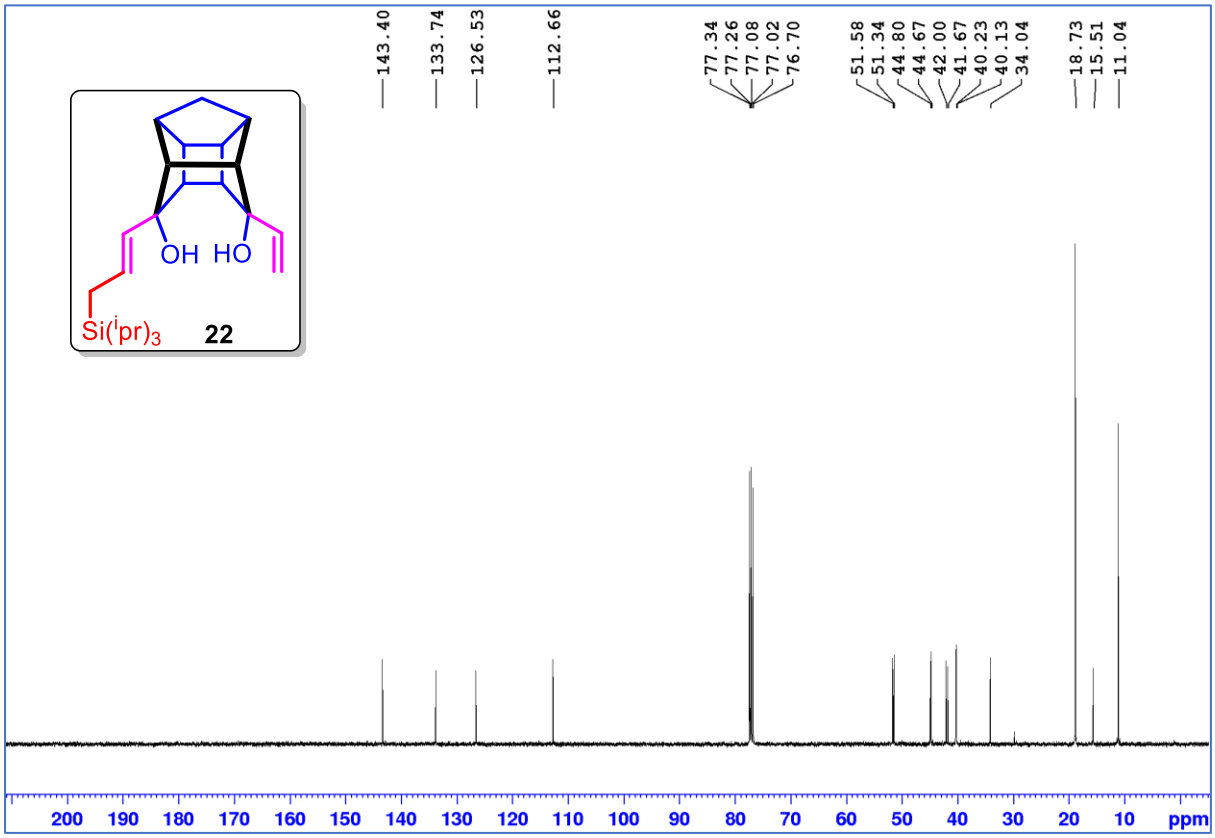
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 21



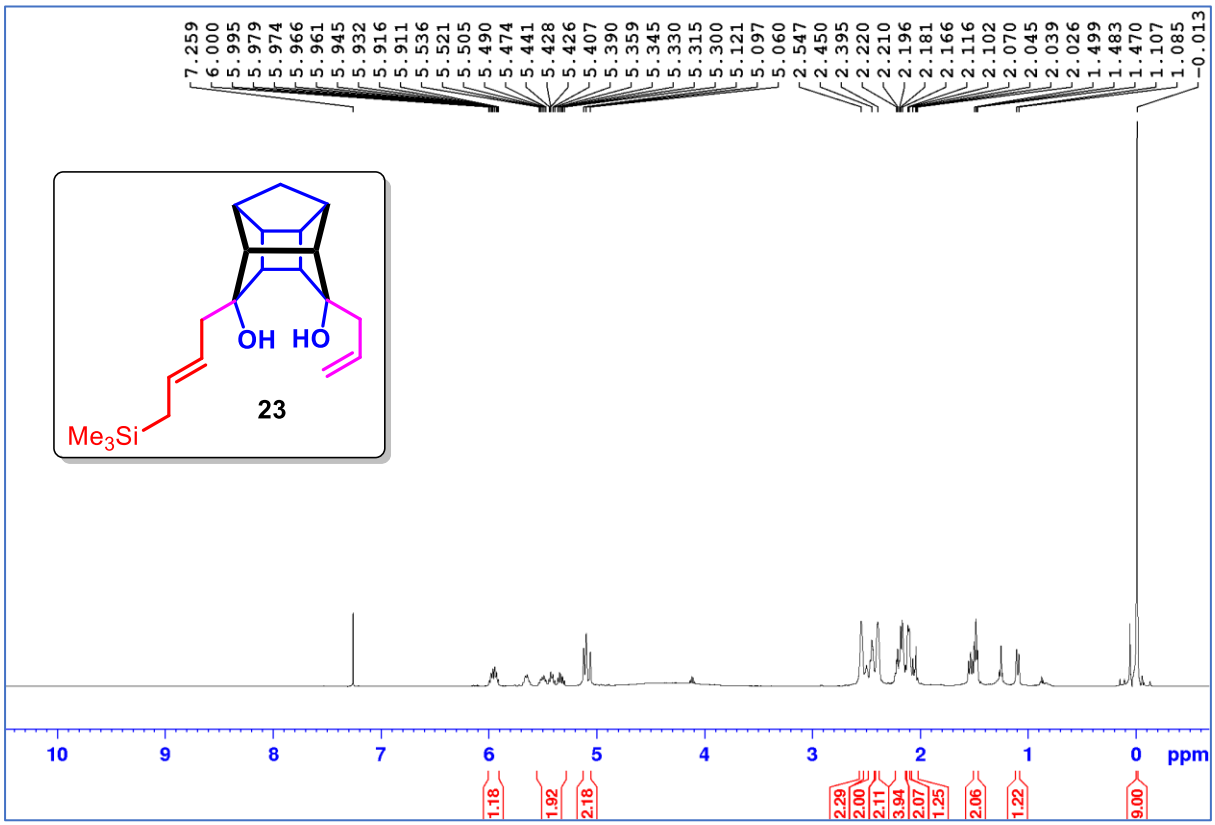


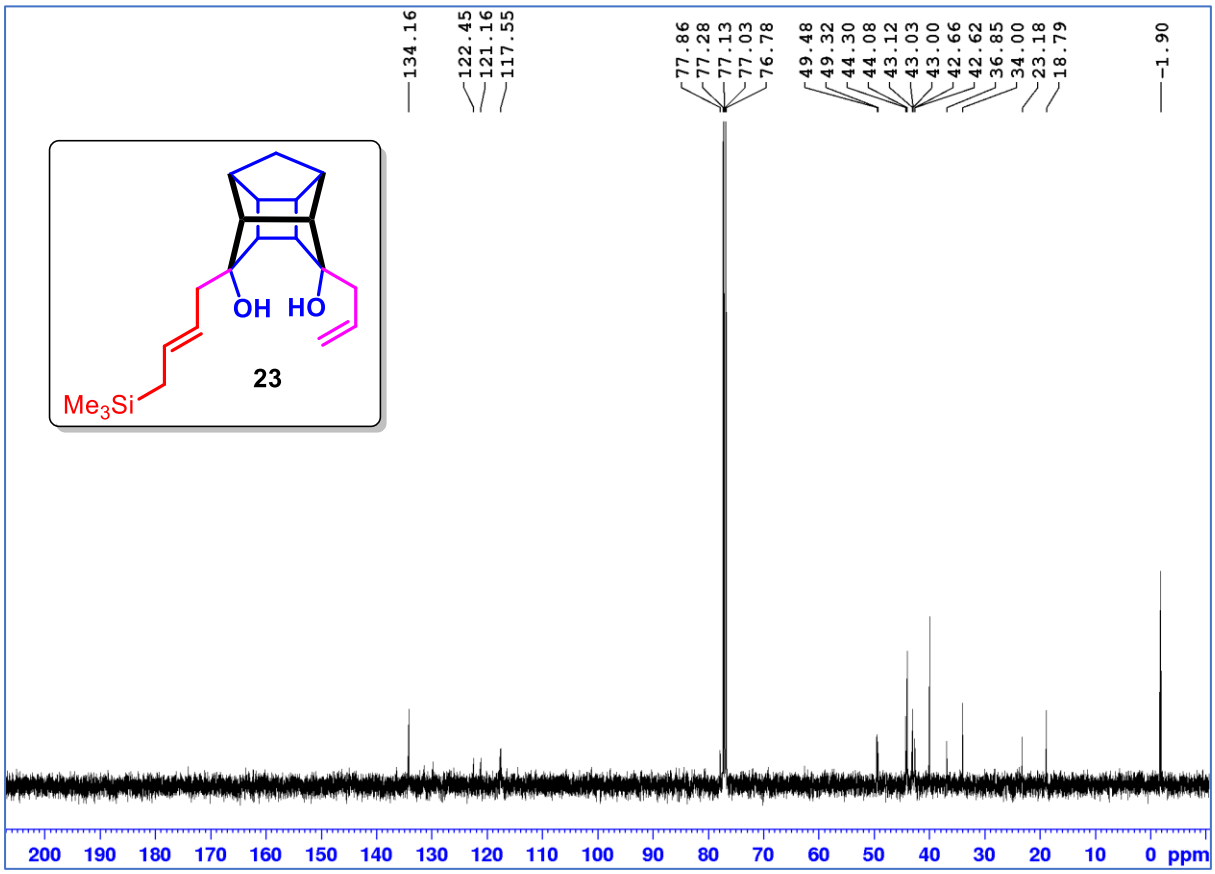
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 22



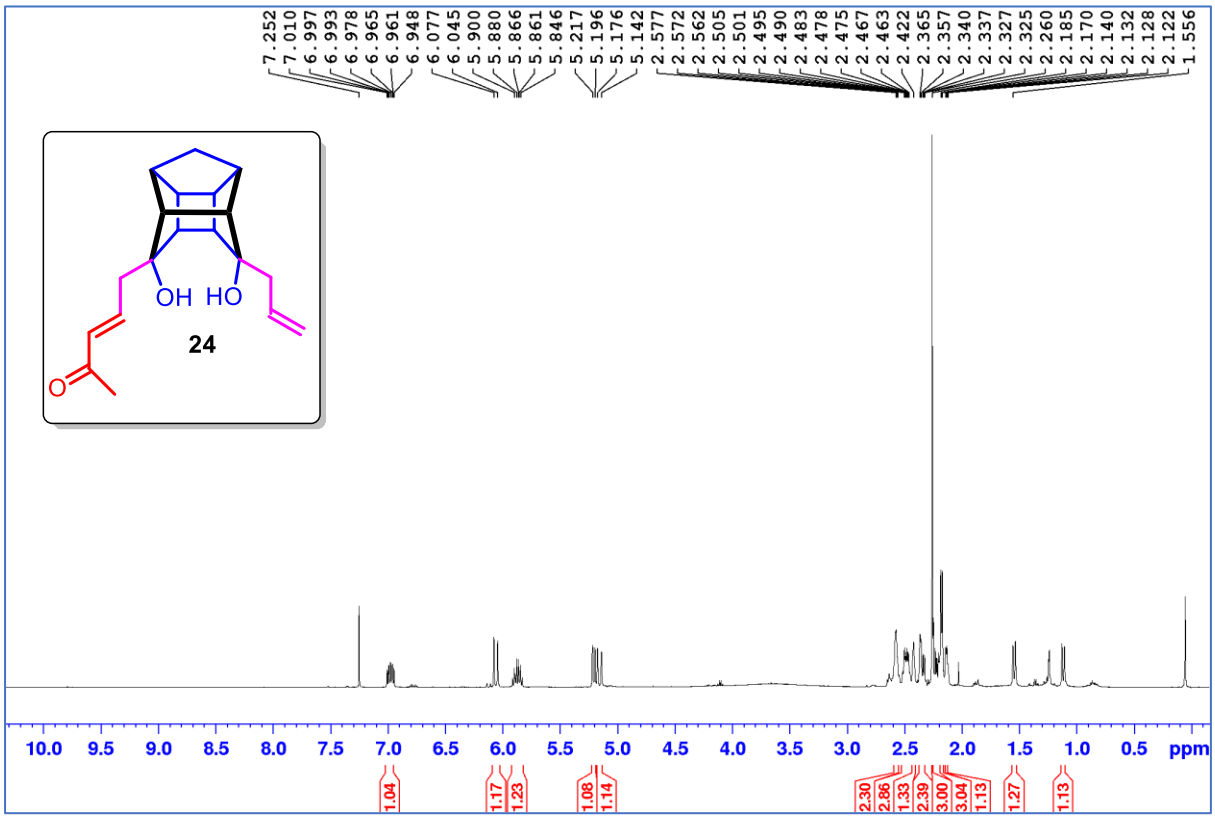


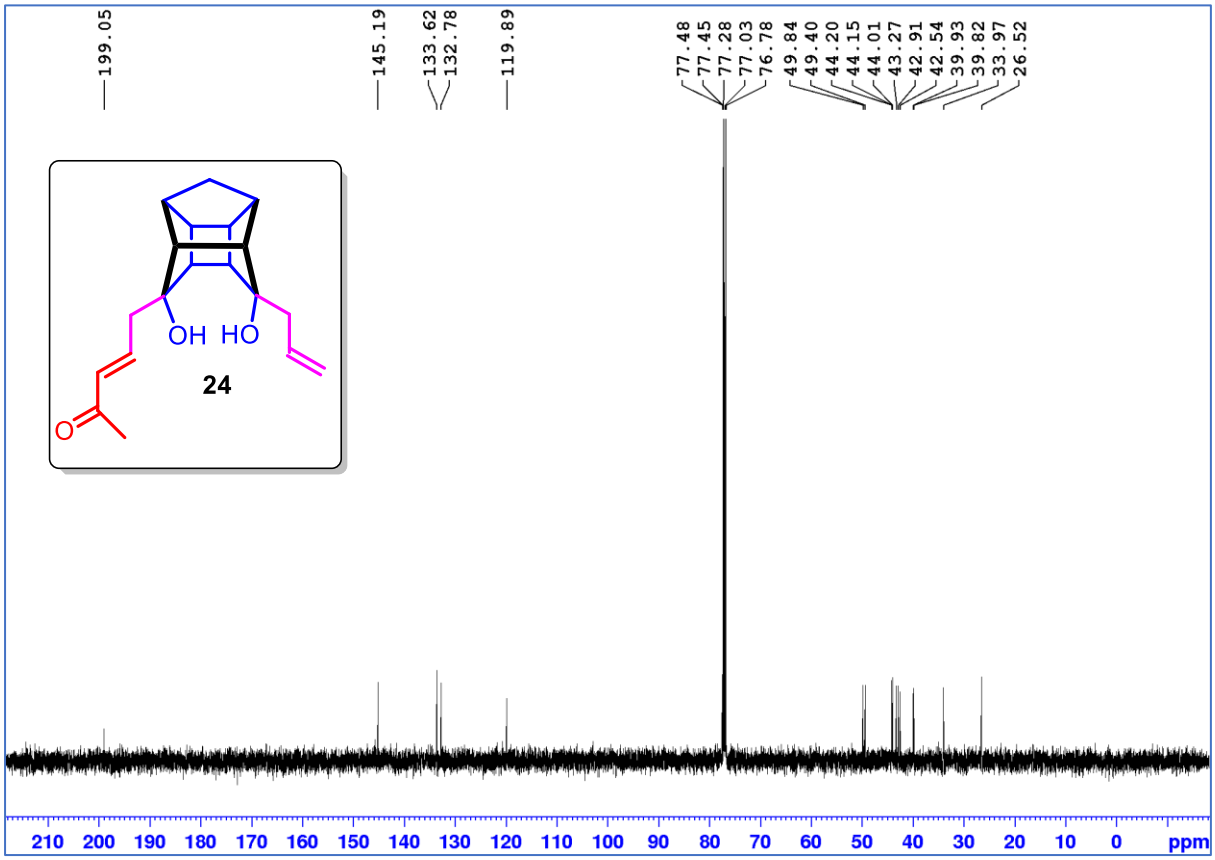
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 23



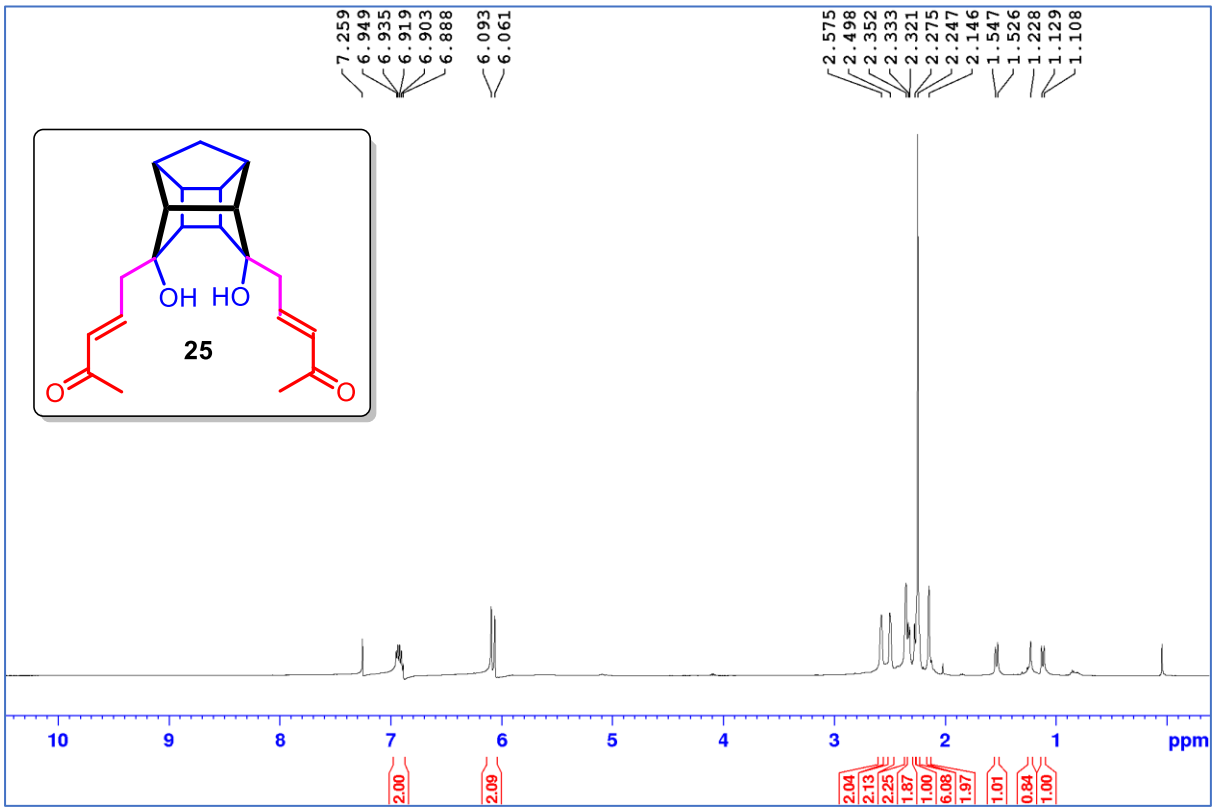


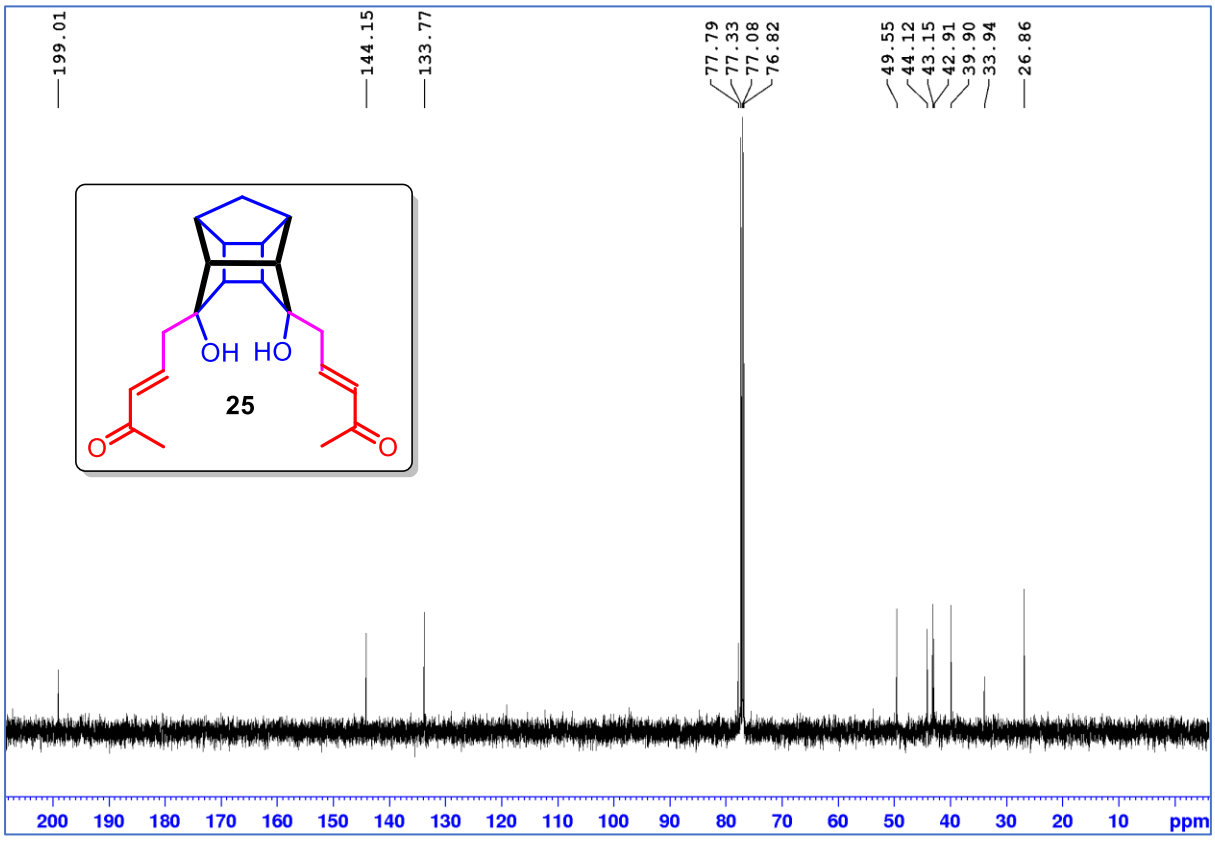
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 24



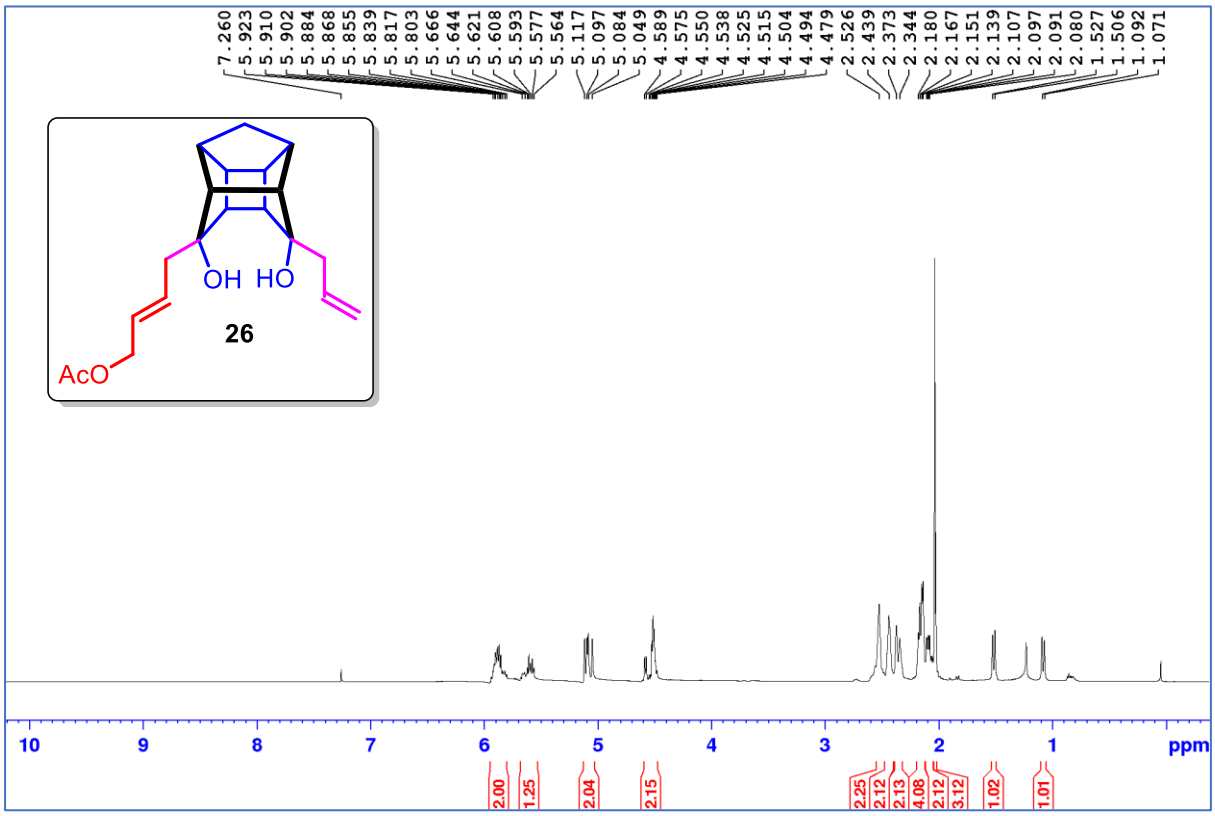


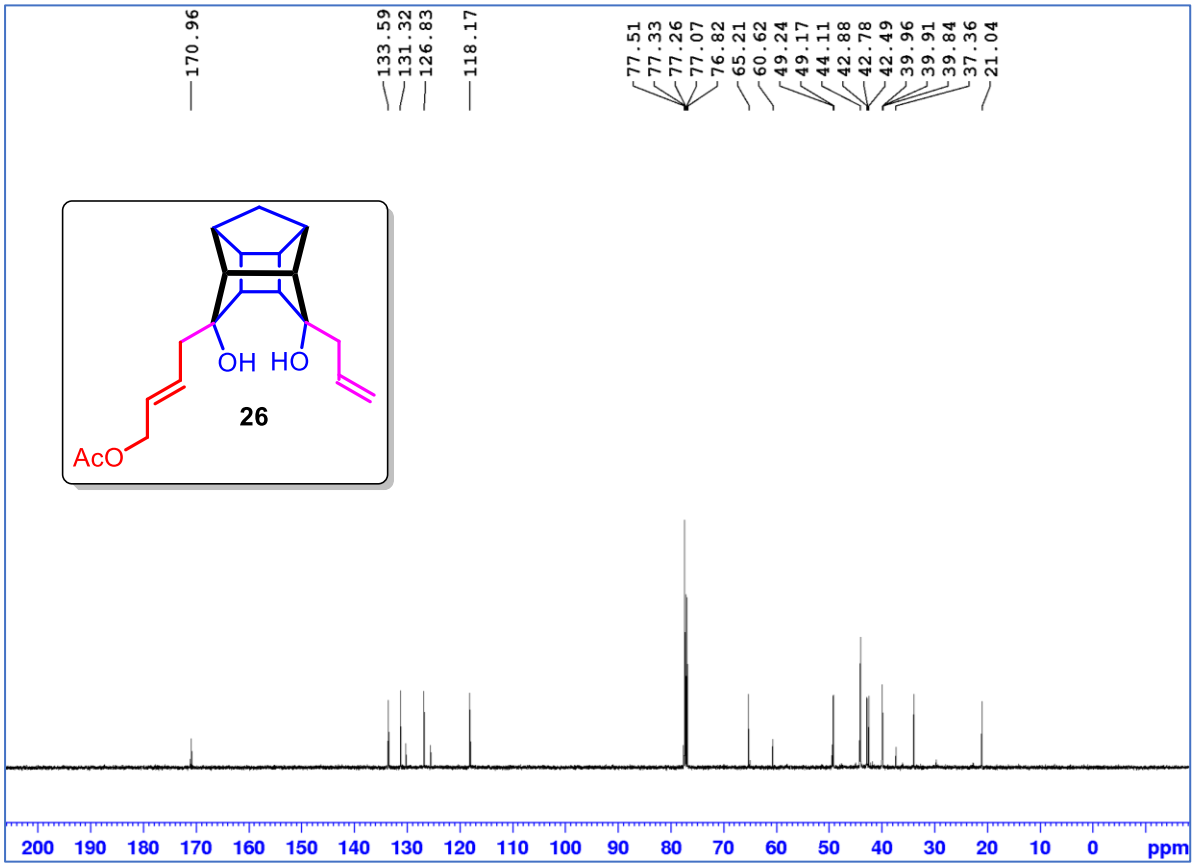
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 25



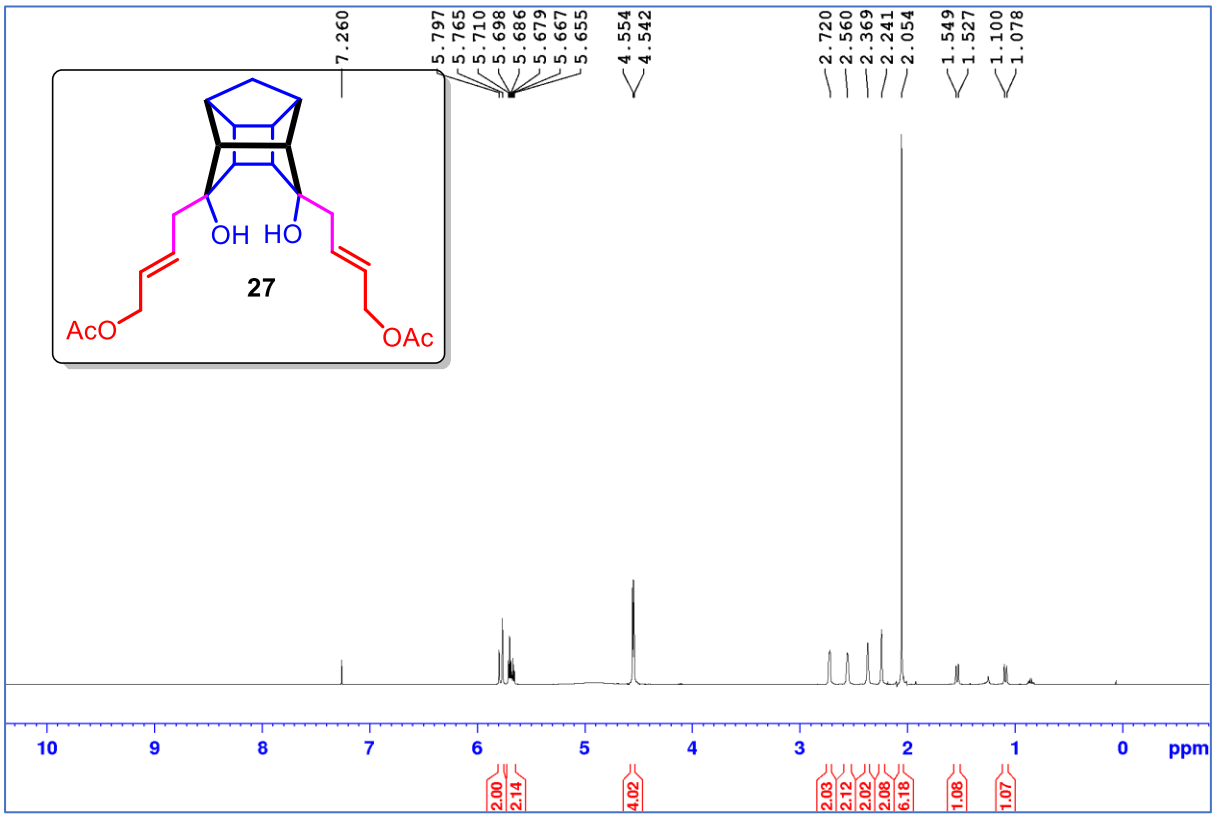


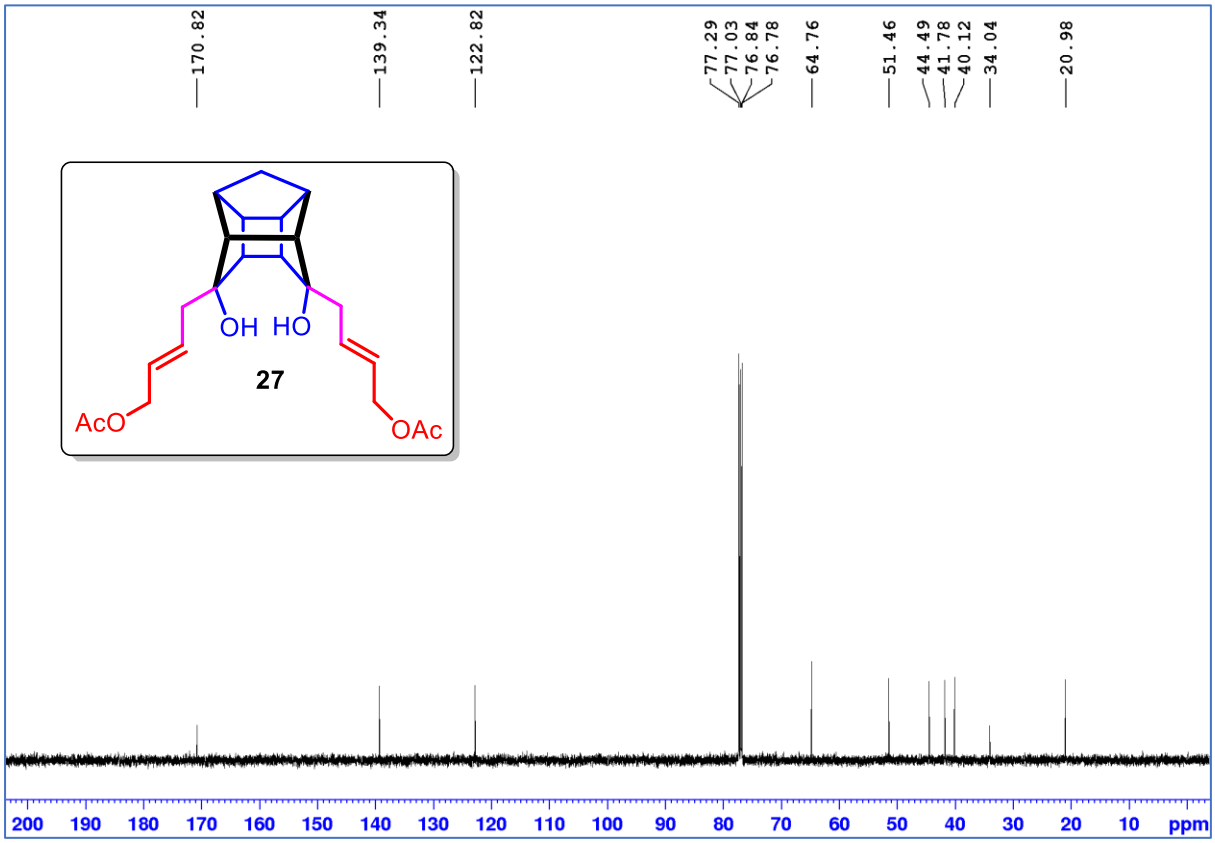
^{1}H and ^{13}CNMR (400 MHz, $CDCl_3$) of compound 26



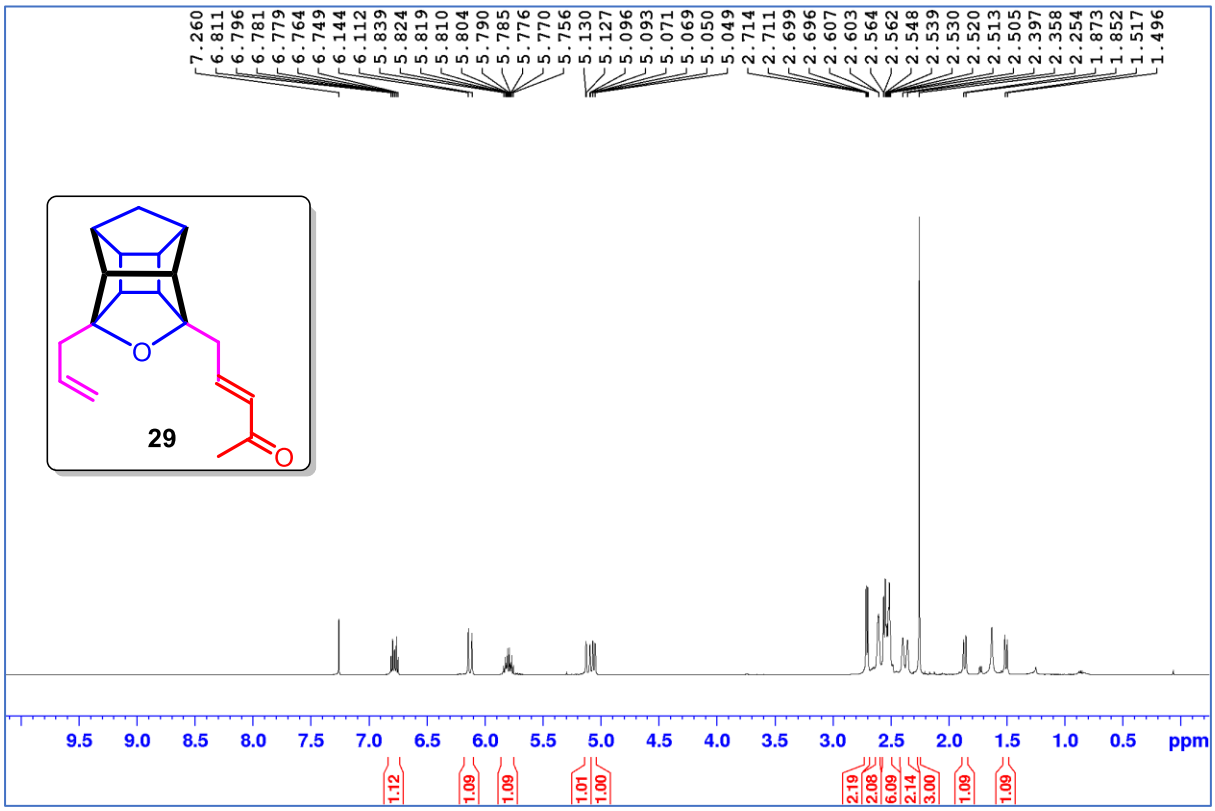


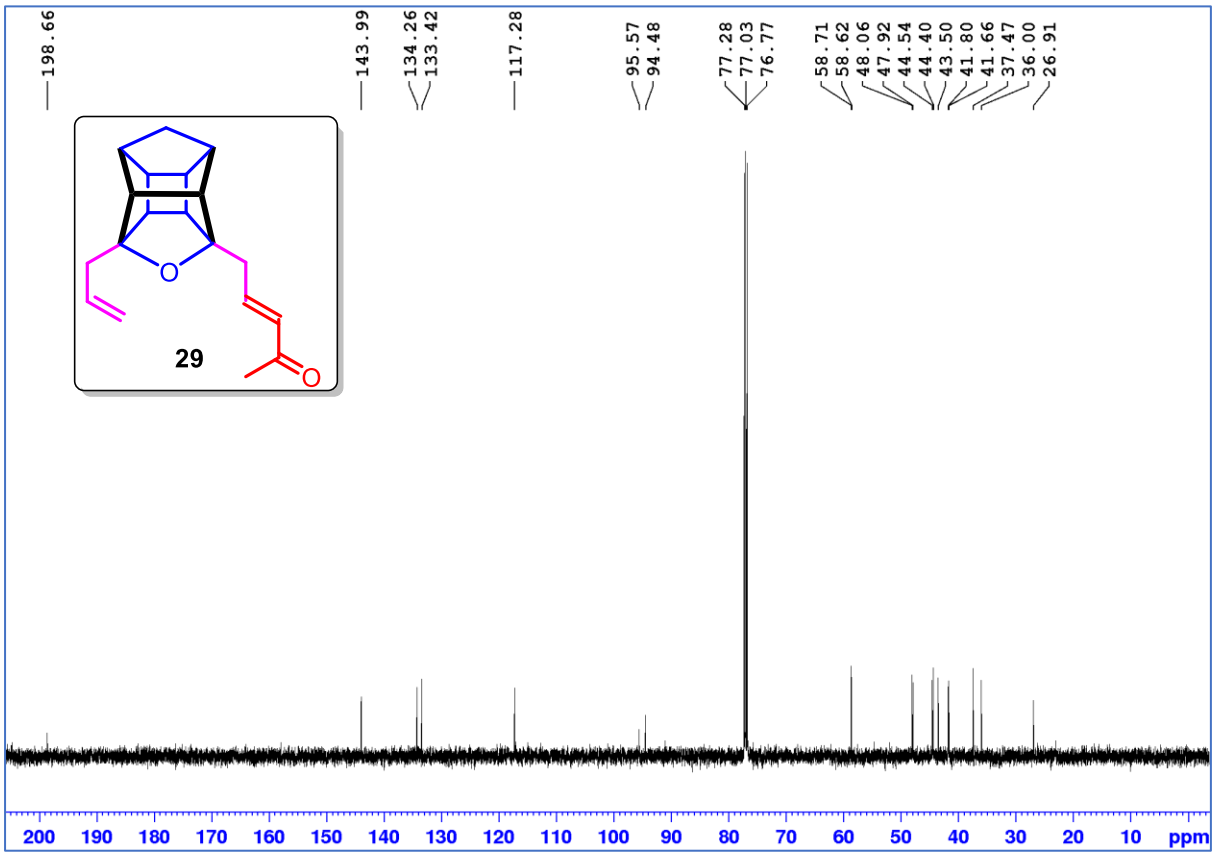
^{1}H and ^{13}CNMR (400 MHz, $CDCl_3$) of compound 27



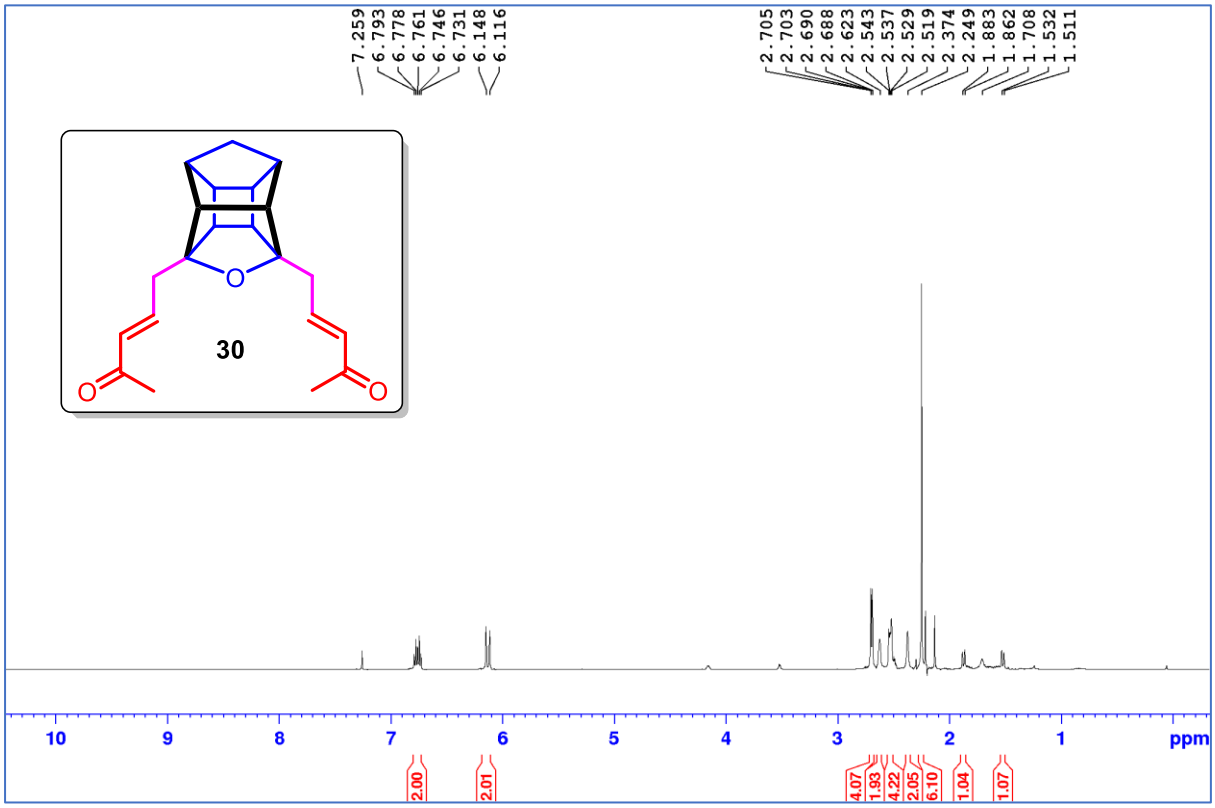


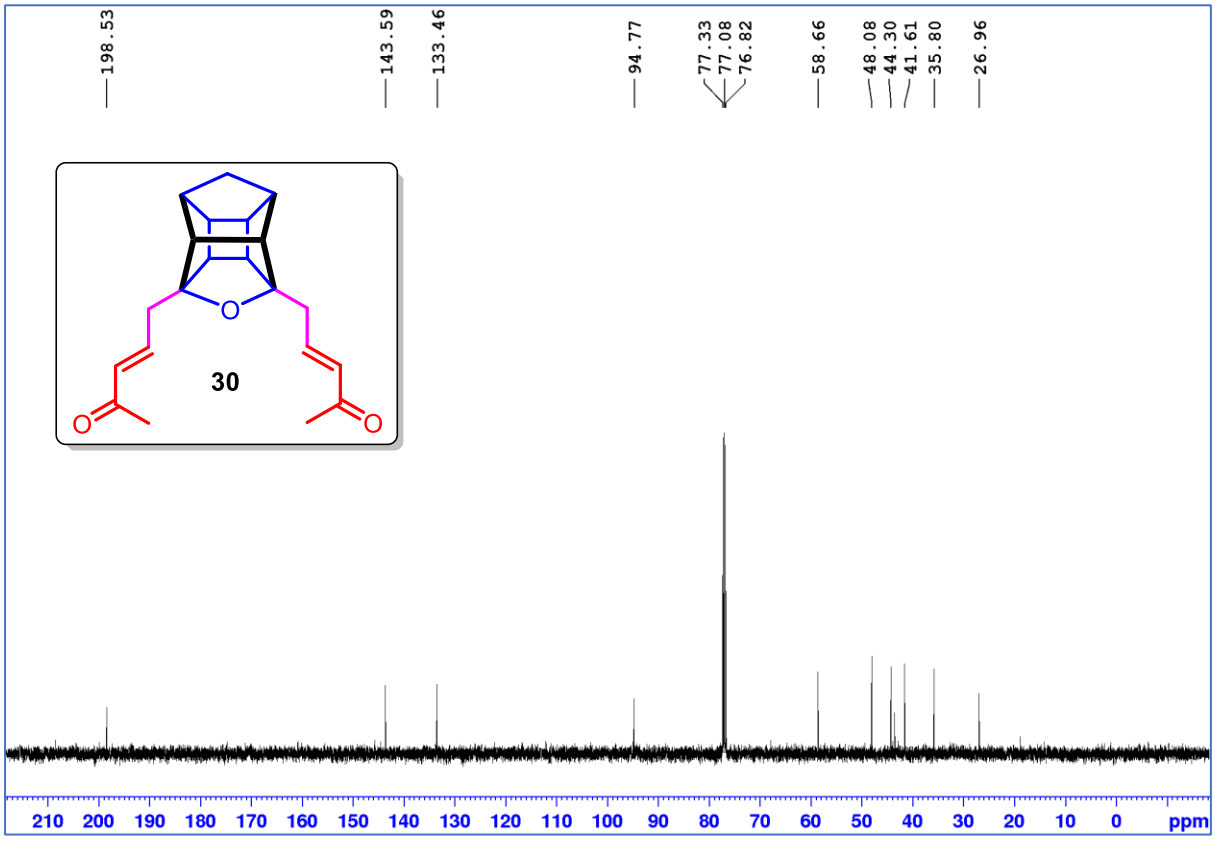
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 29



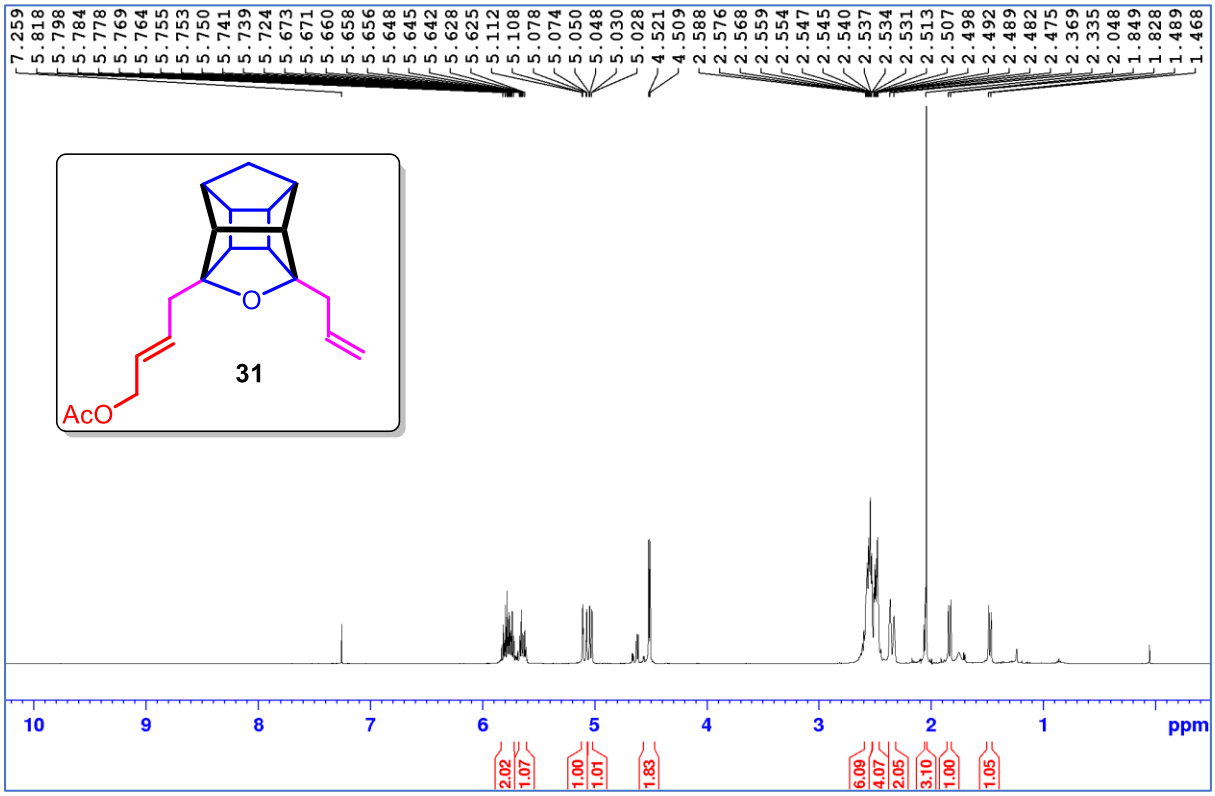


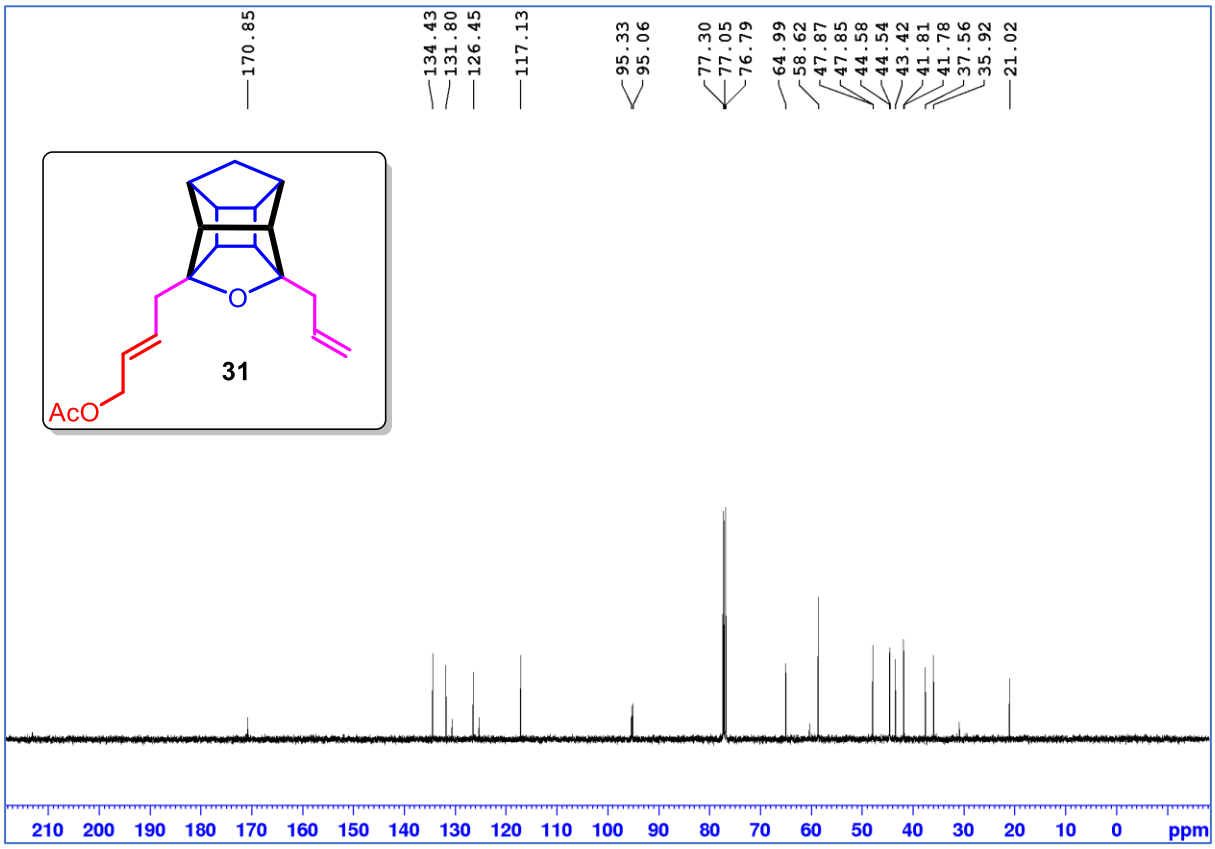
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 30



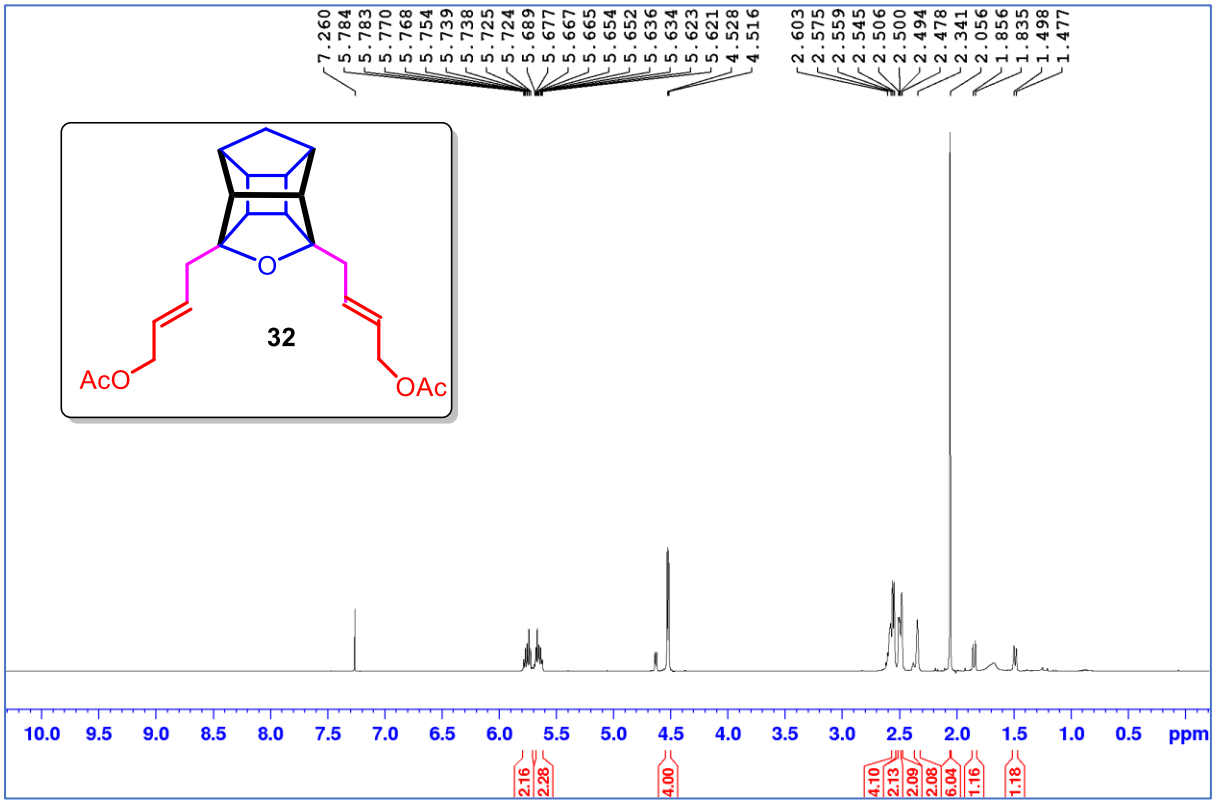


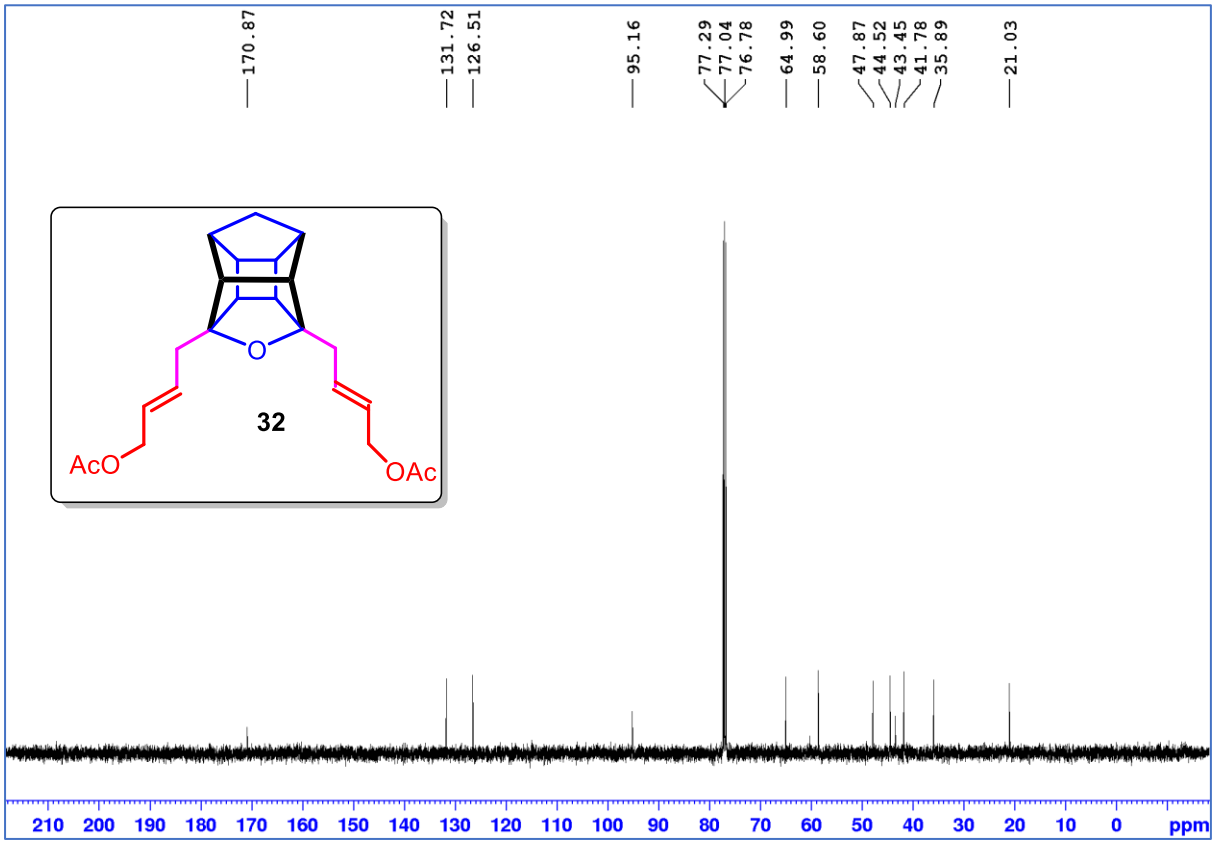
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 31



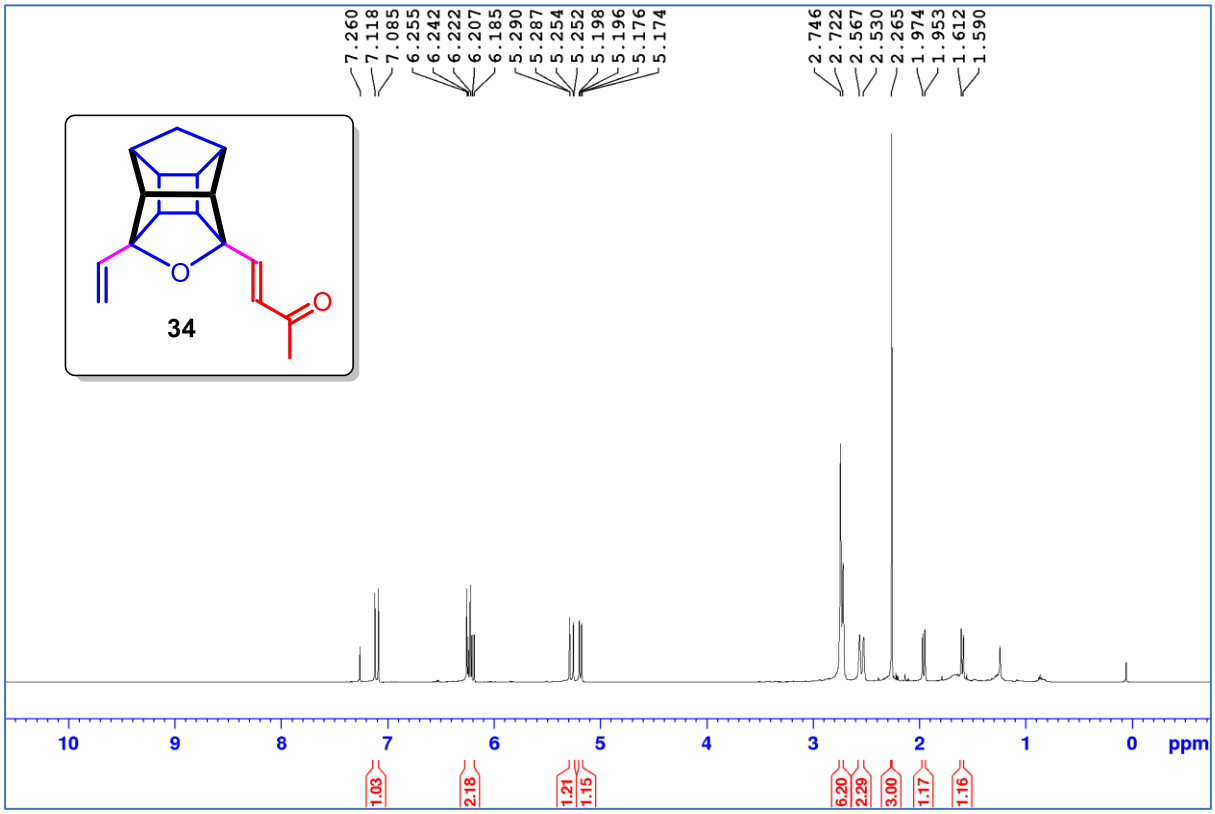


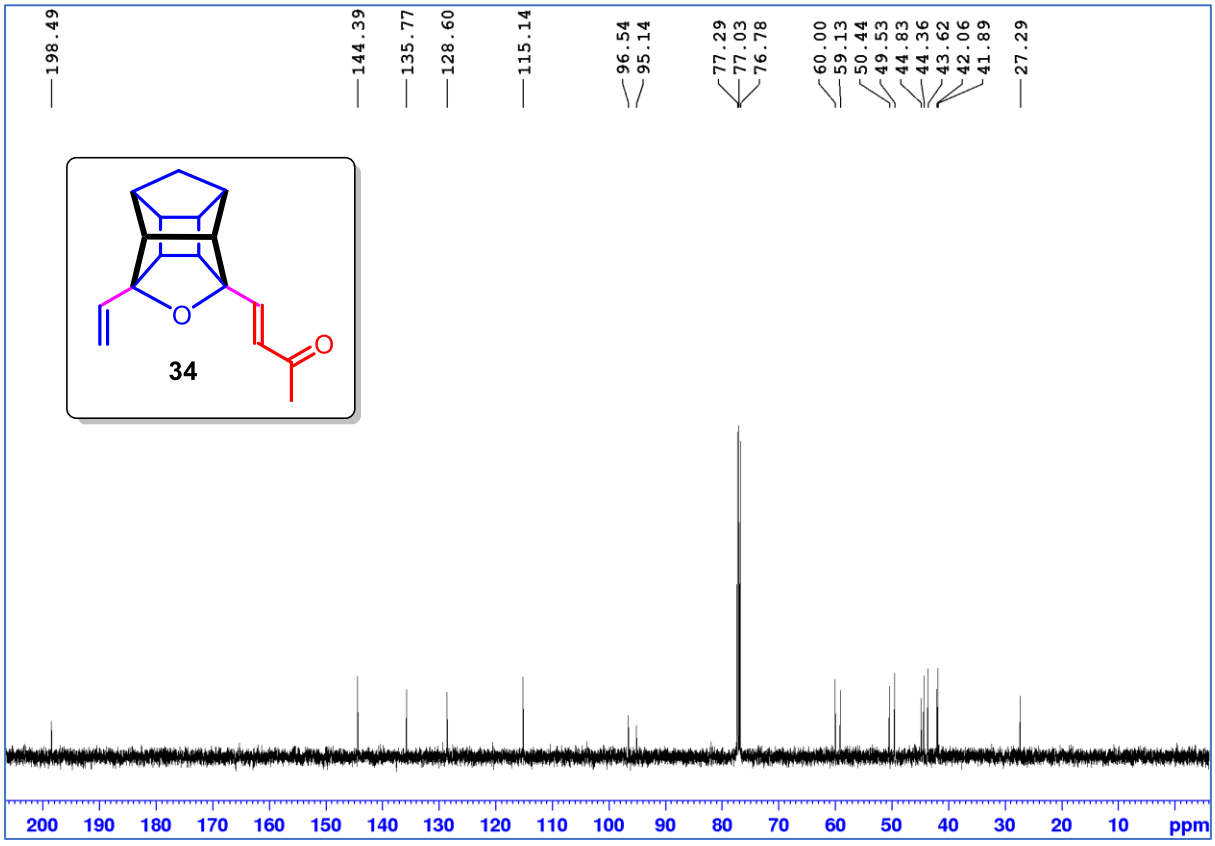
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 32



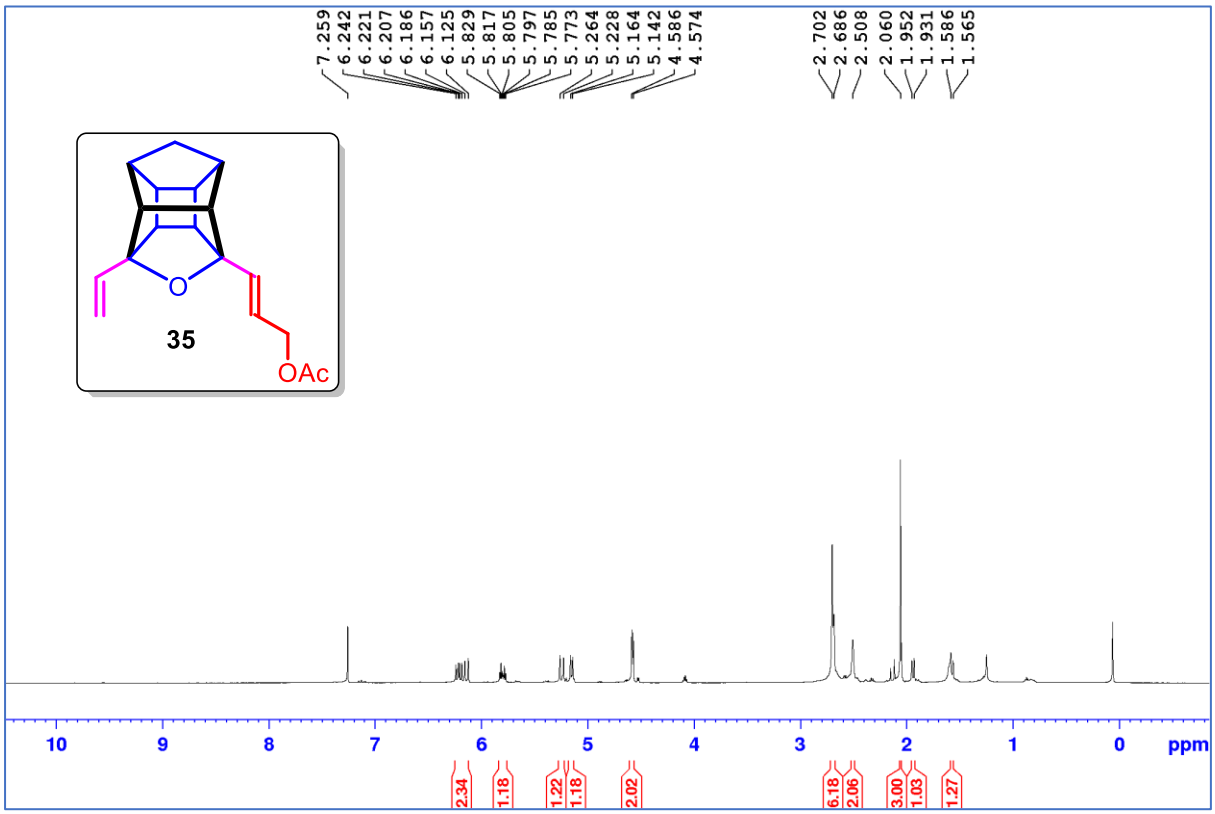


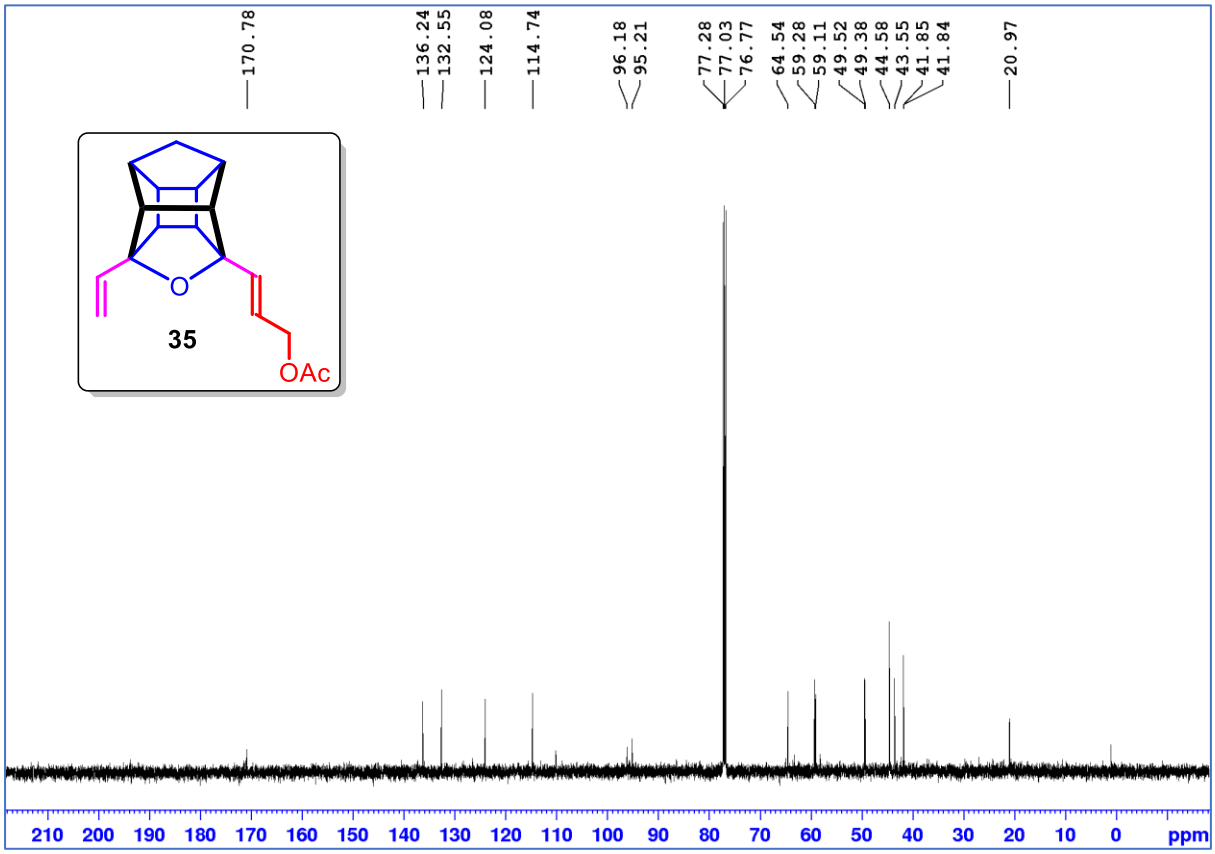
^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 34





^{1}H and ^{13}CNMR (500 MHz, $CDCl_3$) of compound 35

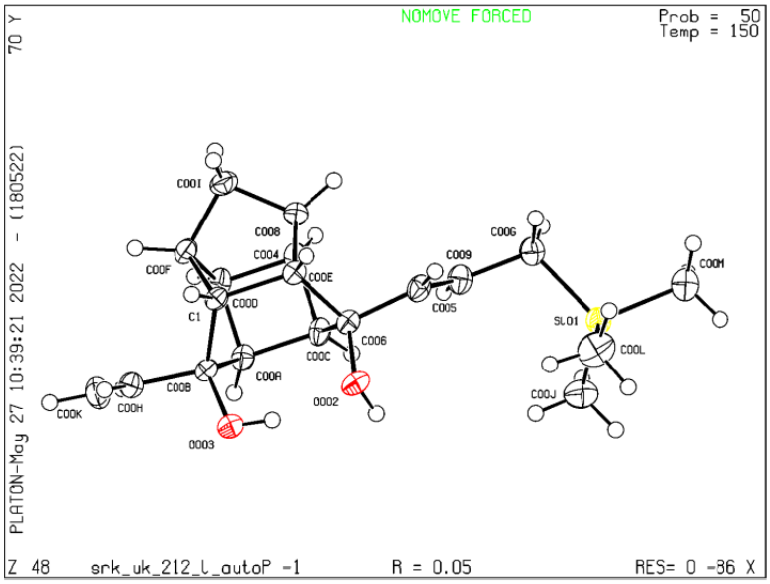




1. X-ray data and refinement parameter for compound

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

CCDC Number = 2176337



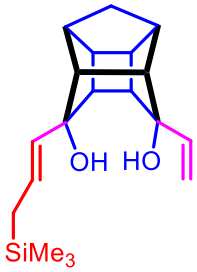


Table S1. X-ray crystallographic data and refinement parameters for **16 (CCDC NO 2176337)**

Identification code	SRK-UK-212(L))	
Empirical formula	$C_{19}H_{28}O_2Si$	
Formula weight	316.50	
Temperature	150.00(10)	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.2865(8) Å	α = 102.270(11)
	b = 10.7960 Å	β = 96.625(11)
	c = 13.3158(18) Å	γ = 93.042(10)
Volume	874.4(2) Å^3	
Z	2	
Density (calculated)	1.202 g/cm^3	
Absorption coefficient (μ)	1.00000mm^{-1}	
Absorption correction	Multi-scan	
Max. and Min. transmission	0.984,0.993	

F (000)	344.0
Crystal size	$0.116 \times 0.11 \times 0.05$ mm^3
Index ranges	$-7 \leq h \leq 7, -12 \leq k \leq 12, -15 \leq l \leq 15$
Theta range for data collection	3.156 to 49.998 °
Reflections collected	31086
Diffraction radiation wavelength	0.71073
Independent reflections	3085 [R_{int} = 0.1056, R_{sigma} = 0.0573]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3085/0/204
Goodness-of-fit on F^2	1.116
Final *R* indices [I>=2σ (I)]	R_1 = 0.0476, wR_2 = 0.1248
R indices (all data)	R_1 = 0.0689, wR_2 = 0.1461
Largest diff. peak and hole	0.28/-0.33 e Å^{-3}