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Experimental

1,7,7-Trimethyl-2-endo-oxiranyl-bicyclo[2.2.1]heptan-2-ol (3a) and 1,7,7-Trimethyl-2-exo-oxiranylbicyclo[2.2.1]heptan-2-ol (3b). To a solution of crude allyl alcohol 2 (500 mg, 2.78 mmol), in dichloromethane (30 mL) was added m-CPBA (1.44 g, 50% by weight, 4.17 mmol) at a time. The mixture was stirred for 18 h at room temperature. Then the reaction mixture was diluted with dichloromethane (50 mL) and washed successively with saturated aqueous sodium bisulphite (2 × 20 mL), saturated aqueous sodium bicarbonate (2 \times 20 mL) and finally with brine (1 \times 20 mL) and then dried (Na₂SO₄). After removal of solvent under reduced pressure the crude material obtained was subjected to column chromatography over silica gel (15% ethyl acetate in light petroleum) to afford the major epoxy alcohol 3a (270 mg, 50%) as a colorless liquid: IR (neat) v 3502, 2954, 2935, 2873, 1732, 1456, 1388, 1371 cm⁻¹; ¹H NMR (300 MHz, CDC_b) δ 0.86 (s, 3H), 1.12 (s, 3H), 1.02-1.98 (m, 7H), 2.70-2.76 (m, 2H), 2.99-3.03 (m, 1H); ¹³C NMR (75 MHz, CDCh) δ 10.5, 20.0, 20.9, 26.9, 29.7, 41.9, 43.6, 44.2, 45.4, 49.7, 55.7, 77.6; HR-MS C₁₂H₂₀O₂Na calcd, 219.1360 (M + Na); found, 219.1299 and the minor epoxy alcohol **3b** (195 mg, 36%) as a colourless liquid: IR (neat) v 3502, 2950, 2937, 2875, 1738, 1456, 1388, 1373 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.86 (s, 3H), 0.89 (s, 3H), 1.09 (s, 3H), 1.03-1.90 (m, 7H), 2.62 (dd, J = 5.16, 4.2 Hz, 1H), 2.78 (dd, J = 5.16, 2.7 Hz, 1H), 3.17 (dd, J = 4.16, 2.8 Hz, 1H); ¹³C NMR (75 MHz, CDCk) δ 10.8, 20.5, 21.1, 27.1, 31.6, 41.9, 43.5, 44.8, 49.6, 52.5, 55.2, 77.4; HR-MS $C_{12}H_{20}O_2Na$ calcd, 219.1360 (M + Na); found, 219.1366.

(3'R)-1,7,7-trimethyl-3'-[(prop-2-ynyloxy)methyl]spiro[bicyclo[2.2.1]heptane-2,2'-oxirane] (5a). To a stirred suspension of NaH (49 mg, 60% dispersion; 2.04 mmol) in dry THF-DMSO (10:1) (3 mL) was added dropwise a solution of epoxy alcohol 3a (200 mg, 1.02 mmol) in dry THF (5 mL) at 0°C under nitrogen. After the evolution of hydrogen ceased (approx. 25 min), a solution of propargyl bromide (145 mg, 1.22 mmol) in THF (5 mL) was added dropwise at 0°C over 20 min. The reaction mixture was then

stirred at room temperature for 8h and then carefully decomposed with ice water. After removal of most of the solvent under reduced pressure, the resulting residue was extracted with diethyl ether (4 × 25 mL). The combined ether extract was washed successively with water (2 × 10 mL) and brine (1 × 10 mL) and then dried (Na₂SO₄). Solvent was removed under reduced pressure, and the oil obtained was purified by column chromatography over silica gel (10% ethyl acetate in light petroleum) to furnish **5a** (186 mg, 78%) as a colorless liquid: IR (neat) v 3305, 3265, 2952, 2873, 2116, 1741, 1475, 1452, 1388, 1371, 1319, 1265 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.62 (s, 3H), 0.86 (s, 3H), 0.97 (s, 3H), 1.10-1.92 (m, 7H), 2.45 (t, J = 2.4 Hz, 1H), 2.94-2.97 (m, 1/2H), 3.03-3.06 (m, 1/2H), 3.46 (dd, J = 10.8, 6.6 Hz, 1H), 3.66 (dd, J = 11.1, 6.7 Hz, 1H), 3.74 (dd, J = 10.9, 4.0 Hz, 1H), 3.87 (dd, J=11.2, 3.6 Hz, 1H), 4.23 (AB_q and each peak splits into doublet, J = 15.8, 2.6 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 8.75, 11.68, 19.28, 19.38, 19.55, 27.29, 27.74, 31.61, 32.17, 35.20, 40.18, 44.32, 44.56, 47.61, 47.62, 53.38, 58.08, 58.21, 59.65, 68.25, 70.11, 70.78, 74.59, 79.39; Anal. Calcd for C₁₅H₂₂O₂: C, 76.88; H, 9.46. Found: C, 76.68; H, 9.48.

(3'S)-1,7,7-trimethyl-3'-[(prop-2-ynyloxy)methyl]spiro[bicyclo[2.2.1]heptane-2,2'-oxirane] (5b): colorless oil; 78% yield; IR (neat) v 2954, 2875, 2200, 17439, 1454, 1390, 1263 cm⁻¹; ¹H NMR (300 MHz, CDC $_{\frac{1}{5}}$) δ 0.75 (s, 1H), 0.85 (s, 3H), 0.95 (s, 3H), 1.14-1.91 (m, 7H), 2.45 (t, J = 2.4 Hz, 1H), 3.03 (dd, J= 6.6, 3.3 Hz, 1H), 3.66 (dd, J = 11.1, 6.7 Hz, 1H), 3.87 (dd, J=11.1, 3.3 Hz, 1H), 4.23 (AB $_{q}$ and each peak splitted into doublet, J = 15.7, 2.4 Hz, 2H); ¹³C NMR (75 MHz, CDC $_{\frac{1}{5}}$) δ 11.75, 19.37, 19.68, 27.81, 31.69, 40.26, 44.6, 49.3, 58.2, 59.7, 68.3, 74.6; Anal. Calcd for $C_{15}H_{22}O_{2}$: C, 76.88; H, 9.46. Found: C, 76.54; H, 9.37.

(1R)-1-(2,2-dimethyl-3-methylenebicyclo[2.2.1]hept-1-yl)-2-(prop-2-ynyloxy)ethanol (6a): A solution of Cp₂TiC½ (225 mg, 0.9 mmol) in THF (5 mL) (dried over Na) was stirred with activated zinc dust (195 mg, 2.99 mmol) for 1h under argon (activated zinc dust was prepared by washing 20 gm of commercially

available zinc dust with 60 mL of 4 N HCl and thorough washing with water untill the washings became neutral and finally with dry acetone and then drying in vacuo). The resulting green solution was then added dropwise to a stirred solution of the epoxide 5a (100 mg, 0.43 mmol) in dry THF (12 mL) at room temperature under argon. It was stirred for an additional 1h and decomposed with saturated sodium dihydrogen phosphate (10 mL). After removal of most of the THF under reduced pressure, the crude material obtained was purified by column chromatography over silica gel (5% ethyl acetate in light petroleum) to furnish 6a (72 mg, 72%) as a colourless liquid. IR (neat) v 3463, 3307, 2931, 2873, 1739, 1654, 1456, 1388, 1369, 1261 cm⁻¹; ¹H NMR (300 MHz, CDCl_b) δ 1.03 (s, 3H), 1.08 (s, 3H), 1.21-1.89 (m, 7H), 2.45 (t, J = 2.4 Hz, 1H), 3.59 (dd, J = 9.6, 8.4 Hz, 1H), 3.83 (dd, J = 9.6, 2.4 Hz, 1H), 4.14-4.30 (m, 3H), 4.72 (s, 1H), 4.85 (s, 1H); ¹³C NMR (75 MHz, CDCl_b) δ 24.9, 26.3, 29.7, 31.2, 38.5, 43.7, 47.1, 57.1, 58.9, 71.4, 72.2, 75.1, 80.0, 100.4, 165.4; Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.26; H, 9.50.

(1*S*)-1-(2,2-dimethyl-3-methylenebicyclo[2.2.1]hept-1-yl)-2-(prop-2-ynyloxy)ethanol (6b) was prepared from 5b by following the same procedure as described for 6a: colorless oil; 75% yield, IR (neat) v 3477, 3307, 2958, 2875, 2115, 1652, 1461, 1361 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.99 (s, 3H), 1.07 (s, 3H), 1.09-2.00 (m, 7H), 2.44 (t, J = 2.4 Hz, 1H), 3.46 (t, J = 9.0 Hz, 1H), 3.78 (dd, J = 9.3, 2.6 Hz, 1H), 4.16 (dd, J=8.7, 2.5 Hz, 1H), 4.19 (d, J= 2.4 Hz, 2H), 4.65 (s, 1H), 4.74 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 23.94, 25.8, 29.1, 29.8, 37.2, 43.1, 46.9, 55.7, 58.3, 70.4, 72.0, 74.5, 79.4, 99.3, 165.7; Anal. Calcd. for C₁₅H₂₂O₂: C, 76.88; H, 9.46. Found: C, 76.16; H, 9.26.

(3'R)-3'-[(benzyloxy)methyl]-1,7,7-trimethylspiro[bicyclo[2.2.1]heptane-2,2'-oxirane] (9a): To a stirred suspension of NaH (49 mg, 60% dispersion; 2.04 mmol) in dry THF-DMSO (10:1) (3 mL) was added dropwise a solution of epoxy alcohol 3a (200 mg, 1.02 mmol) in dry THF (5 mL) at 0°C under nitrogen. After the evolution of hydrogen ceased (approx. 25 min), a solution of benzyl bromide (192

mg, 1.12 mmol) in THF (5 mL) was added dropwise at 0 °C over 20 min. The reaction mixture was then stirred at room temperature for 8 h and carefully decomposed with ice-water (10 mL). After removal of most of the volatiles under reduced pressure, the resulting residue was extracted with diethyl ether (4 × 25 mL). The combined ether extract was washed successively with water (2 × 10 mL), brine (1 × 10 mL) and then dried (Na₂SO₄). Solvent was removed under reduced pressure and the oil obtained was purified by column chromatography over silica gel (5% ethyl acetate in light petroleum) to furnish **9a** (222 mg, 76%) as a colourless liquid: IR (neat) v 3485, 3030, 2952, 2871, 1741, 1496, 1454, 1388, 1361, 1319, 1274, 1203 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.641 (s, 3H), 0.87 (s, 3H), 0.98 (s, 3H), 0.70-1.89 (m, 7H), 2.99-3.02 (m, 1H), 3.45 (dd, J = 10.9, 6.5Hz, 1H), 3.66 (dd, J = 10.9, 4.1 Hz, 1H), 4.5 (ABq, J = 11.8 Hz, 2H), 7.25-7.36 (m, 5H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ 9.28, 20.07, 27.82, 30.33, 32.71, 35.74, 40.74, 43.71, 44.85, 48.12, 54.31, 60.67, 69.18, 71.08, 73.42, 100.34, 120.02, 128.84, 138.54; Anal. Calcd for C₁₉H₂₆O₂: C, 79.68; H, 9.15. Found: C, 79.58; H, 9.16.

(1R)-2-(benzyloxy)-1-(2,2-dimethyl-3-methylenebicyclo[2.2.1]hept-1-yl)ethanol (10a): A solution of Cp₂TiC½ (183 mg, 0.73 mmol) in dry THF (5 mL) was stirred with activated zinc dust (160 mg, 2.45 mmol) for 1h under argon. The resulting green solution was then added dropwise to a stirred solution of the epoxide 9a (100 mg, 0.35 mmol) in dry THF (5 mL) at room temperature under argon during 30 min. After additional stirring for 1h, the reaction mixture was decomposed with saturated di-sodium hydrogen phosphate (10 mL). After removal of most of the THF under reduced pressure, the resulting residue was extracted with diethyl ether (4 × 25 mL). The combined ether extract was washed successively with saturated NaHCO₃ (2 × 10 mL), brine (1 × 10 mL) and then dried (Na₂SO₄). Solvent was removed under reduced pressure and the brown gummy residue obtained was purified by column chromatography over silica gel (5% ethyl acetate in light petroleum) to furnish 10a (74 mg, 74%) as a colorless liquid: IR (neat) v 3444, 3064, 3030, 2950, 2871, 1722, 1651, 1494, 1454, 1386, 1361, 1315, 1274, 1201 cm⁻¹: ¹H NMR

(300 MHz, CDC½) δ 1.02 (s, 3H), 1.07 (s, 3H), 1.20-1.85 (m, 7H), 3.57 (dd, J = 9.4, 8.4 Hz, 1H), 3.73 (dd, J = 9.6, 2.7 Hz, 1H), 4.18 (dd, J = 8.4, 2.5 Hz, 1H), 4.60 (d, J = 2.9 Hz, 2H), 4.69 (s, 1H), 4.82 (s, 1H), 7.25-7.48 (m, 5H, ArH); ¹³C NMR (75 MHz, CDC½) δ 24.9, 26.3, 29.7, 31.1, 38.5, 43.7, 47.1, 57.0, 71.5, 72.5, 73.7, 100.3, 128.1, 128.5, 130.0, 130.1, 133.5, 138.5, 165.5; Anal. Calcd. for C₁₉H₂₆O₂: C, 79.68; H, 9.15. Found C, 79.58; H, 9.16.

(1*R*)-2-(benzyloxy)-1-(2,2-dimethyl-3-methylenebicyclo[2.2.1]hept-1-yl)-1-(3,5-dinitrophenyl)ethyl acetate (13): To a stirred solution of 3,5-dinitrobenzoic acid (100 mg, 0.47 mmol), DCC (180 mg, 0.87 mmol) and DMAP (20 mg, 0.16 mmol) in CH₂Cl₂ (2 mL) at 0 °C was added a solution of the alcohol 10a (120 mg, 0.419 mmol) in CH₂Cl₂ (3 mL). The reaction mixture was allowed to stir for another 6h. It was then diluted with ether (20 mL), filtered and the filtrate obtained was washed successively with saturated aqueous solution of sodium bicarbonate $Q \times 10$ mL), water (2 × 10 mL) and brine (1 × 10 mL) and then dried (Na₂SO₄). After removal of solvent under reduced pressure, the crude mass obtained was purified by column chromatography over silica gel (10% ethyl acetate in petroleum ether) to furnish the ester 13 (200 mg, 99%) as a crystalline solid, m. p. 104-106 °C; IR (KBr) v 3103, 2949, 2877, 1735, 1627, 1548, 1450, 1344, 1280, 1174, 1093, 1072 cm⁻¹; ¹HNMR (300MHz, CDCl₂) δ 1.03(s, 3H), 1.07 (s, 3H), 1.26-1.35 (m, 1H), 1.40 (d, J = 9.7 Hz, 1H), 1.53-1.59 (m, 1H), 1.69-1.93 (m, 4H), 3.88 (d, J = 6.2 Hz, 2H), 4.55 (ABq, J = 12.1, 36.2 Hz, 2H), 4.67 (s, 1H), 4.83 (s, 1H), 5.85 (dd, J = 6.4, 4.6 Hz, 1H), 7.22 (s, 5H), 9.09 (s, 2H), 9.2 (s, 1H); ¹³CNMR (75MHz, CDCl₂); δ 24.2, 25.8, 29.3, 31.3, 39.3, 43.4, 46.6, 55.5, 69.6, 72.8, 76.3, 100.3, 122.1, 127.3, 127.4, 128.3, 129.3, 134.2, 137.7, 148.5, 162.1, 163.6.

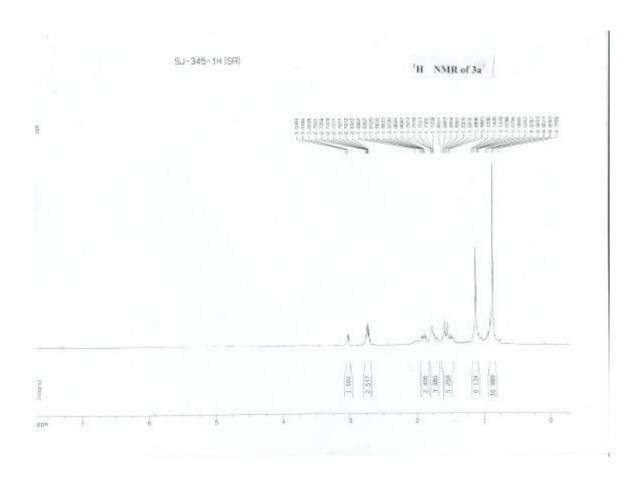
(3'R)-3'-(ethoxymethyl)-1,7,7-trimethylspiro[bicyclo[2.2.1]heptane-2,2'-oxirane] Preparation (11a): To a stirred suspension of NaH (49 mg, 60% dispersion; 2.04 mmol) in dry THF-DMSO (10:1) (3 mL) was added dropwise a solution of epoxy alcohol 3a (200 mg, 1.02 mmol) in dry THF (5 mL) at 0°C under nitrogen. After the evolution of hydrogen ceased (approx. 25 min), a solution of MeI (580 mg, 4.08

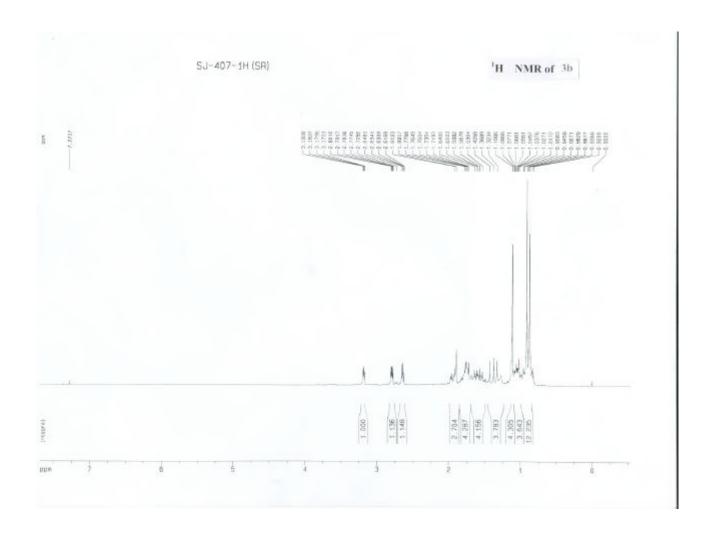
mmol) in THF (5 mL) was added dropwise at 0°C over 20 min. The reaction mixture was then stirred at room temperature for 8 h and carefully decomposed with ice-water (10 mL). After removal of most of the volatiles under reduced pressure, the resulting residue was extracted with diethyl ether (4 × 25 mL). The combined ether extract was washed successively with water (2 × 10 mL), brine (1 × 10 mL) and then dried (Na₂SO₄). Solvent was removed under reduced pressure and the oil obtained was purified by column chromatography over silica gel (5% ethyl acetate in light petroleum) to furnish **11a** (158 mg, 74%) as a colorless liquid: IR (neat) v 2954, 2875, 1732, 1454, 1388, 1371, 1261, 1195, 1124 cm⁻¹; ¹H NMR (300 MHz, CDC\(\frac{1}{2}\)) \delta 0.63 (s, 3H), 0.87 (s, 3H), 0.98 (s, 3H), 1.00-1.91 (m, 7H), 2.94 (dd, J = 6.5, 3.9 Hz., 1H), 3.33 (dd, J = 11.1, 6.5 Hz., 1H), 3.41 (s, 3H), 3.60 (dd, J = 11.2, 3.9 Hz., 1H); ¹³C NMR (75 MHz, CDC\(\frac{1}{2}\)) \delta 9.2, 19.5, 19.7, 27.8, 32.6, 35.7, 40.7, 44.7, 48.1, 54.1, 59.4, 72.1; Anal. Calcd for C₁₃H₂₂O₂: C, 74.24; H, 10.54. Found: C, 74.03; H, 10.41.

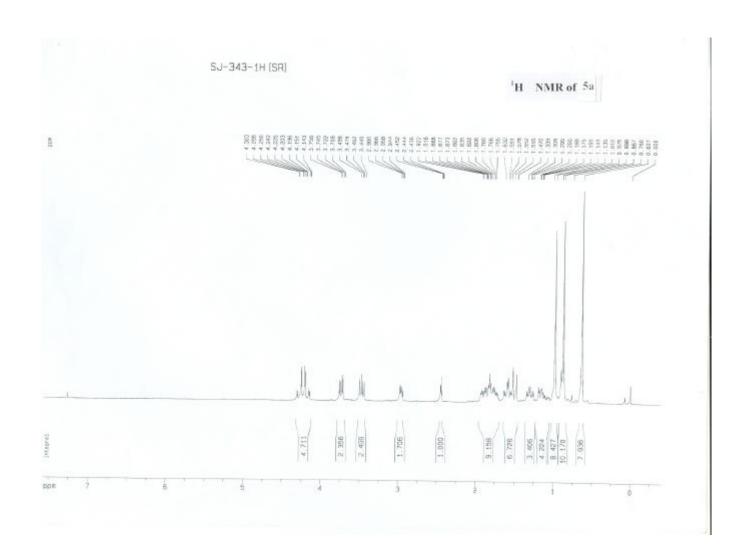
(1R)-1-(2,2-dimethyl-3-methylenebicyclo[2.2.1]hept-1-yl)-2-methoxyethanol (12a): A solution of Cp₂TiCb (250 mg, 1.004 mmol) in dry THF (12.5 mL) was stirred with activated zinc dust (218 mg, 3.33 mmol) for 1h under argon. The resulting green solution was then added dropwise to a stirred solution of the epoxide 11a (100 mg, 0.476 mmol) in dry THF (12 mL) at room temperature under argon. It was stirred for an additional 1h and decomposed with saturated sodium dihydrogen phosphate (10 mL). After removal of most of the THF under reduced pressure, the resulting residue was extracted with diethyl ether (4 × 25 mL). The combined ether extract was washed successively with water (2 × 10 mL), brine (1 × 10 mL) and then dried (Na₂SO₄). Solvent was removed under reduced pressure and the crude material obtained was purified by column chromatography over silica gel (10% ethyl acetate in light petroleum) to furnish 12a (72 mg, 71%): IR (neat) v 3465, 2956, 2927, 2879, 1651, 1458, 1361, 1195, 1124 cm⁻¹; ¹H NMR (300 MHz, CDCl₈) δ 1.03 (s, 3H), 1.08 (s, 3H), 1.16-1.88 (m, 7H), 2.35 (brs, OH), 3.42(s, 3H), 3.47 (dd, J = 9.6, 8.6 Hz, 1H), 3.63 (dd, J = 9.7, 2.6 Hz, 1H), 4.14 (dd, J = 8.5, 2.5Hz, 1H), 4.71 (s, 1H),

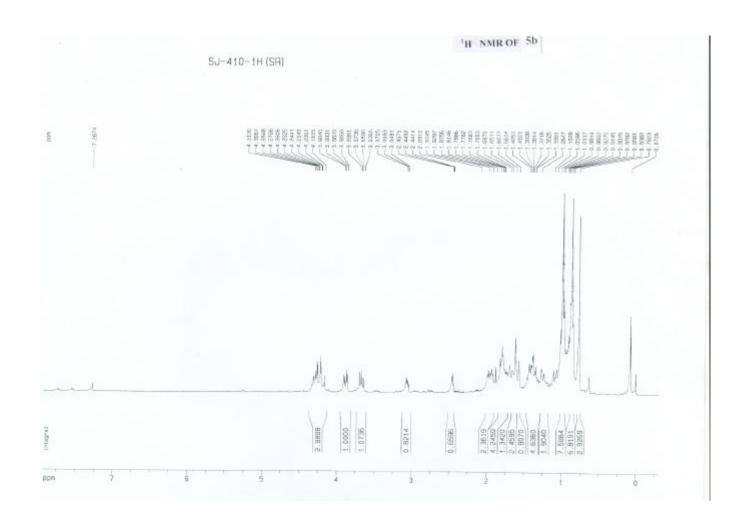
 $4.85~(s,1H); \ ^{13}C~NMR~(75~MHz,CDC\S)~\delta~24.9, \ 26.3, \ 29.6, \ 31.1, \ 38.4, \ 43.7, \ 47.1, \ 57.0, \ 59.4, \ 71.3, \ 74.8, \\ 100.3, \ 165.4; \ Anal.~Calcd.~for~C_{13}H_{22}O_2:~C, \ 74.24;~H, \ 10.54.~Found:~C, \ 74.18;~H, \ 10.55.$

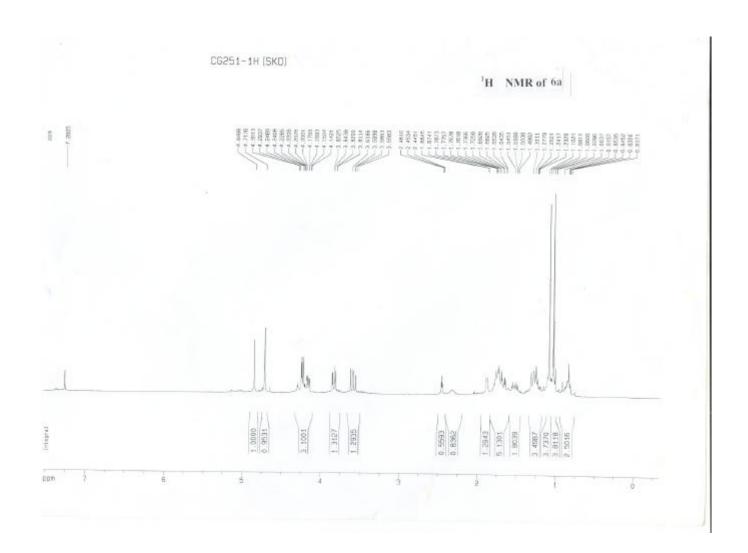
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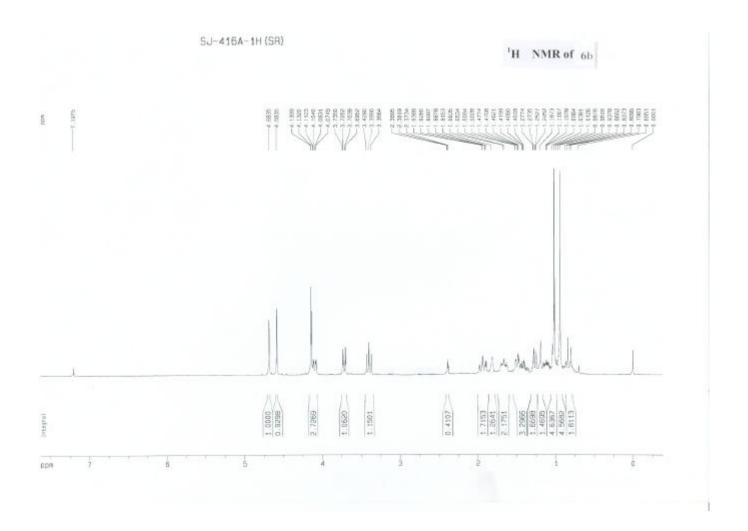


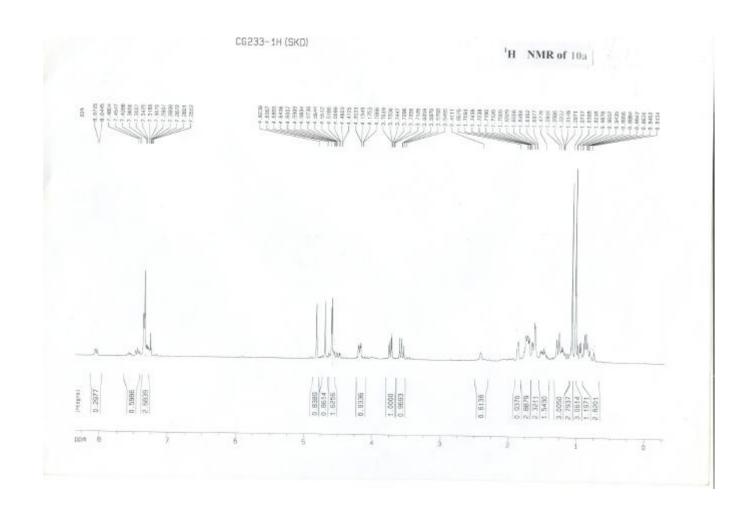


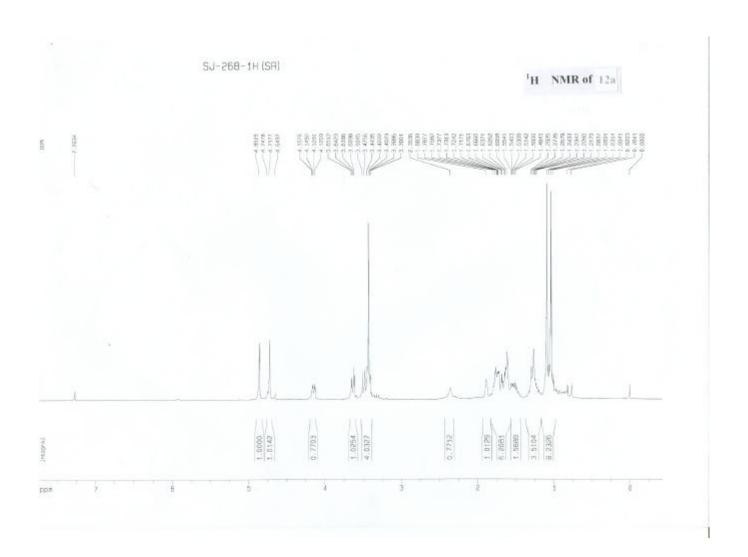


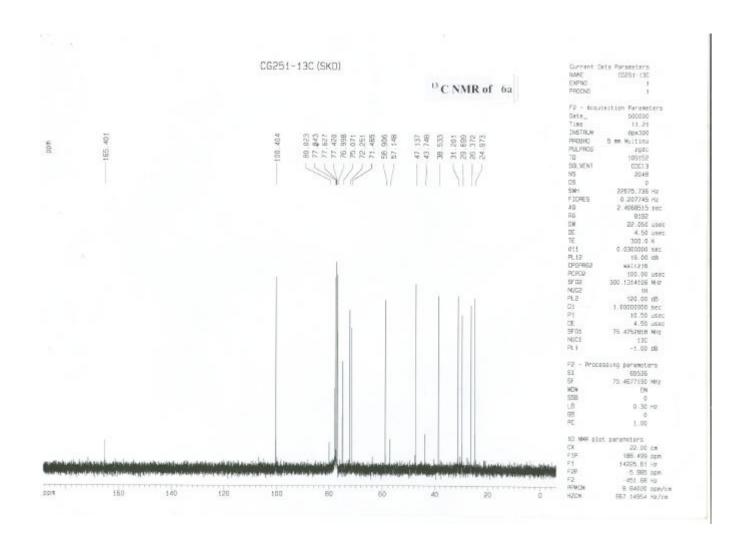


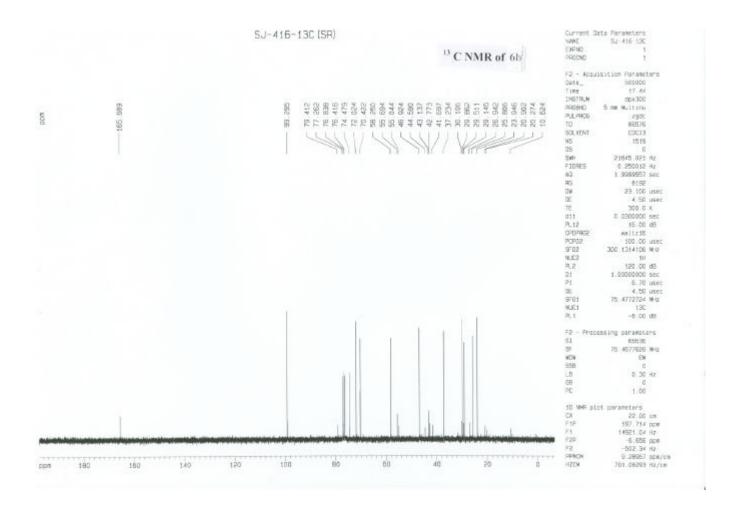


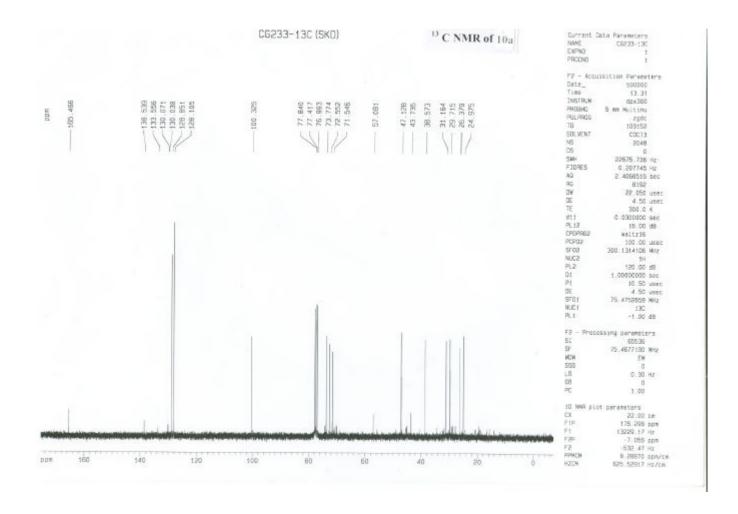


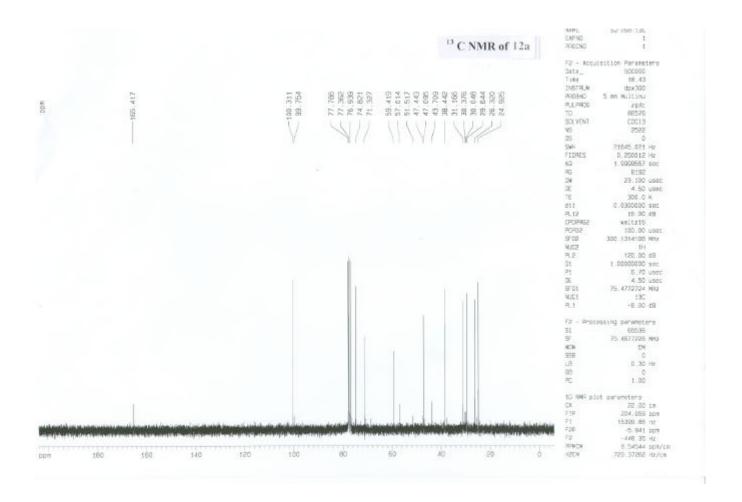












X-Ray picture of 13

