ELECTRONIC SUPPORTING INFORMATION

Stable Bromoallene Oxides

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Cover Page and Contents

General Experimental

Reagents: DMDO solutions were distilled under reduced pressure by reacting acetone (44.1 mL, 600 mmol) together with oxone (27.7 g, 90 mmol) and $NaHCO_3$ (13.4 g, 159 mmol) in H_2O (30 mL) at 0 ^oC for 2 h.[1] The resulting pale yellow distillate was collected at -100 ^oC with concentrations between 0.08 – 0.10 M, determined by iodometric titration and the solution was either used immediately or stored at -20 °C until required. All other reagents were purchased from commercial suppliers and used as received.

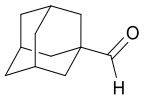
Solvents: Anhydrous tetrahydrofuran, diethyl ether and dichloromethane were obtained from a purification column composed of activated alumina and were used directly. Acetone, extraction solvents and solvents used in column chromatography were used as received at HPLC grade.

Experimental techniques: All synthetic procedures were used or adapted from literature and were conducted in oven-dried glassware under an inert atmosphere of nitrogen, unless otherwise stated. Reaction temperatures other than room temperature were recorded either as oil bath or cooling bath temperature. All volatiles and compounds were removed/concentrated *in vacuo* by rotary evaporation or under reduced pressure (Schlenck line). Kieselgel 60 F254 pre-coated aluminium-backed plates were used for analytical Thin Layer Chromatography and visualized either using UV light (254 or 350 nm) or by chemical staining with potassium permanganate or vanillin. Flash column chromatography was performed using Geduran® silica gel, particle size 40-63 μm.

Characterisation: An ATR-IR spectrometer was used to obtain FT-IR spectra of neat compounds unless otherwise stated. ^1H NMR (400 MHz) spectra and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ at 298 K unless otherwise stated using the NMR facility at Imperial College London on either a Bruker DRX-400 or Bruker AV-400. Chemical shifts (δ) are quoted in parts per million (ppm) and are downfield relative to tetramethylsilane ($SiMe_4$, δ = 0.00 ppm) and referenced to the residual solvent peak (δ 7.26 ppm for $CDCl_3$). Abbreviations used for multiplicity are as follows: s – singlet, d – doublet, br – broad, m – multiplet. Melting points were measured using a Lambda Photometrics MPA100 OptiMelt melting point device. Low resolution MS (CI and EI) and high resolution MS were recorded by the Imperial College Department of Chemistry Mass Spectrometry Service. X-Ray Crystallography studies were conducted on suitable single crystals, grown in hexamethyldisiloxane (HMDS) by slow evaporation, by the Imperial College Department of Chemistry X-Ray Crystallography Facility.

Experimental details and characterising data for compounds 7-9, 11-24.

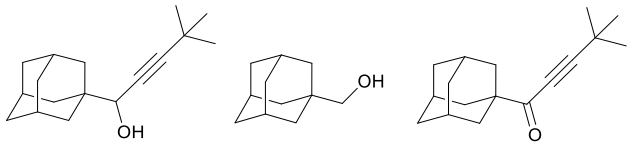
Adamantanecarboxaldehyde



A solution of 1-adamantanemethanol (7.36 g, 44 mmol) in dichloromethane (100 mL) was added dropwise to a suspension of pyridinium chlorochromate (19 g, 89 mmol) in dichloromethane (100 mL). The orange suspension was stirred at room temperature for 4 h and the resulting brown-black mixture was diluted with diethyl ether (300 mL), filtered through Celite and washed with 1 M sodium hydroxide (300 mL). The layers were separated and the aqueous phase was extracted using diethyl ether (200 mL). The combined organics were washed with water (2 x 200 mL), dried over anhydrous sodium sulfate and concentrated *in vacuo* to yield adamantanecarboxaldehyde (6.87 g, 42 mmol, 95%) as a white solid: R_f 0.60 (ethyl acetate : hexane, 1 : 9); m.p. 139.6 – 140.8 °C, (lit. m.p. 140 -142 °C);[2] ATIR 2902, 2848, 1723, 1693, 1451, 649 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H, C<u>H</u>O), 2.07 (br s, 3H, C<u>H</u>), 1.80 – 1.62 (m, 12H, C<u>H</u>$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0 (<u>C</u>=O), 44.9 (<u>C</u>), 36.6 (<u>C</u>H_2), 35.9 (<u>C</u>H_2), 27.4 (<u>C</u>H); HRMS (CI^+) *m/z* calcd for $C_{11}H_{17}O$ $(M + H)^+$ 165.1274, found 165.1273.

1-Adamantan-1-yl-4,4-dimethyl-2-pentyn-1-ol (11), 1-adamantanemethanol,

1-adamantan-1-yl-4,4-dimethyl-2-pentyn-1-one (12)

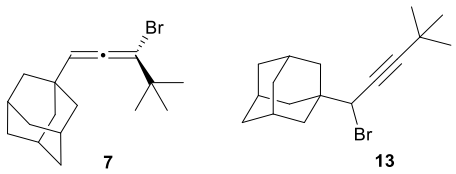


11 **12**

To a solution of terminal alkyne **10** (13.3 mL, 108 mmol) in THF (100 mL) at -78 °C was added *n*-BuLi (17.3 mL, 2.5M, 43.2 mmol) dropwise. The mixture was stirred at -78 °C for 45 min and subsequently warmed to 0 °C for 45 min during which, a colourless to pale yellow colour change was observed. The solution was cooled back down to -78 °C where it was left to stir for an additional 30 min before adding a solution of adamantanecarboxaldehyde (7.1 g, 43.2 mmol) in THF (40 mL). The mixture was left at -78 °C for 5 h and subsequently warmed to room temperature over 18 h. The yellow solution was quenched with saturated ammonium chloride (200 mL) and the aqueous layer was extracted with diethyl ether (2 x 150 mL). The combined organics were washed with brine (3 x 150 mL), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The resulting yellow oil was purified by flash column chromatography (ethyl acetate : hexane, 1 : 9) to give ynol **11** (10.3 g, 42 mmol, 97%) as an amorphous pale yellow solid: R_f 0.45 (ethyl acetate : hexane, 1 : 9); m.p. 86.0 – 88.0 °C; ATIR 3479 – 3134, 2971, 2902, 2848, 2229, 1452, 1361, 1261, 1076, 1011 cm^{-1}; ^1H NMR

(400 MHz, $CDCl_3$) δ 3.81 (s, 1H, C<u>H</u>OH), 2.00 (br s, 3H, Ad-C<u>H</u>), 1.78 – 1.51 (m, 12H, C<u>H</u>$_2$), 1.23 (s, 9H, C<u>H</u>$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 95.1 (<u>C</u>≡C), 77.4 (<u>C</u>≡C), 71.6 (<u>C</u>HOH), 37.8, 37.4 (Ad-<u>C</u>), 37.2 (Ad-<u>C</u>H$_2$), 31.1 (^{t}Bu-<u>C</u>H$_3$), 28.3 (Ad-<u>C</u>H), 27.5 (^{t}Bu-C); MS (CI^+) *m/z* 229 $(M - OH)^+$; HRMS (CI^+) *m/z* calcd for $C_{17}H_{25}$ $(M - OH)^+$ 229.1900, found 229.1952 and also 1-adamantanemethanol (31.8 mg, 0.13 mmol, 3%) – commercially available and ynone **12** (11.6 mg, 0.07 mmol, 1.5%) as an amorphous pale yellow solid: R_f 0.50 (ethyl acetate : hexane, 1 : 9); m.p. 51.6 – 52.8 °C; ATIR 2904, 2850, 2206, 1663, 1452, 1270, 1204, 1057, 908 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (br s, 3H, Ad-C<u>H</u>), 1.83 – 1.65 (m, 12H, Ad-C<u>H</u>$_2$) 1.28 (s, 9H, ^{t}Bu-C<u>H</u>$_3$); ^{13}C NMR (100MHz, $CDCl_3$) δ 194.4 (<u>C</u>=O), 103.1 (<u>C</u>≡C), 77.1 (<u>C</u>≡C), 46.8 (Ad-<u>C</u>) and (^{t}Bu-C), 38.2 (Ad-<u>C</u>H$_2$), 36.5 (^{t}Bu-<u>C</u>H$_3$), 30.2 (Ad-<u>C</u>H$_2$), 27.9 (Ad-<u>C</u>H); MS (CI^+) *m/z* 245 $(M + H)^+$; HRMS (CI^+) *m/z* calcd for $C_{17}H_{25}O$ $(M + H)^+$ 245.1900, found 245.1902.

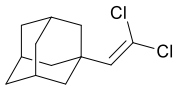
1-Adamantan-1-yl-3-bromo-4,4-dimethyl-1,2-pentadiene (7), 1-adamantan-1-yl-1-bromo-4,4-dimethyl-2-pentyne (13)



7 13

Propylene oxide (4.3 mL, 61 mmol) was added to a solution of ynol **11** (5.01 g, 20.3 mmol) in diethyl ether (100 mL). The solution was left to stir for 5 min, after which thionyl bromide (4.73 mL, 61 mmol) was added. The dark orange solution was left to stir at room temperature for 22 h and was quenched with a 1 : 1 (*v*/*v*) ratio of brine : pH 7.5 phosphate buffer (150 mL : 150 mL) solution. The resulting aqueous layer was extracted with diethyl ether (2 x 150 mL) and the combined yellow-orange organics were washed with brine (3 x 150 mL), dried over anhydrous sodium sulfate and concentrated *in vacuo*. The crude yellow oil was purified by flash column chromatography eluting with neat hexane to yield the title compound **7** (2.43 g, 7.87 mmol, 39%) as an amorphous white solid: R_f 0.62 (neat hexane); m.p. 53.6 – 54.4 °C; ATIR 2971, 2903, 2845, 1956, 1474, 1457, 1360, 880, 838, 781, 558 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (s, 1H, <u>H</u>C=C=C), 2.00 (br s, 3H, Ad-C<u>H</u>), 1.74 – 1.63 (m, 12H, Ad-C<u>H</u>$_2$), 1.17 (s, 9H, ^{t}Bu-C<u>H</u>$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5 (C=<u>C</u>=C), 109.3 (H<u>C</u>=C=C), 107.0 (C=C=<u>C</u>Br), 42.3 (Ad-<u>C</u>H$_2$), 36.9 (^{t}Bu-<u>C</u>), 36.7 (Ad-<u>C</u>H$_2$), 34.7 (Ad-<u>C</u>), 29.3 (^{t}Bu-<u>C</u>H$_3$), 28.5 (Ad-<u>C</u>H); MS (EI^+) *m/z* 310, 308 $(M)^+$; HRMS (EI^+) *m/z* calcd for $C_{17}H_{25}{}^{79}Br$ $(M)^+$ 308.1140, found 308.1139 and also propargyl bromide **13** (3.38 g, 10.9 mmol, 55%) as a yellow oil: R_f 0.38 (neat hexane); ATIR 2970, 2909, 2849, 2231, 1450, 1359, 1265, 661, 568, 530 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (s, 1H, <u>H</u>CBr), 2.01 (br s, 3H, Ad-C<u>H</u>), 1.72 – 1.59 (m, 12H, Ad-C<u>H</u>$_2$), 1.23 (s, 9H, ^{t}Bu-C<u>H</u>$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.5 (<u>C</u>≡C), 75.9 (<u>C</u>≡C), 53.5 (H<u>C</u>Br), 39.3 (Ad-<u>C</u>H$_2$), 37.8 (Ad-<u>C</u>), 36.8 (Ad-<u>C</u>H$_2$), 30.8 (^{t}Bu-<u>C</u>H$_3$), 28.5 (Ad-<u>C</u>H), 27.7 (^{t}Bu-<u>C</u>); MS (EI^+) *m/z* 310, 308 $(M)^+$; HRMS (EI^+) *m/z* calcd for $C_{17}H_{25}{}^{79}Br$ $(M)^+$ 308.1140, found 308.1133.

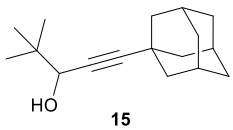
1-Adamantan-1-yl-2,2-dichloroethene (14)



14

Carbon tetrachloride (3.53 mL, 36.5 mmol) was added to a stirred solution of triphenylphosphine (19.2 g, 73 mmol) in dichloromethane (40 mL) at 0 °C. The resulting mixture was left to stir at 0 °C for 0.5 h, during which a colourless to yellow colour change was observed. A solution of adamantanecarboxaldehyde (3 g, 18 mmol) in dichloromethane (20 mL) was then added and the solution was stirred at 0 °C for 1 h. The reaction mixture was subsequently warmed to room temperature and left to stir for 18 h, during which a white precipitate was suspended in an orange-brown solution. The reaction mixture was diluted with dichloromethane (50 mL) and the resulting yellow homogeneous solution was added dropwise into hexane (500 mL). The resulting cloudy white supernatant was separated from the yellow aggregate by filtration through a silica plug, eluting with hexane to yield a colourless solution. The volatiles were subsequently removed *in vacuo* to give the title compound **14** (3.63 g, 15.7 mmol, 87%) as a colourless oil: R_f 0.84 (ethyl acetate : hexane, 1 : 9); ATIR 2907, 2849, 1694, 1605, 1450, 1099, 883, 870, 614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.68 (s, 1H, H<u>C</u>=C), 1.98 (br s, 3H, Ad-C<u>H</u>), 1.86 (br s, 6H, Ad-C<u>H</u>$_2$), 1.69 (br s, 6H, Ad-C<u>H</u>$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8 (H<u>C</u>=C), 40.8 (Ad-<u>C</u>H$_2$), 37.8 (Cl_2<u>C</u>=C), 36.6 (Ad-<u>C</u>H$_2$), 36.1 (Ad-<u>C</u>), 28.4 (Ad-<u>C</u>H); MS (EI^+) *m/z* 234, 232, 230 $(M)^+$; HRMS (EI^+) *m/z* calcd for $C_{12}H_{16}{}^{35}Cl_2$ $(M)^+$ 230.0629, found 230.0622.

1-Adamantan-1-yl-4,4-dimethyl-1-pentyn-3-ol (15)

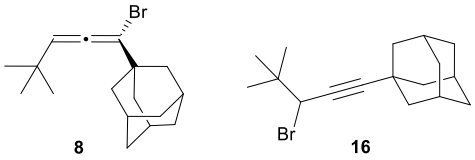


15

n-BuLi (5.2 mL, 2.5 M, 13 mmol) was added dropwise to a stirred solution of vinyl dichloride **14** (1.5 g, 6.48 mmol) in tetrahydrofuran (40 mL) at -78 °C and left to stir for 4 h. The pale yellow solution was then warmed to room temperature and left to stir for 30 min before being cooled back down to -78 °C. Pivaldehyde (0.7 mL, 6.5 mmol) was then added to the mixture which was stirred at -78 °C for 4 h, after which the solution was warmed to room temperature and left to stir for 18 h. The pale yellow solution was quenched with saturated ammonium chloride (100 mL) and the resulting aqueous layer was extracted with diethyl ether (2 x 100 mL). The combined organics were washed with brine (3 x 100 mL), dried over anhydrous sodium sulfate and concentrated *in vacuo*. The resulting pale yellow oil was purified by flash column chromatography eluting with 8% ethyl acetate in hexane to yield the title compound **15** (1.2 g, 4.9 mmol, 75%) as a white solid: R_f 0.35 (ethyl acetate : hexane, 1 : 9); m.p. 148.5 – 149.8 °C; ATIR 3567 – 3170, 2953, 2905, 2852, 2235, 1476, 1450, 1360, 1055,

1009 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 1H, HCOH), 1.94 (br s, 3H, Ad-CH), 1.87 – 1.84 (m, 6H, Ad-CH_2), 1.70 – 1.66 (m, 6H, Ad-CH_2), 0.96 (s, 9H, ^{t}Bu-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 94.4 (C≡C), 78.6 (C≡C), 71.5 (HCOH), 43.0 (Ad-CH_2), 36.4 (Ad-CH_2), 35.9 (Ad-C), 29.5 (^{t}Bu-C), 28.0 (Ad-CH), 25.3 (^{t}Bu-CH_3); MS (CI^+) *m/z* 229 $(M - OH)^+$; HRMS (CI^+) *m/z* calcd for $C_{17}H_{25}O$ $(M - H)^+$ 245.1900, found 245.1900.

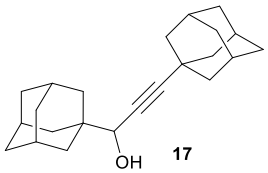
1-Adamantan-1-yl-1-bromo-4,4-dimethyl-1,2-pentadiene (8), 1-adamantan-1-yl-3-bromo-4,4-dimethyl-1-pentyne (16)



8 16

Propylene oxide (0.78 mL, 11 mmol) and thionyl bromide (0.87 mL, 11 mmol) were added dropwise to a stirred solution of ynol **15** (1.1 g, 4.5 mmol) in diethyl ether (30 mL). The orange solution was left to stir at room temperature for 20 h, before it was quenched with a 1 : 1 (*v*/*v*) ratio of brine : pH 7.5 phosphate buffer (100 mL : 100 mL) solution. The resulting aqueous layer was extracted with diethyl ether (2 x 100 mL) and the combined yellow organics were washed with brine (3 x 150 mL), dried over anhydrous sodium sulfate and concentrated *in vacuo*. The resulting yellow-orange oil was purified by flash column chromatography eluting with neat hexane to yield the title compound **8** (0.69 g, 2.2 mmol, 49%) as an amorphous white solid: R_f 0.76 (neat hexane); m.p. 69.3 – 70.4 °C; ATIR 2962, 2890, 2849, 1963, 1471, 1450, 1360, 1344, 887, 838, 743, 660, 565 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.23 (s, 1H, HC=C=C), 2.01 (br s, 3H, Ad-CH), 1.79 – 1.57 (m, 12H, Ad-CH_2), 1.07 (s, 9H, ^{t}Bu-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2 (C=C=C), 109.9 (HC=C=C), 107.6 (C=C=CBr), 41.5 (Ad-CH_2), 38.1 (^{t}Bu-C), 36.6 (Ad-CH_2), 32.7 (Ad-C), 29.7 (^{t}Bu-CH_3), 28.6 (Ad-CH); MS (EI^+) *m/z* 310, 308 $(M)^+$; HRMS (EI^+) *m/z* calcd for $C_{17}H_{25}{}^{79}Br$ 308.1140, found 308.1136 and propargyl bromide **16** (0.40 g, 1.3 mmol, 29%) as a yellow oil: R_f 0.62 (neat hexane); ATIR 2962, 2911, 2851, 2207, 1694, 1449, 1364, 576, 561, 542 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.40 (s, 1H, HCBr), 1.95 (br s, 3H, Ad-CH), 1.86 (br s, 6H, Ad-CH_2), 1.68 (br s, 6H, Ad-CH_2), 1.10 (s, 9H, ^{t}Bu-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 96.7 (C≡C), 65.9 (C≡C), 52.8 (HCBr), 42.6 (Ad-CH_2), 36.7 (Ad-C), 36.3 (Ad-CH_2), 29.8 (^{t}Bu-C), 27.9 (Ad-CH), 26.9 (^{t}Bu-CH_3); MS (EI^+) *m/z* 229 $(M - Br)^+$; HRMS (EI^+) *m/z* calcd for $C_{17}H_{25}$ $(M - Br)^+$ 229.1956, found 229.1954.

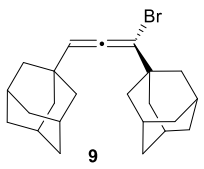
1,3-Diadamantan-1-yl-2-propyn-1-ol (17)



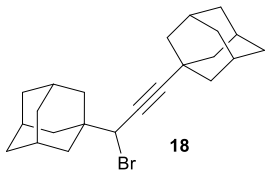
17

n-BuLi (6.9 mL, 2.5 M, 17 mmol) was added dropwise to a stirred solution of vinyl dichloride **14** in tetrahydrofuran (40 mL) at -78 °C and left to stir for 4 h. The pale yellow solution was then warmed to room temperature and left to stir for 30 min before being cooled back down to -78 °C. A 10 mL solution of adamantanecarboxaldehyde (1.4 g, 8.6 mmol) was added to the mixture which was stirred at -78 °C for 4 h, after which the solution was warmed to room temperature and left to stir for 18 h. The yellow solution was quenched with saturated ammonium chloride (100 mL). The resulting aqueous layer was extracted with diethyl ether (2 x 100 mL). The combined organics were washed with brine (3 x 100 mL), dried over anhydrous sodium sulfate, concentrated *in vacuo* and the resulting pale yellow amorphous solid was purified by flash column chromatography (ethyl acetate : hexane, 1 : 9) to yield ynol **17** (2.5 g, 7.7 mmol, 89%) as a white solid: R_f 0.32 (ethyl acetate : hexane, 1 : 9); m.p. 174.3 – 175.9 °C; ATIR 3635 – 3075, 2900, 2848, 2235, 1450, 1360, 1344, 1099, 1049, 1036, 1001 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.82 (br s, 1H, HCOH), 2.00 (s, 3H, Ad-CH), 1.95 (s, 3H, Ad-CH), 1.87 (s, 6H, Ad-CH_2), 1.77 – 1.45 (m, 18H, Ad-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 94.9 (C≡C), 77.7 (C≡C), 71.7 (HCOH), 43.0 (Ad-CH_2), 37.8 (Ad-CH_2), 37.4 (Ad-C), 37.2 (Ad-CH_2), 36.4 (Ad-CH_2), 29.6 (Ad-C), 28.3 (Ad-CH), 28.0 (Ad-CH); MS (CI^+) *m/z* 325 $(M + H)^+$; HRMS (CI^+) *m/z* calcd for $C_{23}H_{33}O$ $(M + H)^+$ 325.2531, found 325.2538.

1,3-Diadamantan-1-yl-1-bromo-1,2-propadiene (9), 1,3-diadamantan-1-yl-3-bromo-1-propyne (18)



9

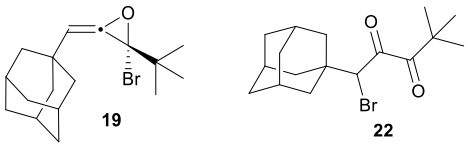


18

Propylene oxide (1.22 mL, 17 mmol) and thionyl bromide (1.36 mL, 17 mmol) were added dropwise to a stirred solution of ynol **17** (2.3 g, 7 mmol) in diethyl ether (35 mL). The orange solution was left to stir at room temperature for 20 h, before it was quenched with a 1 : 1 (*v*/*v*) ratio of brine : pH 7.5 phosphate buffer (150 mL : 150 mL) solution. The resulting aqueous layer was extracted with diethyl ether (2 x 150 mL) and the combined yellow organics were washed with brine (3 x 150 mL), dried over anhydrous sodium sulfate and concentrated *in vacuo*. The resulting yellow-orange oil was purified by flash column chromatography, eluting with neat hexane to yield the title compound **9** (1.8 g, 4.64 mmol, 66%) as an amorphous white solid: R_f 0.50 (neat hexane); m.p. 145.6 – 146.8 °C; ATIR

2899, 2848, 1965, 1448, 1343, 982, 742, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.11 (s, 1H, HC=C=C), 2.00 (br s, 6H, Ad-CH), 1.81 – 1.55 (m, 24H, Ad-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7 (C=C=C), 109.7 (HC=C=C), 107.8 (C=C=CBr), 42.4 (Ad-CH_2), 41.6 (Ad-CH_2), 38.0 (Ad-C), 36.6 (2 x Ad-CH_2), 34.6 (Ad-C), 28.6 (Ad-CH), 28.5 (Ad-CH); MS (EI^+) *m/z* 307 $(M - Br)^+$; HRMS (EI^+) *m/z* calcd for $C_{23}H_{31}$ $(M - Br)^+$ 307.2426, found 307.2416. Bromoallene **9** was recrystallised from hexamethyldisiloxane to give crystals suitable for X-ray crystallography. *Crystal data for* **9**: $C_{23}H_{31}Br$, M = 387.39, monoclinic, $C2/c$ (no. 15), a = 22.7174(12), b = 6.5055(3), c = 25.6670(15) Å, β = 94.802(5)°, V = 3780.0(3) $Å^3$, Z = 8, D_c = 1.361 g cm^{-3}, μ(Mo-Kα) = 2.176 mm^{-1}, T = 173 K, colourless platy needles, Agilent Xcalibur 3 E diffractometer; 3741 independent measured reflections (R_{int} = 0.0196), F^2 refinement,[3,4] R_1(obs) = 0.0484, wR_2(all) = 0.1055, 2927 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 56°], 319 parameters. CCDC 1485934. Propargyl bromide **18** (0.81 g, 2.1 mmol, 30%) was also isolated as an amorphous pale yellow solid: R_f 0.31 (neat hexane); ATIR 2962, 2911, 2851, 2225, 1694, 1449, 1364, 576, 561, 542 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.26 (s, 1H, HCBr), 2.01 (br s, 3H, Ad-CH), 1.95 (br s, 3H, Ad-CH_2), 1.87 (m, 6H, Ad-CH_2), 1.75 – 1.58 (m, 18H, Ad-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.3 (C≡C), 76.3 (C≡C), 53.7 (HCBr), 42.7 (Ad-CH), 39.3 (Ad-CH_2), 37.7 (Ad-C), 36.8 (Ad-CH_2), 36.3 (Ad-CH_2), 29.9 (Ad-C), 28.5 (Ad-CH_2), 27.9 (Ad-CH); MS (EI^+) *m/z* 307 $(M - Br)^+$; HRMS (EI^+) *m/z* calcd for $C_{23}H_{31}$ $(M - Br)^+$ 307.2426, found 307.2429.

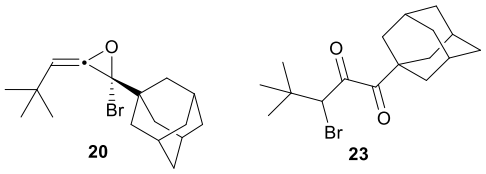
E-1-Adamantan-1-yl-3-bromo-2,3-epoxy-4,4-dimethyl-1-pentene (19), 1-adamantan-1-yl-1-bromo-4,4-dimethyl-2,3-pentanedione (22)



DMDO (4.9 mL, 0.1 M, 0.49 mmol) was added to a solution of bromoallene **7** (50 mg, 0.16 mmol) in dichloromethane (5 mL) at -40 °C. The solution was immediately warmed up to room temperature and left to stir for 20 h. The yellow solution that had formed was reduced *in vacuo* and purified through flash column chromatography, eluting with neat hexane to give bromoallene oxide **19** (16 mg, 0.049 mmol, 30%) as a white crystalline solid: R_f 0.55 (neat hexane); ATIR 2970, 2904, 2838, 1806, 1699, 1453, 1004, 875, 710, 634, 566 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.84 (s, 1H, HC=C), 2.01 (br s, 3H, Ad-CH_2), 1.81 – 1.62 (m, 12H, Ad-CH_2), 1.15 (s, 9H, ^{t}Bu-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6 (C=CO), 100.3 (HC=C), 83.8 (BrCO), 43.0 (Ad-CH_2), 39.6 (Ad-C), 36.7 (Ad-CH_2), 33.4 (^{t}Bu-C), 28.4 (Ad-CH), 26.2 (^{t}Bu-CH_3); MS (CI^+) *m/z* 325 $(M + H)^+$; HRMS (CI^+) *m/z* calcd for $C_{17}H_{26}O^{79}Br$ $(M + H)^+$ 325.1162, found 325.1161. Bromoallene oxide **19** was recrystallised from hexamethyldisiloxane to give crystals suitable for X-ray crystallography. *Crystal data for* **19**: $C_{17}H_{25}BrO$, M = 325.28, monoclinic, $P2_1/n$ (no. 14), a = 10.8427(7), b = 6.8117(4), c = 21.2550(17) Å, β = 94.932(6)°, V = 1564.03(19) $Å^3$, Z = 4, D_c = 1.381 g cm^{-3}, μ(Mo-Kα) = 2.620 mm^{-1}, T = 173

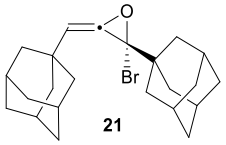
K, colourless plates, Agilent Xcalibur 3 E diffractometer; 3118 independent measured reflections (R_{int} = 0.0355), F^2 refinement,[3,4] R_1(obs) = 0.0663, wR_2(all) = 0.1709, 1998 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 56°], 175 parameters. CCDC 1485935. Diketone **22** (14 mg, 0.053 mmol 33%) as a waxy yellow solid: R_f 0.15 (neat hexane); ATIR 2904, 2848, 1712, 1694, 1451, 1225, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.84 (s, 1H, HCBr), 2.00 (br s, 3H, Ad-CH), 1.93 – 1.87 (m, 3H, Ad-CH_2), 1.72 – 1.62 (m, 9H, Ad-CH_2), 1.30 (s, 9H, ^{t}Bu-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3 (BrC-C=O), 190.9 (^{t}Bu-C=O), 58.8 (Br-CH), 38.9 (Ad-CH_2), 38.6 (Ad-C), 36.6 (Ad-CH), 28.2 (Ad-CH_2), 27.8 (^{t}Bu-C), 26.6 (^{t}Bu-CH_3) as well as the starting material **7** (17 mg, 0.055 mmol, 34%) was also isolated from the column.

***E*-1-Adamantan-1-yl-1-bromo-1,2-epoxy-4,4-dimethyl-2-pentene (20), 1-adamantan-1-yl-3-bromo-4,4-dimethyl-1,2-pentanedione (23)**

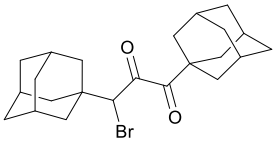


DMDO (4.9 mL, 0.1 M, 0.49 mmol) was added to a solution of bromoallene **8** (50 mg, 0.16 mmol) in dichloromethane (5 mL) at -40 °C. The resulting solution was immediately warmed up to room temperature and left to stir for 20 h. The yellow solution that had formed was reduced *in vacuo* and purified through flash column chromatography, eluting with neat hexane to give bromoallene oxide **20** (14 mg, 0.043 mmol, 27%) as a colourless waxy solid: R_f 0.50 (neat hexane); ATIR 2949, 2905, 2852, 1806, 1450, 1405, 1239, 1201, 924 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.97 (s, 1H, HC=C), 2.03 (br s, 3H, Ad-CH), 1.80 – 1.64 (m, 12H, Ad-CH_2), 1.16 (s, 9H, ^{t}Bu-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6 (C=CO), 100.3 (HC=C), 84.3 (BrCO), 40.6 (Ad-C), 38.0 (Ad-CH_2), 36.5 (Ad-CH_2), 31.5 (^{t}Bu-C), 30.7 (^{t}Bu-CH_3), 28.1 (Ad-CH); MS (CI^+) *m/z* 325 $(M + H)^+$; HRMS (CI^+) *m/z* calcd for $C_{17}H_{26}O^{79}Br$ $(M + H)^+$ 325.1162, found 325.1160 and diketone **23** (15 mg, 0.057 mmol, 35%) as a waxy yellow solid: R_f 0.10 (neat hexane); m.p. 78.8 – 80.3 °C; ATIR 2909, 2852, 1719, 1690, 1450, 1367, 982, 885, 657 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.95 (s, 1H, HCBr), 2.11 – 2.03 (m, 6H, Ad-CH_2 and Ad-CH), 1.96 – 1.91 (m, 3H, Ad-CH_2), 1.74 (m, 6H, Ad-CH_2) 1.17 (s, 9H, ^{t}Bu-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3 (BrC-C=O), 191.0 (Ad-C=O), 58.2 (Br-CH), 38.7 (Ad-C), 37.9 (Ad-CH), 36.4 (Ad-CH_2), 34.3 (^{t}Bu-C), 27.8 (Ad-CH_2), 27.0 (^{t}Bu-CH_3) and the starting material **8** (18 mg, 0.058 mmol, 36%) was also isolated from the column.

***E*-1,3-Diadamantan-1-yl-1-bromo-1,2-epoxy-2-propene (21), 1,3-diadamantan-1-yl-3-bromo-1,2-propanedione (24)**



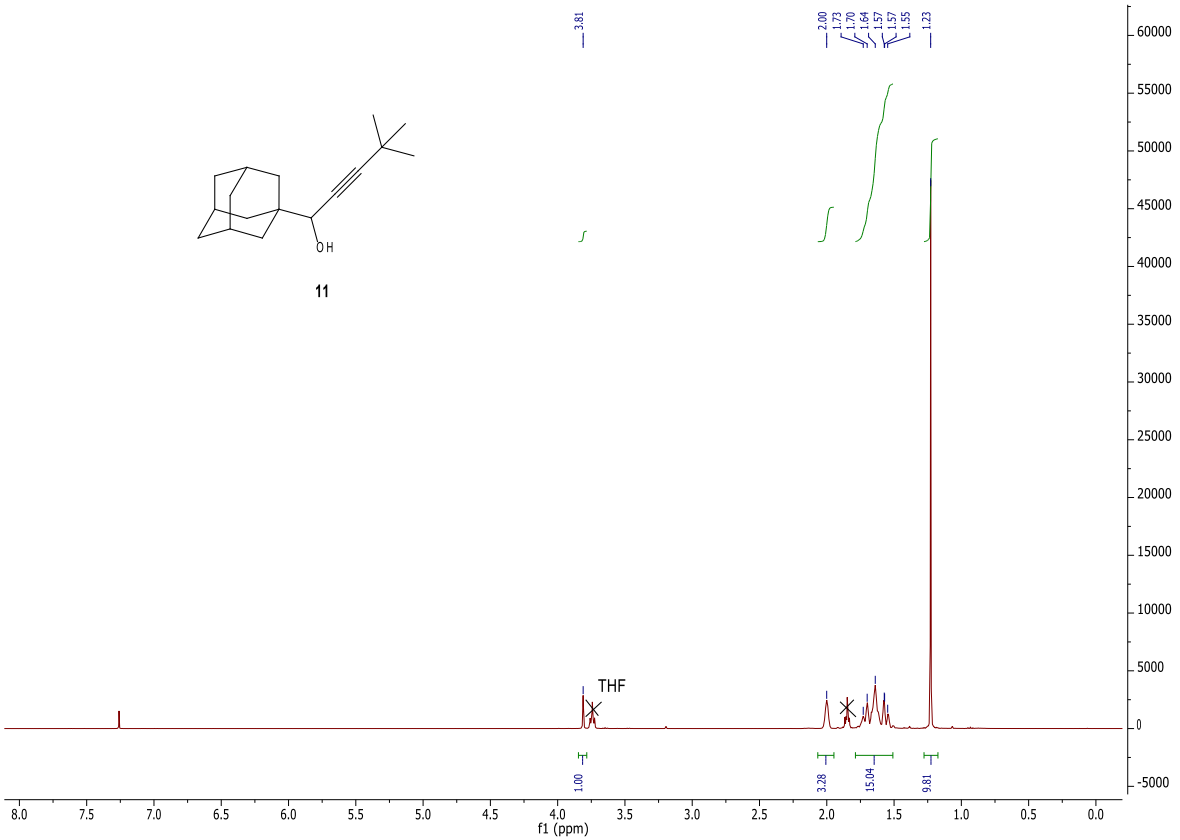
21



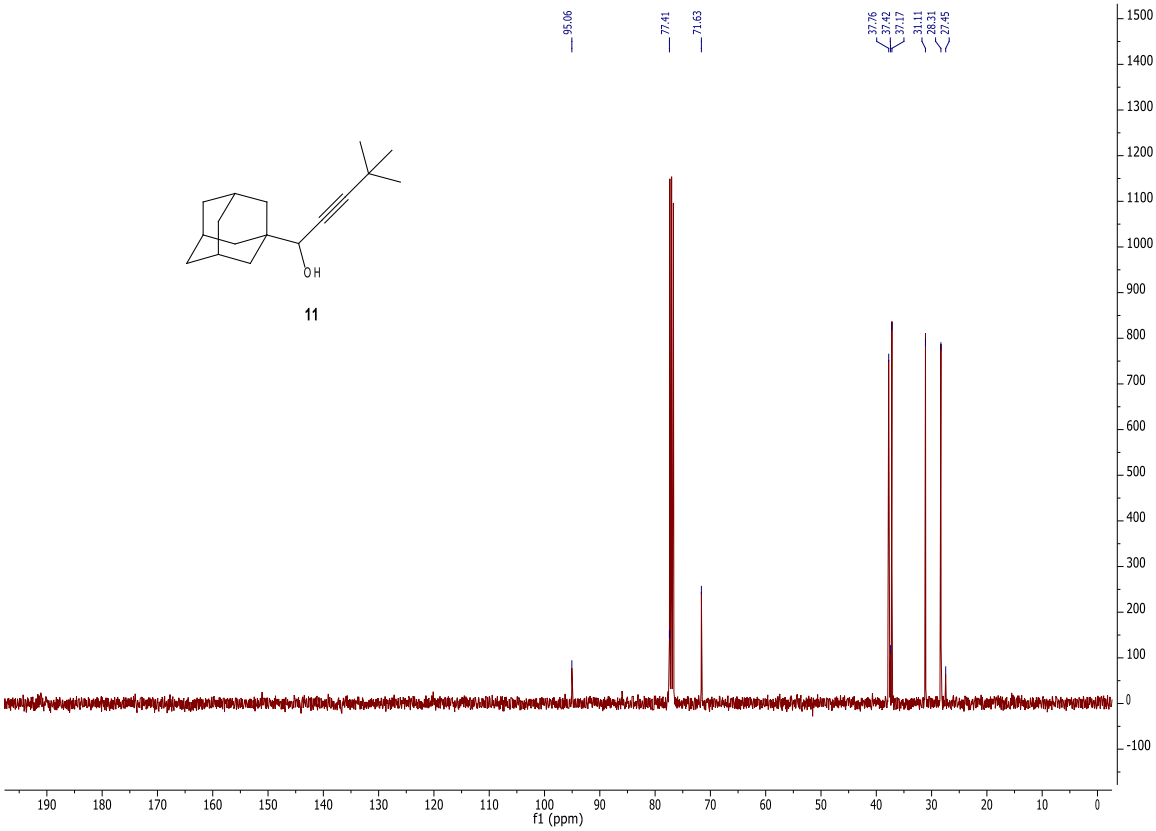
24

DMDO (4.9 mL, 0.1 M, 0.49 mmol) was added to a solution of bromoallene **9** (63 mg, 0.13 mmol) in dichloromethane (5 mL) at -40 °C. The resulting solution was immediately warmed up to room temperature and left to stir for 20 h. The yellow solution that had formed was reduced *in vacuo* and purified through flash column chromatography, eluting with neat hexane to give bromoallene oxide **21** (15 mg, 0.037 mmol, 23%) as a white solid: R_f 0.30 (neat hexane); m.p. 98.5 – 100.2 °C; ATIR: 2901, 2852, 1806, 1450, 1343, 1011, 889, 709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.83 (s, 1H, HCBr), 2.05 – 2.01 (m, 6H, Ad-CH), 1.81 – 1.60 (m, 24H, Ad-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0 (C=CO), 100.4 (HC=C), 84.4 (BrCO), 43.1 (Ad-CH_2), 40.6 (Ad-C), 38.0 (Ad-CH_2), 36.7 (Ad-CH_2), 36.5 (Ad-CH_2), 33.4 (Ad-C), 28.4 (Ad-CH), 28.1 (Ad-CH); MS (CI^+) *m/z* 403 $(M + H)^+$; HRMS (CI^+) *m/z* calcd for $C_{23}H_{32}O^{79}Br$ $(M + H)^+$ 403.1631, found 403.1630 and diketone **24** (19 mg, 0.056 mmol, 35%) as a yellow solid: R_f 0.11 (neat hexane); m.p. 139.8 – 142.2 °C; ATIR 2905, 2856, 1717, 1692, 1450, 980, 891, 659 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.77 (s, 1H, HC=C), 2.10 – 1.88 (m, 15H, Ad-CH_2 and Ad-CH), 1.75 – 1.62 (m, 15H, Ad-CH_2 and Ad-CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9 (BrC-C=O), 191.2 (Ad-C=O), 59.1 (Br-CH), 44.9 (Ad-C), 38.9 (Ad-CH), 37.9 (Ad-CH_2), 36.6 (Ad-CH), 36.4 (Ad-CH_2), 36.1 (Ad-C), 28.3 (Ad-CH_2), 27.8 (Ad-CH_2) and the starting material **9** (20 mg, 0.052 mmol, 32%) was also isolated from the column.

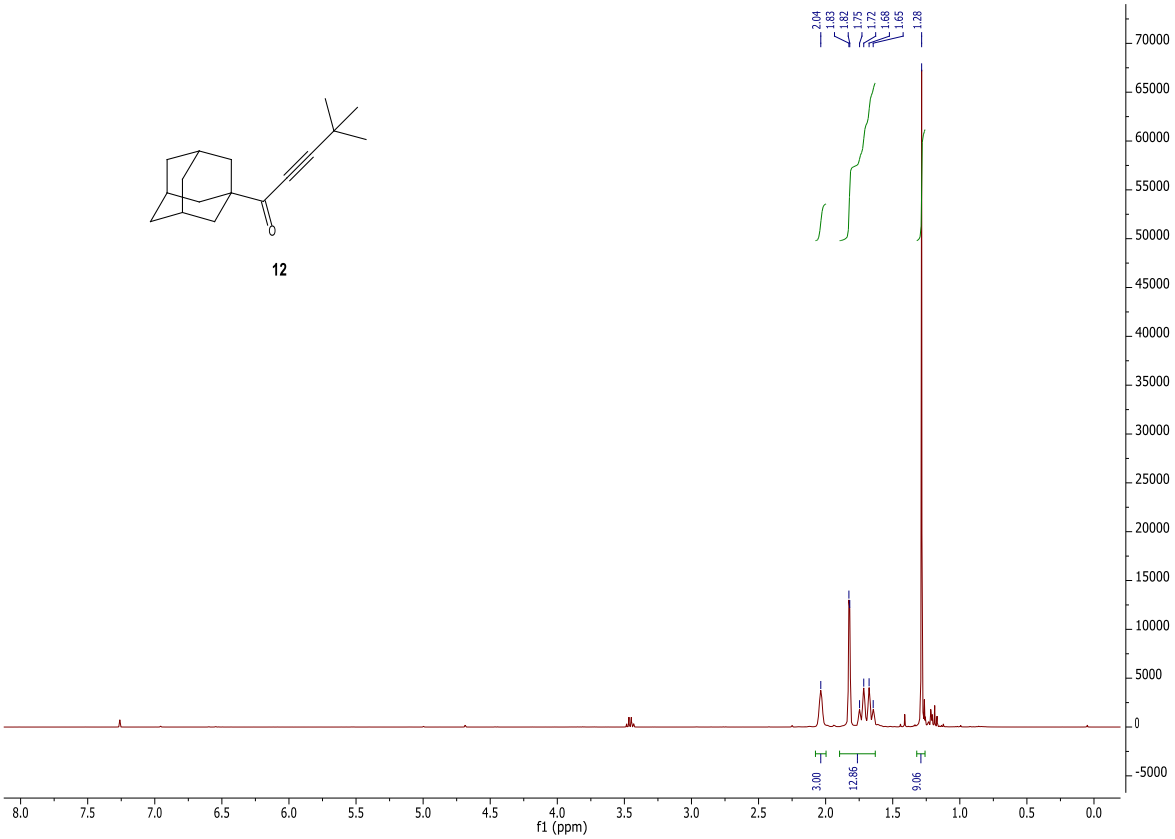
^{1}H NMR spectrum of 1-adamantan-1-yl-4,4-dimethyl-2-pentyn-1-ol (**11**) (400 MHz, $CDCl_3$)



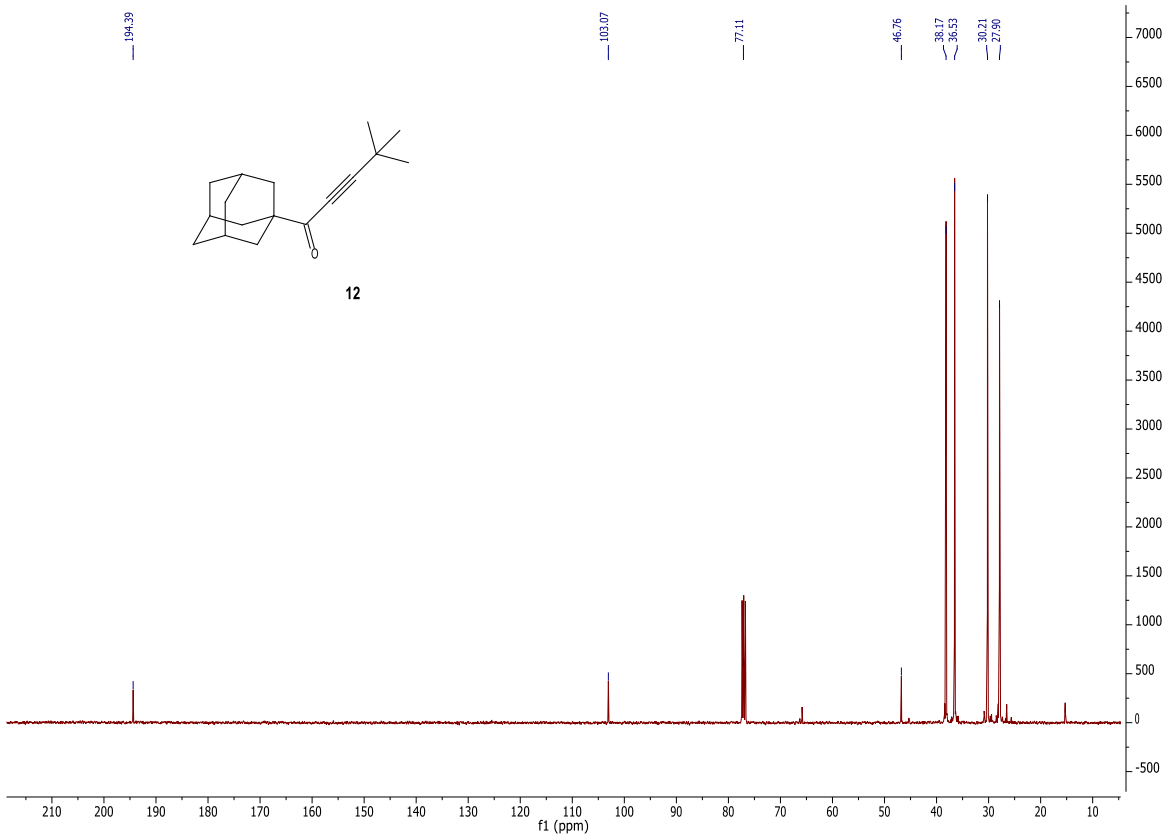
^{13}C NMR spectrum of 1-adamantan-1-yl-4,4-dimethyl-2-pentyn-1-ol (**11**) (100 MHz, $CDCl_3$)



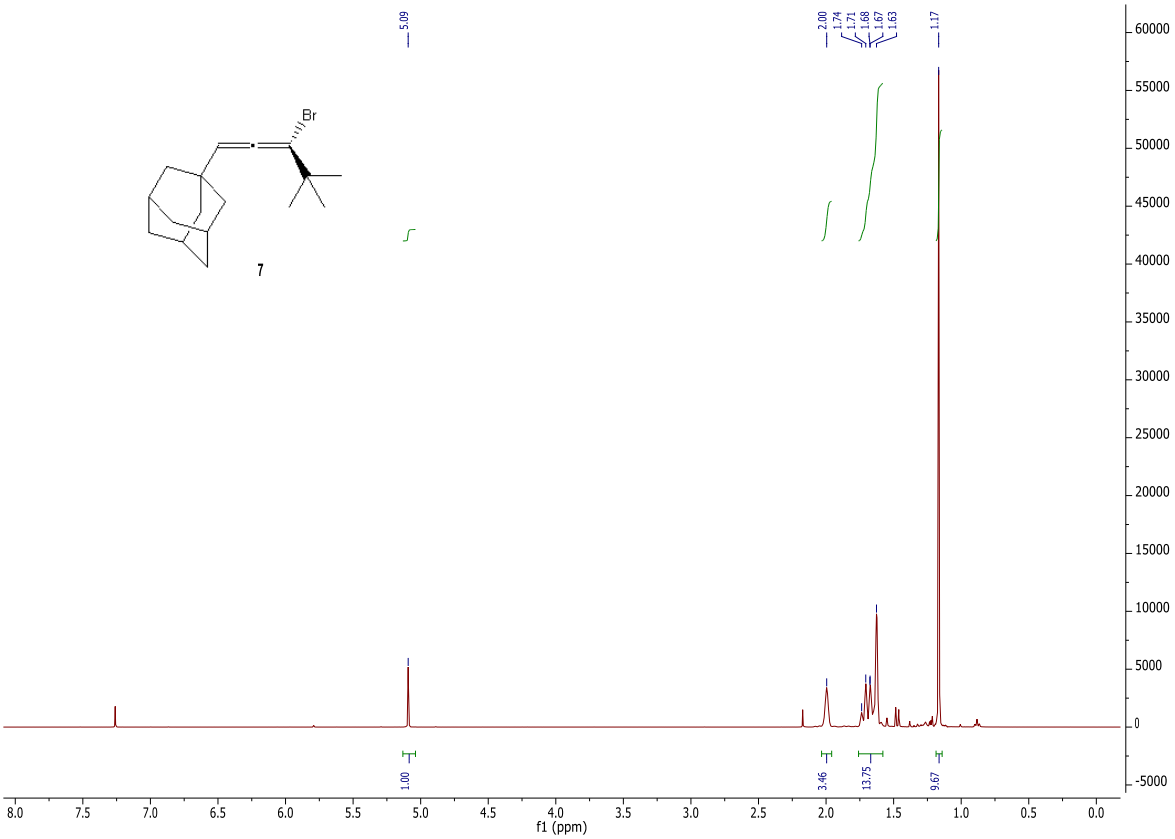
^{1}H NMR spectrum of 1-adamantan-1-yl-4,4-dimethyl-2-pentyn-1-one (**12**) (400 MHz, $CDCl_3$)



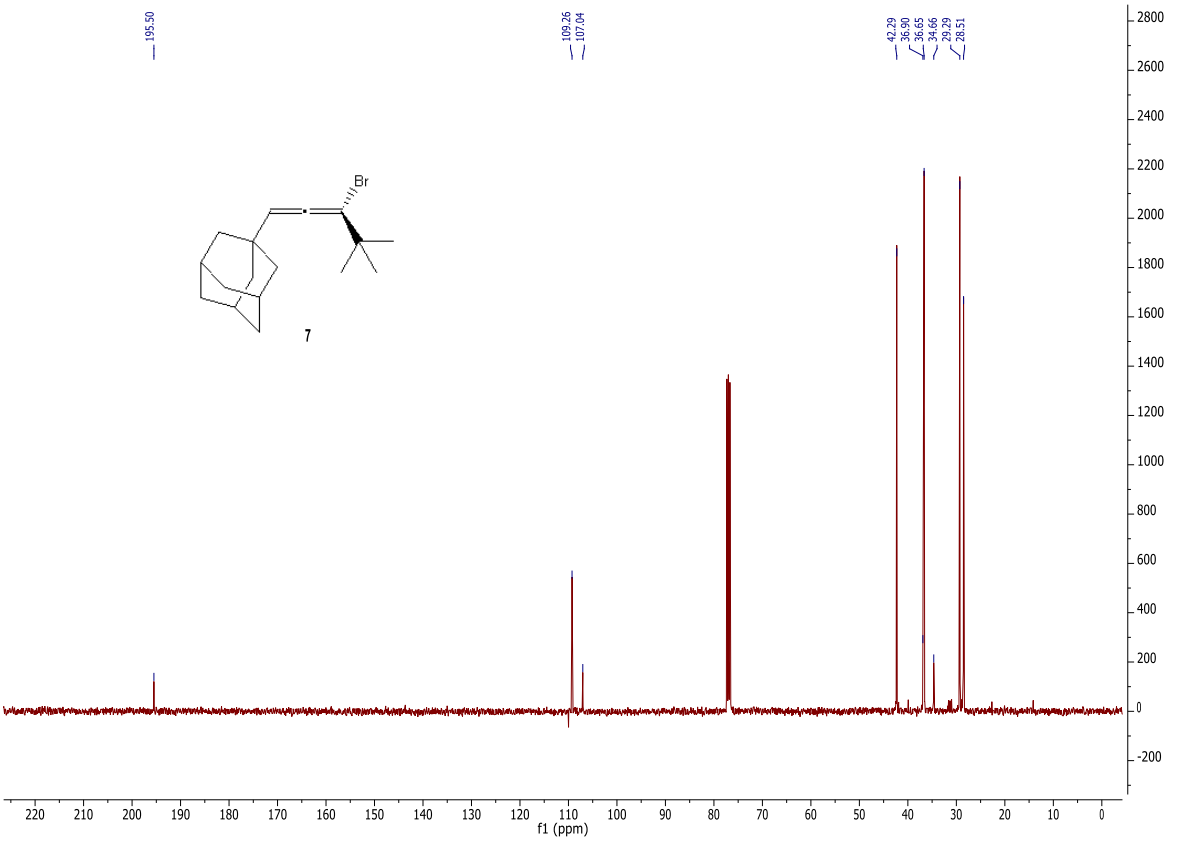
^{13}C NMR spectrum of 1-adamantan-1-yl-4,4-dimethyl-2-pentyn-1-one (**12**) (100 MHz, $CDCl_3$)



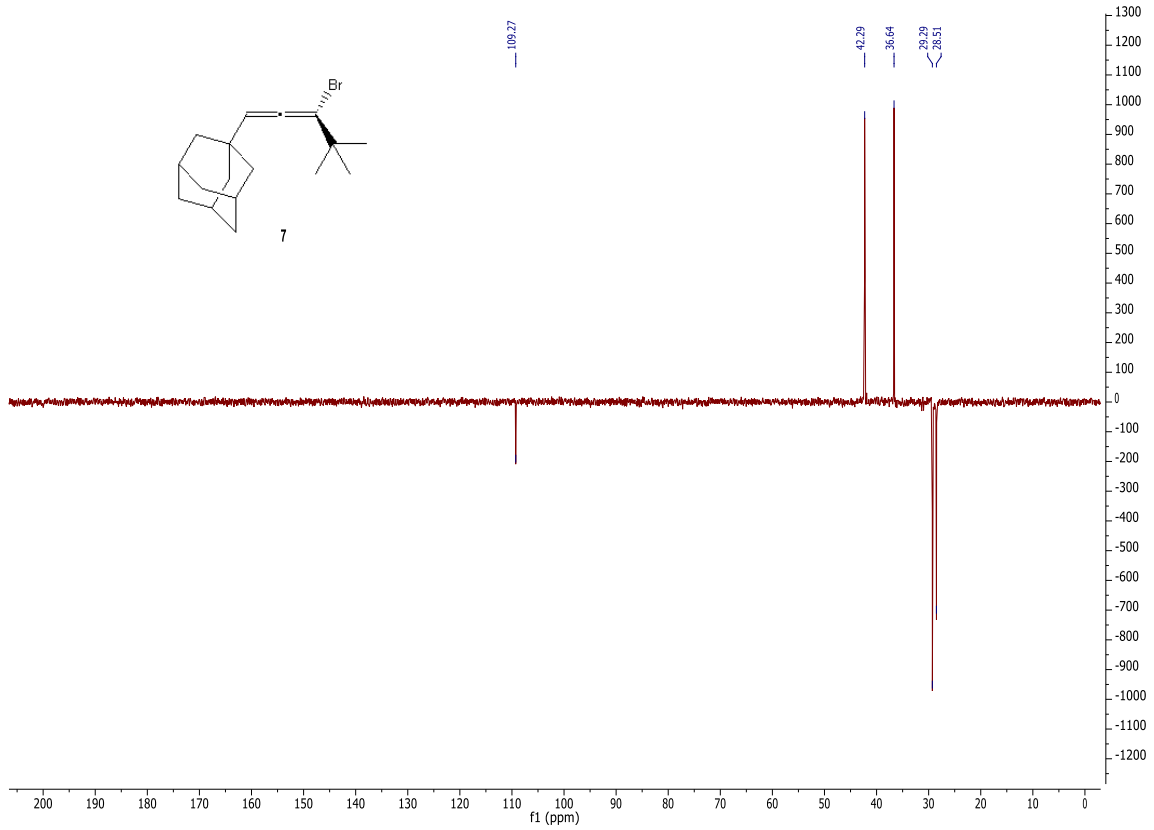
^{1}H NMR spectrum of 1-adamantan-1-yl-3-bromo-4,4-dimethyl-1,2-pentadiene (**7**) (400 MHz, $CDCl_3$)



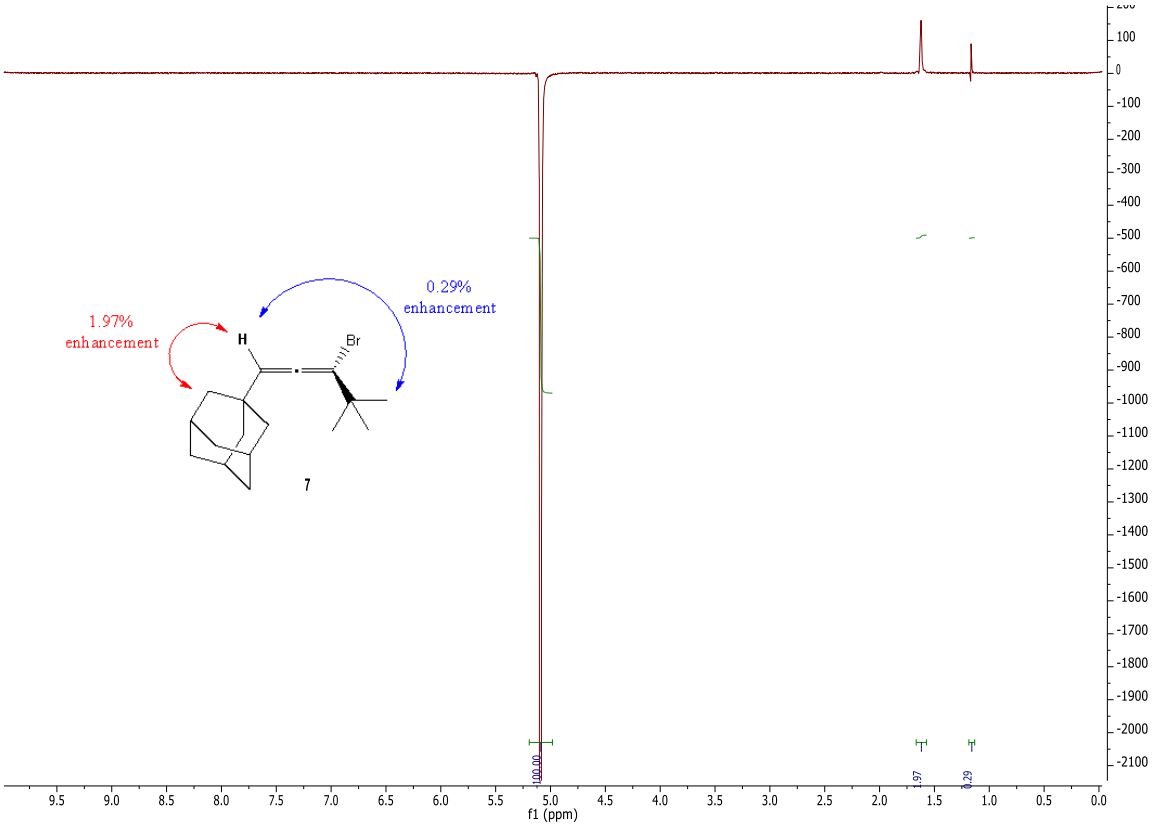
^{13}C NMR spectrum of 1-adamantan-1-yl-3-bromo-4,4-dimethyl-1,2-pentadiene (**7**) (100 MHz, $CDCl_3$)



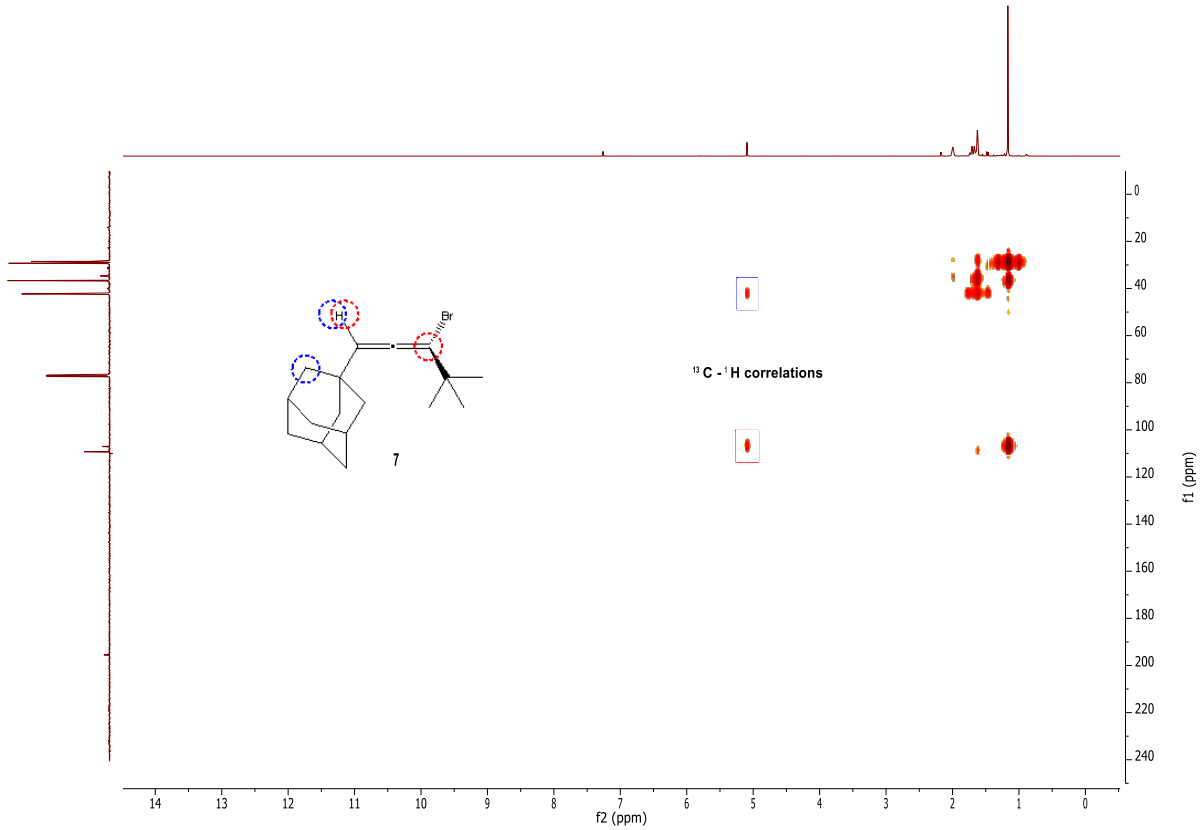
DEPT-135 spectrum of 1-adamantan-1-yl-3-bromo-4,4-dimethyl-1,2-pentadiene (**7**) (100 MHz, $CDCl_3$)



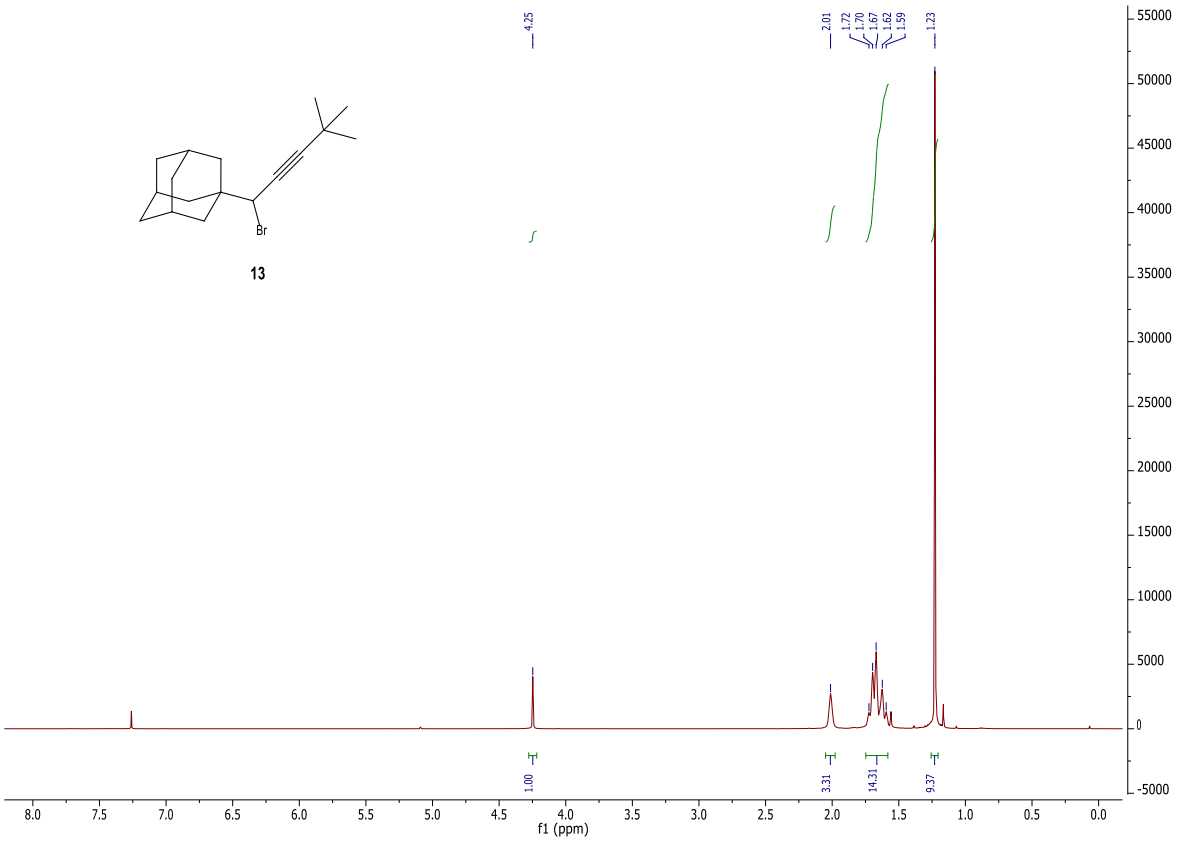
Selective (5.09 ppm) NOE spectrum of 1-adamantan-1-yl-3-bromo-4,4-dimethyl-1,2-pentadiene (**7**) (400 MHz, $CDCl_3$)



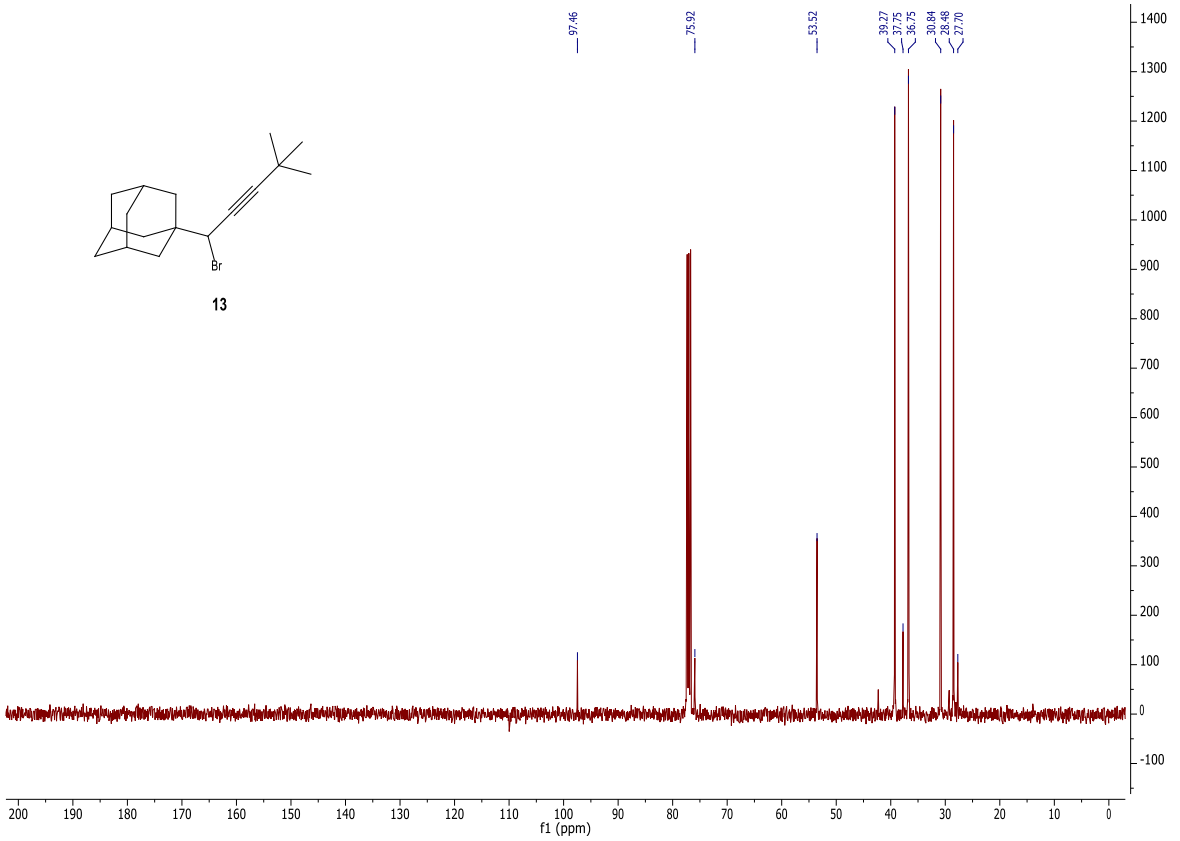
HMBC spectrum of 1-adamantan-1-yl-3-bromo-4,4-dimethyl-1,2-pentadiene (**7**) (400 MHz, $CDCl_3$)



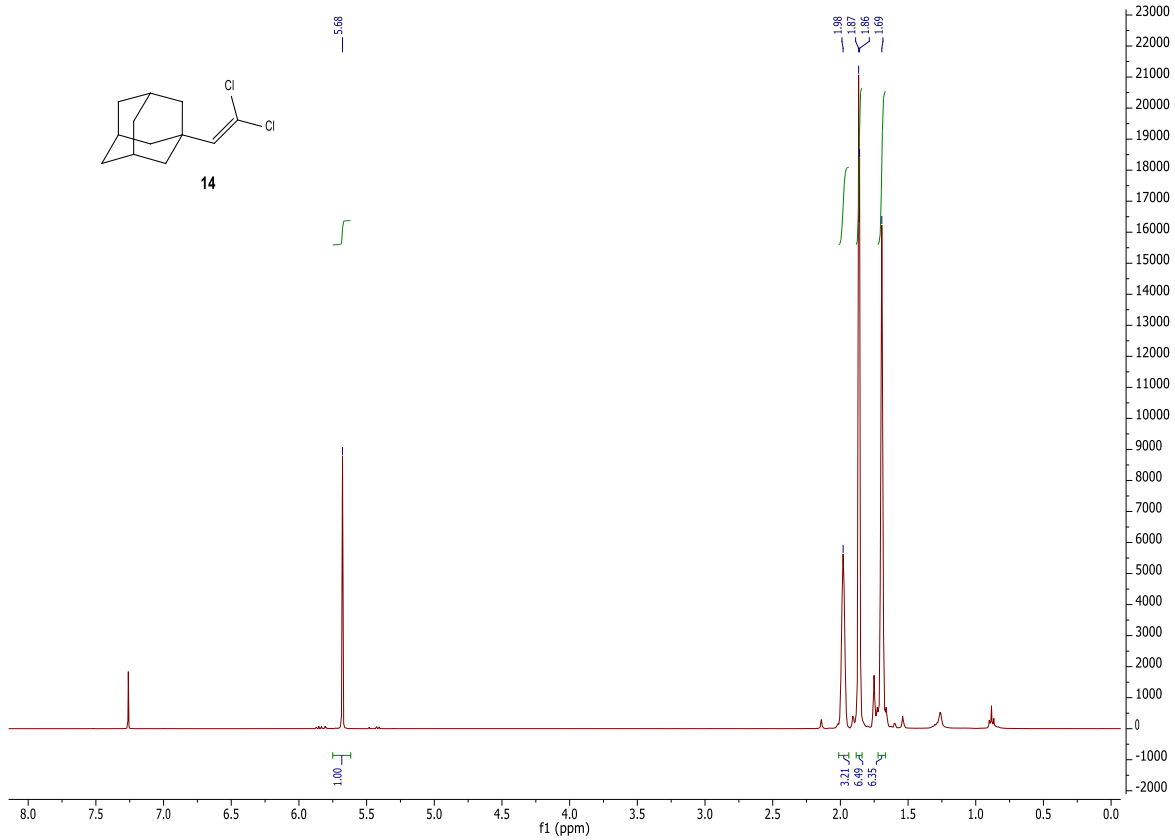
^{1}H NMR spectrum of 1-adamantan-1-yl-1-bromo-4,4-dimethyl-2-pentyne (**13**) (400 MHz, $CDCl_3$)



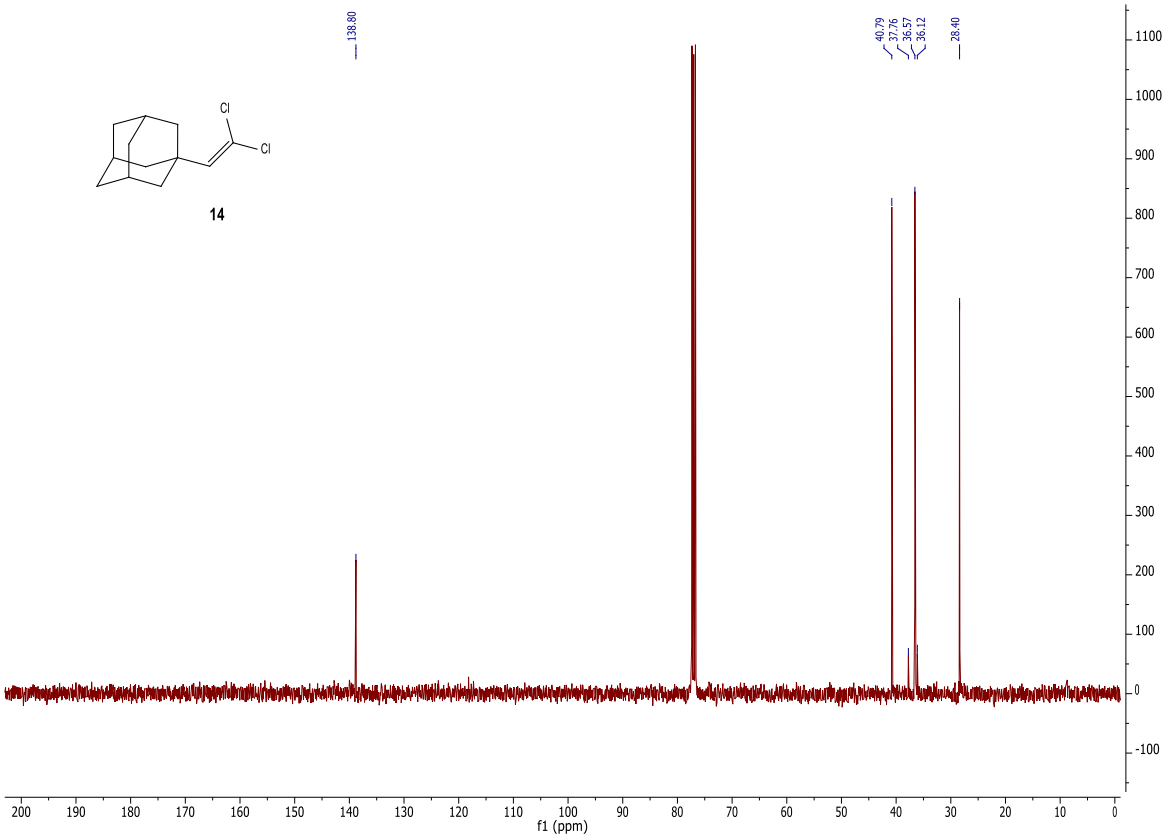
^{13}C NMR spectrum of 1-adamantan-1-yl-1-bromo-4,4-dimethyl-2-pentyne (**13**) (100 MHz, $CDCl_3$)



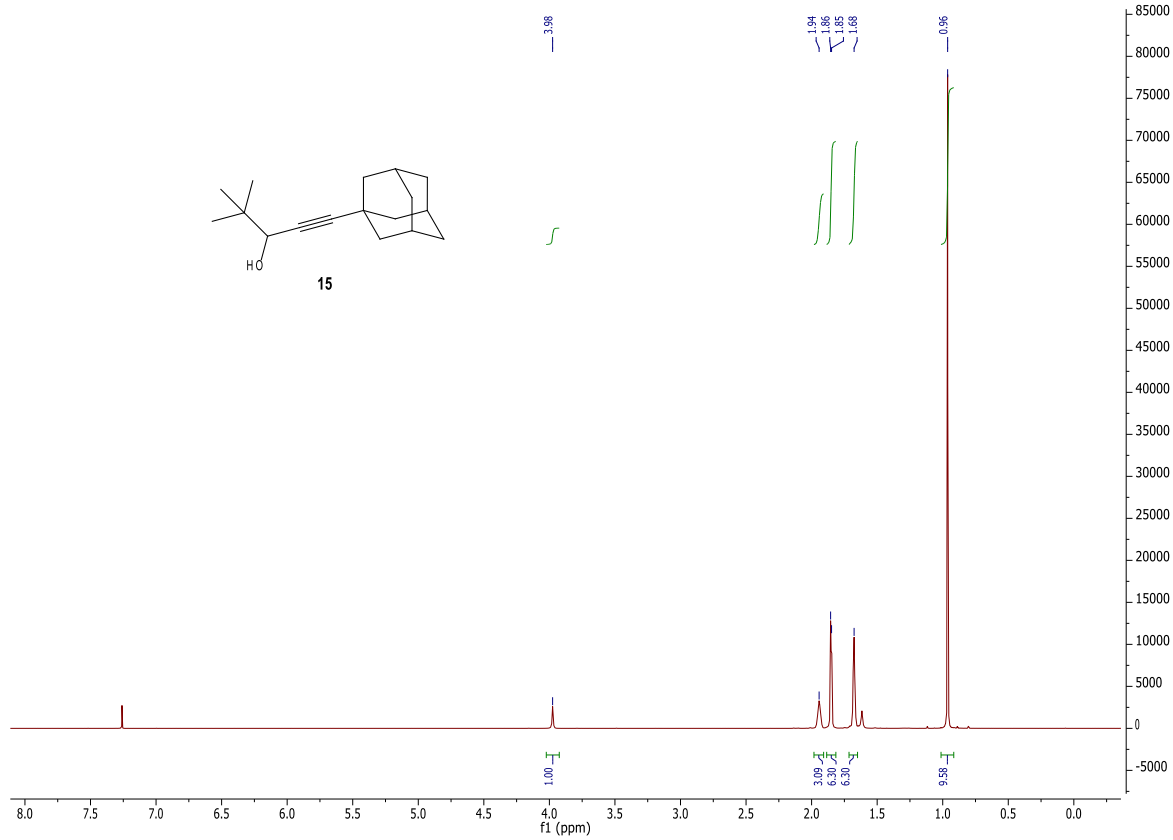
^{1}H NMR spectrum of 1-adamantan-1-yl-2,2-dichloroethene (**14**) (400 MHz, $CDCl_3$)



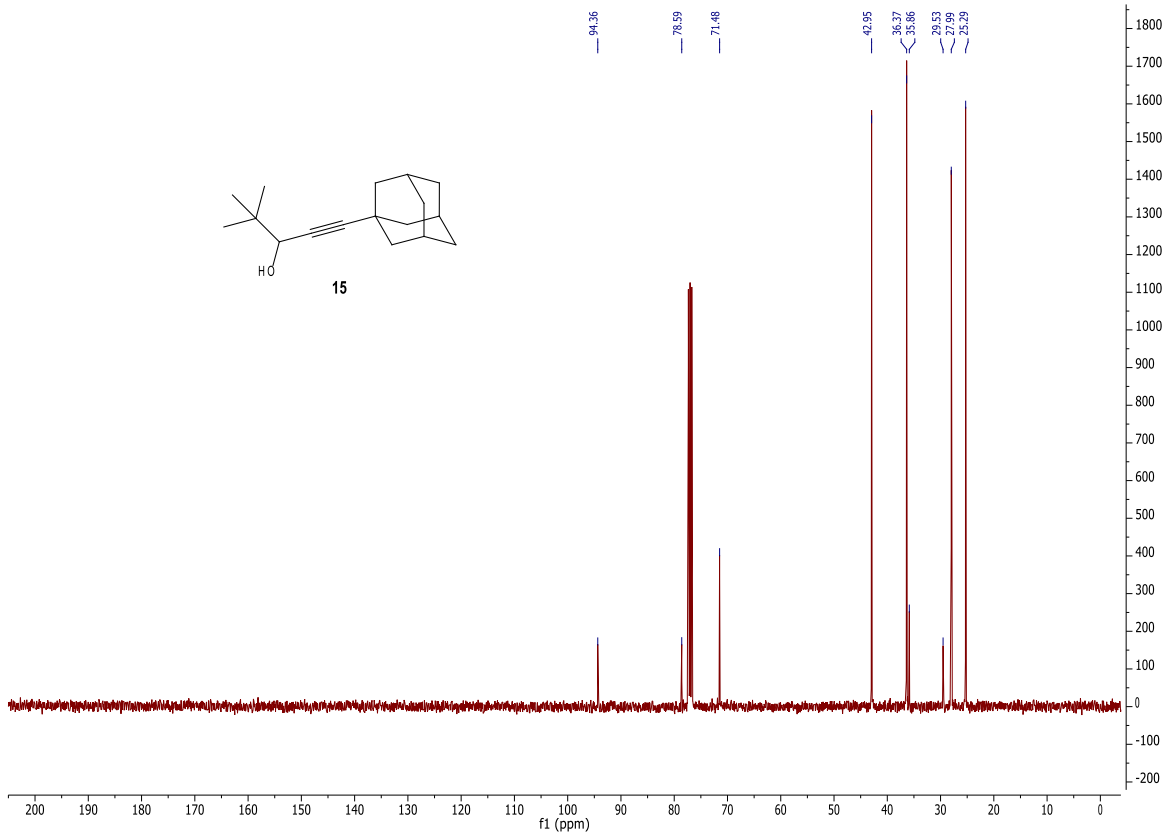
^{13}C NMR spectrum of 1-adamantan-1-yl-2,2-dichloroethene (**14**) (100 MHz, $CDCl_3$)



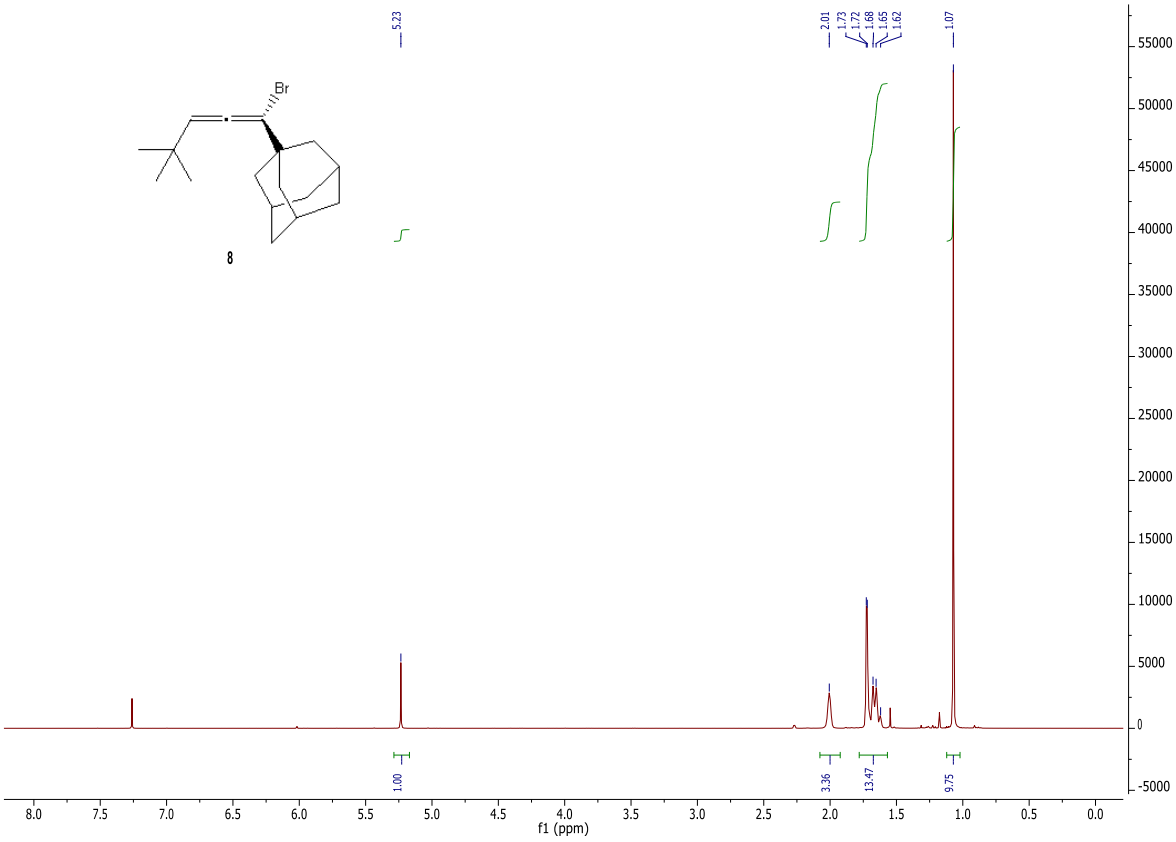
^{1}H NMR spectrum of 1-adamantan-1-yl-4,4-dimethyl-1-pentyn-3-ol (**15**) (400 MHz, $CDCl_3$)



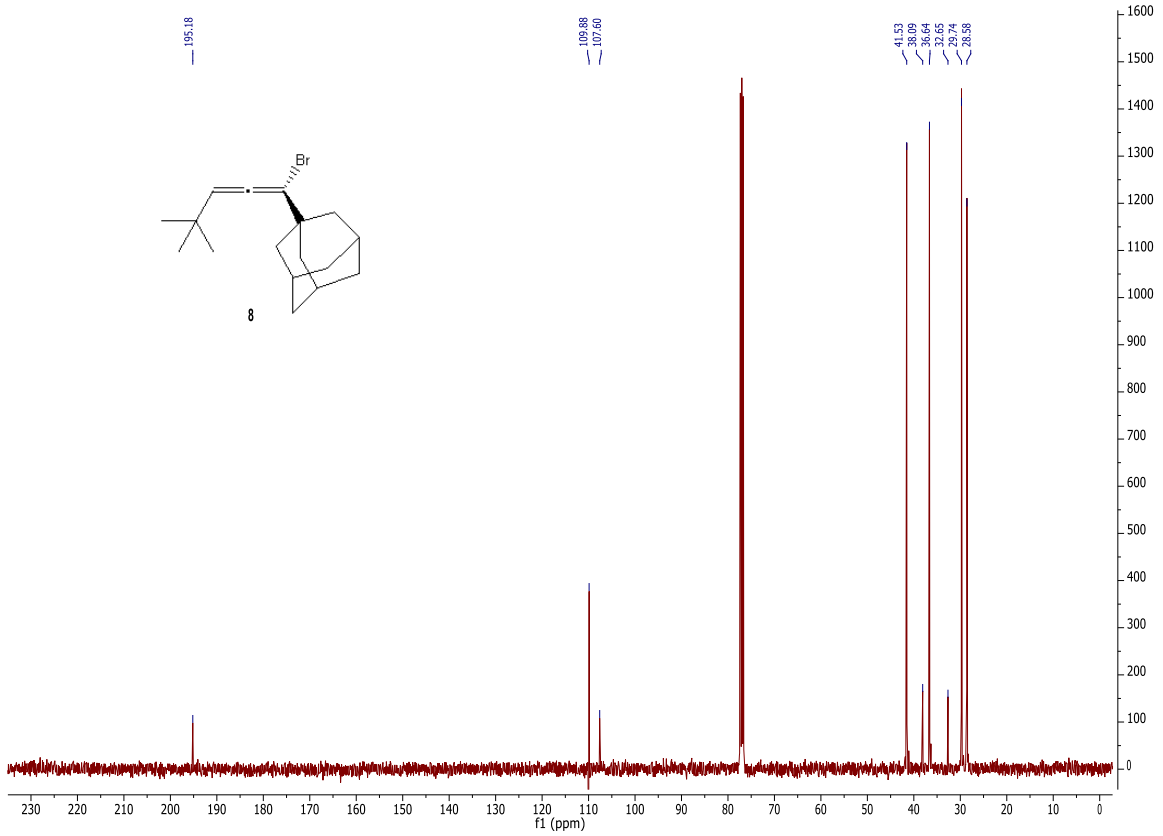
^{13}C NMR spectrum of 1-adamantan-1-yl-4,4-dimethyl-1-pentyn-3-ol (**15**) (100 MHz, $CDCl_3$)



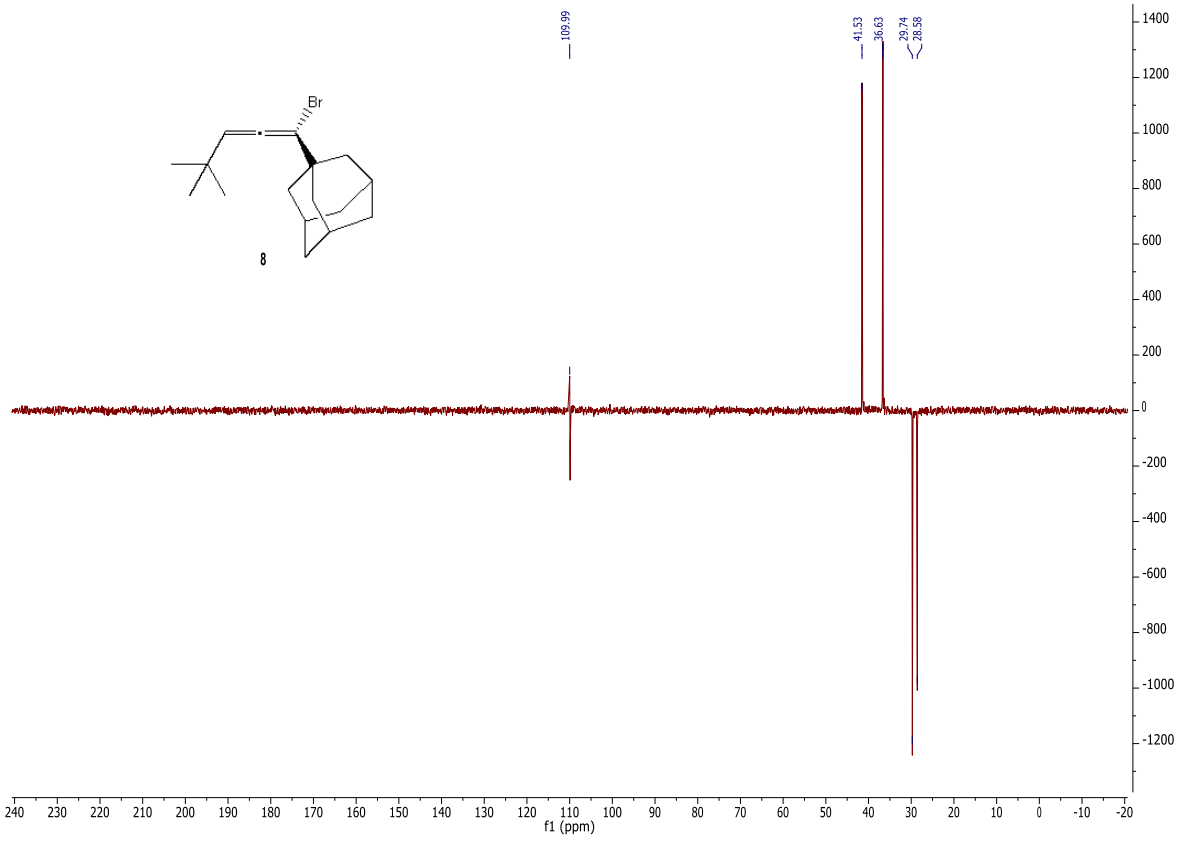
^{1}H NMR spectrum of 1-adamantan-1-yl-1-bromo-4,4-dimethyl-1,2-pentadiene (**8**) (400 MHz, $CDCl_3$)



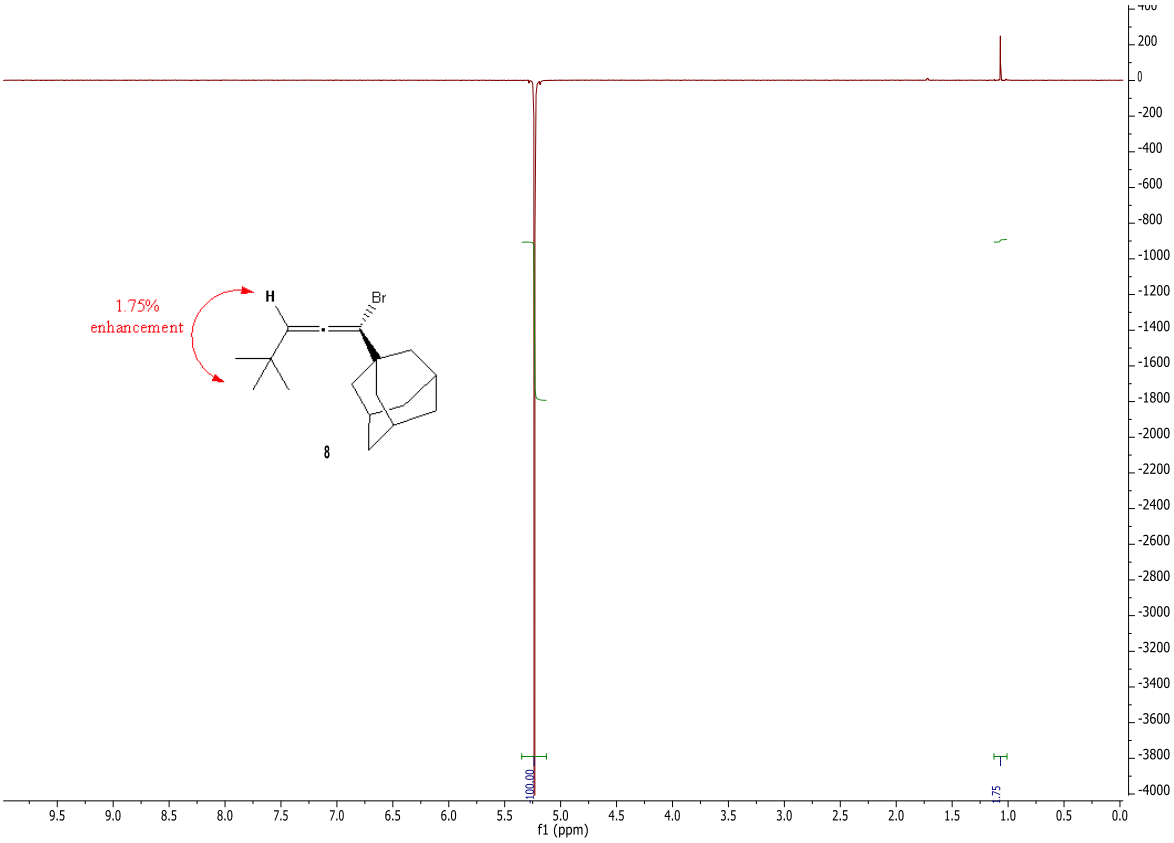
^{13}C NMR spectrum of 1-adamantan-1-yl-1-bromo-4,4-dimethyl-1,2-pentadiene (**8**) (100 MHz, $CDCl_3$)



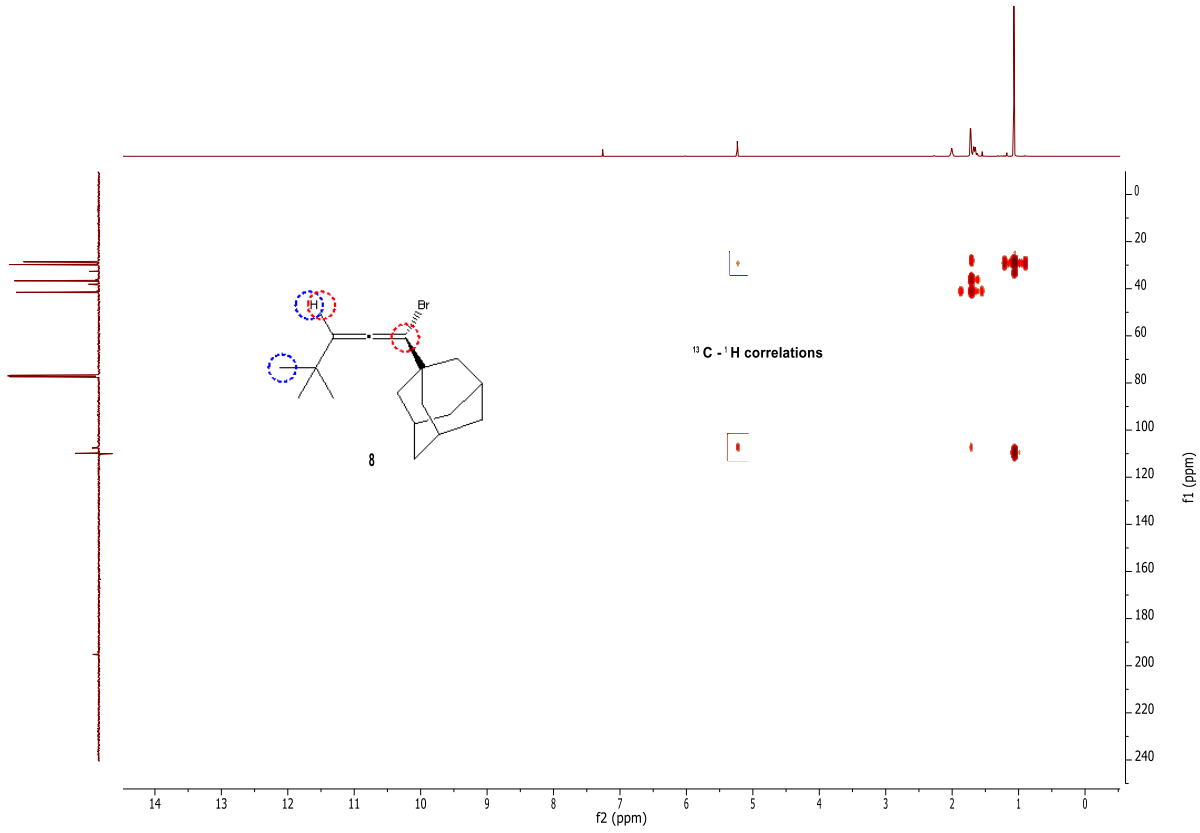
DEPT-135 spectrum of 1-adamantan-1-yl-1-bromo-4,4-dimethyl-1,2-pentadiene (**8**) (100 MHz, $CDCl_3$)



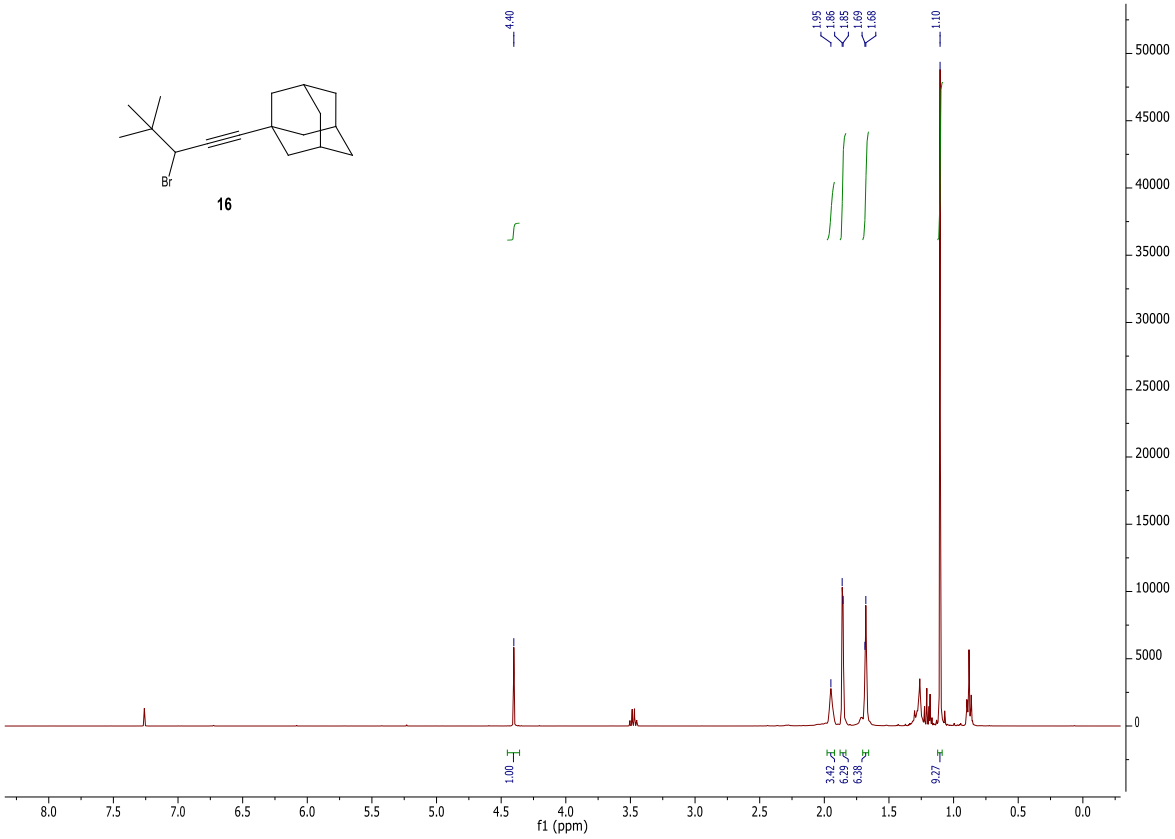
Selective (5.23 ppm) NOE spectrum of 1-adamantan-1-yl-1-bromo-4,4-dimethyl-1,2-pentadiene (**8**) (400 MHz, $CDCl_3$)



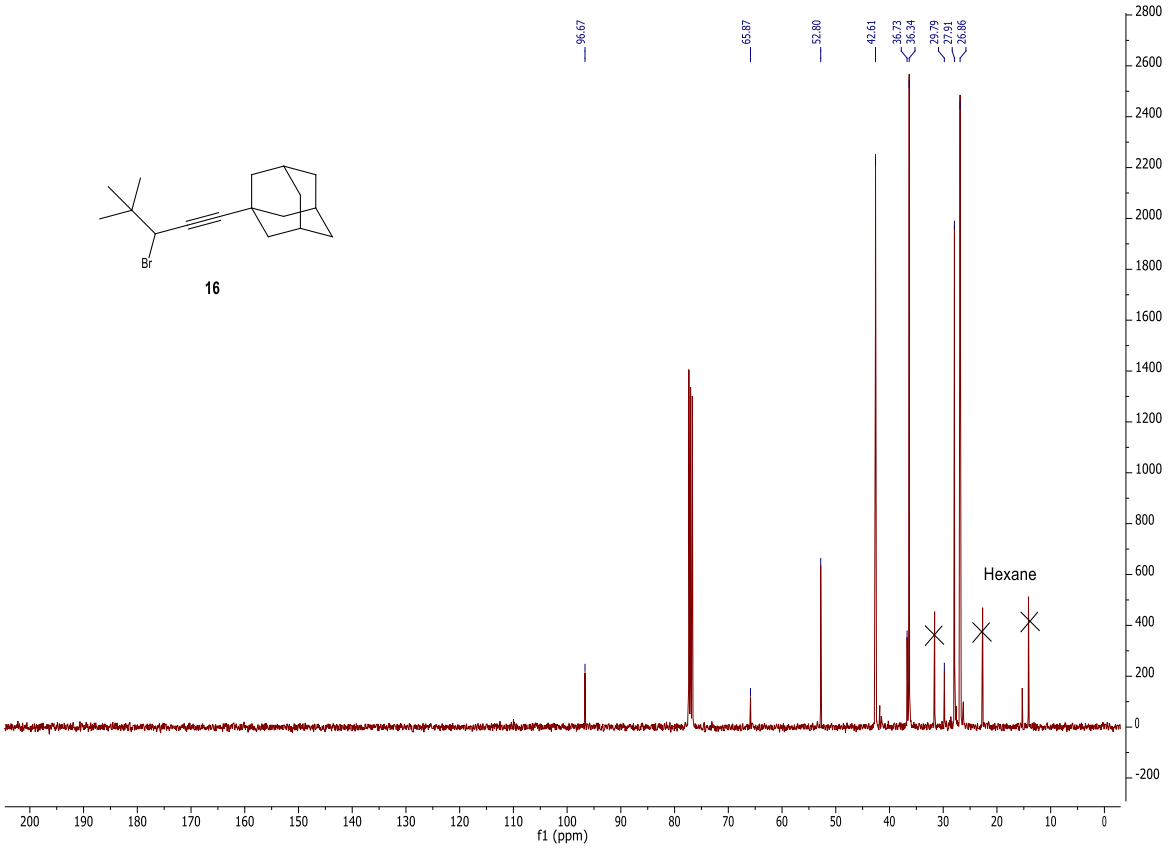
HMBC spectrum of 1-adamantan-1-yl-1-bromo-4,4-dimethyl-1,2-pentadiene (**8**) (400 MHz, $CDCl_3$)



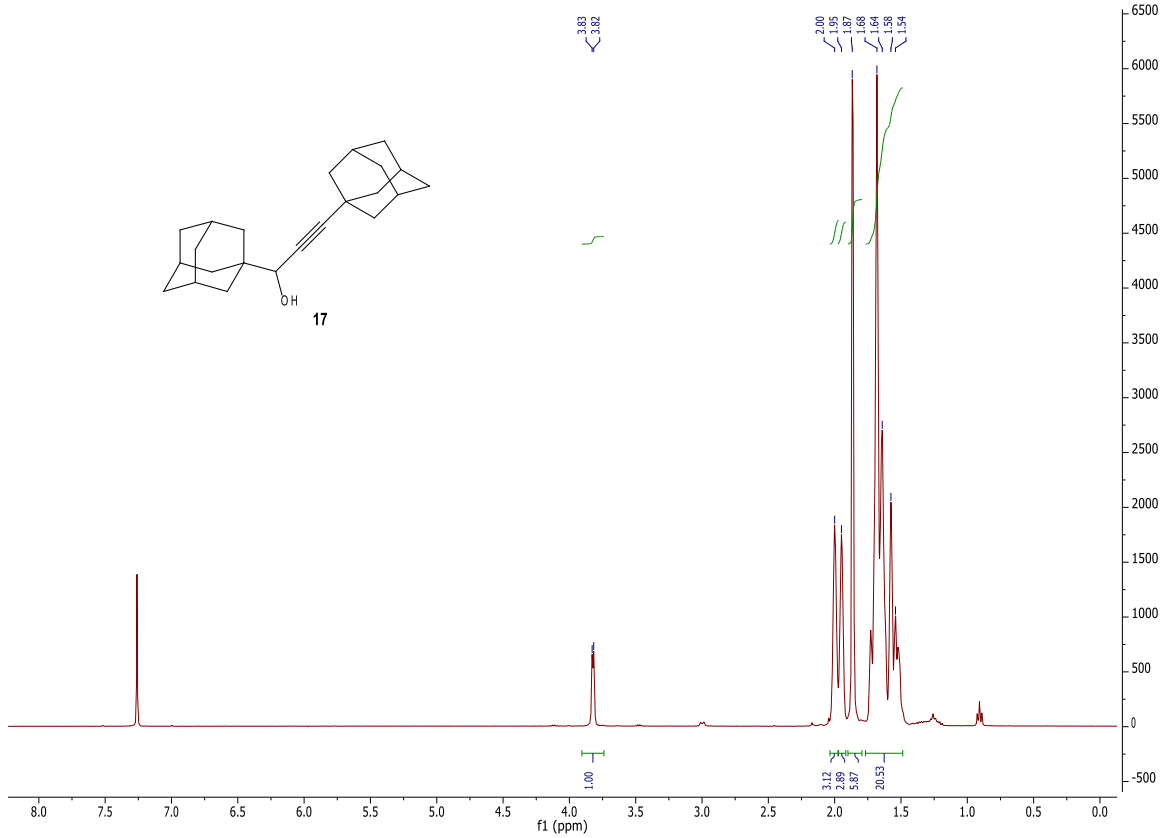
^{1}H NMR spectrum of 1-adamantan-1-yl-3-bromo-4,4-dimethyl-1-pentyne (**16**) (400 MHz, $CDCl_3$)



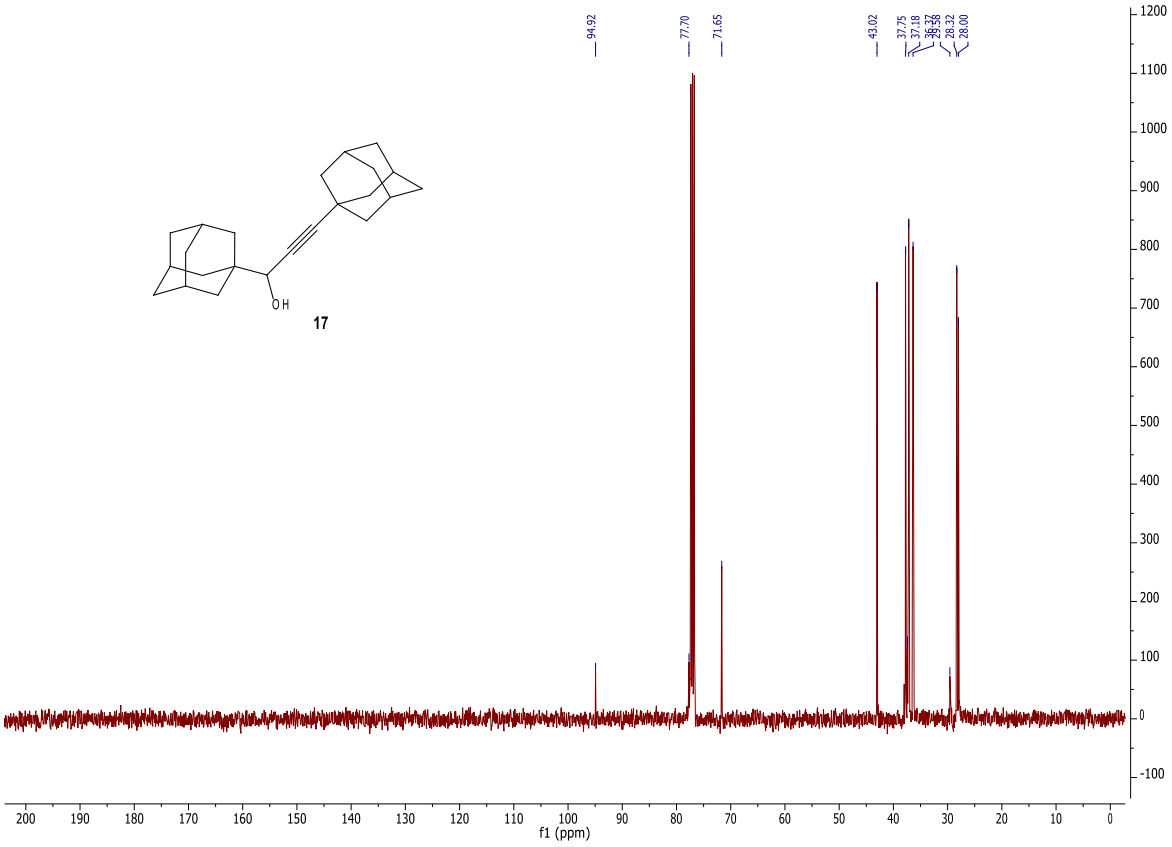
^{13}C NMR spectrum of 1-adamantan-1-yl-3-bromo-4,4-dimethyl-1-pentyne (**16**) (100 MHz, $CDCl_3$)



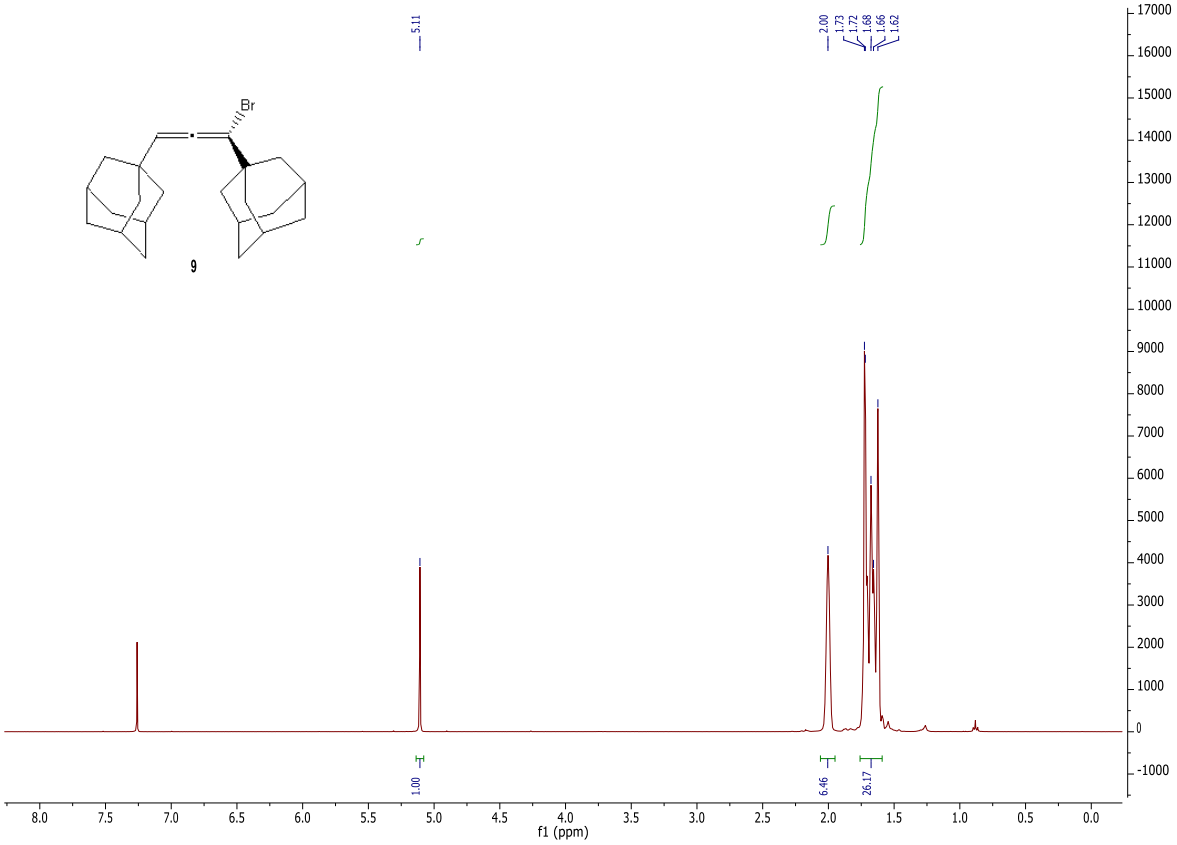
^{1}H NMR spectrum of 1,3-diadamantan-1-yl-2-propyn-1-ol (**17**) (400 MHz, $CDCl_3$)



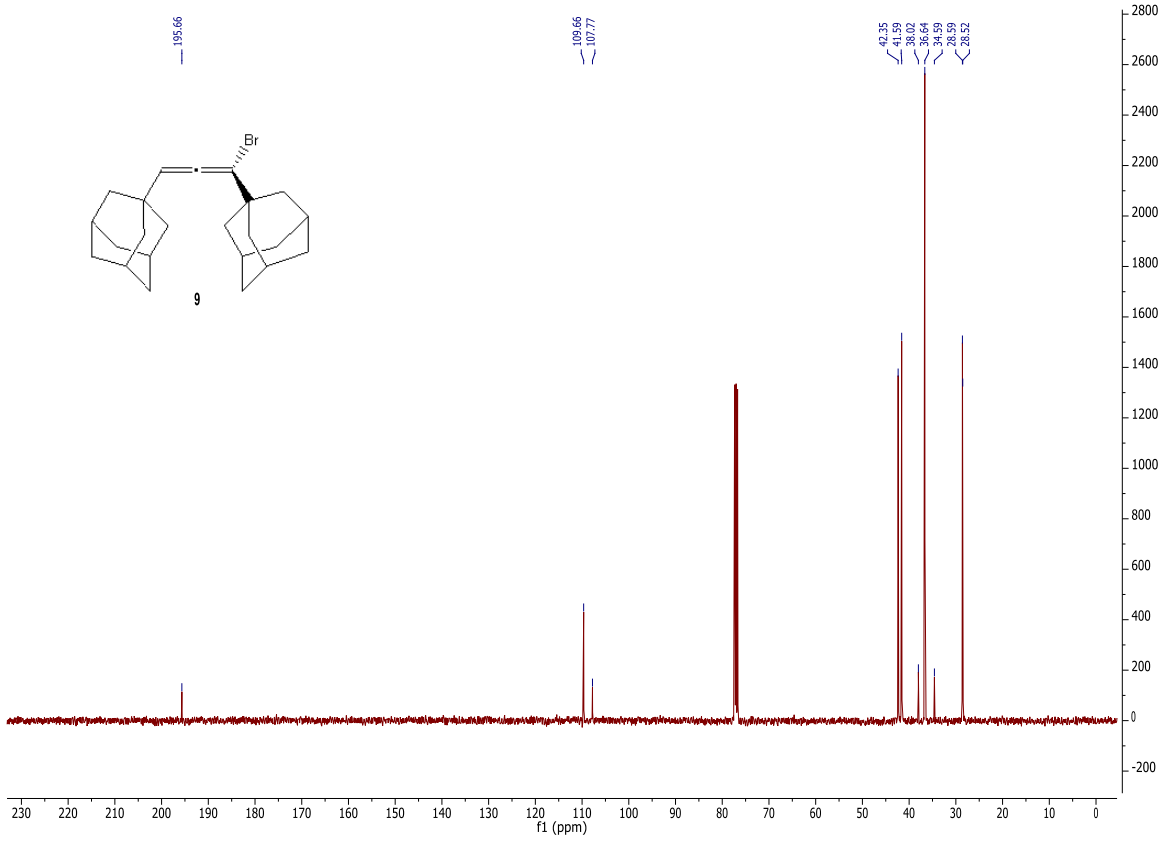
^{13}C NMR spectrum of 1,3-diadamantan-1-yl-2-propyn-1-ol (**17**) (100 MHz, $CDCl_3$)



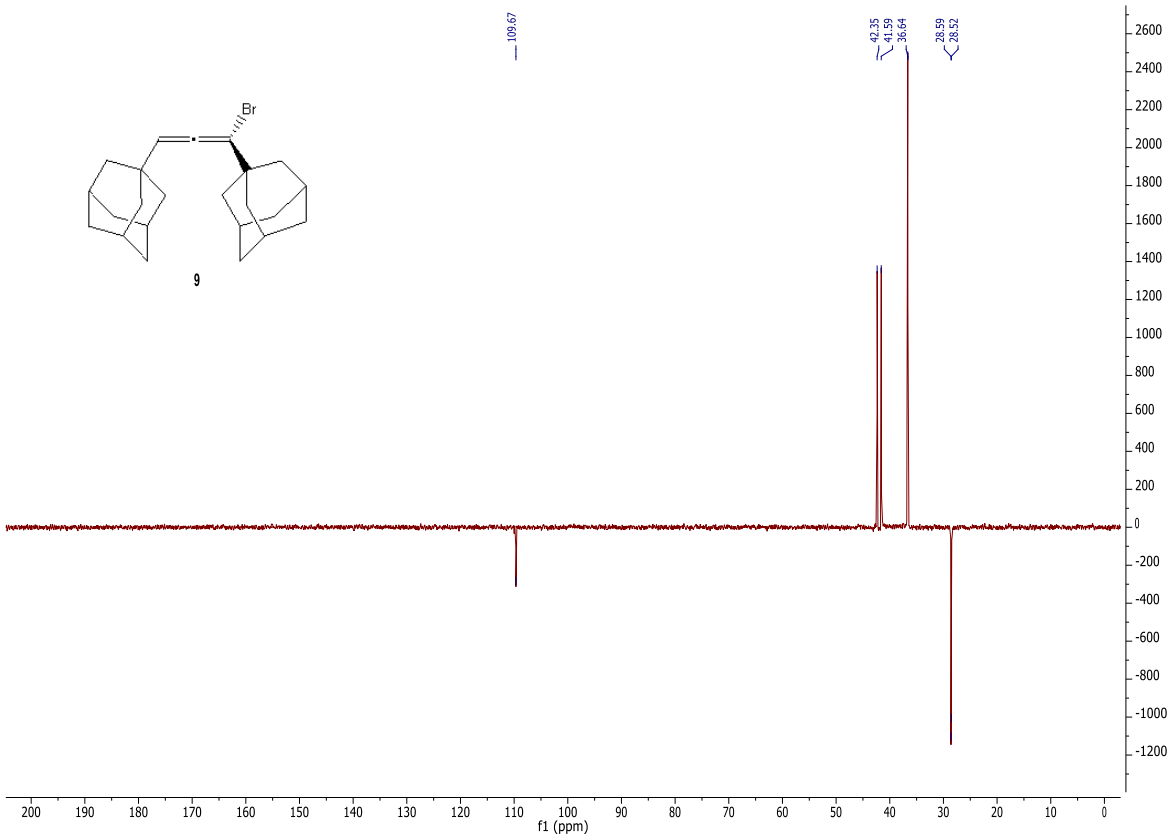
^{1}H NMR spectrum of 1,3-diadamantan-1-yl-1-bromo-1,2-propadiene (**9**) (400 MHz, $CDCl_3$)



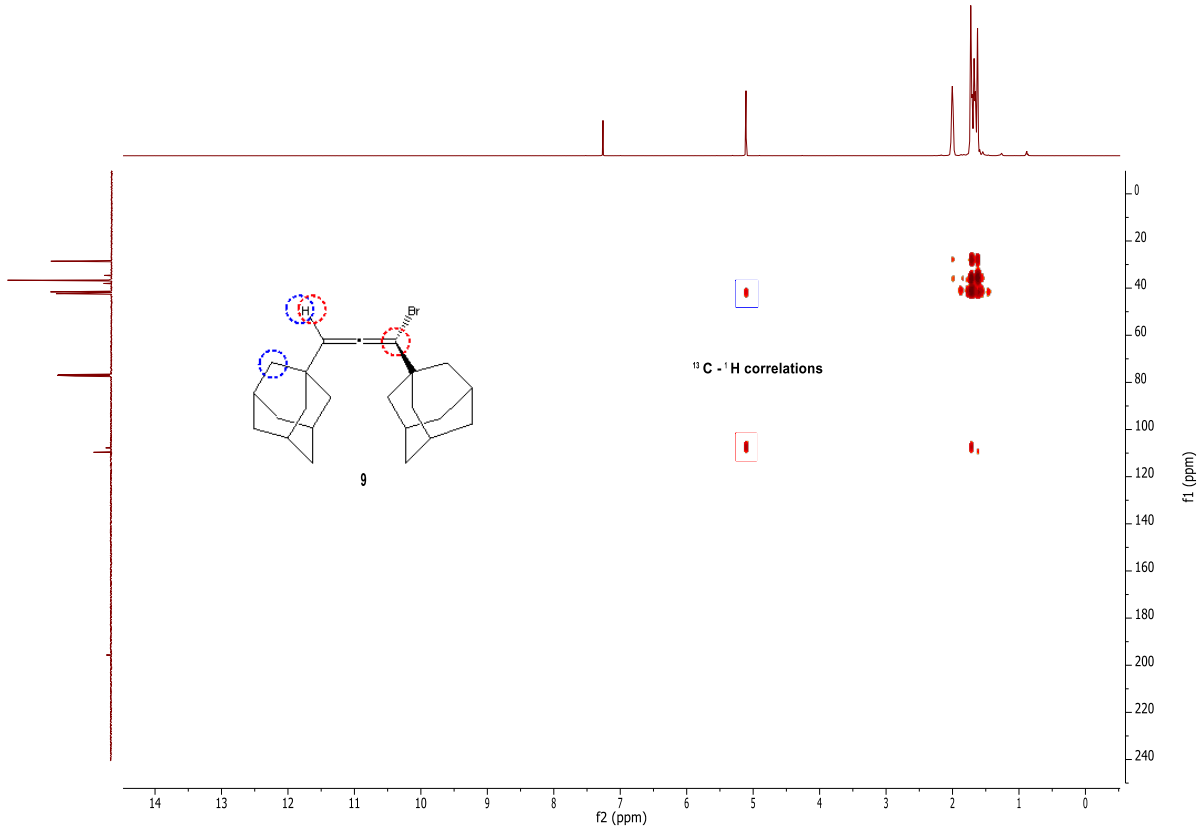
^{13}C NMR spectrum of 1,3-diadamantan-1-yl-1-bromo-1,2-propadiene (**9**) (100 MHz, $CDCl_3$)



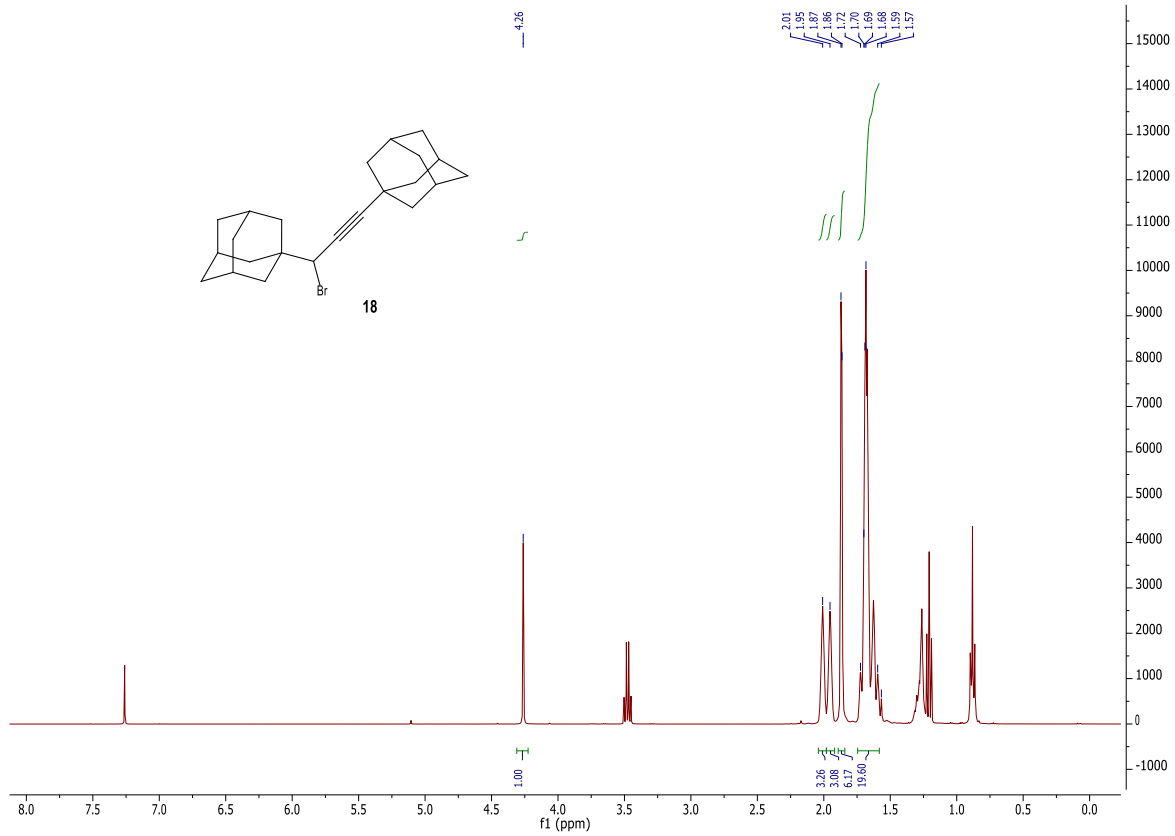
DEPT-135 spectrum of 1,3-diadamantan-1-yl-1-bromo-1,2-propadiene (**9**) (100 MHz, $CDCl_3$)



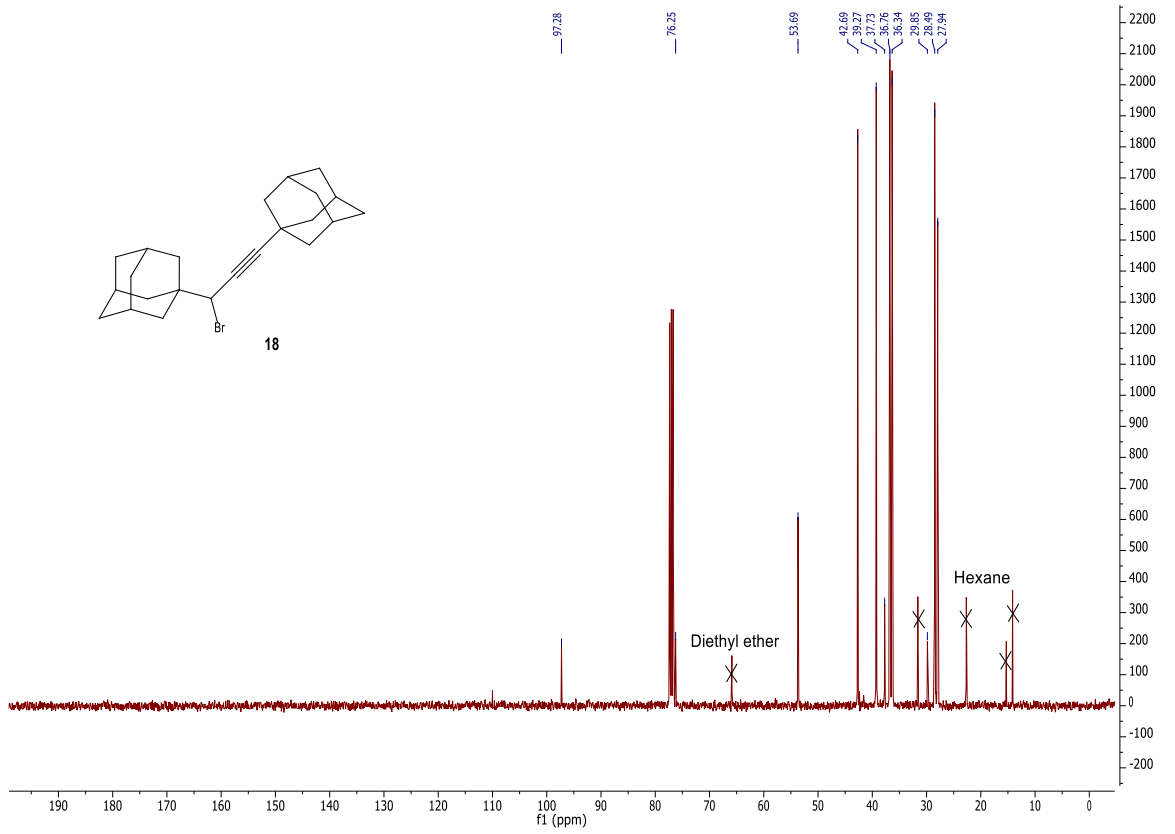
HMBC spectrum of 1,3-diadamantan-1-yl-1-bromo-1,2-propadiene (**9**) (400 MHz, $CDCl_3$)



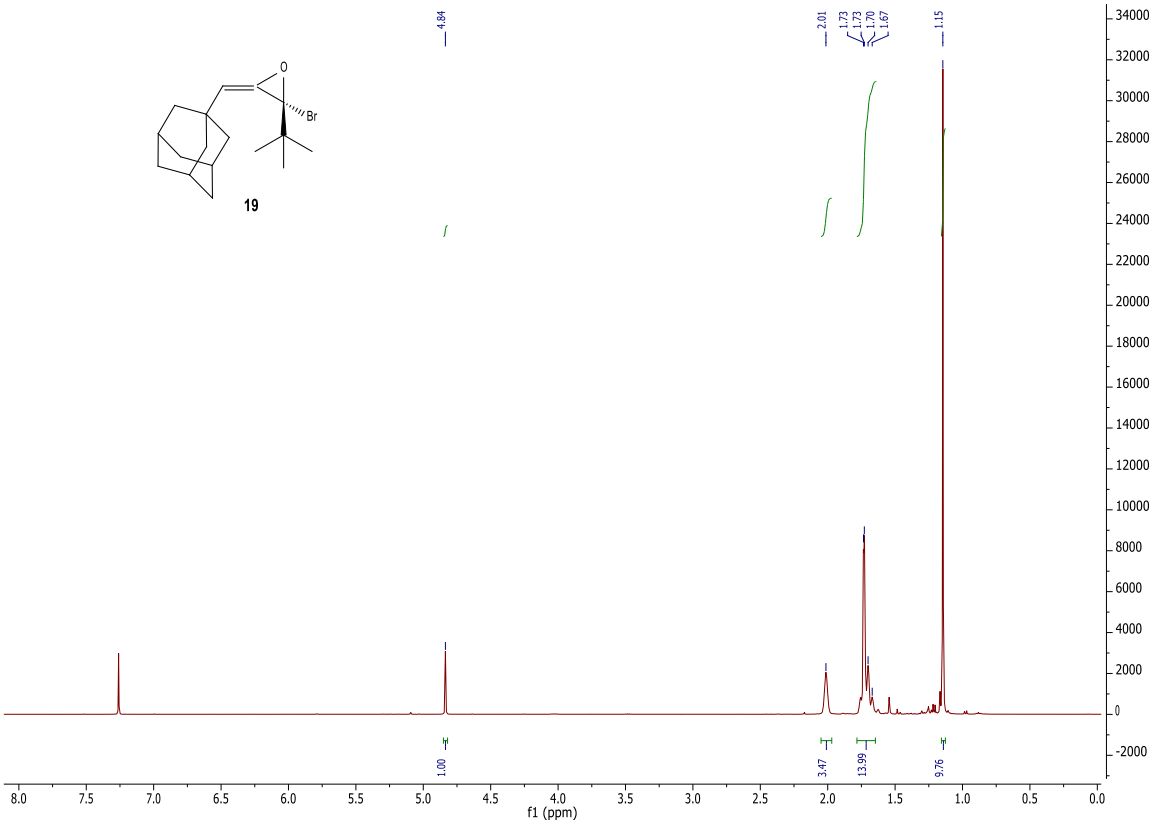
^{1}H NMR spectrum of 1,3-diadamantan-1-yl-3-bromo-1-propyne (**18**) (400 MHz, $CDCl_3$)



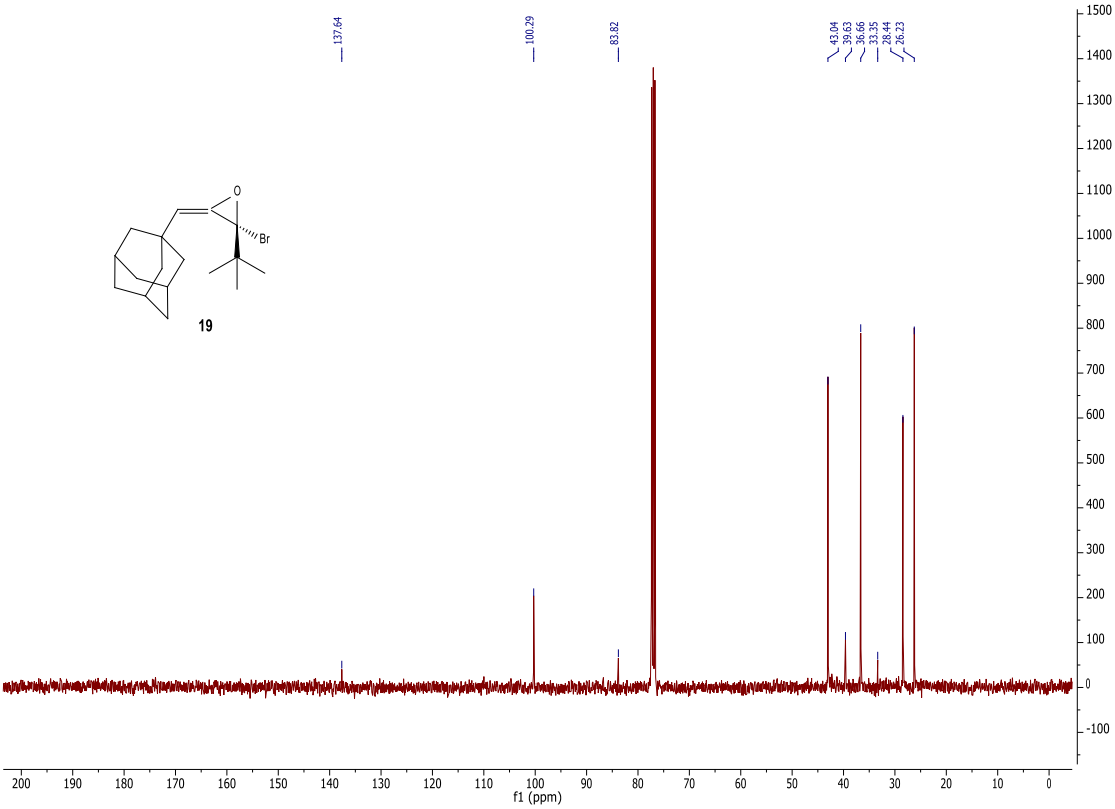
^{13}C NMR spectrum of 1,3-diadamantan-1-yl-3-bromo-1-propyne (**18**) (100 MHz, $CDCl_3$)



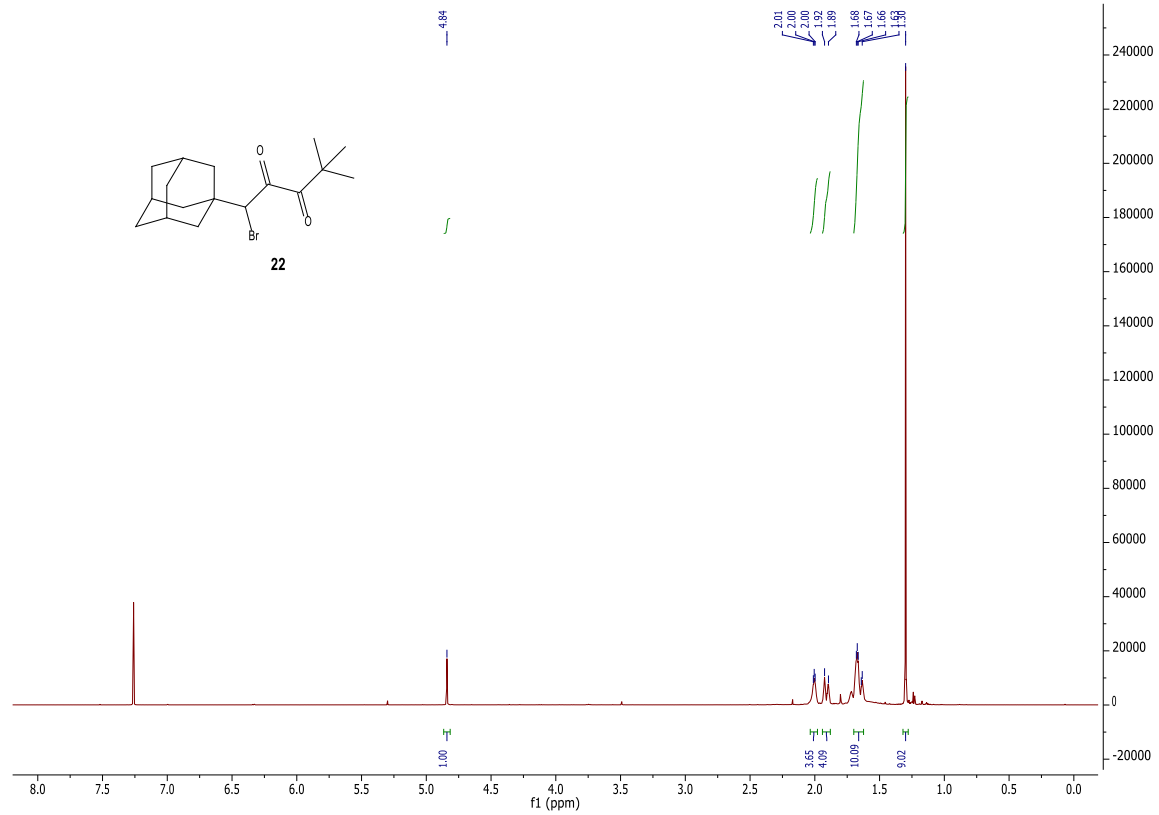
^{1}H NMR spectrum of *E*-1-adamantan-1-yl-3-bromo-2,3-epoxy-4,4-dimethyl-1-pentene (**19**) (400 MHz, $CDCl_3$)



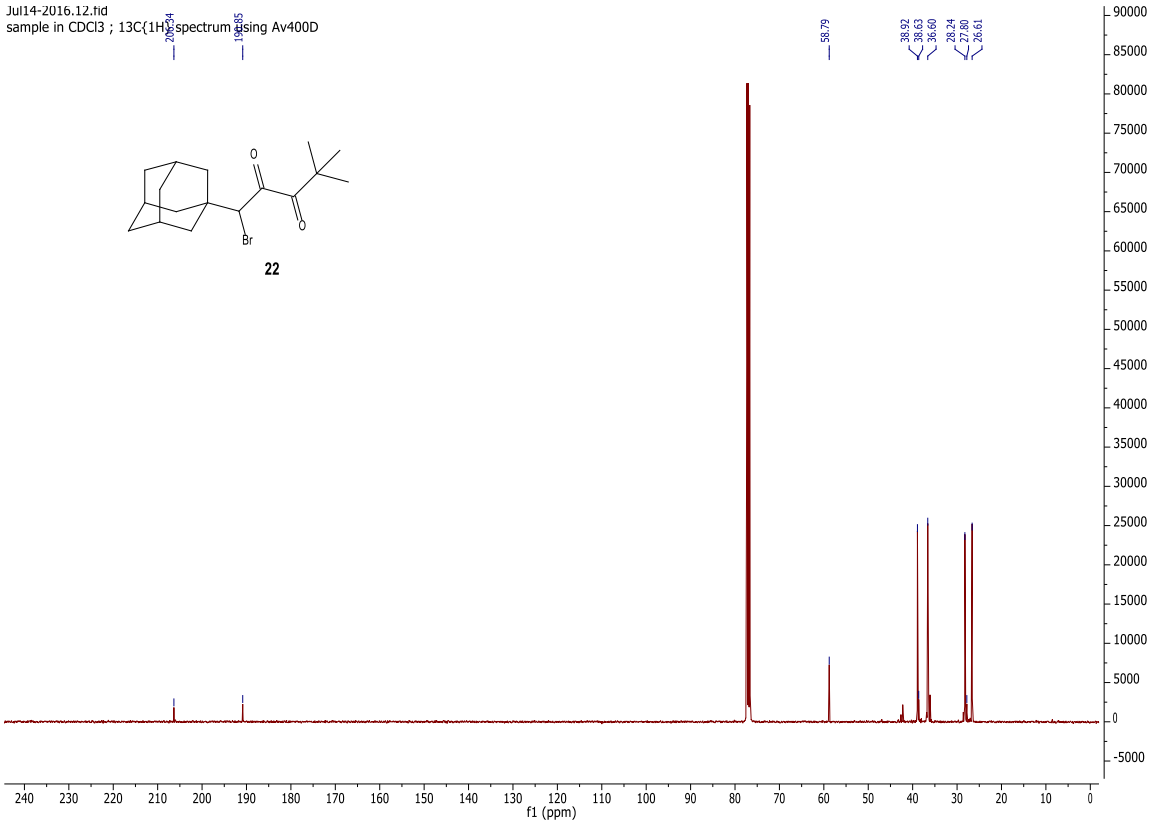
^{13}C NMR spectrum of *E*-1-adamantan-1-yl-3-bromo-2,3-epoxy-4,4-dimethyl-1-pentene (**19**) (100 MHz, $CDCl_3$)



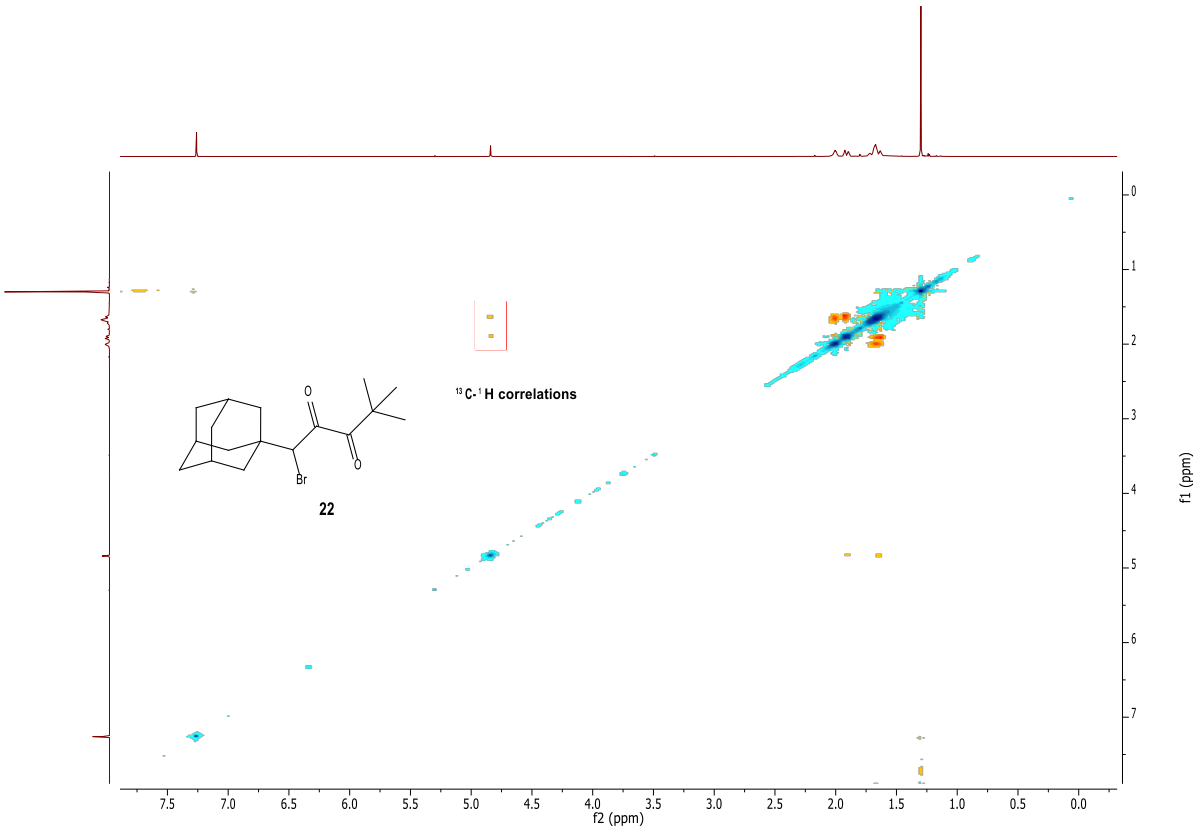
^{1}H NMR spectrum of 1-adamantan-1-yl-1-bromo-4,4-dimethyl-2,3-pentanedione (**22**) (400 MHz, $CDCl_3$)



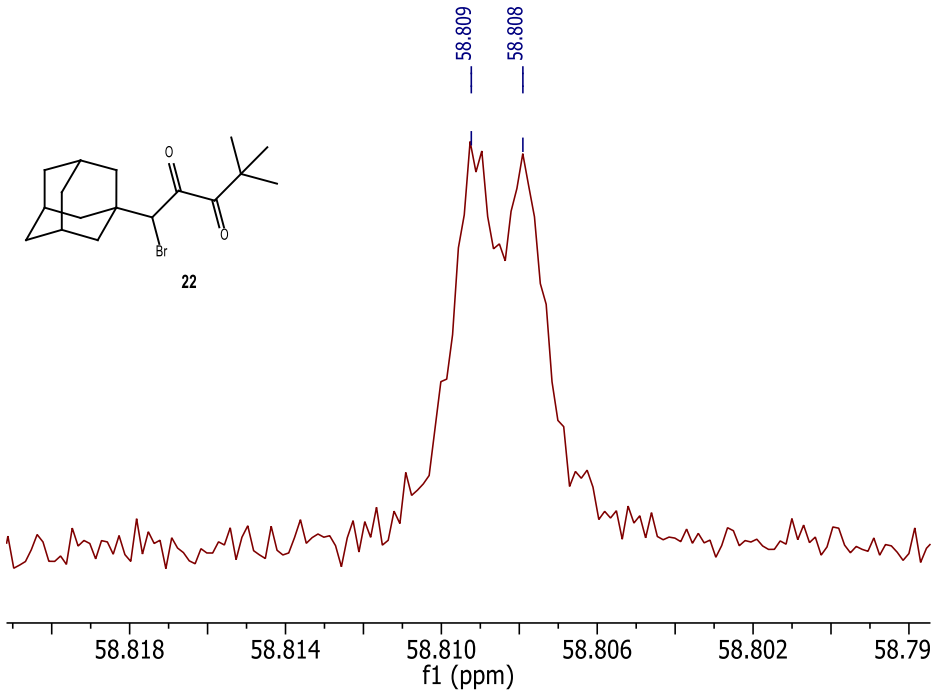
^{13}C NMR spectrum of 1-adamantan-1-yl-1-bromo-4,4-dimethyl-2,3-pentanedione (**22**) (100 MHz, $CDCl_3$)



NOESY spectrum of 1-adamantan-1-yl-1-bromo-4,4-dimethyl-2,3-pentanedione (**22**) (400 MHz, $CDCl_3$)

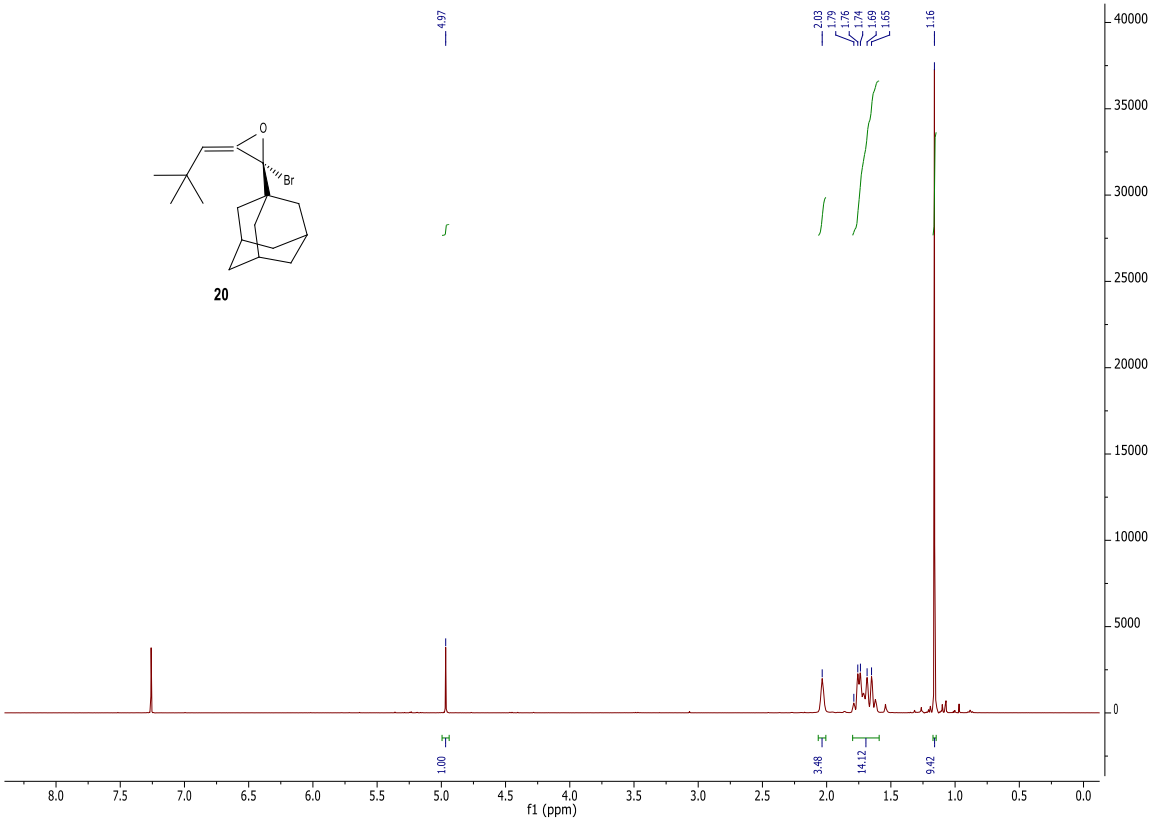


Bromine-induced isotopic shift in ^{13}C NMR spectrum of 1-adamantan-1-yl-1-bromo-4,4-dimethyl-2,3-pentanedione (**22**) (125 MHz, $CDCl_3$)[5]

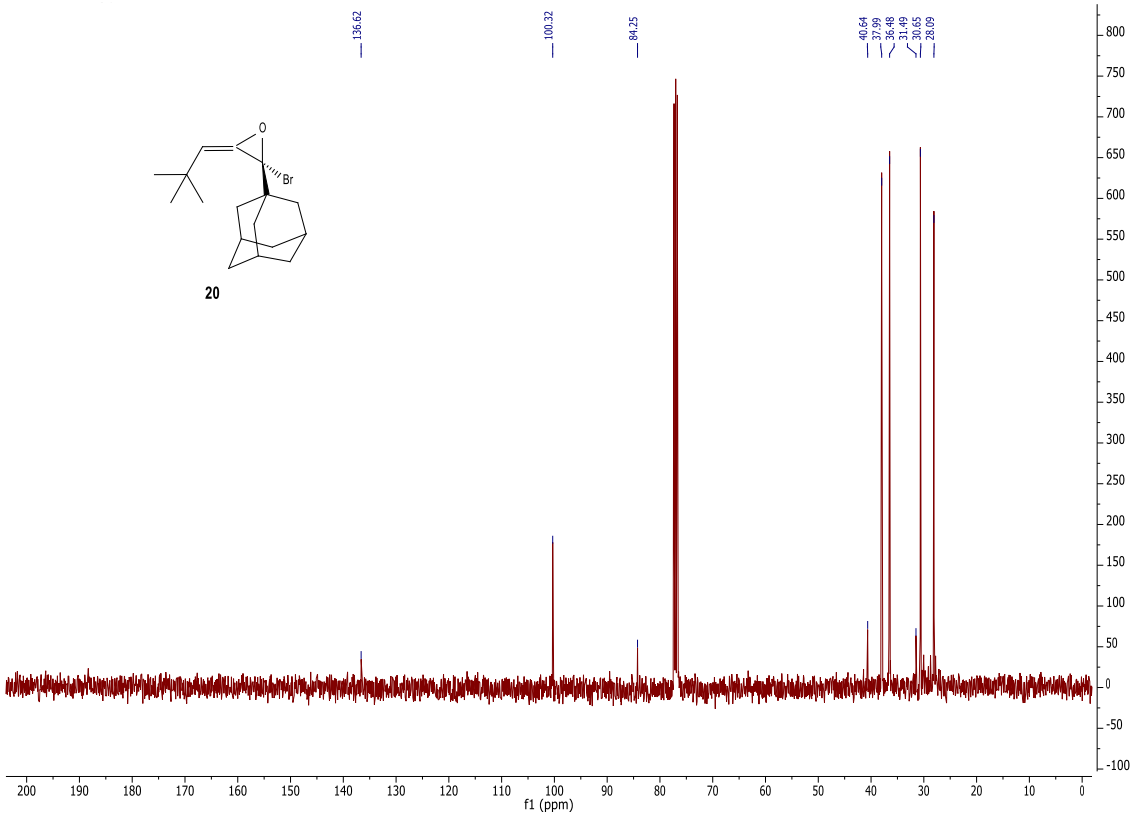


δ 58.8 (CBr) ppm; Δδ ($C^{79}Br$, $C^{81}Br$) = 1.6 ppb

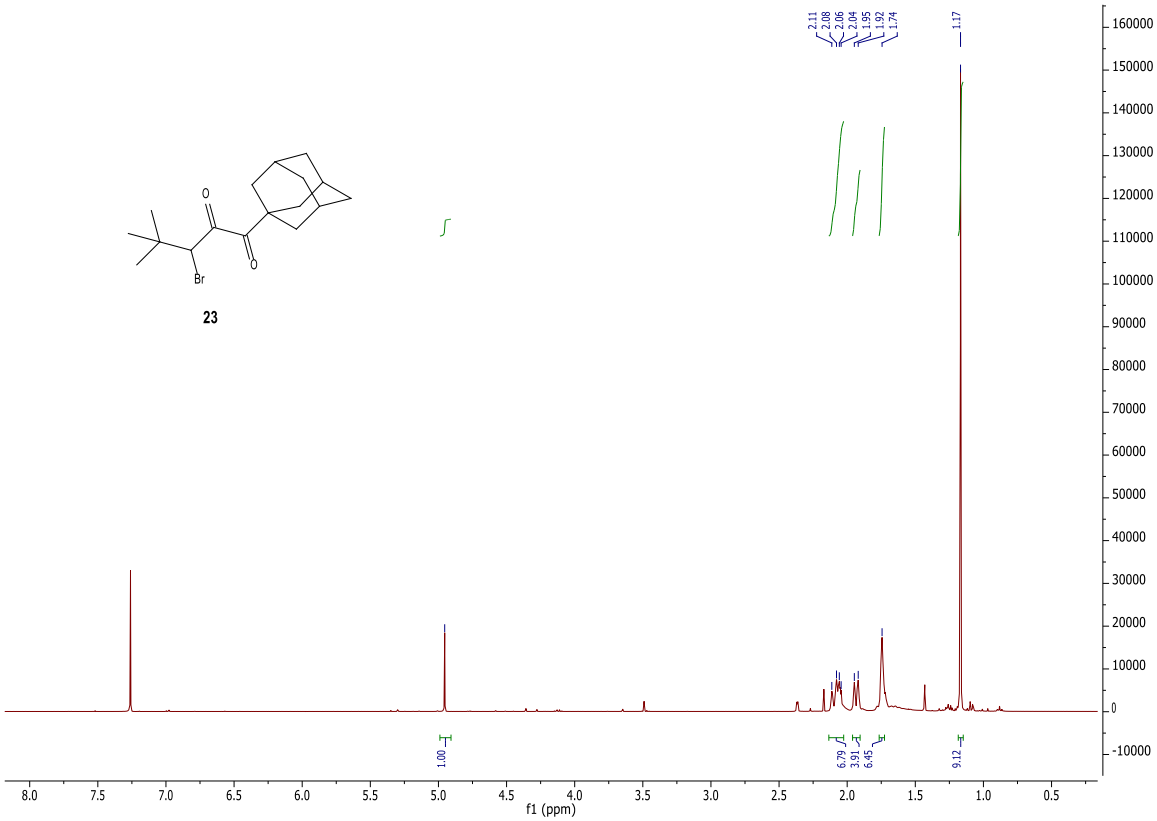
^{1}H NMR spectrum of *E*-1-adamantan-1-yl-1-bromo-1,2-epoxy-4,4-dimethyl-2-pentene (**20**) (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of *E*-1-adamantan-1-yl-1-bromo-1,2-epoxy-4,4-dimethyl-2-pentene (**20**) (100 MHz, $CDCl_3$)

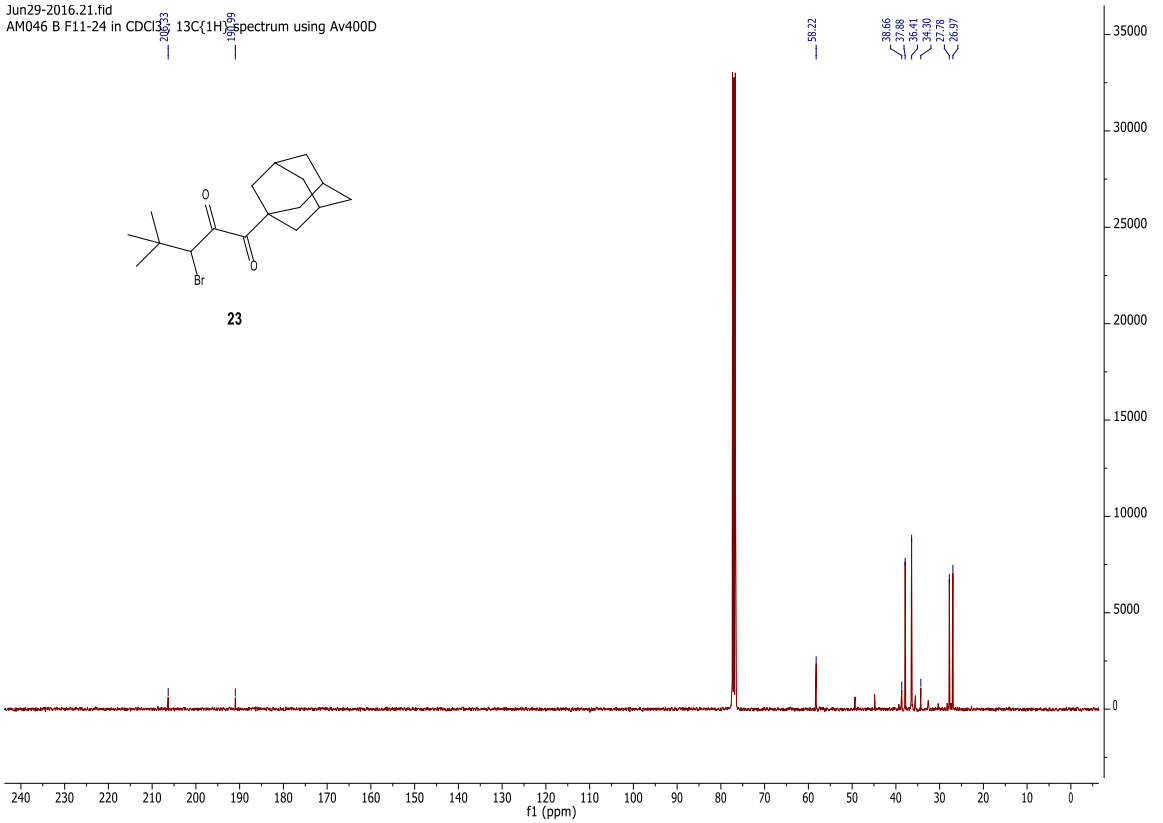


^{1}H NMR spectrum of 1-adamantan-1-yl-3-bromo-4,4-dimethyl-1,2-pentanedione (**23**) (400 MHz, $CDCl_3$)



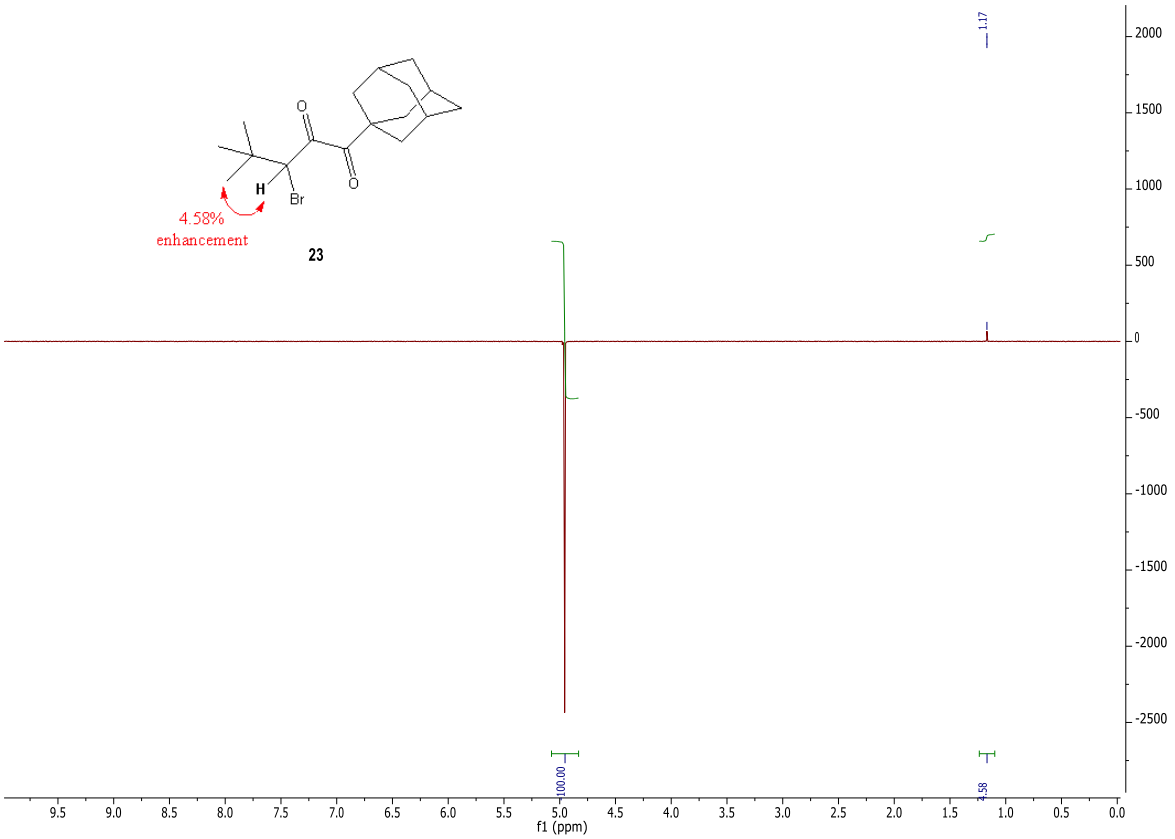
23

^{13}C NMR spectrum of 1-adamantan-1-yl-3-bromo-4,4-dimethyl-1,2-pentanedione (**23**) (100 MHz, $CDCl_3$)

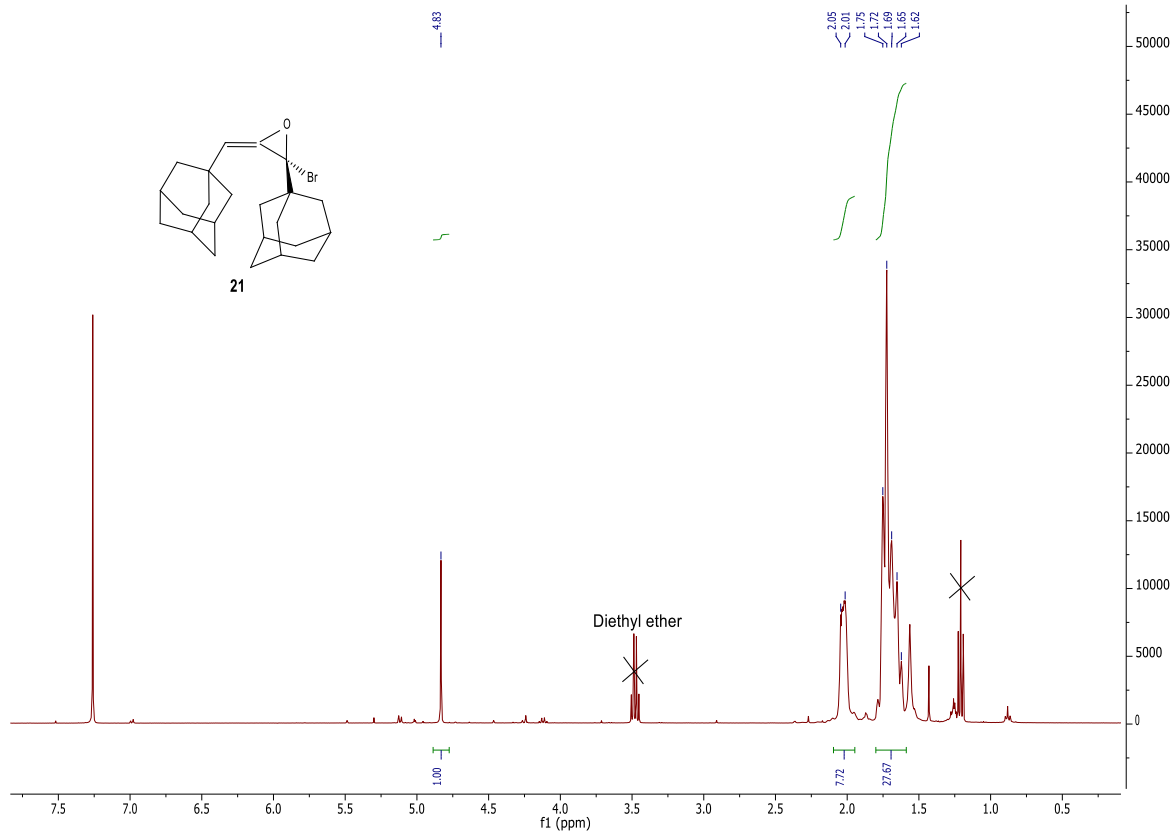


23

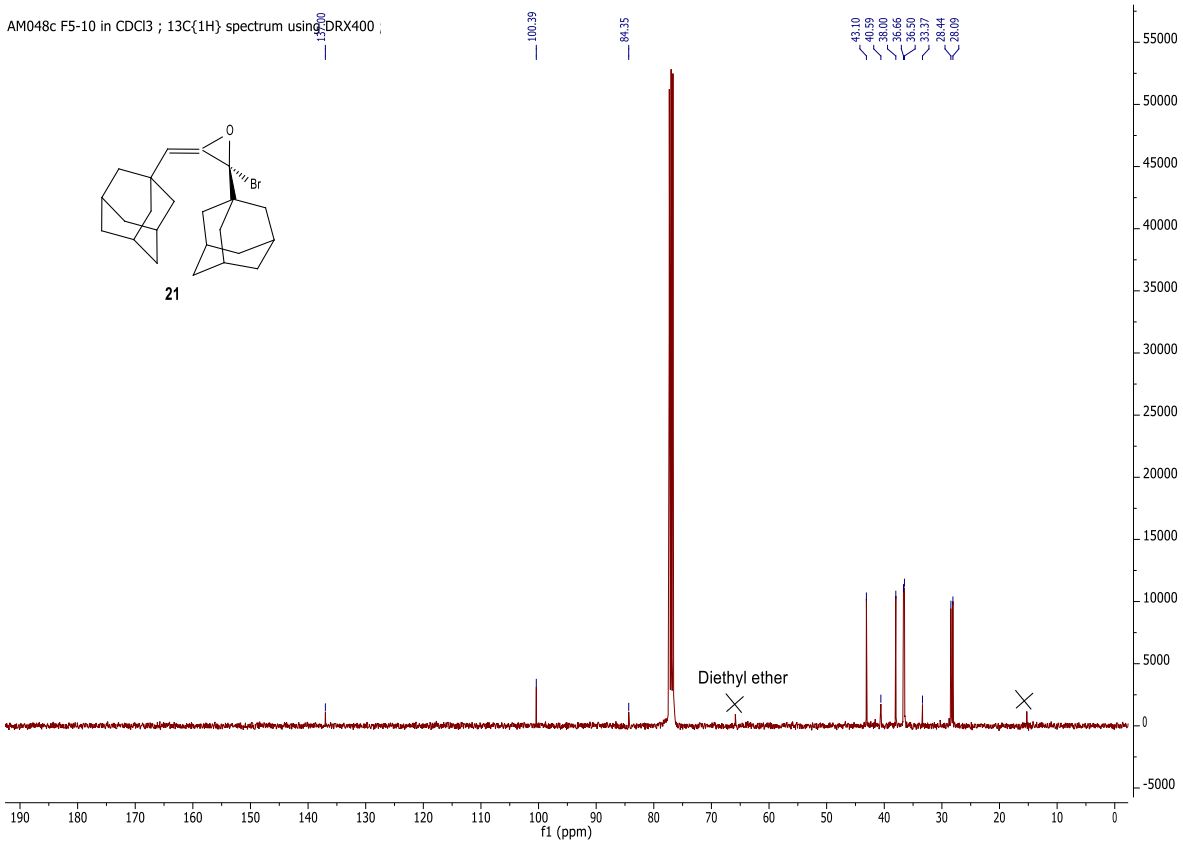
Selective (4.96 ppm) NOE spectrum of 1-adamantan-1-yl-3-bromo-4,4-dimethyl-1,2-pentanedione (**23**) (400 MHz, $CDCl_3$)



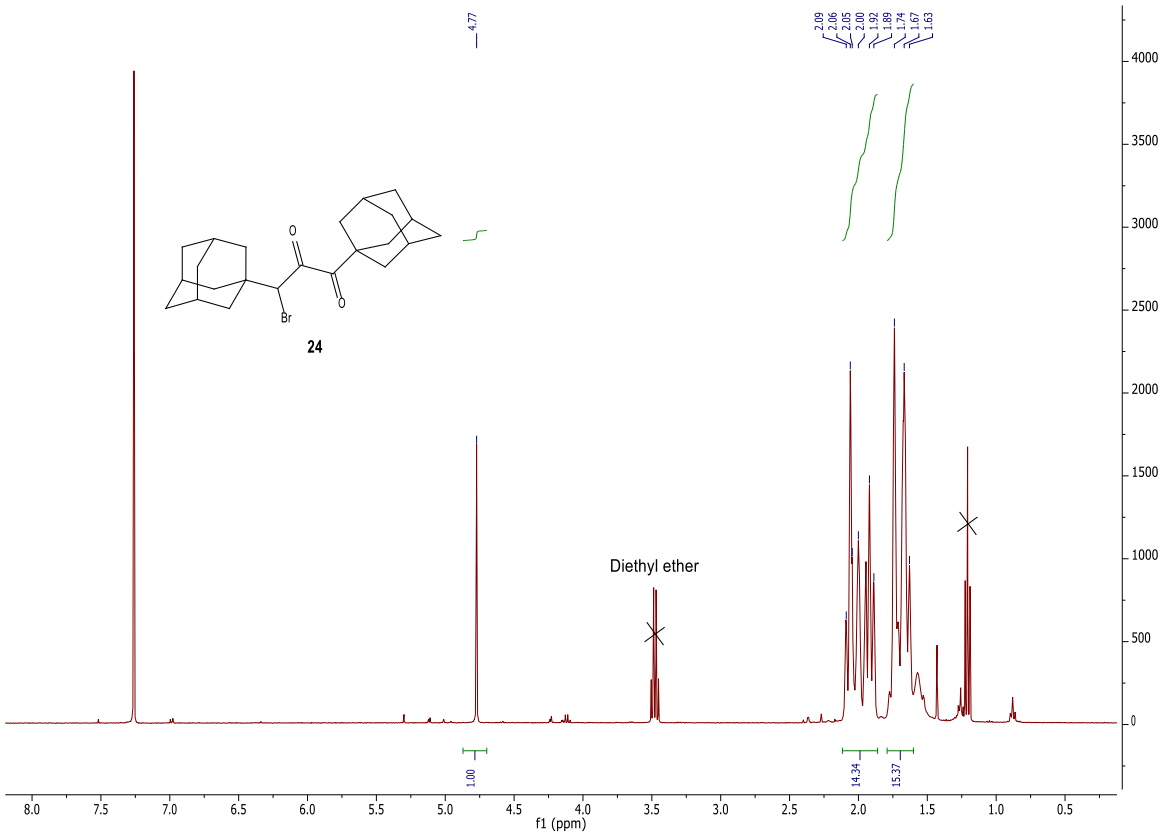
^{1}H NMR spectrum of *E*-1,3-diadamantan-1-yl-1-bromo-1,2-epoxy-2-propene (**21**) (400 MHz, $CDCl_3$)



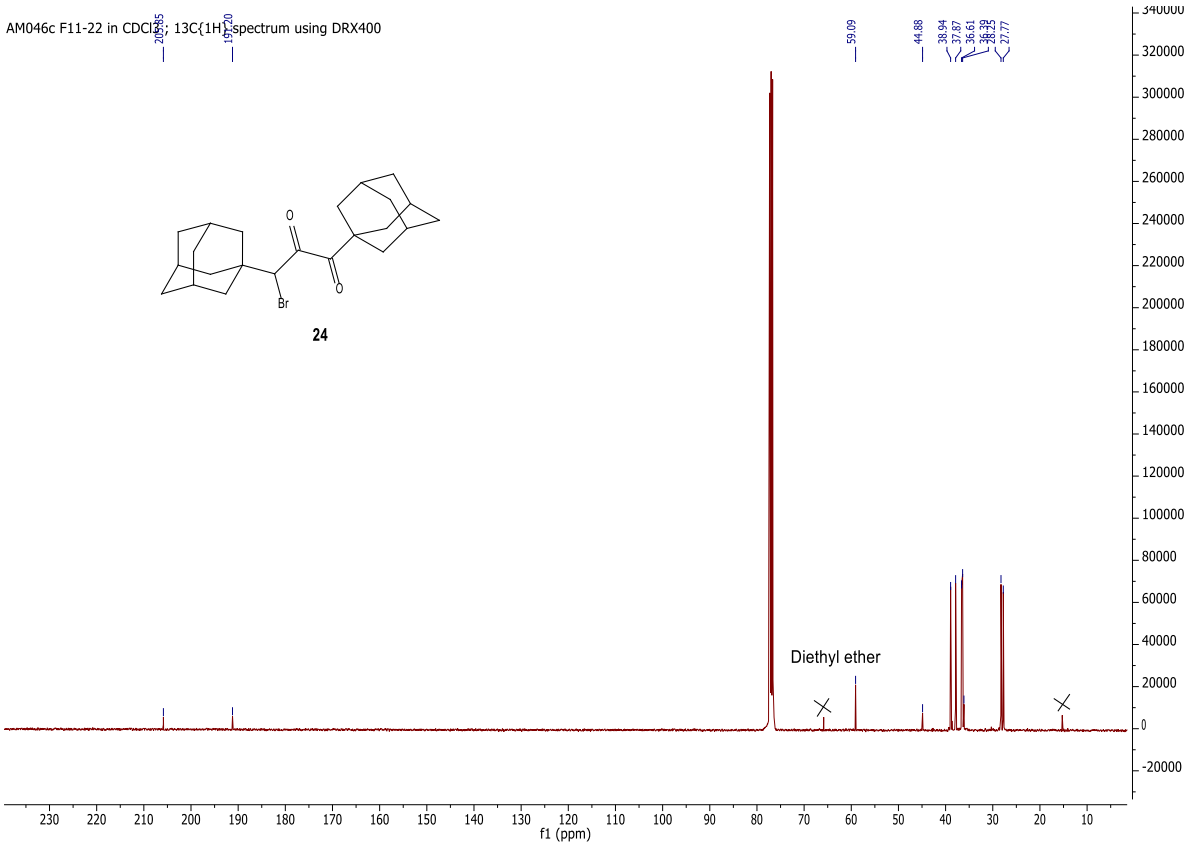
^{13}C NMR spectrum of *E*-1,3-diadamantan-1-yl-1-bromo-1,2-epoxy-2-propene (**21**) (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of 1,3-diadamantan-1-yl-3-bromo-1,2-propanedione (**24**) (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 1,3-diadamantan-1-yl-3-bromo-1,2-propanedione (**24**) (100 MHz, $CDCl_3$)



X-ray crystallographic details for compounds 9 and 19

The X-ray crystal structure of 9

The structure of **9** was found to contain two very different orientations for the complete molecule of *ca*. 85 and 15% occupancy. The geometries of the two orientations were restrained to be similar, as were the thermal parameters of the chemically equivalent atoms in each molecule. The non-hydrogen atoms of the major occupancy orientation were refined anisotropically, whilst those of the minor occupancy orientation were refined isotropically.

Consideration of the packing makes sense of the very different orientations for the two partial occupancy molecules. The basic repeat motif is a pair of centrosymmetrically related molecules approaching side by side such that the positions of the adamantan-1-yl rings forms an approximate rhombus (Fig. S2). This disorder can then be seen as just the opposite pair of linkages between the adamantan-1-yl sites; in Fig. S2 the linkages for the major occupancy orientations are approximately vertical, whilst those for the minor occupancy orientation are approximately horizontal. Since the shape of each pair of molecules is very similar irrespective of the "vertical" or "horizontal" nature of the linkage it is easy to see how the two orientations can co-exist within the crystal.

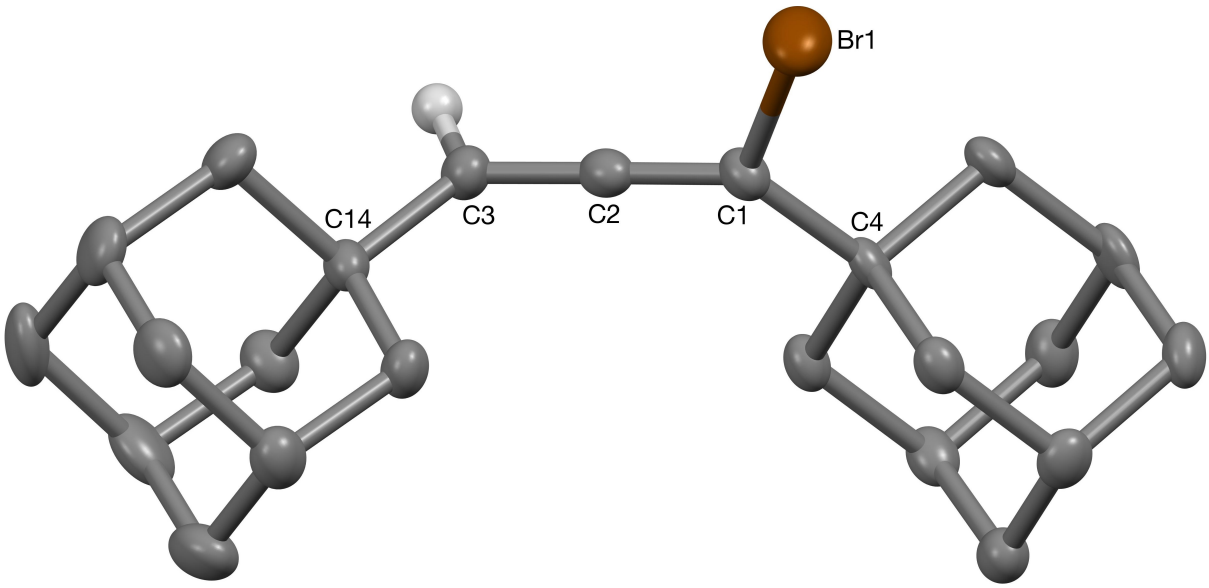


Fig. S1 The crystal structure of **9** showing the major (*ca*. 85%) occupancy orientation (50% probability ellipsoids).

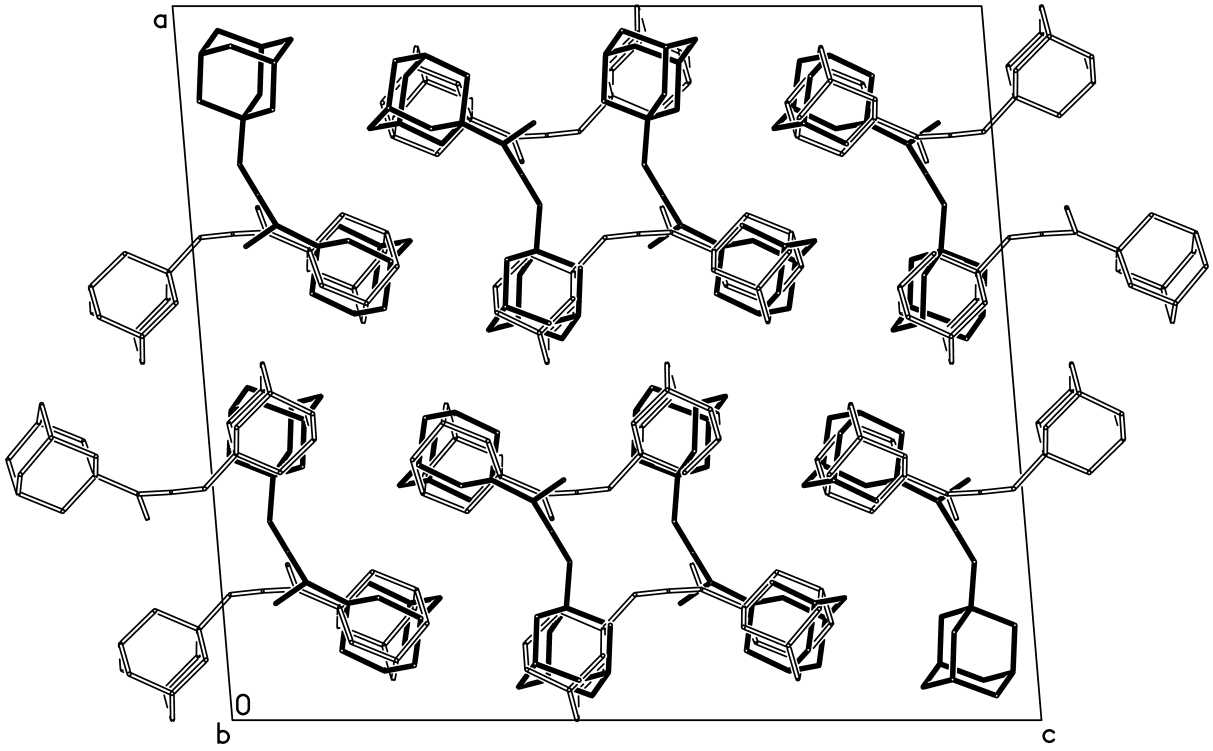


Fig. S2 Part of the extended packing in the crystal structure of **9** (viewed in parallel projection along the *b* axis direction), showing how the two disordered orientations exist in pairs that have very similar molecular shapes (the major and minor occupancy orientations have been drawn with dark and open bonds respectively).

The X-ray crystal structure of 19

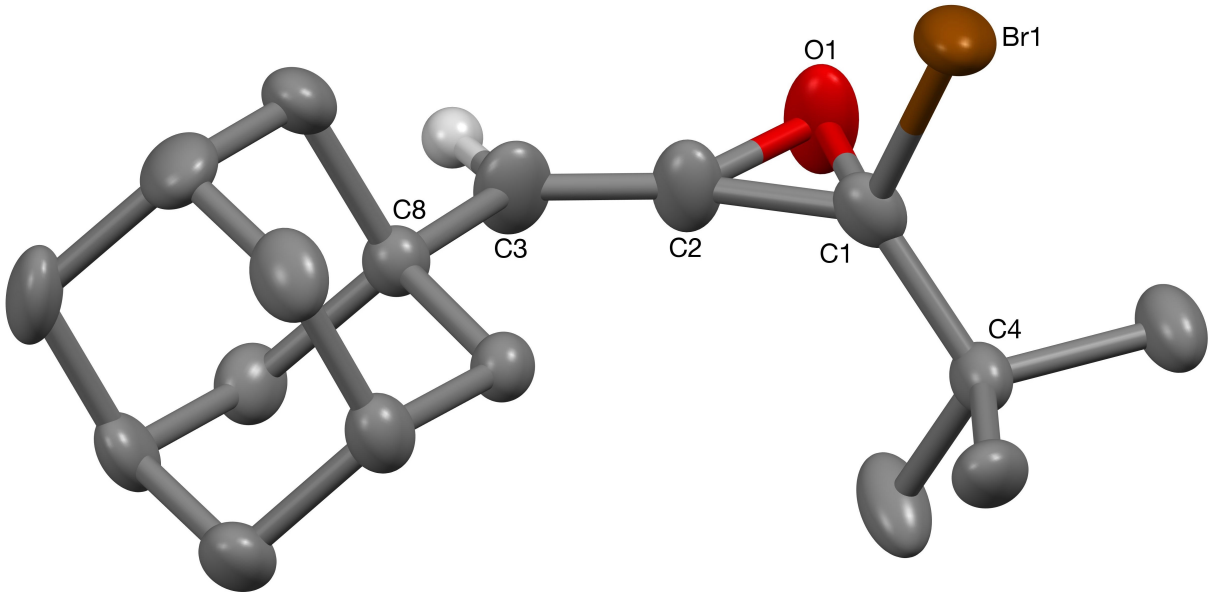


Fig. S3 The crystal structure of **19** (50% probability ellipsoids).

References

(1) Braddock, D. C.; Clarke, J.; Rzepa, H. S. *Chem. Commun. (Camb).* **2013**, *49* (95), 11176–11178.

(2) Iinuma, M.; Moriyama, K.; Togo, H. *Tetrahedron* **2013**, *69* (14), 2961–2970.

(3) SHELXTL, Bruker AXS, Madison, WI

(4) SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

(5) Raynes, W. T.; Sergeyev, N. M.; Sandor, P.; Grayson, M. *Magn. Reson. Chem.* **1997**, *35* (2), 141–143.