Supplementary Material (ESI) for Chemical Communications

Supporting information

Gold Catalysed Reactions with Cyclopropenes

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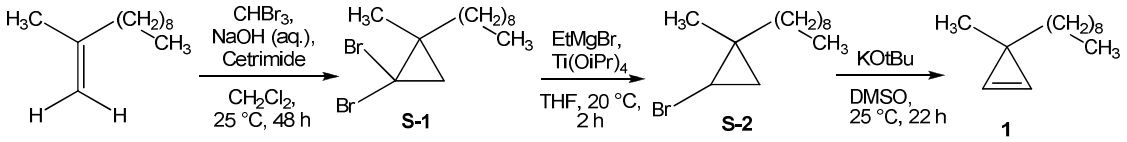
1. General Experimental Section

^{1}H NMR spectra were recorded on Bruker AC 200 and DPX 400 spectrometers at 200 and 400 MHz respectively and referenced to residual solvent. ^{13}C NMR spectra were recorded at 50 and 100 MHz on the same spectrometers. Chemical shift data are quoted in parts per million (δ in ppm), *J* values are given in Hz and s, d, dd, t, q and m represent singlet, doublet, doublet of doublet, triplet, quartet and multiplet. Mass spectra were obtained on a Thermoquest Automass BenchTop mass spectrometer at Heriot-Watt University and a Finnigan MAT 900 XLT at the EPSRC National Mass Spectrometry Service Centre in Swansea. Flash column chromatography was carried out using Matrix silica gel 60 from Fisher Chemicals and TLC was performed using Merck silica gel 60 F254 pre-coated sheets and visualised by UV (254 nm) or stained by the use of aqueous acidic $KMnO_4$ or aqueous acidic ammonium molybdate as appropriate. Chemicals were purchased from Aldrich and Fisher chemical companies and used without further purification unless otherwise stated. Tetrahydrofuran was dried by distillation from sodium – benzophenone under nitrogen, dimethylsulfoxide, acetonitrile, toluene, ethynyltrimethylsilane and dichloromethane were dried over calcium hydride. Petrol ether refers to petroleum ether (40 – 60 %).

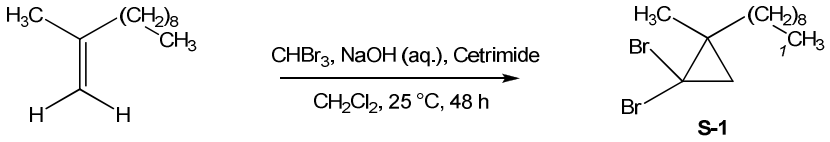
2. Experimental Procedures

Cyclopropene **1** was synthesized following a general procedure by Gevorgyan (Scheme 1).[1-2]



Scheme 1

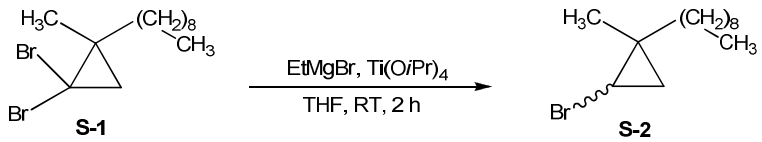
1,1-Dibromo-2-methyl-2-nonylcyclopropane S-1



Bromoform (30.9 g, 122 mmol) and dichloromethane (5 mL) were added dropwise to a stirring mixture of aqueous sodium hydroxide (30 mL, 11.2 g, 280 mmol), cetrimide (2.52 g), 2-methylundec-1-ene (10.3 g, 61.2 mmol) and dichloromethane (10 mL). The mixture was allowed to stir at 25 °C. After 48 h, the reaction mixture was diluted with water (75 mL). Dichloromethane (30 ml) was added and the layers partitioned. The aqueous layer was washed twice with dichloromethane (30 ml). The combined organic layers were washed with brine (50 mL), dried over magnesium sulphate and concentrated under reduced pressure. The resulting material was purified by flash column chromatography (hexanes) and the remaining bromoform was evaporated under high vacuum (10 h, 30 °C) to yield 1,1-dibromo-2-methyl-2-nonylcyclopropane **S-1** (16.8 g, 49.5 mmol, 81%) as a colourless oil.

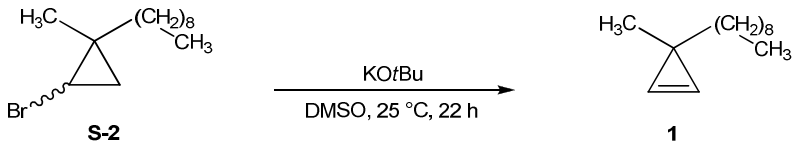
δ_H (200 MHz, $CDCl_3$) 1.67 – 1.18 (21H, m, alkyl-H), 0.88 (3H, t, J = 6.6, H-1); δ_C (50 MHz, $CDCl_3$) 39.9 (C), 38.8 (CH_2), 34.8 (CH_2), 31.8 (CH_2), 29.7 (C), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 26.4 (CH_2), 22.7 (CH_2), 22.5 (CH_3), 14.1 (CH_3); M^+(EI) = 338.0245 required M = 338.0245.

2-Bromo-1-methyl-1-nonylcyclopropane S-2



A solution of ethylmagnesium bromide (1.38 M in Et_2O, 38.6 mL, 53.3 mmol) was added over 1 hour to a strirring solution of 1,1-dibromo-2-methyl-2-nonylcyclopropane **S-1** (14.1 g, 41.5 mmol), $Ti(OiPr)_4$ (0.235 g, 0.827 mmol) and tetrahydrofuran (100 mL). The solution was allowed to stir for an additional hour at 20 °C. The reaction was quenched by slow addition of water (20 mL), then 20% aqueous sulphuric acid (50 mL) was added and the mixture stirred for 30 minutes. Diethyl ether (50 mL) was added and the layers were partitioned. The aqueous layer was washed further three times with diethyl ether (50 mL). The combined organic layers were washed twice with saturated sodium bicarbonate (50 mL), washed with brine (50 mL), dried over magnesium sulphate and concentrated under reduced pressure. The crude material was purified by flash column chromatography (eluent: petrol ether) to yield a mixture of the two diastereomers of 2-bromo-1-methyl-1-nonylcyclopropane **S-2** (8.25 g, 31.6 mmol, 77%) as a colourless oil.
δ_H (200 MHz, $CDCl_3$) 2.82 (1H x 2, m, C*H*Br), 1.55 – 0.82 (22H x 2, m, alkyl-H), 0.62 (2H x 2, m, CHBrCH_2); δ_C (50 MHz, $CDCl_3$) 38.9 (CH_2), 36.4 (CH_2), 31.9 (CH_2), 30.7 (CH_2), 30.1 (CH), 29.8 (CH), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 26.5 (CH_2), 26.3 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 22.1 (CH_3), 21.3 (C), 21.0 (C), 20.2 (CH_3), 14.1 (CH_3); M^+(EI) = 260.1121 required *M* = 260.1140.

3-Methyl-3-nonylcycloprop-1-ene 1



Potassium *tert*-butoxide (1.72 g, 15.3 mmol) and dimethyl sulfoxide (23 mL) were heated to 50 °C and allowed to stir for 30 minutes at this temperature. The solution was cooled to room temperature and 2-bromo-1-methyl-1-nonylcyclopropane **S-2** (2.50 g, 9.58 mmol) was added dropwise. The reaction mixture was allowed to stir for 22 h at 25 °C, then quenched by addition of water (100 mL). Pentane (500 mL) was added and the layers partitioned. The aqueous layer was washed three times with pentane (50 mL). The combined organic layers were washed twice with brine (100 mL), dried over magnesium sulphate and concentrated under reduced pressure. The resulting material was purified by flash column chromatography (pentane) to yield 3-methyl-3-nonylcycloprop-1-ene **1** (1.00 g, 5.55 mmol, 58%) as a colourless oil.

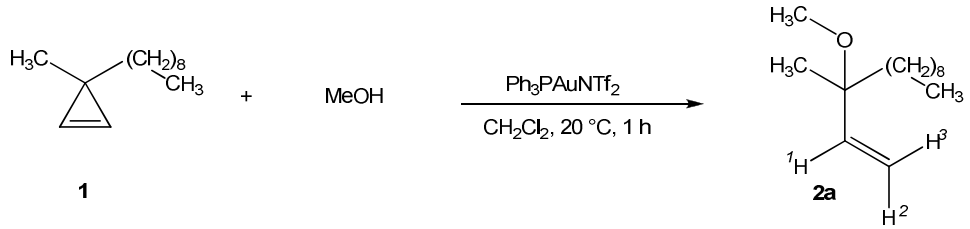
δ_H (200 MHz, $CDCl_3$) 7.34 (2H, s, C=C*H*), 1.54 – 1.03 (19H, m, alkyl-H), 0.88 (3H, t, *J* = 6.4, CH_2CH_3); δ_C (50 MHz, $CDCl_3$) 122.1 (CH), 40.2 (CH_2), 31.9 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.6 (C), 29.4 (CH_2), 27.3 (CH_3), 27.1 (CH_2), 22.7 (CH_2), 14.1 (CH_3); M^+(EI) = 180.1897 required *M* = 180.1878.

General Procedure: Gold(I) catalysed addition of alcohols to cyclopropene 1

Method A: Ph_3PAuCl (5 mol%) and AgOTf (5 mol%) were added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (1 eq.) and ROH (6 eq.) in dichloromethane (0.55 M). The reaction mixture was allowed to stir for 1-2 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography to yield the corresponding *tert*-allylic ether product.

Method B: $Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (5 mol%) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (1 eq.) and ROH (6 eq.) in dichloromethane (0.55 M). The reaction mixture was allowed to stir for 1-2 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography to yield the corresponding *tert*-allylic ether product.

3-Methoxy-3-methyldodec-1-ene 2a

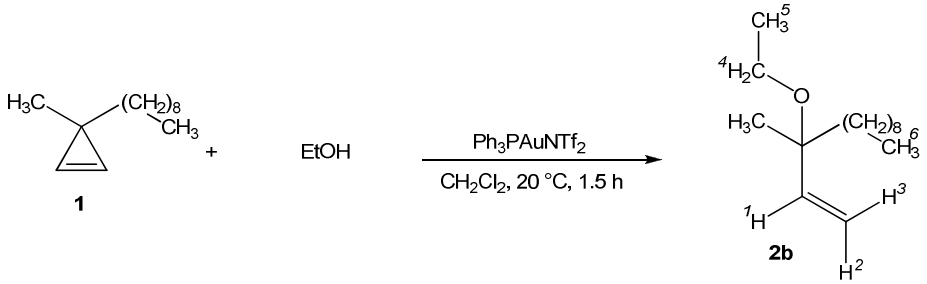


1 **2a**

$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (9.1 mg, 5.79 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (48.2 mg, 0.267 mmol) and methanol (48.5 mg, 1.51 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (95% petrol ether, 5% diethyl ether) to yield 3-methoxy-3-methyldodec-1-ene **2a** (49.0 mg, 0.231 mmol, 86%) as a colourless oil.

δ_H (200 MHz, $CDCl_3$) 5.74 (1H, dd, *J* = 17.4, 10.8, H-1), 5.15 (1H, dd, *J* = 10.8, 1.7, H-2), 5.10 (1H, dd, *J* = 17.4, 1.7, H-3), 3.14 (3H, s, OCH_3), 1.33 - 0.81 (22H, m, alkyl-H); δ_C (50 MHz, $CDCl_3$) 143.0 (CH), 114.5 (CH_2), 77.4 (C), 50.0 (CH_3), 39.7 (CH_2), 31.9 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 21.2 (CH_3), 14.1 (CH_3); M^+(EI) = 212.2153 required *M* = 212.2140.

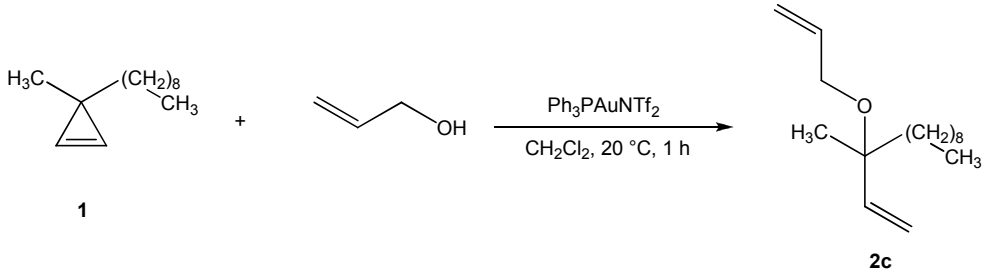
3-Ethoxy-3-methyldodec-1-ene 2b



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.7 mg, 7.45 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (53.6 mg, 0.297 mmol) and ethanol (85.9 mg, 1.86 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 3-ethoxy-3-methyldodec-1-ene **2b** (55.7 mg, 0.246 mmol, 83%) as a colourless oil.

δ_H (200 MHz, $CDCl_3$) 5.76 (1H, dd, *J* = 17.0, 11.2, H-1), 5.12 (1H, dd, *J* = 11.2, 1.2, H-2), 5.08 (1H, dd, *J* = 17.0, 1.2, H-3), 3.32 (2H, q, *J* = 7.1, H-4), 1.62 – 1.19 (19H, m, alkyl-H), 1.14 (3H, t, *J* = 7.1, H-5), 0.87 (3H, t, *J* = 6.4, H-6); δ_C (50 MHz, $CDCl_3$) 143.7 (CH), 113.9 (CH_2), 77.2 (C), 57.3 (CH_2), 39.9 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 27.6 (CH_2), 23.6 (CH_2), 22.6 (CH_2), 22.1 (CH_3), 16.0 (CH_3), 14.1 (CH_3); M^+(EI) = 226.2291 required *M* = 226.2292.

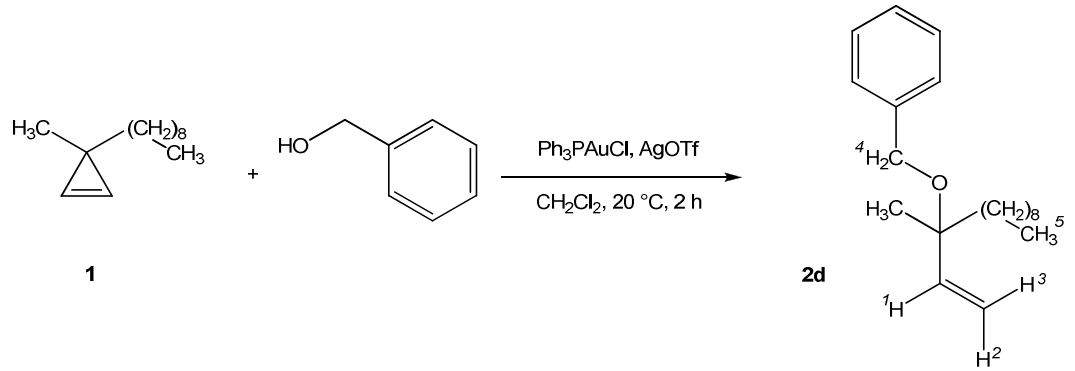
3-(Allyloxy)-3-methyldodec-1-ene 2c



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.0 mg, 7.00 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (50.0 mg, 0.277 mmol) and 2-propen-1-ol (97 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 3-(allyloxy)-3-methyldodec-1-ene **2c** (58.1 mg, 0.244 mmol, 88%) as a colourless oil.

δ_H (200 MHz, $CDCl_3$) 6.00 - 5.70 (2H, m, C*H*=CH_2 x 2), 5.32 – 5.07 (4H, m, CH=C*H*$_2$ x 2), 3.82 (2H, dt, *J* = 5.4, 1.7, OC*H*$_2$), 1.50 – 1.16 (19H, m, alkyl-H), 0.87 (3H, t, *J* = 6.2, CH_2CH_3) ; δ_C (50 MHz, $CDCl_3$) 143.2 (CH), 136.0 (CH), 115.5 (CH_2), 114.4 (CH_2), 77.6 (C), 63.5 (CH_2), 40.1 (CH_2), 31.8 (CH_2), 30.1 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 21.9 (CH_3), 14.1 (CH_3); $[M+NH_4]^+$(ESI) = 256.2636 required *M* = 256.2635.

1-((3-Methyldodec-1-en-3-yloxy)methyl)benzene 2d

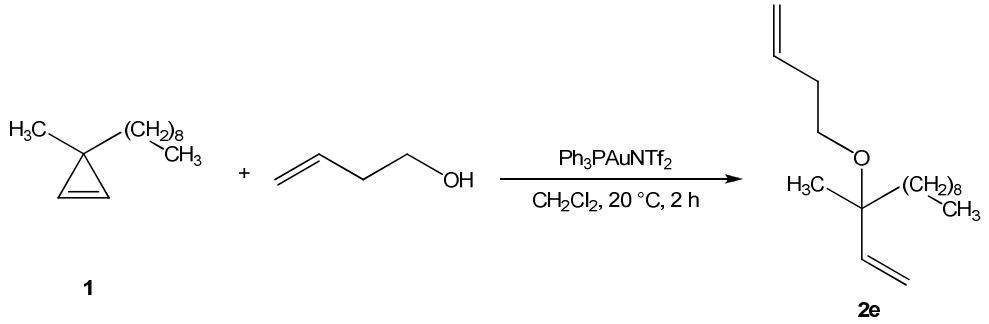


1 **2d**

Ph_3PAuCl (7.2 mg, 14.6 μmol) and AgOTf (3.5 mg, 13.6 μmol) were added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (50.9 mg, 0.282 mmol) and phenylmethanol (180 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 2 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 1-((3-methyldodec-1-en-3-yloxy)methyl)benzene **2d** (63.5 mg, 0.220 mmol, 78%) as a colourless oil.

δ_H (400 MHz, $CDCl_3$) 7.38 – 7.24 (5H, m, aryl-H), 5.89 (1H, dd, *J* = 18.2, 10.3, H-1), 5.22 (1H, dd, *J* = 10.3, 1.2, H-2), 5.21 (1H, dd, *J* = 18.2, 1.2, H-3), 4.40 (2H, s, H-4), 1.67 – 1.25 (19H, m, alkyl-H), 0.91 (3H, t, *J* = 6.9, H-5) ; δ_C (100 MHz, $CDCl_3$) 143.4 (CH), 139.9 (C), 128.2 (CH), 127.2 (CH), 127.0 (CH), 114.6 (CH_2), 77.9 (C), 64.4 (CH_2), 40.2 (CH_2), 31.9 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.7 (CH_2), 22.7 (CH_2), 22,1 (CH_3), 14.1 (CH_3); M^+(EI) = 288.2449 required *M* = 288.2453.

3-(But-3-enyloxy)-3-methyldodec-1-ene 2e

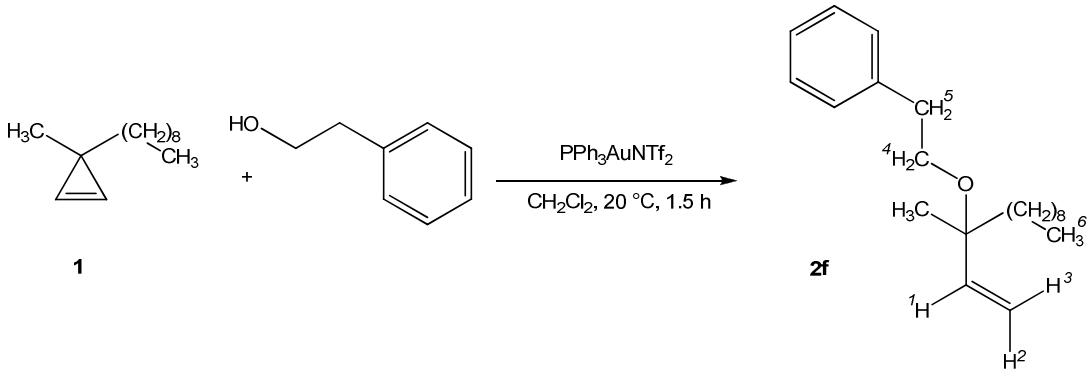


1 **2e**

$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.2 mg, 7.13 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (58.4 mg, 0.268 mmol) and 3-buten-1-ol (119 mg, 1.65 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 3-(but-3-enyloxy)-3-methyldodec-1-ene **2e** (59.6 mg, 0.236 mmol, 88%) as a colourless oil.

δ_H (200 MHz, $CDCl_3$) 5.92 - 5.69 (2H, m, C*H*=CH_2 x), 5.15 – 4.96 (4H, m, CH=C*H*$_2$ x 2), 3.03 (2H, dt, *J* = 1.2, 7.1, OC*H*$_2$), 2.27 (2H, m, C*H*$_2$CH=CH_2), 1.50 – 1.18 (19H, m, alkyl-H), 0.87 (3H, t, *J* = 5.8, CH_2CH_3) ; δ_C (50 MHz, $CDCl_3$) 143.5 (CH), 135.7 (CH), 115.9 (CH_2), 114.1 (CH_2), 77.2 (C), 61.5 (CH_2), 39.9 (CH_2), 35.0 (CH_2), 31.8 (CH_2), 30.1 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 21.9 (CH_3), 14.1 (CH_3); $[M+NH_4]^+$(ESI) = 270.2793 required *M* = 270.2791.

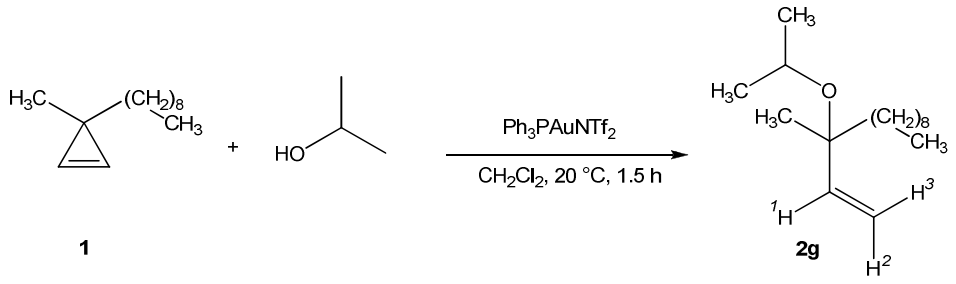
1-(2-(3-Methyldodec-1-en-3-yloxy)ethyl)benzene 2f



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.4 mg, 7.26 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (50.0 mg, 0.277 mmol) and 2-phenylethanol (203 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 1-(2-(3-methyldodec-1-en-3-yloxy)ethyl)benzene **2f** (64.5 mg, 0.213 mmol, 77%) as a colourless oil.

δ_H (200 MHz, $CDCl_3$) 7.25 – 7.07 (5H, m, aryl-H), 5.63 (1H, dd, *J* = 17.4, 10.8, H-1), 5.02 (1H, dd, *J* = 10.8, 1.2, H-2), 4.98 (1H, dd, *J* = 17.4, 1.2, H-3), 3.35 (2H, t, *J* = 7.5, H-4), 2.75 (2H, t, *J* = 7.5, H-5), 1.51 – 1.08 (19H, m, alkyl-H), 0.81 (3H, t, *J* = 6.5, H6) ; δ_C (50 MHz, $CDCl_3$) 143.4 (CH), 139.4 (C), 129.0 (CH), 128.1 (CH), 126.0 (CH), 114.2 (CH_2), 77.4 (C), 63.4 (CH_2), 40.0 (CH_2), 37.2 (CH_2), 31.9 (CH_2), 30.1 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 21.9 (CH_3), 14.1 (CH_3); M^+(EI) = 302.2604 required *M* = 302.2603.

3-Isopropoxy-3-methyldodec-1-ene 2g

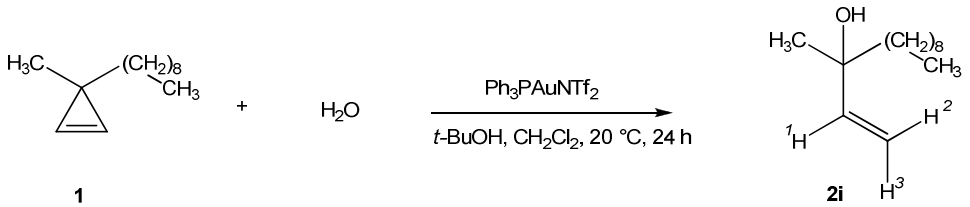


1 **2g**

$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.4 mg, 7.26 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (51.0 mg, 0.283 mmol) and propan-2-ol (107 mg, 1.78 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. ^{1}H-NMR analysis of the crude product showed 97:3 ratio of **2g** and **3g**. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 3-isopropoxy-3-methyldodec-1-ene **2g** (47.7 mg, 0.198 mmol, 70%) as a colourless oil.

δ_H (200 MHz, $CDCl_3$) 5.82 (1H, dd, *J* = 17.4, 11.2, H-1), 5.12 (1H, dd, *J* = 11.2, 1.2, H-2), 5.07 (1H, dd, *J* = 17.4, 1.2, H-3), 3.66 (1H, *septet*, *J* = 6.2, C*H*Me$_2$), 1.62 – 1.19 (19H, m, alkyl-H), 1.09 (3H, d, *J* = 6.2, C*H*$_3$), 1.07 (3H, d, *J* = 6.2, C*H*$_3$), 0.87 (3H, t, *J* = 6.0, CH_2CH_3); δ_C (50 MHz, $CDCl_3$) 144.2 (CH), 114.0 (CH_2), 77.9 (C), 64.2 (CH), 41.2 (CH_2), 31.9 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 25.0 (CH_3), 24.9 (CH_3), 23.9 (CH_2), 22.7 (CH_2), 22.0 (CH_3), 14.1 (CH_3); M^+(EI) = 240.2448 required *M* = 240.2447.

3-Methyldodec-1-en-3-ol 2i



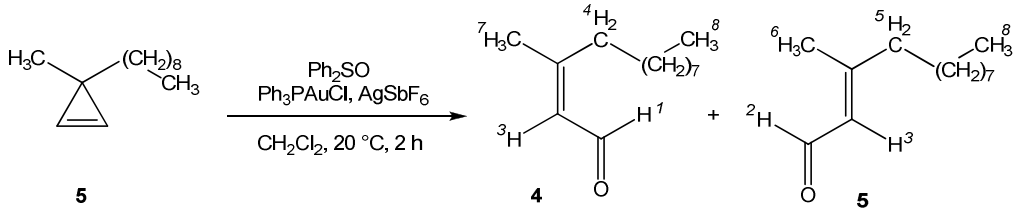
1 **2i**

$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (5.8 mg, 3.69 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (25.2 mg, 0.140 mmol), water (16.1 mg, 0.893 mmol), *tert*-butanol[§] (154 mg, 2.07 mmol) and dichloromethane (0.2 mL). The reaction mixture was allowed to stir for 24 h at 20 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (50% petrol ether, 50% diethyl ether) to yield 3-methyldodec-1-en-3-ol **2i** (9.4 mg, 0.0474 mmol, 34%) as a colourless oil.

δ_H (200 MHz, $CDCl_3$) 5.91 (1H, dd, *J* = 17.4, 10.8, H-1), 5.19 (1H, dd, *J* = 17.4, 1.2, H-2), 5.04 (1H, dd, *J* = 10.8, 1.2, H-3), 1.59 – 1.16 (19H, m, alkyl-H), 0.87 (3H, t, *J* = 6.2, CH_2CH_3); δ_C (50 MHz, $CDCl_3$) 145.2 (CH), 111.4 (CH_2), 73.3 (C), 42.3 (CH_2), 31.8 (CH_2), 30.0 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 27.6 (CH_3), 23.9 (CH_2), 22.6 (CH_2), 14.1 (CH_3); M^+(EI) = 198.1970 required *M* = 198.1984.

[§] *t*-BuOH was added as a co-solvent to homogenize the layers. In the absence of *t*-BuOH co-solvent, a lower yield of 17% was observed. This lower yield is probably due to the biphasic nature (H_2O/CH_2Cl_2) of the resulting reaction mixture.

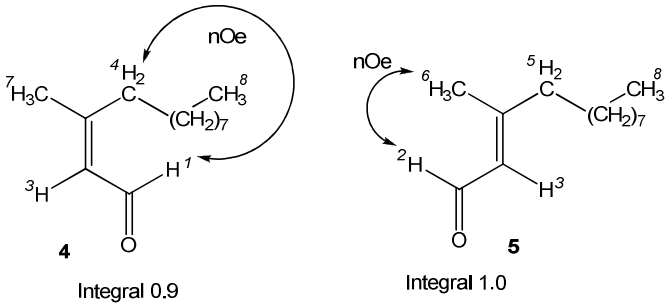
3-Methyldodec-2-enal 4 and 5



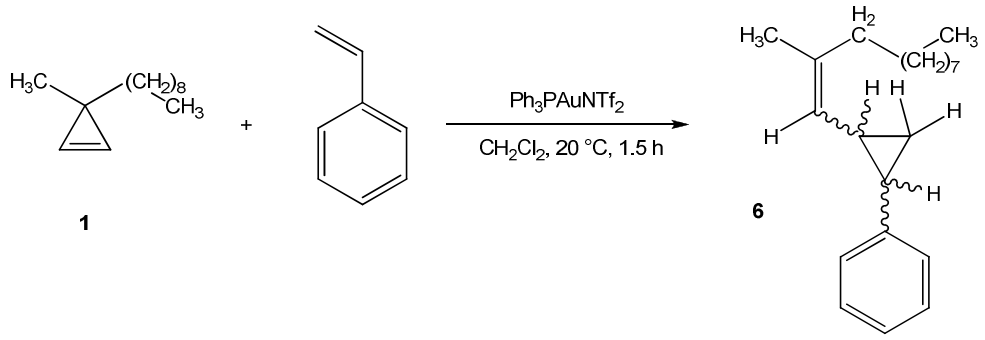
Ph_3PAuCl (7.2 mg, 14.6 µmol) and $AgSbF_6$ (5.6 mg, 16.3 µmol) were added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (54.0 mg, 0.299 mmol) and phenyl sulfoxide (243 mg, 1.20 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 2 h at 20 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (80% petrol ether, 20% diethyl ether) to yield 3-methoxy-3-methyldodec-1-ene as a mixture of the *Z* and *E* isomers **4** and **5** (39.1 mg, 0.199 mmol, 66%) as a colourless oil. The ratio of the *Z* and *E* isomers was 9 : 11.

δ_H (200 MHz, $CDCl_3$) 9.98 (1H, d, *J* = 7.9, H-1), 8.3 (1H, d, *J* = 9.94, H-2), 5.89 – 5.83 (2H, m, H-3), 2.55 (2H, t, *J* = 7.9, H-4), 2.19 (2H, t, *J* = 7.1, H-5), 2.15 (3H, d, *J* = 1.2, H-6), 1.96 (3H, d, *J* = 1.2, H-7), 1.56 – 1.15 (28H, m, alkyl-H), 0.87 (6H, t, *J* = 6.6, H-8); δ_C (50 MHz, $CDCl_3$) 191.3 (CH), 190.8 (CH), 165.0 (C), 164.5 (C), 128.3 (CH), 127.2 (CH), 40.6 (CH_2), 32.5 (CH_2), 31.8 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.8 (CH_2), 27.1 (CH_2), 25.0 (CH_3), 22.6 (CH_2), 17.4 (CH_3), 14.0 (CH_3); M^+(EI) = 196.2.

Proof of stereochemical ratio: gNOESY (400 MHz, $CDCl_3$):



(2-(-2-Methylundec-1-enyl)cyclopropyl)benzene 6

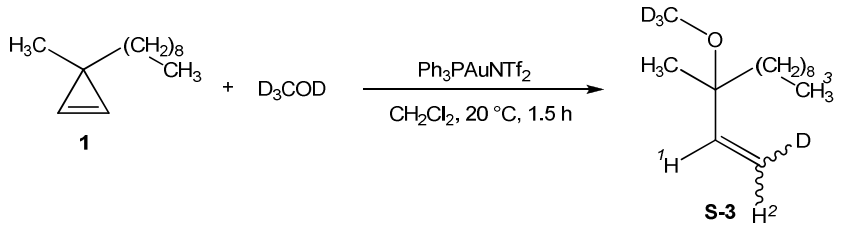


$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (4.6 mg, 2.93 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (21.1 mg, 0.117 mmol) and styrene (77.6 mg, 0.745 mmol) in dichloromethane (0.2 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (petrol ether) to yield a mixture of four diastereomers (23.8 mg, 83.7 μmol, 72%) as a colourless oil. The ratio of the *cis:trans* isomers was 6:1 and ratio of *Z*:*E* isomers was 1.6:1 (determined by ^{1}H-NMR at 400 MHz).[‡]

δ_H (main isomer) (400 MHz, $CDCl_3$) 7.33 – 7.03 (5H, m, aryl-H), 4.48 (1H, d, *J* = 8.8, C=C*H*), 2.25 (1H, m, C*H*Ph), 2.11 (2H, t, *J* = 7.6, CH_2), 1.88 (1H, m, C*H*C=C), 1.53 (3H, s, C=CCH_3), 1.27-0.83 (19H, m, alkyl-H); δ_C (100 MHz, $CDCl_3$) 139.4 (C), 137.0 (C), 129.0 (CH), 128.2 (CH), 127.8 (CH), 125.7 (CH), 125.5 (CH), 125.3 (CH), 123.4 (CH), 123.0 (CH), 39.5 (CH_2), 32.3 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.0 (CH_2), 27.9 (CH_2), 27.8 (CH_2), 23.4 (CH_2), 22.9 (CH), 22.8 (CH_2), 22.7 (CH_2), 18.0 (CH), 16.5 (CH_2), 14.1 (CH_3), 12.5 (CH_2), 12.4 (CH_2); M^+(EI) = 284.2525 required M = 284.2504.

[‡] Assignment with the aid of NOESY, COSY, HMQC and comparison with data of *cis*- and *trans*-2-phenyl-1-(2-methyl-1-propenyl)cyclopropane from C. P. Casey, W. H. Miles, H. Tukada, *J. Am. Chem. Soc.* 1985, **107**, 2924.

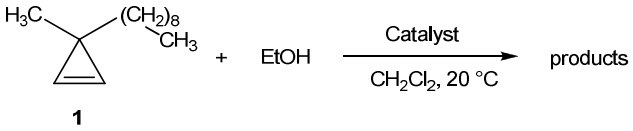
Reaction with CD_3OD



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (4.4 mg, 2.78 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (100 mg, 0.555 mmol) and d_4-methanol (0.14 mL, 3.33 mmol) in dichloromethane (1 mL) with 3 Å molecular sieves. The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the product purified by column chromatography (diethyl ether) to yield **S-3** (47 mg, 0.22 mmol, 40%) as a mixture of the *E* and *Z* isomers (ratio 1:1, 90% D incorporation) as a colourless oil.

δ_H (400 MHz, $CDCl_3$) 5.77 – 5.70 (1H, m, H-1), 5.15 (1H, d, J = 10.9, H-2_{cis}), 5.09 (1H, d, J = 17.7, H-2_{trans}), 1.55 – 1.20 (19H, m, alkyl-H), 0.87 (3H, t, J = 6.7, H-3); δ_C (50 MHz, $CDCl_3$) 142.9 (*C*H=CHD), 114.2 (t, J = 24.0, CH=*C*HD), 77.3 (*C*OCD_3), 49.1 (septet, J = 21.4, *C*D_3), 39.7 (CH_2), 31.9 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 21.3 (CH_3), 14.1 (CH_3); M^+(EI) = 216.2.

Control Reactions



1

Catalyst: Trifluoromethanesulfonic acid

Trifluoromethanesulfonic acid (21 μL of a 0.666 M solution in dichloromethane, 14.0 μmol) were added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (48.9 mg, 0.271 mmol) and ethanol (77.2 mg, 1.68 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir at 20 °C. After 1.5 h the reaction was monitored by TLC (eluent: 90% petrol ether, 10% diethyl ether) and there was no sign of any product formed. After a further 22.5 h at 20 °C the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether). Analysis of the crude mixture by ^{1}H-NMR (200 MHz, $CDCl_3$) showed that no reaction took place (>95% of starting material).

Catalyst: AgOTf

AgOTf (3.7 mg, 14.4 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (48.3 mg, 0.268 mmol) and ethanol (70.1 mg, 1.72 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir at 20 °C. After 1.5 h the reaction was monitored by TLC (eluent: 90% petrol ether, 10% diethyl ether) and only traces of product were detected. After a further 22.5 h at room temperature the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to give 48.4 mg of a mixture of unreacted **1**:**2b** (7:4 ratio) along with traces of **3b**, **4**, **5** and other unidentified by-products. The products were identified and ratios determined by ^{1}H-NMR (200 MHz, $CDCl_3$).

Catalyst: $Rh(OAc)_2$

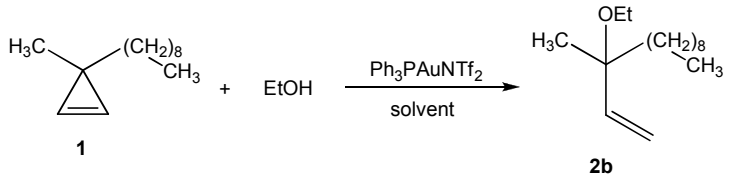
$[Rh(OAc)_2]_2$ (3.1 mg, 7.01 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (47.3 mg, 0.262 mmol) and ethanol (76.3 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir at 20 °C. After 1.5 h the reaction was

monitored by TLC (eluent: 90% petrol ether, 10% diethyl ether) and only traces of products were detected. After a further 22.5 h at 20 °C the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to give 18.4 mg of a mixture of **4** and **5** along with traces of **3b** and **2b**. The products were identified by ^{1}H-NMR (200 MHz, $CDCl_3$) analysis of the crude mixture.

Catalyst: $AuCl_3$

$AuCl_3$ (1.7 mg, 5.60 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (21.7 mg, 0.120 mmol) and ethanol (34.7 mg, 0.753 mmol) in dichloromethane (0.2 mL). The reaction mixture was allowed to stir at 20 °C. After 1.5 h the reaction was monitored by TLC (eluent: 90% petrol ether, 10% diethyl ether) and only traces of product were detected. After a further 22.5 h at 20 °C the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to give 25.3 mg of a mixture mainly **4** and **5** along with traces of **2b**, **3b** and other unidentified by-products. The products were identified by ^{1}H-NMR (200 MHz, $CDCl_3$) analysis of the crude mixture. Purification by column chromatography (9:1 hexane:ether) produced a mixture of **4** and **5** as a colourless oil (12 mg, 61 μmol, 50%).

Other Reactions



tert-Butanol as solvent instead of dichloromethane

$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (3.3 mg, 2.10 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (14.2 mg, 78.7 μmol) and ethanol (23.5 mg, 0.510 mmol) in *tert*-butanol (0.2 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. Then the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to give 13.5 mg of a mixture of mainly unreacted **1** (~90%), **2b** (~5%) and **2h** (~5%) as a colourless oil. The products were identified and ratios determined by ^{1}H-NMR (200 MHz, $CDCl_3$) analysis of the crude mixture. [N.B. The catalyst did not seem to completely dissolve in this solvent mixture.]

1.5 Equivalents of ethanol (instead of 6 equivalents)

$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.2 mg, 7.13 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (52.0 mg, 0.288 mmol) and ethanol (20.4 mg, 0.443 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. Then the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to give 62.0 mg of a mixture of **2b**, **3b** (4:1 ratio) and unidentified by-products as a colourless oil. The products were identified and ratio determined by ^{1}H-NMR (200 MHz, $CDCl_3$) analysis of the crude mixture.

1.1 Equivalents of ethanol and 5 equivalents tert-butanol (instead of 6 equivalents of ethanol)

$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (4.4 mg, 2.80 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (20.5 mg, 0.114 mmol), ethanol (5.8 mg, 0.126 mmol) and *tert*-butanol (44.3 mg, 0.598 mmol) in dichloromethane (0.2 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. Then the solvent was evaporated

and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield **2b** (16.5 mg, 72.9 μmol, 64%) as a colourless oil.

Reaction time of 10 min

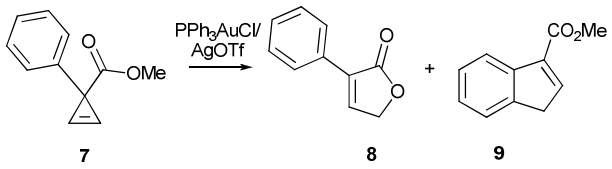
$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (4.7 mg, 2.99 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (21.1 mg, 0.117 mmol) and ethanol (33.1 mg, 0.718 mmol) in dichloromethane (0.2 mL). The reaction mixture was allowed to stir for 10 min at 20 °C. The solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to yield **2b** as colourless oil (24.1 mg, 0.106 mmol, 91%).

1 mol% catalyst

$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (0.9 mg, 0.573 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (23.2 mg, 0.129 mmol) and ethanol (37.3 mg, 0.809 mmol) in dichloromethane (0.2 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to yield **2b** as colourless oil (28.7 mg, 0.127 mmol, 98%).

Cyclopropenes **7** and **10a-d** were synthesised following literature procedures.[1,3,4]

Gold(I)-catalysed rearrangement of cyclopropene 7.



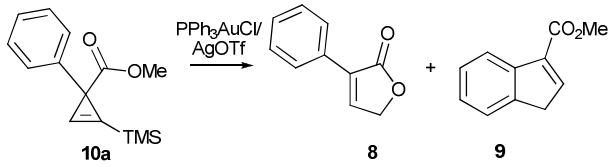
7 **8** **9**

A solution of AgOTf (18.8 mg, 0.07 mmol) and PPh_3AuCl (36.1 mg, 0.07 mmol) in toluene (0.2 ml) was added to a solution of cyclopropene **7** (50 mg, 0.29 mmol) toluene (0.3 ml). The reaction mixture was allowed to stir at 80 ^oC and the reaction monitored using TLC (1:1 hex/ether). Upon completion of the reaction the product was purified using column chromatography (1:1 hex/ether) to yield the product 3-Phenylfuran-2(5H)-one **8**[5] (24 mg, 52%) as an orange solid.

δ_H (200 MHz, $CDCl_3$) 7.90-7.76 (2H, m Ar-H), 7.63 (1H, t, *J* 2.0, C=C*H*), 7.46-7.34 (3H, m, Ar-H), 4.91 (2H, d, *J* 2, OCH_2); δ_C (200 MHz, $CDCl_3$) 172.4 (C), 144.5 (C), 131.8 (C), 129.5 (CH), 129.5 (CH), 128.9 (CH), 127.1 (CH), 69.7 (CH_2); LR-EI: m/z = 160 [$M^{+\cdot}$].

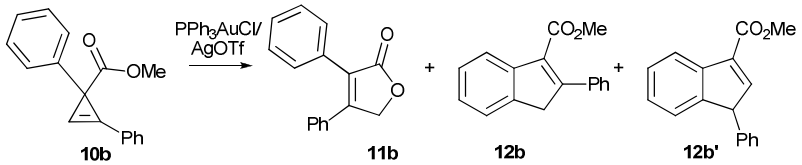
The methyl 1H-indene-3-carboxylate **9**,[6] was also formed as a minor product in 20 % yield; δ_H (200 MHz, $CDCl_3$); - 8.03 (1H, dd, *J* 7.8, 0.6, Ar-H), 7.40 (4H, m, Ar-H, C=C*H*), 3.89 (3H, s, OCH_3), 3.51 (2H, d, *J* 2.0, CH_2); δ_C (50 MHz, $CDCl_3$) 164.5 (C), 144.7 (CH), 143.4 (C), 140.8 (C), 136.1 (C), 126.7 (CH), 125.6 (CH), 123.8 (CH), 122.5 (CH), 51.7 (CH_3), 38.5 (CH_2); LR-EI: m/z = 174 [$M^{+\cdot}$].

Gold(I)-catalysed rearrangement of cyclopropene 10a.



A solution of AgOTf (2.0 mg, 0.008 mmol) and PPh_3AuCl (4 mg, 0.008 mmol) in DCM (0.2 ml) was allowed to stir at 25 ^oC for approx. 2 min. A solution of cyclopropene **10a** (20 mg, 0.08 mmol) in DCM (0.3 ml) was added and the reaction was monitored using TLC (1:1 hex/ether). Upon completion of reaction the mixture was purified using column chromatography (1:1 hex/ether) to produce two products, methyl 1H-indene-3-carboxylate **9**[6] (5.5 mg, 39%) and 3-phenylfuran-2(5H)-one **8**[5] (4.8 mg, 37%).

Gold(I)-catalysed rearrangement of cyclopropene 10b.

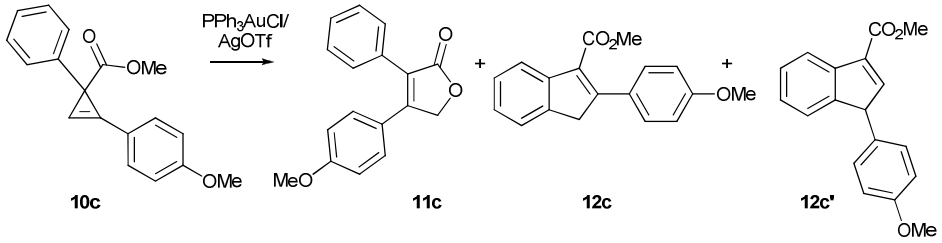


A solution of AgOTf (2 mg, 0.008 mmol) and PPh_3AuCl (3.7 mg, 0.008 mmol) in DCM (0.2 ml) was allowed to stir at 25 ^oC for approx. 2 min. A solution of cyclopropene **10b** (20 mg, 0.08 mmol) in DCM (0.3 ml) was added and the reaction was monitored using TLC (1:1 hex/ether). Upon completion of the reaction (approx 1 h) the crude mixture was purified using column chromatography (1:1 hex/ether) to yield the product 3,4-diphenylfuran-2(5H)-one **11b**[7]as an amber oil (10 mg, 53%).

δ_H (200 MHz, $CDCl_3$) 7.46-7.28 (10H, m, Ar-H), 5.17 (2H, s, O-CH_2); δ_C (100 MHz, $CDCl_3$) 173.4 (C), 156.1 (C), 130.8 (C), 130.6 (CH), 130.1 (C), 129.2 (CH), 129.0 (CH), 128.8 (CH), 128.7 (CH), 127.5 (CH), 126.2 (C), 70.6 (CH_2); LR-EI: m/z = 236 [$M^{+\cdot}$].

The indene products **12b** and **12b'** (ratio ~1:1) were collected as a mixture (3.6 mg, 18%). δ_H (400 MHz, $CDCl_3$); - 7.58-7.18 (9H+10H', m, Ar-H and C=CH), 4.84 (1H', s, C=CHC*H*Ar), 3.58 (2H, s, CH_2), 3.81, (3H, s, OCH_3), 3.62 (3H', s, OCH_3); $[M+NH_4]^+$(HNES) = 268.1337 required $[M+NH_4]^+$ = 268.1332.

Gold(I)-catalysed rearrangement of cyclopropene 10c.

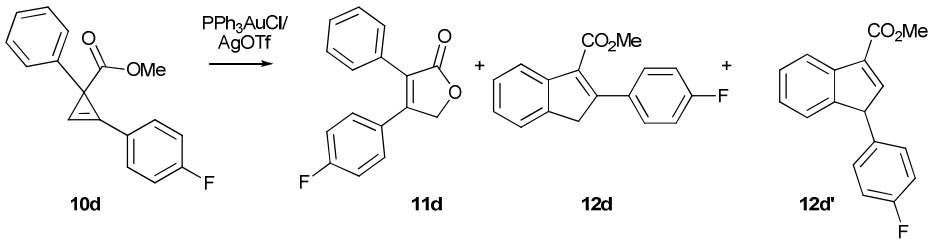


A solution of AgOTf (4.6 mg, 0.018 mmol) and PPh_3AuCl (8.9 mg, 0.018 mmol) in DCM (0.4 ml) was allowed to stir at 25 ^oC for approx. 2 min. A solution of cyclopropene **10c** (50 mg, 0.18 mmol) in DCM (0.8 ml) was added and the reaction was monitored using TLC (1:1 hex/ether). Upon completion of the reaction (approx 2 h) the crude mixture was purified using column chromatography (5:1 hex/ether) to yield the product 4-(4-methoxyphenyl)-3-phenylfuran-2(5H)-one **11c**[8] as a yellow solid (16.8 mg, 35%).

δ_H (200 MHz, $CDCl_3$); - 7.48-7.35 (5H, m, Ph-H), 7.28 (2H, d, *J* 8.3, Ar-H), 6.83 (2H, d, *J* 8.3, Ar-H), 5.16 (2H, s, CH_2), 3.81 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 173.8 (C), 161.4 (C), 155.6 (C), 130.7 (C), 129.4 (CH), 129.1(CH), 128.7 (CH), 128.6 (CH), 124.3 (C), 123.1 (C), 114.4 (CH), 70.4 (CH_2), 55.4 (CH_3); LR-EI: m/z = 266 [$M^{+\cdot}$].

The indene products **12c** and **12c'** (ratio 2.6:1) were collected as a mixture (15.7 mg, 33%). δ_H (200 MHz, $CDCl_3$); - 7.48-6.80 (8H+9H', m, Ar-H and C=CH), 4.73 (1H', s, C=CHC*H*Ar), 3.78 (8H, overlapping s, CH_2, 2xOCH_3), 3.76, (3H', s, OCH_3), 3.56 (3H', s, OCH_3).

Gold(I)-catalysed rearrangement of cyclopropene 10d.



A solution of AgOTf (4.8 mg, 0.019 mmol) and PPh_3AuCl (9.3 mg, 0.019 mmol) in DCM (0.4 ml) was allowed to stir at 25 ^oC for approx. 2 min. A solution of cyclopropene **10d** (50 mg, 0.187 mmol) in DCM (0.8 ml) was added and the reaction was monitored using TLC (1:1 hex/ether). Upon completion of the reaction (approx 2 h) the crude mixture was purified using column chromatography (3:1 hex/ether) to yield the product 4-(4-fluorophenyl)-3-phenylfuran-2(5H)-one **11d** as a yellow solid (22.9 mg, 49%).

δ_H (400 MHz, $CDCl_3$); - 7.43-7.36 (5H, m, Ph-H), 7.32 (2H, dd, *J* 9.0, 5.2, Ar-H), 7.32 (2H, dd, *J* 9.0, 8.4, Ar-H), 5.16 (2H, s, CH_2); δ_C (100 MHz, $CDCl_3$) 173.3 (C), 163.8 (d, *J* 253 Hz, C), 154.8 (C), 130.0 (C), 129.6 (d, *J* 8 Hz, CH), 129.2 (CH), 128.9 (CH), 128.8 (CH), 127.0 (C), 126.2 (C), 116.3 (d, *J* 22 Hz, CH), 70.4 (CH_2); LR-EI: m/z = 254 [$M^{+\cdot}$].

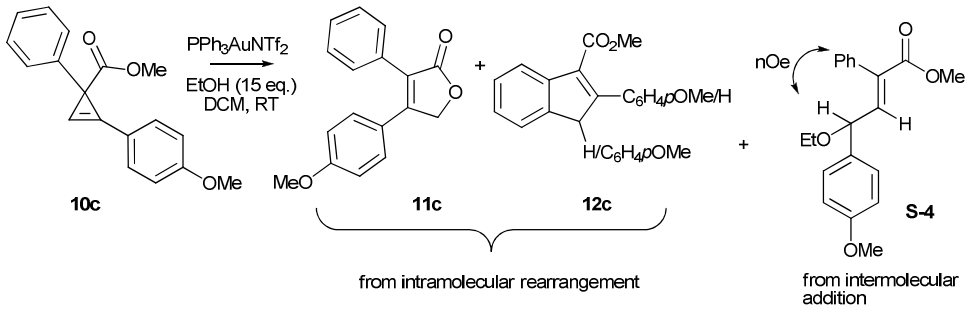
The indene products **12d** and **12d'** (ratio 1:3) were collected as a mixture (8.8 mg, 18%).

δ_H (400 MHz, $CDCl_3$); - 7.55-7.02 (8H+9H', m, Ar-H and C=CH), 4.80 (1H', s, C=CHC*H*Ar), 3.85 (2H, s, CH_2), 3.82, (3H, s, OCH_3), 3.63 (3H', s, OCH_3).

Gold(I)-catalysed reaction of 7 with 15 eq. EtOH

PPh_3AuNTf_2 (19 mg, 12.1 μmol) was added to a solution of **7** (21 mg, 0.121 mmol) in EtOH (83 mg, 1.8 mmol) and DCE (0.4 mL). The reaction mixture was allowed to stir at 50 °C for 18 h. The reaction mixture was concentrated *in vacuo* and passed through a plug of silica (eluent: ether). The products were identified and ratio determined by ^{1}H-NMR (400 MHz, $CDCl_3$) analysis of the crude mixture.

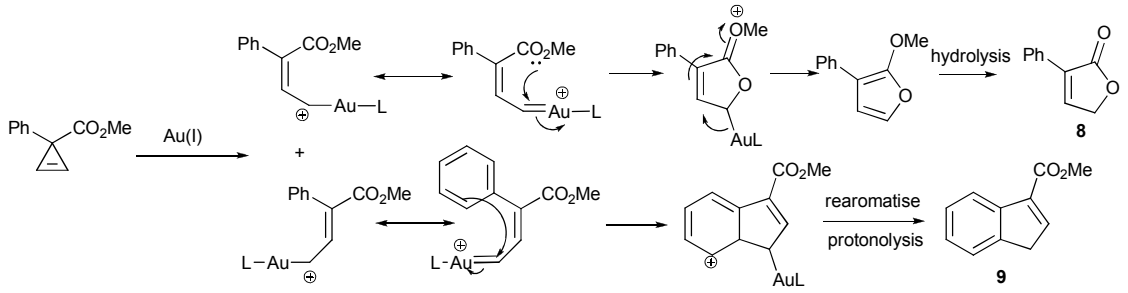
Gold(I)-catalysed reaction of 10c with 15 eq. EtOH



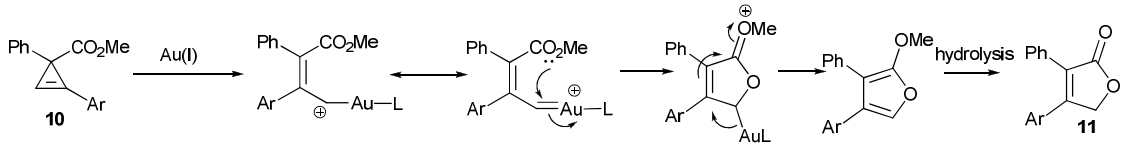
A solution of PPh_3AuNTf_2 (8.4 mg, 0.011 mmol) and EtOH (0.09 mL, 1.6 mmol) in DCM (0.2 ml) was allowed to stir at 25 ^oC for approx. 2 min. A solution of cyclopropene **10c** (30 mg, 0.11 mmol) in DCM (0.3 mL) was added and the reaction was monitored using TLC (1:1 hex/ether). Upon completion of the reaction (approx. 3 h) the crude mixture was filtered through a plug of silica (eluent:ether). The products were identified and ratio determined by ^{1}H-NMR (400 MHz, $CDCl_3$) analysis of the crude mixture. The major products **11c**:**12c**:**S-4** were observed in approximately 1:1.5:2 ratio along with other unidentified by-products. **S-4**: δ_H (400 MHz, $CDCl_3$); - 7.25-7.28 (5H, m, Ph-H), 7.06 (2H, d, *J* 8.9, Ar-H), 6.73 (2H, d, *J* 8.9, Ar-H), 6.38 (1H, s, C=C*H*), 4.96 (1H, s, EtOCC*H*), 3.98-3.84 (2H, m, OCH_2), 3.74 (3H, s, OCH_3), 3.68 (3H, s, OCH_3), 1.28 (3H, t, *J* 7.1, OCH_2CH_3); δ_C (100 MHz, $CDCl_3$) 173.3 (C), 158.3 (C), 144.9 (CH), 137.6 (C), 131.1 (C), 129.2 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 117.1 (C), 113.5 (CH), 68.3 (CH_2), 55.2 (CH_3), 52.0 (CH_3), 51.5 (CH), 15.3 (CH_3).

3. Mechanistic Proposals

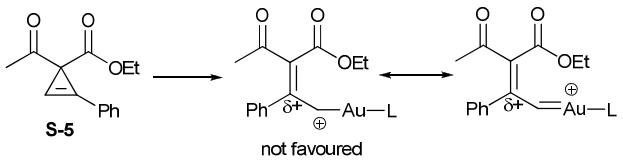
Mechanistic proposal for the gold(I)-catalysed formation of **8** and **9** from cyclopropene **7**:



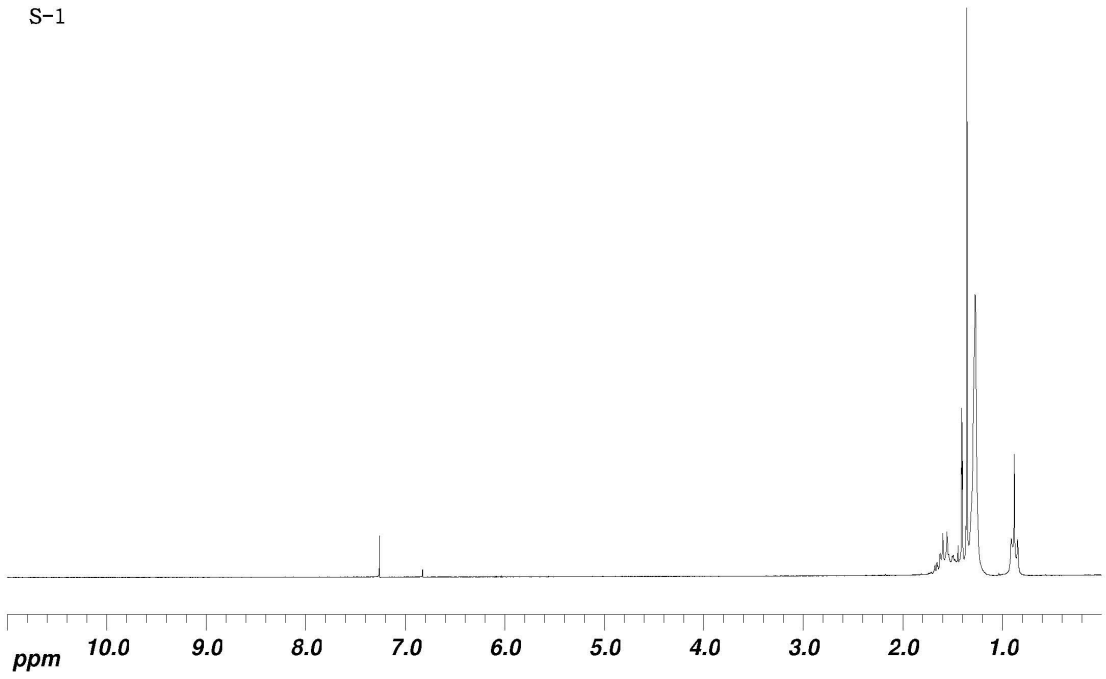
For Ar-substituted cyclopropenes **10b-d**, one regioisomer of furanone **11b-d** is detected. Mechanistic proposal for the gold(I)-catalysed formation of **11** from cyclopropenes **10b**:

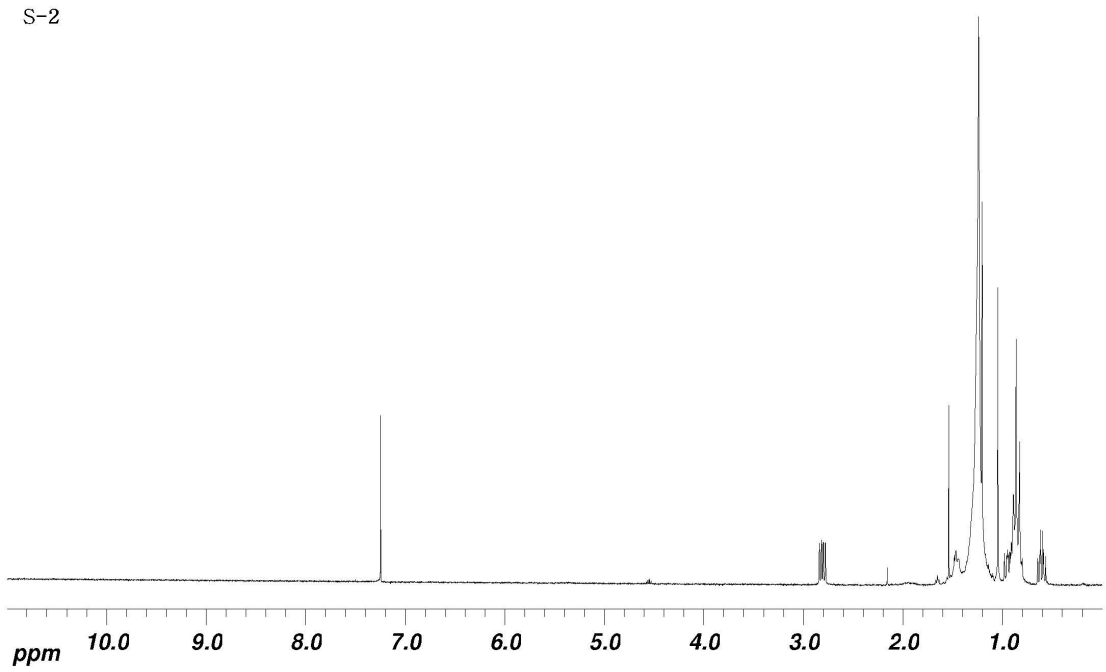


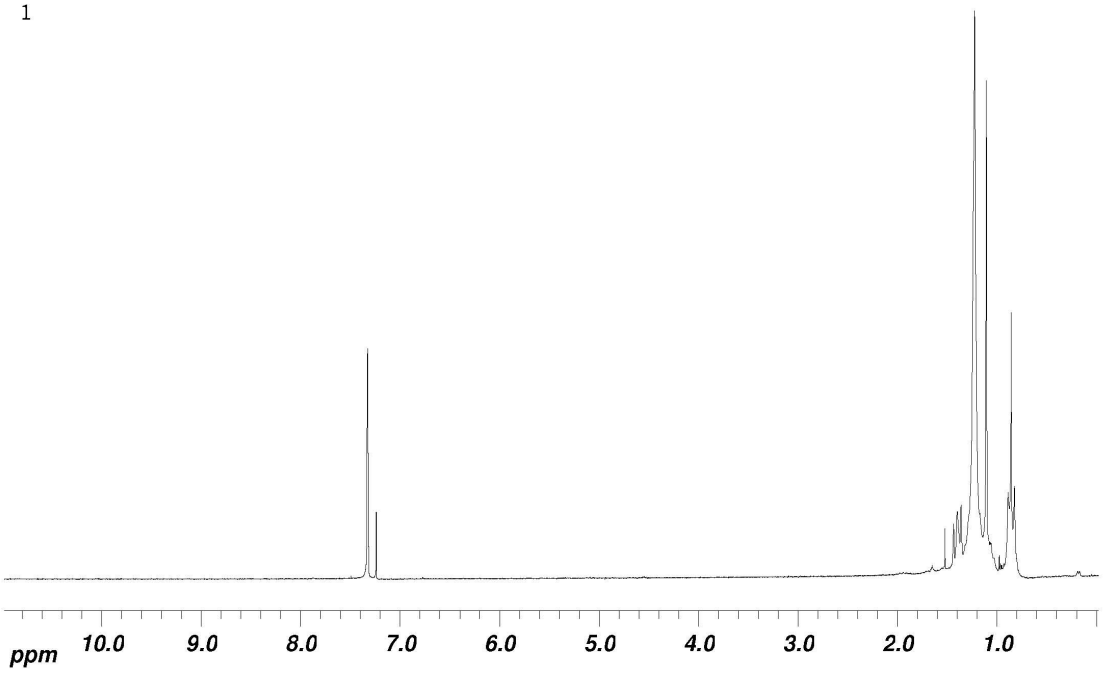
It is of note that 3,3-keto,ester-disubstituted cyclopropene **S-5**, which is known to undergo rearrangement to furans under Cu(I) and Pd(II) catalysis,[9] fails to react under Au(I) catalysis, thereby suggesting a different mechanistic pathway from Cu(I) and Pd(II). Our proposed mechanism is consistent with this result: the corresponding vinyl carbenoid/cation is now disfavoured, since this places a carbocation next to the δ+ carbon atom (β to two carbonyl groups):



4. ^{1}H-NMR Spectra of Synthesised Compounds



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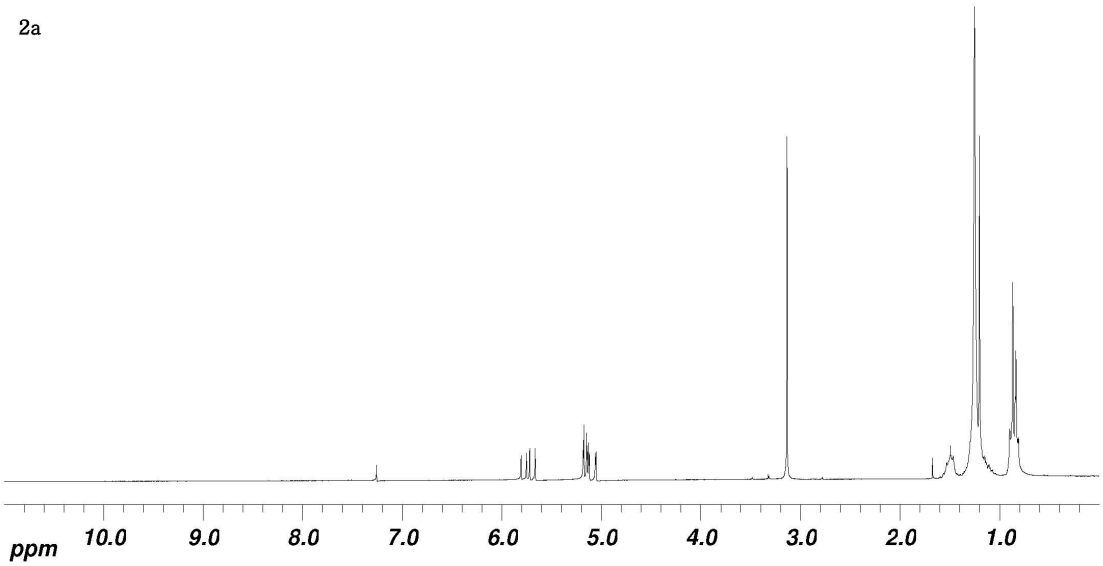
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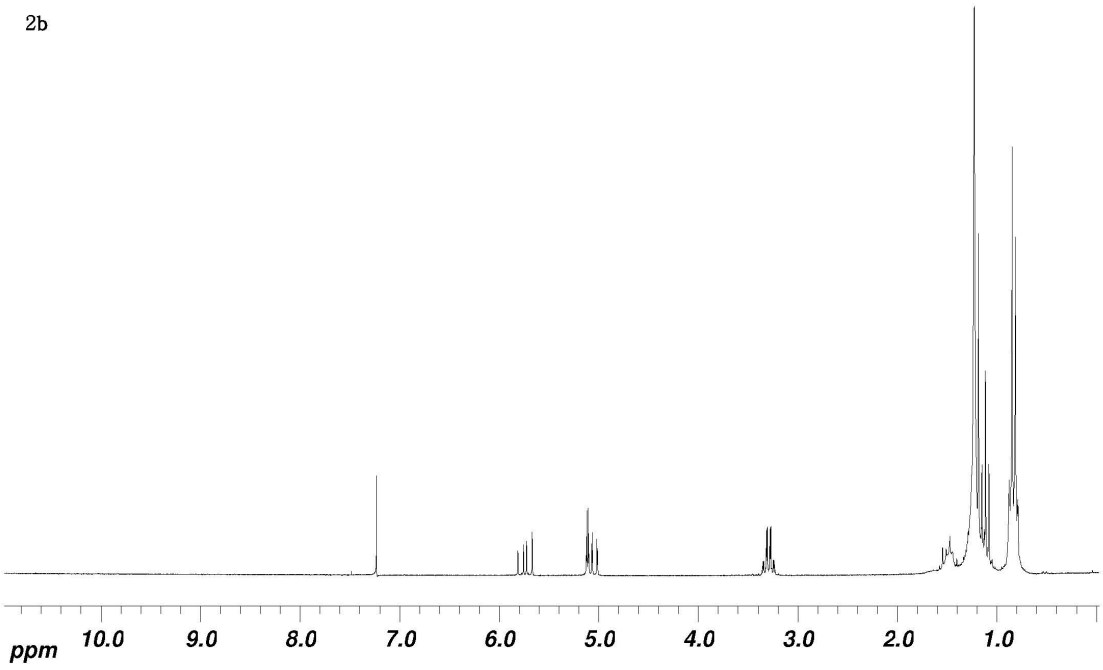
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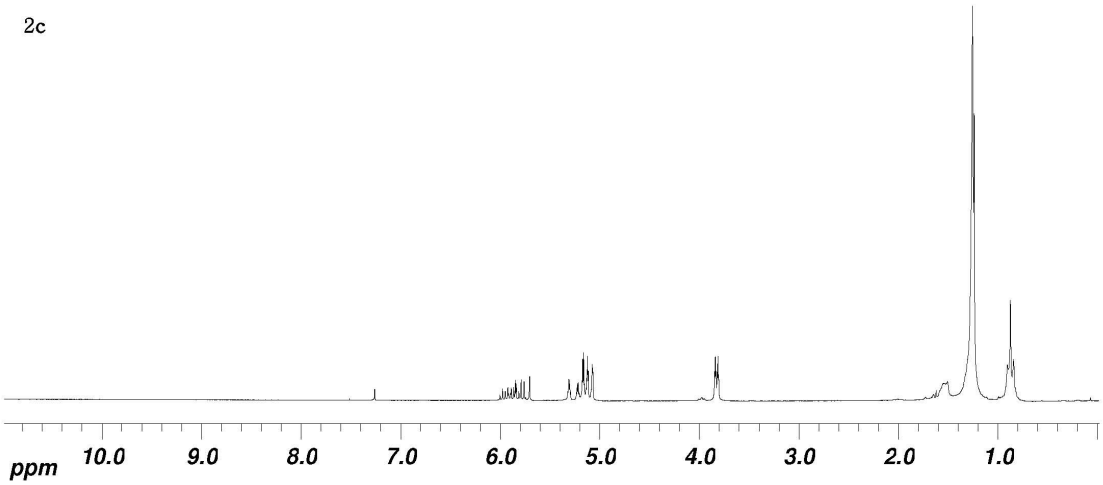
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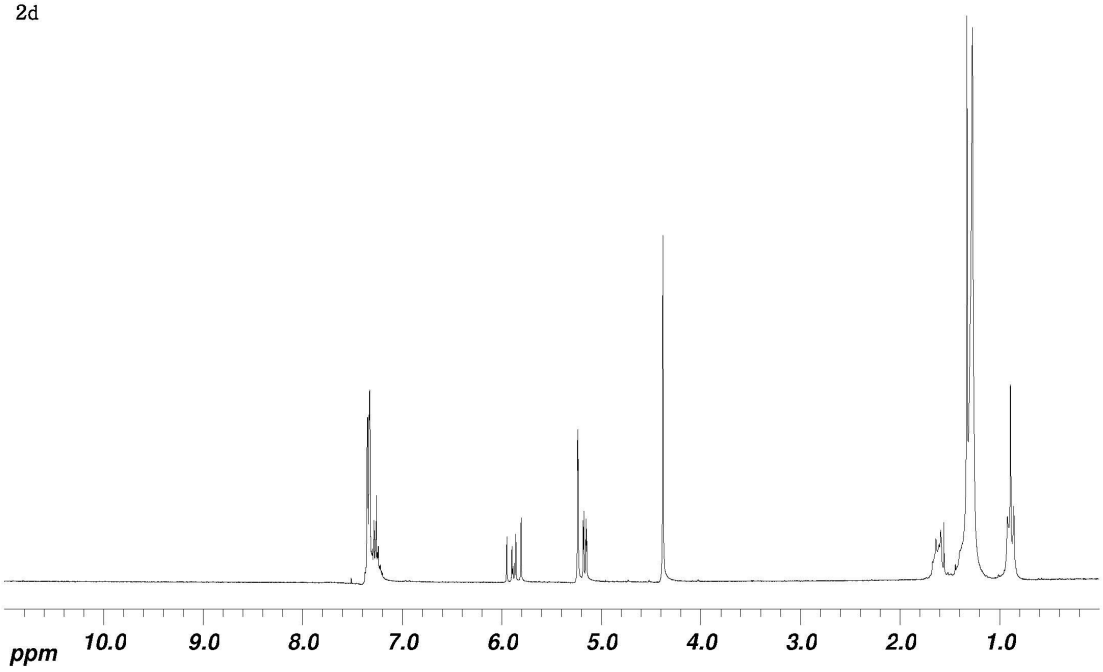

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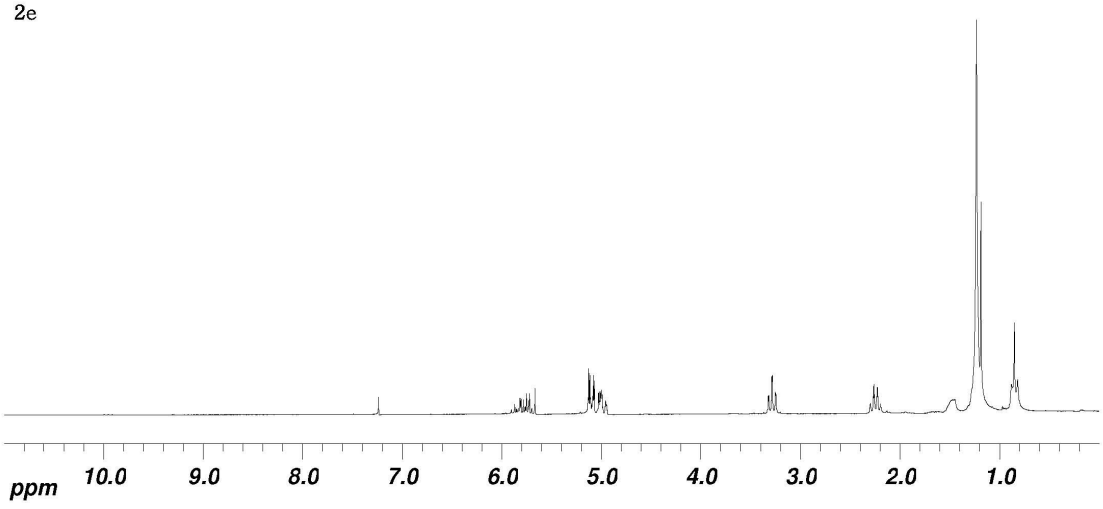

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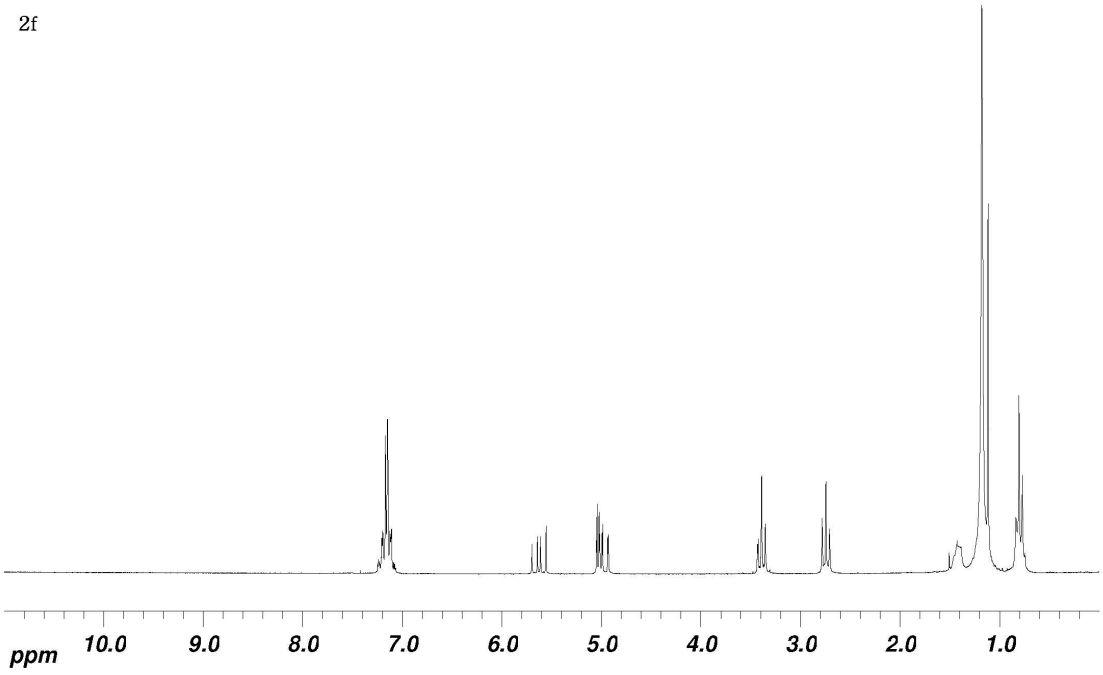

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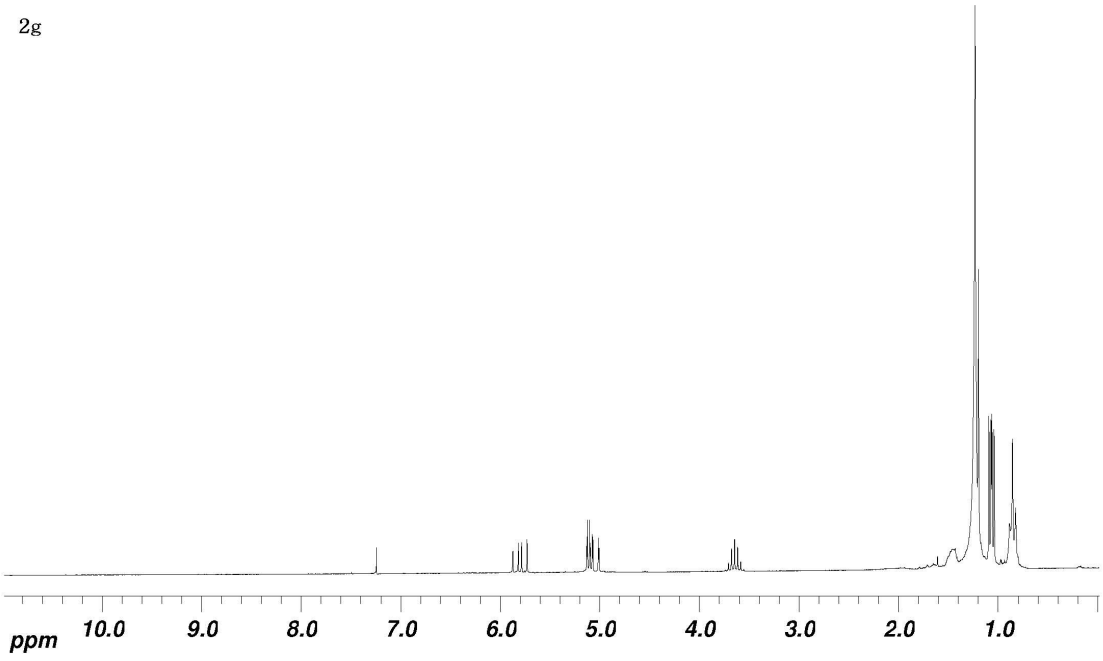

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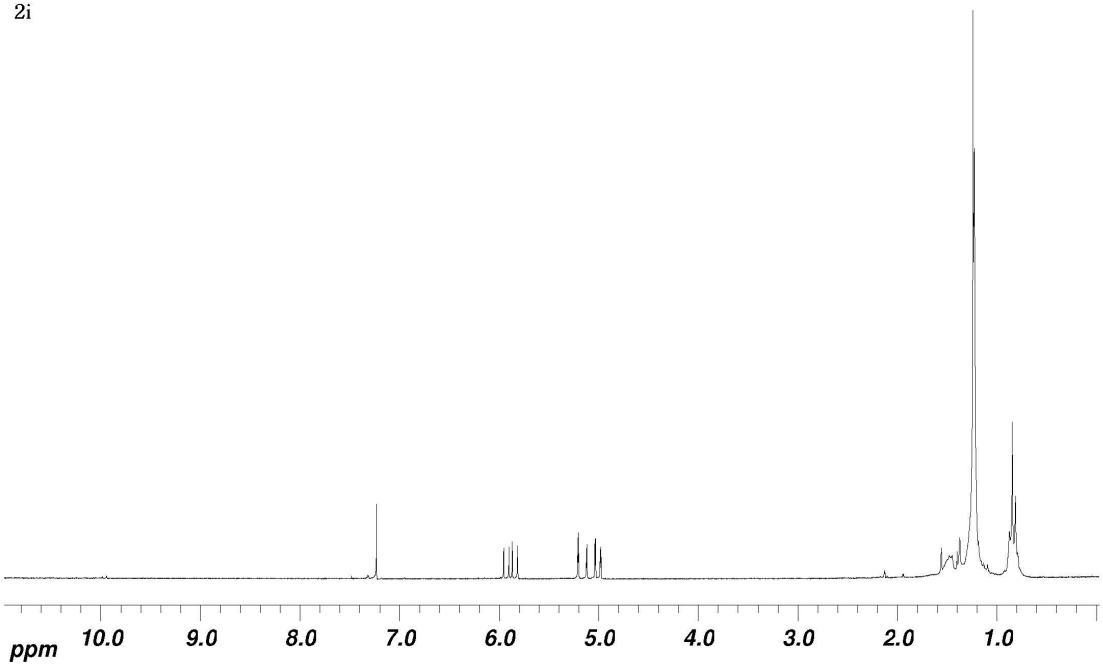

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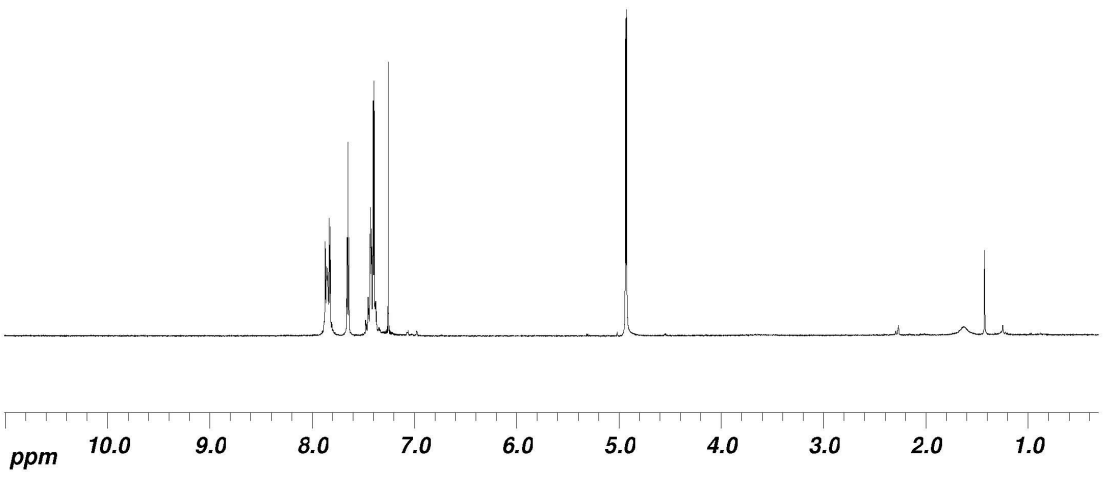

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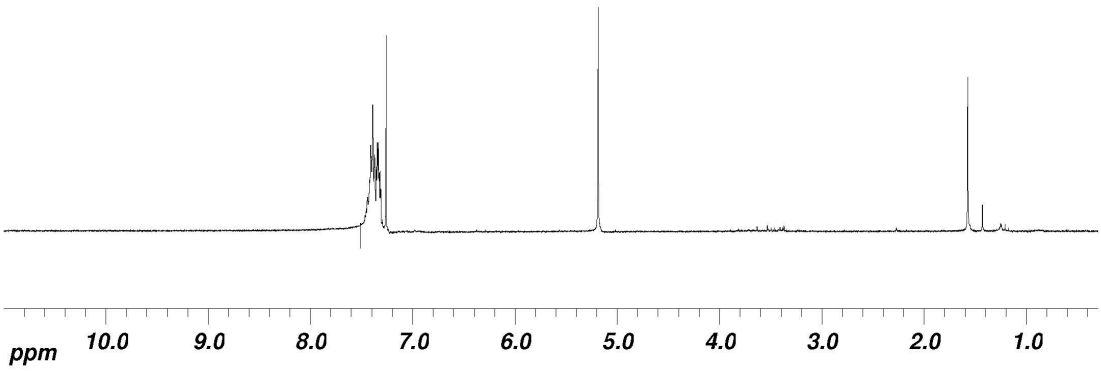

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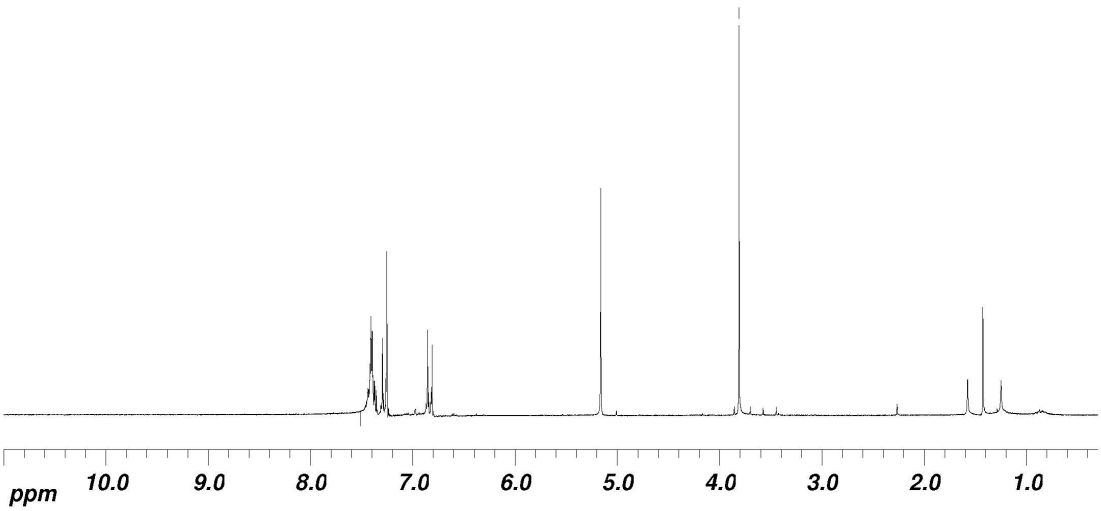

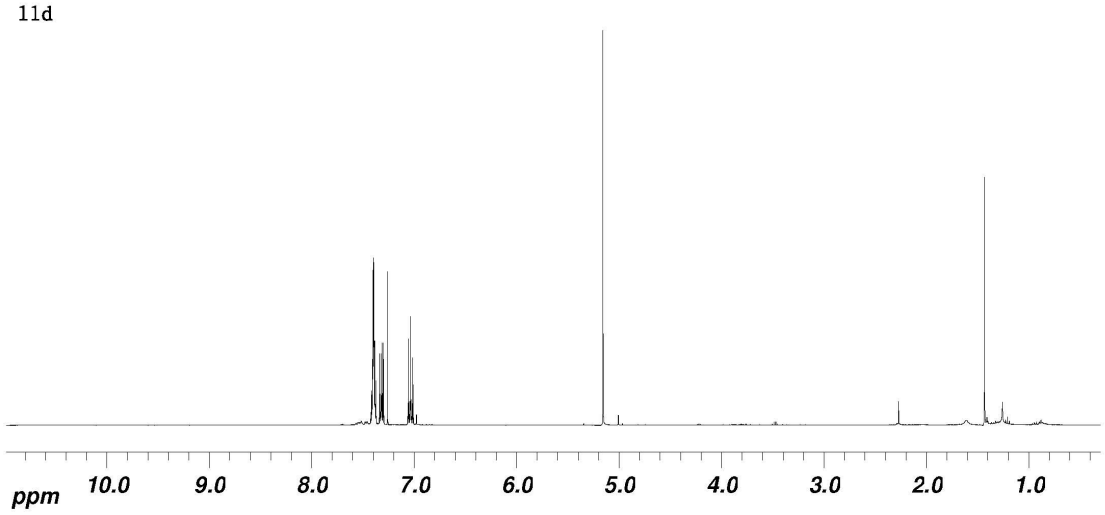
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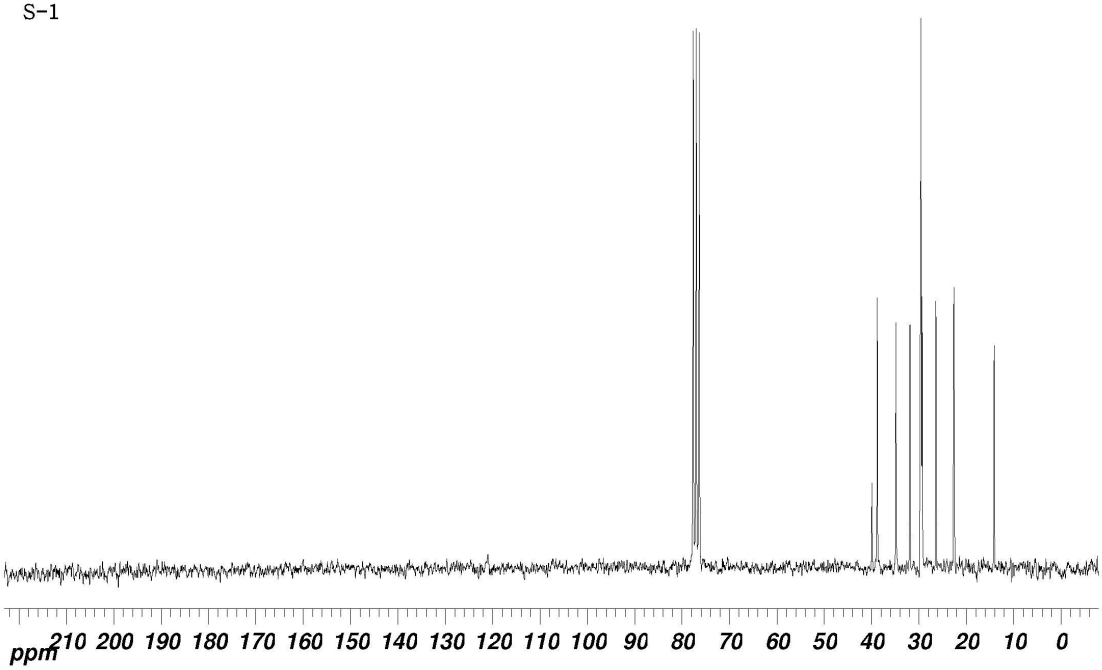
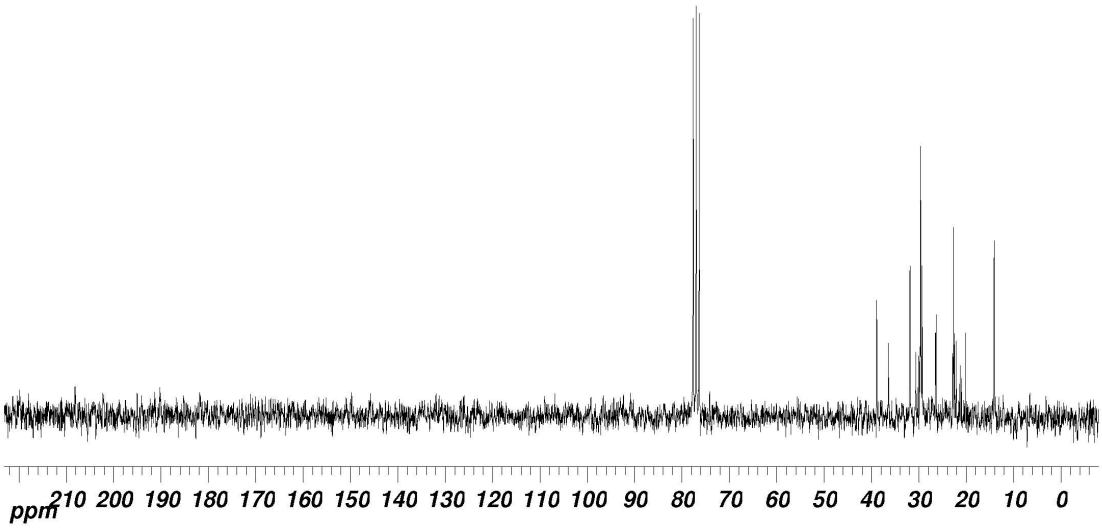
5. ^{13}C-NMR Spectra of Synthesised Compounds

S-1



S-2



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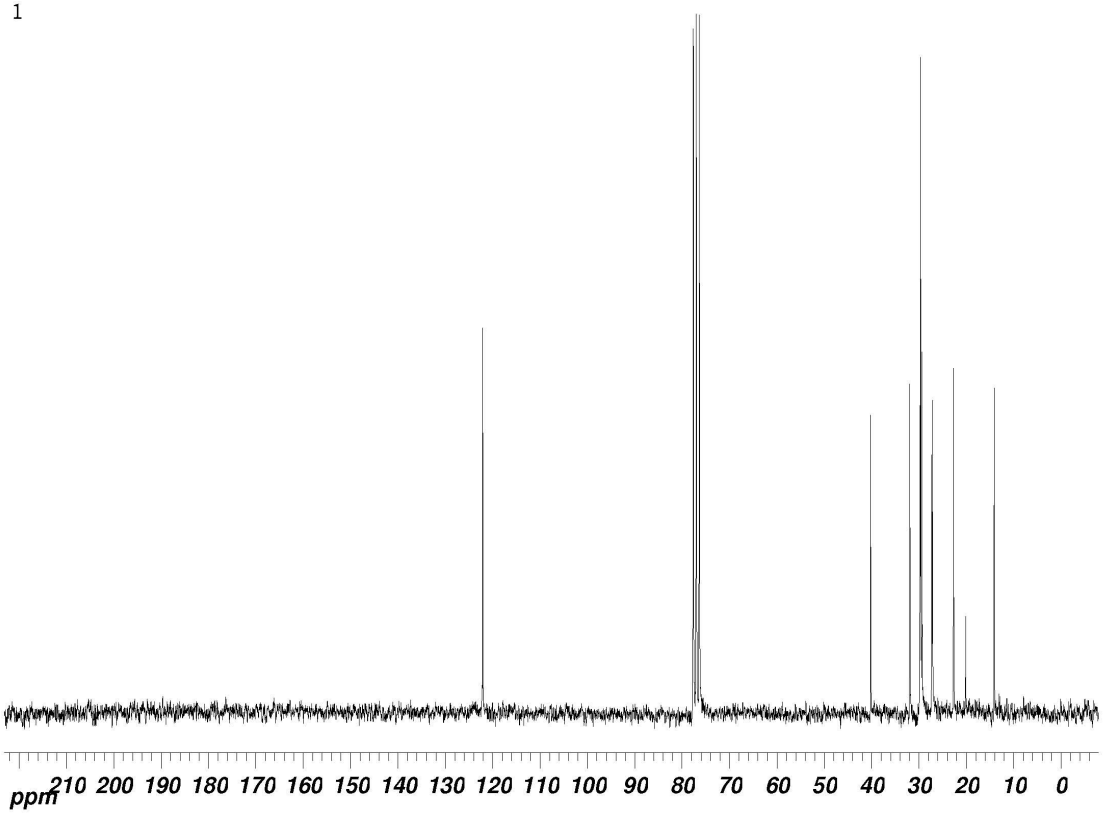
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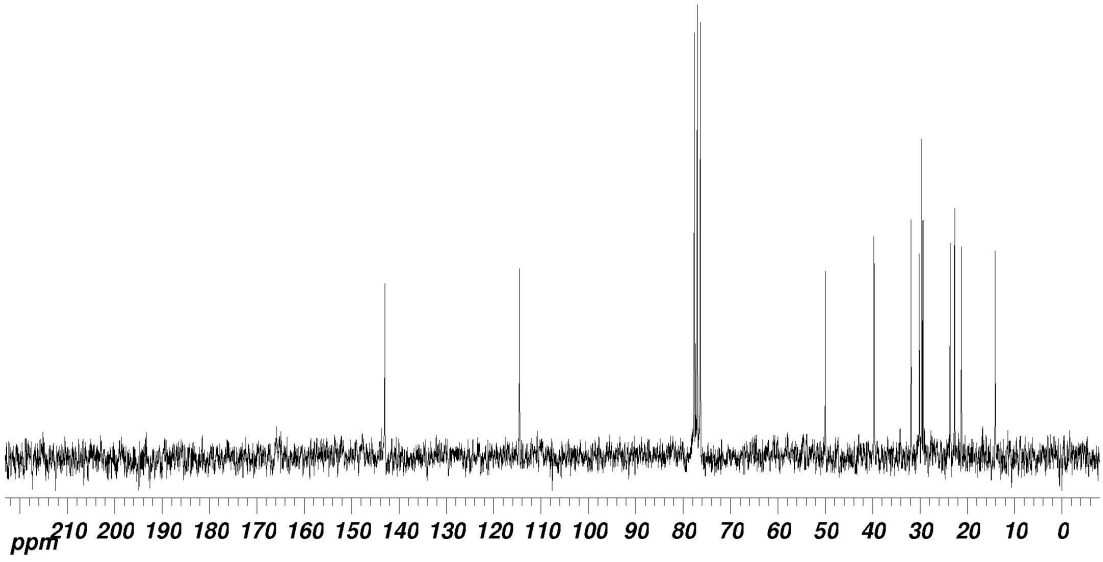
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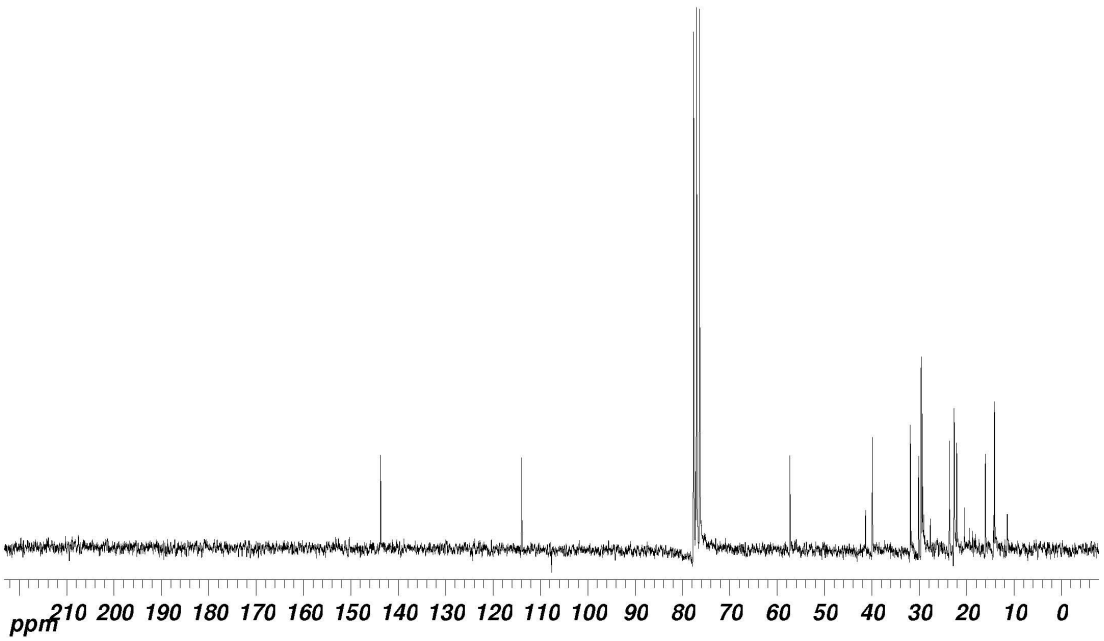
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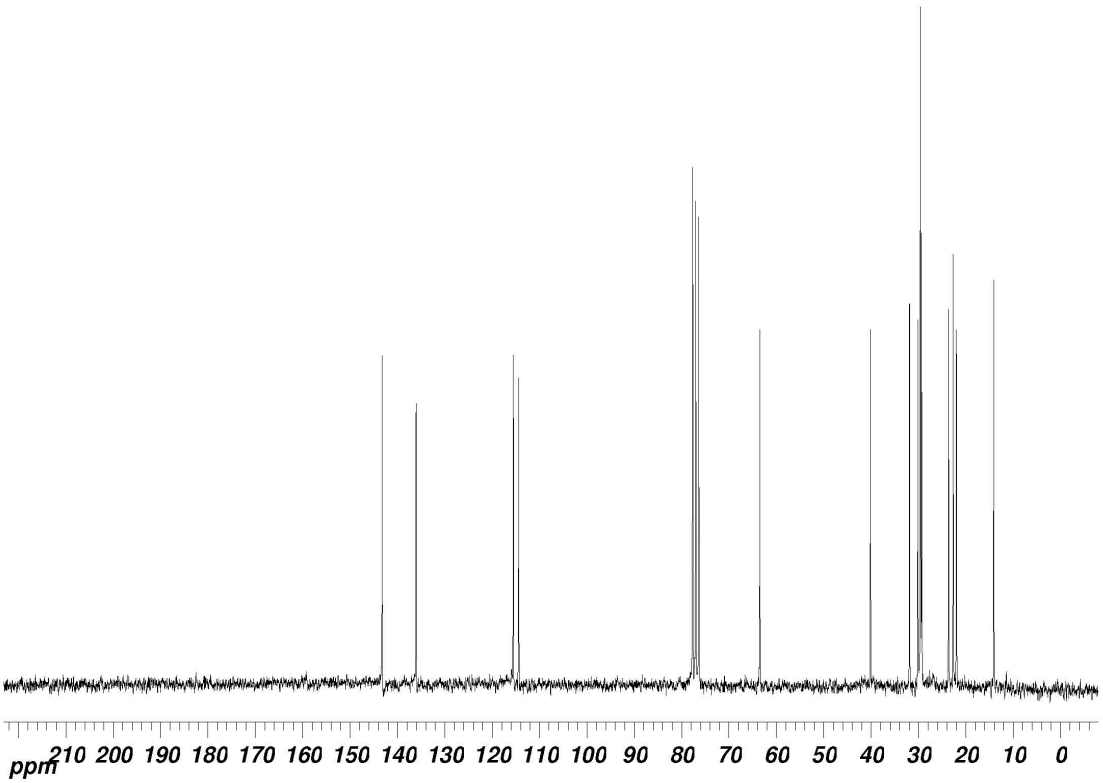
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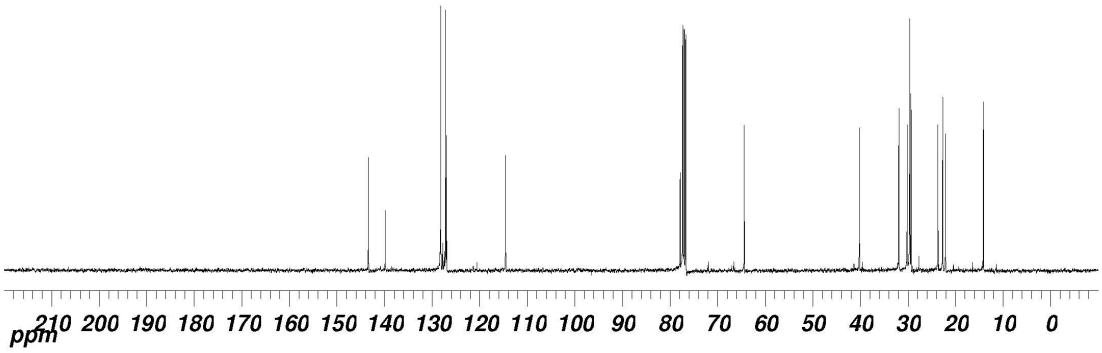
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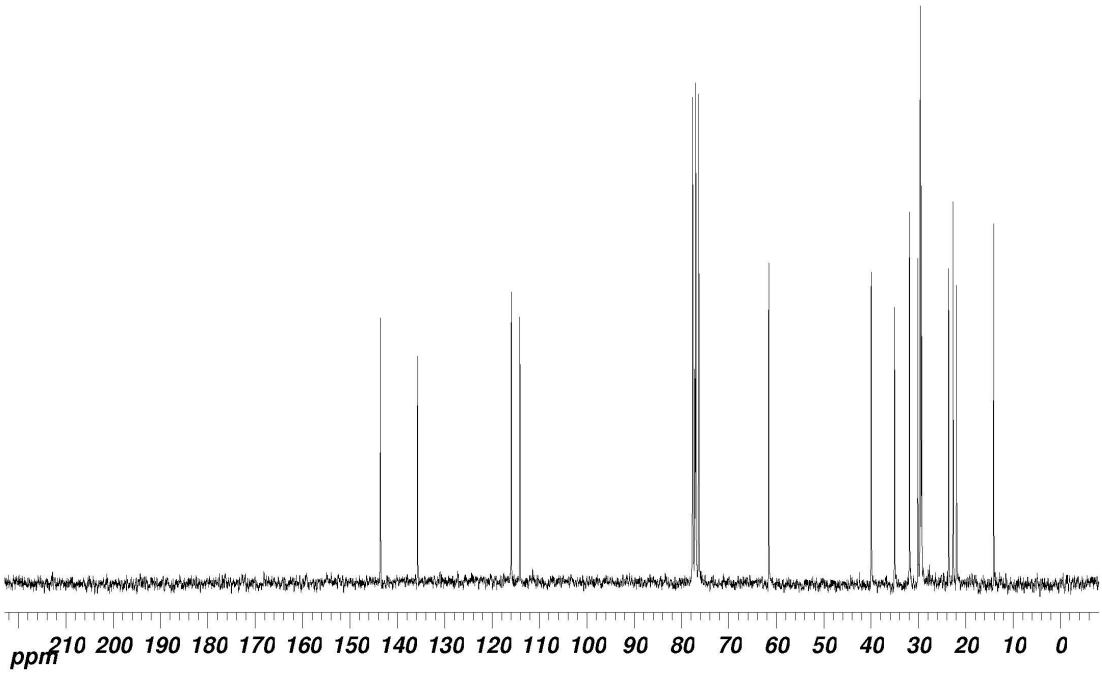
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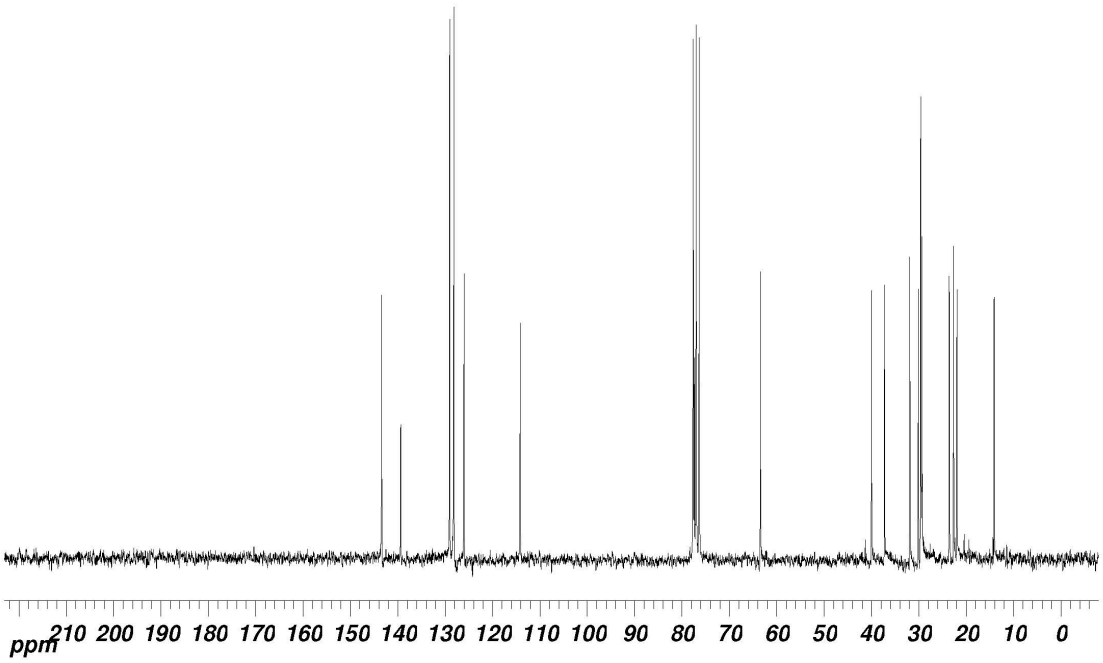
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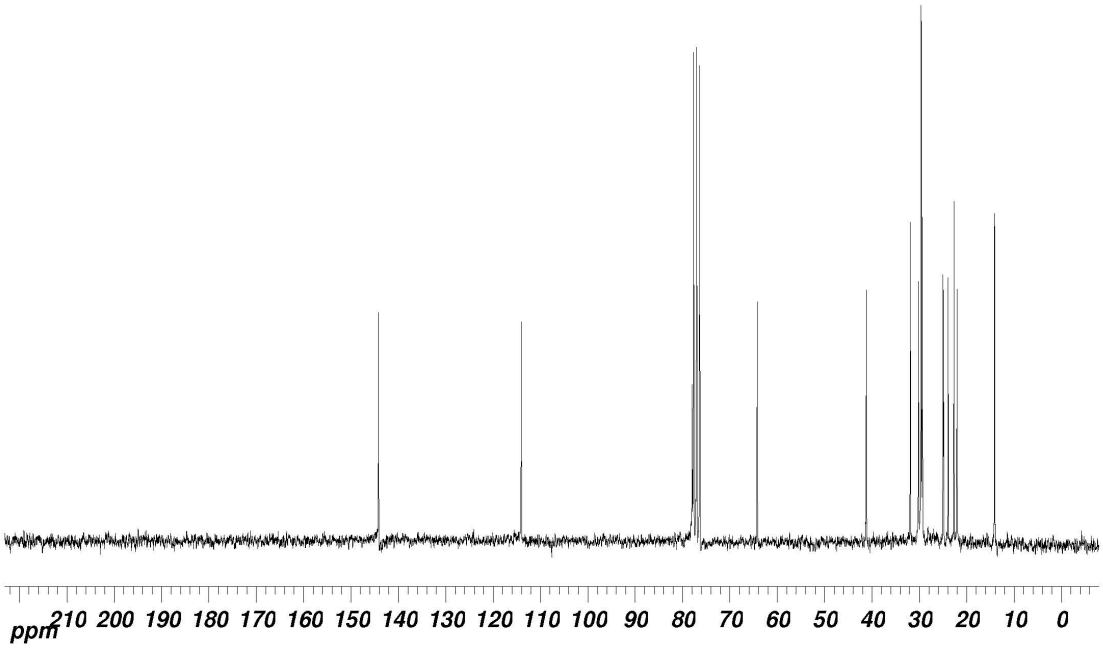
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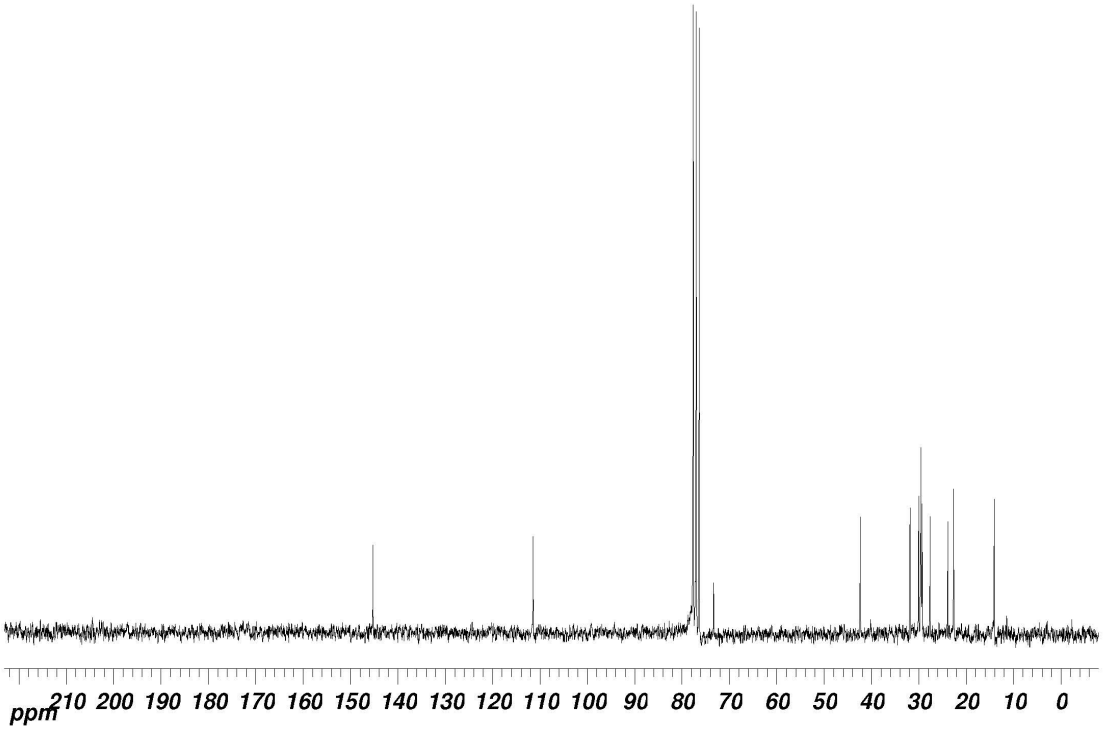
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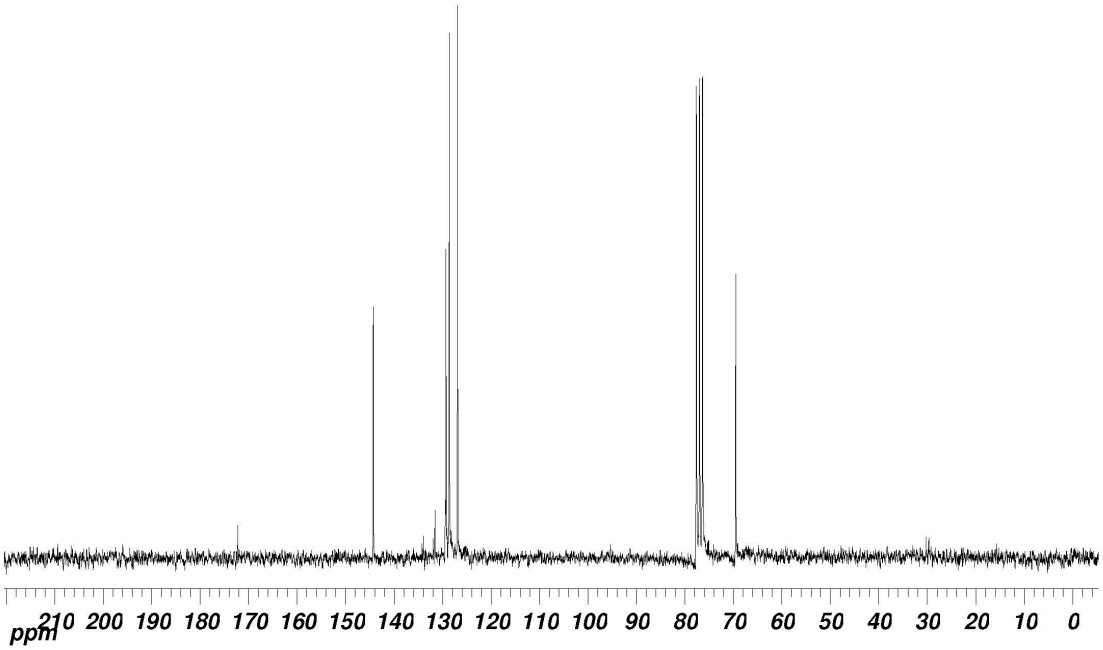
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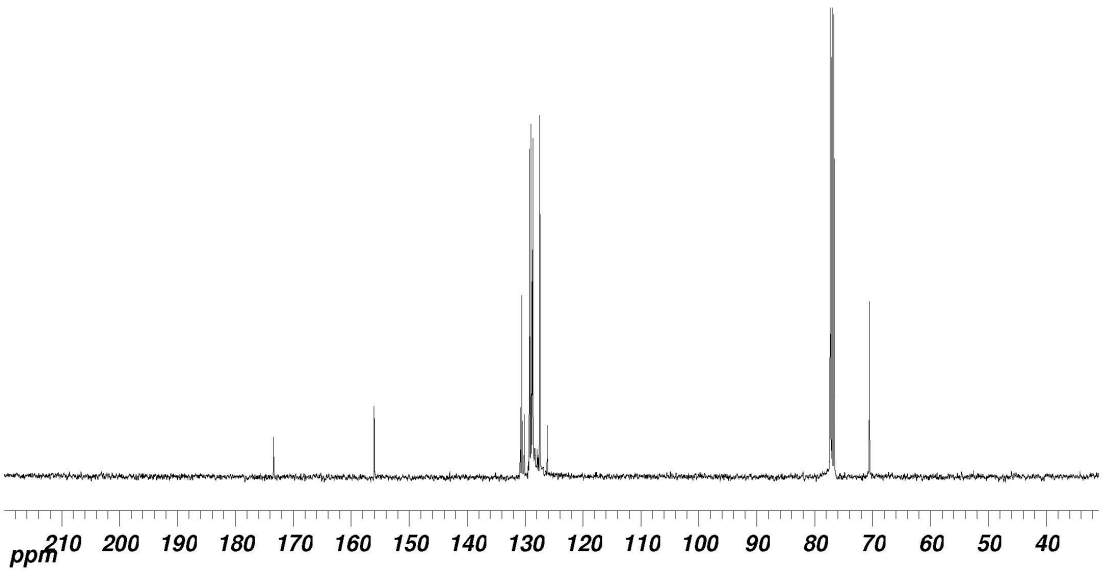
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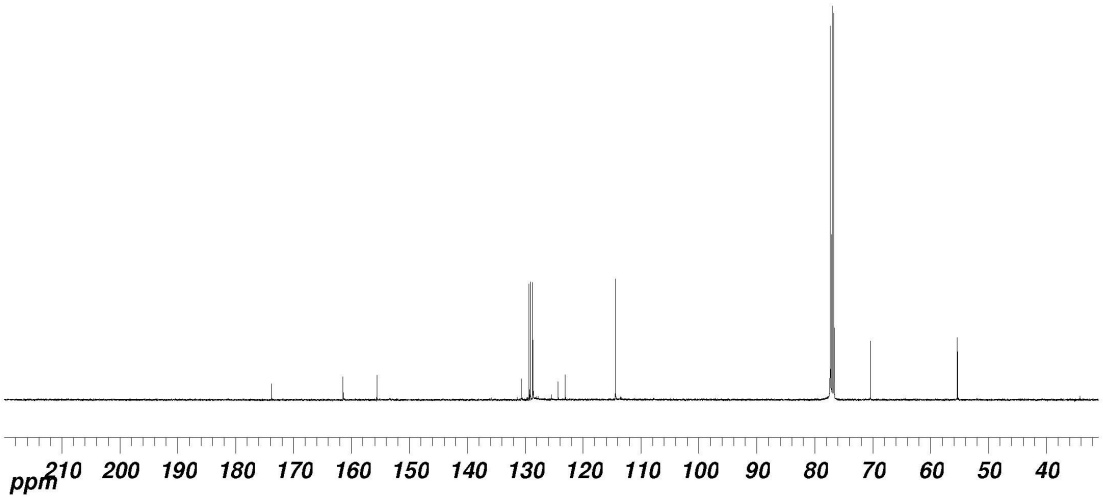
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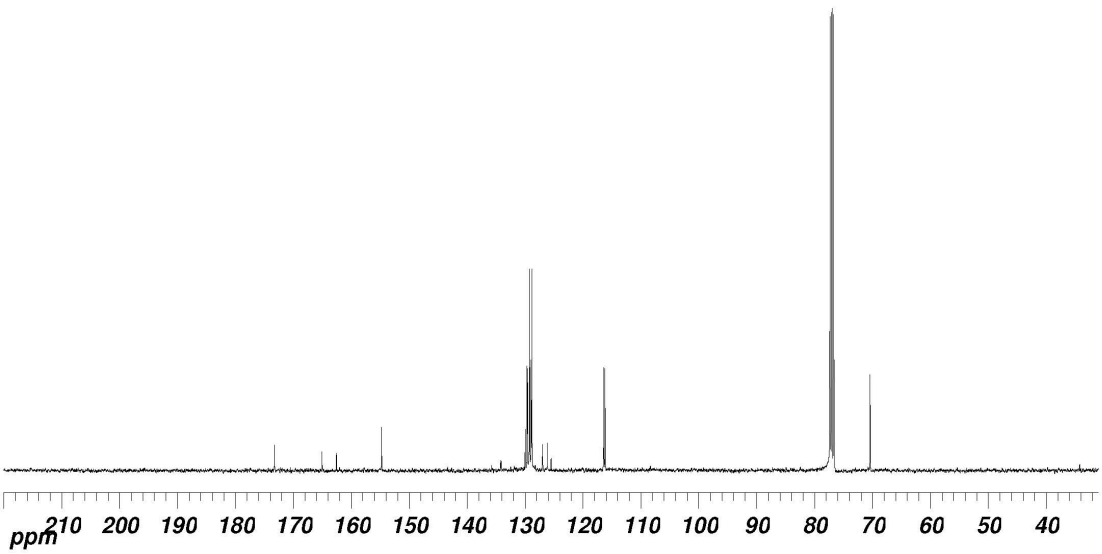
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6. References

1) M. Rubin, V. Gevorgyan, *Synthesis,* 2004, **5**, 796.
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