SUPPORTING INFORMATION

Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

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General Experimental

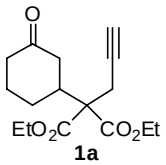
Flash chromatography: Fluorochem silica gel 60 (0.043-0.063 mm). Thin layer chromatography (TLC): Macherey Nagel silica gel $60F_{254}$ analytical plates (plastic support) which were developed using standard visualising agents: UV fluorescence (254 and 366 nm), phosphomolybdic acid /Δ, and potassium permanganate /Δ. IR: Perkin–Elmer Spectrum 100 FTIR spectrometer or a Paragon 1600, only selected absorbencies (υ_{max}) are reported in cm^{-1}. MS and HRMS (EI): VG ProSpec or VG-ZabSpec at 70 eV. High resolution EI spectra were measured using perfluorokerosene (PFK) as an internal calibrant. MS and HRMS (ES): Micromass LCT using a methanol mobile phase. HRMS was obtained using a lock-mass to adjust the calibrated mass scale. MS data are reported as *m/z* (relative intensity). GC-MS were performed using a HP 5890 Series II apparatus. Melting points: Kofler hot stage. Elemental analyses: Carlo Erba EA1110 simultaneous CHNS analyser based on a dynamic flash combustion and GC separation system. Commercially available compounds were purchased from Aldrich, Fluka, Acros, Strem, Alfa Aesar and used without further purification; except for 2-cyclohexen-1-one which was purified by Kugelrohr distillation (oven temperature 90 °C, pressure 50 mBar). All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF (Na benzophenone ketyl), CH_2Cl_2 (CaH_2), toluene (Na), EtOH (Mg turnings). Anhydrous DMF and $ClCH_2CH_2Cl$ were purchased from Aldrich. Asynt DrySin heating blocks on stirrer hotplates were employed for reactions with temperature controlled *via* external probe. NMR: Spectra were recorded on Bruker AC300 (^1H = 300 MHz, ^{13}C = 75.5 MHz), Bruker AV300 (^1H = 300 MHz, ^{13}C = 75.5 MHz), and Bruker AV400 (^1H = 400 MHz, ^{13}C = 101 MHz) in the solvents indicated; Chemical shifts (δ) are given in ppm relative to TMS. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual CH_2Cl_2 in CD_2Cl_2: $\delta_H \equiv 5.32$ ppm). Coupling constants (*J*) are reported in Hz. Multiplicity is denoted in ^1H NMR by: s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet). Multiplicity is denoted in ^{13}C NMR as s, d, t, q for C, CH, CH_2, CH_3 based on PENDANT pulse programme. 1D and 2D spectra were recorded using the following pulse sequences from the Bruker standard pulse program library: JMOD, PENDANT, DEPT 45, DEPT 135; Gradient COSY 90; Gradient HSQC for $^1J(C,H)$ = 145 Hz; Gradient HMBC for correlations via $^nJ(C,H)$. HPLC was performed on a Dionex Summit instrument. When given, NMR signal assignments are based on COSY and HSQC and/or HMBC. The numbering schemes are arbitrary and are shown in the inserts.

Preparation of Alkynyl Ketone Cyclisation Precursors

General Notes

Diethyl propargyl malonate,[1] propargyl malononitrile,[2] and ethyl propargyl acetoacetate[3] were prepared according to literature methods. Diethyl homopropargyl malonate was prepared by a modification of literature method[4] using NaH in place of NaOEt. The alkynyl ketones **1a**, **1d-1h** were prepared by nucleophilic attack of the required nucleophiles onto cyclic enones following the method described by Renaud.[5] The procedure was varied by using a slight excess on enone in some cases as described below for alkynyl ketone **1a**. Methyl 2-oxocyclooctanecarboxylate was prepared using the method of Holmes.[6]

2-(3-Oxocyclohexyl)-2-prop-2-ynylmalonic acid diethyl ester (1a)



1a

2-Cyclohexen-1-one (1.37 mL, 14.14 mmol) and DBU (2.11 mL, 14.14 mmol) were added to a solution of diethyl propargylmalonate (2.15 g, 10.87 mmol) in THF (32 mL). The mixture was heated to 40 °C and stirred for 48 h before saturated NH_4Cl (80 mL) was added, followed by ethyl acetate (80 mL). The two layers were separated. The organic layer was washed with saturated aqueous NaCl (80 mL), dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure. The residue was purified by flash chromatography (hexane/ethyl acetate: 8/2) to afford **1a** as a light yellow oil (2.05 g, 64%); EA (Found: C, 65.43; H, 7.81. Calc. for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53%); υ_{max} /cm^{-1} (neat) 3278, 2981, 2940, 2870, 1727; δ_H(300 MHz; $CDCl_3$) 1.27 (6 H, t, *J* 7.1), 1.36-1.52 (1 H, m), 1.59-1.76 (1 H, m), 2.03 (1 H, t, *J* 2.6), 2.05-2.34 (4 H, m), 2.37-2.48 (1 H, m), 2.53-2.74 (2 H, m), 2.86 (2 H, d, *J* 2.6), 4.23 (4 H, q, *J* 7.1); δ_C(75.5 MHz; $CDCl_3$) 13.9 (2q), 22.6 (t), 24.5 (t), 26.9 (t), 40.6 (d), 40.9 (t), 43.4 (t), 59.5 (s), 61.5 (2t), 71.7 (d), 78.6 (s), 168.9 (2s), 209.8 (s); *m/z* (ES) 317.1369 (calc. for [M$^+$ + Na] $C_{16}H_{22}O_5Na$: 317.1365).

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[1] Padgett, H.; Csendes, I. G.; Rapoport, H. *J. Org. Chem*. **1979**, *44*, 3492.

[2] Diez-Barra, E.; De la Hoz, A.; Moreno, A.; Sánchez-Verdú, P. J. *Chem. Soc. Perkin Trans. 1*, **1991**, 2589.

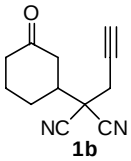
[3] Reynolds, R. C.; Trask, T. W.; Sedwick, W. D. *J. Org. Chem*. **1991**, *56*, 2391.

[4] Eglinton, G.; Whiting, M. C. *J. Chem. Soc*. **1953**, 3052.

[5] Beaufils, F.; Dénès, F.; Becattini, B.; Renaud, P. *Adv. Synth. Catal.* **2005**, *347*, 1587.

[6] Carling, R. W.; Clark, J. S.; Holmes, A. B. *J. Chem. Soc. Perkin Trans 1*. **1992**, 83.

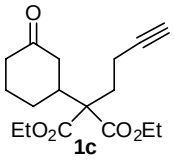
2-(3-Oxocyclohexyl)-2-prop-2-ynyl-malononitrile (1b)



1b

Addition of propargyl malononitrile (200 mg, 1.92 mmol) to 2-cyclohexen-1-one (93 μL, 0.96 mmol) was achieved using a method described by Parham and Czuba.[7] **1b** was obtained after flash chromatography (Hexanes:EtOAc 7:3) as a light yellow solid (170 mg, 89%); mp 96-98 ºC; υ_{max} /cm^{-1} (neat) 3246, 2985, 2930, 2878, 1714; δ_H(300 MHz; $CDCl_3$), 1.63-1.84 (2 H, m), 2.19-2.39 (4 H, m), 2.40 (1 H, t, *J* 2.7), 2.45-2.60 (2 H, m), 2.63-2.74 (1 H, m), 2.92 (1 H, dd, *J* 17.0 and 2.7), 3.02 (1 H, dd, *J* 17.0 and 2.7); δ_C(75.5 MHz; $CDCl_3$) 23.5 (t), 26.0 (t), 26.8 (t), 40.3 (t), 41.4 (s), 42.4 (t), 42.4 (d), 73.7 (s), 75.8 (d), 113.0 (s), 113.4 (s), 206.1 (s); *m/z* (ES) 223.0842 (calc. for [M^+ + Na] $C_{12}H_{12}N_2ONa$: 223.0847).

2-But-3-ynyl-2-(3-oxocyclohexyl)-malonic acid diethyl ester (1c)



1c

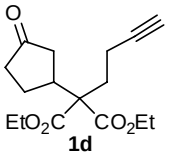
Following the method of Iwasawa[8] diethyl homopropargylmalonate (0.38 g, 1.79 mmol) was added to a suspension of NaH (0.12 g, 3.00 mmol) in THF (2.9 mL) at 0 °C. After the evolution of H_2, 2-cyclohexen-1-one (0.14 mL, 1.45 mmol) was added to the reaction mixture, followed by addition of TMSOTf (0.29 mL, 1.59 mmol) at 0°C. The mixture was stirred at 0°C for 4 h before saturated NH_4Cl (25 mL) was added, followed by ethyl acetate (25 mL). The two layers were separated. The organic layer was washed with saturated aqueous NaCl (40 mL), dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure. The residue was purified by flash chromatography (hexane/ethyl acetate: 8/2) to afford the silyl enol ether as a colourless liquid (0.31 g, 56%). The silyl enol ether (300 mg, 0.79 mmol) was dissolved in THF (8.5 mL) and cooled to -35 °C. TBAF (1 M in THF, 1.0 mL, 1.00 mmol) was added and the mixture stirred for 40 min at -35 °C. The reaction was quenched with saturated NH_4Cl (25 mL) and extracted with ethyl acetate (25 mL). The two layers were separated. The organic layer was washed with saturated aqueous NaCl (25 mL), dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure. The residue was purified by flash chromatography (hexane/ethyl acetate: 8/2) to afford **1c** as a yellow liquid (129 mg, 53%). υ_{max} /cm^{-1} (neat) 3281, 2937, 2870, 1715; δ_H(300 MHz; $CDCl_3$) 1.27 (6 H, t, *J* 7.1), 1.32-1.69 (3 H, m), 1.96 (1 H, t, *J* 2.2), 1.98-2.52 (10 H, m), 4.21 (2 H, q, *J* 7.1), 4.22 (2 H, q, *J* 7.1); δ_C(75.5 MHz; $CDCl_3$) 14.1 (2q),14.5 (t), 24.7 (t), 27.0 (t), 32.5 (t), 41.1 (t), 42.2 (d), 43.6 (t), 60.2 (s), 61.4 (2t), 68.8 (d), 83.1 (s), 169.6

[7] Parham, W. E.; Czuba, L. J. *J. Org. Chem*. **1969**, *34*, 1899.

[8] Iwasawa, N.; Maeyama, K.; Kusama, H. *Org. Lett*. **2001**, *3*, 3871.

(s), 169.8 (s), 210.0 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{17}H_{24}O_5Na$: 331.1521, found 331.1526 [M^+ + Na].

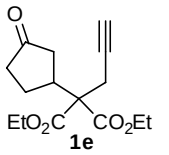
2-But-3-ynyl-2-(3-oxocyclopentyl)-malonic acid diethyl ester (1d)



1d

Using 2-cyclopenten-1-one (0.16 mL, 1.89 mmol) and diethyl homopropargylmalonate (400 mg, 1.89 mmol) and after purification by flash chromatography (Hexanes:EtOAc 8:2) **1d** was obtained as a colourless liquid (400 mg, 72%); υ_{max} /cm^{-1} (neat) 3283, 2981, 2938, 1725; δ_H(300 MHz; $CDCl_3$) 1.27 (6 H, t, *J* 7.1), 1.62-1.79 (1 H, m), 1.97 (1 H, t, *J* 2.4), 2.10-2.40 (8 H, m), 2.50 (1 H, dd, *J* 18.7 and 7.9), 2.74-2.88 (1 H, m), 4.21 (4 H, q, *J* 7.1); δ_C(75.5 MHz; $CDCl_3$) 14.0 (2 q), 14.4 (t), 24.8 (t), 32.7 (t), 38.4 (t), 40.3 (d), 41.1 (t), 59.3 (s), 61.5 (2t), 68.9 (d), 83.0 (s), 169.8 (s), 170.0 (s), 217.2 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{16}H_{22}O_5Na$: 317.1365, found 317.1359 [M^+ + Na].

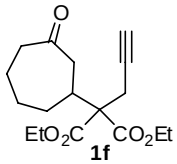
2-(3-Oxocyclopentyl)-2-prop-2-ynylmalonic acid diethyl ester (1e)



1e

Using 2-cyclopenten-1-one (0.21 mL, 2.52 mmol) and diethylpropargyl malonate (0.50 g, 2.52 mmol) and after purification by flash chromatography (Hexanes:EtOAc 8:2) **1e** was obtained as a colourless liquid (623 mg, 88%); υ_{max} /cm^{-1} (neat) 3279, 2982, 2937, 2907, 1729; δ_H(300 MHz; $CDCl_3$) 1.27 (6 H, t, *J* 7.1), 1.62-1.81 (1 H, m), 2.04 (1 H, t, *J* 2.4), 2.14-2.43 (4 H, m), 2.60 (1 H, dd, *J* 18.4 and 7.4), 2.85 (1 H, dd, *J* 17.4 and 2.4), 2.93 (1 H, dd, *J* 17.4 and 2.4), 3.00-3.15 (1 H, m), 4.17-4.32 (4 H, m); δ_C(75.5 MHz; $CDCl_3$) 14.0 (2 q), 23.7 (t), 24.9 (t), 38.5 (t), 39.4 (d), 41.1 (t), 58.8 (s), 61.8 (2t), 71.8 (d), 78.6 (s), 169.2 (s), 169.3 (s), 217.3 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{15}H_{20}O_5Na$: 303.1208, found 303.1199 [M^+ + Na].

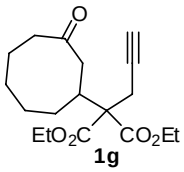
2-(3-Oxocycloheptyl)-2-prop-2-ynyl-malonic acid diethyl ester (1f)



1f

Using 2-cyclohepten-1-one (266 mg, 2.42 mmol) and diethylpropargyl malonate (480 mg, 2.42 mmol) and after purification by flash chromatography (Hexanes:EtOAc 8:2) **1f** was obtained as a yellow oil (418 mg, 56%); υ_{max} /cm^{-1} (neat) 3277, 2935, 1725, 1701; δ_H(300 MHz; $CDCl_3$) 1.13-1.24 (1 H, m), 1.26 (3 H, t, *J* 7.1), 1.28 (3 H, t, *J* 7.1), 1.45-1.60 (2 H, m), 1.91-2.09 (3 H, m), 2.05 (1 H, t, *J* 2.7), 2.42-2.54 (2 H, m), 2.59-2.77 (3 H, m), 2.82 (1 H, dd, *J* 17.5 and 2.7), 2.89 (1 H, dd, *J* 17.5 and 2.7), 4.18-4.28 (4 H, m); δ_C(75.5 MHz; $CDCl_3$) 14.0 (2 q), 23.0 (t), 25.1 (t), 29.4 (t), 32.3 (t), 38.4 (d), 43.1 (t), 46.0 (t), 60.5 (s), 61.7 (2t), 71.8 (d), 78.9 (s), 169.2 (s), 169.4 (s), 212.8 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{17}H_{24}O_5Na$: 331.1521, found 331.1517 [M^+ + Na].

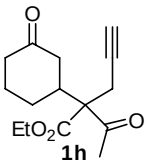
2-(3-Oxocyclooctyl)-2-prop-2-ynyl-malonic acid diethyl ester (1g)



1g

Using 2-cycloocten-1-one (200 mg, 1.61 mmol) and diethylpropargyl malonate (319 mg, 1.61 mmol) and after purification by flash chromatography (Hexanes:EtOAc 8:2) **1g** was obtained as a light yellow oil (218 mg, 42%); υ_{max} /cm^{-1} (neat) 3277, 2937, 2861, 1729, 1699; δ_H(300 MHz; $CDCl_3$) 1.05-1.23 (1 H, m), 1.27 (3 H, t, *J* 7.1), 1.28 (3 H, t, *J* 7.1), 1.32-1.49 (2 H, m), 1.59-1.96 (5 H, m), 2.08 (1 H, t, *J* 2.8), 2.26-2.37 (2 H, m), 2.66-2.74 (1 H, m), 2.82 (1 H, dd, *J* 17.5 and 2.7), 2.80-2.89 (1 H, m), 2.97 (1 H, dd, *J* 17.5 and 2.7), 3.18 (1 H, tt, *J* 12.6, 3.4), 4.14-4.31 (4 H, m); δ_C(75.5 MHz; $CDCl_3$) 14.0 (2 q), 23.0 (t), 23.8 (t), 25.8 (t), 28.0 (t), 29.5 (t), 36.5 (d), 40.6 (t), 46.1 (t), 60.0 (s), 61.7 (2t), 71.8 (d), 79.0 (s), 169.4 (s), 169.8 (s), 215.9 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{18}H_{26}O_5Na$: 345.1678, found 345.1690 [M^+ + Na].

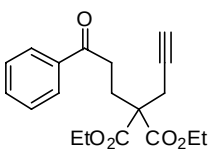
2-Acetyl-2-(3-oxocyclohexyl)-pent-4-ynoic acid ethyl ester (1h)



1h

Using 2-cyclohexen-1-one (0.29 mL, 2.98 mmol) and ethyl propargyl acetoacetate (0.50 g, 2.98 mmol) and after purification by flash chromatography (Hexanes:EtOAc 8:2) **1h** is obtained as a colorless oil in a 1:1.2 mixture of diastereoisomers (357 mg, 45%); υ_{max} /cm^{-1} (neat) 3278, 2940, 1705; δ_H(300 MHz; $CDCl_3$) 1.30 (3 H, t, *J* 7.1, isomer a), 1.31 (3 H, t, *J* 7.2, isomer b), 1.40 (1 H, dt, *J* 12.8 and 3.3, isomer a), 1.43 (1 H, dt, *J* 12.8 and 3.4, isomer b), 1.57-1.75 (2 H, m, both isomers), 1.92-2.01 (2 H, m, both isomers), 2.04 (1 H, t, *J* 2.7, isomer a), 2.04 (1 H, t, *J* 2.7, isomer b), 2.05-2.19 (4 H, m, both isomers), 2.22 (3 H, s, isomer a), 2.22 (3 H, s, isomer b), 2.27 (2 H, dd, *J* 16.8 and 11.5, both isomers), 2.33-2.51 (4 H, m, both isomers), 2.62-2.77 (2 H, m, both isomers), 2.79 (2 H, dd, *J* 4.6 and 2.7, both isomers), 2.82 (2 H, d, *J* 2.7, both isomers), 4.20-4.33 (4 H, m, both isomers); δ_C(75.5 MHz; $CDCl_3$) 13.8 (2 q), 20.9 (t), 21.1 (t), 24.6 (2t), 26.5 (t), 27.3 (t), 27.5 (q), 27.8 (q), 40.1 (d), 40.5 (d), 40.7 (t), 40.9 (t), 42.9 (t), 43.4 (t), 61.6 (t), 61.7 (t), 64.7 (s), 64.9 (s), 71.9 (d), 72.0 (d), 78.6 (s), 79.0 (s), 169.7 (2s), 202.0 (s), 202.1 (s), 209.5 (2s); HR-MS (ES-TOF): *m/z*: calcd for $C_{15}H_{20}O_4Na$: 287.1259, found 287.1251 [M^+ + Na].

Diethyl 2-(3-oxo-3-phenylpropyl)-2-(prop-2-yn-1-yl)malonate (1i)[9]



1i

Na (57.9 mg, 2.52 mmol) was carefully dissolved in absolute EtOH (7 mL). Diethyl propargylmalonate (500 mg, 2.52 mmol) was added dropwise over 15 min, followed by the addition of 3-chloropropiophenone (302 mg,

[9] Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928-1929.

1.79 mmol). The reaction mixture was then stirred at rt for 2 h; before H_2O (30 mL) was added to quench the reaction. The aqueous phase was extracted with Et_2OAc (2 × 30 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc: 8/2) to afford **1i** as a white solid (562 mg, 95%); R_f 0.37 (hexane/EtOAc: 8/2); δ_H(300 MHz; $CDCl_3$) 1.25 (6 H, t, *J* 7.1, CH_2CH_3), 2.01-2.05 (1 H, m, C≡C*H*), 2.45-2.54 (2 H, m, CH_2), 2.89 (2 H, d, *J* 2.7, H_2CC≡CH), 2.99-3.09 (2 H, m), 4.08-4.30 (4 H, m, CH_2CH$_3$), 7.42-7.49 (2 H, m, Ar *H*), 7.53-7.60 (1 H, m, Ar *H*), 7.94-7.99 (2 H, m, Ar *H*); δ_C(75.5 MHz; $CDCl_3$) 14.0 (2 q, CH_2CH_3), 23.8 (t, CH_2), 27.0 (t, CH_2), 33.7 (t, CH_2), 56.1 (s, $C(CO_2Et)_2$), 61.8 (2 t, CH_2CH_3), 71.8 (d, CH_2C≡CH), 78.7 (s, C≡CH), 128.1 (d, Ar *C*H), 128.6 (d, Ar *C*H), 133.1 (d, Ar *C*H), 154.1 (s, Ar *C*H), 170.0 (2 s, CO_2Et), 198.6 (s, *C*O); *m/z* (TOF ES+) 353.2 ($[M+Na]^+$, 100%); HR-MS (ES-TOF): *m/z*: calcd for $C_{19}H_{22}O_5Na$: 353.1365, found 353.1375 [M^+ + Na].

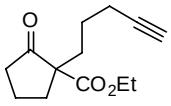
General Procedure 1 (GP1): α-Alkylation of β-ketoesters

Following a modified literature procedure[5] the β-ketoester (1 eq) was added dropwise to a suspension of sodium hydride (1.2 eq) in DMF (0.96 M) at 0°C. The reaction mixture was stirred at rt for 55 min before 5-iodopent-1-yne (1 eq) was added dropwise. After the addition, the mixture was stirred at rt for 24 h before aq 1 M HCl (10 × solvent volume) was added followed by toluene (10 × solvent volume). The two layers were separated. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure. The residue was purified by flash chromatography (hexane/ethyl acetate: 8/2) to afford the alkylated product.

General Procedure 2 (GP2): Decarbethoxylation of alkylated β-ketoesters

Following a modified literature procedure[5] LiI (5 eq) was added to a solution of the alkylated β-ketoesters (1 eq) in DMF (0.76 M). The reaction mixture was stirred at 150 °C. After completion, the reaction mixture was allowed to cool to rt and treated with aq 1 M HCl (10 × solvent volume). Diethyl ether was added (10 × solvent volume) and the two layers were separated. The organic layer was extracted twice, washed with brine, dried over Na_2SO_4, filtered, and the solvent removed carefully under reduced pressure. The residue was purified by flash chromatography (hexane/diethyl ether: 9/1) to give the decarbethoxylated product.

2-(Pentin-4-yl)-2-ethoxycarbonylcyclopentanone (6a)

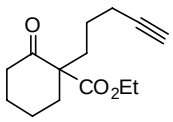


6a

Following GP1 using ethyl 2-oxocyclopentanecarboxylate (403 mg, 2.58 mmol) **6a** was obtained as a colourless liquid (426 mg, 74%). υ_{max} /cm^{-1} (neat) 3282,

2964, 1748, 1722; δ_H(300 MHz; $CDCl_3$) 1.25 (3 H, t, *J* 7.1), 1.37-1.73 (3 H, m), 1.83-2.10 (5 H, m), 2.16-2.33 (3 H, m), 2.36-2.59 (2 H, m), 4.16 (2 H, q, *J* 7.1); δ_C(75.5 MHz; $CDCl_3$) 13.6 (q), 18.2 (t), 19.1 (t), 23.4 (t), 32.4 (2t), 37.3 (t), 59.5 (s), 60.8 (t), 68.4 (d), 83.1 (s), 170.3 (s), 213.8 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{18}O_3Na$: 245.1154, found 245.1156 [M^+ + Na].

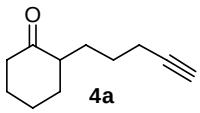
2-Oxo-1-pent-4-ynyl-cyclohexanecarboxylic acid ethyl ester (6b)



6b

Following general procedure 1, using ethyl 2-oxocyclohexanecarboxylate (439 mg, 2.58 mmol) **6b** was obtained as a colourless liquid (454 mg, 75%). υ_{max} /cm^{-1} (neat) 3285, 2940, 2867, 1711; δ_H(300 MHz; $CDCl_3$) 1.26 (3 H, t, *J* 7.1), 1.35-1.56 (3 H, m), 1.57-1.81 (4 H, m), 1.89-2.06 (2 H, m), 1.94 (1 H, t, *J* 2.6), 2.15-2.23 (2 H, m), 2.38-2.56 (3 H, m), 4.21 (2 H, q, *J* 7.1); δ_C(75.5 MHz; $CDCl_3$) 14.1 (q), 18.7 (t), 22.5 (t), 23.4 (t), 27.5 (t), 33.8 (t), 36.0 (t), 41.0 (t), 60.5 (s), 61.2 (t), 68.5 (d), 83.8 (s), 171.8 (s), 207.7 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{14}H_{20}O_3Na$: 259.1310, found 259.1307 [M^+ + Na].

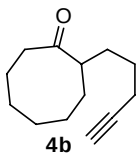
2-Pent-4-ynylcyclohexanone (4a)



4a

Following GP2, using ethyl 2-oxo-1-pent-4-ynylcyclohexanecarboxylate **6b** (300 mg, 1.83 mmol) **4a** was obtained as a colourless liquid (140 mg, 67%). υ_{max} /cm^{-1} (neat) 3291, 2934, 2861, 1709; δ_H(300 MHz; $CDCl_3$) 1.24-1.57 (4 H, m), 1.59-1.76 (2 H, m), 1.80-1.93 (2 H, m), 1.94 (1 H, t, *J* 2.6), 1.98-2.44 (7 H, m); δ_C(75.5 MHz; $CDCl_3$) 18.6 (t), 24.9 (t), 26.1 (t), 28.0 (t), 28.7 (t), 34.0 (t), 42.0 (t), 50.3 (d), 68.3 (d), 84.3 (s), 213.0 (s); MS(EI) 164 (M^+, 5%), 149 (21), 146 (5), 135 (34), 133 (4), 131 (16), 125 (11), 123 (35), 121 (100). Data are identical to those reported in the literature.[5]

2-Pent-4-ynyl-cyclooctanone (4b)



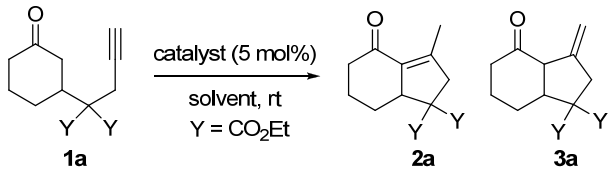
4b

Following GP1, using methyl 2-oxocyclooctanecarboxylate (950 mg, 5.16 mmol) methyl 2-oxo-1-pent-4-ynylcyclooctanecarboxylate was obtained as a colourless liquid (832 mg, 64%). υ_{max} /cm^{-1} (neat) 3286, 2930, 2859, 1736, 1705; δ_H(300 MHz; $CDCl_3$) 0.87-1.03 (1 H, m), 1.21-1.89 (10 H, m), 1.93 (1 H, t, *J* 2.7), 1.96-2.30 (5 H, m), 2.47 (1 H, ddd, *J* 15.7, 11.6, 4.4), 2.69 (1 H, dt, *J* 11.9 and 3.8), 3.68 (3H, s); δ_C(75.5 MHz; $CDCl_3$) 18.8 (t), 23.1 (t), 23.9 (t), 24.2 (t), 25.5 (t), 28.4 (t), 29.3 (t), 30.2 (t), 38.5 (t), 52.3 (q), 62.0 (s), 68.5 (d), 83.9 (s), 172.2 (s), 212.2 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{15}H_{22}O_3Na$: 273.1467, found 273.1457 [M^+ + Na]. Methyl 2-oxo-1-pent-4-ynylcyclooctanecarboxylate (622 mg, 2.49 mmol) was then subjected to GP2 and **4b** was obtained as a yellow liquid (392 mg, 82%); υ_{max} /cm^{-1} (neat) 3292, 2927, 2856, 1696; δ_H(300 MHz; $CDCl_3$) 1.17-1.31 (1 H, m), 1.34-1.88 (12 H, m), 1.90-2.06 (1 H, m), 1.94 (1 H, t,

J 2.7), 2.13-2.21 (2 H, m), 2.26-2.35 (1 H, m), 2.38-2.49 (1 H, m), 2.53-2.63 (1 H, m); δ_C(75.5 MHz; $CDCl_3$) 18.4 (t), 24.7 (t), 25.5 (t), 25.7 (t), 26.3 (t), 27.3 (t), 31.6 (t), 32.7 (t), 42.0 (t), 50.2 (d), 68.5 (d), 84.1 (s), 219.9 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{13}H_{20}ONa$: 215.1412, found 215.1406 [M^+ + Na]

Gold-Catalysed Cyclisation Reactions

Survey table using simple metal salts



Entry	Conditions	Time	Ratio		
			1a	**2a**	**3a**
1	$PtCl_2$, toluene	48 h	>98	<2	-
2[a]	$PtCl_2$, toluene	5 d	92	8	-
3	AuCl, anhydrous toluene at 70°C	2 d	78	22	0
4	AuCl, toluene non-dried at 70°C	2 d	78	-	-
5	AuCl, DCM	2 d	98.6	-	-
6	AuCl, DCM non-dried, rt	2 d	98.6	1.4	-
7	AuCl, THF, 70°C	1 d	100	-	-
8[a]	$AuCl_3$, DCM, rt	2 h 30	71	-	3

Procedure: a 0.1 M solution of the substrate in the required solvent was added onto the catalyst under argon atmosphere in a flame-dried Schlenk tube. [a] The reaction temperature was progressively increased : 3 days at rt, 1 day at 40 °C, 1 day at 70 °C. The ratios were determined by ^{1}H NMR analysis of the crude mixture.

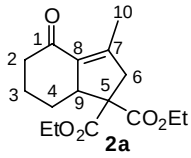
General procedure for gold-catalysed reactions

AgOTf (0.06 eq) was weighed into a flame-dried Schlenk (or carousel tube) under argon atmosphere, followed by the addition of the Ph_3PAuCl (0.06 eq). Immediately after this addition, a 0.1 M solution of the substrate in the desired solvent was added *via* syringe, and the mixture stirred at rt for the required length of time. On completion of the reaction, the solution was either loaded directly onto a silica gel column followed by elution with the appropriate eluent, or filtered through a short pad of silica gel (CH_2Cl_2, diethyl ether or hexane/ethyl acetate: 8/2), the solvent removed under reduced pressure and the residue was purified by flash

chromatography (hexanes/ethyl acetate). When required the ratio of isomers was determined by NMR analysis of the crude reaction.

The following compounds were prepared by this method:

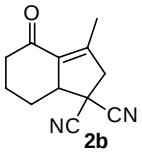
Diethyl 3-methyl-4-oxo-2,4,5,6,7,7a-hexahydroindene-1,1-dicarboxylate (2a)



2a

Using **1a** (117 mg, 0.4 mmol), cyclised product **2a** was obtained as a yellow oil (102 mg, 87%); υ_{max} /cm^{-1} (neat) 2981, 2942, 2871, 1731, 1682, 1626; δ_H(300 MHz; $CDCl_3$) 1.07-1.14 (1 H, m, 4-H), 1.20 (6 H, t, *J* 7.1, 2 × CH_2CH_3), 1.61-1.81 (1 H, m, 3-H), 1.91-2.00 (1 H, m, 3-H), 2.03 (3 H, s, 10-H), 2.05-2.19 (2 H, m, 4-H, 2-H), 2.31-2.44 (1 H, m, 2-H), 2.70 (1 H, br d, *J* 18.3, 6-H), 3.04 (1 H, br d, *J* 18.3, 6-H), 3.59-3.73 (1 H, m, 9-H), 4.02-4.28 (4 H, m, 2 × CH_2CH_3); δ_C(75.5 MHz; $CDCl_3$) 13.9 (q), 14.0 (q), 15.5 (q), 23.4 (t), 27.4 (t), 40.5 (t), 46.0 (t), 51.6 (d), 61.2 (t), 61.3 (t), 61.8 (s), 131.9 (s), 149.3 (s), 170.1 (s), 171.0 (s), 199.1 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{16}H_{22}O_5Na$: 317.1365, found 317.1362 [M^+ + Na].

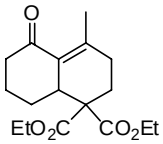
3-Methyl-4-oxo-2,4,5,6,7,7a-hexahydroindene-1,1-dicarbonitrile (2b)



2b

Using **1b** (80 mg, 0.4 mmol), cyclised product **2b** was obtained as a white solid (65 mg, 81%); mp 80-82 ºC; υ_{max} /cm^{-1} (neat) 2964, 2872, 2254, 1681, 1623; δ_H(300 MHz; $CDCl_3$) 1.71-1.94 (2 H, m), 2.14-2.21 (3 H, m), 2.21-2.39 (3 H, m), 2.50-2.62 (1 H, m), 3.12 (1 H, br d, *J* 17.4), 3.24 (1 H, br d, *J* 17.4), 3.43-3.53 (1 H, m); δ_C(75.5 MHz; $CDCl_3$) 15.8 (q), 22.1 (t), 26.8 (t), 38.2 (s), 40.2 (t), 48.5 (t), 54.7 (d), 114.4 (s), 115.0 (s), 130.8 (s), 148.3 (s), 196.8 (s); HR-MS (EI): *m/z*: calcd for $C_{12}H_{12}N_2O$: 200.0949, found 200.0954.

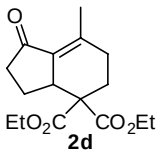
4-Methyl-5-oxo-3,5,6,7,8,8a-hexahydro-2H-naphthalene-1,1-dicarboxylic acid diethyl ester (2c)



2c

Using **1c** (115 mg, 0.37 mmol), cyclised product **2c** was obtained as a light yellow oil (70 mg, 61%); υ_{max} /cm^{-1} (neat) 2940, 2872, 1732, 1694, 1632; δ_H(300 MHz; $CDCl_3$) 1.19-1.29 (6 H, m), 1.59-1.73 (2 H, m), 1.73-2.20 (6 H, m), 1.87-1.92 (3 H, m), 2.32 (1 H, ddd, *J* 15.8, 9.8 and 6.1), 2.53 (1 H, dt, *J* 15.8 and 5.4), 3.02-3.12 (1 H, m), 4.07-4.29 (4 H, m); δ_C(75.5 MHz; $CDCl_3$) 13.9 (2q), 20.8 (q), 22.0 (t), 24.9 (t), 26.8 (t), 30.2 (t), 40.3 (d), 41.2 (s), 56.6 (t), 61.1 (t), 61.3 (t), 132.0 (s), 140.3 (s), 170.1 (s), 170.5 (s), 203.2 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{17}H_{24}O_5Na$: 331.1521, found 331.1518 [M^+ + Na].

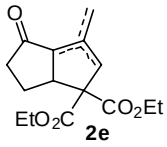
7-Methyl-1-oxo-1,2,3,3a,5,6-hexahydroindene-4,4-dicarboxylic acid diethyl ester (2d)



2d

Using **1d** (117 mg, 0.4 mmol), cyclised product **2d** was obtained as a light yellow liquid (93 mg, 79%); υ_{max} /cm^{-1} (neat) 2981, 1726, 1710, 1643; δ_H(300 MHz; $CDCl_3$) 1.22 (3 H, t, *J* 7.1), 1.28 (3 H, t, *J* 7.1), 1.86-2.10 (2 H, m), 2.10-2.17 (3 H, m), 2.17-2.50 (6 H, m), 3.01-3.13 (1 H, m), 4.15 (2 H, q, *J* 7.1), 4.24 (2 H, qd, *J* 7.1 and 1.7); δ_C(75.5 MHz; $CDCl_3$) 13.9 (q), 14.0 (q), 18.2 (q), 22.8 (t), 29.4 (t), 31.3 (t), 38.5 (t), 43.8 (d), 55.2 (s), 60.7 (t), 61.3 (t), 129.2 (s), 146.5 (s), 169.1 (s), 171.3 (s), 205.9 (s); HR-MS (EI): *m/z*: calcd for $C_{16}H_{22}O_5Na$: 294.1467, found 294.1461 [M^+ + Na].

3-Methyl-4-oxo-4,5,6,6a-tetrahydro-2H-pentalene-1,1-dicarboxylic acid diethyl ester, diethyl 6-oxo-4-methylene-bicyclo[3.3.0]octane-2,2-dicarboxylate, 3-methyl-4-oxo-4,5,6,6a-tetrahydro-3aH-pentalene-1,1-dicarboxylic acid diethyl ester (2e)

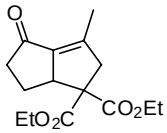


2e

Using **1e** (112 mg, 0.4 mmol), cyclised products **2e** were obtained as a clear yellow oil (111 mg, 98%) in a 3.7:2:1 mixture of isomers. HPLC separation (C_{18} 250 × 4.16 mm, isocratic in CH_3CN/water 40/60, 1.0 mL/min, 230 nm) gave **2e-a** pure and a mixture of **2e-b** and **2e-c**.

HR-MS (ES-TOF) (mixture of the 3 isomers): *m/z*: calcd for $C_{15}H_{20}O_5Na$: 303.1208, found 303.1202.

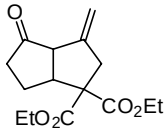
3-Methyl-4-oxo-4,5,6,6a-tetrahydro-2H-pentalene-1,1-dicarboxylic acid diethyl ester (2e-a)



2e-a

3-Methyl-4-oxo-4,5,6,6a-tetrahydro-2H-pentalene-1,1-dicarboxylic acid diethyl ester υ_{max} /cm^{-1} (neat) 2931, 1728, 1713, 1665; δ_H(300 MHz; $CDCl_3$) 1.25 (3 H, t, *J* 7.1), 1.26 (3 H, t, *J* 7.1), 1.30-1.46 (2 H, m), 2.04 (3 H, s), 2.13-2.27 (1 H, m), 2.39-2.54 (2 H, m), 3.07 (1 H, br d, *J* 18.3), 3.41 (1 H, br d, *J* 18.3), 4.08-4.34 (4 H, m); δ_C(75.5 MHz; $CDCl_3$) 14.1 (q), 14.2 (q), 14.6 (q), 26.1 (t), 43.8 (t), 50.7 (t), 53.8 (d), 61.5 (t), 61.7 (t), 62.6 (s), 137.3 (s), 146.1 (s), 169.8 (s), 171.0 (s), 201.0 (s).

Diethyl 6-oxo-4-methylenebicyclo[3.3.0]octane-2,2-dicarboxylate (2e-b)

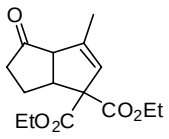


2e-b

υ_{max} /cm^{-1} (neat) 2981, 1726; δ_H(300 MHz; $CDCl_3$) 1.19-1.28 (6 H, m), 1.37-1.67 (2 H, m), 2.12-2.39 (2 H, m), 2.79 (1 H, d, *J* 17.6), 3.20 (1 H, ddd, *J* 17.6, 5.5 and 2.7), 3.26-3.35 (2 H, m), 4.03-4.28 (4 H, m), 5.06 (1 H, br d, *J* 1.6), 5.17 (1 H, td, *J* 2.7 and 1.6); δ_C(75.5 MHz; $CDCl_3$) 13.9 (q), 14.1 (q), 23.1 (t), 38.2

(t), 38.3 (t), 46.9 (d), 56.6 (d), 61.5 (t), 61.6 (t), 62.5 (s), 111.3 (t), 142.9 (s), 169.2 (s), 171.2 (s), 215.2 (s); MS(ES) 303.0 (M^+ + Na. $C_{15}H_{20}O_5Na$). **2e-b** is a known compound and the data is identical to that reported in the literature.[8]

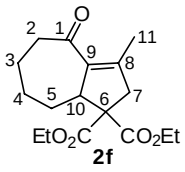
3-Methyl-4-oxo-4,5,6,6a-tetrahydro-3aH-pentalene-1,1-dicarboxylic acid diethyl ester (2e-c)



2e-c

υ_{max} /cm^{-1} (neat) 2981, 1726; δ_H(300 MHz; $CDCl_3$) 1.19-1.28 (6 H, m), 1.79 (3 H, s), 1.96-2.10 (2 H, m), 2.12-2.39 (2 H, m), 3.39 (1 H, dt, *J* 10.1 and 7.7), 3.62 (1 H, dt, *J* 10.1 and 7.7), 4.03-4.28 (4 H, m), 5.51 (1 H, m); δ_C(75.5 MHz; $CDCl_3$) 13.9 (q), 14.1 (q), 14.6 (q), 23.8 (t), 38.4 (t), 44.7 (d), 61.2 (s), 61.3 (d), 61.5 (t), 61.6 (t), 124.3 (d), 142.0 (s), 169.5 (s), 170.0 (s), 215.2 (s); MS(ES) 303.0 (M^+ + Na. $C_{15}H_{20}O_5Na$).

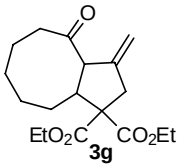
3-Methyl-4-oxo-4,5,6,7,8,8a-hexahydro-2H-azulene-1,1-dicarboxylic acid diethyl ester (2f)



2f

Using **1f** (134 mg, 0.4 mmol), **2f** was obtained as a yellow oil (86 mg, 64%); υ_{max} /cm^{-1} (neat) 2929, 1729, 1675, 1618; δ_H(300 MHz; $CDCl_3$) 1.24 (3 H, t, *J* 7.1, CH_2CH_3), 1.25 (3 H, t, *J* 7.1, CH_2CH_3), 1.28-1.47 (2 H, m, 5-H, 3-H), 1.46-1.67 (1 H, m, 4-H), 1.76-2.01 (3 H, m, 5-H, 4-H, 3-H), 2.03-2.08 (3 H, m, 11-H), 2.44-2.62 (2 H, m, 2-H), 2.79 (1 H, dq, *J* 18.7 and 1.4, 7-H), 3.32 (1 H, dq, *J* 18.7 and 1.4, 7-H), 3.72 (1 H, br d, *J* 11.9, 10-H), 4.08-4.29 (4 H, m, 2 × CH_2CH_3); δ_C(75.5 MHz; $CDCl_3$) 13.9 (q), 14.0 (q), 16.2 (q), 24.6 (t), 30.4 (t), 31.6 (t), 45.3 (2t), 51.4 (d), 61.4 (t), 61.6 (t), 62.7 (s), 137.2 (s), 150.8 (s), 169.7 (s), 171.2 (s), 201.5 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{17}H_{24}O_5Na$: 331.1029, found 331.1042 [M^+ + Na].

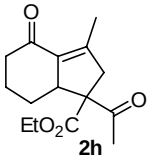
Diethyl 2-oxo-11-methylenebicyclo[6.3.0]undecane-9,9-dicarboxylate (3g)



3g

Using **1g** (77 mg, 0.24 mmol), a number of fractions were collected including recovered **1g** (13 mg, 17%) and a mixture of cyclized isomeric products with **3g** as the major constituent (20 mg, 26%); δ_H(300 MHz; $CDCl_3$) 1.12-1.21 (1 H, m), 1.26 (3 H, t, *J* 7.1), 1.27 (3 H, t, *J* 7.1), 1.31-1.54 (2 H, m), 1.62-2.08 (5 H, m), 2.22-2.37 (1 H, m), 2.58-2.70 (1 H, m), 2.73-2.85 (1 H, m), 3.06 (1 H, dt, *J* 12.6 and 3.3), 3.21 (1 H, bd, *J* 17.4), 3.36 (1 H, dd, *J* 12.9 and 1.9), 4.06-4.32 (4 H, m), 4.76 (1 H, dd, *J* 5.0, 2.4), 5.00 (1 H, dd, *J* 4.8, 2.4); HR-MS (ES-TOF): *m/z*: calcd for $C_{18}H_{26}O_5Na$: 345.1678, found 345.1676 [M^+ + Na]. Spectroscopic data were identical to those reported in the literature.[8]

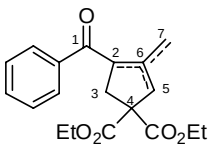
1-Acetyl-3-methyl-4-oxo-2,4,5,6,7,7a-hexahydro-1H-indene-1-carboxylic acid ethyl ester (2h)



2h

Using **1h** (106 mg, 0.4 mmol), **2h** was obtained as a pale yellow oil (47 mg, 44%), in 1.9:1 mixture of two diastereoisomers; υ_{max} /cm^{-1} (neat) 2941, 1709, 1682, 1623; δ_H(300 MHz; $CDCl_3$) *minor diastereoisomer* 1.09-1.25 (1 H, m, 4-H), 1.28 (3 H, t, *J* 7.1, CH_2CH_3), 1.67-1.87 (1 H, m, 3-H), 1.95-2.28 (6 H, m, 3-H, 4-H, 2-H, OCH_3), 2.18 (3 H, s, 10-H), 2.40-2.51 (1 H, m, 2-H), 2.60 (1 H, br d, *J* 18.3, 6-H), 3.12 (1 H, br d, *J* 18.3, 6-H), 3.66-3.83 (1 H, m, 9-H), 4.14-4.31 (2 H, m, CH_2CH_3); δ_H(300 MHz; $CDCl_3$) *major diastereoisomer* 1.09-1.25 (1 H, m, 4-H), 1.29 (3 H, t, *J* 7.1, CH_2CH_3), 1.67-1.87 (1 H, m, 3-H), 1.95-2.28 (6 H, m, 3-H, 4-H, 2-H, OCH_3), 2.17 (3 H, s, 10-H), 2.40-2.51 (1 H, m, 2-H), 2.73 (1 H, br d, *J* 18.4, 6-H), 3.0.2 (1 H, br d, *J* 18.4, 6-H), 3.66-3.83 (1 H, m, 9-H), 4.14-4.31 (2 H, m, CH_2CH_3); δ_C(75.5 MHz; $CDCl_3$) *minor diastereoisomer*: 14.1 (q), 15.7 (q), 23.5 (t), 27.2 (q), 27.6 (t), 40.6 (t), 45.1 (t), 49.6 (d), 61.4 (t), 68.4 (s), 132.4 (s), 147.8 (s), 170.8 (s), 199.3 (s), 202.0 (s); *major diastereoisomer*: 14.0 (q), 15.7 (q), 23.7 (t), 27.1 (t), 28.6 (q), 40.5 (t), 45.3 (t), 51.8 (d), 61.6 (t), 67.5 (s), 131.7 (s), 149.9 (s), 172.5 (s), 199.0 (s), 203.0 (s); HR-MS (ES-TOF): *m/z*: calcd for $C_{15}H_{20}O_4Na$: 287.1259, found 287.1246 [M^+ + Na].

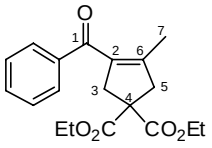
Diethyl 3-benzoyl-4-methylcyclopent-3-ene-1,1-dicarboxylate (2i-a); Diethyl 3-benzoyl-4-methylenecyclopentane-1,1-dicarboxylate (2i-b); and Diethyl 4-benzoyl-3-methyl-cyclopent-2-ene-1,1-dicarboxylate (2i-c)



2i

Using **1i** (215 mg, 0.65 mmol), **2i** as isolated as a light yellow oil (109 mg, 51%), in 10:3:1 mixture of three isomers (**2i-a**: **2i-b**: **2i-c**); These isomers were inseparable by flash column chromatography. Analytically pure samples of each isomer were obtained by preparative HPLC (t = 0 → 65 min CH_3OH/H_2O 60:40).

Diethyl 3-benzoyl-4-methylcyclopent-3-ene-1,1-dicarboxylate (2i-a)

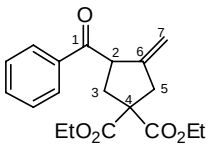


2i-a

HPLC: t_R = 53.2 min; υ_{max} (film)/cm^{-1} 2982 (CH, CH_2, CH_3), 1728 (CO_2Et and CO), 1641 (C=C), 1597, 1579 (C=C Ar); δ_H(300 MHz; $CDCl_3$) 1.26 (6 H, t, *J* 7.1, 2 × CH_2CH_3), 1.66 (3 H, s, 7-H), 3.16-3.21 (2 H, m, CH_2), 3.36-3.43 (2 H, m, CH_2), 4.22 (4 H, q, *J* 7.1, 2 × CH_2CH_3), 7.40-7.48 (2 H, m, Ar-H), 7.50-7.57 (1 H, m, Ar-H), 7.72-7.78 (2 H, m, Ar-H); δ_C(75.5 MHz; $CDCl_3$) 14.0 (2 q, CH_2CH_3), 16.3 (q, 7-C), 42.9 (t, 3 or 5-C), 47.1 (t, 3 or 5-C), 57.3 (s, 4-C), 61.8 (2 t,

CH_2CH$_3$), 128.5 (2 d, Ar-C), 128.9 (2 d, Ar-C), 132.6 (d, Ar-C), 133.1 (s, 6-C), 138.6 (s, 2-C), 146.0 (s, Ar-C), 171.5 (2 s, *C*O_2Et), 195.3 (s, 1-C); *m/z* (TOF ES+) 353.1 ([M^+ + Na], 100%).

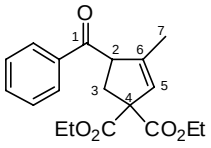
Diethyl 3-benzoyl-4-methylenecyclopentane-1,1-dicarboxylate (2i-b)



2i-b

HPLC: t_R = 60.3 min; υ_{max}(film)/cm^{-1} 2983 (CH, CH_2, CH_3), 1728 (CO_2Et and CO), 1683 (C=C), 1597, 1580 (C=C Ar); δ_H(300 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.1, CH_2CH_3), 1.27 (3 H, t, *J* 7.1, CH_2CH_3), 2.71 (2 H, d, *J* 8.7, 3-H), 2.96 (1 H, d, *J* 16.5, 5-H), 3.16 (1 H, ddt, *J* 16.5, 2.5, 2.5, 5-H), 4.17-4.29 (4 H, m, 2 × CH_2CH$_3$), 4.54-4.63 (1 H, m, 2-H), 4.73 (1 H, dd, *J* 4.0, 2.5, 7-H), 5.05 (1 H, dd, *J* 4.0, 2.5, 7-H), 7.41-7.54 (2 H, m, Ar-H), 7.56-7.62 (1 H, m, Ar-H), 7.97-8.03 (2 H, m, Ar-H); δ_C(75.5 MHz; $CDCl_3$) 14.0 (2 q, CH_2CH_3), 36.5 (t, 3-C), 41.3 (t, 5-C), 49.4 (d, 2-C), 58.9 (s, 4-C), 61.6 (t, *C*H_2CH$_3$), 61.7 (t, *C*H_2CH$_3$), 110.5 (t, 7-C), 128.7 (2 d, Ar-C), 129.1 (2 d, Ar-C), 133.2 (d, Ar-C), 136.9 (s, 6-C), 147.3 (s, Ar-C), 170.7 (s, CO_2Et), 171.7 (s, CO_2Et), 198.7 (s, 1-C); *m/z* (TOF ES+) 353.1 ([M^+ + Na], 100%). Data were identical to those previously reported.**Error! Bookmark not defined.**

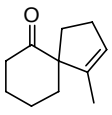
Diethyl 4-benzoyl-3-methyl-cyclopent-2-ene-1,1-dicarboxylate (2i-c)



2i-c

HPLC: t_R = 43.4 min; υ_{max}(film)/cm^{-1} 2921 (CH, CH_2, CH_3), 1730 (CO_2Et and CO), 1682 (C=C), 1597 (C=C Ar); δ_H(300 MHz; $CDCl_3$) 1.20-1.30 (6 H, m, 2 × CH_2CH_3), 1.75-1.78 (3 H, m, 7-C), 2.63 (1 H, dd, J_{AB} 13.6, 6.2, 3-H), 2.94 (1 H, dd, J_{AB} 13.6, 9.1, 3-H), 4.12-4.29 (4 H, m, 2 × CH_2CH$_3$), 4.50-4.59 (1 H, m, 2-H), 5.71-5.75 (1 H, m, 5-H), 7.45-7.52 (2 H, m, Ar-H), 7.55-7.62 (1 H, m, Ar-H), 7.95-8.02 (2 H, m, Ar-H); δ_C(75.5 MHz; $CDCl_3$) 14.0 (2 q, CH_2CH_3), 16.0 (q, 7-C), 36.7 (t, 3-C), 54.9 (d, 2-C), 61.5 (t, *C*H_2CH$_3$), 61.7 (t, *C*H_2CH$_3$), 65.7 (s, 4-C), 126.5 (d, 5-C), 128.6 (2 d, Ar-C), 128.7 (2 d, Ar-C), 133.3 (d, Ar-C), 136.6 (s, 6-C), 144.1 (s, Ar-C), 170.5 (s, *C*O_2Et), 171.2 (s, *C*O_2Et), 199.8 (s, 1-C); *m/z* (TOF ES+) 353.1 ([M^+ + Na], 100%).

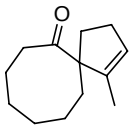
4-Methylspiro[4.5]dec-3-ene-6-one (5a)



5a

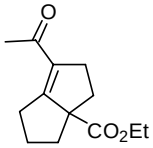
Using **4a** (66 mg, 0.4 mmol), cyclized product **5a** was obtained as a light brown liquid (40 mg, 61%); υ_{max} /cm^{-1} (neat) 2928, 2853, 1704; δ_H(300 MHz; $CDCl_3$) 1.60-1.94 (8 H, m), 1.95-2.08 (3 H, m), 2.19-2.27 (2 H, m), 2.31-2.53 (2 H, m), 5.48-5.53 (1 H, m); δ_C(75.5 MHz; $CDCl_3$) 13.7 (q), 22.1 (t), 26.4 (t), 29.5 (t), 35.7 (t), 36.0 (t), 39.8 (t), 64.3 (s), 126.9 (d), 141.8 (s), 213.7 (s); HR-MS (EI): *m/z*: calcd for $C_{11}H_{16}ONa$: 164.1201, found 164.1203 [M^+ + Na].

1-Methylspiro[4.7]dodec-1-en-6-one (5b)


5b

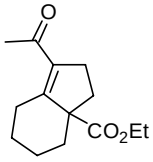
Using **4b** (77 mg, 0.4 mmol), cyclized product **5b** was obtained as a brown liquid (45 mg, 58%); υ_{max} /cm^{-1} (neat) 2924, 2854, 1693; δ_H(300 MHz; $CDCl_3$) 0.93-1.11 (1 H, m), 1.28-1.43 (1 H, m), 1.43-1.74 (7 H, m), 1.74-1.77 (3 H, m), 1.81-1.94 (1 H, m), 2.13-2.28 (2 H, m), 2.32-2.59 (3 H, m), 2.78 (1 H, dt, *J* 11.4, 3.5), 5.41-5.46 (1 H, m); δ_C(75.5 MHz; $CDCl_3$) 14.3 (q), 24.6 (t), 25.8 (t), 26.3 (t), 30.2 (t), 30.5 (t), 32.6 (t), 32.6 (t), 39.2 (t), 66.0 (s), 128.6 (d), 141.3 (s), 218.4 (s); HR-MS (EI): *m/z*: calcd for $C_{13}H_{20}O$: 192.1514, found 192.1508 [M^+].

6-Acetyl-2,3,4,5-tetrahydro-1H-pentalene-3a-carboxylic acid ethyl ester (7a)


7a

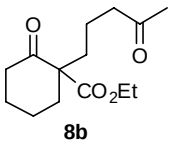
Using **6a** (59.1 mg, 0.2 mmol), cyclized product **7a** was obtained as a clear yellow liquid (29.8 mg, 50%); υ_{max} /cm^{-1} (neat) 2929, 2857, 1723, 1684, 1662; δ_H(300 MHz; $CDCl_3$) 1.23 (3 H, t, *J* 7.1), 1.39-1.53 (1 H, m), 1.68-1.81 (1 H, m), 2.04-2.45 (4 H, m), 2.29 (3 H, s), 2.48-2.74 (2 H, m), 2.73-2.90 (1 H, m), 2.90-3.05 (1 H, m), 4.13 (2 H, q, *J* 7.1); δ_C(75.5 MHz; $CDCl_3$) 14.1 (q), 26.3 (t), 27.8 (t), 29.5 (q), 35.3 (t), 35.6 (t), 36.7 (t), 60.9 (t), 69.1 (s), 135.2 (s), 164.9 (s), 174.6 (s), 196.7 (s); HR-MS (ES): *m/z*: calcd for $C_{13}H_{18}O_3Na$: 245.1154, found 245.1156 [M^+ + Na].

1-Acetyl-2,3,4,5,6,7-hexahydro-3aH-indene-3a-carboxylic acid ethyl ester (7b)


7b

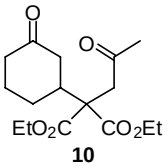
Using **6b** (55.0 mg, 0.2 mmol), cyclised product **7b** was obtained as a clear yellow liquid (26.6 mg, 48%); υ_{max} /cm^{-1} (neat) 2935, 2857, 1725, 1682, 1657, 1621; δ_H(300 MHz; $CDCl_3$) 1.22 (3 H, t, *J* 7.1), 1.28-1.50 (3 H, m), 1.59-1.76 (2 H, m), 1.77-1.89 (1 H, m), 1.94-2.10 (1 H, m), 2.12-2.22 (1 H, m), 2.25 (3 H, s), 2.44-2.74 (3 H, m), 3.32-3.44 (1 H, m), 4.13 (2 H, q, *J* 7.1); δ_C(75.5 MHz; $CDCl_3$) 14.2 (q), 23.4 (t), 26.7 (t), 26.9 (t), 30.6 (q), 32.2 (t), 35.5 (t), 38.3 (t), 60.4 (s), 60.7 (t), 135.7 (s), 155.0 (s), 175.0 (s), 198.8 (s); HR-MS (ES): *m/z*: calcd for $C_{14}H_{20}O_3Na$: 259.1310, found 259.1306 [M^+ + Na].

Ethyl 2-oxo-1-(4-oxopentyl)cyclohexanecarboxylate (8b)


8b

Product **8b** was obtained in small quantities as a side-product in the cyclisation of **6b** to **7b**; υ_{max} /cm^{-1} (neat) 2962, 2940, 2864, 1739, 1706; δ_H(300 MHz; $CDCl_3$) 1.24 (3 H, t, *J* 7.1), 1.36-1.83 (8 H, m), 1.91-2.04 (1 H, m), 2.10 (3 H, s), 2.32-2.54 (5 H, m), 4.18 (2 H, q, *J* 7.1); δ_C(75.5 MHz; $CDCl_3$) 14.1 (q), 18.6 (t), 22.5 (2t), 27.5 (t), 29.8 (q), 33.9 (t), 41.0 (t), 43.7 (t), 60.7 (s), 61.2 (t), 171.8 (s), 207.9 (s), 208.3 (s); HR-MS (ES): *m/z*: calcd for $C_{14}H_{22}O_4Na$: 277.1416, found 277.1411 [M^+ + Na].

2-(3-Oxocyclohexyl)-2-(2-oxopropyl)malonic acid diethyl ester (10)[10]



10

A mixture of 2-(3-oxocyclohexyl)-2-prop-2-ynylmalonic acid diethyl ester (100 mg, 0.34 mmol), $NaAuCl_4.2H_2O$ (4 mg, 0.01 mmol) in 1.36 mL of MeOH-H_2O (10:1) was irradiated by ultrasound at rt for 5 h. Saturated $NH_4Cl_{(aq)}$ (20 mL) was then added, followed by diethyl ether (20 mL). The two layers were separated. The organic layer was washed with saturated aqueous NaCl (20 mL), dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure. The residue was purified by flash chromatography (hexane/ethyl acetate: 8/2) to afford **10** as a light yellow oil (30 mg, 28%); δ_H(300 MHz; $CDCl_3$) 1.25 (6 H, t, *J* 7.1), 1.32-1.50 (2 H, m), 1.50-1.72 (1 H, m), 1.89-2.53 (6 H, m), 2.17 (3 H, s), 3.04 (1 H, d, *J* 17.8), 3.11 (1 H, d, *J* 17.8), 4.20 (4 H, q, *J* 7.1); δ_C(75.5 MHz; $CDCl_3$) 13.9 (2q), 24.6 (t), 27.3 (t), 30.0 (q), 41.0 (t), 42.7 (d), 43.8 (t), 46.0 (t), 58.4 (s), 61.6 (2t), 169.6 (s), 169.7 (s), 204.4 (s), 209.5 (s); *m/z* (ES) 335.1483 (calc. for [M^+ + Na] $C_{16}H_{24}O_6Na$: 335.1471).

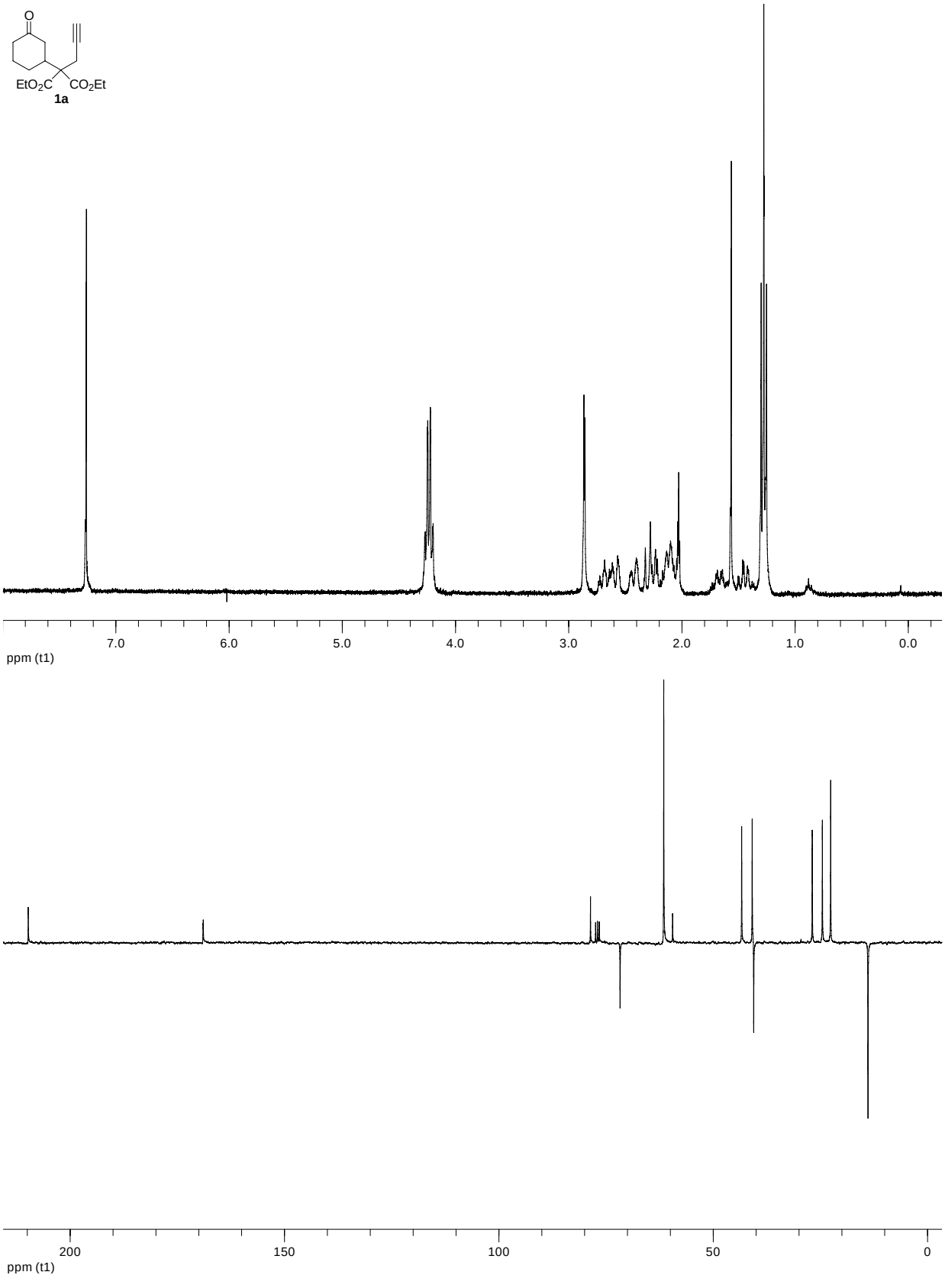
[10] Imi, K.; Imai, K.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 3127.

Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR Spectra of Cyclisation Precursors

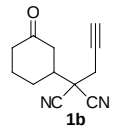
^{1}H and ^{13}C NMR spectra of (1a)



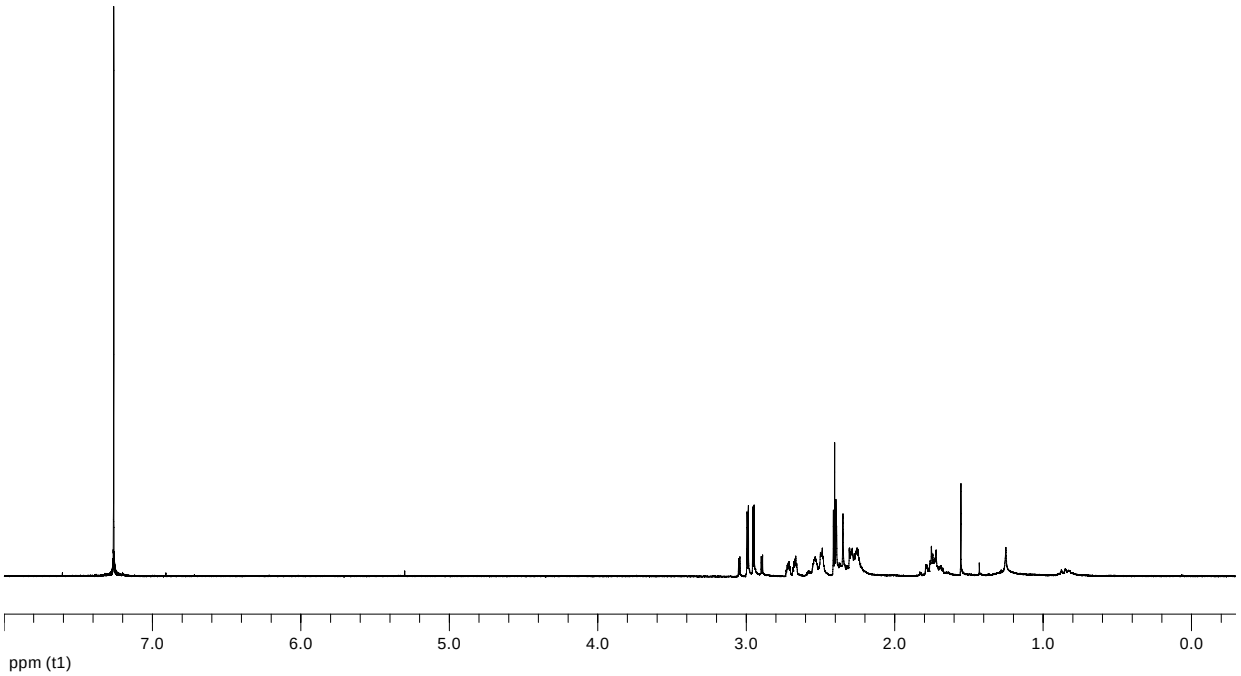
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

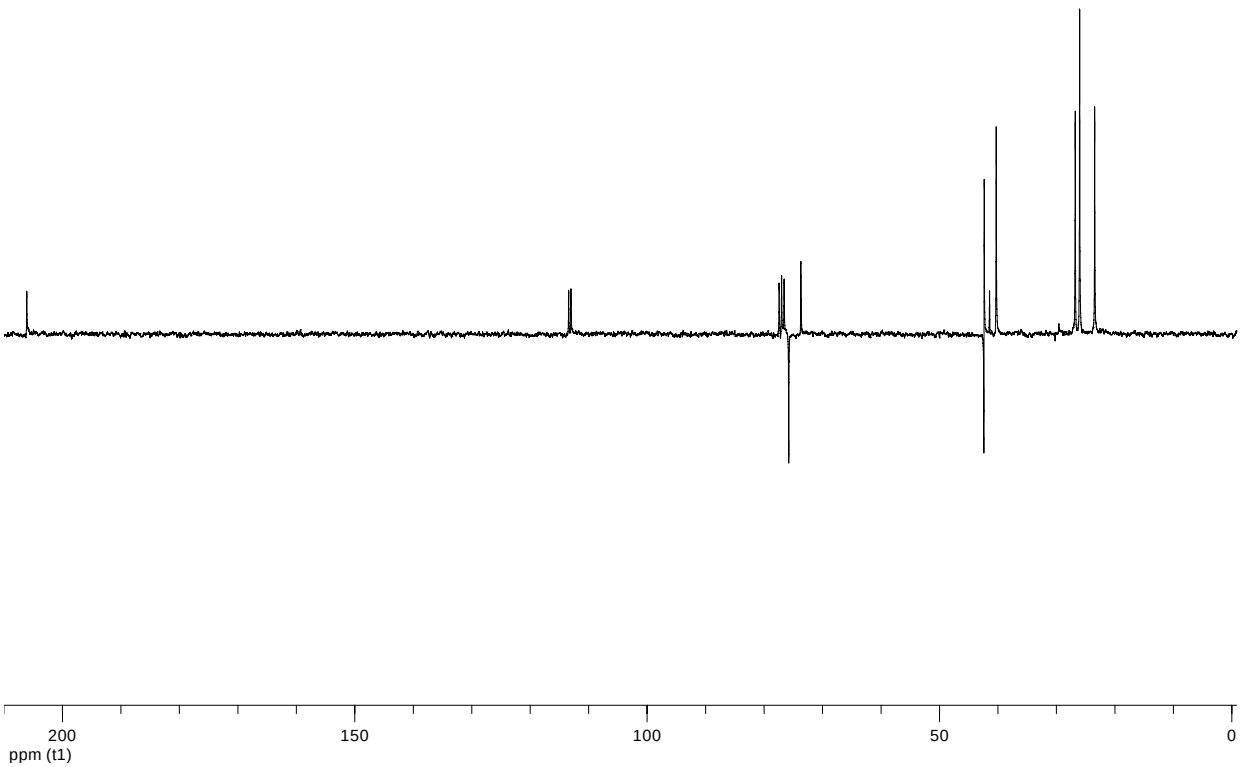
P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (1b)



1b

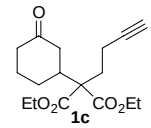




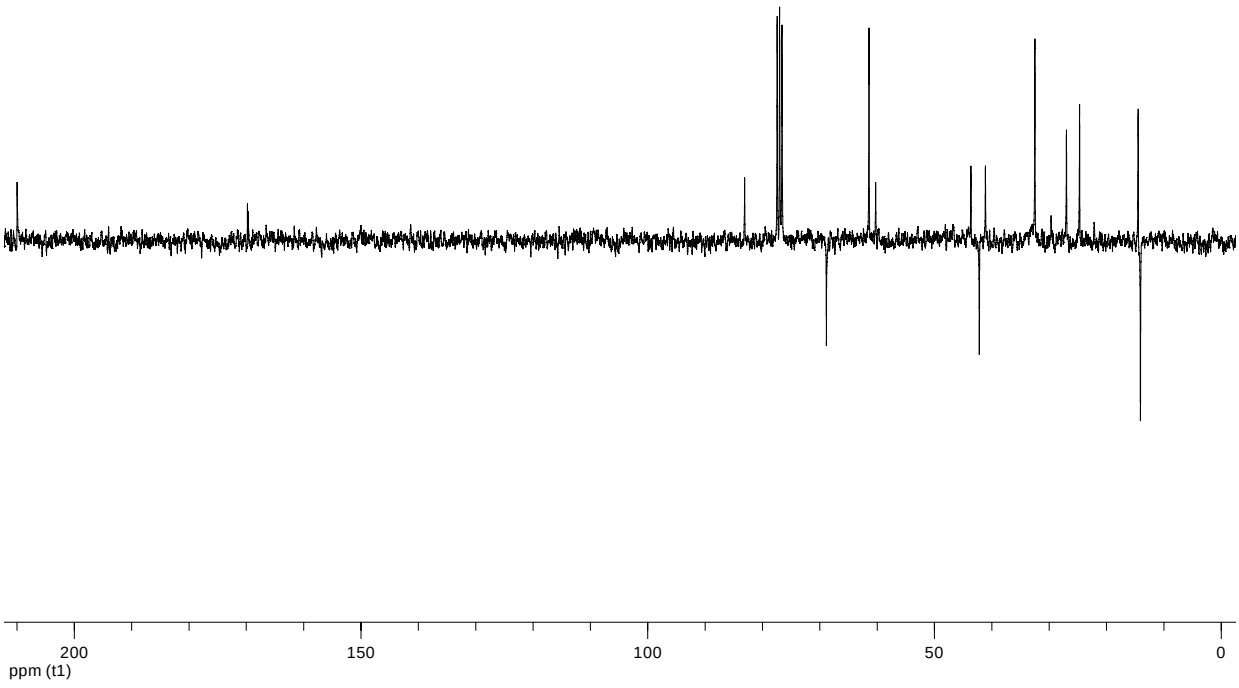
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

P. W. Davies and C. Detty-Mambo

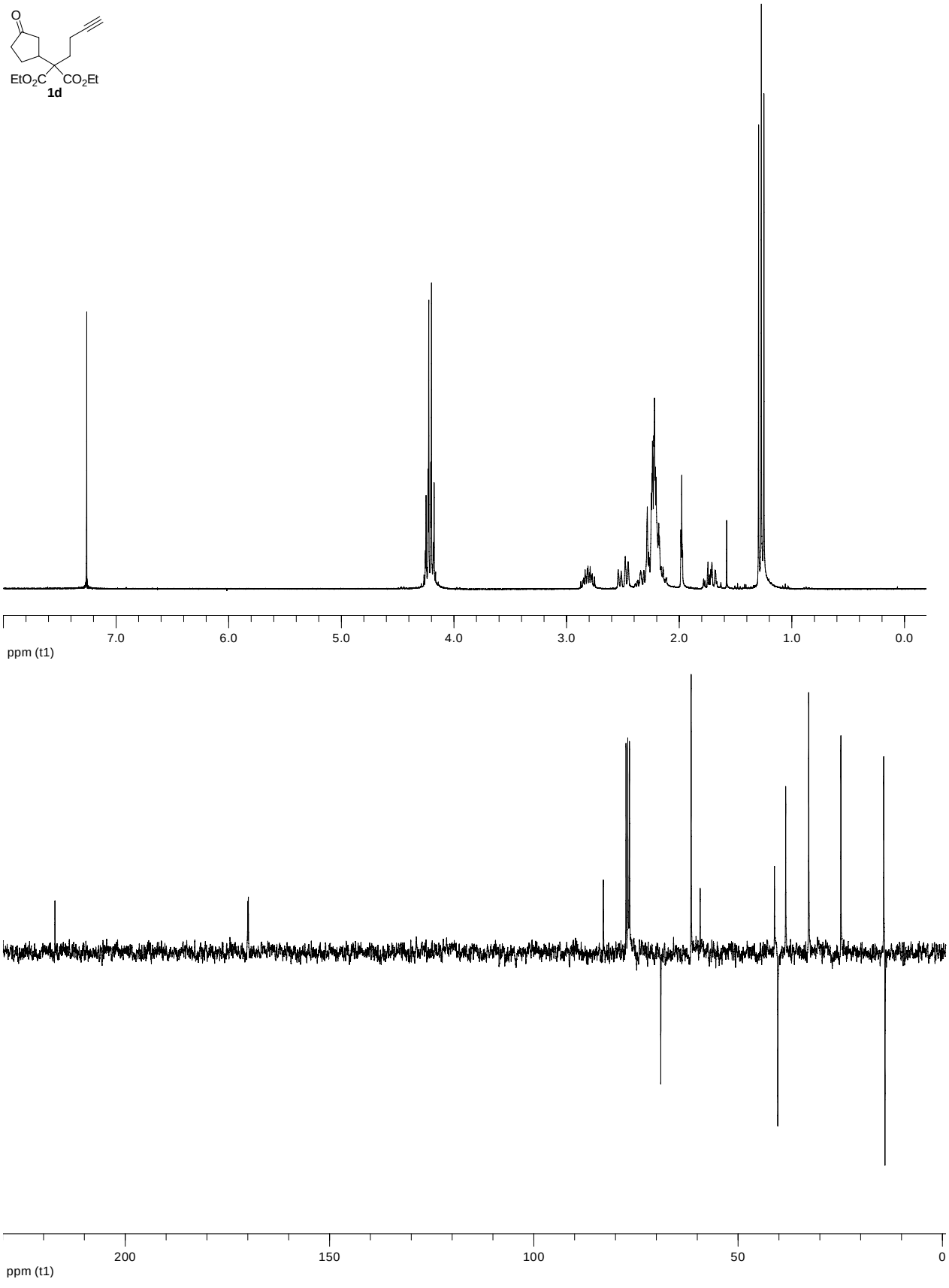
^{1}H and ^{13}C NMR spectra of (1c)



1c



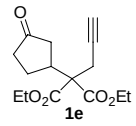
^{1}H and ^{13}C NMR spectra of (1d)



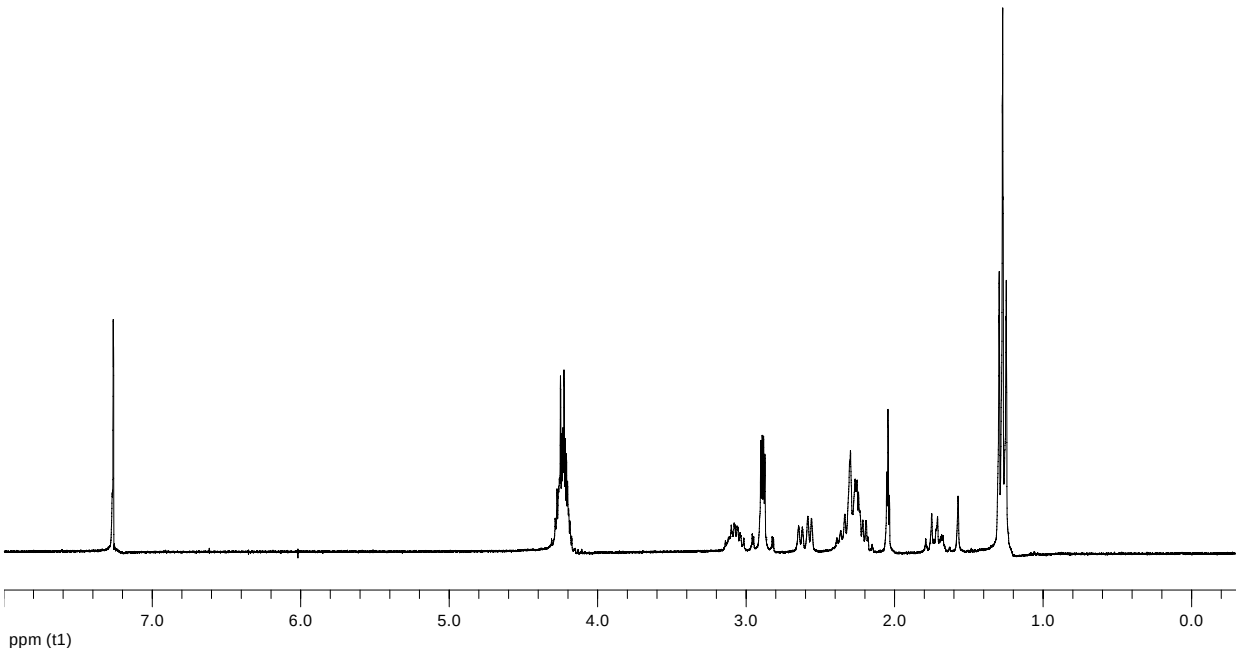
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

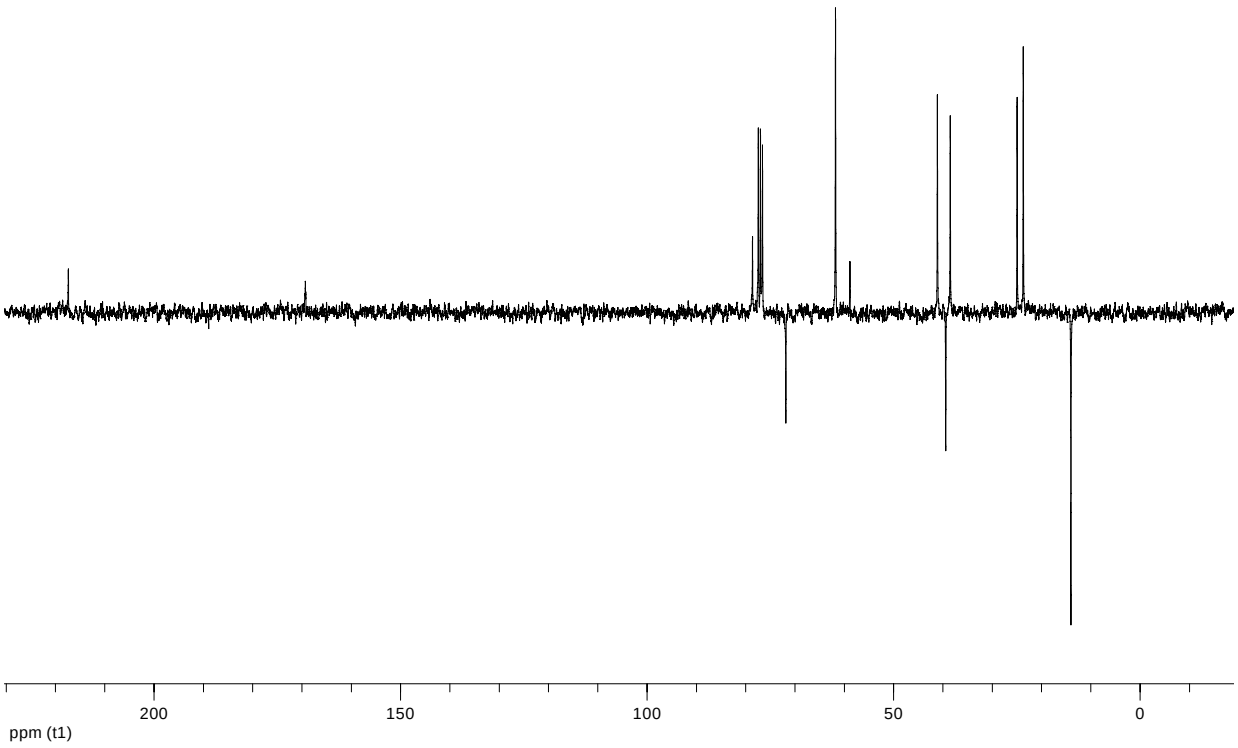
P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (1e)



1e

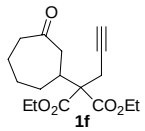




Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (1f)



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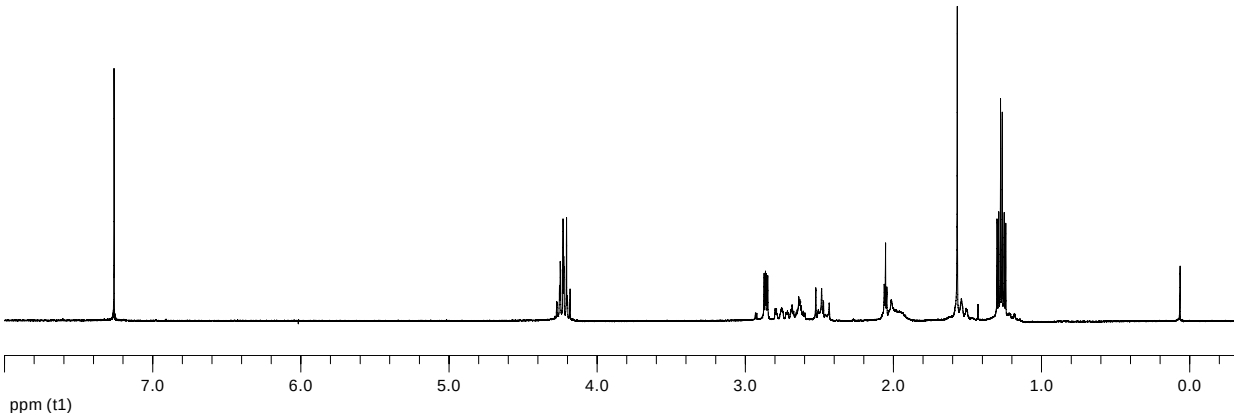
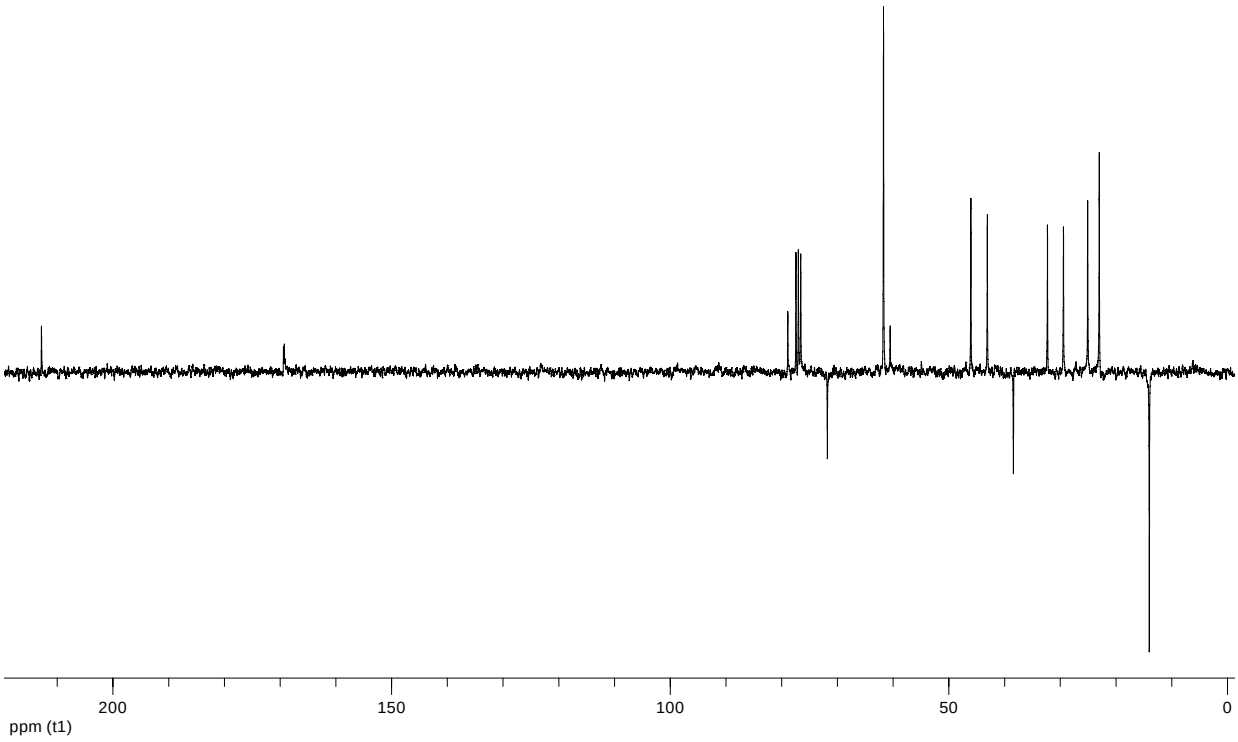
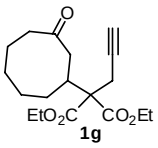




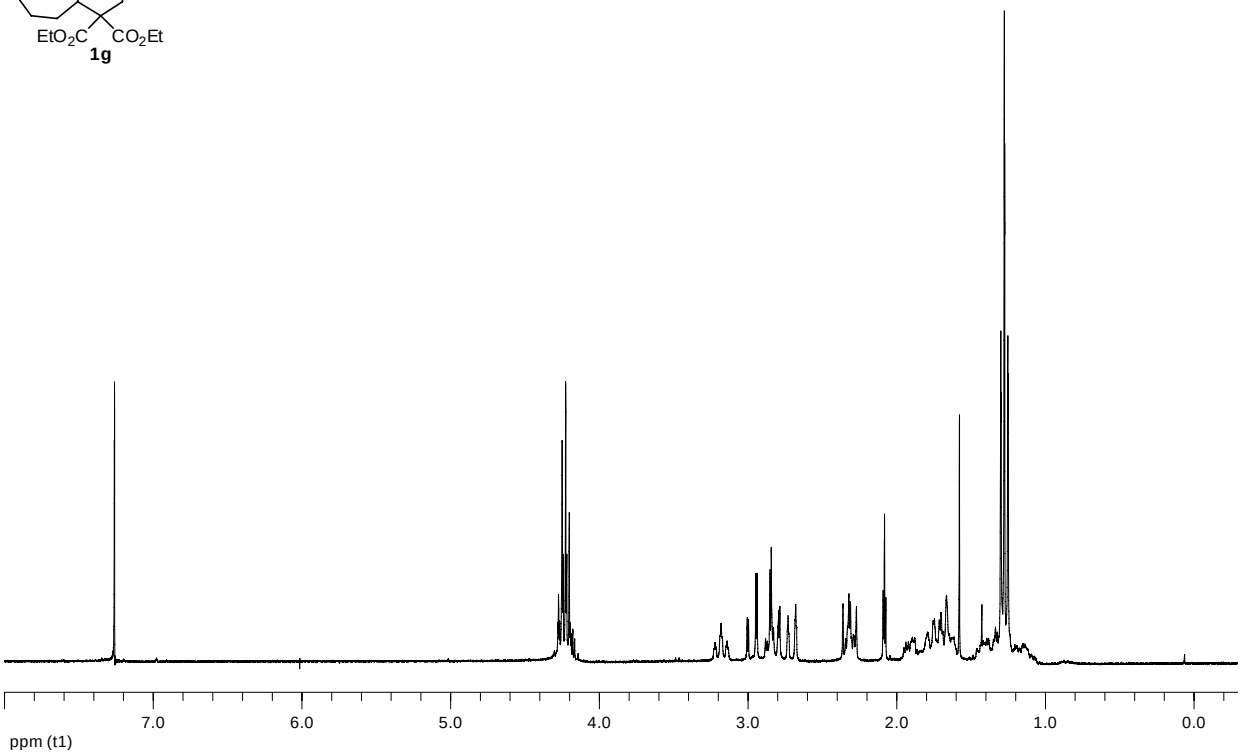
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

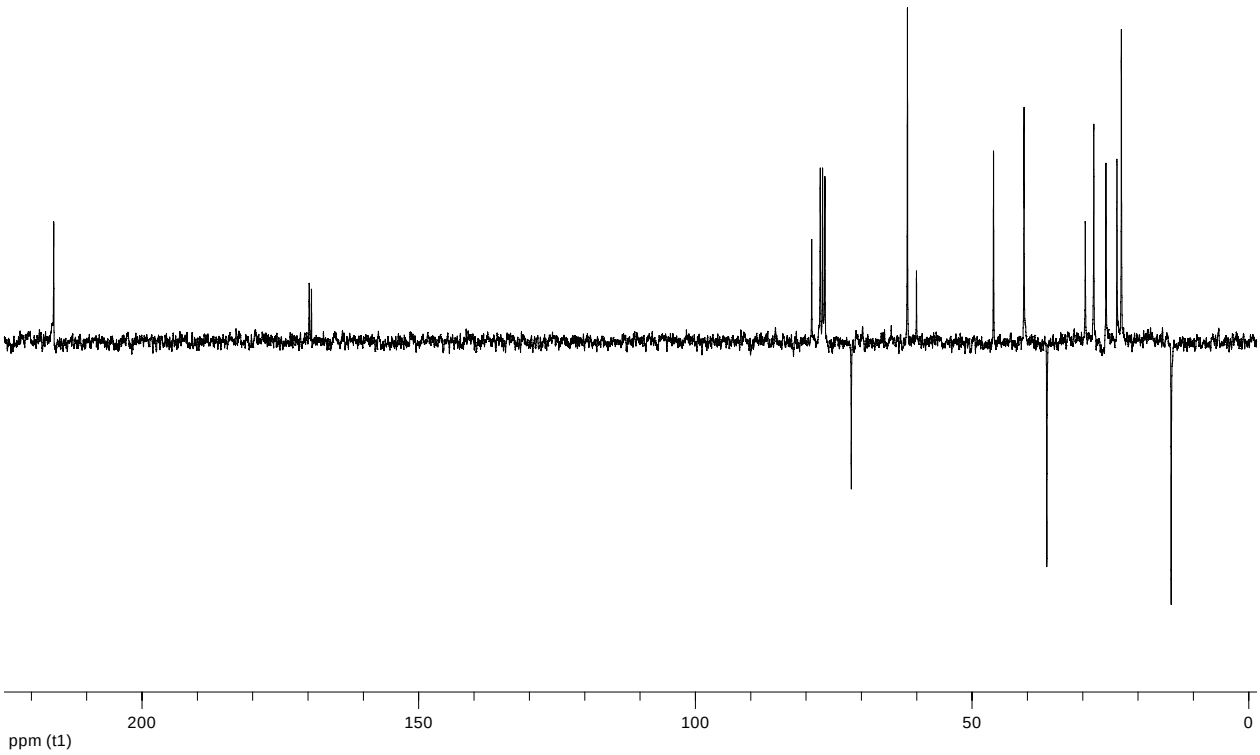
P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (1g)



1g

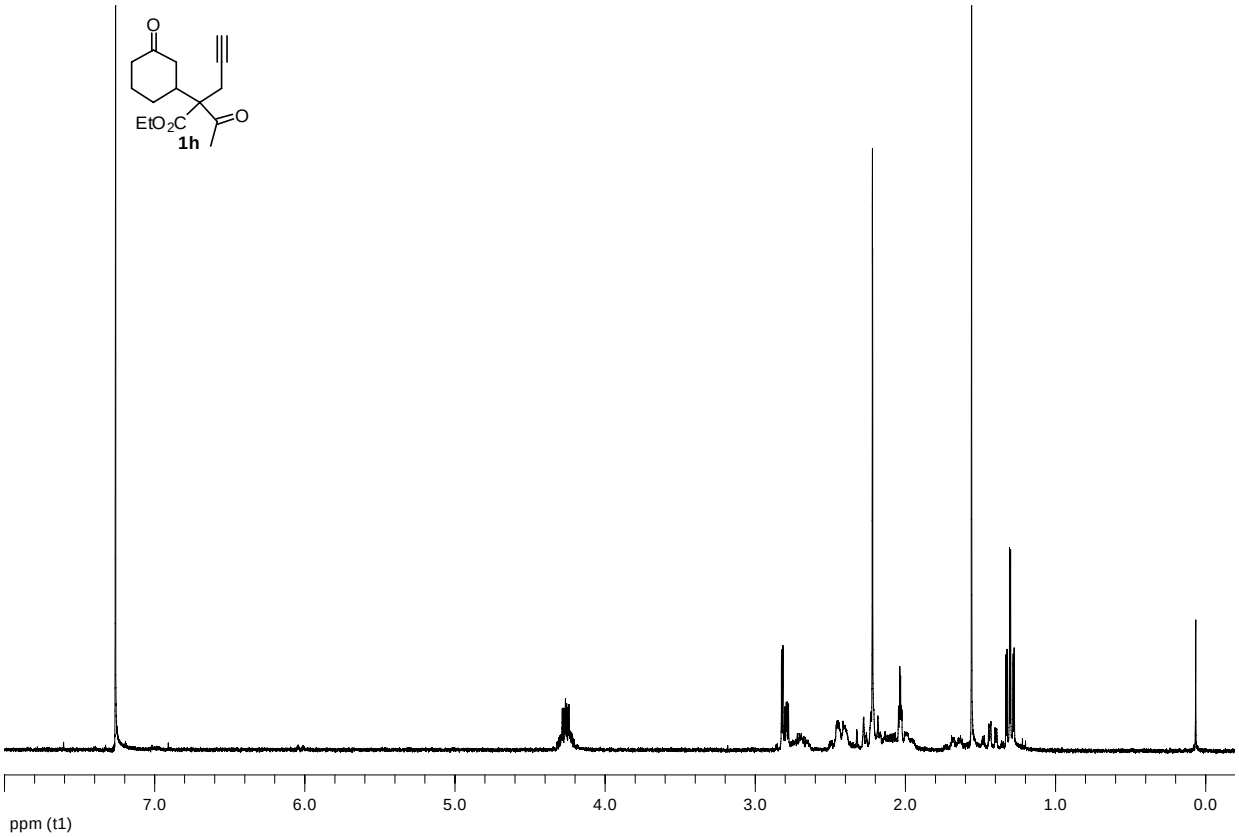


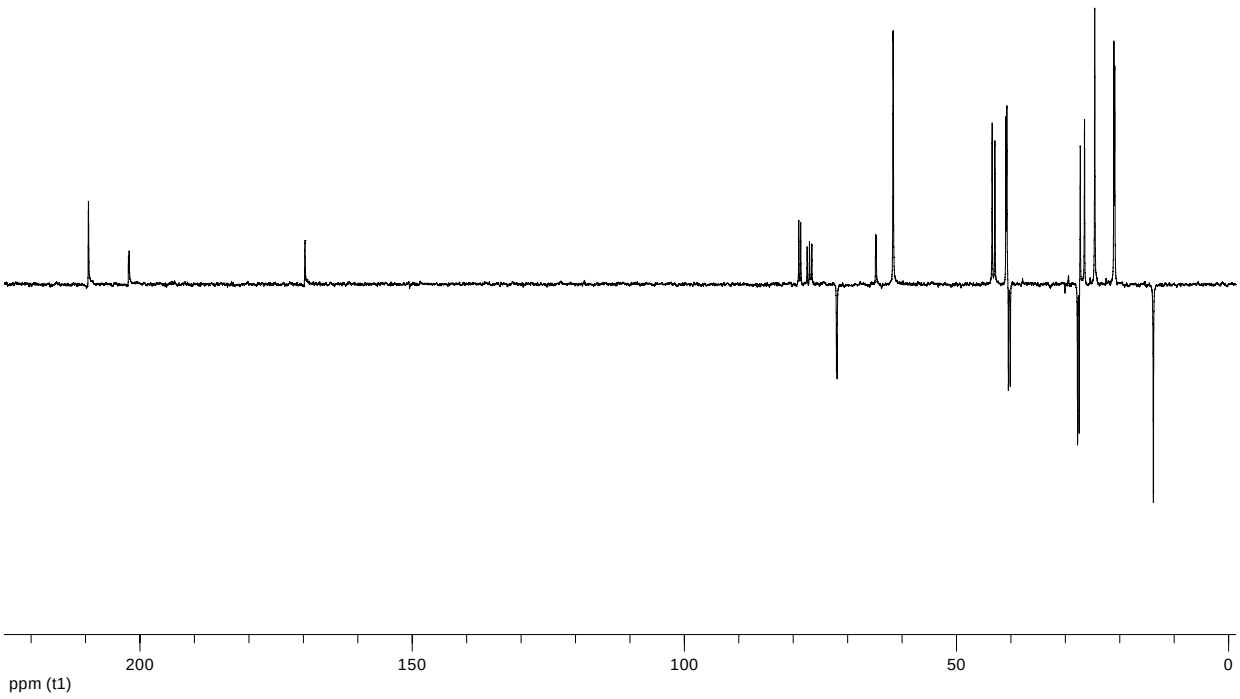


Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

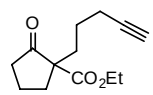
P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (1h)

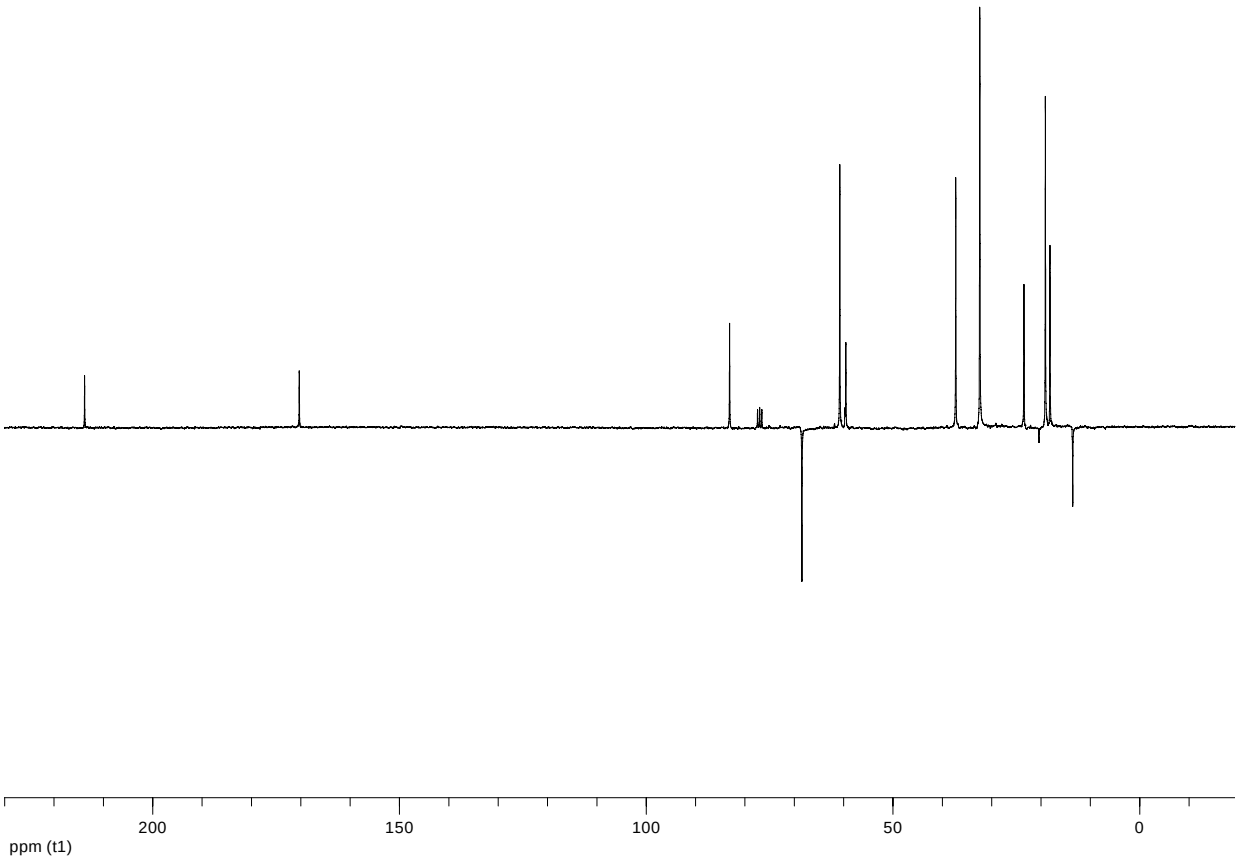




^{1}H and ^{13}C NMR spectra of (6a)



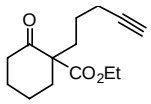
6a



Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (6b)



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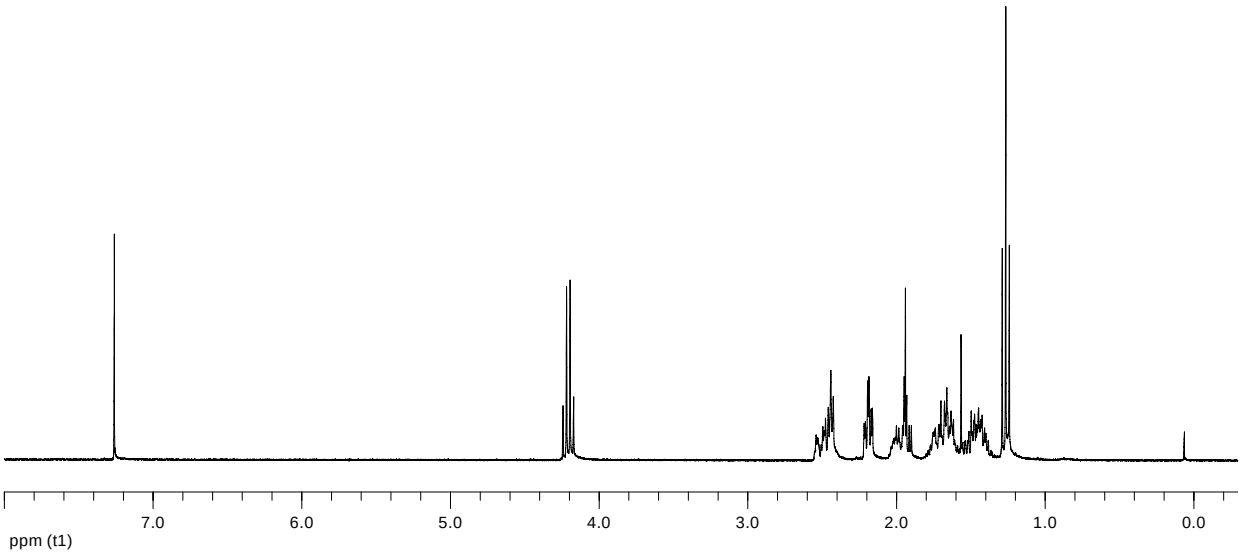
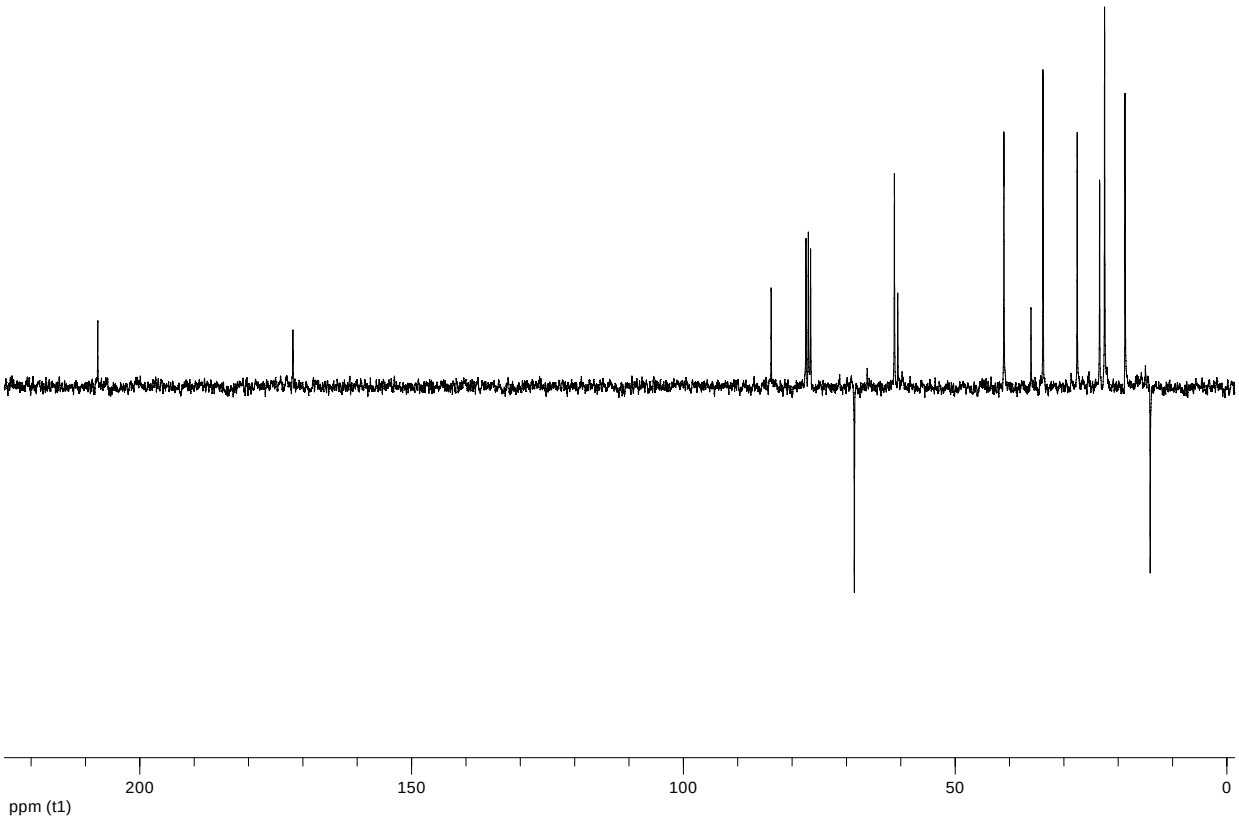
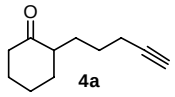


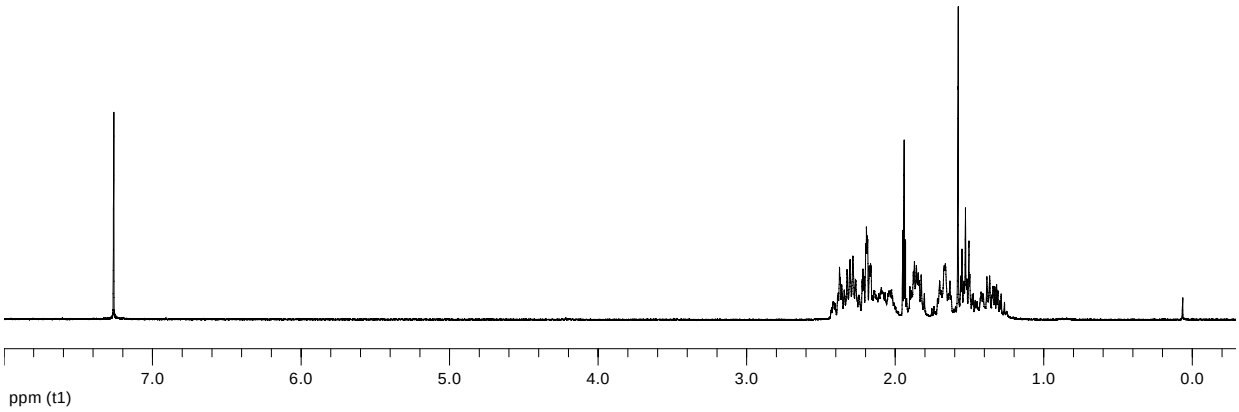


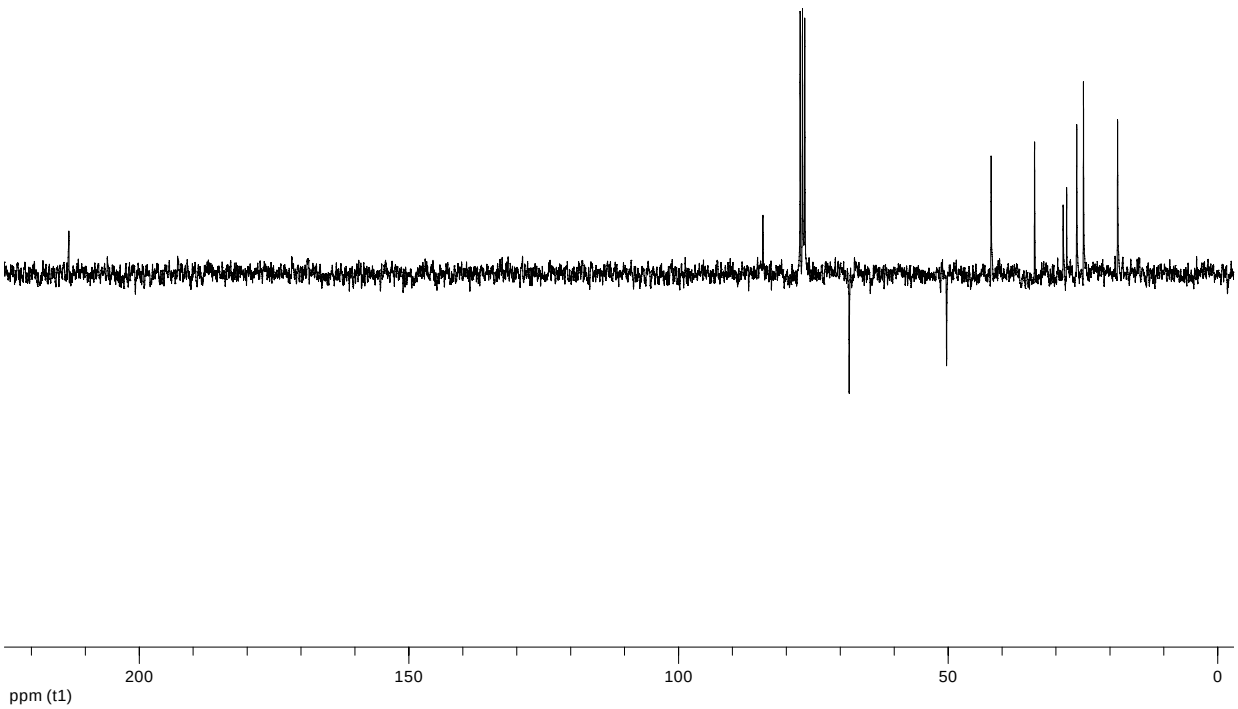
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (4a)



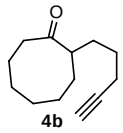




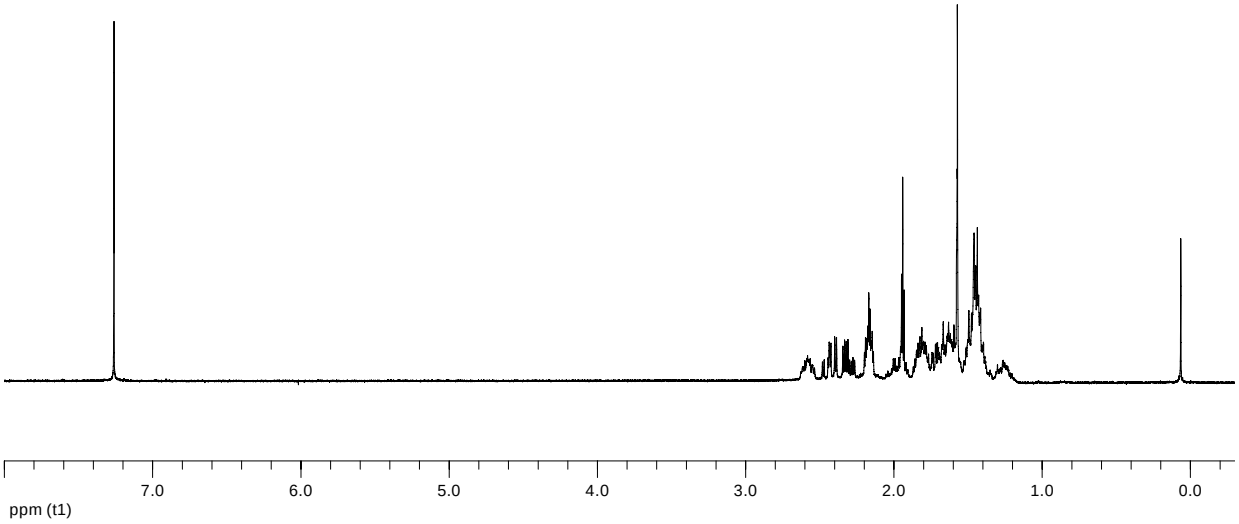
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

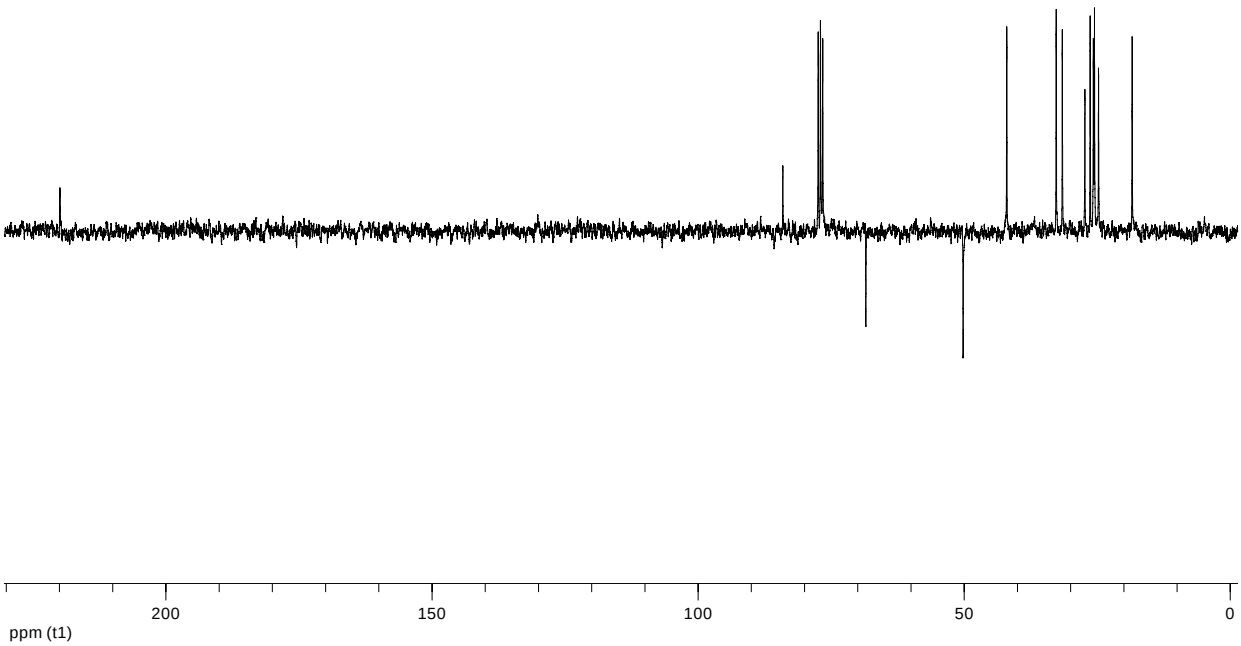
P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (4b)



4b



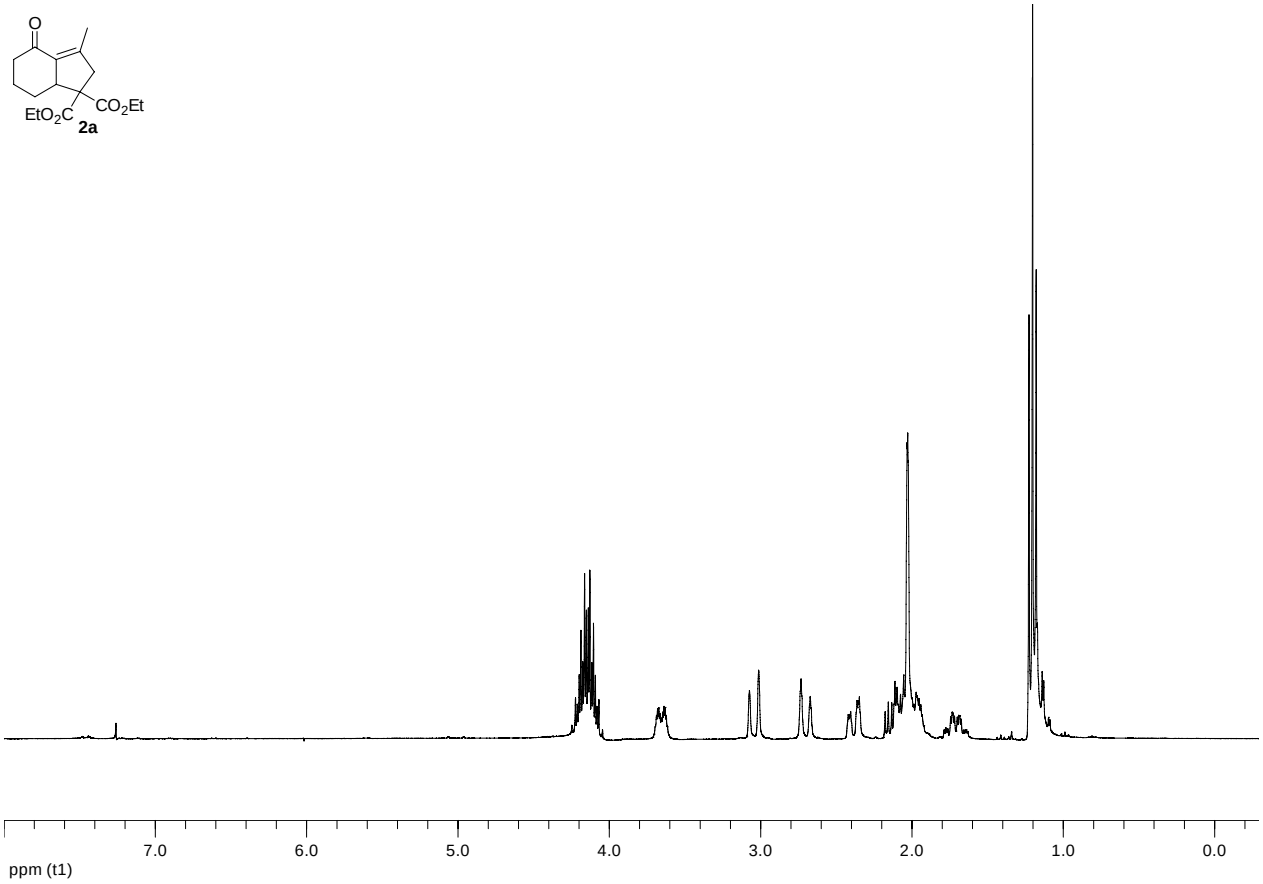


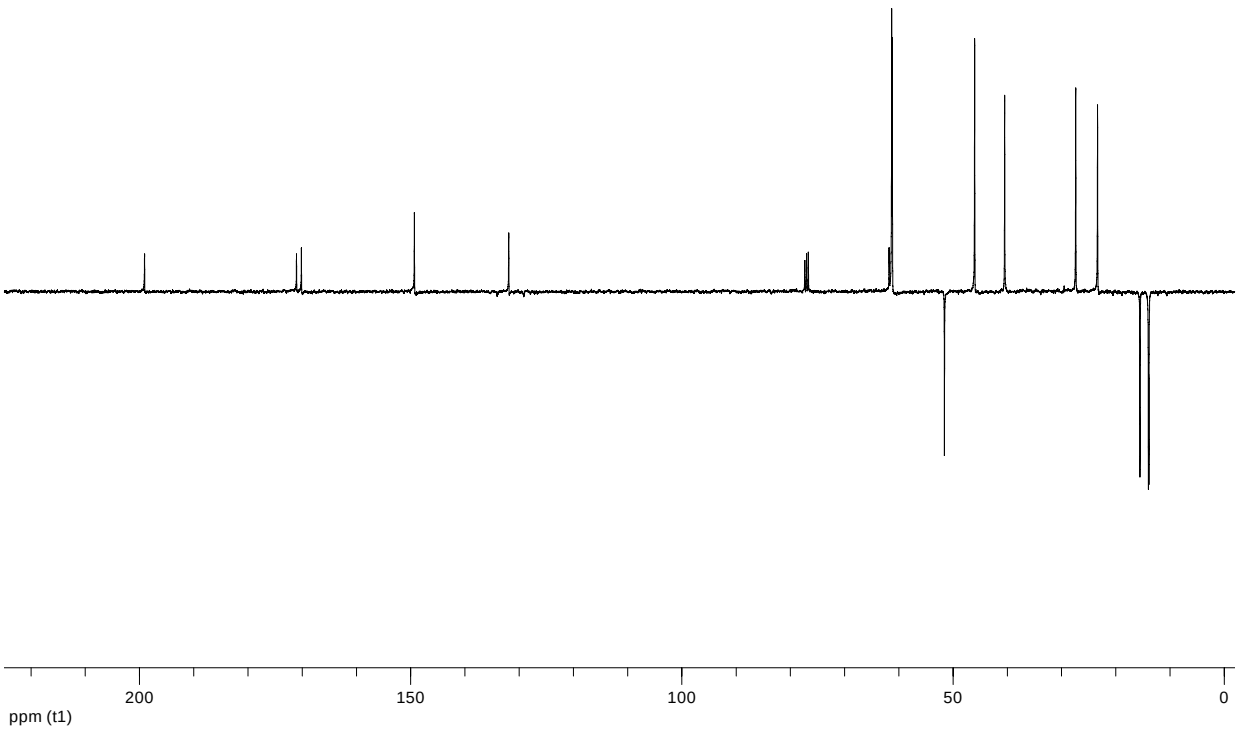
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

P. W. Davies and C. Detty-Mambo

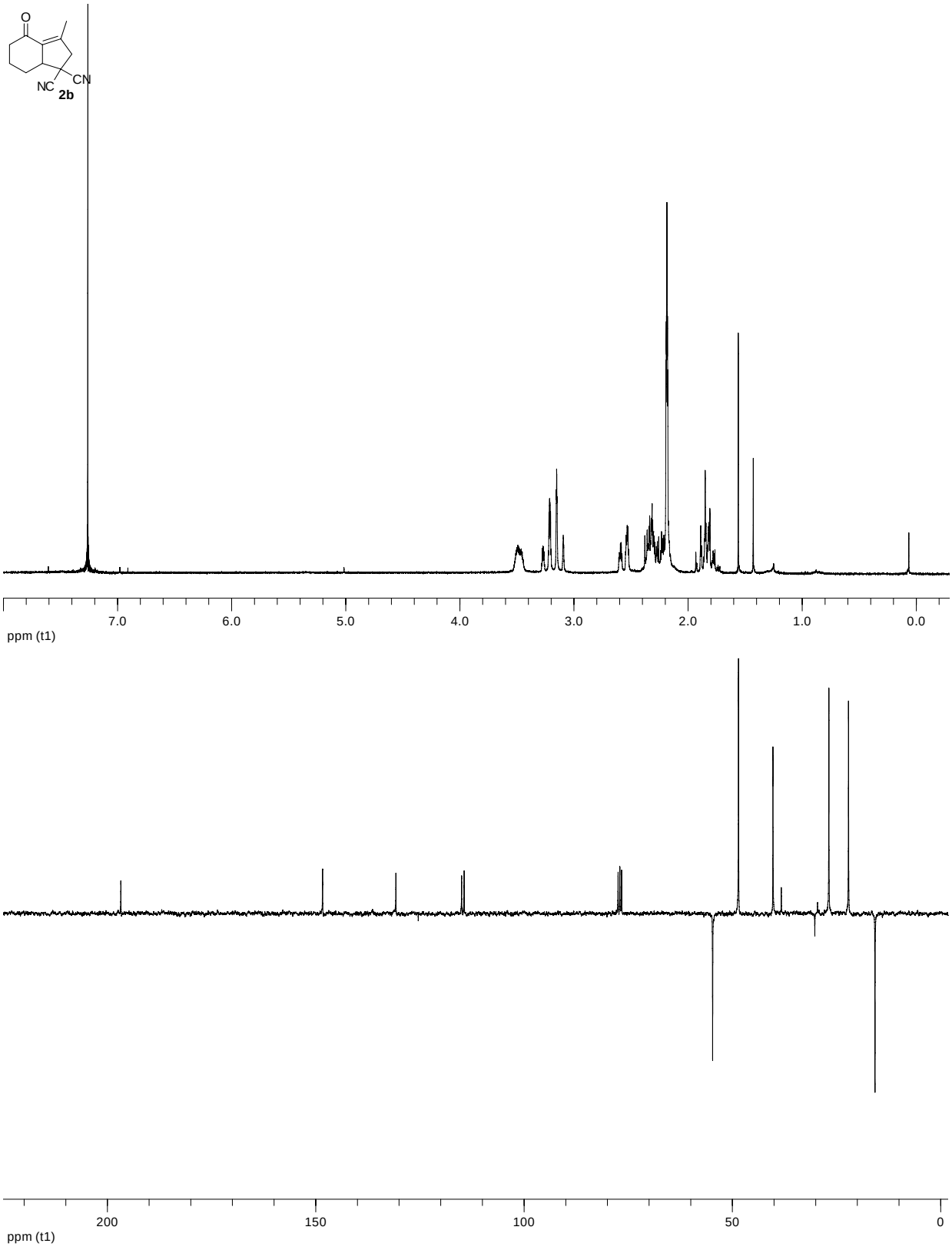
^{1}H and ^{13}C NMR Spectra of Cyclisation Products

^{1}H and ^{13}C NMR spectra of (2a)





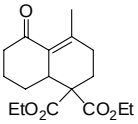
^{1}H and ^{13}C NMR spectra of (2b)



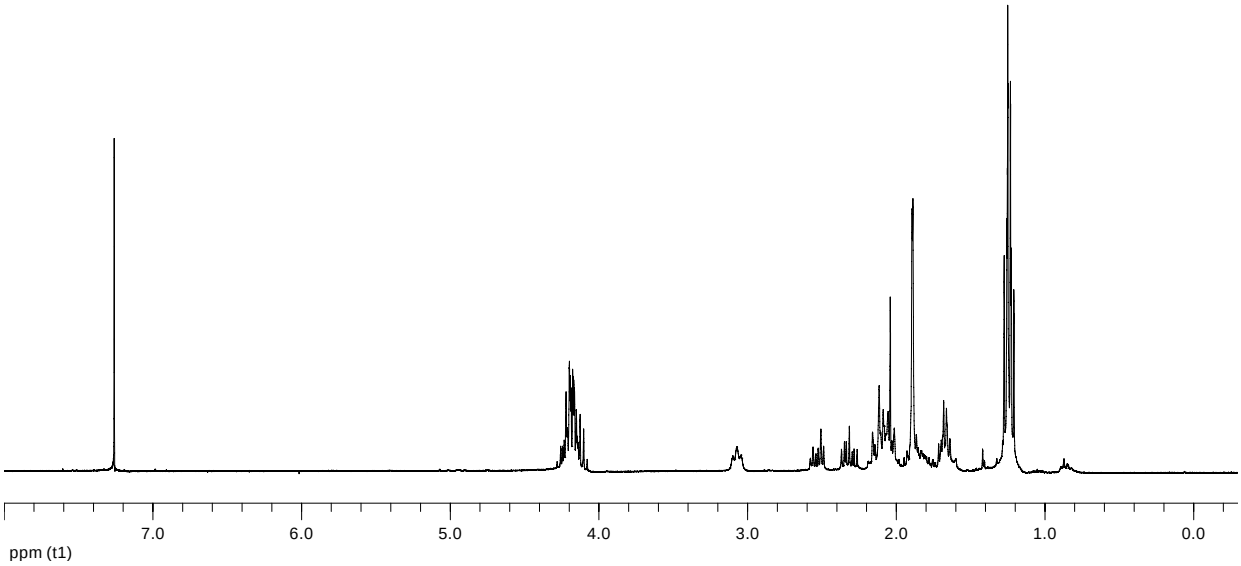
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

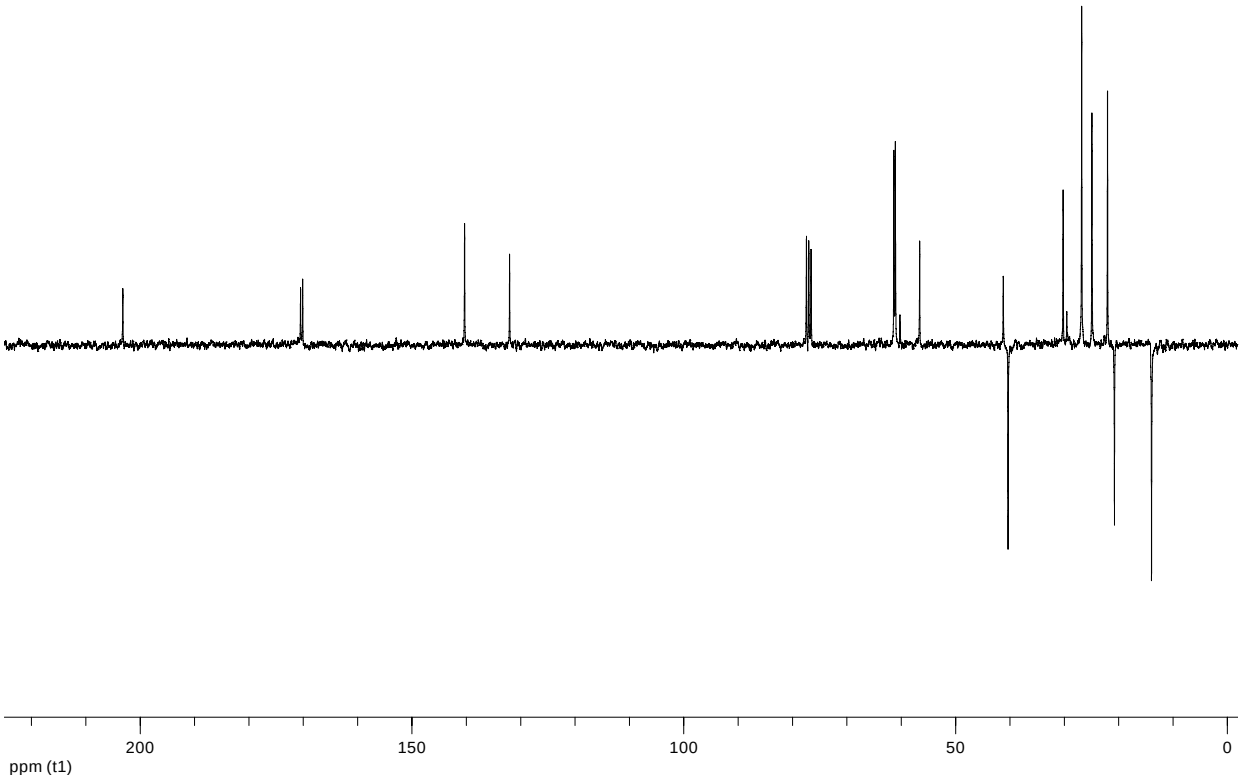
P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (2c)



2c

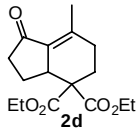




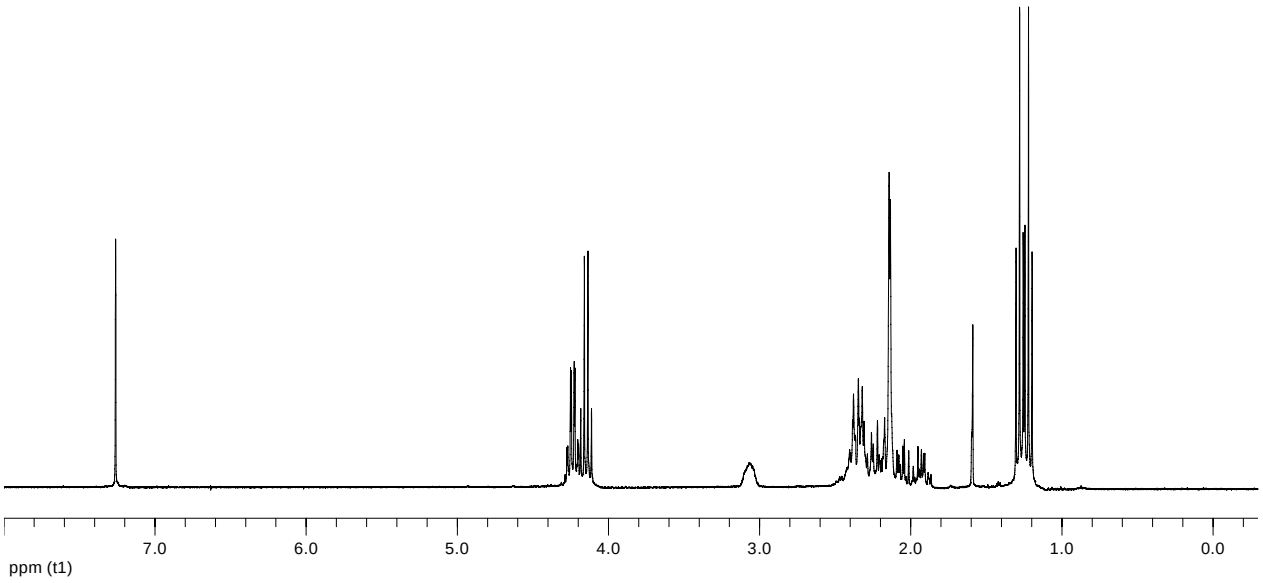
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

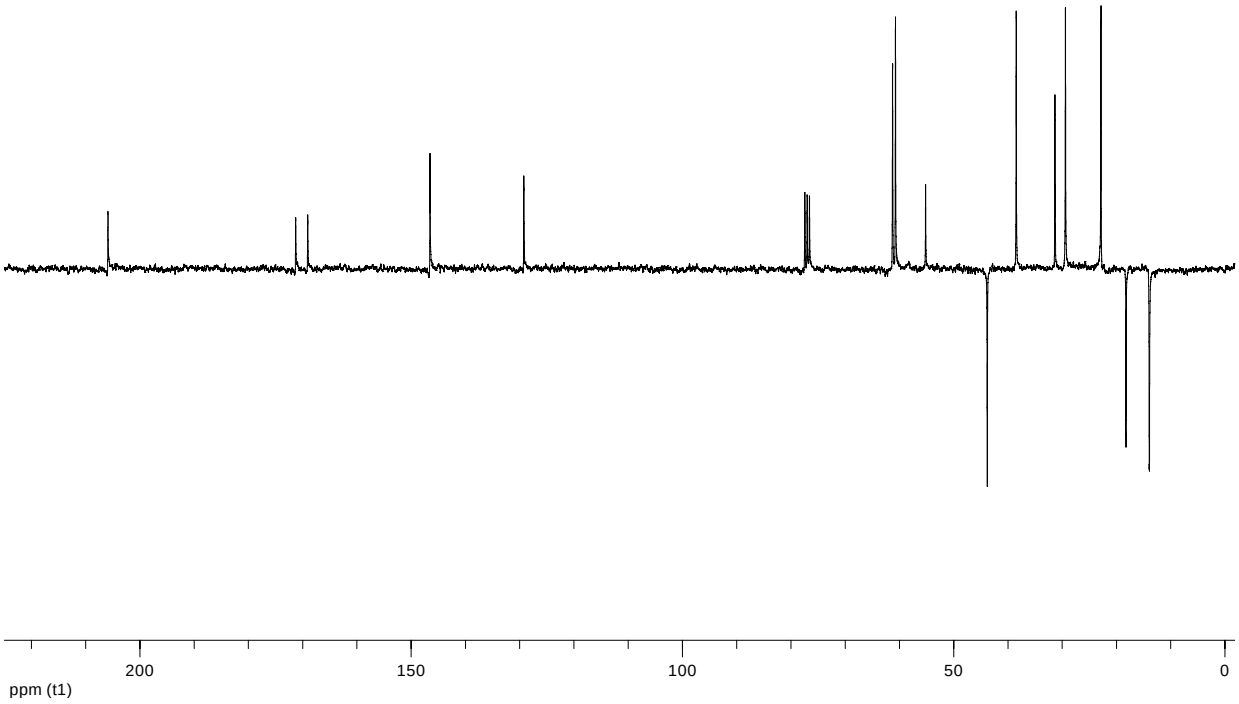
P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (2d)



2d

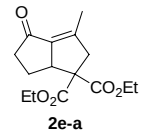




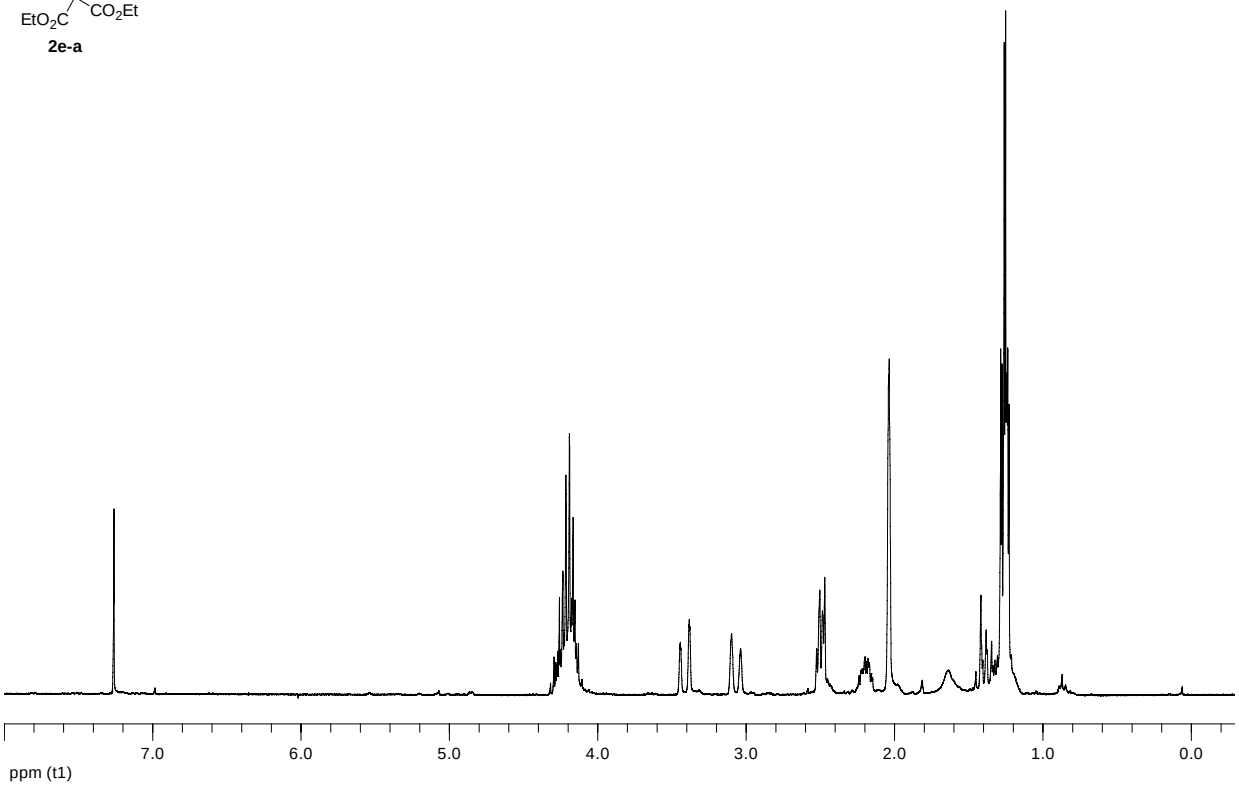
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

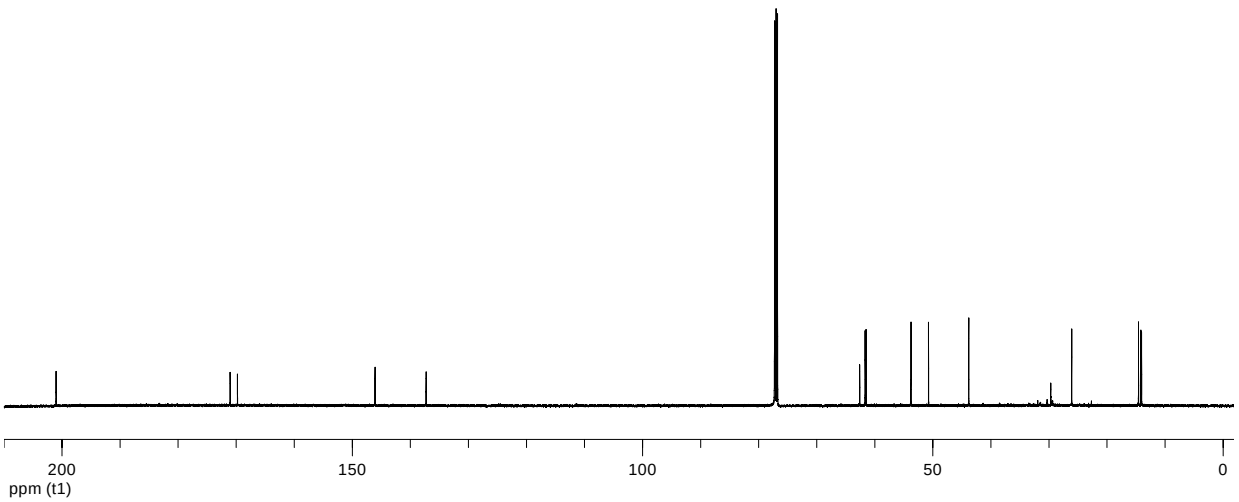
P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (2e-a)



2e-a

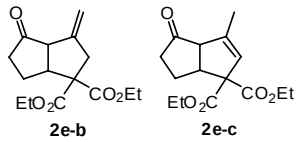




Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

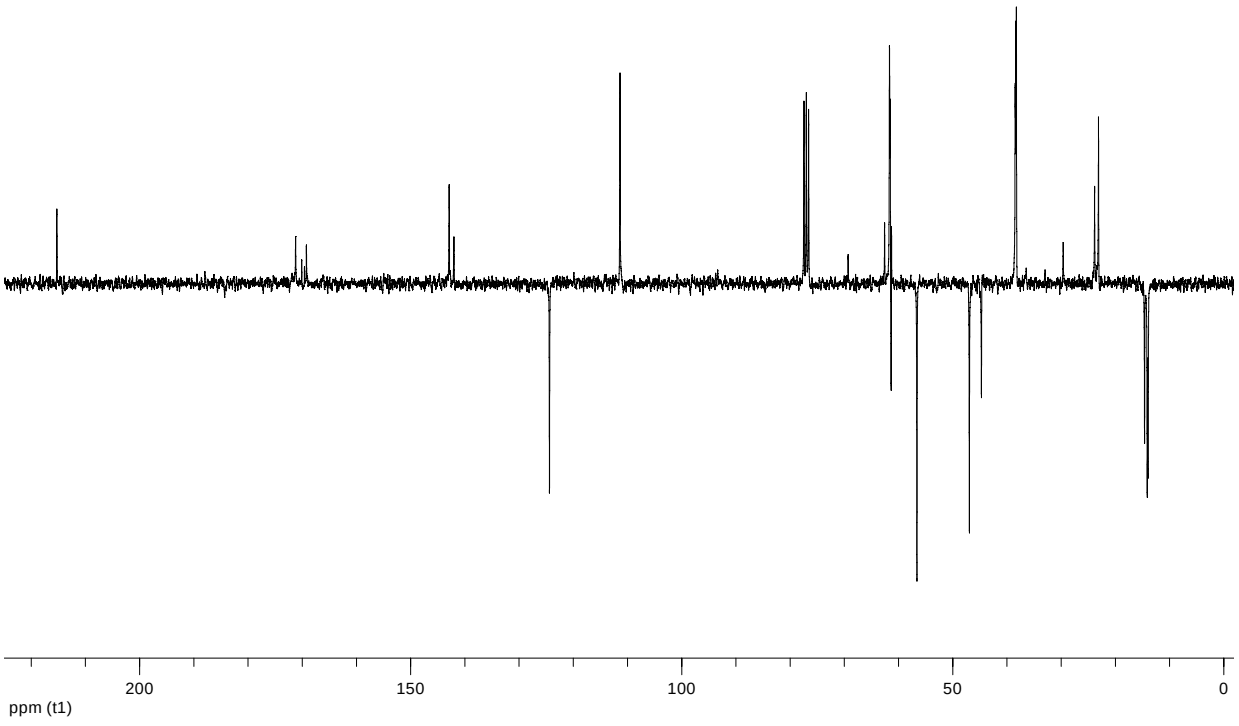
P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (2e-b) and (2e-c)



2e-b

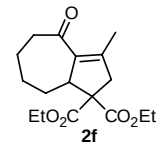
2e-c



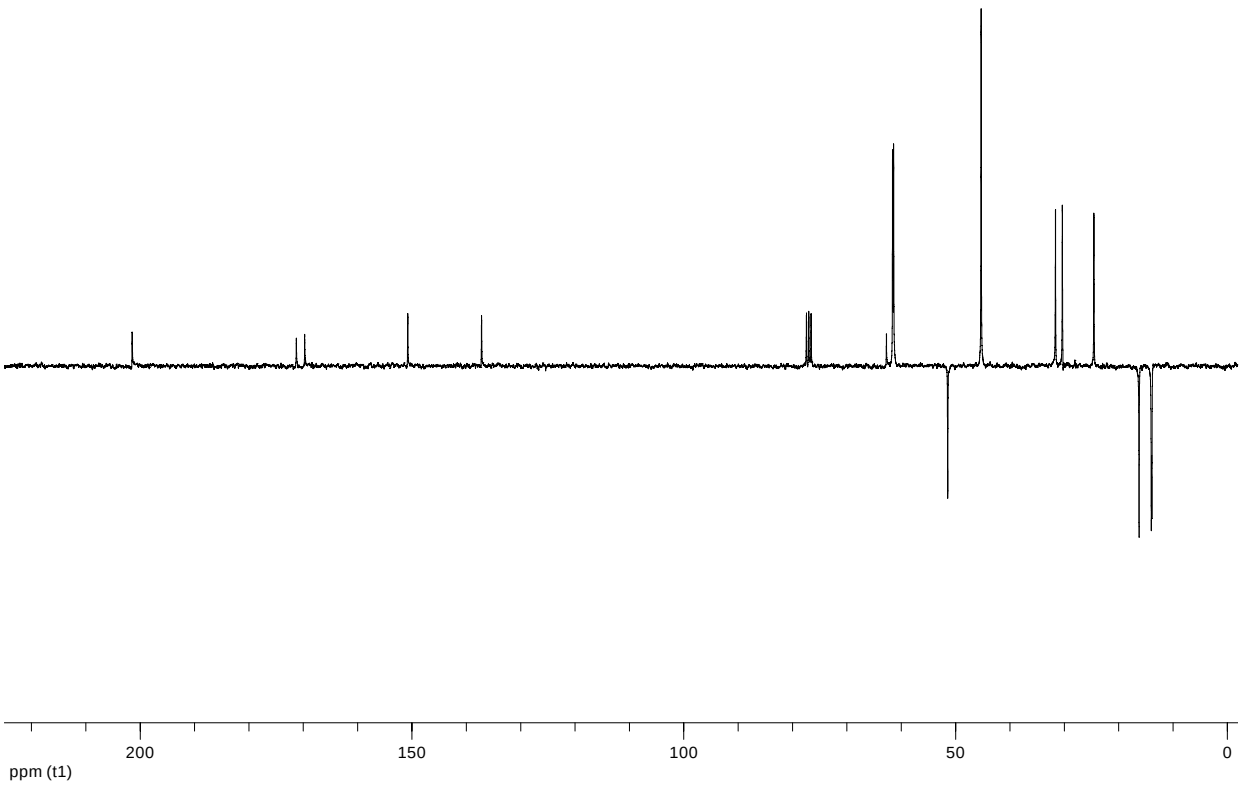
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (2f)



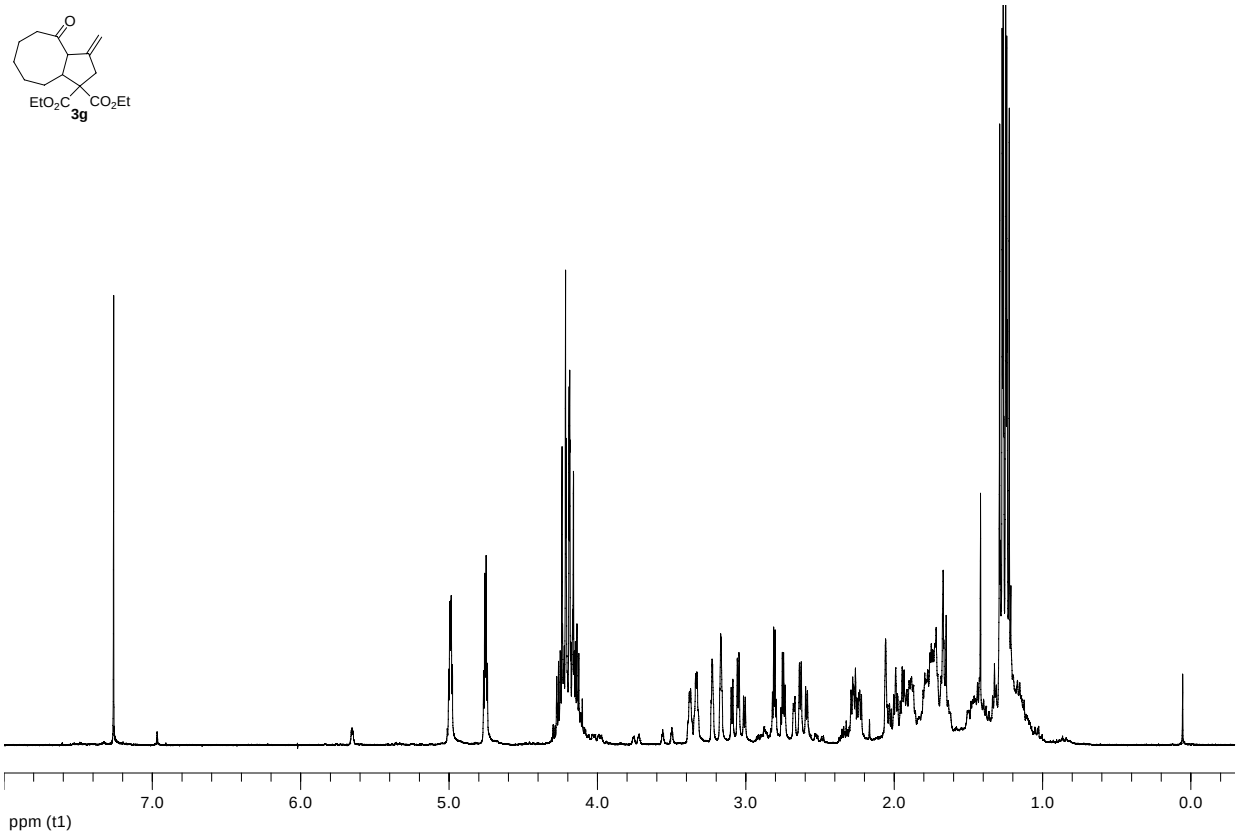
2f



Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

P. W. Davies and C. Detty-Mambo

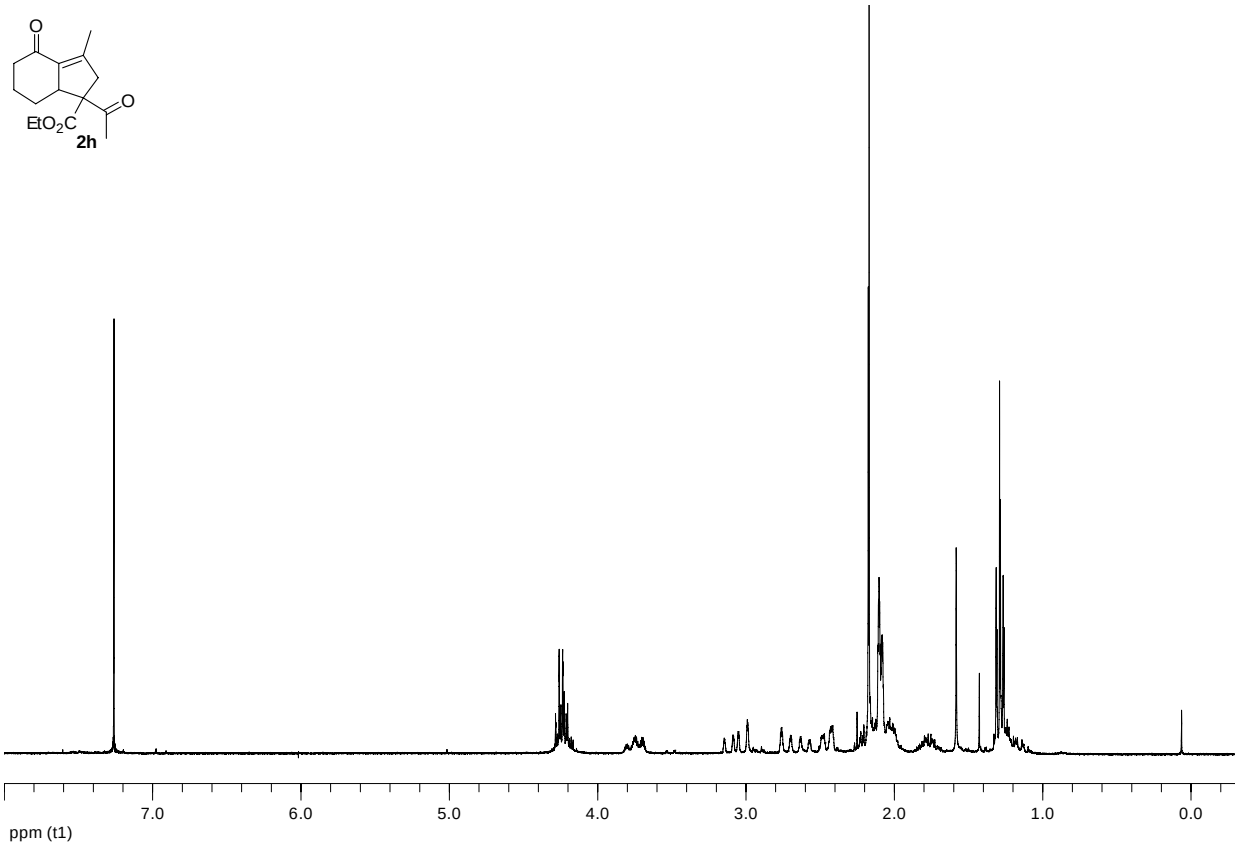
^{1}H spectra of (3g)

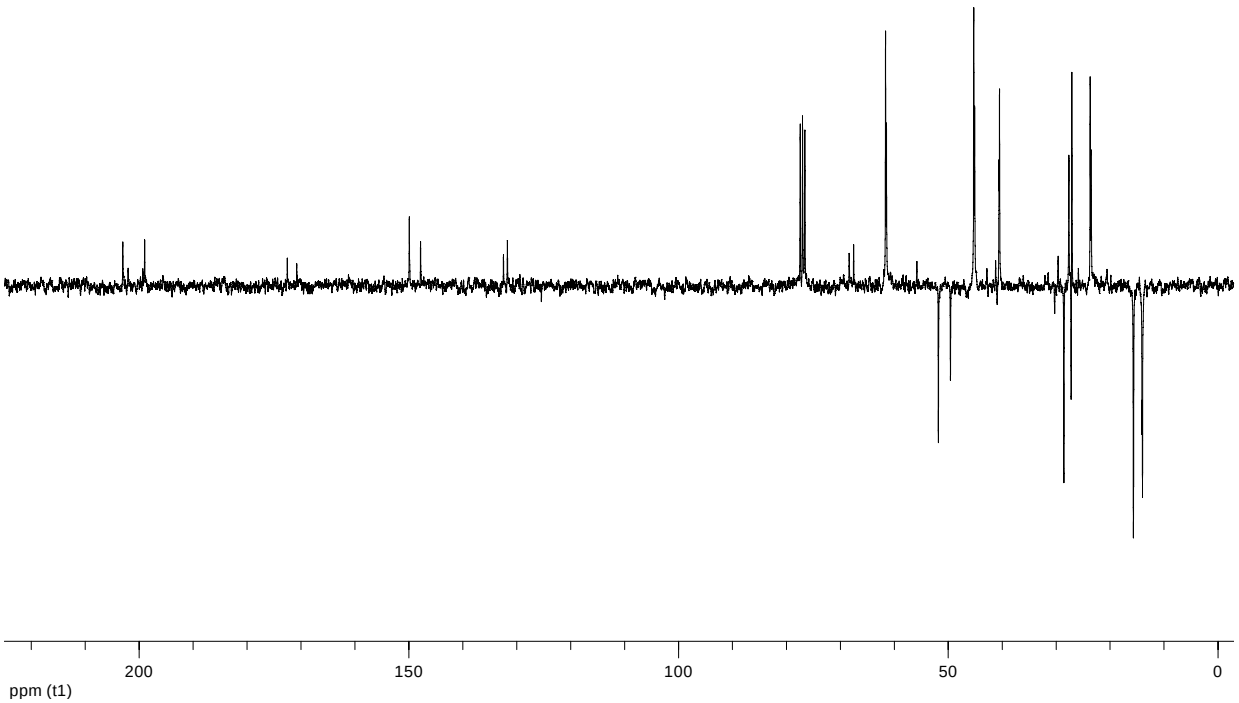


Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (2h)

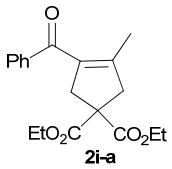




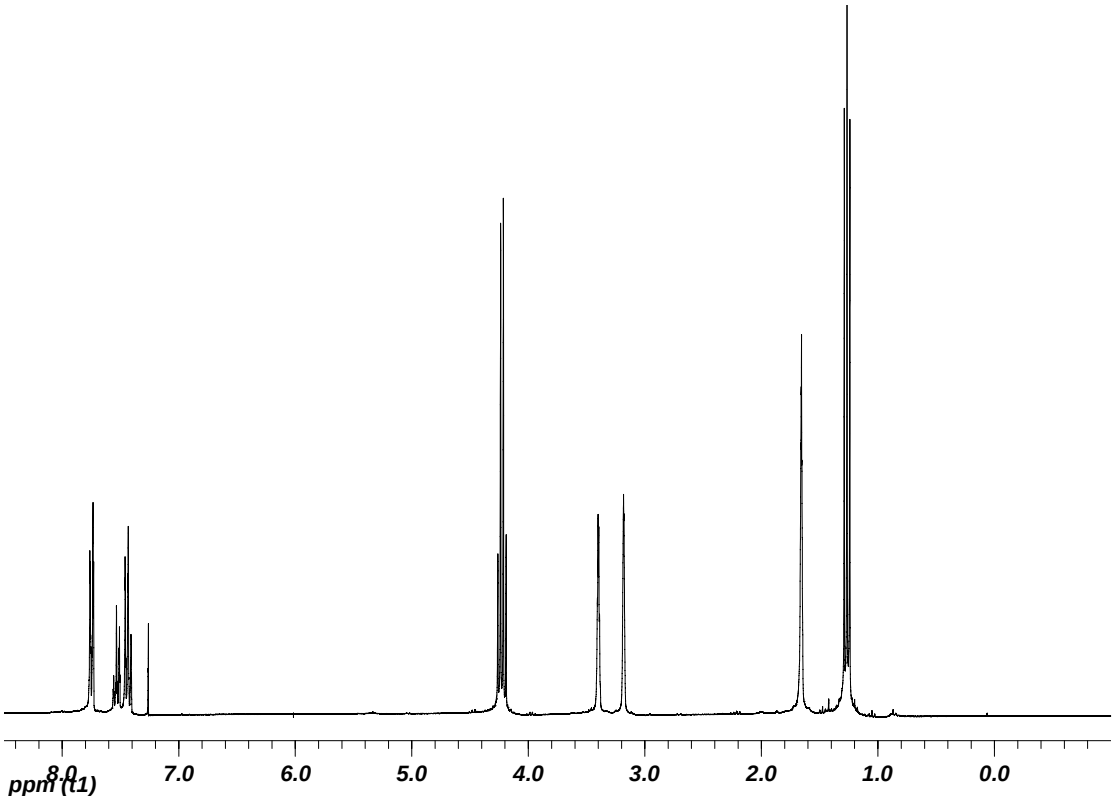
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

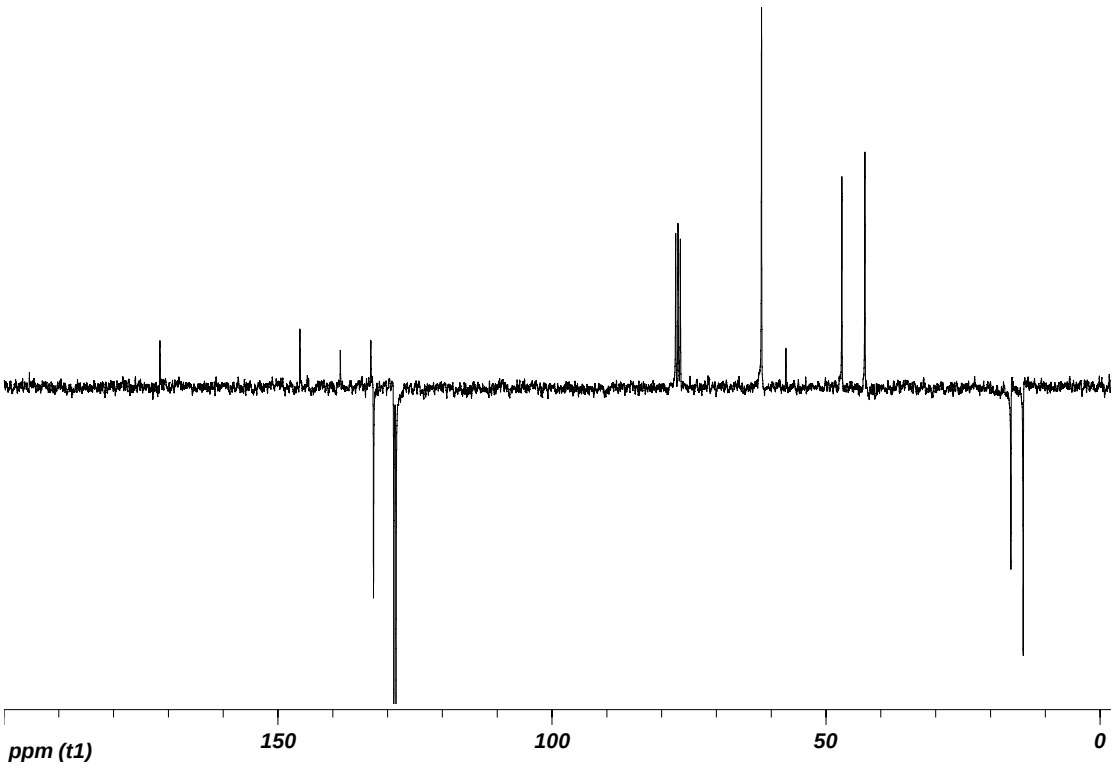
P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (2i-a)



2i-a

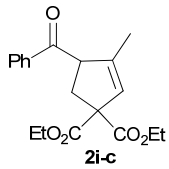




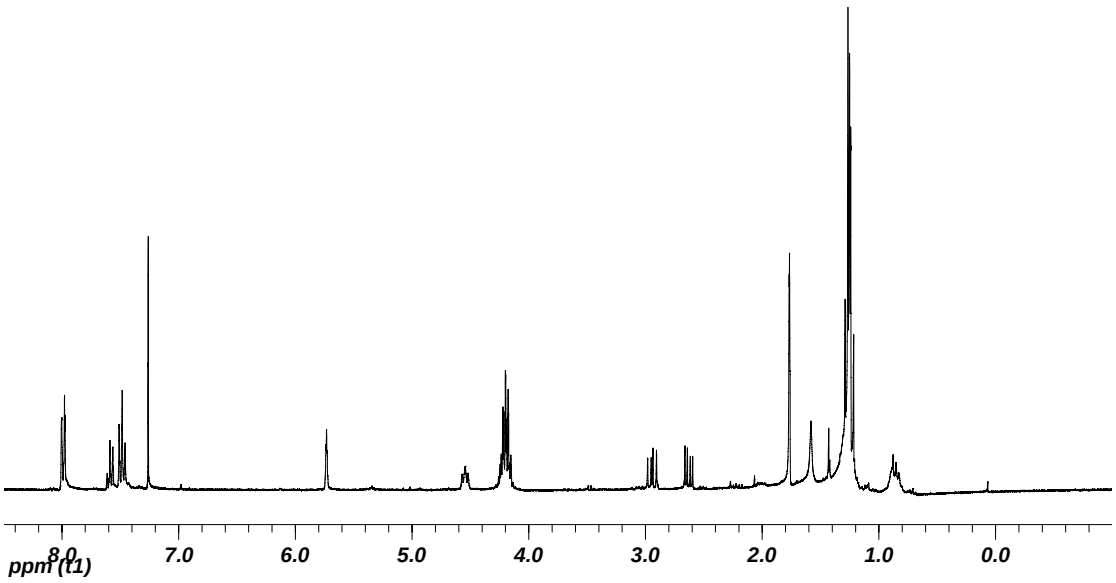
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

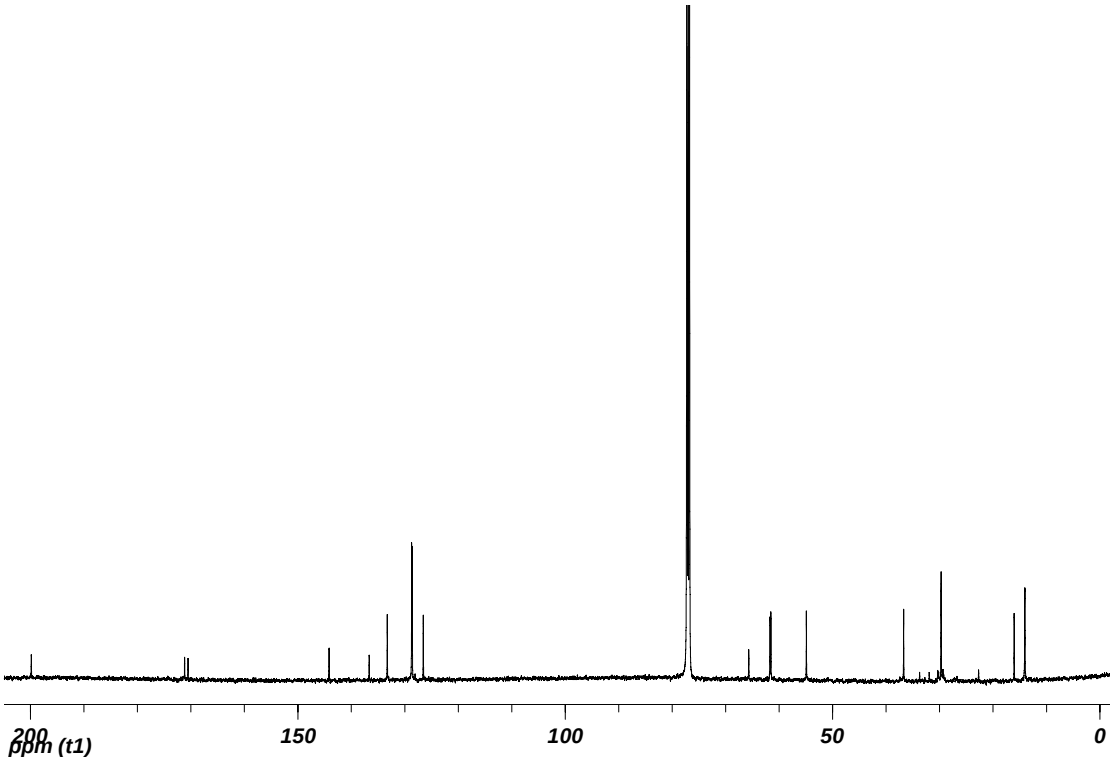
P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (2i-c)



2i-c



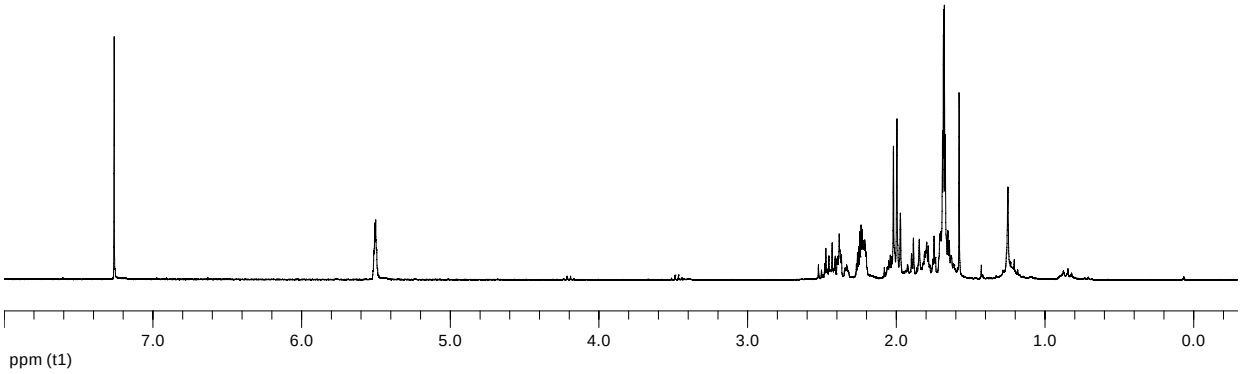


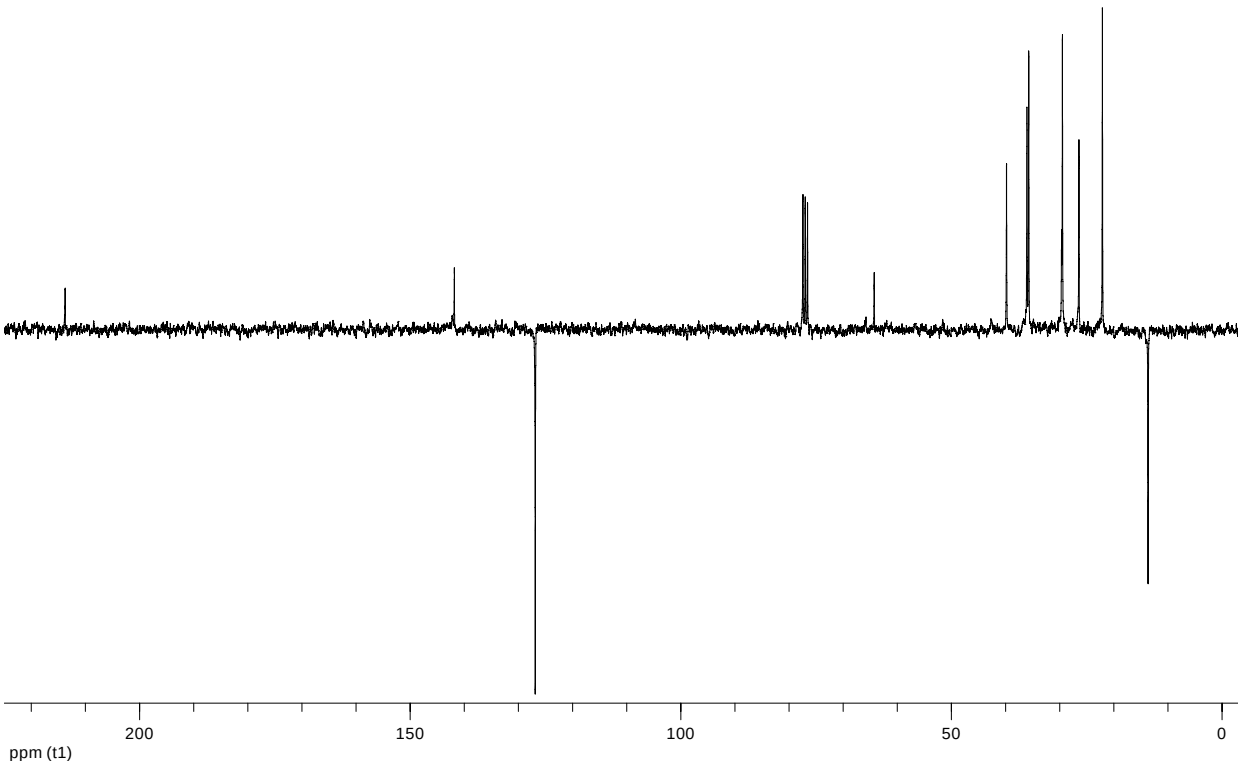
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (5a)

5a

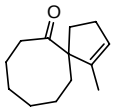




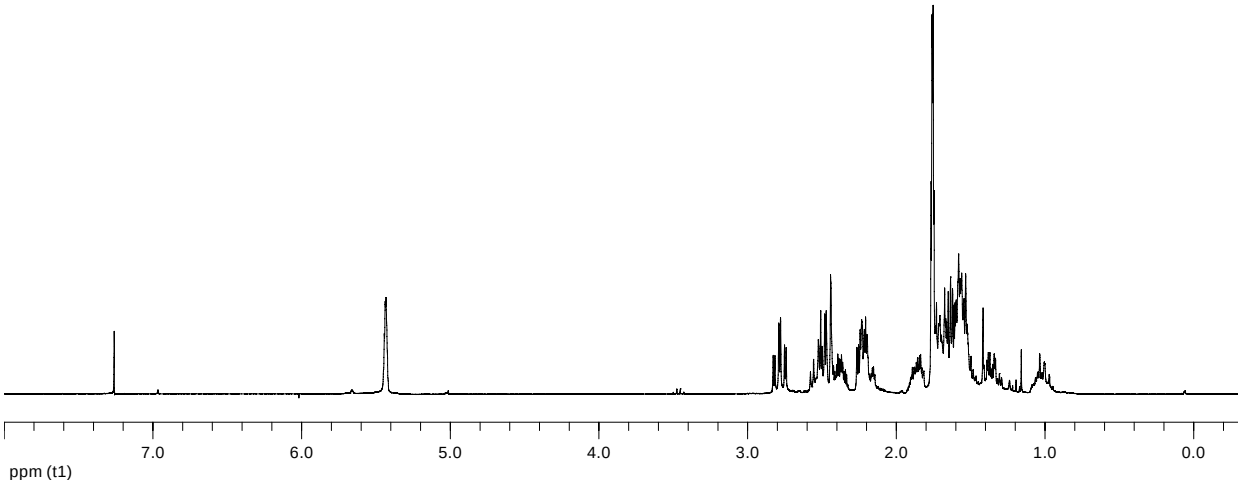
Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

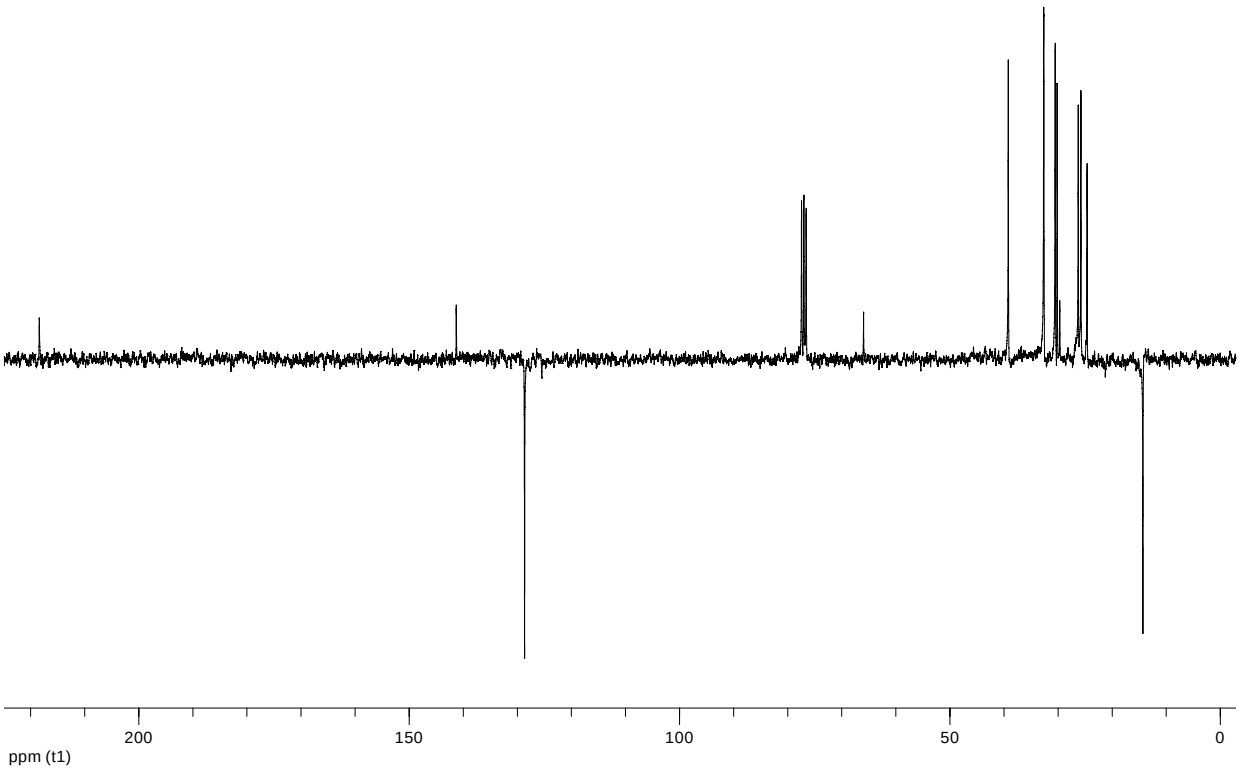
P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (5b)



5b

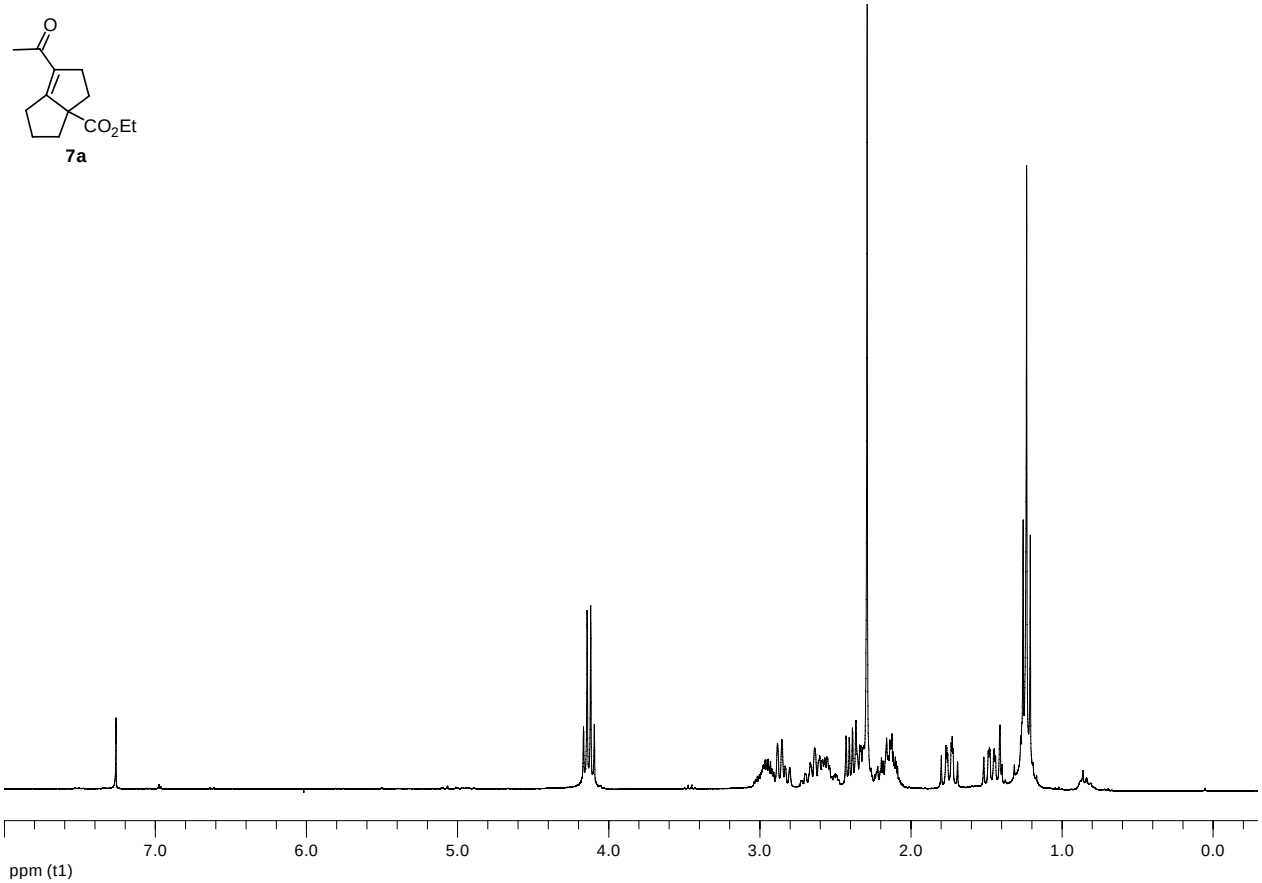


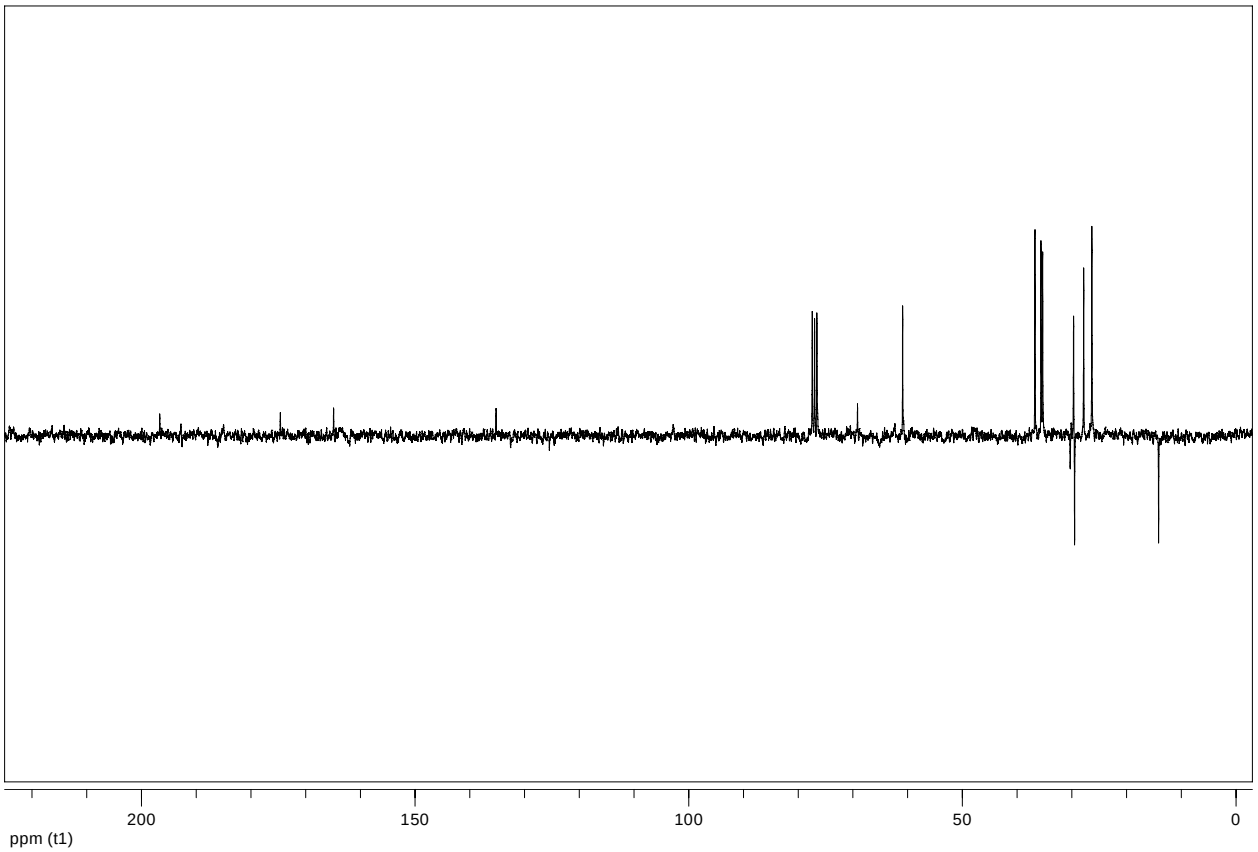


Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

P. W. Davies and C. Detty-Mambo

^{1}H and ^{13}C NMR spectra of (7a)





Gold-Catalysed Room-Temperature Cycloisomerisation of Alkynes and Unactivated Enolisable Ketones

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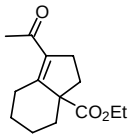
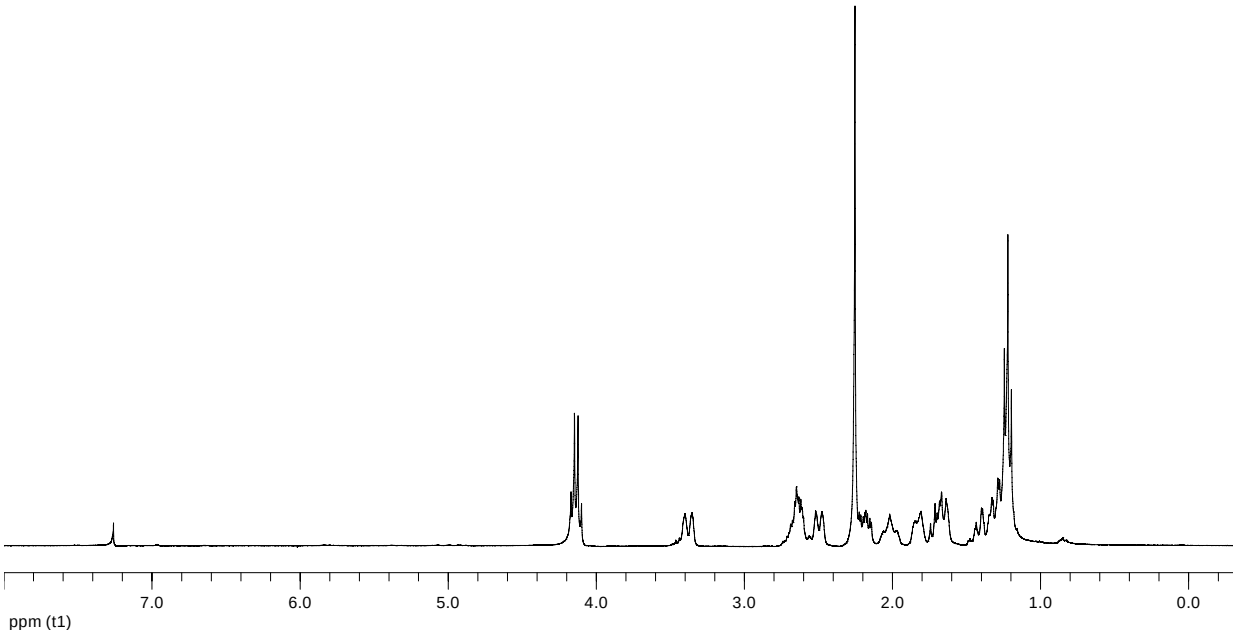
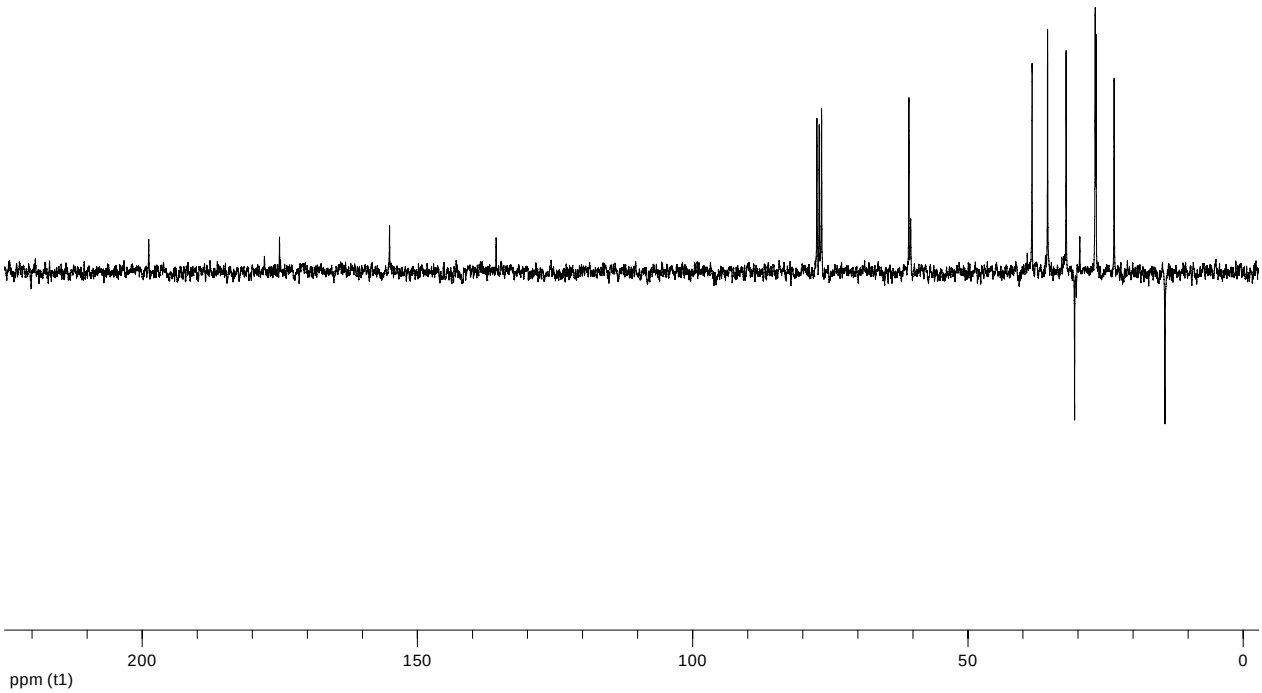
^{1}H and ^{13}C NMR spectra of (7b)

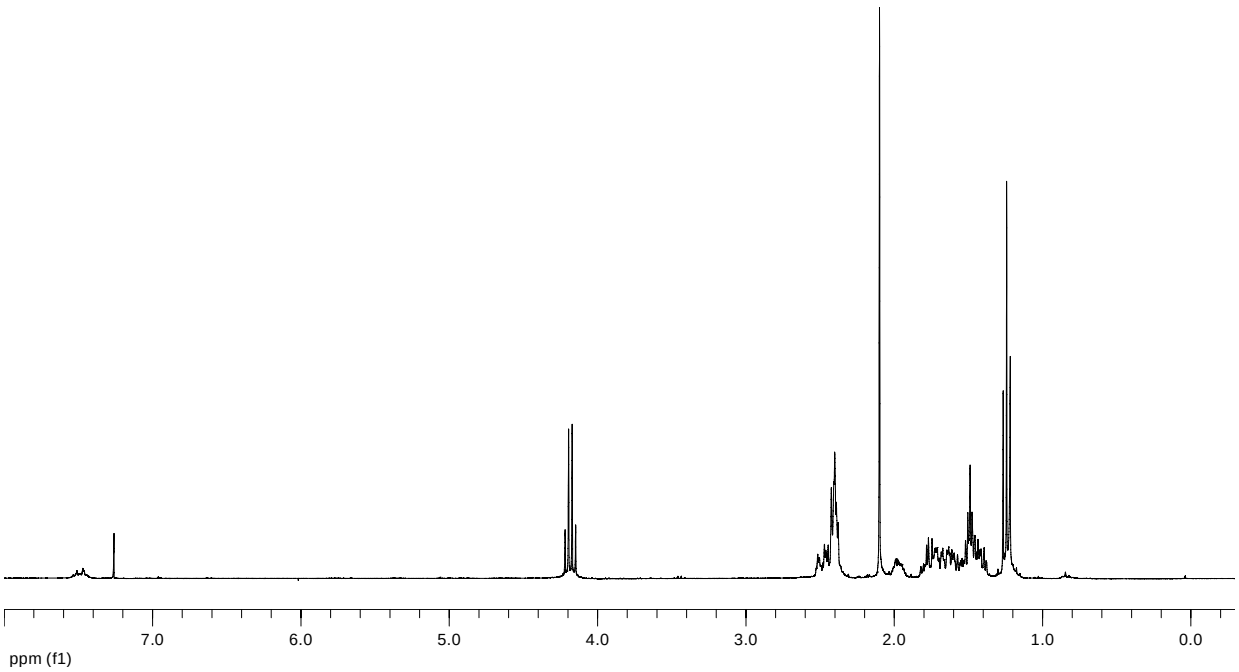


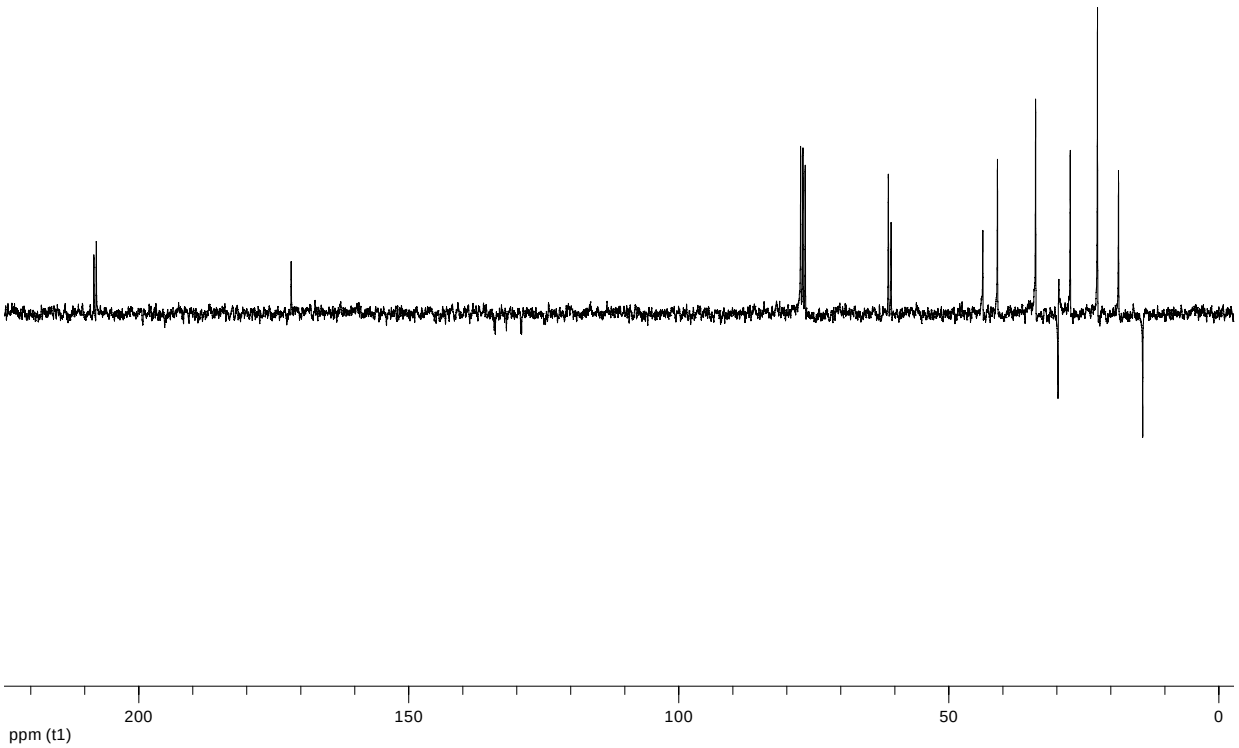
7b





^{1}H and ^{13}C NMR spectra of (8b)





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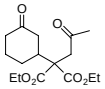
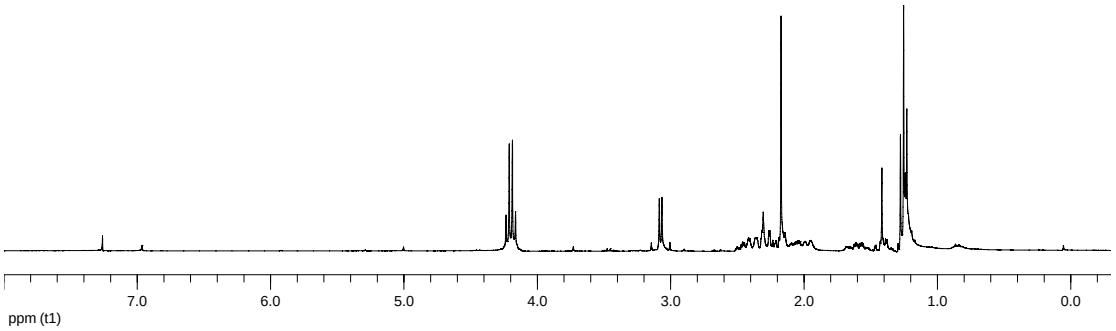
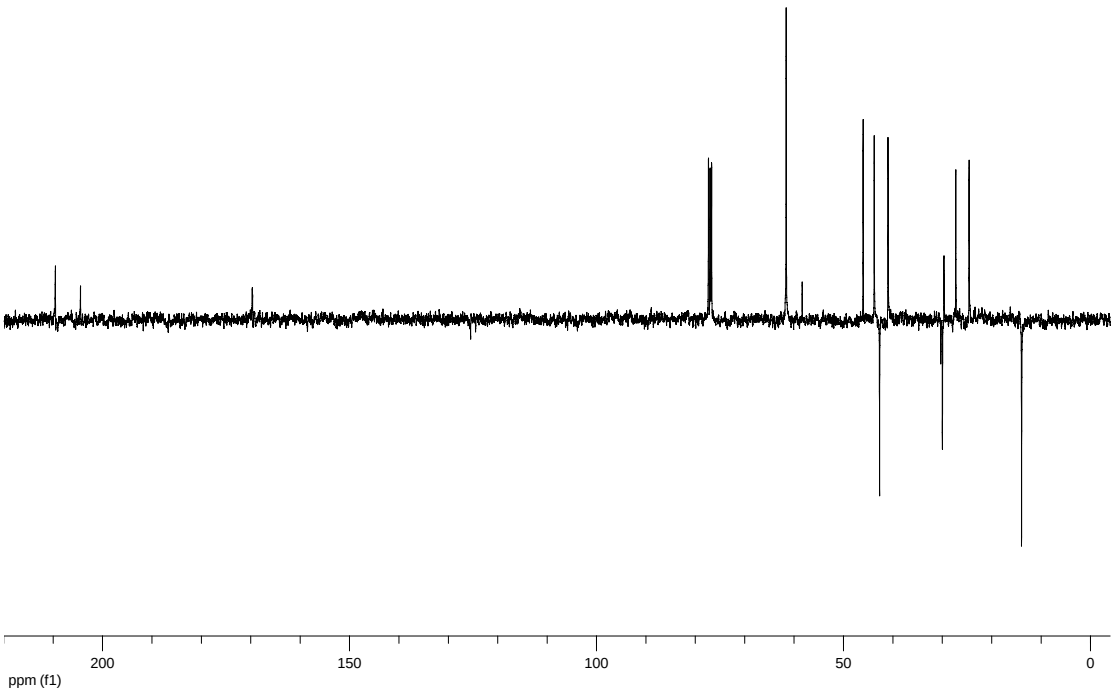
^{1}H and ^{13}C NMR spectra of (10)

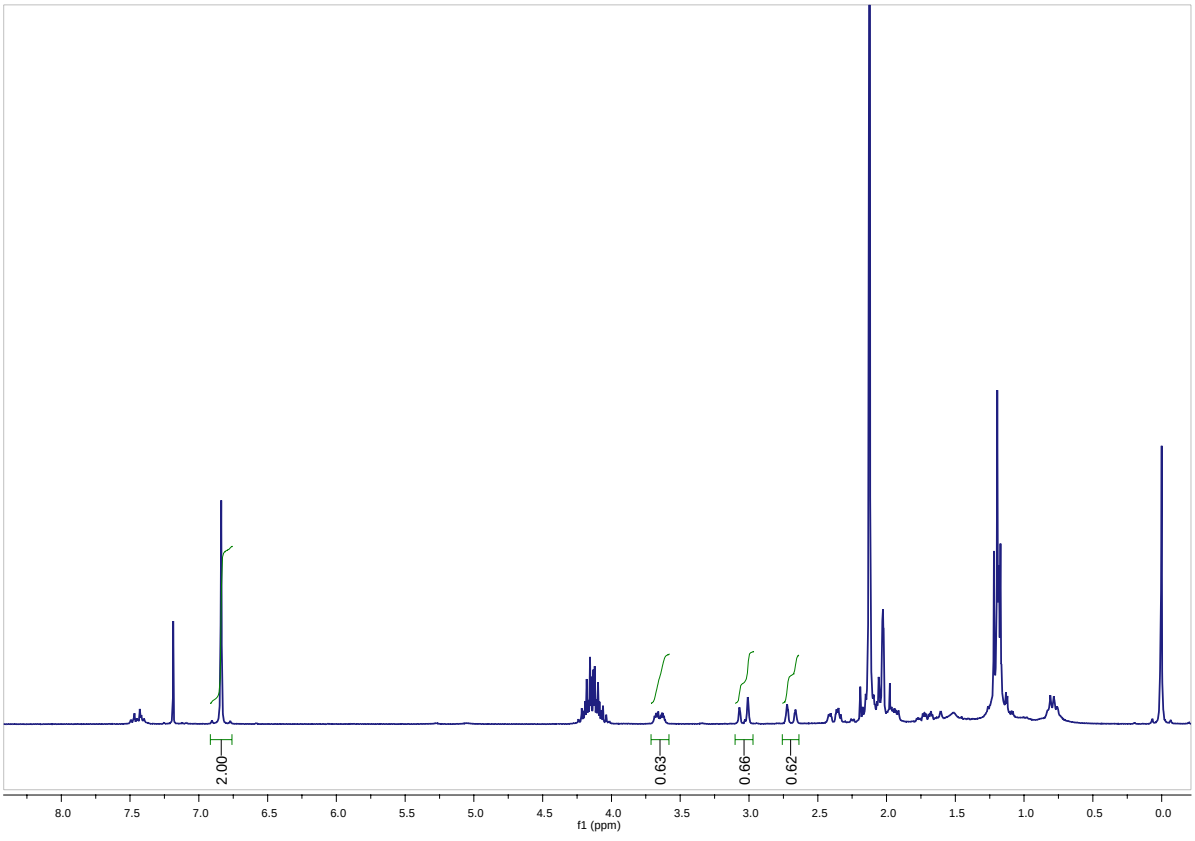




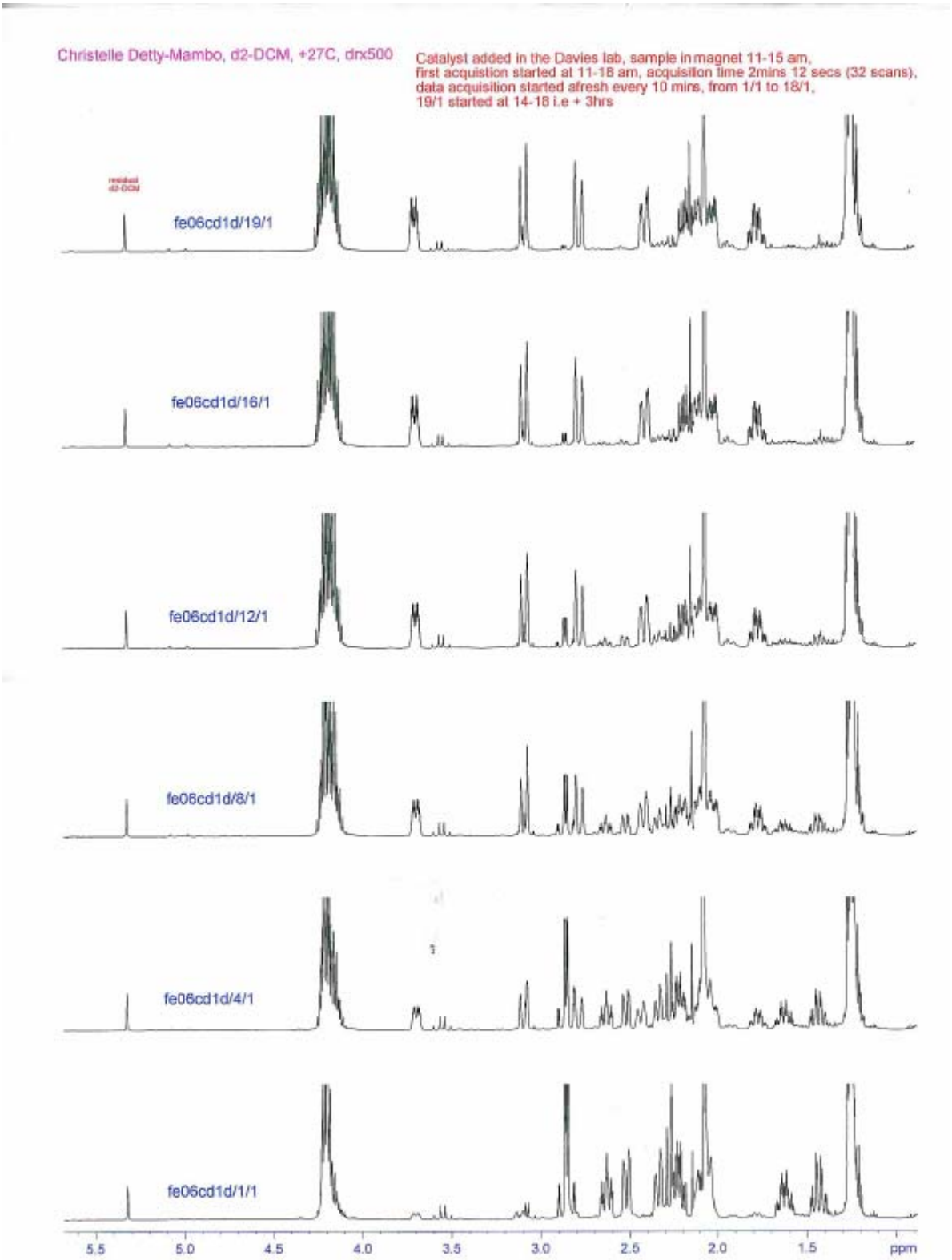


Aldol dehydration of diketone 10

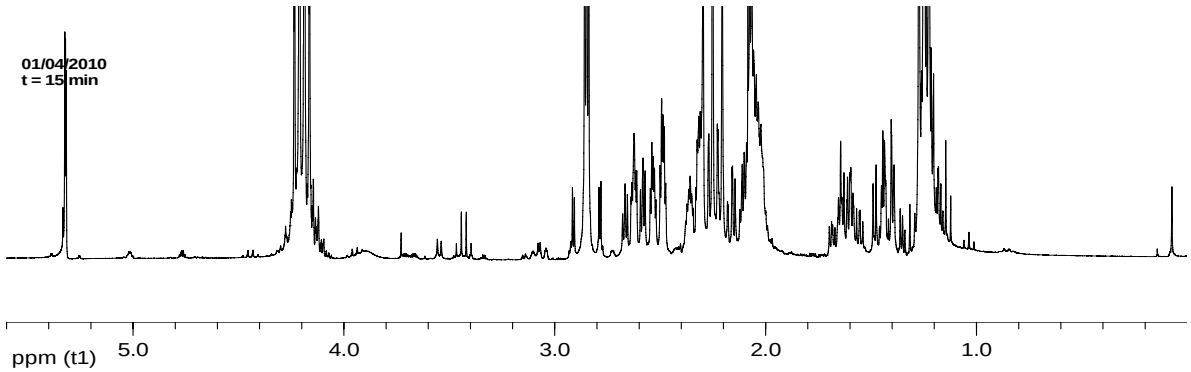
AgOTf (2.6 mg, 0.012 mmol) and Ph_3PAuCl (5.9 mg, 0.012 mmol) were added into a dried Schlenk tube under an argon atmosphere followed by the addition of CH_2Cl_2 (2 mL). The reaction mixture was stirred for 1 min, before a solution of diketone **10** (4.3 mg, 13.7 μmol) diluted in CH_2Cl_2 (14 μL) was added. After 2 h, no consumption of diketone was observed. Ketoalkyne **1a** (2.7 mg, 9.1 μmol) was added to the reaction mixture and after 1 min the formation of cyclised product could be observed by TLC. The reaction was then stirred for 24 h and the solution filtered through a short pad of silica gel (hexane/EtOAc: 6/4). The solvent was removed under reduced pressure [Mass of residue 7.9 mg]. 1,2,4,5-tetramethyl benzene (2.8 mg, 20.8 μmol) was added as internal standard. NMR analysis shows formation of **2a** (13.1 μmol) and unreacted **10** (0.31 μmol).

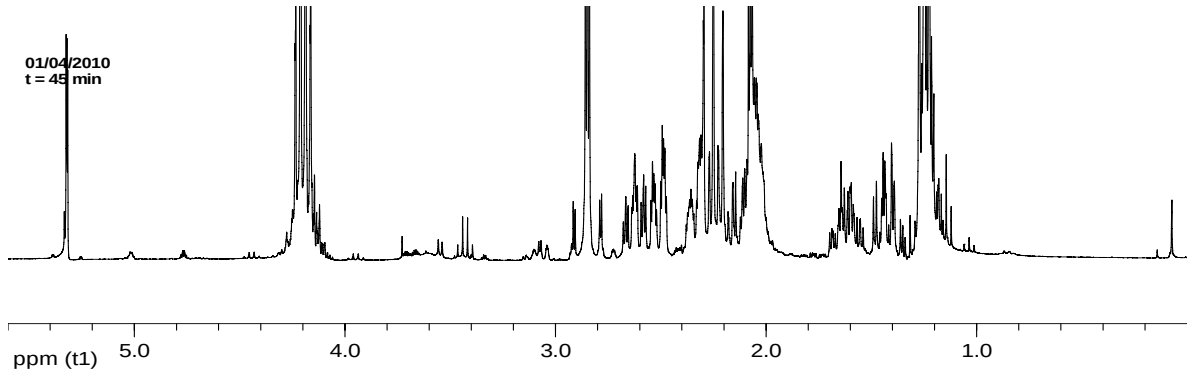


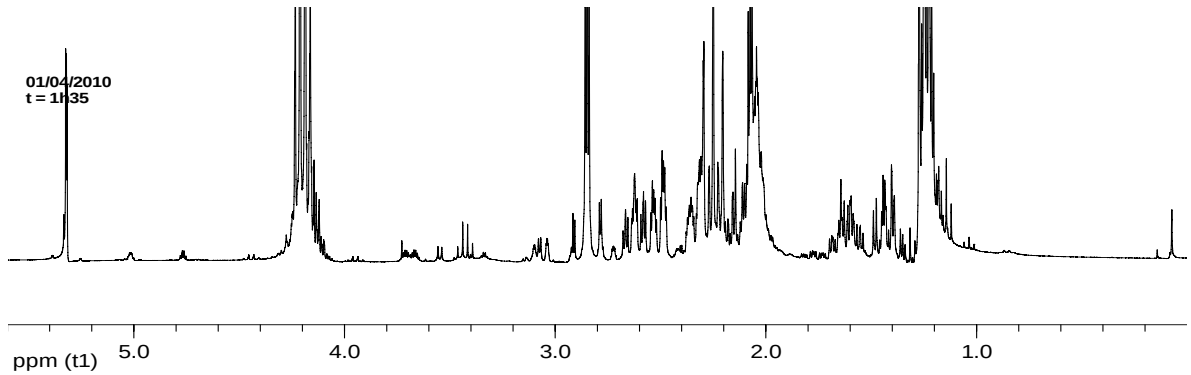
Catalysis reaction of 1a monitored by ^{1}H NMR



AgOTf (2.6 mg, 0.012 mmol) was added into a dried Schlenk under argon atmosphere followed by the addition of Ph_3PAuCl (5.9 mg, 0.012 mmol). Immediately after this addition, a solution of the **1a** (58.7 mg, 0.2 mmol) in CD_2Cl_2 (0.8 mL) was added by syringe. The mixture was stirred at rt for 2 min and then was transferred via a pipette into the NMR tube under argon, filtering through a piece of cotton wool. The Schlenk and the cotton were washed with CD_2Cl_2 (0.2 ml) and this was added to the NMR tube. The NMR tube was capped and the first NMR acquisition was made 15 min after the beginning of the reaction. The reaction was monitored by NMR. After 4.5h, a solution of diketone **10** (0.1 mL, 0.1 M in CD_2Cl_2) was added into the NMR tube. A second addition of **10** (0.05 mL, 0.2 M in CD_2Cl_2) was made after 18.5h. The reaction was monitored until consumption of both **1a** and **10**.







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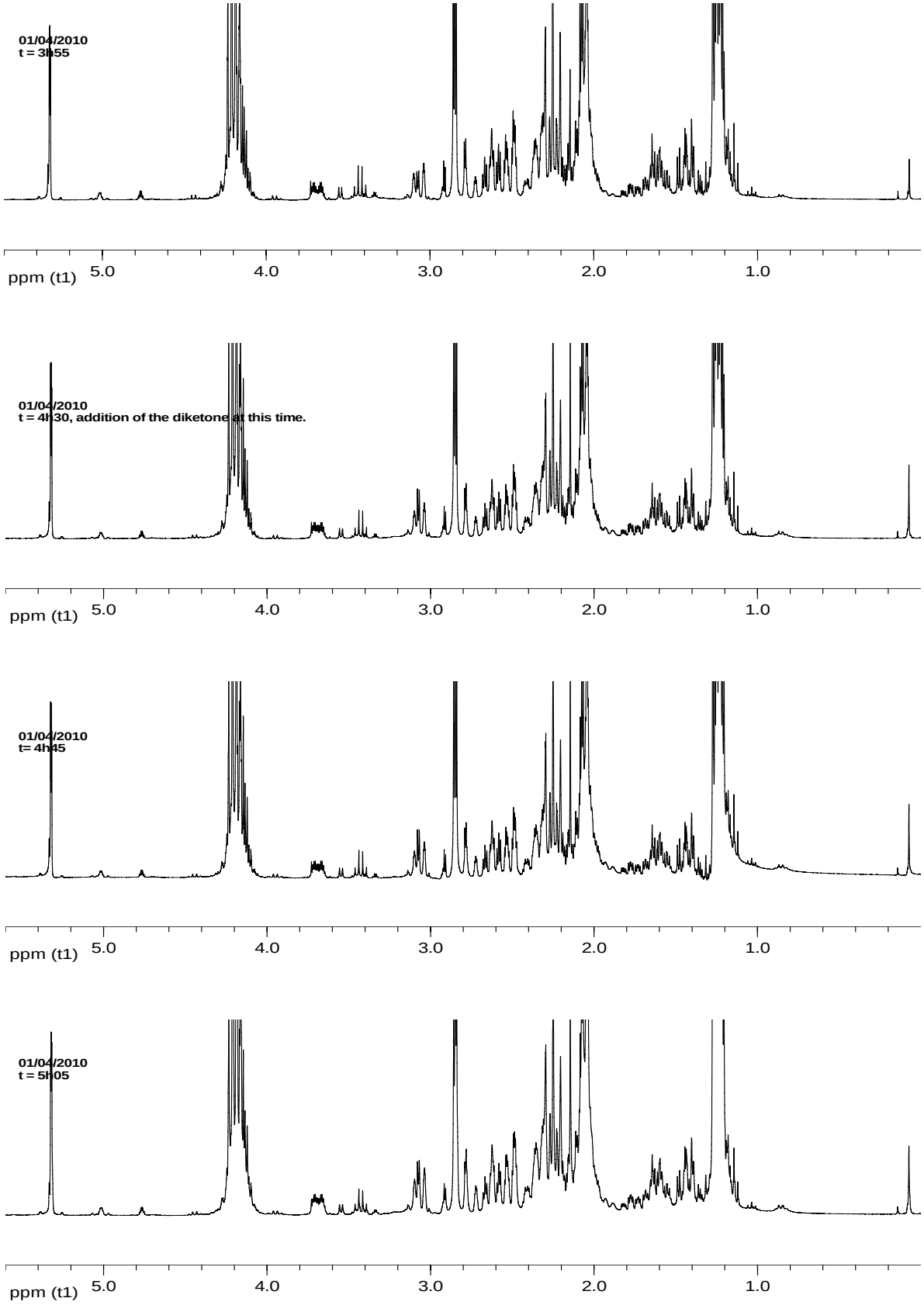

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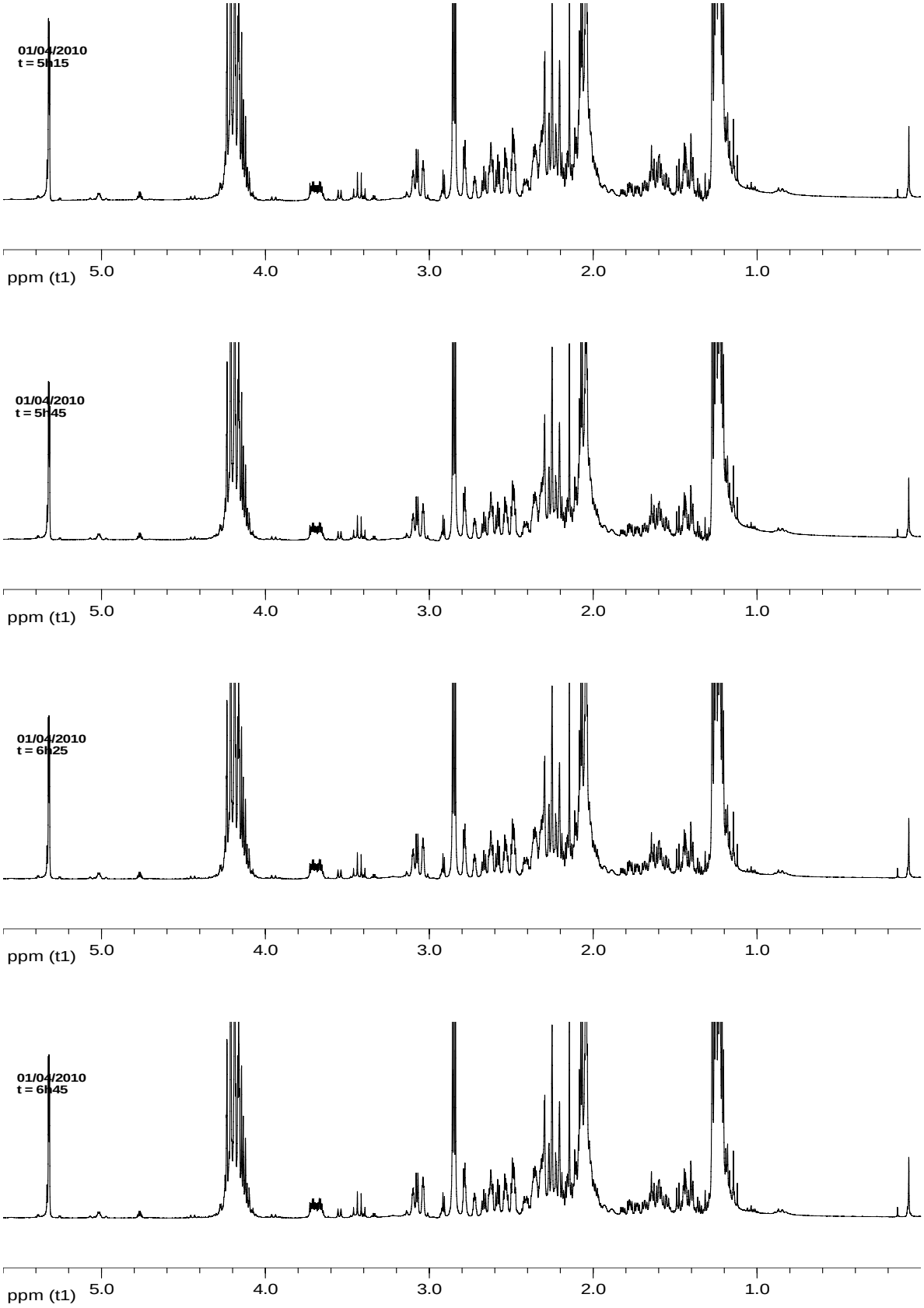

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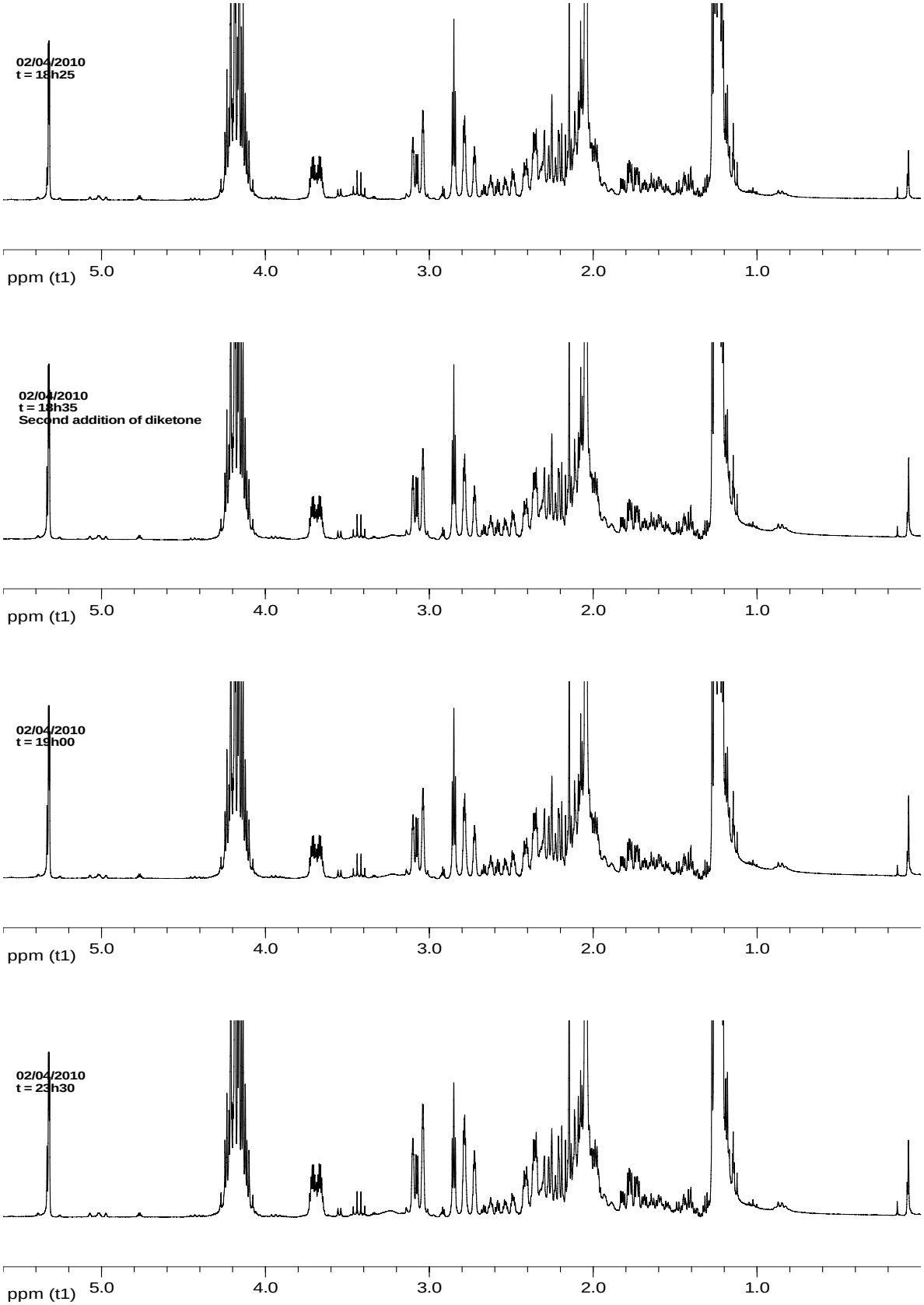

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