Supporting Information

Preparation of Highly Substituted Tetrahydropyrans *via* a Metal Assisted [4+2] Dipolar Cycloaddition Reaction

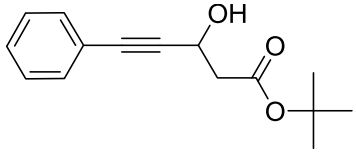
Eric A. Allart, Steven D. R. Christie*, Gareth J. Pritchard* and Mark R. J. Elsegood.

Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

Experimental section

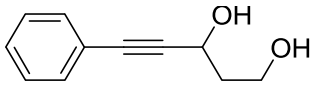
General Information. High resolution mass spectroscopy was carried out on a Jeol SX 102 machine, using fast atom bombardment (FAB^+) ionisation technique. Nuclear magnetic resonance spectroscopy was carried out using a Brucker DPX 400 instrument. The spectra were calibrated where possible to the signals of tetramethylsilane or the small quantity of $CHCl_3$ present in $CDCl_3$. Where possible, coupling constants (*J*) are shown denoting the multiplicity as a singlet (s), doublet (d), triplet (t), quarter (q), multiplet (m). The size of the coupling constant is given in Hertz (Hz). Fourrier transformation Infra Red spectroscopy was recorded using a Paragon 1000 Perkin Elmer FT-IR spectrophotometer in the range of 3500-600 cm^{-1} following a standard background correction. Flash silica column chromatography was used as a standard purification procedure using Fluka Kiesel gel 60, 0.04-0.063 mm particle size. Thin layer chromatography was used where possible as a standard procedure for monitoring the course and rate of a given reaction. TLC plates used were Merck aluminium backed sheets with Kiesel gel 60 F_{254} silica coating. DCM was distilled over CaH_2 for anhydrous reactions. Petrol was distilled collecting the fraction distilling below 60 °C. THF was dried over sodium/benzophenone and freshly distilled before use. Diethyl ether was purchased from Fischer Scientific (99+ %) and used without purification. Ethyl acetate was distilled over $CaCl_2$ for general use. Dicobalt octacarbonyl was purchased from Strem (stabilised by 1-5% hexane) and used without any further purification. Anhydrous reactions were carried out in oven-dried glassware and under an atmosphere of nitrogen. All metal carbonyl complexes were stored under a nitrogen atmosphere and kept at –18 °C in a freezer.

^{t}Butyl-3-hydroxy-5-phenylpent-4-ynoate (3)



Butyl lithium (26.1 mL, 2.5 M solution, 65.2 mmol, 1.1 eq) was added dropwise to a solution of diisopropyl amine (9.1 mL, 6.56 g, 65.2 mmol, 1.1 eq) in THF (90 mL) at 0°C. The reaction mixture was stirred for 30 minutes and *t*butyl acetate (9.6 mL, 8.26 g, 71.1 mmol) was added at −78°C. The reaction mixture was stirred one more hour and a solution of 3-phenylpropiolaldehyde (7.62 g, 58.6 mmol) in THF (20 mL) was slowly added. After 30 minutes, the reaction was quenched with a solution of saturated ammonium chloride (25 mL). Most of the organic solvents were evaporated *in vacuo*. The residue was taken up in ethyl acetate (30 mL) and washed with water (30 mL). The aqueous layer was extracted with ethyl acetate (2×15 mL). The organic extracts were combined and dried over magnesium sulfate. Evaporation of the solvent afforded the desired compound in 99% yield (14.42 g, 58.5 mmol) as a yellow oil; Rf (15% EtOAc/petrol) 0.42; ν_{max} (film)/cm^{-1} 1733 (C=O), 2234 (C≡C), 2931 (ArC–H), 2978 (ArC–H) and 3444 (OH); δ_H(400 MHz; $CDCl_3$) 1.49 (9H, s, C*H*$_3$), 2.61 (1H, d, *J* 6.4 Hz, CHC*H*H), 2.76 (1H, d, *J* 5.2 Hz, CH*CH*H), 3.35 (1H, d, *J* 6.4 Hz, O*H*), 4.93 (1H, dt, *J* 5.2, 6.4 Hz, C*H*OH), 7.27-7.34 (3H, m, ArC*H*) and 7.40-7.45 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 29 (3*C*H$_3$), 42.9 (CH*C*H$_2$), 59.5 (*C*H), 81.5 (O*C*(CH$_3$)$_3$), 84.8 (*C*≡C), 88.2 (C≡*C*), 122.4 (Ar*C*), 128.3 (2Ar*C*H), 128.5 (2Ar*C*H) and 131.7 (1Ar*C*H) and 170.8 (*C*=O); HRMS (EI) (M^+), found 247.1339, $C_{15}H_{19}O_3$ requires 247.1334 (+1.9 ppm); *m*/*z* 247 (10%), 191 (29%), 173 (100%), 131 (44%) and 57 (59%).

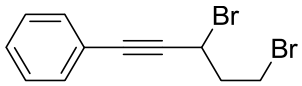
5-Phenylpent-4-yne-1,3-diol (4)



Lithium borohydride (71.0 mL, 142.0 mmol, 2.0 M solution, 2.5 eq) was added over an hour to a solution of *t*butyl-3-hydroxy-5-phenylpent-4-ynoate (14.09 g, 57.2 mmol) in THF (200 mL). Methanol (46.3 mL, 1.1 mol, 20 eq) was then added *via* a syringe pump over an hour at 0°C. The reaction mixture was allowed to stir at room temperature for a further 30 min. Ice cold water (10 mL) was added and the resulting mixture was extracted from ethyl acetate (3×30 mL). The combined organic layers were dried over magnesium sulfate to give the *title compound* in 99% yield (10.04 g, 57.0 mmol) as a yellow oil; Rf (15% EtOAc/petrol) 0.13; ν_{max} (film)/cm^{-1} 1049 (C–O), 2230 (C≡C), 2886 (ArC–H), 2953 (ArC–H) and 3341 (OH); δ_H(400 MHz; $CDCl_3$) 1.92-2.09 (2H,

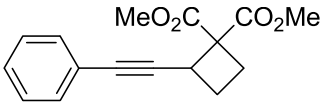
m, CHC*H*$_2$), 2.33 (1H, broad s, OH), 2.99 (1H, broad s, OH), 3.85 (1H, ddd, *J* 4.0, 6.4, 10.8 Hz, C*H*HOH), 4.00 (1H, ddd, *J* 4.0, 7.6, 10.8 Hz, C*H*HOH), 4.81 (1H, dd, *J* 4.4, 6.4 Hz C*H*OH), 7.16-7.29 (3H, ArC*H*) and 7.31-7.42 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 38.9 (CH*C*H$_2$), 60.7 (*C*H$_2$OH), 62.3 (*C*HOH), 85.4 (*C*≡C), 89.2 (C≡*C*), 122.4 (Ar*C*), 128.3 (2Ar*C*H), 128.5 (Ar*C*H) and 131.8 (2Ar*C*H); no mass ion could be observed.

1-(3,5-Dibromopent-1-ynyl)benzene (5)



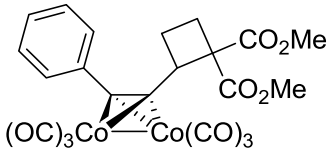
Bromine (5.6 mL, 17.52 g, 114.7 mmol, 2.4 eq) was added dropwise to a solution of triphenylphosphine (31.33 g, 119.5 mmol, 2.5 eq) in DCM (250 mL) at 0°C. The resulting mixture was allowed to stir until the phosphonium salt precipitated (approximately 20 min). A solution of diol **303** (8.42 g, 47.8 mmol) and imidazole (8.13 g, 119.5 mmol, 2.5 eq) in DCM (150 mL) was slowly added *via* a cannula to the phosphonium salt at 0°C and the resulting reaction mixture was allowed to stir overnight at room temperature. The reaction mixture was quenched with ice-cold water (30 mL) and extracted from ethyl acetate (3×15 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated *in vacuo*. Triphenylphosphine oxide and triphenylphosphine were recrystallised thrice from cold petrol using DCM and filtered off. The filtrates were combined and the solvents were removed *in vacuo* affording the *title compound* in 99% (14.41 g, 47.8 mmol) as an orange oil; Rf (petrol) 0.24; ν_{max} (film)/cm^{-1} 755 (C–Br), 689 (C–Br), 2224 (C≡C), 2965 (ArC–H) and 3054 (ArC–H); δ_H(400 MHz; $CDCl_3$) 2.61 (2H, dt, *J* 6.4, 6.8 Hz, CHC*H*$_2$), 3.62 (2H, t, *J* 6.4 Hz, C*H*$_2$Br), 4.97 (1H, t, *J* 6.8 Hz, C*H*Br), 7.24-7.37 (3H, m, ArC*H*) and 7.40-7.47 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 30.0 (CH*C*H$_2$), 35.4 (C*H*Br), 41.9 (C*H*$_2$Br), 86.6 (C≡*C*), 87.7 (*C*≡C), 121.8 (Ar*C*), 128.4 (2Ar*C*H), 129.1 (Ar*C*H) and 131.9 (2Ar*C*H); no mass ion could be observed.

Dimethyl 2-(2-phenylethynyl)cyclobutane-1,1-dicarboxylate (6)



Dimethyl malonate (0.9 mL, 1.08 g, 7.7 mmol, 1.1 eq) was added to a suspension of sodium hydride (620 mg, 15.4 mmol, 60% in mineral oil, 2.2 eq) in THF (140 mL) at 0°C under a nitrogen atmosphere. A solution of 1-(3,5-dibromopent-1-ynyl)benzene (2.11 g, 7.0 mmol) in THF (60 mL) was added *via* a cannula over 5 min and the resulting mixture was allowed to stir at room temperature for 2 hours. The reaction mixture was heated to reflux for 6 hours. Most of the solvent was evaporated *in vacuo* and the residue was taken up in diethyl ether (20 mL). The organic crude solution was washed with water (25 mL), dried over magnesium sulfate and concentrated *in vacuo*. The crude cyclobutane was purified by flash chromatography (5% ethyl acetate/petrol) affording the *title compound* as a yellow oil in 74% yield (1.41 g, 5.2 mmol); Rf (15% EtOAc/petrol) 0.92; ν_{max} (film)/cm^{-1} 1754 (C=O), 1737 (C=O), 2227 (C≡C), 2953 (ArC–H) and 3001 (ArC–H); δ_H(400 MHz; $CDCl_3$) 2.09-2.33 (3H, m, 1H $CHCH_2CHH$ + 2H $CHCH_2CH_2$), 2.73-2.82 (1H, m, $CHCH_2CHH$), 3.71 (3H, s, OCH_3), 3.72 (3H, s, OCH_3), 3.95 (1H, t, *J* 8.8 Hz, C*H*), 7.17-7.24 (3H, m, Ar*CH*) and 7.26-7.41 (2H, m, Ar*CH*); δ_C(100 MHz; $CDCl_3$) 24.4 ($CHCH_2$), 26.1 ($CHCH_2CH_2$), 31.5 (*C*H), 52.7 (CO_2CH_3), 52.8 (CO_2CH_3), 57.7 ($C(CO_2CH_3)_2$), 84.4 (C≡*C*), 88.0 (*C*≡C), 123.1 (Ar*C*), 128.0 (Ar*C*H), 128.2 (2Ar*C*H), 131.6 (2Ar*C*H), 169.6 (*C*=O) and 171.1 (*C*=O); HRMS (EI) (M^+), found 273.1127, $C_{16}H_{16}O_4$ requires 273.1121 (+0.8 ppm); *m*/*z* 273 (24%), 213 (20%), 145 (100%), 141 (37%) and 113 (61%).

Dimethyl 2-(2-phenylethynyl)cyclobutane-1,1-dicarboxylate dicobalt hexacarbonyl (2)



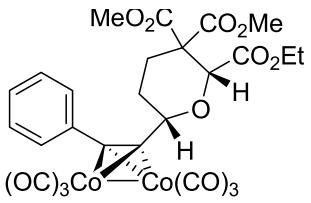
Dicobalt octacarbonyl (1.81 g, 5.3 mmol, 1.2 eq) was added to a solution of dimethyl 2-(2-phenylethynyl)cyclobutane-1,1-dicarboxylate (1.20 g, 4.4 mmol) in DCM (60 mL). The reaction mixture was allowed to stir for 4 hours at room temperature under a nitrogen atmosphere. The solvent was evaporated and the residue was taken up in ethyl acetate (20 mL). The resulting solution was washed with water (25 mL). The aqueous layer was extracted with ethyl acetate (2×10 mL). The combined organic layers were dried over magnesium sulfate, filtered through celite and concentrated *in vacuo*. The crude product was purified by flash chromatography (15 % ethyl acetate/ petrol) affording the desired dicobalt hexacarbonyl complex in 97% yield (2.38 g, 4.3 mmol) as a

dark red oil; Rf (15% ethyl acetate/petrol) 0.83; ν_{max} (film)/cm^{-1} 1731 (C=O), 2018 (C≡O), 2048 (C≡O), 2088 (C≡O) and 2993 (ArC–H); δ_H(400 MHz; $CDCl_3$) 2.15-2.26 (1H, m, $CHCH_2CHH$), 2.35-2.52 (2H, m, $CHCH_2CH_2$), 2.60-2.69 (1H, m, $CHCH_2CHH$), 2.97 (3H, s, OCH_3), 3.65 (3H, s, OCH_3), 4.47 (1H, dd, *J* 9.2, 10.4 Hz, CH_2CH), 7.17-7.28 (3H, m, ArC*H*) and 7.36-7.46 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 26.7 ($CHCH_2$), 28.8 ($CHCH_2CH_2$), 46.5 ($CHCH_2$), 52.3 (CO_2CH_3), 52.6 (CO_2CH_3), 58.6 ($C(CO_2CH_3)_2$), 81.9 (*C*–C), 93.4 (*C*–C), 127.6 (Ar*C*H), 128.6 (2Ar*C*H), 129.7 (2Ar*C*H), 131.8 (Ar*C*), 169.5 (*C*=O), 171.2 (*C*=O) and 199.4 ($CO_{complex}$); HRMS (FAB) (M^+–3CO), found 473.9574, $C_{19}H_{16}Co_2O_7$ requires 473.9560 (+2.6 ppm); *m*/*z* 503 (5%), 475 (4%), 447 (26%), 419 (14%), 391 (21%), 390 (80%), 331 (21%) and 273 (15%).

Typical procedure for cycloaddition reactions (7-21)

Dimethyl 2-(2-phenylethynyl)cyclobutane-1,1-dicarboxylate 6 (70 mg, 0.257 mmol) was dissolved in DCM (5 ml) in a 10 mL oven dried round-bottom flask. Activated 4 Å molecular sieves were added (150 mg). Dicobalt octacarbonyl (100 mg, 0.292, 1.14 eq) was added and the reaction mixture was allowed to stir at room temperature under nitrogen atmosphere for 1.5 hour. The aldehyde (3.0 eq) and scandium triflate (9 mg, 5 mol%) were added successively. The resulting mixture was allowed to stir at room temperature. (Refer to table for reaction times). After complete conversion of the starting material (TLC monitoring) the crude reaction mixture was filtered through a pad of celite and silica and the solvent was evaporated in vacuo. The crude product was purified by flash chromatography on silica gel (5% ethyl acetate/petrol) for all the tetrahydropyrans synthesized.

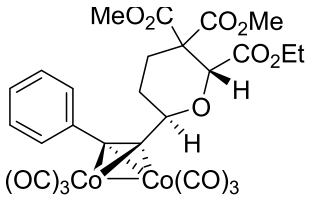
(2R,6S) and (2S,6R)-Dicobalt hexacarbonyl 2-ethyl 3,3-dimethyl dihydro-6-(2-phenylethynyl)-2H-pyran-2,3,3(4H)-tricarboxylate (**7a**) isolated in 34% as a dark red oil.



Rf (15% EtOAc/petrol) 0.34; IR ν_{max} (DCM)/cm^{-1} 1116 (C-O), 1732 (C=O), 2021, 2053, 2091 (C≡$O_{complex}$), 2959 (ArC-H); δ_H(400 MHz; $CDCl_3$) 1.18 (3H, t, *J* 7.2 Hz, OCH_2CH_3), 1.53-1.66 (1H, m, CHC*H*H), 1.98-2.07 (1H, m, CHC*H*H), 2.21-2.31 (1H, m, $CHCH_2CHH$), 2.68 (1H, ddd, *J* 2.8,

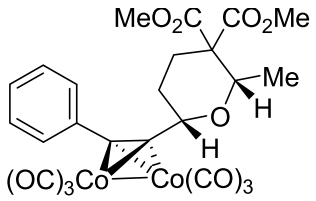
4.0, 13.6 Hz, $CHCH_2CHH$), 4.13-4.23 (2H, m, OCH_2CH_3), 4.63 (1H, s, $OCHCO_2Et$), 4.80 (1H, dd, *J* 2.5, 11.2 Hz, CH_2CHO), 7.18-7.29 (3H, m, ArC*H*) and 7.52-7.58 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 12.9 (OCH_2CH_3), 28.8 ($CHCH_2$), 30.5 ($CHCH_2CH_2$), 51.6 (OCH_3), 52.0 (OCH_3), 56.5 ($C(CO_2CH_3)_2$), 60.2 (OCH_2CH_3), 77.3 (CH_2CHO), 78.0 ($OCHCO_2Et$), 89.3 (Co*C*CCo), 94.1 (CoC*C*Co), 126.8 (Ar*C*H), 127.7 (2Ar*C*H), 128.9 (2Ar*C*H), 136.6 (Ar*C*), 167.4 (CO_2CH_3), 167.7 (CO_2CH_3), 169.4 ($CO_2CH_2CH_3$) and 198.1 ($CO_{complex}$); HRMS (FAB$^+$) (M–3CO), found 575.9890, $C_{23}H_{22}Co_2O_{10}$ requires 575.9877 (+2.2 ppm); *m/z* 548 (100%), 520 (5%) and 492 (92%).

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl 2-ethyl 3,3-dimethyl dihydro-6-(2-phenylethynyl)-2H-pyran-2,3,3(4H)-tricarboxylate (**7b**) isolated in 24% as a dark red oil.



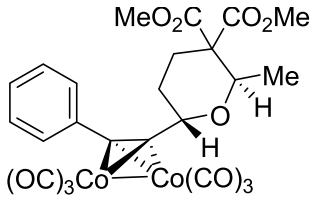
Rf (15% EtOAc/petrol) 0.52; IR ν_{max} (DCM)/cm^{-1} 1069 (C-O), 1737 (C=O), 2021, 2053, 2057 (C≡Ocomplex), and 2991 (ArC-H); δH(400 MHz; CDCl3) 1.23 (3H, t, *J* 7.2 Hz, OCH_2CH_3), 1.50-1.68 (1H, m, CHC*H*H), 1.93-2.06 (1H, m, CHC*H*H), 2.24-2.35 (1H, m, $CHCH_2CHH$), 2.57-2.66 (1H, m, $CHCH_2CHH$), 3.68 (3H, s, OCH_3), 3.72 (3H, s, OCH_3), 4.18 (2H, q, *J* 7.2 Hz, OCH_2CH_3), 4.83 (1H, dd, *J* 2.4, 11.2 Hz, CH_2CHO), 5.42 (1H, s, $OCHCO_2Et$), 7.21-7.30 (3H, m, ArCH) and 7.50-7.56 (2H, m, ArCH); δ_C(100 MHz; $CDCl_3$) 13.0 (OCH_2CH_3), 24.0 ($CHCH_2$), 28.9 ($CHCH_2CH_2$), 51.9 (OCH_3), 52.2 (OCH_3), 54.3 ($C(CO_2CH_3)_2$), 60.6 (OCH_2CH_3), 72.1 (CH_2CHO), 75.3 ($OCHCO_2Et$), 89.0 (CoC*C*Co), 94.9 (Co*C*CCo), 126.8 (Ar*C*H), 127.7 (2Ar*C*H), 128.9 (2Ar*C*H), 136.6 (Ar*C*), 167.3 (CO_2CH_3), 167.6 (CO_2CH_3), 168.6 (CO_2Et) and 198.2 ($CO_{complex}$); HRMS (FAB$^+$) (M–2CO), found 603.9815, $C_{24}H_{22}Co_2O_{11}$ requires 603.9826 (–1.8 ppm); m/z 576 (17%), 548 (100%), 520 (12%) and 492 (52%).

(2S,6R) and (2R,6S)-Dicobalt hexacarbonyl dimethyl dihydro-2-methyl-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (**8a**) isolated in 45% as a dark red crystal.



Rf (15% EtOAc/petrol) 0.76; IR ν_{max} (DCM)/cm^{-1} 1264, (C-O), 1730 (C=O), 2022, 2050, 2090 (C≡O$_{complex}$) and 2953 (ArC-H); δ_H(400 MHz; $CDCl_3$) 1.39 (3H, d, *J* 6.4 Hz, CHC*H*$_3$), 1.91-2.08 (3H, m, 2H CHC*H*$_2$ + 1H CHCH$_2$C*H*H), 2.50-2.58 (1H, m, CHCH$_2$C*H*H), 3.68 (3H, s, CO$_2$C*H*$_3$), 3.70 (3H, s, CO$_2$C*H*$_3$), 4.13 (1H, q, *J* 6.4 Hz, OC*H*CH$_3$), 4.73 (1H, dd, *J* 3.2, 10.0 Hz, CH$_2$C*H*O), 7.21-7.30 (3H, m, ArC*H*) and 7.46-7.51 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 18.2 (CH*C*H$_3$), 29.8 (CH*C*H$_2$), 32.0 (CHCH$_2$*C*H$_2$), 52.0 (CO$_2$*C*H$_3$), 52.6 (CO$_2$*C*H$_3$), 56.7 (*C*(CO$_2$CH$_3$)$_2$), 77.4 (O*C*HCH$_3$), 77.9 (CH$_2$*C*HO), 89.6 (CoC*C*Co), 96.9 (Co*C*CCo), 127.7 (Ar*C*H), 128.7 (2Ar*C*H), 129.8 (2Ar*C*H), 137.8 (Ar*C*), 169.4 (*C*O$_2$CH$_3$), 171.4 (*C*O$_2$CH$_3$) and 199.4 (*C*O$_{complex}$); HRMS (FAB$^+$) (M–2CO), found 545.9782, $C_{22}H_{20}Co_2O_9$ requires 545.9771 (+2.1 ppm); *m/z* 518 (5%), 490 (100%), 462 (5%) and 434 (18%); mp 112-113 °C.

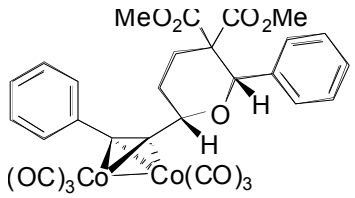
(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-2-methyl-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (**8b**) isolated in 28% as a dark red oil.



Rf (15% EtOAc/petrol) 0.71; IR υ_{max} (DCM)/cm^{-1} 1262, (C-O), 1730 (C=O), 2028, 2050, 2089 (C≡O$_{complex}$) and 2957 (ArC-H); δ_H(400 MHz; $CDCl_3$) 1.29 (3H, d, *J* 6.9 Hz, CHC*H*$_3$), 1.44-1.57 (1H, m, CHC*H*H), 1.92-2.01 (1H, m, CHC*H*H), 2.25-2.35 (1H, m, CHCH$_2$C*H*H), 2.39-2.47 (1H, m, CHCH$_2$C*H*H), 3.66 (3H, s, CO$_2$C*H*$_3$), 3.71 (3H, s, CO$_2$C*H*$_3$), 4.85 (1H, dd, *J* 2.8, 11.2 Hz, CH$_2$C*H*O), 4.97 (1H, q, *J* 6.8 Hz, OC*H*CH$_3$), 7.21-7.30 (3H, m, ArC*H*) and 7.46-7.52 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 14.7 (CH*C*H$_3$), 23.7 (CH*C*H$_2$), 30.2 (CHCH$_2$*C*H$_2$), 52.8 (CO$_2$*C*H$_3$), 52.9 (CO$_2$*C*H$_3$), 57.0 (*C*(CO$_2$CH$_3$)$_2$), 68.6 (CH$_2$C*H*O), 71.2 (O*C*HCH$_3$), 90.0 (CoC*C*Co), 97.8 (Co*C*CCo), 126.9 (Ar*C*H), 128.7 (2Ar*C*H), 129.9 (2Ar*C*H), 137.8 (Ar*C*), 169.5 (*C*O$_2$CH$_3$), 170.0

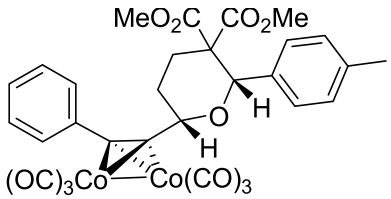
(CO_2CH_3) and 199.4 ($CO_{complex}$); HRMS (FAB$^+$) (M–2CO), found 545.9780, $C_{22}H_{20}Co_2O_9$ requires 545.9771 (+1.7 ppm); *m*/*z* 518 (20%), 490 (100%) and 434 (48%).

(2R,6R) and (2S,6S) Dicobalt hexacarbonyl dimethyl dihydro-2-phenyl-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (**9**) isolated in 34% as a dark red solid.



Rf (15% EtOAc/petrol) 0.68; IR υ_{max} (DCM)/cm^{-1} 1083, 1262 (C-O), 1731, 1736 (C=O), 2020, 2051, 2091 (C≡O$_{complex}$), 2848 and 2913 (ArC-H); δ_H(400 MHz; $CDCl_3$) 2.09-2.18 (2H, m, CHC*H*$_2$), 2.36-2.46 (1H, m, CHCH$_2$C*H*H), 2.72 (1H, dt, *J* 3.6, 13.6 Hz, CHCH$_2$C*H*H), 3.54, (3H, s, CO_2CH_3), 3.69 (3H, s, CO_2CH_3), 4.99-5.05 (1H, m, CH$_2$C*H*O), 5.27 (1H, s, OC*H*Ar), 7.23-7.32 (6H, m, ArC*H*), 7.40-7.45 (2H, m, ArC*H*) and 7.55-7.60 (2H, m, ArCH); δ_C(100 MHz; $CDCl_3$) 30.0 (CH*C*H$_2$), 32.7 (CHCH$_2$*C*H$_2$), 51.7 (CO_2CH_3), 52.6 (CO_2CH_3), 59.1 (*C*(CO$_2$CH$_3$)$_2$), 79.2 (O*C*HAr), 82.8 (CH$_2$*C*HO), 89.9 (CoC*C*Co), 96.0 (Co*C*CCo), 126.0 (2Ar*C*H), 126.4 (2Ar*C*H), 126.5 (Ar*C*H), 126.8 (Ar*C*H), 127.7 (2Ar*C*H), 128.8 (2Ar*C*H), 137.6 (Ar*C*), 138.9 (Ar*C*), 169.0 (CO_2CH_3), 171.2 (CO_2CH_3) and 198.2 ($CO_{complex}$); HRMS (FAB$^+$) *m*/*z* (M–2CO), found 607.9940, $C_{27}H_{22}Co_2O_9$ requires 607.9928 (+2.1 ppm); *m*/*z* 580 (90%), 552 (43%), 524 (100%) and 496 (48%); mp 114-115 °C.

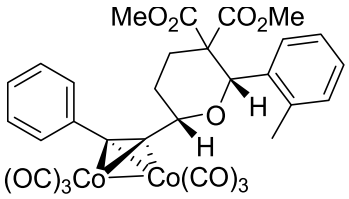
(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-6-(2-phenylethynyl)-2-p-tolyl-2H-pyran-3,3(4H)-dicarboxylate (**10**) isolated in 64% as a dark red cristal.



Rf (15% EtOAc/petrol) 0.75; IR ν_{max} (DCM)/cm^{-1} 1083, 1262 (C-O), 1731, (C=O), 2090, 2051, 2023 (C≡O$_{complex}$) and 2952 (ArCH); δ_H(400 MHz; $CDCl_3$) 2.08-2.18 (2H, m, CHC*H*$_2$), 2.33 (3H, s, ArC*H*$_3$), 2.37-2.49 (1H, m, CHCH$_2$C*H*H), 2.72 (1H, dt, *J* 3.6, 13.2 Hz, CHCH$_2$C*H*H), 3.57 (3H, s,

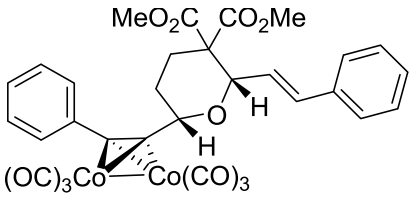
CO_2CH_3), 3.69 (3H, s, CO_2CH_3), 4.94 (1H, dd, *J* 6.0, 8.2 Hz, CH_2CHO), 5.24 (1H, s, OC*H*Ar), 7.27-7.36 (5H, m, ArC*H*), 7.32-7.37 (2H, m, ArC*H*) and 7.56-7.63 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 21.2 (Ar*C*H_3), 30.1 (CH*C*H_2), 32.7 ($CHCH_2CH_2$), 51.7 (CO_2CH_3), 53.3 (CO_2CH_3), 60.4 ($C(CO_2CH_3)_2$), 79.2 (CH_2CHO), 82.9 (O*C*HAr), 89.9 (CoC*C*Co), 96.1 (Co*C*CCo), 127.3 (1Ar*C*H), 127.9 (4Ar*C*H), 128.8 (2Ar*C*H), 129.9 (2Ar*C*H), 136.0 (Ar*C*), 137.0 (Ar*C*), 137.7 (Ar*C*), 169.0 (CO_2CH_3), 171.2 (CO_2CH_3) and 199.3 ($CO_{complex}$); HRMS (FAB$^+$) (M–2CO), found 622.0096, $C_{28}H_{24}Co_2O_9$ requires 622.0084 (+1.9 ppm); *m/z* 594 (100%), 566 (79%), 538 (96%) and 510 (57%); mp 114.1-114.8 °C.

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-6-(2-phenylethynyl)-2-o-tolyl-2H-pyran-3,3(4H)-dicarboxylate, (**11**) isolated in 43% as a dark red oil.



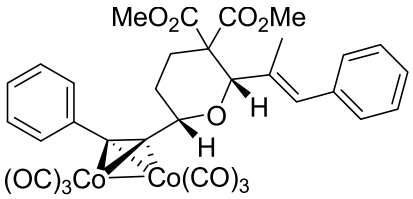
Rf (15% EtOAc/petrol) 0.77; IR ν_{max} (DCM)/cm^{-1} 1261, 1083 (C-O), 1732, (C=O), 2090, 2051, 2022 (C≡$O_{complex}$), 2958 and 3002 (ArC-H); δ_H(400 MHz; $CDCl_3$) 2.01-2.08 (1H, m, CHC*H*H), 2.09-2.21 (1H, m, CHC*H*H), 2.27-2.39 (4H, m, 1H, $CHCH_2CHH$ + ArCH_3), 2.64 (1H, dt, *J* 4.4, 13.6 Hz, $CHCH_2CHH$), 3.49 (3H, s, CO_2CH_3), 3.57 (3H, s, CO_2CH_3), 4.99 (1H, dd, *J* 3.6, 10.4 Hz, CH_2CHO), 5.34 (1H, s, OC*H*Ar), 6.99-7.12 (3H, m, ArC*H*), 7.16-7.24 (4H, m, ArC*H*) and 7.44-7.52 (2H, m, ArCH); δ_C(100 MHz; $CDCl_3$) 20.0 (Ar*C*H_3), 29.7 (CH*C*H_2), 31.9 ($CHCH_2CH_2$), 51.9 (CO_2CH_3), 52.6 (CO_2CH_3), 57.8 ($C(CO_2CH_3)_2$), 78.3 (CH_2CHO), 79.3 (O*C*HAr), 90.1 (CoC*C*Co), 96.3 (Co*C*CCO), 124.8 (Ar*C*H), 127.7 (Ar*C*H), 127.8 (Ar*C*H), 128.7 (2Ar*C*H), 129.0 (Ar*C*H), 129.8 (Ar*C*H), 129.9 (2Ar*C*H), 135.8 (Ar*C*), 136.5 (Ar*C*), 137.7 (Ar*C*), 169.4 (CO_2CH_3), 171.0 (CO_2CH_3) and 199.3 ($CO_{complex}$); HRMS (FAB$^+$) (M–2CO), found 622.0071, $C_{28}H_{24}Co_2O_9$ requires 622.0084 (–2.0 ppm); *m/z* 594 (76%), 566 (72%), 538 (100%) and 510 (65%); mp 114-115 °C.

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-6-(2-phenylethynyl)-2-styryl-2H-pyran-3,3(4H)-dicarboxylate (**12**) isolated in 82% as a dark red oil.



Rf (15% EtOAc/petrol) 0.69; IR ν_{max} (DCM)/cm^{-1} 1084, 1264 (C-O), 1731 (C=O), 2021, 2050, 2088 (C≡O$_{complex}$), 2953 (ArC-H), 3025 and 3058 (=CH); δ_H(400 MHz; $CDCl_3$) 1.97-2.20 (2H, m, CHC*H*$_2$), 2.64-2.55 (2H, m, CHCH$_2$C*H*$_2$), 3.62 (3H, s, CO$_2$C*H*$_3$), 3.66 (3H, s, CO$_2$C*H*$_3$), 4.72 (1H, d, *J* 5.2 Hz, OC*H*CH=CH), 4.84-4.90 (1H, m, CH$_2$C*H*O), 6.49 (1H, dd, *J* 5.2, 16.4 Hz, C*H*=CHPh), 6.60 (1H, d, *J* 16.4 Hz, CH=C*H*Ph), 7.11-7.30 (8H, m, ArC*H*) and 7.48-7.54 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 28.8 (CH*C*H$_2$), 30.7 (CHCH$_2$*C*H$_2$), 51.1 (CO$_2$*C*H$_3$), 51.7 (CO$_2$*C*H$_3$), 56.9 (*C*(CO$_2$CH$_3$)$_2$), 77.2 (CH$_2$*C*HO), 80.3 (O*C*HCH), 88.9 (CoC*C*Co), 95.5 (Co*C*CCo), 125.5 (2Ar*C*H), 125.9 (*C*H=CHPh), 126.4 (Ar*C*H), 126.8 (Ar*C*H), 127.4 (2Ar*C*H), 127.8 (2Ar*C*H), 129.2 (CH=C*H*Ph), 129.8 (2Ar*C*H), 136.2 (Ar*C*), 136.7 (Ar*C*), 168.0 (*C*O$_2$CH$_3$), 170.0 (*C*O$_2$CH$_3$) and 198.3 (*C*O$_{complex}$); HRMS (FAB$^+$) (M–3CO) found 606.0144, $C_{26}H_{24}Co_2O_8$ requires 606.0135 (+1.5 ppm); *m*/*z* 578 (80%), 550 (4%) and 522 (100%).

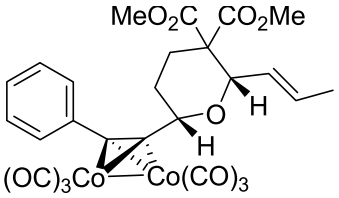
(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-6-(2-phenylethynyl)-2-((E)-1-phenylprop-1-en-2-yl)-2H-pyran-3,3(4H)-dicarboxylate (**13**) isolated in 84% as a dark red oil.



Rf (15% EtOAc/petrol) 0.75; IR ν_{max} (DCM)/cm^{-1} 1075, 1259 (C-O), 1731, 1736 (C=O), 2021, 2050, 2089 (C≡O$_{complex}$), 2952 (ArC-H), 2997, 3027 and 3057 (=CH); δ_H(400 MHz; $CDCl_3$) 1.89 (3H, s, CHCC*H*$_3$), 2.03-2.14 (2H, m, CHC*H*$_2$) , 2.25-2.41 (1H, m, CHCH$_2$C*H*H), 2.66 (1H, dt, *J* 3.6, 13.2 Hz, CHCH$_2$C*H*H), 3.71 (3H, s, CO$_2$C*H*$_3$), 3.74 (3H, s, CO$_2$C*H*$_3$), 4.82 (1H, s, OC*H*C=), 4.94-5.00 (1H, m, CH$_2$C*H*O), 6.66 (1H, s, C=C*H*Ph), 7.16-7.26 (2H, m, ArCH), 7.27-7.38 (6H, m, ArC*H*) and 7.57-7.63 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 15.7 (CHC*C*H$_3$), 29.9 (CH*C*H$_2$), 32.8 (CHCH$_2$*C*H$_2$), 52.0 (CO$_2$*C*H$_3$), 52.6 (CO$_2$*C*H$_3$), 58.4 (*C*(CO$_2$CH$_3$)$_2$), 79.8 (CH$_2$*C*HO), 84.9 (O*C*HCCH$_3$), 90.1 (CoC*C*Co), 96.2 (Co*C*CCo), 126.3 (Ar*C*H), 127.2 (Ar*C*H), 127.9 (=*C*HPh),

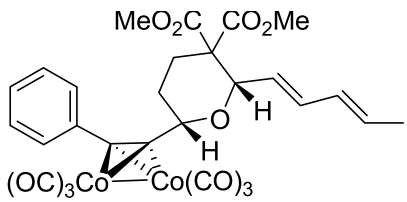
128.0 (2Ar*C*H), 128.8 (2Ar*C*H), 129.1 (2Ar*C*H), 129.9 (2Ar*C*H), 135.9 (CH*C*CH$_3$), 137.7 (Ar*C*), 137.9 (Ar*C*), 169.7 (*C*O$_2$CH$_3$), 171.6 (*C*O$_2$CH$_3$) and 199.3 (*C*O$_{complex}$); HRMS (FAB$^+$) (M–2CO), found 648.0250, $C_{30}H_{26}Co_2O_9$ requires 648.0241 (+1.3 ppm); *m*/*z* 620 (20%), 592 (100%) and 536 (27%).

(2R,6R) and (2S,6S)-Dicolabt octacarbonyl dimethyl dihydro-6-(2-phenylethynyl)-2-((E)-prop-1-enyl)-2H-pyran-3,3(4H)-dicarboxylate (**14**) isolated in 82% as a dark red oil.



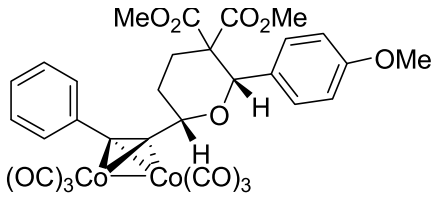
Rf (15% EtOAc/petrol) 0.77; IR ν_{max} (DCM)/cm^{-1} 1082, 1266 (C-O), 1726, 1731 (C=O), 2021, 2051, 2090 (C≡O$_{complex}$), 2954 (ArC-H) and 3058 (=CH); δ_H(400 MHz; $CDCl_3$) 1.62 (3H, d, *J* 6.4 Hz, CHC*H*$_3$), 1.79-2.02 (2H, m, CHC*H*$_2$), 2.13 (1H, dt, *J* 4.8, 13.2 Hz, CHCH$_2$C*H*H), 2.55 (1H, ddd *J* 2.8, 4.0, 13.2 Hz, CHCH$_2$C*H*H), 3.64 (3H, s, CO$_2$C*H*$_3$), 3.67 (3H, s, CO$_2$C*H*$_3$), 4.41 (1H, d, *J* 6.4 Hz, OC*H*CH), 4.78 (1H, dd, *J* 3.2, 11.2 Hz, CH$_2$C*H*O), 5.64 (1H, ddd, *J* 0.8, 6.4, 15.2 Hz, CH=C*H*CH$_3$), 5.83 (1H, ddd, *J* 1.6, 6.4, 15.2 Hz, C*H*=CHCH$_3$), 7.19-7.29 (3H, m, ArC*H*) and 7.46-7.53 (2H, m, ArCH); δ_C(100 MHz; $CDCl_3$) 16.9 (CH*C*H$_3$), 28.8 (CH*C*H$_2$), 30.8 (CHCH$_2$*C*H$_2$), 51.0 (CO$_2$*C*H$_3$), 51.8 (CO$_2$*C*H$_3$), 57.2 (*C*(CO$_2$CH$_3$)$_2$), 77.0 (CH$_2$*C*HO), 81.3 (O*C*HCH), 88.9 (CoC*C*Co), 95.5 (Co*C*CCo), 126.7 (Ar*C*H), 126.9 (CH=*C*HCH$_3$), 127.3 (*C*H=CHCH$_3$), 127.7 (2Ar*C*H), 128.9 (2Ar*C*H), 136.8 (Ar*C*), 168.2 (*C*O$_2$CH$_3$), 170.0 (*C*O$_2$CH$_3$) and 198.3 (*C*O$_{Complex}$); HRMS (FAB$^+$) (M–2CO) found 571.9915, $C_{26}H_{24}Co_2O_8$ requires 571.99278 (–1.4 ppm); *m*/*z* 629 (4%), 572 (19%), 545 (14%), 517 (65%), 516 (100%), 488 (15%) and 460 (30%).

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-2-((1E,3E)-penta-1,3-dienyl)-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (**15**) isolated in 51% as a dark red oil.



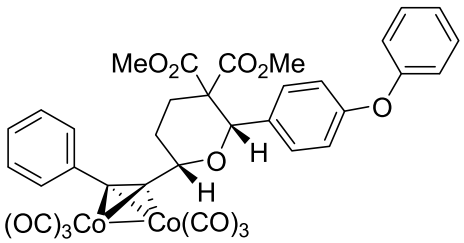
Rf (15% EtOAc/petrol) 0.78; IR ν_{max} (DCM)/cm^{-1} 1083, 1262 (C-O), 1731 (C=O), 2020, 2089 (C≡O$_{complex}$), 2953 (ArC-H), 3019 and 3057 (=CH); δ_H(400 MHz; $CDCl_3$) 1.75 (3H, d, *J* 6.8 Hz, C*H*$_3$), 1.98-2.10 (2H, m, CHC*H*$_2$), 2.19 (1H, dt, *J* 5.2, 13.2 Hz, CHCH$_2$C*H*H), 2.63 (1H, ddd, *J* 2.8, 4.0, 13.2 Hz, CHCH$_2$C*H*H), 3.72 (6H, s, OC*H*$_3$), 4.59 (1H, d, *J* 6.0 Hz, OC*H*CH), 4.87 (1H, dd, *J* 4.0, 10.8 Hz, CH$_2$C*H*O), 5.62 (1H, dd, *J* 6.8, 14.9 Hz, CH$_3$C*H*=CH), 5.92 (1H, dd, *J* 6.0, 15.6 Hz, OCHC*H*), 6.03-6.14 (1H, m, CH$_3$CH=C*H*), 6.24 (1H, dd, *J* 10.4, 15.6 Hz, CH$_3$CH=CHC*H*), 7.27-7.36 (3H, m, ArC*H*) and 7.52-7.59 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 18.2 (CH*C*H$_3$), 29.8 (CH*C*H$_2$), 31.7 (CHCH$_2$*C*H$_2$), 52.1 (CO_2CH_3), 52.6 (CO_2CH_3), 58.1 (*C*(CO$_2$CH$_3$)$_2$), 78.2 (CH$_2$*C*HO), 81.7 (O*C*HCH), 89.9 (CoC*C*Co), 96.5 (Co*C*CCo), 127.4 (OCH*C*H), 127.8 (Ar*C*H), 128.8 (2Ar*C*H), 129.7 (CH$_3$*C*H), 129.8 (2Ar*C*H), 131.2 (CH$_3$CH=C*H*), 131.5 (CH$_3$CH=CH*C*H), 137.8 (Ar*C*), 169.1 (*C*O$_2$CH$_3$), 180.0 (*C*O$_2$CH$_3$) and 199.4 (*C*O$_{complex}$); HRMS (FAB$^+$) (M–2CO), found 598.0071, $C_{26}H_{24}Co_2O_9$ requires 598.0084 (–2.1 ppm); *m*/*z* 570 (37%), 542 (100%), 514 (11%) and 486 (89%).

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-2-(4-methoxyphenyl)-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (**16**) isolated in 85% as a dark red oil.



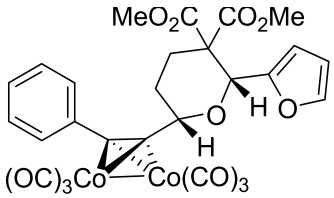
Rf (15% EtOAc/petrol) 0.61; IR ν_{max} (DCM)/cm^{-1} 1085, 1251 (C-O), 1731, 1736 (C=O), 2021, 2090 (C≡O$_{complex}$) and 2954 (ArC-H); δ_H(400 MHz; $CDCl_3$) 2.01-2.11 (2H, m, CHC*H*$_2$), 2.28-2.38 (1H, m, CHCH$_2$C*H*H), 2.64 (1H, dt, *J* 3.2, 13.2 Hz, CHCH$_2$C*H*H), 3.49 (3H, s, CO_2CH_3), 3.61 (3H, s, CO_2CH_3), 3.72 (3H, s, ArOC*H*$_3$), 4.91-4.97 (1H, m, CH$_2$C*H*O), 5.14 (1H, s, OC*H*Ar), 6.70-6.75 (2H, m, ArC*H*), 7.17-7.25 (3H, m, ArC*H*), 7.26-7.31 (2H, m, ArC*H*) and 7.48-7.53 (2H, m, ArCH); δ_C(100 MHz; $CDCl_3$) 29.0 (CH*C*H$_2$), 31.6 (CHCH$_2$*C*H$_2$), 50.7 (CO_2CH_3), 51.5 (CO_2CH_3), 54.0 (ArO*C*H$_3$), 58.0 (*C*(CO$_2$CH$_3$)$_2$), 78.2 (O*C*HAr), 81.6 (CH$_2$*C*HO), 88.9 (CoC*C*Co), 95.1 (Co*C*CCo), 111.4 (2Ar*C*H), 126.7 (Ar*C*H), 127.6 (2Ar*C*H), 127.8 (2Ar*C*H), 128.8 (2Ar*C*H), 130.1 (Ar*C*), 136.6 (Ar*C*), 157.8 (Ar*C*), 168.0 (*C*O$_2$CH$_3$), 170.2 (*C*O$_2$CH$_3$) and 198.4 (*C*O$_{complex}$); HRMS (FAB$^+$) (M –2CO), found 638.0047, $C_{28}H_{24}Co_2O_{10}$ requires 638.0033 (+2.2 ppm); *m*/*z* 610 (77%), 582 (75%), 554 (100%) and 526 (26%).

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-2-(4-phenoxyphenyl)-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (**17**) isolated in 65% as a dark red oil.



Rf (15% EtOAc/petrol) 0.66; IR ν_{max} (DCM)/cm^{-1} 1072, 1240, 1263 (C-O), 1730 (C=O), 2021, 2050, 2089 (C≡O$_{complex}$), 2952 and 3059 (ArC-H); δ_H(400 MHz; $CDCl_3$) 2.09-2.21 (2H, m, CHC*H*$_2$), 2.33-2.45 (1H, m, CHCH$_2$C*H*H), 2.72 (1H, dt, *J* 3.2, 13.6 Hz, CHCH$_2$C*H*H), 3.57, (3H, s, CO$_2$C*H*$_3$), 3.70 (3H, s, CO$_2$C*H*$_3$), 4.94 (1H, dd, *J* 4.0, 10.0 Hz, CH$_2$C*H*O), 5.18 (1H, s, OC*H*Ar), 6.79-6.86 (2H, ArCH), 6.90-6.96 (2H, ArC*H*), 6.97-7.06 (1H, m, ArC*H*), 7.18-7.36 (7H, m, ArC*H*) and 7.47-7.54 (2H, m, ArCH); δ_C(100 MHz; $CDCl_3$) 30 (CH*C*H$_2$), 32.7 (CHCH$_2$*C*H$_2$), 51.7 (CO$_2$*C*H$_3$), 52.6 (CO$_2$*C*H$_3$), 59.0 (*C*(CO$_2$CH$_3$)$_2$), 72.3 (O*C*HAr), 82.5 (CH$_2$*C*HO), 90.0 (CoC*C*Co), 96.0 (Co*C*CCo), 117.3 (2Ar*C*H), 119.1 (2Ar*C*H), 123.2 (Ar*C*H), 127.9 (Ar*C*H), 128.8 (2ArCH), 128.9 (2Ar*C*H), 129.7 (2Ar*C*H), 129.9 (2Ar*C*H), 133.8 (Ar*C*), 137.7 (Ar*C*), 156.6 (Ar*C*), 157.2 (Ar*C*), 168.9 (*C*O$_2$CH$_3$), 171.2 (*C*O$_2$CH$_3$) and 199.4 (*C*O$_{complex}$); HRMS (FAB) (M^+−3CO), found 672.0253, $C_{32}H_{26}Co_2O_9$ requires 672.0241 (+1.8 ppm); *m*/*z* 672 (21%), 644 (11%), 616 (3%) and 588 (100%).

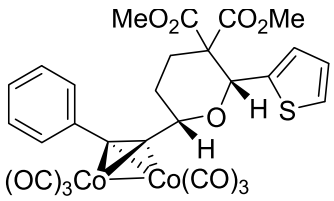
(2R,6S) and (2S,6R)-Dicobalt hexacarbonyl dimethyl 2-(furan-2-yl)-dihydro-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (**18**) isolated in 95% as a dark red crystal.



Rf (15% EtOAc/petrol) 0.62; IR ν_{max} (DCM)/cm^{-1} 1080, 1263 (C-O), 1734 (C=O), 2022, 2052, 2091 (C≡O$_{complex}$) and 2953 (ArCH); δ_H(400 MHz; $CDCl_3$) 1.94-2.06 (1H, m, CHC*H*H), 2.07-2.17

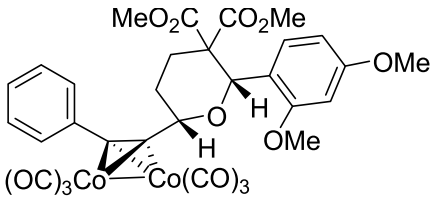
(1H, m, CHC*H*H), 2.34 (1H, dt, *J* 4.4, 13.2 Hz, $CHCH_2CHH$), 2.73 (1H, ddd, *J* 2.8, 4.0, 13.2 Hz, $CHCH_2CHH$), 3.59 (3H, s, CO_2CH_3), 3.80 (3H, s, CO_2CH_3), 5.03 (1H, dd, *J* 2.8, 11.2 Hz, CH_2CHO), 5.34 (1H, s, OC*H*Ar), 6.33 (2H, d, *J* 1.2 Hz, ArC*H*), 7.27-7.36 (4H, m, ArC*H*) and 7.55-7.60 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 29.9 ($CHCH_2$), 31.8 ($CHCH_2CH_2$), 52.1 (CO_2CH_3), 52.9 (CO_2CH_3), 57.6 ($C(CO_2CH_3)_2$), 78.0 (OCHAr), 78.9 (CH_2CHO), 89.9 (CoCCCo), 95.6 (CoCCCo), 106.5 (ArCH), 110.3 (ArCH), 127.9 (ArCH), 128.8 (2ArCH), 129.8 (2ArCH), 137.7 (ArC), 140.9 (ArCH), 152.2 (ArC), 168.5 (CO_2CH_3), 170.8 (CO_2CH_3) and 199.3 ($CO_{complex}$); HRMS (FAB$^+$) (M–2CO), found 597.9734, $C_{25}H_{20}Co_2O_{10}$ requires 597.9720 (+2.2 ppm); *m/z* 570 (22%), 540 (100%) and 486 (42%); mp 119-120.

(2R,6S) and (2S,6R)-Dicobalt hexacarbonyl dimethyl dihydro-6-(2-phenylethynyl)-2-(thiophen-2-yl)-2H-pyran-3,3(4H)-dicarboxylate (**19**) isolated in 89% as a dark red solid.



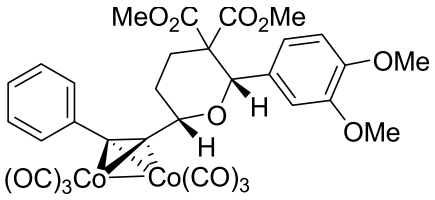
Rf (15% EtOAc/petrol) 0.66; IR ν_{max} (DCM)/cm^{-1} 1077, 1265 (C-O), 1728 (C=O), 2024, 2052, 2091 (C≡O$_{complex}$) and 2952 (ArC-H); δ_H(400 MHz; $CDCl_3$) 1.98-2.19 (2H, m, $CHCH_2$), 2.20-2.32 (1H, dt, *J* 4.0, 12.8 Hz, $CHCH_2CHH$), 2.60-2.70 (1H, broad d, *J* 12.8 Hz, $CHCH_2CHH$), 3.49 (3H, s, CO_2CH_3), 3.70 (3H, s, CO_2CH_3), 4.96 (1H, broad d, *J* 9.8 Hz, CH_2CHO), 5.50 (1H, s, OC*H*Ar), 6.83-6.98 (2H, m, ArC*H*), 7.12-7.31 (4H, m, ArC*H*) and 7.47-7.57 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 29.9 ($CHCH_2$), 32.3 ($CHCH_2CH_2$), 52.0 (CO_2CH_3), 52.7 (CO_2CH_3), 59.2 ($C(CO_2CH_3)_2$), 79.4 (OCHAr), 79.8 (CH_2CHO), 90.2 (CoCCCo), 95.5 (CoCCCo), 124.6 (ArCH), 124.8 (ArCH), 125.8 (ArCH), 127.9 (ArCH), 128.8 (2ArCH), 129.9 (2ArCH), 137.6 (ArC), 142.0 (ArC), 168.6 (CO_2CH_3), 171.1 (CO_2CH_3) and 199.3 ($CO_{complex}$); HRMS (FAB$^+$) (M–2CO), found 613.9482, $C_{25}H_{20}Co_2O_9S$ requires 613.9492 (–1.6 ppm); *m/z* 614 (5%), 586 (77%), 558 (100%), 530 (9%), 502 (27%); mp 122-123.

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-2-(2,4-dimethoxyphenyl)-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (**20**) islolated in 92% as a dark red oil.



Rf (15% EtOAc/petrol) 0.30; IR ν_{max} (DCM)/cm^{-1} 1045, 1085, 1158, 1208, 1255 (C-O), 1732, 1736 (C=O), 2019, 2050, 2089 (C≡O$_{complex}$), 2952 and 3000 (ArC-H); δ_H(400 MHz; $CDCl_3$) 1.58-1.71 (1H, m, CHC*H*H), 2.01-2.12 (1H, m, CHC*H*H), 2.52-2.68 (2H, m, $CHCH_2C\mathit{H}_2$), 3.48 (3H, s, $OC\mathit{H}_3$), 3.58 (3H, s, $OC\mathit{H}_3$), 3.67 (3H, s, $OC\mathit{H}_3$), 3.73 (3H, s, $OC\mathit{H}_3$), 4.88 (1H, dd, *J* 2.6, 11.2 Hz, $CH_2C\mathit{H}O$), 5.13 (1H, s, OC*H*Ar), 6.27 (1H, d, *J* 2.4 Hz, ArCH), 6.42 (1H, dd, *J* 2.0, 8.4 Hz, ArC*H*), 7.20-7.28 (3H, m, ArC*H*), 7.51-7.57 (2H, m, ArC*H*) and 7.72 (1H, d, *J* 8.4 Hz, ArC*H*); δ_C(100 MHz; $CDCl_3$) 29.6 ($CH\mathit{C}H_2$), 30.9 ($CHCH_2\mathit{C}H_2$), 50.9 ($OC\mathit{H}_3$), 51.2 ($OC\mathit{H}_3$), 54.0 ($CO_2\mathit{C}H_3$), 54.2 ($CO_2\mathit{C}H_3$), 57.3 ($\mathit{C}(CO_2CH_3)_2$), 76.4 ($CH_2\mathit{C}HO$), 78.5 (O*C*HAr), 89.0 (CoC*C*Co), 95.0 (Co*C*CCo), 95.4 (Ar*C*H), 102.3 (Ar*C*H), 118.3 (Ar*C*), 126.7 (Ar*C*H), 127.7 (2Ar*C*H), 128.9 (2Ar*C*H), 130.5 (Ar*C*H), 136.7 (Ar*C*), 155.7 (ArOMe), 159.0 (ArOMe), 168.3 ($\mathit{C}O_2CH_3$), 168.6 ($\mathit{C}O_2CH_3$) and 198.4 ($\mathit{C}O_{complex}$); HRMS (FAB$^+$) (M–3CO), found 640.0177, $C_{28}H_{26}Co_2O_{10}$ requires 640.0189 (–2.0 ppm); *m*/*z* 612(100%), 584 (13%) and 556 (12%).

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-2-(3,4-dimethoxyphenyl)-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (**21**) isolated in 92% as a dark red oil.

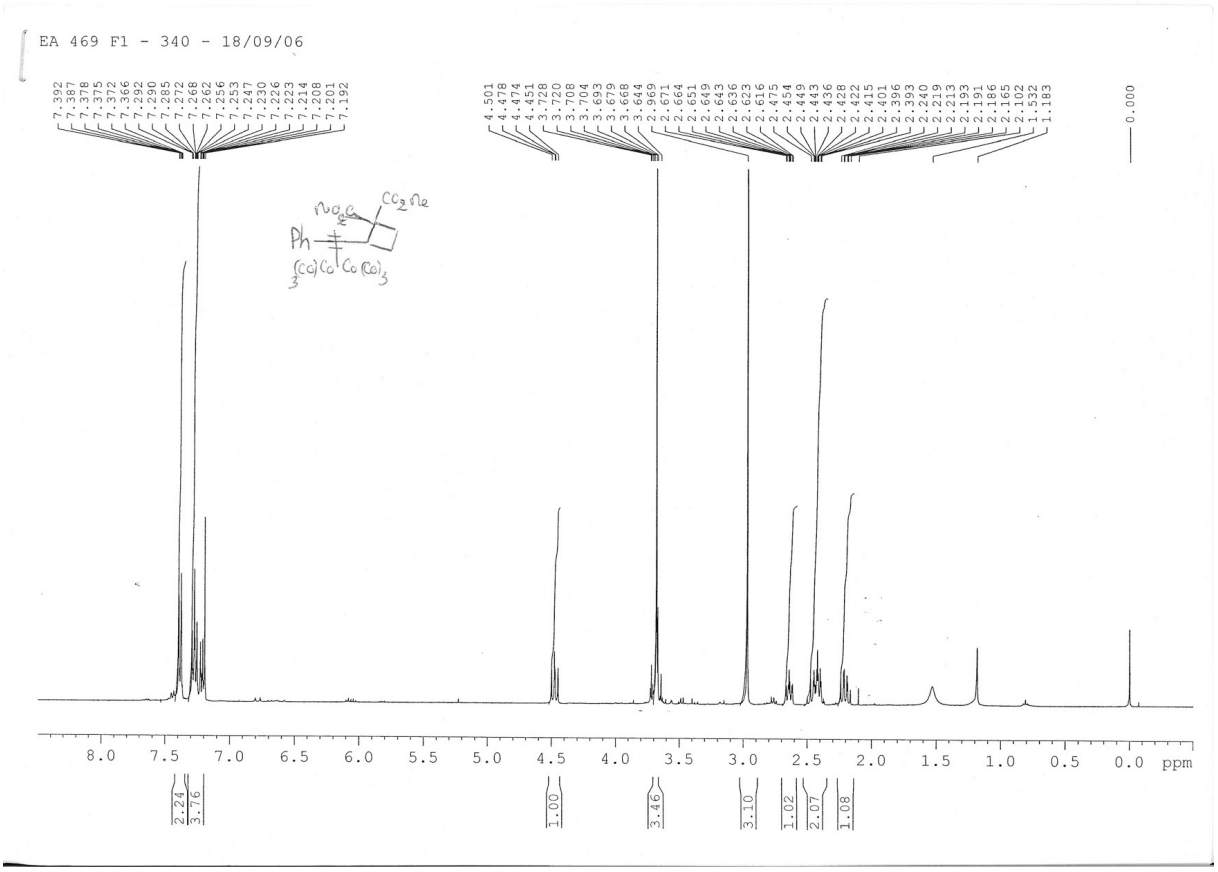


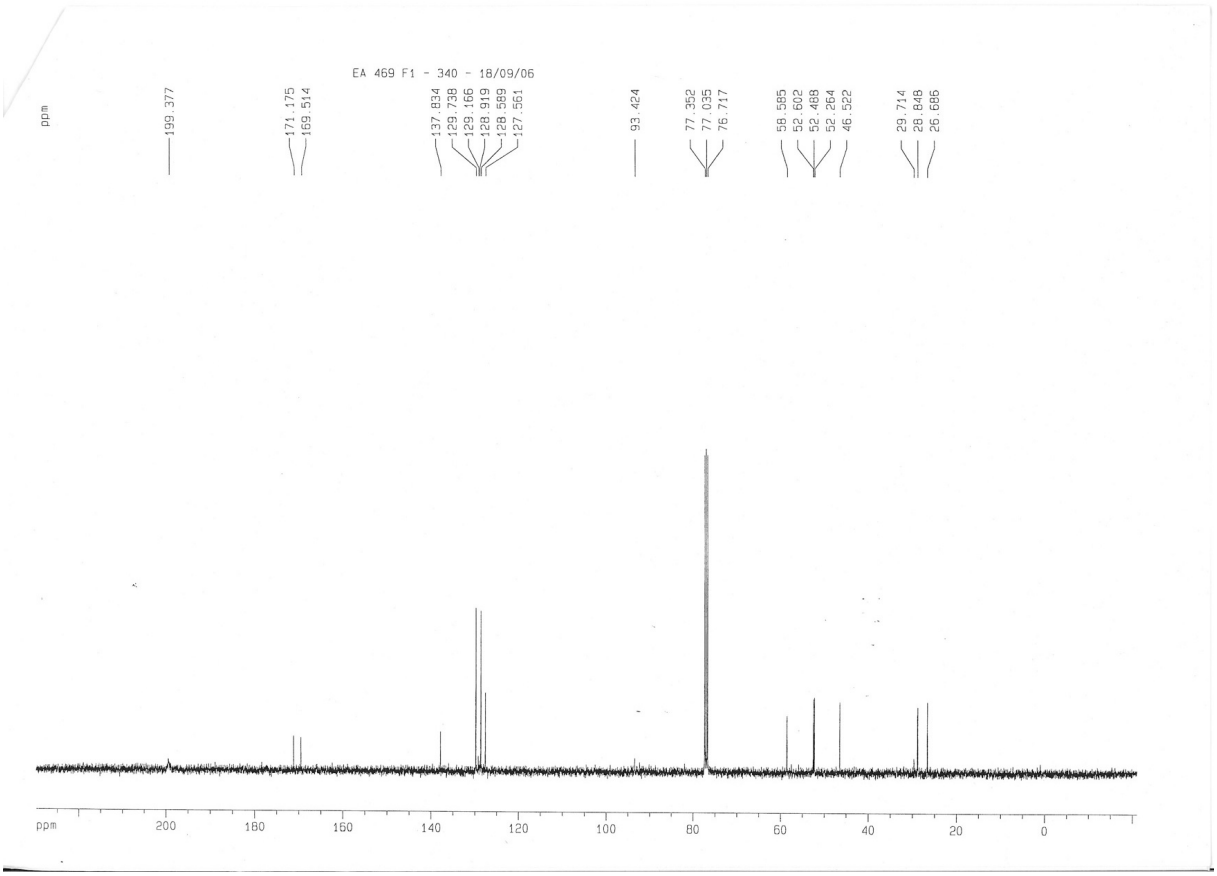
Rf (15% EtOAc/petrol) 0.19; IR ν_{max} (DCM)/cm^{-1} 1029, 1074, 1234, 1264 (C-O), 1731 (C=O), 2022, 2050, 2090 (C≡O), 2953, 3002 and 3075 (ArC-H); δ_H(400 MHz; $CDCl_3$) 2.03-2.11 (2H, m, $CHC\mathit{H}_2$), 2.28-2.37 (1H, m, $CHCH_2C\mathit{H}H$), 2.64 (1H, dd, *J* 3.2, 13.2 Hz, $CHCH_2C\mathit{H}H$), 3.49 (3H, s, $OC\mathit{H}_3$), 3.62 (3H, s, $OC\mathit{H}_3$), 3.66 (3H, s, $OC\mathit{H}_3$), 3.80 (3H, s, $OC\mathit{H}_3$), 4.95 (1H, dd, *J* 6.0, 8.0 Hz, $CH_2C\mathit{H}O$), 5.17 (1H, s, OC*H*Ar), 6.68 (1H, d, *J* 8.4 Hz, ArCH), 6.83 (1H, dd, *J* 2.0, 8.4 Hz, ArC*H*), 7.03 (1H, d, *J* 2.0 Hz, ArC*H*), 7.19-7.27 (3H, m, ArC*H*) and 7.48-7.55 (2H, m, ArC*H*); δ_C(100 MHz; $CDCl_3$) 29.0 ($CH\mathit{C}H_2$), 37.7 ($CHCH_2\mathit{C}H_2$), 50.7 ($CO_2\mathit{C}H_3$), 51.6 ($CO_2\mathit{C}H_3$), 54.4 ($ArO\mathit{C}H_3$),

54.6 (ArO*C*H_3), 58.2 (*C*(CO_2CH_3)$_2$), 78.3 (O*C*HAr), 81.6 (CH_2*C*HO), 89.0 (Co*C*Co), 95.1 (Co*C*Co), 108.4 (Ar*C*H), 109.3 (Ar*C*H), 118.4 (Ar*C*H), 126.9 (Ar*C*H), 127.8 (2Ar*C*H), 128.7 (2Ar*C*H), 130.5 (Ar*C*), 136.6 (Ar*C*), 146.8 (Ar*C*OMe), 147.1 (Ar*C*OMe), 168.1 (*C*O_2CH_3), 170.2 (*C*O_2CH_3) and 198.2 (*C*$O_{complex}$); HRMS (FAB$^+$) (M–3CO), found 640.0178, $C_{28}H_{26}Co_2O_{10}$ requires 640.0189 (–1.8 ppm); *m*/*z*, 612(43%), 584 (100%) and 556 (60%).

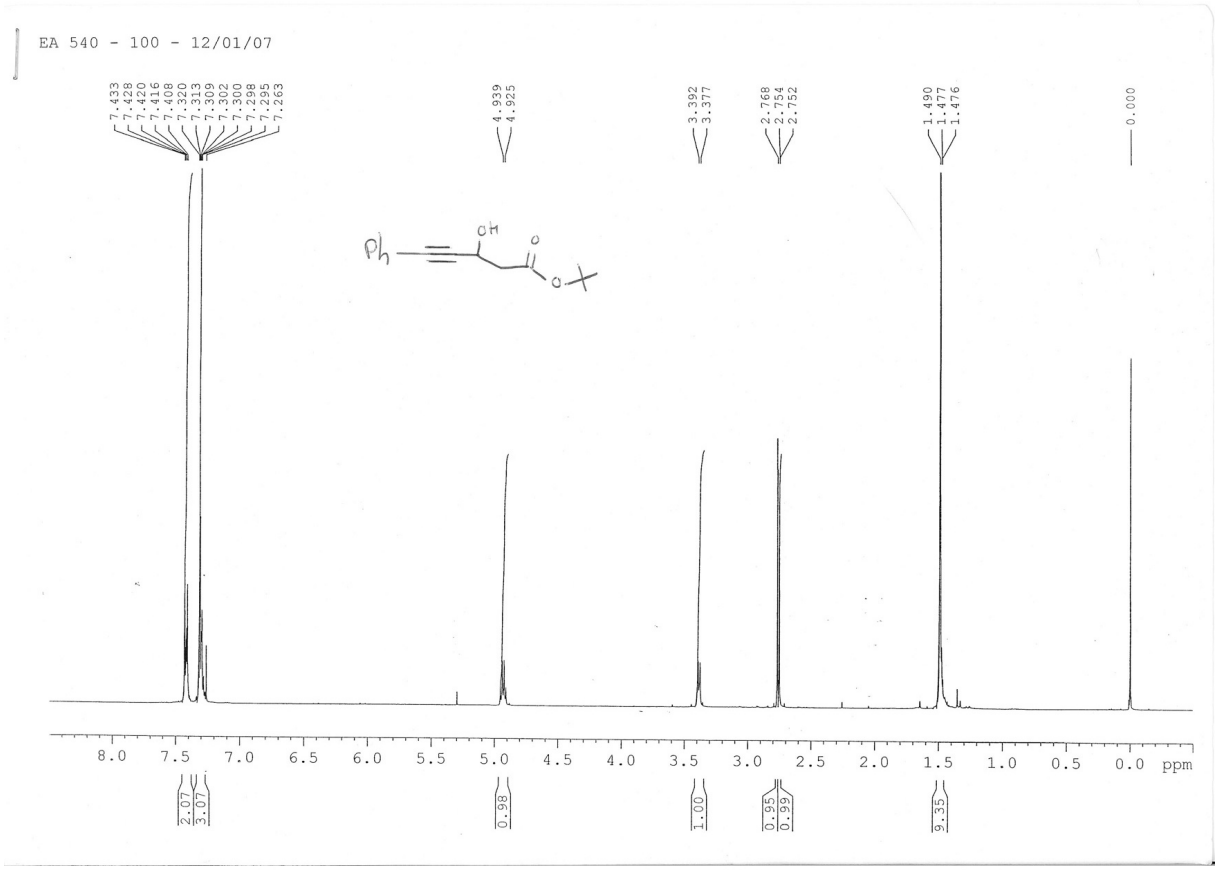
Proton and Carbon Spectra Section

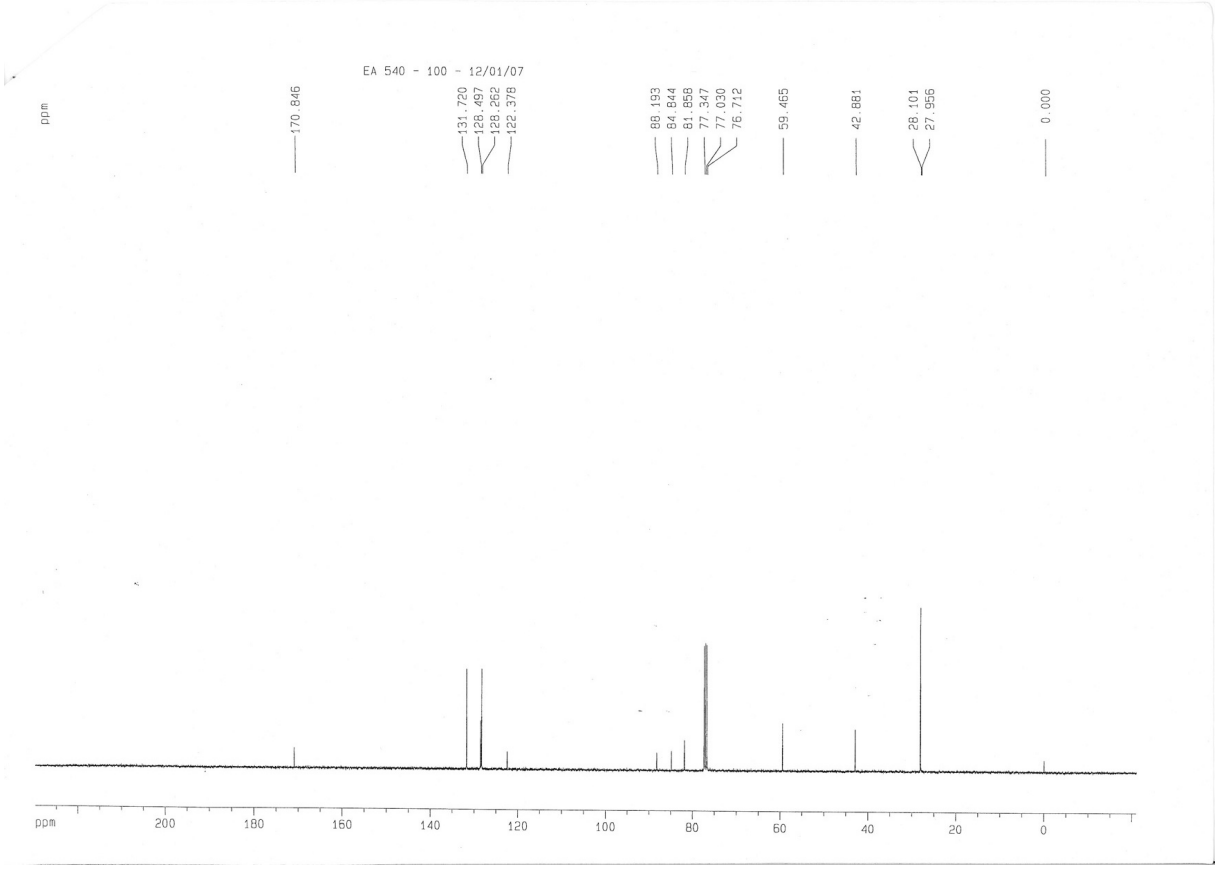
Compound 2



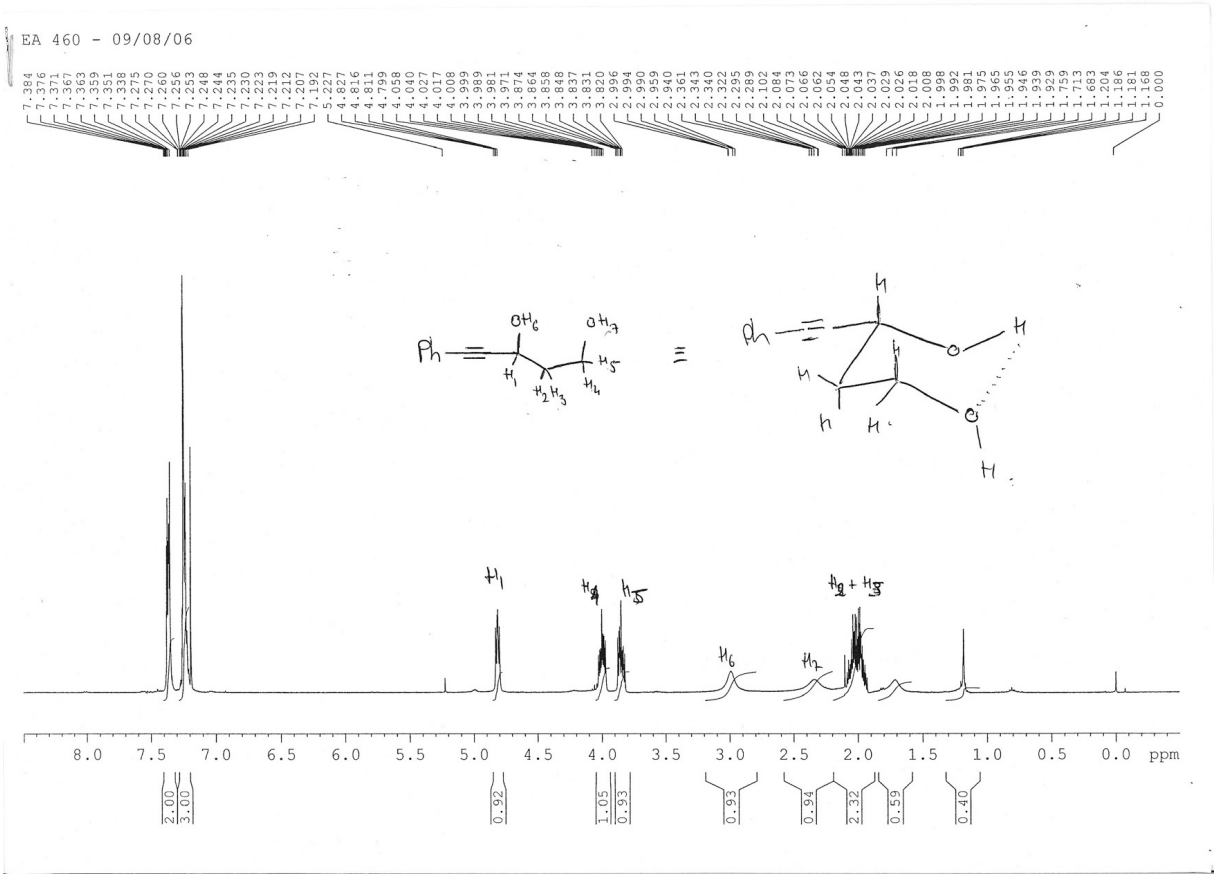


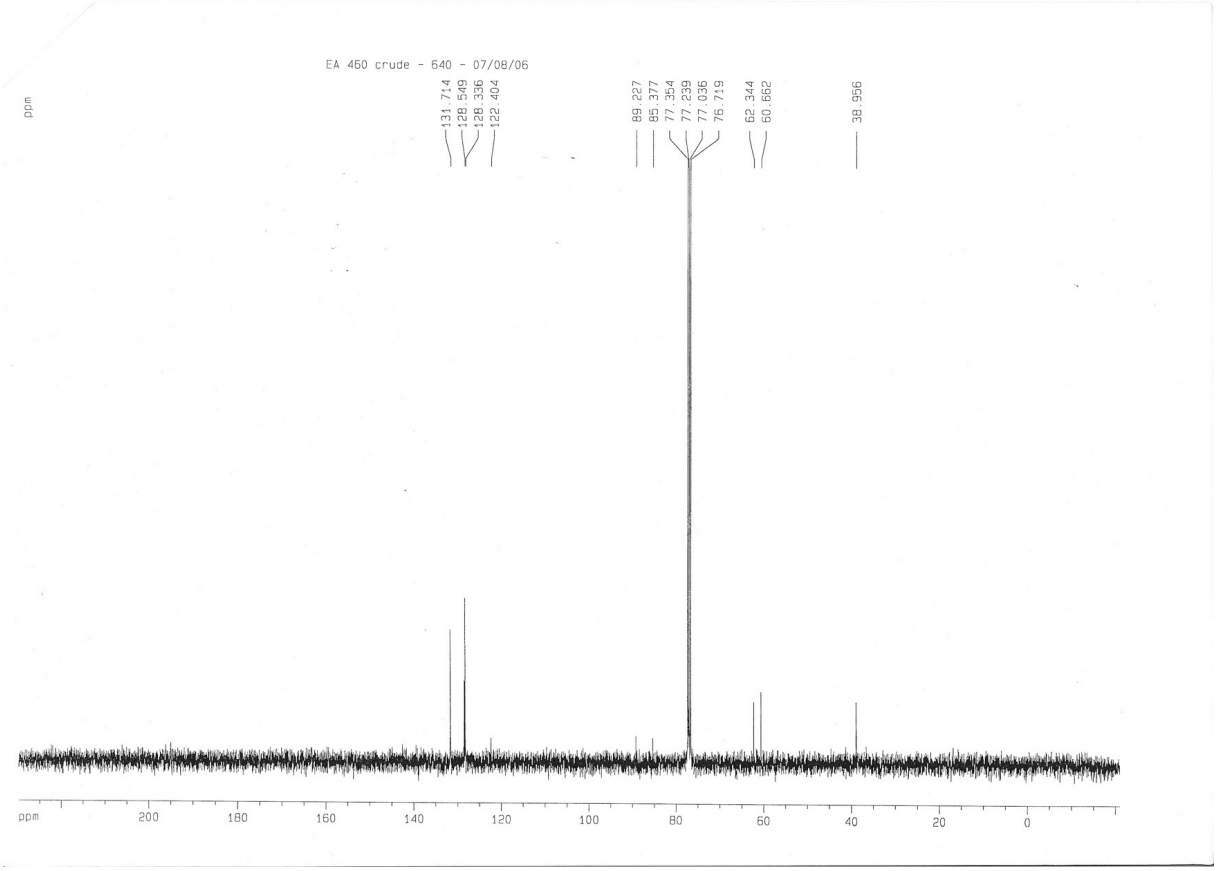
Compound 3


EA 540 - 100 - 12/01/07
7.433
7.428
7.420
7.416
7.408
7.320
7.313
7.309
7.302
7.300
7.298
7.295
7.263
4.939
4.925
3.392
3.377
2.768
2.754
2.752
1.490
1.477
1.476
0.000
Ph
OH
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.07
3.07
0.98
1.00
0.95
0.99
9.35

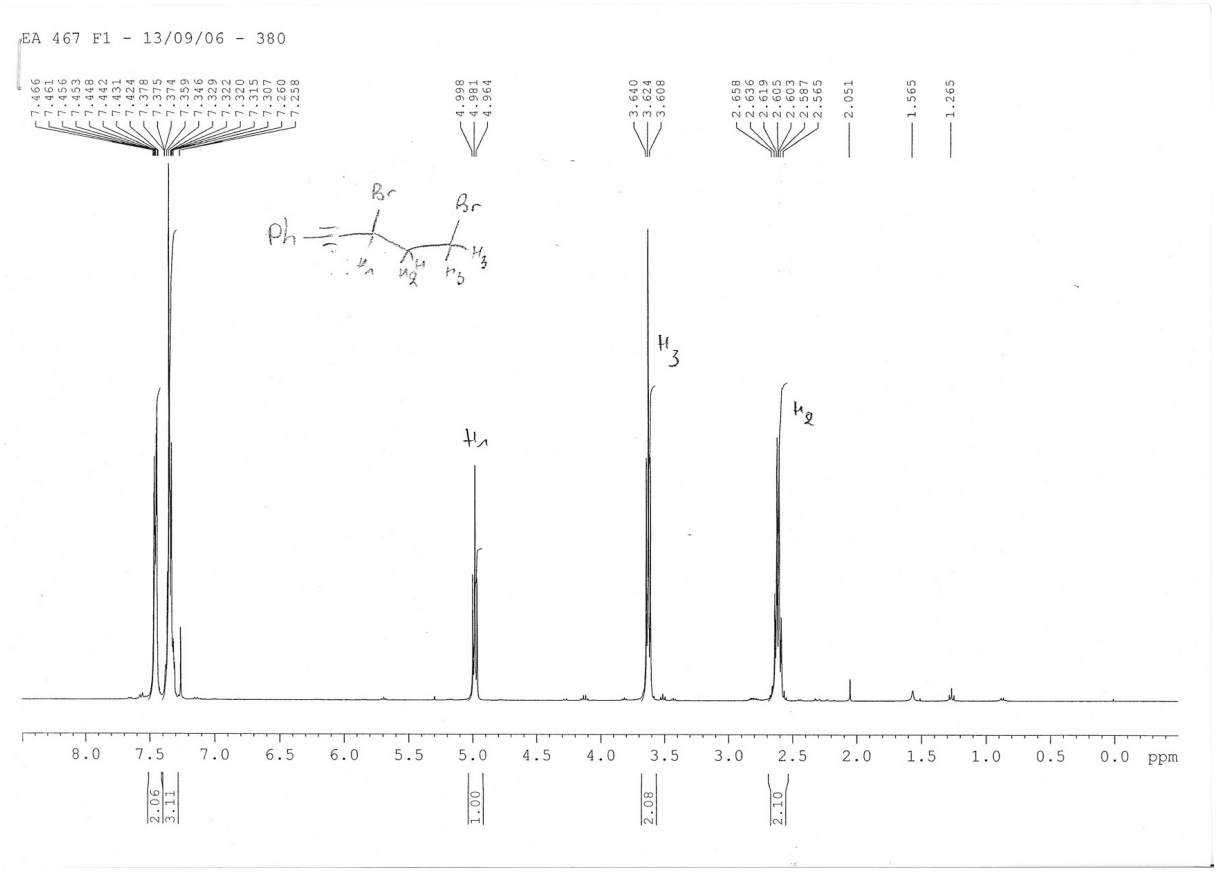

EA 540 - 100 - 12/01/07
ppm
170.846
131.720
128.497
128.262
122.378
88.193
84.844
81.858
77.347
77.030
76.712
59.465
42.881
28.101
27.956
0.000
ppm
200
180
160
140
120
100
80
60
40
20
0

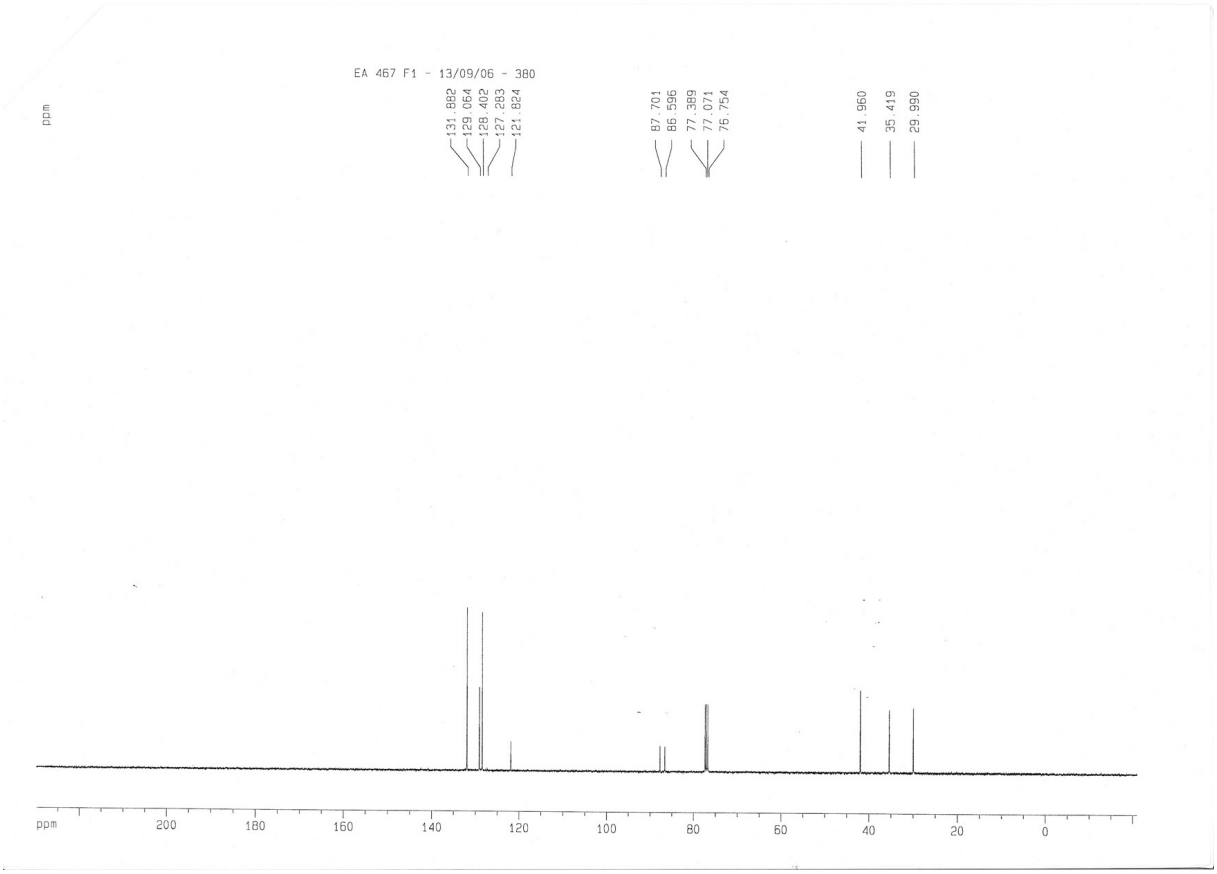
Compound 4


EA 460 - 09/08/06
7.384 7.376 7.371 7.367 7.363 7.359 7.351 7.338 7.275 7.270 7.260 7.256 7.253 7.248 7.244 7.235 7.230 7.223 7.219 7.212 7.207 7.192 5.227 4.827 4.816 4.811 4.799 4.058 4.040 4.027 4.017 4.008 3.999 3.989 3.981 3.971 3.874 3.864 3.858 3.848 3.837 3.831 3.820 2.996 2.994 2.990 2.959 2.940 2.361 2.343 2.340 2.322 2.295 2.289 2.102 2.084 2.073 2.066 2.062 2.054 2.048 2.043 2.037 2.029 2.026 2.018 2.008 1.998 1.992 1.981 1.975 1.965 1.955 1.946 1.939 1.929 1.759 1.713 1.683 1.204 1.186 1.181 1.168 0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00 3.00 0.92 1.05 0.93 0.93 0.94 2.32 0.59 0.40

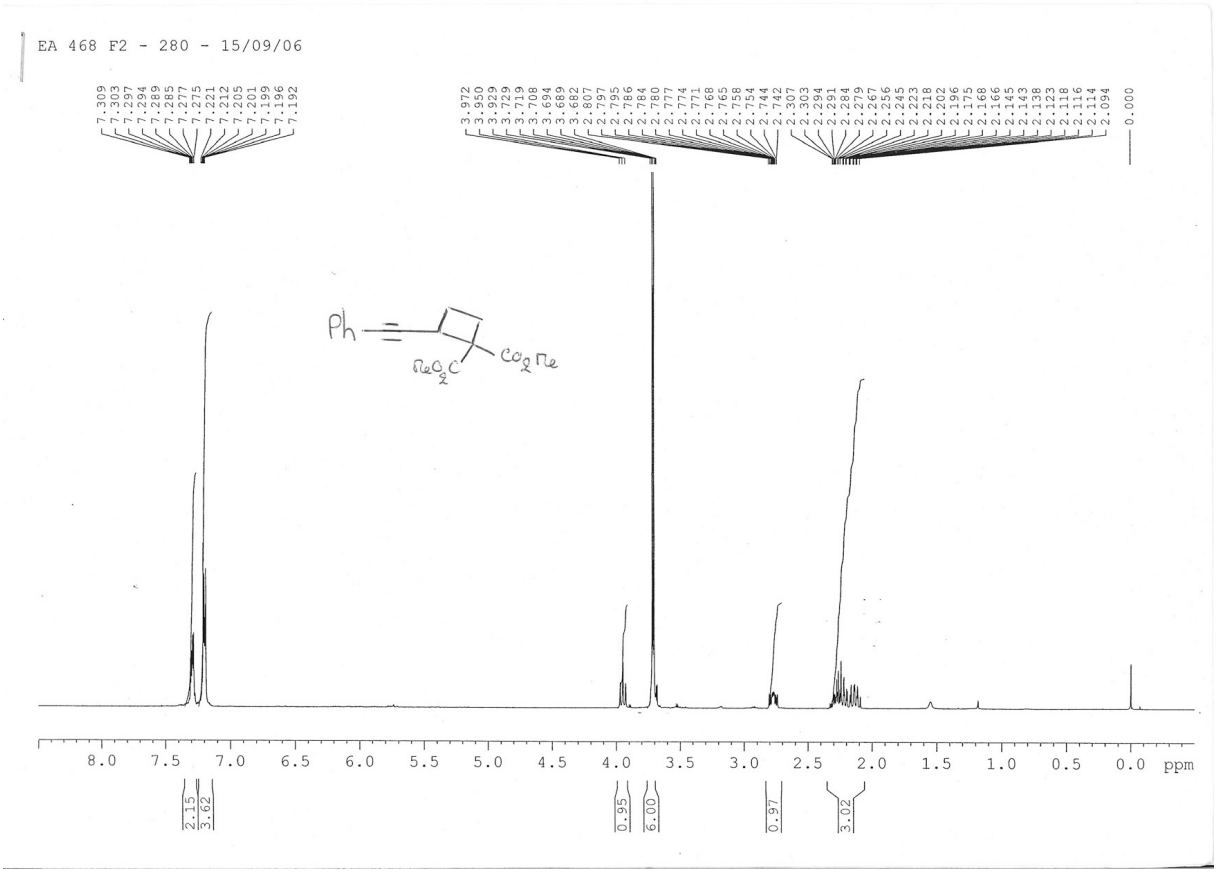

EA 460 crude - 640 - 07/08/06
ppm
131.714 128.549 128.336 122.404 89.227 85.377 77.354 77.239 77.036 76.719 62.344 60.662 38.956
ppm 200 180 160 140 120 100 80 60 40 20 0

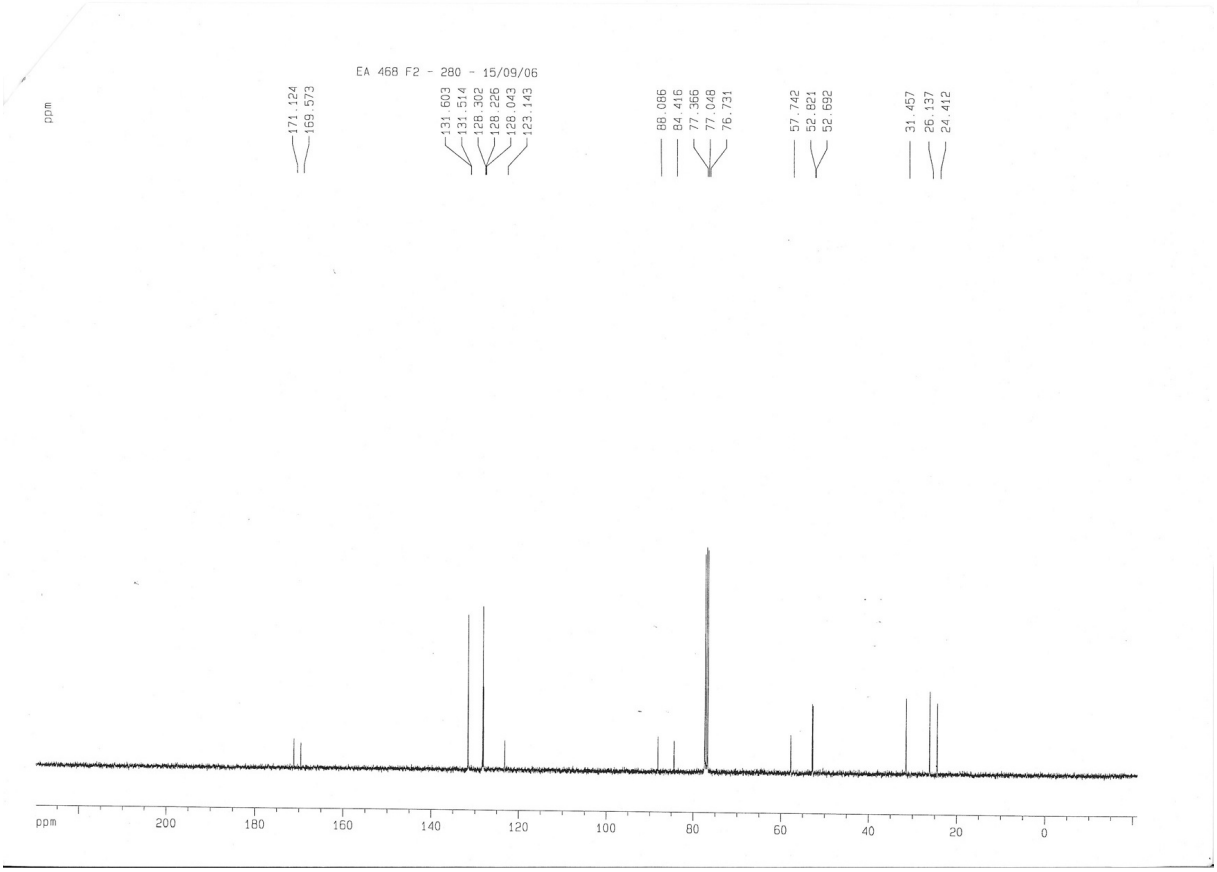
Compound 5


EA 467 F1 - 13/09/06 - 380
7.466
7.461
7.456
7.453
7.448
7.442
7.431
7.424
7.378
7.375
7.374
7.359
7.346
7.329
7.322
7.320
7.315
7.307
7.260
7.258
4.998
4.981
4.964
3.640
3.624
3.608
2.658
2.636
2.619
2.605
2.603
2.587
2.565
2.051
1.565
1.265
Br
Br
Ph
H1
H2
H3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.06
3.11
1.00
2.08
2.10

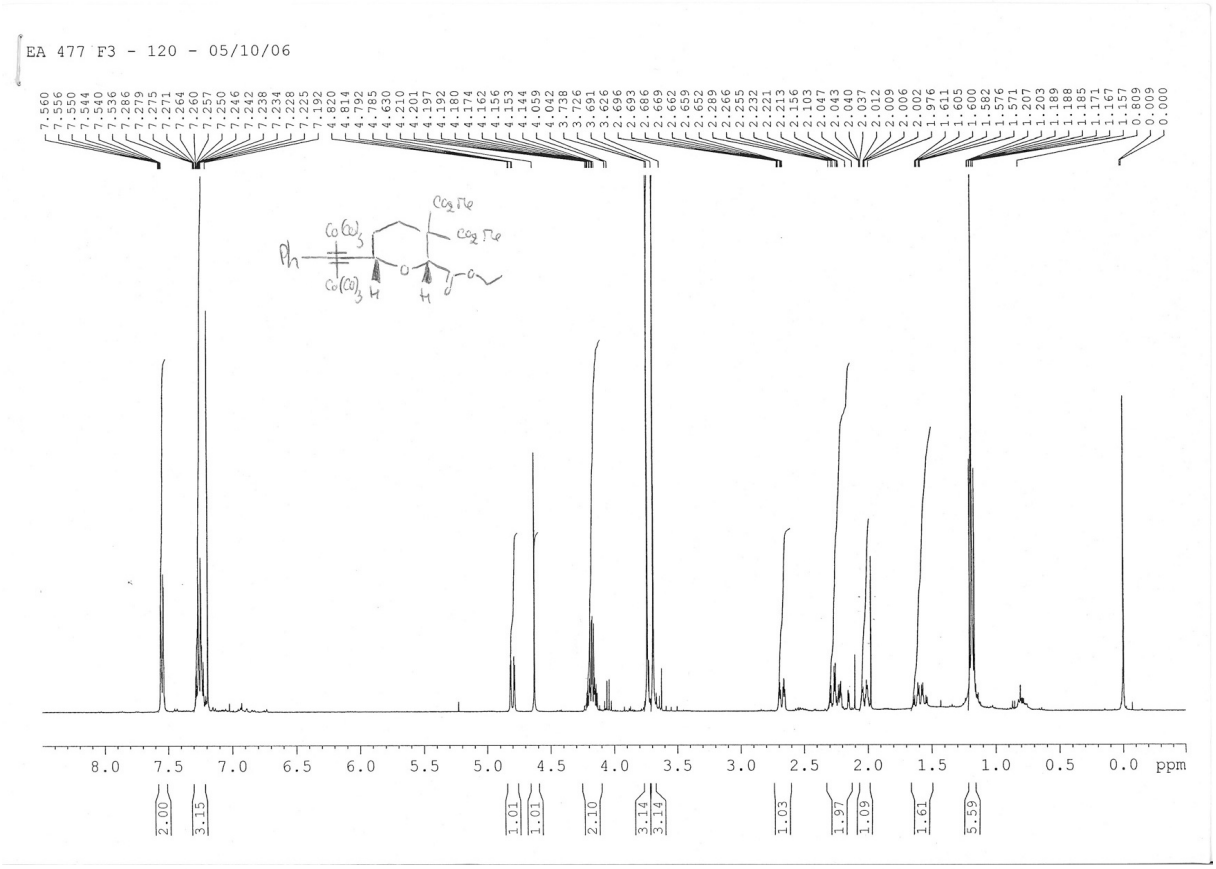

EA 467 F1 - 13/09/06 - 380
ppm
131.882
129.064
128.402
127.283
121.824
87.701
86.596
77.389
77.071
76.754
41.960
35.419
29.990
ppm
200
180
160
140
120
100
80
60
40
20
0

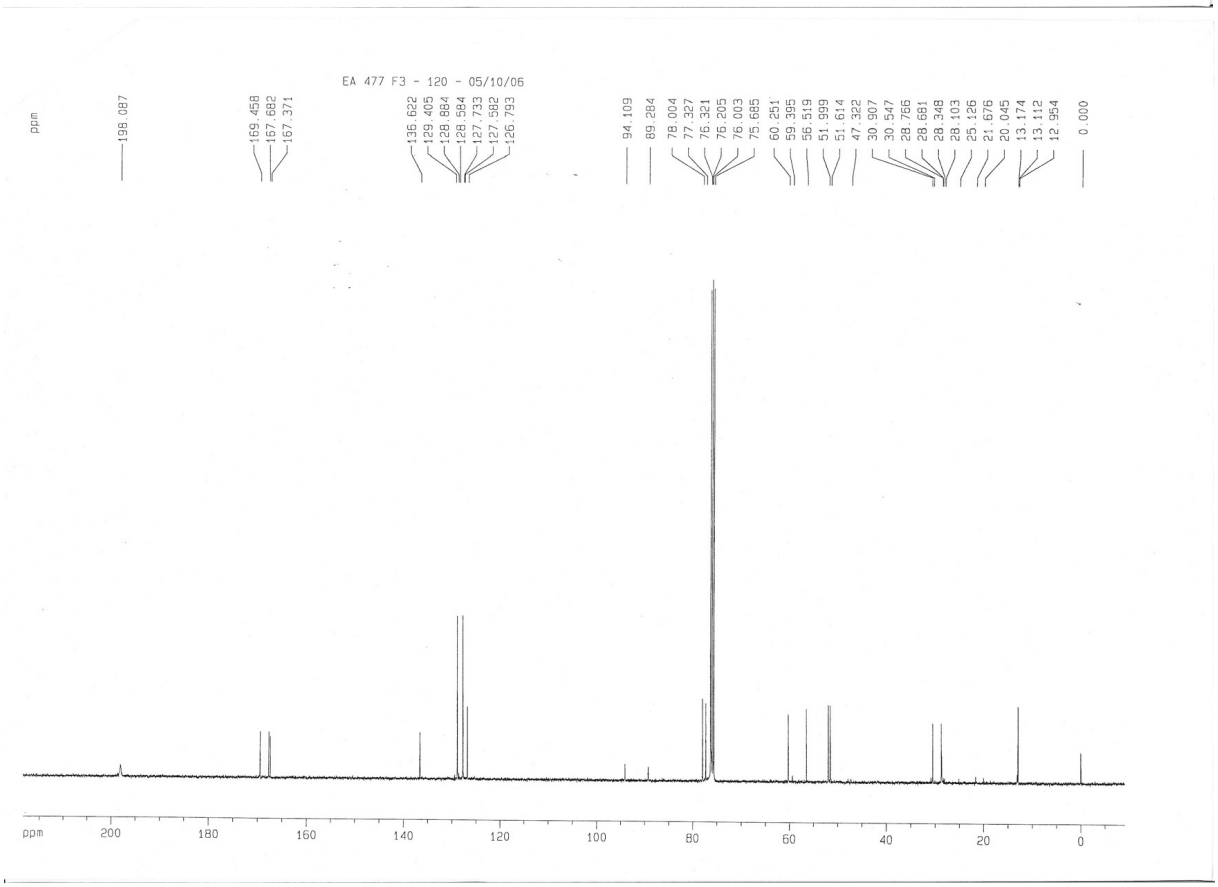
Compound 6


EA 468 F2 - 280 - 15/09/06
7.309
7.303
7.297
7.294
7.289
7.285
7.277
7.275
7.221
7.212
7.205
7.201
7.199
7.196
7.192
3.972
3.950
3.929
3.729
3.719
3.708
3.694
3.689
3.682
2.807
2.797
2.795
2.786
2.784
2.780
2.777
2.774
2.771
2.768
2.765
2.758
2.754
2.744
2.742
2.307
2.303
2.294
2.291
2.284
2.279
2.267
2.256
2.245
2.223
2.218
2.202
2.196
2.175
2.168
2.166
2.145
2.143
2.138
2.123
2.118
2.116
2.114
2.094
0.000
Ph
MeO2C
CO2Me
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.15
3.62
0.95
6.00
0.97
3.02


EA 468 F2 - 280 - 15/09/06
ppm
171.124
169.573
131.603
131.514
128.302
128.226
128.043
123.143
88.066
84.416
77.366
77.048
76.731
57.742
52.821
52.692
31.457
26.137
24.412
ppm
200
180
160
140
120
100
80
60
40
20
0

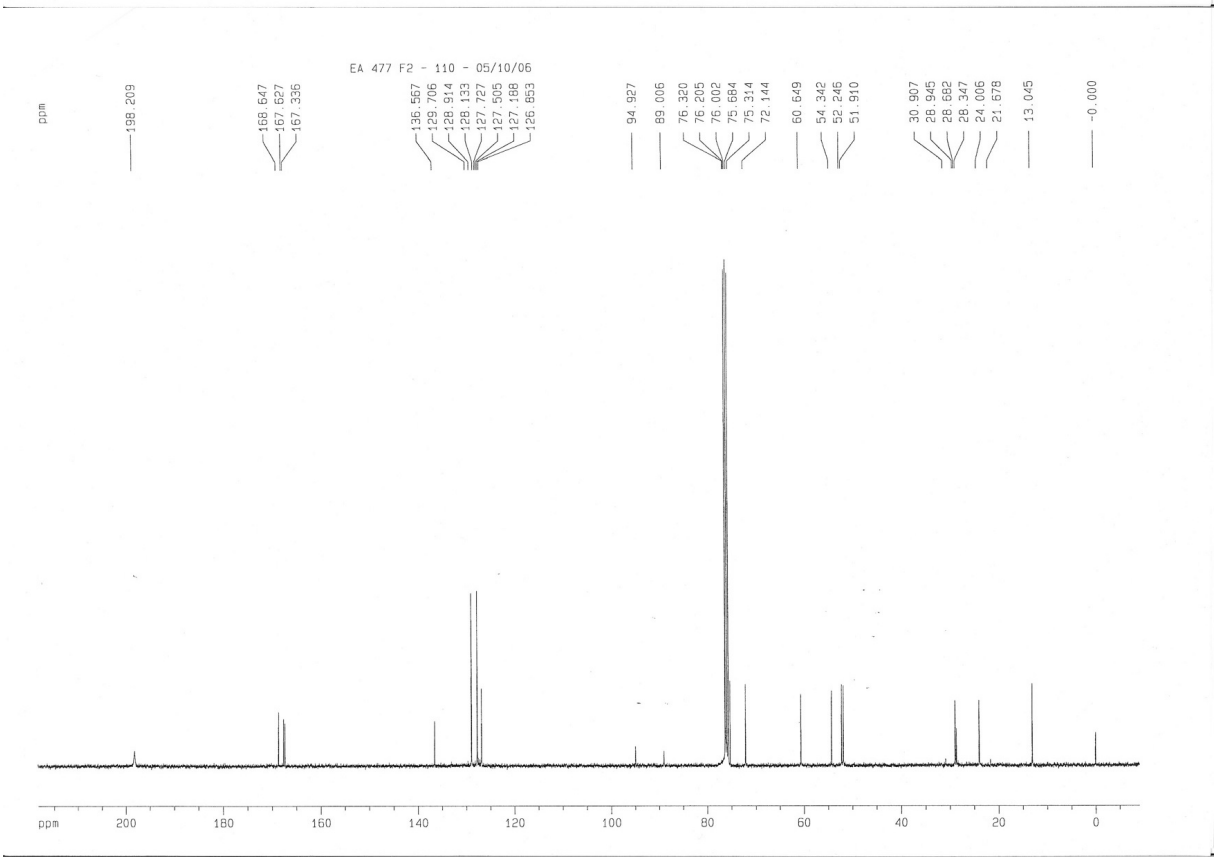
Compound 7a


EA 477 F3 - 120 - 05/10/06
7.560
7.556
7.550
7.544
7.540
7.536
7.286
7.279
7.275
7.271
7.264
7.260
7.257
7.250
7.246
7.242
7.238
7.234
7.225
7.192
4.820
4.814
4.792
4.785
4.630
4.210
4.201
4.197
4.192
4.180
4.174
4.162
4.156
4.153
4.144
4.059
4.042
3.738
3.726
3.691
3.626
2.696
2.693
2.686
2.669
2.662
2.659
2.652
2.289
2.266
2.255
2.232
2.221
2.213
2.156
2.103
2.047
2.043
2.040
2.037
2.012
2.009
2.006
2.002
1.976
1.611
1.605
1.600
1.582
1.576
1.571
1.207
1.203
1.189
1.188
1.185
1.171
1.167
1.157
0.809
0.009
0.000
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
3.15
1.01
1.01
2.10
3.14
3.14
1.03
1.97
1.09
1.61
5.59

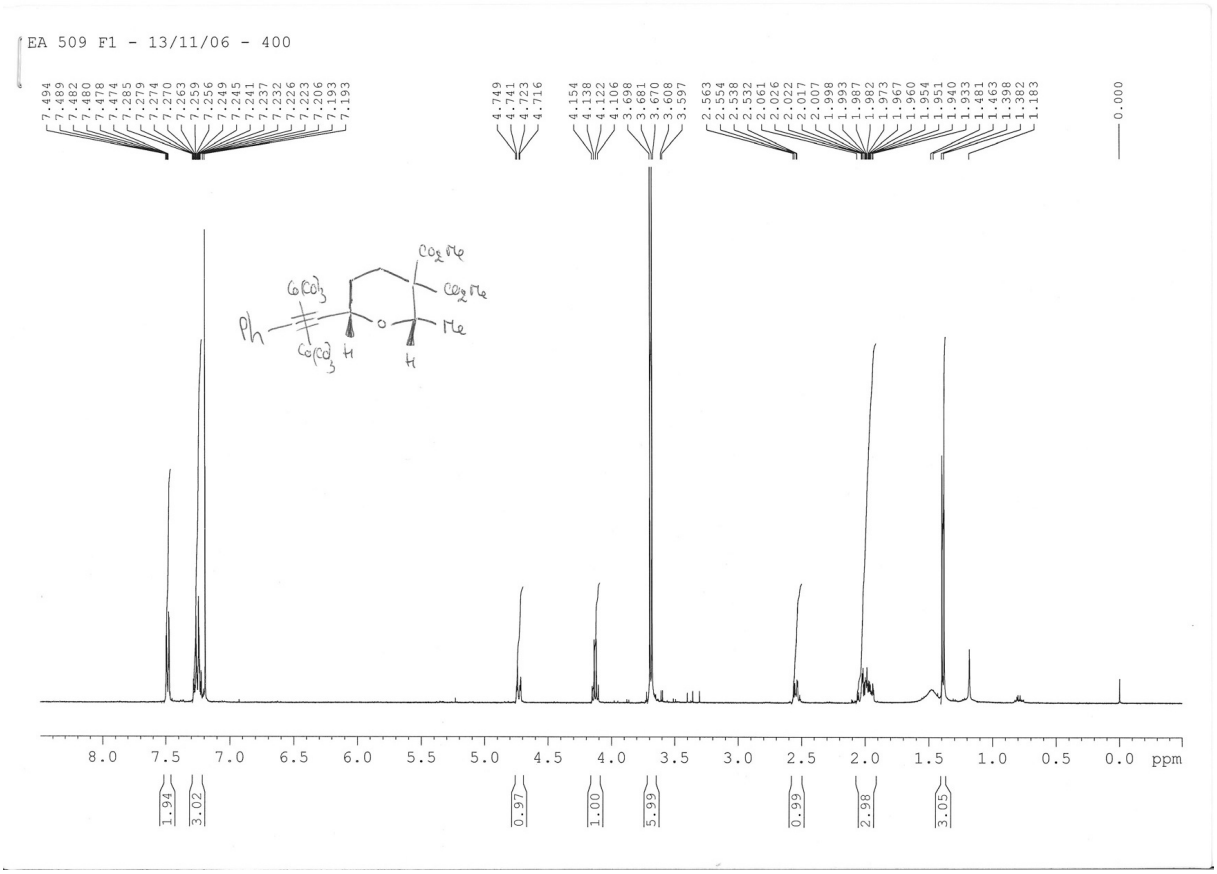

EA 477 F3 - 120 - 05/10/06
ppm
198.087
169.458
167.682
167.371
136.622
129.405
128.884
128.584
127.733
127.582
126.793
94.109
89.284
78.004
77.327
76.321
76.205
76.003
75.685
60.251
59.395
56.519
51.999
51.614
47.322
30.907
30.547
28.766
28.681
28.348
28.103
25.126
21.676
20.045
13.174
13.112
12.954
0.000
ppm
200
180
160
140
120
100
80
60
40
20
0

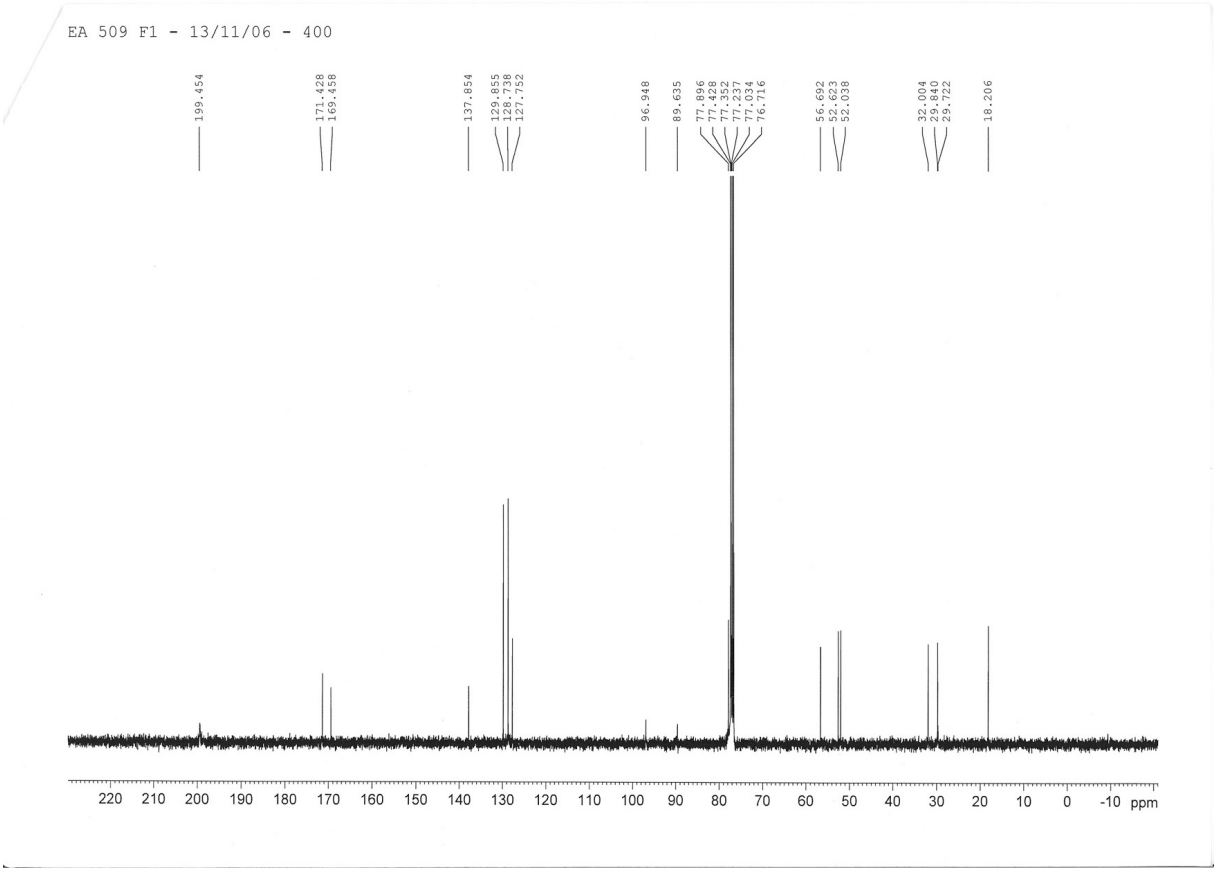
Compound 7b


EA 477 F2 - 210 - 01/02/07
7.540
7.536
7.531
7.524
7.520
7.516
7.510
7.290
7.284
7.279
7.275
7.268
7.265
7.261
7.250
7.247
7.242
7.238
7.231
7.229
7.193
5.419
5.416
4.848
4.842
4.820
4.813
4.213
4.211
4.195
4.193
4.177
4.175
4.159
3.745
3.741
3.721
3.679
3.593
2.636
2.610
2.599
2.336
2.325
2.301
2.291
2.280
2.266
2.260
2.256
2.032
2.024
1.998
1.990
1.979
1.623
1.617
1.612
1.594
1.588
1.583
1.579
1.560
1.549
1.515
1.246
1.228
1.210
1.183
0.826
0.810
0.792
0.000
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.99
3.08
0.96
0.99
2.03
2.97
3.00
1.01
1.15
1.10
1.24
3.76
3.61

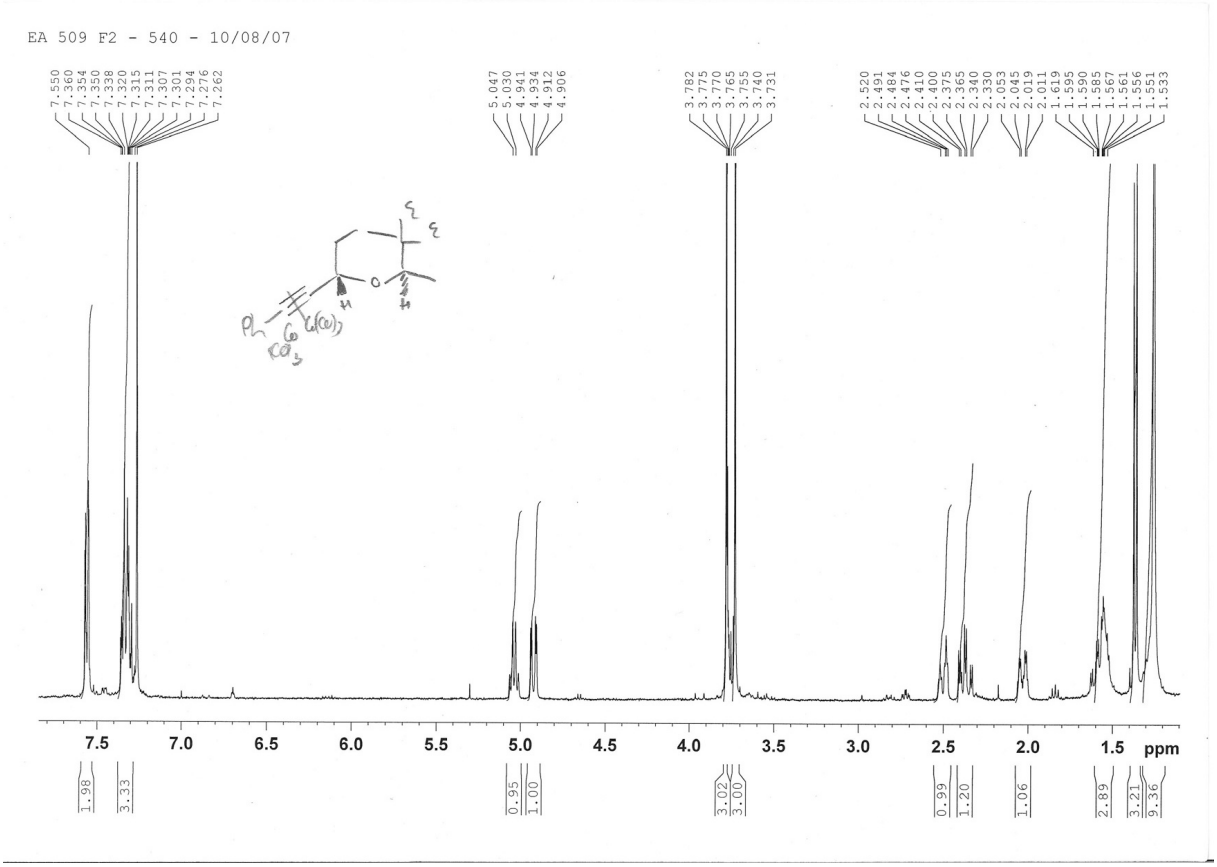

EA 477 F2 - 110 - 05/10/06
ppm
198.209
168.647
167.627
167.336
136.567
129.706
128.914
128.133
127.727
127.505
127.188
126.653
94.927
89.006
76.320
76.205
76.002
75.684
75.314
72.144
60.649
54.342
52.246
51.910
30.907
28.945
28.682
28.347
24.006
21.678
13.045
-0.000
ppm
200
180
160
140
120
100
80
60
40
20
0

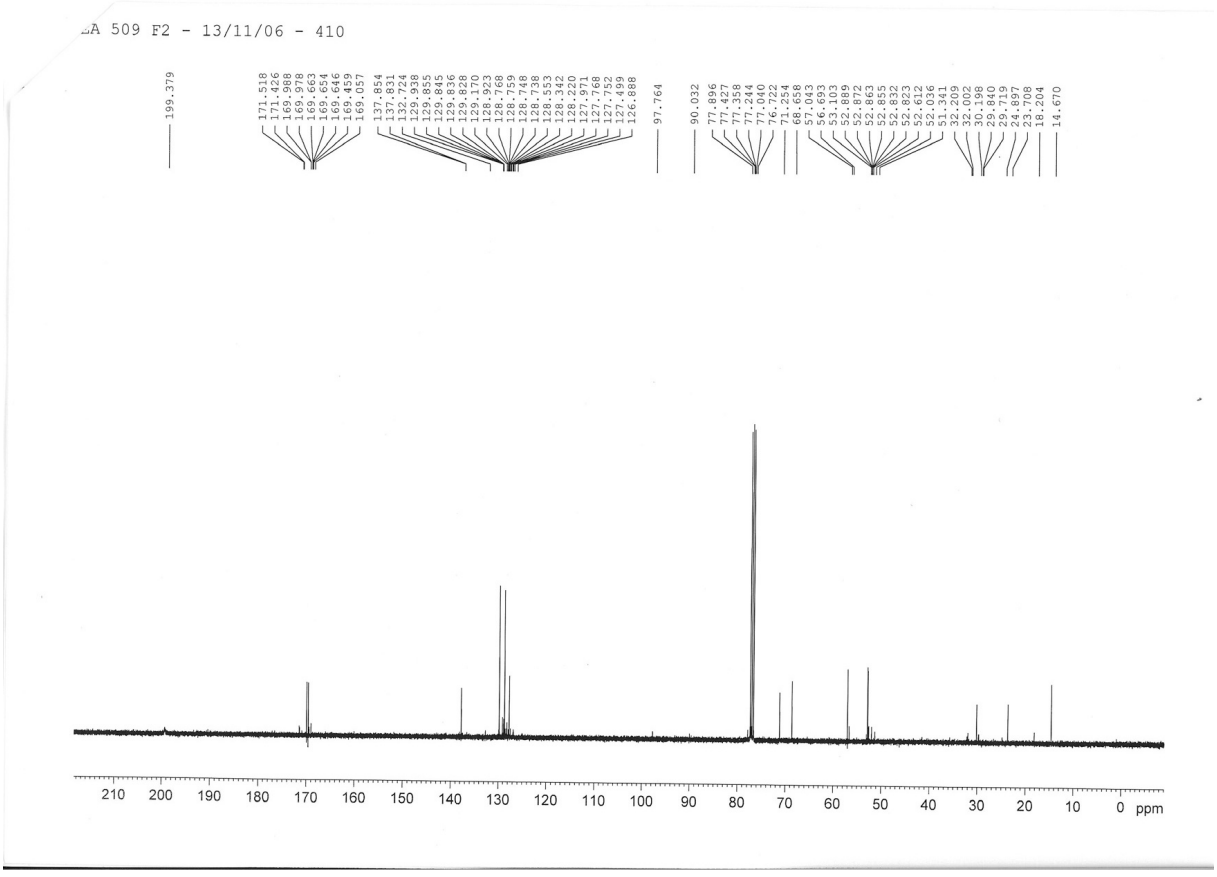
Compound 8a


EA 509 F1 - 13/11/06 - 400
7.494
7.489
7.482
7.480
7.478
7.474
7.285
7.279
7.274
7.270
7.263
7.259
7.256
7.249
7.245
7.241
7.237
7.232
7.226
7.225
7.206
7.193
7.193
4.749
4.741
4.723
4.716
4.154
4.138
4.122
4.106
3.698
3.681
3.670
3.608
3.597
2.563
2.554
2.538
2.532
2.061
2.026
2.022
2.017
2.007
1.998
1.993
1.987
1.982
1.973
1.967
1.960
1.954
1.951
1.940
1.933
1.481
1.463
1.398
1.382
1.183
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.94
3.02
0.97
1.00
5.99
0.99
2.98
3.05

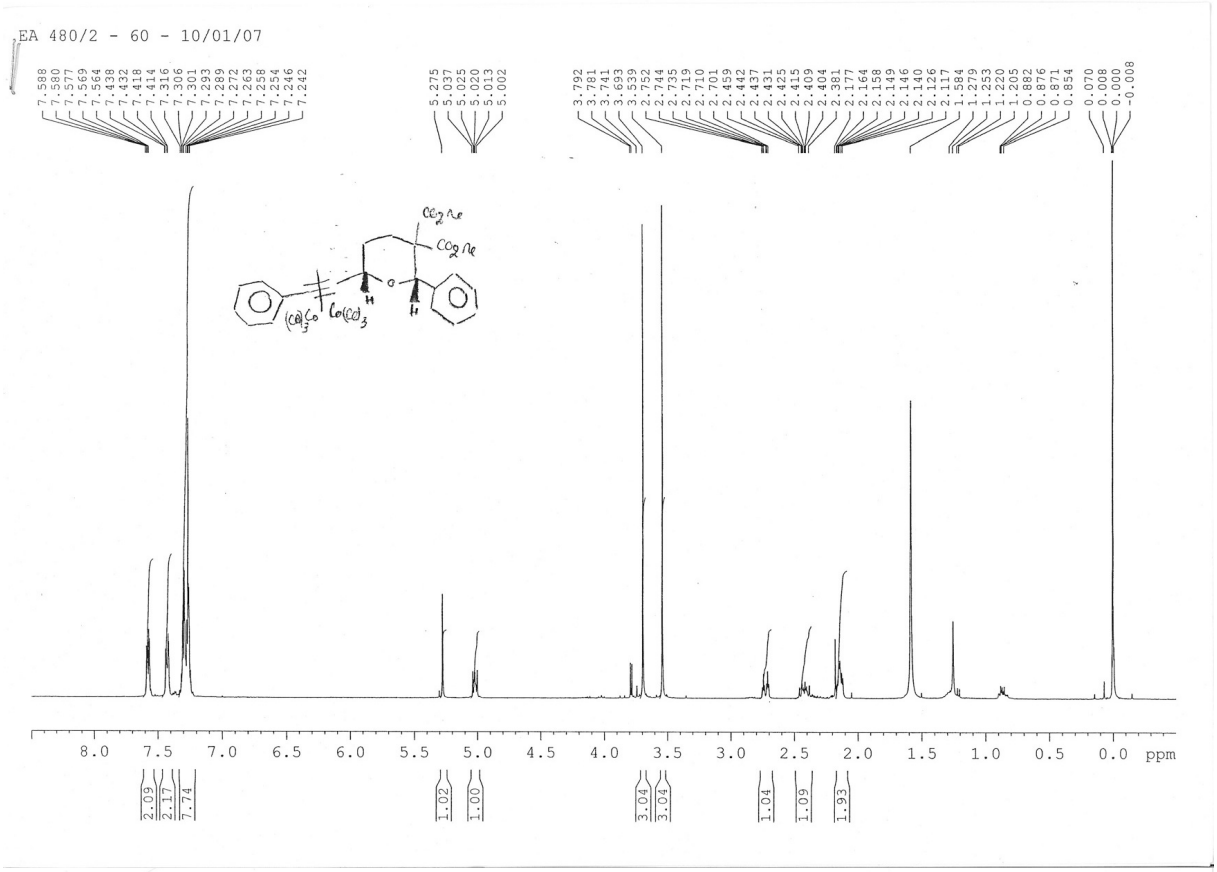

EA 509 F1 - 13/11/06 - 400
199.454
171.428
169.458
137.854
129.855
128.738
127.752
96.948
89.635
77.896
77.428
77.352
77.237
77.034
76.716
56.692
52.623
52.038
32.004
29.840
29.722
18.206
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

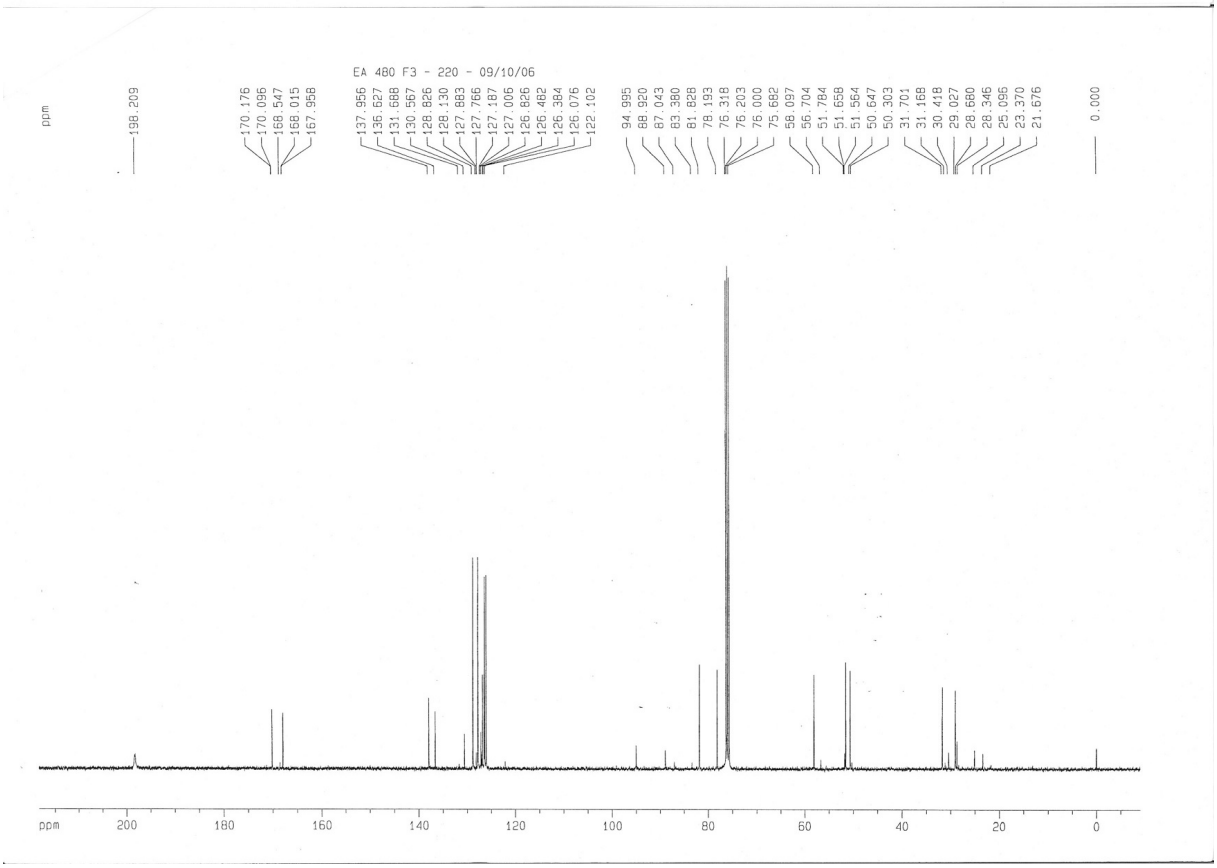
Compound 8b


EA 509 F2 - 540 - 10/08/07
7.550
7.360
7.354
7.350
7.338
7.320
7.315
7.311
7.307
7.301
7.294
7.276
7.262
5.047
5.030
4.941
4.934
4.912
4.906
3.782
3.775
3.770
3.765
3.755
3.740
3.731
2.520
2.491
2.484
2.476
2.410
2.400
2.375
2.365
2.340
2.330
2.053
2.045
2.019
2.011
1.619
1.595
1.590
1.585
1.567
1.561
1.556
1.551
1.533
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.98
3.33
0.95
1.00
3.02
3.00
0.99
1.20
1.06
2.89
3.21
9.36

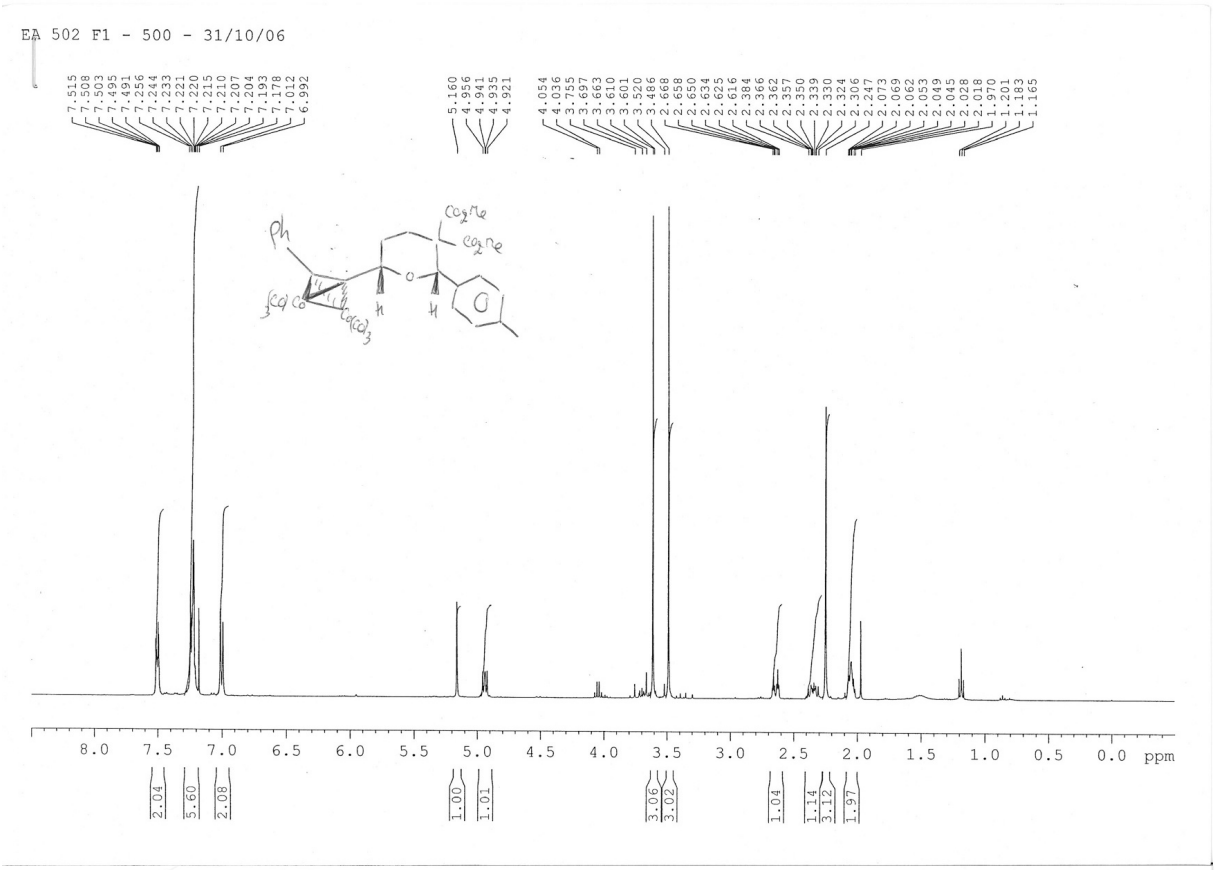

EA 509 F2 - 13/11/06 - 410
199.379
171.518
171.426
169.988
169.978
169.663
169.654
169.646
169.459
169.057
137.854
137.731
132.734
129.938
129.855
129.845
129.836
129.828
129.170
128.923
128.768
128.759
128.748
128.738
128.553
128.342
128.220
127.971
127.768
127.752
127.499
126.888
97.764
90.032
77.896
77.427
77.358
77.244
77.040
76.722
71.254
68.638
67.045
56.693
53.103
52.889
52.872
52.863
52.855
52.832
52.823
52.612
52.036
51.341
32.209
32.002
30.198
30.040
29.719
24.897
23.708
18.204
14.670
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

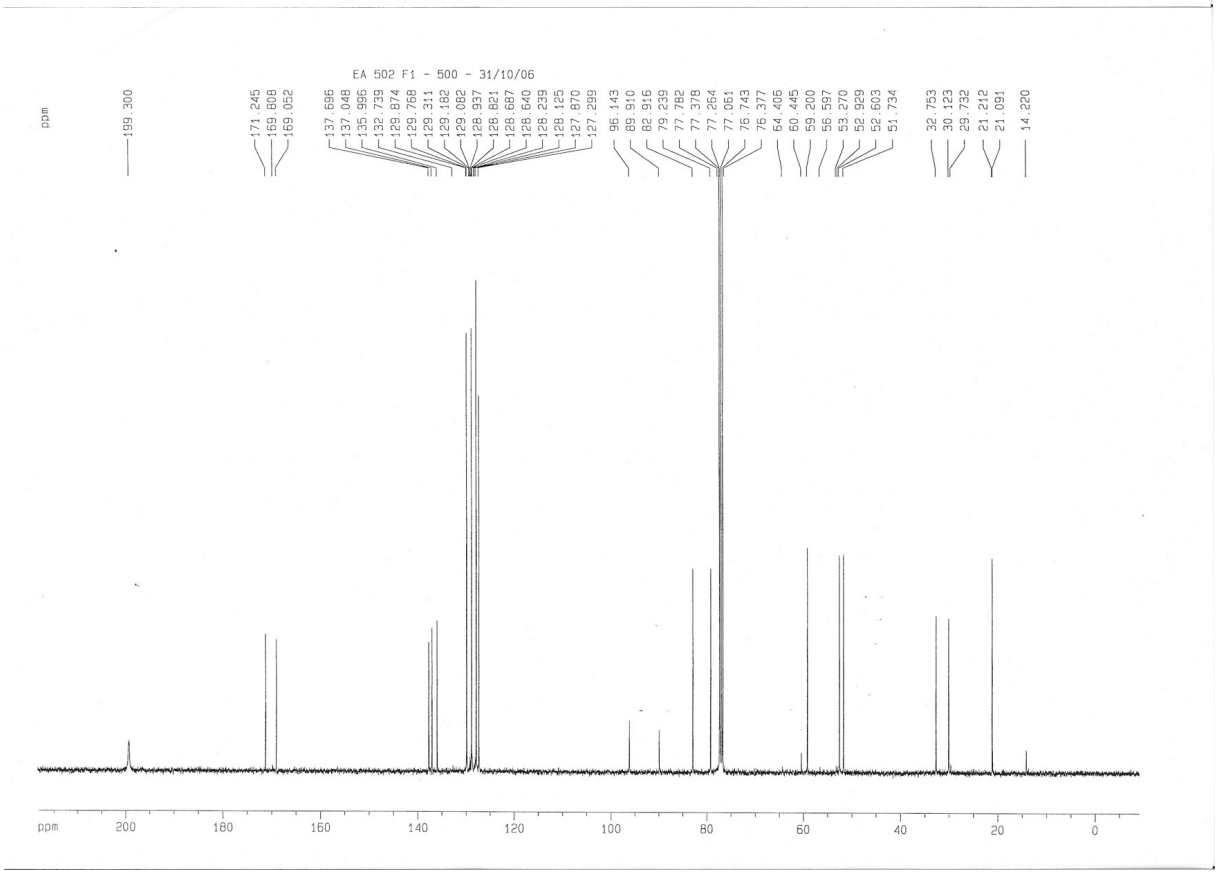
Compound 9


EA 480/2 - 60 - 10/01/07
7.588
7.580
7.577
7.569
7.564
7.438
7.432
7.418
7.414
7.316
7.306
7.301
7.293
7.289
7.272
7.263
7.258
7.254
7.246
7.242
5.275
5.037
5.025
5.020
5.013
5.002
3.792
3.781
3.741
3.693
3.539
2.752
2.744
2.735
2.719
2.710
2.701
2.459
2.442
2.437
2.431
2.415
2.409
2.404
2.381
2.177
2.164
2.158
2.149
2.146
2.140
2.126
2.117
1.584
1.279
1.253
1.220
1.205
0.882
0.876
0.871
0.854
0.070
0.008
0.000
-0.008
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.09
2.17
7.74
1.02
1.00
3.04
3.04
1.04
1.09
1.93

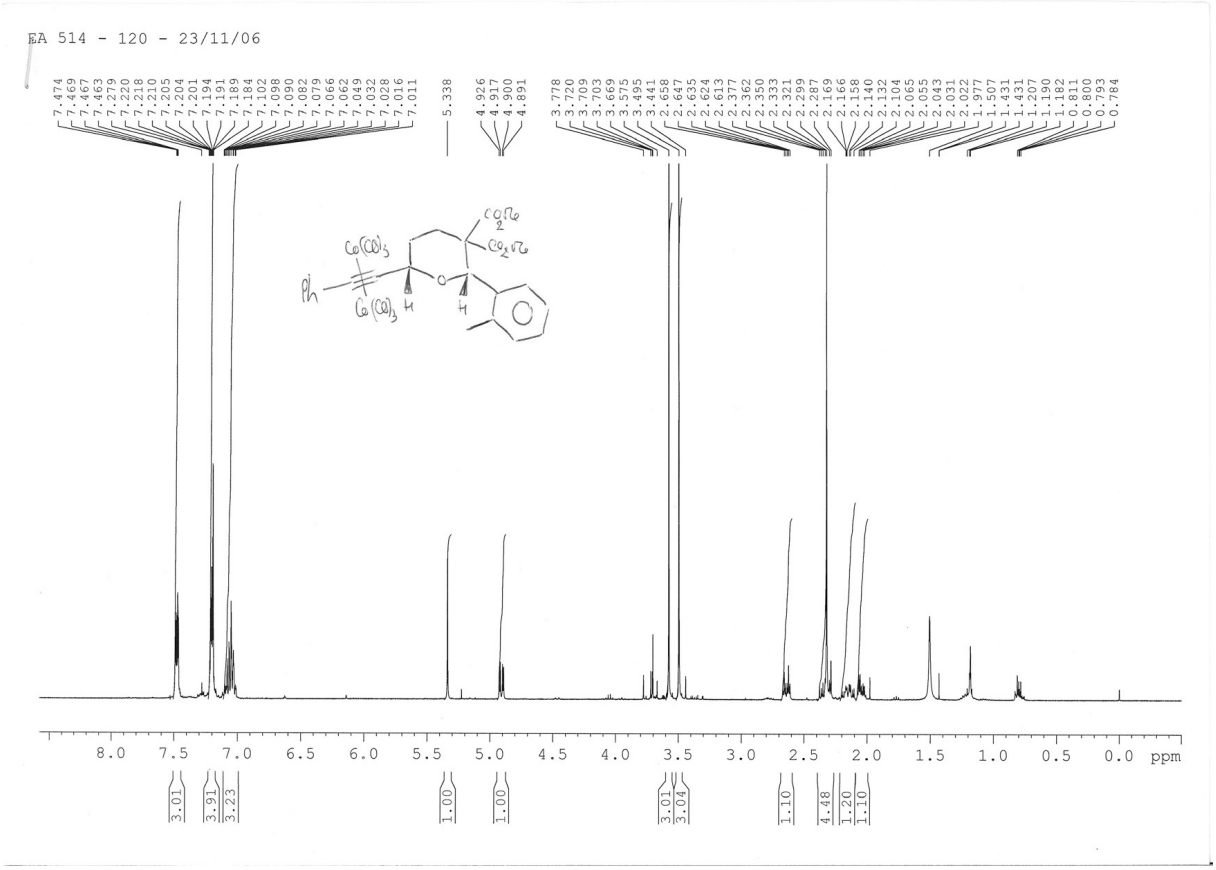

EA 480 F3 - 220 - 09/10/06
ppm
198.209
170.176
170.096
168.547
168.015
167.958
137.956
136.627
131.688
130.567
128.826
128.130
127.883
127.766
127.187
127.006
126.826
126.482
126.384
126.076
122.102
94.995
88.920
87.043
83.380
81.828
78.193
76.318
76.203
76.000
75.682
58.097
56.704
51.784
51.658
51.564
50.647
50.303
31.701
31.168
30.418
29.027
28.680
28.346
25.095
23.370
21.676
0.000
ppm 200 180 160 140 120 100 80 60 40 20 0

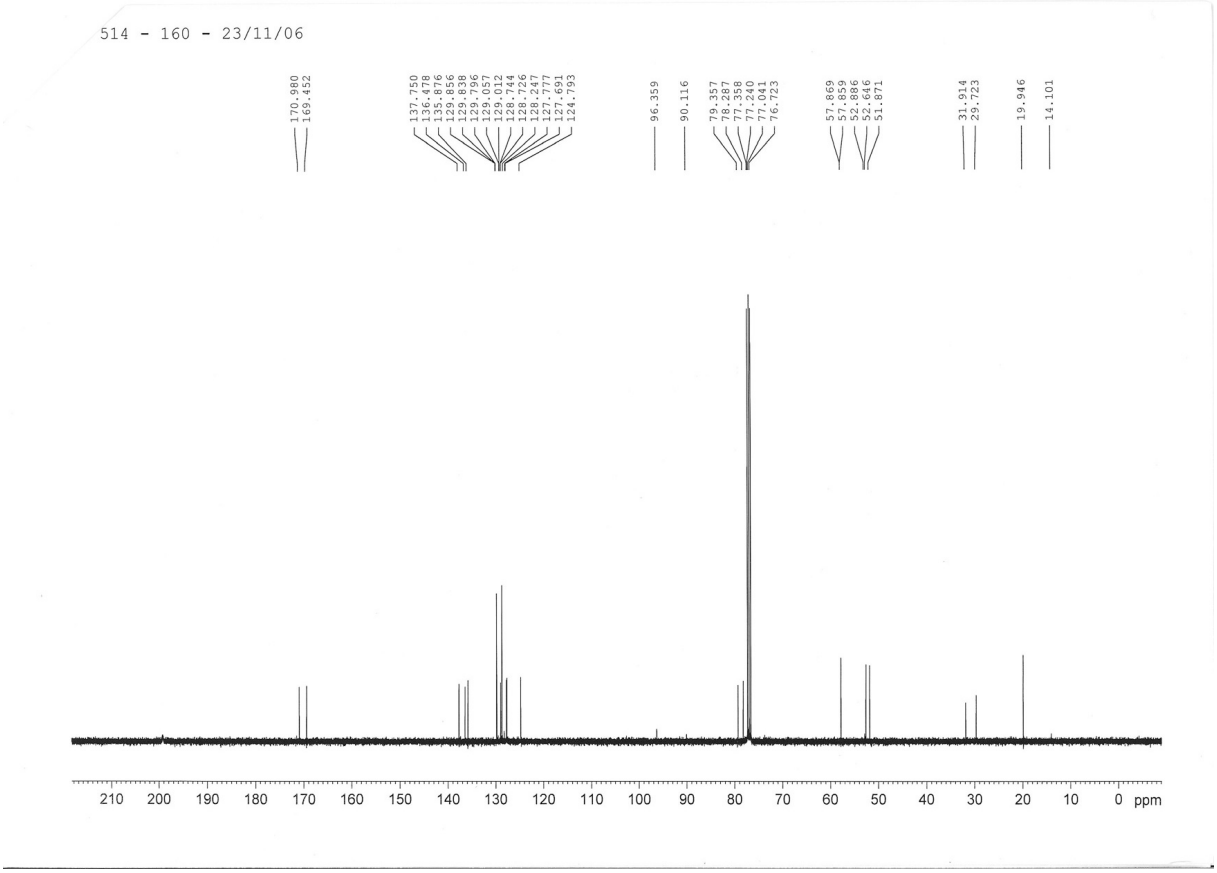
Compound 10


EA 502 F1 - 500 - 31/10/06
7.515
7.508
7.503
7.495
7.491
7.256
7.244
7.233
7.221
7.220
7.215
7.210
7.207
7.204
7.193
7.178
7.012
6.992
5.160
4.956
4.941
4.935
4.921
4.054
4.036
3.755
3.697
3.663
3.610
3.601
3.520
3.486
2.668
2.658
2.650
2.634
2.625
2.616
2.384
2.366
2.362
2.357
2.350
2.339
2.330
2.324
2.306
2.247
2.073
2.069
2.062
2.053
2.049
2.045
2.028
2.018
1.970
1.201
1.183
1.165
Ph
CO2Me
CO2Me
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.04
5.60
2.08
1.00
1.01
3.06
3.02
1.04
1.14
3.12
1.97

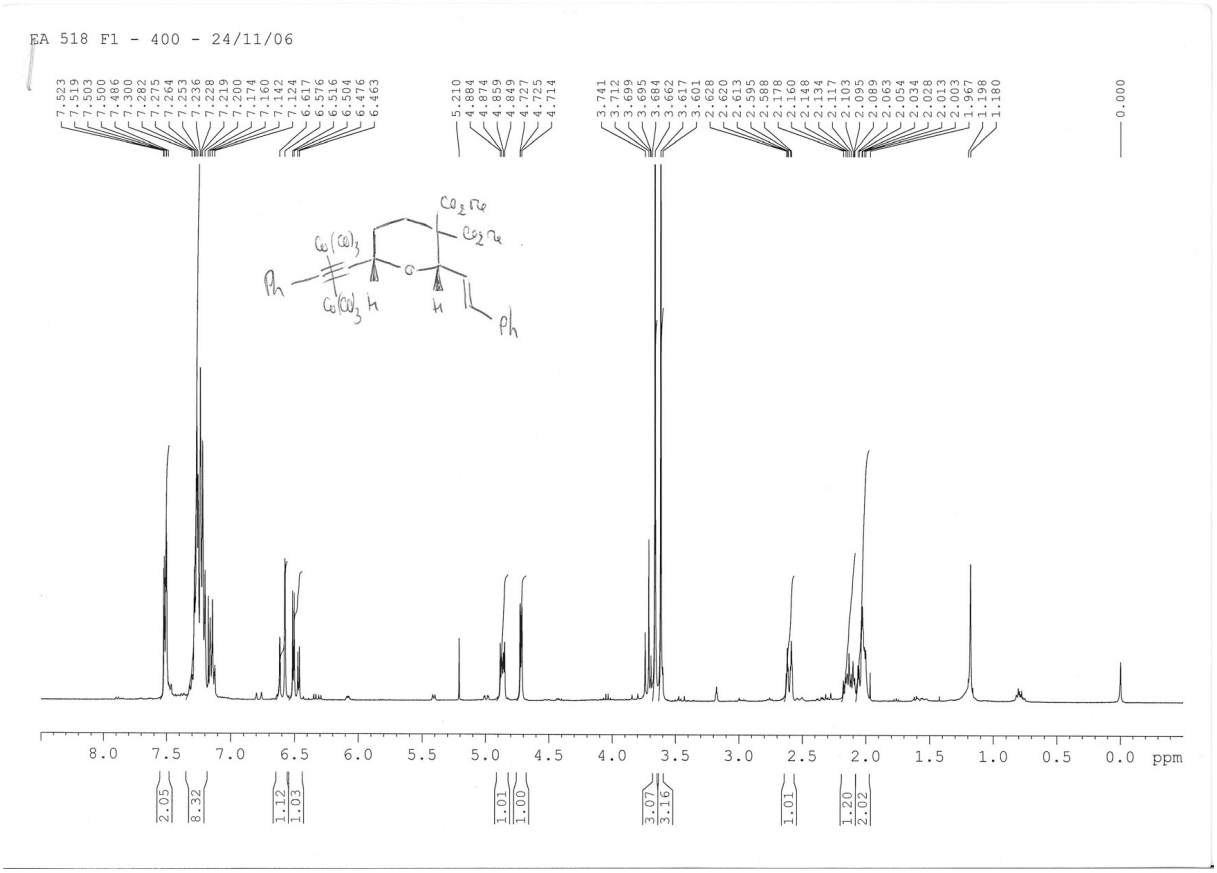

EA 502 F1 - 500 - 31/10/06
ppm
199.300
171.245
169.808
169.052
137.696
137.048
135.996
132.739
129.874
129.768
129.311
129.182
129.082
128.937
128.821
128.687
128.640
128.239
128.125
127.870
127.299
96.143
89.910
82.916
79.239
77.782
77.378
77.264
77.061
76.743
76.377
64.406
60.445
59.200
56.597
53.270
52.929
52.603
51.734
32.753
30.123
29.732
21.212
21.091
14.220
200
180
160
140
120
100
80
60
40
20
0

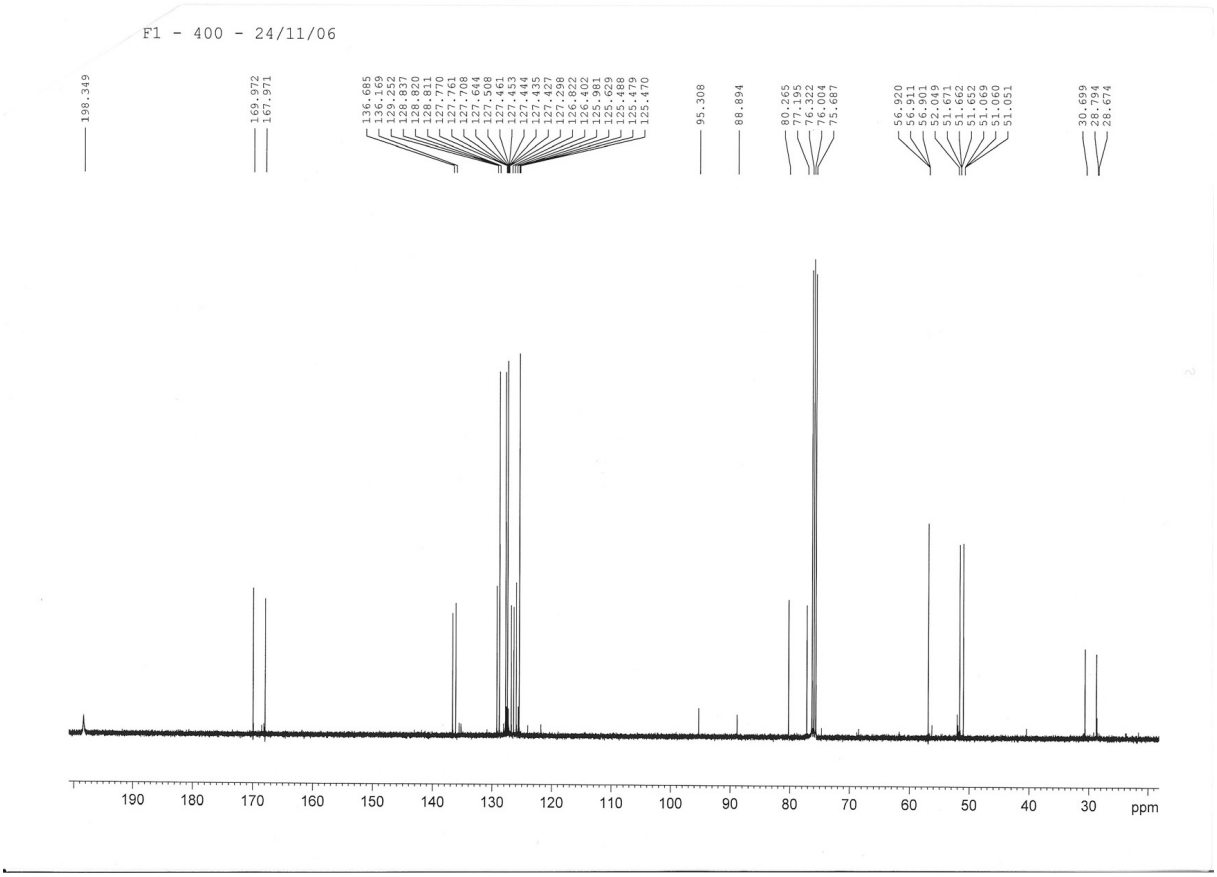
Compound 11


EA 514 - 120 - 23/11/06
7.474
7.469
7.467
7.463
7.279
7.220
7.218
7.210
7.205
7.204
7.201
7.194
7.191
7.189
7.184
7.102
7.098
7.090
7.082
7.079
7.066
7.062
7.049
7.032
7.028
7.016
7.011
5.338
4.926
4.917
4.900
4.891
3.778
3.720
3.709
3.703
3.669
3.575
3.495
3.441
2.658
2.647
2.635
2.624
2.613
2.377
2.362
2.350
2.333
2.321
2.299
2.287
2.169
2.166
2.158
2.140
2.132
2.104
2.065
2.055
2.043
2.031
2.022
1.977
1.507
1.431
1.431
1.407
1.190
1.182
0.811
0.800
0.793
0.784
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.01
3.91
3.23
1.00
1.00
3.01
3.04
1.10
4.48
1.20
1.10

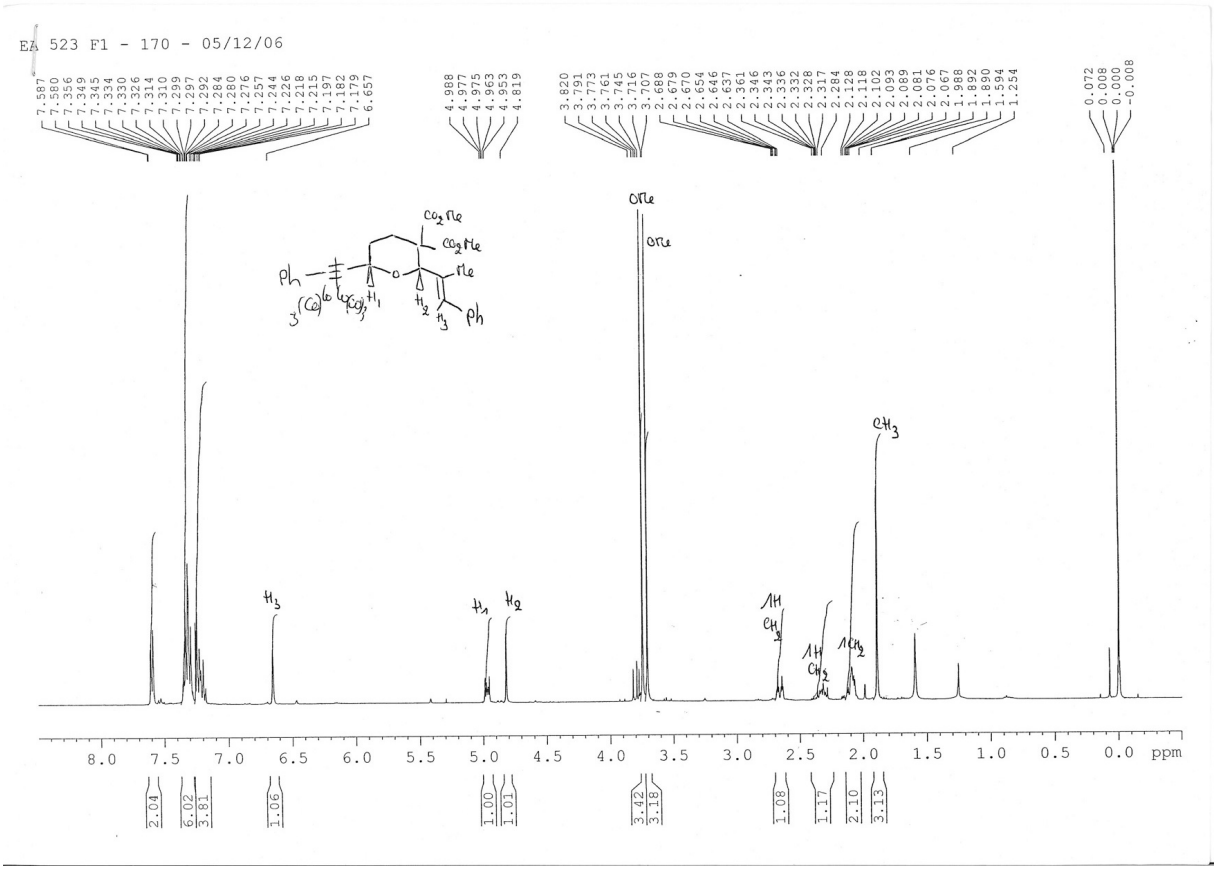

514 - 160 - 23/11/06
170.980
169.452
137.750
136.478
135.876
129.856
129.838
129.756
129.057
129.012
128.744
128.726
128.247
127.777
127.691
124.793
96.359
90.116
79.357
78.387
77.358
77.240
77.041
76.723
57.869
57.859
52.886
52.646
51.871
31.914
29.723
19.946
14.101
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

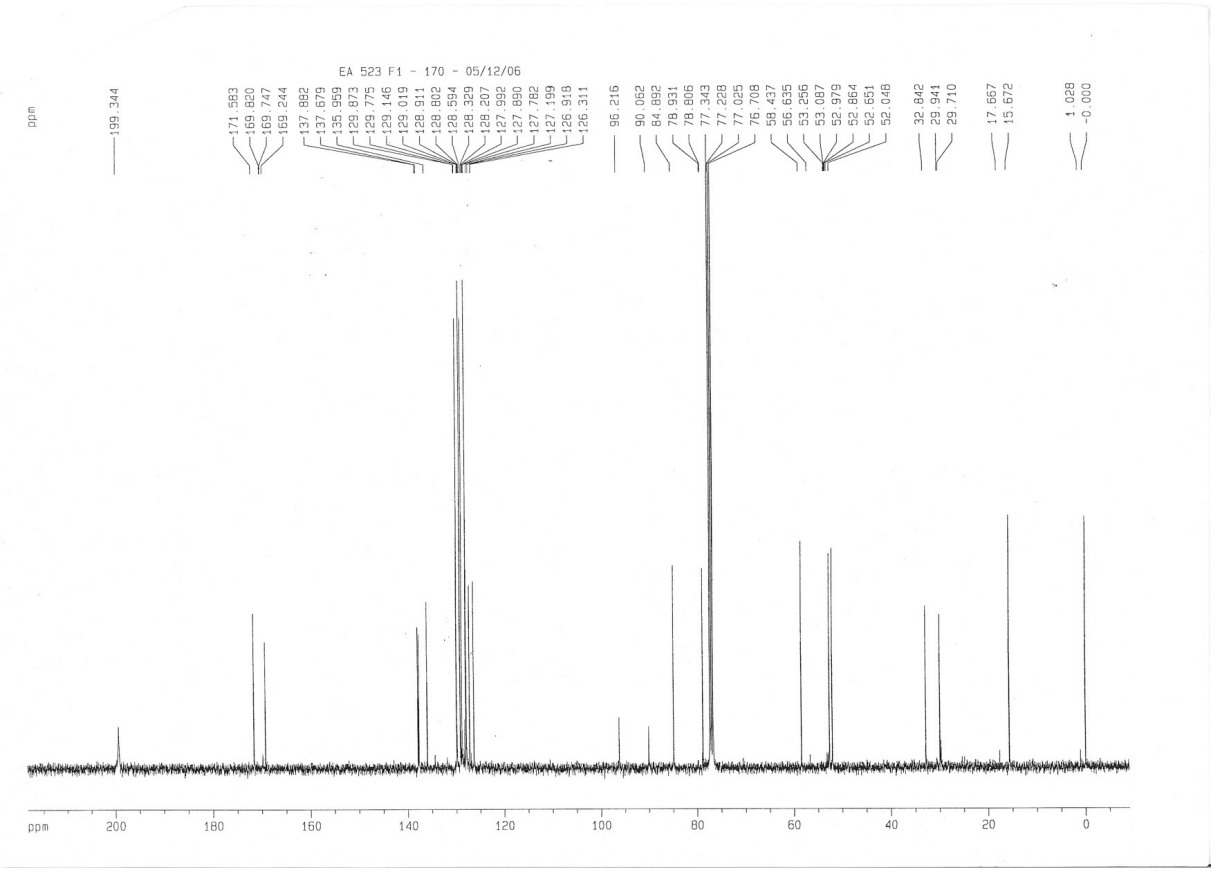
Compound 12


EA 518 F1 - 400 - 24/11/06
7.523 7.519 7.503 7.500 7.486 7.300 7.282 7.275 7.264 7.253 7.236 7.228 7.219 7.200 7.174 7.160 7.142 7.124 6.617 6.516 6.504 6.476 6.463
5.210 4.884 4.874 4.859 4.849 4.727 4.725 4.714
3.741 3.712 3.699 3.695 3.684 3.662 3.617 3.601 2.628 2.620 2.613 2.595 2.588 2.178 2.160 2.148 2.134 2.117 2.103 2.095 2.089 2.063 2.054 2.034 2.028 2.013 2.003 1.967 1.198 1.180
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.05 8.32 1.12 1.03 1.01 1.00 3.07 3.16 1.01 1.20 2.02

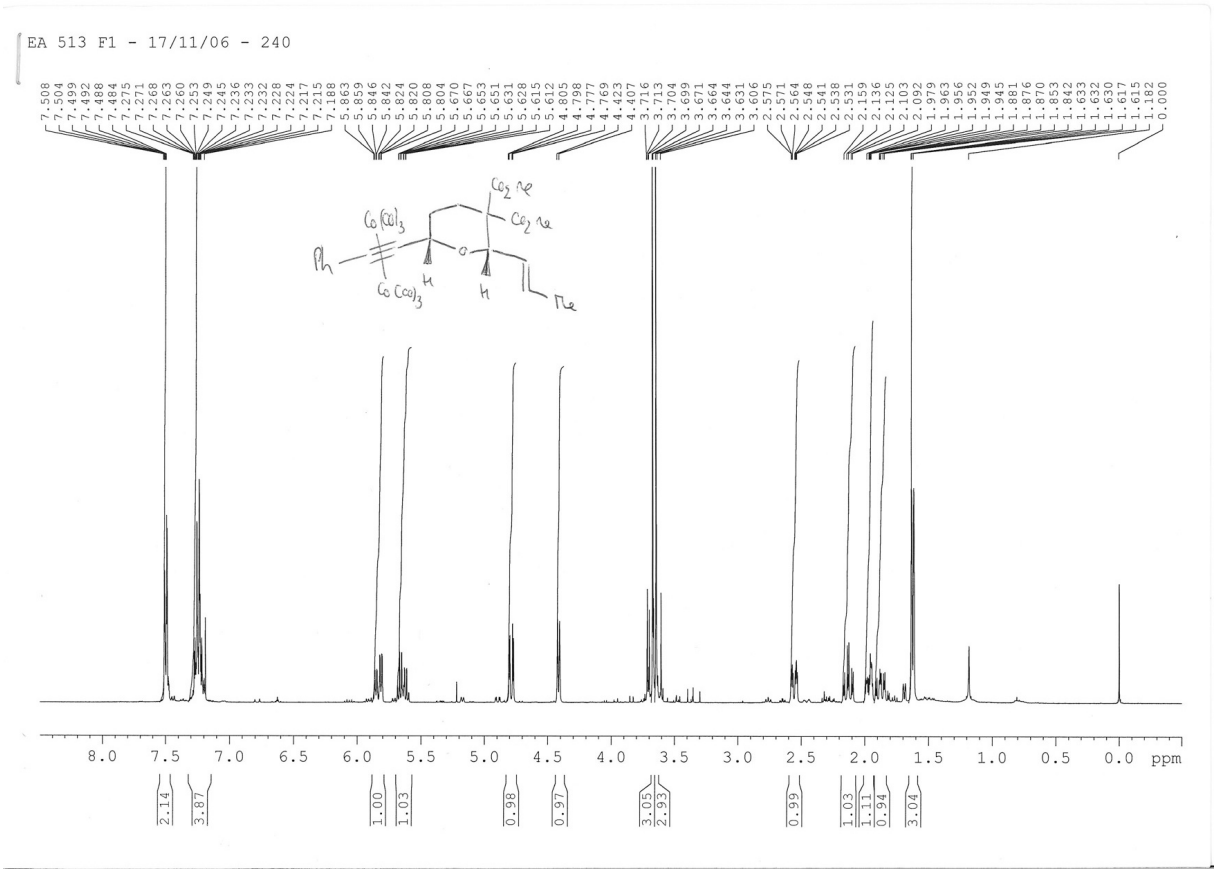

F1 - 400 - 24/11/06
198.349
169.972 167.971
136.685 136.169 129.252 128.837 128.820 128.811 127.770 127.761 127.708 127.644 127.588 127.461 127.453 127.444 127.435 127.427 127.298 126.822 126.402 125.981 125.629 125.488 125.479 125.470
95.308
88.894
80.265 77.195 77.032 76.001 75.687
56.920 56.911 56.901 54.049 51.671 51.662 51.652 51.069 51.060 51.051
30.699 28.794 28.674
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

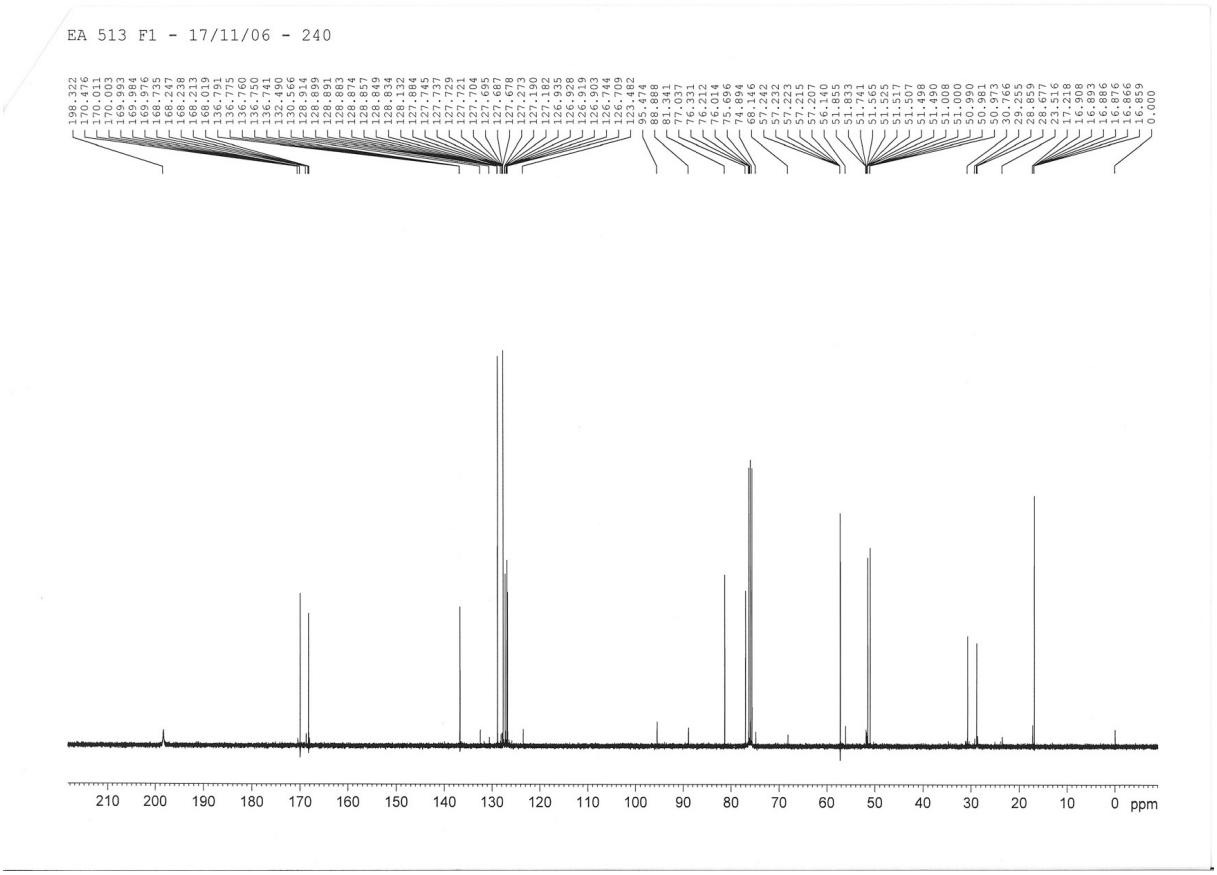
Compound 13


EA 523 F1 - 170 - 05/12/06
7.587 7.580 7.356 7.345 7.334 7.330 7.326 7.314 7.310 7.299 7.297 7.292 7.284 7.280 7.276 7.257 7.244 7.226 7.218 7.215 7.197 7.182 7.179 6.657
4.988 4.977 4.975 4.963 4.953 4.819
3.820 3.791 3.773 3.761 3.745 3.716 3.707 2.688 2.679 2.670 2.654 2.646 2.637 2.361 2.346 2.343 2.336 2.332 2.328 2.317 2.284 2.128 2.118 2.102 2.093 2.089 2.081 2.076 2.067 1.988 1.892 1.890 1.594 1.254
0.072 0.008 0.000 -0.008
OMe
OMe
CH3
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.04 6.02 3.81 1.06 1.00 1.01 3.42 3.18 1.08 1.17 2.10 3.13

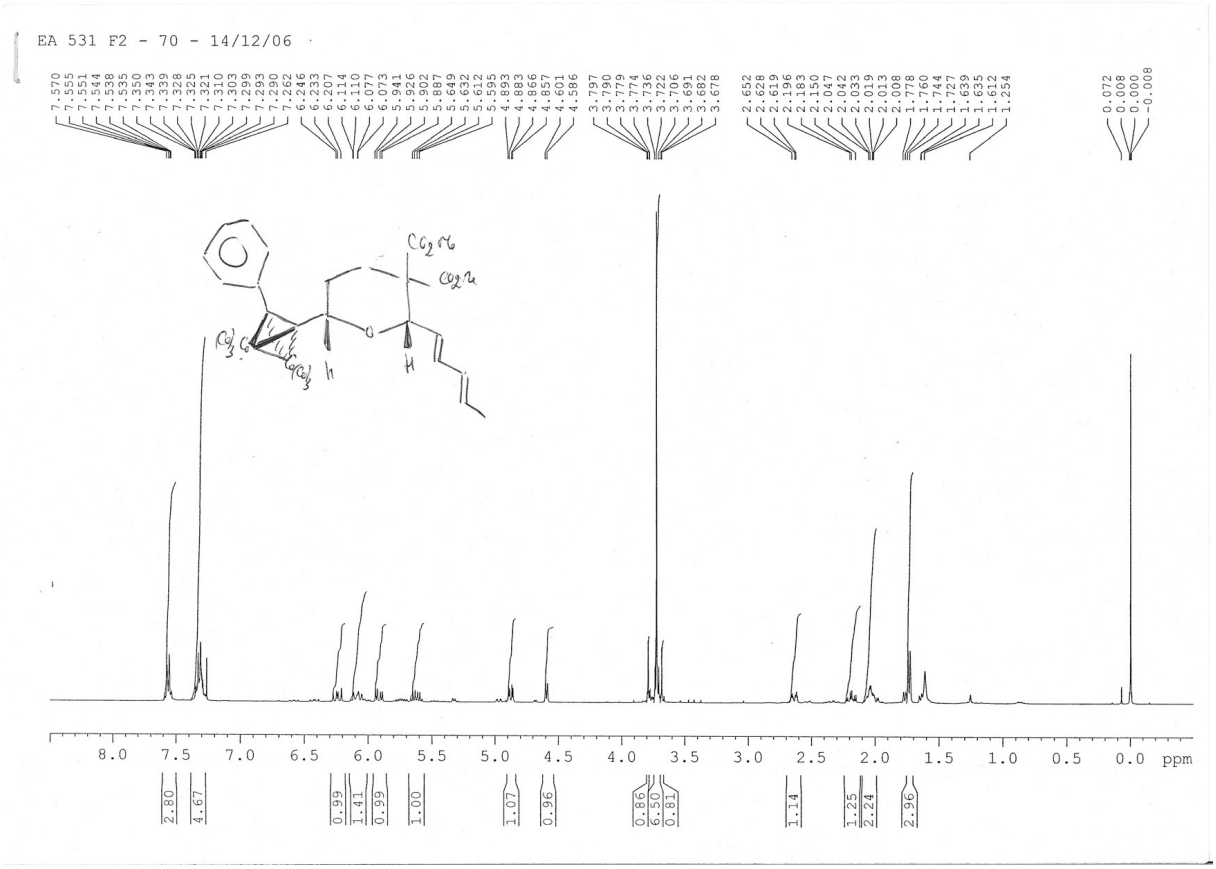

EA 523 F1 - 170 - 05/12/06
ppm
199.344
171.583 169.820 169.747 169.244
137.882 137.679 135.999 129.873 129.775 129.145 129.019 128.911 128.802 128.594 128.329 128.207 127.982 127.890 127.782 127.199 126.918 126.311
96.216
90.052 84.892 78.931 78.806 77.343 77.228 77.025 76.708
58.437 56.635 53.256 53.087 52.979 52.864 52.651 52.048
32.842 29.941 29.710
17.667 15.672
1.028 -0.000
ppm 200 180 160 140 120 100 80 60 40 20 0

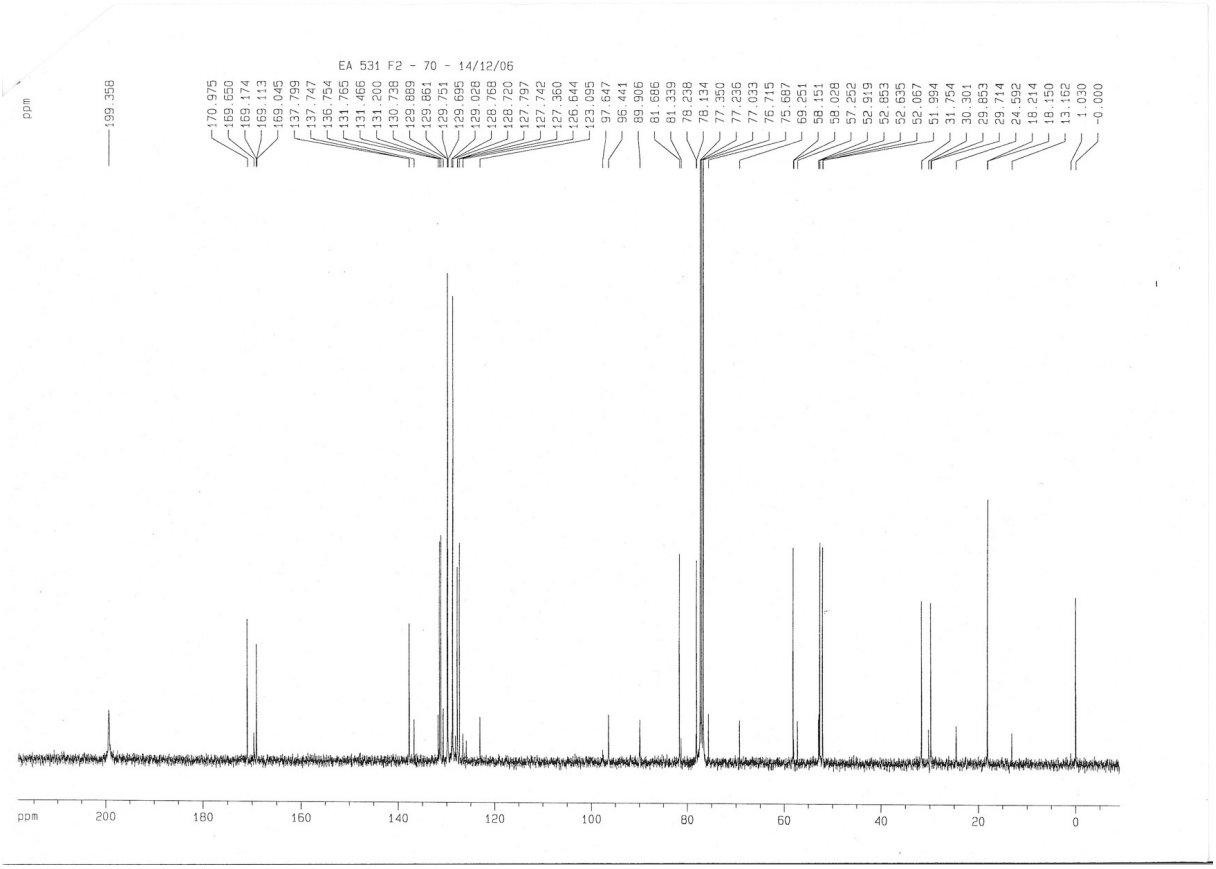
Compound 14



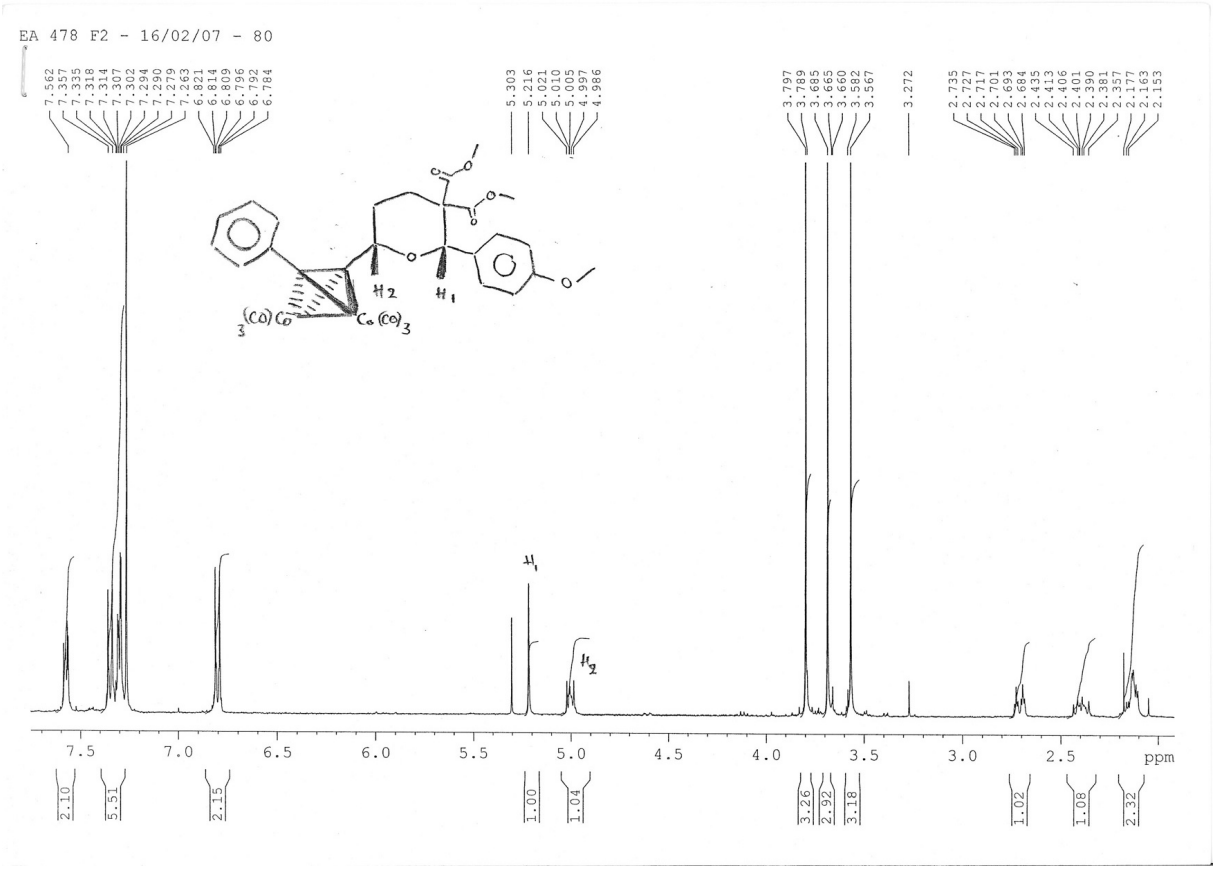


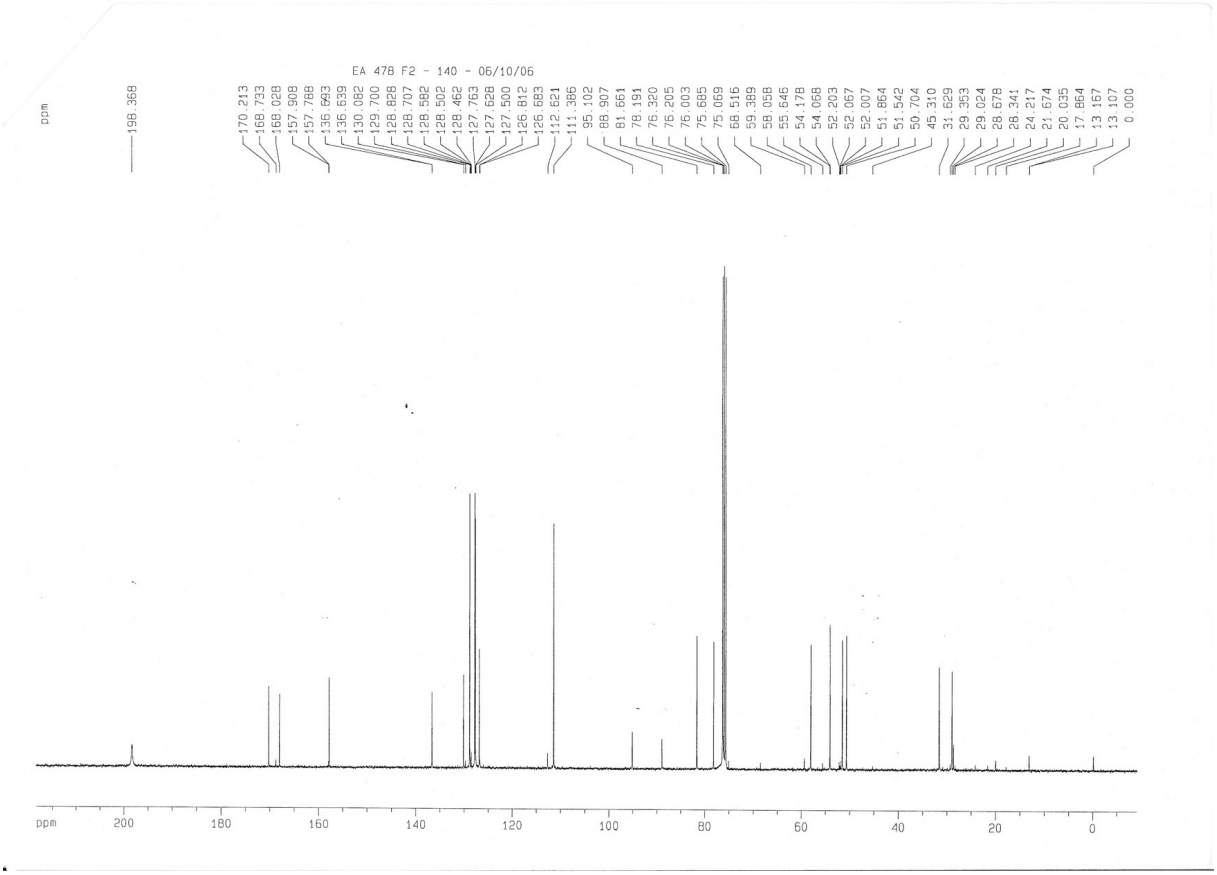
Compound 15


EA 531 F2 - 70 - 14/12/06
7.570
7.555
7.551
7.544
7.538
7.355
7.350
7.343
7.339
7.328
7.325
7.321
7.310
7.303
7.299
7.293
7.290
7.262
6.246
6.233
6.207
6.114
6.110
6.077
6.073
5.941
5.926
5.902
5.887
5.649
5.632
5.612
5.595
4.893
4.883
4.866
4.857
4.601
4.586
3.797
3.790
3.779
3.774
3.736
3.722
3.706
3.691
3.682
3.678
2.652
2.628
2.619
2.196
2.183
2.150
2.047
2.042
2.033
2.019
2.013
2.008
1.778
1.760
1.744
1.727
1.639
1.635
1.612
1.254
0.072
0.008
0.000
-0.008
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.80
4.67
0.99
1.41
0.99
1.00
1.07
0.96
0.86
6.50
0.81
1.14
1.25
2.24
2.96

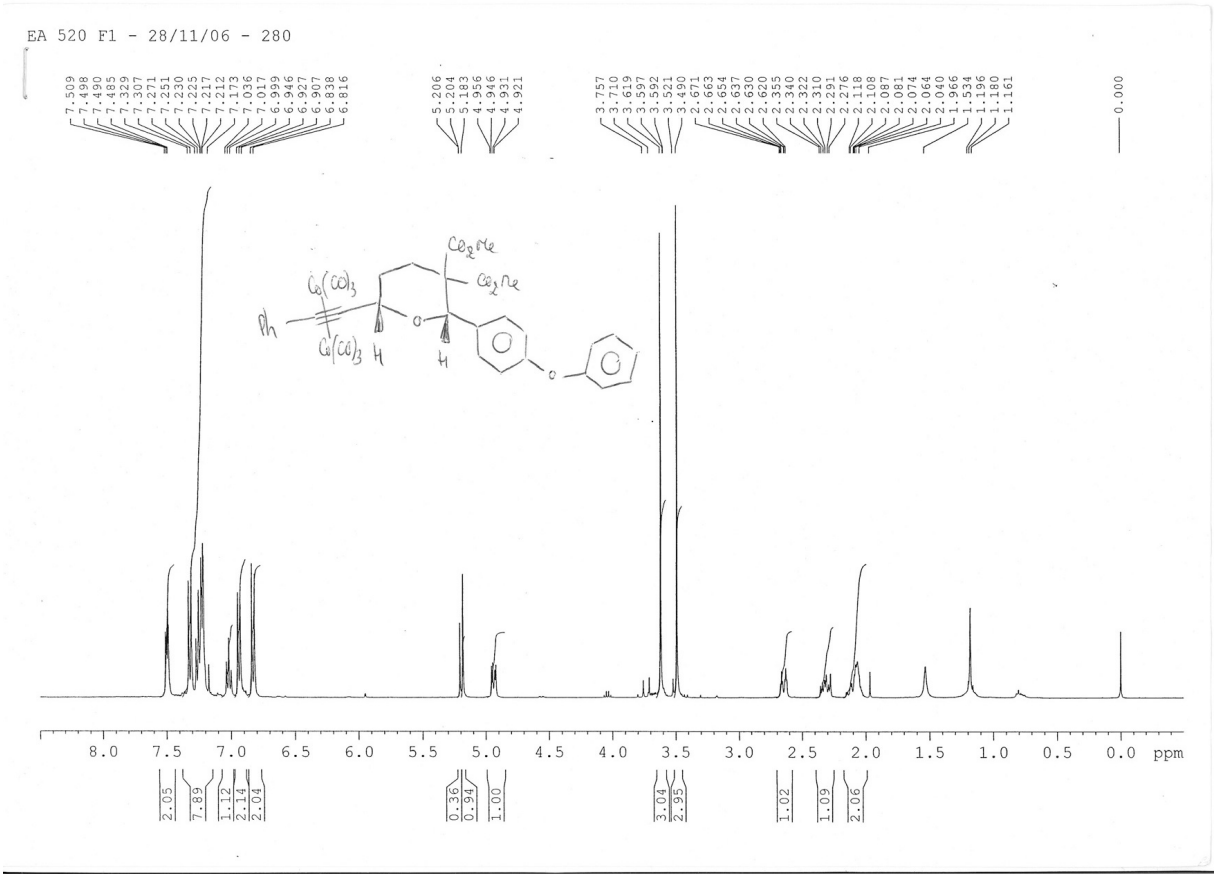

EA 531 F2 - 70 - 14/12/06
ppm
199.358
170.975
169.650
169.174
169.113
169.045
137.799
137.747
136.754
131.765
131.466
131.200
130.738
129.889
129.861
129.751
129.695
129.028
128.768
128.720
127.797
127.742
127.360
126.644
123.095
97.647
96.441
89.906
81.686
81.339
78.238
78.134
77.350
77.236
77.033
76.715
75.687
69.251
58.151
58.028
57.252
52.919
52.853
52.635
52.067
51.984
31.754
30.301
29.853
29.714
24.592
18.214
18.150
13.162
1.030
-0.000
ppm
200
180
160
140
120
100
80
60
40
20
0

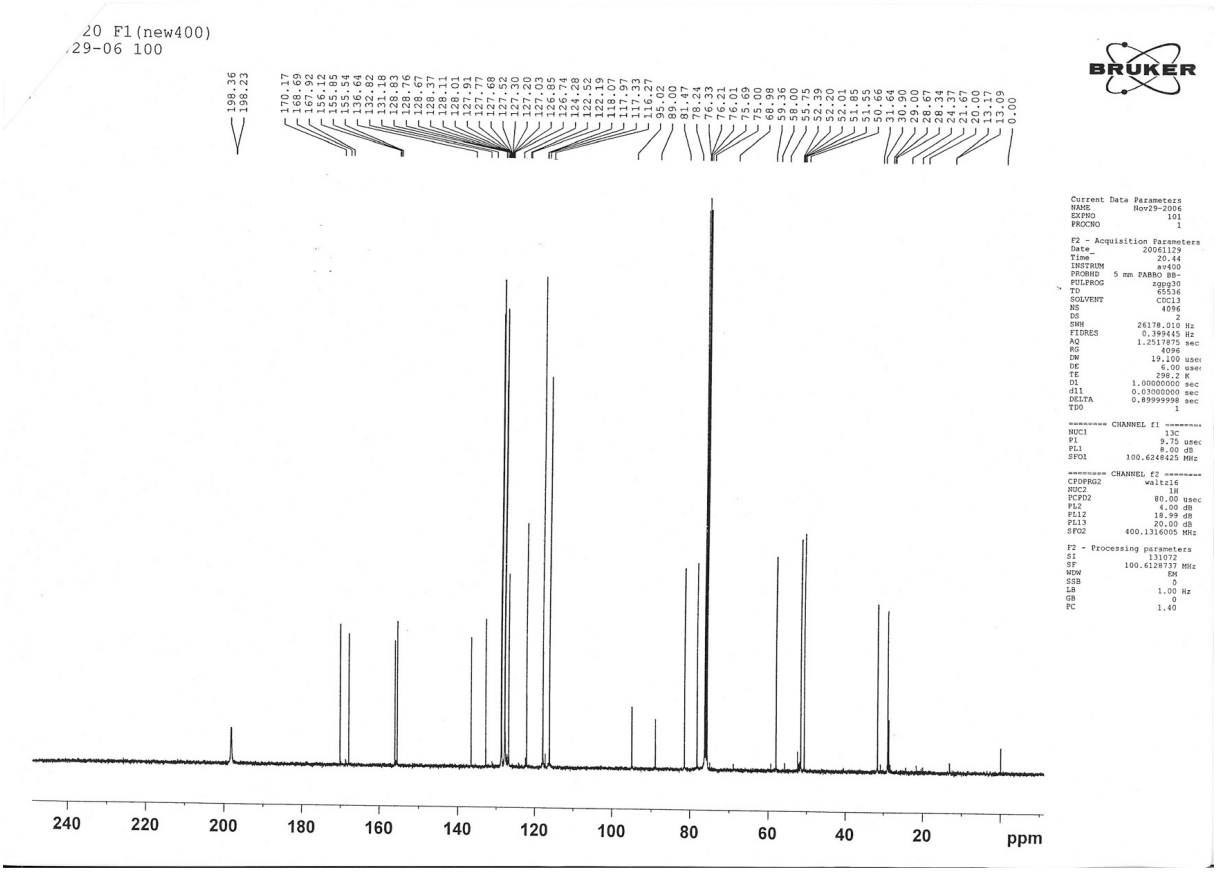
Compound 16


EA 478 F2 - 16/02/07 - 80
7.562
7.357
7.335
7.318
7.314
7.307
7.302
7.294
7.290
7.279
7.263
6.821
6.814
6.809
6.796
6.792
6.784
5.303
5.216
5.021
5.010
5.005
4.997
4.986
3.797
3.789
3.685
3.665
3.660
3.582
3.567
3.272
2.735
2.727
2.717
2.701
2.693
2.684
2.435
2.413
2.406
2.401
2.390
2.381
2.377
2.163
2.153
H2
H1
(CO)3Co
Co(CO)3
H1
H2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
2.10
5.51
2.15
1.00
1.04
3.26
2.92
3.18
1.02
1.08
2.32

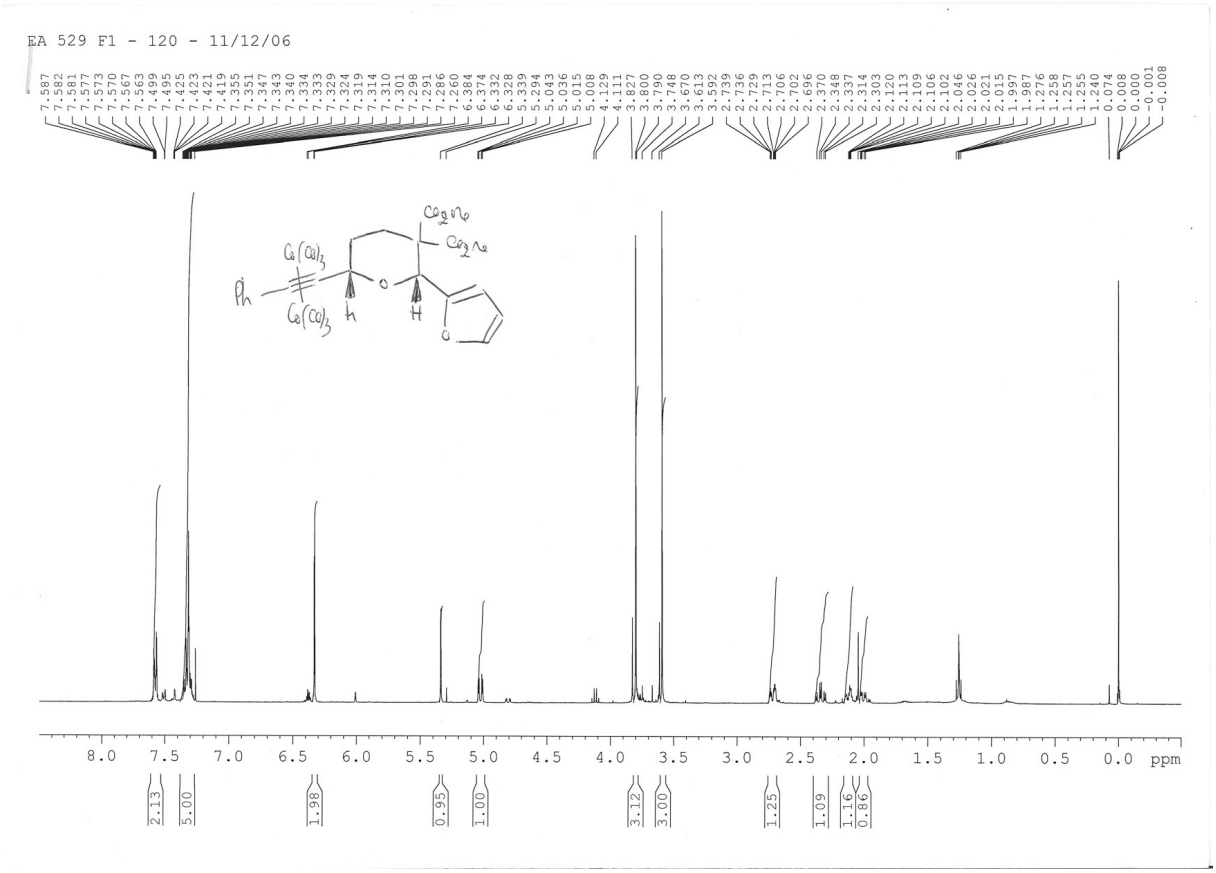

EA 478 F2 - 140 - 06/10/06
ppm
198.368
170.213
168.733
168.028
157.908
157.788
136.693
136.639
130.082
129.700
128.828
128.707
128.582
128.502
128.462
127.763
127.628
127.500
126.812
126.683
112.621
111.386
95.102
88.907
81.661
78.191
76.320
76.205
76.003
75.685
75.069
68.516
59.389
58.058
55.646
54.178
54.068
52.203
52.067
52.007
51.864
51.542
50.704
45.310
31.629
29.353
29.024
28.678
28.341
24.217
21.674
20.035
17.864
13.167
13.107
0.000
ppm
200
180
160
140
120
100
80
60
40
20
0

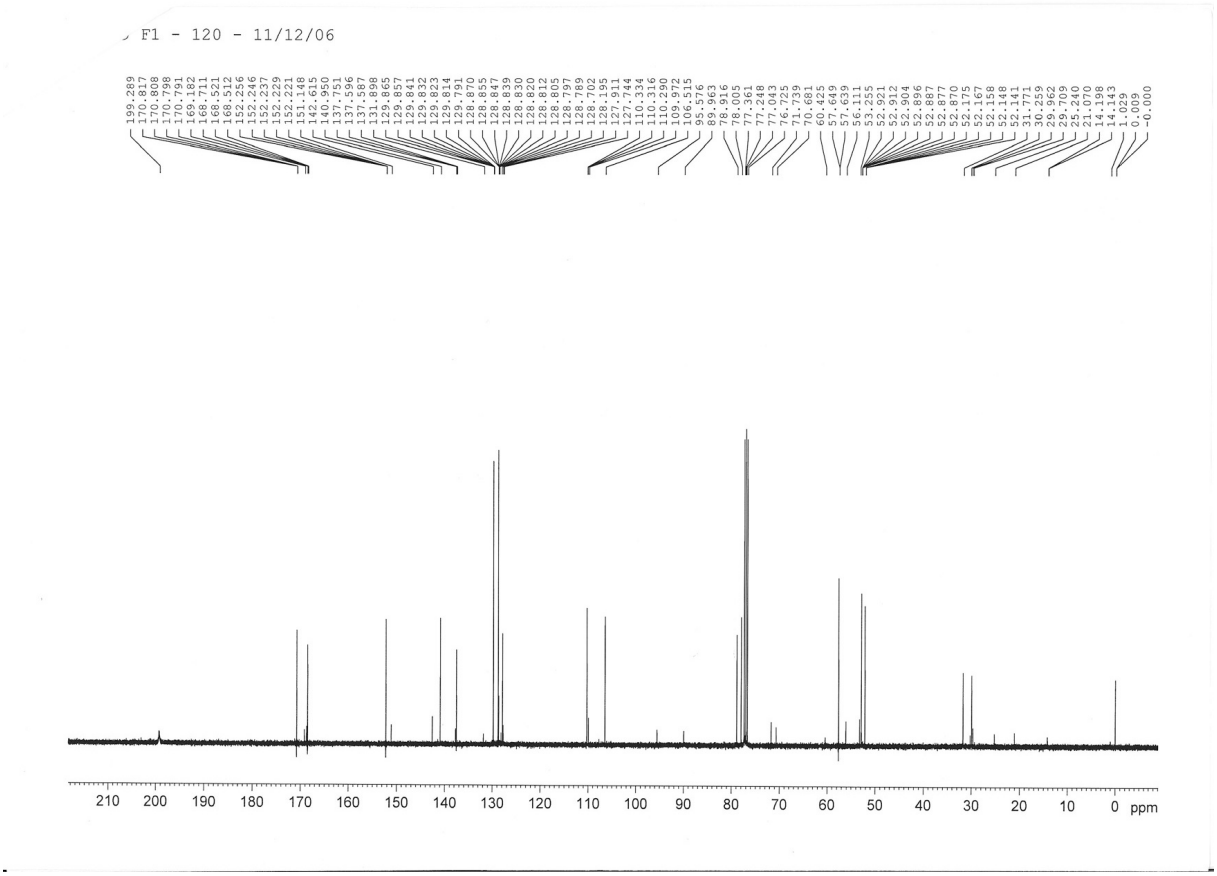
Compound 17


EA 520 F1 - 28/11/06 - 280
7.509
7.498
7.490
7.485
7.329
7.307
7.251
7.230
7.225
7.217
7.212
7.173
7.036
7.017
6.999
6.946
6.927
6.907
6.838
6.816
5.206
5.204
5.183
4.956
4.946
4.931
4.921
3.757
3.710
3.619
3.597
3.592
3.521
3.490
2.671
2.663
2.654
2.637
2.630
2.620
2.355
2.340
2.322
2.310
2.291
2.276
2.118
2.108
2.087
2.081
2.074
2.064
2.040
1.966
1.534
1.196
1.180
1.161
0.000
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.05
7.89
1.12
2.14
2.04
0.36
0.94
1.00
3.04
2.95
1.02
1.09
2.06

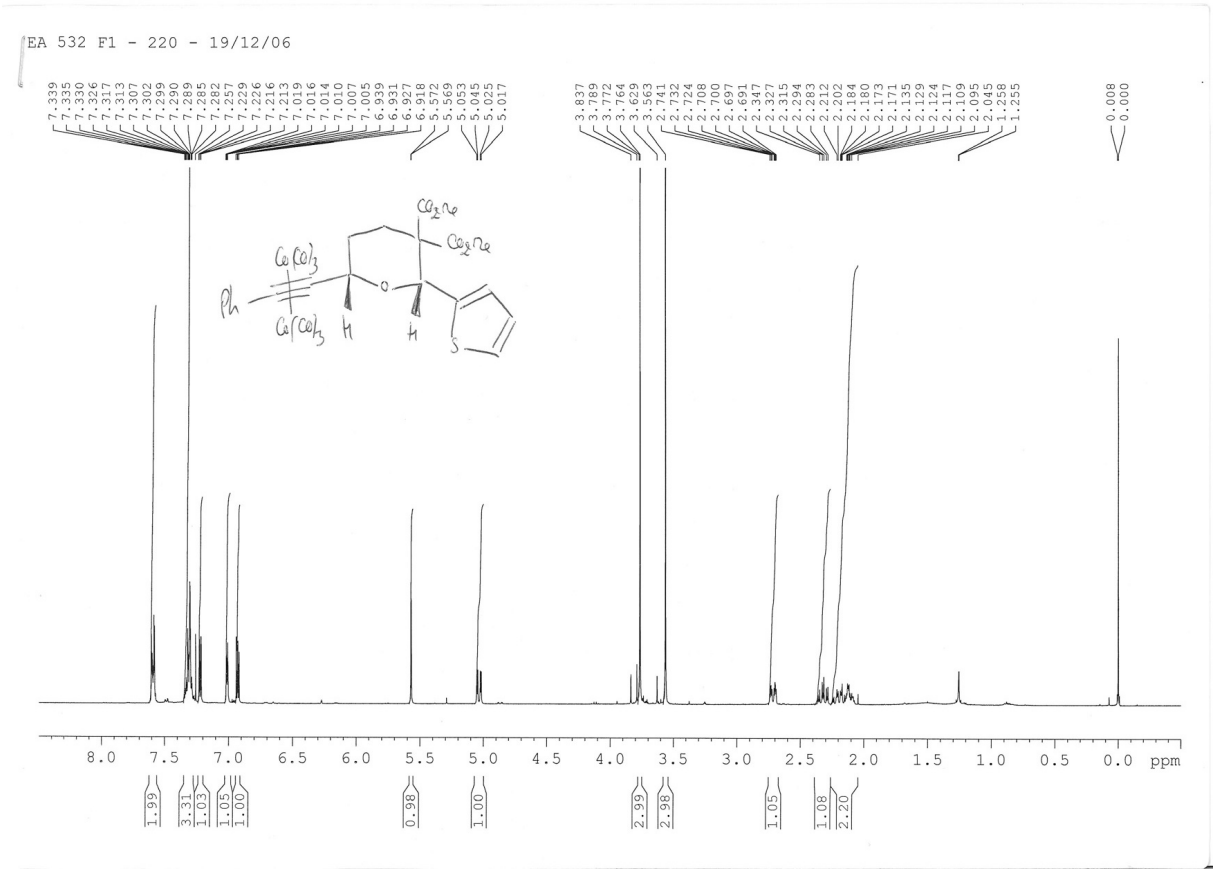

20 F1(new400)
29-06 100
BRUKER
198.36
198.23
170.17
168.69
167.72
156.12
155.85
155.54
136.64
132.82
131.18
128.83
128.76
128.67
128.37
128.11
128.01
127.91
127.77
127.68
127.52
127.30
127.20
127.03
126.85
126.74
122.28
122.22
122.19
118.07
117.97
117.33
116.27
95.02
90.00
81.47
78.24
76.33
76.21
76.01
75.69
75.00
63.88
59.36
58.00
55.75
52.39
52.20
52.01
51.85
51.55
50.66
31.64
30.90
29.00
28.67
24.34
24.17
21.67
20.00
13.17
13.09
0.00
240
220
200
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME Nov29-2006
EXPNO 101
PROCNO 1
F2 - Acquisition Parameters
Date_ 20061129
Time 20.44
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4096
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 4096
DW 19.100 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 2.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6128737 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

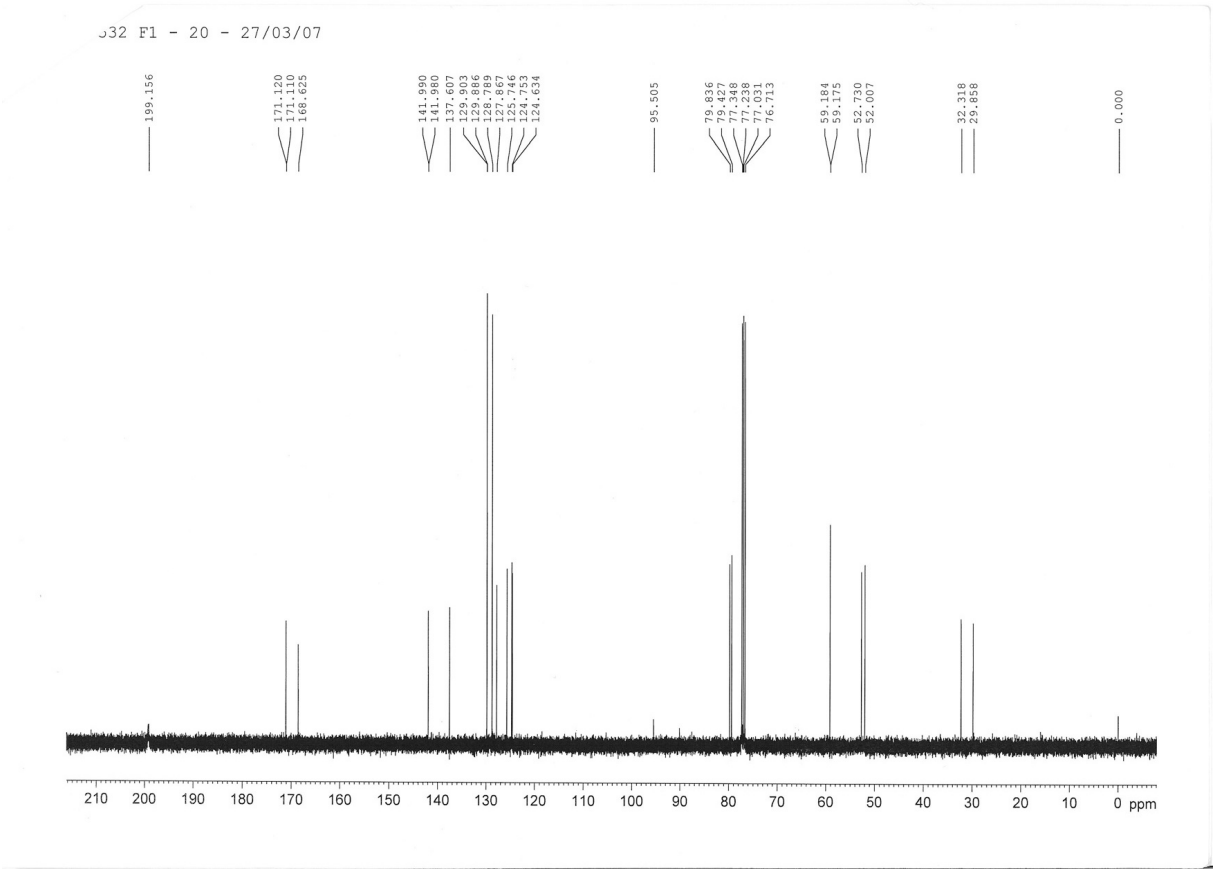
Compound 18


EA 529 F1 - 120 - 11/12/06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.13 5.00 1.98 0.95 1.00 3.12 3.00 1.25 1.09 1.16 0.86

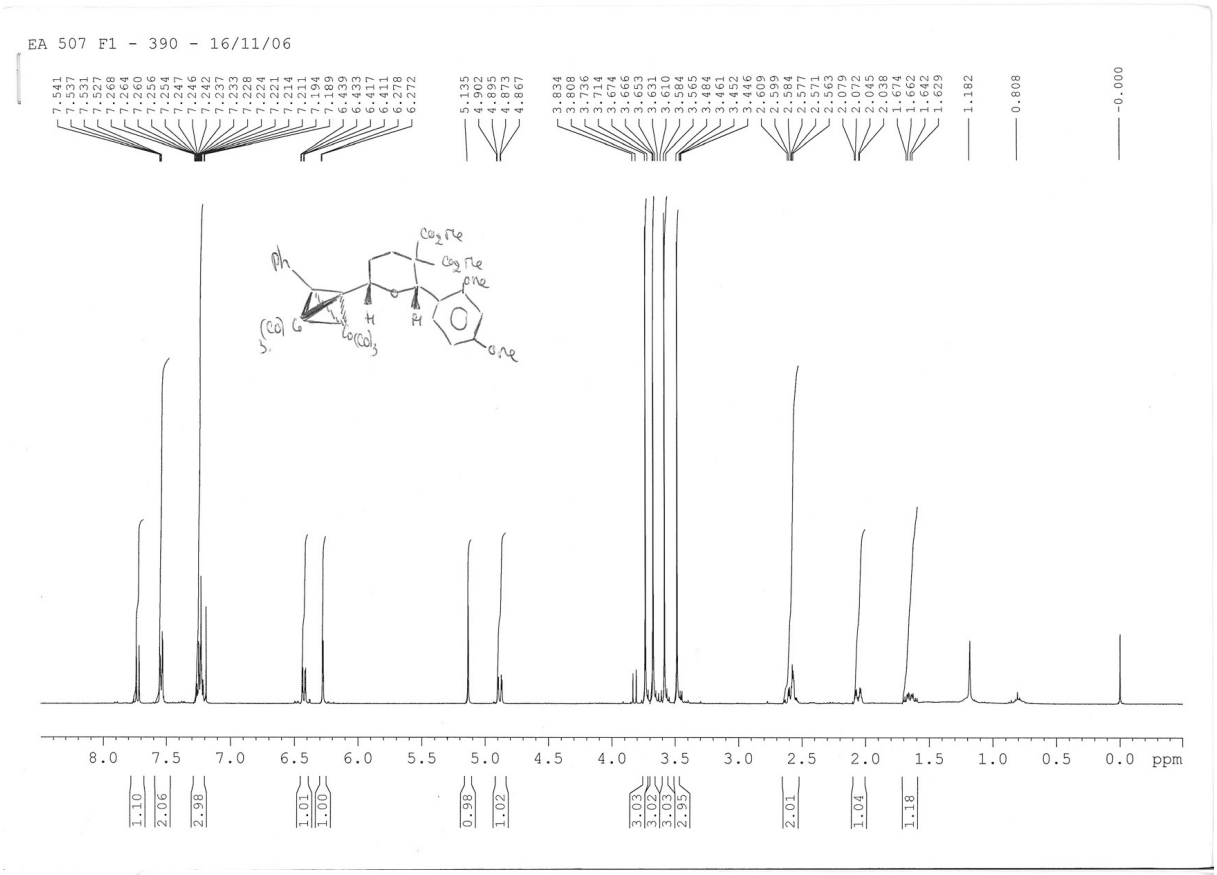

F1 - 120 - 11/12/06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

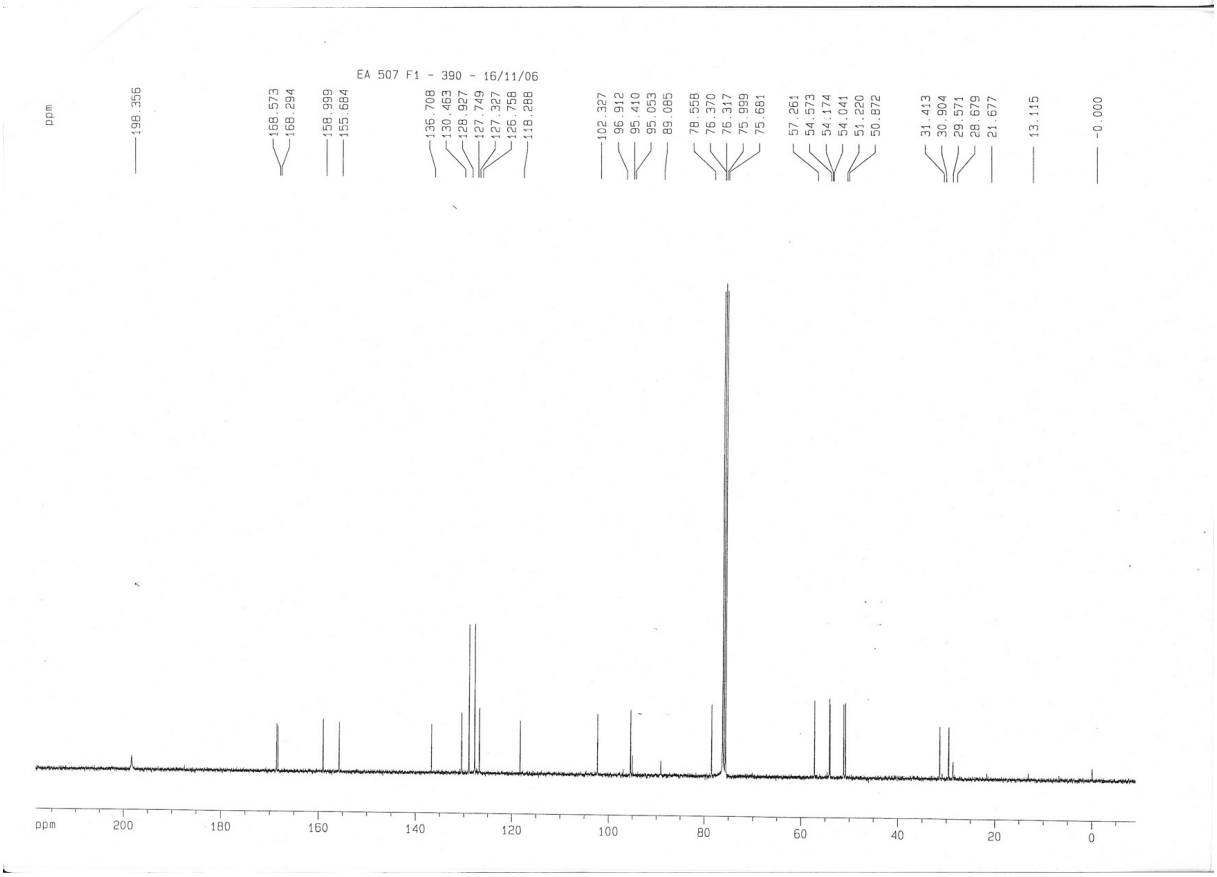
Compound 19


EA 532 F1 - 220 - 19/12/06
7.339
7.335
7.330
7.326
7.317
7.313
7.307
7.302
7.299
7.290
7.289
7.285
7.282
7.257
7.229
7.226
7.216
7.213
7.019
7.016
7.014
7.010
7.007
7.005
6.939
6.931
6.927
6.918
5.572
5.569
5.053
5.045
5.025
5.017
3.837
3.789
3.772
3.764
3.629
3.563
2.741
2.732
2.724
2.708
2.700
2.697
2.691
2.347
2.327
2.315
2.294
2.283
2.212
2.202
2.184
2.180
2.173
2.171
2.135
2.129
2.124
2.117
2.109
2.095
2.045
1.258
1.255
0.008
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.99
3.31
1.03
1.05
1.00
0.98
1.00
2.99
2.98
1.05
1.08
2.20

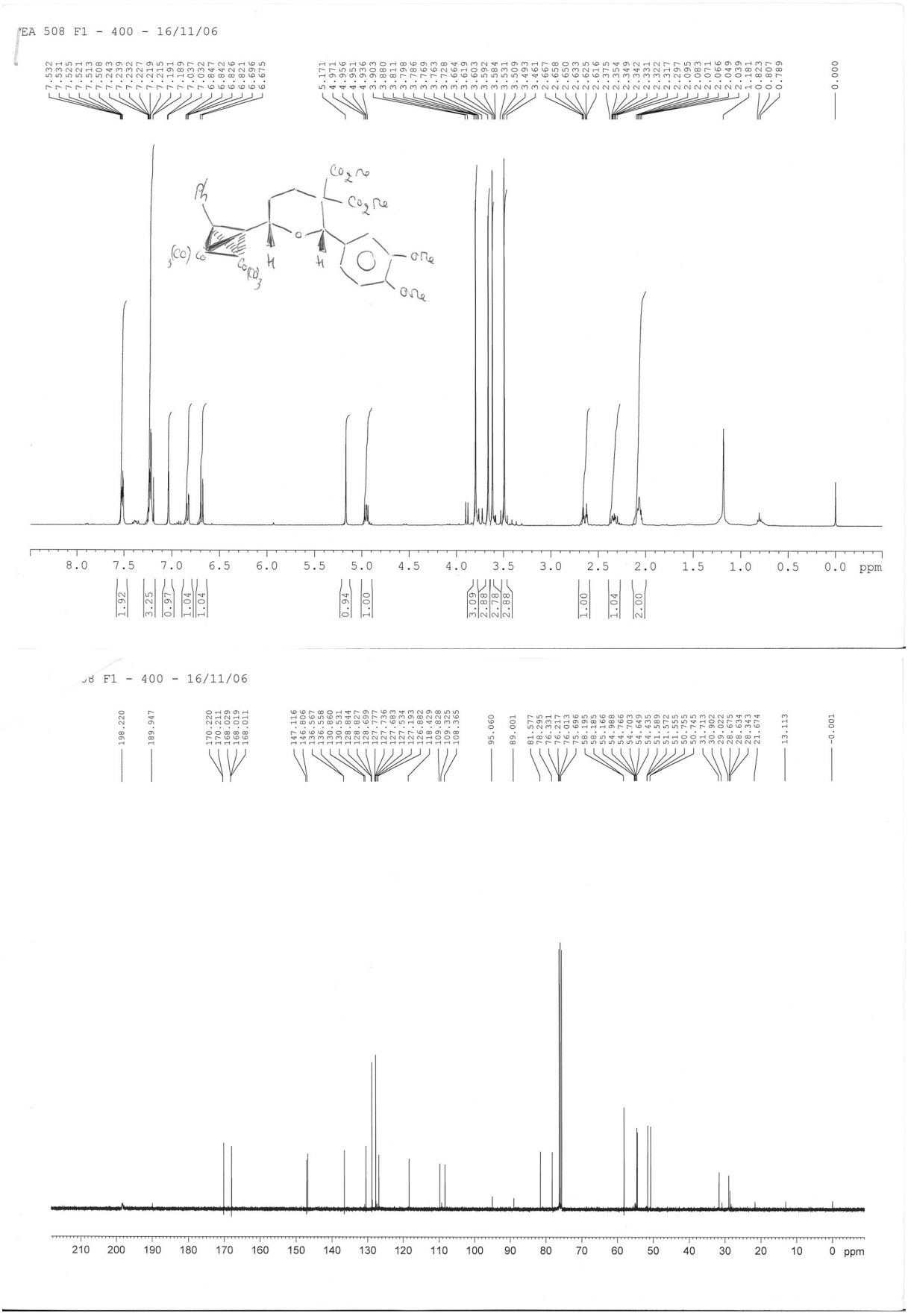

532 F1 - 20 - 27/03/07
199.156
171.120
171.110
168.625
141.990
141.980
137.607
129.903
129.886
129.689
128.787
125.746
124.753
124.634
95.505
79.836
79.427
77.348
77.238
77.031
76.713
59.184
59.175
52.730
52.007
32.318
29.858
0.000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Compound 20

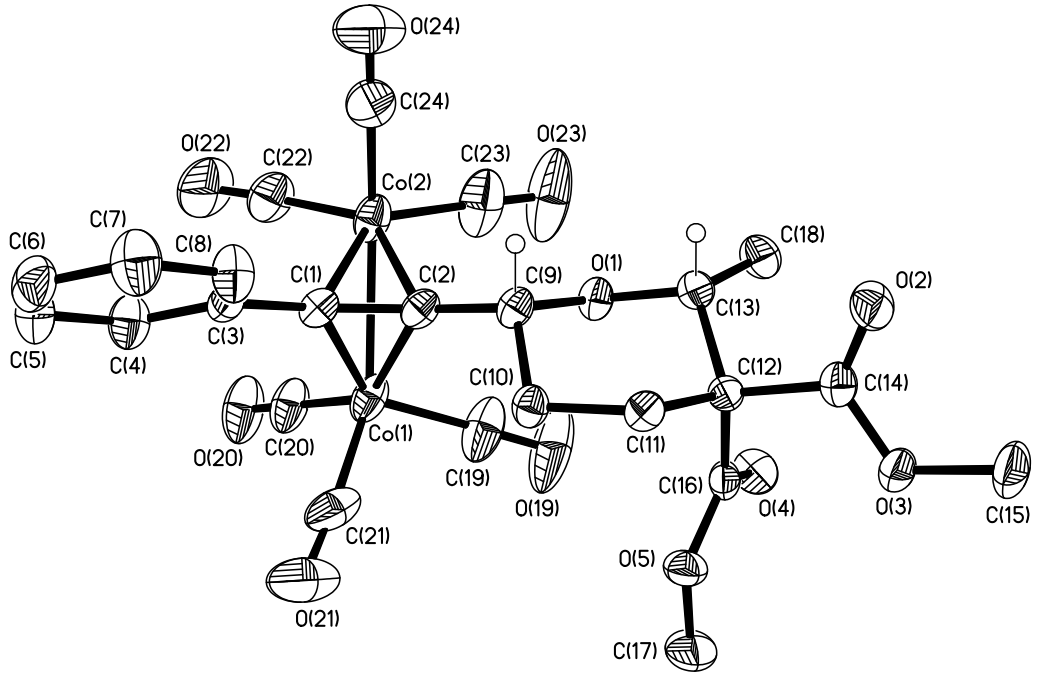

EA 507 F1 - 390 - 16/11/06
7.541
7.537
7.531
7.527
7.268
7.264
7.260
7.254
7.247
7.246
7.242
7.237
7.233
7.228
7.224
7.221
7.214
7.211
7.194
7.189
6.439
6.433
6.417
6.411
6.278
6.272
5.135
4.902
4.895
4.873
4.867
3.834
3.808
3.736
3.714
3.674
3.666
3.653
3.631
3.610
3.584
3.565
3.484
3.461
3.452
3.446
2.609
2.599
2.584
2.577
2.571
2.563
2.079
2.072
2.045
2.038
1.674
1.662
1.642
1.629
1.182
0.808
-0.000
Ph
CO2Me
CO2Me
OMe
OMe
(CO)3Cr
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.10
2.06
2.98
1.01
1.00
0.98
1.02
3.03
3.02
3.03
2.95
2.01
1.04
1.18


EA 507 F1 - 390 - 16/11/06
ppm
198.356
168.573
168.294
158.999
155.684
136.708
130.463
128.927
127.749
127.327
126.758
118.288
102.327
96.912
95.410
95.053
89.085
78.558
76.370
76.317
75.999
75.681
57.261
54.573
54.174
54.041
51.220
50.872
31.413
30.904
29.571
28.679
21.677
13.115
-0.000
ppm
200
180
160
140
120
100
80
60
40
20
0

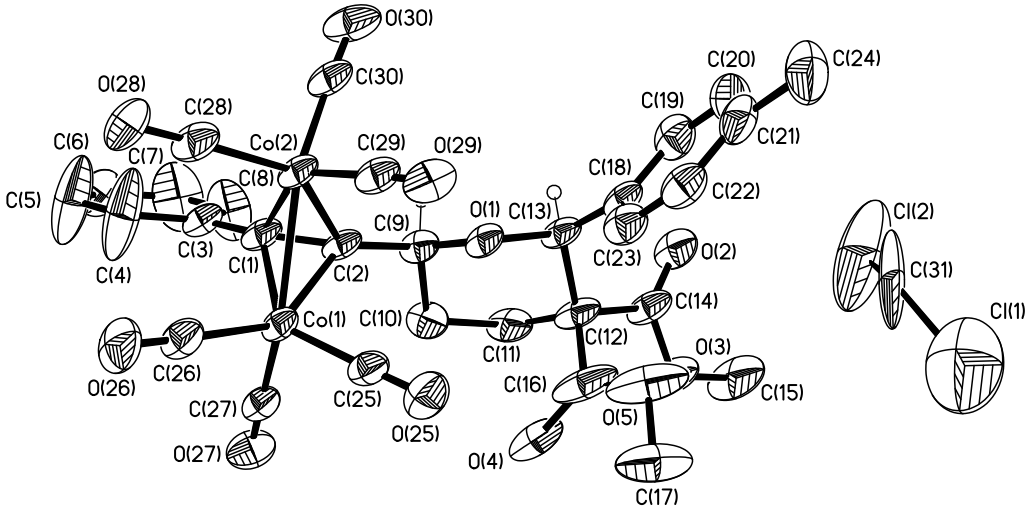
Compound 21


EA 508 F1 - 400 - 16/11/06
7.532 7.531 7.525 7.521 7.513 7.508 7.243 7.239 7.232 7.227 7.219 7.215 7.191 7.189 7.037 7.032 6.847 6.842 6.826 6.821 6.696 6.675
5.171 4.971 4.956 4.951 4.936 3.903 3.880 3.811 3.798 3.786 3.769 3.763 3.728 3.664 3.619 3.603 3.592 3.584 3.531 3.509 3.493 3.461 2.667 2.658 2.650 2.633 2.625 2.616 2.375 2.354 2.349 2.342 2.331 2.322 2.317 2.297 2.095 2.083 2.071 2.066 2.049 2.039 1.181 0.823 0.807 0.789
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.92 3.25 0.97 1.04 1.04 0.94 1.00 3.09 2.88 2.78 2.88 1.00 1.04 2.00
198.220 189.947 170.220 170.211 168.021 168.019 168.011 147.116 146.806 136.568 130.860 130.531 128.844 128.827 128.699 127.776 127.737 127.683 127.534 127.193 126.882 118.429 109.828 109.325 108.365 95.060 89.001 81.577 78.295 76.331 76.217 76.013 75.696 58.195 55.185 55.166 54.988 54.766 54.703 54.649 54.435 51.599 51.572 51.555 50.755 50.745 31.713 30.902 29.022 28.675 28.634 28.343 21.674 13.113 -0.001
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

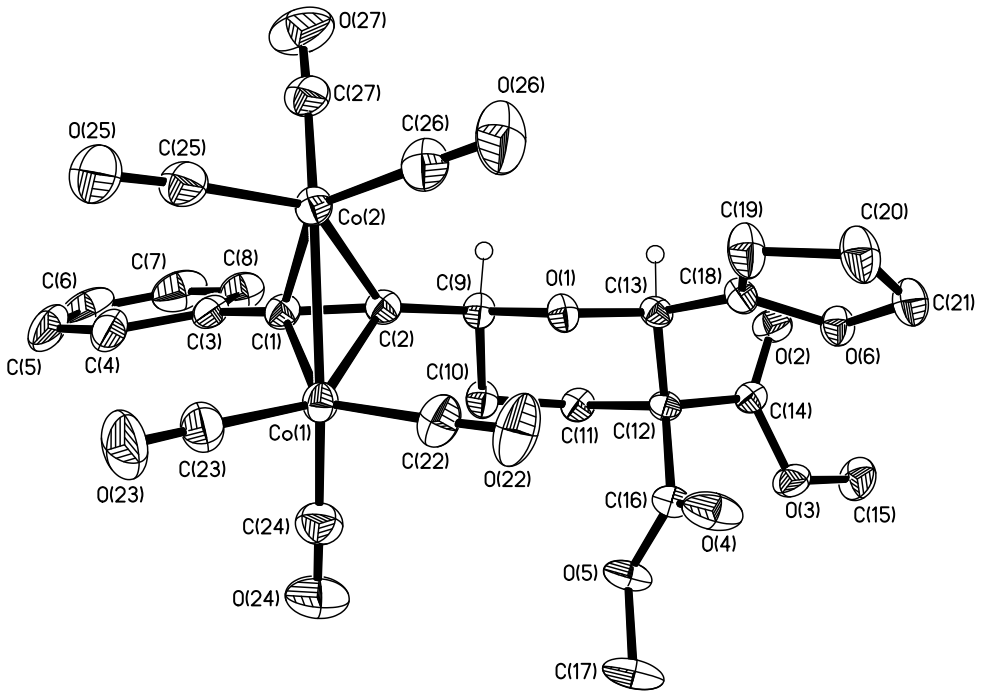
X-ray Crystallography ESI.



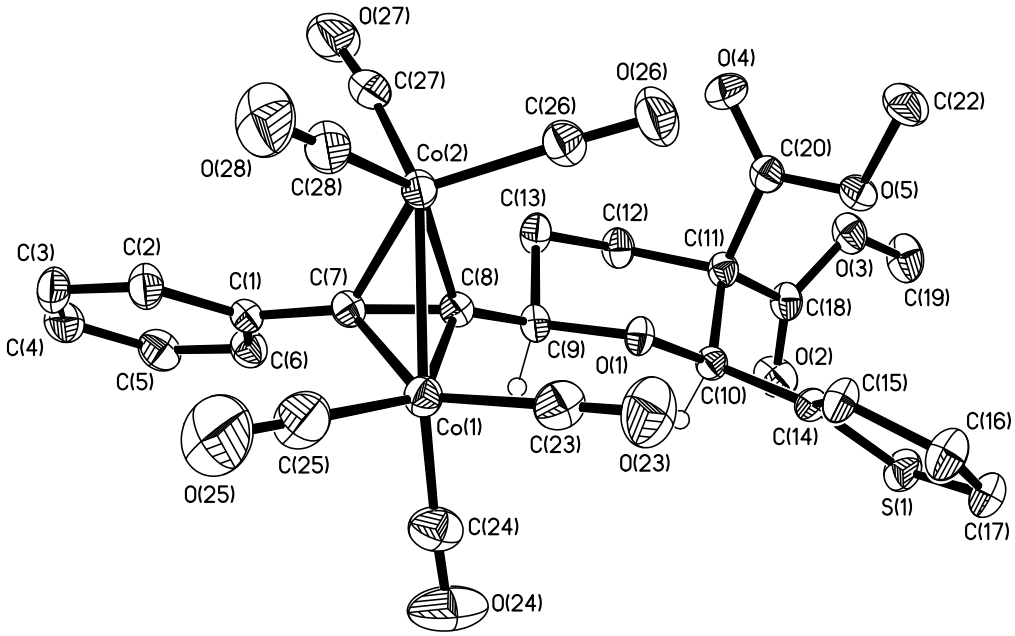
ESIFIG1. Ellipsoid plot at 50% probability level for compound **8**. Most H atoms omitted for clarity



ESIFIG2. Ellipsoid plot at 50% probability level for compound **10**·CH_2Cl_2. Minor disorder components and most H atoms omitted for clarity.



ESIFIG3. Ellipsoid plot at 50% probability level for compound **18**. Most H atoms omitted for clarity.



ESIFIG4. Ellipsoid plot at 50% probability level for compound **19**. Most H atoms omitted for clarity.