Supporting Information

Gold(I)-catalysed Synthesis of Conjugated Trienes

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1. General Experimental Section

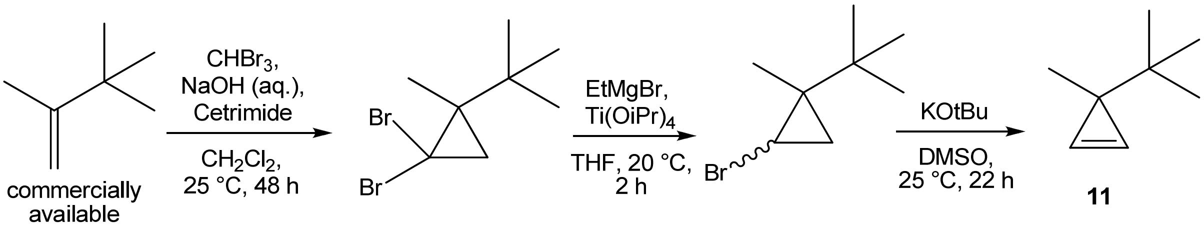
All reactions were performed under an N_2 atmosphere unless otherwise stated. ^{1}H NMR spectra were recorded on Bruker AC200, AV 300, DPX 400 and AV 400 spectrometers at 200, 300 and 400 MHz respectively and referenced to residual solvent. ^{13}C NMR spectrum were recorded using the same spectrometers at 50, 75 and 100 MHz respectively. Chemical shifts (δ in ppm) were referenced to tetramethylsilane (TMS) or to residual solvent peaks ($CDCl_3$ at δ_H 7.26). *J* values are given in Hz and s, d, dd, t, q and m abbreviations correspond to singlet, doublet, doublet of doublet, triplet, quartet and multiplet. Mass spectra were obtained at the EPSRC National Mass Spectrometry Service Centre in Swansea. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat or as a chloroform solution to a diamond/ZnSe plate.

All glassware were oven dried. Flash column chromatography was carried out using Matrix silica gel 60 from Fisher Chemicals and TLC was performed using Merck silica gel 60 F254 precoated sheets and visualised by UV (254 nm) or stained by the use of aqueous acidic $KMnO_4$ or aqueous acidic ammonium molybdate as appropriate. Dichloromethane was purchased from Fisher and used without further purification.

2. Experimental Procedures

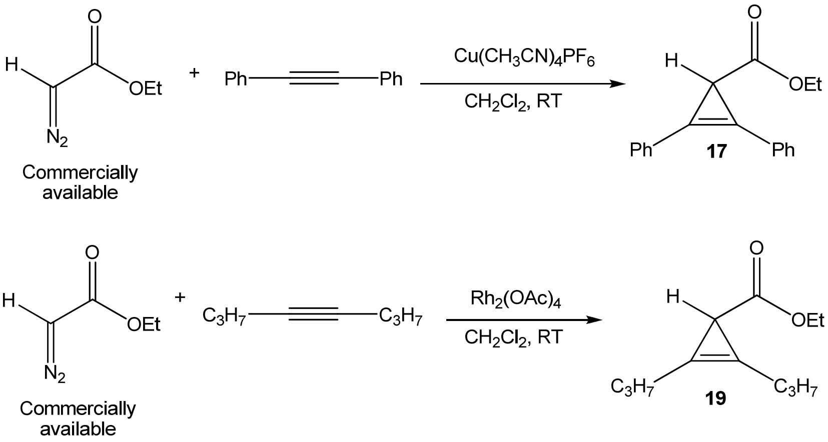
Starting Materials

Cyclopropenes **1,**[1] **5,**[2] **7,**[3] **9,**[1] **11**[4] **and 13**[5, 6] were synthesized following a general procedure by Gevorgyan (Scheme 1).[5, 6] For example:



Scheme 1

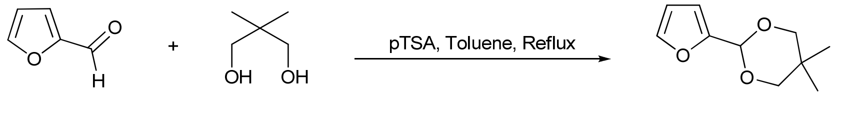
Cyclopropenes **15** ,[5, 6] **17**[7] and **19**[7] were made *via* cyclopropenation of the diazo precursor (Scheme 2).[7] For example:



Scheme 2

Furans **23** used in Table 3 were commercially available and used as purchased, apart from the acetal substituted furans shown below.

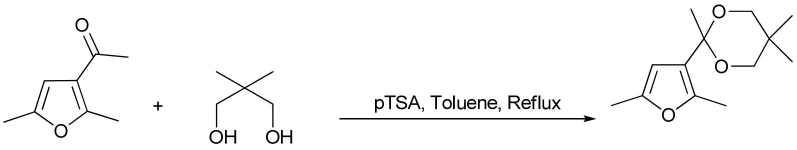
Preperation of 2-(furan-2-yl)-5,5-dimethyl-1,3-dioxane[8]



To a stirred solution of furanaldehyde (1.7 ml, 20 mmol) in dry toluene (30 ml), neopentyl glycol (2.6 g, 25mmol) and para-toluene sulphonic acid (30 mg, 0.17mmol) were added. Dean stark apparatus was attached and the mixture heated to reflux (2 hours). Once all the water was removed the dark solution was washed with 2% Na_2CO_3 and extracted with diethyl ether (3 x 50ml). The combined organic layers were washed once more with 2% Na_2CO_3, brine, dried over Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (95 % n-pentane, 5 % diethyl ether, 1% triethylamine) to yield 2-(furan-2-yl)-5,5-dimethyl-1,3-dioxane (3.54 g, 19.6 mmol, 98%) as a pale yellow liquid.

Rf (95% n-pentane, 5% diethyl ether) 0.40. ν_{max}/cm^{-1} 2956 w (C-H), 1610 vw (C=C), 1149 m (C-O), 1099 s (C-O);δ_H (400 MHz, $CDCl_3$) 2 x 7.43 (1H, d, *J* = 0.9, O-$\underline{H}$C=CH), 2 x 6.52 (1H, t, *J* = 0.9, O-HC=C$\underline{H}$), 2 x 6.40 (1H, d, *J* = 1.8, HC-(CH)=C), 5.51 (1H, s, $\underline{H}$C-$(O)_2$), 3.79 (2H, d, *J* = 11.2, O-CH_2 (axial/equitorial)), 3.65 (2H, d, *J* = 11.2, O-CH_2 (axial/equitorial)), 1.31 (3H, s, C$\underline{H}_3$), 0.82 (3H, s,C$\underline{H}_3$); δ_C (100 MHz, $CDCl_3$) 151.0 (C), 142.5 (CH), 110.2 (CH), 107.4 (CH), 96.1 (CH), 77.5 (CH_2), 23.0 (CH_3), 21.9 (CH_3); HRMS $[M+H]^+$ = 183.1012 required [M+H] = 183.1016.

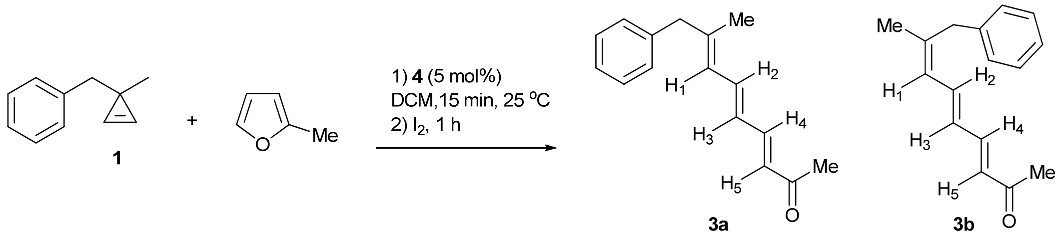
Preperation of 2-(2,5-dimethylfuran-3-yl)-2,5,5-trimethyl-1,3-dioxane



To a stirred solution of 3 acetyl-2,5-dimethylfuran (2.66 ml, 20 mmol) in dry toluene (30 ml), neopentyl glycol (2.6g, 25 mmol) and para-toluene sulphonic acid (30 mg, 0.17 mmol) were added. Dean stark apparatus was attached and the mixture heated to reflux (3 hours). Once all the water was removed the dark solution was washed with 2% Na_2CO_3 and extracted with diethyl ether (3 x 20ml). The combined organic layers were washed once more with 2% Na_2CO_3, brine, dried over Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography (200:1 hexane / diethyl ether, 1% triethylamine) to yield 2-(2,5-dimethylfuran-3-yl)-2,5,5-trimethyl-1,3-dioxane **33** (1.07 g, 4.78 mmol, 24%) as a pale yellow liquid.

Rf (15:1 hexane / diethyl ether) 0.67. ν_{max}/cm^{-1} 2952 w (C-H), 1631 vw (C=C), 1601 s (C=C), 1177 s (C-O), 1081 m (C-O); δ_H (300 MHz, $CDCl_3$) 5.81 (1H, s, $\underline{H}$C=C), 3.53 (2H, d, J = 11.0, OC$\underline{H}_2$), 3.34 (2H, d, J = 11.0, OC$\underline{H}_2$), 2.24 (6H, s, C(C$\underline{H}_3)_2$), 1.50 (3H, s, C$\underline{H}_3$), 1.23 (3H, s, CH_3), 0.65 (3H, s, C$\underline{H}_3$); δ_C (100 MHz, $CDCl_3$) 149.5 (C), 146.3 (C), 119.9 (C), 106.6 (CH), 97.9 (C), 71.7 (CH_2), 30.2 (CH_3), 29.9 (C), 22.8 (CH_3), 21.89 (CH_3), 13.5 (CH_3), 12.2 (CH_3); HRMS $[M+H]^+$ = 225.1485 required [M+H] = 225.1485.

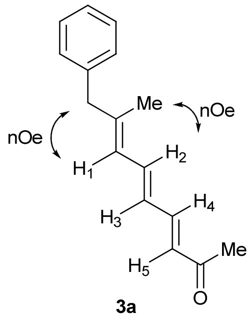
(3E,5E,7E)-8-Methyl-9-phenylnona-3,5,7-trien-2-one 3a, (3E,5E,7Z)-8-methyl-9-phenylnona-3,5,7-trien-2-one 3b



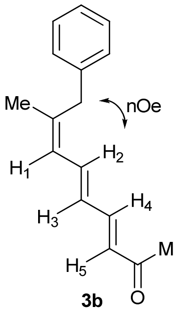
Catalyst **4** (11 mg, 1.40 x 10^{-5} mol) was added to a solution of ((1-methylcycloallyl)methyl)benzene **1** (39 mg, 0.271 mmol) and 2-methylfuran (38 μL, 0.424 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the reaction was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (16:1 n-pentane/diethyl ether, 1% triethylamine) to yield inseparable isomers (3E,5E,7E)-8-methyl-9-phenylnona-3,5,7-trien-2-one **3a** and (3E,5E,7Z)-8-methyl-9-phenylnona-3,5,7-trien-2-one **3b** (56 mg, 0.247 mmol, 91%) as a yellow oil.

Rf (9:1 n-pentane / diethyl ether) 0.20. ν_{max}/cm^{-1} 3027 w (C-H), 1662 m (C=O), 1634 m (C=C), 1600 s (C=C), 1570 m (C=C), 1494 w (Ar C=C), 1452 w (Ar C=C); δ_H (200 MHz, $CDCl_3$) 7.36 – 7.13 ("6H", m, **3a** + **3b** (Ar-H + H-4)), 7.01 (1H, dd, *J* = 14.7, 11.2, **3b** H-2) 6.87 (1H, dd, *J* = 14.8, 11.2, **3a** H-2), 6.35 (1H, dd, J = 14.7, 11.2, **3b** H-3), 6.28 (1H, dd, J = 14.8, 11.2, **3a** H-3), 6.15 (2H, d, J = 15.3, **3b** H-5 + H-1), 6.13 (1H, d, J = 15.3, **3a** H-5), 6.04 (1H, d, J = 11.2, **3a** H-1), 3.58 (2H, s, **3b** $C\underline{H}_2$), 3.43 (2H, s, **3a** $C\underline{H}_2$), 2.29 (3H, s, **3b** (CO)$C\underline{H}_3$), 2.28 (3H, s, **3a** (CO)$C\underline{H}_3$), 1.81 (3H, s, **3b** $C\underline{H}_3$)), 1.80 (3H, s, **3a** $C\underline{H}_3$)); δ_C (100 MHz, $CDCl_3$) 198.1 ($\underline{C}$=O), 144.3 (C), 143.8 (C), 143.7 (C), 143.6 (CH), 138.5 (C), 137.6 (CH), 137.3 (CH), 129.1 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.2 (CH), 128.2 (CH), 128.1 (CH), 126.3 (CH), 126.1 (CH), 126.0 (CH), 125.8 (CH), 46.2 (CH_2), 38.2 (CH_2), 26.9 (CH_3), 26.9 (CH_3), 23.8 (CH_3), 16.8 (CH_3); HRMS [M+H] = 227.1431 required [M+H] = 227.1430.

Stereochemistry confirmed by 400 MHz NOESY

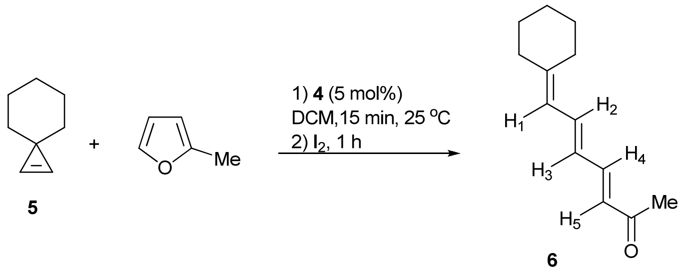


3a
Major



3b
Minor

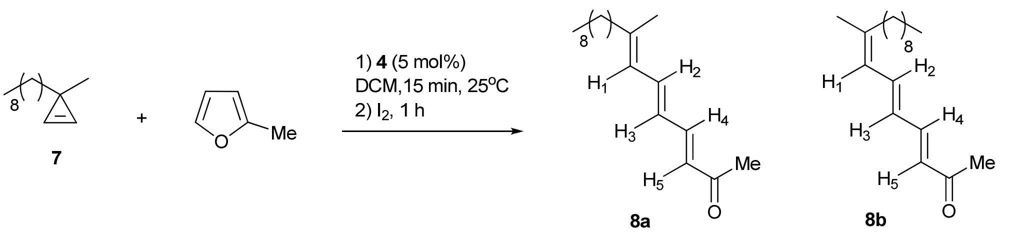
(3E,5E)-7-Cyclohexylidenehepta-3,5-dien-2-one, 6



Catalyst **4** (5 mg, 6.47 x 10^{-6} mol) was added to a solution of spiro[2.5]oct-1-ene **5** (13 mg, 0.123 mmol) and 2-methylfuran (11 μL, 0.123 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the mixture was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (10:1 n-pentane/diethyl ether, 1% triethylamine) to yield (3E,5E)-7-cyclohexylidenehepta-3,5-dien-2-one **6** (19 mg, 0.102 mmol, 83%) as a yellow oil.

Rf (10:1 n-pentane / diethyl ether) 0.19. ν_{max}/cm^{-1} 2931 s, 2857 m (C-H), 1711 s (C=O), 1667 s, 1630 s, 1595 m, (C=C); δ_H (400 MHz, $CDCl_3$) 7.20 (1H, dd, *J* = 15.3, 11.2, H-4), 6.91 (1H, dd, *J* = 14.7, 11.4, H-2), 6.25 (1H, dd, *J* = 14.7, 11.4, H-3), 6.11 (1H, d, *J* = 15.3, H-5), 5.93 (1H, d, *J* = 11.4, H-1), 2.36 (2H, t, *J* = 5.1, $C(CH_2)_2$), 2.28 (3H, s, (CO)$C\underline{H}_3$), 2.21 (2H, t, *J* = 5.1, $C(CH_2)_2$), 1.61 (6H, m, cyclo (CH_2 CH_2CH_2)); δ_C (100 MHz, $CDCl_3$) 198.4 ($\underline{C}$=O), 150.1 (C), 144.3 (CH), 137.7 (CH), 128.7 (CH), 128.1 (CH), 122.1 (CH), 37.7 (CH_2), 29.7 (CH_2), 28.6 (CH_3), 27.9 (CH_2), 27.2 (CH_2), 26.6 (CH_2); HRMS $[M+H]^+$ = 191.1430 required [M+H] = 191.1430.

(3E,5E,7E)-8-Methylheptadeca-3,5,7-trien-2-one 8a, (3E,5E,7Z)-8-methylheptadeca-3,5,7-trien-2-one 8b

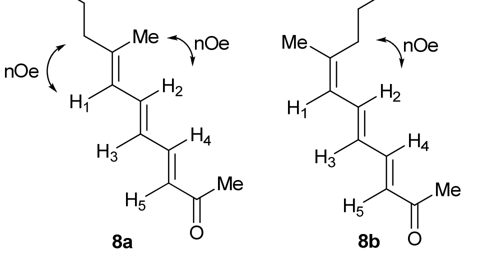


7 **8a** **8b**

Catalyst **4** (6 mg, 7.5 x 10^{-6} mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **7** (26 mg, 0.146 mmol) and 2-methylfuran (20 μL, 0.225 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the mixture was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1 % triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (20:1 n-pentane/diethyl ether, 1 % triethylamine) to yield inseparable isomers (3E,5E,7E)-8-methylheptadeca-3,5,7-trien-2-one **8a**, (3E,5E,7Z)-8-methylheptadeca-3,5,7-trien-2-one **8b** (2:1) (31 mg, 0.12 mmol, 82%) as a yellow oil.

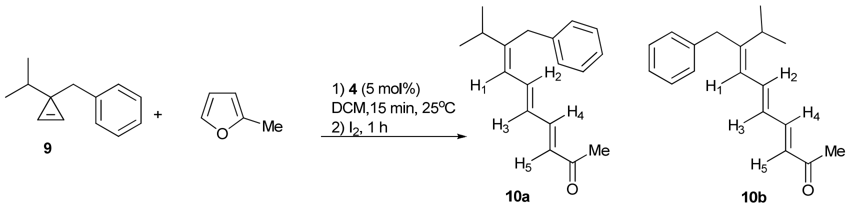
Rf (20:1 (n-pentane / diethyl ether)) 0.20. ν_{max}/cm^{-1} 2924 s, 2854 m (C-H), 1664 m (C=O), 1633 w, 1601 s, 1572 m, (C=C); δ_H (400 MHz, $CDCl_3$) 7.22 (1H, dd, *J* = 15.3, 11.2, (a + b) H-4), 6.88 (1H, dd, *J* = 14.7, 11.2, (a) H-2), 6.86 (1H, dd, *J* = 14.7, 11.2, (b) H-2), 6.25 (1H, dd, *J* = 14.2, 11.2, (a) H-3), 6.23 (1H, dd, *J* = 14.7, 11.2, (b) H-3), 6.12 (1H, d, *J* = 15.3, (a + b) H-5), 5.99 (1H, d, *J* = 11.2, (a + b) H-1), 2.29 (3H, s, (a + b) (CO)$C\underline{H}_3$), 2.25 (2H, t, *J* = 7.6, (b) C-$C\underline{H}_2$-CH_2), 2.13 (2H, t, *J* = 7.6, (a) C-$C\underline{H}_2$-CH_2), 1.87 (3H, s, (b) HC=C-$C\underline{H}_3$), 1.85 (3H, s, (a) HC=C-$C\underline{H}_3$), 1.26-1.46 (14H, m, (a + b) $(C\underline{H}_2)_7$), 0.90 (3H, t, *J* = 6.5, (a + b) CH_2-$C\underline{H}_3$); δ_C (100 MHz, $CDCl_3$) 198.4 ($\underline{C}$=O), 147.0 (C), 146.7 (C), 144.3 (CH), 138.5 (CH), 138.1 (CH), 128.8 (CH), 128.8 (CH), 128.0 (CH), 127.9 (CH), 125.4 (CH), 124.6 (CH), 40.3 (CH_2), 32.8 (CH_2), 31.9 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 28.4 (CH_2), 27.7 (CH_2), 27.2 (CH_2), 27.2 (CH_3), 24.3 (CH_3), 22.7 (CH_2), 17.1 (CH_3), 14.1 (CH_3); HRMS $[M+H]^+$ = 263.2373 required [M+H] = 263.2369.

Stereochemistry confirmed by 400 MHz NOESY



8a **8b**

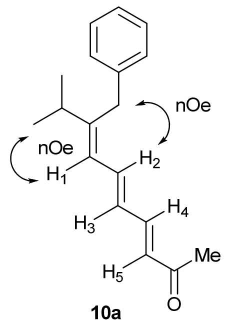
(3E,5E,7E)-8-Benzyl-9-methyldeca-3,5,7-trien-2-one 10a, (3E,5E,7Z)-8-benzyl-9-methyldeca-3,5,7-trien-2-one 10b



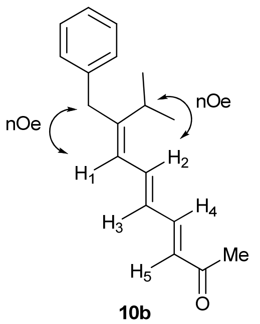
Catalyst **4** (8 mg, 1.08 x 10^{-5} mol) was added to a solution of ((1-isopropylcycloallyl)methyl)benzene **9** (37 mg, 0.215 mmol) and 2-methylfuran (29 μL, 0.323 mmol) in dichloromethane (0.8 mL). The reaction mixture was allowed to stir for 0.25 h at 25 °C. One crystal of iodine was added and continued to stir for 1.0 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1 % triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (11:1 n-pentane/diethyl ether, 1% triethylamine) to yield inseparable isomers (3E,5E,7E)-8-benzyl-9-methyldeca-3,5,7-trien-2-one **10a**, (3E,5E,7Z)-8-benzyl-9-methyldeca-3,5,7-trien-2-one **10b** (3.5:1 ratio) (50 mg, 0.195 mmol, 82%) as a yellow oil.

Rf (10:1 n-pentane / diethyl ether) 0.27. ν_{max}/cm^{-1} 2961 w (C-H), 1662 m (C=O), 1603 s (C=C), 1601 s (C=C), 1569 m, (C=C), 1493 w (Ar C=C), 1452 w (Ar C=C); δ_H (300 MHz, $CDCl_3$) 7.33 – 7.13 (6H, m, (**10a + 10b**) Ar-$\underline{H}$ & H-4), 6.98 (1H, dd, *J* = 14.8, 11.5, **10b** H-2), 6.95 (1H, dd, *J* = 14.7, 11.4, (**10a**) H-2), 6.38 (2H, dd, *J* = 14.7, 11.4, (**10a + 10b**) H-3), 6.24 (1H, d, *J* = 11.4, (**10a**) H-1), 6.14 (1H, d, *J* = 15.4, (**10a**) H-5), 6.08 (1H, d, *J* = 15.4, (**10b**) H-5), 5.66 (1H, d, *J* = 11.6, (**10b**) H-1); 3.66 (2H, s, (**10a**) CH_2Ph), 3.44 (2H, s, (**10b**) CH_2Ph), 3.17 (1H, sept, *J* = 6.9, (**10b**) *CH*Me$_2$), 2.34 (1H, sept, *J* = 6.9, (**10a**) *CH*Me$_2$), 2.29 (3H, s, (**10a**) $COCH_3$), 2.28 (3H, s, (**10b**) $COCH_3$), 1.10 (6H, d, *J* = 6.9, (**10b**) CH*Me*$_2$), 1.04 (6H, d, *J* = 6.9, (**10a**) CH*Me*$_2$), δ_C (100 MHz, $CDCl_3$) 198.5 ($\underline{C}$=O), 154.2 (C), 153.6 (C), 144.1 (CH), 139.4 (C), 138.3 (CH), 129.6 (CH), 129.4 (CH), 129.2 (CH), 129.1 (CH), 128.5 (CH), 128.4 (CH), 126.2 (CH), 124.0 (CH), 38.6 (CH_2), 36.1 (CH_2), 34.7 (CH), 30.1 (CH), 27.2 (CH_3), 27.1 (CH_3), 21.9 (CH_3), 21.4 (CH_3); HRMS $[M+H]^+$ = 255.1743 required [M+H] = 255.1743.

Stereochemistry confirmed by 400 MHz NOESY

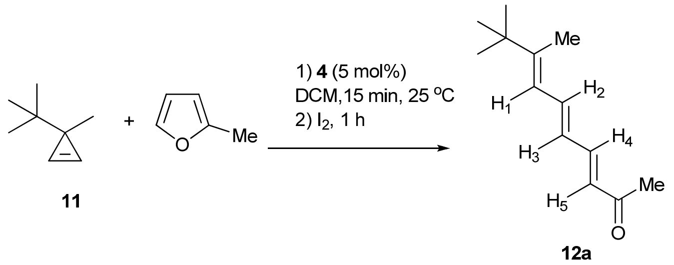


10a



10b

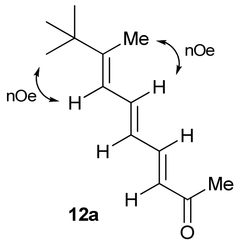
(3E,5E,7E)-8,9,9-Trimethyldeca-3,5,7-trien-2-one, 12a



Catalyst **4** (11 mg, 1.40 x 10^{-5} mol) was added to a solution of 3-tert-butyl-3-methylcycloprop-1-ene **11** (30 mg, 0.275 mmol) and 2-methylfuran (38 μL, 0.424 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the mixture was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (12:1 n-pentane/diethyl ether, 1% triethylamine) to yield (3E,5E,7E)-8,9,9-trimethyldeca-3,5,7-trien-2-one **12a** (45 mg, 0.233 mmol, 85%) as a yellow oil.

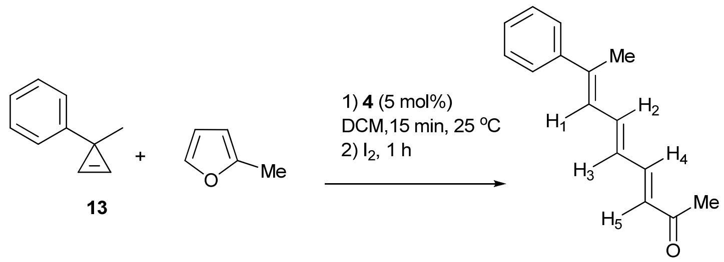
Rf (10:1 n-pentane / diethyl ether) 0.39. ν_{max}/cm^{-1} 2965 m (C-H), 1663 s (C=O), 1603 s (C=C), 1592 s (C=C), 1570 m (C=C); δ_H (400 MHz, $CDCl_3$) 7.24 (1H, dd, *J* = 15.6, 11.2, H-4), 6.92 (1H, dd, *J* = 14.7, 11.2, H-2), 6.31 (1H, dd, *J* = 14.7, 11.2, H-3), 6.13 (1H, d, *J* = 15.6, H-5), 6.09 (1H, d, *J* = 12.6, H-1), 2.29 (3H, s, (CO)C$\underline{H}_3$), 1.87 (3H, d, *J* = 1.2, HC=C-C$\underline{H}_3$), 1.11 (9H, s, C(C$\underline{H}_3$)$_3$); δ_C (100 MHz, $CDCl_3$) 198.5 ($\underline{C}$=O), 153.8 (C), 144.3 (CH), 139.1 (CH), 128.9 (CH), 128.8 (CH), 121.5 (CH), 37.1 (C), 28.8 (3 x CH_3), 27.2 (CH_3), 13.8 (CH_3); HRMS $[M+H]^+$ = 193.1586 required [M+H] = 193.1587.

Stereochemistry confirmed by 400 MHz NOESY



12a

(3E,5E,7E)-8-Phenylnona-3,5,7-trien-2-one, 14a

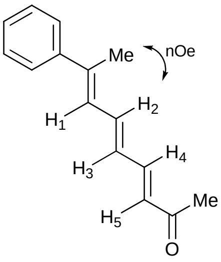


14a

Catalyst **4** (6 mg, 7.7 x 10^{-6} mol) was added to a solution of (1-methylcycloallyl)benzene **13** (20 mg, 0.154 mmol) and 2-methylfuran (21 μL, 0.231 mmol) in dichloromethane (0.4 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the mixture was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether. The solvent was evaporated and the residue was purified by flash column chromatography (15:1 n-pentane/diethyl ether, 1% triethylamine) to yield (3E,5E,7E)-8-phenylnona-3,5,7-trien-2-one **14a** (21 mg, 0.099 mmol, 64%) as a yellow oil. Product **14a** is not particularly stable and decomposes upon standing.

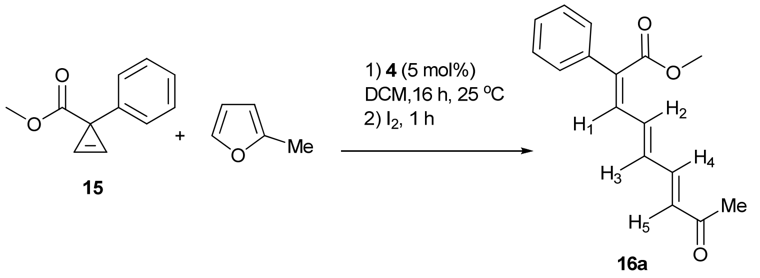
Rf (9:1 n-pentane / diethyl ether) 0.16. ν_{max}/cm^{-1} 1661 s (C=O), 1599 s (C=C/Ar C=C), 1559 m (C=C/Ar C=C), 1493 w (Ar C=C); δ_H (300 MHz, $CDCl_3$) 7.55 – 7.22 (6H, m, Ar-H + H-4), 7.05 (1H, dd, *J* = 14.7, 11.4, H-2), 6.61 (1H, d, *J* = 11.4, H-1), 6.46 (1H, dd, *J* = 14.7, 11.2, H-3), 6.19 (1H, d, *J* = 15.4, H-5), 2.31 (3H, s, (CO)C$\underline{H}_3$), 2.27 (3H, d, *J* = 1.1, HC=C-C$\underline{H}_3$); δ_C (100 MHz, $CDCl_3$) 198.4 ($\underline{C}$=O), 143.7 (CH), 142.2 (C), 141.8 (C), 138.2 (CH), 130.8 (CH), 129.7 (CH), 128.5 (CH), 128.0 (CH), 126.5 (CH), 125.8 (CH), 27.4 (CH_3), 16.4 (CH_3); HRMS $[M]^+$ = 212.1197 required $[M]^+$ = 212.1196.

Stereochemistry confirmed by 400 MHz NOESY



14a

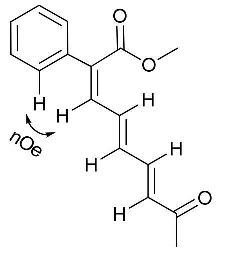
(2Z,4E,6E)-Methyl 8-oxo-2-phenylnona-2,4,6-trienoate, 16a



Catalyst **4** (8 mg, 1.10 x 10^{-5} mol) was added to a solution of methyl 1-phenylcycloprop-2-enecarboxylate **15** (38 mg, 0.218 mmol) and 2-methylfuran (30 μL, 0.328 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 16 h at 25 °C. A crystal of iodine was added and the reaction was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (10:1 n-pentane/diethyl ether, 1% triethylamine) to yield (2Z,4E,6E)-methyl 8-oxo-2-phenylnona-2,4,6-trienoate **16a** (42 mg, 0.164 mmol, 75%) as a yellow oil.

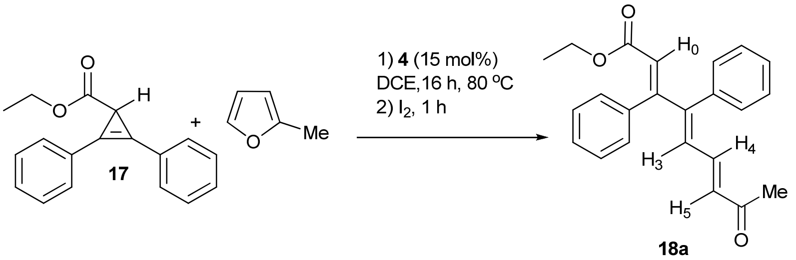
Rf (10:1 n-pentane / diethyl ether) 0.21. ν_{max}/cm^{-1} 1710 s (C=O), 1663 s (C=O), 1599 m (C=C/Ar C=C), 1561 w (C=C/Ar C=C), 1497 w (Ar C=C), 1205 s (C-O); δ_H (300 MHz, $CDCl_3$) 7.44-7.20 (7H, m, Ar-H, H-2, H-4), 6.78 (1H, d, *J* = 11.7, H-1), 6.60 (1H, dd, *J* = 15.0, 11.0, H-3), 6.25 (1H, d, *J* = 15.5, H-5), 3.89 (3H, s, (OC$\underline{H}_3$), 2.32 (3H, s, (CO)C$\underline{H}_3$); δ_C (100 MHz, $CDCl_3$) 196.1 ($\underline{C}$=O), 167.8 ($\underline{C}$=O), 142.4 (CH), 137.0 (CH), 136.6 (C), 136.1 (CH), 134.9 (CH), 132.3 (CH), 128.6 (CH), 128.5 (CH), 127.5 (CH), 113.7 (C), 52.2 (O$\underline{C}H_3$), 27.3 (CH_3); HRMS $[M+H]^+$ = 257.1175required [M+H] = 257.1172.

Stereochemistry confirmed by 400 MHz NOESY



16a

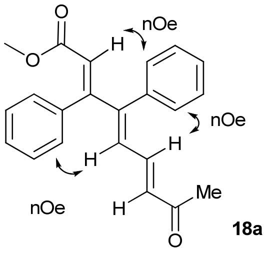
(2E,4E,6E)-Ethyl 8-oxo-3,4-diphenylnona-2,4,6-trienoate, 18a



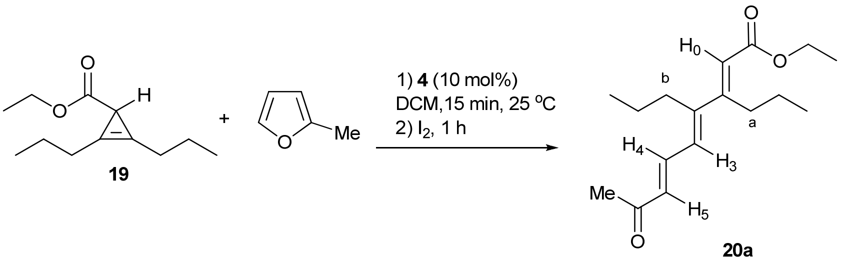
Catalyst **4** (7 mg, 8.85 x 10^{-6} mol) was added to a solution of ethyl 2,3-diphenylcycloprop-2-enecarboxylate **17** (16 mg, 0.059 mmol) and 2-methylfuran (8.1 μL, 0.090 mmol) in DCE (0.3 mL). The reaction mixture was allowed to stir for 16 h at 80 °C. A crystal of iodine was added and the mixture allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (20:1 n-pentane/diethyl ether, 1% triethylamine) to yield (2E,4E,6E)-methyl 8-oxo-3,4-diphenylnona-2,4,6-trienoate **18a** (16 mg, 0.046 mmol, 77%) as a yellow oil.

Rf (6:1 n-pentane / diethyl ether) 0.41. ν_{max}/cm^{-1} 1720 m (C=O), 1687 m (C=O), 1667 m (C=C), 1597 (C=C), 1464 (Ar C=C), 1222 s (C-O); δ_H (300 MHz, $CDCl_3$) 7.54 - 7.41 (6H, m, Ar-H), 7.29 – 7.21 (4 H, m, Ar-H), 6.89 (1H, dd, *J* = 15.6, 11.7, H-4), 6.17 (1H, d, *J* = 11.7, H-3),6.06 (1H, d, *J* = 15.6, H-5), 5.71 (1H, s, H-0), 3.92 (2H, q, *J* = 7.0, ($OC\underline{H}_2$), 2.08 (3H, s, (CO)$C\underline{H}_3$), 1.00 (3H, t, *J* = 7.0 ($CH_2C\underline{H}_3$)); δ_C (100 MHz, $CDCl_3$) 198.1 ($\underline{C}$=O), 155.9 ($\underline{C}$=O), 152.0 (C), 139.5 (CH), 137.5 (C), 136.6 (C), 134.2 (CH), 133.2 (CH), 130.0 (CH), 128.7 (CH), 128.7 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 123.8 (CH), 60.1 (CH_2), 27.5 (CH_3), 13.8 (CH_3); HRMS $[M+H]^+$ = 347.1648 required [M+H] = 347.1642.

Stereochemistry confirmed by 400 MHz NOESY



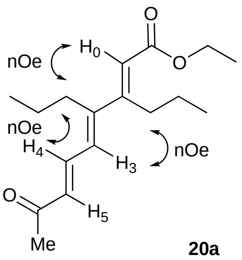
(2E,4E,6E)-Ethyl 8-oxo-3,4-dipropylnona-2,4,6-trienoate, 20a



Catalyst **4** (8 mg, 1.0 x 10^{-5} mol) was added to a solution of 3ethyl 2,3-dipropylcycloprop-2-enecarboxylate **19** (19 mg, 0.097 mmol) and 2-methylfuran (107 μL, 1.2 mmol) in dichloromethane (0.2 mL). The reaction mixture was allowed to stir for 24 h at 15 °C. A crystal of iodine was added and the reaction allowed to stir for a further 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1 % triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (10:1 n-pentane/diethyl ether, 1 % triethylamine) to yield (2E,4E,6E)-ethyl 8-oxo-3,4-dipropylnona-2,4,6-trienoate, **20a** (10 mg, 0.036 mmol, 37 %) as a yellow oil.

20a Rf (4:1 n-pentane / diethyl ether) 0.38. ν_{max}/cm^{-1} 2961 m, 2933 m, 2873 w (C-H), 1712 s (C=O), 1688 m (C=O), 1607 m (C=C), 1145 s (C-O); δ_H (400 MHz, $CDCl_3$) 7.48 (1H, dd, *J* = 15.3, 11.4, H-4), 6.38 (1H, d, *J* = 11.4, H-3), 6.28 (1H, d, *J* = 15.3, H-5), 5.91 (1H, s, H-0), 4.19 (2H, q, *J* = 7.1, $OC\underline{H}_2CH_3$), 2.81 (2H, m, $CH_2C\underline{H}_2{}^aC=CH$), 2.47 (2H, m, $CH_2C\underline{H}_2{}^bC=CH$), 2.31 (3H, s, $(CO)C\underline{H}_3$), 1.31 (3H, t, *J* = 7.1, $OCH_2C\underline{H}_3$), 1.48 – 1.38 (4H, m, (CH_2)x2), 1.05 – 0.90 (6H, m, (CH_3) x 2); δ_C (100 MHz, $CDCl_3$) 198.2 ($\underline{C}$=O), 166.4 ($\underline{C}$=O), 160.4 (C), 152.2 (C), 138.1 (CH), 131.7 (CH), 127.3 (CH), 117.7 (CH), 60.0 (CH_2), 30.8 (CH_2), 28.1 (CH_3), 22.6 (CH), 22.5 (CH_2), 14.5 (CH_3), 14.3 (CH_3), 13.9 (CH_3); HRMS $[M+H]^+$ = 279.1958 required [M+H] = 279.1955.

Stereochemistry confirmed by 400 MHz NOESY:

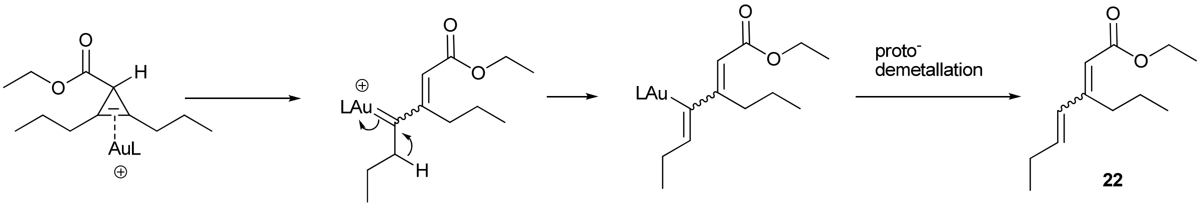


20a

Major by-product, (2E,4E)-ethyl 3-propylhepta-2,4-dienoate, 22 Rf (4:1 n-pentane / diethyl ether) 0.38. ν_{max}/cm^{-1} 2961 m (C-H), 1711 m (C=O), 1620 m (C=C), 1506 (C=C), 1269 (C-O); δ_H (300 MHz, $CDCl_3$) 6.17 (1H, dt, *J* = 15.4, 6.6, H-3), 6.00 (1H, d, *J* = 15.4, H-2), 5.67 (1H, s, H-1), 4.16 (2H, q, *J* = 7.3, $O\underline{CH_2}$), 2.76 (2H, t, *J* = 8.1, (H-1)C=C($\underline{CH_2}$), 2.20 (2H, m, (H-3)C-$\underline{CH_2}CH_3$), 1.49 (2H, m, $CH_2\underline{CH_2}CH_3$), 1.28 (3H, t, *J* = 7.0, $CH_2\underline{CH_3}$), 1.05 (3H, t, *J* = 7.5, $CH_2\underline{CH_3}$), 0.98 (3H, t, *J* = 7.3, $CH_2\underline{CH_3}$); δ_C (100 MHz, $CDCl_3$) 166.9 (C=O), 157.3 (C), 138.4 (CH), 131.6 (CH), 117.0 (CH), 59.5 (OCH_2), 29.8 (CH_2), 26.1 (CH_2), 23.1 (CH_2), 14.4 (CH_3), 14.3 (CH_3), 13.3 (CH_3); HRMS $[M+H]^+$= 197.1535 required [M+H] = 197.1536.

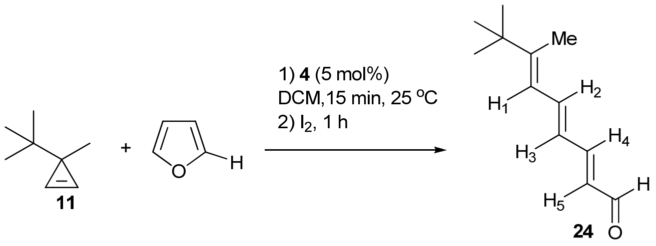
Isolated as a 5:1 mix of (E,E) and (Z,E) isomers, major isomer is (E,E).

Proposed mechanism for formation of 22:



At room temperature under the standard conditions, the desired triene **20b** is formed in only 20% yield, the major product being a rearrangement product, the diene **22** (69%). At elevated temperature (60 °C), the rearrangement product **22** forms as the major product (82%), whereas at 0 °C, no reaction is observed. Thus, cooling the reaction to 10-15 °C and increasing the equivalents of furan **2** to 12 equivalents is the best compromise, producing the desired triene **20a** as one isomer in 37% yield, with the diene **22** being formed as the major by-product.

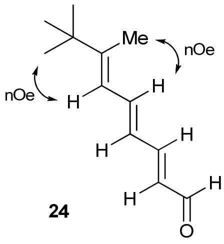
(2E,4E,6E)-7,8,8-Trimethylnona-2,4,6-trienal, 24



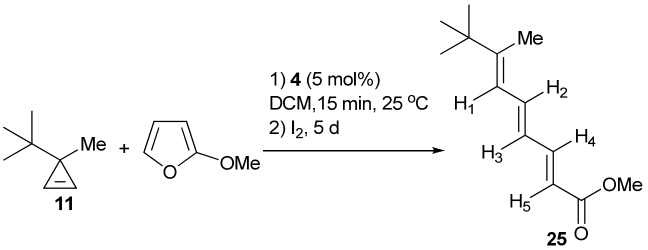
Catalyst **4** (11 mg, 1.40 x 10^{-5} mol) was added to a solution of 3-tert-butyl-3-methylcycloprop-1-ene **11** (30 mg, 0.268 mmol) and furan (31 μL, 0.426 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the reaction was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (20:1 n-pentane/diethyl ether, 1% triethylamine) to yield (2E,4E,6E)-7,8,8-trimethylnona-2,4,6-trienal **24** (29 mg, 0.164 mmol, 61%) as a yellow oil.

Rf (10:1 n-pentane / diethyl ether) 0.29. ν_{max}/cm^{-1} 2965 (C-H), 1680 m (C=O), 1671 m (C=C), 1602 s (C=C); δ_H (400 MHz, $CDCl_3$) 9.58 (1H, d, *J* = 8.2, O=C-$\underline{H}$), 7.22 (1H, dd, *J* = 15.3, 11.2, H-4), 7.00 (1H, dd, *J* = 14.7, 11.2, H-2), 6.44 (1H, dd, *J* = 14.7, 11.2, H-3), 6.16 (1H, dd, *J* = 15.3, 8.2 H-5), 6.14 (1H, d, *J* = 11.2, H-1), 1.91 (3H, d, *J* = 1.2, HC=C-C$\underline{H}_3$), 1.14 (9H, s, C(C$\underline{H}_3$)$_3$); δ_C (100 MHz, $CDCl_3$) 193.6 ($\underline{C}$=O), 155.5 (C), 153.0 (CH), 140.2 (CH), 130.1 (CH), 128.5 (CH), 121.5 (CH), 37.2 (C), 28.8 (3 x CH_3), 14.0 (CH_3); HRMS $[M+H]^+$ = 179.1429 required $[M+H]^+$ = 179.1430.

Stereochemistry confirmed by 400 MHz NOESY



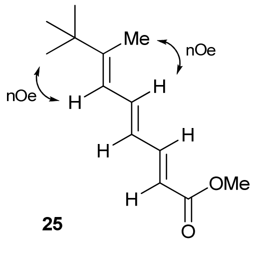
(2E,4E,6E)-Methyl 7,8,8-trimethylnona-2,4,6-trienoate, 25



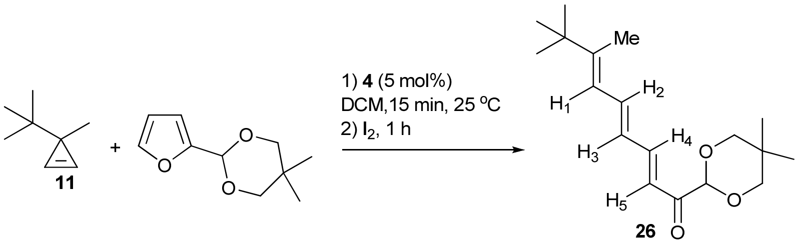
Catalyst **4** (11 mg, 1.40 x 10^{-5} mol) was added to a solution of 3-tert-butyl-3-methylcycloprop-1-ene **11** (30 mg, 0.274 mmol) and 2-methoxyfuran (39 μL, 0.423 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the reaction was allowed to stir for 5 days. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (18:1 n-pentane/diethyl ether, 1% triethylamine) to yield (2E,4E,6E)-methyl 7,8,8-trimethylnona-2,4,6-trienoate **25** (40 mg, 0.191 mmol, 70%) as a yellow oil.

Rf (18:1 n-pentane / diethyl ether, 1% Et_3N) 0.36. ν_{max}/cm^{-1} 2953 (C-H), 1714 s (C=O), 1608 s (C=C), 1580 w (C=C), 1135 s, (C-O); δ_H (400 MHz, $CDCl_3$) 7.40 (1H, dd, *J* = 15.3, 11.3, H-4), 6.87 (1H, dd, *J* = 14.7, 11.2, H-2), 6.30 (1H, dd, *J* = 14.7, 11.3, H-3), 6.06 (1H, d, *J* = 11.2, H-1), 5.86 (1H, d, *J* = 15.3, H-5), 3.76 (3H, s, $OC\underline{H}_3$), 1.86 (3H, d, *J* = 1.2, $HC=C-C\underline{H}_3$), 1.11 (9H, s, $C(C\underline{H}_3)_3$); δ_C (100 MHz, $CDCl_3$) 167.8 ($\underline{C}=O$), 153.3 (C), 145.6 (CH), 138.4 (CH), 128.4 (CH), 121.3 (CH), 118.8 (CH), 51.4 (CH_3), 37.0 (C), 28.8 (3 x CH_3), 13.8 (CH_3); HRMS $[M+H]^+$ = 209.1535 required [M+H] = 209.1536.

Stereochemistry confirmed by 400 MHz NOESY



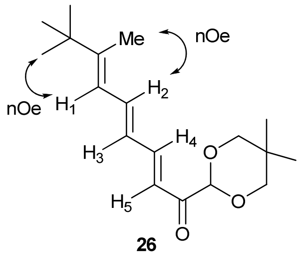
(2E,4E,6E)-1-(5,5-Dimethyl-1,3-dioxan-2-yl)-7,8,8-trimethylnona-2,4,6-trien-1-one, 26



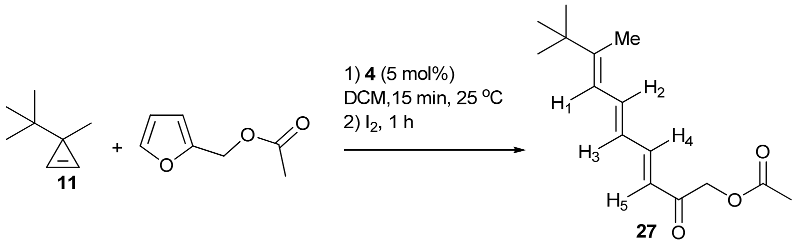
Catalyst **4** (5 mg, 6.75 x 10^{-6} mol) was added to a solution of 3-tert-butyl-3-methylcycloprop-1-ene **11** (15 mg, 0.135 mmol) and 2-(furan-2-yl)-5,5-dimethyl-1,3-dioxane (37 mg, 0.203 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the mixture was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (10:1 n-pentane/diethyl ether, 1% triethylamine) to yield (((2E,4E,6E)-1-(5,5-dimethyl-1,3-dioxan-2-yl)-7,8,8-trimethylnona-2,4,6-trien-1-one, **26** (28 mg, 0.096 mmol, 71%) as a beige solid.

Mp = 96-98 ^{o}C. Rf (10:1 n-pentane / diethyl ether) 0.17. ν_{max}/cm^{-1} 2954 m (C-H), 1692 m (C=O), 1586 s, 1561 s, (C=C), 1088 s (C-O); δ_H (400 MHz, $CDCl_3$) 7.54 (1H, dd, *J* = 15.4, 11.4, H-4), 6.96 (1H, dd, *J* = 14.6, 11.4, H-2), 6.54 (1H, d, *J* = 15.4, H-5), 6.34 (1H, dd, *J* = 14.6, 11.4, H-3), 6.08 (1H, d, *J* = 11.4, H-1), 4.83 (1H, s, $C\underline{H}$-$(O)_2$), 3.76 (2H, d, *J* = 11.4, O-C*H*H), 3.55 (2H, d, *J* = 11.4, O-CH*H*), 1.86 (3H, d, *J* = 1.1, HC=C-$C\underline{H}_3$), 1.25 (3H, s, $C\underline{H}_3$), 1.11 (9H, s, $C(C\underline{H}_3)_3$), 0.79 (3H, s, $C\underline{H}_3$); δ_C (100 MHz, $CDCl_3$) 191.8 ($\underline{C}$=O), 154.7 (C), 146.4 (CH), 140.8 (CH), 129.1 (CH), 121.9 (CH), 121.7 (CH), 100.5 (C) 37.1 (C), 30.5 (CH_2), 28.9 (C), 28.8 (3 x CH_3), 23.0 (CH_3), 21.9 (2 x CH_3); HRMS $[M+H]^+$= 293.2115 required [M+H] = 293.2111.

Stereochemistry confirmed by 400 MHz NOESY



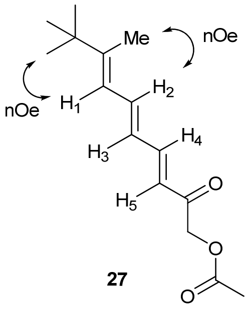
(3E,5E,7E)-8,9,9-Trimethyl-2-oxodeca-3,5,7-trienyl acetate, 27



Catalyst **4** (5 mg, 6.75 x 10^{-6} mol) was added to a solution of 3-tert-butyl-3-methylcycloprop-1-ene **11** (15 mg, 0.133 mmol) and furan-2-ylmethyl acetate (68 mg, 0.203 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the mixture was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (12:1 n-pentane/diethyl ether, 1% triethylamine) to yield (3E,5E,7E)-8,9,9-trimethyl-2-oxodeca-3,5,7-trienyl acetate **27** (26 mg, 0.104 mmol, 78 %) as a yellow oil.

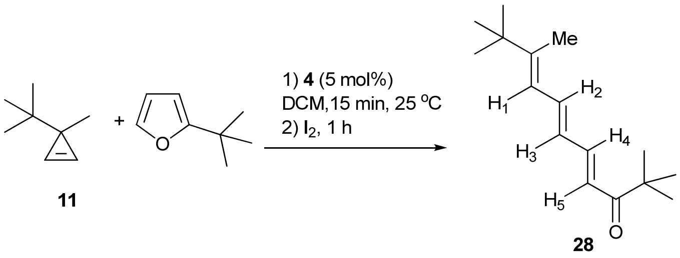
Rf (8:1 n-pentane / diethyl ether) 0.24. ν_{max}/cm^{-1} 2963 (C-H), 1748 s (C=O), 1677 m (C=O), 1590 s (C=C), 1570 m, (C=C), 1219 (C-O); δ_H (300 MHz, $CDCl_3$) 7.38 (1H, dd, *J* = 15.3, 11.4, H-4), 6.97 (1H, dd, *J* = 14.6, 11.4, H-2), 6.30 (1H, dd, *J* = 14.6, 11.4, H-3), 6.19 (1H, d, *J* = 15.3, H-5), 6.09 (1H, d, *J* = 11.4, H-1), 4.85 (2H, s, ($C\underline{H}_2O$)), 2.21 (3H, s, (CO)$C\underline{H}_3$), 1.87 (3H, d, *J* = 1.1, HC=C-$C\underline{H}_3$), 1.11 (9H, s, $C(C\underline{H}_3)_3$); δ_C (100 MHz, $CDCl_3$) 192.4 ($\underline{C}$=O), 170.3 ($\underline{C}$=O), 155.0 (C), 144.9 (CH), 140.7 (CH), 128.5 (CH), 122.9 (CH), 121.5 (CH), 67.2 (CH_2), 37.1 (C), 28.8 (3 x CH_3), 20.6 (CH_3), 13.9 (CH_3); $[M+H]^+$(EI) = 251.1640 required [M+H] = 251.1642.

Stereochemistry confirmed by 400 MHz NOESY



27

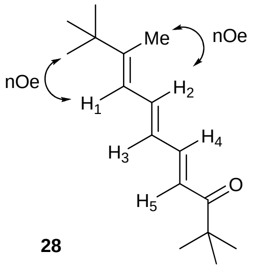
(4E,6E,8E)-2,2,9,10,10-Pentamethylundeca-4,6,8-trien-3-one, 28



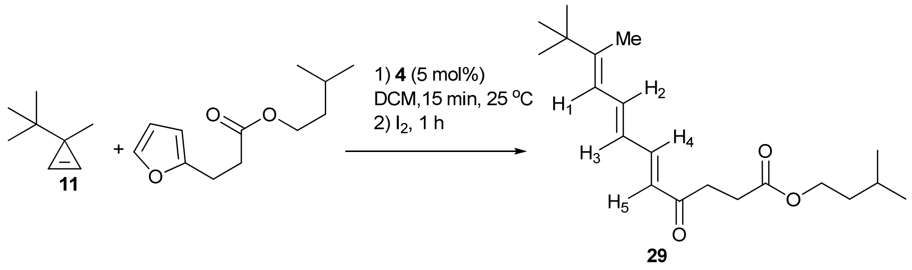
Catalyst **4** (5 mg, 6.75 x 10^{-6} mol) was added to a solution of 3-tert-butyl-3-methylcycloprop-1-ene **11** (15 mg, 0.135 mmol) and 2-*tert*butylfuran (29 μL, 0.203 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. Ae crystal of iodine was added and the mixture was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (10:1 n-pentane/diethyl ether, 1% triethylamine) to yield (4E,6E,8E)-2,2,9,10,10-pentamethylundeca-4,6,8-trien-3-one, **28** (28 mg, 0.120 mmol, 89%) as a colourless oil.

Rf (5:1 n-pentane / diethyl ether) 0.39. ν_{max}/cm^{-1} 2964 m (C-H), 1674 m (C=O), 1603 s (C=C), 1590 s (C=C), 1567 s (C=C); δ_H (300 MHz, $CDCl_3$) 7.39 (1H, dd, *J* = 15.0, 11.2, H-4), 6.90 (1H, dd, *J* = 14.7, 11.2, H-2), 6.52 (1H, d, *J* = 15.0, H-5), 6.31 (1H, dd, *J* = 14.7, 11.2, H-3), 6.06 (1H, d, *J* = 11.2, H-1), 1.85 (3H, d, *J* = 1.1, HC=C-C$\underline{H}_3$), 1.17 (9H, s, (CO)C(C$\underline{H}_3$)$_3$) 1.11 (9H, s, C(C$\underline{H}_3$)$_3$); δ_C (100 MHz, $CDCl_3$) 204.6 ($\underline{C}$=O), 153.2 (C), 143.6 (CH), 139.1 (CH), 128.9 (CH), 128.8 (CH), 121.5 (CH), 42.9 (C), 37.1 (C), 28.8 (CH_3), 27.2 (CH_3), 13.8 (CH_3); HRMS $[M]^+$= 234.1981 required $[M]^+$ = 234.1978.

Stereochemistry confirmed by 400 MHz NOESY



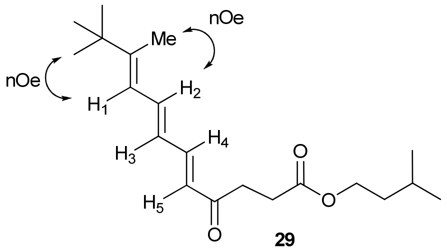
(5E,7E,9E)-Isopentyl 10,11,11-trimethyl-4-oxododeca-5,7,9-trienoate, 29



Catalyst **4** (5 mg, 6.75 x 10^{-6} mol) was added to a solution of 3-tert-butyl-3-methylcycloprop-1-ene **11** (15 mg, 0.135 mmol) and isoamyl 3-(2-furan)propionate (43 μL, 0.203 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the mixture was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (10:1 n-pentane/diethyl ether, 1% triethylamine) to yield (5E,7E,9E)-isopentyl 10,11,11-trimethyl-4-oxododeca-5,7,9-trienoate **29** (39 mg, 0.120 mmol, 89%) as a yellow oil.

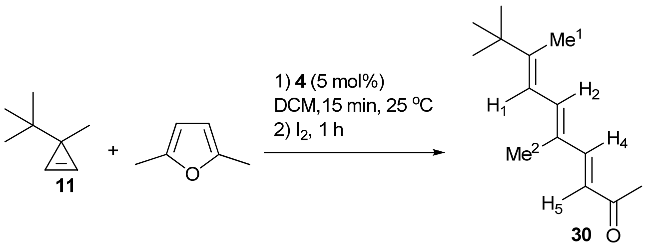
Rf (6:1 n-pentane / diethyl ether) 0.19. ν_{max}/cm^{-1} 2955 m (C-H), 1733 m (C=O), 1692 m (C=O), 1662 w, 1587 s, 1564 s (C=C), 1089 s (C-O); δ_H (300 MHz, CDCl$_3$) 7.29 (1H, dd, *J* = 15.6, 11.2, H-4), 6.90 (1H, dd, *J* = 14.7, 11.2, H-2), 6.28 (1H, dd, *J* = 14.7, 11.2, H-3), 6.15 (1H, d, *J* = 15.6, H-5), 6.07 (1H, d, *J* = 11.2, H-1), 4.11 (2H, t, *J* = 6.8, $\mathrm{OC\underline{H}_2CH_2}$), 2.90 (2H, t, *J* = 6.0, $\mathrm{C\underline{H}_2CH_2}$), 2.64 (2H, t, *J* = 6.0, $\mathrm{CH_2C\underline{H}_2}$), 1.85 (3H, d, *J* = 0.9, $\mathrm{HC{=}C\text{-}C\underline{H}_3}$), 1.68 (1H, m, $\mathrm{\underline{H}C(CH_3)_2}$), 1.52 (2H, dt, *J* = 6.8, 6.8, $\mathrm{CH_2C\underline{H}_2CH}$), 1.10 (9H, s, $\mathrm{C(C\underline{H}_3)_3}$), 0.91 (6H, d, *J* = 6.8, $\mathrm{HC(C\underline{H}_3)_2}$); δ_C (100 MHz, CDCl$_3$) 198.0 ($\underline{\mathrm{C}}$=O), 173.0 ($\underline{\mathrm{C}}$=O), 153.8 (C), 143.7 (CH), 139.4 (CH), 128.8 (CH), 127.5 (CH), 121.5 (CH), 63.3 (CH$_2$), 37.3 (CH$_2$), 37.1 (C), 34.9 (CH$_2$), 28.8 (CH$_3$), 28.3 (CH$_2$), 25.0 (CH), 22.4 (CH$_3$), 13.8 (CH$_3$); HRMS [M+H]$^+$ = 321.2439 required [M+H] = 321.2424

Stereochemistry confirmed by 400 MHz NOESY



29

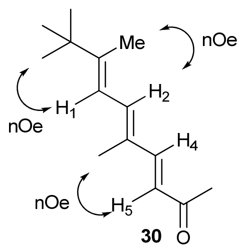
(3E,5E,7E)-5,8,9,9-Tetramethyldeca-3,5,7-trien-2-one, 30



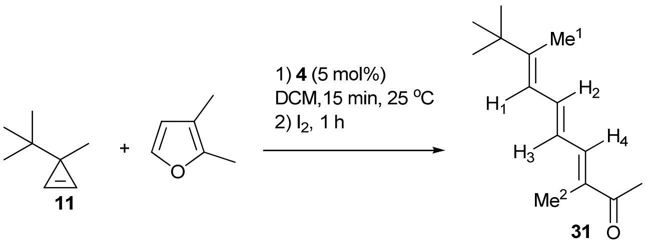
Catalyst **4** (5 mg, 6.75 x 10^{-6} mol) was added to a solution of 3-tert-butyl-3-methylcycloprop-1-ene **11** (15 mg, 0.135 mmol) and 2,5-dimethylfuran (22 μL, 0.203 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the mixture was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (10:1 n-pentane/diethyl ether, 1% triethylamine) to yield ((3E,5E,7E)-5,8,9,9-tetramethyldeca-3,5,7-trien-2-one **30** (23 mg, 0.111 mmol, 82%) as a yellow oil.

Rf (10:1 n-pentane / diethyl ether) 0.27. ν_{max}/cm^{-1} 2956 s (C-H), 1666 m (C=O), 1587 s (C=C), 1567 s (C=C); δ_H (400 MHz, $CDCl_3$) 7.27 (1H, d, *J* = 15.8, H-4), 6.70 (1H, d, *J* = 11.4, H-2), 6.31 (1H, dq, *J* = 11.4, 1.2, H-1), 6.15 (1H, d, *J* = 15.8, H-5), 2.31 (3H, s, (CO)$C\underline{H}_3$), 1.93 (3H, d, *J* = 0.9, $C\underline{H}_3$(Me-2)), 1.90 (3H, d, *J* = 1.2, $C\underline{H}_3$(Me-1)), 1.12 (9H, s, $C(C\underline{H}_3)_3$); δ_C (100 MHz, $CDCl_3$) 198.6 ($\underline{C}$=O), 153.8 (C), 149.0 (CH), 136.8 (CH), 132.0 (C), 124.9 (CH), 117.7 (CH), 37.4 (C), 28.9 (CH_3), 27.4 (CH_3), 13.8 (CH_3); HRMS $[M+H]^+$ = 207.1741 required [M+H] = 207.1743.

Stereochemistry confirmed by 400 MHz NOESY



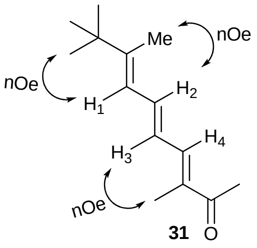
(3E,5E,7E)-3,8,9,9-Tetramethyldeca-3,5,7-trien-2-one, 31



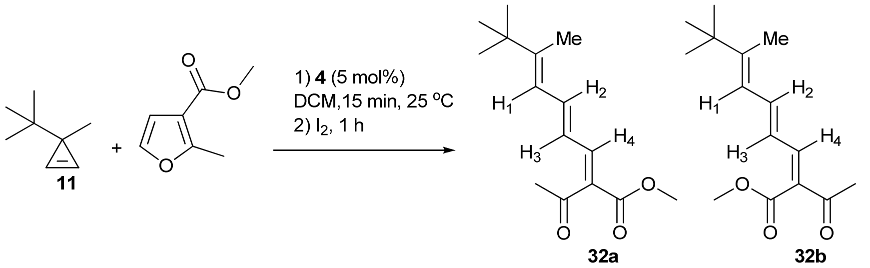
Catalyst **4** (5 mg, 6.75 x 10^{-6} mol) was added to a solution of 3-tert-butyl-3-methylcycloprop-1-ene **11** (15 mg, 0.135 mmol) and 2,3-dimethylfuran (21 μL, 0.203 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the mixture was allowed to stir for 1.h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (10:1 n-pentane /diethyl ether, % triethylamine) to yield (3E,5E,7E)-3,8,9,9-tetramethyldeca-3,5,7-trien-2-one **31** (24 mg, 0.117 mmol, 87%) as a yellow oil.

R_f (5:1 n-pentane / diethyl ether) 0.38. ν_{max}/cm^{-1} 2962 m (C-H), 1714 m (C=O), 1657 s (C=C), 1601 s (C=C); δ_H (400 MHz, $CDCl_3$) 7.14 (1H, d, *J* = 11.2, H-4), 6.87 (1H, dd, *J* = 14.7, 11.2, H-2), 6.53 (1H, dd, *J* = 14.7, 11.2, H-3), 6.13 (1H, d, *J* = 11.2, H-1), 2.36 (3H, s, (CO)C$\underline{H}$3), 1.91 (3H, d, *J* = 1.2, C$\underline{H}_3$(Me-2)), 1.88 (3H, d, *J* = 1.2, C$\underline{H}_3$(Me-1)), 1.11 (9H, s, C(C$\underline{H}_3$)$_3$); δ_C (100 MHz, $CDCl_3$) 199.5 ($\underline{C}$=O), 152.8 (C), 140.1, (CH), 137.5 (CH), 134.9 (C), 126.8 (CH), 121.8, (CH) 37.0 (C), 28.8 (CH_3), 25.5 (CH_3), 13.8 (CH_3), 11.4 (CH_3); HRMS $[M+H]^+$ = 207.1742 required [M+H] = 207.1743.

Stereochemistry confirmed by 400 MHz NOESY



(2E,4E,6E)-Methyl 2-acetyl-7,8,8-trimethylnona-2,4,6-trienoate 32a, (2Z,4E,6E)-methyl 2-acetyl-7,8,8-trimethylnona-2,4,6-trienoate 32b



Catalyst **4** (3 mg, 4.10 x 10^{-6} mol) was added to a solution of 3-tert-butyl-3-methylcycloprop-1-ene **11** (15 mg, 0.135 mmol) and methyl 2-methyl-3-furancarboxylate (19 mg, 0.135 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 15 min at 25 °C. A crystal of iodine was added and the mixture was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (17:1 hexane/diethyl ether, 1% triethylamine) to yield isomers (2E,4E,6E)-methyl 2-acetyl-7,8,8-trimethylnona-2,4,6-trienoate **32a**, (2Z,4E,6E)-methyl 2-acetyl-7,8,8-trimethylnona-2,4,6-trienoate **32b** (1:1.5) (25 mg, 0.101 mmol, 75%) as a yellow oil. The isomers were partially separable for ^{1}H-NMR assignment purposes, however, both trienes isomerise to a ~1:1 mixture of **32a**:**32b** upon standing, so a full characterisation of the separated trienes was not possible. Full characterisation was thus carried out on the mixture.

(2E,4E,6E)-methyl 2-acetyl-7,8,8-trimethylnona-2,4,6-trienoate 32a

Rf (5:1 hexane / diethyl ether) 0.39. δ_H (300 MHz, $CDCl_3$) 7.43 (1H, d, *J* = 12.5, H-4), 7.04 (1H, dd, J = 15.0, 11.6, H-2), 6.74 (1H, dd, *J* = 15.0, 12.5, H-3), 6.14 (1H, d, *J* = 11.6, H-1), 3.82 (3H, s, $OC\underline{H}_3$), 2.43 (3H, s, $(CO)C\underline{H}_3$), 1.88 (3H, d, *J* = 1.1, $HC{=}C{-}C\underline{H}_3$), 1.10 (9H, s, $C(C\underline{H}_3)_3$).

(2Z,4E,6E)-methyl 2-acetyl-7,8,8-trimethylnona-2,4,6-trienoate, 32b

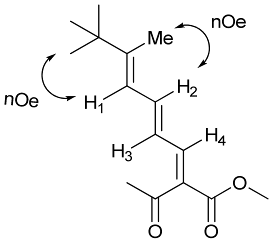
Rf (5:1 hexane / diethyl ether) 0.27. δ_H (300 MHz, $CDCl_3$) 7.40 (1H, d, *J* = 12.3, H-4), 7.04 (1H, dd, *J* = 15.0, 11.2, H-2), 6.66 (1H, dd, *J* = 15.0, 12.3, H-3), 6.17 (1H, d, *J* = 11.2, H-1), 3.88 (3H, s, $OC\underline{H}_3$), 2.38 (3H, s, $(CO)C\underline{H}_3$), 1.89 (3H, d, *J* = 1.1, $HC{=}C{-}C\underline{H}_3$), 1.11 (9H, s, $C(C\underline{H}_3)_3$).

32a+32b

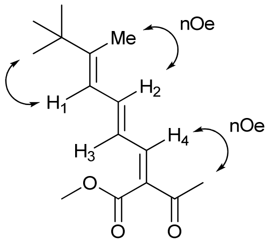
ν_{max}/cm^{-1} 2956 m (C-H), 1708 m (C=O), 1683 (C=O), 1584 s (C=C), 1547 m, (C=C), 1221 (C-O). δ_C (100 MHz, $CDCl_3$) 195.5 ($\underline{C}$=O), 167.1 (C=O) 157.2 (C), 156.8 (C), 146.6, (CH), 146.2, (CH), 144.2 (CH), 143.9

(CH), 130.2 (C), 129.4 (C), 126.0 (CH), 121.9 (CH), 52.0 (CH_3), 37.4 (C), 37.3 (C), 31.2 (CH_3) 28.8 (CH_3), 27.9 (CH_3), 25.8 (CH_3), 14.1 (CH_3), 14.0 (CH_3). HRMS $[M+H]^+$ = 251.1644 required [M+H] = 251.1642.

Stereochemistry confirmed by 400 MHz NOESY

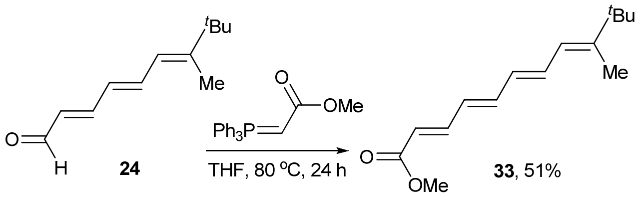


32a



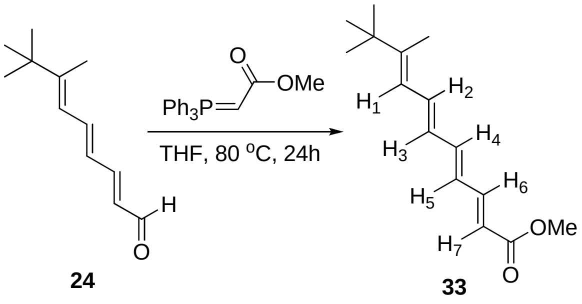
32b

The functionalised triene products are useful building blocks which can be further elaborated.[9] For example, a simple Wittig reaction on triene **24** produces the (*EEEE*)-tetraene **33**:



Further elaboration of triene **24** to form tetraene **33**.

(2E,4E,6E,8E)-Methyl 9,10,10-trimethylundeca-2,4,6,8-tetraenoate, 33

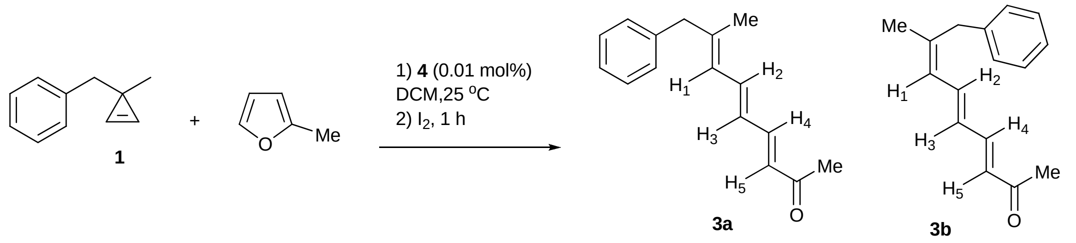


To a stirred solution of (2E,4E,6E)-7,8,8-trimethylnona-2,4,6-trienal, **24** (12 mg, 0.067 mmol) in dry THF (7 ml), $PPh_3CHCO_2CH_3$ (134 mg, 0.402mmol) was added and the resulting mixture was heated to reflux (24 h). The reaction mixture was then filtered through a plug of silica and washed with diethyl ether (1 % triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (13:1 n-pentane/diethyl ether, 1% triethylamine) to yield (2E,4E,6E,8E)-methyl 9,10,10-trimethylundeca-2,4,6,8-tetraenoate **33** (8 mg, 0.034 mmol, 51%) as a white crystalline solid.

M.p. 74 – 76 ^{o}C; Rf (4:1 n-pentane / diethyl ether) 0.63. ν_{max}/cm^{-1} 2952 (C-H), 1712 s (C=O), 1614 m (C=C), 1589 s (C=C), 1130 (C-O) δ_H (300 MHz, $CDCl_3$) 7.34 (1H, dd, *J* = 15.0, 11.6, H-6), 6.66 (2H, m, H-2 and H4), 6.28 (2H, m, H-5 and H-3), 6.04 (1H, d, *J* = 11.0, H-1), 5.86 (1H, d, *J* = 15.0, H-7), 3.75 (3H, s, $OC\underline{H}_3$), 1.84 (3H, d, *J* = 1.1, $C\underline{H}_3$), 1.09 (9H, s, $(C\underline{H}_3)_3$); δ_C (100 MHz, $CDCl_3$) 167.7(C=O), 151.4 (C) 145.0 (CH), 141.8 (CH), 134.8 (CH), 130.2 (CH), 128.5 (CH), 121.6 (CH), 119.2 (CH), 51.5 (OCH_3), 36.9 (C), 28.9 (CH_3), 13.7 (CH_3).

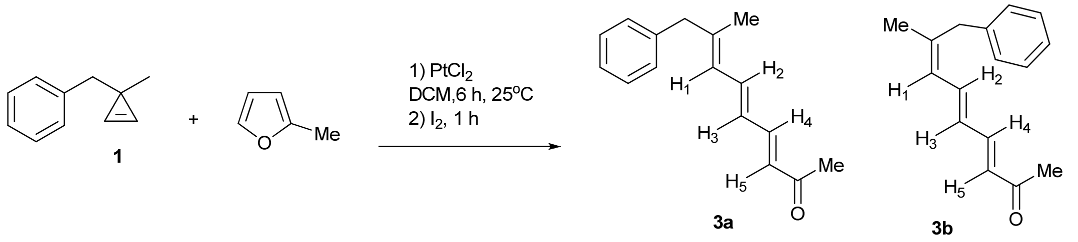
Metal Catalyst Screen

0.01 mol% Au (I)



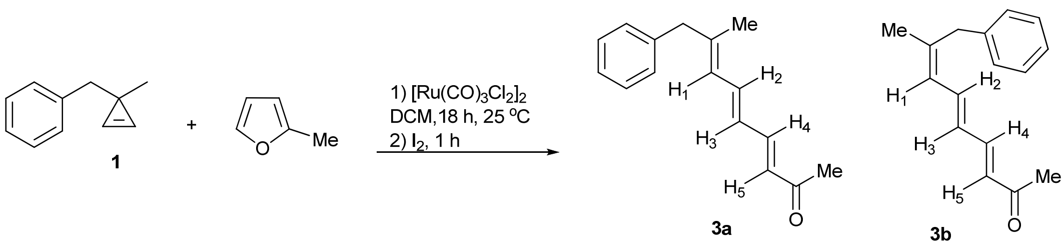
2-Methylfuran (87 μL, 0.972 mmol) was added to((1-methylcycloallyl)methyl)benzene **1** (93 mg, 0.648 mmol). A solution of catalyst **4** [2.5 mL of a solution of **4** (0.5 mg, 6.48 x 10^{-7} mol) in DCM (25 mL)] was added and the reaction mixture was allowed to stir for at 25 °C. Reaction monitoring showed that the reaction was complete within <2 min. A crystal of iodine was added and the mixture was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1 % triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (9:1 hexane/diethyl ether, 1% triethylamine) to yield inseparable isomers (3E,5E,7E)-8-methyl-9-phenylnona-3,5,7-trien-2-one **3a** and (3E,5E,7Z)-8-methyl-9-phenylnona-3,5,7-trien-2-one **3b** (2:1) (130 mg, 0.575 mmol, 89%) as a yellow oil.

$PtCl_2$



$PtCl_2$ (1.4 mg, 5.2 x 10^{-6} mol) was added to a solution of ((1-methylcycloallyl)methyl)benzene **1** (16 mg, 0.110 mmol) and 2-methylfuran (14 μL, 0.156 mmol) in dichloromethane (0.4 mL). The reaction mixture was allowed to stir at 25 °C and was monitored by TLC. After 6 h, a crystal of iodine was added and the mixture was allowed to stir for 1 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (10:1 n-pentane/diethyl ether, 1% triethylamine) to yield inseparable isomers (3E,5E,7E)-8-methyl-9-phenylnona-3,5,7-trien-2-one **3a** and (3E,5E,7Z)-8-methyl-9-phenylnona-3,5,7-trien-2-one **3b** (19 mg, 0.085 mmol, 77%) as a yellow oil.

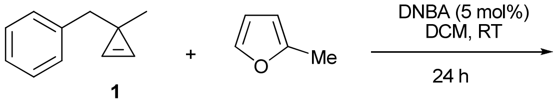
$[Ru(CO)_3Cl_2]_2$



$[Ru(CO)_3Cl_2]_2$ (5.3 mg, 1.04 x 10^{-5} mol) was added to a solution of ((1-methylcycloallyl)methyl)benzene **1** (16 mg, 0.108 mmol) and 2-methylfuran (14 µL, 0.156 mmol) in dichloromethane (0.4 mL). The reaction mixture was allowed to stir at 25 °C and was monitored by TLC. After 24 h, a crystal of iodine was added and the mixture was allowed to stir for 1.0 h. The reaction mixture was filtered through a plug of silica and washed with diethyl ether (1% triethylamine). The solvent was evaporated and the residue was purified by flash column chromatography (10:1 n-pentane / diethyl ether, 1 % triethylamine) to yield inseparable isomers (3E,5E,7E)-8-methyl-9-phenylnona-3,5,7-trien-2-one **3a** and (3E,5E,7Z)-8-methyl-9-phenylnona-3,5,7-trien-2-one **3b** (11 mg, 0.047 mmol, 44%) as a yellow oil.

Bronsted Acid

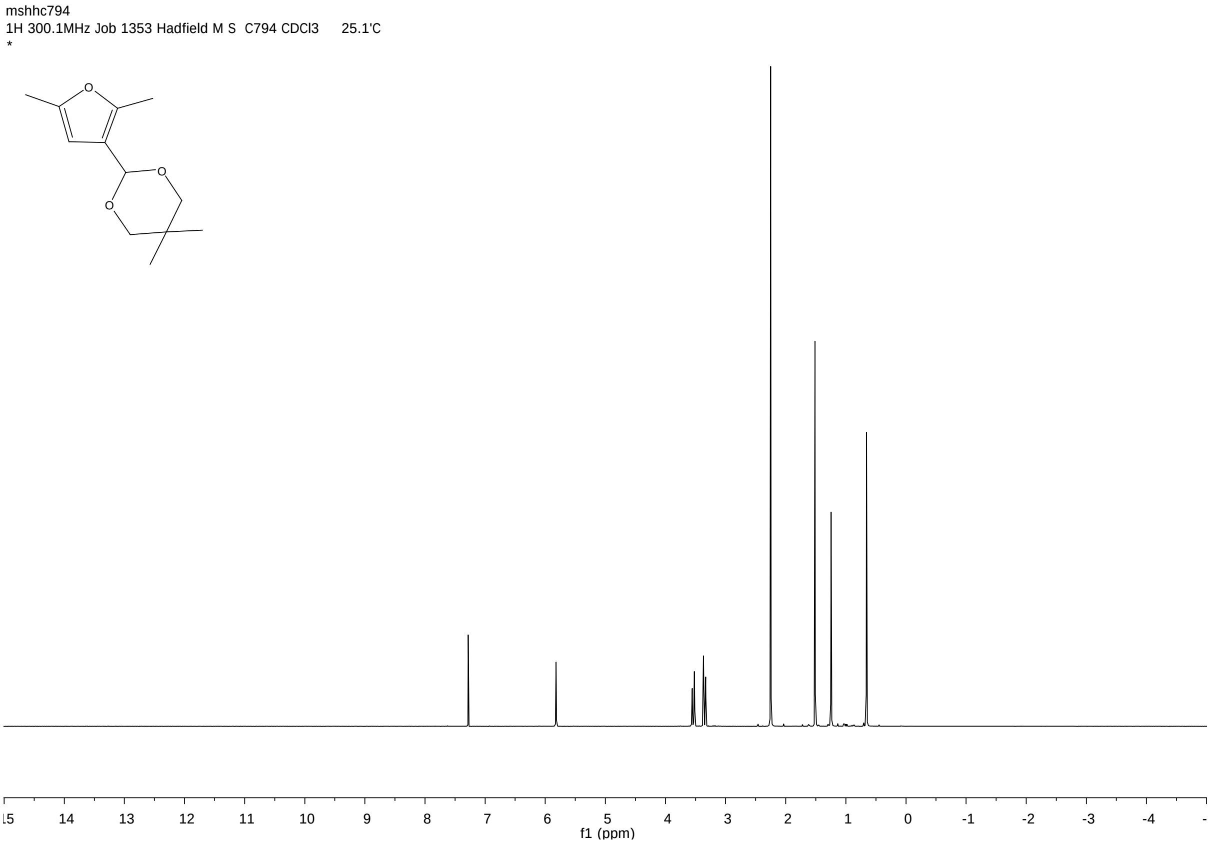
An experiment was also carried out with a Bronsted acid: no desired trienes were observed.

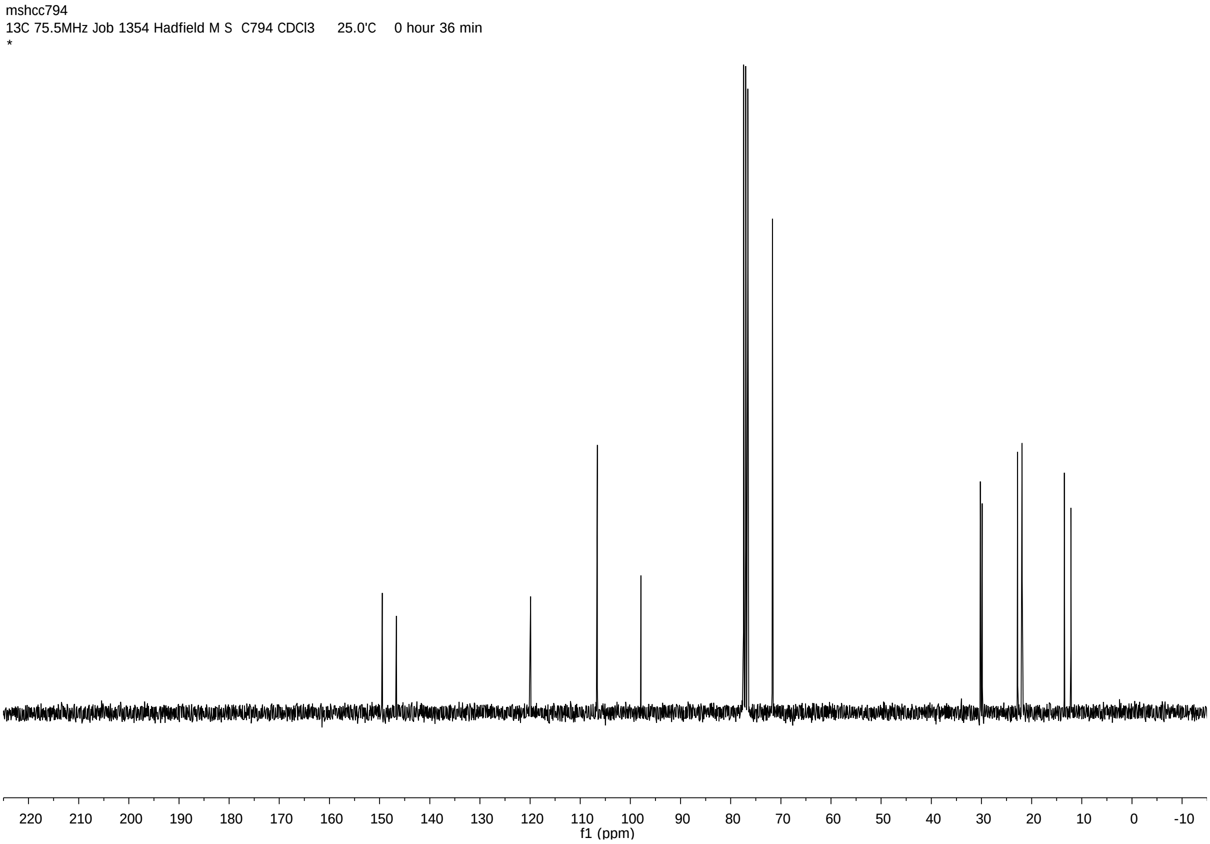


Recovered starting material **1**
No sign of desired triene products **3a** or **3b**.

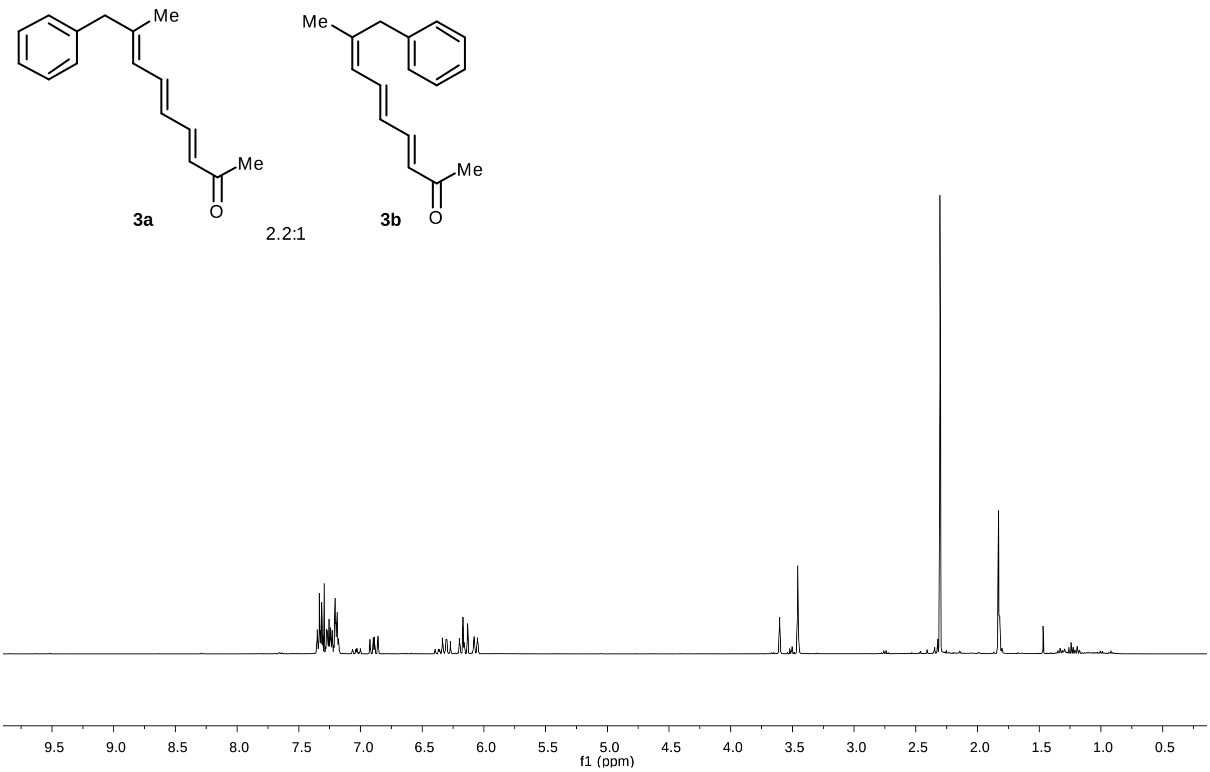
DNBA=2,4-dinitrobenzenesulfonic acid

3. ^{1}H-NMR and ^{13}C-NMR Spectra of Synthesized Compounds

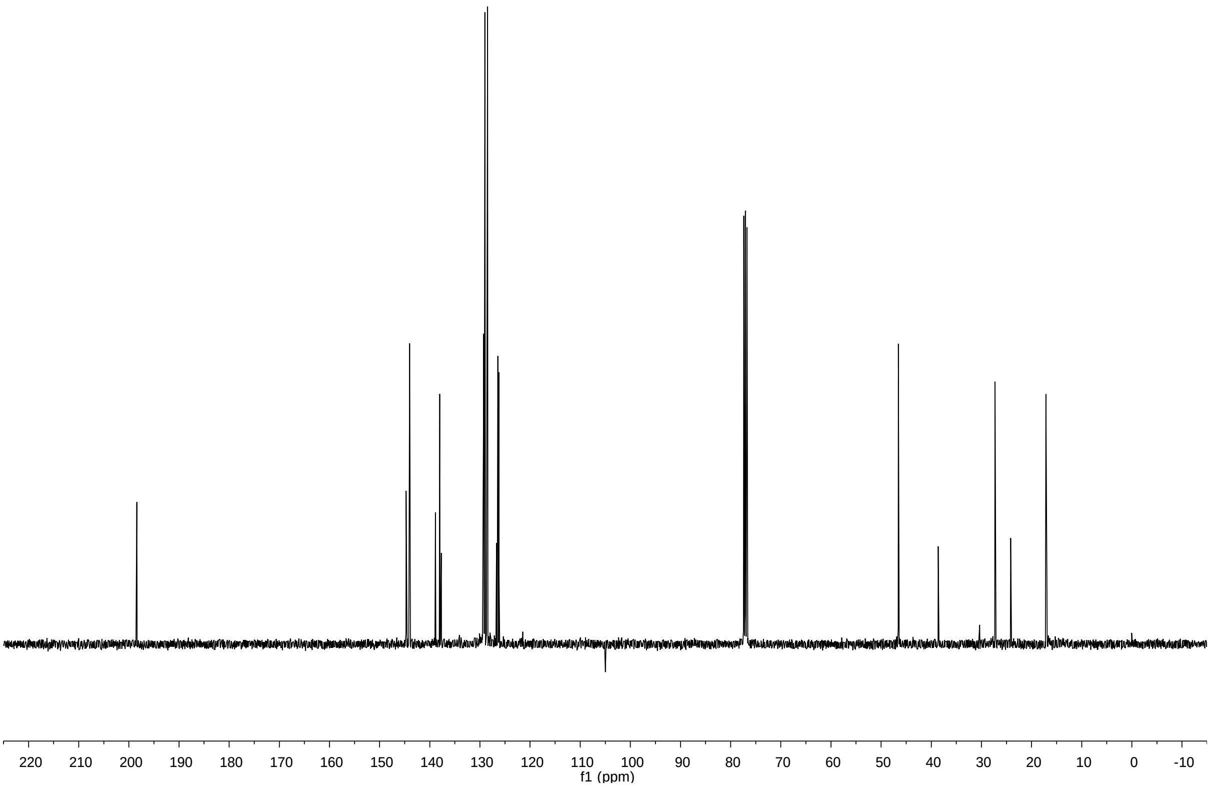




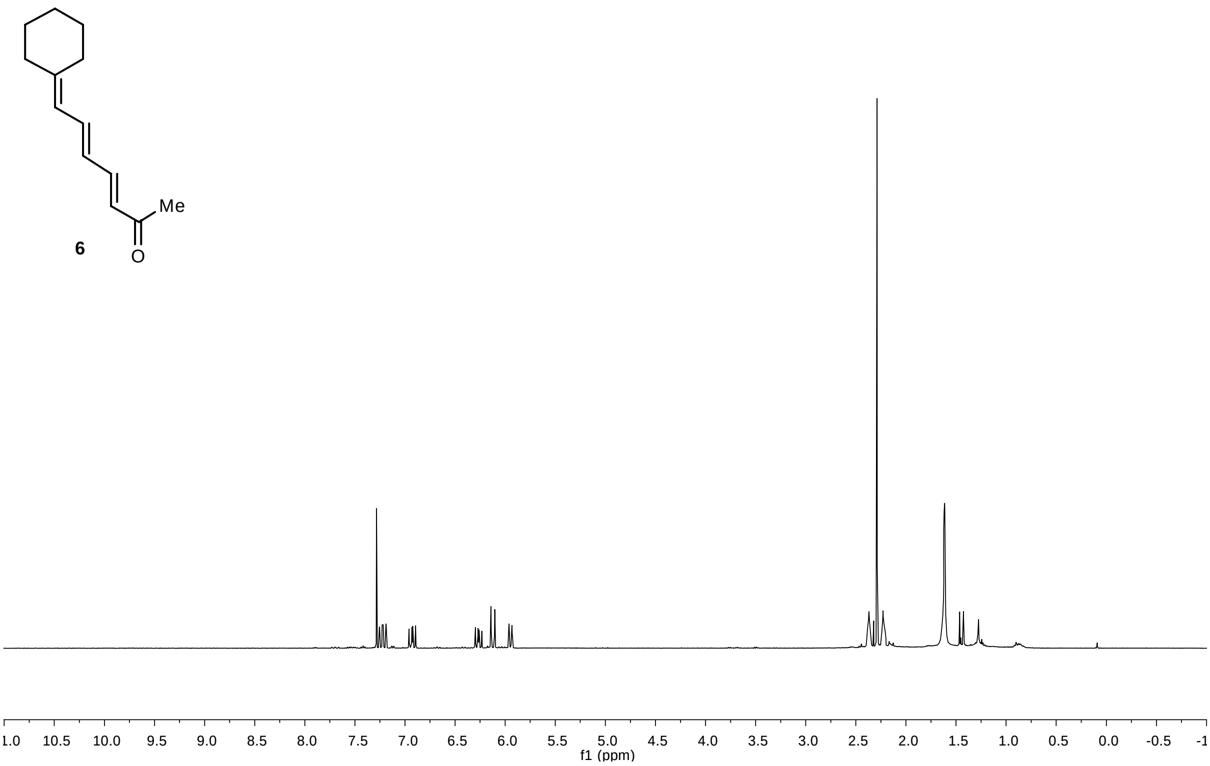
mshhc667
1H 400.1MHz Job 17106 Hadfield M S C667 CDCl3 25.0'C



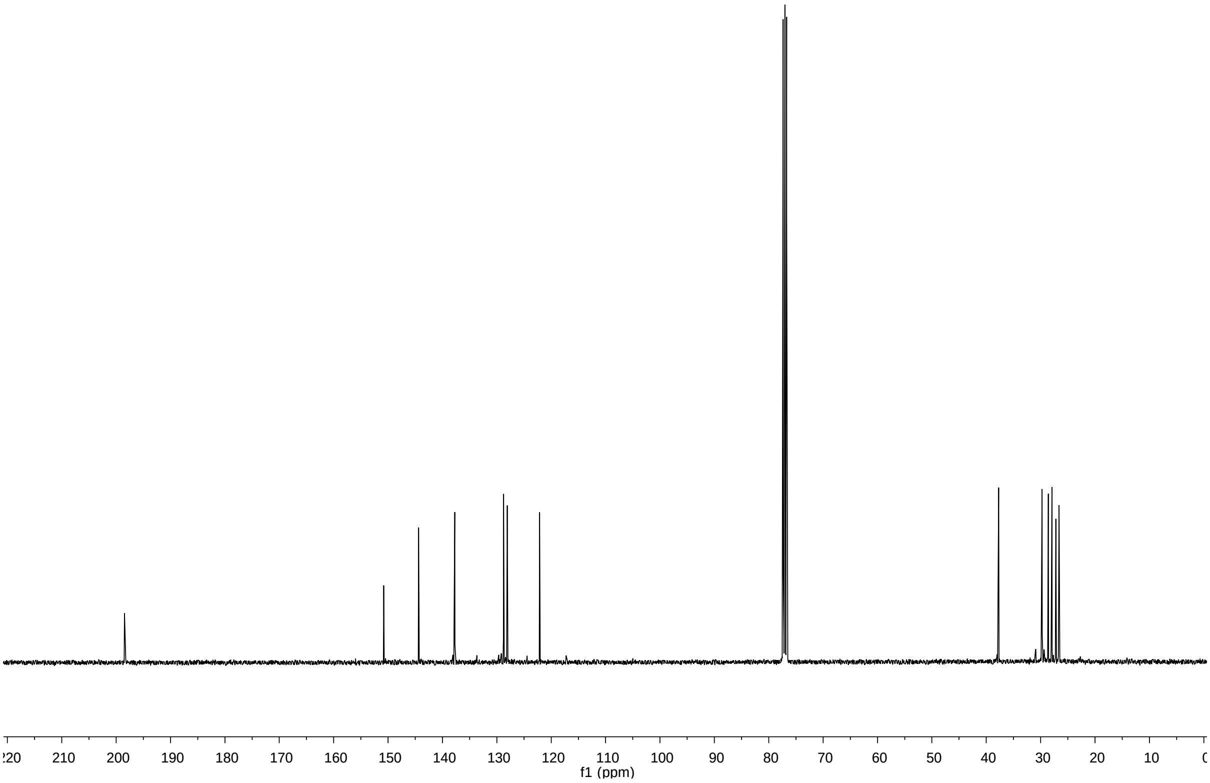
mshcc667
13C 100.6MHz Job 17107 Hadfield M S C667 CDCl3 25.0'C 0 hour 59 min



mshhb723
1H 400.1MHz Job 17987 Hadfield M S B723 CDCl3   25.0'C



mshcb723
13C 100.6MHz Job 18035 Hadfield M S B723 CDCl3   25.0'C   5 hours 35 min



mshha722
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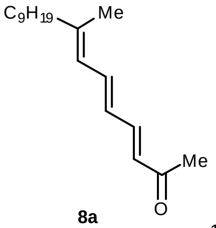
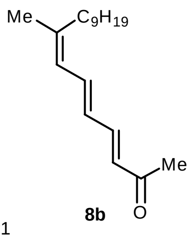
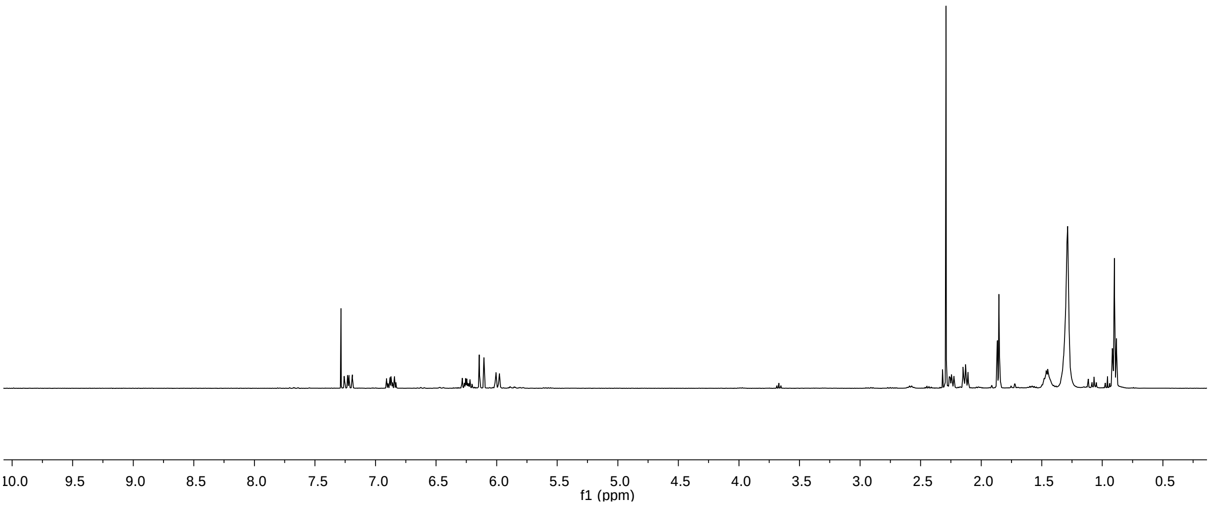


8a

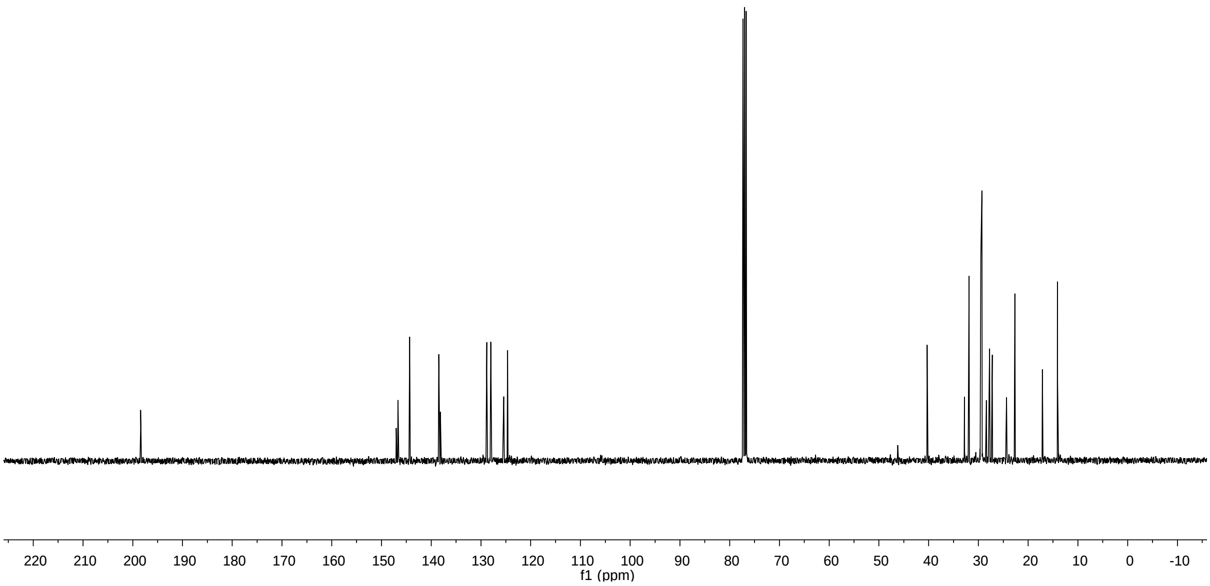
1.5:1



8b



mshca722
13C 100.6MHz Job 17976 Hadfield M S A722 CDCl3 25.0'C 0 hour 58 min



mshhc744
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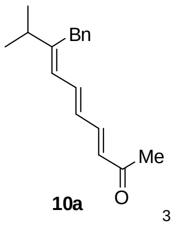
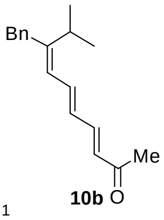
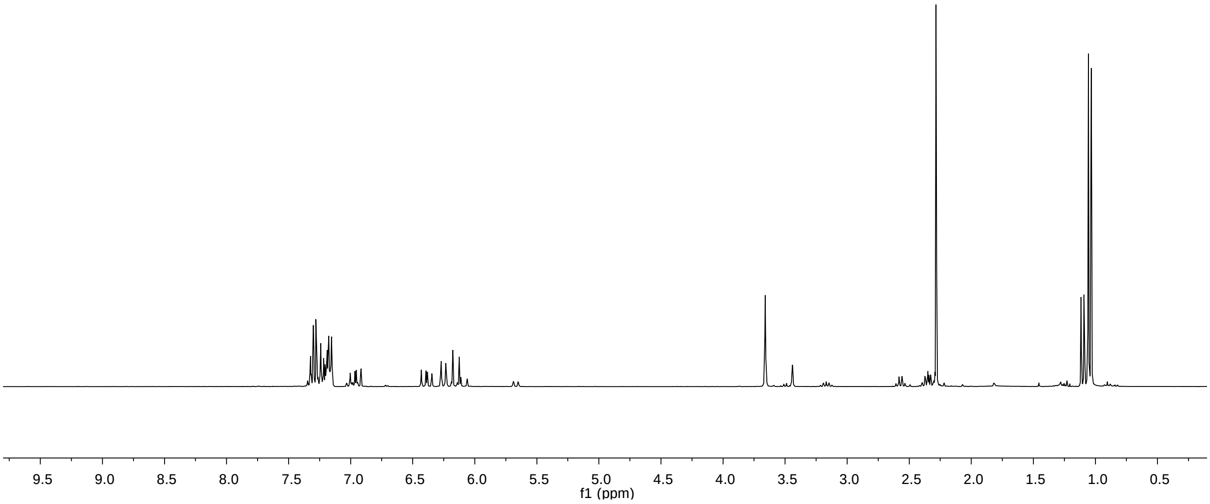


10a

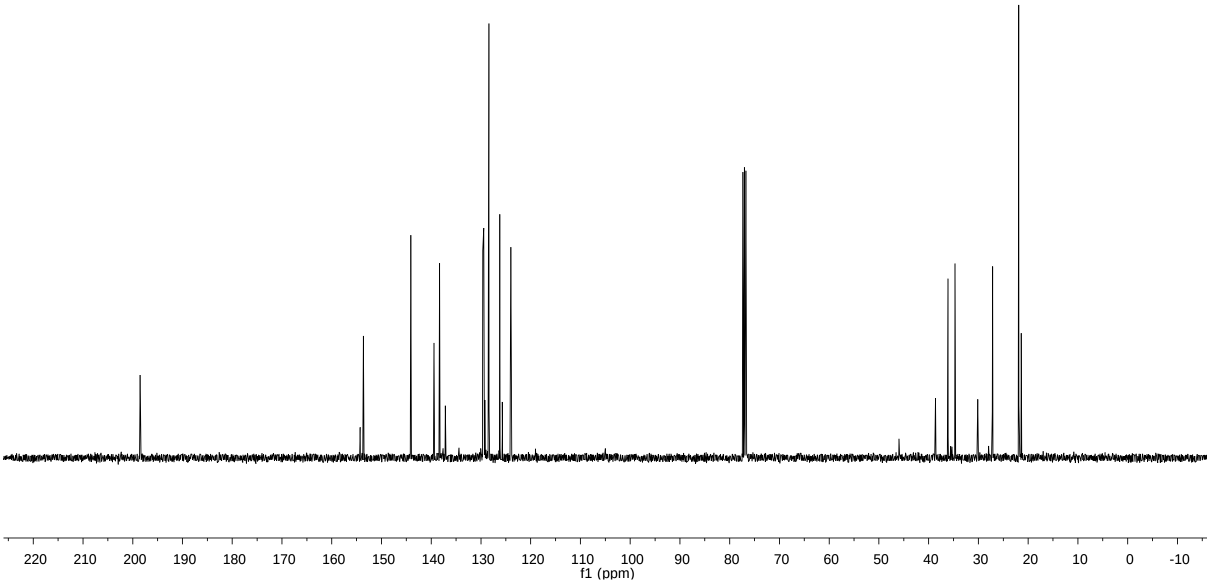
3.5:1



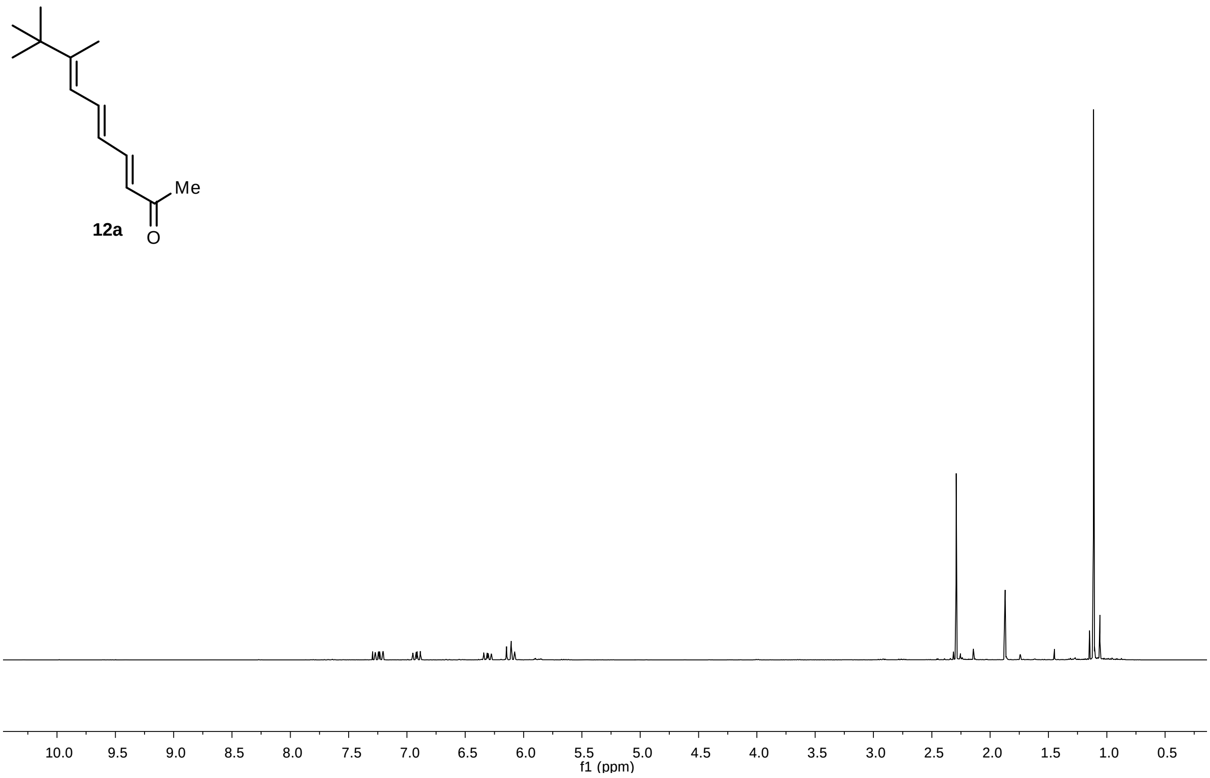
10b



mshcc744
13C 100.6MHz Job 18205 Hadfield M S C744 CDCl3 25.0'C 0 hour 29 min



mshhe668
1H 400.1MHz Job 17175 Hadfield M S E668 CDCl3 25.0'C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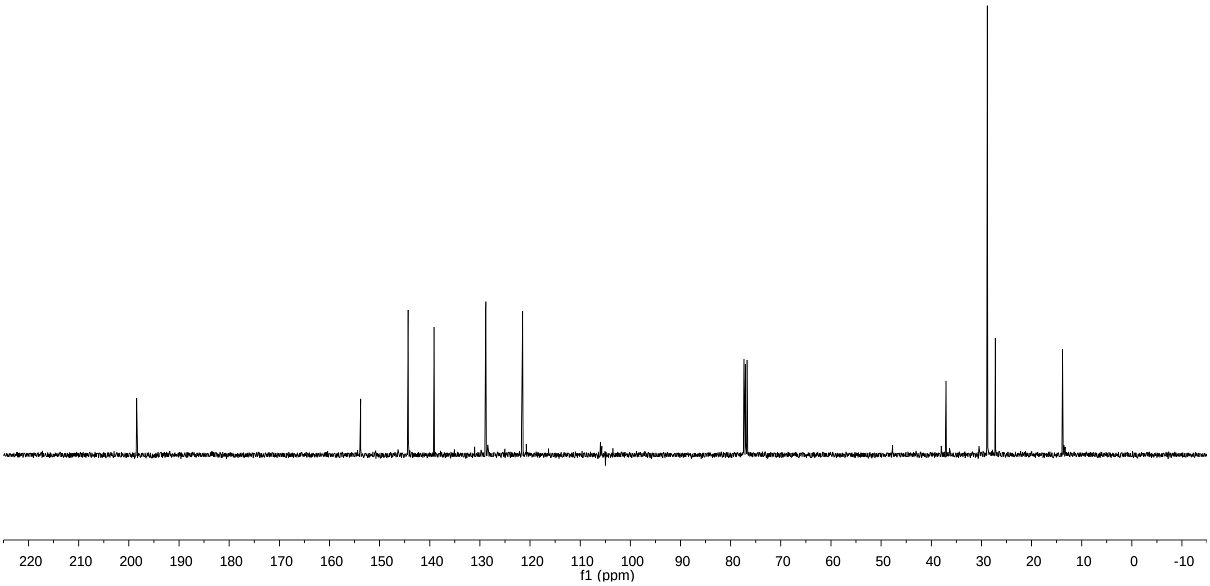
mshce668
13C 100.6MHz Job 17183 Hadfield M S E668 CDCl3 25.0'C 0 hour 14 min



mshha818
1H 300.1MHz Job 1640 Hadfield M S A818 CDCl3 25.1'C
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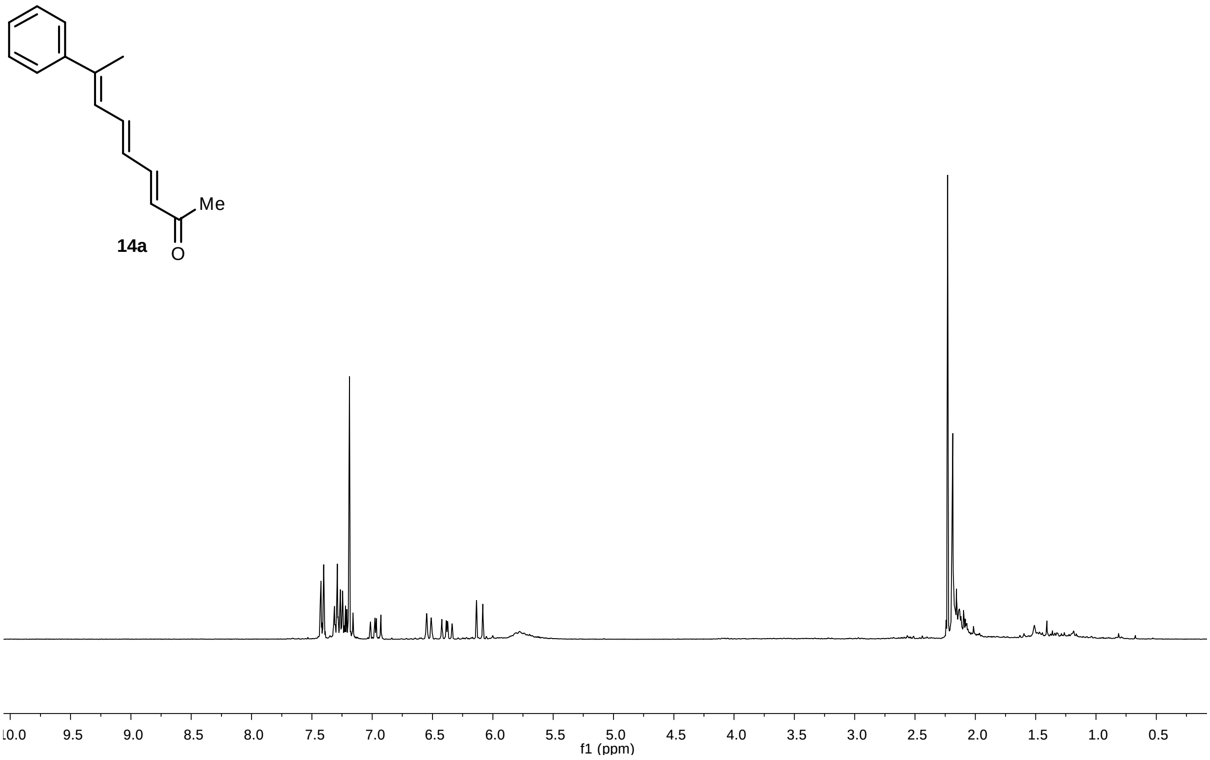
14a

mshca818
13C 75.5MHz Job 1641 Hadfield M S A818 CDCl3 25.0'C 0 hour 18 min
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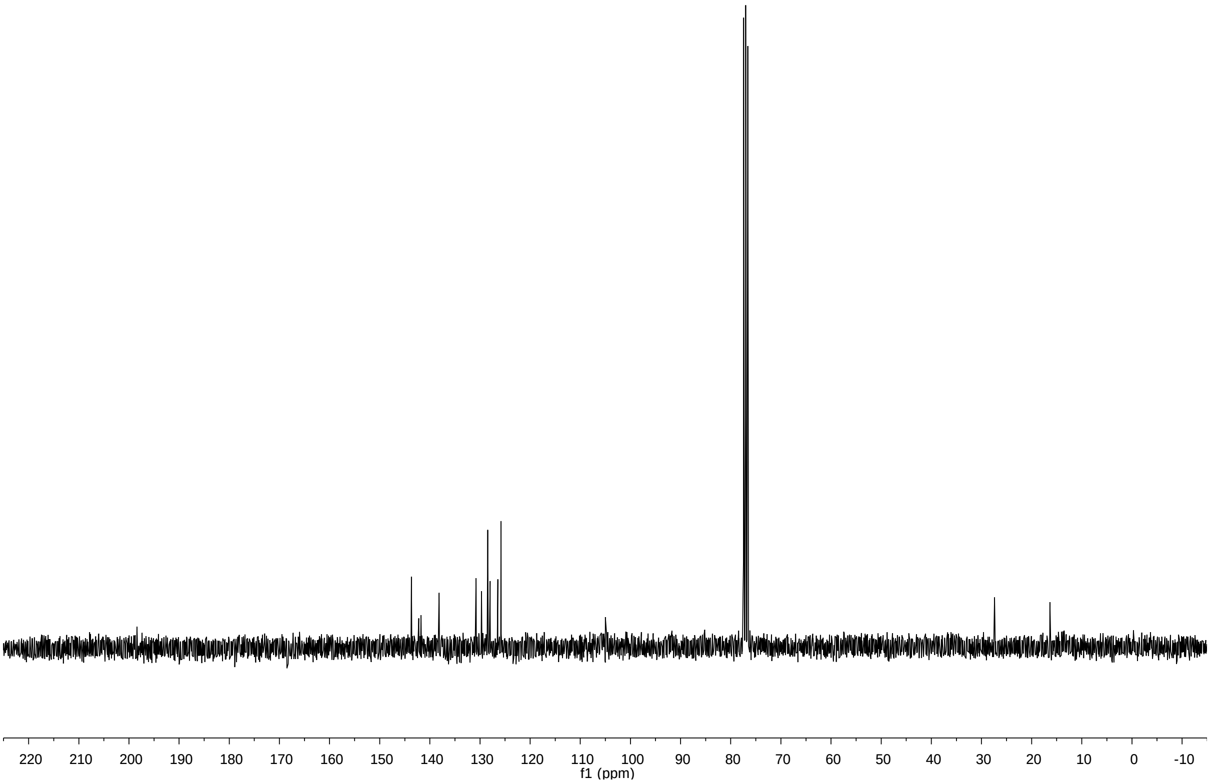

mshhc756
1H 300.1MHz Job 578 Hadfield M S C756 CDCl3 25.1'C
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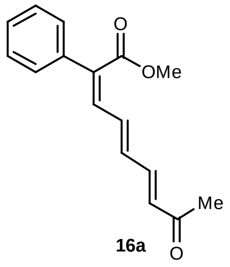
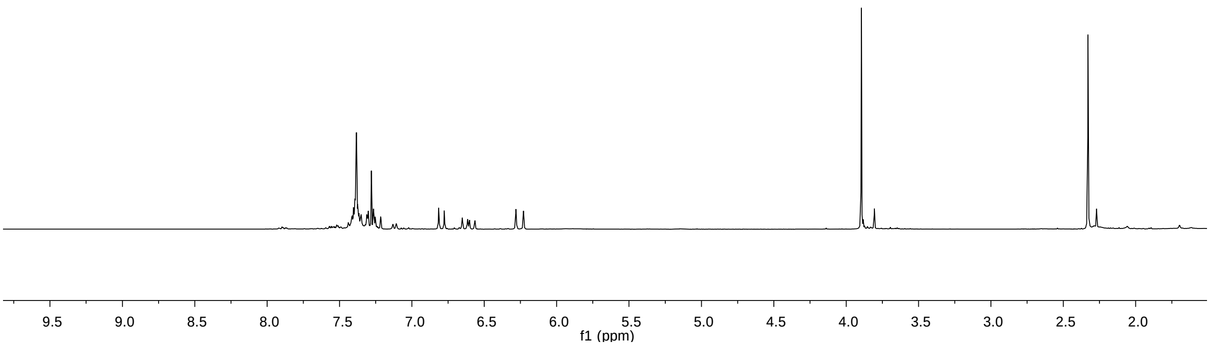
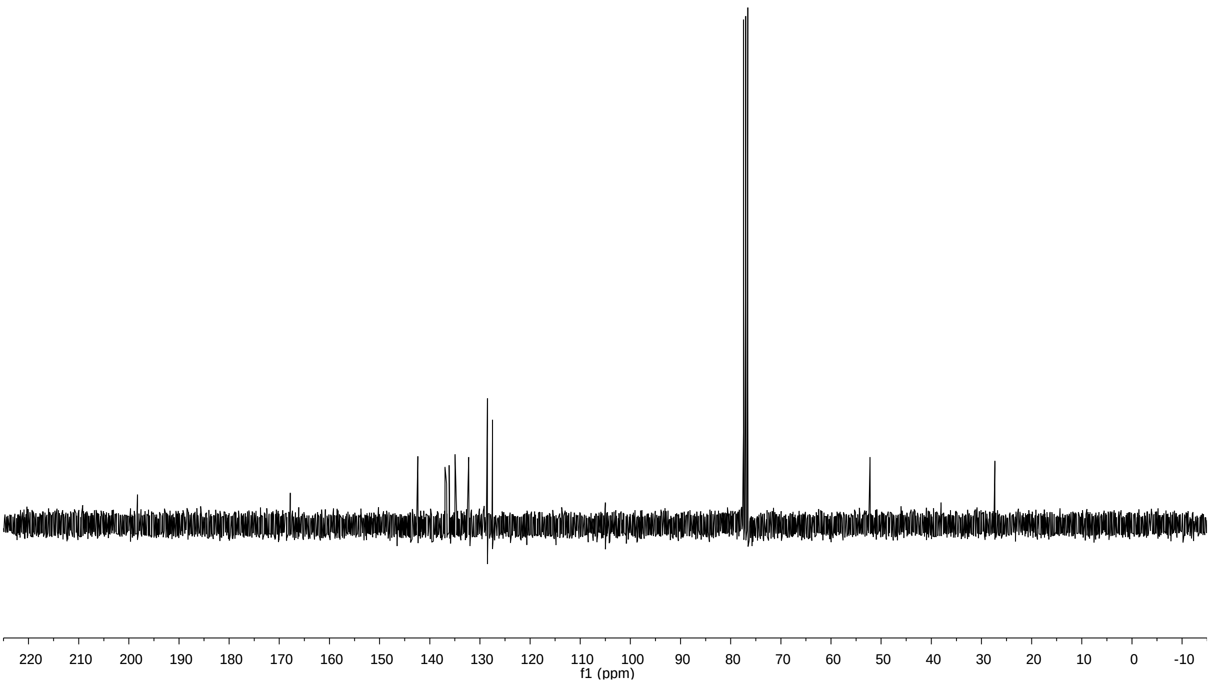


16a



mshce756



mshhc760
1H 300.1MHz Job 640 Hadfield M S C760 CDCl3 25.1'C
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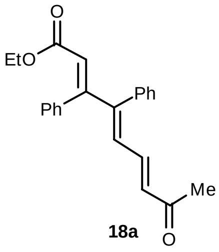
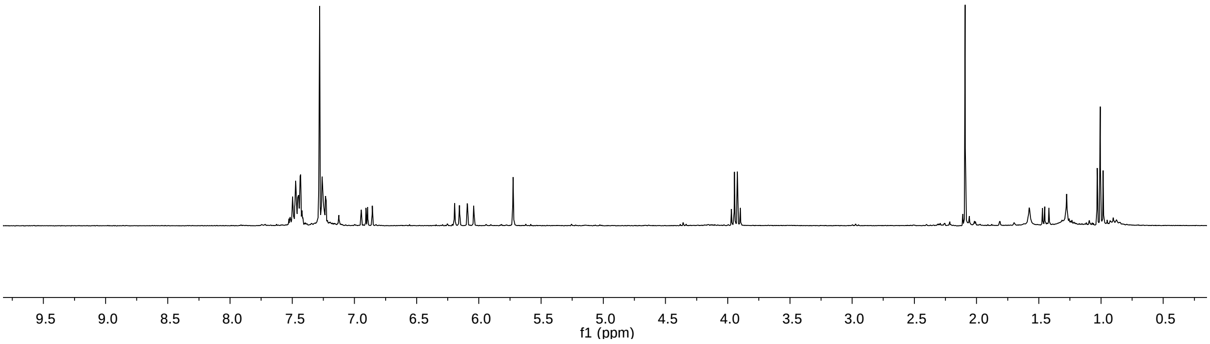
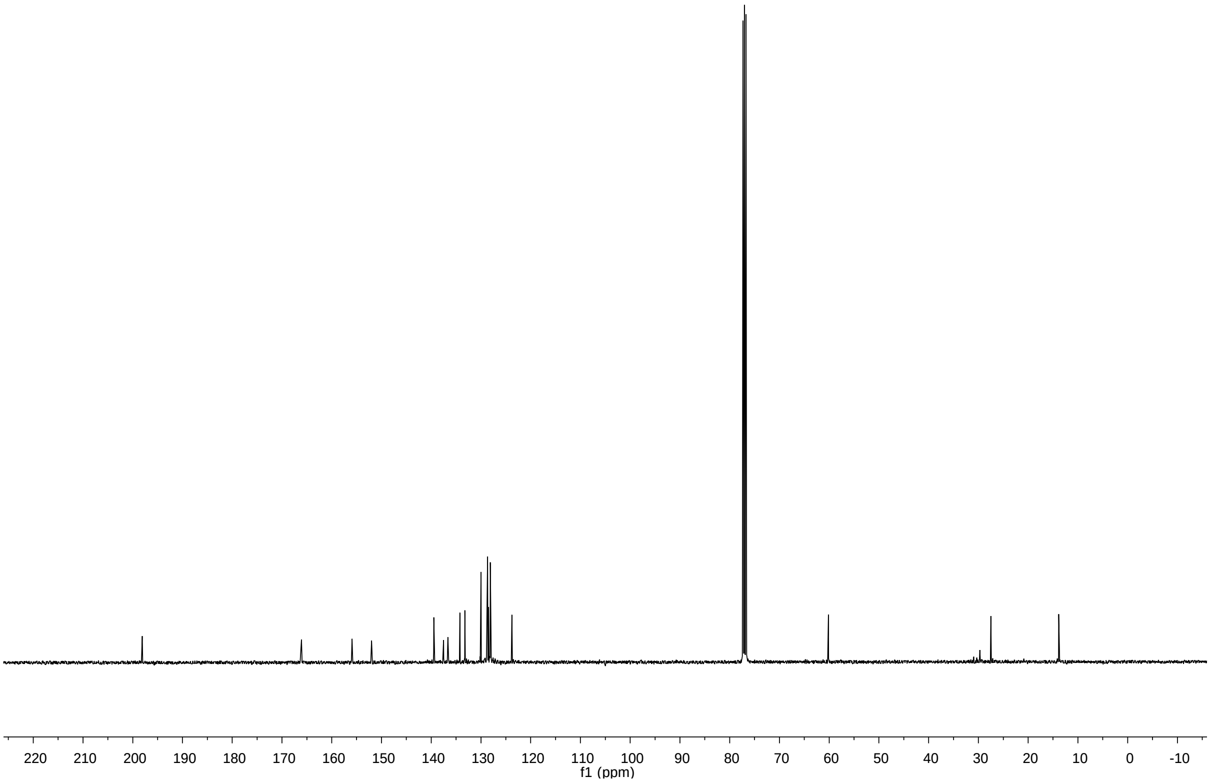


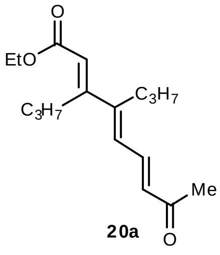
18a



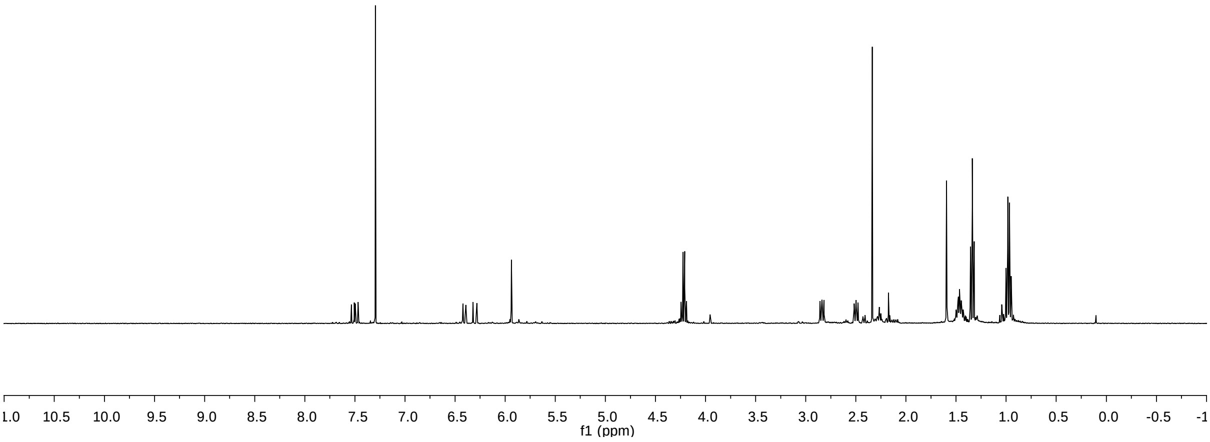
mshcc760
13C 100.6MHz Job 18240 Hadfield M S C760 CDCl3 25.0'C 8 hours 15 min



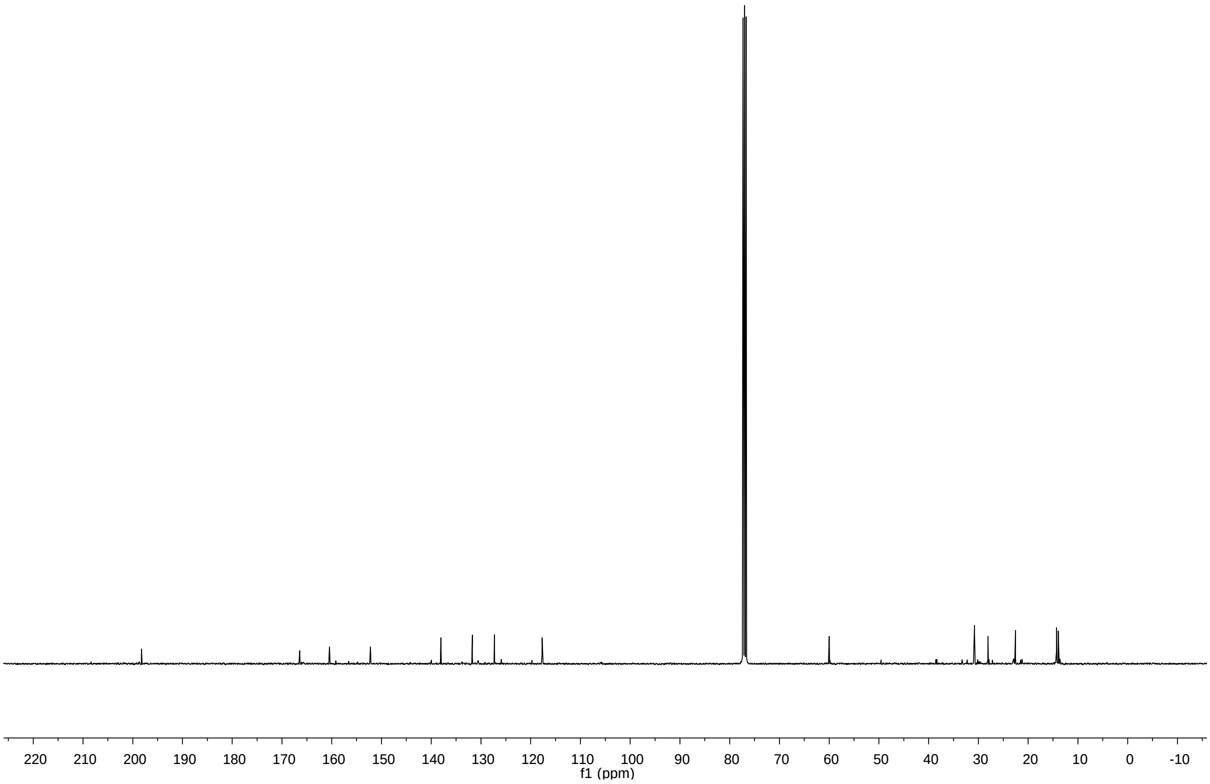
mshhc776
1H 400.1MHz Job 18315 Hadfield M S C776 CDCl3   25.0'C



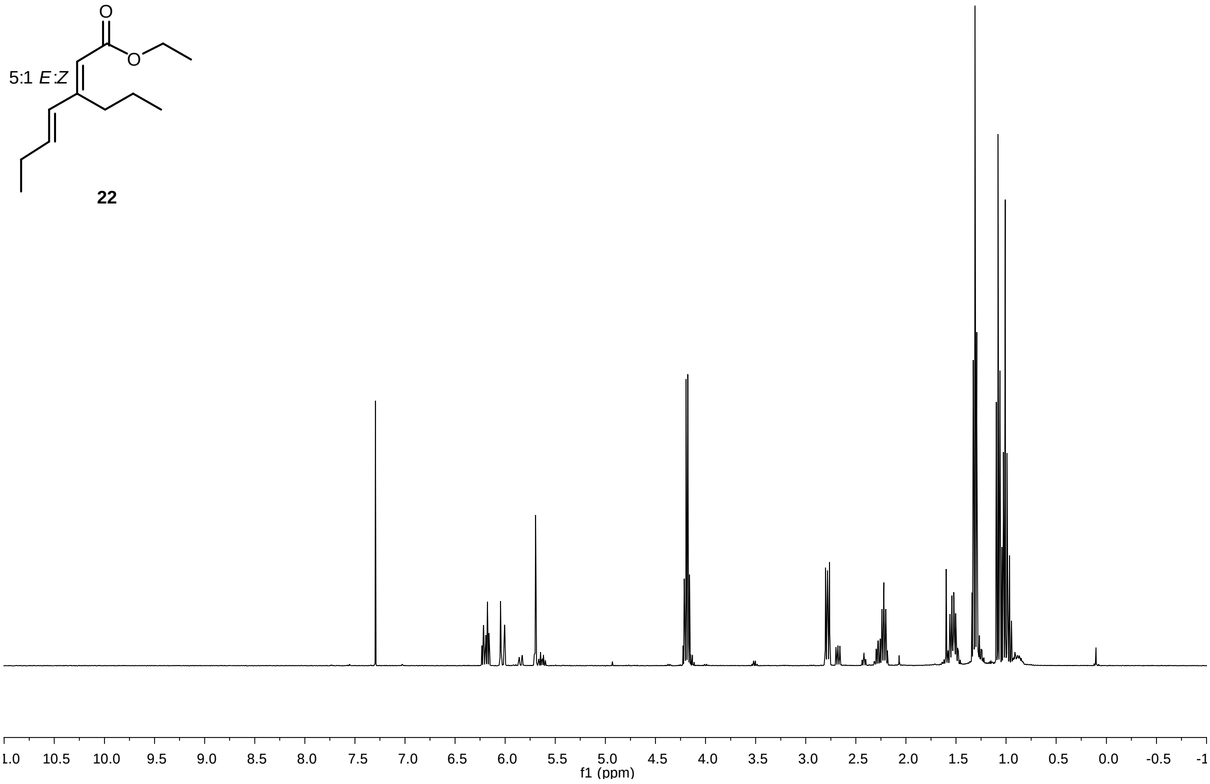
20a



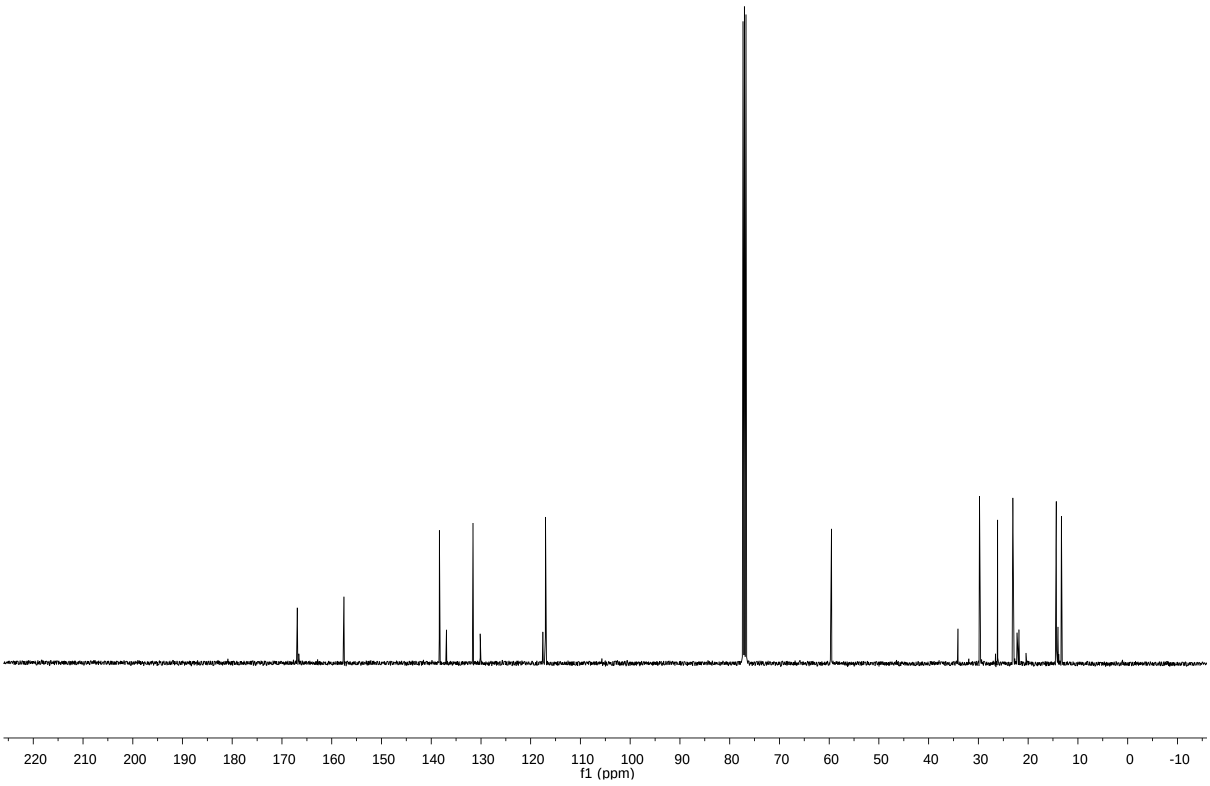
mshcc776
13C 100.6MHz Job 18302 Hadfield M S C776 CDCl3   25.0'C 32 hours 5 min



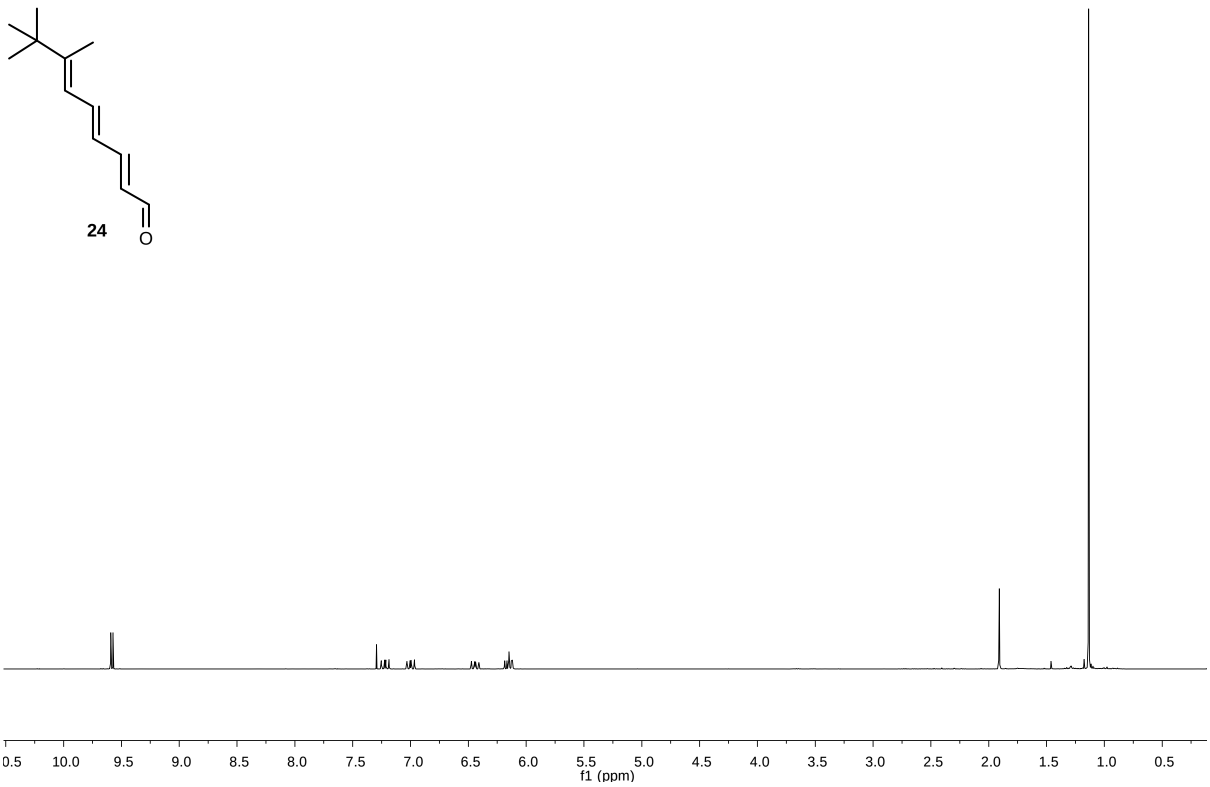
mshha766
1H 400.1MHz Job 18259 Hadfield M S A766 CDCl3   25.0'C



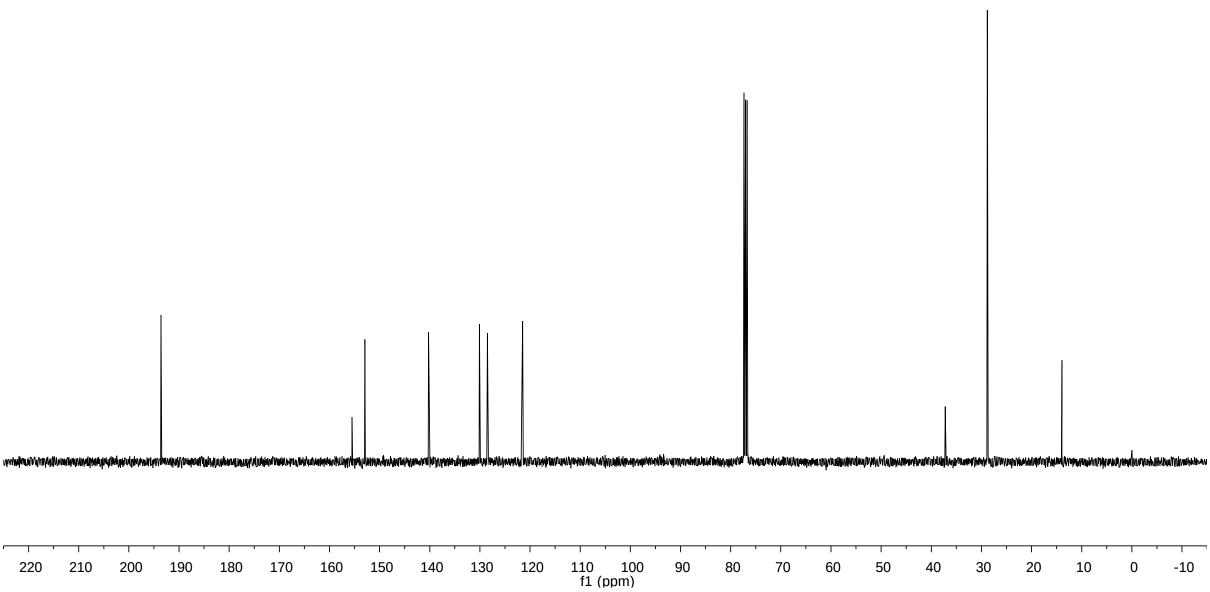
mshca766
13C 100.6MHz Job 18260 Hadfield M S A766 CDCl3   25.0'C   4 hours 22 min



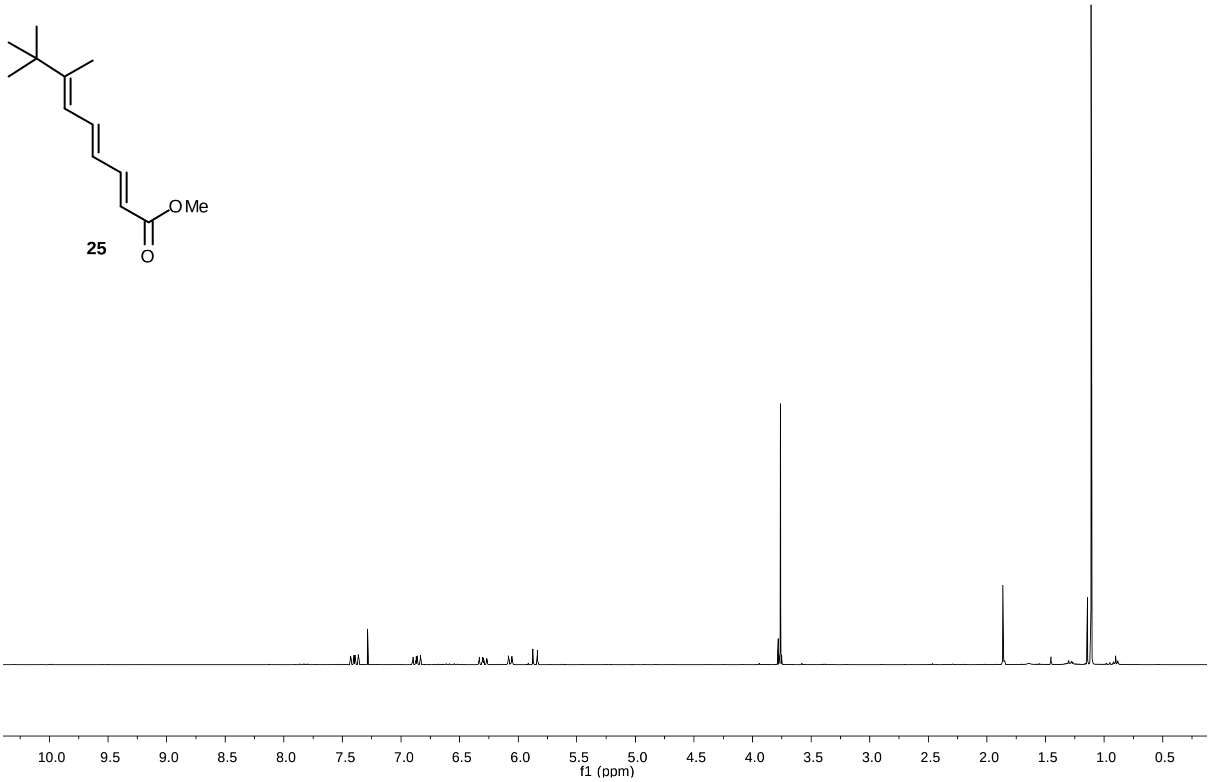
mshhb671
1H 400.1MHz Job 17262 Hadfield M S B671 CDCl3 25.0'C



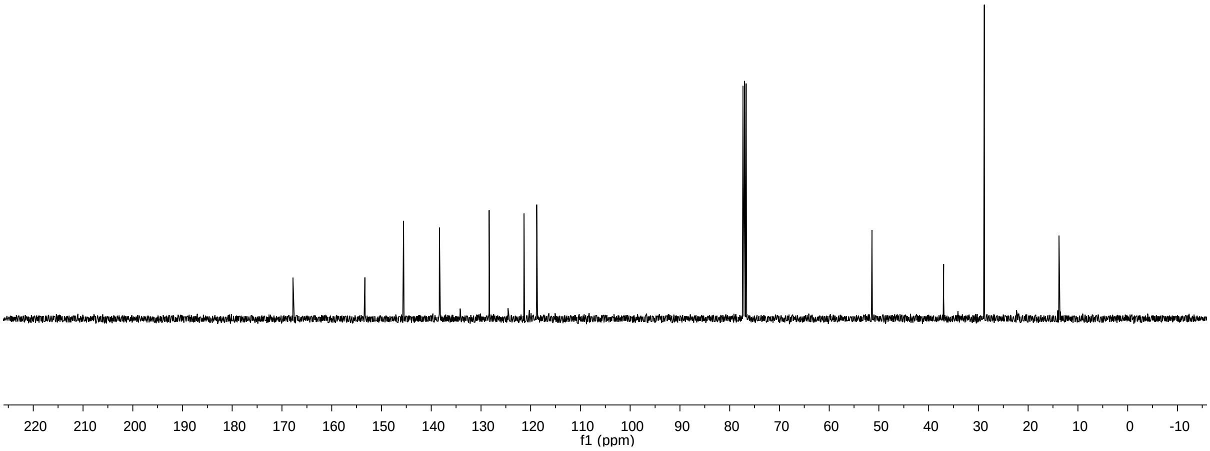
mshcb671
13C 100.6MHz Job 17263 Hadfield M S B671 CDCl3 25.0'C 0 hour 29 min



mshhd669
1H 400.1MHz Job 17964 Hadfield M S D669 CDCl3   25.0'C



mshcd669
13C 100.6MHz Job 17977 Hadfield M S D669 CDCl3   25.0'C   0 hour 14 min



mshhb731
1H 300.1MHz Job 5 Hadfield M S B731 CDCl3   25.0'C
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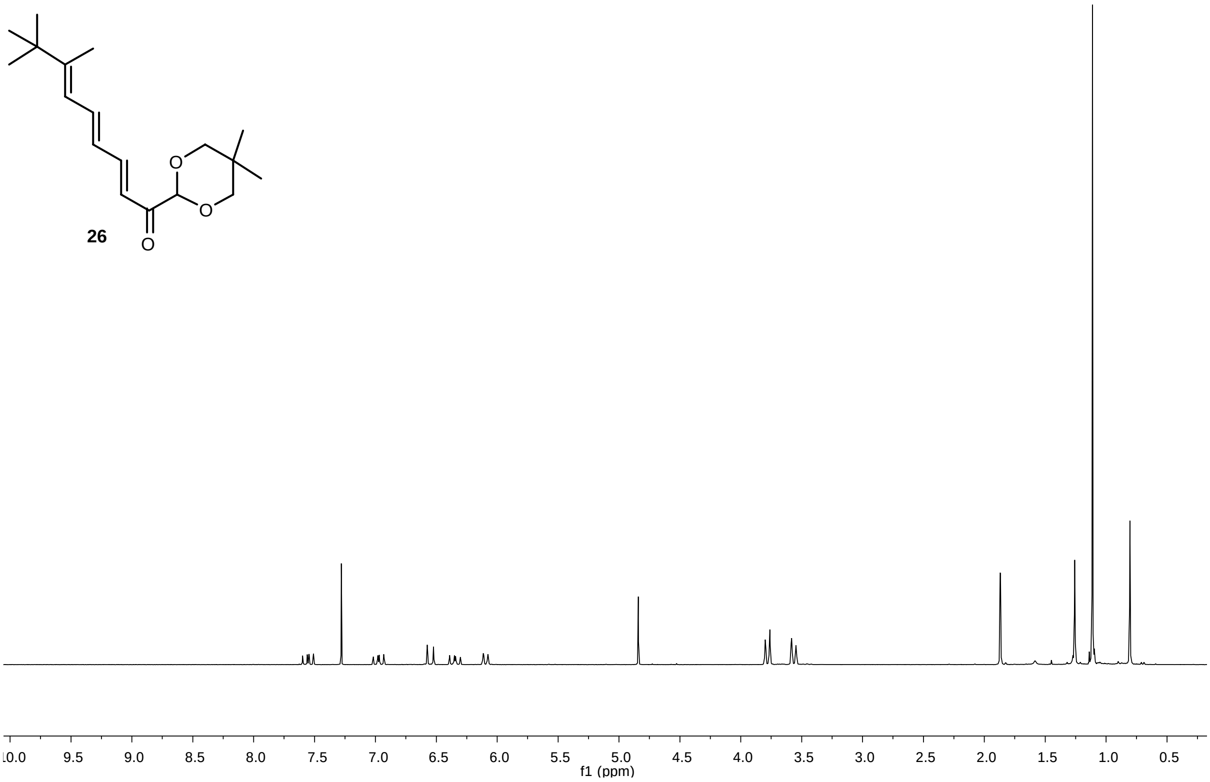
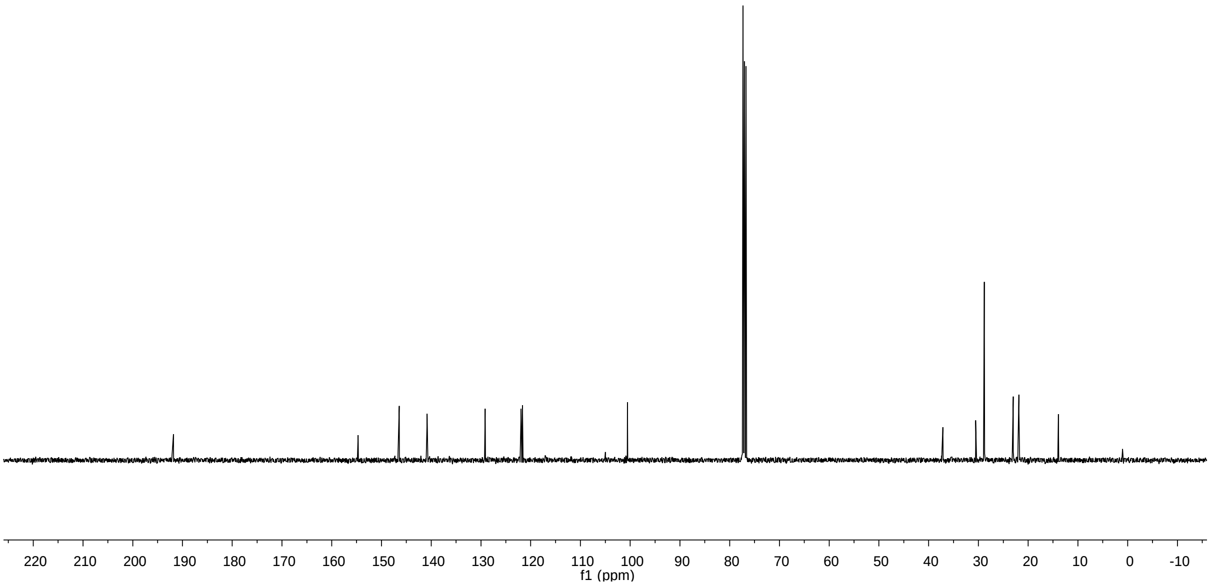


26

mshcb731
13C 100.6MHz Job 18166 Hadfield M S B731 CDCl3   25.0'C   1 hour 12 min



mshha741
1H 300.1MHz Job 153 Hadfield M S A741 CDCl3 25.0'C
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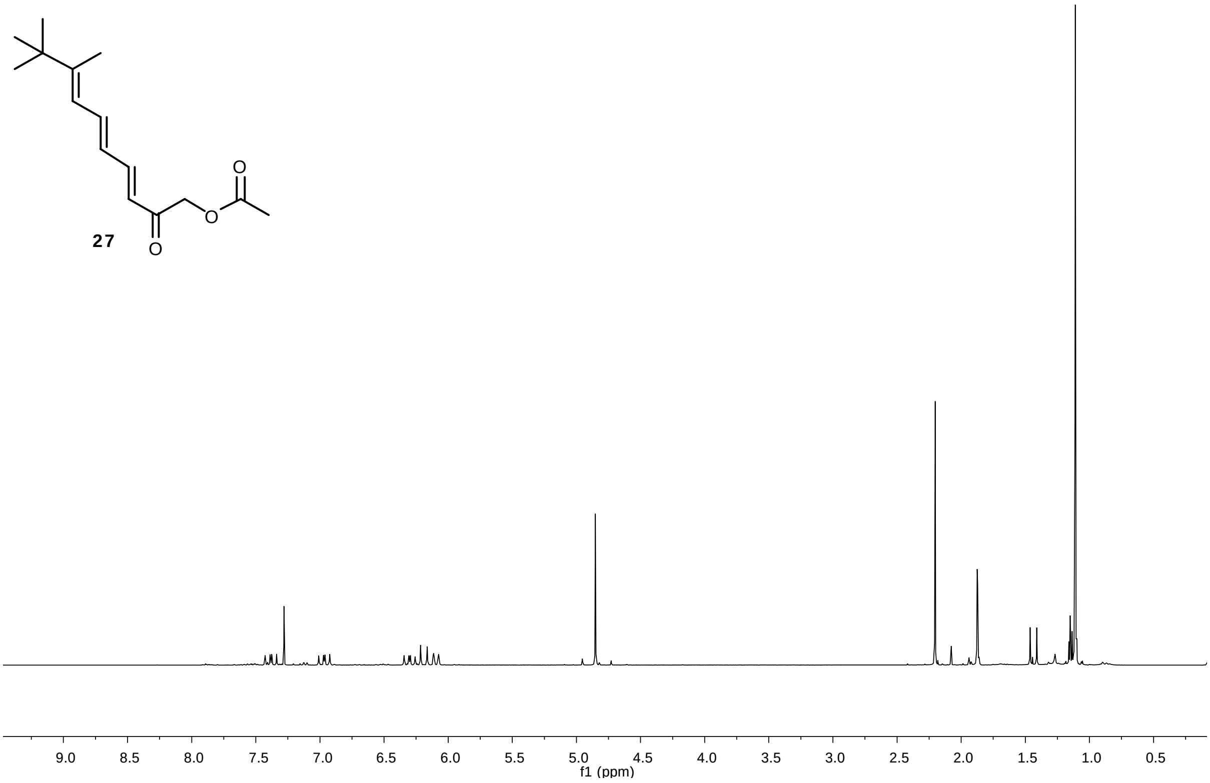
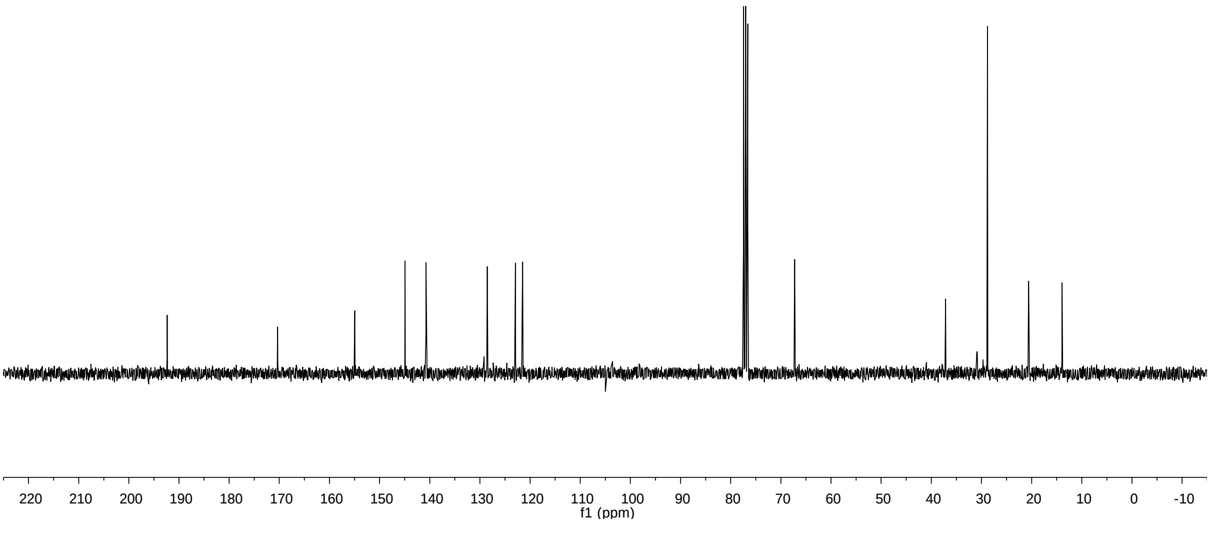
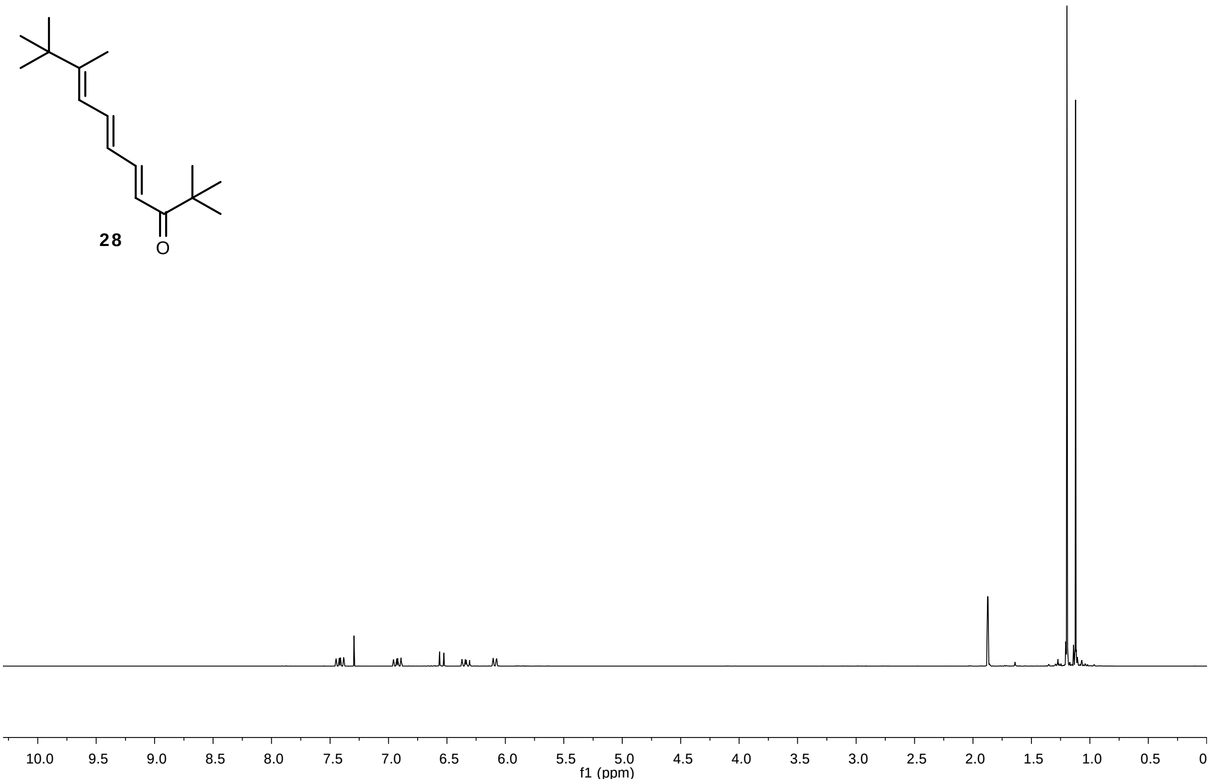


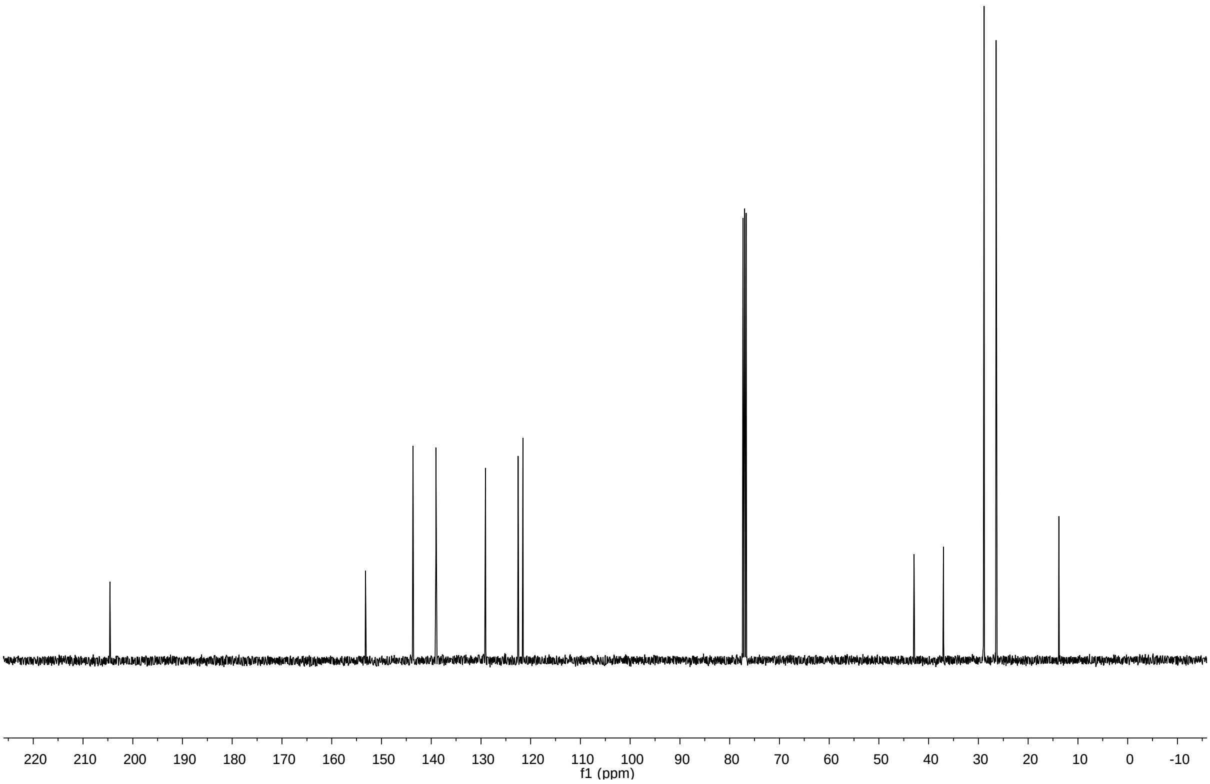
mshca741
13C 75.5MHz Job 154 Hadfield M S A741 CDCl3 25.0'C 0 hour 18 min
*



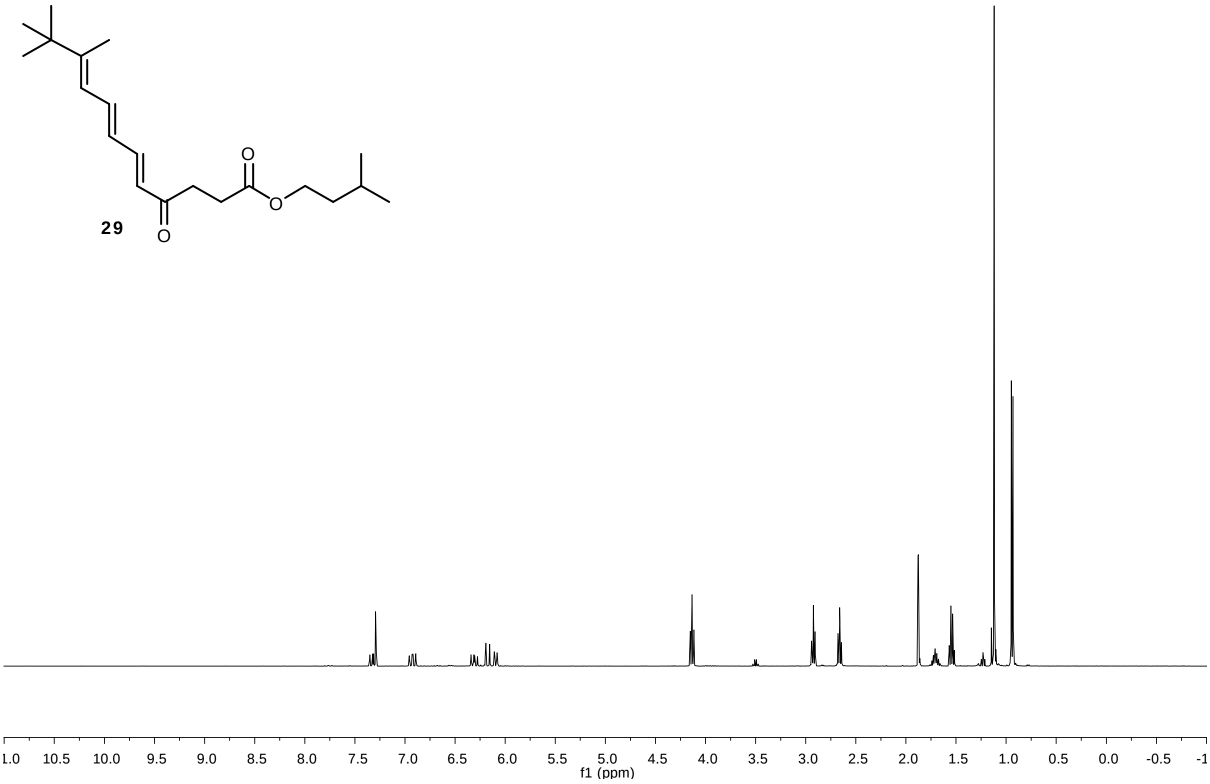
MSHHB801
1H 400.1MHz Job 18368 Hadfield M S B801 CDCl3   25.0'C



MSHCB801
13C 100.6MHz Job 18371 Hadfield M S B801 CDCl3   25.0'C   0 hour 43 min

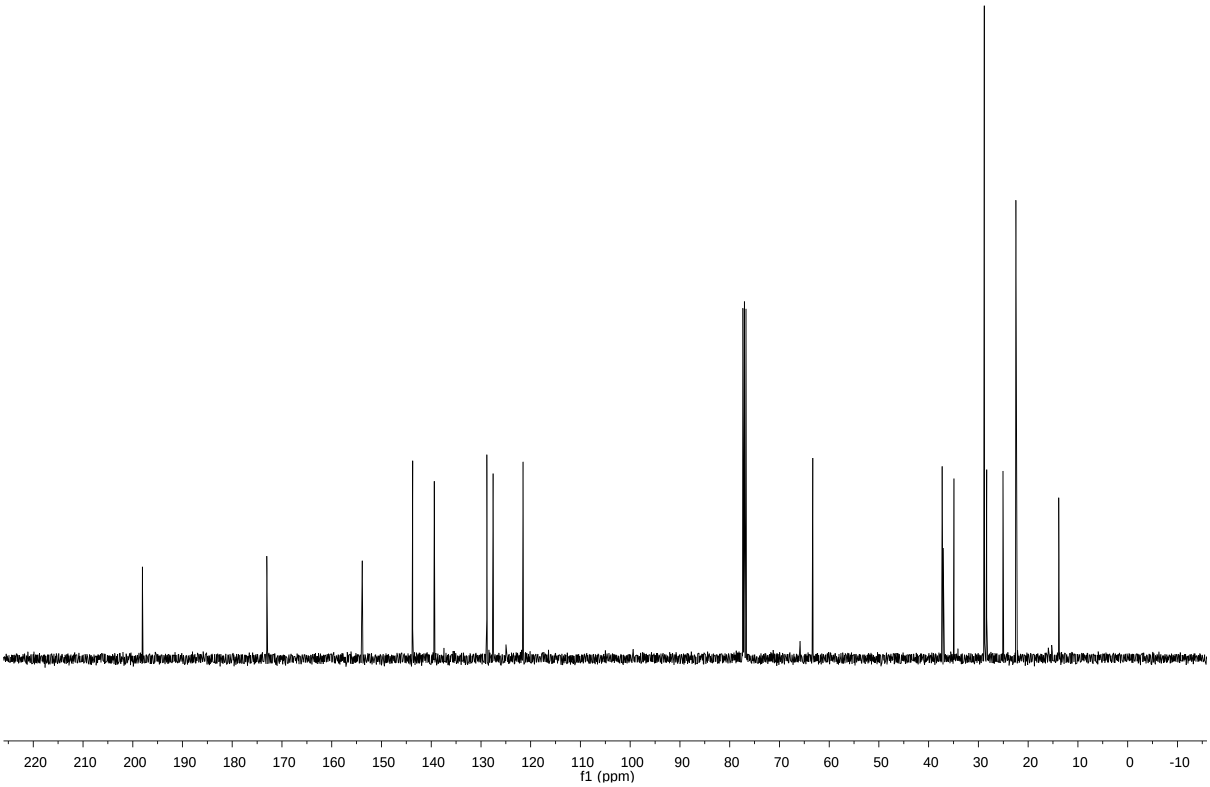


mshhb783

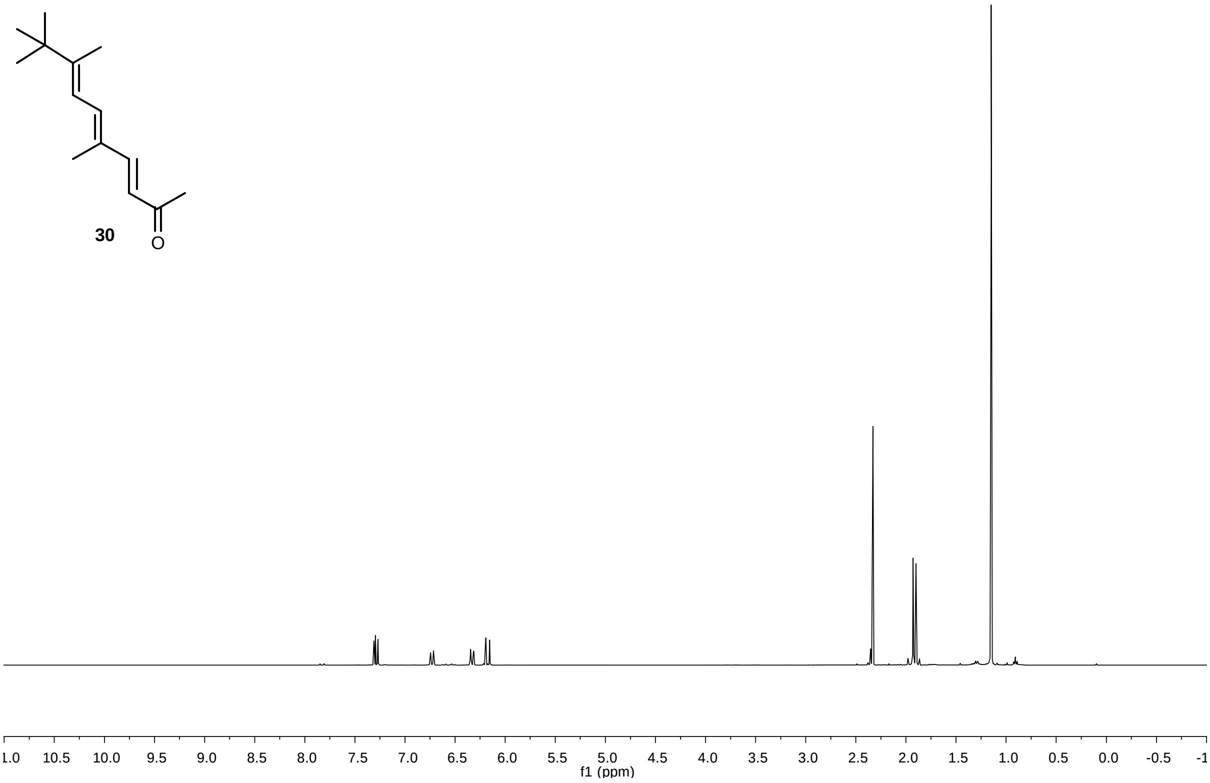


29

mshcb783
13C 100.6MHz Job 18318 Hadfield M S B783 CDCl3 25.0'C 0 hour 14 min



mshha727
1H 400.1MHz Job 18045 Hadfield M S A727 CDCl3   25.0'C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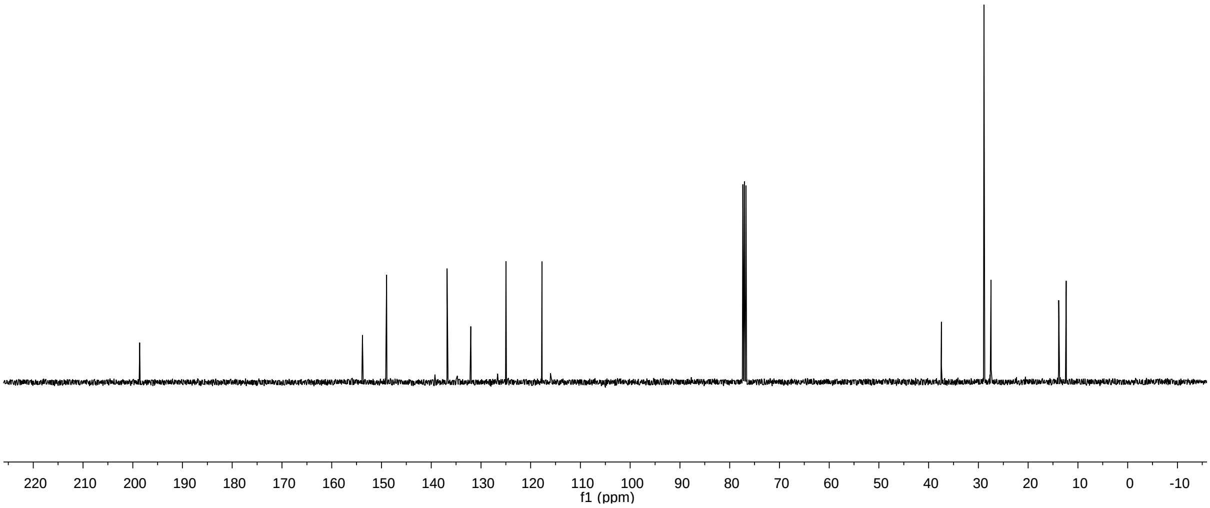
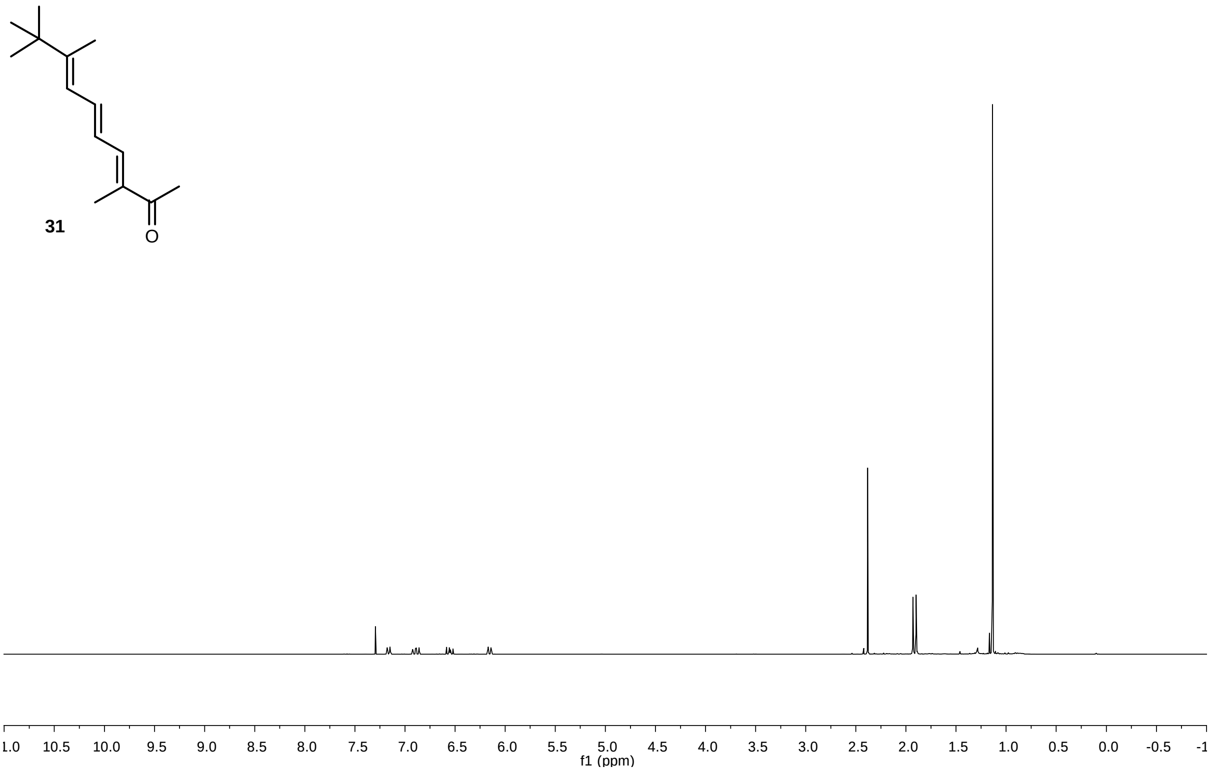
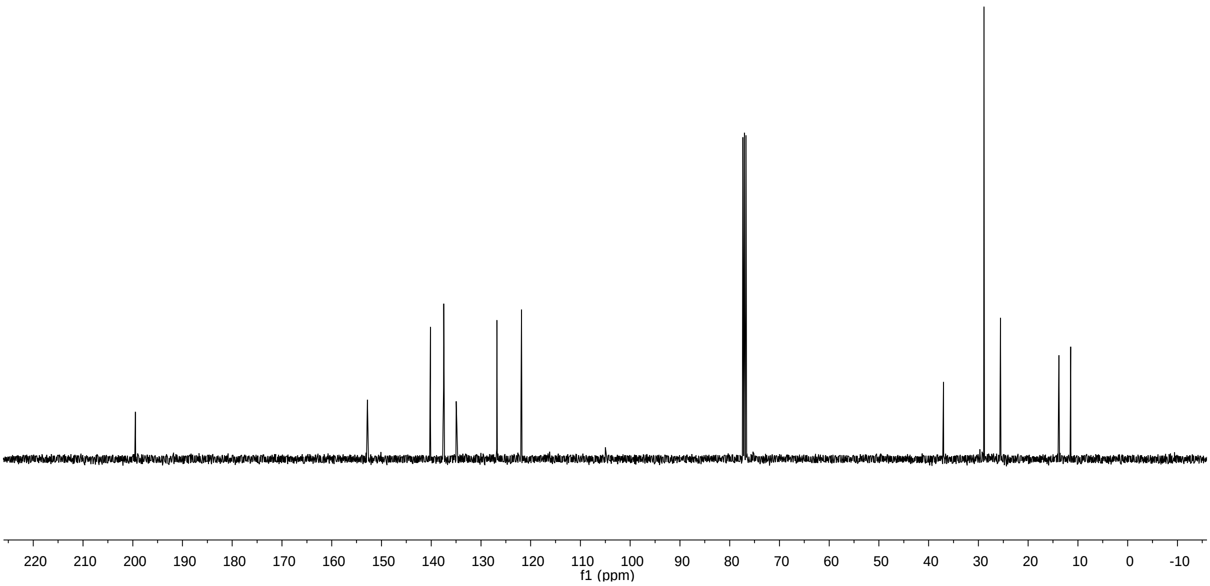
mshca727
13C 100.6MHz Job 18050 Hadfield M S A727 CDCl3   25.0'C   0 hour 14 min



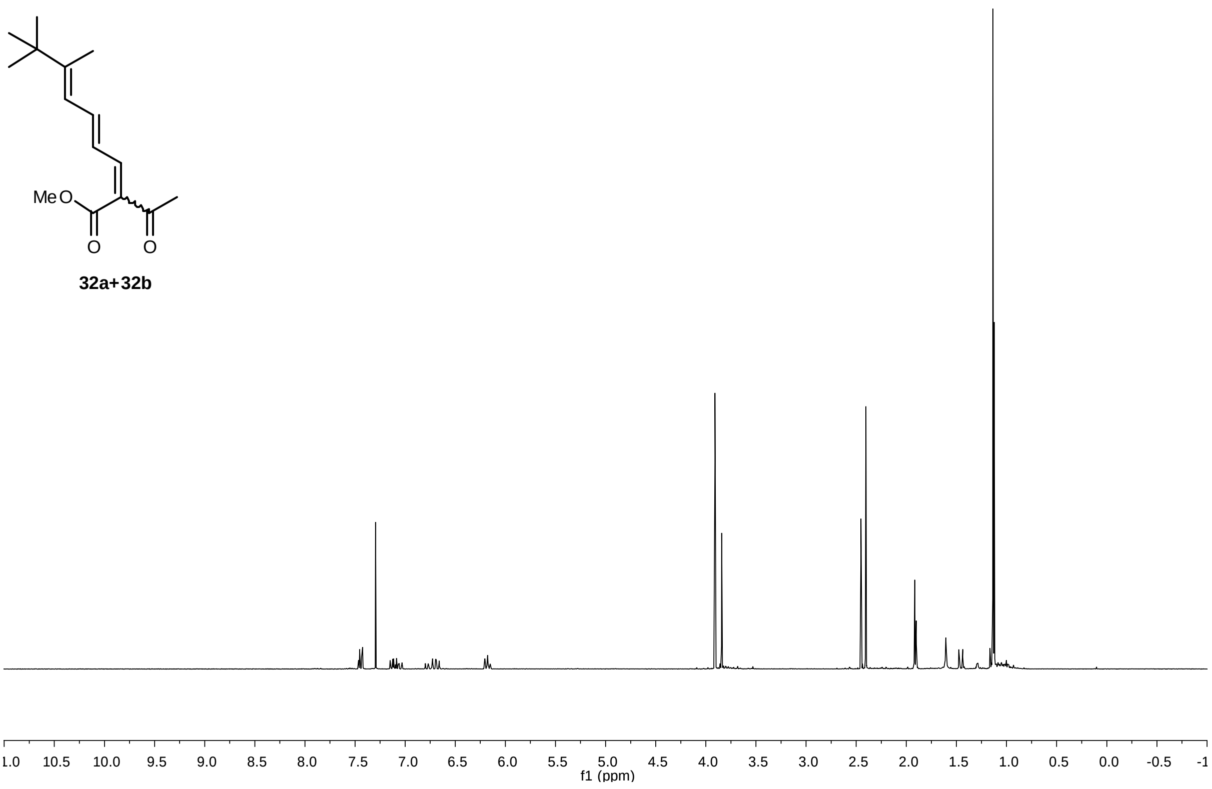
mshha728
1H 400.1MHz Job 18155 Hadfield M S A728 CDCl3   25.0'C



mshca728
13C 100.6MHz Job 18157 Hadfield M S A728 CDCl3   25.0'C   0 hour 14 min

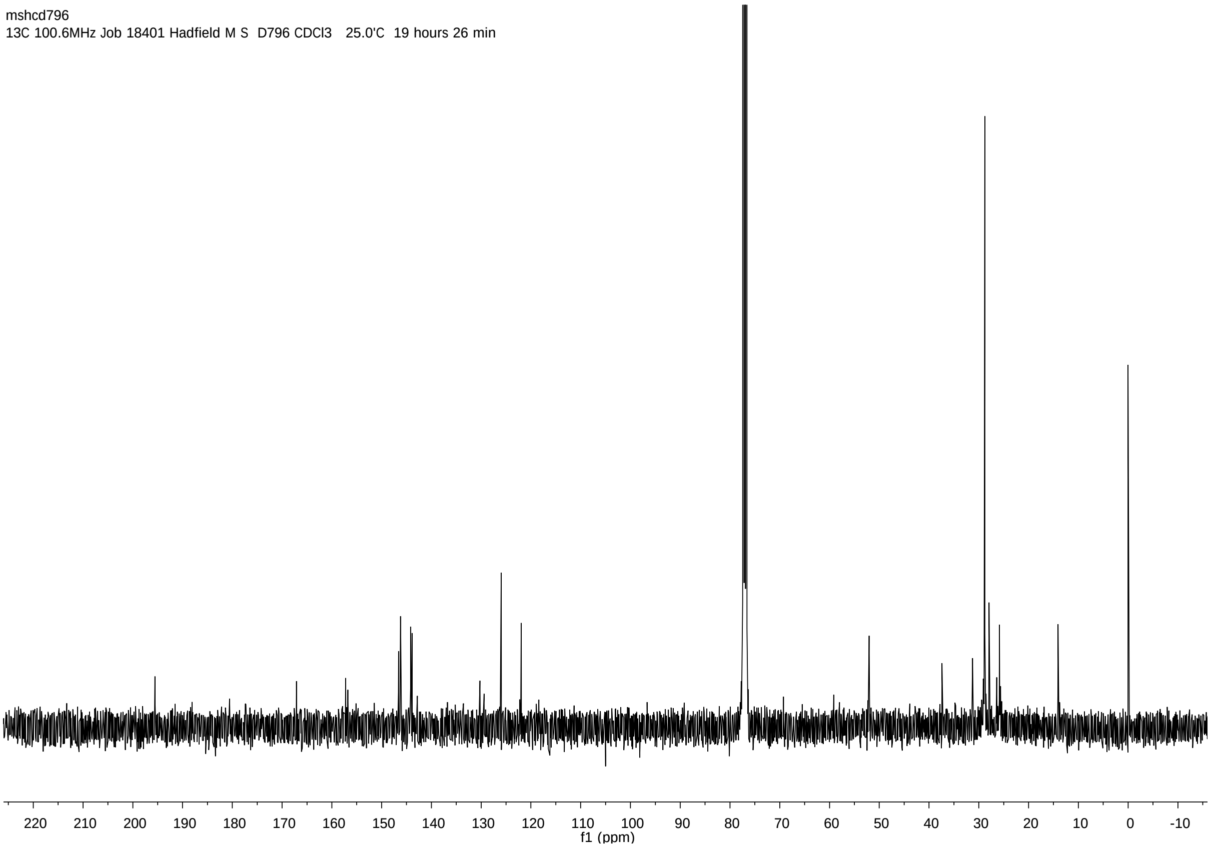


mshhd796
1H 400.1MHz Job 18348 Hadfield M S D796 CDCl3 25.0'C



32a+32b

mshcd796
13C 100.6MHz Job 18401 Hadfield M S D796 CDCl3 25.0'C 19 hours 26 min



mshhb774
1H 300.1MHz Job 964 Hadfield M S B774 CDCl3   25.0'C
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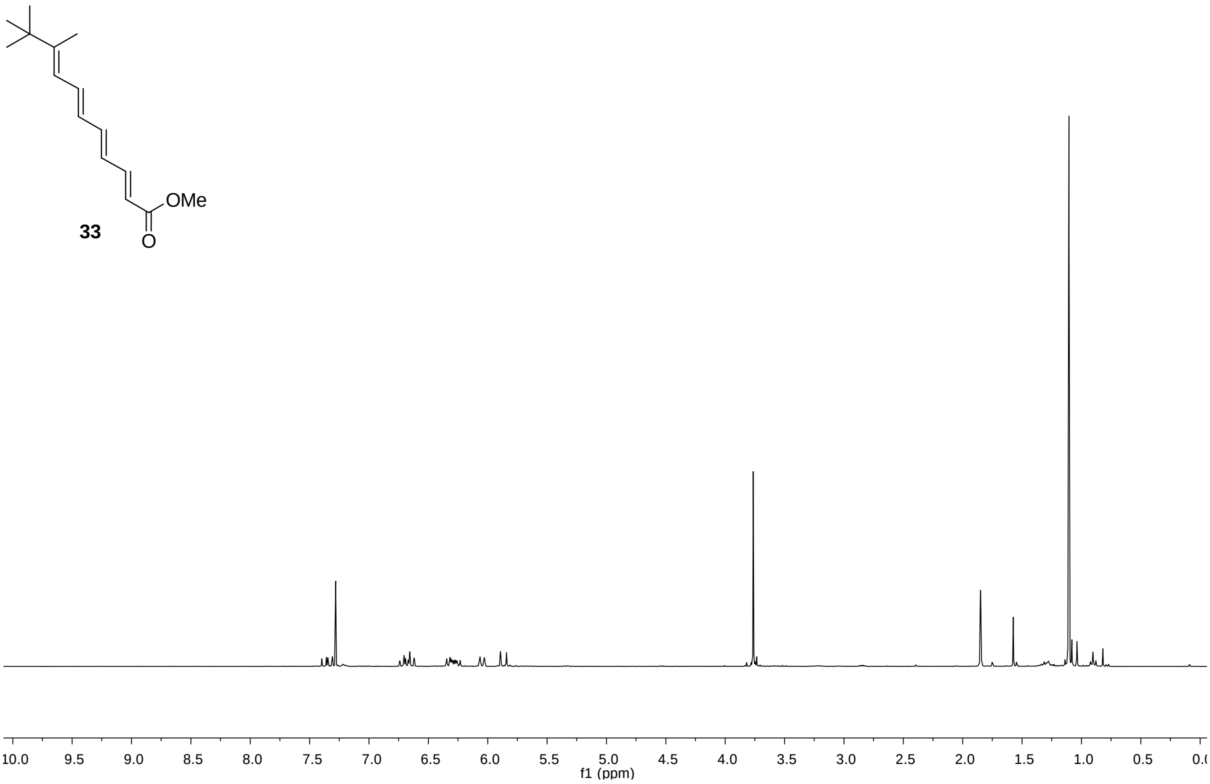
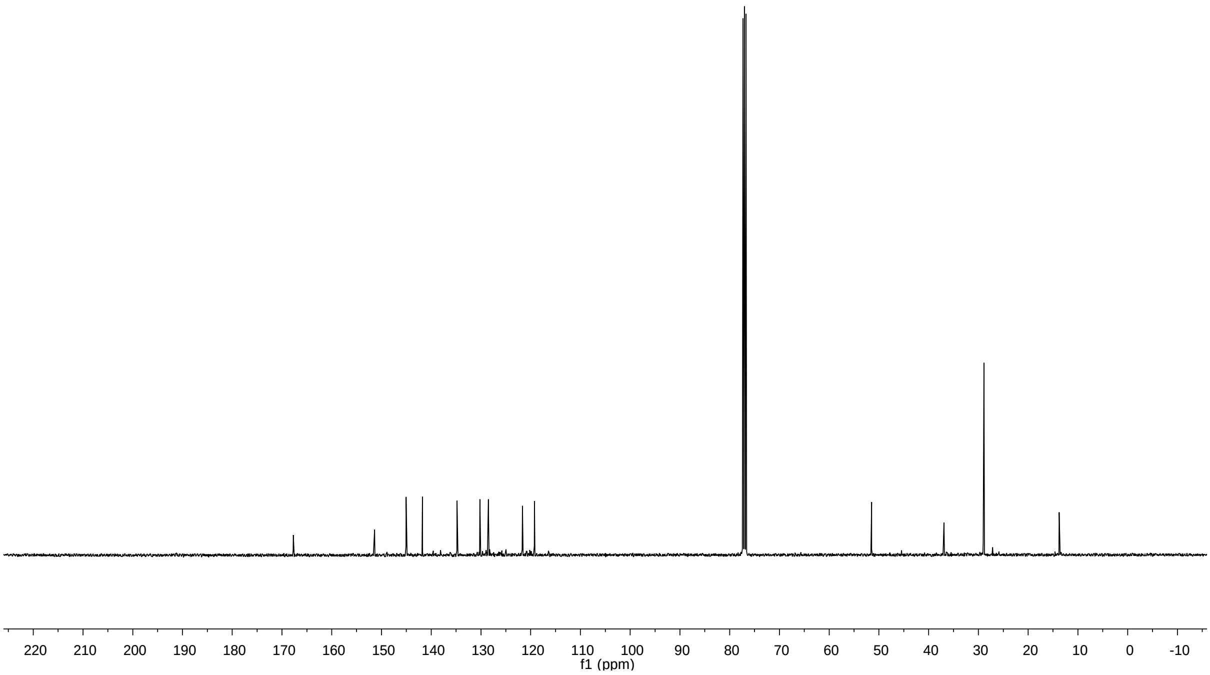


mshcb774
13C 100.6MHz Job 18301 Hadfield M S B774 CDCl3   25.0'C   6 hours 4 min



4. References

1. M. S. Hadfield, J. T. Bauer, P. E. Glen and A. L. Lee, *Org. Biomol. Chem.*, 2010, **8**, 4090-4095.
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3. J. T. Bauer, M. S. Hadfield and A. L. Lee, *Chem. Commun.*, 2008, 6405-6407.
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7. C. Li, H. Zhang, J. Feng, Y. Zhang and J. Wang, *Org. Lett.*, 2010, **12**, 3082.
8. G. C. G. Pals, A. Keshavaraja, K. Saravanan and P. Kumar, *J. Chem. Res.* , 1996, **9**, 426-427.
9. For example, see: P. Charoenying, H. Davies, D. McKerrecher and R. J. K. Taylor, *Tetrahedron Lett.*, 1996, **37**, 1913 and ref. 1, 3 and 4 within the communication.