*ELECTRONIC SUPPLEMENTARY INFORMATION FOR:*

# Total syntheses of the furanosesquiterpenes crassifolone and dihydrocrassifolone *via* an Au(I)-catalysed intramolecular Michael addition reaction

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## 1. General Experimental Procedures

Proton ($^{1}$H) and carbon ($^{13}$C) NMR spectra were recorded on Varian machines operating at 300 or 400 MHz. Unless otherwise specified, the spectra were recorded at 20 °C in deuterochloroform. Chemical shifts are recorded as δ values in parts per million (ppm). Infrared spectra ($\nu_{max}$) were recorded as thin films on NaCl plates using a Perkin–Elmer 1800 Series FTIR spectrometer. Low-resolution ESI mass spectra were recorded on a Micromass–Waters LC-ZMD single quadrupole liquid chromatograph mass spectrometer while low and hig resolution EI mass spectra were recorded on a VG Fisons AUTOSPEC three-sector double focussing instrument. Flash chromatographic separations were carried out using the protocols defined by Still *et. al*.[1] with silica gel 60 (40–63 μm) as the stationary phase and using the AR- or HPLC-grade solvents indicated. Melting points were measured using a Reichert hot stage microscope and are uncorrected. Analytical thin layer chromatography (TLC) was performed on aluminium-backed 0.2 mm thick silica gel 60 F254 plates as supplied by Merck. Eluted plates were visualised using a 254 nm UV lamp and/or by treatment with a suitable dip followed by heating. The retardation factor ($R_f$) values cited here have been rounded at the first decimal point. Starting materials and reagents were generally available from the Sigma–Aldrich, Merck, TCI, Strem or Lancaster Chemical companies and were used as supplied. Most of the solvents were dried using a Glass contour solvent purification system that is based upon a technology originally described by Grubbs *et. al*.[2]

All the reactions were performed under an inert atmosphere of nitrogen.

## 2. Specific Experimental Procedures and Product Characterisation

Acid **4**,[3] allylic alcohol **5**,[4] saturated alcohol **6**[5] and iodide **7**[6] were prepared according to literature procedures or minor modifications thereof (as specified below).

### (*E*)-Furyl-3-acrylic acid (**4**)

A solution of 3-furaldehyde (**3**) (1.00 g, 10.4 mmol) and malonic acid (1.50 g, 1.44 mmol) in pyridine (2 mL) was heated at 90 °C for 2 h. The resulting solution was cooled to 18 °C then poured into HCl (10 mL of a cold 1 M aqueous solution). The precipitate was collected by filtration, dissolved in ethyl acetate (20 mL) and the resulting solution was washed with HCl (2 × 10 mL of a 1 M aqueous solution). The separated organic layer was dried ($Na_2SO_4$) then filtered and concentrated under reduced pressure to give a pale-brown solid that was dried under high vacuum to give the title compound **4**[3] (1.38 g, 96%) as a light-brown solid. This material was used, without purification, in the next step of the reaction sequence.

**$R_f$** = 0.3 (in 1:1 v/v ethyl acetate/hexane)

**IR** $\nu_{max}$ (NaCl) 1677, 1640, 1419, 1323, 1274, 1159, 1084, 1021, 978, 942, 805 $cm^{-1}$

**$^1$H NMR** ($CD_3OD$, 300 MHz) δ 7.81 (s, 1 H), 7.59 (d, *J* = 15.0 Hz, 1H), 7.53 (m, 1H), 6.73 (m, 1H), 6.19 (d, *J* = 15.0 Hz, 1H) (signal due to carboxylic acid group proton not observed)

**$^{13}$C NMR** ($CD_3OD$, 75 MHz) δ 170.4, 146.4, 145.9, 136.6, 124.0, 118.8, 108.4

**Mass spectrum** (ESI, –ve ionisation) *m/z* 137 [$(M–H^+)^-$, 31%], 97 (14), 93 (90), 80 (8), 67 (93), 65 (100)

**HRESIMS** Found: $(M–H^+)^-$, 137.0239. $C_7H_6O_3$ requires $(M–H^+)^-$, 137.0239.

### (*E*)-3-(3'-Furanyl) prop-2-en-1-ol (**5**)

A solution of acid **4** (1.00 g, 7.25 mmol) in THF (10 mL) was added, dropwise, to a magnetically slurry of lithium aluminium hydride (400 mg, 10.50 mmol) in THF (5 mL) maintained at 18 °C. After 1 h the reaction mixture was cooled to 0 °C then treated with methanol (10 mL) and Celite™/$Na_2SO_4$•$10H_2O$ (15 g of a 1:1 w/w mixture). The resulting slurry was stirred at 18 °C for 16 h then subjected to vacuum filtration. Concentration of the filtrate under reduced pressure afforded a light-yellow oil that was subjected to flash chromatography (silica gel, 3:7 v/v ethyl acetate/hexane elution) to yield, after concentration of the appropriate fractions, alcohol **5**[4] (683 mg, 76%) as a clear, colourless oil.

**$R_f$** = 0.45 (1:1 v/v ethyl acetate/hexane)

**IR** $\nu_{max}$ (NaCl) 3337 (broad), 2923, 2866, 1666, 1508, 1380, 1159, 1074, 1021, 965, 871, 778 $cm^{-1}$

**$^1$H NMR** (300 MHz) δ 7.39 (s, 1H), 7.35 (broad s, 1H), 6.50 (broad s, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 6.06 (dt, *J* = 15.9 and 5.7 Hz, 1H), 4.22 (m, 2H), 2.49 (broad s, 1H)

**$^{13}$C NMR** (75 MHz) δ 143.5, 140.5, 128.1, 123.6, 120.9, 107.5, 63.3

**Mass spectrum** (EI, 70 eV) *m/z* 124 ($M^{+\bullet}$, 63%), 107 (35), 95 (95), 82 (92), 81 (100), 77 (46), 67 (58), 41 (53), 39 (74)

**HREIMS** Found: $M^{+\bullet}$, 124.0522. $C_7H_8O_2$ requires $M^{+\bullet}$, 124.0524.

**3-(3-Furyl)-propanol** (**6**)

A magnetically stirred slurry of the allylic alcohol **5** (650 mg, 5.24 mmol) and 10% palladium on charcoal (32 mg, 5 wt %) in methanol (10 mL) was degassed then treated with dihydrogen (1 atmosphere). The ensuing mixture was stirred at 18 °C for 3 h then filtered through a pad of Celite™ that was washed thoroughly with dichloromethane (50mL). The combined filtrates were concentrated under reduced pressure and the residue so obtained subjected to flash chromatography (silica gel, 1:5 v/v ethyl acetate/hexane) to afford, after concentration of the appropriate fractions, alcohol **6**[5] (542 mg, 82%) as clear, colourless liquid.

**$R_f$** = 0.45 (1:1 v/v ethyl acetate/hexane)

**IR** $\nu_{max:}$ (NaCl) 3350 (broad), 2940, 2865, 1501, 1450, 1383, 1158, 1059, 1024, 973, 911, 874, 778, 599 $cm^{-1}$

**$^1$H NMR** (300 MHz) δ 7.35 (m, 1H), 7.23 (m, 1H), 6.27 (m, 1H), 3.66 (t, *J* = 6.6 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 1.86–1.77 (complex m, 2H) (signal due to hydroxyl group proton not observed)

**$^{13}$C NMR** (75 MHz): δ 142.8, 138.8, 124.3, 110.9, 62.1, 32.7, 20.9

**Mass spectrum** (EI, 70 eV) *m/z* 126 ($M^{+\bullet}$, 20%), 107 (5), 95(15), 82 (100), 81 (68), 53 (25), 44 (7), 39 (26)

**HREIMS** Found: $M^{+\bullet}$, 126.0675. $C_7H_{10}O_2$ requires $M^{+\bullet}$, 126.0681.

**3-(3-Furyl)-propyl-1-iodide** (**7**)

A magnetically stirred solution of the alcohol **6** (280 mg, 2.22 mmol) in dichloromethane (5 mL) was cooled to 0 °C then treated with triphenylphosphine (756 mg, 2.89 mmol), triethylamine (0.40 mL, 2.89 mmol) and molecular iodine (733 mg, 2.89 mmol). The resulting mixture was stirred at 0 °C for a minute then imidazole (20 mg, catalytic) was added. The ensuing mixture was stirred vigorously and

allowed to warm to 18 °C over 0.5 h, kept at this temperature for 2 h then poured into water (30 mL) and extracted with diethyl ether (3 × 30 mL). The combined organic extracts were washed with sodium thiosulfate solution (1 × 30 mL of a 10% w/v aqueous solution) and brine (1 × 30 mL) then dried ($Na_2SO_4$), filtered and concentrated under reduced pressure. Subjection of the resulting light-yellow oil to flash chromatography (silica gel, 1:49 v/v ethyl acetate/hexane elution) gave, after concentration of the appropriate fractions, iodide **7**[6] (393 mg, 73%) as a clear, colourless oil.

**$R_f$** = 0.6 (in 5:95 v/v ethyl acetate/hexane)
**IR** $\nu_{max}$ (NaCl) 2926, 2852, 1500, 1447, 1424, 1383, 1211, 1164, 1066, 1024, 873, 781, 599 $cm^{-1}$
**$^1$H NMR** (300 MHz) δ 7.37 (t, *J* = 1.5 Hz, 1H), 7.27 (m, 1H), 6.28 (broad s, 1H), 3.19 (t, *J* = 7.2 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.05 (p, *J* = 7.2 Hz, 2H)
**$^{13}$C NMR** (75 MHz) δ 143.0. 139.3, 122.9, 110.7, 33.3, 25.3, 6.3
**Mass spectrum** (EI, 70 eV) *m/z* 236 ($M^{+\bullet}$, 64%), 109 (9), 82 (72), 81 (100), 53 (49), 39 (26)
**HREIMS** Found: $M^{+\bullet}$, 235.9700. $C_7H_9IO$ requires $M^{+\bullet}$, 235.9698.

**Hex-1-yn-5-methyl-3-ol** (**9**)
Ethynyl magnesium bromide (13.7 mL of a 0.5 M solution in THF, 6.84 mmol) was added, dropwise, to a magnetically stirred solution of 3-methylbutyraldehyde (**8**) (490 mg, 5.70 mmol) in anhydrous diethyl ether (5 mL) maintained at 0 °C. The resulting mixture was warmed to 18 °C over a period of 0.5 h then poured into ammonium chloride (10 ml of a chilled and saturated aqueous solution) and extracted with diethyl ether (3 × 15 mL). The combined organic phases were washed with brine (1 × 10 mL) before being dried ($Na_2SO_4$), filtered and concentrated under reduced pressure. The resulting light-yellow oil was subjected to flash chromatography (silica gel, 1:4 v/v ethyl acetate/hexane elution) to yield, after concentration of the appropriate fractions, alcohol **9**[7] (403 mg, 63%) as clear, colourless liquid.

**$R_f$** = 0.3 (in 1:4 v/v ethyl acetate/hexane)
**IR** $\nu_{max}$ (NaCl) 3311, 2959, 2935, 2872, 1469, 1386, 1368, 1298, 1136, 1059, 1023, 654, 628 $cm^{-1}$
**$^1$H NMR** (300 MHz) δ 4.41 (m, 1H), 2.46 (dm, *J* = 2.1 Hz, 1H), 2.02 (broad s, 1H), 1.84 (septet, *J* = 6.6 Hz, 1H), 1.70–1.51 (complex m, 2H), 0.92 (m, 6H)
**$^{13}$C NMR** (75 MHz) δ 85.2, 72.8, 60.8, 46.6, 24.6, 22.5
**Mass spectrum** (EI, 70 eV) *m/z* 112 ($M^{+\bullet}$, <1%), 111 (~1), 97 (18), 79 (20), 57 (72), 55 (65), 41 (57), 32 (100)
**HREIMS** Found: $M^{+\bullet}$, 112.0883. $C_7H_{12}O$ requires $M^{+\bullet}$, 112.0888.

***tert*-Butyldimethyl-(5-methylhex-1-yn-3-yloxy)silane (10)**

A magnetically stirred solution of alcohol **9** (280 mg, 2.50 mmol) in anhydrous THF (5 mL) was treated with imidazole (340 mg, 5.00 mmol) and TBSCl (563 mg, 3.75 mmol). The resulting mixture was stirred at 18 °C for 6 h then quenched with sodium bicarbonate (10 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 15 mL). The combined organic phases was washed with brine (1 × 50 mL) then dried ($Na_2SO_4$), filtered and concentrated under reduced pressure. The resulting light-yellow oil was subjected to flash chromatography (silica gel, hexane elution) to give, after concentration of the appropriate fractions, *silyl ether **10*** (385 mg, 68%) as clear, colourless liquid.

**$R_f$** = 0.3 (in hexane)

**IR** $\nu_{max}$ (NaCl) 3313, 2957, 2932, 2858, 1471, 1361, 1252, 1125, 1089, 1005, 938, 900, 837, 777 $cm^{-1}$

**$^1$H NMR** (300 MHz) δ 4.39 (m, 1H), 2.37 (d, *J* = 2.4 Hz, 1H), 1.90–1.77 (complex m, 1H), 1.68–1.46 (complex m, 2H), 0.92 (d, *J* = 1.5 Hz, 6H), 0.90 (s, 9H), 0.13 (d, *J* = 7.5 Hz, 6H)

**$^{13}$C NMR** (75 MHz) δ 85.9, 71.9, 61.2, 47.6, 25.8, 24.3, 22.8, 22.2, 18.2, –4.5, –5.1

**Mass spectrum** (EI, 70 eV) *m/z* 226 ($M^{+\bullet}$, 1%), 211 (2), 169 (38), 113 (100), 101 (10), 93 (5), 83 (37), 75 (87), 69 (17)

**HREIMS** Found: $M^{+\bullet}$, 226.1742. $C_{13}H_{26}OSi$ requires $M^{+\bullet}$, 226.1753.

**[*tert*-Butyl-(9-(furan-3-yl)-2-methylnon-5-yn-4-yloxy]dimethylsilane (11)**

A magnetically stirred solution of the alkyne **10** (210 mg, 0.93 mmol) in THF (2 mL) was cooled to −78 °C then treated with *n*-BuLi (1.2 mL of a 1.6 M solution in hexane, 1.90 mmol). After 0.5 h anhydrous DMPU (5 mL) then a solution of iodide **5** (200 mg, 0.85 mmol) in THF (3 mL) were added to the reaction mixture which was then allowed to warm to 18 °C over 3 h before being quenched with ammonium chloride (10 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 15 mL). The combined organic phases were washed with brine (1 × 20 mL) then dried ($Na_2SO_4$), filtered and concentrated under reduced pressure to give a light-yellow oil. Subjection of this material to flash chromatography (silica gel, 1:99 v/v ethyl acetate/hexane elution) gave, after concentration of the appropriate fractions, *alkyne **11*** (218 mg, 77%) as clear, colourless liquid.

**$R_f$** = 0.3 (in 1:99 v/v ethyl acetate/hexane)

**IR** $\nu_{max}$ (NaCl) 2955, 2930, 2857, 1470, 1254, 1083, 1026, 836, 776 $cm^{-1}$

**$^1$H NMR** (300 MHz) δ 7.35 (m, 1H), 7.22 (m, 1H), 6.26 (m, 1H), 4.42–4.36 (complex m, 1H), 2.53 (t, $J$ = 1.5 Hz, 2H), 2.22 (m, 2H), 1.87–1.69 (complex m, 3H), 1.65–1.56 (complex m, 1H), 1.51–1.42 (complex m, 1H), 0.92 (s, 3H), 0.91 (s, 9H), 0.90 (s, 3H), 0.13 (d, $J$ = 6.9 Hz, 6H)

**$^{13}$C NMR** (75 MHz) δ 142.7, 139.0, 124.2, 110.9, 83.7, 82.7, 61.6, 48.1, 29.0, 25.8, 24.5, 23.7, 22.8, 22.3, 18.3, 18.1, –4.4, –5.0

**Mass spectrum** (EI, 70 eV) *m/z* 334 ($M^{+\bullet}$, 4 %), 319 (4), 277 (97), 221 (29), 203 (13), 191 (100), 163 (12), 129 (14), 117 (15), 105 (13), 91 (15), 81 (21), 75 (95), 73 (67), 57 (21), 41 (28).

**HRMS** Found: $M^{+\bullet}$, 334.2328. $C_{20}H_{34}O_2Si$ requires $M^{+\bullet}$, 334.2328.

**9-(Furan-3-yl)-2-methylnon-5-yn-4-ol** (**12**)

A magnetically stirred solution of the silyl ether **11** (668 mg, 2.0 mmol) in THF (5 mL) maintained at 18 °C was treated, *via* syringe, with tetra-*n*-butylammonium fluoride (3 mL of a 1.0 M solution in THF, 3.0 mmol). After 1 h the reaction mixture was treated with sodium bicarbonate (20 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 15 mL). The combined organic phases was washed with brine (1 × 50 mL) then dried ($Na_2SO_4$), filtered and concentrated under reduced pressure to give a light-yellow oil. Subjection of this material to flash chromatography (silica gel, 1:9 v/v ethyl acetate/hexane elution) and concentration of the appropriate fractions afforded *alcohol **12*** (213 mg, 97%) as a clear, colourless liquid.

**$R_f$** = 0.3 (in 15:85 v/v ethyl acetate/hexane)

**IR** $\nu_{max}$ (NaCl) 3363, 2954, 2869, 1501, 1467, 1384, 1367, 1154, 1113, 1025, 873, 779 $cm^{-1}$

**$^1$H NMR** (300 MHz) δ 7.35 (t, $J$ = 1.8 Hz, 1H), 7.22 (m, 1H), 6.26 (m, 1H), 4.43–4.37 (complex m, 1H), 2.51 (t, $J$ = 7.8 Hz, 2H), 2.23 (m, 2H), 1.88–1.46 (complex m, 5H), 0.93 (m, 6H) (signal due to hydroxyl group proton not observed)

**$^{13}$C NMR** (75 MHz) δ 142.8, 139.0, 124.1, 110.9, 84.7, 82.1, 61.2, 47.2, 28.8, 24.8, 23.7, 22.5, 22.5, 18.1.

**Mass spectrum** (EI, 70 eV) *m/z* 220 ($M^{+\bullet}$, < 1 %), 205 (3), 187 (8), 177 (18), 164 (88), 163 (80), 149 (29), 135 (54), 117 (41), 107 (72), 91 (65), 82 (98), 81 (90), 67 (47), 53 (60), 41 (100).

**HRMS** Found: $M^{+\bullet}$, 220.1466. $C_{14}H_{20}O_2$ requires $M^{+\bullet}$, 220.1463.

**9-(Furan-3-yl)-2-methylnon-5-yn-4-one** (**13**)

Pyridinium chlorochromate (322 mg, 1.50 mmol) was added to a magnetically stirred solution of the alcohol **12** (220 mg, 1 mmol) in dichloromethane maintained at 18 °C. After 2.5 h TL-grade silica gel

(500 mg) was added to the reaction mixture that was then concentrated under reduced pressure. The resulting free-flowing solid was loaded directly on to the top of a flash chromatography (silica gel, 5:95 v/v ethyl acetate/hexane elution) and concentration of the appropriate fractions afforded *ketone **13*** (196 mg, 90%) as a clear, colourless liquid.

**$R_f$** = 0.4 (in 8:92 v/v ethyl acetate/hexane)

**IR** $\nu_{max}$ (NaCl) 2957, 2871, 2211, 1670, 1598, 1571, 1465, 1366, 1247, 1166, 1113, 1066, 1024 $cm^{-1}$

**$^1$H NMR** (300 MHz) δ 7.36 (m, 1H), 7.23 (m, 1H), 6.26 (s, 1H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.43–2.33 (complex m, 4H), 2.24 (m, 1H), 1.82 (p, *J* = 7.2 Hz, 2H), 0.95 (d, *J* = 6.6 Hz, 6H)

**$^{13}$C NMR** (75 MHz) δ 188.1, 143,0, 139.1, 123.5, 110.7, 93.2, 81.5, 54.4, 27.9, 25.1, 23.7, 22.4, 18.2

**Mass spectrum** (EI, 70 eV) *m/z* 218 ($M^{+\bullet}$, 30 %), 203 (26), 175 (28), 162 (55), 161 (76), 147 (30), 134 (60), 133 (81), 119 (32), 105 (80), 91 (37), 82 (65), 81 (65), 79 (100), 65 (29), 57 (49), 53 (62), 41 (89)

**HRMS** Found: $M^{+\bullet}$, 218.1308. $C_{14}H_{18}O_2$ requires $M^{+\bullet}$, 218.1307.

**(*E*)-1-(5,6-Dihydrobenzofuran-7(4*H*)-ylidene)-4-methylpentan-2-one** (**14**)

A magnetically stirred solution of ketone **13** (218 mg, 1 mmol) in dichloromethane (5 mL) maintained at 18 °C was treated with (acetonitrile)[(2-biphenyl)-di-*tert*-butylphosphine]gold(I)hexafluoro-antimonate (7 mg, 0.01 mmol). The resulting greenish-yellow reaction mixture was stirred at 18 °C for 5 minutes then concentrated under reduced pressure to give a greenish-yellow oil. Subjection of this material to flash chromatography (silica gel, 1:49 v/v ethyl acetate/hexane elution) and concentration of the appropriate fractions gave *enone **14*** (218 mg, 100%) as a clear, colourless oil.

**$R_f$** = 0.4 (in 2:23 v/v ethyl acetate/hexane)

**IR** $\nu_{max}$ (NaCl) 2954, 2869, 1671, 1598, 1570, 1338, 1150 $cm^{-1}$

**$^1$H NMR** (300 MHz) δ 7.37 (m, 1H), 6.47 (s, 1H), 6.32 (m, 1H), 3.11 (m, 2H), 2.58 (t, *J* = 6.0 Hz, 2H), 2.37 (d, *J* = 6.9 Hz, 2H), 2.18 (septet, *J* = 6.8 Hz, 1H), 1.84 (p, *J* = 6.3 Hz, 2H), 0.94 (d, *J* = 6.6 Hz, 6H)

**$^{13}$C NMR** (75 MHz) δ 201.2, 143.9, 142.2, 129.6, 113.8, 112.1, 110.0, 53.9, 26.9, 25.5, 23.5, 22.7, 22.6

**Mass spectrum** (EI, 70 eV) *m/z* 218 ($M^{+\bullet}$, 48 %), 203 (12), 176 (14), 161 (100), 147 (7), 134 (63), 115 (6), 105 (31), 91 (17), 77 (30), 51 (17), 41 (22)

**HRMS** Found: $M^{+\bullet}$, 218.1306. $C_{14}H_{18}O_2$ requires $M^{+\bullet}$, 218.1307.

**(±)-Dihydrocrassifolone [(±)-2]**

*Step i*: A magnetically stirred slurry of CuBr•$SMe_2$ (10 mg, 0.05 mmol) in THF (2 mL) was cooled to −78 °C then treated with methylmagnesium bromide (0.2 mL of a 3 M solution in THF, 0.60 mmol) and HMPA (224 mg, 1.25 mmol). After 10 minutes, a solution of enone **14** (114 mg. 0.50 mmol) and TMSCl (108 mg, 1.0 mmol) in THF (4 mL) was added dropwise to the reaction mixture reaction which was then allowed to warm to 0 °C over 3 h. After this time, the reaction mixture was treated with ammonium chloride (20 mL of a cold and saturated aqueous solution) and extracted with ether (3 × 20 mL). The combined organic phases were washed with brine (1 × 60 mL) then dried ($Na_2SO_4$), filtered and concentrated under reduced pressure. The yellow oil thus obtained was filtered through a pad of TLC-grade silica gel that was eluted with diethyl ether to afford the *silylenol ether **15*** (93 mg, 61%) as a clear, colourless oil. This material was used directly in the next step of the reaction sequence.

*Step ii*: The crude mixture of the silylenol ethers **15** obtained as described immediately above was dissolved in THF (5 mL) and the resulting solution treated, at 18 °C, with TBAF (1.5 mL of a 1 M solution in THF, 1.5 mmol). The ensuing mixture was stirred at 18 °C for 0.5 h then treated with sodium bicarbonate (10 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 15 mL). The combined organic phases were washed with brine (1 × 50 mL) then dried ($Na_2SO_4$), filtered and concentrated under reduced pressure to give a pale-yellow oil. Subjection of this material to flash column chromatography (silica gel, 1:99 v/v ethyl acetate/hexane elution) afforded, after concentration of the appropriate fractions, dihydrocrassifolone (±)-**2** (47 mg, 66 %) as a clear, colourless liquid.

**$R_f$** = 0.3 (in 1:49 v/v ethyl acetate/hexane)

**IR** $\nu_{max}$ (NaCl) 2958, 2932, 2870, 1711, 1505, 1462, 1365, 1260, 1152, 1103, 1055, 1044, 890, 733 $cm^{-1}$

**$^1$H NMR** (300 MHz) see Table S1

**$^{13}$C NMR** (75 MHz) see Table S2

**Mass spectrum** (EI, 70 eV) *m/z* 234 ($M^{+\bullet}$, 23 %), 135 (100), 134 (45), 91 (20), 85 (20), 77 (8), 65 (6), 57 (26), 41 (17).

**HRMS** Found: $M^{+\bullet}$, 234.1627. $C_{15}H_{22}O_2$ requires $M^{+\bullet}$, 234.1620.

**Table S1: Comparison of $^1$H NMR spectral data derived from the natural and synthetic samples of dihydrocrassifolone (2)**

| Natural (–)-dihydrocrassifolone[8] (recorded in $CDCl_3$ at 400 MHz) δ | Synthetic (±)-dihydrocrassifolone (recorded in $CDCl_3$ at 300 MHz) δ |
|---|---|
| 7.16 (d, *J* = 1.8 Hz, 1H) | 7.22 (d, *J* = 1.8 Hz, 1H) |
| 6.09 (d, *J* = 1.8 Hz, 1H) | 6.15 (d, *J* = 1.8 Hz, 1H) |
| 2.59 (ABq, *J* = 13.5 Hz, 2H) | 2.66 (ABq, *J* = 13.5 Hz, 2H) |
| 2.32 (m, 2H) | 2.41–2.35 (m, 2H) |
| 2.00 (m, 3H) | 2.13–2.01 (m, 3H) |
| 1.82 (m, 1H) | 1.92–1.86 (complex m, 1H) |
| 1.68 (m, 2H and 1.61, m, 1H) | 1.78–1.64 (complex m, 3H) |
| 1.25 (s, 3H) | 1.32 (s, 3H) |
| 0.79 (d, *J* = 6.3 Hz, 3H) | 0.85 (d, *J* = 6.6 Hz, 3H) |
| 0.76 (d, *J* = 6.3 Hz, 3H) | 0.82 (d, *J* = 6.6 Hz, 3H) |

**Table S2: Comparison of $^{13}C$ NMR spectral data derived from the natural and synthetic samples of dihydrocrassifolone (2)**

| Natural<br>(–)-dihydrocrassifolone[8]<br>(recorded in $CDCl_3$ at 100 MHz)<br>δ | Synthetic<br>(±)-dihydrocrassifolone<br>(recorded in $CDCl_3$ at 100 MHz)<br>δ |
|---|---|
| 210.6 | 210.2 |
| 155.5 | 155.1 |
| 140.6 | 140.2 |
| 116.9 | 116.4 |
| 110.8 | 110.4 |
| 53.6 | 53.2 |
| 52.5 | 52.1 |
| 36.3 | 35.9 |
| 35.3 | 35.0 |
| 26.5 | 26.1 |
| 24.7 | 24.3 |
| 23.0 | 22.5 |
| 22.9 | 22.5 |
| 22.8 | 22.4 |
| 20.6 | 20.2 |

**(±)-Crassifolone [(±)-1]**

Following a protocol defined by Lalic and Corey,[9] a magnetically stirred solution of (±)-dihydrocrassifolone [(±)-**2**] (47 mg, 0.20 mmol) in dichloromethane (2 mL) was cooled to 0 °C then treated with triethylamine (242 mg, 2.40 mmol) and TMSOTf (266 mg, 1.20 mmol). The ensuing mixture was allowed to warm to 18 °C over 3 then treated with sodium bicarbonate (10 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 10 mL). The combined organic extracts were washed with brine (1 × 30 mL) before being dried ($Na_2SO_4$), filtered and then concentrated under reduced pressure to give a light-yellow oil (59 mg). A magnetically stirred solution of this oil in anhydrous DMSO (1 mL) maintained at 18 °C was treated with IBX (80 mg, 0.29 mmol) and MPO (36 mg, 0.29 mmol). The ensuing mixture was stirred vigorously for 24 h then

treated with sodium bicarbonate (10 mL of a saturated aqueous solution) and extracted with diethyl ether (3 × 15 mL). The combined organic extracts were washed with brine (1 × 50 mL) then dried ($Na_2SO_4$), filtered and concentrated under reduced pressure. The residue thus obtained was subjected to flash chromatography (silica gel, 0.5:99.5 v/v ethyl acetate/hexane) and thus affording two fractions, A and B.

Concentration of fraction A ($R_f$ = 0.3 in 1:49 v/v ethyl acetate/hexane) afforded (±)-dihydrocrassifolone [(±)-**2**] (12 mg, 27% recovery) as a clear, colourless oil that was identical, in all respects, with an authentic sample.

Concentration of fraction B ($R_f$ = 0.4 in 5:95 v/v ethyl acetate/hexane) afforded (±)-crassifolone [(±)-**1**] (29 mg, 83% at 73% conversion) as a clear, colourless oil.

**$R_f$** = 0.4 (in 5:95 v/v ethyl acetate/hexane)
**IR** $\nu_{max}$ (NaCl) 2962, 2931, 2853, 1679, 1617, 1504, 1444, 1377, 1152, 1105, 1043, 890, 731 $cm^{-1}$
**$^1$H NMR** (300 MHz) see Table S3
**$^{13}$C NMR** (75 MHz) see Table S4
**Mass spectrum** (EI, 70 eV) *m/z* 232 ($M^{+\bullet}$, 15 %), 148 (8), 135 (100), 134 (49), 105 (9), 91 (15), 83 (23)
**HRMS** Found: $M^{+\bullet}$, 232.1466. $C_{15}H_{20}O_2$ requires $M^{+\bullet}$, 232.1463.

**Table S3: Comparison of $^1$H NMR spectral data derived from the natural and synthetic samples of crassifolone (1)**

| Natural (–)-crassifolone[8] (recorded in $CDCl_3$ at 400 MHz) δ | Synthetic (±)-crassifolone (recorded in $CDCl_3$ at 300 MHz) δ |
|---|---|
| 7.14 (d, *J* = 1.8 Hz, 1H) | 7.23 (d, *J* = 1.8 Hz, 1H) |
| 6.06 (d, *J* = 1.8 Hz, 1H) | 6.14 (d, *J* = 1.8 Hz, 1H) |
| 5.74 (broad s, 1H) | 5.82 (m, 1H) |
| 2.59 (ABq, *J* = 13.5 Hz, 2H) | 2.67 (ABq, *J* = 13.5 Hz, 2H) |
| 2.30 (m, 2H) | 2.37 (m, 2H) |
| 2.00 (d, *J* = 0.7 Hz, 3H) | 2.07 (d, *J* = 1.2 Hz, 3H) |
| 1.82 (m, 1H) | 1.96–1.88 (complex m, 1H) |
| 1.71 (d, *J* = 0.7 Hz, 3H) | 1.78 (d, *J* = 1.2 Hz, 3H) |
| 1.65 (m, 2H) | 1.77–1.61 (m, 3H) |
| 1.56 (m, 1H) | – |
| 1.24 (s, 3H) | 1.32, s, 3H |

**Table S4: Comparison of $^{13}C$ NMR spectral data derived from the natural and synthetic samples of crassifolone (1)**

| Natural<br>(–)-crassifolone[8]<br>(recorded in $CDCl_3$ at 100 MHz)<br>δ | Synthetic<br>(±)-crassifolone<br>(recorded in $CDCl_3$ at 100 MHz)<br>δ |
|---|---|
| 200.7 | 200.3 |
| 155.5 | 155.2 |
| 154.6 | 154.3 |
| 140.6 | 140.1 |
| 125.6 | 125.1 |
| 116.8 | 116.3 |
| 110.8 | 110.3 |
| 53.9 | 53.4 |
| 36.4 | 35.9 |
| 35.8 | 35.4 |
| 28.0 | 27.6 |
| 26.6 | 26.2 |
| 22.9 | 22.4 |
| 21.0 | 20.5 |
| 20.6 | 20.2 |

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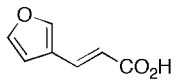
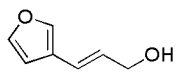
75 MHz $^{13}C$ NMR Spectrum of Compound **4** Recorded in $CD_3OD$



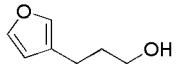

**4**

75 MHz $^{13}C$ NMR Spectrum of Compound **5** Recorded in $CDCl_3$

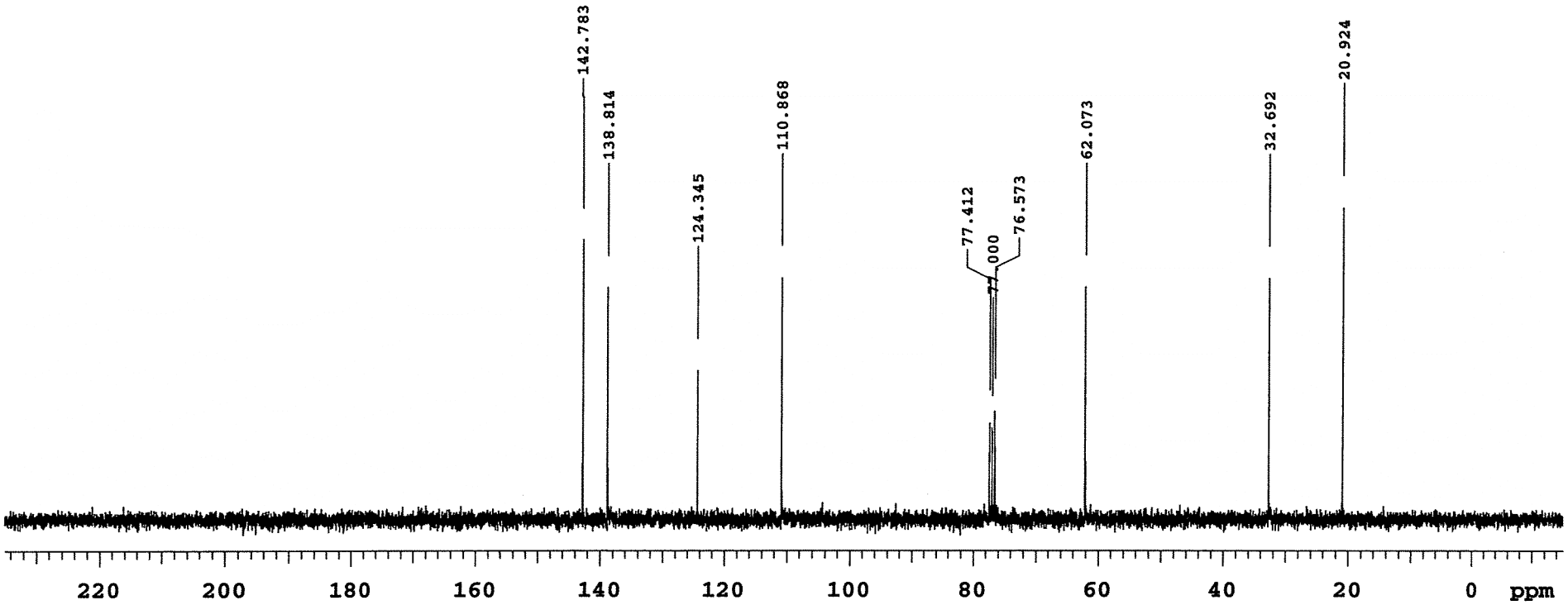



**5**

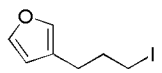
75 MHz $^{13}C$ NMR Spectrum of Compound **6** Recorded in $CDCl_3$



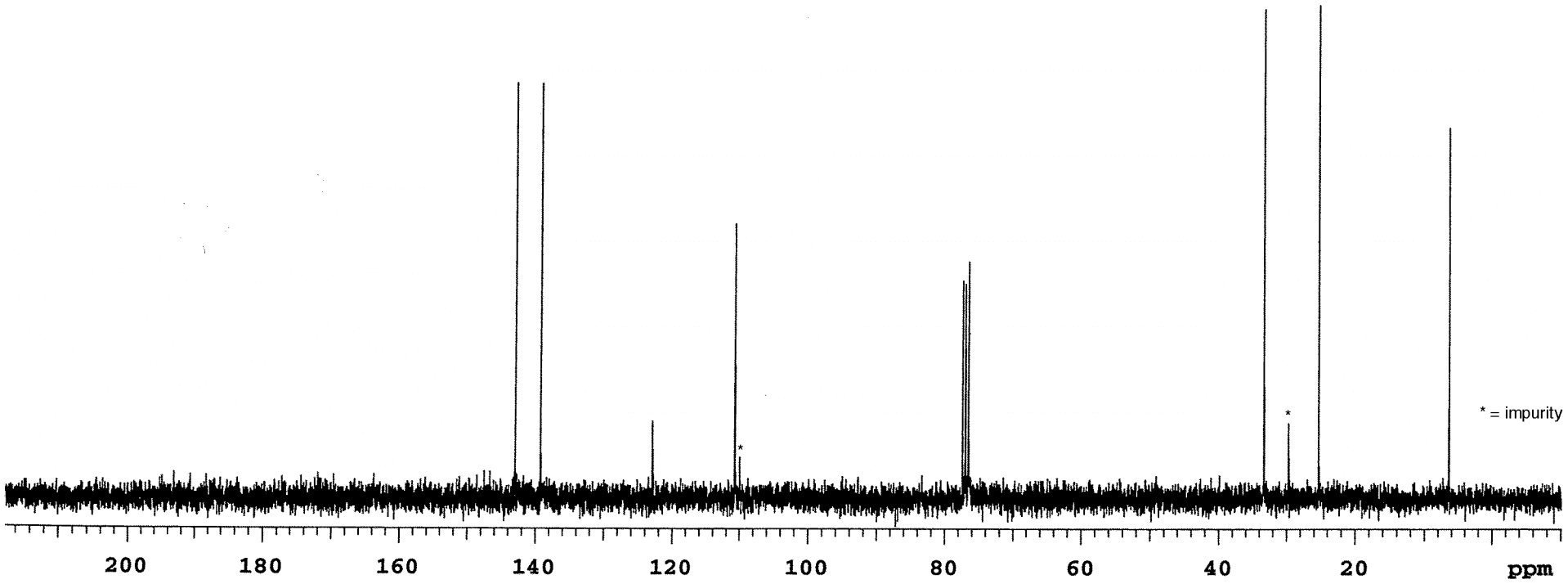

**6**



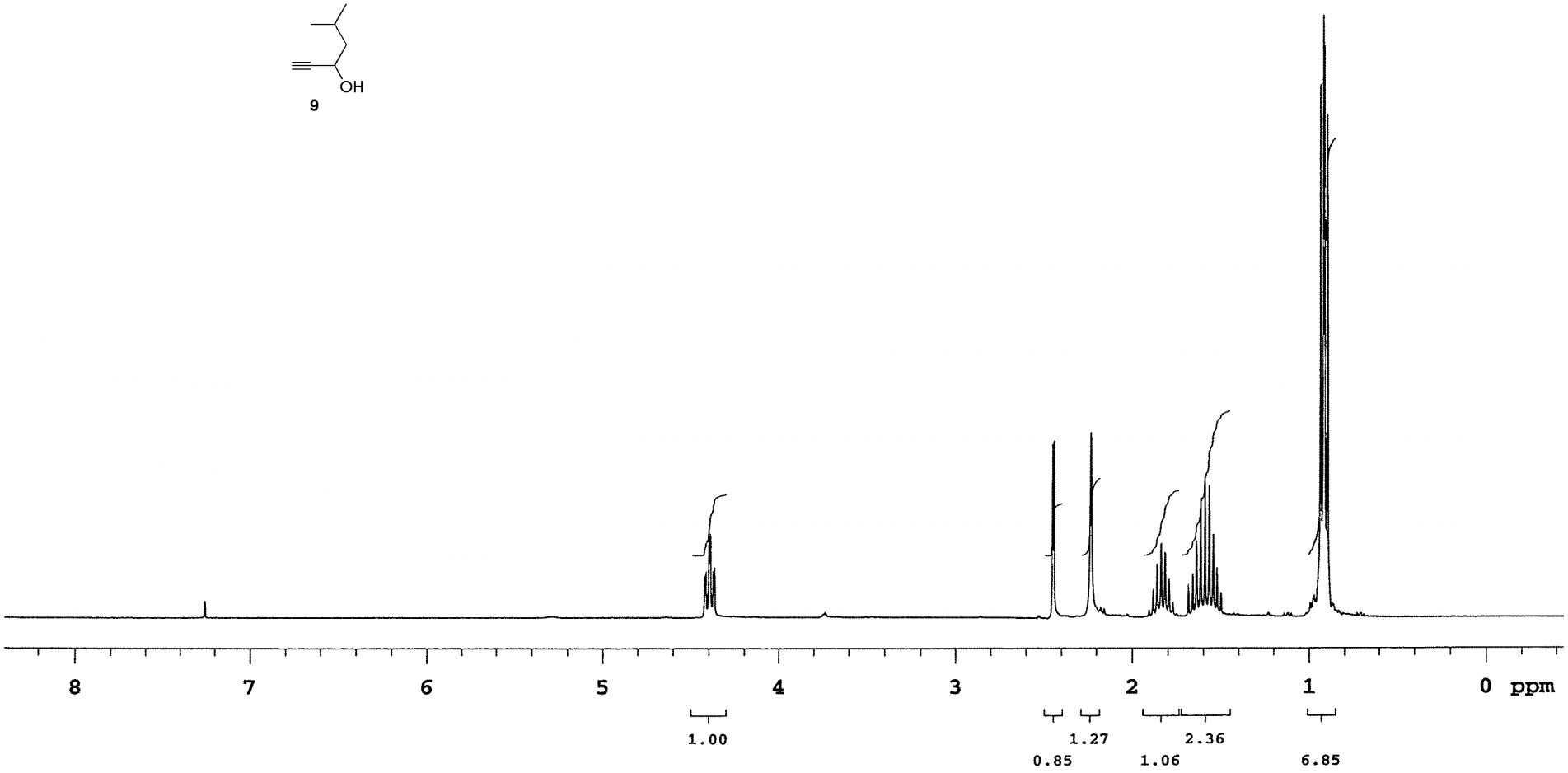
75 MHz $^{13}C$ NMR Spectrum of Compound **7** Recorded in $CDCl_3$



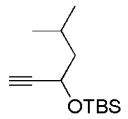
**7**



300 MHz $^{1}H$ NMR Spectrum of Compound **9** Recorded in $CDCl_3$

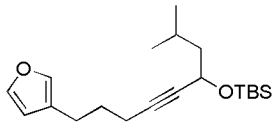


300 MHz $^{1}H$ NMR Spectrum of Compound **10** Recorded in $CDCl_3$



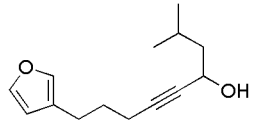

**10**

300 MHz $^{1}H$ NMR Spectrum of Compound **11** Recorded in $CDCl_3$



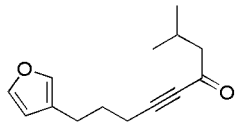

**11**

300 MHz $^{1}H$ NMR Spectrum of Compound **12** Recorded in $CDCl_3$



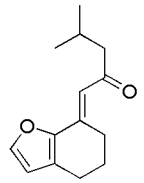

**12**

300 MHz $^{1}H$ NMR Spectrum of Compound **13** Recorded in $CDCl_3$



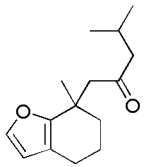
**13**

300 MHz $^{1}H$ NMR Spectrum of Compound **14** Recorded in $CDCl_3$



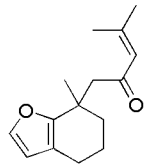
**14**

75 MHz $^{13}C$ NMR Spectrum of Compound (±)-**2** Recorded in $CDCl_3$



(±)-**2**

75 MHz $^{13}C$ NMR Spectrum of Compound (±)-**1** Recorded in $CDCl_3$



(±)-**1**