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Supplementary Information

Total Syntheses of (±)-(Z)-,(E)-9-(Bromomethylene)-1,5,5-trimethylspiro[5.5]-undeca-1,7-dien-3-one and (±)-Majusculone

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CONTENTS

I) $^{1}$H and $^{13}$C-NMR spectra of 6, 11-20 ($^{1}$H-NMR spectrum for crude 17), (±)-1, (±)-2 and (±)-3………………………………………………………………………………………………………(S3-S29)

II) Spectral data and $^{1}$H and $^{13}$C-NMR spectra of (3$^{S*}$,5$^{S*}$)-3,5-dimethyl-4-acetyl-cyclohexanone derived from 11…………(S30-S32)

III) 2D-NOSEY spectrum of 12……………………………………………………………(S33)
I) $^1$H and $^{13}$C-NMR spectra of 6, 11-20 ($^1$H-NMR spectrum for crude 17), (±)-1, (±)-2 and (±)-31

1) Compound 6
2) Compound 11
3) Compound 12
4) Compound 13
5) Compound 14
6) Compound 15

![Diagram of Compound 15 with chemical structure and NMR spectrum]
7) Compound 16
8) Compound 17 (only the crude $^1$H-NMR spectra included)
9) Compound 18
10) Compound 19
11) Compound 20
12) (±)-1
13) (±)-2
II) Spectral data and $^1$H and $^{13}$C-NMR spectra of (3$^S*$,5$^S*$)-3,5-dimethyl-4-acetyl-cyclohexanone derived from 11

To a solution of 11 (210 mg, 0.74 mmol) in THF (4 mL) was added tetra-$n$-butylammonium fluoride (75 wt.% in H$_2$O, 0.41 mL, 1.48 mmol). The mixture was stirred at rt for 2 h, then diluted with EtOAc (60 mL), and washed with water (10 mL) and brine (10 mL). After concentration, the crude residue was purified by flash chromatography on silica gel (hexane-EtOAc 10:1) to give (3$^S*$,5$^S*$)-3,5-dimethyl-4-acetyl-cyclohexanone in 67% yield (84 mg).

IR (neat) 2962, 2935, 1708, 1707, 1461, 1421 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.72 (dd, $J = 9.1, 3.7$ Hz, 1H), 2.56-2.31 (m, 5H), 2.17 (s, 3H), 1.96 (dd, $J = 13.3, 9.5$ Hz, 1H), 0.93 (d, $J = 6.2$ Hz, 3H), 0.79 (d, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 210.2, 209.6, 58.7, 47.6, 47.2 32.0, 30.8, 29.5, 20.7, 15.7; HRMS-FAB m/z calcd for C$_{10}$H$_{17}$O$_2$ [M + H]$^+$: 169.1229, found: 169.1222.
III) 2D-NOSEY spectrum (including an extension) of 12