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Supplementary Information

Allylic Chlorination of Terpenic Olefins using a Combination of $MoCl_5$ and NaOCl

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The monoterpene substrates, commercially available, were used in the experiments as received without further purification : *S*-(−)-limonene, 96%, $[\alpha]_D^{20}$ −94 (Aldrich); (−)-limonene oxide, mixture of *cis* and *trans*, 97%; $[\alpha]_D^{20}$ −69 (Aldrich); *R*-(−)-larvone, 98%, $[\alpha]_D^{20}$ −61 (Aldrich); (−)-β-pinene, 98%, $[\alpha]_D^{20}$ −20 (Acros); (−)-α-pinene, 97%, $[\alpha]_D^{20}$ −42 (Fluka).

*(4S)-1-Chloromethyl-4-isopropenylcyclohexene, (**2**)*

$[\alpha]_D^{20}$ −68 (1.96, $CHCl_3$); Ref. 16: $[\alpha]_D^{20}$ −72 (1.78, $CHCl_3$) from β-pinene; −67 (1.95, $CHCl_3$) from α-pinene; −88 (2.13, $CHCl_3$) from limonene; ^{1}H NMR (300 MHz) δ 5.75 (m, 1H, =CH), 4.80 (s, 2H, CH_2–Cl), 3.85 (s, 2H, $=CH_2$), 1.0-2.30 (m, 7H), 0.8 (s, 3H, $–CH_3$).^{13}C NMR (75 MHz) δ 148.9 (=C–), 134.2 (=C–), 126.5 (=CH–), 113.6 ($=CH_2$), 50.2 (CH_2Cl), 39.7 (CH), 30.1 (CH_2), 27.4 (CH_2), 26.5 (CH_2), 21.0 (CH_3). *m/z*: 172 (4%, M+2⎤$^+$), 170 (10%, M⎤$^+$).

*(4S)-1-Chloromethyl-4-(1-chloromethylvinyl) cyclohexene, (**3**)*

$[\alpha]_D^{20}$ −62 (2.01, $CHCl_3$); Ref. 16: $[\alpha]_D^{20}$ −66 (1.82, $CHCl_3$) from β-pinene; −58 (1.73, $CHCl_3$) from α-pinene; −83 (1.91, $CHCl_3$) from limonene; ^{1}H NMR (300 MHz) δ 5.83 (m, 1H, =CH), 5.2 (s, 1H, $=CH_2$), 5.0 (s, 1H, $=CH_2$), 4.11 (s, 2H, CH_2-Cl), 4.01 (s, 2H, CH_2–Cl), 0.8-2.4 (m, 7H). ^{13}C NMR (75 MHz) δ 149.5 (=C–), 134.4 (=C–), 127.3 (=CH–), 109.1 ($=CH_2$), 50.5 (CH_2Cl), 47.5 (CH_2Cl), 38.0 (CH), 27.5 (CH_2), 27.6 (CH_2), 26.5 (CH_2). *m/z*: 208 (2%, M+4⎤$^+$), 206 (13%, M+2⎤$^+$), 204 (21%, M⎤$^+$).

*(5R)-5-(1-Chloromethylvinyl)-2-methylcyclohex-2-enone, (**7**)*

$[\alpha]_D^{20}$ −56 (2.13, $CHCl_3$); Ref. 16: $[\alpha]_D^{20}$ −54 (1.84, $CHCl_3$); ^{1}H NMR (300 MHz) δ 6.7 (m, 1H, =CH), 5.15 (s, 1H, $=CH_2$), 4.9 (s, 1H, $=CH_2$), 3.9 (s, 2H, Cl–CH_2–), 2.85 (m, 1H, CH), 2.5 (m, 2H, CH_2), 2.3 (m, 2H, CH_2), 1.65 (s, 3H, $–CH_3$). ^{13}C NMR (75 MHz) δ 197.8 (C=O), 146.8 (=C–), 143.4 (=C–), 135.7 (=CH–), 115.0 ($=CH_2$), 46.8 (CH_2Cl), 43.0 (CH_2), 38.0 (CH), 31.5 (CH_2), 15.8 (CH_3). *m/z*: 186 (4%, M+2⎤$^+$), 184 (13%, M⎤$^+$).

*(4S)-4-[1-(chloromethyl)vinyl]-1-methyl-7-oxabicyclo[4.1.0] heptanes, (**9**)*

$[\alpha]_D^{20}$ −43 (2.0, $CHCl_3$); Ref.16 $[\alpha]_D^{20}$ −47 (1.64, $CHCl_3$); ^{1}H NMR (300 MHz) δ 4.71 (s, 1H, $=CH_2$), 4.64 (s, 1H, $=CH_2$), 3.80 (s, 2H, Cl–CH_2–), 2.90 (m, 1H, –O–CH–), 2.3 (m, 1H, CH), 1.60-1.85 (m, 6H), 1.20 (s, 3H, $–CH_3$). ^{13}C NMR (75 MHz) δ 149.10 (=C–), 110.20 ($=CH_2$), 59.23 (O–C), 57.40 (O–CH), 51.20 (CH_2Cl), 40.60 (CH), 30.40 (CH_2), 28.0 (CH_2), 25.20 (CH_2), 23.7 (CH_3). *m/z*: 188 (3%, M+2⎤$^+$), 186 (10%, M⎤$^+$).

*6-Chloro-3,7-dimethylocta-2,7-dien-1-ol, (**11**)*

^{1}H NMR (300 MHz) δ 5.42 (t, *J* 6.8, 1H, =CH–), 5.01 (s, 1H, CH_2), 4.90 (s, 1H, CH_2), 4.35 (t, *J* 6.5, 1H, CH), 4.16 (d, *J* 6.8, 2H, CH_2–O–), 1.80-2.24 (m, 4H), 1.81 (s, 3H, $–CH_3$), 1.68 (s, 3H, $-CH_3$). ^{13}C NMR (75 MHz) δ 144.2 (=C–), 138.0 (=C–), 124.3 (=CH–), 114.3 ($=CH_2$), 59.3 (CH_2OH), 66.2 (CHCl), 34.5 (CH_2), 29.7 (CH_2), 17.0 (CH_3), 16.3 (CH_3). *m/z*: 190 (4%, M+2⎤$^+$), 188 (13%, M⎤$^+$).

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(4*S*)-1-Chloromethyl-4-isopropenylcyclohexene **2**

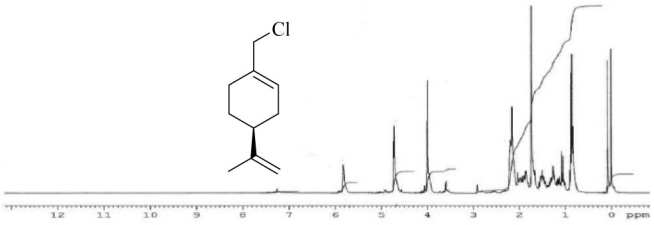

Figure S1. ^{1}H NMR spectrum of **2**.

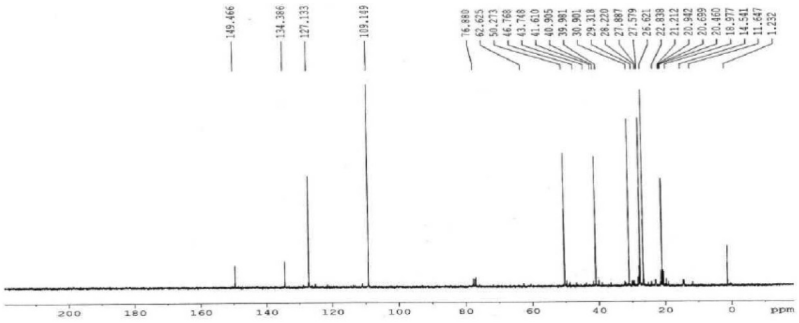

Figure S2. $^{13}C\{^{1}H\}$ spectrum of **2**.

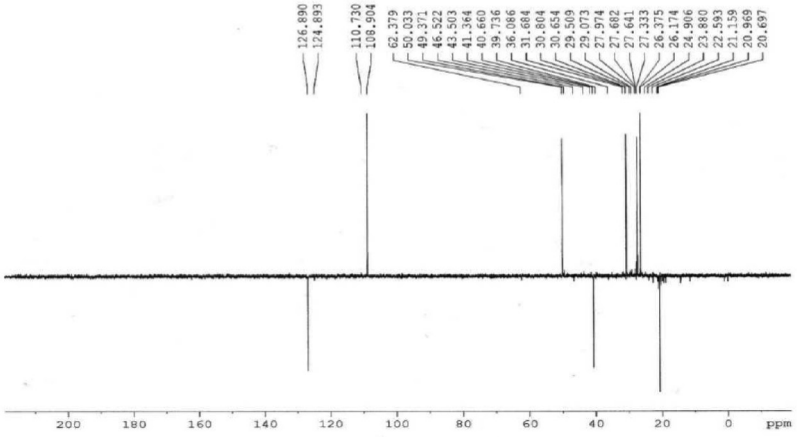

Figure S3. Dept 135 NMR spectrum of **2**.

(4*S*)-1-Chloromethyl-4-(1-chloromethylvinyl)cyclohexene **3**

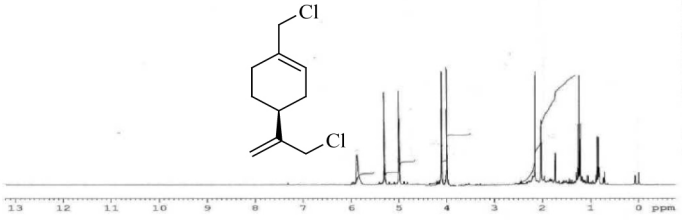

Figure S4. ^{1}H NMR spectrum of **3**.

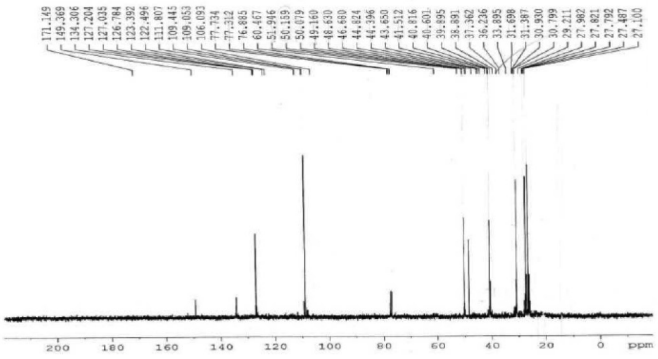

Figure S5. $^{13}C\{^{1}H\}$ spectrum of **3**.

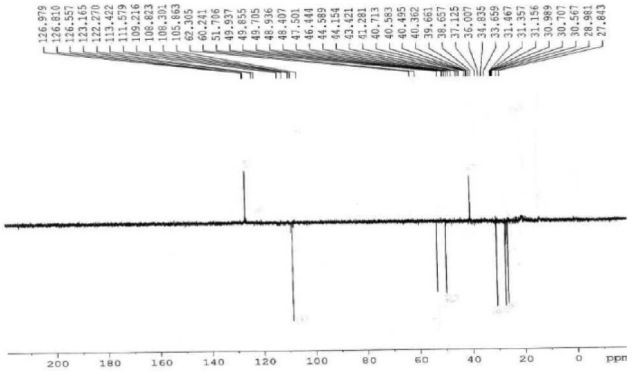

Figure S6. Dept 135 NMR spectrum of **3**.

(5*R*)-5-(1-Chloromethylvinyl)-2-methylcyclohex-2-enone **7**

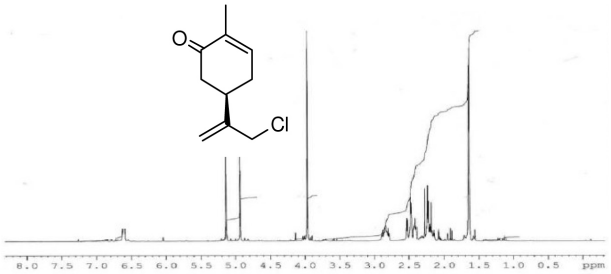

Figure S7. ^{1}H NMR spectrum of **7**.

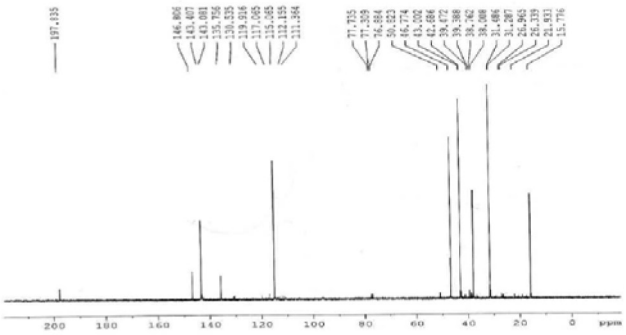

Figure S8. $^{13}C\{^{1}H\}$ spectrum of **7**.

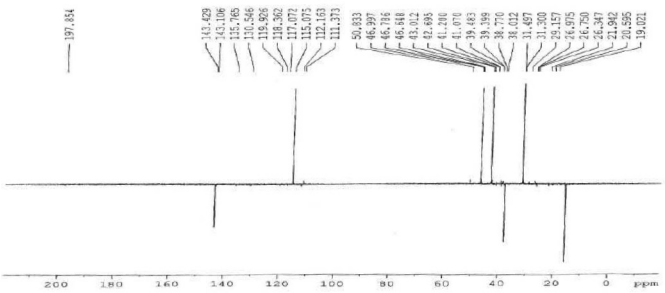

Figure S9. Dept 135 NMR spectrum of **7**.

(4*S*)-4-[1-(chloromethyl)vinyl]-1-methyl-7-oxabicyclo[4.1.0]heptanes **9**

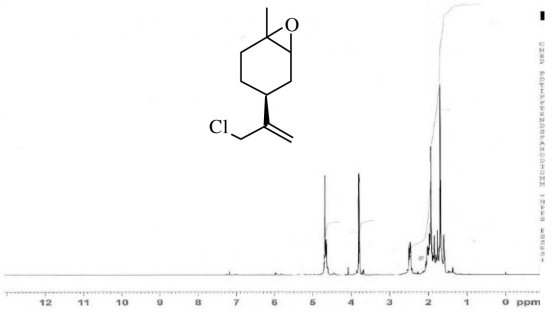

Figure S10. ^{1}H NMR spectrum of **9**.

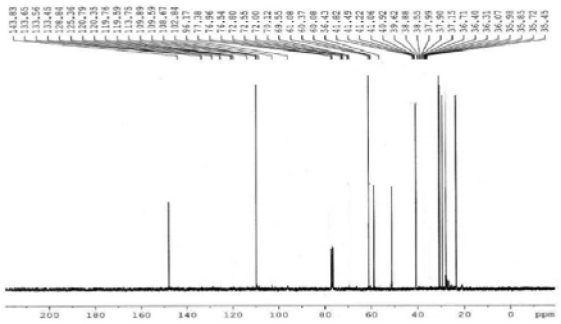

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **9**.

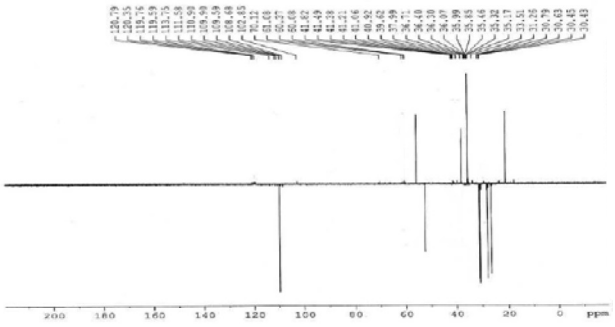

Figure S12. Dept 135 NMR spectrum of **9**.

6-Chloro-3,7-dimethylocta-2,7-dien-1-ol **11**

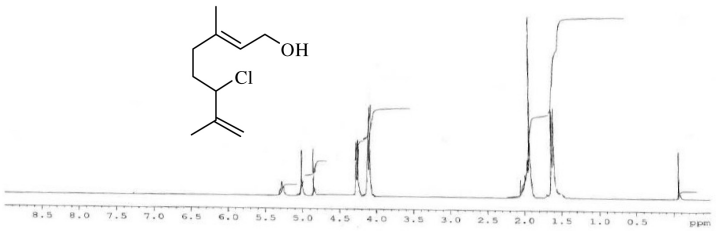

Figure S13. ^{1}H NMR NMR spectrum of **11**.

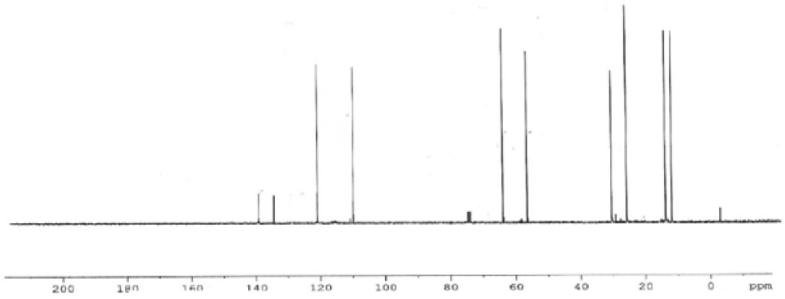

Figure S14. ^{13}C{^{1}H} NMR spectrum of **11**.

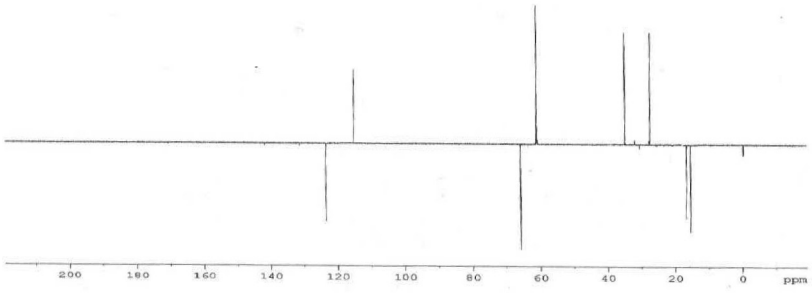

Figure S15. Dept 135 NMR spectrum of **11**.