Supporting information

The salt-free Nickel-Catalysed α-Allylation Reaction of Ketones with Allyl Alcohol and Diallylether

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1-General informations

Chemicals were purchased from Aldrich, Alfa Aesar, Acros, Strem. Common solvents were distilled and degassed before use.

Conversions were determined by gas chromatography on Shimadzu 2010 equipped with a Zebron zb-5 column (30 m, i.d. = 0.32 mm, film thickness: 0,25 μm) and N_2 as gas vector. The GC was equipped with a FID detector.

NMR spectra were recorded using a Bruker AC 300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported to the solvent resonance [$CDCl_3$: 7.27 (^{1}H), 77.0 (^{13}C) ppm].

High Resolution Mass Spectra (HR-MS) were measured in REALACAT, Université de Lille. The experiments were performed on a Synapt G2Si (Waters) equipped with an ion mobility cell. The molecules were analyzed through direct infusion in sensitivity and positive mode with the following tune parameters: 3.00 kV as capillary voltage, 60 and 90 respectively set for the sampling cone and source offset. The source temperature was of 100 °C, with a desolvation temperature of 250 °C. The cone gas flow was set to 50 L/h, with a desolation gas flow of 600 L/h and the nebulizer set to 6.5 Bars. The mass range was set to 50 to 500 g/mol for the analysis.

2- General Procedures

*2.1- α-Allylation of propiophenone **1a** with allyl alcohol **2a** or diallyl ether **2b***

α-allylation reactions of ketones were carried out under nitrogen atmosphere as follows: a glass reactor closed with a Rotaflo® stopcock was filled in a glovebox under argon atmosphere with the precursor $Ni(cod)_2$. The other reactants were added under nitrogen outside the glove box by using Schlenk tube techniques.

In a Schlenk tube were placed first the catalytic precursor $Ni(cod)_2$ (1.5 mol %), then the ligand (3 mol %), the ketone (1.8 mmol, 1 equiv.). Freshly distilled and degassed allyl alcohol (2 eq.) or diallyl ether (1 eq.) were then added. MeOH (0.5 mL) was added and the reaction mixture was stirred at 80°C for 18 h. The reaction mixture was then concentrated under reduced pressure. Trimethoxybenzene (1 mmol) was added as internal standard for NMR analysis.

For determination of ketones conversions by GC, the crude was homogenized by 0.5 mL methanol addition and a precise quantity of anisole (1 mmol) was added as internal standard. Conversions were calculated from the GC analysis of the homogeneous mixture.

*2.2- α-Allylation of ketones **1b-h** with allyl alcohol **2a***

The products ***3b-h*** were synthesized according to the same procedure as those for α-allylation of propiophenone.

The products were purified by silica gel column chromatography using petroleum ether/ethyl acetate (98/2) as eluent. The physical state of all products is liquid.

3- NMR spectra of products 3a-h and HR-MS analyses of the new compounds

1-Phenyl-2-methyl-4-peS-1-one **(3a)** Rdt : 70 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.08 – 7.86 (m, 2H, H_1+H_3), 7.56 (d, *J* = 0.6 Hz, 1H, H_5), 7.50 – 7.36 (m, 2H, H_4+H_6), 5.88 – 5.71 (m, 1H, H_{12}), 5.12 – 4.99 (m, 2H, H_{13}), 3.54 (h, *J* = 6.9 Hz, 1H, H_8), 2.56 (dddt, *J* = 14.4, 7.7, 6.9, 1.3 Hz, 1H, H_{10}), 2.20 (dddt, *J* = 14.4, 7.7, 6.9, 1.3 Hz, 1H, H_{10}), 1.21 (d, *J* = 6.9 Hz, 3H, H_{11}).

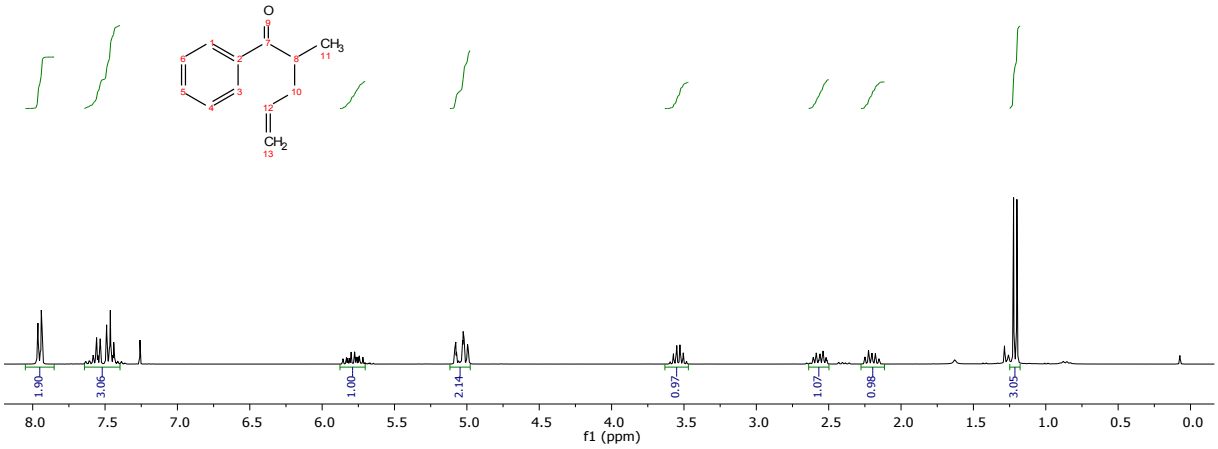

Figure 1. ^{1}H NMR spectrum of **3a**

1-Phenyl-2-methyl-4-penten-1-one **(3a) :** ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.61 (C_7), 136.52 (C_{ar}), 135.83 (C_{ar}), 132.90 (C_{ar}), 128.65 (C_{ar}), 128.29 (C_{12}), 116.74 (C_{13}), 40.37 (C_8), 37.63 (C_{10}), 17.01 (C_{11}).

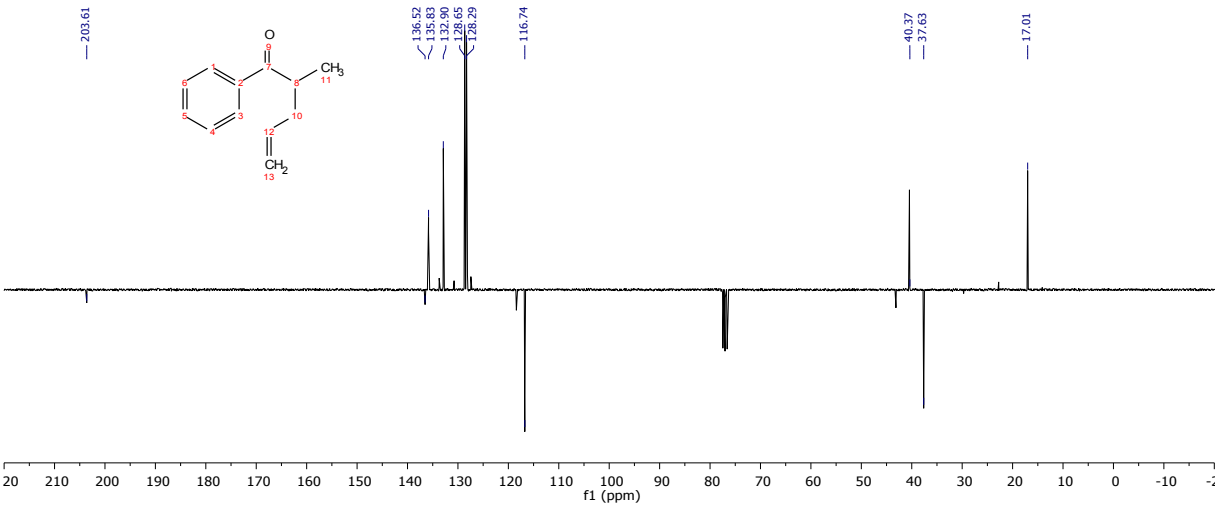

Figure 2. APT NMR spectrum of **3a**

1-phenyl-2-methyl-2-(2-propen-1-yl)- 4-penten-1-one (4a) Rdt : 11 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.63 (dd, *J* = 8.2, 1.5 Hz, 2H, H_1+H_3), 7.40 (d, *J* = 7.2 Hz, 3H, H_4+H_5+H_6), 5.85 – 5.56 (m, 2H, H_{14}+ H_{15}), 5.13 – 4.95 (m, 4H, H_{16}+ H_{17}), 2.62 (ddt, *J* = 14.0, 7.1, 1.3 Hz, 2H, H_{12}, H_{13}), 2.40 (ddt, *J* = 14.0, 7.6, 1.2 Hz, 2H, H_{13}, H_{12}), 1.29 (s, 3H, H_{11}).

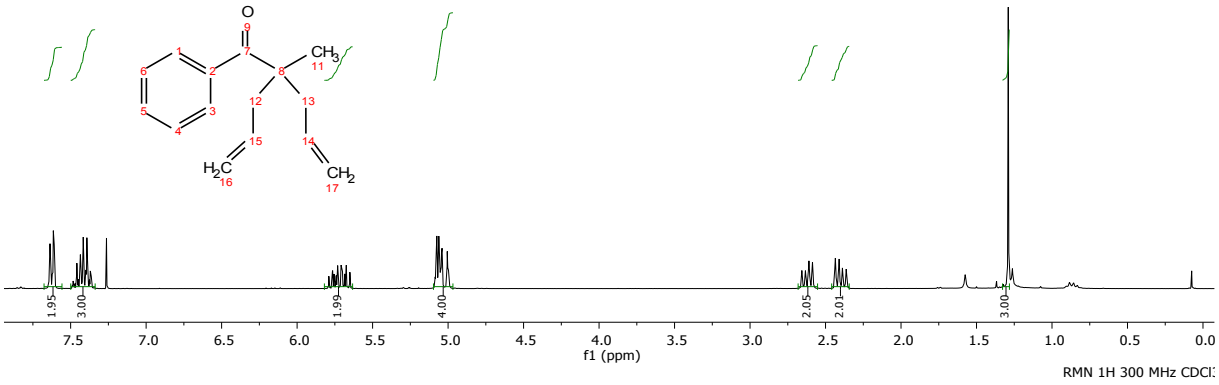

Figure 3. ^{1}H NMR spectrum of **4a**

1-phenyl-2-methyl-2-(2-propen-1-yl)-4-penten-1-one (4a) **:** ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.13 (C_7), 139.58 (C_{ar}), 133.72 (C_{ar}), 130.76 (C_{ar}), 128.11 (C_{ar}), 127.43 ($C_{14,15}$), 118.41, 51.20 ($C_{16,17}$), 43.14 (C_8), 29.70 ($C_{12,13}$), 22.76 (C_{11}).

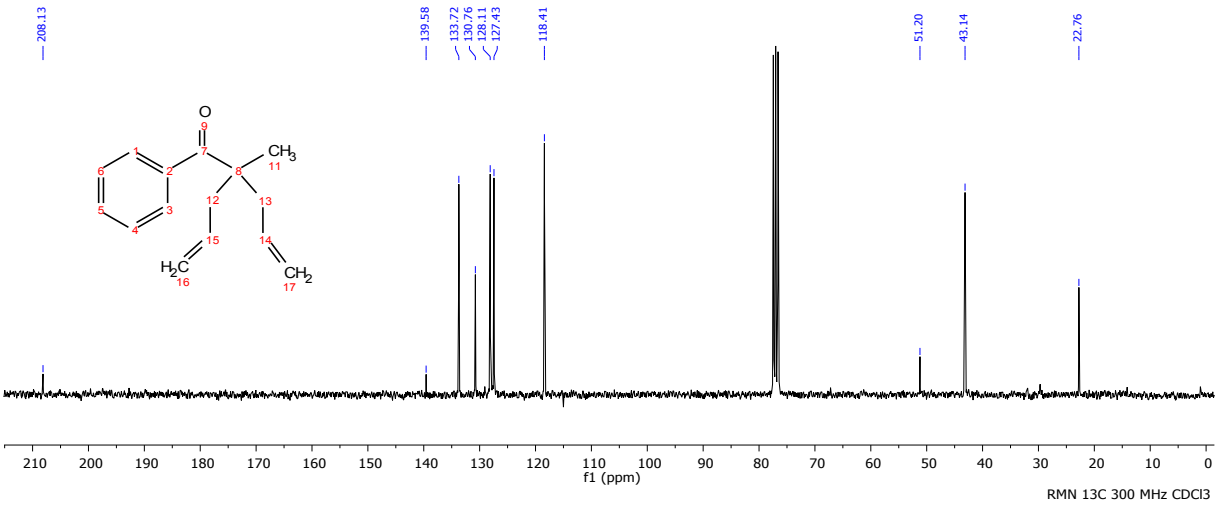

Figure 4. ^{13}C NMR spectrum of **4a**

1-(4-methylphenyl)-2-methyl-4-penten-1-one **(3b)** Rdt : 67 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.93 – 7.78 (m, 2H, H_1+H_3), 7.31 – 7.23 (m, 2H, H_4+H_6), 5.78 (dddd, *J* = 16.8, 10.1, 7.5, 6.5 Hz, 1H, H_{12}), 5.10 – 4.97 (m, 2H, H_{13}), 3.51 (h, *J* = 6.9 Hz, 1H, H_8), 2.55 (dddt, *J* = 14.4, 7.7, 6.9, 1.3 Hz, 1H, H_{11}), 2.41 (s, 1H, H_{14}), 2.27 – 2.12 (m, 1H, H_{11}), 1.20 (d, *J* = 6.9 Hz, 3H, H_9).

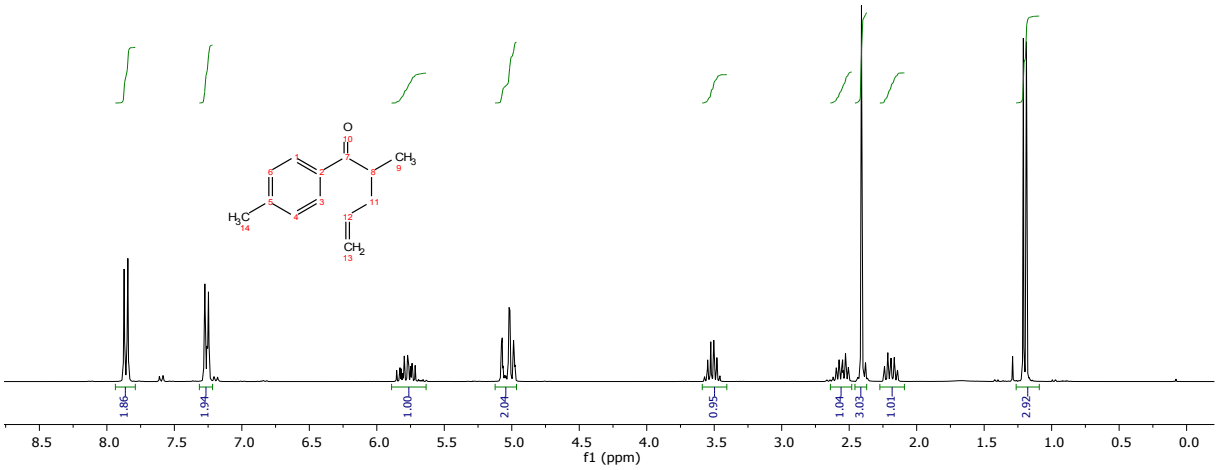

Figure 5. ^{1}H NMR spectrum of **3b**

1-(4-methylphenyl)-2-methyl-4-penten-1-one **(3b):**^{13}C NMR (75 MHz, $CDCl_3$) δ 203.24 (C_7), 143.66 (C_2), 135.95 (C_{ar}), 133.98 (C_{ar}), 129.34 (C_{ar}), 128.43 (C_{12}), 116.62 (C_{13}), 40.29 (C_{14}), 37.71(C_8), 21.60(C_{11}), 17.09(C_9).

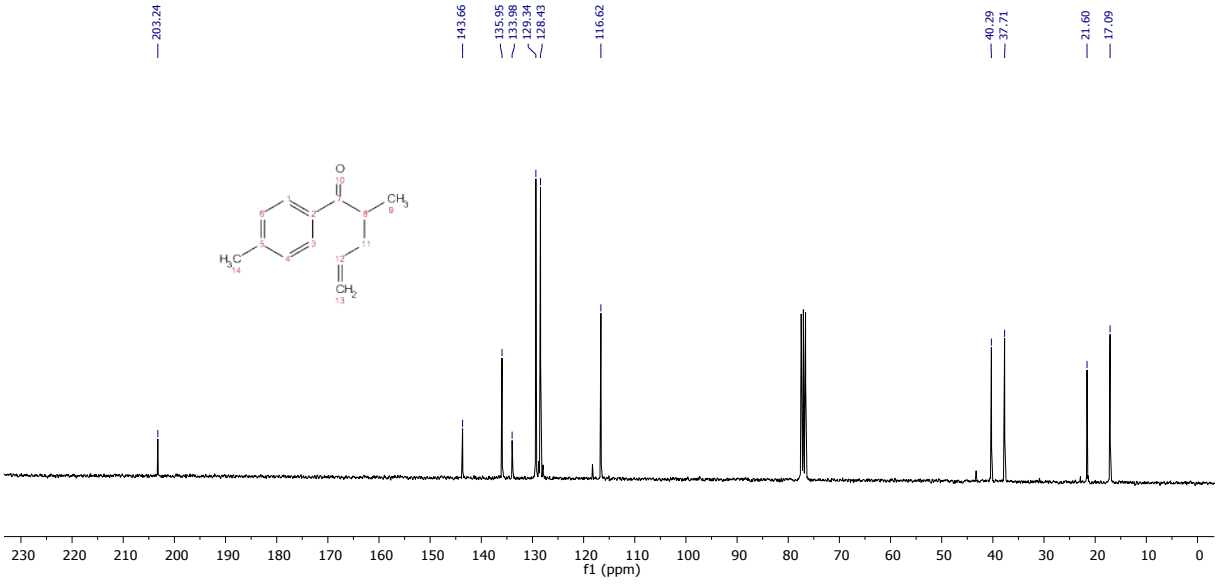

Figure 6. ^{13}C NMR spectrum of **3b**

1-(4-methoxyphenyl)-2-methyl-4-penten-1-one (3c) Rdt : 70 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.03 – 7.89 (m, 2H, H_1+H_3), 7.03 – 6.87 (m, 2H, H_4+H_6), 5.89 – 5.67 (m, 1H, H_{14}), 5.14 – 4.90 (m, 2H, H_{14}), 3.86 (s, 3H, H_{11}), 3.49 (h, *J* = 6.9 Hz, 1H, H_8), 2.61 – 2.47 (m, 1H, H_{13}), 2.29 – 2.10 (m, 1H, H_{13}), 1.19 (d, *J* = 6.9, 3H, H_9).

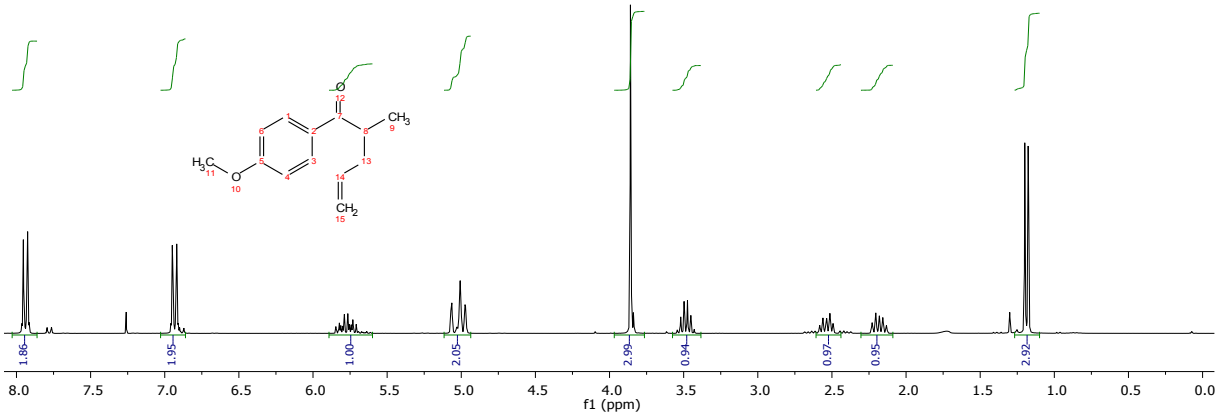

Figure 7. ^{1}H NMR spectrum of **3c**

1-(4-methoxyphenyl)-2-methyl-4-penten-1-one (3c): ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.14, 163.39 (C_{ar}), 136.03 (C_{ar}), 130.56 (C_{ar}), 129.45 (C_{ar}), 116.56 (C_{14}), 113.80 (C_{15}), 55.45 (C_{11}), 40.03 (C_8), 37.80 (C_{13}), 17.19 (C_9).

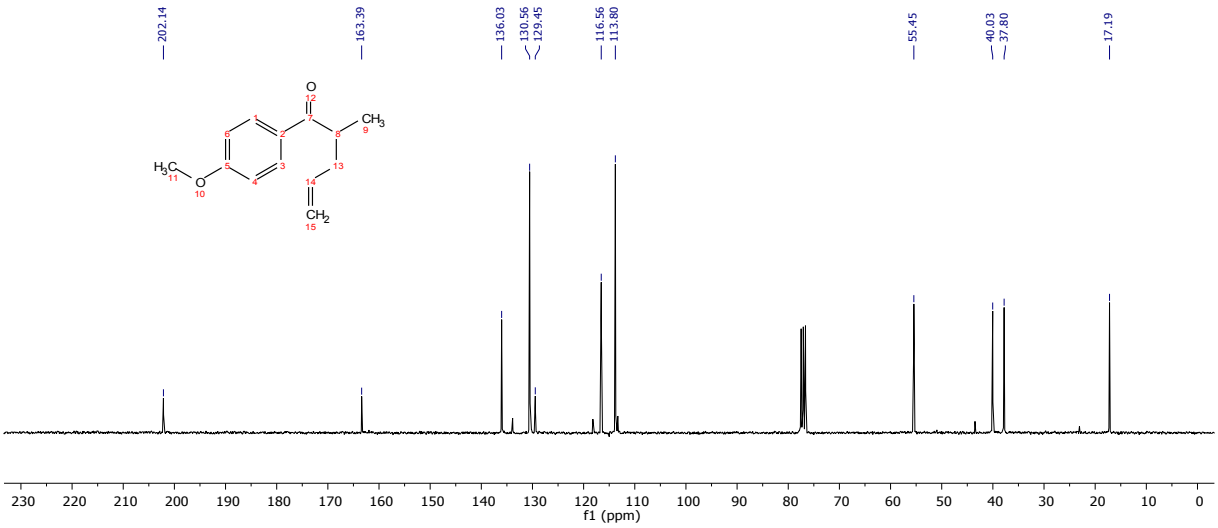

Figure 8. ^{13}C NMR spectrum of **3c**

1-(4-methoxyphenyl)-2-methyl-4-penten-1-one (3c) ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.14 (C_7), 163.39 (C_2), 136.03 (C_{ar}), 130.56 (C_{ar}), 129.45 (C_{ar}), 116.56 (C_{14}), 113.80 (C_{15}), 55.45 (C_{11}), 40.03 (C_8), 37.80 (C_{13}), 17.19 (C_9).

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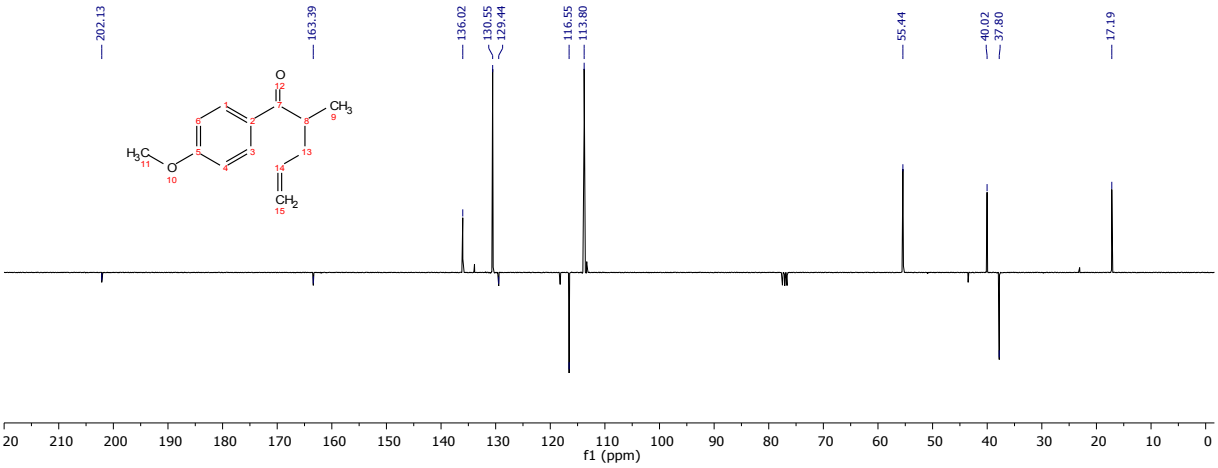

Figure 9. APT NMR spectrum of **3c**

1-phenyl-2-(2-phenylethyl)-4-penten-1-one (3d) Rdt : 65 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.87 – 7.74 (m, 2H, H_1+H_3), 7.53 – 7.42 (m, 1H, H_5), 7.36 (dd, *J* = 8.2, 6.7 Hz, 2H, H_4+H_6), 7.23 – 7.00 (m, 5H, H_{23}+ H_{24} + H_{25} + H_{26}+ H_{27}), 5.65 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H, H_{14}), 5.02 – 4.81 (m, 2H, H_{15}), 3.59 – 3.32 (m, 1H, H_8), 2.66 – 2.39 (m, 3H, H_9 + H_{13}), 2.30 – 2.13 (m, 1H, H_9), 2.10 – 1.95 (m, 1H, H_{10}), 1.77 (dddd, *J* = 13.6, 9.6, 6.4, 5.3 Hz, 1H, H_{10}).

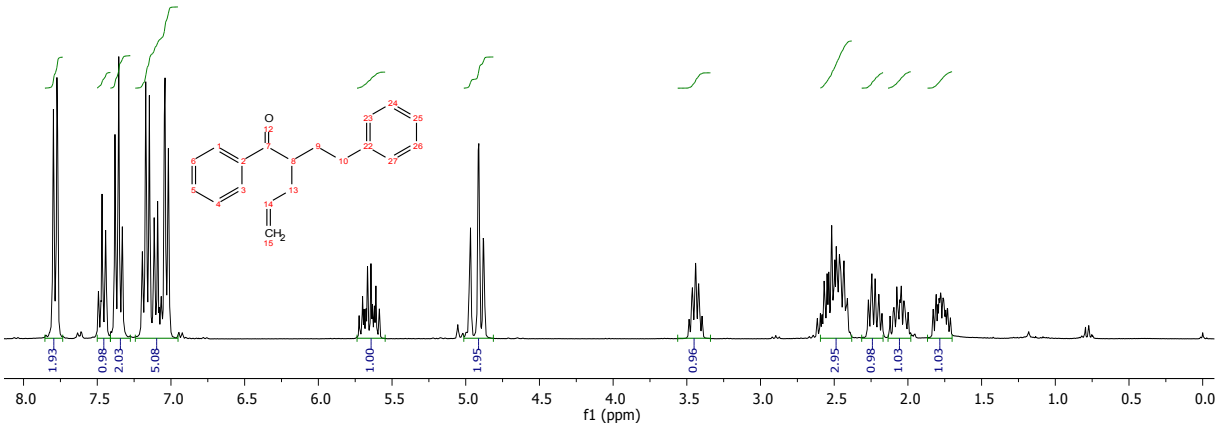

Figure 10. ^{1}H NMR spectrum of **3d**

1-phenyl-2-(2-phenylethyl) -4-penten-1-one (3d): ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.27(C_7), 141.69 (C_{ar}), 137.23 (C_{ar}), 135.53 (C_{ar}), 133.00 (C_{ar}), 128.67 (C_{ar}), 128.49 (C_{ar}), 128.40 (C_{ar}), 128.28 (C_{ar}), 125.98 (C_{14}), 116.90 (C_{15}), 45.06 (C_8), 36.39 (C_{13}), 33.45 (C_9), 33.29 (C_{10}).

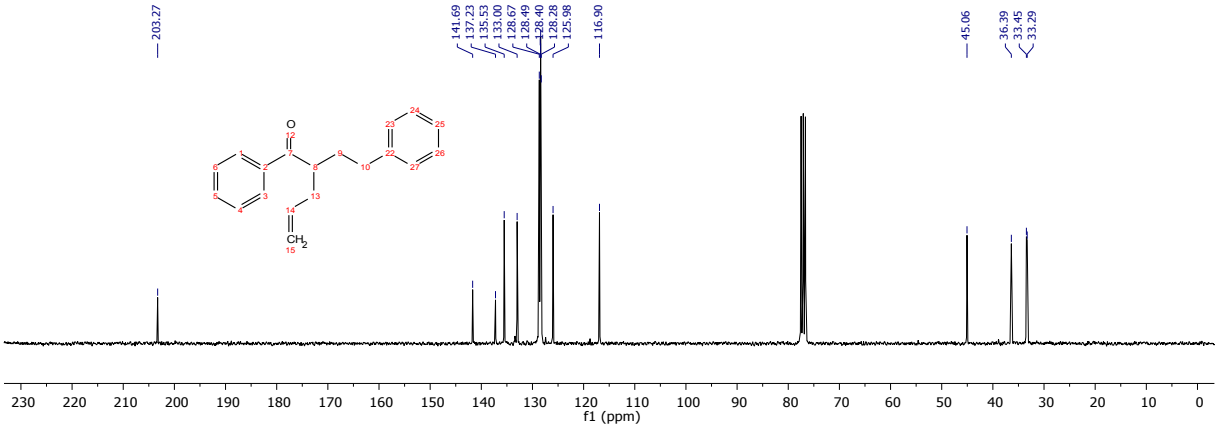

Figure 11.^{13}C NMR spectrum of **3d**

1-phenyl-2-(2-phenylethyl)-4-penten-1-one (3d) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.27 (C_7), 141.69 (C_2), 137.23 (C_{22}), 135.53 (C_{ar}), 133.00 (C_{ar}), 128.67 (C_{ar}), 128.49 (C_{ar}), 128.40 (C_{ar}), 128.28 (C_{ar}), 125.98 (C_{14}), 116.90 (C_{15}), 45.06 (C_8), 36.39 (C_{13}), 33.45 (C_9), 33.29 (C_{10}).

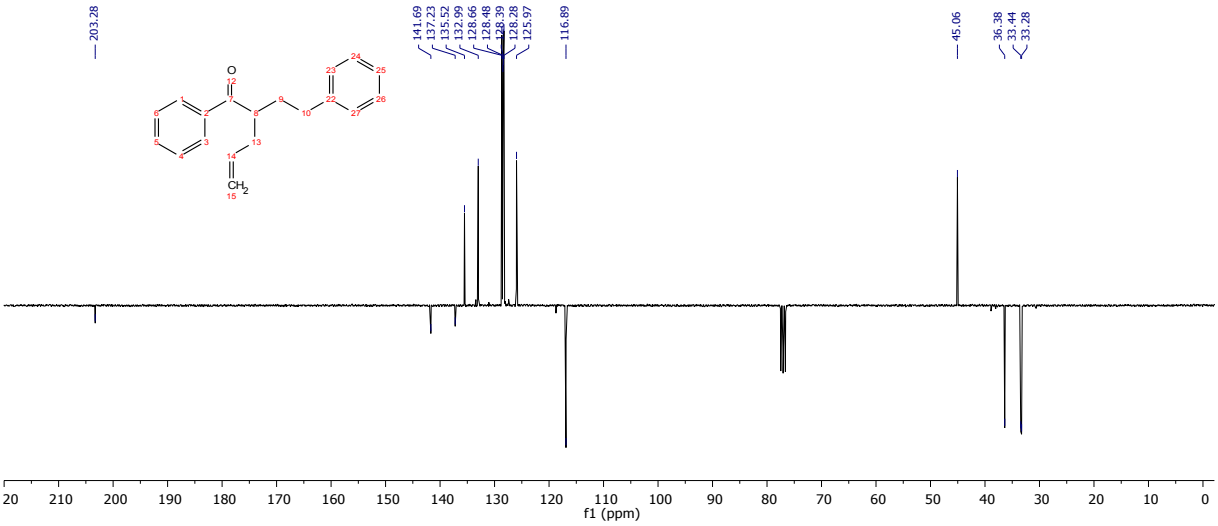

Figure 12. APT NMR spectrum of **3d**

3-phenyl-3-(2-propen-1-yl)-5-hexen-2-one (4e) Rdt : 65 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.42 – 7.30 (m, 2H, H_1+H_3), 7.33 – 7.24 (m, 1H, H_5), 7.23 – 7.14 (m, 1H, H_4+H_6), 5.45 (dddd, *J* = 17.0, 10.1, 7.6, 6.8 Hz, 2H, H_{13}+H_{14}), 5.13 – 4.99 (m, 4H, H_{15}+H_{16}), 2.82 – 2.65 (m, 4H, H_{11}+H_{12}), 1.90 (s, 3H, H_9).

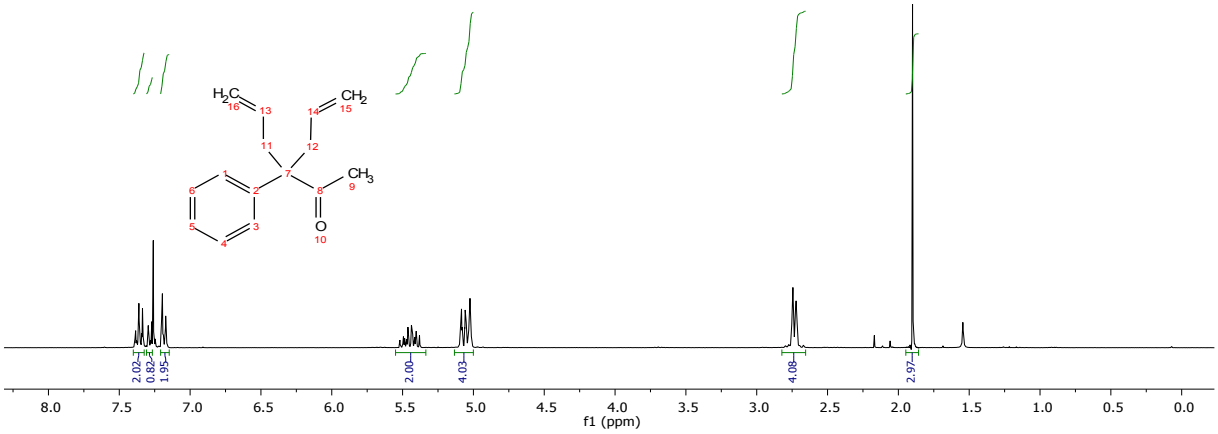

Figure 13. ^{1}H NMR spectrum of **4e**

3-phenyl-3-(2-propen-1-yl)-5-hexen-2-one (4e) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.26 (C_8), 141.15 (C_2), 133.26 ($2C_{ar}$), 128.80 ($2C_{ar}$), 127.12 (C_3), 126.66 (C_{13} + C_{14}), 118.53 (C_{15} + C_{16}), 58.93 (C_7), 37.47(C_{11} + C_{12}), 26.20 (C_9).

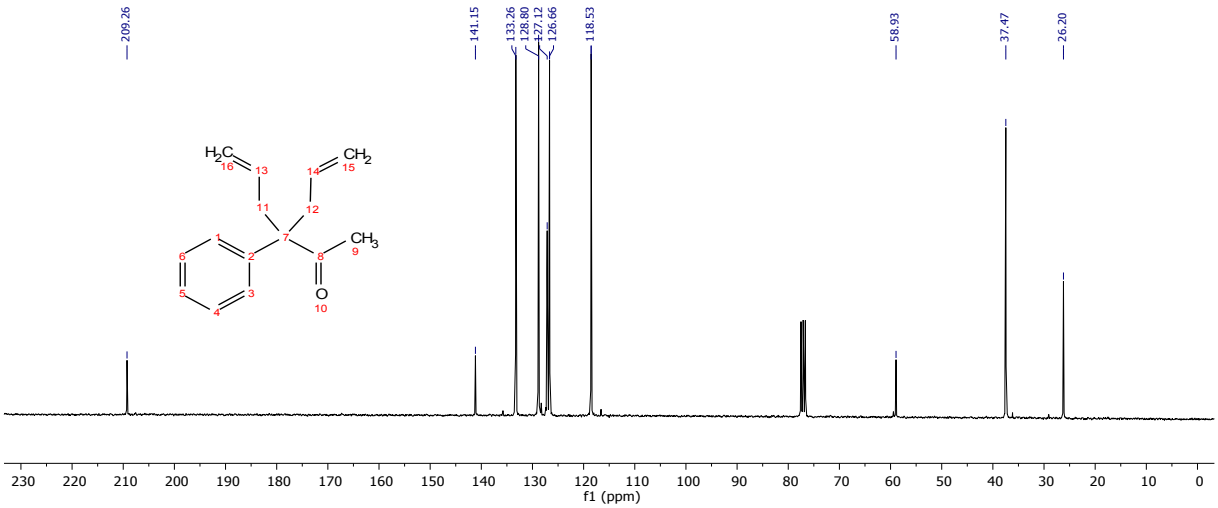

Figure 14. ^{13}C NMR spectrum of **4e**

3-(4-methoxyphenyl)-3-(2-propen-1-yl)-5-hexen-2-one (4f) Rdt : 67 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.9 Hz, 2H, H_1+ H_3), 6.88 (d, *J* = 8.9 Hz, 2H, H_4+ H_5), 5.57 – 5.33 (m, 2H, H_{13} + H_{14}), 5.15 – 4.96 (m, 4H, H_{15} + H_{16}), 3.80 (s, 3H, H_{18}), 2.70 (dt, *J* = 6.6, 1.2 Hz, 4H, H_{11} + H_{12}), 1.89 (s, 3H, H_9).

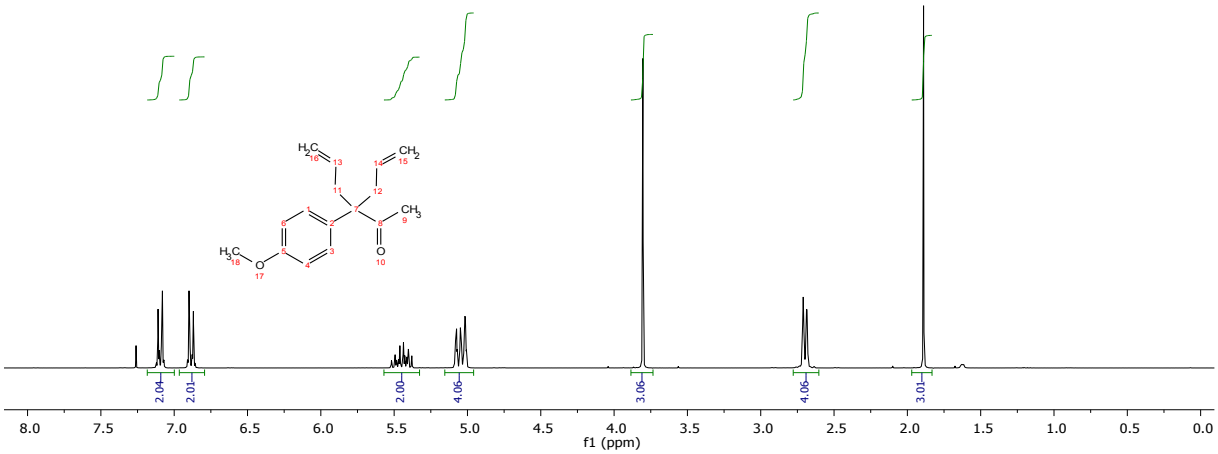

Figure 15. ^{1}H NMR spectrum of **4f**

3-(4-methoxyphenyl)-3-(2-propen-1-yl)-5-hexen-2-one (4f) *:* ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.59 (C_7), 158.58 (C_2), 133.40 (C_{ar}), 133.07 (C_{ar}), 127.73 (C_{ar}), 118.42 (C_{13} + C_{14}), 114.15 (C_{15} + C_{16}), 58.20 (C_{18}), 55.22 (C_8), 37.49 (C_{11} + C_{12}), 26.00 (C_9).

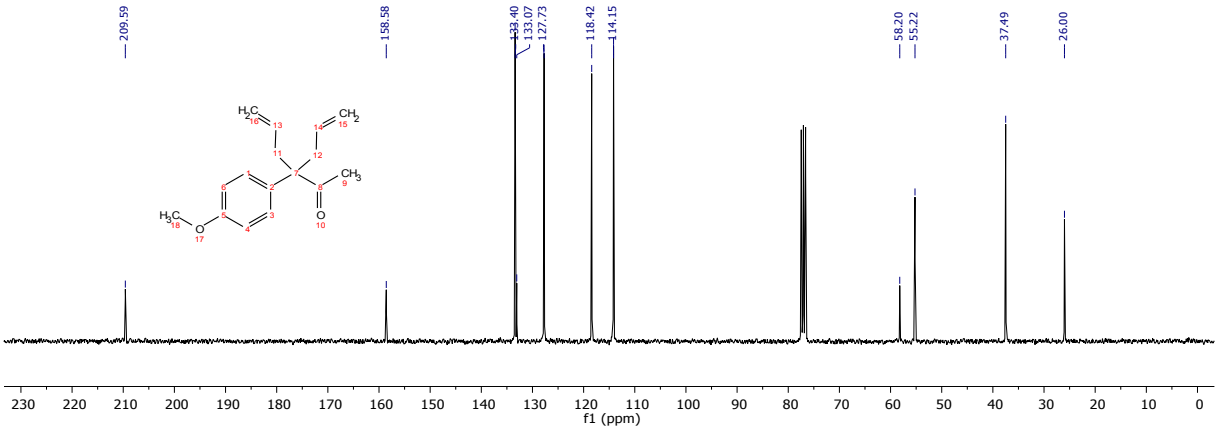

Figure 16^{13}C NMR spectrum of **4f**

3-(4-methoxyphenyl)-3-(2-propen-1-yl)-5-hexen-2-one (4f) *:* ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.59 (C_8), 158.58 (C_2), 133.40 (C_{ar}), 133.07 (C_{ar}), 127.73 (C_{ar}), 118.42 (C_{13} + C_{14}), 114.15 (C_{15} + C_{16}), 58.20 (C_{18}), 55.22 (C_4), 37.49 (C_{11} + C_{12}), 26.00 (C_9).

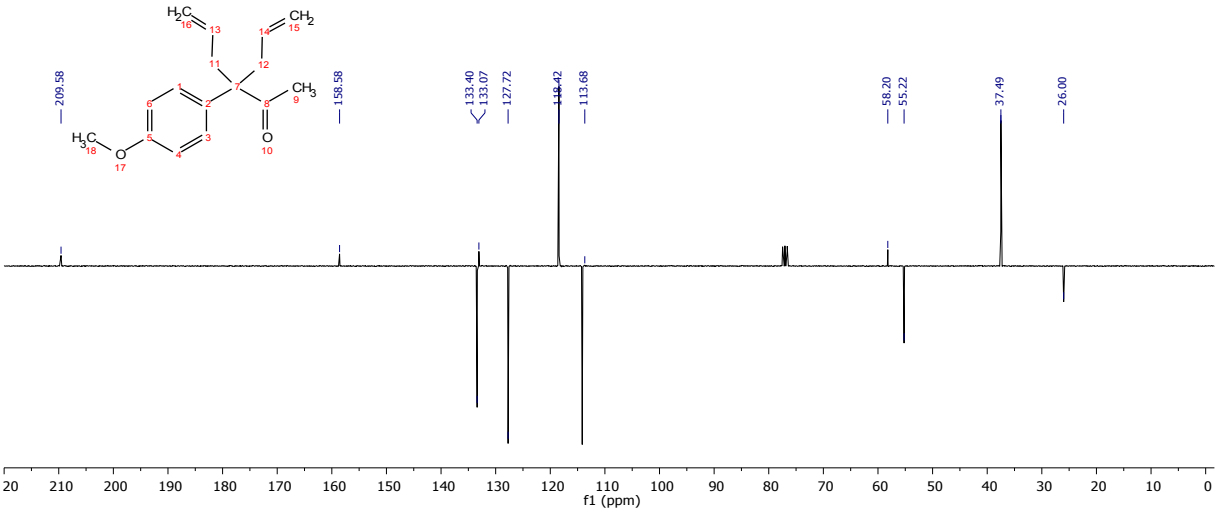

Figure 17. APT NMR spectrum of **4f**

3-(4-methoxyphenyl)-5-hexen-2-one (3f) Rdt : 16 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 6.6 Hz, 2H, H_{1+3}), 6.86 (d, *J* = 8.7 Hz, 2H, H_{4+6}), 5.66 (ddt, *J* = 17.1, 10.1, 6.9 Hz, 1H, H_{11}), 5.04 – 4.91 (m, 2H, H_{12}), 3.78 (s, 3H, H_{15}), 3.63 (t, *J* = 7.5 Hz, 1H, H_{7}), 2.82 – 2.70 (m, 1H, H_{10}), 2.39 (dddt, *J* = 14.4, 7.7, 6.9, 1.3 Hz, 1H, H_{10}), 2.04 (s, 3H, H_{9}).

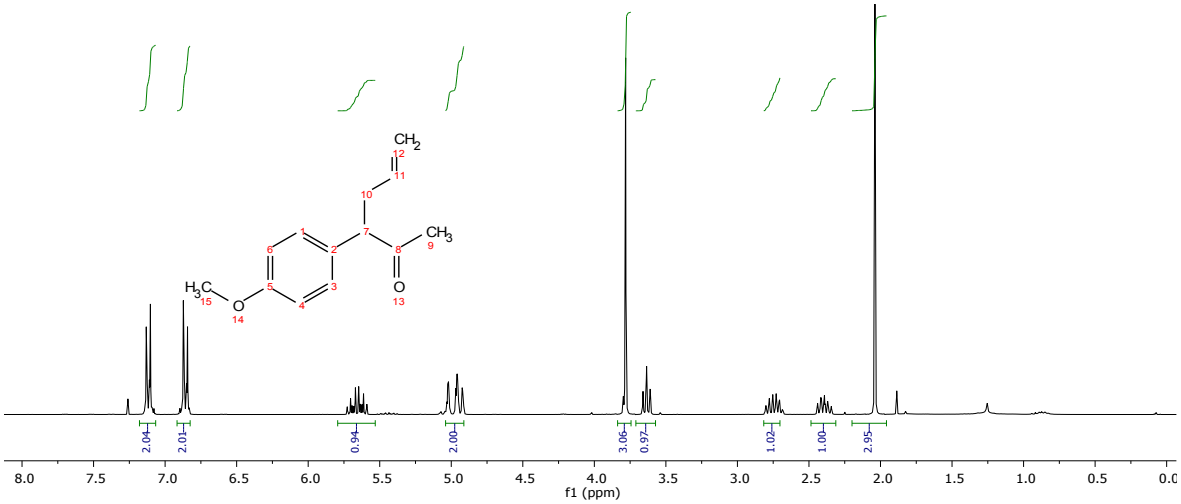

Figure 18. ^{1}H NMR spectrum of **3f**

3-(4-methoxyphenyl)-5-hexen-2-one (3f) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.92 (C_8), 158.90 (C_2), 135.89 (C_{ar}), 130.38 (C_{ar}), 129.27 (C_{ar}), 116.50 (C_{11}), 114.33 (C_{12}), 58.53 (C_{15}), 55.22 (C_7), 36.16 (C_{10}), 28.92 (C_9).

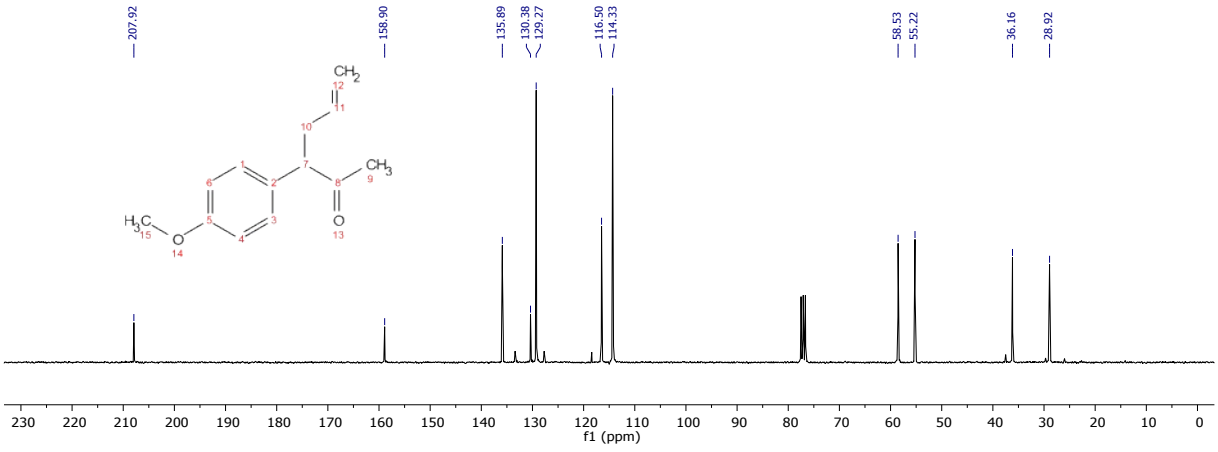

Figure 19. ^{13}C NMR spectrum of **3f**

3-(4-trifluoromethylphenyl)-3-(2-propen-1-yl)-5-hexen-2-one (4g) Rdt : 72 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.61 – 7.43 (m, 3H, H_1 + H_3 + H_6), 7.36 (dddd, *J* = 7.6, 2.0, 1.5, 0.7 Hz, 1H, H_5), 5.43 (ddt, *J* = 17.5, 9.6, 7.2 Hz, 2H, H_{13} + H_{14}), 5.17 – 4.99 (m, 4H, H_{15} + H_{16}), 2.75 (dt, *J* = 7.1, 1.1 Hz, 4H, H_{11} + H_{12}), 1.91 (s, 3H, H_9).

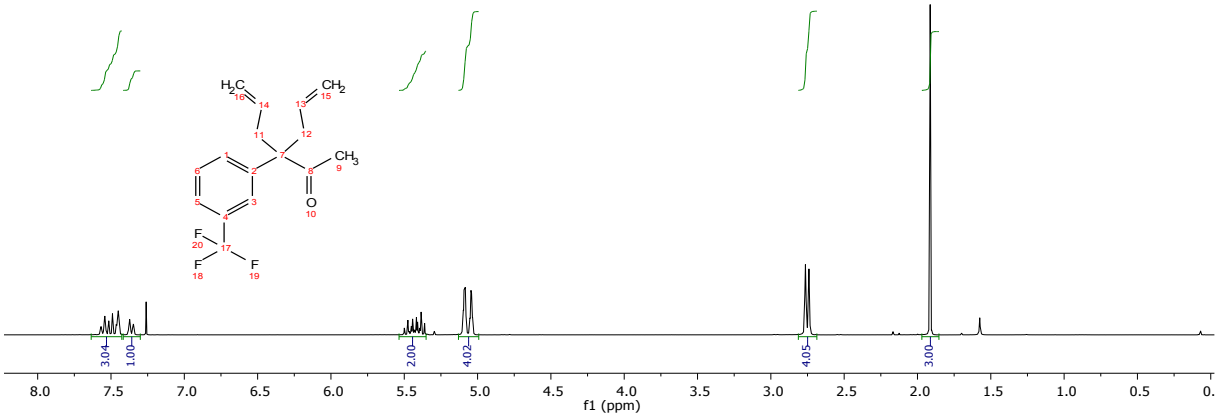

Figure 20. ^{1}H NMR spectrum of **4g**

3-(4-trifluoromethylphenyl)-3-(2-propen-1-yl)-5-hexen-2-one (4g) : ^{13C} NMR (75 MHz, $CDCl_3$) δ 208.34 (C_8), 142.36 (C_{17}), 132.46 (C_{ar}), 130.28 (C_{ar}), 129.29 (C_{13}+C_{14}), 124.13 (C_{ar}), 124.09 (C_{ar}), 123.34 (C_{ar}), 123.30 (C_{ar}), 119.14 (C_{15} + C_{16}), 59.03 (C_7), 37.48 (C_{11} + C_{12}), 26.26(C_9).

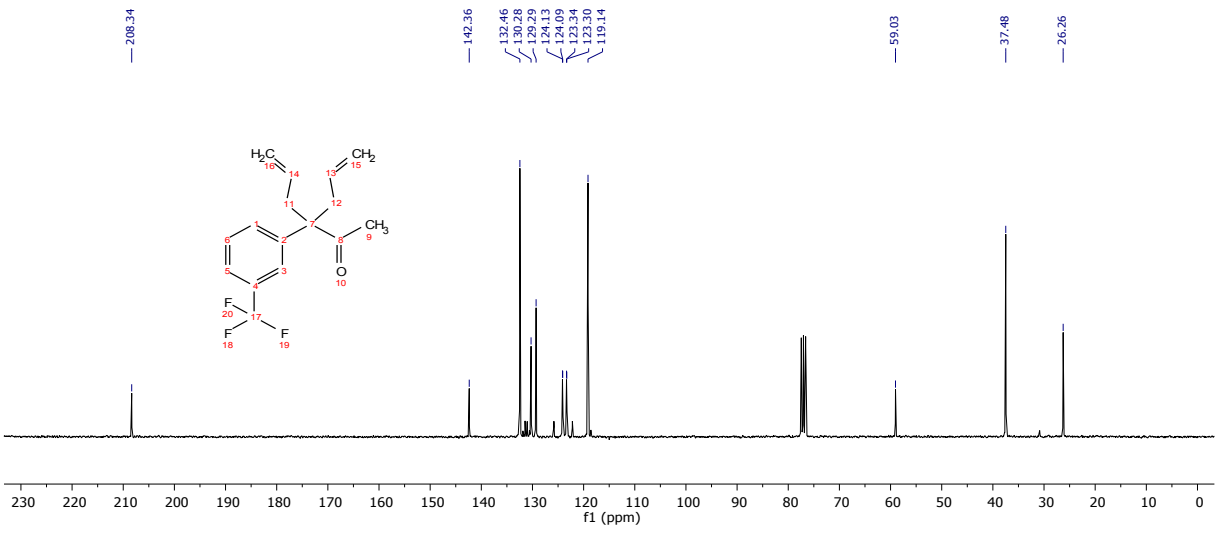

Figure 21: ^{13}C NMR spectrum of **4g**

HRMS (ESI) m/z: Calcd for $[M+H]^+$ $C_{16}H_{17}OF_3$ 282,1231; Found 282.2789.

3-(4-trifluoromethylphenyl)-5-Hexen-2-one (3g) : ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.58 – 7.41 (m, 4H, H_{Ph}), 5.64 (ddt, *J* = 17.1, 10.1, 6.9 Hz, 1H, H_{12}), 5.07 – 4.95 (m, 2H, H_{13}), 3.78 (t, *J* = 7.5 Hz, 1H, H_7), 2.89 – 2.75 (m, 1H, H_{11}), 2.43 (dddt, *J* = 14.4, 7.7, 6.9, 1.3 Hz, 1H, H_{11}), 2.09 (s, 3H, H_9).

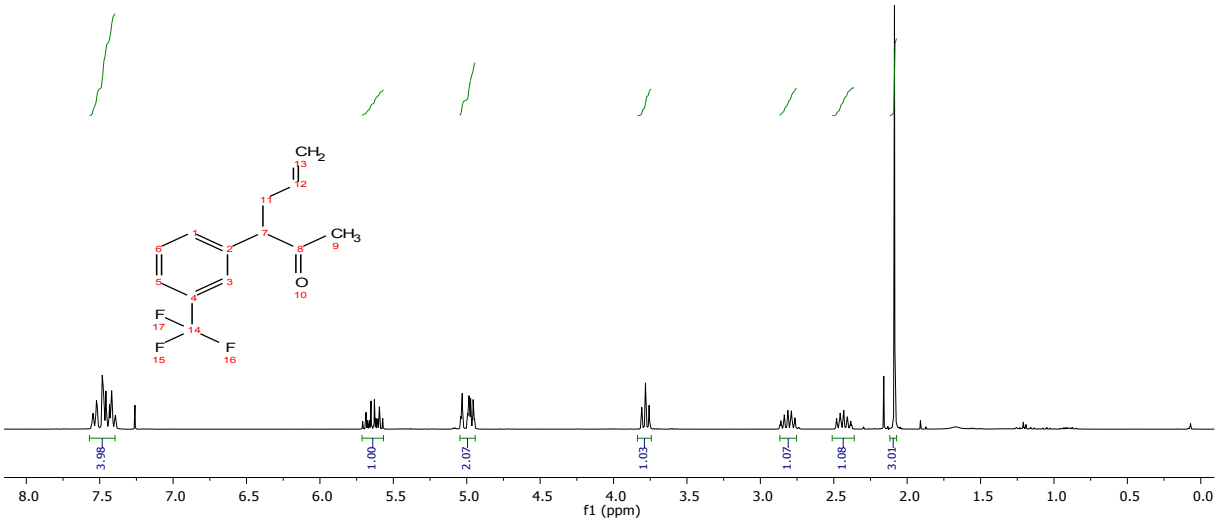

Figure 22. ^{1}H NMR spectrum of **3g**

3-(4-trifluoromethylphenyl)-5-hexen-2-one (3g) Rdt : 14 %, ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.79 (C_8), 139.31 (C_{14}), 134.97 (C_{ar}), 131.57 (C_{ar}), 129.40 (C_{12}), 124.33 (C_{ar}), 124.28 (C_{ar}), 117.26 (C_{ar}), 59.01 (C_7), 36.30 (C_{11}), 29.36 (C_9).

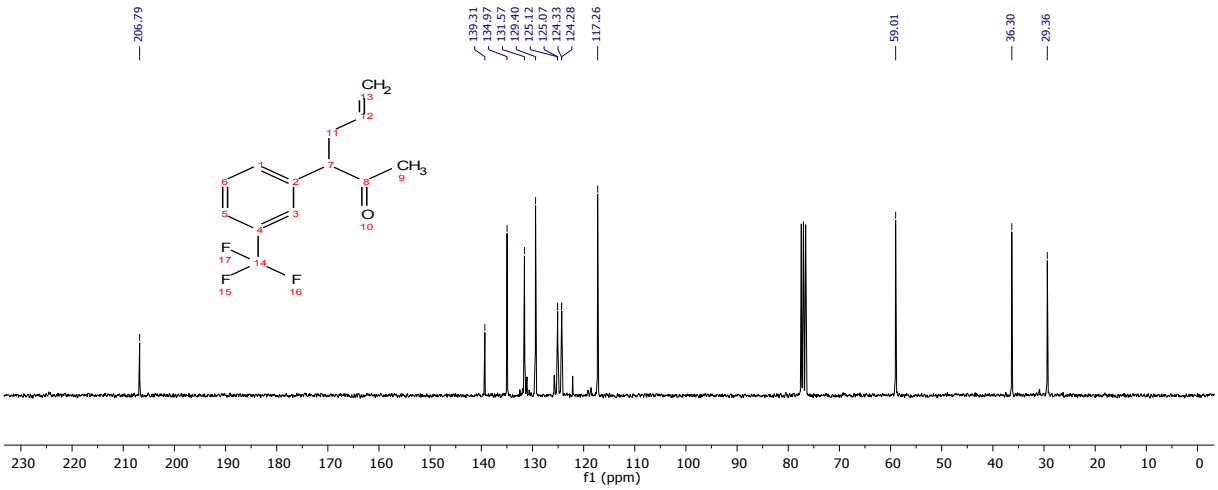

Figure 23. ^{13}C NMR spectrum of **3g**

3-(2-methoxyphenyl)-5-hexen-2-one (3h) Rdt : 91 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.21 – 7.13 (m, 1H, H_1), 7.02 (dd, *J* = 7.5, 1.8 Hz, 1H, H_5), 6.90 – 6.79 (m, 2H, H_4+ H_6), 5.62 (ddt, *J* = 17.0, 10.1, 6.9 Hz, 1H, H_{14}), 4.96 – 4.79 (m, 2H, H_{15}), 4.03 (t, *J* = 7.4 Hz, 1H, H_7), 3.76 (s, 3H, H_{12}), 2.72 (m, 1H, H_{13}), 2.40 – 2.24 (m, 1H, H_{13}), 1.94 (s, 3H, H_9).

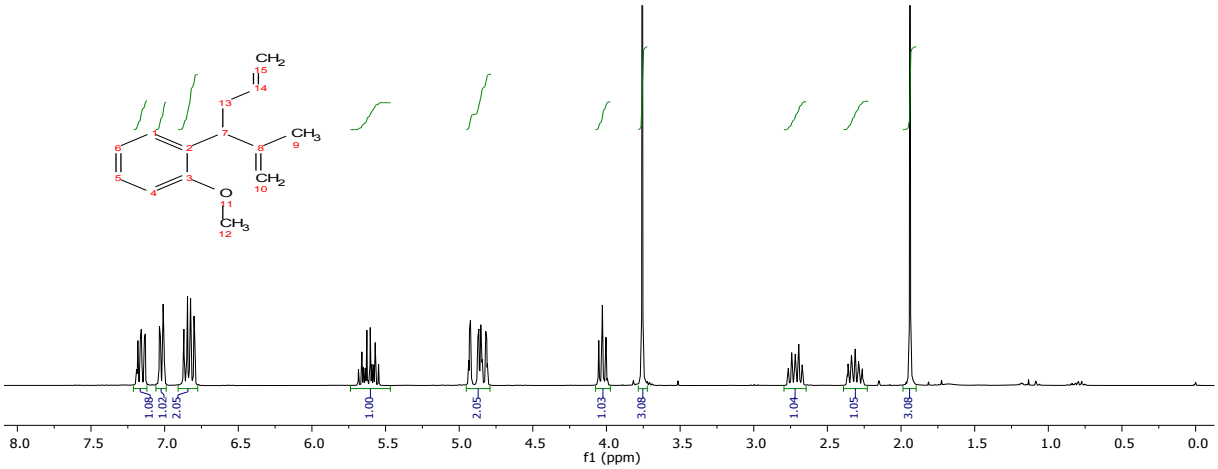

Figure 24. ^{1}H NMR spectrum of **3h**

3-(2-methoxyphenyl)-5-hexen-2-one (3h): ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.17 (C_8), 156.98 (C_3), 136.32 (C_{ar}), 128.74 (C_{ar}), 128.00 (C_{ar}), 127.26 (C_2), 120.93 (C_{ar}), 116.07 (C_{12}), 110.80 (C_{13}), 55.43 (C_{15}), 51.98 (C_7), 34.80 (C_{11}), 28.94 (C_9).

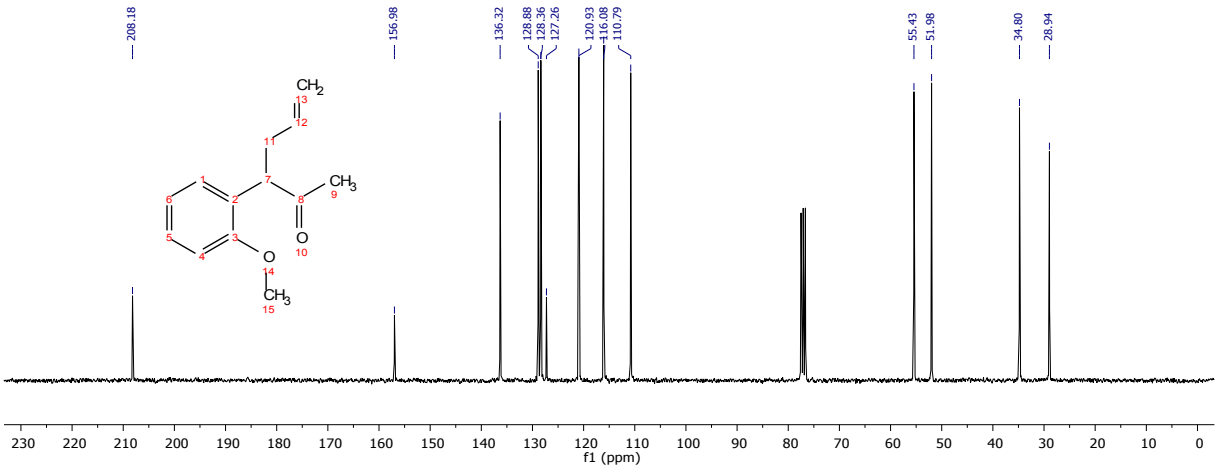

Figure 25. ^{13}C NMR spectrum of **3h**

3-(2-methoxyphenyl-5-hexen-2-one (3h): ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.17(C_8), 156.98 (C_3), 136.32 (C_{ar}), 128.74 (C_{ar}), 128.00 (C_{ar}), 127.26 (C_2), 120.93 (C_{ar}), 116.07 (C_{12}), 110.80 (C_{13}), 55.43 (C_{15}), 51.98 (C_7), 34.80 (C_{11}), 28.94 (C_9).

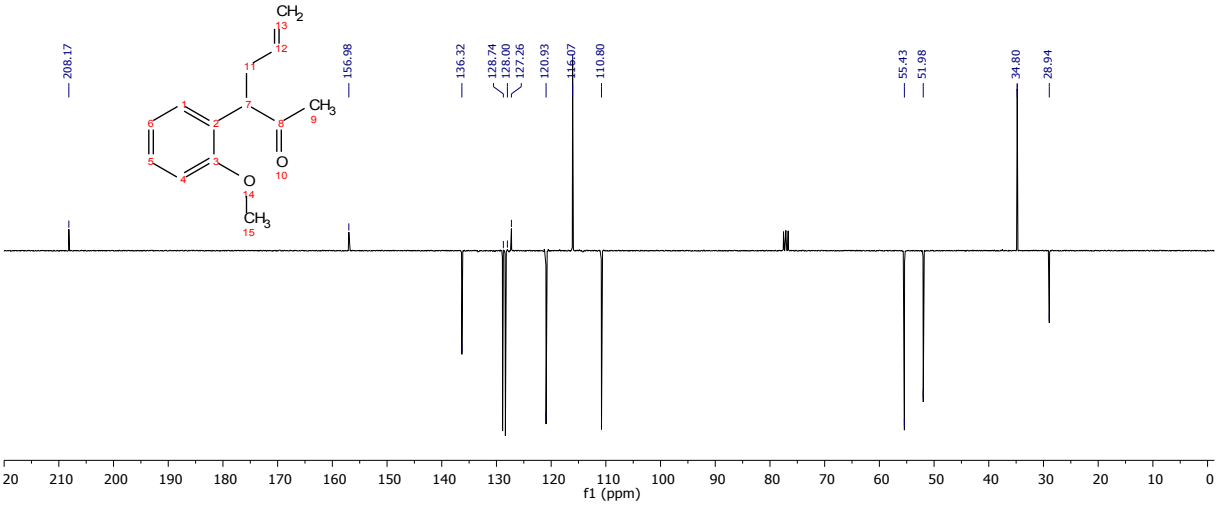

Figure 26. APT NMR spectrum of **3h**

HRMS (ESI) m/z : Calcd for $[M+H]^+$ $C_{13}H_{17}O$ 205.1229; Found 205.1186.

3,4-dihydro-2-methyl-2-(2-propen-1-yl)-1-(2H)-naphthalenone (6a) Rdt : 72 %,: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 7.9, 1.4 Hz, 1H, H_1), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H, H_4), 7.35 – 7.17 (m, 2H, H_5+H_6), 5.89 – 5.70 (m, 1H, H_{12}), 5.15 – 5.01 (m, 2H, H_{13}), 3.09 – 2.86 (m, 2H, H_9), 2.46 (ddt, *J* = 13.8, 7.2, 1.2 Hz, 1H, H_{11}), 2.28 (ddt, *J* = 13.8, 7.5, 1.1 Hz, 1H, H_{11}), 2.08 (ddd, *J* = 13.7, 7.0, 5.9 Hz, 1H, H_{10}), 1.90 (ddd, *J* = 13.7, 6.9, 5.7 Hz, 1H, H_{10}), 1.19 (s, 3H, H_{14}).

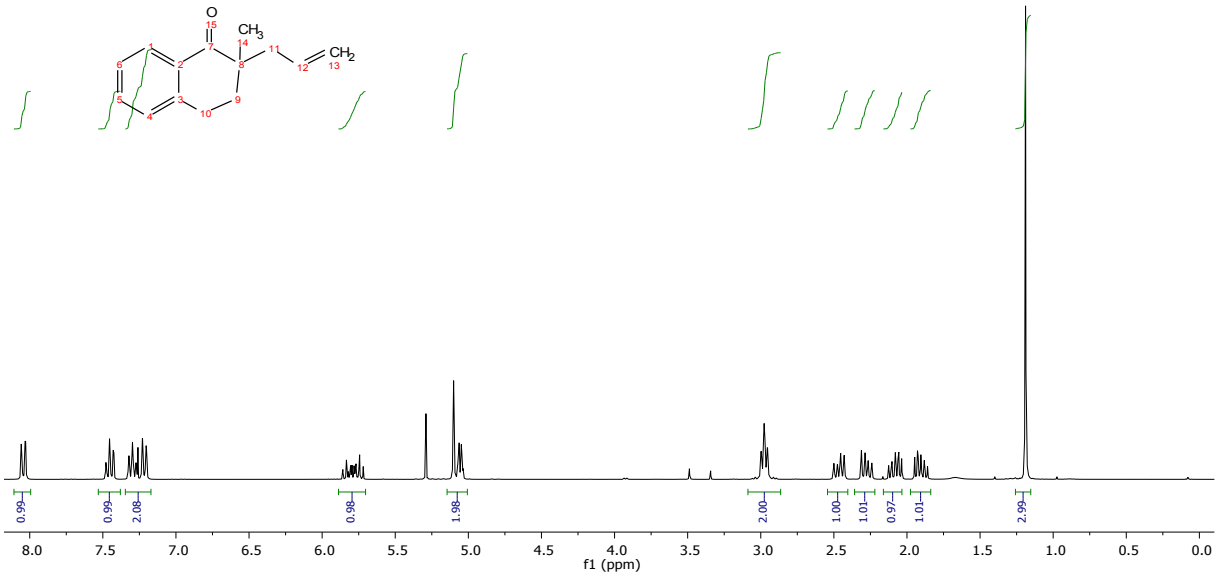

Figure 27. ^{1}H NMR spectrum of **6a**

3,4-dihydro-2-methyl-2-(2-propen-1-yl)-1-(2H)-naphthalenone (6a) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.04 (C_7), 143.32 (C_2), 133.98 (C_{ar}), 133.06 (C_{ar}), 131.62 (C_3), 128.66 (C_{ar}), 128.03 (C_{ar}), 126.64 (C_{13}), 118.19 (C_{12}), 44.6 (C_8), 41.14 (C_9), 33.38 (C_{11}), 25.36 (C_{10}), 21.92 (C_{14}).

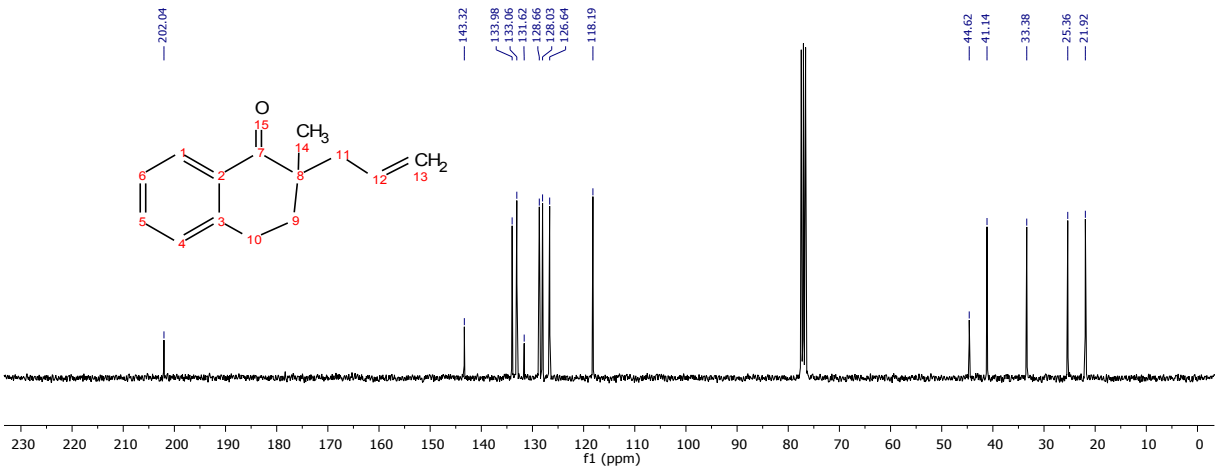

Figure 28. ^{13}C NMR spectrum of **6a**

3,4-dihydro-2,2-di-2-propen-1-yl-1-(2H)-naphthalenone (6b) Rdt : 72 %,: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 7.9, 1.5 Hz, 1H, H_1), 7.36 (td, *J* = 7.4, 1.5 Hz, 1H, H_4), 7.27 – 7.18 (m, 1H, H_6), 7.15 – 7.06 (m, 1H, H_5), 5.69 (ddt, *J* = 18.8, 9.0, 7.3 Hz, 2H, H_{14}+H_{16}), 5.03 – 4.91 (m, 4H, H_{15}+H_{17}), 2.89 (t, *J* = 6.4 Hz, 2H, H_{10}), 2.41 (ddt, *J* = 14.0, 7.1, 1.3 Hz, 2H, H_{13}, H_{12}), 2.19 (ddt, *J* = 13.9, 7.5, 1.2 Hz, 2H, H_{12},H_{13}), 1.94 (t, *J* = 6.4 Hz, 2H, H_9).

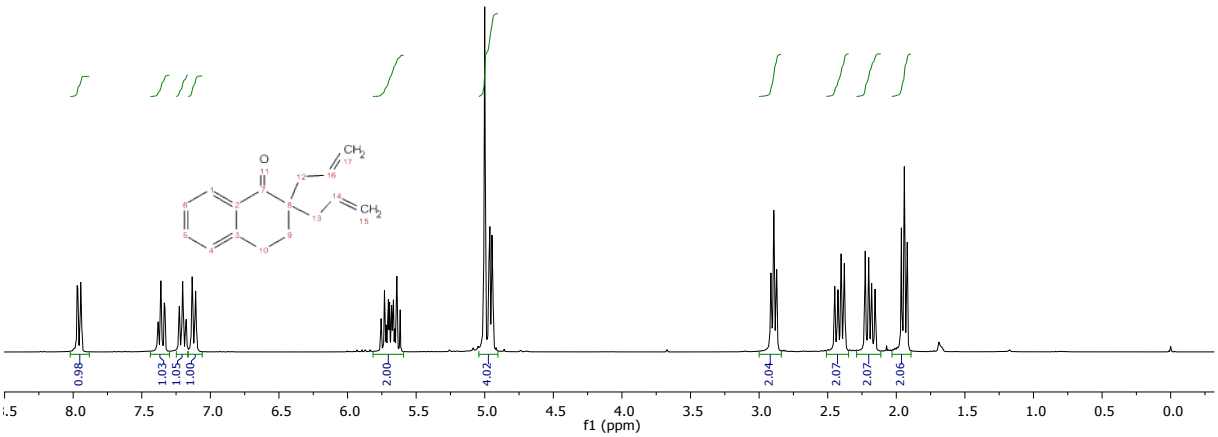

Figure 29. ^{1}H NMR spectrum of **6b**

3,4-dihydro-2,2-di-2-propen-1-yl-1-(2H)-naphthalenone (6b) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.80 (C_7), 143.18 (C_2), 133.84 (C_{ar}), 131.90 (C_{ar}), 128.67 (C_3), 127.97 (C_{ar}), 126.63 (C_{ar}), 118.27 (C_{14}+C_{15}), 115.96 (C_{16}+C_{17}), 47.76 (C_8), 39.19 (C_9), 30.64 (C_{12}+C_{13}), 25.13 (C_{10}),.

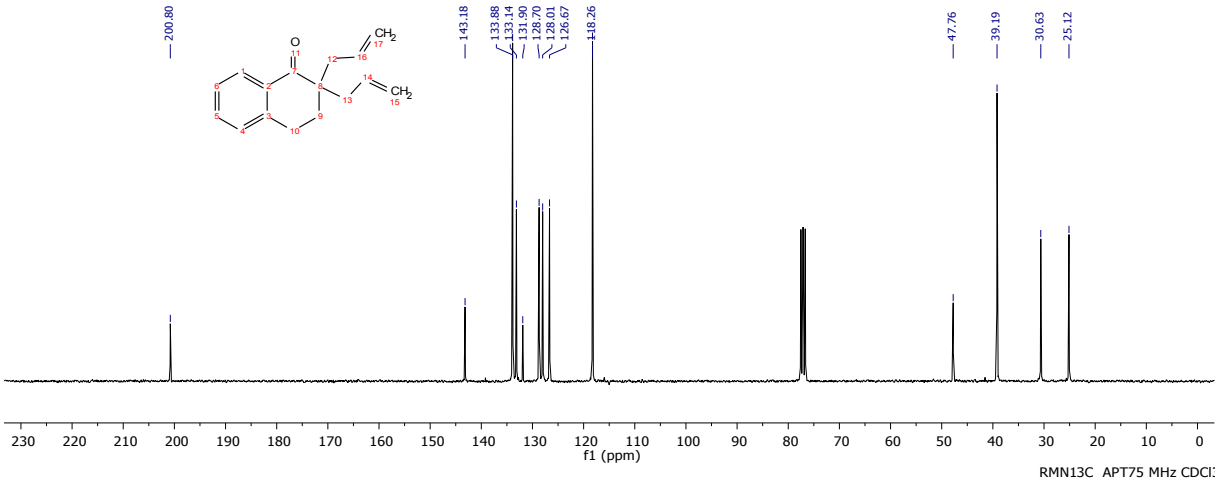

Figure 30. ^{13}C NMR spectrum of **6b**

3,4-dihydro-2,2-di-2-propen-1-yl-1-(2H)-naphthalenone (6b) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.80 (C_7), 143.18 (C_2), 133.84 (C_{ar}), 131.90 (C_{ar}), 128.67 (C_3), 127.97 (C_{ar}), 126.63 (C_{ar}), 118.27 (C_{14}+C_{15}), 115.96 (C_{16}+C_{17}), 47.76 (C_8), 39.19 (C_9), 30.64 (C_{12}+C_{13}), 25.13 (C_{10}).

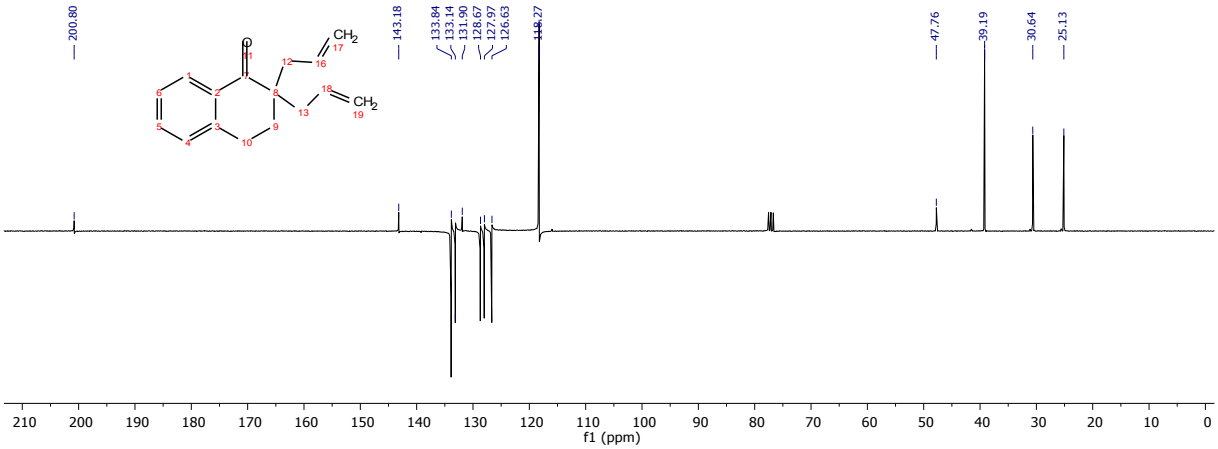

Figure 31. APT NMR spectrum of **6b**

4-methyl-3,4-dihydro-2,2-di-2-propen-1-yl-1-(2H)-naphthalenone (6c) Rdt : 78 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.8, 1.5 Hz, 1H, H_1), 7.52 (ddd, *J* = 7.8, 7.1, 1.6 Hz, 1H, H_4), 7.40 – 7.28 (m, 2H, H_5+H_6), 5.89 – 5.68 (m, 2H, H_{14}+H_{15}), 5.17 – 4.97 (m, 4H, H_{16}+H_{17}), 3.30 – 3.10 (m, 1H, H_{10}), 2.65 (ddt, *J* = 13.8, 6.3, 1.4 Hz, 1H, $H_{12,13}$), 2.37 – 2.20 (m, 3H, $H_{12,13}$), 1.99 – 1.80 (m, 2H, H_9), 1.40 (d, *J* = 6.8 Hz, 3H, H_{18}).

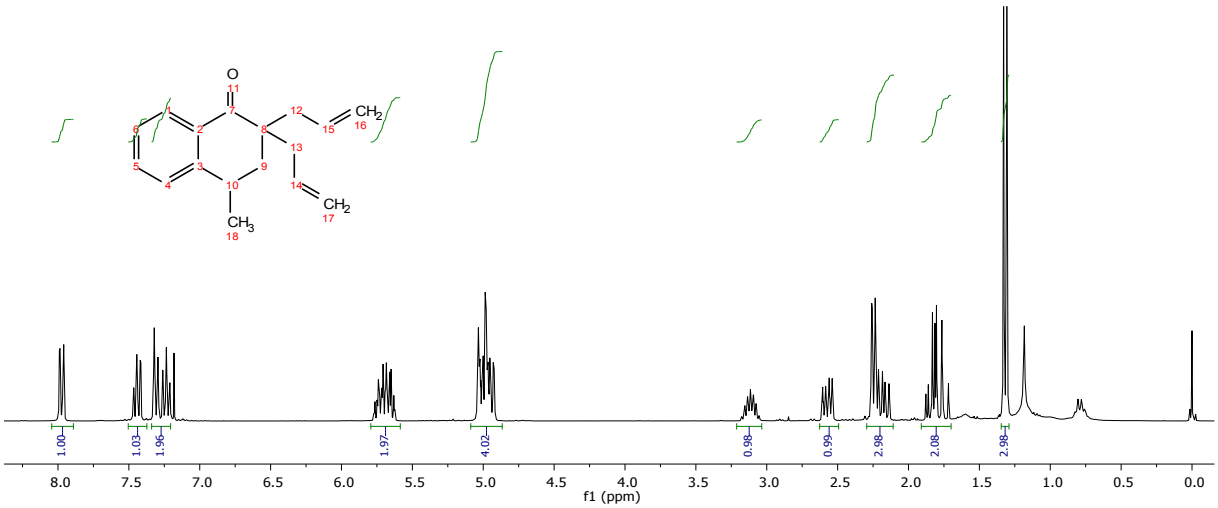

Figure 32. ^{1}H NMR spectrum of **6c**

4-methyl-3,4-dihydro-2,2-di-2-propen-1-yl-1-(2H)-naphthalenone (6c) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.13 (C_7), 147.22 (C_2), 134.53 (C_{ar}), 133.37 (C_{ar}), 133.23 (C_3), 131.54 (C_{ar}), 128.02 (C_{ar}), 126.54 (C_{14},C_{15}), 126.50 (C_{14},C_{15}), 118.46 (C_{16},C_{17}), 118.04 (C_{16},C_{17}), 48.22 (C_8), 40.13 (C_{12},C_{13}), 39.97 (C_{12},C_{13}), 39.10 (C_9), 28.15 (C_{10}), 20.63 (C_{18}).

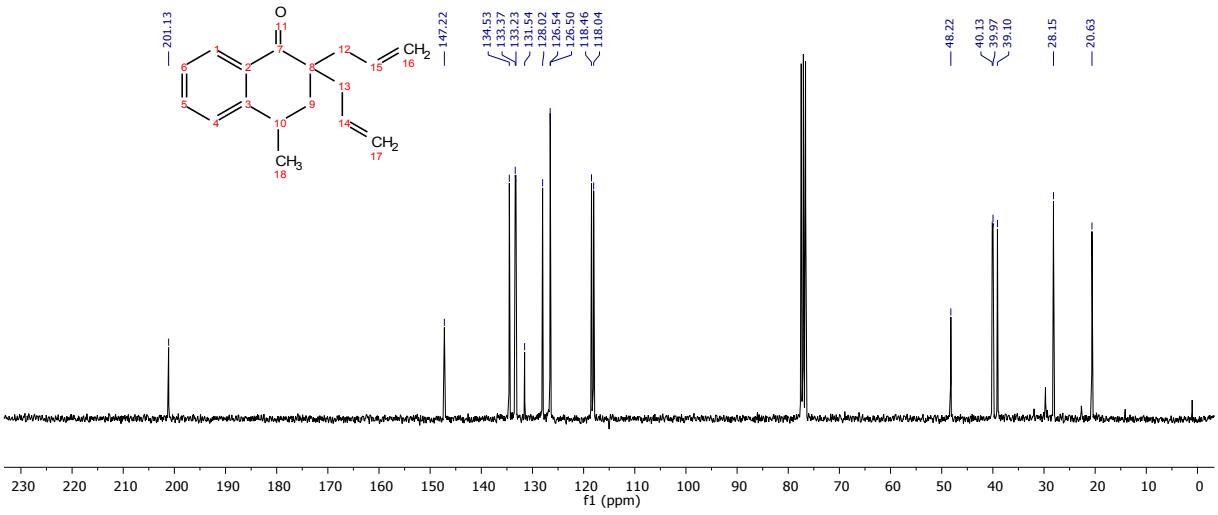

Figure 33.^{13}C NMR spectrum of **6c**

4-methyl-3,4-dihydro-2,2-di-2-propen-1-yl-1-(2H)-naphthalenone (6c) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.13 (C_7), 147.22 (C_2), 134.53 (C_{ar}), 133.37 (C_{ar}), 133.23 (C_3), 131.54 (C_{ar}), 128.02 (C_{ar}), 126.54(C_{14},C_{15}), 126.50 (C_{14},C_{15}), 118.46 (C_{16},C_{17}), 118.04 (C_{16},C_{17}), 48.22 (C_8), 40.13 (C_{12},C_{13}), 39.97 (C_{12},C_{13}), 39.10 (C_9), 28.15 (C_{10}), 20.63 (C_{18}).

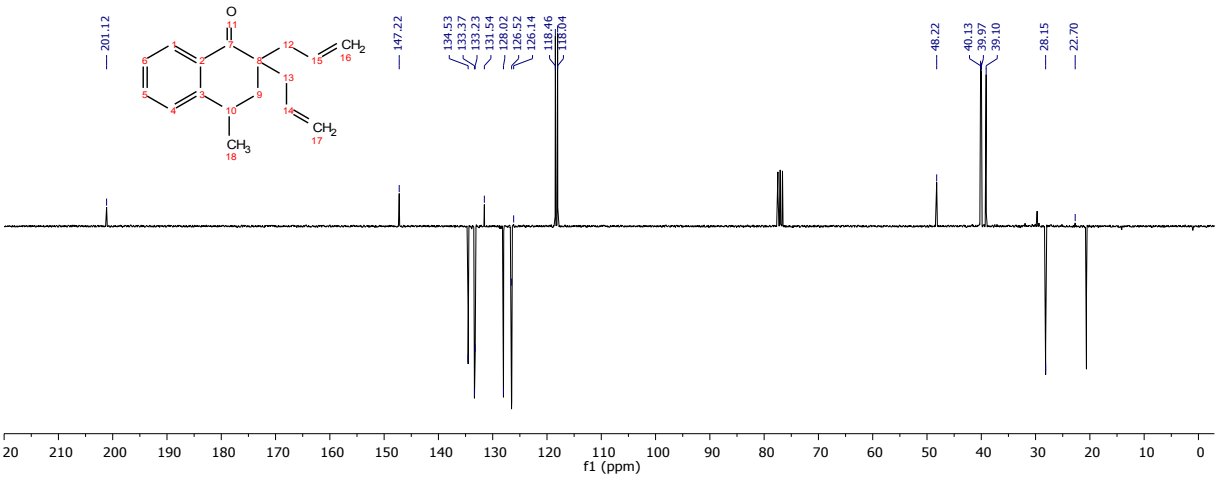

Figure 34. APT NMR spectrum of **6c**

HRMS (ESI) m/z : Calcd for $[M+H]^+$ $C_{17}H_{21}O$ 241.1592; Found 241.1543

2,3-dihydro-2,2-di-2-propen-1-yl-1H-inden-1-one (6d) Rdt : 94 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.7 Hz, 1H, H_1), 7.57 (td, *J* = 7.5, 1.2 Hz, 1H, H_4), 7.48 – 7.31 (m, 2H, H_5+H_6), 5.59 (dddd, *J* = 16.8, 10.0, 8.1, 6.6 Hz, 2H, H_{13}+H_{14}), 5.13 – 4.89 (m, 4H, H_{15}+H_{16}), 3.03 (s, 2H, H_9), 2.45 (ddt, *J* = 13.6, 6.6, 1.2 Hz, 2H, H_{12}, H_{11}), 2.31 (ddt, *J* = 13.7, 8.1, 1.1 Hz, 2H, H_{11}, H_{12}).

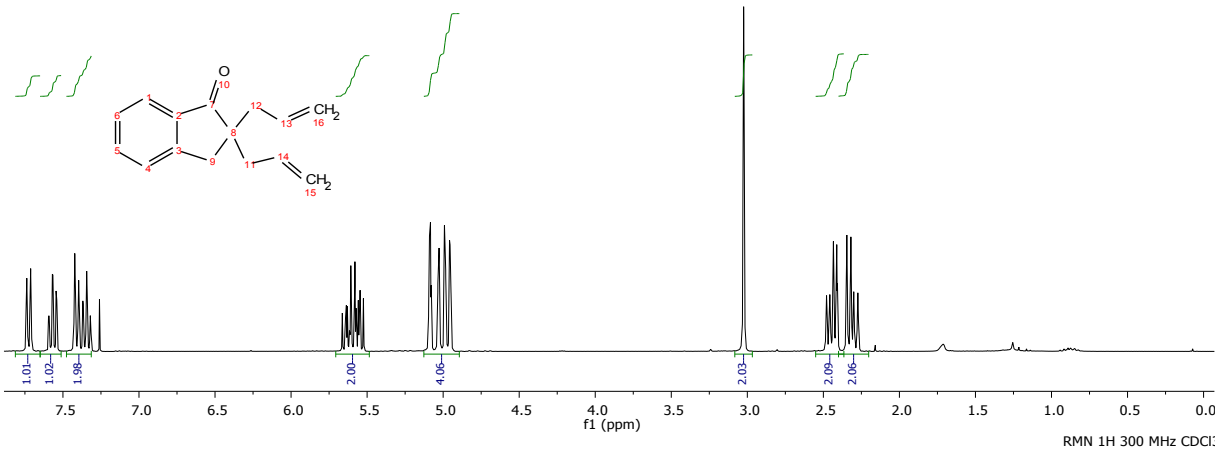

Figure 35. ^{1}H NMR spectrum of **6d**

2,3-dihydro-2,2-di-2-propen-1-yl-1H-inden-1-one (6d) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.01 (C_7), 153.03 (C_2), 136.74 (C_3), 134.93 (C_{ar}), 133.41 (C_{ar}), 127.36 (C_{ar}), 126.06 (C_{ar}), 123.89 (C_{13}+C_{14}), 118.50 (C_{15}+C_{16}), 52.24 (C_8), 41.73 (C_{11}+C_{12}), 36.08 (C_9).

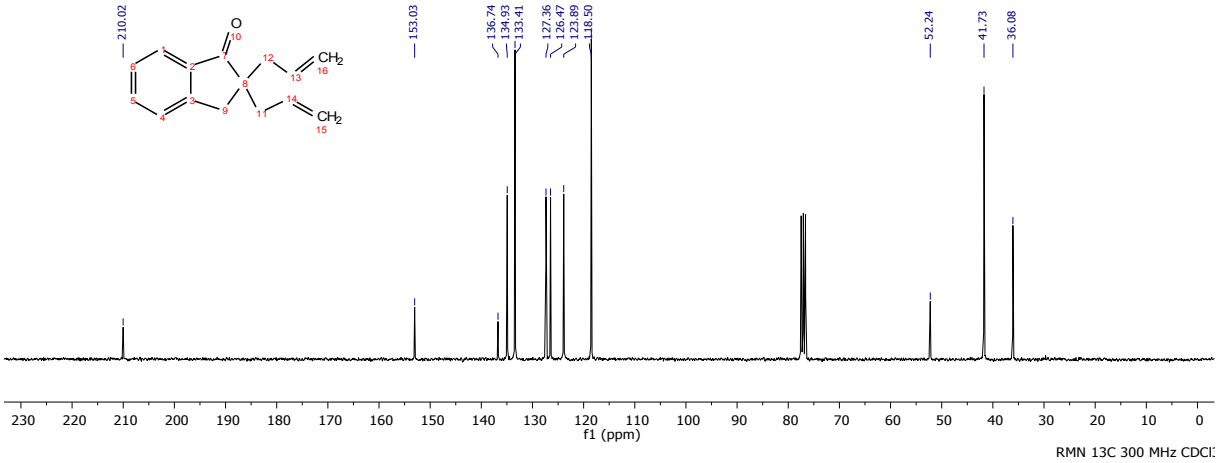

Figure 36 .^{13}C NMR spectrum of **6d**

2,3-dihydro-2,2-di-2-propen-1-yl-1H-inden-1-one (6d) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.01 (C_7), 153.03 (C_2), 136.74 (C_3), 134.93 (C_{ar}), 133.41 (C_{ar}), 127.36 (C_{ar}), 126.06 (C_{ar}), 123.89 (C_{13}+C_{14}), 118.50 (C_{15}+C_{16}), 52.24 (C_8), 41.73 (C_{11}+C_{12}), 36.08 (C_9).

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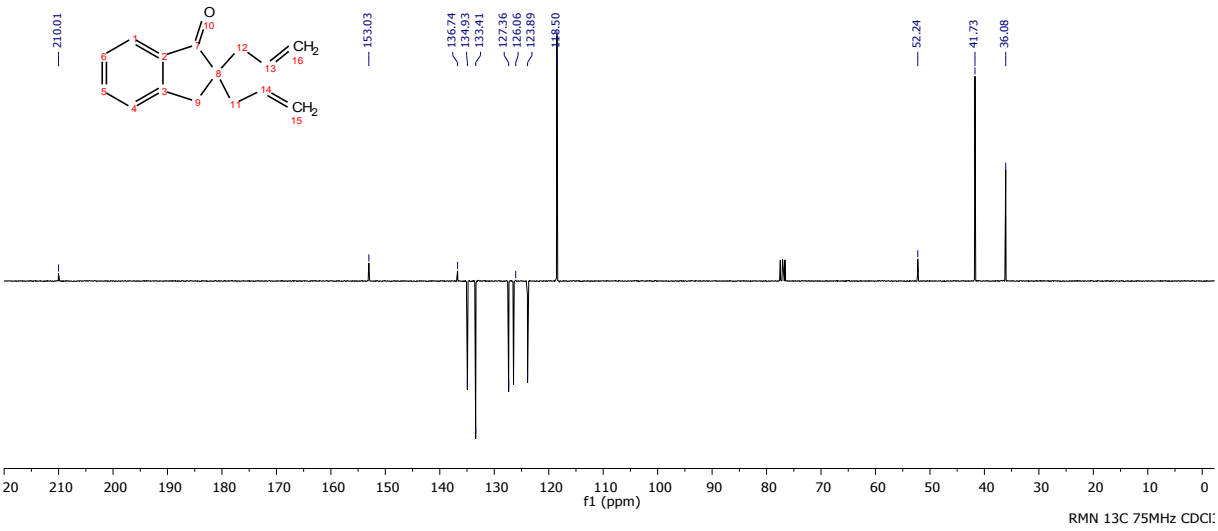

Figure 37. APT NMR spectrum of **6d**

2,3-dihydro-2-methyl-2-(2-propen-1-yl)-1H-inden-1-one (6e) Rdt : 97 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.75 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 1H, H_1), 7.58 (td, *J* = 7.4, 1.3 Hz, 1H, H_4), 7.47 – 7.29 (m, 2H, H_5+H_6), 5.65 (dddd, *J* = 16.9, 10.1, 7.9, 6.7 Hz, 1H, H_{13}), 5.15 – 4.95 (m, 2H, H_{14}), 3.16 (d, *J* = 16.9 Hz, 1H, H_9), 2.83 (d, *J* = 17.2 Hz, 1H, H_9), 2.34 (dddd, *J* = 14.7, 13.6, 7.3, 1.1 Hz, 2H, H_{12}), 1.22 (s, 3H, H_{11}).

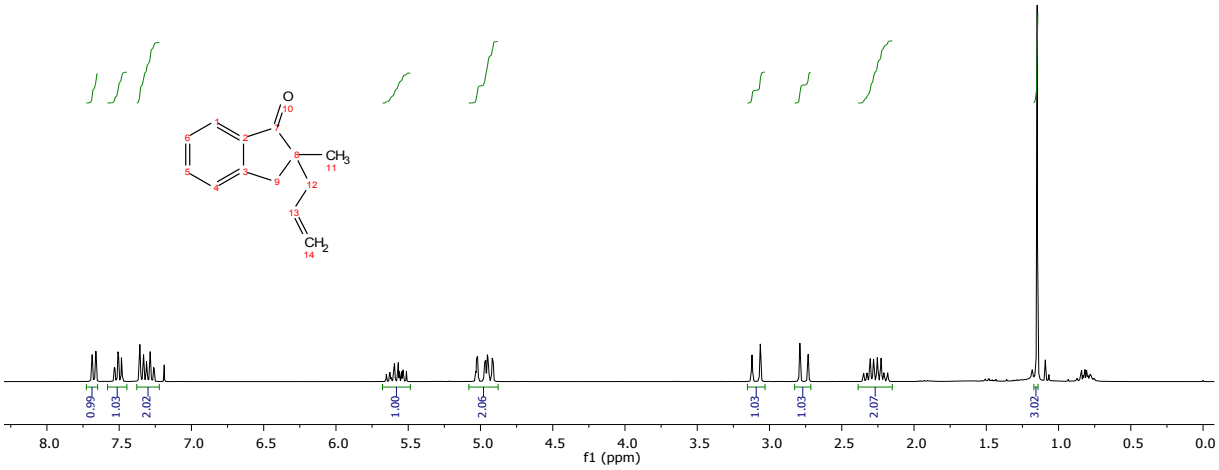

Figure 38. ^{1}H NMR spectrum of **6e**

2,3-dihydro-2-methyl-2-(2-propen-1-yl)-1H-inden-1-one (6e) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.74 (C_7), 152.58 (C_2), 135.88 (C_3), 134.89 (C_{ar}), 133.87 (C_{ar}), 127.41 (C_{ar}), 126.59 (C_{ar}), 124.25 (C_{13}), 118.32 (C_{14}), 48.83 (C_8), 42.53 (C_{12}), 39.44 (C_9), 23.78 (C_{11}).

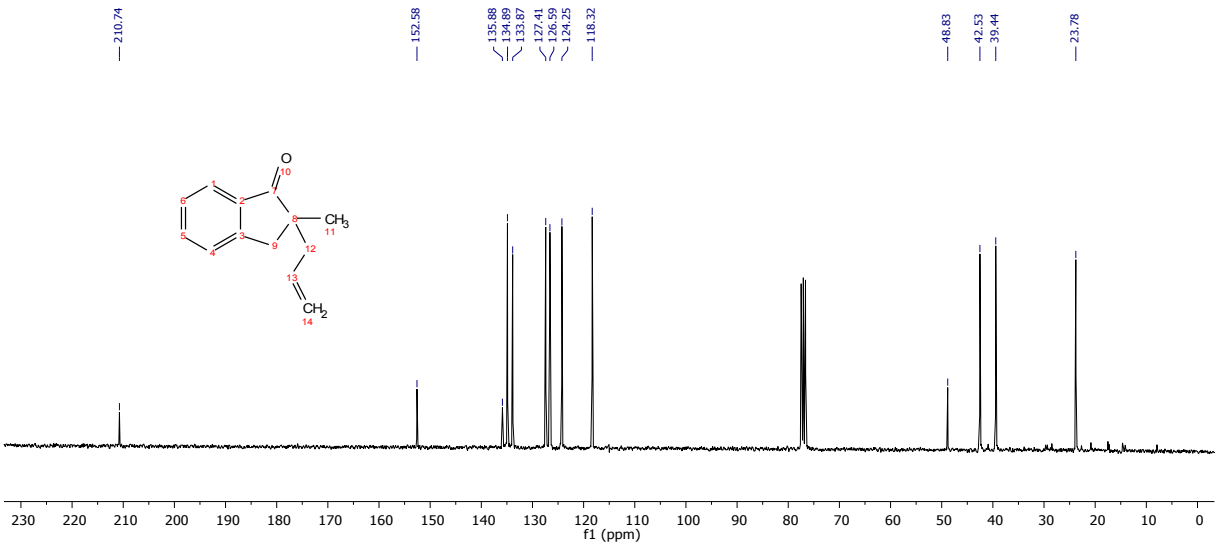

Figure 39. ^{13}C NMR spectrum of **6e**

2,3-dihydro-5,6-dimethoxy-2,2-di-2-propen-1-yl-1H-Inden-1-one (6f) Rdt : 88 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.15 (s, 1H, H_1), 6.83 (d, *J* = 0.9 Hz, 1H, H_4), 5.59 (dddd, *J* = 16.7, 10.0, 8.2, 6.5 Hz, 2H, H_{13}+ H_{15}), 5.11 – 4.94 (m, 4H, H_{14}+H_{16}), 3.95 (s, 3H, H_{18}), 3.90 (s, 3H, H_{22}), 2.93 (d, *J* = 0.9 Hz, 2H, H_9), 2.44 (ddt, *J* = 13.6, 6.4, 1.3 Hz, 2H, H_{11}, H_{12}), 2.29 (ddt, *J* = 13.6, 8.2, 1.0 Hz, 2H, H_{11}, H_{12}).

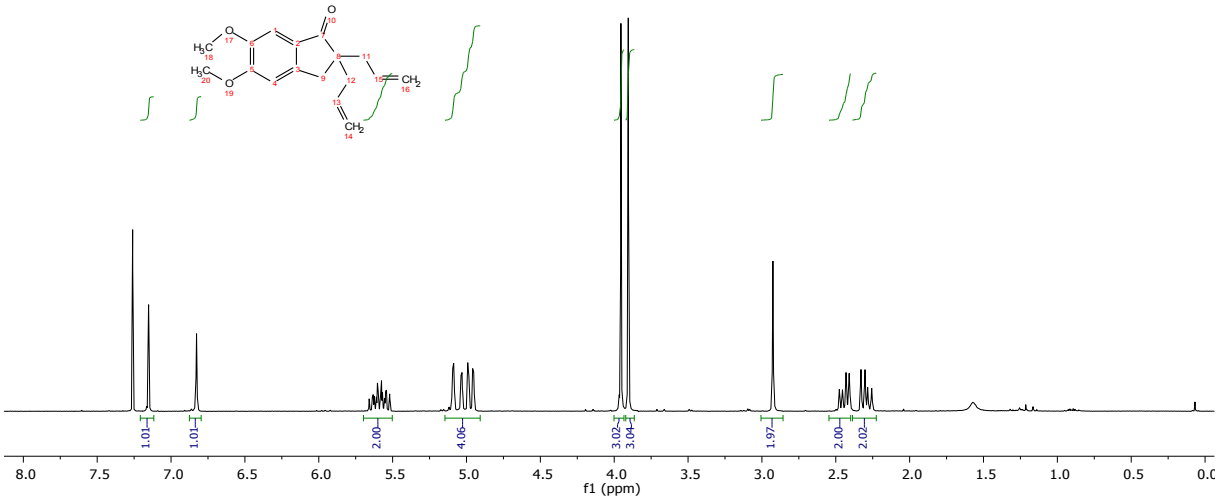

Figure 40. ^{1}H NMR spectrum of **6f**

2,3-dihydro-5,6-dimethoxy-2,2-di-2-propen-1-yl-1H-Inden-1-one (6f) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.53 (C_7), 155.75 (C_2), 149.47 (C_5), 148.25 (C_6), 133.61 (C_{13}+C_{15}), 129.50 (C_3), 118.30 (C_1), 107.27 (C_1), 104.27 (C_4), 56.18 (C_{18}), 56.06 (C_{18}), 52.51 (C_8), 41.91 (C_{11}+C_{12}), 35.69 (C_9).

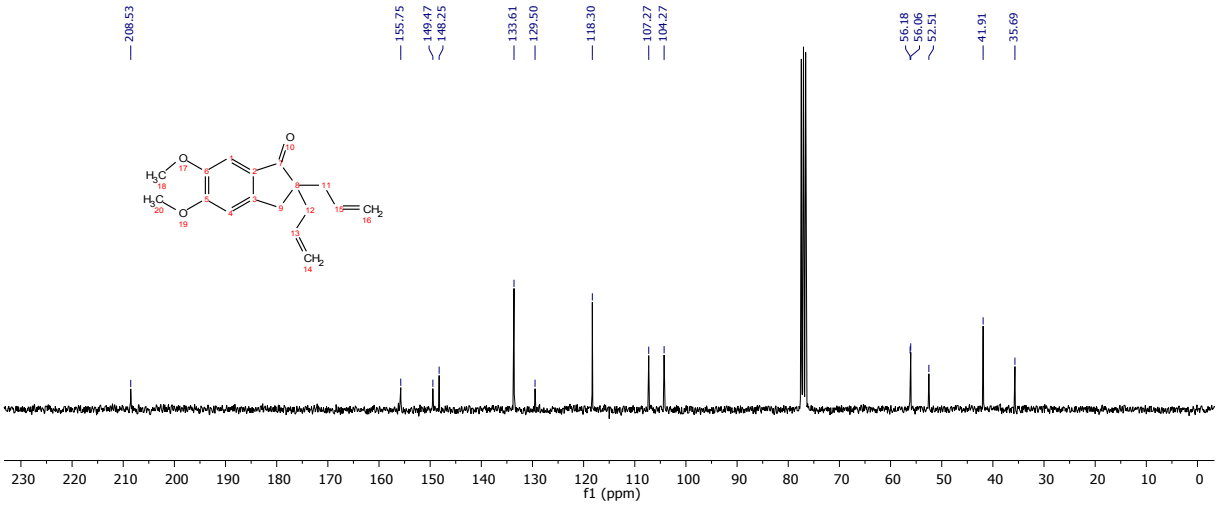

Figure 41.^{13}C NMR spectrum of **6f**

6,6-dimethyl-2,2--Diallylcyclopentanone (6g) Rdt : 87 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.66 (dddd, *J* = 16.9, 10.4, 7.8, 7.1 Hz, 2H, H_{11}+H_{13}), 5.13 – 4.92 (m, 4H, H_{12}+H_{14}), 2.15 (m, 4H, H_9+H_{10}), 1.83 – 1.76 (m, 2H, H_4), 1.76 – 1.68 (m, 2H,H_3), 0.99 (s, 6H, H_7+ H_8).

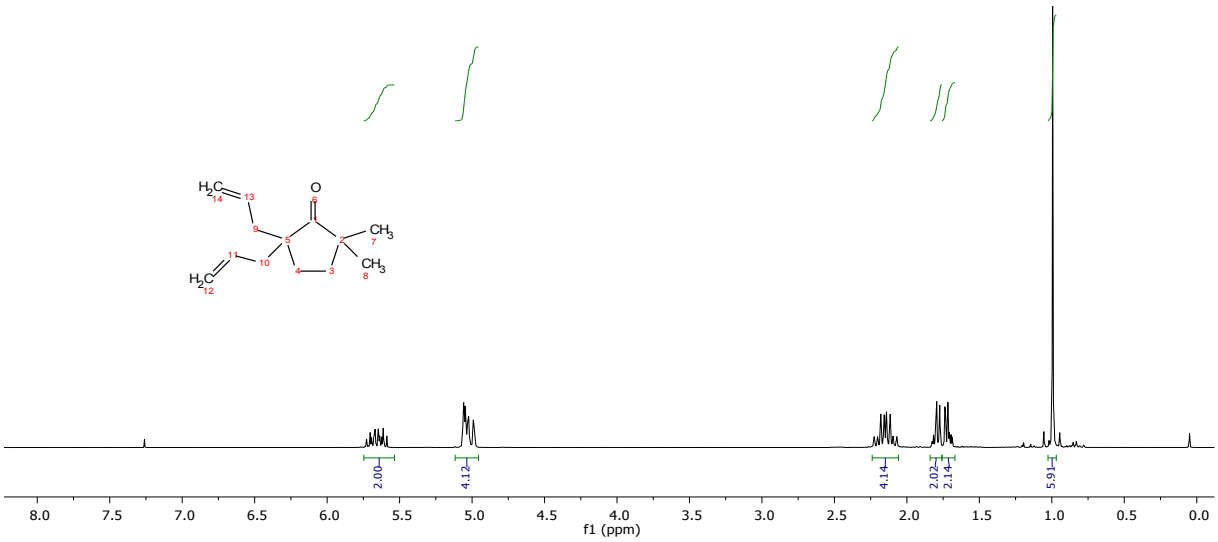

Figure 42. ^{1}H NMR spectrum of **6g**

6,6-dimethyl-2,2--Diallylcyclopentanone (6g) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 225.28 (C_1), 133.92 (C_{11}+C_{13}), 118.25 (C_{12}+C_{14}), 52.56 (C_5), 45.27 (C_2), 40.46 (C_9+C_{10}), 34.84 (C_4), 28.24 (C_3), 24.47 (C_7+C_8).

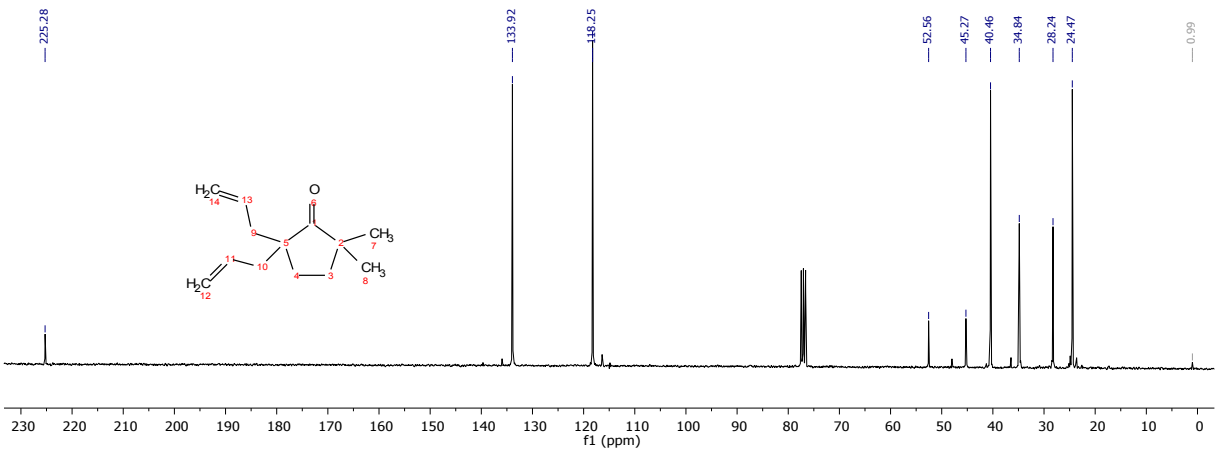

Figure 43. ^{13}C NMR spectrum of **6g**

HRMS (ESI) m/z : Calcd for $[M]^+$ $C_{13}H_{21}O$ 192.1592; Found 192.1552

2,2-Diallylcyclohexanone (6h) Rdt : 66 %, ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.61 (ddt, *J* = 16.1, 11.0, 7.4 Hz, 2H, H_{10}+H_{11}), 5.08 – 4.91 (m, 4H, H_{12}+H_{13}), 2.30 (m, 4H, H_8+H_9), 2.19 (ddt, *J* = 14.2, 7.0, 1.5 Hz, 2H, H_6), 1.80 – 1.60 (m, 6H, H_3+H_4+H_5).

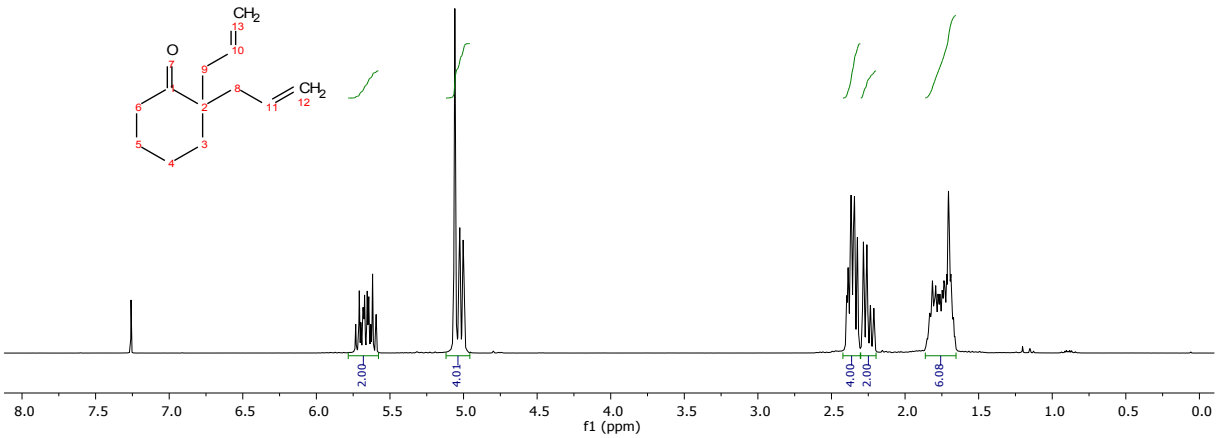

Figure 44. ^{1}H NMR spectrum of **6h**

2,2-Diallylcyclohexanone (6h) : ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.09 (C_1), 133.66 (C_{10}+C_{11}), 118.04 (C_{12}+C_{13}), 51.48 (C_2), 39.32 (C_6), 39.28 (C_8+C_9), 35.97 (C_3), 27.06 (C_5), 20.80 (C_4).

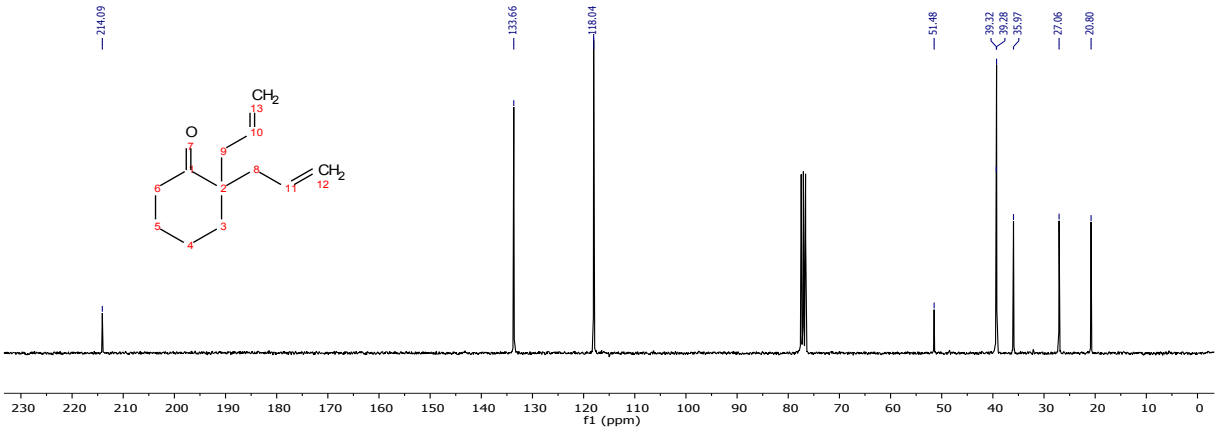

Figure 45. ^{13}C NMR spectrum of **6h**

Spiro[3-cyclopentene-1,2'-[2H]inden]-1'(3'H)-one Rdt : 86 %,: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.7 Hz, 1H, H_1), 7.52 (td, *J* = 7.4, 1.3 Hz, 1H, H_4), 7.44 – 7.27 (m, 1H, H_5+H_6), 5.66 (s, 1H, H_{12}+H_{14}), 3.10 (s, 1H, H_9), 2.92 – 2.73 (m, 1H, H_{11}), 2.34 – 2.20 (m, 1H, H_{13}).

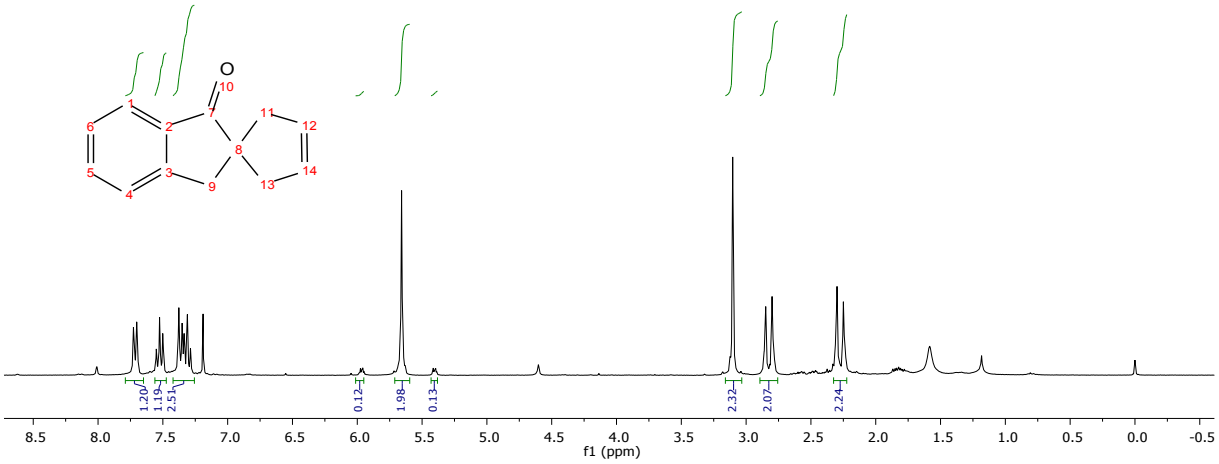

Figure 46. ^{1}H NMR spectrum of **7e**

Spiro[3-cyclopentene-1,2'-[2H]inden]-1'(3'H)-one : ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.46 (C_7), 152.81(C_2), 136.28 (C_3), 134.74 (C_{ar}), 128.74 ($C_{12+}C_{14}$), 127.46 (C_{ar}), 126.45 (C_{ar}), 124.23 (C_{ar}), 55.48 (C_8), 45.49 (C_{10}+C_{11}+C_9).

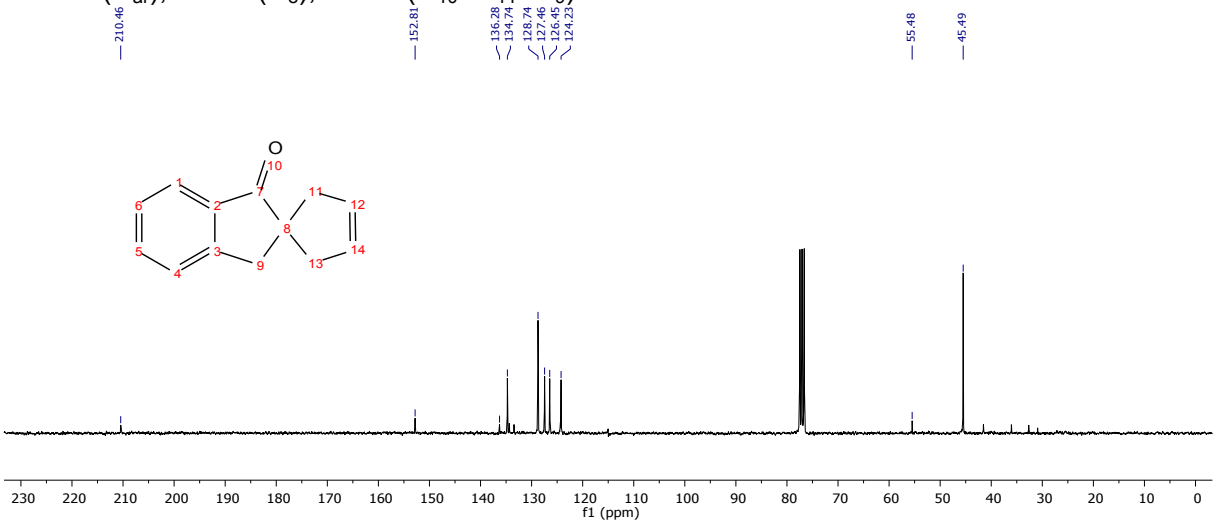

Figure 47. ^{13}C NMR spectrum of **7e**

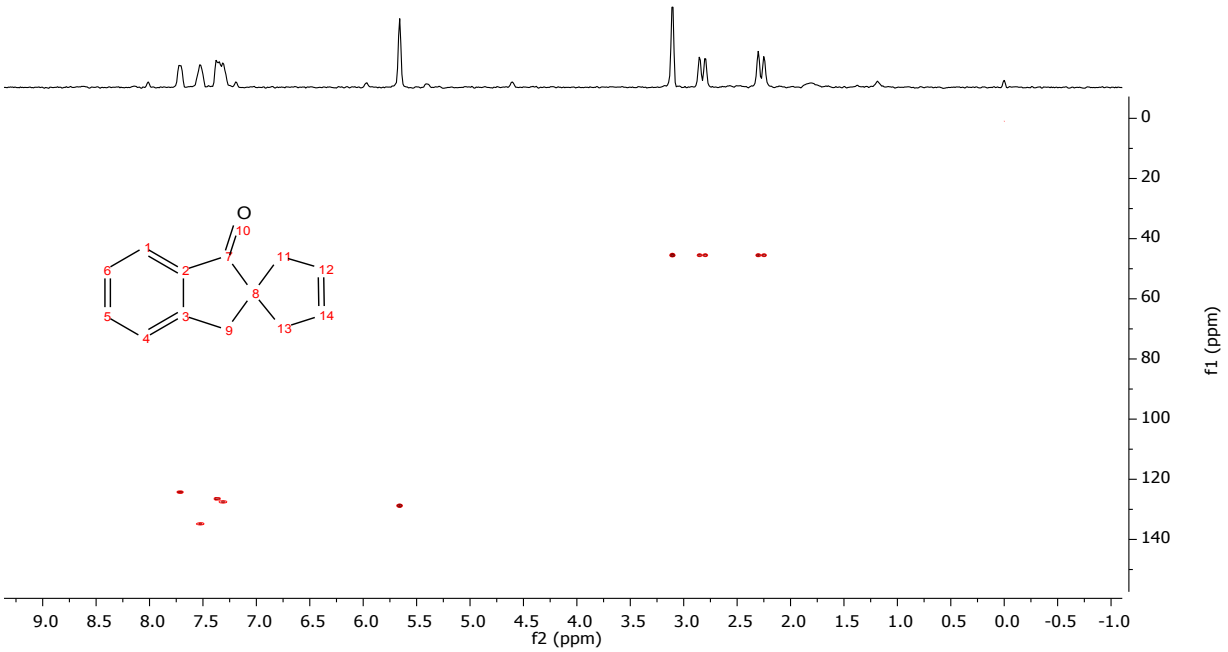

Figure 48. 2D NMR (HSQC) spectrum of **7e**