Supporting Information

for

N-Heterocyclic Carbene Catalyzed (4+2) Cycloaddition/Decarboxylation of Silyl Dienol Ethers with α,β-Unsaturated Acid Fluorides.

Sarah J. Ryan, Lisa Candish and David W. Lupton*

School of Chemistry, Monash University, Clayton 3800, Victoria, AUSTRALIA

SI-1. Experimental Procedures

Index

I. General Procedures

Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300 MHz for proton and 75 MHz for carbon nuclei. 2D correlation spectra were recorded on a Bruker DRX400 spectrometer. Infrared spectra (ν_{max}) were recorded on a Perkin-Elmer RXI FTIR Spectrometer. High resolution mass spectra (HRMS) (ESI) were recorded on a Bruker BioApex 47e FTMS fitted with an Analytical electrospray source using NaI for accurate mass calibration. High Resolution (EI) mass spectra were recorded on an Agilent 7890A GC, Waters GCT Premier TOF-MS with an ion source temperature of 200ºC and electron impact energy (70eV). Flash column chromatography was performed on silica gel (Davisil LC60A, 40-63 μm silica media) using compressed air or nitrogen. Thin layer chromatography (TLC) was performed using aluminum-backed plates coated with 0.2 mm silica (Merck, DC-Platten, Kieselgel; 60 F_{254} plates). Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable stain followed by heating. Starting materials and reagents were purchased from Sigma-Aldrich and were used as supplied or, in the case of some liquids, distilled. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl, dichloromethane was distilled from calcium hydride and diisopropylamine (DIPA) was distilled from sodium. Precursors to NHCs **A1** and **A2** were prepared using the procedure of Arduengo,[1] to **B** using the procedure of Grubbs.[2] The triazolium precursor to NHC **C**

[1] Arduengo, A. J; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523

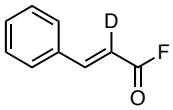
[2] Kuhn, K. M.; Grubbs, R. H. *Org. Lett.* **2008**, *10*, 2075

was prepared using the procedure of Smith.[3] **D1** was prepared according to Kotschy,[4] and **D2** prepared using the procedure of Lyapkalo.[5] (*E*)-((2,2-Dimethyl-6-methylenecyclohexylidene)methoxy)trimethylsilane was prepared according to the procedure of Fehr.[6]

II. Synthesis of acid fluorides

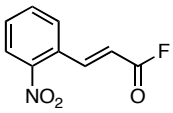
Following the procedure of Chen,[7] a mixture of the appropriate carboxylic acid (10 mmol) and pyridine (2 mL) in CH_2Cl_2 (30 mL) was added to a stirred solution of 70% HF in pyridine (0.3 mL, 11 mmol) and DCC (2.06 g, 10 mmol) in CH_2Cl_2 (6 mL). The reaction mixture was stirred for 2 hours at room temperature, filtered and the volatiles removed *in vacuo*. The crude residue was purified *via* distillation under reduced pressure to provide acid fluorides in 32-75% yield. (*E*)-Cinnamoyl fluoride (**4a**)[8] and (*E*)-3-(furan-2-yl)acryloyl fluoride (**4l**)[7] have been reported previously.

α-D-(*E*)-Cinnamoyl fluoride (αD-4a)



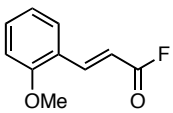
IR ν_{max} 1805, 1616, 1575, 1450 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.1 Hz, 1H), 7.57-7.54 (m, 2H), 7.48-7.40 (m, 3H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 156.2 (d, *J* = 336.2 Hz), 150.8 (d, 6.1 Hz), 132.6, 131.3, 128.7, 128.2, 111.6 (dt, *J* = 67.1, 19.8 Hz)

(*E*)-3-(2-Nitoxyphenyl)acryloyl fluoride (4j)



IR ν_{max} 2927, 1806, 1627, 1525, 1355, 1261, 1197 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 15.9 Hz, 1H), 8.14-8.11 (m, 1H), 7.44-7.12 (m, 1H), 7.68-7.65 (m, 2H), 6.31 (dd, *J* = 15.9, 8.7 Hz, 1H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 160.3, 155.8 (d, *J* = 336 Hz), 147.0 (d, *J* = 6.5 Hz), 134.0, 131.6, 129.3, 129.2, 125.2, 117.1 (d, *J* = 66 Hz) HRMS (EI) *m/z* Found $(M^{\bullet})^+$, 195.0324, $C_9H_6FNO_3$ requires $(M^{\bullet})^+$, 195.0332

(*E*)-3-(2-Methoxyphenyl)acryloyl fluoride (4k)



IR ν_{max} 2939, 1794, 1624, 1599, 1489, 1467, 1326, 1255, 1111 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 15.9 Hz, 1H), 7.52-7.40 (m, 2H), 7.02-6.94 (m, 2H), 6.48 (dd, *J* = 15.9, 8.7 Hz, 1H), 3.91 (s, 3H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 159.1, 157.9 (d, *J* = 336 Hz), 147.1 (d, *J* = 6.5 Hz), 133.3, 130.0, 122.2, 121.0, 112.4 (d, *J* = 66 Hz), 111.5, 55.7 HRMS (EI) *m/z* Found $M^{\bullet+}$, 180.0526, $C_{10}H_9FO_2$ requires $M^{\bullet+}$, 180.0587

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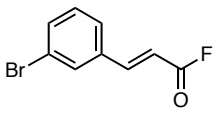
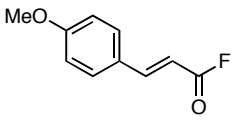
[3] Thomson, J. E.; Rix, K.; Smith, A. D. *Org. Lett.* **2006**, *8*, 3785
[4] Bostai, B.; Novák, Z.; Bényei, A.; Kotschy, A. *Org. Lett.* **2007**, *9*, 3437
[5] Kunetskiy, R. A.; Císarová, I.; Saman, D.; Lyapkalo, I. M. *Chem, Eur. J.* **2009**, *15*, 9477
[6] Fehr, C.; Jose, J. *J. Org. Chem.*, **1988**, *53*, 1828
[7] Chen, C.; Chien, C-T.; Su, C-H. *J. Fluor. Chem.* **2002**, *115*, 75
[8] Bappert, E.; Müller, P.; Fu, G. C. *Chem. Commun.* **2006**, *24*, 2604

(*E*)-3-(3-Bromophenyl)acryloyl fluoride (4l)



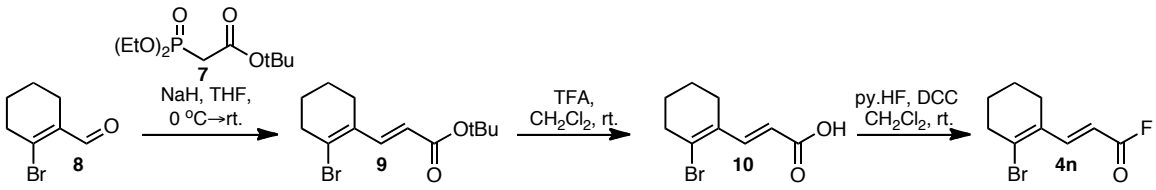
IR ν_{max} 2930, 1799, 1634, 1562, 1218, 1191 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 16.0 Hz, 1H), 7.69 (s, 1H), 7.59 (d, *J* = 7.9, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 6.36 (dd, *J* = 16.0, 6.9 Hz, 1H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 159.1, 152.2 (d, *J* = 364 Hz), 149.8 (d, *J* = 6.0 Hz), 134.9, 131.6, 131.0, 127.6, 123.6, 114.0 (d, *J* = 68 Hz) HRMS (EI) Found $M^{\bullet+}$, 227.9599, C_9H_6BrFO requires $M^{\bullet+}$, 227.9586

(*E*)-3-(4-Methoxyphenyl)acryloyl fluoride (4m)[9]



IR ν_{max} 2940, 1798, 1602, 1426, 1257, 1094 **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 15.9, 1H), 7.50 (m, 2H), 6.93 (m, 2H), 6.19 (dd, *J* = 15.9, 7.2 Hz, 1H), 3.85 (s, 3H) **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 163.0, 157.9 (d, *J* = 334 Hz), 151.4 (d, *J* = 6.3 Hz), 131.0, 126.2, 114.9, 109.4 (d, *J* = 66.8), 55.78

(*E*)-3-(2-Bromocyclohex-1-en-1-yl)acryloyl fluoride (4n)



t-Butyl phosphonate **7**[10] (2.52 g, 10 mmol) was slowly added to a stirred solution of NaH (400 mg of a 60% dispersion in mineral oil, 10 mmol) in THF (20 mL) at 0 °C. The mixture was maintained at this temperature for 15 minutes after which time bromo aldehyde **8**[11] (1.88 g, 10 mmol) was added and the mixture allowed to warm to room temperature. The reaction was quenched with NH_4Cl (5 mL of a saturated aqueous solution), extracted with CH_2Cl_2 (3 x 20 mL), dryed ($MgSO_4$), filtered, concentrated, and the crude residue purified *via* flash column chromatography (1:9, v/v EtOAc : hexanes) to provide *t*-butyl ester **9** in 87% yield IR ν_{max} 2933, 1708, 1621, 1312, 1292 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 15.9 Hz, 1H), 5.82 (d, *J* = 15.9 Hz, 1H), 2.66-2.65 (m, 2H), 2.25-2.22 (m, 2H), 1.73-1.68 (m, 4H), 1.48 (s, 9H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 166.4, 143.3, 132.0, 131.1, 120.6, 80.3, 38.0, 28.1, 27.1, 24.3, 21.8 HRMS (EI) *m/z* Found $M^{\bullet+}$, 286.0567, $C_{13}H_{19}BrO_2$ requires $M^{\bullet+}$, 286.0568

t-Butyl ester **9** (2.30 g, 8 mmol) was dissolved in CH_2Cl_2 (4 mL) and TFA (8 mL) added. The mixture was stirred for 1 hour at room temperature, and the volatiles removed *in vacuo*. The crude solid was converted to acid fluoride **4n** without purification using the general procedure IR ν_{max} 2939, 1799, 1614, 1201, 1116 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 15.9 Hz, 1H), 5.82 (dd, *J* = 15.9,

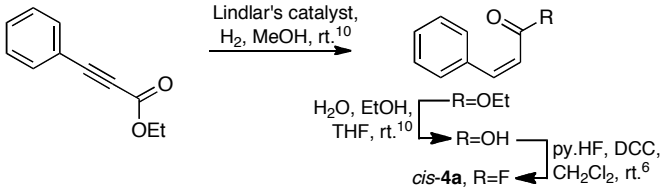
[9] Lin, F. F. S.; Servis, K. L. *J. Am. Chem. Soc.* **1972***, 94*, 5794

[10] Shelkov, R.; Nahmany, M.; Melman, A. *Org. Biomol. Chem*. **2004**, *2*, 397

[11] Harrowven, D. C.; Pascoe, D. D. *Angew. Chem. Int. Ed.* **2007**, *46*, 425

8.7 Hz, 1H), 2.73-2.71 (m, 2H), 2.29-2.25 (m, 2H), 1.77-1.73 (m, 4H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 157.2 (d, *J* = 337 Hz), 150.7 (d, *J* = 6.0 Hz), 137.1, 131.0, 112.5 (d, *J* = 66 Hz), 38.4, 26.9, 24.0, 21.5 HRMS (EI) *m/z* Found $M^{\bullet+}$, 231.9926, $C_9H_{10}BrFO$ requires $M^{\bullet+}$, 231.9899

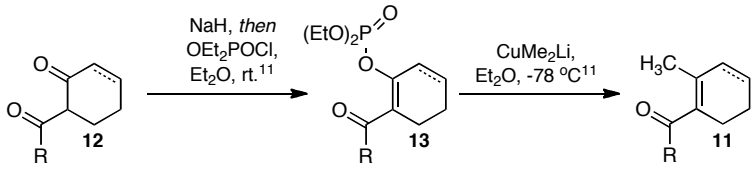
(*Z*)-Cinnamoyl fluoride (***cis*-4a**)



(*Z*)-Cinnamic acid was prepared from ethyl phenylpropiolate following the procedure of Nagasawa.[12] The acid was subjected to a modified version of the general method for acid fluoride synthesis. It was found that removal of pyridine was necessary to avoid isomerization to the (*E*) isomer. IR ν_{max} 1802, 1630, 1204, 1107 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H), 7.49-7.42 (m, 3H), 7.30 (dd, *J* = 12.9, 6.3 Hz, 1H), 5.92 (d, *J* = 12.9 Hz, 1H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 157.4 (d, *J* = 364 Hz), 151.3 (d, *J* = 13 Hz), 130.5, 130.2, 128.7, 128.3, 112.8 (d, *J* = 74 Hz)

III. Synthesis of β-methyl enones

Procedure A: Preparation of β-alkyl enones **11** *from β-diketones* **12**

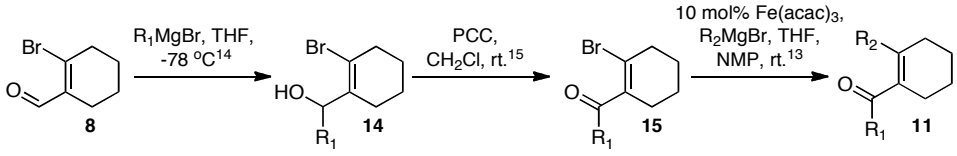


Scheme 1: General strategy for β-methyl enones from β-diketones[13]

β-Methyl ketones **11** were prepared according to the procedure of Weiler,[11] from the corresponding phosphonate intermediate **13**. Thus, MeLi (4.0 eq. of a 1.6M solution in Et_2O) was added to a stirred solution of CuI (2.0 eq.) in dry Et_2O at 0 °C. The resulting clear solution was cooled to -78 °C and phosphonate **13** (1.0 eq.), itself prepared from the corresponding β-diketone **12**,[14] slowly added. The mixture was maintained at this temperature for 1 hour after which time it was quenched with NH_4Cl (saturated aqueous solution), extracted with Et_2O, washed with dilute NH_3 in brine, then brine. The organics were dried ($MgSO_4$), filtered, concentrated, and the crude residue purified *via* flash column chromatography.

[12] Ueda, S.; Okada, T.; Nagasawa, H. *Chem. Commun.* **2010**, *46*, 2462
[13] Sum, F-W.; Weiler, L. *Can. J. Chem.* **1979**, *57*, 1431
[14] Fos, E.; Borràs, L.; Gasull, M.; Mauleón, D.; Carganico, G. *J. Heteroyclic Chem.* **1992**, *29*, 203

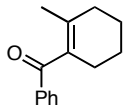
Procedure B



Scheme 2: General strategy for β-alkyl enones from β-halo enals

β-Alkyl ketones **11** were prepared according to Cahiez,[15] through iron catalyzed coupling with the corresponding β-bromo ketones **15**. Hence, R_2MgBr (1.5 eq.) was slowly added to a stirred solution of $Fe(acac)_3$ (0.01 eq.), NMP (9.0 eq.) and β-bromoketone **15** (1.0 eq.), itself prepared from the corresponding aldehyde **8** *via* Grignard addition and oxidation,[16,17] in THF at room temperature. The mixture was stirred at room temperature for 1 hour then quenched with HCl (1M aqueous solution) and the phases separated. The aqueous layer was extracted with Et_2O and washed with $NaHCO_3$ (saturated aqueous solution). The combined organic layers were dryed ($MgSO_4$), filtered, concentrated, and the crude residue purified *via* flash column chromatography

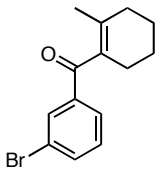
(2-Methylenecyclohex-1-en-1-yl)(phenyl)methanone (11a)[18]



The title compound was prepared using both procedure A and B.

R_f 0.3 (1:9, v/v EtOAc : hexanes) IRν_{max} 2931, 1664, 1596, 1580, 1448, 1280, 1249 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2H), 7.52-7.48 (m, 1H), 7.45-7.39 (m, 2H), 2.20-2.19 (m, 2H), 2.08-2.04 (m, 2H), 1.71-1.66 (m, 4H), 1.51 (t, J = 0.6 Hz, 3H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 201.5, 137.0, 134.7, 133.0, 132.4, 129.3, 128.7, 31.2, 27.5, 22.6, 22.3, 21.2

(3-Bromoyphenyl)(2-methylcyclohex-1-en-1-yl)methanone (11b)

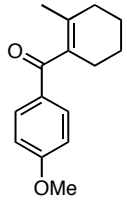


The title compound was prepared following procedure A.

R_f 0.3 (1:9, v/v EtOAc : hexanes) IR ν_{max} 2931, 1666, 1565, 1419, 1279, 1240 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.95 (t, J = 1.5 Hz, 1H), 7.73 (dt, J = 7.5, 1.5 Hz, 1H), 7.61 (dt, J = 7.5, 1.5 Hz, 1H), 7.28 (tt, J = 7.5, 1.5 Hz, 1H), 2.19-2.12 (m, 2H), 2.09-2.01 (m, 2H), 1.68-1.64 (m, 4H), 1.49 (brs, 3H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 199.6, 138.8, 135.9, 135.6, 131.8, 131.6, 130.1, 127.7, 122.8, 31.1, 27.2, 22.3, 22.0, 21.2 HRMS (ESI) *m/z* Found $(M+H)^+$, 279.0382, $C_{14}H_{15}BrO$ requires $(M+H)^+$, 279.0385

[15] Cahiez, G.; Avedissian, H. *Synthesis*, **1998**, *8*, 1199
[16] Murai, M.; Yoshida, S.; Miki, K.; Ohe, K. *Chem. Commun.* **2010**, *46*, 3366
[17] Tang, J-M.; Bhunia, S.; Sohel, S. M. A.; Lin, M-Y.; Liao, H-Y.; Datta, S.; Das, A.; Liu, R-S. *J. Am. Chem. Soc.* **2007**, *129*, 15677
[18] Dufort, N.; Jodoin, B.; Lafontaine, J. *Can. J. Chem.* **1971**, *49*, 1785

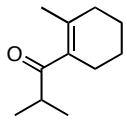
(4-Methoxyphenyl)(2-methylcyclohex-1-en-1-yl)methanone (11c)



The title compound was prepared following procedure B.

R_f 0.3 (1:9, v/v EtOAc : hexanes) IR ν_{max} 2931, 1651, 1599, 1255, 1168 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.19-2.17 (m, 2H), 2.05 (brs, 2H), 1.70-1.66 (m, 4H), 1.50-1.48 (m, 3H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 200.4, 163.6, 133.4, 132.4, 131.7, 129.7, 113.9, 55.5, 31.0, 27.5, 22.7, 22.3, 21.1 HRMS (ESI) *m/z* Found $(M+H)^+$, 231.1379, $C_{15}H_{18}O_2$ requires $(M+H)^+$, 231.1385

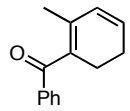
2-Methyl-1-(2-methylenecyclohex-1-en-1-yl)propan-1-one (11d)[19]



The title compound was prepared following procedure B.

R_f 0.3 (1:9, v/v EtOAc : hexanes) IR ν_{max} 2932, 1686, 1449, 1381, 1216, 1152 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.81 (p, *J* = 6.9 Hz, 1H), 2.12-2.11 (m, 2H), 1.97-1.95 (m, 2H), 1.64-1.62 (m, 3H), 1.56-1.52 (m, 4H), 1.00 (d, *J* = 6.6 Hz, 6H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 212.2, 137.0, 133.3, 38.3, 32.0, 26.8, 22.33, 22.30, 21.1, 18.1

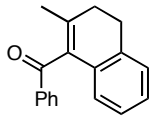
(2-Methylenecyclohexa-1,3-dien-1-yl)(phenyl)methanone (11e)



The title compound was prepared following procedure A.

R_f 0.3 (1:9, v/v EtOAc : hexanes) IR ν_{max} 2929, 1663, 1595, 1579, 1448, 1245 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.85-7.80 (m, 2H), 7.53-7.49 (m, 1H), 7.46-7.40 (m, 2H), 6.10-6.04 (m, 1H), 5.94-5.90 (m, 1H), 2.42-2.35 (m, 2H), 2.26-2.18 (m, 2H), 1.70 (d, *J* = 1.8 Hz, 3H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 200.0, 138.4, 135.7, 132.8, 130.7, 130.3, 129.7, 129.2, 128.7, 25.7, 23.1, 20.0 HRMS (ESI) *m/z* Found $(M-H)^-$, 197.0957, $C_{14}H_{14}O$ requires $(M-H)^-$, 197.0972

(2-Methyl-3,4-dihydronaphthalen-1-yl)(phenyl)methanone (11f)

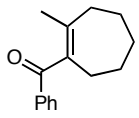


The title compound was prepared following procedure B.

R_f 0.3 (1:9, v/v EtOAc : hexanes) IR ν_{max} 3062, 2930, 2833, 1659, 1448, 1259 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.06-8.02 (m, 2H), 7.58-7.52 (m, 1H), 7.46-7.41 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.12 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.06 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.85 (s, 3H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 199.3, 136.9, 136.6, 133.7, 133.3, 133.1, 132.7, 129.3, 128.5, 127.4, 126.5, 126.3, 124.0, 29.5, 27.7, 20.8 HRMS (ESI) *m/z* Found $(M+H)^+$, 249.1270, $C_{18}H_{16}O$ requires $(M+H)^+$, 249.1279

[19] Ha, H-J.; Park, K-P. *Bull. Kor. Chem. Soc.* **1988**, *9*, 411

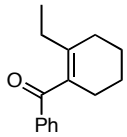
(2-Methylcyclohept-1-en-1-yl)(phenyl)methanone (11g)



The title compound was prepared following procedure B.

R_f 0.3 (1:9, v/v EtOAc : hexanes) IR ν_{max} 2964, 2877, 1713, 1492, 1448, 1183 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.89-7.86 (m, 2H), 7.53-7.41 (m, 3H), 2.36-2.28 (m, 3H), 1.83-1.77 (m, 3H), 1.69-1.56 (m, 4H), 1.63 (s, 3H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 201.4, 142.8, 137.3, 137.1, 132.7, 129.3, 128.5, 36.3, 32.2, 31.2, 26.9, 25.6, 23.4 HRMS (ESI) *m/z* Found $(M+H)^+$, 215.1424, $C_{15}H_{18}O$ requires $(M+H)^+$, 215.1430

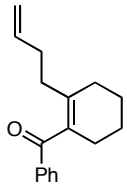
(2-Ethylcyclohex-1-en-1-yl)(phenyl)methanone (11h)[20]



The title compound was prepared following procedure B.

R_f 0.3 (1:9, v/v EtOAc : hexanes) IR ν_{max} 2933, 1664, 1596, 1579, 1148, 1278, 1246 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.92-7.88 (m, 2H), 7.56-7.50 (m, 1H), 7.47-7.41 (m, 2H), 2.20-2.18 (m, 2H), 2.14-2.09 (m, 2H), 1.90 (q, *J* = 7.5 Hz, 2H), 1.74-1.69 (m, 4H), 0.87 (t, *J* = 7.5 Hz, 3H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 201.6, 139.4, 136.9, 133.1, 132.0, 129.4, 128.6, 28.1, 27.8, 27.6, 22.6, 22.3, 12.7

(2-Ethylcyclohex-1-en-1-yl)(phenyl)methanone (11i)



The title compound was prepared following procedure B.

R_f 0.3 (1:9, v/v EtOAc : hexanes) IR ν_{max} 2931, 1664, 1596, 1580, 1148, 1279, 1247 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.90-7.87 (m, 2H), 7.56-7.50 (m, 1H), 7.46-7.41 (m, 2H), 5.67-5.54 (m, 1H), 4.90-4.61 (m, 2H), 2.20-1.94 (m, 8H), 1.73-1.67 (m, 4H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 201.4, 138.1, 137.4, 136.8, 133.2, 133.1, 129.4, 128.6, 114.7, 34.4, 32.3, 28.4, 27.7, 22.6, 22.2 HRMS (ESI) *m/z* Found $(M+H)^+$, 241.1593, $C_{17}H_{20}O$ requires $(M+H)^+$, 241.1592

IV. Synthesis of TMS dienol ethers

Procedure A

n-BuLi (1.6 M in hexane, 1.1 equivalent) was added to a stirred solution of DIPA (1.1 equivalents) in THF at -78 °C. The mixture was stirred at this temperature for 20 minutes after which time the appropriate ketone (1.0 equivalent) was added. Stirring was continued for an additional 15 minutes then TMSCl (1.1 equivalent) added and the mixture allowed to warm slowly to room temperature. The volatiles were removed *in vacuo* and the crude residue purified *via* distillation under reduced pressure.

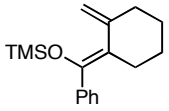
Procedure B:

n-BuLi (1.6M solution in hexane, 1.1 equivalents) was added to a stirred solution of DIPA (1.1 equivalents) in THF at 0 °C. The mixture was stirred for 10 minutes after which time ketone (1.0

[20] Jin, T.; Yamamota, Y. *Org. Lett.* **2007**, *9*, 5259

equivalents) was added. Following a further 30 minutes of continued stirring TMSCl (1.1 equivalents) was added and the solution allowed to slowly warm to room temperature. The volatiles were removed *in vacuo* and the crude residue purified *via* distillation under reduced pressure.

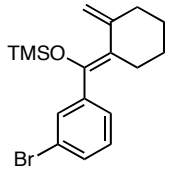
(*Z*)-Trimethyl((2-methylenecyclohexylidene)(phenyl)methoxy)silane (5a)



Following procedure A the title compound was prepared in 76% yield.

IR ν_{max} 2930, 1635, 1444, 1273, 1251, 1139, 1105 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33-7.23 (m, 5H), 5.09 (s, 2H), 2.29 (t, *J* = 5.7 Hz, 2H), 2.15 (t, *J* = 5.7 Hz, 2H), 1.69-1.62 (m, 2H), 1.58-1.52 (m, 2H), -0.03 (s, 9H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 145.2, 143.3, 139.1, 129.5, 127.9, 127.6, 120.6, 111.8, 37.1, 31.1, 27.9, 27.3, 0.7 HRMS (ESI) *m/z* Found $(M+H)^+$, 273.1669, $C_{17}H_{24}OSi$ requires $(M+H)^+$, 273.1675

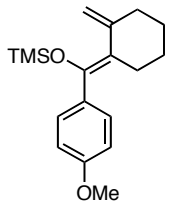
(*Z*)-((3-Bromophenyl)(2-methylenecyclohexylidene)methoxy)trimethylsilane (5b)



Following procedure A the title compound was prepared in 52% yield.

IR ν_{max} 2929, 1636, 1590, 1560, 1470, 1251, 1140 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.47 (t, *J* = 1.5 Hz, 1H), 7.40 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.27-7.17 (m, 2H), 5.08-5.05 (m, 2H), 2.27 (t, *J* = 6.3 Hz, 2H), 2.13 (t, *J* = 6.3 Hz, 2H), 1.67-1.51 (m, 4H), -0.02 (s, 9H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.7, 141.5, 141.0, 132.2, 130.5, 129.3, 127.8, 121.8, 121.5, 112.0, 36.9, 30.9, 27.6, 27.1, 0.51 HRMS (ESI) *m/z* Found $(M+H)^+$, 351.0773, $C_{17}H_{23}BrOSi$ requires $(M+H)^+$, 351.0780

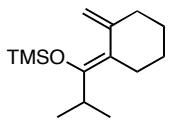
(*Z*)-((4-Methoxyphenyl)(2-methylenecyclohexylidene)methoxy)trimethylsilane (5c)



Following procedure A the title compound was prepared in 46% yield.

IR ν_{max} 2931, 1599, 1255, 1445, 1250, 1168 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.07 (s, 2H), 3.82 (s, 3H), 2.28 (t, *J* = 6.3 Hz, 2H), 2.15 (t, *J* = 6.3 Hz, 2H), 1.65-1.62 (m, 2H), 1.55-1.51 (m, 2H), -0.03 (s, 9H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 159.0, 145.3, 143.0, 131.5, 130.7, 120.1, 113.2, 111.6, 55.3, 37.1, 31.1, 27.9, 27.3, 0.70 HRMS (ESI) *m/z* Found $(M+H)^+$, 303.1793, $C_{18}H_{26}O_2Si$ requires $(M+H)^+$, 303.1780

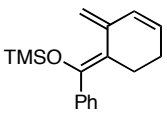
(*Z*)-Trimethyl(2-methylenecyclohexylidene)propoxy)silane (5d)



Following procedure A the title compound was prepared in 29% yield.

IR ν_{max} 2961, 2930, 1637, 1445, 1290, 1250, 1230, 1143, 1080 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.97-4.95 (m, 1H), 4.90 (d, *J* = 2.7 Hz, 1H), 2.81 (p, *J* = 6.9 Hz, 1H), 2.16 (t, *J* = 6.0 Hz, 4H), 1.64-1.47 (m, 4H), 1.00 (d, *J* = 6.9 Hz, 6H), 0.14 (s, 9H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 148.5, 145.6, 116.9, 113.2, 37.0, 30.3, 29.3, 28.2, 27.7, 20.5, 1.24 HRMS (ESI) *m/z* Found $(M+H)^+$, 239.1824, $C_{14}H_{26}OSi$ requires $(M+H)^+$, 239.1831

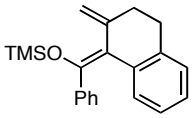
(*Z*)-Trimethyl((2-methylenecyclohex-3-en-1-ylidene)(phenyl)methoxy)silane (5e)



Following procedure A the title compound was prepared in 58% yield.

IR ν_{max} 2960, 1641, 1599, 1490, 1445, 1251, 1111, 844 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.45-7.26 (m, 5H), 6.14 (d, *J* = 9.6 Hz, 1H), 5.83 (dt, *J* = 9.6, 3.9 Hz, 1H), 5.67 (s, 1H), 5.22 (s, 1H), 2.28 (t, *J* = 5.7 Hz, 2H), 2.17 (t, *J* = 5.7 Hz, 2H) -0.02 (s, 9H) δ HRMS (ESI) *m/z* Found $(M+H)^+$, 271.1507, $C_{17}H_{22}OSi$ requires $(M+H)^+$, 271.1518

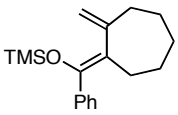
(*E*)-Trimethyl((2-methylene-3,4-dihydronaphthalen-1(2H)-ylidene)(phenyl)methoxy)silane (5f)



Following procedure A the title compound was prepared in 47% yield. The product was contaminated by an inseparable impurity that had no affect on the subsequent step.

IR ν_{max} 3021, 2944, 2838, 1556, 1487, 1236 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.52-7.48 (m, 1H), 7.22-7.13 (m, 4H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.02 (td, *J* = 7.5, 1.5 Hz, 1H), 6.80 (td, *J* = 7.5, 1.5 Hz, 1H), 6.71 (d, *J* = 7.5 Hz, 1H), 5.85 (q, *J* = 2.1 Hz, 1H), 5.36 (q, *J* = 2.1 Hz, 1H), 2.82-2.77 (m, 2H), 2.68-2.65 (m, 2H) 0.05 (s, 9H) HRMS (ESI) *m/z* Found $(M+H)^+$, 321.1673, $C_{21}H_{24}OSi$ requires $(M+H)^+$, 321.1675

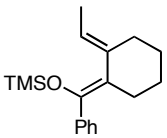
(*Z*)-Trimethyl((2-methylenecycloheptylidene)(phenyl)methoxy)silane (5g)



Following procedure A the title compound was prepared in 41% yield.

IR ν_{max} 3060, 2923, 2851, 1443, 1250, 1153 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.38-7.27 (m, 5H), 5.30 (d, *J* = 3.0 Hz, 1H), 5.14 (d, *J* = 3.0 Hz, 1H), 2.40-2.37 (m, 2H), 2.22-2.21 (m, 2H), 1.67-1.52 (m, 6H), -0.04 (s, 9H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 148.2, 139.4, 129.1, 128.5, 127.7, 127.5, 122.6, 113.4, 37.5, 31.2, 29.8, 29.7, 29.3, 0.50 HRMS (EI) *m/z* Found $(M^{\bullet})^+$, 286.1750, $C_{18}H_{26}OSi$ requires $(M^{\bullet})^+$, 286.1753

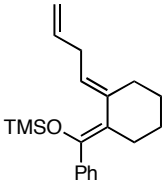
((*Z*)-((*E*)-2-Ethylideneclohexylidene(phenyl)methoxy)trimethylsilane (5h)



Following procedure B the title compound was prepared in 35% yield. The product was contaminated by an inseparable impurity that had no affect on the subsequent step.

IR ν_{max} 2927, 1599, 1491, 1444, 1294, 1250 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.37-7.20 (m, 5H), 5.62 (q, *J* = 6.9 Hz, 1H), 2.29 (t, *J* = 6.0 Hz, 2H), 2.14 (t, *J* = 6.0 Hz, 2H), 1.73 (d, *J* = 6.9 Hz, 3H), 1.63-1.49 (m, 4H), -0.03 (s, 9H) HRMS (ESI) *m/z* Found $(M+H)^+$, 287.1826, $C_{18}H_{26}OSi$ requires $(M+H)^+$, 287.

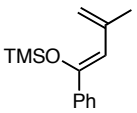
((*Z*)-((*E*)-2-(But-3-en-1-ylidene)cyclohexylidene)(phenyl)methoxy)trimethylsilane (5i)



Following procedure B the title compound was prepared in 27% yield. The product was contaminated by an inseparable impurity that had no affect on the subsequent step.

IR ν_{max} 2927, 1640, 1599, 1492, 1445, 1251, 1140 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.39-7.21 (m, 5H), 5.93-5.83 (m, 1H), 5.59 (t, *J* = 7.5 Hz, 1H), 5.14-5.08 (m, 1H), 5.04-4.97 (m, 1H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.31-2.21 (m, 2H), 2.14 (t, *J* = 7.2 Hz, 2H), 1.64-1.48 (m, 4H), -0.05 (s, 9H) HRMS (EI) *m/z* Found $M^{\bullet+}$, 312.1916, $C_{20}H_{28}OSi$ requires $M^{\bullet+}$, 312.1909

(*Z*)-Trimethyl((3-methyl-1-phenylbuta-1,3-dien-1-yl)oxy)silane



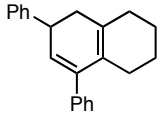
Following procedure A the title compound was prepared in 71% yield.

IR ν_{max} 2962, 1631, 1339, 1252, 1080, 845 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.34-7.28 (m, 3H), 5.66 (s, 1H), 5.20 (q, *J* = 0.9 Hz, 1H), 4.94 (q, *J* = 0.9 Hz, 1H), 2.06 (t, *J* = 0.9 Hz, 3H), 0.12 (s, 9H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 150.5, 140.5, 140.1, 128.1, 128.0, 126.5, 114.5, 112.9, 23.6, 0.90 HRMS (ESI) *m/z* Found $(M+H)^+$, 233.1352, $C_{24}H_{20}OSi$ requires $(M+H)^+$, 233.1362

V. NHC catalyzed (4 + 2) cycloaddition/decarboxylation

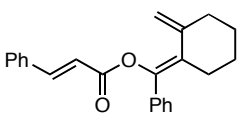
A solution of IPrMe **D2** (0.3 mL of a 0.1 M solution in THF, 0.03 mmol) was added to a stirred solution of acid fluoride **4** (0.3 mmol) and TMS dienol ether **5** (0.3 mmol) in THF (4 mL) at -78 °C. While both substrates tolerate low levels of moisture the reaction is highly sensitive to any trace of water, hence freshly prepared substrates are recommended. The mixture was stirred for 1 hour, allowing the temperature to slowly rise to -10 °C. The volatiles were then evaporated and the crude residue purified *via* flash column chromatography

6,8-Diphenyl-1,2,3,4,5,6-hexahydronaphthalene (3a)



R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2926, 1601, 1491, 1450 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.36-7.27 (m, 10H), 5.76 (d, *J* = 3.3 Hz, 1H), 3.71 (ddd, *J* = 12.3, 9.3, 3.3 Hz, 1H), 2.40-2.24 (m, 4H), 2.10-2.03 (m, 2H), 1.87-1.60 (m, 4H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 145.9, 141.7, 141.4, 131.6, 128.6, 128.5, 127.9, 127.7, 127.2, 127.0, 126.7, 126.3, 41.2, 38.1, 31.0, 27.5, 23.6, 23.1 HRMS (EI) *m/z* Found $M^{\bullet+}$, 286.1685, $C_{22}H_{22}$ requires $M^{\bullet+}$, 286.1722

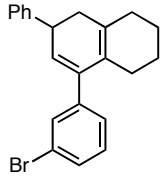
(*Z*)-(2-Methylenecyclohexylidene)(phenyl)methyl cinnamate (6a)



R_f 0.3 (1:19, v/v EtOAc : hexanes) IR ν_{max} 2931, 2856, 1729, 1635, 1447, 1310, 1229, 1200, 1136 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 15.9 Hz,

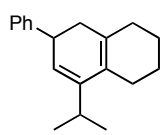
1H), 7.54-7.51 (m, 2H), 7.46-7.43 (m, 2H), 7.40-7.26 (m, 6H), 6.49 (d, *J* = 15.9 Hz, 1H), 4.97 (s, 2H), 2.41 (t, *J* = 5.4 Hz, 2H), 2.34 (t, *J* = 5.4 Hz, 2H), 1.72-1.64 (m, 4H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 155.8, 145.8, 145.3, 139.4, 135.8, 134.4, 130.5, 130.3, 129.2, 129.0, 128.8, 128.3, 128.2, 117.9, 111.2, 36.5, 31.4, 27.8, 27.2 HRMS (ESI) *m/z* Found $(M+Na)^+$, 353.1518, $C_{23}H_{22}O_2$ requires $(M+Na)^+$, 353.1518

8-(3-Bromophenyl)-6-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3b)



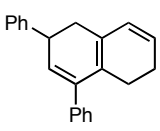
R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2926, 1592, 1557, 1471, 1451, 1070 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 7.33-7.26 (m, 4H), 7.26-7.22 (m, 1H), 7.19-7.17 (m, 2H), 5.72 (d, *J* = 3.6 Hz, 1H), 3.67 (ddd, *J* = 12.6, 9.6, 3.6 Hz, 1H), 2.36-2.22 (m, 4H), 2.06-1.96 (m, 2H), 1.84-1.56 (m, 4H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 145.3, 143.4, 140.4, 132.0, 131.4, 129.5, 129.3, 128.4, 127.7, 127.6, 127.1, 126.5, 126.3, 121.9, 40.9, 37.7, 30.8, 27.3, 23.4, 22.8 MS (EI) *m/z* Found $M^{\bullet+}$, 364.0648, $C_{22}H_{21}Br$ requires $M^{\bullet+}$, 364.0827

8-Isopropyl-6-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3d)



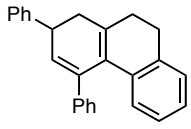
R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2927, 1601, 1492, 1451, 1382, 1076 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.34-7.22 (m, 5H), 5.50 (d, *J* = 3.0 Hz, 1H), 3.74 (brt, *J* = 9.9 Hz, 1H), 2.58 (p, *J* = 6.9 Hz, 1H), 2.18-2.15 (m, 6H), 1.77-1.50 (m, 4H), 1.06 (d, *J* = 6.9 Hz, 6H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 146.7, 145.4, 130.9, 128.4, 127.9, 127.8, 126.1, 119.9, 40.7, 38.4, 31.0, 27.9, 25.1, 23.7, 23.6, 22.9, 22.5 HRMS (EI) *m/z* Found $M^{\bullet+}$, 252.1809, $C_{19}H_{24}$ requires $M^{\bullet+}$, 252.1878

2,4-Diphenyl-1,2,5,6-tetrahydronaphthalene (3e)



R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 3029, 2930, 2922, 1603, 1493, 1454 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.39-7.23 (m, 10H), 5.98 (d, *J* = 9.3 Hz, 1H), 5.91-5.86 (m, 1H), 5.88 (d, *J* = 3.3 Hz, 1H), 3.78 (ddd, *J* = 13.2, 9.0, 3.3 Hz, 1H), 2.55-2.50 (m, 2H), 2.33-2.04 (m, 4H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 145.3, 141.1, 140.5, 128.9, 128.7, 128.6, 128.4, 128.3, 127.9, 127.7, 127.4, 126.8, 126.5, 126.3, 41.4, 35.9, 24.4, 23.6, HRMS (EI) *m/z* Found $M^{\bullet+}$, 284.1542, $C_{22}H_{20}$ requires $M^{\bullet+}$, 284.1565

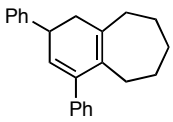
2,4-Diphenyl-1,2,9,10-tetrahydrophenanthrene (3f)



R_f 0.2 (1:99, v/v EtOAc : hexanes) IR ν_{max} 3022, 2928, 2813, 1802, 1629, 1490 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.43-7.36 (m, 4H), 7.33-7.27 (m, 6H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), 6.25 (d, *J* = 3.6 Hz, 1H), 3.82-3.74 (m, 1H), 2.99-2.78 (m, 2H), 2.62-2.53 (m, 2H), 2.36-2.27 (m,

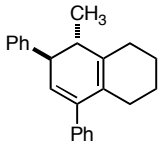
2H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.8, 141.3, 139.3, 138.4, 136.2, 133.6, 130.9, 129.2, 128.5, 128.0, 127.7, 127.3, 127.0, 126.5, 126.4, 126.2, 125.4, 125.3, 41.0, 38.0, 29.5, 28.8 HRMS (EI) *m/z* Found $M^{\bullet+}$, 334.1729 $C_{26}H_{22}$, requires $M^{\bullet+}$, 334.1722

2,4-Diphenyl-2,5,6,7,8,9-hexahydro-1H-benzo[7]annulene (3g)



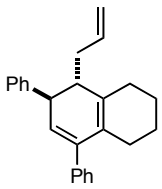
R_f 0.2 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2922, 2847, 1600, 1493, 1451, 1260 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.36-7.22 (m, 10H), 5.78 (d, *J* = 3.6, 1H), 3.62 (ddd, *J* = 12.3, 9.3, 3.6 Hz, 1H), 2.49-2.43 (m, 2H), 2.37-2.12 (m, 4H), 1.79-1.70 (m, 3H), 1.57-1.53 (m, 1H), 1.52-1.48 (m, 2H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 145.4, 143.0, 141.8, 138.1, 133.3, 128.3, 128.1, 127.9, 127.7, 126.8, 126.5, 126.2, 41.5, 40.5, 36.1, 32.2, 30.4, 27.2, 26.1 HRMS (EI^+) *m/z* Found $M^{\bullet+}$, 300.1915 $C_{23}H_{24}$, requires $M^{\bullet+}$, 300.1878

(5*R*,6*S*)-5-Methyl-6,8-diphenyl-1,2,3,4,5,6-hexahydronaphthalene and **(5*S*,6*R*)-5-Methyl-6,8-diphenyl-1,2,3,4,5,6-hexahydronaphthalene (3h)**



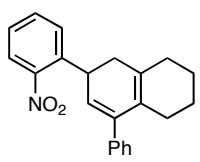
R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2927, 1600, 1491, 1450, 1250 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.30-7.26 (m, 10H), 5.67 (d, *J* = 5.7 Hz, 1H), 3.27 (dd, *J* = 5.7, 3.9 Hz, 1H), 2.21-1.44 (m, 9H), 1.18 (d, *J* = 7.2 Hz, 3H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.5, 141.6, 140.9, 135.7, 128.5, 128.4, 128.0, 127.9, 126.7, 126.3, 125.9, 124.3, 46.9, 41.1, 29.6, 27.7, 23.5, 23.2, 18.8 HRMS (EI) *m/z* Found $M^{\bullet+}$, 300.1833, $C_{23}H_{24}$ requires $M^{\bullet+}$, 300.1878

(5*R*,6*S*)-5-Allyl-6,8-diphenyl-1,2,3,4,5,6-hexahydronaphthalene and **(5*S*,6*R*)-5-Allyl-6,8-diphenyl-1,2,3,4,5,6-hexahydronaphthalene (3i)**



R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2928, 1720, 1638, 1599, 1490, 1448, 1250 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.42-7.18 (m, 10H), 5.96-5.86 (m, 1H), 5.65 (d, *J* = 6.3 Hz, 1H), 5.14-5.06 (m, 2H), 3.46 (d, *J* = 6.3 Hz, 1H), 2.35-2.02 (m, 7H), 1.81-1.38 (m, 4H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 143.7, 141.3, 141.2, 137.3, 133.8, 128.2(8), 128.2(7), 127.8, 127.7, 126.6, 126.5, 126.1, 123.5, 116.7, 46.5, 41.8, 36.6, 30.3, 27.5, 23.4, 22.9 HRMS (EI) *m/z* Found $M^{\bullet+}$, 326.2028, $C_{25}H_{26}$ requires $M^{\bullet+}$, 326.2035.

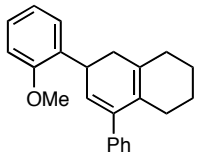
6-(2-Nitrophenyl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3j)



R_f 0.3 (1:19, v/v EtOAc : hexanes) IR ν_{max} 2929, 1606, 1525, 1444. 1352 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.66 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.52 (td, *J* = 7.8, 1.5 Hz, 1H), 7.37-7.22 (m, 6H), 5.59 (d, *J* = 3.6 Hz, 1H), 4.23 (ddd, *J* = 12.3, 8.1, 3.6 Hz, 1H), 2.59-2.50 (m, 1H), 2.40-2.18 (m, 3H),

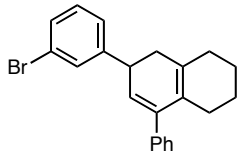
2.02-1.97 (m, 2H), 1.83-1.54 (m, 4H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 149.6, 142.6, 140.8, 140.0, 132.5, 131.1, 130.3, 128.4, 127.8, 127.0, 126.9, 126.7, 125.1, 124.0, 37.1, 35.9, 30.8, 27.3, 23.3, 22.8 HRMS (EI) *m/z* Found $M^{\bullet+}$, 331.1572, $C_{22}H_{21}NO_2$ requires $M^{\bullet+}$, 331.1572

6-(2-Methoxyphenyl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3k)



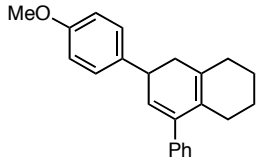
R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2928, 1599, 1493. 1463, 1438, 1240 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.37-7.19 (m, 7H), 6.96-6.88 (m, 2H), 5.71 (d, *J* = 3.6 Hz, 1H), 4.15 (ddd, *J* = 12.3, 8.1, 3.6 Hz, 1H), 3.87 (s, 3H), 2.38-2.20 (m, 4H), 2.05-1.99 (m, 2H), 1.87-1.56 (m, 4H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 157.0, 141.7, 133.6, 131.6, 128.6, 128.5, 127.8, 127.3, 127.2, 126.9, 126.5, 120.6, 110.4, 55.5, 36.1, 33.5, 31.0, 27.6, 23.6, 23.1 (one signal overlapping) HRMS (EI) *m/z* Found $M^{\bullet+}$, 316.1826, $C_{23}H_{24}O$ requires $M^{\bullet+}$, 316.1827

6-(3-Bromophenyl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3l)



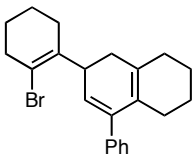
R_f 0.3 (1:99, v/v EtOAc : hexane) IR ν_{max} 2927, 1593, 1475, 1319, 1251, 1071 ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.37-7.16 (m, 8H), 5.67 (d, *J* = 3.6 Hz, 1H), 3.65 (dt, *J* = 10.4, 3.6 Hz, 1H), 2.33 (d, *J* = 10.4 Hz, 1H), 2.26-2.18 (m, 1H), 2.05-1.99 (m, 2H), 1.86-1.75 (m, 1H), 1.75-1.57 (m, 5H) ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.0, 142.1, 141.0, 131.3, 130.8, 129.9, 129.3, 128.4, 127.8, 126.7, 126.3, 125.8, 125.8, 122.4, 40.7, 37.7, 30.8, 27.3, 23.5, 22.9 MS Found $M^{\bullet+}$, 364.1, $C_{22}H_{21}Br$ requires $M^{\bullet+}$, 364.1

6-(4-Methoxyphenyl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3m)



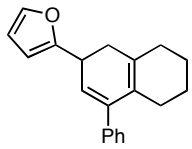
R_f 0.1 (1:99, v/v EtOAc : hexane) **IR ν_{max}** 2929, 1513, 1442, 1249, 1037 **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.36-7.25 (m, 7H), 6.88 (d, *J* = 9.0 Hz, 2H), 5.72 (d, *J* = 3.0 Hz, 1H), 3.82 (s, 3H), 3.65 (dt, *J* = 9.0, 3.0 Hz, 1H), 2.33 (d, *J* = 12.0 Hz, 2H), 2.30-2.23 (m, 1H), 2.08-2.00 (m, 2H), 1.86-1.56 (m, 5H) **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 158.0, 143.0, 138.4, 134.9, 133.3, 129.6, 128.4, 128.0, 127.7, 126.3, 124.2, 113.8, 55.2, 41.0, 40.1, 39.0, 27.8, 26.0, 23.4 HRMS (EI) Found $M^{\bullet+}$, 316.1823, $C_{23}H_{24}O$ requires $M^{\bullet+}$, 316.1827

6-(2-Bromocyclohex-1-en-1-yl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3n)



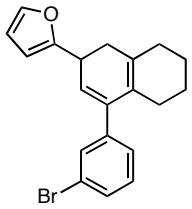
R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2930, 1648, 1490, 1441, 1332, 1260 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32-7.18 (m, 5H), 5.40 (d, *J* = 3.3 Hz, 1H), 3.91 (ddd, *J* = 11.1, 8.1, 3.3 Hz, 1H), 2.55-2.51 (m, 2H), 2.29-2.15 (m, 5H), 2.08-1.94 (m, 3H), 1.73-1.49 (m, 8H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 141.6, 141.3, 138.1, 131.6, 128.4, 127.7, 126.6, 126.4, 124.8, 119.2, 41.8, 37.0, 32.2, 30.8, 28.2, 27.4, 24.5, 23.4, 22.9, 22.7 MS (EI) *m/z* Found $M^{\bullet+}$, 368.1, $C_{22}H_{25}Br$ requires $M^{\bullet+}$, 368.1

2-(4-Phenyl-1,2,5,6,7,8-hexahydronaphthalen-2-yl)furan (3o)



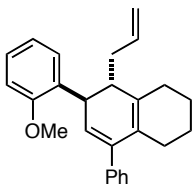
R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2928, 1598, 1505, 1493, 1443, 1013 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.34-7.20 (m, 6H), 6.30 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.07 (dd, *J* = 3.0, 0.9 Hz, 1H), 5.73 (d, *J* = 3.6 Hz, 1H), 3.74 (ddd, *J* = 12.6, 8.7, 3.6 Hz, 1H), 2.40-1.49 (m, 10H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 158.3, 141.9, 141.2, 131.8, 128.6, 127.9, 127.4, 126.8, 123.5, 110.2, 104.3, 34.4, 34.2, 31.0, 27.5, 23.5, 23.0 (one signal overlapping) HRMS (ESI) *m/z* Found $(M+H)^+$, 277.1584, $C_{20}H_{20}O$ requires $(M+H)^+$, 277.1592

2-(4-(3-Bromophenyl)-1,2,5,6,7,8-hexahydronaphthalene-2-yl)furan (3p)



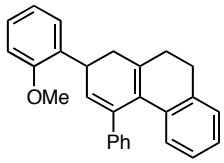
R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2928, 2858, 1583, 1445, 1259, 1071 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.41-7.37 (m, 2H), 7.34 (dd, *J* = 2.1, 0.9 Hz, 1H), 7.20-7.14 (m, 2H), 6.30 (dd, *J* = 3.3, 2.1 Hz, 1H), 6.06 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.73 (d, *J* = 3.6 Hz, 1H), 3.73 (ddd, *J* = 12.6, 8.4, 3.6 Hz, 1H), 2.42-1.49 (m, 10H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 157.7, 143.2, 141.2, 140.6, 132.2, 131.4, 129.7, 129.3, 127.1, 126.6, 124.2, 121.9, 110.1, 104.2, 34.2, 33.9, 30.8, 27.2, 23.3, 22.8 HRMS (EI) *m/z* Found $M^{\bullet+}$, 354.0648, $C_{20}H_{19}BrO$ requires $M^{\bullet+}$, 354.0619

(5*R*,6*S*)-5-Allyl-6-(2-methoxyphenyl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene and **(5*R*,6*S*)-5-allyl-6-(2-methoxyphenyl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3q)**



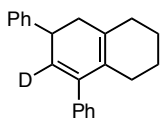
R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2928, 1669, 1598, 1490, 1458, 1240, 1030 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33-7.16 (m, 7H), 6.88 (t, *J* = 8.1 Hz, 2H), 6.03-5.92 (m, 1H), 5.57 (d, *J* = 6.3 Hz, 1H), 5.12-5.04 (m, 2H), 3.94 (d, *J* = 6.3 Hz, 1H), 3.85 (s, 3H), 2.34 (t, *J* = 7.2 Hz, 2H), 2.22-2.04 (m, 4H), 2.01 (t, *J* = 7.2 Hz, 1H), 1.71-1.34 (m, 4H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 156.7, 141.8, 141.5, 137.8, 134.3, 130.9, 128.4, 128.3, 127.7, 127.0, 126.5, 126.2, 123.2, 120.2, 115.7, 110.3, 55.3, 44.5, 37.0, 34.6, 30.4, 27.5, 23.5, 23.0 HRMS (EI) *m/z* Found $M^{\bullet+}$, 356.2119 $C_{26}H_{28}O$, requires $M^{\bullet+}$, 356.2140

2-(2-Methoxyphenyl)-4-phenyl-1,2,9,10-tetrahydrophenanthrene (**3r**)



R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2928, 2812, 1560, 1490, 1240 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.26-7.21 (m, 6H), 7.15 (d, *J* = 6.6 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 7.5 Hz, 1H), 6.20 (d, *J* = 4.5 Hz, 1H), 4.26-4.18 (m, 1H), 3.78 (s, 3H), 2.88-2.78 (m, 2H), 2.62-2.54 (m, 2H), 2.32-2.23 (m, 2H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 156.9, 141.6, 139.6, 138.4, 136.2, 133.8, 132.3, 131.0, 128.7, 128.2, 127.9, 127.2(6), 127.2(5), 126.9, 126.4, 126.2, 125.4, 125.1, 120.5, 110.3, 55.4, 36.1, 33.4, 29.6, 28.9 HRMS (EI) *m/z* Found $M^{\bullet+}$, 364.1827 $C_{27}H_{24}O$, requires $M^{\bullet+}$, 364.1827

7-Deutero-6,8-diphenyl-1,2,3,4,5,6-hexahydronaphthalene (7D-**3a**)



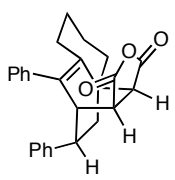
R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2926, 1857, 1602, 1490, 1451, 1073, 1030 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.36-7.24 (m, 10H), 3.70 (dd, *J* = 12.0, 9.6 Hz, 1H), 2.38-2.23 (m, 3H), 2.07-2.01 (m, 2H), 1.87-1.60 (m, 5H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 145.7, 141.5, 141.3, 131.4, 128.7, 128.5, 128.4, 127.7, 127.6, 127.2 (t, *J* = 12.0 Hz), 126.5, 126.2, 40.9, 37.9, 30.8, 27.4, 23.4, 22.9 HRMS (EI) *m/z* Found $M^{\bullet+}$, 287.1773, $C_{22}H_{21}D$ requires $M^{\bullet+}$, 287.1784

VI. Derivatization studies

i) Diels Alder Reaction

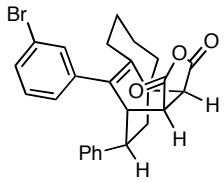
Maleic anhydride (39 mg, 0.4 mmol) was added to a stirred solution of diene **3a** or **b** (0.2 mmol) in toluene (1 mL). The flask was fitted with a condenser and heated to reflux for 16 hours. After cooling to room temperature the volatiles were evaporated and the crude residue purified *via* flash column chromatography (1:5, v/v EtOAc : hexanes) to yield tricyclic compounds **8a** and **8b** in 58 and 47 % yield respectively.

(3a*S*,9a*S*,9b*S*,11*R*)-5,11-diphenyl-3a,4,6,7,8,9-hexahydro-1*H*-4,9a-ethanonaphtho[1,2-*c*]furan-1,3(9b*H*)-dione and **(3a*R*,9a*R*,9b*R*,11*S*)-5,11-diphenyl-3a,4,6,7,8,9-hexahydro-1*H*-4,9a-ethanonaphtho[1,2-*c*]furan-1,3(9b*H*)-dione** (**8a**)



R_f 0.3 (1:5, v/v EtOAc : hexanes) IR ν_{max} 2937, 1777, 1223, 1079, 938 ^{1}H-NMR (300 MHz, CD Cl_3) δ 7.34-7.27 (m, 3H), 7.18-7.15 (m, 2H), 7.11-7.08 (m, 2H), 6.48-6.45 (m, 2H), 3.50-3.44 (m, 2H), 3.26 (ddd, *J* = 9.9, 4.8, 2.1 Hz, 1H), 3.04 (d, *J* = 8.4 Hz, 1H), 2.82 (ddd, *J* = 17.0, 11.1, 5.2 Hz, 1H), 2.61 (ddd, *J* = 15.8, 5.6, 4.1 Hz, 1H), 2.35 (17.0, 11.1, 5.6 Hz, 1H), 2.10 (dd, *J* = 14.1, 4.8 Hz, 1H), 1.95-1.57 (m, 7H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.7, 171.4, 144.1, 140.3, 128.3, 133.6, 128.7, 128.6, 128.0, 127.9, 127.0, 126.8, 48.9, 46.8, 46.7, 43.0, 41.0, 38.2, 27.9, 24.8, 20.4, 18.2 HRMS (ESI) *m/z* Found $(M+H)^+$, 385.1800, $C_{26}H_{24}O_3$ requires $(M+H)^+$, 385.1804

(3a*S*,9a*S*,9b*S*)-5-(3-bromophenyl)-11-phenyl-3a,4,6,7,8,9-hexahydro-1H-4,9a-ethanonaphtho[1,2-c]furan-1,3(9bH)-dione and **(3a*R*,9a*R*,9b*R*)-5-(3-bromophenyl)-11-phenyl-3a,4,6,7,8,9-hexahydro-1H-4,9a-ethanonaphtho[1,2-c]furan-1,3(9bH)-dione** (**8b**)

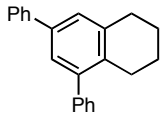


R_f 0.3 (1:5, v/v EtOAc : hexanes) IR ν_{max} 2938, 1841, 1770, 1557, 1229, 1078, 939 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33-7.25 (m, 3H), 7.21 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.15-7.11 (m, 2H), 6.95 (t, *J* = 15.6 Hz, 1H), 6.40 (d, *J* = 7.8 Hz, 1H), 6.31 (t, *J* = 1.8 Hz, 1H), 3.47 (dd, *J* = 9.0, 3.3 Hz, 1H), 3.37 (t, *J* = 2.7 Hz, 1H), 3.27 (ddd, *J* = 9.9, 4.5, 2.7 Hz, 1H), 3.02 (d, *J* = 9.0 Hz, 1H), 2.80 (ddd, *J* = 16.0, 10.8, 5.7 Hz, 1H), 2.54 (ddd, *J* = 16.0, 5.7, 4.5 Hz, 1H), 2.38-2.20 (m, 2H), 2.11 (dd, *J* = 13.8, 4.5 Hz, 1H), 1.96-1.54 (m, 5H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.7, 171.2, 143.7, 141.6, 140.3, 132.3, 130.8, 129.8, 129.4, 128.8, 127.8, 127.2, 126.6, 122.1, 48.8, 46.8, 46.5, 42.8, 41.0, 37.5, 27.8, 24.8, 20.3, 18.1 HRMS (ESI) *m/z* Found $(M+Na)^+$, 485.0726, $C_{26}H_{23}BrO_3$ requires $(M+Na)^+$, 485.0728

ii) Aromatization

DDQ (50 mg, 0.22 mmol) was added to a stirred solution of **3a** or **3e** (0.20 mmol or in the case of triene **3e** 0.10 mmol) in toluene (1 mL). The mixture was stirred for 2 hours at room temperature, after which time the volatiles were evaporated. The crude residue was purified *via* flash column chromatography (1:99, v/v EtOAc : hexanes) to provide compounds **7a** and **7e** in 75% and 92% yield. Naphthalene **7e** was consistent with previously reported data from the litrature.[21]

5,7-diphenyl-1,2,3,4-tetrahydronaphthalene (**7a**)



R_f 0.3 (1:99, v/v EtOAc : hexanes) IR ν_{max} 2930, 1599, 1567, 1497, 1561, 1439, 908 ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.66-7.63 (m, 2H), 7.47-7.34 (m, 10H), 2.97 (t, *J* = 6.3 Hz, 2H), 2.68 (t, *J* = 6.3 Hz, 2H), 1.89-1.76 (m, 4H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 142.8, 142.2, 141.2, 138.4, 138.1, 134.3, 130.3, 129.5, 128.9, 128.3, 127.7, 127.3, 127.0, 126.2, 30.4, 28.3, 23.7, 23.2 HRMS (EI) *m/z* Found $M^{\bullet+}$, 284.1554, $C_{22}H_{20}$ requires $M^{\bullet+}$, 284.1565

[21] Kabalka, G. W.; Ju, Y.; Wu, Z. *J. Org. Chem.*, **2003**, *68*, 7195

VII. Mechanistic studies

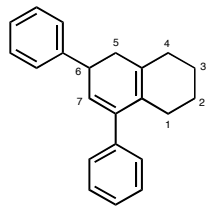
Cross over experiment

IPrMe **D2** (0.5 mL of a 0.1M solution, 0.05 mmol) was added to a stirred solution of TMS ether **5a** (1 equivalent, 137 mg, 0.5 mmol), (α-D)cinnamoyl fluoride αD-**4a** (0.5 equivalents, 38 mg, 0.25 mmol) and (*E*)-3-(4-methoxyphenyl)acryloyl fluoride **4m** (0.5 equivalents, 45 mg, 0.25 mmol) in THF (5 mL) at -78 ^{o}C. The temperature was allowed to slowly rise to -10 ^{o}C at which point the volatiles were evaporated. The crude residue was purified *via* gradient flash column chromatography (1:99→1:19, v/v EtOAc: hexanes) to afford only deuterated cyclohexadiene 7D-**3a** and protio cyclohexadiene **3m**.

Kinetic Isotope Effect

Using approaches developed by Singleton[22] kinetic isotope effects (KIEs) were determined through the comparison of ^{12}C enriched samples on reactions taken to 10% conversions[22b,23] with those taken to complete conversion. From these studies KIEs for the carbons from the α,β-unsaturated acid fluoride **4a** could be determined. Thus, IPrMe **D2** (0.5 mL of a 0.1M solution, 0.05 mmol) was added to a stirred solution of cinnamoyl fluoride (**4a**) (10 equivalents, 750 mg, 5.0 mmol) and TMS ether **5a** (1 equivalent, 137 mg, 0.5 mmol) in THF (20 mL) at -78 ^{o}C. The temperature was allowed to slowly rise to -10 ^{o}C over 1 hour. The volatiles were then evaporated and the crude residue purified *via* flash column chromatography (1:99, v/v EtOAc: hexanes) to provide the ^{12}C enriched product **3a**.

The ^{13}C-NMR spectra from the enriched product were compared to that of a standard product made from the same batch of TMS ether and acid fluoride. Samples for analysis were prepared in the same manner using 30 mg of cyclohexadiene **3a** and 0.6 mL $CDCl_3$. The ^{13}C NMR spectra were recorded at 75MHz on a Bruker DPX300 spectrometer with a 40 second delay between pulses using protocols similar to those reported by Denmark.[23] This allowed analysis with only very minor decomposition by aromatization. Integration was measured at 10Hz for each peak except that at 127.0 which was measured at 6 Hz due to close proximity of peaks. The peak at 27.5 ppm was set at 1.000 as its isotopic composition was assumed to remain consistent throughout the reaction. Assignment of carbons was made based on HSQC and HMBC analysis. KIEs were calculated based on the ratio of standard to enriched[22b] and standard deviations were determined using the formula ΔKIE = ratio$[(\Delta\text{enriched/enriched})^2 + (\Delta\text{standard/standard})^2]^{1/2}$.[22,23]



[22] (a) Singleton, D. A.; Thomas, A. A. *J. Am. Chem. Soc.* **1995***, 117*, 9357 (b) Frantz, D. E.; Singleton, D. A. *J. Am. Chem. Soc.* **2000***, 122*, 3288

[23] Denmark, S. E.; Pham, S. M.; Stavenger, R. A.; Su, X.; Wong, K.-T.; Nishigaichi, Y. *J. Org. Chem.* **2007***, 71*, 3904

Table 1. Integrations and deviations with the standard

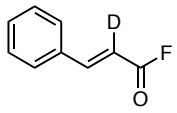
peak ppm	run 1	run 2	run 3	average	stdev
127.0	1.0054	0.9977	1.0074	1.0035	0.0051
126.7	0.9958	0.9930	0.9994	0.9961	0.0032
126.3	0.9969	0.9862	0.9946	0.9926	0.0056
41.2	0.9859	0.9751	0.9700	0.9770	0.0081
38.1	0.9491	0.9494	0.9455	0.9480	0.0022
31.0	0.9987	1.0122	0.9986	1.0032	0.0078
27.5	1.0000	1.0000	1.0000	1.0000	0.0000

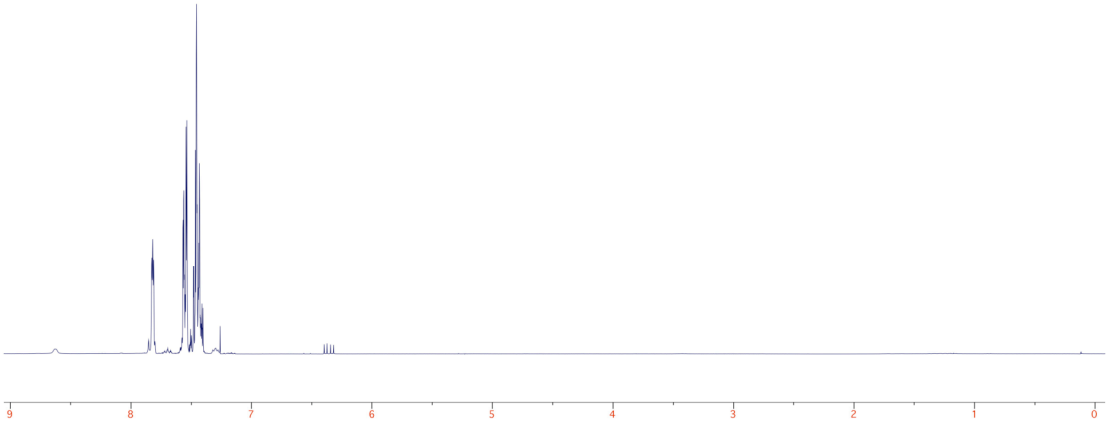
Table 2. Integration from the enriched sample, deviations and KIEs

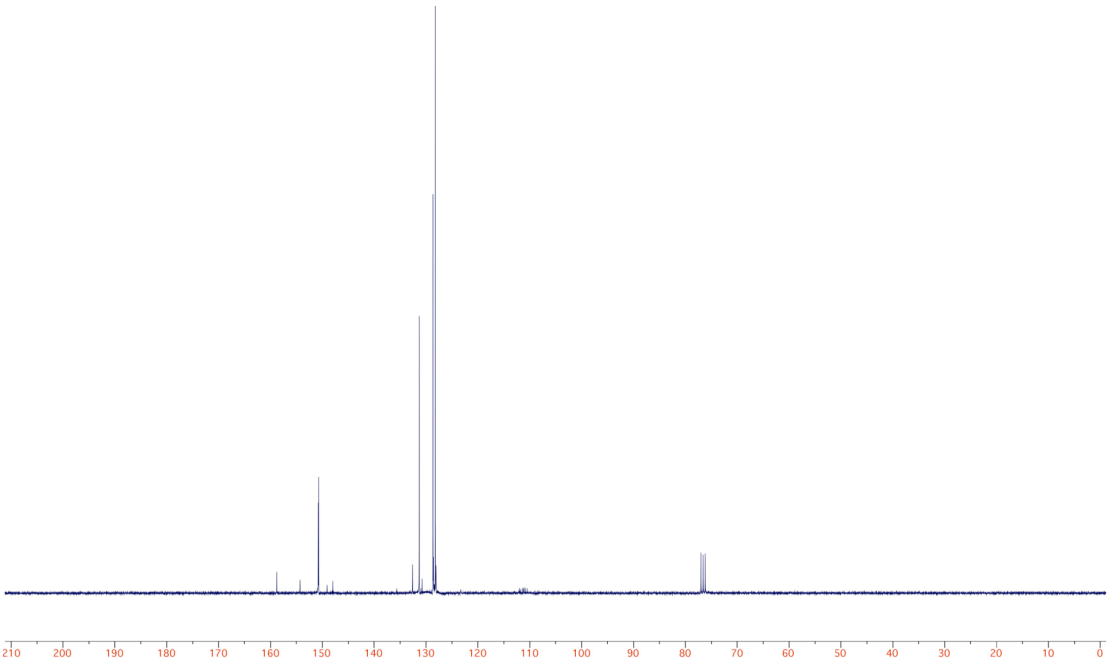
peak ppm	carbon	run 1	run 2	run 3	average	stdev	KIE	stdev
127.0	7	0.9798	0.9920	0.9895	0.9871	0.0064	**1.017**	**0.008**
126.7	aryl	0.9987	1.0010	0.9863	0.9953	0.0079	**1.001**	**0.009**
126.3	aryl	0.9702	1.0033	0.9727	0.9821	0.0184	**1.011**	**0.020**
41.2	6	0.9578	0.9663	0.9488	0.9576	0.0088	**1.020**	**0.013**
38.1	5	0.9495	0.9633	0.9818	0.9649	0.0162	**0.983**	**0.017**
31.0	4	1.0134	1.0154	0.9956	1.0081	0.0109	**0.995**	**0.013**
27.5	1	1.0000	1.0000	1.0000	1.0000	0.0000	**1.000**	**0.000**

VIIII. ^{1}H and ^{13}C NMR spectra

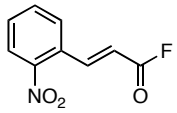
α-D-(*E*)-Cinnamoyl fluoride (αD-4a)

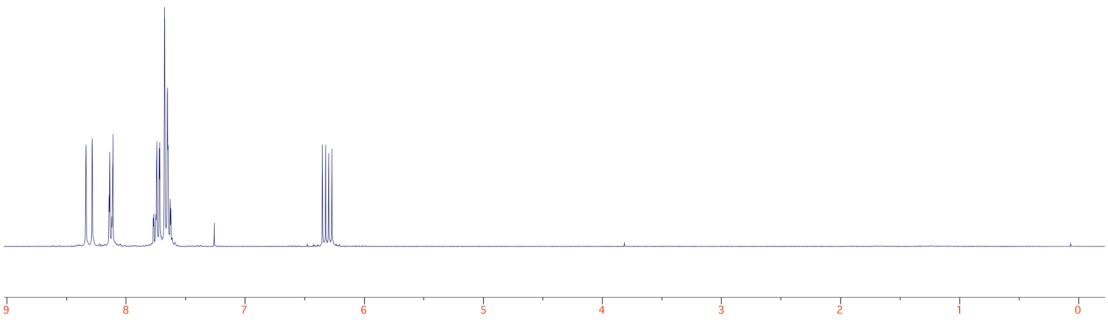


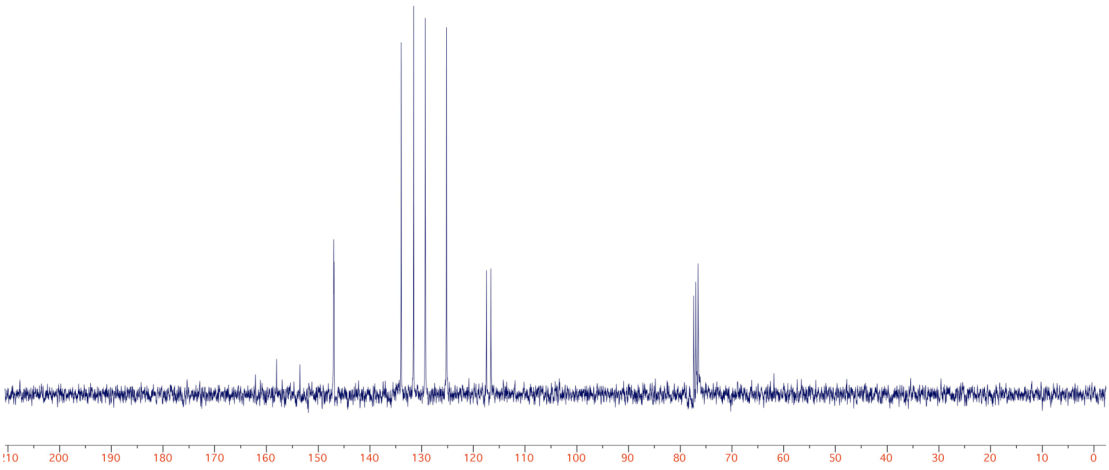




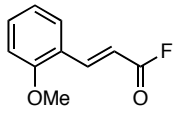
(*E*)-3-(2-Nitoxyphenyl)acryloyl fluoride (4j)

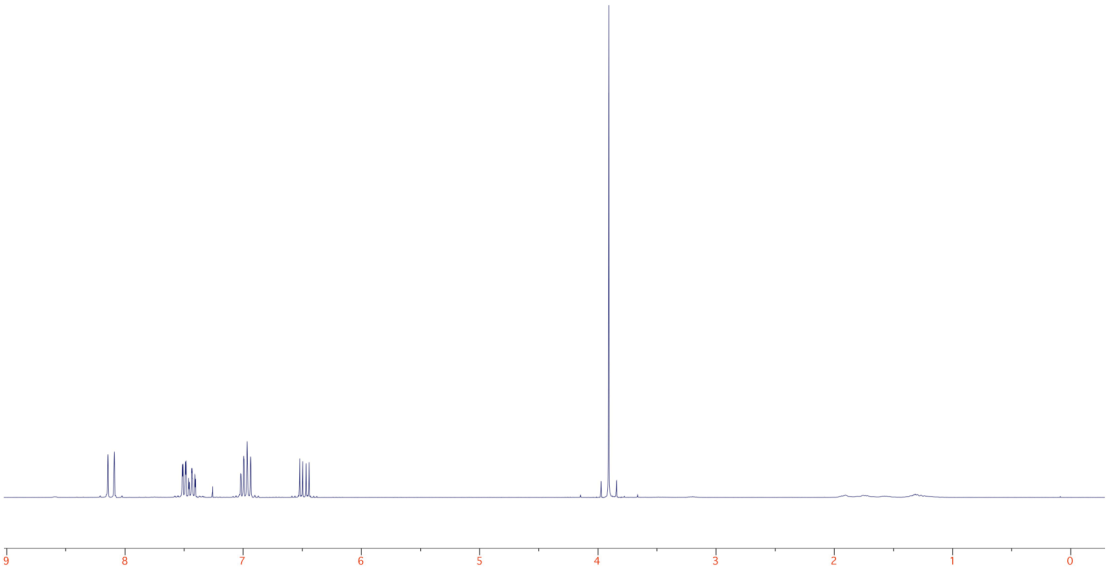


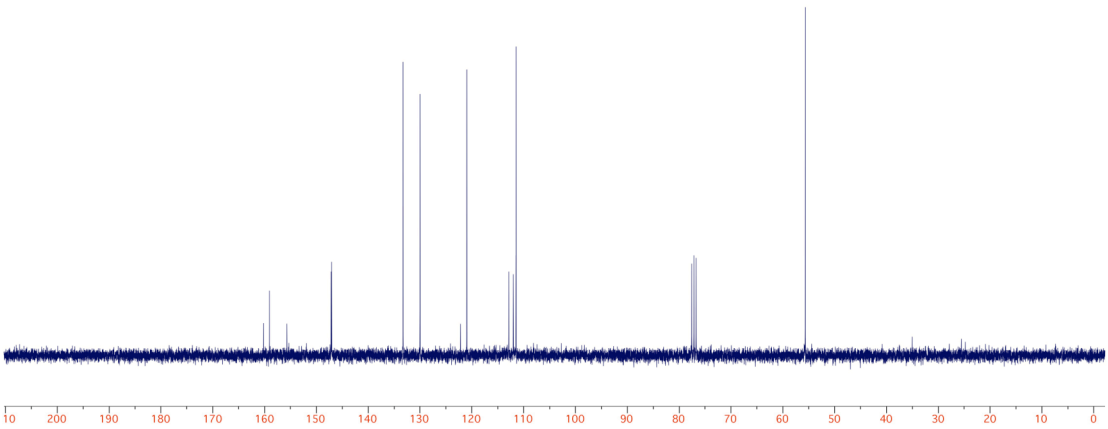




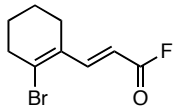
(*E*)-3-(2-Methoxyphenyl)acryloyl fluoride (4k)

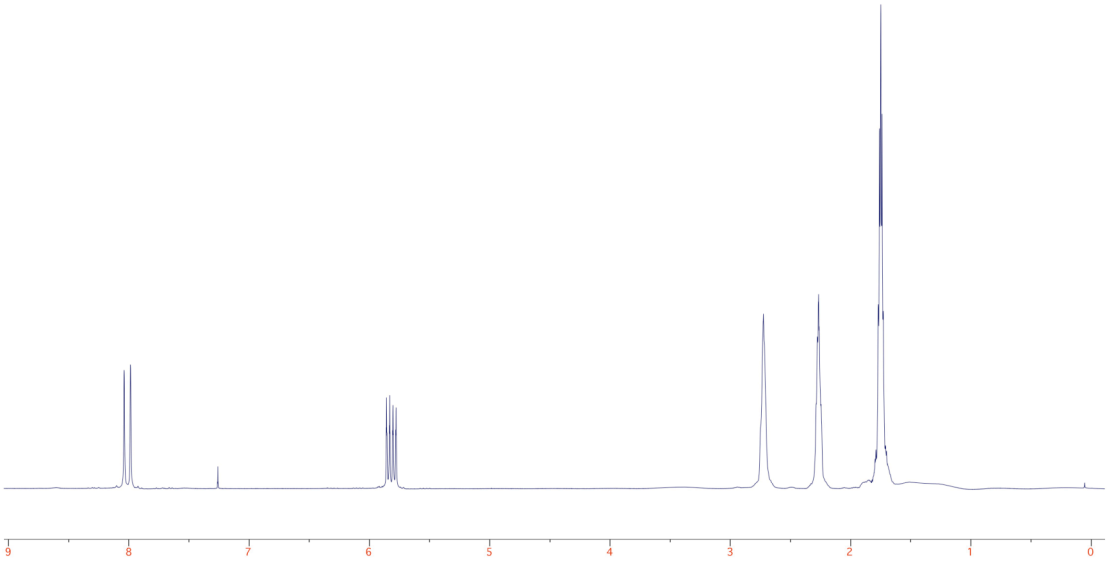


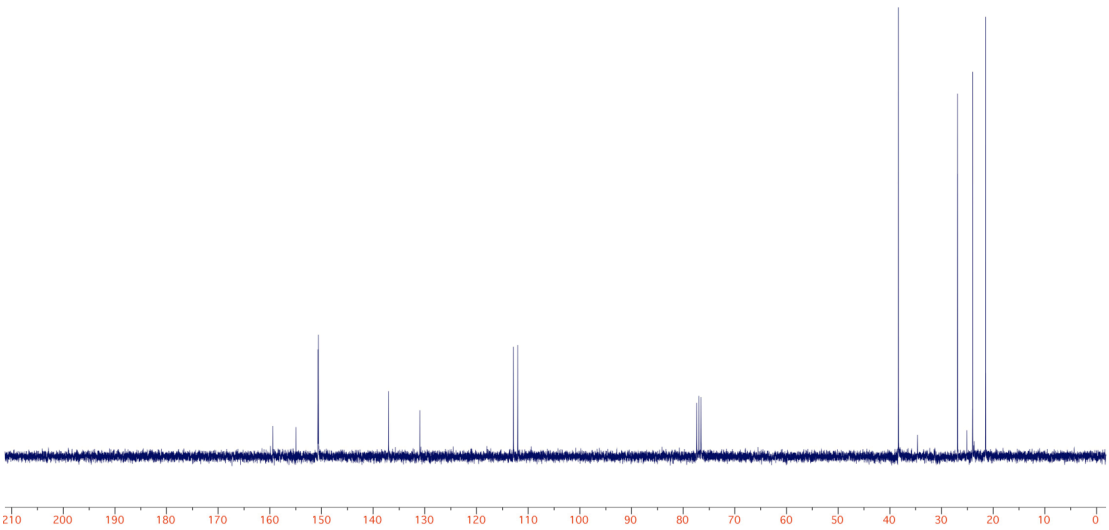




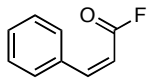
(*E*)-3-(2-Bromocyclohex-1-en-1-yl)acryloyl fluoride (4n)

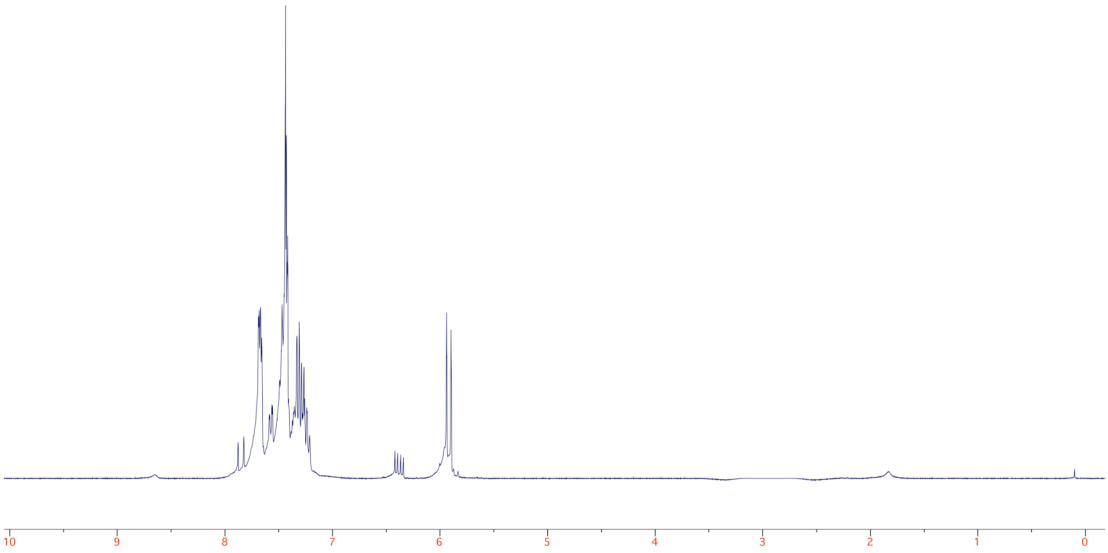


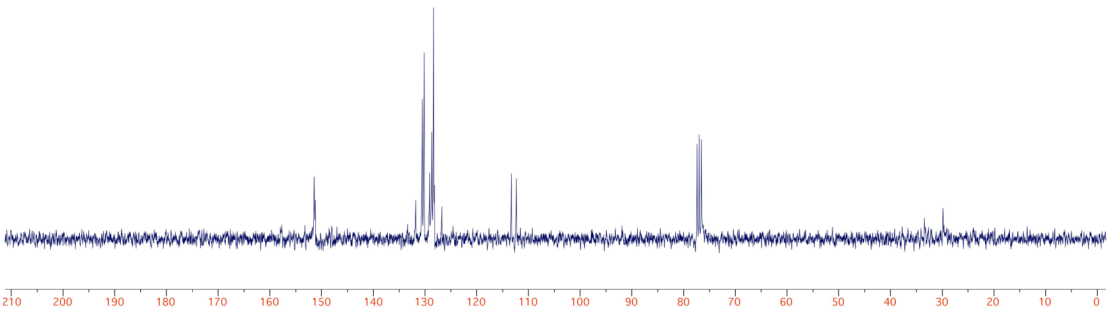




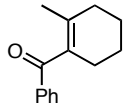
(*Z*)-Cinnamoyl fluoride (*cis*-4a)

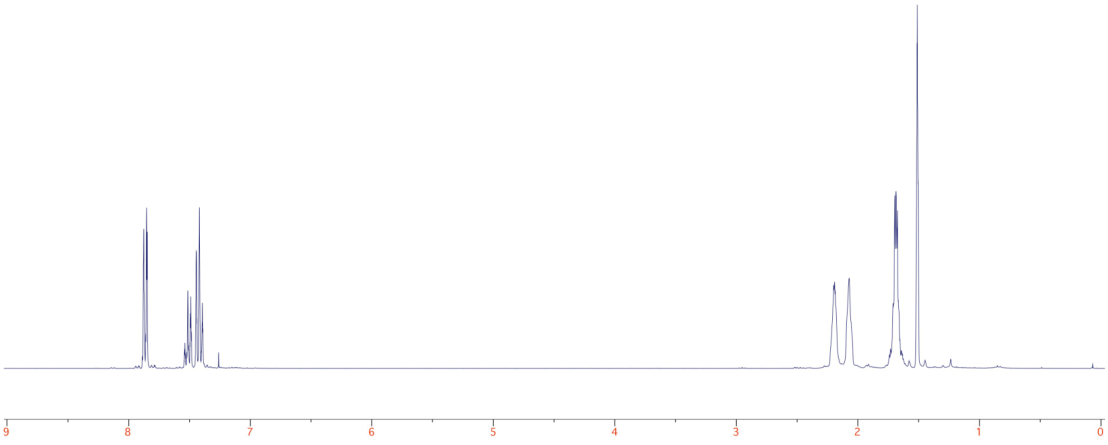


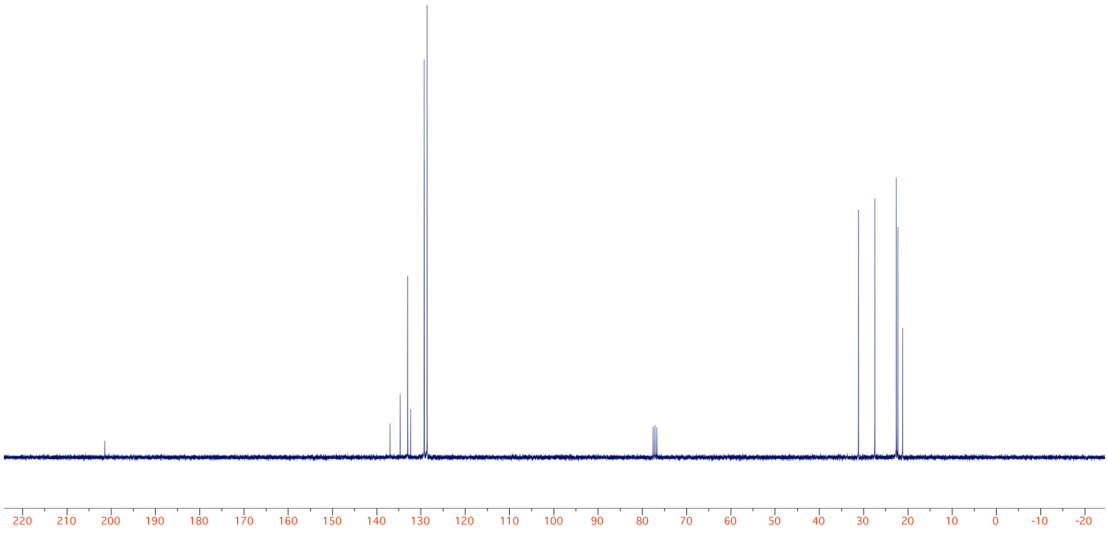




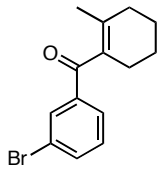
(2-Methylenecyclohex-1-en-1yl)(phenyl)methanone (11a)

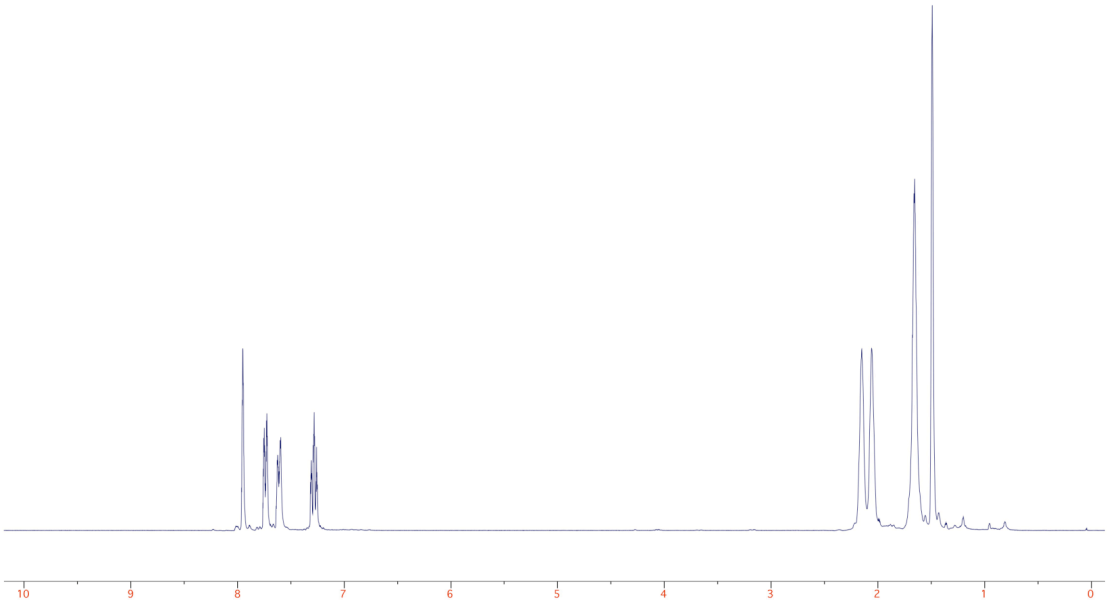


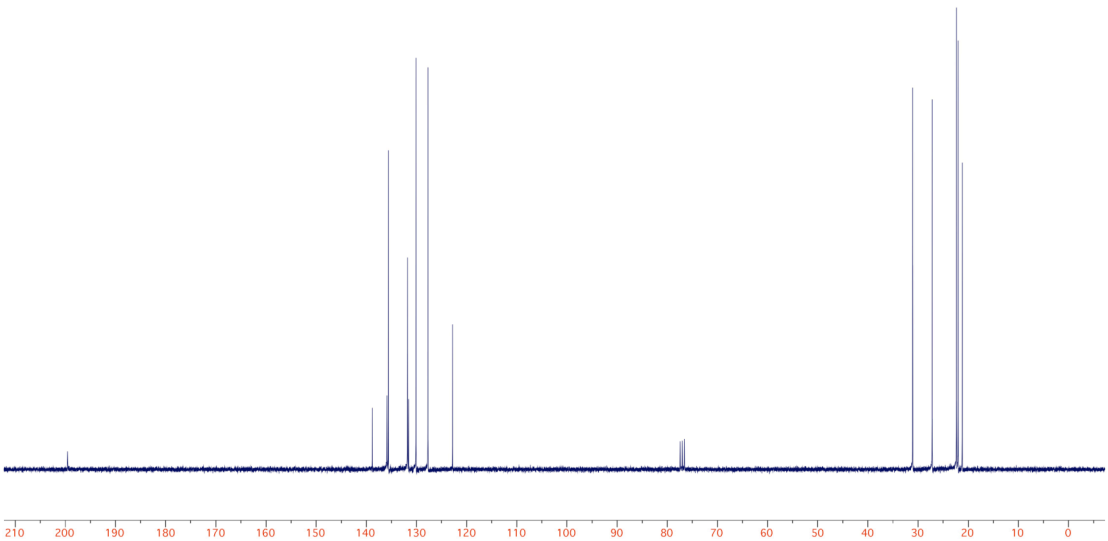




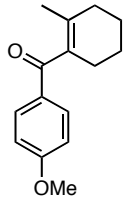
(3-Bromophenyl)(2-methylcyclohex-1-en-1yl)methanone (11b)

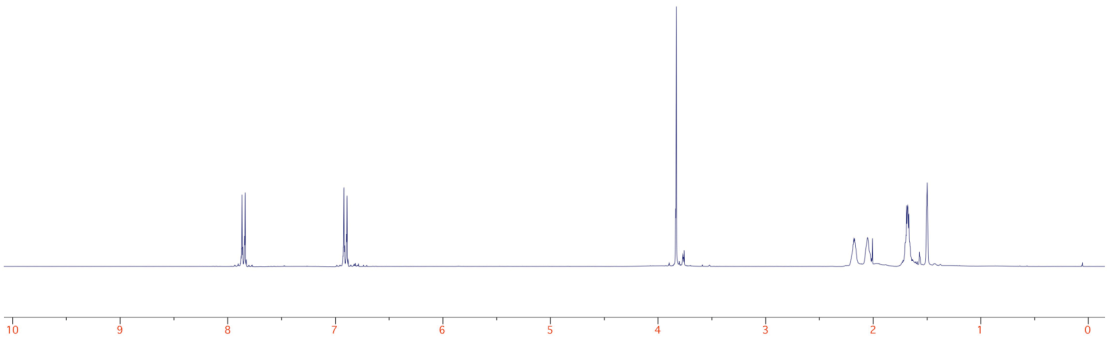


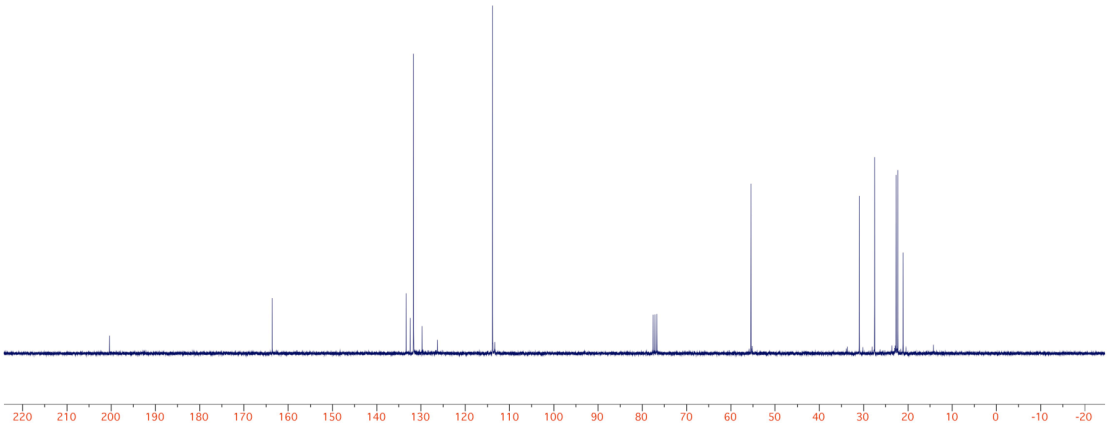




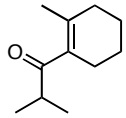
(4-Methoxyphenyl)(2-methylcyclohex-1-en-1yl)methanone (11c)

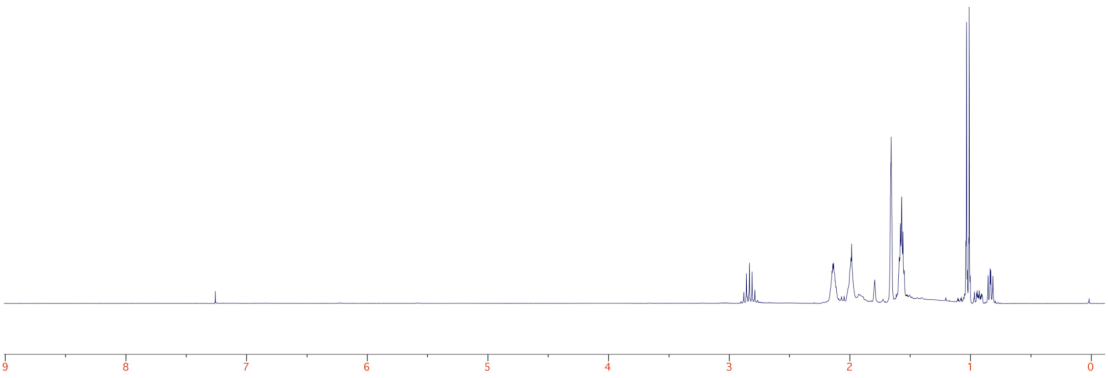


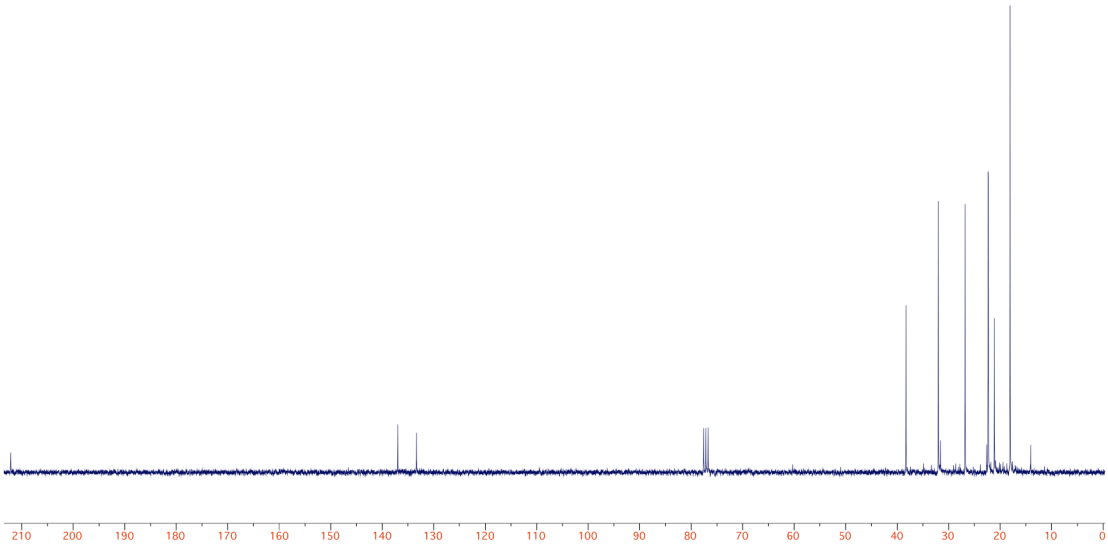




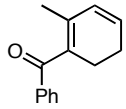
2-Methyl-1-(2-methylenecyclohex-1-en-1-yl)propan-1-one (11d)

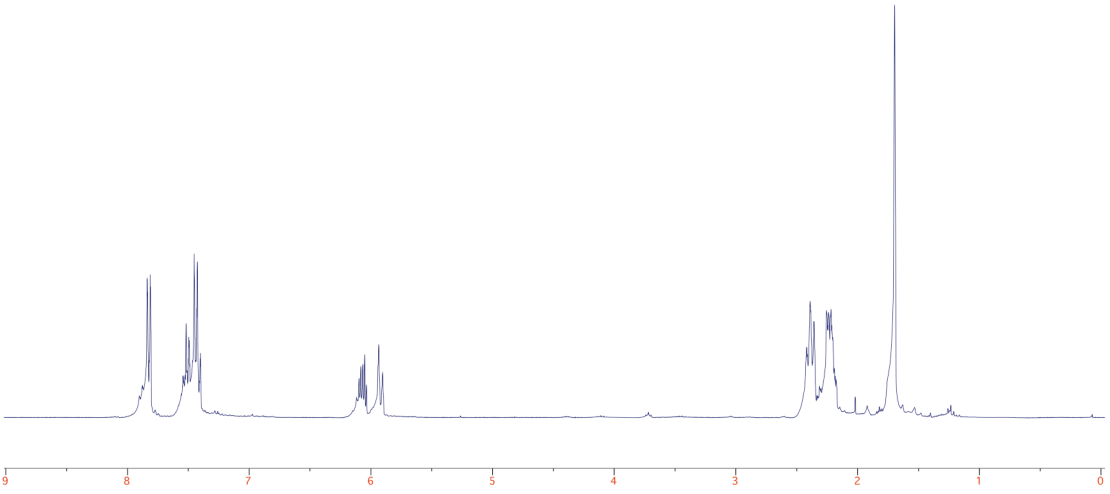


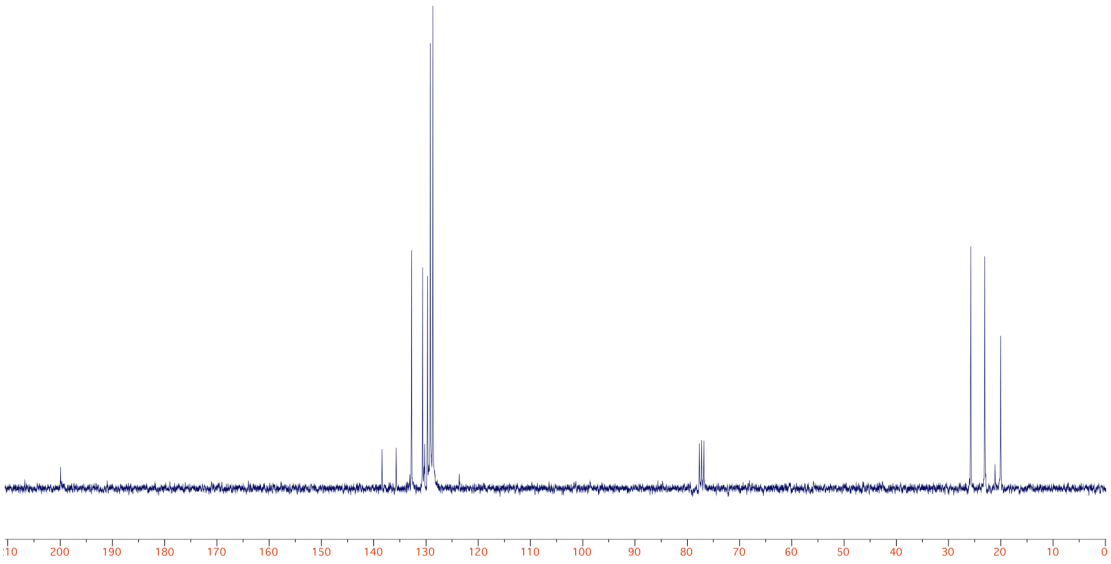




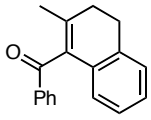
(2-Methylenecyclohex1-1,3-dien-1yl)(phenyl)methanone (11e)

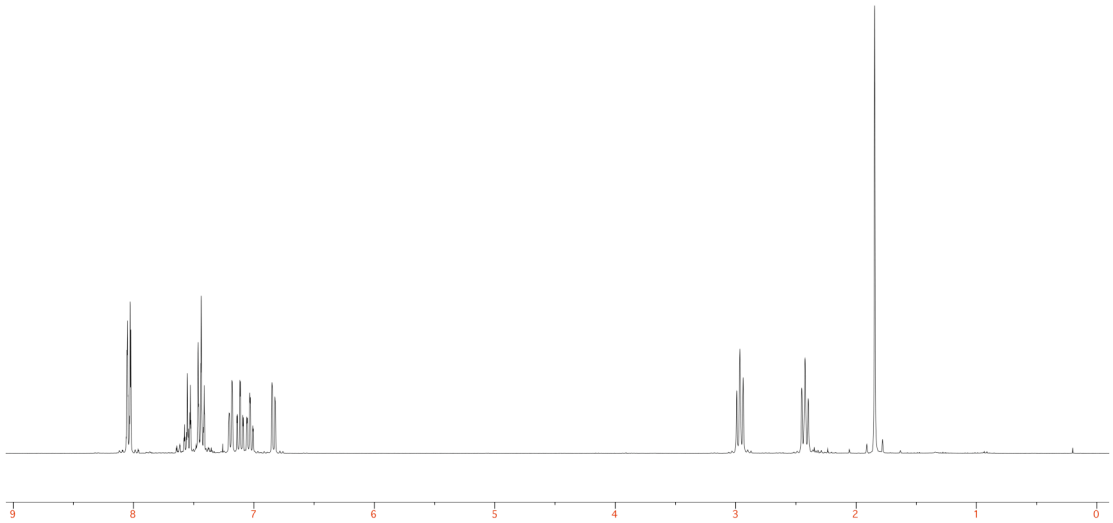


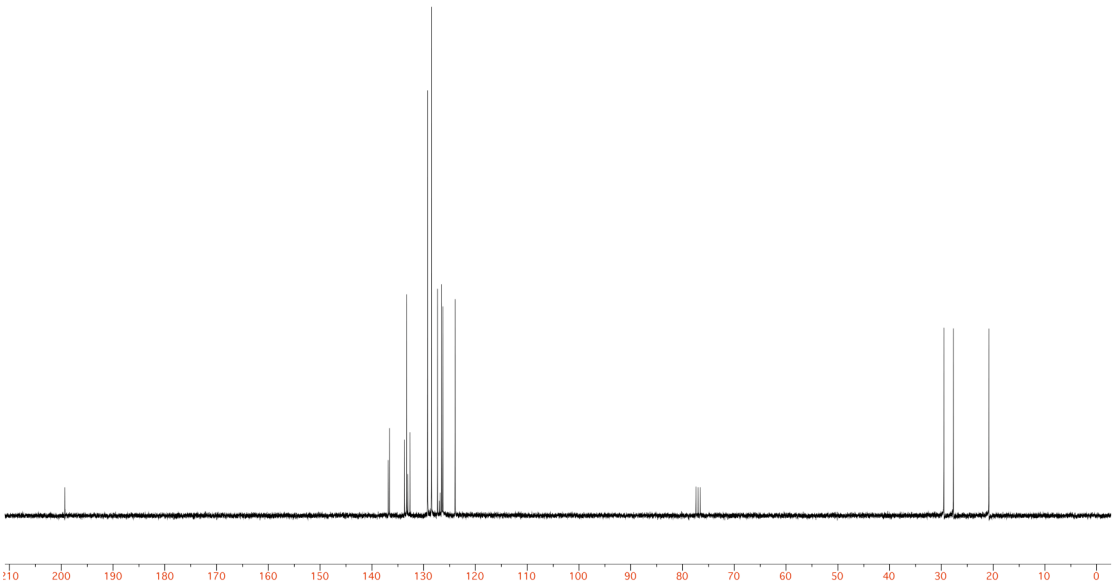




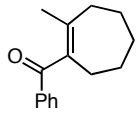
(2-Methyl-3,4-dihydronaphthalen-1-yl)(phenyl)methanone (11f)

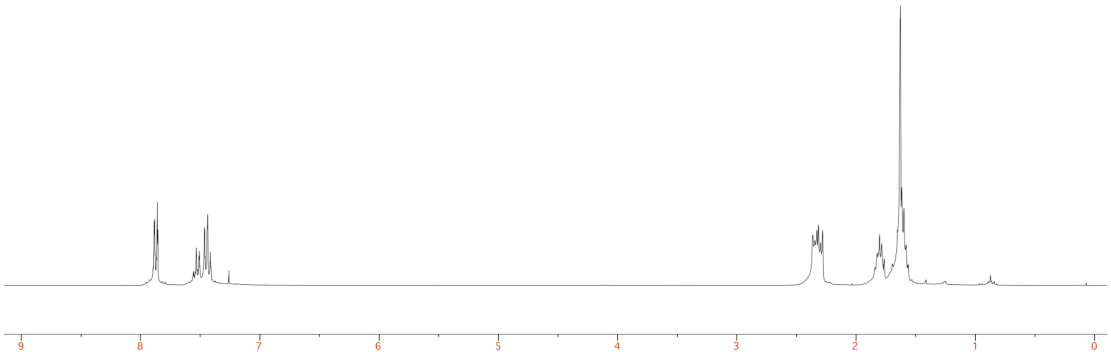


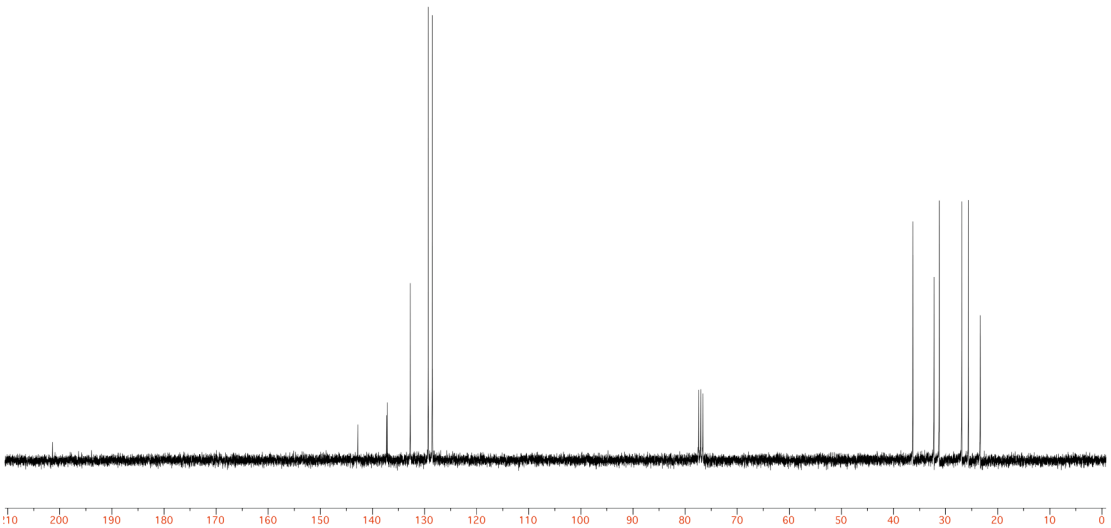




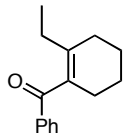
(2-Methylcyclohept-1-en-1-yl)(phenyl)methanone (11g)

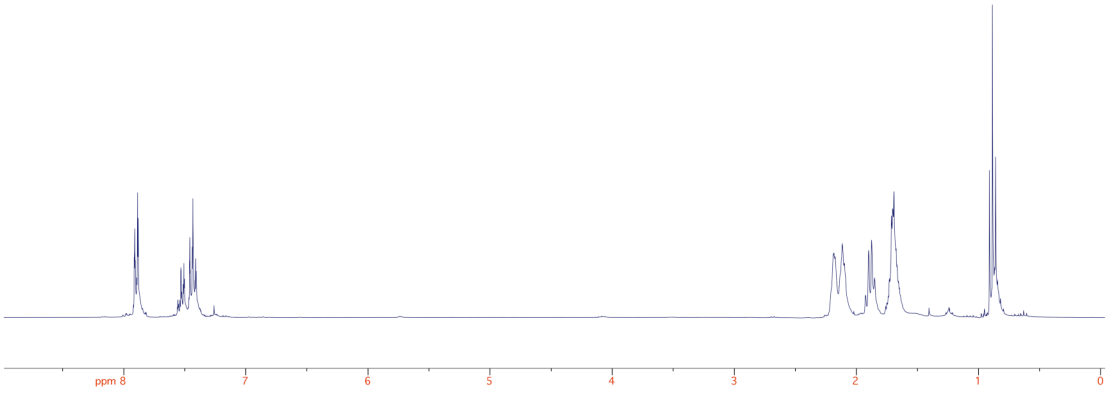


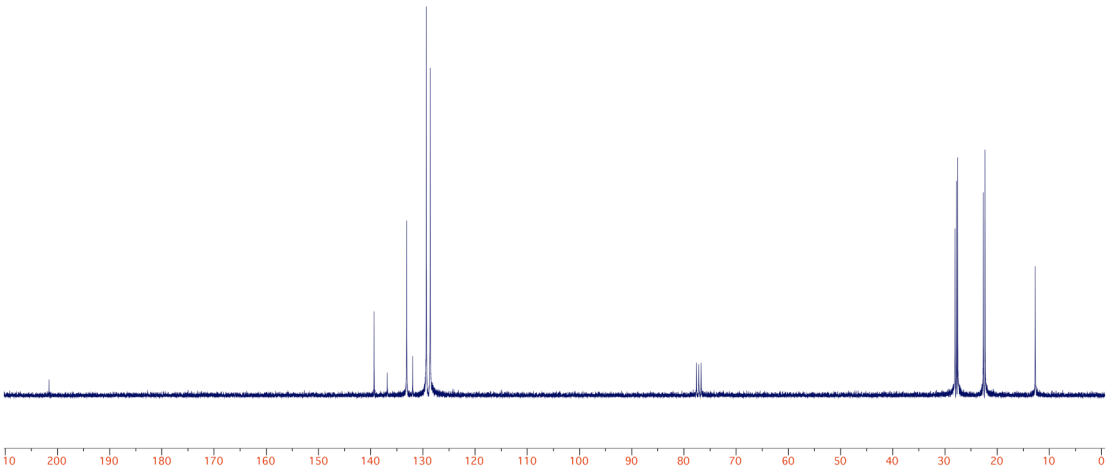




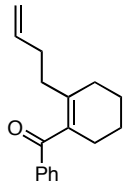
(2-ethylcyclohex-1-en-1-yl)(phenyl)methanone (11h)

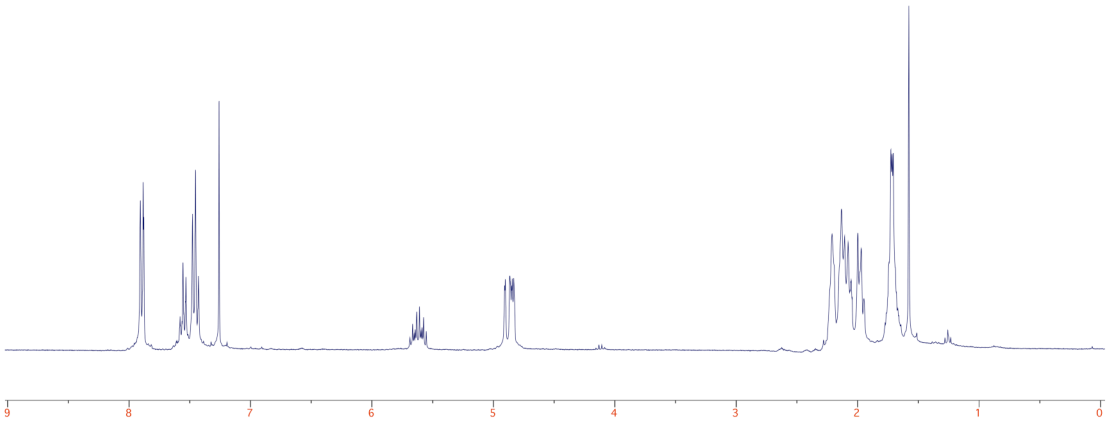


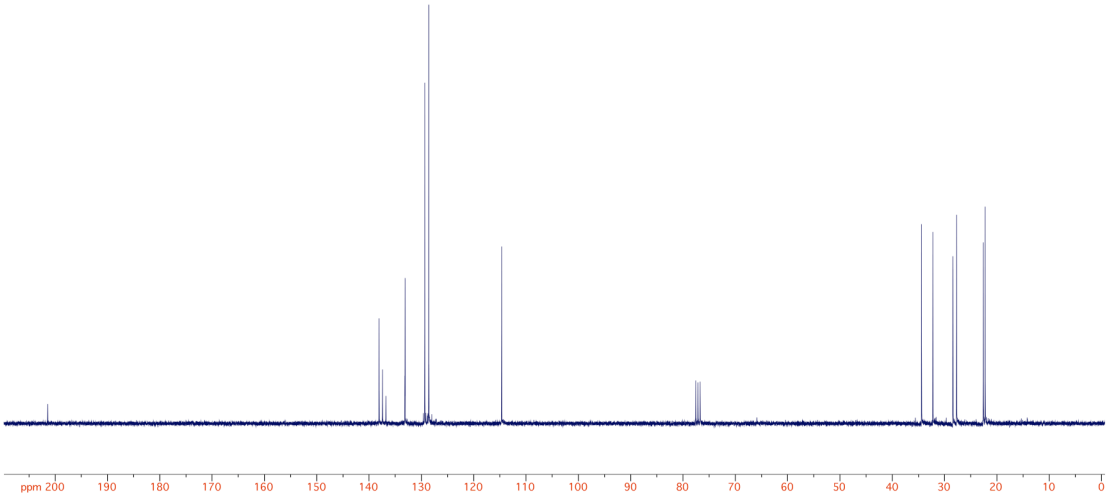




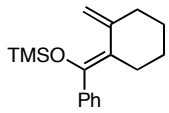
(2-Ethylcyclohex-1-en-1-yl)(phenyl)methanone (11i)

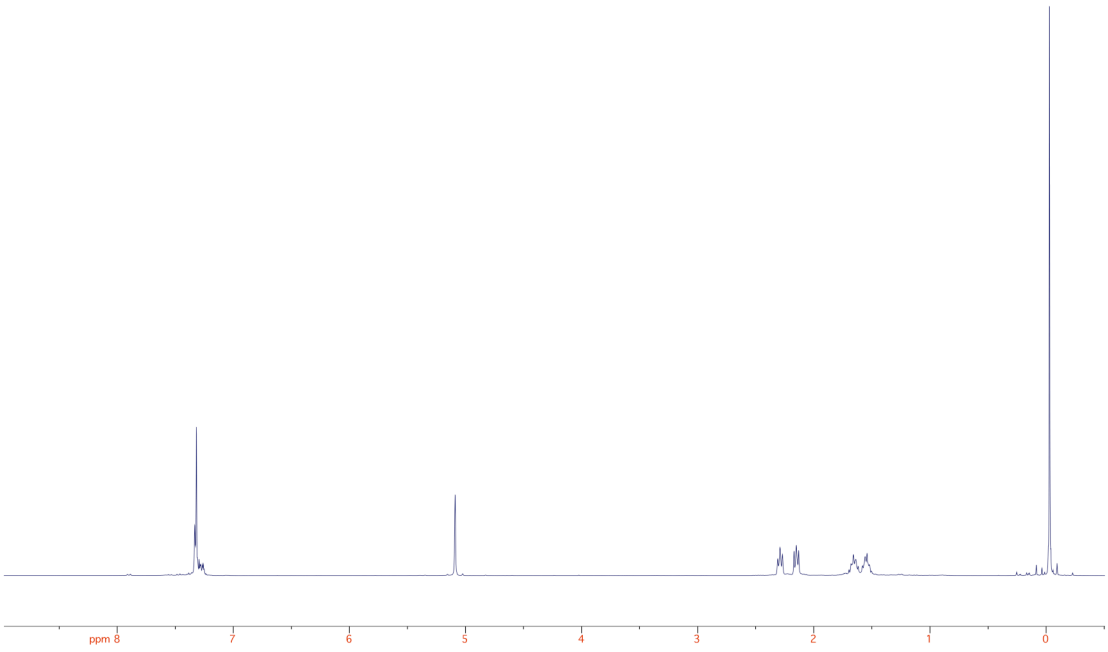


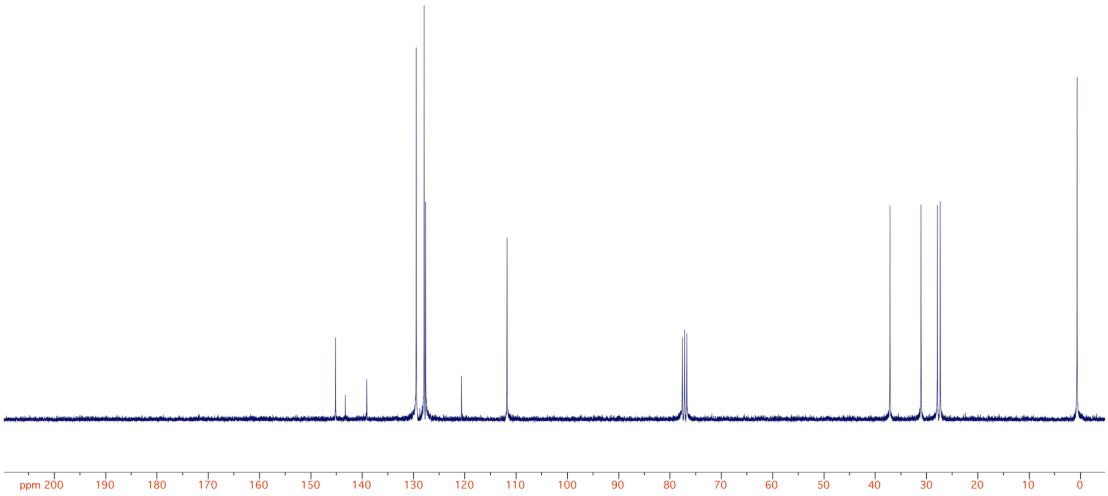




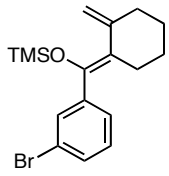
(*Z*)-Trimethyl((2-methylenecyclohexylidene)(phenyl)methoxy)silane (5a)

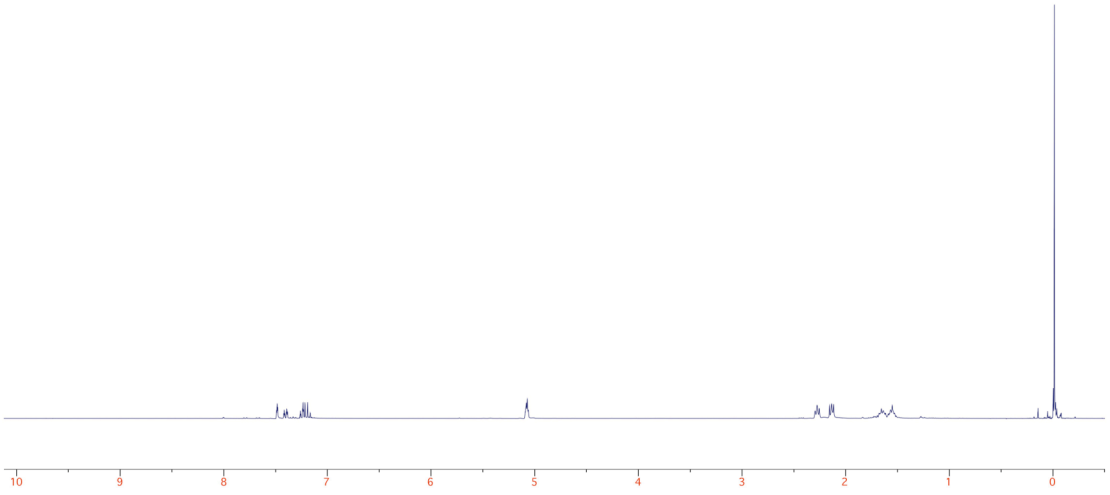


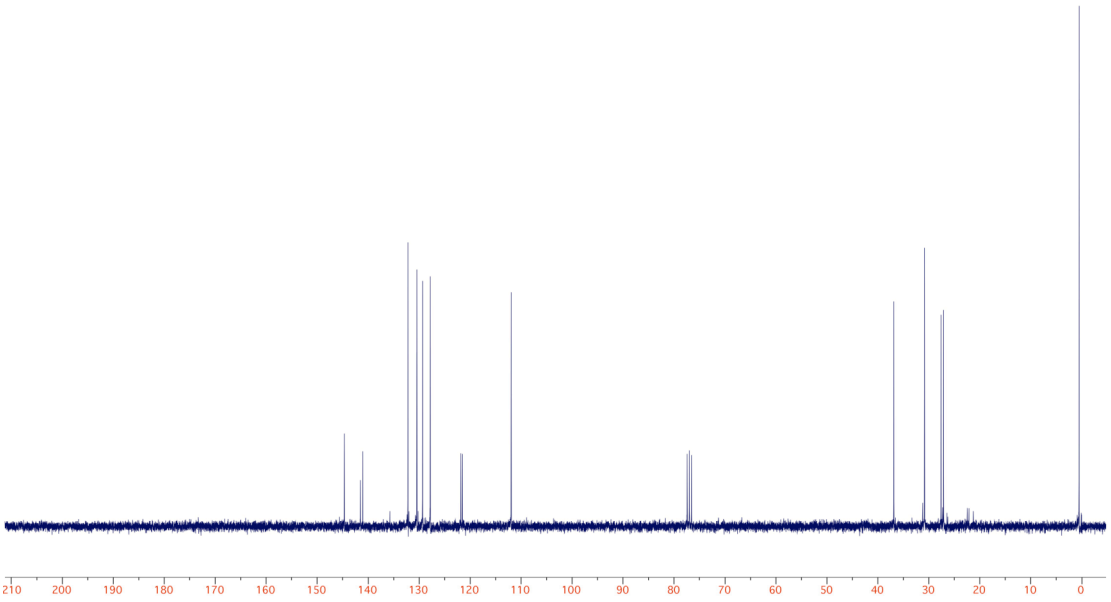




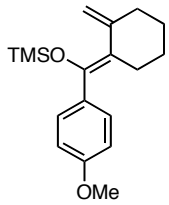
(*Z*)-((3-Bromophenyl)(2-methylenecyclohexylidene)methoxy)trimethylsilane (5b)

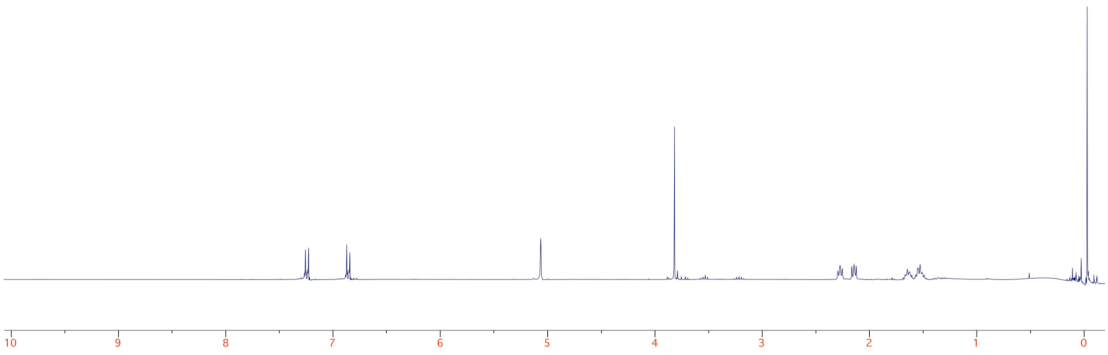


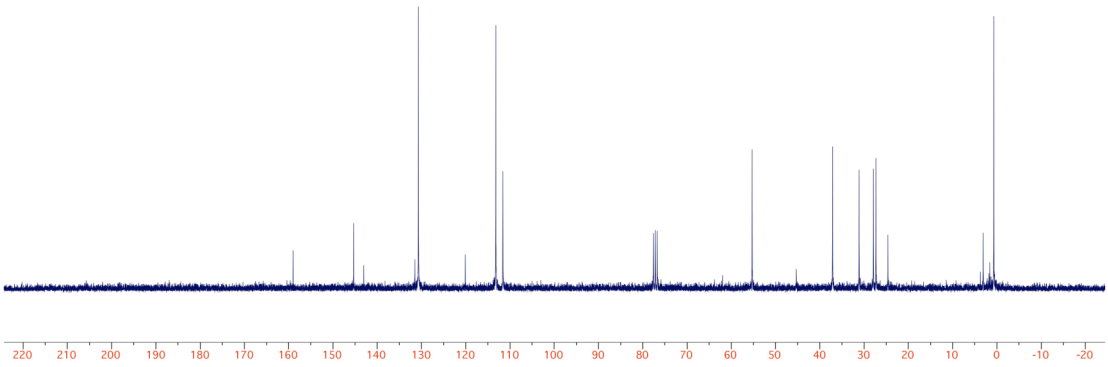




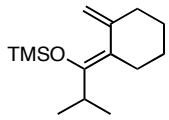
(*Z*)-((4-Methoxyphenyl)(2-methylenecyclohexylidene)methoxy)trimethylsilane (5c)

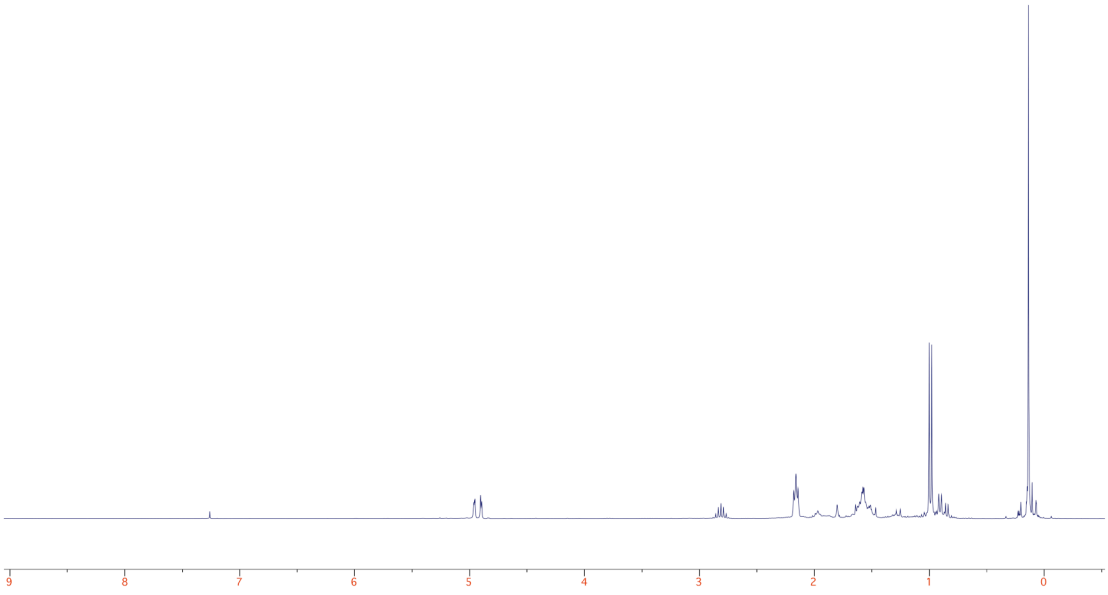


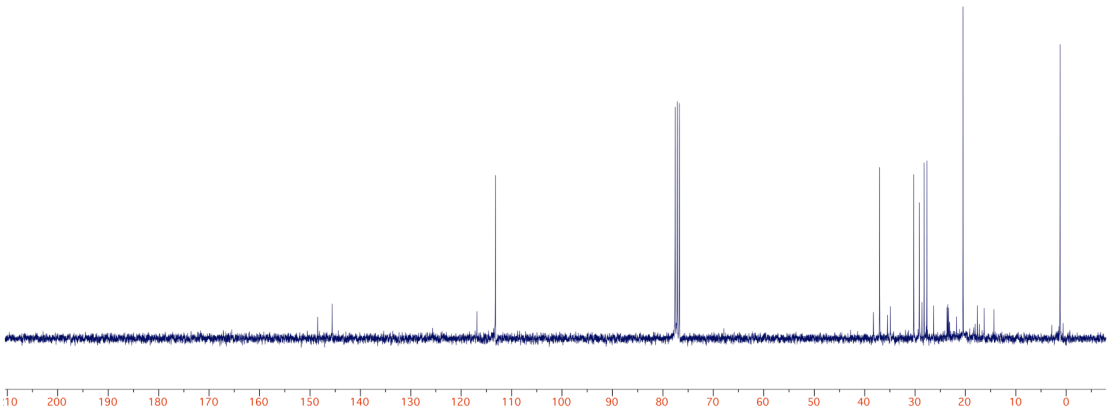




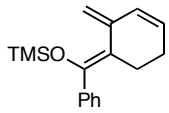
(*Z*)-Trimethyl(2-methylenecyclohexylidene)propoxy)silane (5d)

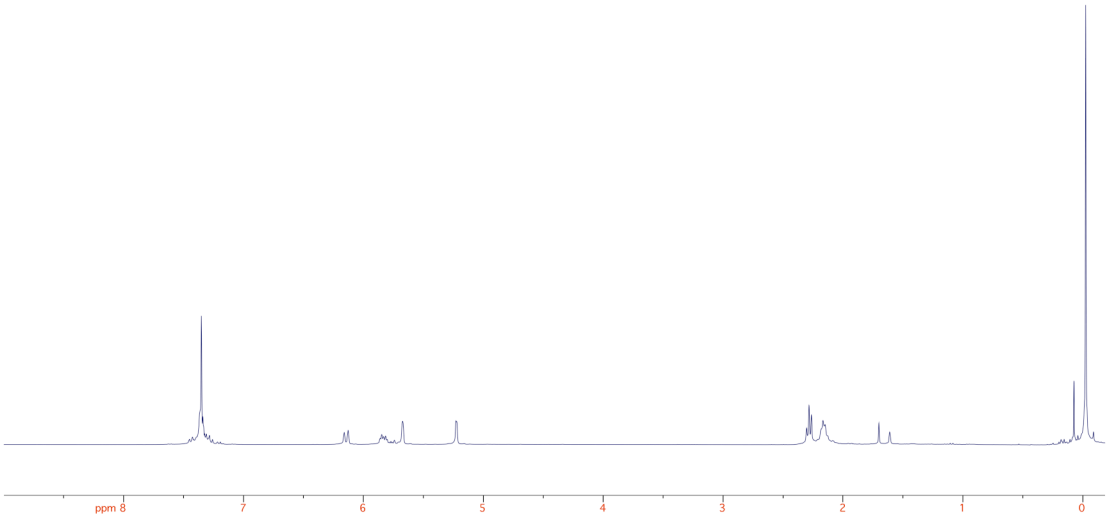


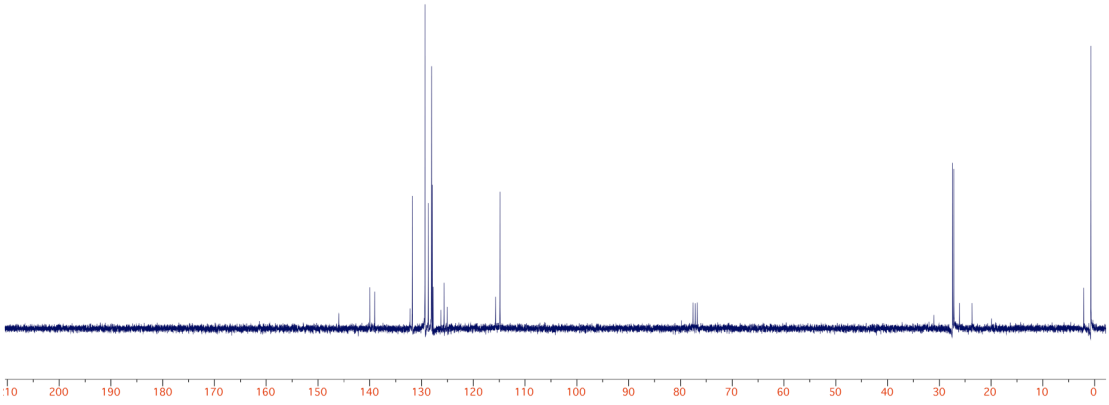




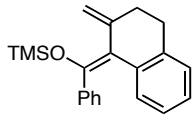
(*Z*)-Trimethyl((2-methylenecyclohex-3-en-1-ylidene)(phenyl)methoxy)silane (5e)

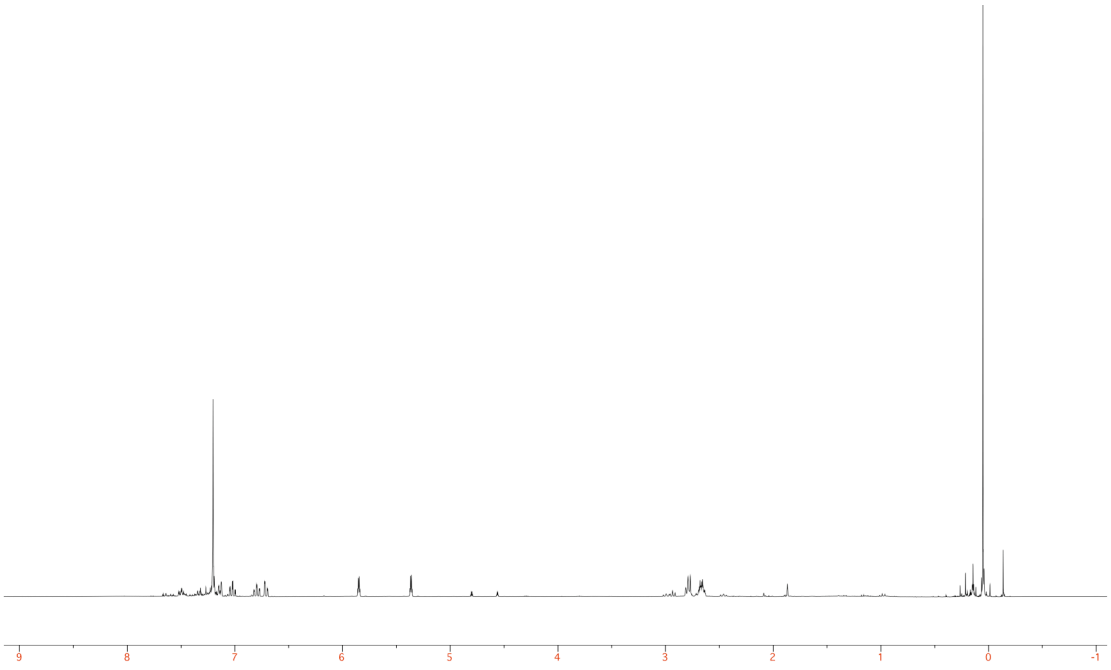




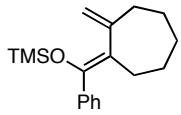


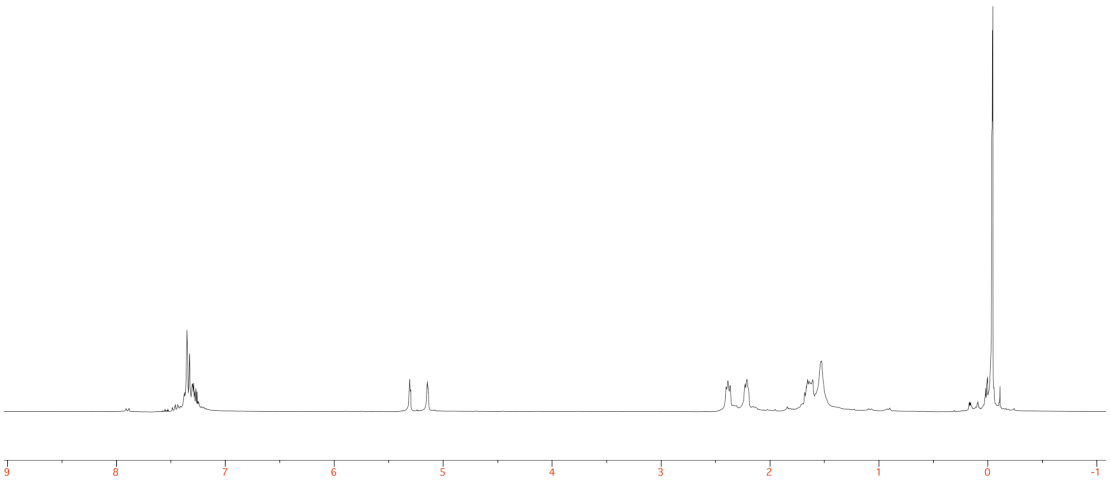
(*E*)-Trimethyl((2-methylene-3,4-dihydronaphthalen-1(2H)-ylidene)(phenyl)methoxy)silane (5f)

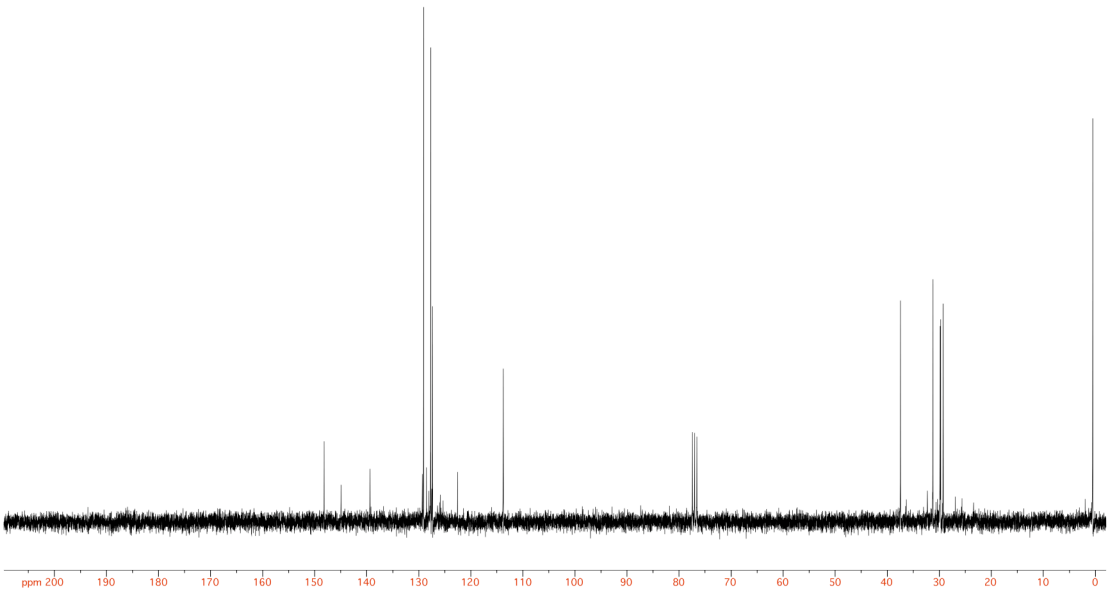




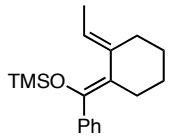
(*Z*)-Trimethyl((2-methylenecycloheptylidene)(phenyl)methoxy)silane (5g)

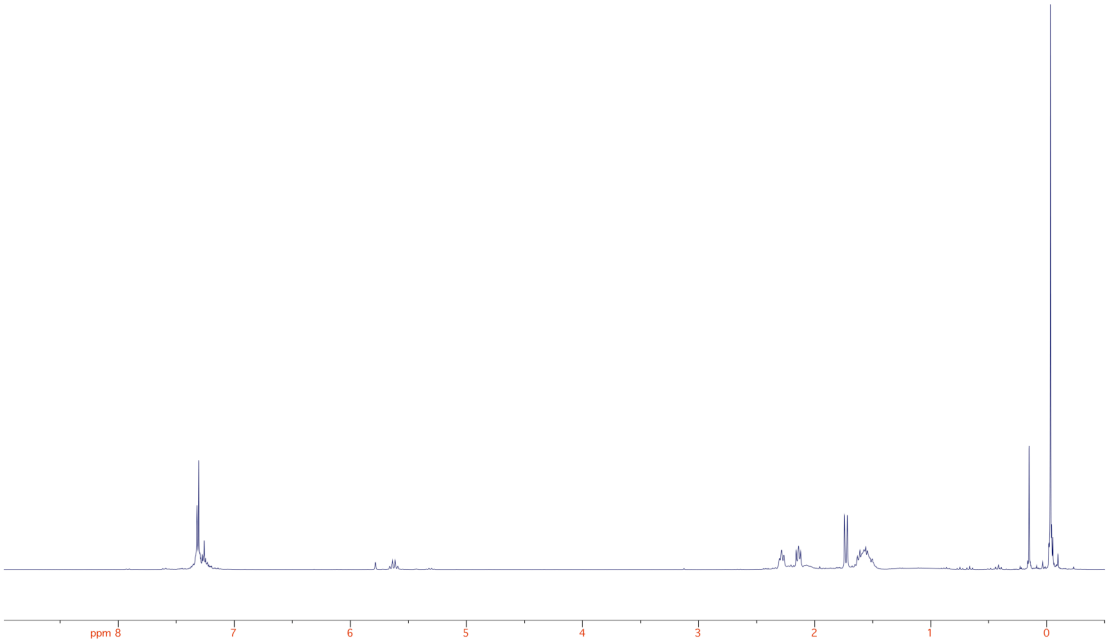


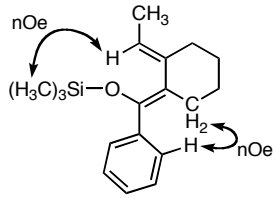




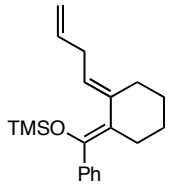
((*Z*)-((*E*)-2-Ethylideneclohexylidene(phenyl)methoxy)trimethylsilane (5h)

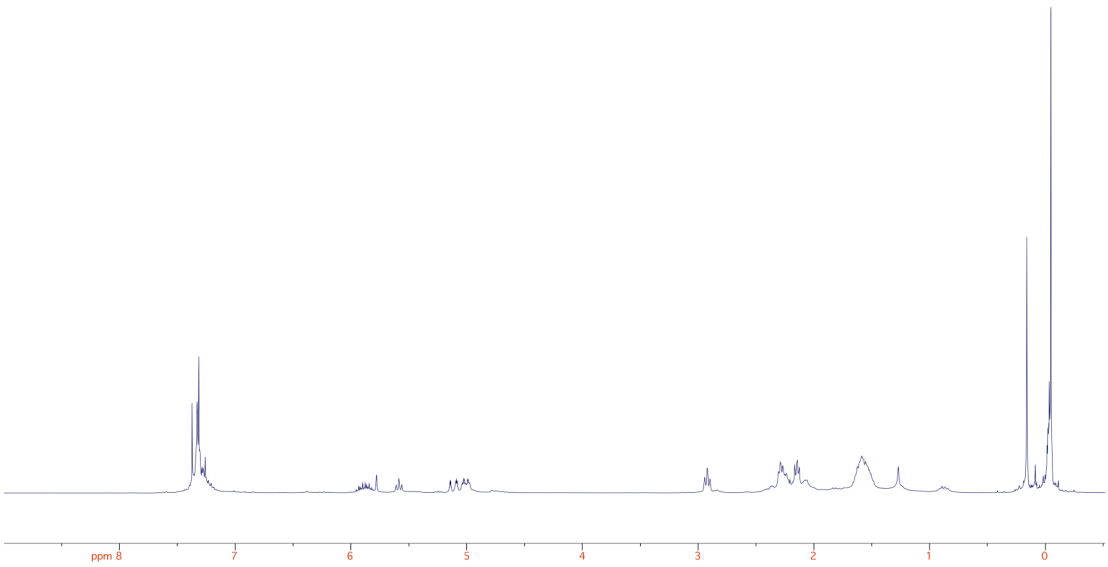




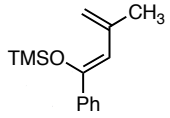


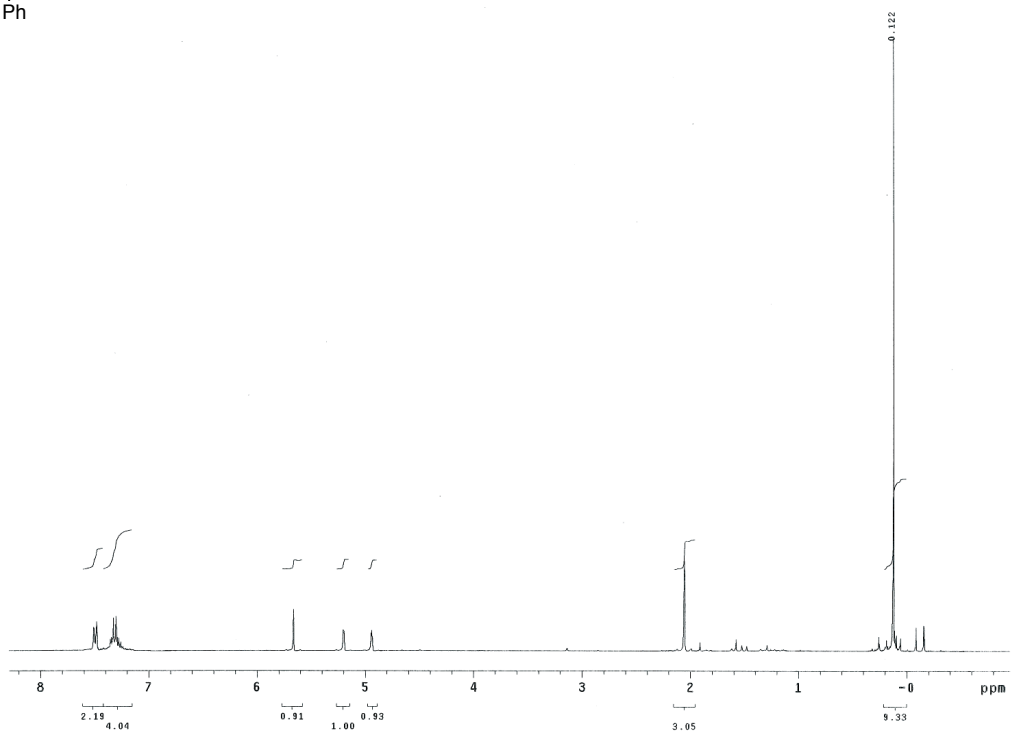
((*Z*)-((*E*)-2-(But-3-en-1-ylidene)cyclohexylidene)(phenyl)methoxy)trimethylsilane (5i)

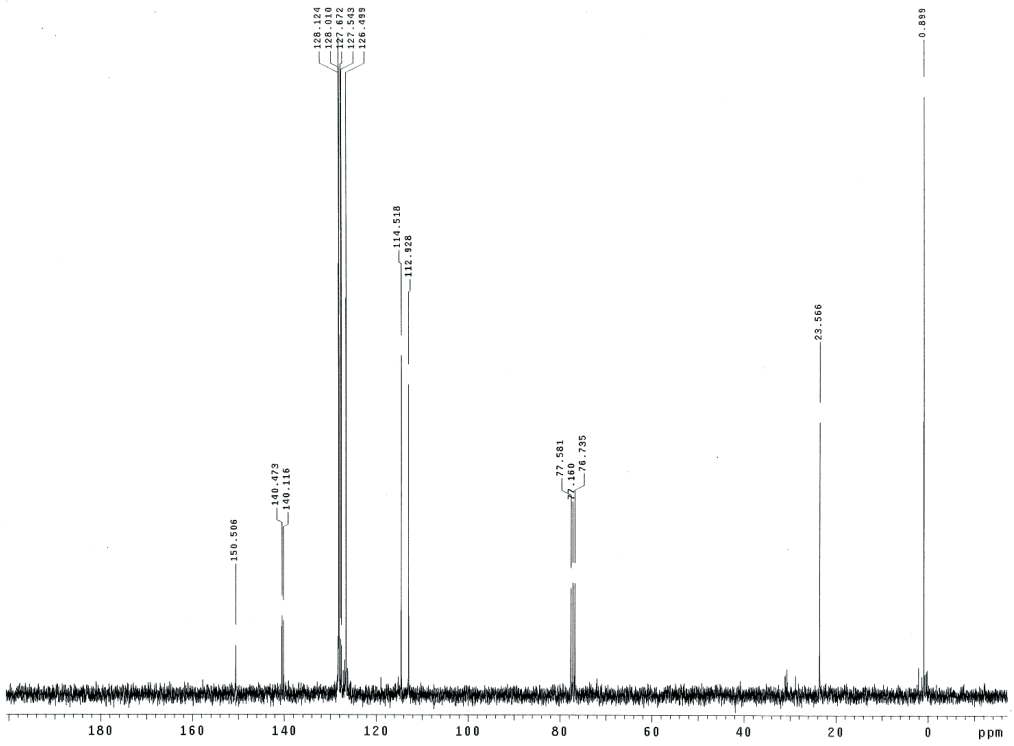




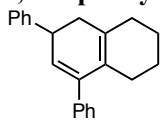
(*Z*)-Trimethyl((3-methyl-1-phenylbuta-1,3-dien-1-yl)oxy)silane

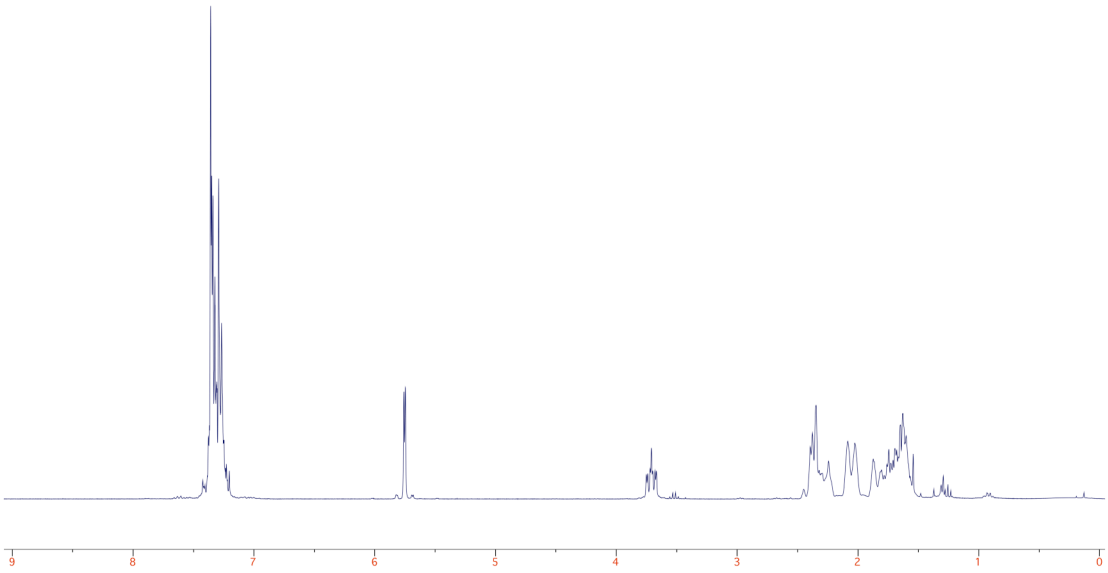


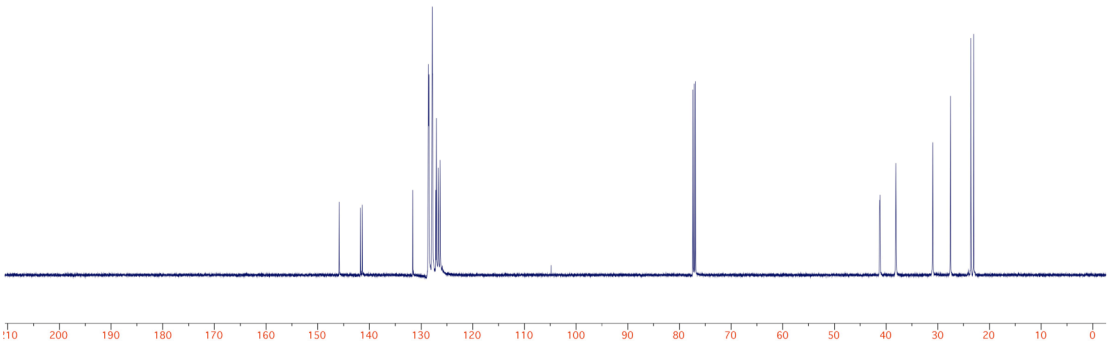




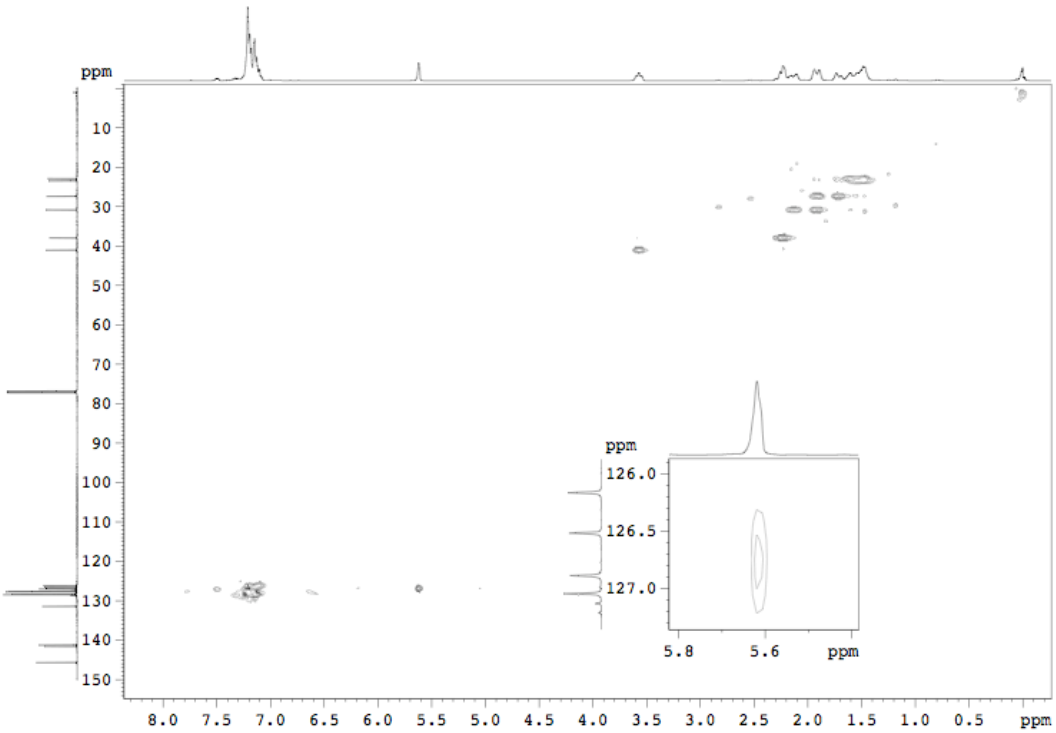
6,8-Diphenyl-1,2,3,4,5,6-hexahydronaphthalene (3a)



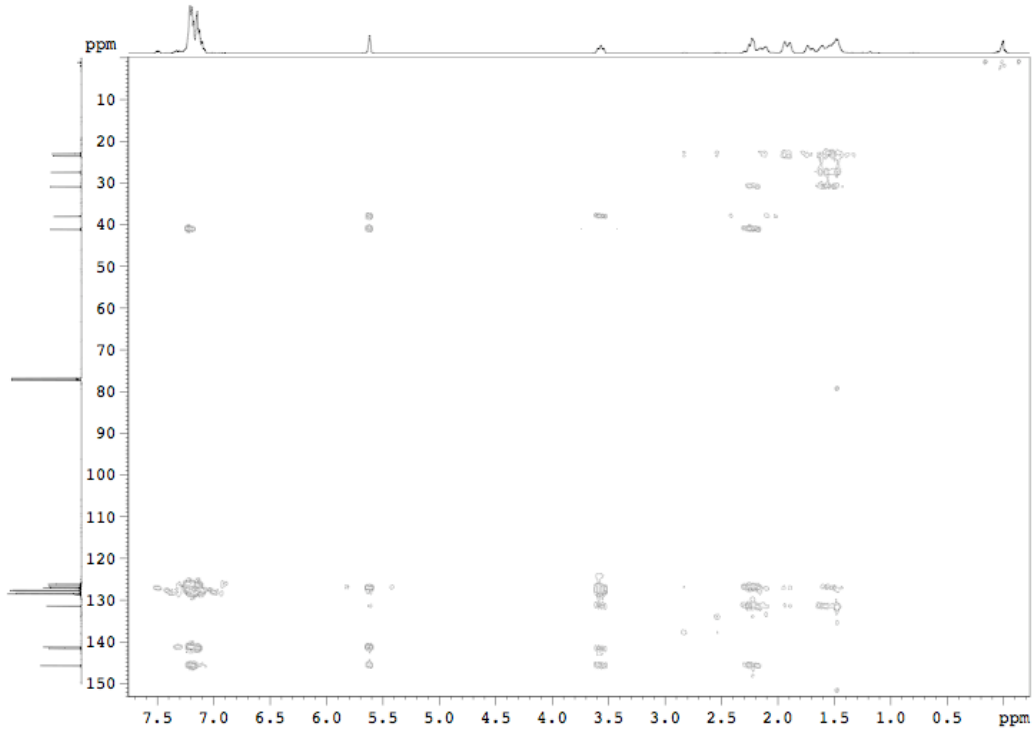




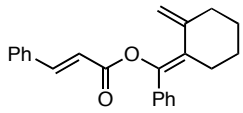
HSQC analysis of 3a

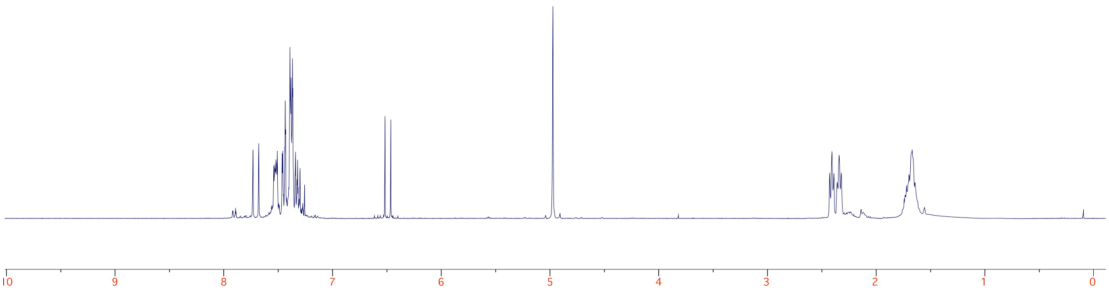


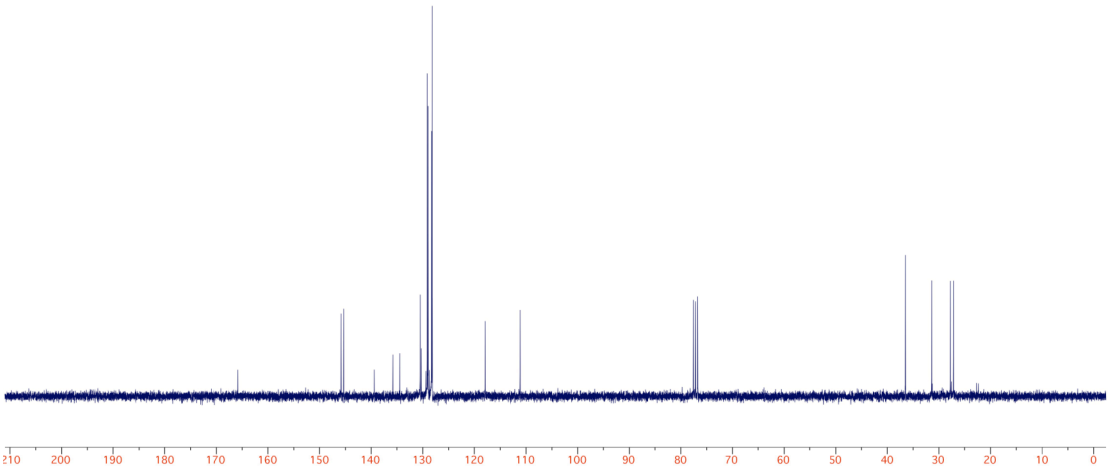
HMBC analysis of 3a



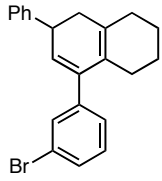
(*Z*)-(2-Methylenecyclohexylidene)(phenyl)methyl cinnamate (6a)

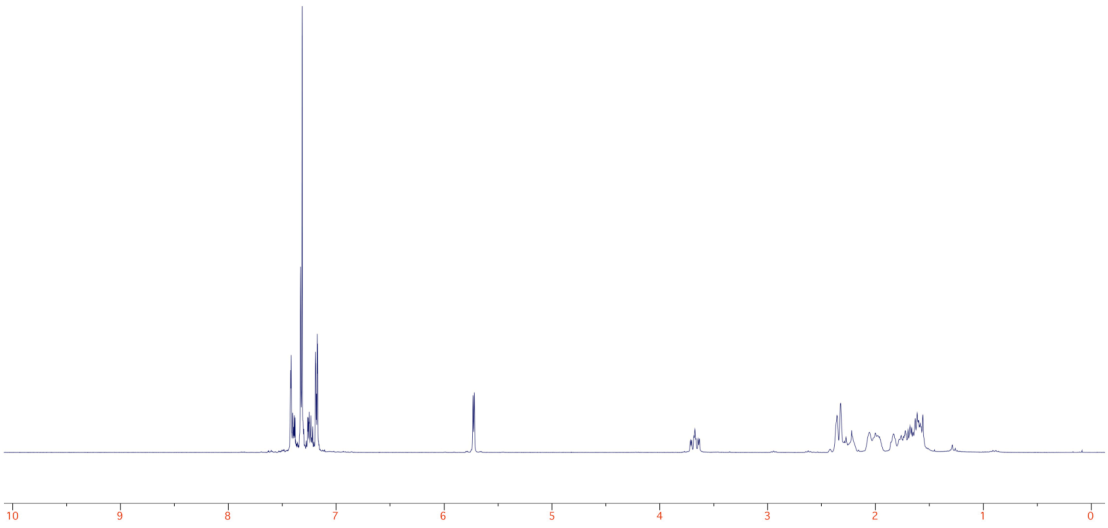


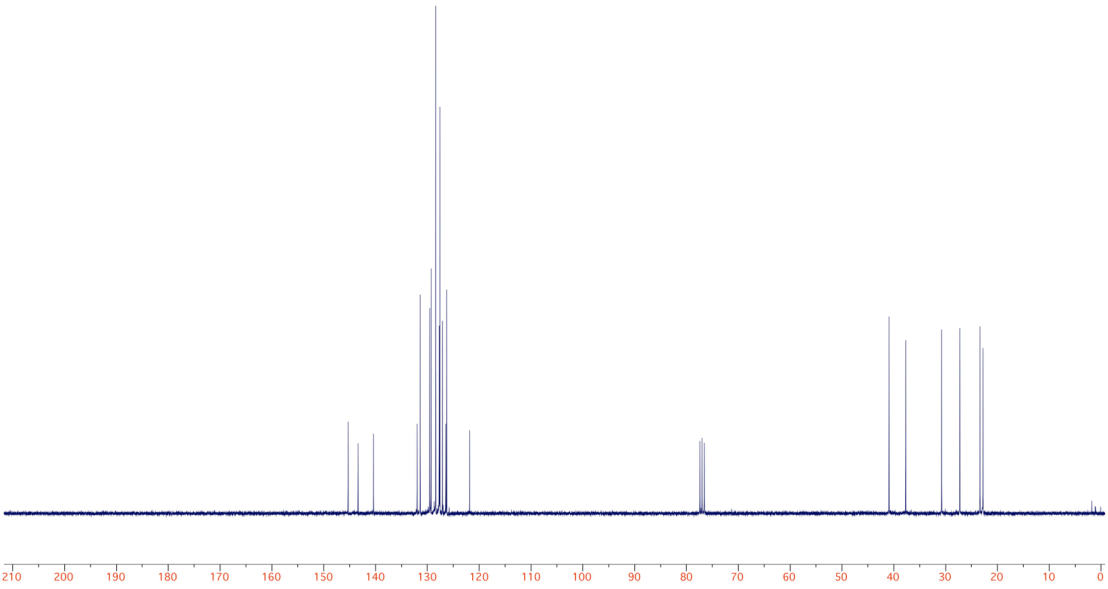




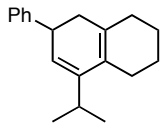
8-(3-Bromophenyl)-6-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3b)

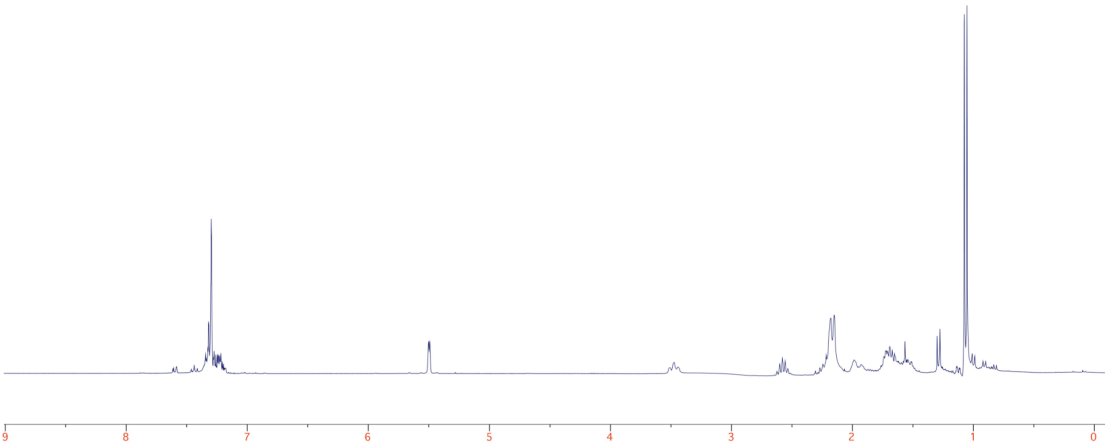


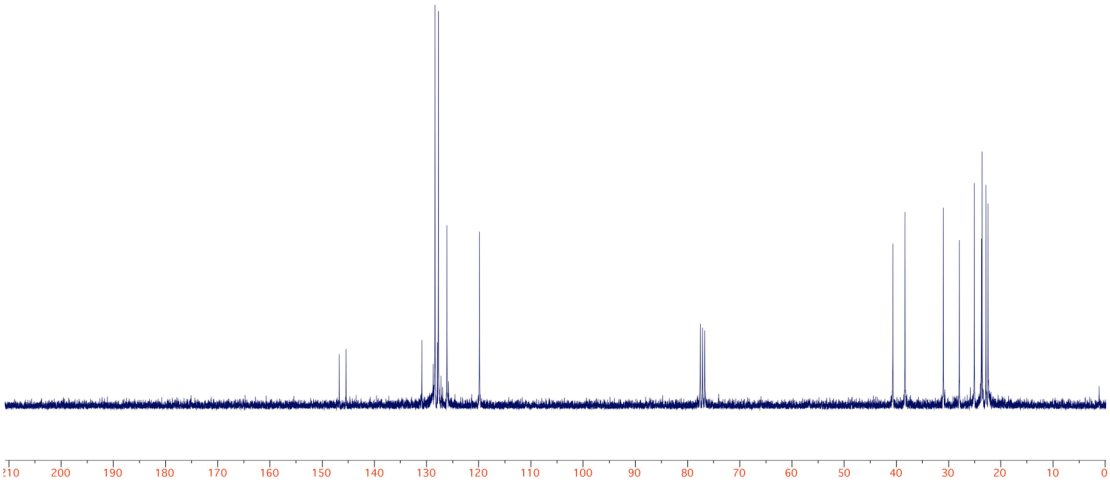




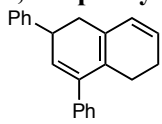
8-Isopropyl-6-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3d)

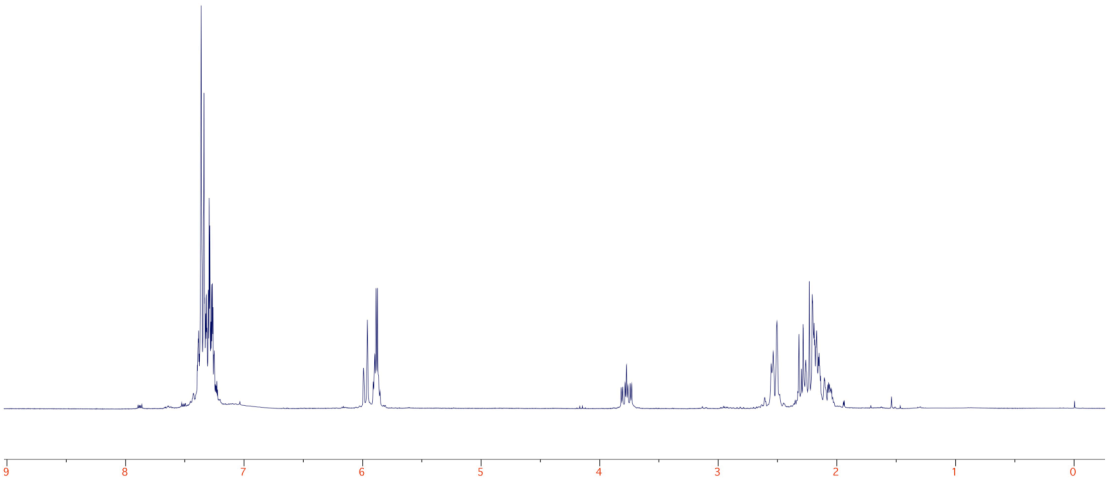


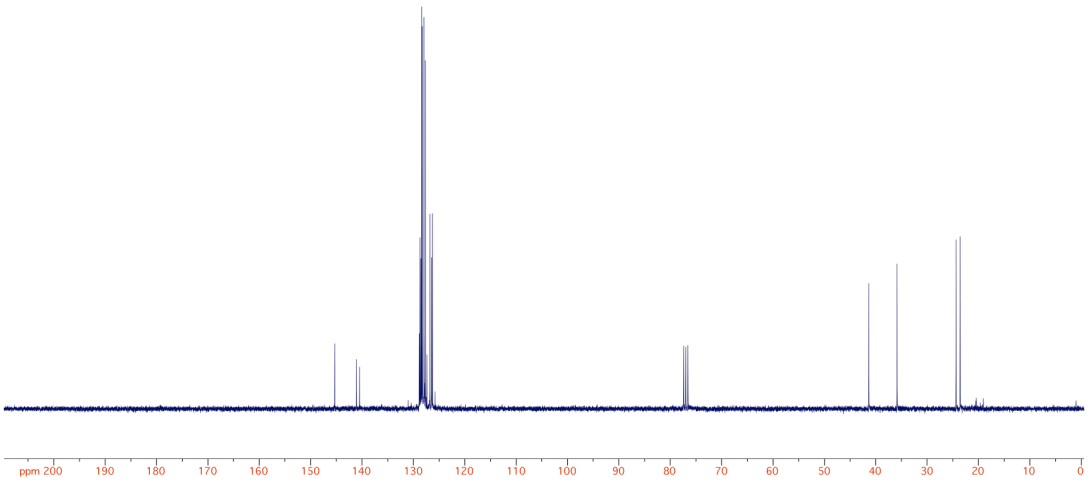




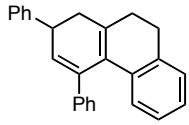
2,4-Diphenyl-1,2,5,6-tetrahydronapthalene (3e)

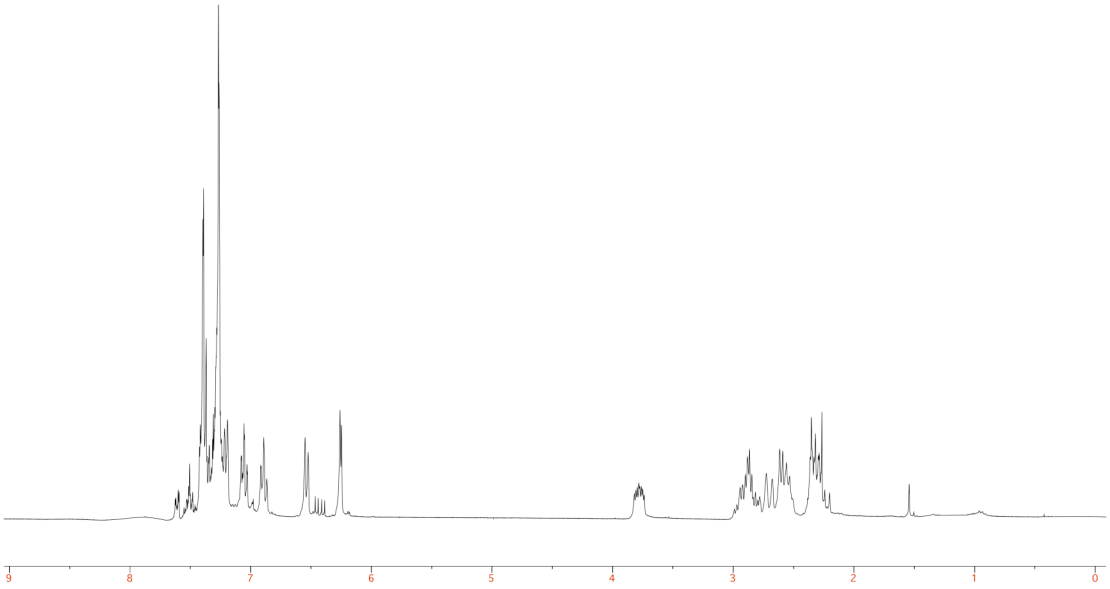


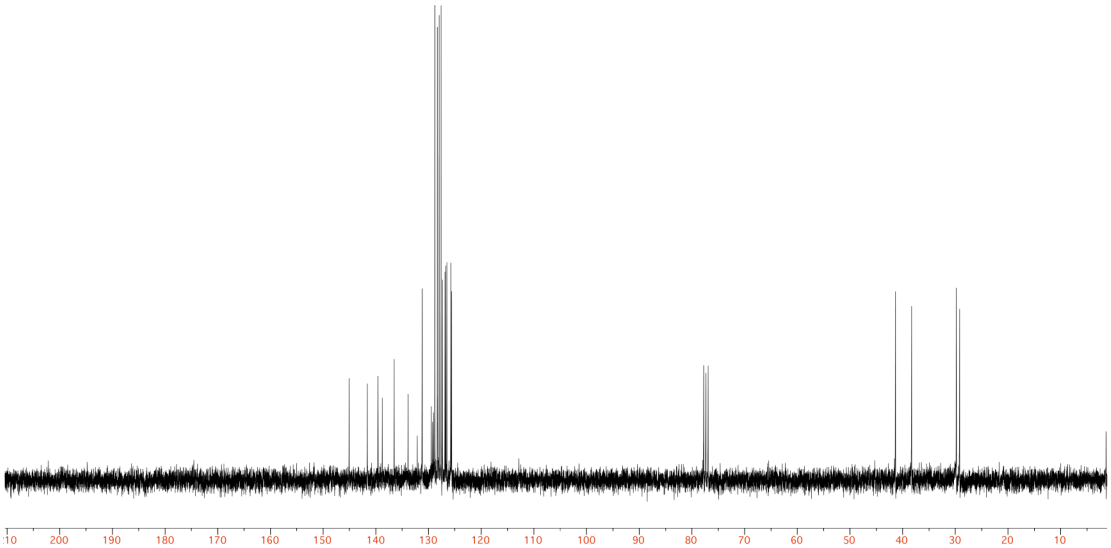




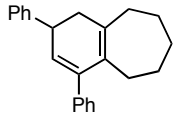
2,4-Diphenyl-1,2,9,10-tetrahydrophenanthrene (3f)

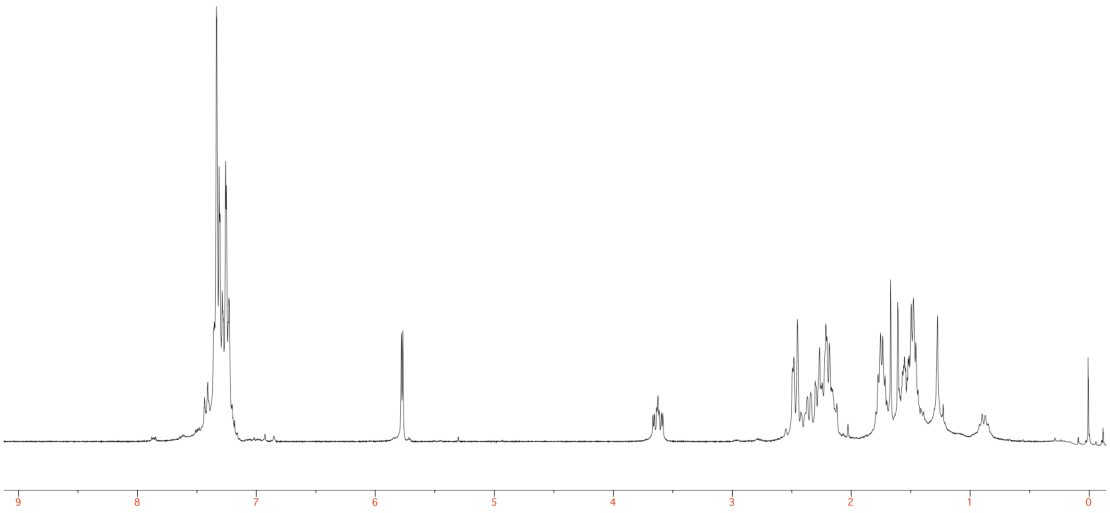


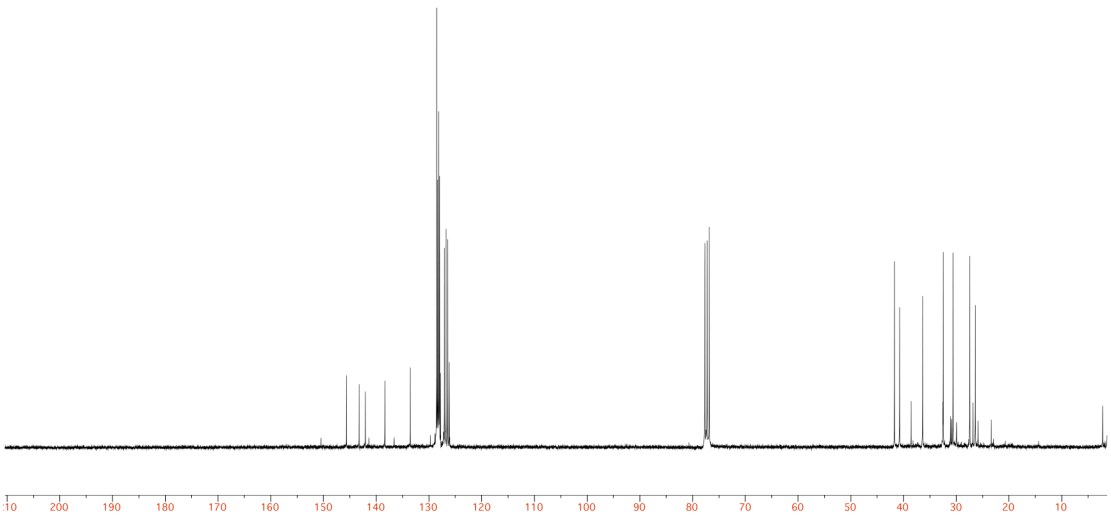




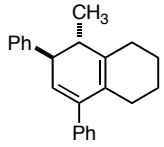
2,4-Diphenyl-2,5,6,7,8,9-hexahydro-1H-benzo[7]annulene (3g)

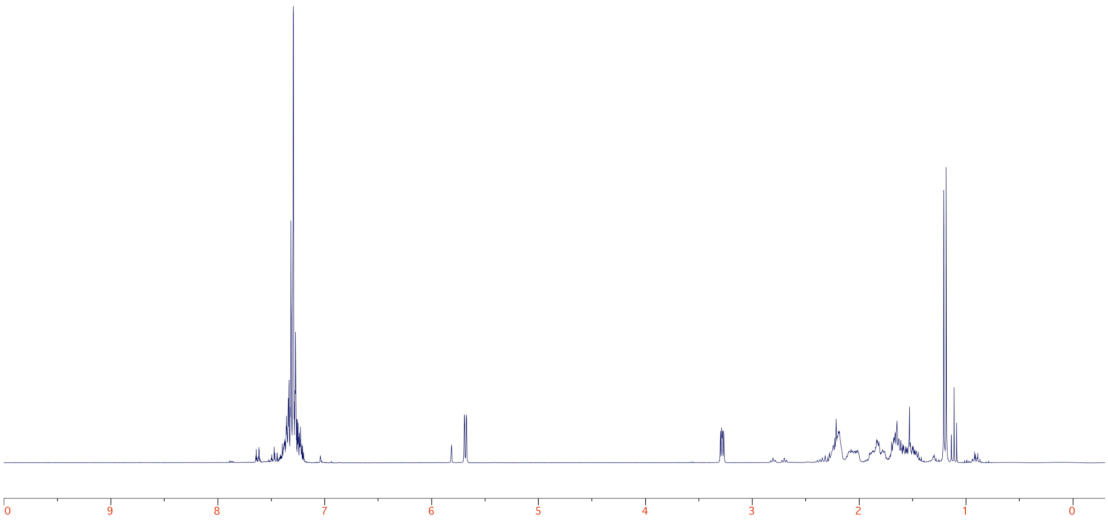


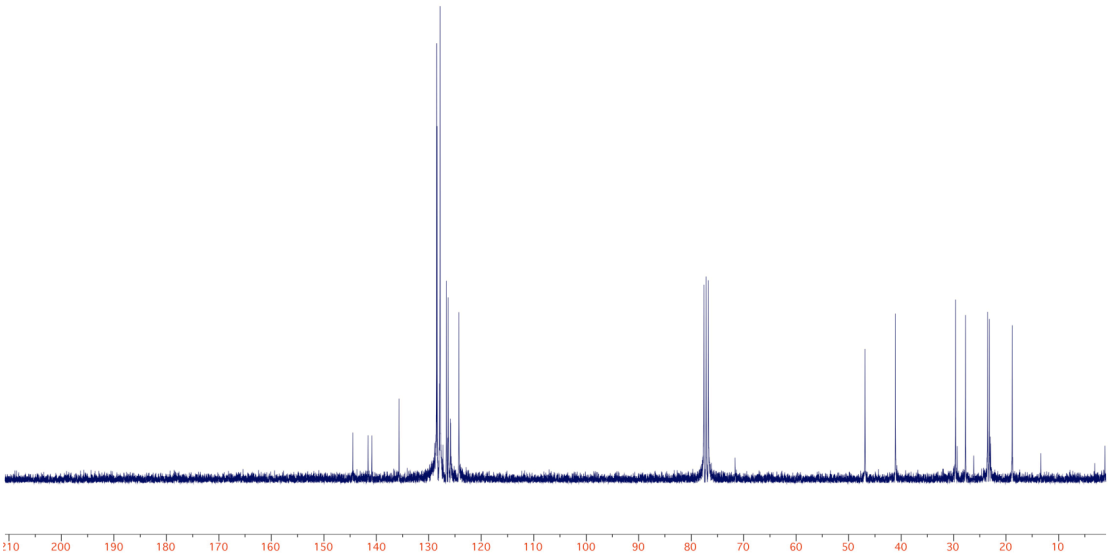


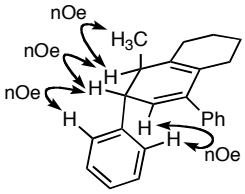


(5*R*,6*S*)-5-Methyl-6,8-diphenyl-1,2,3,4,5,6-hexahydronaphthalene and **(5*S*,6*R*)-5-methyl-6,8-diphenyl-1,2,3,4,5,6-hexahydronaphthalene** (**3h**)





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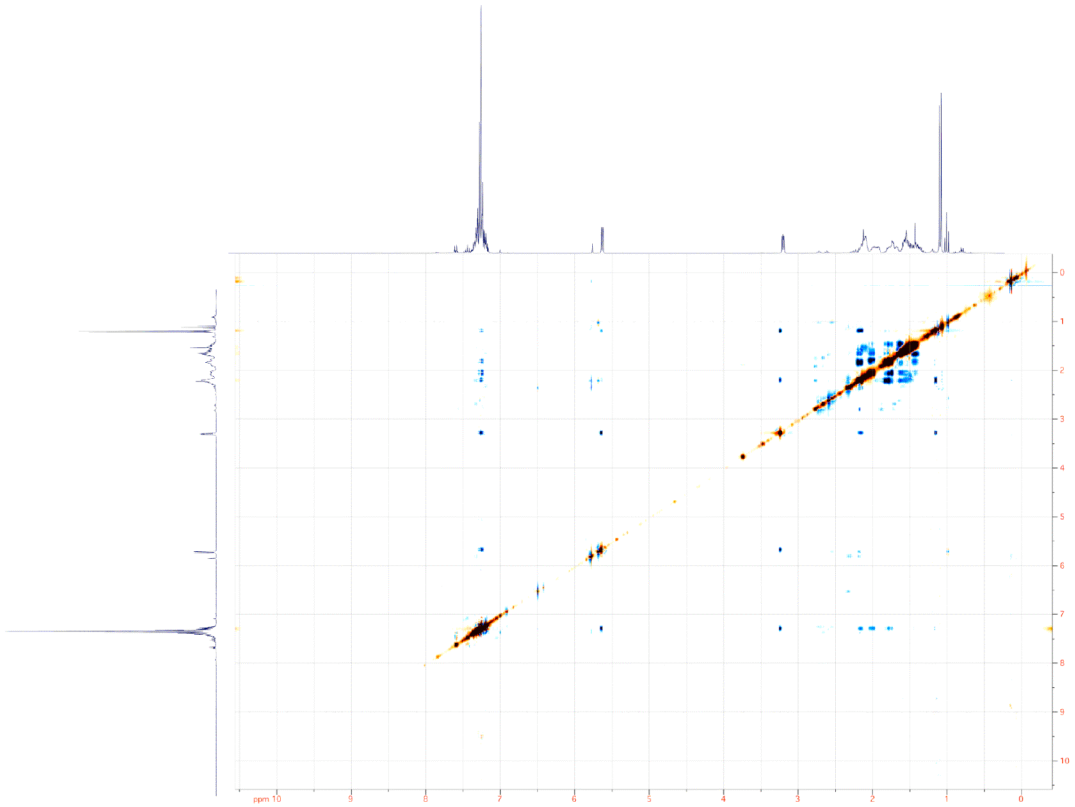
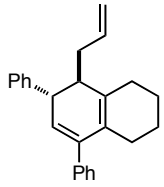
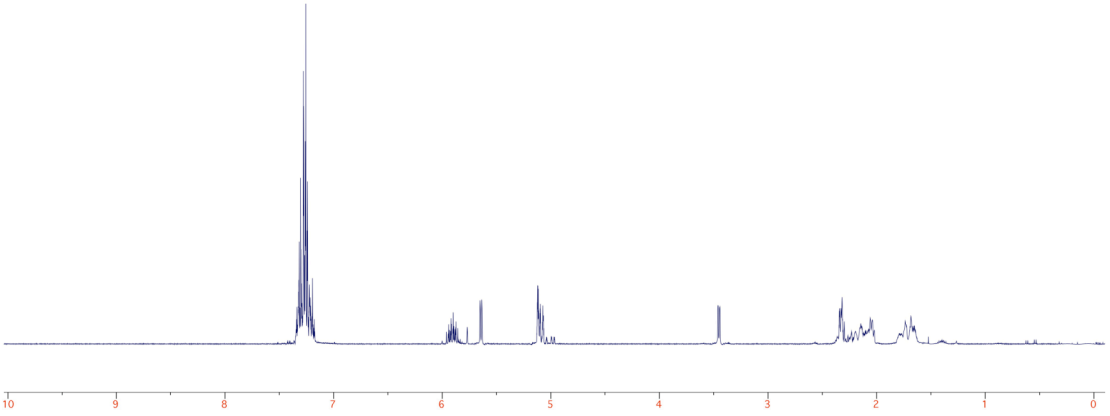
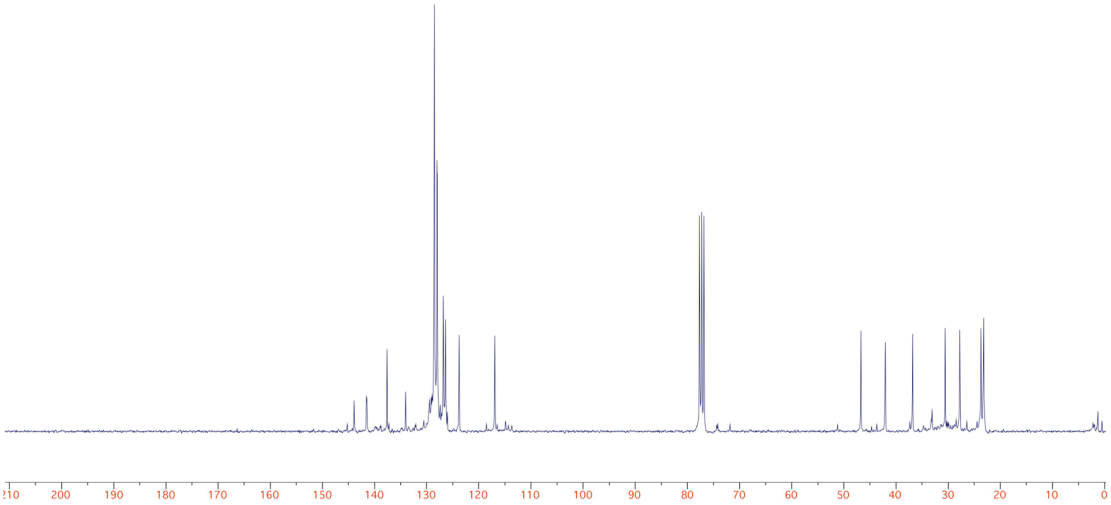
nOe
H
H
nOe
H
H
Ph
H
nOe



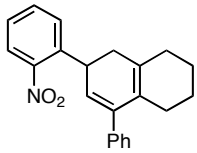
(5*R*,6*S*)-5-Allyl-6,8-diphenyl-1,2,3,4,5,6-hexahydronaphthalene and **(5*S*,6*R*)-5-allyl-6,8-diphenyl-1,2,3,4,5,6-hexahydronaphthalene** (**3i**)

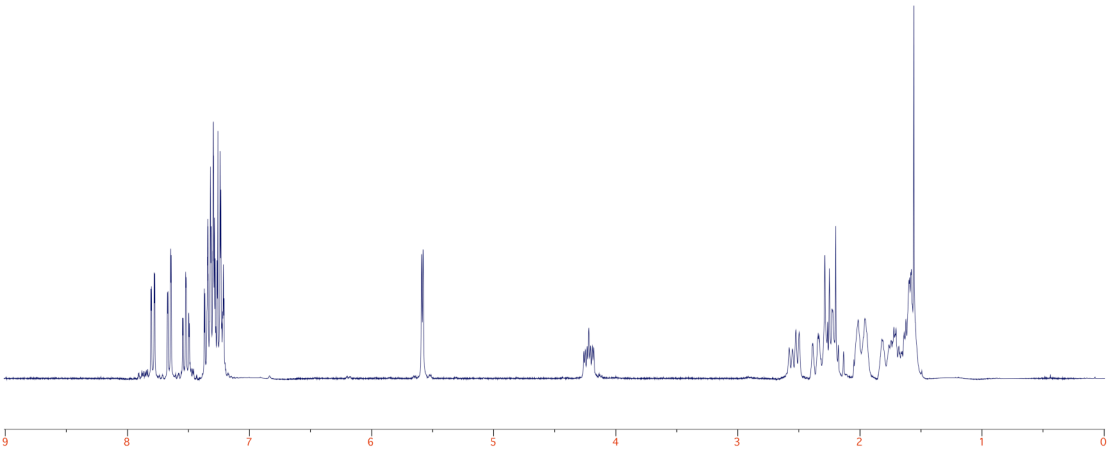


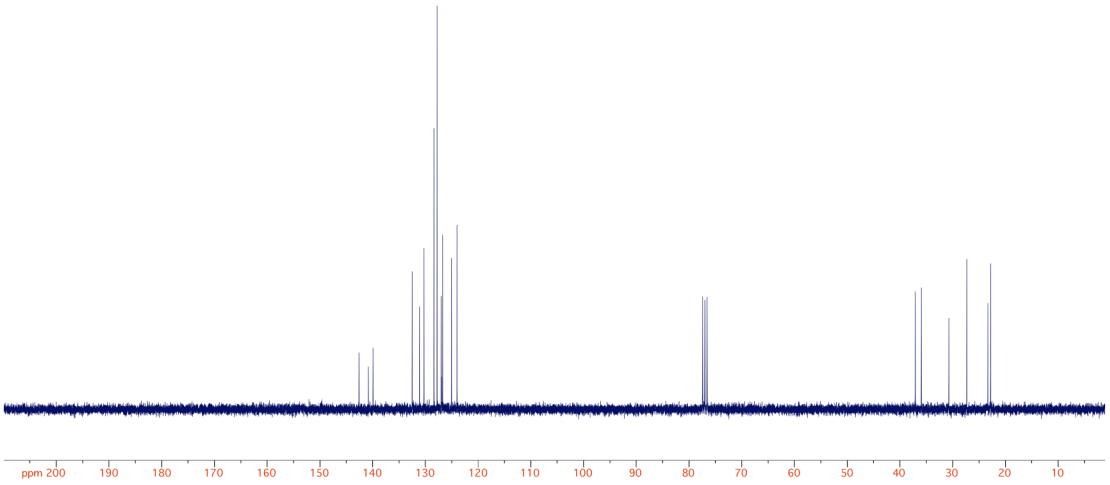




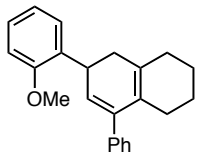
6-(2-Nitrophenyl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3j)

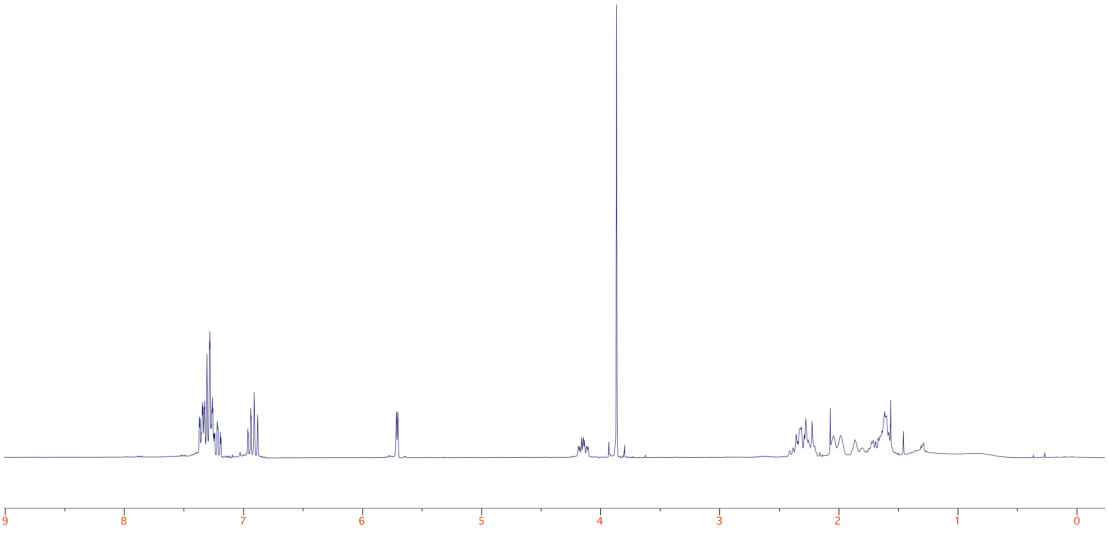


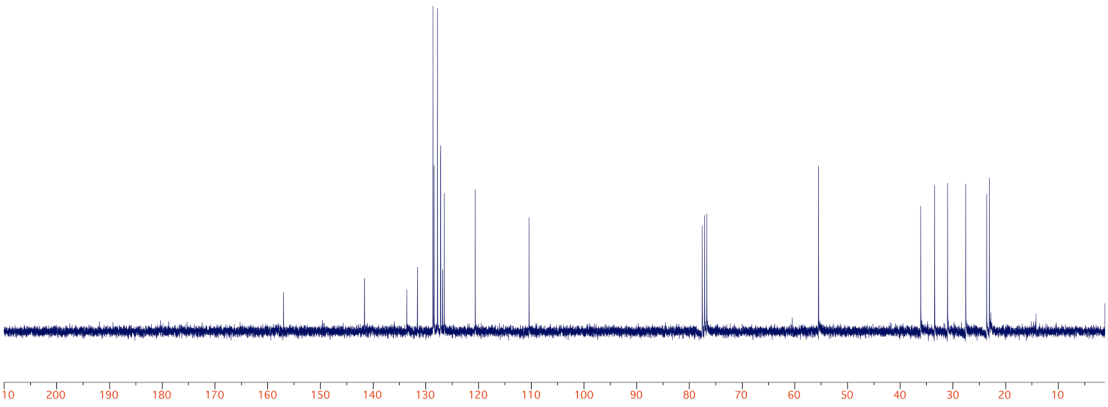




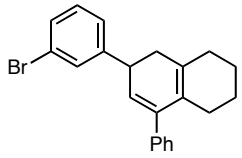
6-(2-Methoxyphenyl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3k)

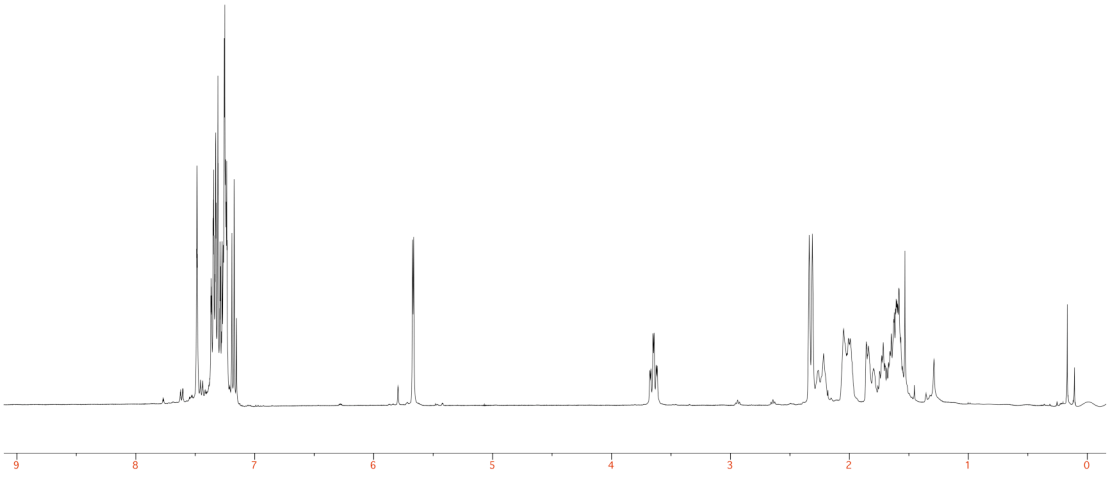


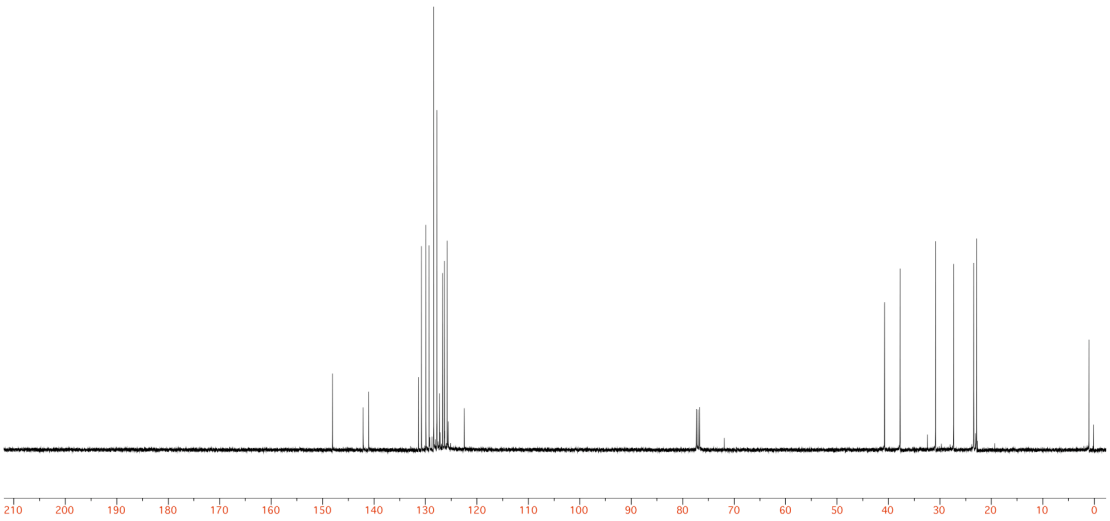




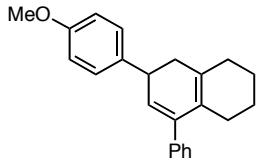
6-(3-Bromophenyl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3l)

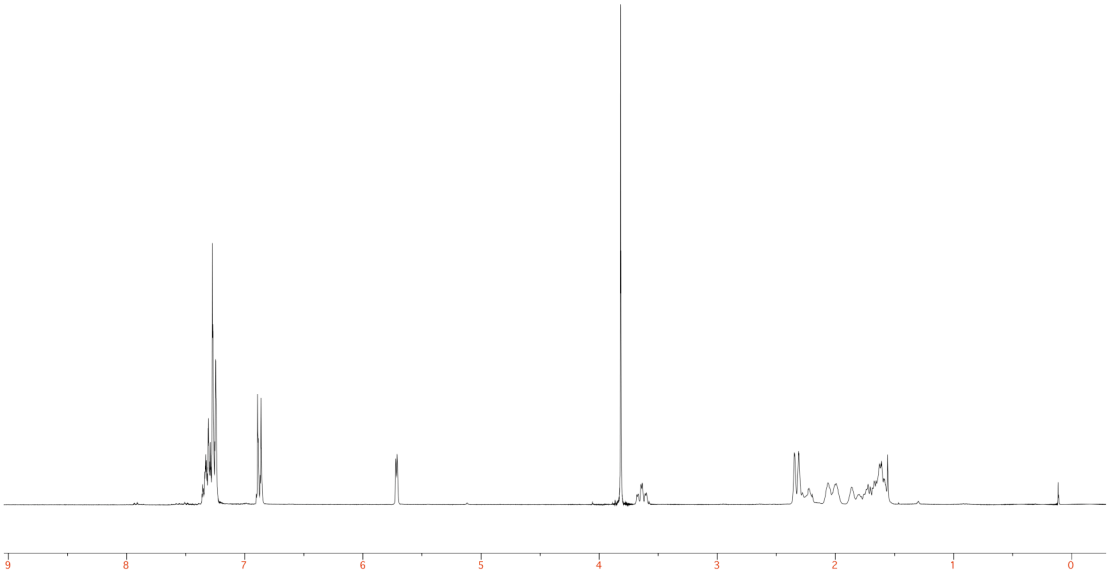


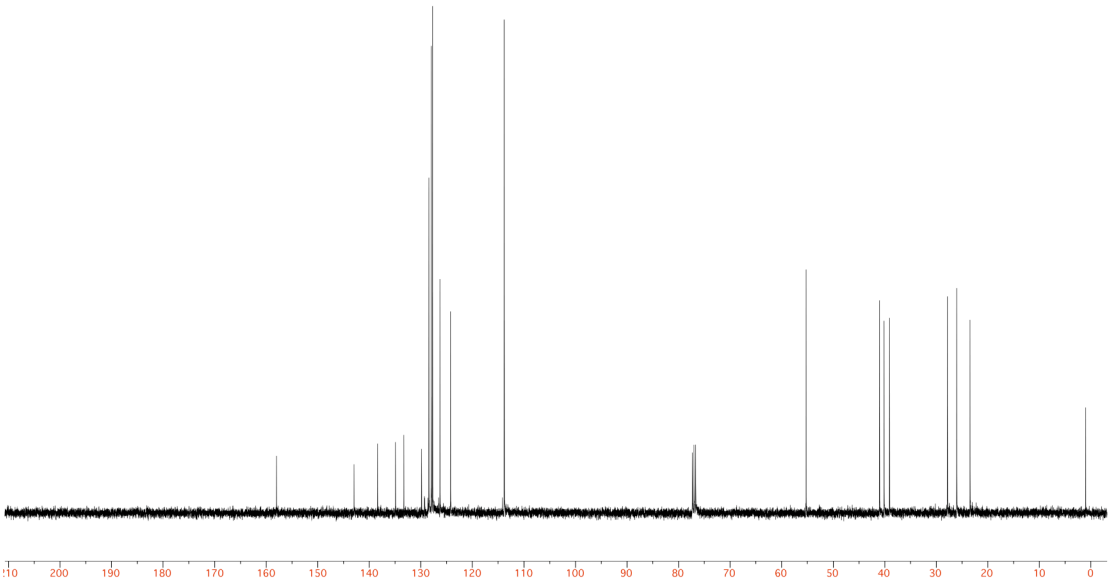




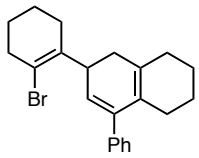
6-(4-Methoxyphenyl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3m)

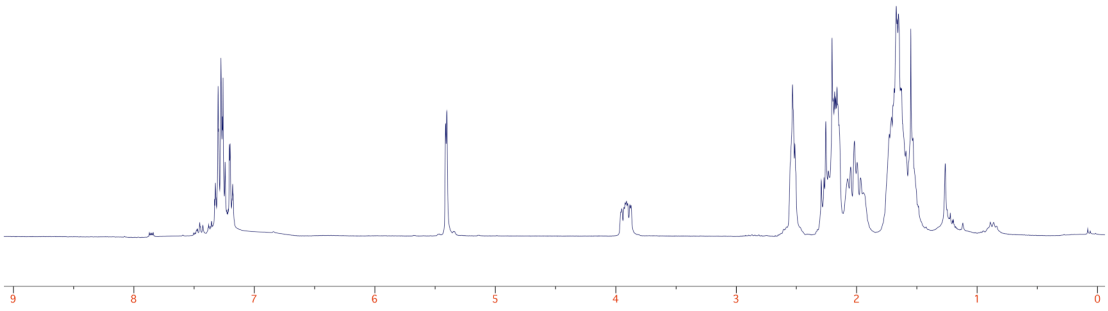


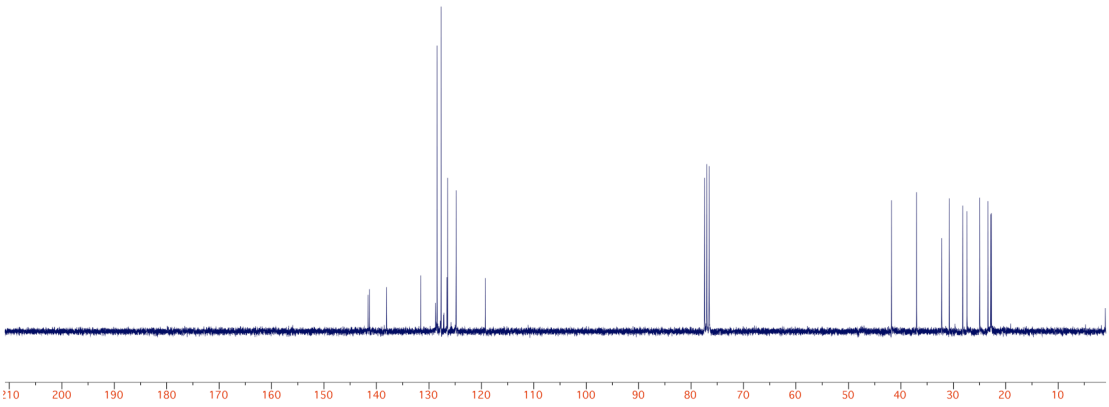




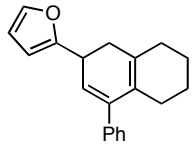
6-(2-Bromocyclohex-1-en-1-yl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene (3n)

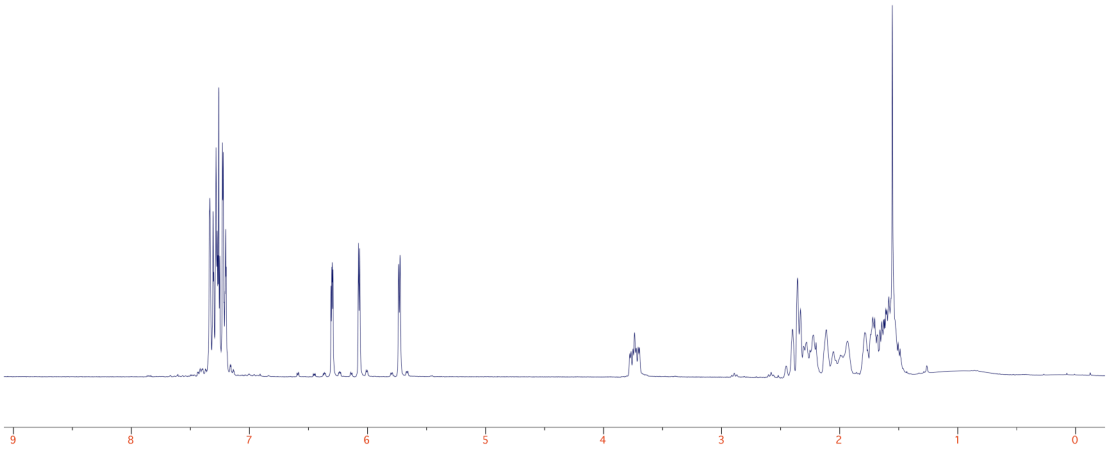


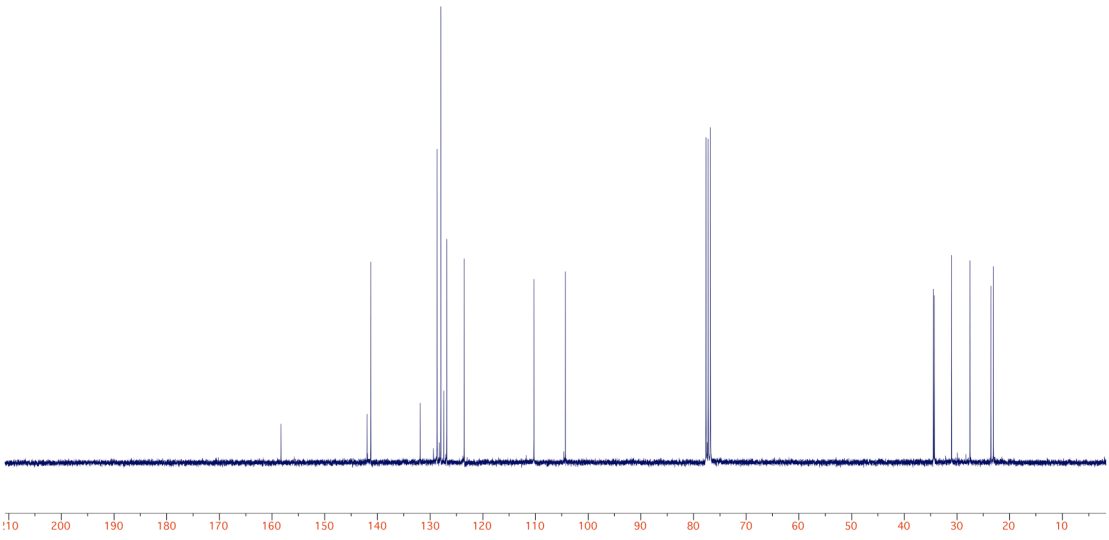




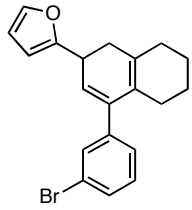
2-(4-Phenyl-1,2,5,6,7,8-hexahydronaphthalen-2-yl)furan (3o)

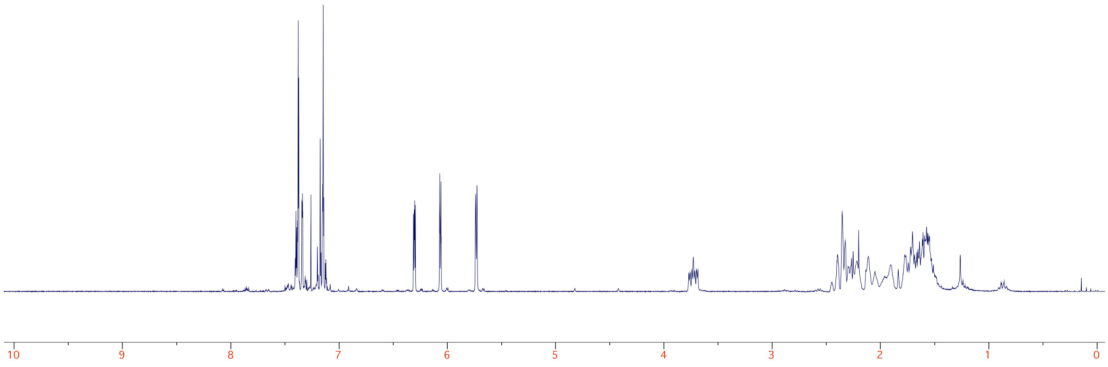


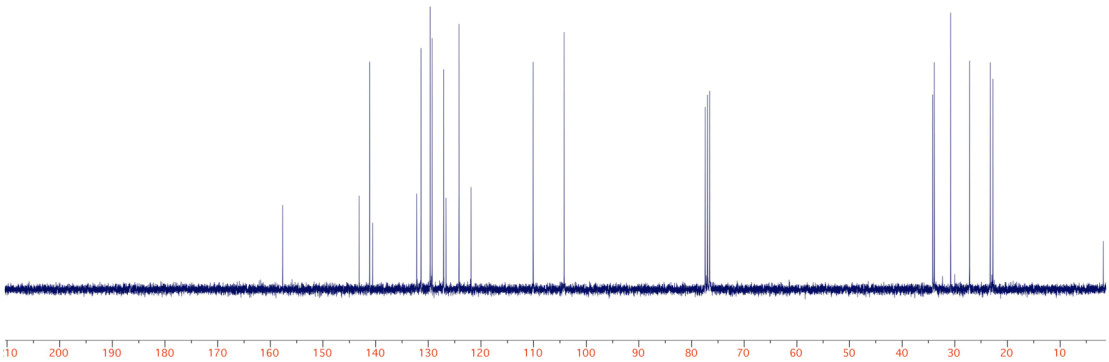




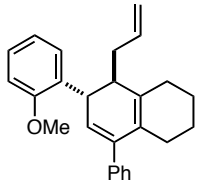
2-(4-(3-Bromophenyl)-1,2,5,6,7,8-hexahydronaphthalen-2-yl)furan (3p)

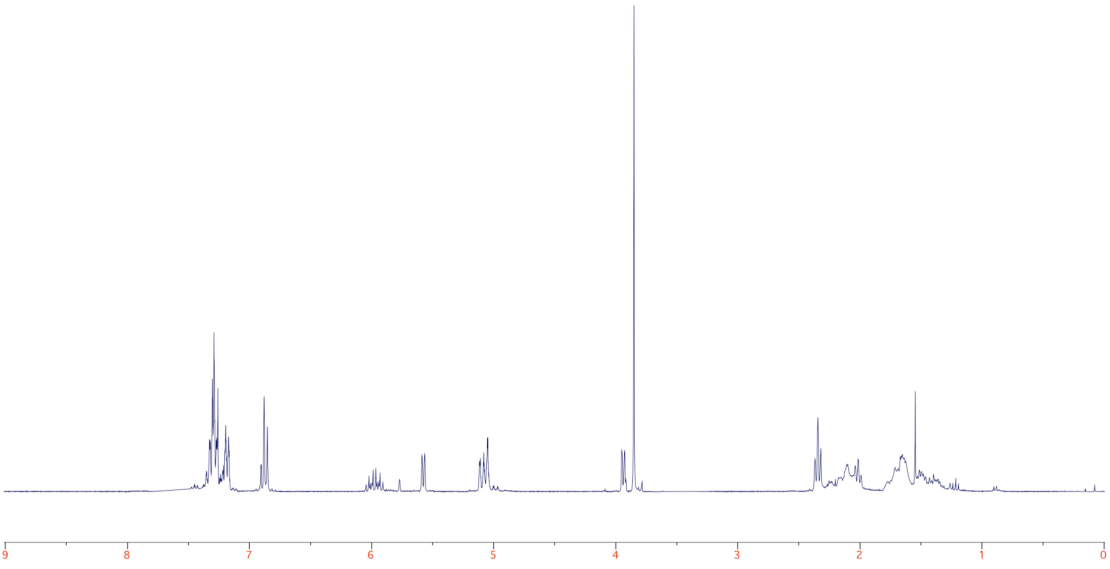


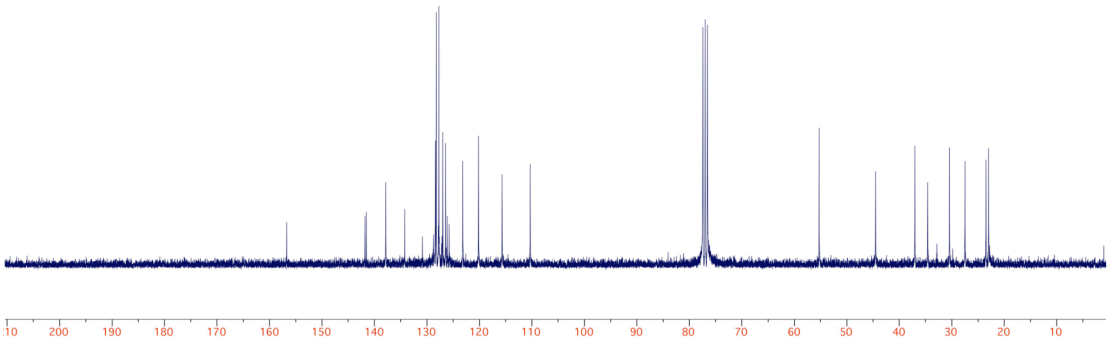


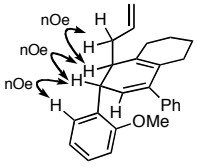


(5*R*,6*S*)-5-Allyl-6-(2-methoxyphenyl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene and **(5*S*,6*R*)-5-allyl-6-(2-methoxyphenyl)-8-phenyl-1,2,3,4,5,6-hexahydronaphthalene** (**3q**)








nOe
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OMe

ppm 9
8
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4
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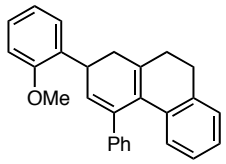
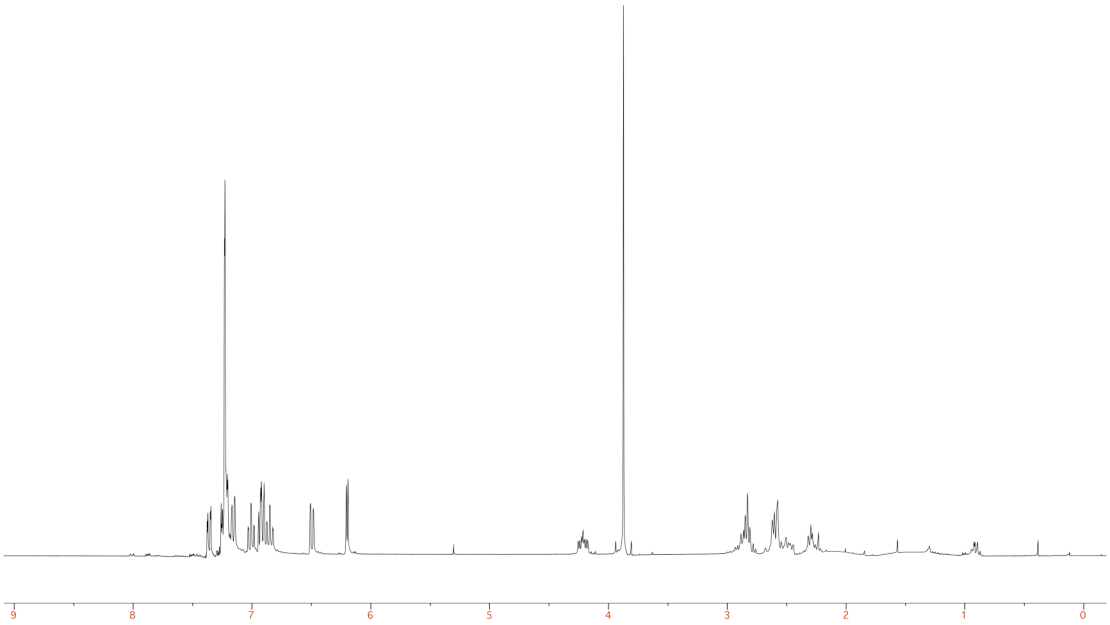
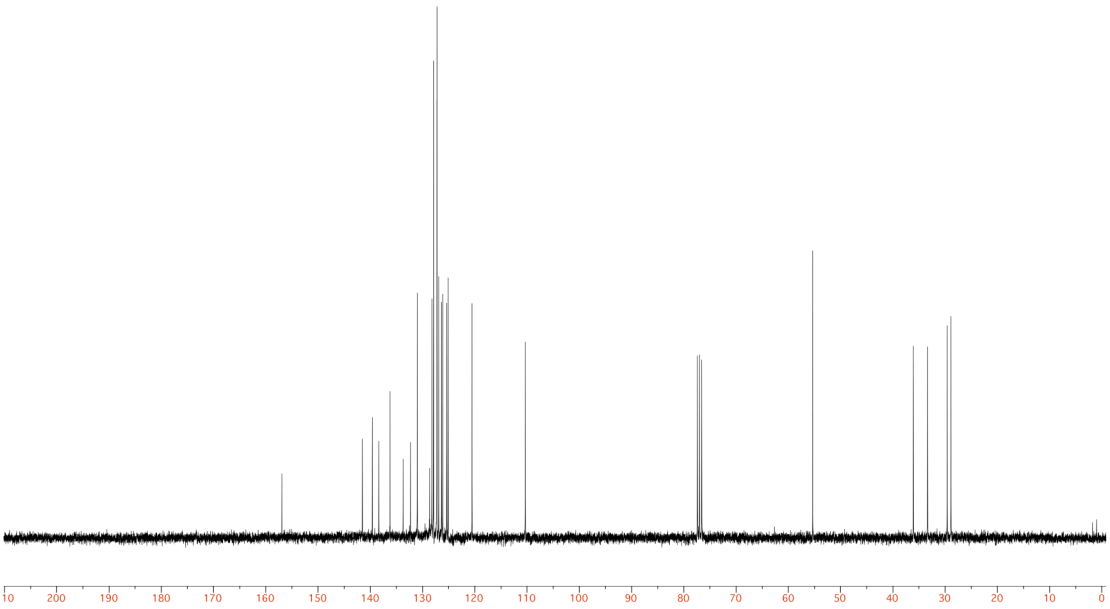
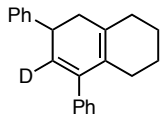
2
1
0

2-(2-Methoxyphenyl)-4-phenyl-1,2,9,10-tetrahydrophenanthrene (3r)





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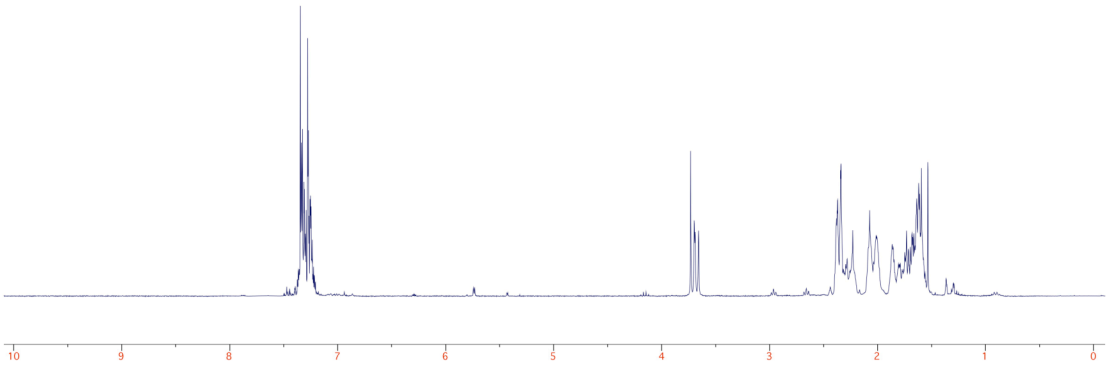
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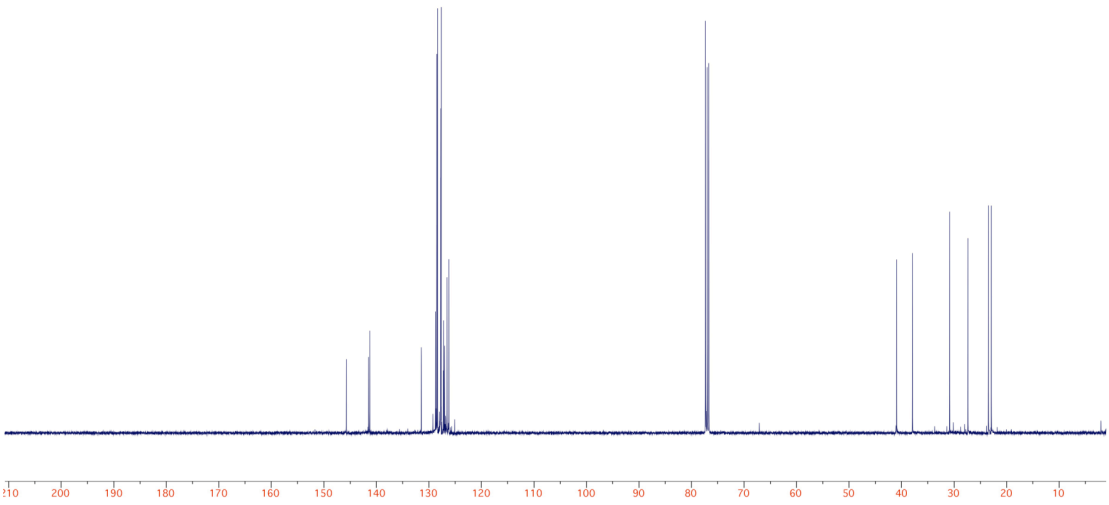
210
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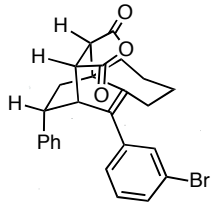
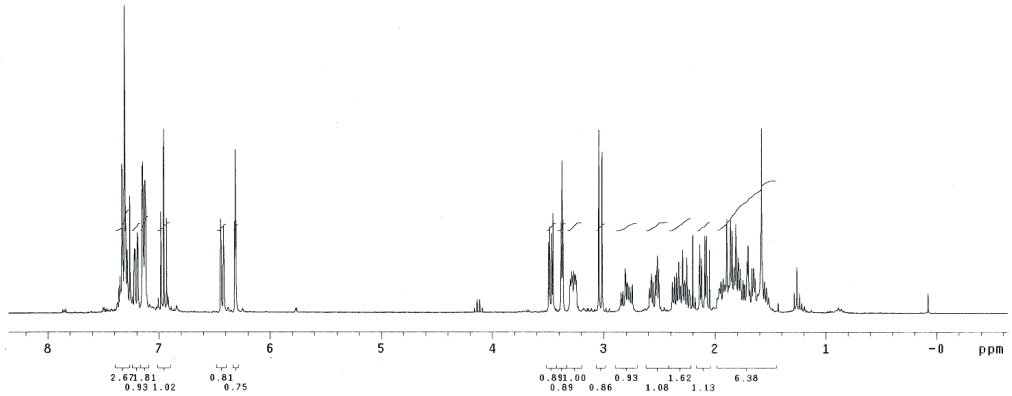
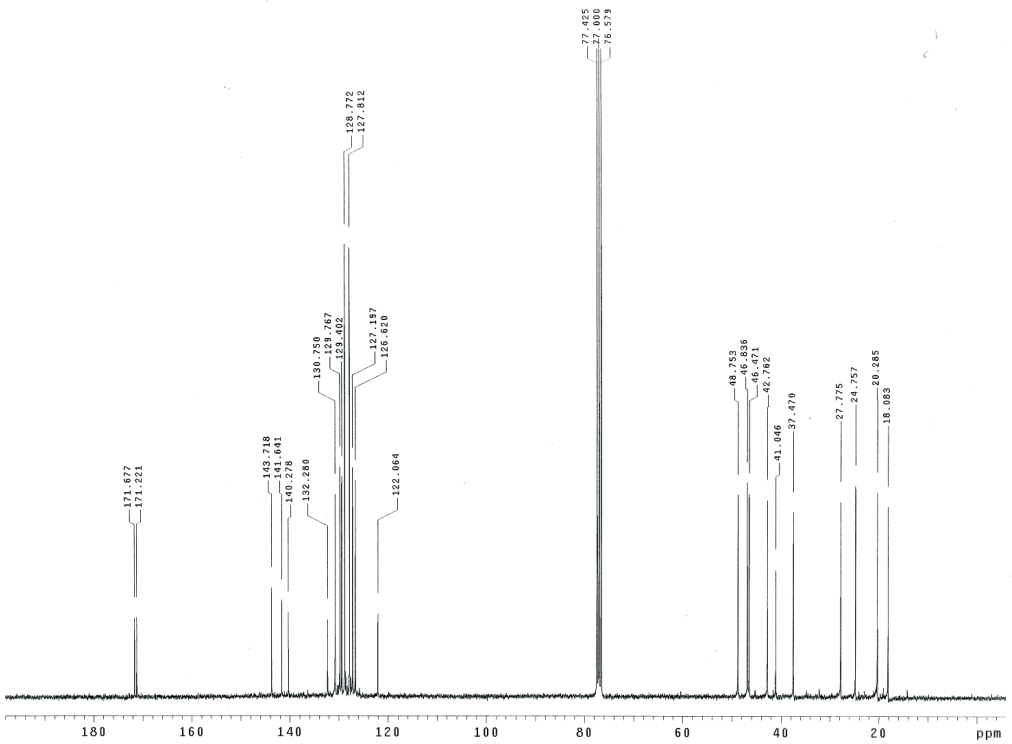
10

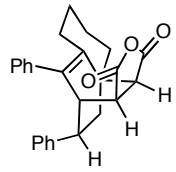
(3a*R*,9a*R*,9b*R*,11*S*)-5-(3-bromophenyl)-11-phenyl-3a,4,6,7,8,9-hexahydro-1*H*-4,9a-ethanonaphtho[1,2-*c*]furan-1,3(9b*H*)-dione and (3a*S*,9a*S*,9b*S*,11*R*)-5-(3-bromophenyl)-11-phenyl-3a,4,6,7,8,9-hexahydro-1*H*-4,9a-ethanonaphtho[1,2-*c*]furan-1,3(9b*H*)-dione (8b)

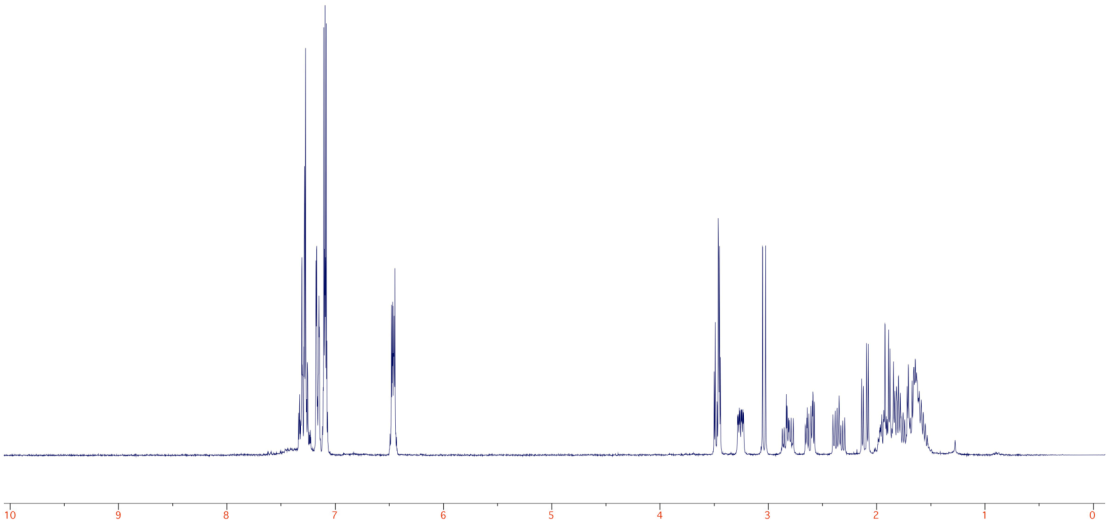


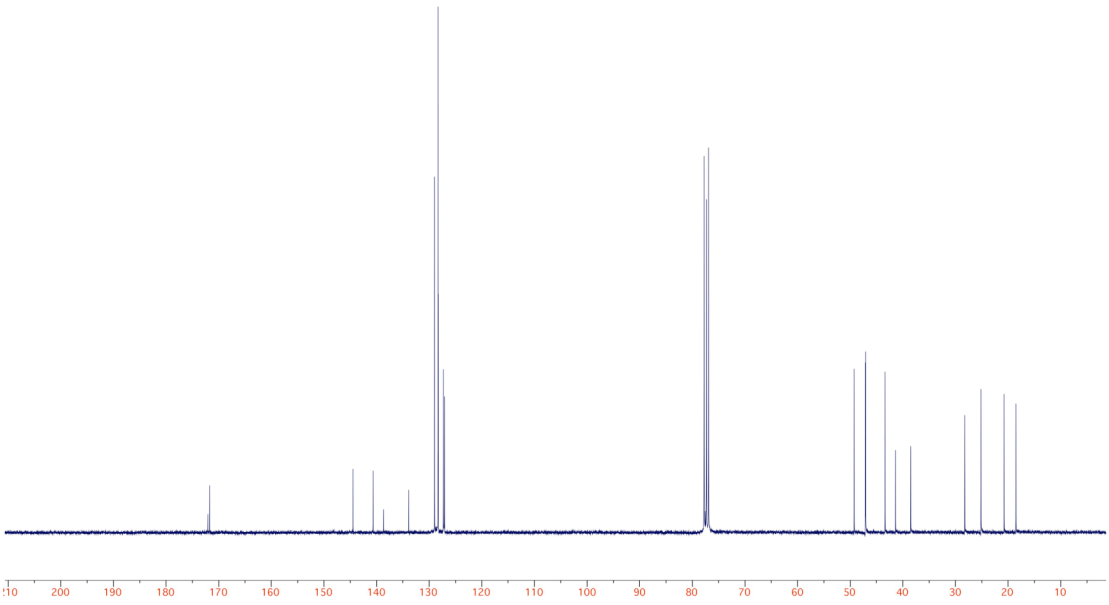




(3a*S*,9a*S*,9b*S*,11*R*)-5,11-diphenyl-3a,4,6,7,8,9-hexahydro-1*H*-4,9a-ethanonaphtho[1,2-*c*]furan-1,3(9b*H*)-dione and **(3a*R*,9a*R*,9b*R*,11*S*)-5,11-diphenyl-3a,4,6,7,8,9-hexahydro-1*H*-4,9a-ethanonaphtho[1,2-*c*]furan-1,3(9b*H*)-dione** (**8a**)







5,7-iphenyl-1,2,3,4-tetrahydronaphthalene (7a)