Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Transition-metal–free Heck-type reaction between alkenes and alkyl iodides enabled by light in water

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Table of Contents

• *General Information*

Solvents and reagents were purchased from Sigma-Aldrich chemical company and were used without further purification unless otherwise specified. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 300 MHz, 400 MHz, or 500 MHz spectrometers and ^{19}F NMR spectra were recorded on Bruker 400 MHz spectrometer. All signals are reported in ppm with the internal reference of 7.26 ppm or 77.0 ppm for chloroform as standard. Data are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet), coupling constant (*J*/Hz) and integration. All NMR spectrums were recorded at room temperature (23°C) unless otherwise indicated. High-resolution mass spectrometry was conducted through using atmospheric pressure chemical ionization (APCI) or electro-spraying ionization (ESI), and was performed by McGill University on a Thermo-Scientific Exactive Orbitrap. Protonated molecular ions $(M+H)^+$ or sodium adducts $(M+Na)^+$, were used for empirical formula confirmation. All preparative chromatography were performed through using gradient elution (hexanes and ethyl acetate) on a Biotage Isolera™ One automated chromatography system with SNAP ultra silica gel cartridges and sample cartridges. All the reactions were conducted in a 5 mL quartz tube unless the control experiments. The UV lamp (left picture in Figure S1) employed in this investigation was purchased at Atlas Specialty Lighting and the photo reactor (middle picture in Figure S1) mentioned in the screening was purchased in Luzchem, both of whose pictures are shown below. The setup of the apparatus we used in the investigation was shown in Figure S1 (right picture).

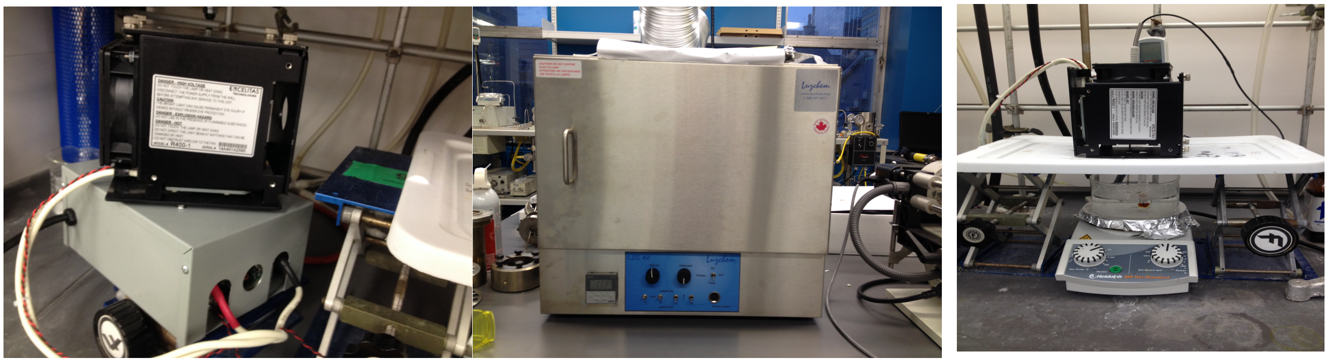


Figure S1: UV lamp we used in this study and the photo reactor mentioned in the screening as the control

- ***General protocol for the preparation of secondary and primary iodide***

Iodine chips (1.2 equiv) were added to a solution of Ph_3P (1.2 equiv) and imidazole (1.2 equiv) in dry CH_2Cl_2 (0.2 M) at 0 °C. The alcohol (neat or a solution in CH_2Cl_2) was added dropwise to the reaction mixture at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. Next, the solvent was removed on a rotary evaporator. The residue was diluted with hexanes/Et_2O (4:1), filtered, concentrated, and purified by flash column chromatography with hexanes. (*J. Am. Chem. Soc.* **135**, 624-627)

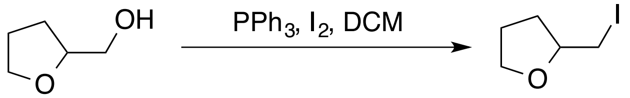


Figure S2: Appel reaction scheme to prepare the primary iodide

Tetrahydrofurfuryl alcohol (3 mL, 0.031mol) was added into 150 mL DCM, into which 9.8 g PPh_3 (1.2 equiv), 2.6 g imidazole (1.2 equiv) and 9.3 g I_2 (1.2 equiv) were added subsequently. After stirring 10 min, a yellow clean solution was obtained. When TLC analysis showed all the tetrahydrofurfuryl alcohol was consumed, the reaction was stopped and water, sodium carbonate, sodium thiosulfate and brine were employed to wash the organic extraction. Then flush column chromatography was conducted by using 10% ethyl acetate in hexane as the eluent to purify the desired product as a colorless oil (4.2 g, 64% yield).

TLC Rf value: 0.50 (EtOAc: Hexane=1:10)

^{1}HNMR: 3.90 (m, 2H), 3.76 (m, 1H), 3.16 (m, 2H), 2.10-1.82 (m, 3H), 1.60 (m, 1H)

^{13}CNMR: 78.4, 68.9, 31.9, 26.1, 10.6

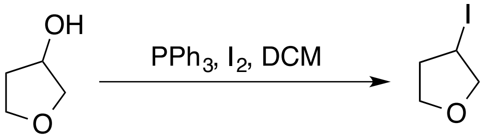


Figure S3: Appel reaction scheme to prepare the secondary iodide

3-Hydroxyltetrhydrfuran (3 mL, 0.037 mol) was added into 185 mL dry DCM, into which 11.6 g PPh_3 (1.2 equiv), 3.0 g imidazole (1.2 equiv) and 11.3 g I_2 (1.2 equiv) were added subsequently. After stirring 10 min, a yellow cloudy solution was obtained. When TLC analysis showed all 3-hydroxyltetrhydrfuran was consumed, the reaction was stopped and the water, sodium carbonate, sodium thiosulfate and brine were employed to wash the organic extraction. Then flush column chromatography was conducted by using 10% ethyl acetate in hexane as the eluent to purify the desired product as a colorless oil (6.0 g, 82% yield).

TLC Rf value: 0.28 (EtOAc: Hexane=1:10)

^{1}HNMR: 4.26-4.19 (m, 1H), 4.12-4.07(m, 1H), 3.96-3.79(m, 3H), 2.42-2.31(m, 1H), 2.26-2.16(m, 1H)

^{13}CNMR: 77.78, 67.27, 38.62, 19.22

- ***General protocol for the preparation of alkene***

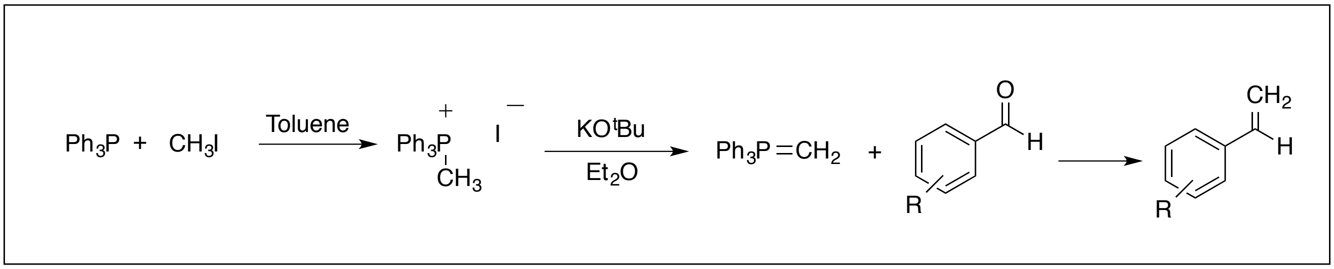


Figure S4: Wittig reaction to prepare the styrene derivatives

Step 1: 36 g PPh_3 and 100 mL toluene were added into a 500 mL round bottom flask, which produced a clean solution. Then 11 mL CH_3I was added into the above clean solution at 0°C drop wisely. Then a condenser was put on the round bottom flask and the solution was heated to reflux for 4 hr, which would produce white solid. The white solid was filtered and dried under the vacuum, which was used directly without further purification (100% yield, white solid).

Step 2 and Step 3: Triphenylphosphine methyliodide salt (2.5 g, 6.2 mmol) prepared in step 1 was added into 30 mL Et_2O, which resulted a cloudy solution and KO^tBu (1.57 g, 14 mmol) was added into the round bottom flask at 0°C, the color of which changed from white into yellow immediately. The mixture remained stirring for 4 hr. Then 0.6 g (4.65 mmol) 4-cyanobenzaldehyde was added into the round bottom flask and kept reacting for 10 hr at room temperature. After TLC analysis showed all the aldehyde was consumed completely, the reaction was terminated and filtrated, washed by Et_2O. Organic solvent was removed on the rota-vapor and the residue was purified by flash column chromatography (pure hexane) to get the desired olefin product, which was confirmed by GCMS and HNMR (60% unoptimized yield).

- ***General protocol for the coupling reaction***

To a 5 mL quartz tube with a rubber septum and a stir bar was added the NaO^tBu (80 mg, 0.83 mmol). Following this, 1.5 mL distilled water was added into the tube. After the salt was dissolved and a clear solution was obtained, the solution was degassed and refilled with pre-purified Argon for three times through using thaw-frozen technique. Then 100 μL (0.77 mmol) iodocyclohexane and 10 μL 4-methoxystyrene (0.077 mmol) were added successively which resulted in a two-phase mixture. The rubber septum was replaced by a screw cap quickly and settled in a pre-heated 50°C water bath. Thereafter, the UV lamp, 10 cm away from the tube was turned on. After 40 min, when GC analysis showed the starting material (4-methoxystyrene) was completely consumed, the reaction was stopped and EtOAc (3x3 mL) was added to extract the organic products. After dried over Na_2SO_4, evaporated on rota-vapor, the residue was subjected to a flush column chromatography (Still protocol) by using pure hexane as the eluent to isolate the desired product and the E/Z isomers ratio was determined by GC analysis.

- ***Failed alkenes***

The substrates shown below cannot give the desired Heck coupling products under the current conditions.

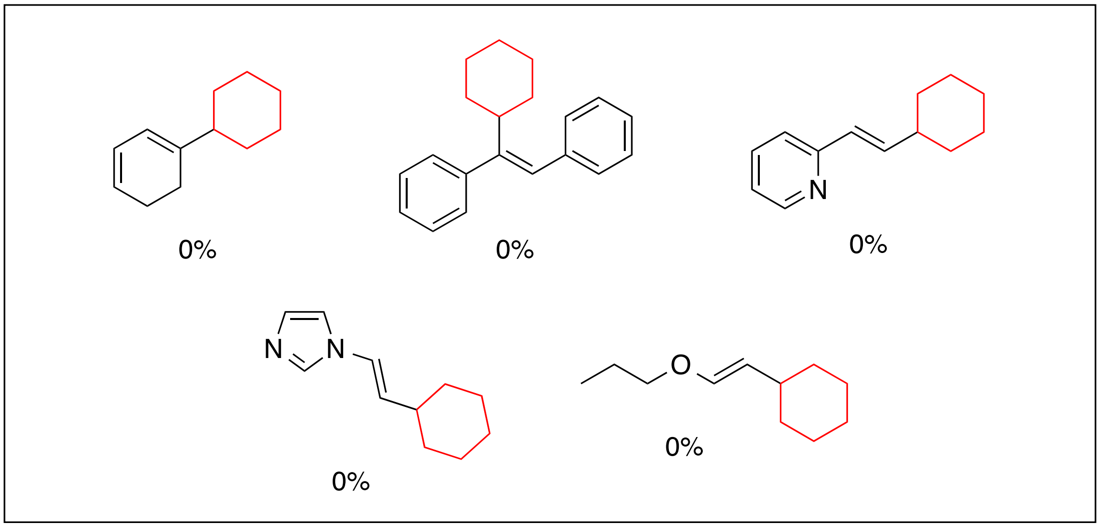


Figure S5: Failed alkenes under current conditions

- ***α-Methyl styrene reacting with 4-methoxystyrene***

When α-methyl styrene was reacted with 4-methoxystyrene, according to GC/MS (Gas Chromatography/mass spectrometry), we obtained five different coupling products as shown in Figure S6. The ratio of different products were calculated based on GC/MS through using dodecane as an internal standard.

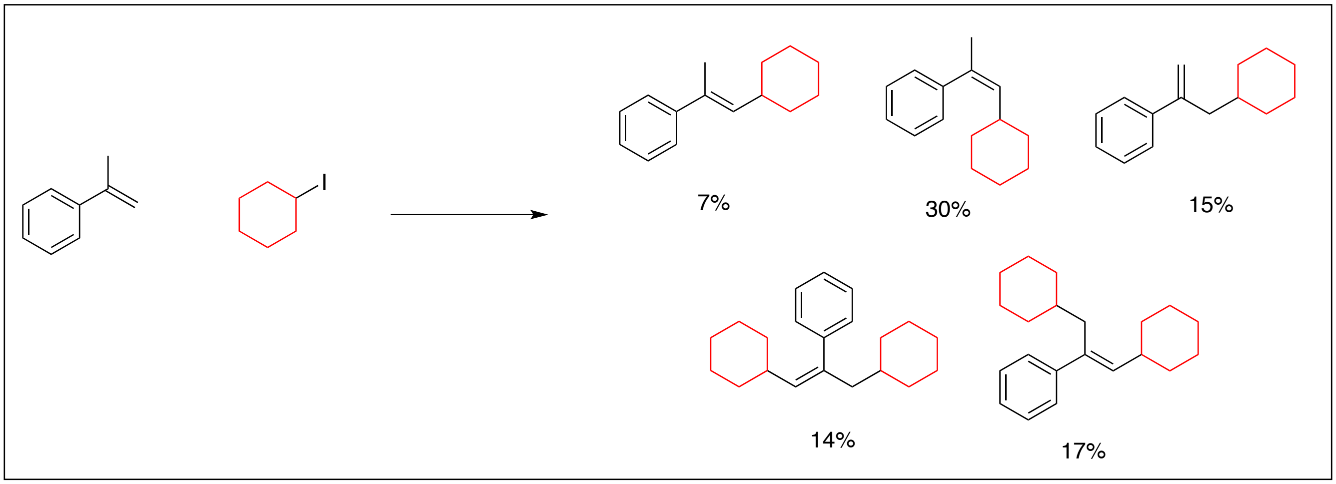


Figure S6: Five coupling products were obtained when α-methyl styrene was reacted with cyclohexyl iodide under the present conditions

- ***Typical GC trace for our coupling reaction***

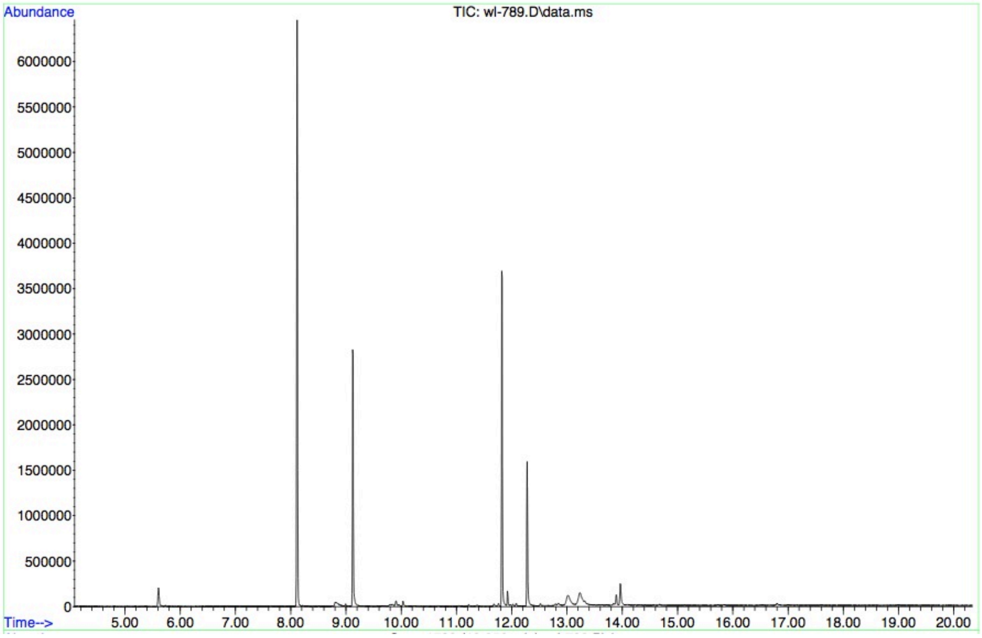


Figure S7: Representative GC/MS trace of the reaction for electron rich styrenes

This GC/MS trace was obtained from the crude reaction mixture of 4-methoxystyrene with cyclohexyl iodide. Based on the mass of every peak, peak at *t* = 8.1 s is the unconsumed cyclohexyl iodide, peak at *t* = 9.2 s is the added internal standard dodecane, peak at *t* = 11.9 s is the Z product and peak at t=12.2s is the E product. Confirmation of E and Z isomers were through the synthesis of E and Z isomers by Wittig reaction to determine the retention time of both isomers.

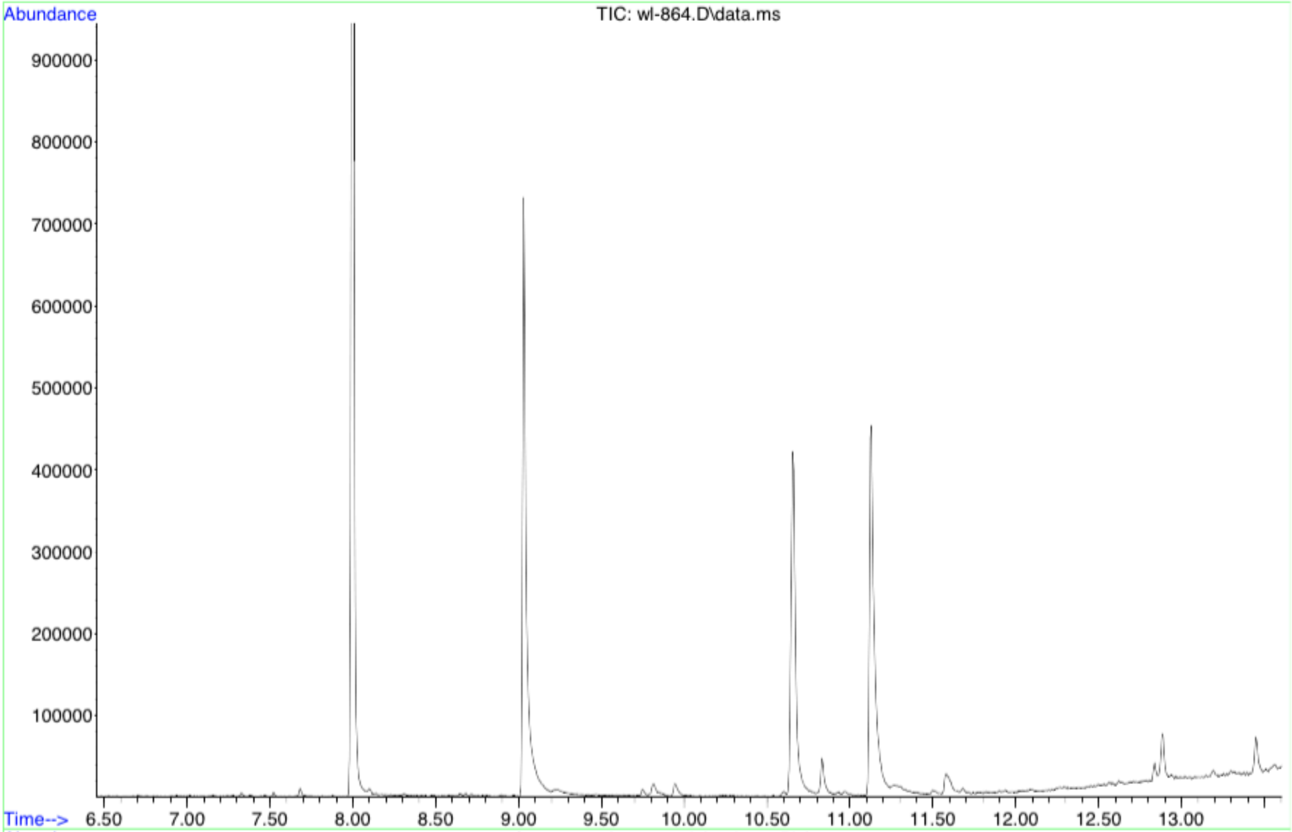
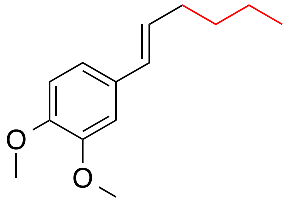


Figure S8: Representative GC/MS trace of the reaction for the electron deficient styrenes

This GC/MS trace was obtained from the crude reaction mixture of 4-F-styrene with cyclohexyl iodide. Based on the mass of every peak, peak at *t* = 8.1 s is the unconsumed cyclohexyl iodide, peak at *t* = 9.2 s is the added internal standard dodecane, peak at *t* = 10.6 s is the Z product and peak at *t* = 10.8 s is the reduction product and peak at *t* = 11.2 s is the E product. Confirmation of E and Z isomers were through the synthesis of E and Z isomers by Wittig reaction to determine the retention time of both isomers.

- ***Supplementary characteristic data***

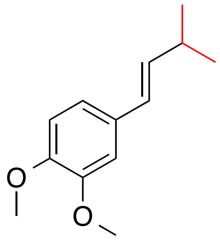


4-(hex-1-en-1-yl)-1,2-dimethoxybenzene (E/Z mixtures) (3x)

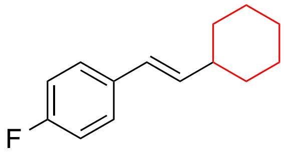
^{1}H NMR (CDCl$_3$, 400MHz): δ 6.90–6.78 (m, 5.53 H), 6.37-6.27 (m, 1.62H), 6.13-6.05 (m, 0.56H), 5.63-5.55 (m, 1H), 3.92-3.85 (m, 10.1H), 2.35-2.31 (m, 2.22H), 2.21-2.13 (m, 1.37H), 1.50-1.30 (m, 8.12H), 0.95-0.85 (m, 5.90H);

^{13}C NMR (CDCl$_3$, 100MHz): δ 151.0, 149.1, 135.0, 132.5, 127.9, 120.0, 111.8, 11.3, 57.0, 56.2, 38.0, 27.0, 22.8, 14.0.

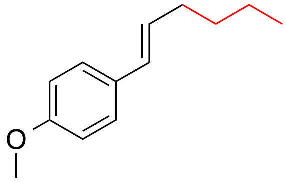
HRMS (APCI): $C_{14}H_{21}O_2$ [M+H$^+$], theoretical mass: 221.15361, found: 221.15297.



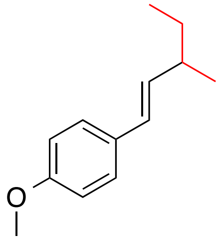
1,2-dimethoxy-4-(3-methylbut-1-en-1-yl)benzene (E/Z mixtures) (3w)
^{1}H NMR ($CDCl_3$, 400MHz): δ 6.93-6.78 (m, 4.1 H), 6.21-6.32 (m, 1H), 6.10-6.02 (m, 0.6H), 3.92-3.84 (m, 9.3H), 2.96-2.86 (m, 0.28H), 2.50-2.40 (m, 0.48H), 1.14-1.00 (m, 7.9H);
^{13}C NMR ($CDCl_3$, 100MHz): δ 151.0, 149.1, 135.0, 132.5, 127.9, 120.0, 111.8, 56.0, 34.5, 23.3.
HRMS (APCI): $C_{13}H_{19}O_2$ [M+H$^+$], theoretical mass: 207.13796, found: 207.13758.



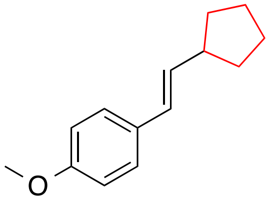
1-(2-cyclohexylvinyl)-4-fluorobenzene (E/Z mixtures)[1] (3q)
^{1}H NMR ($CDCl_3$, 400MHz): δ 7.32-7.19 (m, 5.7 H), 7.08-6.94 (m, 7.0H), 6.83-6.70 (m, 1.1H), 6.33-6.24 (m, 2.3H), 6.12-6.04 (m, 1.2H), 5.51-5.43 (m, 1H), 2.67-2.40 (m, 1.4H), 2.20-2.05 (m, 1.5H), 1.85-1.50 (m, 15H), 1.40-1.10 (m, 15H);
^{13}C NMR ($CDCl_3$, 100MHz): δ 149.7, 149.3, 136.2, 135.3, 135.0, 128.6, 128.3, 127.8, 126.8, 125.6, 125.4, 124.7, 123.9, 33.3, 33.0, 31.3, 26.1.
MS (EI): $C_{14}H_{17}F$, theoretical mass: 204.1, found: 204.1.



1-(hex-1-en-1-yl)-4-methoxybenzene (E/Z mixtures) (3ai)
^{1}H NMR ($CDCl_3$, 400MHz): δ 7.29-7.22 (m, 3.15H), 6.89-6.83 (m, 3.29H), 6.36-6.31 (m, 1.40H), 6.13-6.05 (m, 0.45H), 5.61-5.54 (m, 1.00H), 3.82-3.80 (m, 5.51H), 2.36-2.30 (m, 2.08H), 2.22-2.17 (m, 1.26H), 1.39-1.33 (m, 7.13H), 0.95-0.89 (m, 5.36H).
^{13}C NMR ($CDCl_3$, 100MHz): δ 158.60, 158.13, 131.66, 129.92, 129.05, 128.07, 126.94, 113.90, 113.53, 55.24, 32.23, 28.37, 22.45, 13.99, 13.98.
HRMS (APCI): $C_{13}H_{19}O$ [M+H$^+$], theoretical mass: 191.14304, found: 191.14239.



1-methoxy-4-(3-methylpent-1-en-1-yl)benzene (E/Z mixtures) (3ac)
^{1}H NMR ($CDCl_3$, 400MHz): δ 7.31-7.20 (m, 2.63 H), 6.88-6.83 (m, 2.44H), 6.34-6.27 (m, 1.00H), 5.99-5.91 (m, 0.31H), 5.38-5.31 (m, 0.71H), 3.81-3.80 (m, 4.15H), 2.71-2.58 (m, 1.03H), 2.20-2.15 (m, 0.47H), 1.40-1.33 (m, 4.20H), 1.08-1.02 (m, 4H), 0.93-0.84 (m, 4.83H);
^{13}C NMR ($CDCl_3$, 100MHz): δ 158.57, 158.08, 138.03, 134.67, 127.40, 126.90, 113.87, 113.52, 55.28, 55.21, 38.84, 29.89, 20.65, 20.30, 11.83, 11.80.
HRMS (APCI): $C_{13}H_{19}O$ [M+H$^+$], theoretical mass: 191.14304, found: 191.14247.

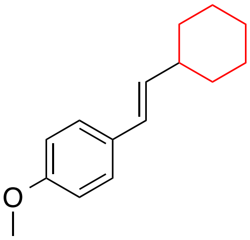


1-(2-cyclopentylvinyl)-4-methoxybenzene (E/Z mixtures) (3aa)

^{1}H NMR (CDCl$_3$, 400MHz): δ 7.29-7.21 (m, 2.68 H), 6.88-6.82 (m, 2.38H), 6.34-6.27 (m, 1.00H), 6.10-6.02 (m, 0.38H), 5.53-5.46 (m, 0.61H), 3.81-3.79 (m, 3.92H), 2.99-2.91 (m, 0.62H), 2.61-2.53 (m, 0.62H), 1.89-1.82 (m, 2.44H), 1.72-1.54 (m, 5.93H), 1.40-1.31 (m, 2.71H);

^{13}C NMR (CDCl$_3$, 100MHz): δ 158.54, 158.13, 136.96, 129.80, 129.76, 127.14, 126.73, 113.86, 113.62, 113.51, 55.27, 55.23, 43.80, 38.79, 34.21, 33.29, 32.63, 25.54, 25.20.

HRMS (APCI): $C_{14}H_{19}O$ [M+H$^+$], theoretical mass: 203.14304, found: 203.14256.

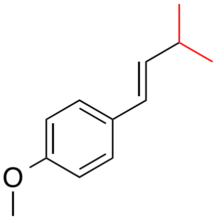


1-(2-cyclohexylvinyl)-4-methoxybenzene (E/Z mixtures) (3c)

^{1}H NMR (CDCl$_3$, 400MHz): δ 7.29-7.20 (m, 2.90 H), 6.89-6.82 (m, 2.81H), 6.31-6.23 (m, 1.23H), 6.07-6.01 (m, 0.28H), 5.43-5.38 (m, 1.00H), 3.82-3.80 (m, 4.70H), 2.61-2.52 (m, 1.09H), 2.17-2.07 (m, 0.25H), 1.78-1.65 (m, 7.43H), 1.31-1.15 (m, 7.46H);

^{13}C NMR (CDCl$_3$, 100MHz): δ 158.56, 158.13, 137.54, 134.78, 129.73, 126.96, 126.21, 113.87, 113.59, 55.27, 55.26, 41.11, 36.87, 33.30, 33.08, 26.19, 25.73.

HRMS (APCI): $C_{15}H_{21}O$ [M+H$^+$], theoretical mass: 217.15869, found: 217.15811.

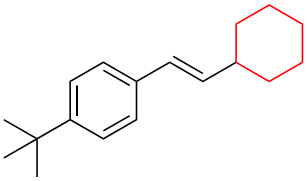


1-methoxy-4-(3-methylbut-1-en-1-yl)benzene (E/Z mixtures) (3u)

^{1}H NMR (CDCl$_3$, 400MHz): δ 7.30-7.15 (m, 2.63 H), 6.90-6.80 (m, 2.80H), 6.30-6.20(m, 1H), 6.10-6.00(m, 0.41H), 5.65-5.55(m, 0.04H), 5.45-5.35(m, 0.45H), 5.15-5.10(m, 0.07H), 3.85-3.78(m, 4.83H), 2.95-2.82(m, 0.38H), 2.50-2.40(m, 0.40H), 1.12-1.02(m, 7.38H);

^{13}C NMR (CDCl$_3$, 100MHz): δ 158.58, 158.13, 139.07, 135.93, 129.76, 126.98, 125.79, 113.87, 113.55, 55.27, 55.23, 31.46, 27.07, 23.21, 22.55.

HRMS (APCI): $C_{12}H_{17}O$ [M+H$^+$], theoretical mass: 177.12739, found: 177.12682.

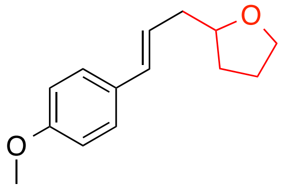


(*E*)-1-(*tert*-butyl)-4-(2-cyclohexylvinyl)benzene (E/Z mixtures)[2] (3m)

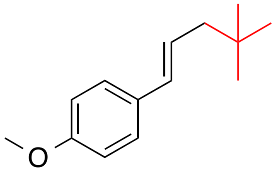
^{1}H NMR (CDCl$_3$, 400MHz): δ 7.45-7.20 (m, 5.64 H), 7.15-7.0(m, 0.87H), 6.72-6.69(m, 0.29H), 6.35-6.25(m, 1H), 6.18-6.12(m, 0.59), 5.50-5.42(m, 0.36H), 2.63-2.56(m, 0.68H), 2.21-2.06 (m, 0.75H), 1.85-1.65 (m, 6.61H), 1.62-1.42 (m, 2.8H), 1.40-1.28(m, 17.61H), 1.25-1.18(m, 4H);

^{13}C NMR (CDCl$_3$, 100MHz): δ 149.73, 149.32, 138.42, 136.15, 135.30, 135.07, 128.35, 127.84, 126.90, 126.55, 125.42, 125.11, 124.78, 123.94, 41.17, 36.96, 34.50, 34.48, 33.04, 31.43, 26.74, 26.28, 26.21, 26.08, 25.72.

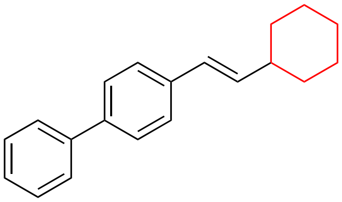
MS (EI): $C_{18}H_{26,}$ theoretical mass: 242.2, found: 242.2.



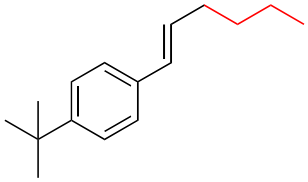
2-(3-(4-methoxyphenyl)allyl)tetrahydrofuran (E/Z mixtures) (3af)
^{1}H NMR (CDCl$_3$, 400MHz): δ 7.35-7.18 (m, 3.64 H), 6.92-6.80 (m, 3.10H), 6.50-6.35(m, 1.32H), 6.13-6.03(m, 0.32H), 5.66-5.56(m, 1H), 4.01-3.69(m, 9.98H), 2.70-2.30 (m, 3.35H), 2.10-1.80 (m, 5.65H), 1.62-1.40 (m, 3.21H);
^{13}C NMR (CDCl$_3$, 100MHz): δ 158.26, 129.95, 129.90, 127.14, 126.90, 124.54, 113.85, 113.54, 113.51, 79.03, 67.89, 55.26, 55.23, 39.20, 34.66, 30.97, 25.71.
HRMS (APCI): $C_{14}H_{19}O_2$ [M+H$^+$], theoretical mass: 219.13796, found: 219.13744.



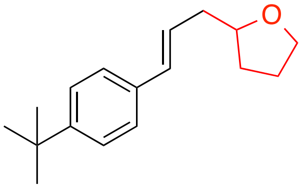
1-(4,4-dimethylpent-1-en-1-yl)-4-methoxybenzene (E/Z mixtures) (3ah)
^{1}H NMR (CDCl$_3$, 400MHz): δ 7.54-7.46 (m, 3.8 H), 7.12-7.08 (m, 3.24H), 6.69-6.64 (d, *J* = 11.6Hz, 0.94H), 4.05 (m, 5.5H), 2.48-2.46 (m, 2.02H), 2.31-2.29 (m, 0.69H), 1.25-1.20 (m,11.6H);
^{13}C NMR (CDCl$_3$, 100MHz): δ 161.1, 130.5, 128.7, 127.9, 123.1, 115.1, 55.8, 49.9, 31.0, 29.9.
HRMS (APCI): $C_{14}H_{21}O$ [M+H$^+$], theoretical mass: 205.15869, found: 205.15812.



4-(2-cyclohexylvinyl)-1,1'-biphenyl (E/Z mixtures) (3l)
^{1}H NMR (CDCl$_3$, 400MHz): δ 7.65-7.41 (m, 27 H), 7.39-7.30 (m, 5.6H), 6.40-6.30 (m, 2.40H), 6.21-6.18(m, 1.44H), 5.56-5.49(t, *J* =10 Hz, 1H), 2.21-2.13 (m, 1H), 2.70-2.55(m, 1.88H), 2.10-2.10(m, 1.49H), 1.83-1.71 (m, 17.7H), 1.40-1.18 (m, 18.9H);
^{13}C NMR (CDCl$_3$, 100MHz): δ 140.91, 139.49, 139.26, 139.19, 137.15, 137.08, 137.01, 128.77, 128.73, 127.17, 127.11, 126.88, 126.63, 126.33, 41.23, 37.06, 33.28, 32.98, 26.19, 26.06, 25.71.
HRMS (APCI): $C_{20}H_{23}$ [M+H$^+$], theoretical mass: 263.17943, found: 263.17860.



1-(*tert*-butyl)-4-(hex-1-en-1-yl) benzene (E/Z mixtures) (3ab)
^{1}H NMR (CDCl$_3$, 400MHz): δ 7.41-7.21 (m, 10 H), 7.20-7.10 (m, 2H), 6.85-6.75(m, 0.35H), 6.50-6.35(m, 1,95H), 6.30-6.20(m, 0.86H), 5.70-5.60 (m, 1H), 2.80-2.70 (m, 0.25H), 2.65-2.55(m, 0.75H), 2.43-2.33(m, 2.15H), 2.30-2.13 (m, 2.88H), 1.50-1.23 (m, 21H), 1.05-0.85 (m, 11H);
^{13}C NMR (CDCl$_3$, 100MHz): δ 149.73, 149.30, 148.55, 148.42, 148.11, 135.22, 134.99, 132.63, 128.49, 127.86, 125.59, 125.37, 125.02, 124.94, 124.86, 124.09, 51.80, 51.20, 37.15, 34.51, 34.48, 31.69, 31.47, 31.35, 28.51, 27.69, 27.22, 22.58, 22.49, 22.26, 14.13, 14.08, 14.03, 14.01, 13.97.
HRMS (APCI): $C_{16}H_{25}$ [M+H$^+$], theoretical mass: 217.19508, found: 217.19510.

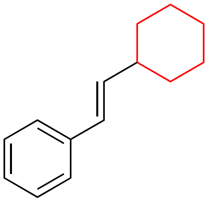


(*E*)-2-(3-(4-(*tert*-butyl) phenyl)allyl)tetrahydrofuran (3z)

^{1}H NMR (CDCl$_3$, 400MHz): δ 7.41-7.15 (m, 4 H), 6.51 (d, *J* = 10 Hz, 1H), 5.75-5.65 (m, 1H), 3.93-3.82 (m, 2H), 3.53-3.42 (m, 1H), 2.70-2.60 (m, 1H), 2.58-2.48 (m, 1H), 2.05-1.95 (m, 1H), 1.92-1.82 (m, 2H), 1.55-1.49 (m, 1H), 1.22-1.20 (s, 9H);

^{13}C NMR (CDCl$_3$, 100MHz): δ 149.55, 134.62, 130.27, 128.50, 127.89, 125.05, 79.06, 67.90, 34.75, 34.51, 31.32, 30.99, 25.74.

HRMS (APCI): C$_{17}$H$_{25}$O [M+H$^+$], theoretical mass: 245.18999, found: 245.19819.

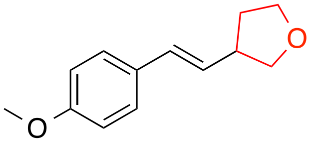


(*E/Z mixture*)-(2-cyclohexylvinyl) benzene (3a)

^{1}H NMR (CDCl$_3$, 400MHz): δ 7.42-7.10 (m, 10 H), 6.41-6.31 (m, 1.3 H), 6.20-6.10 (m, 0.67H), 5.50-5.45 (m, 0.65 H), 2.55-2.50 (m, 1H), 2.25-2.10 (m, 1.13H), 1.80-1.55 (m, 10.8H), 1.45-1.10 (m, 10.8H);

^{13}C NMR (CDCl$_3$, 100MHz): δ 145.9, 143.1,139.8, 138.2, 137.0, 128.1, 127.8, 126.3, 125.4, 123.2, 48.7, 42.2, 41.2, 36.5, 32.3, 31.5, 30.3, 26.1, 25.7.

HRMS (APCI): C$_{14}$H$_{19}$ [M+H$^+$], theoretical mass: 187.14813, found: 187.14710.

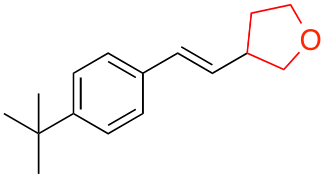


(*E/Z mixture*)-3-(4-methoxystyryl) tetrahydrofuran (3aj)

^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.21-7.18 (d, *J* = 8.7 Hz, 1.6H), 6.89-6.83 (d, J = 8.1 Hz, 2.5H), 6.45-6.37 (m, 1H), 6.03-5.95 (m, 0.2 H), 5.54-5.47 (t, *J* = 11.1 Hz, 0.62 H), 4.01-3.92 (m, 2.3 H), 3.82-3.80 (m, 5.6H), 3.48-3.31 (m, 2H), 3.03-2.95 (m, 0.24 H), 2.17-2.11 (m, 1.3H), 1.83-1.70 (m, 1.3H);

^{13}C NMR (CDCl$_3$, 75 MHz): δ 158.93, 158.48, 131.68, 129.95, 129.80, 129.76, 129.73, 129.41, 129.17, 128.41, 127.15, 73.55, 73.04, 68.36, 68.27, 55.28, 55.26, 43.16, 38.36, 34.18, 33.36, 29.69.

HRMS (APCI): C$_{13}$H$_{17}$O$_2$ [M+H$^+$], theoretical mass: 205.12231, found: 205.12191.

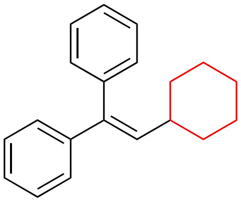


E-3-(4-(*tert*-butyl) styryl) tetrahydrofuran (3ag)

^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.39-7.36 (d, *J* = 8.4 Hz, 2H), 7.22-7.19 (d, J = 8.1 Hz, 2H), 6.46 (d, J = 11.7 Hz, 1H), 5.59-5.52 (dd, J_1 = 9.9 Hz, J_2 = 11.4 Hz, 1H), 4.01-3.92 (m, 2H), 3.85-3.77 (m, 1H), 3.52-3.35 (m, 2H), 2.20-2.14 (m, 1H), 1.78-1.73 (m, 1H), 1.33, (s, 9H) ;

^{13}C NMR (CDCl$_3$, 75 MHz): δ 149.87, 134.26, 132.54, 129.73, 128.28, 125.17, 73.55, 68.36, 38.44, 34.52, 34.20, 31.30.

HRMS (APCI): C$_{16}$H$_{23}$O [M+H$^+$], theoretical mass: 205.12231, found: 205.12259.



(2-cyclohexylethene-1,1-diyl)dibenzene[3] (3h)
^{1}H NMR ($CDCl_3$, 400MHz): δ 7.41-7.21 (m, 10 H), 5.94 (d, *J* = 10 Hz, 1H), 2.21-2.13 (m, 1H), 1.73-1.71 (m, 5H), 1.22-1.20 (m, 5H);
^{13}C NMR ($CDCl_3$, 100MHz):
δ 142.95, 140.59, 139.60, 135.97, 129.79, 128.13, 128.03, 127.19, 126.77, 126.71, 38.32, 33.35, 26.01, 25.61
MS (EI): $C_{20}H_{22}$, theoretical mass: 262.2, found: 262.2.

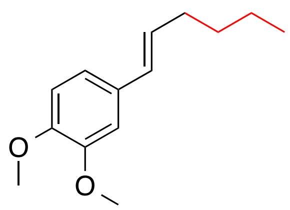
Reference:

1: C. M. McMahen and E. J. Alexanian, *Angew. Chem. Int. Ed.*, 2014, **53**, 5974;

2: Y. Zhu and Y. Wei, *Chem. Sci.*, 2014, **5**, 2379;

3: Y. Zou and J. Zhou, *Chem. Comm.*, 2014, **50**, 3725;

- ***^{1}HNMR spectrum and ^{13}CNMR Spectrum for new compounds***



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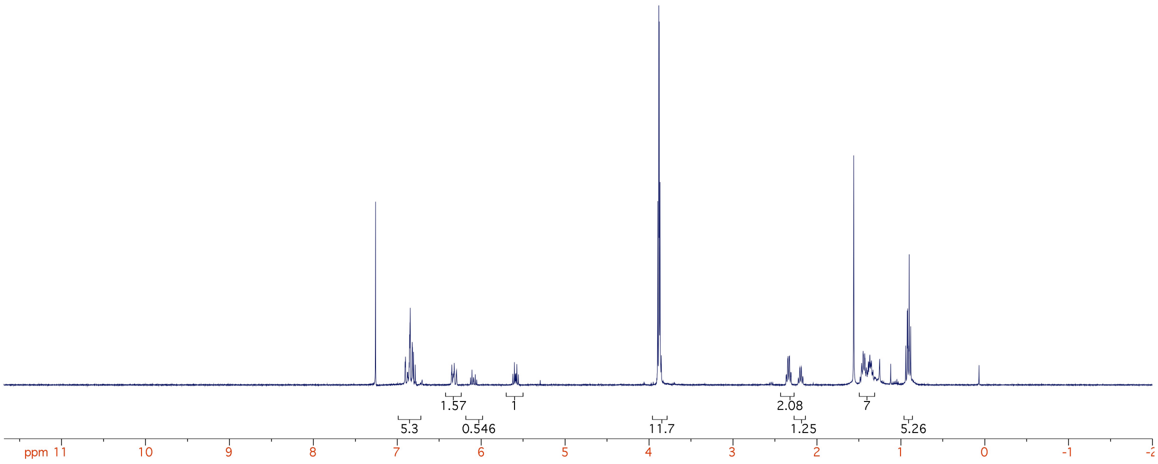

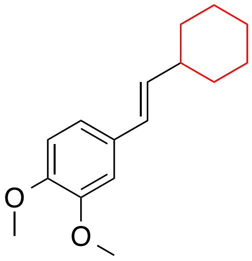

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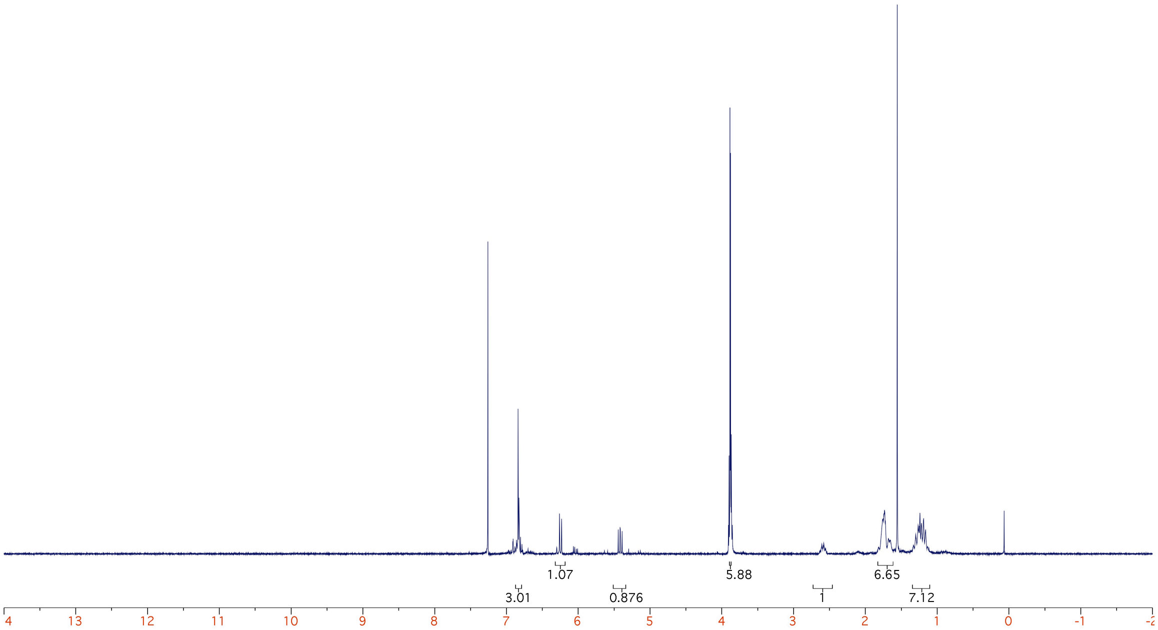

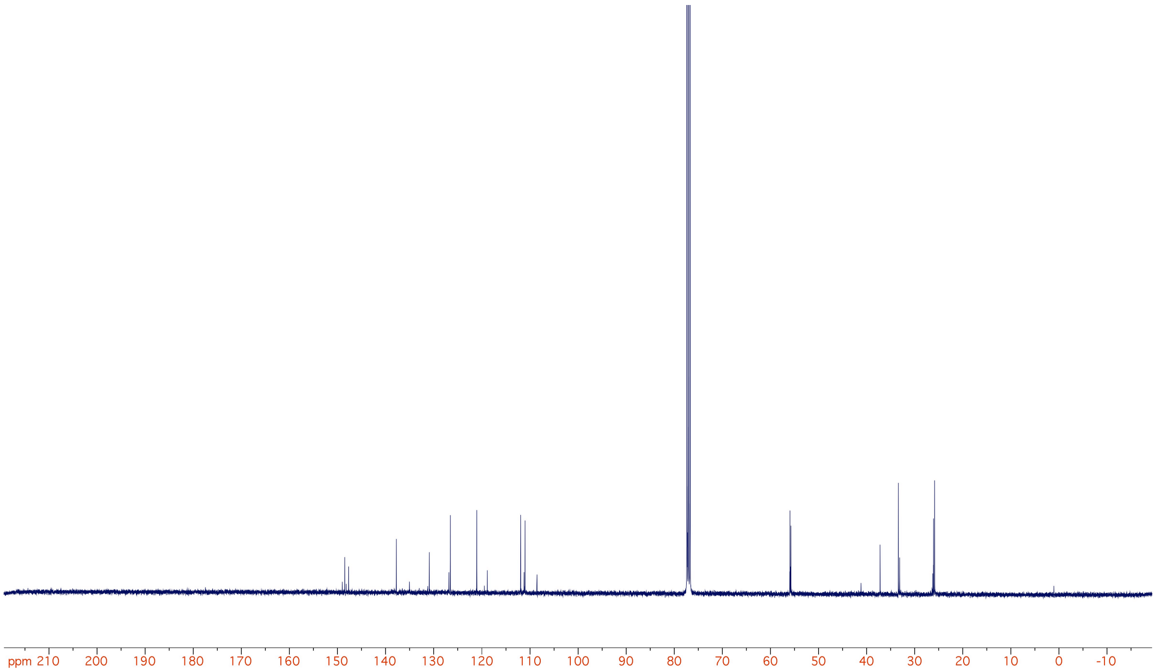

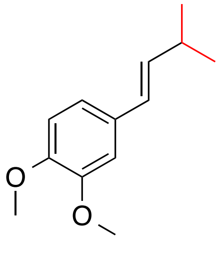

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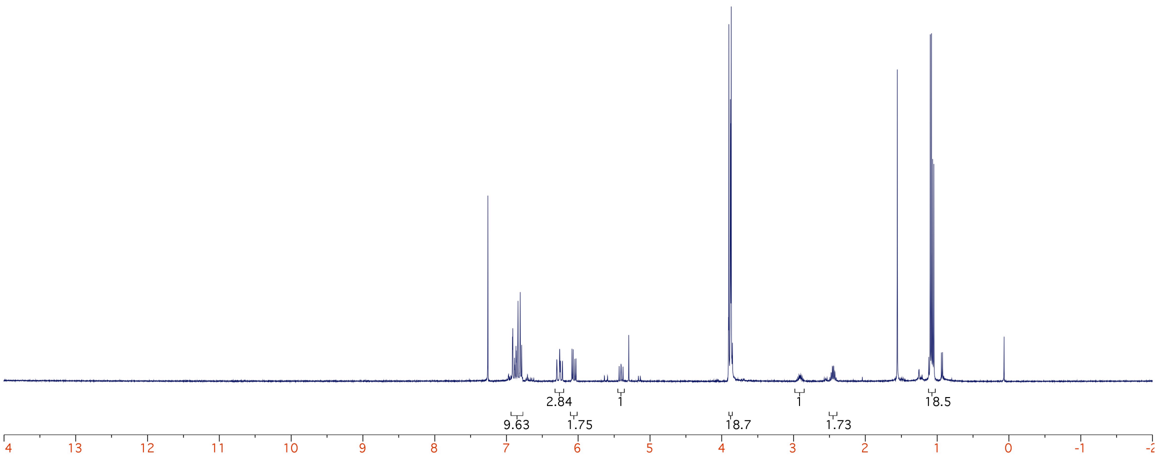

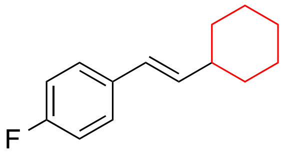

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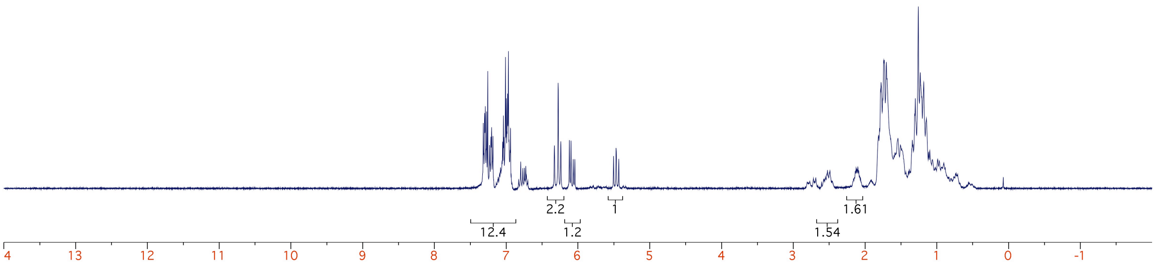

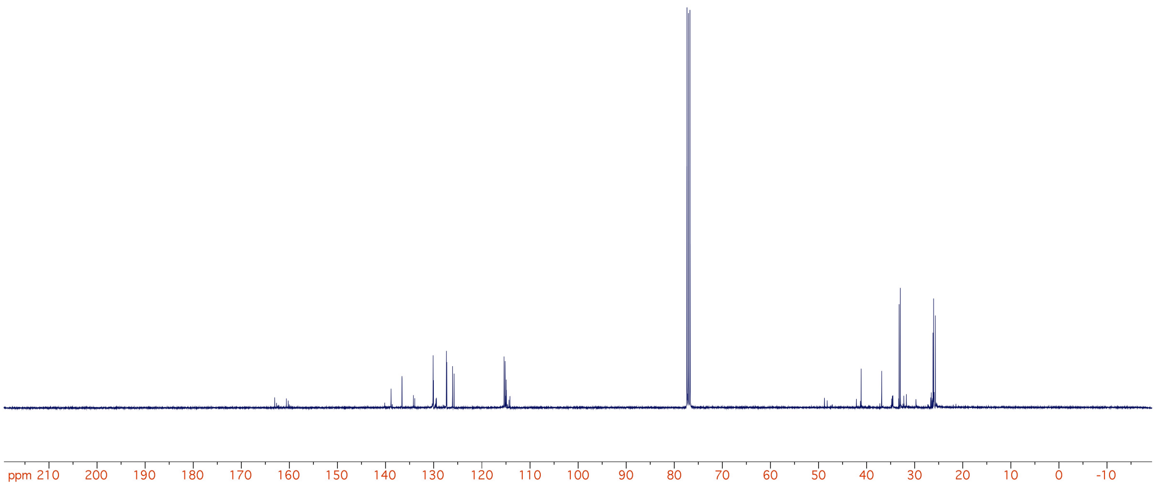

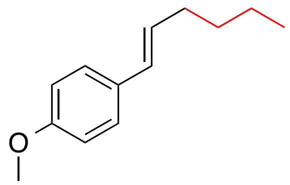

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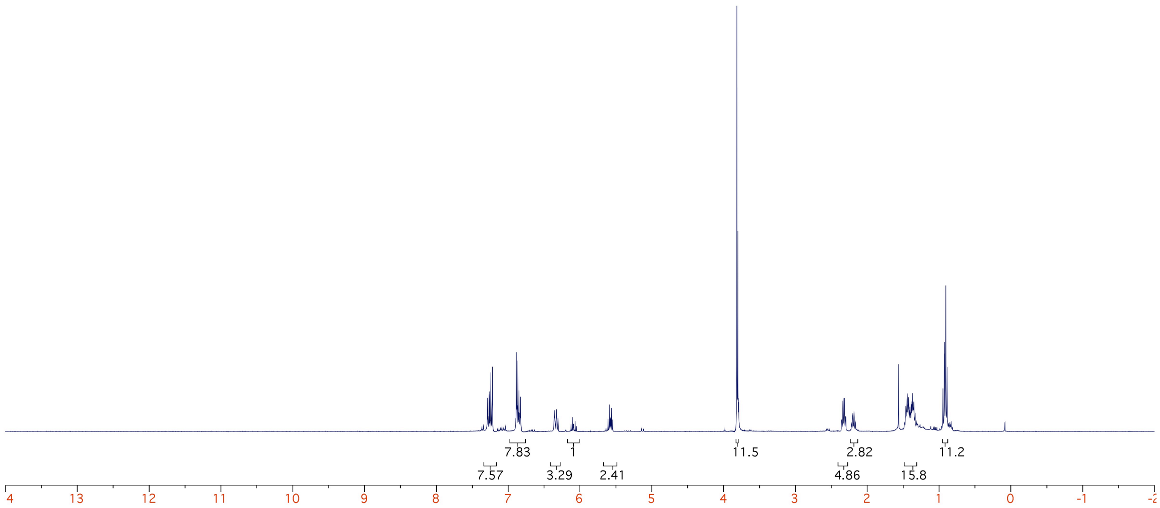

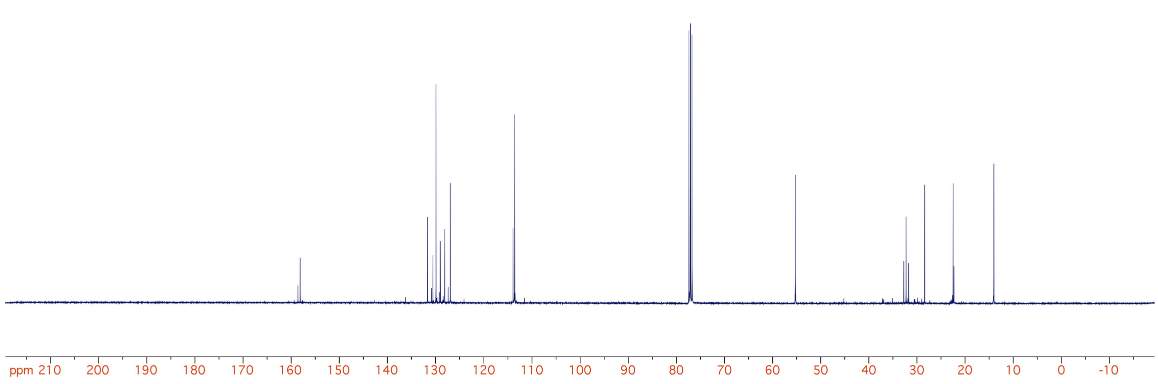

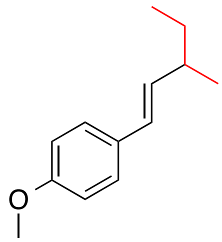

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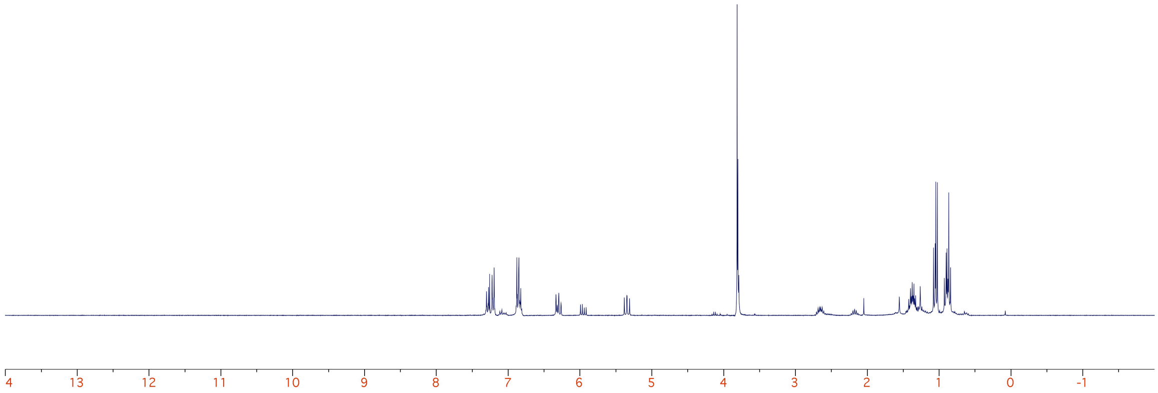

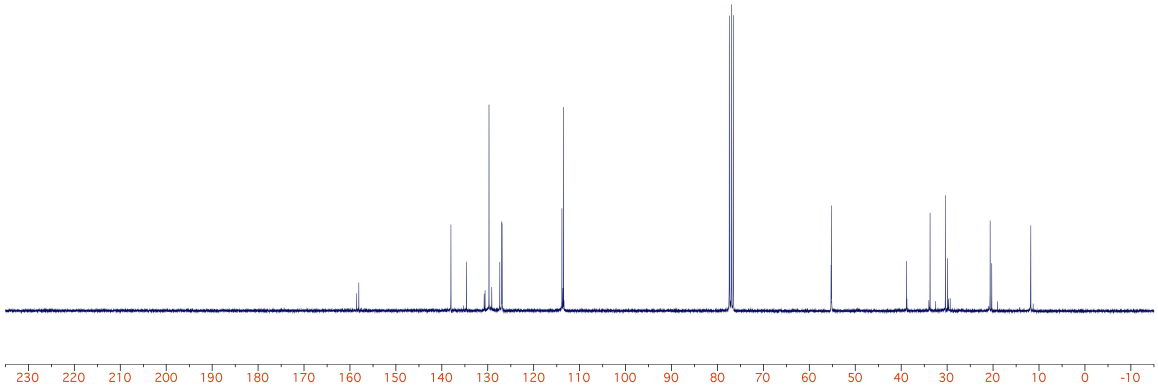

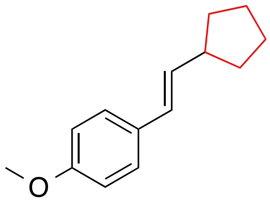

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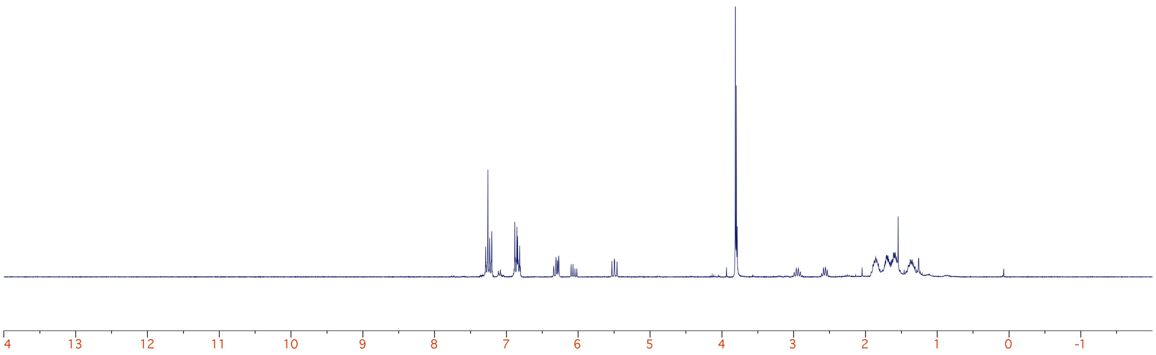

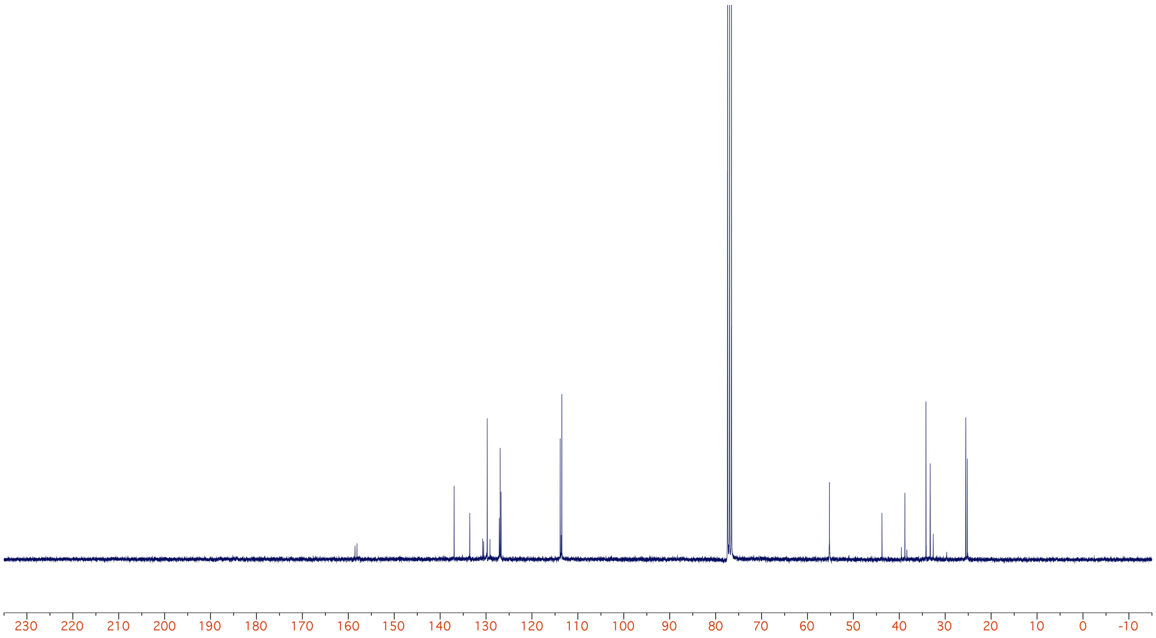

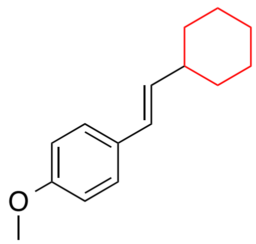

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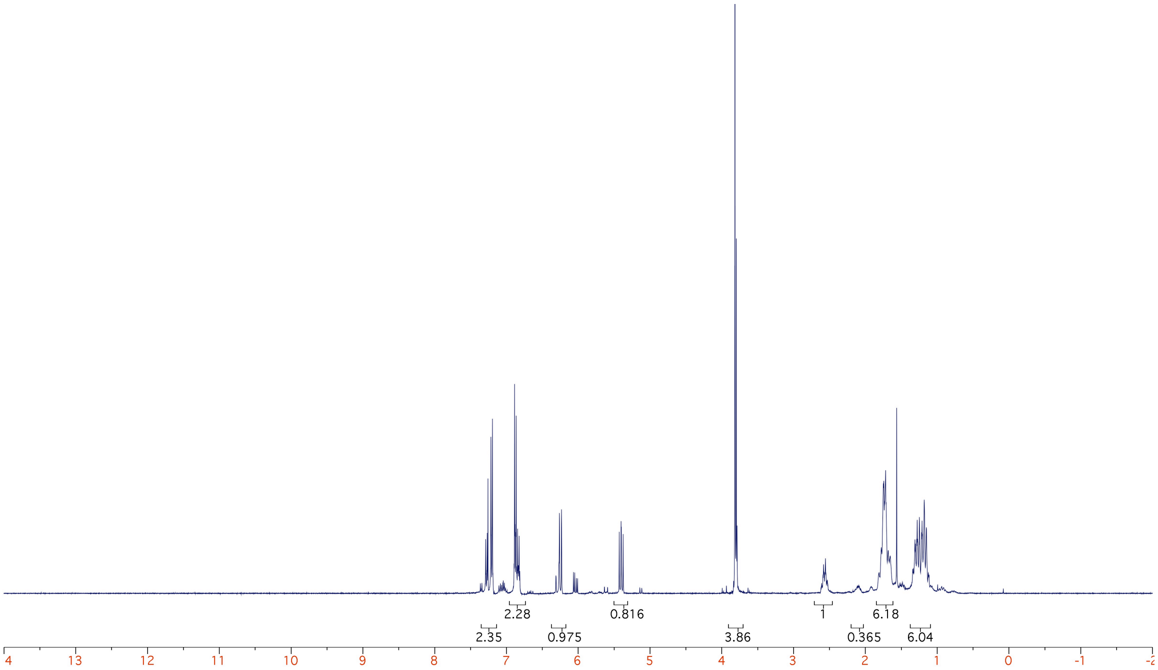

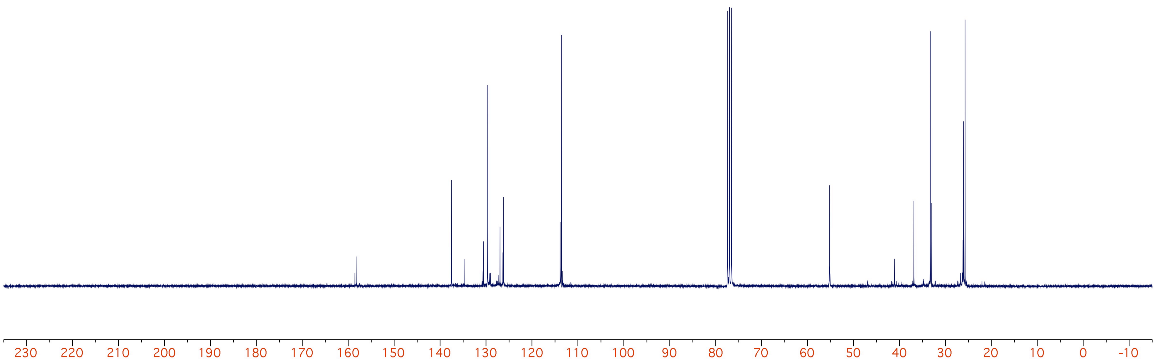

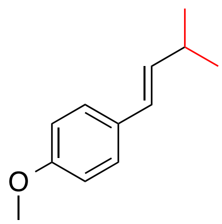

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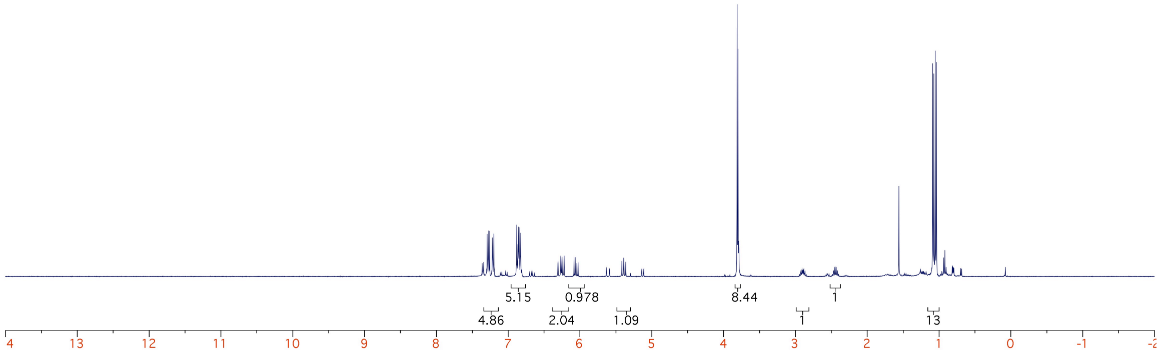

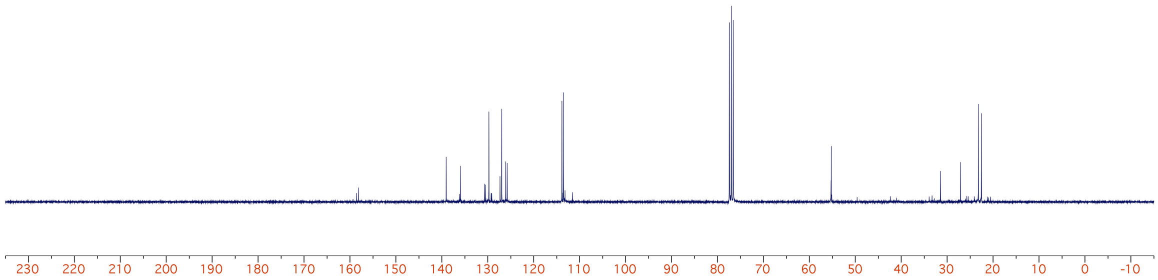

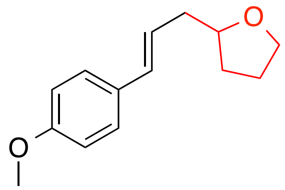

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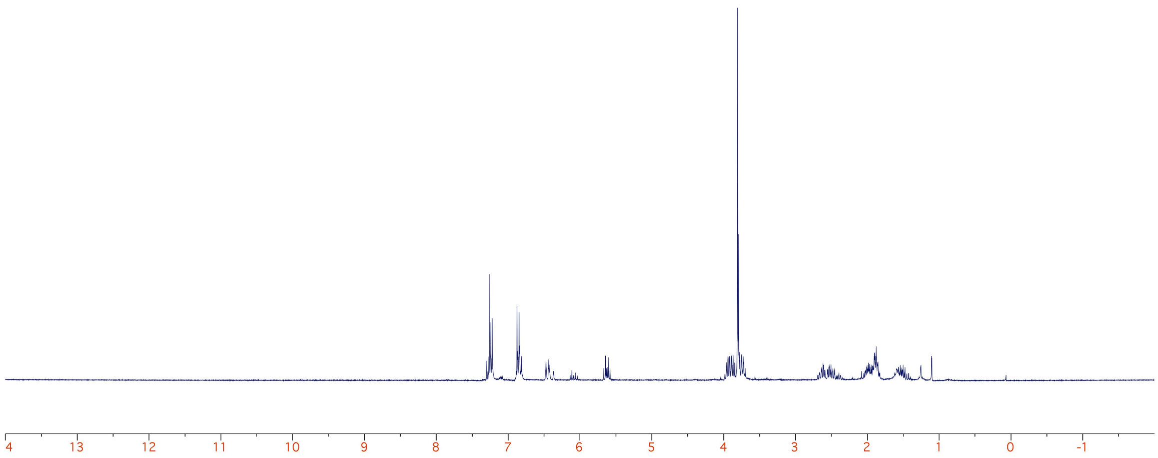

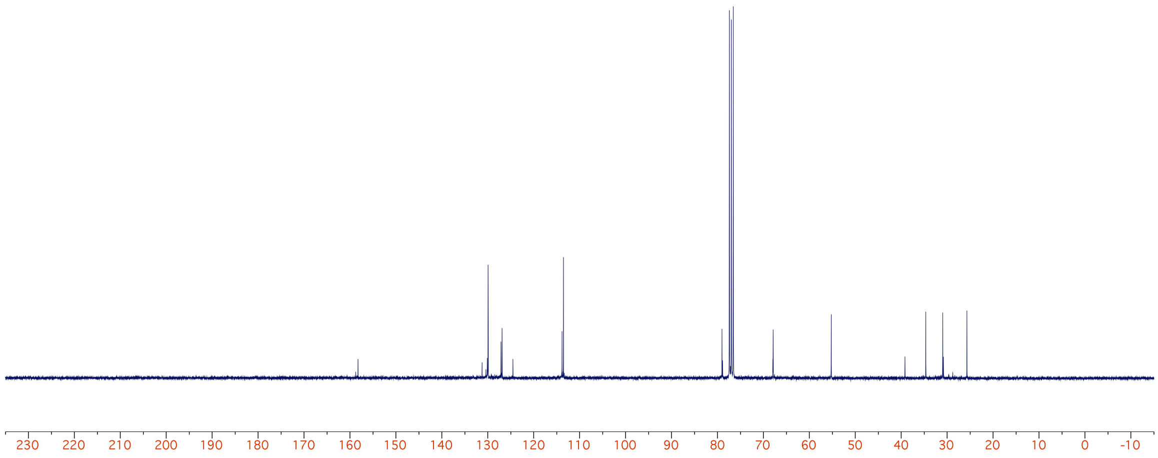

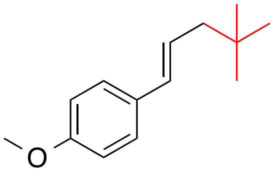

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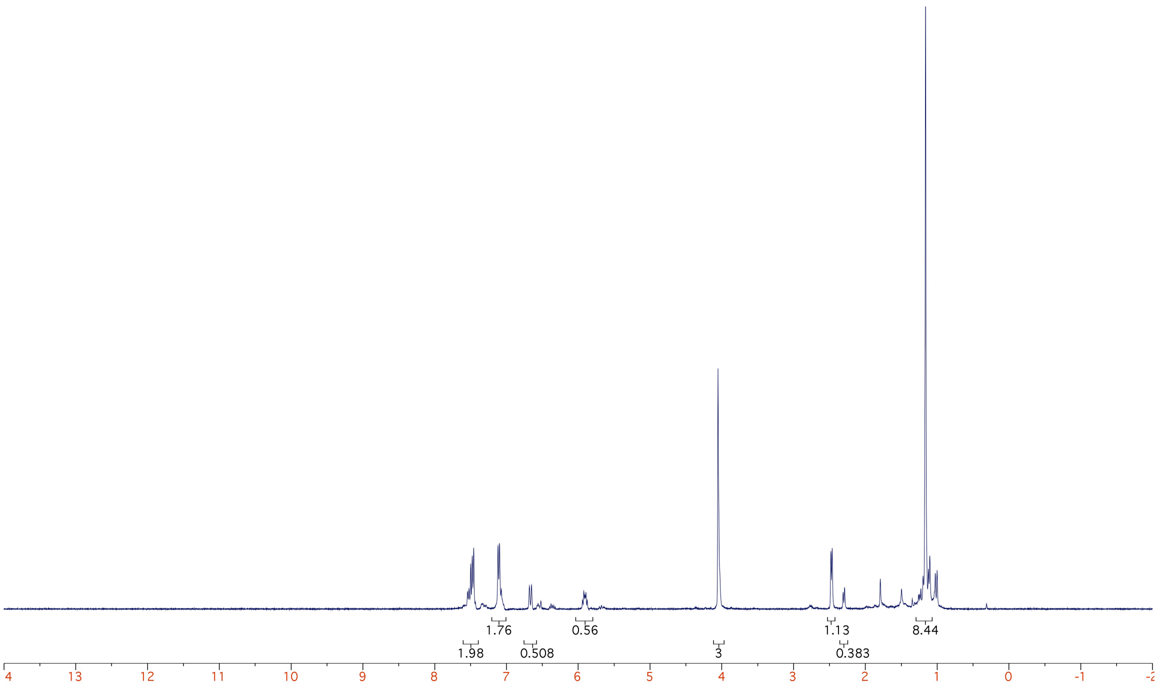

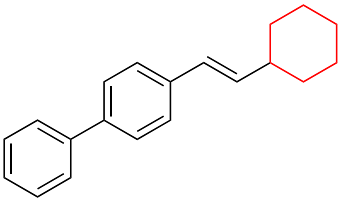

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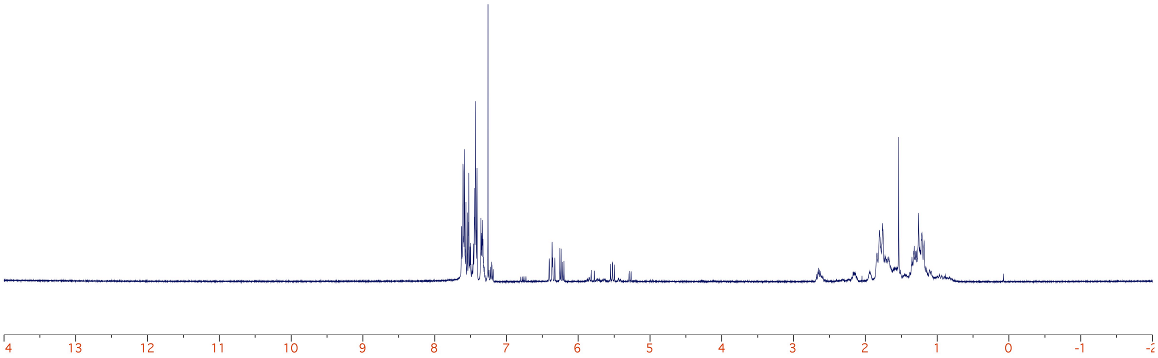

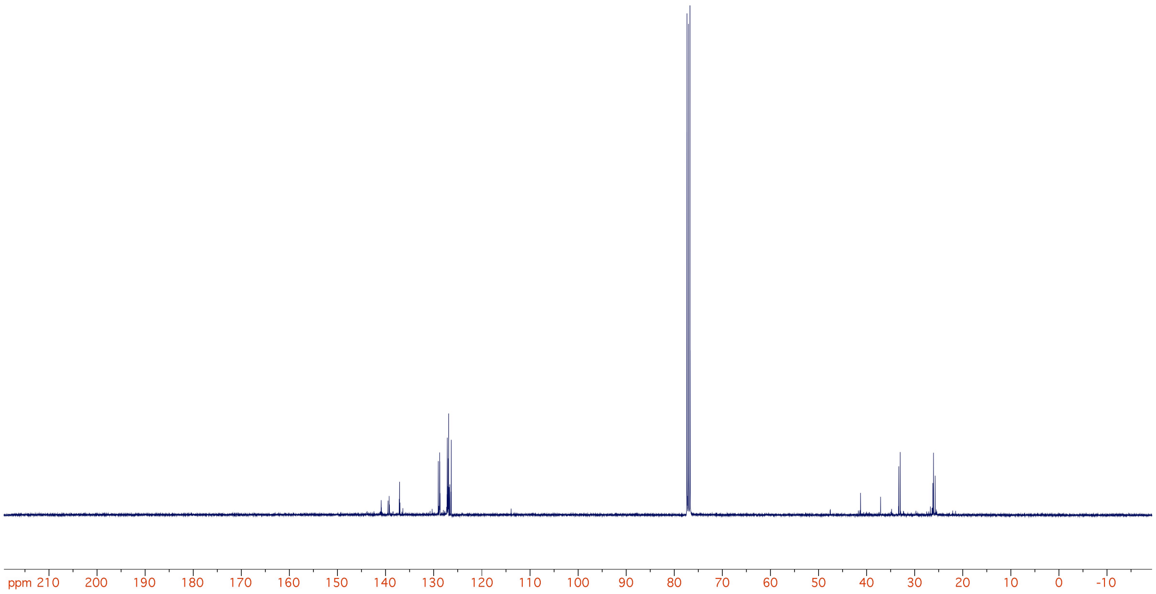

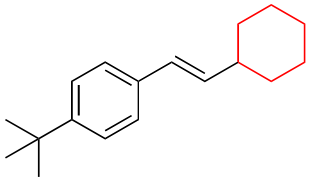

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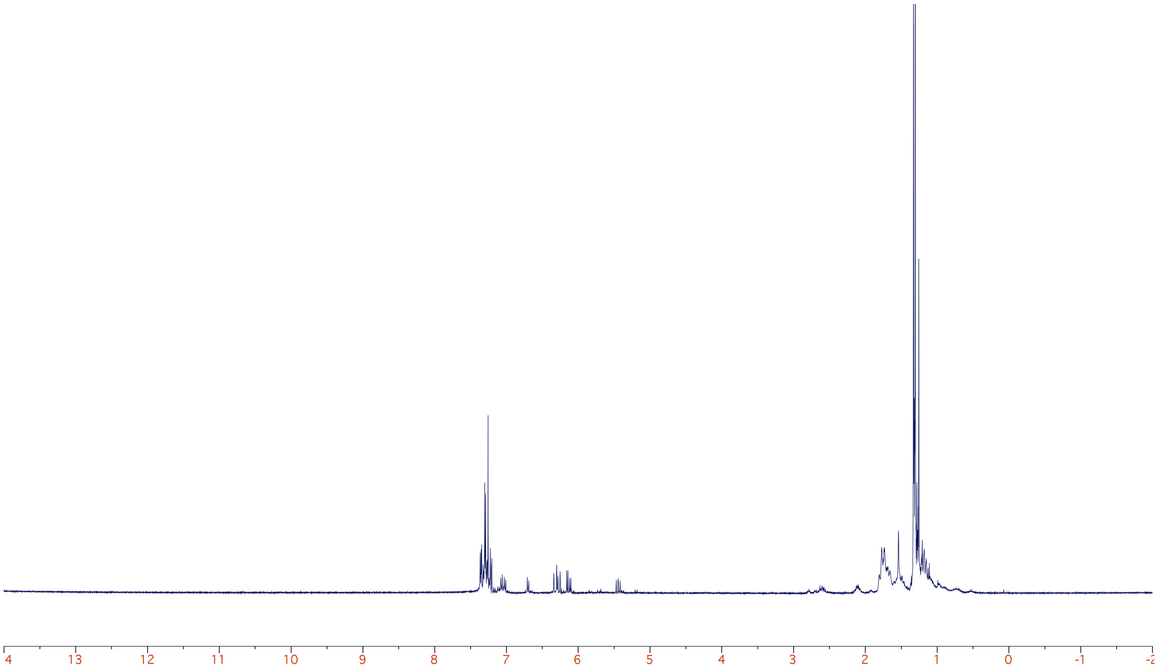

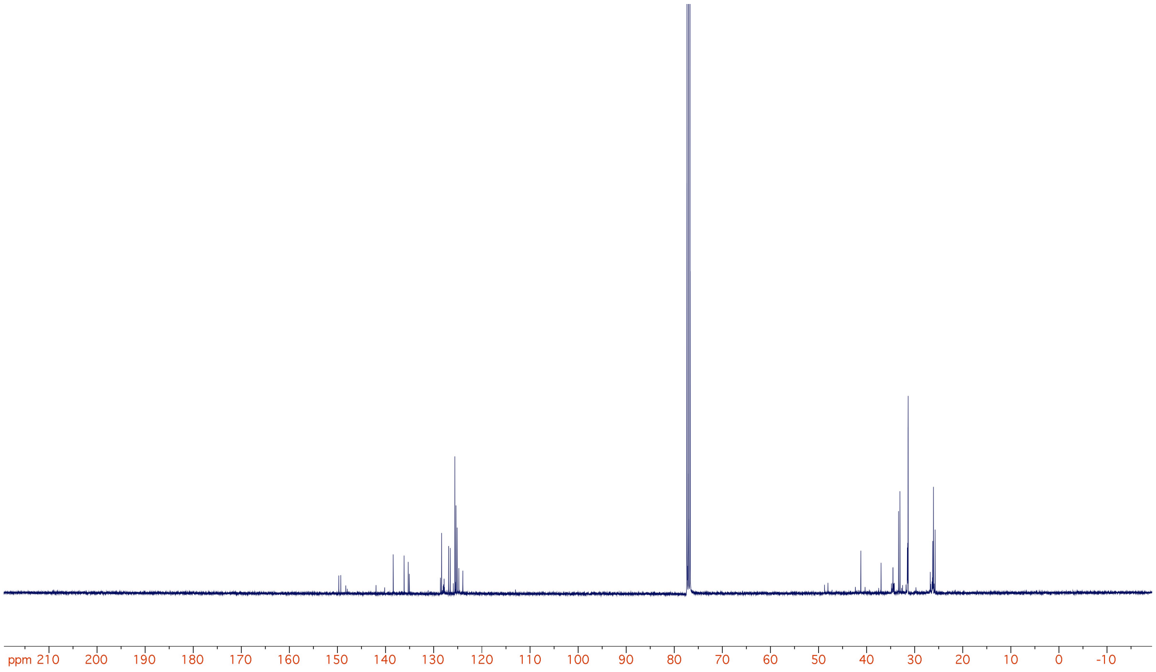

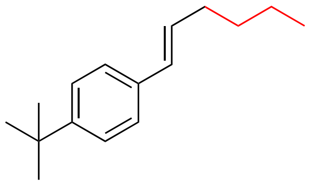

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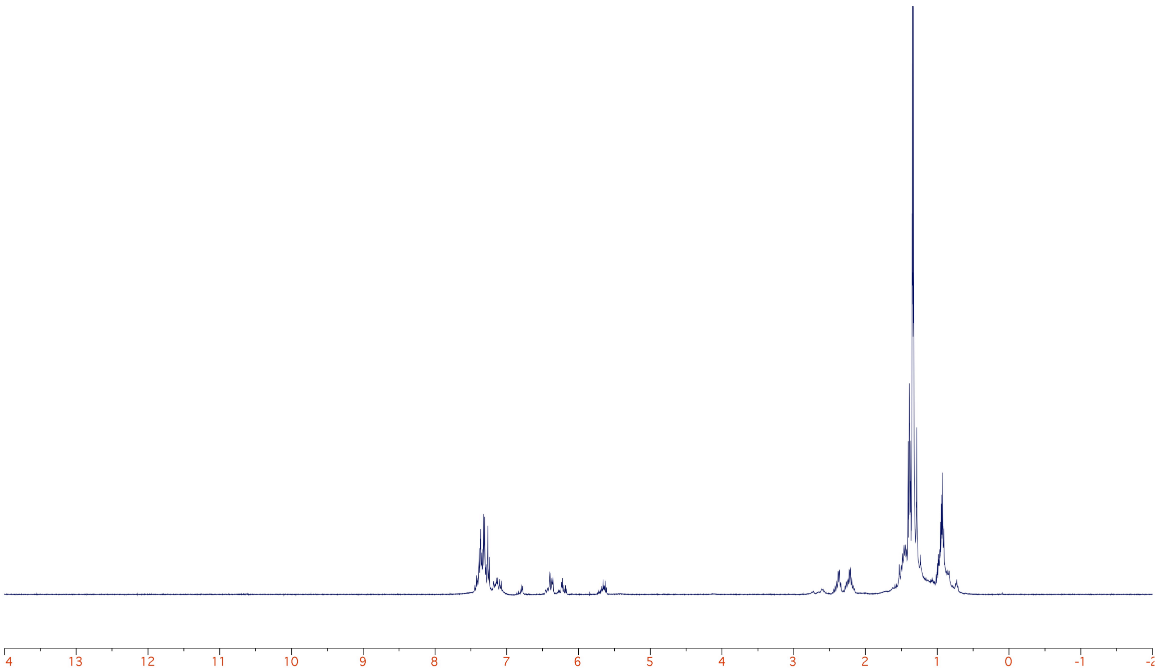

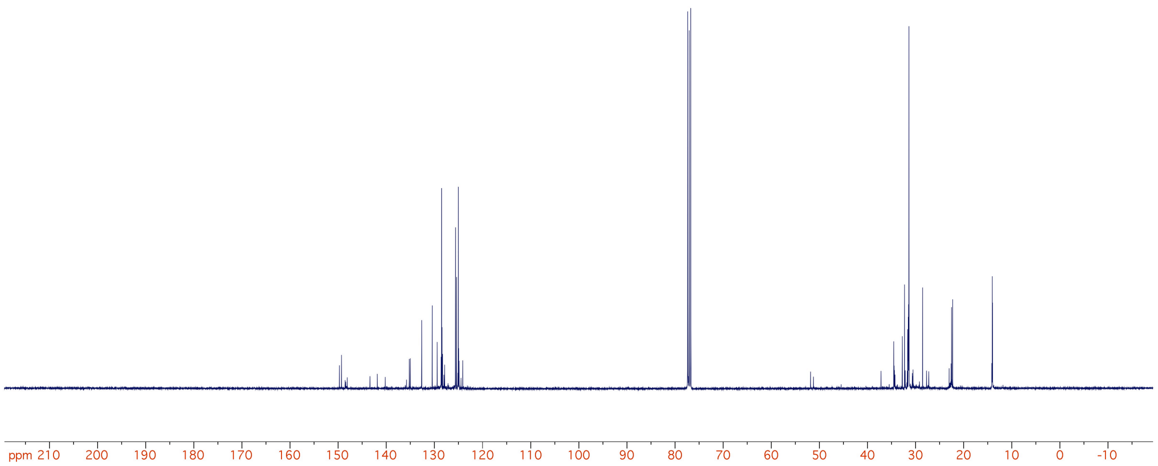

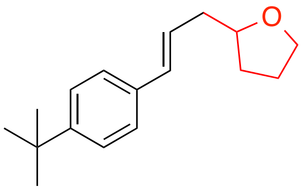

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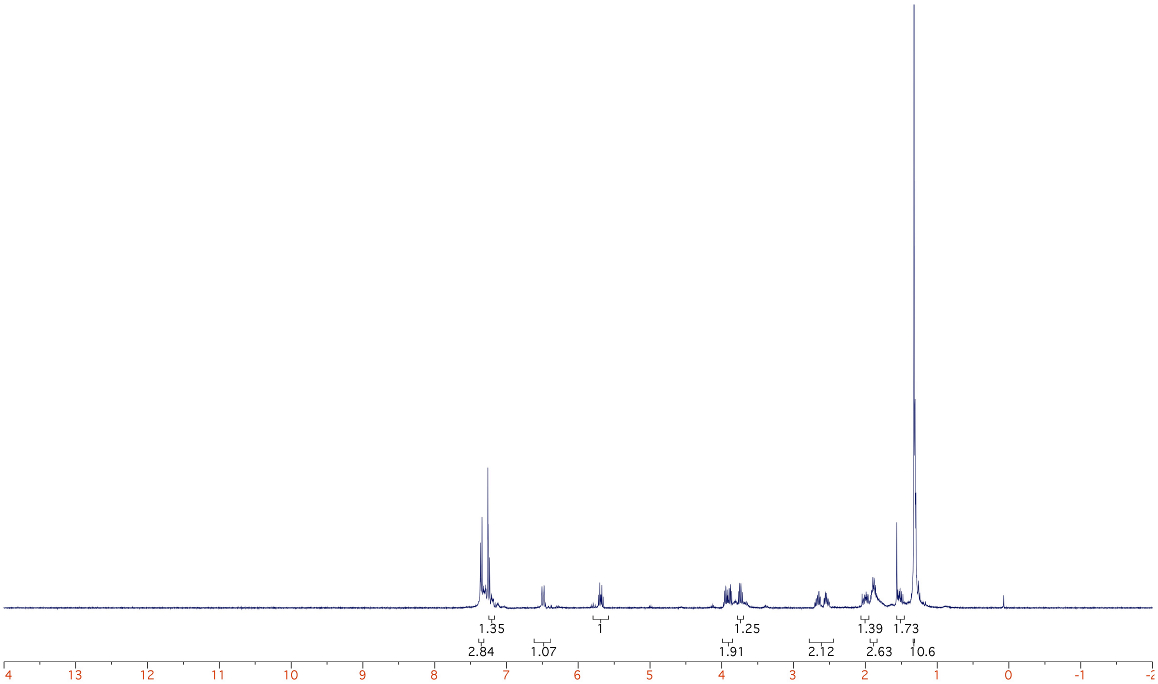

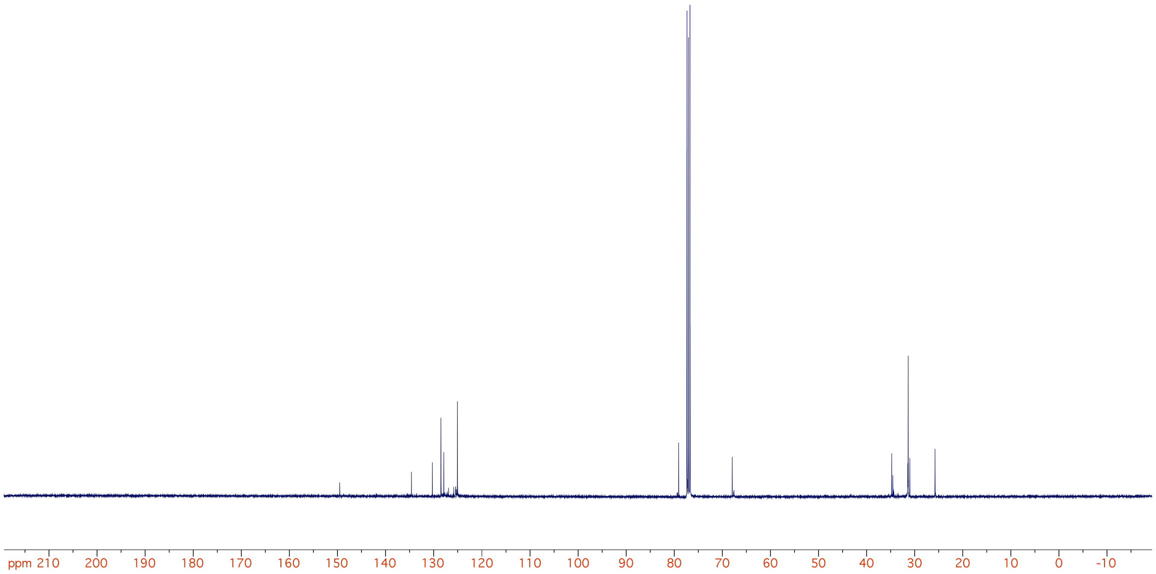

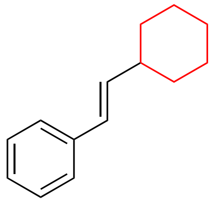

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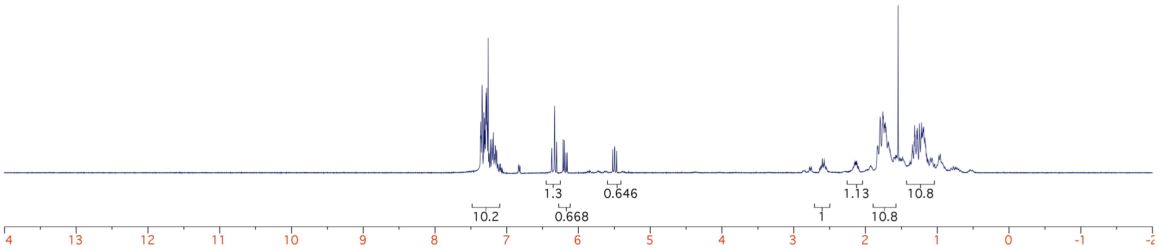

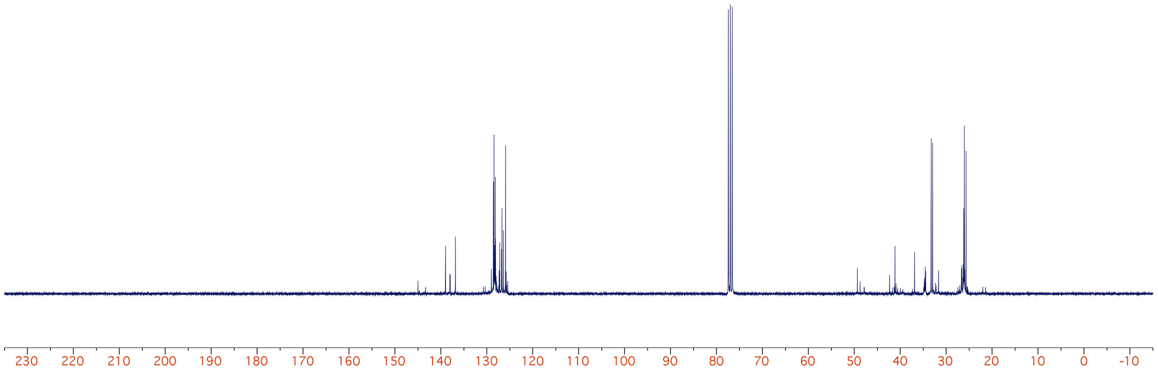

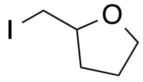
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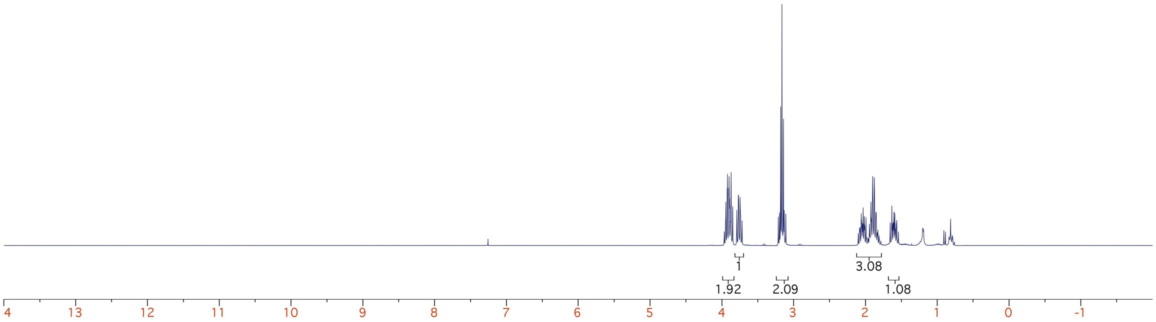
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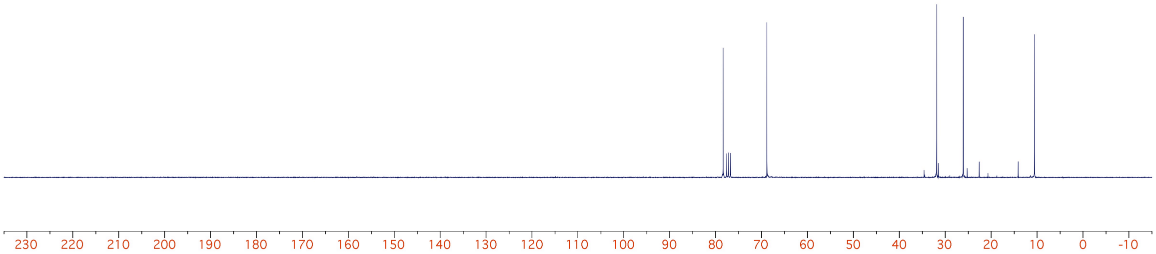
-1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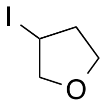
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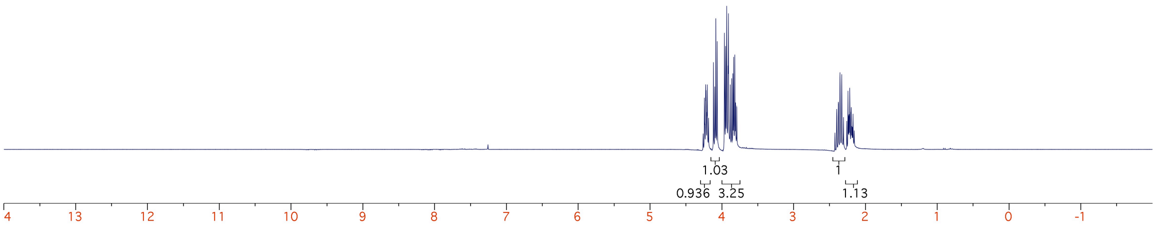
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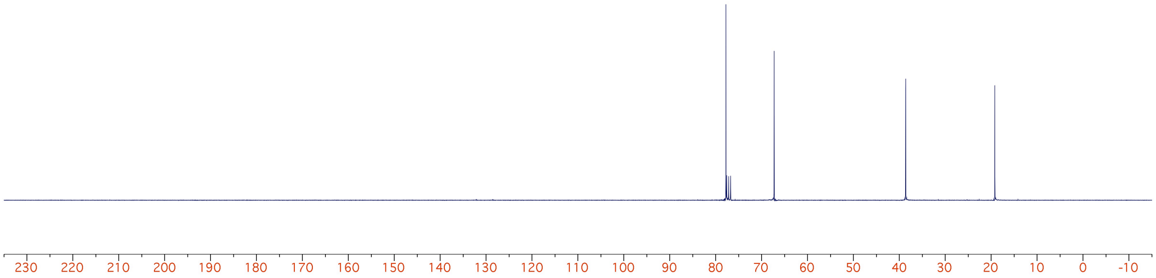
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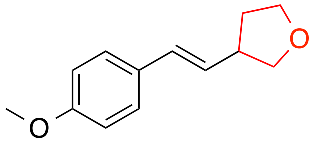
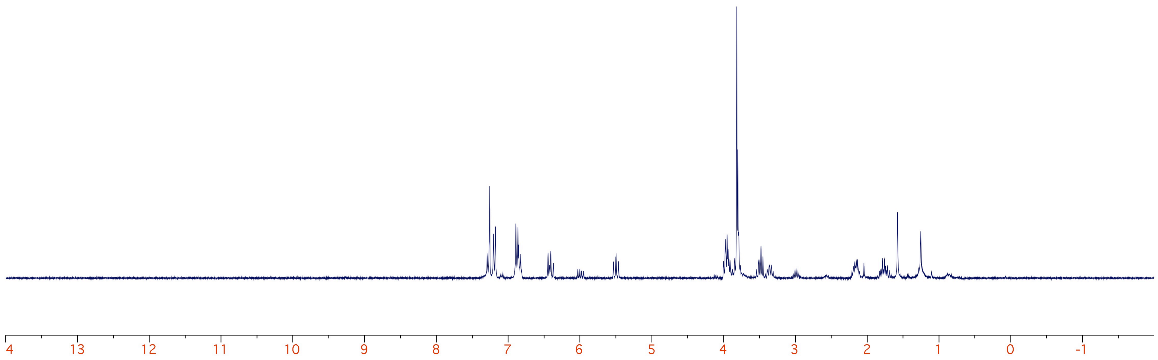
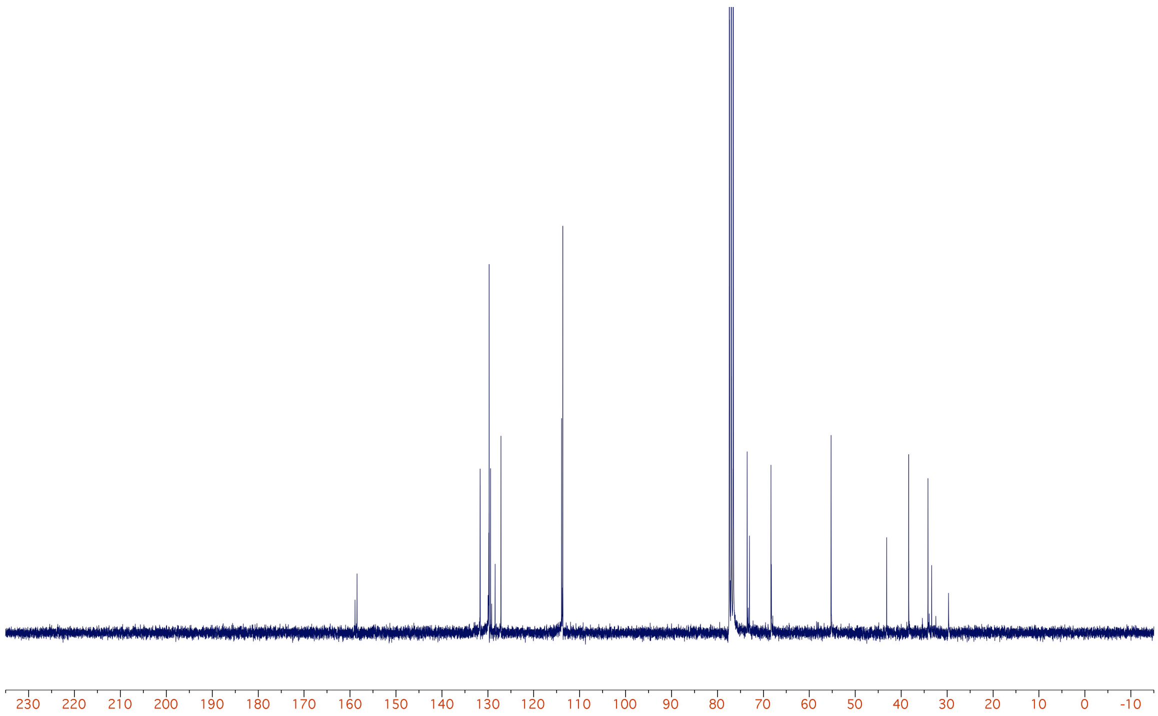
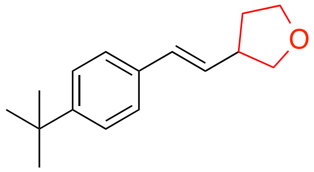


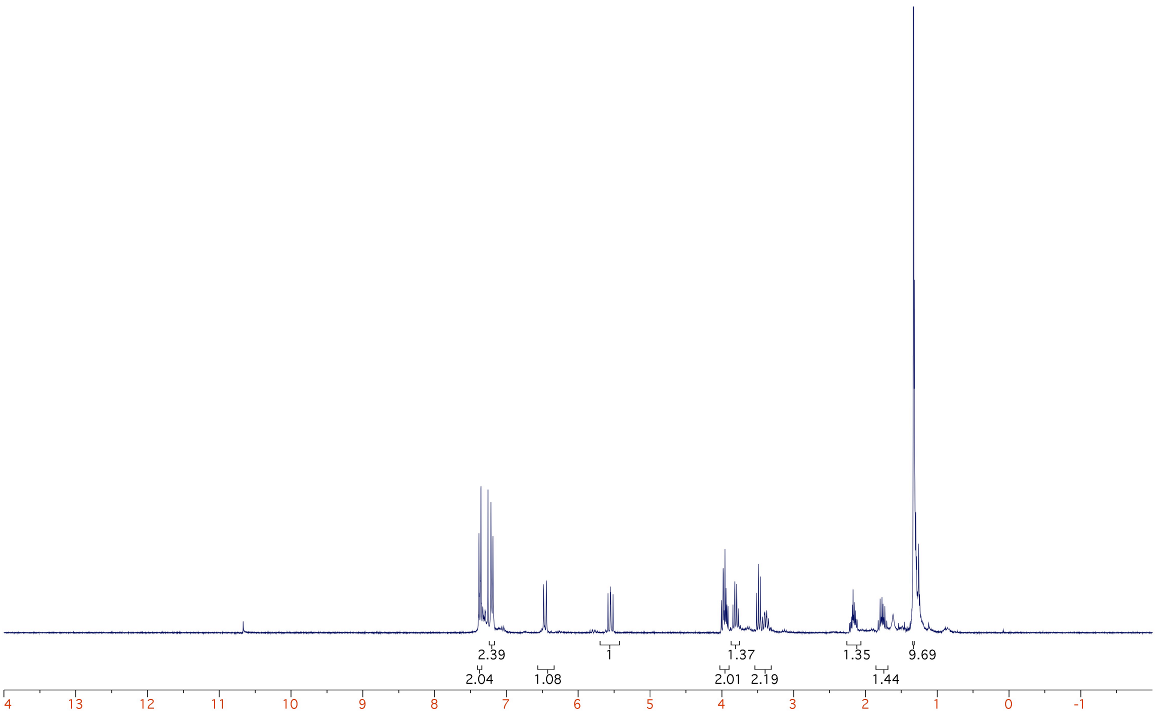
(E/Z isomers mixture)

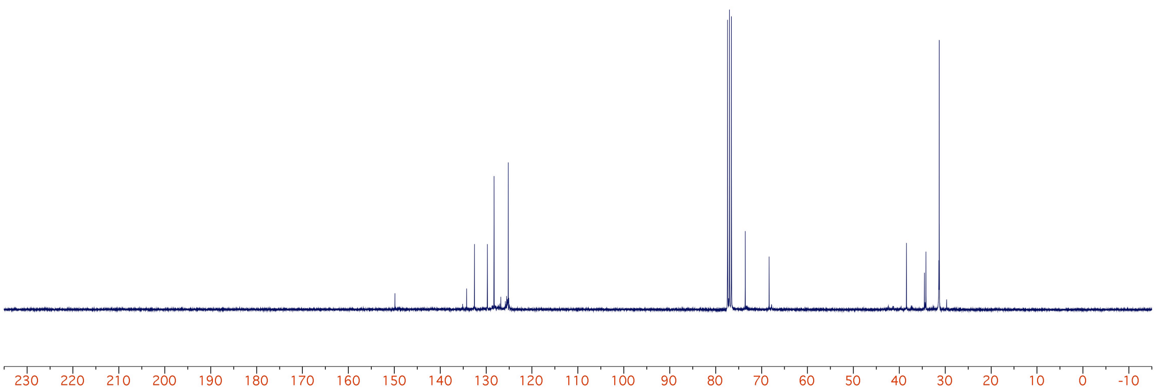


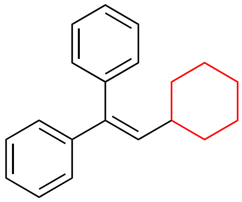


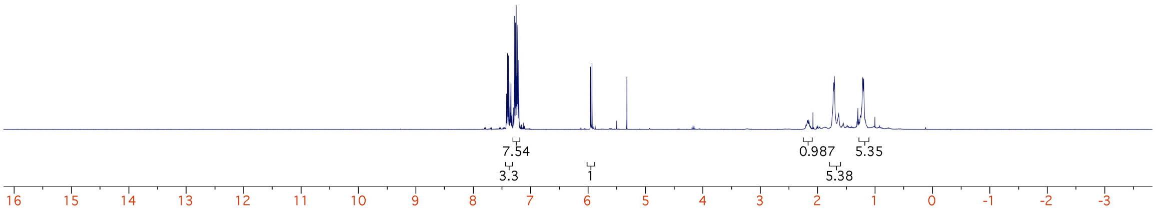


(E/Z isomers mixture)





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5.35
5.38
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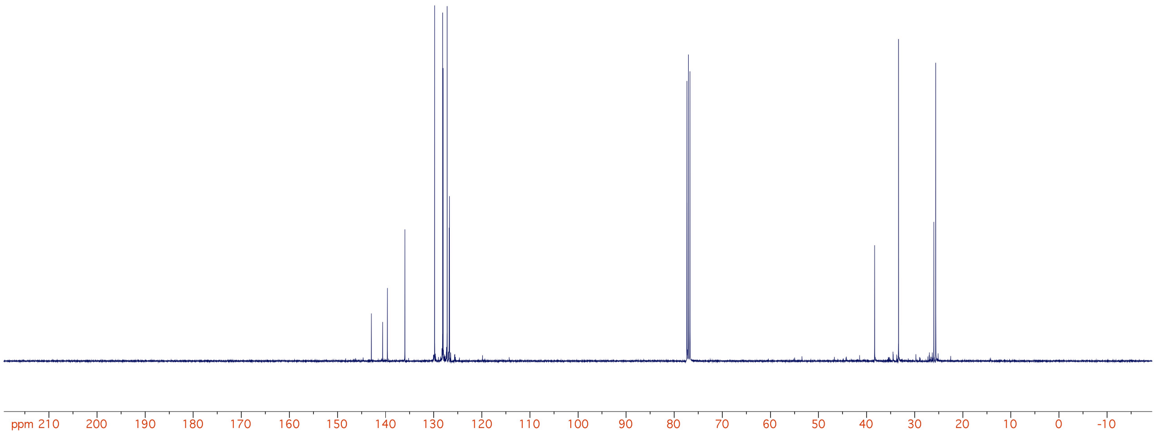
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