

Supporting Information File 1

for

**Cyclization–endoperoxidation cascade reactions of
dienes mediated by a pyrylium photoredox catalyst**

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Experimental procedures and characterization data

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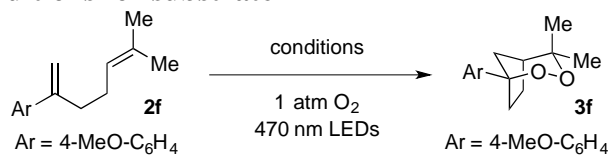
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I. General information. Proton and carbon nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded on a Bruker model DRX 400 or AVANCE III 600 CryoProbe (^1H NMR at 400 MHz or 600 MHz and ^{13}C NMR at 100 MHz or 150 MHz) spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in solvent (^1H NMR: CHCl_3 at 7.24 ppm). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the residual solvent peak (^{13}C NMR: CDCl_3 at 77.0 ppm). NMR data are represented as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublet, t = triplet, ddd = doublet of doublet of doublet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Mass spectra were obtained using a Micromass Quattro II (triple quad) instrument with nanoelectrospray ionization. Analytical thin layer chromatography (TLC) was performed on SiliaPlate 250 μm thick silica gel plates provided by Silicycle. Visualization was accomplished using fluorescence quenching, KMnO_4 stain, or ceric ammonium molybdate (CAM) stain followed by heating. Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator. Purification of the reaction products was carried out by chromatography using Siliaflash-P60 (40–63 μm) or Siliaflash-T60 (5–20 μm) silica gel purchased from Silicycle. All reactions were carried out under an inert atmosphere of nitrogen in flame-dried glassware with magnetic stirring or under an atmosphere of oxygen in flame-dried glassware with magnetic stirring unless otherwise noted. Irradiation of photochemical reactions was carried out using a SE-WFLS-B60 blue (470 nm) LED flexible light strip purchased from Super Bright LEDs Inc. (St. Louis, MO, USA), with standard borosilicate glass vials purchased from Fisher Scientific. Yield refers to isolated yield of analytically pure material unless otherwise noted. NMR yields were determined using hexamethyldisiloxane, $(\text{Me}_3\text{Si})_2\text{O}$, as an internal standard.

Procedure for yield determination using $(\text{Me}_3\text{Si})_2\text{O}$ NMR internal standard: upon consumption of starting material (as determined by TLC), crude reaction mixture was passed through a short silica gel plug with DCM. The crude mixture was concentrated and then taken up in deuterated NMR solvent (CDCl_3). A carefully measured amount of $(\text{Me}_3\text{Si})_2\text{O}$ was then added to the solution via micro syringe and a ^1H NMR spectrum acquired.

Materials. Commercially available reagents were purchased from Sigma–Aldrich, Acros, Alfa Aesar, or TCI, and used as received unless otherwise noted. Diethyl ether (Et_2O), dichloromethane (DCM), tetrahydrofuran (THF), toluene (PhMe), and dimethylformamide (DMF) were dried by passing through activated alumina columns under nitrogen prior to use. Other common solvents and chemical reagents were purified by standard published methods where noted.

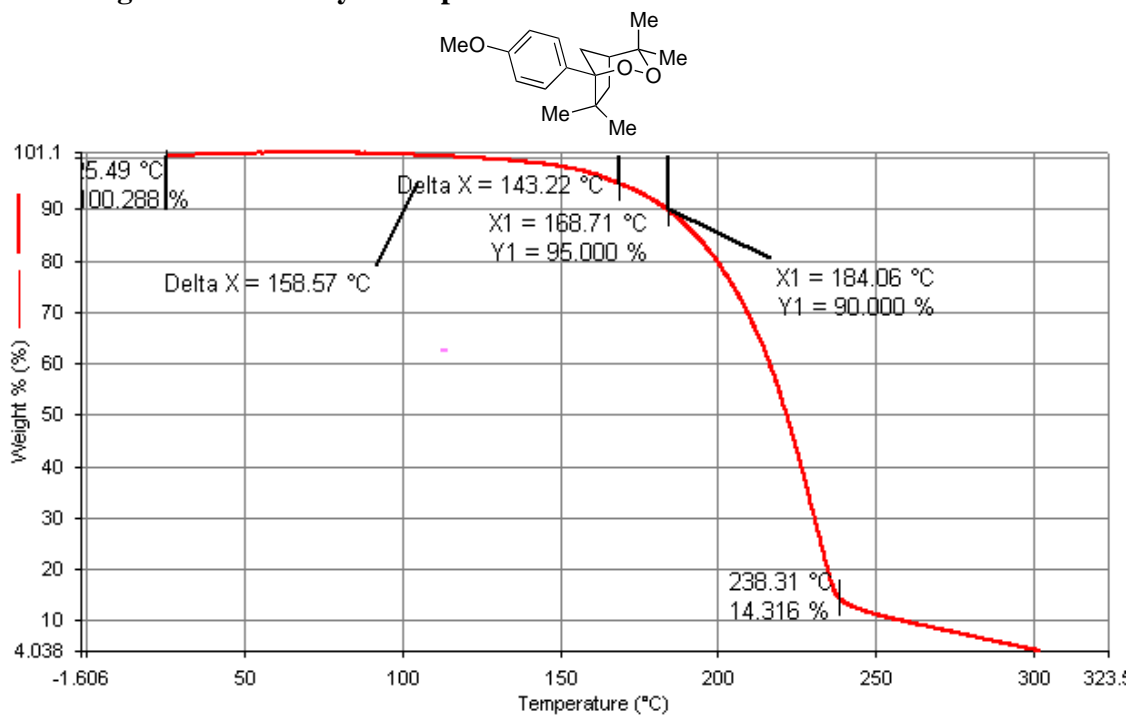
II. Optimization of conditions for substrate **2f**



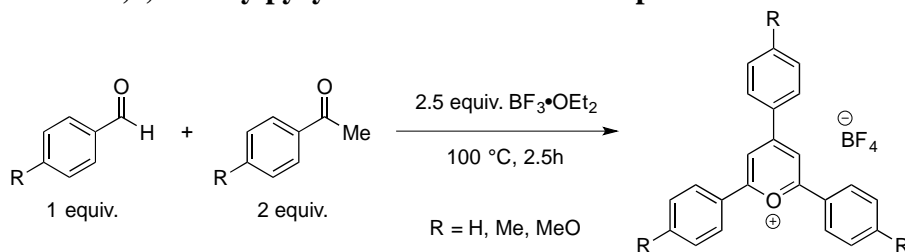
Entry	Conditions	Conversion	Yield ^a
1	2 mol% 1c 0.01 M DCM, -41 °C	100%	22%
2	2 mol% 1c 0.01 M DCM, -78 °C	100%	10%
3 ^b	2 mol% 1c 0.01 M DCM, -41 °C, 1 atm Air	100%	20%
4	2 mol% 1c 0.02 M DCM, -41 °C	100%	16%
5	2 mol% 1c 0.02 M DCM, -10 °C	100%	20%
6	2 mol% 1c 0.02 M CHCl ₃ , -10 °C	100%	22%
7	2 mol% 1c 0.02 M DCE, -10 °C	100%	30%
8	2 mol% 1c 0.02 M DCE, rt	100%	28%

All reactions carried out in oxygen saturated solvents unless otherwise noted. ^aYields reported with respect to (Me₃Si)₂O ¹H NMR internal standard. ^bReaction carried out under balloon of air, in air saturated DCM.

III. Thermogravimetric analysis for product 3a



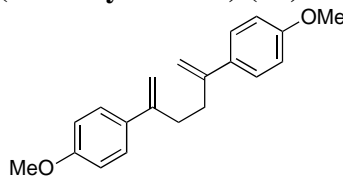
IV. Preparation of 2,4,6-triarylpyrylium tetrafluoroborate photosensitizers



All variants prepared according to a published procedure; spectral data were in agreement with the literature values.¹

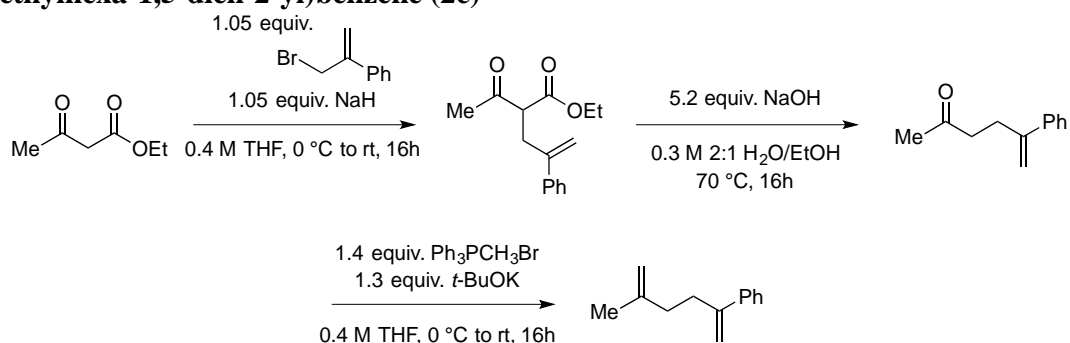
V. Preparation of unconjugated diene substrates

4,4'-(Hexa-1,5-diene-2,5-diyl)bis(methoxybenzene) (2b)



Prepared according to a published procedure; spectral data were in agreement with the literature values.²

(5-Methylhexa-1,5-dien-2-yl)benzene (2c)



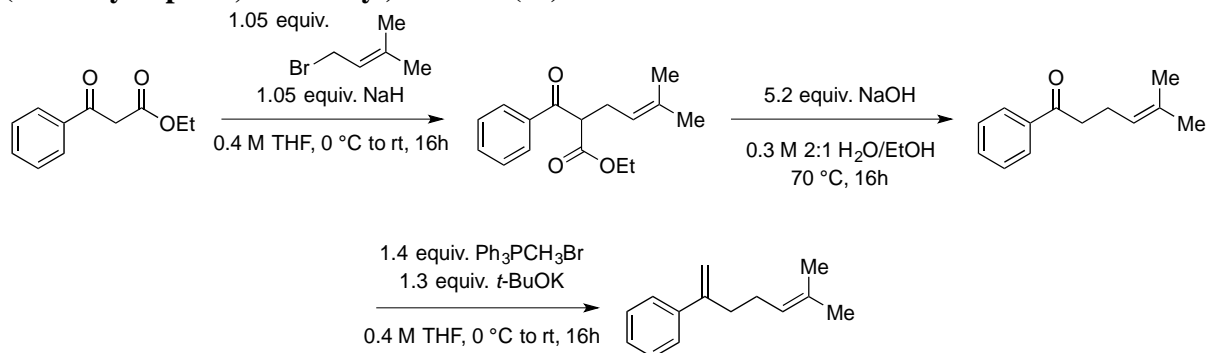
1.05 equiv of sodium hydride were dispensed into a flame-dried round bottom flask, which was subsequently purged with N_2 . The sodium hydride was suspended in dry THF (0.4 mmol/mL) and the stirred suspension was cooled to 0 °C in an ice bath. At 0 °C, ethyl acetoacetate was added dropwise with stirring. The solution was stirred at 0 °C for 30 minutes after effervescence ceased. At 0 °C, (3-bromoprop-1-en-2-yl)benzene (1.05 equiv) was added to the mixture dropwise. The reaction was allowed to warm to room temperature and stirred for 16 hours overnight. The reaction was then quenched with concentrated NH_4Cl solution and diluted with DI water and diethyl ether. The organic layer was separated and aqueous layer extracted three times with diethyl ether in a separatory funnel. The combined organics were washed with brine, dried with anhydrous $MgSO_4$, filtered, and concentrated to afford a crude oil, which was taken on to the next step without further purification.

Decarboxylation of the crude alkylation product was carried out as follows: sodium hydroxide (5.2 equiv) was weighed into a round bottom flask containing a 2:1 water/ethanol mixture (approx. concentration 0.3 mmol/mL) and stirred to dissolution. At room temperature the crude alkylation product was introduced dropwise, then the reaction was heated to 70 °C overnight. The reaction was cooled to room temperature and quenched with concentrated NH_4Cl . The organic phase was separated and the aqueous phase extracted three times with diethyl ether. The combined organics were washed with brine, dried with anhydrous $MgSO_4$, filtered, and concentrated to afford a crude oil, which was taken on to the next step without further purification.

The crude aryl ketone was converted to the diene product by Wittig olefination. Olefination procedure for this substrate was identical to the Wittig olefination procedure in **General procedure A** below (step 2). The final product was purified using silica gel column chromatography (20% EtOAc/hexanes) to furnish 0.78 g of pure product (47% overall) as a colorless oil. Spectral data were in agreement with the reported literature values.³ Analytical data

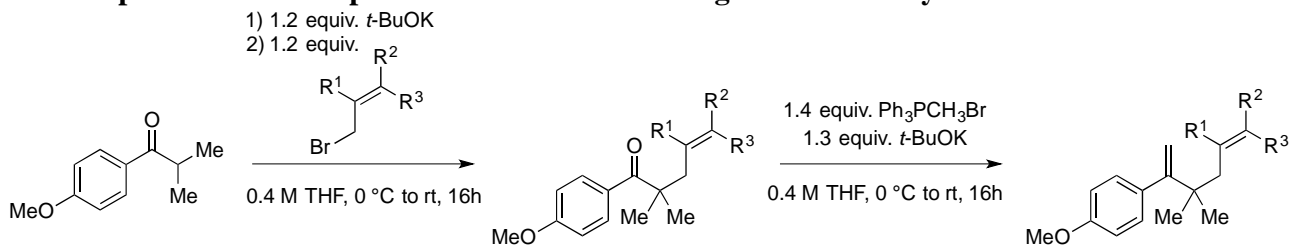
for **2c**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.40 (m, 2H), 7.32 (m, 2H), 7.26 (m, 1H), 5.28 (d, $J = 1.2$ Hz, 1H), 5.08 (d, $J = 1.2$ Hz, 1H), 4.73 (d, $J = 1.2$ Hz, 1H), 4.68 (d, $J = 1.2$ Hz, 1H), 2.64 (dt, $J = 7.8$ Hz, $J = 1.2$ Hz, 2H), 2.16 (t, $J = 7.8$ Hz, 2H), 1.74 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 148.2, 145.4, 141.2, 128.3, 127.3, 126.1, 112.3, 110.0, 36.5, 33.6, 22.5

(6-Methylhepta-1,5-dien-2-yl)benzene (**2e**)



Carried out using the procedure above for synthesis of **2c**. In the initial alkylation, ethyl benzoyl acetate was used in place of ethyl acetoacetate and 3,3-dimethylallyl bromide in place of (3-bromoprop-1-en-2-yl)benzene. The remaining steps were carried out without alteration. The final product was purified using silica gel column chromatography (20% Et_2O /hexanes) to furnish 0.67 g of pure product (50% overall) as a colorless oil. Spectral data were in agreement with the reported literature values.³ Analytical data for **2e**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.41 (m, 2H), 7.32 (m, 2H), 7.26 (m, 1H), 5.27 (s, 1H), 5.14 (m, 1H), 5.06 (s, 1H), 2.51 (t, $J = 7.2$ Hz, 2H), 2.13 (q, $J = 7.2$ Hz, 2H), 1.67 (s, 3H), 1.54 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 148.3, 141.3, 131.9, 128.2, 127.2, 126.1, 123.8, 112.2, 35.4, 26.9, 25.7, 17.7

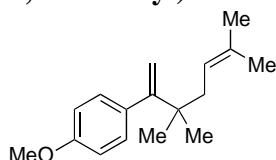
General procedure A: Preparation of substrates with geminal dimethyl tether



A flame-dried round bottom flask equipped with magnetic stirbar containing potassium *tert*-butoxide (1.2 equiv) was purged with nitrogen. Dry THF was added via syringe (approximate concentration 0.4 mmol/mL) and the solution was cooled to 0 °C in an ice bath with stirring. At 0 °C, 1-(4-methoxyphenyl)-2-methylpropan-1-one (prepared according to literature procedure⁴) was added to the stirring solution via syringe dropwise and stirred for 1 hour. At 0 °C, the appropriate allylic bromide was added dropwise via syringe and stirred at room temperature for 16 hours. The reaction was then quenched with concentrated NH_4Cl solution and diluted with DI water and diethyl ether. The organic layer was separated and aqueous layer extracted three times with diethyl ether in a separatory funnel. The combined organics were washed with brine, dried with anhydrous MgSO_4 , filtered, and concentrated to afford a crude oil, which was taken on to the next step without further purification (acceptable purity confirmed by TLC and $^1\text{H NMR}$).

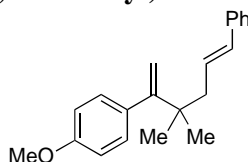
The crude allylation product was converted to the desired diene by Wittig olefination. Potassium *tert*-butoxide (1.3 equiv) and methyltriphenylphosphonium bromide (1.4 equiv) were dispensed into a flame-dried round bottom flask equipped with a magnetic stirbar. The flask was purged with nitrogen and cooled to 0 °C with stirring. At 0 °C, dry THF was added via syringe (approximate concentration 0.4 mmol/mL) and the solution was stirred at 0 °C for 1 hour. At 0 °C, the crude allylation product was added via syringe (in THF) dropwise. The reaction was warmed to room temperature and stirred overnight. Upon completion, the reaction was quenched with concentrated NH₄Cl solution and then diluted with DI water and diethyl ether. The organic layer was separated and aqueous layer extracted three times with diethyl ether in a separatory funnel. The combined organics were washed with brine, dried with anhydrous MgSO₄, filtered, and concentrated to afford the crude product. The product was purified by silica gel column chromatography.

1-Methoxy-4-(3,3,6-trimethylhepta-1,5-dien-2-yl)benzene (2a)



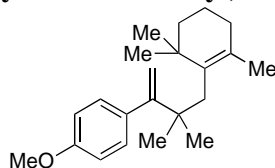
Diene prepared according to **general procedure A** using 3,3-dimethylallyl bromide as the electrophile in the first step. The final product was purified by silica gel column chromatography (20% diethyl ether/hexanes) to furnish 2.16 g of pure product (88%) as a colorless oil. Analytical data for **2a**: ¹H NMR (600 MHz, CDCl₃): δ 7.05 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 5.18 (m, 1H), 5.11 (s, 1H), 4.83 (s, 1H), 3.79 (s, 3H), 2.03 (d, *J* = 7.2 Hz, 2H), 1.73 (s, 3H), 1.56 (s, 3H), 1.06 (s, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 158.0, 157.6, 135.8, 132.6, 129.9, 121.5, 113.3, 112.7, 55.1, 39.7, 39.0, 27.4, 26.0, 18.1

(*E*)-1-(3,3-Dimethyl-6-phenylhexa-1,5-dien-2-yl)-4-methoxybenzene (2m)



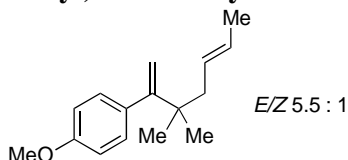
Diene prepared according to **general procedure A** using cinnamyl bromide as the electrophile in the first step. The final product was purified by silica gel column chromatography (20% diethyl ether/hexanes) to furnish 2.73 g of pure product (93%) as a yellow oil. Analytical data for **2m**: ¹H NMR (600 MHz, CDCl₃): δ 7.36 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.23 (m, 1H), 5.18 (s, 1H), 4.90 (s, 1H), 3.82 (s, 3H), 2.29 (d, *J* = 6.6 Hz), 1.15 (s, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 158.2, 157.3, 137.8, 135.6, 132.0, 130.0, 128.5, 127.8, 126.9, 126.0, 113.7, 112.8, 55.2, 44.4, 39.7, 27.5

1-(3,3-Dimethyl-4-(2,6,6-trimethylcyclohex-1-en-1-yl)but-1-en-2-yl)-4-methoxybenzene (2n)



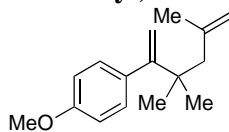
Diene prepared according to **general procedure A** using 2-(bromomethyl)-1,3,3-trimethylcyclohex-1-ene (prepared according to literature procedure⁵) as the electrophile in the first step. The final product was purified by silica gel column chromatography (20% Et₂O/hexanes) to furnish 1.10 g of pure product (50%) as a colorless oil. Analytical data for **2n**: ¹H NMR (600 MHz, CDCl₃): δ 7.18 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 5.14 (d, *J* = 1.2 Hz, 1H), 4.81 (d, *J* = 1.2 Hz, 1H), 3.80 (s, 3H), 2.32 (s, 2H), 1.95 (t, *J* = 6.6 Hz, 2H), 1.56 (m, 2H), 1.55 (s, 3H), 1.40 (m, 2H), 1.14 (s, 3H), 0.94 (s, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 158.4, 158.1, 143.6, 135.8, 130.0, 114.0, 113.2, 112.7, 55.2, 48.4, 39.3, 28.0, 25.3

(*E*)-1-(3,3-Dimethylhepta-1,5-dien-2-yl)-4-methoxybenzene (2o)



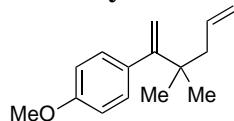
Diene prepared according to **general procedure A** using crotyl bromide as the electrophile in the first step. The final product was purified by silica gel column chromatography (20% diethyl ether/hexanes) to furnish 1.86 g of pure product (81%) as a colorless oil (5.5:1 mixture of isomers). Analytical data for **2o**: ¹H NMR for *E* isomer (600 MHz, CDCl₃): δ 7.05 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.41 (m, 1H), 5.10 (d, *J* = 1.2 Hz, 1H), 4.82 (d, *J* = 1.2 Hz, 1H), 3.79 (s, 3H), 2.03 (m, 2H), 1.66 (m, 3H), 1.04 (s, 6H); ¹³C NMR for *E* isomer (150 MHz, CDCl₃): δ 158.1, 157.6, 135.8, 130.0, 128.0, 127.2, 113.3, 112.7, 55.2, 43.9, 39.3, 27.3, 18.1

1-Methoxy-4-(3,3,5-trimethylhexa-1,5-dien-2-yl)benzene (2p)



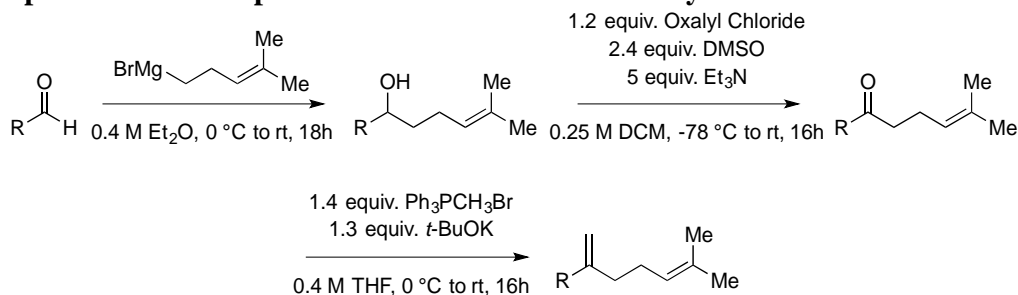
Diene prepared according to **general procedure A** using methallyl bromide as the electrophile in the first step. The final product was purified by silica gel column chromatography (20% EtOAc/hexanes) to furnish 1.55 g of pure product (67%) as a colorless oil. Analytical data for **2p**: ¹H NMR (600 MHz, CDCl₃): δ 7.10 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.17 (s, 1H), 4.85 (s, 1H), 4.83 (s, 1H), 4.71 (s, 1H), 3.79 (s, 3H), 2.14 (s, 2H), 1.75 (s, 3H), 1.11 (s, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 158.4, 158.1, 143.6, 135.8, 130.0, 114.0, 113.2, 112.7, 55.2, 48.4, 39.2, 28.0, 25.3

1-(3,3-Dimethylhexa-1,5-dien-2-yl)-4-methoxybenzene (2q)



Diene prepared according to **general procedure A** using allyl bromide as the electrophile in the first step. The final product was purified by silica gel column chromatography (20% EtOAc/hexanes) to furnish 1.94 g of pure product (90%) as a colorless oil. Analytical data for **2q**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.06 (d, $J = 7.8$ Hz, 2H), 6.81 (d, $J = 7.8$ Hz, 2H), 5.81 (m, 1H), 5.12 (s, 1H), 5.02 (m, 2H), 4.84 (s, 1H), 3.79 (s, 3H), 2.11 (d, $J = 7.2$ Hz, 2H), 1.07 (s, 6H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 158.1, 157.3, 135.8, 135.6, 130.0, 116.7, 113.5, 112.7, 55.2, 45.2, 39.1, 27.3

General procedure B: Preparation of substrates with methylene tether



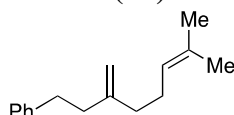
Freshly activated and dried magnesium turnings (1.38 equiv relative to aldehyde) were weighed into a flame-dried round bottom flask equipped with a stir bar. The flask was purged with nitrogen, cooled to 0 °C, and diethyl ether dispensed (to approximate concentration 0.6 mmol/mL). Seventy microliters 1,2-dibromoethane were added to activate the magnesium and stirred for 15 minutes. At 0 °C, 5-bromo-2-methyl-2-pentene (1.25 equiv relative to aldehyde) was added dropwise to the stirring magnesium turnings and stirred for 2 hours (consumption of magnesium observed). After formation of the Grignard reagent, the necessary aldehyde (freshly distilled to ensure purity), in diethyl ether, was added to the reaction mixture dropwise at 0 °C and stirred for 18 hours. The reaction was quenched with concentrated NH_4Cl solution dropwise and diluted with DI water and diethyl ether. The organic layer was separated and aqueous layer extracted three times with diethyl ether in a separatory funnel. The combined organics were washed with brine, dried with anhydrous MgSO_4 , filtered, and concentrated to afford a crude oil, which was taken on to the next step without further purification (acceptable purity confirmed by TLC and $^1\text{H NMR}$).

The crude alkenol product was then converted to the aryl ketone via Swern oxidation. A flame-dried round bottom flask containing a stir bar was charged with dry DCM (to approximate concentration of 0.25 mmol/mL) and cooled to -78 °C. At -78 °C, the flask was charged with oxalyl chloride (1.2 equiv) and stirred. After 10 minutes, DMSO (2.4 equiv) was added to the flask dropwise then stirred for 25 minutes at -78 °C. The alkenol substrate was next added to the reaction mixture dropwise and stirred for additional 25 minutes at -78 °C. Finally, triethylamine (5 equiv) was added to the reaction dropwise. The reaction was warmed to room temperature and stirred overnight. The reaction was quenched with concentrated NH_4Cl , the organic layer was separated, and the aqueous layer extracted three times with DCM. The combined organics were

washed with brine, dried with anhydrous MgSO_4 , filtered, and concentrated to afford the crude aryl ketone, which was further purified by silica gel column chromatography.

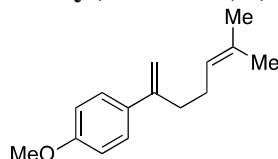
The purified aryl ketone was converted to the desired unconjugated diene by Wittig olefination. Wittig olefination procedure for general procedure B is identical to Wittig olefination procedure in **general procedure A** (step 2).

(7-Methyl-3-methyleneoct-6-en-1-yl)benzene (2d)



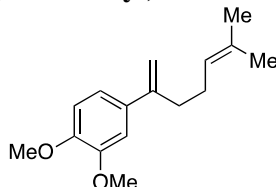
Diene prepared according to **general procedure B** using hydrocinnamaldehyde in the Grignard addition step. The alkyl ketone product from oxidation was purified by silica gel column chromatography (20% EtOAc/hexanes). The final product was purified using silica gel column chromatography (20% EtOAc/hexanes) to furnish 2.06 g of the desired diene (68%) as a colorless oil. Analytical data for **2d**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.27 (m, 2H), 7.18 (m, 3H), 5.12 (m, 1H), 4.76 (s, 2H), 2.74 (t, $J = 7.8$ Hz, 2H), 2.32 (t, $J = 8.4$ Hz, 2H), 2.12 (m, 2H), 2.07 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 149.1, 142.3, 131.7, 128.3, 128.3, 125.7, 124.1, 109.2, 38.0, 36.3, 34.7, 26.5, 25.7, 17.7

1-Methoxy-4-(6-methylhepta-1,5-dien-2-yl)benzene (2f)



Diene prepared according to **general procedure B** using 4-anisaldehyde in the Grignard addition step. The aryl ketone product from oxidation was purified by silica gel column chromatography (20% EtOAc/hexanes). The final product was purified using silica gel column chromatography (20% Et₂O/hexanes) to furnish 2.46 g of the desired diene (59%) as a colorless oil. Spectral data were in agreement with the reported literature values.⁶ Analytical data for **2f**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.35 (d, $J = 9.0$ Hz, 2H), 6.85 (d, $J = 9.0$ Hz, 2H), 5.20 (s, 1H), 5.14 (m, 1H), 4.97 (s, 1H), 3.80 (s, 3H), 2.48 (t, $J = 7.2$ Hz, 2H), 2.13 (q, $J = 7.2$ Hz, $J = 7.8$ Hz, 2H), 1.68 (s, 3H), 1.55 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 158.9, 147.6, 133.7, 131.8, 127.1, 123.9, 113.5, 110.6, 55.2, 35.5, 27.0, 25.7, 17.7

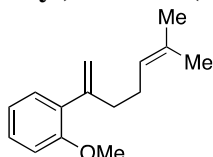
1,2-Dimethoxy-4-(6-methylhepta-1,5-dien-2-yl)benzene (2h)



Diene prepared according to **general procedure B** using 3,4-dimethoxybenzaldehyde in the Grignard addition step. The aryl ketone product from oxidation was purified by silica gel column chromatography (20% EtOAc/hexanes). The final product was purified using silica gel column chromatography (20% Et₂O/hexanes) to furnish 1.29 g of the desired diene (42%) as a colorless oil. Analytical data for **2h**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 6.95 (m, 2H), 6.81 (d, $J =$

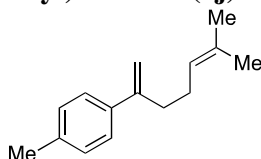
8.4 Hz, 1H), 5.20 (d, $J = 1.8$ Hz, 1H), 5.14 (m, 1H), 4.98 (d, $J = 1.8$ Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.47 (t, $J = 7.2$ Hz, 2H), 2.13 (q, $J = 7.2$ Hz, 2H), 1.67 (s, 3H), 1.54 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3); δ 148.6, 148.5, 147.9, 134.2, 131.8, 123.9, 118.4, 110.9, 110.8, 109.4, 55.9, 55.8, 35.5, 27.0, 25.7, 17.7

1-Methoxy-2-(6-methylhepta-1,5-dien-2-yl)benzene (2i)



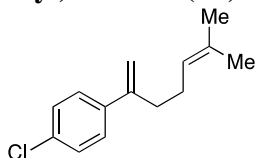
Diene prepared according to **general procedure B** using *o*-anisaldehyde in the Grignard addition step. The aryl ketone product from oxidation was purified by silica gel column chromatography (10% EtOAc/hexanes). The final product was purified using silica gel column chromatography (hexanes) to furnish 1.58 g of the desired diene (47%) as a colorless oil. Spectral data were in agreement with the reported literature values.⁷ Analytical data for **2i**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.24 (m, 1H), 7.13 (m, 1H), 6.91 (m, 1H), 6.86 (m, 1H), 5.14 (s, 1H), 5.12 (m, 1H), 5.02 (s, 1H), 3.82 (s, 3H), 2.51 (t, $J = 7.8$ Hz, 2H), 2.04 (q, $J = 7.8$ Hz, 2H), 1.67 (s, 3H), 1.53 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3); δ 156.5, 149.0, 132.1, 131.4, 130.2, 128.2, 124.2, 120.4, 114.0, 110.5, 55.4, 36.3, 26.8, 25.7, 17.6

1-Methyl-4-(6-methylhepta-1,5-dien-2-yl)benzene (2j)



Diene prepared according to **general procedure B** using 4-tolualdehyde in the Grignard addition step. The aryl ketone product from oxidation was purified by silica gel column chromatography (10% Et_2O /hexanes). The final product was purified using silica gel column chromatography (hexanes) to furnish 1.27 g of the desired diene (52%) as a colorless oil. Spectral data were in agreement with the reported literature values.⁷ Analytical data for **2j**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.31 (d, $J = 7.8$ Hz, 2H), 7.13 (d, $J = 7.8$ Hz, 2H), 5.25 (d, $J = 1.2$ Hz, 1H), 5.15 (m, 1H), 5.01 (d, $J = 1.2$ Hz, 1H), 2.49 (dt, $J = 7.8$ Hz, $J = 1.2$ Hz, 2H), 2.34 (s, 3H), 2.13 (q, $J = 7.8$ Hz, 2H), 1.68 (s, 3H), 1.55 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3); δ 148.1, 138.3, 137.0, 131.8, 128.9, 125.9, 123.9, 111.4, 35.4, 27.0, 25.7, 21.1, 17.7

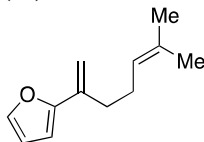
1-Chloro-4-(6-methylhepta-1,5-dien-2-yl)benzene (2k)



Diene prepared according to **general procedure B** using 4-chlorobenzaldehyde in the Grignard addition step. The aryl ketone product from oxidation was purified by silica gel column chromatography (5% Et_2O /hexanes). The final product was purified using silica gel column chromatography (hexanes) to furnish 1.44 g of the desired diene (40%) as a colorless oil. Analytical data for **2k**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.32 (d, $J = 9.0$ Hz, 2H), 7.27 (d, $J = 9.0$

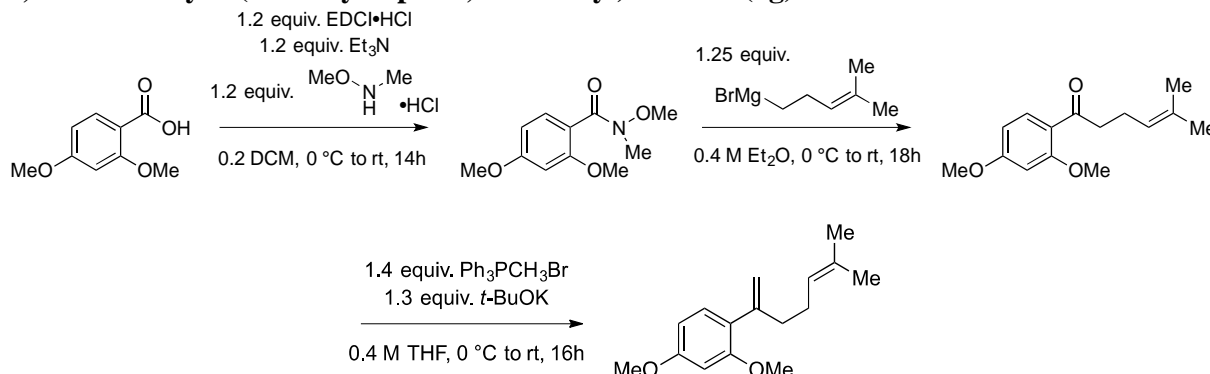
Hz, 2H), 5.25 (d, $J = 1.2$ Hz, 1H), 5.11 (m, 1H), 5.06 (d, $J = 1.2$ Hz, 1H), 2.47 (t, $J = 7.8$ Hz, 2H), 2.10 (q, $J = 7.8$ Hz, 2H), 1.66 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3); δ 147.0, 139.5, 132.8, 131.8, 128.1, 127.2, 123.4, 112.5, 35.1, 26.6, 25.5, 17.5

2-(6-Methylhepta-1,5-dien-2-yl)furan (2l)



Diene prepared according to **general procedure B** using furfural in the Grignard addition step. The aryl ketone product from oxidation was purified by silica gel column chromatography (10% Et_2O /hexanes). The final product was purified using silica gel column chromatography (hexanes) to furnish 0.61 g of the desired diene (14%) as a yellow oil. Analytical data for **2l**: ^1H NMR (600 MHz, CDCl_3): δ 7.34 (d, $J = 1.8$ Hz, 1H), 6.36 (m, 1H), 6.29 (d, $J = 3.6$ Hz, 1H), 5.51 (s, 1H), 5.16 (m, 1H), 4.96 (s, 1H), 2.36 (t, $J = 7.8$ Hz, 2H), 2.23 (q, $J = 7.8$ Hz, 2H), 1.68 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3); δ 154.8, 141.7, 137.3, 132.1, 123.7, 111.0, 109.2, 105.8, 33.3, 27.3, 25.7, 17.7

2,4-Dimethoxy-1-(6-methylhepta-1,5-dien-2-yl)benzene (2g)

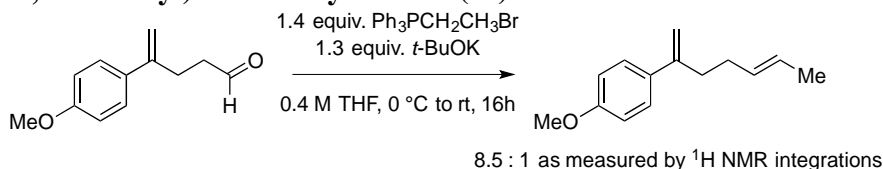


A flame-dried round bottom flask, containing 2,4-dimethoxybenzoic acid (1.0 equiv) and *N,O*-dimethylhydroxylamine hydrochloride (1.2 equiv) dissolved in anhydrous dichloromethane (0.2 M), was cooled to 0 °C with stirring. At 0 °C, triethylamine (1.2 equiv) was added to the solution dropwise via syringe and stirred for 15 minutes. Next, at 0 °C, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI·HCl, 1.2 equiv) was added to the stirring solution in one portion. The reaction was allowed warm to room temperature and stir overnight. The reaction was then quenched with 2 N HCl and diluted with DCM. The organic layer was separated and washed twice with DI water. The combined organics were then washed with brine, dried with anhydrous MgSO_4 , filtered, and concentrated to afford a crude oil, which was taken on to the Grignard addition without further purification.

Grignard addition into the Weinreb amide and Wittig olefination were carried out according the equivalent procedures in **general procedure B**. The aryl ketone produced from Grignard addition into the Weinreb amide was purified by column chromatography (20% EtOAc /hexanes) to yield a colorless oil (1.76 g, 47%). The Wittig olefination product was purified by column chromatography (20% Et_2O /hexanes) to give 1.42 g (81%) of the desired unconjugated diene as a colorless oil. Analytical data for **2g**: ^1H NMR (600 MHz, CDCl_3): δ 7.03 (m, 1H), 6.42 (m, 2H), 5.08 (m, 2H), 4.96 (d, $J = 2.4$ Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H),

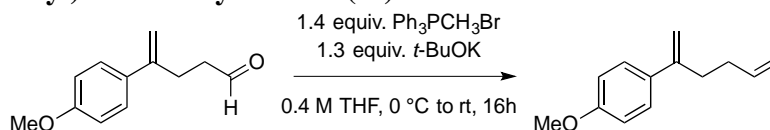
2.45 (t, $J = 7.8$ Hz, 2H), 2.00 (q, $J = 7.8$ Hz, 2H), 1.64 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3); δ 160.0, 157.5, 148.5, 131.3, 130.5, 124.8, 124.3, 113.9, 103.9, 98.5, 55.4, 55.3, 36.5, 26.9, 25.7, 17.6

(Z)-1-(Hepta-1,5-dien-2-yl)-4-methoxybenzene (2r)



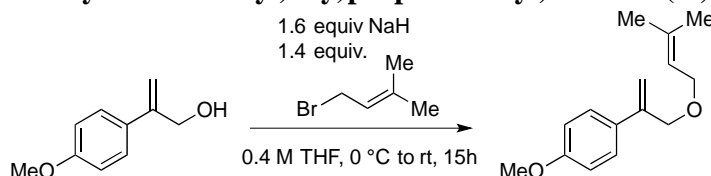
4-(4-methoxyphenyl)pent-4-enal was prepared according to a procedure published by Hartwig and coworkers.⁸ Wittig olefination of the terminal aldehyde carried out using ethyltriphenylphosphonium bromide following the procedure in **general procedure A** above. The desired diene product was purified by column chromatography (20% Et_2O /hexanes) to furnish 1.13 g (67%) of pure product as a colorless oil (8.5:1 mixture of *E/Z* isomers). Analytical data for **2r**: ^1H NMR (400 MHz, CDCl_3): δ 7.34 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 5.41 (m, 2H), 5.21 (d, $J = 1.6$ Hz, 1H), 4.98 (d, $J = 1.6$ Hz, 1H), 3.80 (s, 3H), 2.51 (m, 2H), 2.20 (m, 2H), 1.53 (d, $J = 5.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3); δ 158.9, 147.3, 133.5, 129.8, 127.1, 124.1, 113.5, 110.7, 55.1, 35.1, 25.7, 12.7

1-(Hexa-1,5-dien-2-yl)-4-methoxybenzene (2s)



4-(4-methoxyphenyl)pent-4-enal was prepared according to a procedure published by Hartwig and coworkers.⁸ Wittig olefination of the terminal aldehyde carried out using methyltriphenylphosphonium bromide following the procedure in **general procedure A** above. The diene product was purified by column chromatography (20% Et_2O /hexanes) to furnish 1.13 g of pure product (75%) as a colorless oil. Spectral data were in agreement with the reported literature values.⁹ Analytical data for **2s**: ^1H NMR (600 MHz, CDCl_3): δ 7.24 (d, $J = 7.2$ Hz, 2H), 6.85 (d, $J = 7.2$ Hz, 2H), 5.83 (m, 1H), 5.21 (s, 1H), 4.98 (m, 3H), 3.80 (s, 3H), 2.56 (t, $J = 7.8$ Hz, 2H), 2.20 (q, $J = 7.8$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3); δ 159.0, 147.1, 138.2, 133.6, 127.2, 114.6, 113.6, 110.9, 55.2, 34.8, 32.5

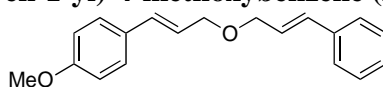
1-methoxy-4-(3-((3-methylbut-2-en-1-yl)oxy)prop-1-en-2-yl)benzene (2t)



1.6 equiv sodium hydride was dispensed into a flame-dried round bottom flask, which was subsequently purged with N_2 . The sodium hydride was suspended in dry THF (0.4 mmol/mL relative to substrate) and the stirred suspension was cooled to 0 °C in an ice bath. At 0 °C, a solution of 2-(4-methoxyphenyl)prop-2-en-1-ol (prepared according to literature procedure¹⁰) in THF was added dropwise with stirring. The solution was stirred at 0 °C for 30 minutes after effervescence ceased. At 0 °C, prenyl bromide (1.4 equiv) was added to the mixture dropwise.

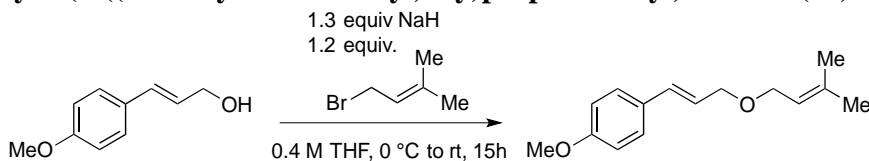
The reaction was allowed to warm to room temperature and stirred for 15 hours overnight. The reaction was then quenched with concentrated NH₄Cl solution, and diluted with DI water and diethyl ether. The organic layer was separated and aqueous layer extracted three times with diethyl ether in a separatory funnel. The combined organics were washed with brine, dried with anhydrous MgSO₄, filtered, and concentrated to afford a crude oil. The crude allylic ether was purified by silica gel column chromatography (20% Et₂O/hexanes) to yield 2.16 g (70%) of the desired product as an off-white oil. Analytical data for **2t**: ¹H NMR (600 MHz, CDCl₃): δ 7.41 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.43 (d, *J* = 1.2 Hz, 1H), 5.35 (m, 1H), 5.22 (d, *J* = 1.2 Hz, 1H), 4.32 (s, 2H), 3.98 (d, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 1.72 (s, 3H), 1.62 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 159.2, 143.7, 137.1, 131.4, 127.2, 121.0, 113.6, 112.7, 72.0, 65.3, 55.3, 25.8, 18.0

1-((*E*)-3-(Cinnamyloxy)prop-1-en-1-yl)-4-methoxybenzene (2u)



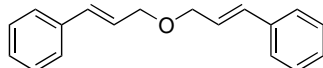
Prepared according to a published procedure; spectral data were in agreement with the literature values.¹¹

(*E*)-1-Methoxy-4-(3-((3-methylbut-2-en-1-yl)oxy)prop-1-en-1-yl)benzene (2v)



Prepared according to published procedure for **2u** above, however using 3,3-dimethylallyl bromide in place of cinnamyl bromide. The desired product was purified by column chromatography (10% Et₂O/hexanes) to furnish 1.81 g of pure product (78%) as a yellow oil. Analytical data for **2v**: ¹H NMR (600 MHz, CDCl₃): δ 7.30 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 16.2 Hz, 1H), 6.16 (m, 1H), 5.38 (m, 1H), 4.09 (dd, *J* = 6.6 Hz, *J* = 1.8 Hz, 2H), 3.99 (d, *J* = 6.6 Hz, 2H), 3.78 (s, 3H), 1.74 (s, 3H), 1.67 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 159.2, 137.0, 132.0, 129.5, 127.6, 124.0, 121.1, 113.9, 70.8, 66.4, 55.2, 25.8, 18.0

((1*E*,1'*E*)-Oxybis(prop-1-ene-3,1-diyl)dibenzene (2w)

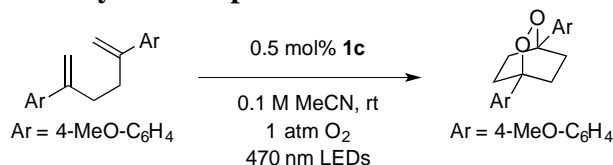


Prepared according to a published procedure; spectral data were in agreement with the literature values.¹¹

VI. General procedures for PET endoperoxidation

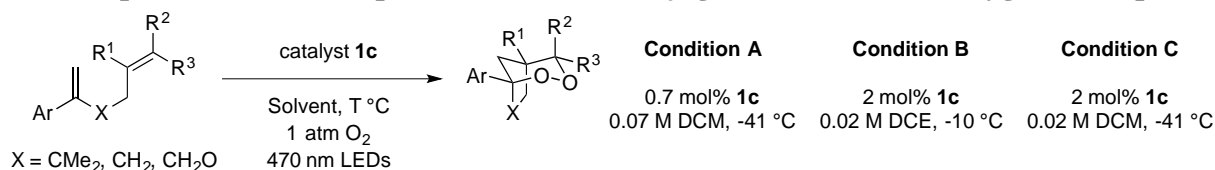
Isolated products of cyclization–endoperoxidation cascade reactions

Procedure for synthesis of bicyclic endoperoxide **3a** from diene **2a**



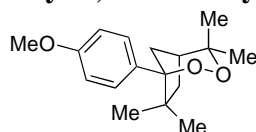
A flame dried 1-dram vial equipped with a magnetic stir bar and 0.25 mg and 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate catalyst, then sealed with a septum cap. 0.5 mL dry acetonitrile was then added via syringe under an atmosphere of nitrogen. Finally, 30 mg diene **3a** was added to the stirring reaction mixture in 0.5 mL acetonitrile. A balloon of oxygen was fitted to the vial and bubbled through the stirring solution for 2 minutes. After bubbling was suspended, an atmosphere of oxygen was maintained over the solution and the reaction was irradiated for two hours at ambient temperature using 470 LEDs. Upon completion, the desired product was isolated using silica gel column chromatography (33% Et₂O/hexanes). Spectral data were in agreement with the literature values.¹²

General procedure for endoperoxidation of unconjugated dienes under oxygen atmosphere.



A flame dried flask (2-dram vial, scintillation vial, or round-bottom flask) was equipped with a magnetic stir bar and 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate catalyst (**1c**, 4-MeO-TPT, see conditions above for catalyst loading), then sealed with a septum. The solvent (DCM for conditions A and C, DCE for condition B, see conditions above for concentration) was then added to the flask via syringe under an atmosphere of nitrogen. Substrate was then added to the flask via microsyringe and stirred to ensure a homogeneous reaction mixture. A balloon of oxygen was fitted to the reaction flask and oxygen was bubbled through the stirring solution for 3 minutes to ensure oxygen saturation in the solvent. After bubbling was suspended the reaction was fitted with a balloon of oxygen to ensure an oxygen atmosphere and submerged in a temperature-controlled bath (-41 °C for conditions A and C, -10 °C for condition B). The reaction was irradiated with 470 nm LEDs until completion (as monitored by TLC). Upon completion, the reaction mixture was concentrated under reduced pressure and the products isolated by silica gel column chromatography.

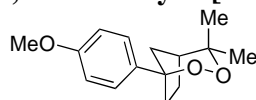
1-(4-Methoxyphenyl)-4,4,7,7-tetramethyl-2,3-dioxabicyclo[3.2.1]octane (**3a**)



The average yield for the title compound was 66% (2 trials) at the 0.72 mmol scale, using **condition A**, and an irradiation time of 3.5 hours. The title compound was purified by column

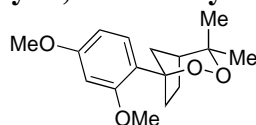
chromatography on silica gel (10% EtOAc/hexanes) to yield a white solid. Analytical data for **3a**: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.28 (d, $J = 8.8$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H), 2.35 (dd, $J = 12.0$ Hz, $J = 5.6$ Hz, 1H), 2.24 (dd, $J = 12.0$ Hz, $J = 2.8$ Hz, 1H), 2.03 (t, $J = 6.0$ Hz, 1H), 1.98 (dd, $J = 13.2$ Hz, $J = 2.8$ Hz, 1H), 1.66 (dd, $J = 13.2$ Hz, $J = 6.4$ Hz), 1.41 (s, 3H), 1.32 (s, 3H), 1.13 (s, 3H), 0.58 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 159.2, 130.3, 127.5, 113.2, 93.4, 80.3, 55.2, 42.5, 42.4, 41.6, 33.7, 31.6, 24.9, 23.4, 21.6; **MS** (+ESI): m/z calculated for $\text{C}_{17}\text{H}_{24}\text{O}_3$ $[\text{M}+\text{H}]^+$ 277.18, found 277.11.

1-(4-Methoxyphenyl)-4,4-dimethyl-2,3-dioxabicyclo[3.2.1]octane (**3f**)



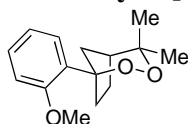
The average yield for the title compound was 32% (2 trials) at the 1.0 mmol scale, using **condition B**, and an irradiation time of 3.5 hours. The title compound was purified by column chromatography on silica gel (20% EtOAc/hexanes) to yield a white solid. Analytical data for **3f**: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.35 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H), 2.49 (m, 2H), 2.16 (t, $J = 5.4$ Hz, 1H), 2.09 (m, 1H), 1.84 (dt, $J = 12.4$ Hz, $J = 3.6$ Hz, 1H), 1.74 (m, 2H), 1.45 (s, 3H), 1.16 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 159.4, 132.2, 127.9, 113.6, 90.0, 80.6, 55.2, 43.7, 35.6, 34.8, 26.3, 24.8, 23.4; **MS** (+ESI): m/z calculated for $\text{C}_{15}\text{H}_{20}\text{O}_3$ 249.15, found 249.15.

1-(2,4-Dimethoxyphenyl)-4,4-dimethyl-2,3-dioxabicyclo[3.2.1]octane (**3g**)



The average yield for the title compound was 9% (2 trials) at the 0.5 mmol scale, using **condition B**, and an irradiation time of 3 hours. The title compound was purified by column chromatography on silica gel (10% to 20% Et₂O/pentane) to yield a colorless oil. Analytical data for **3g**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.25 (s, 1H), 6.42 (m, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 2.78 (m, 1H), 2.58 (dt, $J = 11.4$ Hz, $J = 3.0$ Hz, 1H), 2.09 (t, $J = 5.4$ Hz, 1H), 2.05 (m, 1H), 1.88 (m, 1H), 1.80 (dd, $J = 11.4$ Hz, $J = 5.4$ Hz, 1H), 1.66 (m, 1H), 1.43 (s, 3H), 1.15 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 161.0, 160.0, 129.1, 120.4, 103.6, 99.4, 89.6, 80.6, 55.5, 55.3, 43.4, 36.2, 33.4, 26.3, 24.9, 23.5; **MS** (+ESI): m/z calculated for $\text{C}_{16}\text{H}_{22}\text{O}_4$ $[\text{M}+\text{H}]^+$ 279.15, found 279.15.

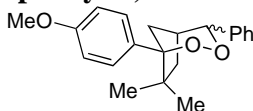
1-(2-methoxyphenyl)-4,4-dimethyl-2,3-dioxabicyclo[3.2.1]octane (**3i**)



The average yield for the title compound was 16% (2 trials) at the 0.5 mmol scale, using **condition B**, and an irradiation time of 5 hours. The title compound was purified by column chromatography on silica gel (20% EtOAc/hexanes) to yield a white solid. Analytical data for **3i**: $^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.34 (dd, $J = 7.8$ Hz, $J = 1.8$ Hz, 1H), 7.26 (m, 1H), 6.89 (m, 2H), 3.81 (s, 3H), 2.77 (m, 1H), 2.57 (dt, $J = 12.0$ Hz, $J = 2.4$ Hz, 1H), 2.10 (t, $J = 5.4$ Hz, 1H), 2.06 (m, 1H), 1.94 (m, 1H), 1.89 (dd, $J = 11.4$ Hz, $J = 5.4$ Hz, 1H), 1.69 (m, 1H), 1.44 (s, 3H),

1.16 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 158.7, 129.6, 128.2, 127.7, 120.2, 111.8, 89.9, 80.8, 55.6, 42.4, 36.1, 33.3, 26.3, 24.8, 23.5; **MS** (+ESI): m/z calculated for $\text{C}_{15}\text{H}_{20}\text{O}_3$ $[\text{M}+\text{H}]^+$ 249.15, found 249.09.

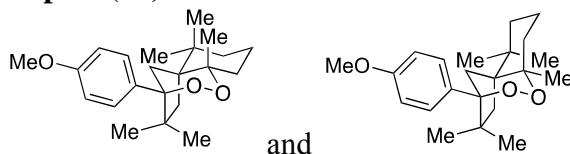
1-(4-Methoxyphenyl)-7,7-dimethyl-4-phenyl-2,3-dioxabicyclo[3.2.1]octane (**3m**)



The average yield for the title compound was 68% (2 trials, 1:1 mixture of diastereomers) at the 0.5 mmol scale, using **condition C**, and an irradiation time of 3 hours. The title compound was purified by column chromatography on silica gel (10% Et_2O /pentane) to yield a white solid.

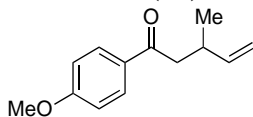
Analytical data for **3m**: ^1H NMR for diastereomer 1 (400 MHz, CDCl_3): δ 7.48 (d, $J = 8.8$ Hz, 2H), 7.31 (t, $J = 7.2$ Hz, 2H), 7.23 (m, 3H), 6.81 (d, $J = 8.8$ Hz, 2H), 5.0 (d, $J = 3.6$ Hz, 1H), 3.76 (s, 3H), 2.80 (m, 1H), 2.28 (dd, $J = 12.0$ Hz, $J = 6.0$ Hz, 1H), 2.07 (m, 2H), 1.83 (dd, $J = 12.0$ Hz, $J = 2.0$ Hz, 1H), 1.47 (s, 3H), 0.62 (s, 3H); ^{13}C NMR for diastereomer 1 (150 MHz, CDCl_3) δ 159.3, 140.5, 130.4, 128.2, 127.5, 126.7, 126.1, 113.2, 94.9, 86.2, 55.2, 45.8, 43.4, 37.3, 32.0, 31.4, 21.6; ^1H NMR for diastereomer 2 (400 MHz, CDCl_3): δ 7.35 (m, 4H), 7.27 (m, 3H), 6.87 (d, $J = 8.8$ Hz, 2H), 5.26 (s, 1H), 3.80 (s, 3H), 2.82 (dd, $J = 11.6$ Hz, $J = 5.9$ Hz, 1H), 2.59 (t, $J = 6.3$ Hz, 1H), 2.12 (dd, $J = 11.6$ Hz, $J = 2.3$ Hz, 1H), 1.87 (dd, $J = 13.2$ Hz, $J = 2.3$ Hz, 1H), 1.58 (dd, $J = 13.2$ Hz, $J = 6.7$ Hz, 1H); ^{13}C NMR for diastereomer 2 (150 MHz, CDCl_3) δ 159.4, 138.8, 129.7, 128.2, 127.6, 127.5, 126.1, 113.3, 94.3, 85.5, 55.2, 43.6, 40.3, 39.4, 38.3, 31.6, 20.8; **MS** (+ESI): m/z calculated for $\text{C}_{21}\text{H}_{24}\text{O}_3$ $[\text{M}+\text{H}]^+$ 325.18, found 325.18

3-(4-Methoxyphenyl)-4,4,6,6,9a-pentamethylhexahydro-3H,6H-3,5a-methanobenzo[*c*][1,2]dioxepine (**3n**)



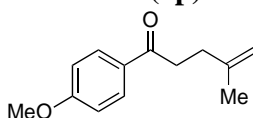
The average yield for the title compound was 64% (2 trials) at the 0.5 mmol scale, using **condition C**, and an irradiation time of 4 hours. The polycyclic product was isolated as 6.5:1 mixture of inseparable diastereomers (shown above, left thought to be major diastereomer). The title compound was purified by column chromatography on silica gel (10% Et_2O /pentane) to yield a colorless oil. Analytical data for **3n**: ^1H NMR for major diastereomer (600 MHz, CDCl_3): δ 7.28 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 8.8$ Hz, 2H), 3.77 (s, 3H), 2.46 (d, $J = 12.0$ Hz, 1H), 2.31 (dt, $J = 13.2$ Hz, 5.4 Hz, 1H), 2.17 (dd, $J = 12.0$ Hz, 2.4 Hz, 1H), 1.84 (dd, $J = 13.2$ Hz, 2.5 Hz, 1H), 1.72-1.57 (m, 3H), 1.55 (d, $J = 13.2$ Hz, 1H), 1.48 (dt, $J = 13.8$ Hz, 4.8 Hz, 1H), 1.41 (dt, $J = 13.2$ Hz, 3.4 Hz, 1H), 1.31 (s, 3H), 1.25 (s, 3H), 1.01 (s, 3H), 0.96 (s, 3H), 0.57 (s, 3H); ^{13}C NMR for major diastereomer (150 MHz, CDCl_3) δ 159.1, 130.9, 127.3, 113.2, 113.1, 92.8, 85.0, 55.2, 50.4, 43.8, 42.6, 37.0, 36.6, 35.5, 31.7, 30.7, 27.7, 25.3, 23.5, 21.7, 20.4; **MS** (+ESI): m/z calculated for $\text{C}_{22}\text{H}_{32}\text{O}_3$ $[\text{M}+\text{H}]^+$ 345.24, found 345.24

1-(4-Methoxyphenyl)-3-methylpent-4-en-1-one (3o)



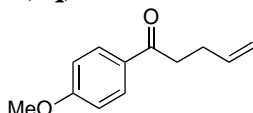
The yield for the title compound was 36% (1 trial) at the 0.5 mmol scale, using **condition C**, and an irradiation time of 23 hours (-41 °C to rt). The title compound was purified by column chromatography on silica gel (20% Et₂O/pentane) to yield a colorless oil. Analytical data for **3o**: ¹H NMR (600 MHz, CDCl₃): δ 7.91 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.82 (m, 1H), 5.00 (d, *J* = 17.2 Hz, 1H), 4.92 (d, *J* = 10.4 Hz, 1H), 3.84 (s, 3H), 2.95 (dd, *J* = 14.9 Hz, *J* = 5.8 Hz, 1H), 2.86 (m, 1H), 2.81 (dd, *J* = 14.9 Hz, *J* = 7.2 Hz, 1H), 1.06 (d, *J* = 6.5 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 197.9, 163.3, 143.2, 130.4, 130.3, 113.6, 112.9, 55.4, 44.8, 33.8, 19.8; MS (+ESI): *m/z* calculated for C₁₃H₁₇O₂ [M+H]⁺ 205.12, found 205.09

1-(4-Methoxyphenyl)-4-methylpent-4-en-1-one (3p)



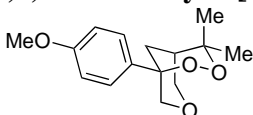
The yield for the title compound was 37% (1 trial) at the 0.5 mmol scale, using **condition C**, and an irradiation time of 23 hours (-41 °C to rt). The title compound was purified by column chromatography on silica gel (20% Et₂O/pentane) to yield a colorless oil. Spectral data were in agreement with the literature values.¹³ Analytical data for **3p**: ¹H NMR (600 MHz, CDCl₃): δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.74 (s, 1H), 4.70 (s, 1H), 3.84 (s, 3H), 3.04 (m, 2H), 2.41 (t, *J* = 7.8 Hz, 2H), 1.76 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 198.3, 163.3, 144.8, 130.3, 130.0, 113.7, 110.0, 55.4, 36.4, 32.1, 22.7

1-(4-Methoxyphenyl)pent-4-en-1-one (3q)



The yield for the title compound was 27% (1 trial) at the 0.5 mmol scale, using **condition C**, and an irradiation time of 23 hours (-41 °C to rt). The title compound was purified by column chromatography on silica gel (20% Et₂O/pentane) to yield a colorless oil. Spectral data were in agreement with the literature values.¹³ Analytical data for **3q**: ¹H NMR (600 MHz, CDCl₃): δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.88 (m, 1H), 5.06 (dq, *J* = 17.1, *J* = 1.8 Hz, 1H), 4.98 (dq, *J* = 10.2, *J* = 1.8 Hz, 1H), 3.85 (s, 3H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.47 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 198.0, 163.4, 137.5, 130.3, 130.0, 115.1, 113.7, 55.4, 37.4, 28.3

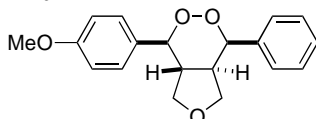
1-(4-Methoxyphenyl)-4,4-dimethyl-2,3,7-trioxabicyclo[3.3.1]nonane (3t)



The average yield for the title compound was 16% (2 trials) at the 0.5 mmol scale, using modified **condition C** (0.04 M DCE, other conditions unaltered), and an irradiation time of 4 hours. The title compound was purified by column chromatography on silica gel (20% Et₂O/pentane) to yield a white solid. Analytical data for **3t**: ¹H NMR (400 MHz, CDCl₃): δ 6.96

(d, $J = 8.7$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 4.19 (m, 2H), 4.01 (dd, $J = 9.6$ Hz, $J = 2.4$ Hz, 1H), 3.77 (s, 3H), 3.72 (d, $J = 9.6$ Hz, 1H), 2.53 (m, 1H), 1.97 (dt, $J = 6.7$ Hz, $J = 2.0$ Hz, 1H), 1.87 (d, $J = 9.2$ Hz, 1H), 1.26 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.1, 134.5, 127.2, 113.6, 74.6, 68.3, 55.2, 50.1, 40.9, 39.3, 30.4, 23.6, 19.7; MS (GC-MS): m/z calculated for $\text{C}_{15}\text{H}_{20}\text{O}_4$ 264.14, found 264.1

1-(4-Methoxyphenyl)-4-phenyltetrahydro-1*H*,4*H*-furo[3,4-*d*][1,2]dioxine (3u)

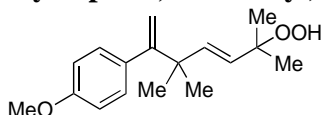


The average yield for the title compound was 79% (2 trials, 5.7:1 mixture of diastereomers) at the 0.5 mmol scale, using **condition C**, and an irradiation time of 3 hours. The title compound was purified by column chromatography on silica gel (33% to 50% EtOAc/hexanes) to yield a colorless oil. Spectral data were in agreement with the literature values.¹¹ Analytical data for **3u**: ^1H NMR major diastereomer (600 MHz, CDCl_3): δ 7.49 (d, $J = 7.0$ Hz, 2H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.30 (m, 3H), 6.90 (d, $J = 8.7$ Hz, 2H), 5.55 (d, $J = 5.8$ Hz, 1H), 5.03 (d, $J = 9.9$ Hz, 1H), 4.16 (t, $J = 7.3$ Hz, 1H), 3.80 (s, 3H), 3.77 (m, 1H), 3.42 (dd, $J = 11.4$ Hz, $J = 8.4$ Hz, 1H), 3.24 (dd, $J = 11.4$ Hz, $J = 7.8$ Hz, 1H), 2.83 (m, 1H), 2.60 (m, 1H); ^1H NMR minor diastereomer (600 MHz, CDCl_3): δ 7.37 (s, 5H), 7.33 (d, $J = 8.7$ Hz, 2H), 6.90 (d, $J = 8.7$ Hz, 2H), 5.14 (d, $J = 9.4$ Hz, 1H), 5.11 (d, $J = 9.4$ Hz, 1H), 3.90 (m, 2H), 3.80 (s, 3H), 3.53 (m, 2H), 2.63 (m, 2H)

VII. Hydroperoxide via $^1\text{O}_2$

$^1\text{O}_2$ Control Experiment (Table 1, entry 10)

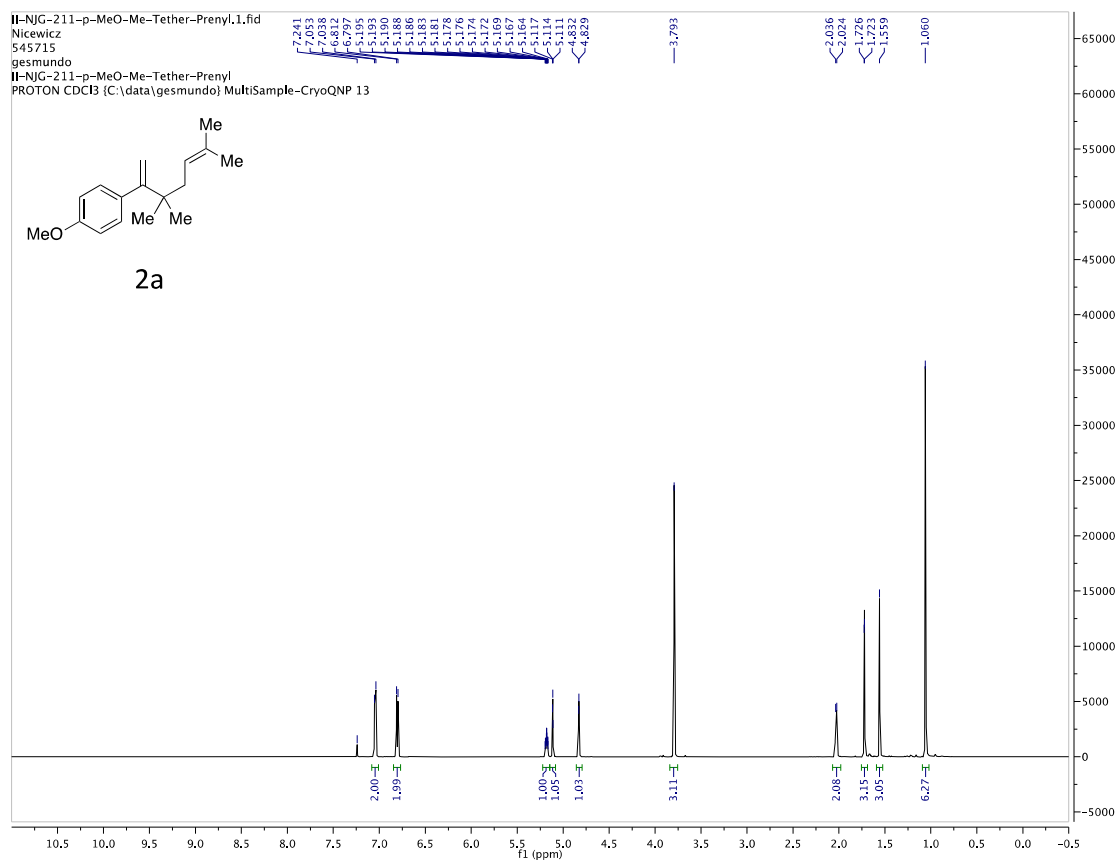
(*E*)-1-(6-Hydroperoxy-3,3,6-trimethylhepta-1,4-dien-2-yl)-4-methoxybenzene

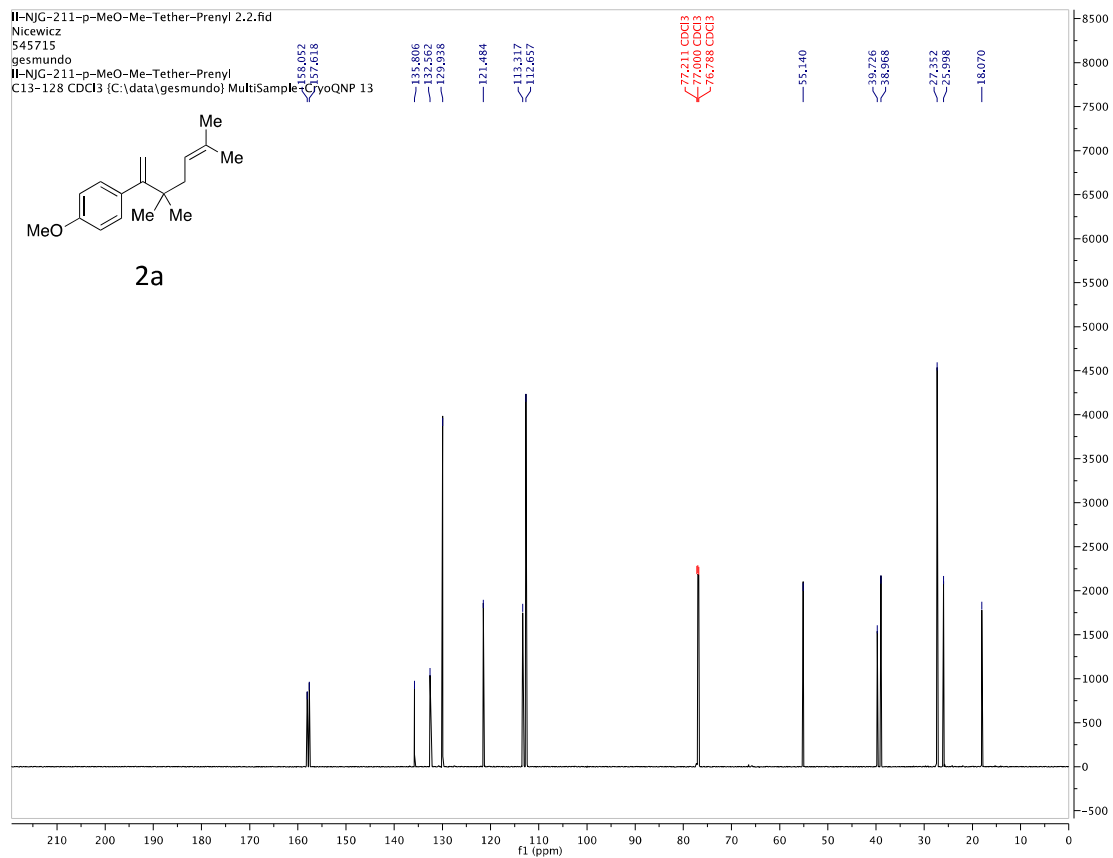


The yield for the title compound was 65% (1 trial) at the 0.36 mmol scale, using modified **condition A**, and an irradiation time of 3.5 hours. Rose Bengal was used in place of catalyst **1c** and dry MeOH as solvent in place of DCM. The reaction was carried out at ambient temperature. The title compound was purified by column chromatography on silica gel (20% Et₂O/hexanes) to yield a colorless oil. It should be noted that the shown tertiary allylic hydroperoxide was the major product in a transformation possibly producing multiple oxidation products (complete consumption of starting material was observed by ^1H NMR). No endoperoxidation/cyclization products were observed. Analytical data for shown hydroperoxide: ^1H NMR (600 MHz, CDCl_3): δ 7.16 (s, 1H) 7.07 (d, $J = 8.7$ Hz, 2H), 6.77 (d, $J = 8.7$ Hz, 2H), 5.78 (d, $J = 16.2$ Hz, 1H), 5.42 (d, $J = 16.2$ Hz, 1H), 5.17 (d, $J = 1.5$ Hz, 1H), 4.90 (d, $J = 1.5$ Hz, 1H), 3.77 (s, 3H), 1.32 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 158.3, 156.6, 140.4, 135.2, 130.0, 129.8, 113.1, 112.7, 82.3, 55.2, 41.6, 27.2, 24.3; MS (+ESI): m/z calculated for $\text{C}_{17}\text{H}_{24}\text{O}_3$ $[\text{M}+\text{H}]^+$ 277.18, found 277.11

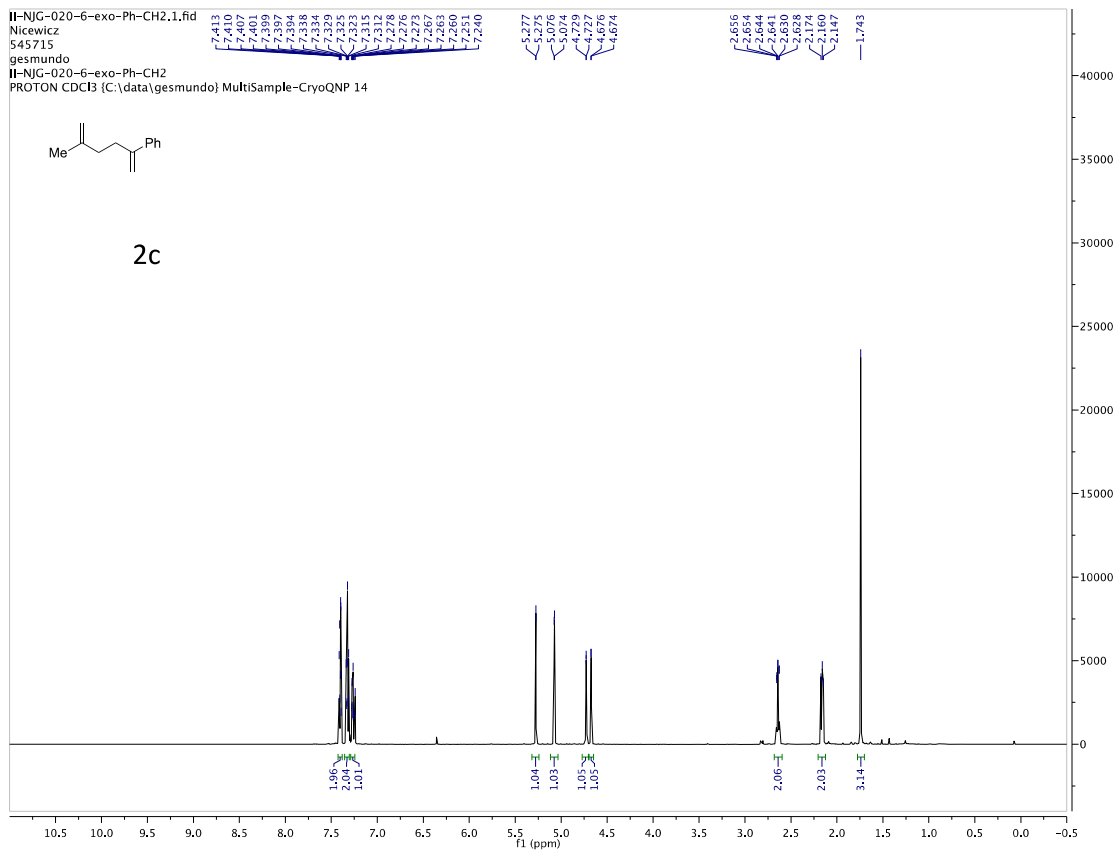
VIII. ^1H and ^{13}C NMR Spectra

1-Methoxy-4-(3,3,6-trimethylhepta-1,5-dien-2-yl)benzene (2a)

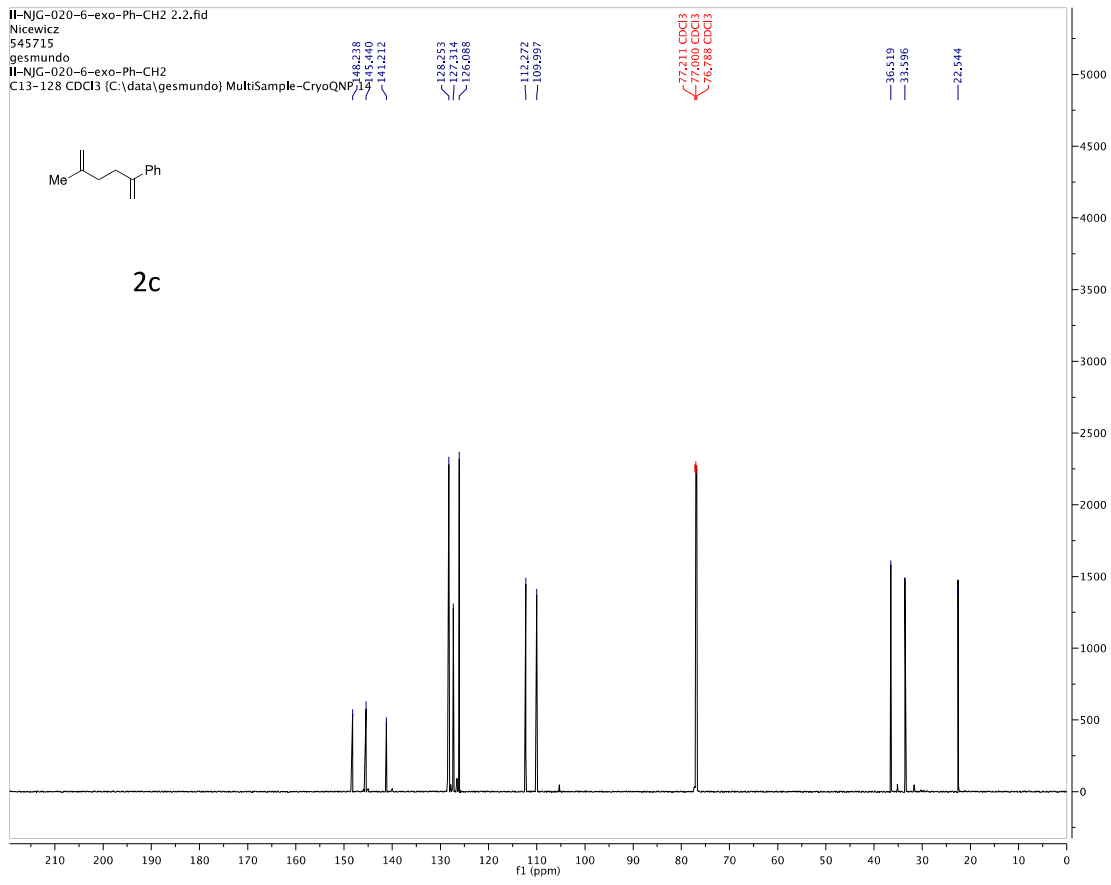




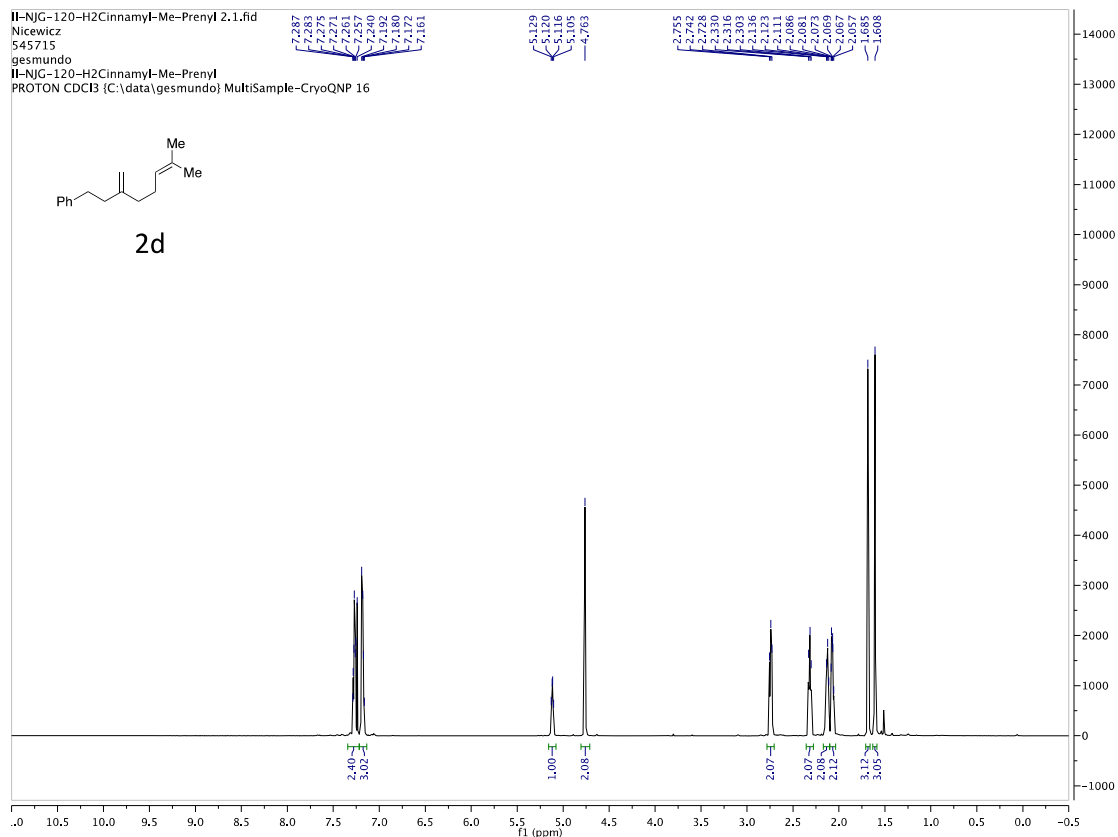
(5-Methylhexa-1,5-dien-2-yl)benzene (2c)

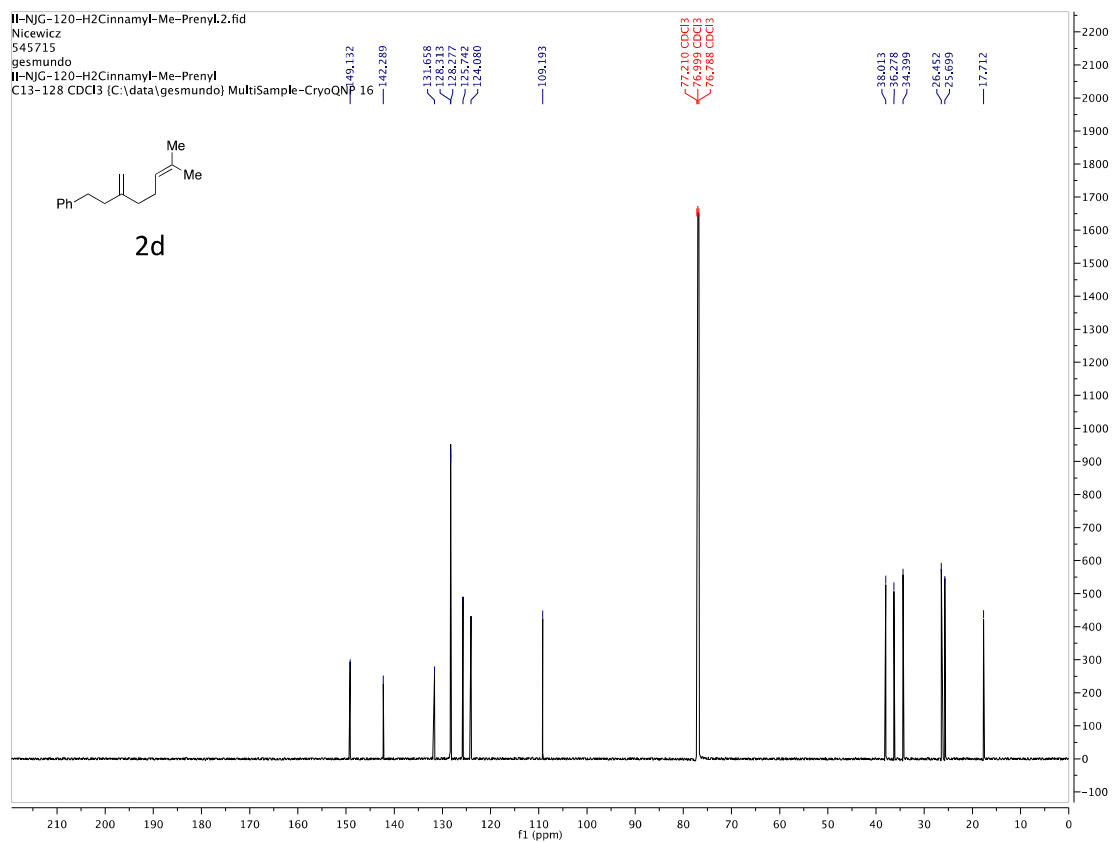


II-NJG-020-6-exo-Ph-CH2 2.2.fid
Nicewicz
545715
gesmundo
II-NJG-020-6-exo-Ph-CH2
C13-128 CDCl3 {C:\data\gesmundo} MultiSample-CryoQNP1

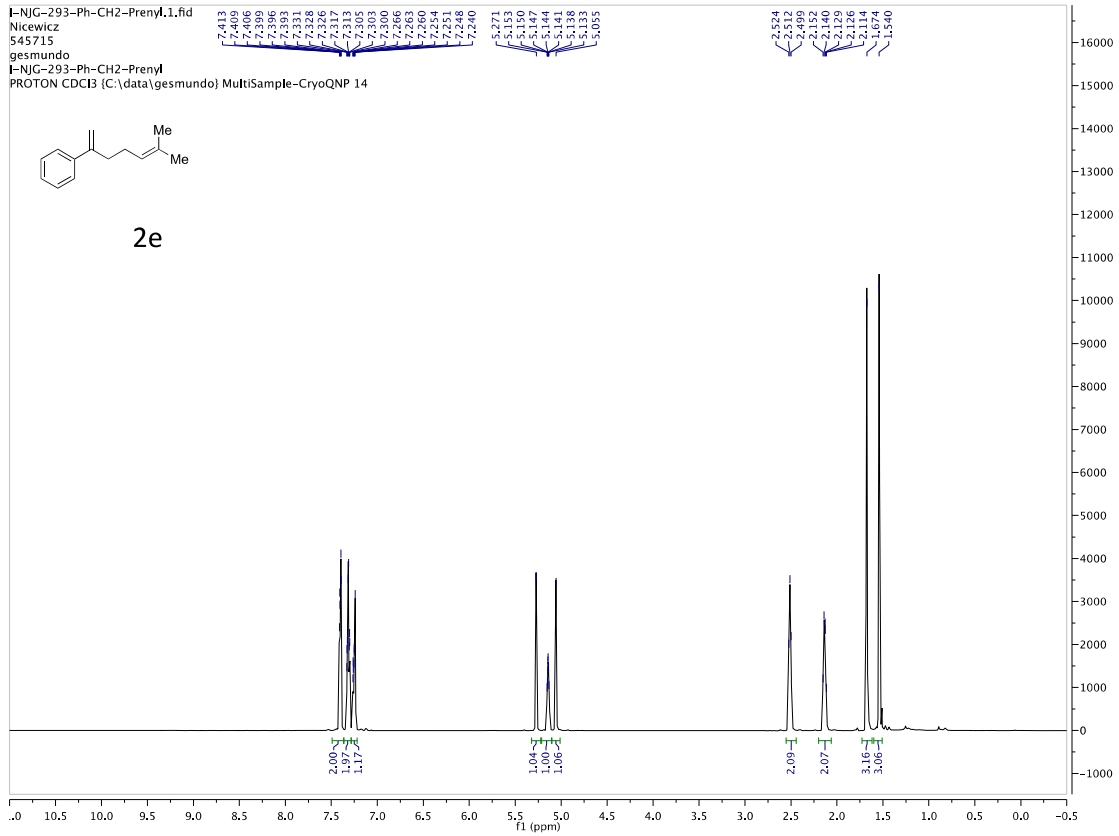


(7-Methyl-3-methyleneoct-6-en-1-yl)benzene (2d)

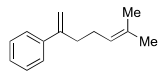




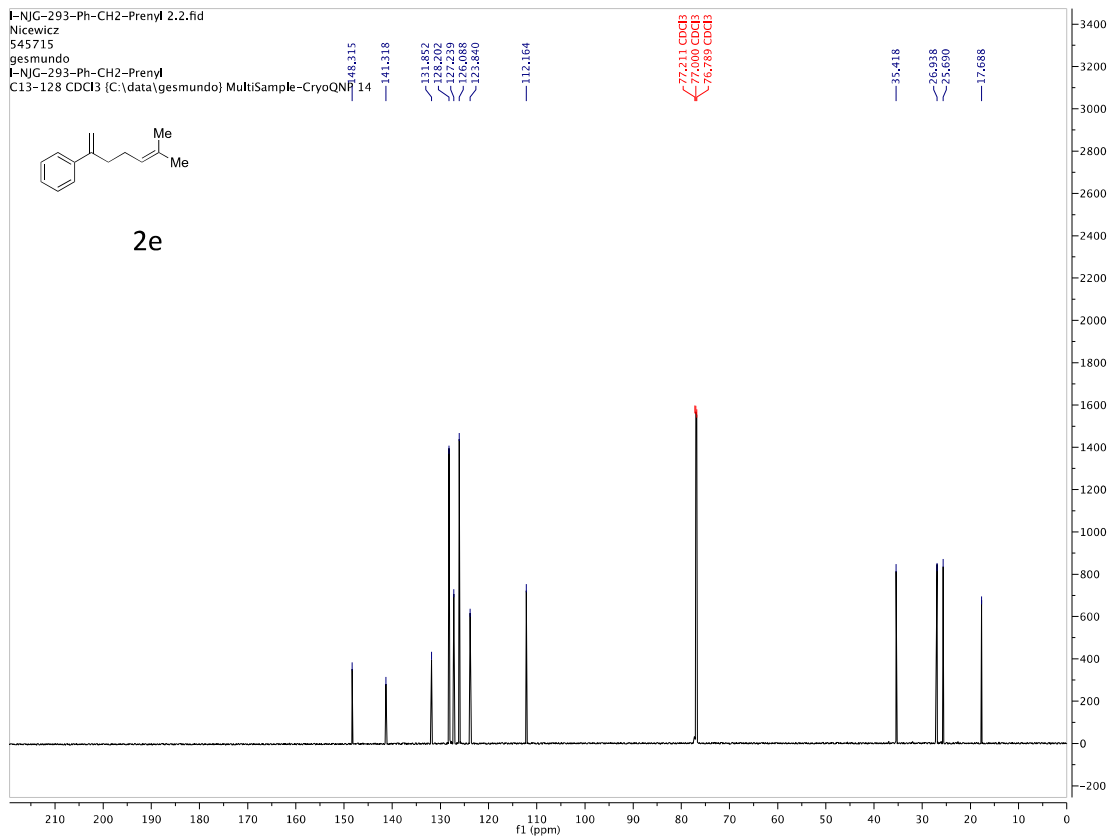
(6-Methylhepta-1,5-dien-2-yl)benzene (2e)



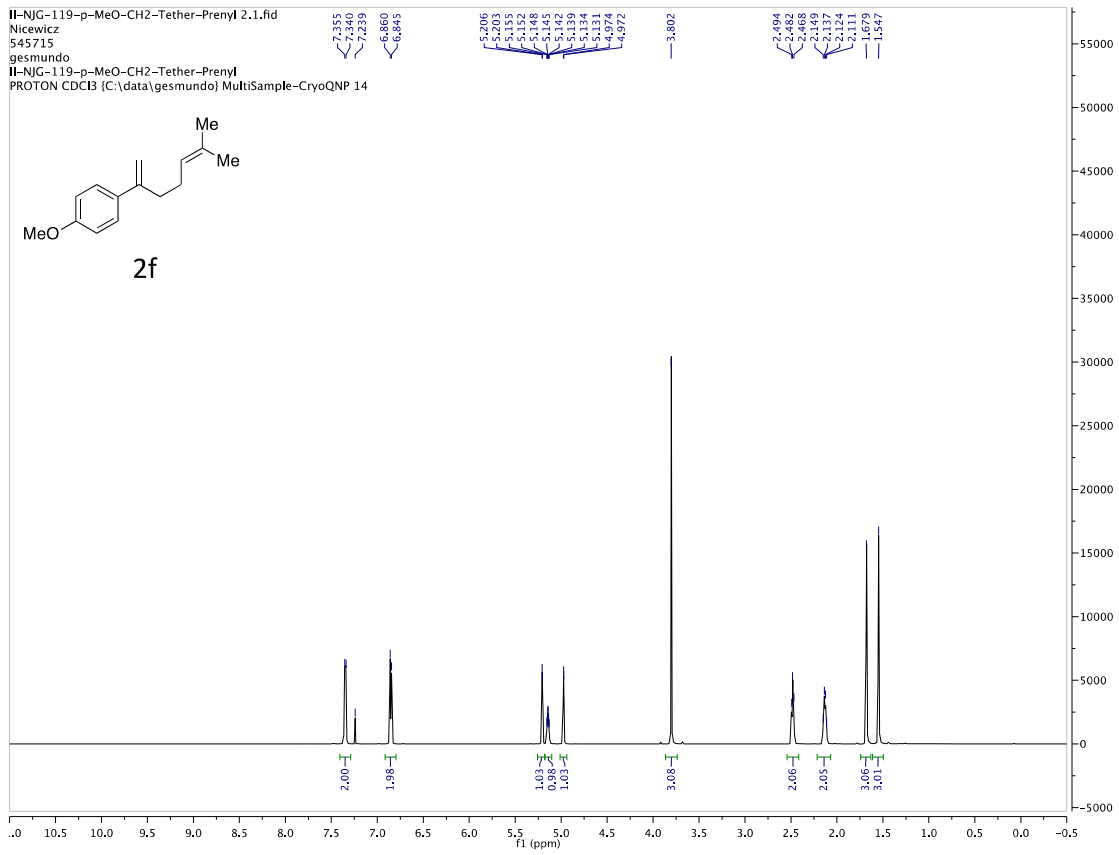
I-NJG-293-Ph-CH2-Prenyl 2.2.fid
Nicewicz
545715
gesmundo
I-NJG-293-Ph-CH2-Prenyl
C13-128 CDCl3 (C:\data\gesmundo) MultiSample-CryoQNP 14

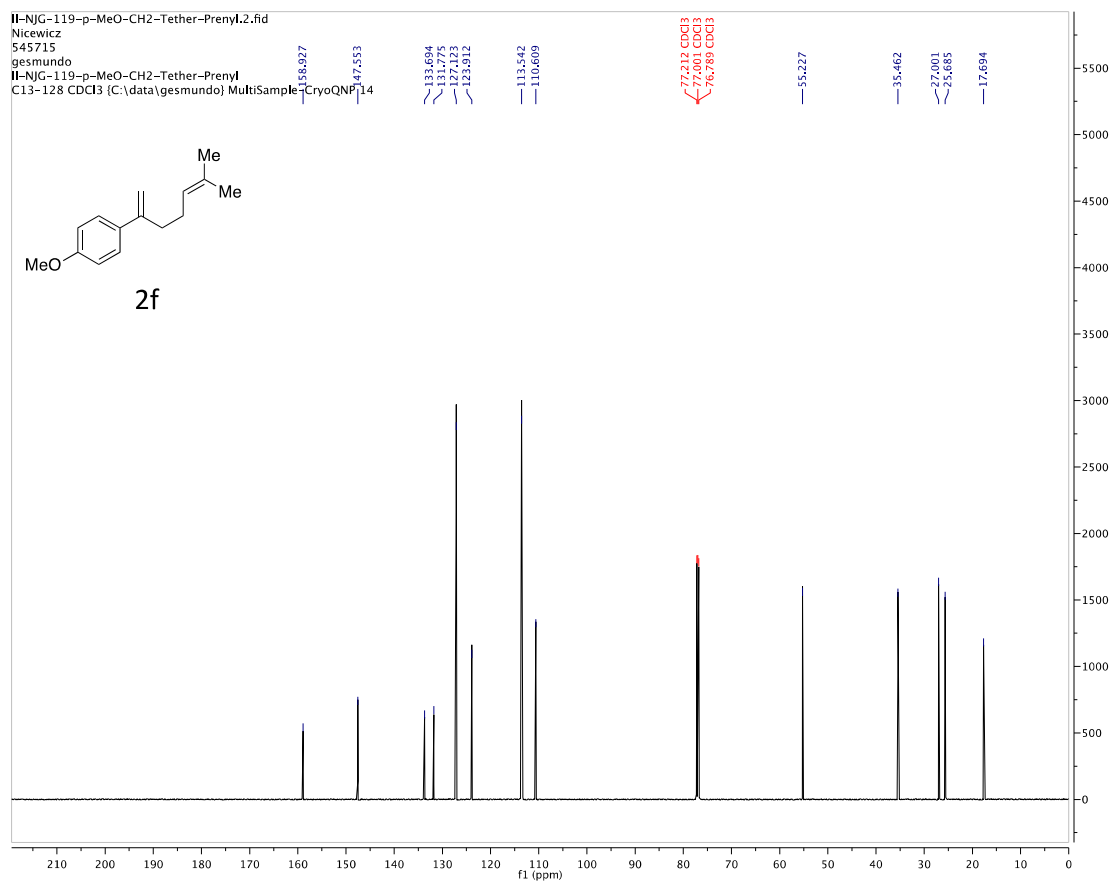


2e

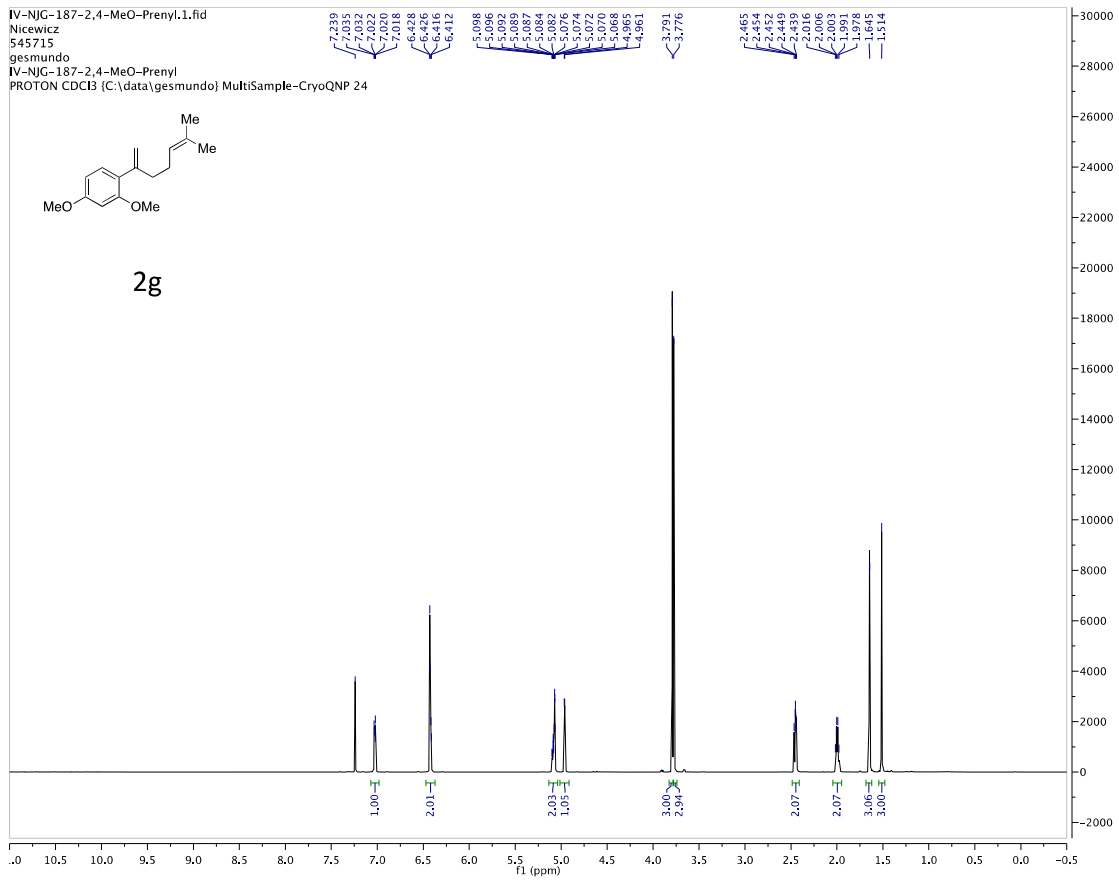


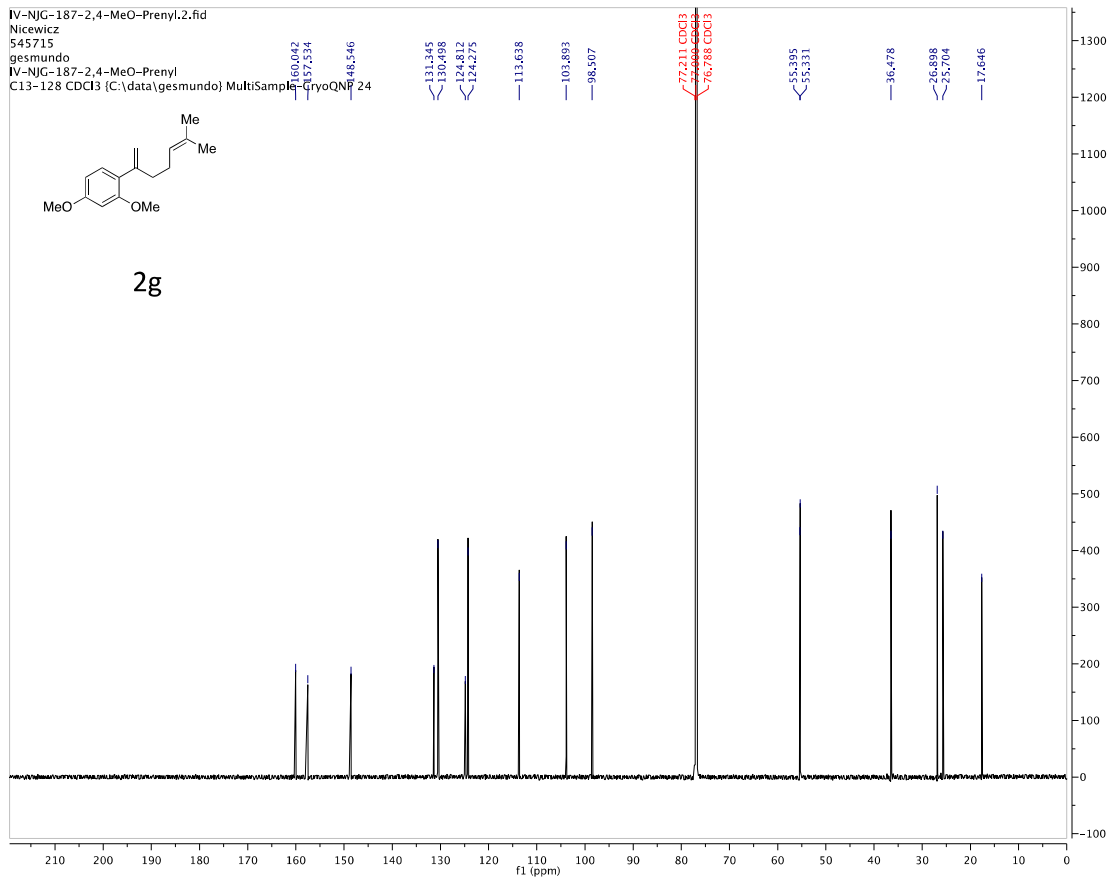
1-Methoxy-4-(6-methylhepta-1,5-dien-2-yl)benzene (2f)



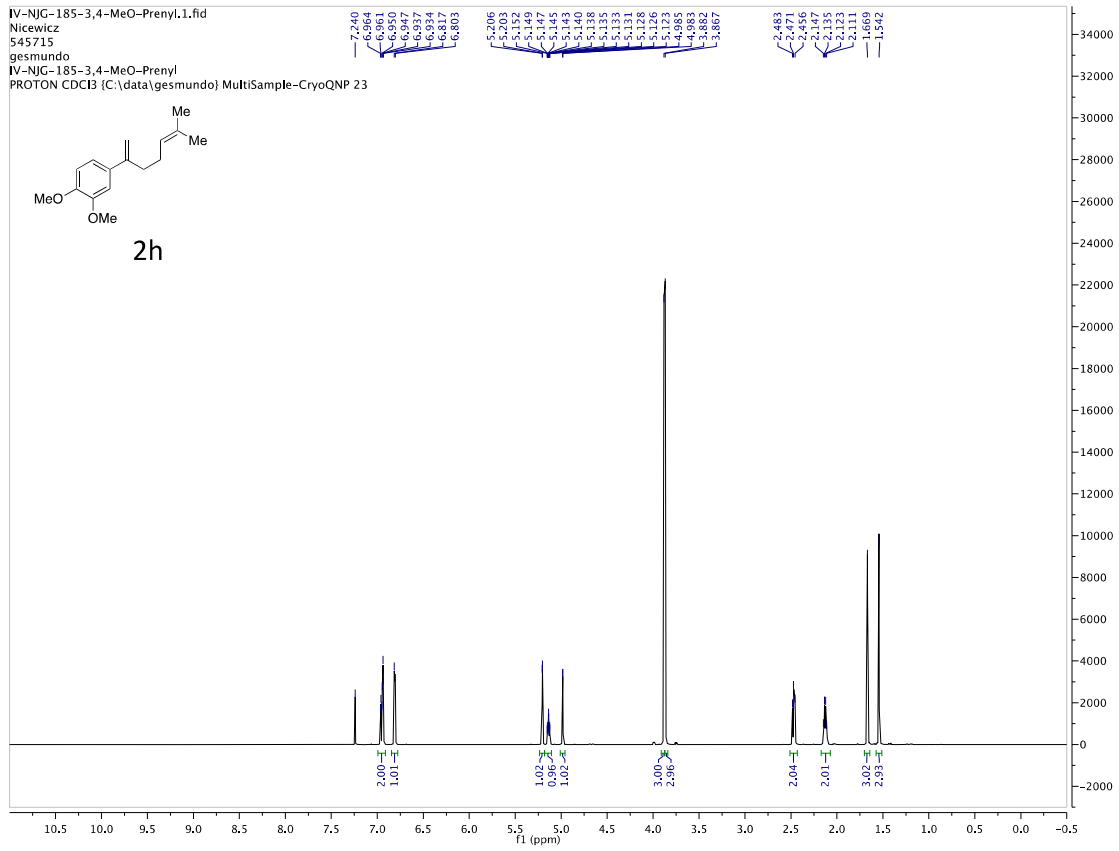


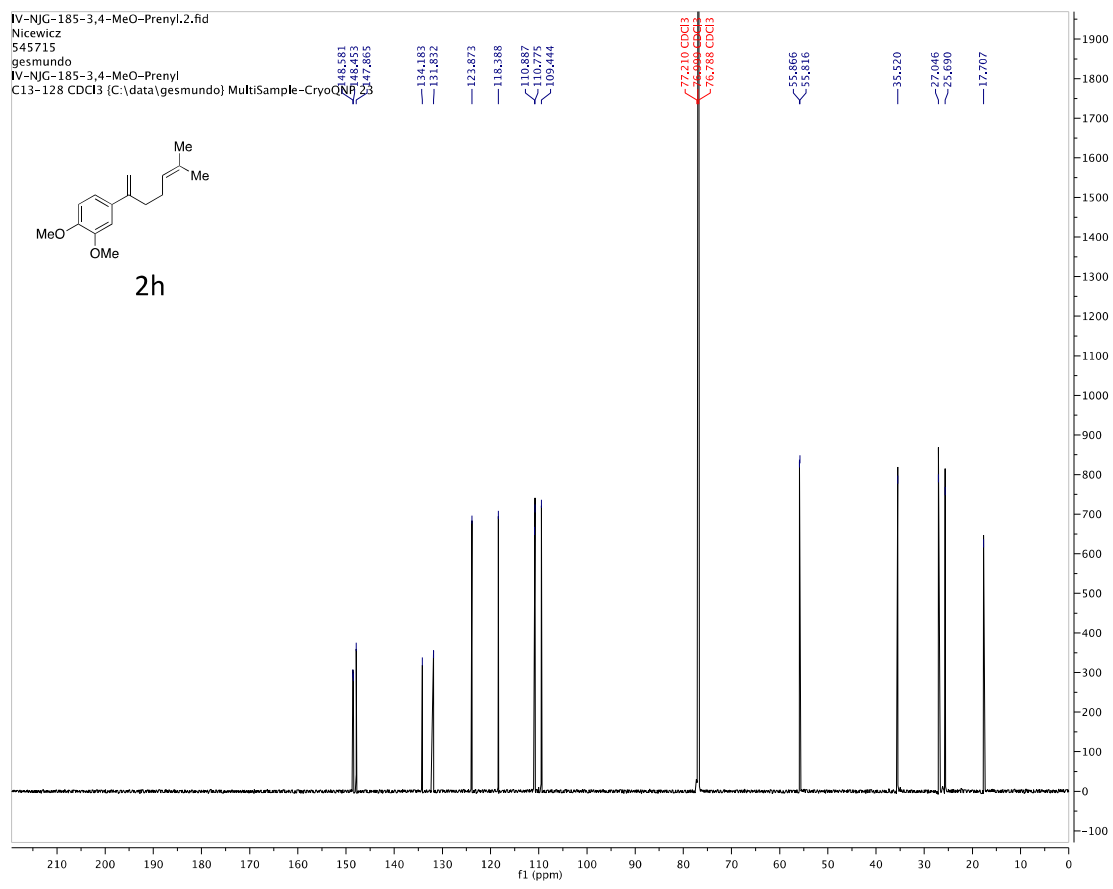
2,4-Dimethoxy-1-(6-methylhepta-1,5-dien-2-yl)benzene (2g)



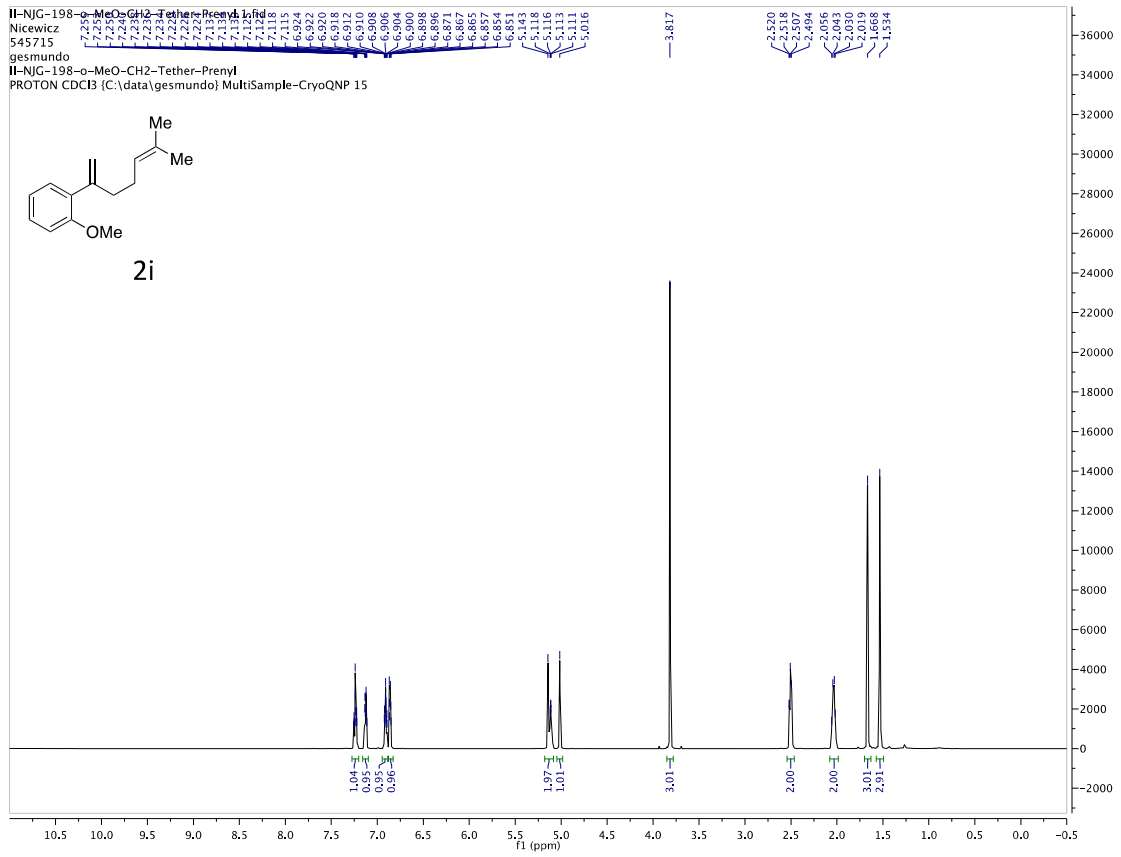


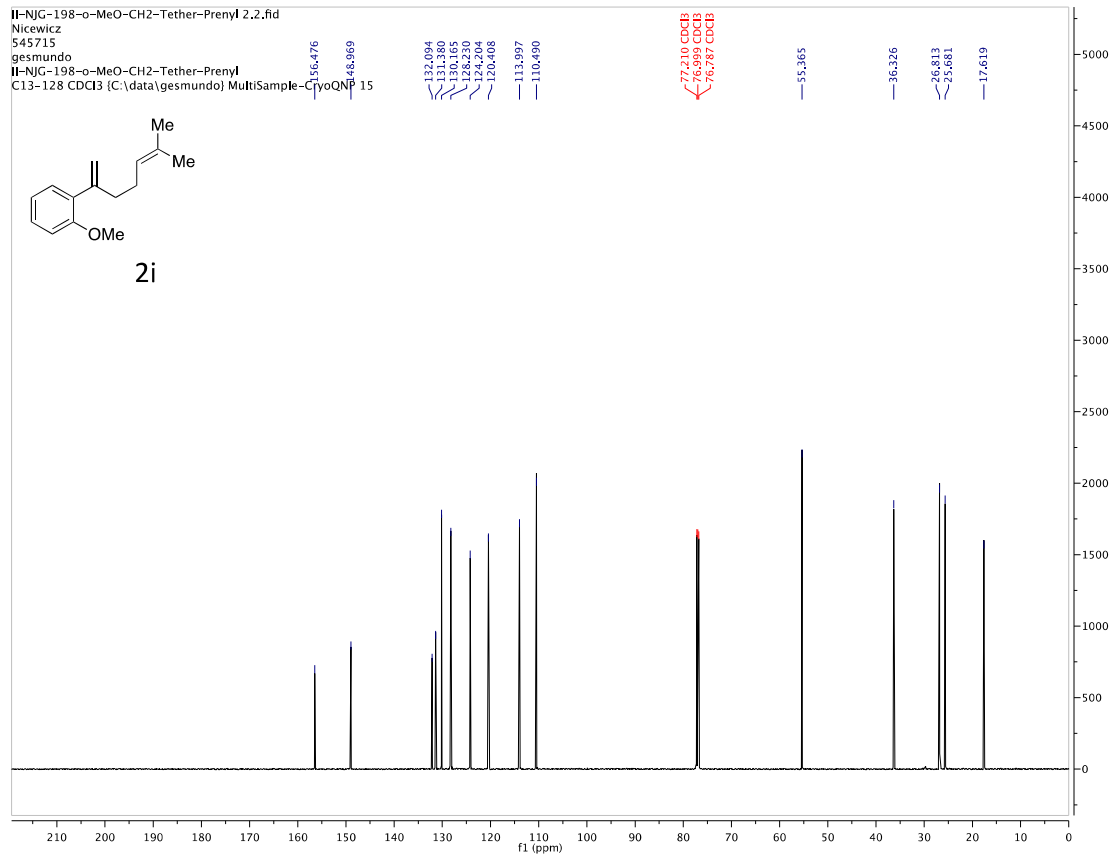
1,2-Dimethoxy-4-(6-methylhepta-1,5-dien-2-yl)benzene (2h)



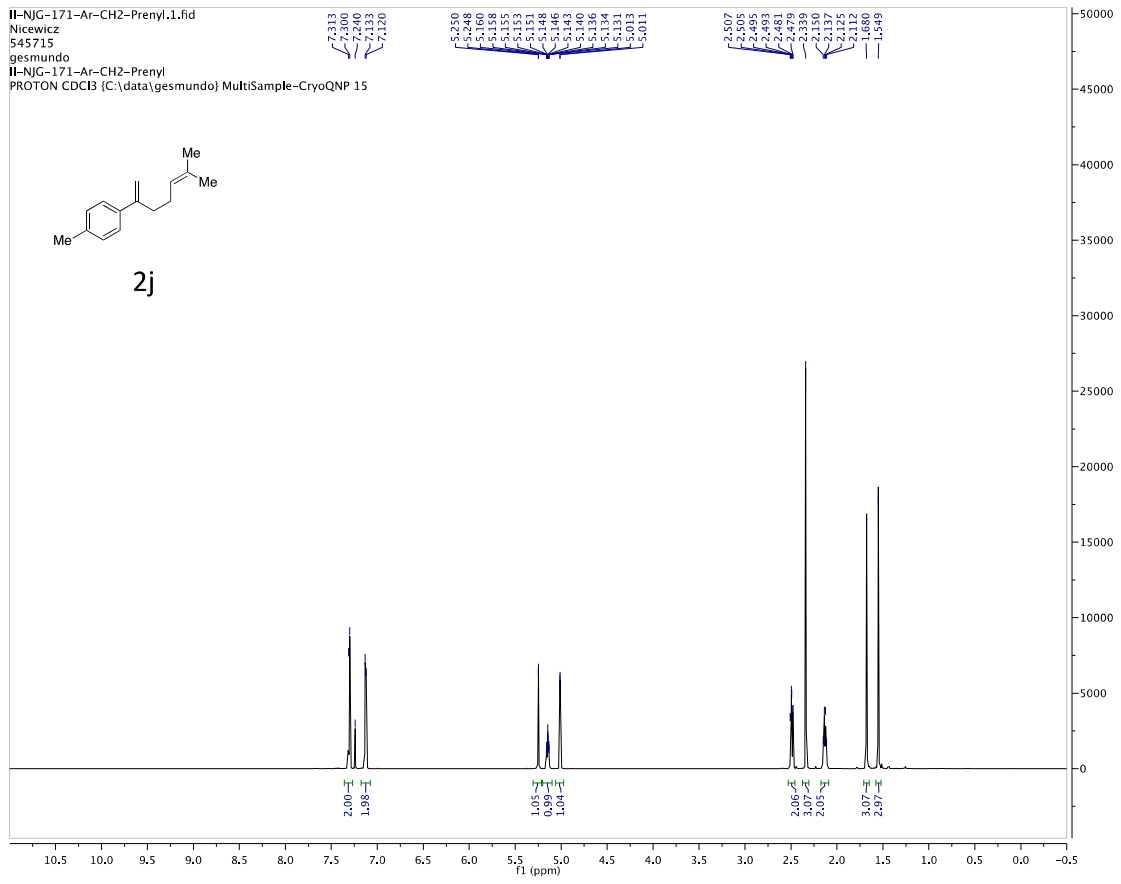


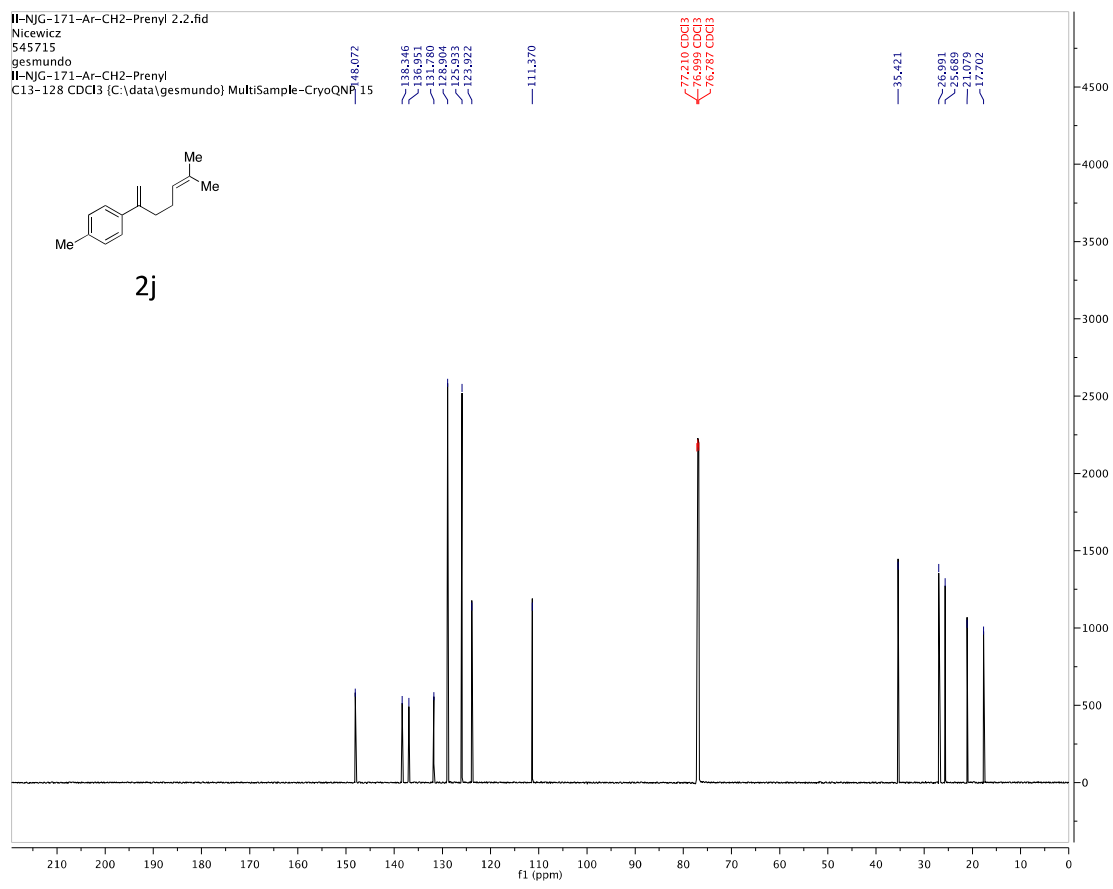
1-Methoxy-2-(6-methylhepta-1,5-dien-2-yl)benzene (2i)



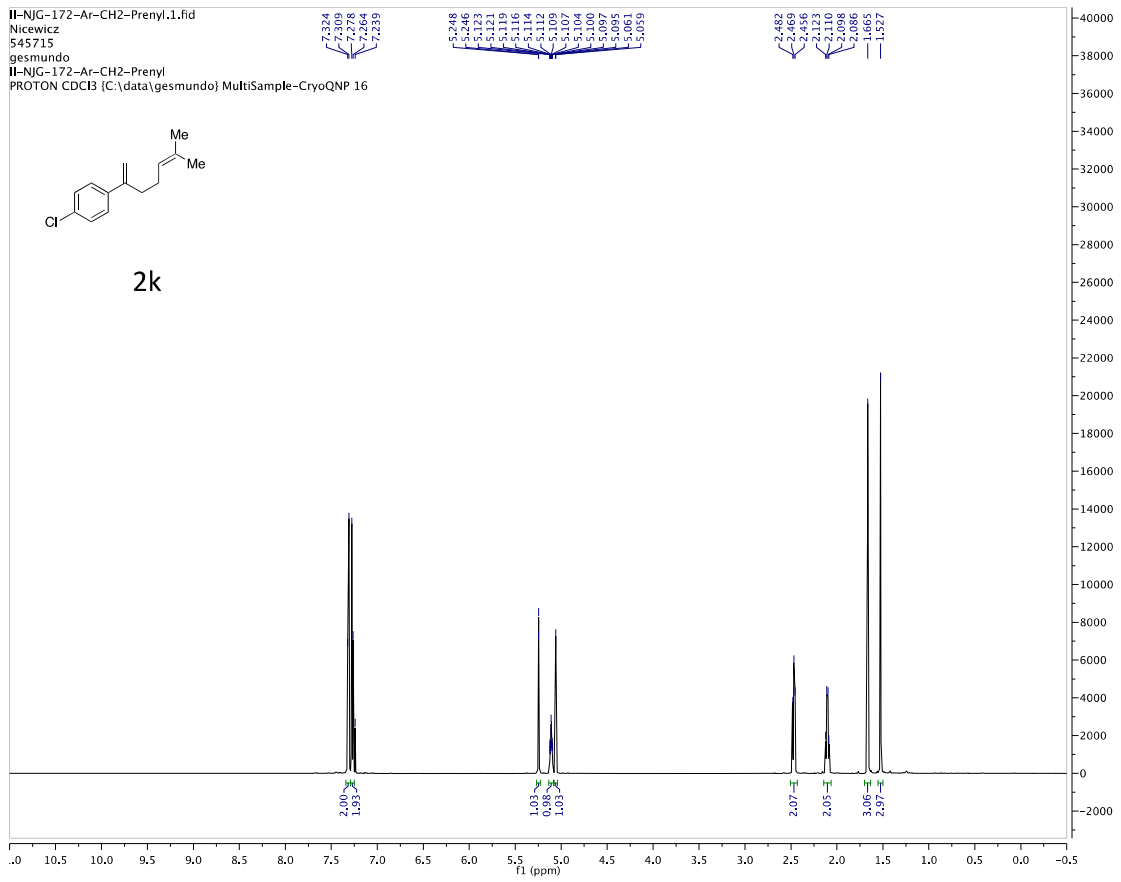


1-Methyl-4-(6-methylhepta-1,5-dien-2-yl)benzene (2j)

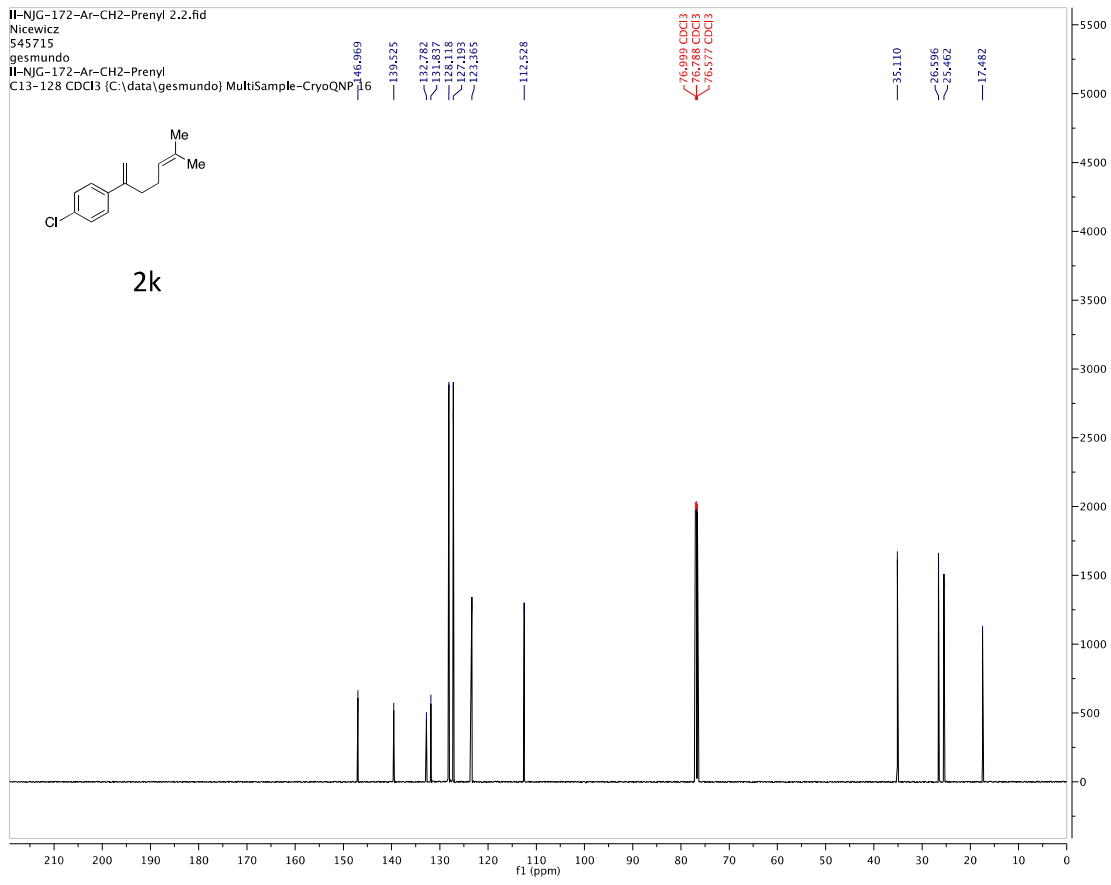




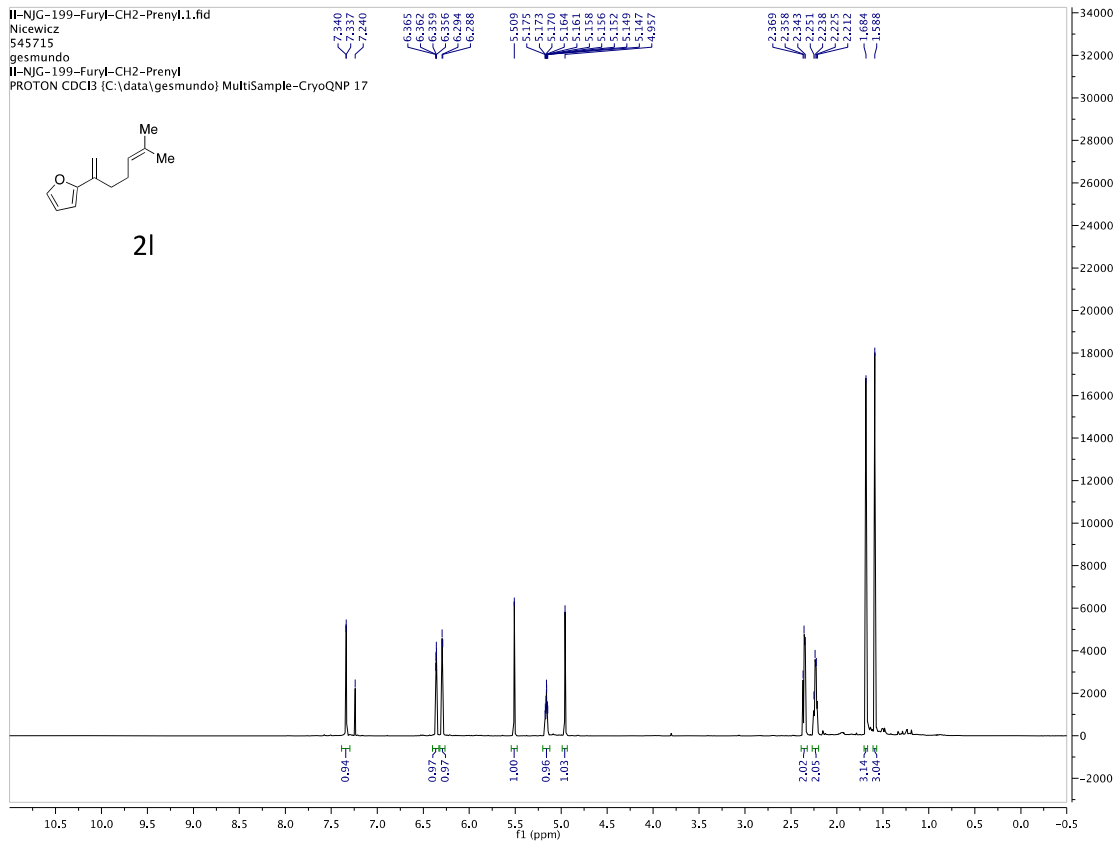
1-Chloro-4-(6-methylhepta-1,5-dien-2-yl)benzene (2k)

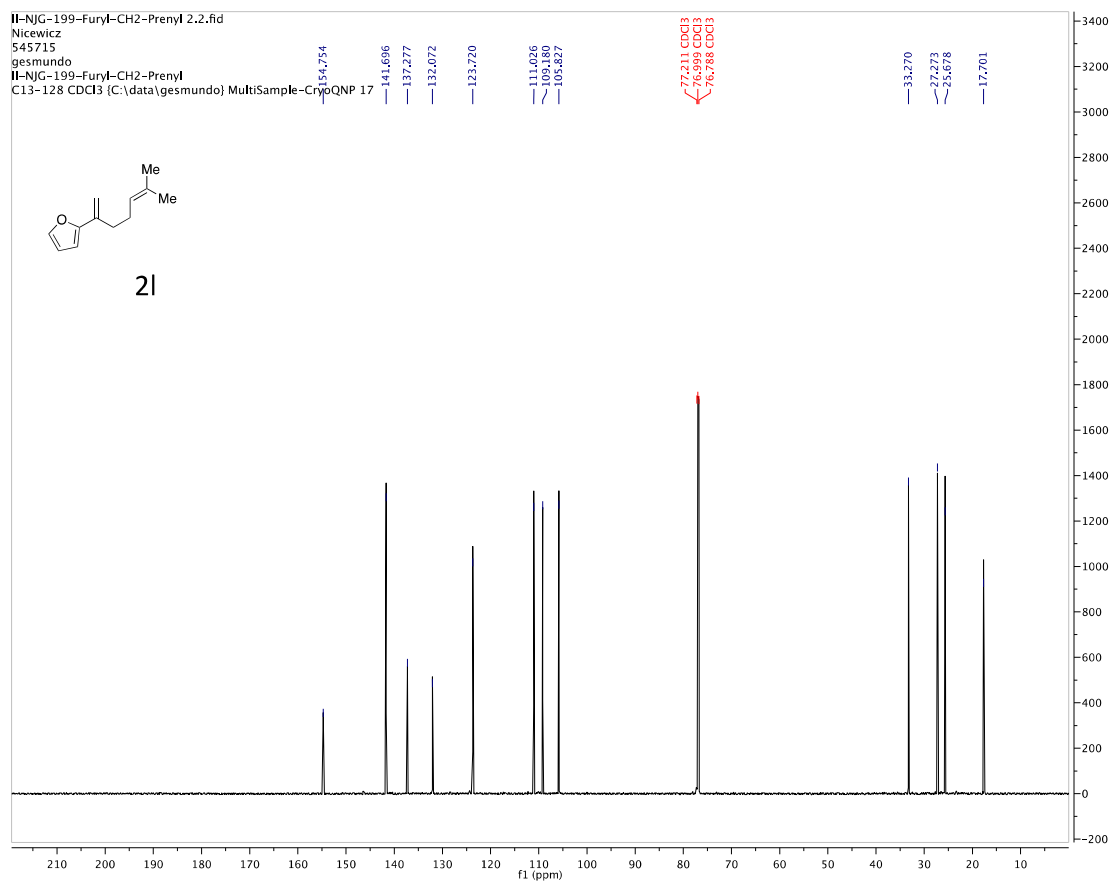


II-NJG-172-Ar-CH2-Prenyl 2.2.fid
Nicewicz
545715
gesmundo
II-NJG-172-Ar-CH2-Prenyl
C13-128 CDCl3 {C:\data\gesmundo} MultiSample-CryoQNP 1.6

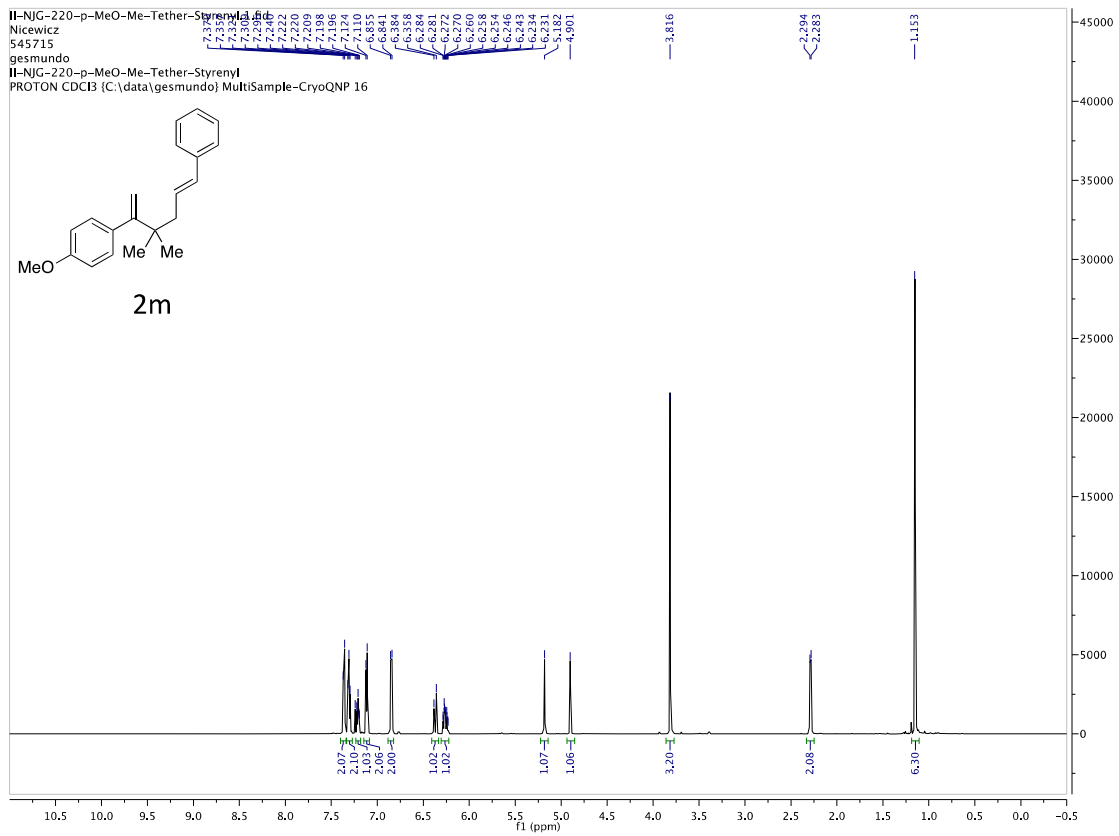


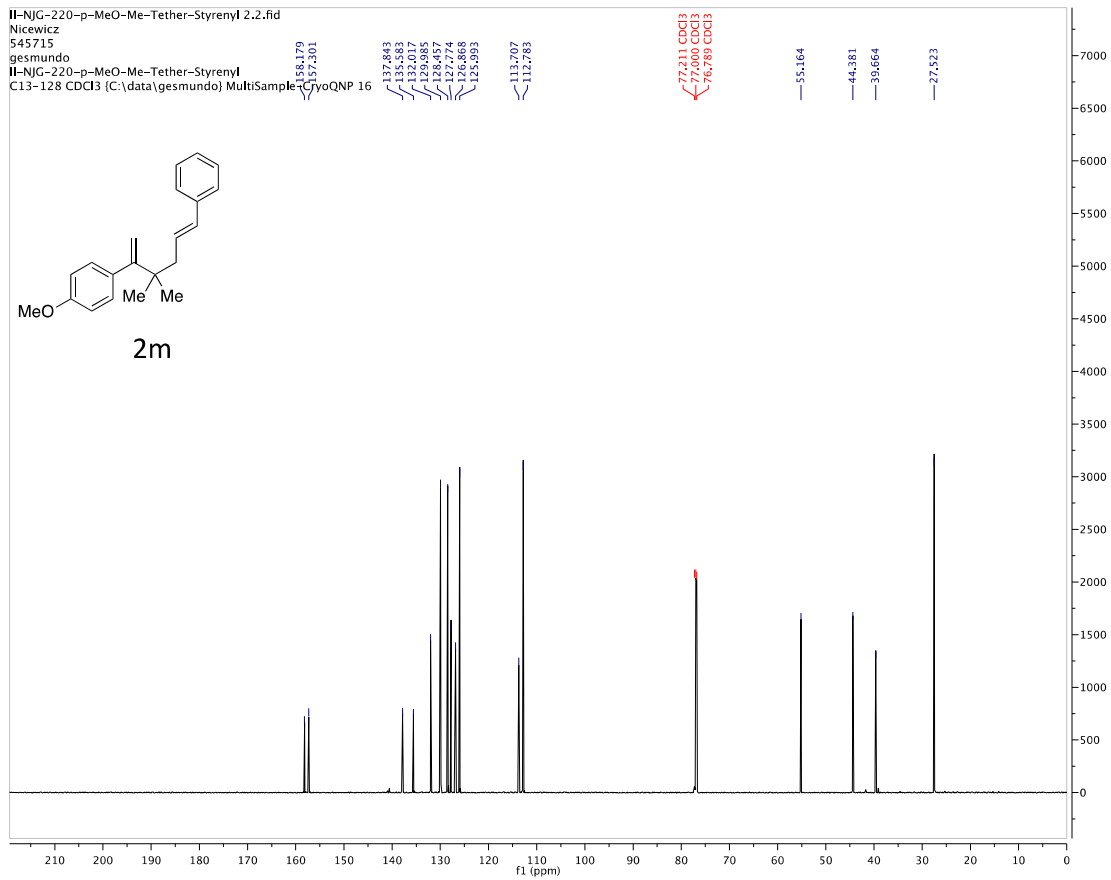
2-(6-Methylhepta-1,5-dien-2-yl)furan (2l)



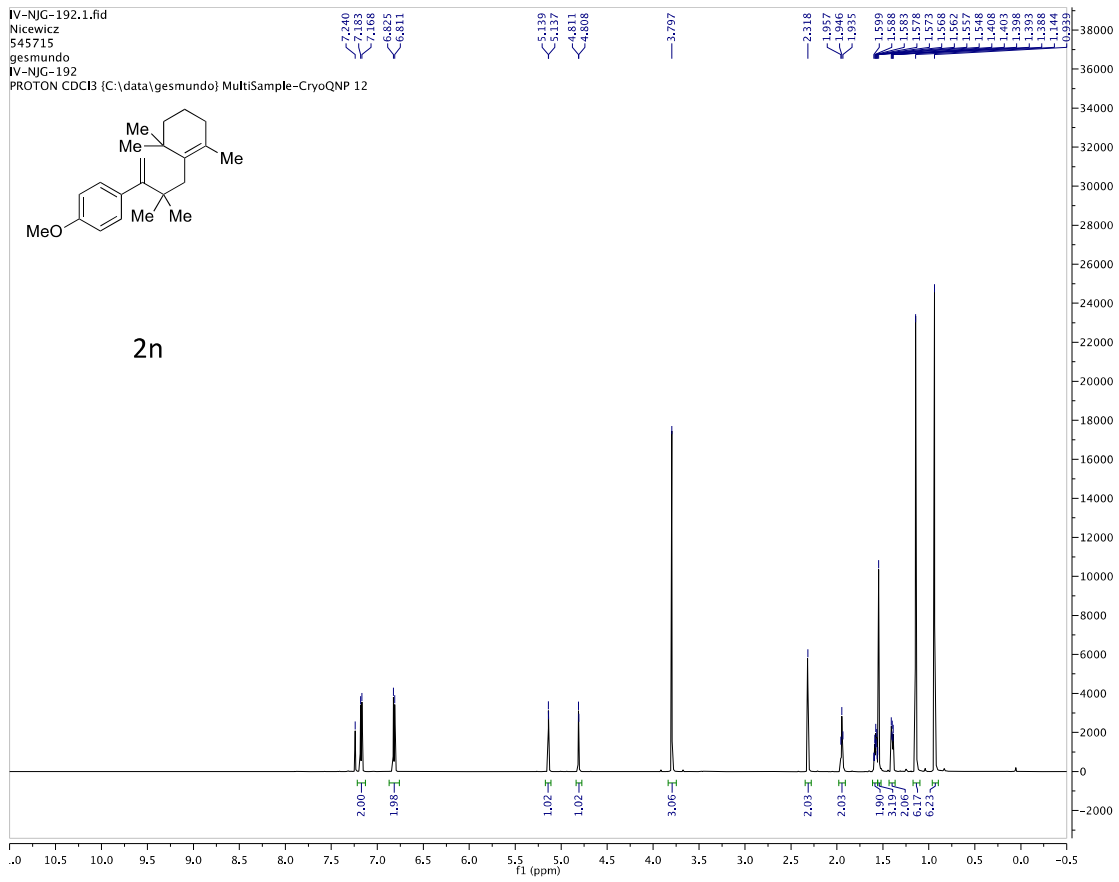


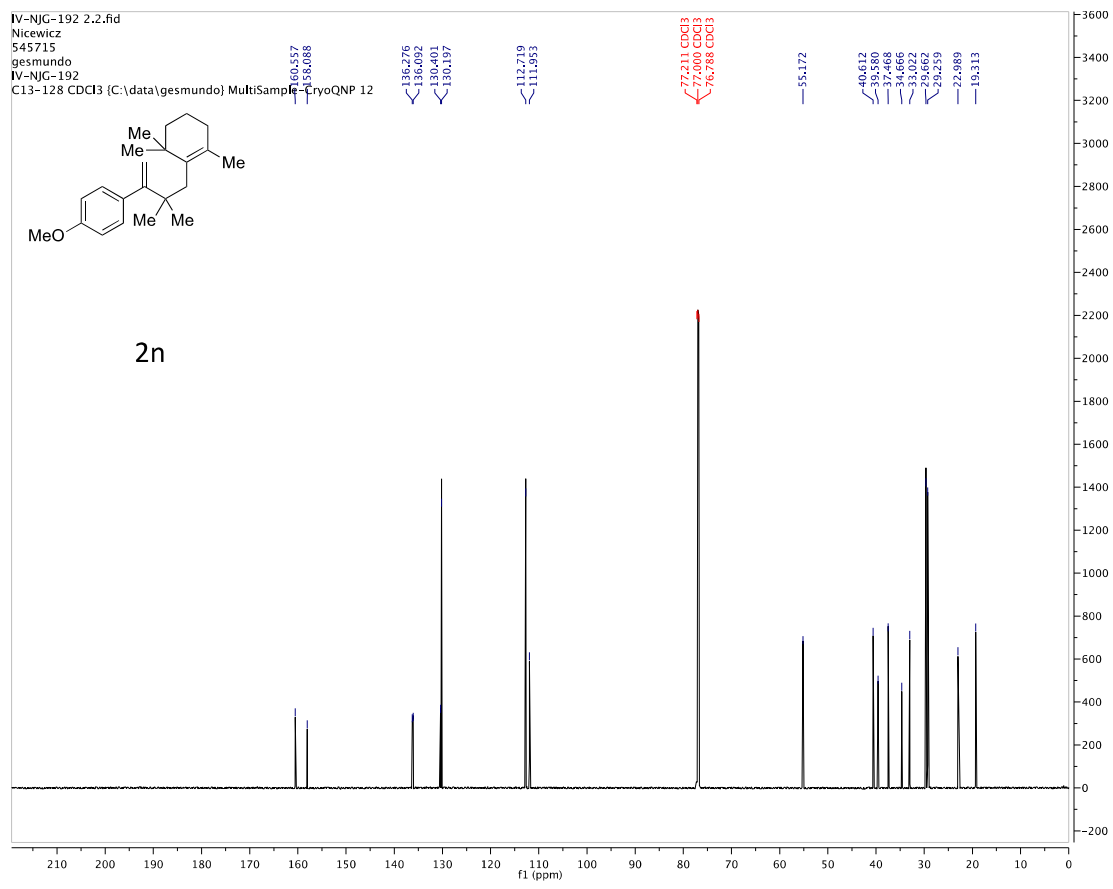
(E)-1-(3,3-Dimethyl-6-phenylhexa-1,5-dien-2-yl)-4-methoxybenzene (2m)



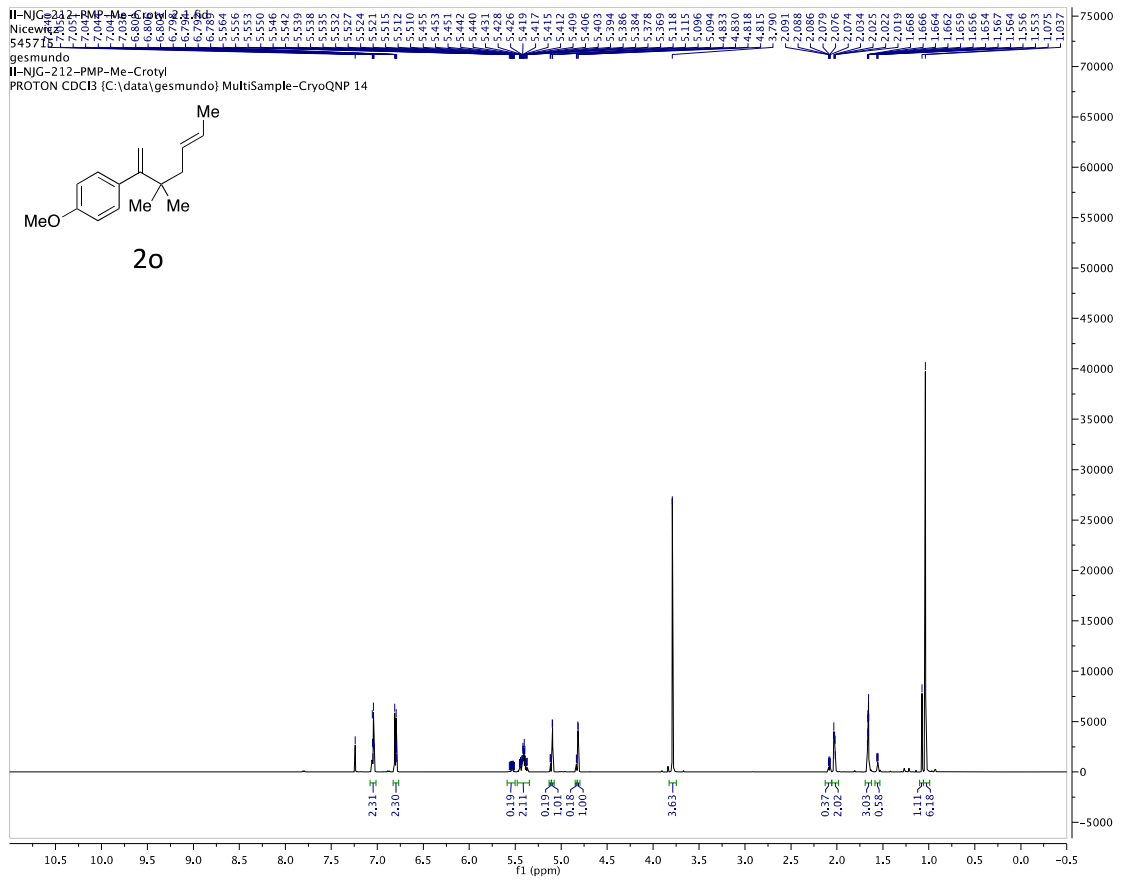


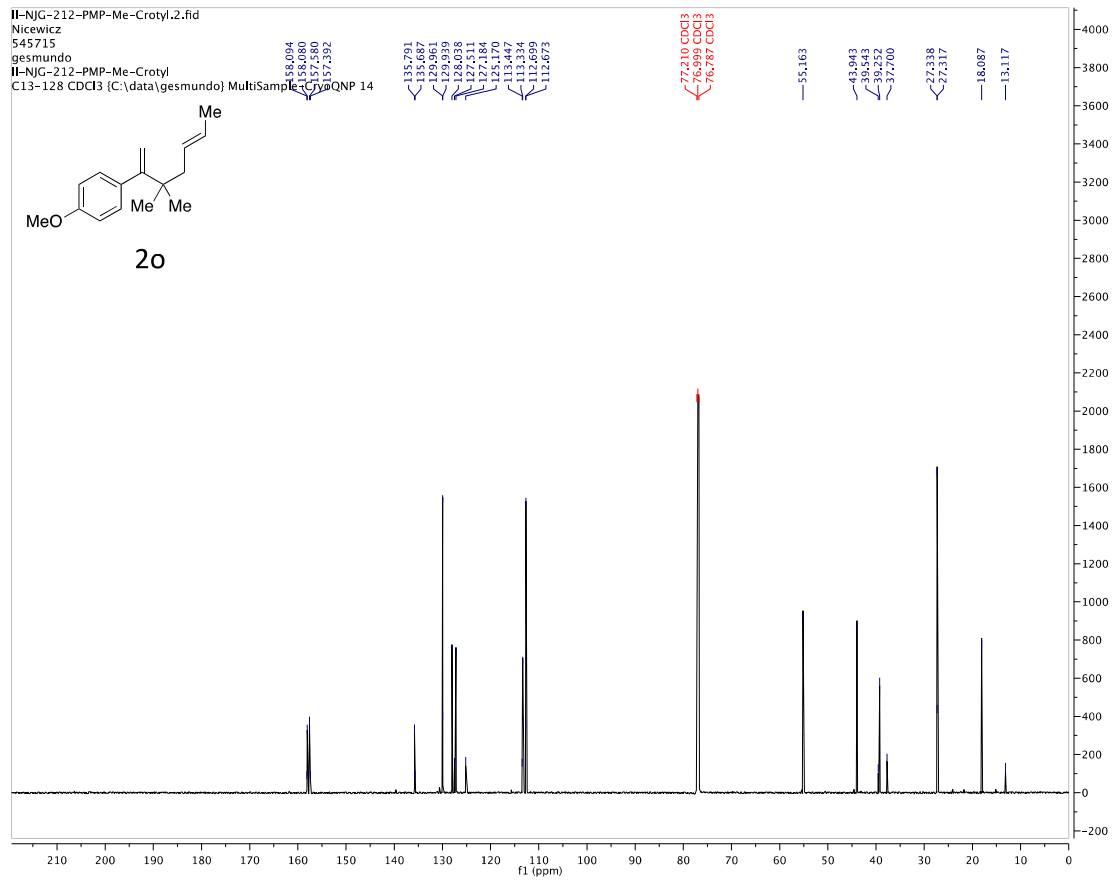
1-(3,3-Dimethyl-4-(2,6,6-trimethylcyclohex-1-en-1-yl)but-1-en-2-yl)-4-methoxybenzene (2n)



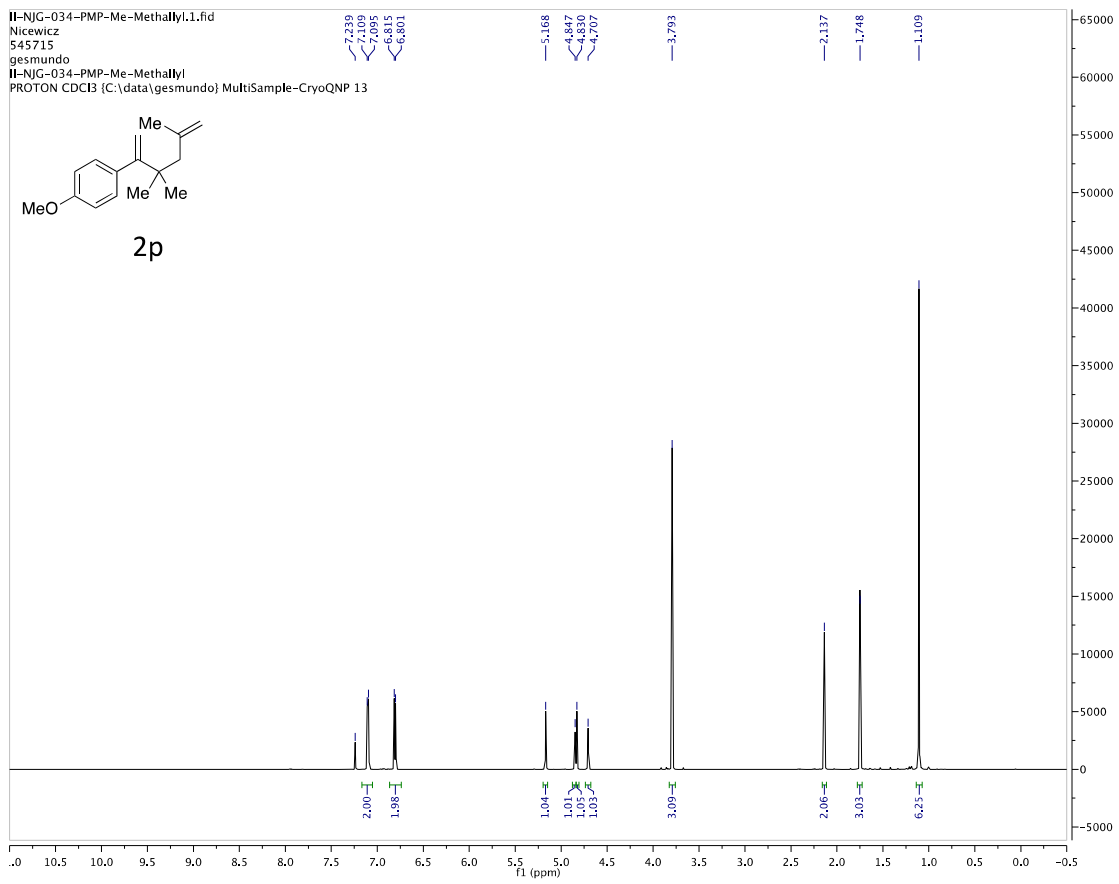


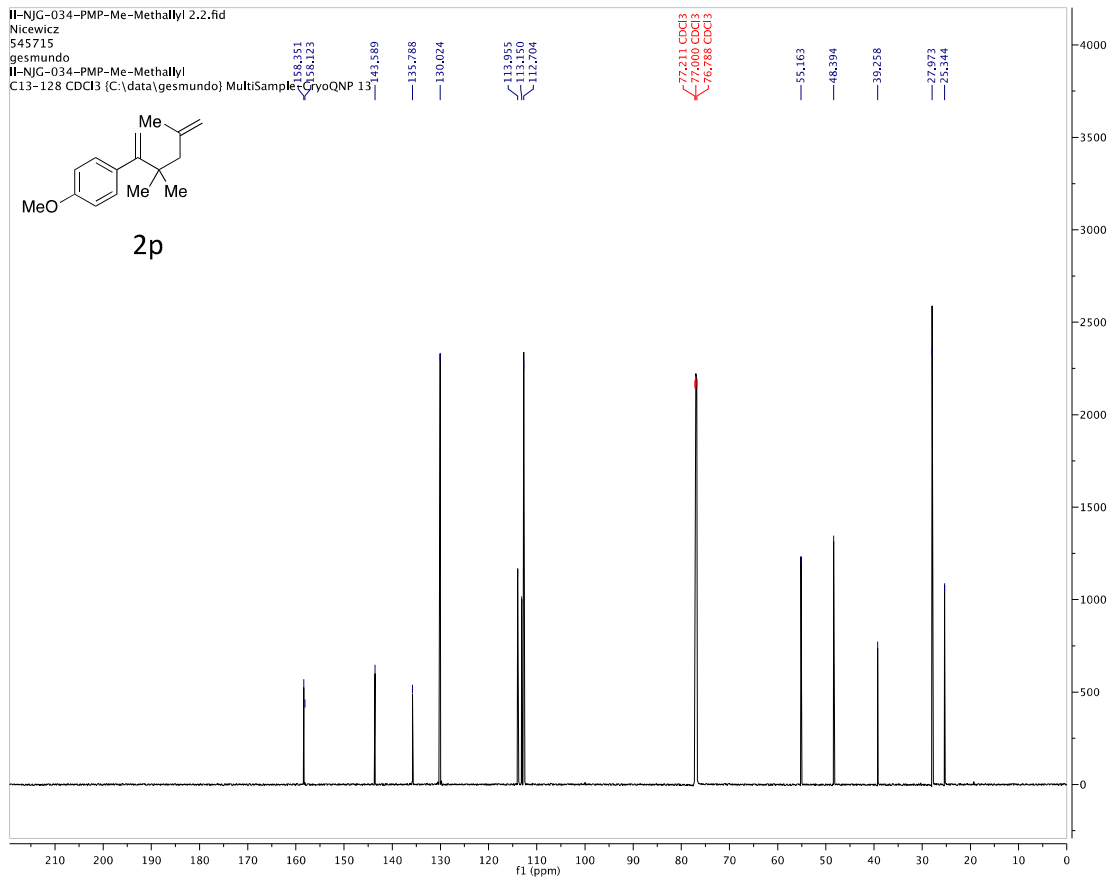
(E)-1-(3,3-Dimethylhepta-1,5-dien-2-yl)-4-methoxybenzene (2o)



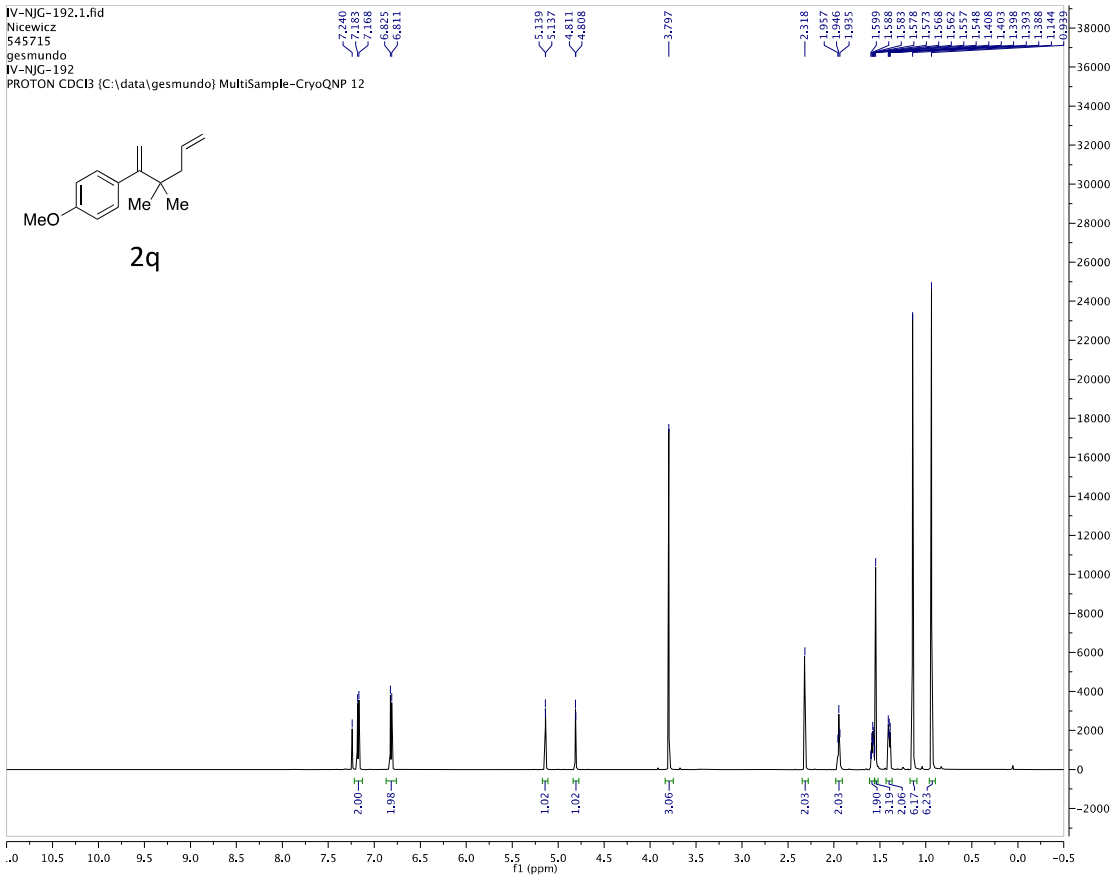


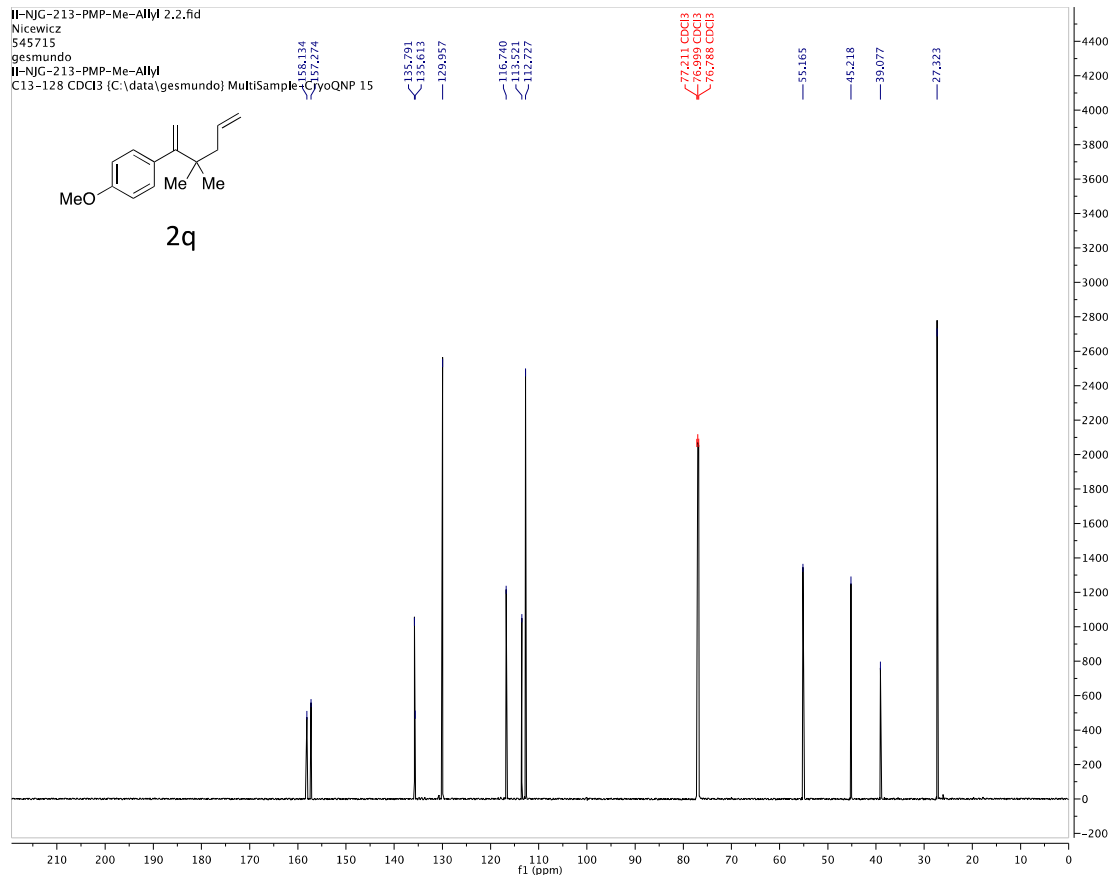
1-Methoxy-4-(3,3,5-trimethylhexa-1,5-dien-2-yl)benzene (2p)



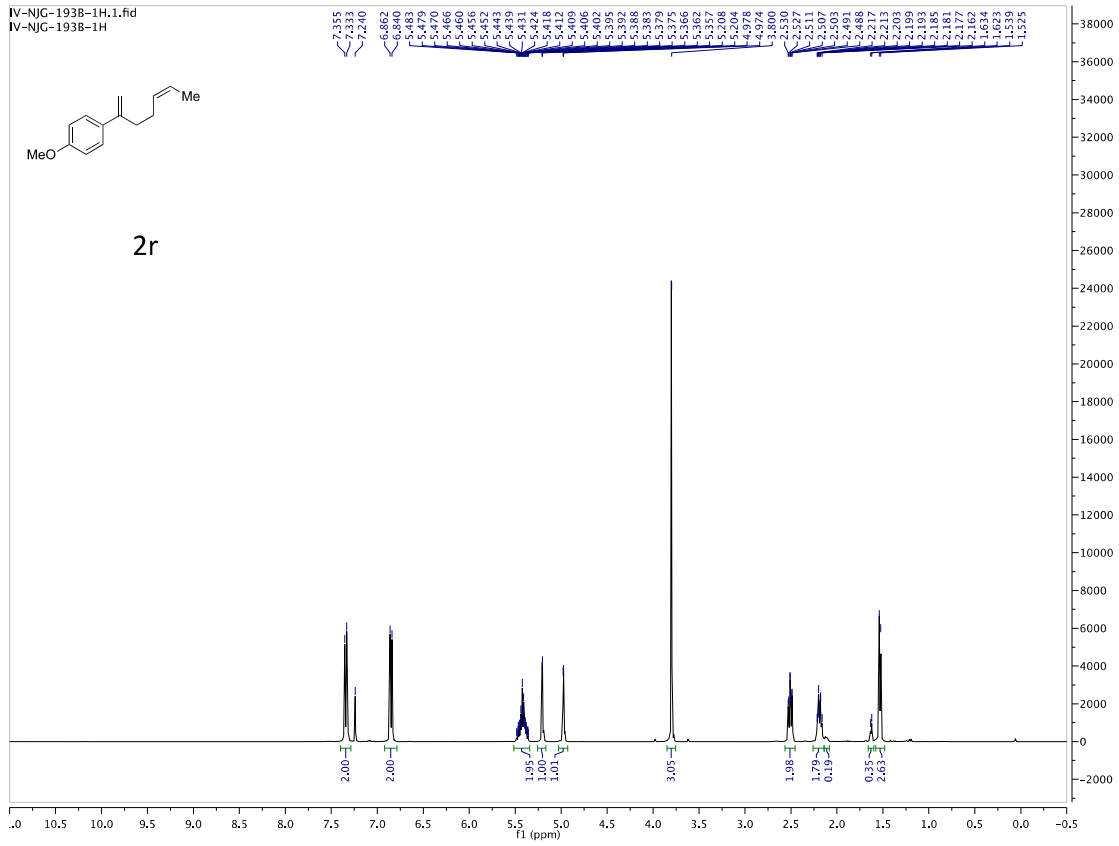


1-(3,3-Dimethylhexa-1,5-dien-2-yl)-4-methoxybenzene (2q)

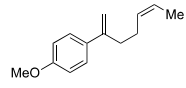




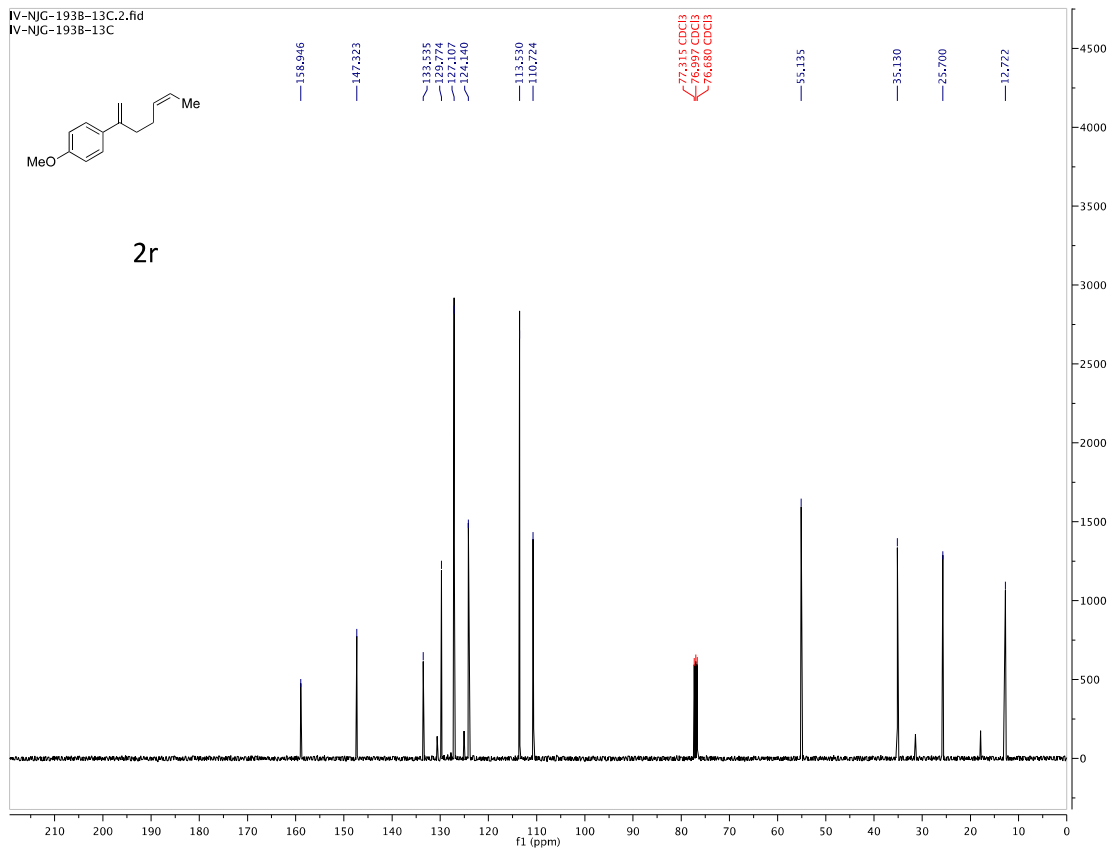
(Z)-1-(Hepta-1,5-dien-2-yl)-4-methoxybenzene (2r)



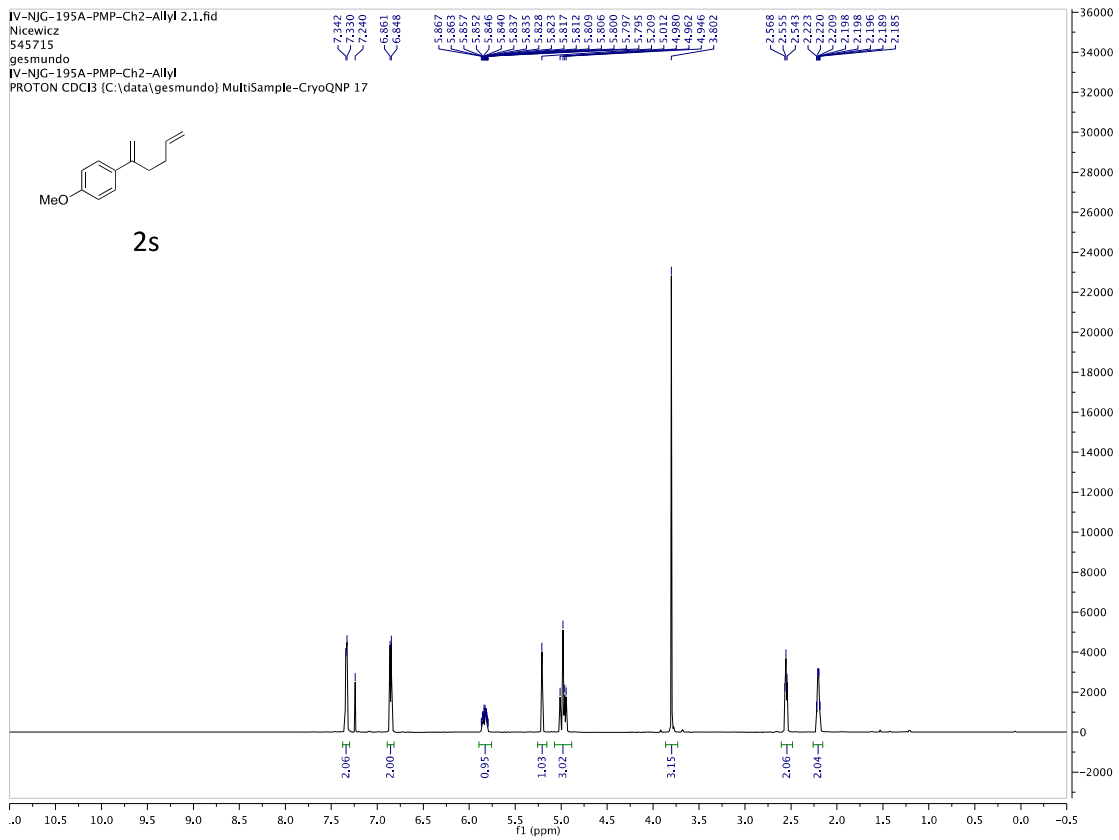
IV-NJC-193B-13C.2.fid
IV-NJC-193B-13C



2r



1-(Hexa-1,5-dien-2-yl)-4-methoxybenzene (2s)



IV-NJG-195A-PMP-Ch2-Allyl.2.fid

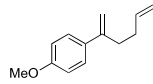
Nicewicz

545715

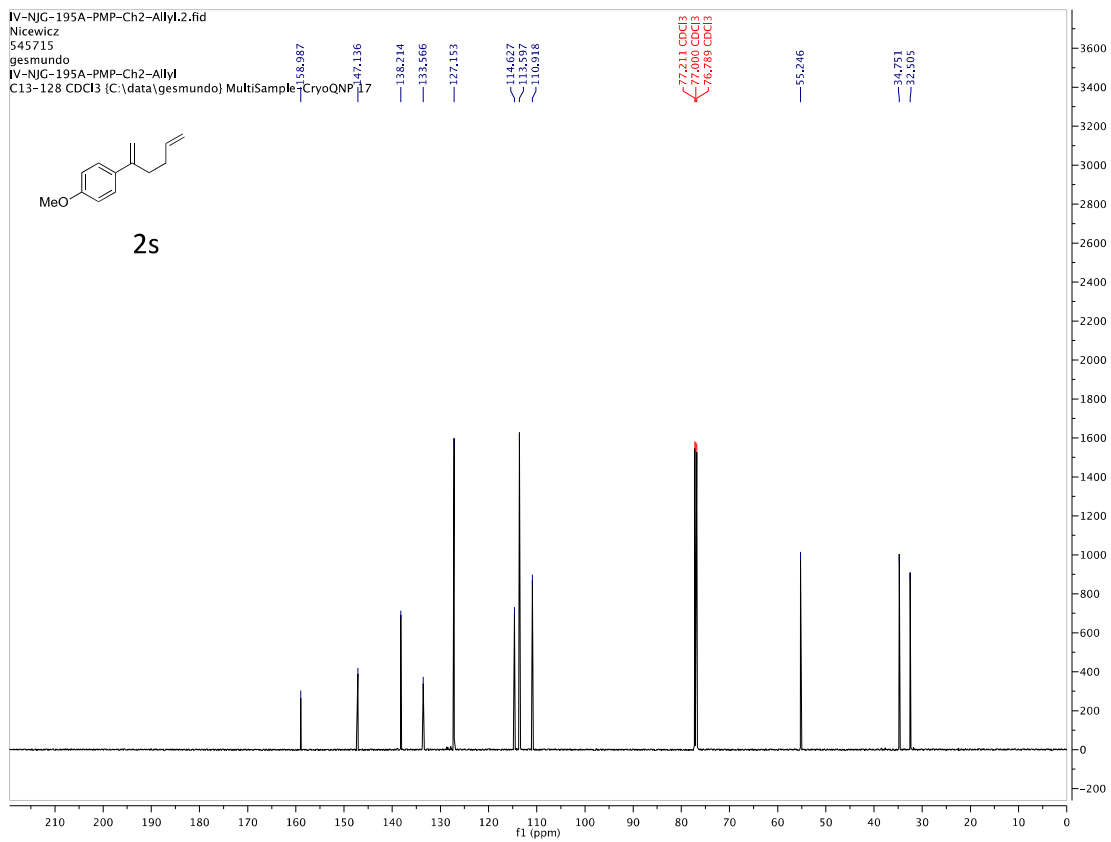
gesmundo

IV-NJG-195A-PMP-Ch2-Allyl

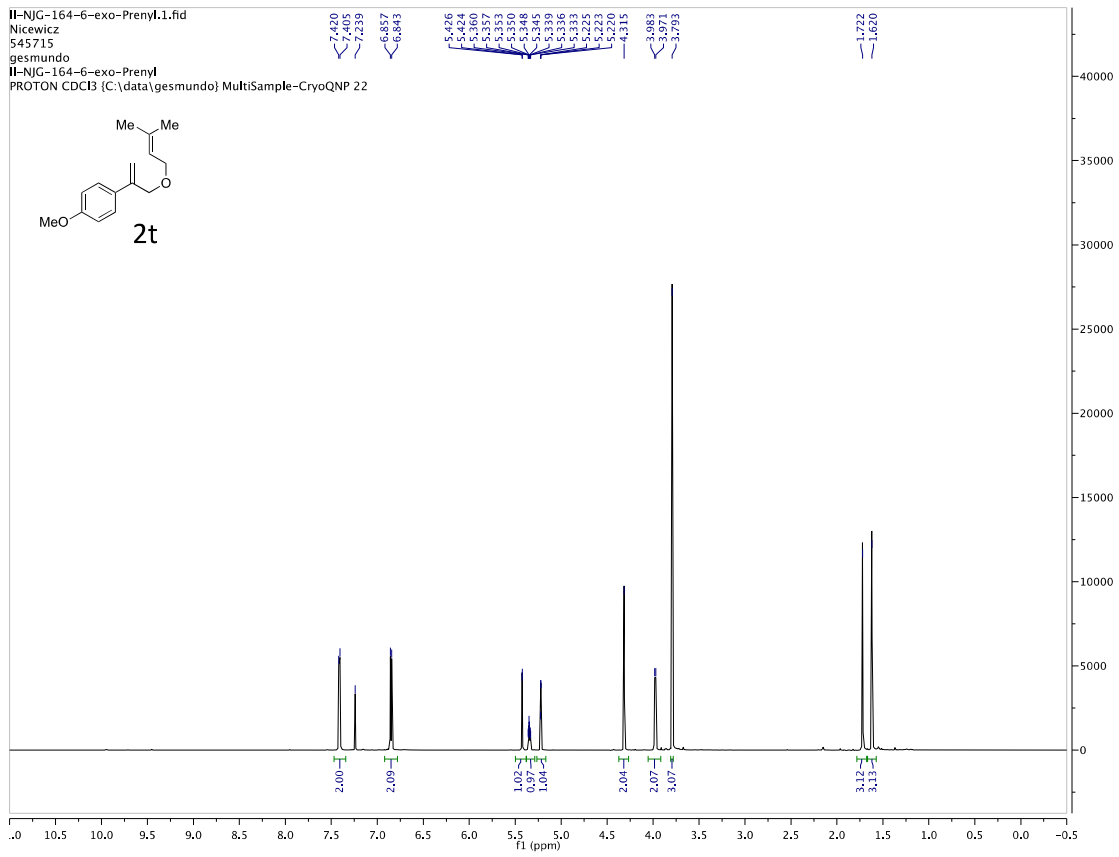
C13-128 CDCl3 (C:\data\gesmundo) MultiSample-CryoQNP 1.7

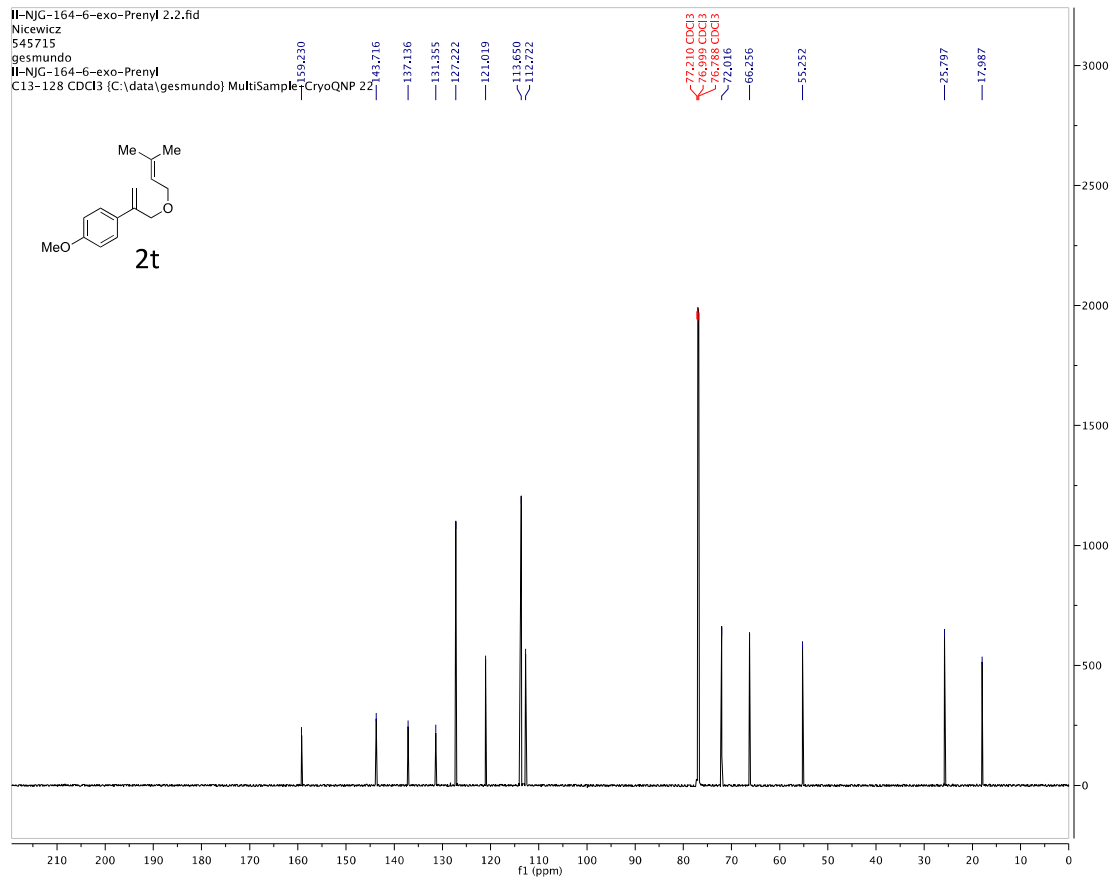


2s

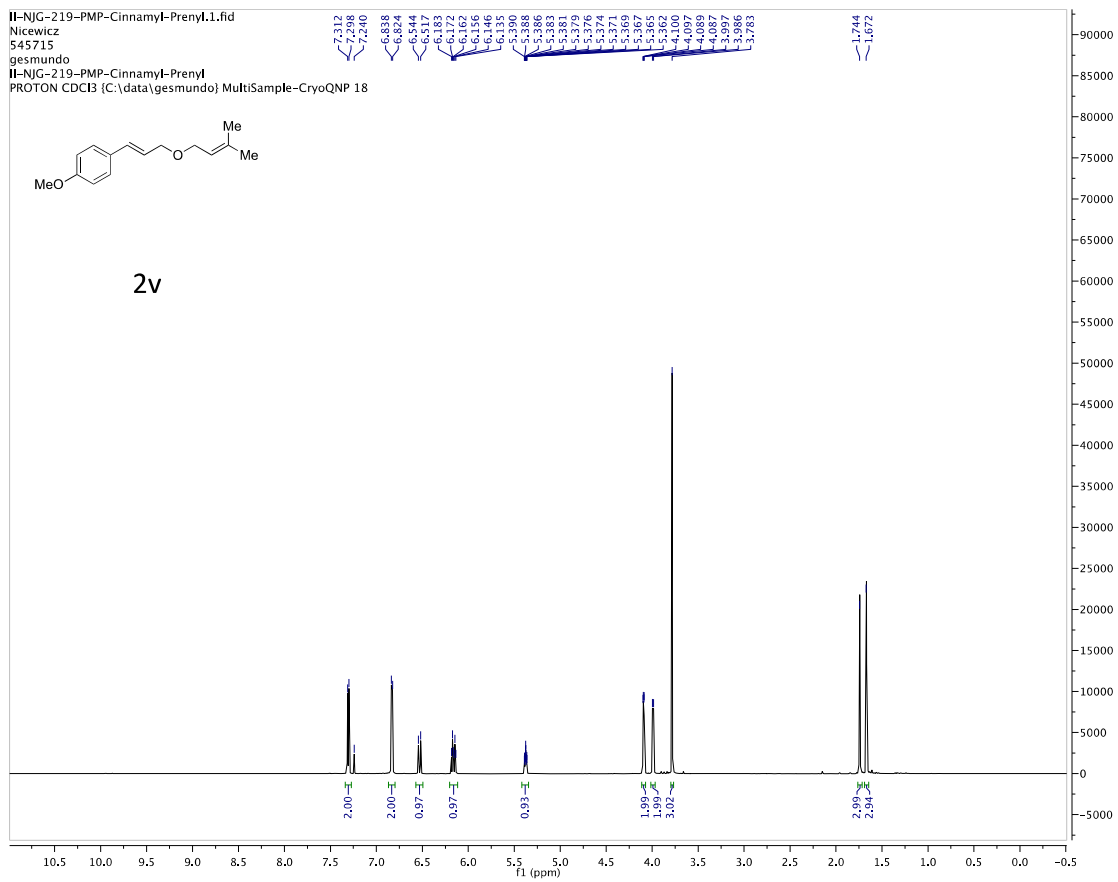


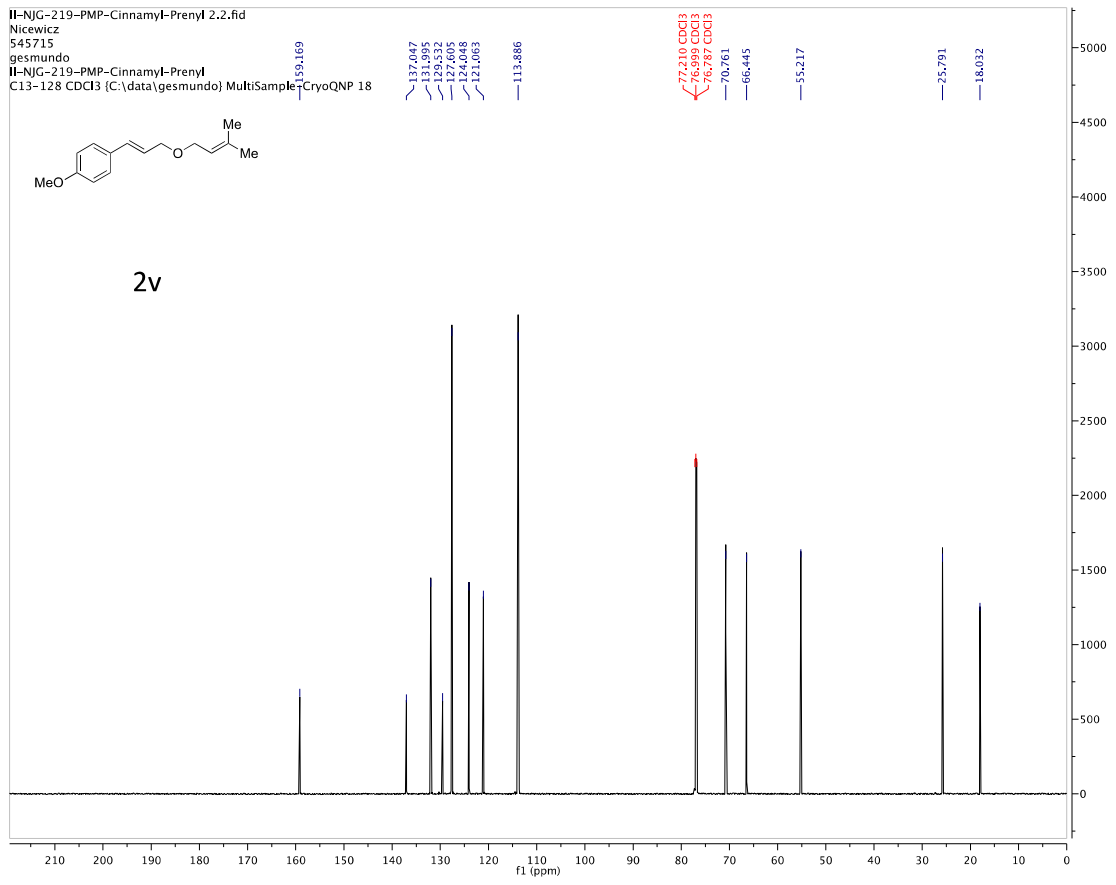
1-Methoxy-4-(3-((3-methylbut-2-en-1-yl)oxy)prop-1-en-2-yl)benzene (2t)



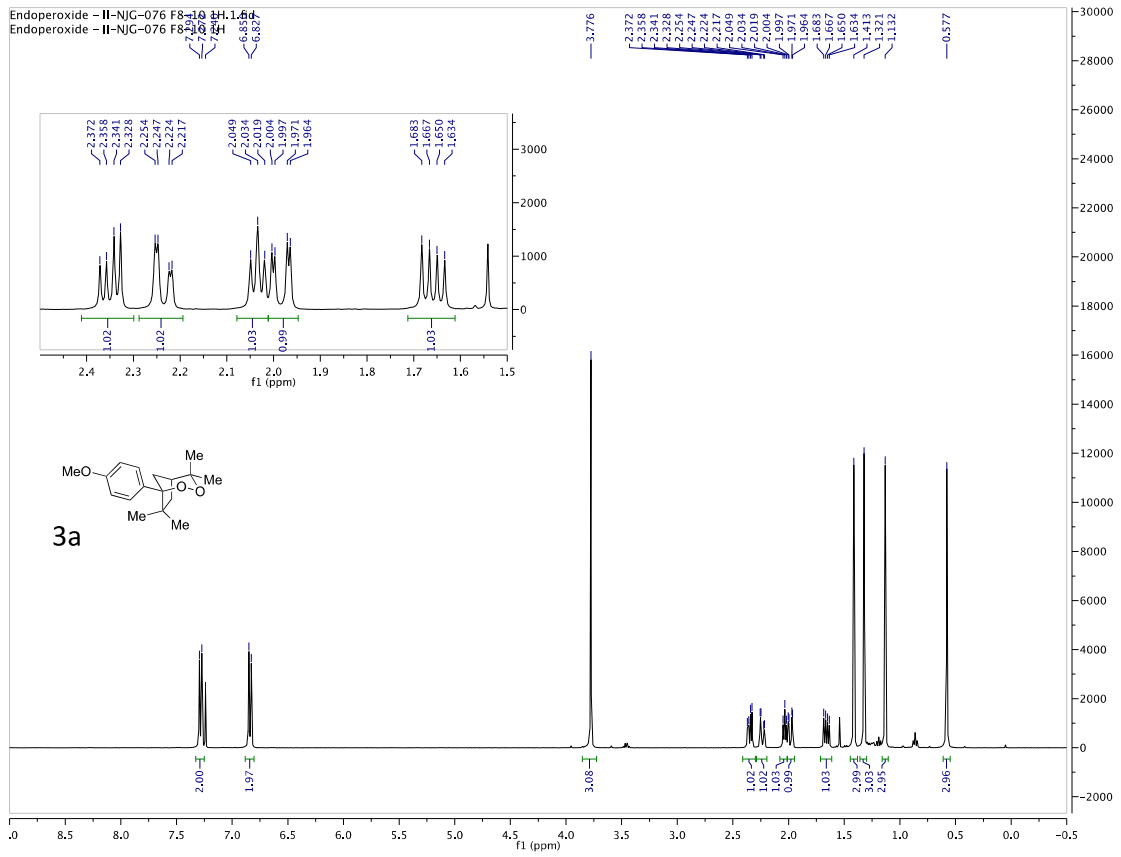


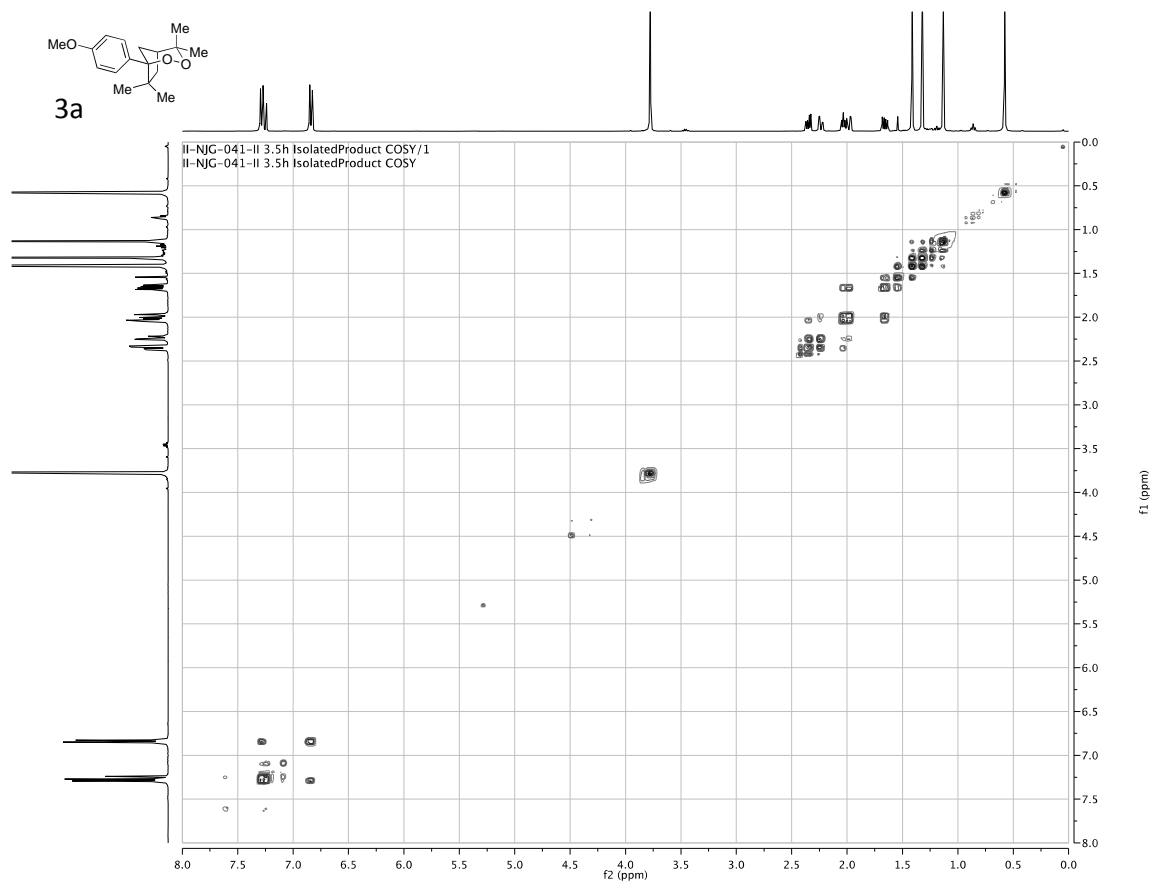
(E)-1-Methoxy-4-(3-((3-methylbut-2-en-1-yl)oxy)prop-1-en-1-yl)benzene (2v)

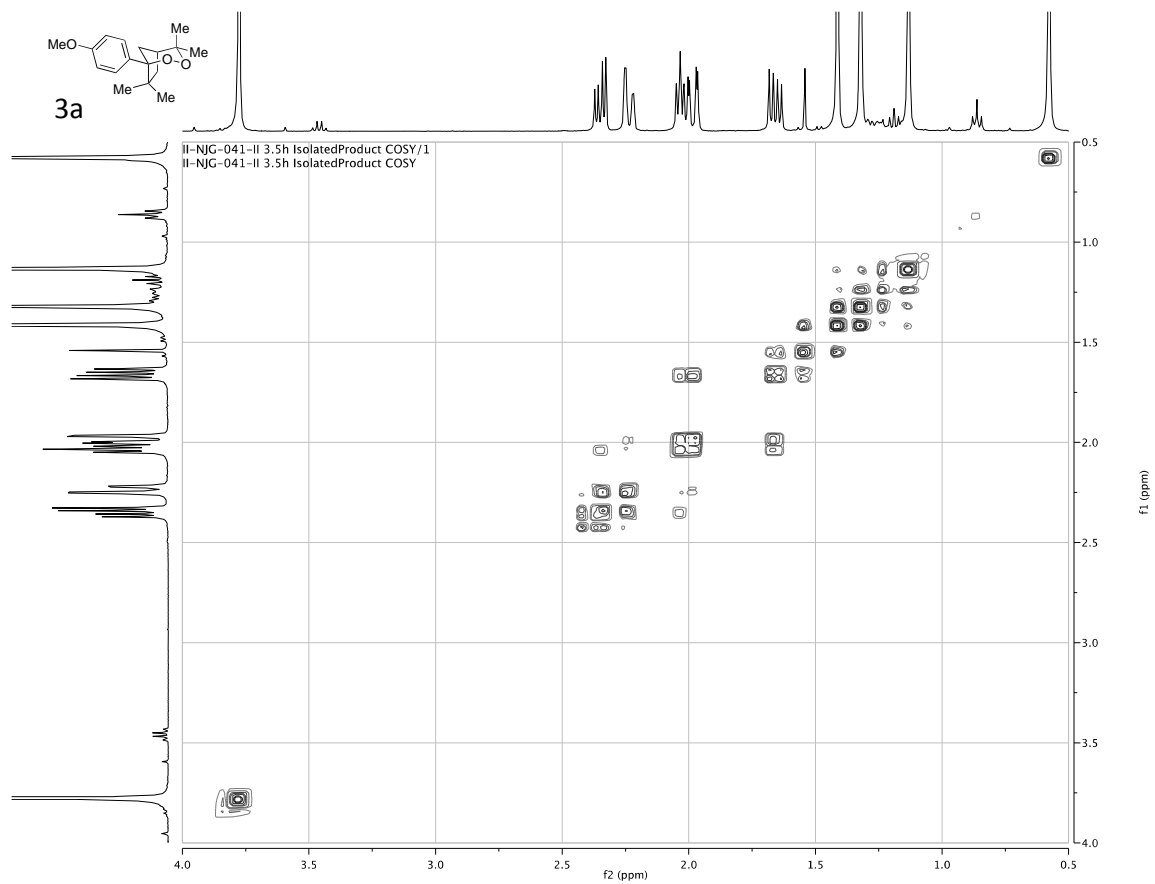




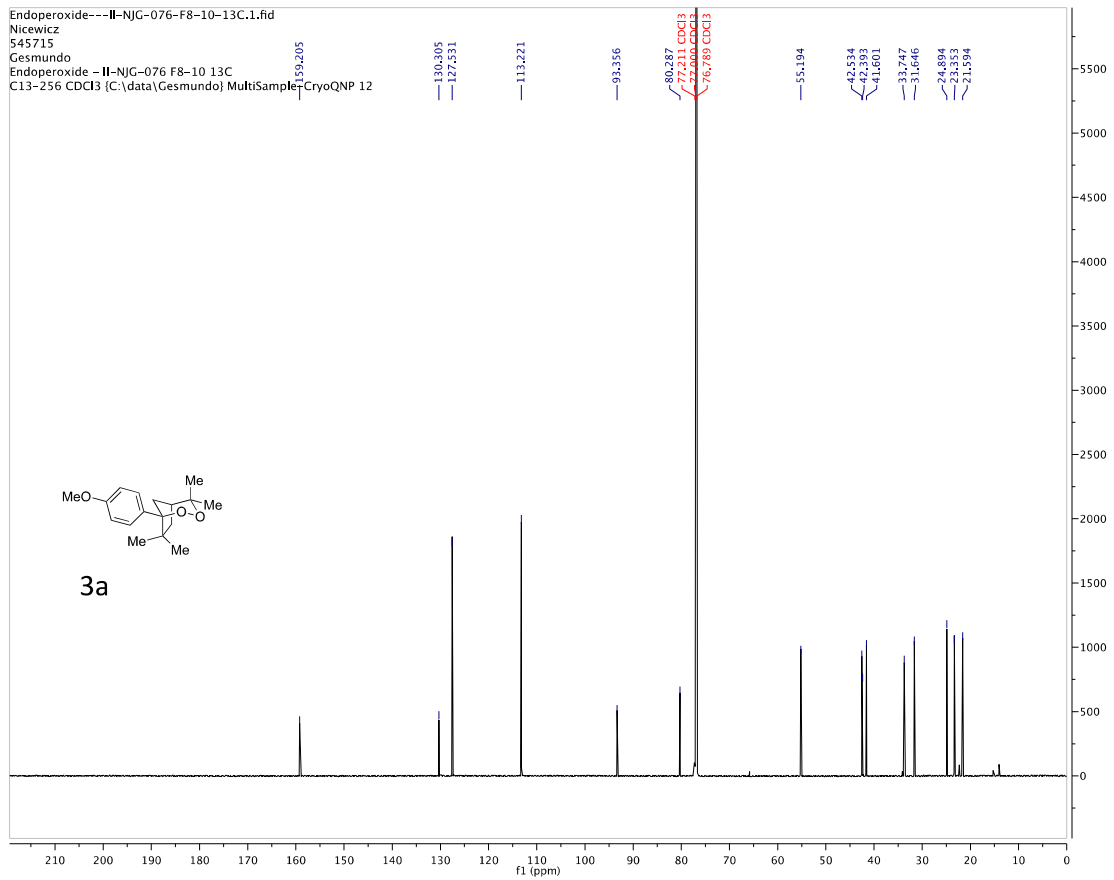
1-(4-Methoxyphenyl)-4,4,7,7-tetramethyl-2,3-dioxabicyclo[3.2.1]octane (3a)



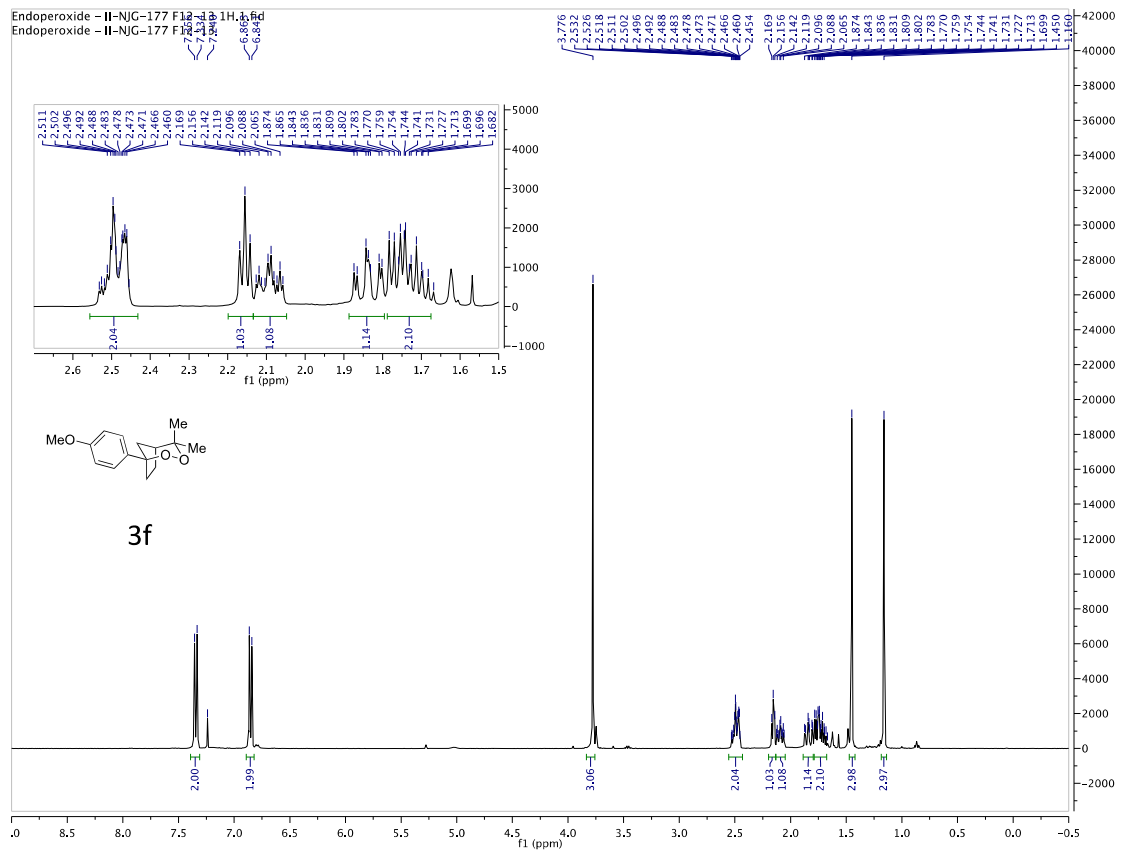


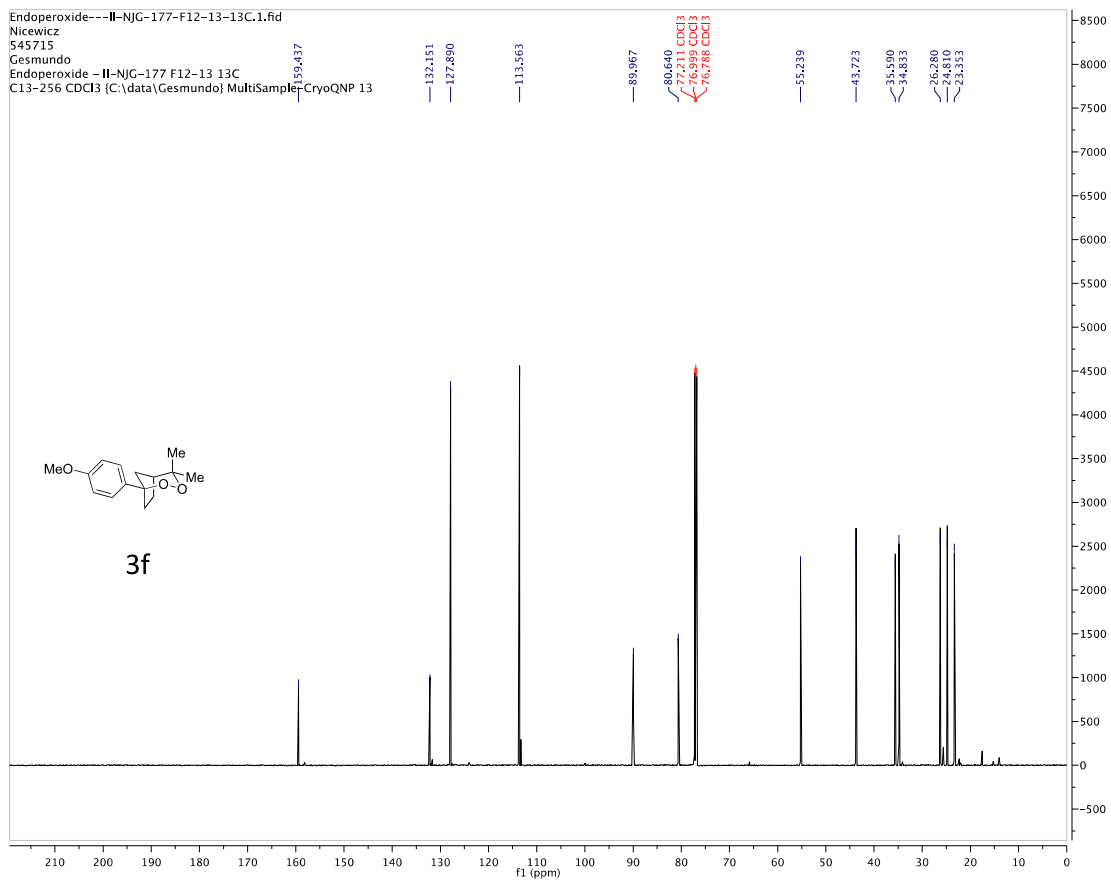


Endoperoxide---II-NJG-076-F8-10-13C.1.fid
545715
Nicewicz
Gesmundo
Endoperoxide - II-NJG-076 F8-10 13C
C13-256 CDCl3 {C:\data\Gesmundo} MultiSample CryoQNP 12

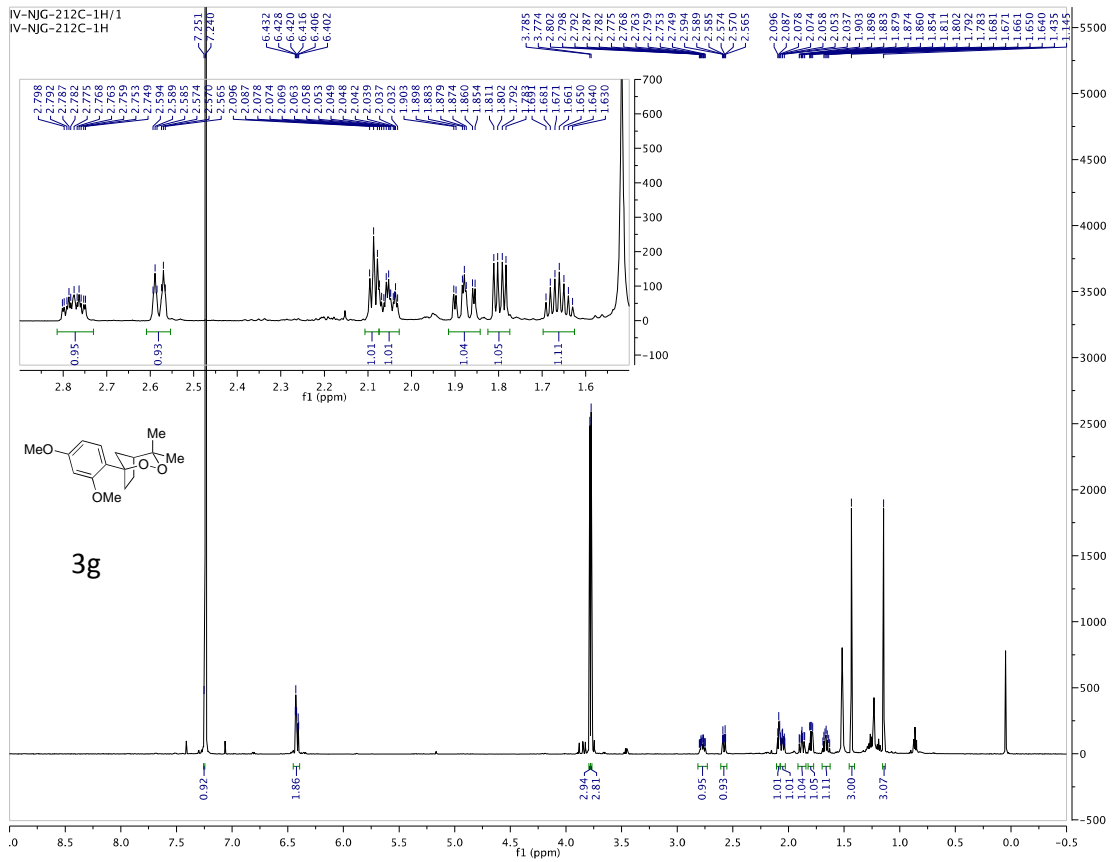


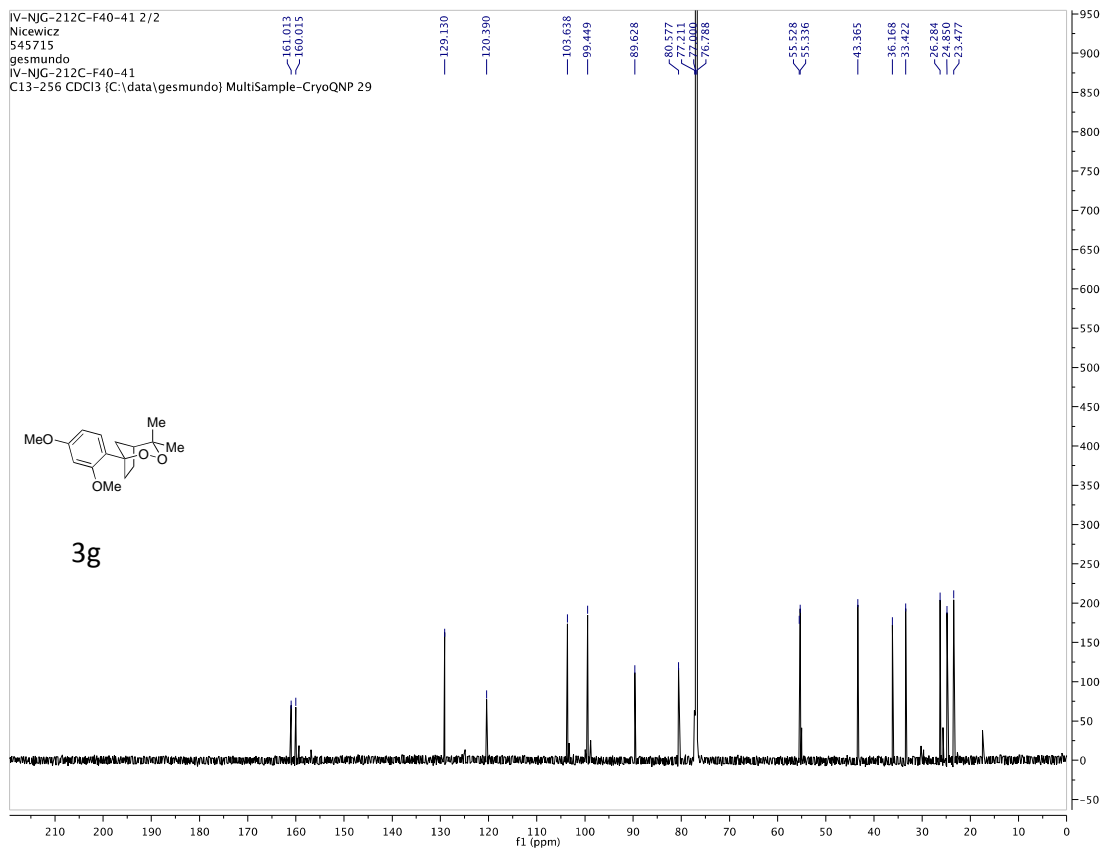
1-(4-Methoxyphenyl)-4,4-dimethyl-2,3-dioxabicyclo[3.2.1]octane (3f)

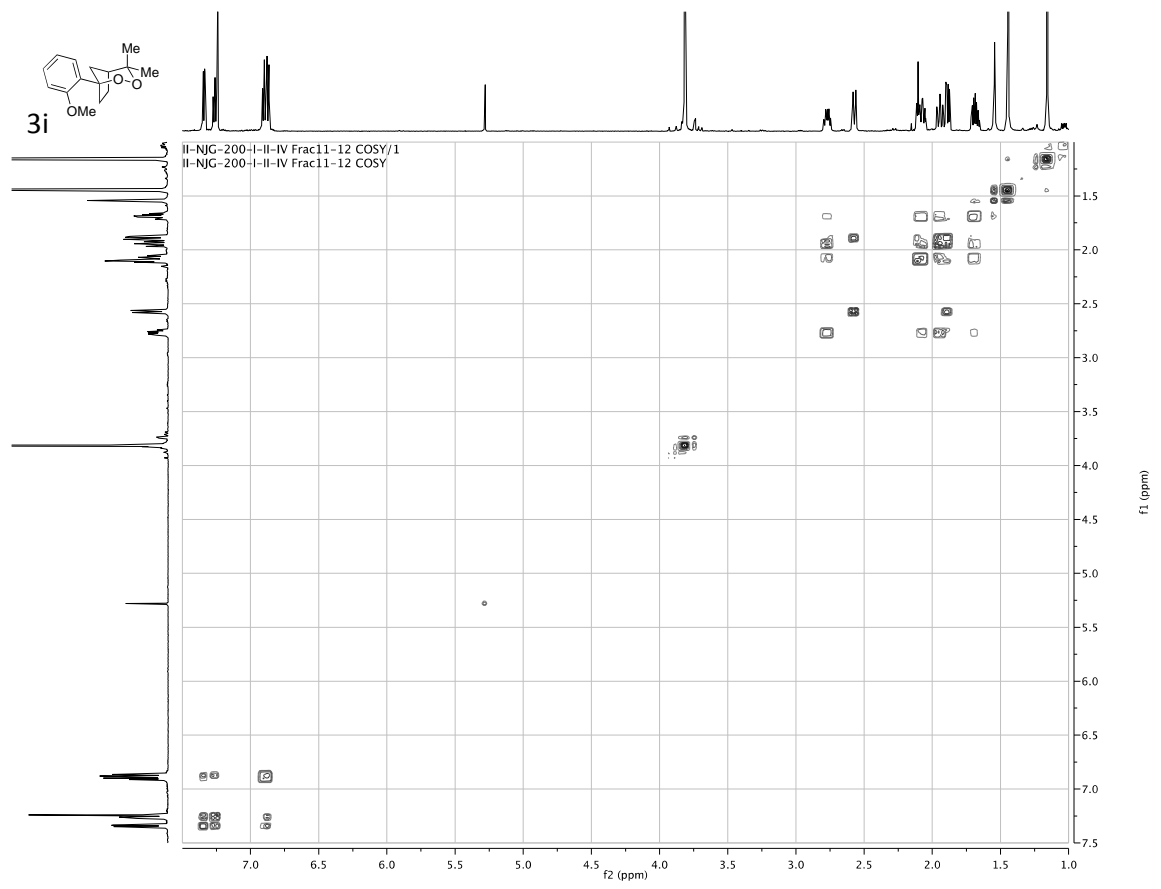
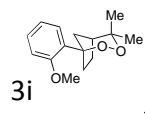




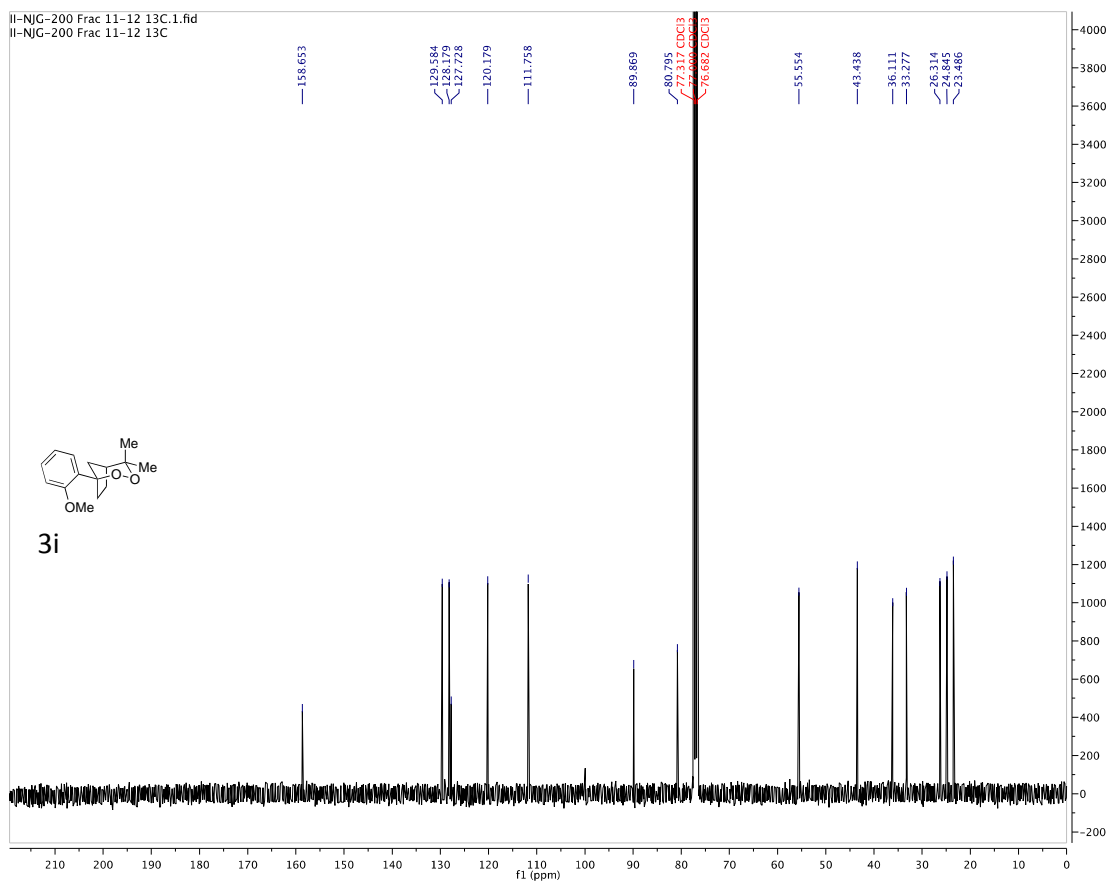
1-(2,4-Dimethoxyphenyl)-4,4-dimethyl-2,3-dioxabicyclo[3.2.1]octane (3g)



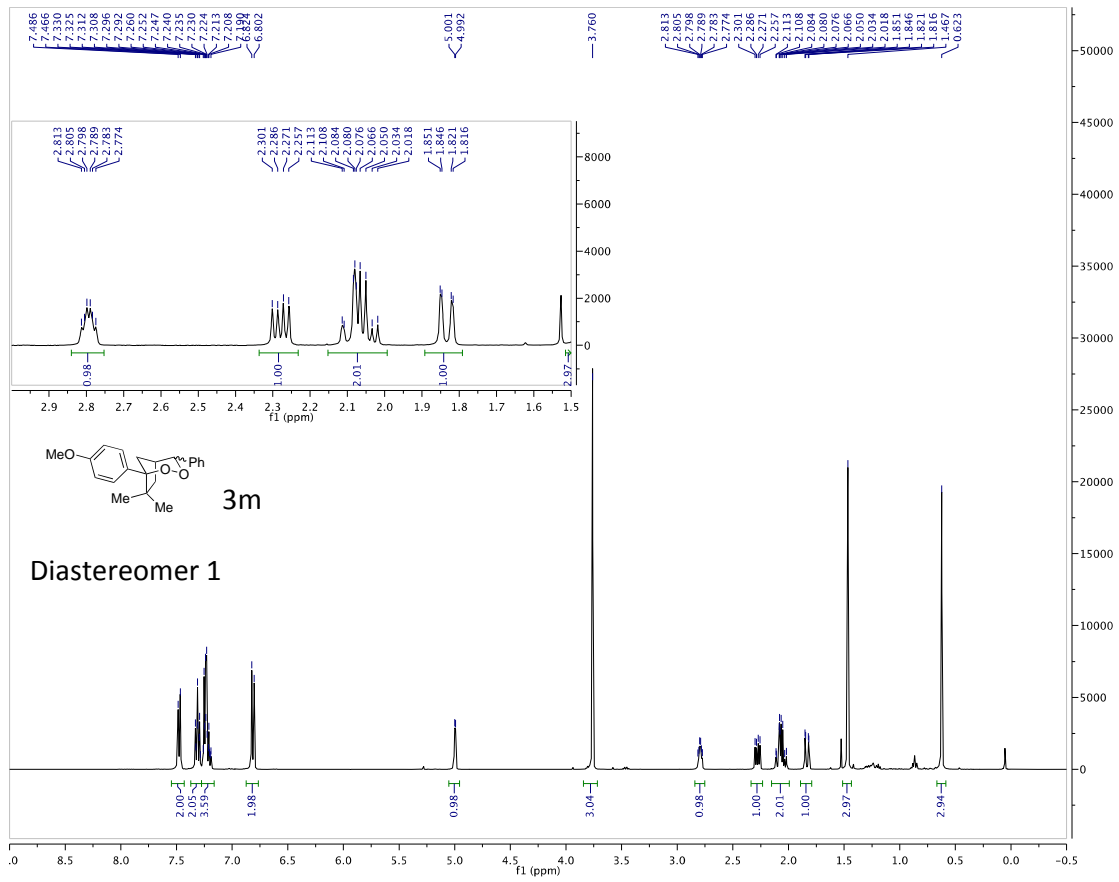


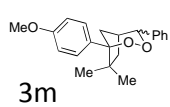


II-NJG-200 Frac 11-12 13C.1.fid
II-NJG-200 Frac 11-12 13C

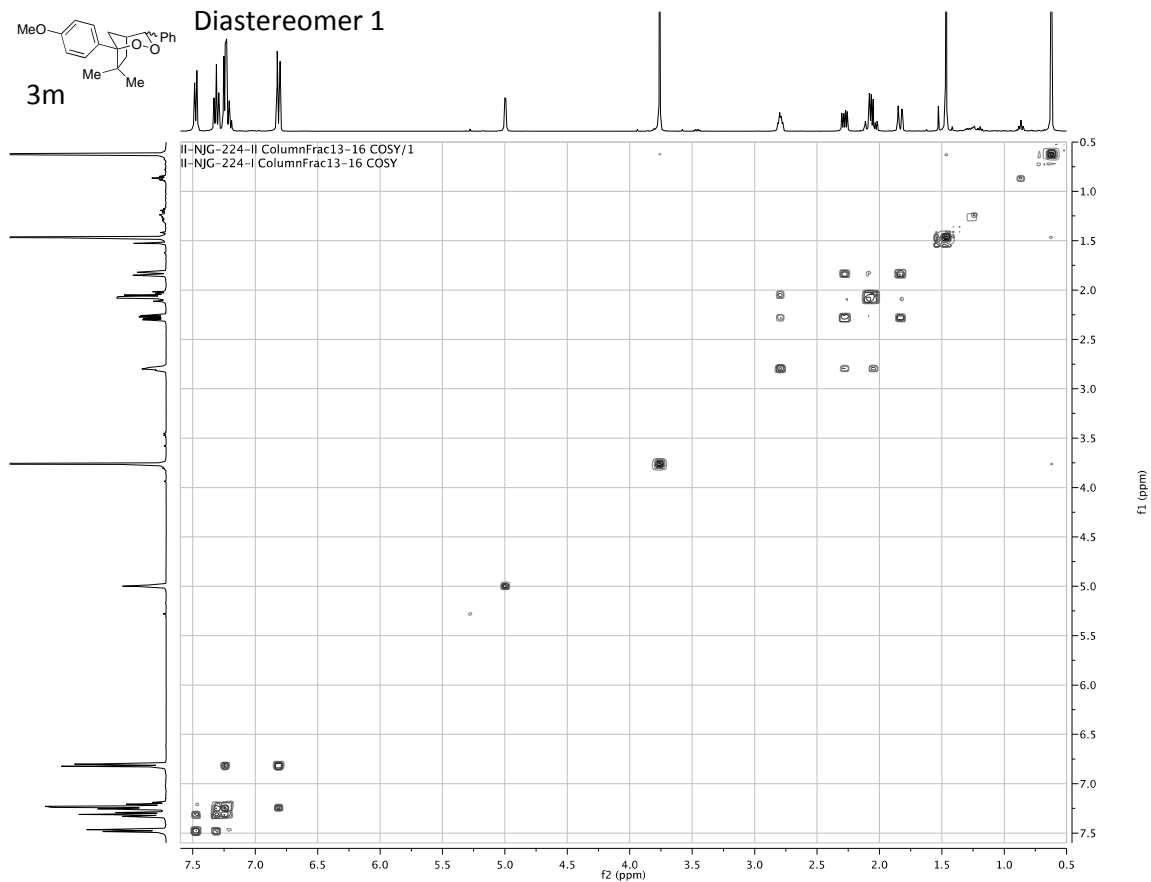


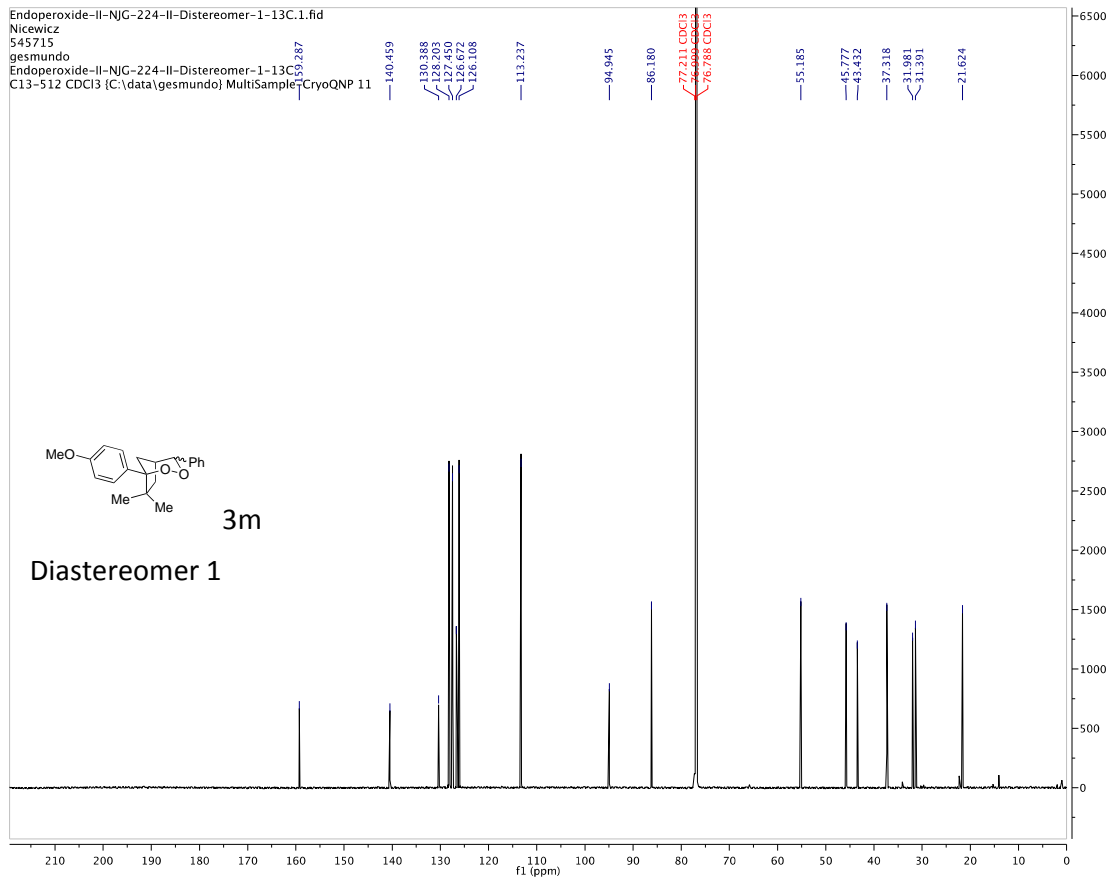
1-(4-Methoxyphenyl)-7,7-dimethyl-4-phenyl-2,3-dioxabicyclo[3.2.1]octane (3m)

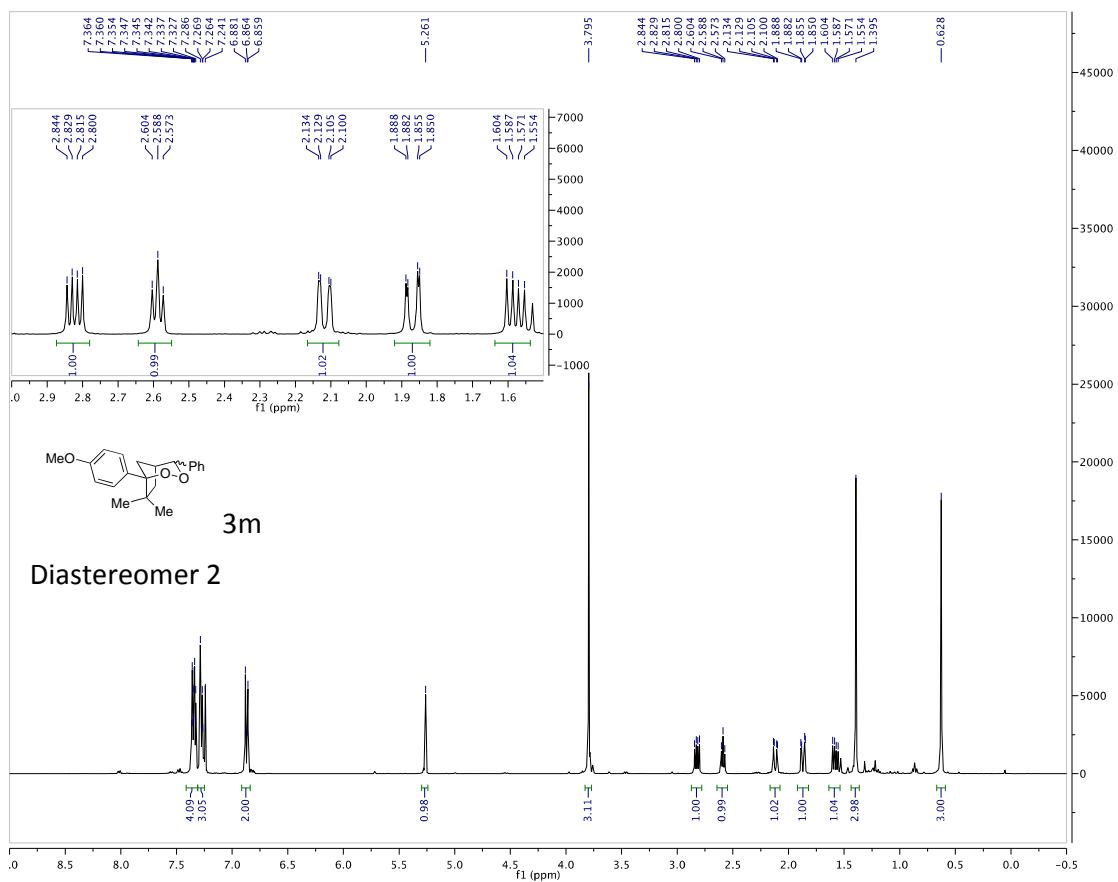


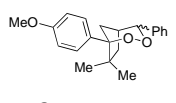


Diastereomer 1



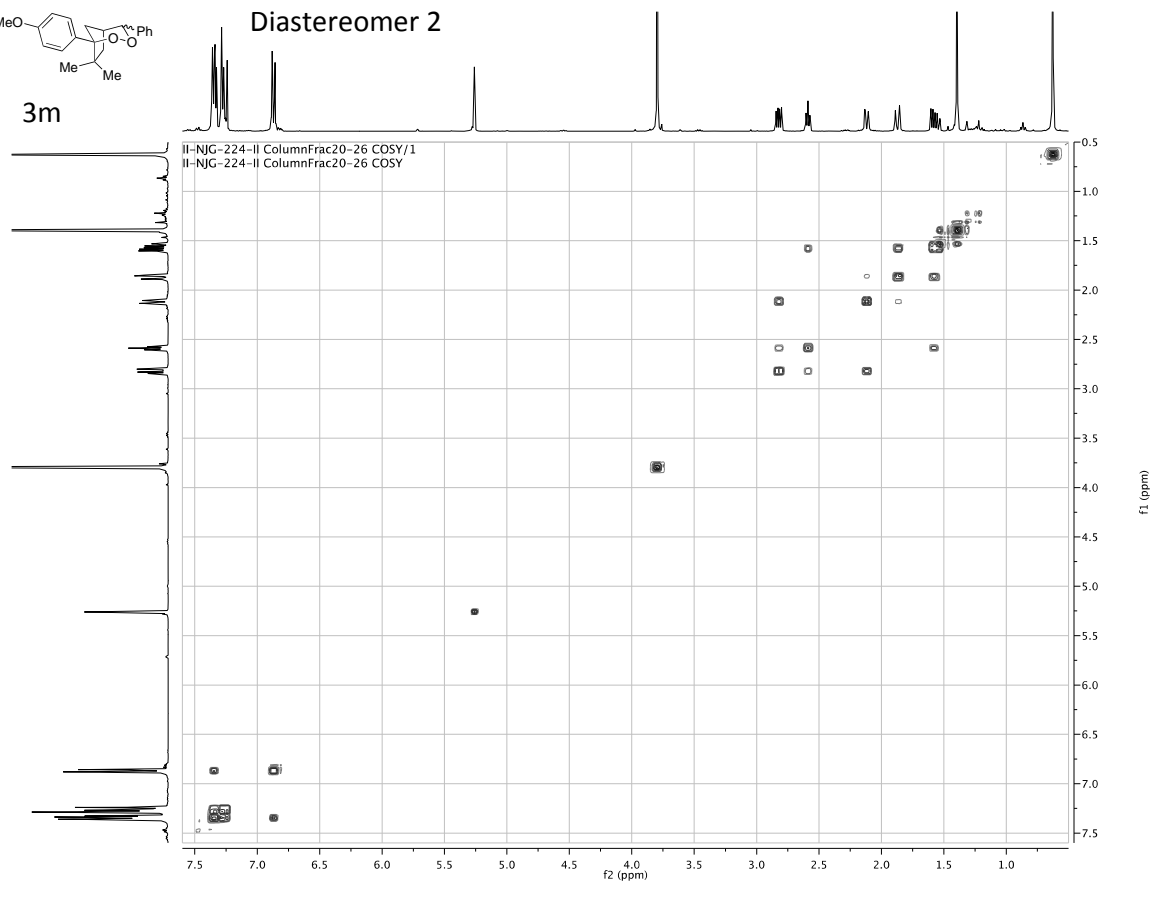


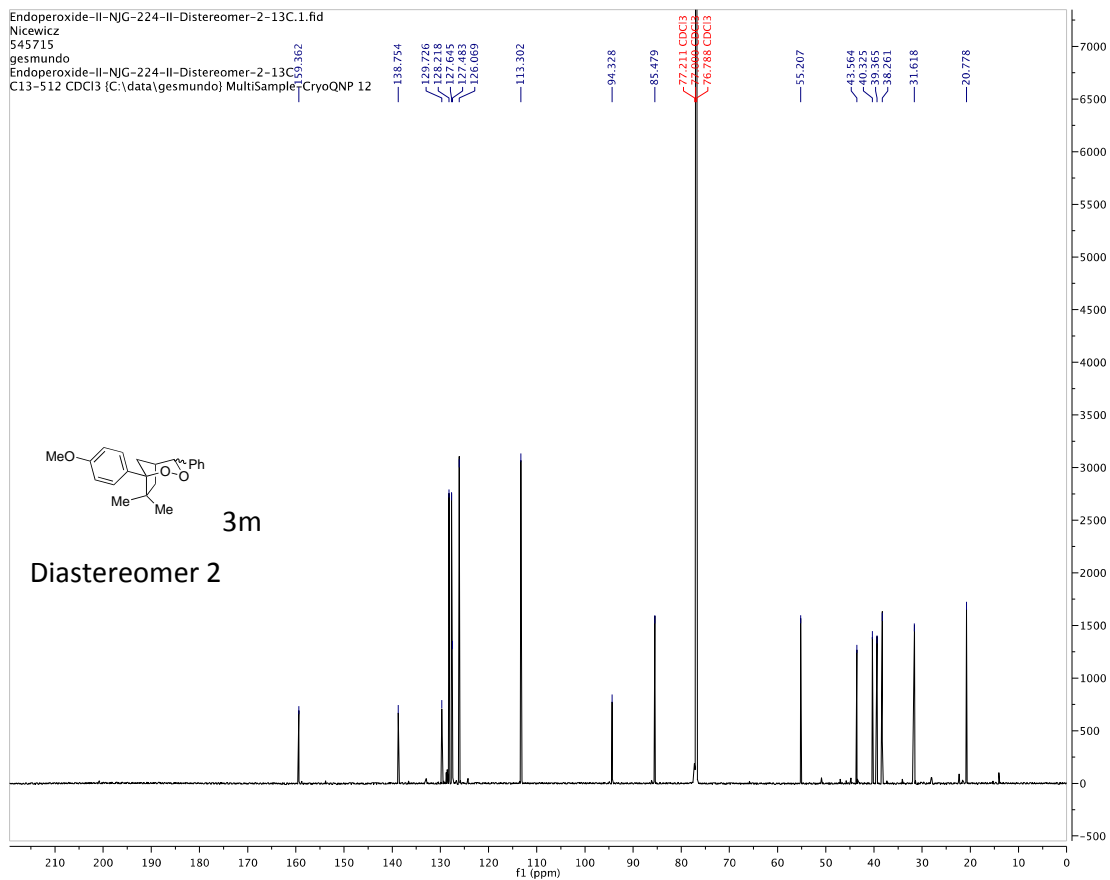




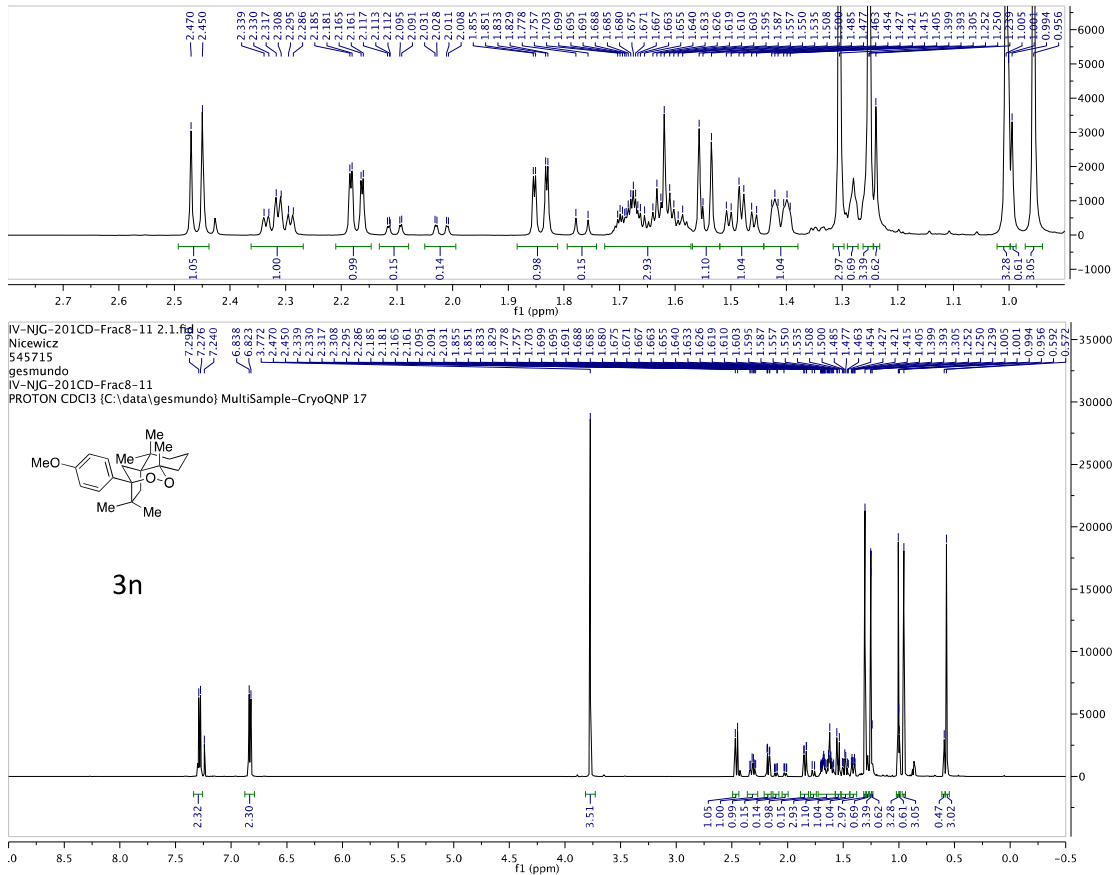
3m

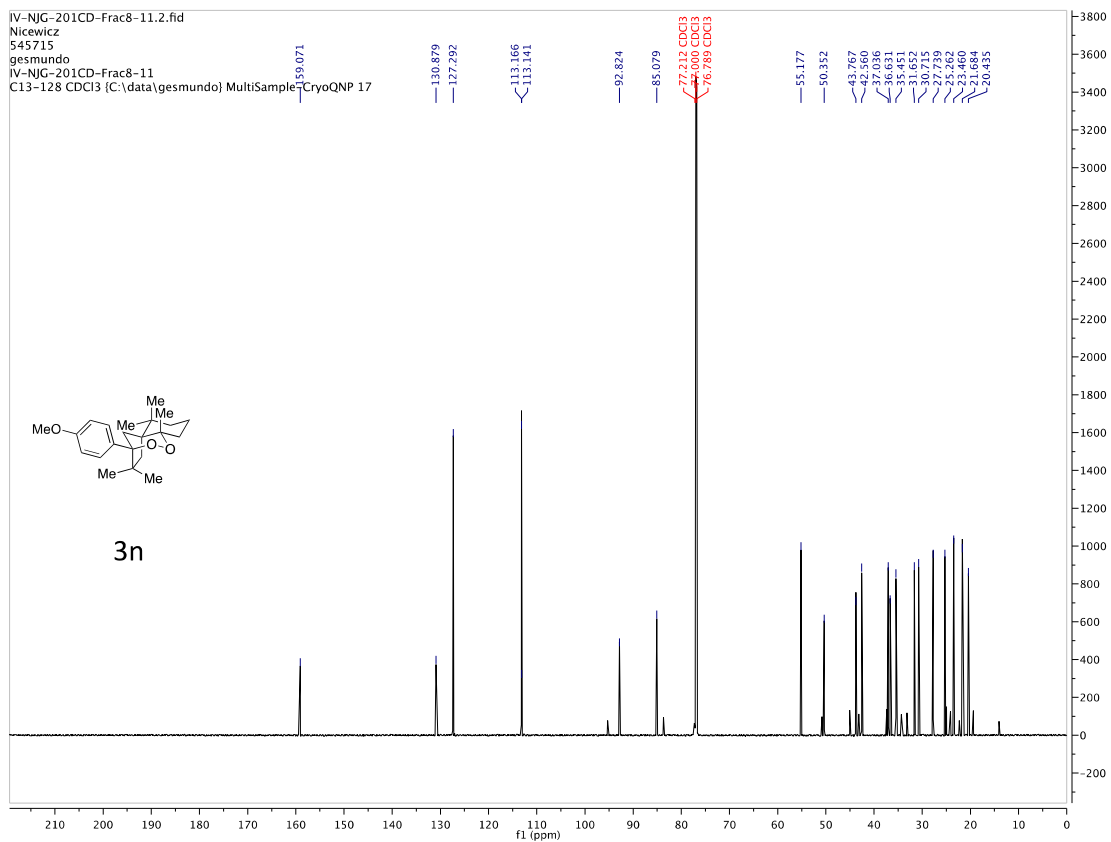
Diastereomer 2



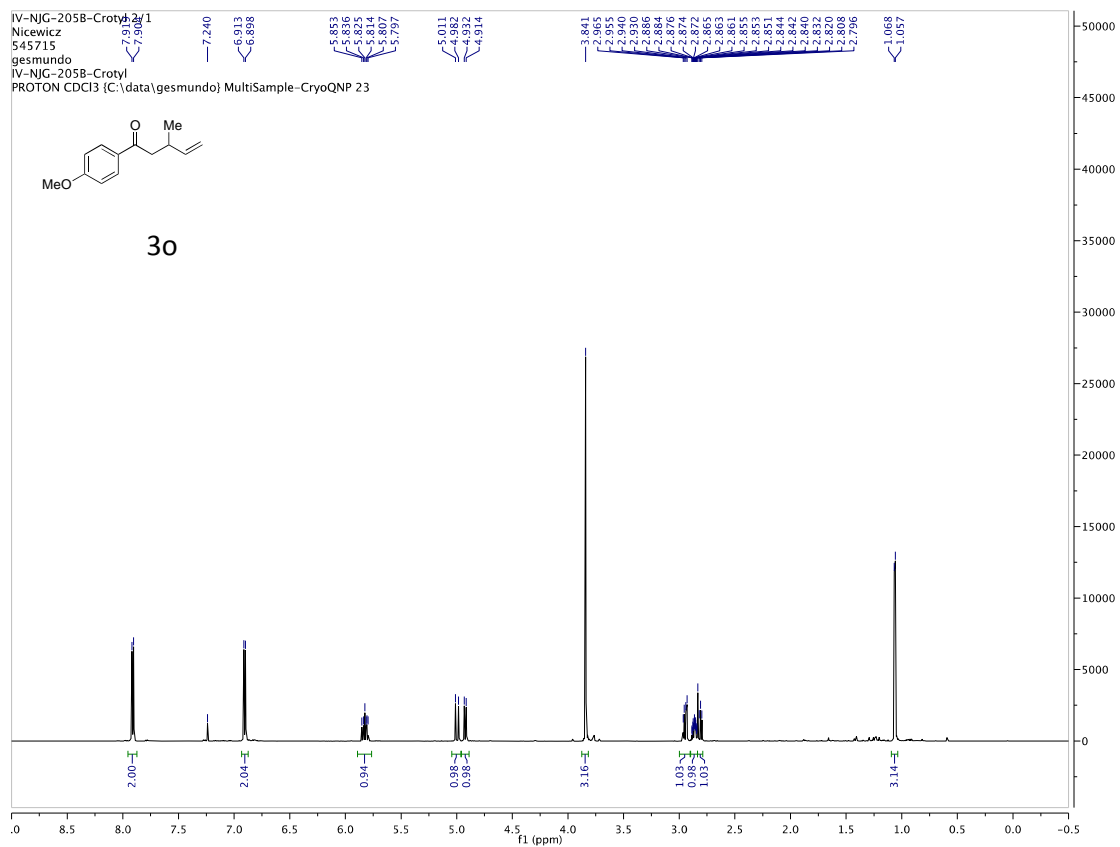


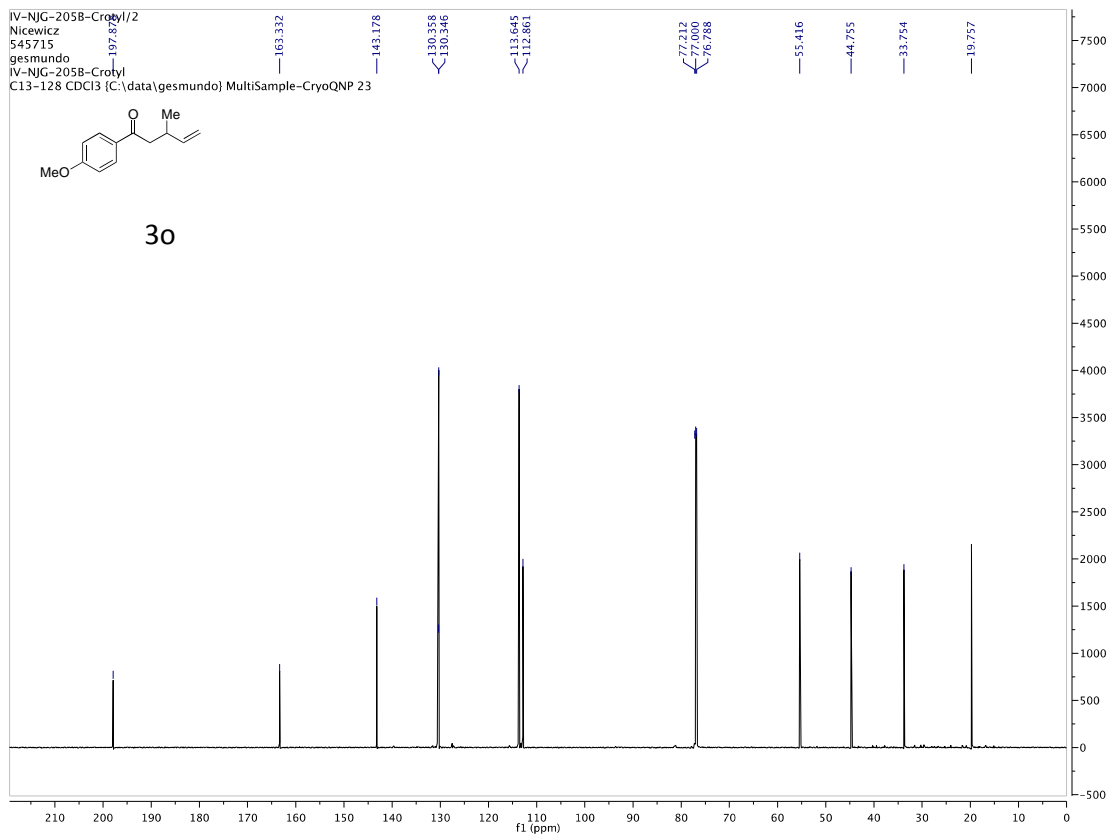
3-(4-Methoxyphenyl)-4,4,6,6,9a-pentamethylhexahydro-3H,6H-3,5a-methanobenzo[c][1,2]dioxepine (3n)



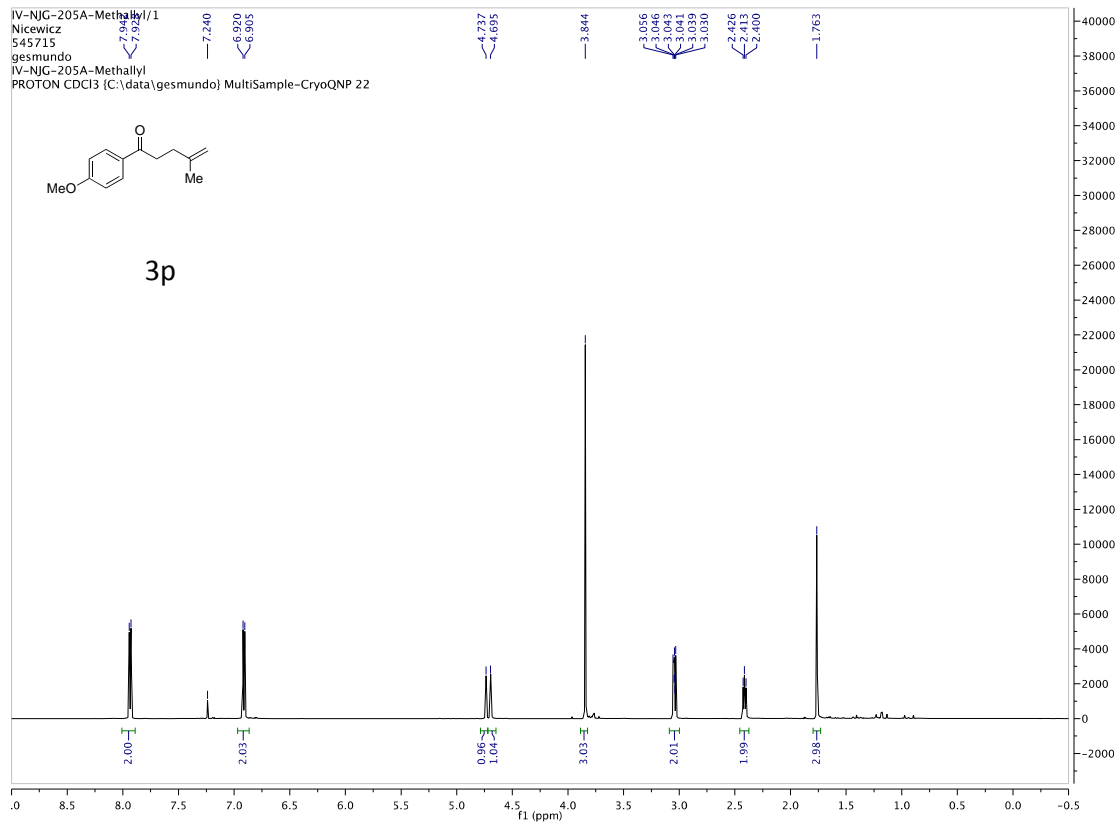


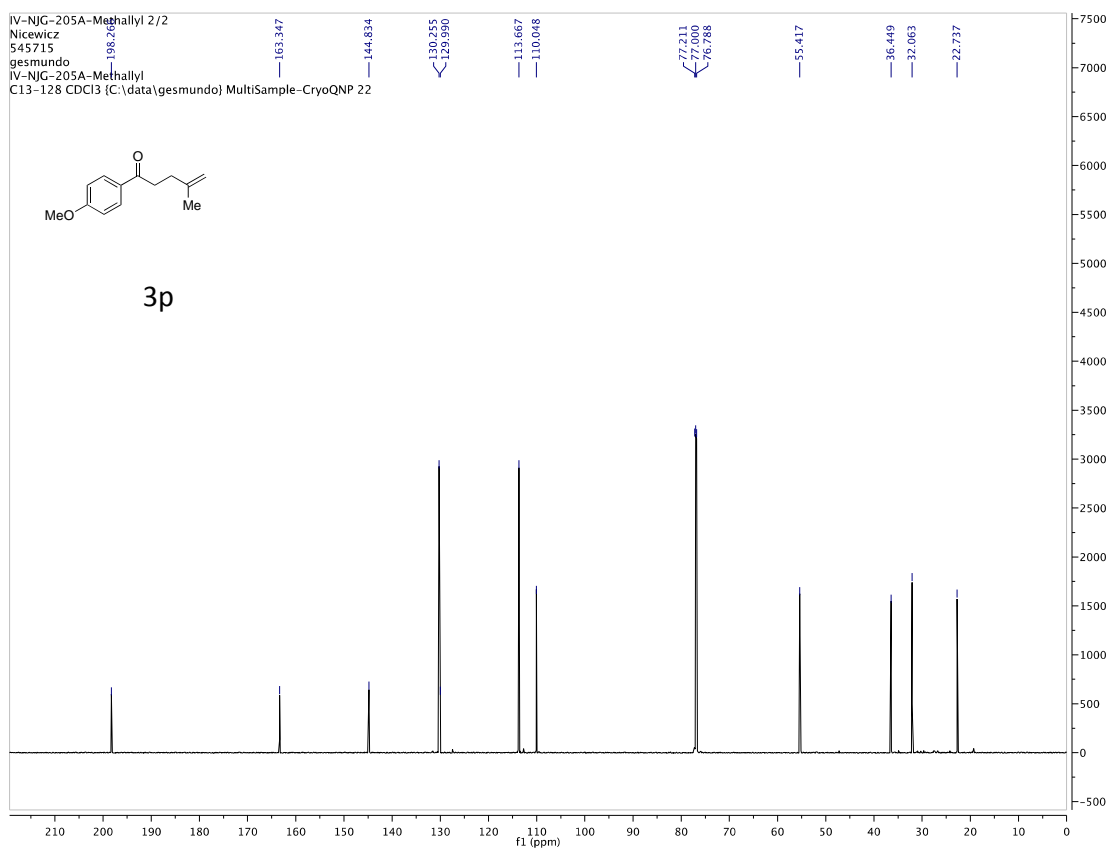
1-(4-Methoxyphenyl)-3-methylpent-4-en-1-one (30)



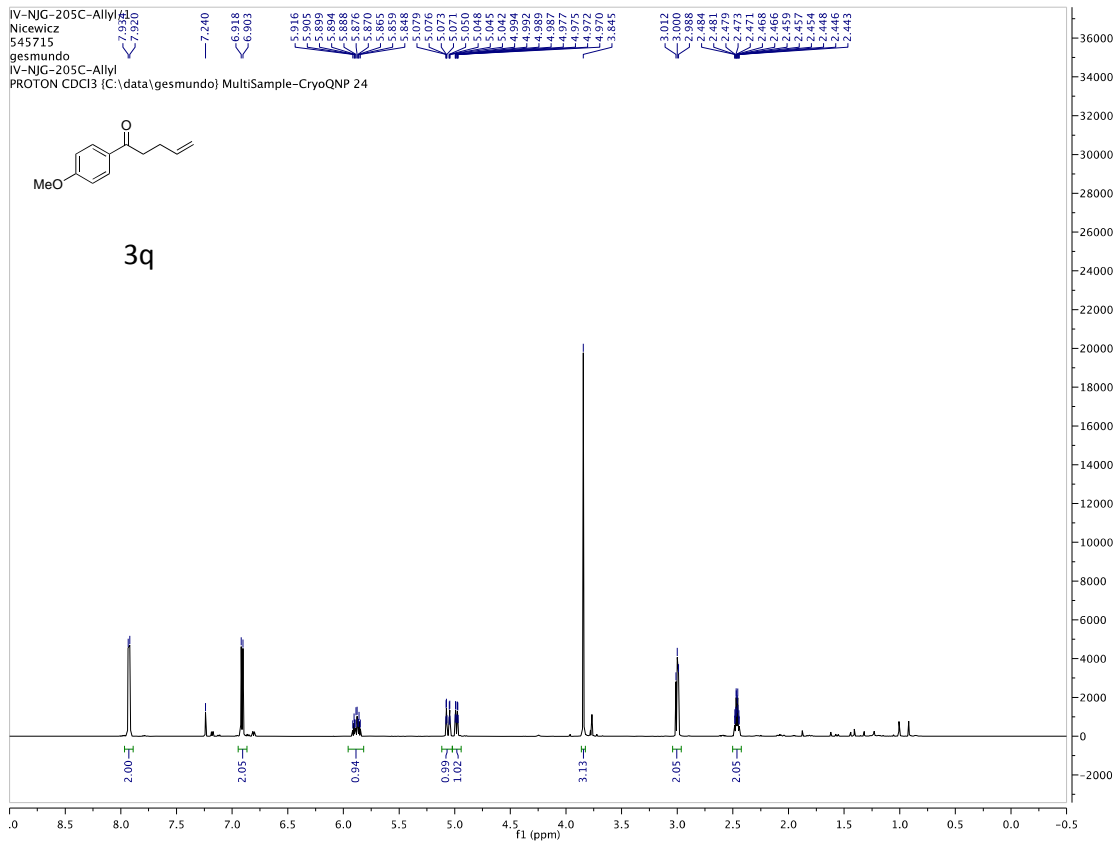


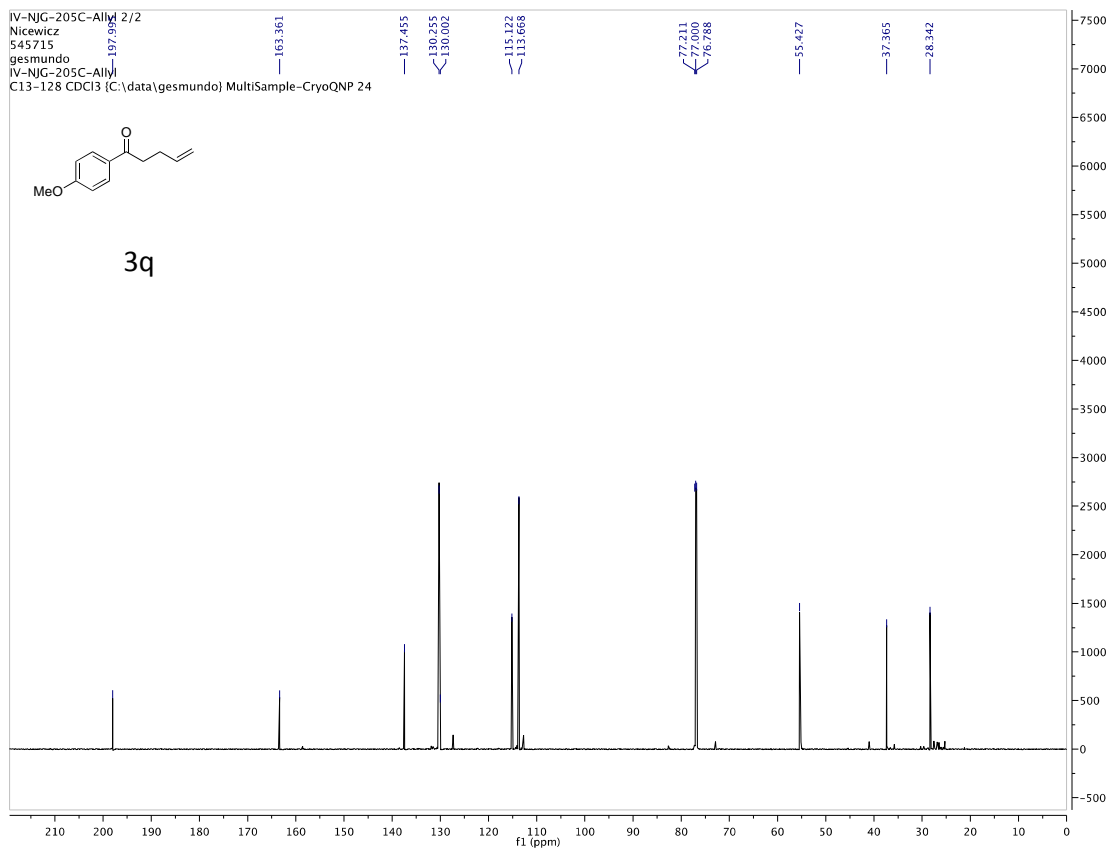
1-(4-Methoxyphenyl)-4-methylpent-4-en-1-one (3p)



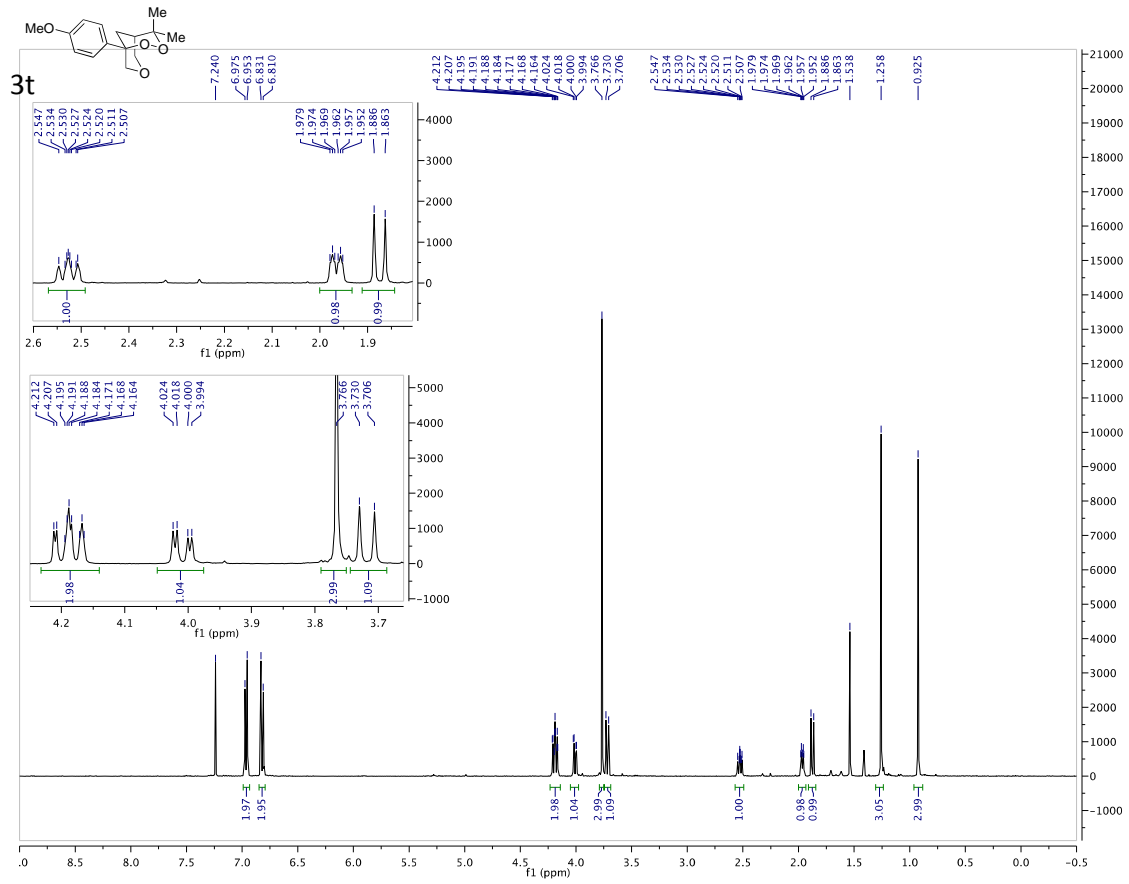


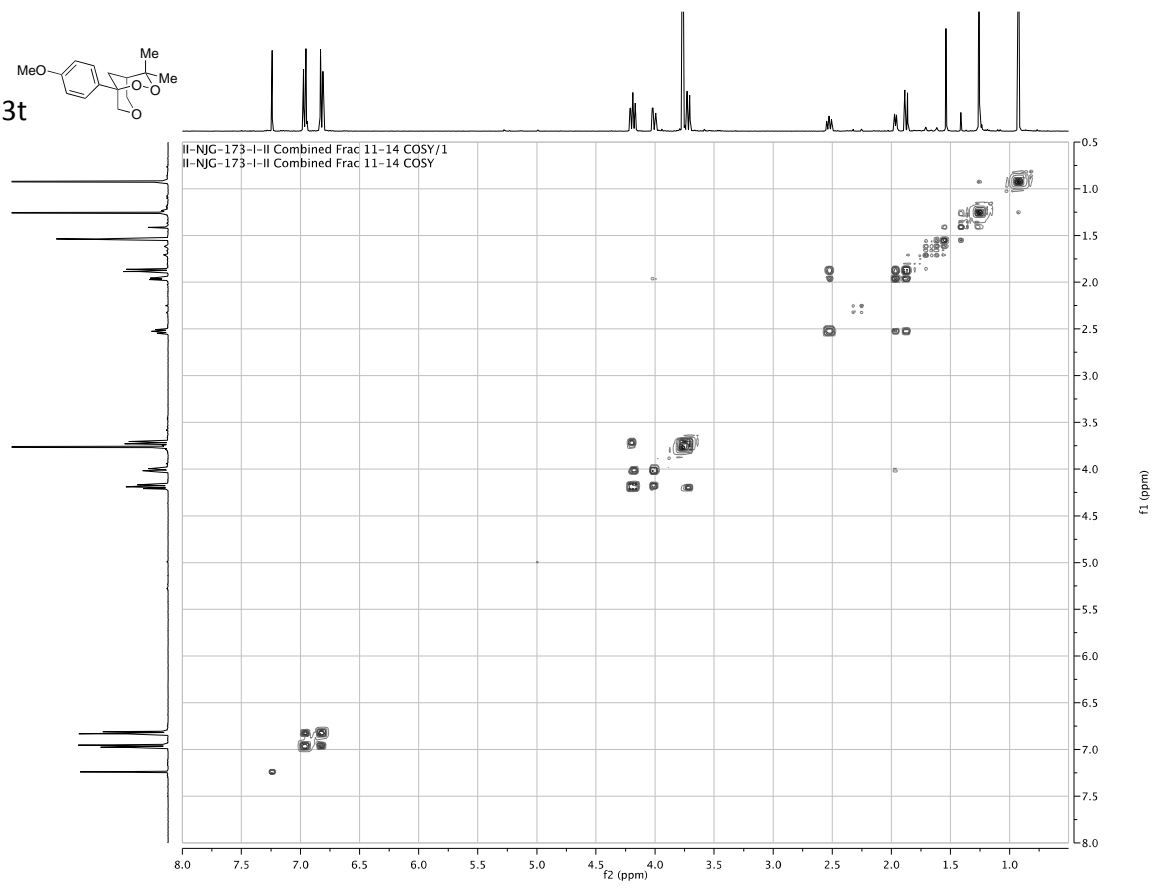
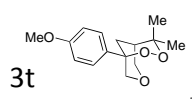
1-(4-Methoxyphenyl)pent-4-en-1-one (3q)

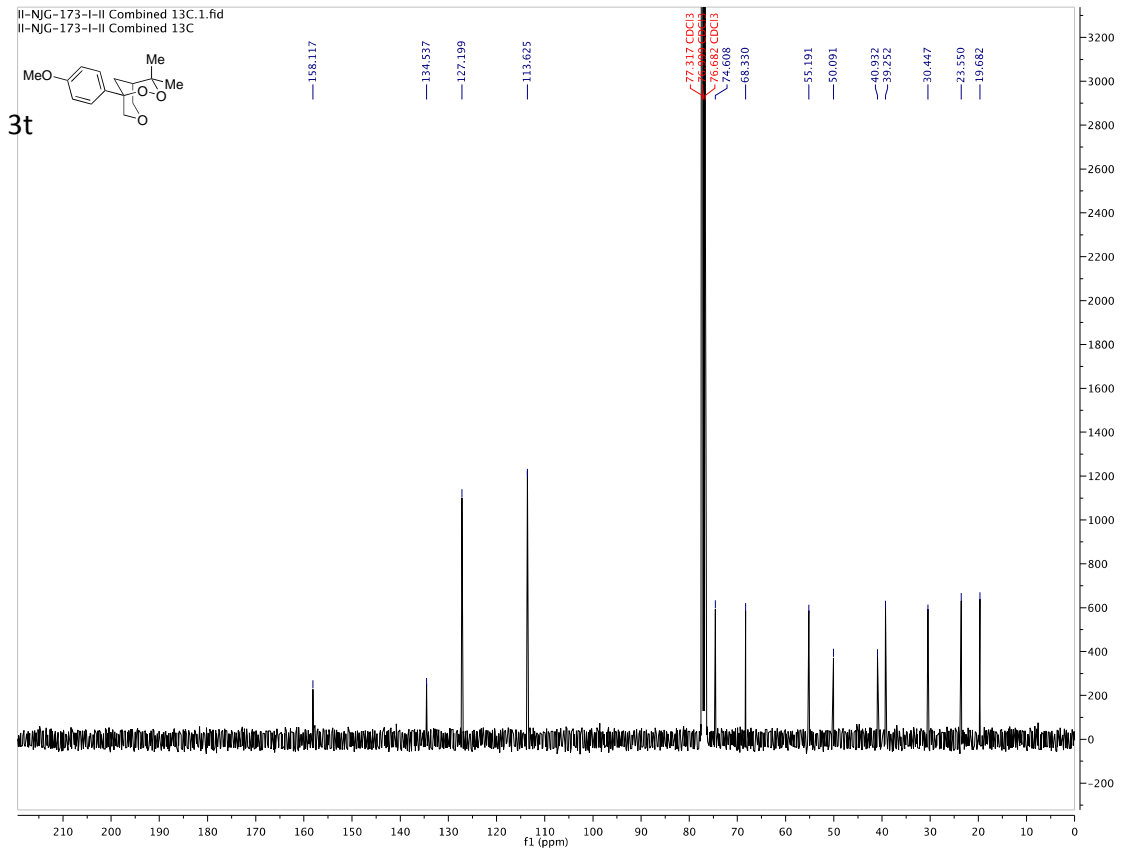




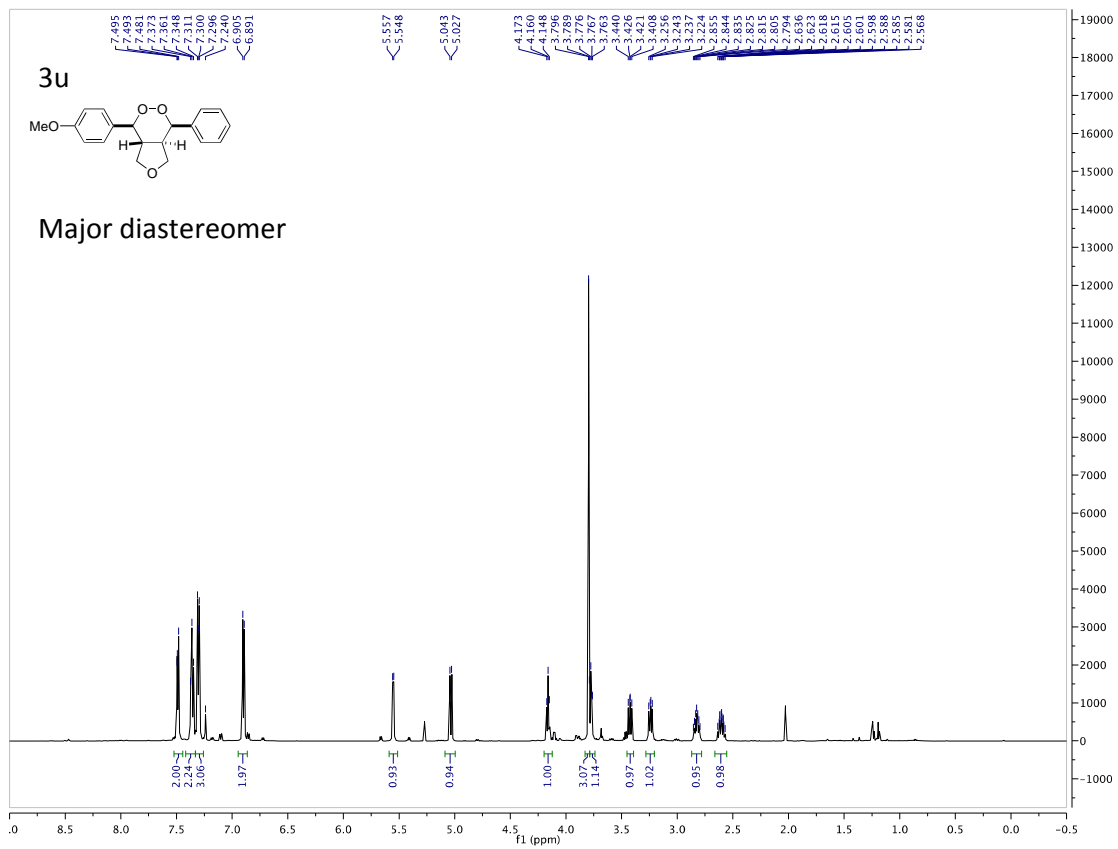
1-(4-Methoxyphenyl)-4,4-dimethyl-2,3,7-trioxabicyclo[3.3.1]nonane (3t)

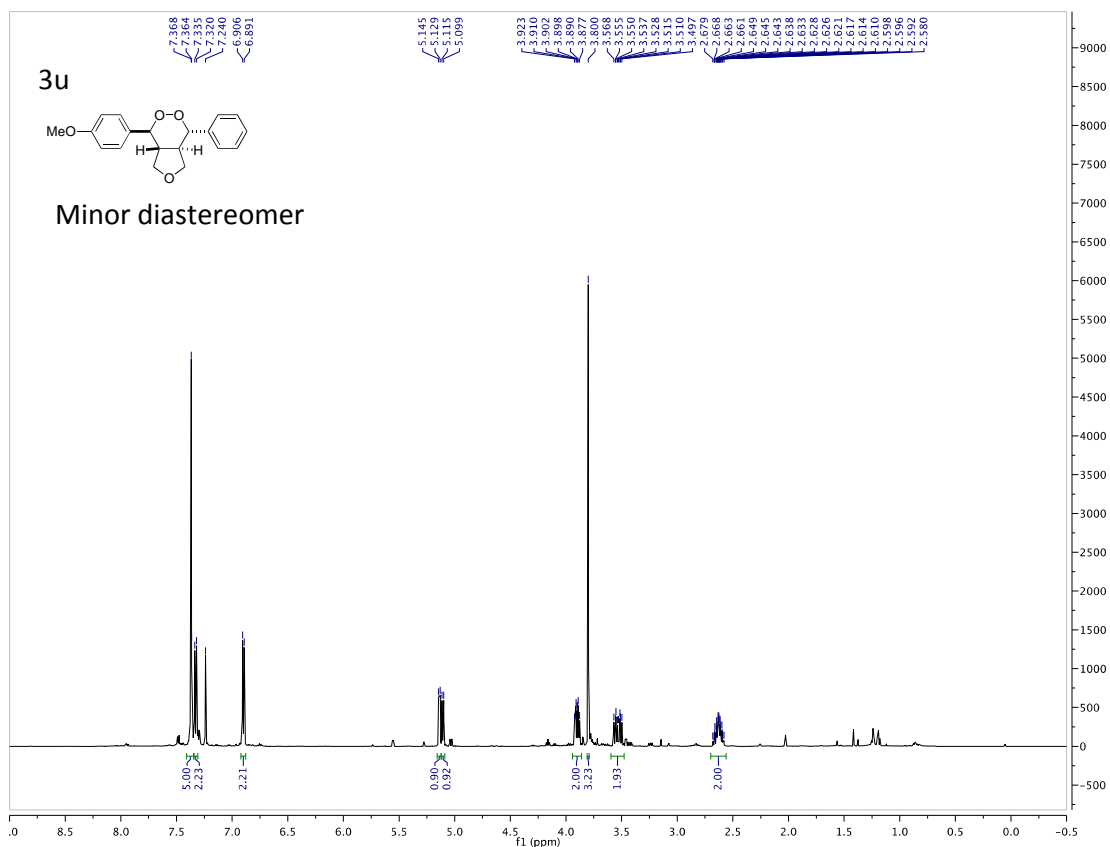




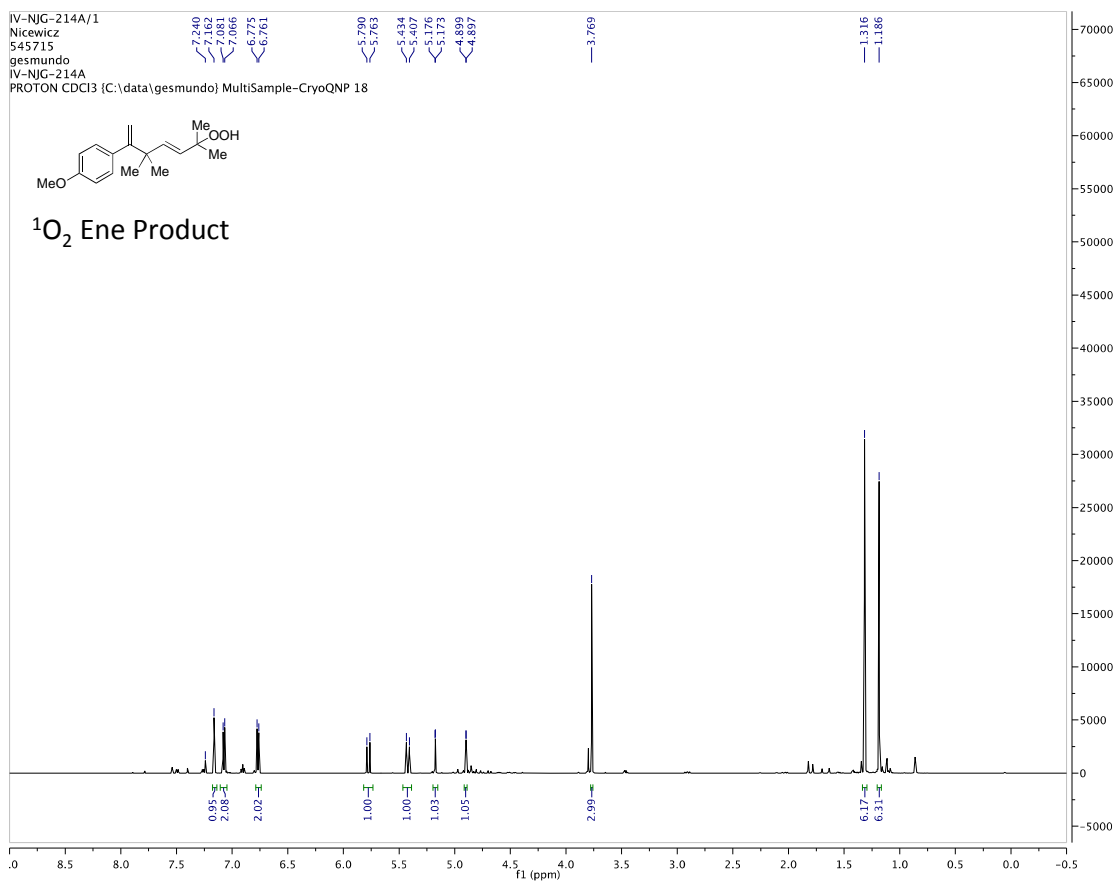


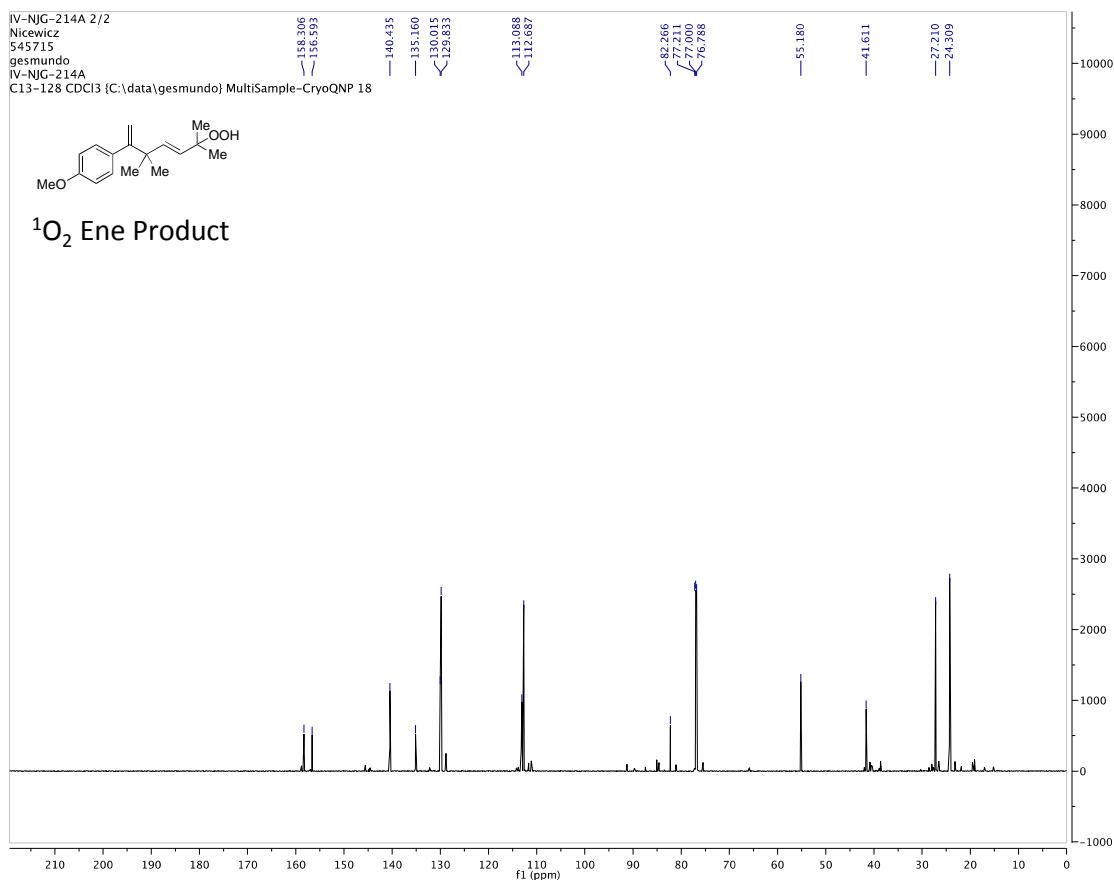
1-(4-Methoxyphenyl)-4-phenyltetrahydro-1*H*,4*H*-furo[3,4-*d*][1,2]dioxine (3u)





(E)-1-(6-Hydroperoxy-3,3,6-trimethylhepta-1,4-dien-2-yl)-4-methoxybenzene





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