General Considerations

(A) General Analytical Information

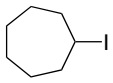
Nuclear Magnetic Resonance spectra were recorded on a Bruker Avance 400 MHz instruments at ambient temperature. All ^{1}H NMR spectra were measured in part per million (ppm) relative to the signals for tetramethylsilane (TMS) added into the deuterated chloroform ($CDCl_3$) (0 ppm) unless otherwise stated. Data for ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, m = multiplet, ovrlp = overlap; br = broad), coupling constants, and integration. All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.16 ppm) unless otherwise stated, and were obtained with complete ^{1}H decoupling. All GC analyses were performed on a Perkin-Elmer Clarus 400 GC system with a FID detector. All GC-MS analyses were performed on an Agilent Technologies 7890A GC system equipped with a 5975C MS detector. High-resolution mass spectra (HRMS) by electrospray ionization (ESI) method were performed at the EPFL ISIC Mass Spectroscopy Service with a Micro Mass QTOF Ultima spectrometer.

(B) General Reagent Information

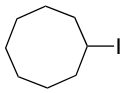
Unless otherwise noted, all chemicals used in the reactions were commercially available and were used as received without further purifications. Tetrahydrofuran (THF) was purified and dehydrated using a two-column solid-state purification system (Innovative Technology, NJ, U.S.A.) and transferred to the nitrogen-filled glove box and further dried with activated 3Å molecular sieves (beads) for storage. Anhydrous dimethylacetamide (DMA) (99.8% purity) were purchased from Acros Chemicals in Sure-Seal bottles and stored under nitrogen. Iron(II) bromide ($FeBr_2$, 98% purity) was purchased from Aldrich Chemical Co.. Copper(I) iodide (98% purity) was purchased from Strem Chemicals. Bis(1,5-cyclooctadiene)nickel(0) (98% purity) was purchased from abcr GmbH. Anhydrous cobalt(II) bromide (99% purity) was purchased from Aldrich Chemical Co.. All alkyl halides (starting materials) and the resulting alkene products were in form of racemic mixtures unless otherwise noted.

The following known starting materials (alkyl halides, bromoalkynes, aryl halides and triflates, and alkenyl halides) were prepared according to the literature procedures;[1-32]

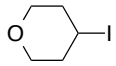
(i) Alkyl Halides



iodocycloheptane[1]

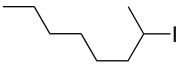


iodocyclooctane[2]

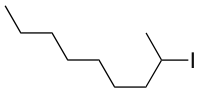


4-iodotetrahydro-2*H*-pyran[3]

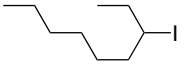
2-iodobicyclo[2.2.1]heptane (d.r.: *exo*:*endo* = 4.3:1)[4]



2-iodooctane[5]



2-iodononane[4]



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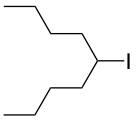
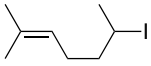
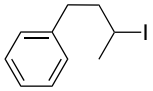


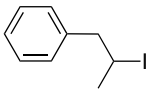
5-iodononane[4]



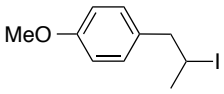
6-iodo-2-methylhept-2-ene[6]



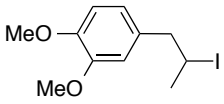
(3-iodobutyl)benzene[4]



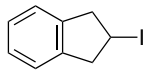
(2-iodopropyl)benzene[7]



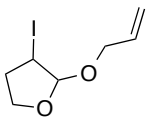
1-(2-iodopropyl)-4-methoxybenzene[4]



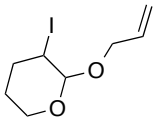
4-(2-iodopropyl)-1,2-dimethoxybenzene[4]



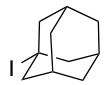
2-iodo-2,3-dihydro-1*H*-indene[8]



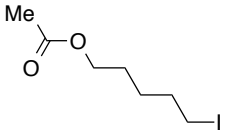
2-(allyloxy)-3-iodotetrahydrofuran[9]



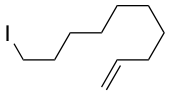
2-(allyloxy)-3-iodotetrahydro-2*H*-pyran[9]



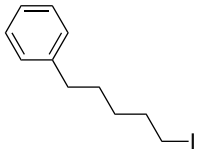
1-iodoadamantane[10]



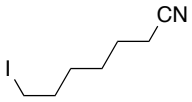
5-iodopentyl acetate[11]



10-iododec-1-ene[12]

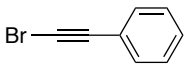


(5-iodopentyl)benzene[13]

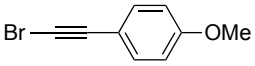


7-iodoheptanenitrile[14]

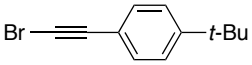
(ii) Bromoalkynes



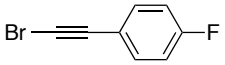
(bromoethynyl)benzene[15]



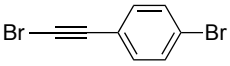
1-(bromoethynyl)-4-methoxybenzene[15]



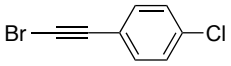
1-(bromoethynyl)-4-(*tert*-butyl)benzene[16]



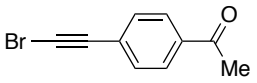
1-(bromoethynyl)-4-fluorobenzene[16]



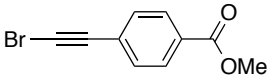
1-bromo-4-(bromoethynyl)-benzene[15]



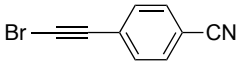
1-bromo-4-(bromoethynyl)-benzene[16]



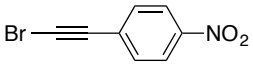
1-(4-(bromoethynyl)phenyl)-ethan-1-one[17]



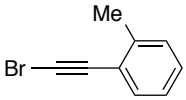
methyl 4-(bromoethynyl)-benzoate[18]



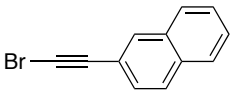
4-(bromoethynyl)-benzonitrile[19]



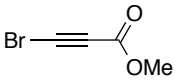
1-(bromoethynyl)-4-nitrobenzene[19]



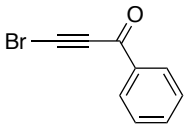
1-(bromoethynyl)-2-methylbenzene[20]



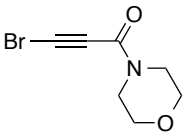
2-(bromoethynyl)-naphthalene[21]



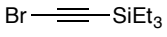
methyl 3-bromopropiolate[15]



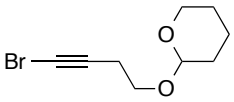
3-bromo-1-phenylprop-2-yn-1-one[15]



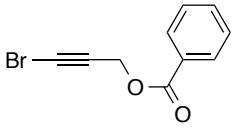
3-bromo-1-morpholino-prop-2-yn-1-one[22]



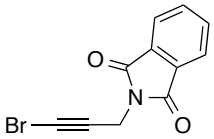
(bromoethynyl)triethylsilane[23]



2-((4-bromobut-3-yn-1-yl)oxy)-tetrahydro-2*H*-pyran[24]

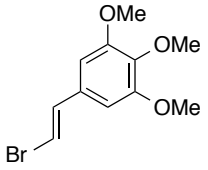


3-bromoprop-2-yn-1-yl benzoate[25]

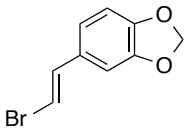


2-(3-bromoprop-2-yn-1-yl)-isoindoline-1,3-dione[26]

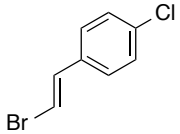
(iii) Aryl and Alkenyl Halides



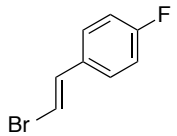
(*E*)-5-(2-bromovinyl)-1,2,3-trimethoxybenzene[27]



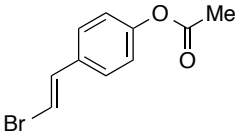
(*E*)-5-(2-bromovinyl)-benzo[*d*][1,3]dioxole[28]



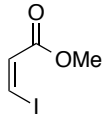
(*E*)-1-(2-bromovinyl)-4-chlorobenzene[29]



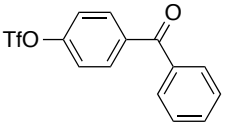
(*E*)-1-(2-bromovinyl)-4-fluorobenzene[28]



(*E*)-4-(2-bromovinyl)phenyl acetate[30]



methyl (*Z*)-3-iodoacrylate[31]



4-benzoylphenyl trifluoromethanesulfonate[32]

(C) General Manipulation Considerations

All manipulations for the (i) Fe-catalyzed reductive coupling reactions of alkyl iodides with terminal alkynes to alkenylzinc reagents, and (ii) the subsequent transition metal-catalyzed cross-couplings of alkenylzinc reagents, were set up in a 30 mL Teflon-screw cap test tube under an inert nitrogen atmosphere using the glove-box techniques. The test tubes were then sealed with airtight electrical tapes and the reaction mixtures were stirred under nitrogen atmosphere at room temperature on bench-top or heated in a preheated oil bath. Flash column chromatography was performed using silica gel (Silicycle, ultrapure grade). Preparative thin layer chromatography (preparative TLC) was used to purify the trisubstituted alkene products using TLC silica gel 60 F_{254} glass plate (Merck). The eluents for column chromatography and preparative TLC are presented as a ratio of solvent volumes.

The yields reported in the publication are of isolated materials unless otherwise noted. All new trisubstituted alkene products were characterized by ^{1}H NMR and ^{13}C NMR spectroscopies and high-resolution mass spectrometry (HRMS); in case the molecular ions could not be detected by HRMS, GC-MS was used instead.

The major stereoisomers of trisubstituted alkene products (Figures 1 and 3 in the main text; Figure S1 and S3 in Supporting Information) and the corresponding minor stereoisomers were differentiated by comparing the chemical shifts of the olefinic protons of product isomers with the stereochemically similar, known compounds.[33,34] The stereospecific trisubstituted alkenes products (Figure 2 in the main text; Figure S2 in Supporting Information) were supported by comparing the ^{1}H NMR spectrum of product **S3a** (Table S2) with the authentic compound.[35] The ratio of the stereoisomers of trisubstituted alkene product was determined by comparing the ratio of the integrations of olefinic protons by ^{1}H NMR spectroscopy.

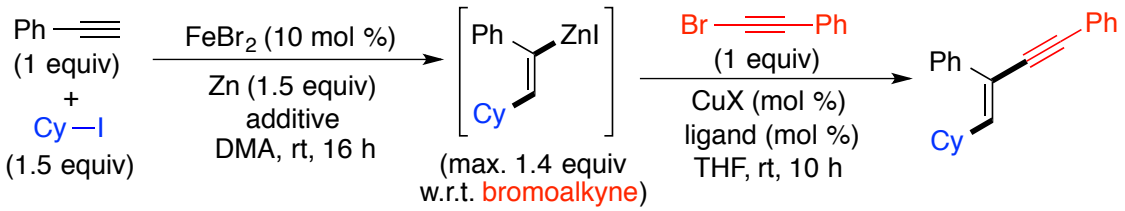
In case diastereomers exist in 1:1 ratio in the α-alkylated styene products (Figures 3 and S3), the multiplicity of the splitting of proton signals in the ^{1}H NMR spectra were not shown due to the complexity of the proton signals. Moreover, the chemical shifts of carbon signals in the ^{13}C NMR spectra were represented as “number (number)” for the same carbons of the diastereomers.

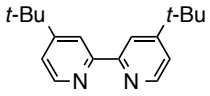
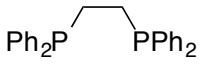
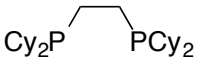
Supplementary Experimental Results

(A) Optimization of Cu-Catalyzed Cross-Coupling of Alkenylzinc Reagents with Bomoalkynes

The *Z*-disubstituted alkenylzinc reagent was prepared by using a procedure similar to that used in our previous study[36] (by using ethynylbenzene (0.14 mmol, 1 equiv) and excess iodocyclohexane (1.5 equiv) as reagents, $FeBr_2$ (10 mol %) as catalyst, Zn as redundant (1.5 equiv), iodine (~2 mol %) as zinc activating reagent, and DMA (~0.3 mL) as solvent). The *in-situ* formed alkenylzinc reagent was then diluted with THF (volume ratio THF to DMA ~ 6:1). In the reaction of excess alkenylzinc reagent (up to 1.4 equiv assuming 100% conversion in the first step) with (2-bromoethynyl)benzene (test substrate, 1 equiv, 0.10 mmol), the use of CuCl catalyst (20 mol %) in conjunction with 2,2-dibypridyl (20 mol %) could catalyze the reaction to give the *E*-enyne product in 49% GC yield (Table S1, entry 1). Other bidentate nitrogen and phosphine ligands did not promote the reaction as efficiently as bipy (Table S1, entries 2-6). By using iodotrimethylsilane as Zn activating reagent, the yield of enyne was significantly enhanced to 87% yield (Table S1, entry 7). The product yield can be further slightly increased to 91% when a lower loading of CuCl (15 mol %) was used (Table S1, entry 8). By switching the catalyst to CuI, the highest yield (95%) was obtained (Table S1, entry 9). However, the lowering of the loading of bipy or CuI led to the decrease of yields (Table S1, entries 10 and 11). Other Cu catalysts were also screened but they did not catalyze the reactions as efficiently as CuI (Table S1, entries 12-18). The use of other Zn activating reagents, bromo- and chlorotrimethylsilane (TMSBr and TMSCl), did not lead to a higher yielder yield compared to TMSI (Table S1, entries 19 and 20). Without CuI, the reaction was sluggish and only a modest yield was obtained (Table S1, entry 21). The conditions in entry 9 were used as the optimal general conditions for substrate scope study.

Table S1. Complete Optimization of Cu-Catalyzed Cross-Coupling of Alkenylzinc Reagents with Bomoalkynes



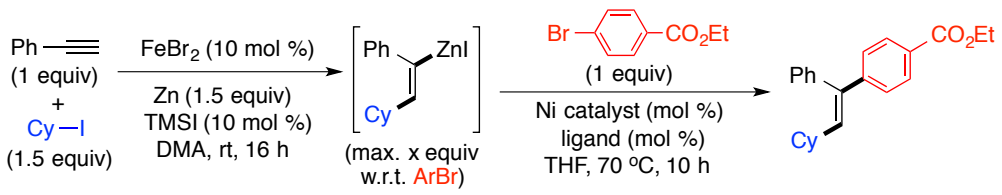
entry	additive (mol %)	CuX (mol %)	ligand (mol %)	GC yield (%)[a]
1	I_2 (2)	CuCl (20)	bipy (20)	49
2	I_2 (2)	CuCl (20)	 (20)	27
3	I_2 (2)	CuCl (20)	phenanthroline (20)	46
4	I_2 (2)	CuCl (20)	TMEDA (80)	48
5	I_2 (2)	CuCl (20)	 (20)	28
6	I_2 (2)	CuCl (20)	 (20)	24
7	TMSI (10)	CuCl (20)	bipy (20)	87
8	TMSI (10)	CuCl (15)	bipy (20)	91
9	**TMSI (10)**	**CuI (15)**	**bipy (20)**	**95**
10	TMSI (10)	CuI (15)	bipy (15)	79
11	TMSI (10)	CuI (10)	bipy (20)	83
12	TMSI (10)	CuBr (15)	bipy (20)	83
13	TMSI (10)	$Cu(MeCN)_4PF_6$ (15)	bipy (20)	94
14	TMSI (10)	1/2 $[Cu(OTf)]_2 \cdot$ benzene (15)	bipy (20)	78
15	TMSI (10)	CuSCN (15)	bipy (20)	87
16	TMSI (10)	CuCN (15)	bipy (20)	89
17	TMSI (10)	CuOAc (15)	bipy (20)	90
18	TMSI (10)	CuTc (15)	bipy (20)	84
19	TMSBr (10)	CuI (15)	bipy (20)	89
20	TMSCl (10)	CuI (15)	bipy (20)	81
21	TMSI (10)	CuI (0)	bipy (20)	41

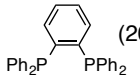
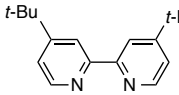
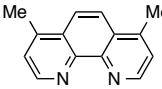
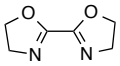
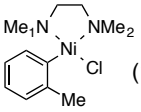
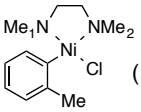
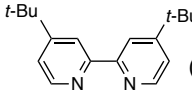
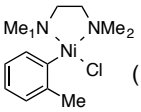
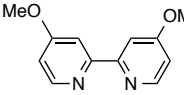
(a) GC yield using *n*-dodecane as internal standard.

(B) Optimization of Ni-Catalyzed Cross-Coupling of Alkenylzinc Reagents with Aryl Halides

The *in-situ* formed alkenylzinc reagent solution was prepared using conditions optimized in Table S1.[36] In the reaction of excess alkenylzinc reagents (up to 1.25 equiv assuming 100% conversion in the first step) with ethyl 4-bromobenzoate (test substrate, 1 equiv, 0.10 mmol), the effect of ligand was first studied in the presence of $Ni(cod)_2$ catalyst (20 mol %). The use of phosphine-type ligands only led to the formation of the α-phenylstyrene product in low yields (Table S2, entries 1-8). On the contrary, the use of bidentate nitrogen-type ligands could generally give higher yields (Table S2, entries 9-13), and 2,2'-dipyridiyl ligand was found to be the optimal ligand to give the product in 64% yield (Table S2, entry 9). Further screening demonstrated that the yield was highest (76%) when $Ni(cod)_2$ (10 mol %) and bipy (15 mol %) were used (Table S2, entry 14). Without a Ni catalyst, only a low yield of was obtained (Table S2, entry 16). Nickel(II) precatalysts, Ni^{II}(TMEDA)(*o*-tolyl)(Cl)[37] and $Ni^{II}Br_2$(diglyme), did not efficiently catalyze the reaction as compared to $Ni(cod)_2$ despite the use of other derivatives of 2,2'-dipyridiyl ligands (Table S2, entries 17-21). The conditions in entry 14 were used as the optimal general conditions for substrate scope study of aryl halides and other sp^2-carbon halogen bonds.

Table S2. Complete Optimization of Ni-Catalyzed Cross-Coupling of Alkenylzinc Reagents with ArBr



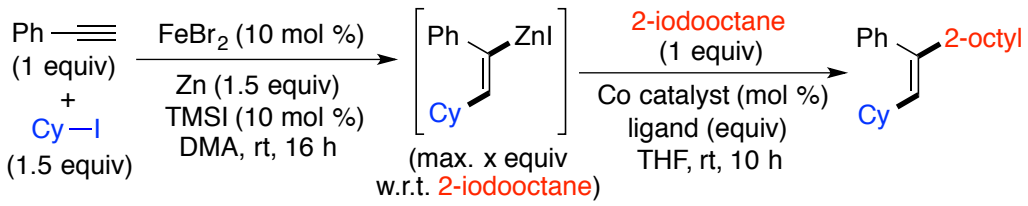
entry	alkenyl-ZnI (x equiv)	Ni catalyst (mol %)	ligand (mol %)	GC yield (%)[a]
1	1.25	$Ni(cod)_2$ (20)	dppe (20)	9
2	1.25	$Ni(cod)_2$ (20)	dppp (20)	8
3	1.25	$Ni(cod)_2$ (20)	dppb (20)	16
4	1.25	$Ni(cod)_2$ (20)	dppf (20)	16
5	1.25	$Ni(cod)_2$ (20)	PPh_3 (80)	22
6	1.25	$Ni(cod)_2$ (20)	BINAP (20)	8
7	1.25	$Ni(cod)_2$ (20)	Xantphos (20)	11
8	1.25	$Ni(cod)_2$ (20)	 (20)	15
9	1.25	$Ni(cod)_2$ (20)	bipy (20)	64
10	1.25	$Ni(cod)_2$ (20)	 (20)	36
11	1.25	$Ni(cod)_2$ (20)	phen (20)	18
12	1.25	$Ni(cod)_2$ (20)	 (20)	59
13	1.25	$Ni(cod)_2$ (20)	 (20)	28
14	**1.4**	**$Ni(cod)_2$ (10)**	**bipy (15)**	**76**
15	1.4	$Ni(cod)_2$ (15)	bipy (15)	62
16	1.4	$Ni(cod)_2$ (0)	bipy (15)	18
17	1.4	 (10)	bipy (15)	68
18	1.4	 (10)	 (15)	62
19	1.4	 (10)	 (15)	49
20	1.25	$Ni(cod)_2$ (10)	bipy (10)	42
21	1.25	$NiBr_2$(diglyme) (10)	bipy (10)	27

(a) GC yield using *n*-dodecane as an internal standard.

(C) Optimization of Co-Catalyzed Cross-Coupling of Alkenylzinc Reagents with Alkyl Iodides

The *in-situ* formed alkenylzinc reagent solution was prepared using optimized conditions in Table S1.[36] In the reaction of excess alkenylzinc reagent (up to 1.4 equiv assuming 100% conversion in the first step) with 2-iodooctane (test substrate, 1 equiv, 0.10 mmol), the use of $CoBr_2$ (10 mol %) in conjunction with TEMDA (2 equiv) were found to catalyze the reaction to give the α-alkylstyrene product in 47% yield (Table S3, entry 1). The increase of loading of $CoBr_2$ to 20 mol % further increased the yield to 57% (Table S3, entry 2), but the further increase of loading of $CoBr_2$ (30 and 40 mol %) could not further enhance the yield (Table S3, entries 3 and 4). The use of TMEDA derivatives, *N*,*N*,*N'*,*N'*-tetramethyl-1,3-propanediamine (TMPDA) and *N*,*N*,*N'*,*N'*-tetraethylethylenediamine (TEEDA), only led to modest yields (Table S3, entries 5 and 6). The incorporation of flame-dried LiCl into either alkenylzinc reagent or various cobalt halide catalysts could not promote the yields (Table S3, entries 7-9). The additional use of 3 equiv of pyridine co-ligand was found to further enhance the yield to 67% yield (Table S3, entry 10). By using a higher loading of alkenylzinc reagent (1.7 equiv), the use of $CoBr_2$/TMEDA/pyridine catalyst system could led to a highest yield of product in 76% yield (Table S3, entry 12). The subsequent tuning of loading of either TMEDA or pyridine did not promote the yield further (Table S3, entries 13-15). Additionally, the conditions in entry 12 also allowed for the coupling of primary alkyl iodide, 1-iodooctane (test substrate, 0.10 mmol), to give the desired product in 76% yield Table S3, entry 12). Without $CoBr_2$ catalyst, only trace amounts of products were obtained (Table S3, entry 16). The conditions in entry 12 were used as the optimal general conditions for study of substrate scope of alkyl halides.

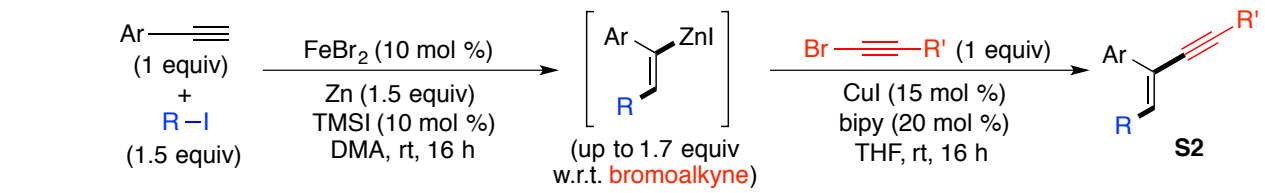
Table S3. Complete Optimization of Co-Catalyzed Cross-Coupling of Alkenylzinc Reagents with Alkyl Iodides

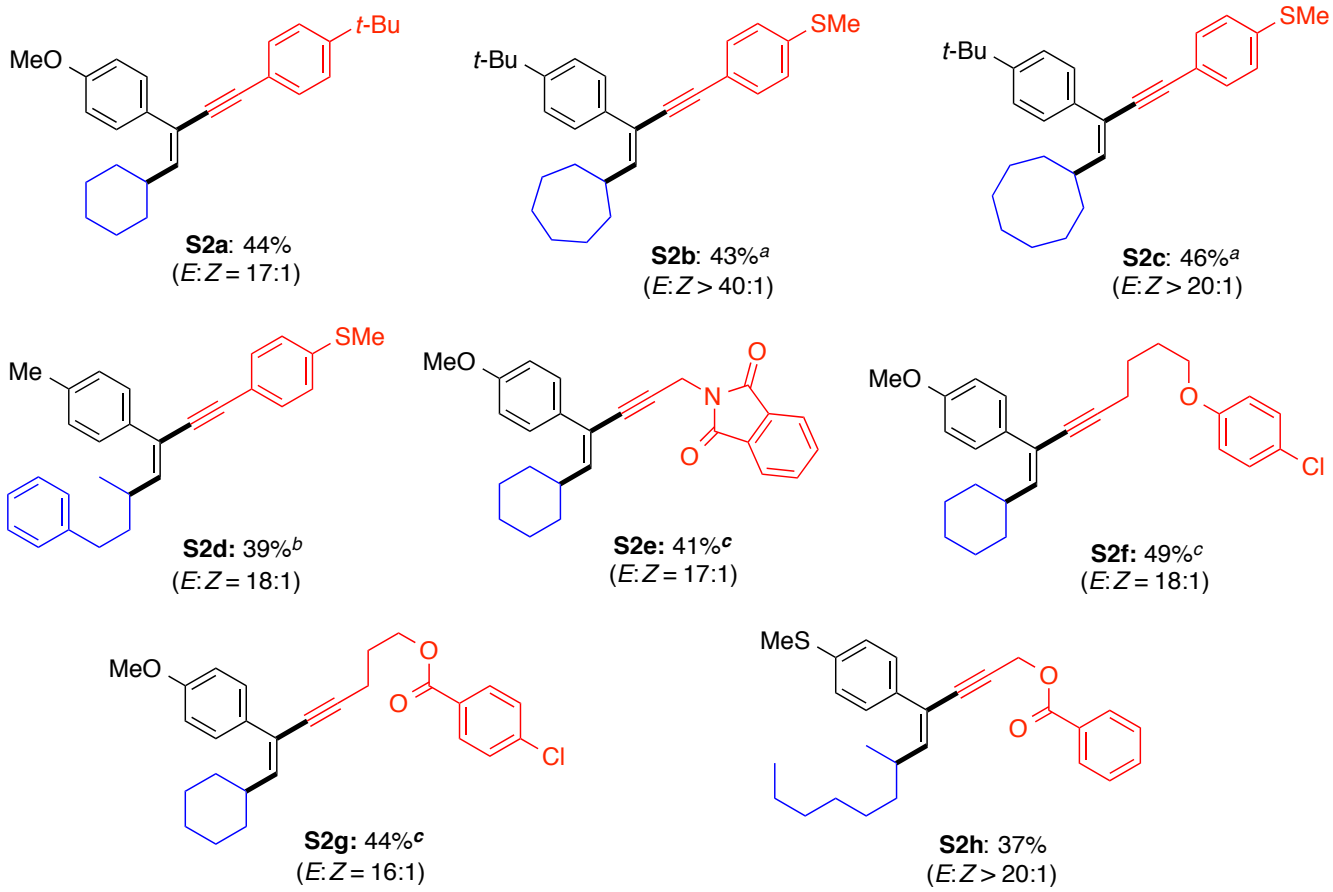


entry	alkenyl-ZnI (x equiv)	Co catalyst (mol %)	ligand(s) (equiv)	GC yield (%)[a]
1	1.4	$CoBr_2$ (10)	TMEDA (2)	47
2	1.4	$CoBr_2$ (20)	TMEDA (2)	57
3	1.4	$CoBr_2$ (30)	TMEDA (2)	57
4	1.4	$CoBr_2$ (40)	TMEDA (2)	53
5	1.4	$CoBr_2$ (30)	TMPDA (2)	26
6	1.4	$CoBr_2$ (30)	TEEDA (2)	37
7	1.4 (+ 1.4 equiv LiCl)	$CoBr_2$ (20)	TMEDA (2)	49
8	1.4	$CoBr_2 \cdot 2LiCl$(30)	TMEDA (2)	22
9	1.4	$CoCl_2 \cdot 2LiCl$(30)	TMEDA (2)	5
10	1.4	$CoBr_2$ (20)	TMEDA (2), py (3)	67
11	1.4	$CoBr_2$ (20)	TMEDA (1.5), py (3)	45
12	**1.7**	**$CoBr_2$ (20)**	**TMEDA (2), py (3)**	**76 (76)[b]**
13	1.7	$CoBr_2$ (20)	TMEDA (2), pyridine (4)	66
14	1.7	$CoBr_2$ (20)	TMEDA (1.5), pyridine (4)	70
15	1.7	$CoBr_2$ (20)	TMEDA (1.5), pyridine (2)	70
16	1.7	$CoBr_2$ (0)	TMEDA (2), py (3)	<5 (<1)[b]

(a) GC yield using *n*-dodecane as an internal standard. (b) 1-Iodooctane was used instead of 2-iodooctane.

(D) Supplementary Results of Cu-Catalyzed Cross-Coupling of Alkenylzinc Reagents with Bromoalkynes

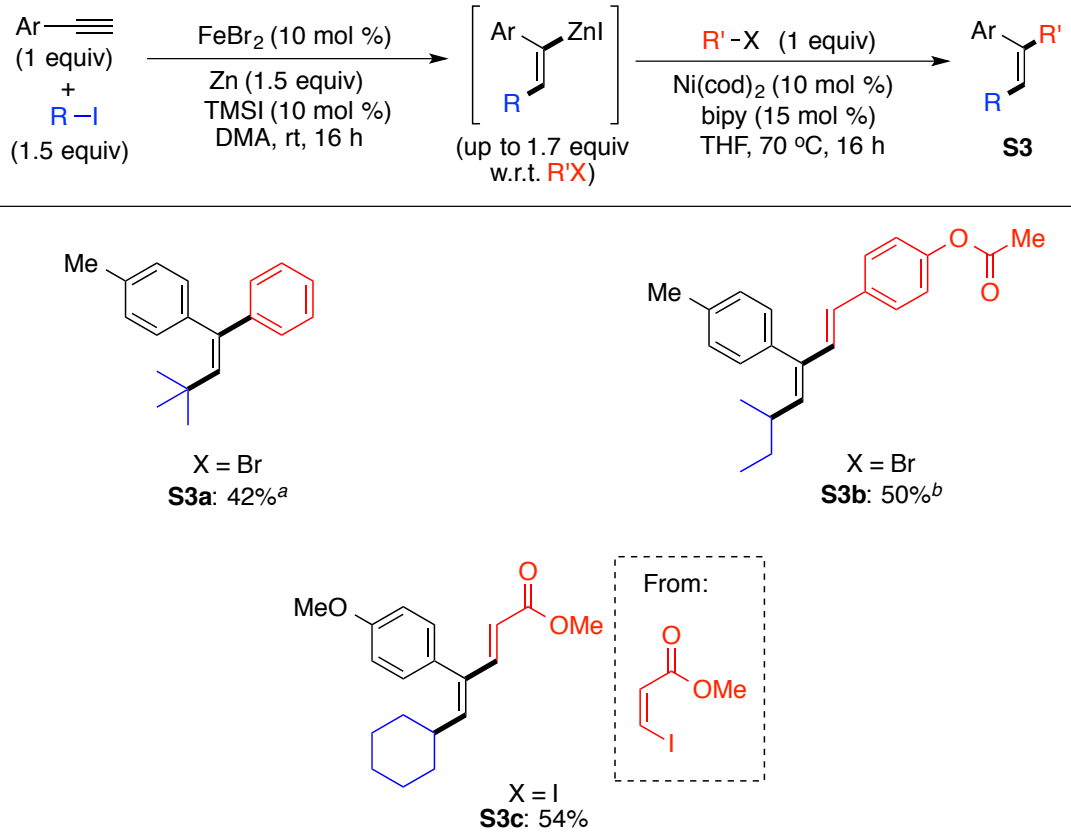




(a) Alkyl iodide (2 equiv) and Zn (2 equiv) were used in the first step. (b) Alkyl iodide (3 equiv), Zn (3 equiv) and TMSI (20 mol %) were used in the first step. (c) CuI (25 equiv) and bipy (35 equiv) were used in the second step.

Figure S1. Cu-catalyzed cross-coupling of alkenylzinc reagents with bromoalkynes.

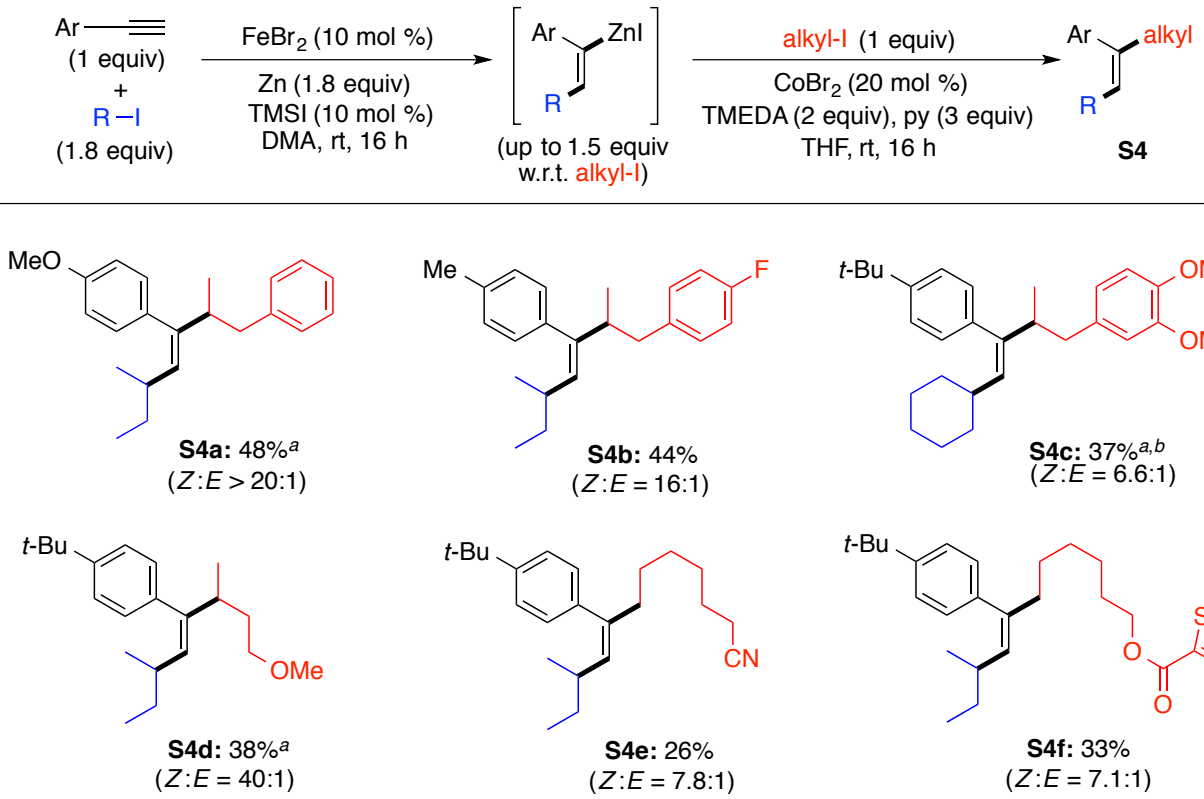
(E) Supplementary Results of of Ni-Catalyzed Cross-Coupling of Alkenylzinc Reagents with sp^2-Carbon-Halogen Bonds



(a) Alkyl iodide (3 equiv), Zn (3 equiv), and TMSI (20 mol %) were used in the first step. (b) Alkyl iodide (1.8 equiv) and Zn (1.8 equiv) were used in the first step.

Figure S2. Ni-catalyzed cross-coupling of alkenylzinc reagents with sp^2-carbon-halogen bonds. In all products, the ratios of major to minor isomer are more than 50:1.

(F) Supplementary Results of of Co-Catalyzed Cross-Coupling of Alkenylzinc Reagents with Alkyl Iodides

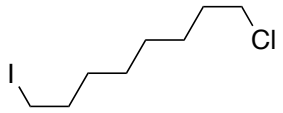


(a) Alkenylzinc reagent (1.7 equiv with repsect to alkyl iodide) was used in the second step. (b) Alkyl iodide (1.5 equiv) and Zn (1.5 equiv) were used in the first step.

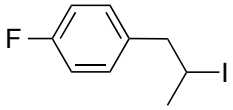
Figure S3. Co-catalyzed cross-coupling of alkenylzinc reagents with alkyl iodides.

Experimental Section

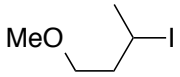
General Procedure for the Preparation of Alkyl Halide from Alkyl Alcohol.[4] A 1 L round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with triphenylphosphine (1.4 equiv), imidazole (1.4 equiv), and dichloromethane (~300 mL). The reaction mixture was stirred at room temperature until most of the white solids dissolved. Iodine (1.4 equiv) was then added slowly in a few portions into the reaction mixture, and the resulting mixture was stirred until the iodine granules almost dissolved. Alkyl alcohol (1.0 equiv) was then slowly added into the reaction mixture, and the resulting mixture was stirred overnight. After the reaction, the reaction mixture was concentrated with the aid of a rotary evaporator, and it was further diluted with hexanes and filtered to remove the solid residues. The filtrate was concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using hexanes and ethyl acetate as eluent to afford the following alkyl iodides. The following compounds were synthesized using the general procedures:



1-chloro-8-iodooctane



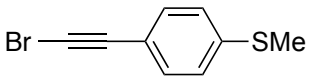
1-fluoro-4-(2-iodopropyl)benzene



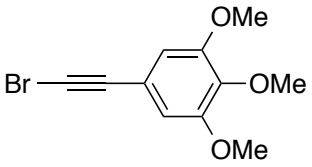
3-iodo-1-methoxybutane

General Procedure for the Preparation of Bromoalkyne.

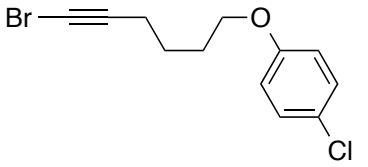
(i) From Terminal Alkynes.[15,16] A 100 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with alkyne (1 equiv) and silver nitrate (10 mol %). Acetone (~30 mL) and water (~1 mL) were then added into the flask, followed by the addition of *N*-bromosuccinimide (NBS) (1.1 equiv). The resulting mixture was stirred overnight. After the reaction, the reaction mixture was washed with NaOH solution (~1 M, 50 mL) and dichloromethane (20 mL). The aqueous layer was further washed with dichloromethane (2 x 20 mL). The organic fractions were combined and concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using hexanes and ethyl acetate as eluent to afford the following bromoalkynes. The following compounds were synthesized using the general procedures:



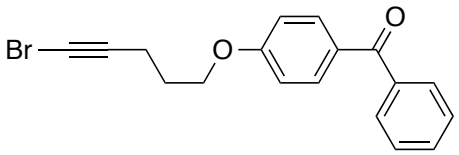
(4-(bromoethynyl)phenyl)-(methyl)sulfane



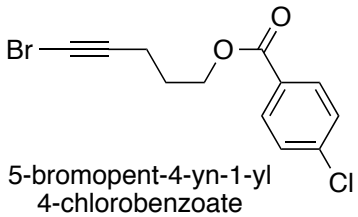
5-(bromoethynyl)-1,2,3-trimethoxybenzene



1-((6-bromohex-5-yn-1-yl)oxy)-4-chlorobenzene

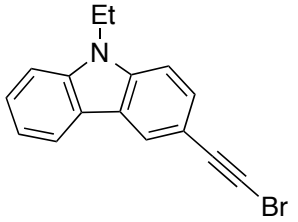


(4-((5-bromopent-4-yn-1-yl)oxy)phenyl)-(phenyl)methanone



5-bromopent-4-yn-1-yl 4-chlorobenzoate

(ii) From Aryl-aldehyde.[20] A 1 L round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with triphenylphosphine (3 equiv) and dichloromethane (~300 mL). Tetrabromomethane (1.5 equiv) was then added slowly into the reaction mixture, and the reaction mixture was stirred at room temperature until most of the solids dissolved. Aryl-aldehyde (1 equiv) was added into the reaction mixture, and the resulting mixture was stirred overnight. After the reaction, the reaction mixture was concentrated with the aid of a rotary evaporator, and it was further diluted with hexanes and filtered to remove the solid residues. The filtrate was concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using hexanes and ethyl acetate as eluent to afford the (2,2-dibromovinyl)arene. A 500 mL round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with (2,2-dibromovinyl)arene (1 equiv, prepared from the previous procedure), benzyltriethylammonium chloride (0.88 equiv), and dichloromethane (~100 mL). A solution of KOH (~50 equiv) in water (~30-40 mL) was slowly added into the reaction mixture, and the resulting mixture was stirred vigorously at room temperature overnight. The reaction conversion was monitored by GC analysis. After the reaction, the reaction mixture was diluted with water (~200 mL). The organic fraction was isolated, and the aqueous layer was further washed with dichloromethane (2 x 50 mL). The organic fractions were combined and concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using hexanes and ethyl acetate as eluent to afford the following bromoalkynes. The following compound was synthesized using the general procedures:



3-(bromoethynyl)-9-ethyl-9*H*-carbazole

General Procedure for the Iron-Catalyzed Reductive Coupling of Terminal Alkyne and Alkyl Iodide to Prepare *in-situ* Formed *Z*-Substituted Alkenylzinc Reagent (General Procedure A). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with zinc powder (Zn, 69 mg, 1.05 mmol, 1.5 equiv), iron(II) bromide ($FeBr_2$, 15 mg, 0.07 mmol, 10 mol %), and DMA solvent (1.5 mL). Iodotrimethylsilane (TMSI, 14 mg, 0.07 mmol, 10 mol %) was then added into the reaction mixture, and the mixture was stirred at room temperature for ~1 min (**Caution:** white fume was generated when iodotrimethylsilane was once added; no more fume was produced upon prolonged stirring). Ethynylarene (0.70 mmol, 1.0 equiv) was added into the reaction mixture followed by the addition of alkyl iodide (1.05 mmol, 1.5 equiv). The resulting mixture was stirred at room temperature for 16 h. After the reaction, THF (9 mL) was added into the resulting mixture to form the *in-situ* formed *Z*-disubstituted alkenylzinc reagent.

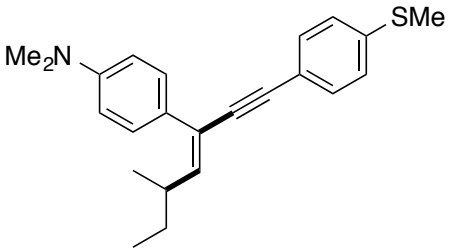
General Procedure for the Copper-Catalyzed Cross-Coupling of *in-situ* Formed Alkenylzinc Reagent with Bromoalkyne (General Procedure B). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with bromoalkyne (0.41 mmol, 1.0 equiv), copper(I) iodide (CuI, 12 mg, 0.062 mmol, 15 mol %), and 2,2'-dipyridyl (bipy, 13 mg, 0.082 mmol, 20 mol %). The solution of *in-situ* formed *Z*-disubstituted alkenylzinc reagent in THF/DMA (prepared in **General Procedure A**; ~0.7 mmol (assuming 100% conversion, ~**1.7 equiv**) was transferred into the tube via a syringe. The resulting reddish brown mixture was stirred at room temperature for 16 h. After the reaction, the crude product was washed with EtOAc (~20 mL) and saturated $NaHCO_3$ solution (~50 mL). The aqueous fraction was further washed with EtOAc (2 x ~10 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by preparative TLC using a solvent mixture (hexanes and EtOAc) as eluent to afford the isolated *E*-enyne product.

General Procedure for the Nickel-Catalyzed Cross-Coupling of *in-situ* Formed Alkenylzinc Reagent with sp^2-Carbon—Halogen Bond (General Procedure C). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with aryl halide / alkenyl halide / acyl chloride (0.41 mmol, 1.0 equiv), bis(cyclooctadiene)nickel(0) ($Ni(cod)_2$, 11.3 mg, 0.041 mmol, 10 mol %), and 2,2'-dipyridyl (bipy, 10 mg, 0.062 mmol, 15 mol %). The solution of *in-situ* formed *Z*-disubstituted alkenylzinc reagent in THF/DMA (prepared in **General Procedure A**; ~0.7 mmol assuming 100% conversion, ~**1.7 equiv**) was transferred into the tube via a syringe. The resulting dark mixture was stirred at 70 ^oC in a preheated oil bath for 16 h. After the reaction, the tube was cooled to room temperature, and the crude product was washed with EtOAc (~20 mL) and saturated $NaHCO_3$ solution (~50 mL). The aqueous fraction was further washed with EtOAc (2 x ~10 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by preparative TLC using a solvent mixture (hexanes and EtOAc) as eluent to afford the isolated α-arylated styrene product.

General Procedure for the Cobalt-Catalyzed Cross-Coupling of *in-situ* Formed Alkenylzinc Reagent with Alkyl Halide (General Procedure D). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with alkyl halide (0.41 mmol, 1.0

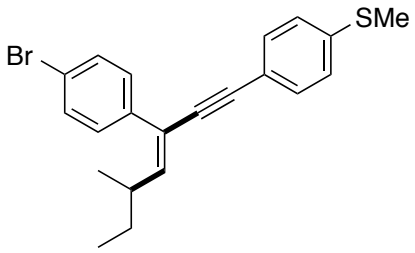
equiv), anhydrous cobalt(II) bromide ($CoBr_2$, 18 mg, 0.082 mmol, 20 mol %), *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA, 95 mg, 123 μL, 0.82 mmol, 2 equiv), and pyridine (py, 95 mg, 99 μL, 1.23 mmol, 3 equiv). The solution of *in-situ* formed *Z*-disubstituted alkenylzinc reagent in THF/DMA (prepared in **General Procedure A**; ~0.7 mmol assuming 100% conversion, ~**1.7 equiv**) was transferred into the tube via a syringe. The resulting deep green mixture was stirred at room temperature for 16 h. After the reaction, the crude product was washed with EtOAc (~20 mL) and saturated $NaHCO_3$ solution (~50 mL). The aqueous fraction was further washed with EtOAc (2 x ~10 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by preparative TLC using a solvent mixture (hexanes and EtOAc) as eluent to afford the isolated α-alkylated styrene product.

General Procedure for the Cobalt-Catalyzed Cross-Coupling of *in-situ* Formed Alkenylzinc Reagent with Alkyl Halide (General Procedure E). An oven-dried 30 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with alkyl halide (0.47 mmol, 1.0 equiv), anhydrous cobalt(II) bromide ($CoBr_2$, 20 mg, 0.094 mmol, 20 mol %), *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA, 109 mg, 141 μL, 0.94 mmol, 2 equiv), and pyridine (py, 112 mg, 114 μL, 1.41 mmol, 3 equiv). The solution of *in-situ* formed *Z*-disubstituted alkenylzinc reagent in THF/DMA (prepared in **General Procedure A**; ~0.7 mmol assuming 100% conversion, ~**1.5 equiv**) was transferred into the tube via a syringe. The resulting deep green mixture was stirred at room temperature for 16 h. After the reaction, the crude product was washed with EtOAc (~20 mL) and saturated $NaHCO_3$ solution (~50 mL). The aqueous fraction was further washed with EtOAc (2 x ~10 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by preparative TLC using a solvent mixture (hexanes and EtOAc) as eluent to afford the isolated α-alkylated styrene product.

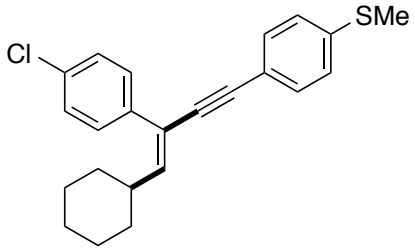


(*E*)-*N*,*N*-Dimethyl-4-(5-methyl-1-(4-(methylthio)phenyl)hept-3-en-1-yn-3-yl)aniline (2a). Following the general procedure A, the alkenylzinc reagent was prepared using 4-ethynyl-*N*,*N*-dimethylaniline (102 mg, 0.70 mmol, 1 equiv), Zn (138 mg, 2.1 mmol, 3 equiv), TMSI (28 mg, 0.14 mmol, 20 mol %), and 2-iodobutane (386 mg, 2.1 mmol, 3 equiv). Following the general procedure B, the title compound was prepared using (4-(bromoethynyl)phenyl)(methyl)sulfane (93 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (50:1) as an eluent to afford the title compound (**2a**) as viscous brown oil (78 mg, 55%; ***E*:*Z*** = 15:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.3 Hz, 2 H), 7.30 (d, *J* = 8.7 Hz, 2 H), 7.14 (d, *J* = 8.3 Hz, 2 H), 6.72 (d, *J* = 8.6 Hz, 2 H), 5.94 (d, *J* = 10.6 Hz, 1 H), 2.96 (s, 6 H), 2.58-2.50 (m, 1 H), 2.45 (s, 3 H), 1.36 (qu, *J* = 7.2 Hz, 2 H), 1.03 (d, *J* = 6.6 Hz, 3 H), 0.85 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.8,

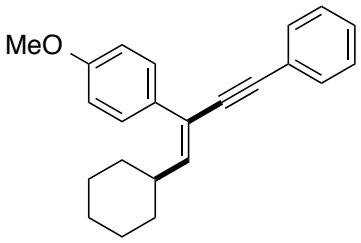
144.9, 138.5, 131.9, 129.6, 126.05, 125.96, 122.3, 120.4, 112.0, 92.5, 86.5, 40.6, 35.1, 30.4, 20.6, 15.6, 11.9. **HRMS** (ESI): Calcd for $C_{23}H_{28}NS$ [M]: 350.1941; Found: 350.1937.



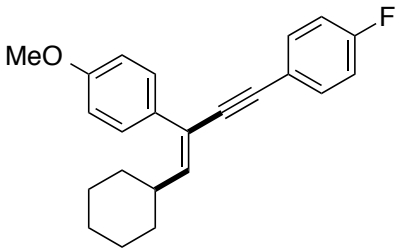
(*E*)-4-(3-(4-Bromophenyl)-5-methylhept-3-en-1-yn-1-yl)phenyl)(methyl)sulfane (2b). Following the general procedure A, the alkenylzinc reagent was prepared using 1-bromo-4-ethynylbenzene (127 mg, 0.70 mmol, 1 equiv), Zn (138 mg, 2.1 mmol, 3 equiv), TMSI (28 mg, 0.14 mmol, 20 mol %), and 2-iodobutane (386 mg, 2.1 mmol, 3 equiv). Following the general procedure B, the title compound was prepared using (4-(bromoethynyl)phenyl)(methyl)sulfane (93 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2b**) as pale brown solid (112 mg, 71%; ***E*:*Z*** >30:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.1 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.25 (d, *J* = 8.1 Hz, 2 H), 7.14 (d, *J* = 8.1 Hz, 2 H), 6.04 (d, *J* = 10.7 Hz, 1 H), 2.45 (s, 3 H), 2.41-2.33 (m, 1 H), 1.38-1.30 (m, 2 H), 1.01 (d, *J* = 6.6 Hz, 3 H), 0.82 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.8, 139.1, 137.0, 131.8, 131.5, 130.4, 125.9, 121.6, 121.4, 119.8, 91.1, 87.6, 35.3, 30.1, 20.5, 15.5, 12.0. **HRMS** (ESI): Calcd for $C_{21}H_{22}BrS$ [M+H]: 387.0602; Found: 387.0599.



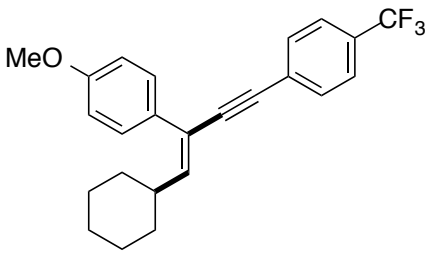
(*E*)-(4-(3-(4-Chlorophenyl)-4-cyclohexylbut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane (2c). Following the general procedure A, the alkenylzinc reagent was prepared using 1-chloro-4-ethynylbenzene (96 mg, 0.70 mmol, 1 equiv), Zn (92 mg, 1.4 mmol, 2 equiv), and iodocyclohexane (294 mg, 1.4 mmol, 2 equiv). Following the general procedure B, the title compound was prepared using (4-(bromoethynyl)phenyl)(methyl)sulfane (93 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2c**) as a yellow solid (79 mg, 52%; ***E*:*Z*** > 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36-7.31 (ovrlp, 6 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 6.09 (d, *J* = 10.5 Hz, 1 H), 2.45 (s, 3 H), 2.34-2.25 (m, 1 H), 1.73-1.61 (ovrlp, 5 H), 1.25-1.13 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.3, 139.1, 136.5, 133.3, 131.8, 130.1, 128.5, 125.9, 120.8, 119.8, 91.3, 87.5, 38.3, 32.9, 25.9, 25.5, 15.5. **HRMS** (ESI): Calcd for $C_{23}H_{24}ClS$ [M]: 367.1287; Found: 367.1288.



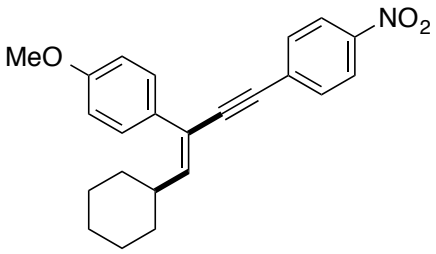
(*E*)-1-(1-Cyclohexyl-4-phenylbut-1-en-3-yn-2-yl)-4-methoxybenzene (2d). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using (bromoethynyl)benzene (74 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2d**) as pale brown oil (81 mg, 63%; ***E*:*Z*** = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 6.1 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.29-7.24 (ovrlp, 3 H), 6.91 (d, *J* = 8.4 Hz, 2 H), 6.05 (d, *J* = 10.4 Hz, 1 H), 3.81 (s, 3 H), 2.46-2.33 (m, 1 H), 1.75-1.60 (ovrlp, 5 H), 1.26-1.12 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.0, 145.3, 131.6, 130.4, 129.9, 128.3, 127.9, 123.8, 121.3, 113.7, 92.0, 87.1, 55.4, 38.2, 33.0, 26.0, 25.6. **HRMS** (ESI): Calcd for $C_{23}H_{25}O$ [M+H]: 317.1906; Found: 317.1906.



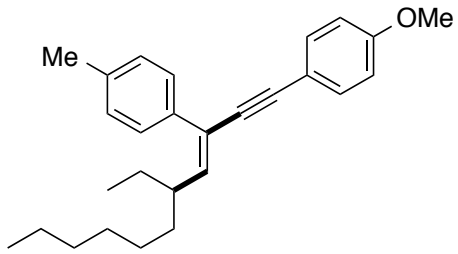
(*E*)-1-(4-Cyclohexyl-3-(4-methoxyphenyl)but-3-en-1-yn-1-yl)-4-fluorobenzene (2e). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 1-(bromoethynyl)-4-fluorobenzene (82 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2e**) as low-melting pale brown solid (80 mg, 58%; ***E*:*Z*** = 16:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39 (dd, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HF}$ = 5.6 Hz, 2 H), 7.34 (d, *J* = 8.5 Hz, 2 H), 6.97 (dd, $^{3}J_{HH}$ = 8.6 Hz, $^{3}J_{HF}$ = 8.6 Hz, 2 H), 6.91 (d, *J* = 8.5 Hz, 2 H), 6.04 (d, *J* = 10.4 Hz, 1 H), 3.82 (s, 3 H), 2.44-2.34 (m, 1 H), 1.80-1.54 (ovrlp, 5 H), 1.27-1.12 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.3 (d, $^{1}J_{CF}$ = 247.3 Hz), 159.0, 145.4, 133.4 (d, $^{3}J_{CF}$ = 8.2 Hz), 130.3, 129.9, 121.2, 119.9 (d, $^{4}J_{CF}$ = 3.5 Hz), 115.6 (d, $^{2}J_{CF}$ = 21.9 Hz), 113.8, 91.7, 86.0, 55.4, 38.2, 33.0, 26.0, 25.6. **HRMS** (ESI): Calcd for $C_{23}H_{24}FO$ [M+H]: 335.1804; Found: 335.1806.



(*E*)-1-(4-Cyclohexyl-3-(4-methoxyphenyl)but-3-en-1-yn-1-yl)-4-(trifluoromethyl)benzene (2f). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 1-(bromoethynyl)-4-(trifluoromethyl)benzene (102 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2f**) as yellow oil (122 mg, 77%; ***E*:*Z*** = 8.1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.4 Hz, 2 H), 7.51 (d, *J* = 8.5 Hz, 2 H), 7.34 (d, *J* = 8.5 Hz, 2 H), 6.93 (d, *J* = 8.5 Hz, 2 H), 6.10 (d, *J* = 10.4 Hz, 1 H), 3.84 (s, 3 H), 2.46-2.36 (m, 1 H), 1.75-1.60 (ovrlp, 5 H), 1.26-1.13 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.1, 146.6, 131.8, 130.0, 129.9, 129.6 (q, J_{CF} = 32.4 Hz), 127.7 (q, J_{CF} = 1.3 Hz), 125.3 (q, J_{CF} = 3.8 Hz), 124.1 (q, J_{CF} = 270.3 Hz), 121.0, 113.9, 94.5, 85.8, 55.4, 38.3, 33.0, 26.0, 25.6. **HRMS** (ESI): Calcd for $C_{24}H_{24}F_3O$ [M+H]: 385.1779; Found: 385.1777.

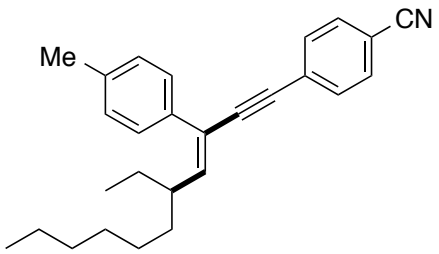


(*E*)-1-(4-Cyclohexyl-3-(4-methoxyphenyl)but-3-en-1-yn-1-yl)-4-nitrobenzene (2g). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 1-(bromoethynyl)-4-nitrobenzene (93 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (50:1) as an eluent to afford the title compound (**2g**) as viscous brown oil (66 mg, 45%; ***E*:*Z*** = 9.6:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.6 Hz, 2 H), 7.53 (d, *J* = 8.6 Hz, 2 H), 7.33 (d, *J* = 8.5 Hz, 2 H), 6.93 (d, *J* = 8.6 Hz, 2 H), 6.14 (d, *J* = 10.5 Hz, 1 H), 3.84 (s, 3 H), 2.47-2.36 (m, 1 H), 1.78-1.60 (ovrlp, 5 H), 1.27-1.15 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.2, 147.5, 146.8, 132.2, 130.9, 129.8, 129.6, 129.7, 120.9, 113.9, 97.6, 85.3, 55.4, 38.3, 32.9, 25.9, 25.5. **HRMS** (ESI): Calcd for $C_{23}H_{24}NO_3$ [M+H]: 362.1756; Found: 362.1758.

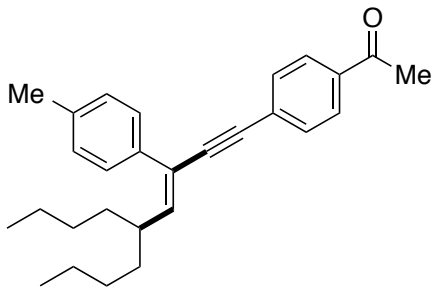


(*E*)-1-(5-Ethyl-1-(4-methoxyphenyl)undec-3-en-1-yn-3-yl)-4-methylbenzene (2h). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg) and 3-iodononane (267 mg). Following the general procedure B, the title compound was prepared using 1-(bromoethynyl)-4-methoxybenzene (93 mg, 0.44 mmol, 1 equiv), CuI (13 mg, 15 mol %), bipy (14 mg, 20 mol %), and the alkenylzinc reagent prepared in the general procedure A (~1.6 equiv). The crude product was purified using hexanes as an eluent to afford the title compound (**2h**) as a low-melting

yellow solid (111 mg, 67%; ***E*:*Z*** > 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 7.8 Hz, 2 H), 7.15 (d, *J* = 7.8 Hz, 2 H), 6.80 (d, *J* = 8.4 Hz, 2 H), 5.94 (d, *J* = 10.8 Hz, 1 H), 3.77 (s, 3 H), 2.36-2.29 (ovrlp, 4 H), 1.48-1.12 (ovrlp, 12 H), 0.88-0.83 (ovrlp, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.4, 144.8, 136.9, 135.7, 133.0, 128.9, 128.7, 123.8, 116.0, 113.9, 90.6, 87.2, 55.3, 40.3, 35.4, 32.0, 29.7, 28.5, 27.4, 22.8, 21.3, 14.2, 12.0. **HRMS** (ESI): Calcd for $C_{27}H_{35}O$ [M+H]: 375.2688; Found: 375.2683.

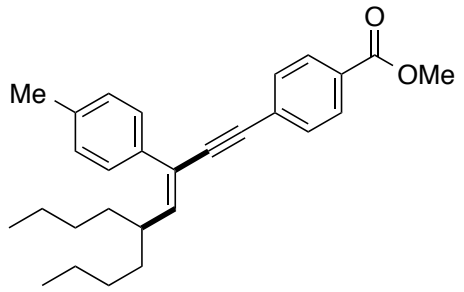


(*E*)-4-(5-Ethyl-3-(*p*-tolyl)undec-3-en-1-yn-1-yl)benzonitrile (2i). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg) and 3-iodononane (267 mg). Following the general procedure B, the title compound was prepared using 4-(bromoethynyl)benzonitrile (91 mg, 0.44 mmol, 1 equiv), CuI (13 mg, 15 mol %), bipy (14 mg, 20 mol %), and the alkenylzinc reagent prepared in the general procedure A (~1.6 equiv). The crude product was purified using hexanes/EtOAc (50:1) as an eluent to afford the title compound (**2i**) as viscous yellow oil (105 mg, 65%; ***E*:*Z*** > 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.2 Hz, 2 H), 7.47 (d, *J* = 8.2 Hz, 2 H), 7.25 (d, *J* = 7.8 Hz, 2 H), 7.18 (d, *J* = 7.8 Hz, 2 H), 6.05 (d, *J* = 10.8 Hz, 1 H), 2.41-2.31 (ovrlp, 4 H), 1.50-1.12 (ovrlp, 12 H), 0.87-0.84 (ovrlp, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.6, 137.3, 134.7, 132.0, 129.1, 128.9, 128.6, 123.1, 118.7, 111.0, 96.5, 85.8, 40.4, 35.2, 31.9, 29.6, 28.4, 27.4, 22.8, 21.3, 14.2, 12.0. **HRMS** (ESI): Calcd for $C_{27}H_{32}N$ [M]: 370.2528; Found: 370.2529.

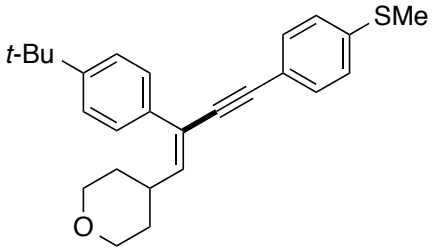


(*E*)-1-(4-(5-Butyl-3-(*p*-tolyl)non-3-en-1-yn-1-yl)phenyl)ethan-1-one (2j). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg) and 5-iodononane (267 mg). Following the general procedure B, the title compound was prepared using 1-(4-(bromoethynyl)phenyl)ethan-1-one (98 mg, 0.44 mmol, 1 equiv), CuI (13 mg, 15 mol %), bipy (14 mg, 20 mol %), and the alkenylzinc reagent prepared in the general procedure A (~1.6 equiv). The crude product was purified using hexanes as an eluent to afford the title compound (**2j**) as viscous yellow oil (111 mg, 65%; ***E*:*Z*** > 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.9 Hz, 2 H), 7.48 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 7.6 Hz, 2 H), 7.18 (d, *J* = 7.5 Hz, 2 H), 6.05 (d, *J* = 10.8 Hz, 1 H), 2.57 (s, 3 H), 2.46-2.40 (m, 1 H), 2.37 (s, 3 H), 1.43-1.13 (ovrlp, 12 H), 0.85 (t, *J* = 6.7 Hz, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.4, 147.3, 137.2, 135.9, 135.0, 131.6, 129.0, 128.9, 128.6, 128.3, 123.1, 95.5, 86.6, 38.8, 35.4, 29.6, 26.7, 23.0, 21.3, 14.1. **HRMS** (ESI): Calcd for $C_{28}H_{35}O$ [M+H]: 387.2688; Found:

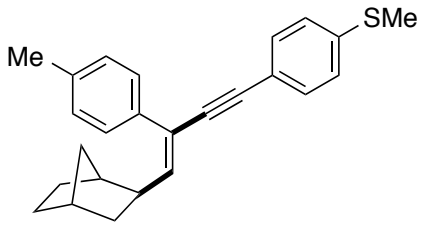
387.2682.



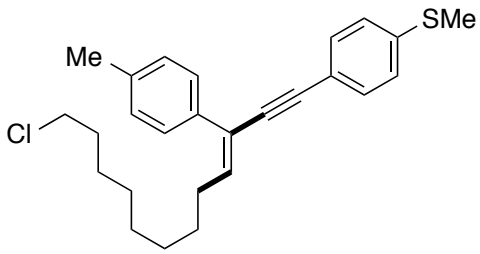
Methyl (*E*)-4-(5-Butyl-3-(*p*-tolyl)non-3-en-1-yn-1-yl)benzoate (2k). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg) and 5-iodononane (267 mg). Following the general procedure B, the title compound was prepared using methyl 4-(bromoethynyl)benzoate (105 mg, 0.44 mmol, 1 equiv), CuI (13 mg, 15 mol %), bipy (14 mg, 20 mol %), and the alkenylzinc reagent prepared in the general procedure A (~1.6 equiv). The crude product was purified using hexanes as an eluent to afford the title compound (**2k**) as viscous yellow oil (106 mg, 60%; ***E*:*Z*** > 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.1 Hz, 2 H), 7.47 (d, *J* = 8.1 Hz, 2 H), 7.26 (d, *J* = 7.8 Hz, 2 H), 7.17 (d, *J* = 7.8 Hz, 2 H), 6.04 (d, *J* = 10.8 Hz, 1 H), 3.89 (s, 3 H), 2.46-2.38 (m, 1 H), 2.36 (s, 3 H), 1.42-1.12 (ovrlp, 12 H), 0.85 (t, *J* = 7.0 Hz, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.7, 147.1, 137.1, 135.0, 131.4, 129.5, 129.1, 129.0, 128.68, 128.65, 123.1, 95.1, 86.6, 52.2, 38.8, 35.4, 29.6, 23.0, 21.3, 14.1. **HRMS** (ESI): Calcd for $C_{28}H_{35}O_2$ [M+H]: 403.2627; Found: 403.2632.



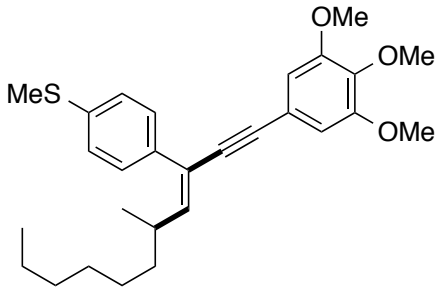
(*E*)-4-(2-(4-(*tert*-Butyl)phenyl)-4-(4-(methylthio)phenyl)but-1-en-3-yn-1-yl)tetrahydro-2*H*-pyran (2l). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (92 mg, 1.4 mmol, 2 equiv), and 4-iodotetrahydro-2*H*-pyran (297 mg, 1.4 mmol, 2 equiv). Following the general procedure B, the title compound was prepared using (4-(bromoethynyl)phenyl)(methyl)sulfane (93 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2l**) as viscous pale-brown oil (103 mg, 64%; ***E*:*Z*** = 19:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.9 Hz, 2 H), 7.34-7.32 (ovrlp, 4 H), 7.14 (d, *J* = 7.8 Hz, 2 H), 6.05 (d, *J* = 10.2 Hz, 1 H), 3.93 (d, *J* = 11 Hz, 2 H), 3.38-3.32 (m, 2 H), 2.73-2.61 (m, 1 H), 2.45 (s, 3 H), 1.61-1.54 (ovrlp, 4 H), 1.35 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.7, 143.1, 139.0, 134.7, 131.9, 128.3, 126.0, 125.5, 123.1, 119.9, 91.6, 87.6, 67.3, 35.4, 34.8, 32.7, 31.5, 15.6. **HRMS** (ESI): Calcd for $C_{26}H_{31}OS$ [M]: 391.2096; Found: 391.2093.



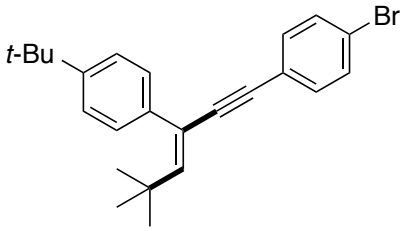
(4-((*E*)-4-(Bicyclo[2.2.1]heptan-2-yl)-3-(*p*-tolyl)but-3-en-1-yn-1 yl)phenyl)(methyl)sulfane (2m). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (92 mg, 1.4 mmol, 2 equiv), and 2-iodobicyclo[2.2.1]heptane (311 mg, 1.4 mmol, 2 equiv). Following the general procedure B, the title compound was prepared using (4-(bromoethynyl)phenyl)(methyl)sulfane (93 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2m**) as viscous pale-brown oil (87 mg, 59%; ***E*:*Z*** > 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43-7.31 (ovrlp, 4 H), 7.18 (d, *J* = 7.8 Hz, 2 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 6.11 (d, *J* = 10.6 Hz, 1 H), 2.44 (s, 3 H), 2.44-2.34 (ovrlp, 4 H), 2.27 (s, 1 H), 2.11 (s, 1 H), 1.55-1.47 (m, 4 H), 1.39-1.32 (m, 1 H), 1.25-1.09 (m, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.2, 138.7, 137.2, 134.9, 131.8, 128.9, 126.0, 120.9, 120.2, 92.1, 86.9, 43.3, 41.8, 39.6, 36.7, 36.4, 29.5, 29.0, 21.3, 15.5. **HRMS** (ESI): Calcd for $C_{25}H_{27}S$ [M+H]: 359.1833; Found: 359.1833.



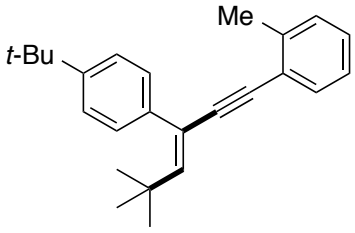
(*E*)-(4-(12-Chloro-3-(*p*-tolyl)dodec-3-en-1-yn-1-yl)phenyl)(methyl)sulfane (2n). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (138 mg, 2.1 mmol, 3 equiv), TMSI (28 mg, 0.14 mmol, 20 mol %), and 1-chloro-8-iodooctane (577 mg, 2.1 mmol, 3 equiv), along with the additional use of $CuBr_2$ (15 mg, 10 mol %). Following the general procedure B, the title compound was prepared using (4-(bromoethynyl)phenyl)(methyl)sulfane (93 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2n**) as viscous brown oil (69 mg, 41%; ***E*:*Z*** = 9.4:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34-7.30 (ovrlp, 4 H), 7.19-7.14 (ovrlp, 4 H), 6.23 (t, *J* = 7.6 Hz, 1 H), 3.51 (t, *J* = 6.6 Hz, 2 H), 2.47 (s, 3 H), 2.37 (s, 3 H), 2.25 (q, *J* = 7.4 Hz, 2 H), 1.74 (qu, *J* = 7.4 Hz, 2 H), 1.45-1.25 (ovrlp, 10 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.2, 138.8, 137.3, 134.9, 131.9, 129.0, 128.8, 126.0, 123.5, 120.2, 91.9, 87.0, 45.3, 32.7, 29.8, 29.7, 29.4, 29.3, 28.9, 21.4, 15.6. **HRMS** (ESI): Calcd for $C_{26}H_{32}ClS$ [M]: 411.1913; Found: 411.1908.



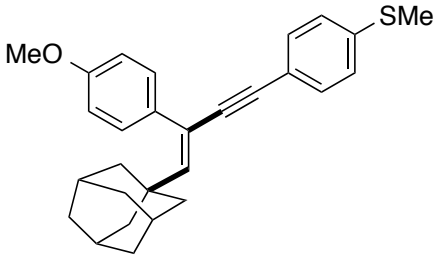
Methyl(4-(5-methyl-1-(3,4,5-trimethoxyphenyl)undec-3-en-1-yn-3-yl)phenyl)sulfane (2o). Following the general procedure A, the alkenylzinc reagent was prepared using (4-ethynylphenyl)(methyl)sulfane (104 mg, 0.70 mmol, 1 equiv), Zn (92 mg, 1.4 mmol, 2 equiv), and 2-iodooctane (336 mg, 1.4 mmol, 2 equiv). Following the general procedure B, the title compound was prepared using 5-(bromoethynyl)-1,2,3-trimethoxybenzene (111 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (100:1) as an eluent to afford the title compound (**2o**) as viscous brown oil (97 mg, 52%; ***E*:*Z*** > 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.2 Hz, 2 H), 7.25 (d, *J* = 8.1 Hz, 2 H), 6.66 (s, 2 H), 6.03 (d, *J* = 10.6 Hz, 1 H), 3.84 (s, 3 H), 3.83 (s, 6 H), 2.55-2.48 (ovrlp, 4 H), 1.33-1.13 (ovrlp, 10 H), 1.02 (d, *J* = 6.6 Hz, 3 H), 0.86 (t, *J* = 6.9 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.1, 146.8, 138.6, 137.7, 134.9, 129.2, 126.3, 121.7, 118.7, 108.8, 90.5, 87.4, 61.0, 56.2, 37.4, 33.6, 31.9, 29.5, 27.4, 22.8, 20.9, 15.8, 14.2. **HRMS** (ESI): Calcd for $C_{28}H_{37}O_3S$ [M+H]: 453.2463; Found: 453.2460.



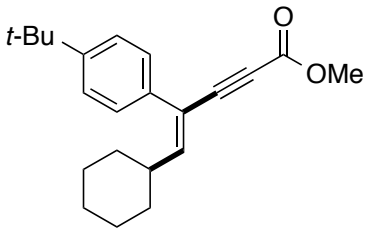
(*E*)-1-Bromo-4-(3-(4-(*tert*-butyl)phenyl)-5,5-dimethylhex-3-en-1-yn-1-yl)benzene (2p). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (126 mg, 0.80 mmol, 1 equiv), Zn (157 mg, 2.4 mmol, 3 equiv), $FeBr_2$ (17 mg, 0.08 mmol, 10 mol %), TMSI (32 mg, 0.16 mmol, 20 mol %), and 2-iodo-2-methylpropane (442 mg, 2.4 mmol, 3 equiv). Following the general procedure B, the title compound was prepared using 1-bromo-4-(bromoethynyl)benzene (122 mg, 0.47 mmol, 1 equiv), CuI (13.4 mg, 15 mol %), bipy (15 mg, 20 mol %), and the alkenylzinc reagent prepared in the general procedure A (~0.8 mmol, ~1.7 equiv). The crude product was purified using hexanes as an eluent to afford the title compound (**2p**) as yellow solid (116 mg, 62%; ***E*:*Z*** > 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.3 Hz, 2 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.24-7.19 (ovrlp, 4 H), 6.27 (s, 1 H), 1.33 (s, 9 H), 0.95 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.4, 150.3, 135.4, 132.9, 131.4, 128.8, 124.8, 122.8, 122.0, 121.9, 94.0, 85.9, 34.7, 34.6, 31.4, 31.0. **HRMS** (ESI): Calcd for $C_{24}H_{28}Br$ [M]: 395.1375; Found: 395.1380.



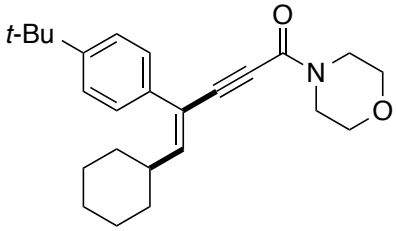
(*E*)-1-(3-(4-(*tert*-Butyl)phenyl)-5,5-dimethylhex-3-en-1-yn-1-yl)-2-methylbenzene (2q). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (126 mg, 0.80 mmol, 1 equiv), Zn (157 mg, 2.4 mmol, 3 equiv), $FeBr_2$ (17 mg, 0.08 mmol, 10 mol %), TMSI (32 mg, 0.16 mmol, 20 mol %), and 2-iodo-2-methylpropane (442 mg, 2.4 mmol, 3 equiv). Following the general procedure B, the title compound was prepared using 1-(bromoethynyl)-2-methylbenzene (92 mg, 0.47 mmol, 1 equiv), CuI (13.4 mg, 15 mol %), bipy (15 mg, 20 mol %), and the alkenylzinc reagent prepared in the general procedure A (~0.8 mmol, ~1.7 equiv). The crude product was purified using hexanes as an eluent to afford the title compound (**2q**) as viscous yellow oil (94 mg, 60%; ***E*:*Z*** > 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35-7.31 (ovrlp, 3 H), 7.25 (d, *J* = 8.2 Hz, 2 H), 7.15-7.10 (ovrlp, 2 H), 7.09-7.04 (m, 1 H), 6.25 (s, 1 H), 2.35 (s, 3 H), 1.33 (s, 9 H), 0.97 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.2, 149.4, 140.1, 136.0, 131.7, 129.4, 128.8, 127.9, 125.5, 124.8, 123.6, 122.6, 97.1, 86.2, 34.69, 34.68, 31.6, 21.2, 20.8. **HRMS** (ESI): Calcd for $C_{25}H_{31}$ [M+H]: 331.2420; Found: 331.2420.



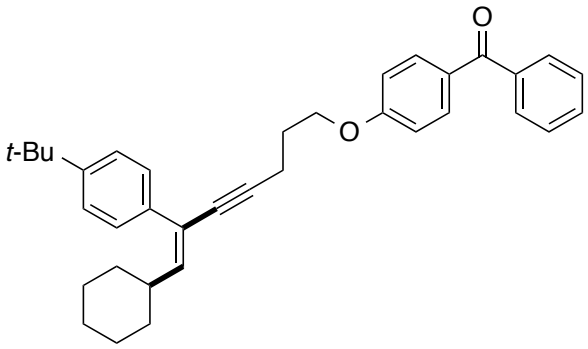
(4-((*E*)-4-(Adamantan-1-yl)-3-(4-methoxyphenyl)but-3-en-1-yn-1 yl)phenyl)(methyl)sulfane (2r). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (53 mg, 0.40 mmol, 1 equiv), Zn (131 mg, 2.0 mmol, 5 equiv), $FeBr_2$ (9 mg, 10 mol %), TMSI (24 mg, 0.12 mmol, 30 mol %), 1-iodoadamantane (524 mg, 2.0 mmol, 5 equiv), and DMA (0.8 mL), and the reaction mixture was stirred at room temperature for 4 d. THF (4.5 mL) was then added into the reaction mixture to form an *in-situ* alkenylzinc reagent. Following the general procedure B, the title compound was prepared using (4-(bromoethynyl)phenyl)(methyl)sulfane (54.5 mg, 0.24 mmol, 1 equiv), CuI (6.8 mg, 15 mol %), bipy (7.5 mg, 20 mol %), and the alkenylzinc reagent prepared in the general procedure A (~0.4 mmol, ~1.7 equiv). The crude product was purified using hexanes as an eluent to afford the title compound (**2r**) as a white solid (54 mg, 54%; ***E*:*Z*** > 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.1 Hz, 2 H), 7.22 (d, *J* = 8.3 Hz, 2 H), 7.11 (d, *J* = 8.1 Hz, 2 H), 6.85 (d, *J* = 8.3 Hz, 2 H), 6.00 (s, 1 H), 3.82 (s, 3 H), 2.44 (s, 3 H), 1.88-1.82 (m, 3 H), 1.62-1.52 (ovrlp, 12 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.8, 150.3, 138.6, 131.8, 131.5, 130.3, 125.9, 121.7, 120.3, 113.3, 93.4, 86.8, 55.3, 42.8, 37.3, 36.7, 28.5, 15.6. **HRMS** (ESI): Calcd for $C_{28}H_{31}OS$ [M+H]: 415.2088; Found: 415.2090.



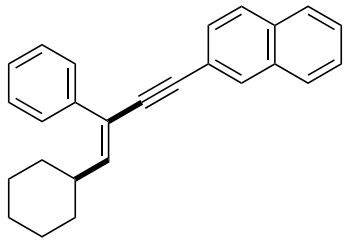
Methyl (*E*)-4-(4-(*tert*-Butyl)phenyl)-5-cyclohexylpent-4-en-2-ynoate (2s). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using methyl 3-bromopropiolate (67 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2s**) as viscous brown oil (64 mg, 48%; ***E*:*Z*** > 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.2 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 6.33 (d, *J* = 10.6 Hz, 1 H), 3.80 (s, 3 H), 2.57-2.45 (m, 1 H), 1.80-1.64 (ovrlp, 5 H), 1.37 (s, 9 H), 1.29-1.16 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.7, 151.9, 151.0, 132.8, 128.3, 125.5, 119.3, 89.4, 78.3, 52.7, 38.4, 34.8, 32.5, 31.4, 25.8, 25.3. **HRMS** (ESI): Calcd for $C_{22}H_{29}O_2$ [M+H]: 325.2168; Found: 325.2168.



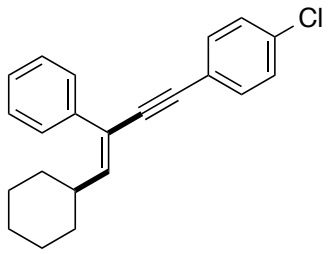
(*E*)-4-(4-(*tert*-Butyl)phenyl)-5-cyclohexyl-1-morpholinopent-4-en-2-yn-1-one (2t). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 3-bromo-1-morpholinoprop-2-yn-1-one (89 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (50:1) as an eluent to afford the title compound (**2t**) as viscous yellow oil (104 mg, 67%; ***E*:*Z*** = 12:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 8.1 Hz, 2 H), 6.22 (d, *J* = 10.6 Hz, 1 H), 3.72-3.67 (m, 4 H), 3.66-3.62 (ovrlp, 4 H), 2.50-2.41 (m, 1 H), 1.76-1.61 (ovrlp, 5 H), 1.34 (s, 9 H), 1.34-1.14 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.5, 150.8, 150.2, 133.2, 128.1, 125.4, 119.6, 93.9, 78.6, 66.9, 66.5, 47.2, 41.9, 38.2, 34.6, 32.6, 31.3, 25.8, 25.2. **HRMS** (ESI): Calcd for $C_{25}H_{34}NO_2$ [M+H]: 380.2589; Found: 380.2592.



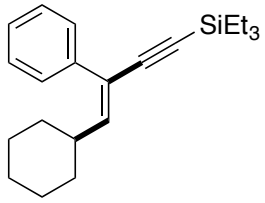
(*E*)-(4-((6-(4-(*tert*-Butyl)phenyl)-7-cyclohexylhept-6-en-4-yn-1-yl)oxy)phenyl)(phenyl)methanone (2u). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using (4-((5-bromopent-4-yn-1-yl)oxy)phenyl)(phenyl)methanone (141 mg), CuI (20 mg, 25 mol %), bipy (22 mg, 35 mol %), and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2u**) as viscous yellow oil (115 mg, 56%; ***E*:*Z*** = 18:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.3 Hz, 2 H), 7.75 (d, *J* = 7.4 Hz, 2 H), 7.55 (t, *J* = 7.1 Hz, 1 H), 7.46 (t, *J* = 7.3 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.27 (d, *J* = 7.8 Hz, 2 H), 6.95 (d, *J* = 8.3 Hz, 2 H), 4.15 (t, *J* = 5.9 Hz, 2 H), 2.55 (t, *J* = 6.6 Hz, 2 H), 2.42-2.31 (m, 1 H), 2.04 (qu, *J* = 6.3 Hz, 2 H), 1.74-1.58 (ovrlp, 5 H), 1.31 (s, 9 H), 1.22-1.08 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.6, 162.8, 150.2, 144.5, 138.4, 135.3, 132.6, 131.9, 130.1, 129.8, 128.3, 128.2, 125.1, 121.5, 114.2, 86.1, 83.9, 66.8, 37.9, 34.6, 33.1, 31.4, 28.4, 26.0, 25.5, 16.2. **HRMS** (ESI): Calcd for $C_{36}H_{41}O_2$ [M+H]: 505.3099; Found: 505.3101.



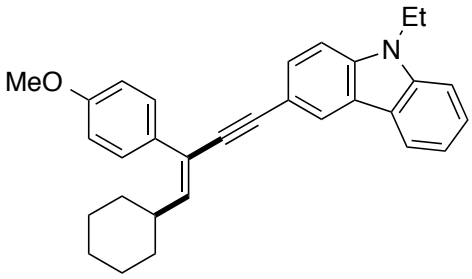
(*E*)-2-(4-Cyclohexyl-3-phenylbut-3-en-1-yn-1-yl)naphthalene (2v). Following the general procedure A, the alkenylzinc reagent was prepared using 1 ethynylbenzene (72 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 2-(bromoethynyl)naphthalene (95 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2v**) as viscous brown oil (75 mg, 54%; ***E*:*Z*** > 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (s, 1 H), 7.78-7.72 (ovrlp, 3 H), 7.49-7.43 (ovrlp, 5 H), 7.40 (t, *J* = 7.6 Hz, 2 H), 7.31 (t, *J* = 7.3 Hz, 1 H), 6.17 (d, *J* = 10.5 Hz, 1 H), 2.45-2.36 (m, 1 H), 1.73-1.60 (ovrlp, 5 H), 1.26-1.16 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.3, 138.1, 133.2, 132.7, 131.3, 128.8, 128.6, 128.4, 128.0, 127.85, 127.81, 127.5, 126.6, 122.0, 121.1, 38.2, 33.0, 26.0, 25.6. **HRMS** (ESI): Calcd for $C_{26}H_{24}$ [M]: 336.1878; Found: 336.1869.



(*E*)-1-Chloro-4-(4-cyclohexyl-3-phenylbut-3-en-1-yn-1-yl)benzene (2w). Following the general procedure A, the alkenylzinc reagent was prepared using ethynylbenzene (72 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 1-(bromoethynyl)-4-chlorobenzene (88 mg), CuI (16 mg, 20 mol %), bipy (19 mg, 30 mol %), and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2w**) as yellow solid (74 mg, 57%; ***E*:*Z*** > 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41-7.30 (ovrlp, 7 H), 7.24 (d, *J* = 8.2 Hz, 2 H), 6.11 (d, *J* = 10.4 Hz, 1 H), 2.43-2.32 (m, 1 H), 1.77-1.58 (ovrlp, 5 H), 1.28-1.10 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.5, 137.8, 133.9, 132.8, 128.69, 128.66, 128.4, 127.6, 122.3, 121.7, 92.7, 86.3, 38.2, 33.0, 26.0, 25.5. **HRMS** (ESI): Calcd for $C_{22}H_{22}Cl$ [M+H]: 321.1410; Found: 321.1407.

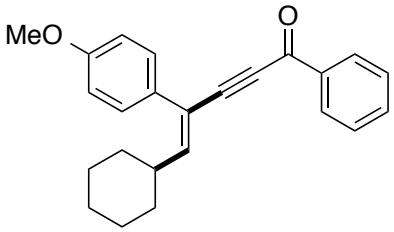


(*E*)-(4-Cyclohexyl-3-phenylbut-3-en-1-yn-1-yl)triethylsilane (2x). Following the general procedure A, the alkenylzinc reagent was prepared using 1 ethynylbenzene (72 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using (bromoethynyl)triethylsilane (90 mg), CuI (16 mg, 20 mol %), bipy (19 mg, 30 mol %), and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2x**) as colorless oil (85 mg, 64%; ***E*:*Z*** = 9.9:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.32 (ovrlp, 4 H), 7.26 (t, *J* = 7.3 Hz, 1 H), 6.06 (d, *J* = 10.5 Hz, 1 H), 2.39-2.31 (m, 1 H), 1.78-1.58 (ovrlp, 5 H), 1.23-1.13 (ovrlp, 5 H), 0.99 (t, *J* = 7.9 Hz, 9 H), 0.61 (d, *J* = 7.9 Hz, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.6, 137.9, 128.7, 128.2, 127.4, 122.1, 108.2, 89.0, 38.1, 33.0, 26.0, 25.8, 7.7, 4.7. **HRMS** (ESI): Calcd for $C_{22}H_{33}Si$ [M]: 325.2351; Found: 325.2348.

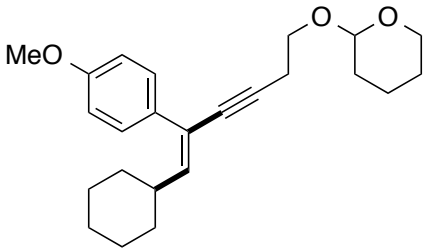


(*E*)-3-(4-Cyclohexyl-3-(4-methoxyphenyl)but-3-en-1-yn-1-yl)-9-ethyl-9*H*-carbazole (2y). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92

mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 3-(bromoethynyl)-9-ethyl-9*H*-carbazole (122 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (100:1) as an eluent to afford the title compound (**2y**) as viscous brown oil (119 mg, 67%; ***E*:*Z*** > 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.19 (s, 1 H), 8.02 (d, *J* = 7.7 Hz, 1 H), 7.52 (d, *J* = 8.4 Hz, 1 H), 7.45-7.40 (ovrlp, 3 H), 7.33 (d, *J* = 8.1 Hz, 1 H), 7.26 (d, *J* = 8.4 Hz, 1 H), 7.20 (d, *J* = 7.4 Hz, 1 H), 6.93 (d, *J* = 8.2 Hz, 2 H), 6.08 (d, *J* = 10.4 Hz, 1 H), 4.25 (q, *J* = 7.1 Hz, 2 H), 3.80 (s, 3 H), 2.46-2.37 (m, 1 H), 1.76-1.59 (ovrlp, 5 H), 1.36 (t, *J* = 7.1 Hz, 3 H), 1.26-1.13 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.9, 144.3, 140.3, 139.4, 130.9, 129.9, 129.3, 126.1, 124.0, 123.0, 122.6, 121.7, 120.6, 119.3, 113.8, 113.7, 108.7, 108.4, 90.1, 88.5, 55.3, 38.2, 37.7, 33.2, 26.0, 25.6, 13.9. **HRMS** (ESI): Calcd for $C_{31}H_{32}NO$ [M]: 434.2484; Found: 434.2481.

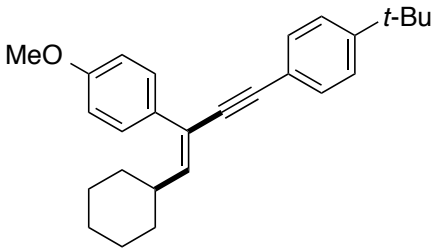


(*E*)-5-Cyclohexyl-4-(4-methoxyphenyl)-1-phenylpent-4-en-2-yn-1-one (2z). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 3-bromo-1-phenylprop-2-yn-1-one (86 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**2z**) as viscous brown oil (69 mg, 49%; ***E*:*Z*** = 8.7:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.6 Hz, 2 H), 7.58 (t, *J* = 6.8 Hz, 1 H), 7.46 (d, *J* = 7.5 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 6.94 (d, *J* = 8.4 Hz, 2 H), 6.39 (d, *J* = 10.5 Hz, 1 H), 3.84 (s, 3 H), 2.53-2.42 (m, 1 H), 1.80-1.58 (ovrlp, 5 H), 1.31-1.13 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 178.1, 159.4, 152.0, 137.2, 139.9, 129.9, 129.6, 128.6, 128.5, 119.8, 114.0, 96.3, 85.3, 55.4, 38.6, 32.6, 25.8, 25.4. **HRMS** (ESI): Calcd for $C_{24}H_{25}O_2$ [M+H]: 345.1855; Found: 345.1855.

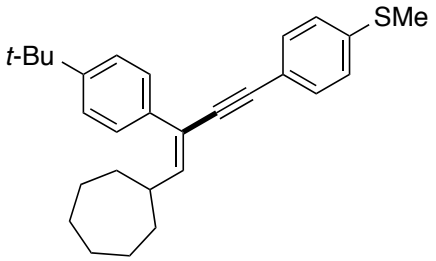


(*E*)-2-((6-Cyclohexyl-5-(4-methoxyphenyl)hex-5-en-3-yn-1-yl)oxy)tetrahydro-2*H*-pyran (2aa). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 2-((4-bromobut-3-yn-1-yl)oxy)tetrahydro-2*H*-pyran (96 mg), CuI (20 mg, 25 mol %), bipy (22 mg, 35 mol %), and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (50:1) as an eluent to afford the title compound (**2aa**) as viscous yellow oil (82 mg, 54%; ***E*:*Z*** = 16:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.6

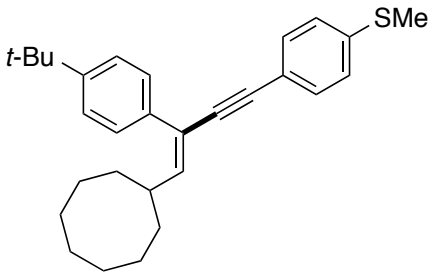
Hz, 2 H), 6.87 (d, J = 8.6 Hz, 2 H), 5.87 (d, J = 10.4 Hz, 1 H), 4.64 (t, J = 3.0 Hz, 1 H), 3.88-3.79 (ovrlp, 5 H), 3.60-3.54 (m, 1 H), 3.50-3.45 (m, 1 H), 2.62 (d, J = 7.2 Hz, 2 H), 2.35-2.28 (m, 1 H), 1.85-1.46 (ovrlp, 11 H), 1.21-1.07 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.8, 144.1, 130.8, 129.8, 121.3, 113.6, 98.7, 84.4, 83.9, 65.9, 62.2, 55.3, 37.9, 33.1, 30.7, 26.0, 25.57, 25.56, 21.0, 19.5. **HRMS** (ESI): Calcd for $C_{24}H_{33}O_3$ [M]: 369.2430; Found: 369.2432.



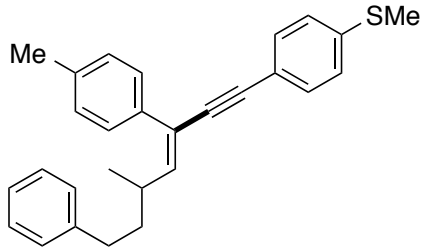
(*E*)-1-(*tert*-Butyl)-4-(4-cyclohexyl-3-(4-methoxyphenyl)but-3-en-1-yn-1-yl)benzene (S2a). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 1-(bromoethynyl)-4-(*tert*-butyl)benzene (97 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S2a**) as viscous yellow oil (67 mg, 44%; ***E*:*Z*** = 17:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36-7.35 (ovrlp, 4 H), 7.30 (d, J = 8.2 Hz, 2 H), 6.90 (d, J = 8.4 Hz, 2 H), 6.03 (d, J = 10.4 Hz, 1 H), 3.82 (s, 3 H), 2.44-2.36 (ovrlp, 1 H), 1.77-1.57 (ovrlp, 5 H), 1.29 (s, 9 H), 1.25-1.12 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.9, 151.1, 144.9, 131.3, 130.6, 129.9, 125.3, 121.5, 120.8, 113.7, 91.4, 87.3, 55.4, 38.2, 34.8, 33.1, 31.3, 26.0, 25.6.



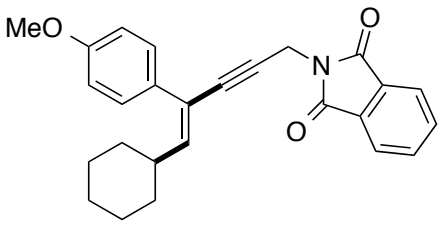
(*E*)-(4-(3-(4-(*tert*-Butyl)phenyl)-4-cycloheptylbut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane (S2b). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (92 mg, 1.4 mmol, 2 equiv), and iodocycloheptane (314 mg, 1.4 mmol, 2 equiv). Following the general procedure B, the title compound was prepared using (4-(bromoethynyl)phenyl)(methyl)sulfane (93 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S2b**) as viscous brown oil (71 mg, 43%; ***E*:*Z*** > 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42-7.30 (ovrlp, 6 H), 7.14 (d, J = 8.1 Hz, 2 H), 6.17 (d, J = 10.8 Hz, 1 H), 2.65-2.56 (m, 1 H), 2.45 (s, 3 H), 1.79-1.64 (m, 4 H), 1.59-1.40 (ovrlp, 8 H), 1.34 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.3, 146.3, 138.7, 134.9, 131.9, 128.5, 126.0, 125.2, 120.3, 120.2, 92.3, 86.7, 39.2, 34.9, 34.7, 31.5, 28.7, 26.2, 15.6.



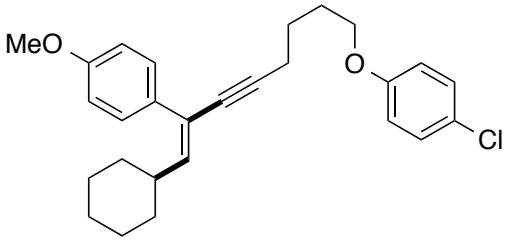
(*E*)-(4-(3-(4-(*tert*-Butyl)phenyl)-4-cyclooctylbut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane (S2c). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (92 mg, 1.4 mmol, 2 equiv), and iodocyclooctane (333 mg, 1.4 mmol, 2 equiv). Following the general procedure B, the title compound was prepared using (4-(bromoethynyl)phenyl)(methyl)sulfane (93 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S2c**) as viscous brown oil (78 mg, 46%; ***E*:*Z*** > 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40-4.32 (ovrlp, 6 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 6.18 (d, *J* = 10.8 Hz, 1 H), 2.71-2.63 (m, 1 H), 2.45 (s, 3 H), 1.73-1.63 (ovrlp, 4 H), 157-1.42 (ovrlp, 10 H), 1.34 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.3, 146.4, 138.7, 134.9, 131.9, 128.5, 126.0, 125.2, 120.31, 120.27, 92.3, 86.7, 37.4, 34.7, 32.1, 31.5, 27.4, 26.2, 25.0, 15.6.



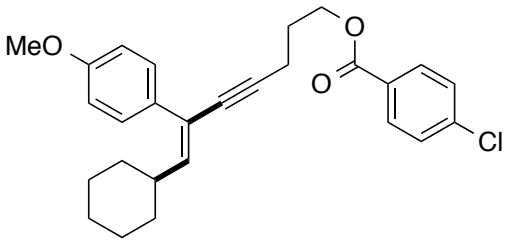
(*E*)-Methyl(4-(5-methyl-7-phenyl-3-(*p*-tolyl)hept-3-en-1-yn-1-yl)phenyl)sulfane (S2d). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (137 mg, 2.1 mmol, 3 equiv), and (3-iodobutyl)benzene (546 mg, 2.1 mmol, 3 equiv). Following the general procedure B, the title compound was prepared using (4-(bromoethynyl)phenyl)(methyl)sulfane (93 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S2d**) as viscous pale-brown oil (93 mg, 39%; ***E*:*Z*** = 18:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* =7.8 Hz, 2 H), 7.21-7.11 (ovrlp, 7 H), 7.05 (d, *J* =7.3 Hz, 2 H), 6.06 (d, *J* =10.6 Hz, 1 H), 2.64-2.56 (m, 2 H), 2.49-2.42 (ovrlp, 4 H), 2.36 (s, 3 H), 1.63 (q, *J* =7.6 Hz, 2 H), 1.07 (d, *J* = 6.5 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.6, 142.4, 138.9, 137.2, 135.1, 131.9, 129.1, 128.6, 128.5, 128.3, 126.0, 125.7, 123.0, 120.1, 91.8, 87.3, 39.4, 33.8, 33.2, 21.4, 21.0, 15.5.



(*E*)-2-(5-Cyclohexyl-4-(4-methoxyphenyl)pent-4-en-2-yn-1-yl)isoindoline-1,3-dione (S2e). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 2-(3-bromoprop-2-yn-1-yl)isoindoline-1,3-dione (117 mg), CuI (20 mg, 25 mol %), bipy (22 mg, 35 mol %), and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (50:1) as an eluent to afford the title compound (**S2e**) as low-melting yellow solid (67 mg, 41%; ***E*:*Z*** = 17:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90-7.84 (m, 2 H), 7.74-7.69 (m, 2 H), 7.25 (d, *J* = 8.6 Hz, 2 H), 6.86 (d, *J* = 8.5 Hz, 2 H), 5.94 (d, *J* = 10.5 Hz, 1 H), 4.58 (s, 2 H), 3.80 (s, 3 H), 2.36-2.27 (m, 1 H), 1.72-1.57 (ovrlp, 5 H), 1.24-1.07 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.2, 158.9, 145.9, 134.2, 132.2, 130.0, 129.8, 123.5, 120.4, 113.6, 85.4, 80.1, 55.3, 38.0, 32.9, 28.0, 25.9, 25.5.

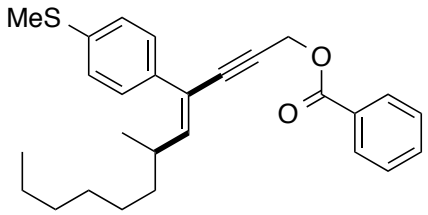


(*E*)-1-Chloro-4-((8-cyclohexyl-7-(4-methoxyphenyl)oct-7-en-5-yn-1-yl)oxy)benzene (S2f). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 1-((6-bromohex-5-yn-1-yl)oxy)-4-chlorobenzene (118 mg), CuI (20 mg, 25 mol %), bipy (22 mg, 35 mol %), and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S2f**) as viscous yellow oil (86 mg, 49%; ***E*:*Z*** = 18:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.6 Hz, 2 H), 6.87 (d, *J* = 8.4 Hz, 2 H), 6.79 (d, *J* = 8.6 Hz, 2 H), 5.85 (d, *J* = 10.4 Hz, 1 H), 3.93 (t, *J* = 6.2 Hz, 2 H), 3.80 (s, 3 H), 2.39 (d, *J* = 6.9 Hz, 2 H), 2.35-2.27 (m, 1 H), 1.89 (qu, *J* = 7.6 Hz, 2 H), 1.74-1.56 (ovrlp, 7 H), 1.24-1.08 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.8, 157.7, 143.9, 131.0, 129.7, 129.4, 125.5, 121.4, 115.8, 113.6, 87.1, 83.5, 67.8, 55.3, 38.0, 33.1, 28.5, 26.0, 25.6, 25.4, 19.3.

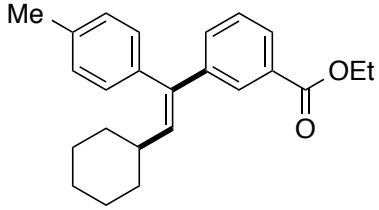


(*E*)-7-Cyclohexyl-6-(4-methoxyphenyl)hept-6-en-4-yn-1-yl 4-chlorobenzoate (S2g). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure B, the title compound was prepared using 5-bromopent-4-yn-1-yl 4-chlorobenzoate (124 mg), CuI (20 mg, 25 mol %), bipy (22 mg, 35 mol %), and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S2g**) as viscous yellow oil (80 mg, 44%; ***E*:*Z*** = 16:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.3 Hz, 2 H), 7.39 (d, *J* = 8.3 Hz, 2 H), 7.26 (d, *J* =

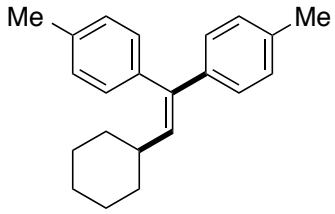
8.3 Hz, 2 H), 6.87 (d, *J* = 8.4 Hz, 2 H), 5.86 (d, *J* = 10.4 Hz, 1 H), 4.42 (t, *J* = 6.2 Hz, 2 H), 3.81 (s, 3 H), 2.51 (t, *J* = 7.0 Hz, 2 H), 2.34-2.27 (m, 1 H), 2.00 (qu, *J* = 6.6 Hz, 2 H), 1.74-1.57 (ovrlp, 5 H), 1.20-1.08 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.8, 158.8, 144.2, 139.5, 131.1, 130.8, 129.7, 128.9, 128.8, 121.2, 113.6, 86.0, 83.8, 64.2, 55.4, 38.0, 33.1, 28.1, 26.0, 25.6, 16.5.



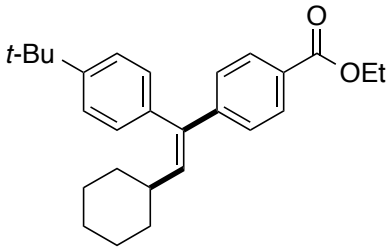
(*E*)-6-Methyl-4-(4-(methylthio)phenyl)dodec-4-en-2-yn-1-yl benzoate (S2h). Following the general procedure A, the alkenylzinc reagent was prepared using (4-ethynylphenyl)(methyl)sulfane (104 mg) and 2-iodooctane (252 mg). Following the general procedure B, the title compound was prepared using 3-bromoprop-2-yn-1-yl benzoate (98 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S2h**) as viscous yellow oil (64 mg, 37%; ***E*:*Z*** > 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (d, *J* =7.7 Hz, 2 H), 7.56 (t, *J* =7.2 Hz, 1 H), 7.44 (t, *J* =7.6 Hz, 2 H), 7.27-7.22 (ovrlp, 4 H), 6.00 (d, *J* =10.7 Hz, 1 H), 5.06 (s, 2 H), 2.51-2.43 (ovrlp, 4 H), 1.30-1.13 (ovrlp, 10 H), 0.98 (d, *J* =6.5 Hz, 3 H), 0.85 (d, *J* =6.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 148.0, 137.8, 134.4, 133.3, 129.9, 129.8, 129.1, 128.5, 126.4, 120.9, 88.6, 80.9, 53.6, 37.3, 33.5, 31.9, 29.5, 27.4, 22.8, 20.8, 15.9, 14.2.



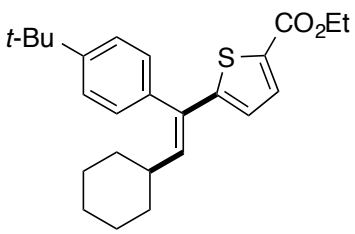
Ethyl (*E*)-3-(2-Cyclohexyl-1-(*p*-tolyl)vinyl)benzoate (3a). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using ethyl 3-iodobenzoate (113 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3a**) as viscous brown oil (88 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (s, 1 H), 7.89-7.85 (m, 1 H), 7.27-7.25 (ovrlp, 2 H), 7.16 (d, *J* = 7.6 Hz, 2 H), 7.05 (d, *J* = 8 Hz, 2 H), 5.92 (d, *J* = 10.0 Hz, 1 H), 4.37 (qu, *J* = 7.2 Hz, 2 H), 2.38 (s, 3 H), 2.26-2.11 (m, 1 H), 1.77-1.59 (ovrlp, 5 H), 1.28 (t, *J* = 6.8 Hz, 3 H), 1226-1.17 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.0, 143.8, 138.9, 137.2, 137.0, 136.7, 132.2, 130.5, 129.7, 129.1, 128.12, 128.08, 127.8, 61.1, 38.5, 33.4, 26.1, 25.7, 21.4, 14.5. **HRMS** (ESI): Calcd for $C_{24}H_{29}O_2$ [M]: 349.2168; Found: 349.2159.



4,4'-(2-Cyclohexylethene-1,1-diyl)bis(methylbenzene) (3b). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using 1-iodo-4-methylbenzene (89 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3b**) as white solid (74 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.14 (d, *J* = 7.8 Hz, 2 H), 7.08 (d, *J* = 8.1 Hz, 2 H), 7.06-7.03 (ovrlp, 4 H), 5.81 (d, *J* = 10.0 Hz, 1 H), 2.38 (s, 3 H), 2.30 (s, 3 H), 2.16-2.13 (m, 1 H), 1.66-1.59 (ovrlp, 5 H), 1.22-1.15 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.6, 139.4, 137.9, 136.4, 136.3, 135.2, 129.8, 128.9, 128.8, 127.3, 38.4, 33.6, 26.2, 25.8, 21.4, 21.2. **HRMS** (ESI): Calcd for $C_{22}H_{27}$ [M+H]: 291.2113; Found: 291.2110.

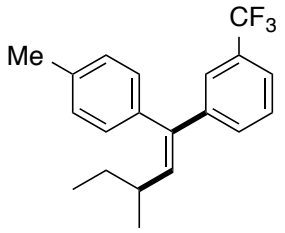


Ethyl (*E*)-4-(1-(4-(*tert*-Butyl)phenyl)-2-cyclohexylvinyl)benzoate (3c). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using ethyl 4-bromobenzoate (94 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3c**) as viscous brown oil (97 mg, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 8.2 Hz, 2 H), 7.07 (d, *J* = 8.1 Hz, 2 H), 5.96 (d, *J* = 10.1 Hz, 1 H), 4.34 (q, *J* = 7.1 Hz, 2 H), 7.27-2.17 (m, 1 H), 1.74-1.58 (ovrlp, 5 H), 1.36 (s, 9 H), 1.26-1.13 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.8, 150.0, 148.0, 139.1, 138.0, 136.9, 129.5, 129.4, 128.6, 127.3, 125.2, 60.9, 38.5, 34.8, 33.4, 31.6, 26.1, 25.7, 14.5. **HRMS** (ESI): Calcd for $C_{27}H_{35}O_2$ [M]: 391.2637; Found: 391.2639.

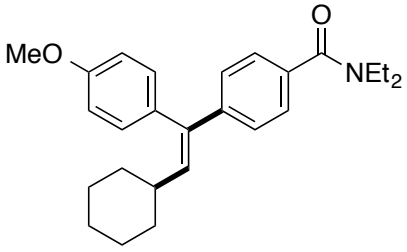


Ethyl (*E*)-5-(1-(4-(*tert*-Butyl)phenyl)-2-cyclohexylvinyl)thiophene-2-carboxylate (3d). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was

prepared using ethyl 5-bromothiophene-2-carboxylate (96 mg), $Ni(cod)_2$ (17 mg, 15 mol %), bipy (16 mg, 25 mol %), and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3d**) as viscous brown oil (86 mg, 53%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 3.7 Hz, 1 H), 7.39 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 7.9 Hz, 2 H), 6.60 (d, *J* = 3.7 Hz, 1 H), 6.09 (d, *J* = 10.0 Hz, 1 H), 4.31 (q, *J* = 7.1 Hz, 2 H), 2.15-2.00 (m, 1 H), 1.70-1.59 (ovrlp, 5 H), 1.42-1.29 (ovrlp, 12 H), 1.23-1.11 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.6, 154.8, 150.5, 137.4, 135.6, 133.68, 133.66, 130.9, 129.1, 125.3, 125.0, 38.2, 34.7, 33.1, 31.5, 26.0, 25.5, 14.5. **HRMS** (ESI): Calcd for $C_{25}H_{33}O_2S$ [M+H]: 397.2196; Found: 397.2193.

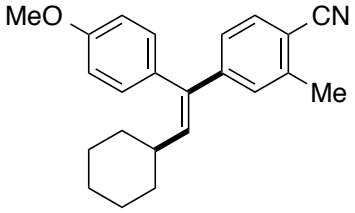


(*E*)-1-(3-Methyl-1-(*p*-tolyl)pent-1-en-1-yl)-3-(trifluoromethyl)benzene (3e). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure C, the title compound was prepared using 1-iodo-3-(trifluoromethyl)benzene (112 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3e**) as viscous colorless oil (85 mg, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (s, 1 H), 7.44-7.41 (m, 1 H), 7.35-7.29 (ovrlp, 2 H), 7.18 (d, *J* = 7.7 Hz, 2 H), 7.04 (d, *J* = 7.9 Hz, 2 H), 5.87 (d, *J* = 10.2 Hz, 1 H), 2.38 (s, 3 H), 2.30-2.19 (m, 1 H), 1.36 (qu, *J* = 7.3 Hz, 2 H), 1.01 (d, *J* = Hz, 2 H), 1.01 (d, *J* = 6.6 Hz, 3 H), 0.84 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ144.0, 139.4, 137.8, 136.9, 130.7, 130.6 (q, *J* = 31.7 Hz), 129.8, 129.2, 128.6, 124.4 (q, *J* = 270.8 Hz), 123.6 (q, *J* = 3.8 Hz), 123.4 (q, *J* = 3.7 Hz), 35.7, 30.5, 21.4, 21.0, 12.2. **GCMS:** $[M]^+$ = 318 was detected which corresponds to $C_{20}H_{21}F_3$.

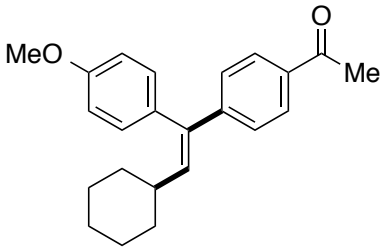


(*Z*)-4-(2-Cyclohexyl-1-(4-methoxyphenyl)vinyl)-*N*,*N*-diethylbenzamide (3f). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using 4-bromo-*N*,*N*-diethylbenzamide (105 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3f**) as low-melting yellow solid (98 mg, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27-7.21 (ovrlp, 4 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 5.91 (d, *J* = 10.0 Hz, 1 H), 3.83 (s, 3 H), 3.52 (br s, 2 H), 3.28 (br s, 2 H), 2.27-2.10 (m, 1 H), 1.80-1.55 (ovrlp, 5 H), 1.38-1.17 (ovrlp, 11 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.3, 158.6, 144.2, 138.7, 136.6, 135.5, 132.5, 130.9, 127.2, 126.2, 113.6, 55.2, 43.3, 39.4,

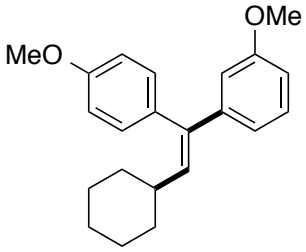
38.4, 33.4, 26.0, 25.7, 14.3, 13.1. **HRMS** (ESI): Calcd for $C_{26}H_{34}NO_2$ [M+H]: 392.2584; Found: 392.2584.



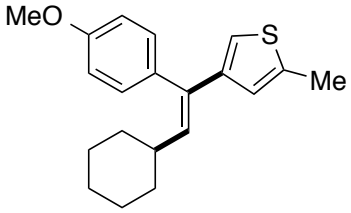
(*E*)-4-(2-Cyclohexyl-1-(4-methoxyphenyl)vinyl)-2-methylbenzonitrile (3g). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using 4-bromo-2-methylbenzonitrile (76 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (100:1) as an eluent to afford the title compound (**3g**) as low-melting colorless solid (76 mg, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.1 Hz, 1 H), 7.13 (s, 1 H), 7.07 (d, *J* = 8.2 Hz, 1 H), 7.04 (d, *J* = 8.4 Hz, 2 H), 6.93 (d, *J* = 8.3 Hz, 2 H), 5.95 (d, *J* = 10.0 Hz, 1 H), 3.84 (s, 3 H), 2.47 (s, 3 H), 2.26-2.16 (m, 1 H), 1.68-1.61 (ovrlp, 5 H), 1.26-1.16 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.8, 147.8, 141.6, 138.8, 138.3, 132.3, 131.7, 130.9, 128.9, 125.2, 118.6, 113.9, 110.5, 55.3, 38.6, 33.2, 26.0, 25.6, 20.6. **HRMS** (ESI): Calcd for $C_{23}H_{26}NO$ [M]: 332.2009; Found: 332.2009.



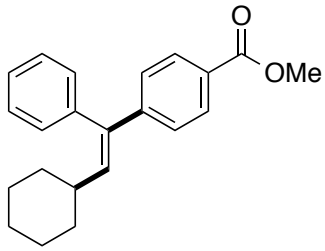
(*Z*)-1-(4-(2-Cyclohexyl-1-(4-methoxyphenyl)vinyl)phenyl)ethan-1-one (3h). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using 1-(4-iodophenyl)ethan-1-one (101 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3h**) as viscous pale-yellow oil (85 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.1 Hz, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.08 (d, *J* = 8.3 Hz, 2 H), 6.92 (d, *J* = 8.3 Hz, 2 H), 5.99 (d, *J* = 10.0 Hz, 1 H), 3.83 (s, 3 H), 2.55 (s, 3 H), 2.25-2.17 (m, 1 H), 1.69-1.61 (ovrlp, 5 H), 1.25-1.17 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.7, 158.7, 148.1, 138.6, 138.2, 135.4, 132.1, 130.9, 128.3, 127.3, 113.8, 55.3, 38.6, 33.3, 26.6, 26.0, 25.6. **HRMS** (ESI): Calcd for $C_{23}H_{27}O_2$ [M+H]: 335.2003; Found: 335.2006.



(*E*)-1-(2-Cyclohexyl-1-(4-methoxyphenyl)vinyl)-3-methoxybenzene (3i). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using 1-iodo-3-methoxybenzene (96 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3i**) as low-melting colorless solid (78 mg, 59%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 (t, *J* = 8.2 Hz, 1 H), 7.10 (d, *J* = 8.3 Hz, 2 H), 6.91 (d, *J* = 8.3 Hz, 2 H), 6.82 (d, *J* = 7.7 Hz, 1 H), 6.76-7.74 (ovrlp, 2 H), 5.88 (d, *J* = 9.8 Hz, 1 H), 3.84 (s, 3 H) 3.75 (s, 3 H), 2.24-2.08 (m, 1 H), 1.75-1.60 (ovrlp, 5 H), 1.1-1.16 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.5, 158.6, 145.0, 139.1, 136.2, 132.9, 131.0, 129.0, 120.1, 113.6, 113.4, 112.0, 55.34, 55.33, 38.4, 33.5, 26.2, 25.8. **HRMS** (ESI): Calcd for $C_{22}H_{27}O_2$ [M+H]: 323.2011; Found: 323.2005.

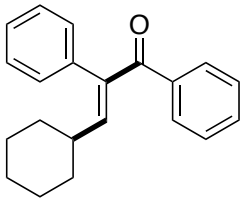


(*E*)-4-(2-Cyclohexyl-1-(4-methoxyphenyl)vinyl)-2-methylthiophene (3j). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using 4-bromo-2-methylthiophene (73 mg), $Ni(cod)_2$ (17 mg, 15 mol %), bipy (16 mg, 25 mol %), and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3j**) as viscous brown oil (70 mg, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.5 Hz, 2 H), 6.90 (d, *J* = 8.5 Hz, 2 H), 6.86 (s, 1 H), 6.42 (s, 1 H), 5.86 (d, *J* = 9.9 Hz, 1 H), 3.84 (s, 3 H), 2.44 (s, 3 H), 2.11-1.96 (m, 1 H), 1.70-1.58 (ovrlp, 5 H), 1.19-1.14 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 144.8, 139.7, 134.7, 134.4, 132.7, 130.6, 124.0, 119.6, 113.6, 55.4, 38.0, 33.5, 26.1, 25.8, 15.6. **HRMS** (ESI): Calcd for $C_{20}H_{25}OS$ [M+H]: 313.1617; Found: 313.1621.

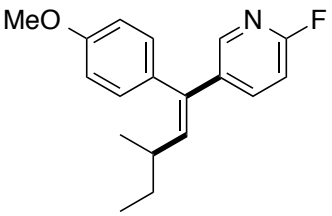


Methyl (*E*)-4-(2-Cyclohexyl-1-phenylvinyl)benzoate (3k). Following the general procedure A, the

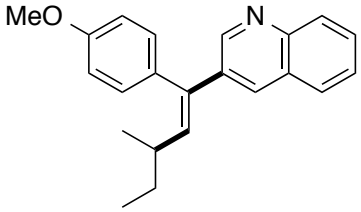
alkenylzinc reagent was prepared using ethynylbenzene (72 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using methyl 4-iodobenzoate (107 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3k**) as viscous pale-brown oil (107 mg, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 2 H), 7.39-7.32 (ovrlp, 3 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 7.2 Hz, 2 H), 6.0 (d, *J* = 10.0 Hz, 1 H), 3.88 (s, 3 H), 2.22-2.13 (m, 1 H), 1.68-1.60 (ovrlp, 5 H), 1.25-1.15 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.1, 147.5, 139.9, 139.1, 138.1, 129.8, 129.5, 128.4, 128.3, 127.2, 127.1, 52.1, 38.6, 33.3, 26.0, 25.6. **HRMS** (ESI): Calcd for $C_{22}H_{25}O_2$ [M+H]: 321.1855; Found: 321.1860.



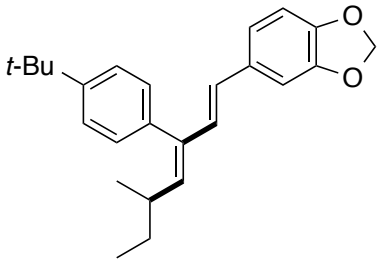
(*E*)-3-Cyclohexyl-1,2-diphenylprop-2-en-1-one (3l).[38] Following the general procedure A, the alkenylzinc reagent was prepared using ethynylbenzene (72 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using benzoyl chloride (58 mg) and the alkenylzinc reagent prepared in the general procedure A by stirring at rt. The crude product was purified using hexanes as an eluent to afford the title compound (**3l**) as pale yellow oil (62 mg, 52%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.6 Hz, 2 H), 7.50 (t, *J* = 7.3 Hz, 1 H), 7.42-7.36 (ovrlp, 4 H), 7.31 (t, *J* = 7.5 Hz, 1 H), 7.25 (d, *J* = 7.6 Hz, 2 H), 6.26 (d, *J* = 10.4 Hz, 1 H), 2.39-2.30 (m, 1 H), 1.74-1.57 (ovrlp, 5 H), 1.24-1.08 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.6, 150.2, 139.6, 138.6, 136.5, 132.0, 129.8, 129.5, 128.3, 128.2, 127.5, 38.4, 32.5, 25.8, 25.3.



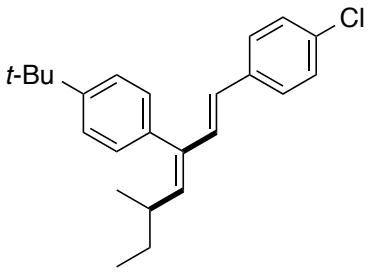
(*E*)-2-Fluoro-5-(1-(4-methoxyphenyl)-3-methylpent-1-en-1-yl)pyridine (3m). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure C, the title compound was prepared using 5-bromo-2-fluoropyridine (72 mg), $Ni(cod)_2$ (17 mg, 15 mol %), bipy (16 mg, 25 mol %), and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (50:1) as an eluent to afford the title compound (**3m**) as viscous pale-yellow oil (60 mg, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15 (s, 1 H), 7.65-7.61 (m, 1 H), 7.12 (d, *J* = 8.3 Hz, 2 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 6.87-6.84 (m, 1 H), 5.87 (d, *J* = 10.2 Hz, 1 H), 3.90 (s, 3 H), 2.40-2.29 (m, 1 H), 1.47-1.39 (m, 2 H), 1.08 (d, *J* = 6.6 Hz, 3 H), 0.90 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.7 (d, J_{CF} = 236.9 Hz), 158.9, 145.8 (d, J_{CF} = 14.5 Hz), 139.8 (d, J_{CF} = 7.7 Hz), 137.8, 137.0 (d, J_{CF} = 4.7 Hz), 136.0, 131.7, 130.8, 114.0, 108.7 (d, J_{CF} = 37.3 Hz), 55.4, 35.6, 30.4, 21.0, 12.1. **HRMS** (ESI): Calcd for $C_{18}H_{21}FNO$ [M]: 286.1607; Found: 286.1608.



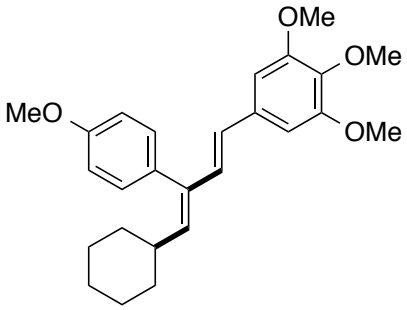
(*E*)-3-(1-(4-Methoxyphenyl)-3-methylpent-1-en-1-yl)quinolone (3n). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure C, the title compound was prepared using 3-bromoquionline (85 mg), $Ni(cod)_2$ (17 mg, 15 mol %), bipy (16 mg, 25 mol %), and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3n**) as viscous yellow oil (71 mg, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.94 (d, *J* = 1.6 Hz, 1 H), 8.06 (d, *J* = 8.4 Hz, 1 H), 7.76 (s, 1 H), 7.69 (d, *J* = 8.1 Hz, 1 H), 7.63 (t, *J* = 8.0 Hz, 1 H), 7.47 (t, *J* = 7.7 Hz, 1 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 6.94 (d, *J* = 8.4 Hz, 2 H), 6.01 (d, *J* = 10.2 Hz, 1 H), 3.85 (s, 3 H), 2.40-2.29 (m, 1 H), 1.41 (qu, *J* = 7.2 Hz, 2 H), 1.06 (d, *J* = 6.6 Hz, 3 H), 0.88 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.9, 150.1, 147.1, 138.4, 137.4, 135.9, 133.4, 131.9, 131.0, 129.2, 129.0, 128.0, 127.9, 126.7, 114.0, 55.4, 35.8, 30.5, 21.0, 12.2. **HRMS** (ESI): Calcd for $C_{22}H_{24}NO$ [M+H]: 318.1858; Found: 318.1854.



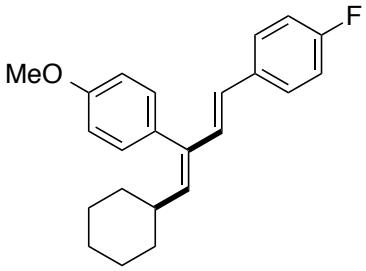
5-((1*E*,3*Z*)-3-(4-(*tert*-Butyl)phenyl)-5-methylhepta-1,3-dien-1-yl)benzo[*d*][1,3]dioxole (3o). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure C, the title compound was prepared using (*E*)-5-(2-bromovinyl)benzo[*d*][1,3]dioxole (93 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (100:1) as an eluent to afford the title compound (**3o**) as viscous brown oil (95 mg, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 6.90 (s, 1 H), 6.81 (d, *J* = 15.9 Hz, 1 H), 6.71-6.66 (ovrlp, 2 H), 5.92-5.88 (ovrlp, 3 H), 5.54 (d, *J* = 10.2 Hz, 1 H), 2.10-2.03 (m, 1 H), 1.36 (s, 9 H), 1.32-1.24 (m, 2 H), 0.93 (d, *J* = 6.6 Hz, 3 H), 0.80 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.5, 148.1, 146.8, 140.5, 140.2, 135.5, 132.6, 132.4, 129.3, 128.8, 125.1, 121.1, 108.3, 105.5, 101.0, 35.1, 34.7, 31.6, 30.4, 21.2, 12.1. **HRMS** (ESI): Calcd for $C_{25}H_{31}O_2$ [M+H]: 363.2324; Found: 363.2320.



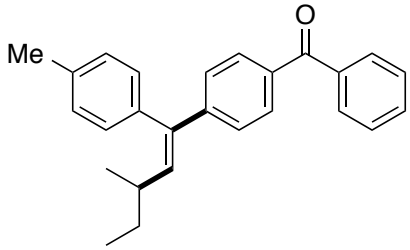
1-(*tert*-Butyl)-4-((1*E*,3*Z*)-1-(4-chlorophenyl)-5-methylhepta-1,3-dien-3-yl)benzene (3p). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure C, the title compound was prepared using (*E*)-1-(2-bromovinyl)-4-chlorobenzene (89 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3p**) as viscous brown oil (92 mg, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.8 Hz, 2 H), 7.24-7.19 (ovrlp, 4 H), 7.07 (d, *J* = 7.8 Hz, 2 H), 6.93 (d, *J* = 16.0 Hz, 1 H), 5.93 (d, *J* = 16.0 Hz, 1 H), 5.60 (d, *J* = 10.2 Hz, 1 H), 2.13-2.02 (m, 1 H), 1.37 (s, 9 H), 1.33-1.25 (m, 2 H), 0.93 (d, *J* = 6.6 Hz, 3 H), 0.80 (t, *J* = 7.4 Hz, 3 H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.7, 141.8, 140.1, 136.5, 135.2, 134.6, 132.5, 129.2, 128.7, 127.8, 127.5, 125.2, 35.2, 34.7, 31.6, 30.3, 21.1, 12.1. **HRMS** (ESI): Calcd for $C_{24}H_{29}Cl$ [M]: 352.1913; Found: 352.1913.



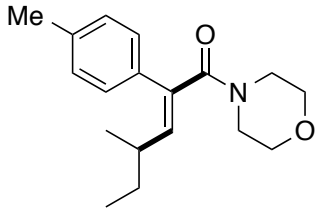
5-((1*E*,3*Z*)-4-Cyclohexyl-3-(4-methoxyphenyl)buta-1,3-dien-1-yl)-1,2,3-trimethoxybenzene (3q). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using (*E*)-5-(2-bromovinyl)-1,2,3-trimethoxybenzene (112 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (50:1) as an eluent to afford the title compound (**3q**) as yellow solid (122 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.2 Hz, 2 H), 6.95 (d, *J* = 8.2 Hz, 2 H), 6.87 (d, *J* = 15.8 Hz, 1 H), 6.53 (s, 2 H), 5.91 (d, *J* = 15.8 Hz, 1 H), 5.67 (d, *J* = 9.8 Hz, 1 H), 3.85 (s, 3 H), 3.84-3.79 (ovrlp, 9 H), 2.06-1.99 (m, 1 H), 1.71-1.52 (ovrlp, 5 H), 1.20-1.11 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.5, 153.3, 140.8, 138.9, 137.4, 133.61, 133.60, 130.61, 130.57, 129.2, 113.7, 103.2, 60.9, 56.0, 55.2, 38.0, 33.2, 26.0, 25.6. **HRMS** (ESI): Calcd for $C_{26}H_{33}O_4$ [M]: 409.2371; Found: 409.2373.



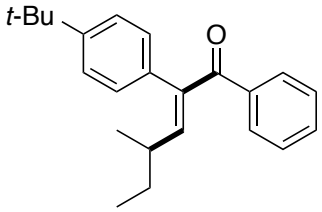
1-((1*E*,3*Z*)-4-Cyclohexyl-3-(4-methoxyphenyl)buta-1,3-dien-1-yl)-4-fluorobenzene (3r). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using (*E*)-1-(2-bromovinyl)-4-fluorobenzene (82 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**3r**) as white solid (94 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{CF}$ = 7.0 Hz, 2 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 6.96-6.92 (ovrlp, 4 H), 6.85 (d, *J* = 16.0 Hz, 1 H), 5.94 (d, *J* = 16.0 Hz, 1 H), 5.64 (d, *J* = 9.9 Hz, 1 H), 3.86 (s, 3 H), 2.04-1.92 (m, 1 H), 1.81-1.55 (ovrlp, 5 H), 1.20-1.05 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.9 (d, *J* = 244.6 Hz), 158.6, 141.1, 139.0, 134.1 (d, *J* = 3.3 Hz), 134.0 (d, *J* = 2.1 Hz), 130.7, 130.6, 128.1, 127.7 (d, *J* = 5.8 Hz), 115.5 (d, *J* = 21.4 Hz), 113.8, 55.4, 38.0, 33.3, 26.1, 25.7. **HRMS** (ESI): Calcd for $C_{23}H_{26}FO$ [M+H]: 337.1960; Found: 337.1962.



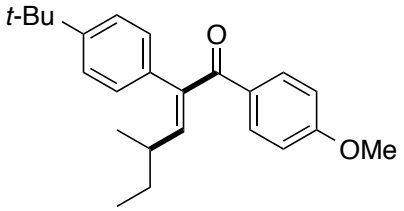
(*E*)-(4-(3-Methyl-1-(*p*-tolyl)pent-1-en-1-yl)phenyl)(phenyl)methanone (3s). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure C, the title compound was prepared using 4-benzoylphenyl trifluoromethanesulfonate (135 mg), $Ni(cod)_2$ (23 mg, 20 mol %), bipy (20 mg, 30 mol %), and the alkenylzinc reagent prepared in the general procedure A by stirring at rt. The crude product was purified using hexanes as an eluent to afford the title compound (**3s**) as viscous brown oil (126 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.2 Hz, 2 H), 7.70 (d, *J* = 8.3 Hz, 2 H), 7.56 (t, *J* = 7.3 Hz, 1 H), 7.45 (t, *J* = 7.4 Hz, 2 H), 7.32 (d, *J* = 8.3 Hz, 2 H), 7.20 (d, *J* = 7.8 Hz, 2 H), 7.07 (d, *J* = 7.9 Hz, 2 H), 5.78 (d, *J* = 10.2 Hz, 1 H), 2.39 (s, 3 H), 2.31-2.20 (m, 1 H), 1.37 (qu, *J* = 7.4 Hz, 2 H), 1.02 (d, *J* = 6.6 Hz, 3 H), 0.85 (t, *J* = 7.5 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.4, 147.2, 139.8, 138.5, 138.0, 137.0, 136.8, 135.7, 132.3, 130.2, 130.1, 129.8, 129.2, 128.3, 126.9, 35.8, 30.5, 21.4, 21.0, 12.2. **HRMS** (ESI): Calcd for $C_{26}H_{27}O$ [M]: 355.2062; Found: 355.2064.



(*E*)-4-Methyl-1-morpholino-2-(*p*-tolyl)hex-2-en-1-one (3t). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure C, the title compound was prepared using morpholine-4-carbonyl chloride (70 mg), $Ni(cod)_2$ (17 mg, 15 mol %), bipy (16 mg, 25 mol %), and the alkenylzinc reagent prepared in the general procedure A by stirring at rt. The crude product was purified using hexanes as an eluent to afford the title compound (**3t**) as viscous brown oil (75 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.21-7.15 (ovrlp, 4 H), 5.61 (d, *J* = 10.5 Hz, 1 H), 3.64 (br s, 2 H), 3.46 (br s, 2 H), 2.51-2.42 (m, 1 H), 2.35 (s, 3 H), 1.36 (qu, *J* = 7.2 Hz, 2 H), 1.01 (d, *J* = 6.6 Hz, 3 H), 0.85 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.7, 139.4, 137.5, 135.3, 133.0, 129.3, 128.4, 66.8, 47.6, 42.4, 34.2, 30.1, 21.3, 20.4, 12.0. **HRMS** (ESI): Calcd for $C_{18}H_{26}NO_2$ [M+H]: 288.1960; Found: 288.1958.

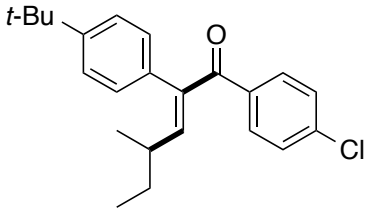


(*E*)-2-(4-(*tert*-Butyl)phenyl)-4-methyl-1-phenylhex-2-en-1-one (3u). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure C, the title compound was prepared using benzoyl chloride (57 mg) and the alkenylzinc reagent prepared in the general procedure A by stirring at rt. The crude product was purified using hexanes as an eluent to afford the title compound (**3u**) as viscous brown oil (102 mg, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.5 Hz, 2 H), 7.50 (t, *J* = 7.2 Hz, 1 H), 7.43-7.37 (ovrlp, 4 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 6.16 (d, *J* = 10.5 Hz, 1 H), 2.53-2.42 (m, 1 H), 1.40-1.28 (ovrlp, 11 H), 1.02 (d, *J* = 6.6 Hz, 3 H), 0.86 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.8, 150.5, 150.2, 140.5, 138.7, 133.4, 132.0, 129.8, 129.1, 128.2, 125.2, 35.5, 34.7, 31.5, 29.9, 20.4, 12.1. **HRMS** (ESI): Calcd for $C_{23}H_{29}O$ [M+H]: 321.2218; Found: 321.2220.

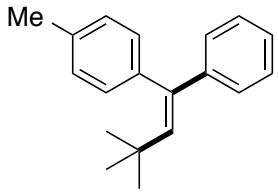


(*E*)-2-(4-(*tert*-Butyl)phenyl)-1-(4-methoxyphenyl)-4-methylhex-2-en-1-one (3v). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol,

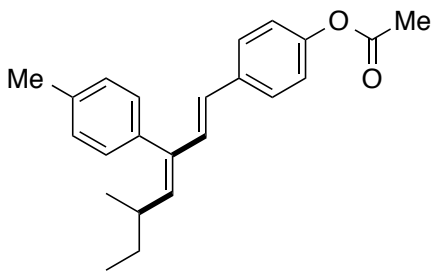
1.8 equiv). Following the general procedure C, the title compound was prepared using 4-methoxybenzoyl chloride (70 mg) and the alkenylzinc reagent prepared in the general procedure A by stirring at rt. The crude product was purified using hexanes as an eluent to afford the title compound (**3v**) as viscous brown oil (80 mg, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.6 Hz, 2 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 6.90 (d, *J* = 8.5 Hz, 2 H), 6.05 (d, *J* = 10.5 Hz, 1 H), 3.84 (s, 3 H), 2.54-2.43 (m, 1 H), 1.40-1.26 (ovrlp, 11 H), 1.03 (d, *J* = 6.6 Hz, 3 H), 0.88 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.5, 163.0, 150.1, 147.7, 140.3, 133.7, 132.3, 131.0, 129.0, 125.2, 113.5, 55.5, 35.2, 34.6, 31.5, 30.0, 20.5, 12.1. **GCMS:** $[M]^+$ = 350 was detected which corresponds to $C_{24}H_{30}O_2$.



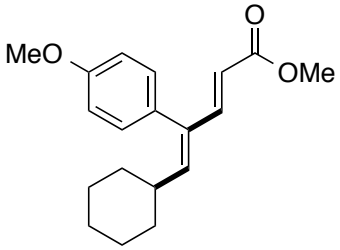
(*E*)-2-(4-(*tert*-Butyl)phenyl)-1-(4-chlorophenyl)-4-methylhex-2-en-1-one (3w). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure C, the title compound was prepared using 4-chlorobenzoyl chloride (72 mg) and the alkenylzinc reagent prepared in the general procedure A by stirring at rt. The crude product was purified using hexanes as an eluent to afford the title compound (**3w**) as viscous brown oil (77 mg, 53%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2 H), 7.40-7.37 (ovrlp, 4 H), 7.16 (d, *J* = 8.2 Hz, 2 H), 6.15 (d, *J* = 10.5 Hz, 1 H), 2.53-2.42 (m, 1 H), 1.40-1.31 (ovrlp, 11 H), 1.02 (d, *J* = 6.6 Hz, 3 H), 0.86 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.4, 150.6, 150.4, 140.3, 138.3, 137.0, 133.1, 131.2, 129.1, 128.6, 125.4, 35.5, 34.7, 31.5, 29.9, 20.4, 12.1. **HRMS** (ESI): Calcd for $C_{23}H_{28}ClO$ [M+H]: 355.1829; Found: 355.1823.



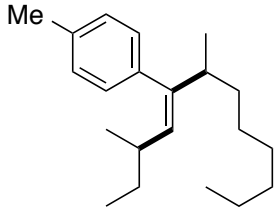
(*Z*)-1-(3,3-Dimethyl-1-phenylbut-1-en-1-yl)-4-methylbenzene (S3a).[35] Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (137 equiv, 2.1 mmol, 3 equiv), TMSI (28 mg, 0.14 mmol, 20 mol %) and 2-iodo-2-methylpropoane (386 mg, 2.1 mmol, 3 equiv). Following the general procedure C, the title compound was prepared using bromobenzene (65 mg, 0.70 mmol, 1 equiv) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S3a**) as viscous pale yellow oil (44 mg, 42%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.23-7.17 (ovrlp, 5 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 7.06 (d, *J* = 7.8 Hz, 2 H), 6.06 (s, 1 H), 2.37 (s, 3 H), 0.96 (s, 12 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.4, 140.1, 139.1, 137.8, 136.3, 130.2, 128.5, 128.0, 126.9, 126.5, 34.0, 31.4, 21.3.



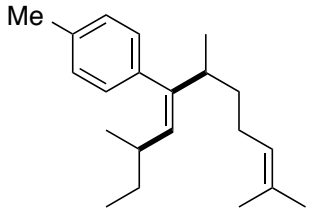
4-((1*E*,3*Z*)-5-methyl-3-(*p*-tolyl)hepta-1,3-dien-1-yl)phenyl acetate (S3b). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure C, the title compound was prepared using (*E*)-4-(2-bromovinyl)phenyl acetate (99 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S3d**) as brown solid (68 mg, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 7.6 Hz, 2 H), 7.04 (d, *J* = 7.7 Hz, 2 H), 6.98 (d, *J* = 8.4 Hz, 2 H), 6.92 (d, *J* = 15.9 Hz, 1 H), 5.94 (d, *J* = 16.0 Hz, 1 H), 5.58 (d, *J* = 10.2 Hz, 1 H), 2.39 (s, 3 H), 2.25 (s, 3 H), 2.11-2.00 (m, 1 H), 1.34-1.20 (m, 2 H), 0.93 (d, *J* = 6.6 Hz, 3 H), 0.79 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.5, 149.6, 141.3, 140.2, 136.4, 135.8, 135.5, 134.2, 129.5, 129.0, 128.2, 127.1, 121.6, 35.3, 30.3, 21.4, 21.2, 21.0, 12.1.



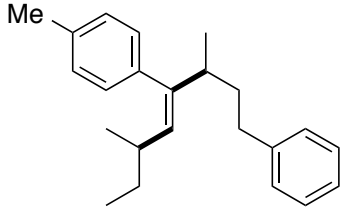
Methyl (2*E*,4*Z*)-5-Cyclohexyl-4-(4-methoxyphenyl)penta-2,4-dienoate (S3c). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg) and iodocyclohexane (221 mg). Following the general procedure C, the title compound was prepared using methyl (*Z*)-3-iodoacrylate (87 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S3e**) as pale yellow solid (66 mg, 54%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 15.5 Hz, 1 H), 7.00 (d, *J* = 8.4 Hz, 2 H), 6.91 (d, *J* = 8.4 Hz, 2 H), 5.91 (d, *J* = 10.1 Hz, 1 H), 5.38 (d, *J* = 15.5 Hz, 1 H), 3.83 (s, 3 H), 3.69 (s, 3 H), 2.10-1.96 (m, 1 H), 1.70-1.53 (ovrlp, 5 H), 1.21-1.05 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.0, 158.9, 149.9, 148.6, 137.8, 130.3, 129.0, 118.3, 113.9, 55.3, 51.4, 38.4, 32.6, 25.9, 25.4.



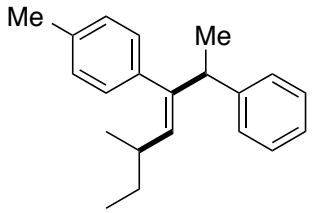
1-((*Z*)-3,6-Dimethyldodec-4-en-5-yl)-4-methylbenzene (4a). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure D, the title compound was prepared using 2-iodooctane (98 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**4a**) as viscous colorless oil (65 mg, 55%; ***Z*:*E*** > 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.10 (d, *J* = 7.6 Hz, 2 H), 6.92 (d, *J* = 7.9 Hz, 2 H), 5.09 (d, *J* = 10.0 Hz, 1 H), 2.34-2.26 (ovrlp, 4 H), 1.92-1.80 (m, 1 H), 1.36-1.14 (ovrlp, 12 H), 0.98-0.95 (m, 3 H), 0.91-0.84 (ovrlp, 6 H), 0.76 (t, *J* = 7.3 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.6, 138.6 (138.4), 135.5, 132.9 (132.8), 129.1, 128.4, 42.22 (42.18), 35.5 (35.4), 34.72 (34.68), 32.1, 30.51 (30.49), 29.64 (29.62), 27.7 (27.6), 22.8, 21.6, 21.3, 20.5 (20.3), 14.3, 12.21 (12.19). **HRMS** (ESI): Calcd for $C_{21}H_{34}$ [M]: 286.2661; Found: 286.2648.



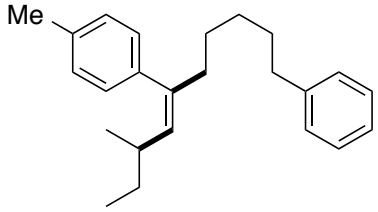
1-Methyl-4-((*Z*)-3,6,10-trimethylundeca-4,9-dien-5-yl)benzene (4b). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure D, the title compound was prepared using 6-iodo-2-methylhept-2-ene (98 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**4b**) as viscous colorless oil (64 mg, 55%; ***Z*:*E*** = 7.5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.10 (d, *J* = 7.6 Hz, 2 H), 6.93 (d, *J* = 7.2 Hz, 2 H), 5.12-5.07 (ovrlp, 2 H), 2.40-2.27 (ovrlp, 4 H), 2.05-1.95 (ovrlp, 2 H), 1.95-1.83 (m, 1 H), 1.68 (s, 3 H), 1.60 (s, 3 H), 1.45-1.36 (m, 1 H), 1.26-1.13 (ovrlp, 3 H), 0.98 (d, *J* = 6.7 Hz, 3 H), 0.85 (d, *J* = 6.6 Hz, 3 H), 0.77 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.4, 138.40 (138.36), 135.6, 133.1 (133.0), 131.2, 129.2 (129.1), 128.5, 125.11 (125.09), 41.93 (41.87), 35.5 (35.4), 34.72 (34.70), 30.49 (30.47), 26.29 (26.26), 25.9, 21.65 (21.60), 21.3, 20.5 (20.3), 17.89 (17.86), 12.23 (12.20). **HRMS** (ESI): Calcd for $C_{21}H_{33}$ [M]: 285.2582; Found: 285.2586.



1-((*Z*)-3,6-Dimethyl-1-phenyloct-4-en-4-yl)-4-methylbenzene (4c). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure E, the title compound was prepared using (3-iodobutyl)benzene (122 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**4c**) as viscous colorless oil (84 mg, 58%; ***Z*:*E*** = 14:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 7.2 Hz, 2 H), 7.17-7.10 (ovrlp, 5 H), 6.96 (d, *J* = 7.7 Hz, 2 H), 5.16 (d, *J* = 9.7 Hz, 1 H), 2.72-2.58 (m, 2 H), 2.39-2.29 (ovrlp, 4 H), 1.96-1.88 (m, 1 H), 1.74-1.65 (m, 1 H), 1.55-1.47 (m, 1 H), 1.29-1.16 (m, 2 H), 1.04-1.02 (m, 3 H), 0.89-0.86 (m, 3 H), 0.82-0.76 (m, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.0, 143.1, 138.2 (138.1), 135.7, 133.6 (133.5), 129.1, 128.6 (128.5), 128.4, 125.7, 42.0 (41.9), 37.2 (37.1), 34.8 (34.7), 34.1, 30.5, 21.62 (21.56), 21.3, 20.6 (20.4), 12.32 (12.28). **HRMS** (ESI): Calcd for $C_{23}H_{31}$ [M+H]: 307.2426; Found: 307.2421.

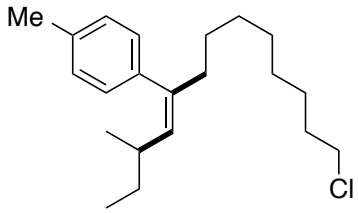


1-Methyl-4-((*Z*)-5-Methyl-2-phenylhept-3-en-3-yl)benzene (4d). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure E, the title compound was prepared using (1-bromoethyl)benzene (80 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**4d**) as viscous colorless oil (66 mg, 50%; ***Z*:*E*** > 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.23-7.21 (m, 2 H), 7.17-7.12 (ovrlp, 3 H), 7.01-6.95 (m, 2 H), 6.73-6.68 (m, 2 H), 5.28-5.20 (m, 1 H), 3.71-3.63 (m, 1 H), 2.29-2.27 (ovrlp, 3 H), 1.97-1.87 (m, 1 H), 1.38-1.35 (ovrlp, 3 H), 1.30-1.15 (m, 2 H), 0.91-0.84 (m, 3 H), 0.80-0.73 (ovrlp, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.2, 144.2 (144.1), 138.5 (138.3), 135.59 (135.58), 133.5, 129.01 (128.97), 128.38 (128.34), 128.10 (128.09), 128.1 (128.0), 125.94 (125.93), 47.8 (47.7), 34.81 (34.78), 30.5, 21.5 (21.4), 21.3, 20.35 (20.29), 12.24 (12.16). **HRMS** (ESI): Calcd for $C_{21}H_{27}$ [M]: 279.2113; Found: 279.2091.

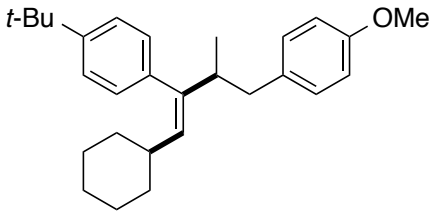


(*Z*)-1-methyl-4-(3-methyl-10-phenyldec-4-en-5-yl)benzene (4e). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure E, the title compound was prepared using (5-iodopentyl)benzene (129 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**4e**) as colorless oil (90 mg, 60%; ***Z*:*E*** = 6.3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28-7.23 (m, 2 H), 7.18-7.09 (ovrlp, 5 H), 6.98 (d, *J* = 7.6 Hz, 2 H), 5.11 (d, *J* = 10.0

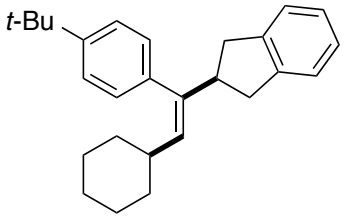
Hz, 1 H), 2.56 (t, *J* = 7.6 Hz, 2 H), 2.34 (s, 3 H), 2.26 (t, *J* = 7.1 Hz, 2 H), 2.07-1.96 (m, 1 H), 1.57 (qu, *J* = 6.3 Hz, 2 H), 1.36-1.28 (ovrlp, 4 H), 1.26-1.14 (m, 2 H), 0.87 (d, *J* = 6.6 Hz, 3 H), 0.76 (t, *J* = 7.3 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.0, 139.8, 139.1, 135.7, 133.6, 128.7, 128.5, 128.4, 128.3, 125.7, 39.6, 36.1, 34.6, 31.4, 30.5, 28.9, 28.1, 21.4, 21.3, 12.1. **HRMS** (ESI): Calcd for $C_{24}H_{33}$ [M]: 321.2582; Found: 321.2580.



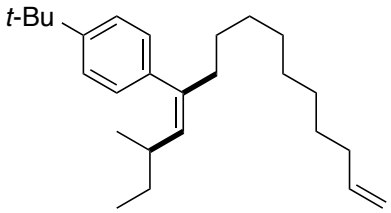
(*Z*)-1-(13-Chloro-3-methyltridec-4-en-5-yl)-4-methylbenzene (4f). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure E, the title compound was prepared using 1-chloro-8-iodooctane (129 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**4f**) as pale yellow oil (84 mg, 55%; ***Z*:*E*** = 6.5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 7.5 Hz, 2 H), 6.99 (d, *J* = 7.8 Hz, 2 H), 5.12 (d, *J* = 10.0 Hz, 1 H), 3.51 (t, *J* = 6.8 Hz, 2 H), 2.34 (s, 3 H), 2.26 (d, *J* = 6.1 Hz, 2 H), 2.08-1.97 (m, 1 H), 1.74 (qu, *J* = 7.4 Hz, 2 H), 1.39 (qu, *J* = 7.6 Hz, 2 H), 1.31-1.15 (ovrlp, 10 H), 0.88 (d, *J* = 6.7 Hz, 3 H), 0.77 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.8, 139.2, 135.7, 133.5, 128.7, 128.4, 45.3, 39.7, 34.7, 32.8, 30.5, 29.4, 29.1, 29.0, 28.2, 27.0, 21.5, 21.3, 12.1. **HRMS** (ESI): Calcd for $C_{21}H_{33}Cl$ [M]: 320.2271; Found: 320.2271.



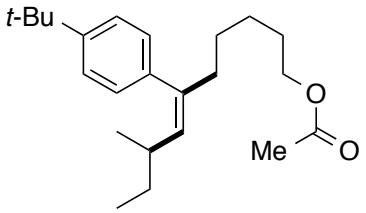
(*Z*)-1-(*tert*-Butyl)-4-(1-cyclohexyl-4-(4-methoxyphenyl)-3-methylbut-1-en-2-yl)benzene (4g). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg) and iodocyclohexane (221 mg). Following the general procedure D, the title compound was prepared using 1-(2-iodopropyl)-4-methoxybenzene (113 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**4g**) as viscous yellow oil (84 mg, 52%; ***Z*:*E*** = 8.2:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 8.4 Hz, 2 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 6.78 (d, *J* = 8.3 Hz, 2 H), 5.19 (d, *J* = 9.8 Hz, 1 H), 3.77 (s, 3 H), 2.77-2.72 (m, 1 H), 2.62-2.53 (m, 1 H), 2.35-2.29 (m, 1 H), 1.92-1.83 (m, 1 H), 1.64-1.49 (ovrlp, 5 H), 1.33 (s, 9 H), 1.13-1.02 (ovrlp, 5 H), 0.94 (d, *J* = 6.8 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.7, 148.9, 143.4, 138.6, 133.7, 132.6, 130.2, 128.5, 124.7, 113.5, 55.4, 43.5, 41.5, 37.3, 34.5, 33.8 (33.7), 31.6, 26.2 (25.8), 19.6. **HRMS** (ESI): Calcd for $C_{28}H_{39}O$ [M+H]: 391.2991; Found: 391.2995.



(*Z*)-2-(1-(4-(*tert*-Butyl)phenyl)-2-cyclohexylvinyl)-2,3-dihydro-1*H*-indene (4h). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg) and iodocyclohexane (221 mg). Following the general procedure D, the title compound was prepared using 1-(2-iodopropyl)-4-methoxybenzene (113 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**4h**) as white crystallize solid (89 mg, 61%; ***Z*:*E*** > 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.9 Hz, 2 H), 7.16-7.11 (m, 2 H), 7.10-7.06 (m, 2 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 5.35 (d, *J* = 9.6 Hz, 1 H), 3.39-3.30 (m, 1 H), 2.93-2.80 (m, 4 H), 1.97-1.88 (m, 1 H), 1.63-1.52 (ovrlp, 5 H), 1.33 (s, 9 H), 1.14-1.05 (ovrlp, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.9, 143.5, 141.2, 138.3, 132.8, 128.5, 126.1, 124.9, 124.3, 48.8, 38.3, 37.4, 34.6, 33.7, 31.6, 26.2, 25.8. **GCMS**: $[M]^+$ = 358 was detected which corresponds to $C_{27}H_{34}$.

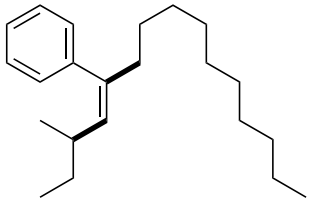


(*Z*)-1-(*tert*-Butyl)-4-(3-methylpentadeca-4,14-dien-5-yl)benzene (4i). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure E, the title compound was prepared using 10-iododec-1-ene (125 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**4i**) as colorless oil (93 mg, 56%; ***Z*:*E*** = 6.7:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.1 Hz, 2 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 5.85-5.75 (m, 1 H), 5.12 (d, *J* = 10.1 Hz, 1 H), 4.98 (d, *J* = 17.2 Hz, 1 H), 4.92 (d, *J* = 10.1 Hz, 1 H), 2.26 (t, *J* = 6.9 Hz, 2 H), 2.09-2.00 (ovrlp, 3 H), 1.36-1.19 (ovrlp, 23 H), 0.88 (d, *J* = 6.5 Hz, 3 H), 0.78 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.8, 139.9, 139.4, 139.1, 133.4, 128.1, 124.8, 114.2, 39.7, 34.6, 34.5, 34.0, 31.6, 30.6, 29.6, 29.5, 29.3, 29.1, 28.3, 21.5, 12.1. **HRMS** (ESI): Calcd for $C_{26}H_{43}$ [M+H]: 355.3365; Found: 355.3361.

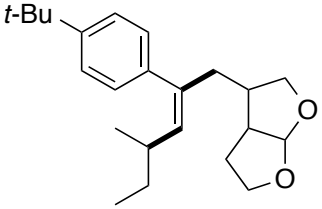


(*Z*)-6-(4-(*tert*-Butyl)phenyl)-8-methyldec-6-en-1-yl acetate (4j). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1

equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure E, the title compound was prepared using 5-iodopentyl acetate (120 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**4j**) as pale-brown oil (86 mg, 53%; ***Z*:*E*** = 7.1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.0 Hz, 2 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 5.13 (d, *J* = 10.1 Hz, 1 H), 4.02 (t, *J* = 6.7 Hz, 2 H), 2.28 (t, *J* = 6.8 Hz, 2 H), 2.10-2.00 (ovrlp, 4 H), 1.59 (d, *J* = 6.4 Hz, 2 H), 1.37-1.19 (ovrlp, 15 H), 0.88 (d, *J* = 6.6 Hz, 3 H), 0.78 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.4, 149.0, 139.5, 138.8, 133.7, 128.1, 124.9, 64.8, 39.5, 34.6, 34.5, 31.6, 30.5, 28.5, 27.9, 25.5, 21.5, 21.2, 12.1. **HRMS** (ESI): Calcd for $C_{23}H_{37}O_2$ [M]: 345.2794; Found: 345.2789.

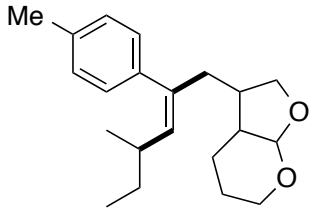


(*Z*)-(3-Methylpentadec-4-en-5-yl)benzene (4k). Following the general procedure A, the alkenylzinc reagent was prepared using ethynylbenzene (71 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure E, the title compound was prepared using 1-iodooctane (126 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**4k**) as colorless oil (70 mg, 50%; ***Z*:*E*** = 8.5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 7.2 Hz, 2 H), 7.21 (d, *J* = 6.9 Hz, 1 H), 7.10 (d, *J* = 7.6 Hz, 2 H), 5.15 (d, *J* = 10.1 Hz, 1 H), 2.28 (t, *J* = 6.8 Hz, 2 H), 2.06-1.95 (m, 1 H), 1.31-1.19 (ovrlp, 18 H), 0.89-0.86 (ovrlp, 6 H), 0.77 (d, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.3, 140.1, 133.6, 128.6, 128.0, 126.2, 39.7, 34.7, 32.1, 30.5, 29.81, 29.77, 29.6, 29.5, 29.3, 28.2, 22.9, 21.4, 14.3, 12.1. **GCMS** (ESI): $[M]^+$ = 300 was detected which corresponds to $C_{22}H_{36}$.

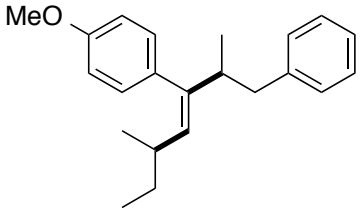


3-((*Z*)-2-(4-(*tert*-Butyl)phenyl)-4-methylhex-2-en-1-yl)hexahydrofuro[2,3-*b*]furan (4l). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure E, the title compound was prepared using 2-(allyloxy)-3-iodotetrahydrofuran (119 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (100:1) as an eluent to afford the title compound (**4l**) as viscous pale brown oil (80 mg, 50%; ***Z*:*E*** = 7.3:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 5.64 (d, *J* = 4.9 Hz, 1 H), 5.20 (d, *J* = 10.2 Hz, 1 H), 3.92-3.79 (ovrlp, 3 H), 3.42 (t, *J* = 9.2 Hz, 1 H), 2.74-2.63 (m, 1 H), 2.48-2.25 (ovrlp, 3 H), 2.13-2.04 (m, 1 H), 1.96-1.88 (m, 1 H), 1.84-1.73 (m, 1 H), 1.33 (s, 9 H), 1.27-1.17 (m, 2 H), 0.89 (d, *J* = 6.5 Hz, 3 H), 0.79 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.5, 138.0, 137.6, 135.0, 128.0, 125.1,

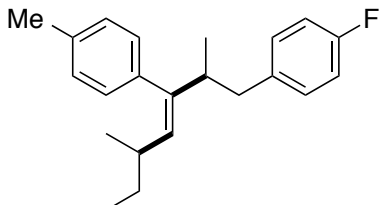
110.0, 72.53 (72.47), 69.3, 45.6 (45.5), 40.4, 38.0, 34.6, 34.54 (34.45), 31.5, 30.4, 25.3, 21.4 (21.3), 12.1. **HRMS** (ESI): Calcd for $C_{21}H_{31}O_2$ [M]: 343.2637; Found: 343.2684.



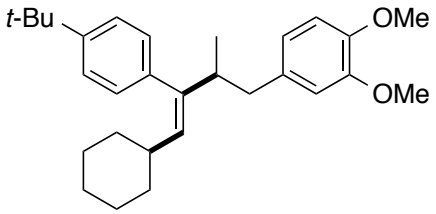
3-((*Z*)-4-Methyl-2-(*p*-tolyl)hex-2-en-1-yl)hexahydro-4*H*-furo[2,3-*b*]pyran (4m). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure E, the title compound was prepared using 2-(allyloxy)-3-iodotetrahydro-2*H*-pyran (126 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (100:1) as an eluent to afford the title compound (**4m**) as viscous pale brown oil (75 mg, 45%; ***Z*:*E*** = 7.2:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.13 (d, *J* = 7.8 Hz, 2 H), 6.99 (d, *J* = 7.8 Hz, 2 H), 5.19-5.13 (ovrlp, 2 H), 3.81 (t, *J* = 7.4 Hz, 1 H), 3.74 (td, *J* = 9.6 Hz, *J* = 2.0 Hz, 1 H), 3.68-3.58 (ovrlp, 2 H), 2.49-2.40 (m, 1 H), 2.35 (s, 3 H), 2.32-2.25 (m, 2 H), 2.09-1.98 (m, 1 H), 1.89-1.80 (m, 1 H), 1.73-1.51 (ovrlp, 3 H), 1.50-1.38 (m, 1 H), 1.33-1.14 (m, 2 H), 0.89-0.85 (m, 3 H), 0.80-0.74 (m, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.2, 137.70 (137.68), 136.3, 134.95 (134.93), 129.0, 128.3, 102.1, 70.0 (69.9), 61.18 (61.16), 38.87 (38.85), 37.8 (37.7), 36.9 (36.8), 34.7 (34.6), 30.4, 23.4, 21.33, 21.29, 19.61 (19.57), 12.12 (12.07). **HRMS** (ESI): Calcd for $C_{21}H_{31}O_2$ [M+H]: 315.2324; Found: 315.2328.



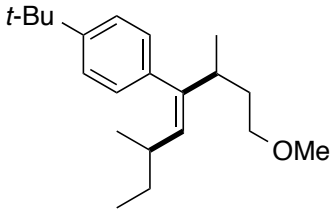
1-((*Z*)-2,5-Dimethyl-1-phenylhept-3-en-3-yl)-4-methoxybenzene (S4a). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methoxybenzene (92 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure D, the title compound was prepared using (2-iodopropyl)benzene (101 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S4a**) as colorless oil (61 mg, 48%; ***Z*:*E*** > 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26-7.23 (m, 2 H), 7.17-1.12 (ovrlp, 3 H), 6.98-6.95 (m, 2 H), 6.85 (d, *J* = 8.4 Hz, 2 H), 5.13 (d, *J* = 10.0 Hz, 1 H), 3.81 (s, 3 H), 2.84-2.76 (m, 1 H), 2.69-2.60 (m, 1 H), 2.42-2.36 (m, 1 H), 1.94-1.83 (m, 1 H), 1.26-1.15 (m, 2 H), 0.98-0.95 (ovrlp, 3 H), 0.86-0.80 (m, 3 H), 0.74-0.66 (ovrlp, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.1, 143.8, 141.6 (141.5), 133.81 (133.79), 133.4 (133.3), 130.23 (130.31), 129.34 (129.31), 128.1, 125.7, 113.3, 55.3, 43.71 (43.70), 42.4 (42.2), 34.7 (34.6), 30.43 (30.42), 21.4 (21.3), 19.7 (19.5), 12.1 (12.0).



1-((*Z*)-2,5-dimethyl-3-(*p*-tolyl)hept-3-en-1-yl)-4-fluorobenzene (S4b). Following the general procedure A, the alkenylzinc reagent was prepared using 1-ethynyl-4-methylbenzene (81 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure E, the title compound was prepared using 1-fluoro-4-(2-iodopropyl)benzene (108 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S4b**) as colorless oil (57 mg, 44%; ***Z*:*E*** = 16:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 7.7 Hz, 2 H), 7.09-7.05 (m, 2 H), 6.95-6.91 (ovrlp, 4 H), 5.11 (d, *J* = 10.0 Hz, 1 H), 2.79-2.72 (m, 1 H), 2.65-2.59 (m, 1 H), 2.40-2.30 (ovrlp, 4 H), 1.93-1.83 (m, 1 H), 1.23-1.05 (m, 2 H), 0.98-0.95 (ovrlp, 3 H), 0.85-0.79 (m, 3 H), 0.74-0.66 (ovrlp, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.4 (J_{CF} = 241.6 Hz), 143.9, 138.43 (138.37), 137.12 (137.06) (J_{CF} = 3.3 Hz), 135.8, 133.34 (133.31), 130.60 (130.56) (J_{CF} = 7.7 Hz), 129.1 (129.0), 128.6, 114.84 (113.83) (J_{CF} = 20.9 Hz), 43.71 (43.68), 41.5 (41.3), 34.7 (34.6), 30.42 (30.40), 21.45 (21.33), 21.31, 19.7 (19.5), 12.1 (12.0).

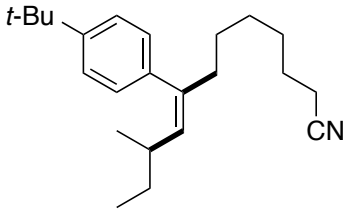


(*Z*)-4-(3-(4-(*tert*-butyl)phenyl)-4-cyclohexyl-2-methylbut-3-en-1-yl)-1,2-dimethoxybenzene (S4c). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg) and iodocyclohexane (221 mg). Following the general procedure D, the title compound was prepared using 4-(2-iodopropyl)-1,2-dimethoxybenzene (126 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (200:1) as an eluent to afford the title compound (**S4c**) as viscous yellow oil (64 mg, 37%; ***Z*:*E*** = 6.6:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 7.7 Hz, 2 H), 6.97 (d, *J* = 7.8 Hz, 2 H), 6.75 (d, *J* = 7.8 Hz, 1 H), 6.70-6.63 (ovrlp, 2 H), 5.22 (d, *J* = 9.7 Hz, 1 H), 3.84 (ovrlp, 6 H), 2.80-2.70 (m, 1 H), 2.65-2.55 (m, 1 H), 2.37-2.31 (m, 1 H), 1.92-1.82 (m, 1 H), 1.68-1.48 (ovrlp, 5 H), 1.34 (s, 9 H), 1.13-1.10 (ovrlp, 5 H), 0.96 (d, *J* = 6.6 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.9, 128.6, 147.1, 143.5, 138.6, 134.3, 132.7, 128.5, 124.7, 121.3, 112.6, 111.0, 56.0, 55.9, 43.5, 42.0, 37.3, 34.5, 33.8 (33.7), 31.6, 26.2, 25.8, 19.8.

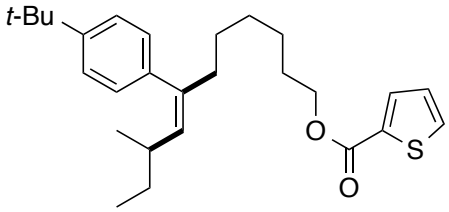


1-(*tert*-Butyl)-4-((*Z*)-1-methoxy-3,6-dimethyloct-4-en-4-yl)benzene (S4d). Following the general

procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure D, the title compound was prepared using 3-iodo-1-methoxybutane (88 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes as an eluent to afford the title compound (**S4d**) as viscous yellow oil (47 mg, 38%; ***Z*:*E*** > 40:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.0 Hz, 2 H), 6.97 (d, *J* = 8.1 Hz, 2 H), 5.18-5.14 (m, 1 H), 3.34-3.26 (ovrlp, 4 H), 3.16 (d, *J* = 8.2 Hz, 1 H), 2.43-2.36 (m, 1 H), 1.99-1.88 (m, 1 H), 1.48-1.41 (m, 1 H), 1.32 (s, 9 H), 1.27-1.14 (ovrlp, 3 H), 0.98-0.94 (ovrlp, 3 H), 0.89-0.86 (m, 3 H), 0.81-0.76 (m, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.9, 139.6 (139.5), 137.6, 136.0 (135.9), 128.8 (128.7), 124.6, 75.7 (75.6), 58.60 (58.56), 50.1, 34.8 (34.7), 34.5, 31.6, 30.5 (30.4), 22.9 (22.8), 21.7 (21.5), 12.22 (12.18), 11.98 (11.97).



(*Z*)-8-(4-(*tert*-Butyl)phenyl)-10-methyldodec-8-enenitrile (S4e). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure E, the title compound was prepared using 7-iodoheptanenitrile (111 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (50:1) as an eluent to afford the title compound (**S4e**) as viscous yellow oil (41 mg, 26%; ***Z*:*E*** = 7.8:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.0 Hz, 2 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 5.13 (d, *J* = 10.1 Hz, 1 H), 2.29 (ovrlp, 4 H), 2.12-2.01 (m, 1 H), 1.61 (qu, *J* = 7.6 Hz, 2 H), 1.41 (qu, *J* = 7.3 Hz, 2 H), 1.35-1.28 (ovrlp, 13 H), 1.26-1.40 (m, 2 H), 0.88 (d, *J* = 6.6 Hz, 3 H), 0.78 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.0, 139.4, 138.8, 133.7, 128.0, 124.9, 119.9, 39.9, 34.6, 34.5, 31.5, 30.5, 28.6, 28.3, 27.9, 25.5, 21.5, 17.2, 12.1.



(*Z*)-7-(4-(*tert*-Butyl)phenyl)-9-methylundec-7-en-1-yl thiophene-2-carboxylate (S4f). Following the general procedure A, the alkenylzinc reagent was prepared using 1-(*tert*-butyl)-4-ethynylbenzene (111 mg, 0.70 mmol, 1 equiv), Zn (82 equiv, 1.26 mmol, 1.8 equiv), and 2-iodobutane (232 mg, 1.26 mmol, 1.8 equiv). Following the general procedure E, the title compound was prepared using 6-iodohexyl thiophene-2-carboxylate (145 mg) and the alkenylzinc reagent prepared in the general procedure A. The crude product was purified using hexanes/EtOAc (100:1) as an eluent to afford the title compound (**S4f**) as viscous yellow oil (67 mg, 33%; ***Z*:*E*** = 7.1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 3.6 Hz, 1 H), 7.53 (d, *J* = 4.9 Hz, 1 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 7.08 (t, *J* = 4.4 Hz, 1 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 5.13 (d, *J* = 10.1 Hz, 1 H), 4.26 (d, *J* = 6.6 Hz, 2 H), 2.28 (t, *J* = 7.3 Hz, 2 H), 2.11-2.00 (m, 1 H),

1.70 (qu, J = 7.1 Hz, 2 H), 1.42-1.28 (ovrlp, 15 H), 1.28-1.15 (m, 2 H), 0.88 (d, J = 6.5 Hz, 3 H), 0.78 (t, J = 7.4 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.5, 148.9, 139.6, 138.9, 134.3, 133.6, 133.3, 132.3, 128.1, 127.8, 124.8, 65.4, 39.5, 34.55, 34.51, 31.6, 31.5, 30.5, 28.8, 28.1, 25.9, 21.5, 12.1.

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(33) For enyne products, the major *E*-stereoisomers (as shown in Figures 1 and S1) have more upfield olefinic protons than the minor *Z*-stereoisomers. For the ^{1}H NMR spectrometric data of structurally similar products, see: (a) Ikeda, S.-i.; Kondo, K.; Sato, Y. *Chem. Lett.* **1999**, *28*, 1227-1228. (b)

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(34) For *α*-alkylated styrene products generated from secondary alkyl iodides in the second step, the major *Z*-stereoisomers (as shown in Figures 3 and S3) have more downfield olefinic protons than the minor *E*-stereoisomers. On the contrary, for *α*-alkylated styrene products generated from primary alkyl iodides in the second step, the major *Z*-stereoisomers (as shown in Figures 3 and S3) have more upfield olefinic protons than the minor *E*-stereoisomers. For the ^{1}H NMR spectrometric data of structurally similar products, see: (a) Liu, J.-T.; Jang, Y.-J.; Shih, Y.-K.; Hu, S.-R.; Chu, C.-M.; Yao, C.-F. *J. Org. Chem.* **2001,** *66,* 6021-6028. (b) Huang, T.-H.; Chang, H.-M.; Wu, M.-Y.; Cheng, C.-H. *J. Org. Chem.* **2002,** *67,* 99-105.

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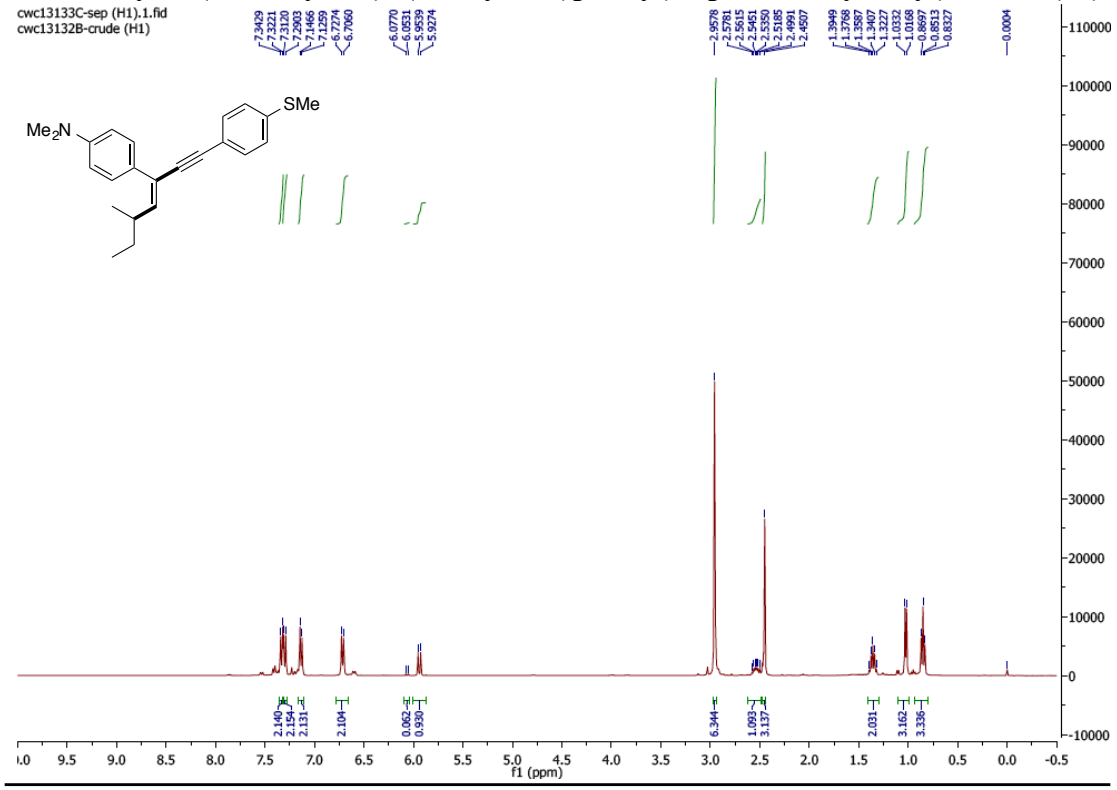
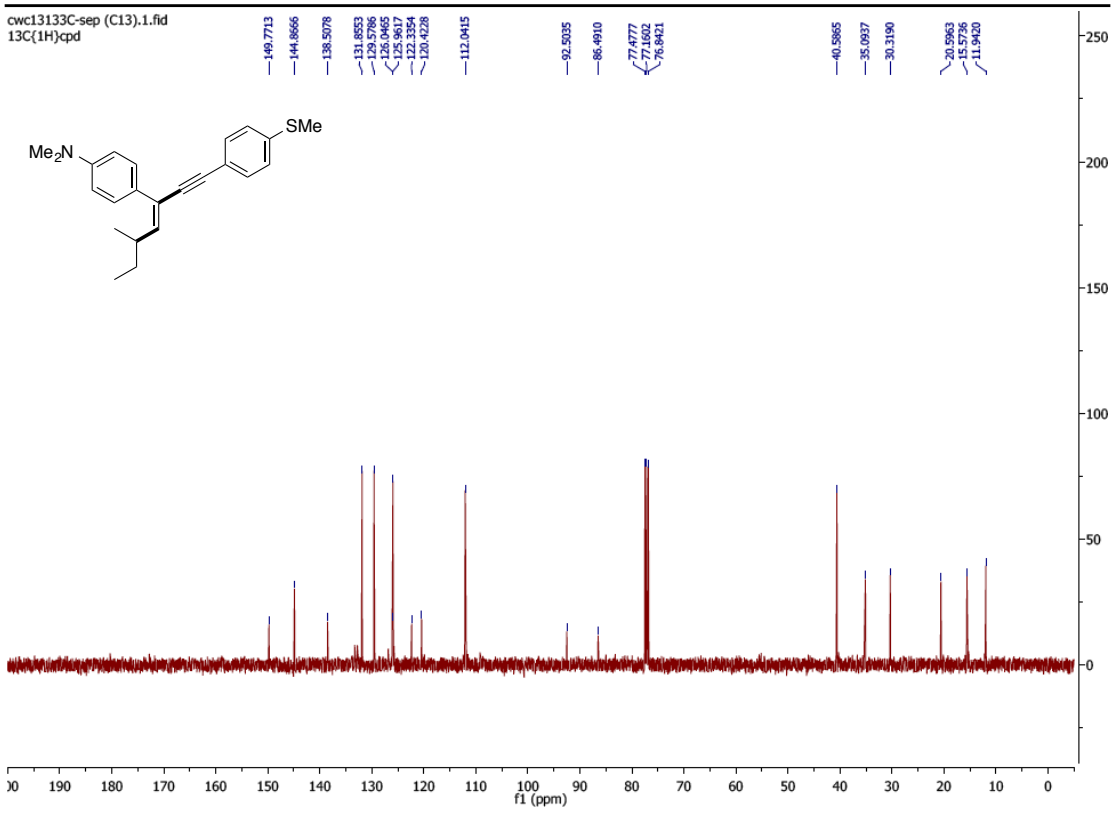
Lists of NMR Spectra

(*E*)-*N*,*N*-Dimethyl-4-(5-methyl-1-(4-(methylthio)phenyl)hept-3-en-1-yn-3-yl)aniline (2a)





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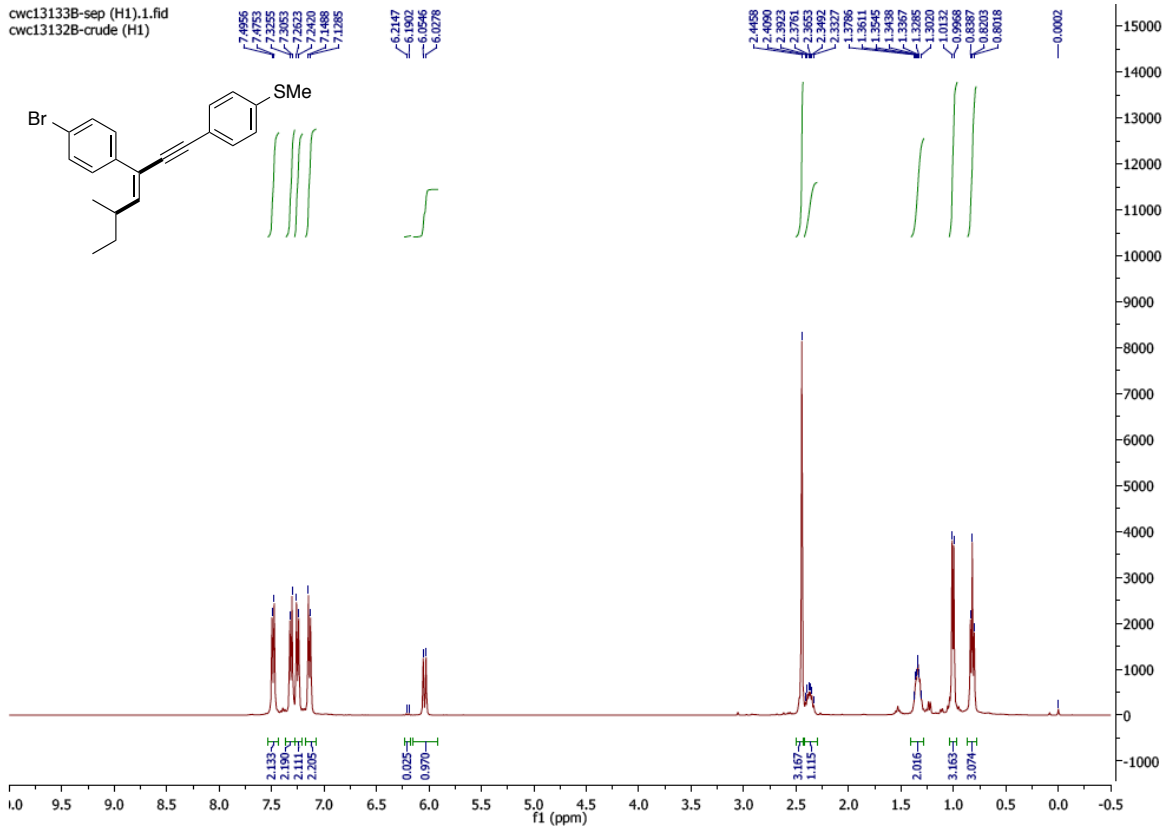

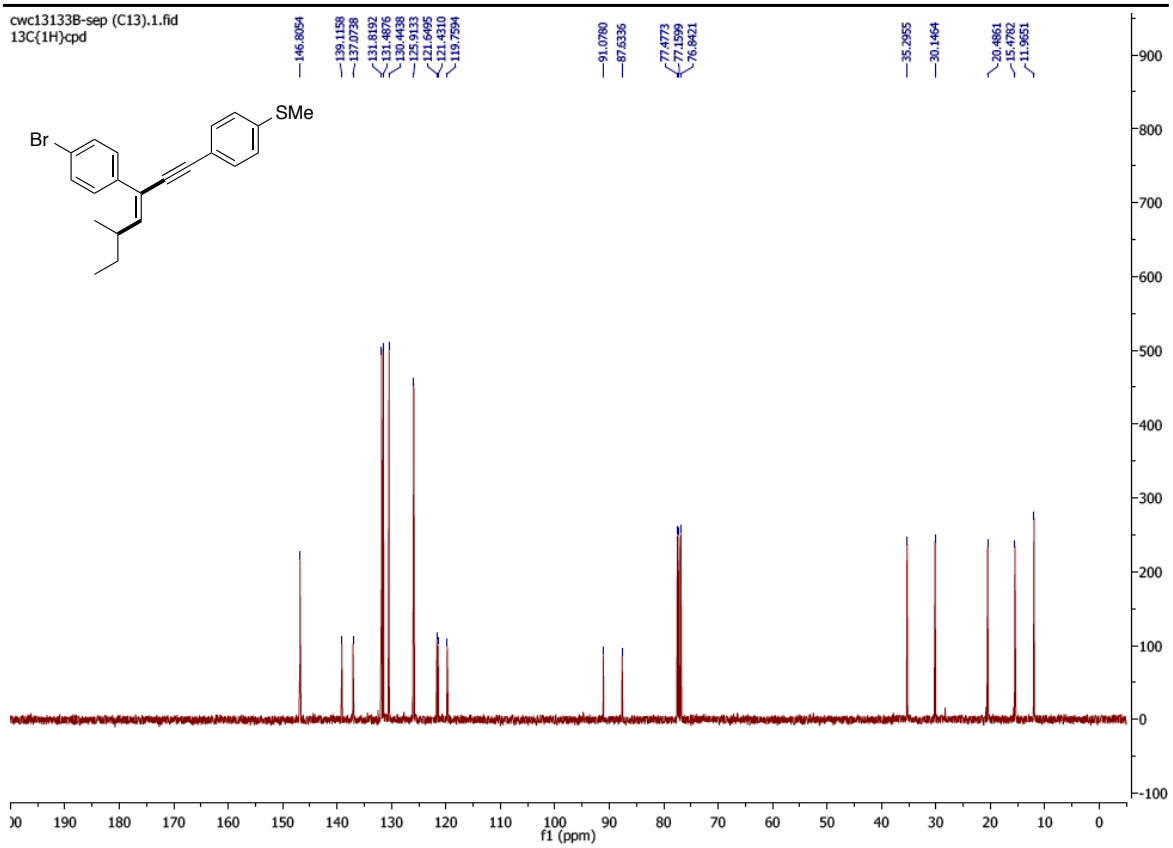

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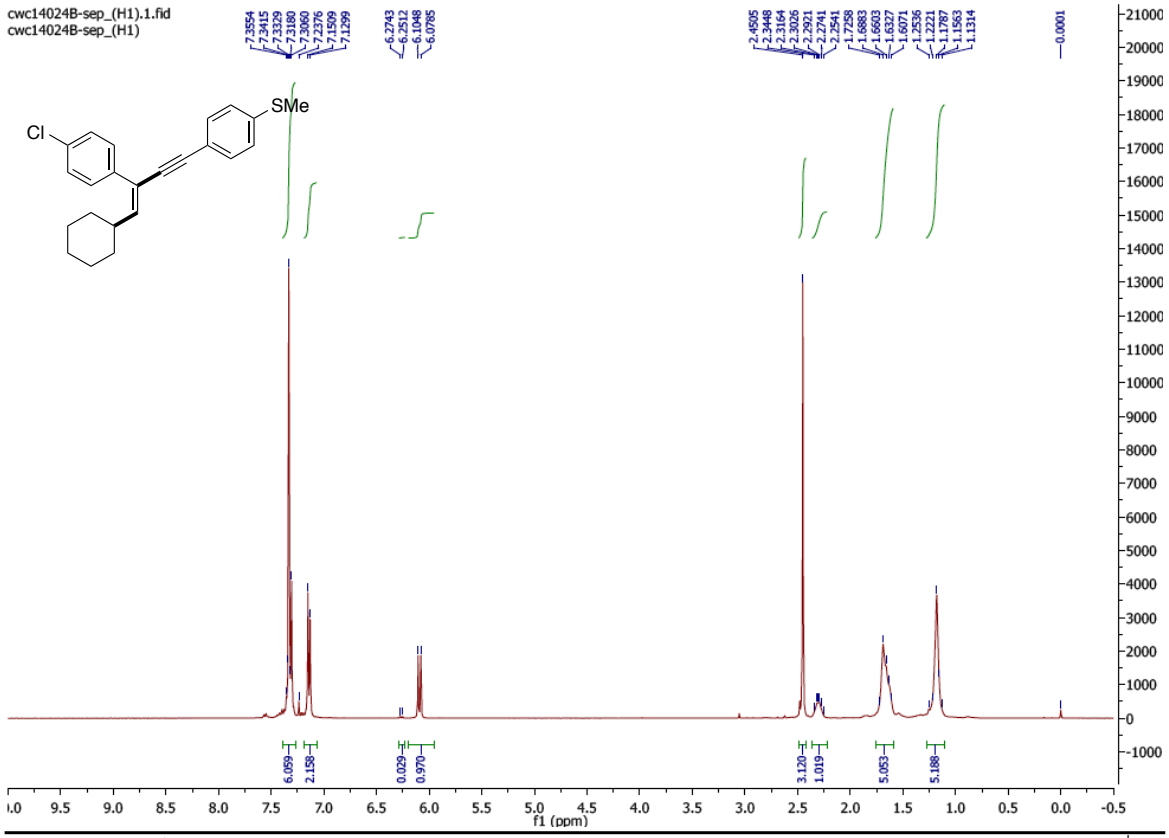

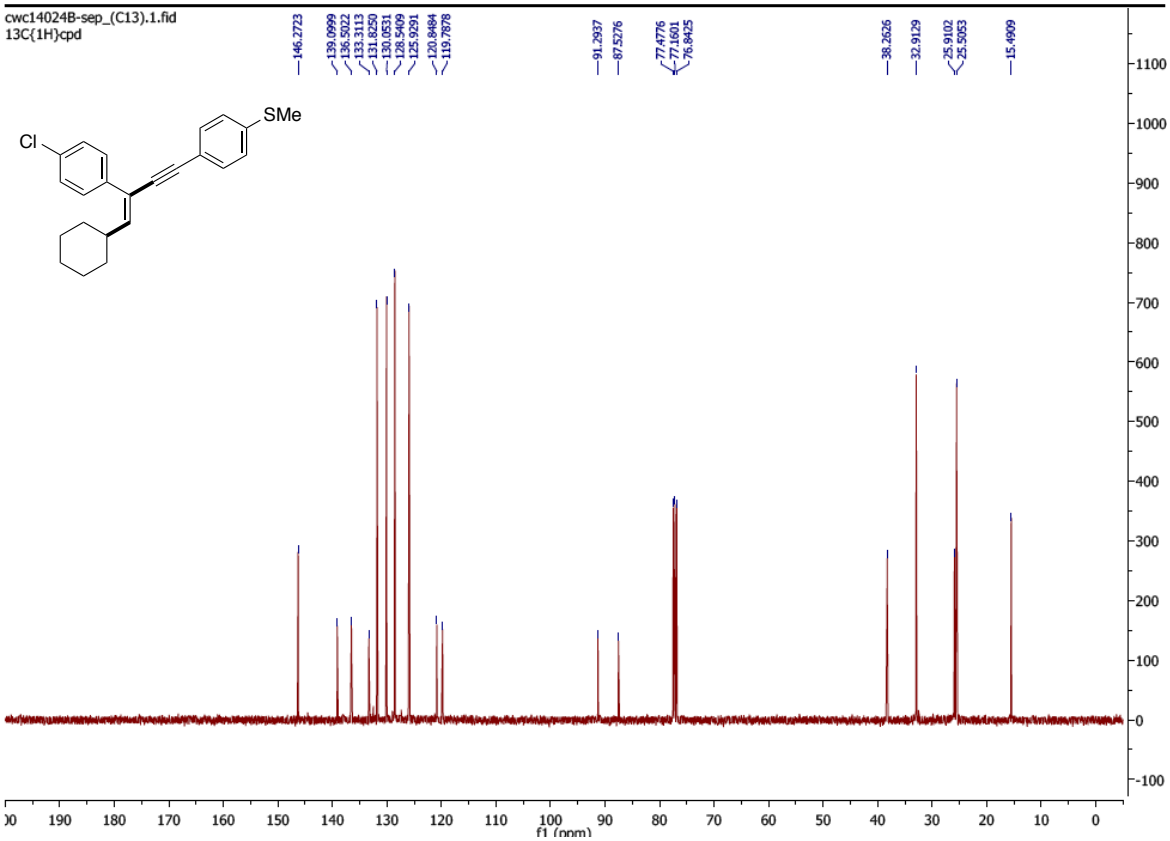

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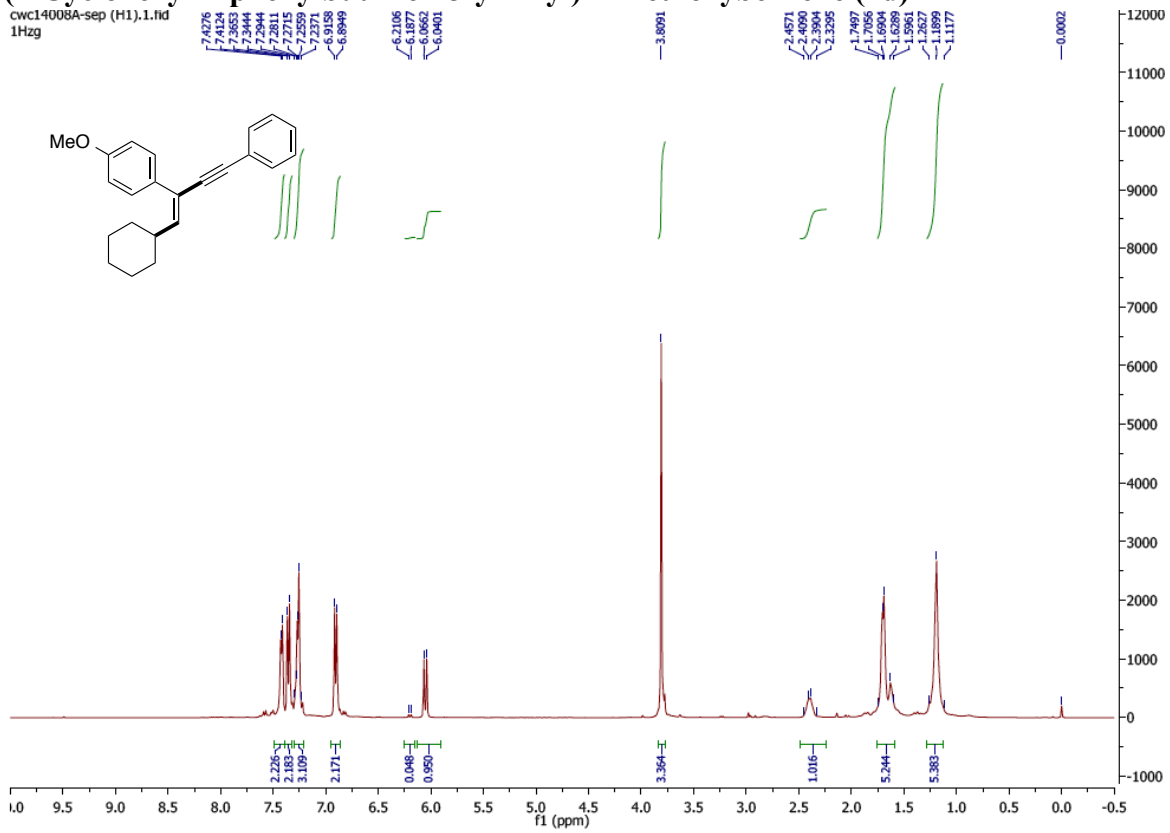

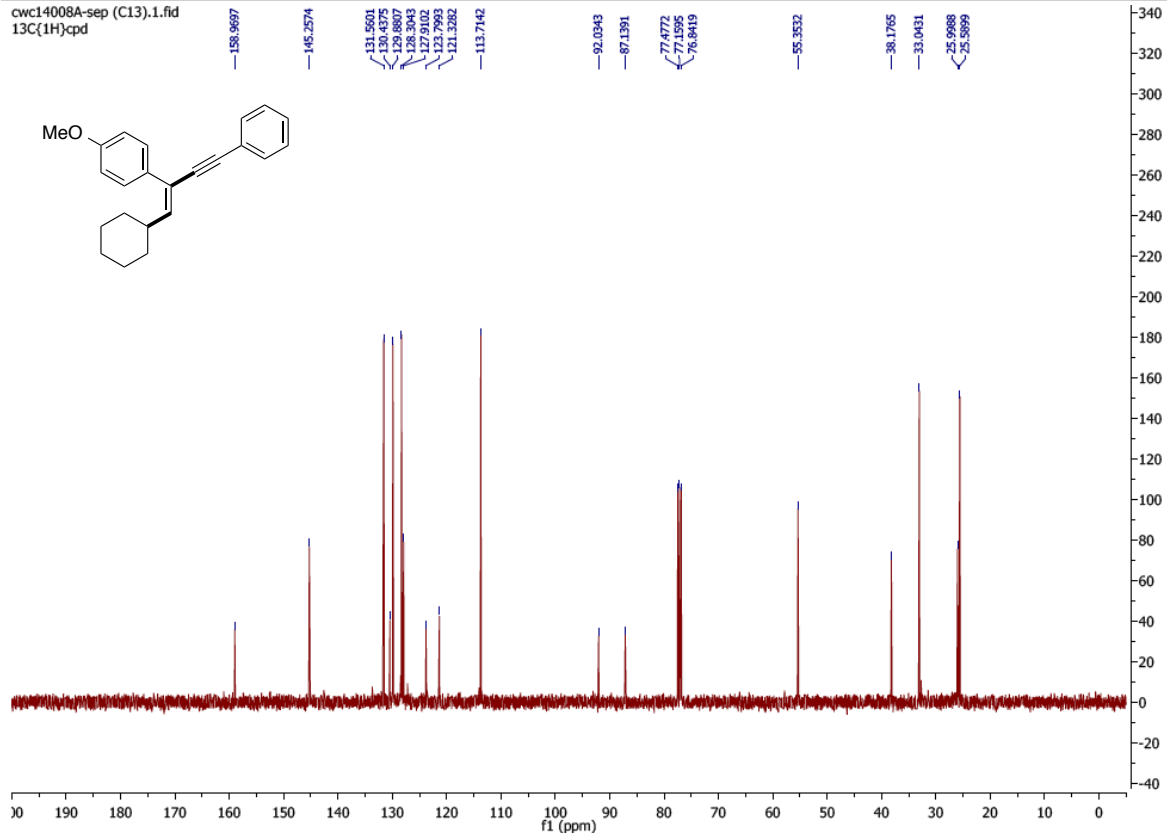

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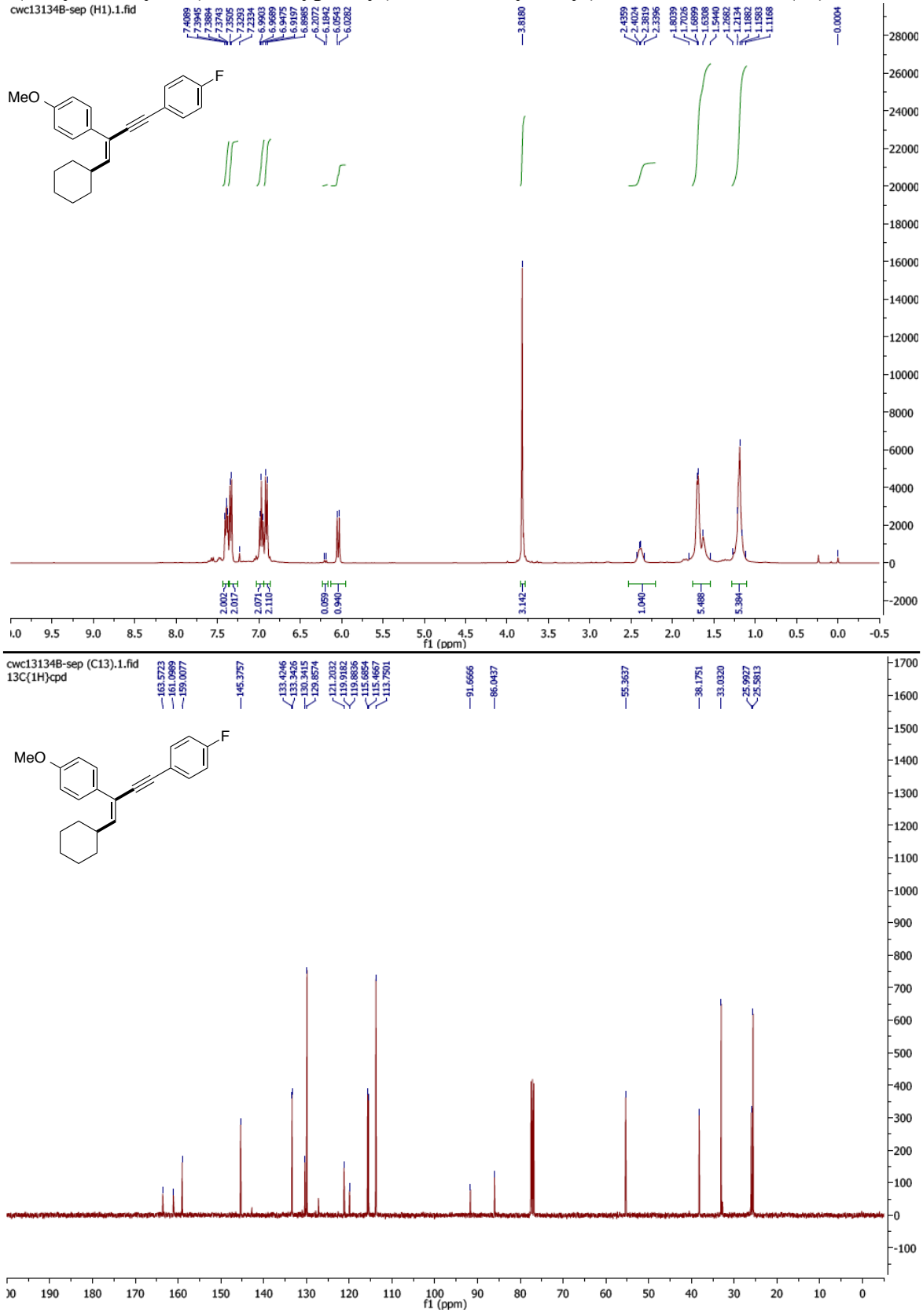

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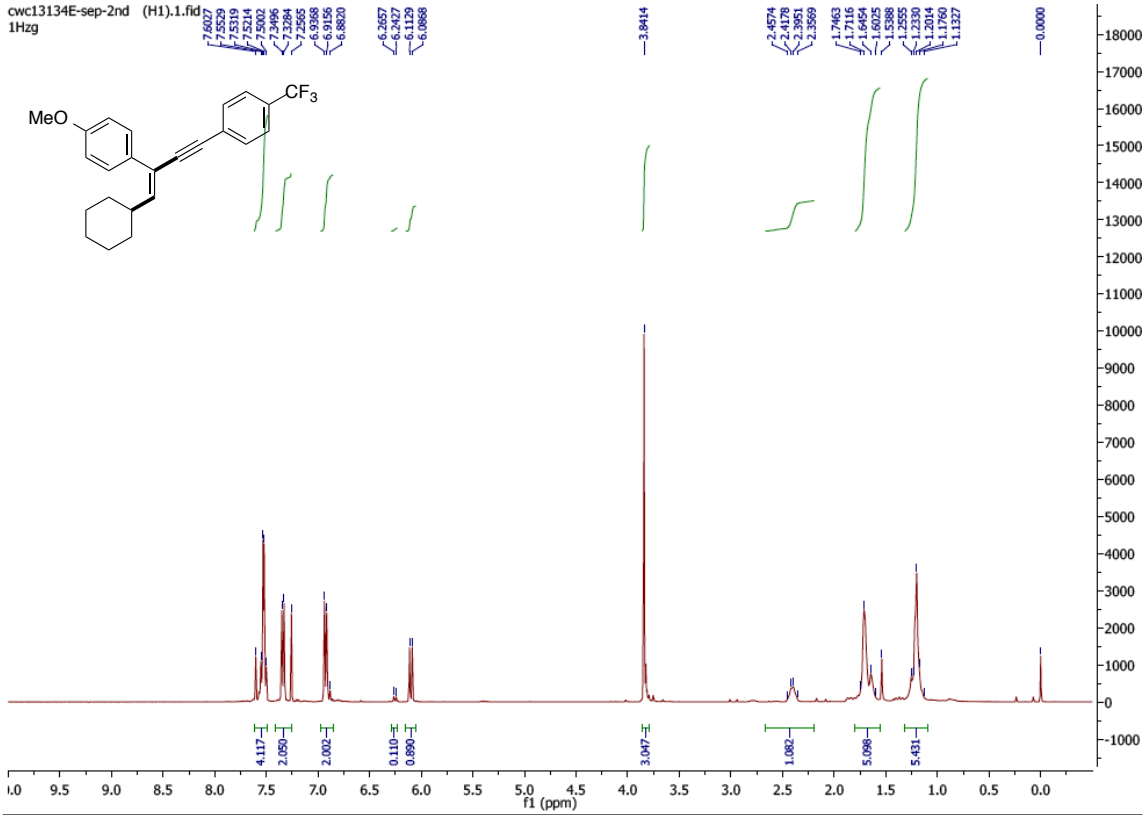

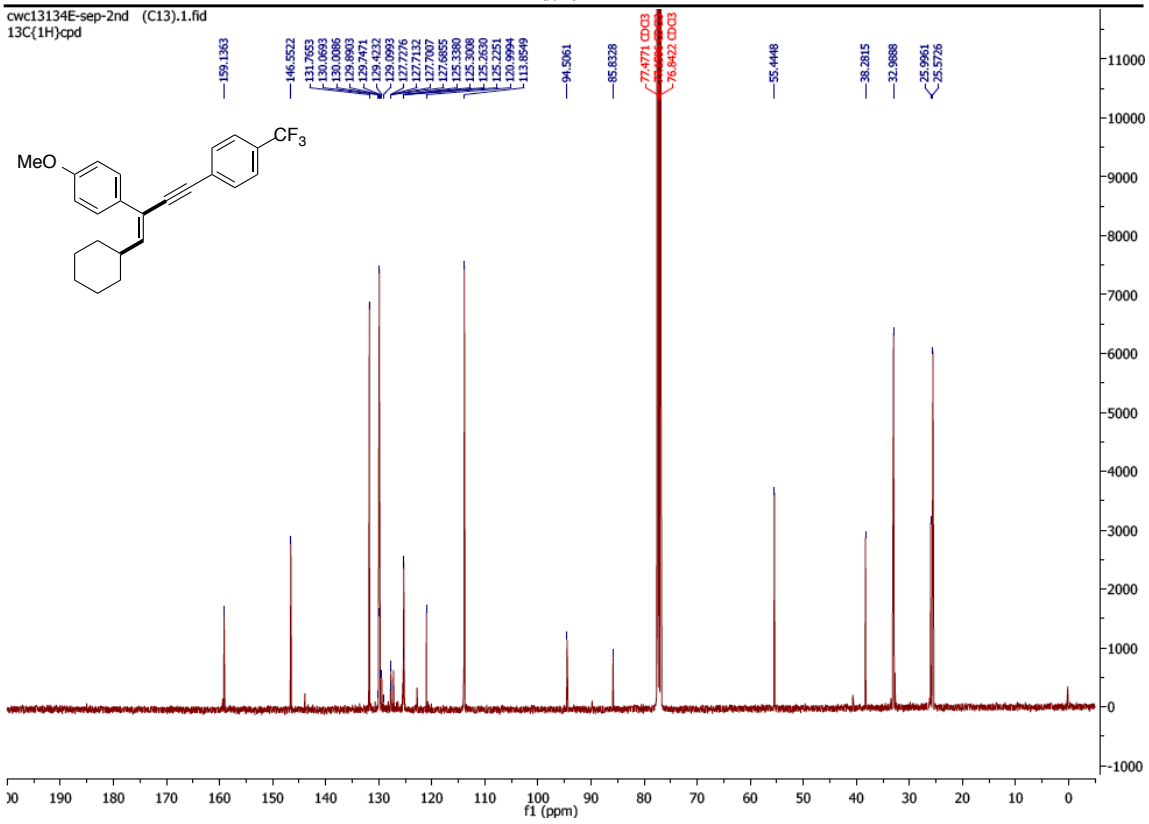

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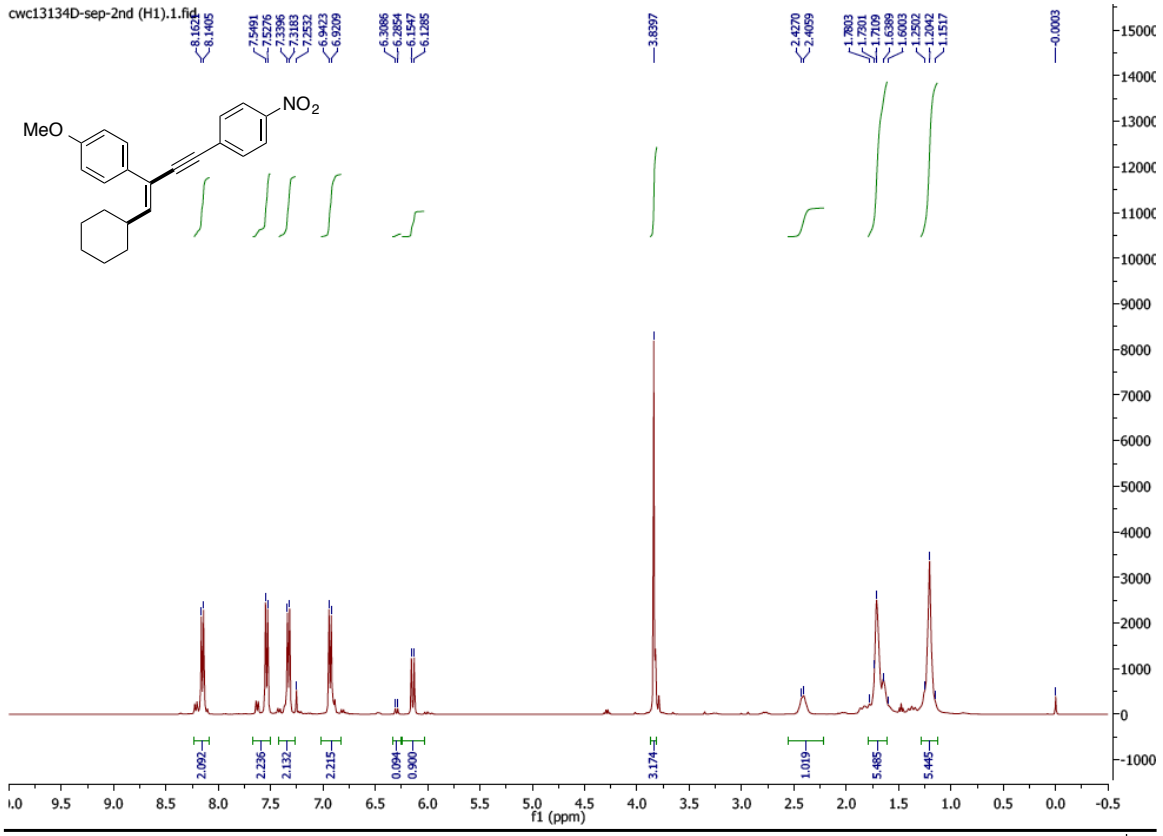

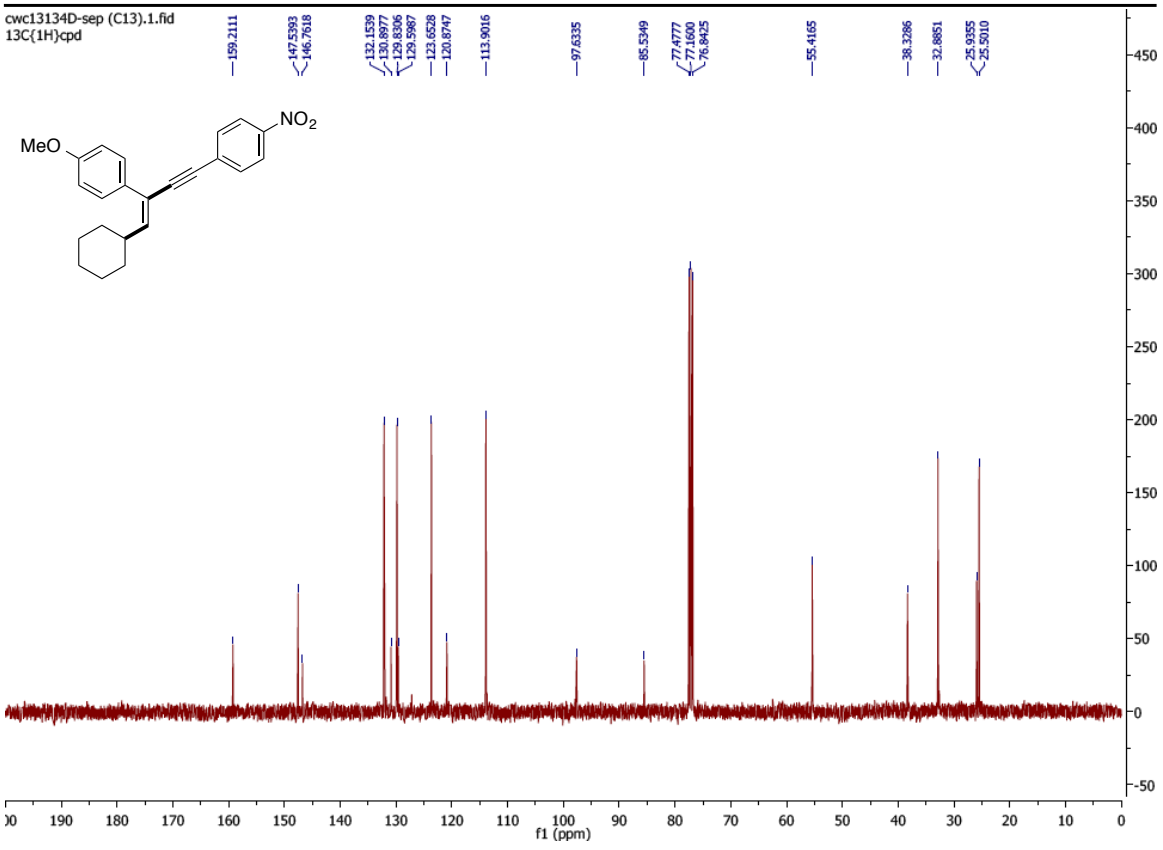

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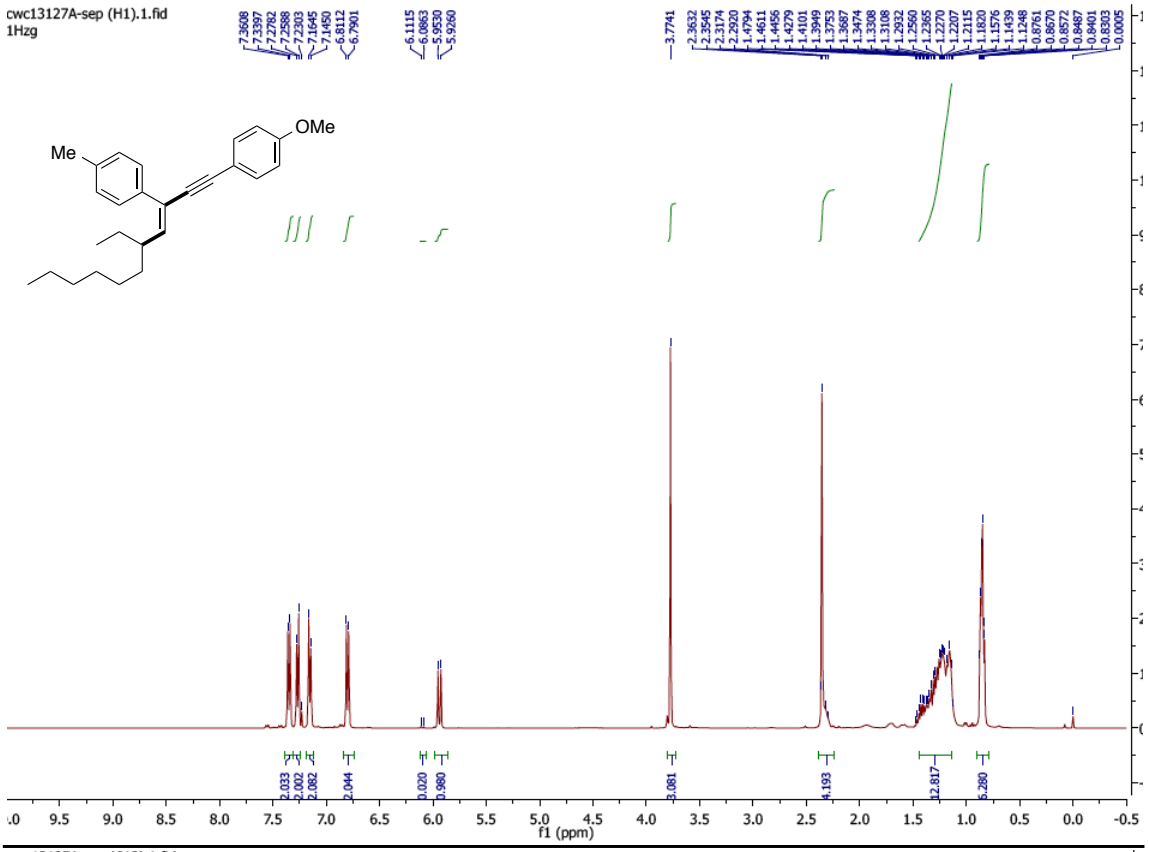
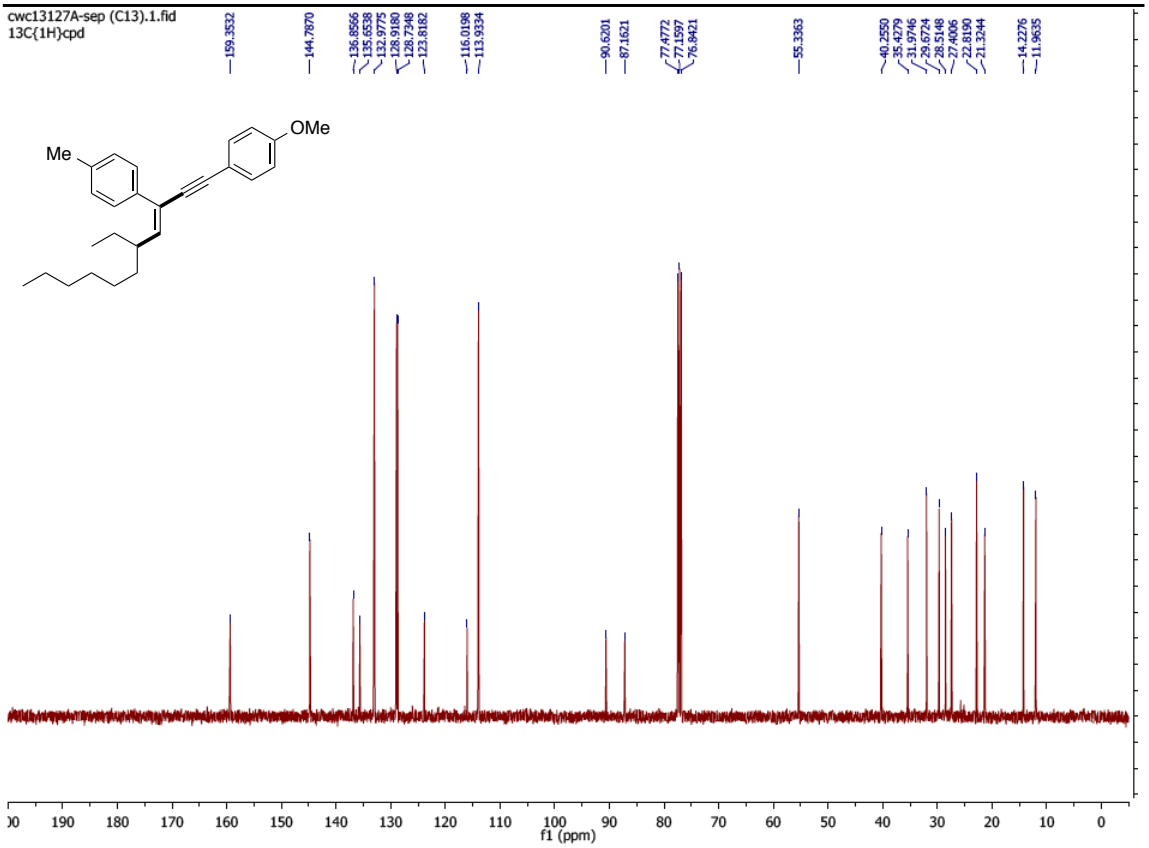
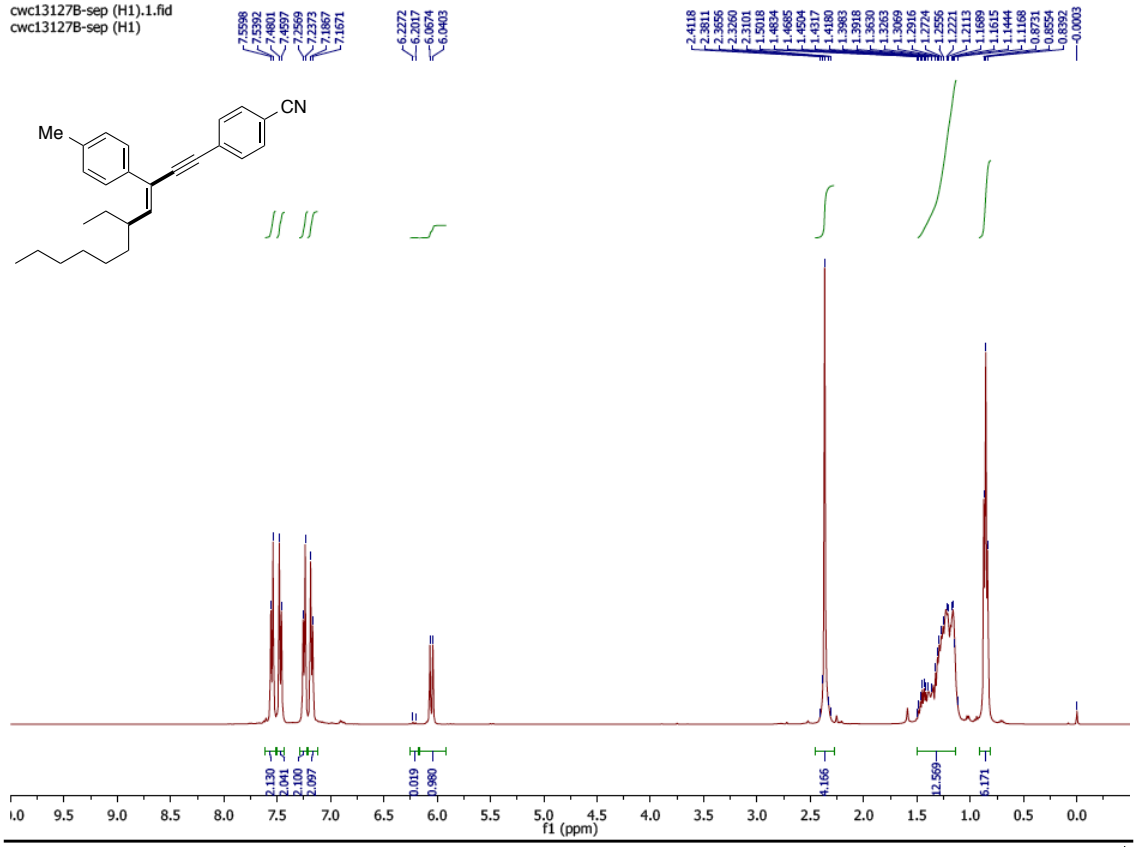
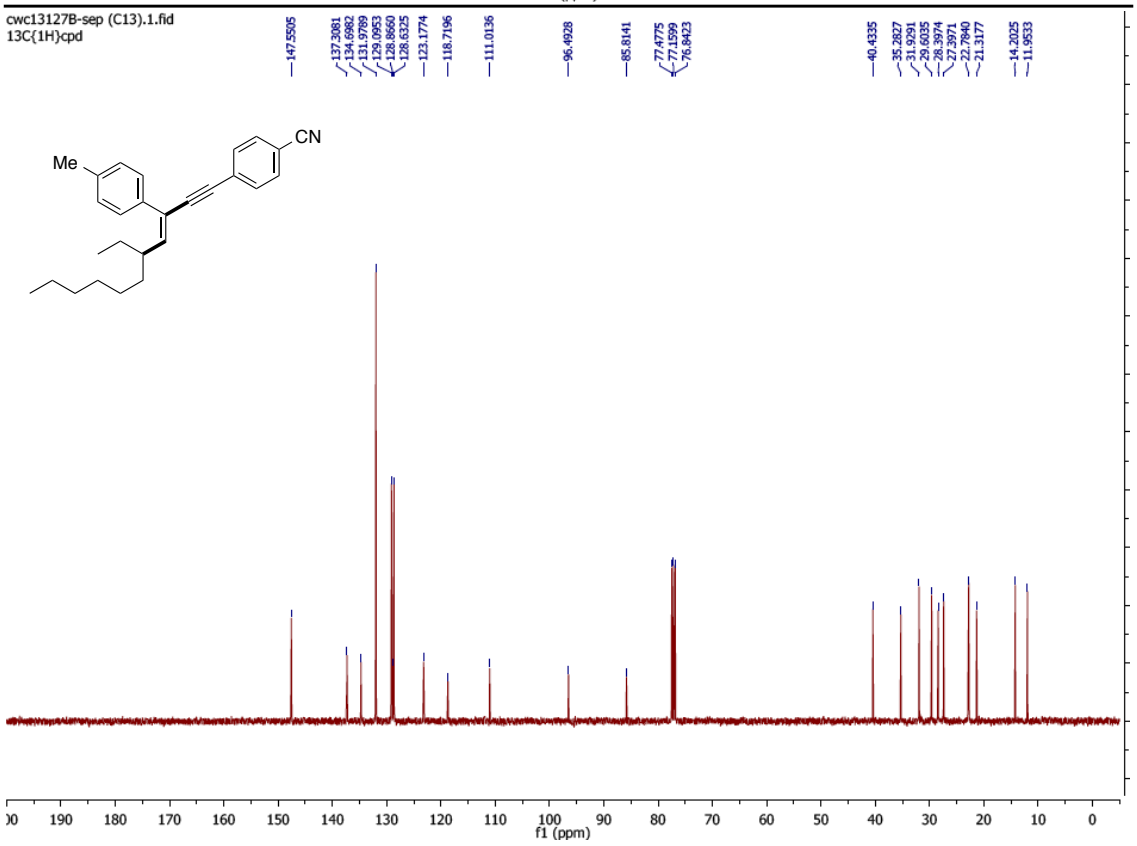


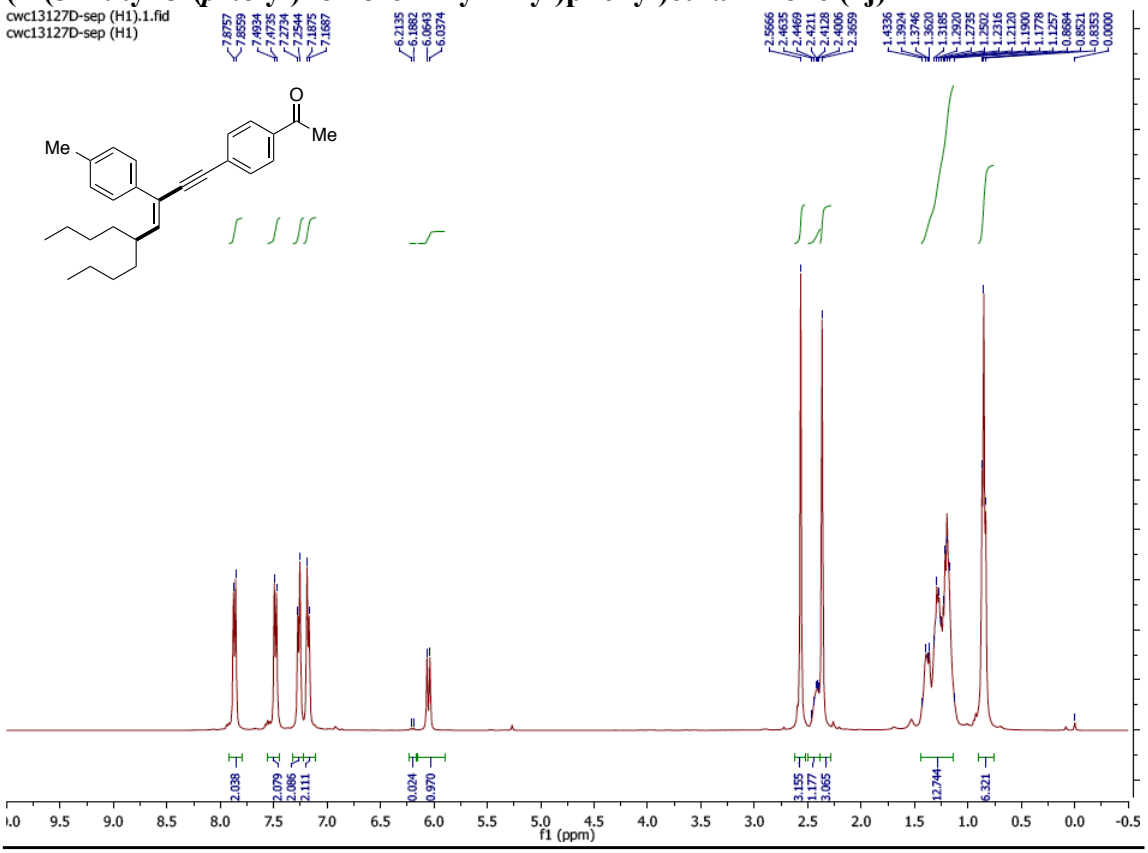


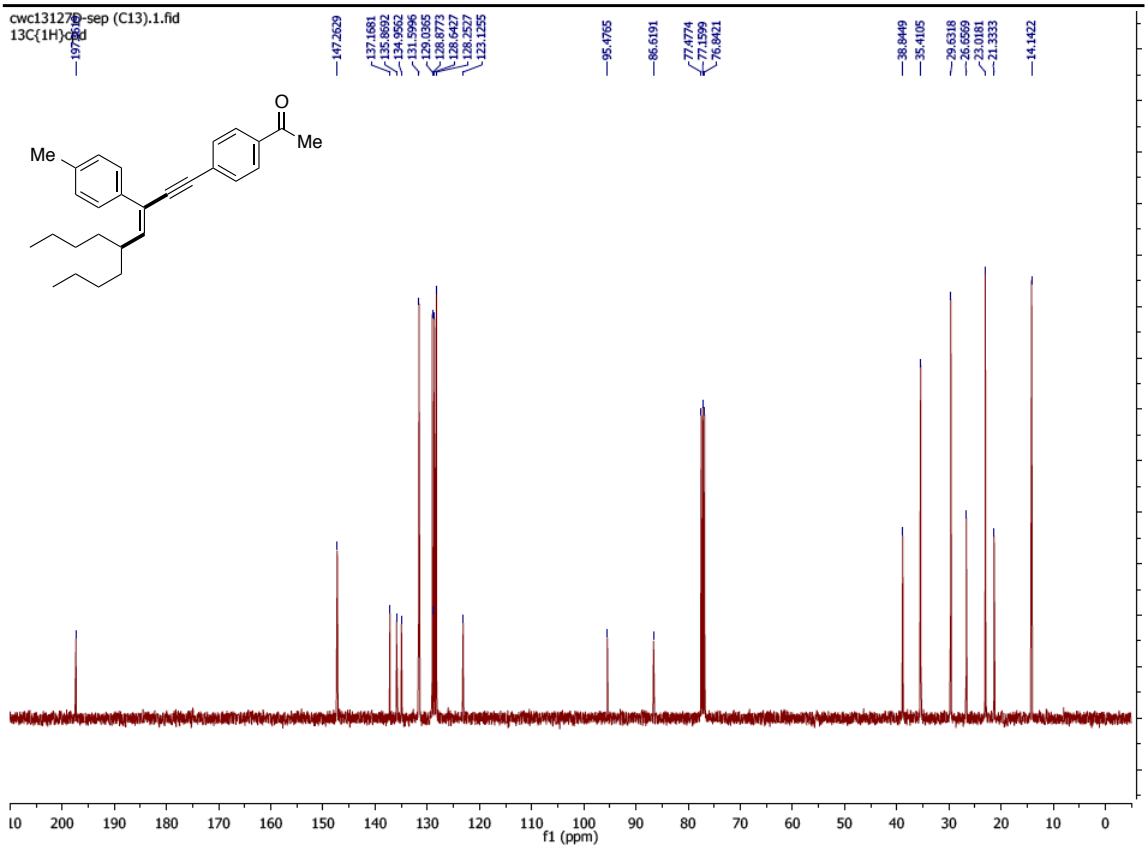
(*E*)-4-(5-Ethyl-3-(*p*-tolyl)undec-3-en-1-yn-1-yl)benzonitrile (2i)



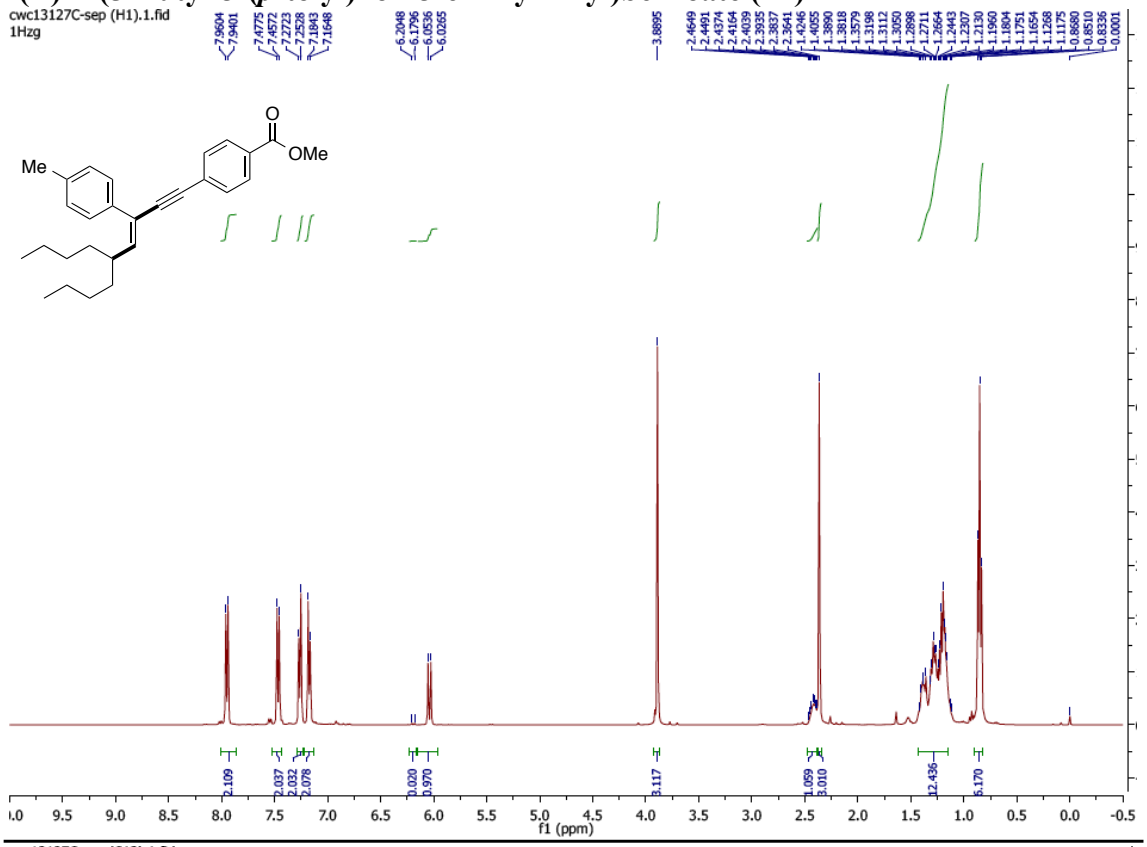


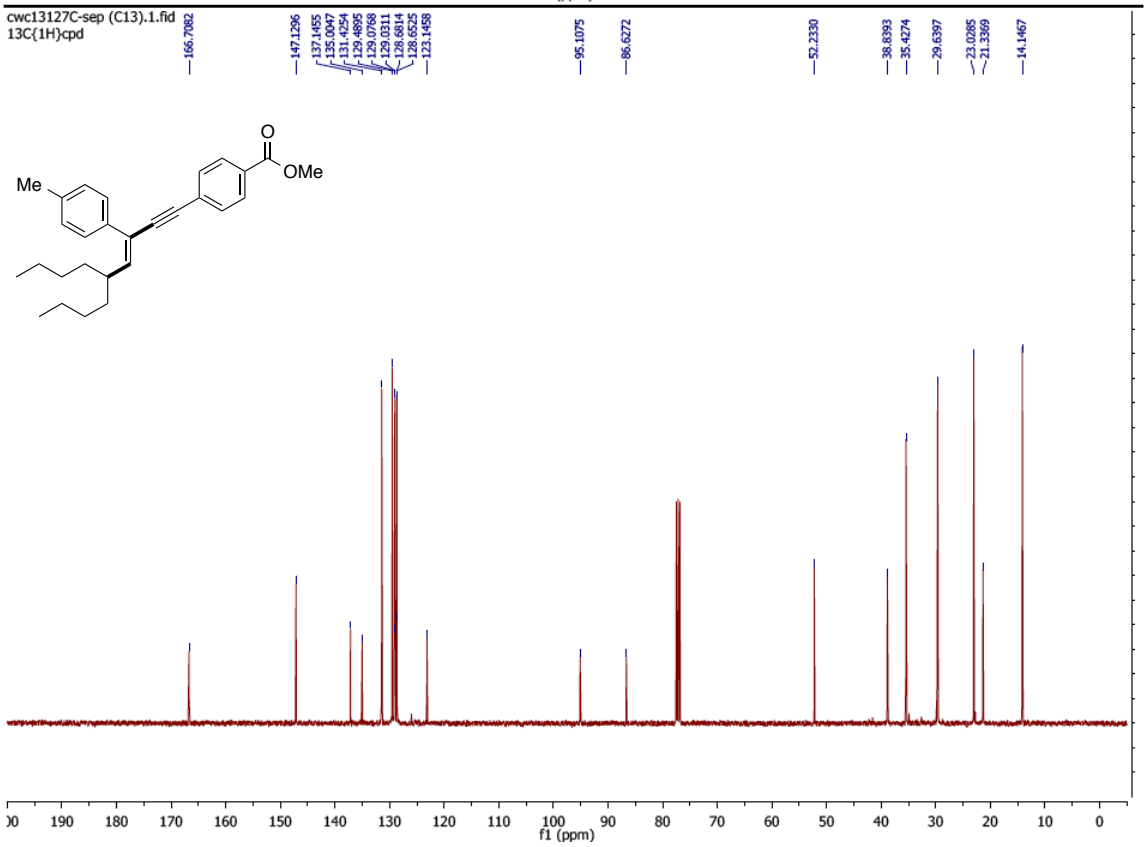
(*E*)-1-(4-(5-Butyl-3-(*p*-tolyl)non-3-en-1-yn-1-yl)phenyl)ethan-1-one (2j)



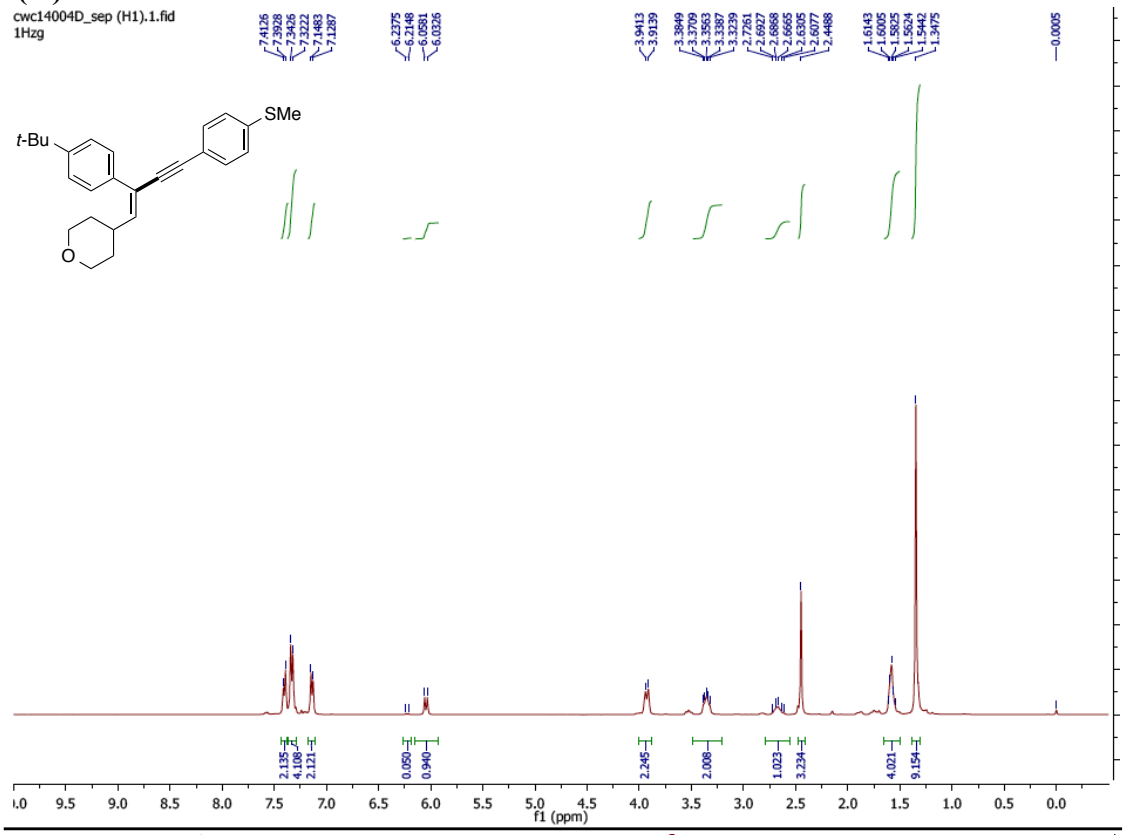


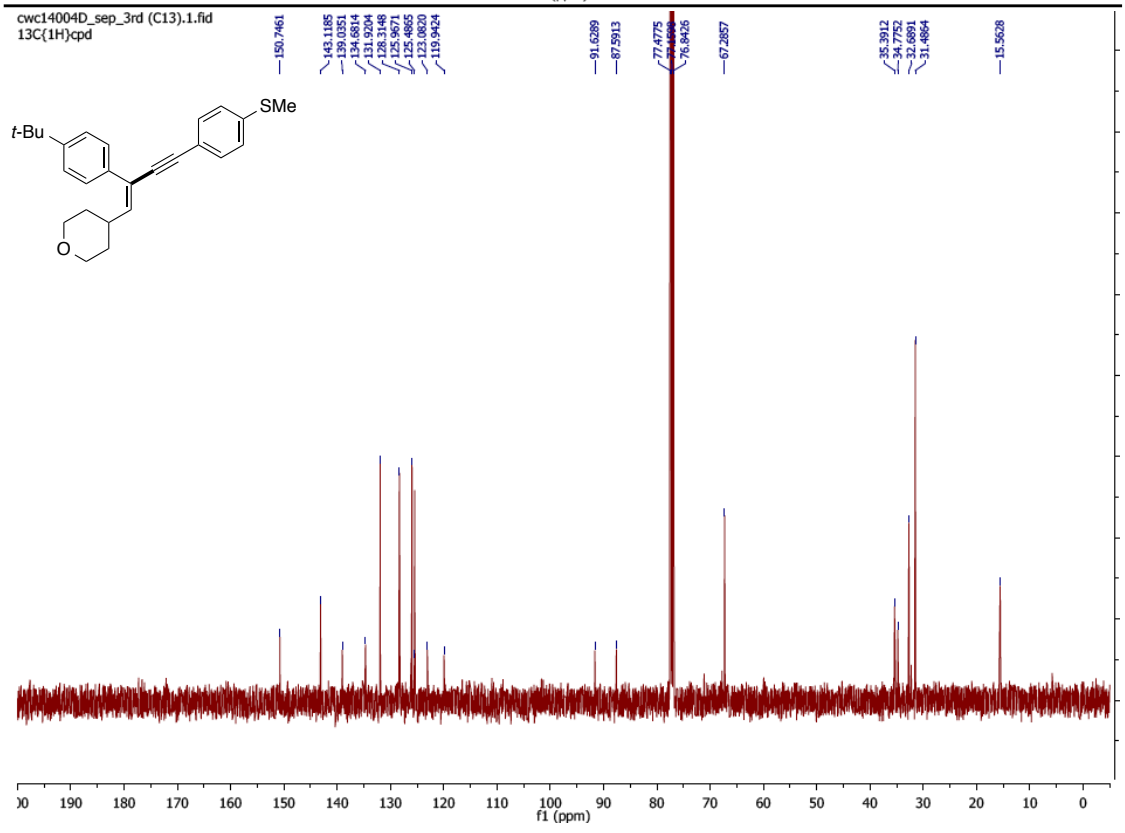
Methyl (*E*)-4-(5-Butyl-3-(*p*-tolyl)non-3-en-1-yn-1-yl)benzoate (2k)



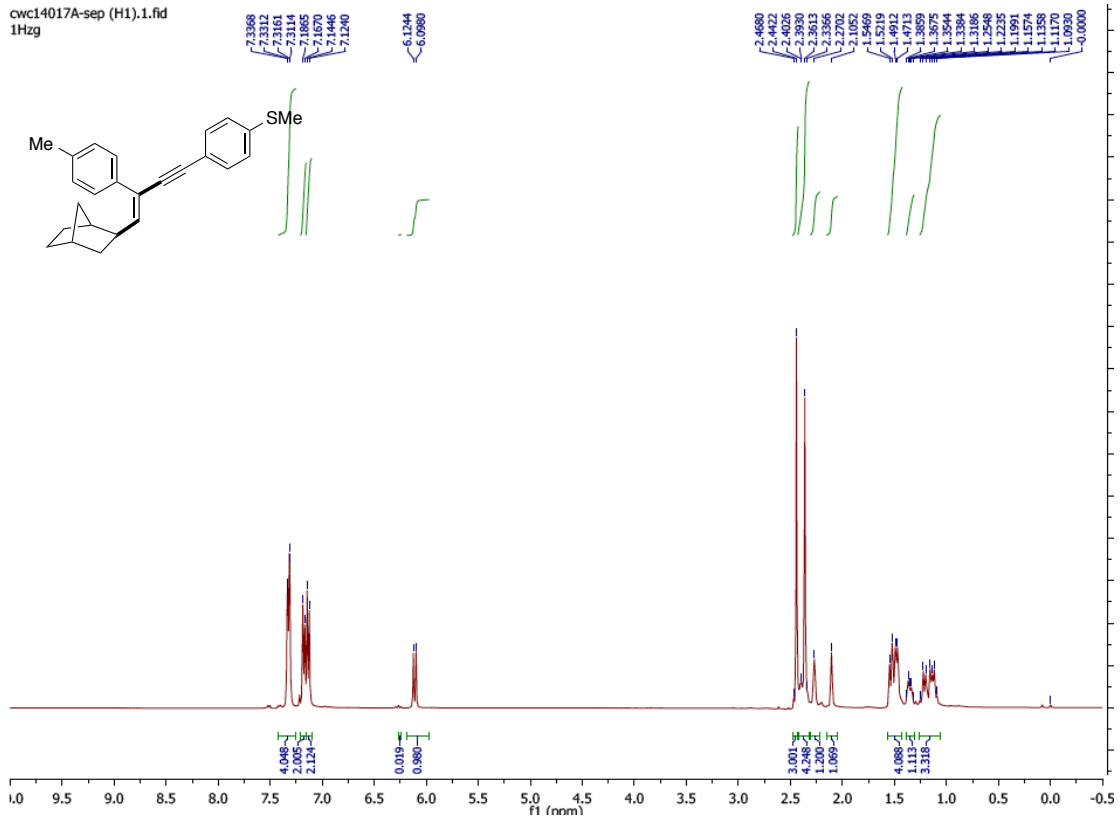


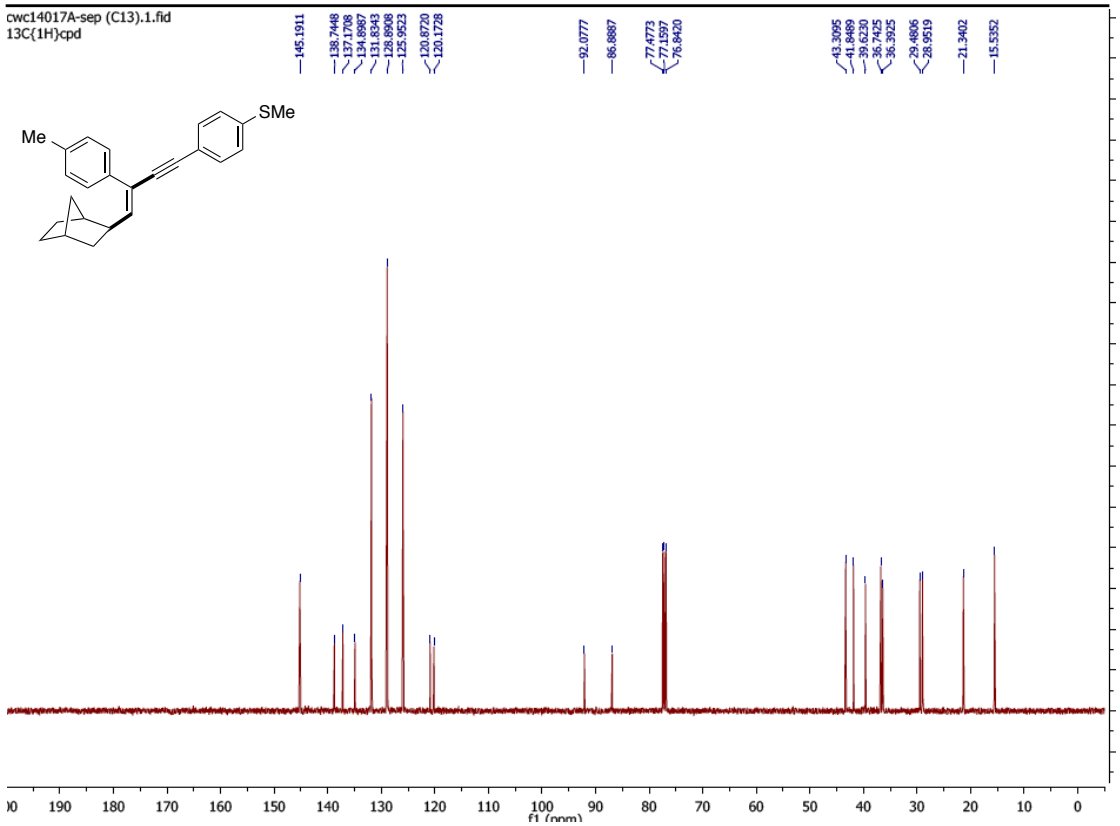
(*E*)-4-(2-(4-(*tert*-Butyl)phenyl)-4-(4-(methylthio)phenyl)but-1-en-3-yn-1-yl)tetrahydro-2*H*-pyran (2l)



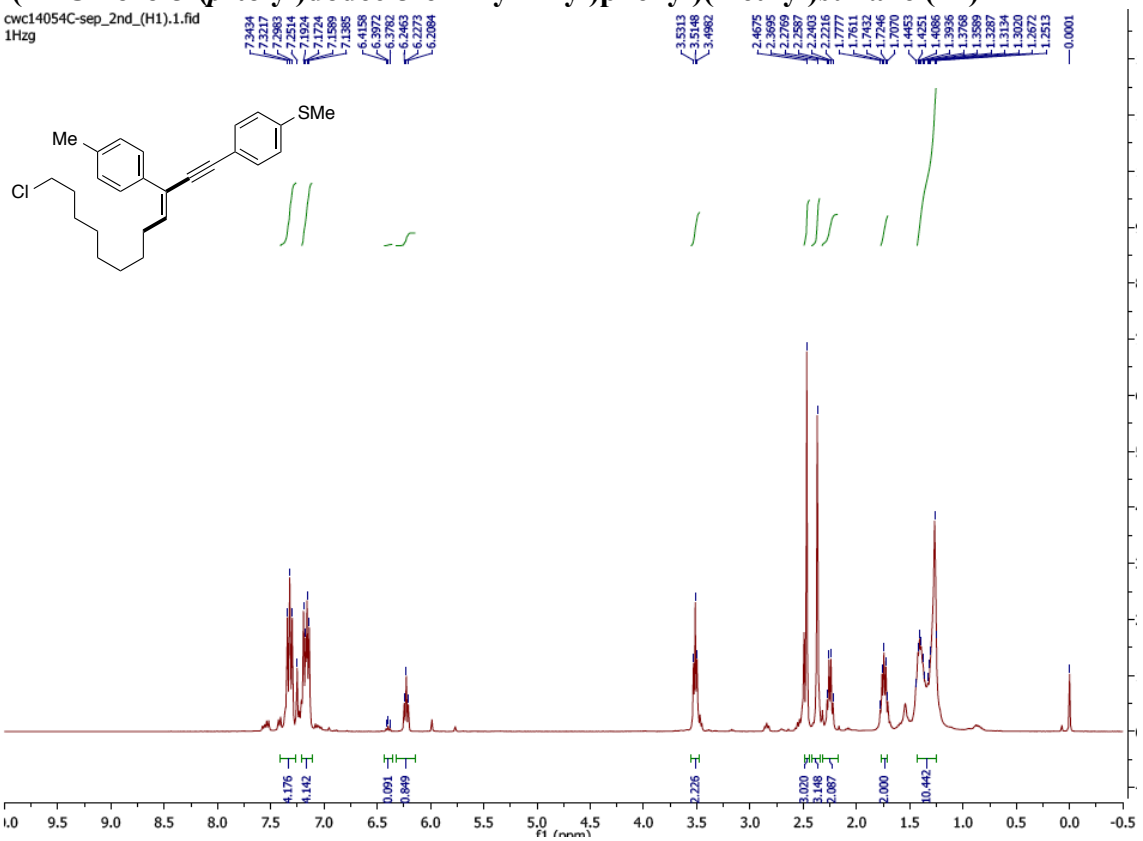


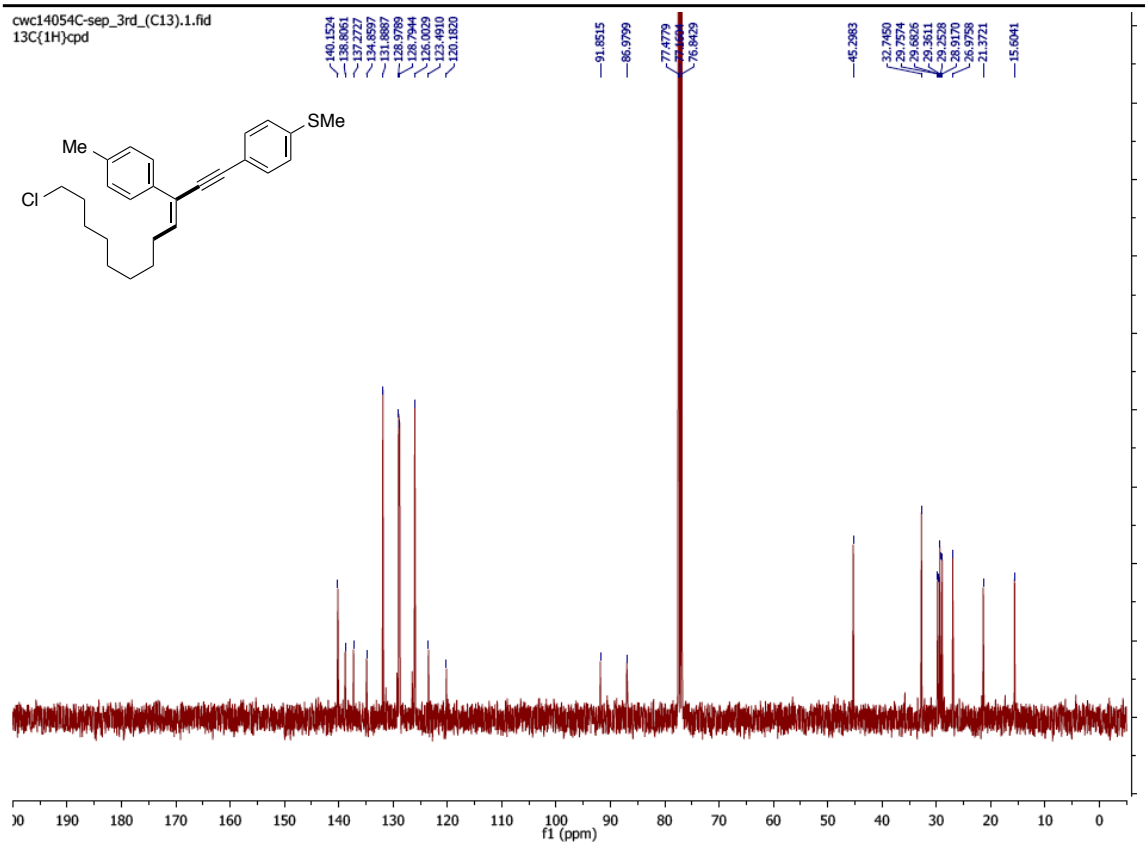
(4-((*E*)-4-(Bicyclo[2.2.1]heptan-2-yl)-3-(*p*-tolyl)but-3-en-1-yn-1 yl)phenyl)(methyl)sulfane (2m)



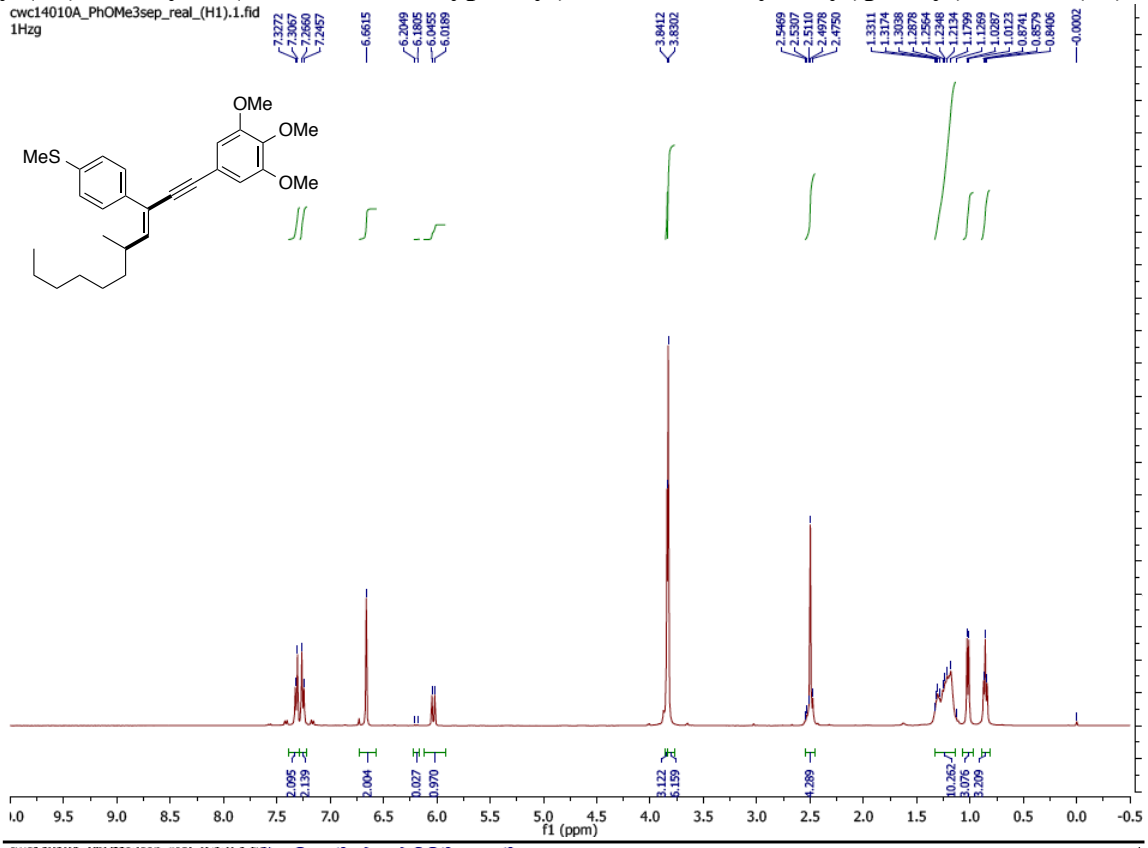


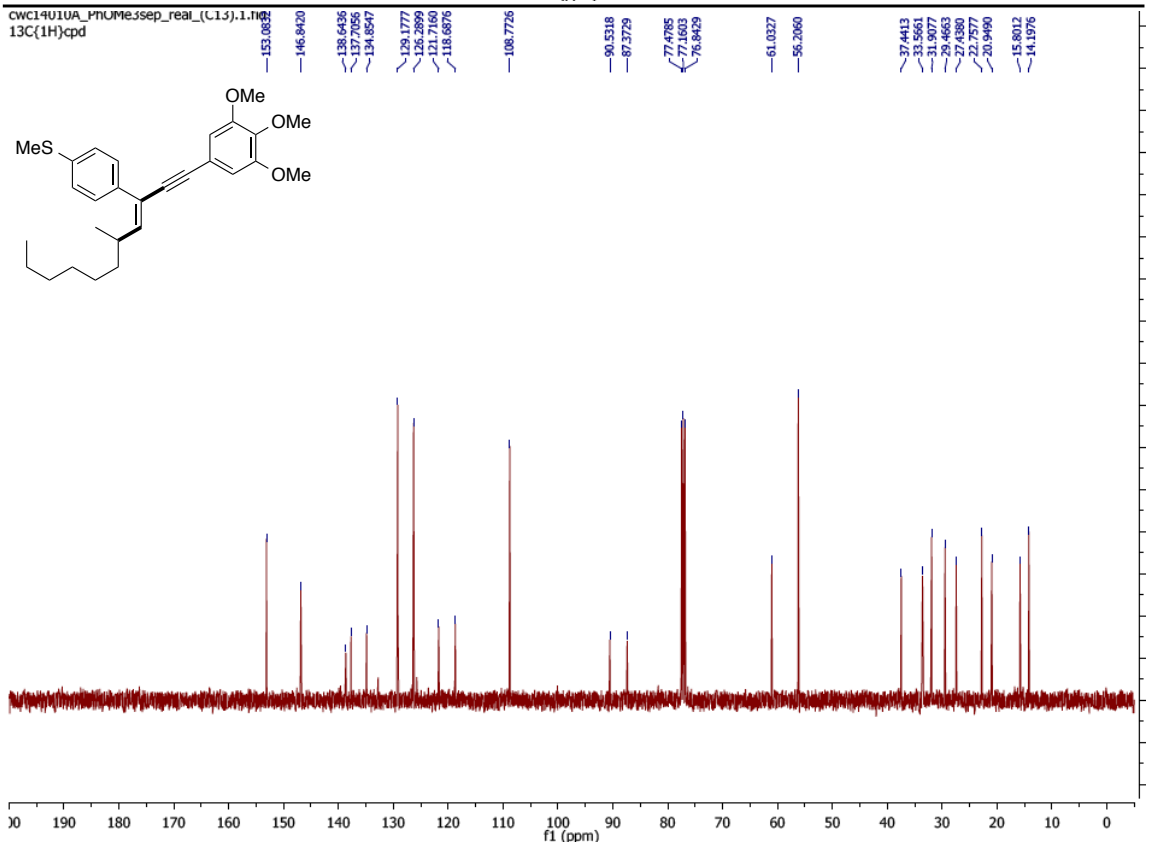
(*E*)-(4-(12-Chloro-3-(*p*-tolyl)dodec-3-en-1-yn-1-yl)phenyl)(methyl)sulfane (2n)



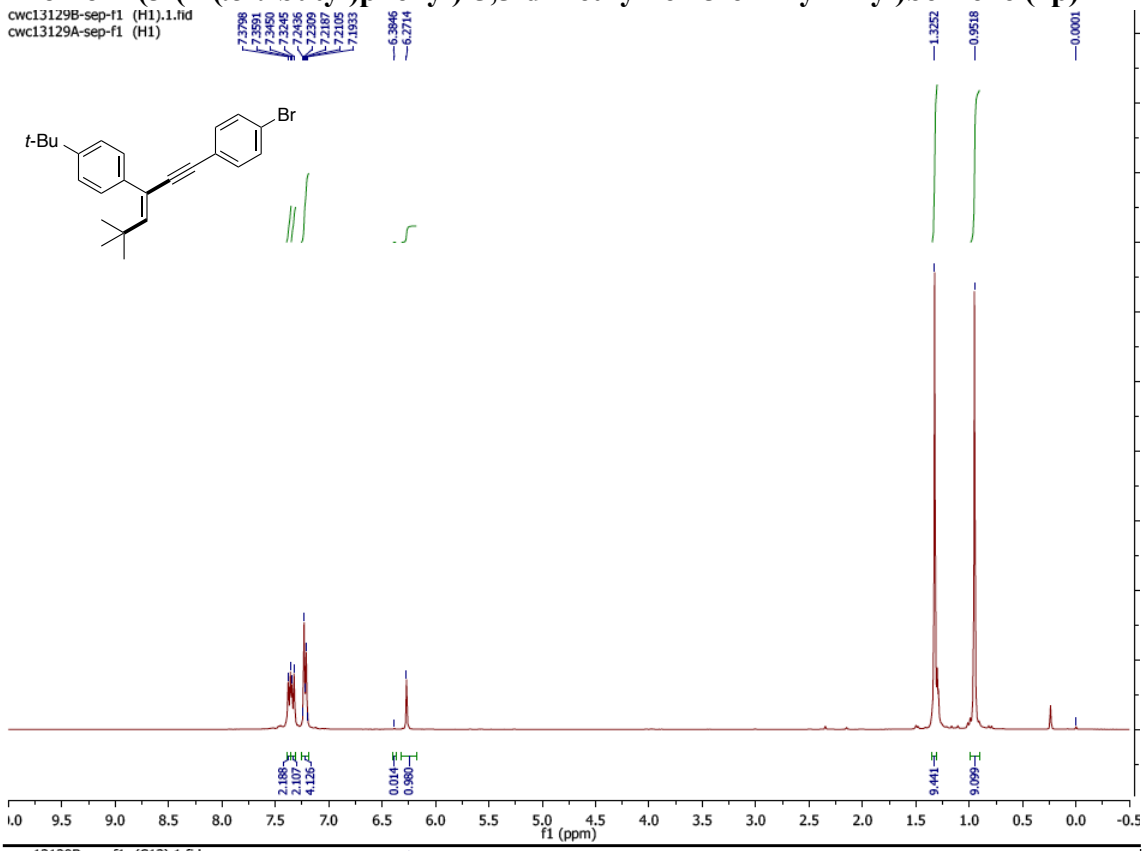


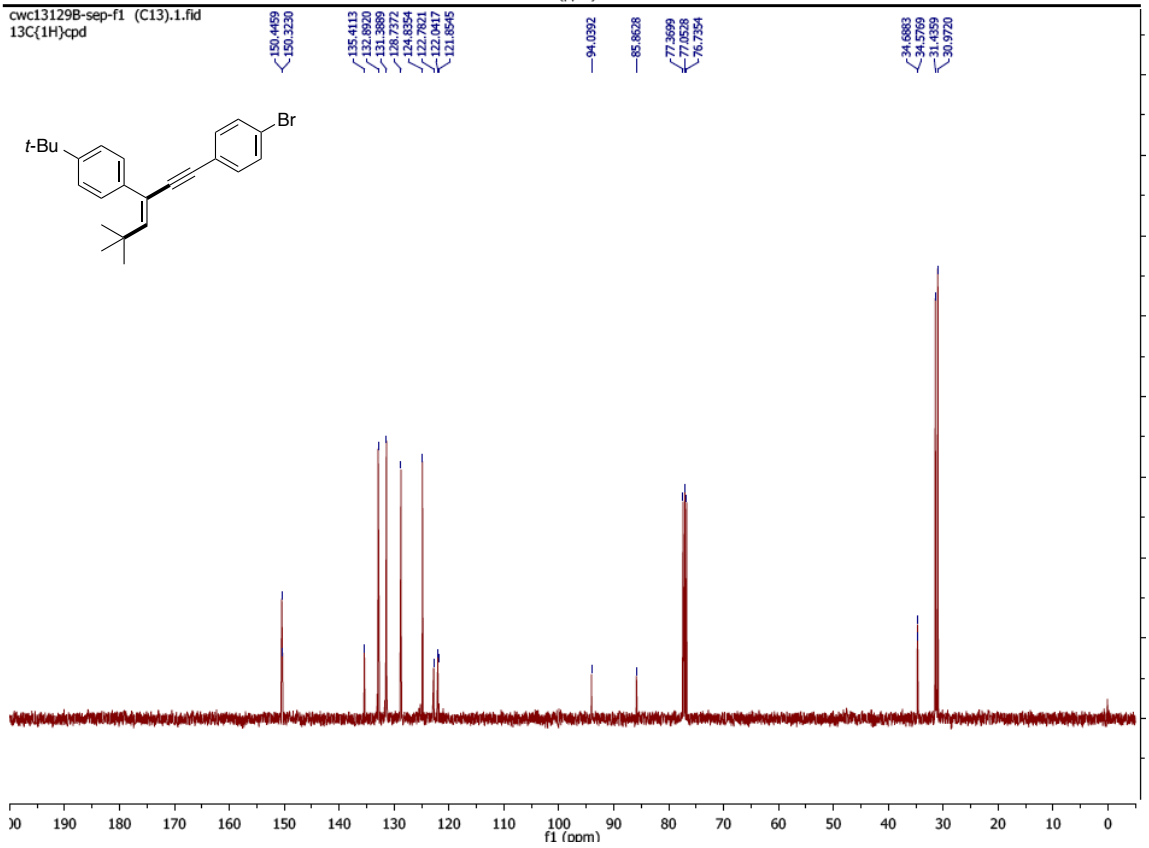
Methyl(4-(5-methyl-1-(3,4,5-trimethoxyphenyl)undec-3-en-1-yn-3-yl)phenyl)sulfane (2o)



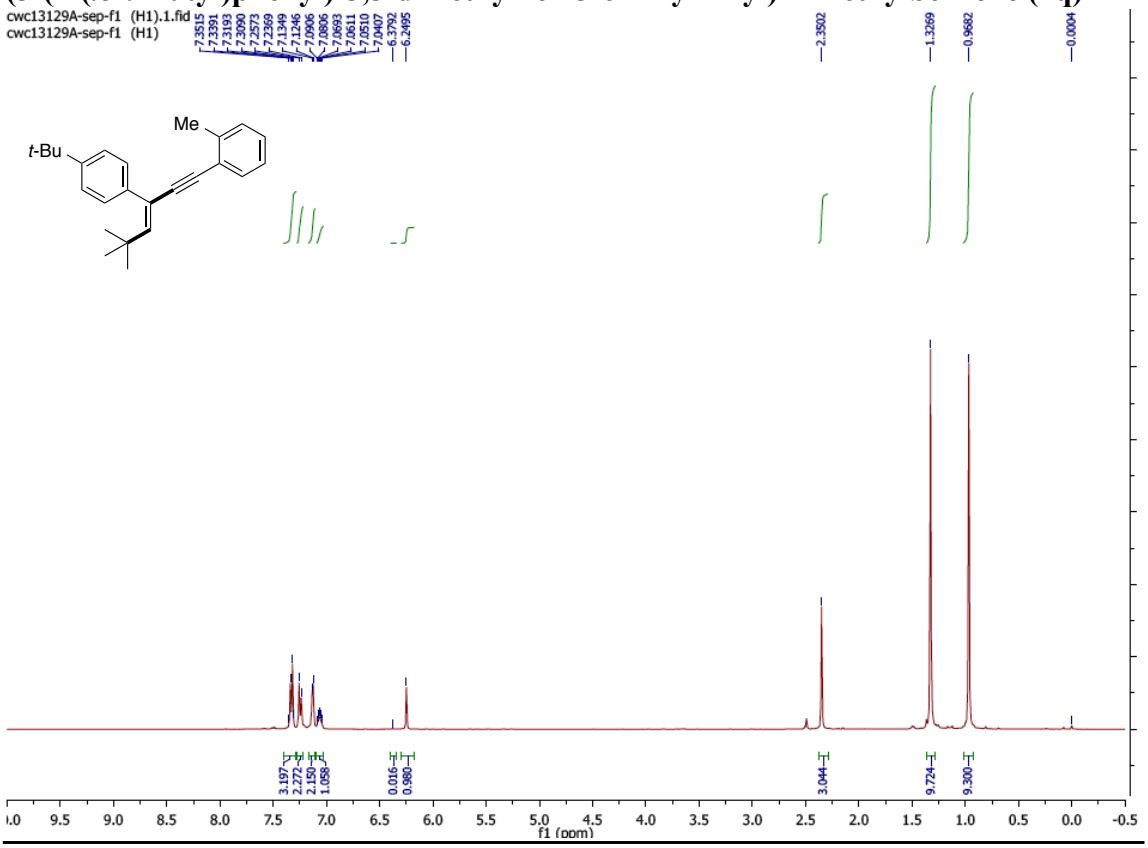


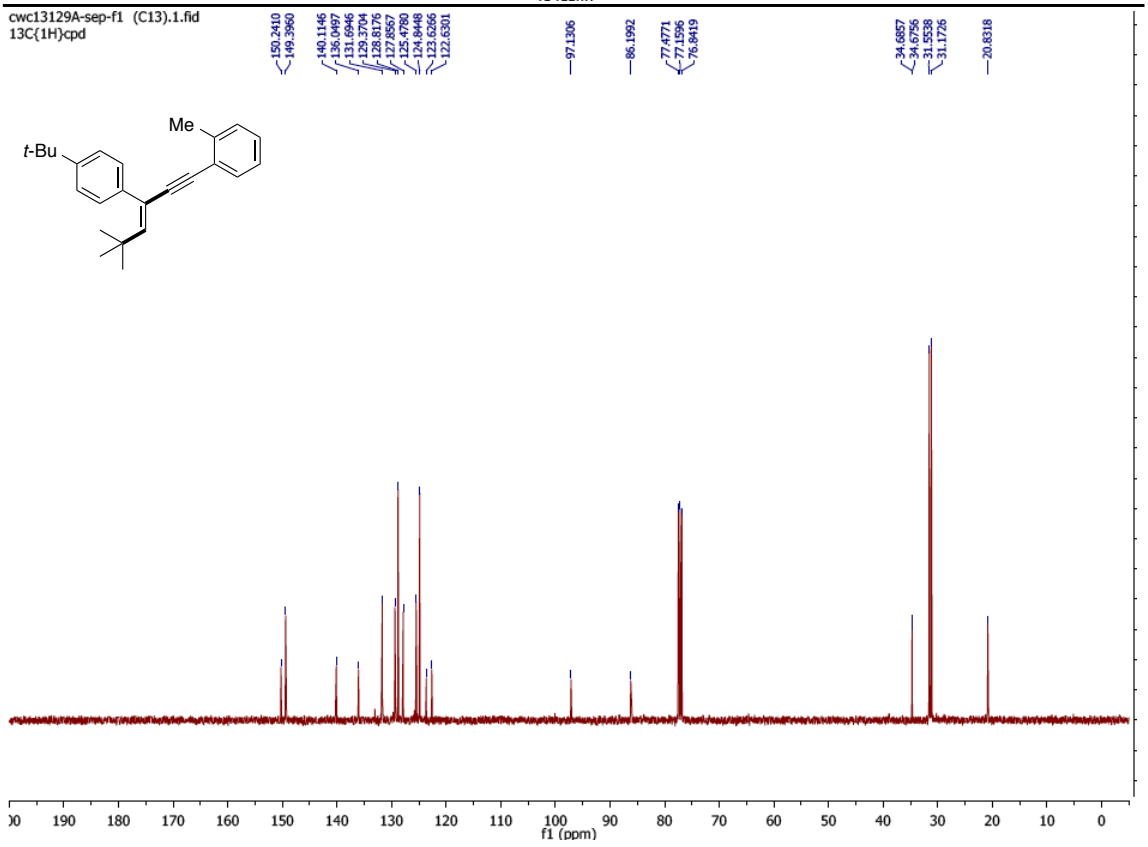
(*E*)-1-Bromo-4-(3-(4-(*tert*-butyl)phenyl)-5,5-dimethylhex-3-en-1-yn-1-yl)benzene (2p)



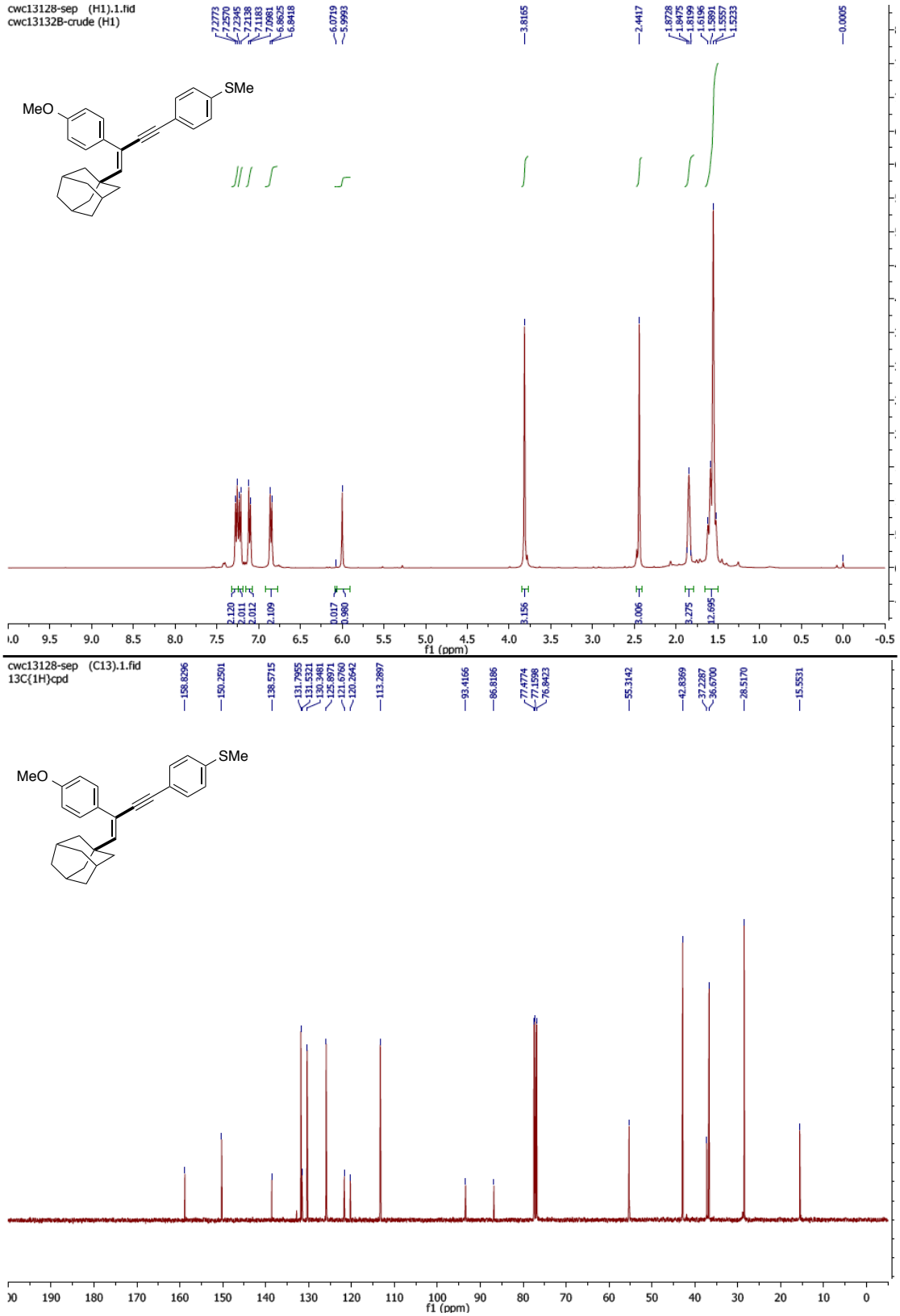


(*E*)-1-(3-(4-(*tert*-Butyl)phenyl)-5,5-dimethylhex-3-en-1-yn-1-yl)-2-methylbenzene (2q)

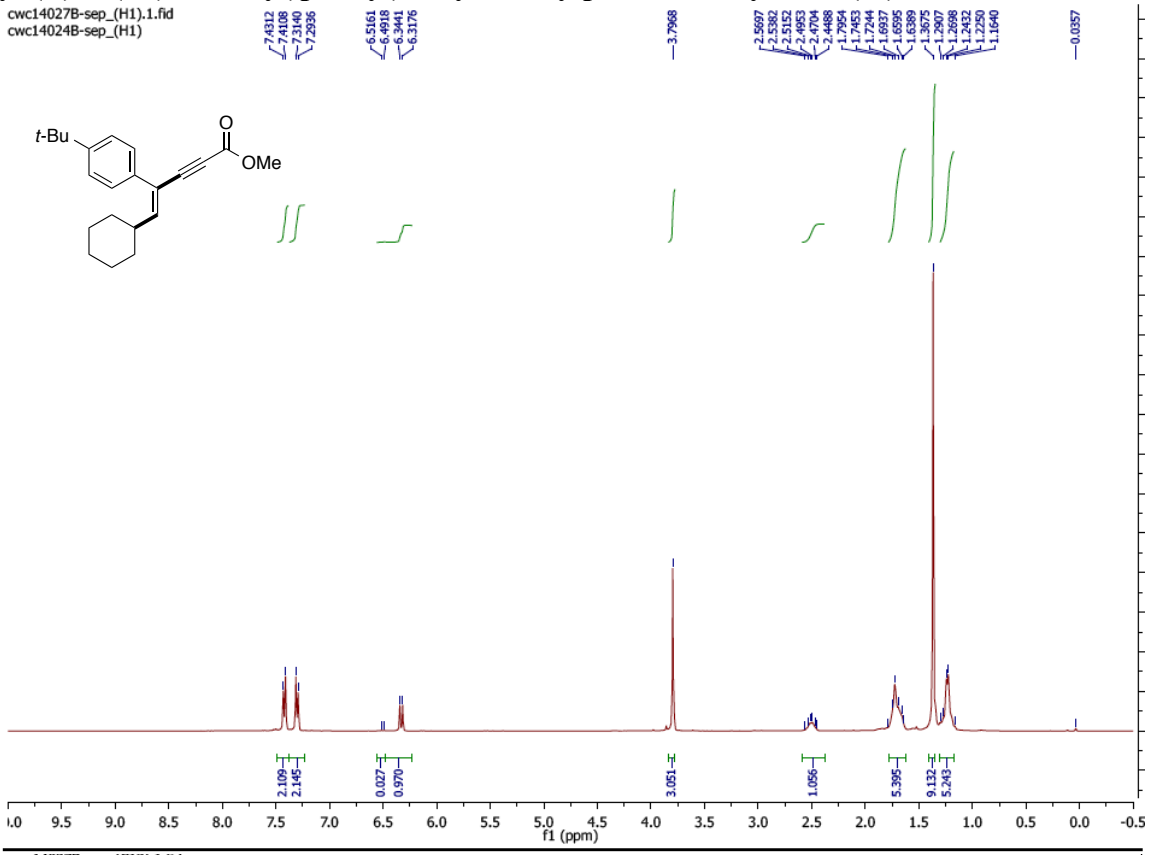


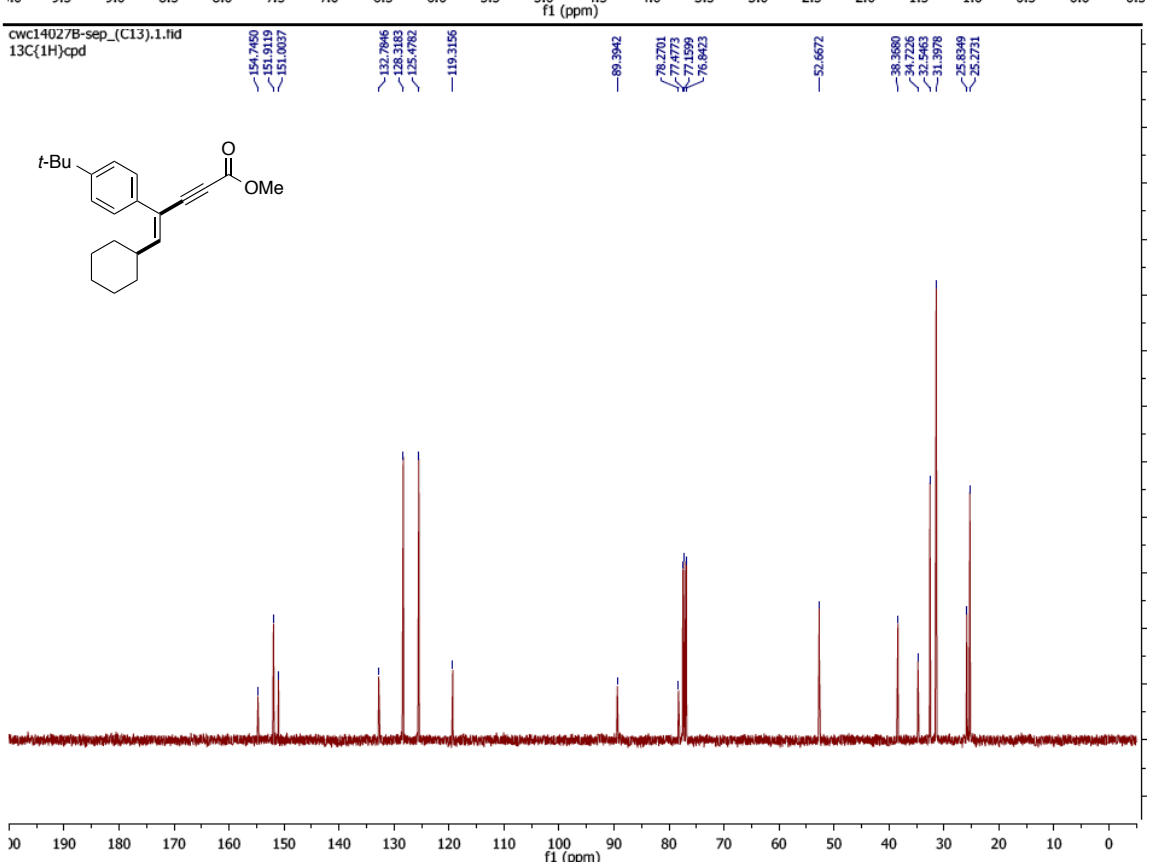


(4-((*E*)-4-(Adamantan-1-yl)-3-(4-methoxyphenyl)but-3-en-1-yn-1 yl)phenyl)(methyl)sulfane (2r)

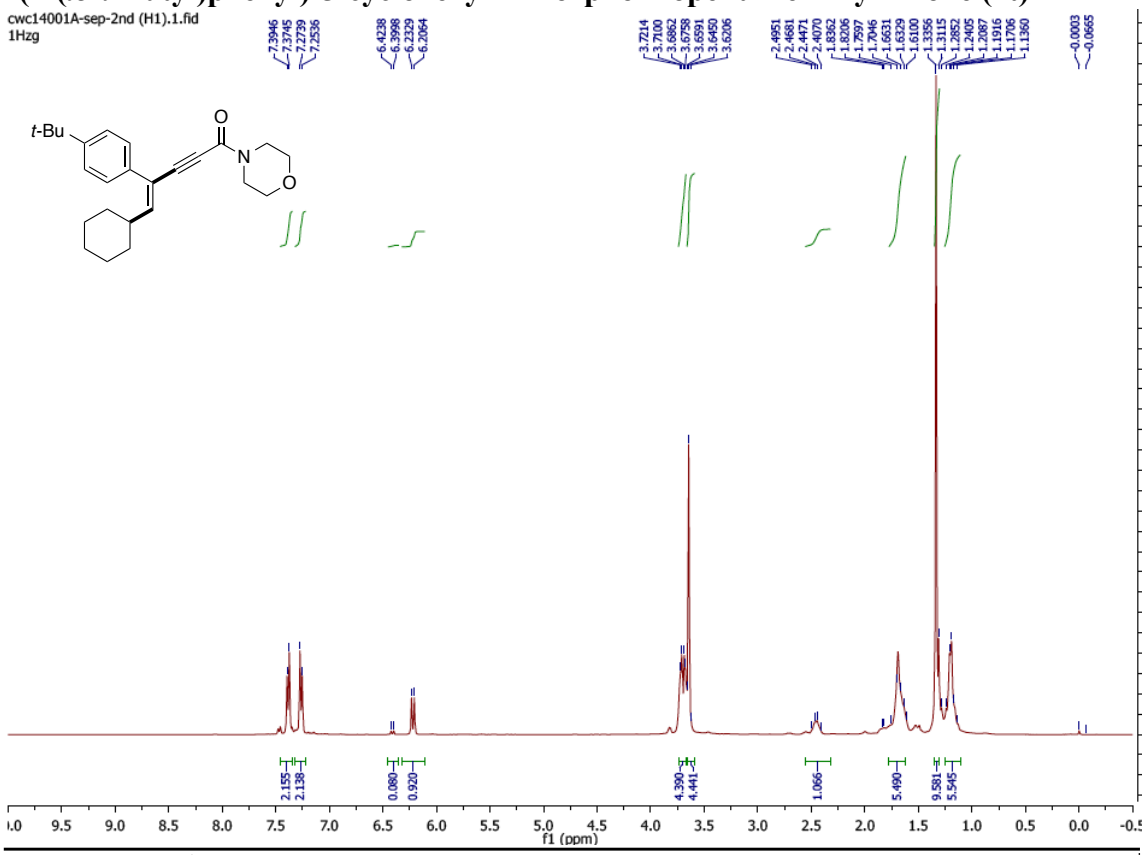


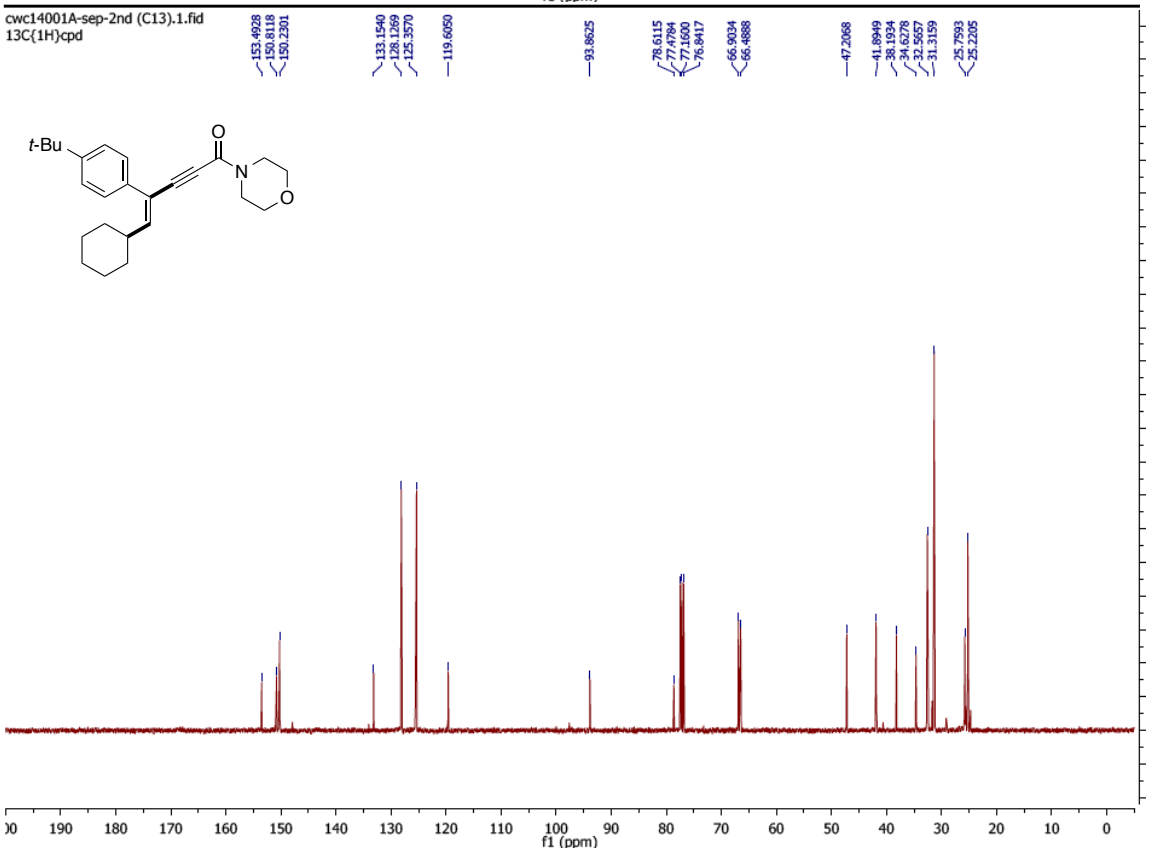
Methyl (*E*)-4-(4-(*tert*-Butyl)phenyl)-5-cyclohexylpent-4-en-2-ynoate (2s)



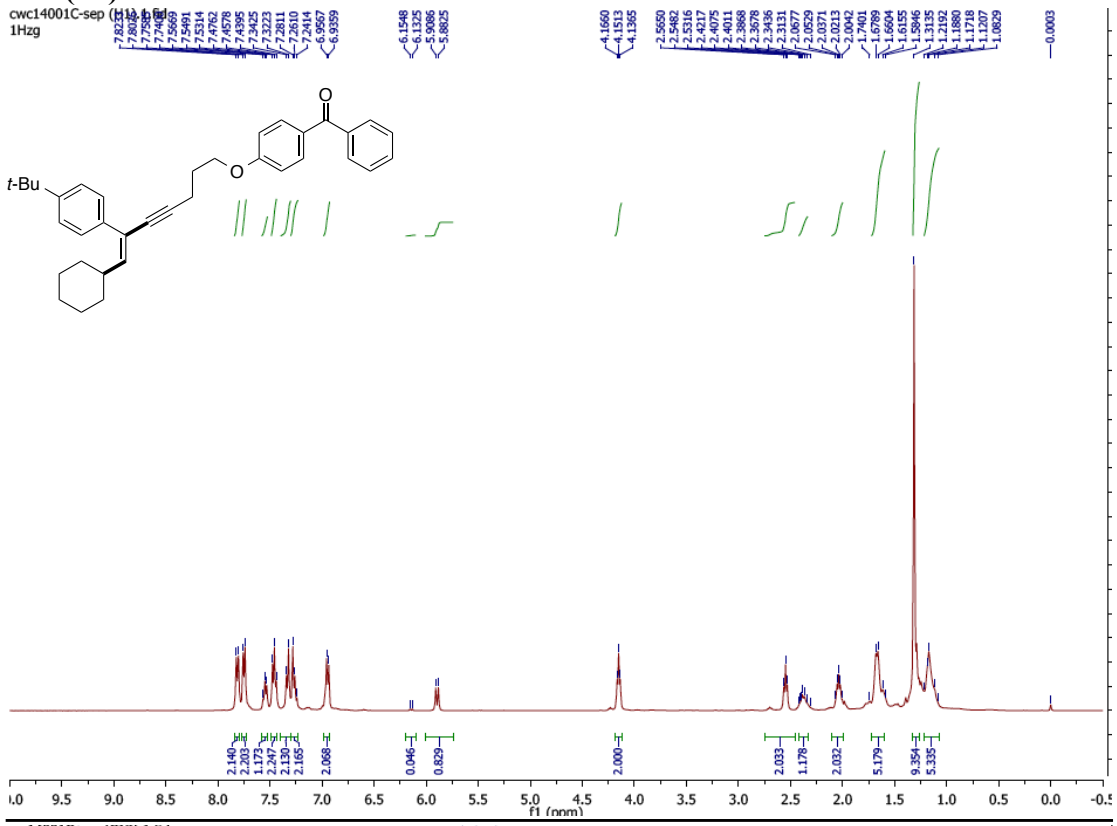


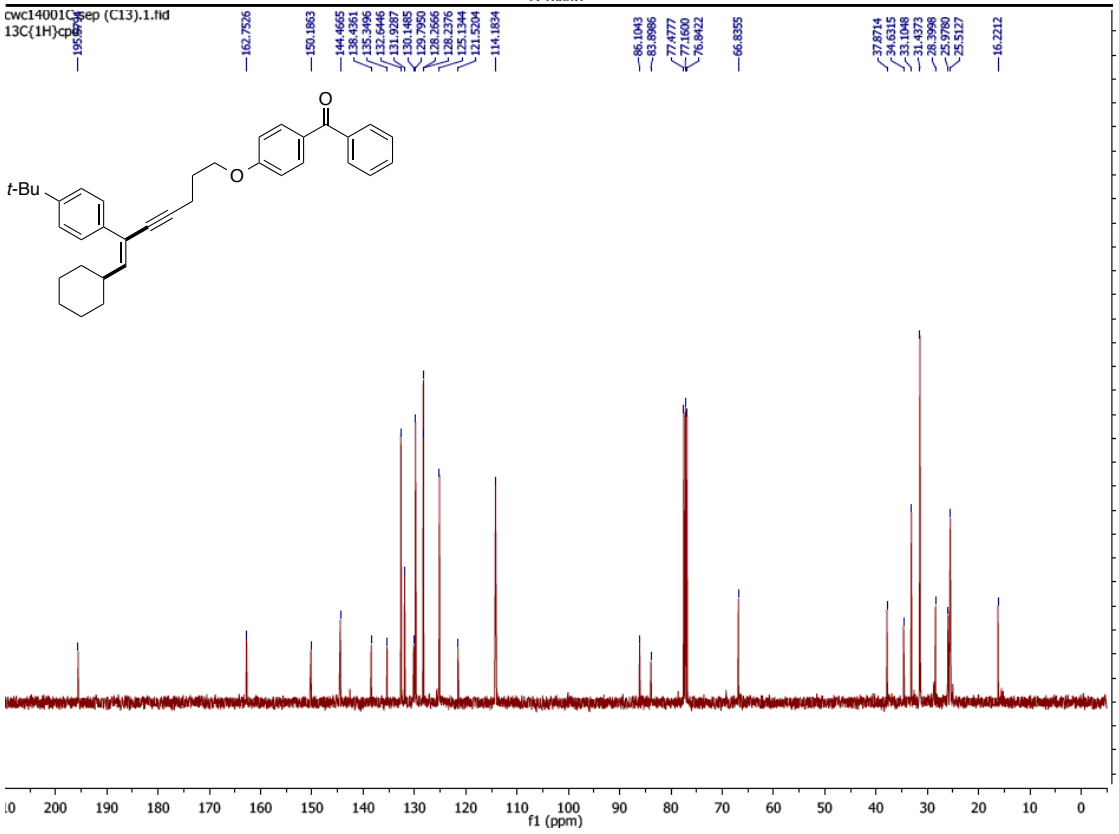
(*E*)-4-(4-(*tert*-Butyl)phenyl)-5-cyclohexyl-1-morpholinopent-4-en-2-yn-1-one (2t)



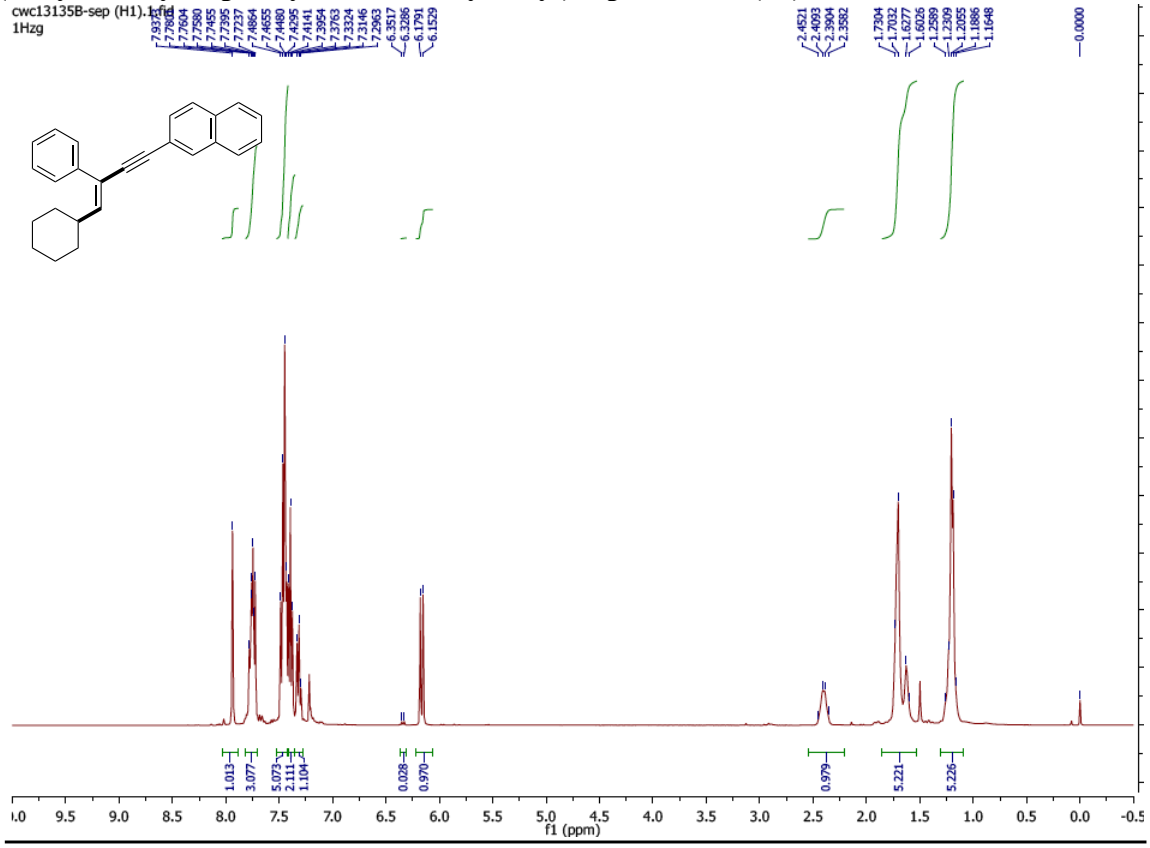


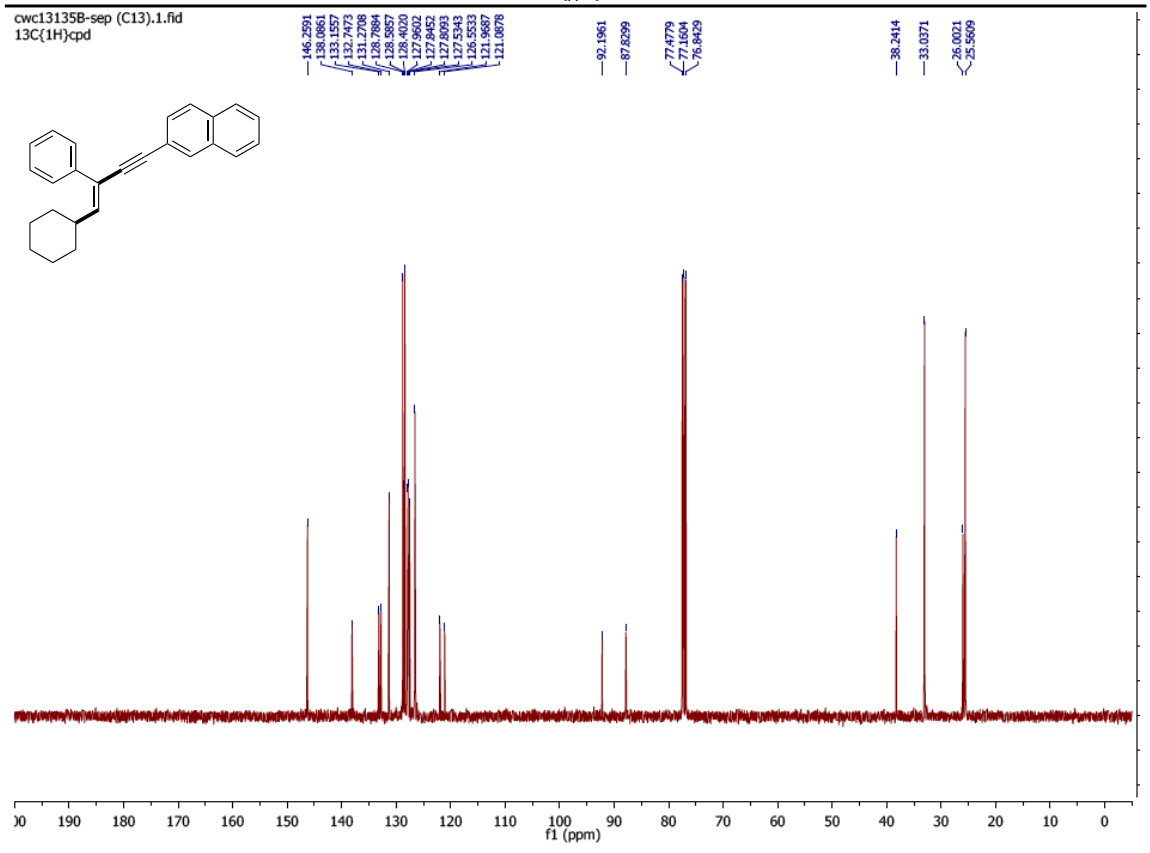
(*E*)-(4-((6-(4-(*tert*-Butyl)phenyl)-7-cyclohexylhept-6-en-4-yn-1-yl)oxy)phenyl)(phenyl)-methanone (2u)



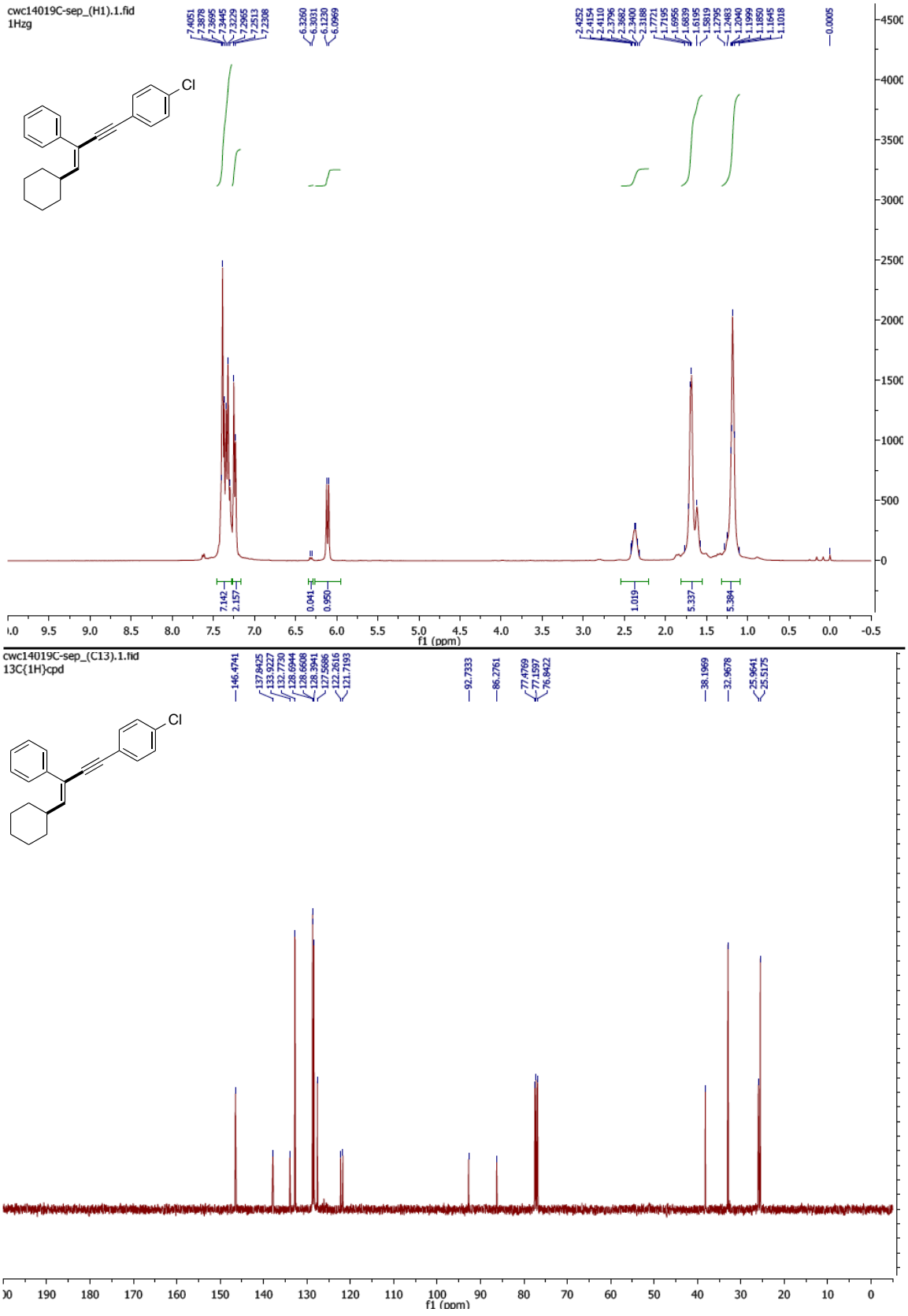


(*E*)-2-(4-Cyclohexyl-3-phenylbut-3-en-1-yn-1-yl)naphthalene (2v)

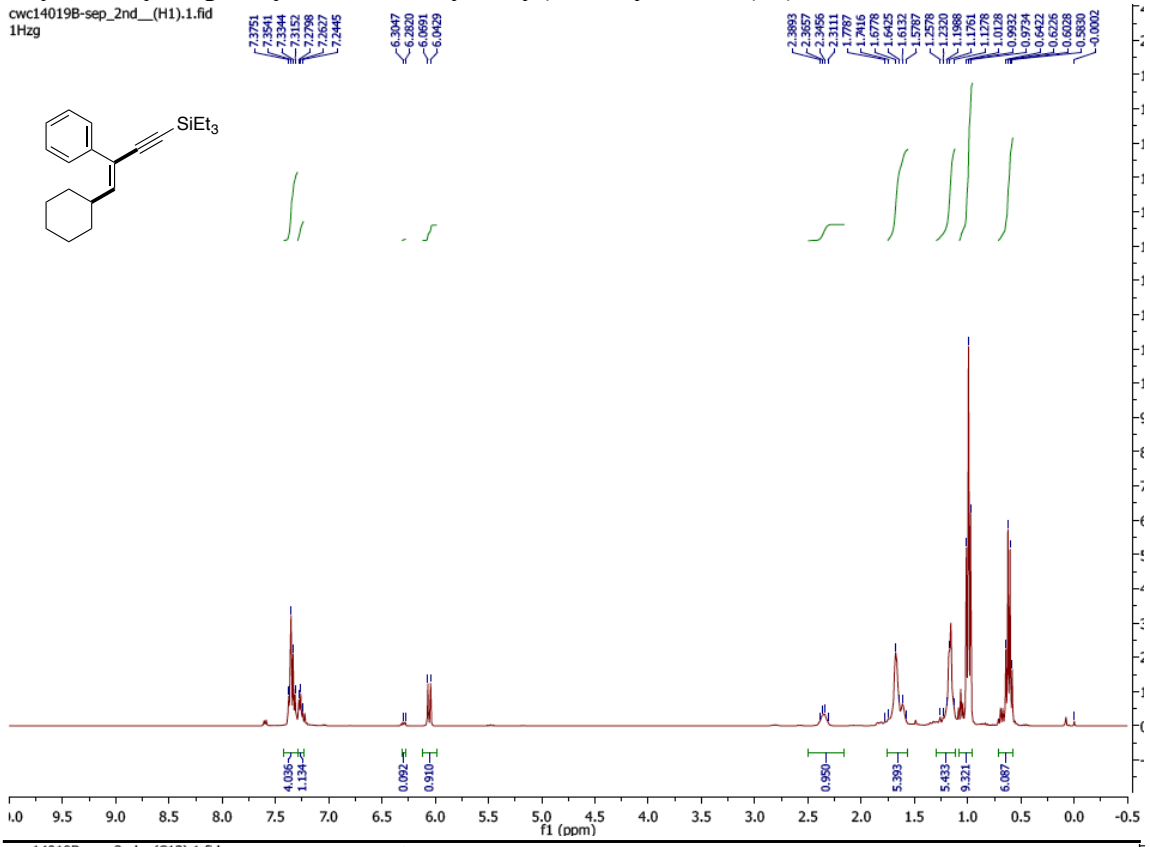


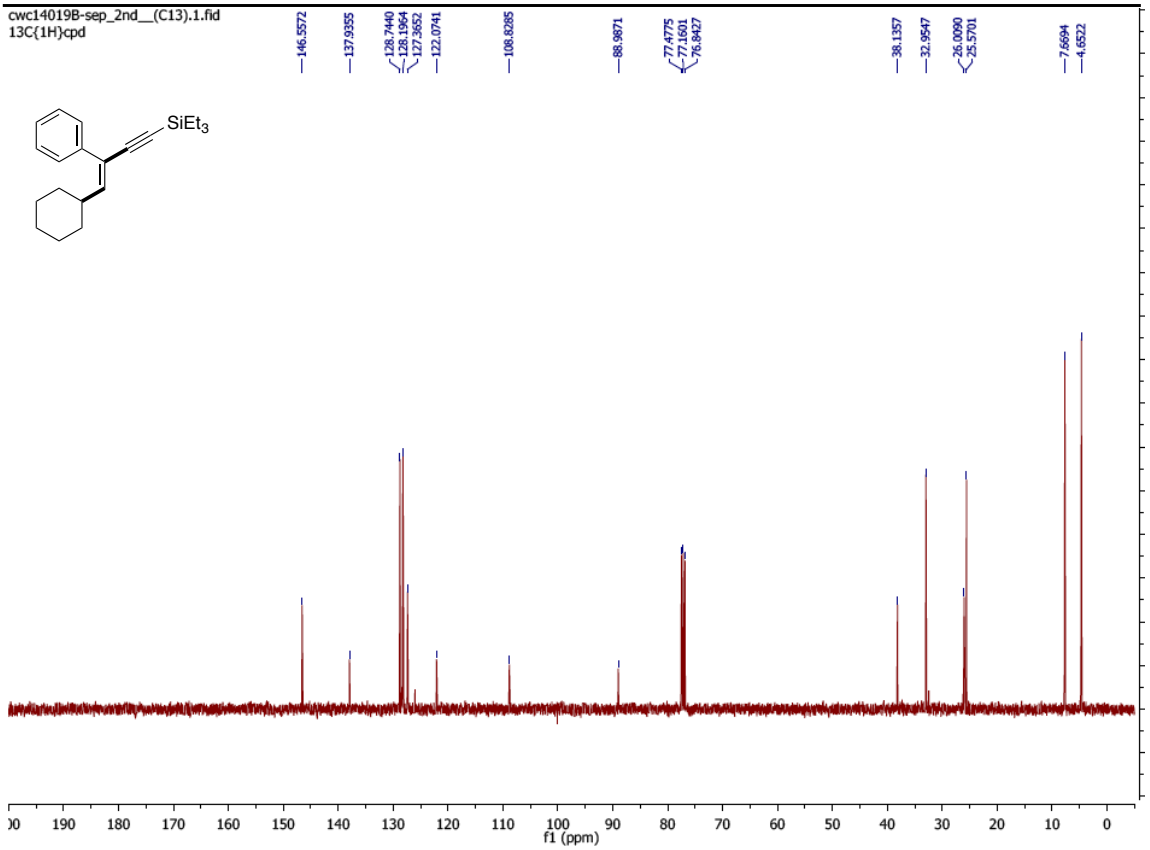


(*E*)-1-Chloro-4-(4-cyclohexyl-3-phenylbut-3-en-1-yn-1-yl)benzene (2w)

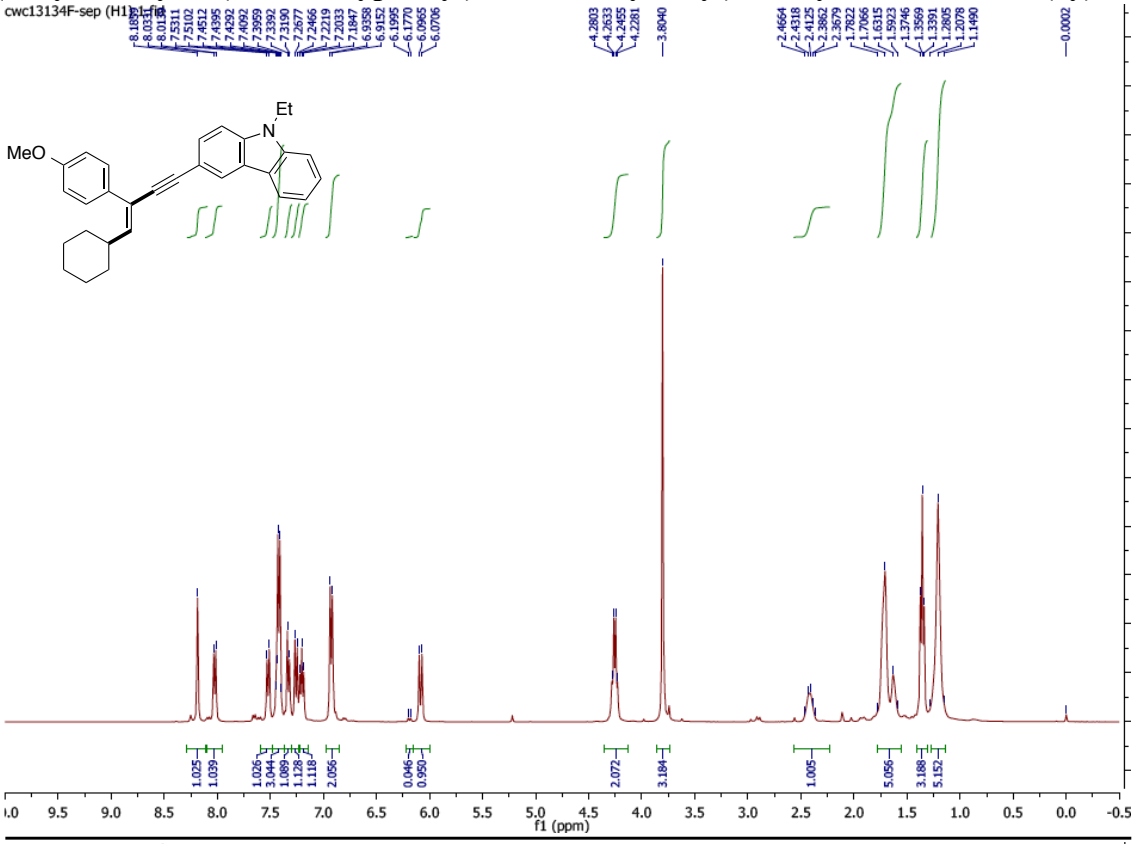


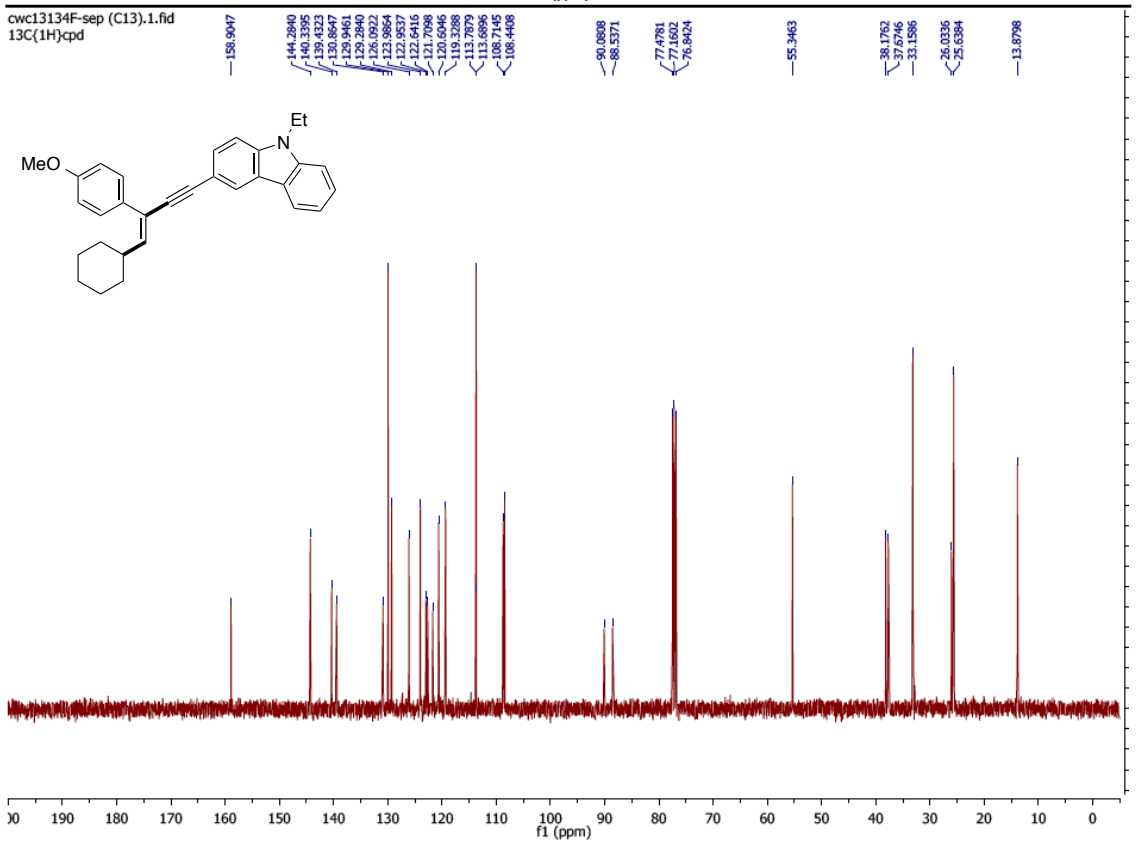
(*E*)-(4-Cyclohexyl-3-phenylbut-3-en-1-yn-1-yl)triethylsilane (2x)



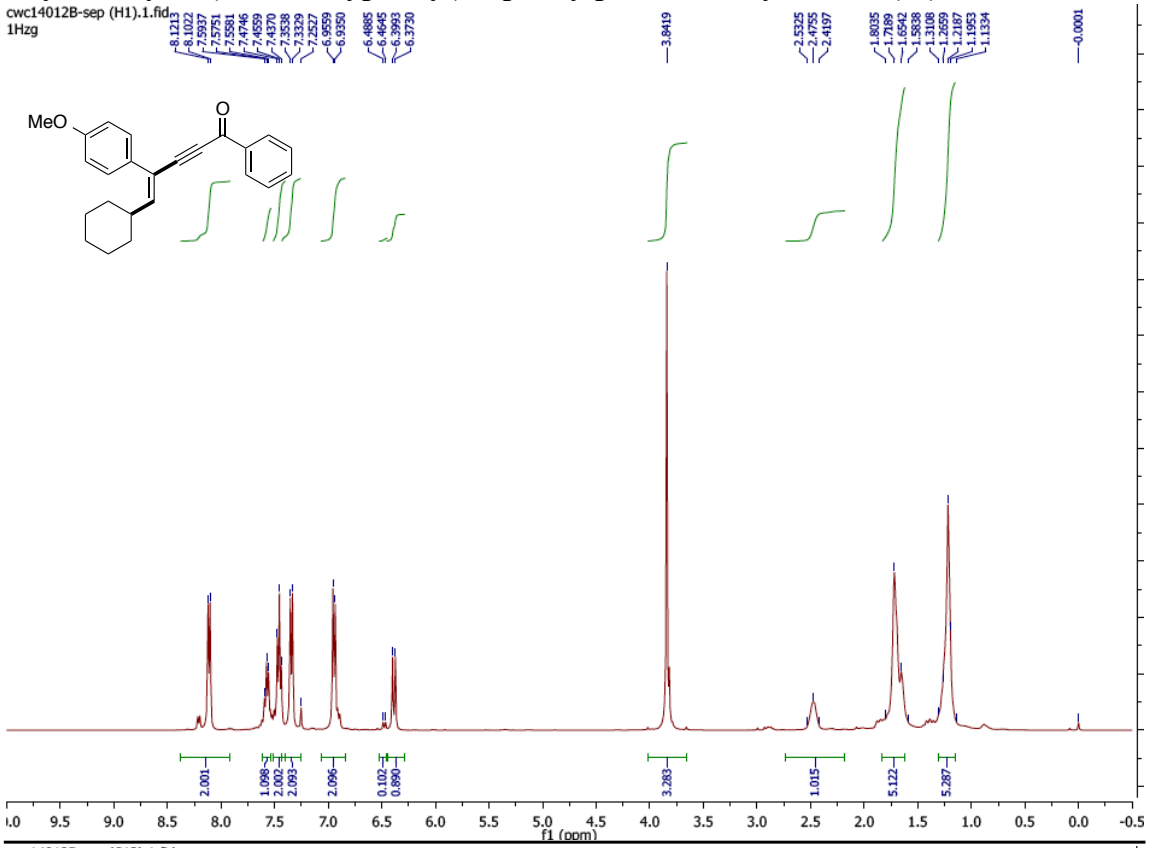


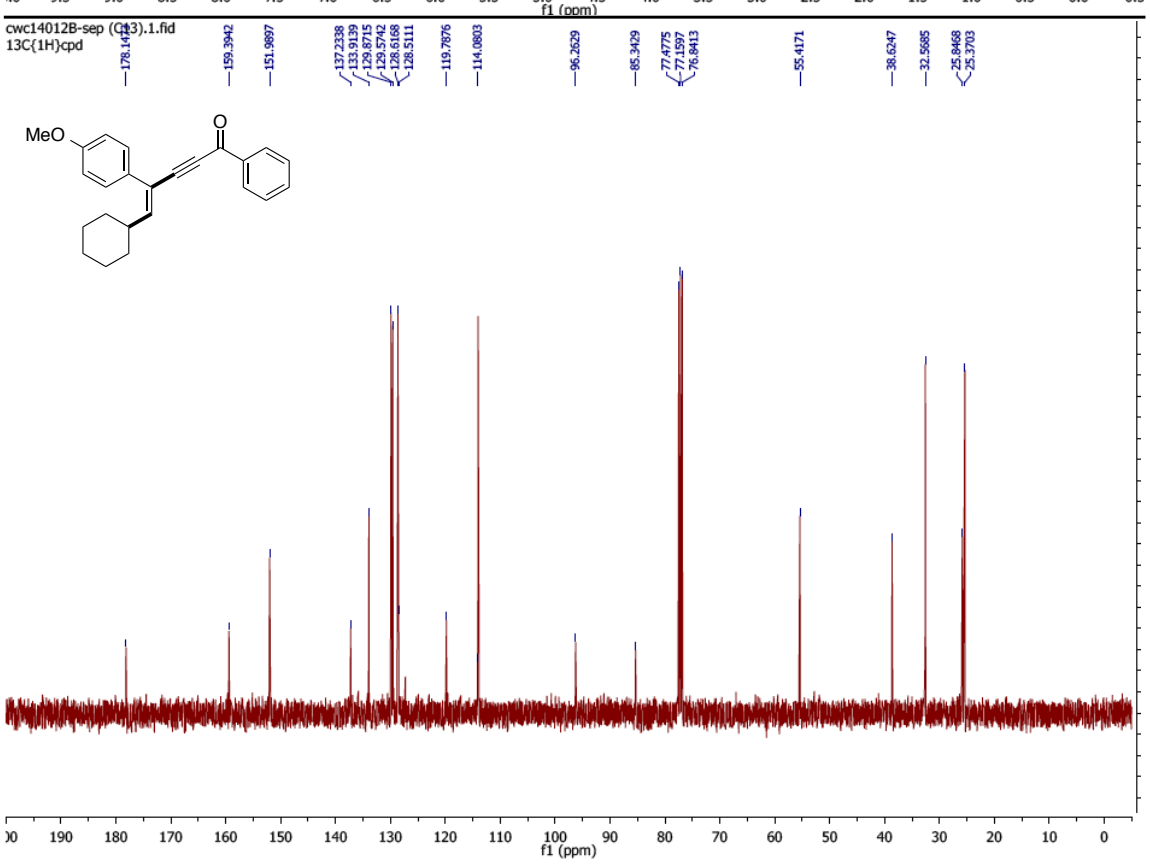
(*E*)-3-(4-Cyclohexyl-3-(4-methoxyphenyl)but-3-en-1-yn-1-yl)-9-ethyl-9*H*-carbazole (2y)



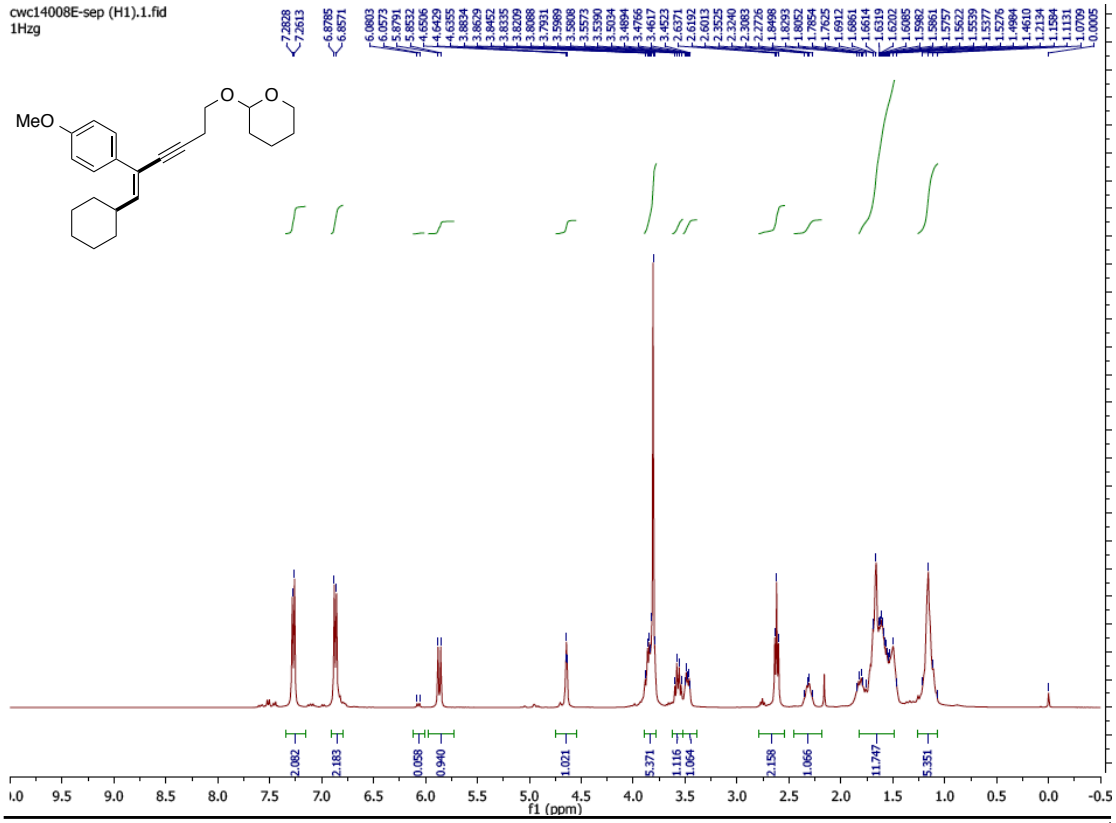


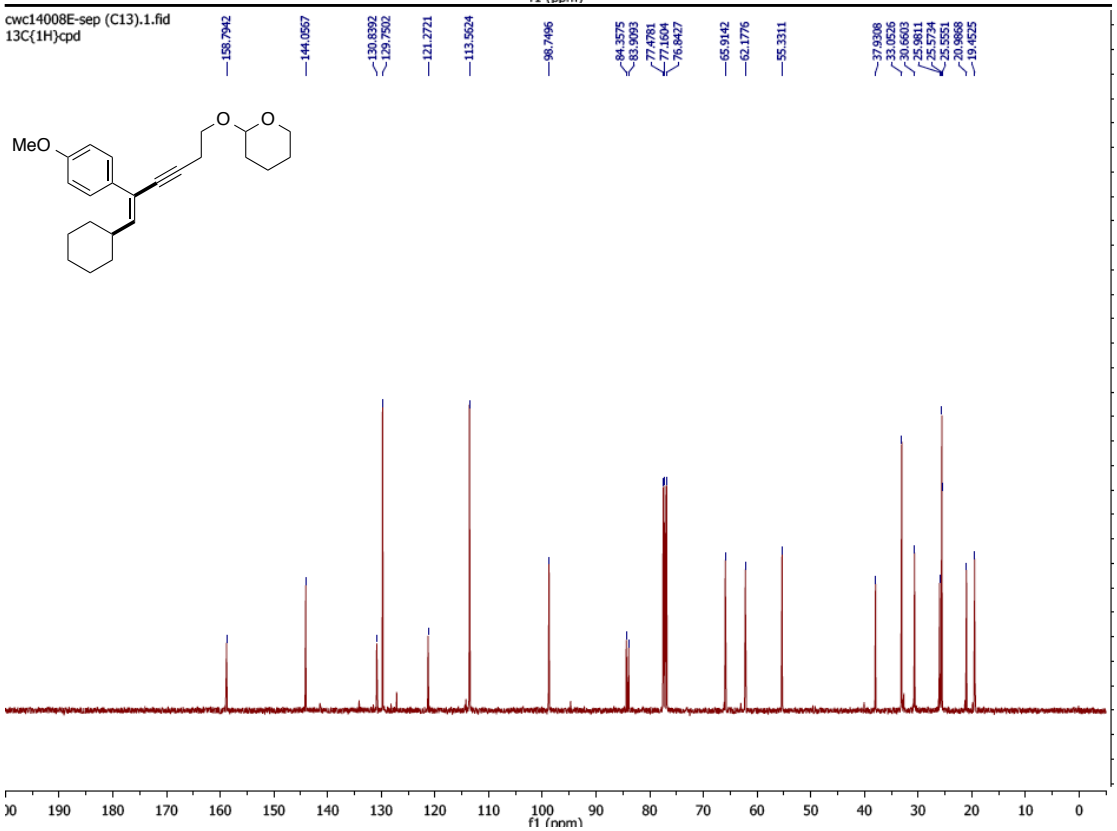
(*E*)-5-Cyclohexyl-4-(4-methoxyphenyl)-1-phenylpent-4-en-2-yn-1-one (2z)



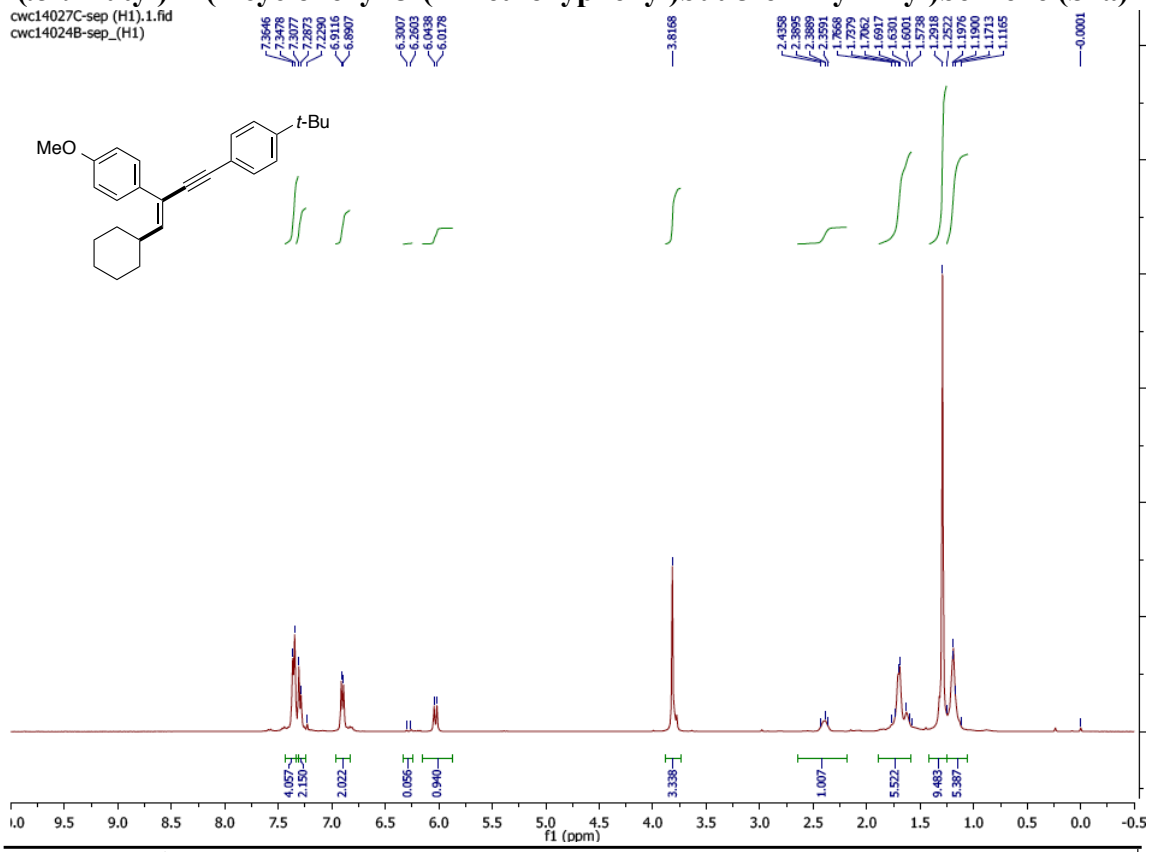


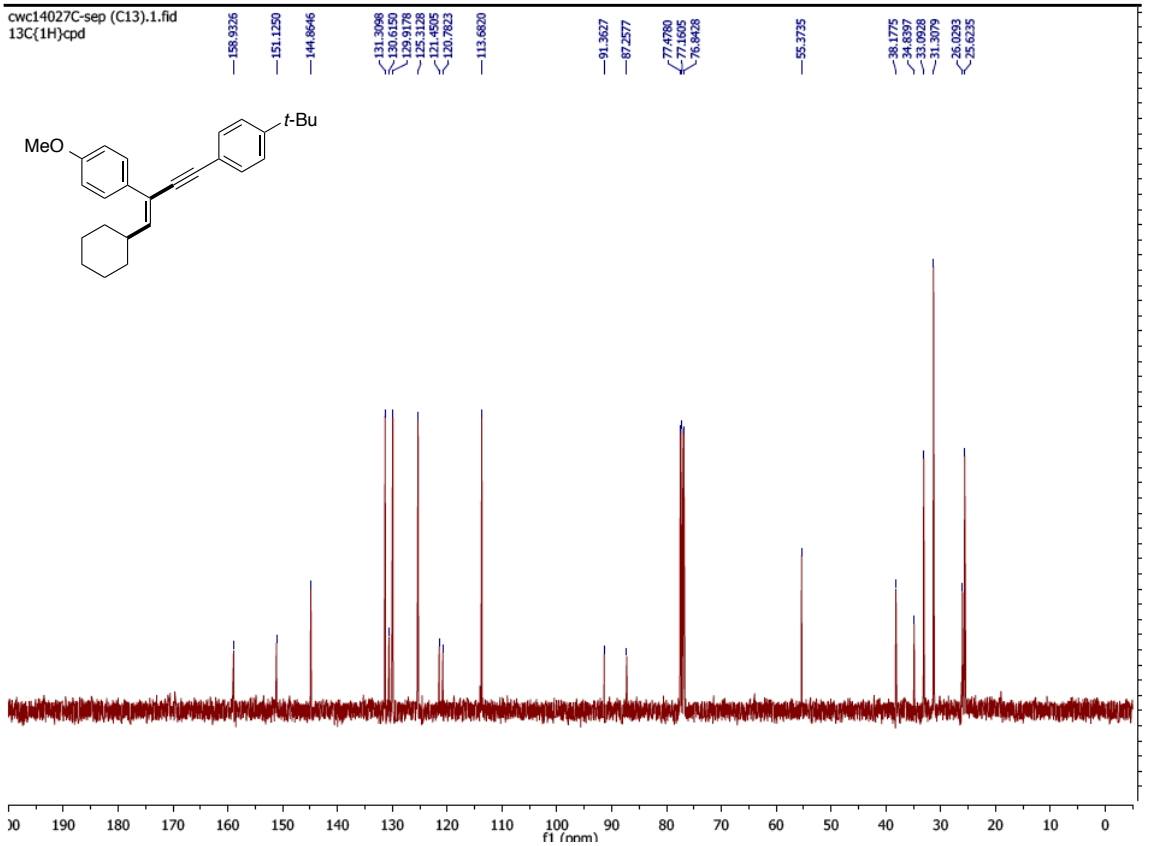
(*E*)-2-((6-Cyclohexyl-5-(4-methoxyphenyl)hex-5-en-3-yn-1-yl)oxy)tetrahydro-2*H*-pyran (2aa)



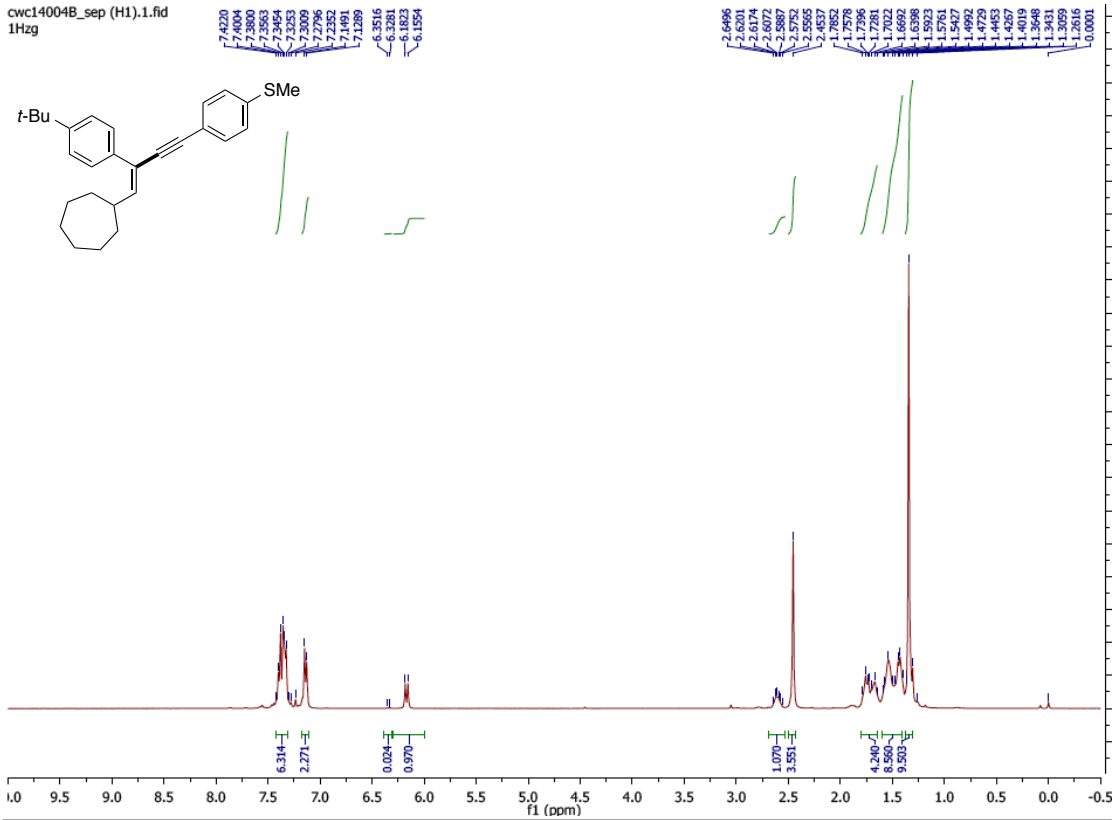


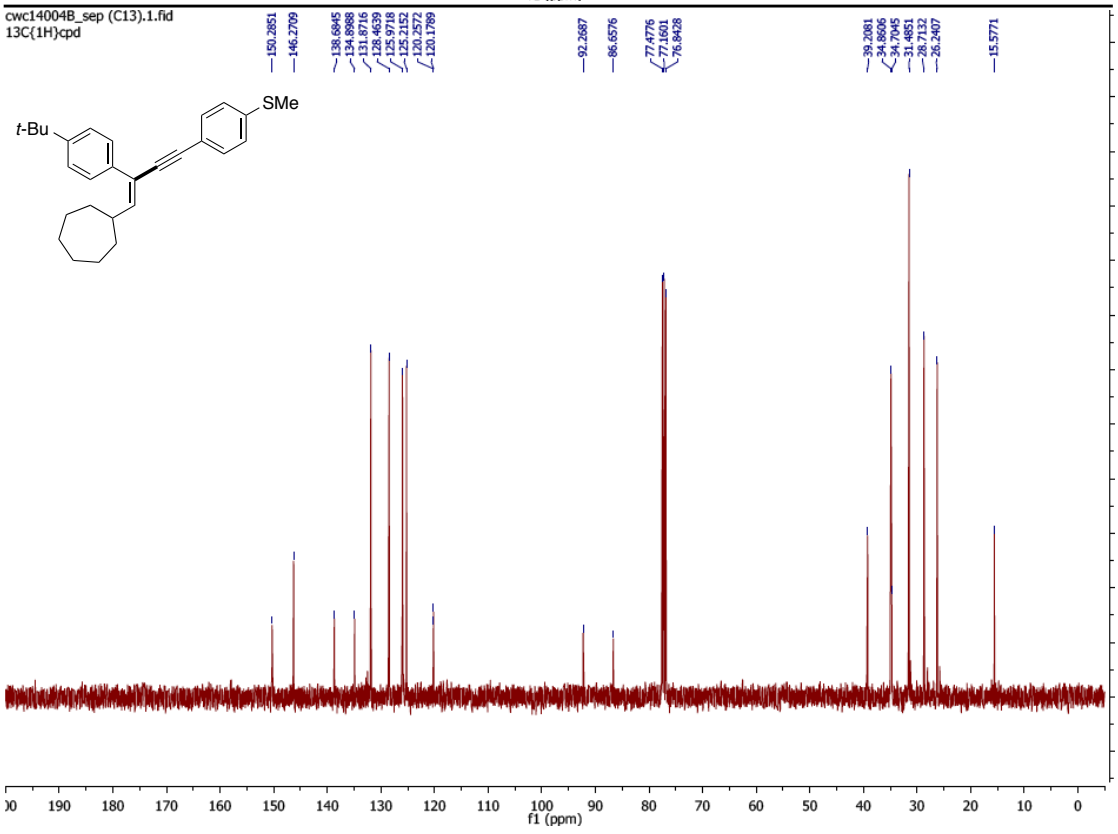
(*E*)-1-(*tert*-Butyl)-4-(4-cyclohexyl-3-(4-methoxyphenyl)but-3-en-1-yn-1-yl)benzene (S2a)



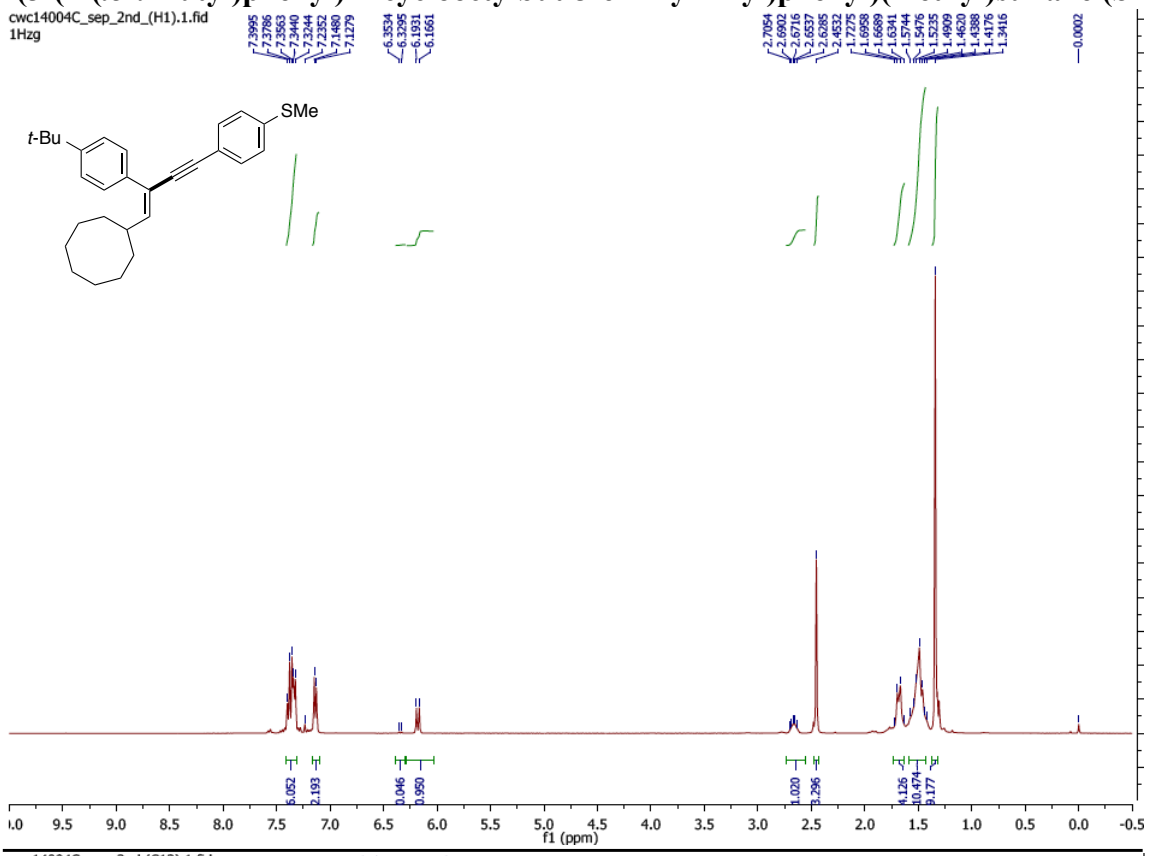


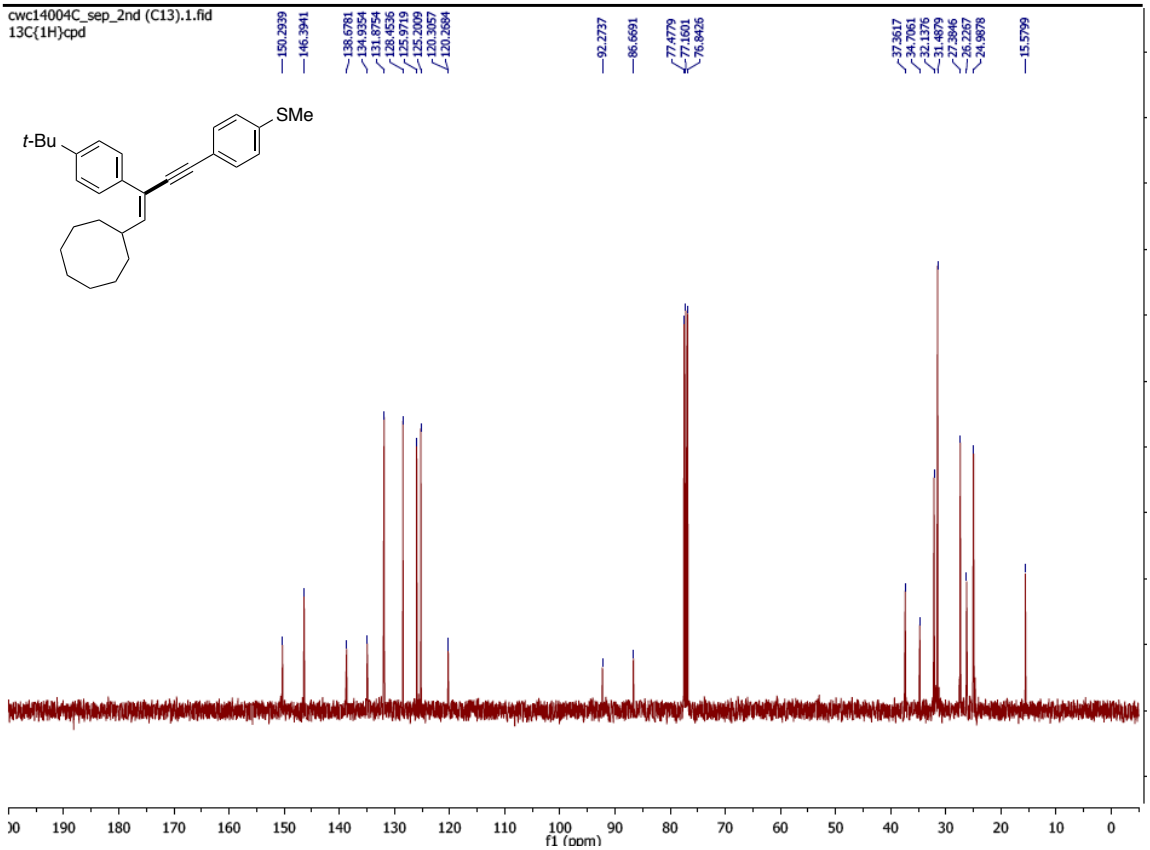
(*E*)-(4-(3-(4-(*tert*-Butyl)phenyl)-4-cycloheptylbut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane (S2b)



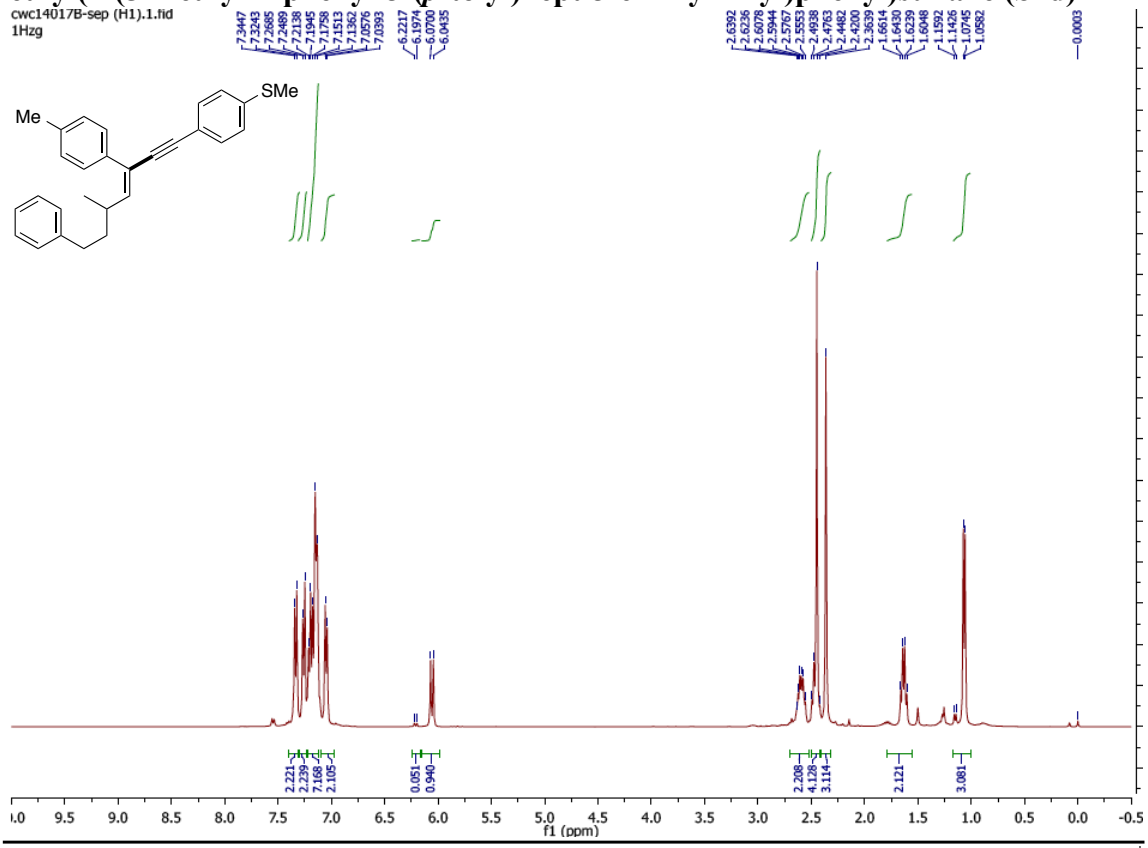


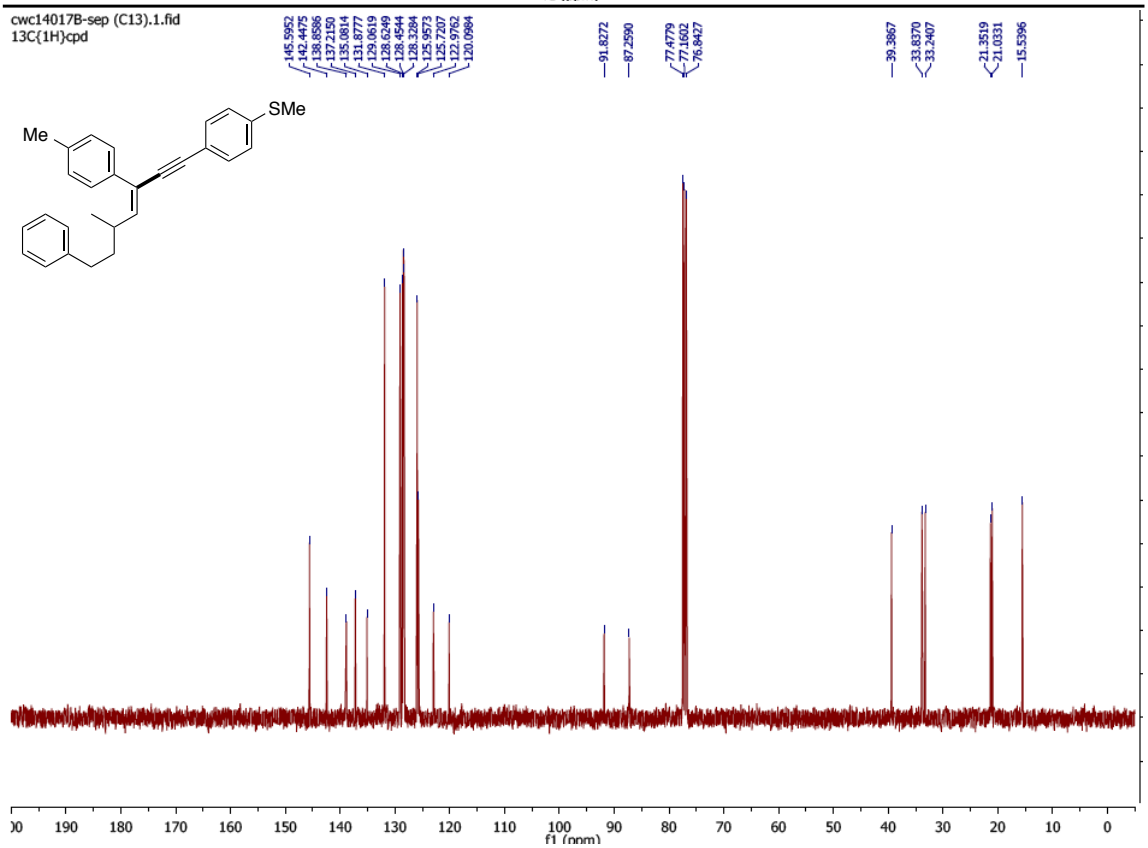
(*E*)-(4-(3-(4-(*tert*-Butyl)phenyl)-4-cyclooctylbut-3-en-1-yn-1-yl)phenyl)(methyl)sulfane (S2c)



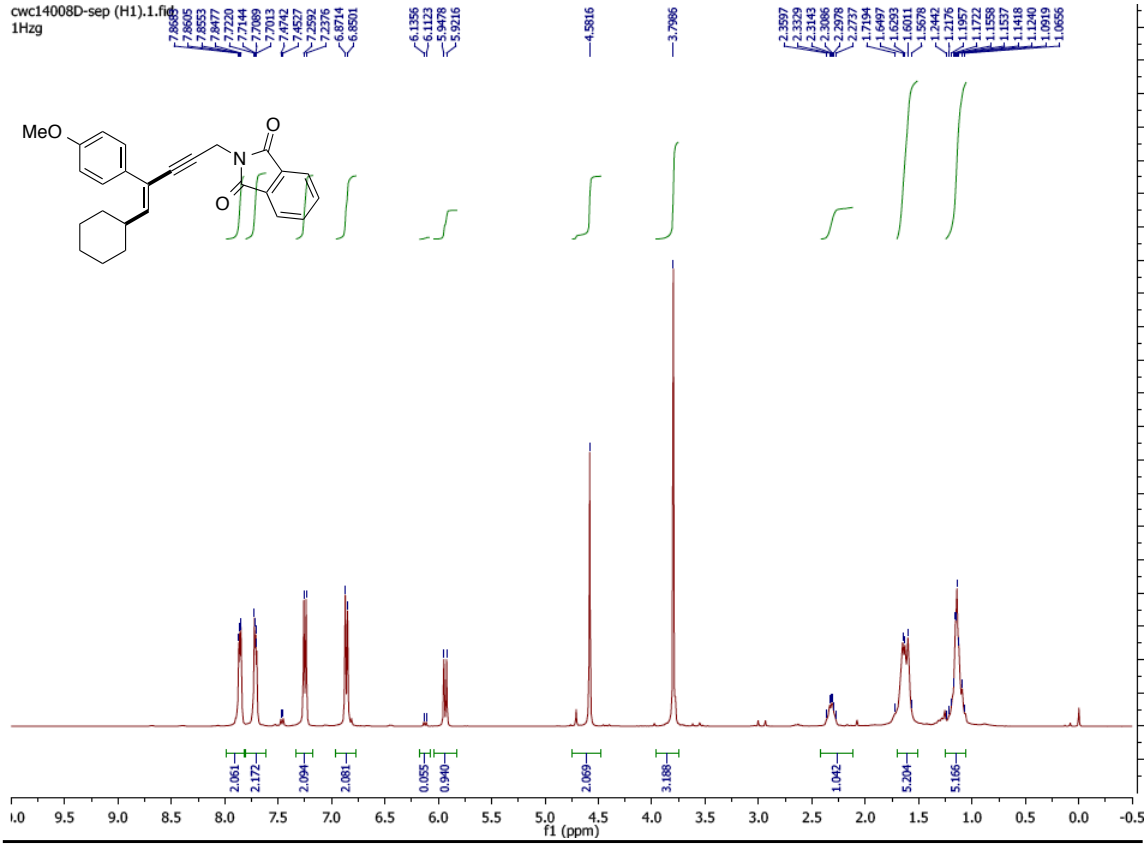


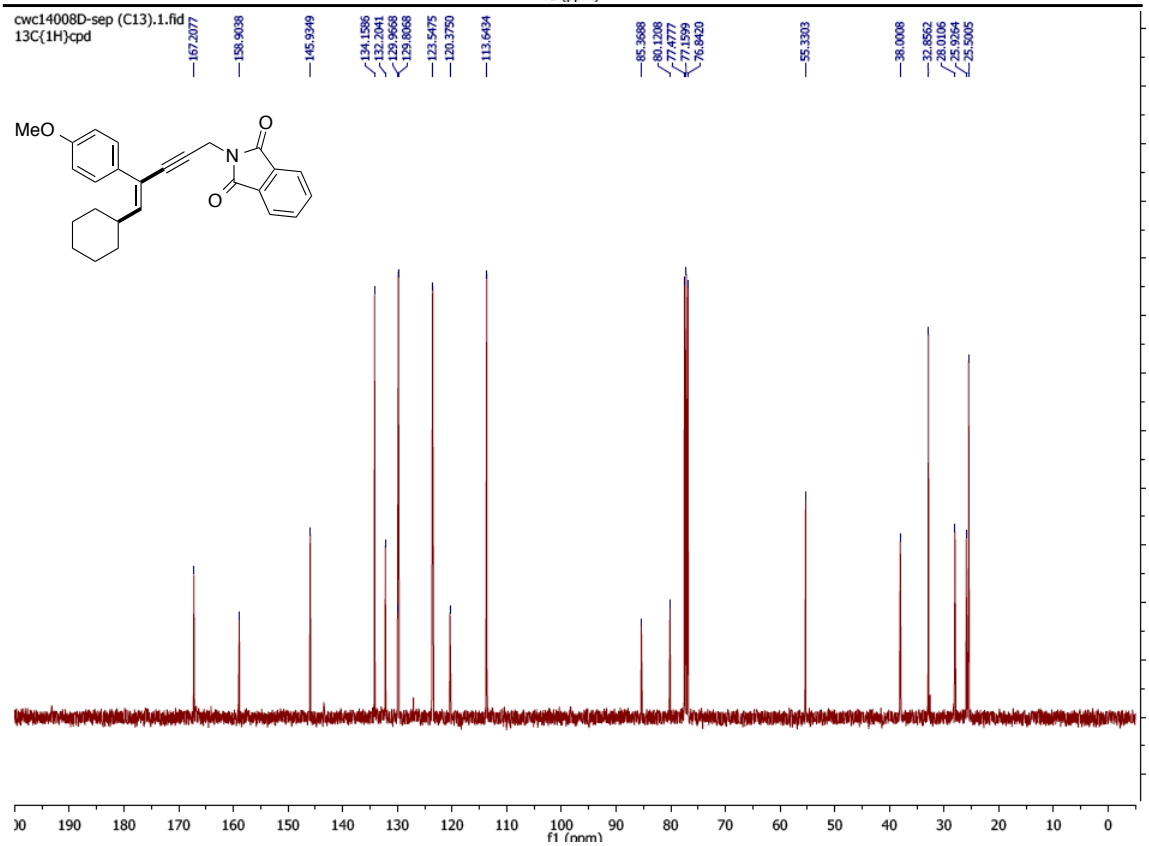
(*E*)-Methyl(4-(5-methyl-7-phenyl-3-(*p*-tolyl)hept-3-en-1-yn-1-yl)phenyl)sulfane (S2d)



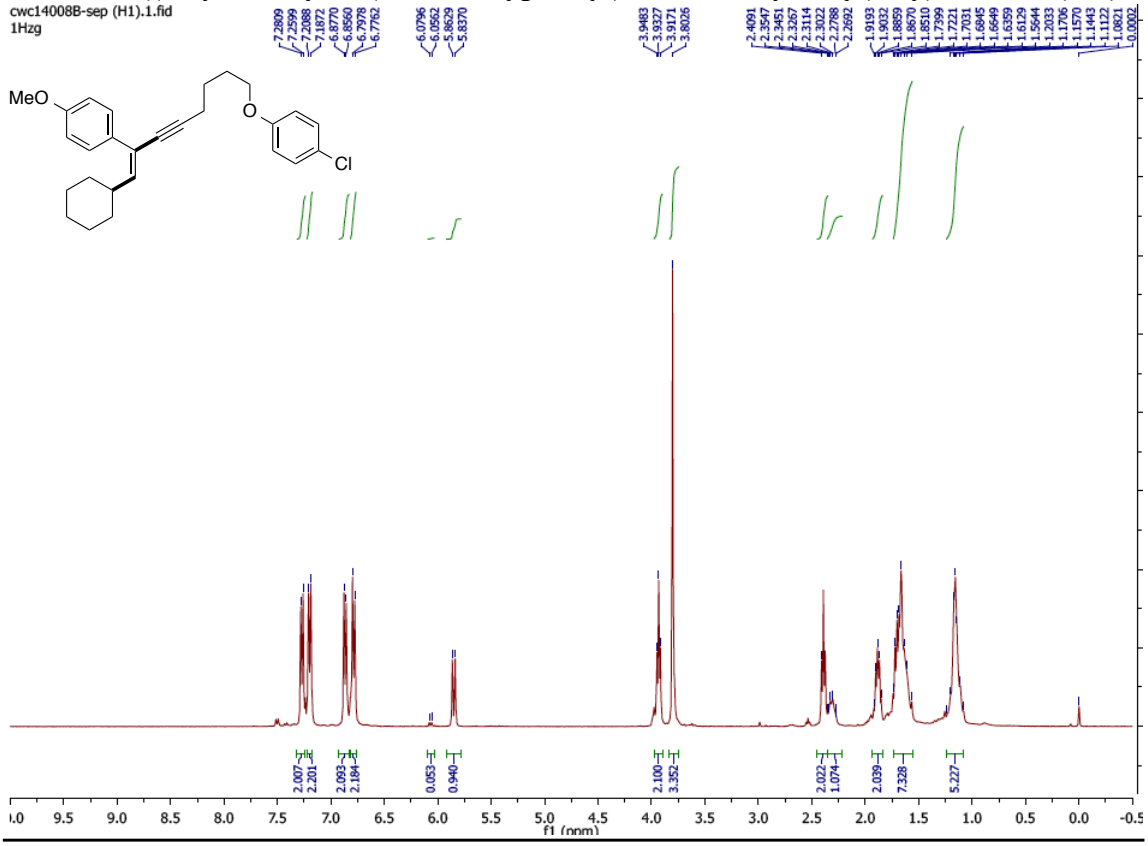


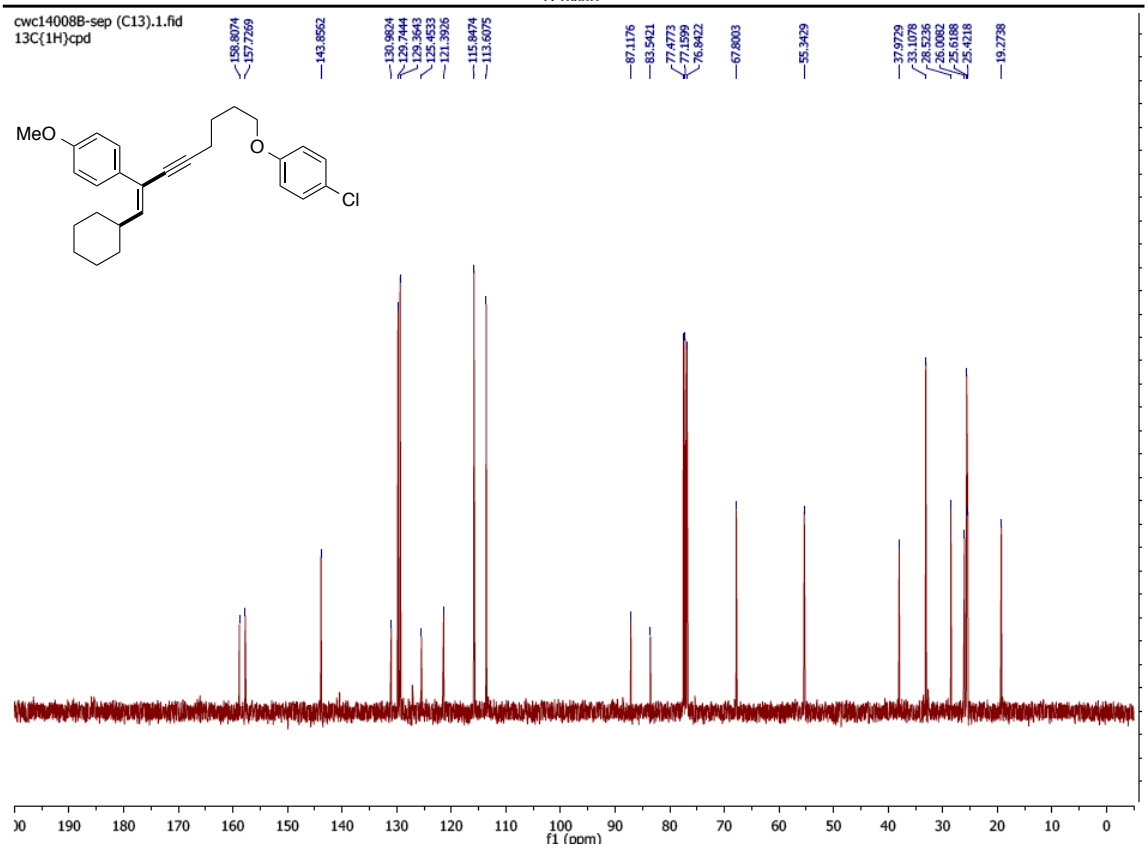
(*E*)-2-(5-Cyclohexyl-4-(4-methoxyphenyl)pent-4-en-2-yn-1-yl)isoindoline-1,3-dione (S2e)



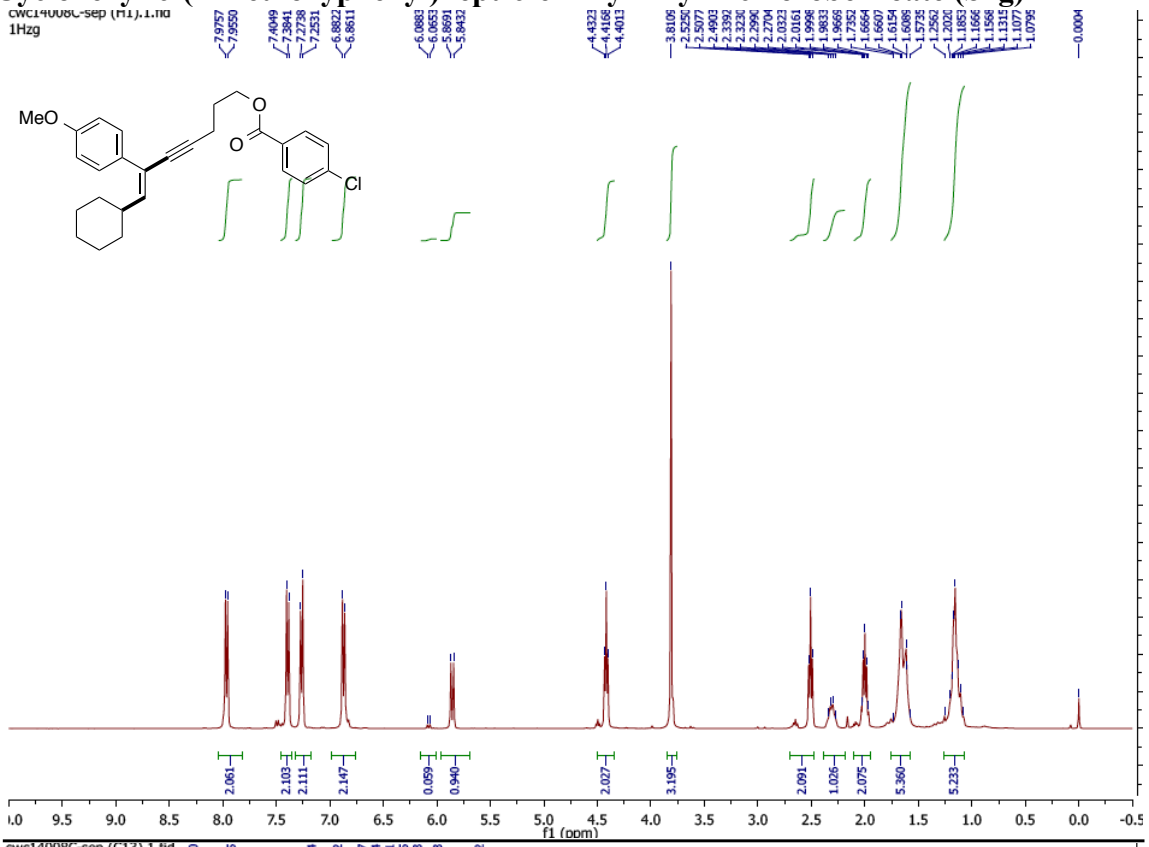


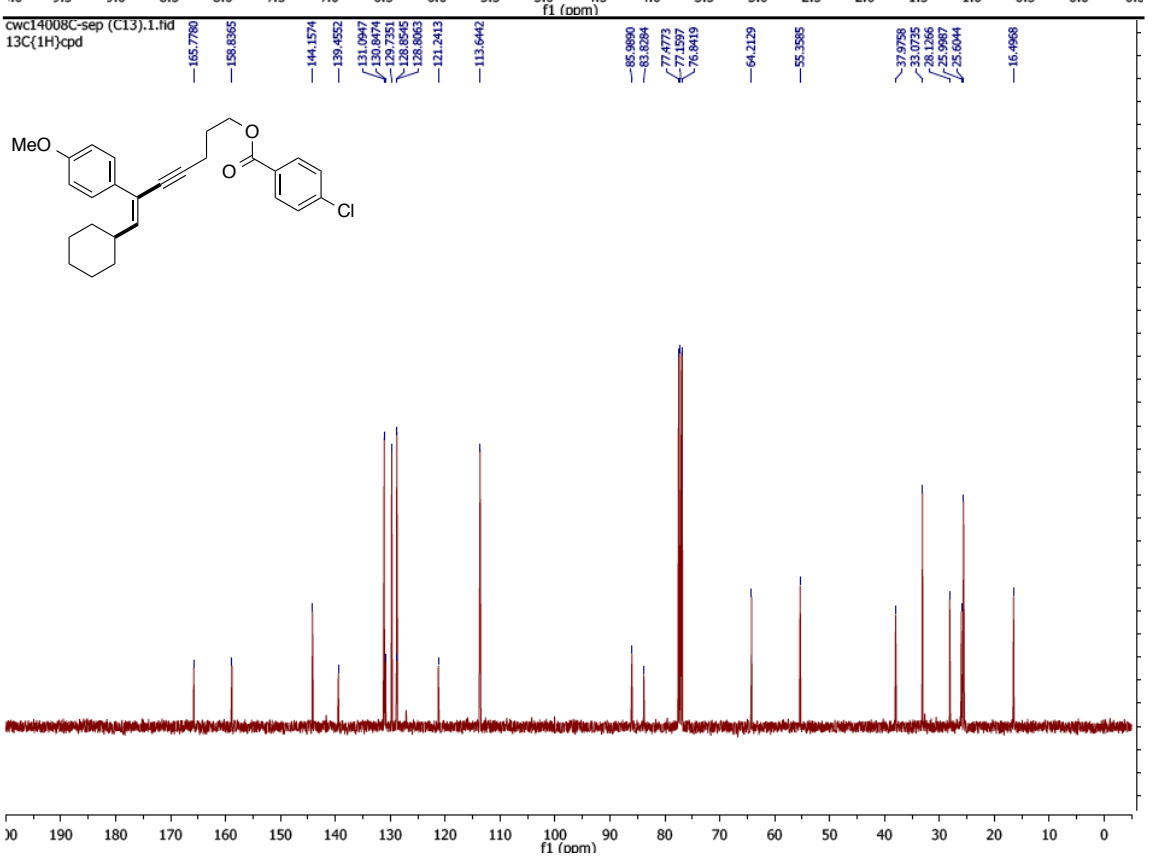
(*E*)-1-Chloro-4-((8-cyclohexyl-7-(4-methoxyphenyl)oct-7-en-5-yn-1-yl)oxy)benzene (S2f)



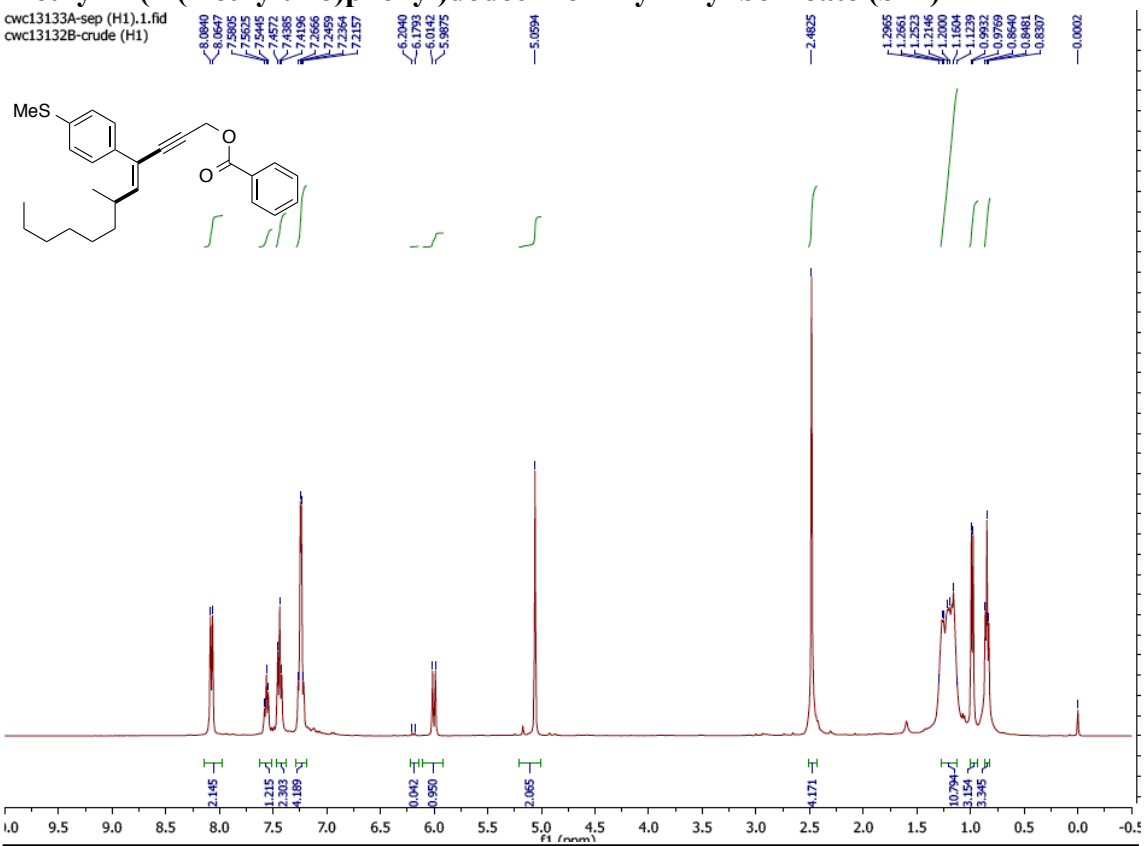


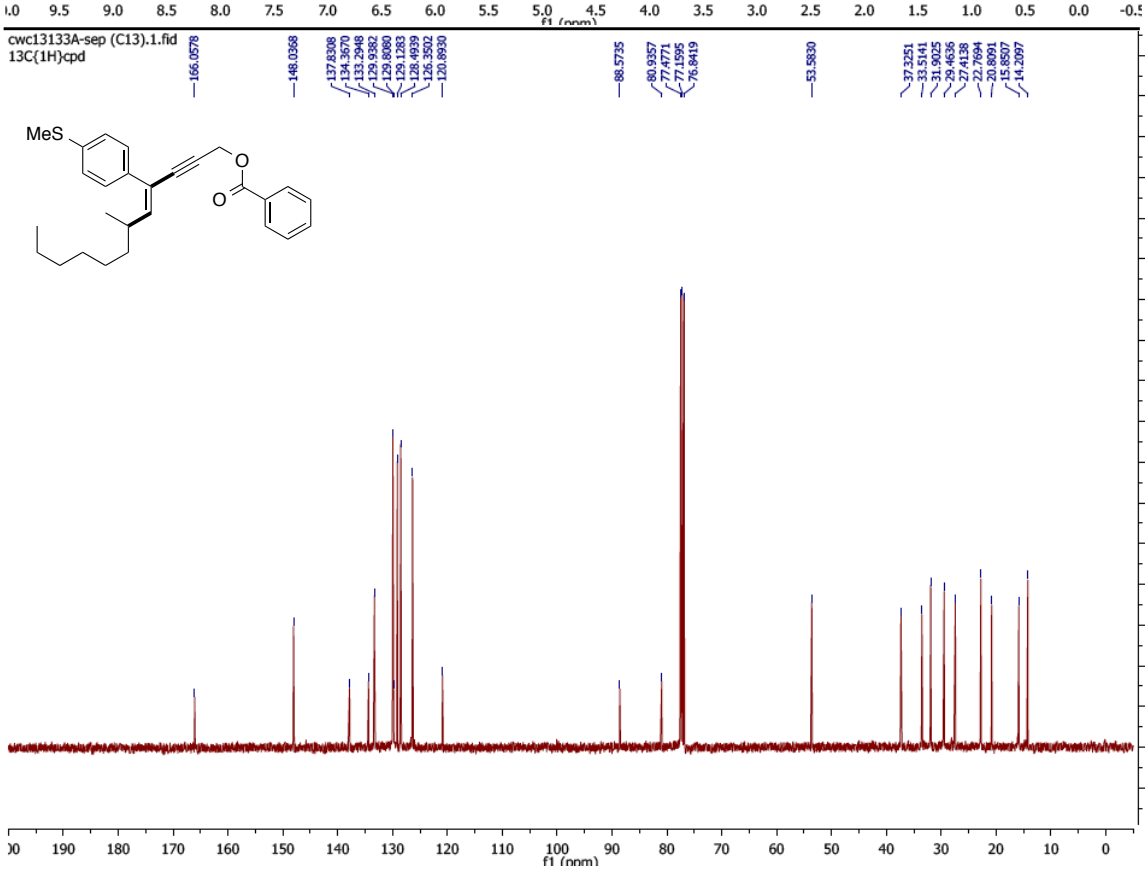
(*E*)-7-Cyclohexyl-6-(4-methoxyphenyl)hept-6-en-4-yn-1-yl 4-chlorobenzoate (S2g)



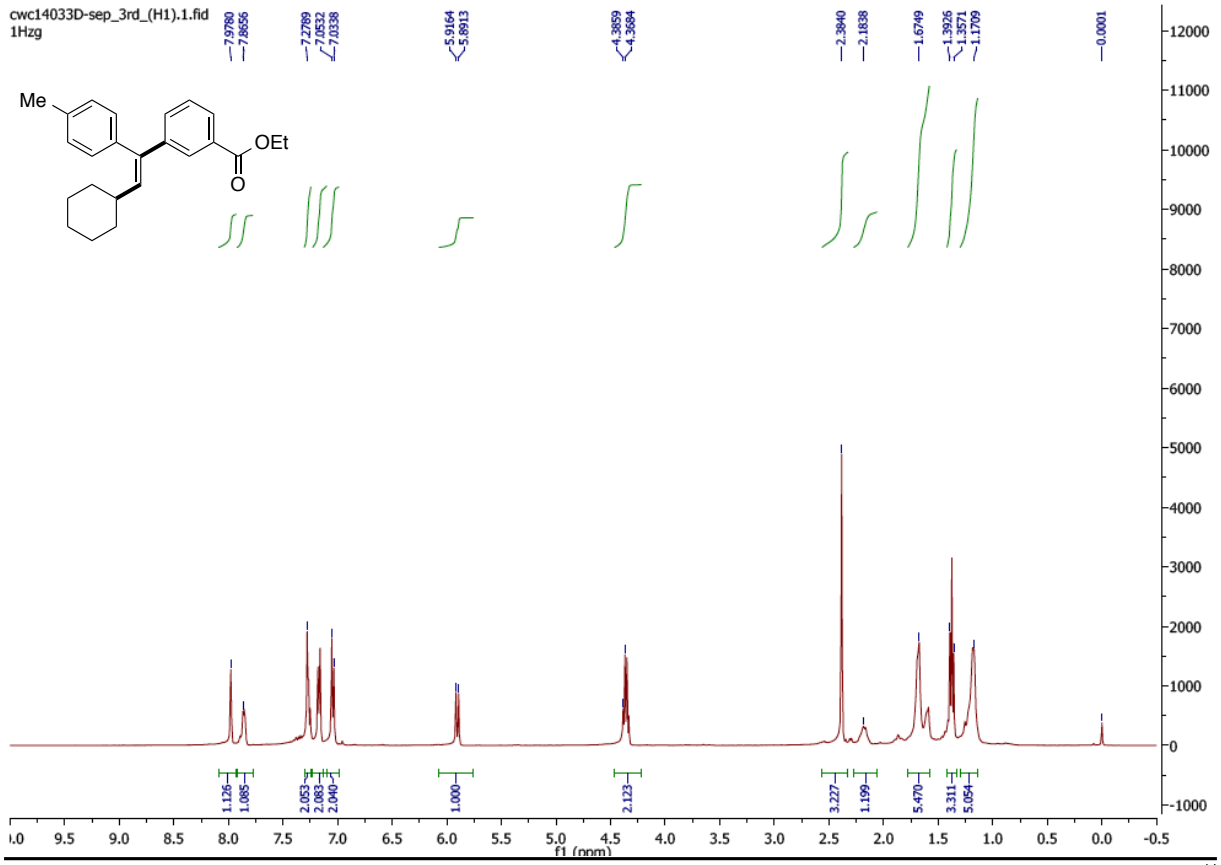


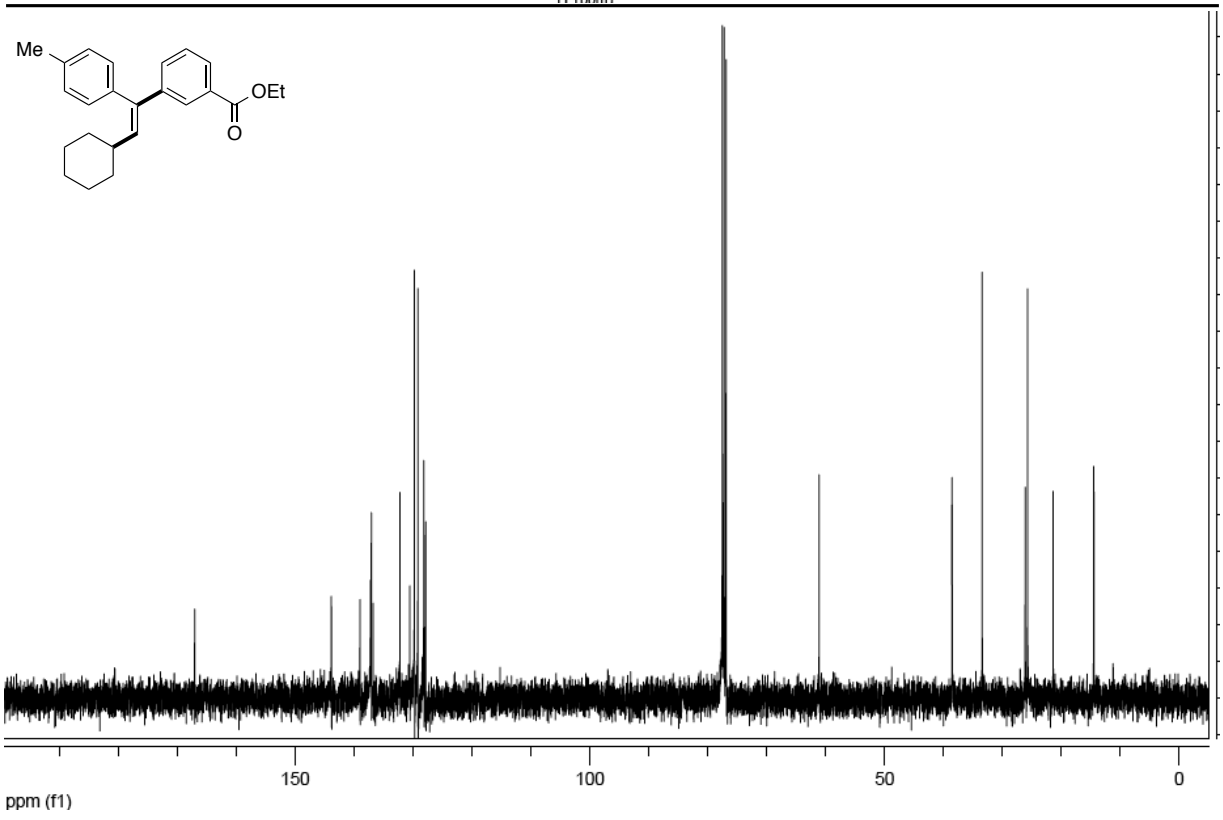
(*E*)-6-Methyl-4-(4-(methylthio)phenyl)dodec-4-en-2-yn-1-yl benzoate (S2h)



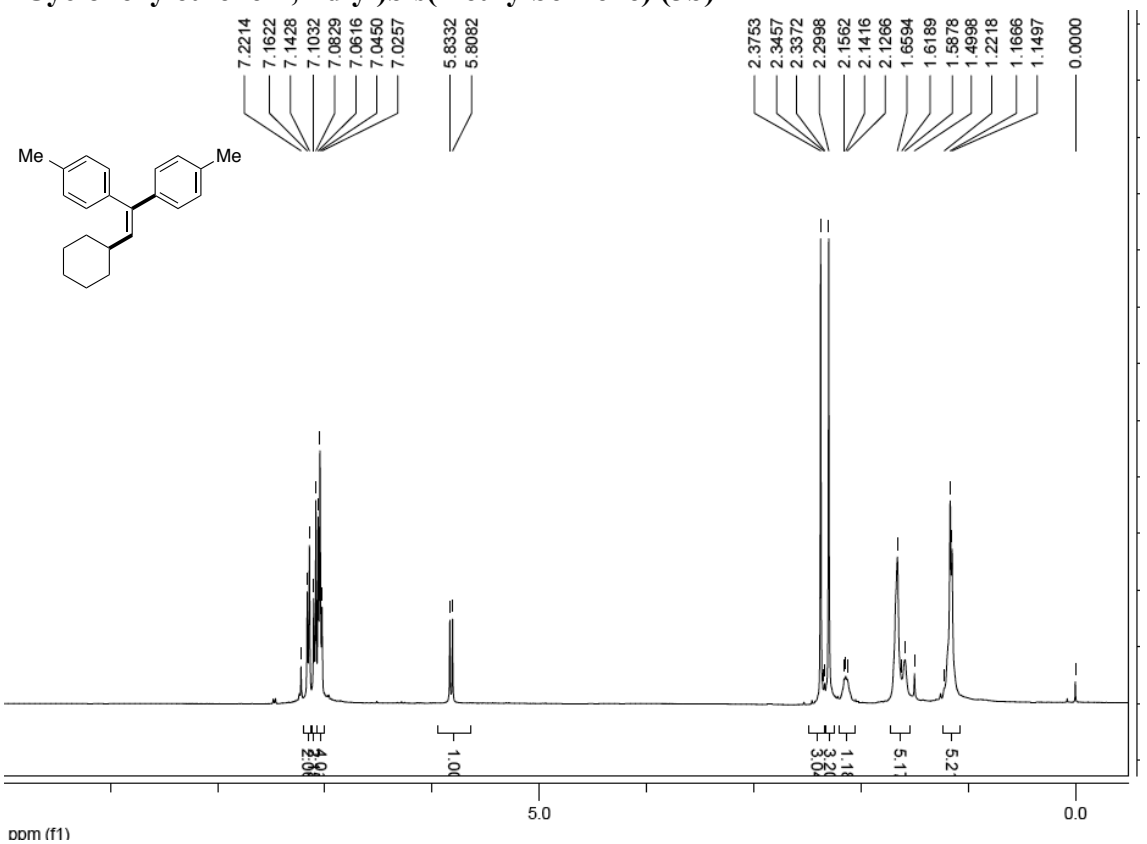


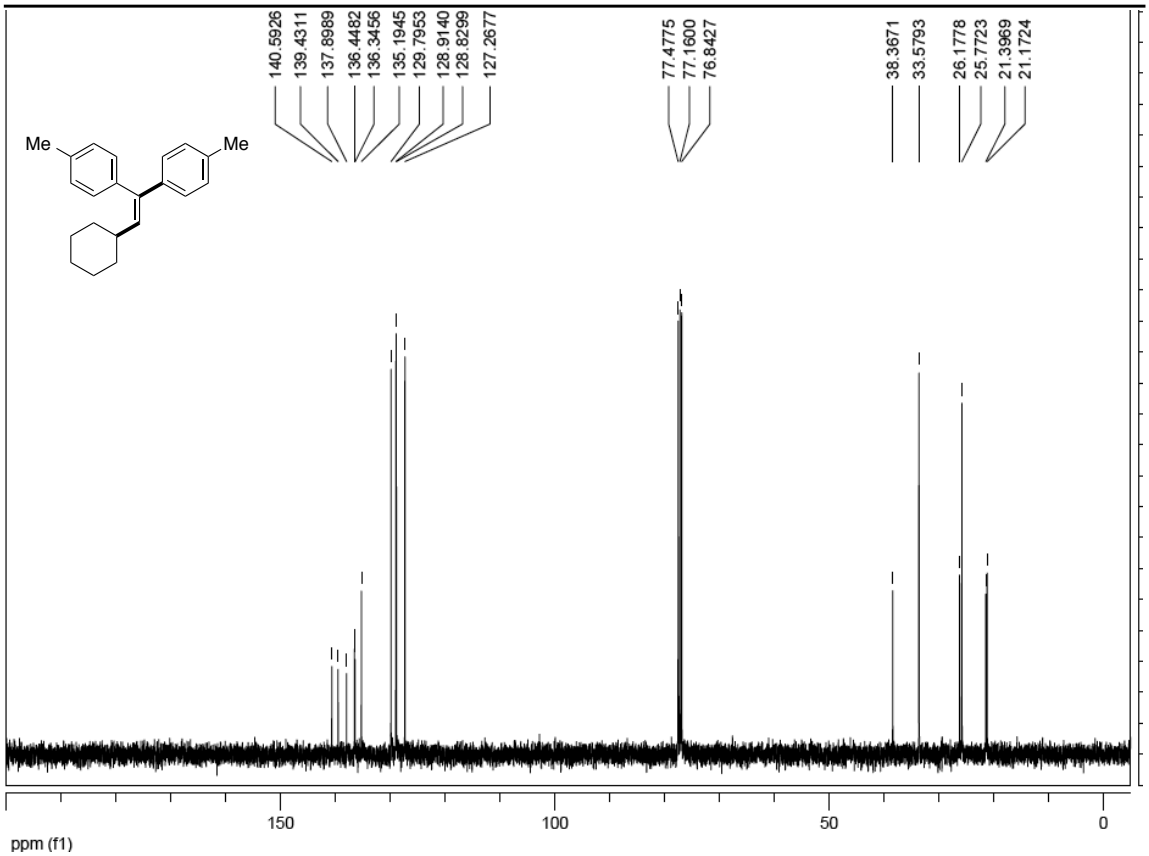
Ethyl (*E*)-3-(2-Cyclohexyl-1-(*p*-tolyl)vinyl)benzoate (3a)



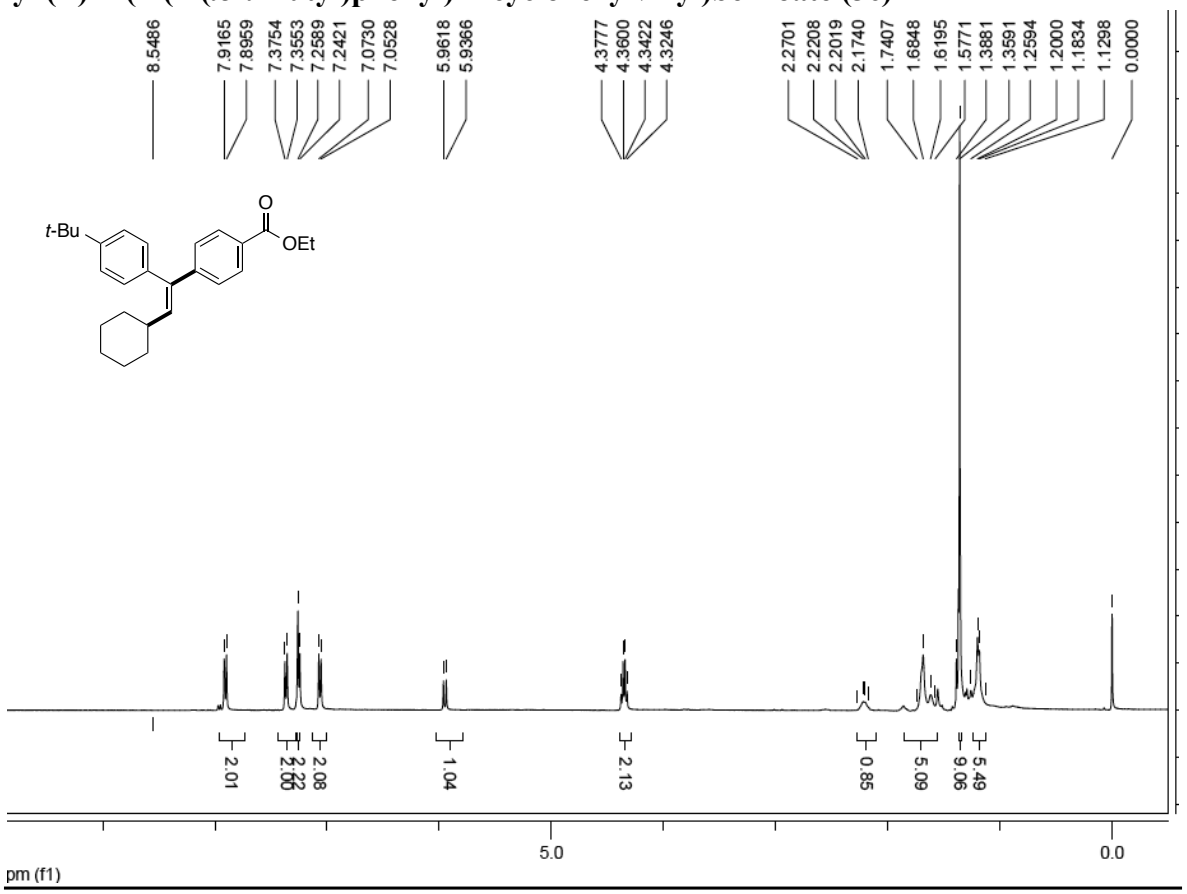


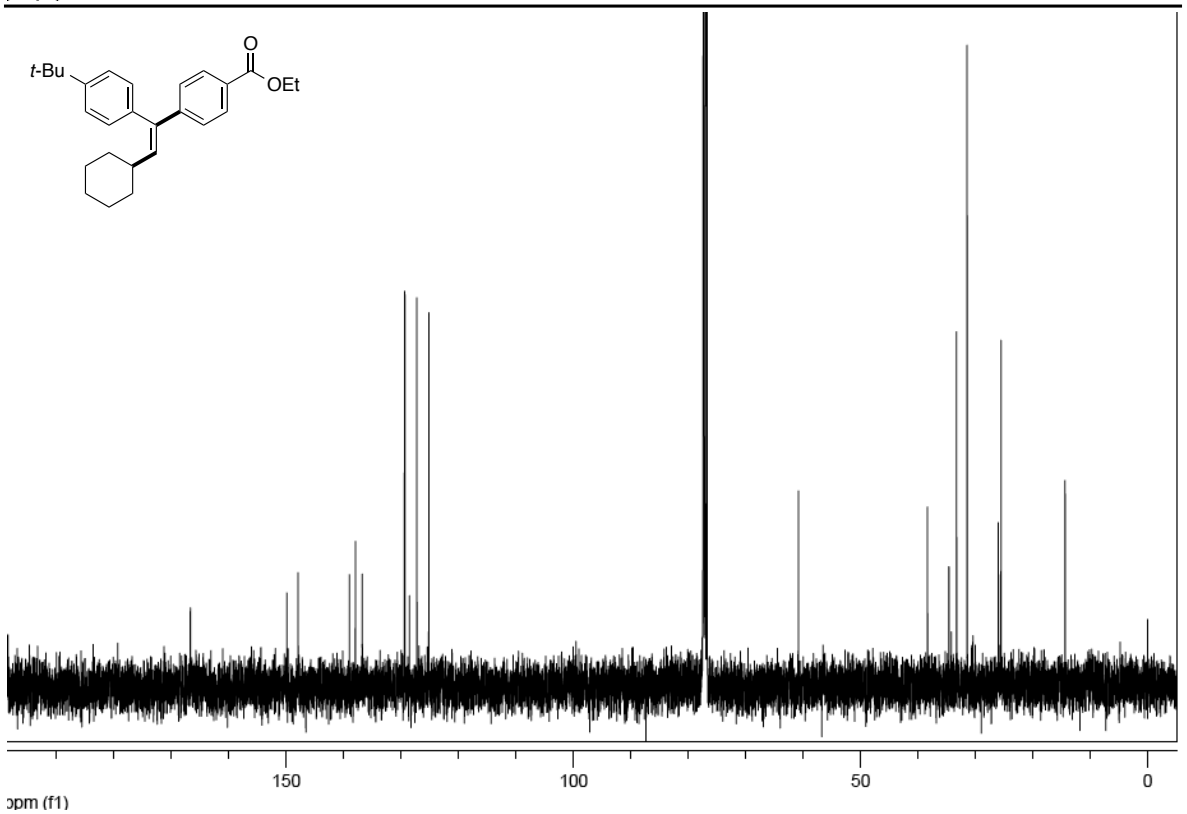
4,4'-(2-Cyclohexylethene-1,1-diyl)bis(methylbenzene) (3b)



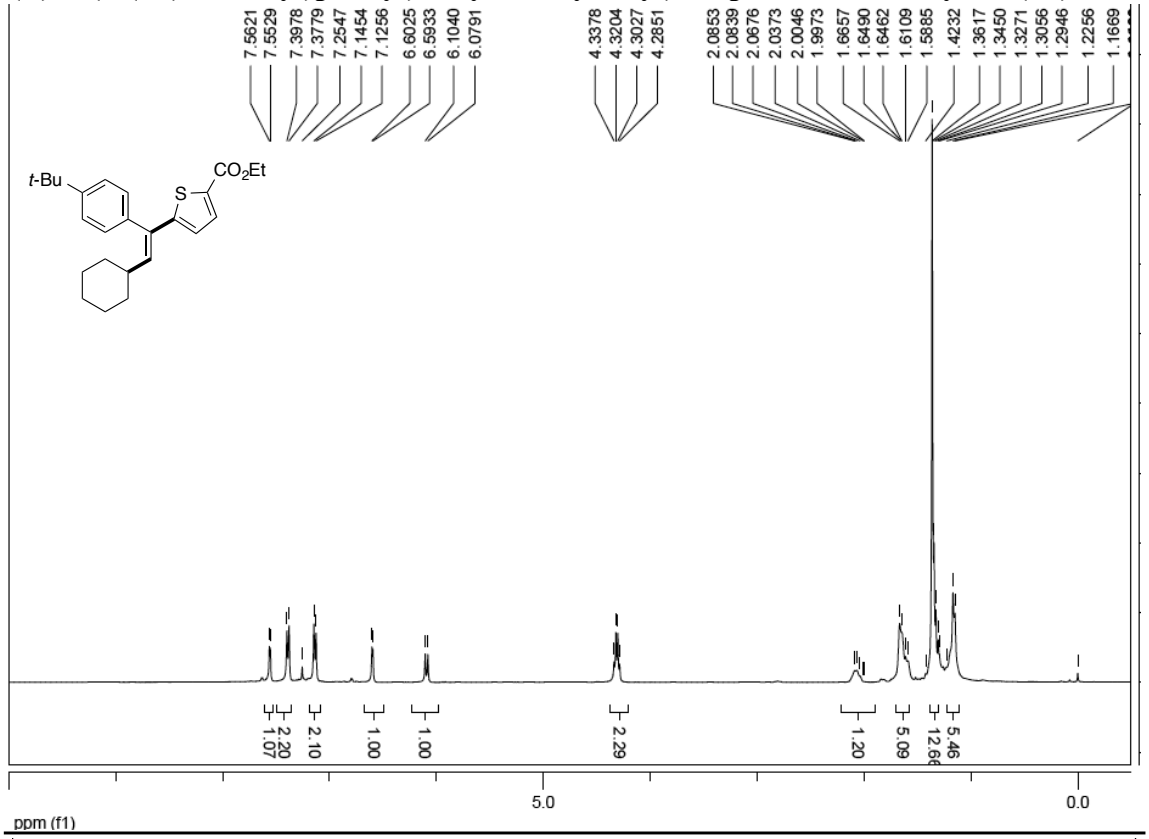


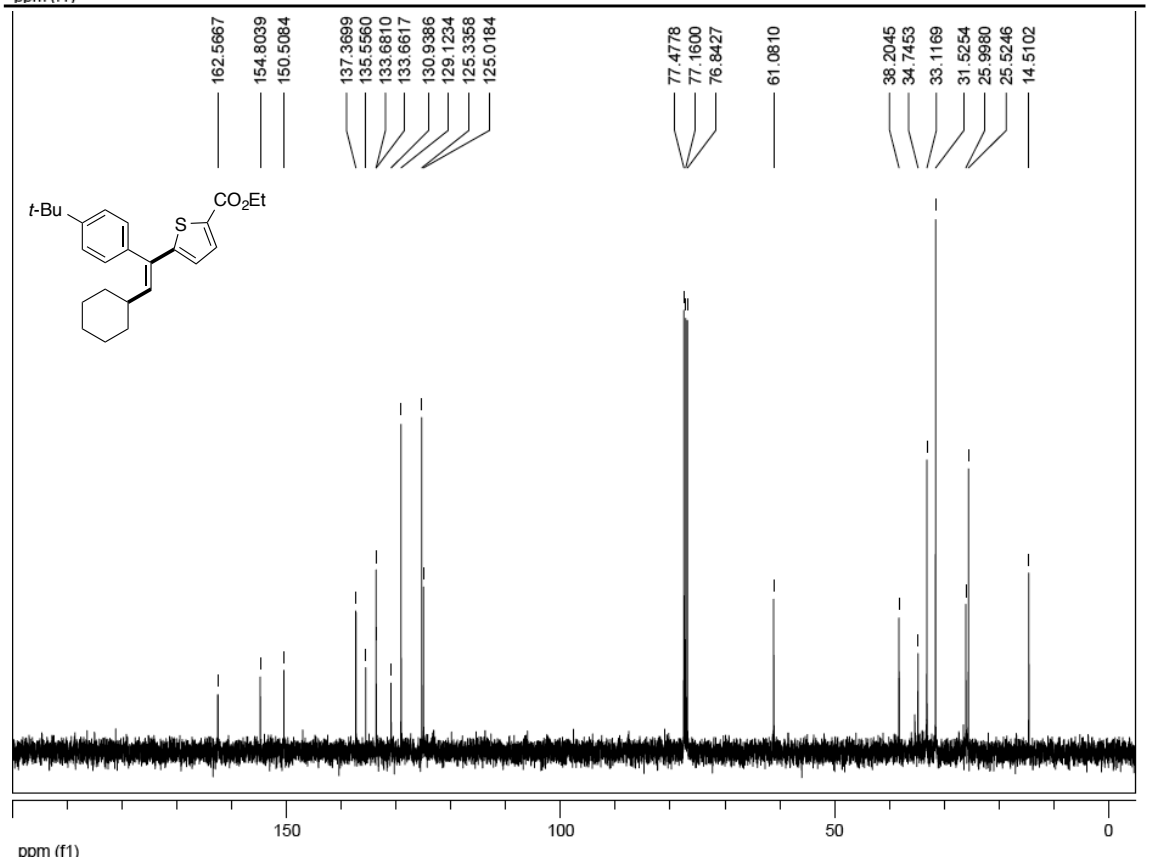
Ethyl (*E*)-4-(1-(4-(*tert*-Butyl)phenyl)-2-cyclohexylvinyl)benzoate (3c)



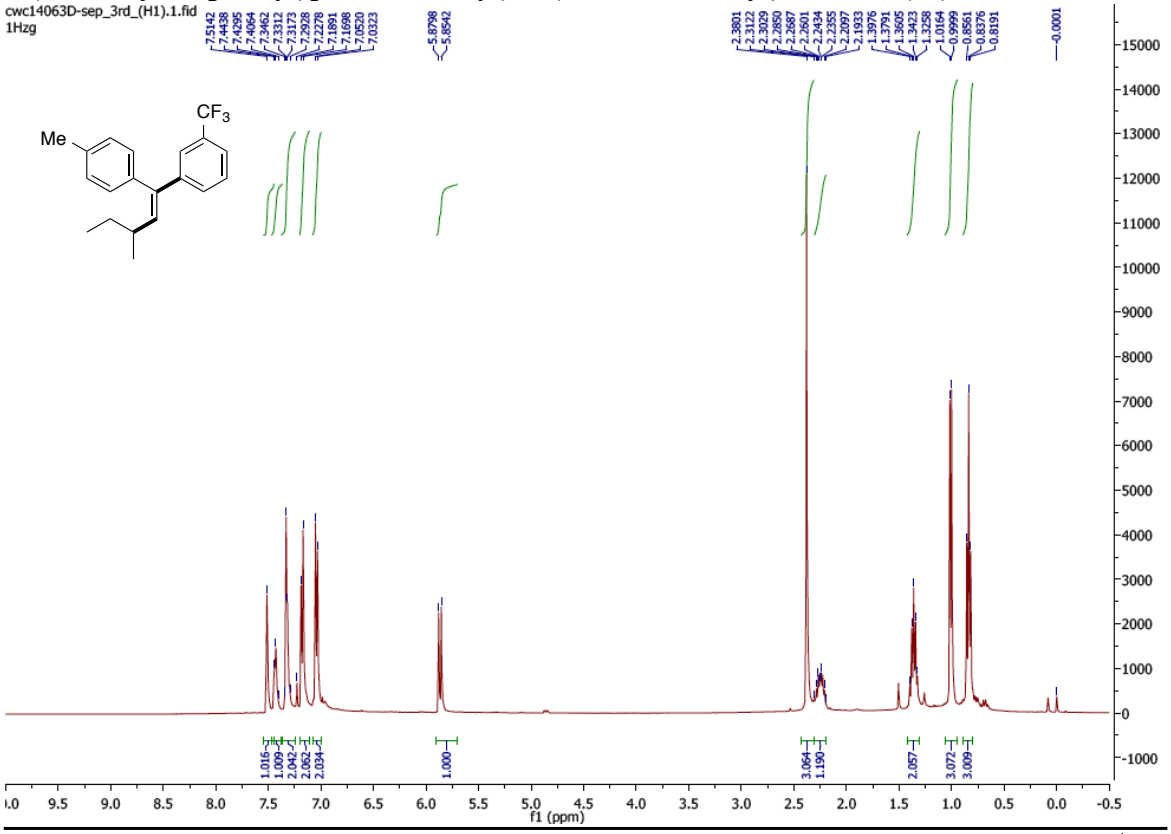


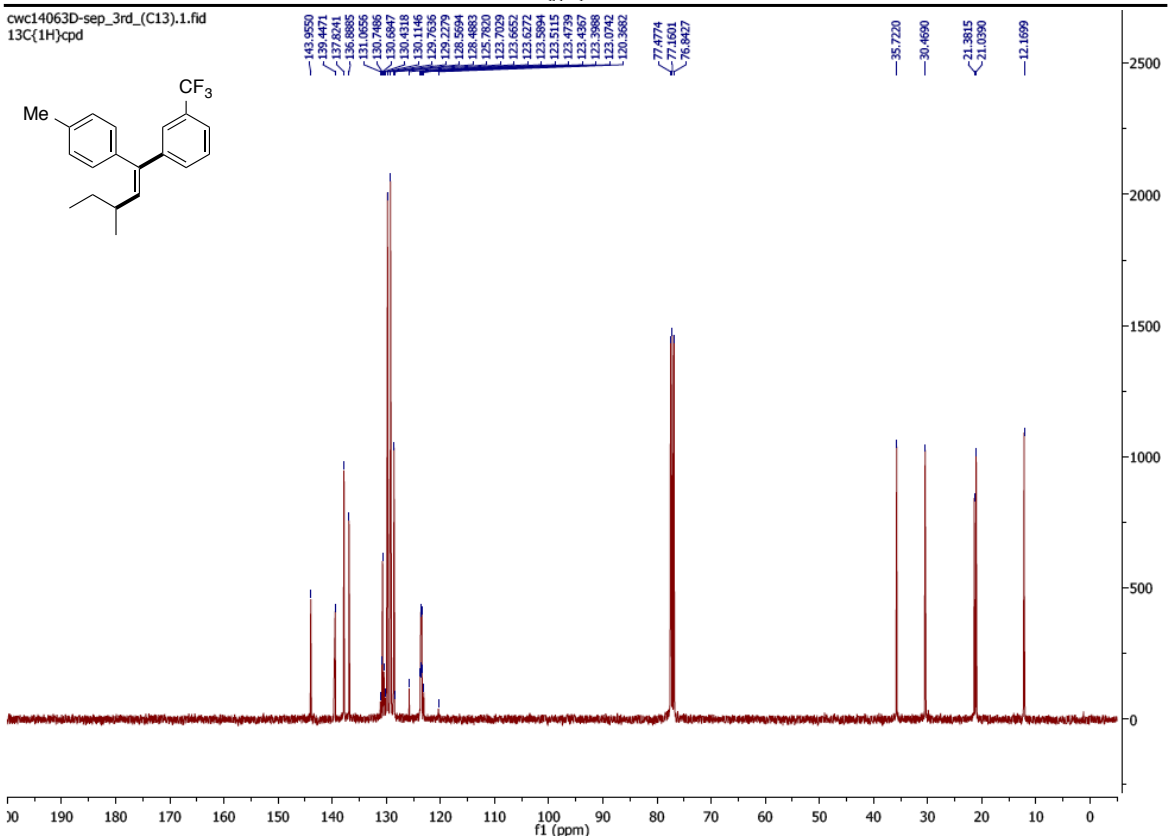
Ethyl (*E*)-5-(1-(4-(*tert*-Butyl)phenyl)-2-cyclohexylvinyl)thiophene-2-carboxylate (3d)



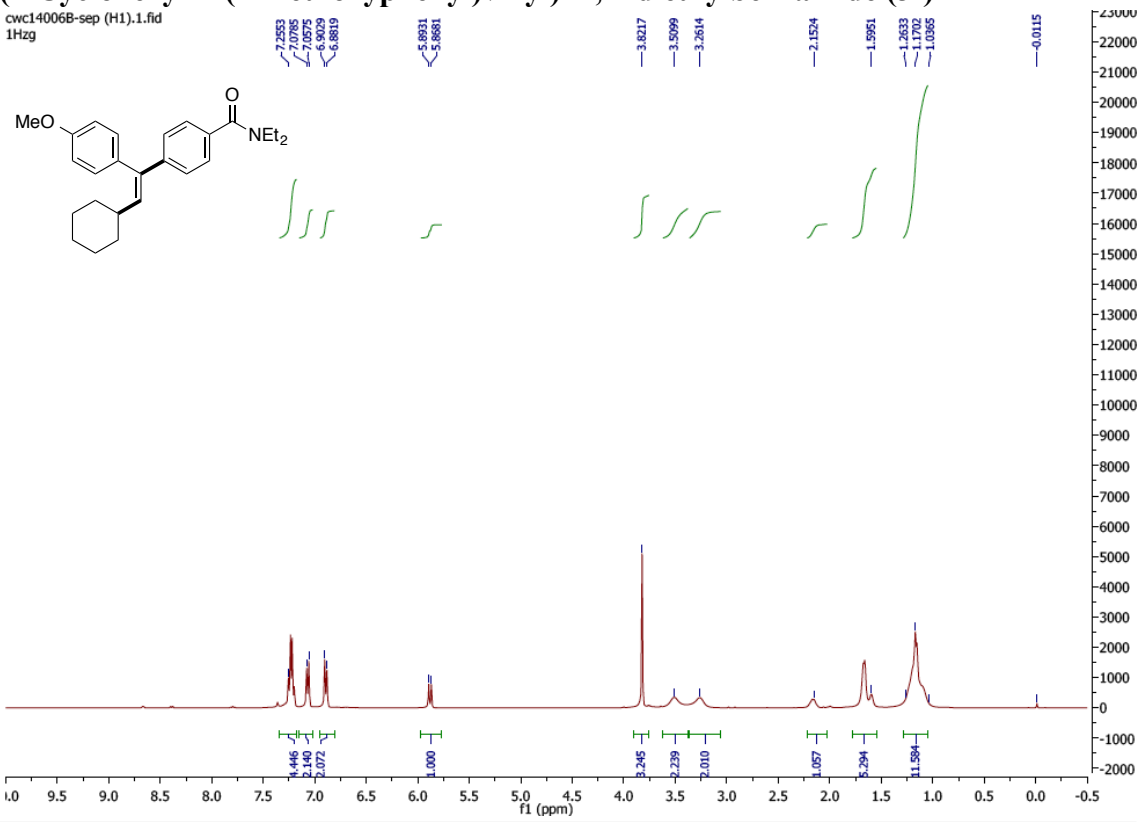


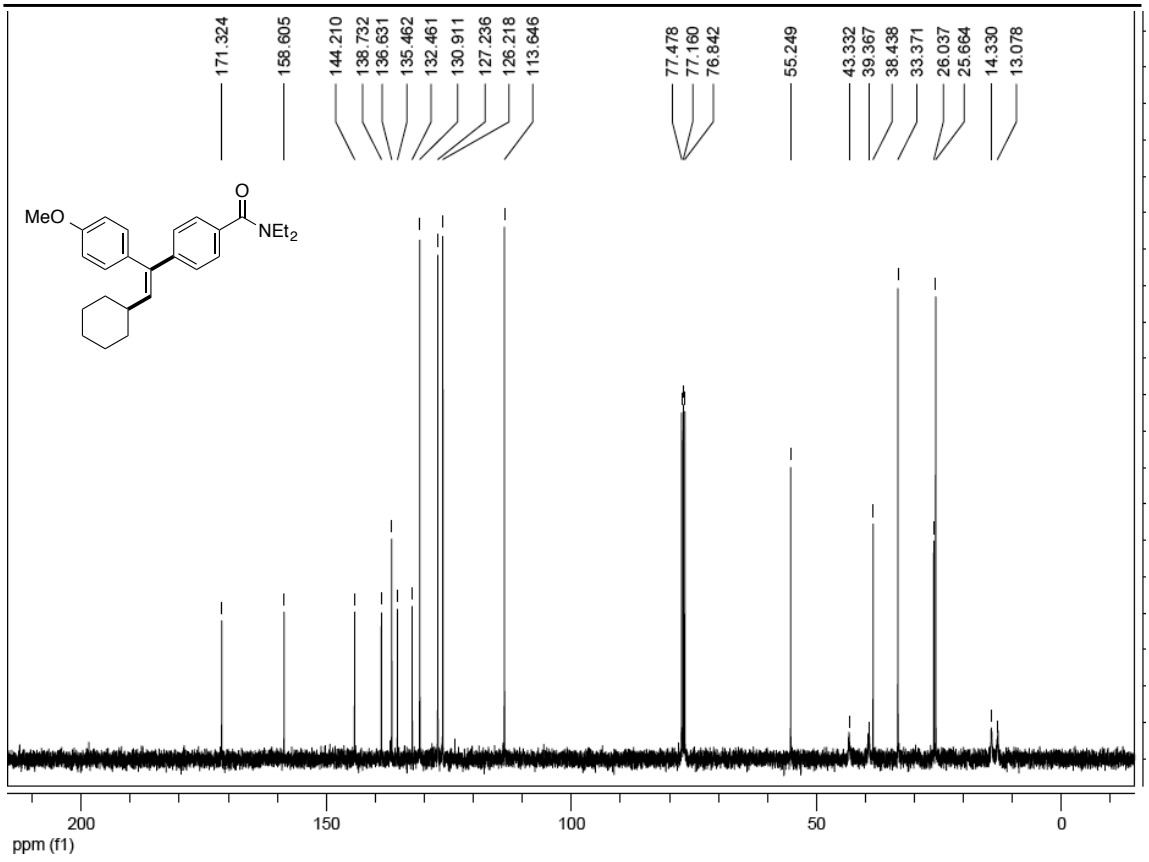
(*E*)-1-(3-Methyl-1-(*p*-tolyl)pent-1-en-1-yl)-3-(trifluoromethyl)benzene (3e)



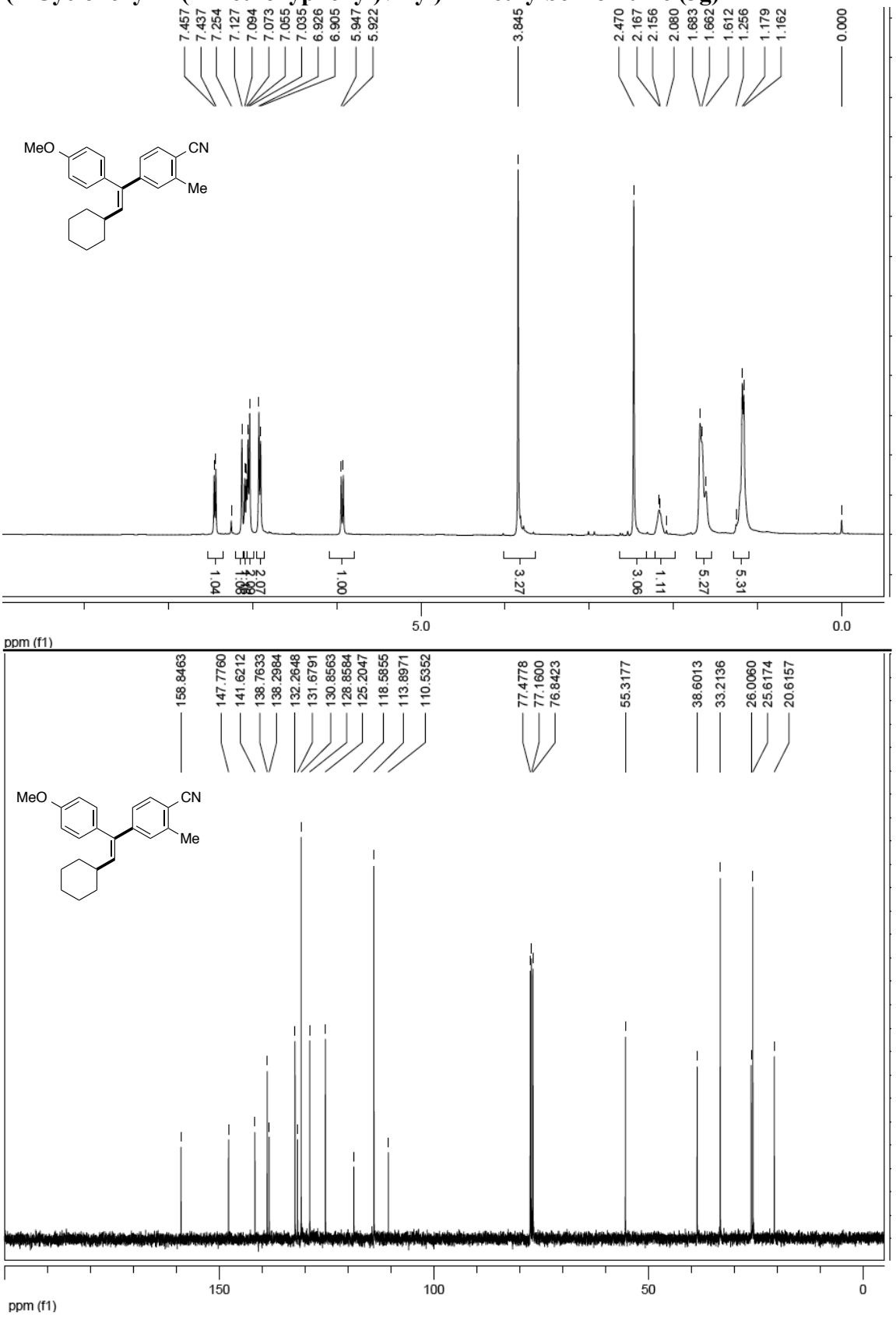


(*Z*)-4-(2-Cyclohexyl-1-(4-methoxyphenyl)vinyl)-*N*,*N*-diethylbenzamide (3f)

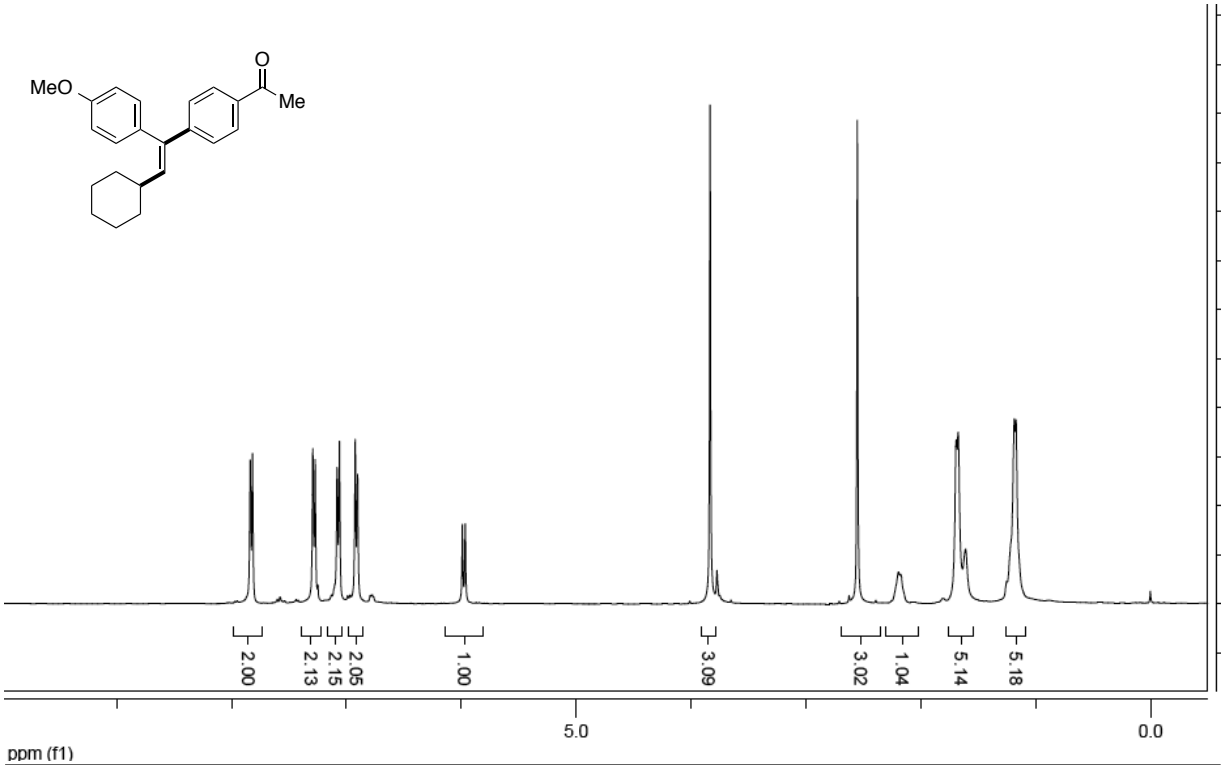


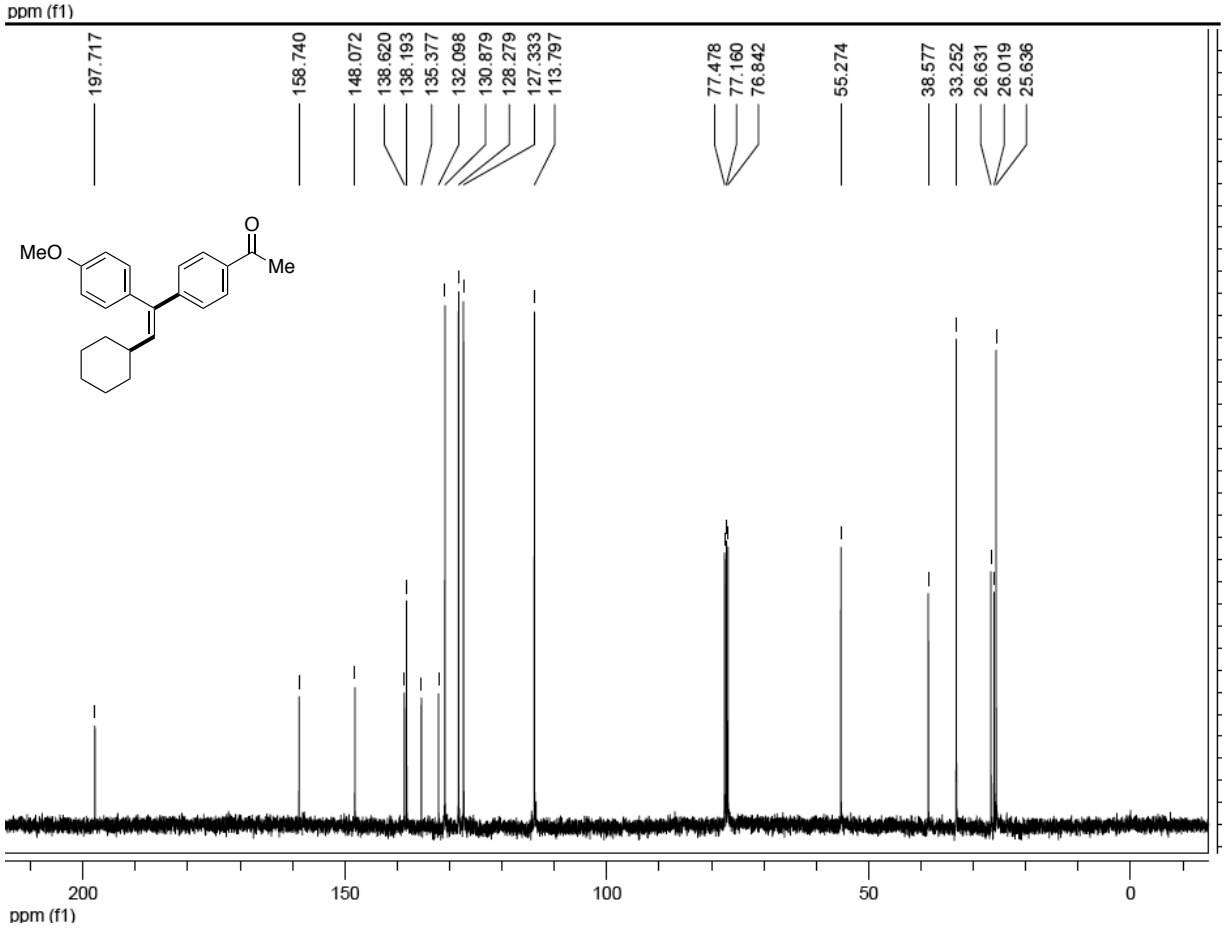


(*E*)-4-(2-Cyclohexyl-1-(4-methoxyphenyl)vinyl)-2-methylbenzonitrile (3g)

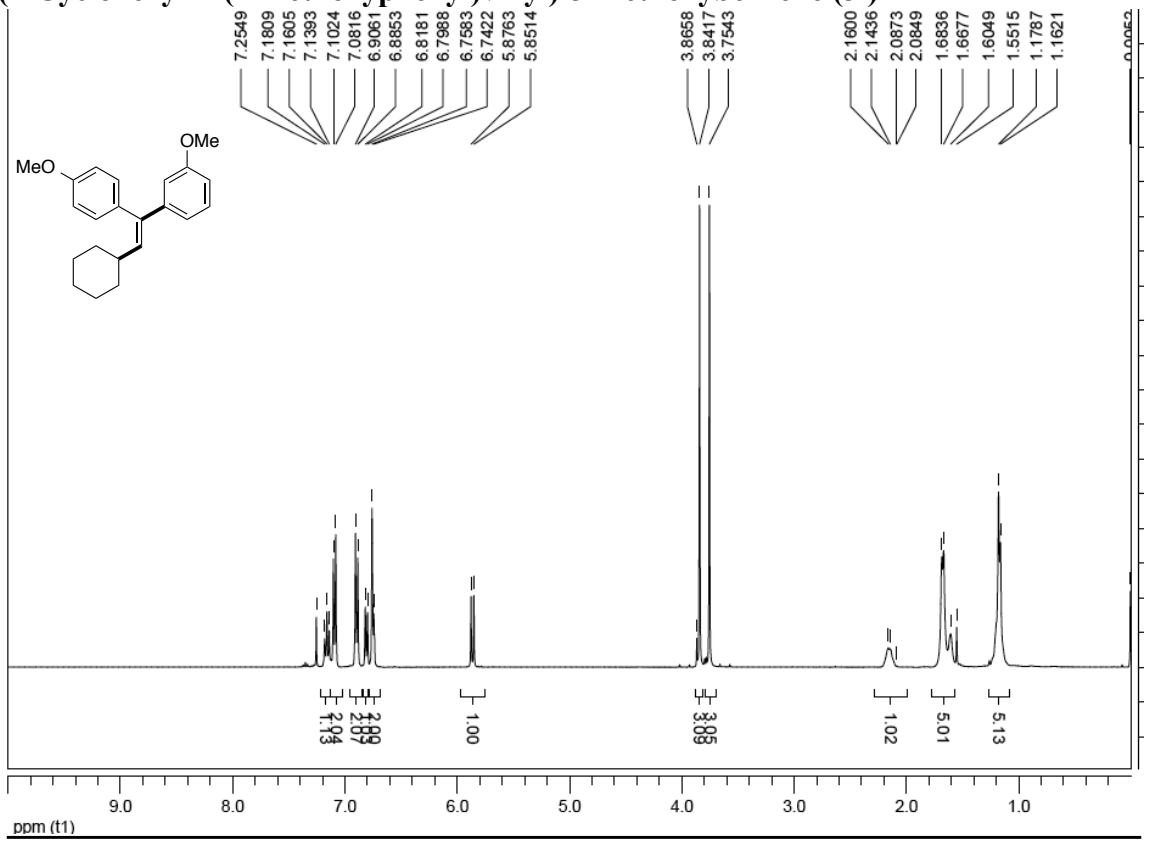


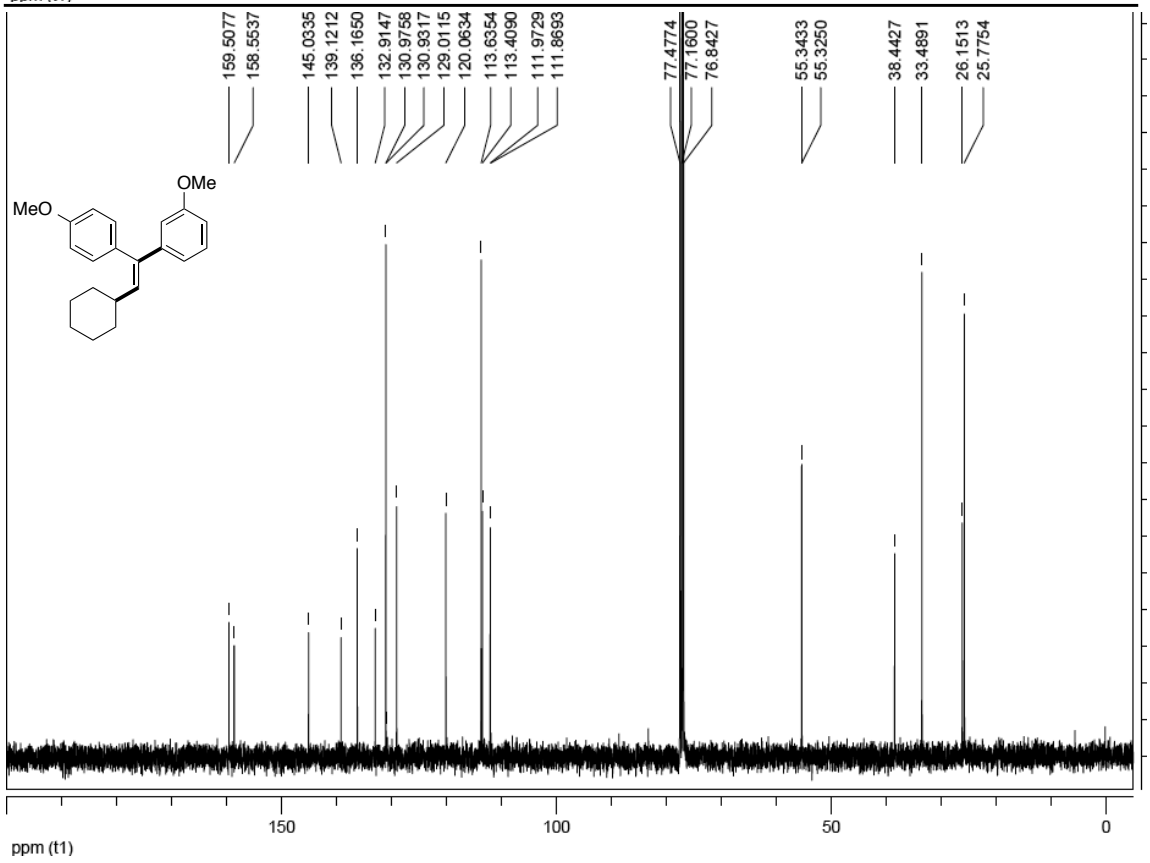
(*Z*)-1-(4-(2-Cyclohexyl-1-(4-methoxyphenyl)vinyl)phenyl)ethan-1-one (3h)



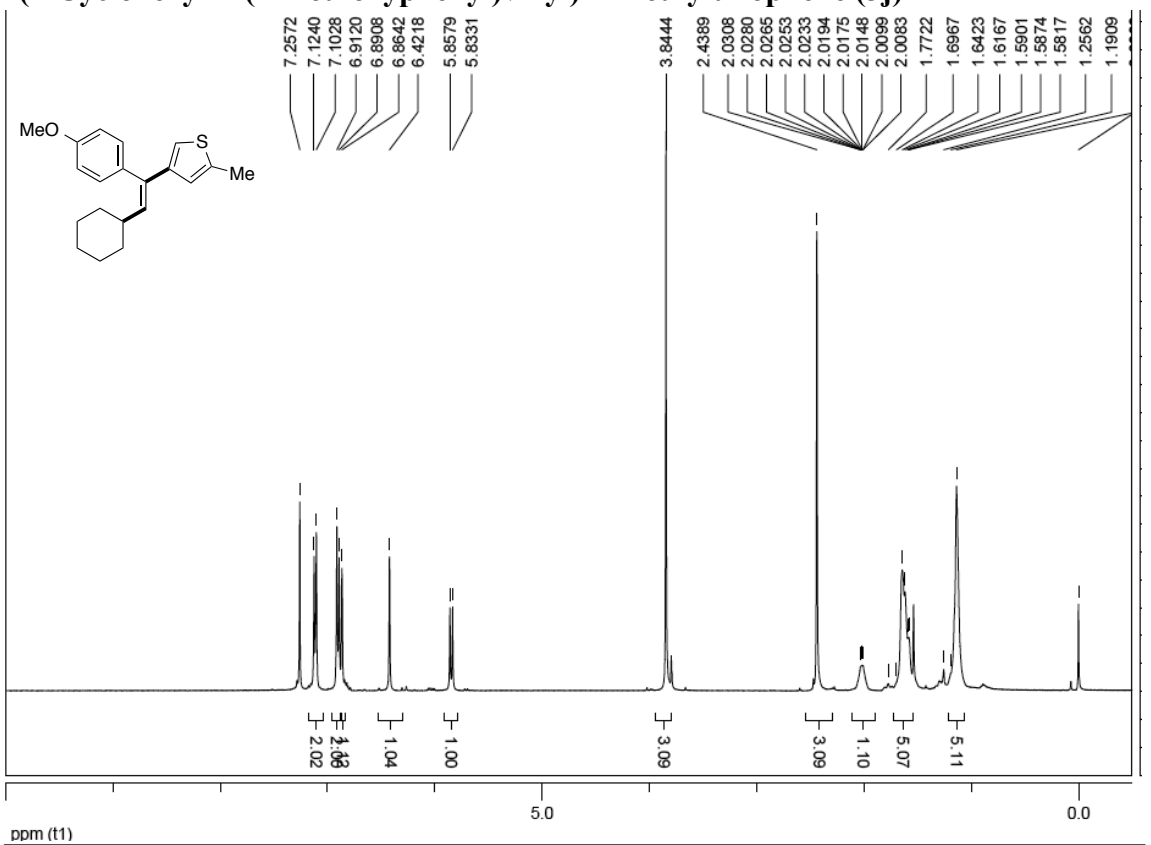


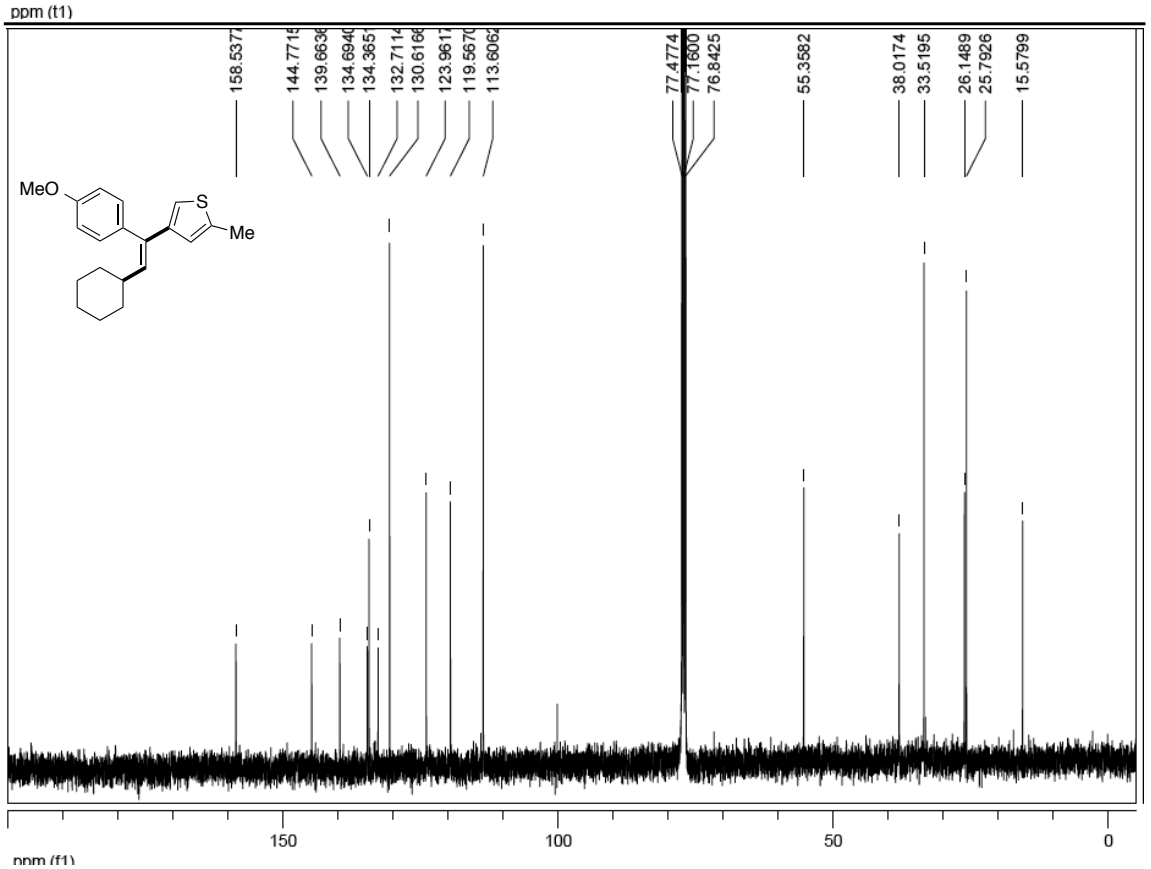
(*E*)-1-(2-Cyclohexyl-1-(4-methoxyphenyl)vinyl)-3-methoxybenzene (3i)



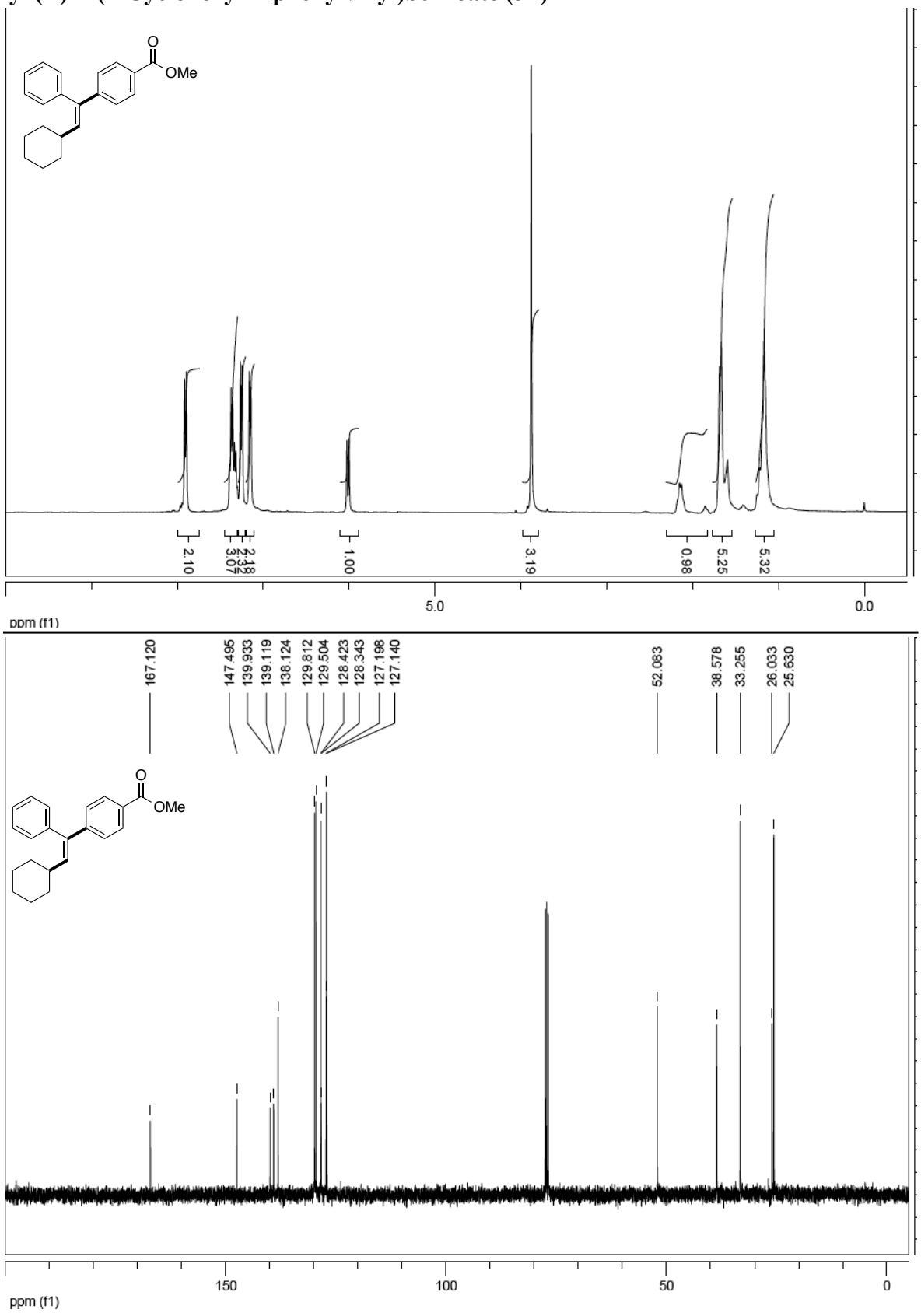


(*E*)-4-(2-Cyclohexyl-1-(4-methoxyphenyl)vinyl)-2-methylthiophene (3j)

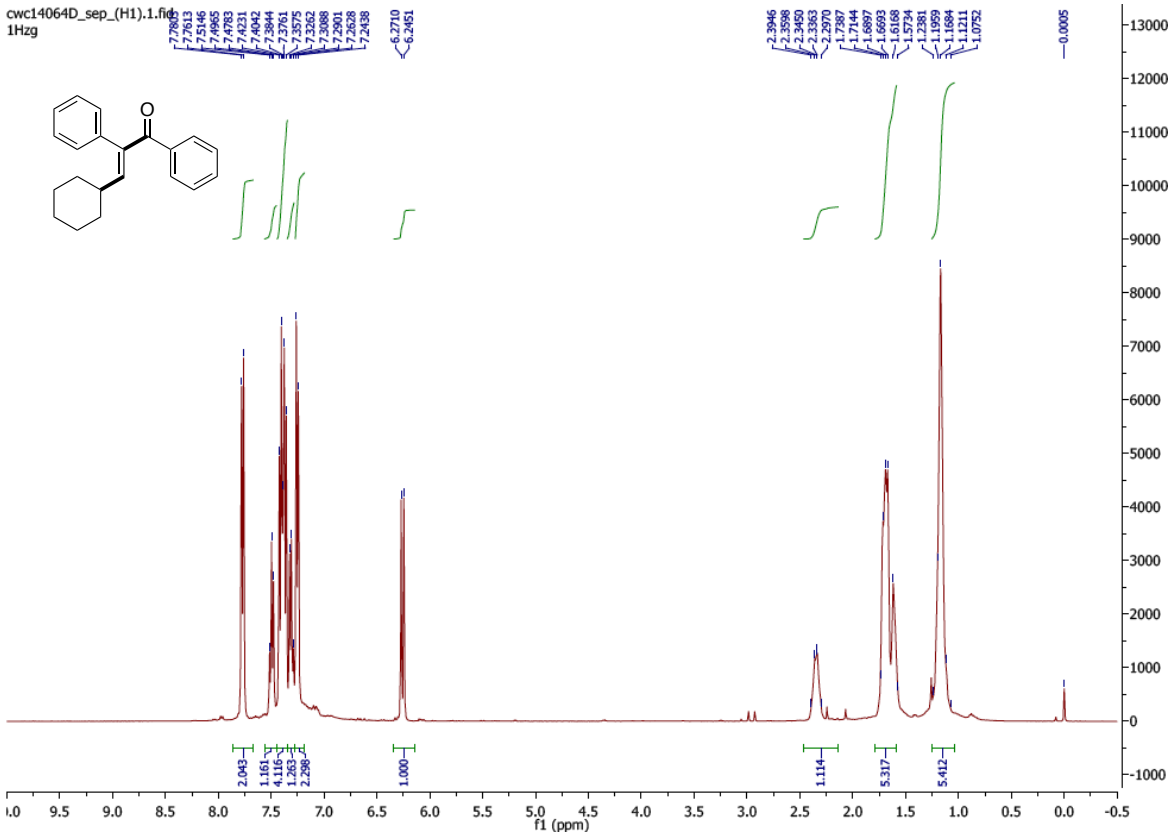


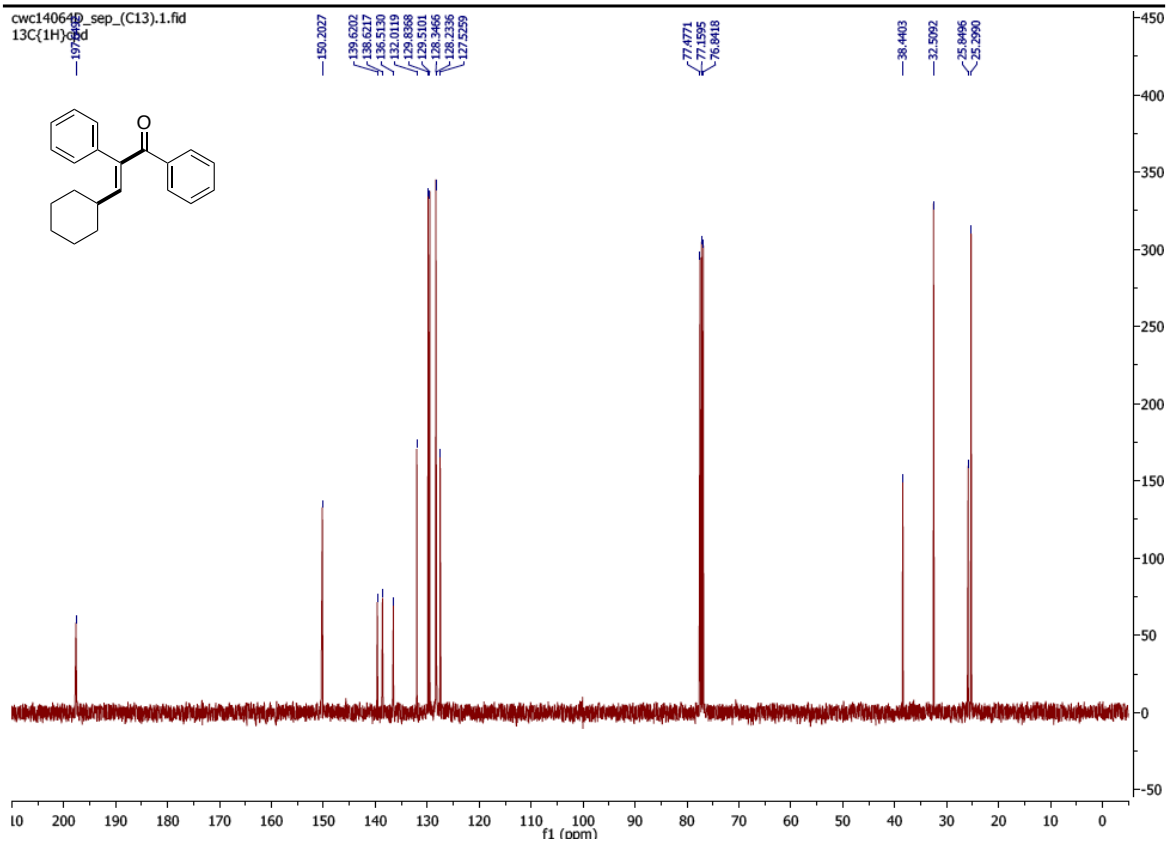


Methyl (*E*)-4-(2-Cyclohexyl-1-phenylvinyl)benzoate (3k)

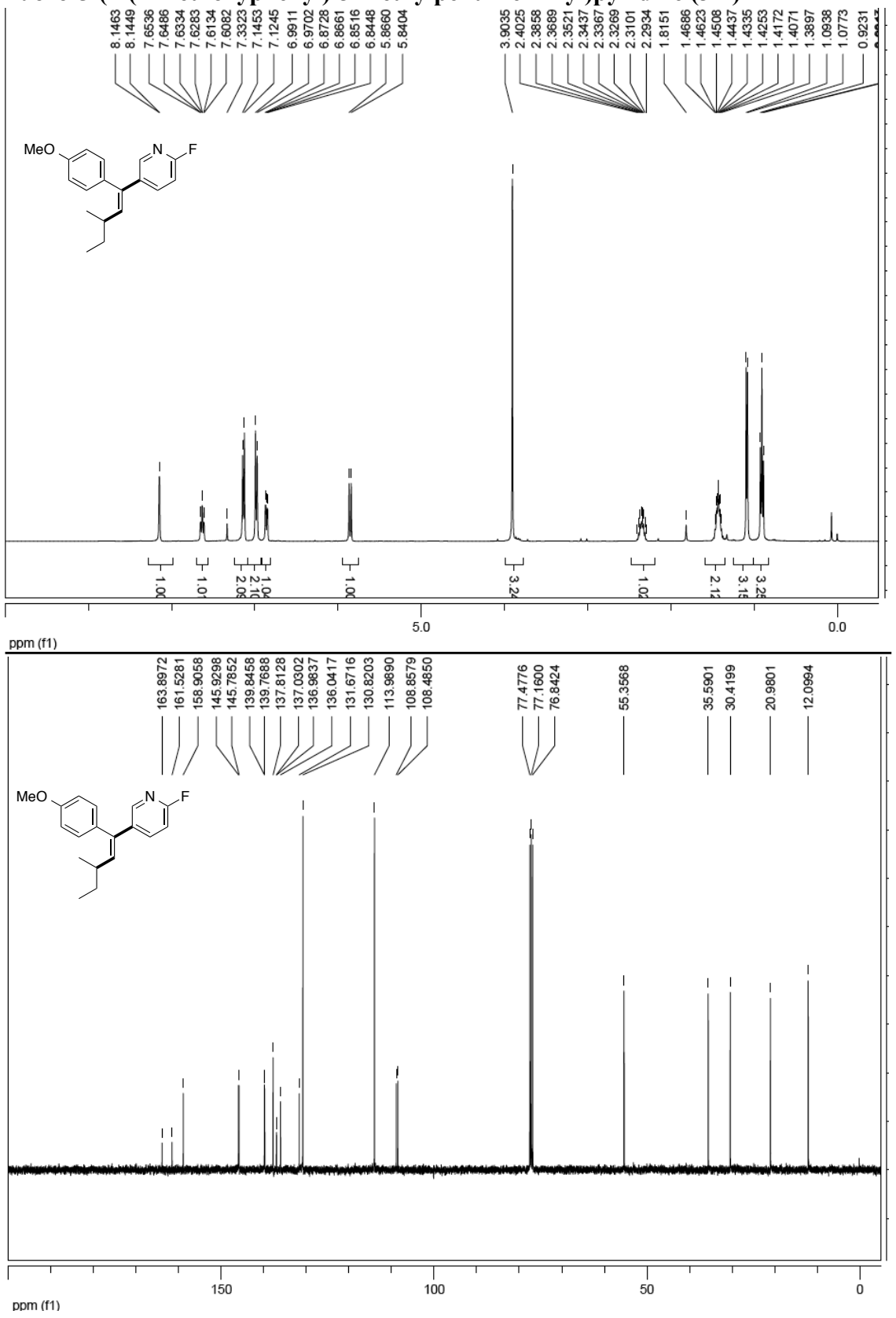


(*E*)-3-Cyclohexyl-1,2-diphenylprop-2-en-1-one (3l)

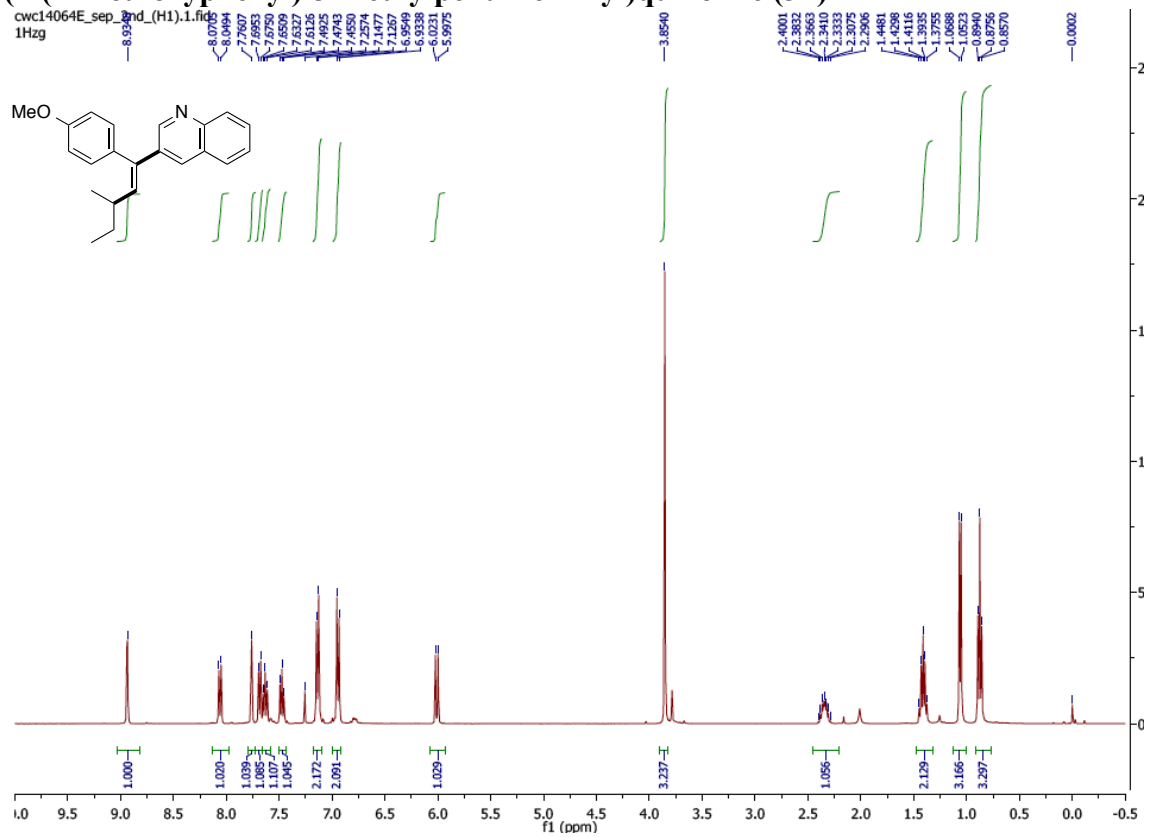


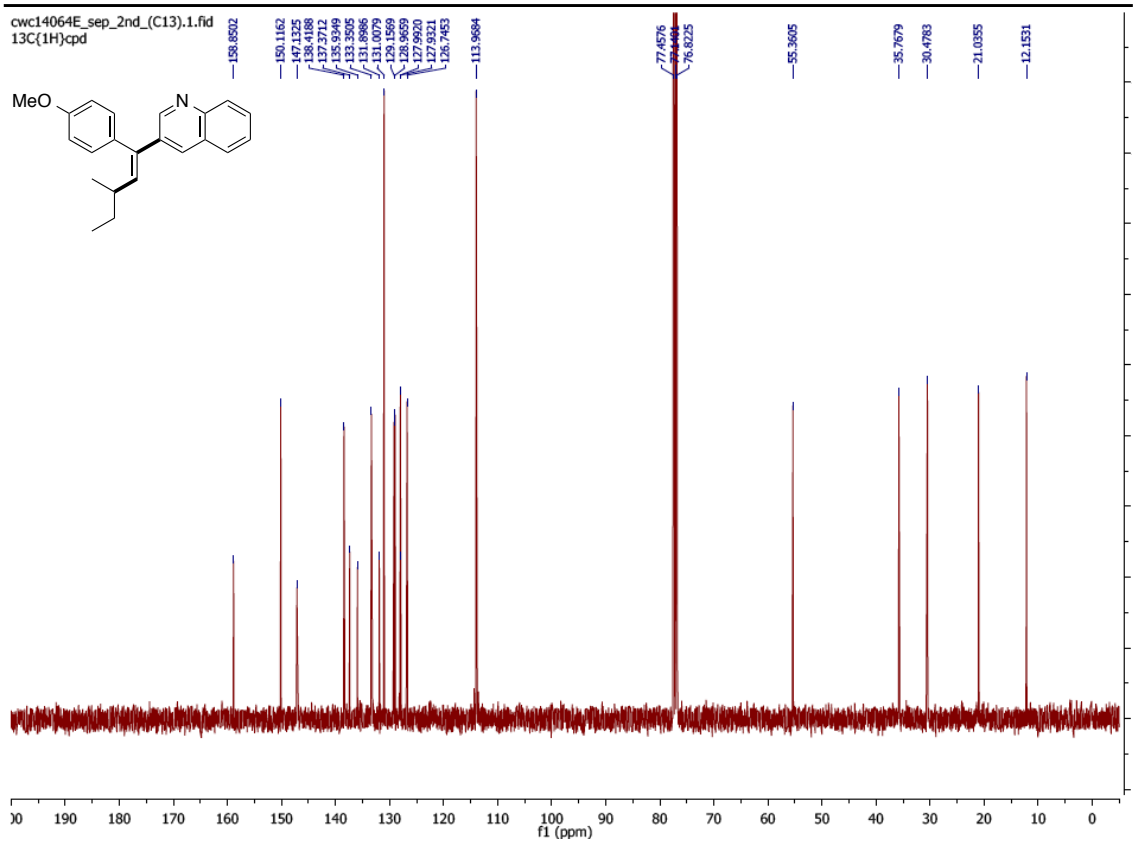


(*E*)-2-Fluoro-5-(1-(4-methoxyphenyl)-3-methylpent-1-en-1-yl)pyridine (3m)

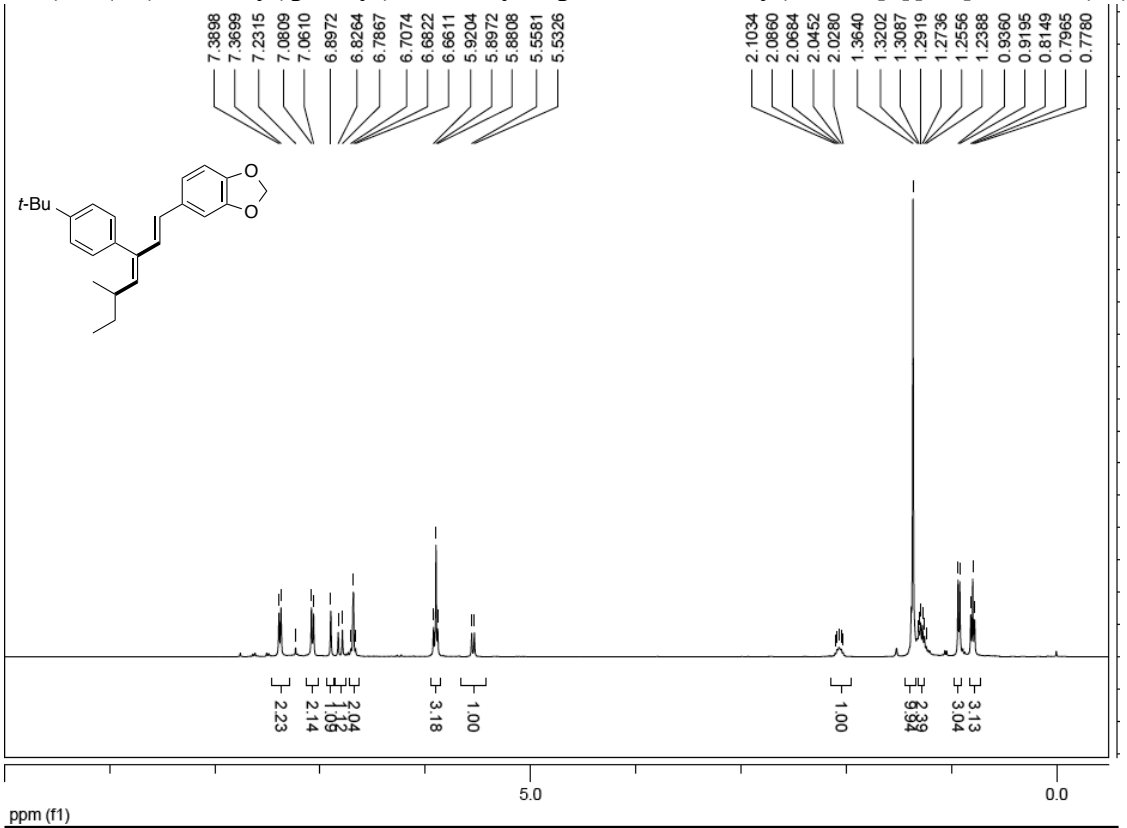


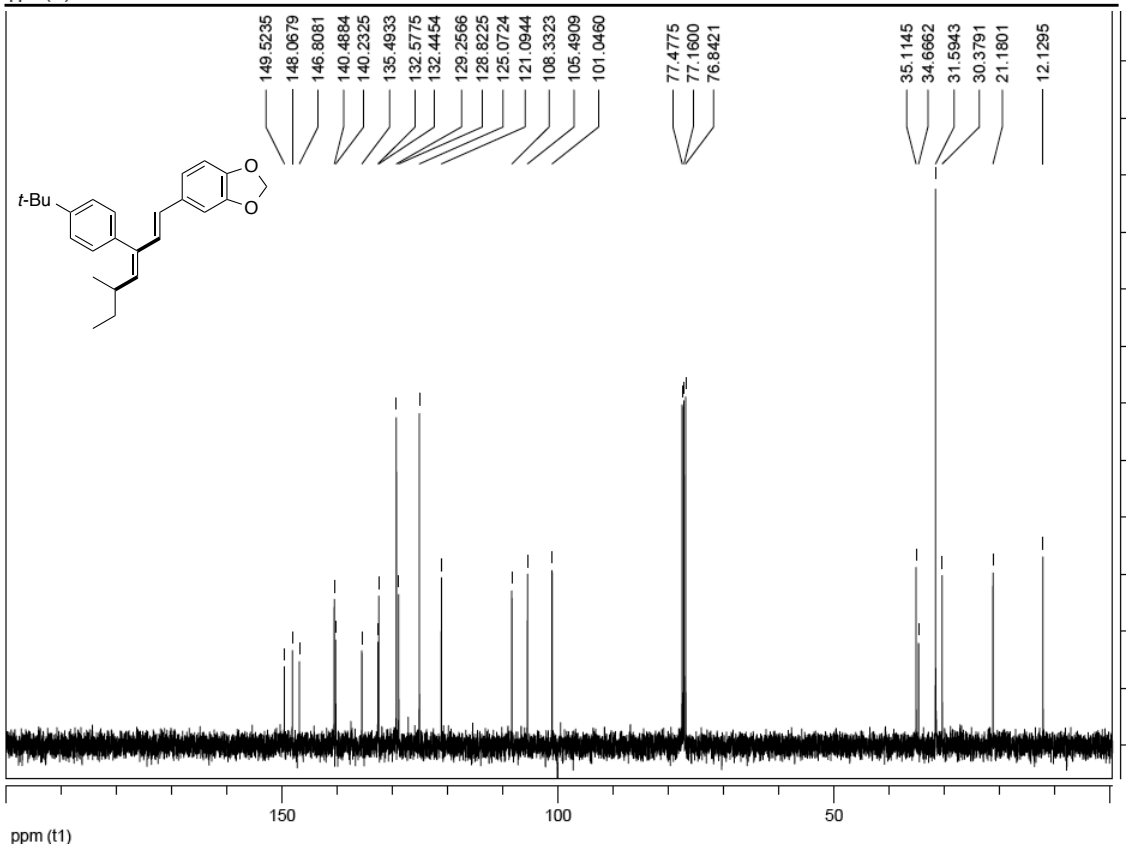
(*E*)-3-(1-(4-Methoxyphenyl)-3-methylpent-1-en-1-yl)quinoline (3n)



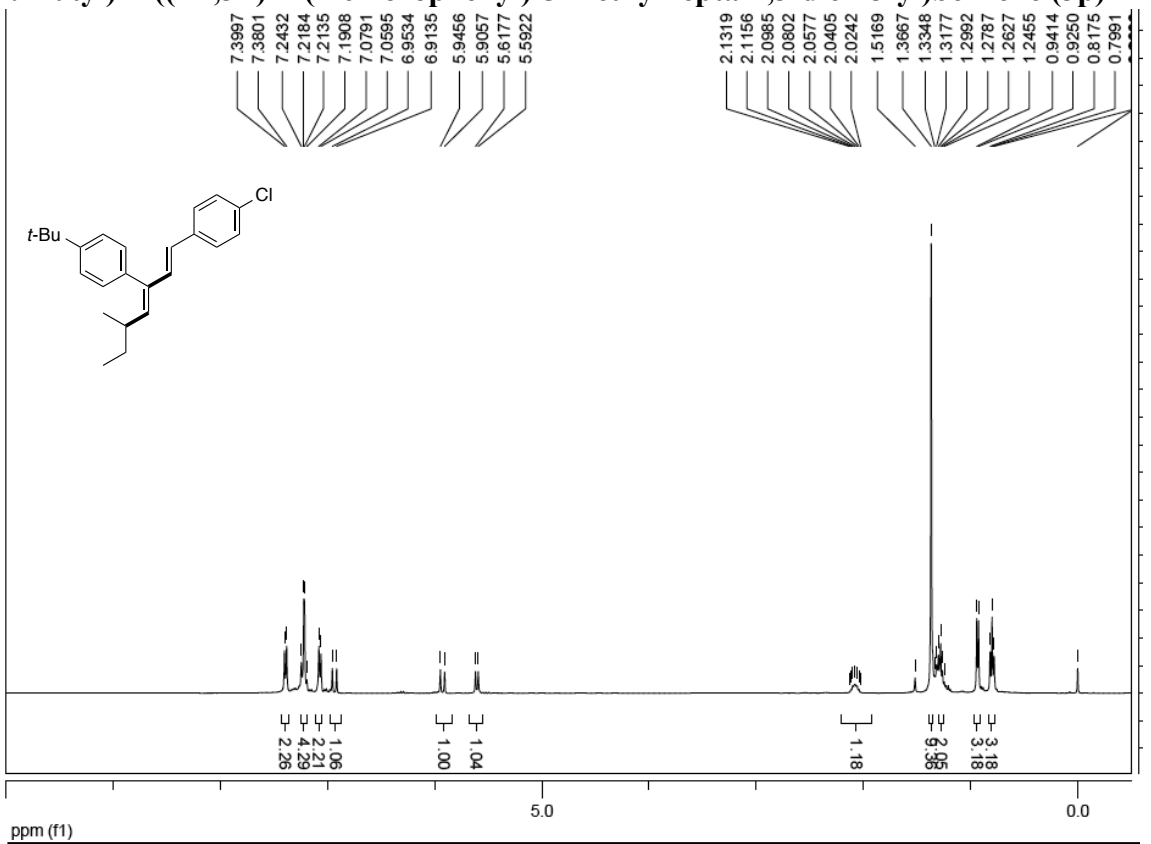


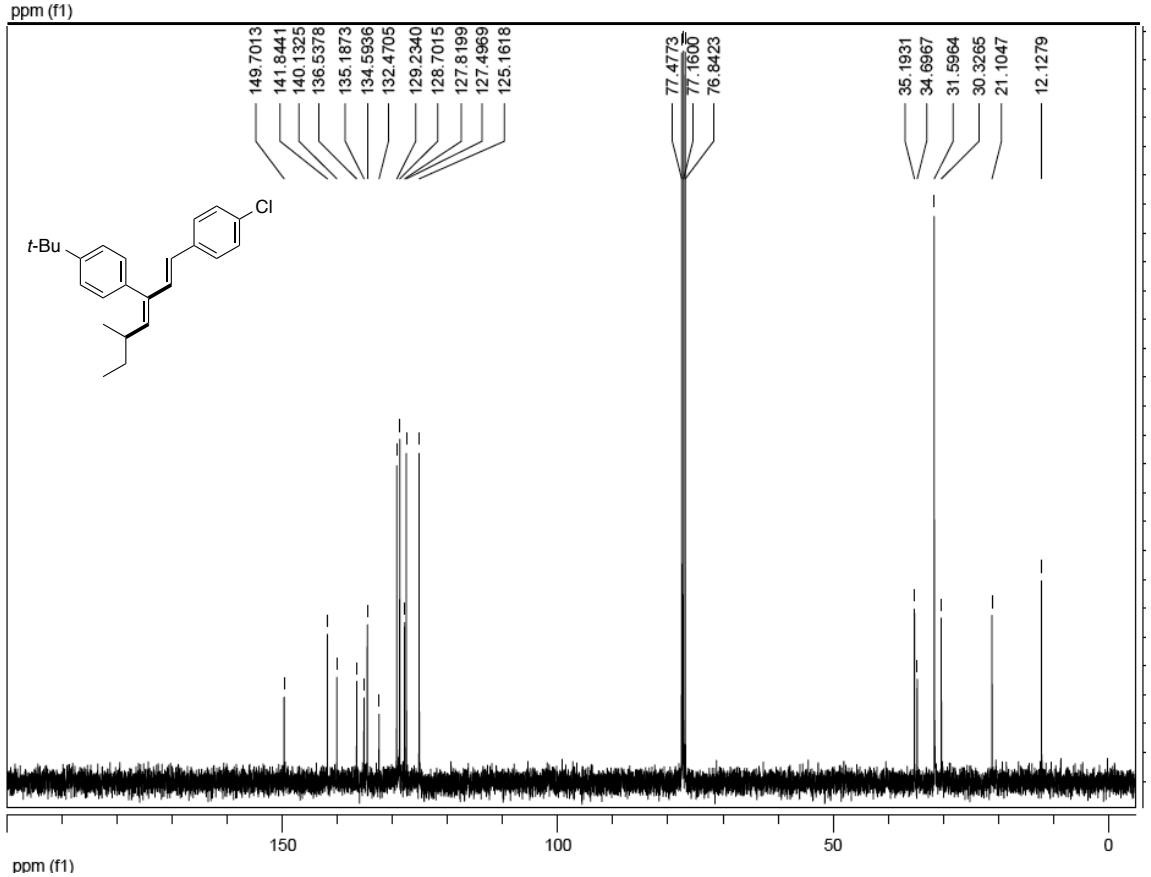
5-((1*E*,3*Z*)-3-(4-(*tert*-Butyl)phenyl)-5-methylhepta-1,3-dien-1-yl)benzo[*d*][1,3]dioxole (3o)



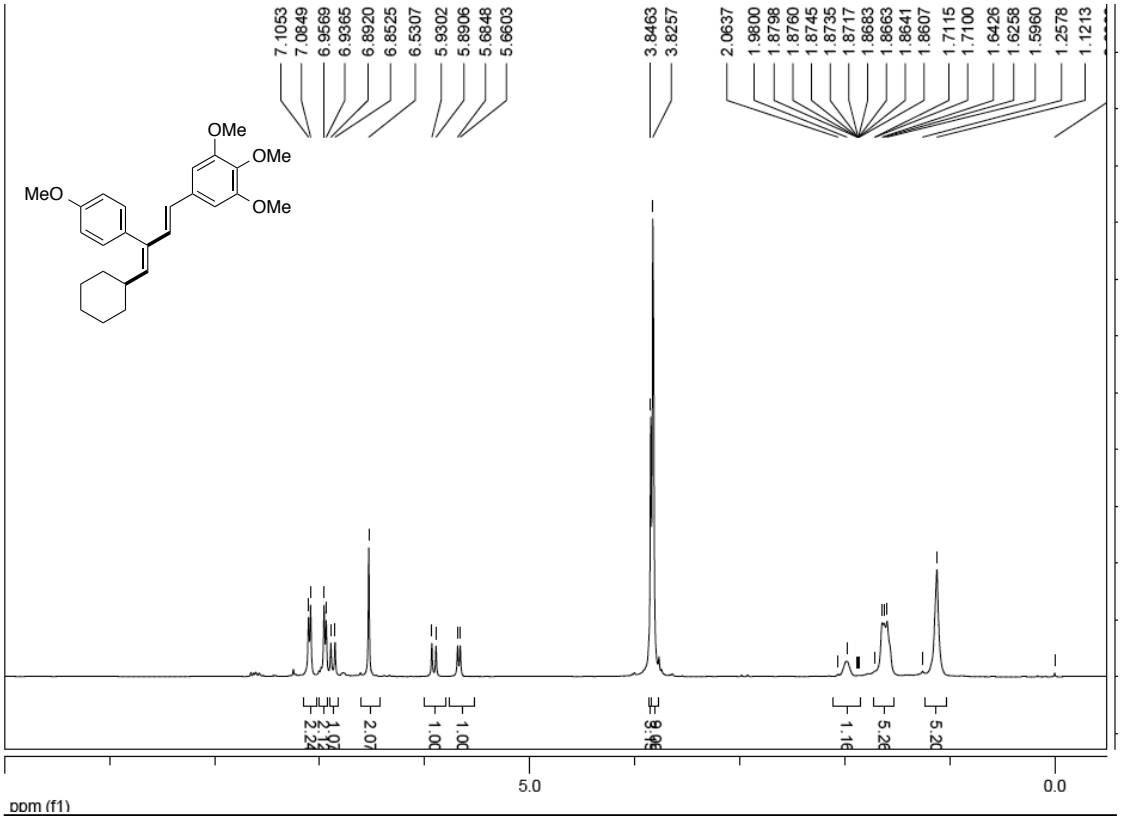


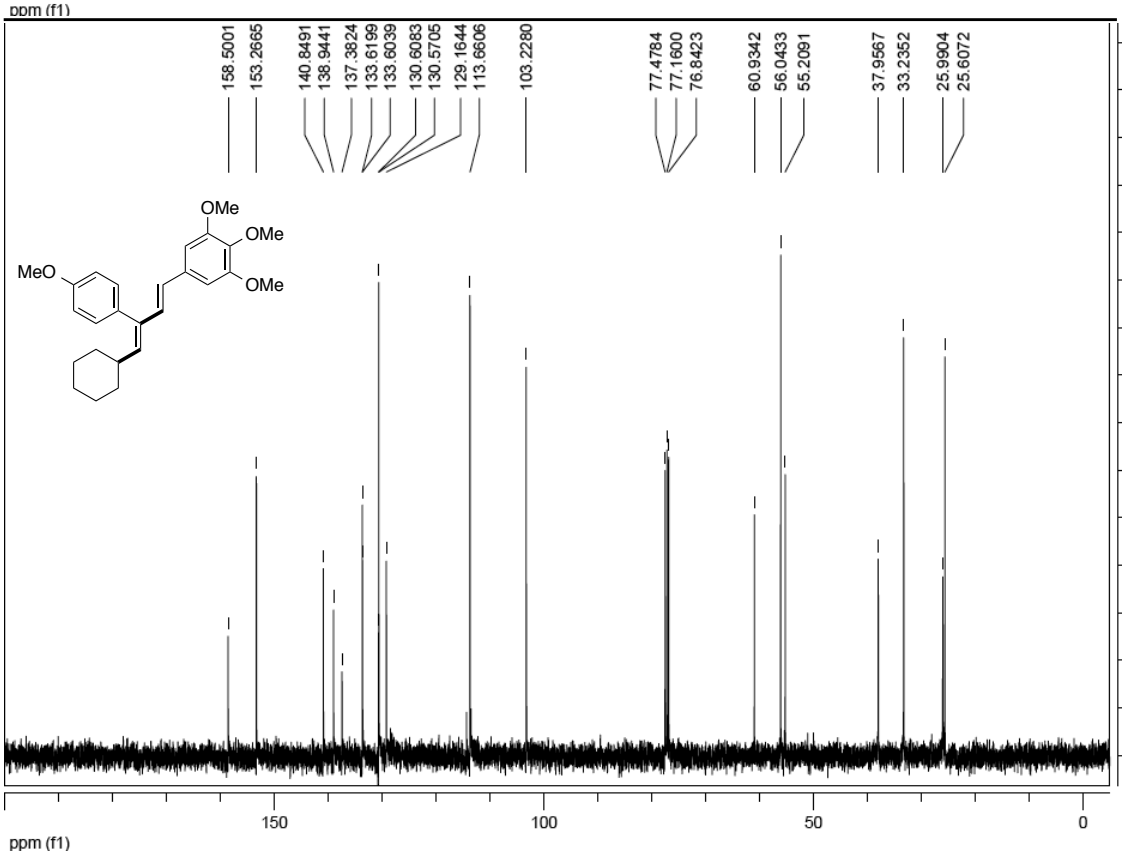
1-(*tert*-Butyl)-4-((1*E*,3*Z*)-1-(4-chlorophenyl)-5-methylhepta-1,3-dien-3-yl)benzene (3p)



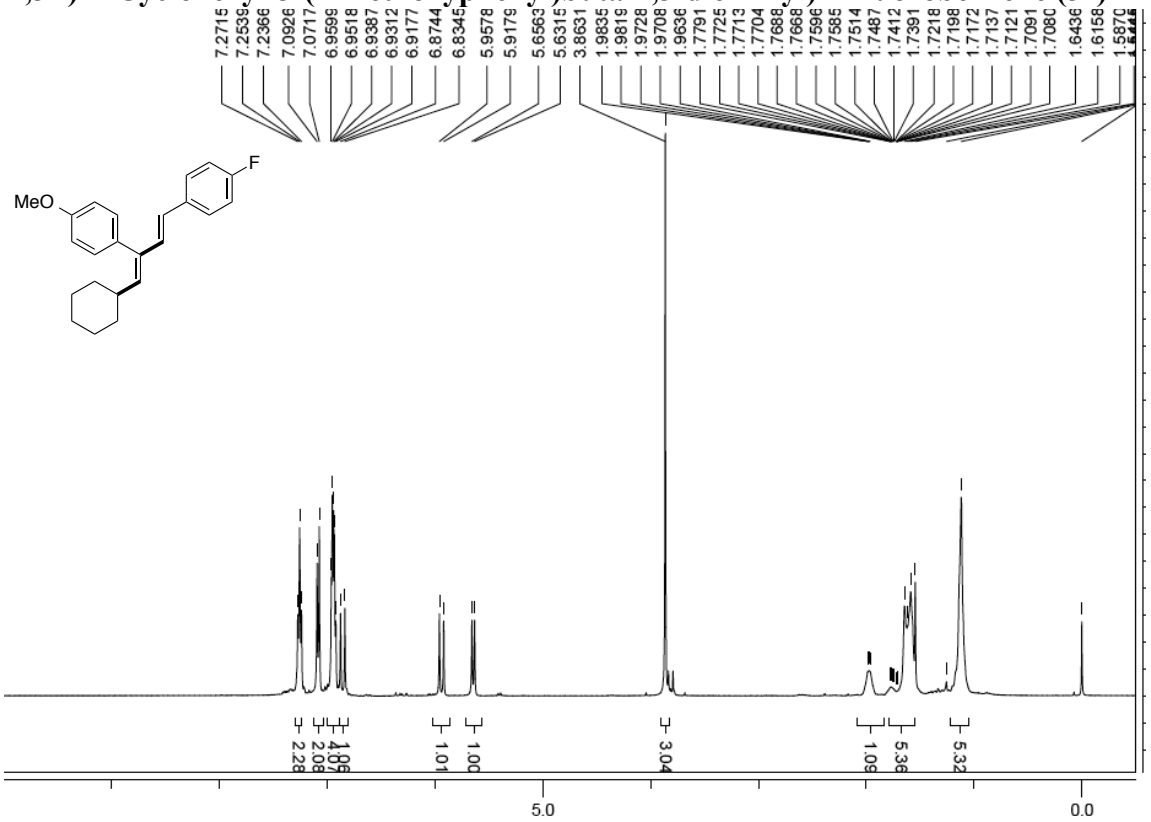


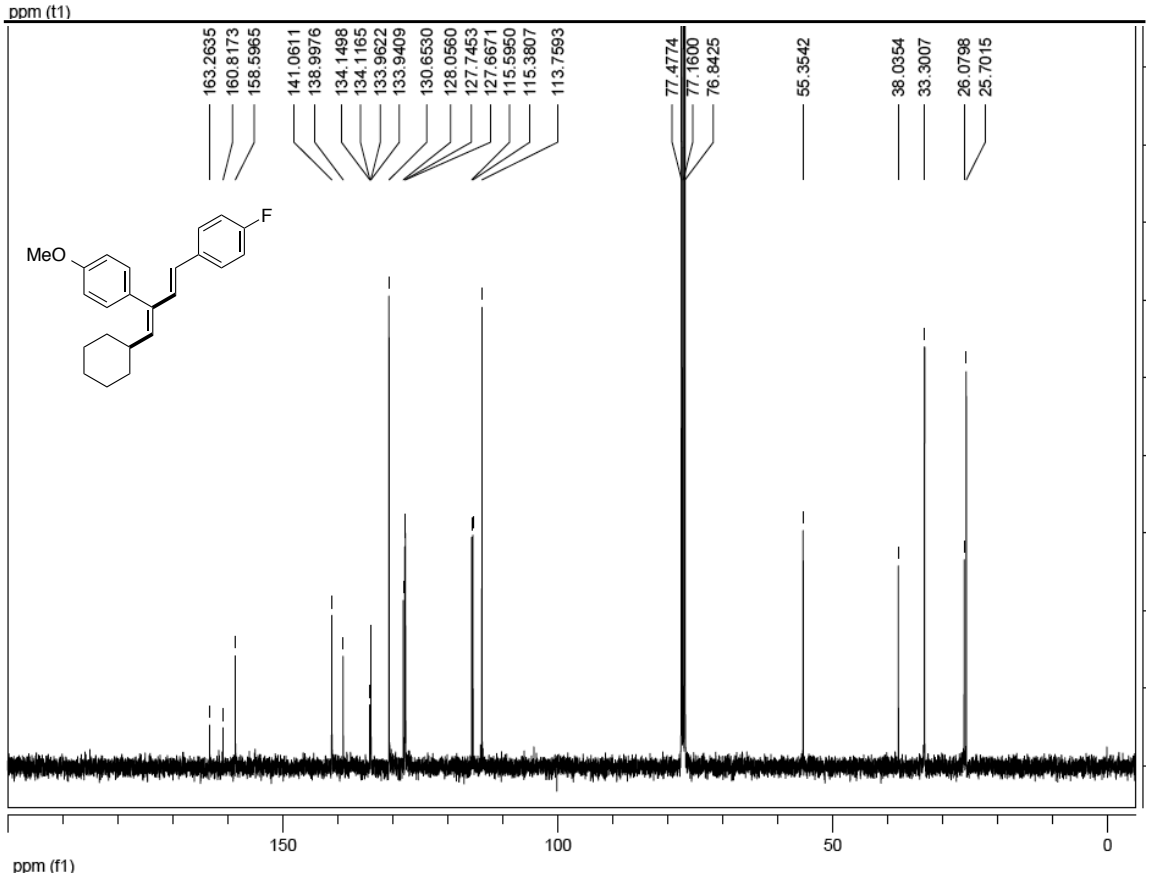
5-((1*E*,3*Z*)-4-Cyclohexyl-3-(4-methoxyphenyl)buta-1,3-dien-1-yl)-1,2,3-trimethoxybenzene (3q)



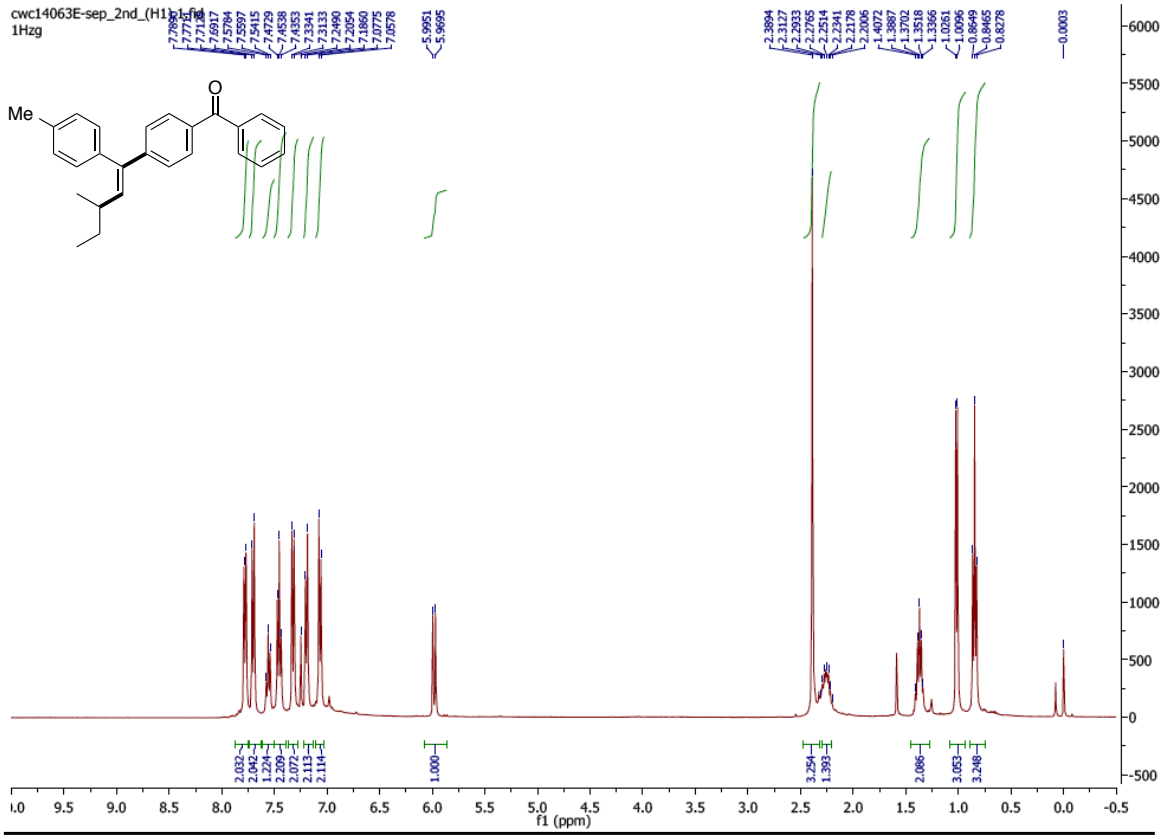


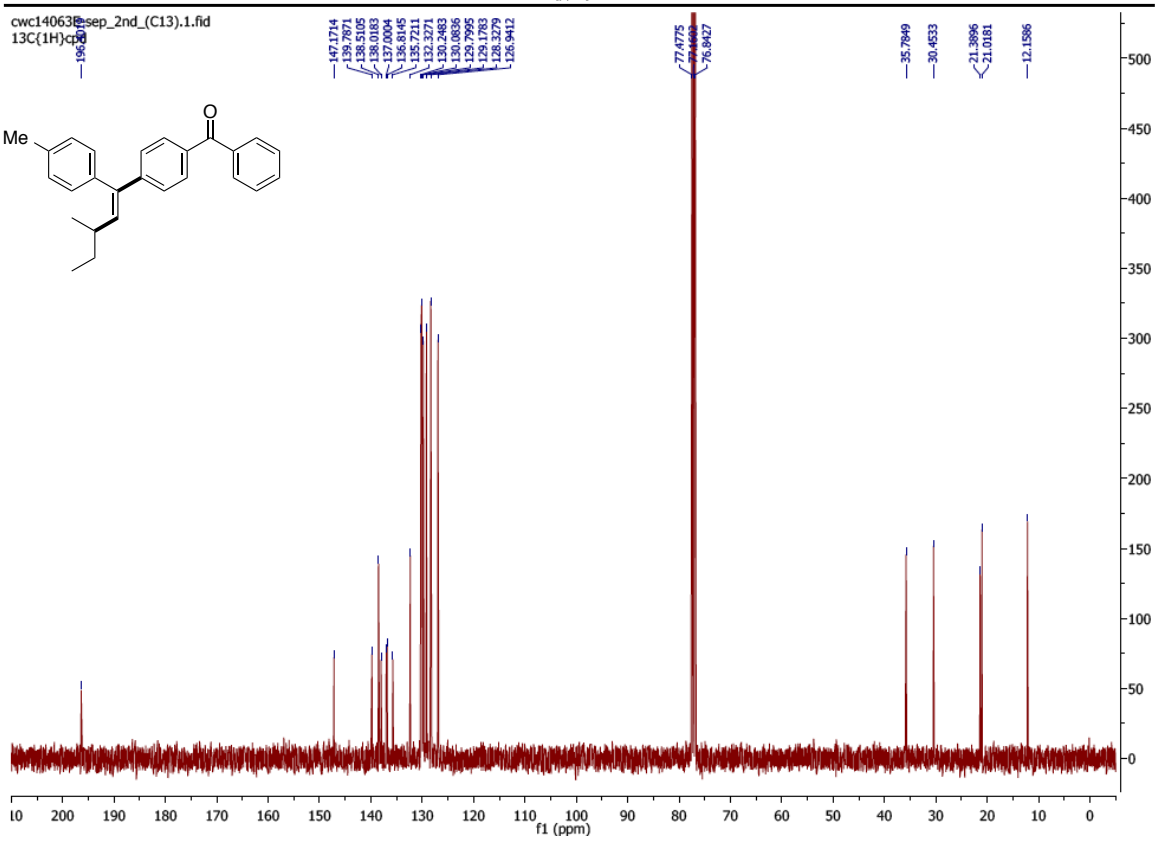
1-((1*E*,3*Z*)-4-Cyclohexyl-3-(4-methoxyphenyl)buta-1,3-dien-1-yl)-4-fluorobenzene (3r)



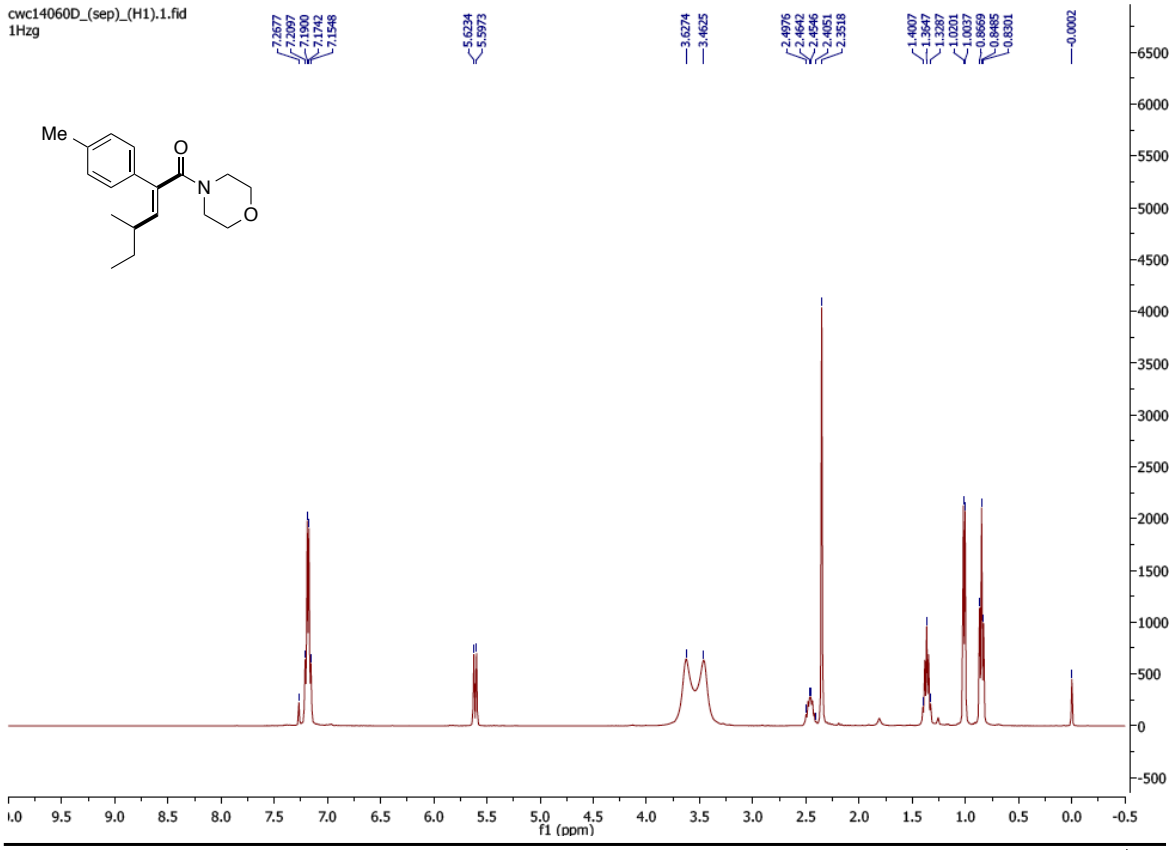


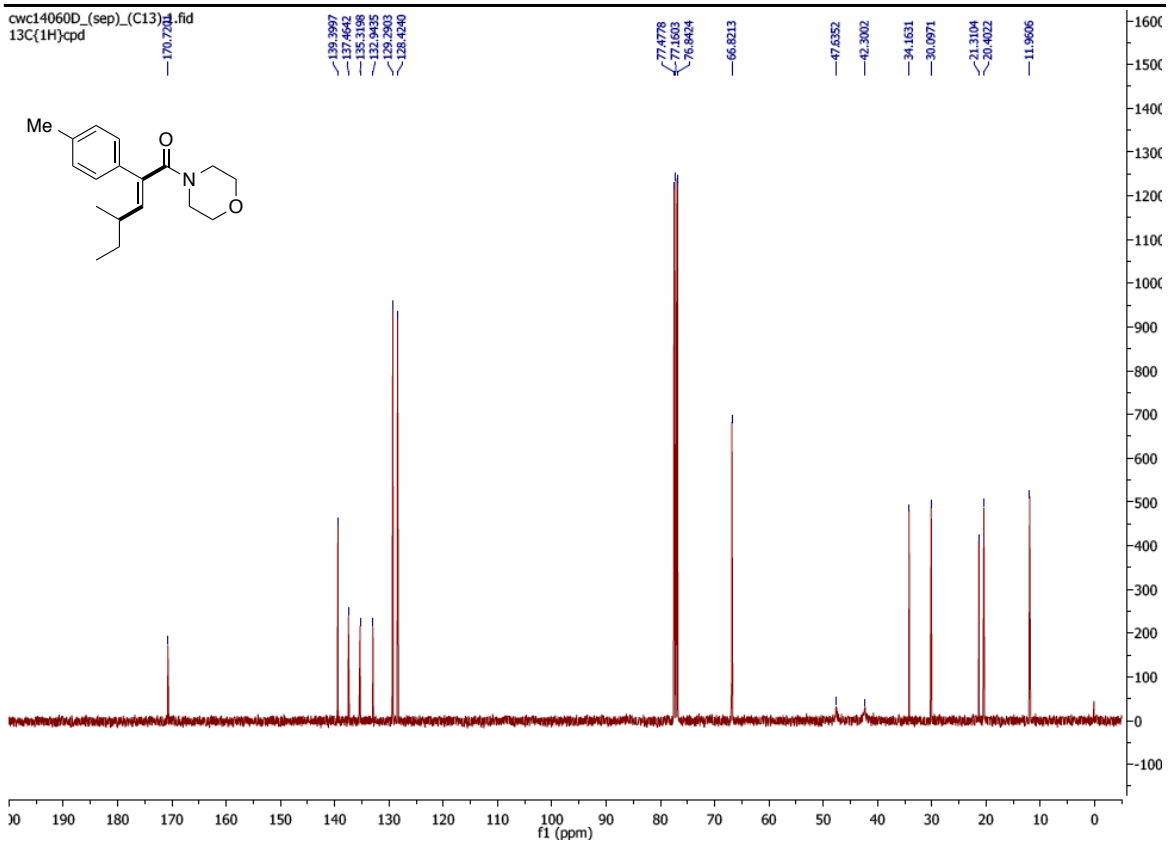
(*E*)-(4-(3-Methyl-1-(*p*-tolyl)pent-1-en-1-yl)phenyl)(phenyl)methanone (3s)



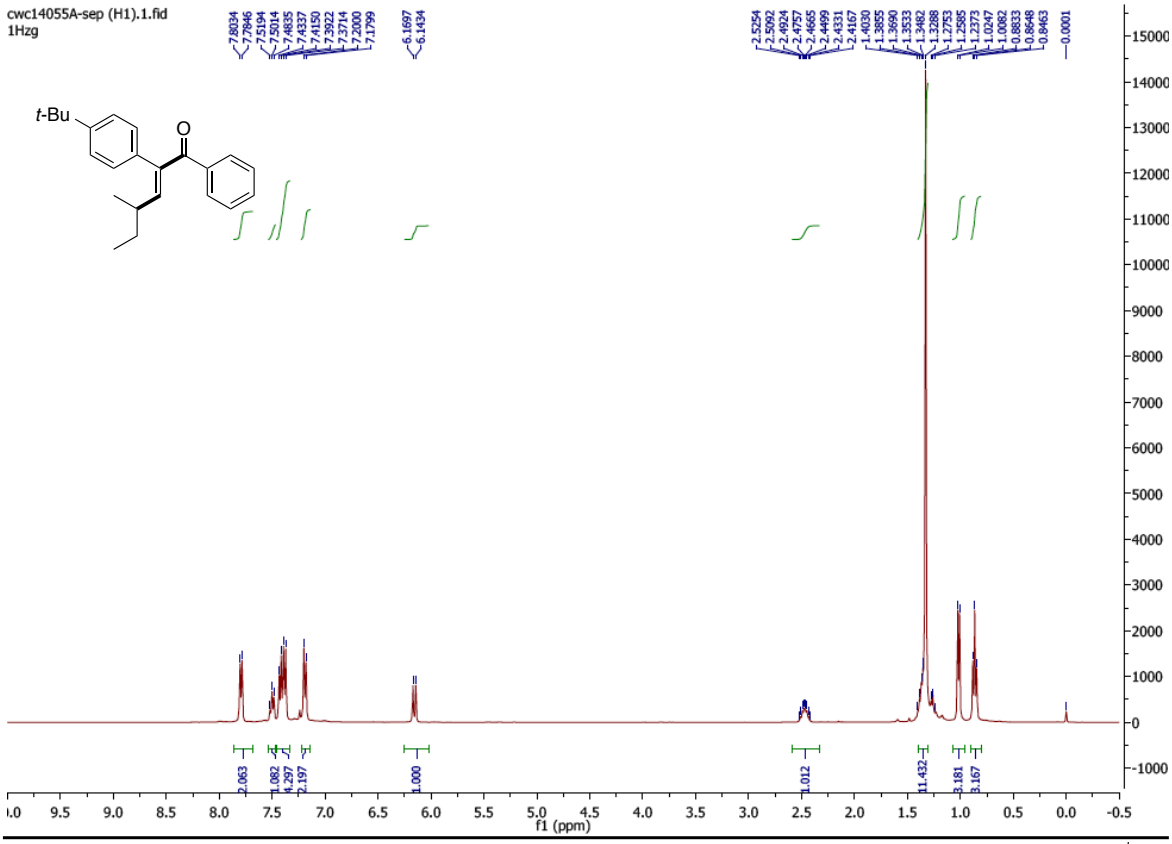


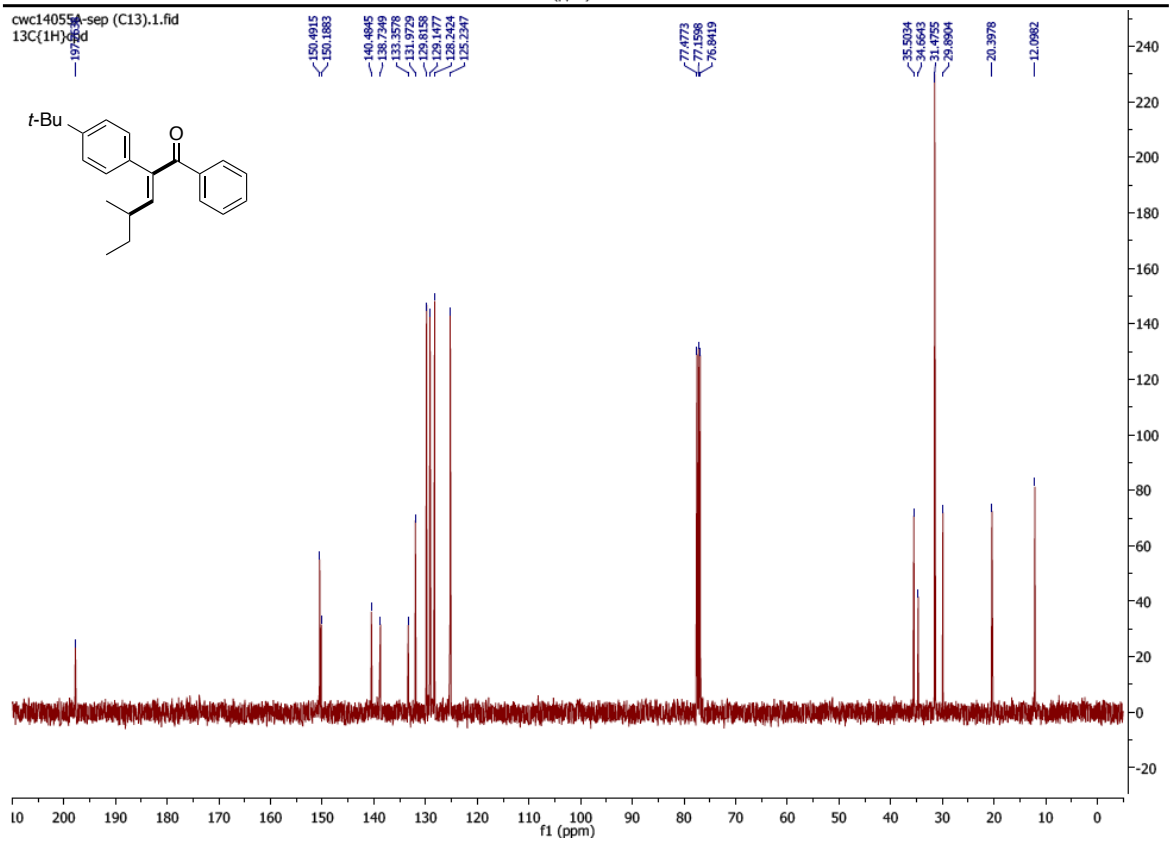
(*E*)-4-Methyl-1-morpholino-2-(*p*-tolyl)hex-2-en-1-one (3t)



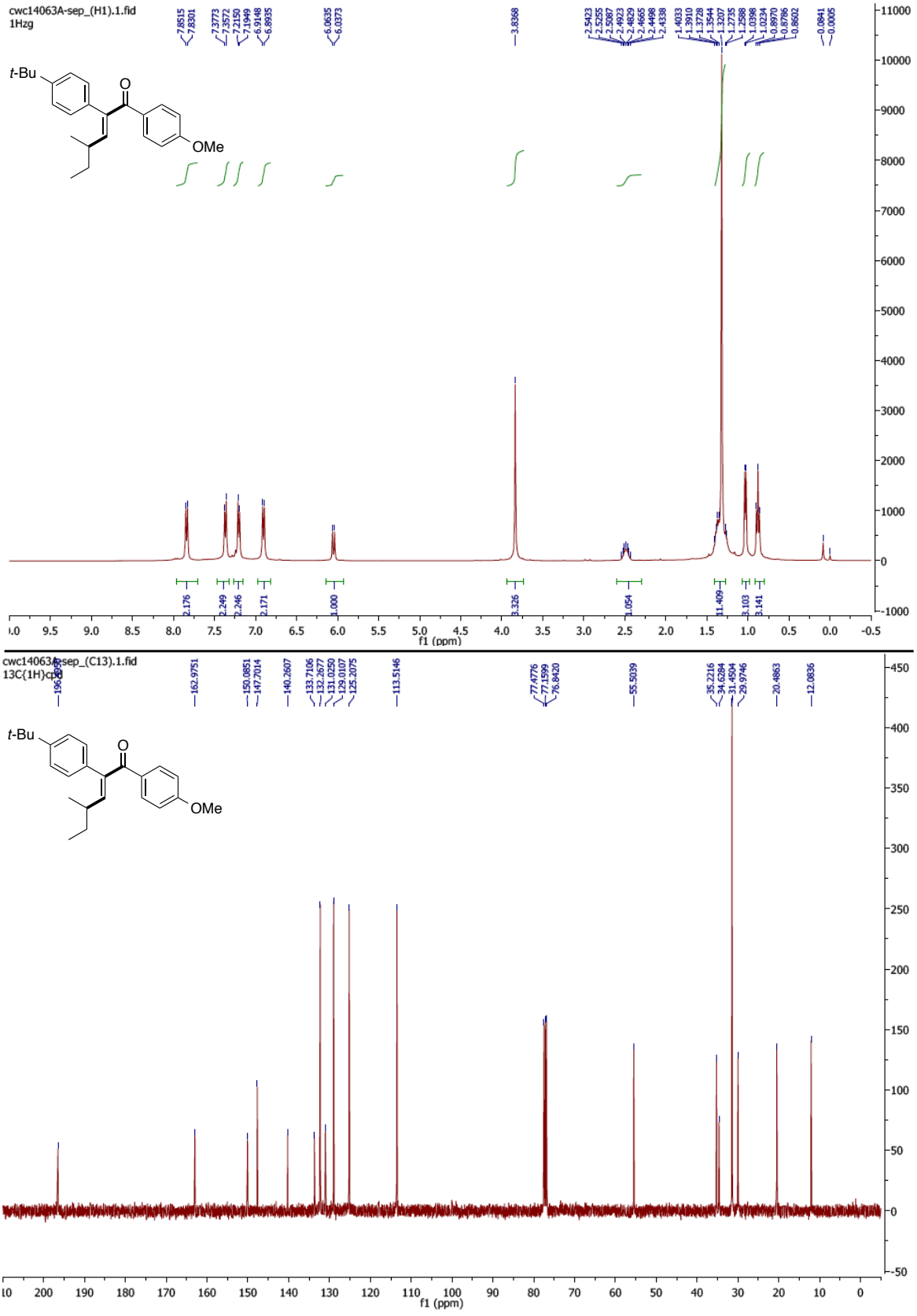


(*E*)-2-(4-(*tert*-Butyl)phenyl)-4-methyl-1-phenylhex-2-en-1-one (3u)

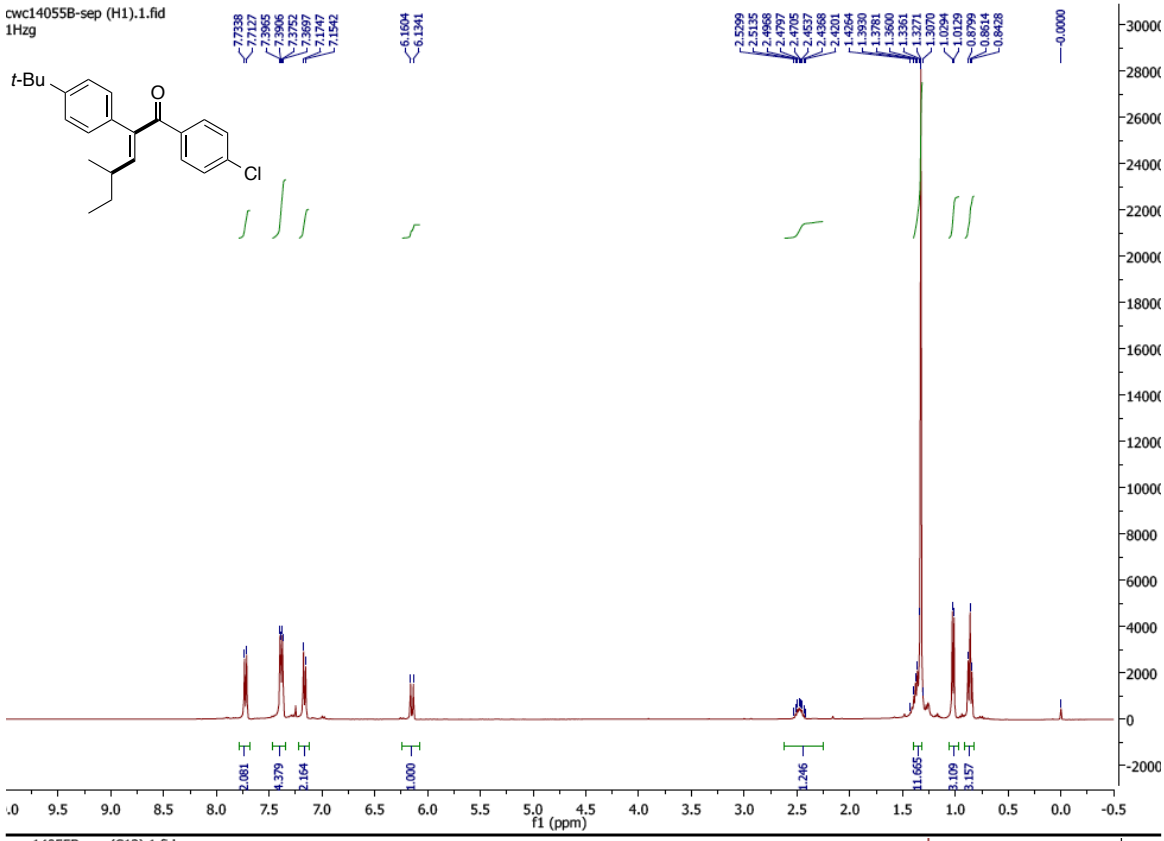


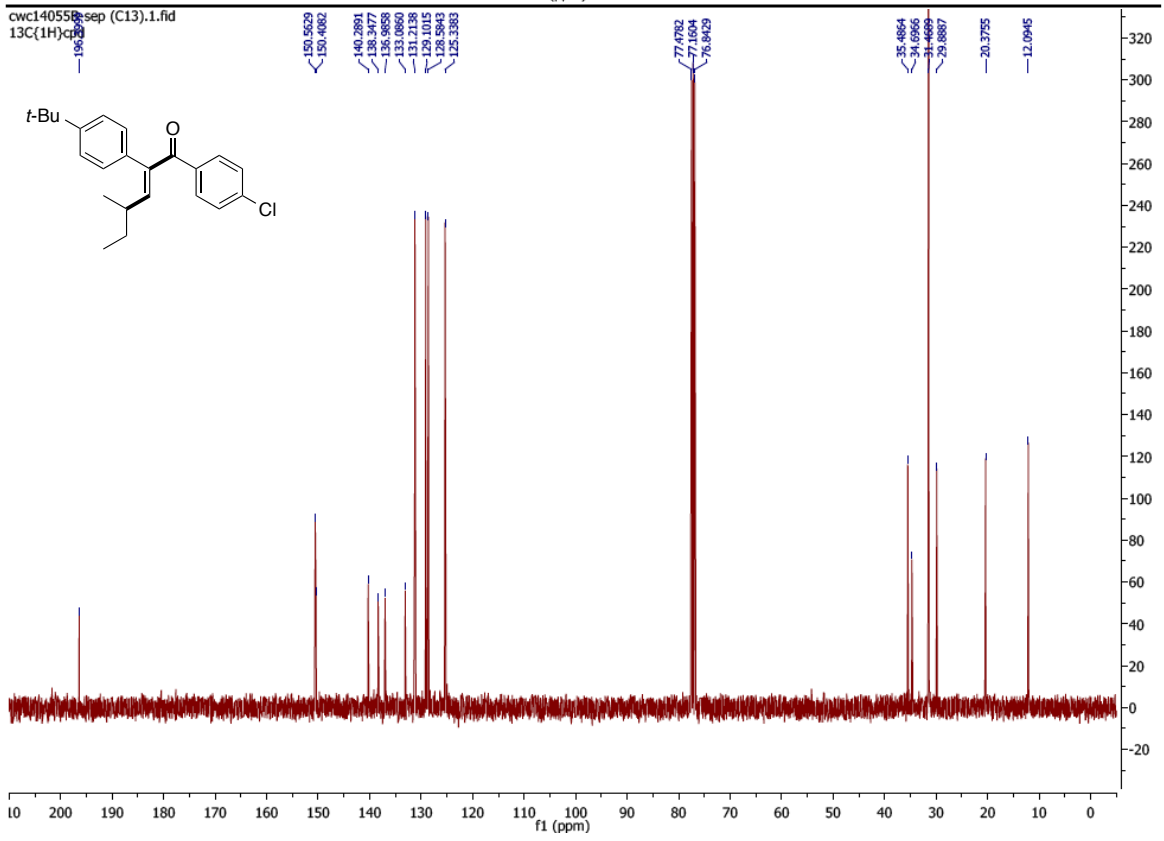


(*E*)-2-(4-(*tert*-Butyl)phenyl)-1-(4-methoxyphenyl)-4-methylhex-2-en-1-one (3v)

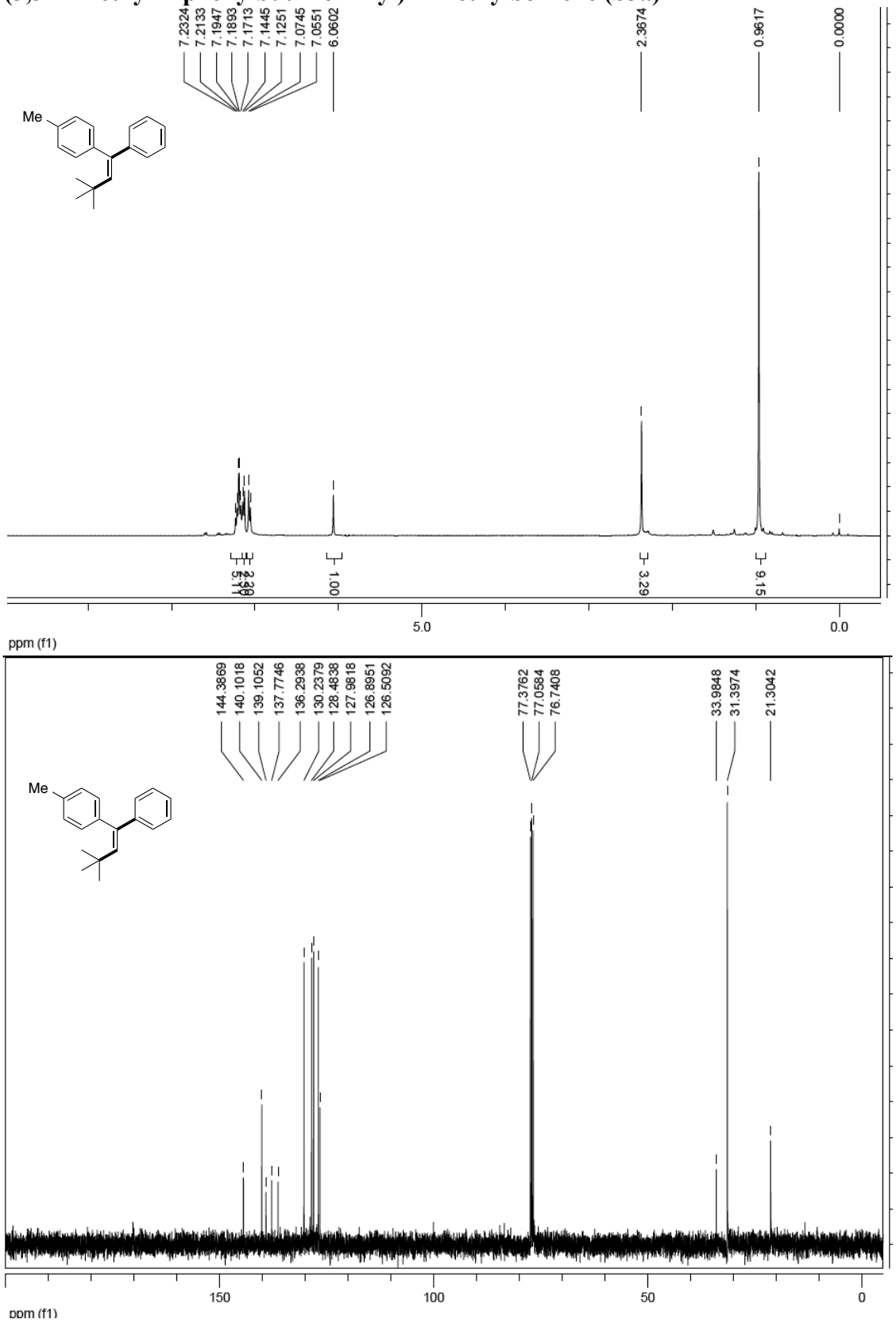


(*E*)-2-(4-(*tert*-Butyl)phenyl)-1-(4-chlorophenyl)-4-methylhex-2-en-1-one (3w)

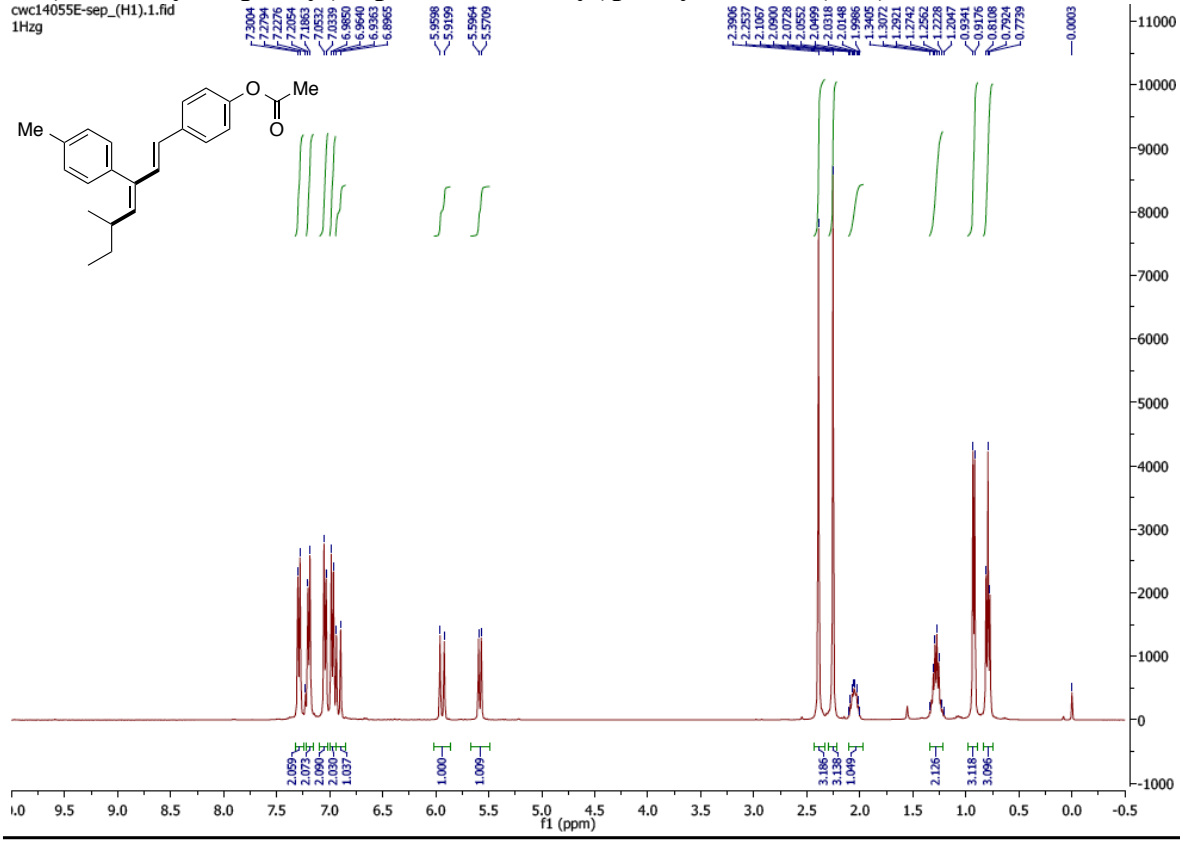


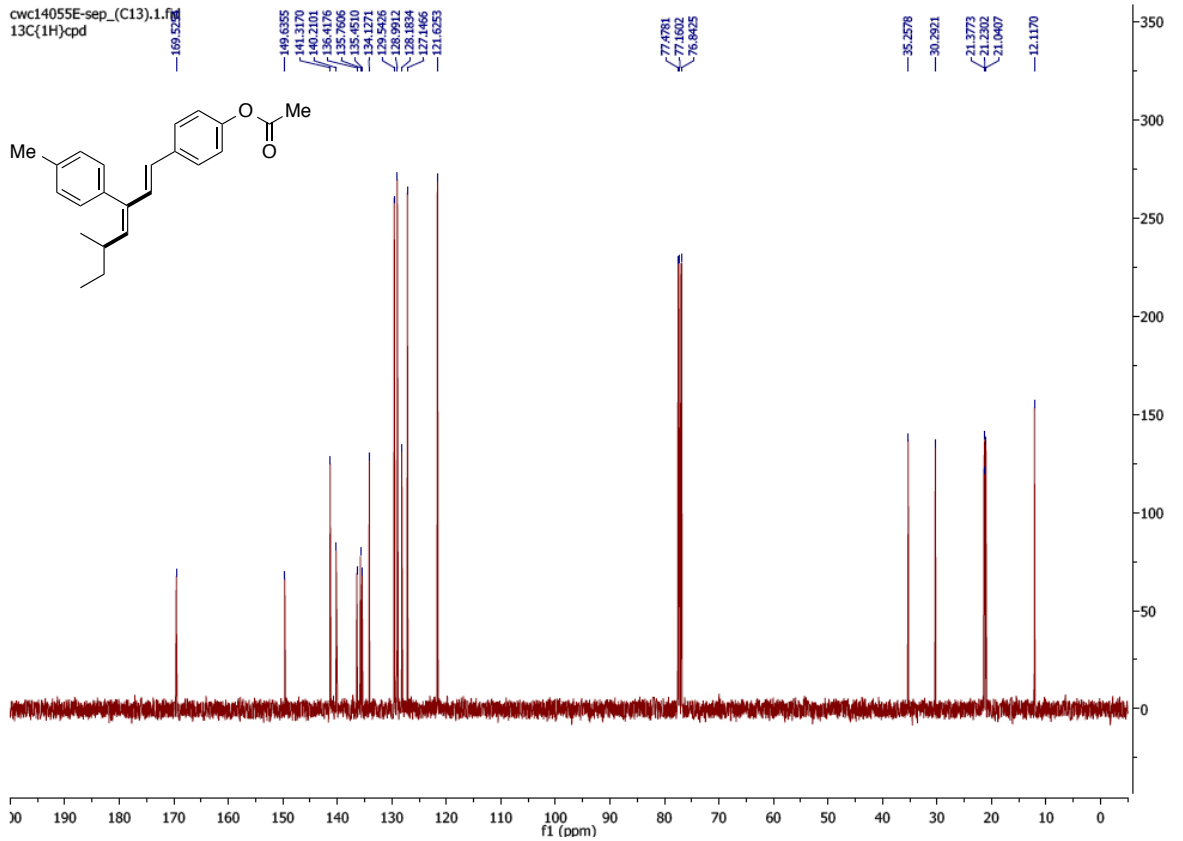


(*Z*)-1-(3,3-Dimethyl-1-phenylbut-1-en-1-yl)-4-methylbenzene (S3a)

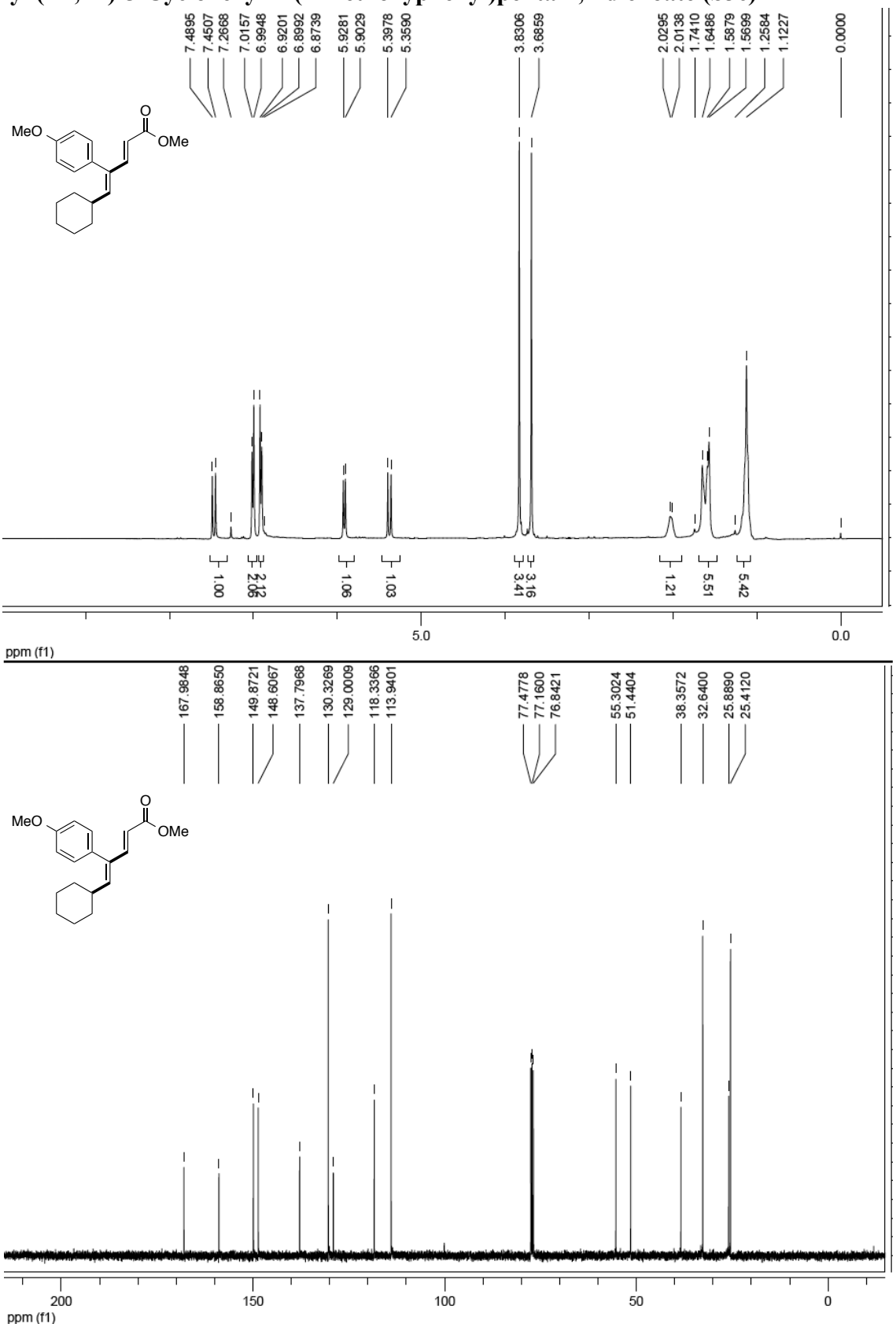


4-((1*E*,3*Z*)-5-methyl-3-(*p*-tolyl)hepta-1,3-dien-1-yl)phenyl acetate (S3b)

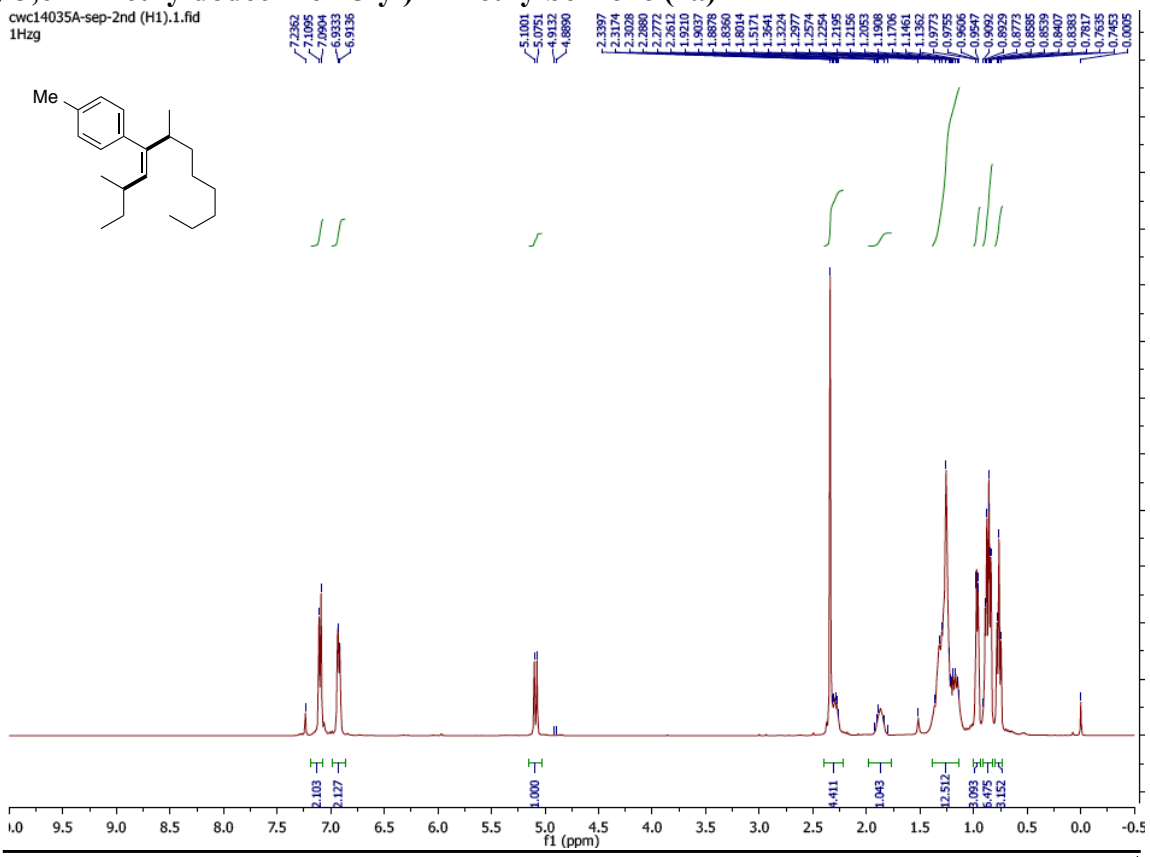


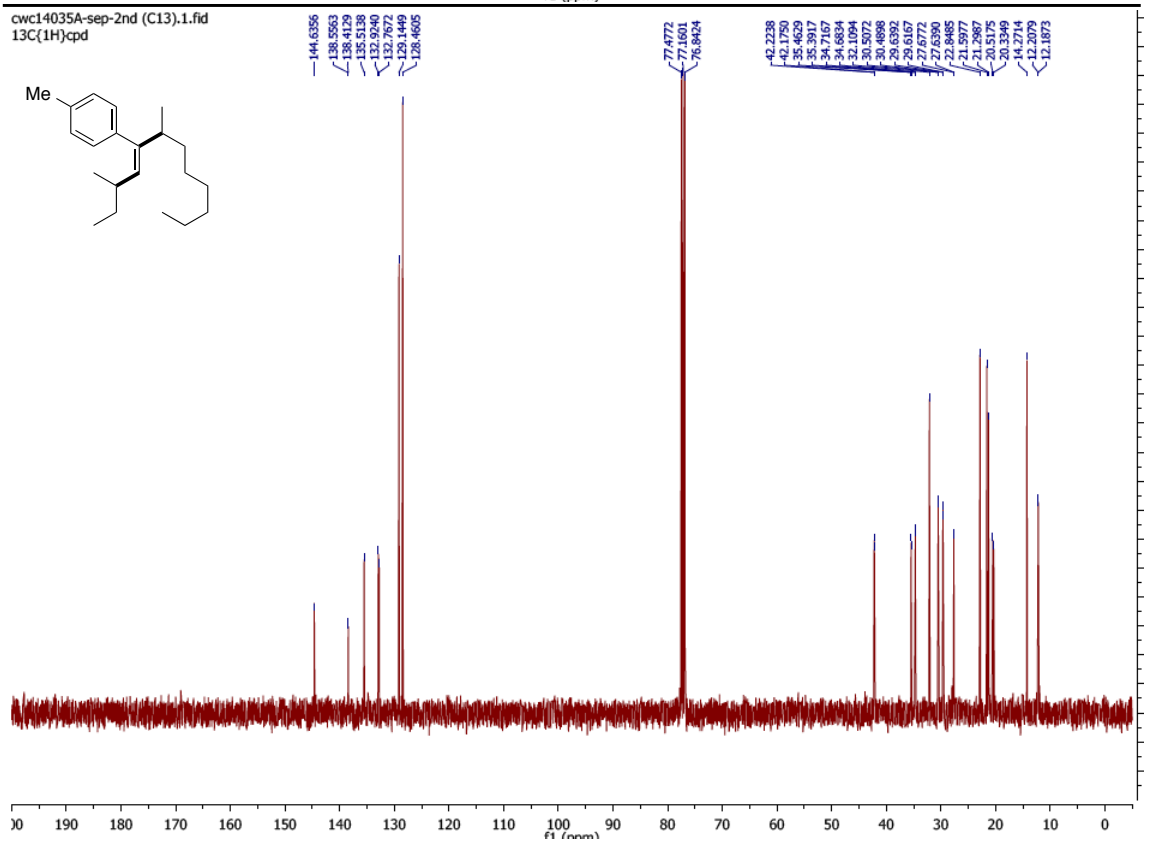


Methyl (2*E*,4*Z*)-5-Cyclohexyl-4-(4-methoxyphenyl)penta-2,4-dienoate (S3c)

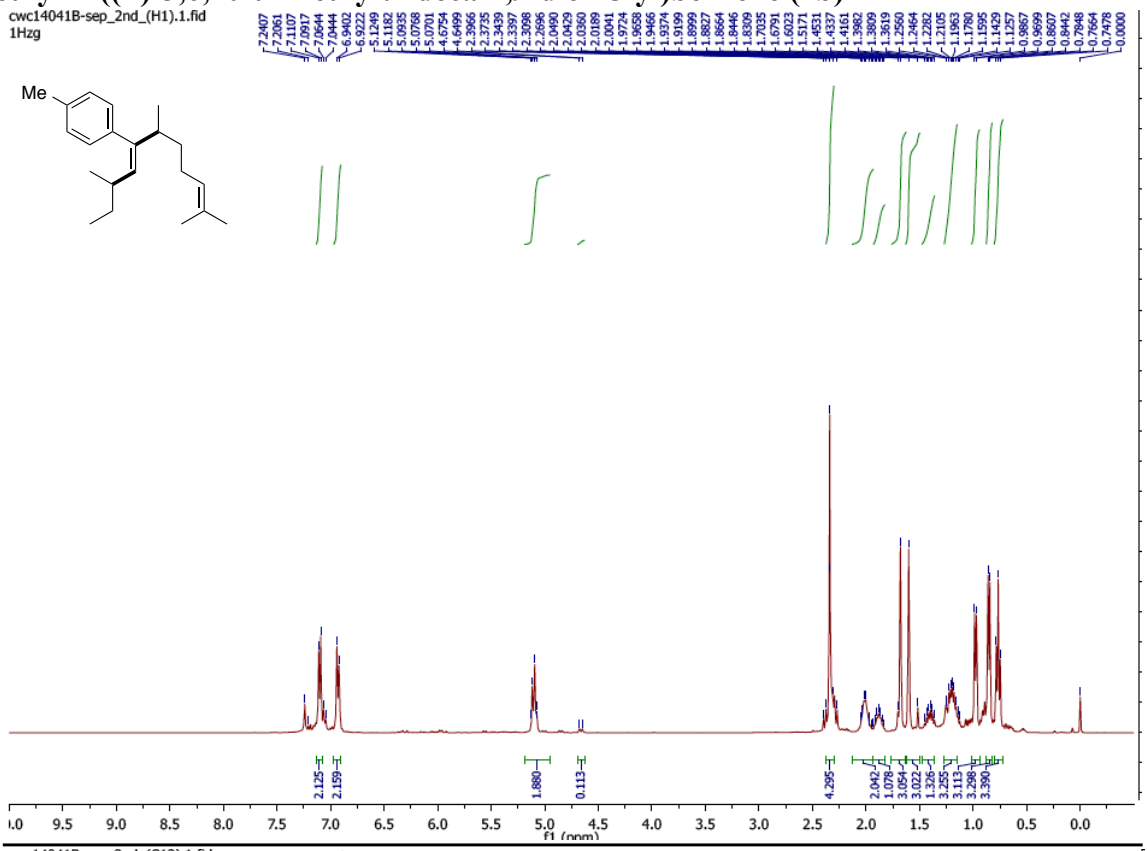


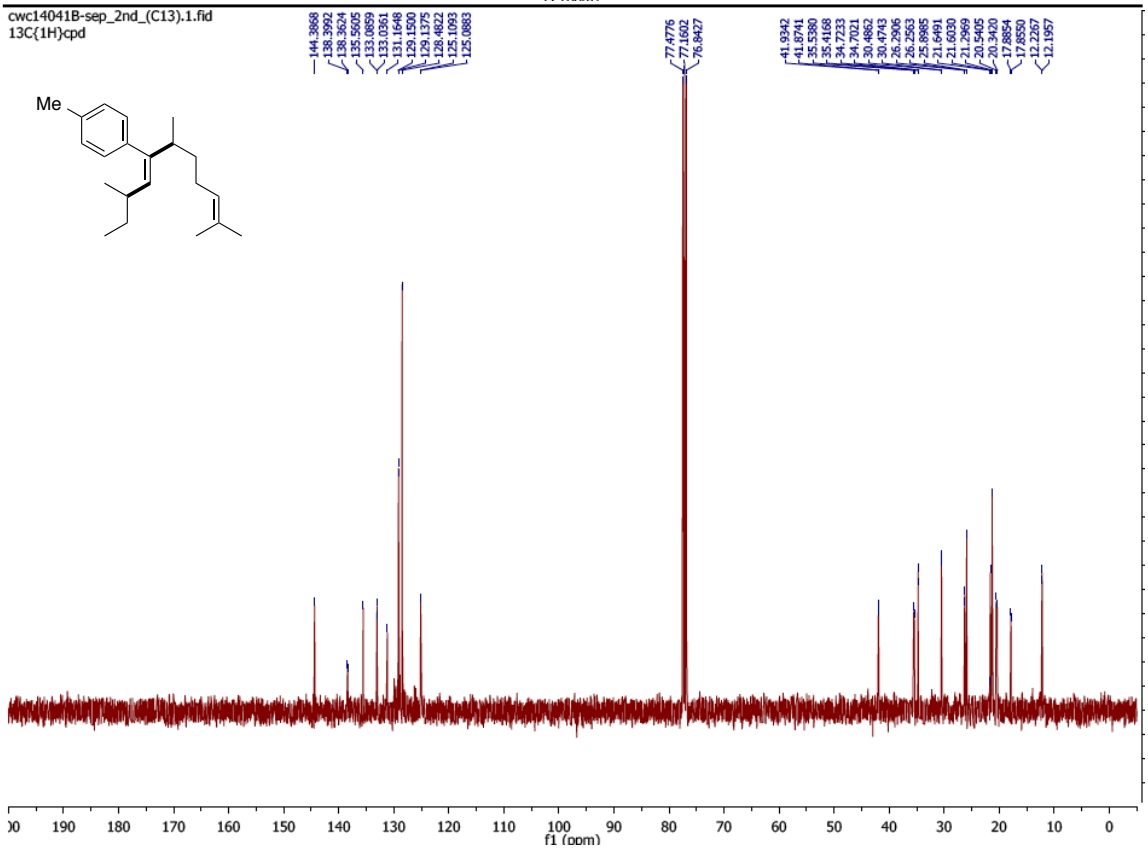
1-((*Z*)-3,6-Dimethyldodec-4-en-5-yl)-4-methylbenzene (4a)



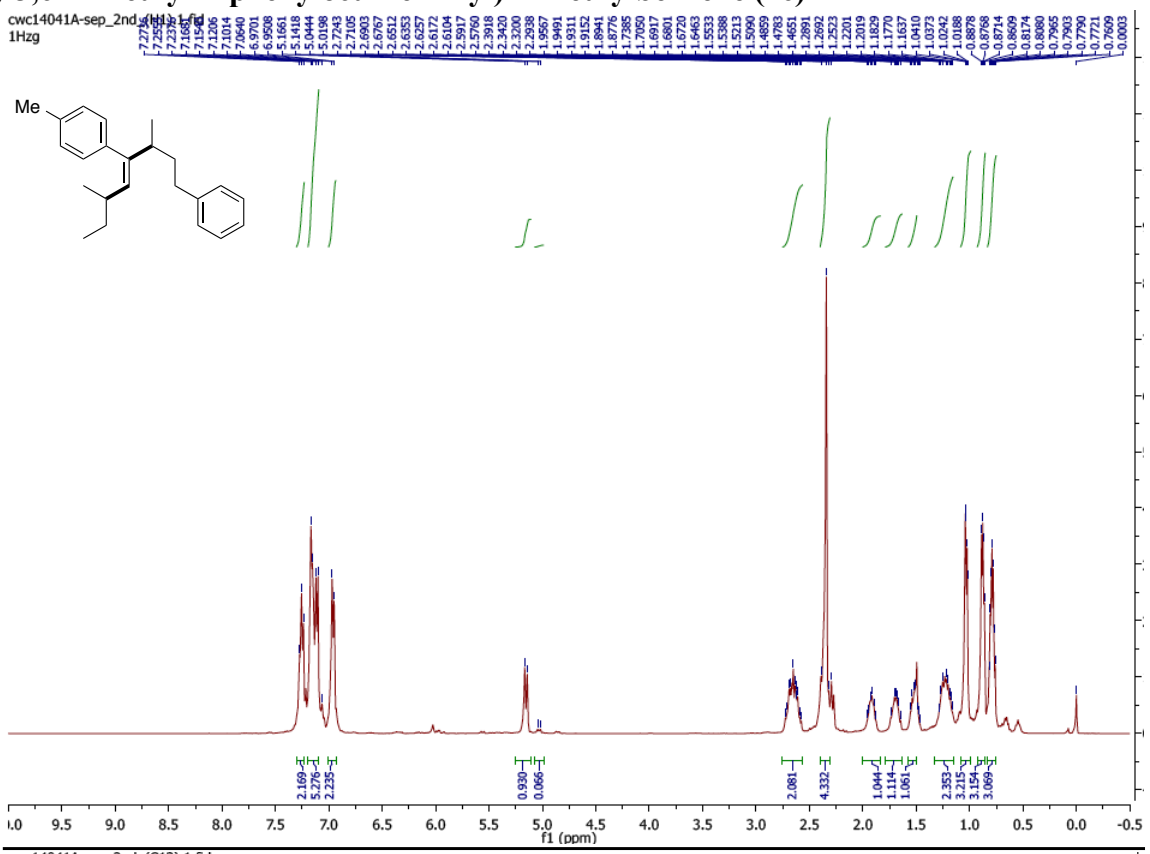


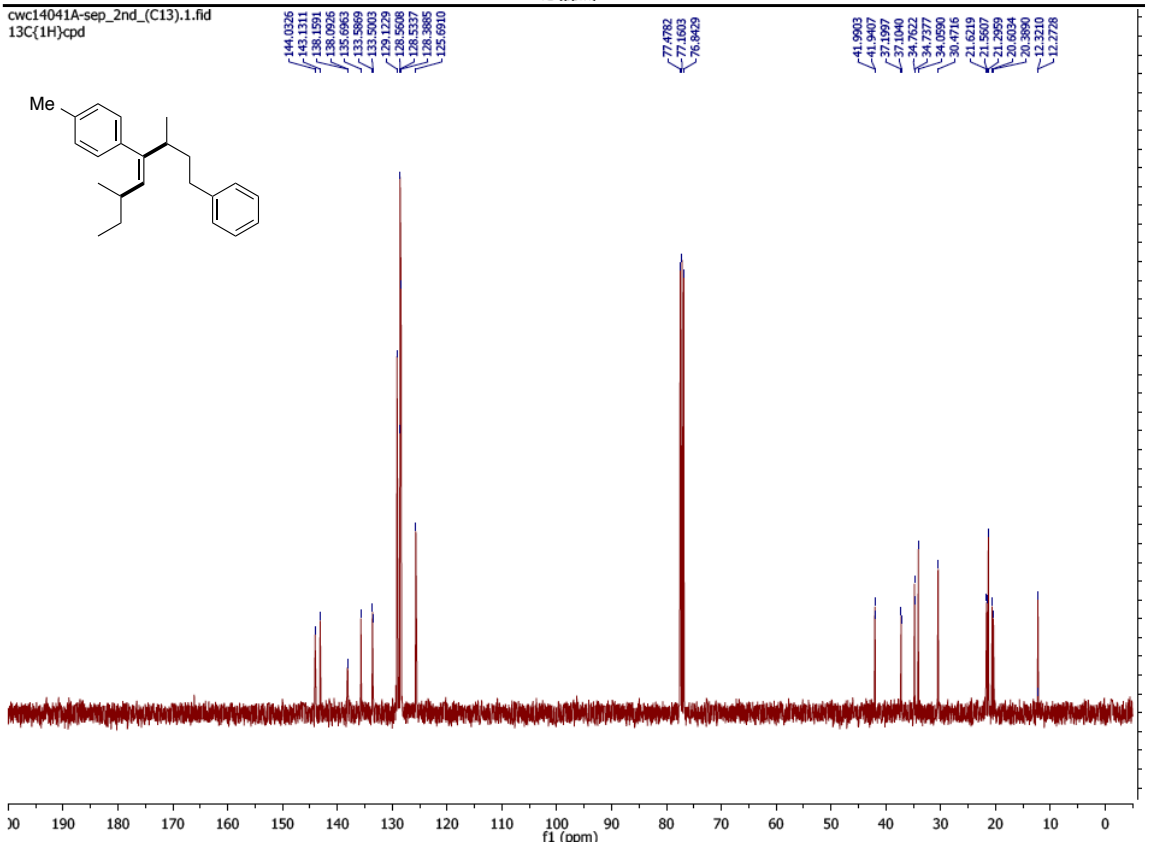
1-Methyl-4-((*Z*)-3,6,10-trimethylundeca-4,9-dien-5-yl)benzene (4b)



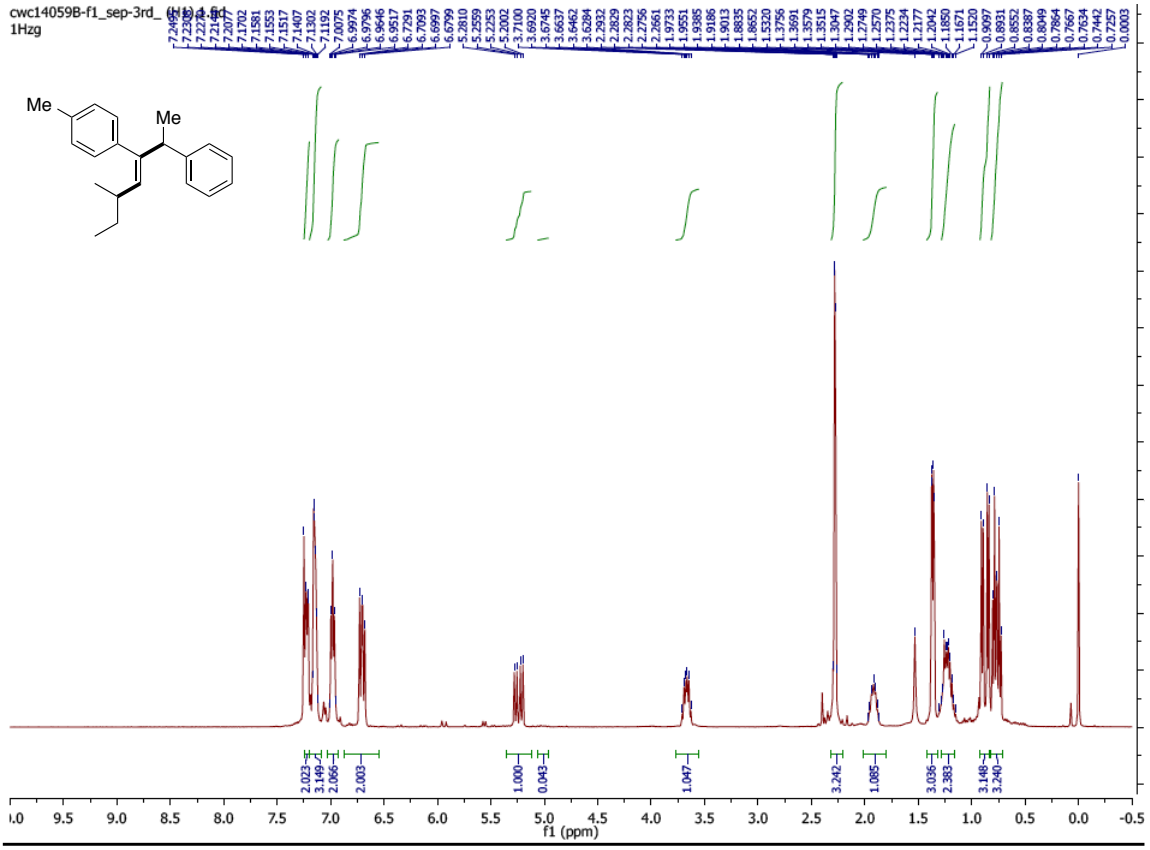


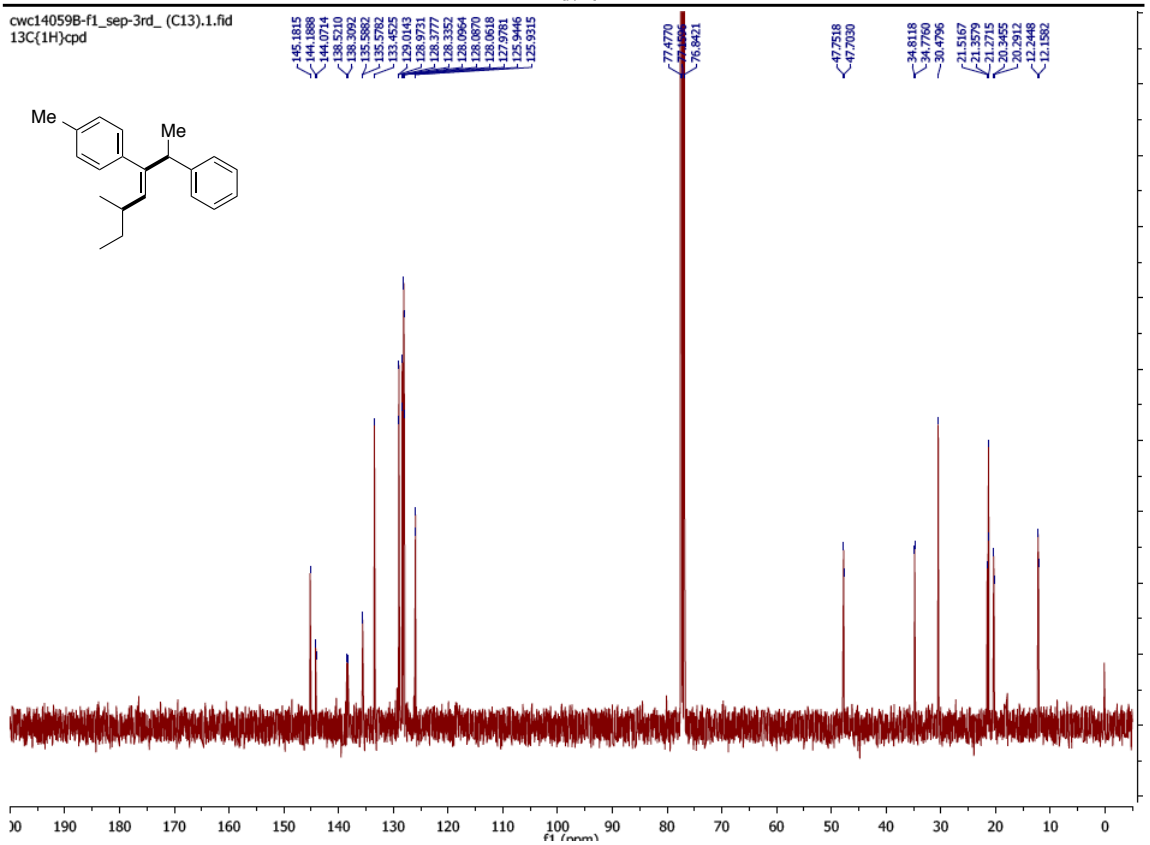
1-((*Z*)-3,6-Dimethyl-1-phenyloct-4-en-4-yl)-4-methylbenzene (4c)



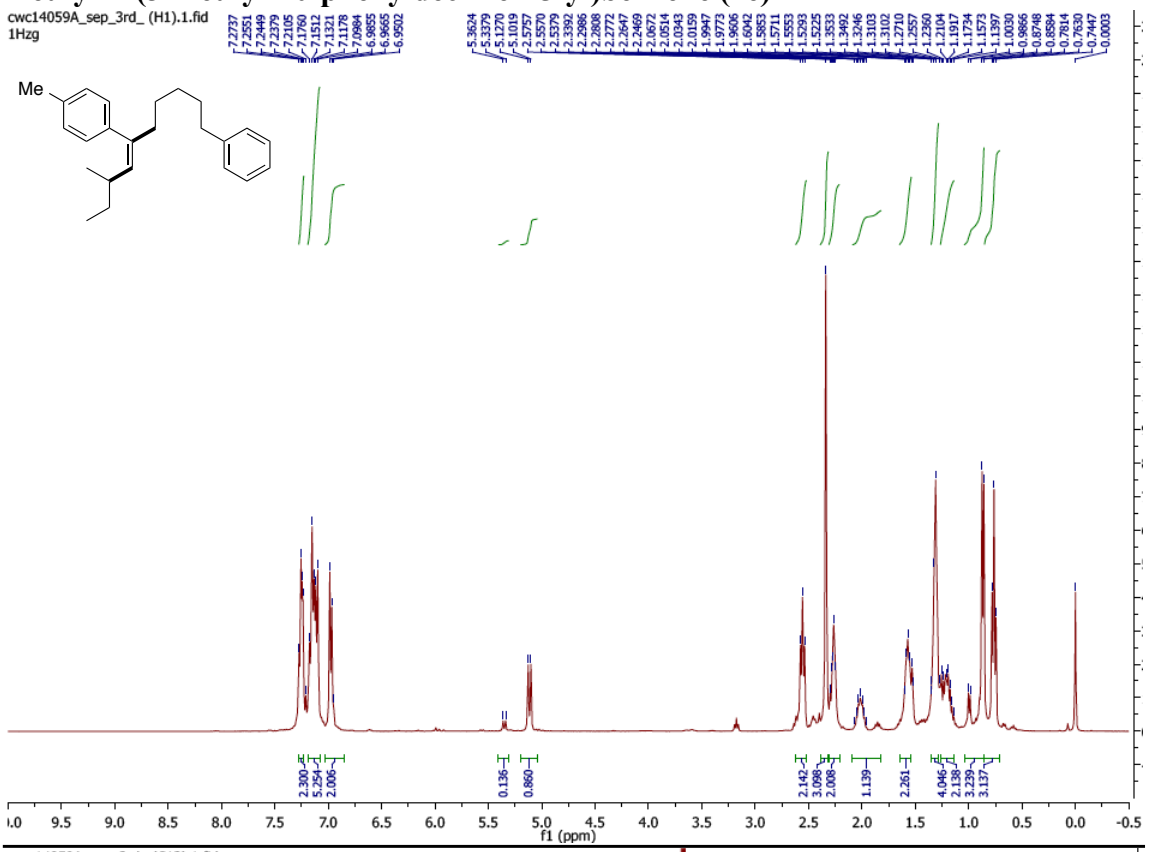


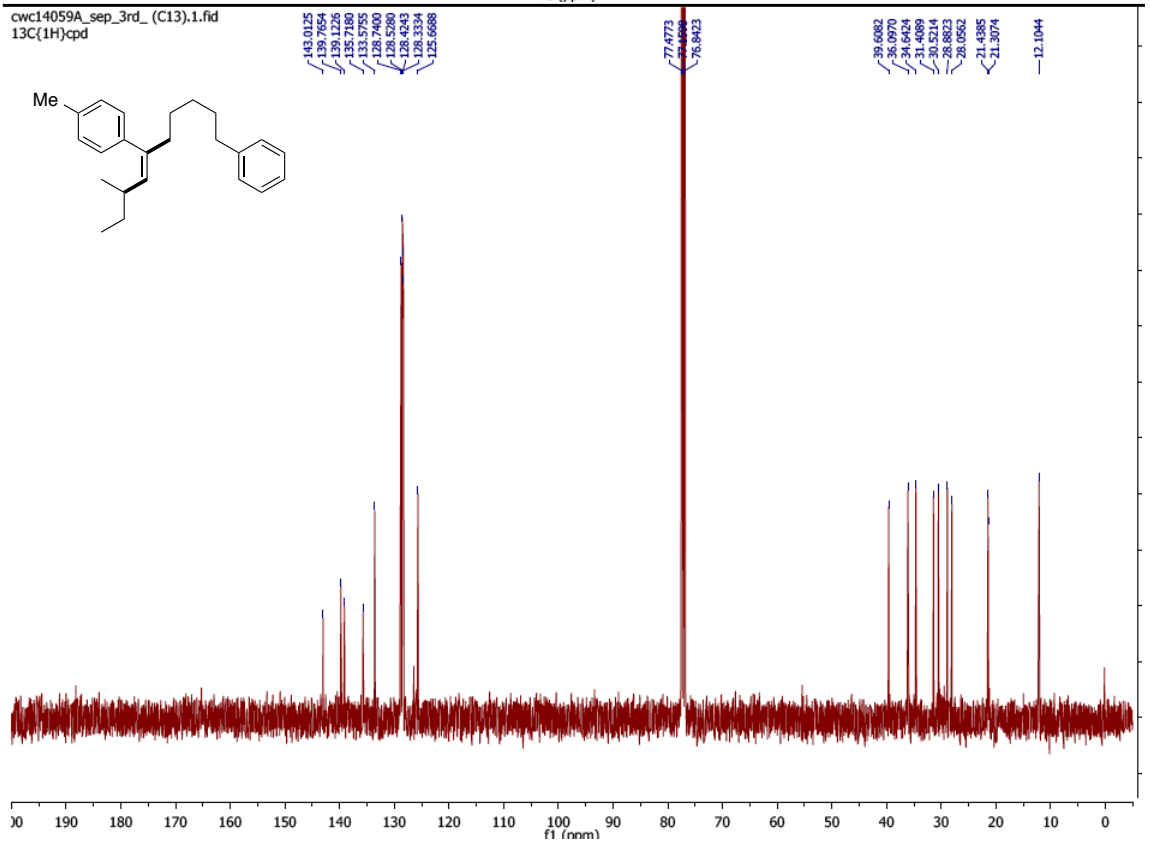
1-Methyl-4-((*Z*)-5-Methyl-2-phenylhept-3-en-3-yl)benzene (4d)



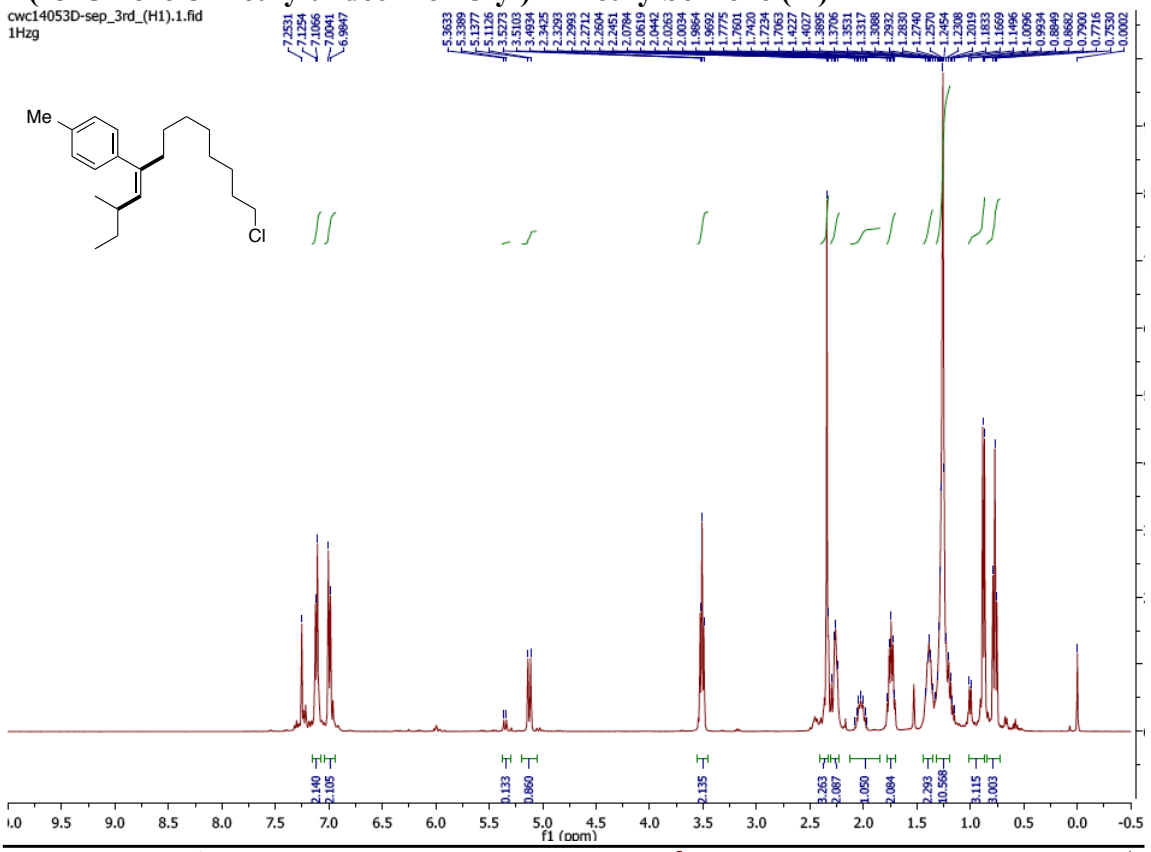


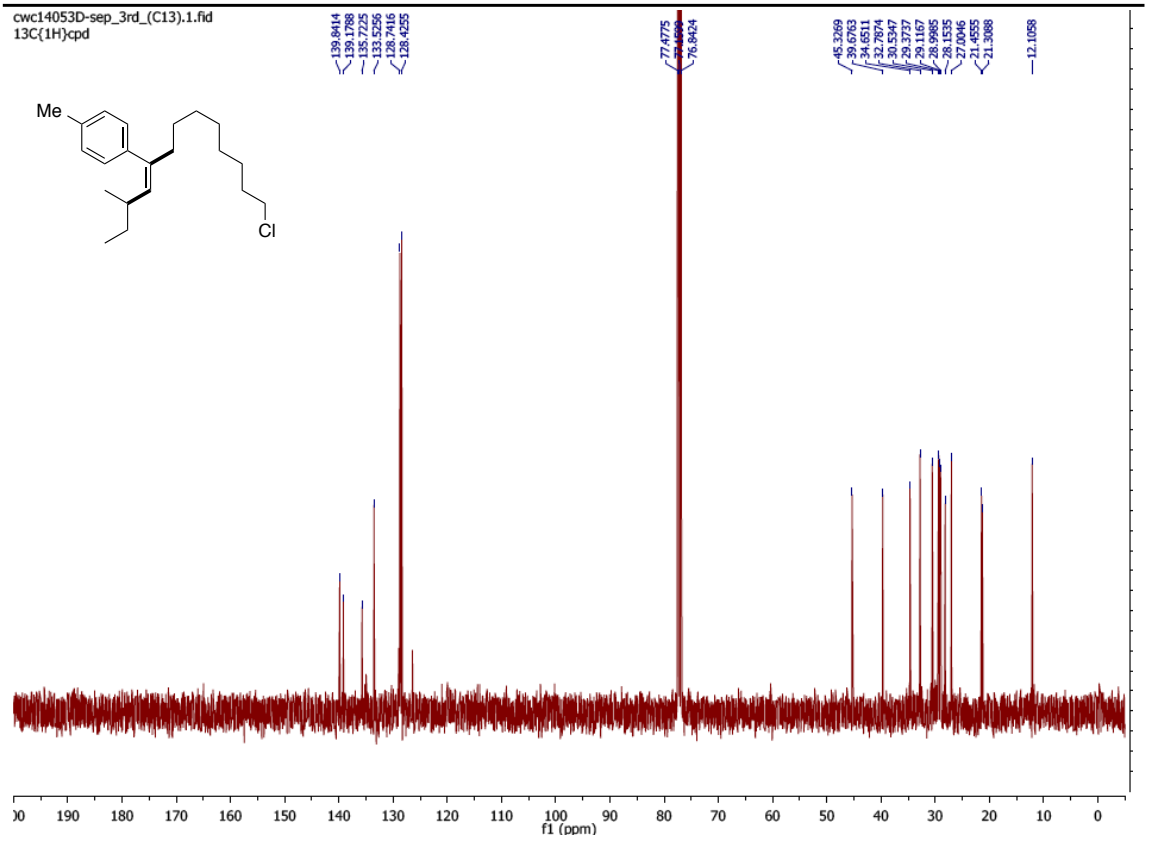
(*Z*)-1-methyl-4-(3-methyl-10-phenyldec-4-en-5-yl)benzene (4e)



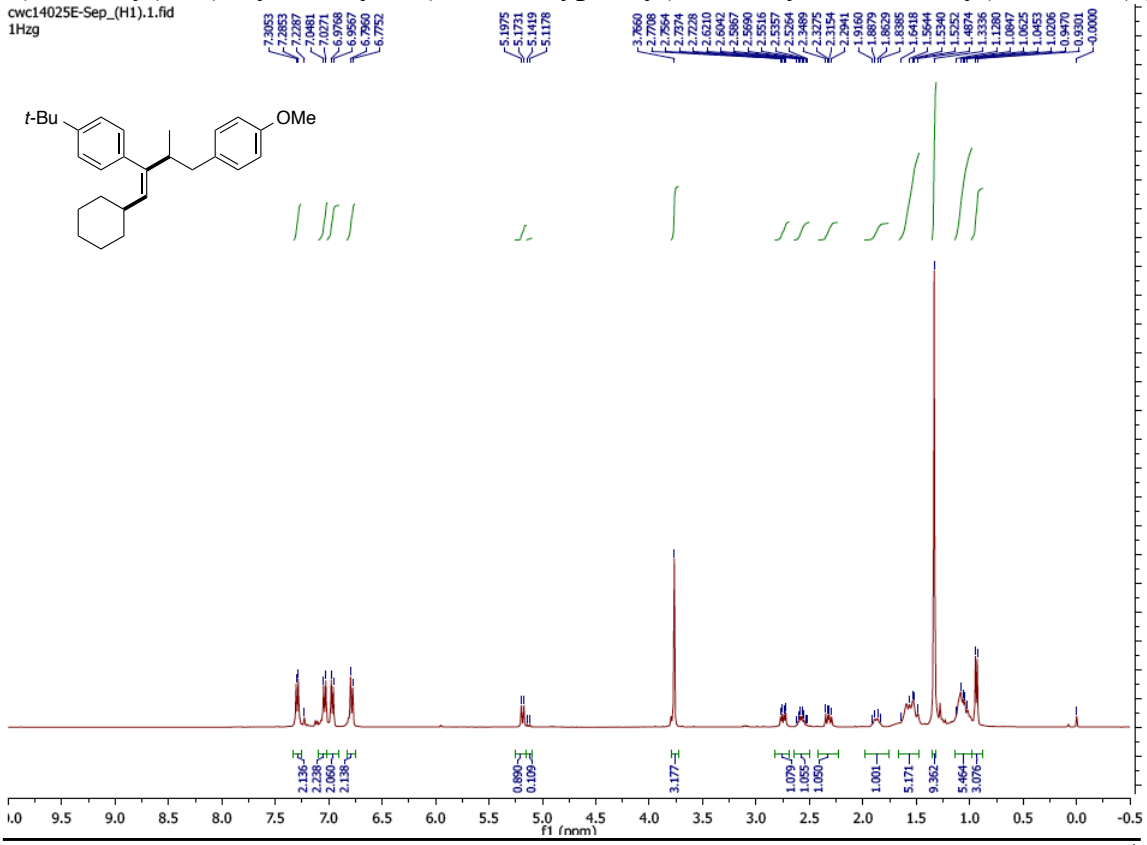


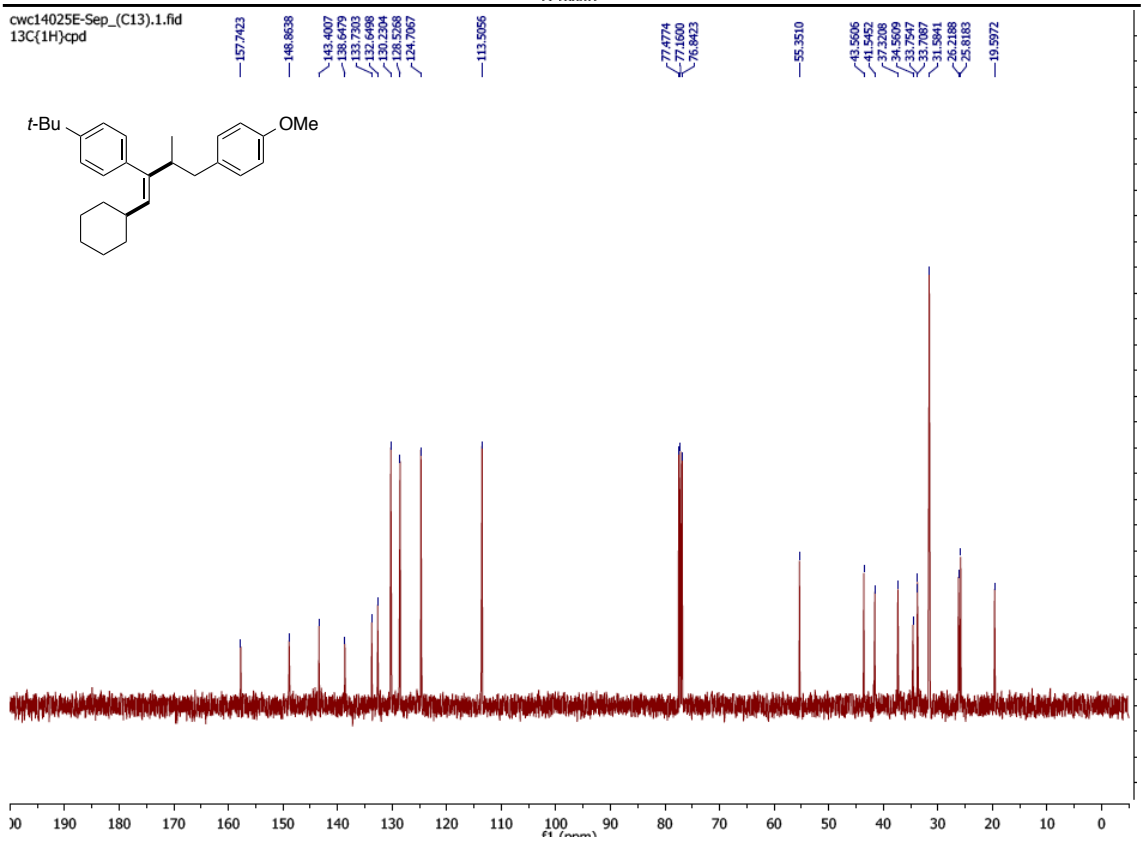
(*Z*)-1-(13-Chloro-3-methyltridec-4-en-5-yl)-4-methylbenzene (4f)



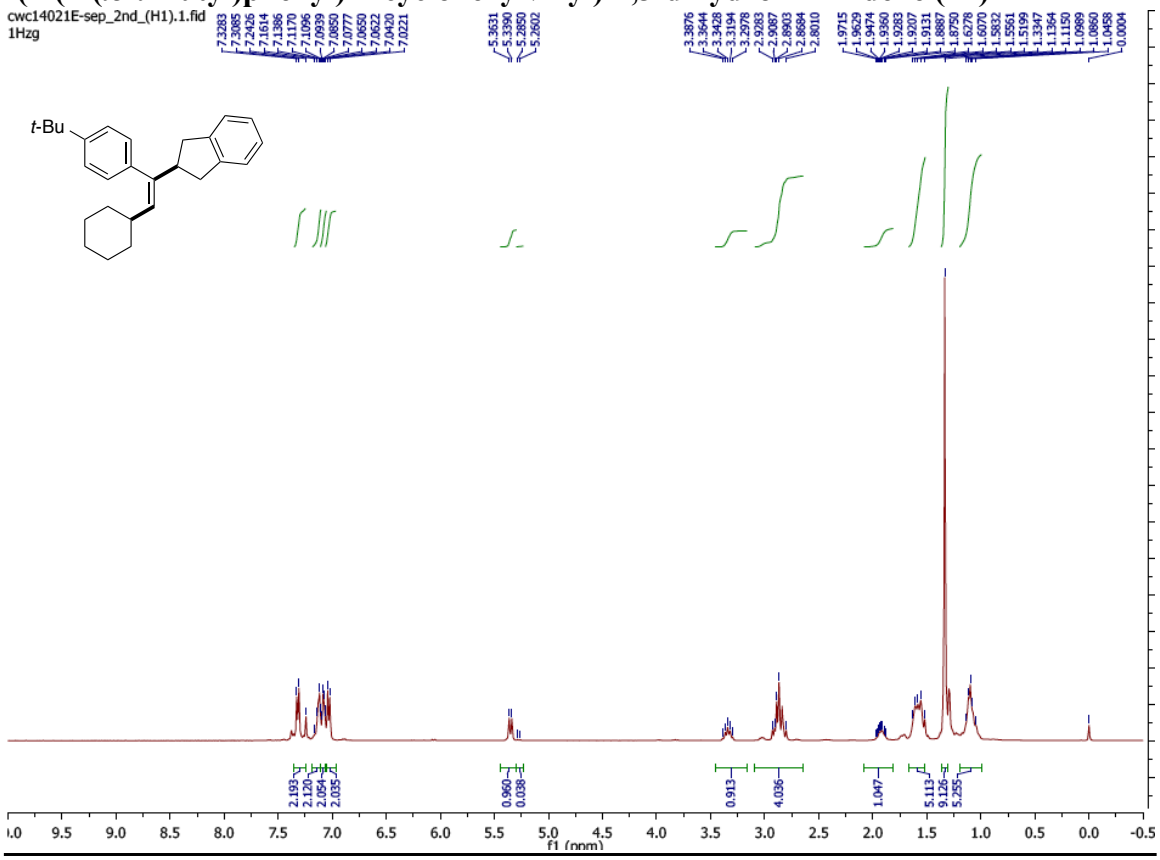


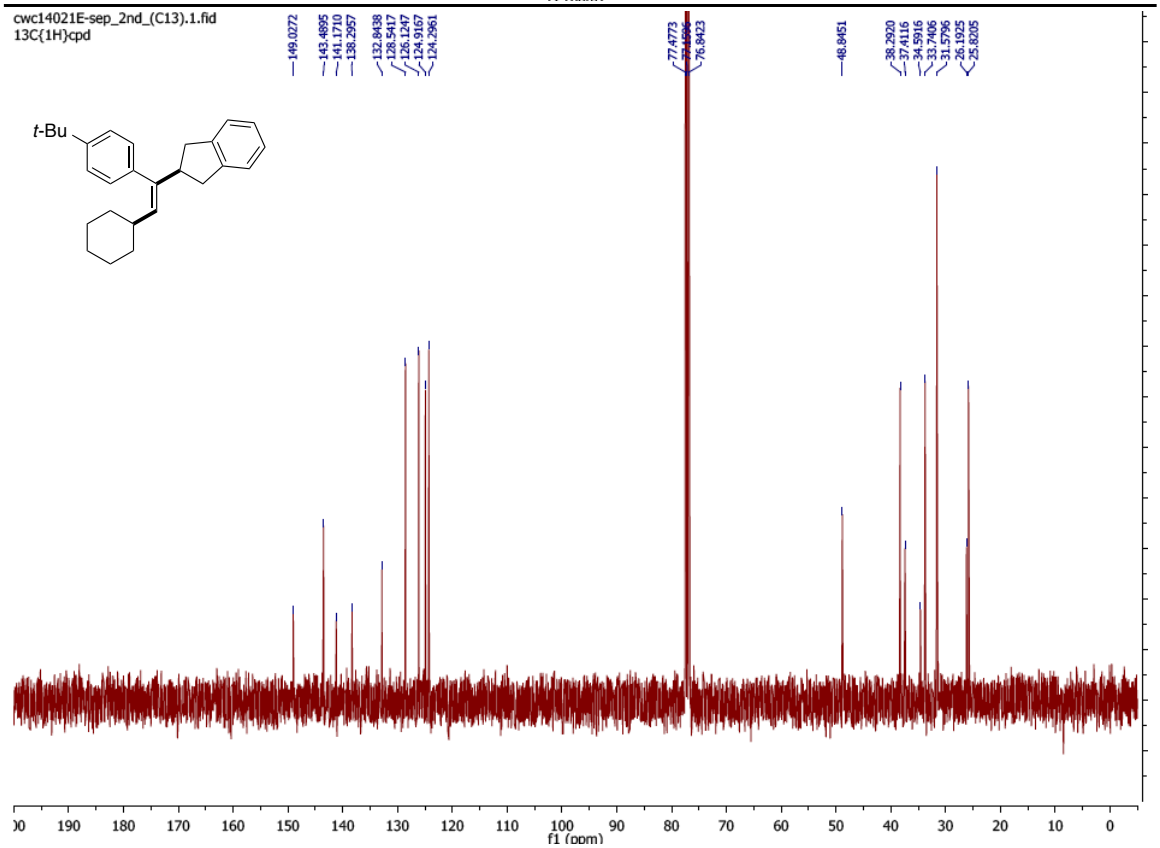
(*Z*)-1-(*tert*-Butyl)-4-(1-cyclohexyl-4-(4-methoxyphenyl)-3-methylbut-1-en-2-yl)benzene (4g)



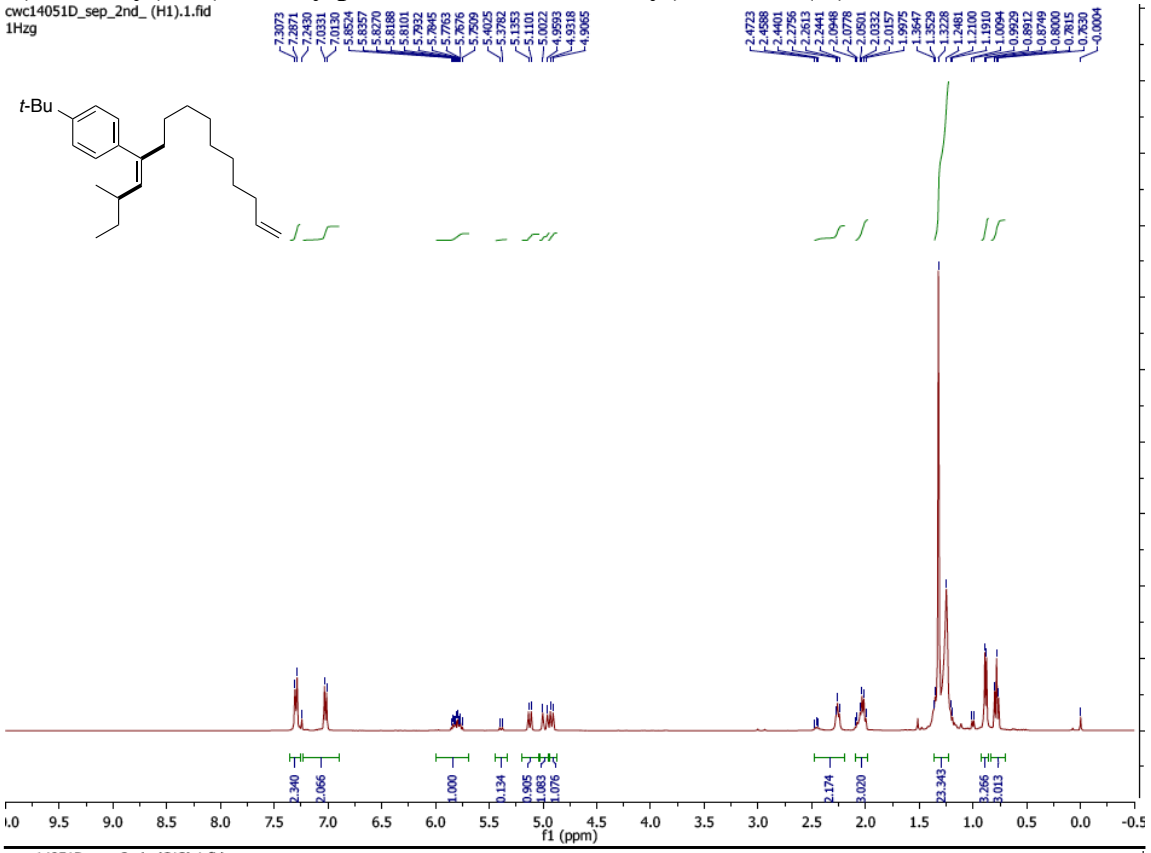


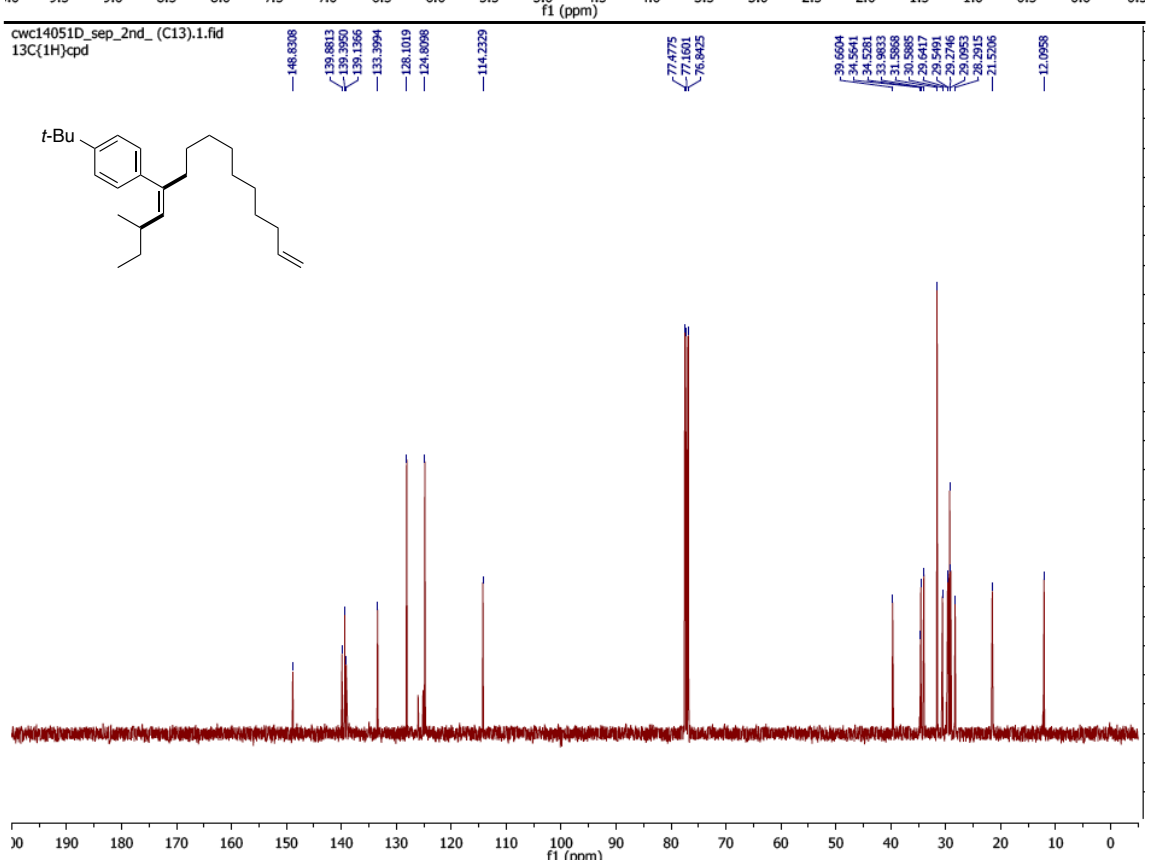
(*Z*)-2-(1-(4-(*tert*-Butyl)phenyl)-2-cyclohexylvinyl)-2,3-dihydro-1*H*-indene (4h)



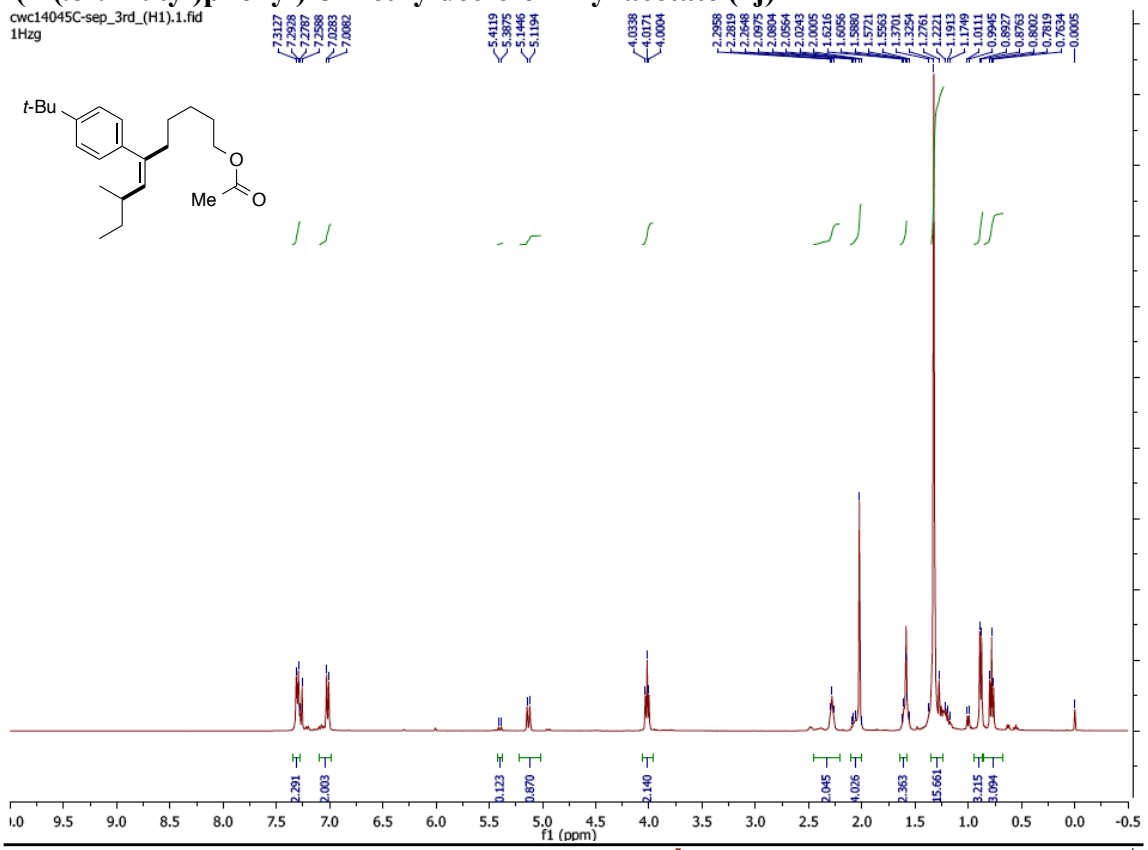


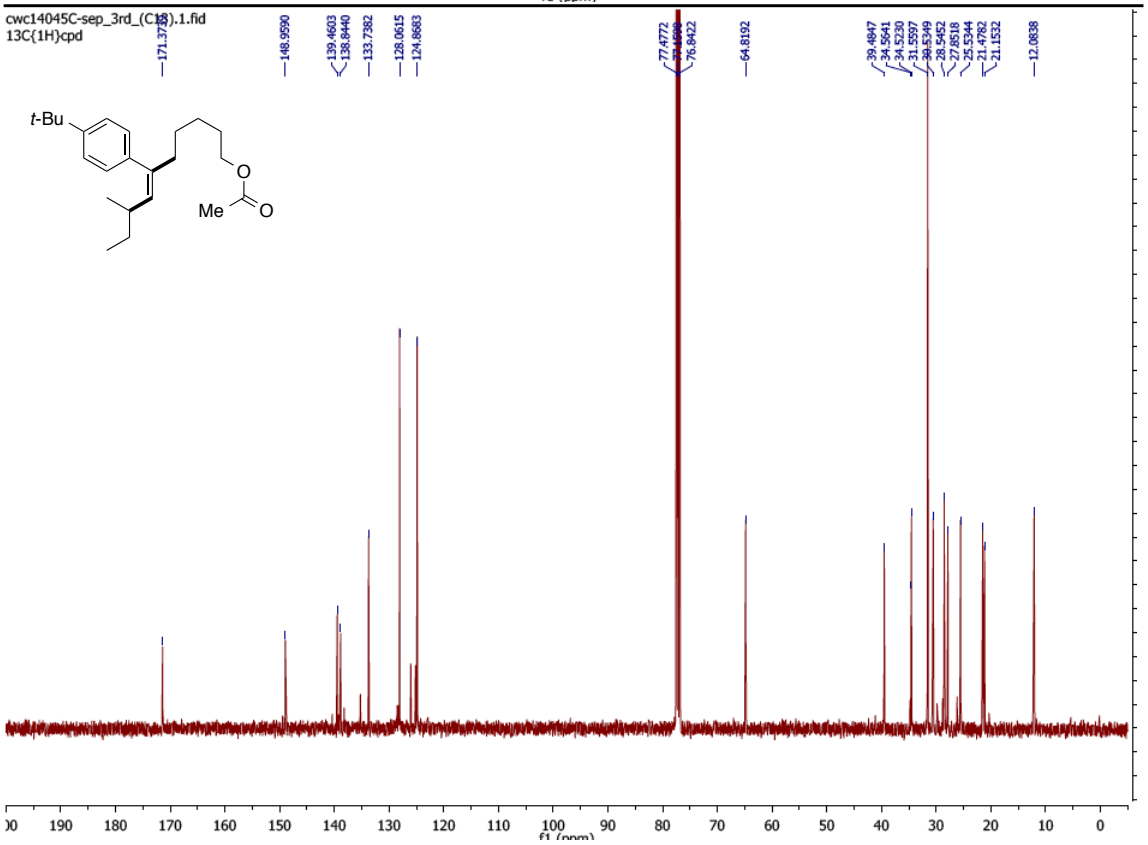
(*Z*)-1-(*tert*-Butyl)-4-(3-methylpentadeca-4,14-dien-5-yl)benzene (4i)



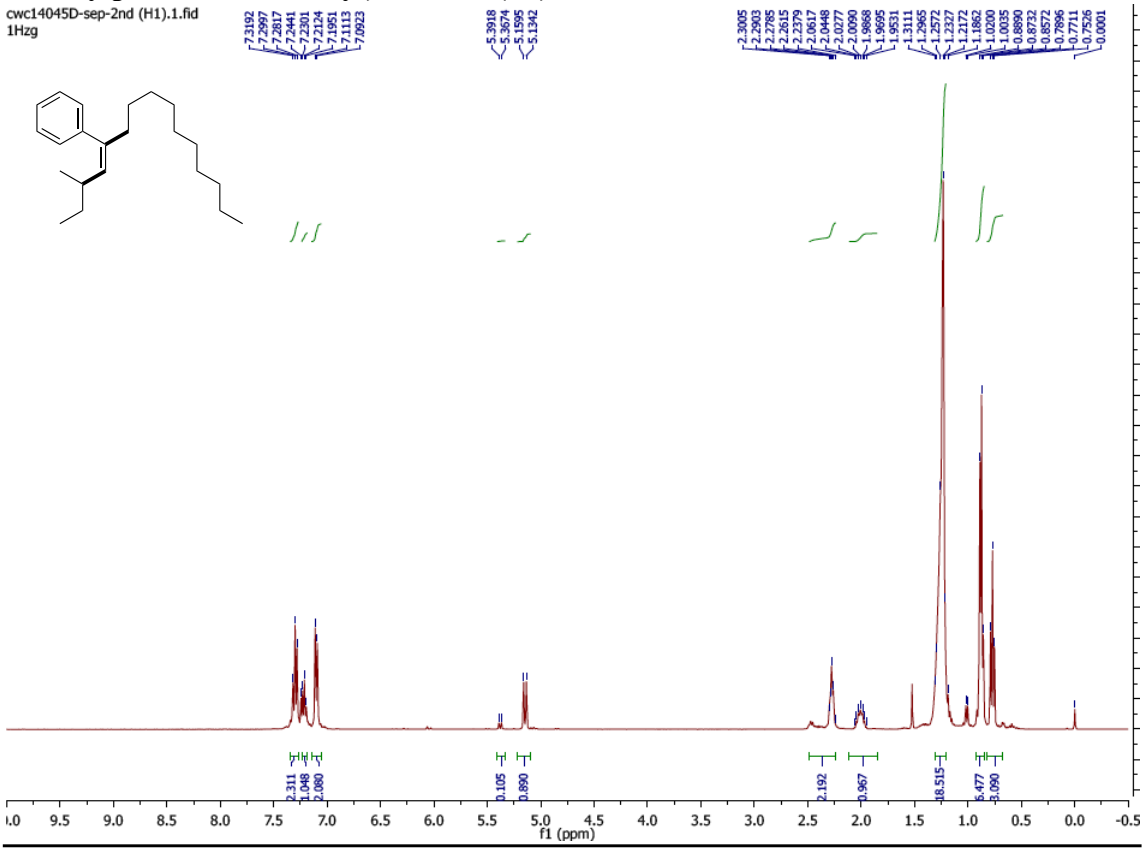


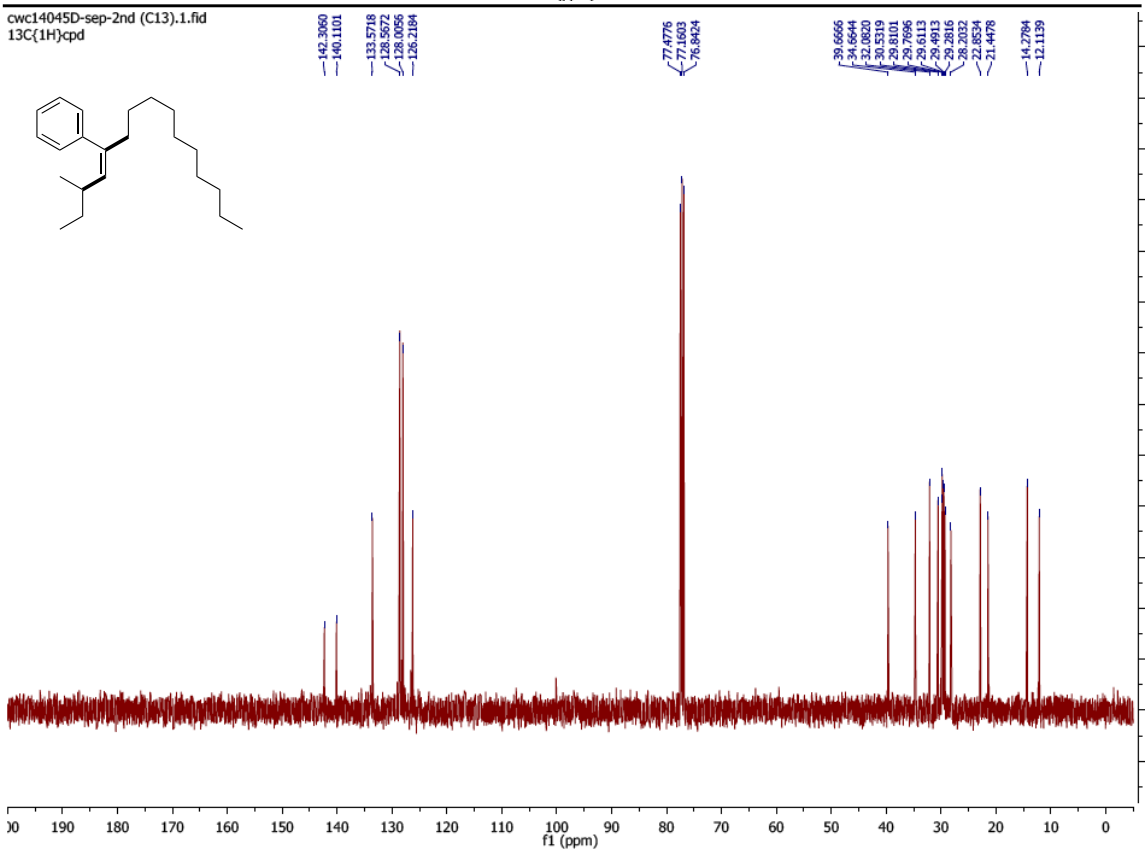
(*Z*)-6-(4-(*tert*-Butyl)phenyl)-8-methyldec-6-en-1-yl acetate (4j)



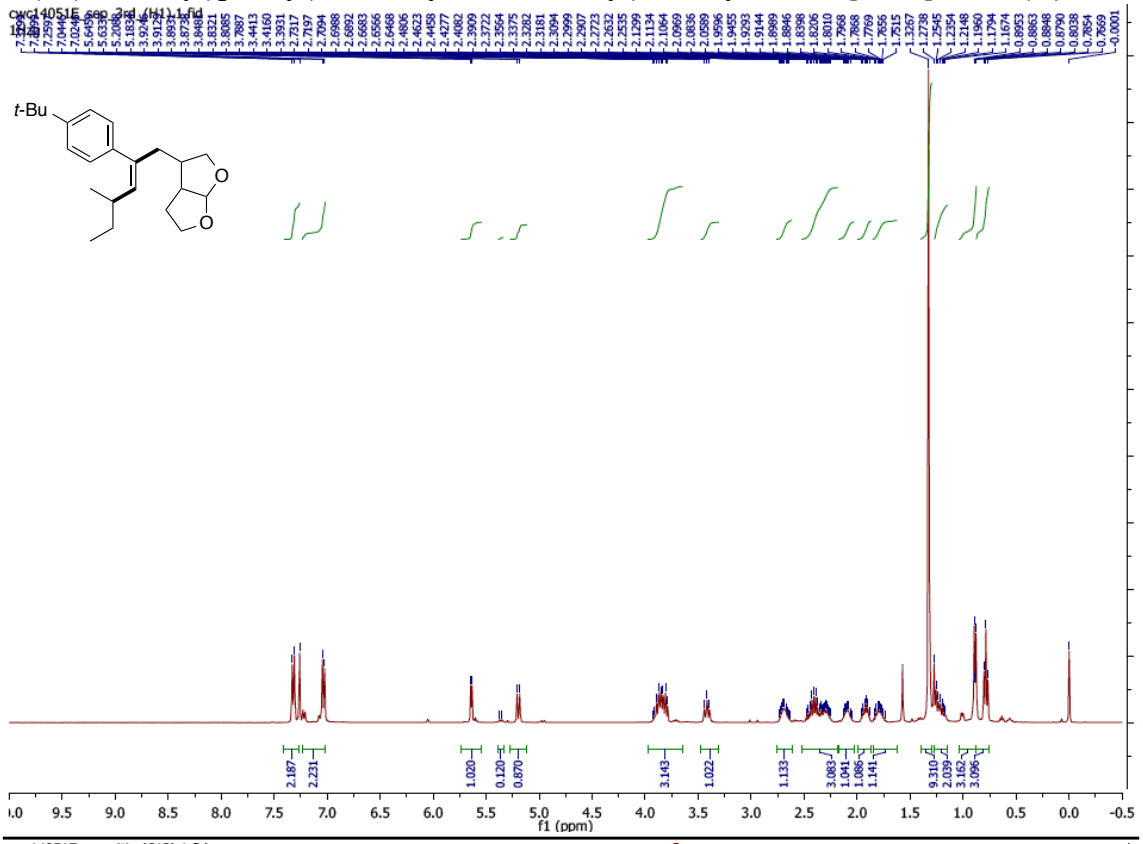


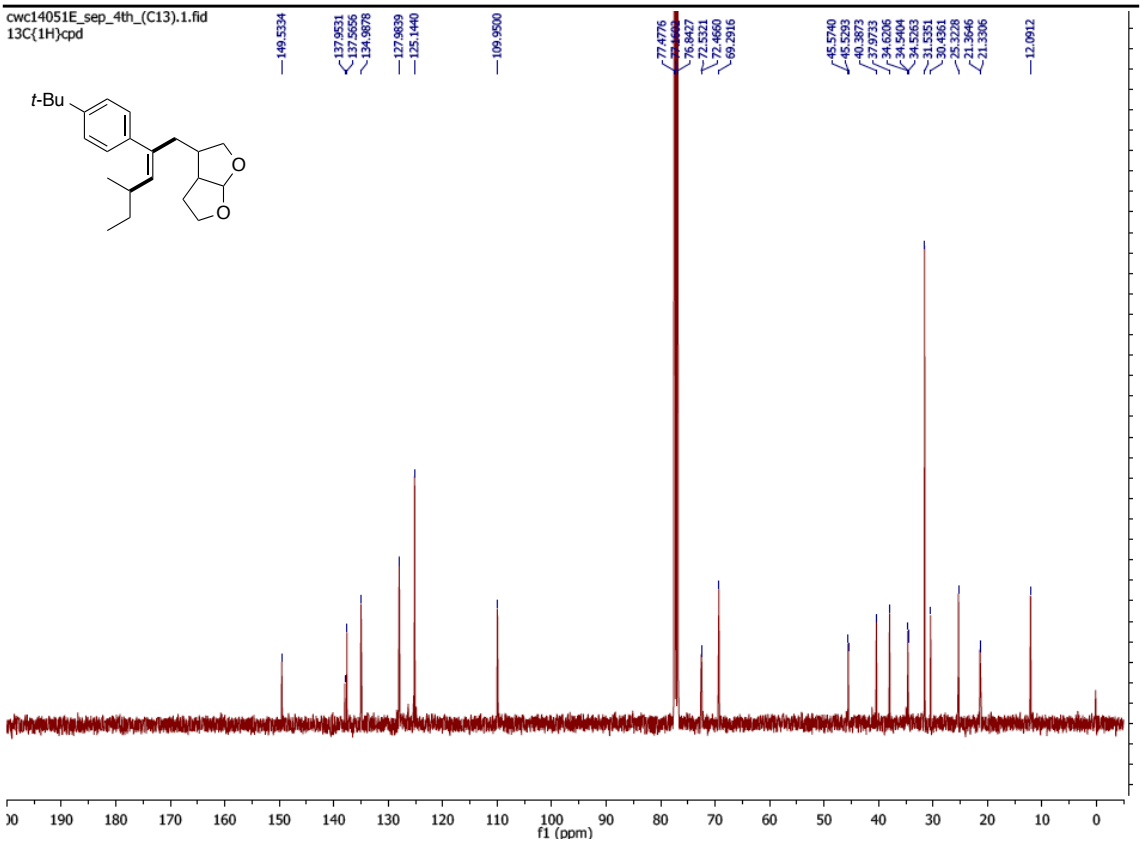
(*Z*)-(3-Methylpentadec-4-en-5-yl)benzene (4k)



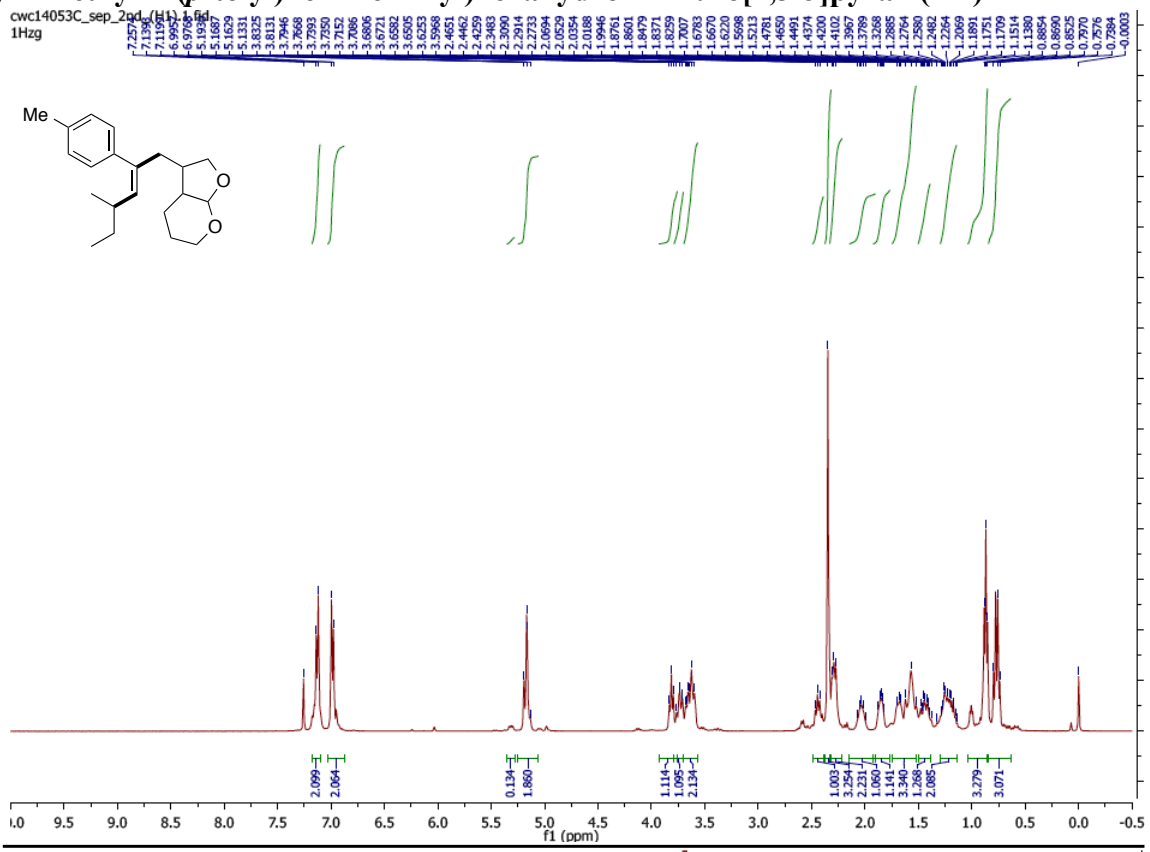


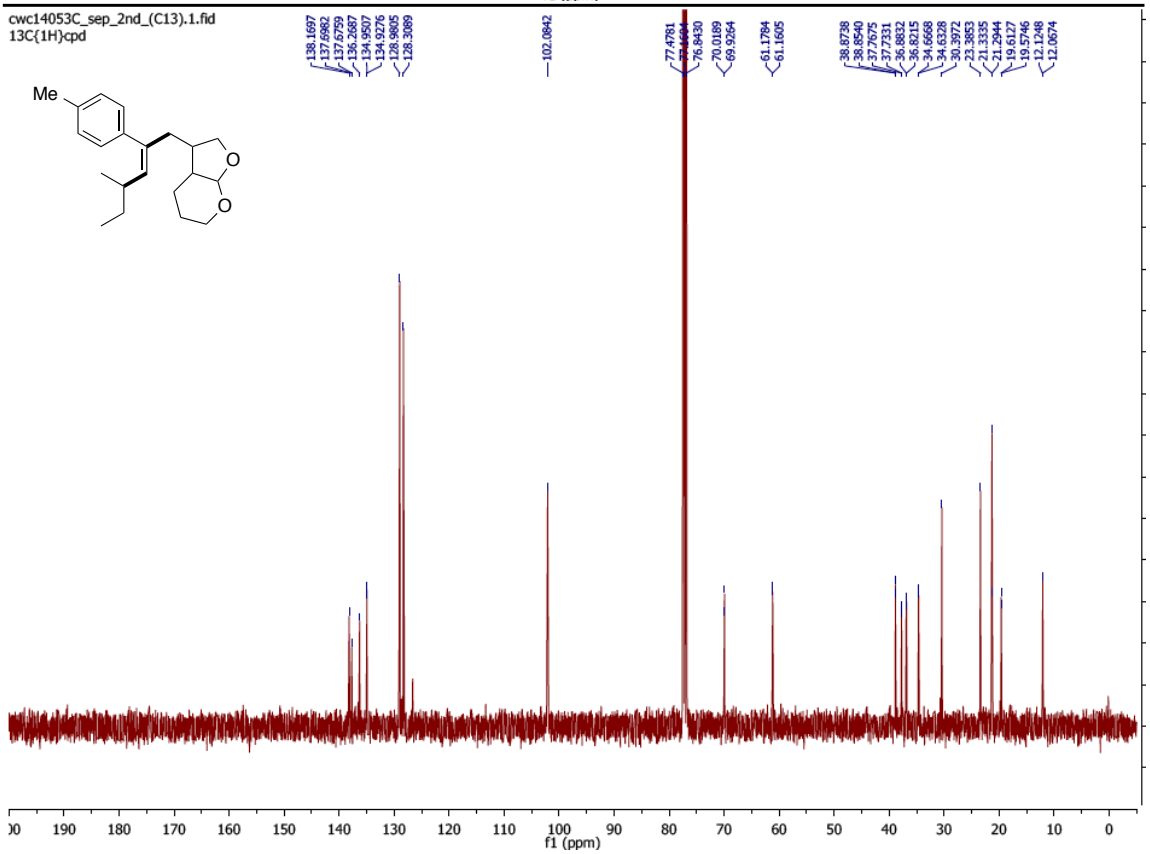
3-((*Z*)-2-(4-(*tert*-Butyl)phenyl)-4-methylhex-2-en-1-yl)hexahydrofuro[2,3-*b*]furan (4l)



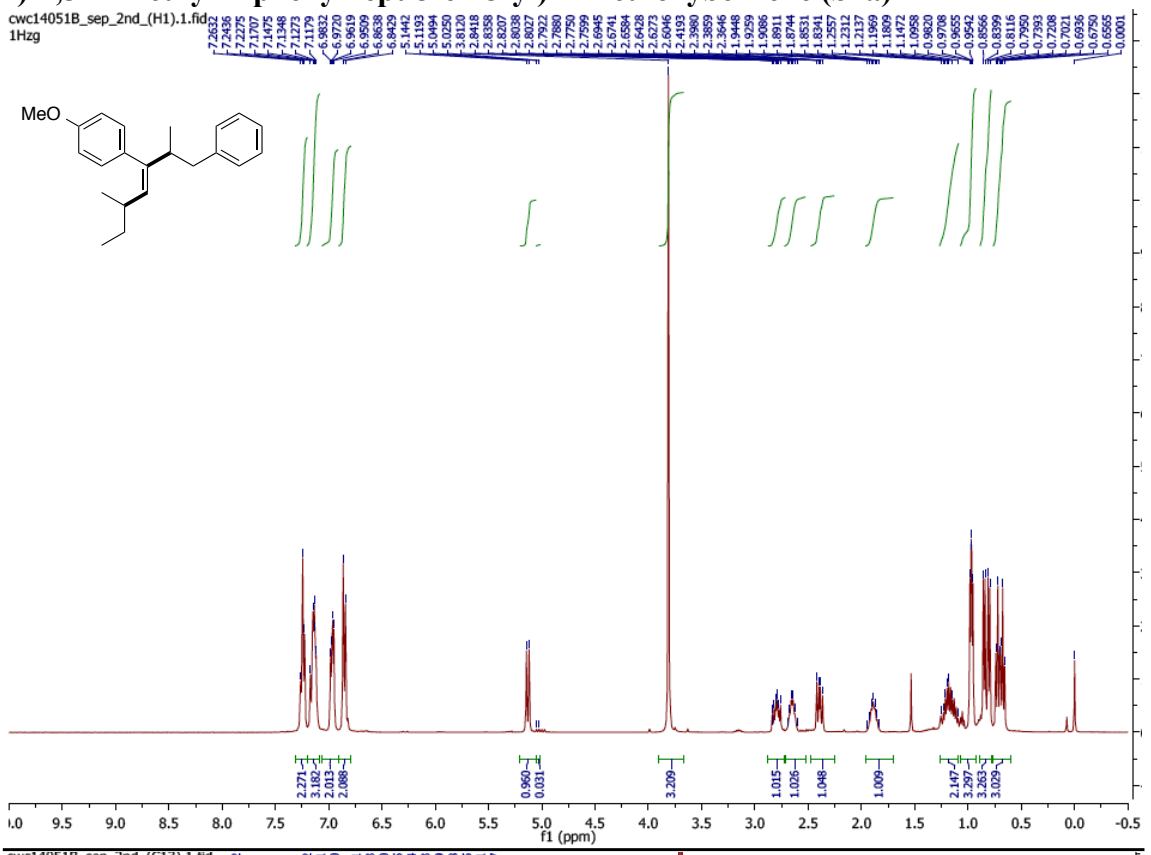


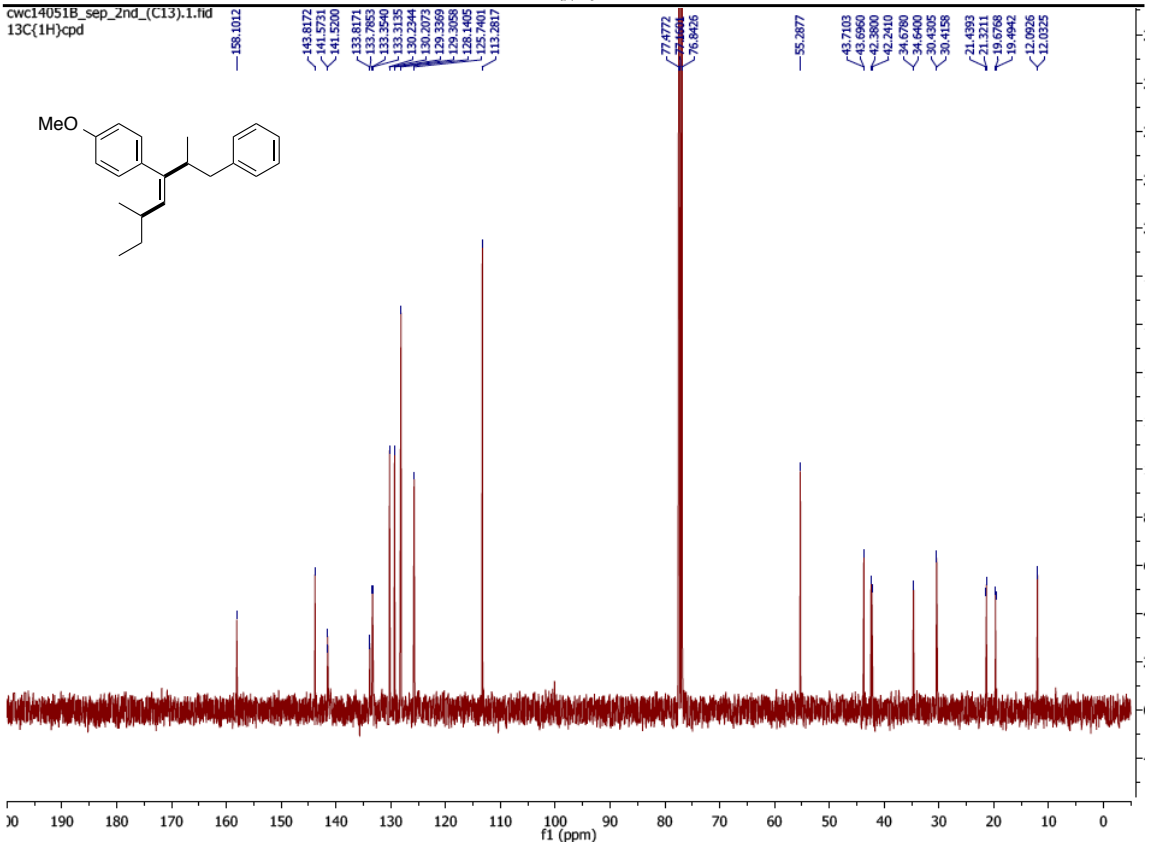
3-((*Z*)-4-Methyl-2-(*p*-tolyl)hex-2-en-1-yl)hexahydro-4*H*-furo[2,3-*b*]pyran (4m)



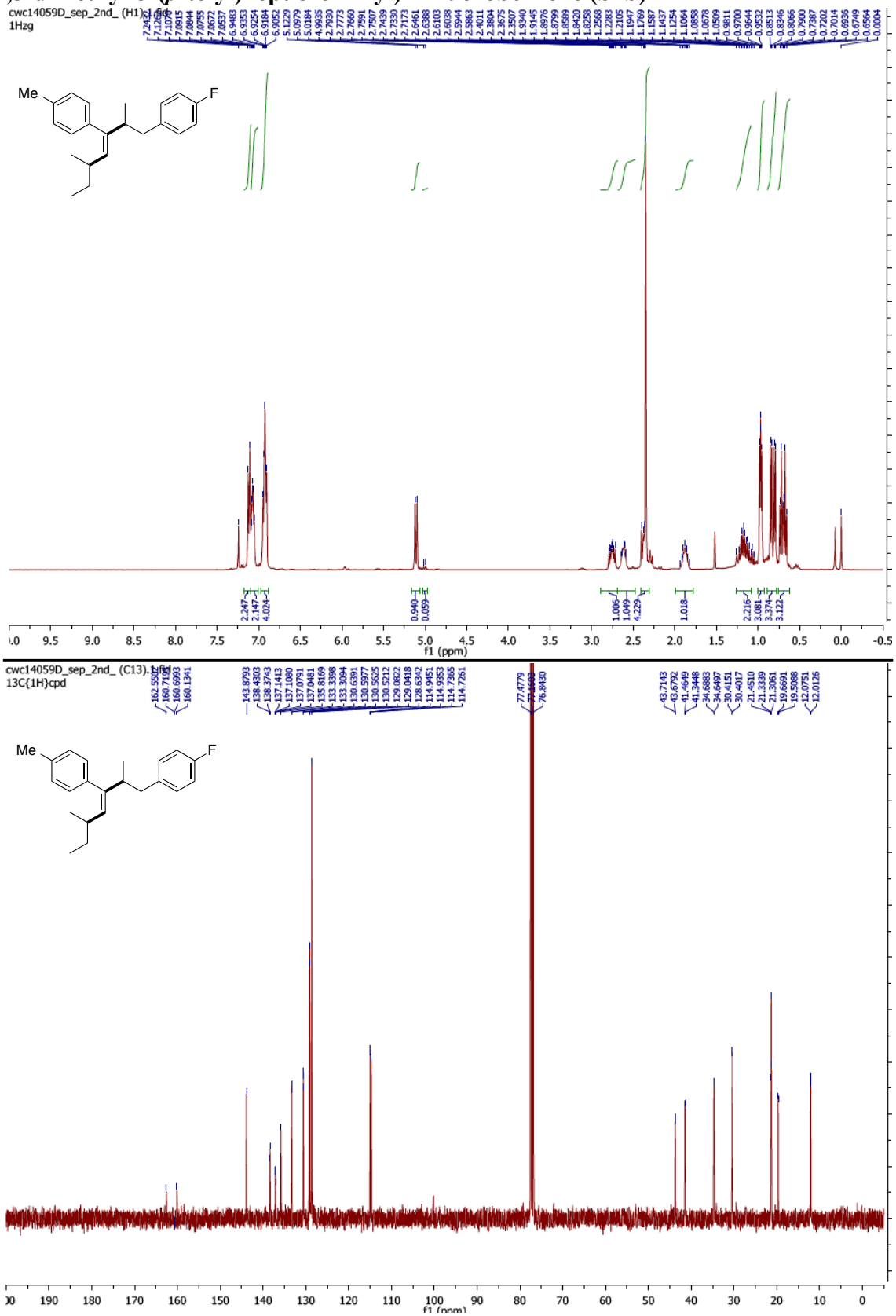


1-((*Z*)-2,5-Dimethyl-1-phenylhept-3-en-3-yl)-4-methoxybenzene (S4a)

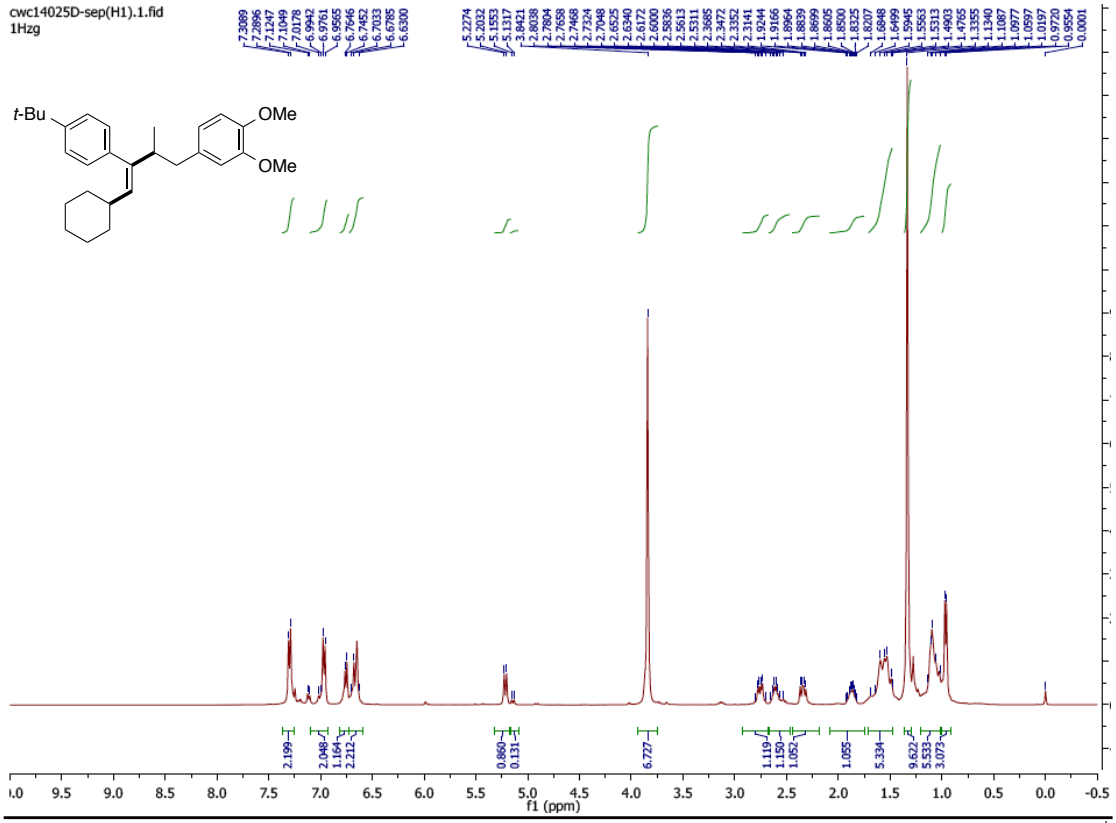


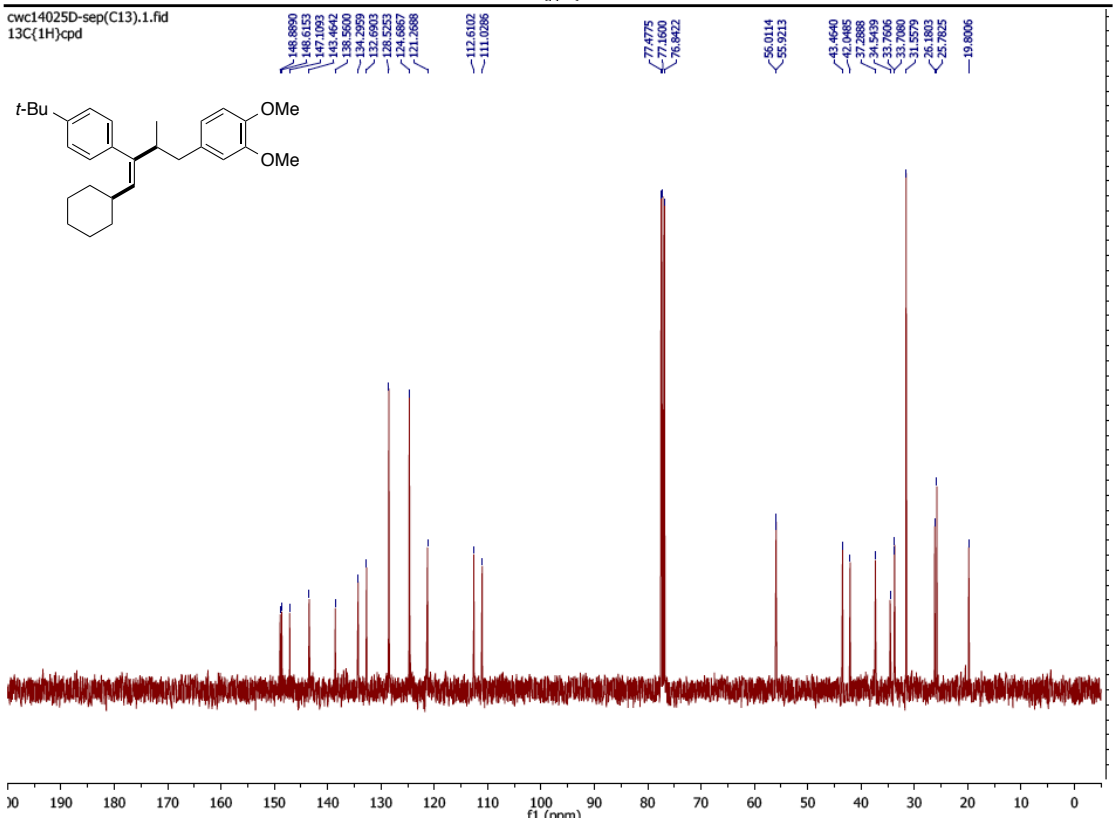


1-((*Z*)-2,5-dimethyl-3-(*p*-tolyl)hept-3-en-1-yl)-4-fluorobenzene (S4b)

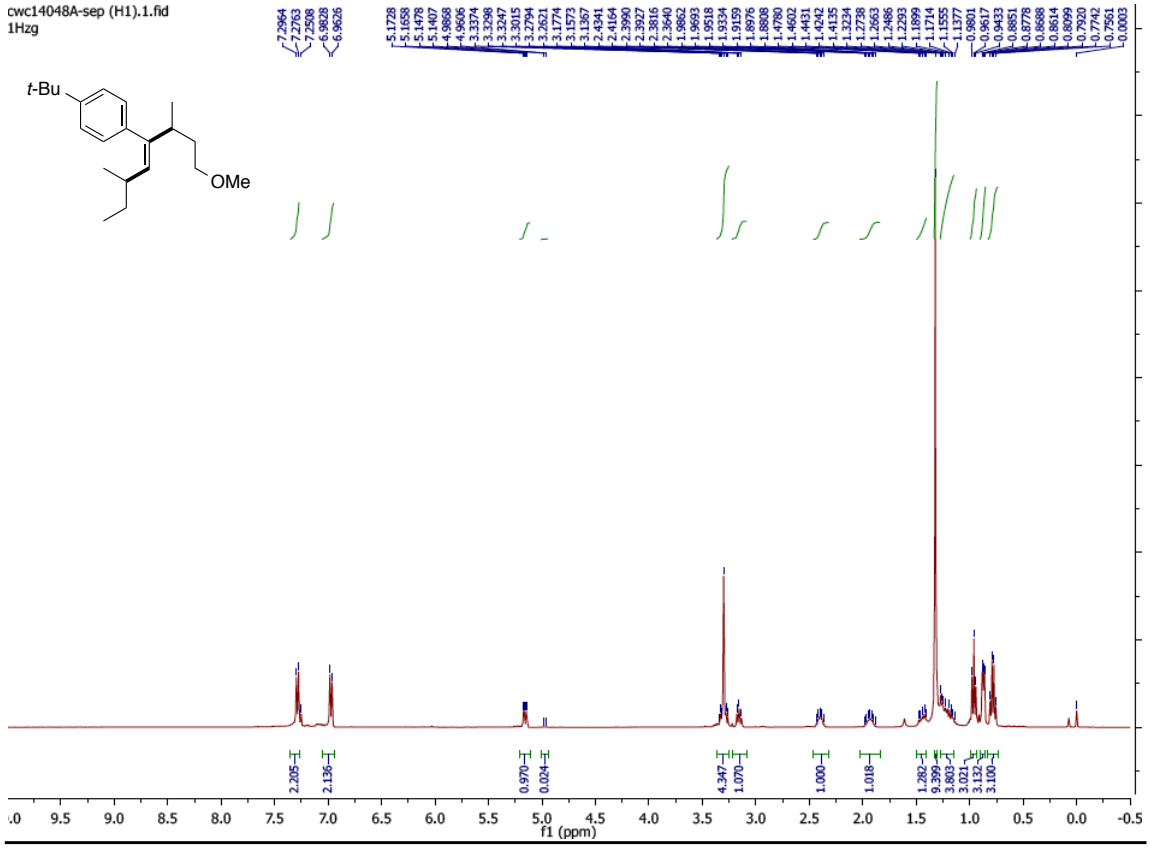


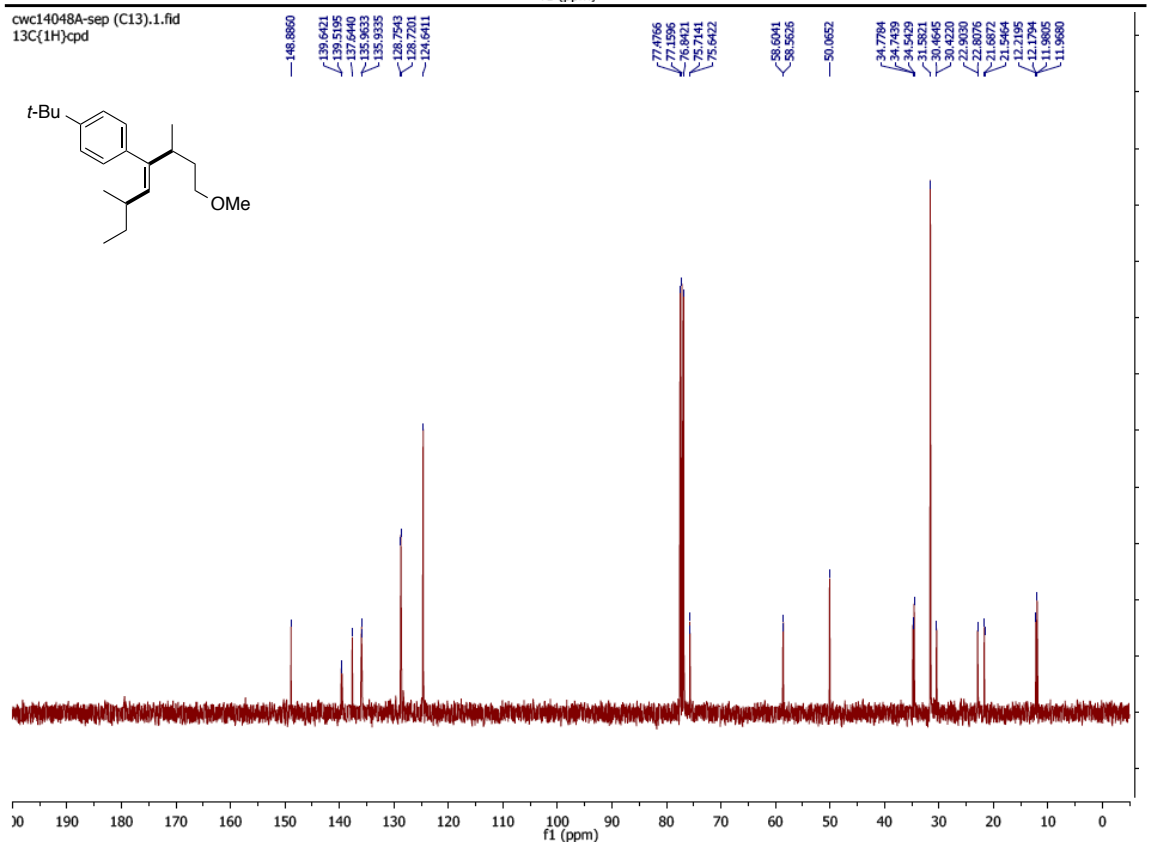
(*Z*)-4-(3-(4-(*tert*-butyl)phenyl)-4-cyclohexyl-2-methylbut-3-en-1-yl)-1,2-dimethoxybenzene (S4c)



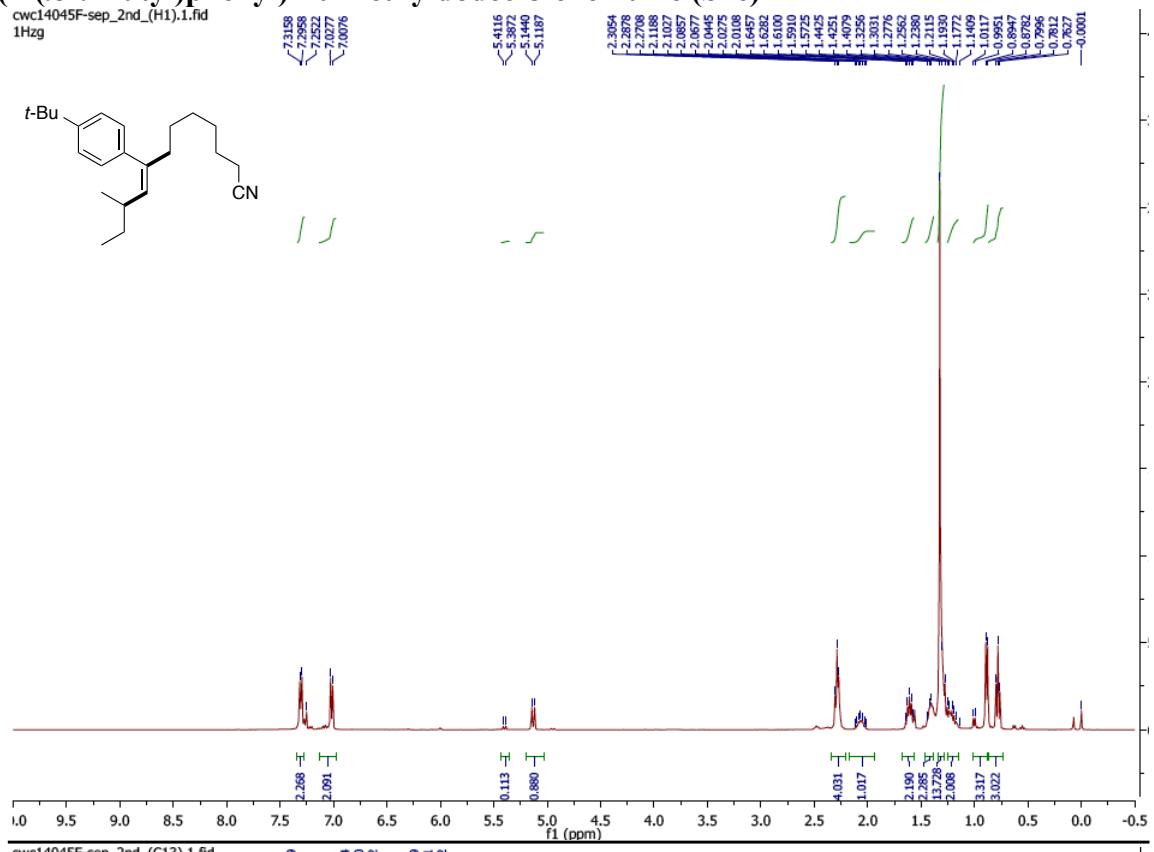


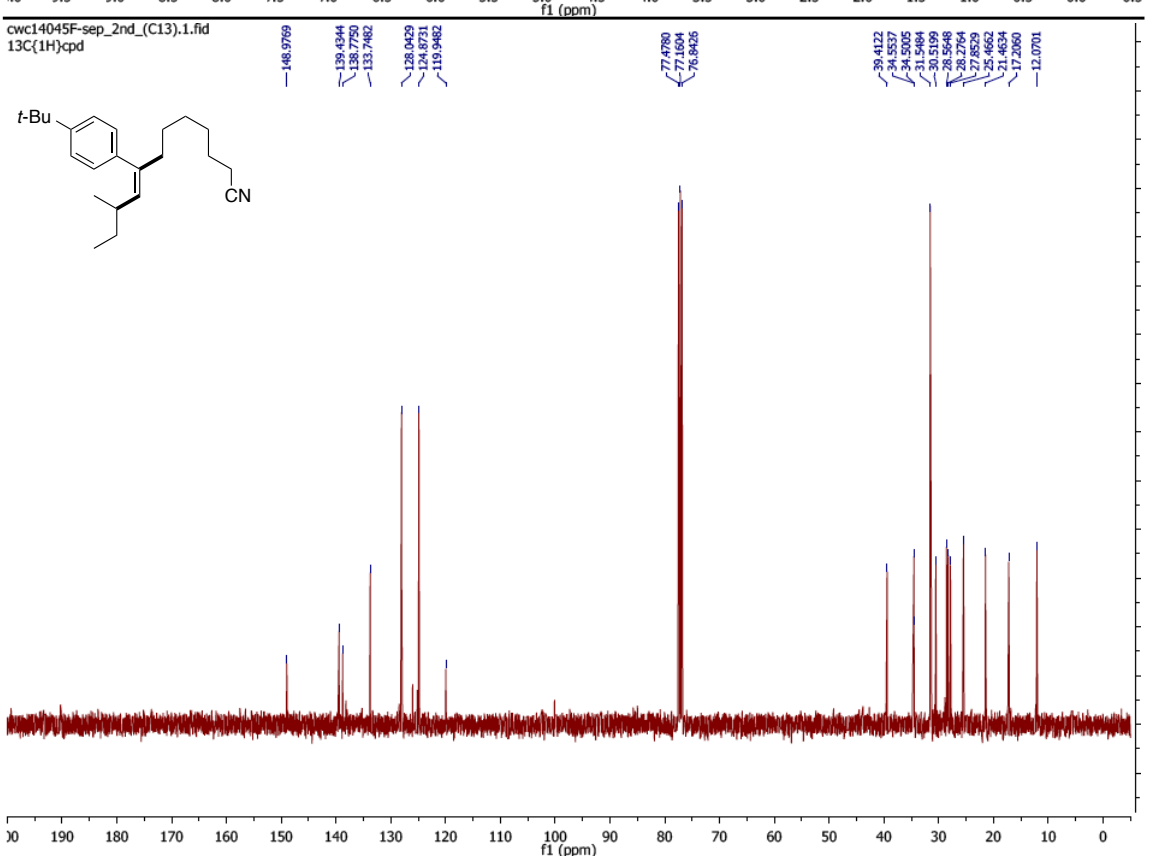
1-(*tert*-Butyl)-4-((*Z*)-1-methoxy-3,6-dimethyloct-4-en-4-yl)benzene (S4d)





(*Z*)-8-(4-(*tert*-Butyl)phenyl)-10-methyldodec-8-enenitrile (S4e)





(*Z*)-7-(4-(*tert*-Butyl)phenyl)-9-methylundec-7-en-1-yl thiophene-2-carboxylate (S4f)