

# Supporting Information

## Enantioselective reductive allylic alkylation enabled by dual photoredox/palladium catalysis

Sheng Tang,<sup>a</sup> Hong-Hao Zhang,<sup>\*ab</sup> Shouyun Yu<sup>\*a</sup>

<sup>a</sup> State Key Laboratory of Analytical Chemistry for Life Science, Jiangsu Key Laboratory of Advanced Organic Materials, Chemistry and Biomedicine Innovation Centre (ChemBIC), School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China.

E-mail: yushouyun@nju.edu.cn

<sup>b</sup> School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China.

E-mail: zhanghonghao@cczu.edu.cn

### Table of Contents

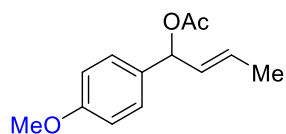
1. General information.....	S2
2. Numberings and structures of all compounds.....	S3
3. General procedure for the synthesis of racemic products <b>3</b> .....	S7
4. General procedure for asymmetric allylic alkylation.....	S8
5. Gram-scale preparation of <b>3a</b> .....	S10
6. Optimization of the conditions for <b>3a</b> .....	S11
7. Proof of stereochemistry.....	S15
8. Mechanism Study.....	S18
9. Product characterization.....	S21
10. Attempt of other alkyl bromides.....	S38
11. References.....	S39
12. NMR spectra for all compounds.....	S40
13. HPLC spectra.....	S72

## 1. General information

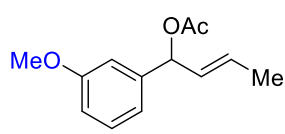
Commercial reagents were purchased from Aldrich Chemical, Alfa Aesar, TCI, Strem, Acros, Energy Chemical, J&K Chemical, Innochem and were used as received. All catalytic reactions were run in dried glassware. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate, respectively. Column chromatography was performed on EMD Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar.  $^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}$  NMR (100 MHz) and  $^{19}\text{F}$  (376 MHz) were measured on a Bruker AVANCE III–400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC-MS spectra were performed on Agilent 5977A Series (EI Source). High Resolution Mass spectra were performed on Agilent 1260 Series (ESI Source). High-pressure liquid chromatography (HPLC) was performed on Agilent 1260 Series chromatographs using chiral columns as noted for each compound. Optical rotations were measured on an automatic polarimeter with  $[\alpha]_{\text{D}}^{20}$  values reported in degrees; concentration (c) is in g/100 mL.

The allylic acetates (**1**)<sup>1</sup> and alkyl bromides (**2**)<sup>2</sup> and chiral allylic acetate (*S*)-**10**'<sup>3</sup> were prepared according to the literature procedure.

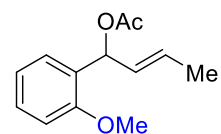
## 2. Numberings and structures of all compounds



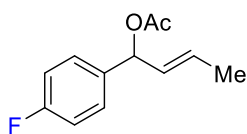
1a



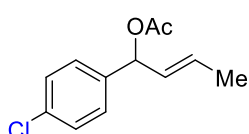
1b



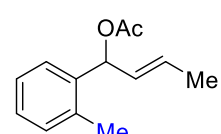
1c



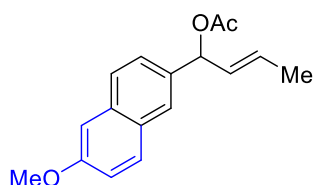
1d



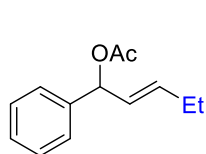
1e



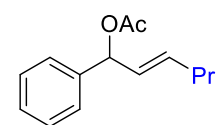
1f



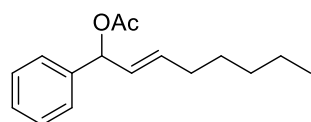
1g



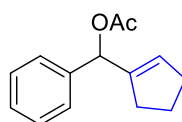
1h



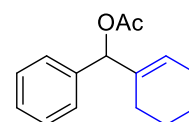
1i



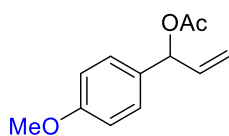
1j



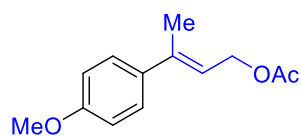
1k



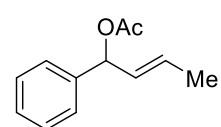
1l



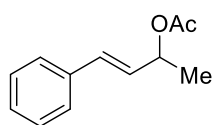
1m



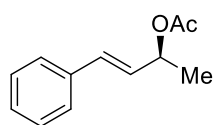
1n



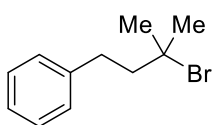
1o



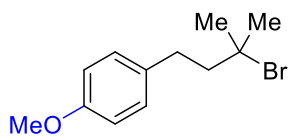
1o'



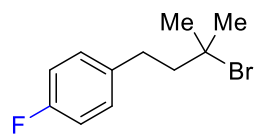
(S)-1o'



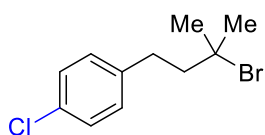
2a



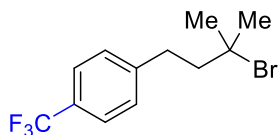
2b



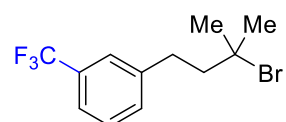
2c



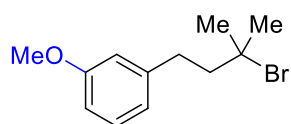
2d



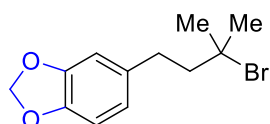
2e



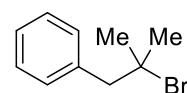
2f



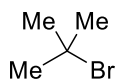
2g



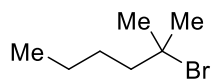
2h



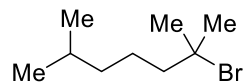
2i



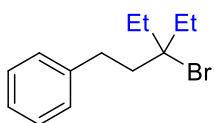
2j



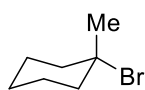
2k



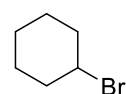
2l



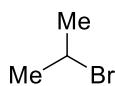
2m



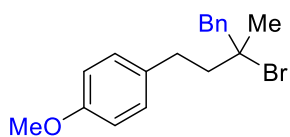
2n



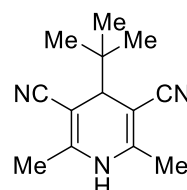
2o



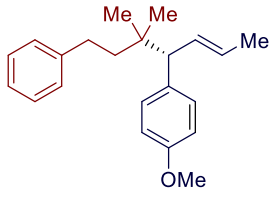
2p



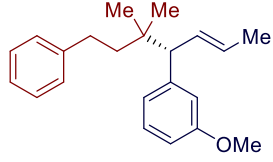
2q



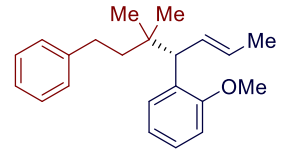
6



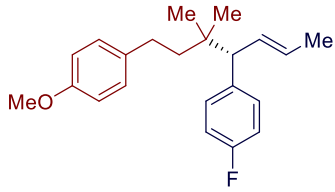
3a



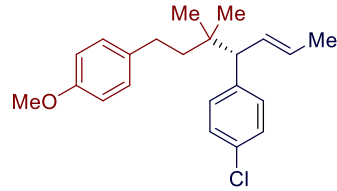
3b



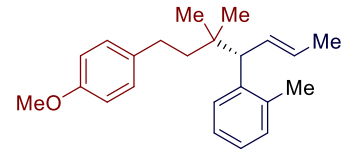
3c



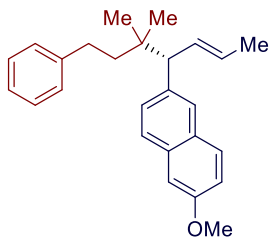
3d



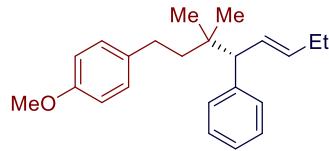
3e



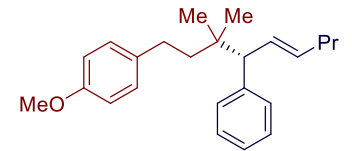
3f



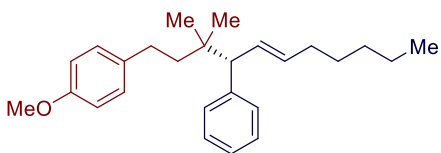
3g



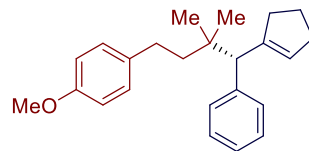
3h



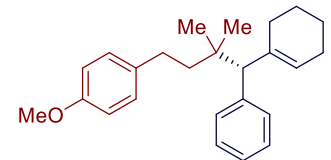
3i



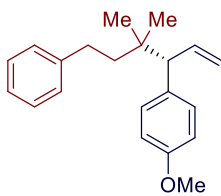
3j



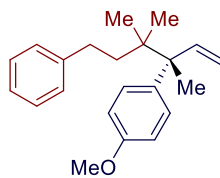
3k



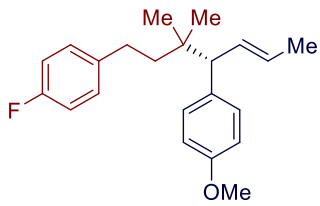
3l



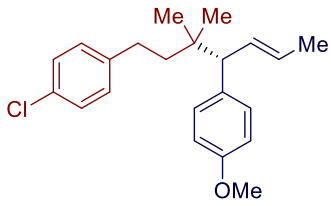
3m



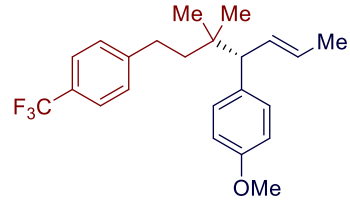
3n



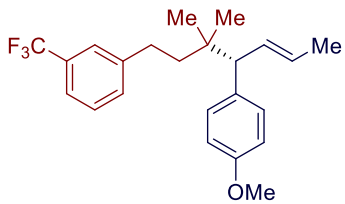
**3o**



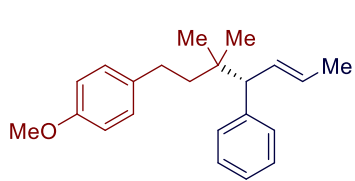
**3p**



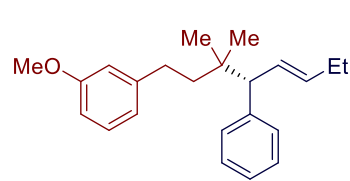
**3q**



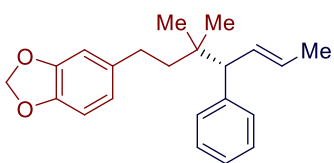
**3r**



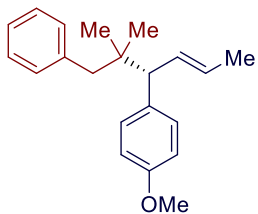
**3s**



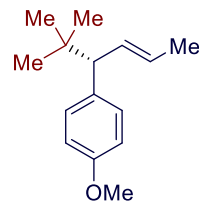
**3t**



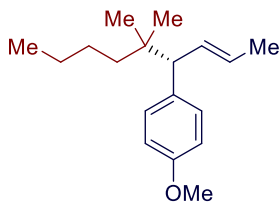
**3u**



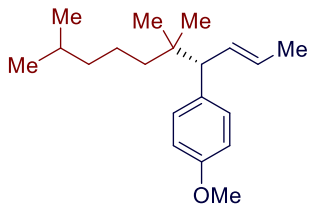
**3v**



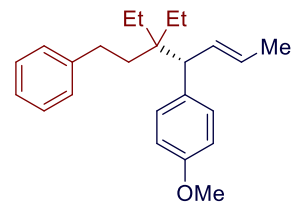
**3w**



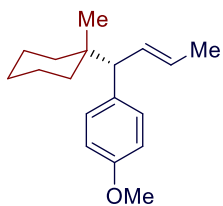
**3x**



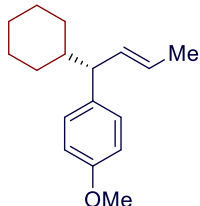
**3y**



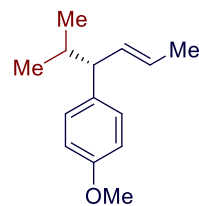
**3z**



**3aa**

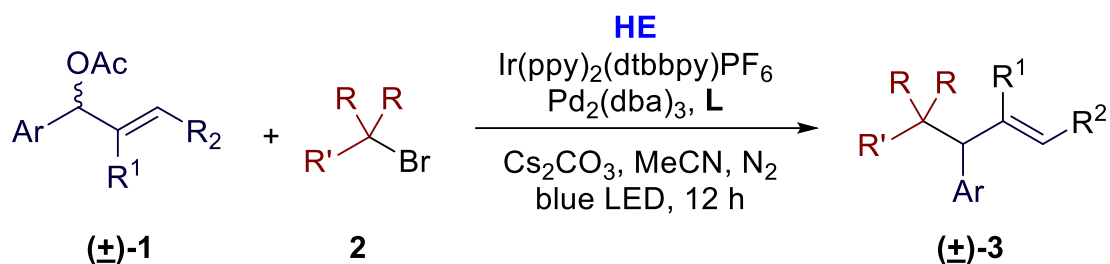


**3ab**



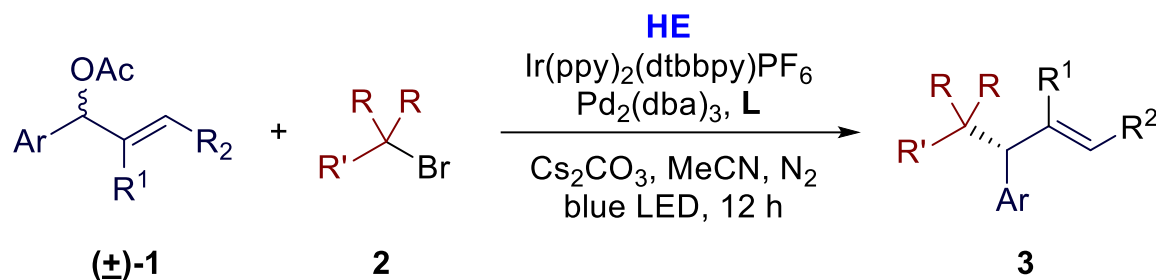
**3ac**

### 3. General procedure for the synthesis of racemic products 3



**General Procedure A:** In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with Pd<sub>2</sub>(dba)<sub>3</sub> (2.3 mg, 0.0025 mmol, 2.5 mol%), racemic-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (3.7 mg, 0.006 mmol, 6 mol%), anhydrous MeCN (2.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.0 mg, 0.002 mmol, 2.0 mol%), Cs<sub>2</sub>CO<sub>3</sub> (65.2 mg, 0.2 mmol, 2.0 equiv), HE (50.7 mg, 0.2 mmol, 2.0 equiv), allylic acetates **1** (0.1 mmol, 1.0 equiv), alkyl bromides **2** (0.3 mmol, 3.0 equiv) and anhydrous MeCN (2.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

#### 4. General procedure for asymmetric allylic alkylation



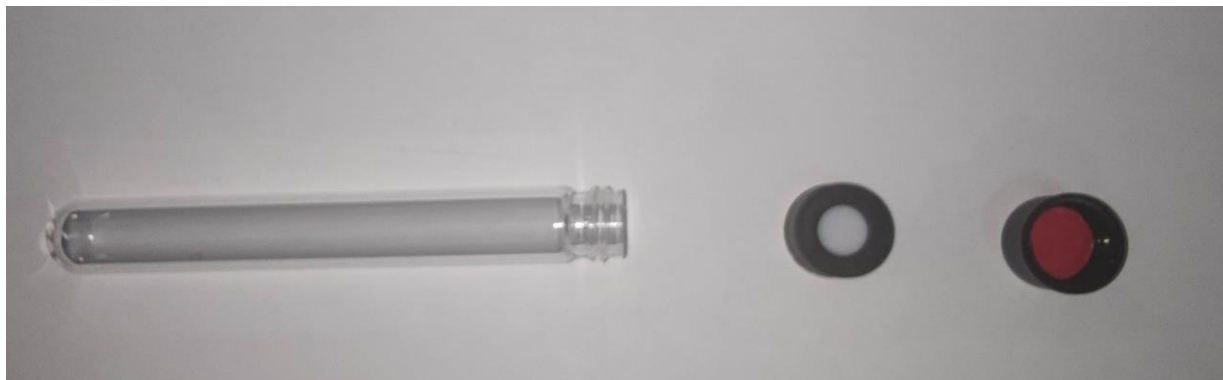
**General Procedure B (in-glovebox):** In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with Pd<sub>2</sub>(dba)<sub>3</sub> (2.3 mg, 0.0025 mmol, 2.5 mol%), (*R*)-2,2'-bis((3,5-di-*tert*-butyl-4-methoxyphenyl)-λ<sup>2</sup>-phosphaneyl)-1,1'-binaphthalene (**L1**) (7.4 mg, 0.006 mmol, 6 mol%), anhydrous MeCN (2.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.0 mg, 0.002 mmol, 2.0 mol%), Cs<sub>2</sub>CO<sub>3</sub> (65.2 mg, 0.2 mmol, 2.0 equiv), HE (50.7 mg, 0.2 mmol, 2.0 equiv), allylic acetates **1** (0.1 mmol, 1.0 equiv), alkyl bromides **2** (0.3 mmol, 3.0 equiv) and anhydrous MeCN (2.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

**General Procedure B':** In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with Pd<sub>2</sub>(dba)<sub>3</sub> (2.3 mg, 0.0025 mmol, 2.5 mol%), (*R*)-2,2'-bis((3,5-di-*tert*-butyl-4-methoxyphenyl)-λ<sup>2</sup>-phosphaneyl)-1,1'-binaphthalene (**L1**) (7.4 mg, 0.006 mmol, 6 mol%), anhydrous MeCN (2.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.0 mg, 0.002 mmol, 2.0 mol%), Cs<sub>2</sub>CO<sub>3</sub> (65.2 mg, 0.2 mmol, 2.0 equiv), HE (50.7 mg, 0.2 mmol, 2.0 equiv), allylic acetates **1** (0.1 mmol, 1.0 equiv), alkyl bromides **2** (0.3 mmol, 3.0 equiv) and anhydrous MeCN (2.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at 0 °C for 12h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

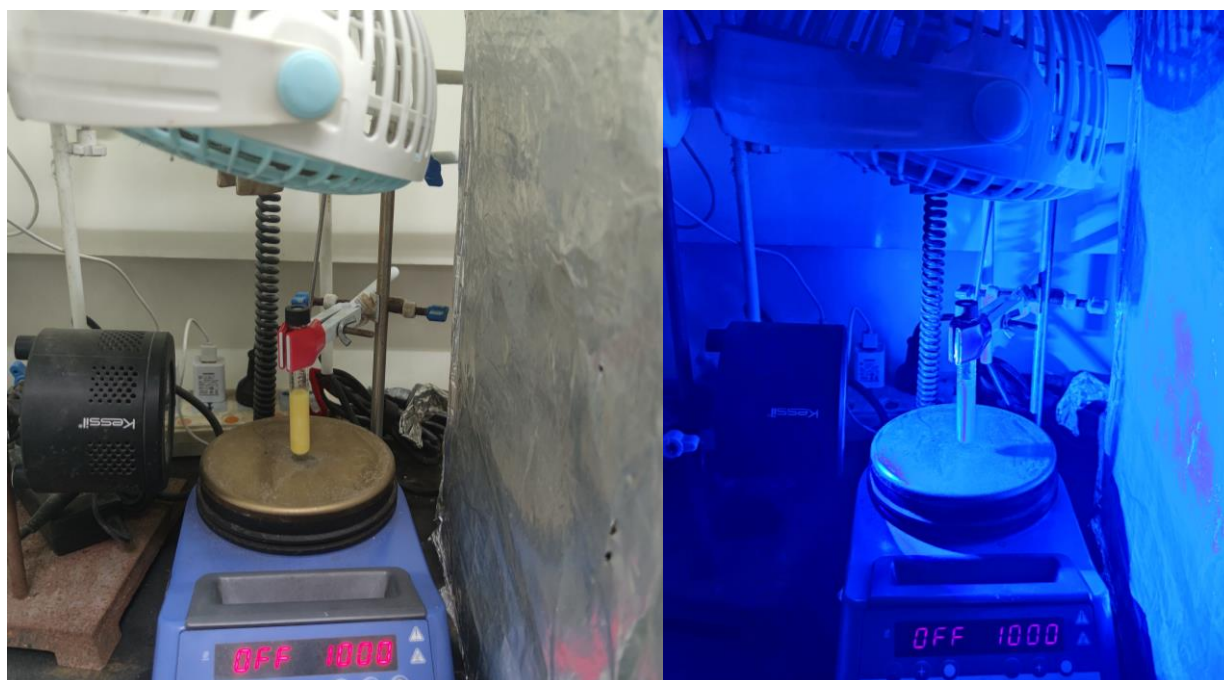
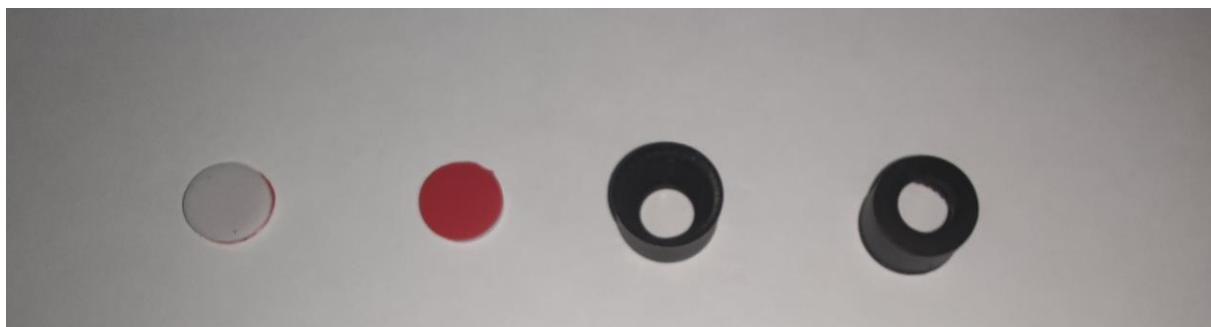


## Reaction Setup

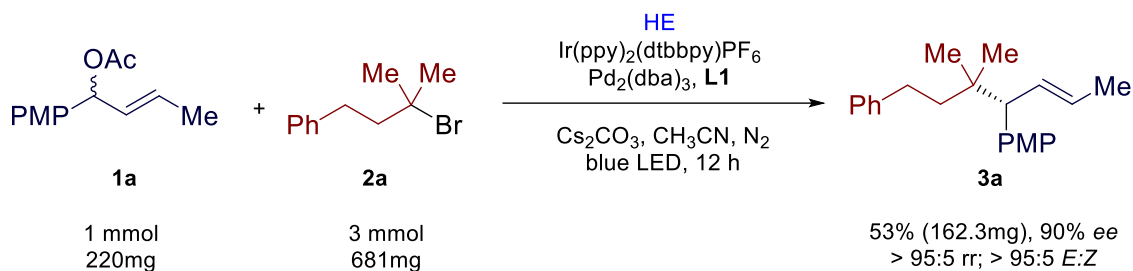
Medium-sized screw-cap test tubes (8 mL) were used for all 0.1 mmol scale reactions: Fisher 13 x 100 mm tubes (Cat. No. 14-959-35C)



Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No. 03378316)



## 5. Gram-scale preparation of 3a

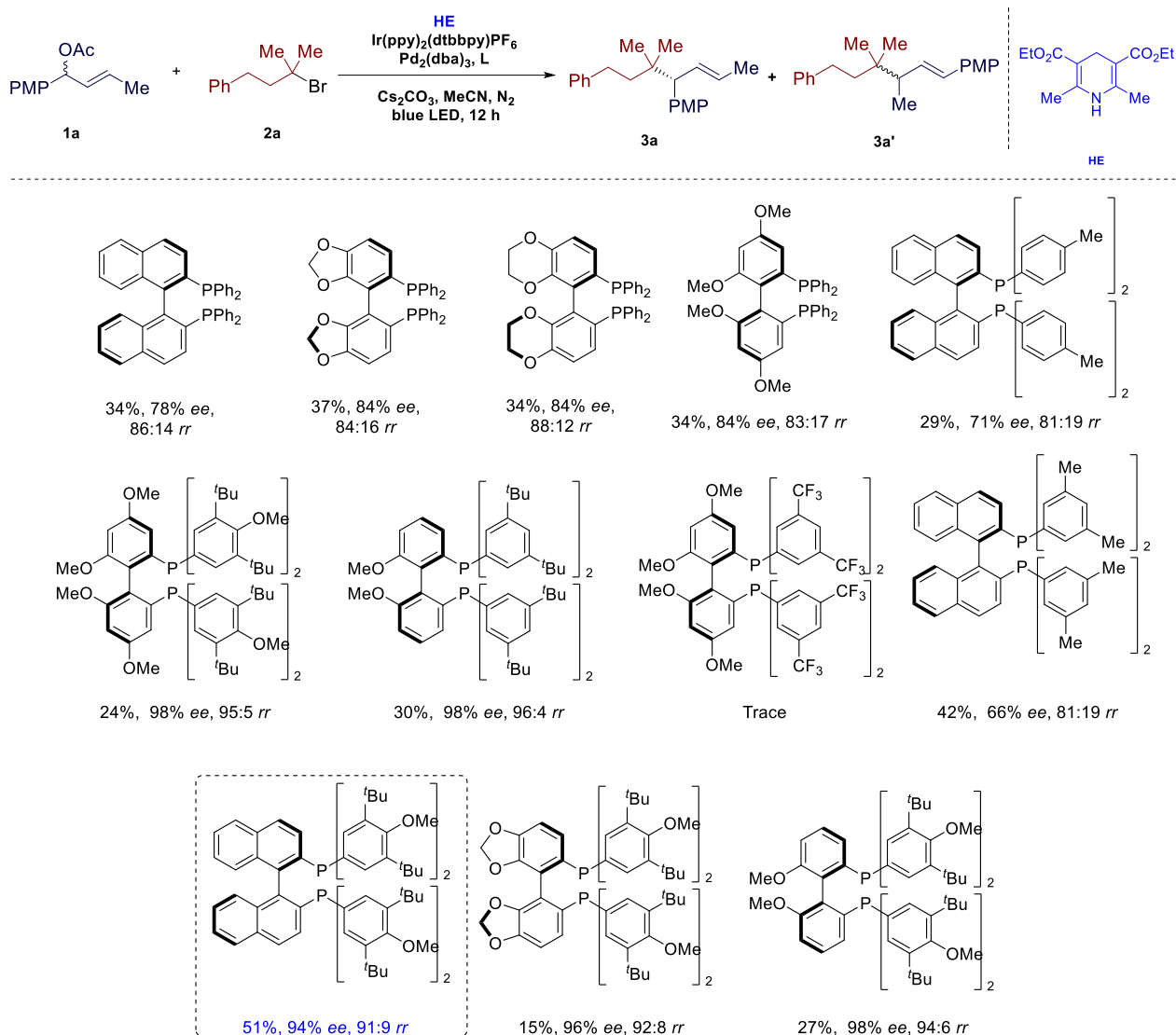


In a nitrogen-filled glovebox, a 500 mL round bottom flask, equipped with a magnetic stir bar, charged with  $\text{Pd}_2(\text{dba})_3$  (23 mg, 0.025 mmol, 2.5 mol%), (*R*)-2,2'-bis((3,5-di-*tert*-butyl-4-methoxyphenyl)- $\lambda^2$ -phosphaneyl)-1,1'-binaphthalene (**L1**) (74 mg, 0.06 mmol, 6 mol%), anhydrous  $\text{CH}_3\text{CN}$  (50.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn:  $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$  (20.0 mg, 0.02 mmol, 2.0 mol%),  $\text{Cs}_2\text{CO}_3$  (652 mg, 2 mmol, 2.0 equiv), **HE** (50.7 mg, 2 mmol, 2.0 equiv), allylic acetates **1a** (220 mg, 1 mmol, 1.0 equiv), alkyl bromides **2a** (681 mg, 3 mmol, 3.0 equiv) and anhydrous  $\text{CH}_3\text{CN}$  (50.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12h.

The reaction mixture was then transferred to a 500 mL separatory funnel, rinsed/diluted with 200 mL ether, and washed with 200 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography (53% (162.3mg); 90% *ee*; > 95:5 *rr*; > 95:5 *E:Z*).

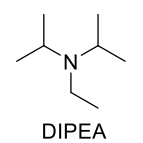
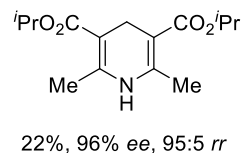
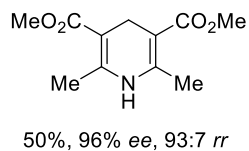
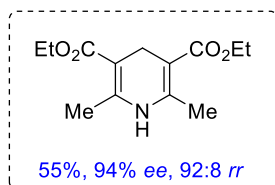
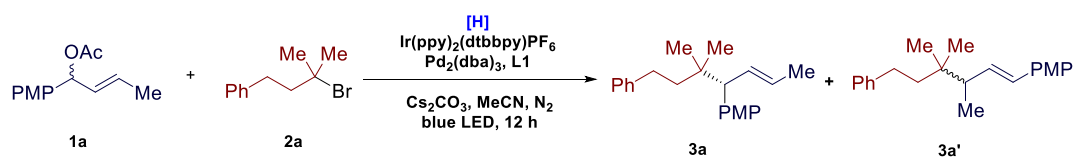
## 6. Optimization of the conditions for 3a

**Table S1.** Screening of the chiral ligands<sup>a</sup>

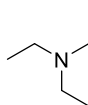


<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), HE (0.2 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (2.5 mol %), ligand (6 mol %), and Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2 mol %) in MeCN (4.0 mL) was irradiated by 45 W blue LEDs for 12 h. <sup>b</sup>The yield and regioselectivity (*rr*) were determined by GC. <sup>c</sup>Enantiomeric excess (*ee*) values determined by HPLC on a chiral stationary phase. PMP = *para*-methoxyphenyl.

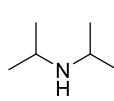
**Table S2.** Screening of the reductant<sup>a</sup>



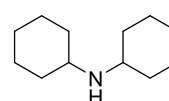
23%, 92% ee,  
92:8 rr



15%, 94% ee,  
92:8 rr

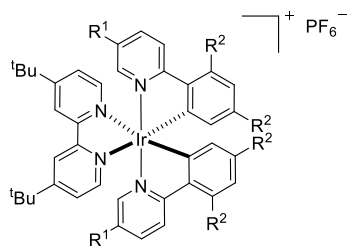
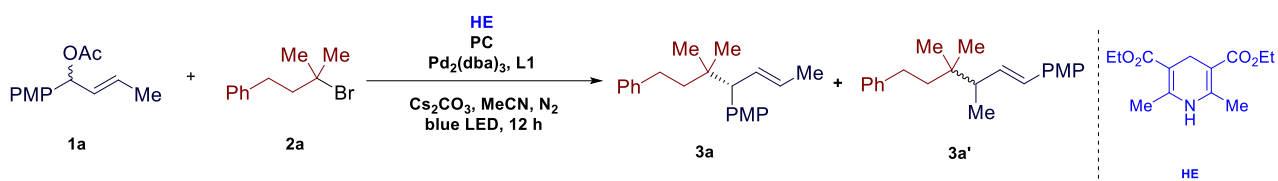


trace

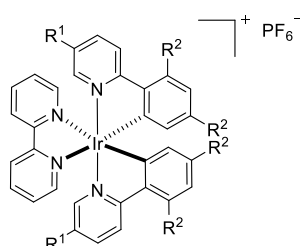


trace

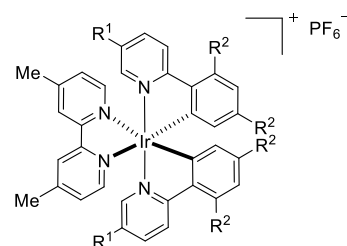
<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), the reductant (0.2 mmol),  $\text{Cs}_2\text{CO}_3$  (0.2 mmol),  $\text{Pd}_2(\text{dba})_3$  (2.5 mol %), ligand (6 mol %), and  $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$  (2 mol %) in MeCN (4.0 mL) was irradiated by 45 W blue LEDs for 12 h. <sup>b</sup>The yield and regioselectivity (*rr*) were determined by GC. <sup>c</sup>Enantiomeric excess (*ee*) values determined by HPLC on a chiral stationary phase. PMP = *para*-methoxyphenyl.

**Table S3: Examination of Photocatalysts<sup>a</sup>**

R<sup>1</sup> = R<sup>2</sup> = H, Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (I):  
51%, 94% ee, 92:8 rr



R<sup>1</sup> = R<sup>2</sup> = H, Ir(ppy)<sub>2</sub>(bpy)PF<sub>6</sub> (IV):  
30%, 94% ee, 94:6 rr



R<sup>1</sup> = R<sup>2</sup> = H, Ir(ppy)<sub>2</sub>(dMebpy)PF<sub>6</sub> (VII):  
30%, 94% ee, 94:6 rr

R<sup>1</sup> = CF<sub>3</sub>; R<sup>2</sup> = F, Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (II):  
N.D.

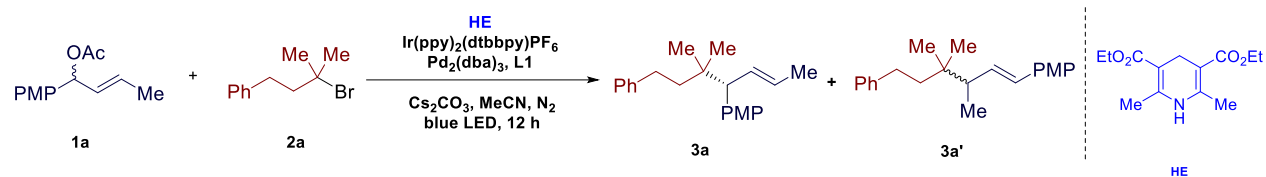
R<sup>1</sup> = CF<sub>3</sub>; R<sup>2</sup> = F, Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>(bpy)PF<sub>6</sub> (V):  
N.D.

R<sup>1</sup> = CF<sub>3</sub>; R<sup>2</sup> = F, Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>(dMebpy)PF<sub>6</sub> (VIII):  
N.D.

R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = F, Ir(dFMepPy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (III):  
29%, 96% ee, 93:7 rr

R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = F, Ir(dFMepPy)<sub>2</sub>(bpy)PF<sub>6</sub> (VI):  
27%, 94% ee, 93:7 rr

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), HE (0.2 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (2.5 mol %), L1 (6 mol %), and PC (2 mol %) in MeCN (4.0 mL) was irradiated by 45 W blue LEDs for 12 h. <sup>b</sup>The yield and regioselectivity (*rr*) were determined by GC. <sup>c</sup>Enantiomeric excess (*ee*) values determined by HPLC on a chiral stationary phase. PMP = *para*-methoxyphenyl.

**Table S4.** Reaction conditions optimization<sup>a</sup>

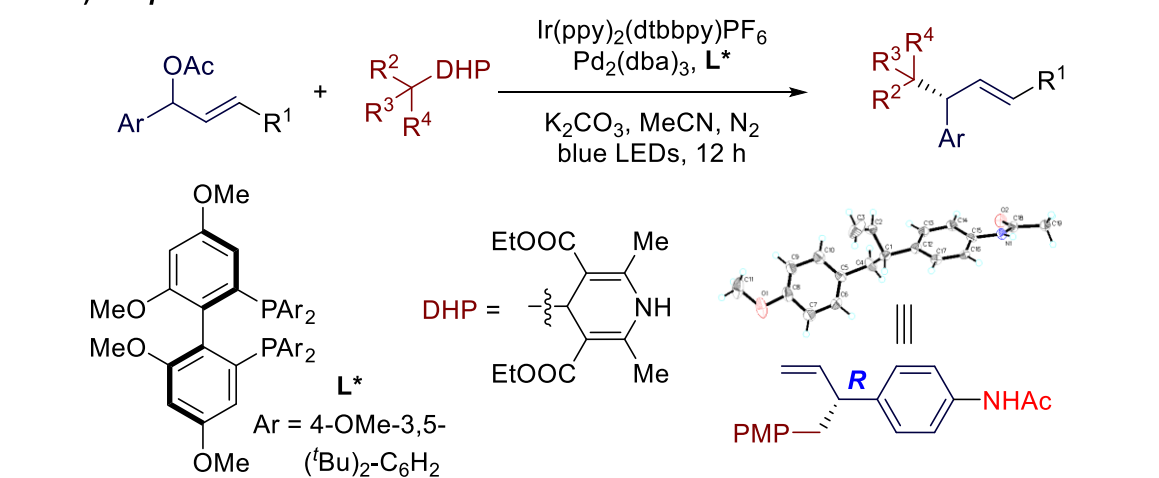
Entry	<b>2a</b> (x mmol)	<b>1a</b> (y mmol)	<b>HE</b> (z mmol)	yield <sup>b</sup>	<i>ee</i> <sup>c</sup>	<i>rr</i> <sup>b</sup>
1	0.1	0.15	0.2	53%	96%	93:7
2	0.1	0.2	0.2	58%	96%	95:5
3	0.1	0.2	0.3	64%	96%	95:5
4	0.1	0.3	0.2	63%	96%	>95:5
5	0.1	0.3	0.3	60%	96%	>95:5
6	0.2	0.1	0.2	56%	96%	>95:5
7	0.2	0.1	0.3	63%	96%	>95:5
8	0.3	0.1	0.2	70%	96%	>95:5
9	0.3	0.1	0.3	66%	96%	>95:5

<sup>a</sup>Reaction conditions: **1a**, **2a**, **HE**, Cs<sub>2</sub>CO<sub>3</sub>, Pd<sub>2</sub>(dba)<sub>3</sub> (2.5 mol %), ligand (6 mol %), and Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2 mol %) in MeCN (4.0 mL) was irradiated by 45 W blue LEDs for 12 h. <sup>b</sup>The yield and regioselectivity (*rr*) were determined by GC. <sup>c</sup>Enantiomeric excess (*ee*) values determined by HPLC on a chiral stationary phase. PMP = *para*-methoxyphenyl.

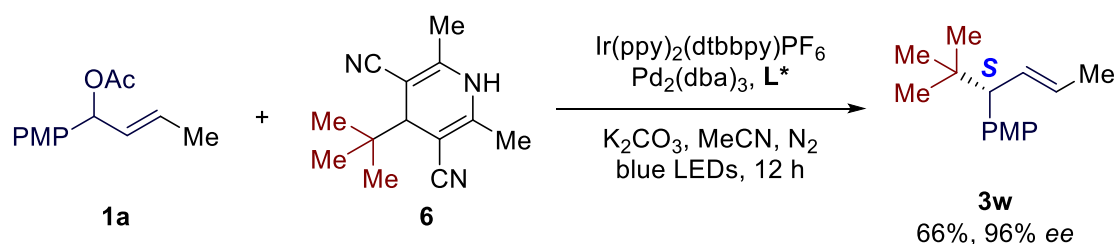
## 7. Proof of stereochemistry

In our previous work<sup>4</sup>, we described photoredox/Pd-cocatalyzed enantioselective coupling of allyl esters with 4-alkyl-1,4-dihydropyridines. The (*R*)-configuration of the product was established unambiguously by single crystal X-ray diffraction analysis (**Figure S1a**). When **1a** was alkylated with 4-alkyl-1,4-dihydropyridines **6** under the same conditions, the absolute configuration of (*S*)-**3w** was also assigned as “*S*” based on the assumption that the two reactions proceed through a similar pathway (**Figure S1b**).

### a) our previous work:

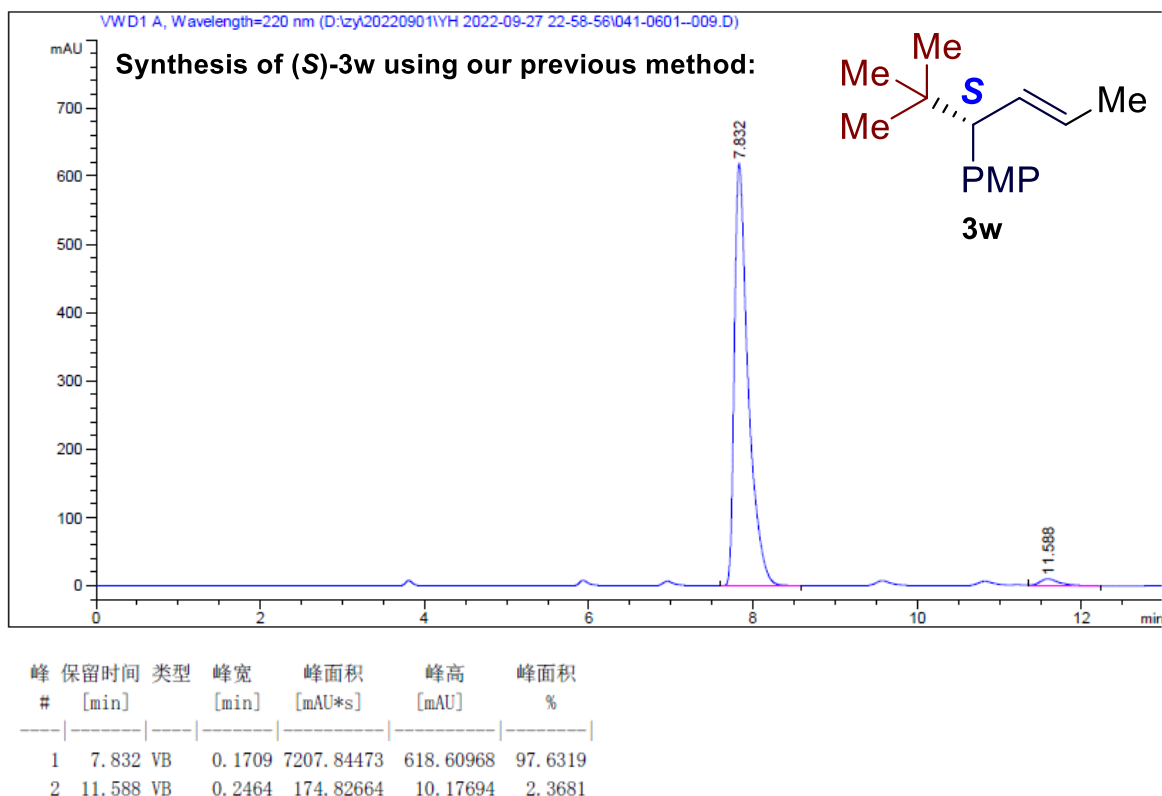


### b) Synthesis of (*S*)-**3w** using our previous method:



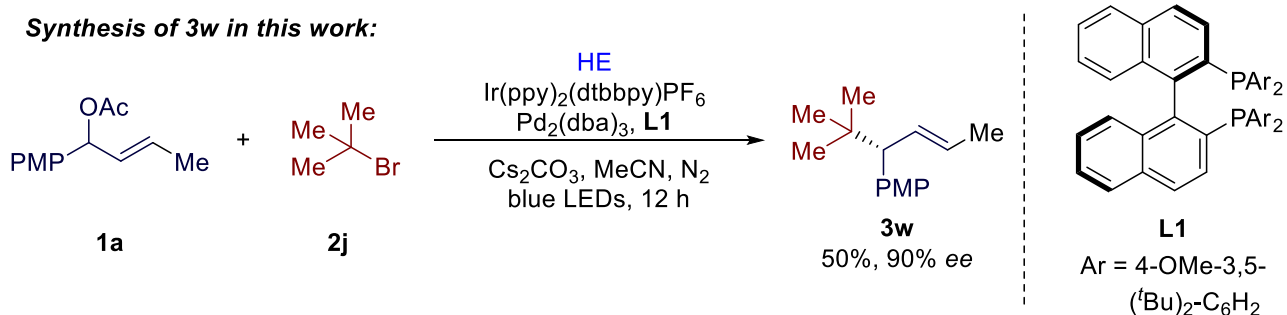
**Figure S1.** Synthesis of (*R*)-**3w** using our previous method.

The enantioselectivity of (*S*)-**3w** (96% ee) synthesized according to our previous methods could be determined by the HPLC analysis (Daicel Chiralpak OD-H, hexane/ethanol = 100/0, flow rate 1.0 mL/min, T = 25 °C, 220 nm). As shown in **Figure S2**, the retention time of (*S*)-**3w** under this HPLC conditions is 7.83 min, and the retention time of (*R*)-**3w** is 11.59 min.



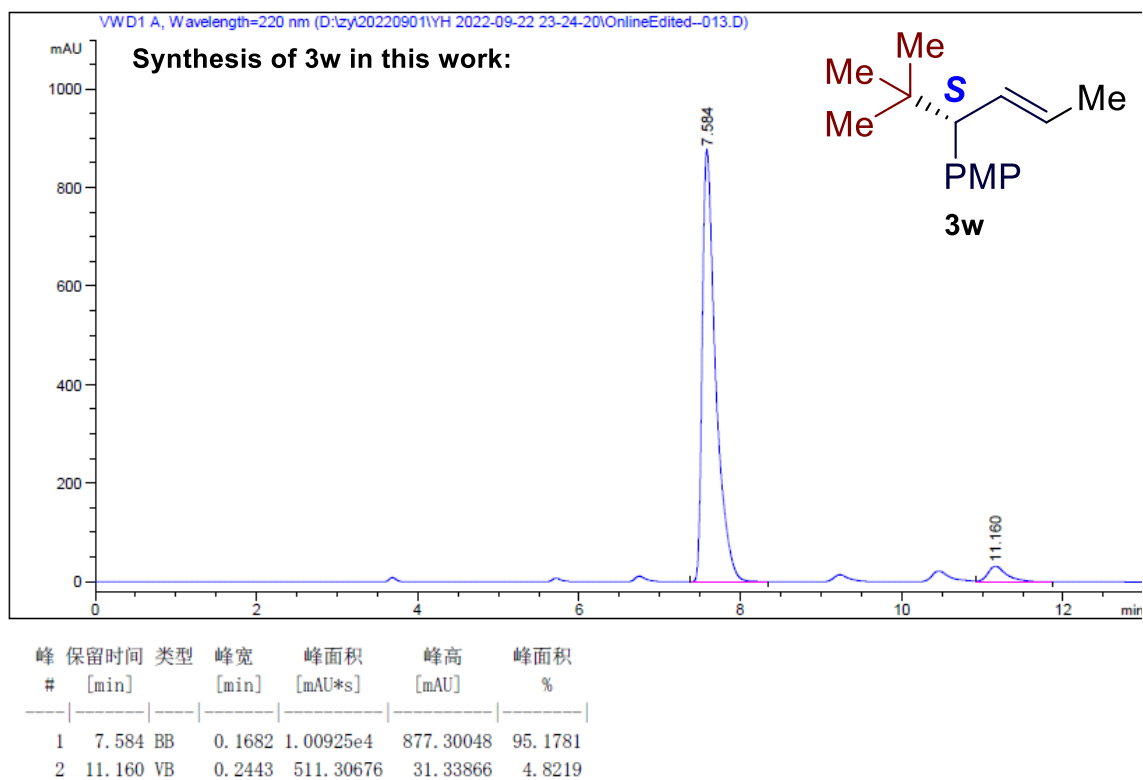
**Figure S2.** The HPLC spectrum of (S)-3w. HPLC conditions: Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min, T = 25 °C, 220 nm.

3w was synthesized under the standard conditions of this work (Figure S3), and its enantioselectivity was determined under the same HPLC conditions (Daicel Chiralpak OD-H, hexane/ethanol = 100/0, flow rate 1.0 mL/min, T = 25 °C, 220 nm).



**Figure S3.** Synthesis of 3w in this work.

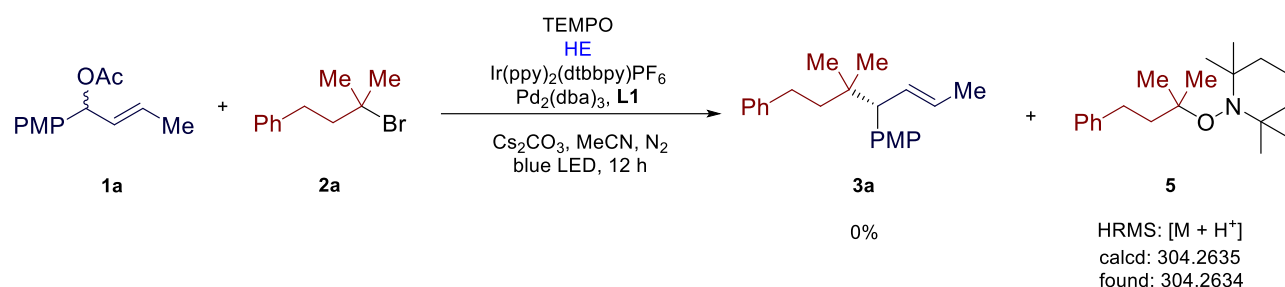




**Figure S4.** The HPLC spectrum of **3w** in this work. HPLC conditions: Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min, T = 25 °C, 220 nm.

## 8. Mechanism Study

### Radical Trapping Experiment with TEMPO

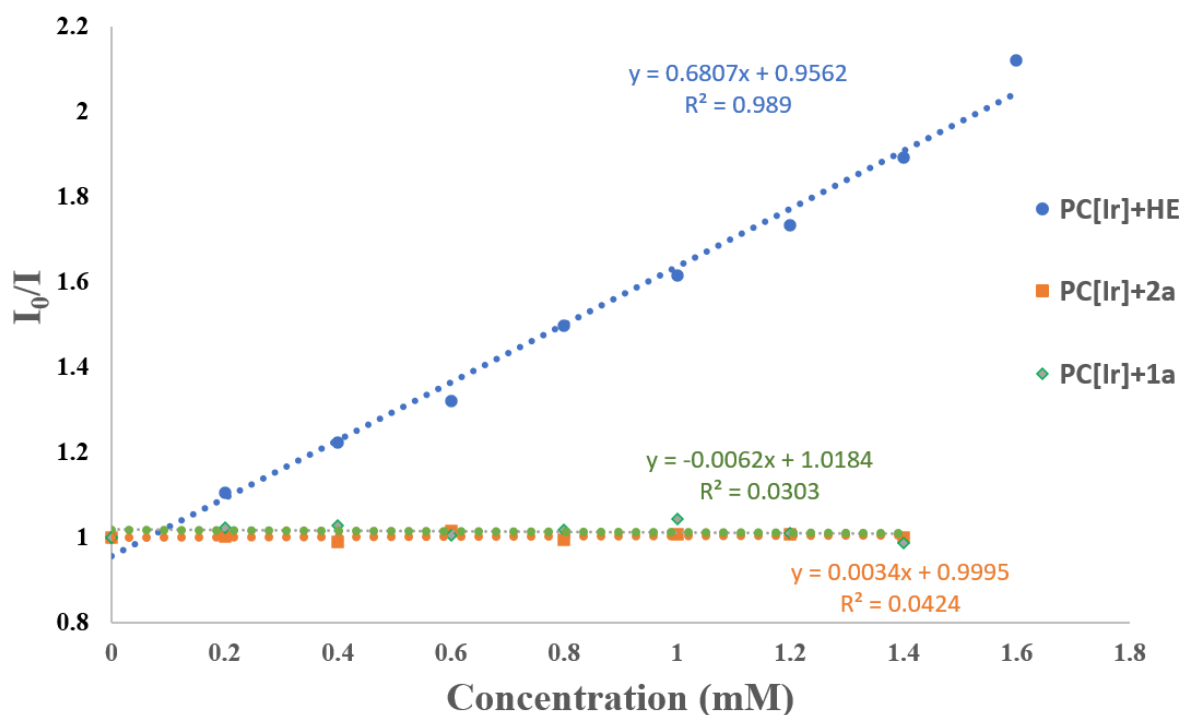


### Procedure C

In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with Pd<sub>2</sub>(dba)<sub>3</sub> (2.3 mg, 0.0025 mmol, 2.5 mol%), (*R*)-2,2'-bis((3,5-di-*tert*-butyl-4-methoxyphenyl)-λ<sup>2</sup>-phosphaneyl)-1,1'-binaphthalene (**L1**) (7.4 mg, 0.006 mmol, 6 mol%), anhydrous MeCN (2.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.0 mg, 0.002 mmol, 2.0 mol%), Cs<sub>2</sub>CO<sub>3</sub> (65.2 mg, 0.2 mmol, 2.0 equiv), HE (50.7 mg, 0.2 mmol, 2.0 equiv), allylic acetates **1a** (0.1 mmol, 1.0 equiv), alkyl bromides **2a** (0.3 mmol, 3.0 equiv), TEMPO (46.9 mg, 0.3 mmol, 3.0 equiv) and anhydrous MeCN (2.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum to afford a residue. The HRMS of the crude reaction mixture did not show the formation of product **3a**, while a TEMPO-alkyl adduct **5** was observed.

### Stern-Volmer fluorescence quenching experiments

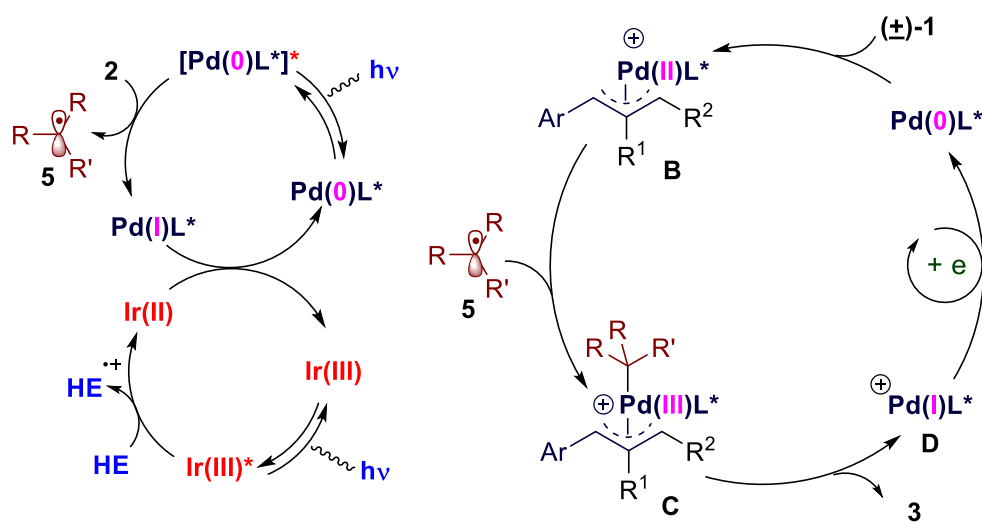
A Hitachi F-7000 fluorescence spectrometer was used to record the emission intensities. All  $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$  solutions were excited at 410 nm and the emission intensity at 572 nm was observed. MeCN was degassed with a stream of Ar for 30 min. In a typical experiment, the emission spectrum of a  $2 \times 10^{-5}$  M solution of  $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$  in MeCN was collected. Then, appropriate amount of quencher was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was collected.  $I_0$  and  $I$  represent the intensities of the emission in the absence and presence of the quencher at 572 nm.



**Figure S5.** The Stern–Volmer plot.

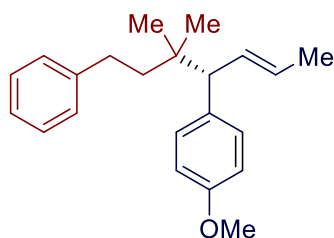
Stern–Volmer quenching experiments indicate that HE quenches photoexcited catalyst.

### Excited-state palladium catalysis pathway



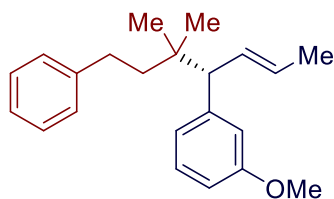
**Figure S6.** Proposed mechanisms for excited-state palladium catalysis pathway.

## 9. Product characterization



**3a**

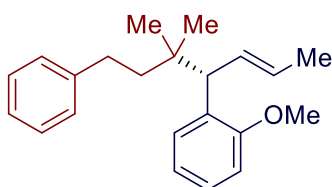
**(*S,E*)-1-(5,5-dimethyl-7-phenylhept-2-en-4-yl)-4-methoxybenzene (3a):** According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 70% (21.6 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_{\text{D}}^{20} = -18.4$  (c 0.55,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.23 (m, 2H), 7.18 – 7.08 (m, 5H), 6.83 – 6.79 (m, 2H), 5.86 (m, 1H), 5.48 (m, 1H), 3.78 (s, 3H), 3.11 (d,  $J = 9.9$  Hz, 1H), 2.62 – 2.54 (m, 2H), 1.68 (m, 3H), 1.53 – 1.43 (m, 2H), 0.92 (s, 3H), 0.88 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.76, 143.54, 135.23, 131.32, 130.17, 128.36, 128.29, 126.55, 125.51, 113.18, 57.66, 55.20, 43.03, 36.60, 30.49, 25.06, 24.75, 18.15; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{22}\text{H}_{28}\text{NaO}$  requires  $m/z$  331.2032; found  $m/z$  331.2023; Enantiomeric ratio: 98:2, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min,  $T = 25$  °C, 220 nm):  $t_{\text{R}} = 18.29$  min (major),  $t_{\text{R}} = 43.53$  min (minor). ( $\pm$ )-**3a**: According to *General Procedure A*.



**3b**

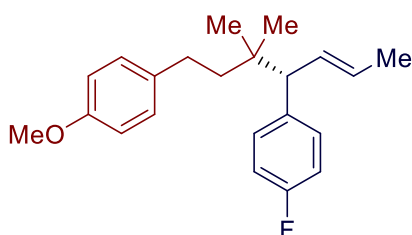
**(*S,E*)-1-(5,5-dimethyl-7-phenylhept-2-en-4-yl)-3-methoxybenzene (3b):** According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 63% (19.4 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_{\text{D}}^{20} = -15.8$  (c 0.44,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.23 (m, 2H), 7.21 – 7.09 (m, 4H), 6.80 – 6.71 (m, 3H), 5.87 (m, 1H), 5.50 (m, 1H), 3.79 (s, 3H), 3.13 (d,  $J = 9.9$  Hz, 1H), 2.58 (t,  $J = 8.8$  Hz, 2H), 1.69 (m, 3H), 1.58 – 1.44 (m, 2H), 0.95 (s, 3H), 0.91 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.04, 144.74, 143.47, 130.98, 128.60, 128.36, 128.29, 126.89, 125.52, 121.98, 115.64, 110.76,

58.56, 55.14, 43.13, 36.61, 30.48, 25.19, 24.83, 18.15.; HRMS (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{22}H_{28}NaO$  requires  $m/z$  331.2032; found  $m/z$  331.2025; Enantiomeric ratio: 96:4, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min,  $T = 25\text{ }^\circ\text{C}$ , 220 nm):  $t_R = 14.58$  min (major),  $t_R = 29.12$  min (minor). ( $\pm$ )-**3b**: According to *General Procedure A*.



**3c**

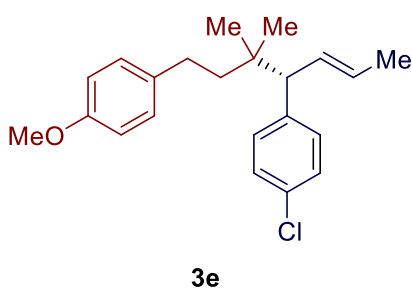
**(*S,E*)-1-(5,5-dimethyl-7-phenylhept-2-en-4-yl)-2-methoxybenzene (3c)**: According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 68% (21.0 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20} = -17.0$  (c 0.39,  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.28 – 7.23 (m, 2H), 7.21 (m, 2H), 7.18 – 7.11 (m, 3H), 6.93 – 6.82 (m, 2H), 5.93 – 5.79 (m, 1H), 5.50 (m, 1H), 3.90 (d,  $J = 9.9$  Hz, 1H), 3.78 (s, 3H), 2.65 – 2.55 (m, 2H), 1.67 (m, 3H), 1.55 (m, 2H), 0.94 (s, 3H), 0.87 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  157.09, 143.87, 131.88, 131.56, 129.78, 128.37, 128.23, 126.58, 125.39, 119.92, 110.68, 55.37, 42.94, 37.22, 30.54, 29.72, 24.59, 18.15; HRMS (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{22}H_{28}NaO$  requires  $m/z$  331.2032; found  $m/z$  331.2027; Enantiomeric ratio: 97:3, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min,  $T = 25\text{ }^\circ\text{C}$ , 220 nm):  $t_R = 8.26$  min (major),  $t_R = 12.35$  min (minor). ( $\pm$ )-**3c**: According to *General Procedure A*.



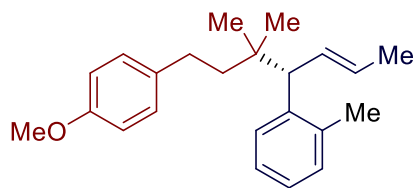
**3d**

**(*S,E*)-1-fluoro-4-(7-(4-methoxyphenyl)-5,5-dimethylhept-2-en-4-yl)benzene (3d)**: According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 54% (17.6 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20} = -10.2$  (c 0.33,  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.16 – 7.10 (m, 2H), 7.07 – 7.01 (m, 2H), 6.99 – 6.91 (m, 2H), 6.84 – 6.79 (m, 2H), 5.85 (m, 1H), 5.49 (m, 1H), 3.78 (s, 3H), 3.14 (d,  $J =$

9.8 Hz, 1H), 2.56 – 2.45 (m, 2H), 1.69 (m, 3H), 1.53 – 1.40 (m, 2H), 0.91 (s, 3H), 0.87 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.25 (d,  $J = 243.7$  Hz), 157.61, 138.74 (d,  $J = 3.4$  Hz), 135.37, 130.90, 130.57 (d,  $J = 7.7$  Hz), 129.15, 127.06, 114.48 (d,  $J = 20.9$  Hz), 113.76, 57.74, 55.26, 43.20, 36.51, 29.46, 24.99, 24.66, 18.14.;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -117.71; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{22}\text{H}_{27}\text{FNaO}$  requires  $m/z$  349.1938; found  $m/z$  349.1927; Enantiomeric ratio: 96:4, determined by HPLC (Daicel Chiralpak OJ-H, hexane/ethanol = 99/1, flow rate 1.0 mL/min,  $T = 25$  °C, 220 nm):  $t_{\text{R}} = 21.87$  min (major),  $t_{\text{R}} = 20.21$  min (minor). ( $\pm$ )-**3d**: According to **General Procedure A**.

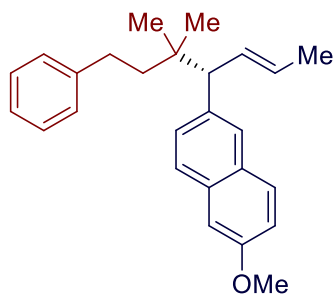


**(S,E)-1-chloro-4-(7-(4-methoxyphenyl)-5,5-dimethylhept-2-en-4-yl)benzene (3e)**: According to **General Procedure B** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100;0 to 100:1; Reaction time = 12 h; yield: 51% (17.5 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_{\text{D}}^{20} = -12.2$  (c 0.34,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 – 7.20 (m, 2H), 7.12 – 7.08 (m, 2H), 7.06 – 7.01 (m, 2H), 6.84 – 6.79 (m, 2H), 5.84 (m, 1H), 5.49 (m, 1H), 3.78 (s, 3H), 3.12 (d,  $J = 9.8$  Hz, 1H), 2.56 – 2.46 (m, 2H), 1.69 (dd,  $J = 6.4, 1.5$  Hz, 3H), 1.53 – 1.40 (m, 2H), 0.91 (s, 3H), 0.87 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.62, 141.60, 135.31, 131.62, 130.63, 130.59, 129.15, 127.85, 127.34, 113.78, 57.94, 55.27, 43.18, 36.53, 29.45, 24.97, 24.65, 18.13; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{22}\text{H}_{27}\text{ClNaO}$  requires  $m/z$  365.1643, found  $m/z$  365.1638; Enantiomeric ratio: 97:3, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 99.7/0.3, flow rate 1.0 mL/min,  $T = 25$  °C, 220 nm):  $t_{\text{R}} = 45.04$  min (major),  $t_{\text{R}} = 35.85$  min (minor). ( $\pm$ )-**3e**: According to **General Procedure A**.



**3f**

**(*S,E*)-1-(7-(4-methoxyphenyl)-5,5-dimethylhept-2-en-4-yl)-2-methylbenzene (3f):** According to **General Procedure B** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 57% (18.4 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20} = -16.6$  (c 0.41,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (dd,  $J = 8.2, 1.5$  Hz, 1H), 7.16 – 7.11 (m, 2H), 7.09 – 7.03 (m, 3H), 6.83 – 6.79 (m, 2H), 5.81 (m, 1H), 5.50 – 5.40 (m, 1H), 3.78 (s, 3H), 3.53 (d,  $J = 9.6$  Hz, 1H), 2.58 – 2.47 (m, 2H), 2.36 (s, 3H), 1.66 (m, 3H), 1.60 – 1.55 (m, 2H), 0.99 (s, 3H), 0.89 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.58, 141.77, 136.12, 135.54, 132.03, 130.51, 129.18, 128.69, 126.41, 125.47, 125.30, 113.75, 55.27, 52.23, 43.46, 37.71, 29.59, 24.70, 24.48, 20.94, 18.14; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{23}\text{H}_{30}\text{NaO}$  requires  $m/z$  345.2189, found  $m/z$  345.2181; Enantiomeric ratio: 94:6, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min,  $T = 25$  °C, 220 nm):  $t_R = 9.51$  min (major),  $t_R = 8.88$  min (minor). ( $\pm$ )-**3f**: According to **General Procedure A**.

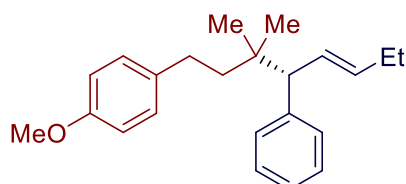


**3g**

**(*S,E*)-2-(5,5-dimethyl-7-phenylhept-2-en-4-yl)-6-methoxynaphthalene (3g):** According to **General Procedure B** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 34% (12.2 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20} = -17.0$  (c 0.27,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (m, 2H), 7.54 (m, 1H), 7.31 (m, 1H), 7.28 – 7.22 (m, 2H), 7.19 – 7.07 (m, 5H), 6.05 – 5.95 (m, 1H), 5.59 – 5.48 (m, 1H), 3.90 (s, 3H), 3.30 (d,  $J = 9.8$  Hz, 1H), 2.61 (m, 2H), 1.70 (m, 3H), 1.62 – 1.50 (m, 2H), 0.99 (s, 3H), 0.94 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.21, 143.49, 138.42, 133.05, 131.16, 129.20, 128.67,

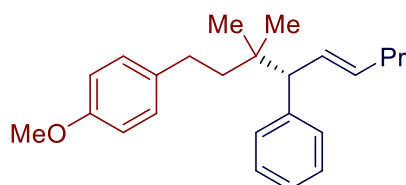


128.37, 128.30, 127.52, 126.96, 125.93, 125.52, 118.55, 105.46, 58.39, 55.31, 43.17, 36.89, 30.53, 25.22, 24.88, 18.19; HRMS (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{26}H_{30}NaO$  requires  $m/z$  381.2189, found  $m/z$  381.2182; Enantiomeric ratio: 91:9, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 99.5/0.5, flow rate 0.8 mL/min,  $T = 25\text{ }^\circ\text{C}$ , 220 nm):  $t_R = 7.82$  min (major),  $t_R = 8.49$  min (minor). ( $\pm$ )-**3g**: According to *General Procedure A*.



**3h**

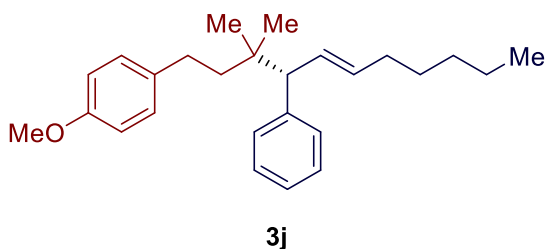
**(*S,E*)-1-(3,3-dimethyl-4-phenyloct-5-en-1-yl)-4-methoxybenzene (3h)**: According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 60% (19.4 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20} = -18.1$  ( $c$  0.48,  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.28 – 7.24 (m, 2H), 7.20 – 7.15 (m, 4H), 6.79 – 6.65 (m, 3H), 5.87 (m, 1H), 5.54 (m, 1H), 3.78 (s, 3H), 3.16 (d,  $J = 9.9$  Hz, 1H), 2.57 (m, 2H), 2.10 – 1.99 (m, 2H), 1.57 – 1.43 (m, 2H), 0.98 (t,  $J = 7.4$  Hz, 3H), 0.94 (s, 3H), 0.89 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  159.60, 145.17, 143.14, 134.06, 129.41, 129.22, 128.79, 127.72, 125.88, 120.80, 114.13, 110.82, 58.25, 55.12, 42.93, 36.60, 30.53, 25.77, 25.17, 24.87, 13.90; HRMS (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{23}H_{30}NaO$  requires  $m/z$  345.2189, found  $m/z$  345.2182; Enantiomeric ratio: 97:3, determined by HPLC (Daicel Chiralpak OJ-H, hexane/ethanol = 99/1, flow rate 1.0 mL/min,  $T = 25\text{ }^\circ\text{C}$ , 220 nm):  $t_R = 18.55$  min (major),  $t_R = 14.86$  min (minor). ( $\pm$ )-**3h**: According to *General Procedure A*.



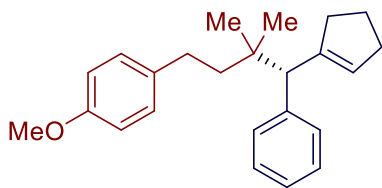
**3i**

**(*S,E*)-1-(3,3-dimethyl-4-phenylnon-5-en-1-yl)-4-methoxybenzene (3i)**: According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 54% (18.2 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20} = -$

13.7 (c 0.45, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 – 7.23 (m, 2H), 7.20 – 7.14 (m, 3H), 7.07 – 7.02 (m, 2H), 6.83 – 6.78 (m, 2H), 5.88 (m, 1H), 5.48 (m, 1H), 3.78 (s, 3H), 3.15 (d, *J* = 9.9 Hz, 1H), 2.53 (m, 2H), 2.05 – 1.94 (m, 2H), 1.55 – 1.44 (m, 2H), 1.38 (m, 2H), 0.93 (s, 3H), 0.90 – 0.84 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.56, 143.20, 135.52, 132.30, 130.05, 129.40, 129.16, 127.68, 125.83, 113.72, 58.37, 55.26, 43.26, 36.56, 34.88, 29.48, 25.14, 24.87, 22.64, 13.77; HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>32</sub>NaO requires *m/z* 359.2345, found *m/z* 359.2338; Enantiomeric ratio: 97:3, determined by HPLC (Daicel Chiralpak OJ-H, hexane/ethanol = 99/1, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t<sub>R</sub> = 16.25 min (major), t<sub>R</sub> = 14.06 min (minor). (±)-**3i**: According to *General Procedure A*.

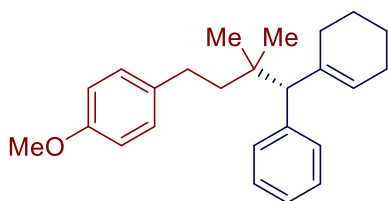


(*S,E*)-1-(3,3-dimethyl-4-phenylundec-5-en-1-yl)-4-methoxybenzene (**3j**): According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 62% (20.7 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil; [α]<sub>D</sub><sup>20</sup> = -13.1 (c 0.38, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 – 7.23 (m, 2H), 7.20 – 7.15 (m, 3H), 7.07 – 7.02 (m, 2H), 6.83 – 6.77 (m, 2H), 5.87 (m, 1H), 5.48 (m, 1H), 3.77 (s, 3H), 3.15 (d, *J* = 9.9 Hz, 1H), 2.53 (m, 2H), 2.05 – 1.98 (m, 2H), 1.55 – 1.43 (m, 2H), 1.39 – 1.32 (m, 2H), 1.26 (m, 4H), 0.93 (s, 3H), 0.88 (s, 3H), 0.86 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.57, 143.20, 135.53, 132.54, 129.83, 129.41, 129.16, 127.68, 125.83, 113.72, 58.35, 55.26, 43.29, 36.56, 32.74, 31.44, 29.48, 29.19, 25.16, 24.82, 22.52, 14.07; HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>36</sub>NaO requires *m/z* 387.2658, found *m/z* 387.2652; Enantiomeric ratio: 97:3, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t<sub>R</sub> = 13.22 min (major), t<sub>R</sub> = 17.18 min (minor). (±)-**3j**: According to *General Procedure A*.



**3k**

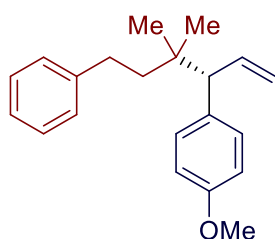
**(R)-1-(4-(cyclopent-1-en-1-yl)-3,3-dimethyl-4-phenylbutyl)-4-methoxybenzene (3k):** According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 54% (18.0 mg); > 95:5 *rr*; a colourless sticky oil;  $[\alpha]_{\text{D}}^{20} = -11.0$  (c 0.22,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.20 (m, 5H), 7.03 (m, 2H), 6.84 – 6.75 (m, 2H), 5.77 – 5.57 (m, 1H), 3.77 (s, 3H), 3.39 (s, 1H), 2.59 – 2.47 (m, 2H), 2.36 – 2.26 (m, 4H), 1.82 – 1.73 (m, 2H), 1.72 – 1.61 (m, 2H), 1.52 (m, 2H), 1.04 (s, 3H), 0.96 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.56, 144.55, 141.84, 135.54, 130.19, 129.17, 127.57, 126.37, 125.97, 113.74, 57.60, 55.26, 44.06, 37.43, 32.75, 29.76, 26.35, 25.57, 23.23; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{24}\text{H}_{30}\text{NaO}$  requires  $m/z$  357.2189, found  $m/z$  357.2183; Enantiomeric ratio: 84:16, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 99.9/0.1, flow rate 1.0 mL/min,  $T = 25$  °C, 220 nm):  $t_{\text{R}} = 14.61$  min (major),  $t_{\text{R}} = 12.73$  min (minor). ( $\pm$ )-**3k**: According to *General Procedure A*.



**3l**

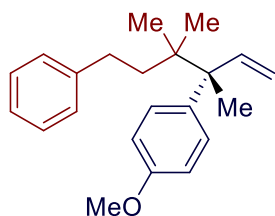
**(R)-1-(4-(cyclohex-1-en-1-yl)-3,3-dimethyl-4-phenylbutyl)-4-methoxybenzene (3l):** According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50:1; Reaction time = 12 h; yield: 45% (15.7 mg); > 95:5 *rr*; a colourless sticky oil;  $[\alpha]_{\text{D}}^{20} = -9.5$  (c 0.27,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (m, 3H), 7.24 – 7.18 (m, 2H), 7.05 – 6.99 (m, 2H), 6.83 – 6.78 (m, 2H), 5.91 – 5.79 (m, 1H), 3.78 (s, 3H), 3.06 (s, 1H), 2.52 (m, 2H), 2.12 – 2.04 (m, 2H), 2.01 – 1.94 (m, 2H), 1.74 – 1.66 (m, 2H), 1.56 – 1.47 (m, 4H), 1.05 (s, 3H), 0.98 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.53, 142.32, 138.44, 135.64, 130.32, 129.16, 127.49, 125.86, 123.90, 113.72, 62.75, 55.26, 44.45, 37.29, 30.53, 29.80, 27.07, 26.10, 25.60, 23.43,

22.30; HRMS (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{25}H_{32}NaO$  requires  $m/z$  371.2345, found  $m/z$  371.2337; Enantiomeric ratio: 82:18, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 0.5 mL/min,  $T = 25\text{ }^\circ\text{C}$ , 220 nm):  $t_R = 29.20$  min (major),  $t_R = 27.47$  min (minor). ( $\pm$ )-**3l**: According to *General Procedure A*.



**3m**

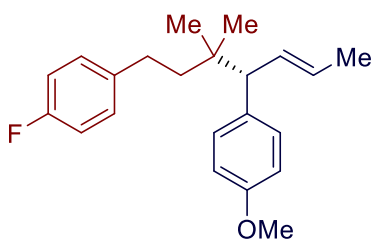
**(S)-1-(4,4-dimethyl-6-phenylhex-1-en-3-yl)-4-methoxybenzene (3m)**: According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 32% (9.4 mg); > 95:5 *rr*; a colourless sticky oil;  $[\alpha]_D^{20} = -23.4$  (c 0.35,  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.25 (m, 3H), 7.20 – 7.05 (m, 4H), 6.89 – 6.70 (m, 2H), 6.26 (d,  $J = 16.7$  Hz, 1H), 5.15 – 5.00 (m, 2H), 3.79 (s, 3H), 3.16 (d,  $J = 9.8$  Hz, 1H), 2.59 (t,  $J = 8.8$  Hz, 2H), 1.60 – 1.46 (m, 2H), 0.95 (s, 3H), 0.91 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  160.77, 143.39, 138.76, 134.53, 130.20, 128.36, 128.30, 125.54, 116.12, 113.25, 58.93, 55.20, 42.98, 36.43, 30.45, 24.98, 24.70; HRMS (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{21}H_{26}NaO$  requires  $m/z$  317.1876, found  $m/z$  317.1872; Enantiomeric ratio: 94:6, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min,  $T = 25\text{ }^\circ\text{C}$ , 220 nm):  $t_R = 17.14$  min (major),  $t_R = 22.61$  min (minor). ( $\pm$ )-**3m**: According to *General Procedure A*.



**3n**

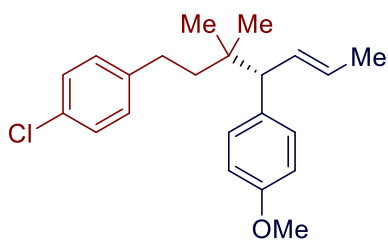
**(S)-1-methoxy-4-(3,4,4-trimethyl-6-phenylhex-1-en-3-yl)benzene (3n)**: According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 30% (9.3 mg); > 95:5 *rr*; a colourless sticky oil;  $[\alpha]_D^{20} = -16.2$  (c 0.25,

CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31 – 7.21 (m, 4H), 7.20 – 7.09 (m, 3H), 6.83 – 6.75 (m, 2H), 6.72 (m, 1H), 5.14 (m, 1H), 5.02 (m, 1H), 3.79 (s, 3H), 2.51 – 2.42 (m, 2H), 1.60 – 1.49 (m, 2H), 1.45 (s, 3H), 0.93 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.30, 144.47, 143.59, 137.93, 130.02, 128.39, 128.28, 125.51, 113.66, 112.26, 55.14, 49.27, 39.57, 38.99, 31.36, 29.71, 22.31, 22.24, 20.42; HRMS (ESI) m/z: [M+Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>28</sub>NaO requires m/z 331.2032, found m/z 331.2028; Enantiomeric ratio: 89:11, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t<sub>R</sub> = 22.00 min (major), t<sub>R</sub> = 28.61 min (minor). (±)-**3n**: According to *General Procedure A*.



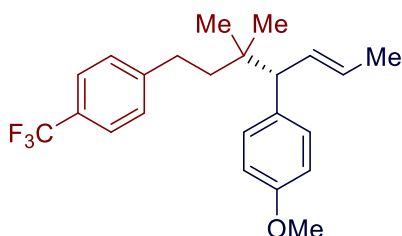
**3o**

(*S,E*)-1-fluoro-4-(4-(4-methoxyphenyl)-3,3-dimethylhept-5-en-1-yl)benzene (**3o**): According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 56% (18.3 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil; [α]<sub>D</sub><sup>20</sup> = -18.1 (c 0.40, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.08 (m, 4H), 6.97 – 6.90 (m, 2H), 6.84 – 6.79 (m, 2H), 5.86 (m, 1H), 5.48 (m, 1H), 3.78 (s, 3H), 3.10 (d, *J* = 9.9 Hz, 1H), 2.58 – 2.50 (m, 2H), 1.68 (m, 3H), 1.52 – 1.40 (m, 2H), 0.92 (s, 3H), 0.88 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.09 (d, *J* = 243.0 Hz), 159.88, 139.04 (d, *J* = 2.6 Hz), 135.13, 131.26, 130.15, 129.58 (d, *J* = 7.7 Hz), 126.59, 114.97 (d, *J* = 21.0 Hz), 113.19, 57.65, 55.19, 43.19, 36.57, 29.67, 25.01, 24.76, 18.15; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -118.29. HRMS (ESI) m/z: [M+Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>27</sub>FNaO requires m/z 349.1938, found m/z 349.1935 Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak OJ-H, hexane/ethanol = 99/1, flow rate 0.8 mL/min, T = 25 °C, 220 nm): t<sub>R</sub> = 8.69 min (major), t<sub>R</sub> = 10.28 min (minor). (±)-**3o**: According to *General Procedure A*.



**3p**

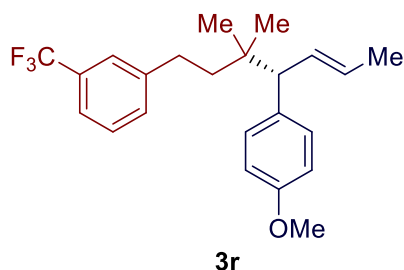
**(*S,E*)-1-chloro-4-(4-(4-methoxyphenyl)-3,3-dimethylhept-5-en-1-yl)benzene (3p):** According to **General Procedure B** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 60% (20.6 mg); a colourless sticky oil; > 95:5 *rr*; > 95:5 *E:Z*;  $[\alpha]_D^{20} = -8.8$  (c 0.36,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 – 7.18 (m, 2H), 7.11 – 7.02 (m, 4H), 6.84 – 6.79 (m, 2H), 5.85 (m, 1H), 5.47 (m, 1H), 3.78 (s, 3H), 3.09 (d,  $J = 9.9$  Hz, 1H), 2.62 – 2.43 (m, 2H), 1.68 (m, 3H), 1.52 – 1.40 (m, 2H), 0.91 (s, 3H), 0.87 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.80, 141.94, 135.07, 131.21, 130.14, 129.68, 128.36, 126.64, 113.20, 113.12, 57.68, 55.20, 43.00, 36.58, 29.89, 24.98, 24.75, 18.14; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{22}\text{H}_{27}\text{ClNaO}$  requires  $m/z$  365.1643, found  $m/z$  365.1637; Enantiomeric ratio: 96:4, determined by HPLC (Daicel Chiralpak OJ-H, hexane/ethanol = 99/1, flow rate 1.0 mL/min,  $T = 25$  °C, 220 nm):  $t_R = 10.44$  min (major),  $t_R = 13.01$  min (minor). ( $\pm$ )-**3p**: According to **General Procedure A**.



**3q**

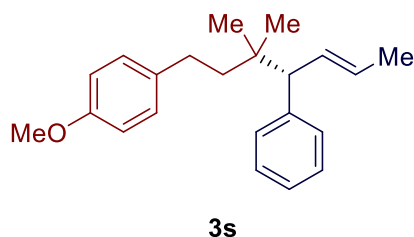
**(*S,E*)-1-(5,5-dimethyl-7-(4-(trifluoromethyl)phenyl)hept-2-en-4-yl)-4-methoxybenzene (3q):** According to **General Procedure B** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 68% (25.6 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20} = -9.4$  (c 0.30,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (m, 2H), 7.23 (m, 2H), 7.12 – 7.07 (m, 2H), 6.82 (m, 2H), 5.92 – 5.81 (m, 1H), 5.49 (m, 1H), 3.78 (s, 3H), 3.10 (d,  $J = 9.9$  Hz, 1H), 2.63 (t,  $J = 8.8$  Hz, 2H), 1.69 (m, 3H), 1.49 (m, 2H), 0.93 (s, 3H), 0.89 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.83, 147.67, 135.00, 131.15, 130.13, 128.63, 126.72, 125.21 (q,  $J = 4.0$  Hz), 124.41 (q,  $J = 270.0$  Hz), 113.23, 57.67, 55.20, 42.83, 36.62, 30.45, 24.97, 24.74, 18.13;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.25. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for

$C_{23}H_{27}F_3NaO$  requires  $m/z$  399.1906, found  $m/z$  399.1898; Enantiomeric ratio: 96:4, determined by HPLC (Daicel Chiralpak OJ-H, hexane/ethanol = 99/1, flow rate 1.0 mL/min,  $T = 25\text{ }^\circ\text{C}$ , 220 nm):  $t_R = 9.23$  min (major),  $t_R = 12.92$  min (minor). ( $\pm$ )-**3q**: According to *General Procedure A*.



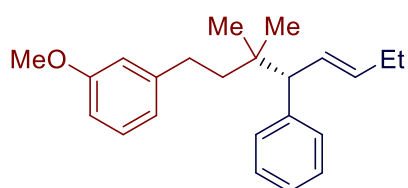
**(*S,E*)-1-(4-(4-methoxyphenyl)-3,3-dimethylhept-5-en-1-yl)-3-(trifluoromethyl)benzene (3r):**

According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 66% (24.8 mg); a colourless sticky oil; > 95:5 *rr*; > 95:5 *E:Z*;  $[\alpha]_D^{20} = -10.3$  (c 0.30,  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.45 – 7.27 (m, 4H), 7.14 – 7.06 (m, 2H), 6.87 – 6.78 (m, 2H), 5.87 (m, 1H), 5.50 (m, 1H), 3.78 (s, 3H), 3.12 (d,  $J = 9.9$  Hz, 1H), 2.70 – 2.55 (m, 2H), 1.69 (m, 3H), 1.55 – 1.42 (m, 2H), 0.93 (s, 3H), 0.89 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  157.85, 144.36, 135.01, 131.74, 131.16, 130.39, 130.14, 128.66, 126.73, 125.05 (q,  $J = 4.2$  Hz), 124.30 (q,  $J = 270.0$  Hz) 122.42 (q,  $J = 4.2$  Hz), 113.23, 57.52, 55.19, 42.98, 36.60, 30.37, 29.71, 25.03, 24.76, 18.10;  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -62.54. HRMS (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{23}H_{27}F_3NaO$  requires  $m/z$  399.1906, found  $m/z$  399.1898; Enantiomeric ratio: 98:2, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min,  $T = 25\text{ }^\circ\text{C}$ , 220 nm):  $t_R = 11.52$  min (major),  $t_R = 22.36$  min (minor). ( $\pm$ )-**3r**: According to *General Procedure A*.



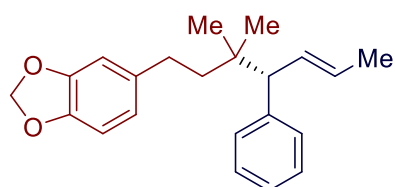
**(*S,E*)-1-(3,3-dimethyl-4-phenylhept-5-en-1-yl)-4-methoxybenzene (3s):** According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 54% (16.7 mg); a colourless sticky oil; > 95:5 *rr*; > 95:5 *E:Z*;  $[\alpha]_D^{20} = -12.6$  (c 0.41,  $CHCl_3$ );  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.28 – 7.23 (m, 2H), 7.21 – 7.14 (m, 3H), 7.07

– 7.01 (m, 2H), 6.84 – 6.78 (m, 2H), 5.89 (m, 1H), 5.55 – 5.43 (m, 1H), 3.78 (s, 3H), 3.15 (d,  $J = 9.9$  Hz, 1H), 2.57 – 2.48 (m, 2H), 1.68 (m, 3H), 1.52 – 1.41 (m, 2H), 0.93 (s, 3H), 0.89 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.57, 143.11, 135.53, 131.12, 129.39, 129.17, 127.73, 126.83, 125.88, 113.74, 58.55, 55.26, 43.29, 36.56, 29.49, 25.11, 24.78, 18.15; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{22}\text{H}_{28}\text{NaO}$  requires  $m/z$  331.2032, found  $m/z$  331.2028; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak OJ-H, hexane/ethanol = 99/1, flow rate 1.0 mL/min,  $T = 25$  °C, 220 nm):  $t_{\text{R}} = 12.54$  min (major),  $t_{\text{R}} = 11.19$  min (minor). (+)-**3s**: According to *General Procedure A*.



**3t**

(*S,E*)-1-(3,3-dimethyl-4-phenyloct-5-en-1-yl)-3-methoxybenzene (**3t**): According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 56% (18.1 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_{\text{D}}^{20} = -13.3$  (c 0.29,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.24 (m, 2H), 7.20 – 7.15 (m, 4H), 6.79 – 6.65 (m, 3H), 5.87 (m, 1H), 5.54 (m, 1H), 3.78 (s, 3H), 3.16 (d,  $J = 9.9$  Hz, 1H), 2.57 (m, 2H), 2.10 – 1.99 (m, 2H), 1.57 – 1.43 (m, 2H), 0.98 (t,  $J = 7.4$  Hz, 3H), 0.94 (s, 3H), 0.89 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.60, 145.17, 143.14, 134.06, 129.41, 129.22, 128.79, 127.72, 125.88, 120.80, 114.13, 110.82, 58.25, 55.12, 42.93, 36.60, 30.53, 25.77, 25.17, 24.87, 13.90; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{23}\text{H}_{30}\text{NaO}$  requires  $m/z$  345.2189, found  $m/z$  345.2180; Enantiomeric ratio: 97:3, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 99.3/0.7, flow rate 0.8 mL/min,  $T = 25$  °C, 220 nm):  $t_{\text{R}} = 11.28$  min (major),  $t_{\text{R}} = 10.65$  min (minor). (+)-**3t**: According to *General Procedure A*.

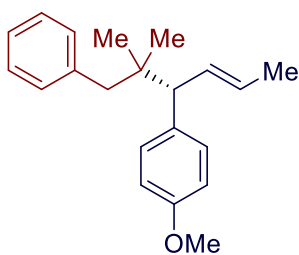


**3u**

(*S,E*)-5-(3,3-dimethyl-4-phenylhept-5-en-1-yl)benzo[*d*][1,3]dioxole (**3u**): According to *General*

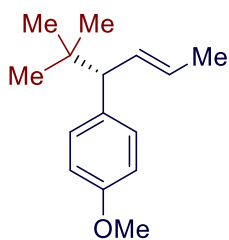


**Procedure B** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 48% (15.5 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20} = -17.5$  (c 0.26, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27 – 7.23 (m, 2H), 7.21 – 7.15 (m, 3H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.64 – 6.53 (m, 2H), 5.96 – 5.80 (m, 1H), 5.90 (s, 2H), 5.49 (m, 1H), 3.13 (d, *J* = 9.9 Hz, 1H), 2.54 – 2.45 (m, 2H), 1.69 (m, 3H), 1.50 – 1.41 (m, 2H), 0.92 (s, 3H), 0.88 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.45, 145.36, 143.05, 137.34, 131.08, 129.37, 127.75, 126.88, 125.92, 120.89, 108.85, 108.10, 100.69, 58.55, 43.35, 36.54, 30.21, 25.09, 24.78, 18.15; HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>26</sub>NaO<sub>2</sub> requires *m/z* 345.1825, found *m/z* 345.1817; Enantiomeric ratio: 96:4, determined by HPLC (Daicel Chiralpak OJ-H, hexane/ethanol = 99/1, flow rate 1.0 mL/min, T = 25 °C, 220 nm): *t<sub>R</sub>* = 12.47 min (major), *t<sub>R</sub>* = 9.92 min (minor). (±)-**3u**: According to **General Procedure A**.



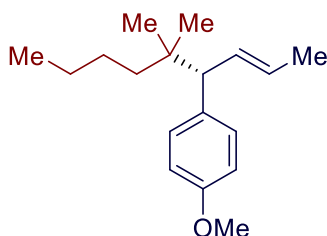
**3v**

**(*S,E*)-1-(2,2-dimethyl-1-phenylhex-4-en-3-yl)-4-methoxybenzene (3v)**: According to **General Procedure B** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 64% (18.8 mg); a colourless sticky oil; > 95:5 *rr*; > 95:5 *E:Z*;  $[\alpha]_D^{20} = -17.6$  (c 0.46, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26 – 7.20 (m, 2H), 7.20 – 7.15 (m, 1H), 7.13 – 7.06 (m, 4H), 6.85 – 6.81 (m, 2H), 5.99 – 5.90 (m, 1H), 5.55 – 5.45 (m, 1H), 3.79 (s, 3H), 3.07 (d, *J* = 9.8 Hz, 1H), 2.60 – 2.43 (m, 2H), 1.72 (m, 3H), 0.81 (s, 3H), 0.72 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.82, 139.42, 135.21, 131.34, 130.90, 130.31, 127.52, 127.15, 125.65, 113.22, 59.45, 55.20, 46.57, 37.74, 24.51, 23.96, 18.22; HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>26</sub>NaO requires *m/z* 317.1876, found *m/z* 317.1877; Enantiomeric ratio: 96:4, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min, T = 25 °C, 220 nm): *t<sub>R</sub>* = 16.94 min (major), *t<sub>R</sub>* = 26.57 min (minor). (±)-**3v**: According to **General Procedure A**.



**3w**

**(*S,E*)-1-(2,2-dimethylhex-4-en-3-yl)-4-methoxybenzene (3w):** According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0; Reaction time = 12 h; yield: 50% (10.9 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20} = -18.2$  (c 0.37, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.10 – 7.04 (m, 2H), 6.84 – 6.78 (m, 2H), 5.94 – 5.75 (m, 1H), 5.49 – 5.37 (m, 1H), 3.78 (s, 3H), 2.92 (d, *J* = 9.8 Hz, 1H), 1.67 (m, 3H), 0.85 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.70, 135.68, 131.64, 129.95, 126.36, 113.09, 59.35, 55.19, 34.02, 29.70, 28.01, 27.74, 18.07 ; HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>22</sub>NaO requires *m/z* 241.1563, found *m/z* 241.1564; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min, T = 25 °C, 220 nm): *t*<sub>R</sub> = 7.58 min (major), *t*<sub>R</sub> = 11.16 min (minor). (±)-**3w**: According to *General Procedure A*.

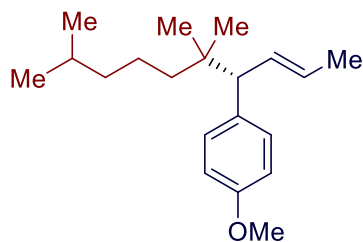


**3x**

**(*S,E*)-1-(5,5-dimethylnon-2-en-4-yl)-4-methoxybenzene (3x):** According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0; Reaction time = 12 h; yield: 64% (16.6 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20} = -24.7$  (c 0.48, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.13 – 7.01 (m, 2H), 6.86 – 6.74 (m, 2H), 5.88 – 5.78 (m, 1H), 5.47 – 5.36 (m, 1H), 3.78 (s, 3H), 3.02 (d, *J* = 9.8 Hz, 1H), 1.66 (m, 3H), 1.25 – 1.10 (m, 6H), 0.91 – 0.85 (m, 3H), 0.83 (s, 3H), 0.76 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.64, 135.55, 131.55, 130.16, 126.22, 113.06, 57.75, 55.17, 40.34, 36.36, 26.07, 24.90, 24.75, 23.63, 18.11, 14.23; HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>28</sub>NaO requires *m/z* 283.2032, found *m/z* 283.2027; Enantiomeric ratio: 97:3, determined by HPLC (Daicel Chiralpak OD-H, pentane/isopropanol =

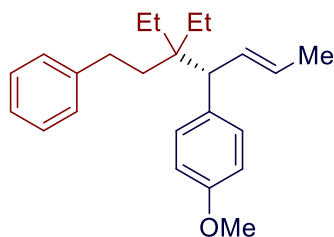
100/0, flow rate 1.0 mL/min, T = 25 °C, 220 nm):  $t_R$  = 7.20 min (major),  $t_R$  = 11.88 min (minor).

(±)-**3x**: According to *General Procedure A*.



**3y**

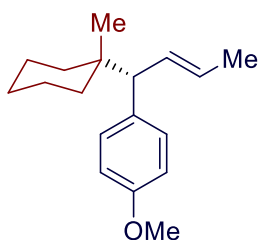
(*S,E*)-1-methoxy-4-(5,5,9-trimethyldec-2-en-4-yl)benzene (**3y**): According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 59% (17.0 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20}$  = -24.8 (c 0.53, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.16 – 6.98 (m, 2H), 6.89 – 6.73 (m, 2H), 5.83 (m, 1H), 5.42 (m, 1H), 3.78 (s, 3H), 3.02 (d, *J* = 9.9 Hz, 1H), 1.66 (m, 3H), 1.55 – 1.46 (m, 1H), 1.25 – 1.18 (m, 2H), 1.16 – 1.05 (m, 4H), 0.86 (m, 6H), 0.83 (s, 3H), 0.77 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.64, 135.54, 131.55, 130.15, 126.23, 113.06, 57.82, 55.17, 40.86, 39.99, 36.46, 27.98, 24.90, 24.76, 22.72, 22.66, 21.48, 18.13; HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>32</sub>NaO requires *m/z* 311.2345, found *m/z* 311.2338; Enantiomeric ratio: 98:2, determined by HPLC (Daicel Chiralpak OD-H, hexane/ isopropanol = 100/0, flow rate 1.0 mL/min, T = 25 °C, 220 nm):  $t_R$  = 5.76 min (major),  $t_R$  = 9.66 min (minor). (±)-**3y**: According to *General Procedure A*.



**3z**

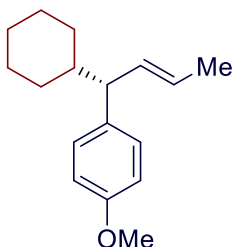
(*S,E*)-1-(5,5-diethyl-7-phenylhept-2-en-4-yl)-4-methoxybenzene (**3z**): According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 65% (21.9 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20}$  = -23.6 (c 0.53, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 – 7.23 (m, 2H), 7.15 (m, 5H), 6.85 – 6.79 (m, 2H), 6.00 – 5.89 (m, 1H), 5.43 (m, 1H), 3.78 (s, 3H), 3.28 (d, *J* = 9.8 Hz, 1H), 2.55 – 2.43 (m, 2H), 1.67 (m, 3H), 1.58 – 1.48 (m, 2H), 1.37 (m, 4H), 0.86 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ

157.78, 143.78, 135.30, 132.32, 130.34, 128.33, 128.28, 125.90, 125.55, 113.25, 55.24, 55.20, 41.23, 37.55, 30.52, 27.70, 27.49, 18.18, 8.72, 8.67; HRMS (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{24}H_{32}NaO$  requires  $m/z$  359.2345, found  $m/z$  359.2339; Enantiomeric ratio: 97:3, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min,  $T = 25\text{ }^\circ\text{C}$ , 220 nm):  $t_R = 9.04$  min (major),  $t_R = 10.41$  min (minor). ( $\pm$ )-**3z**: According to *General Procedure A*.



**3aa**

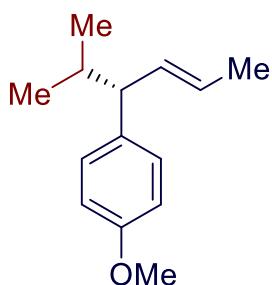
**(*S,E*)-1-methoxy-4-(1-(1-methylcyclohexyl)but-2-en-1-yl)benzene (3aa)**: According to *General Procedure B* Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0; Reaction time = 12 h; yield: 25% (6.5 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_D^{20} = -5.5$  (c 0.23,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.11 – 7.04 (m, 2H), 6.84 – 6.77 (m, 2H), 5.89 – 5.78 (m, 1H), 5.48 – 5.37 (m, 1H), 3.78 (s, 3H), 3.03 (d,  $J = 9.9$  Hz, 1H), 1.67 (m, 3H), 1.59 – 1.51 (m, 4H), 1.41 – 1.30 (m, 4H), 1.12 – 0.97 (m, 2H), 0.84 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.66, 135.13, 131.13, 130.24, 126.38, 113.03, 58.71, 55.18, 36.19, 36.16, 29.70, 26.35, 21.99, 21.93, 20.67, 18.13; HRMS (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{18}H_{26}NaO$  requires  $m/z$  281.1876, found  $m/z$  281.1874; Enantiomeric ratio: 98:2, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min,  $T = 25\text{ }^\circ\text{C}$ , 220 nm):  $t_R = 7.39$  min (major),  $t_R = 10.98$  min (minor). ( $\pm$ )-**3aa**: According to *General Procedure A*.



**3ab**

**(*R,E*)-1-(1-cyclohexylbut-2-en-1-yl)-4-methoxybenzene (3ab)**: According to *General Procedure*

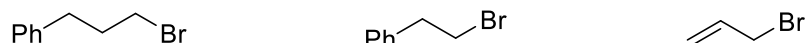
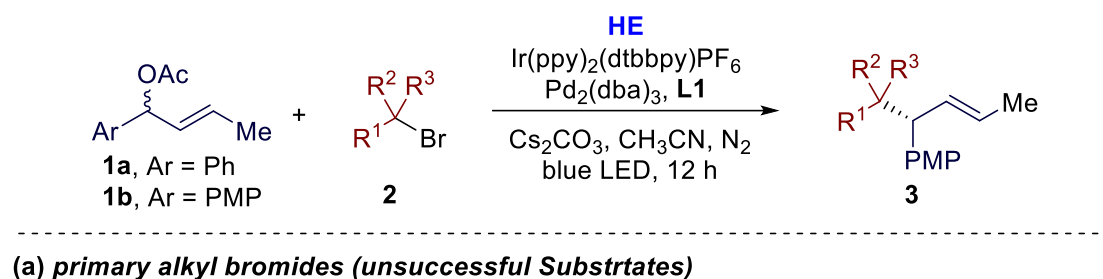
**B'** (at °C) Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0; Reaction time = 12 h; yield: 40% (9.8 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_{\text{D}}^{20} = -7.7$  (c 0.40, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.08 – 7.01 (m, 2H), 6.85 – 6.80 (m, 2H), 5.60 – 5.52 (m, 1H), 5.39 (m, 1H), 3.78 (s, 3H), 2.82 (m, 1H), 1.89 – 1.83 (m, 1H), 1.75 – 1.69 (m, 1H), 1.65 – 1.59 (m, 5H), 1.47 – 1.38 (m, 2H), 1.22 – 1.18 (m, 1H), 1.14 – 1.08 (m, 2H), 0.92 – 0.83 (m, 1H), 0.81 – 0.70 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.63, 137.05, 134.16, 128.67, 125.02, 113.67, 55.41, 55.20, 42.64, 31.39, 26.60, 26.44, 17.97; HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>24</sub>NaO requires *m/z* 267.1719, found *m/z* 267.1718; Enantiomeric ratio: 97:3, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 1.0 mL/min, T = 25 °C, 220 nm): *t<sub>R</sub>* = 7.38 min (major), *t<sub>R</sub>* = 8.59 min (minor). (±)-**3ab**: According to *General Procedure A*.



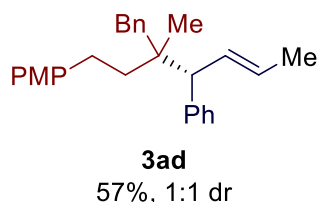
**3ac**

**(*R,E*)-1-methoxy-4-(2-methylhex-4-en-3-yl)benzene (3ac)**: According to *General Procedure B'* (at °C) Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0; Reaction time = 12 h; yield: 42% (8.6 mg); > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $[\alpha]_{\text{D}}^{20} = -9.0$  (c 0.48, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.05 – 6.92 (m, 2H), 6.81 – 6.68 (m, 2H), 5.58 – 5.46 (m, 1H), 5.38 – 5.31 (m, 1H), 3.71 (s, 3H), 2.73 – 2.69 (m, 1H), 1.79 – 1.72 (m, 1H), 1.58 (m, 3H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.66 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.65, 137.30, 134.13, 128.65, 125.15, 113.66, 56.37, 55.21, 33.10, 21.07, 20.77, 17.98; HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>20</sub>NaO requires *m/z* 227.1406, found *m/z* 227.1407; Enantiomeric ratio: 94:6, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 100/0, flow rate 0.8 mL/min, T = 25 °C, 220 nm): *t<sub>R</sub>* = 9.56 min (major), *t<sub>R</sub>* = 13.11 min (minor). (±)-**3ac**: According to *General Procedure A*.

## 10. Attempt of other alkyl bromides

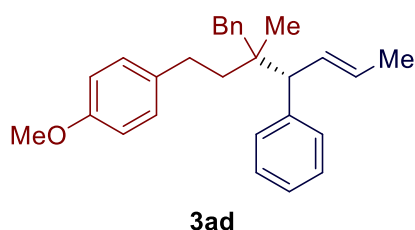


**(b) unsymmetric tertiary alkyl bromide**



**Figure S7.** Attempt of other alkyl bromides.

Some alkyl bromides other than tertiary alkyl bromides were explored. As shown in Figure S7, Under the standard conditions, we were unable to obtain the reductive cross-coupling products with primary alkyl bromides. Unsymmetric tertiary alkyl bromide **2q** was also suitable for this reaction, although no diastereoselectivity (1: 1 dr) was observed.



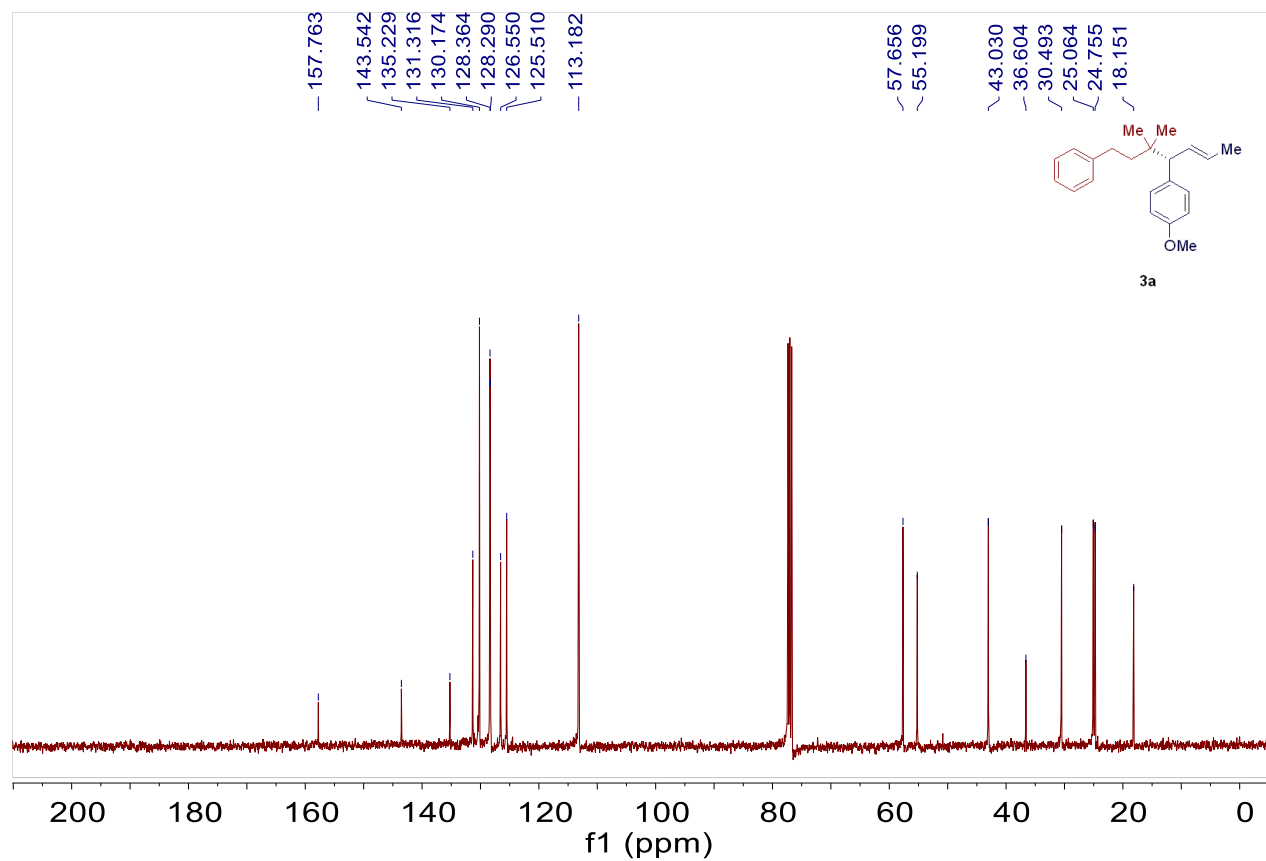
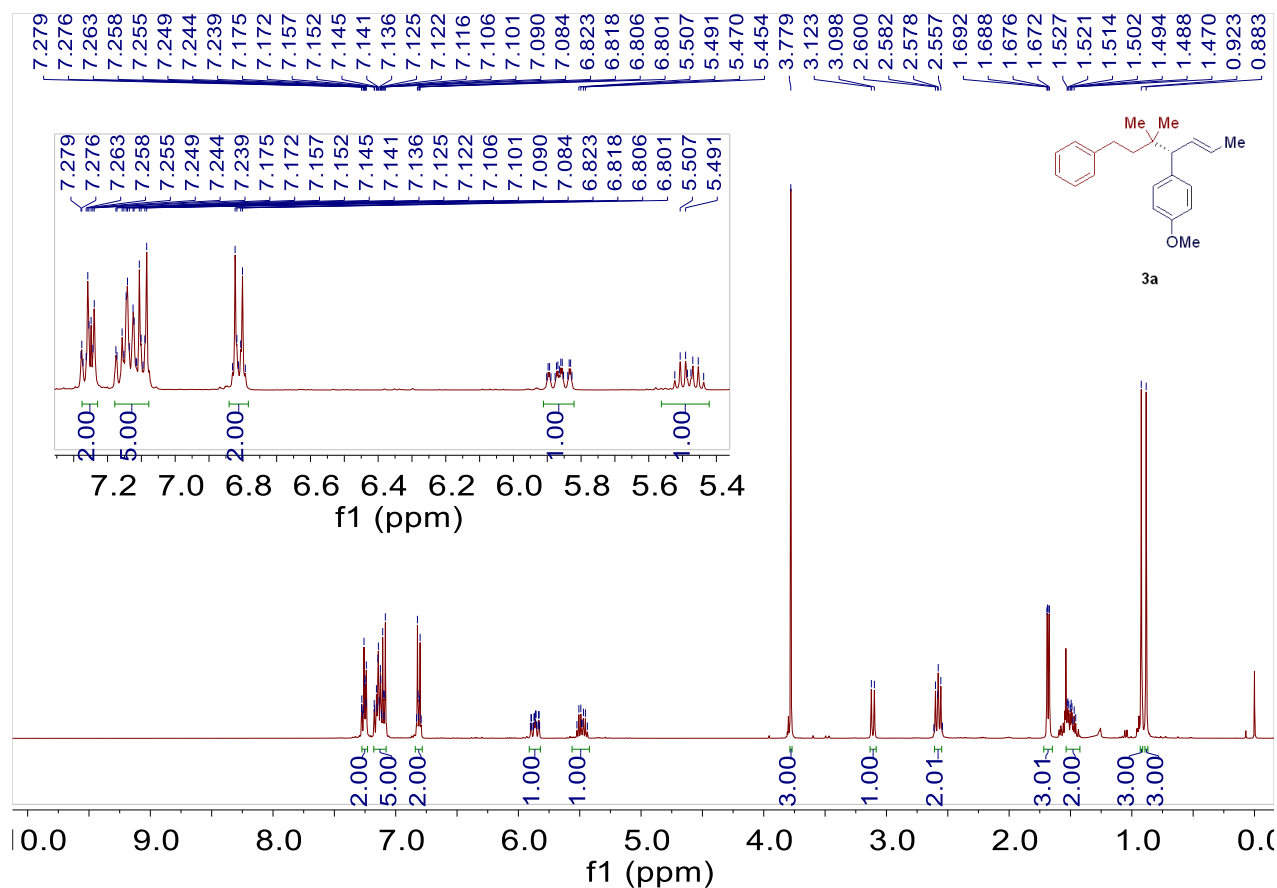
**((3*S*,*E*)-2-(4-methoxyphenethyl)-2-methylhex-4-ene-1,3-diyl)dibenzene (3ad):** According to **General Procedure B'** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0; Reaction time = 12 h; yield: 57% (21.9 mg); inseparable diastereoisomers 1:1 *dr*; > 95:5 *rr*; > 95:5 *E:Z*; a colourless sticky oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.17 (m, 16H), 7.13 – 7.07 (m, 4H), 7.05 – 7.01 (m, 2H), 6.97 – 6.93 (m, 2H), 6.82 – 6.75 (m, 4H), 6.12 – 5.97 (m, 2H), 5.67 – 5.54 (m, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.43 (dd,  $J = 9.9, 7.6$  Hz, 2H), 2.77 – 2.68 (m, 4H), 2.66 – 2.56 (m, 2H), 2.51 – 2.40 (m, 2H), 1.84 – 1.67 (m, 6H), 1.60 – 1.53 (m, 2H), 1.45 – 1.31 (m, 2H),

0.88 (s, 3H), 0.85 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.65, 142.83, 138.95, 135.22, 131.00, 130.88, 130.82, 130.76, 129.81, 129.76, 129.12, 127.86, 127.68, 127.47, 127.32, 126.09, 125.84, 125.79, 113.79, 113.71, 56.63, 56.34, 55.27, 55.25, 43.05, 40.23, 40.15, 39.21, 38.66, 28.92, 22.35, 18.30.

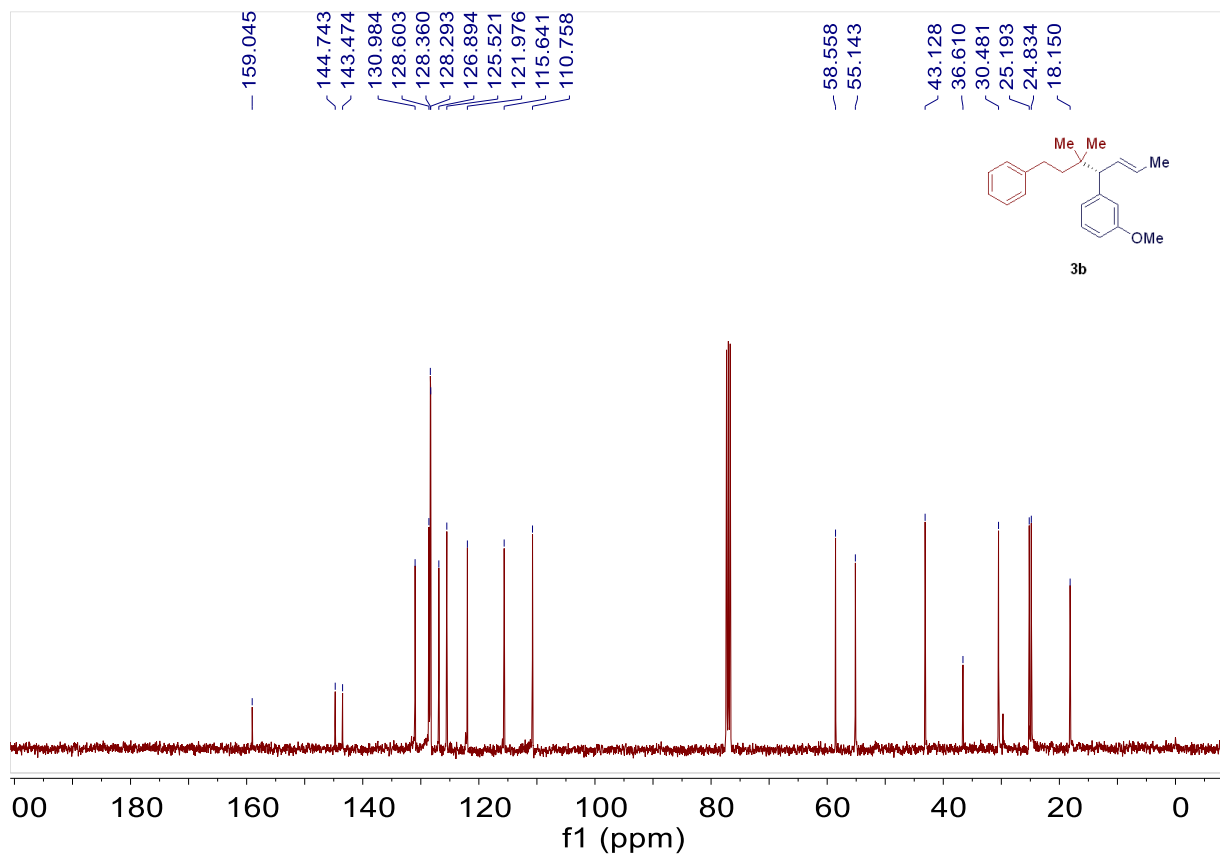
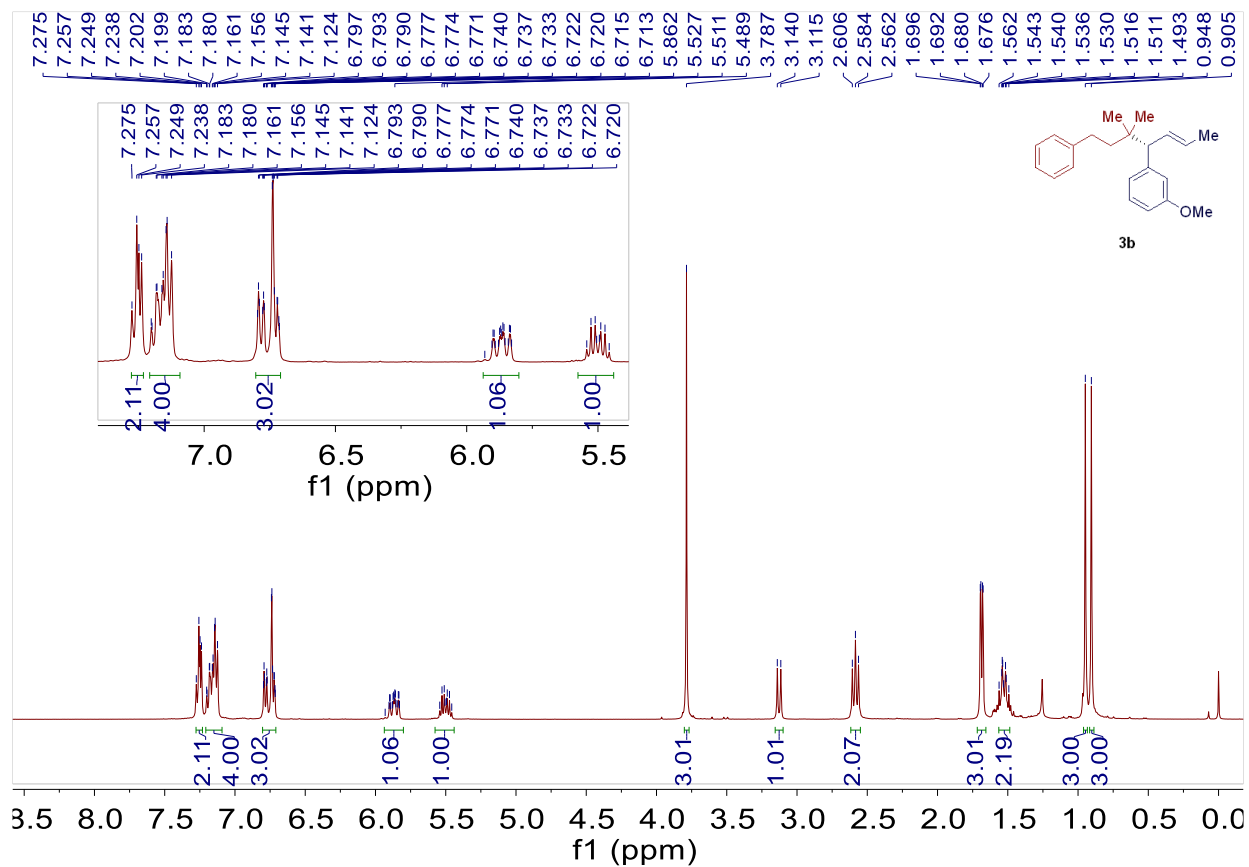
## 11. References

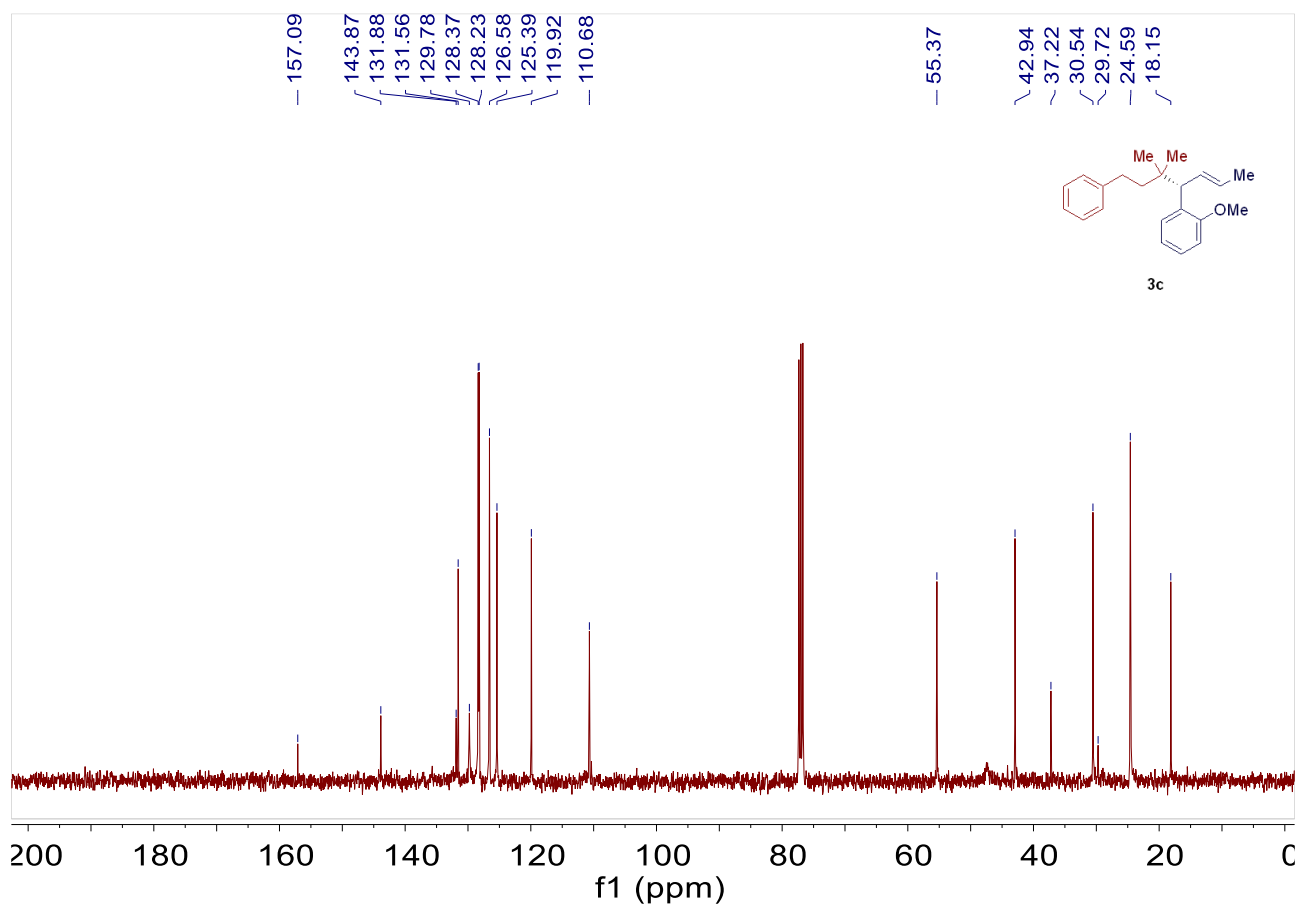
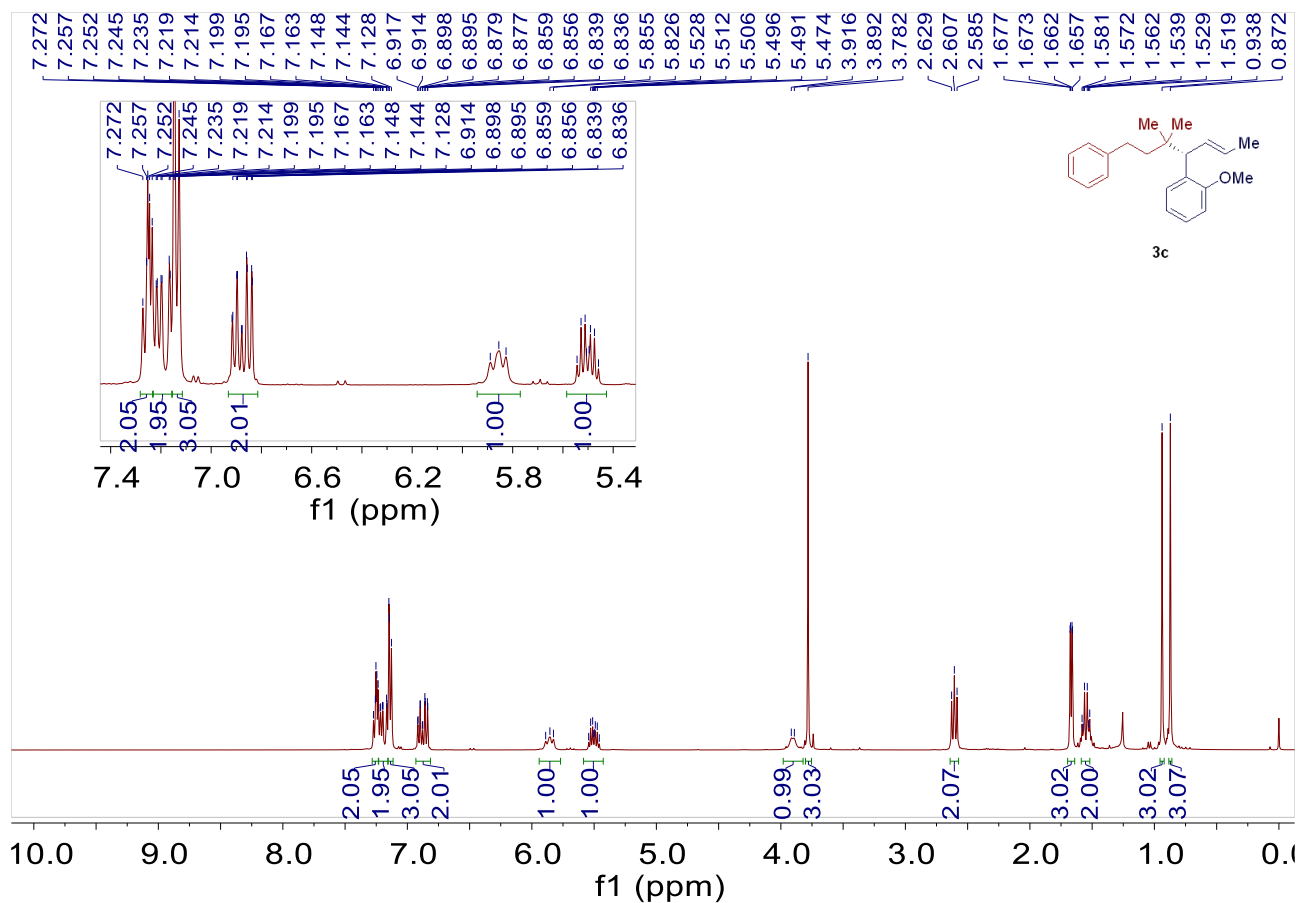
- [1] (a) A. Serra-Muns, A. Guerinot, S. Reymond and J. Cossy, *Chem. Commun.*, 2010, **46**, 4178-4180. (b) Marion, Nicolas, R. Gealageas, and S. P. Nolan, *Org. Lett.*, 2007, **9**, 2653-2656.
- [2] (a) H. M. Huang, P. Bellotti, P. M. Pfluger, J. L. Schwarz, B. Heidrich and F. Glorius, *J. Am. Chem. Soc.*, 2020, **142**, 10173-10183. (b) A. S. Dudnik and G. C. Fu, *J. Am. Chem. Soc.*, 2012, **134**, 10693-10697. (c) L. Wang and C. Wang, *Org. Lett.*, 2020, **22**, 8829-8835.
- [3] F. Chen, Y. Zhang, L. Yu and S. Zhu, *Angew. Chem. Int. Ed.*, 2017, **56**, 2022-2025.
- [4] H.-H. Zhang, J.-J. Zhao and S. Yu, *J. Am. Chem. Soc.*, 2018, **140**, 16914-16919.

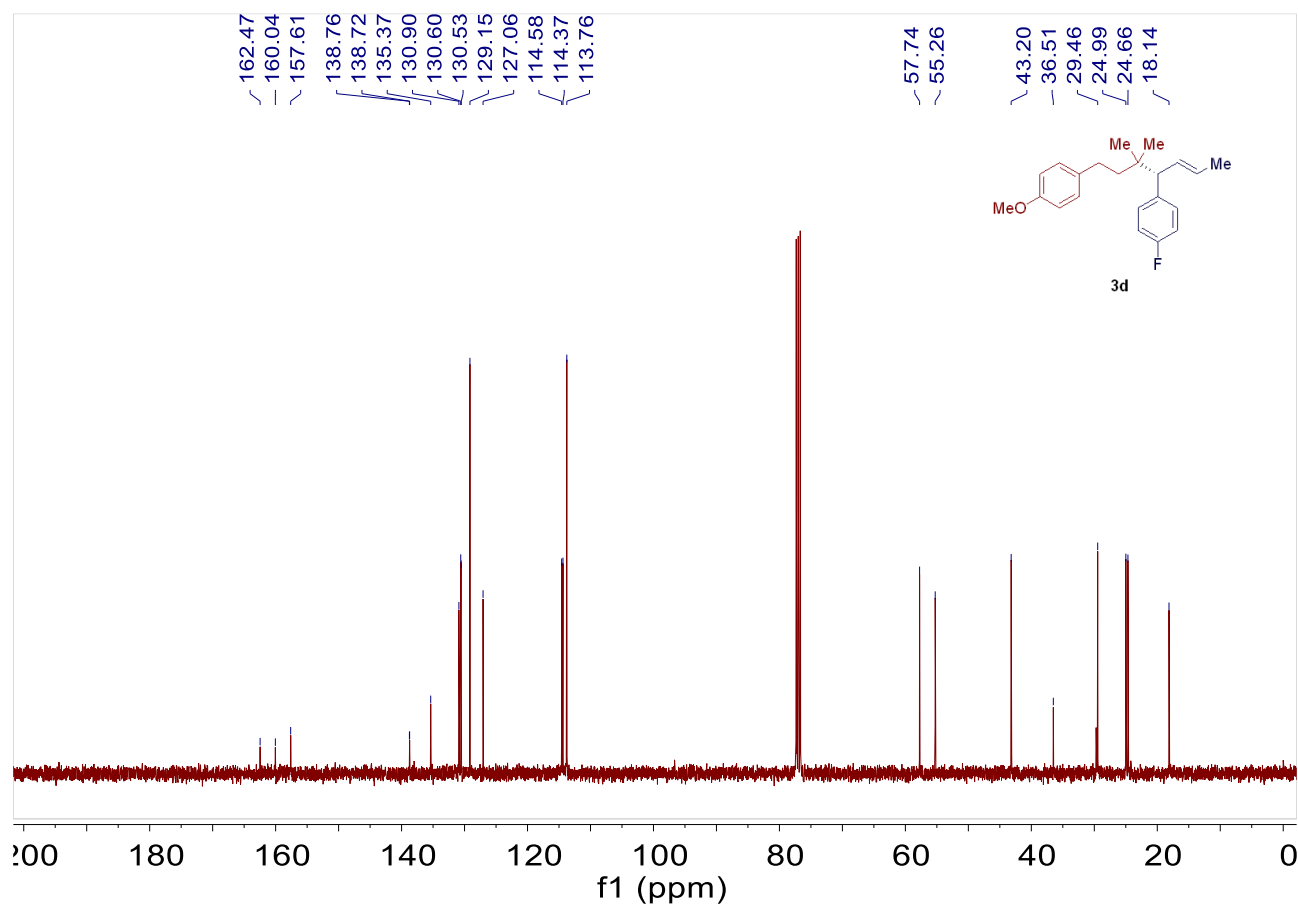
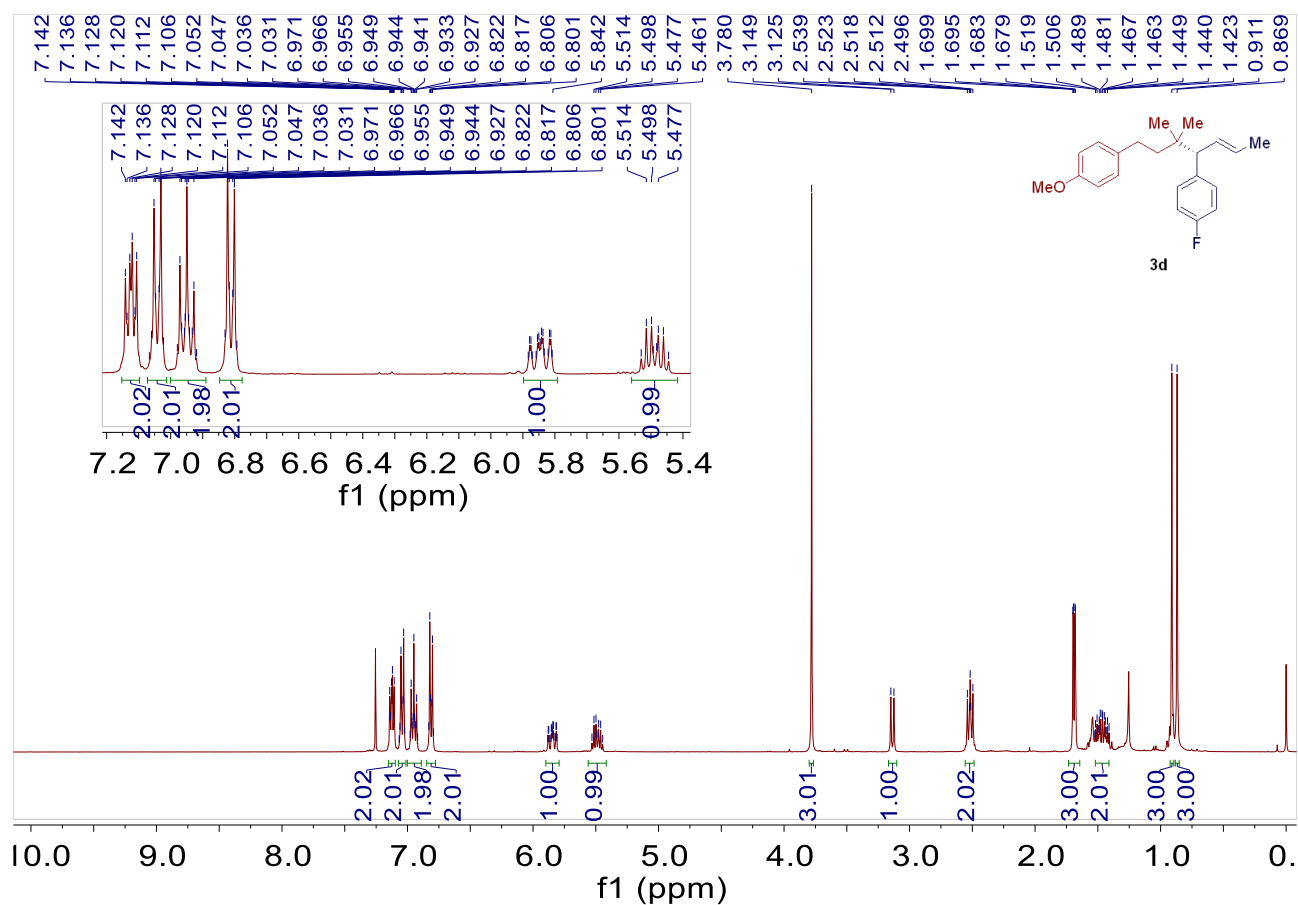
## 12. NMR spectra for all compounds

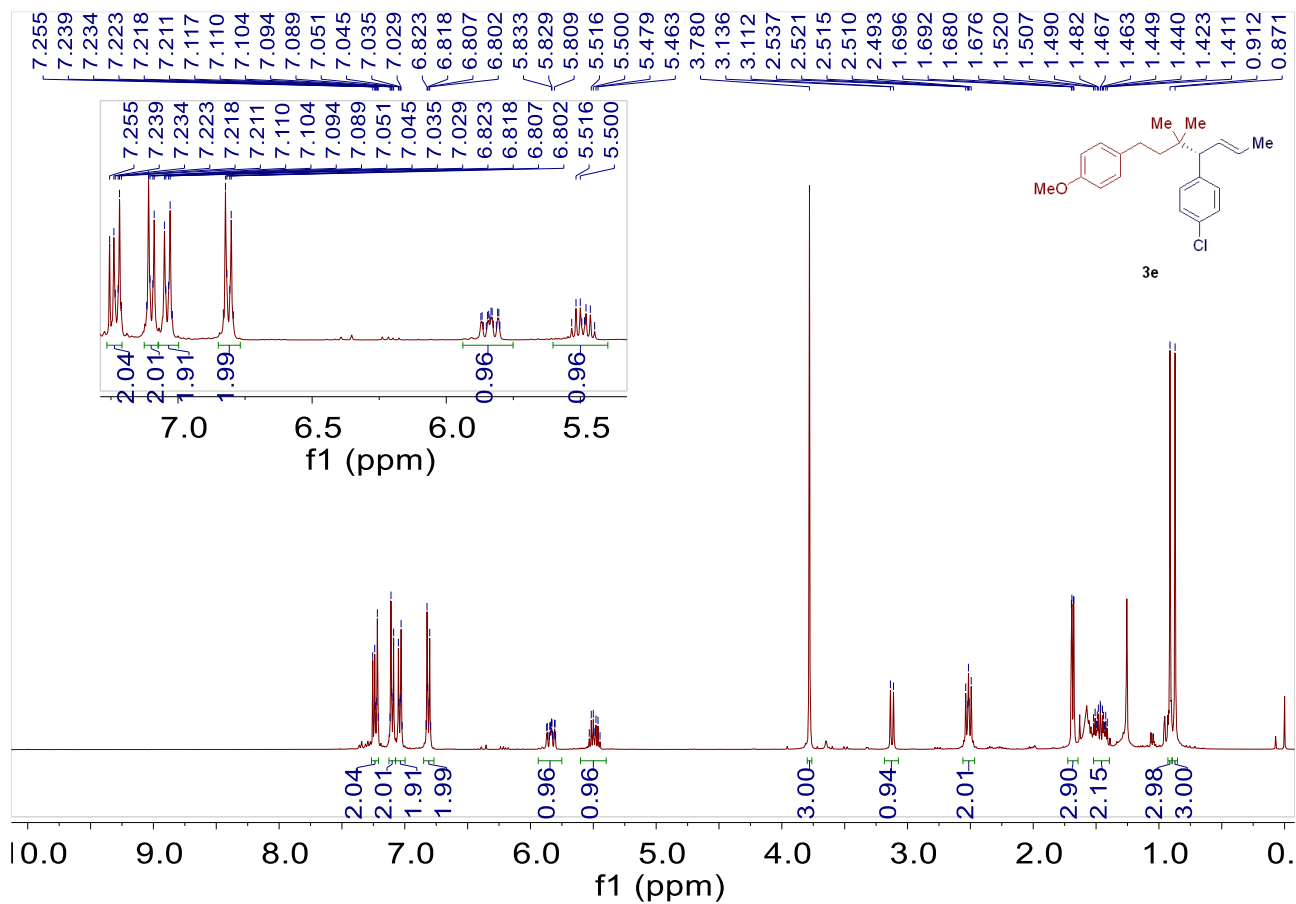
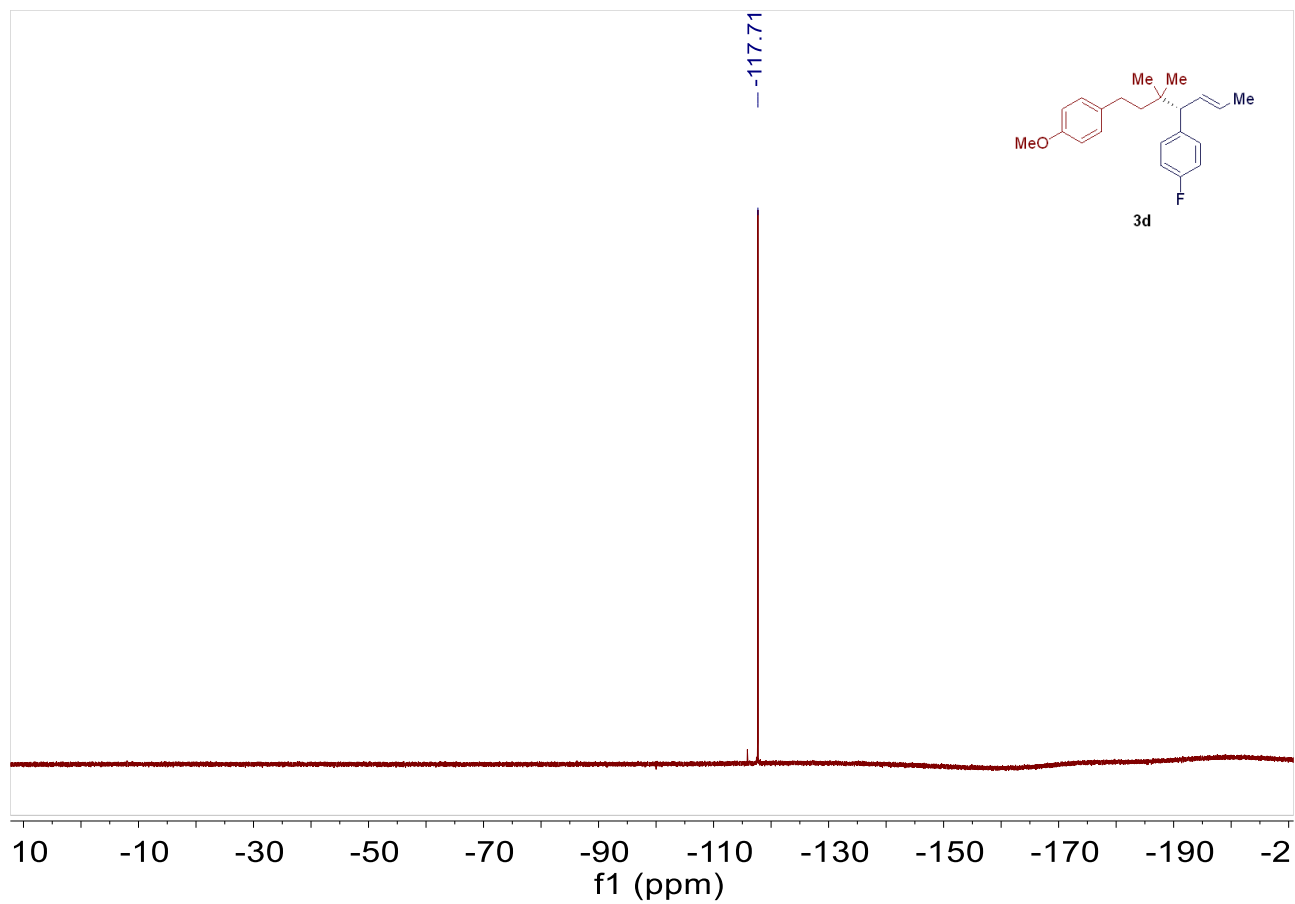


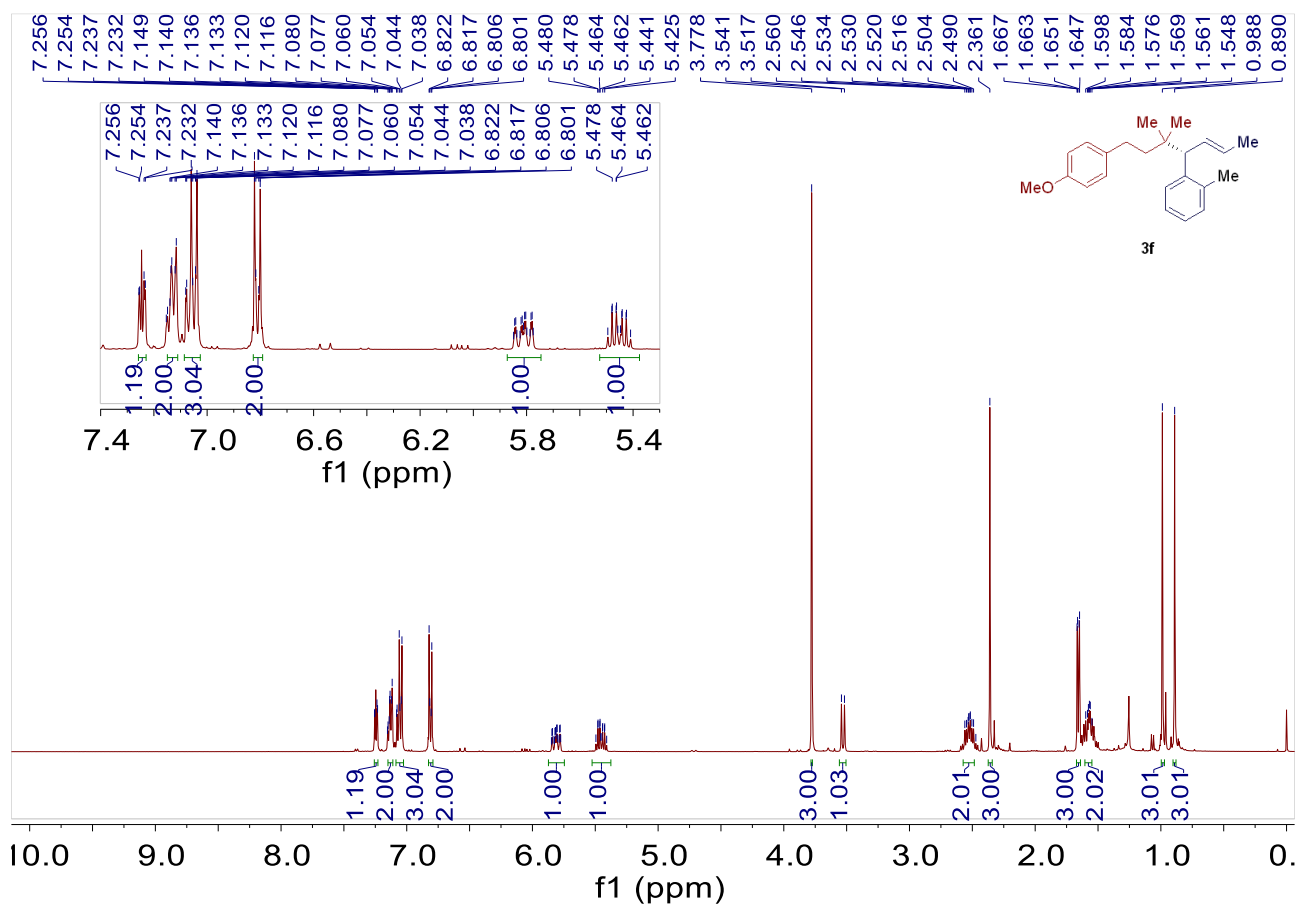
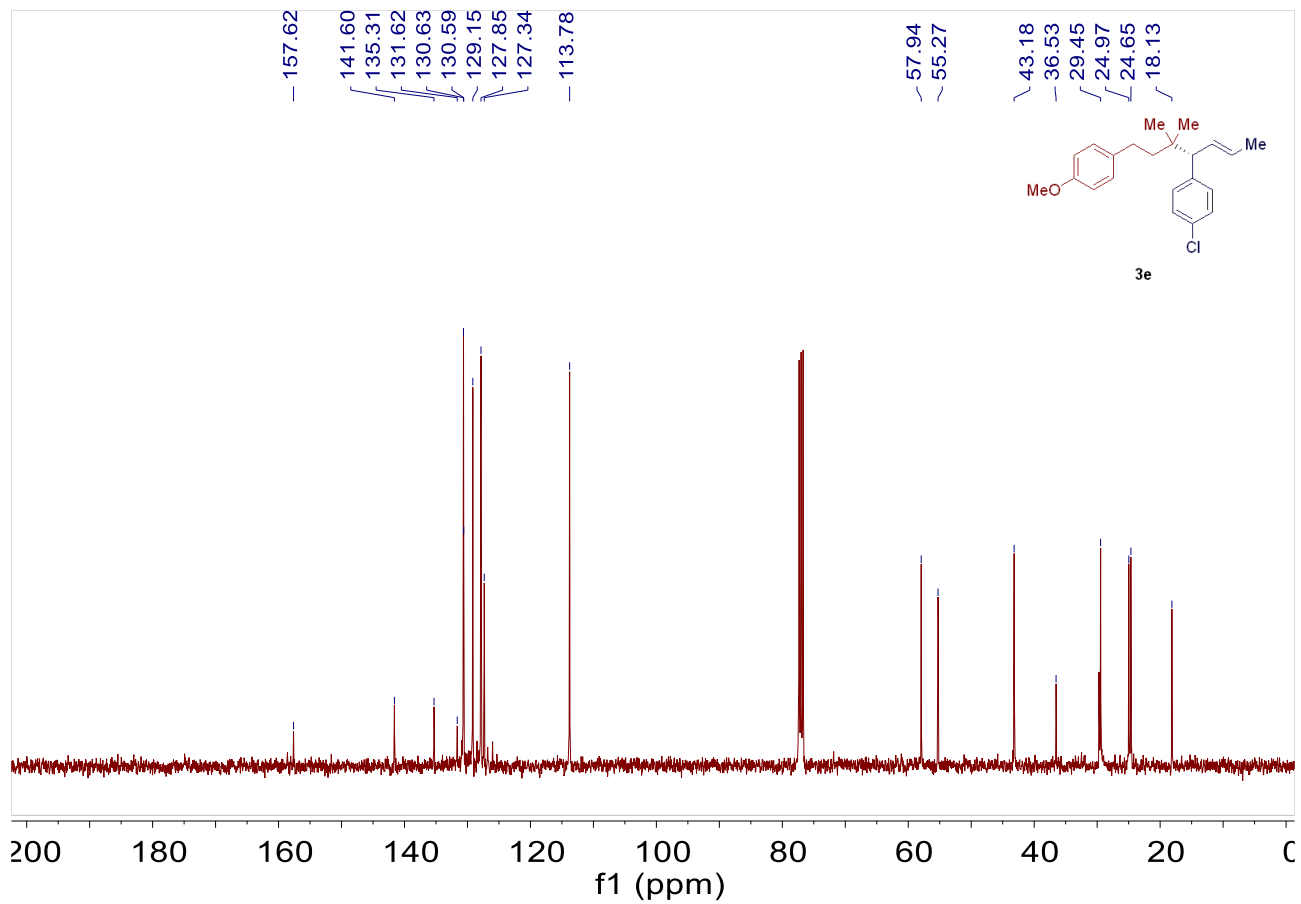


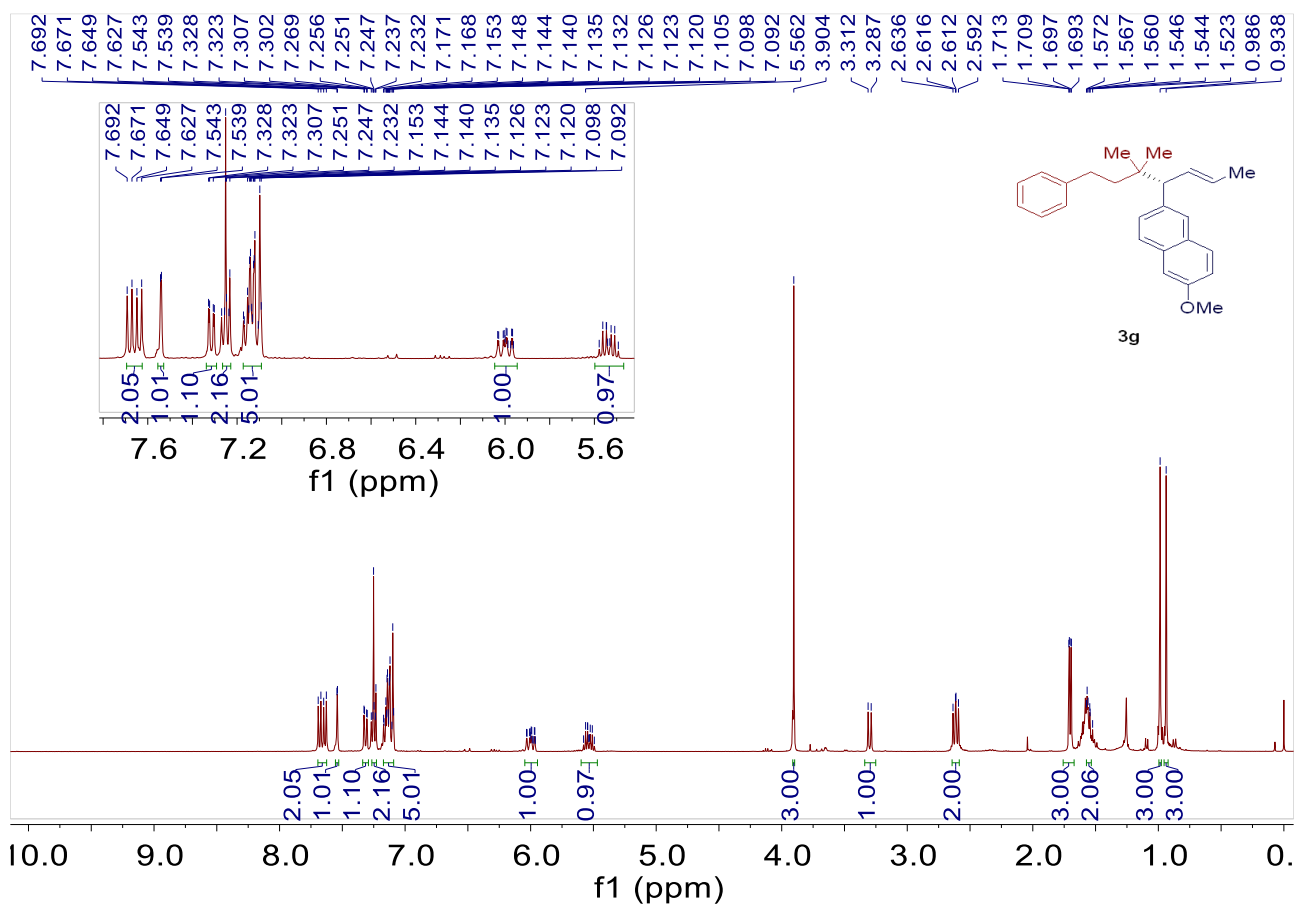
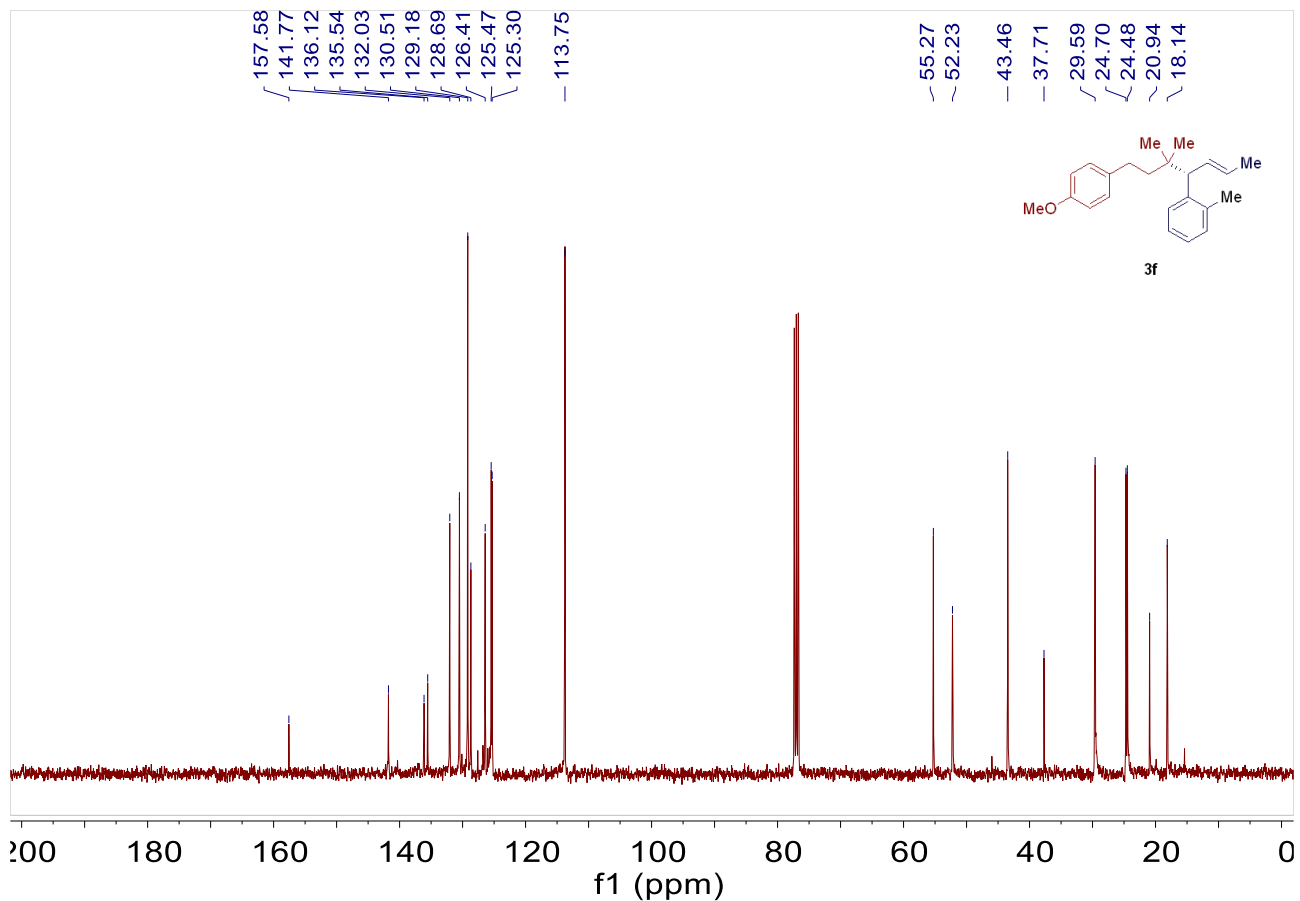


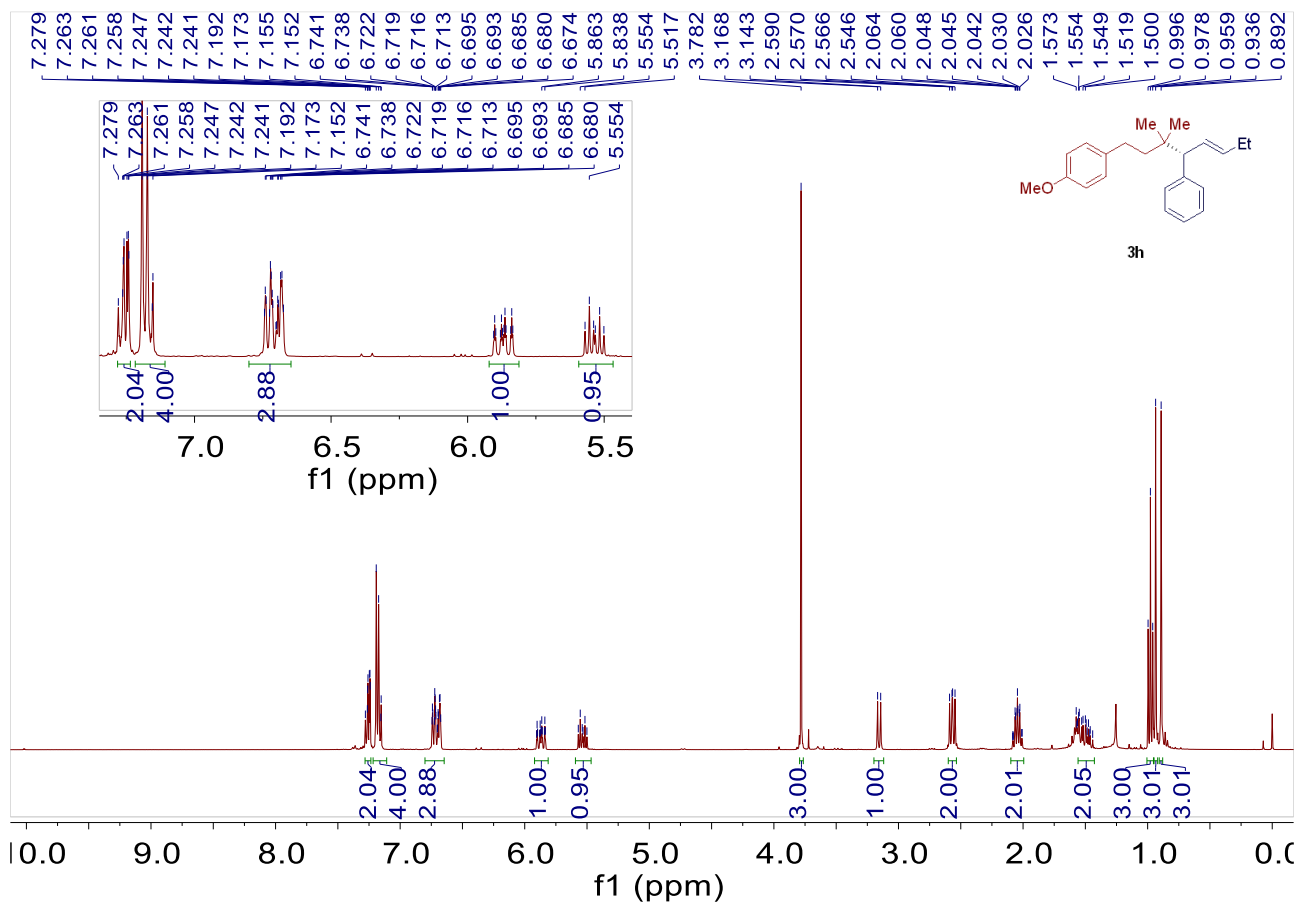
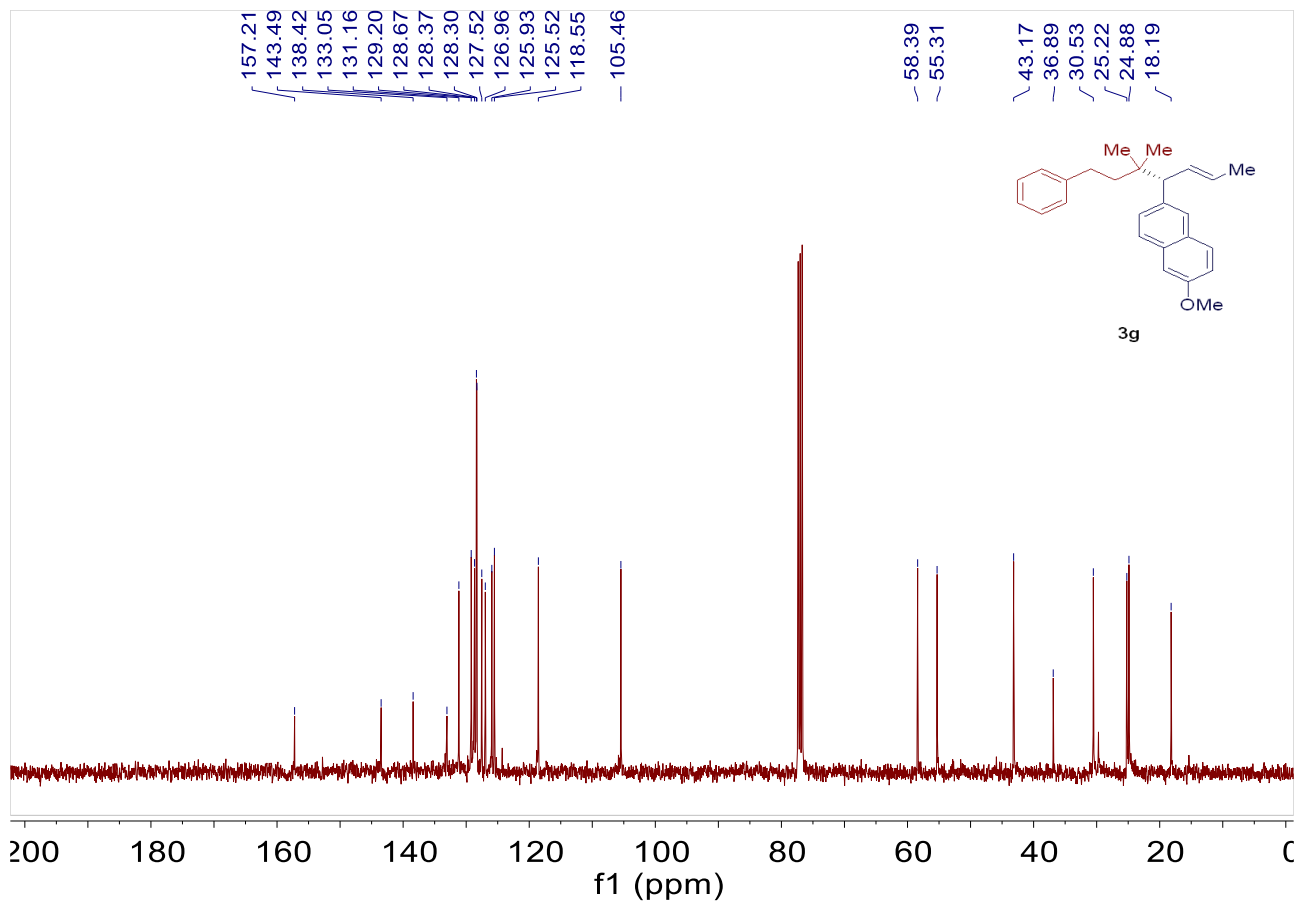


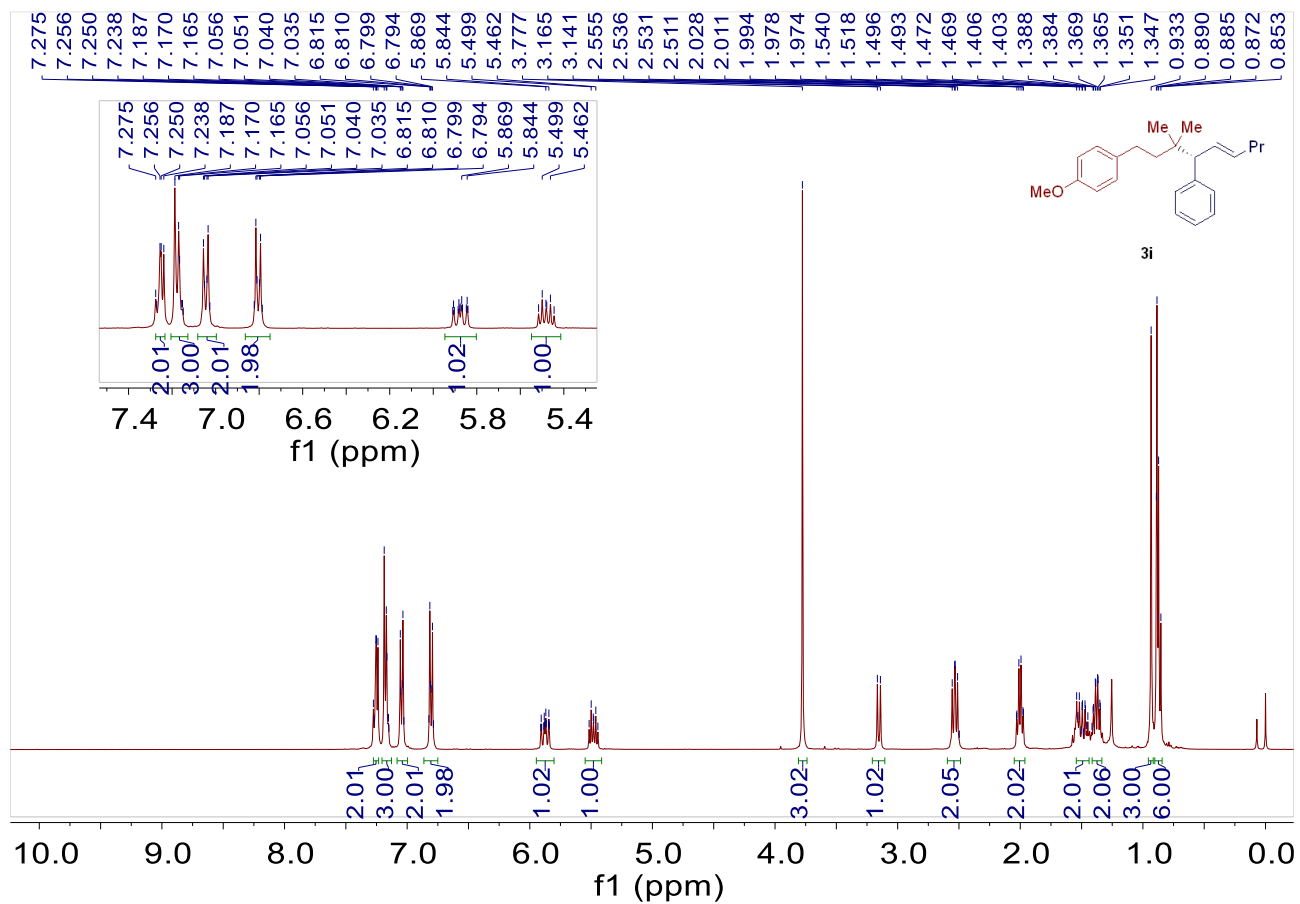
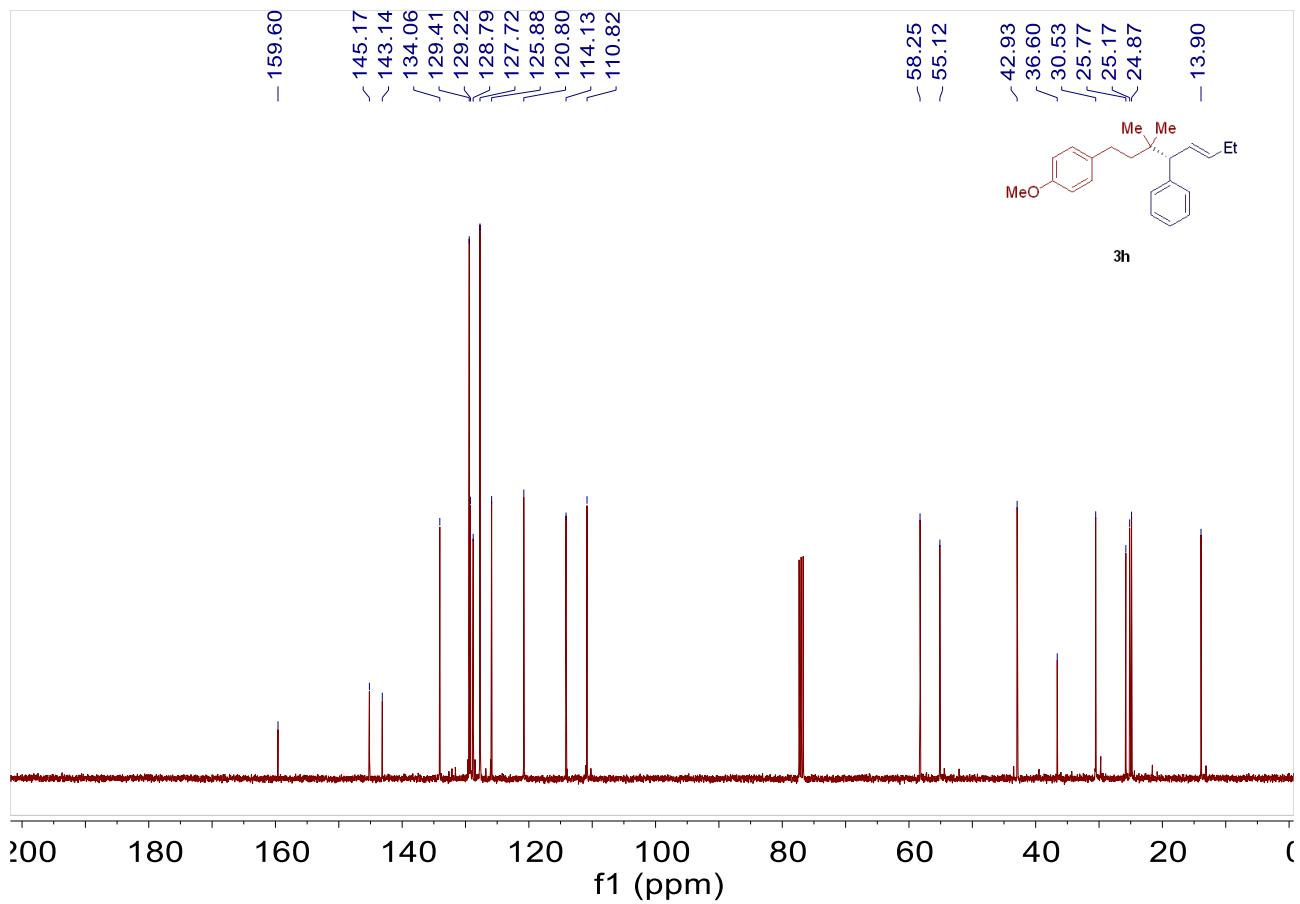




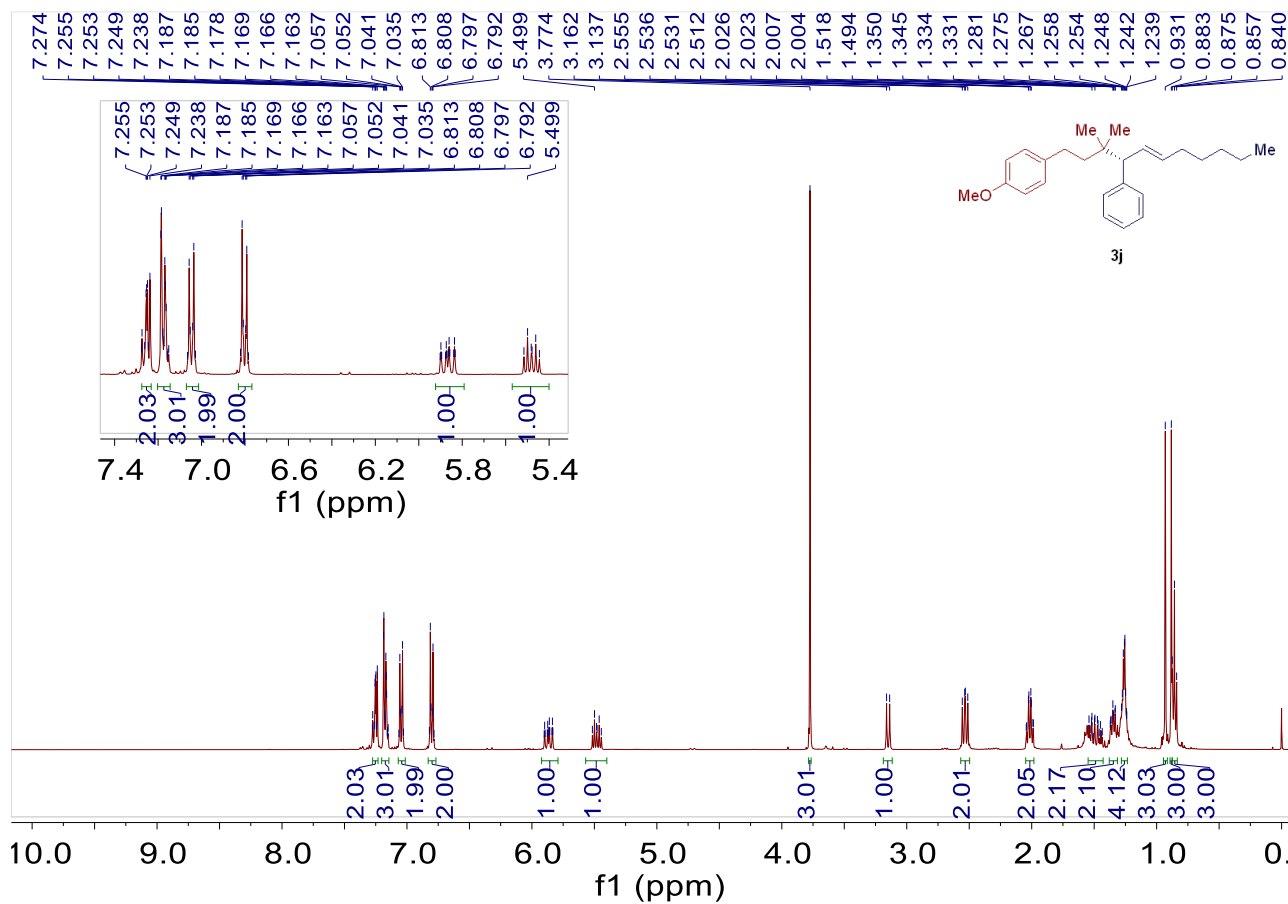
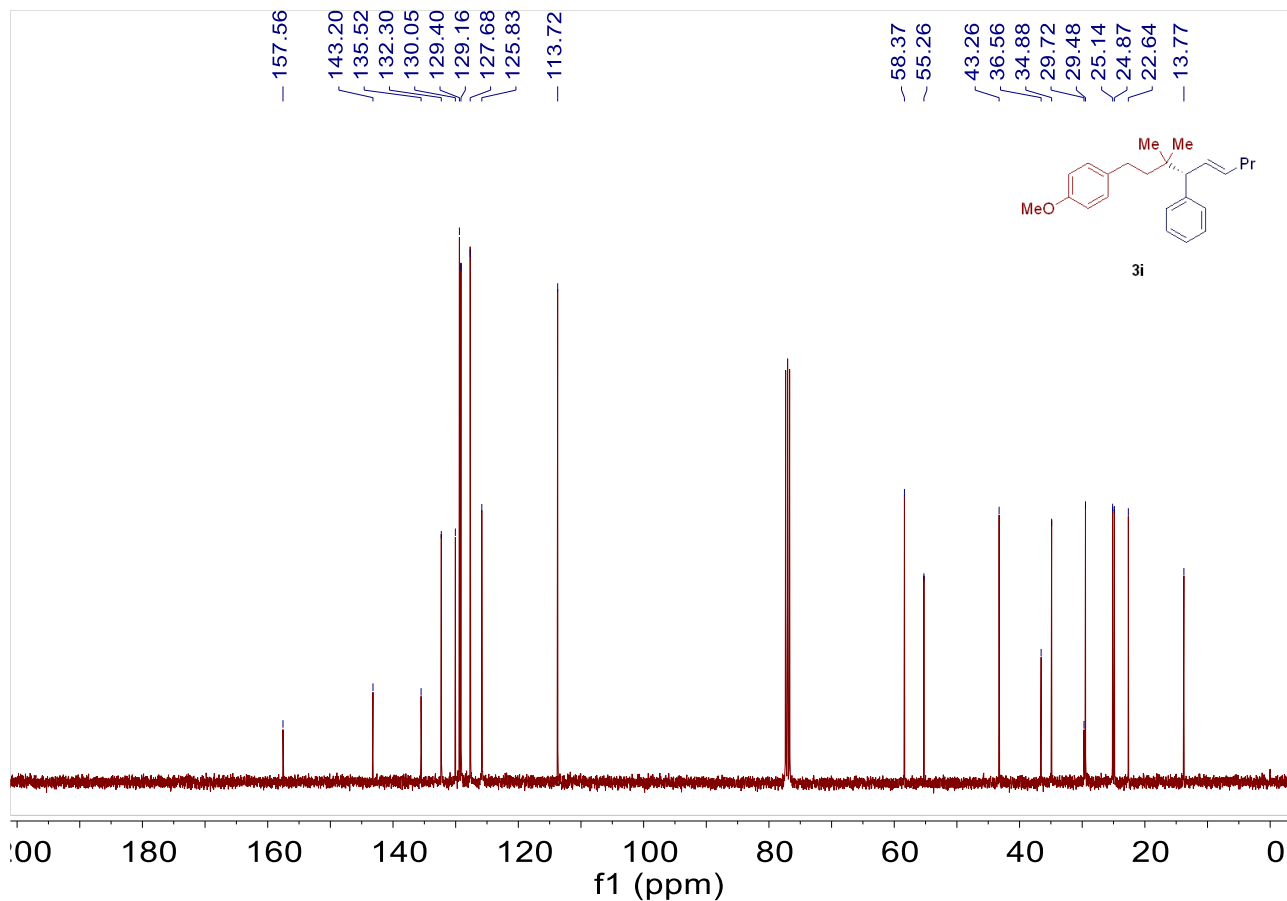


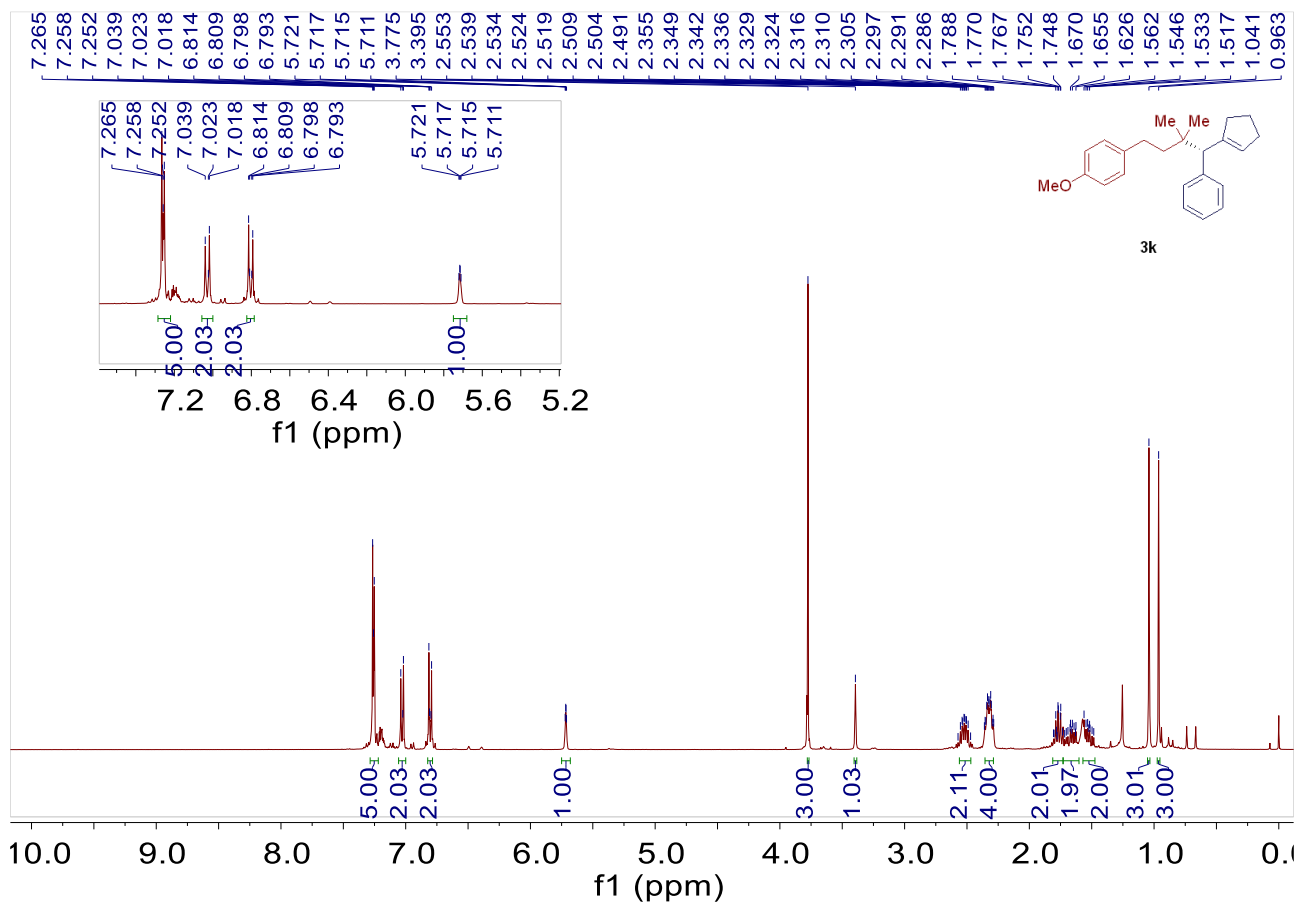
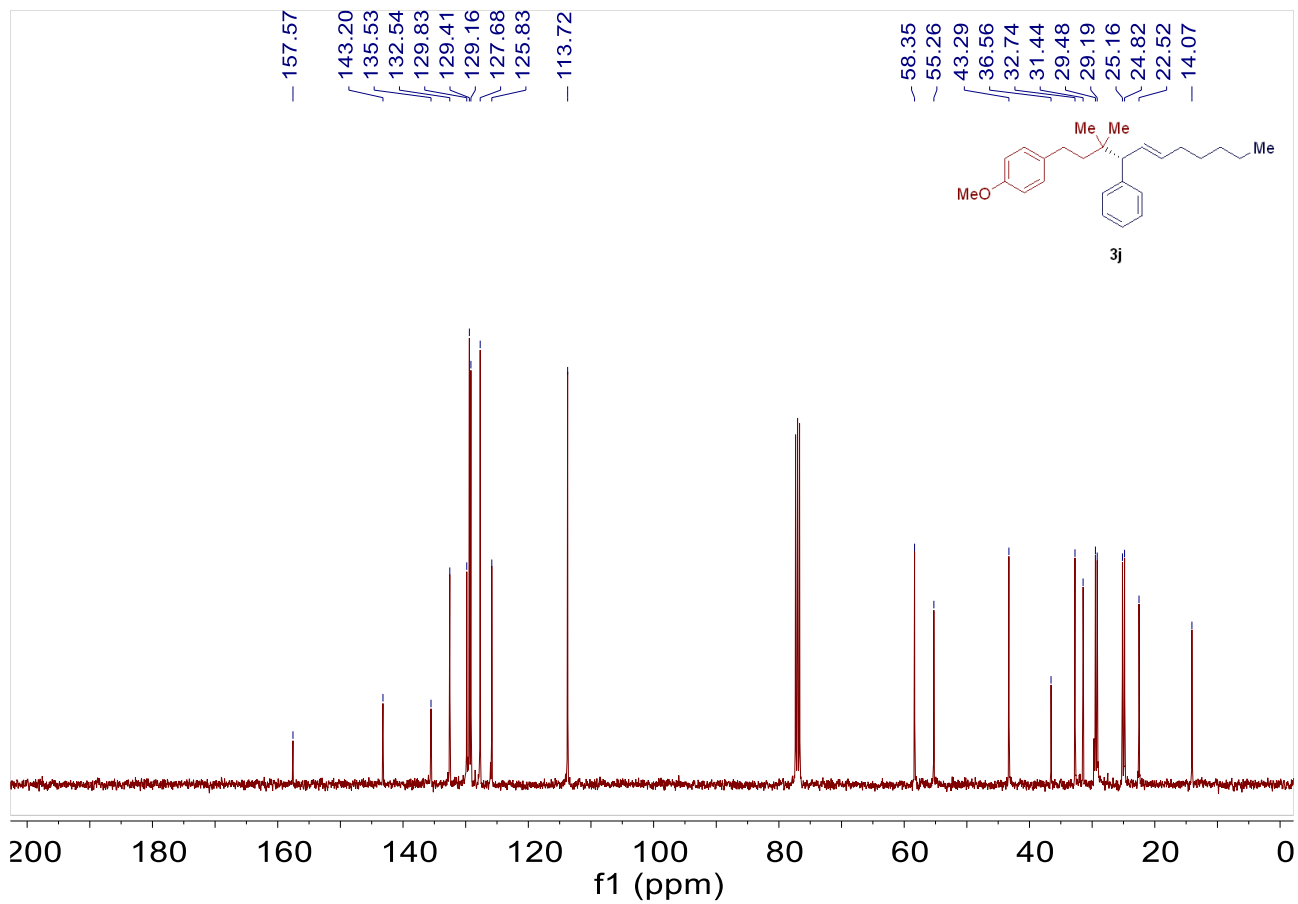


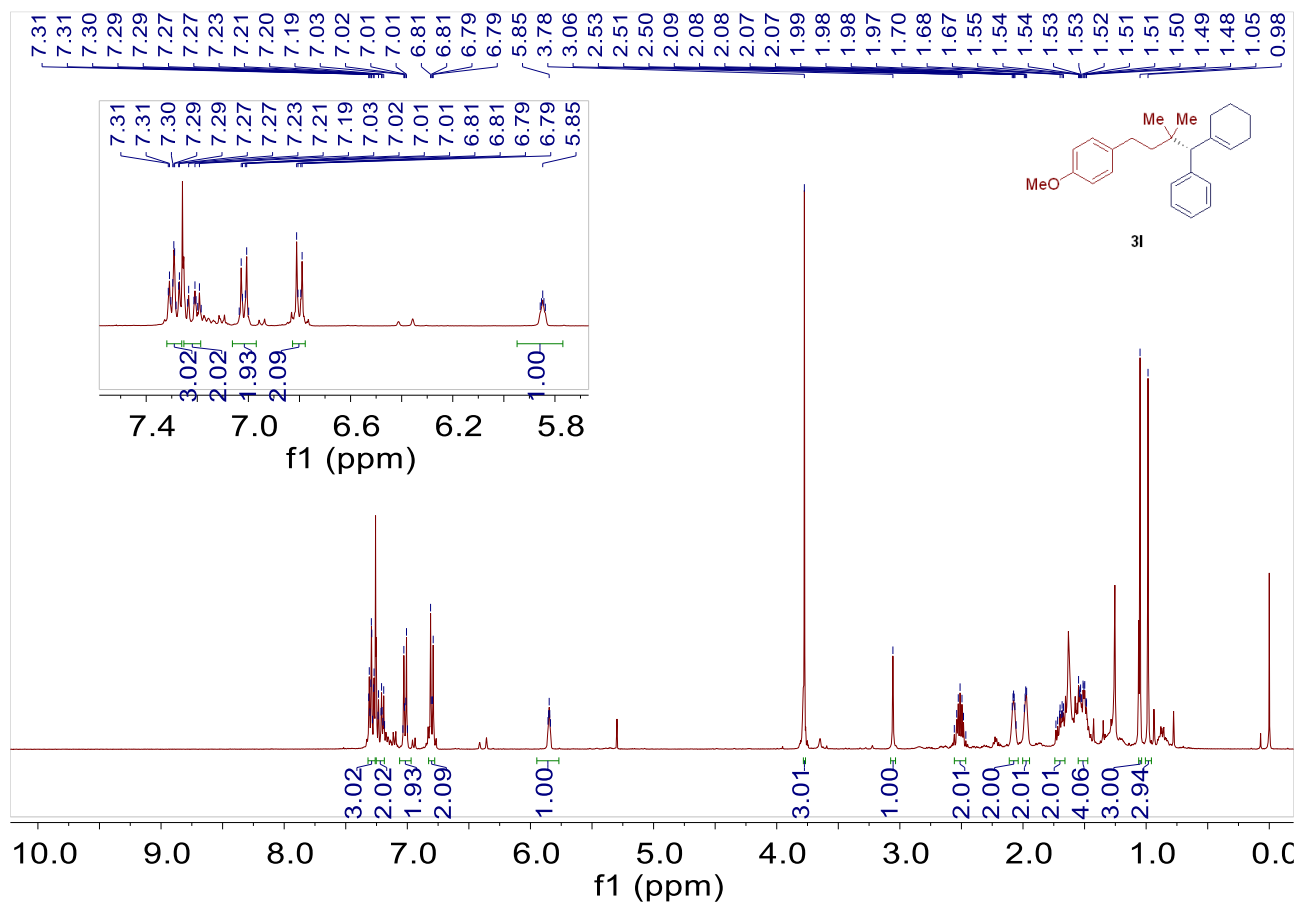
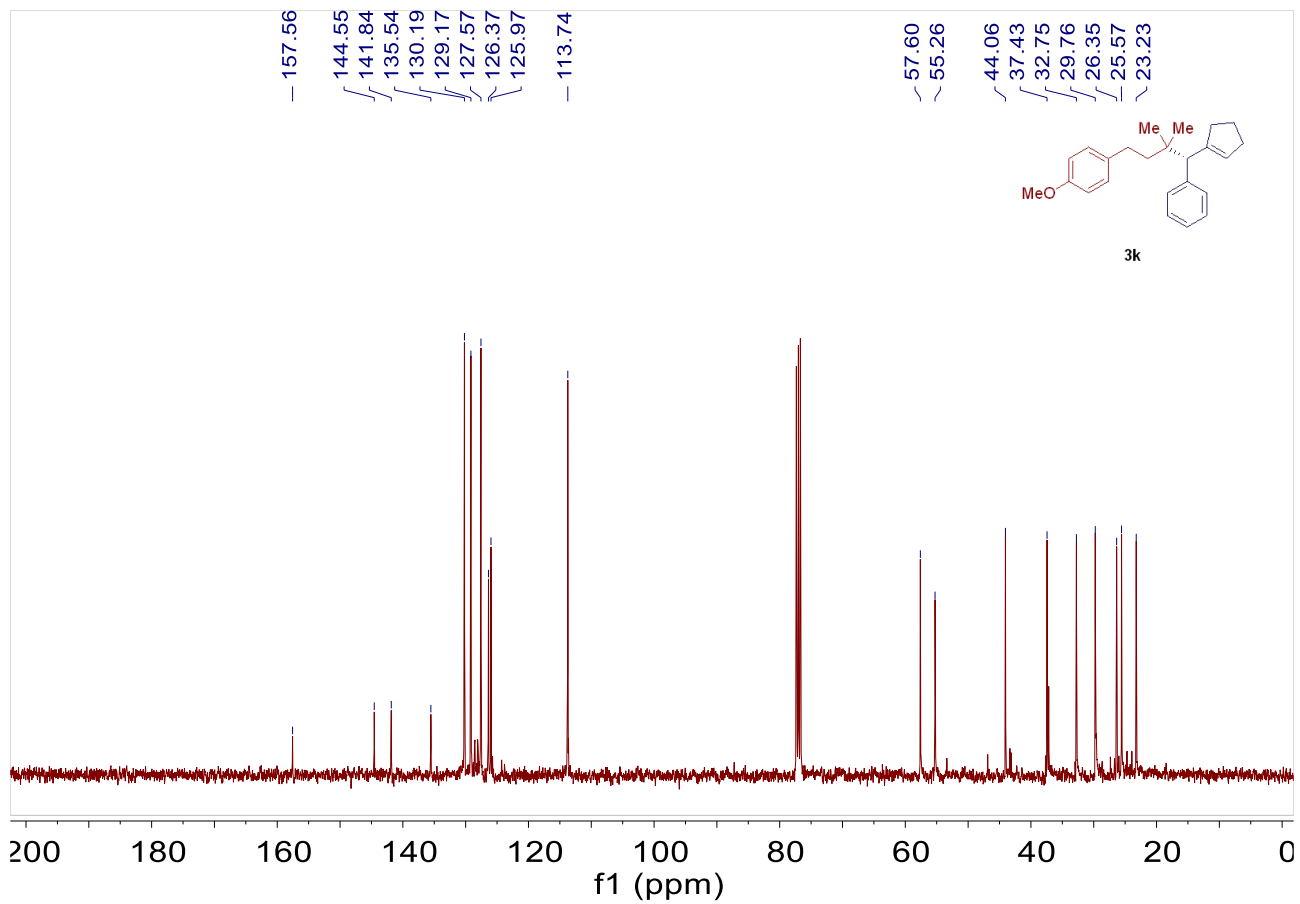


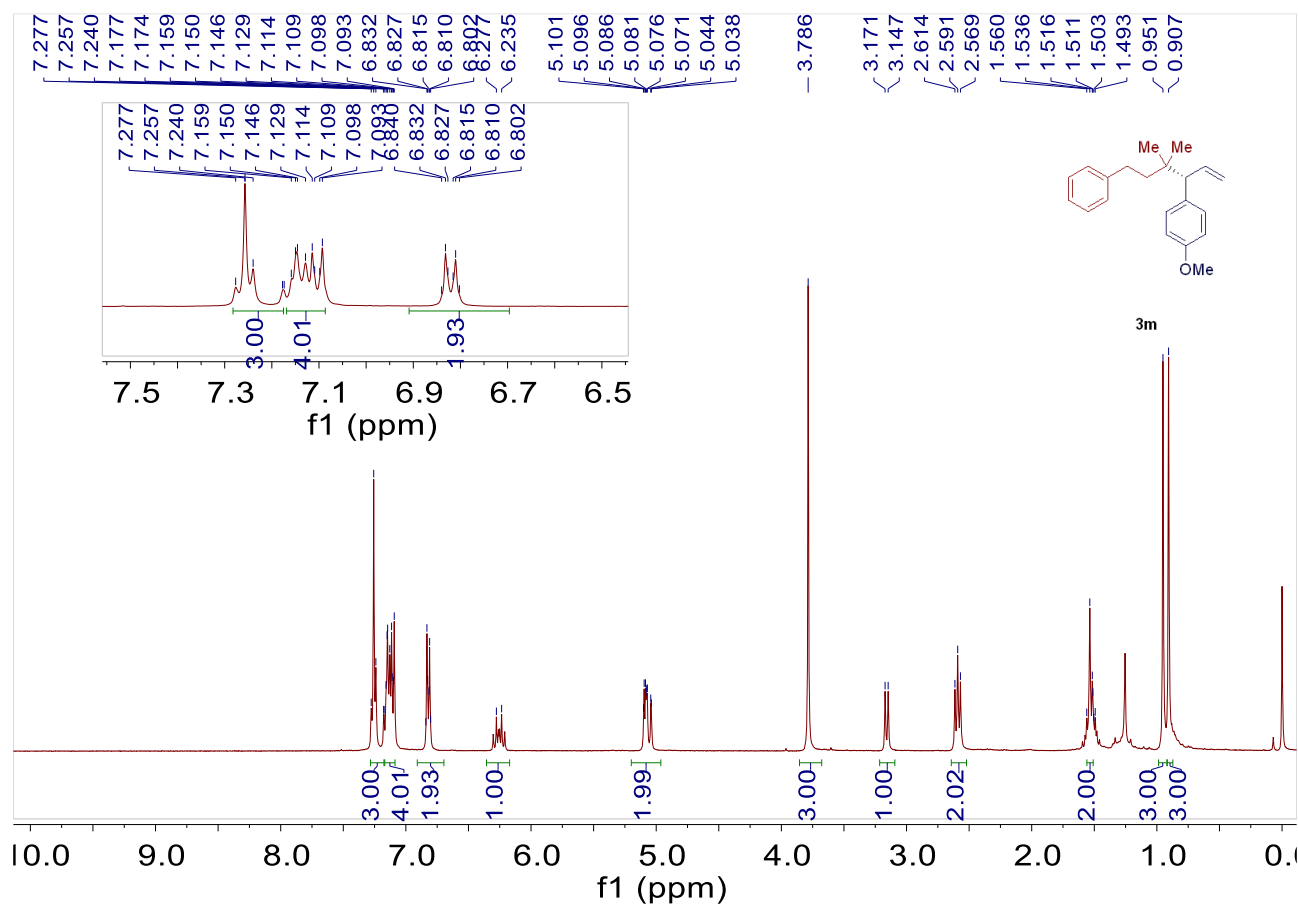
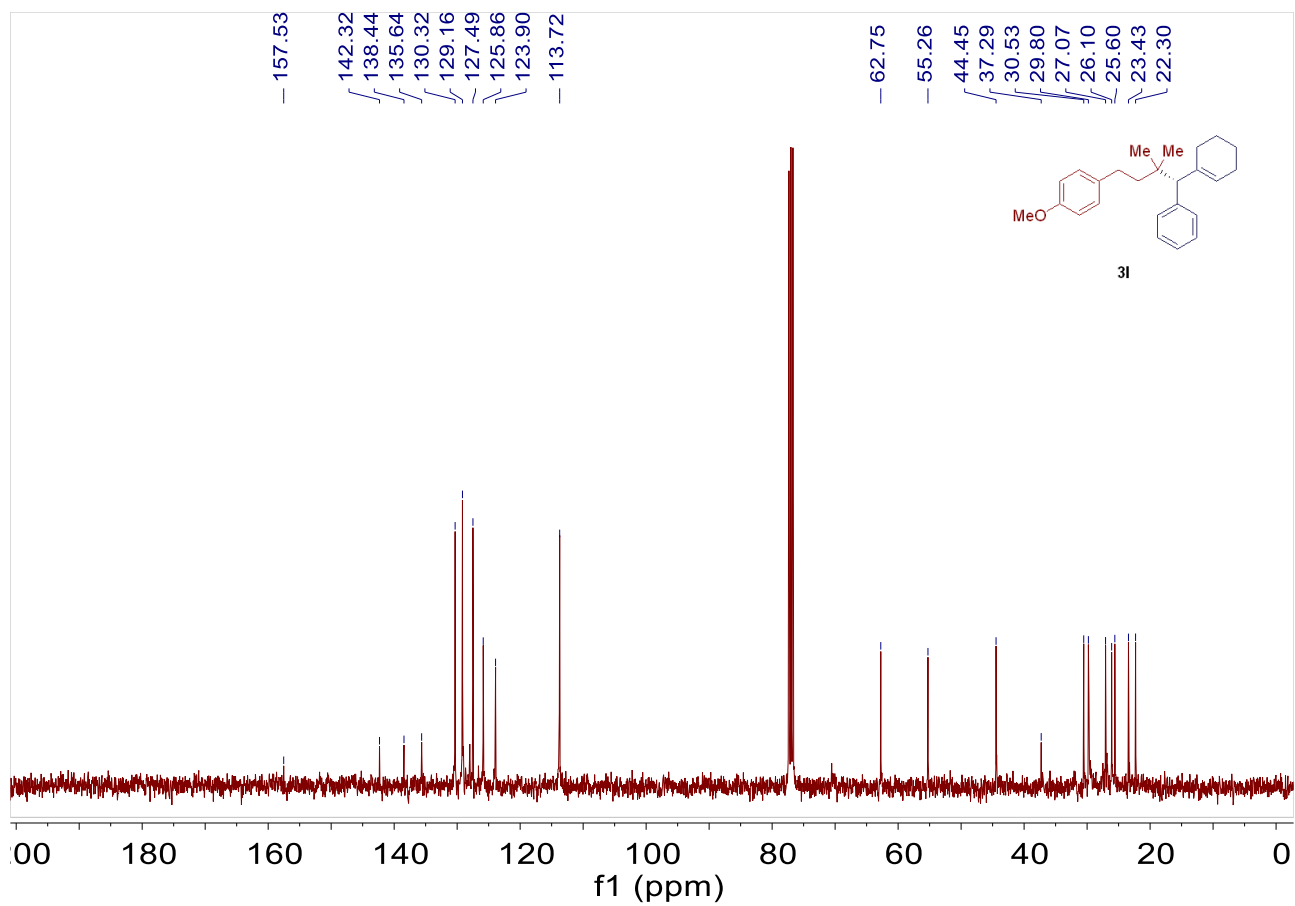


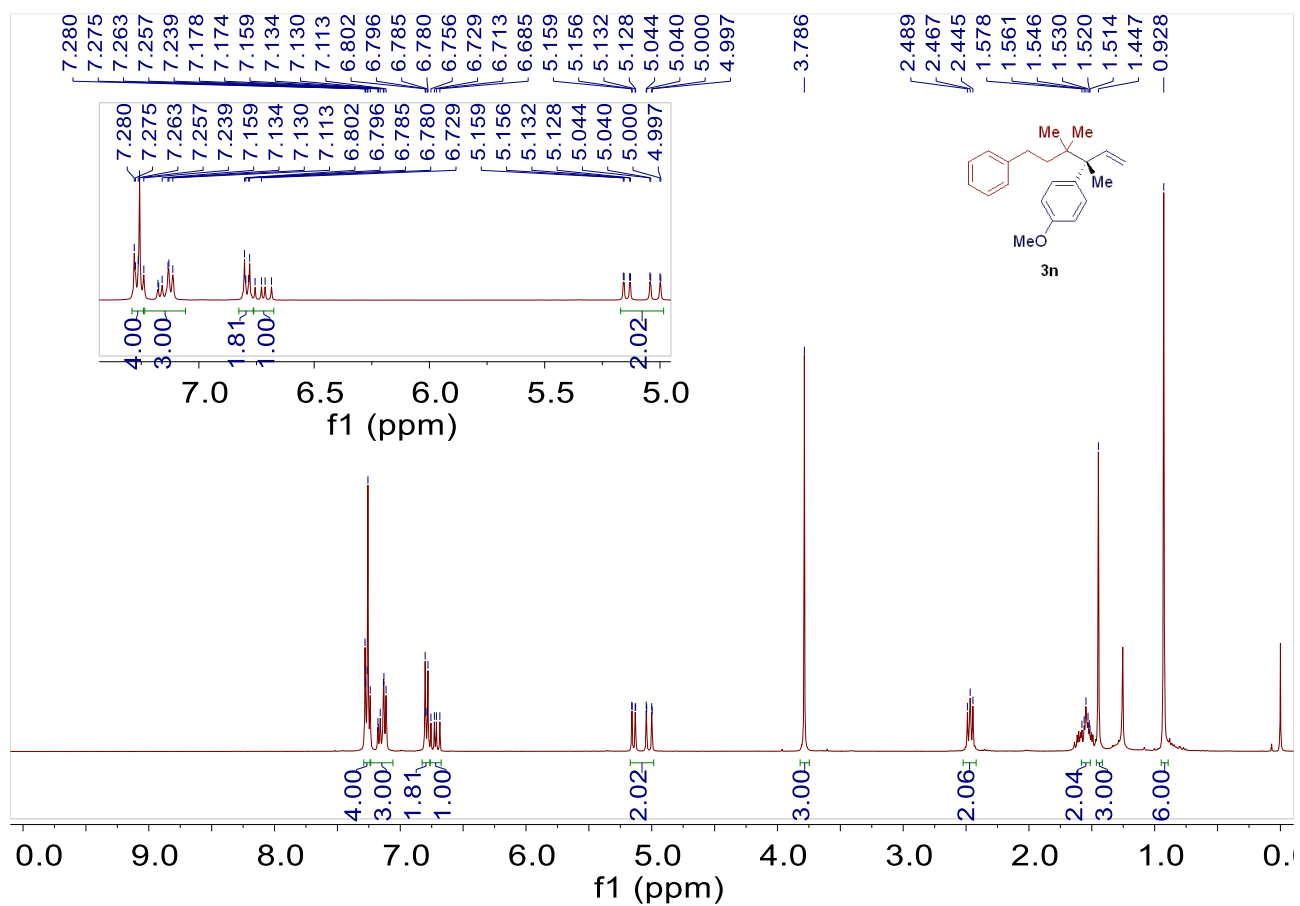
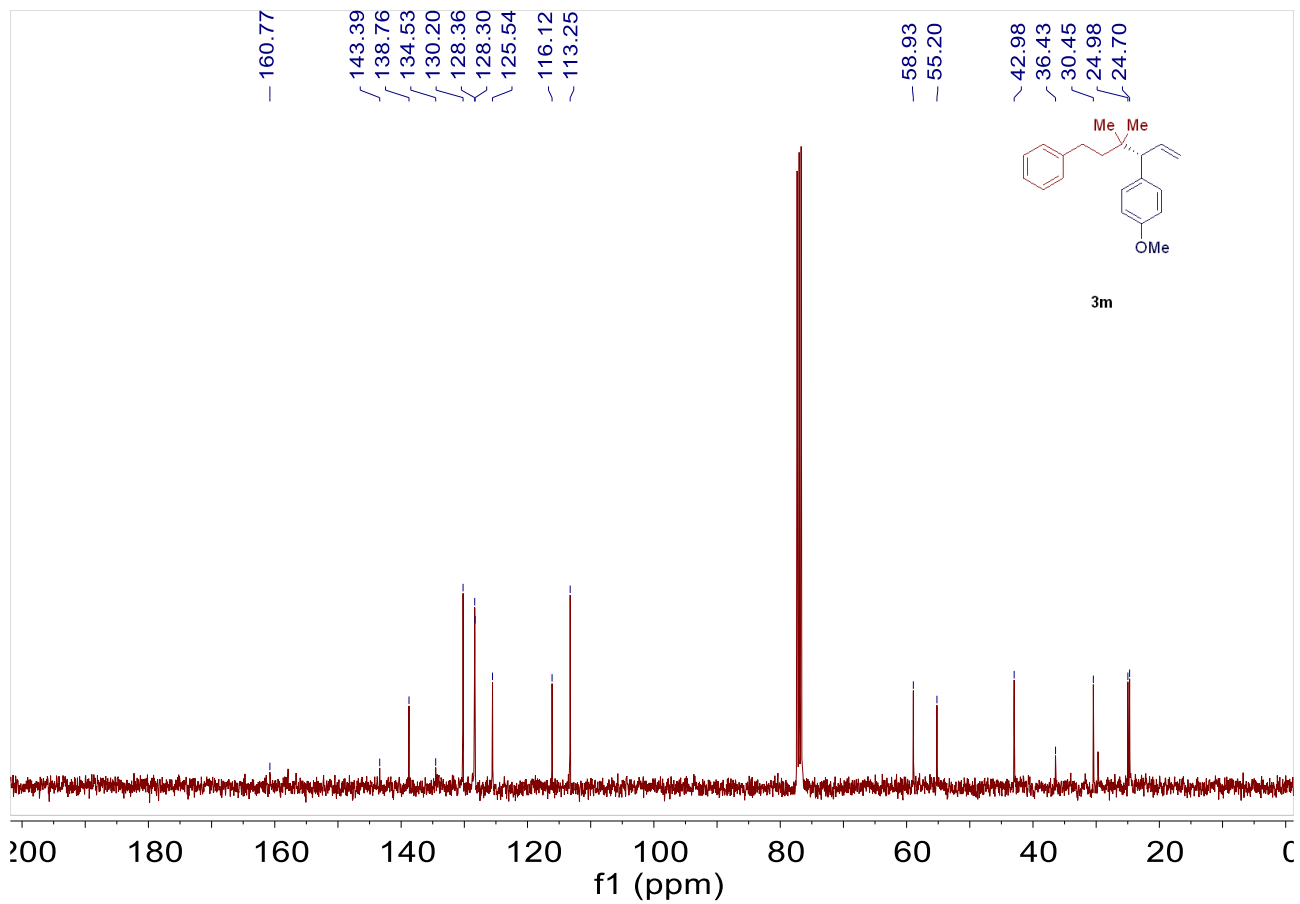


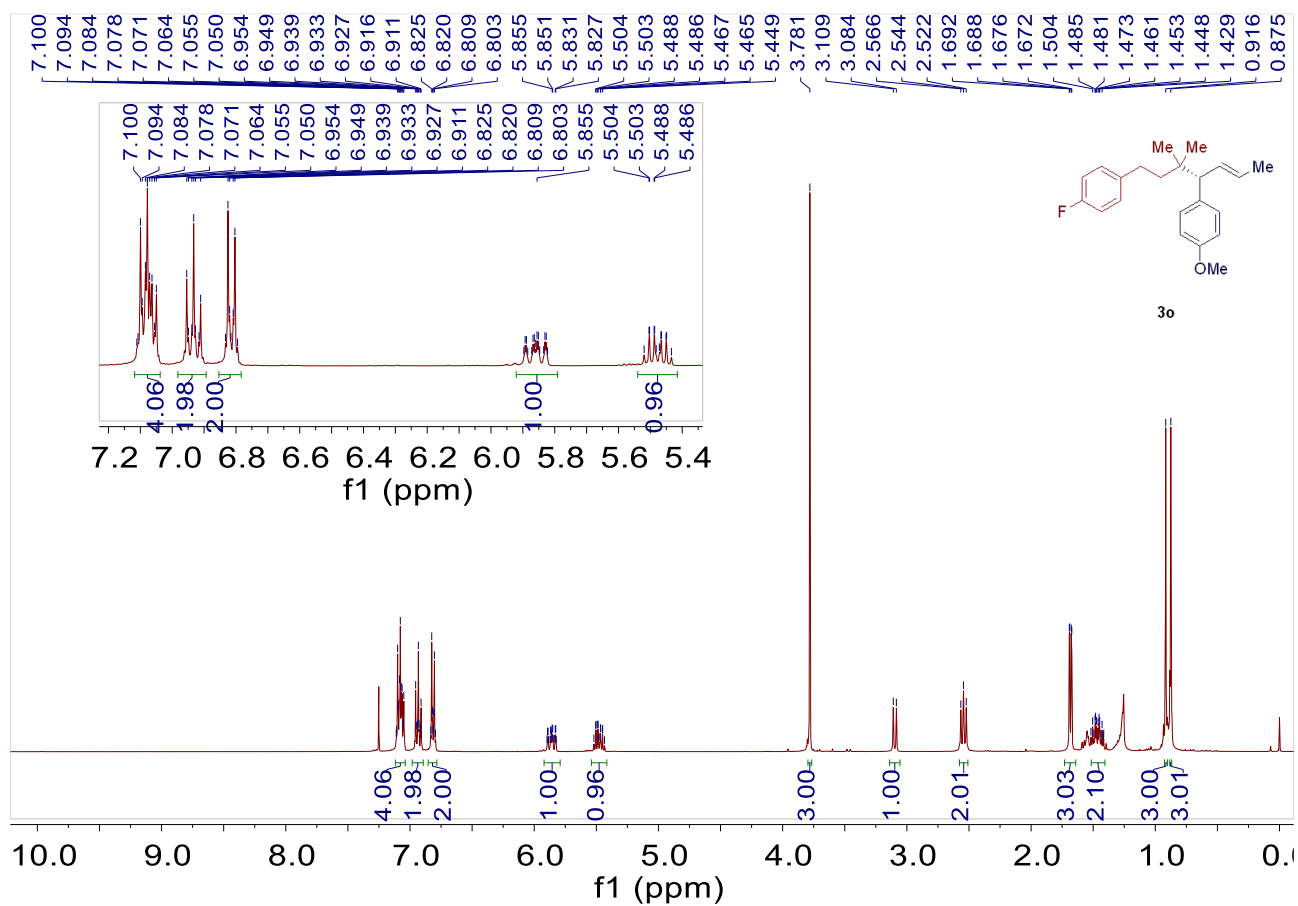
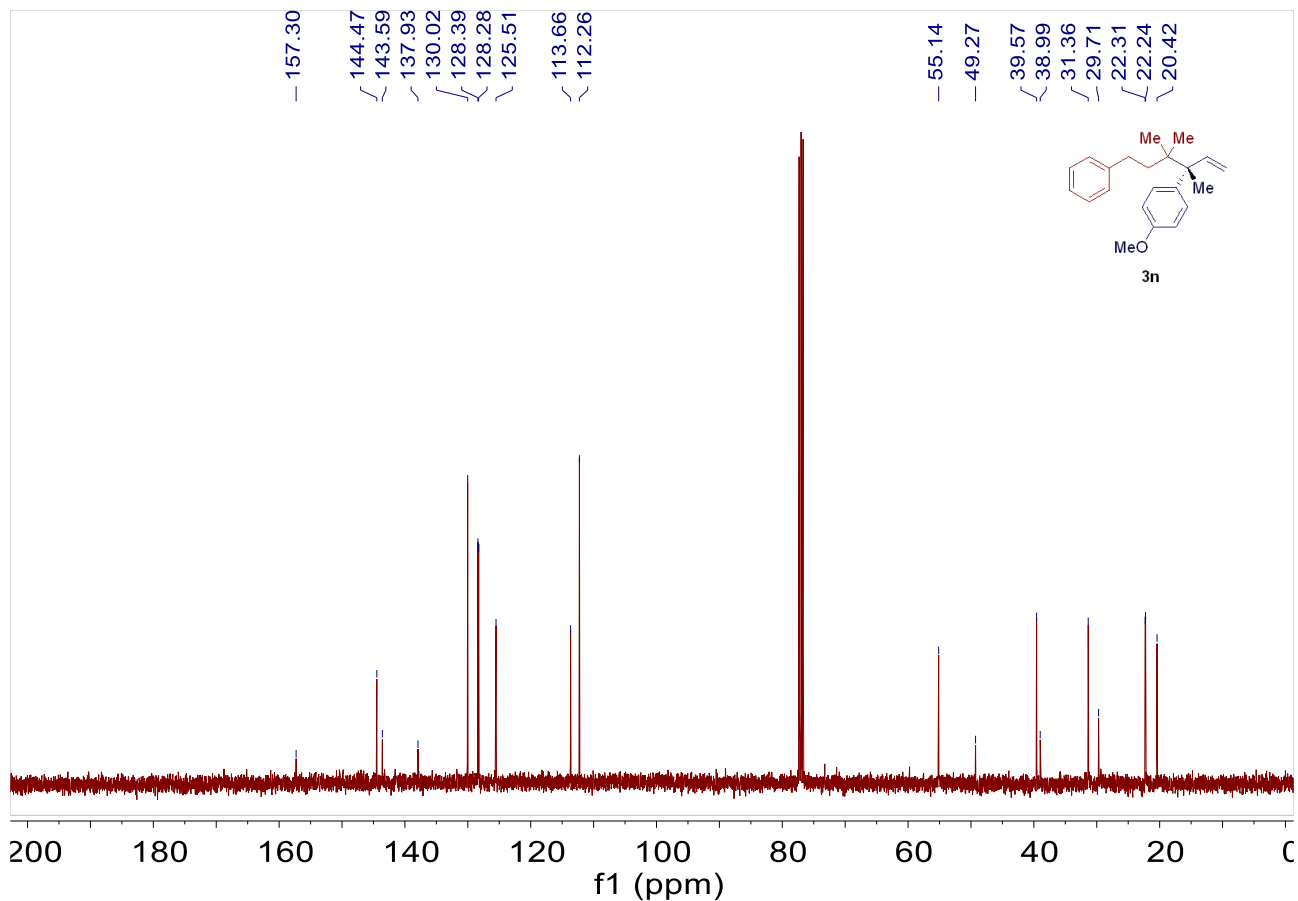


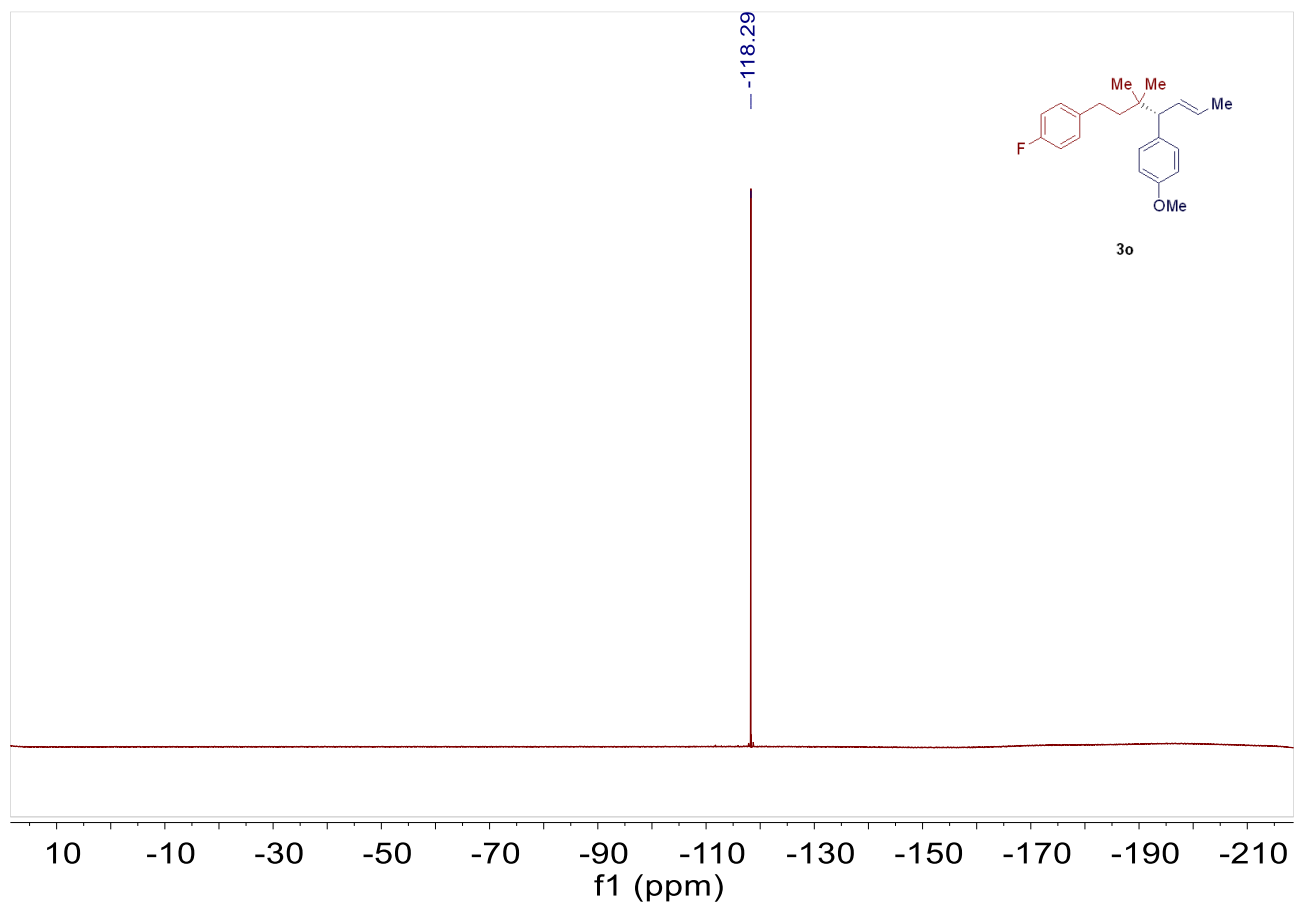
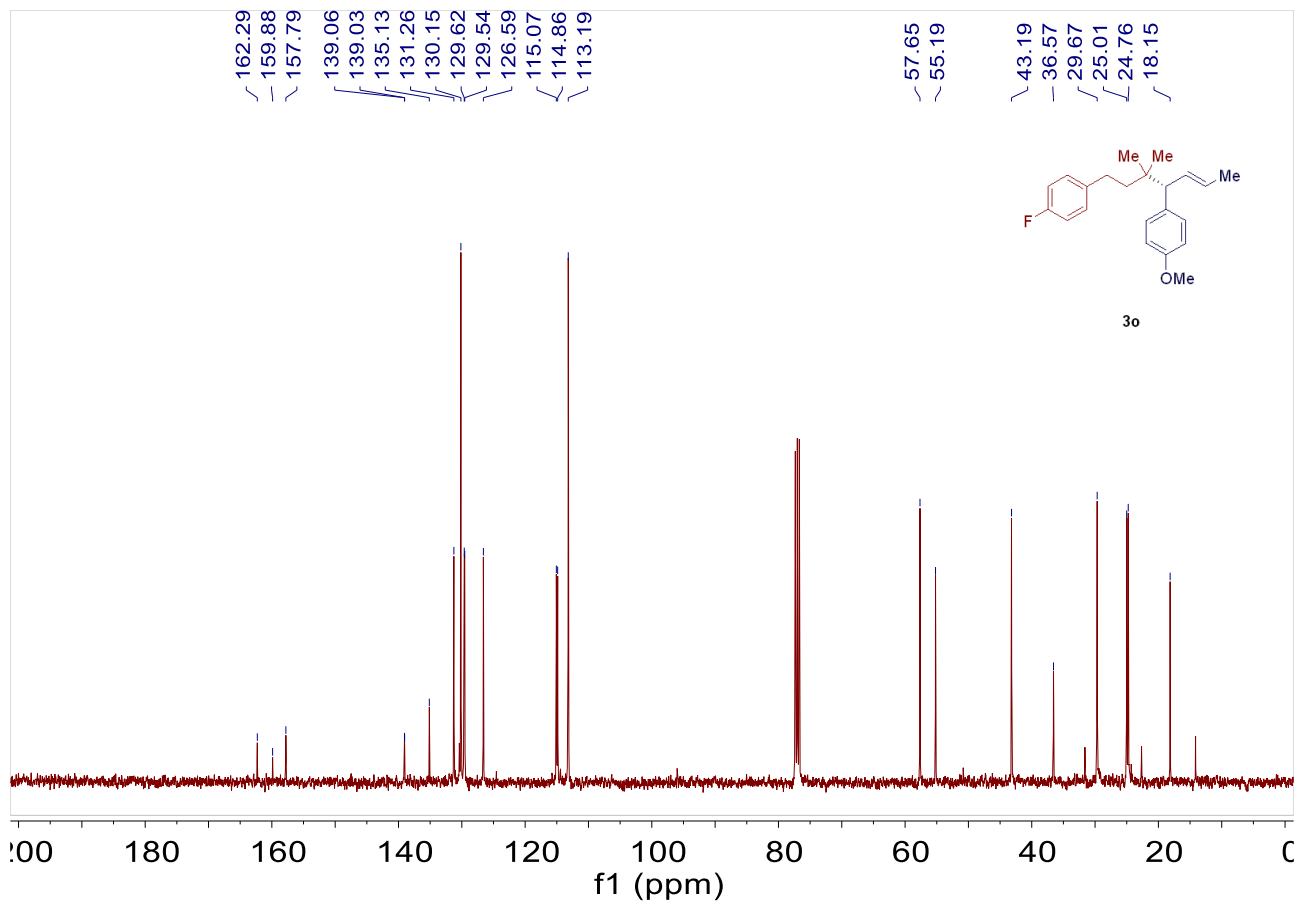


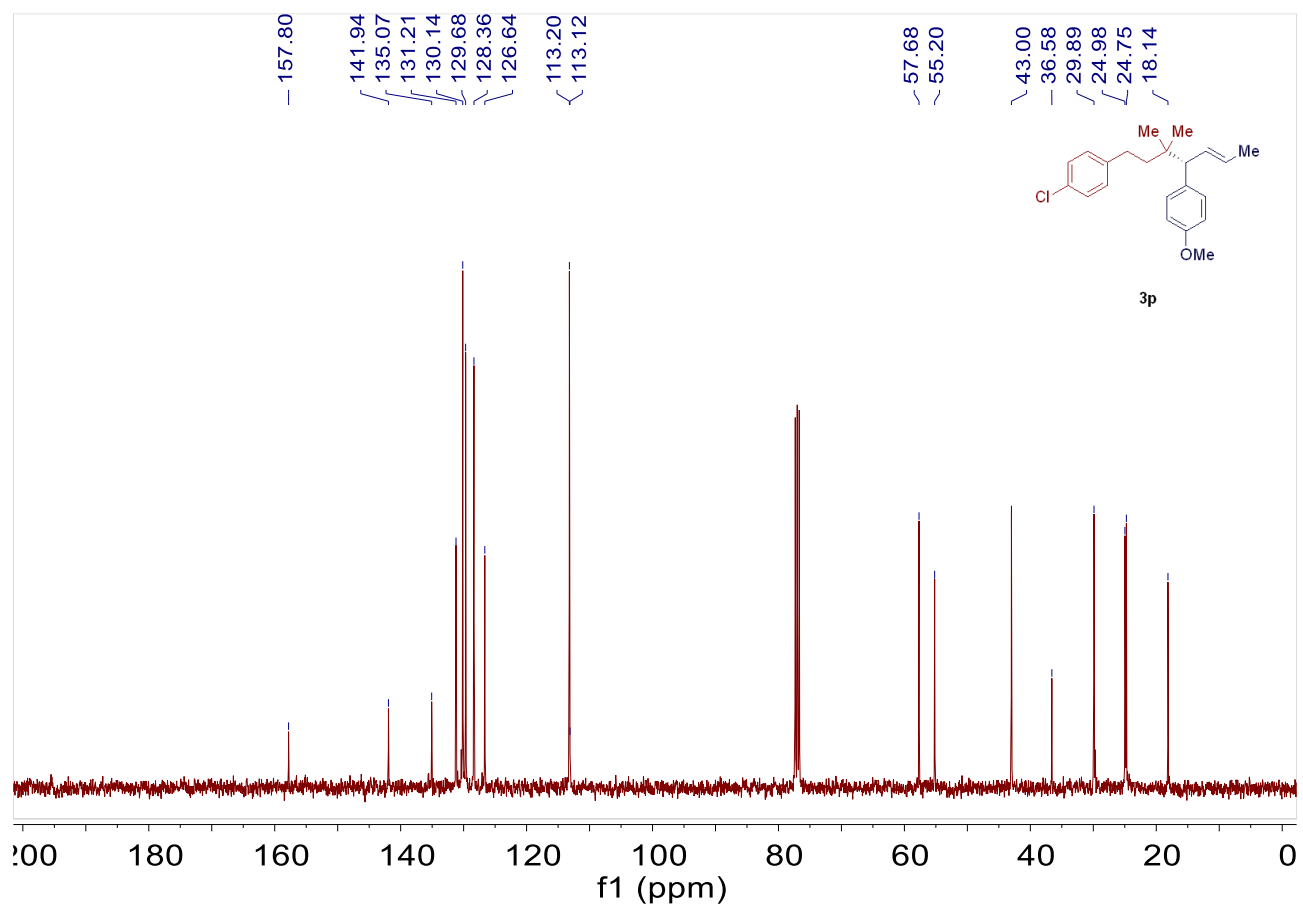
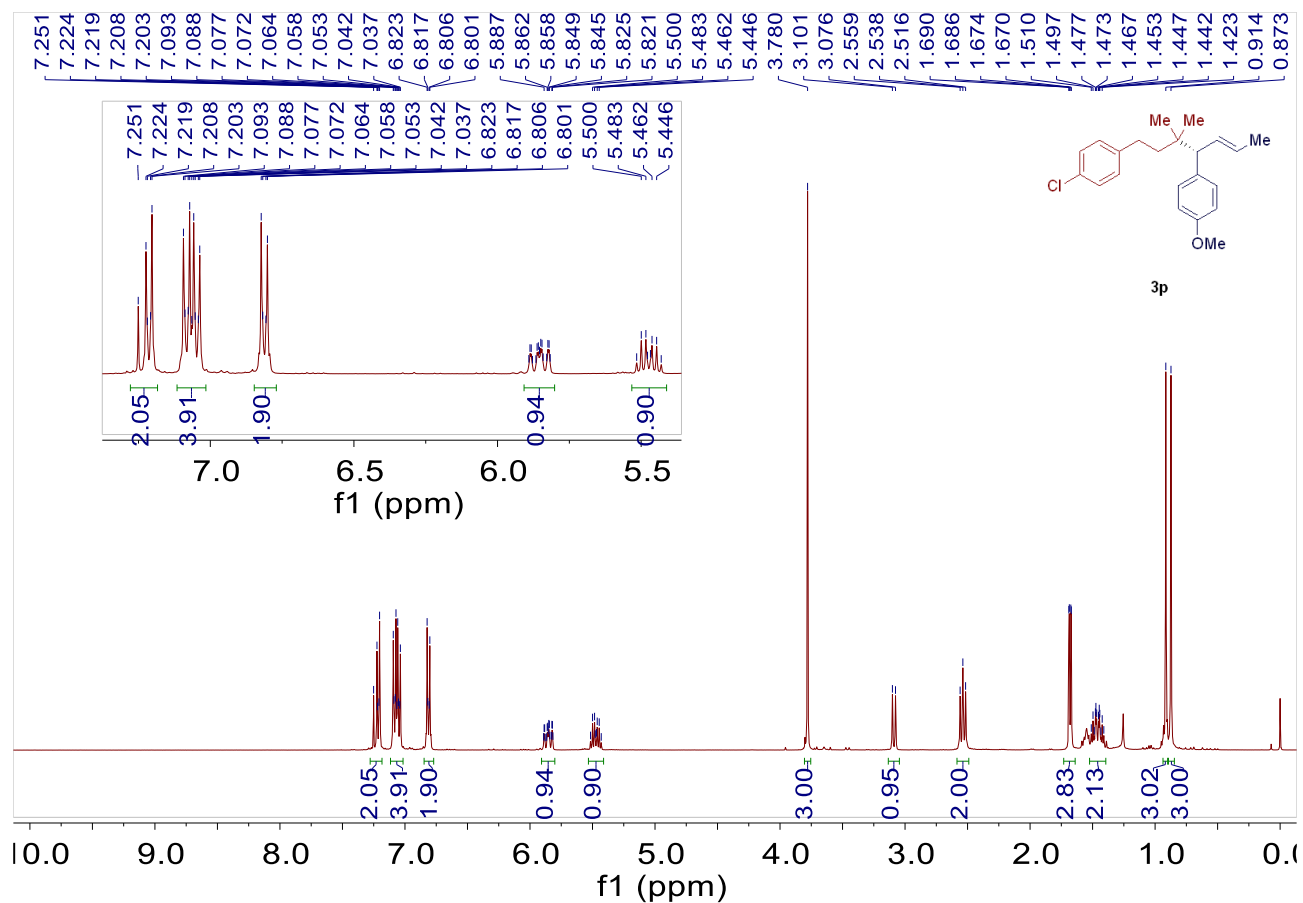




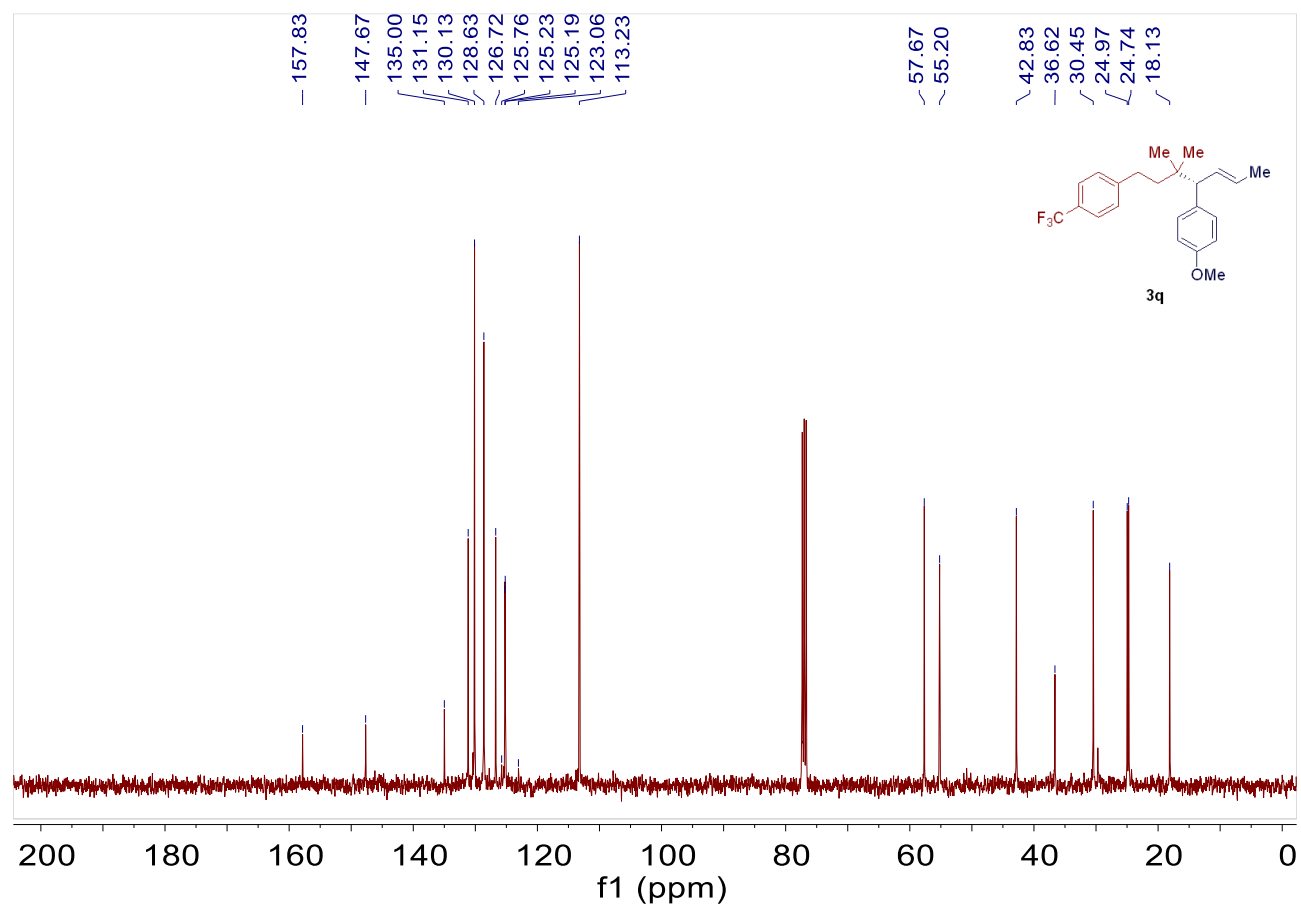
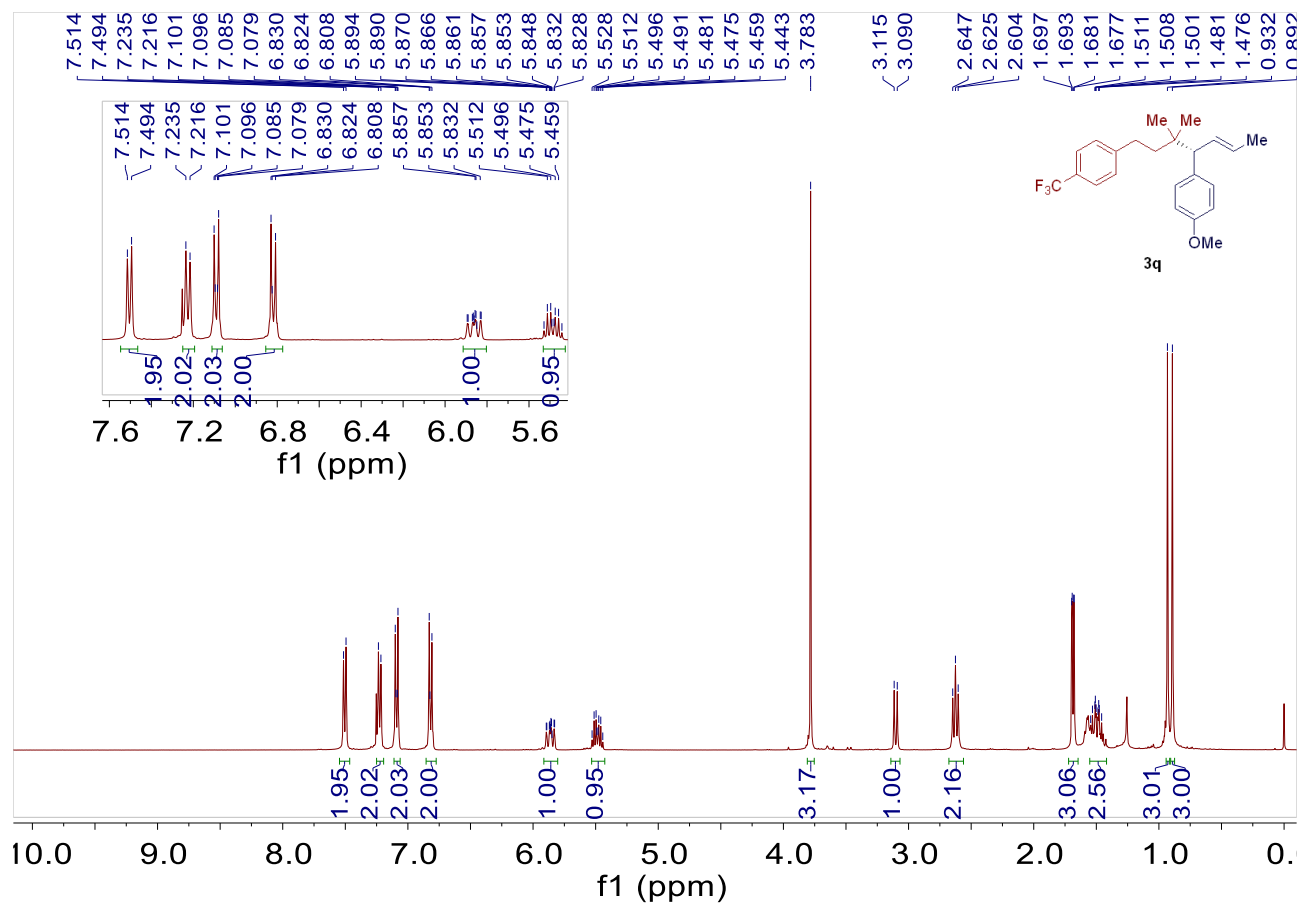


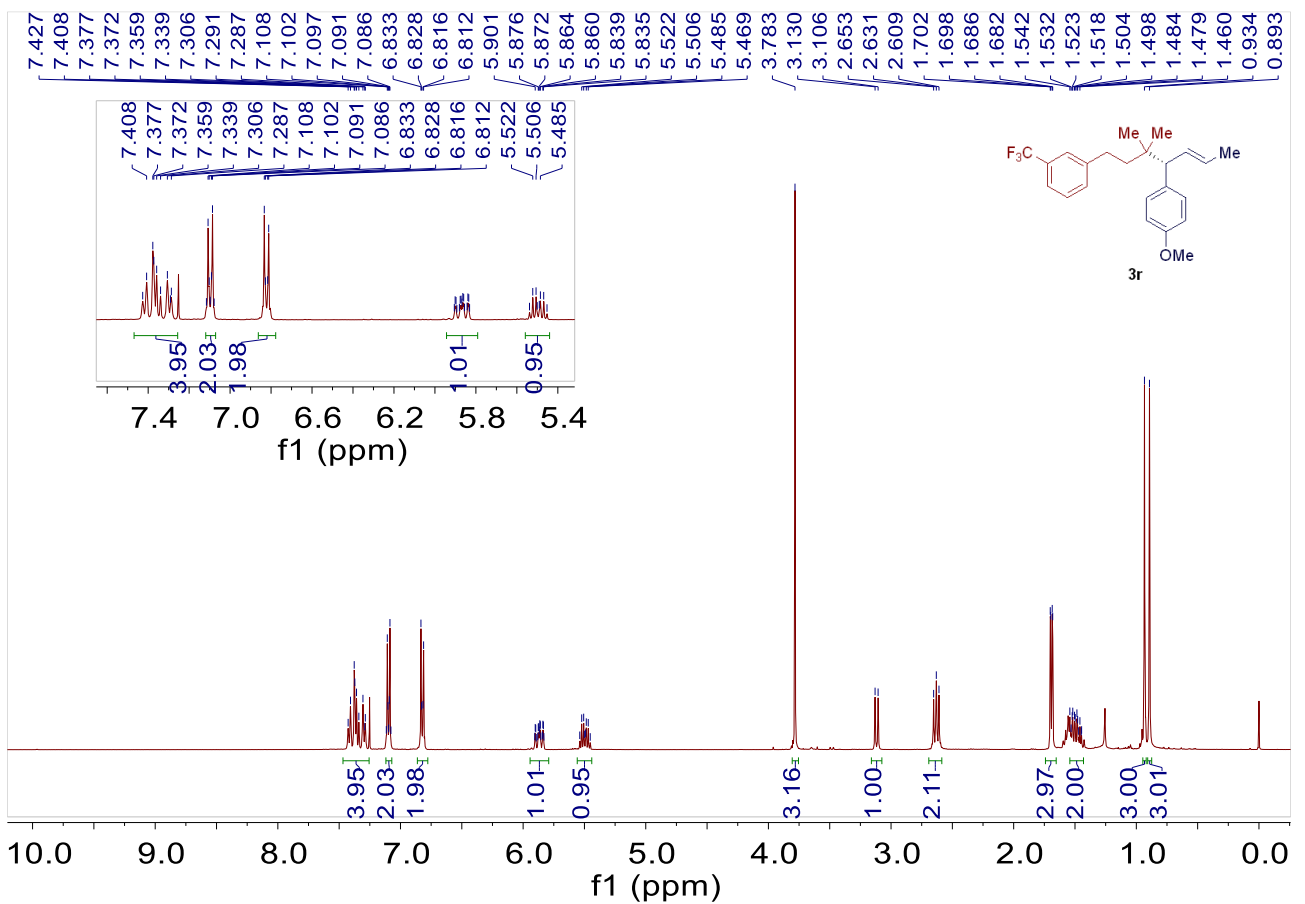
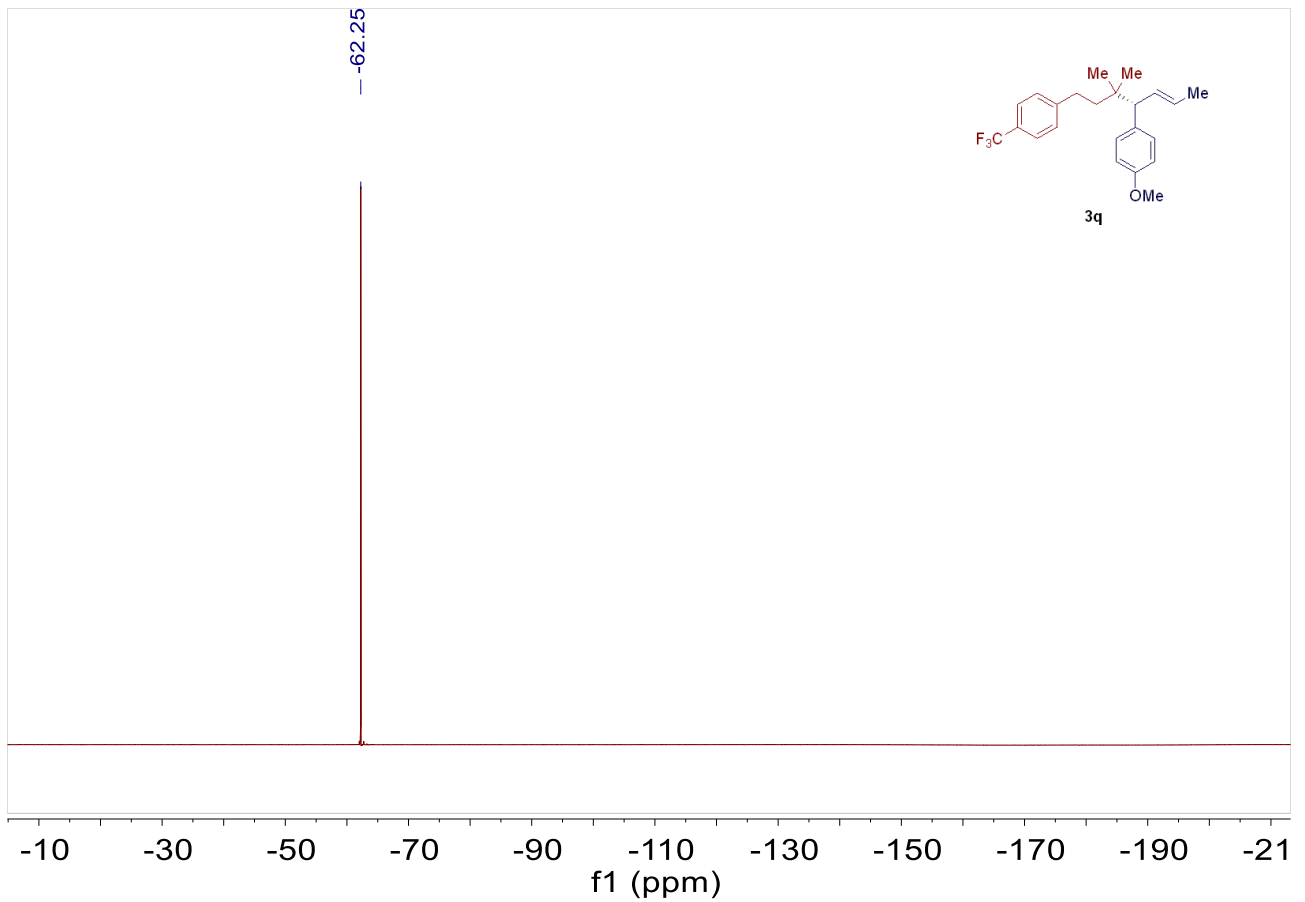


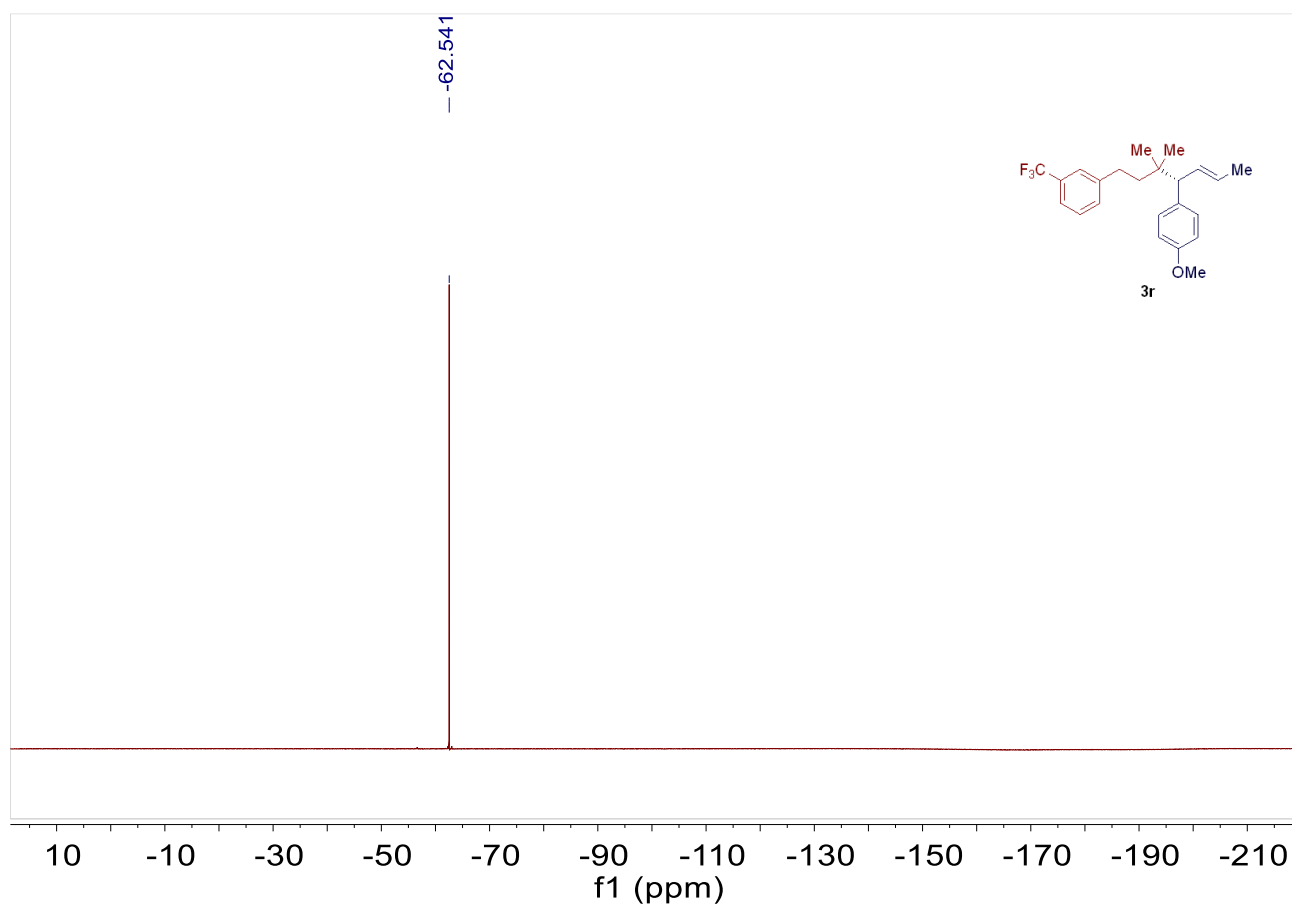
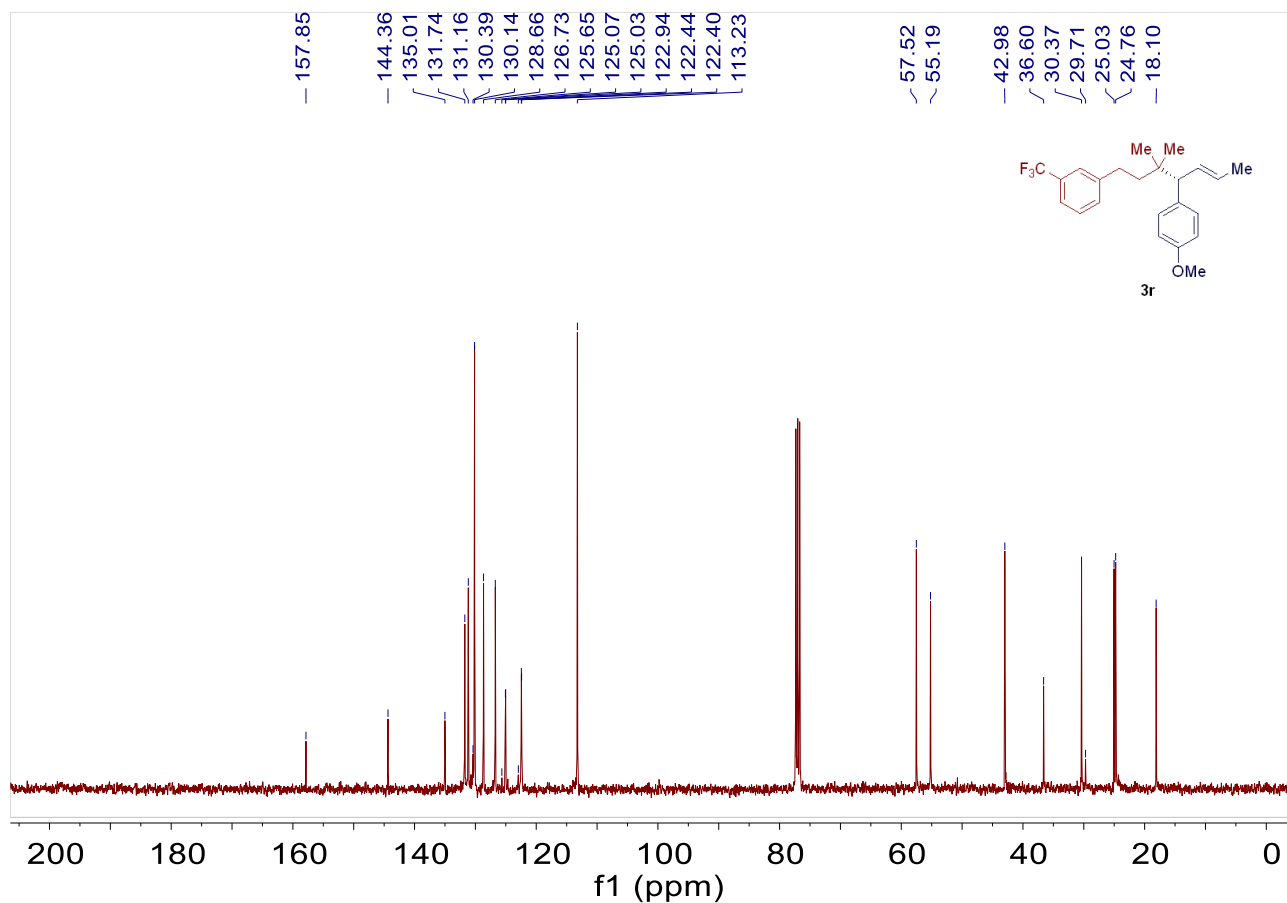


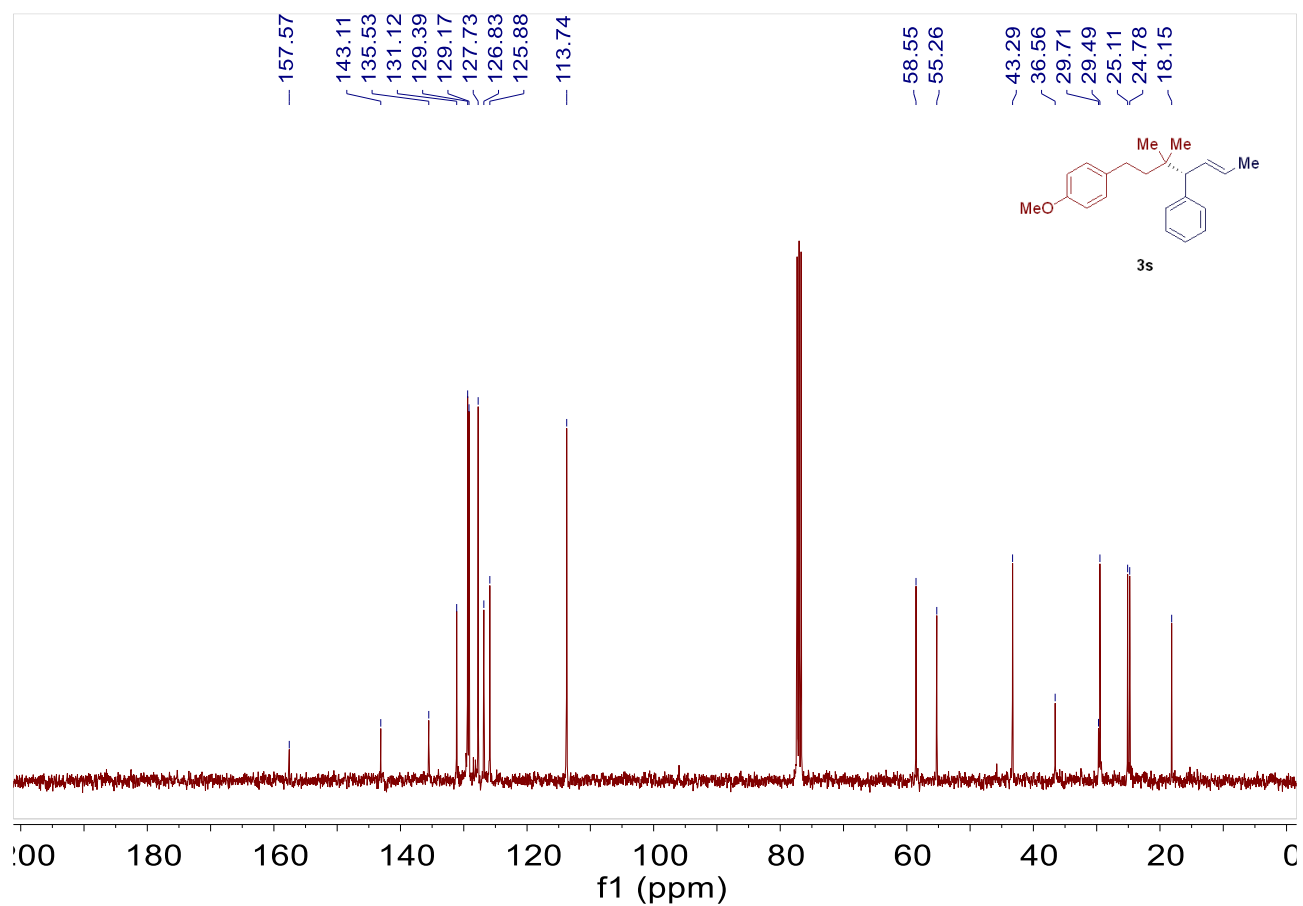
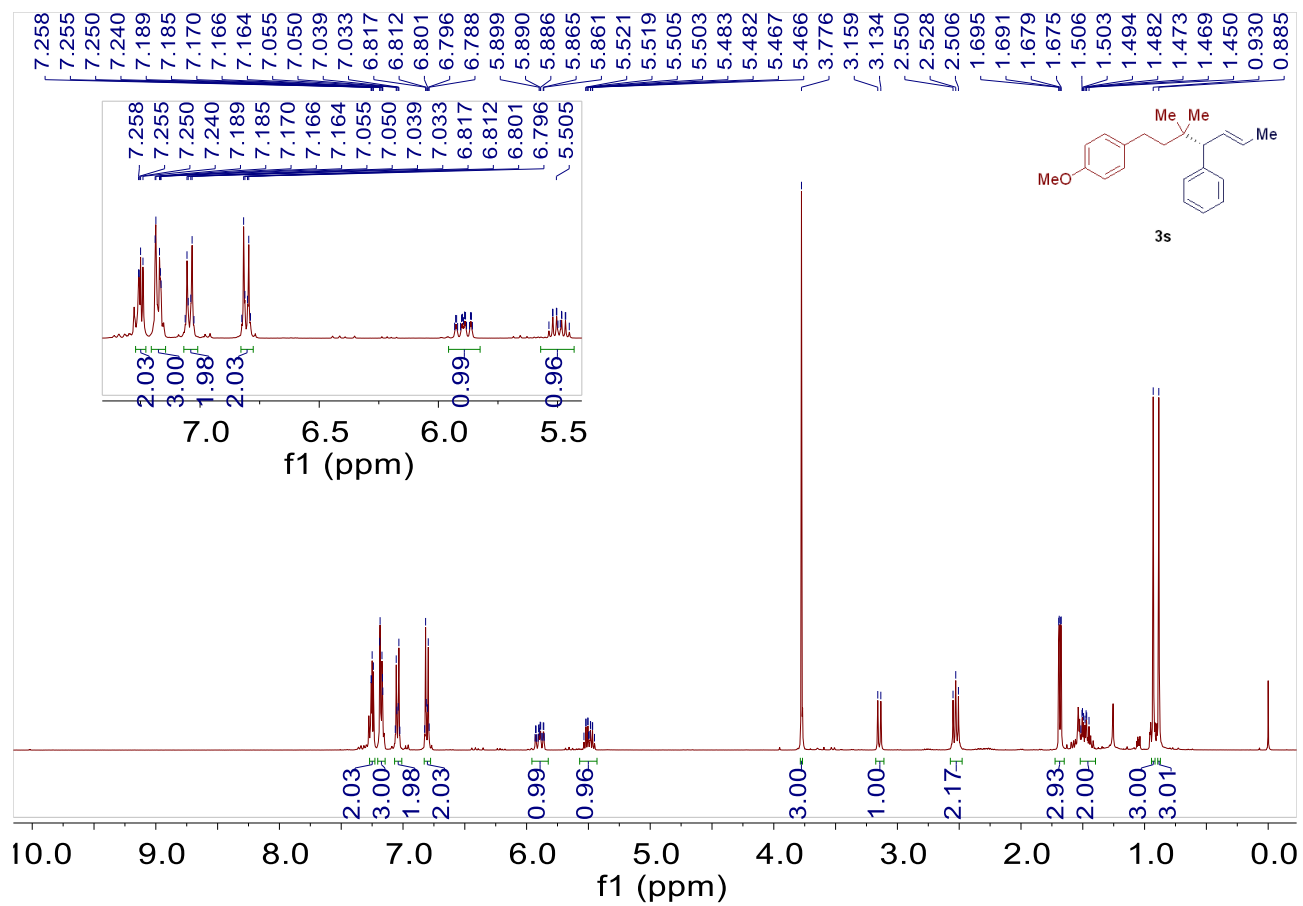


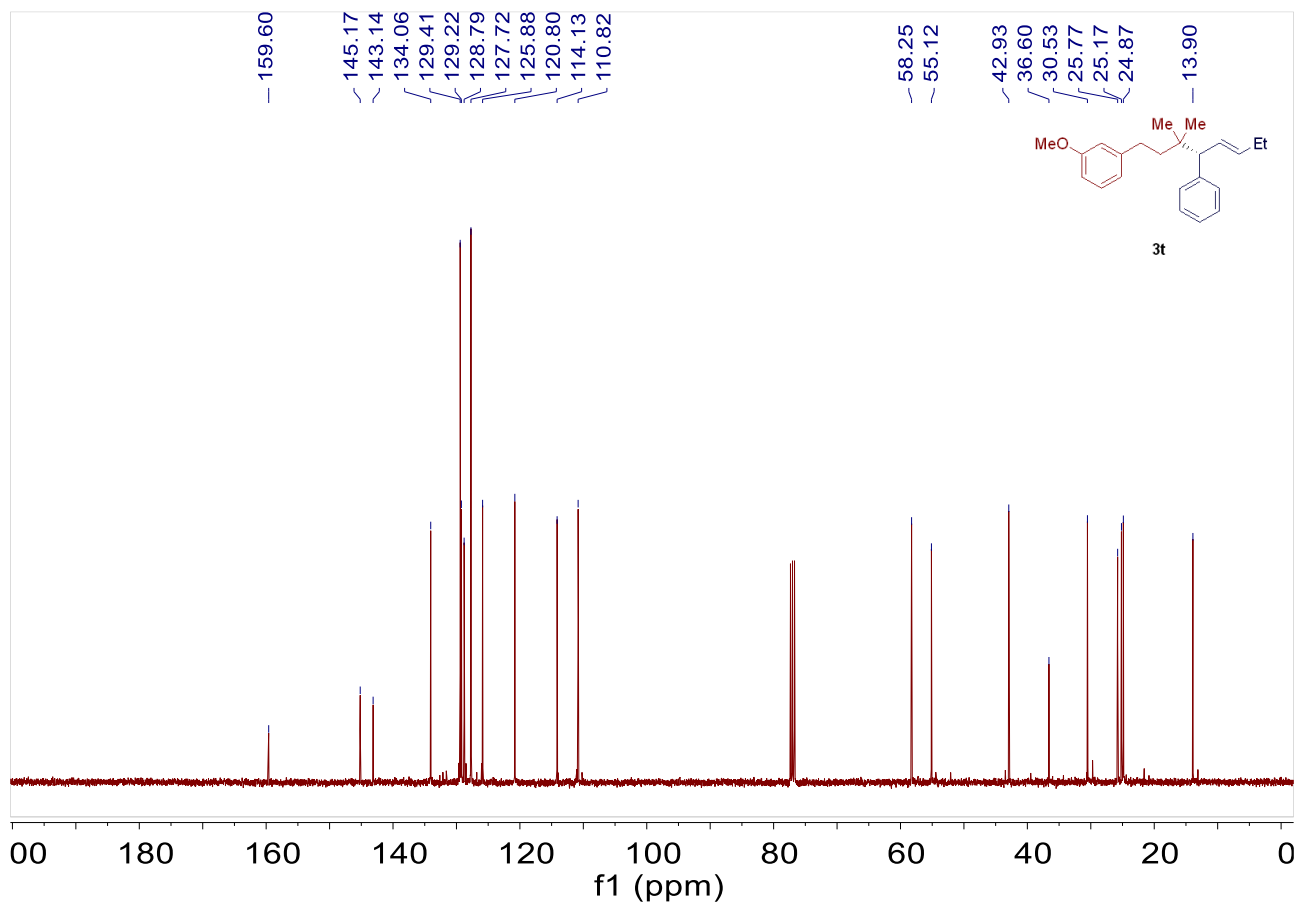
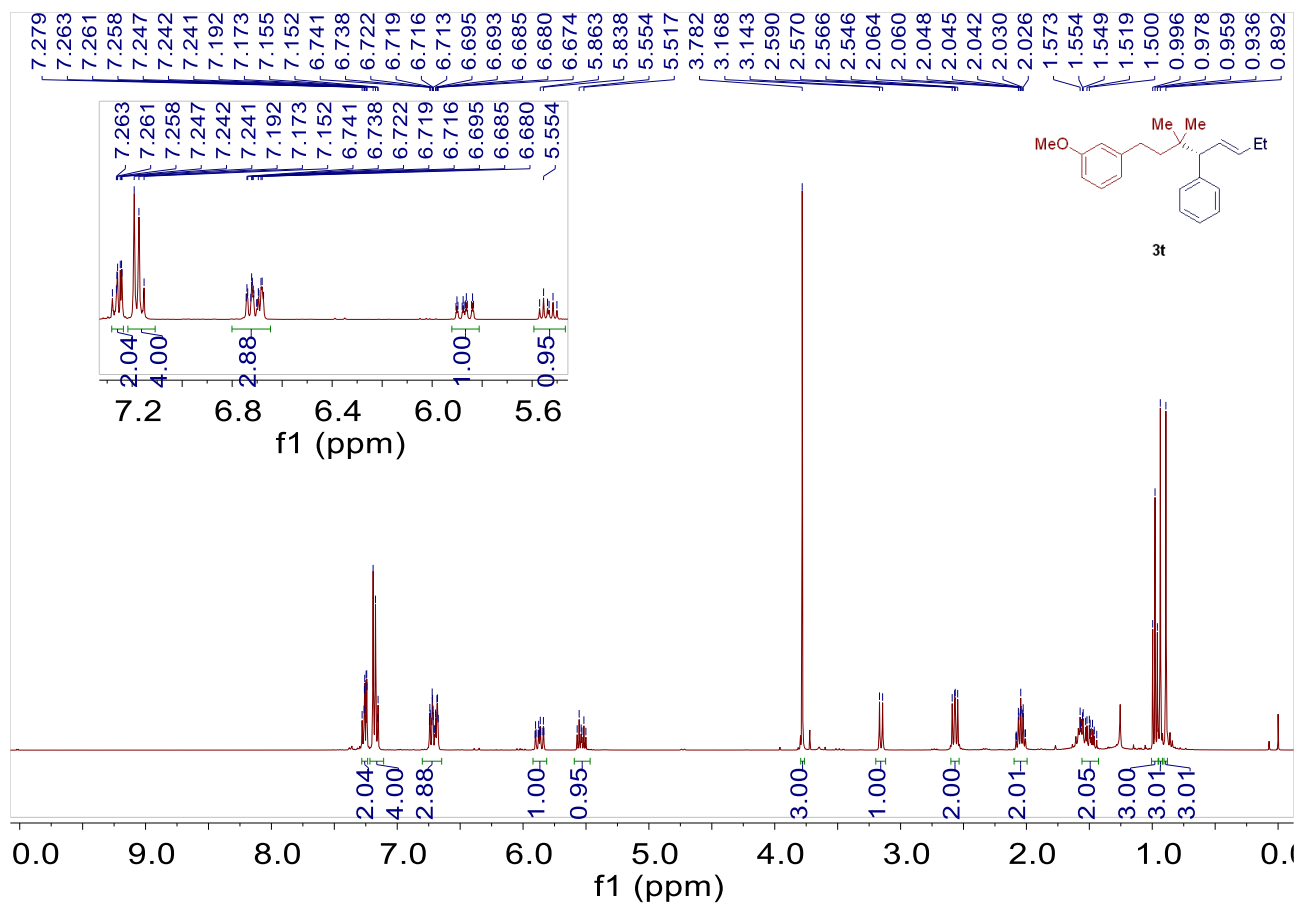


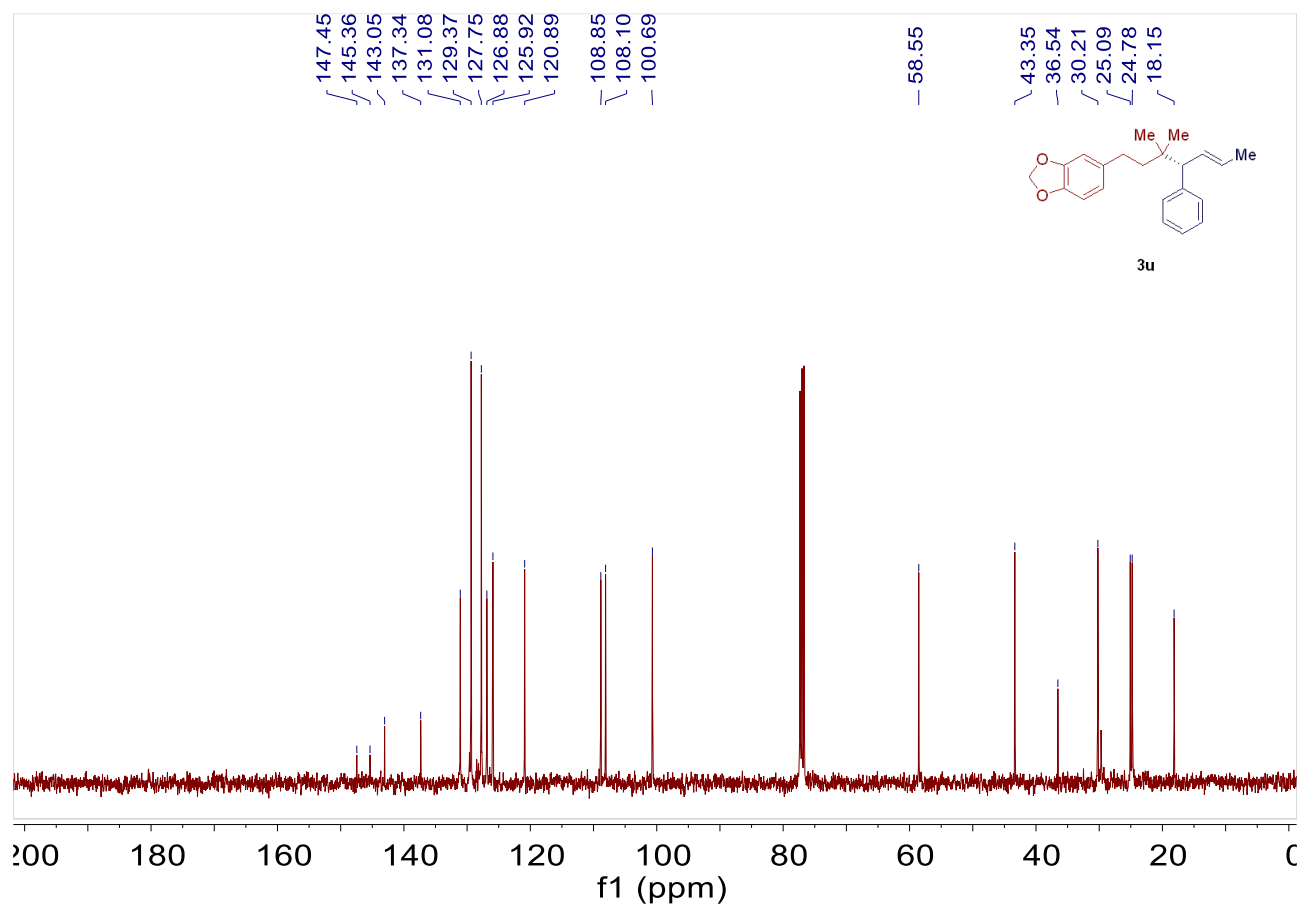
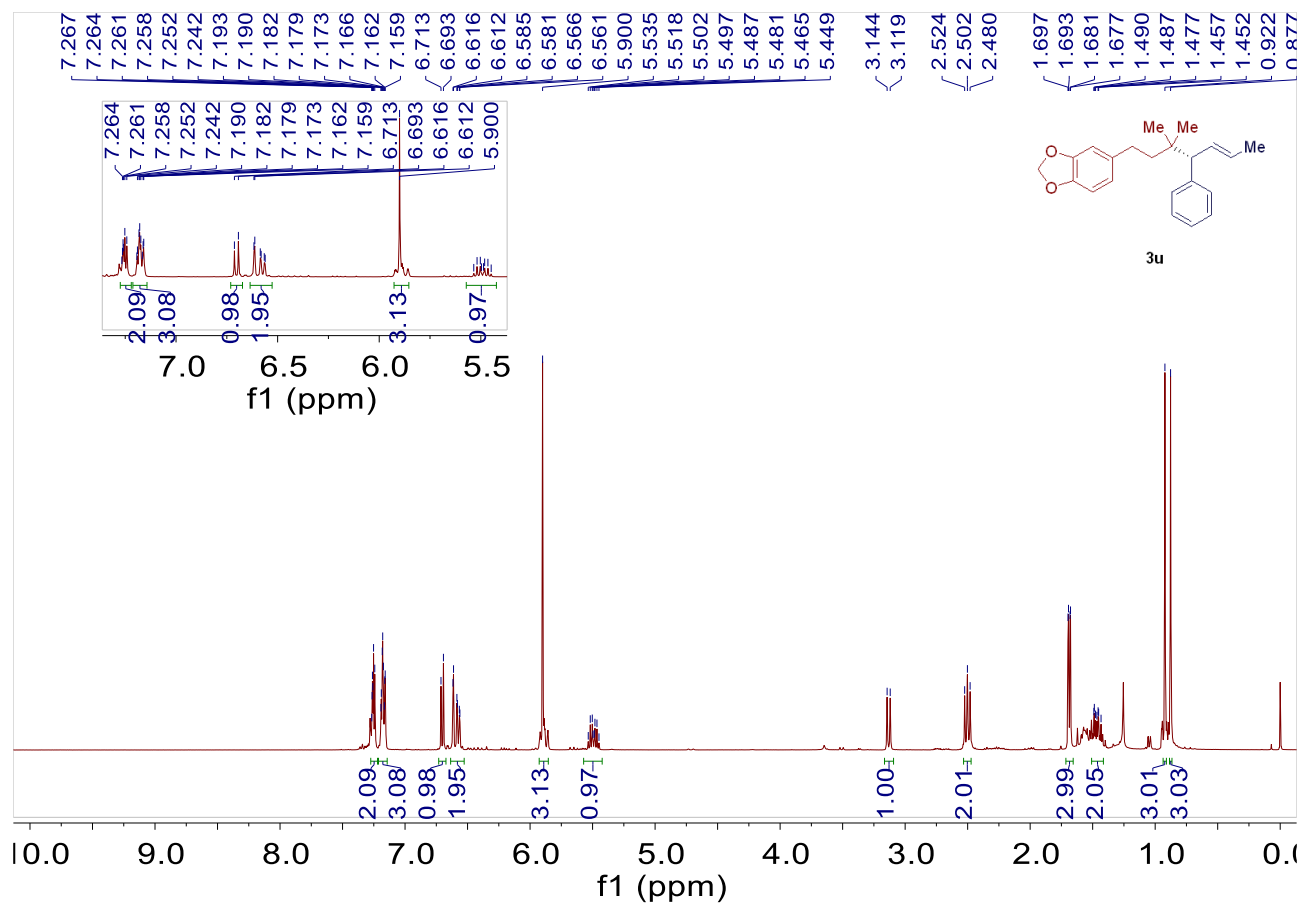


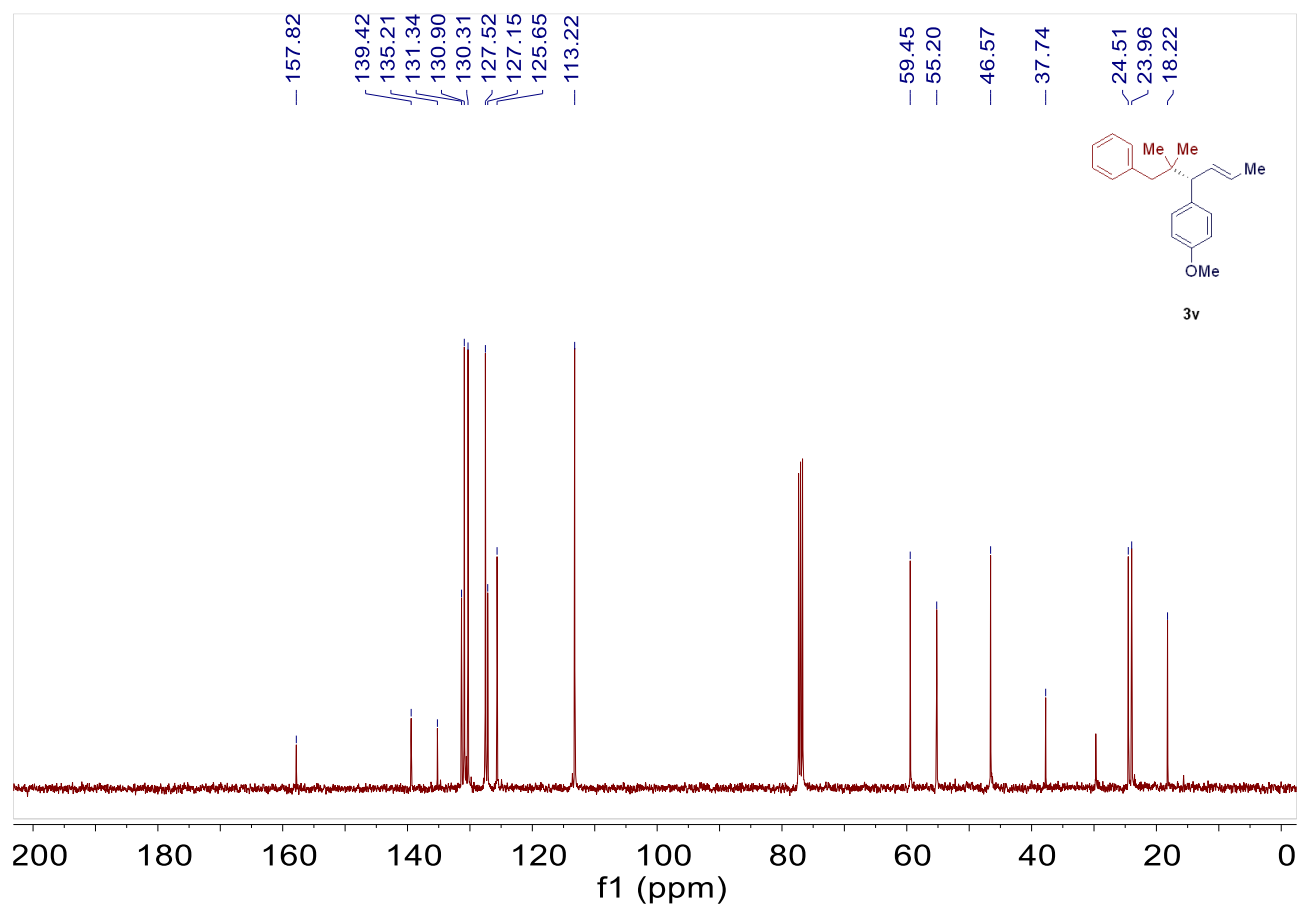
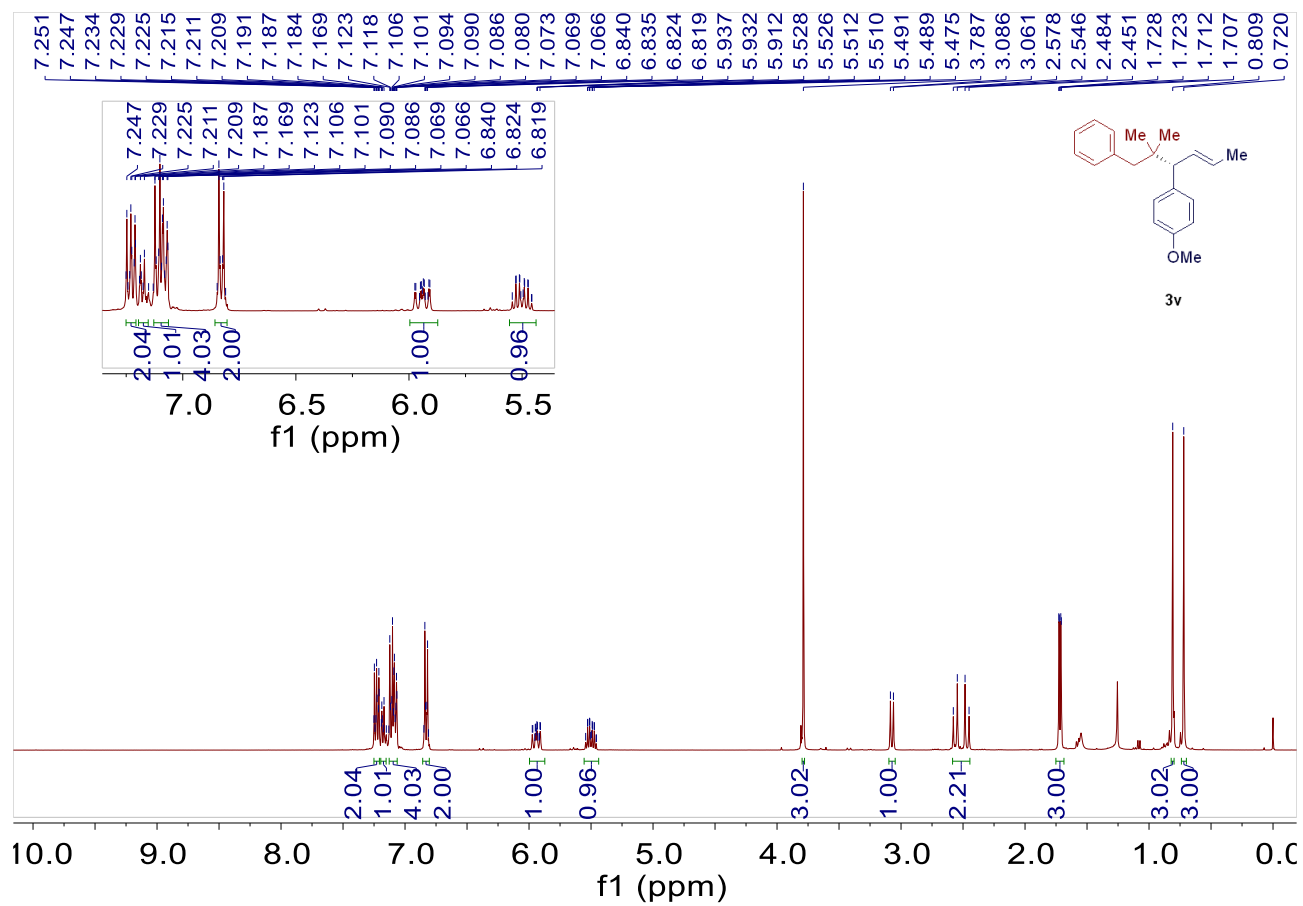


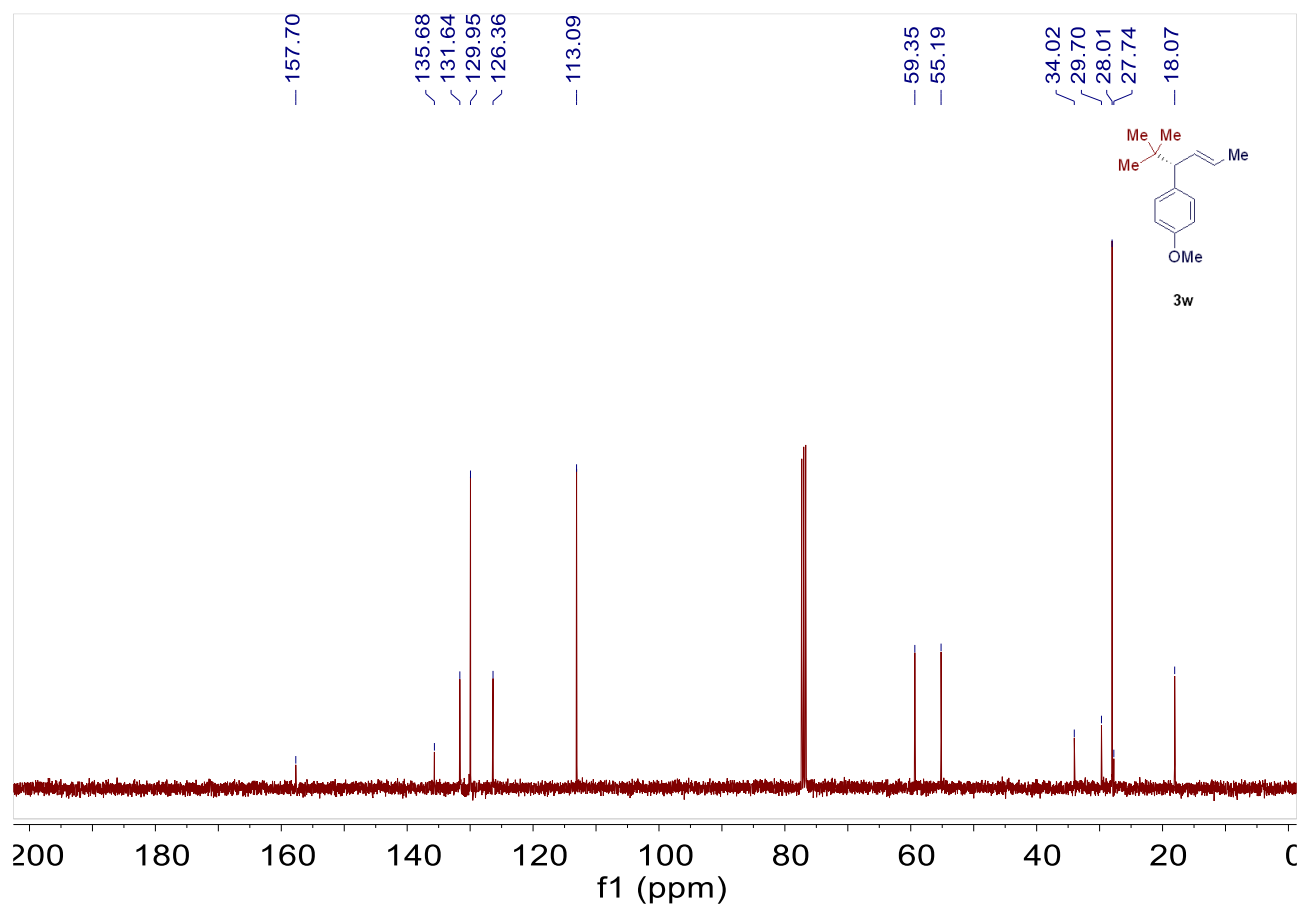
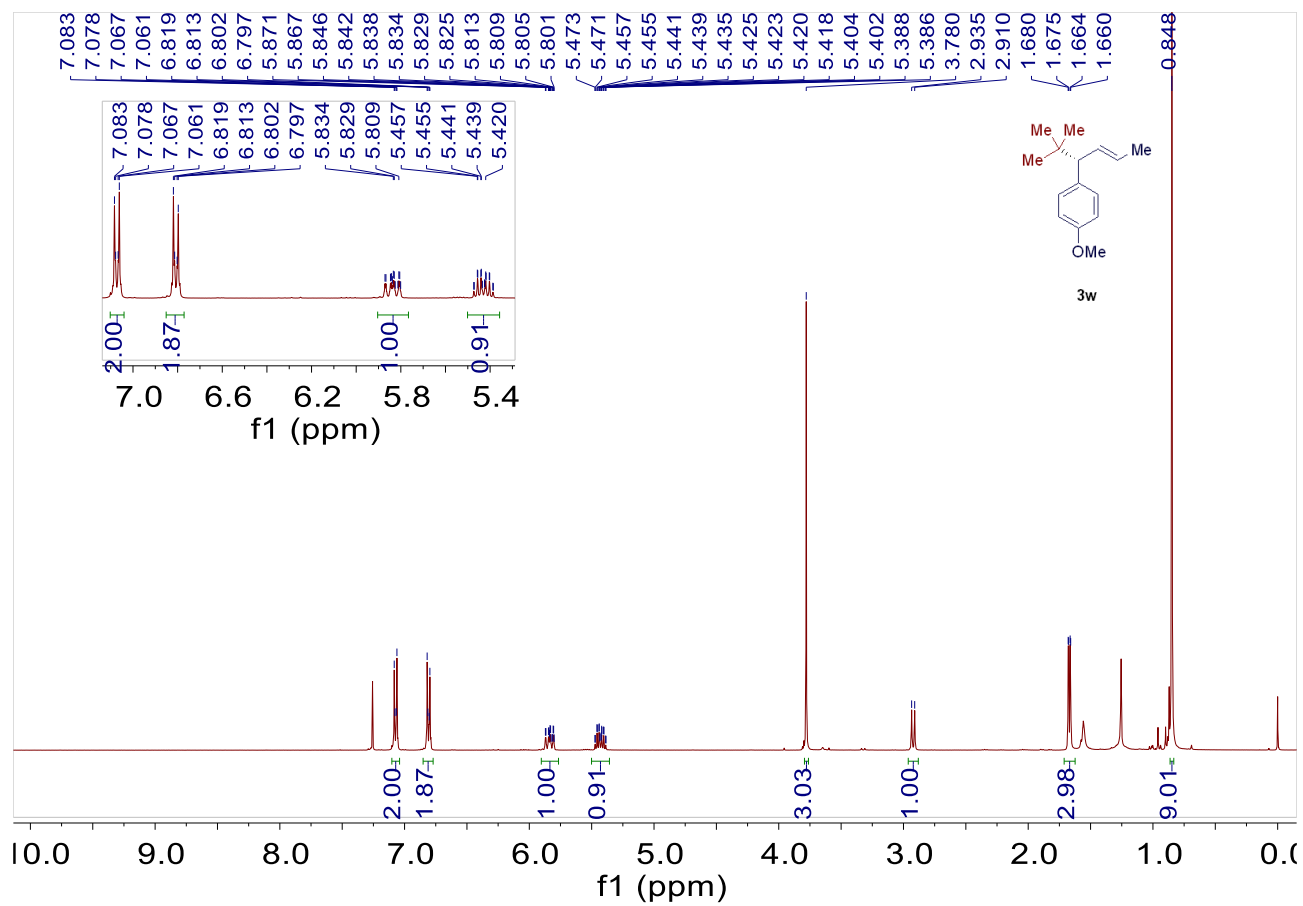




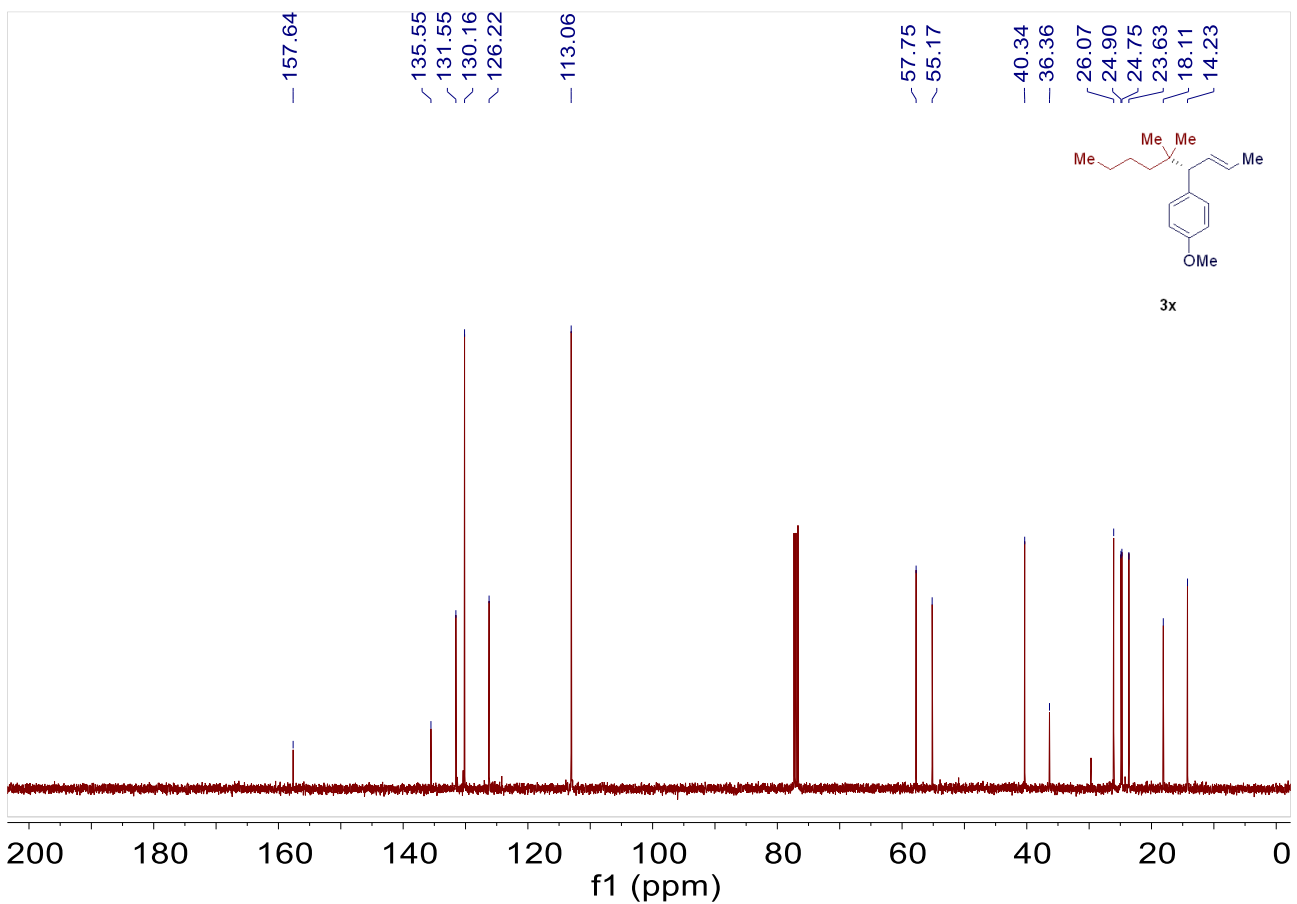
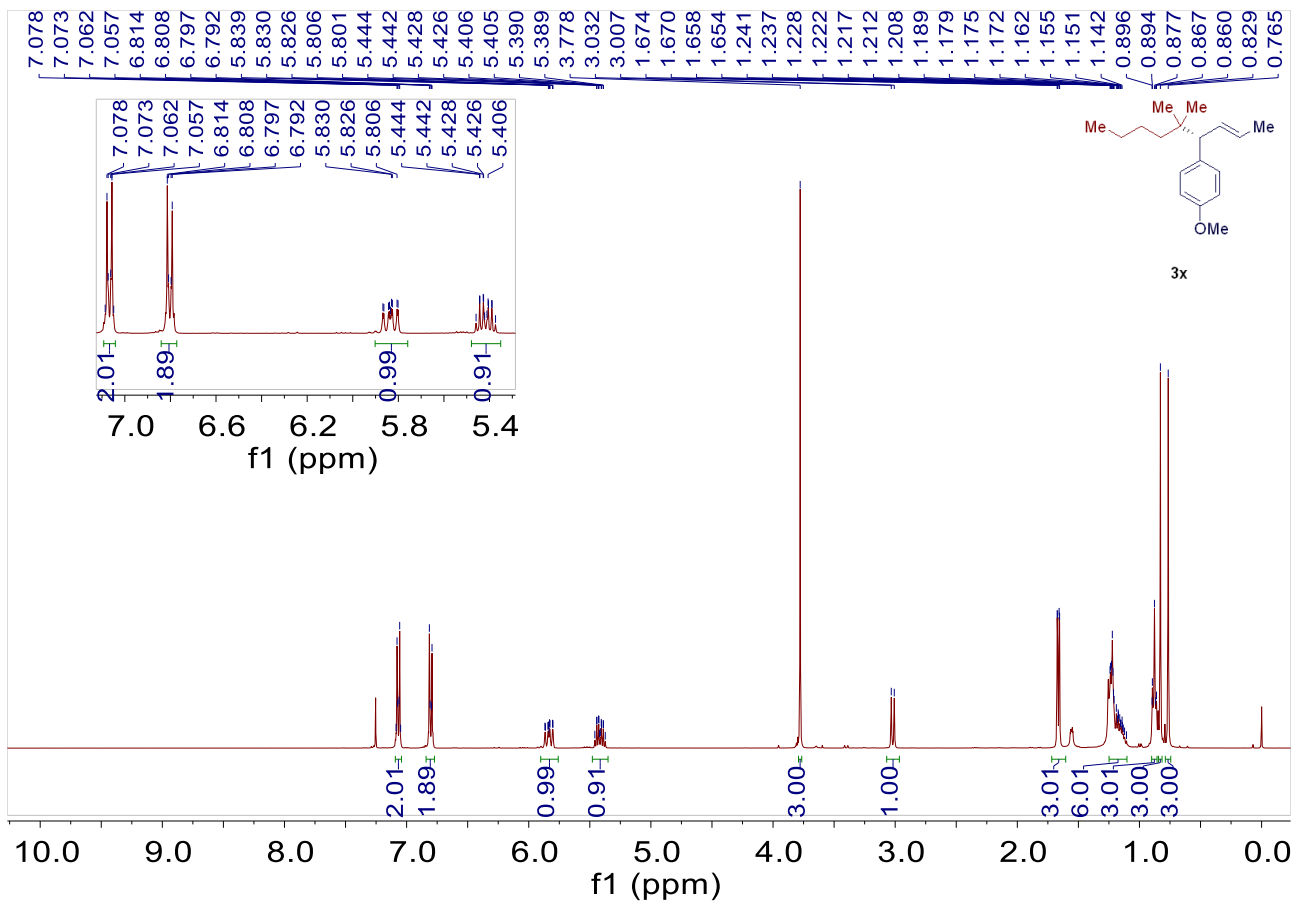


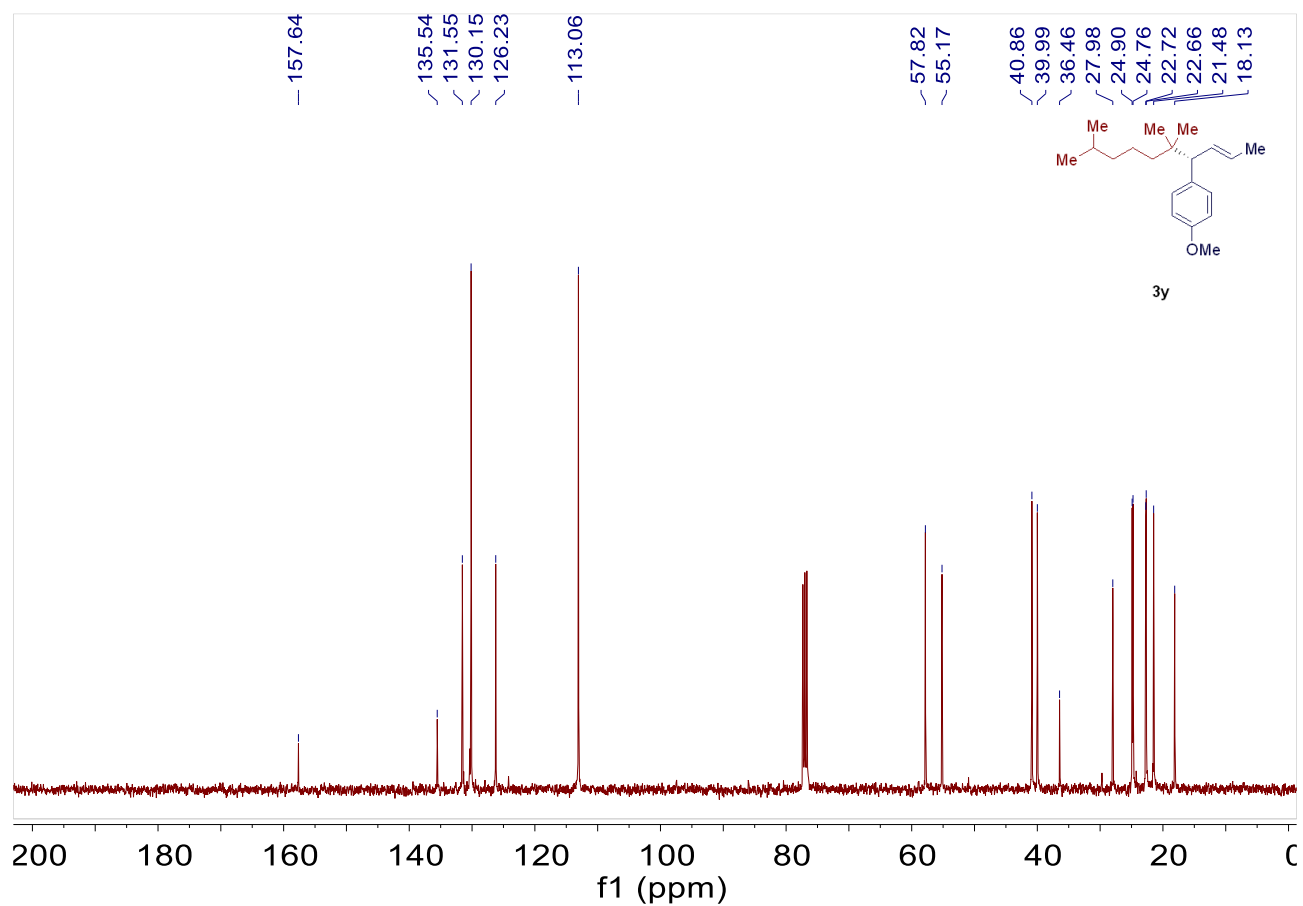
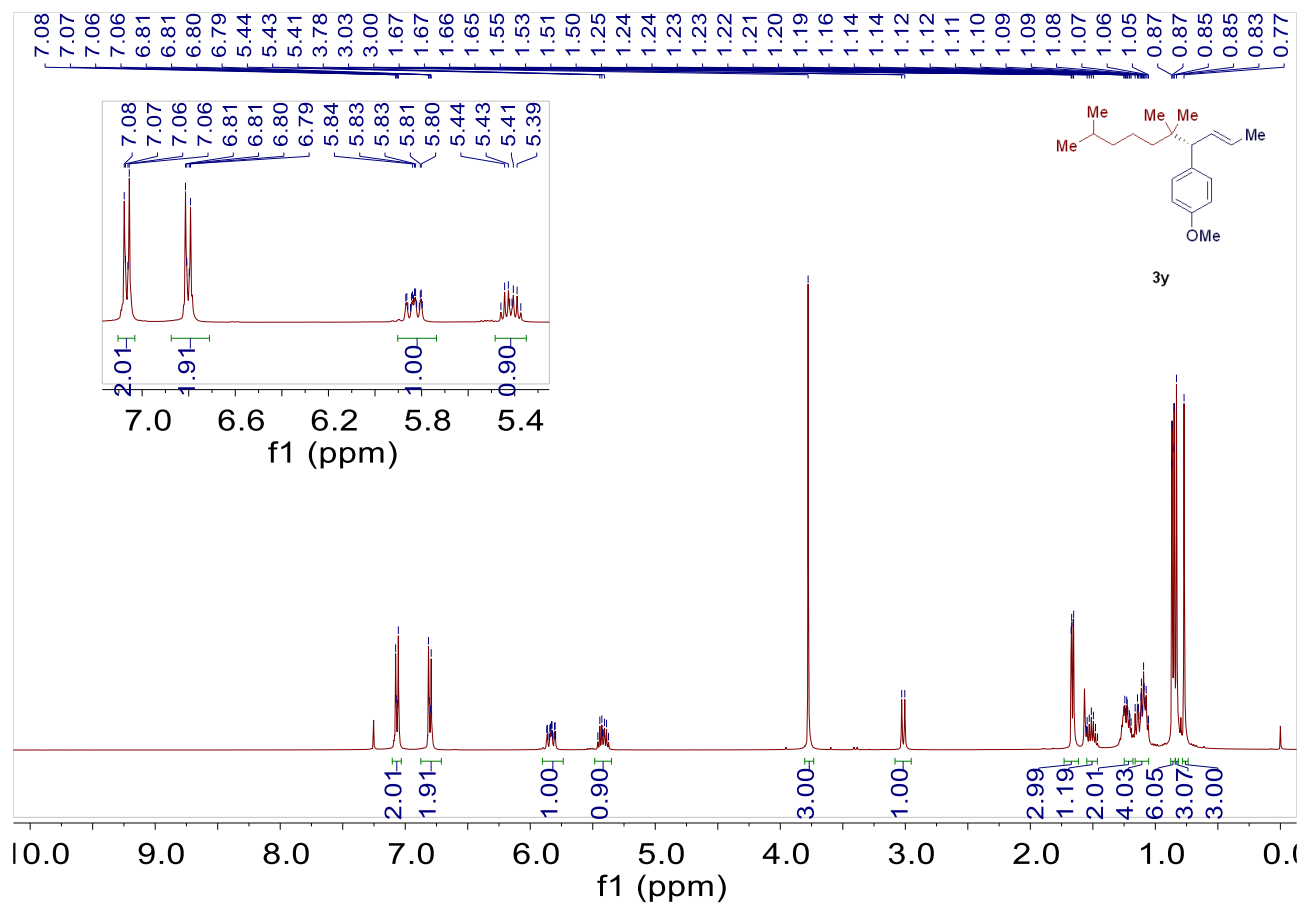


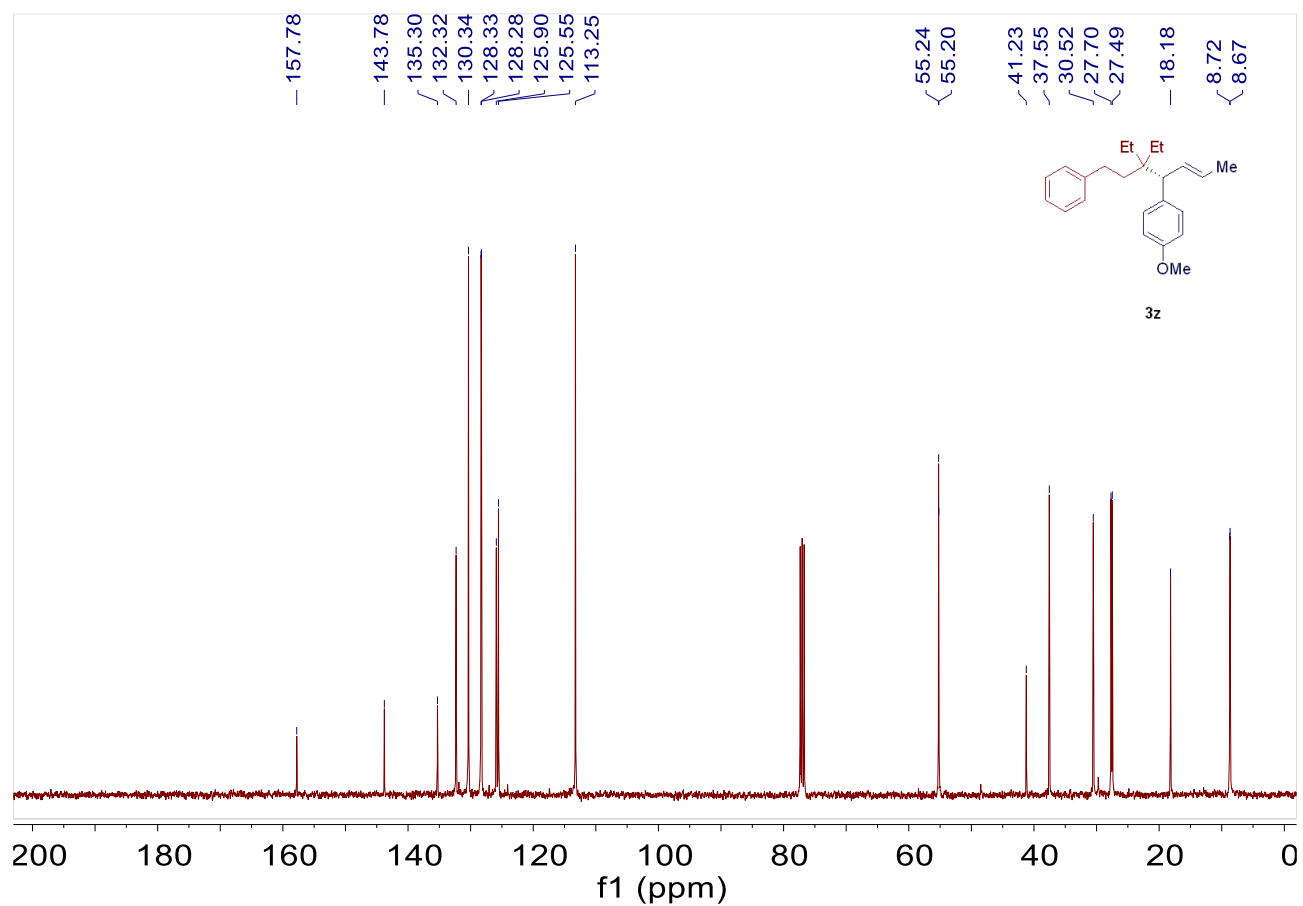
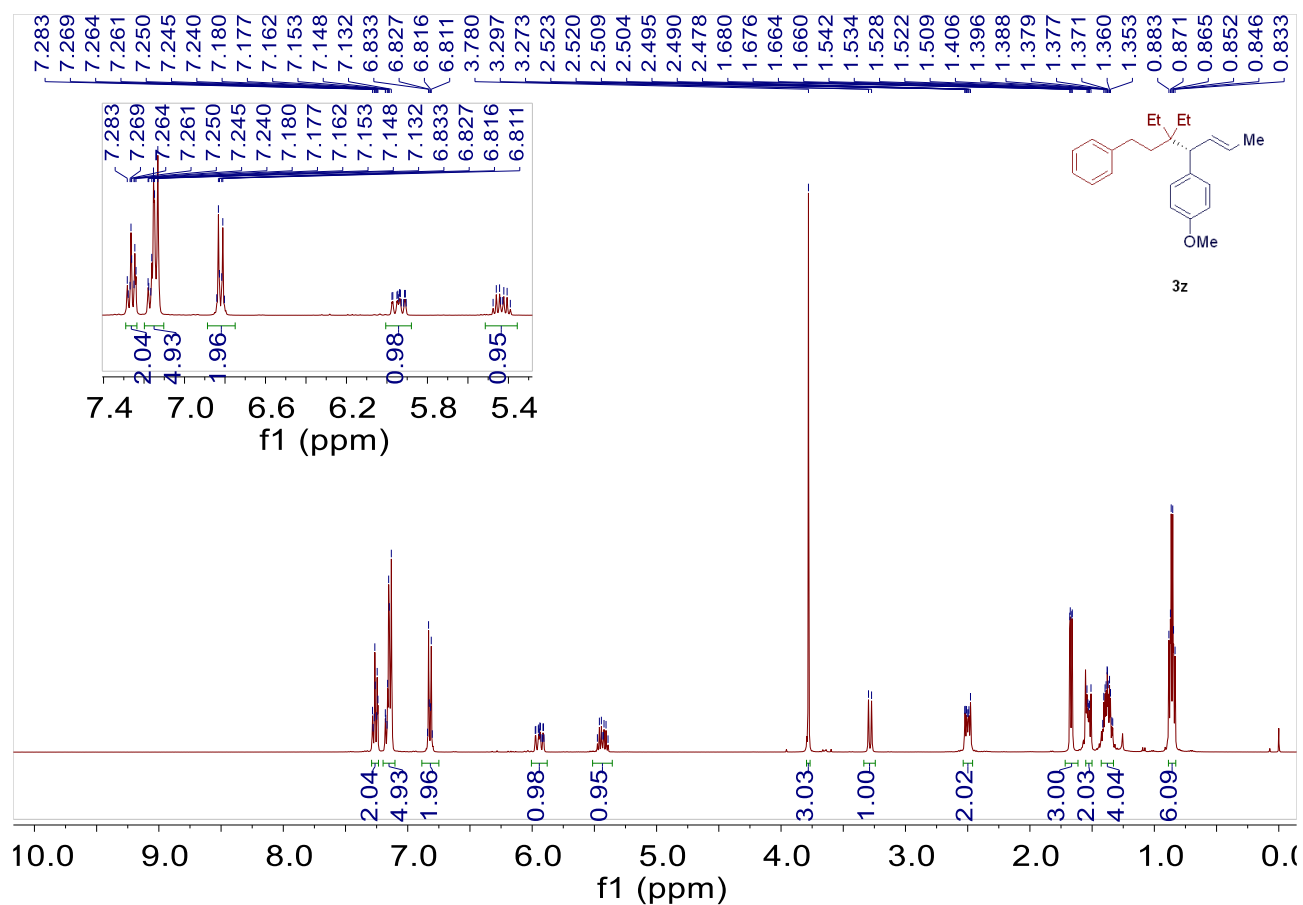


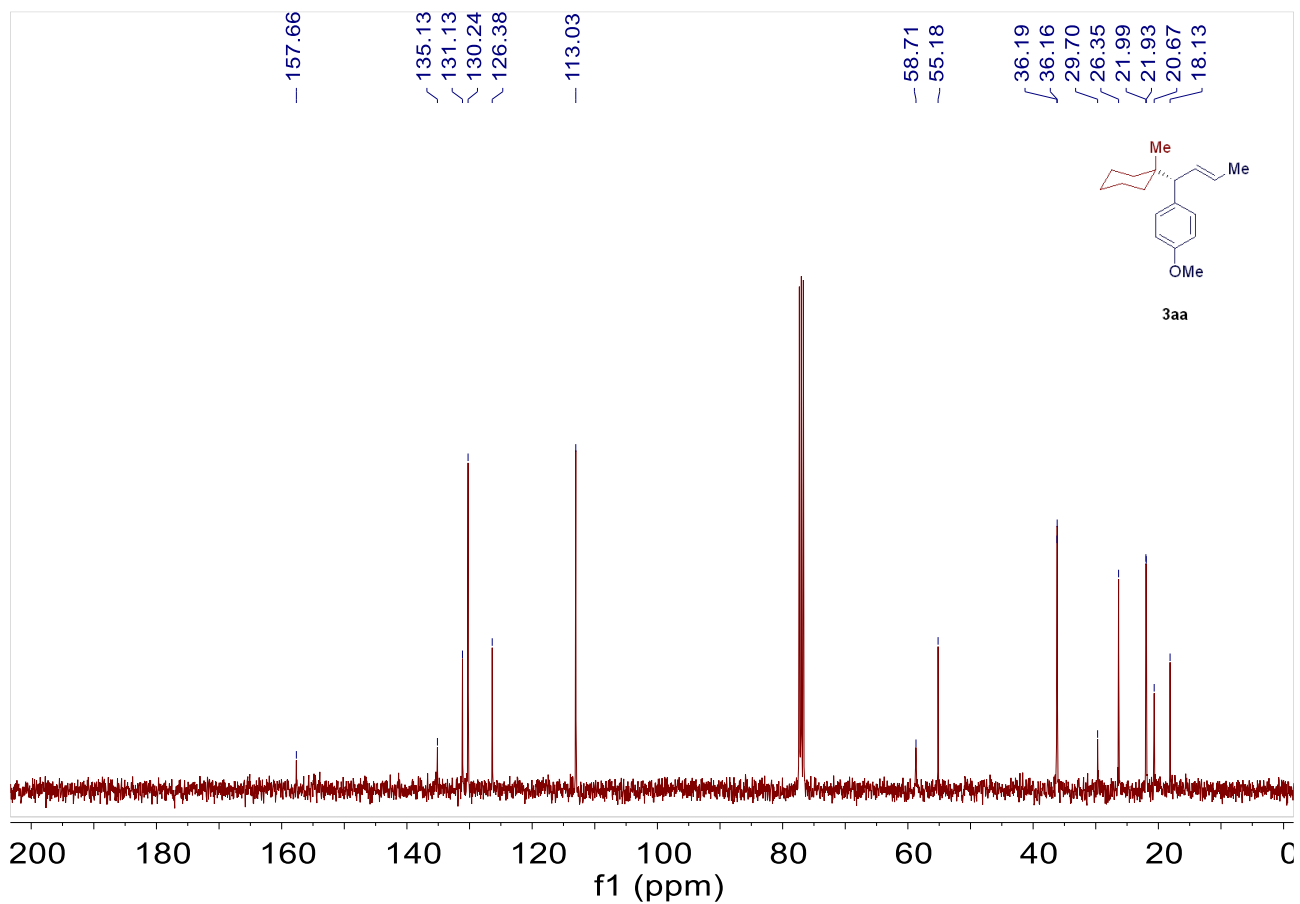
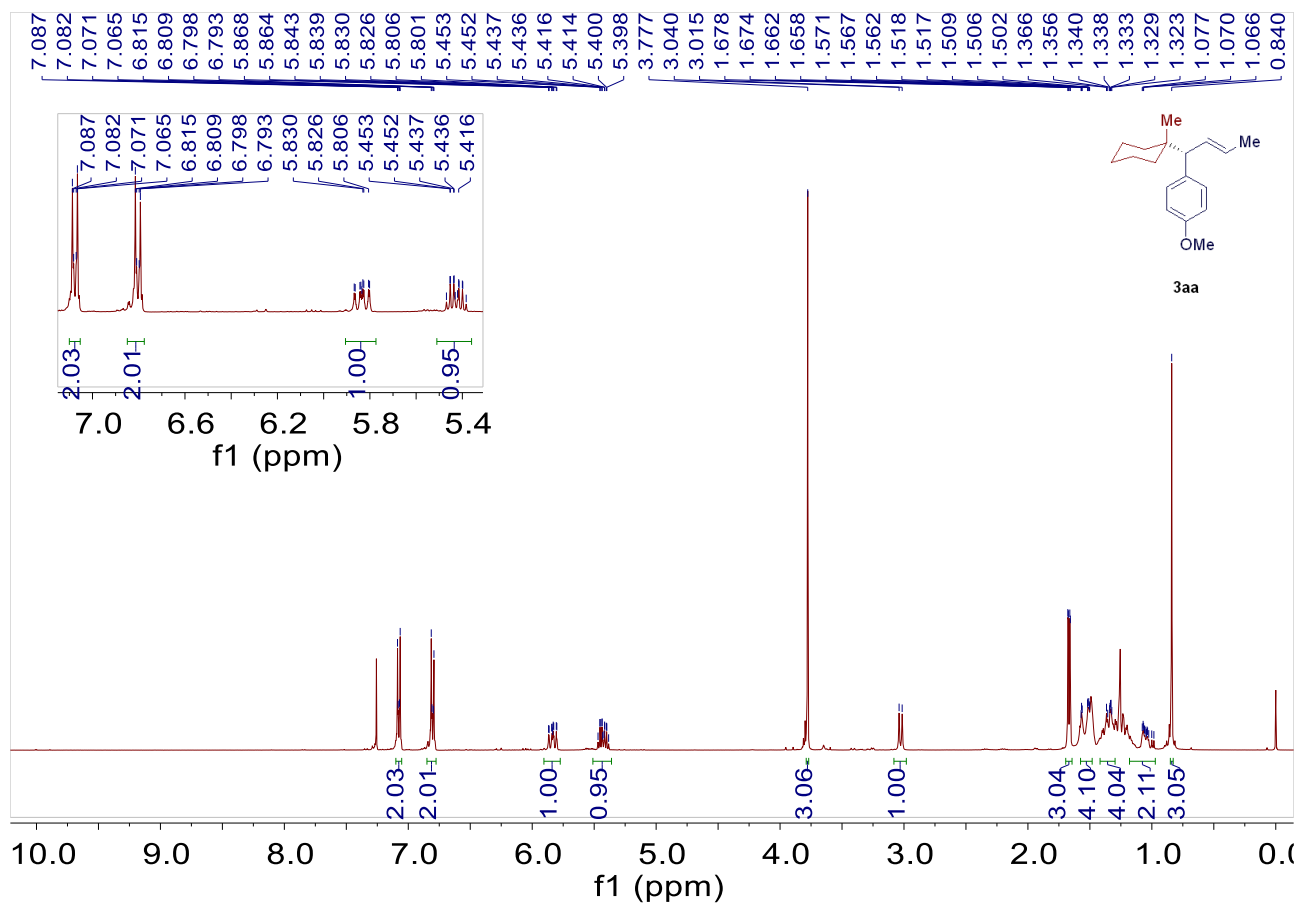


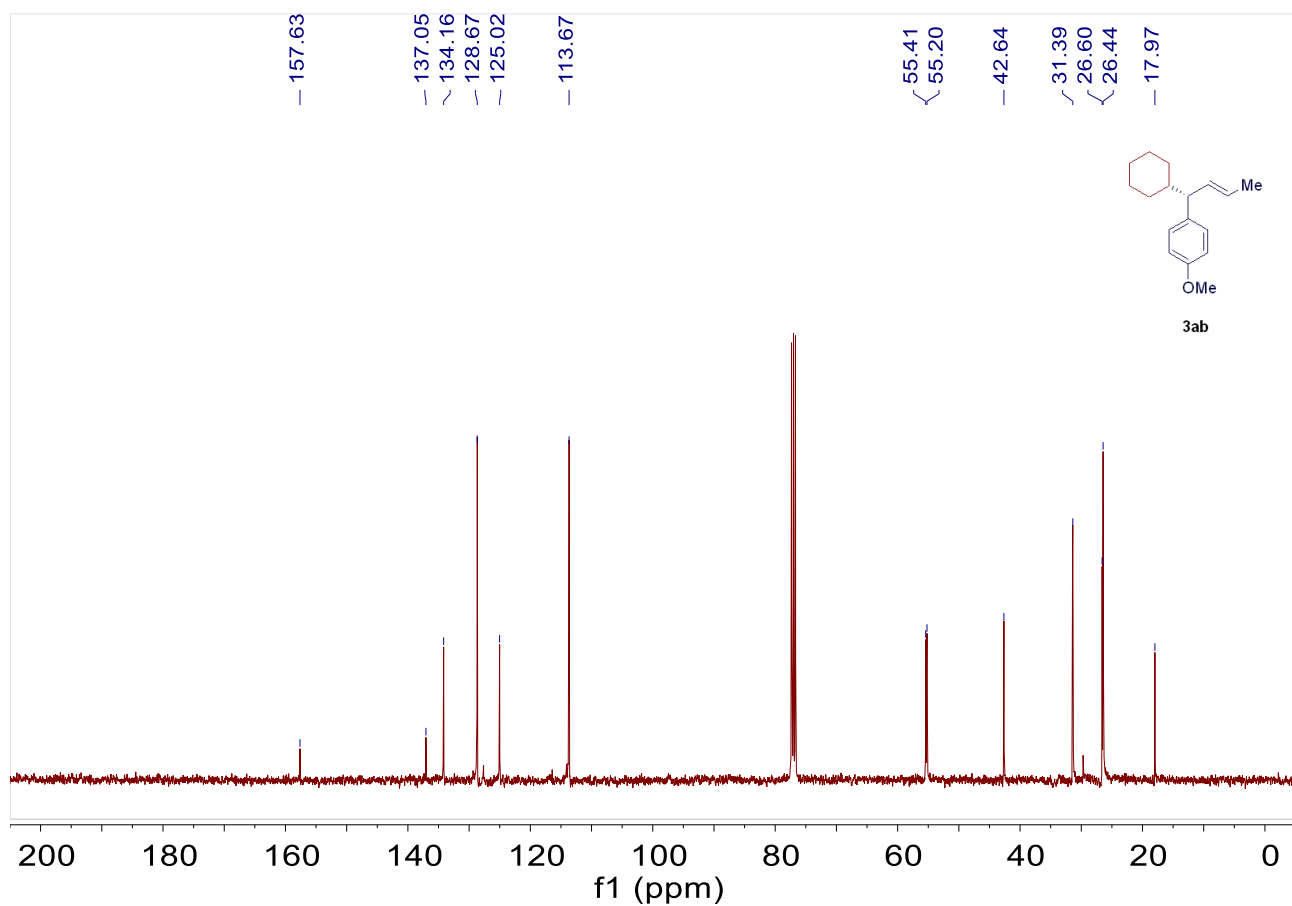
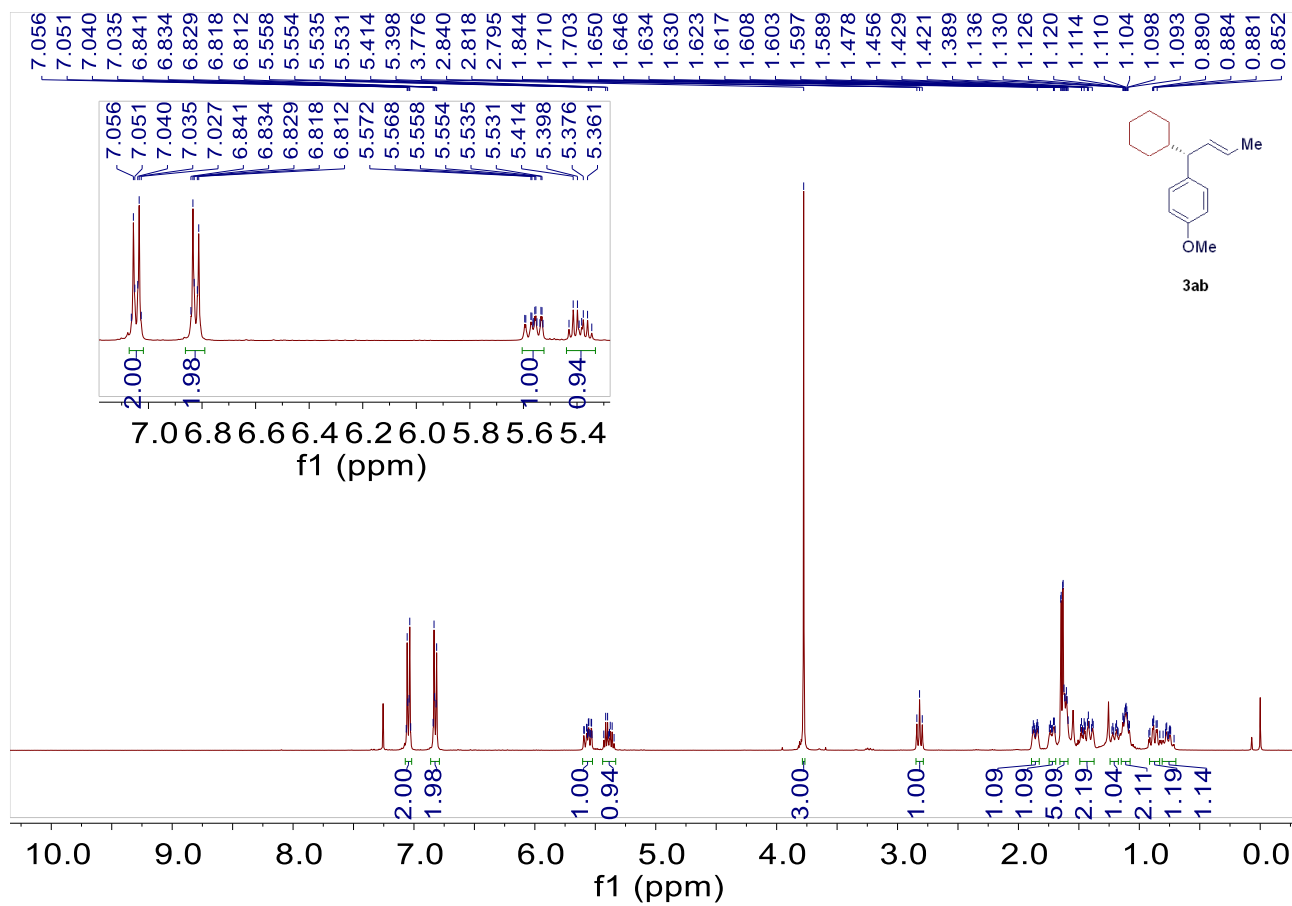


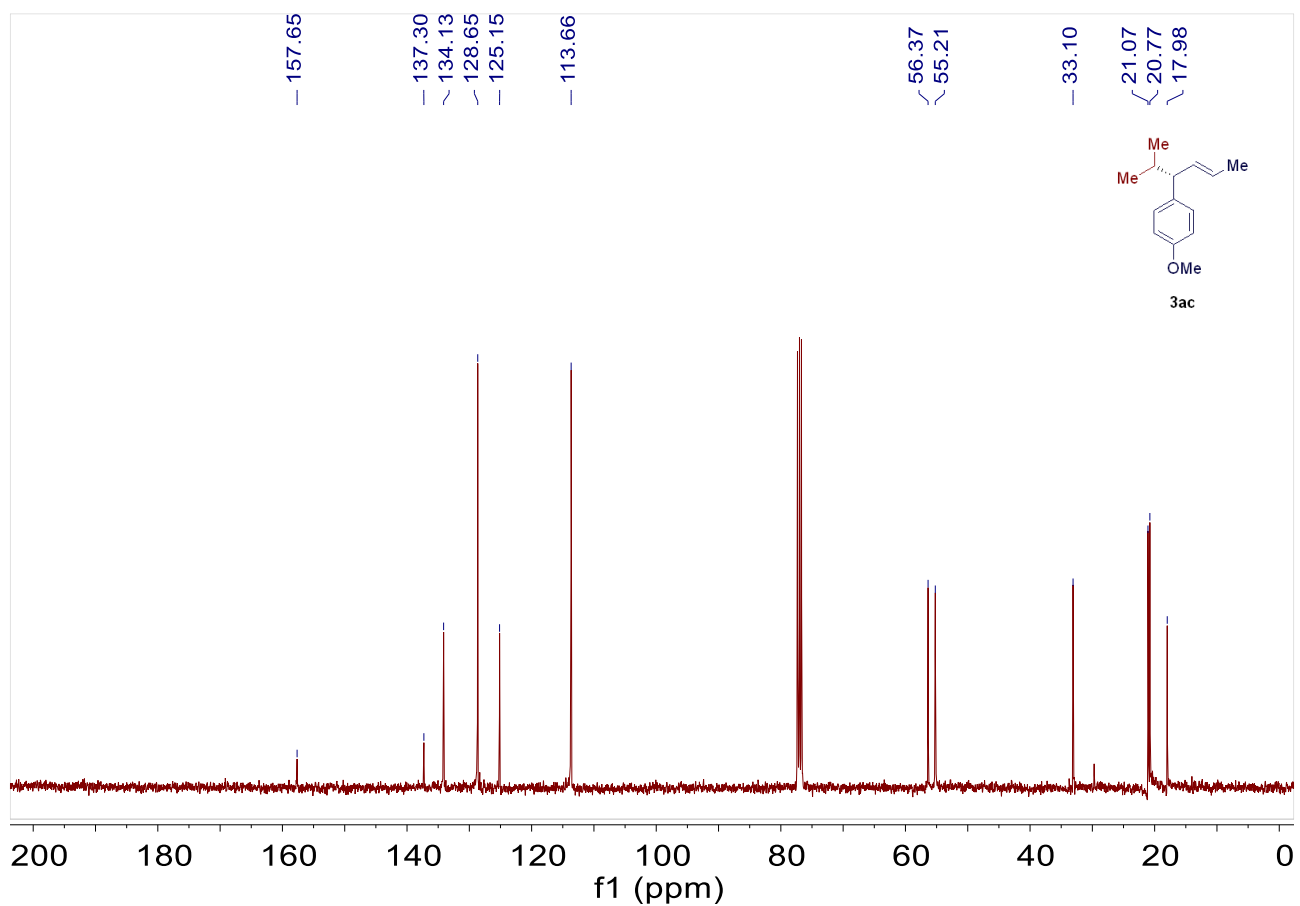
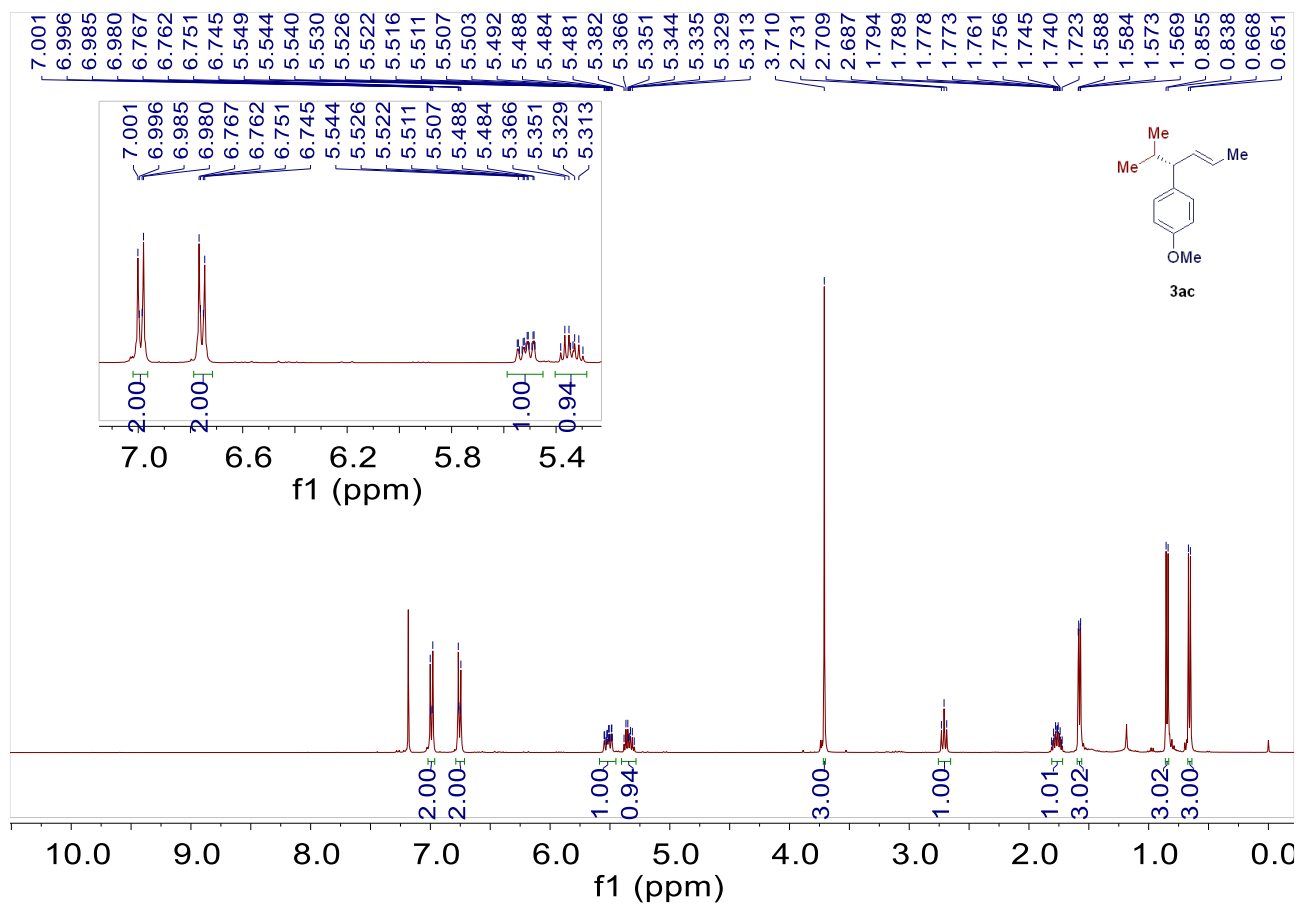


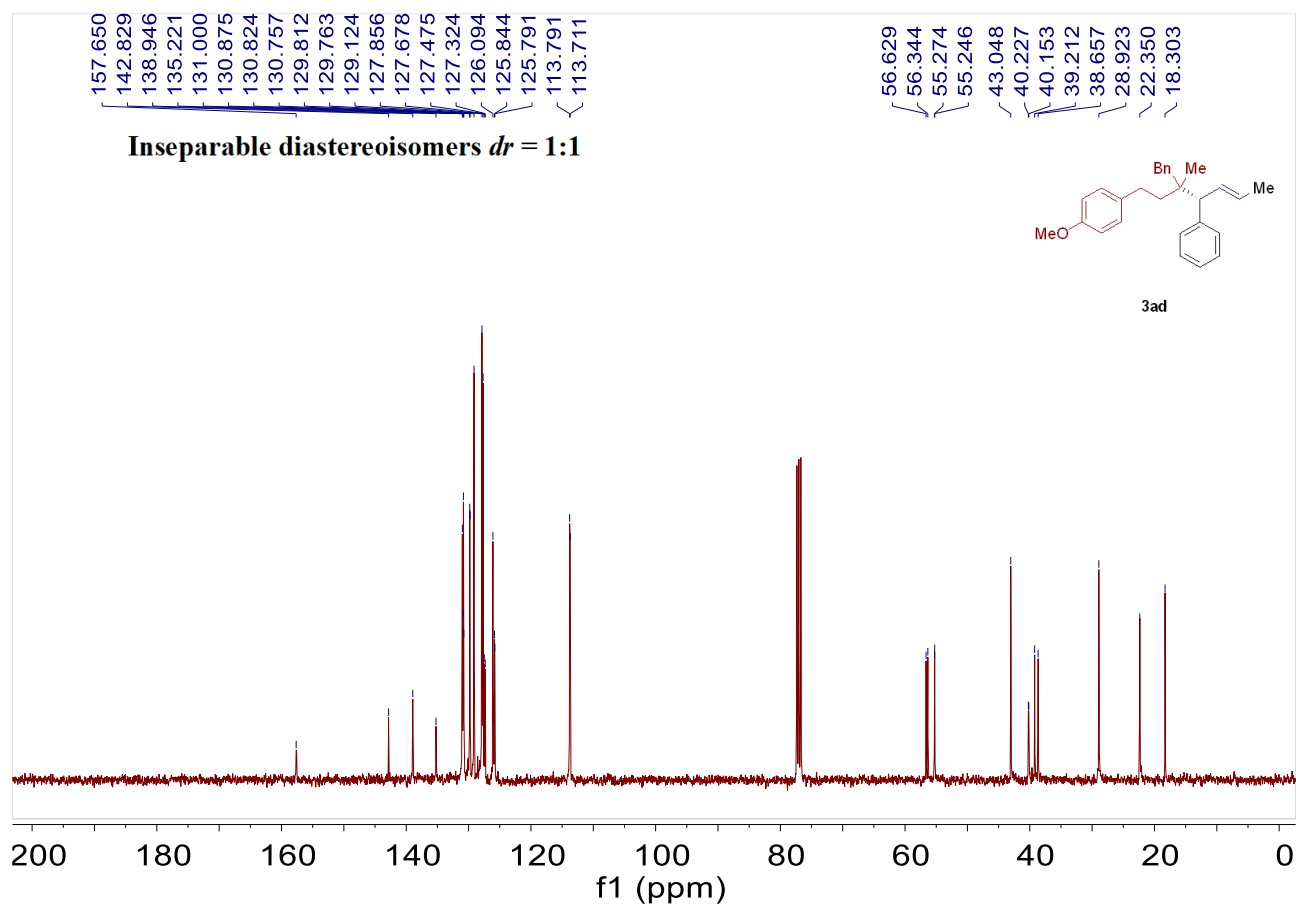
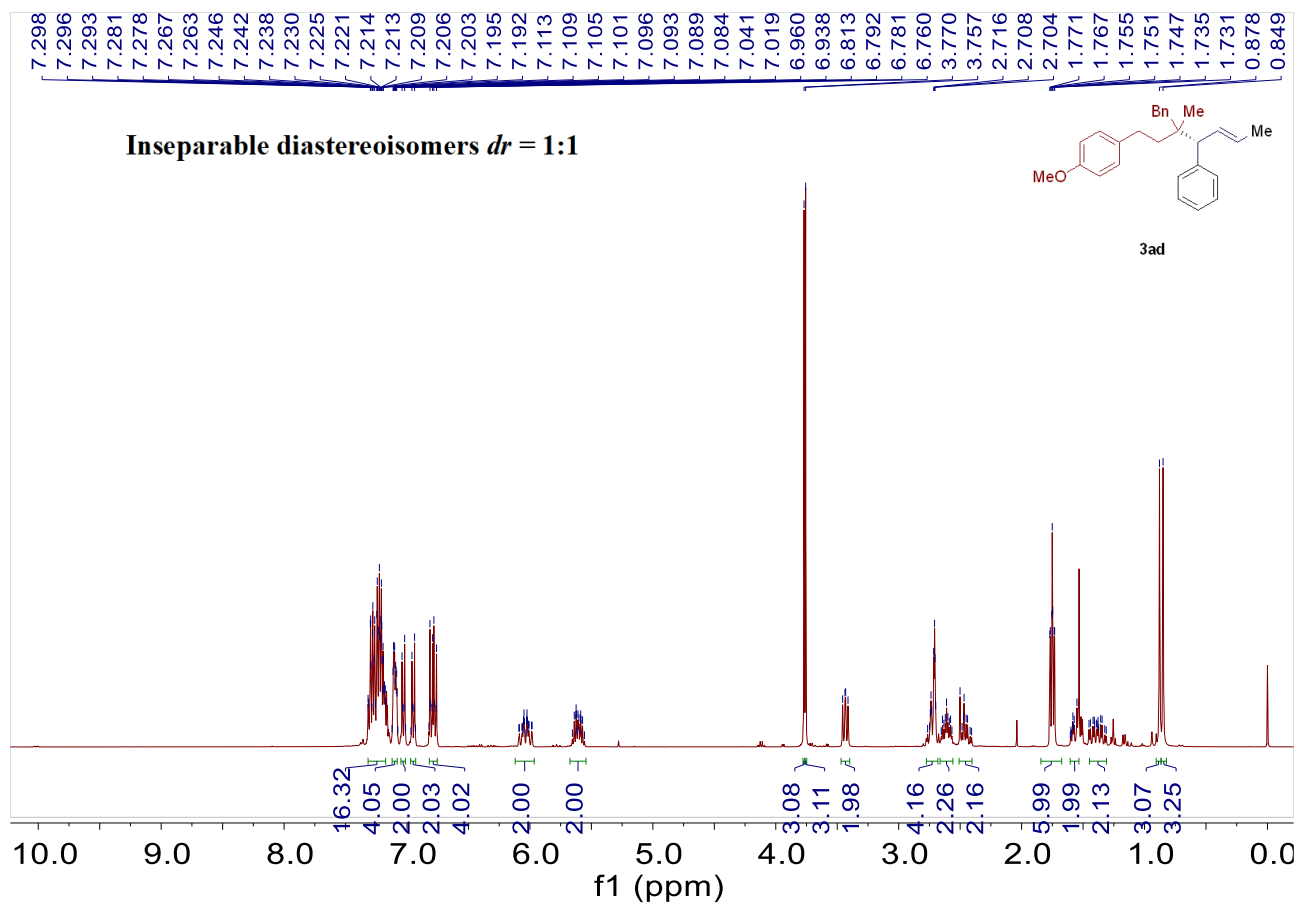




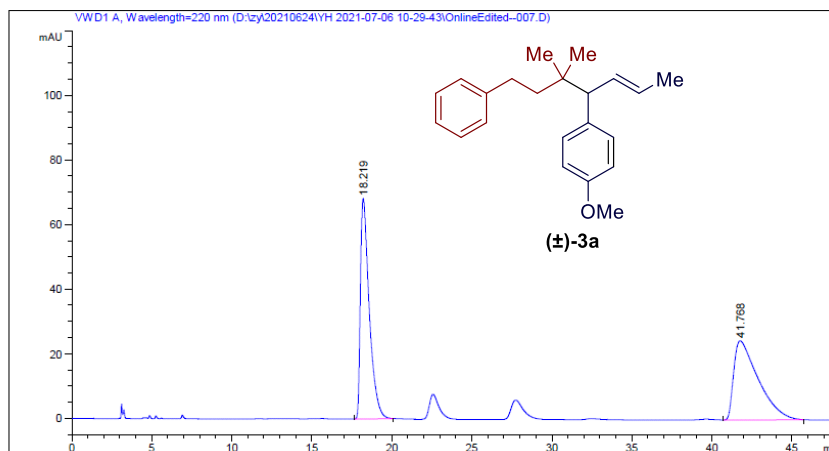




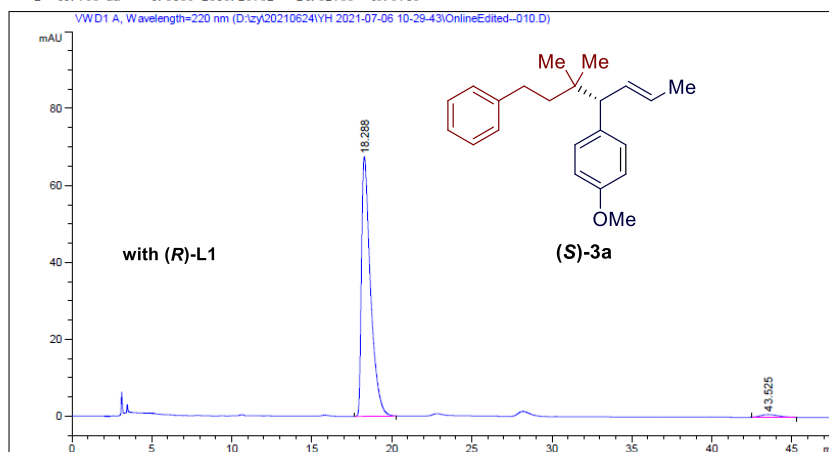




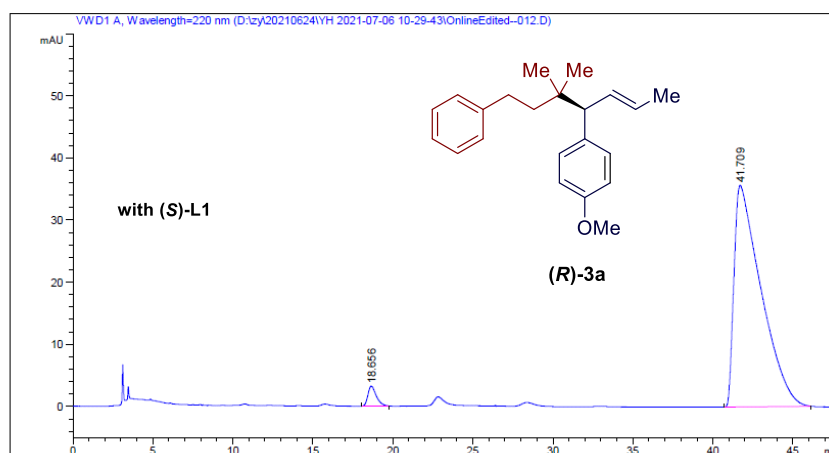
# 13. HPLC spectra



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.219	BB	0.5711	2616.20630	68.26635	50.0287
2	41.768	BB	1.5130	2613.20752	24.52783	49.9713

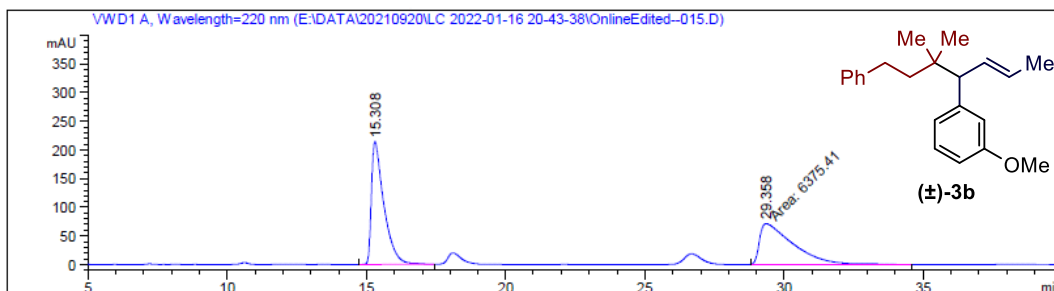


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.288	BB	0.5846	2654.10547	67.52473	97.9020
2	43.525	BB	0.9099	56.87577	7.37347e-1	2.0980

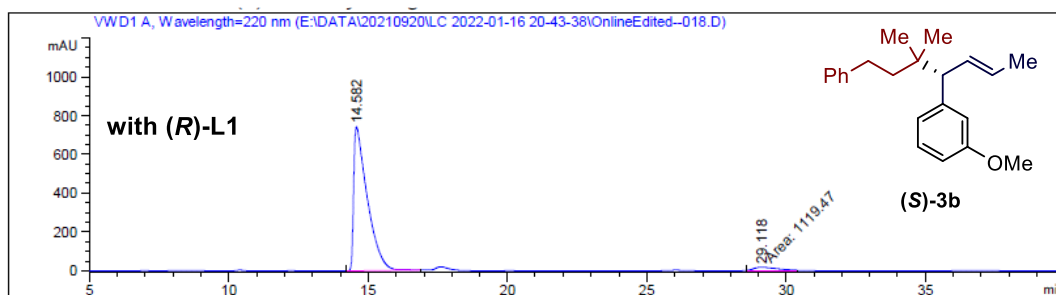


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.656	BB	0.5400	119.39038	3.23964	2.7708
2	41.709	BB	1.6082	4189.44678	35.67170	97.2292

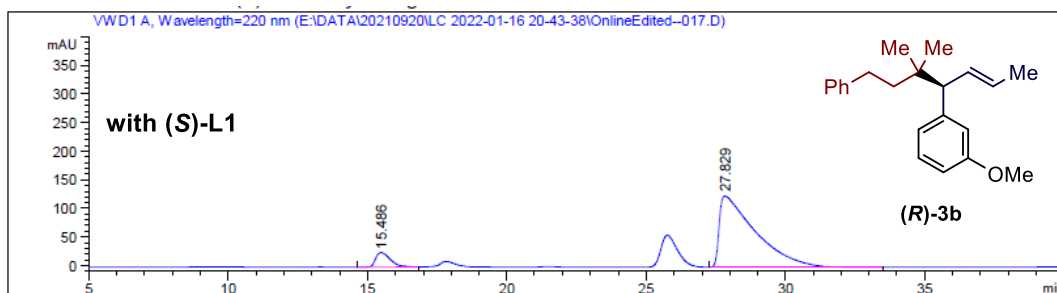




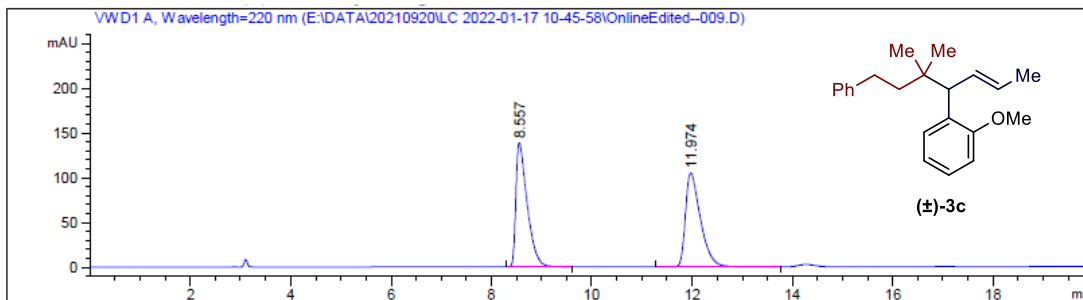
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.308	BB	0.4479	6655.06787	214.55164	51.0731
2	29.358	MM	1.4668	6375.41406	72.44096	48.9269



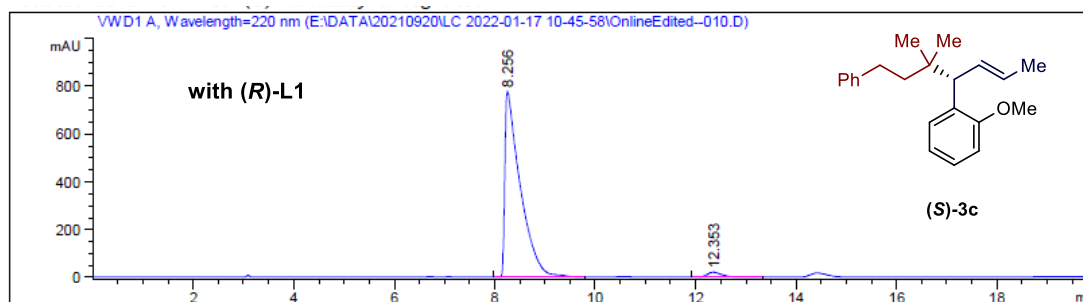
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.582	BV R	0.4794	2.52905e4	743.24207	95.7612
2	29.118	MF	1.0236	1119.47192	18.22857	4.2388



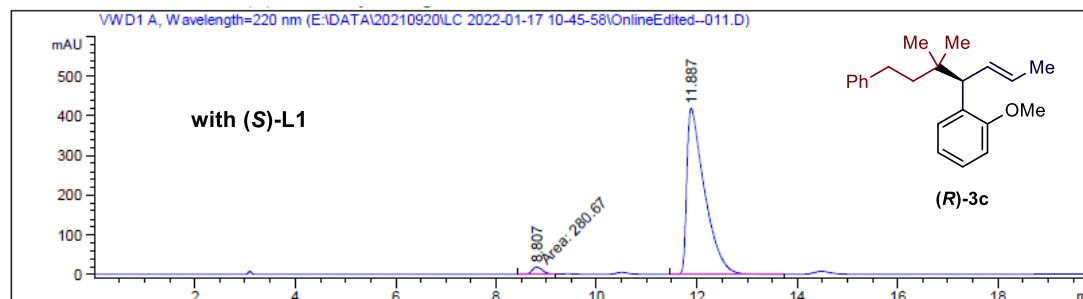
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.486	BB	0.5863	963.41742	25.64508	7.8629
2	27.829	BB	1.2395	1.12893e4	124.77864	92.1371



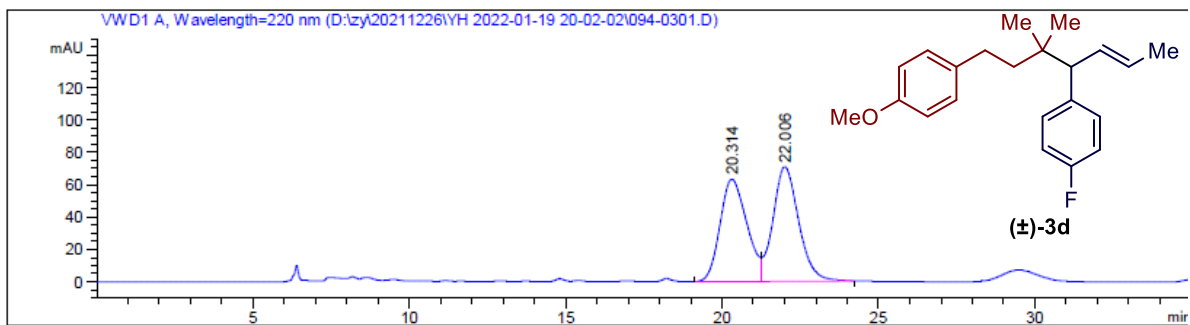
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.557	BB	0.2297	2162.60889	138.88603	49.8307
2	11.974	BB	0.3108	2177.30322	105.03326	50.1693



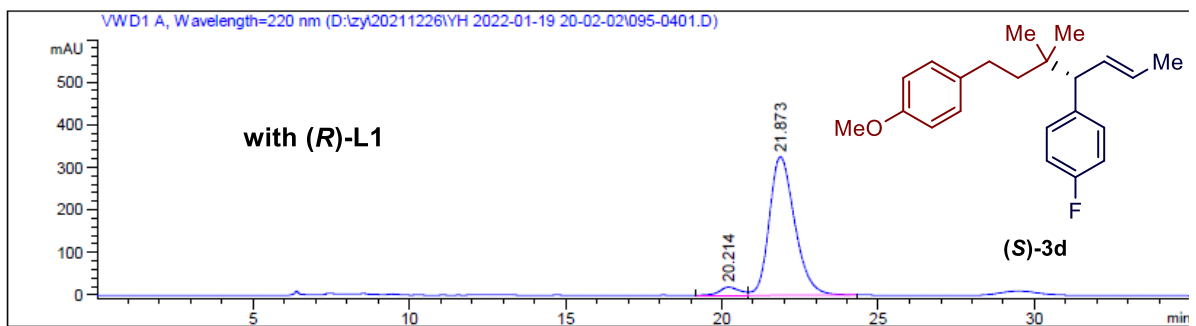
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.256	BB	0.2902	1.65802e4	779.42249	97.4365
2	12.353	BB	0.3176	436.20856	21.05996	2.5635



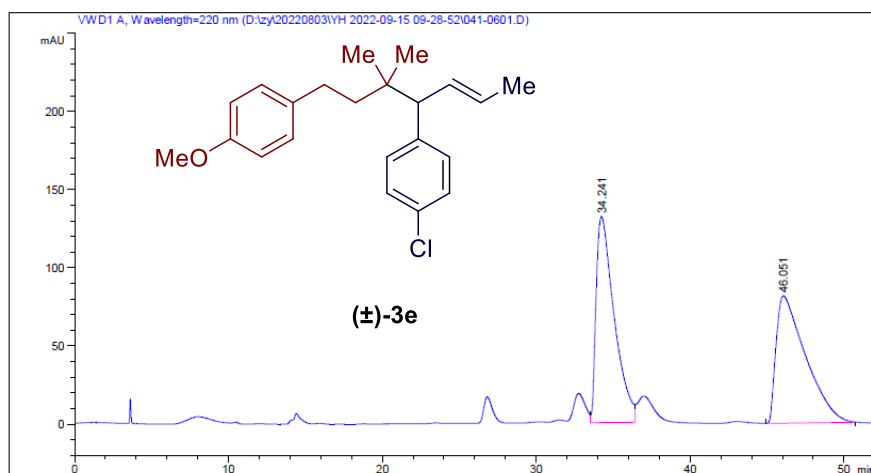
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.807	MF	0.2472	280.67047	18.92015	2.6565
2	11.887	BB	0.3520	1.02848e4	419.52045	97.3435



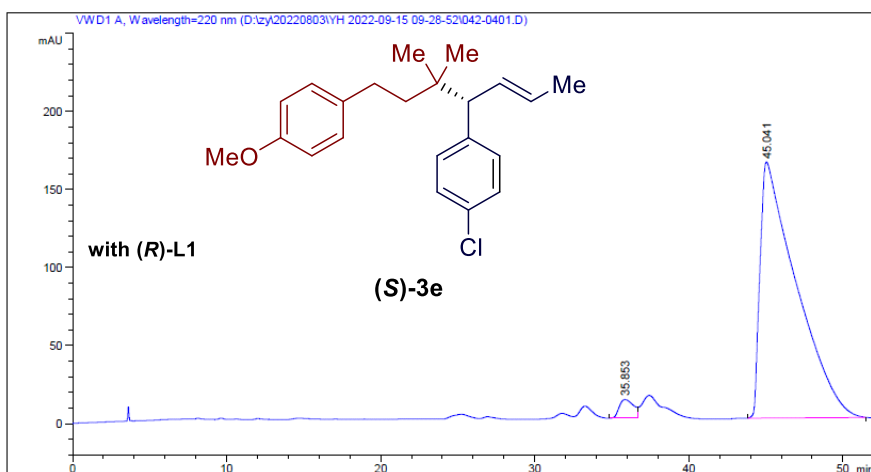
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.314	BV	0.8817	3759.93237	63.05514	48.1096
2	22.006	VB	0.8625	4055.42114	70.67263	51.8904



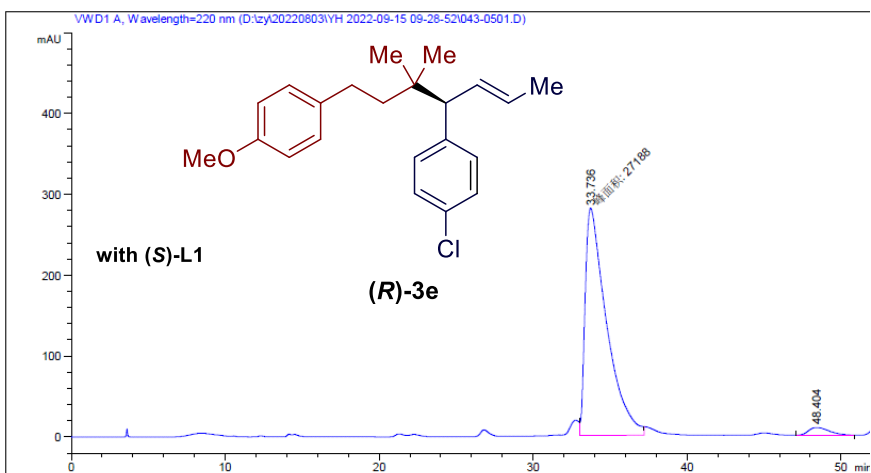
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.214	BV	0.6258	850.14056	19.22800	4.4110
2	21.873	VB	0.8602	1.84231e4	325.54718	95.5890



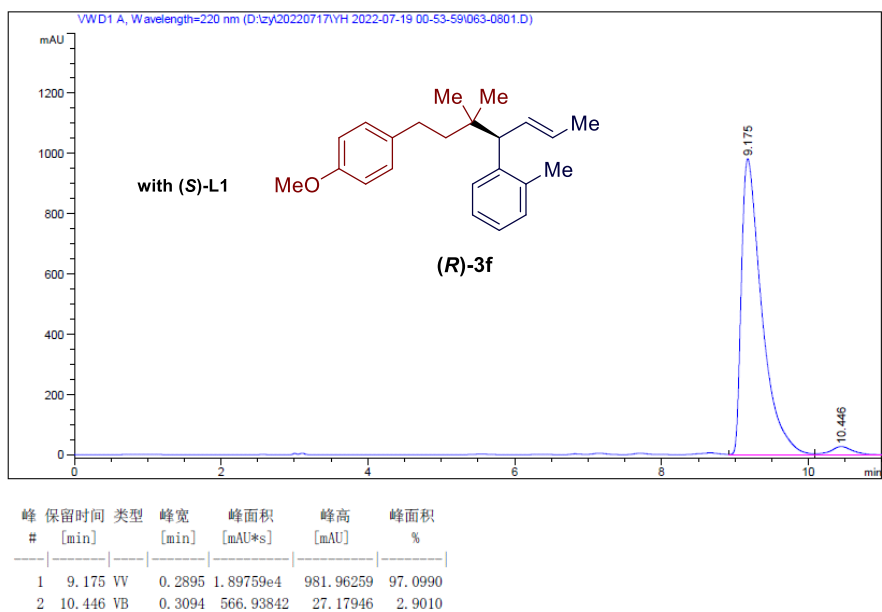
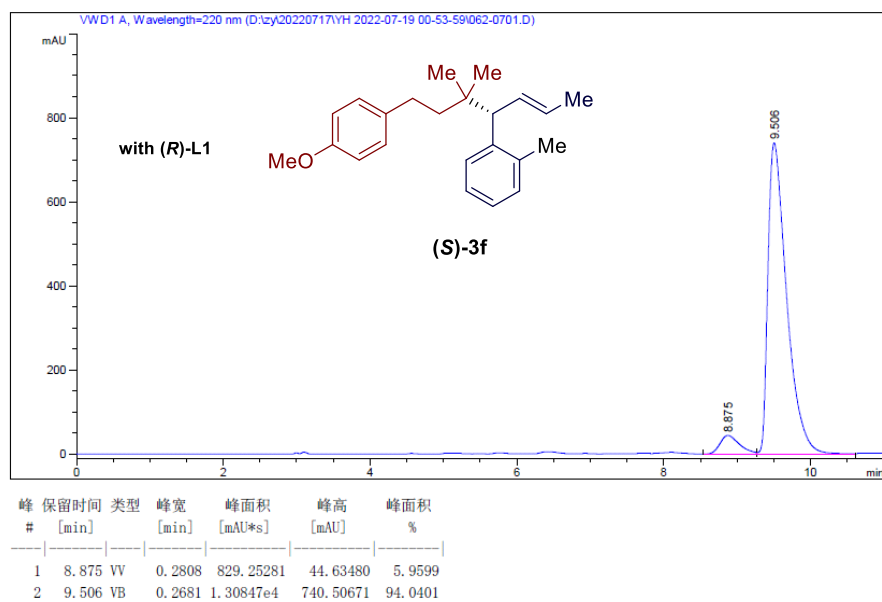
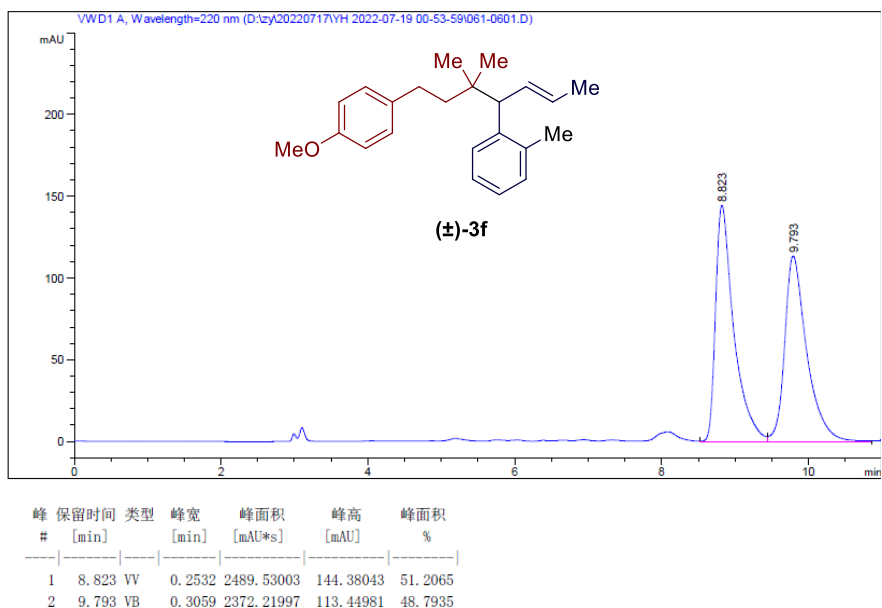
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	34.241	VV	0.9618	1.07870e4	132.07971	49.8999
2	46.051	BB	1.5589	1.08303e4	81.52178	50.1001

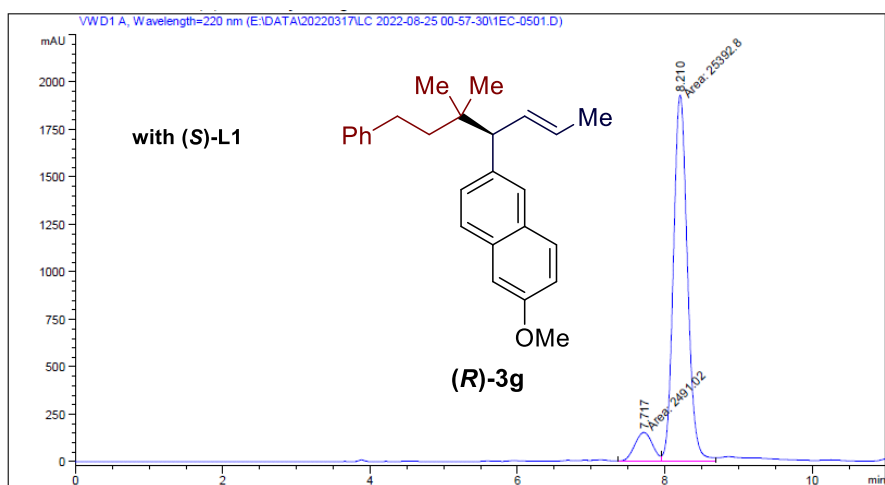
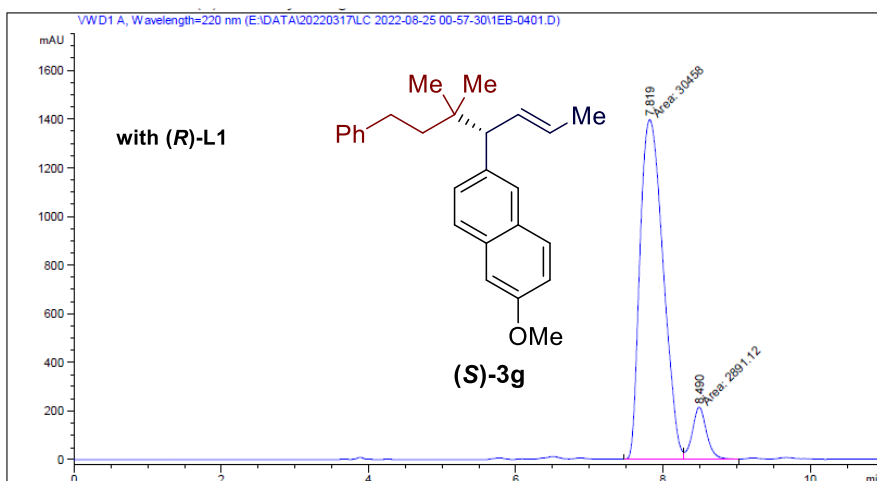
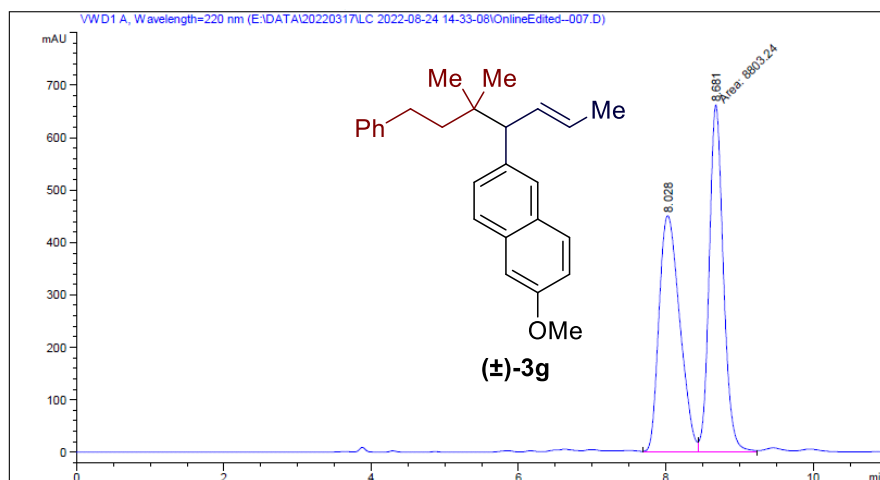


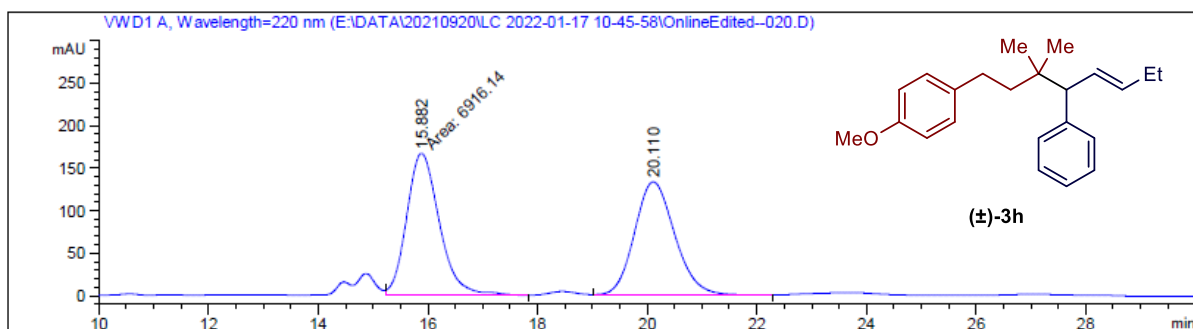
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	35.853	BV	0.7586	776.34174	12.01866	2.8087
2	45.041	BB	1.9308	2.68641e4	164.19289	97.1913



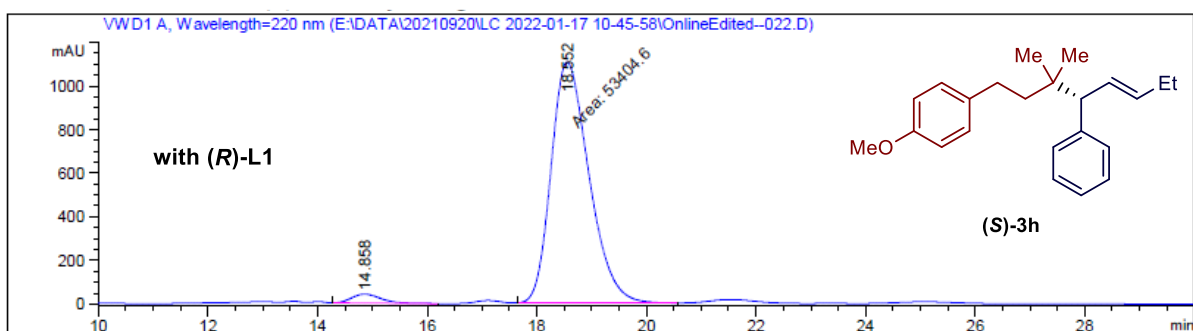
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	33.736	MF	1.6108	2.71880e4	281.30637	96.7880
2	48.404	BB	1.0898	902.25824	9.70365	3.2120



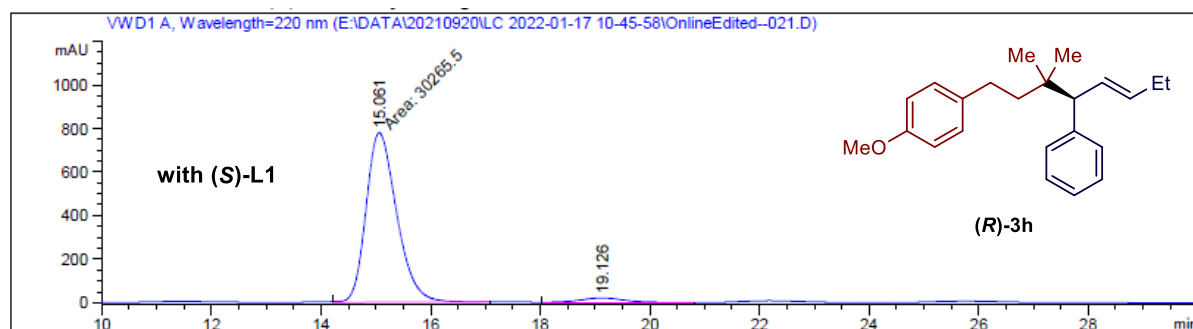




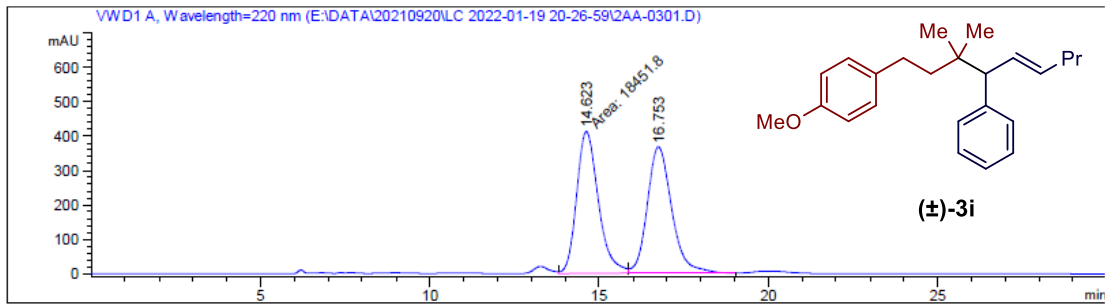
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.882	FM	0.6904	6916.13867	166.96463	50.6442
2	20.110	BB	0.7862	6740.19824	132.78203	49.3558



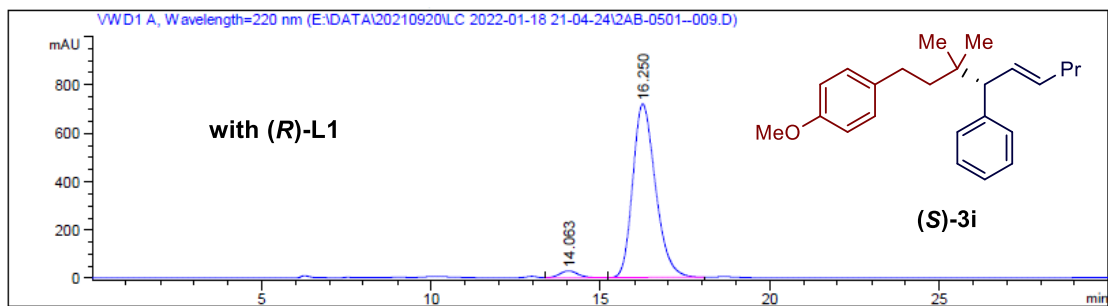
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.858	BB	0.5735	1518.11206	40.94632	2.7641
2	18.552	FM	0.8036	5.34046e4	1107.59863	97.2359



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.061	FM	0.6471	3.02655e4	779.50464	96.5549
2	19.126	BB	0.7990	1079.88989	20.51896	3.4451

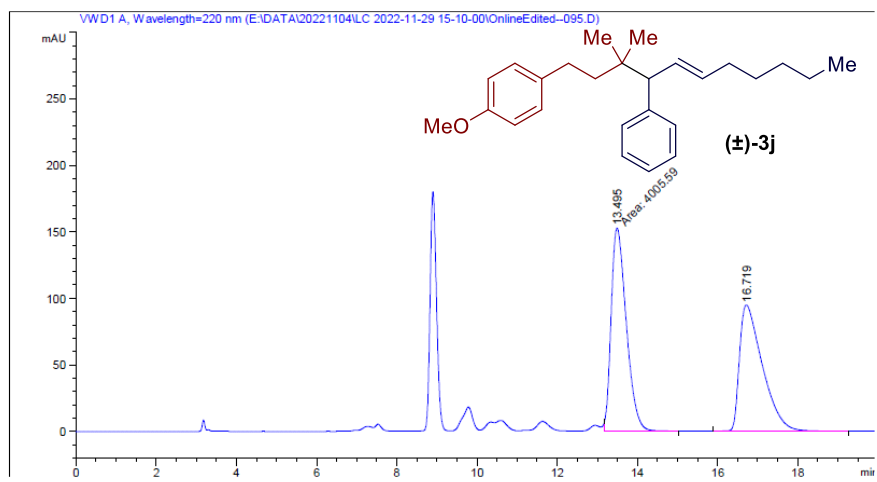


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.623	FM	0.7452	1.84518e4	412.69940	49.9744
2	16.753	VB	0.7721	1.84707e4	367.65771	50.0256

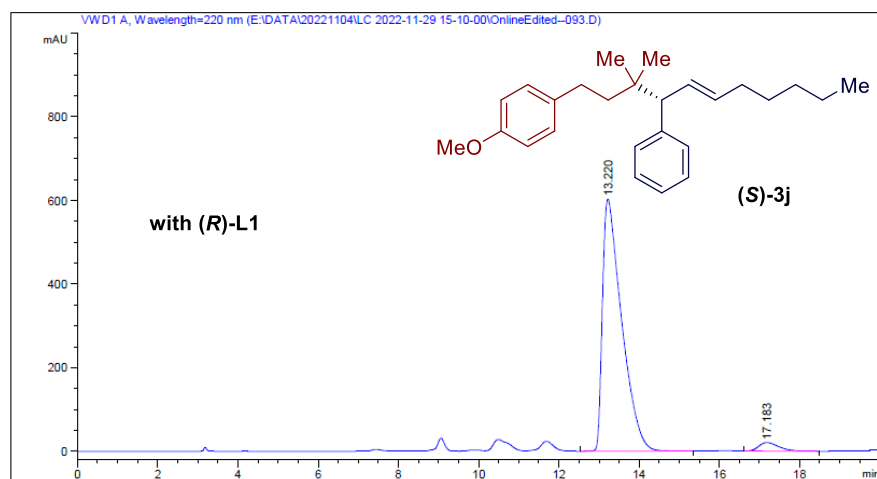


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.063	VB	0.5995	1133.54663	29.03459	3.2602
2	16.250	BB	0.7211	3.36352e4	718.59766	96.7398

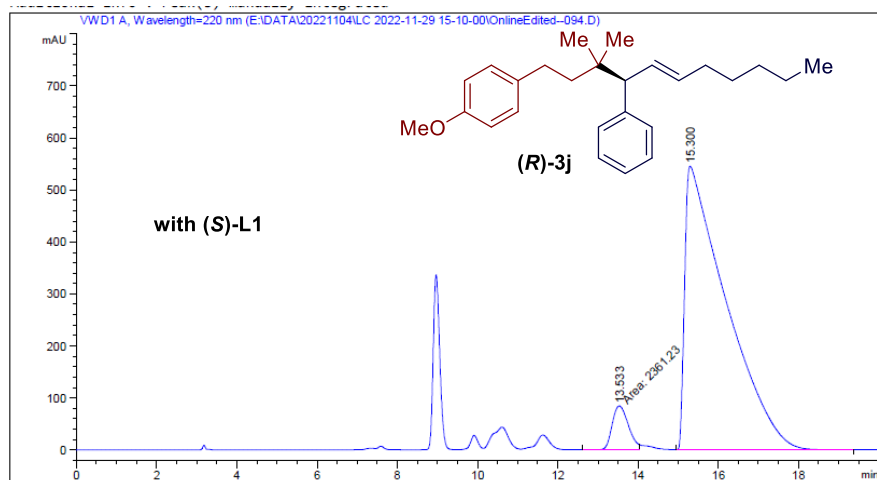




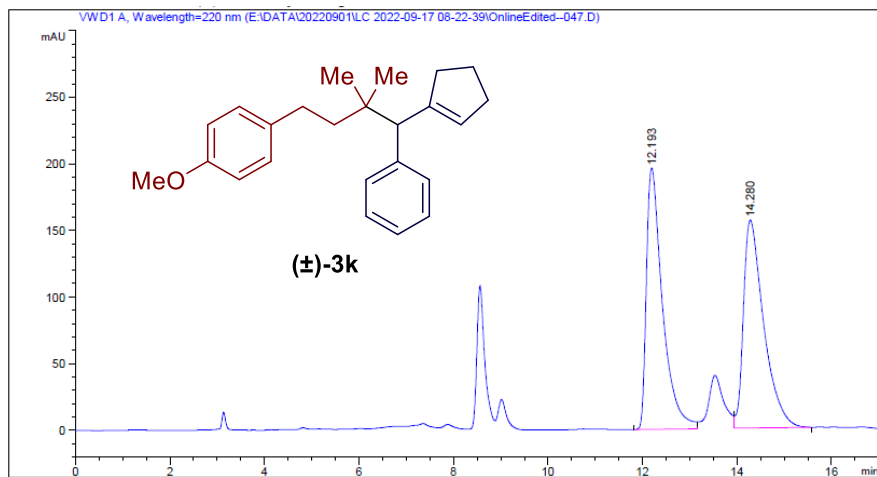
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.495	FM	0.4373	4005.58545	152.65329	51.6836
2	16.719	BB	0.5918	3744.61743	94.81467	48.3164



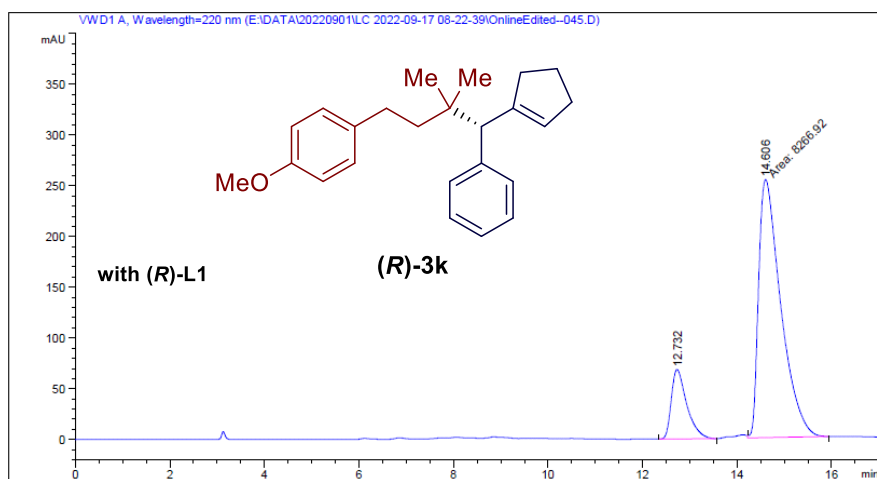
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.220	BB	0.4881	1.99968e4	602.73242	96.6700
2	17.183	BB	0.5256	688.83740	20.11166	3.3300



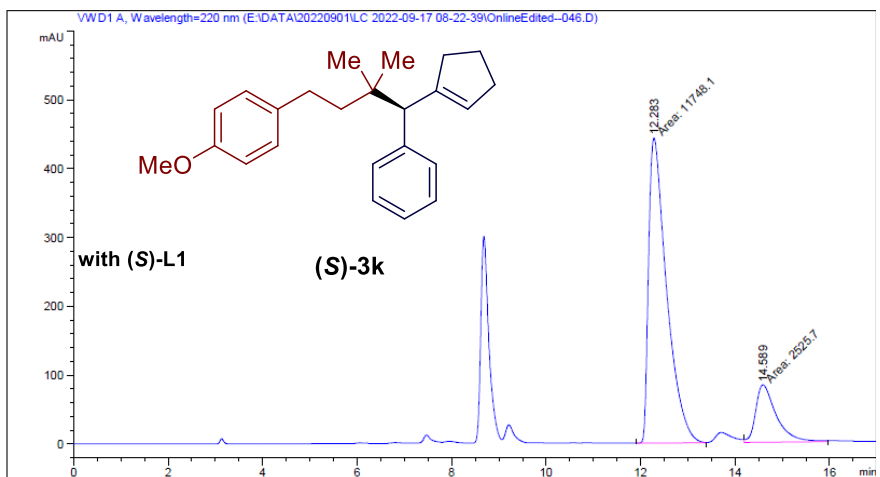
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.533	MF	0.4676	2361.23193	84.16882	5.6944
2	15.300	VB	0.9629	3.91047e4	545.11444	94.3056



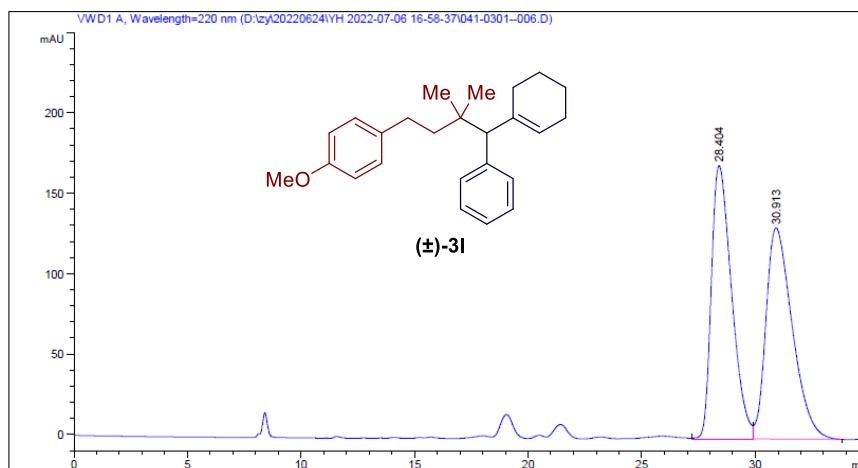
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.193	BV	0.3509	4642.11621	196.29243	49.9580
2	14.280	VB	0.4447	4649.91455	156.00333	50.0420



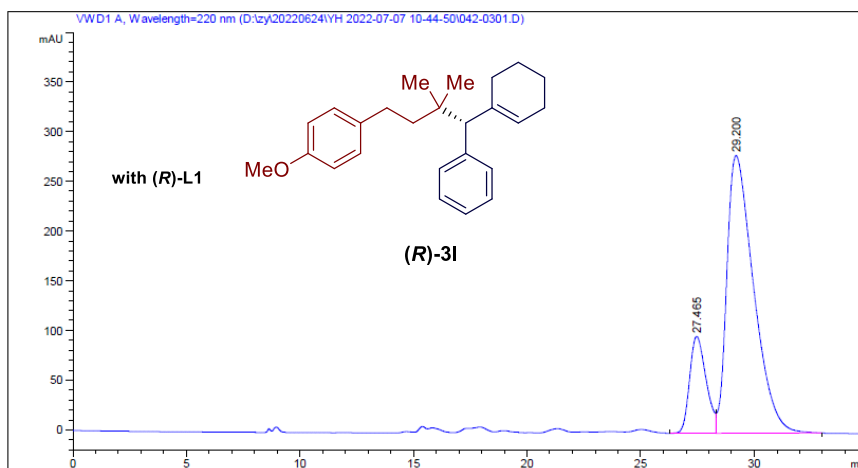
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.732	BB	0.3406	1551.86694	68.41867	15.8051
2	14.606	FM	0.5422	8266.91992	254.13066	84.1949



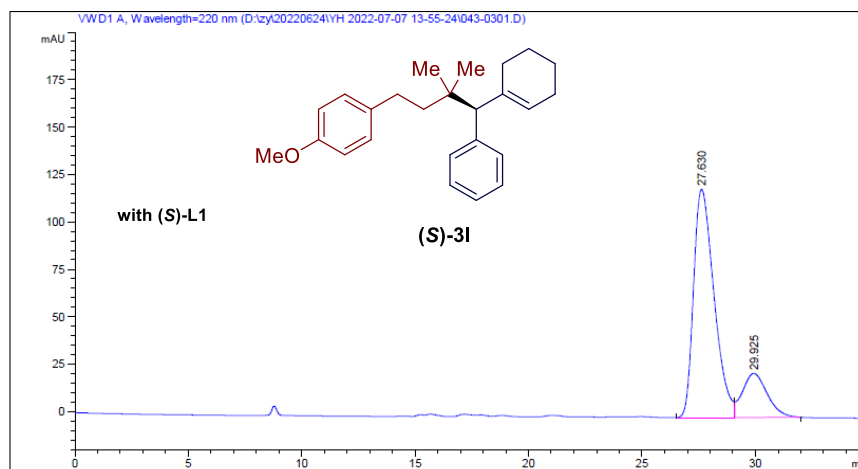
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.283	FM	0.4413	1.17481e4	443.68225	82.3054
2	14.589	MF	0.5047	2525.70483	83.39798	17.6946



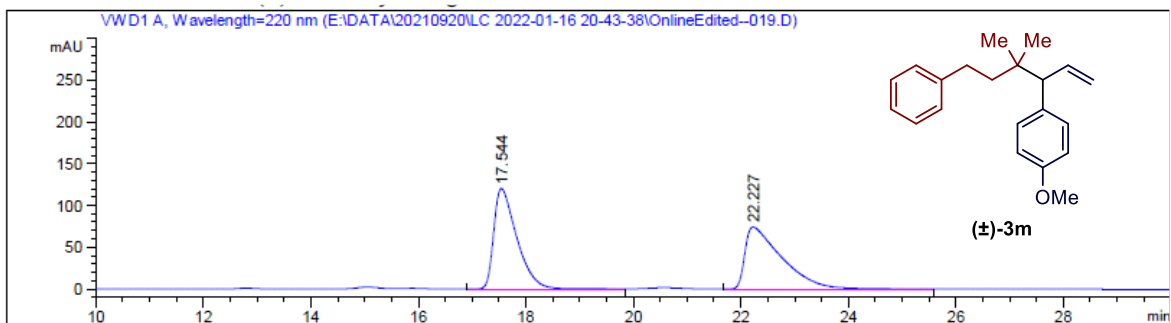
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.404	VV	0.9274	1.05045e4	169.89044	49.7828
2	30.913	VB	1.1440	1.05962e4	131.36908	50.2172



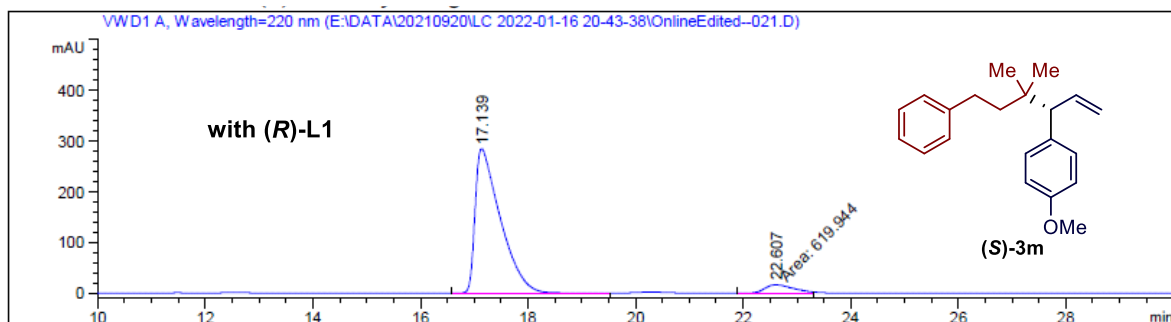
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	27.465	VV	0.7487	4917.62012	97.45625	17.6842
2	29.200	VB	1.1570	2.28903e4	279.34198	82.3158



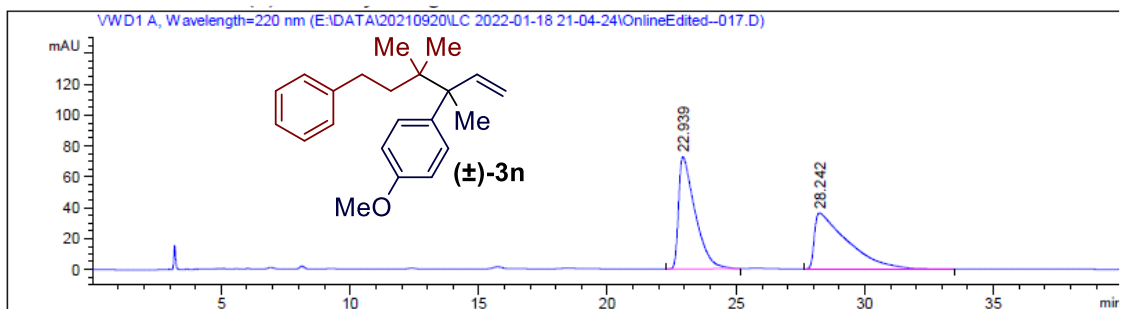
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	27.630	BV	0.9121	7553.36621	120.37693	80.9813
2	29.925	VB	0.9330	1773.93018	23.22763	19.0187



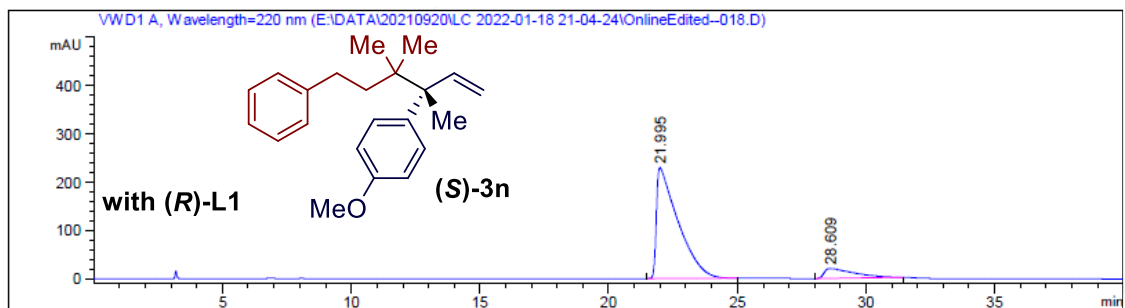
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.544	BB	0.4452	3598.37817	120.55315	50.3979
2	22.227	BB	0.6794	3541.55298	74.39710	49.6021



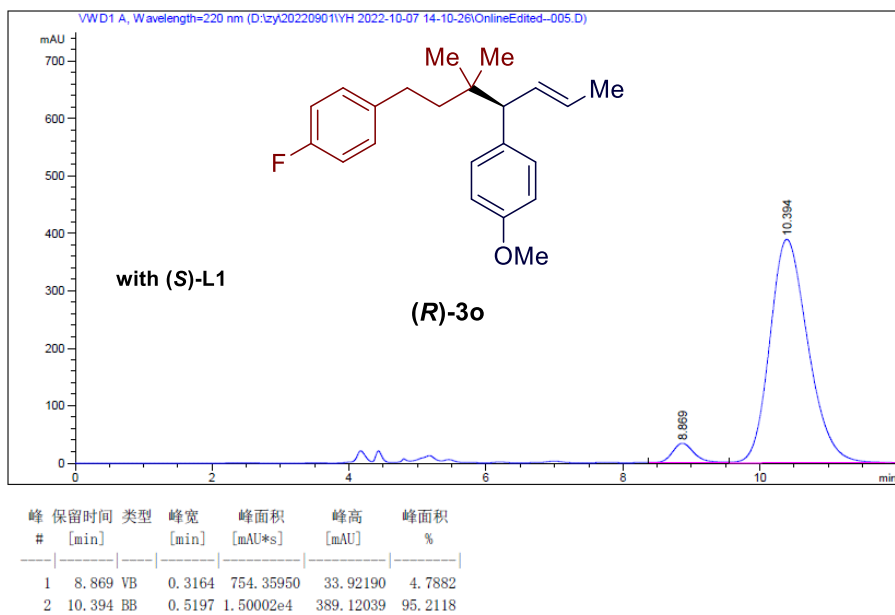
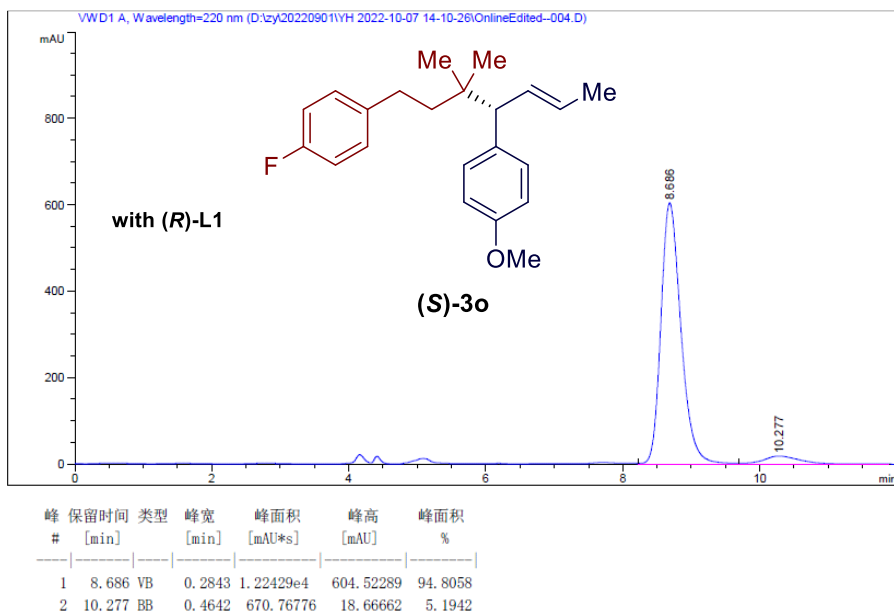
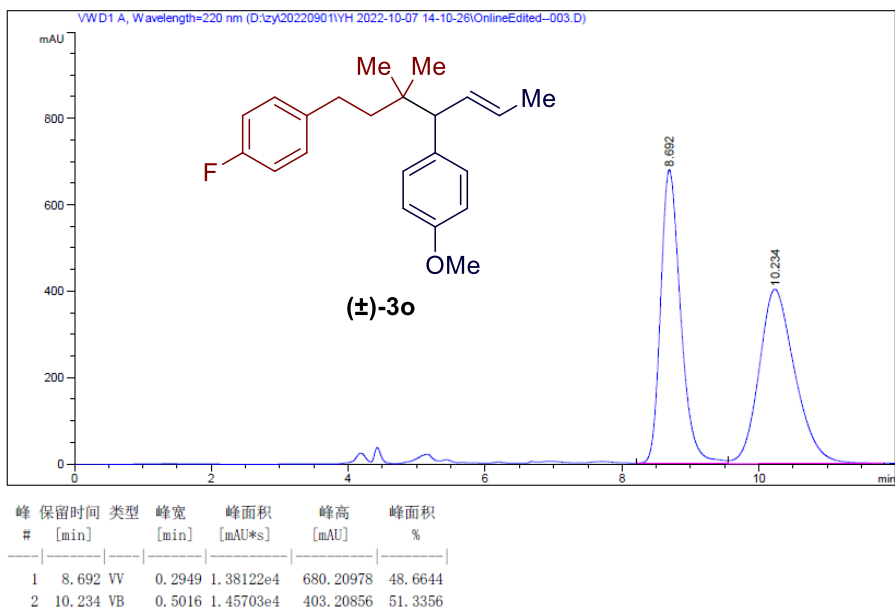
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.139	BB	0.4737	9252.26563	284.26569	93.7203
2	22.607	MF	0.6199	619.94385	16.66792	6.2797

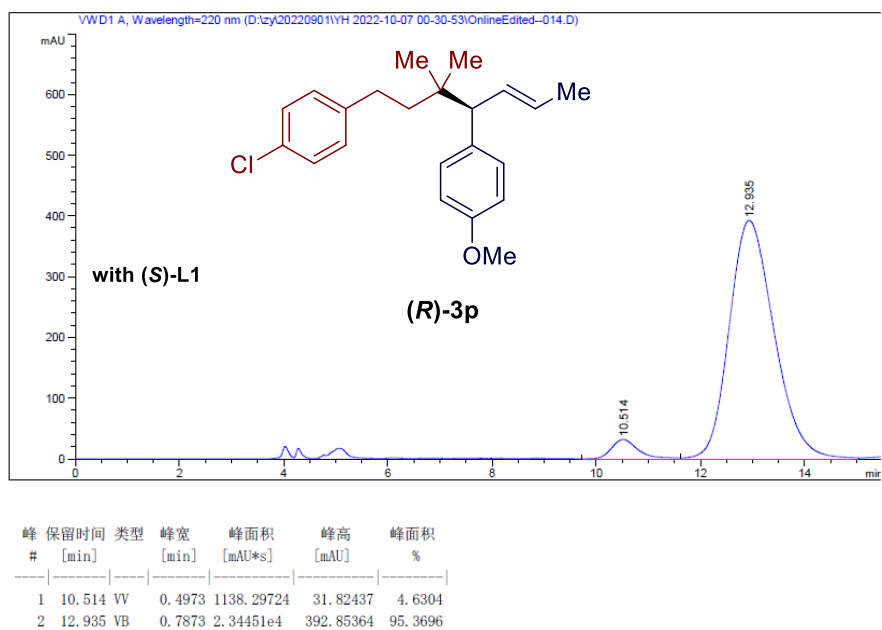
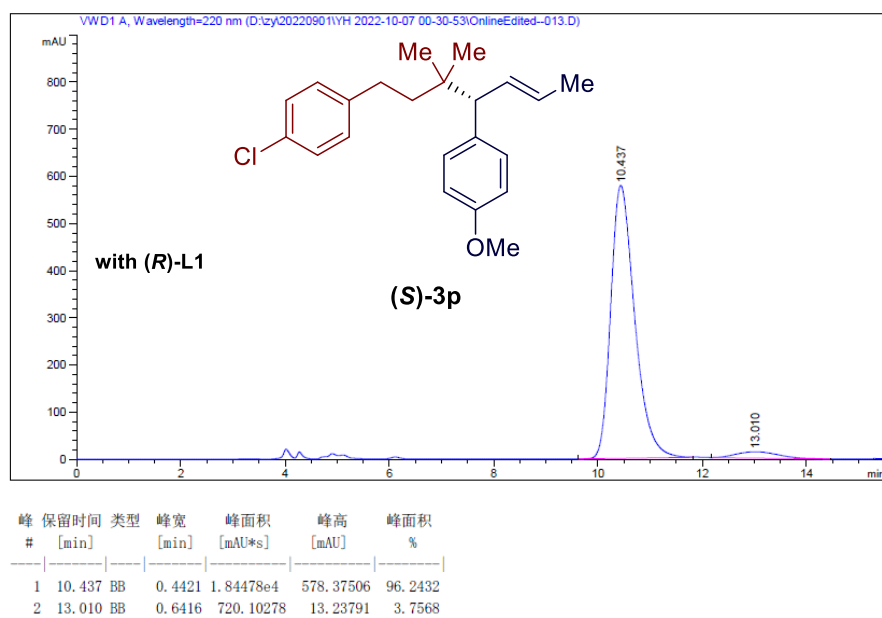
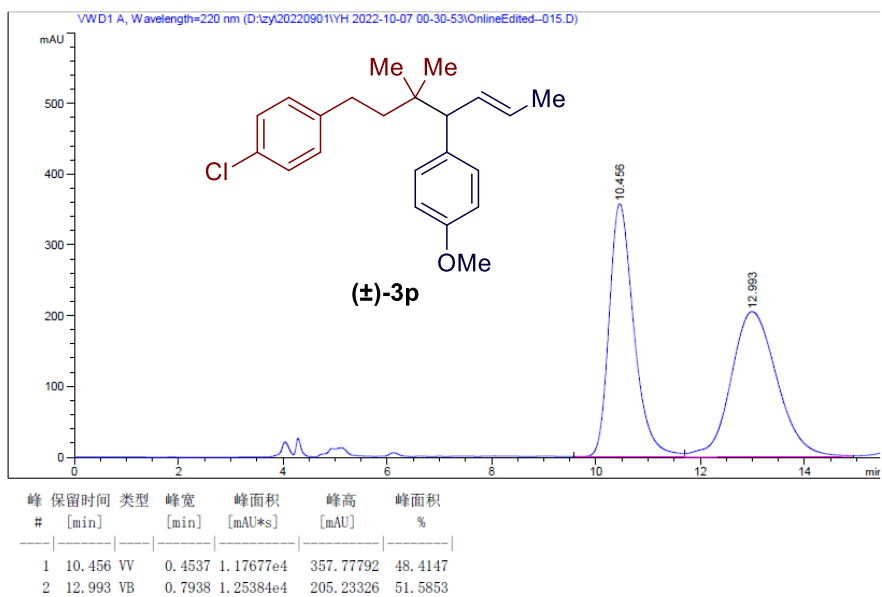


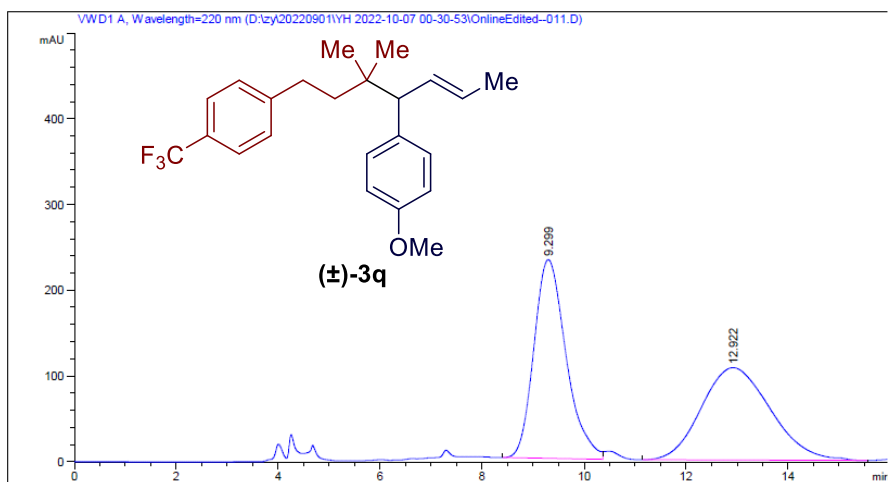
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.939	BB	0.6500	3239.38599	72.53445	50.1514
2	28.242	BB	1.1781	3219.82861	36.25635	49.8486



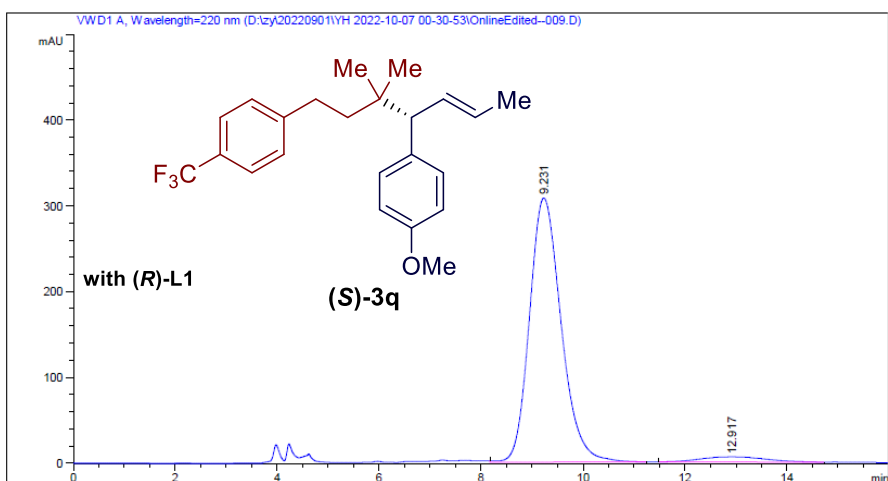
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.995	BB	0.8084	1.34040e4	228.81059	89.1556
2	28.609	BB	1.0853	1630.39087	20.38013	10.8444



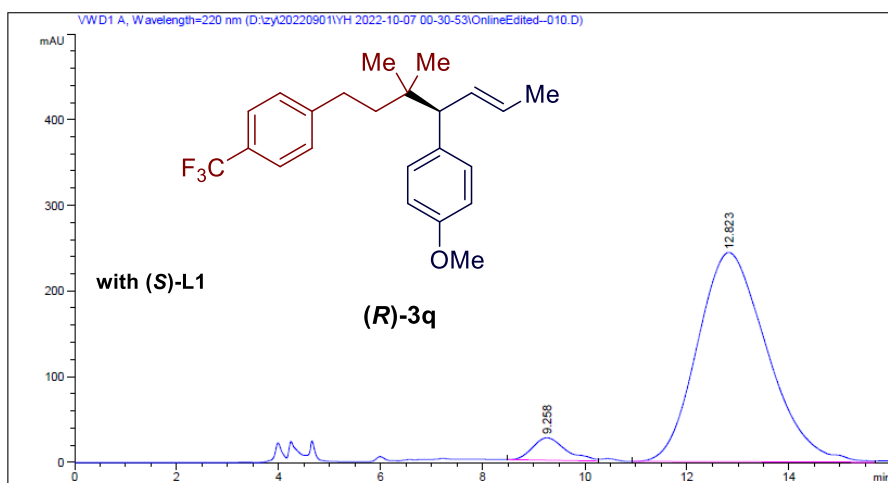




峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.299	BV	0.5927	1.01700e4	231.89560	50.0997
2	12.922	BB	1.1636	1.01295e4	107.86082	49.9003

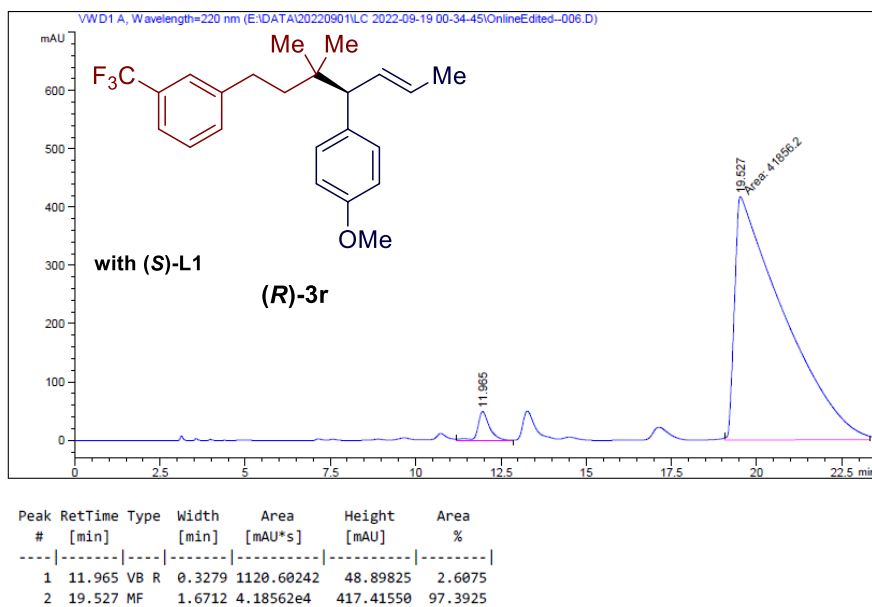
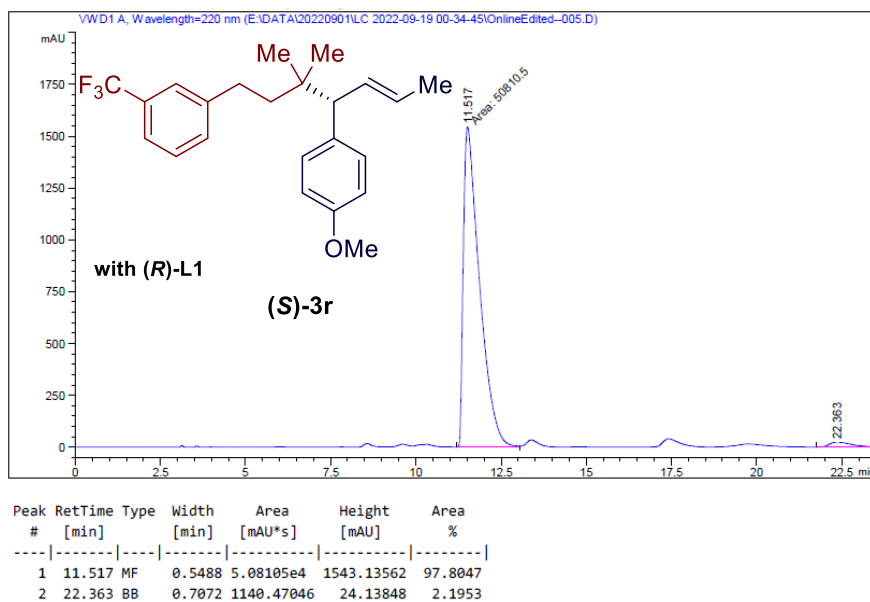
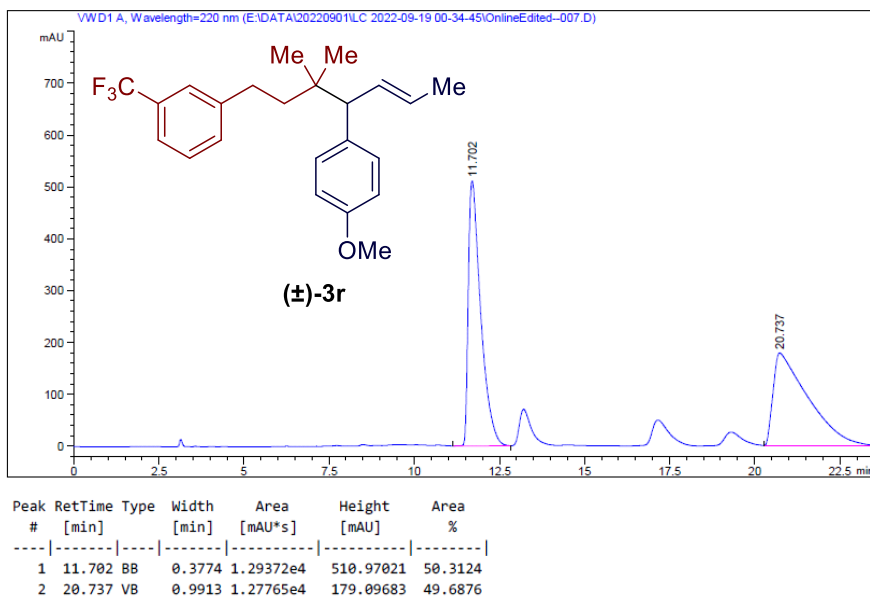


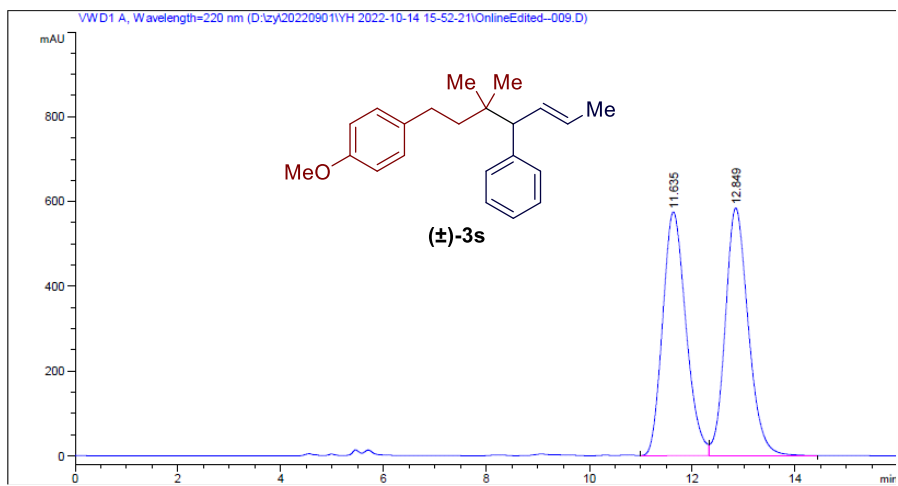
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.231	VB	0.6073	1.33137e4	307.98404	96.0494
2	12.917	BV	1.0558	547.60236	6.09148	3.9506



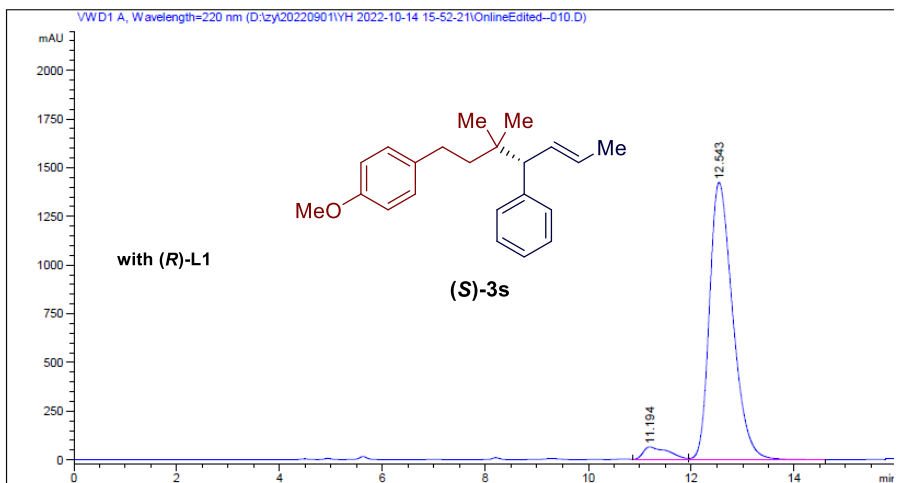
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.258	BV	0.5977	1188.54211	26.18013	4.9023
2	12.823	VB	1.2033	2.30558e4	244.23891	95.0977



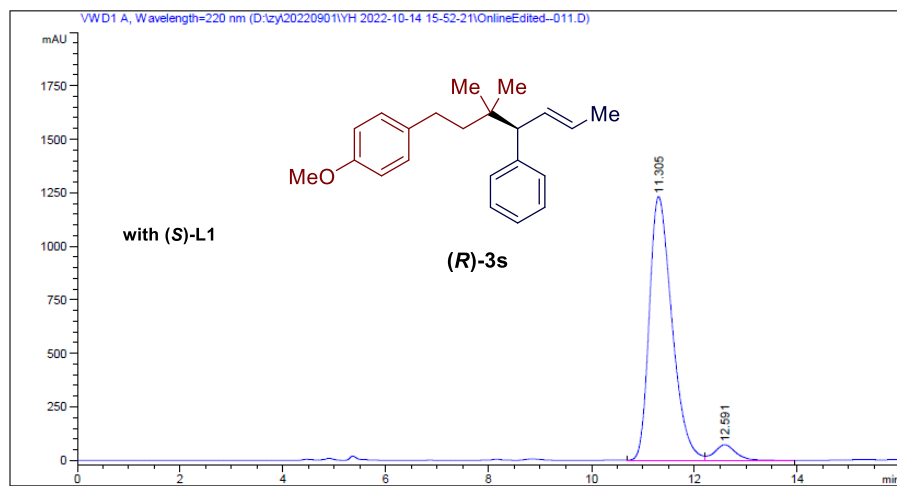




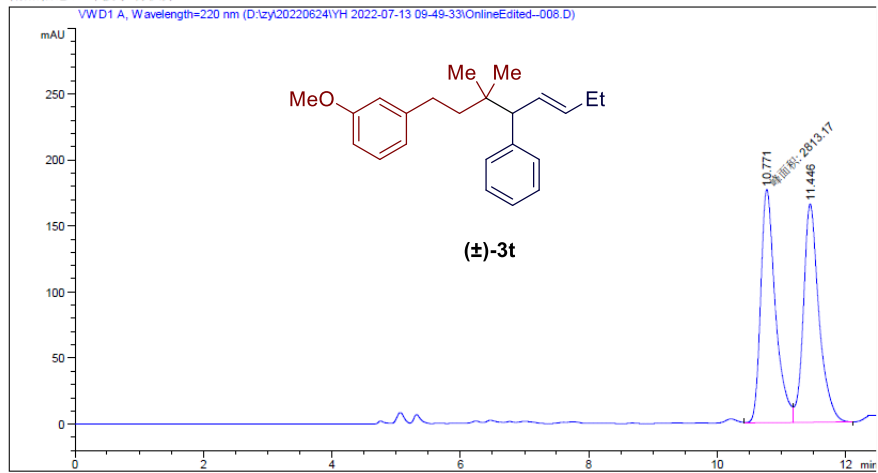
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.635	VV	0.4244	1.80617e4	575.03711	49.8387
2	12.849	VB	0.4201	1.81786e4	584.11682	50.1613



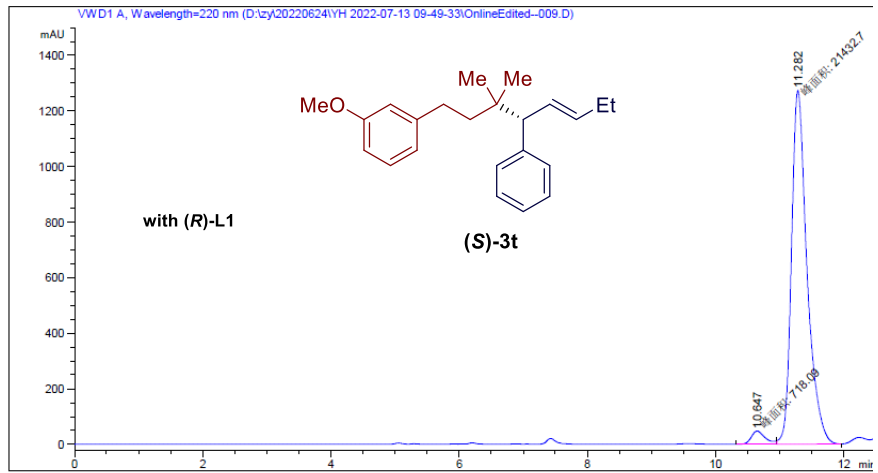
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.194	VV	0.4597	2286.98975	66.08847	4.8750
2	12.543	VB	0.4346	4.46261e4	1424.19861	95.1250



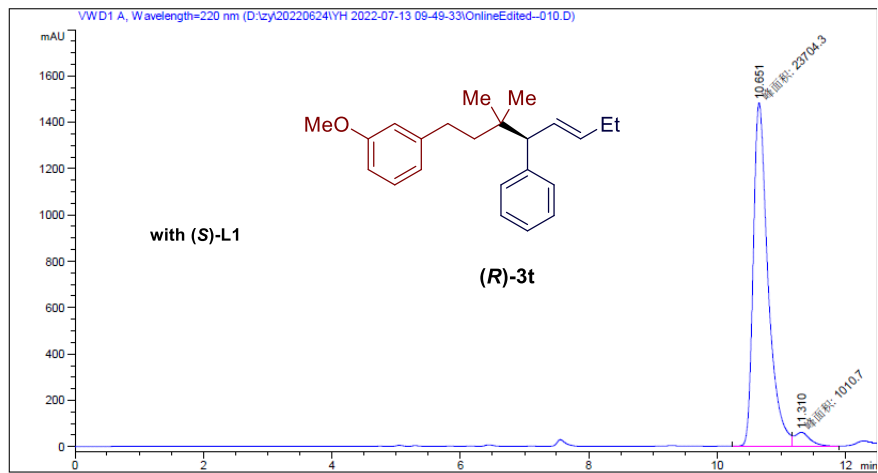
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.305	VV	0.4257	3.76744e4	1232.35144	94.7490
2	12.591	VB	0.3940	2087.92236	72.49850	5.2510



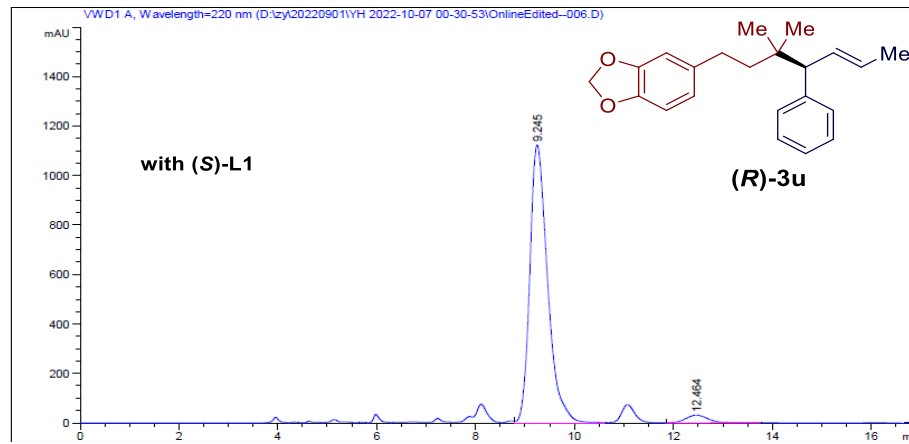
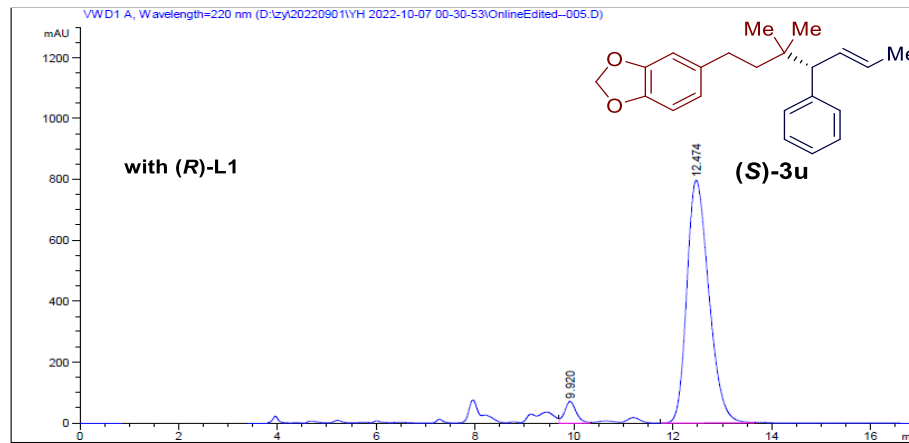
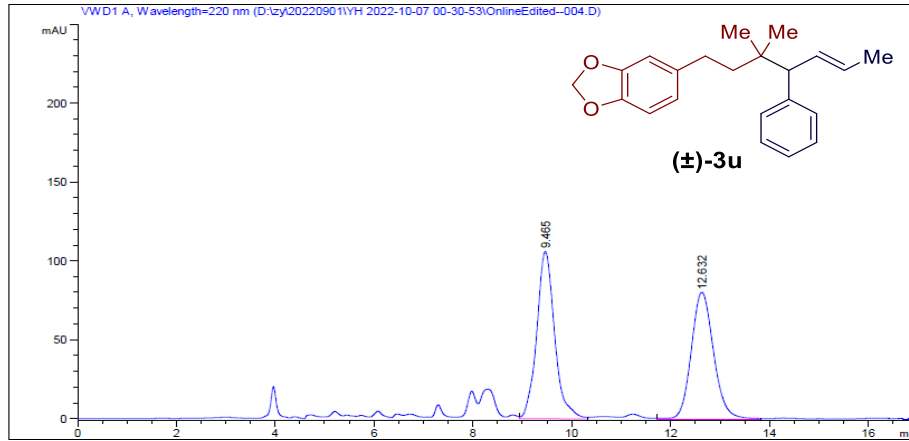
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.771	FM	0.2652	2813.16846	176.77815	50.2587
2	11.446	VB	0.2498	2784.21143	165.47011	49.7413

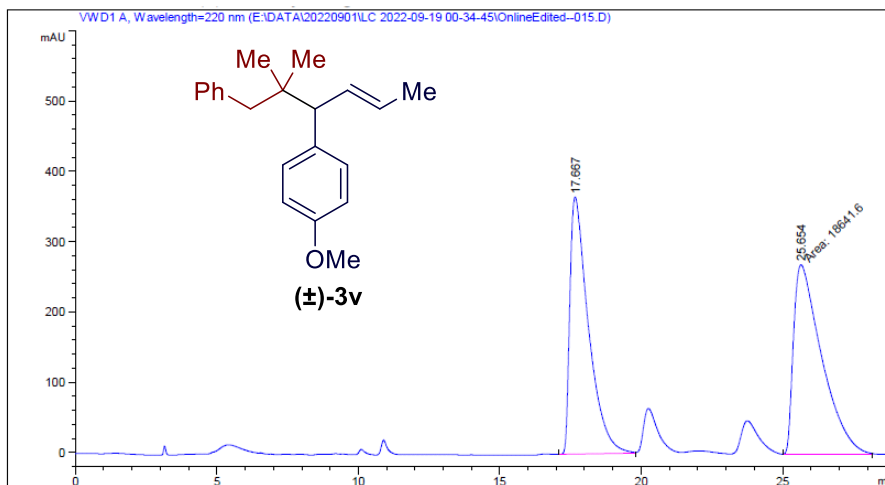


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.647	MF	0.2540	718.09027	47.12522	3.2418
2	11.282	FM	0.2810	2.14327e4	1271.21509	96.7582

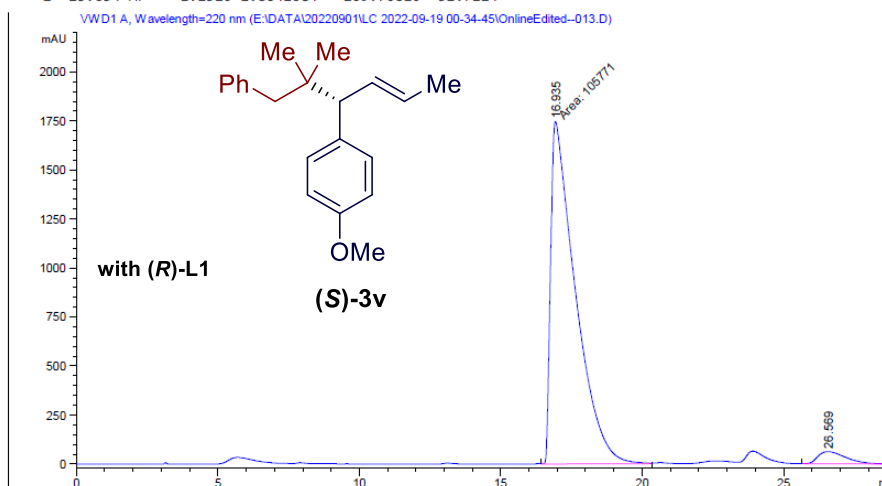


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.651	MF	0.2666	2.37043e4	1482.07568	95.9106
2	11.310	FM	0.2851	1010.70020	59.07620	4.0894

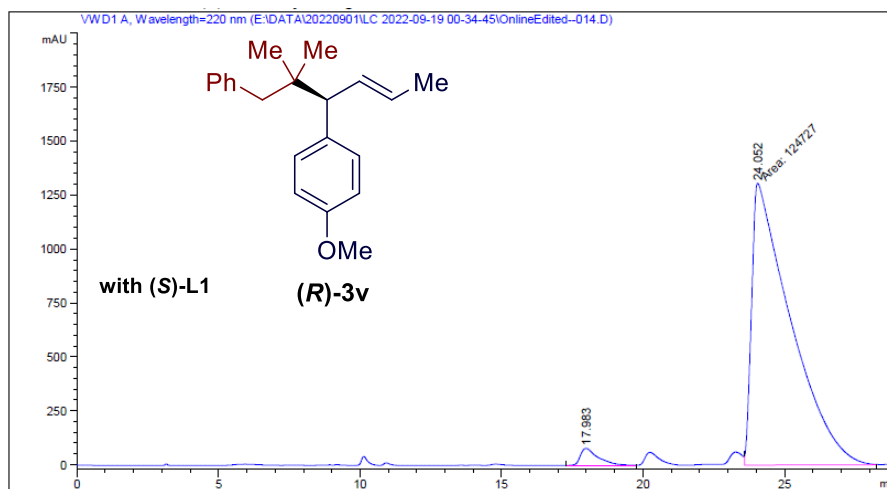




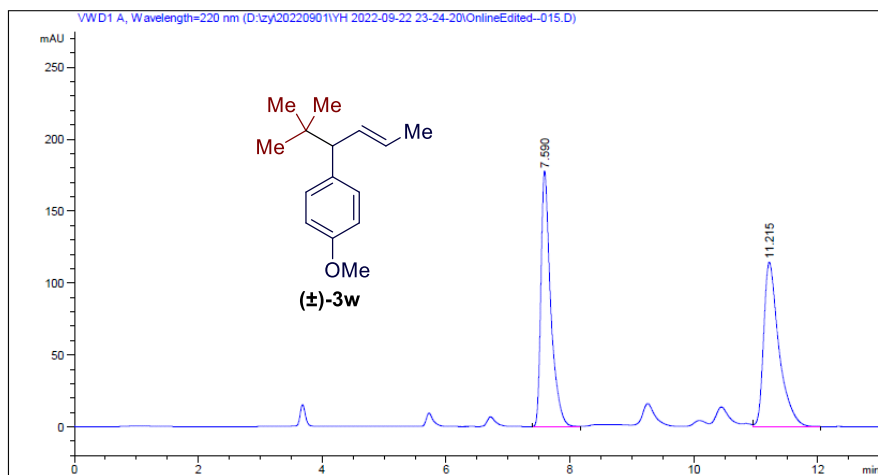
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.667	BV	0.6731	1.67232e4	365.98392	47.2876
2	25.654	MF	1.1520	1.86416e4	269.70810	52.7124



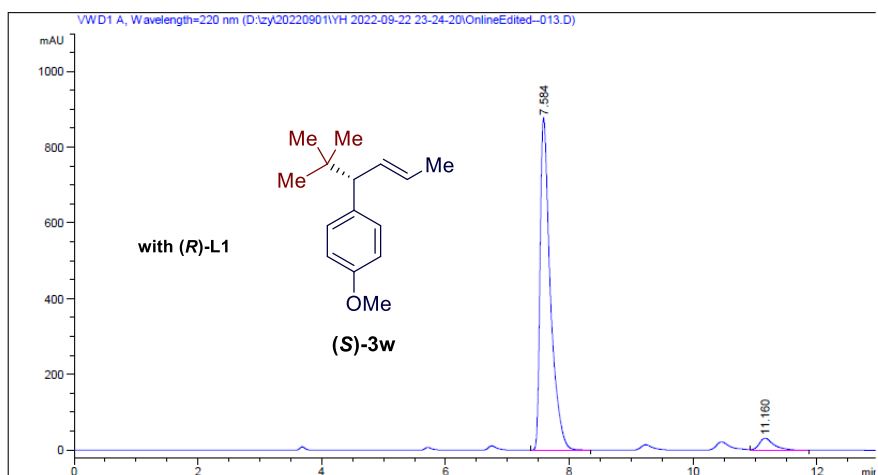
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.935	MF	1.0096	1.05771e5	1746.17456	96.1289
2	26.569	BB	1.0519	4259.40869	62.20335	3.8711



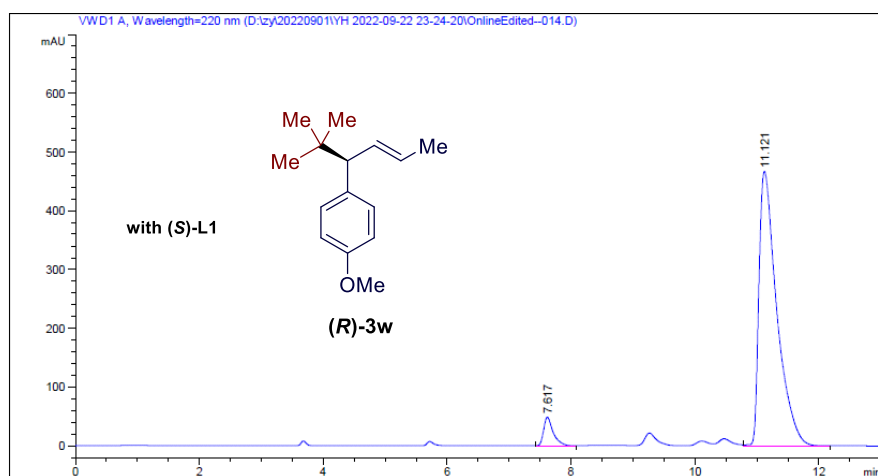
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.983	BV	0.6281	3422.35889	78.73964	2.6706
2	24.052	MF	1.5919	1.24727e5	1305.83105	97.3294



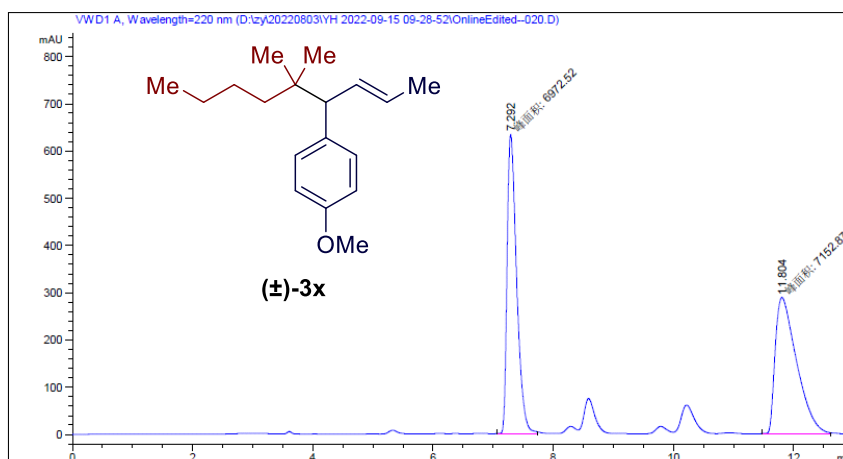
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.590	BB	0.1618	1950.30652	178.03227	49.9746
2	11.215	VB	0.2532	1952.28870	114.36316	50.0254



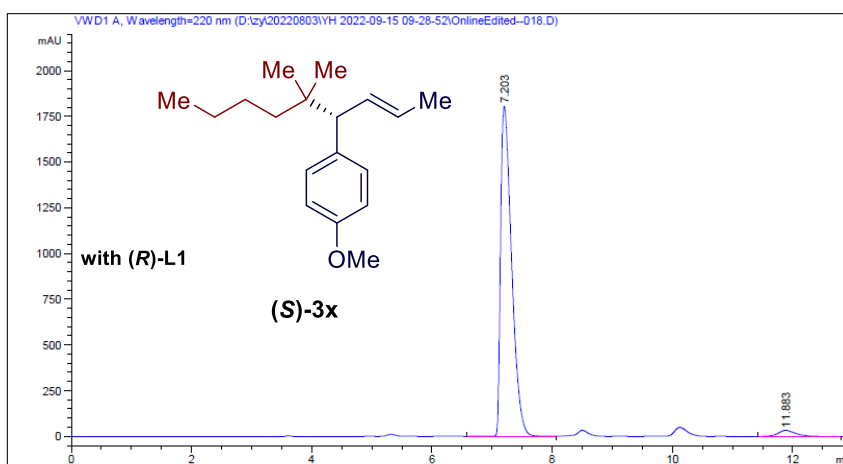
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.584	BB	0.1682	1.00925e4	877.30048	95.1781
2	11.160	VB	0.2443	511.30676	31.33866	4.8219



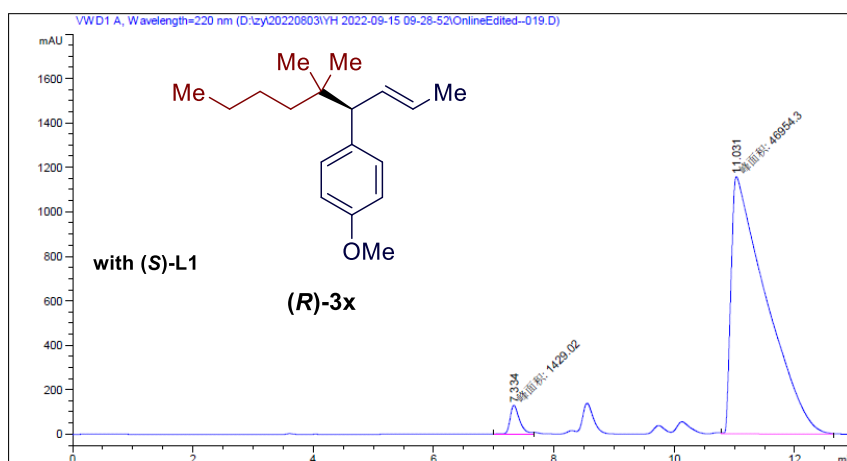
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.617	BB	0.1588	526.09283	48.80503	5.3450
2	11.121	VB	0.2889	9316.60352	466.72687	94.6550



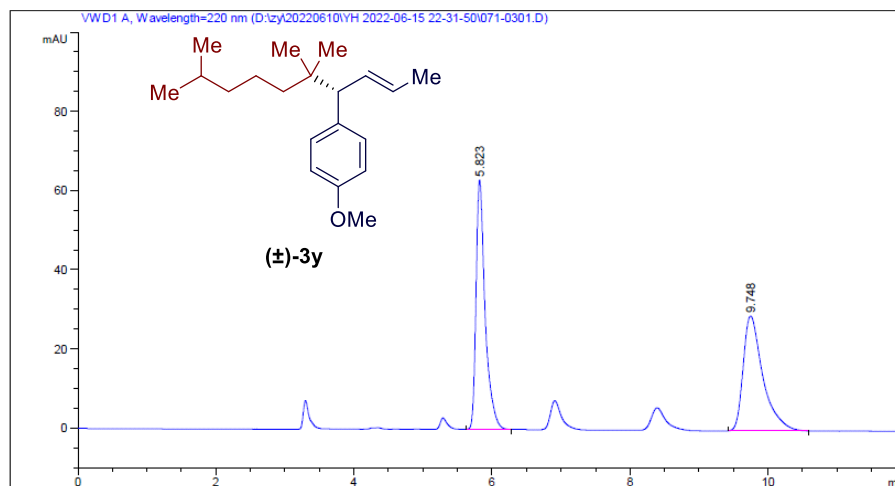
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.292	FM	0.1835	6972.51611	633.36646	49.3616
2	11.804	FM	0.4130	7152.87256	288.62186	50.6384



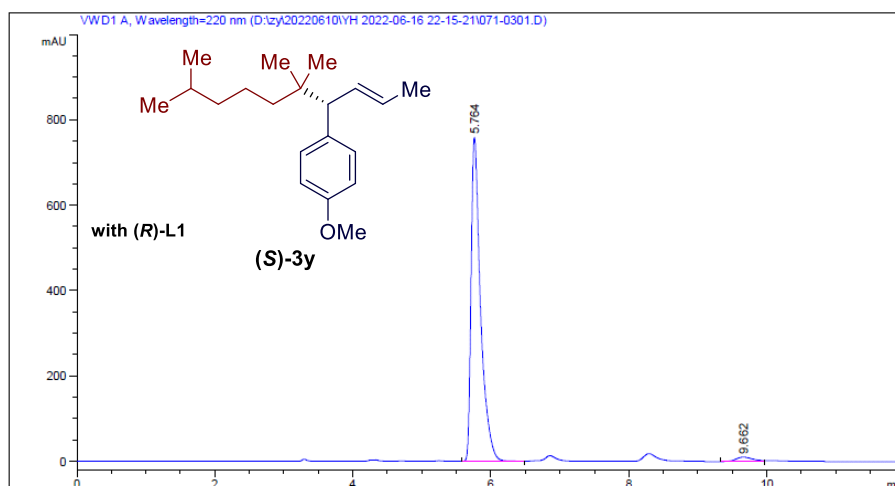
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.203	VV R	0.1932	2.29199e4	1804.09949	97.2379
2	11.883	BB	0.2905	651.05457	32.38744	2.7621



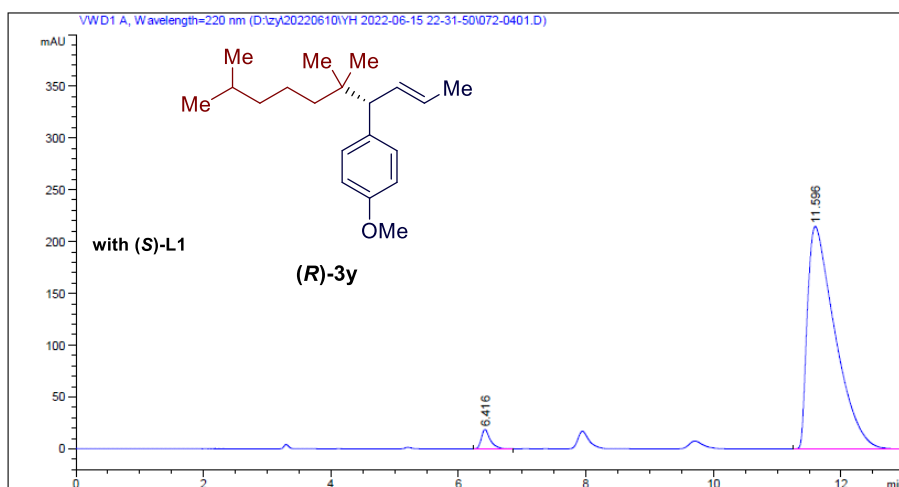
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.334	FM	0.1836	1429.02173	129.71706	2.9535
2	11.031	MF	0.6766	4.69543e4	1156.53870	97.0465



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.823	BB	0.1344	575.71326	63.09723	49.9978
2	9.748	BB	0.2972	575.76337	29.04870	50.0022

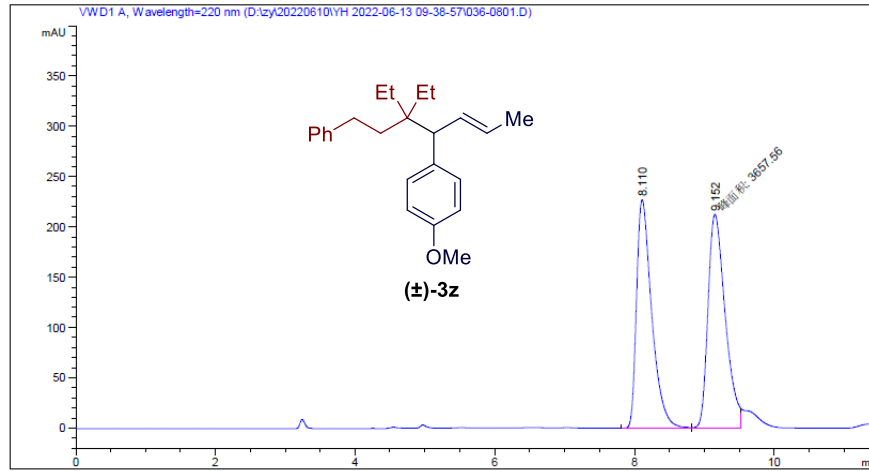


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.764	BV	0.1426	7262.29199	759.13556	97.5773
2	9.662	BV	0.2644	180.31424	10.34189	2.4227

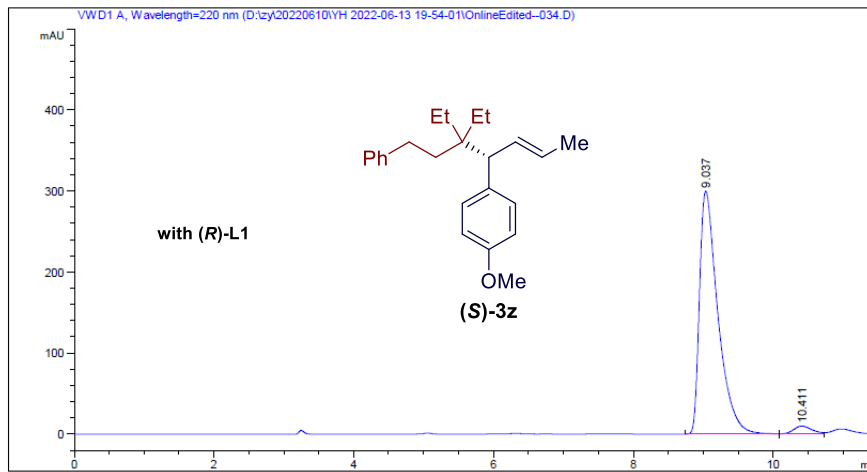


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.416	BB	0.1430	180.80946	18.66933	2.7275
2	11.596	BB	0.4491	6448.20996	214.84837	97.2725

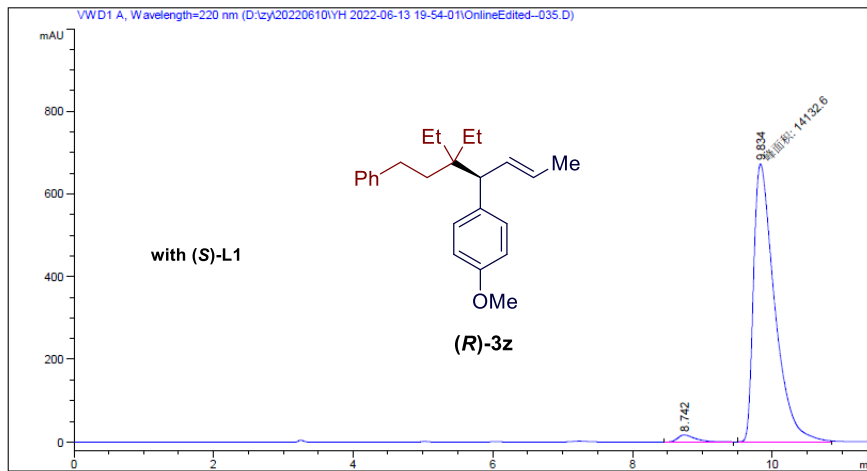




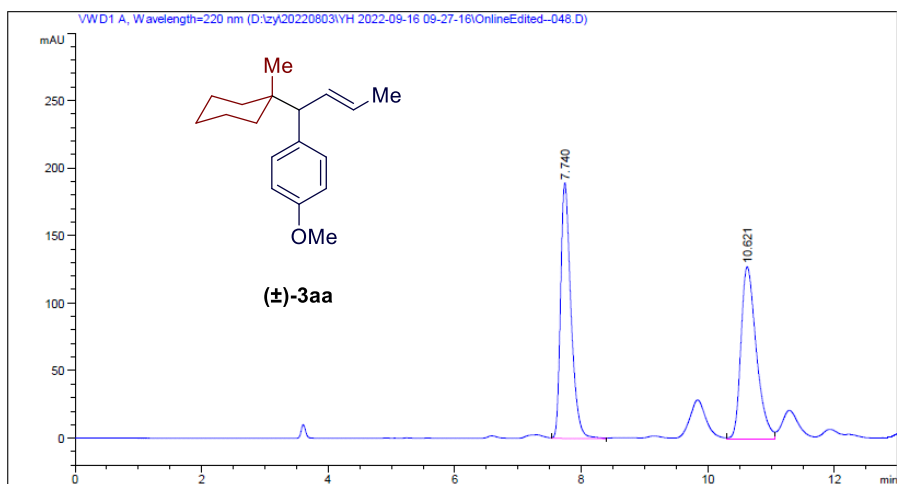
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.110	BV	0.2256	3430.09351	227.20183	48.3953
2	9.152	MF	0.2867	3657.56299	212.59645	51.6047



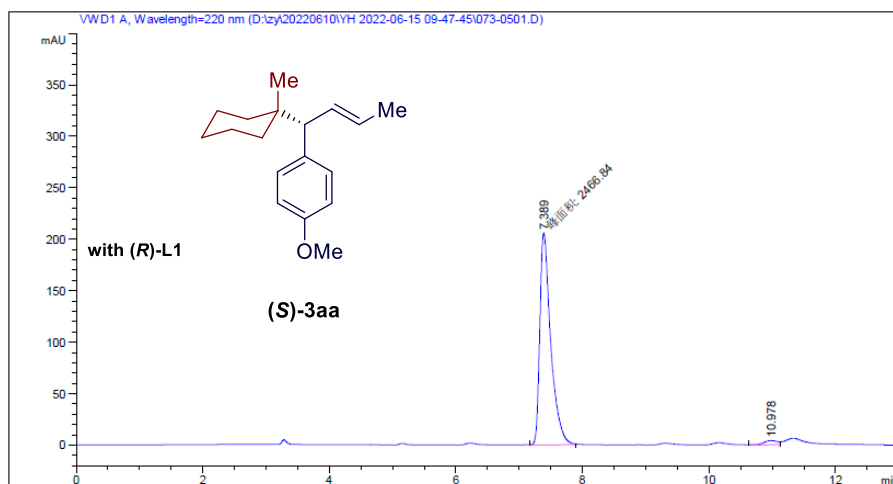
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.037	BV	0.2709	5469.47168	299.68872	96.7326
2	10.411	VV	0.2850	184.74428	9.84127	3.2674



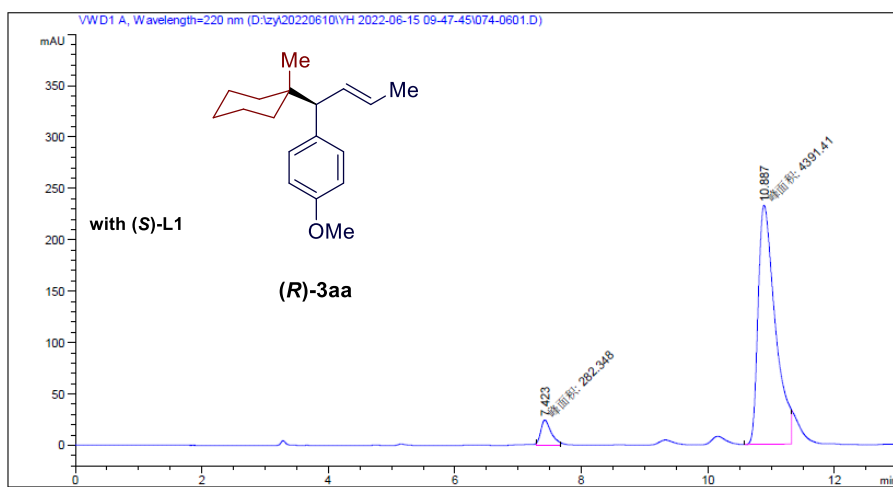
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.742	BB	0.2623	312.27695	17.32033	2.1619
2	9.834	MF	0.3504	1.41326e4	672.21332	97.8381



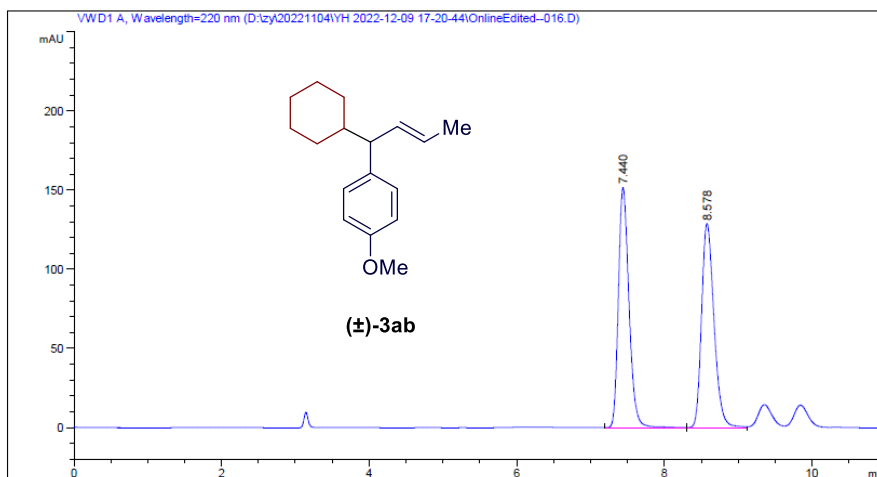
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.740	VB	0.1746	2153.05396	189.42548	50.0537
2	10.621	VV	0.2527	2148.42993	127.45947	49.9463



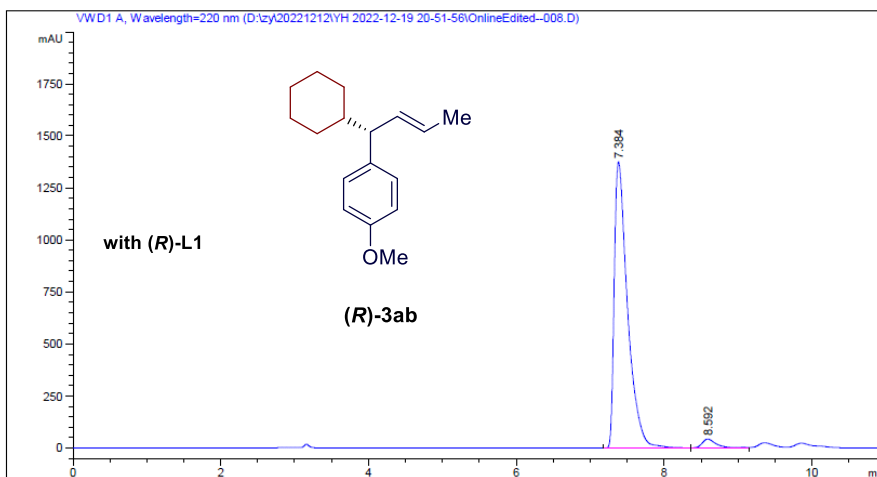
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.389	FM	0.1998	2466.83936	205.78412	97.6381
2	10.978	BV	0.2083	59.67376	4.00491	2.3619



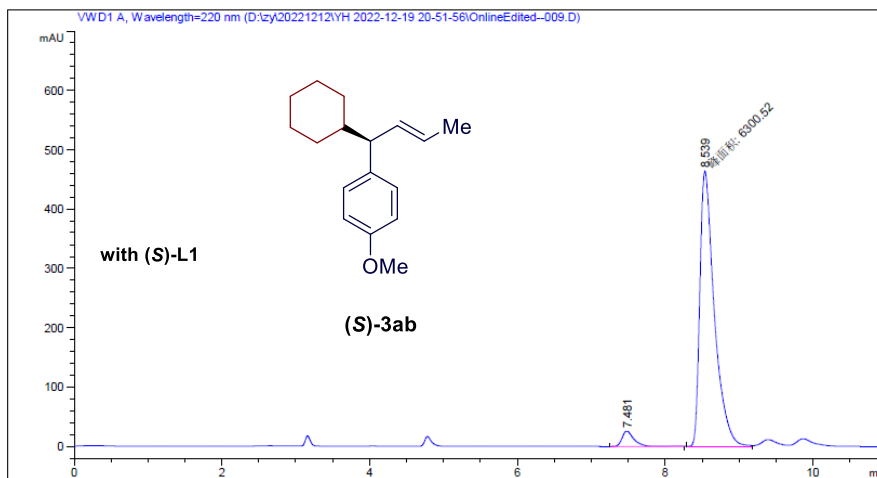
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.423	MF	0.1921	282.34793	24.49025	6.0411
2	10.887	MF	0.3146	4391.41357	232.66273	93.9589



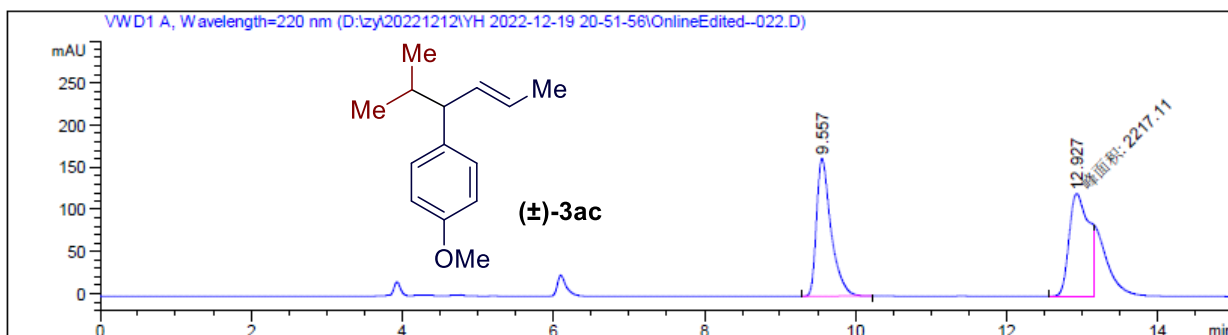
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.440	BB	0.1536	1511.25232	151.83400	50.0388
2	8.578	BV	0.1805	1508.90613	129.00020	49.9612



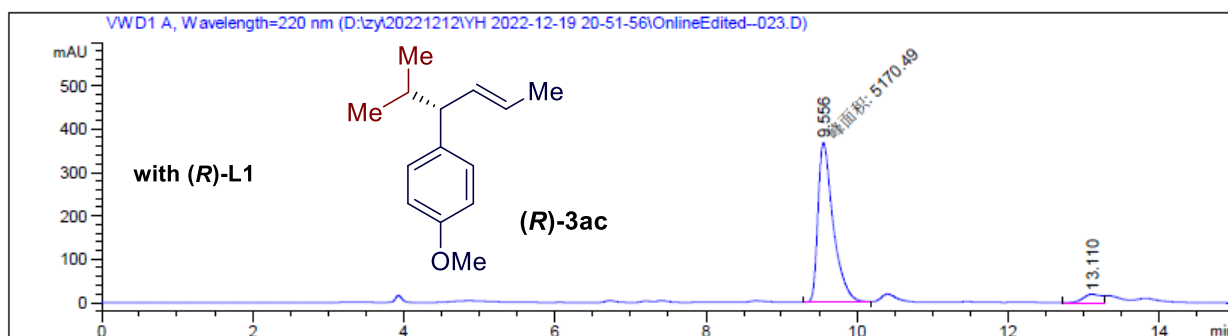
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.384	BB	0.1858	1.71275e4	1375.55969	96.8280
2	8.592	BV R	0.1923	561.09070	41.78769	3.1720



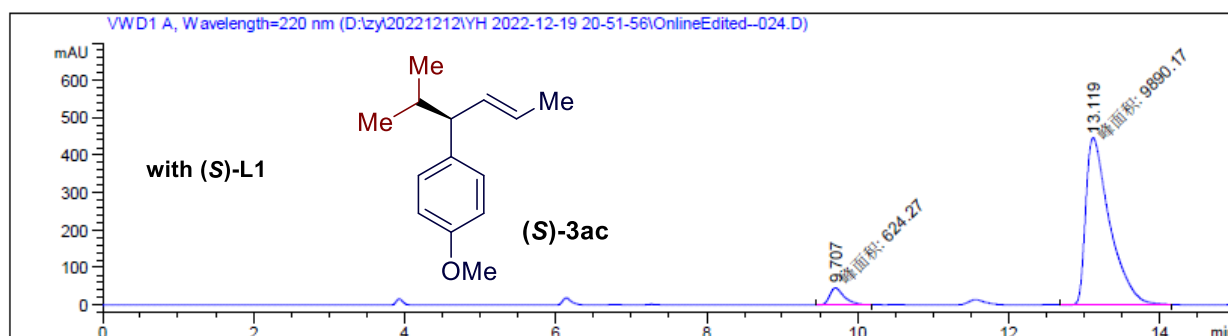
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.481	BB	0.1654	290.47113	25.99231	4.4071
2	8.539	MF	0.2265	6300.51758	463.63486	95.5929



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.557	BB	0.1999	2179.84082	163.10854	49.5762
2	12.927	MF	0.3035	2217.11182	121.74976	50.4238



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.556	MF	0.2344	5170.48730	367.69540	94.2132
2	13.110	BV	0.2468	317.58459	19.02051	5.7868



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.707	MF	0.2280	624.27020	45.63062	5.9373
2	13.119	MF	0.3692	9890.17188	446.45493	94.0627