

## ***Supporting Information***

### **Enantioselective and site-specific copper-satalyzed reductive allyl-allyl cross-coupling of allenes**

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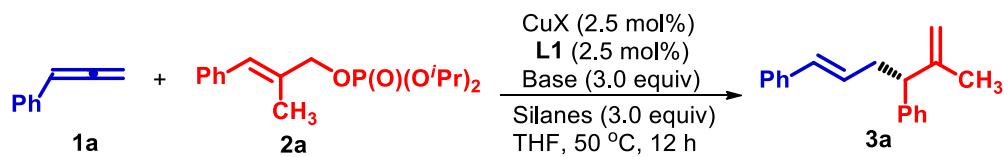
## 1. General Considerations

All reactions were performed under nitrogen atmosphere in flame dried flasks. All reactions were monitored by thin layer chromatography (TLC) using Macherey-Nagel 0.20 mm silica gel 60 plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Taizhou, China).  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  nuclear magnetic resonance (NMR) spectra were recorded on Varian (400/500 MHz) or Bruker 600 MHz NMR spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm for  $^1\text{H}$ ) and  $\text{CHCl}_3$  (77.0 ppm for  $^{13}\text{C}$ ), respectively. High resolution mass spectra were recorded on Bruck microtof. High-pressure liquid chromatography (HPLC) was performed on Agilent 1260 Series chromatographs using a chiral column (25 cm) as noted for each compound. HPLC analysis carried on Chiraldak OZ-H, OD-H, AD-H, IA column (Daicel Chemical Industries, LTD). Optical rotations were measured on a Perkin–Elmer 341 polarimeter.

Unless otherwise stated, all commercially available compounds were purchased from Aldrich or Energy–Chemical Limited and used as supplied without further purification. THF was purified by distillation from sodium benzophenone ketyl immediately prior to use. 1,4–Dioxane was distilled over sodium, degassed, and stored over activated molecular sieves.  $(\text{Me}_2\text{SiH})_2\text{O}$  (TMDS) was purchased from Energy–Chemical Limited and vacuum transferred over calcium hydride before use. **L1** and **L2** have been reported by Amir H. Hoveyda.<sup>1</sup> To obtain racemic samples of the hydroallylation products, rac-**L1** was used as the ligand. Allenes were prepared according to the procedure reported by Gérard Buono.<sup>2</sup> Primary allylic phosphates and (*Z*)-allylic phosphate were prepared according to the reported procedures.<sup>3</sup>

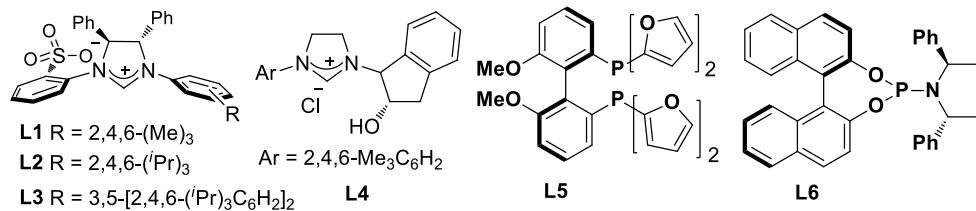
## 2. Optimization Studies for Asymmetric Hydroallylation of Allenes<sup>a</sup>.

**Table S1.** Screening of the catalysts, bases and hydrosilanes<sup>a,b</sup>

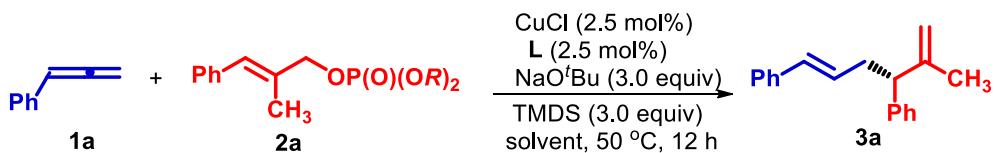


entry	cat.	base	silanes	yield (%)	ee <sup>c</sup>
1	CuCl	NaO'Bu	TMDS	50	33
2	CuBr	NaO'Bu	TMDS	14	33
3	CuOAc	NaO'Bu	TMDS	30	33
4	CuI	NaO'Bu	TMDS	24	32
5	Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub>	NaO'Bu	TMDS	30	nd
6	CuCl <sub>2</sub>	NaO'Bu	TMDS	42	nd
7	CuCl	LiO'Bu	TMDS	50	26
8	CuCl	KO'Bu	TMDS	nr	---
9	CuCl	NaOMe	TMDS	nr	---
10	CuCl	NaO'Bu	DEMS	nr	---
11	CuCl	NaO'Bu	PMHS	58	27
12	CuCl	NaO'Bu	PhSiH <sub>3</sub>	nr	---

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), allyl phosphate (1.5 equiv), catalyst (2.5 mol%), **L1** (2.5 mol%), base (3.0 equiv) and silane (3.0 equiv) in 2.0 mL THF at 50 °C. <sup>b</sup>Isolated yields. <sup>c</sup>ee determined by HPLC. TMDS = (Me<sub>2</sub>HSi)<sub>2</sub>O, DEMS = (EtO)<sub>2</sub>MeSiH.



**Table S2. Screening of the ligands, leaving groups and solvents<sup>a,b</sup>**

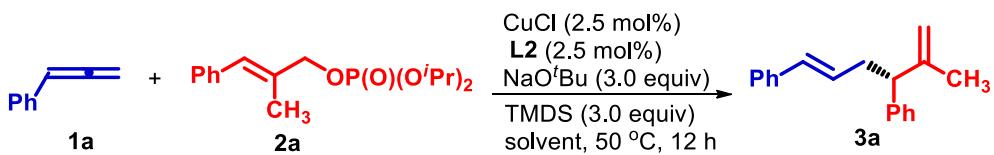


entry	solvent	R	L	yield (%)	ee <sup>d</sup>
1	THF	Me	<b>L1</b>	50	33
2	THF	Me	<b>L2</b>	50	85
3	THF	Me	<b>L3</b>	0	---
4	THF	Me	<b>L4</b>	0	---
5	THF	Me	<b>L5</b>	0	---
6	THF	Me	<b>L6</b>	0	---
7	THF	Me	<b>L2</b>	50	85
8	THF	iBu	<b>L2</b>	50	78
9	THF	Et	<b>L2</b>	50	87
<b>10</b>	<b>THF</b>	<i>i</i> Pr	<b>L2</b>	<b>50</b>	<b>89</b>
11	CyH	<i>i</i> Pr	<b>L2</b>	66	77
12	MTBE	<i>i</i> Pr	<b>L2</b>	trace	nd
13	Toluene	<i>i</i> Pr	<b>L2</b>	70	76
14	Et <sub>2</sub> O	<i>i</i> Pr	<b>L2</b>	trace	nd
15	Dioxane	<i>i</i> Pr	<b>L2</b>	60	93
<b>16<sup>c</sup></b>	<b>Dioxane</b>	<i>i</i> Pr	<b>L2</b>	<b>73</b>	<b>93</b>

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), allyl phosphate (1.5 equiv), catalyst (2.5 mol%), **L2** (2.5 mol%), base (3.0 equiv) and silane (3.0 equiv) in 2.0 mL solvent at 50 °C. MTBE = methyl tert-butyl ether.

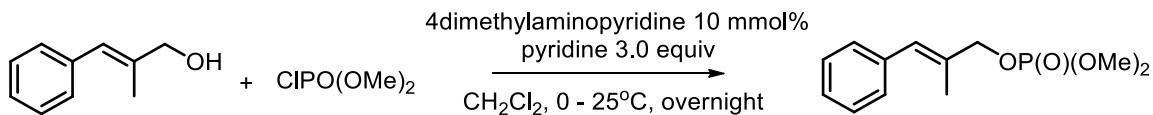
<sup>b</sup>Isolated yields. <sup>c</sup>**1a** (1.5 equiv), allyl phosphate (0.2 mmol). <sup>d</sup>ee determined by HPLC.

### 3. General Procedure for Enantioselective Hydroallylation of Allene



In a nitrogen-filled glove box, a screw-cap test tube was charged with **L2** (9 mg, 0.010 mmol) and  $\text{NaO}'\text{Bu}$  (60 mg, 0.6 mmol). Anhydrous dioxane (2.0 mL) was added and the mixture was stirred for 30 minutes at 50 °C after the addition of  $\text{CuCl}$  (1 mg, 0.010 mmol). TMDS (80 mg, 0.6 mmol) was added, after 5 minutes, **1a** (34.8 mg, 0.3 mmol) and **2c** (62.4 mg, 0.2 mmol) was added to the mixture. The reaction tube was sealed with a Teflon screw cap, removed from the glove box and stirred at 50 °C for 12 h. Then, the mixture was quenched by 1M  $\text{NaOH}$  (10.0 mL), extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5.0$  mL), combined the organic phases, and dried over anhydrous  $\text{MgSO}_4$ . The solvents were evaporated under vacuum and the crude product was purified on silica gel column chromatography to give the corresponding product **3a** (36.2 mg, 73% yield, 93% ee) as a colorless oil.

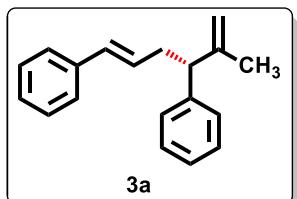
### 4. Preparation of Primary Allyl Phosphates



In a 50 ml dry two-neck flask equipped with a magnetic bar was added 4-dimethylaminopyridine (DMAP, 0.042 mmol, 51 mg). The flask was then evacuated and back-filled with argon three times. Dry dichloromethane (10 mL), pyridine (24.9 mmol, 2.0 mL) and *(E*)-2-methyl-3-phenylprop-2-en-1-ol (8.3 mmol, 1.2 g) were added in turn to the flask. The reaction mixture was cooled to 0 °C and then diisopropyl phosphorochloridate (12.5 mmol, 2.5 g) was added dropwise. After the reaction was slowly

warmed to room temperature through overnight with stirring, it was quenched with water (10.0 mL) at 0 °C. The organic layer was separated and the water layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>(3×15 mL). The solution was concentrated in vacuo, which afforded an oil that was purified by flash chromatography (ethyl acetate : petroleum ether = 10:90) to give (*E*)-diisopropyl (2-methyl-3-phenylallyl) phosphate (1.55 g, 60%) as a colorless oil.

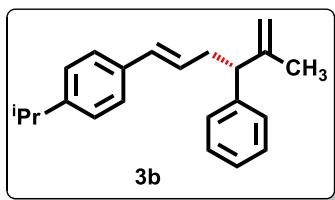
## 5. Compounds Characterization



**(*R,E*)-(5-methylhexa-1,5-diene-1,4-diyl)dibenzene (3a)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (36.2 mg, 73%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.31 - 7.27 (m, 5H), 7.24 - 7.22 (m, 3H), 7.20 - 7.15 (m, 2H), 6.38 (d, *J* = 16.2 Hz, 1H), 6.14 - 6.09 (m, 1H), 4.97 (s, 1H), 4.89 (s, 1H), 3.36 (t, *J* = 7.2 Hz, 1H), 2.78 - 2.73 (m, 1H), 2.67 - 2.60 (m, 1H), 1.61 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 147.3, 143.1, 137.7, 131.0, 129.1, 128.4, 128.3, 127.8, 126.9, 126.3, 126.0, 110.8, 53.0, 36.8, 21.2. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>19</sub>H<sub>20</sub>Na ([M + Na]<sup>+</sup>): 271.1457; found: 271.1462. [α]<sub>D</sub><sup>14</sup> = 21.3, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 31.0 min, *t*<sub>R</sub> (major) = 37.9 min); ee = 93%.

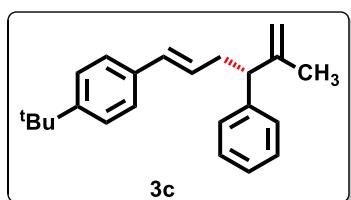
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**(*R,E*)-1-isopropyl-4-(5-methyl-4-phenylhexa-1,5-dien-1-yl)benzene (3b)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (41.8 mg, 72%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.28 (t, *J* = 7.2 Hz, 2H), 7.23 - 7.18 (m, 5H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.09 - 6.04 (m, 1H), 4.96 (s, 1H), 4.87 (s, 1H), 3.35 (t, *J* = 7.8 Hz, 1H), 2.88 - 2.83 (m, 1H), 2.76 - 2.71 (m, 1H), 2.65 - 2.60 (m, 1H), 1.60 (s, 3H), 1.22 (d, *J* = 6.6 Hz, 6H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 147.7, 147.4, 143.1, 135.4, 130.8, 128.3, 128.1, 127.8, 126.5, 126.3, 126.0, 110.8, 53.1, 36.8, 33.8, 23.9, 21.1. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>22</sub>H<sub>26</sub>Na ([M + Na]<sup>+</sup>): 313.1928; found: 313.1927. [α]<sub>D</sub><sup>14</sup> = 2.8, (c = 0.5, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 23.6 min, *t*<sub>R</sub> (major) = 26.8 min); ee = 90%.

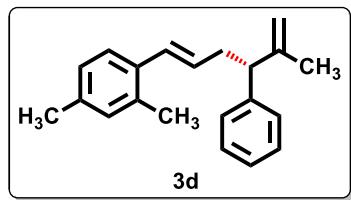
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**(*R,E*)-1-(tert-butyl)-4-(5-methyl-4-phenylhexa-1,5-dien-1-yl)benzene (3c)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (56.0 mg, 92%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.29 – 7.26 (m, 4H), 7.22 (t, *J* = 8.4 Hz, 4H), 7.20 – 7.17 (m, 1H), 6.35 (d, *J* = 16.2 Hz, 1H), 6.09 – 6.04 (m, 1H), 4.96 (s, 1H), 4.87 (s, 1H), 3.34 (t, *J* = 7.2 Hz, 1H), 2.76 – 2.71 (m, 1H), 2.65 – 2.60 (m, 1H), 1.60 (s, 3H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 149.9, 147.4, 143.1, 135.0, 130.7, 128.3, 128.2, 127.8, 126.3, 125.7, 125.3, 110.8, 53.1, 36.8, 34.4, 31.3, 21.2. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>23</sub>H<sub>28</sub>K ([M + K]<sup>+</sup>): 343.1828; found: 343.1823. [α]<sub>D</sub><sup>14</sup> = 30.7, (c = 2.5, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 20.8 min, *t*<sub>R</sub> (major) = 23.5 min); ee = 92%.

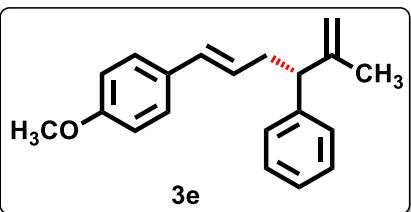
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**(*R,E*)-2,4-dimethyl-1-(5-methyl-4-phenylhexa-1,5-dien-1-yl)benzene (3d)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (36.4 mg, 66%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.28 (t, *J* = 7.2 Hz, 2H), 7.24 (s, 2H), 7.19 (t, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 6.6 Hz, 2H), 6.49 (d, *J* = 15.6 Hz, 1H), 5.94 – 5.89 (m, 1H), 4.97 (s, 1H), 4.88 (s, 1H), 3.36 (t, *J* = 7.8 Hz, 1H), 2.78 – 2.73 (m, 1H), 2.67 – 2.62 (m, 1H), 2.27 (s, 3H), 2.20 (s, 3H), 1.61 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 147.5, 143.1, 136.5, 134.8, 134.1, 130.8, 129.4, 128.9, 128.2, 127.9, 126.6, 126.2, 125.5, 110.7, 53.1, 37.1, 21.2, 21.0, 19.6. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>21</sub>H<sub>24</sub>K ([M + K]<sup>+</sup>): 315.1503; found: 315.1509. [α]<sub>D</sub><sup>14</sup> = 57.7, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 34.2 min, *t*<sub>R</sub> (major) = 39.8 min); ee = 94%.

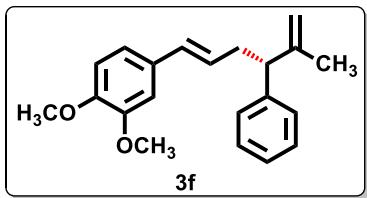
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**(*R,E*)-1-methoxy-4-(5-methyl-4-phenylhexa-1,5-dien-1-yl)benzene (3e)**

Purified by flash column chromatography (eluent: Petroleum ether / dichloromethane = 20:1). Colorless oil

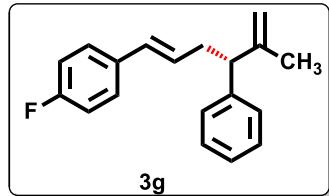
(30.0 mg, 54%);  **$^1\text{H NMR}$**  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.29 (t,  $J = 7.5$  Hz, 2H), 7.24 – 7.22 (m, 3H), 7.20 – 7.19 (m, 2H), 6.80 (d,  $J = 8.5$  Hz, 2H), 6.32 (d,  $J = 15.5$  Hz, 1H), 6.00 – 6.94 (m, 1H), 4.96 (s, 1H), 4.88 (s, 1H), 3.78 (s, 3H), 3.34 (t,  $J = 7.5$  Hz, 1H), 2.76 – 2.70 (m, 1H), 2.64 – 2.59 (m, 1H), 1.61 (s, 3H).  **$^{13}\text{C NMR}$**  (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 158.7, 147.4, 143.2, 130.6, 130.3, 128.2, 127.8, 127.1, 126.9, 126.3, 113.8, 110.7, 55.3, 53.1, 36.8, 21.16. **HRMS** (ESI-TOF) (m/z): Calcd for  $\text{C}_{20}\text{H}_{22}\text{ONa}$  ([M + Na] $^+$ ): 301.1549; found: 301.1562.  $[\alpha]_D^{14} = 94.0$ , (c = 1.5,  $\text{CHCl}_3$ ). **HPLC** analysis (Chiralpak IA column, hexanes/i-PrOH = 100/0, 1.0 mL/min, 250 nm,  $t_R$  (minor) = 19.0 min,  $t_R$  (major) = 20.6 min); ee = 94%.



**(*R,E*)-1,2-dimethoxy-4-(5-methyl-4-phenylhexa-1,5-dien-1-yl)benzene (3f)**

Purified by flash column chromatography (eluent: Petroleum ether / dichloromethane = 20:1). Colorless oil (38.2 mg, 62%);

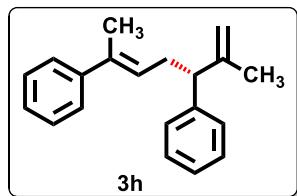
**$^1\text{H NMR}$**  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.30 (t,  $J = 7.0$  Hz, 2H), 7.25 – 7.19 (m, 3H), 6.83 – 6.76 (m, 3H), 6.32 (d,  $J = 16.0$  Hz, 1H), 6.01 – 5.95 (m, 1H), 4.97 (s, 1H), 4.89 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.36 (t,  $J = 7.5$  Hz, 1H), 2.77 – 2.71 (m, 1H), 2.65 – 2.59 (m, 1H), 1.61 (s, 3H).  **$^{13}\text{C NMR}$**  (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 148.9, 148.3, 147.3, 143.1, 130.9, 130.6, 128.2, 127.8, 127.2, 126.3, 118.8, 111.1, 110.8, 108.7, 55.9, 55.8, 53.1, 36.8, 21.2. **HRMS** (ESI-TOF) (m/z): Calcd for  $\text{C}_{21}\text{H}_{25}$  ([M + H] $^+$ ): 309.1846; found: 309.1849.  $[\alpha]_D^{14} = 26.2$ , (c = 1.0,  $\text{CHCl}_3$ ). **HPLC** analysis (Chiralpak AD-H column, hexanes/i-PrOH = 99/1, 0.5 mL/min, 250 nm,  $t_R$  (minor) = 21.6 min,  $t_R$  (major) = 25.1 min); ee = 92%.



**(*R,E*)-1-fluoro-4-(5-methyl-4-phenylhexa-1,5-dien-1-yl)benzen  
e (3g)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (22.9 mg, 43%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.31 – 7.28 (m, 2H), 7.25 – 7.20 (m, 5H), 6.94 (t, J = 8.4 Hz, 2H), 6.33 (d, J = 15.6 Hz, 1H), 6.04 – 5.99 (m, 1H), 4.96 (s, 1H), 4.89 (3) – 4.88 (8) (m, 1H), 3.35 (t, J = 7.2 Hz, 1H), 2.76 – 2.71 (m, 1H), 2.65 – 2.60 (m, 1H), 1.61 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 161.9 (J = 244.2 Hz), 147.3, 143.0, 129.8, 128.8 (J = 2.1 Hz), 128.3, 127.8, 127.4 (J = 117.0 Hz) 126.35, 115.2 (J = 20.9 Hz,), 110.80, 53.0, 36.8, 21.2. **<sup>19</sup>F NMR** (564 MHz; CDCl<sub>3</sub>) δ: -115.63 – -115.68 (m). **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>19</sub>H<sub>20</sub>F ([M + H]<sup>+</sup>): 267.1543; found: 267.1544. [α]<sub>D</sub><sup>15</sup> = 58.3, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiraldak OD-H column, hexanes/i-PrOH = 100/0, 1.0 mL/min, 250 nm, t<sub>R</sub> (minor) = 10.6 min, t<sub>R</sub> (major) = 12.4 min); ee = 93%.

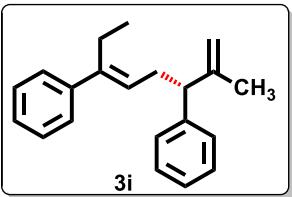
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**(*R,E*)-(6-methylhepta-2,6-diene-2,5-diyl)dibenzene (3h)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (45.6 mg, 63%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.30 – 7.26 (m, 6H), 7.25 – 7.23 (m, 2H), 7.21 – 7.17 (m, 2H), 5.70 – 5.68 (m, 1H), 4.97 (s, 1H), 4.91 (s, 1H), 3.35 (t, J = 7.8 Hz, 1H), 2.75 – 2.70 (m, 1H), 2.64 – 2.59(m, 1H), 1.96 (s, 3H), 1.62 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 147.5, 143.9, 143.3, 135.4, 128.2, 128.1, 127.9, 126.7, 126.5, 126.3, 125.7, 110.8, 52.7, 32.7, 21.3, 16.0. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>20</sub>H<sub>22</sub>Na ([M + Na]<sup>+</sup>): 285.1619; found: 285.1614. [α]<sub>D</sub><sup>14</sup> = 41.3, (c = 1.5, CHCl<sub>3</sub>). **HPLC** analysis (Chiraldak IA column, hexanes/i-PrOH = 100/0, 1.0 mL/min, 250 nm, t<sub>R</sub> (minor) = 5.4 min, t<sub>R</sub> (major) = 5.6 min); ee = 90%.

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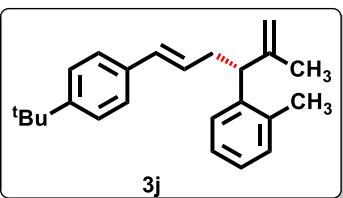


**(*R,E*)-(2-methylocta-1,5-diene-3,6-diyl)dibenzene (3i)**

Purified by flash column chromatography (eluent: Petroleum ether).

Colorless oil (42.0 mg, 76%); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ: 7.31 – 7.26 (2) (m, 4H), 7.25 (5) – 7.24 (m, 4H), 7.21 – 7.18 (m, 2H), 5.55 (t, J = 6.4 Hz, 1H), 5.01 (s, 1H), 4.91 (d, J = 6.4 Hz, 1H), 3.34 (t, J = 6.4 Hz, 1H), 3.76 – 2.70 (m, 1H), 2.65 – 2.59 (m, 1H), 2.45 (q, J = 6.0 Hz, 2H), 1.62 (s, 3H), 0.89 (t, J = 6.0 Hz, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ: 147.5, 143.3, 143.0, 142.2, 128.2, 128.1, 127.9, 126.5, 126.3, 126.3, 110.8, 53.1, 32.3, 23.0, 21.4, 13.3. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>21</sub>H<sub>24</sub>Na ([M + Na]<sup>+</sup>): 299.1767; found: 299.1770. [α]<sub>D</sub><sup>14</sup> = 43.1, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiraldak IA column, hexanes/i-PrOH = 100/0, 0.4 mL/min, 250 nm, t<sub>R</sub> (minor) = 11.8 min, t<sub>R</sub> (major) = 12.1 min); ee = 92%.

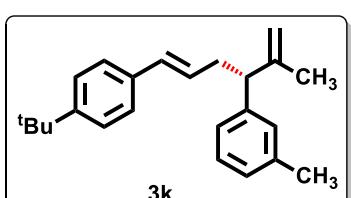
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**(*R,E*)-1-(6-(4-(tert-butyl)phenyl)-2-methylhexa-1,5-dien-3-yl)-2-methylbenzene (3j)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (51.5 mg, 81%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.31 – 7.27 (m, 2H), 7.23 – 7.20 (m, 3H), 7.18 – 7.15 (m, 1H), 7.13 – 7.08 (m, 2H), 6.36 (d, J = 15.6 Hz, 1H), 6.10 – 6.05 (m, 1H), 4.91 (s, 2H), 3.59 (t, J = 7.8 Hz, 1H), 2.77 – 2.72 (m, 1H), 2.61 – 2.56 (m, 1H), 2.32 (s, 3H), 1.60 (s, 3H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 149.9, 146.8, 141.2, 136.4, 135.0, 130.7, 130.3, 128.3, 126.5, 126.0, 125.7, 125.3, 111.1, 48.3, 37.2, 34.5, 31.3, 21.6, 19.8. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>24</sub>H<sub>30</sub>Na ([M + Na]<sup>+</sup>): 341.2245; found: 341.2242. [α]<sub>D</sub><sup>14</sup> = 23.1, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiraldak OD-H column, hexanes/i-PrOH = 100/0, 1.0 mL/min, 250 nm, t<sub>R</sub> (minor) = 11.0 min, t<sub>R</sub> (major) = 12.3 min); ee = 94%.

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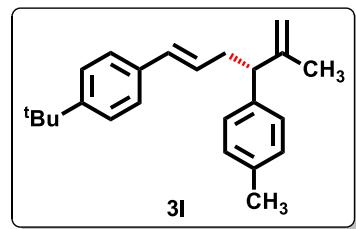


**(*R,E*)-1-(6-(4-(tert-butyl)phenyl)-2-methylhexa-1,5-dien-3-yl)-3-methylbenzene (3k)**

Purified by flash column chromatography (eluent: Petroleum

ether). Colorless oil (36.3 mg, 57%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.29 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.04 – 7.00 (m, 3H), 6.36 (d, *J* = 16.2 Hz, 1H), 6.10 – 6.05 (m, 1H), 4.95 (s, 1H), 4.89 – 4.86 (m, 1H), 3.31 (t, *J* = 7.8 Hz, 1H), 2.75 – 2.70 (m, 1H), 2.64 – 2.59 (m, 1H), 2.33 (s, 3H), 1.60 (s, 3H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 149.9, 147.4, 143.1, 137.7, 135.0, 130.6, 128.6, 128.4, 128.1, 127.0, 125.7, 125.3, 124.8, 110.7, 53.1, 36.8, 34.5, 31.3, 21.5, 21.2. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>24</sub>H<sub>30</sub>Na ([M + Na]<sup>+</sup>): 341.2245; found: 341.2241. [α]<sub>D</sub><sup>14</sup> = 8.1, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 1.0 ml/min, 250 nm, *t*<sub>R</sub> (minor) = 9.5 min, *t*<sub>R</sub> (major) = 10.7 min); ee = 93%.

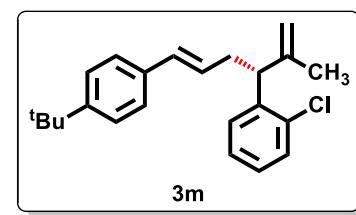
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**(*R,E*)-1-(tert-butyl)-4-(5-methyl-4-(p-tolyl)hexa-1,5-dien-1-yl)benzene (3l)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (36.3 mg, 57%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.29 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.11 – 7.09 (m, 4H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.10 – 6.05 (m, 1H), 4.94 (s, 1H), 4.86 – 4.85 (m, 1H), 3.31 (t, *J* = 7.2 Hz, 1H), 2.74 – 2.69 (m, 1H), 2.63 – 2.58 (m, 1H), 2.32 (s, 3H), 1.60 (s, 3H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 149.9, 147.6, 140.1, 135.7, 135.0, 130.6, 128.9, 128.4, 127.7, 125.7, 125.3, 110.6, 52.7, 36.9, 34.5, 31.3, 21.1, 21.0. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>24</sub>H<sub>30</sub>Na ([M + Na]<sup>+</sup>): 341.2245; found: 341.2242. [α]<sub>D</sub><sup>14</sup> = 18.4, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak IA column, hexanes/i-PrOH = 99.9/0.1, 1.0 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 7.7 min, *t*<sub>R</sub> (major) = 9.7 min); ee = 90%.

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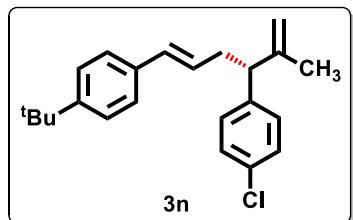


**(*R,E*)-1-(6-(4-(tert-butyl)phenyl)-2-methylhexa-1,5-dien-3-yl)-2-chlorobenzene (3m)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (58.8 mg, 87%); **<sup>1</sup>H NMR** (600 MHz,

$\text{CDCl}_3$ )  $\delta$ : 7.34 – 7.33 (m, 1H), 7.29 – 7.27 (m, 3H), 7.22 – 7.20 (m, 3H), 7.13 – 7.10 (m, 1H), 6.33 (d,  $J$  = 15.6 Hz, 1H), 6.11 – 6.06 (m, 1H), 4.96 (s, 2H), 3.97 (t,  $J$  = 7.2 Hz, 1H), 2.77 – 2.72 (m, 1H), 2.61 – 2.56 (m, 1H), 1.64 (s, 3H), 1.29 (s, 9H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 149.9, 146.2, 140.6, 134.9, 134.7, 130.9, 129.5, 128.3, 127.7, 127.4, 126.8, 125.7, 125.3, 111.6, 47.9, 37.0, 34.5, 31.3, 22.1. HRMS (ESI-TOF) (m/z): Calcd for  $\text{C}_{23}\text{H}_{28}\text{Cl}$  ( $[\text{M} + \text{H}]^+$ ): 339.1876; found: 339.1874.  $[\alpha]_D^{14} = 48.5$ , (c = 1.0,  $\text{CHCl}_3$ ). HPLC analysis (Chiralpak IA column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm,  $t_R$  (minor) = 12.3 min,  $t_R$  (major) = 13.0 min); ee = 92%.

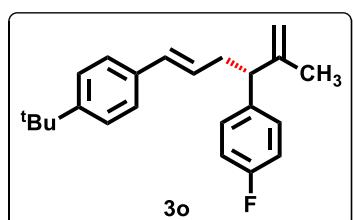
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**(*R,E*)-1-(tert-butyl)-4-(4-chlorophenyl)-5-methylhexa-1,5-dien-1-ylbenzene (3n)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (52.1 mg, 77%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.29 (d,  $J$  = 8.4 Hz, 2H), 7.25 (d,  $J$  = 8.4 Hz, 2H), 7.21 (d,  $J$  = 8.4 Hz, 2H), 7.15 (d,  $J$  = 8.4 Hz, 2H), 6.34 (d,  $J$  = 15.6 Hz, 1H), 6.05 – 6.00 (m, 1H), 4.94 (s, 1H), 4.89 – 4.88 (m, 1H), 3.31 (t,  $J$  = 7.8 Hz, 1H), 2.74 – 2.67 (m, 1H), 2.60 – 2.55 (m, 1H), 1.58 (s, 3H), 1.29 (s, 9H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 150.0, 146.9, 141.6, 134.8, 131.9, 131.1, 129.2, 128.4, 127.7, 125.7, 125.3, 111.1, 52.5, 36.8, 34.5, 31.3, 21.1. HRMS (ESI-TOF) (m/z): Calcd for  $\text{C}_{23}\text{H}_{28}\text{Cl}$  ( $[\text{M} + \text{H}]^+$ ): 339.1877; found: 339.1874.  $[\alpha]_D^{14} = 78.3$ , (c = 2.0,  $\text{CHCl}_3$ ). HPLC analysis (Chiralpak IA column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm,  $t_R$  (minor) = 21.7 min,  $t_R$  (major) = 24.6 min); ee = 91%.

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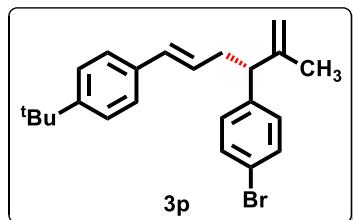


**(*R,E*)-1-(tert-butyl)-4-(4-fluorophenyl)-5-methylhexa-1,5-dien-1-ylbenzene (3o)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (39.9 mg, 62%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.30 – 7.28 (m, 2H), 7.22 – 7.20 (m, 2H), 7.18 – 7.16 (m, 2H), 6.98 – 6.95 (m, 2H), 6.34 (d,  $J$  = 16.2 Hz, 1H), 6.06 – 6.01 (m, 1H), 4.94 (s, 1H), 4.88 –

4.87 (m, 1H), 3.32 (t,  $J = 7.8$  Hz, 1H), 2.72 – 2.69 (m, 1H), 2.61 – 2.56 (m, 1H), 1.59 (s, 3H), 1.29 (s, 9H).  **$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 161.5 (d,  $J = 242.6$  Hz), 150.0, 147.3, 138.7 (d,  $J = 3.0$  Hz), 134.9, 130.9, 129.2 (d,  $J = 7.65$  Hz), 127.9, 125.7, 125.4, 115.0 (d,  $J = 20.85$  Hz), 110.9, 52.31, 36.97, 34.47, 31.28, 21.12.  **$^{19}\text{F}$  NMR** (564 MHz;  $\text{CDCl}_3$ )  $\delta$ -117.02 – (-117.07) (m). **HRMS** (ESI-TOF) (m/z): Calcd for  $\text{C}_{23}\text{H}_{27}\text{FK}$  ( $[\text{M} + \text{K}]^+$ ): 361.1723; found: 361.1728.  $[\alpha]_D^{14} = 90.5$ , (c = 2.0,  $\text{CHCl}_3$ ). **HPLC** analysis (Chiralpak OZ-H column, hexanes/i-PrOH = 100/0, 1.0 mL/min, 250 nm,  $t_R$  (minor) = 7.2 min,  $t_R$  (major) = 7.8 min); ee = 92%.

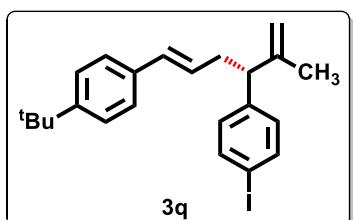
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**(R,E)-1-bromo-4-(6-(tert-butyl)phenyl)-2-methylhexa-1,5-dien-3-ylbenzene (3p)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (55.0 mg, 72%);  **$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.40 (d,  $J = 7.8$  Hz, 2H), 7.29 (d,  $J = 7.8$  Hz, 2H), 7.21 (d,  $J = 8.4$  Hz, 2H), 7.09 (d,  $J = 8.4$  Hz, 2H), 6.34 (d,  $J = 15.6$  Hz, 1H), 6.05 – 6.00 (m, 1H), 4.94 (s, 1H), 4.88 (s, 1H), 3.30 (t,  $J = 7.2$  Hz, 1H), 2.73 – 2.69 (m, 1H), 2.60 – 2.55 (m, 1H), 1.58 (s, 3H), 1.29 (s, 9H).  **$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 150.0, 146.9, 142.1, 134.8, 131.3, 131.1, 129.7, 127.6, 125.7, 125.4, 120.1, 111.2, 52.5, 36.7, 34.5, 31.3, 21.2. **HRMS** (ESI-TOF) (m/z): Calcd for  $\text{C}_{23}\text{H}_{27}\text{BrK}$  ( $[\text{M} + \text{K}]^+$ ): 421.0924; found: 421.0910.  $[\alpha]_D^{14} = 21.8$ , (c = 1.0,  $\text{CHCl}_3$ ). **HPLC** analysis (Chiralpak IA column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm,  $t_R$  (minor) = 22.9 min,  $t_R$  (major) = 33.1 min); ee = 94%.

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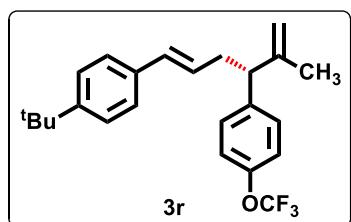


**(R,E)-1-(tert-butyl)-4-(4-(4-iodophenyl)-5-methylhexa-1,5-dien-1-yl)benzene (3q)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (26.7 mg, 31%);  **$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.32 – 7.26 (m, 4H), 7.23 – 7.21 (m, 4H), 6.35 (d,  $J = 13.8$  Hz, 1H), 6.01 – 6.0 (m, 1H), 4.96 (s, 1H), 4.88 – 4.87 (m, 1H), 3.35 (t,  $J = 7.8$  Hz, 1H), 2.76

– 2.71 (m, 1H), 2.66 – 2.60 (m, 1H), 1.60 (s, 3H), 1.29 (s, 11H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 149.9, 147.4, 143.1, 135.0, 130.7, 128.3, 128.3, 127.9, 126.3, 125.7, 125.3, 110.8, 53.1, 36.8, 34.5, 31.3, 21.2. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>23</sub>H<sub>27</sub>IK ([M + K]<sup>+</sup>): 469.0786; found: 469.0789. [α]<sub>D</sub><sup>15</sup> = 2.5, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 1.0 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 9.6 min, *t*<sub>R</sub> (major) = 10.6 min); ee = 84%.

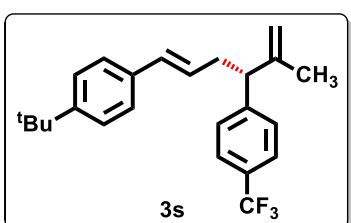
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**(R,E)-1-(tert-butyl)-4-(5-methyl-4-(4-(trifluoromethoxy)phenyl)hexa-1,5-dien-1-yl)benzene (3r)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (38.0 mg, 49%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.34 (d, *J* = 16.2 Hz, 1H), 6.06 – 6.01 (m, 1H), 4.96 (s, 1H), 4.90 (s, 1H), 3.36 (t, *J* = 7.8 Hz, 1H), 2.75 – 2.70 (m, 1H), 2.62 – 2.57 (m, 1H), 1.59 (s, 3H), 1.29 (s, 10H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 150.1, 147.7, 146.9, 141.8, 134.8, 131.1, 129.1, 127.6, 125.7, 125.4, 120.7, 120.5 (q, *J* = 255.0 Hz), 111.3, 52.5, 36.8, 34.5, 31.3, 21.1. **<sup>19</sup>F NMR** (564 MHz; CDCl<sub>3</sub>) δ: -57.82. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>24</sub>H<sub>27</sub>F<sub>3</sub>ONa ([M + Na]<sup>+</sup>): 411.1904; found: 411.1904. [α]<sub>D</sub><sup>20</sup> = 23.5, (c = 2.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak IA column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 12.3 min, *t*<sub>R</sub> (major) = 13.3 min); ee = 93%.

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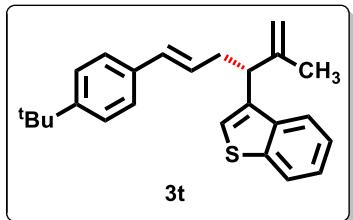


**(R,E)-1-(tert-butyl)-4-(5-methyl-4-(4-(trifluoromethyl)phenyl)hexa-1,5-dien-1-yl)benzene (3s)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (27.5 mg, 37%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.54 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.01 – 6.0 (m, 1H), 4.98 (s, 1H), 4.93 – 4.92 (m, 1H), 3.41 (t, *J* = 7.8 Hz, 1H), 2.79 – 2.74 (m, 1H), 2.65 – 2.60 (m,

1H), 1.60 (s, 3H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 150.1, 147.2, 146.5, 134.7, 131.3, 128.2, 127.4, 125.7, 125.4, 125.2, 125.2, 111.6, 52.9, 36.7, 34.5, 31.3, 21.2. **<sup>19</sup>F NMR** (564 MHz; CDCl<sub>3</sub>) δ: -62.29. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>24</sub>H<sub>27</sub>F<sub>3</sub>Na ([M + Na]<sup>+</sup>): 395.1952; found: 395.1957. [α]<sub>D</sub><sup>14</sup> = 13.4, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak IA column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 15.3 min, *t*<sub>R</sub> (major) = 19.4 min); ee = 98%.

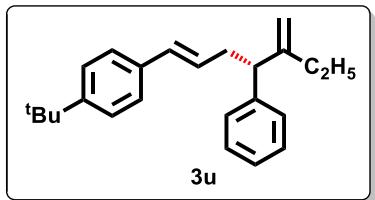
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**(*R,E*)-3-(6-(4-(tert-butyl)phenyl)-2-methylhexa-1,5-dien-3-yl)benzo[b]thiophene (3t)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (25.2 mg, 35%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.85 – 7.82 (m, 2H), 7.37 – 7.20 (m, 4H), 7.24 – 7.23 (m, 2H), 7.20 (s, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.20 – 6.15 (m, 1H), 5.03 (s, 1H), 4.94 (d, *J* = 1.8 Hz, 1H), 3.84 (t, *J* = 7.2 Hz, 1H), 2.82 (t, *J* = 7.2 Hz, 2H), 1.63 (s, 3H), 1.29 (d, *J* = 1.8 Hz, 9H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 150.0, 145.7, 140.5, 138.9, 137.6, 134.8, 131.0, 127.9, 125.8, 125.4, 124.2, 123.7, 122.8, 122.3, 121.6, 112.4, 47.2, 36.2, 34.5, 31.3, 20.2. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>25</sub>H<sub>28</sub>SNa ([M + Na]<sup>+</sup>): 383.1806; found: 383.1806. [α]<sub>D</sub><sup>14</sup> = 2.4, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak IA column, hexanes/i-PrOH = 100/0, 1.0 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 12.3 min, *t*<sub>R</sub> (major) = 16.4 min); ee = 85%.

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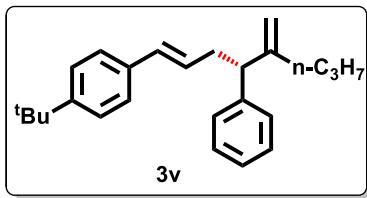


**(*R,E*)-1-(tert-butyl)-4-(5-methylene-4-phenylhept-1-en-1-yl)benzene (3u)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (33.7 mg, 53%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.28 (t, *J* = 8.4 Hz, 4H), 7.23 – 7.17 (m, 5H), 6.33 (d, *J* = 16.2 Hz, 1H), 6.08 – 6.03 (m, 1H), 5.01 (s, 1H), 4.93 (d, *J* = 1.2 Hz, 1H), 3.36 (t, *J* = 7.6 Hz, 1H), 2.77 – 2.72 (m, 1H), 2.64 – 2.59 (m, 1H), 1.98 – 1.92 (m, 1H), 1.89 – 1.84 (m, 1H), 1.29 (s, 9H), 0.96 (t, *J* = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 153.0, 149.9, 143.5, 135.0, 130.7, 128.4, 128.2, 128.0, 126.2, 125.7,

125.3, 108.2, 52.2, 37.7, 34.5, 31.3, 27.7, 12.2. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>24</sub>H<sub>30</sub>K ([M + K]<sup>+</sup>): 357.1977; found: 357.1979. [α]<sub>D</sub><sup>14</sup> = 16.8, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 1.0 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 8.0 min, *t*<sub>R</sub> (major) = 8.7 min); ee = 84%.

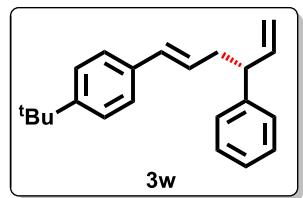
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**(R,E)-1-(tert-butyl)-4-(5-methylene-4-phenyloct-1-en-1-yl)benzene (3v)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (41.2 mg, 62%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.27 (t, *J* = 7.8 Hz, 4H), 7.22 – 7.17 (m, 5H), 6.33 (d, *J* = 16.2 Hz, 1H), 6.08 – 6.03 (m, 1H), 5.02 (s, 1H), 4.93 (s, 1H), 3.33 (t, *J* = 7.8 Hz, 1H), 2.76 – 2.72 (m, 1H), 2.63 – 2.58 (m, 1H), 1.91 – 1.81 (m, 2H), 1.45 – 1.34 (m, 2H), 1.29 (s, 9H), 0.83 (t, *J* = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 151.3, 149.8, 143.5, 135.0, 130.7, 128.4, 128.2, 128.0, 126.2, 125.7, 125.3, 109.3, 51.9, 37.8, 37.3, 34.5, 31.3, 20.8, 13.8. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>25</sub>H<sub>32</sub>K ([M + K]<sup>+</sup>): 371.2131; found: 371.2136. [α]<sub>D</sub><sup>14</sup> = 31.7, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 1.0 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 7.6 min, *t*<sub>R</sub> (major) = 8.2 min); ee = 88%.

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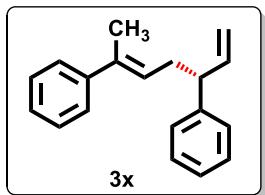


**(R,E)-1-(tert-butyl)-4-(4-phenylhexa-1,5-dien-1-yl)benzene (3w)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (40.6 mg, 70%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.32 – 7.29 (m, 5H), 7.24 – 7.20 (m, 5H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.11 – 5.99 (m, 2H), 5.08 – 5.04 (m, 2H), 3.42 (q, *J* = 7.8 Hz, 1H), 2.67 – 2.60 (m, 2H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 150.0, 143.8, 141.5, 134.9, 131.1, 128.5, 127.7, 126.3, 125.7, 125.3, 114.6, 50.2, 39.1, 34.5, 31.3. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>22</sub>H<sub>26</sub>Na ([M + Na]<sup>+</sup>): 313.1932; found: 313.1931. [α]<sub>D</sub><sup>14</sup> = 3.0, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 99.9/0.1, 0.5 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 23.9 min, *t*<sub>R</sub> (major) = 25.7 min); ee

= 71%.

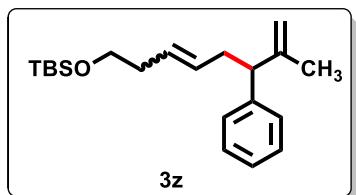
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**(*R,E*)-hepta-2,6-diene-2,5-diylbenzene (3x)**

Purified by flash column chromatography (eluent: Petroleum ether).

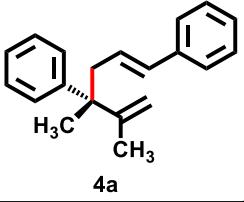
Colorless oil (35.2 mg, 71%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.32 – 7.28 (m, 5H), 7.26 – 7.22 (m, 3H), 7.20 – 7.18 (m, 2H), 6.08 – 6.02 (m, 1H), 5.72 (t, *J* = 7.2 Hz, 1H), 5.10 (d, *J* = 4.2 Hz, 1H), 5.07 (s, 1H), 3.43 (q, *J* = 7.2 Hz, 1H), 2.67 – 2.57 (m, 2H), 1.96 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 143.9, 141.6, 135.8, 128.4, 128.1, 127.7, 126.5, 126.3, 126.1, 125.7, 114.5, 49.8, 34.7, 16.0. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>19</sub>H<sub>20</sub>Na ([M + Na]<sup>+</sup>): 271.1463; found: 271.1462. [α]<sub>D</sub><sup>20</sup> = 22.9, (c = 1.0, CHCl<sub>3</sub>). Enantiomeric purity was determined by chiral HPLC analysis in comparison with authentic racemic material obtained from the derived alcohol **7**, which was synthesized by hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H<sub>2</sub>O<sub>2</sub>. **HPLC** analysis (chiralpak IB column, hexanes/i-PrOH = 97/3, 1.0 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 10.0 min, *t*<sub>R</sub> (major) = 11.6 min); ee = 93%.



**tert-butyldimethyl((7-methyl-6-phenylocta-3,7-dien-1-yl)oxy)silane (3z)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (52.8 mg, 80%, *Z:E* = 2:1); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.29 – 7.25 (m, 3.56H), 7.21 – 7.18 (m, 4.72H), 5.40 – 5.34 (m, 3.19H), 4.92 (s, 1H), 4.91 (s, 0.6H), 4.87 (s, 1H), 4.84 (s, 0.59H), 3.55 – 3.52 (m, 3.25H), 3.23 (t, *J* = 7.2 Hz, 1H), 2.61 – 2.40 (m, 3.38H), 2.26 – 2.13 (m, 3.46H), 1.58 (s, 3H), 1.57 (s, 1.69H), 0.04 (s, 6H), 0.03 (s, 3.22H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 147.6, 147.5, 143.3, 143.2, 130.5, 129.7, 128.2, 128.1, 128.0, 127.8 (8), 127.8 (7), 126.6, 126.2, 126.1, 110.5, 63.3, 62.8, 53.1, 52.8, 36.5, 36.3, 31.3, 31.2, 25.9 (6), 25.9 (5), 21.3, 21.1, 18.4, 18.3, -5.3. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>21</sub>H<sub>34</sub>NaOSi ([M + Na]<sup>+</sup>): 353.2277; found: 353.2275.

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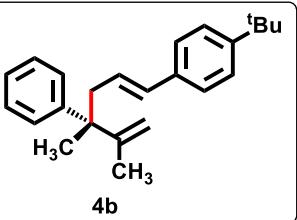


**(*R,E*)-(4,5-dimethylhexa-1,5-diene-1,4-diyl)dibenzene (**4a**)**

Purified by flash column chromatography (eluent: Petroleum ether).

Colorless oil (39.8 mg, 55%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.31 – 7.30 (m, 3H), 7.28 – 7.23 (m, 5H), 7.20 – 7.17 (m, 2H), 6.39 (d, *J* = 15.6 Hz, 1H), 6.01 – 5.96 (m, 1H), 5.02 (s, 1H), 4.99 (s, 1H), 2.79 – 2.70 (m, 2H), 1.54 (s, 3H), 1.39 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 150.8, 147.0, 137.8, 132.2, 128.4, 128.1, 127.5, 126.9, 126.4, 126.0, 125.9, 111.0, 47.2, 42.5, 25.4, 20.3. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>20</sub>H<sub>22</sub>Na ([M + Na]<sup>+</sup>): 285.1619; found: 285.1617. [α]<sub>D</sub><sup>20</sup> = 20.9, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H then OD-H column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t<sub>R</sub>* (minor) = 46.3 min, *t<sub>R</sub>* (major) = 47.5 min); ee = 87%.

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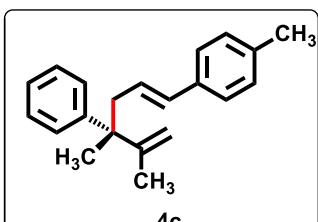


**(*R,E*)-1-(tert-butyl)-4-(4,5-dimethyl-4-phenylhexa-1,5-dien-1-yl)benzene (**4b**)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (38.8 mg, 61%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)

δ: 7.31 – 7.29 (m, 5H), 7.24 – 7.19 (m, 4H), 6.37 (d, *J* = 16.2 Hz, 1H), 5.97 – 5.92 (m, 1H), 5.00 (d, *J* = 18.0 Hz, 2H), 2.78 – 2.69 (m, 2H), 1.53 (s, 3H), 1.38 (s, 3H), 1.30 (s, 9H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 150.8, 149.9, 147.1, 135.0, 131.9, 128.1, 126.6, 126.5, 125.8, 125.7, 125.3, 111.0, 47.2, 42.5, 34.5, 31.3, 25.3, 20.3. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>24</sub>H<sub>30</sub>Na ([M + Na]<sup>+</sup>): 341.2245; found: 341.2242. [α]<sub>D</sub><sup>14</sup> = 22.7, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t<sub>R</sub>* (minor) = 15.0 min, *t<sub>R</sub>* (major) = 15.2 min); ee = 91%.

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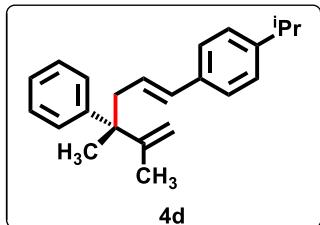


**(*R,E*)-1-(4,5-dimethyl-4-phenylhexa-1,5-dien-1-yl)-4-methylbenzene (**4c**)**

Purified by flash column chromatography (eluent: Petroleum

ether). Colorless oil (27.0 mg, 49%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.32 – 7.29 (m, 5H), 7.24 – 7.20 (m, 5H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.11 – 5.99 (m, 2H), 5.08 – 5.04 (m, 2H), 3.42 (q, *J* = 7.8 Hz, 1H), 2.67 – 2.60 (m, 2H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 150.0, 143.8, 141.5, 134.9, 131.1, 128.5, 127.7, 126.3, 125.7, 125.3, 114.6, 50.2, 39.1, 34.5, 31.3. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>21</sub>H<sub>24</sub>Na ([M + Na]<sup>+</sup>): 299.1773; found: 299.1770. [α]<sub>D</sub><sup>15</sup> = 66.1, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak IA column, hexanes/i-PrOH = 100/0, 1.0 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 5.2 min, *t*<sub>R</sub> (major) = 5.8 min); ee = 88%.

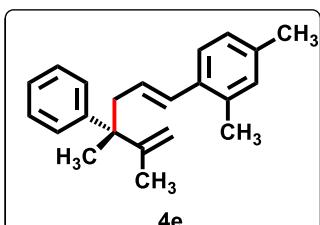
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**(*R,E*)-1-(4,5-dimethyl-4-phenylhexa-1,5-dien-1-yl)-4-isopropylbenzene (4d)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (37.1 mg, 61%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.39 – 7.29 (m, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.37 (d, *J* = 15.6 Hz, 1H), 5.96 – 5.91 (m, 1H), 5.01 (s, 1H), 4.98 (s, 1H), 2.90 – 2.94 (m, 1H), 2.78 – 2.69 (ddd, *J* = 31.3, 13.7, 7.3 Hz, 2H), 1.53 (s, 3H), 1.38 (s, 3H), 1.22 (d, *J* = 6.6 Hz, 6H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 150.8, 147.7, 147.1, 135.4, 132.0, 128.1, 126.5, 126.5, 126.0, 125.8, 111.0, 47.2, 42.5, 33.8, 25.3, 23.9, 20.3. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>23</sub>H<sub>28</sub>Na ([M + Na]<sup>+</sup>): 327.2083; found: 327.2083. [α]<sub>D</sub><sup>14</sup> = 1.4, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 16.9 min, *t*<sub>R</sub> (major) = 17.5 min); ee = 91%.

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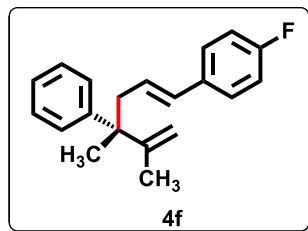


**(*R,E*)-1-(4,5-dimethyl-4-phenylhexa-1,5-dien-1-yl)-2,4-dimethylbenzene (4e)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (31.9 mg, 55%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.30 – 7.29 (m, 4H), 7.20 – 7.18 (m, 2H), 6.92 (d, *J* = 7.8 Hz, 2H), 6.52 (d, *J* = 15.6 Hz, 1H), 5.93 – 5.79 (m, 1H), 5.02 (s, 1H), 4.98 (s, 1H), 2.80 – 2.71 (m, 2H),

2.27 (s, 3H), 2.24 (s, 3H), 1.54 (s, 3H), 1.40 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 150.9, 147.1, 136.5, 134.8, 134.2, 130.8, 130.1, 128.1, 127.9, 126.7, 126.5, 125.8, 125.7, 111.0, 47.2, 42.8, 25.3, 21.0, 20.3, 19.7. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>22</sub>H<sub>26</sub>Na ([M + Na]<sup>+</sup>): 313.1932; found: 313.1934. [α]<sub>D</sub><sup>14</sup> = 17.9, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak IA column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 9.2 min, *t*<sub>R</sub> (major) = 9.4 min); ee = 91%.

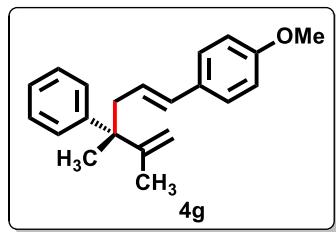
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**(*R,E*)-1-(4,5-dimethyl-4-phenylhexa-1,5-dien-1-yl)-4-fluorobenzene (4f)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (34.2 mg, 61%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.31 – 7.30 (m, 4H), 7.24 – 7.19 (m, 3H), 6.95 (t, *J* = 9.0 Hz, 2H), 6.35 (d, *J* = 15.6 Hz, 1H), 5.91 – 5.86 (m, 1H), 5.02 (s, 1H), 5.00 (s, 1H), 2.78 – 2.69 (m, 2H), 1.53 (s, 3H), 1.38 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 161.9 (*J* = 244.4 Hz), 150.8, 146.9, 133.9, 131.0, 128.1, 127.4 (*J* = 7.8 Hz), 127.2 (*J* = 2.1 Hz), 126.4, 125.9, 115.3 (*J* = 21.5 Hz), 111.0, 47.2, 42.5, 25.3, 20.3. **<sup>19</sup>F NMR** (564 MHz; CDCl<sub>3</sub>) δ: -115.59 – -115.64. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>20</sub>H<sub>21</sub>F ([M + Na]<sup>+</sup>): 303.1525; found: 303.1523. [α]<sub>D</sub><sup>14</sup> = 8.5, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 1.0 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 9.5 min, *t*<sub>R</sub> (major) = 10.2 min); ee = 90%.

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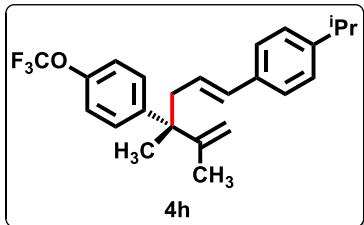


**(*R,E*)-1-(4,5-dimethyl-4-phenylhexa-1,5-dien-1-yl)-4-methoxybenzene (4g)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (28.0 mg, 48%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.31 – 7.30 (m, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.15 (m, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 6.33 (d, *J* = 16.2 Hz, 1H), 5.86 – 5.81 (m, 1H), 5.02 – 4.98 (m, 2H), 3.78 (s, 3H), 2.79 – 2.58 (m, 2H), 1.53 (d, *J* = 0.6 Hz, 3H), 1.38 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 158.7, 150.9, 147.1, 131.5, 130.7, 128.1, 127.1, 126.5, 125.8, 125.2, 113.9, 111.0, 55.3, 47.2, 42.5, 25.3, 20.3. **HRMS** (ESI-TOF) (m/z):

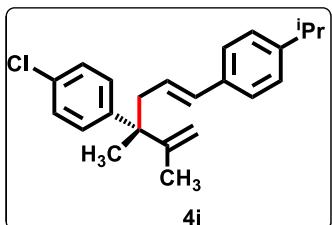
Calcd for C<sub>21</sub>H<sub>25</sub>O ([M + H]<sup>+</sup>): 293.1505; found: 293.1508. [α]<sub>D</sub><sup>15</sup> = 40.1, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak IB column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t<sub>R</sub>* (minor) = 32.7 min, *t<sub>R</sub>* (major) = 34.6 min); ee = 91%.

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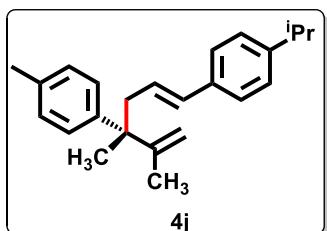
**(*R,E*)-1-(4,5-dimethyl-4-(trifluoromethoxy)phenyl)hexa-1,5-dien-1-yl)-4-isopropylbenzene (4h)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (37.2 mg, 55%); <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ: 7.32 (d, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 6.4 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 4H), 6.36 (d, *J* = 12.8 Hz, 1H), 5.93 – 5.87 (m, 1H), 5.02 – 5.00 (m, 2H), 2.77 – 2.73 (m, 1H), 2.70 – 2.65 (m, 2H), 1.53 (s, 3H), 1.38 (s, 3H), 1.23 (d, *J* = 6.4 Hz, 6H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ: 149.8, 147.4, 146.9, 145.4, 134.8, 132.0, 127.4, 126.0, 125.5, 125.3, 120.0, 111.0, 46.5, 42.1, 33.3, 24.9, 23.5, 19.8. <sup>19</sup>**F NMR** (470 MHz; CDCl<sub>3</sub>) δ: -71.11. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>24</sub>H<sub>27</sub>F<sub>3</sub>NaO ([M + Na]<sup>+</sup>): 411.1912; found: 411.1913. [α]<sub>D</sub><sup>14</sup> = 38.5, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H then OD-H column in series, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t<sub>R</sub>* (minor) = 45.8 min, *t<sub>R</sub>* (major) = 46.9 min); ee = 90%.



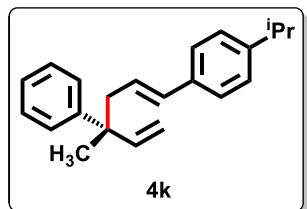
**(*R,E*)-1-(4-(4-chlorophenyl)-4,5-dimethylhexa-1,5-dien-1-yl)-4-isopropyl-2-methylbenzene (4i)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (37.2 mg, 55%); <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.26 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.20 (m, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.36 (d, *J* = 15.6 Hz, 1H), 5.92 – 5.87 (m, 1H), 5.01 (s, 1H), 4.99 (s, 1H), 2.90 – 2.84 (m, 1H), 2.74 – 2.65 (m, 2H), 1.52 (s, 3H), 1.36 (s, 3H), 1.23 (d, *J* = 6.6 Hz, 6H). <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 150.4, 147.8, 145.7, 135.3, 132.4, 131.6, 128.2, 128.0, 126.5, 126.0, 125.9, 111.3, 46.9, 42.6, 33.8, 25.2, 23.9, 20.2. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>23</sub>H<sub>28</sub>Cl ([M + H]<sup>+</sup>): 339.1874; found: 339.1874. [α]<sub>D</sub><sup>14</sup> = 60.5, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t<sub>R</sub>* (minor) = 21.6 min, *t<sub>R</sub>* (major) = 22.7 min); ee = 91%.



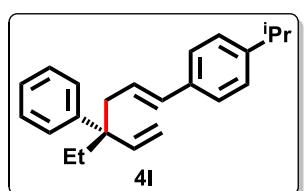
**(*R,E*)-1-(4,5-dimethyl-4-(p-tolyl)hexa-1,5-dien-1-yl)-4-isopropylbenzene (4j)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (46.4 mg, 73%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.22 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.37 (d, *J* = 15.6 Hz, 1H), 5.97 – 5.92 (m, 1H), 4.99 – 4.96 (m, 2H), 2.89 – 2.84 (m, 1H), 2.78 – 2.67 (m, 2H), 2.32 (s, 3H), 1.53 (d, *J* = 0.6 Hz, 3H), 1.36 (s, 3H), 1.22 (d, *J* = 7.8 Hz, 6H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 150.9, 147.6, 144.2, 135.5, 135.2, 131.9, 128.8, 126.7, 126.5, 126.3, 126.0, 110.9, 46.8, 42.5, 33.8, 25.5, 23.9, 20.9, 20.3. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>24</sub>H<sub>31</sub> ([M + H]<sup>+</sup>): 319.2426; found: 319.2424. **[ $\alpha$ ]<sub>D</sub><sup>14</sup>** = 20.4, (*c* = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 0.5 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 14.5 min, *t*<sub>R</sub> (major) = 15.3 min); ee = 92%.



**(*R,E*)-1-isopropyl-4-(4-methyl-4-phenylhexa-1,5-dien-1-yl)benzene (4k)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (38.9 mg, 67%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.36 (d, *J* = 7.2 Hz, 2H), 7.33 – 7.30 (m, 3H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.35 (d, *J* = 16.2 Hz, 1H), 6.02 – 6.07 (m, 1H), 6.00 – 5.94 (m, 1H), 5.14 – 5.06 (m, 2H), 2.89 – 2.84 (m, 1H), 2.70 – 2.61 (m, 2H), 1.40 (s, 3H), 1.22 (d, *J* = 7.2 Hz, 6H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 147.7, 147.1, 146.6, 135.3, 132.3, 128.1, 126.7, 126.5, 126.1, 126.0, 125.9, 112.1, 44.7, 44.6, 33.8, 25.0, 23.9. **[ $\alpha$ ]<sub>D</sub><sup>14</sup>** = 19.7, (*c* = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 1.0 mL/min, 250 nm, *t*<sub>R</sub> (minor) = 11.4 min, *t*<sub>R</sub> (major) = 12.1 min); ee = 91%.

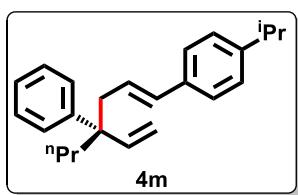


**(*R,E*)-1-(4-ethyl-4-phenylhexa-1,5-dien-1-yl)-4-isopropylbenzene**

**(4l)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (37.1 mg, 61%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.32 – 7.31 (m, 4H), 7.19 (d, J = 8.4 Hz, 3H), 7.12 (d, J = 9.0 Hz, 2H), 6.34 (d, J = 16.2 Hz, 1H), 6.00 – 5.92 (m, 2H), 5.23 (d, J = 11.4 Hz, 1H), 5.12 (d, J = 17.4 Hz, 1H), 2.88 – 2.83 (m, 1H), 2.67 (d, J = 7.2 Hz, 2H), 1.87 – 1.78 (m, 2H), 1.22 (d, J = 6.6 Hz, 6H), 0.76 (t, J = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 147.7, 145.5, 145.3, 135.4, 131.9, 128.0, 127.4, 126.5, 126.7, 126.0, 125.9, 113.1, 48.1, 40.5, 33.8, 29.5, 23.9, 8.4. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>23</sub>H<sub>28</sub>Na ([M + Na]<sup>+</sup>): 327.2089; found: 327.2088. [α]<sub>D</sub><sup>14</sup> = 6.7, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak OD-H column, hexanes/i-PrOH = 100/0, 1.0 ml/min, 250 nm, t<sub>R</sub> (minor) = 9.7 min, t<sub>R</sub> (major) = 10.1 min); ee = 90%.

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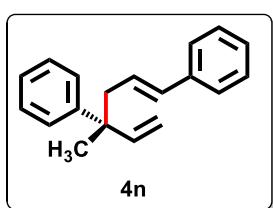


**(R,E)-1-isopropyl-4-(4-phenyl-4-vinylhept-1-en-1-yl)benzene**

**(4m)**

Purified by flash column chromatography (eluent: Petroleum ether). Colorless oil (36.9 mg, 58%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.32 – 7.31 (m, 4H), 7.19 (d, J = 8.4 Hz, 3H), 7.12 (d, J = 7.8 Hz, 2H), 6.33 (d, J = 16.2 Hz, 1H), 6.01 – 5.92 (m, 2H), 5.61 (t, J = 7.2 Hz, 0.23H), 5.21 (dd, J = 10.8, 1.2 Hz, 1H), 5.11 (dd, J = 17.4, 1.2Hz, 1H), 2.89 – 2.84 (m, 1H), 2.67 (dd, J = 7.2, 1.2 Hz, 2H), 1.79 – 1.70 (m, 2H), 1.22 (d, J = 6.6 Hz, 6H), 1.19 – 1.01 (m, 2H), 0.84 (t, J = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 147.7, 145.8, 145.5, 135.4, 131.9, 128.0, 127.3, 126.5, 126.1, 126.0, 125.8, 112.9, 48.0, 41.2, 39.6, 33.8, 23.9, 17.2, 14.7. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>24</sub>H<sub>30</sub>Na ([M + Na]<sup>+</sup>): 341.2245; found: 341.2243. [α]<sub>D</sub><sup>14</sup> = 27.7, (c = 1.0, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak IB column, hexanes/i-PrOH = 100/0, 1.0 ml/min, 250 nm, t<sub>R</sub> (minor) = 9.1 min, t<sub>R</sub> (major) = 9.7 min); ee = 85%. A structure undetermined compound and compound **4m** were obtained and can not isolated by flash column chromatography.

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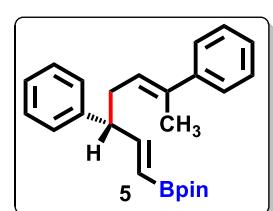
**(R,E)-(4-methylhexa-1,5-diene-1,4-diyl)dibenzene (4n)**

Purified by flash column chromatography (eluent: Petroleum ether).

Colorless oil (46.4 mg, 73%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.36 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 3H), 7.26 – 7.24 (m, 2H), 7.22 – 7.16 (m, 3H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.10 (dd, *J* = 17.4, 10.8 Hz, 1H), 6.04 – 5.99 (m, 1H), 5.15 (d, *J* = 10.8 Hz, 1H), 5.09 (d, *J* = 17.4 Hz, 1H), 2.72 – 2.64 (m, 2H), 1.41 (s, 3H).. **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 147.0, 146.5, 137.7, 132.4, 128.4, 128.1, 127.1, 126.9, 126.6, 126.0 (3), 125.9 (6), 112.2, 44.7, 44.6, 25.0. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>19</sub>H<sub>20</sub>Na ([M + Na]<sup>+</sup>): 271.1463; found: 271.1462. [α]<sub>D</sub><sup>20</sup> = 7.8, (c = 0.5, CHCl<sub>3</sub>). **HPLC** analysis (Chiralpak IB column, hexanes/i-PrOH = 100/0, 0.3 ml/min, 250 nm, *t*<sub>R</sub> (minor) = 25.7 min, *t*<sub>R</sub> (major) = 26.9 min); ee = 90%.

### Proof of Stereochemistry:

Spectra data are in accordance with literature.<sup>4</sup> Based on the optical rotation of **6** in ref 4 (which was assigned to possess *S* absolute stereochemistry, [α]<sub>D</sub><sup>20</sup> = -45.342, (c = 2.1, CHCl<sub>3</sub>), the absolute stereochemistry of product **4n** was determined as *R*.

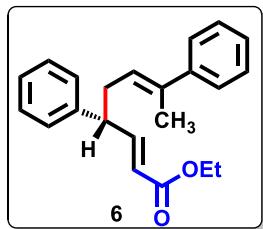


**2-((R,1E,5E)-3,6-diphenylhepta-1,5-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)**

Hoveyda-Grubbs Catalyst 2nd (6.26 mg, 0.01 mmol), pinacol vinylboronate (61.6 mg, 0.4 mmol) were weighed out into a flamedried 50 mL round-bottom flask under a N<sub>2</sub> atmosphere in a glove box. The flask was fitted with a reflux condenser and removed from the glove box. A solution of **3y** (49.6 mg, 0.2 mmol) dissolved in DCM (5.0 mL) was added through a plastic syringe and the resulting mixture was allowed to stir at reflux (50 °C) for 24 h. The mixture was allowed to cool to 22 °C and the volatiles were removed in vacuo and the crude product was purified by flash column chromatography (using 1% diethyl ether / *n*-hexane) to give the corresponding product **5** colorless oil (56.1 mg, 75%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.31 – 7.25 (m, 6H), 7.22 – 7.18 (m, 4H), 6.81 (dd, *J* = 18.0, 7.2 Hz, 1H), 5.67 (t, *J* = 7.7 Hz, 1H), 5.48 (d, *J* = 17.4 Hz, 1H), 3.49 (d, *J* = 7.2 Hz, 1H), 2.72 – 2.67 (m, 1H), 2.65 – 2.59 (m, 1H), 1.95 (s, 3H), 1.25 (s, 12H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 156.2, 143.9, 143.0, 136.0, 128.4, 128.1, 128.0, 126.5, 126.4, 125.9, 125.7, 83.1, 51.7, 34.3, 24.8, 24.8, 16.1. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>19</sub>H<sub>20</sub>BNaO<sub>2</sub> ([M + Na]<sup>+</sup>):

397.2135; found: 397.2131.

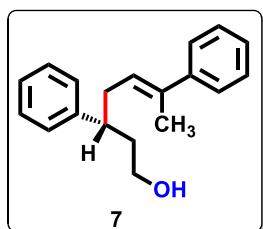
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**(*R*,2*E*,6*E*)-ethyl 4,7-diphenylocta-2,6-dienoate (6)**

Hoveyda-Grubbs Catalyst 2nd (6.26 mg, 0.01 mmol), ethyl acrylate (40.0 mg, 0.4 mmol) were weighed out into a flamedried 50 mL round-bottom flask under a N<sub>2</sub> atmosphere in a glove box. The flask was fitted with a reflux condenser and removed from the glove box. A solution of **3y** (49.6 mg, 0.2 mmol) dissolved in DCM (5.0 mL) was added through a plastic syringe and the resulting mixture was allowed to stir at reflux (50 °C) for 24 h. The mixture was allowed to cool to 22 °C and the volatiles were removed in vacuo and the crude product was purified by flash column chromatography (using 1% diethyl ether / *n*-hexane) to give the corresponding product **6** colorless oil (49.5 mg, 77%); **1H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.32 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 4.2 Hz, 4H), 7.24 – 7.22 (m, 3H), 7.11 – 7.14 (m, 1H), 5.83 (d, *J* = 15.6 Hz, 1H), 5.66 (t, *J* = 6.6 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.57 (q, *J* = 7.2 Hz, 1H), 2.74 – 2.64 (m, 2H), 1.97 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). **13C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 166.6, 151.0, 143.7, 141.8, 137.0, 128.7, 128.1, 127.9, 126.9, 126.7, 125.7, 124.9, 121.2, 60.3, 48.5, 34.3, 16.1, 14.2. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>19</sub>H<sub>24</sub>O<sub>2</sub>Na ([M + Na]<sup>+</sup>): 343.1674; found: 343.1670.

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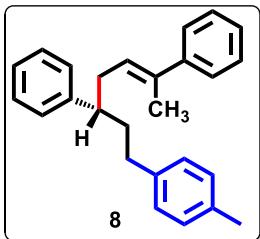


**(*R*,*E*)-3,6-diphenylhept-5-en-1-ol (7)**

A dry 25 mL flask equipped with a magnetic stirring bar was flushed with nitrogen. To the flask were added **3y** (49.6 mg, 0.2 mmol) and dry THF (2.0 mL) and then a solution of 9-BBN (0.5 M solution in THF, 0.4 mL) at 0 °C. Then the reaction flask was stirred for 6 h at rt. NaOH (80 mg) and H<sub>2</sub>O<sub>2</sub> (30%, 1.2 mL) were added to the reaction. After 3 h, the mixture was extracted with DCM (3 × 5.0 mL). The residue was purified by chromatography on silica gel (using 5% EtOAc/*n*-hexane) to afford **7** (colorless oil, 39.4 mg, 74 %); **1H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.30 (t, *J* = 7.2 Hz, 2H), 7.27 – 7.25 (m, 4H), 7.22 – 7.19 (m, 4H), 5.68 (t, *J* = 7.8 Hz, 1H), 3.59 – 3.56 (m, 1H),

3.52 – 3.48 (m, 1H), 2.90 – 2.85 (m, 1H), 2.58 – 2.53 (m, 1H), 2.50 – 2.46 (m, 1H), 2.08 – 2.02 (m, 1H), 1.95 – 1.85 (m, 4H), 1.16 (s, 1H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 144.6, 143.9, 135.9, 128.5, 128.1, 127.6, 126.9, 126.5, 126.3, 126.2, 126.1, 125.6, 61.2, 42.8, 38.6, 36.3, 15.9. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>19</sub>H<sub>20</sub>Na ([M + Na]<sup>+</sup>): 289.1563; found: 289.1580.

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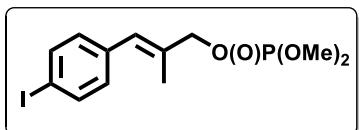


**(S,E)-(7-(p-tolyl)hept-2-ene-2,5-diyl)dibenzene (8)**

To the dry 25 mL flask with a magnetic stirring bar was added **3y** (49.6 mg, 0.2 mmol) and dry THF (2.0 mL) and then added the solution of 9-BBN (0.5 M solution in THF, 0.4 mL) at 0 °C under N<sub>2</sub> atmosphere.

After 12 h at rt, Pd(dppf)Cl<sub>2</sub> (14.5 mg, 10 mol%), 4-bromotoluene (51.3 mg, 1.5 equiv.) and aqueous NaOH (3.0 mL of 3 M) were added successively to the above mixture at rt and then reacted 16 h under reflux. The reaction mixture was diluted with hexane (10.0 mL), and the residual borane was oxidized by addition of H<sub>2</sub>O<sub>2</sub> (30%, 4.0 mL) at rt. The mixture was extracted with DCM (3 × 5.0 mL). The residue was purified by chromatography on silica gel (using 1% diethyl ether / n-hexane) to afford **8** (colorless oil, 39.4 mg, 59%); **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.31 (t, J = 7.8 Hz, 2H), 7.26 – 7.21 (m, 7H), 7.19 – 7.17 (m, 1H), 7.06 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 5.65 (t, J = 6.6 Hz, 1H), 2.74 – 2.69 (m, 1H), 2.57 – 2.40 (m, 4H), 2.30 (s, 3H), 2.07 – 1.93 (m, 2H), 1.90 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 145.1, 144.0, 139.3, 135.7, 135.1, 129.0, 128.3, 128.2, 128.1, 127.8, 126.5, 126.1, 125.6, 45.8, 37.6, 36.4, 33.3, 21.0, 15.9. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>26</sub>H<sub>28</sub>Na ([M + Na]<sup>+</sup>): 363.2089; found: 363.2086.

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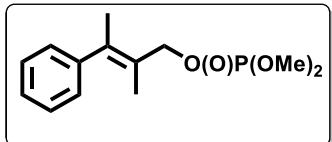


**(E)-3-(4-iodophenyl)-2-methylallyl dimethyl phosphoroperoxoite**

Following the general procedure **4**. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ: 7.67 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.49 (s, 1H), 4.57 (d, J = 7.8 Hz, 2H), 3.80 (d, J = 9.6 Hz, 6H), 1.90 (d, J = 1.2 Hz, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 137.3, 136.2, 133.7 (d, J = 6.75

Hz), 130.7, 127.2, 92.3, 72.9(d,  $J = 5.55$  Hz), 54.3(d,  $J = 6.0$  Hz), 15.1. **HRMS** (ESI-TOF) (m/z): Calcd for  $C_{12}H_{16}NaIO_4P$  ([M + Na]<sup>+</sup>): 404.9723; found: 404.9722.

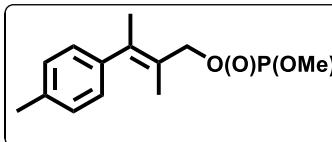
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**(E)-dimethyl (2-methyl-3-phenylbut-2-en-1-yl)  
phosphoroperoxoite**

Following the general procedure **4**. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.33 (t,  $J = 7.8$  Hz, 2H), 7.24 (t,  $J = 7.8$  Hz, 1H), 7.13 (d,  $J = 6.6$  Hz, 2H), 4.73 (d,  $J = 7.2$  Hz, 2H), 3.81 (d,  $J = 10.8$  Hz, 6H), 2.07 (s, 3H), 1.67 (d,  $J = 1.2$  Hz, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 143.8, 137.2, 128.2, 127.7, 126.6, 126.1 (d,  $J = 6.6$  Hz), 68.4 (d,  $J = 5.55$  Hz), 54.2 (d,  $J = 6.0$  Hz), 20.6, 17.8. **HRMS** (ESI-TOF) (m/z): Calcd for  $C_{13}H_{19}NaO_4P$  ([M + Na]<sup>+</sup>): 293.0913; found: 293.0914.

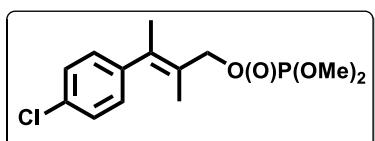
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**(E)-dimethyl (2-methyl-3-(p-tolyl)but-2-en-1-yl)  
phosphoroperoxoite**

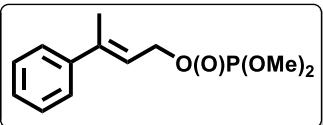
Following the general procedure **4**. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.14 (d,  $J = 7.8$  Hz, 2H), 7.02 (d,  $J = 7.8$  Hz, 2H), 4.72 (d,  $J = 7.2$  Hz, 2H), 3.80 (d,  $J = 11.4$  Hz, 6H), 2.35 (s, 4H), 2.05 (d,  $J = 1.8$  Hz, 3H), 1.68 (d,  $J = 1.8$  Hz, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.8, 137.1, 136.1, 128.8, 127.7, 125.9 (d,  $J = 6.6$  Hz), 68.5 (d,  $J = 5.7$  Hz), 54.2 (d,  $J = 6.0$  Hz), 21.1, 20.6, 17.9. **HRMS** (ESI-TOF) (m/z): Calcd for  $C_{14}H_{21}NaO_4P$  ([M + Na]<sup>+</sup>): 307.1075; found: 307.1074.

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**(E)-3-(4-chlorophenyl)-2-methylbut-2-en-1-yl dimethyl  
phosphoroperoxoite**

Following the general procedure **4**. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.30 (d,  $J = 8.5$  Hz, 2H), 7.07 (d,  $J = 8.5$  Hz, 2H), 4.72 (d,  $J = 7.5$  Hz, 2H), 3.81 (d,  $J = 11.0$  Hz, 6H), 2.04 (s, 3H), 1.67 (d,  $J = 1.0$  Hz, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 141.9, 135.7, 132.1, 129.0, 128.1, 126.6 (d,  $J = 6.45$  Hz), 67.9 (d,  $J = 5.55$  Hz), 54.0 (d,  $J = 6.0$  Hz), 20.2, 17.5. **HRMS** (ESI-TOF) (m/z): Calcd for  $C_{13}H_{18}ClNaO_4P$  ([M + Na]<sup>+</sup>): 327.0529; found: 327.0524.

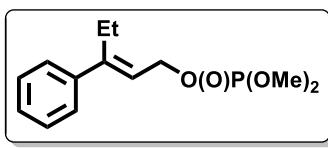


**(*E*)-dimethyl (3-phenylbut-2-en-1-yl) phosphoroperoxoite**

Following the general procedure **4**. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ:

7.40 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 1H), 5.96 – 5.93 (m, 1H), 4.77 (t, *J* = 7.2 Hz, 2H), 3.77 (d, *J* = 10.8 Hz, 6H), 2.12 (s, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 142.1, 140.7, 128.1, 127.5, 125.7, 121.3 (d, *J* = 6.45 Hz), 64.4 (d, *J* = 5.4 Hz), 54.1 (d, *J* = 6.0 Hz), 16.0. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>12</sub>H<sub>17</sub>NaO<sub>4</sub>P ([M + Na]<sup>+</sup>): 279.0757; found: 279.0765.

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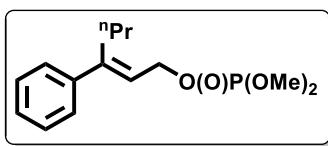


**(*E*)-dimethyl (3-phenylpent-2-en-1-yl) phosphoroperoxoite**

Following the general procedure **4**. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ:

7.37 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 5.81 (t, *J* = 7.2 Hz, 1H), 4.77 (t, *J* = 7.2 Hz, 2H), 3.78 (d, *J* = 11.4 Hz, 6H), 2.59 – 2.86 (m, 2H), 1.00 (t, *J* = 7.8 Hz, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 147.6, 141.4, 128.3, 127.6, 126.4, 121.2 (d, *J* = 6.6 Hz), 64.3 (d, *J* = 5.4 Hz), 54.2 (d, *J* = 5.85 Hz), 23.3, 13.7. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>13</sub>H<sub>19</sub>NaO<sub>4</sub>P ([M + Na]<sup>+</sup>): 293.0913; found: 293.0909.

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**(*E*)-dimethyl (3-phenylhex-2-en-1-yl) phosphoroperoxoite**

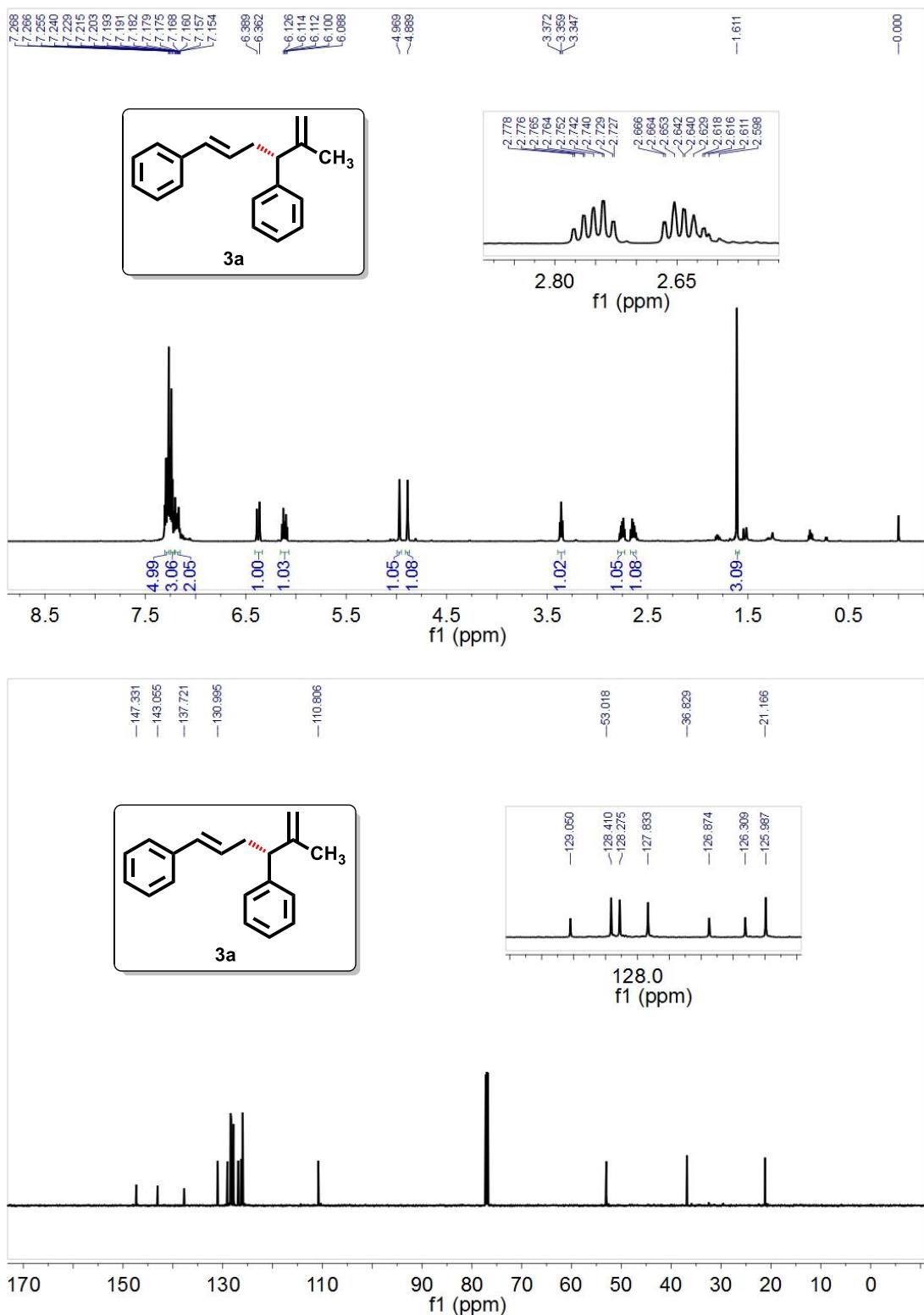
Following the general procedure **4**. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ:

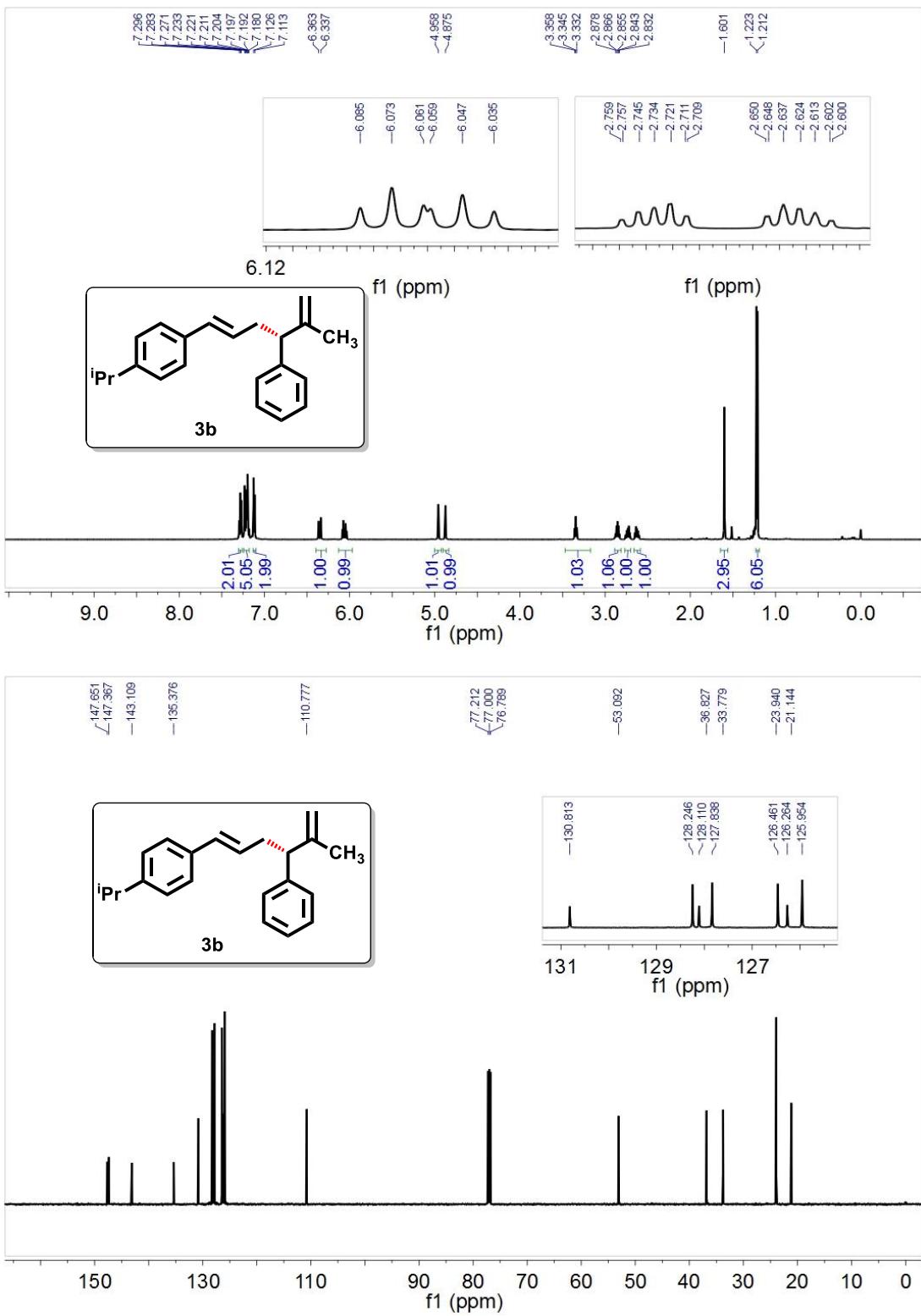
7.36 – 7.31 (m, 4H), 7.29 – 7.26 (m, 1H), 5.84 (t, *J* = 6.6 Hz, 1H), 4.77 (t, *J* = 7.2 Hz, 2H), 3.78 (d, *J* = 10.8 Hz, 6H), 2.53 (t, *J* = 7.8 Hz, 2H), 1.41 – 1.35 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ: 145.9, 141.7, 128.3, 127.5, 126.4, 122.1 (d, *J* = 6.75 Hz), 64.4 (d, *J* = 5.4 Hz, 6H), 54.2 (d, *J* = 6.0 Hz, 6H), 32.0, 21.8, 13.7. **HRMS** (ESI-TOF) (m/z): Calcd for C<sub>14</sub>H<sub>21</sub>NaO<sub>4</sub>P ([M + Na]<sup>+</sup>): 3071070; found: 3071056.

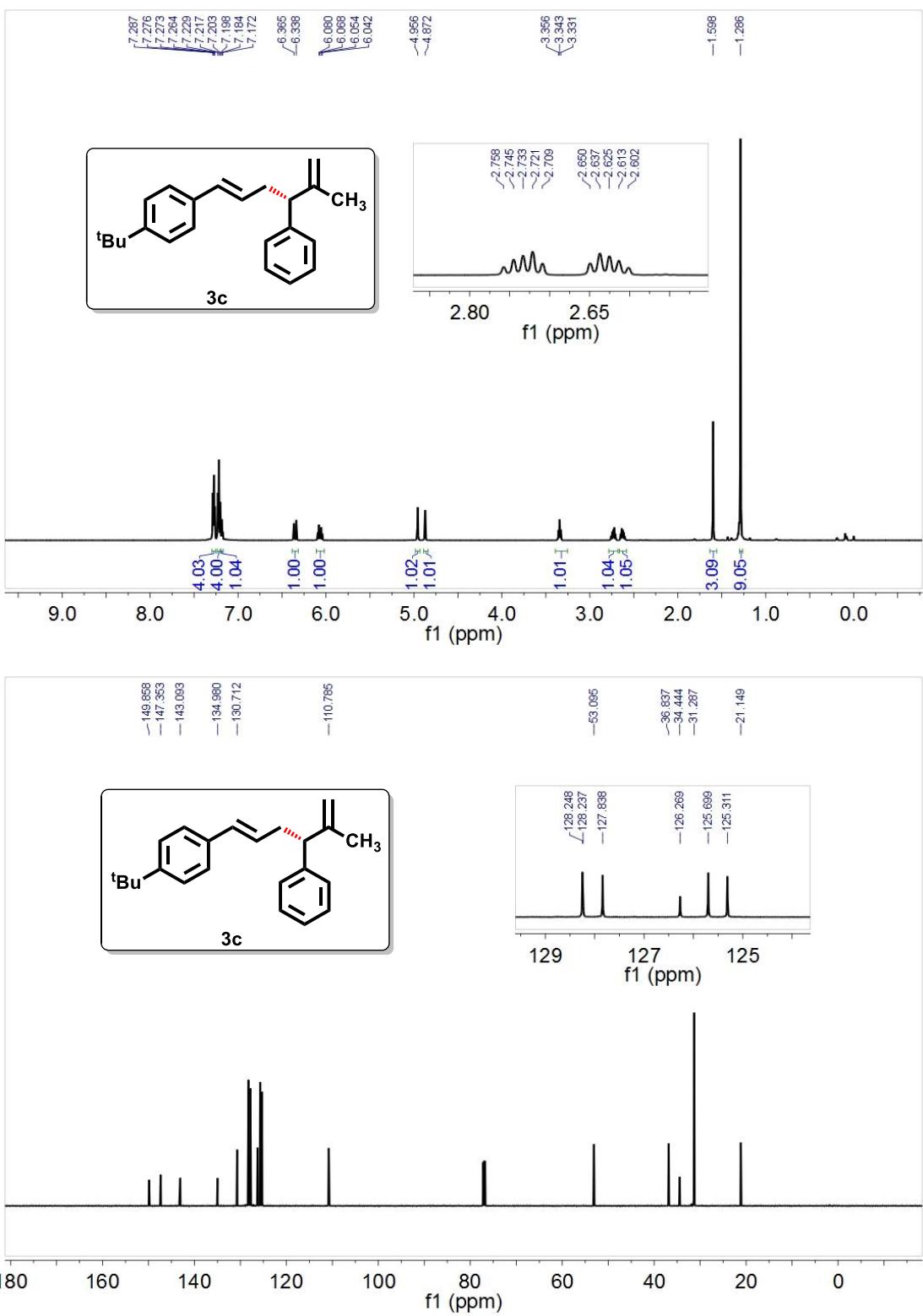
## 6. References

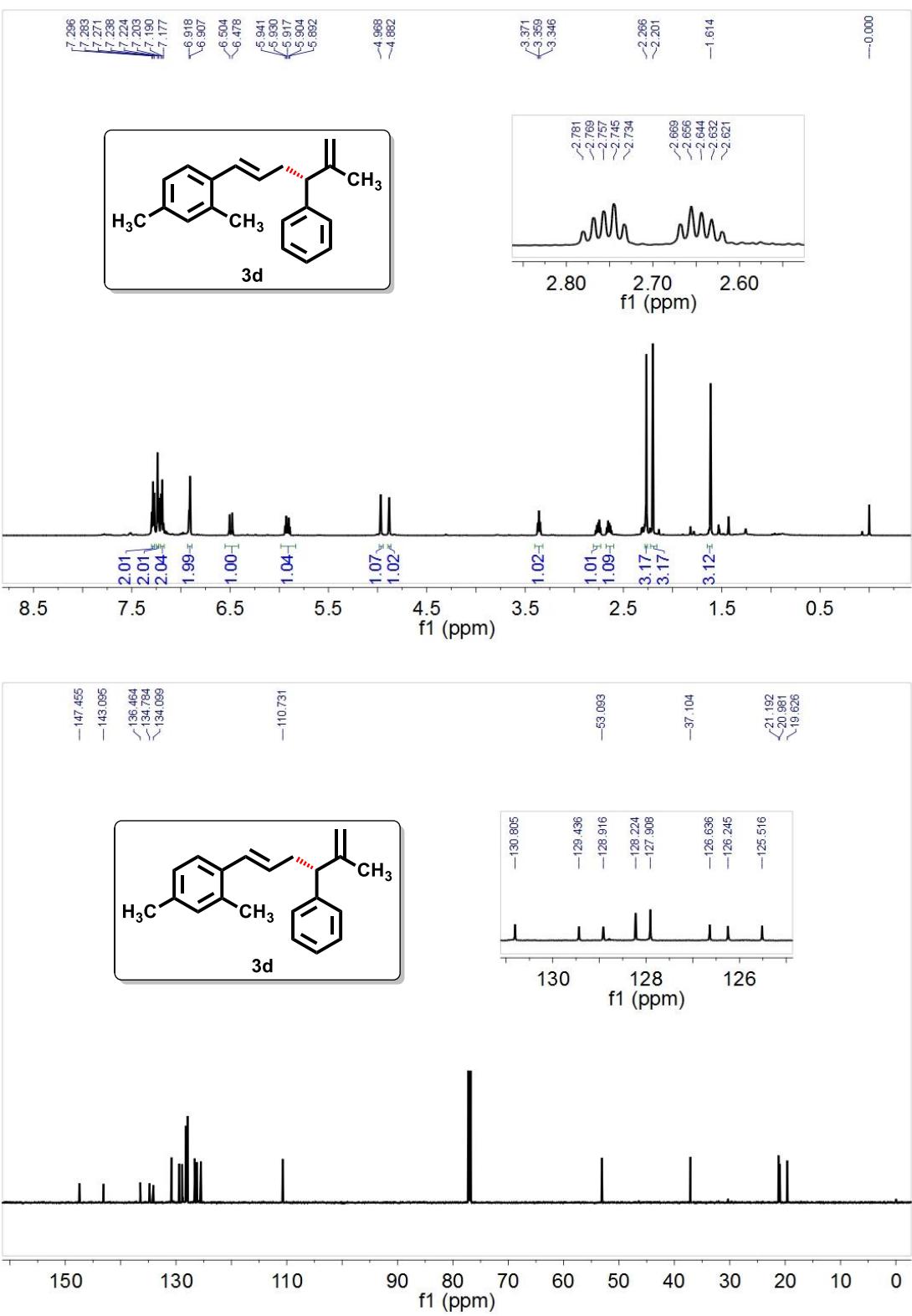
1. B. Jung and A. H. Hoveyda, *J. Am. Chem. Soc.* 2012, **134**, 1490.
2. M. S. Baird, A. V. Nizovtsev and I. G. Bolesov, *Tetrahedron* 2002, **58**, 1581.
3. C.-M. Zhong, S. Kunii, Y. Kosaka, M. Sawamura and H. Ito, *J. Am. Chem. Soc.* 2010, **132**, 11440.
4. P. Zhang, H. Le, R. E. Kyne and J. P. Morken, *J. Am. Chem. Soc.* 2011, **133**, 9716.

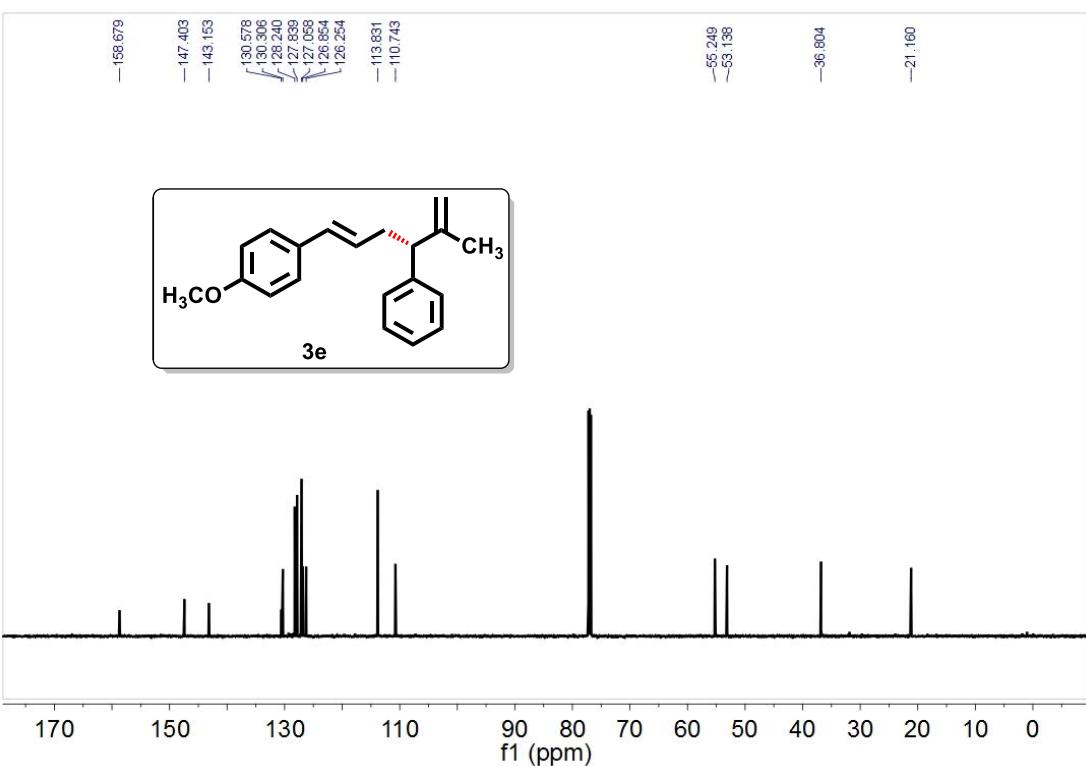
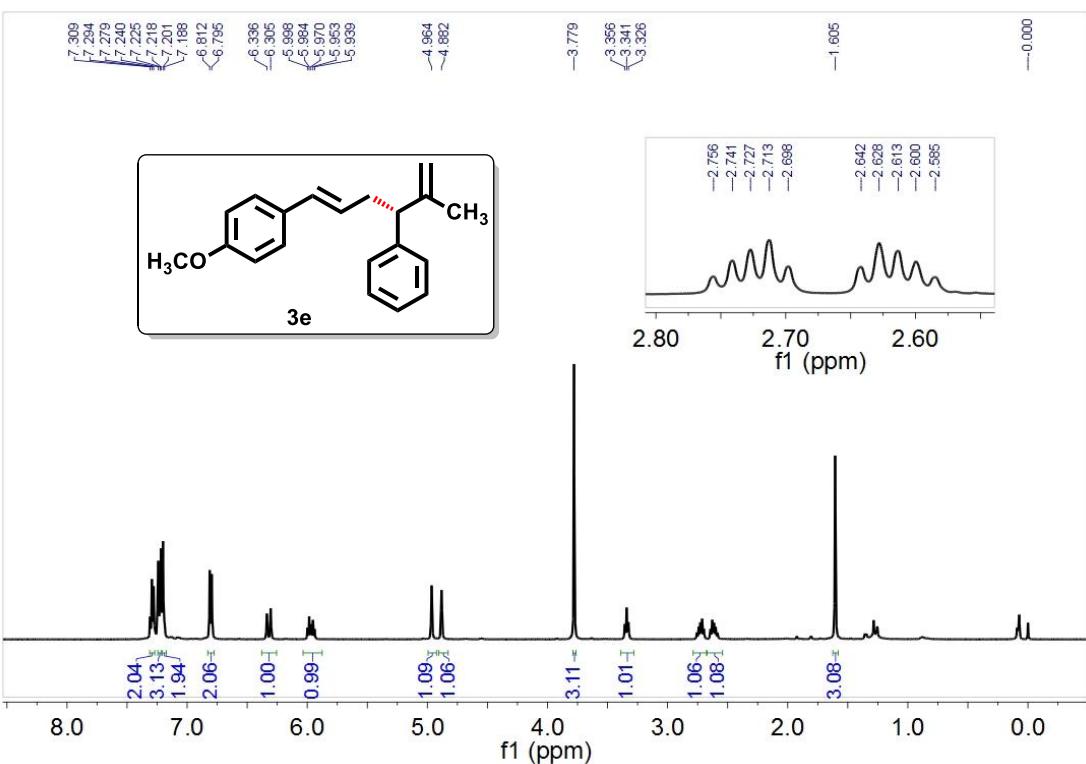
## 7. $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ Spectra of New Compounds

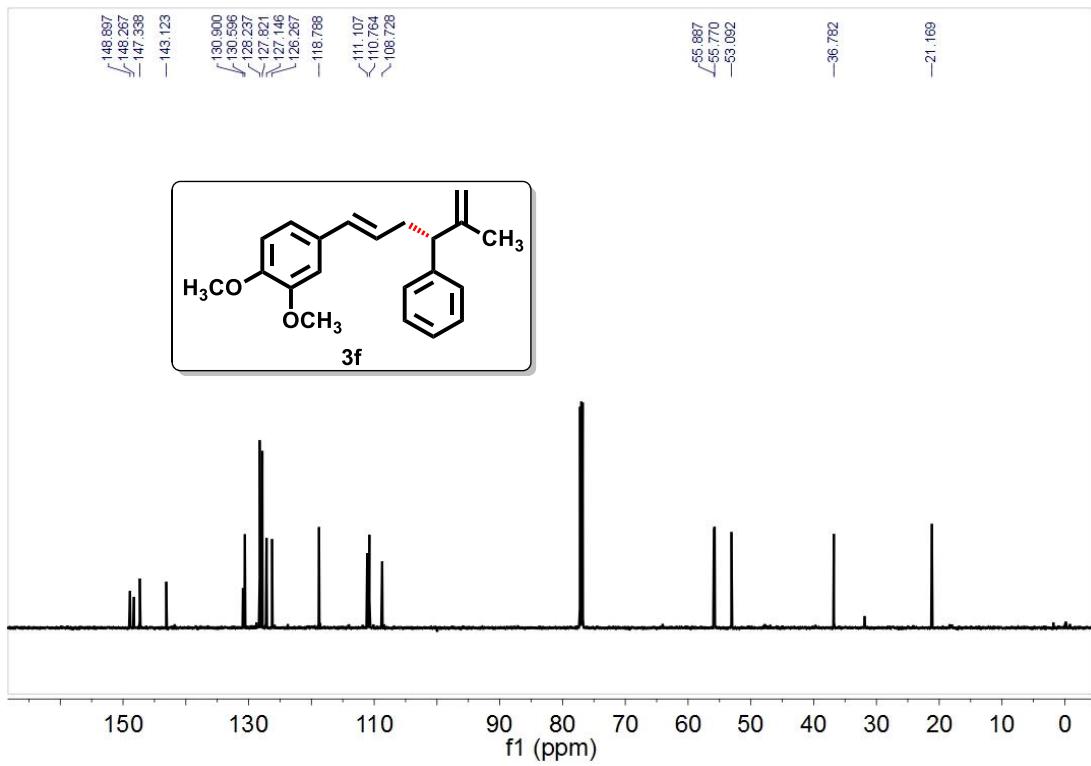
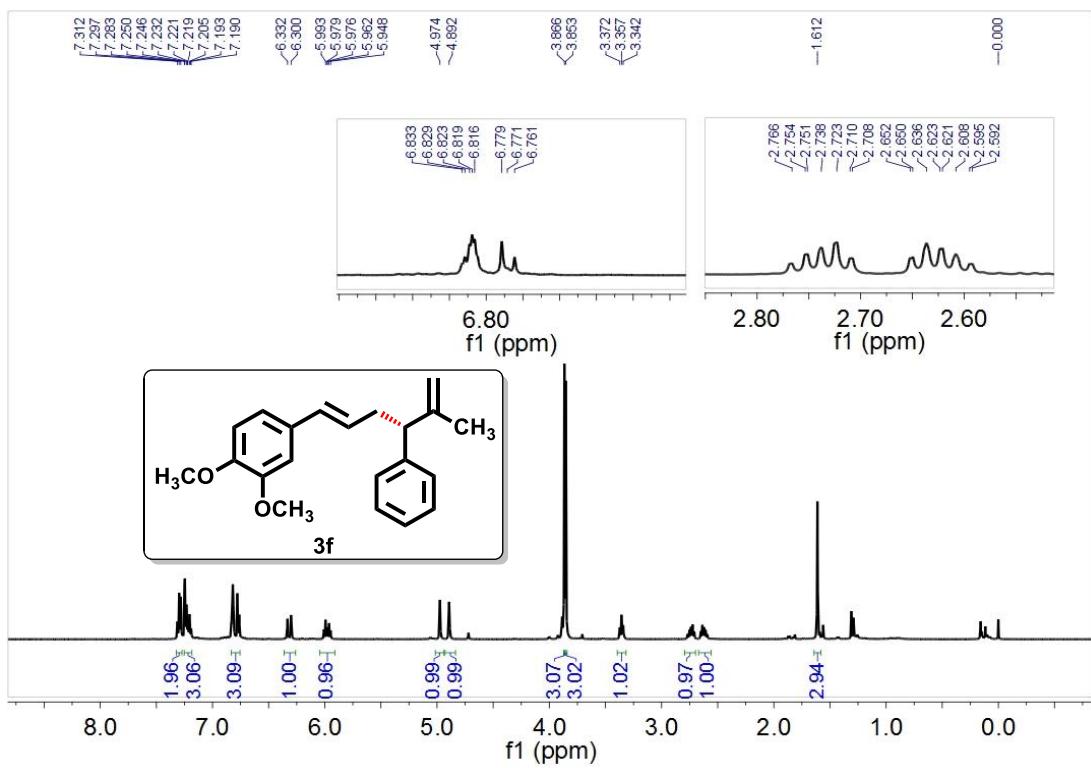


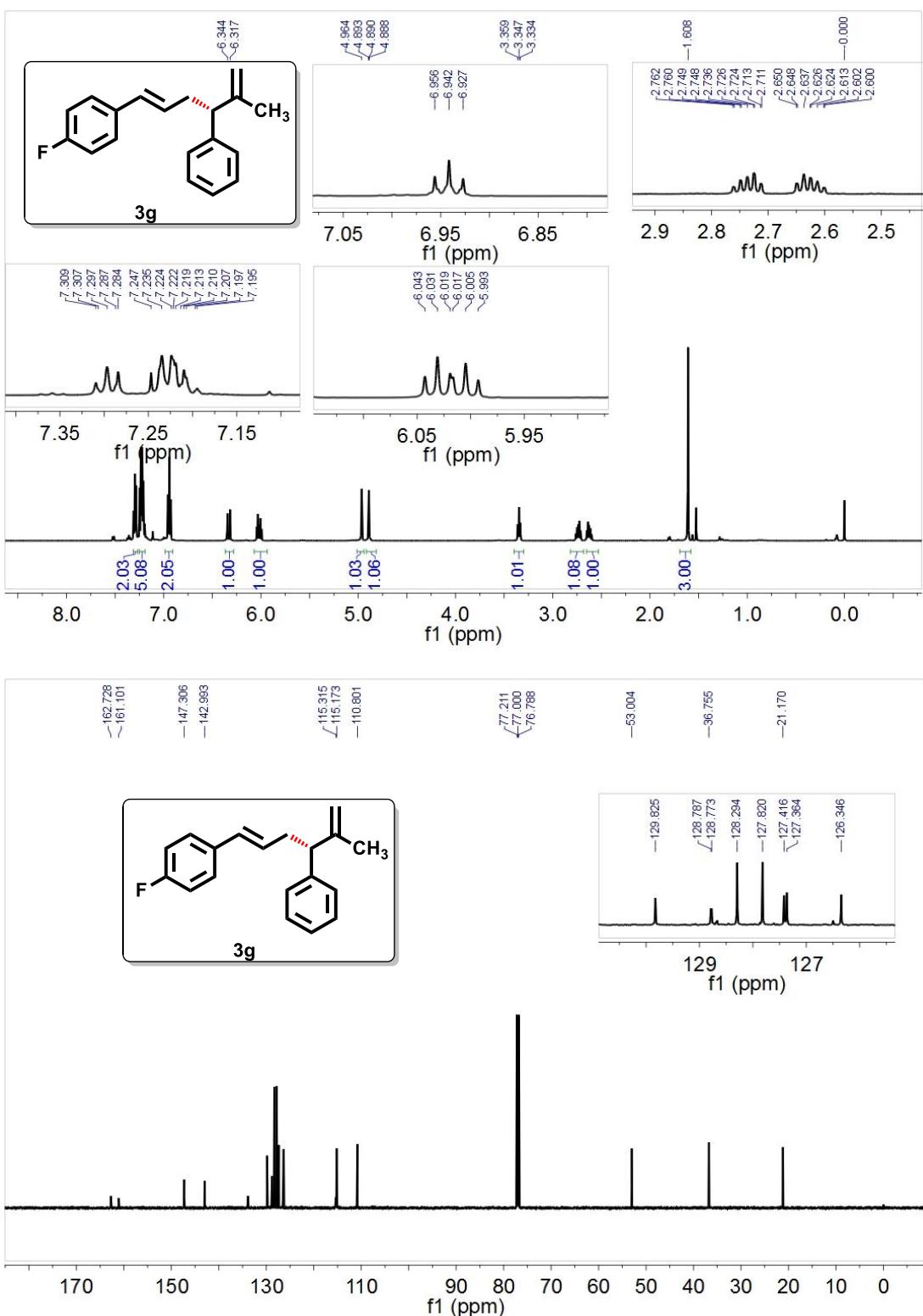


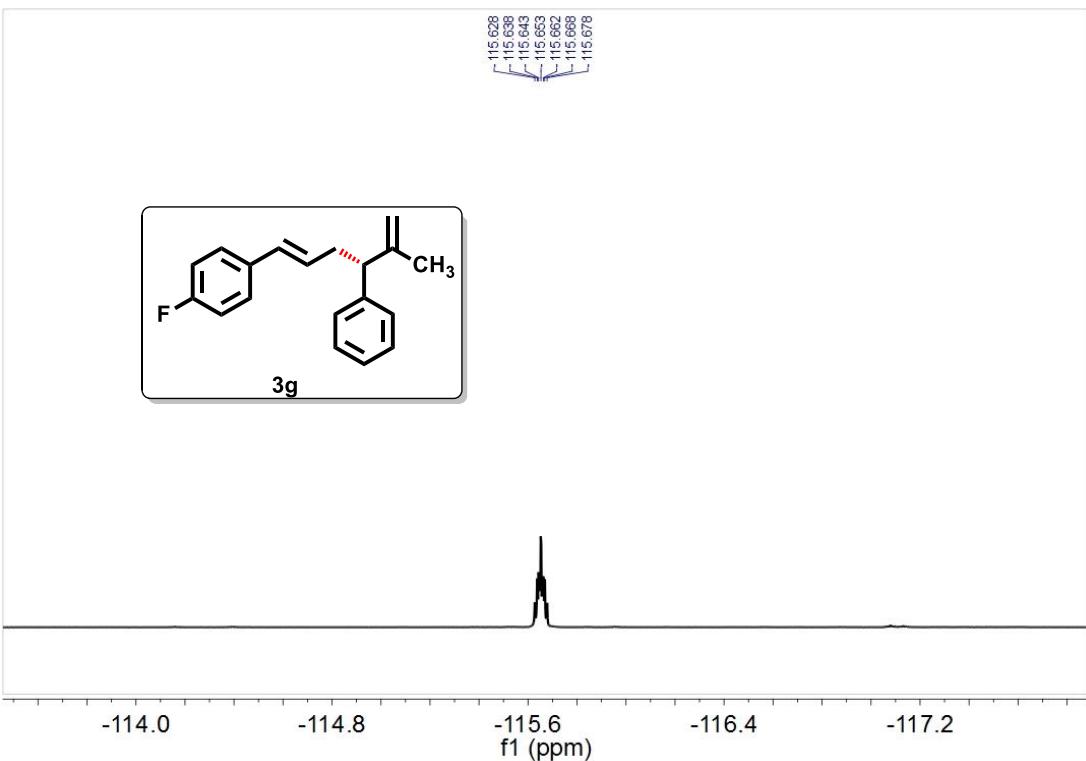


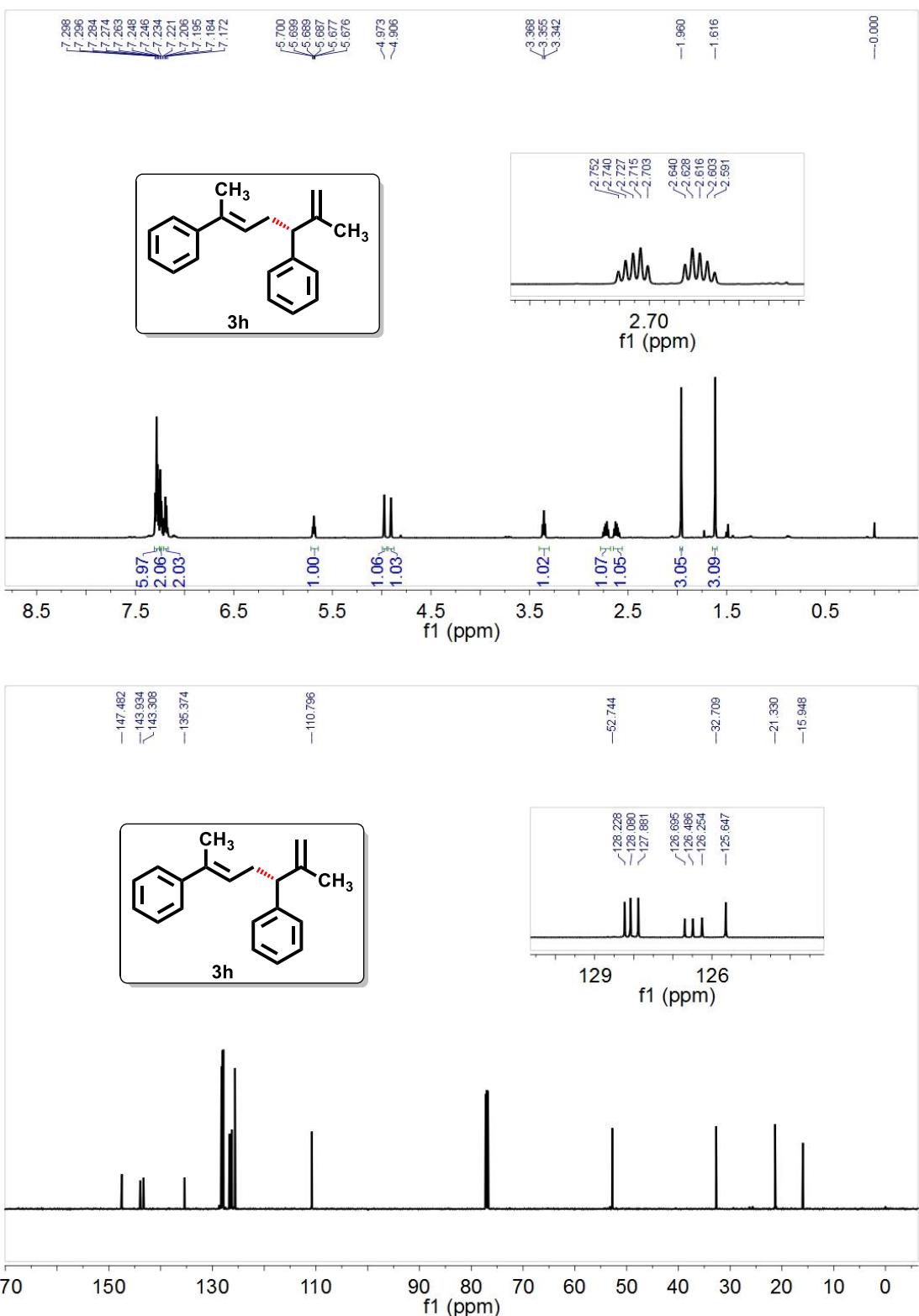


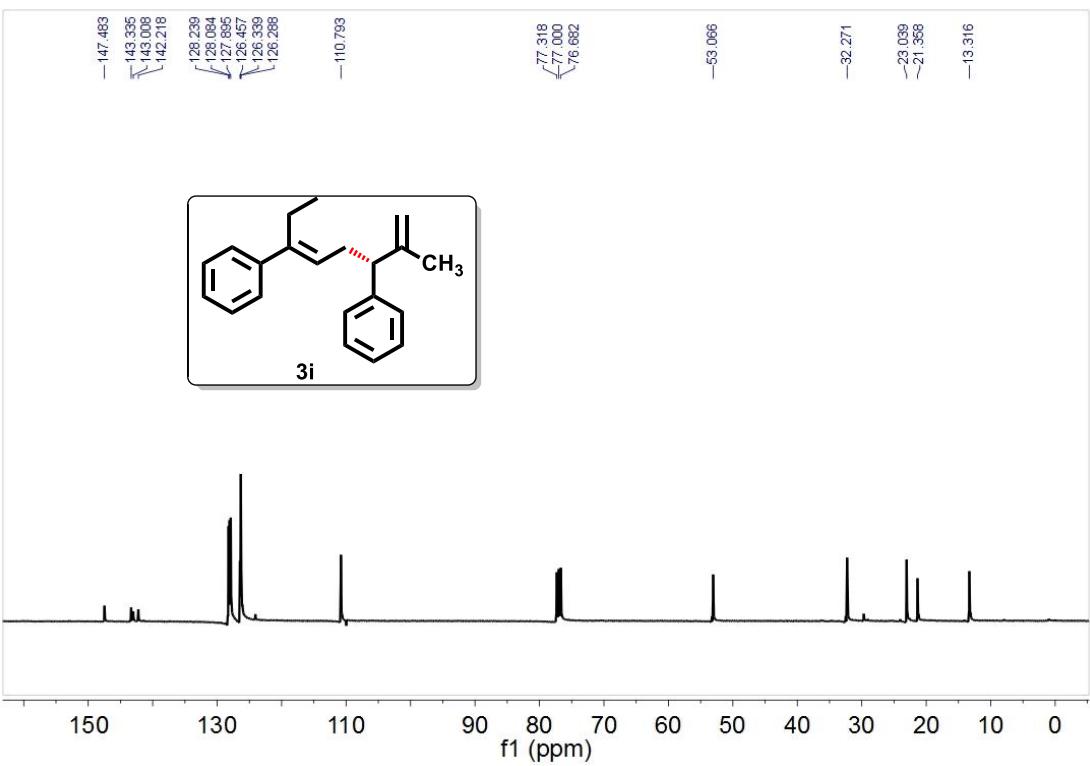
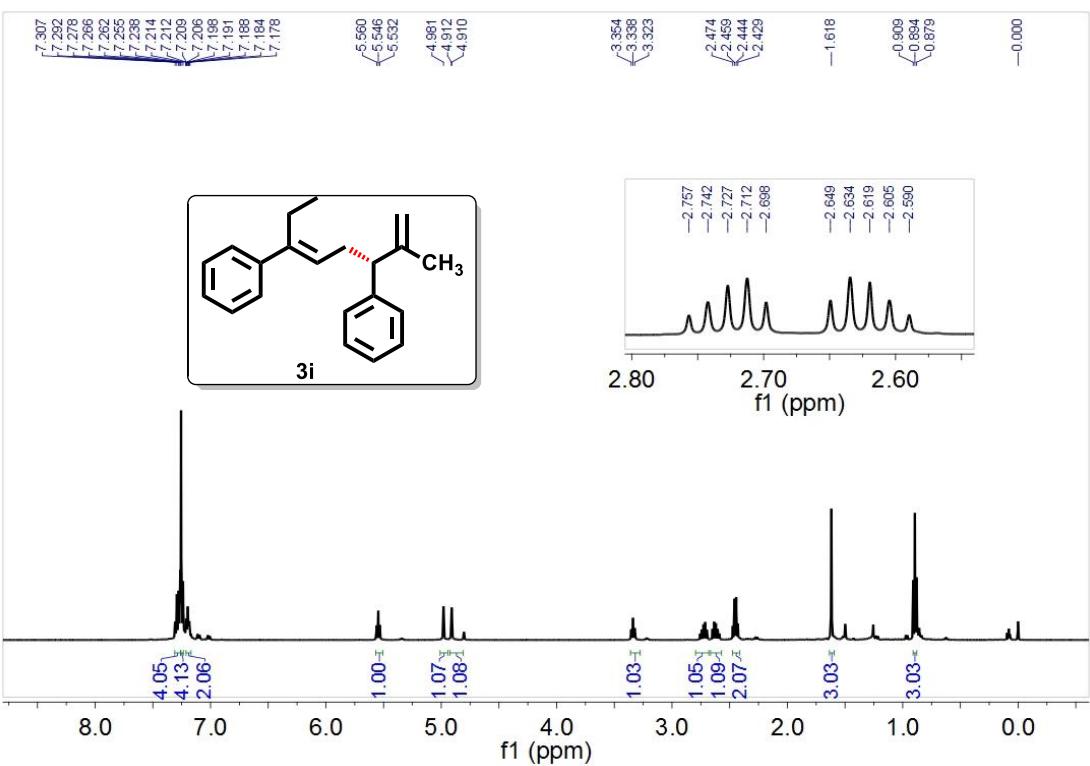


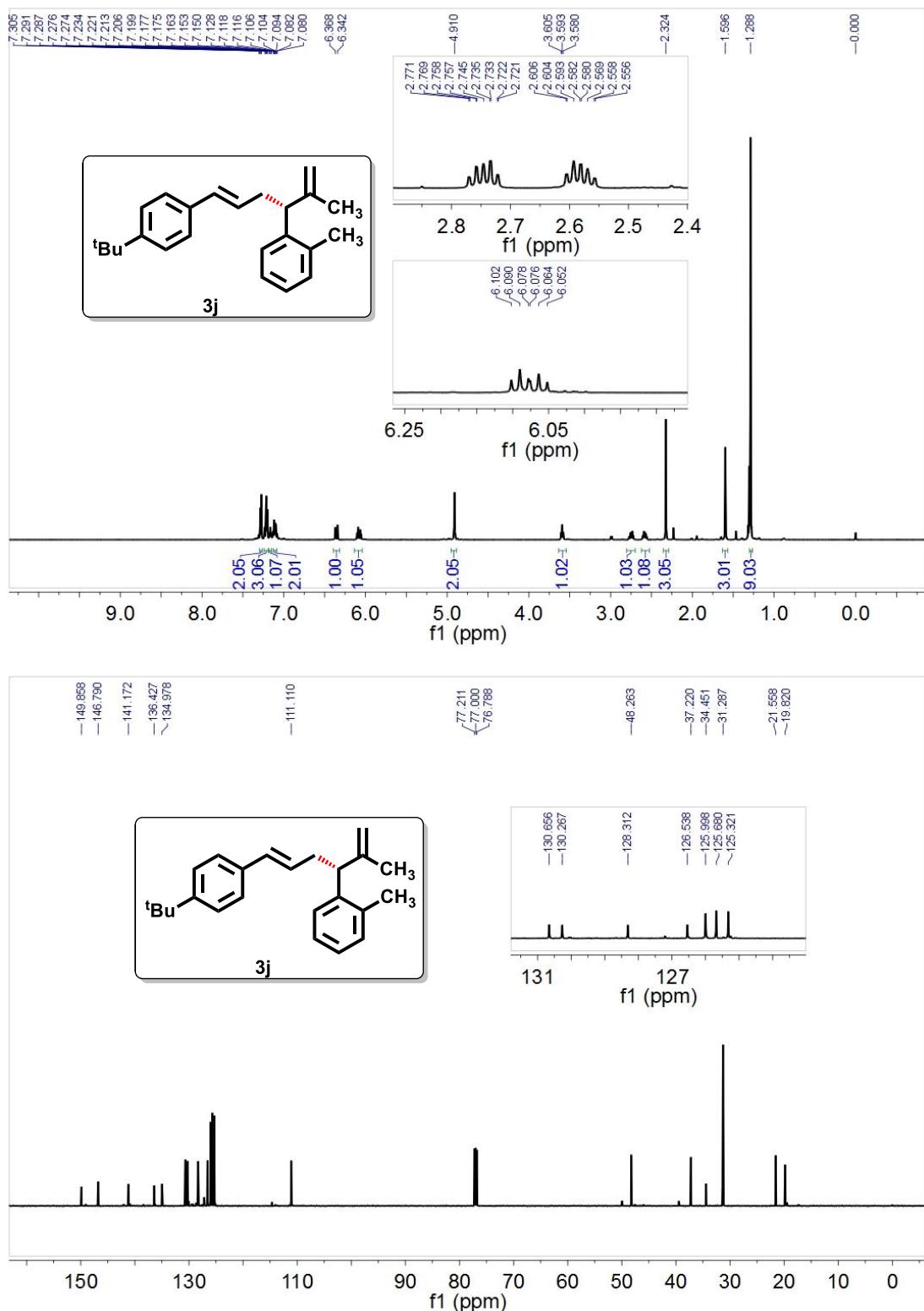


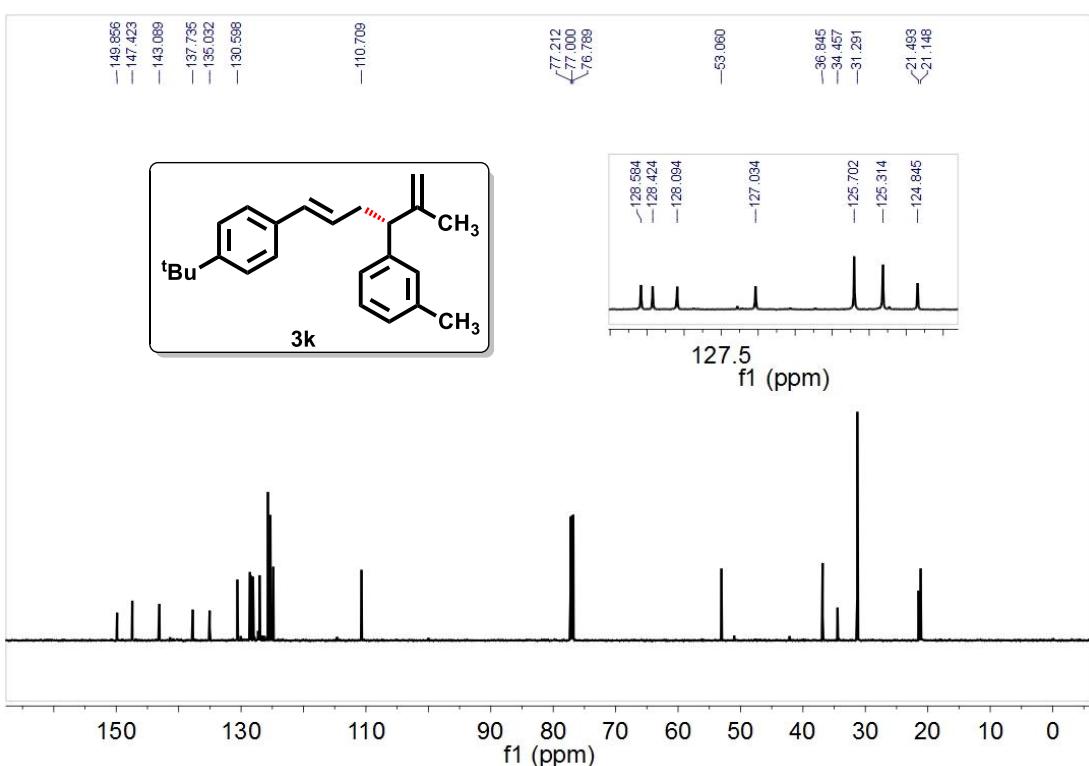
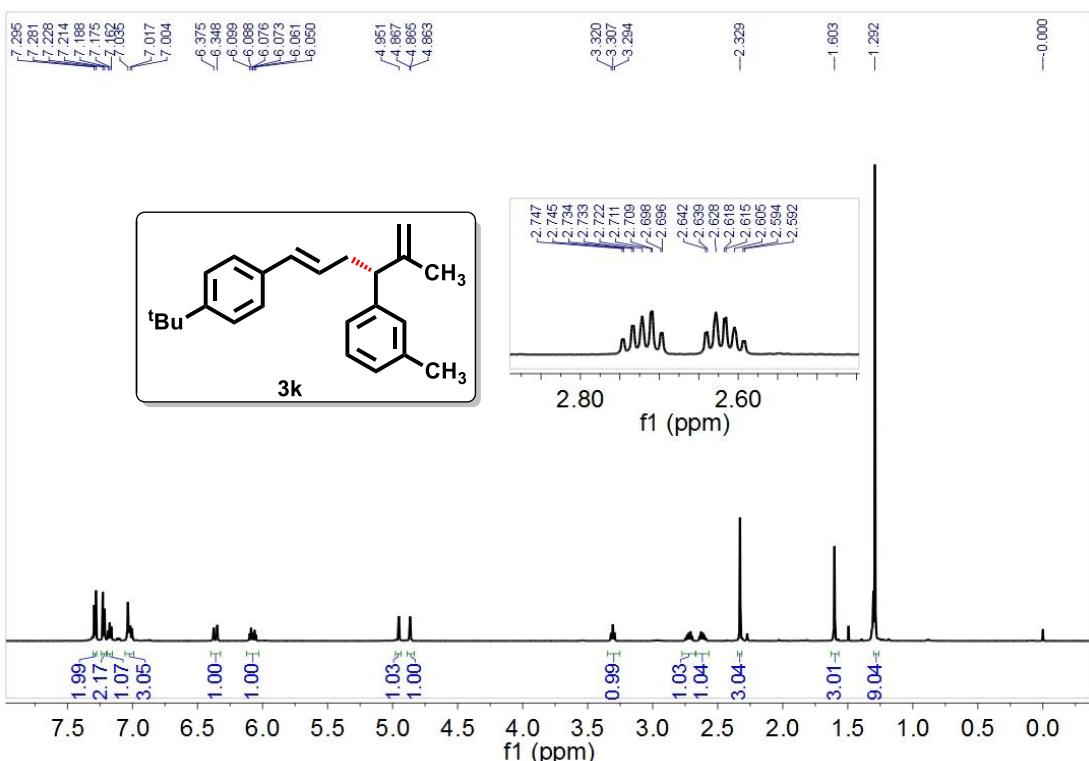


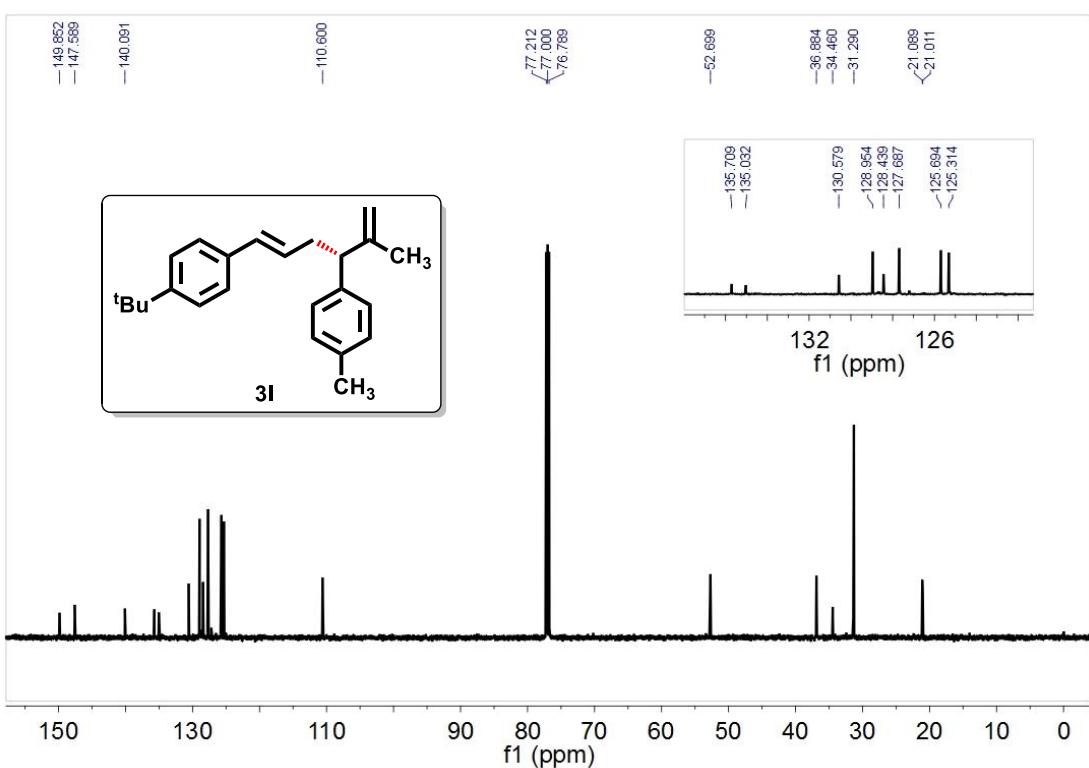
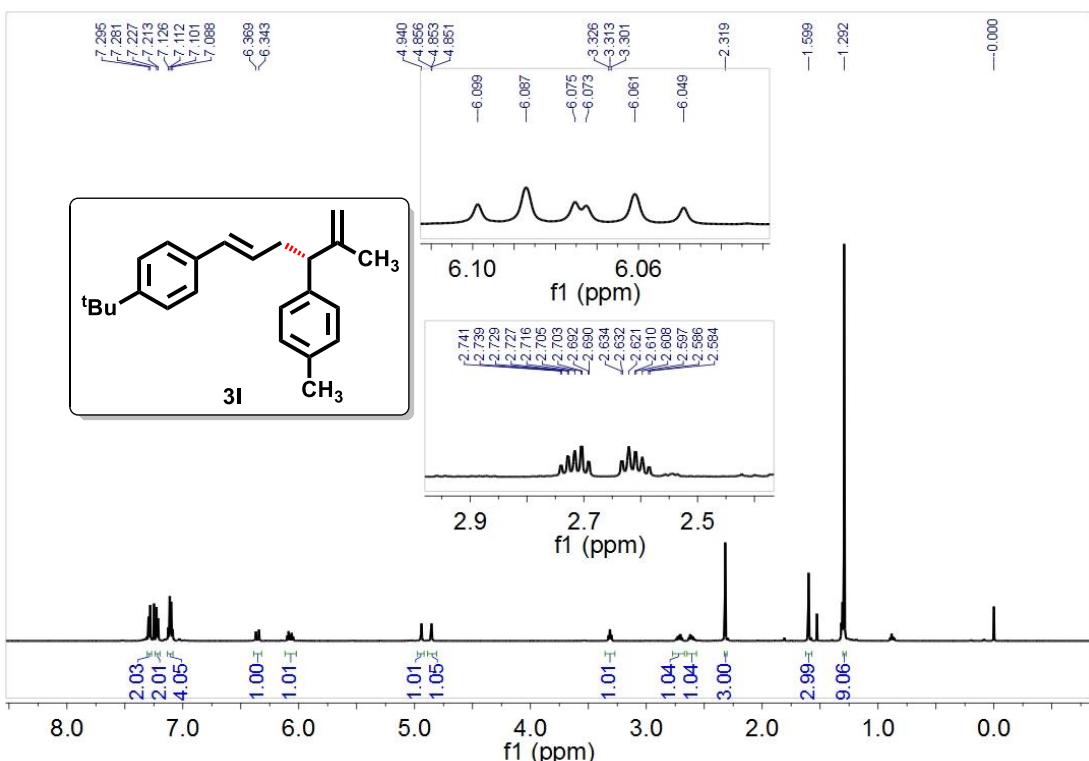


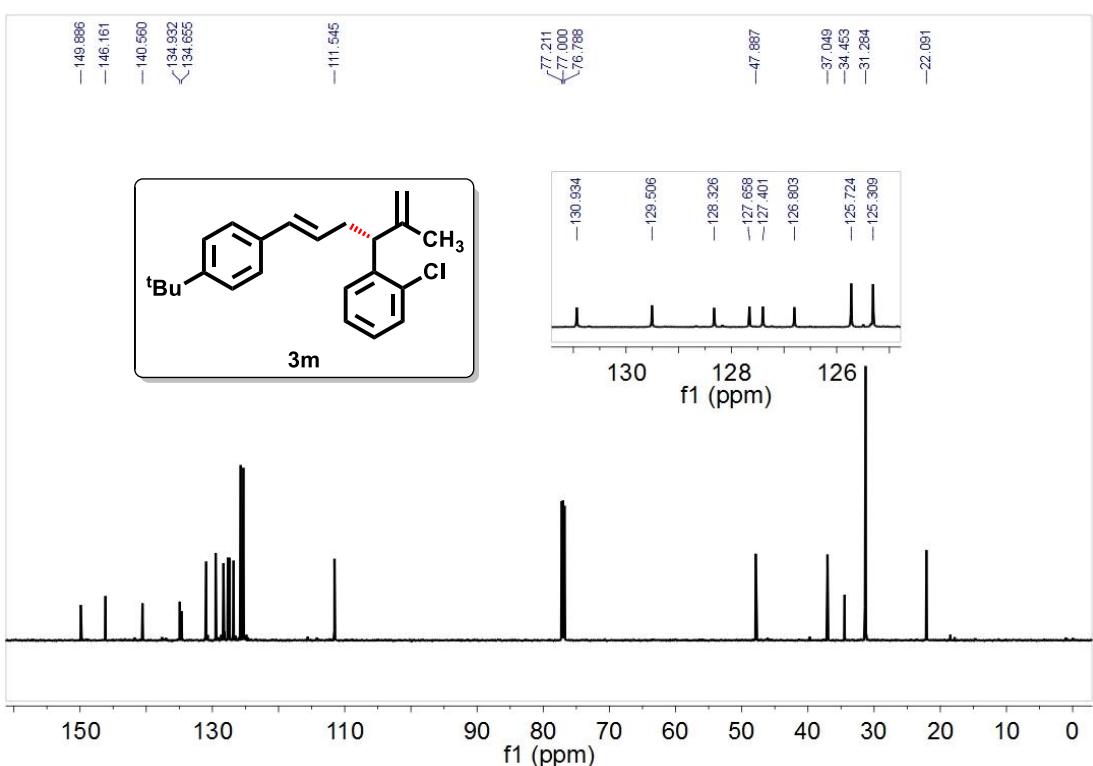
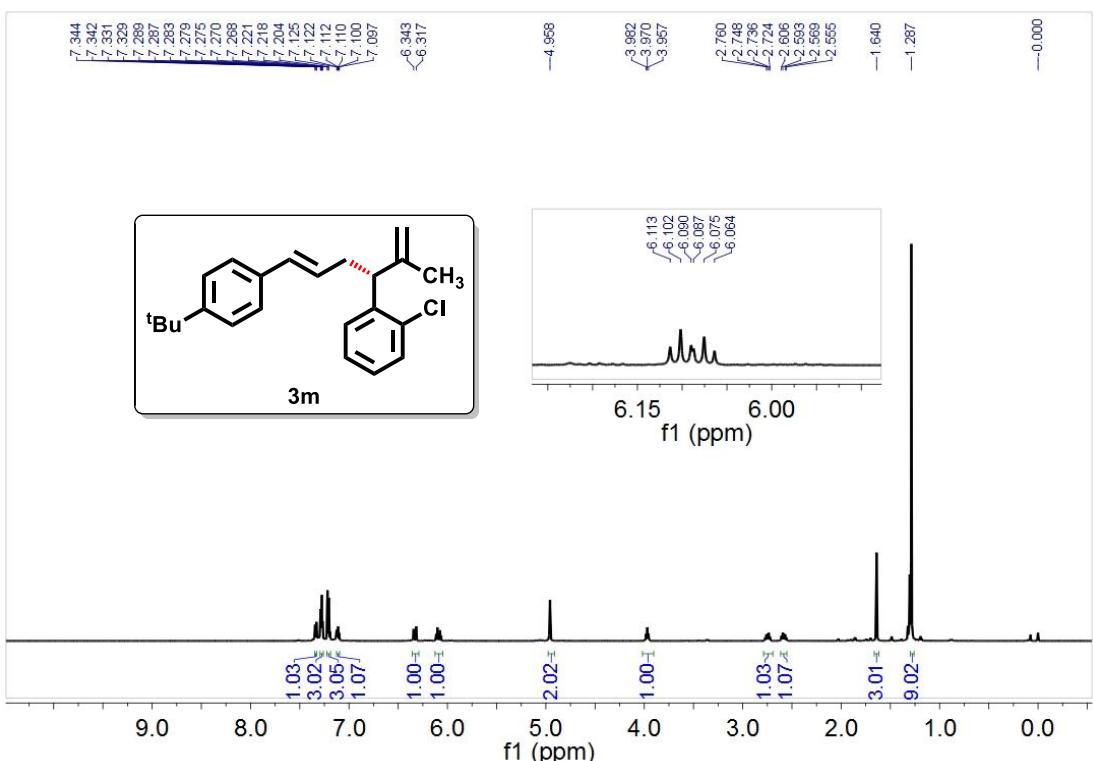


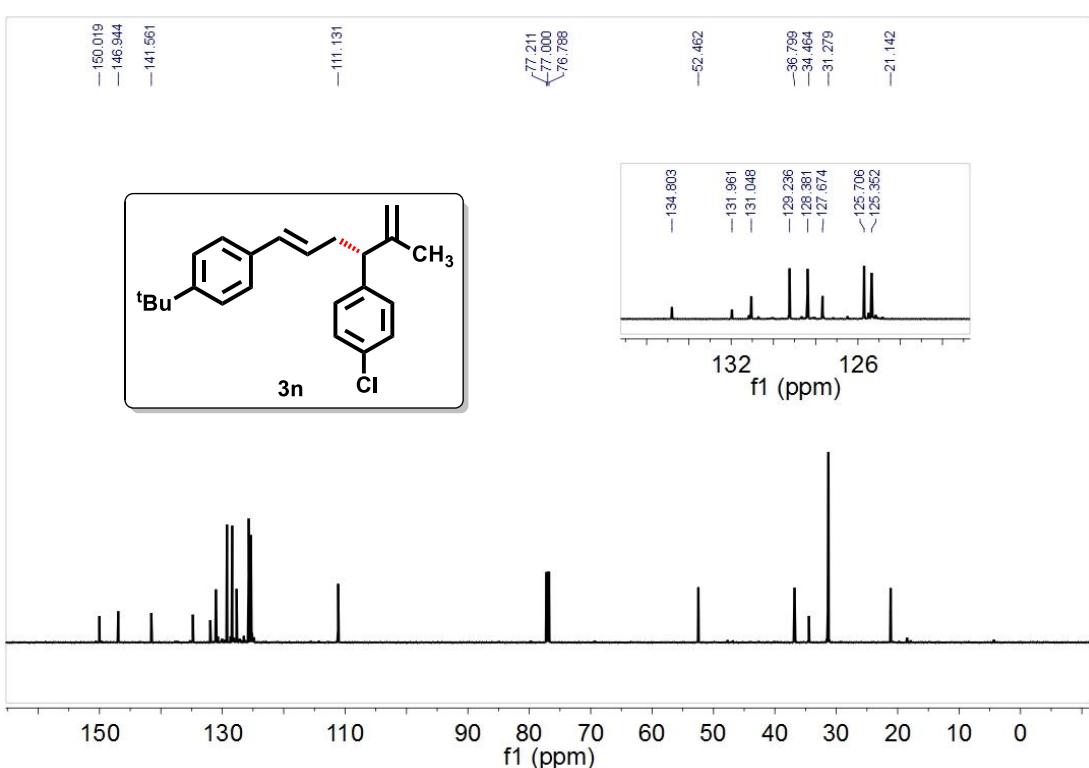
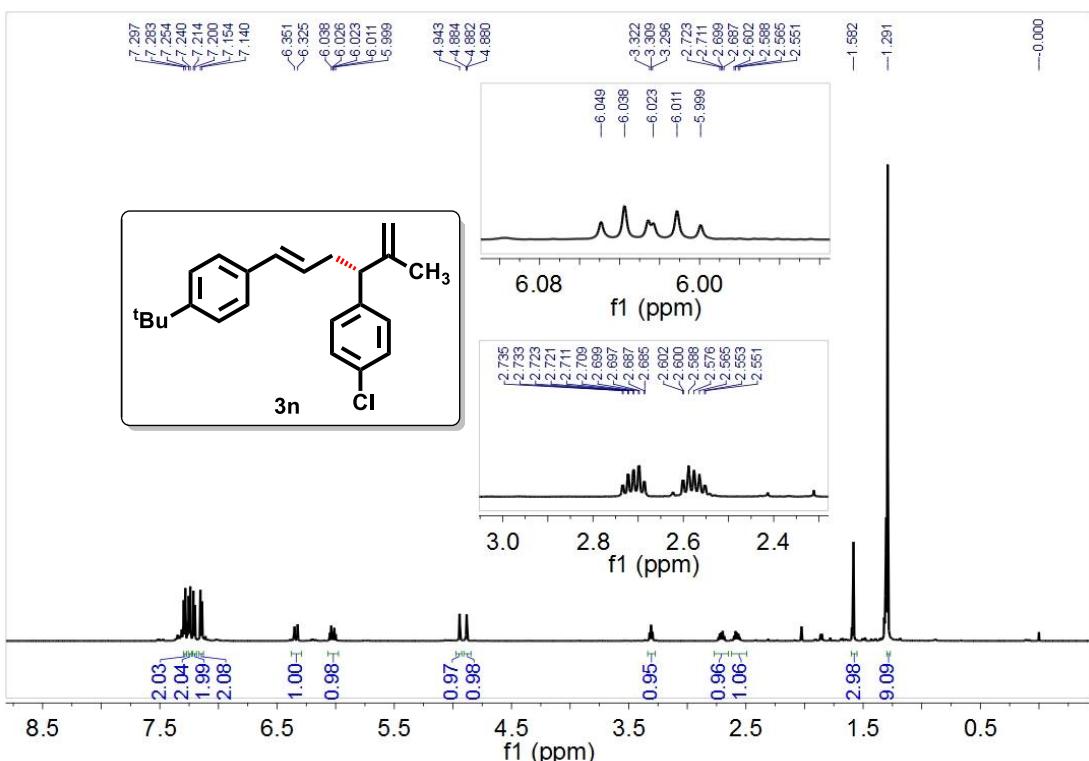


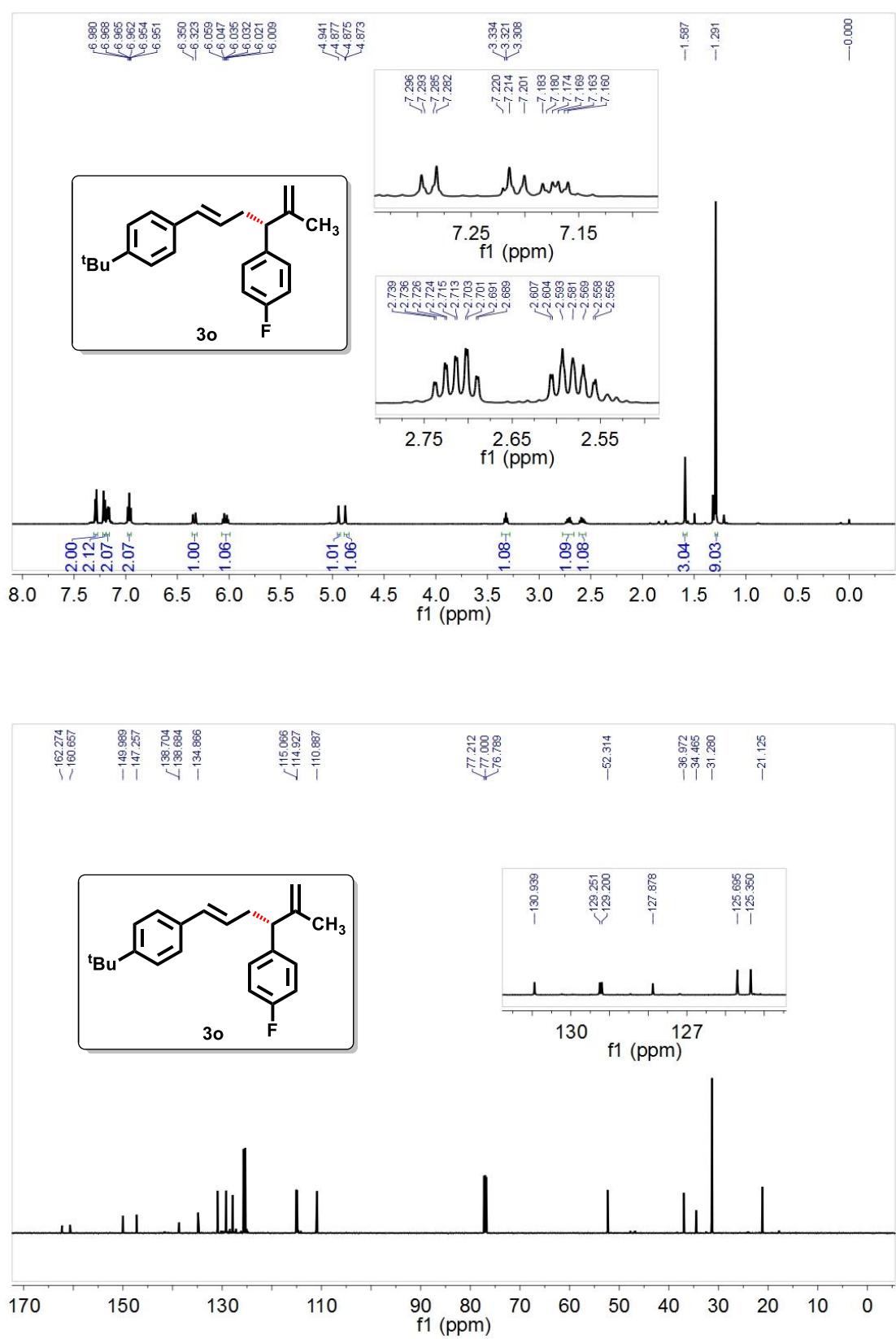


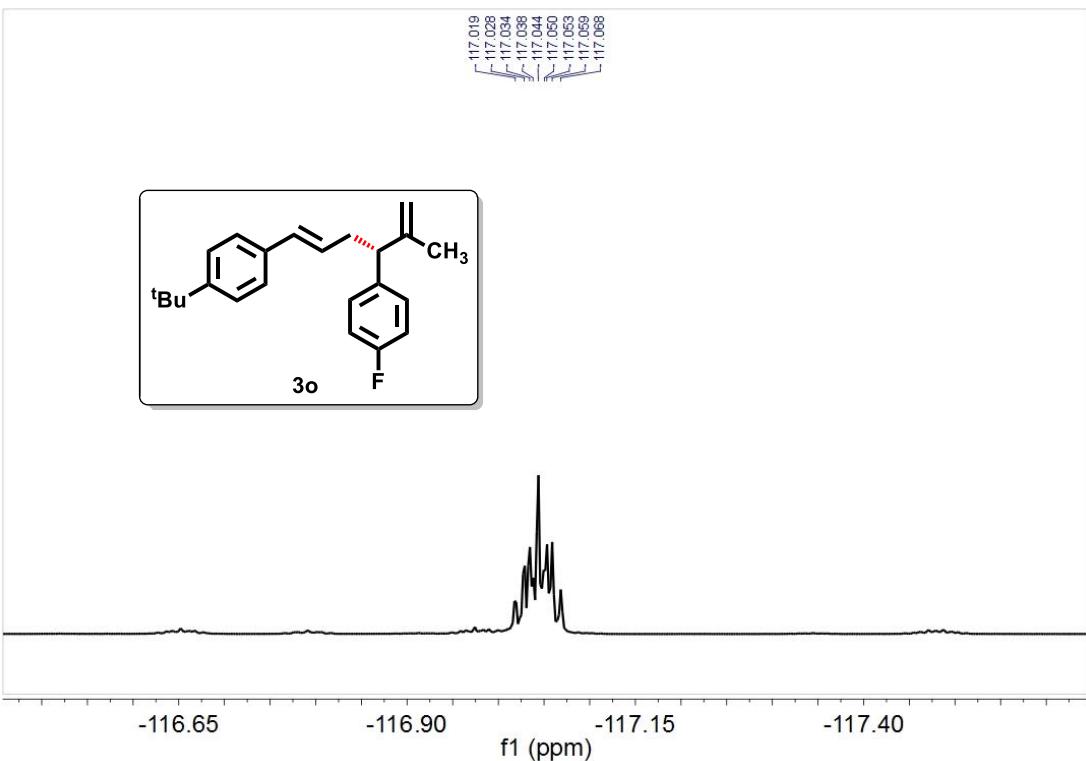


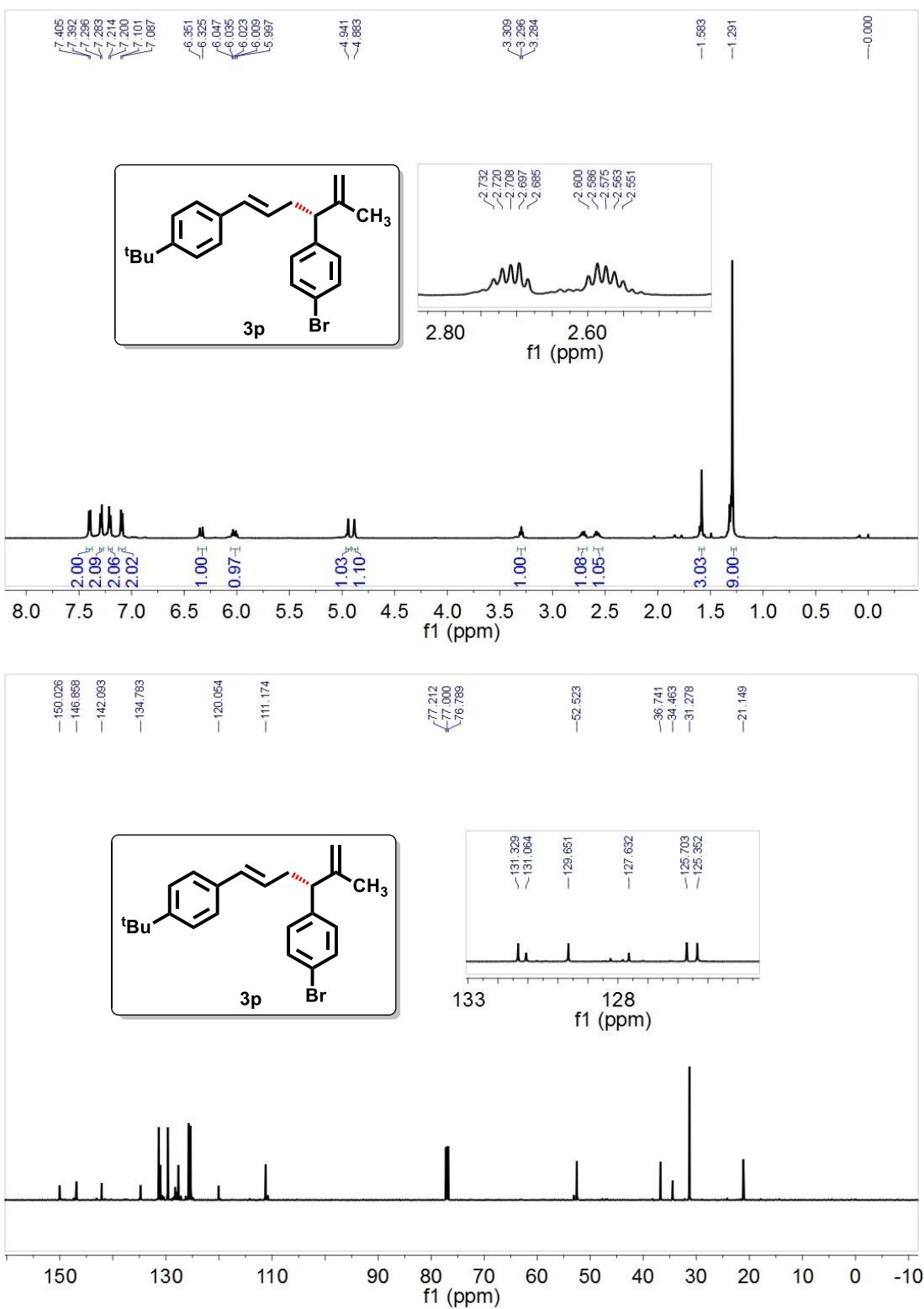


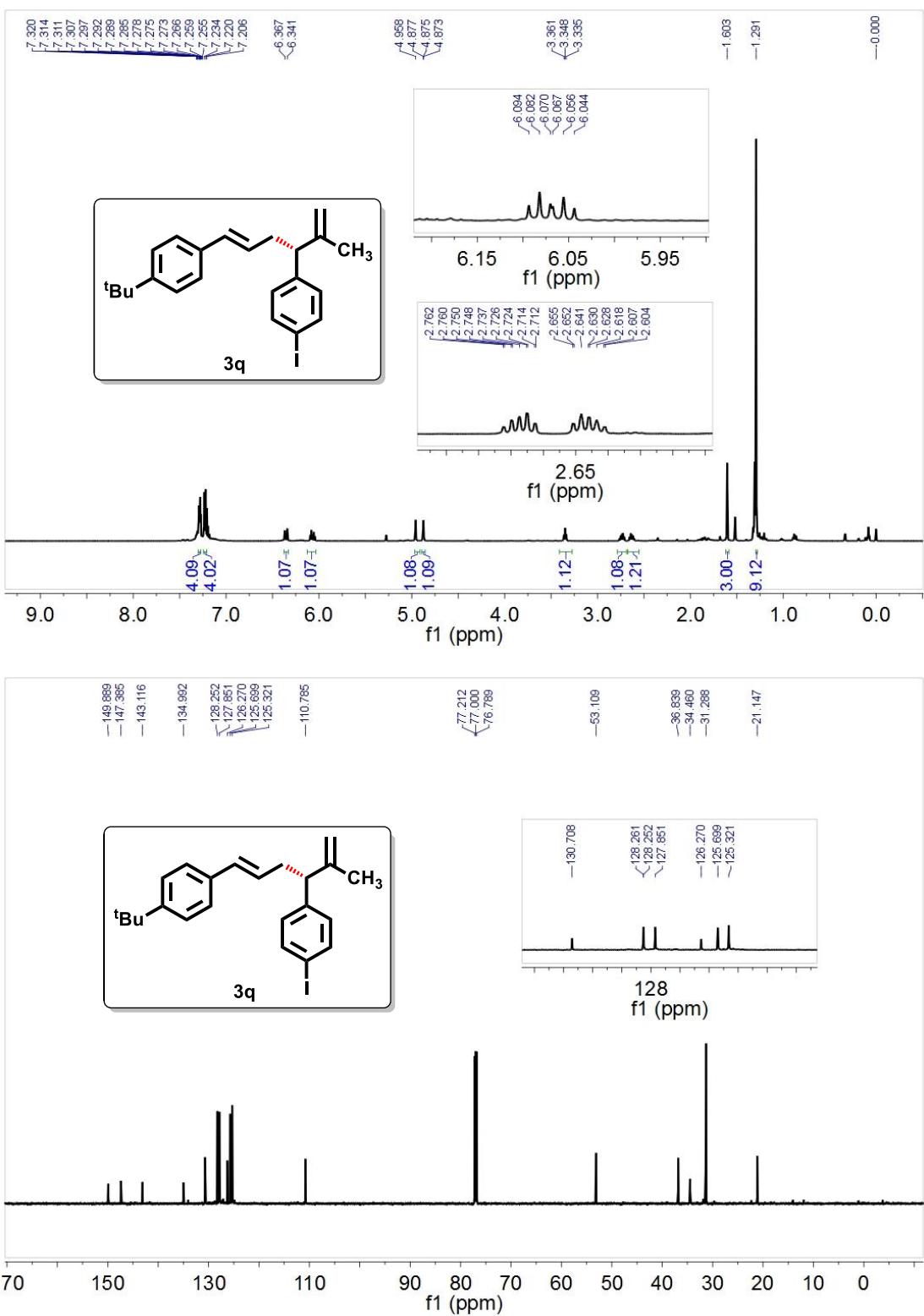


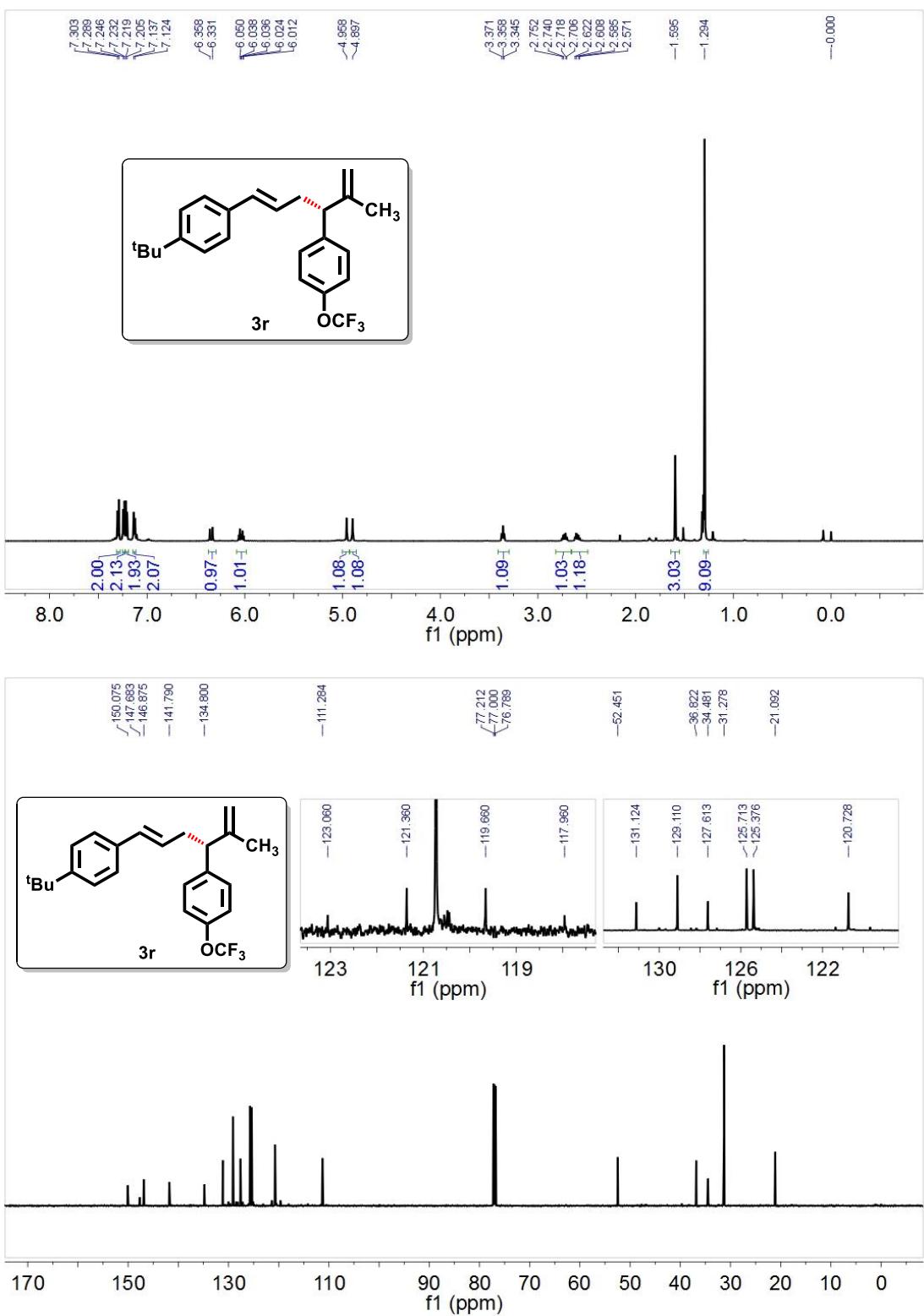


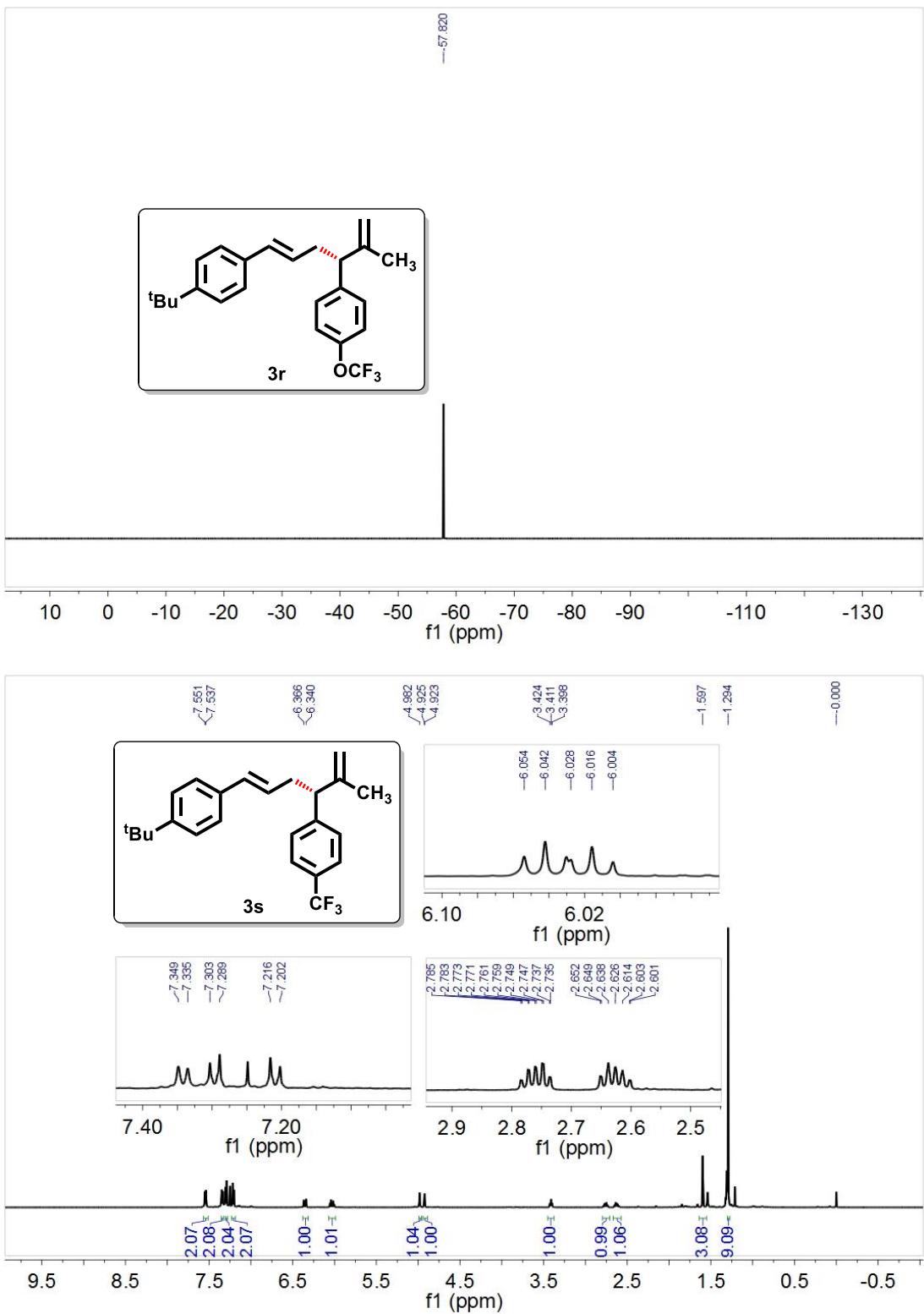


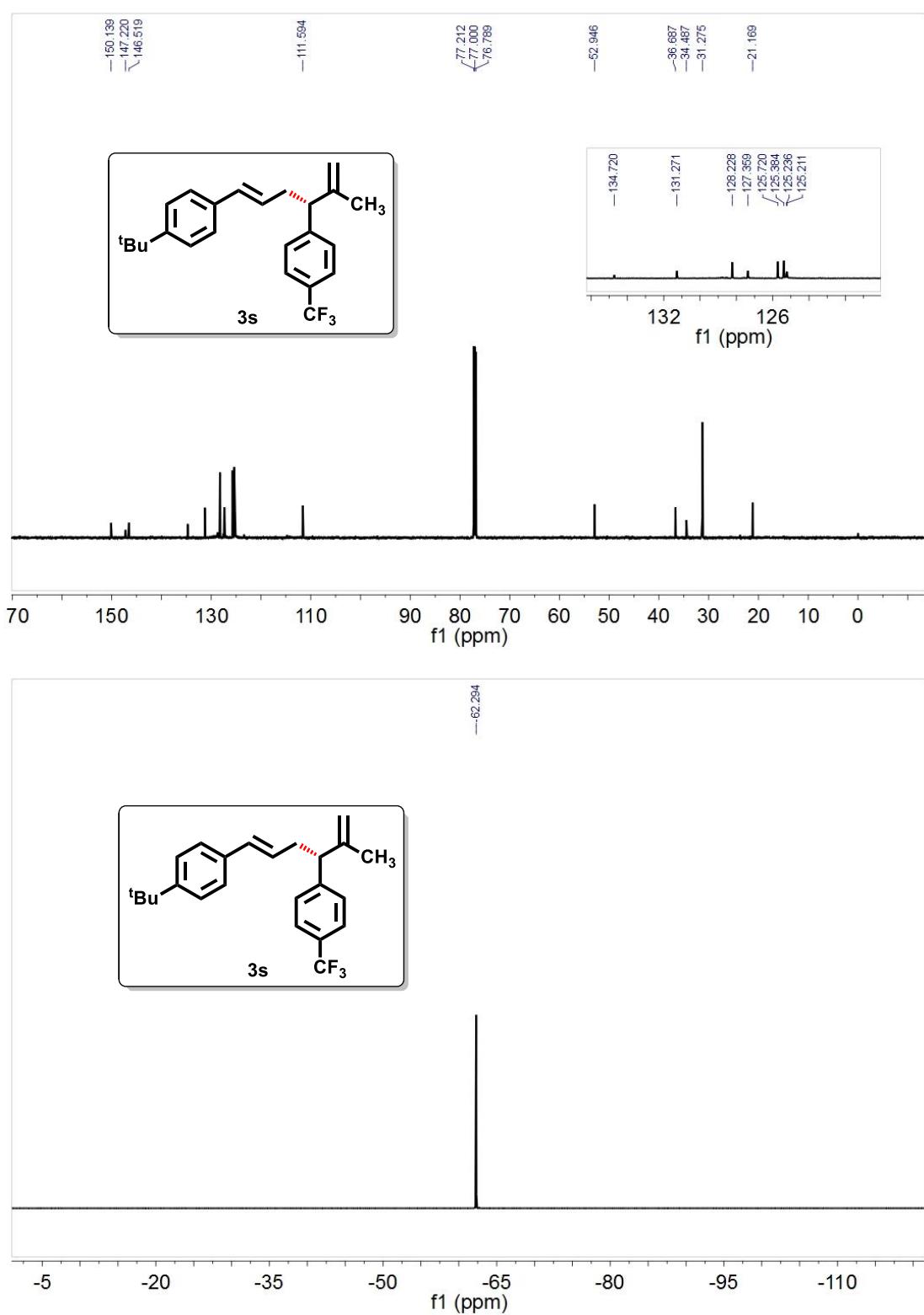


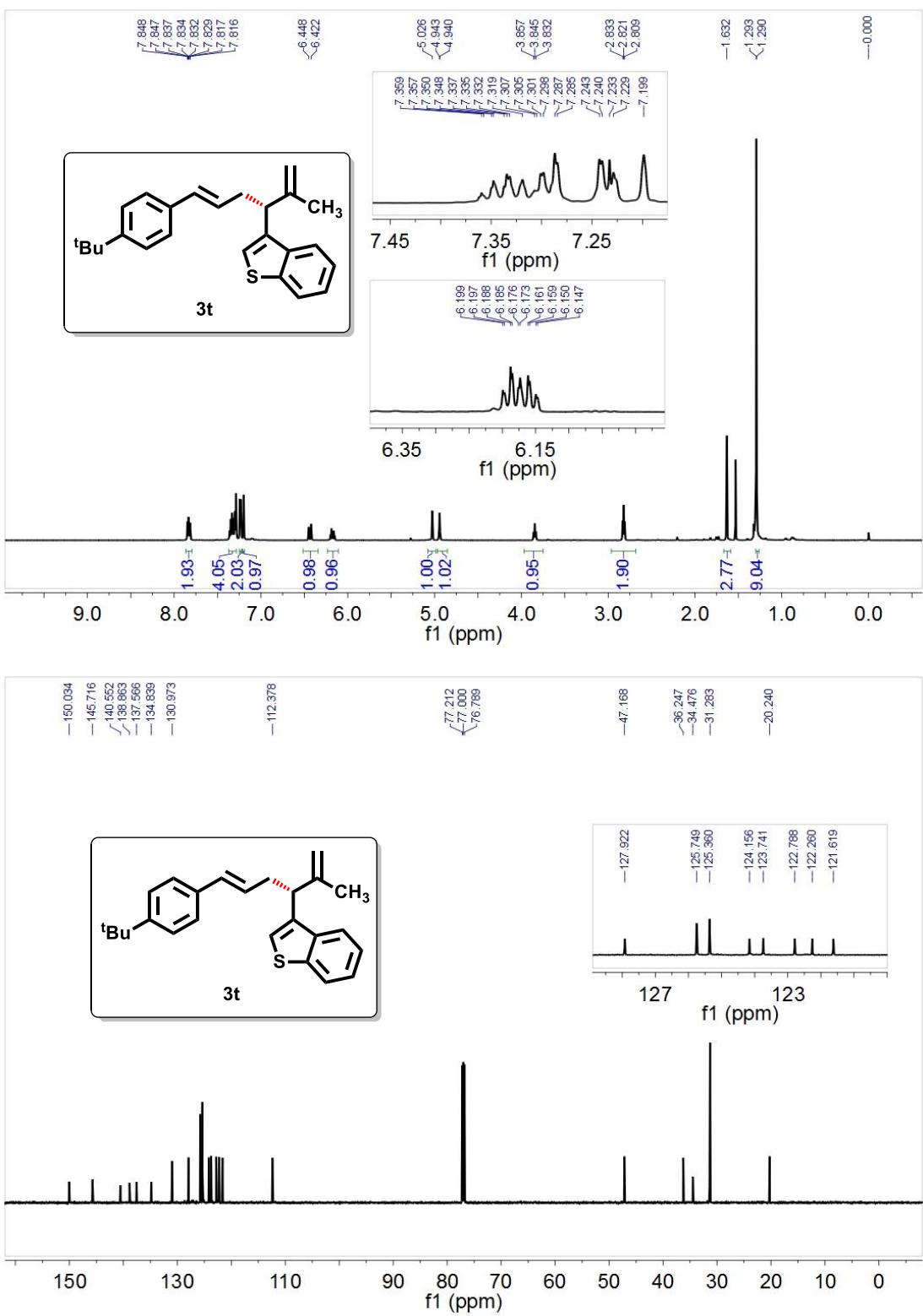


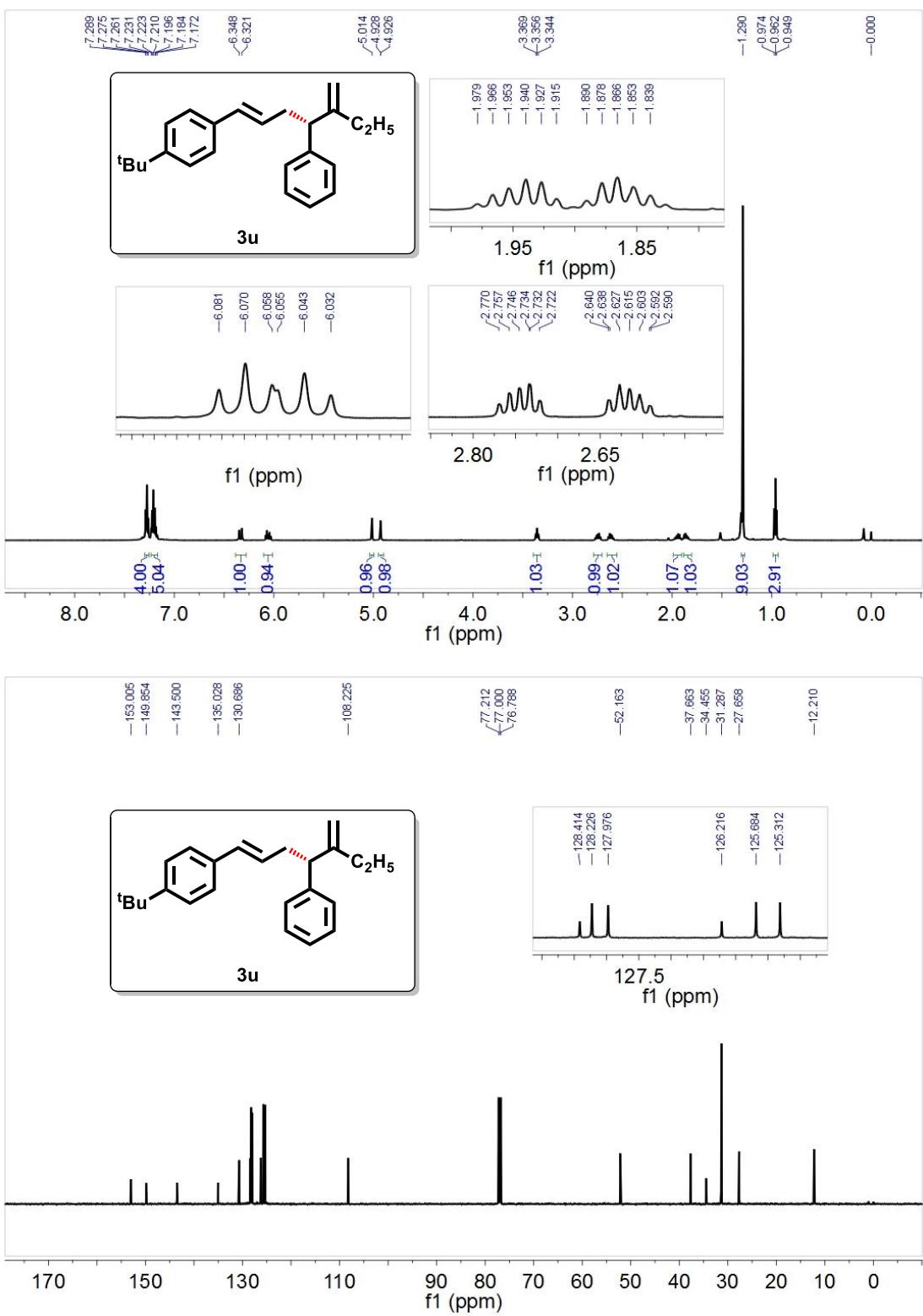


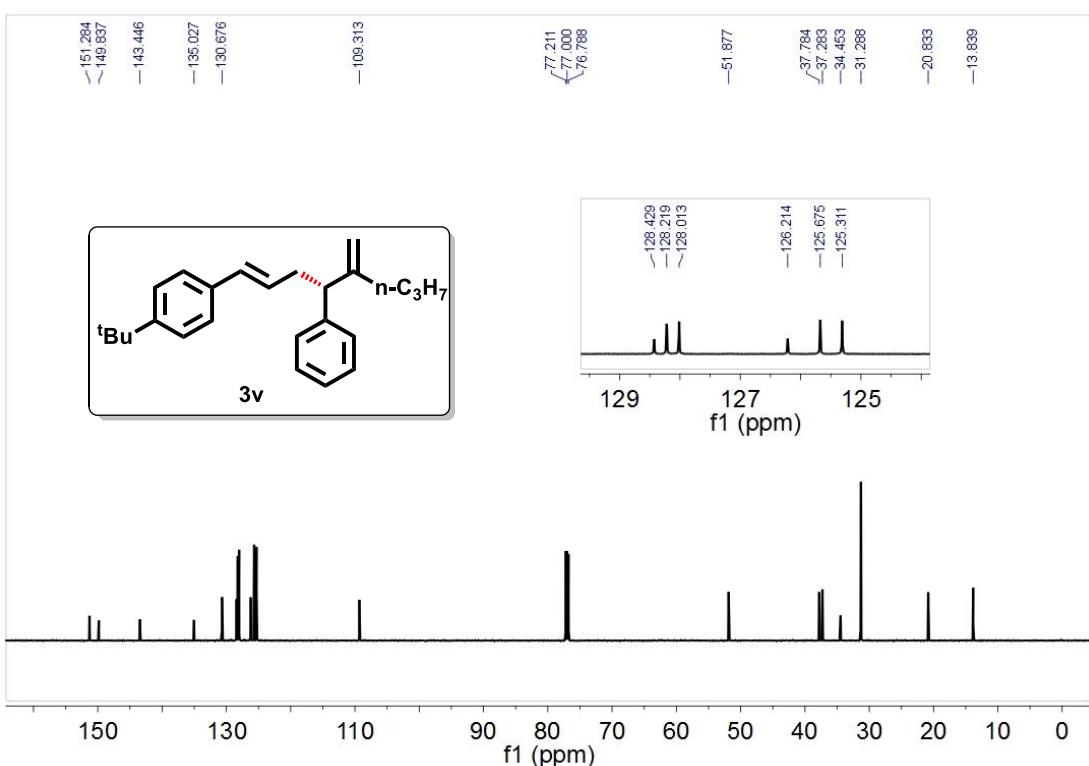
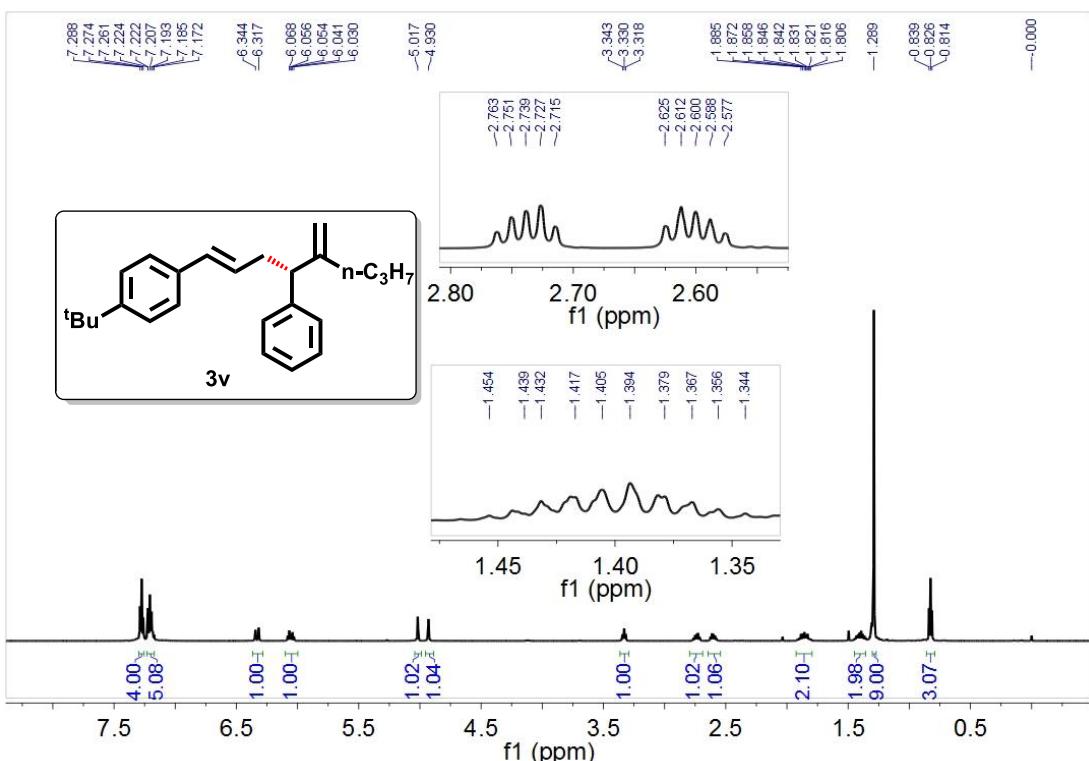


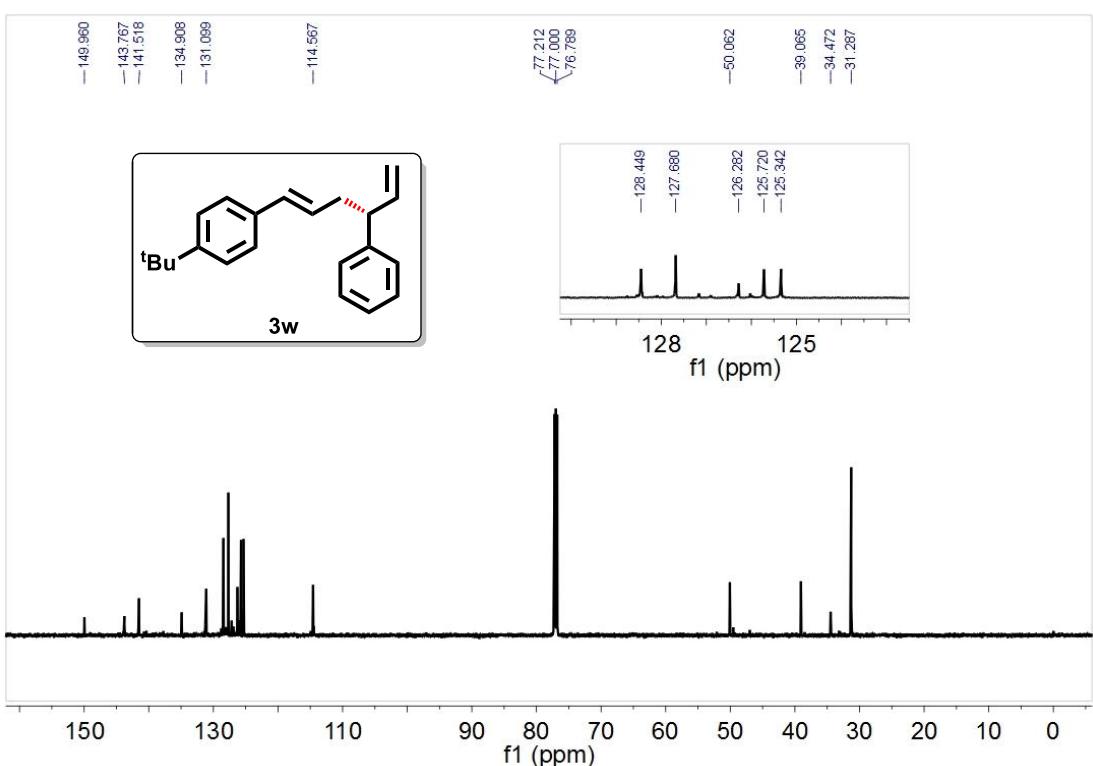
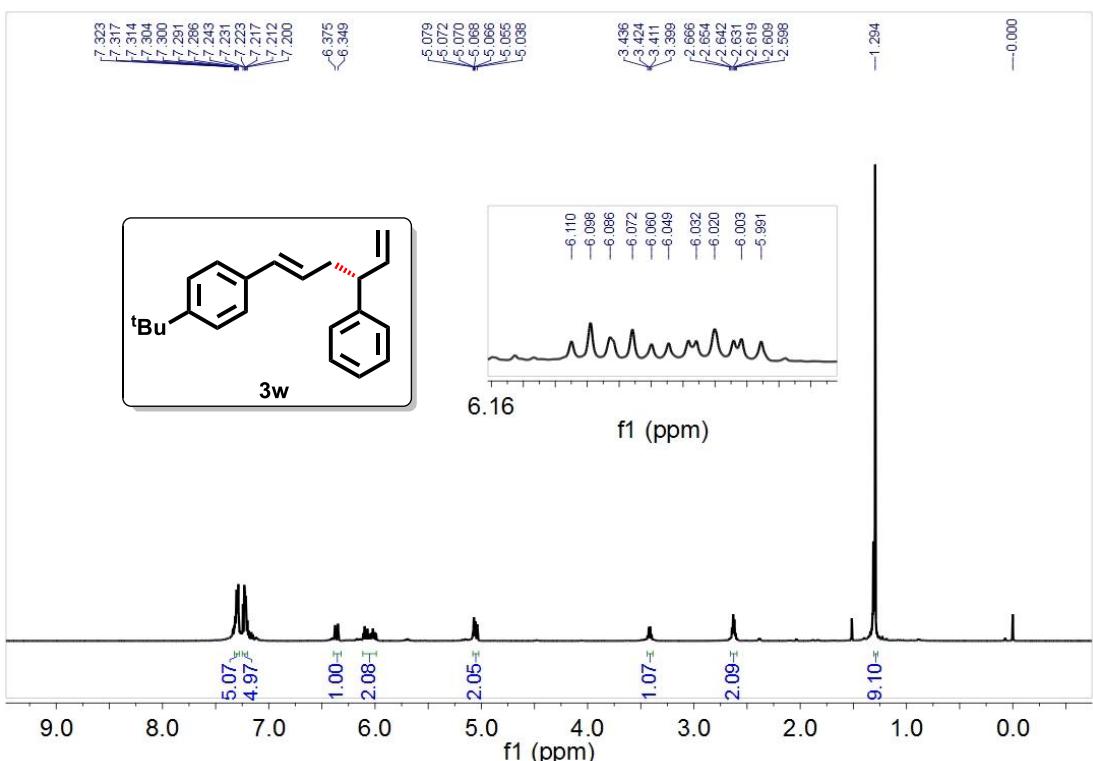


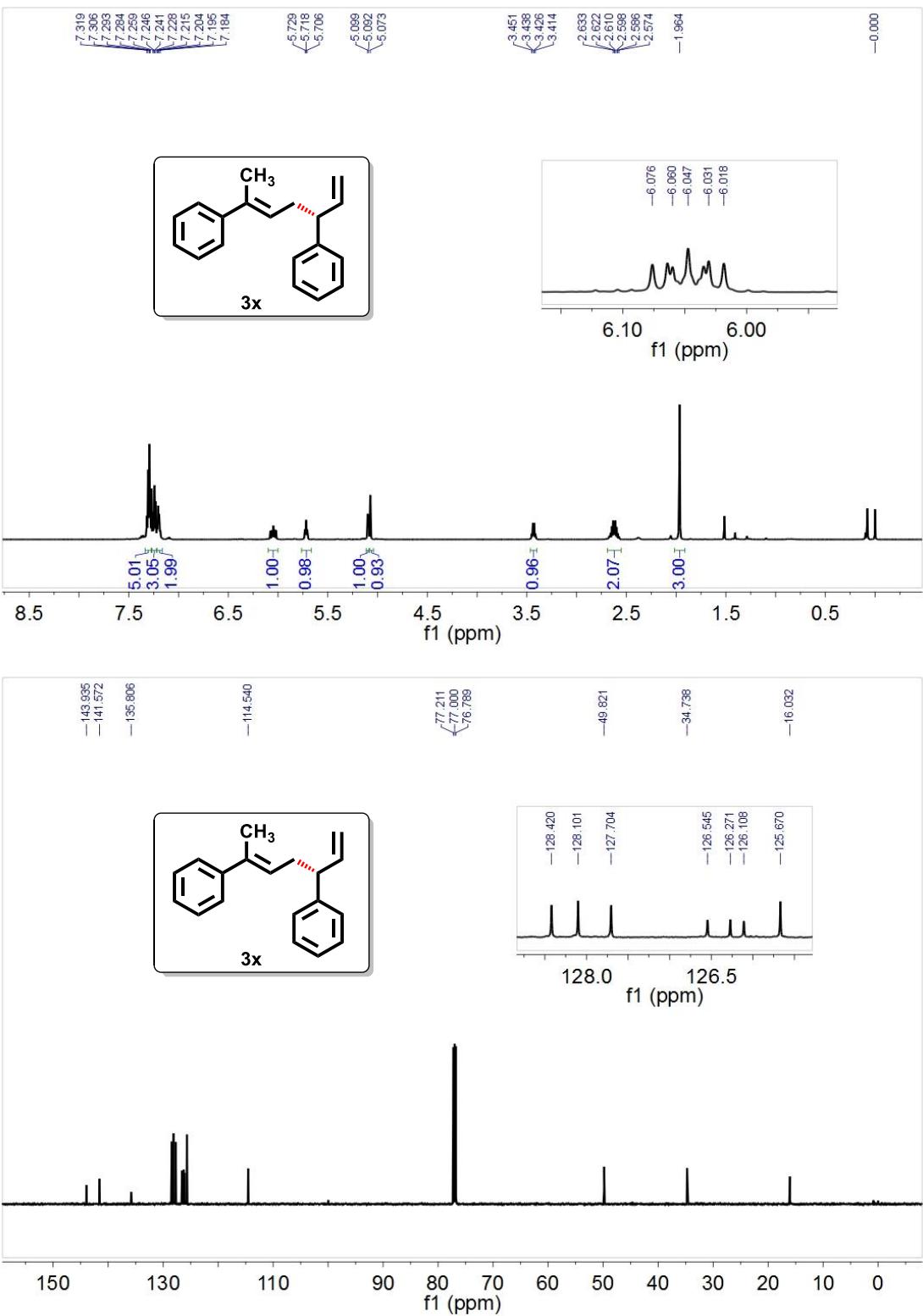


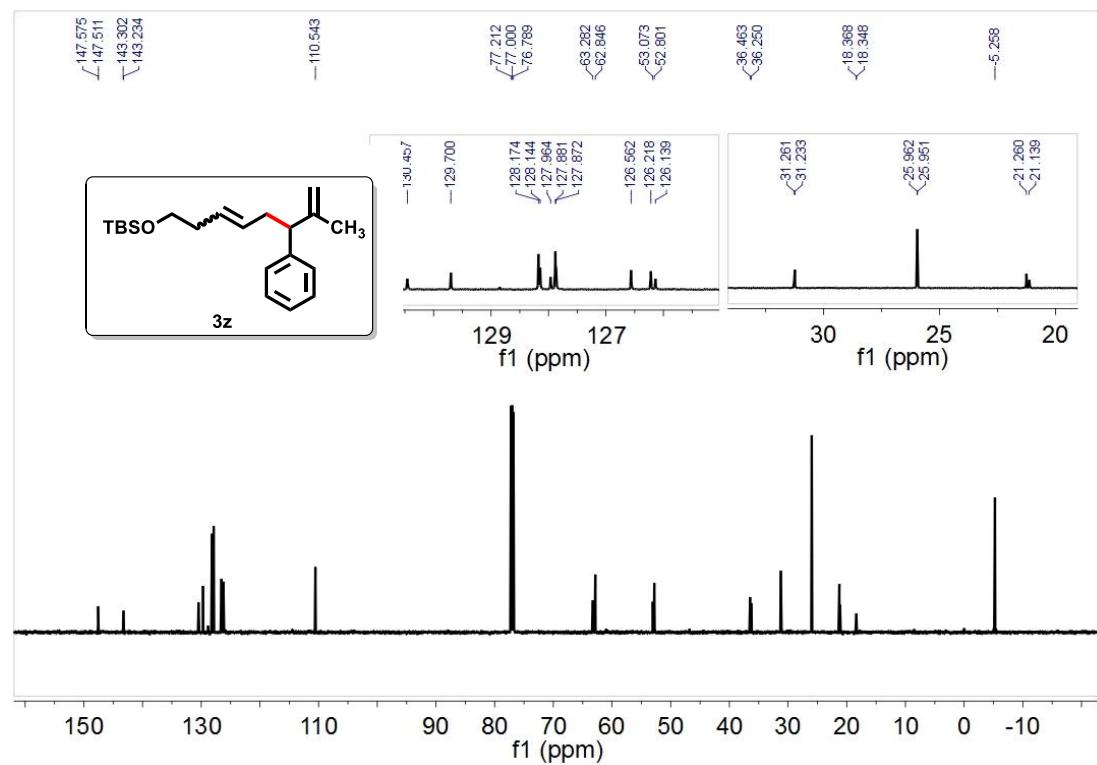
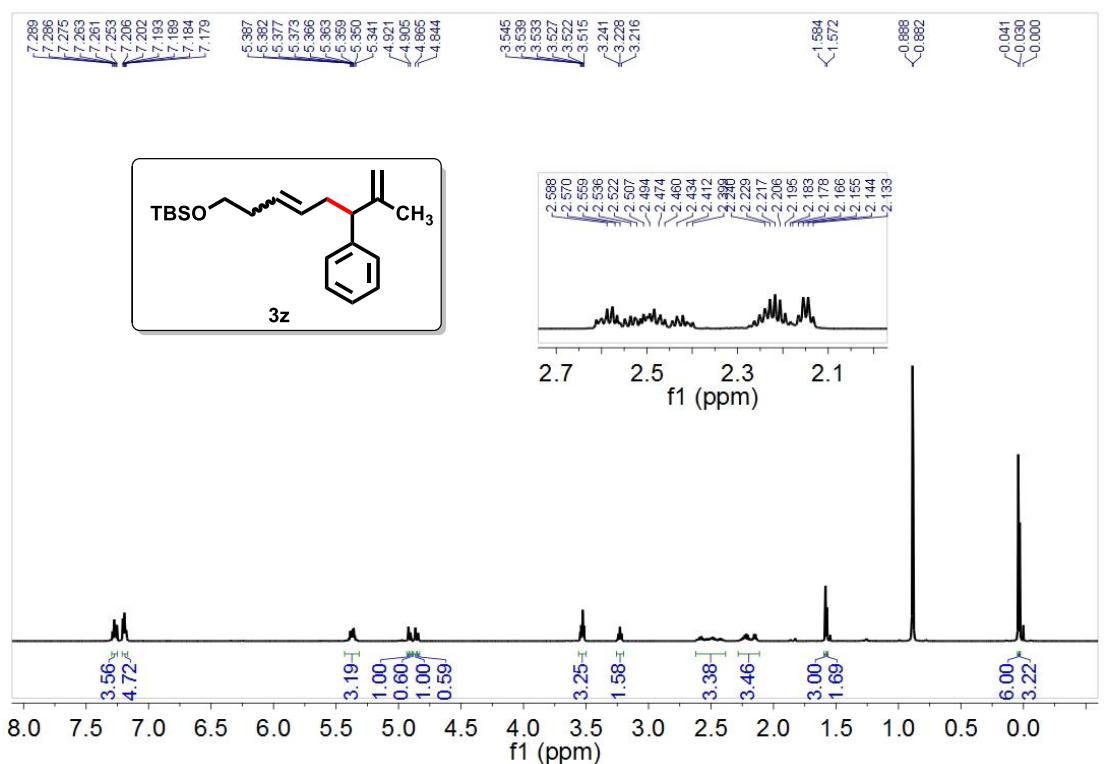


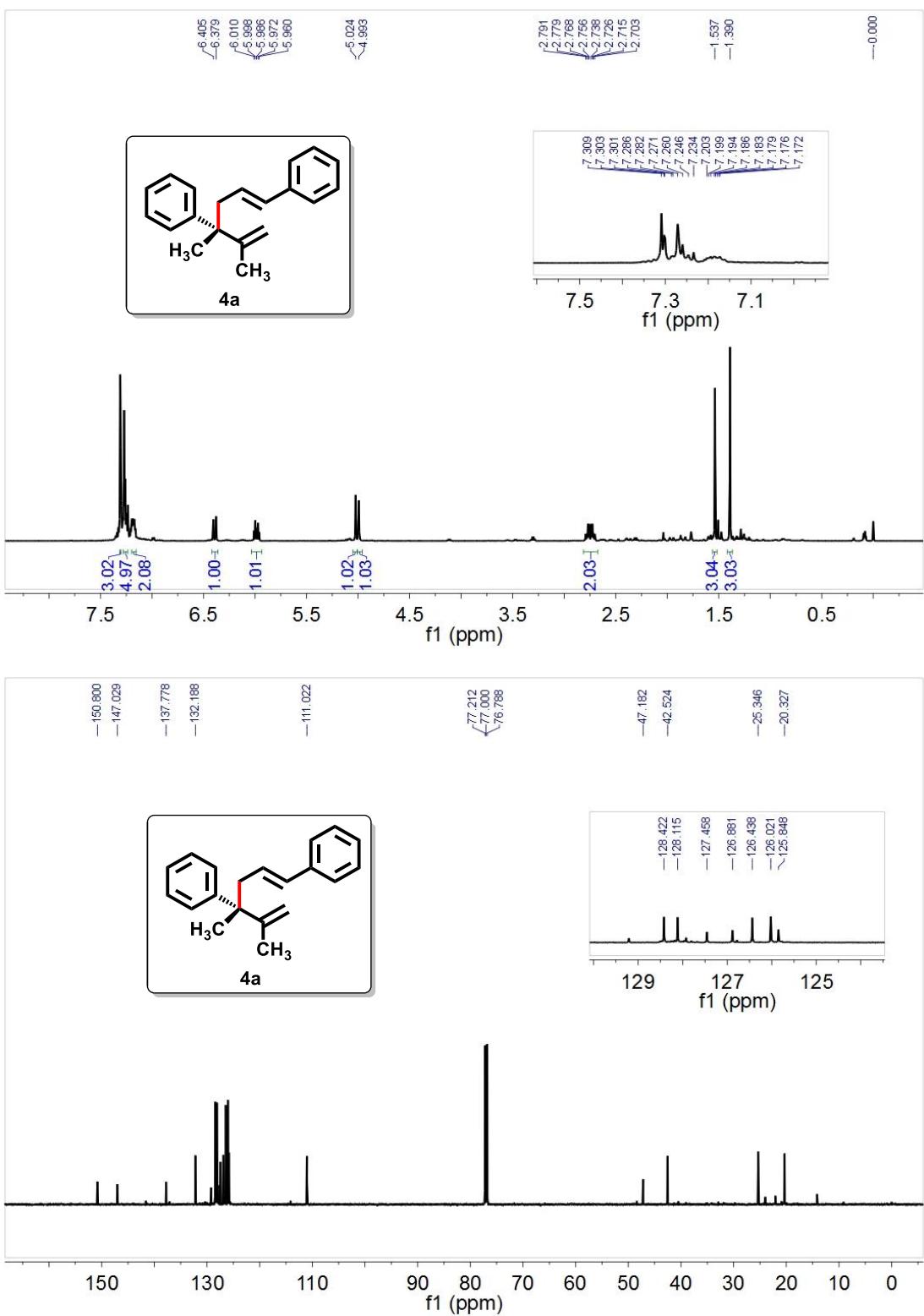


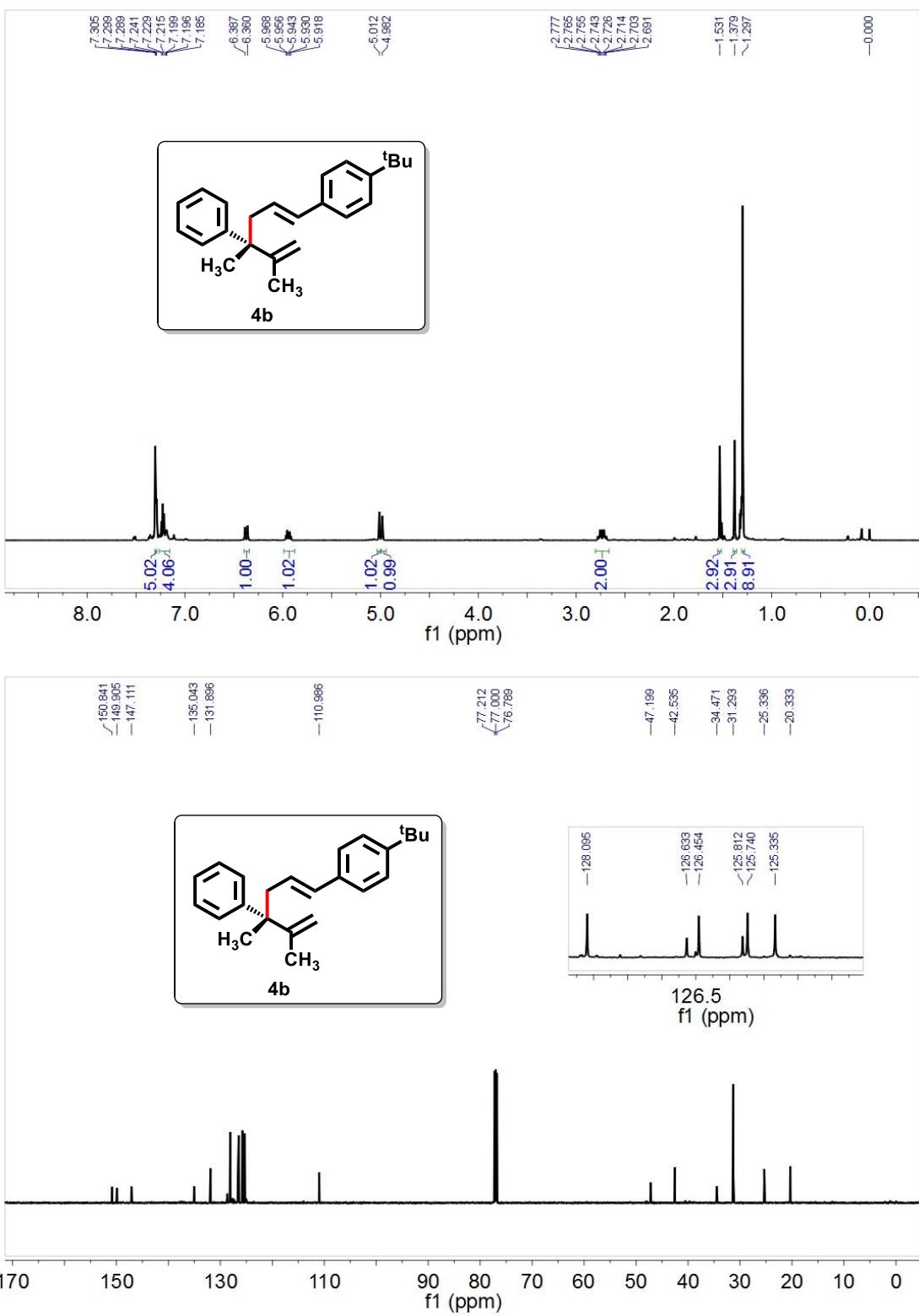


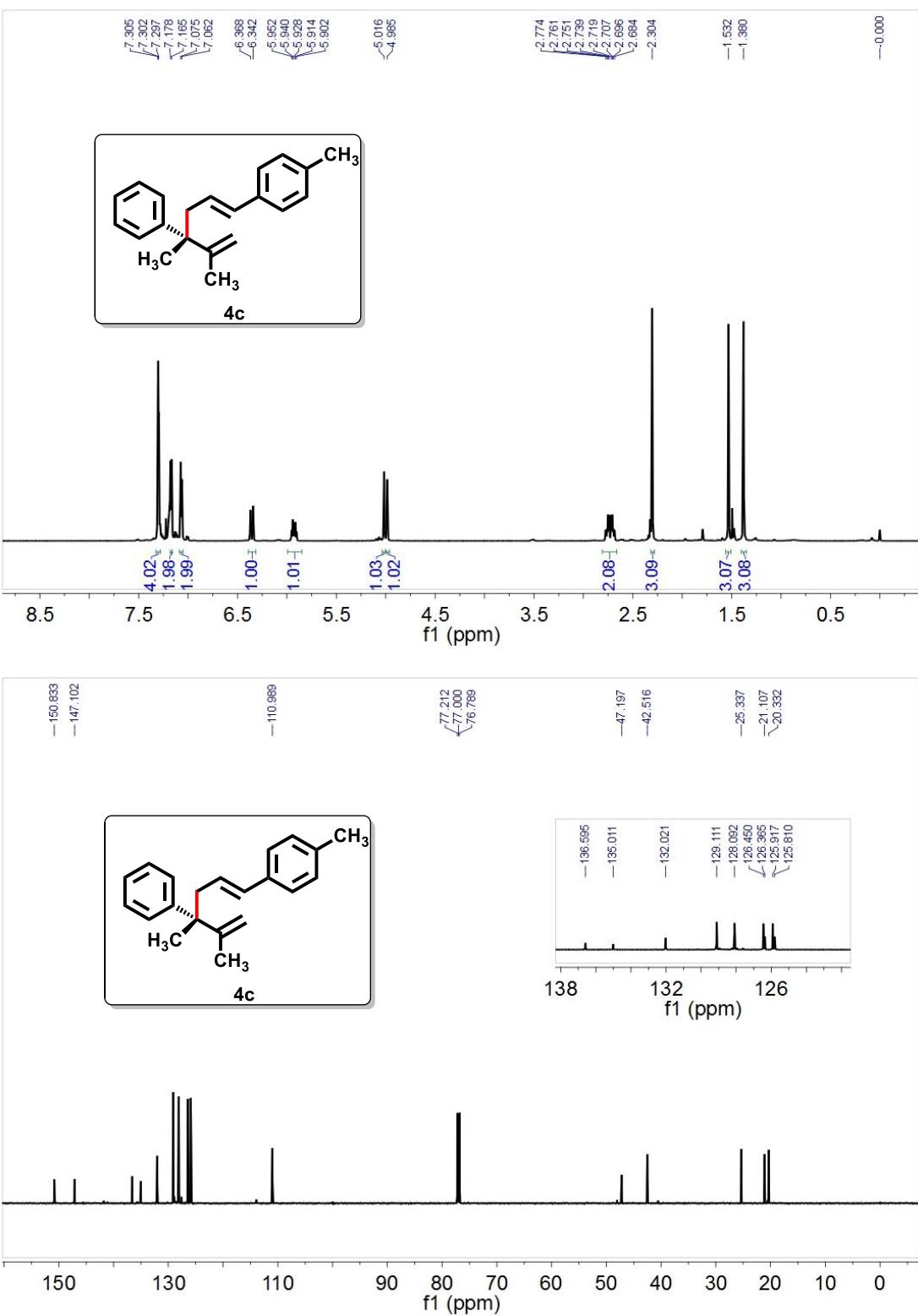


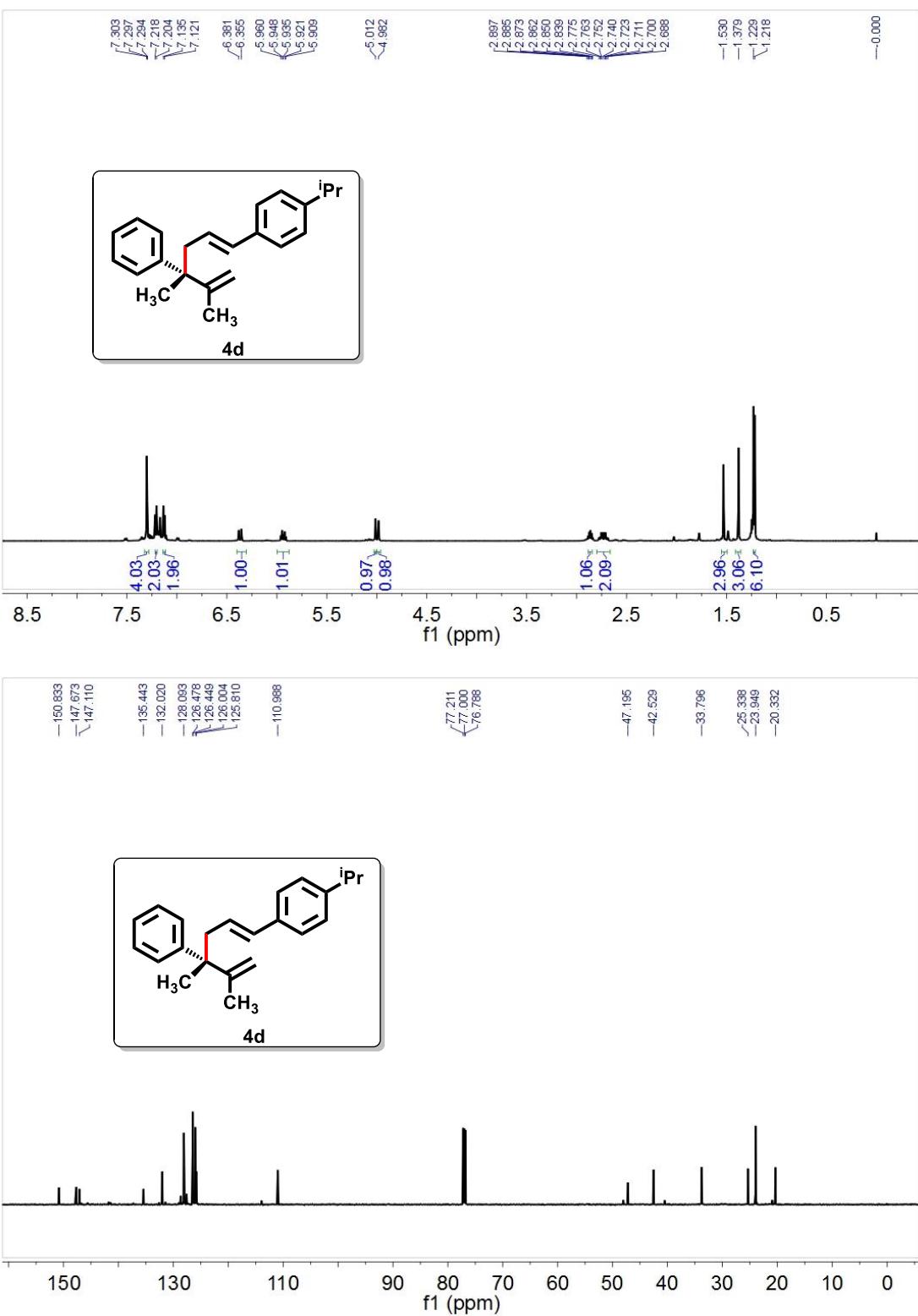


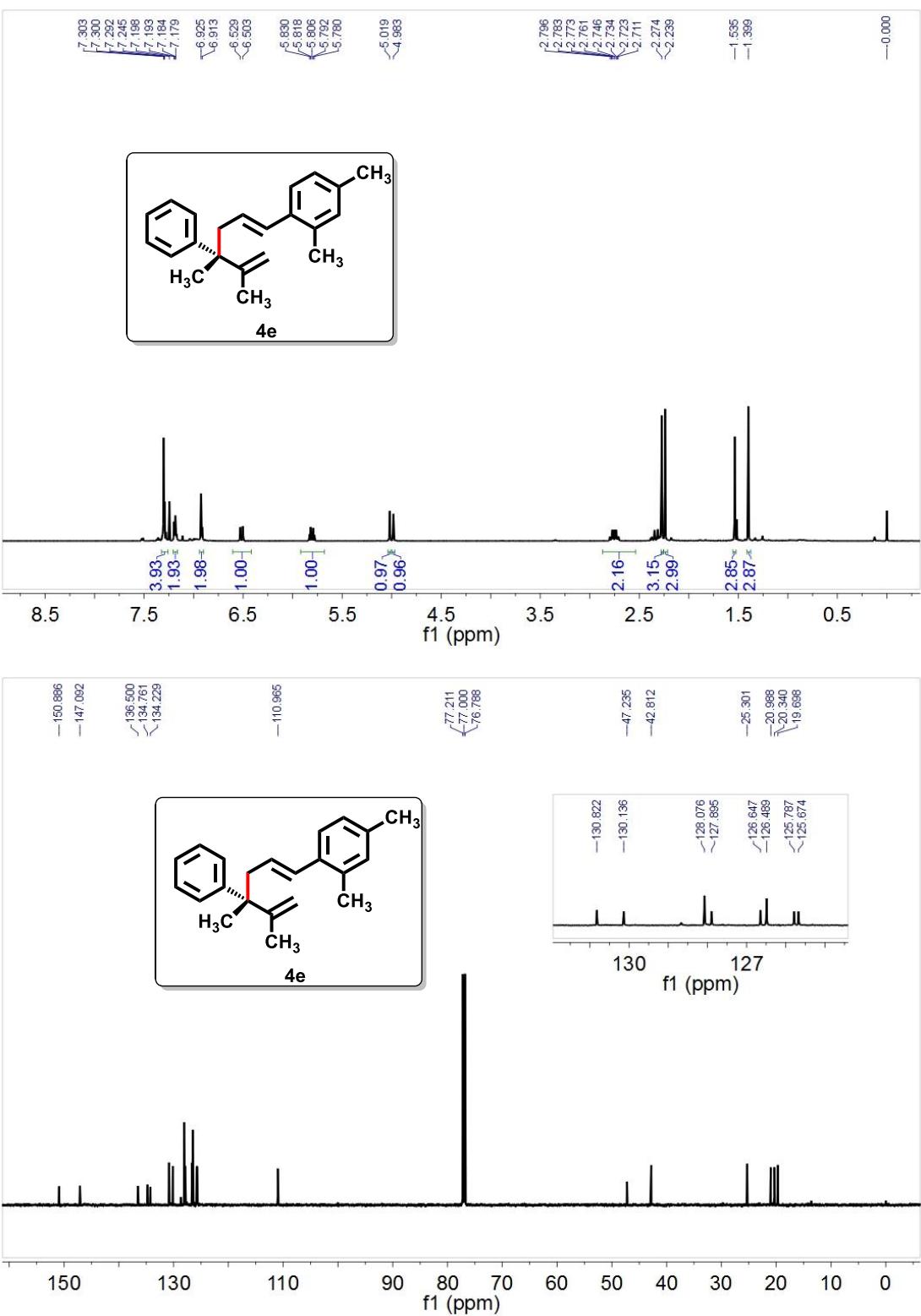


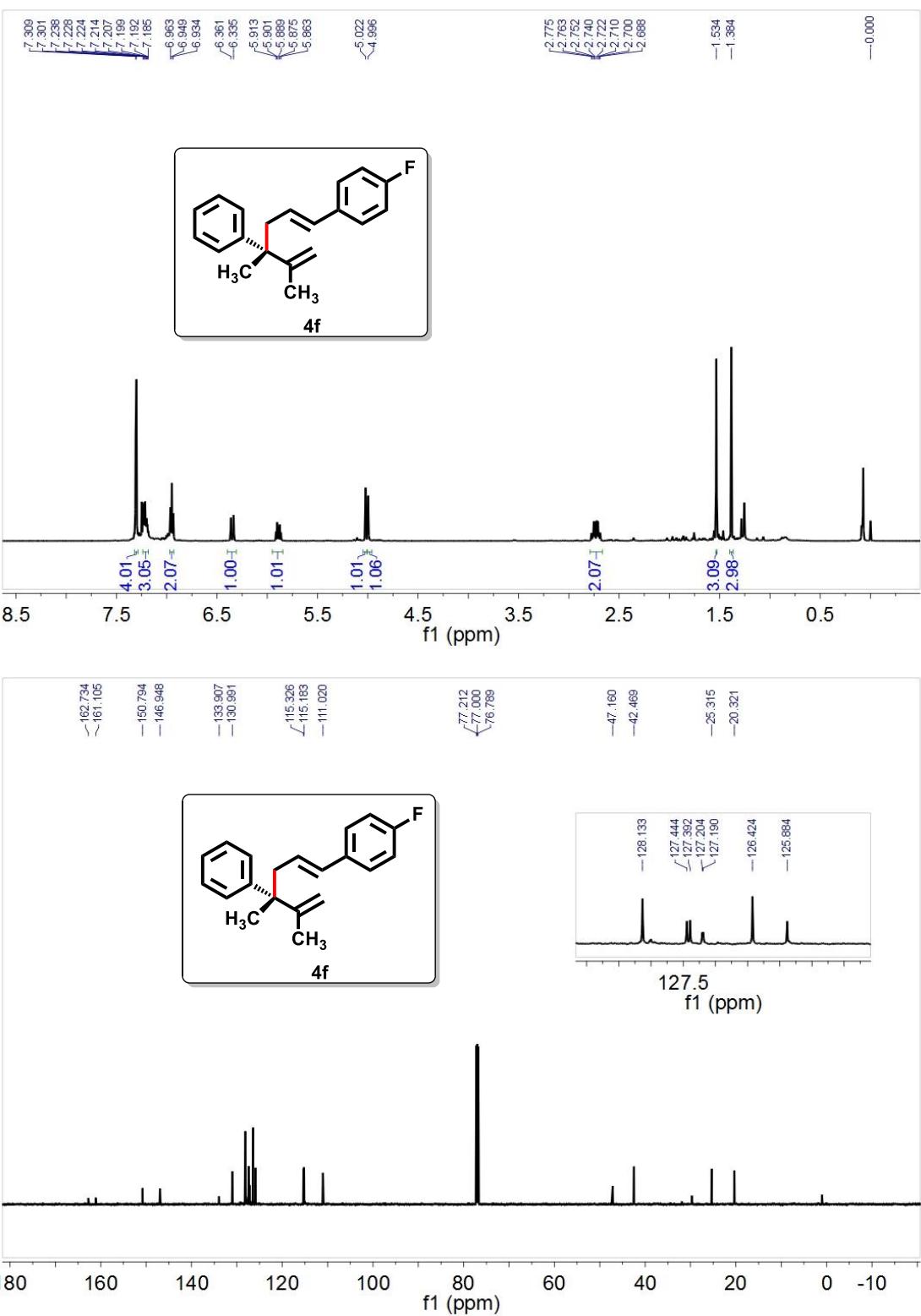


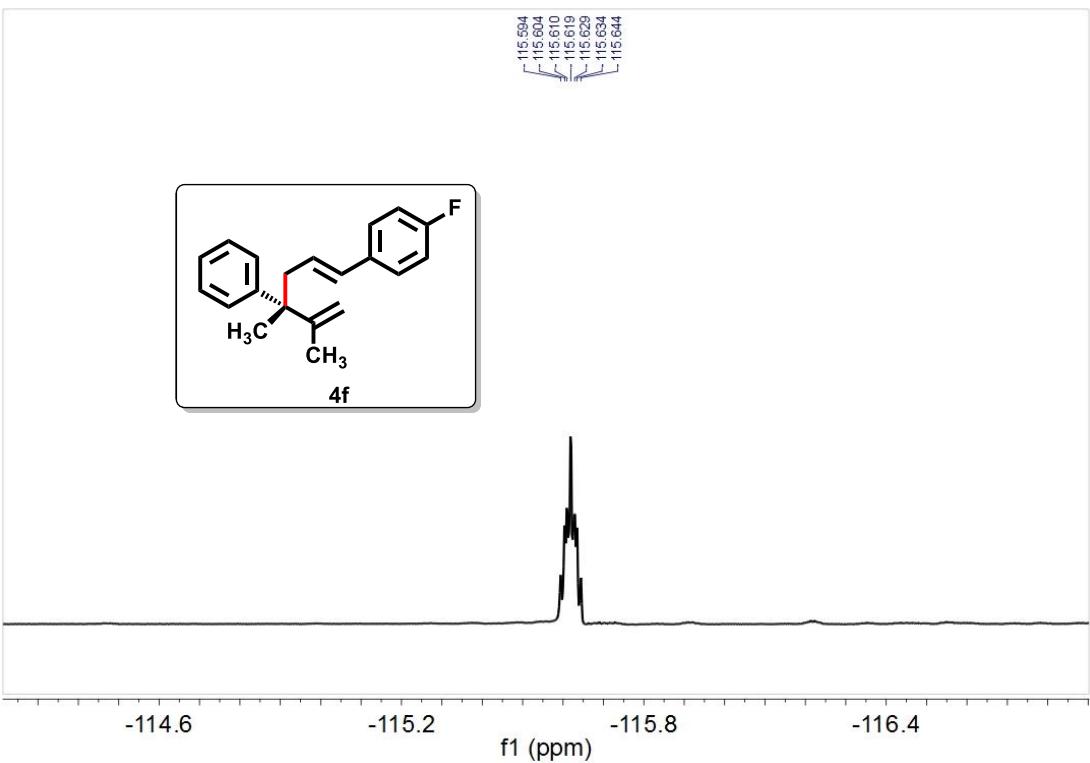


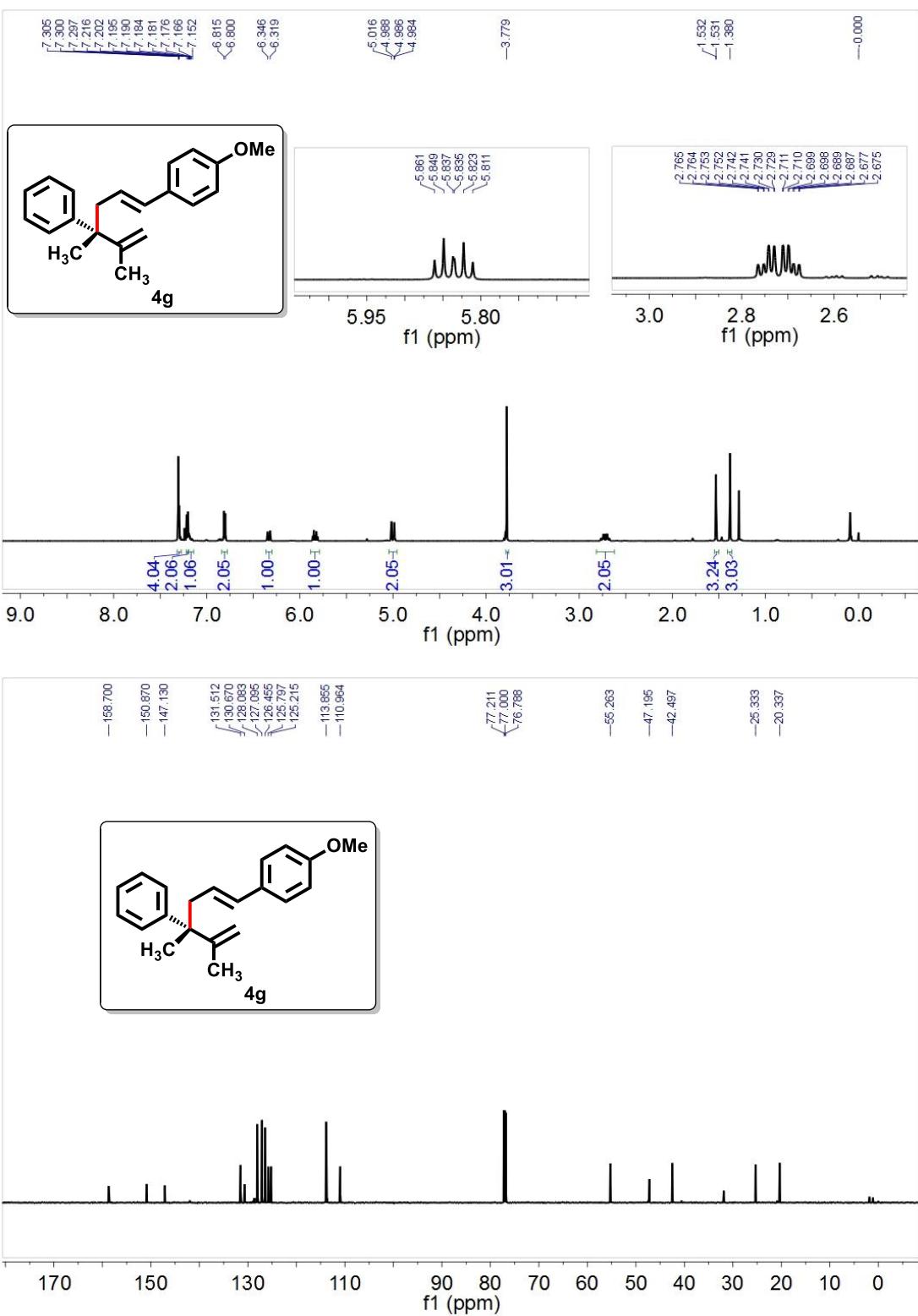


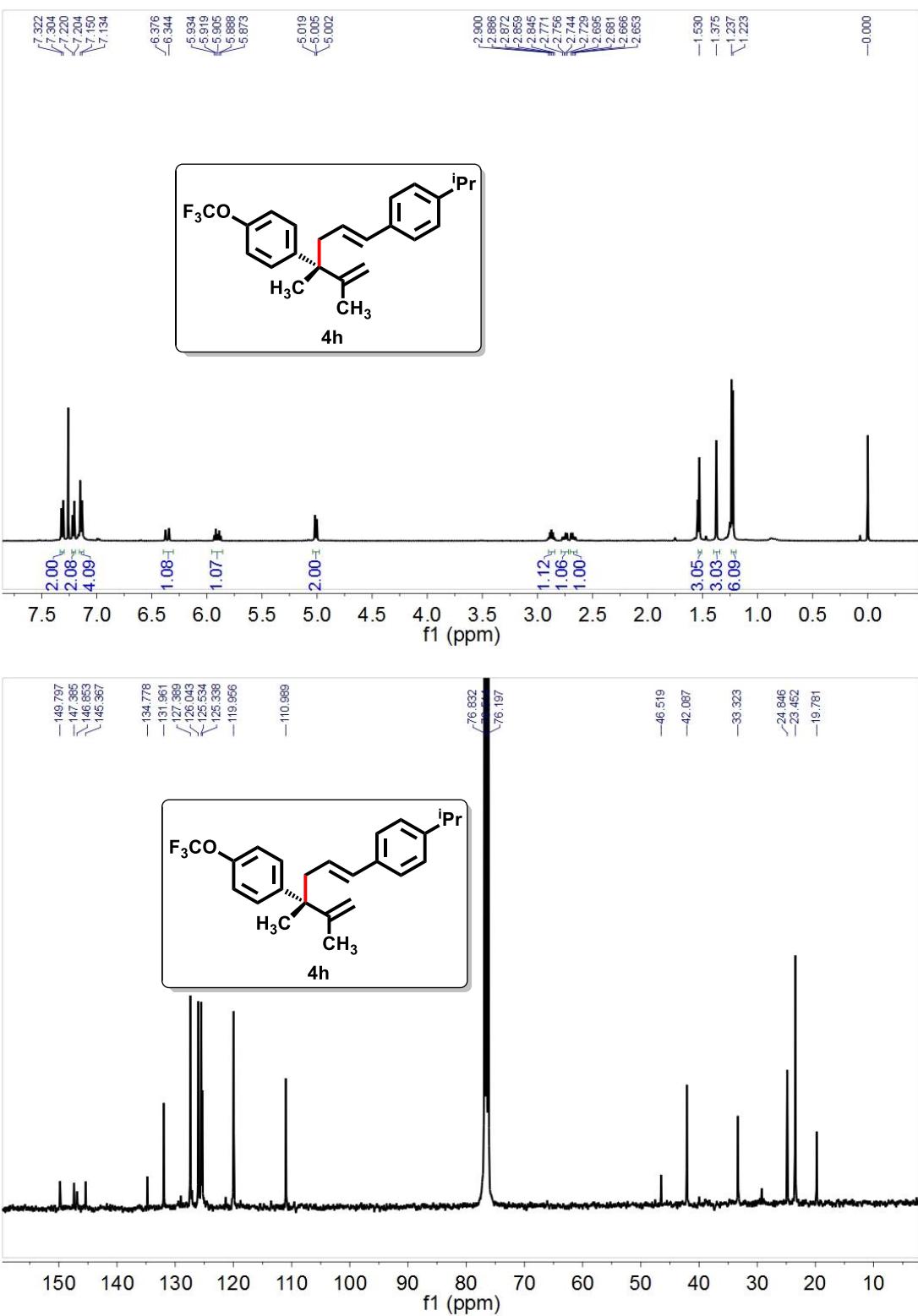




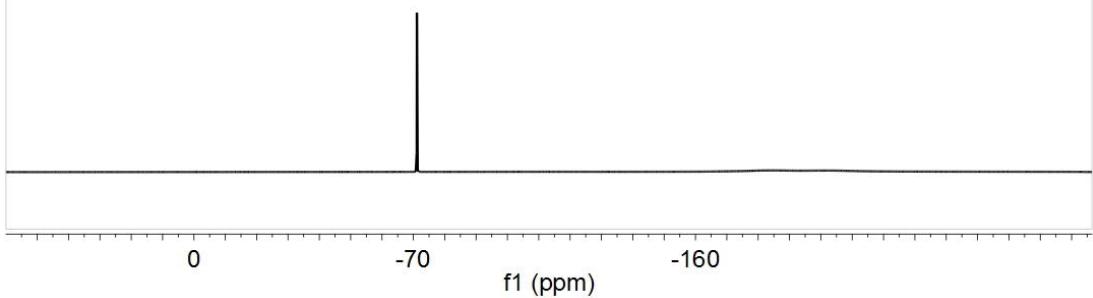
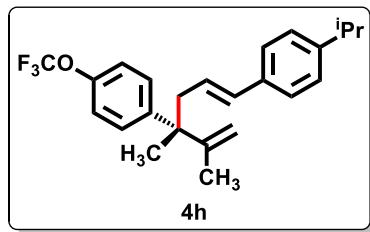


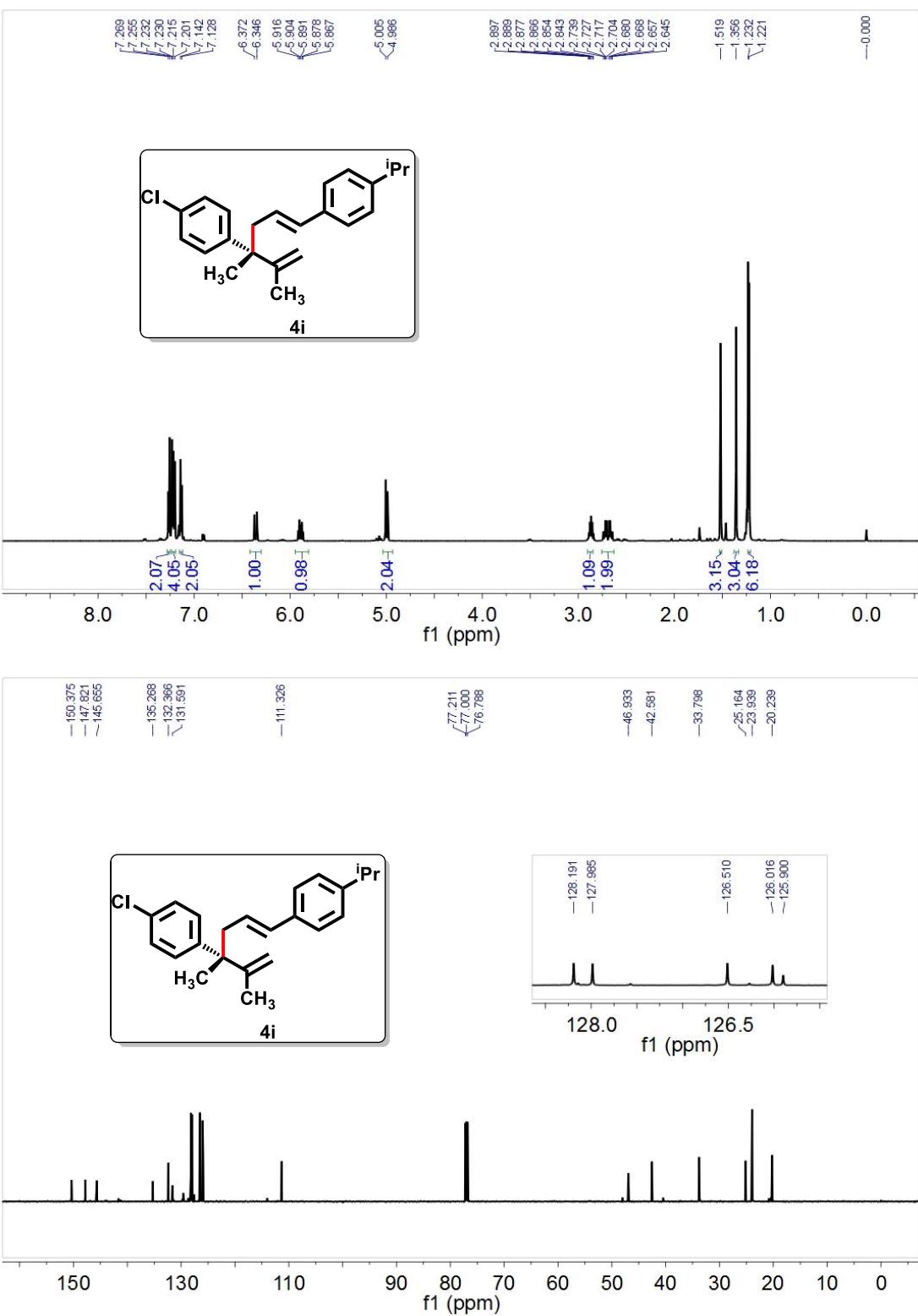


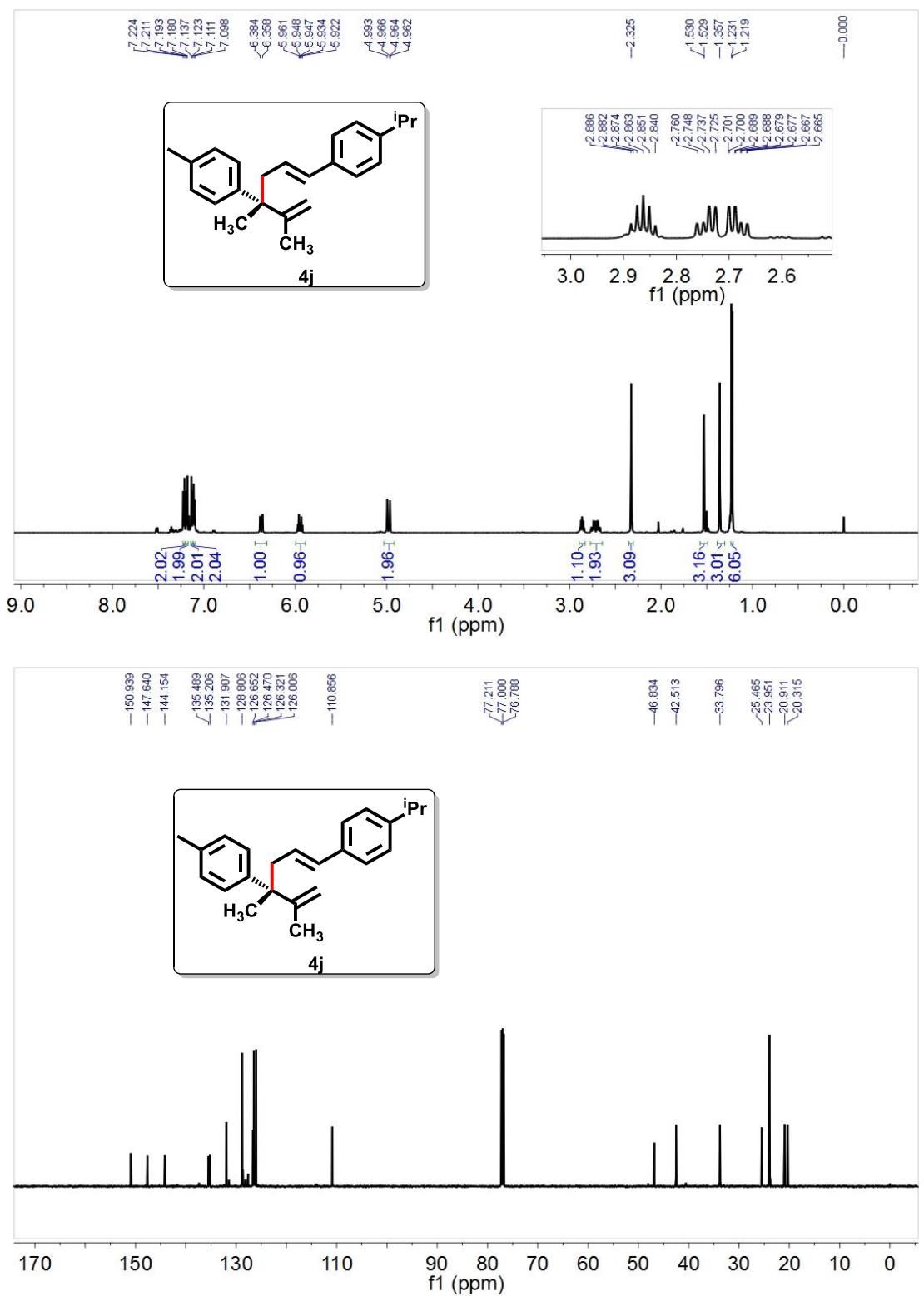


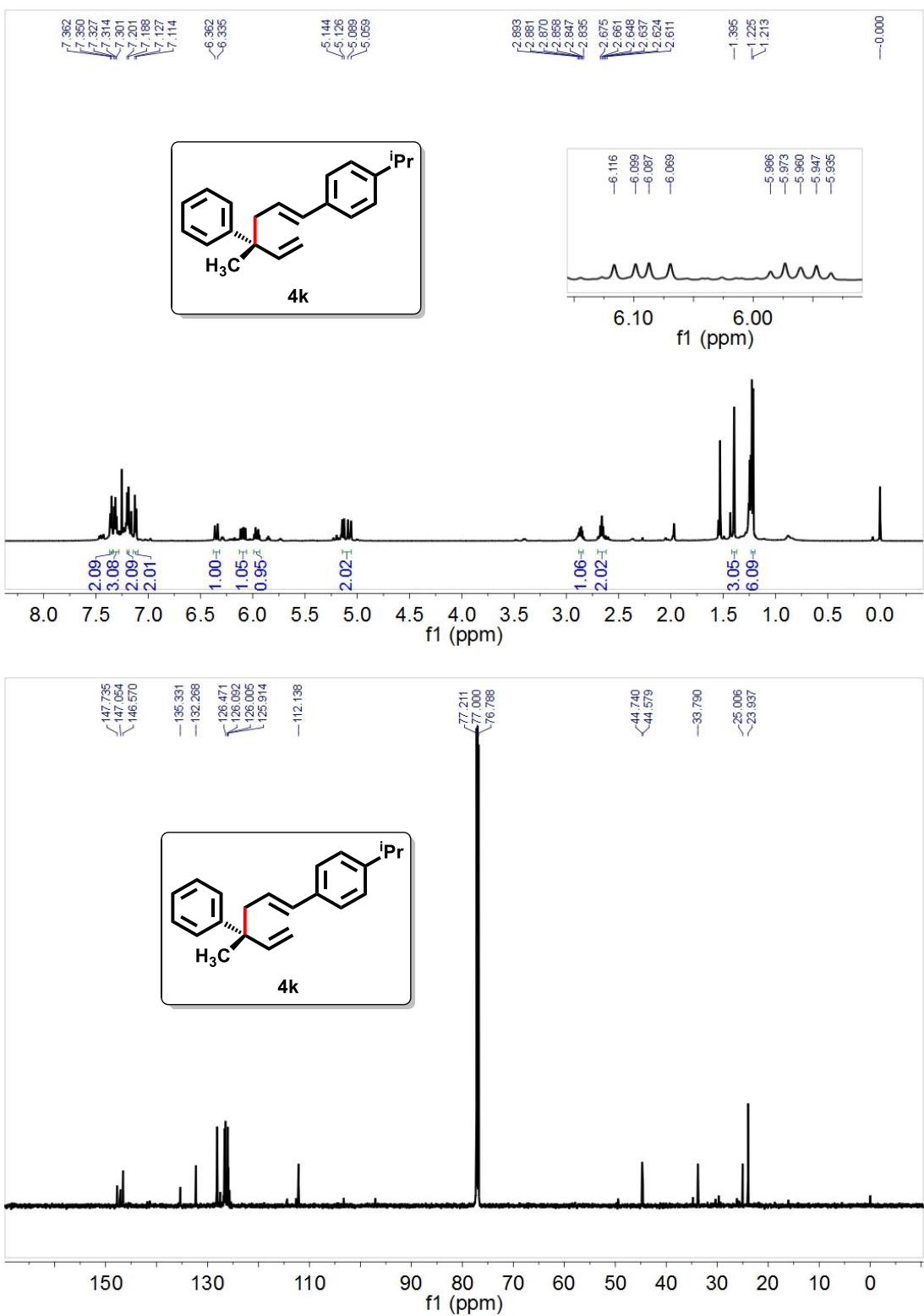


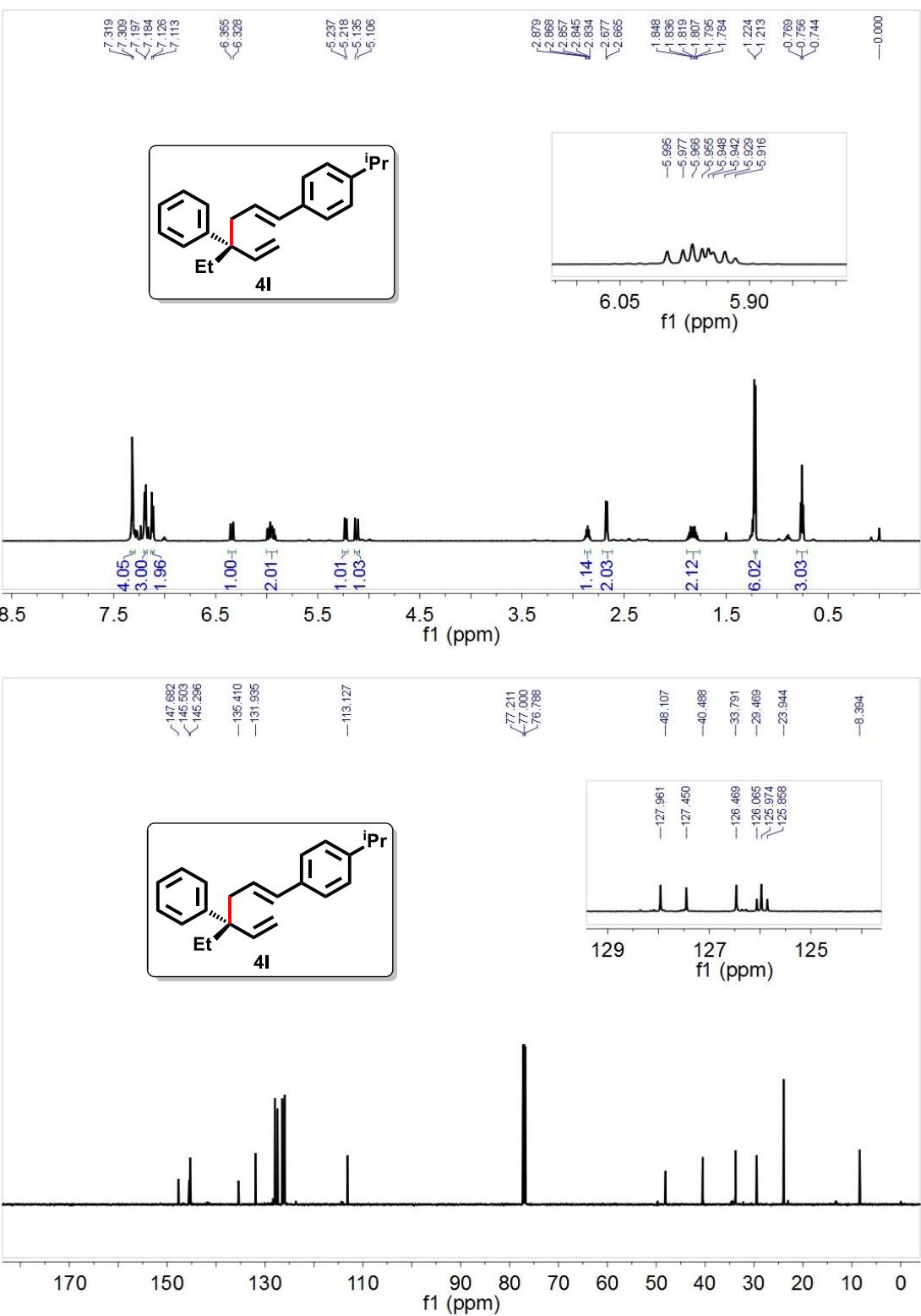
—71.121

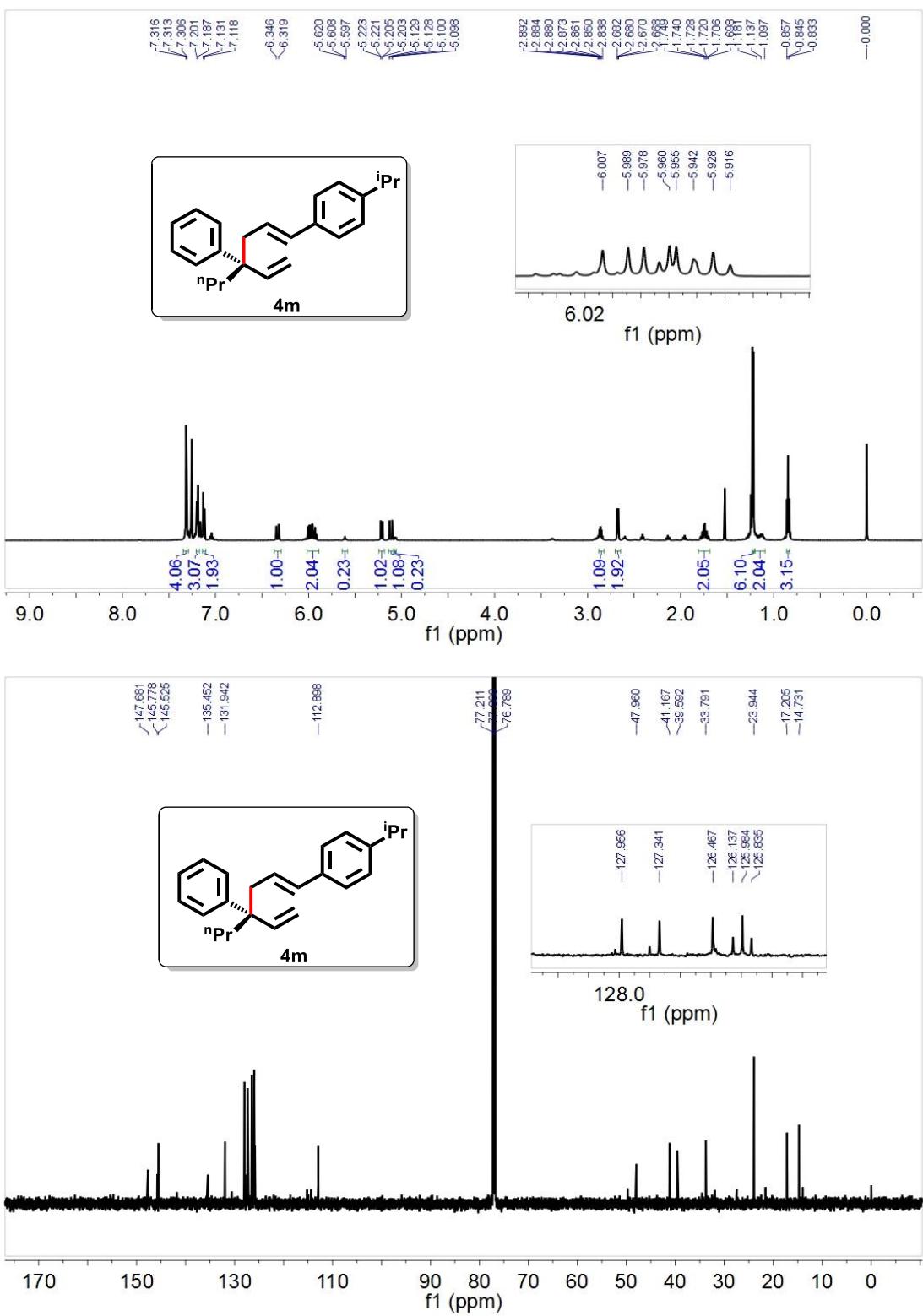


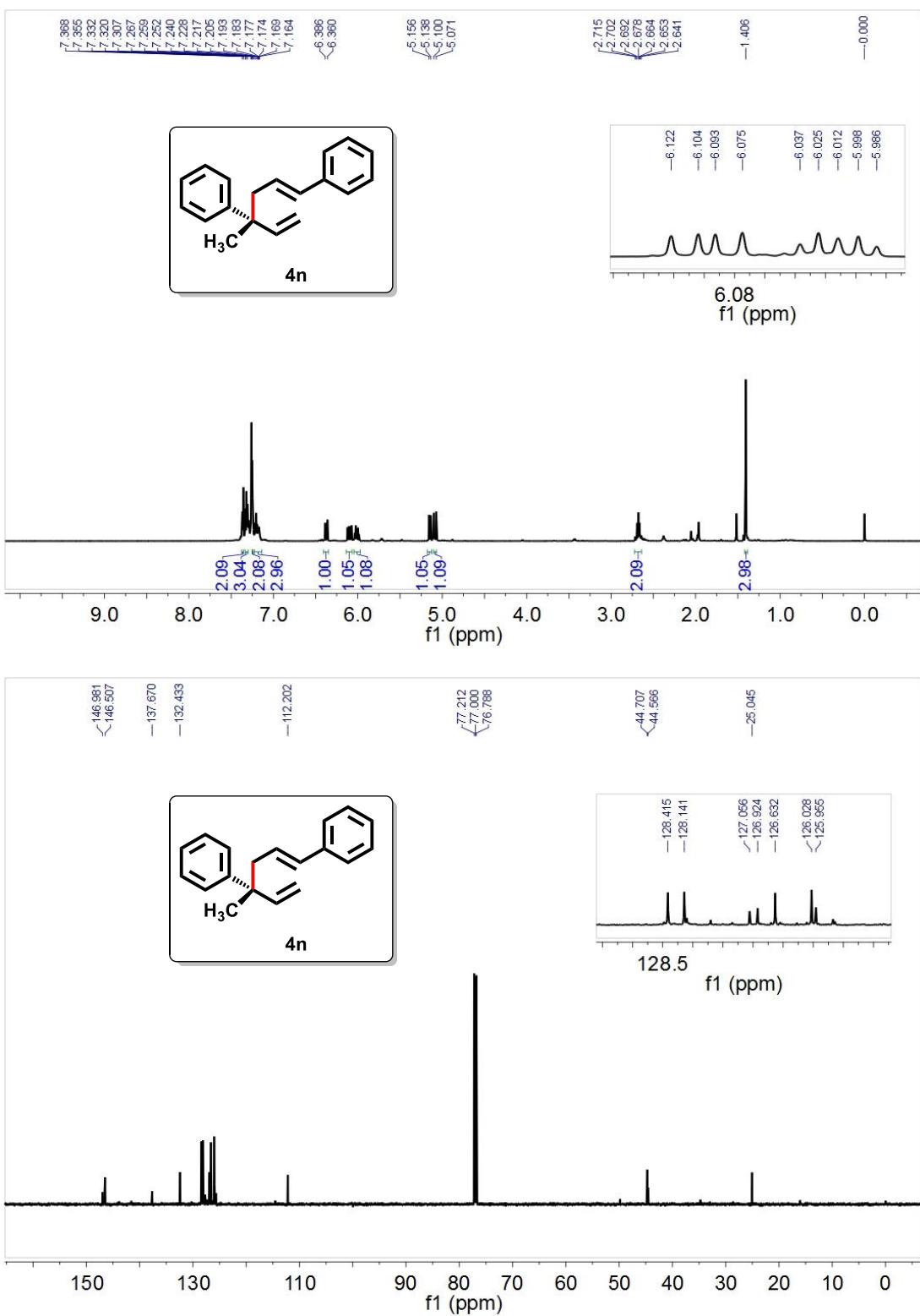


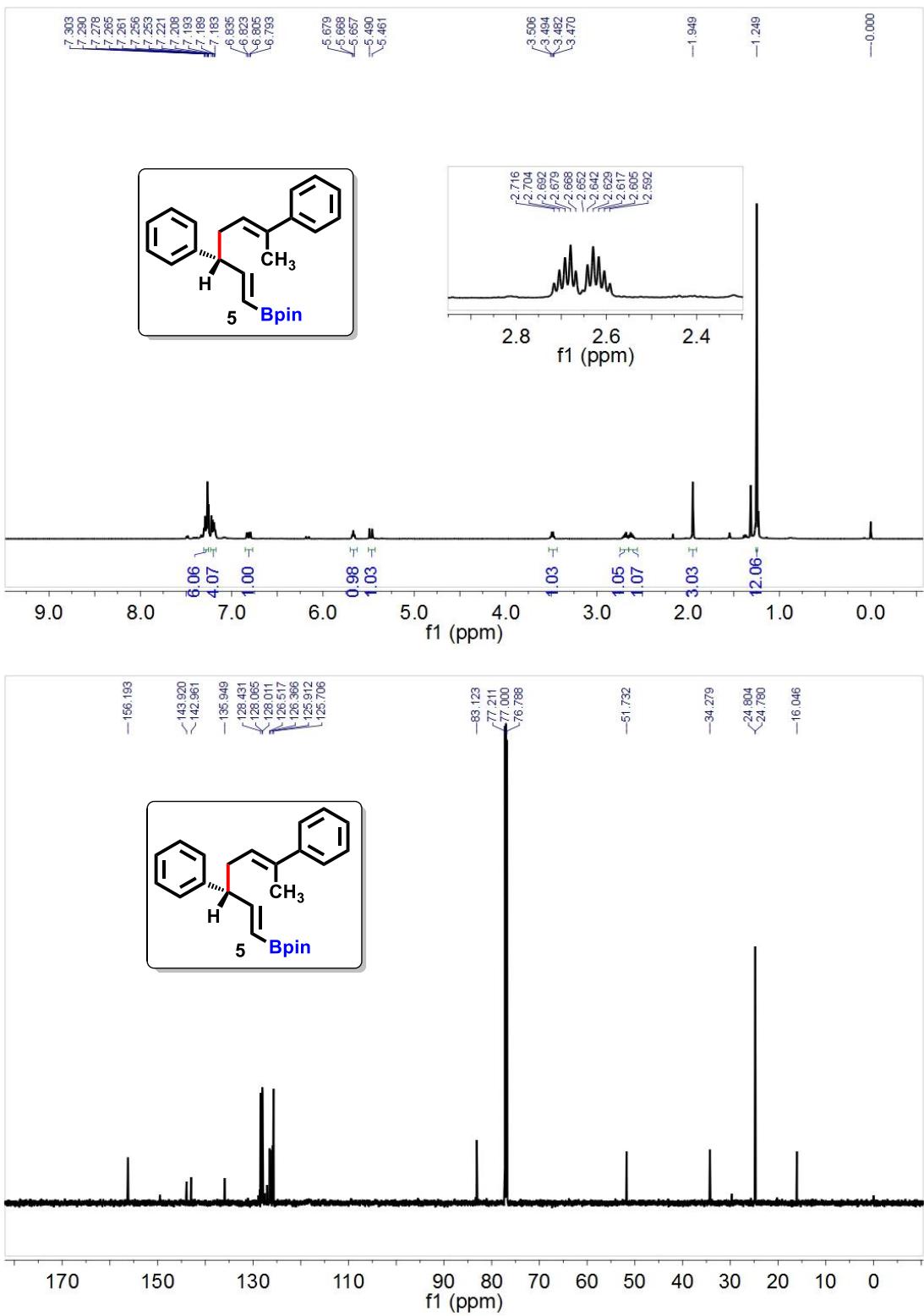


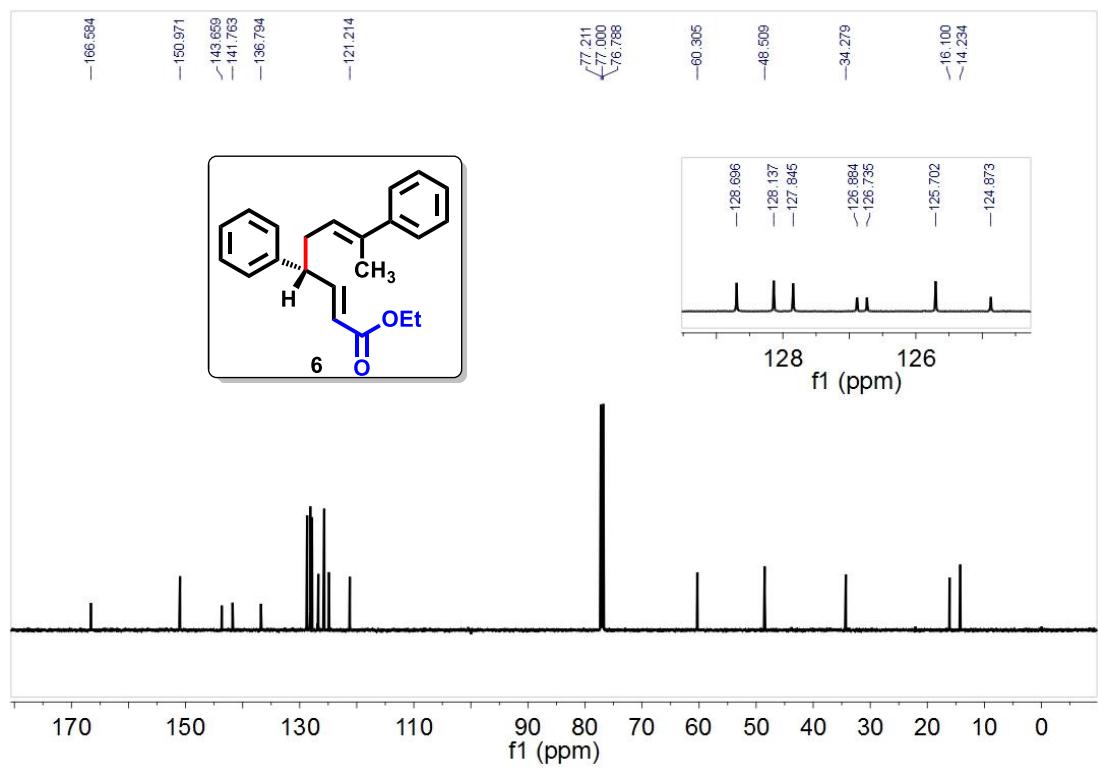
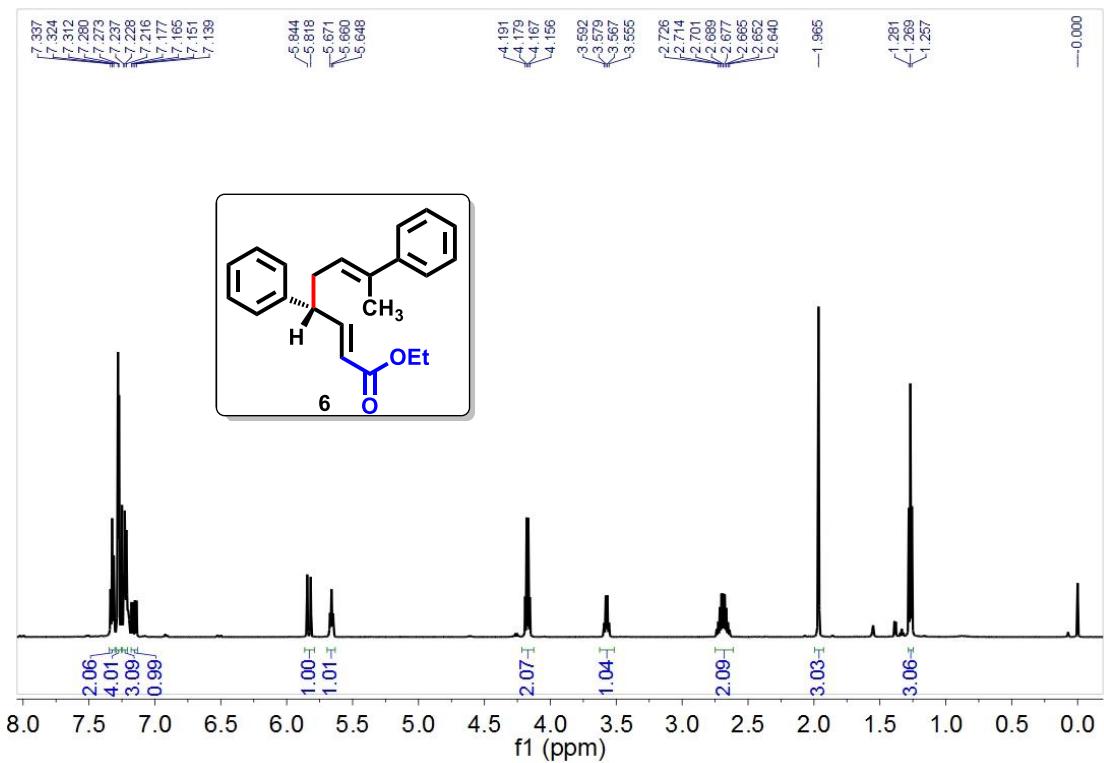


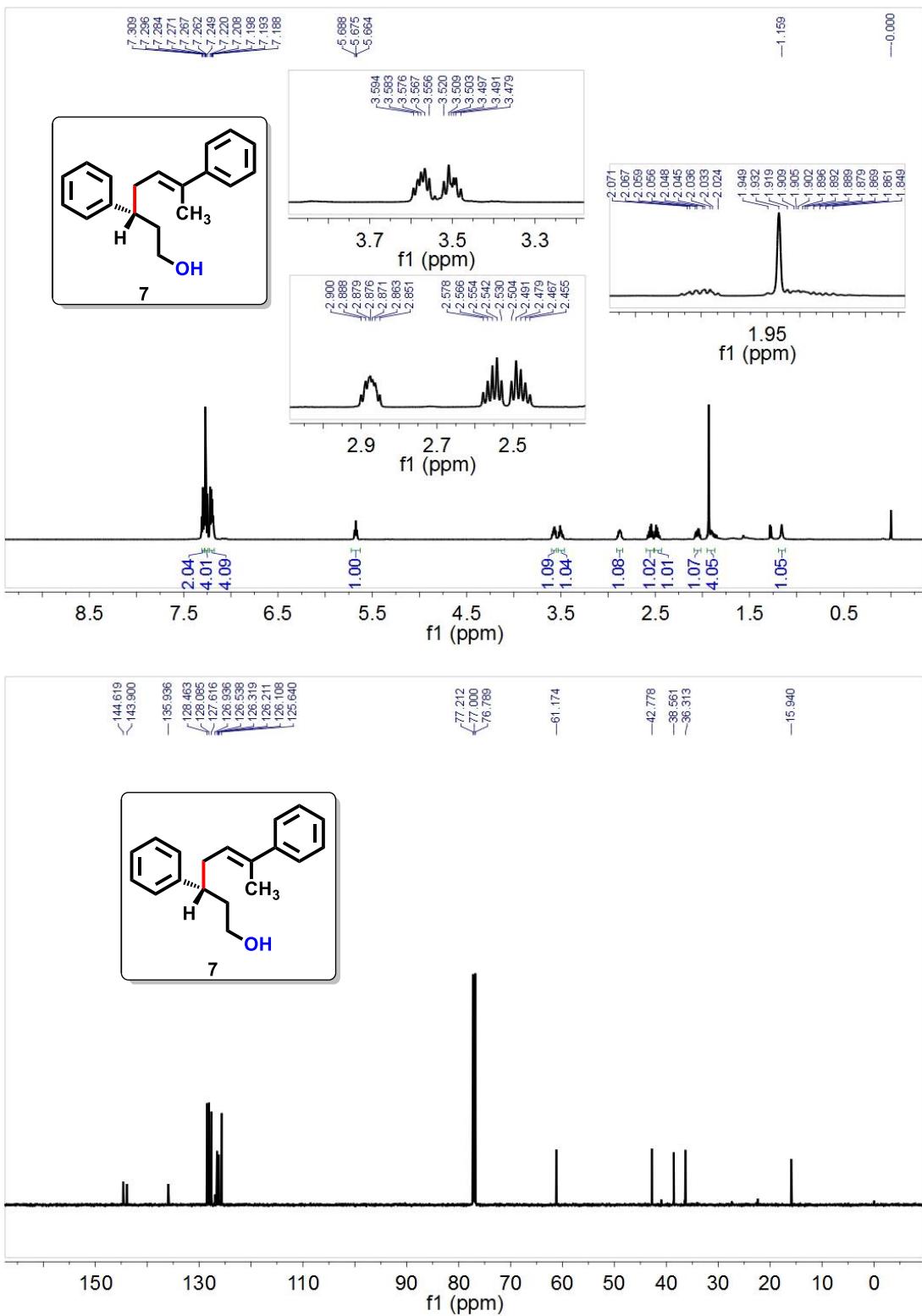


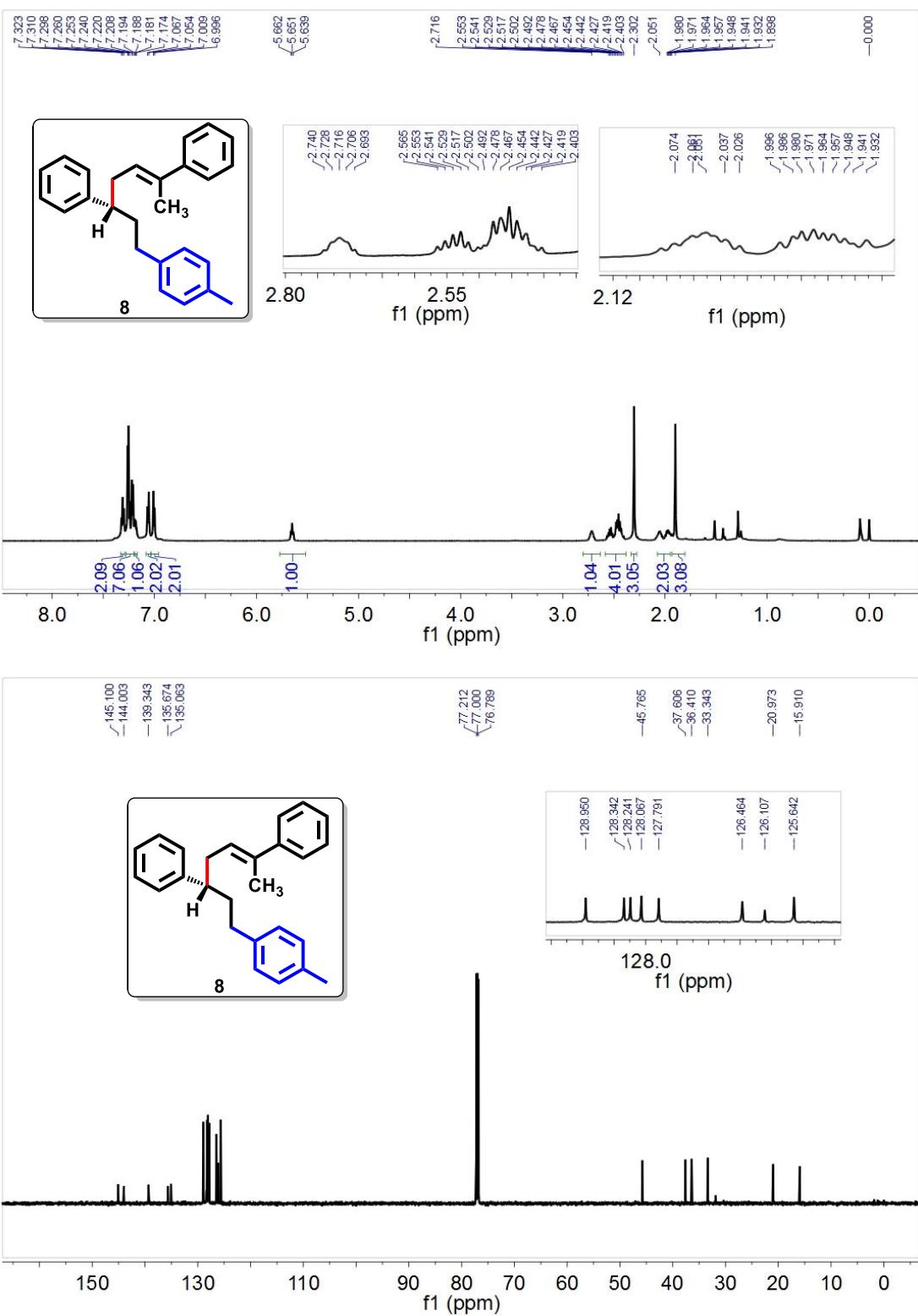


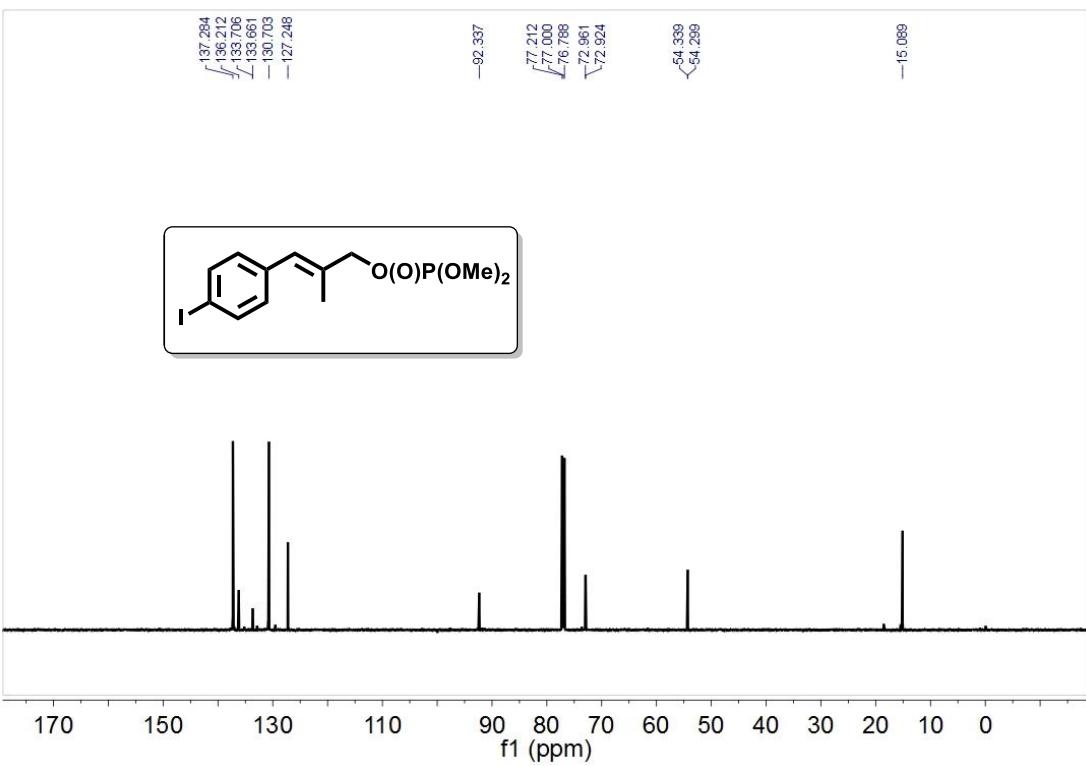
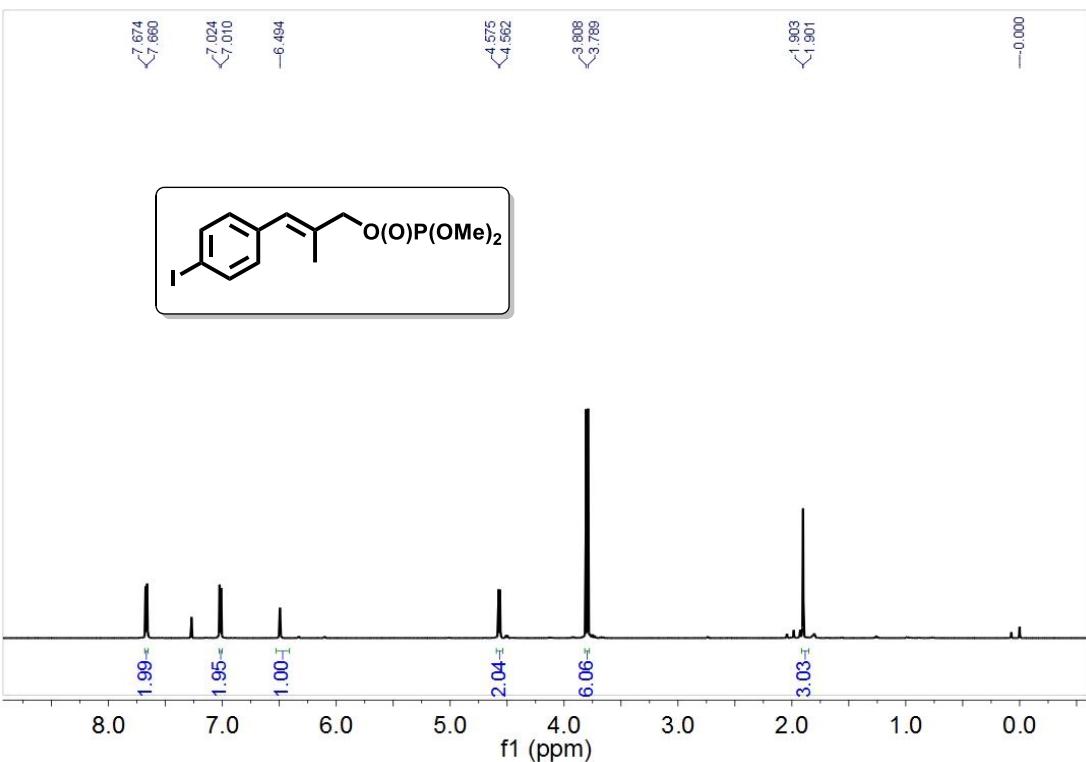


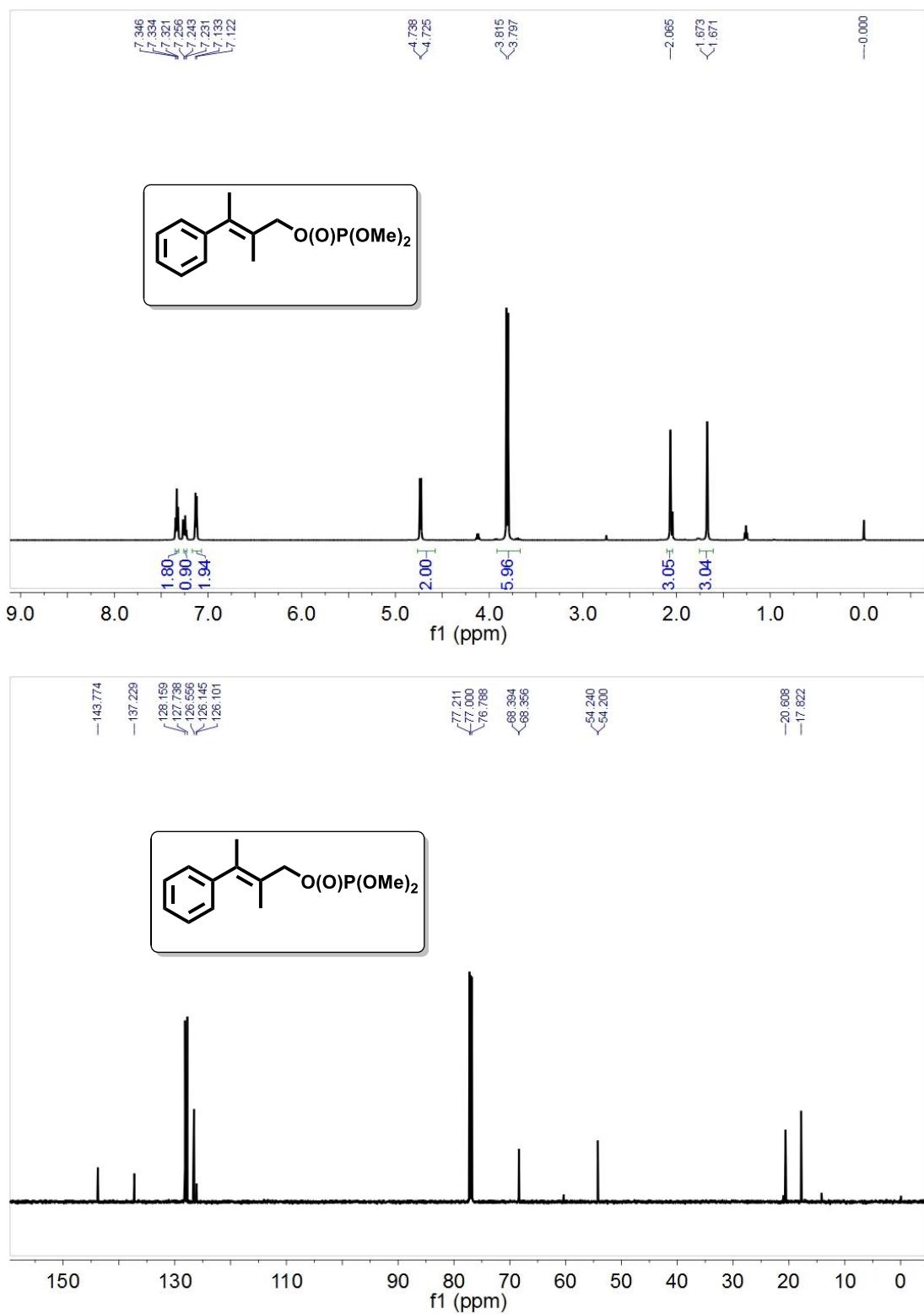


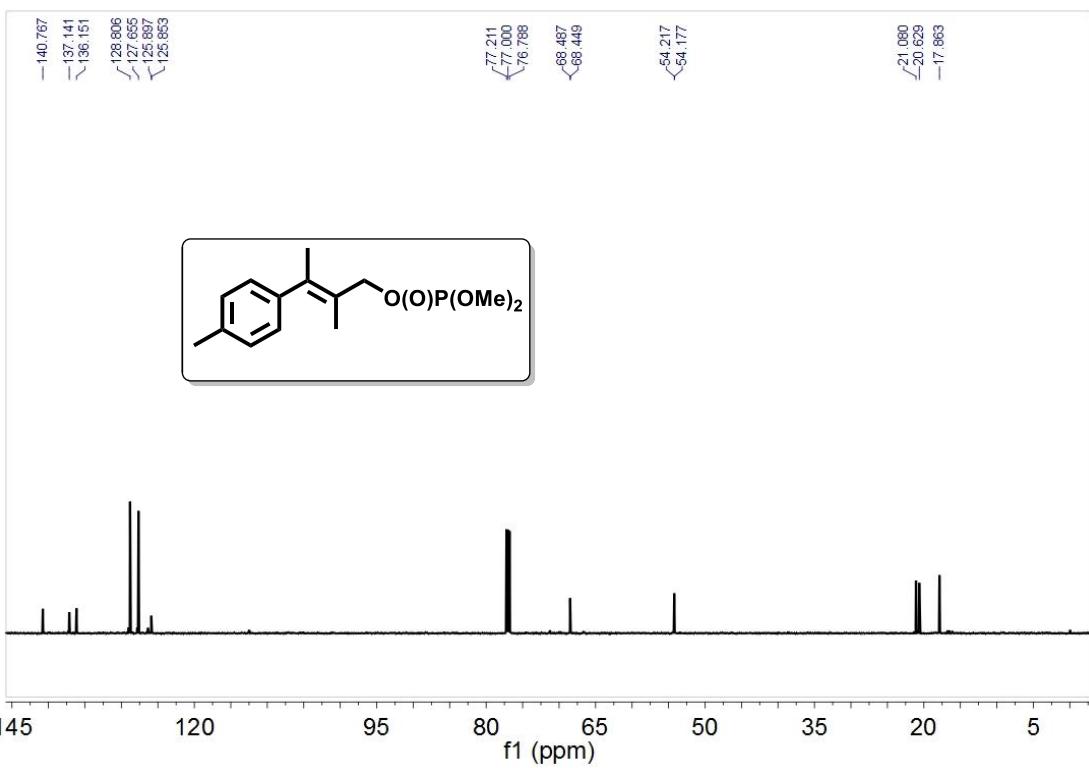
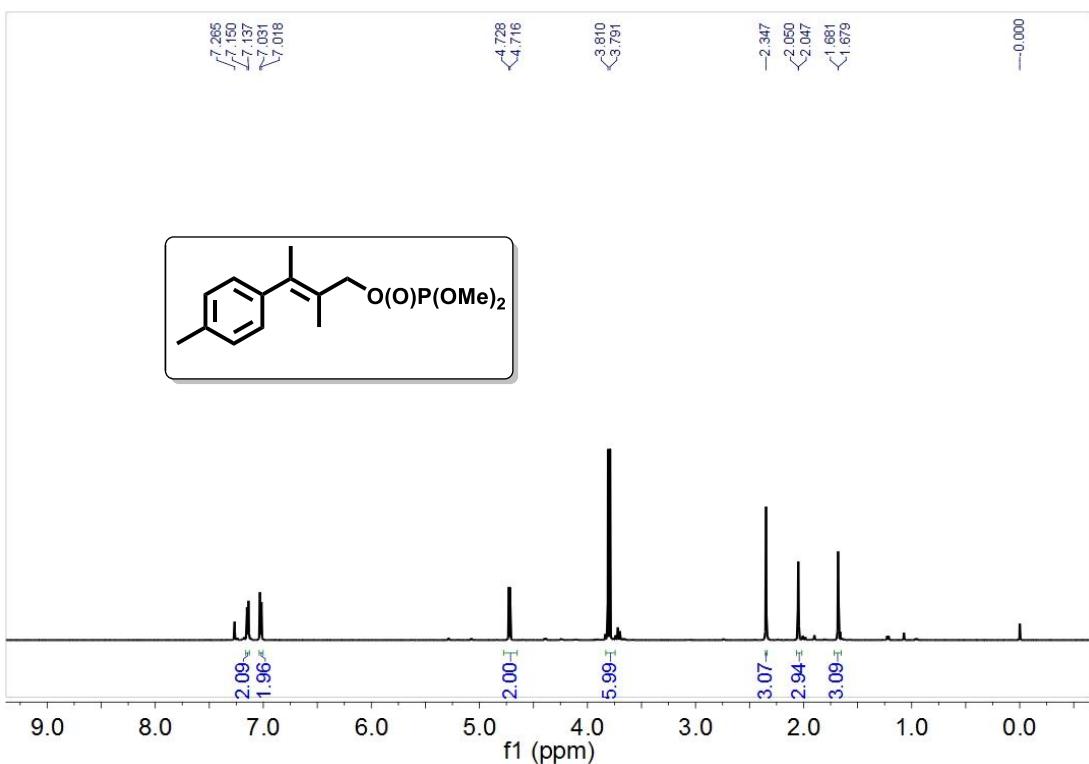


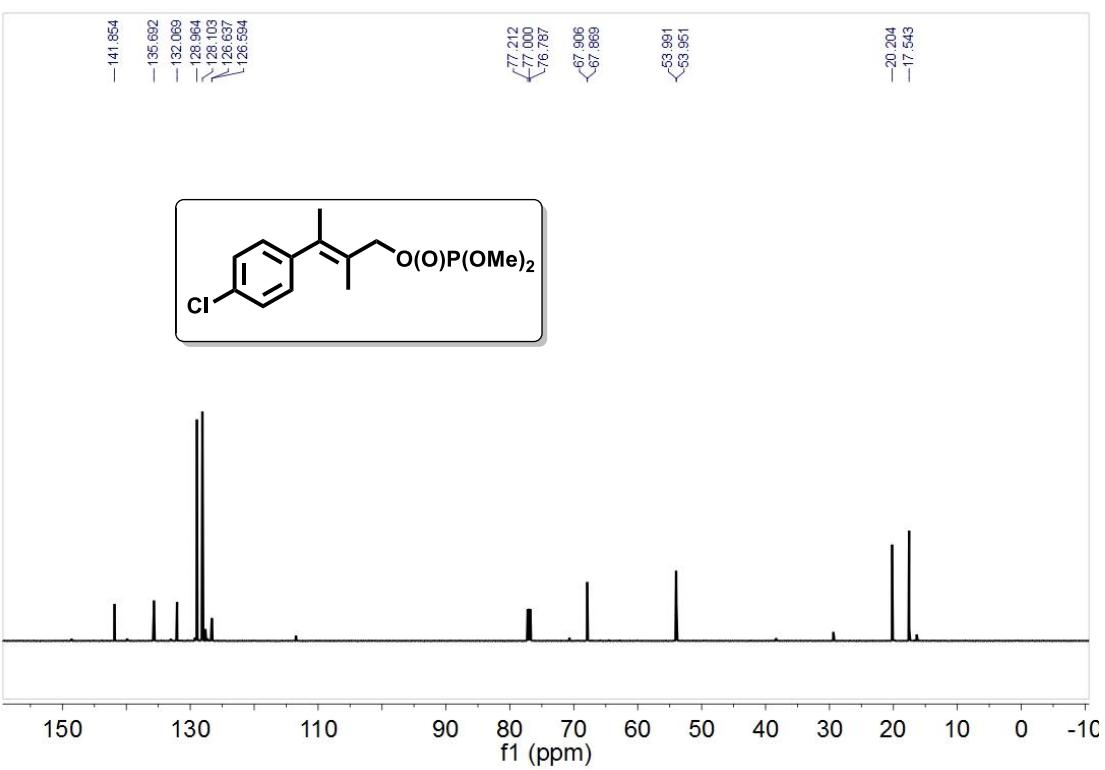
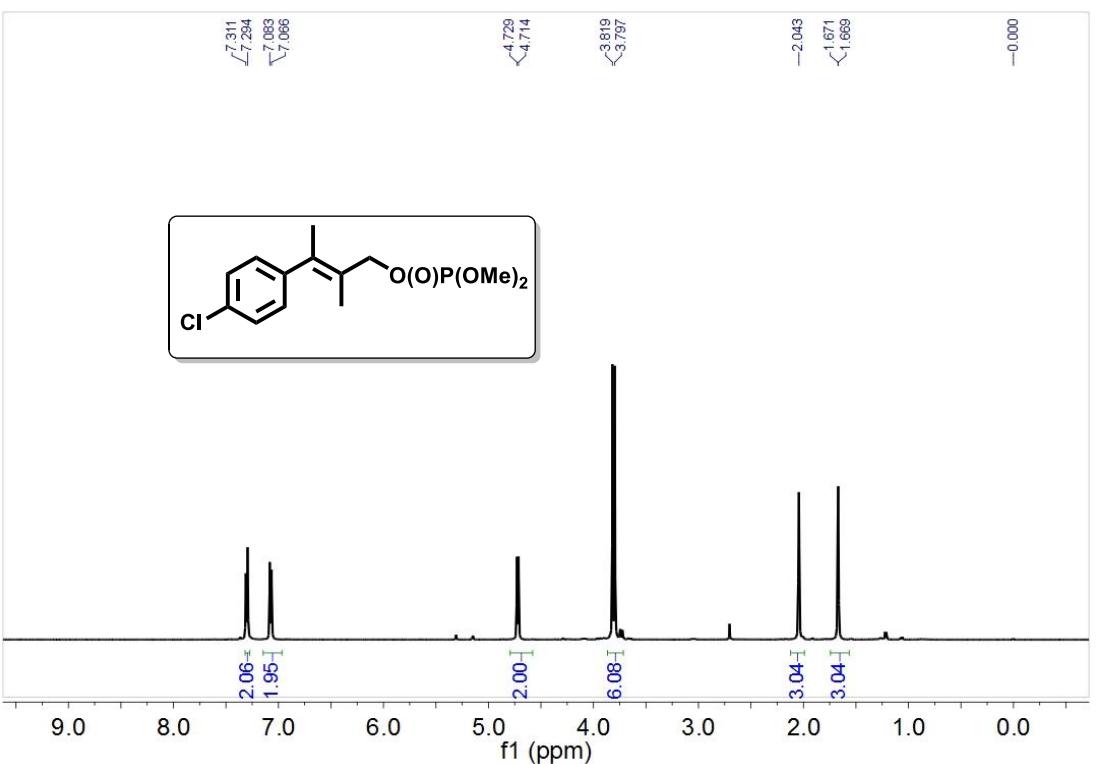


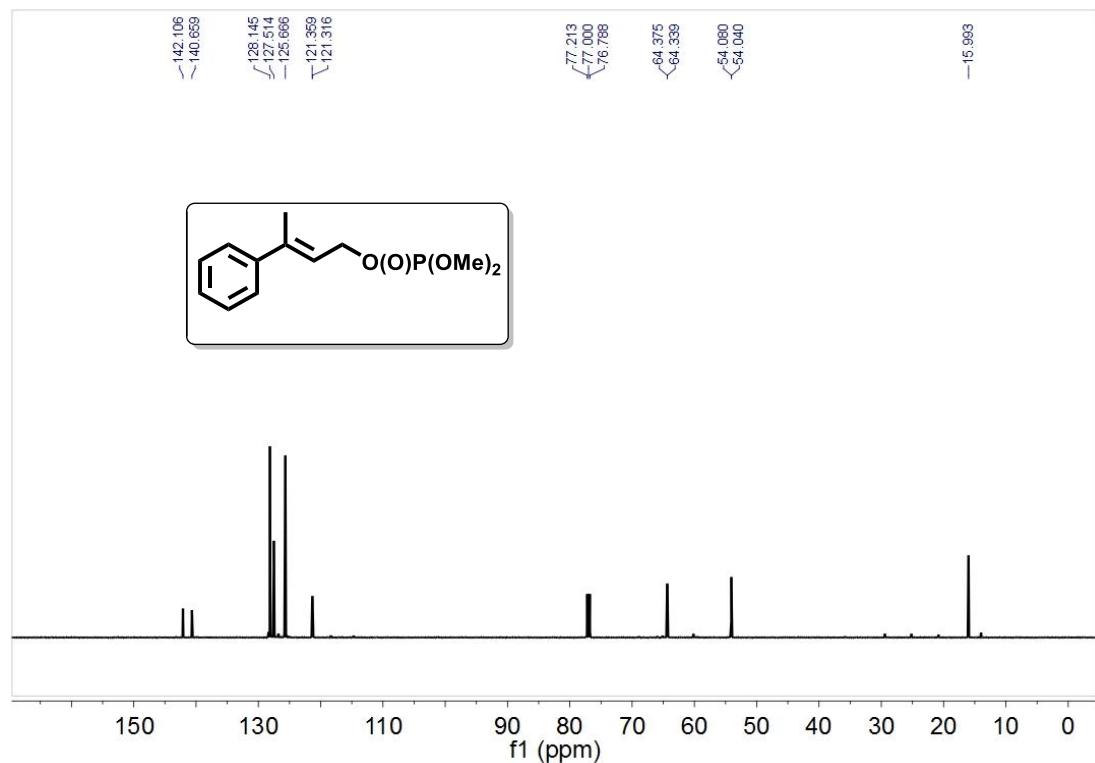
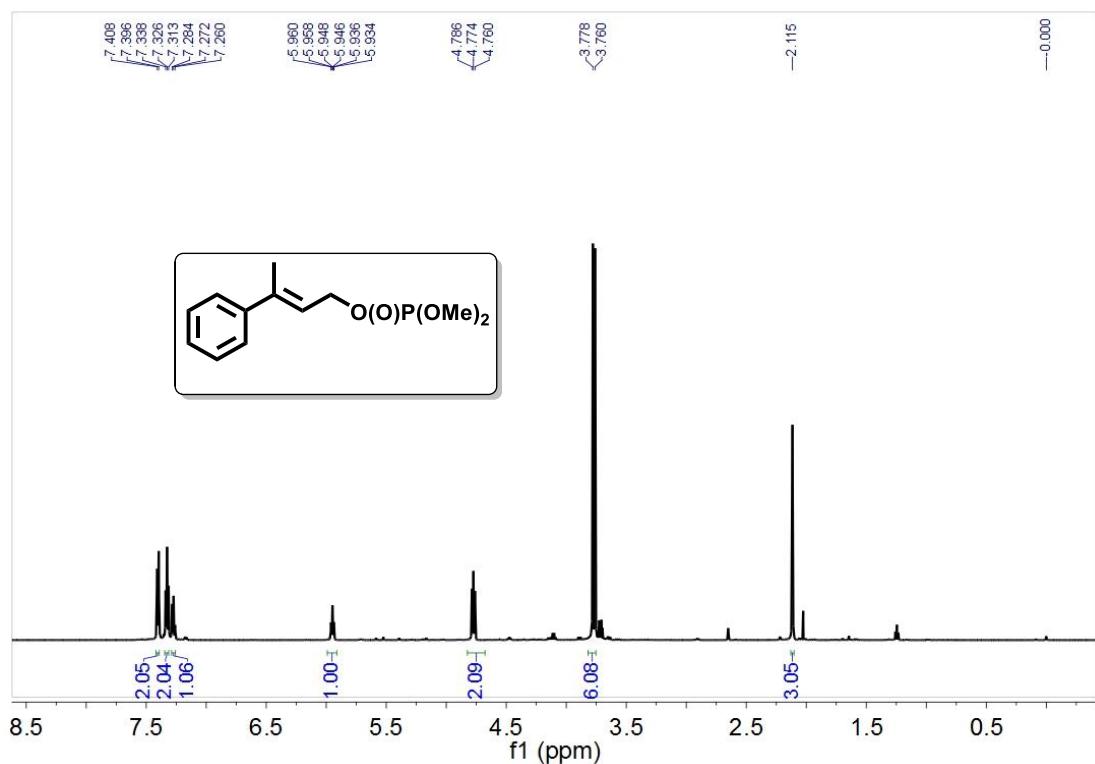


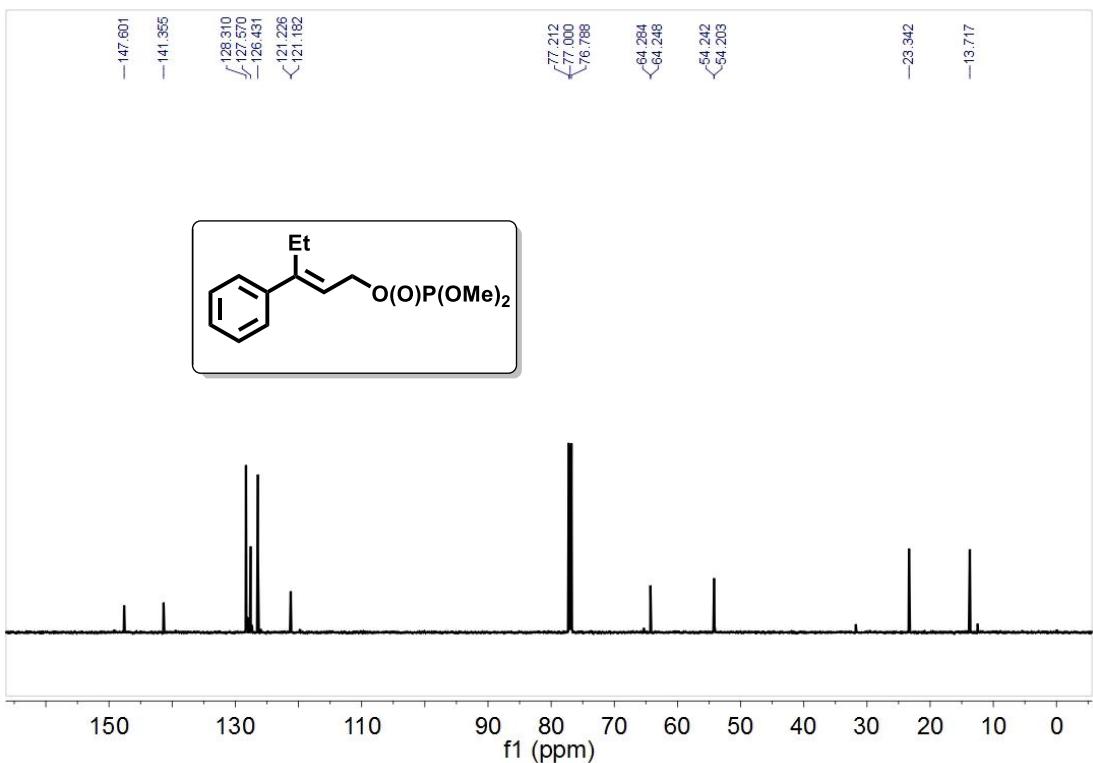
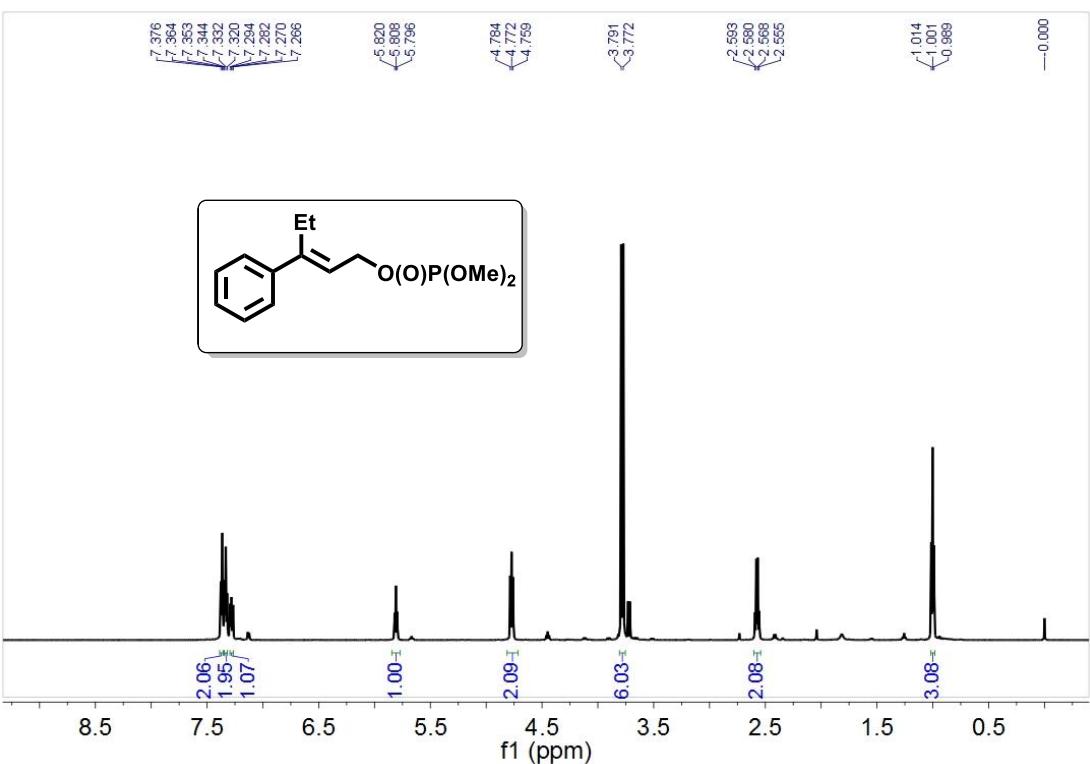


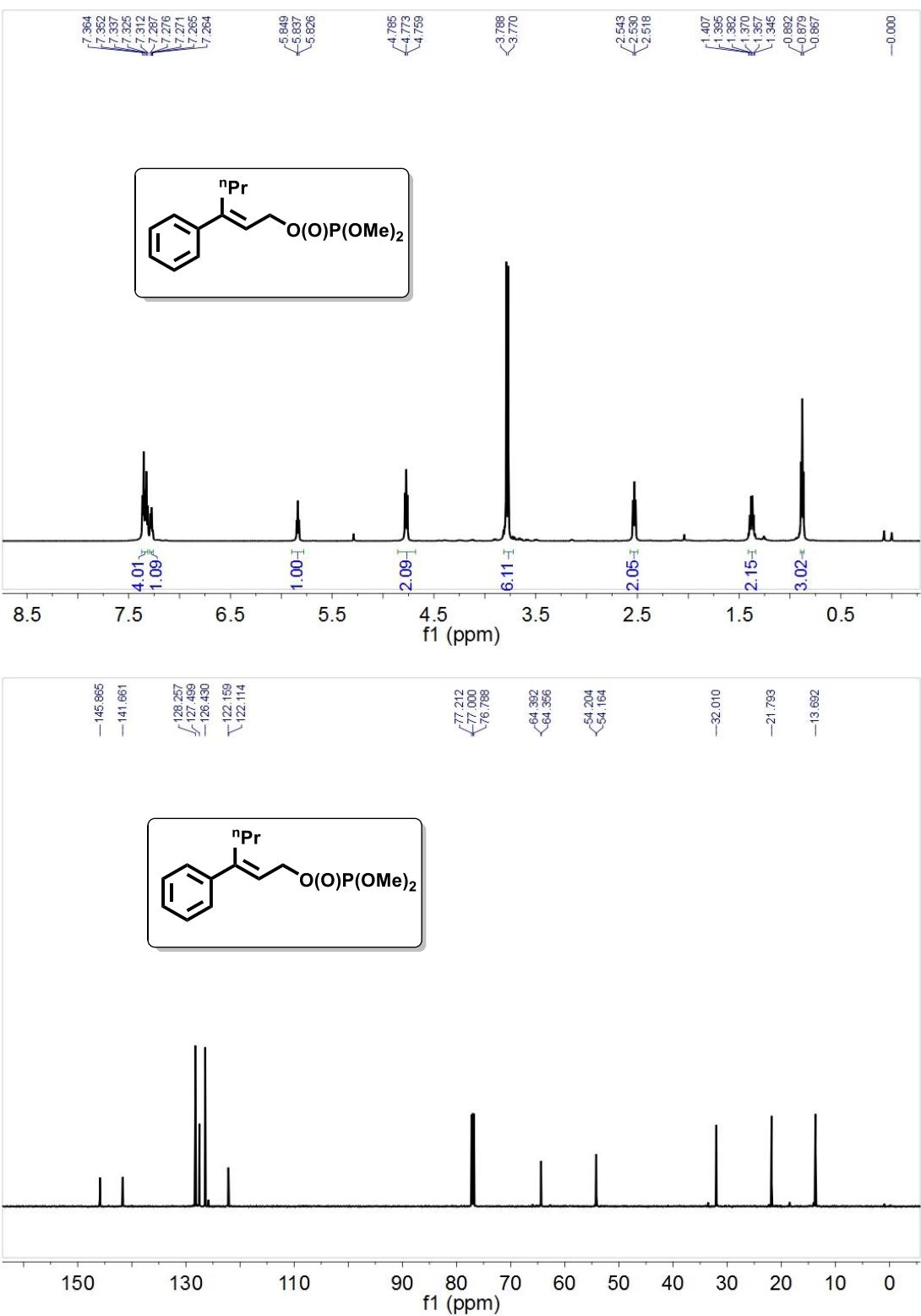




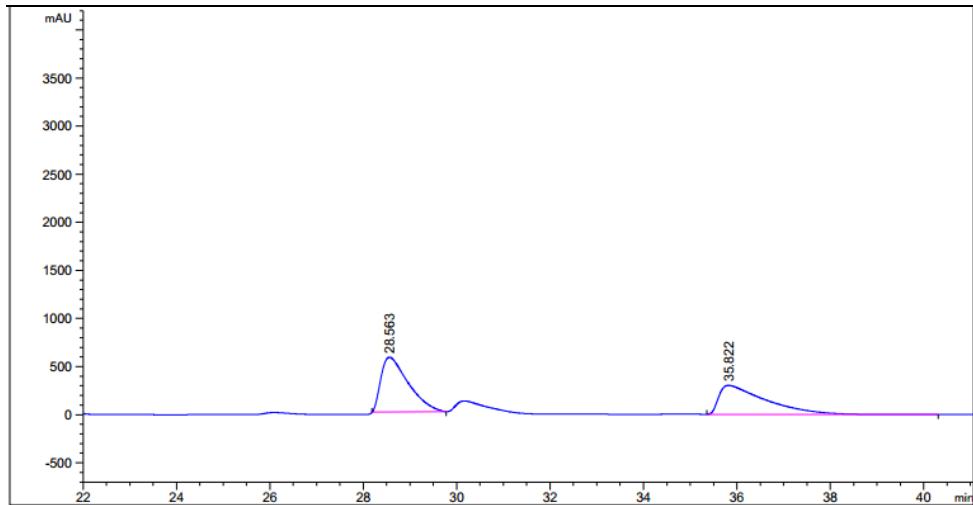
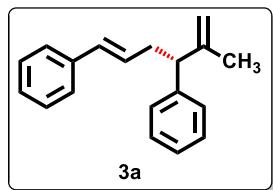




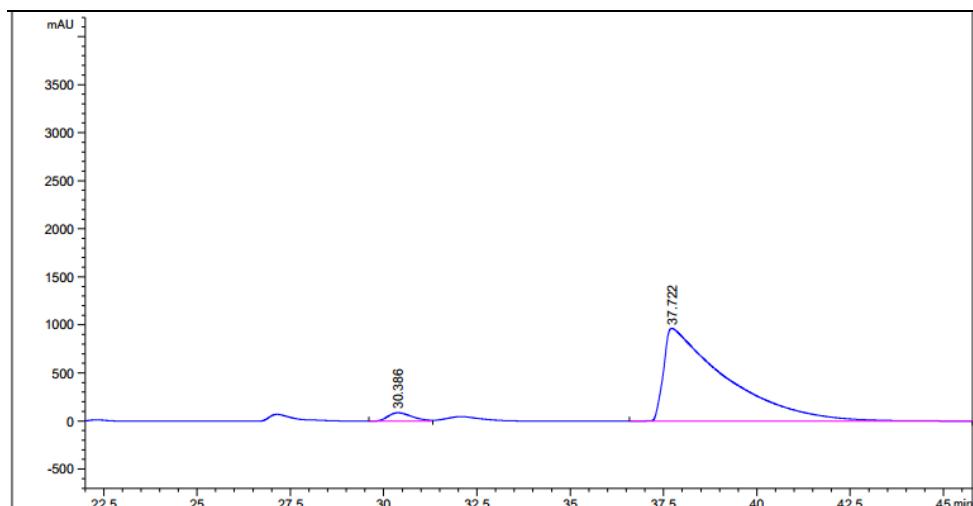




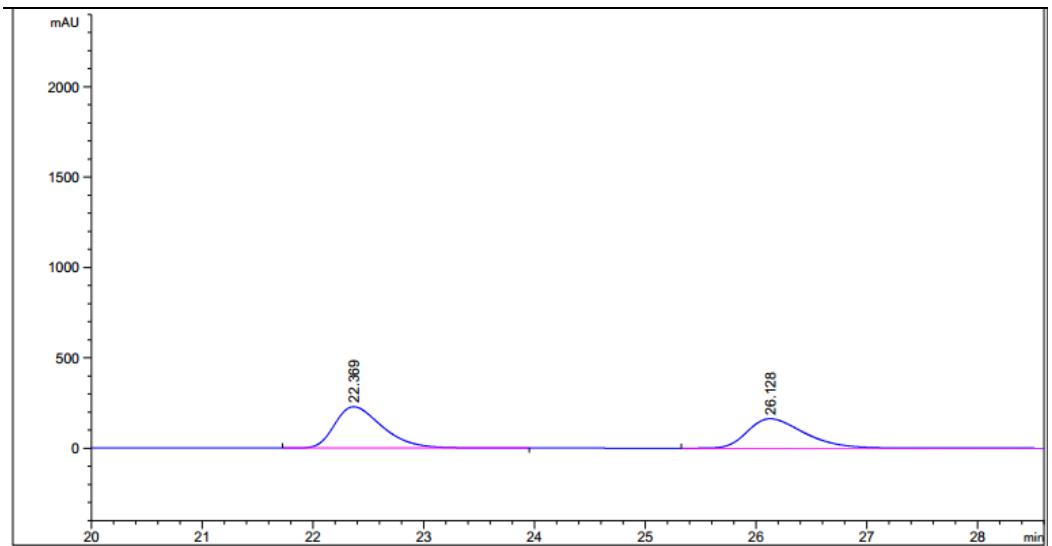
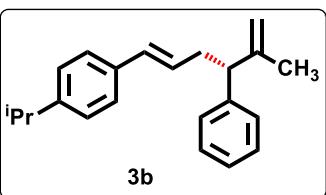
## 8. Copies of HPLC Traces for Chiral Products



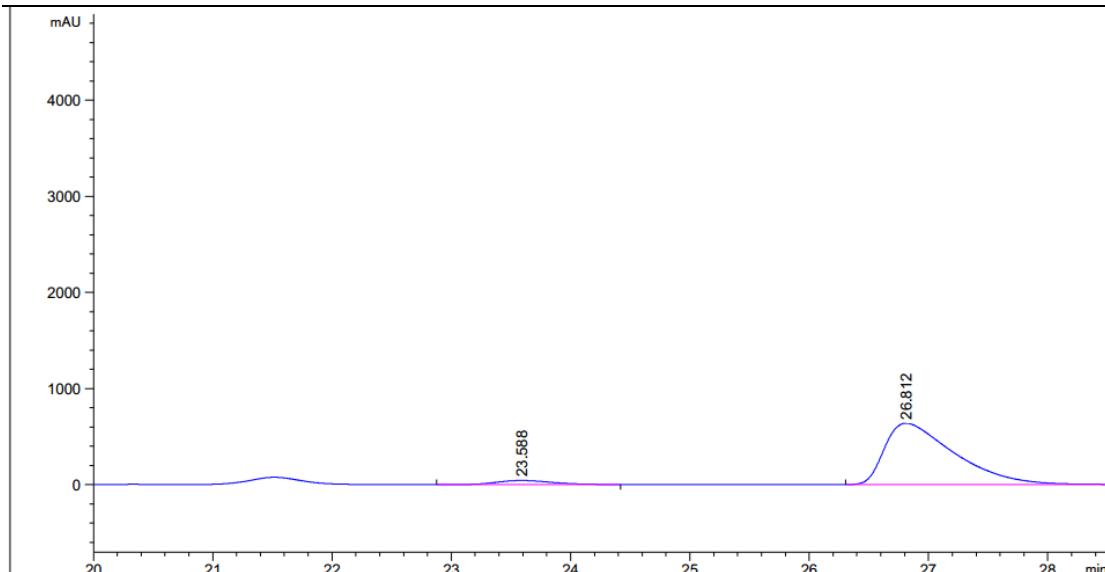
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	28.563	0.6777	2.32029e <sup>4</sup>	570.64282	52.2796
2	35.822	1.1649	2.11794e <sup>4</sup>	302.61514	47.7204

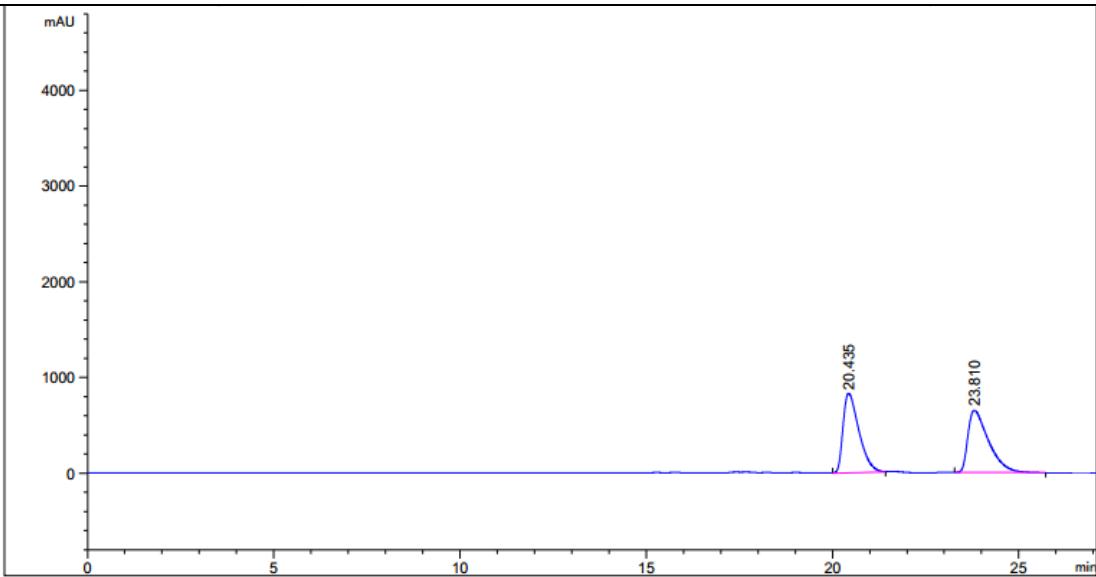
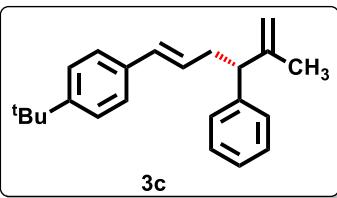


Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	30.386	0.6945	3916.02148	87.27412	3.4094
2	37.722	1.4854	1.10945e <sup>5</sup>	965.63922	96.5906

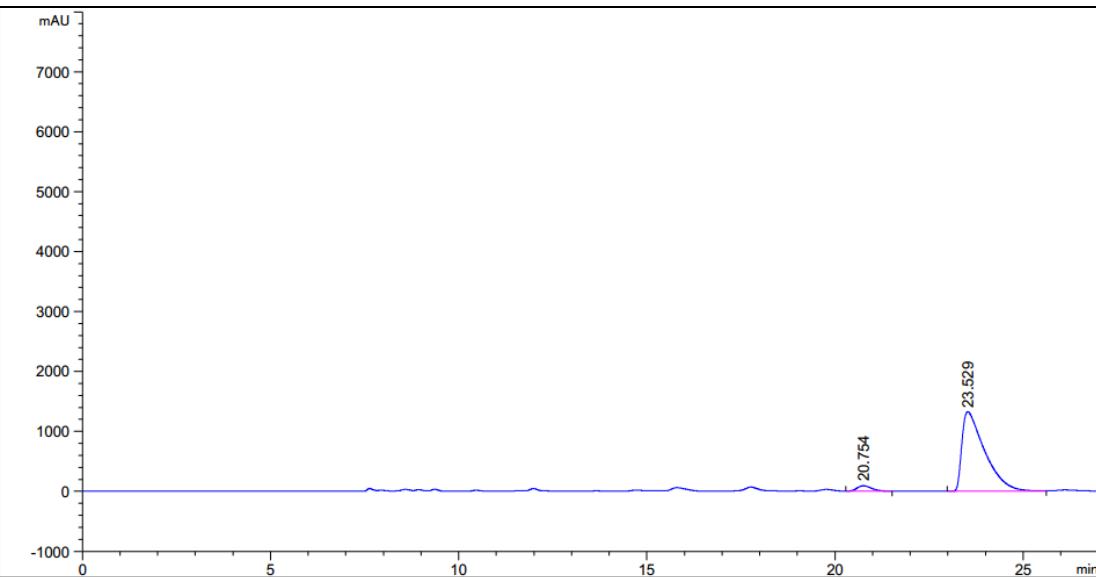


Peak	Ret. Time [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.369	0.4584	6850.30371	228.74400	54.1361
2	26.128	0.5494	5803.55469	162.60884	45.8639

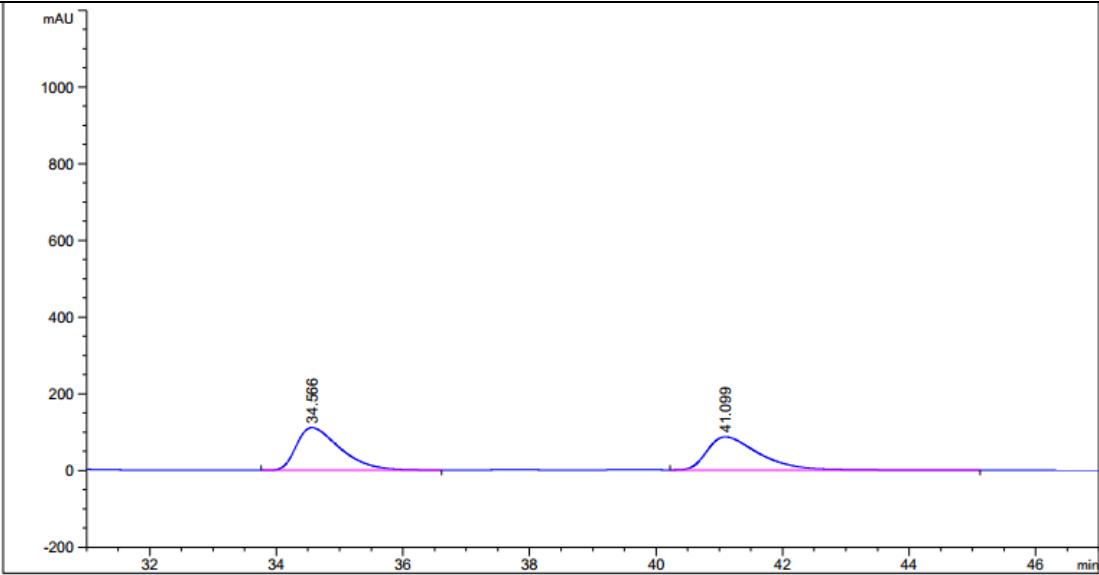
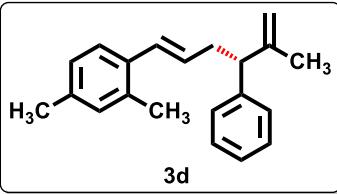




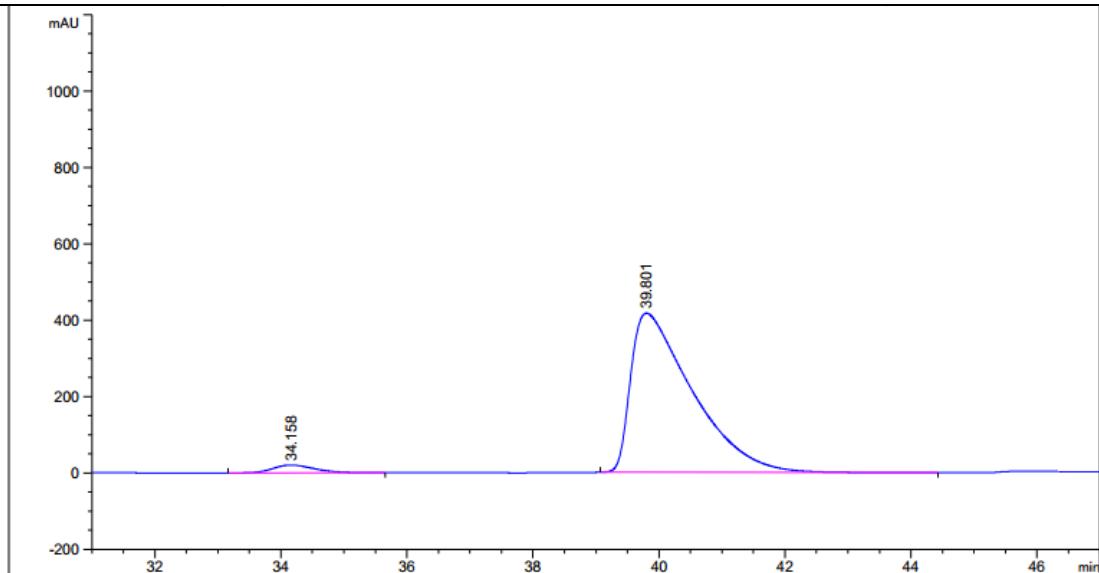
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	20.435	0.4919	2.45441e <sup>4</sup>	830.17517	49.7105
2	23.810	0.6372	2.48300e <sup>4</sup>	648.14868	50.2895



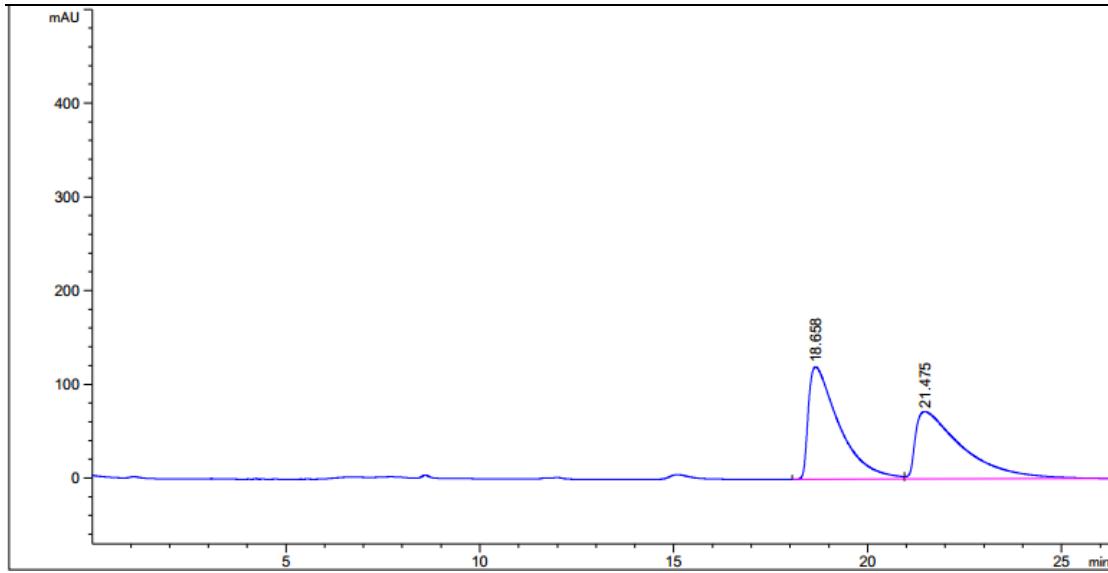
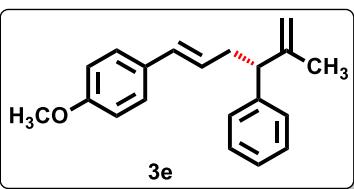
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	20.754	0.4480	2431.55615	90.07298	4.1595
2	23.529	0.7006	5.60265e <sup>4</sup>	1329.33398	95.8405



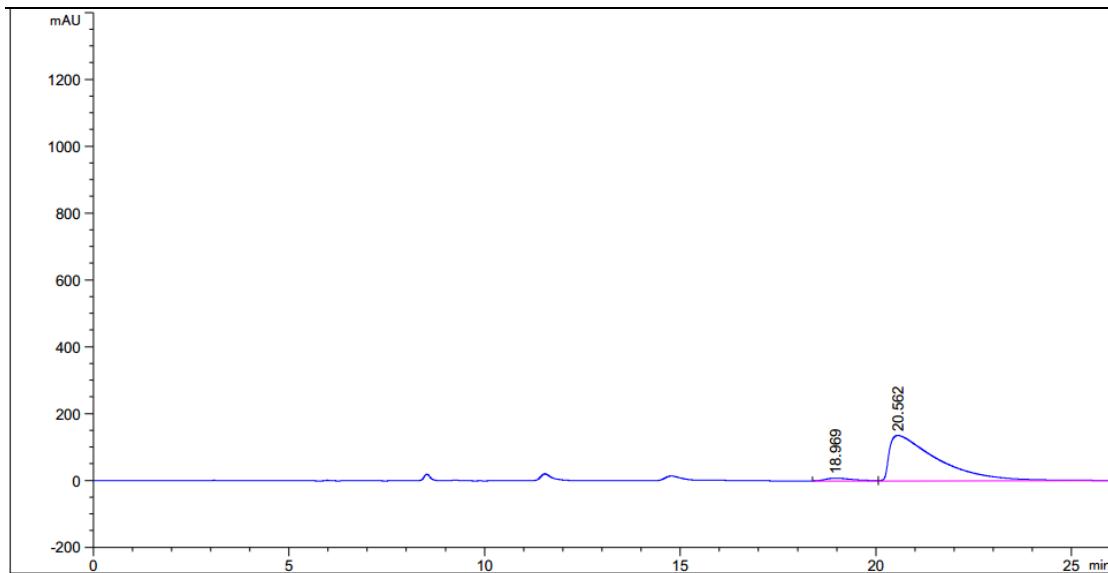
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	<b>34.566</b>	<b>0.7235</b>	<b>5318.93652</b>	<b>111.10107</b>	<b>51.8534</b>
2	<b>41.099</b>	<b>0.8603</b>	<b>4938.71533</b>	<b>86.46931</b>	<b>48.1466</b>



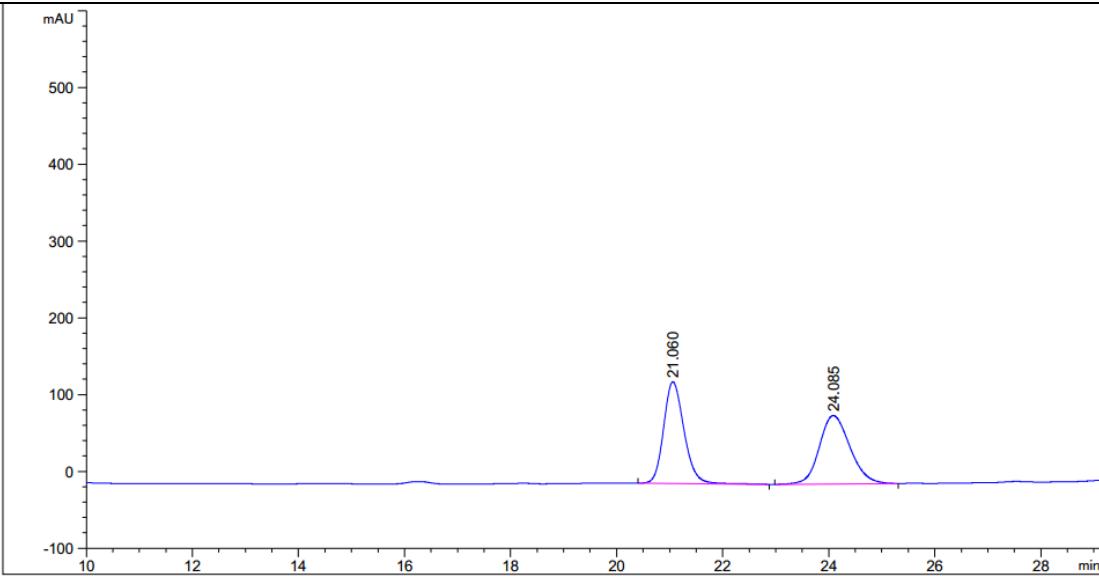
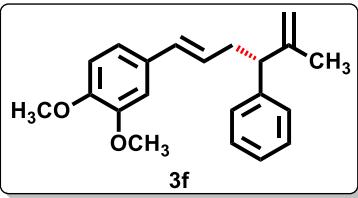
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	<b>34.158</b>	<b>0.7031</b>	<b>934.13037</b>	<b>20.44251</b>	<b>3.1962</b>
2	<b>39.801</b>	<b>0.9401</b>	<b>2.82921e<sup>4</sup></b>	<b>416.72687</b>	<b>96.8038</b>



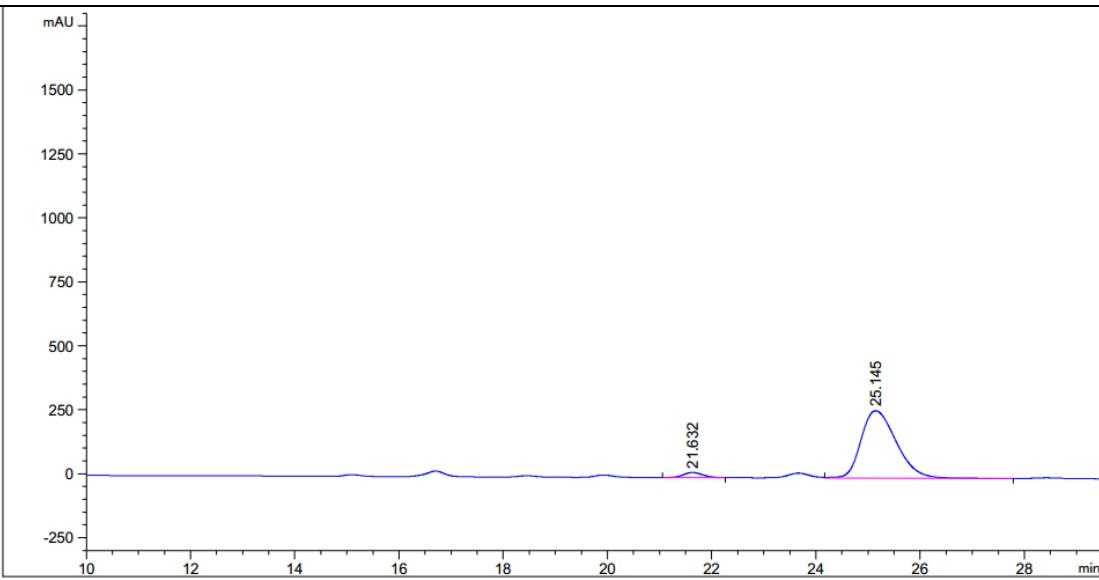
Peak #	Ret. Time [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.658	0.8041	6629.76172	120.08854	52.3172
2	21.475	1.1932	6042.47314	71.91923	47.6828



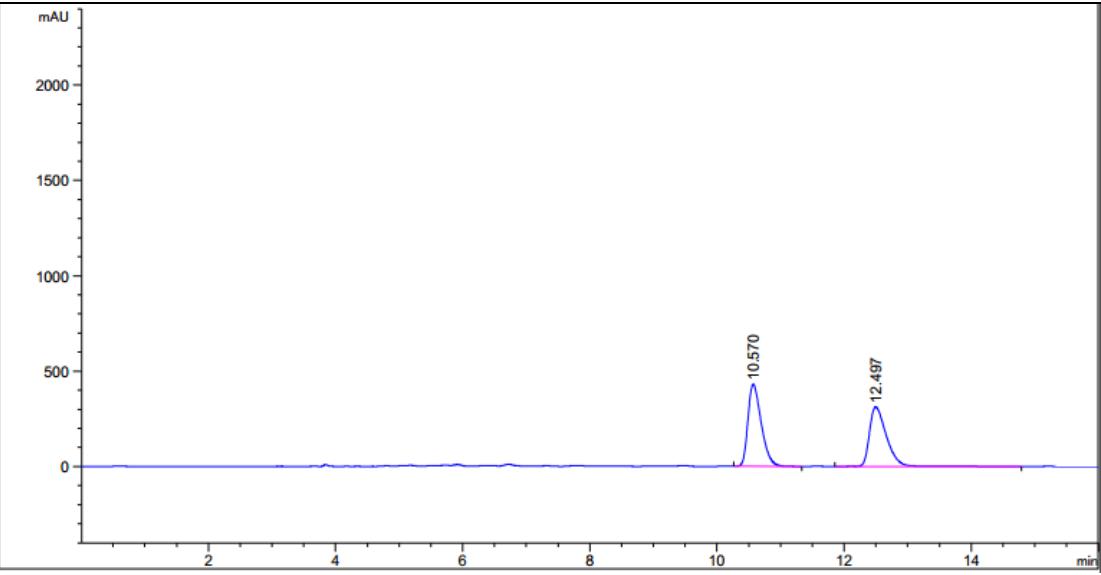
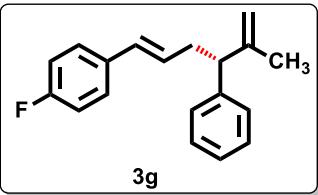
Peak #	Ret. Time [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.969	0.7625	389.39426	8.38979	3.2410
2	20.562	1.4194	1.16251e <sup>4</sup>	135.62494	96.7590



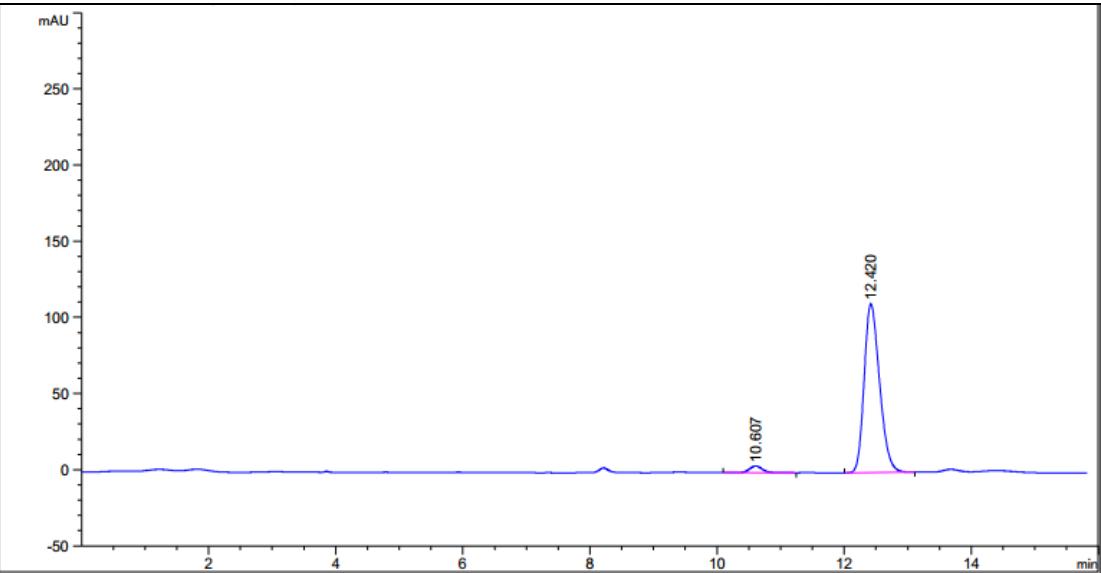
Peak #	Ret. Time [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.060	0.4126	3530.24976	132.19418	49.7755
2	24.085	0.6219	3562.08813	89.01189	50.2245



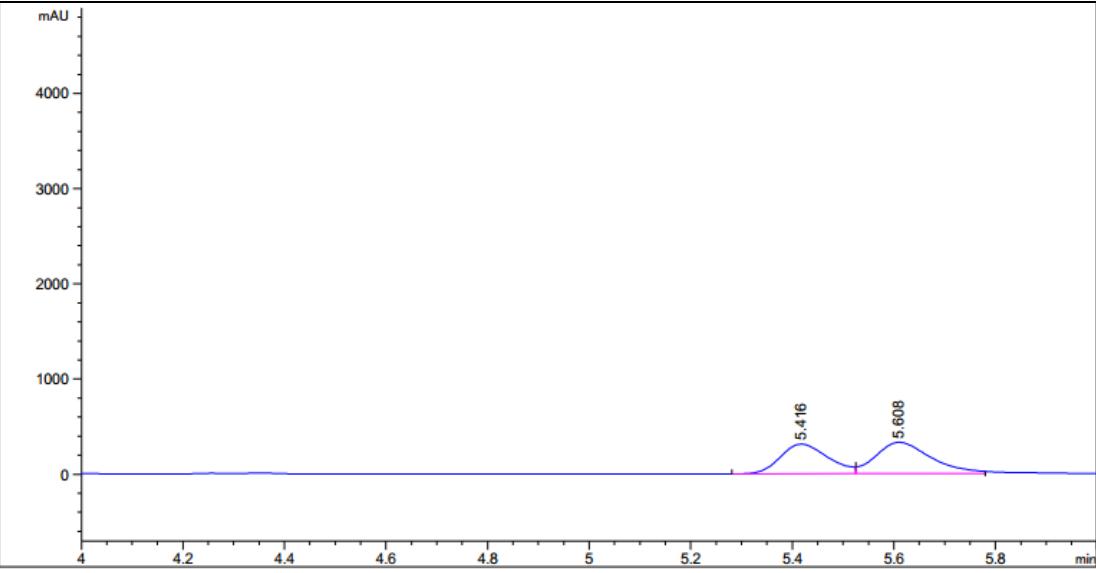
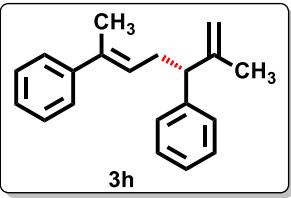
Peak #	Ret. Time [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.632	0.4272	506.44952	19.66724	3.9299
2	25.145	0.7827	1.23807e <sup>4</sup>	263.52487	96.0701



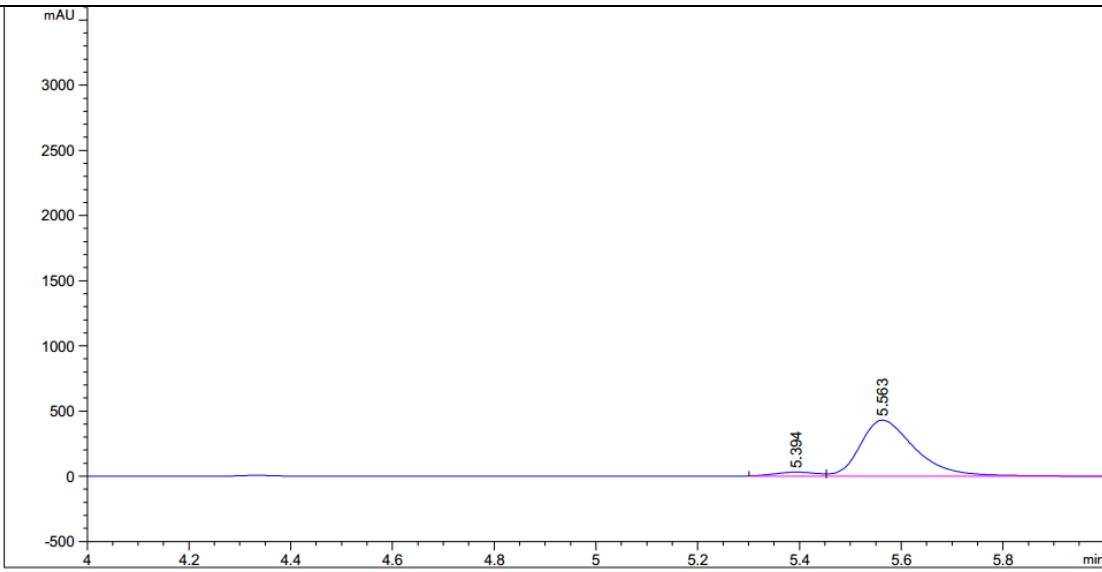
Peak #	Ret. Time [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.570	0.2427	6269.53564	430.27206	51.3084
2	12.497	0.2823	5949.77246	313.57324	48.6916



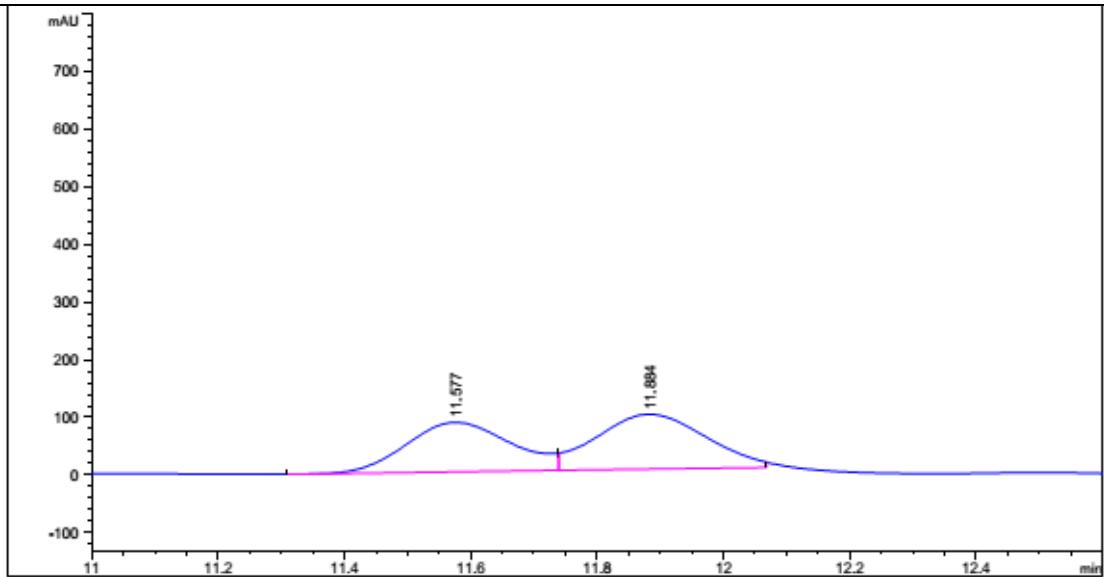
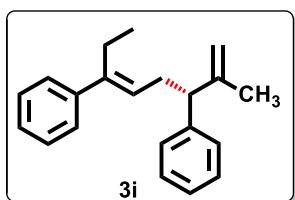
Peak #	Ret. Time [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.607	0.2230	64.14311	4.40324	3.3199
2	12.420	0.2598	1867.94470	110.71239	96.6801



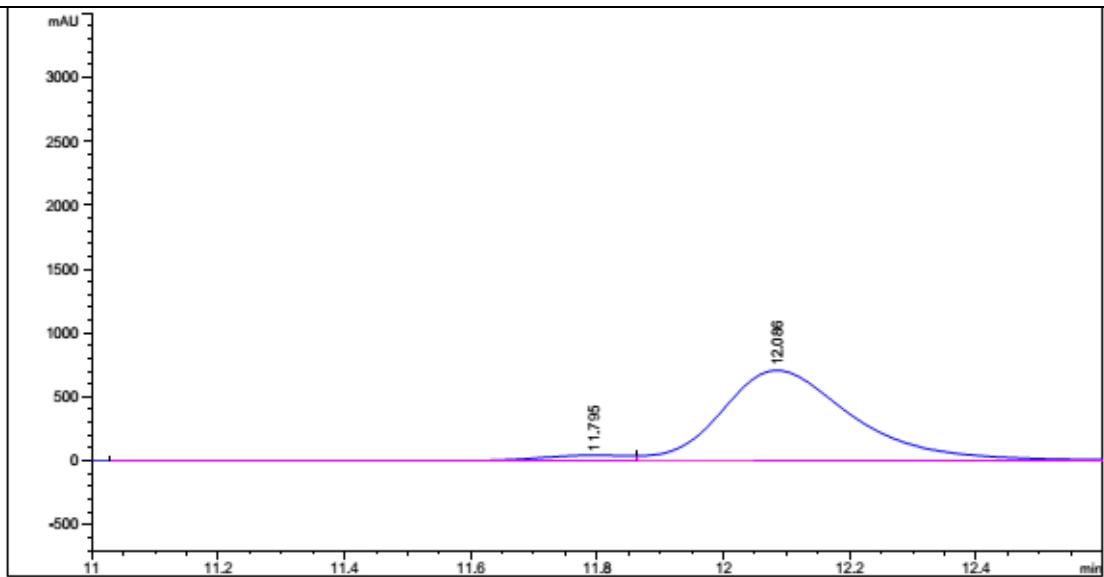
Peak	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
#					
1	5.416	0.1089	2067.66772	312.21786	45.5663
2	5.608	0.1225	2470.04077	329.90192	54.4337



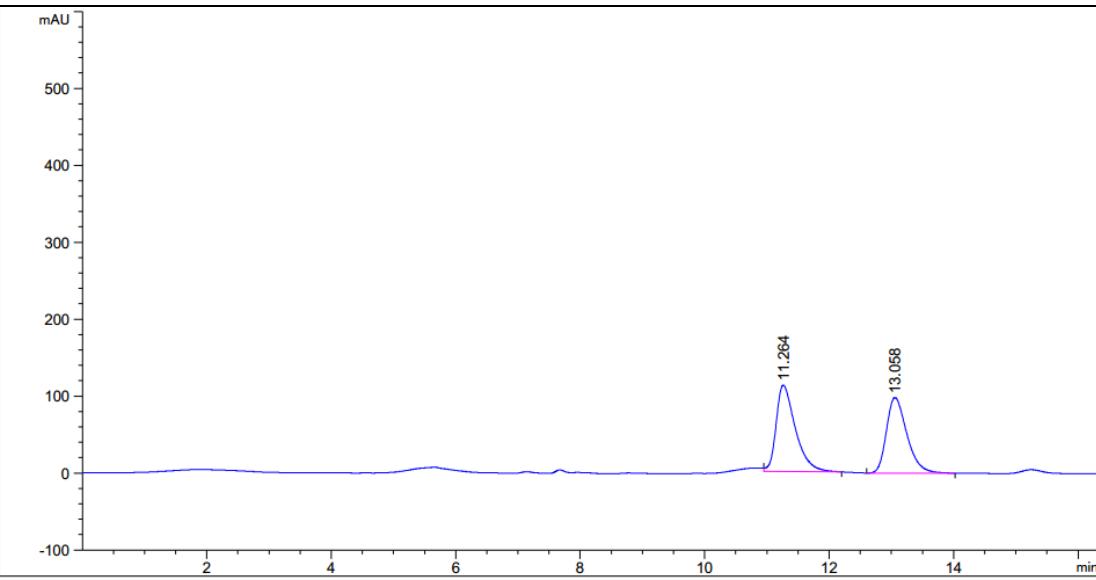
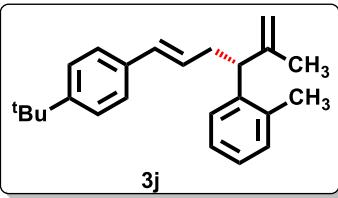
Peak	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
#					
1	5.394	0.0961	173.87526	30.15701	5.1460
2	5.563	0.1232	3204.98340	429.35303	94.8540



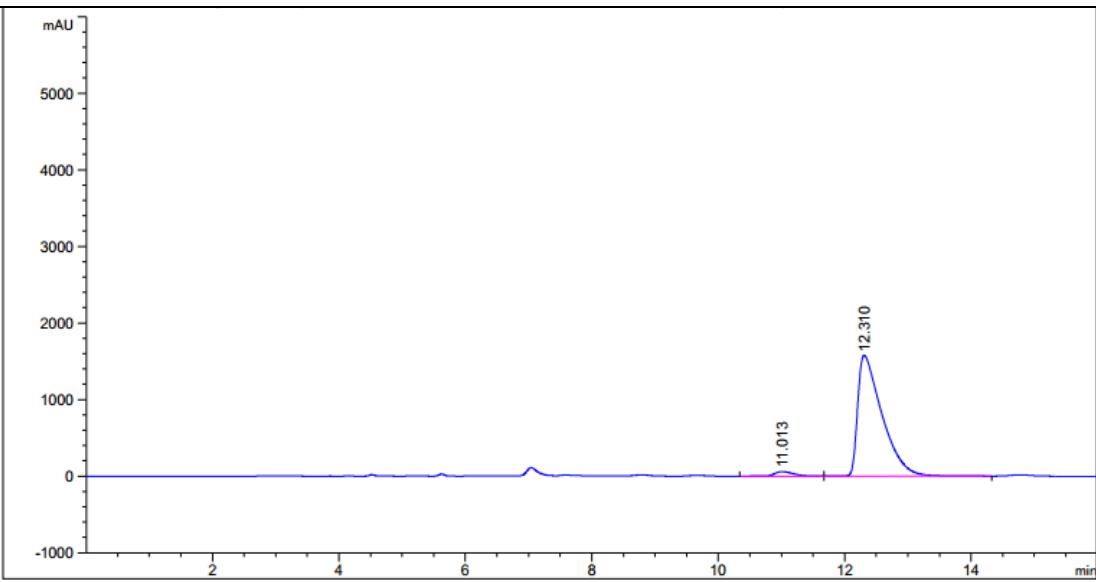
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	11.577	0.1927	995.23657	85.84478	46.5720
2	11.884	0.2002	1141.74878	95.05934	53.4280



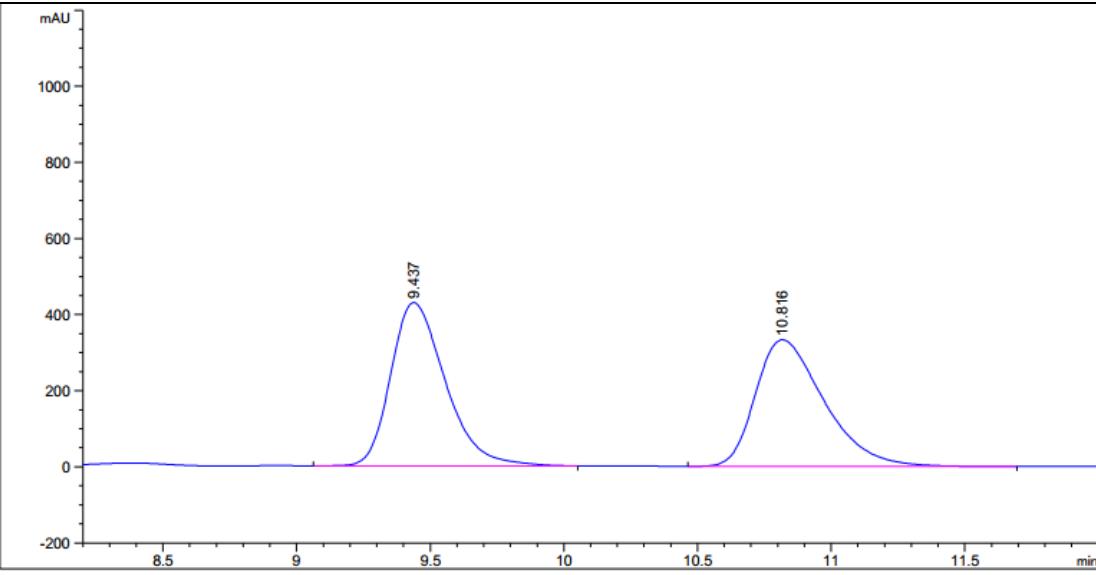
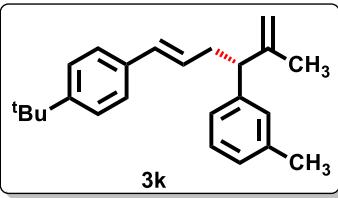
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	11.795	0.1710	435.83896	42.47535	4.0607
2	12.086	0.2419	1.02972e4	708.24408	95.9393



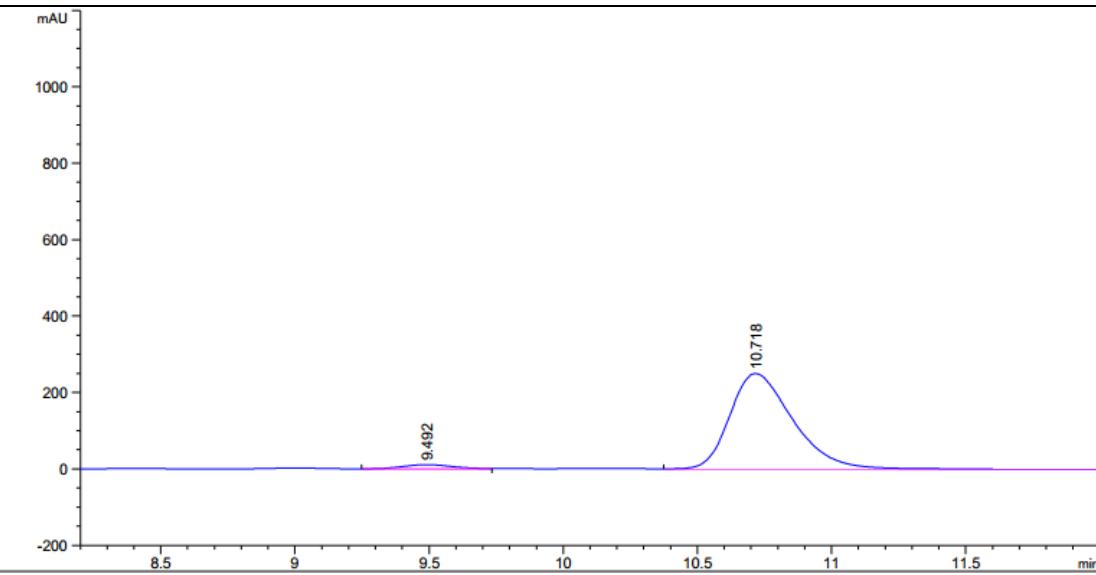
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	11.264	0.3541	2418.16724	112.32983	51.7921
2	13.058	0.3798	2250.81689	98.32371	48.2079



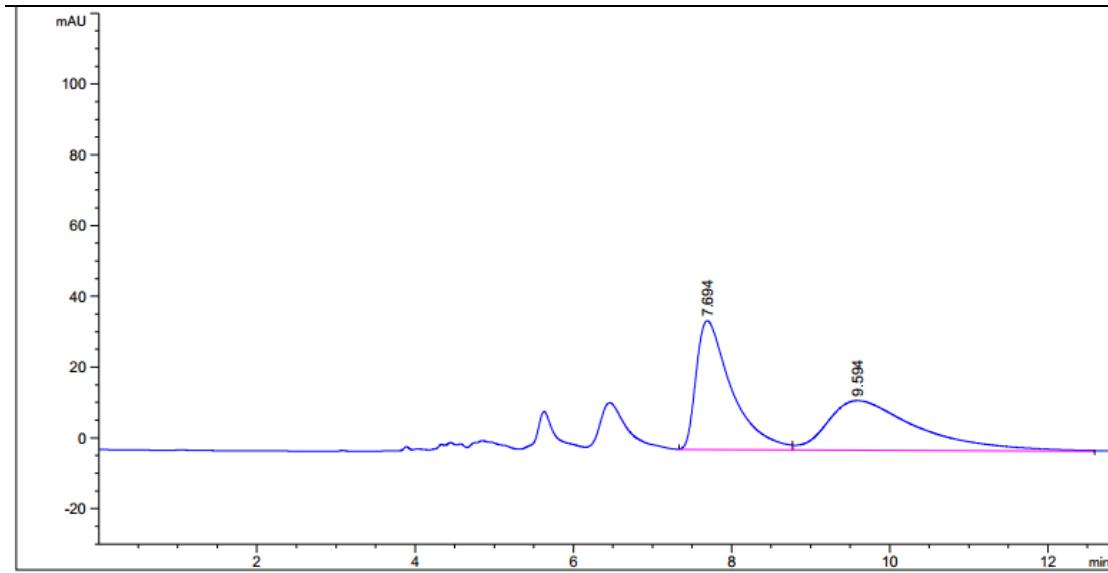
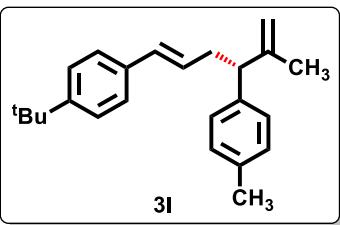
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	11.013	0.3162	1257.21277	60.07287	2.8993
2	12.310	0.3903	4.21051e <sup>4</sup>	1577.94177	97.1007



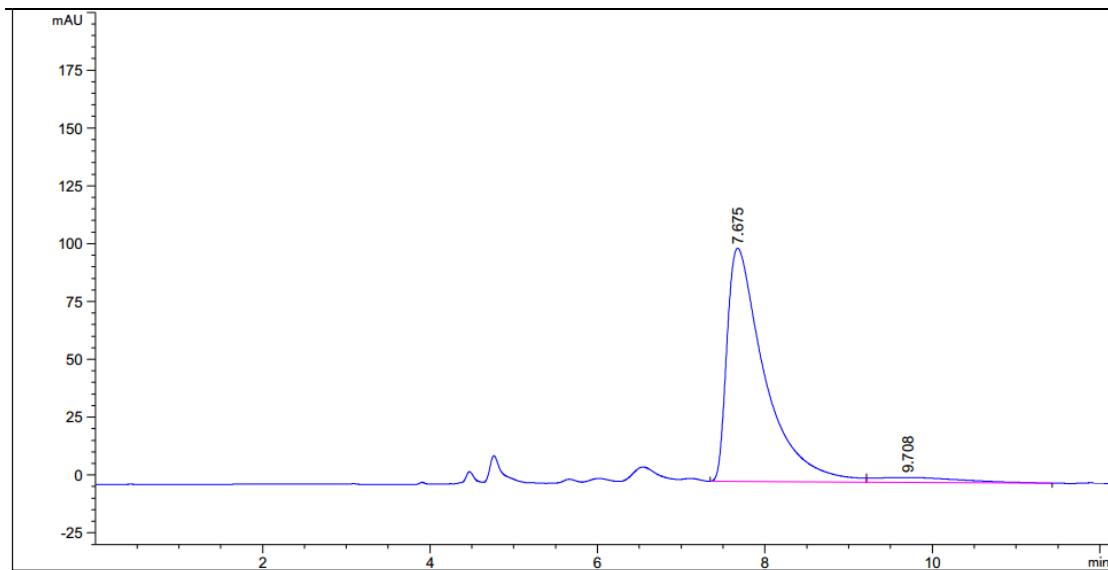
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	9.437	0.2366	6099.33398	429.36243	50.7244
2	10.816	0.2727	5925.12305	332.74637	49.2756



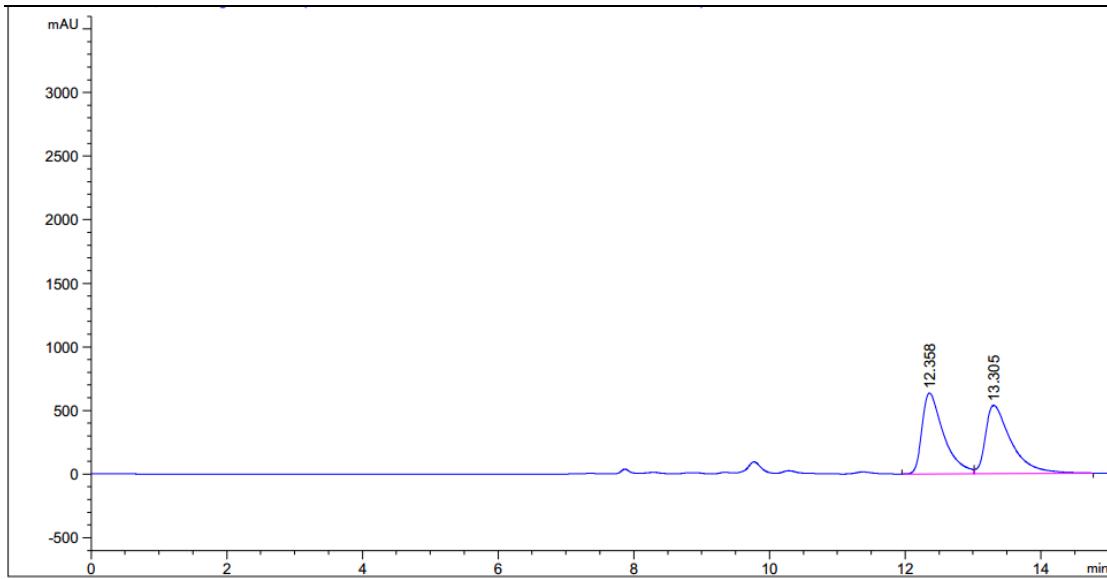
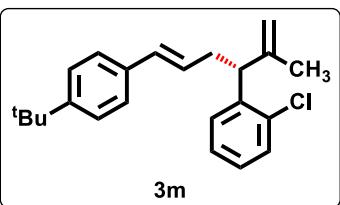
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	9.492	0.2152	142.09402	11.00443	3.3876
2	10.718	0.2705	4052.43335	249.37569	96.6124



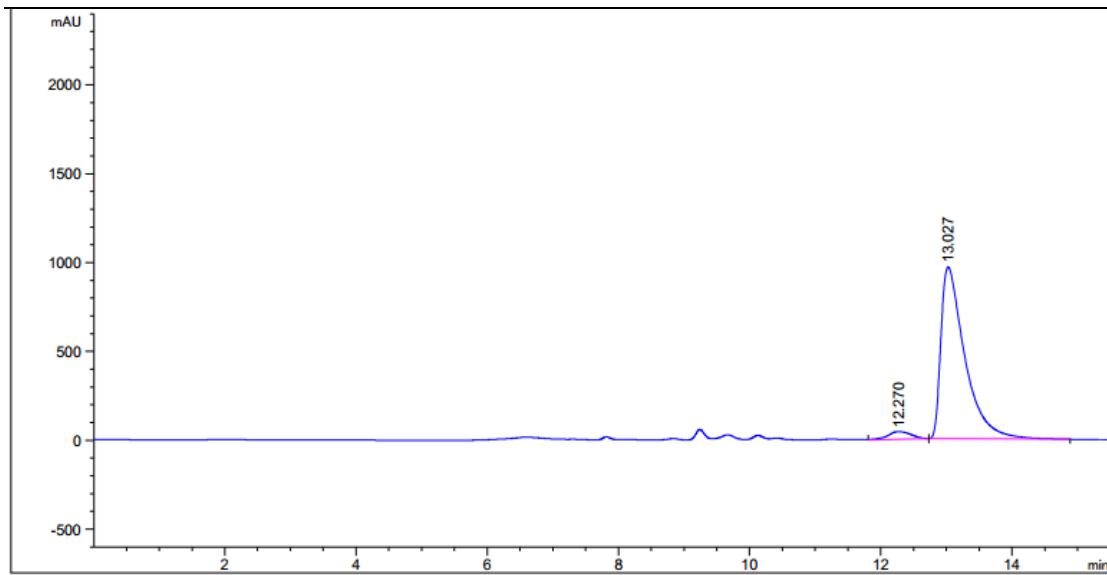
Peak	Ret. Time	Width	Area	Height	Area
#	[min]	[min]	[mAU * s]	[mAU]	%
1	7.694	0.5207	1138.80261	36.45444	50.5467
2	9.594	1.3114	1114.16956	14.04941	49.4533



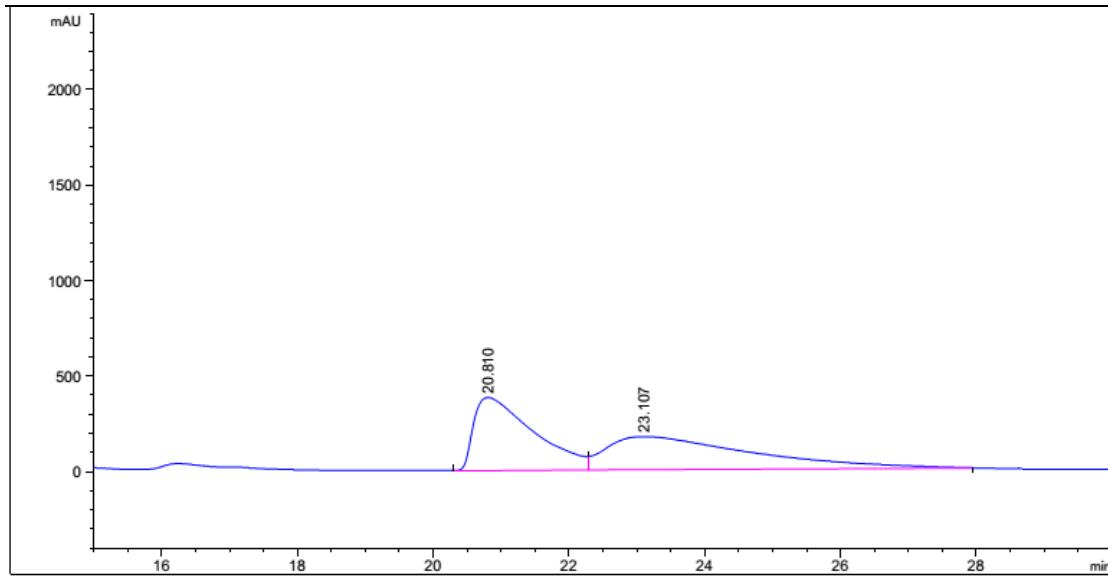
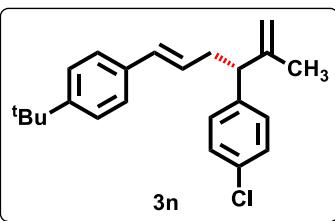
Peak	Ret. Time	Width	Area	Height	Area
#	[min]	[min]	[mAU * s]	[mAU]	%
1	7.675	0.5149	3149.39136	100.89886	95.1456
2	9.708	1.2185	160.68565	2.19779	4.8544



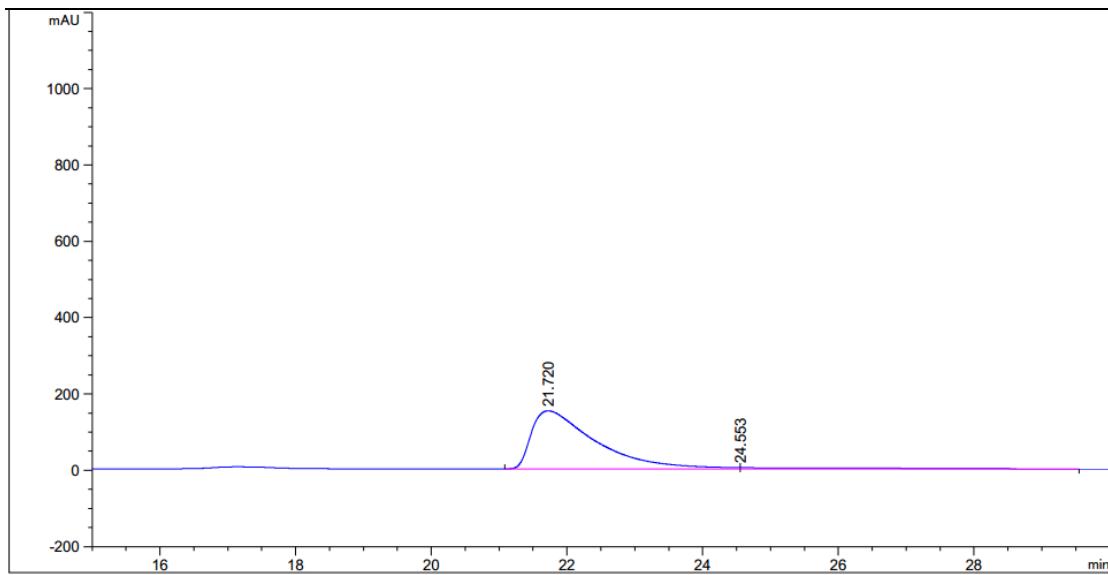
Peak	Ret. Time	Width	Area	Height	Area
#	[min]	[min]	[mAU * s]	[mAU]	%
1	12.358	0.3688	1.40713e <sup>4</sup>	635.88507	49.9516
2	13.305	0.4380	1.40986e <sup>4</sup>	536.50537	50.0484



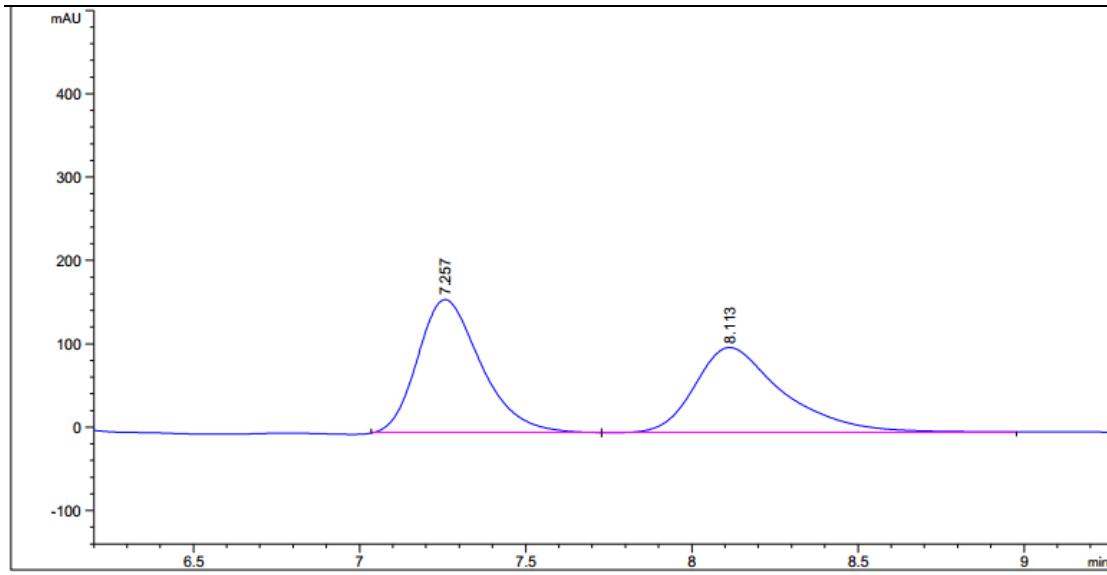
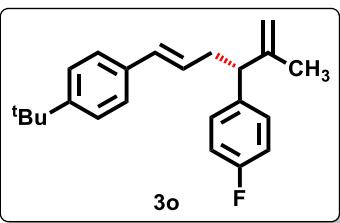
Peak	Ret. Time	Width	Area	Height	Area
#	[min]	[min]	[mAU * s]	[mAU]	%
1	12.270	0.3978	1030.33337	43.17025	4.0329
2	13.027	0.4065	2.45179e <sup>4</sup>	966.39618	95.9671



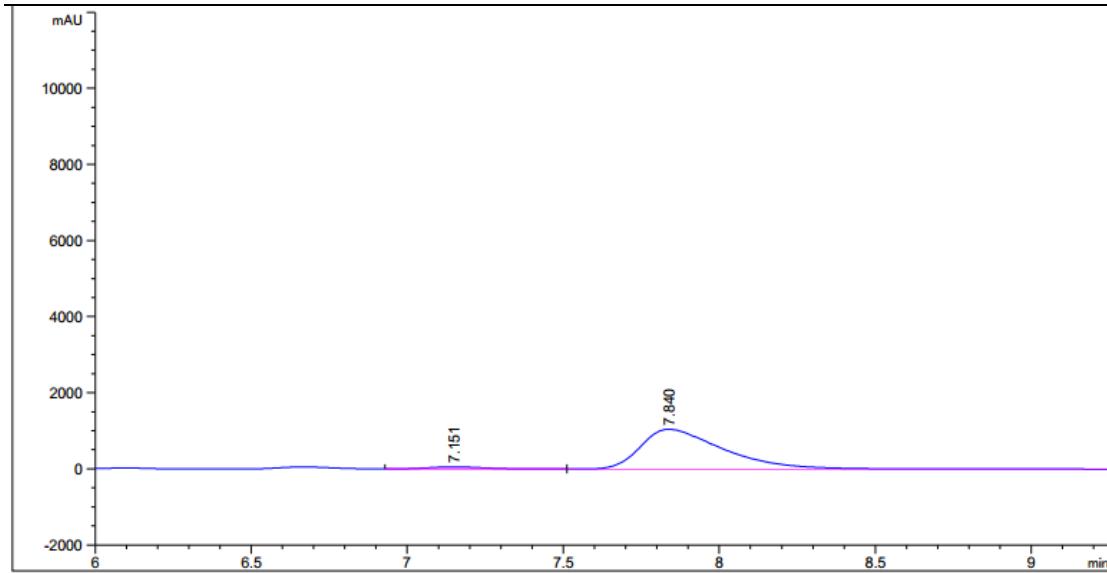
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	20.810	1.0234	2.34716e4	381.78271	47.8665
2	23.107	2.4518	2.55639e4	173.71227	52.1335



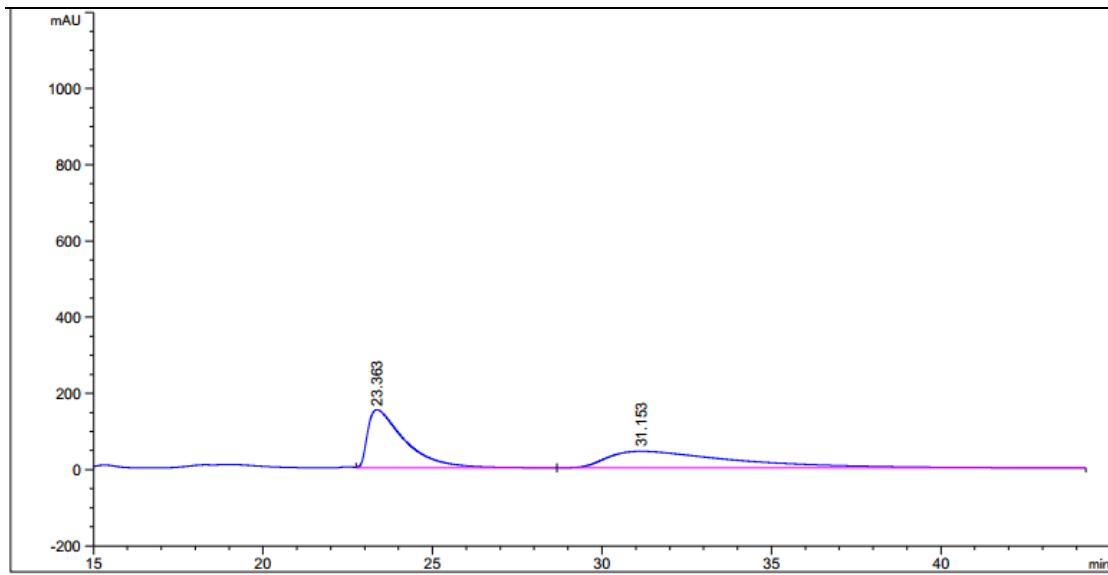
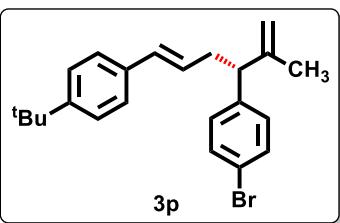
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	21.720	1.0965	1.00623e4	152.55455	95.3245
2	24.553	2.4180	493.53549	3.40177	4.6755



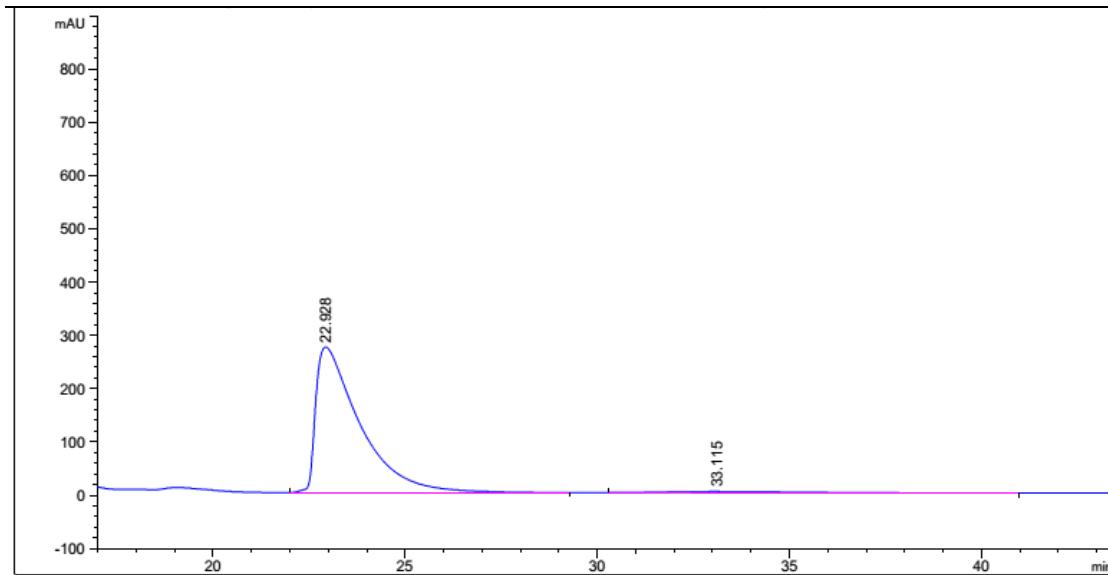
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	7.257	0.2183	2088.07104	159.07199	52.8867
2	8.113	0.3046	1860.12622	101.56214	47.1133



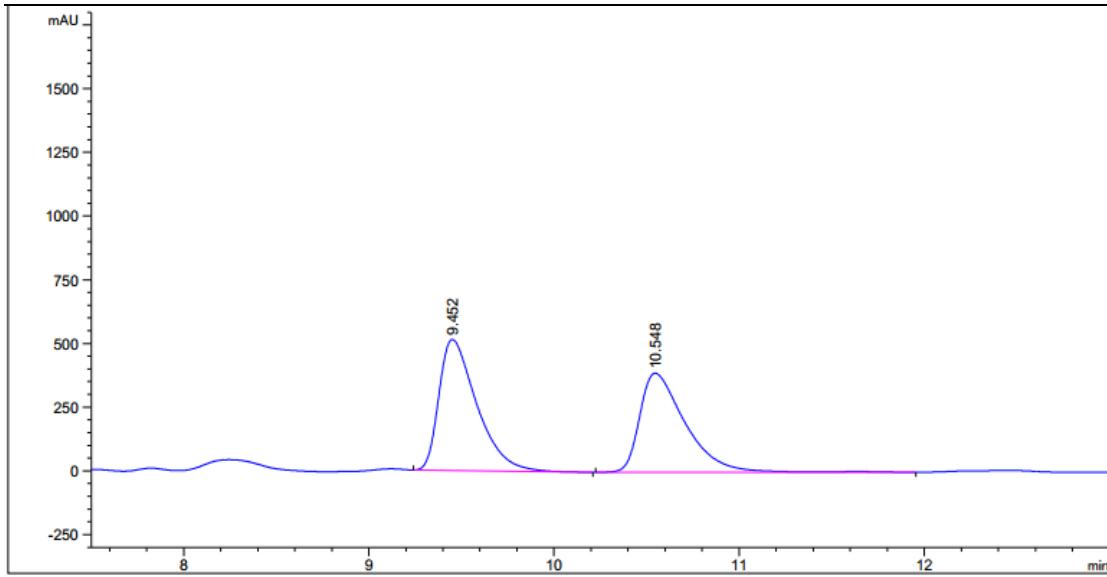
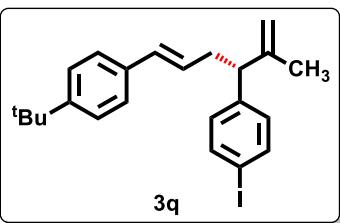
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	7.151	0.2033	778.33716	58.47493	3.8840
2	7.840	0.2748	1.92611e <sup>4</sup>	1046.29395	96.1160



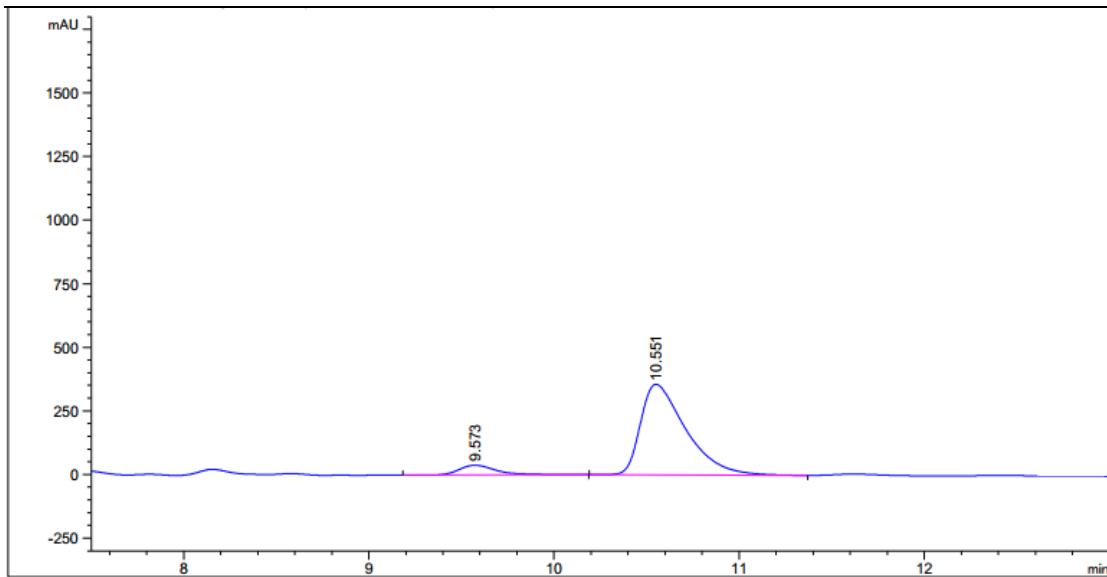
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	23.363	1.2586	1.16557e4	152.84065	50.6791
2	31.153	3.3407	1.13433e4	43.18190	49.3209



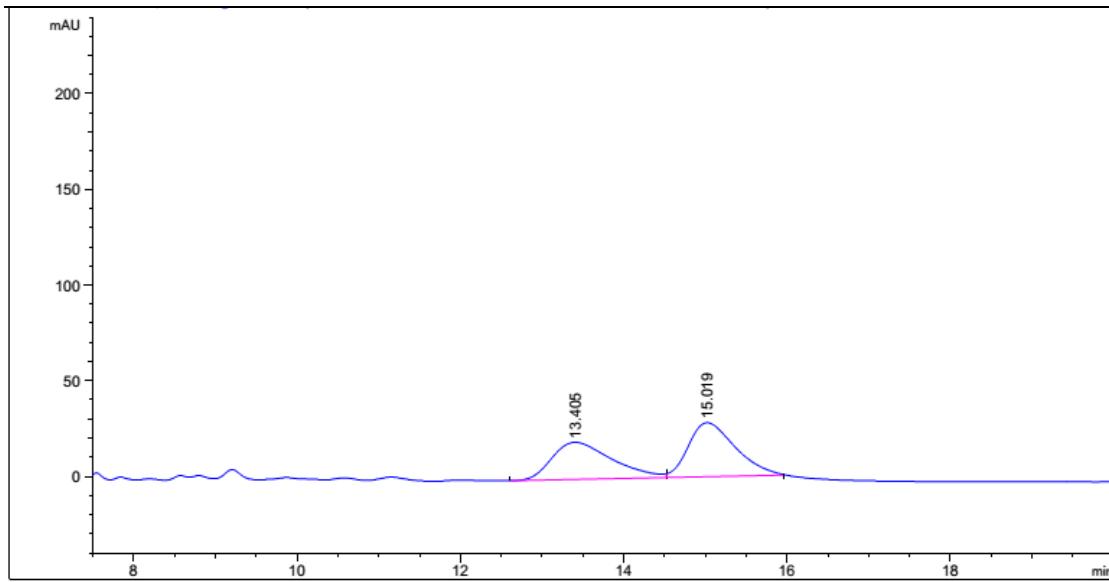
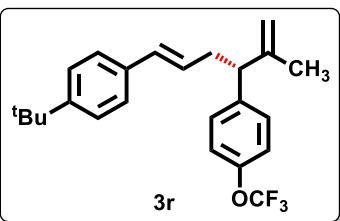
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	22.928	1.3278	2.18193e4	273.37143	96.9034
2	33.115	4.4716	697.25415	2.59884	3.0966



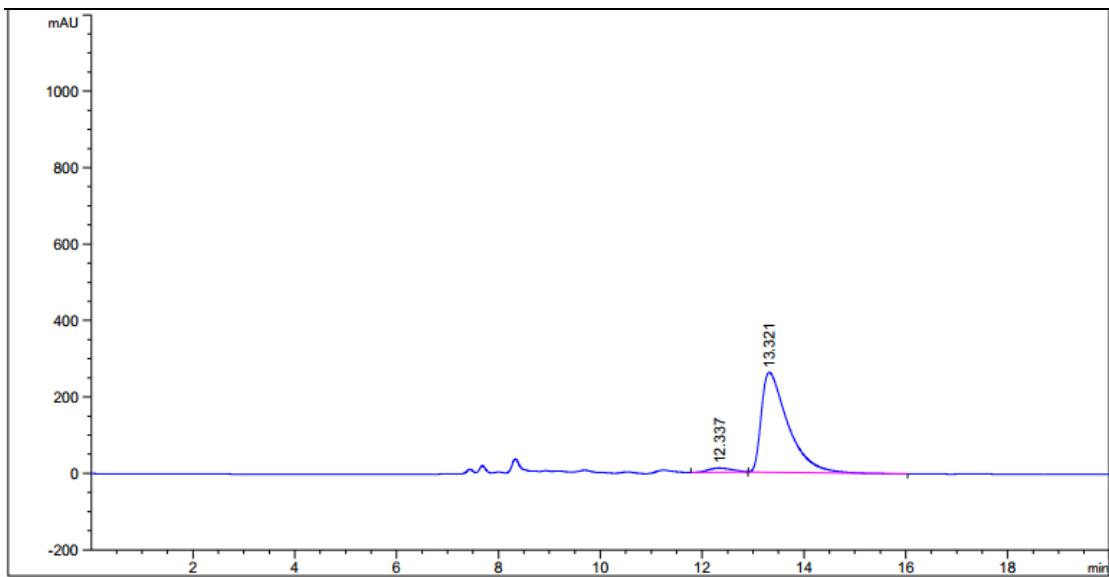
Peak	Ret. Time	Width	Area	Height	Area
#	[min]	[min]	[mAU * s]	[mAU]	%
1	9.452	0.2358	7279.04834	514.03363	52.2215
2	10.548	0.2544	6659.73926	388.60910	47.7785



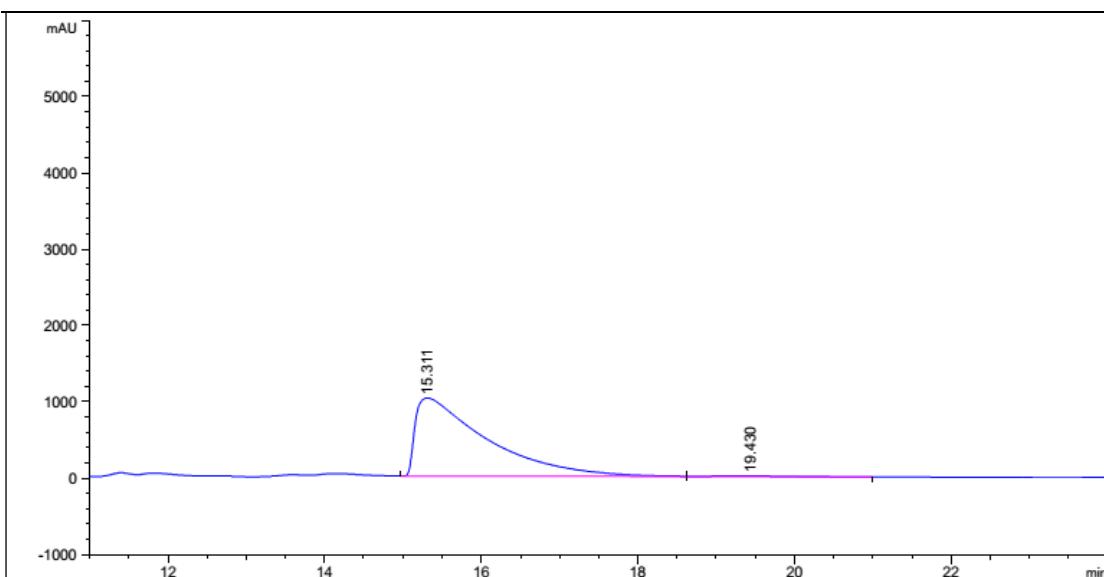
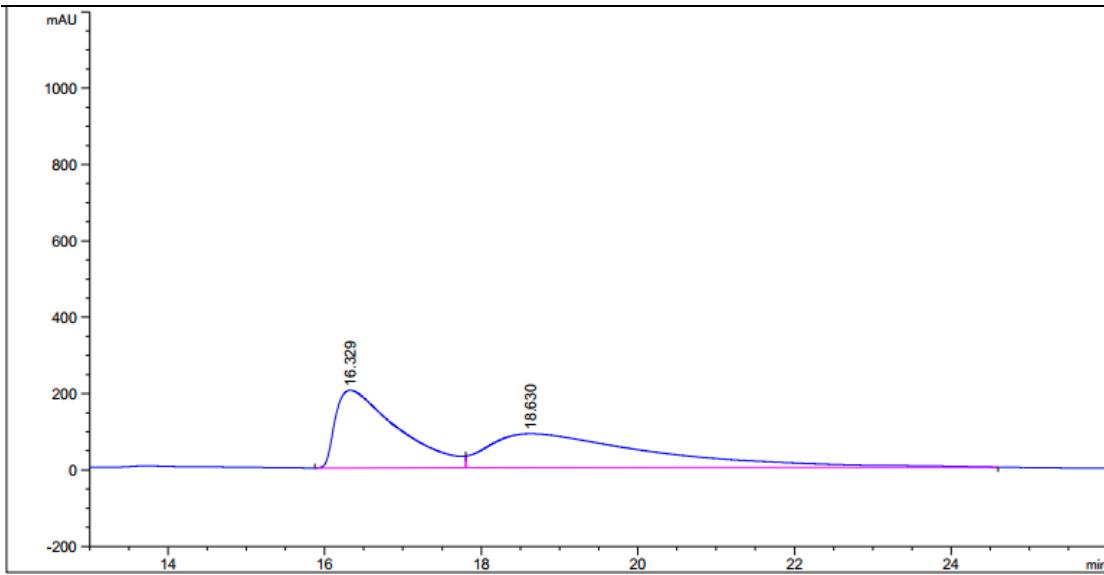
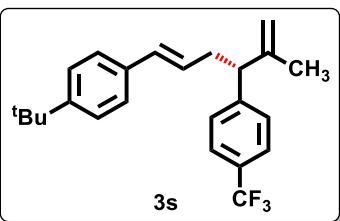
Peak	Ret. Time	Width	Area	Height	Area
#	[min]	[min]	[mAU * s]	[mAU]	%
1	9.573	0.2139	533.79907	38.22643	8.1154
2	10.551	0.2541	6043.78174	355.98837	91.8846

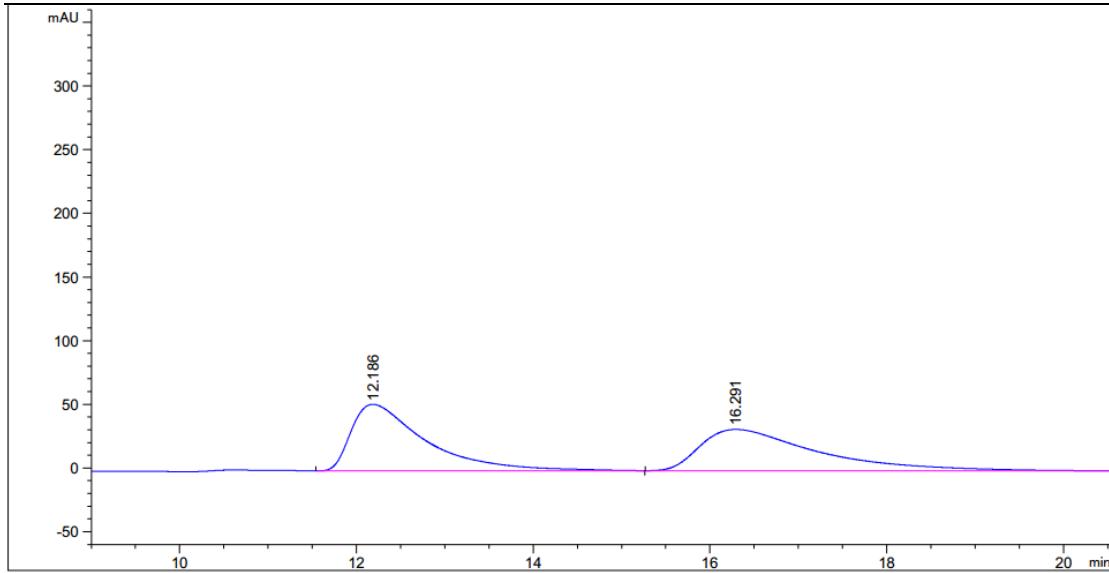
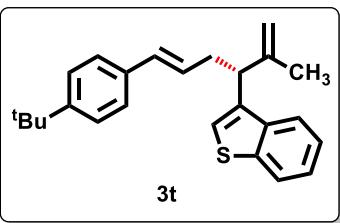


Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	13.405	0.8506	987.11475	19.34062	46.6464
2	15.019	0.6670	1129.05164	28.21390	53.3536

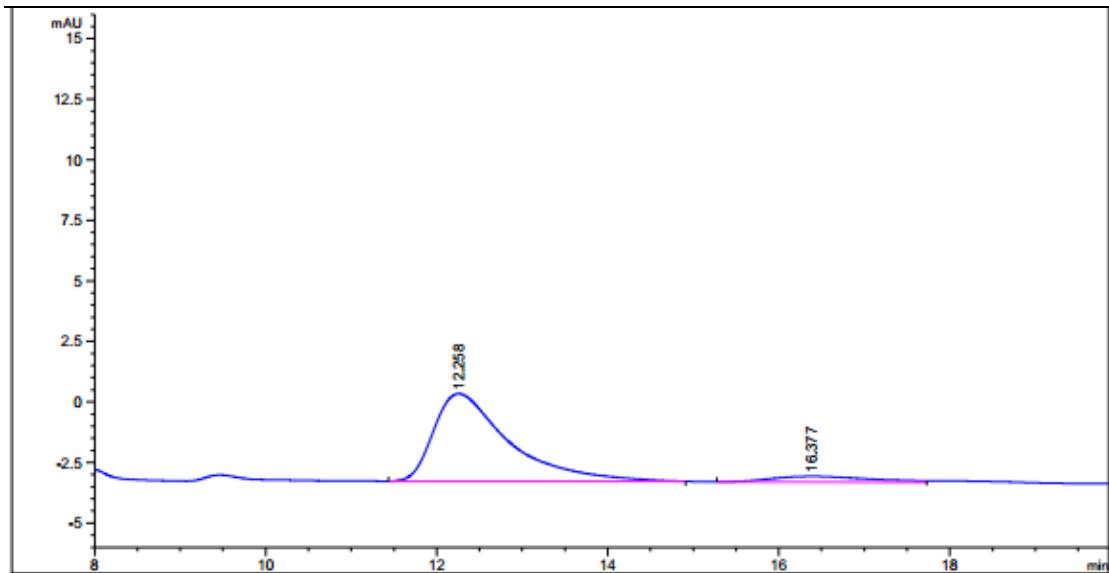


Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	12.337	0.5349	352.91824	10.85855	3.5911
2	13.321	0.6041	9474.75879	261.34335	96.4089

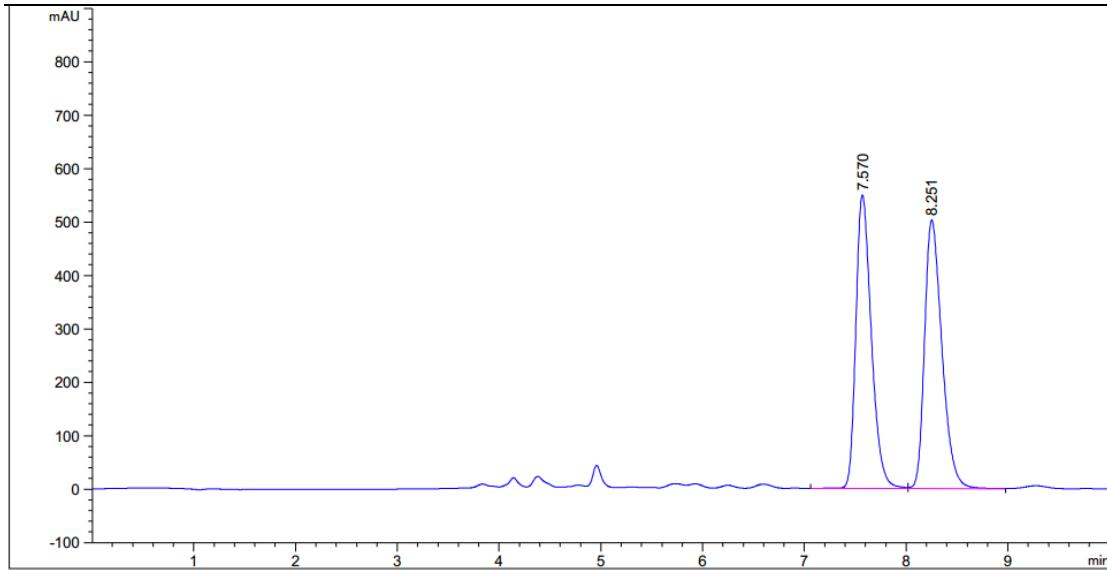
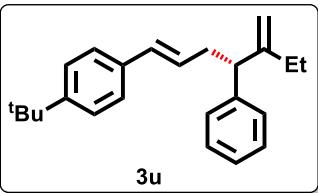




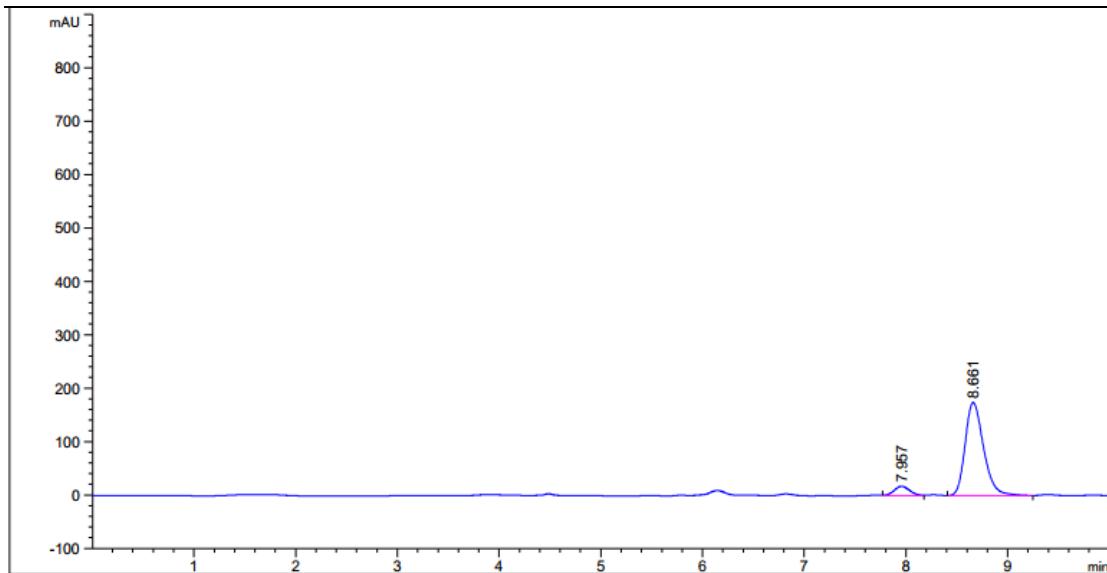
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	12.186	0.8456	3044.01489	52.33733	50.5982
2	16.291	1.3233	2972.04419	32.42663	49.4018



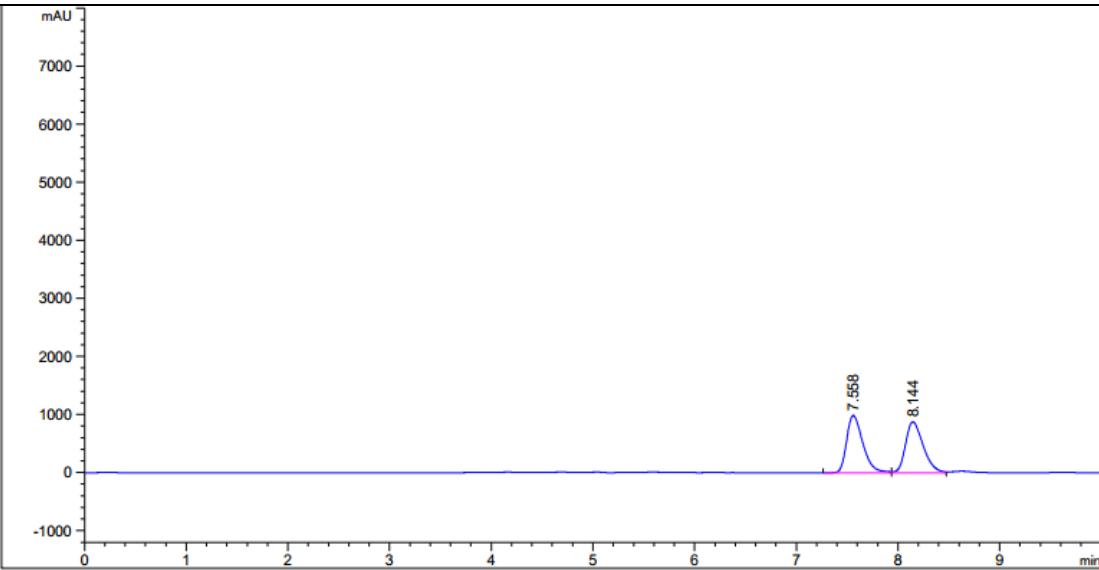
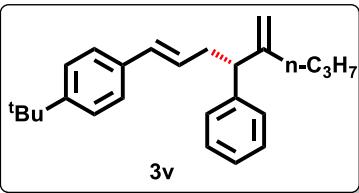
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	12.258	0.8702	220.61562	3.61885	92.3454
2	16.377	1.3100	18.28707	2.32665e-1	7.6546



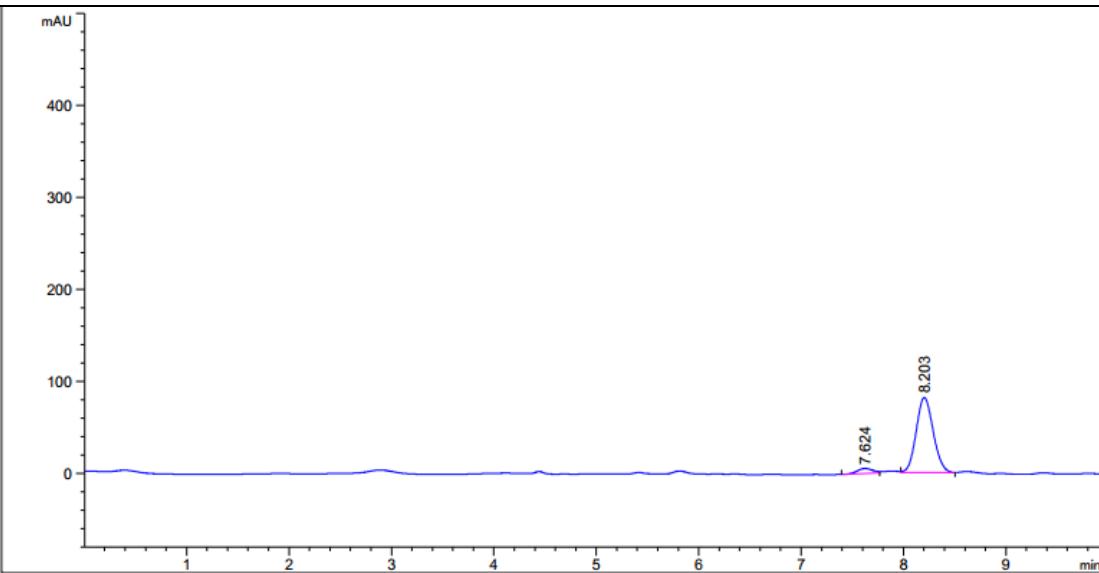
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	7.570	0.1625	5819.43262	549.81604	49.3688
2	8.251	0.1825	5968.23389	502.61896	50.6312



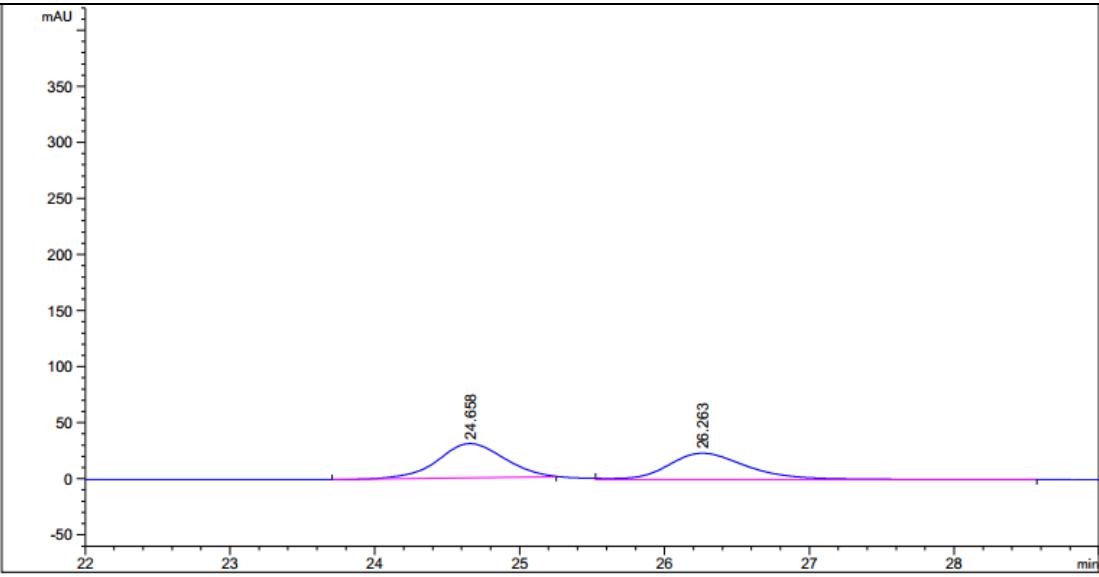
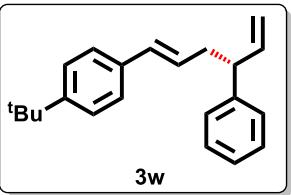
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	7.957	0.1810	192.38066	17.71098	8.0309
2	8.661	0.2100	2203.12329	174.72110	91.9691



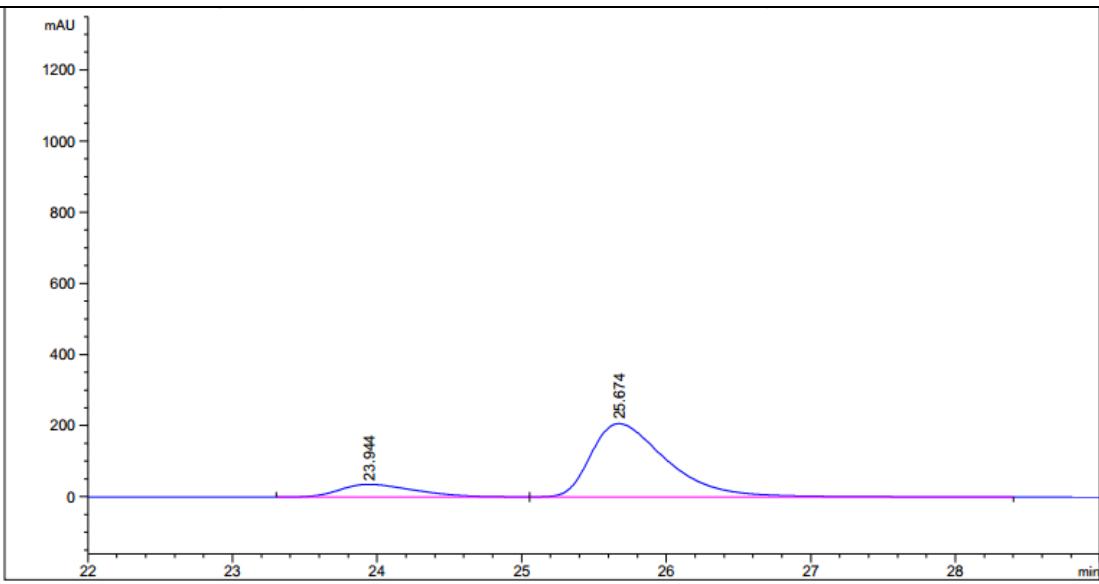
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	7.558	0.1706	1.09612e <sup>4</sup>	986.73853	50.8010
2	8.144	0.2017	1.06155e <sup>4</sup>	876.72778	49.1990



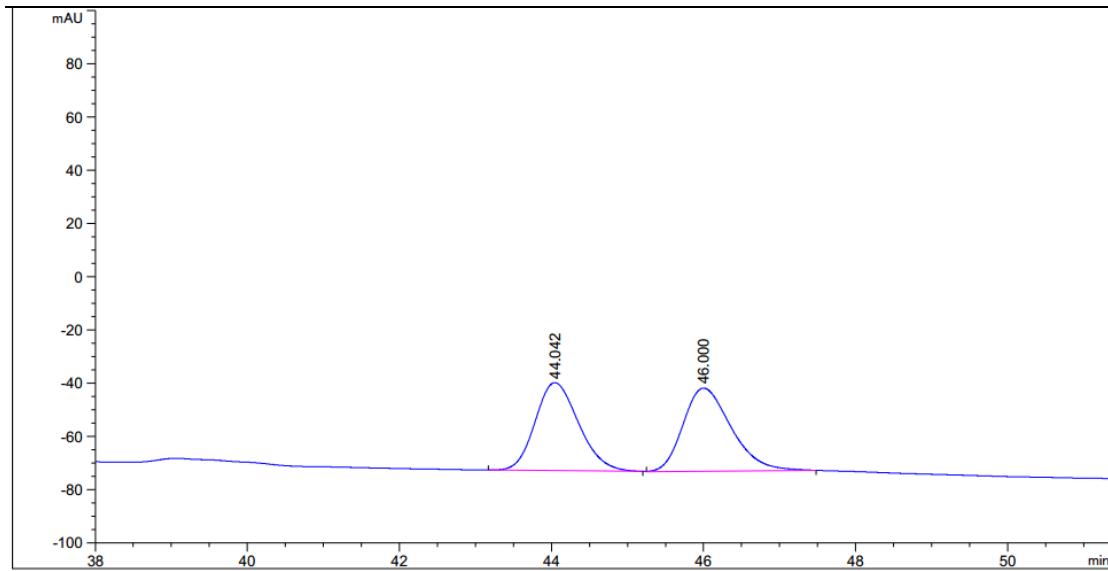
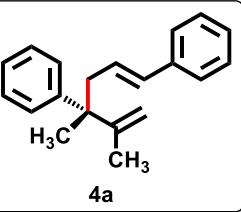
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	7.624	0.1771	58.58163	5.51326	5.8571
2	8.203	0.1925	941.60486	81.53452	94.1429



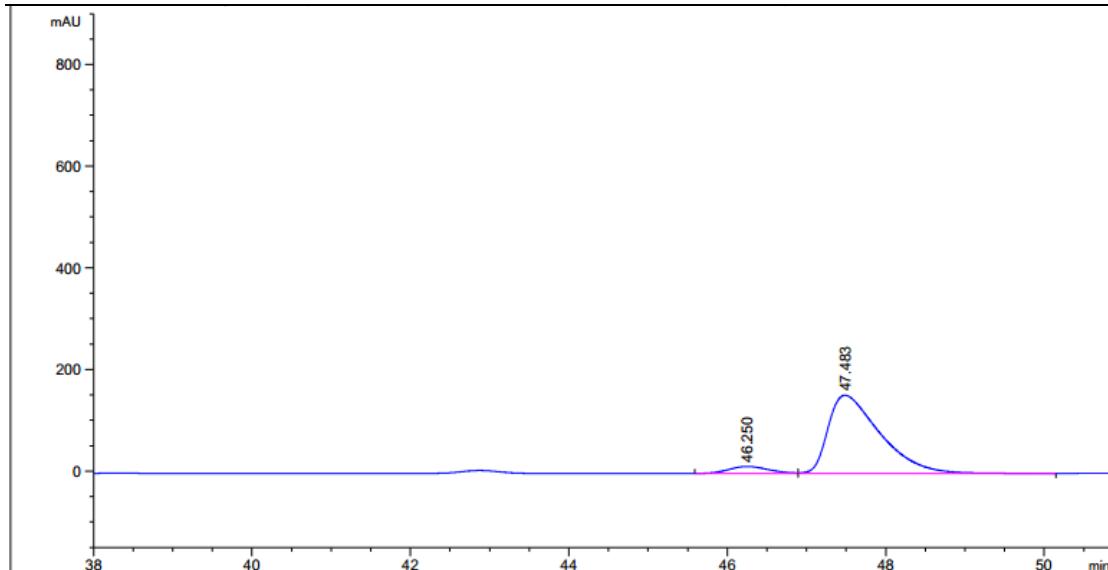
Peak #	Ret. Time [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.658	0.5275	971.43060	30.50536	51.4262
2	26.263	0.6476	917.54871	23.61549	48.5738



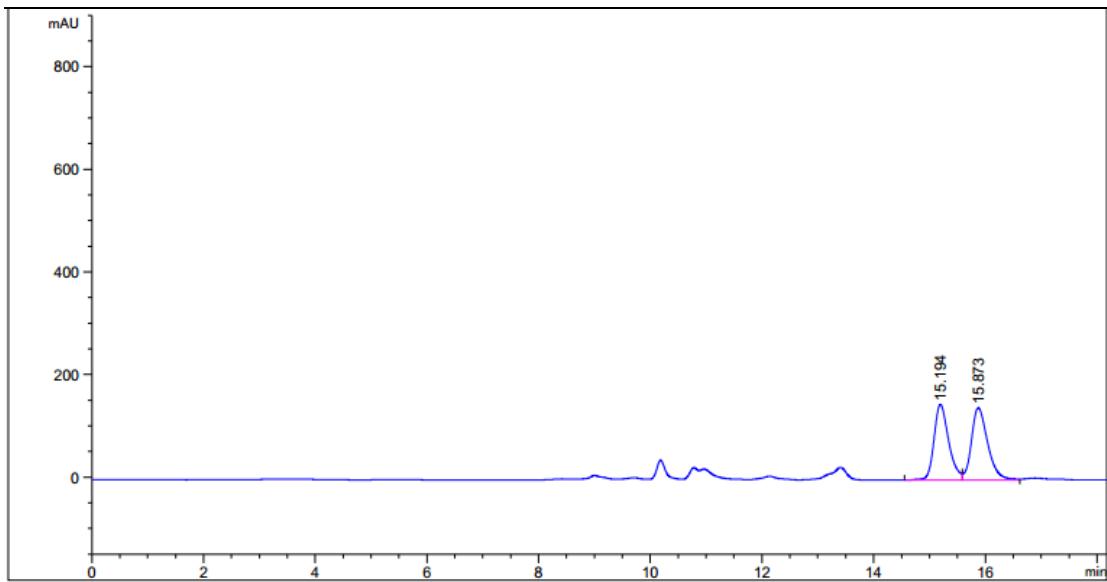
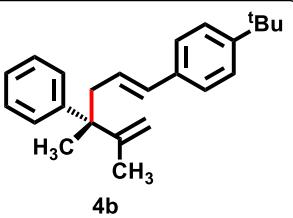
Peak #	Ret. Time [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.944	0.5521	1294.80981	35.78869	14.6473
2	25.674	0.5607	7545.11523	206.27385	85.3527



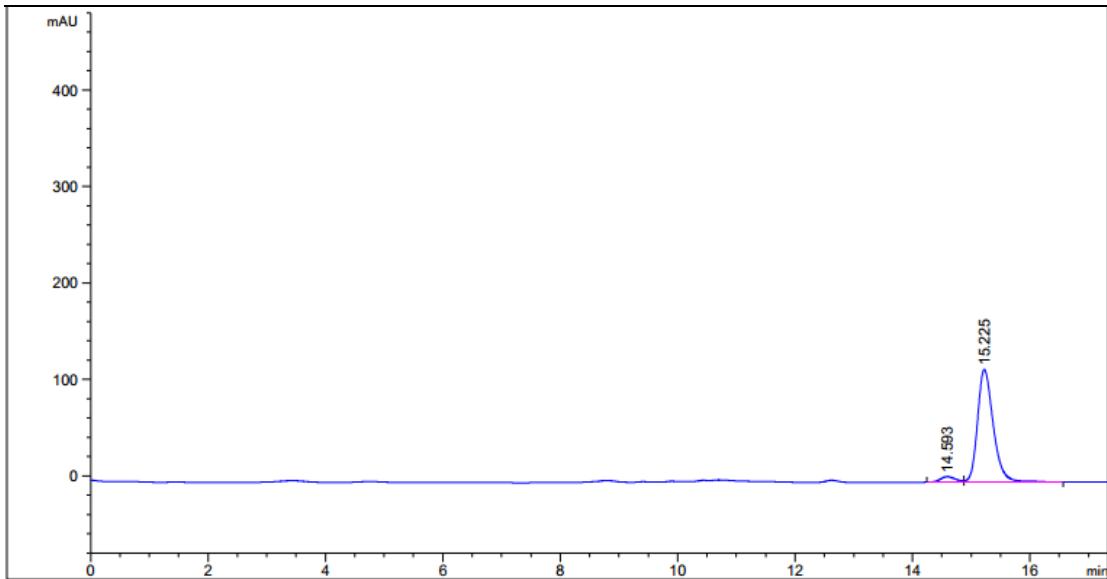
<b>Peak</b>	<b>Ret. Time</b>	<b>Width</b>	<b>Area</b>	<b>Height</b>	<b>Area</b>
#	[min]	[min]	[mAU * s]	[mAU]	%
1	<b>44.042</b>	<b>0.6160</b>	<b>1311.97595</b>	<b>33.05962</b>	<b>48.9612</b>
2	<b>46.000</b>	<b>0.7301</b>	<b>1367.65051</b>	<b>31.21997</b>	<b>51.0388</b>



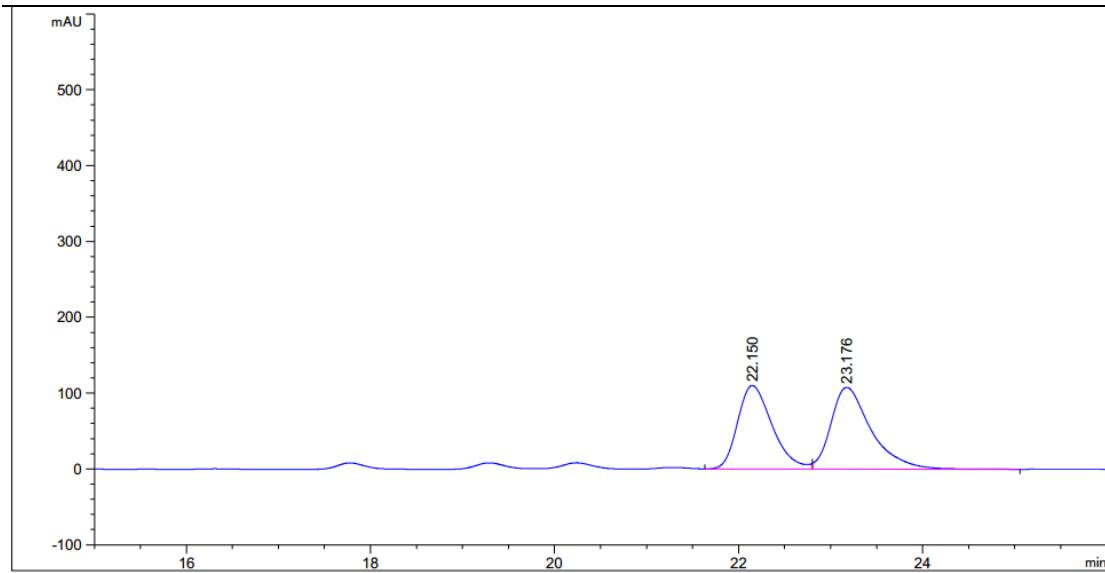
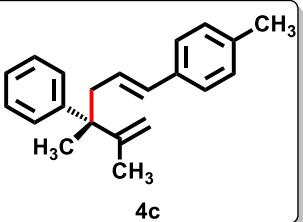
<b>Peak</b>	<b>Ret. Time</b>	<b>Width</b>	<b>Area</b>	<b>Height</b>	<b>Area</b>
#	[min]	[min]	[mAU * s]	[mAU]	%
1	<b>46.250</b>	<b>0.5834</b>	<b>488.85046</b>	<b>13.89795</b>	<b>6.5168</b>
2	<b>47.483</b>	<b>0.7593</b>	<b>7012.57080</b>	<b>153.84323</b>	<b>93.4832</b>



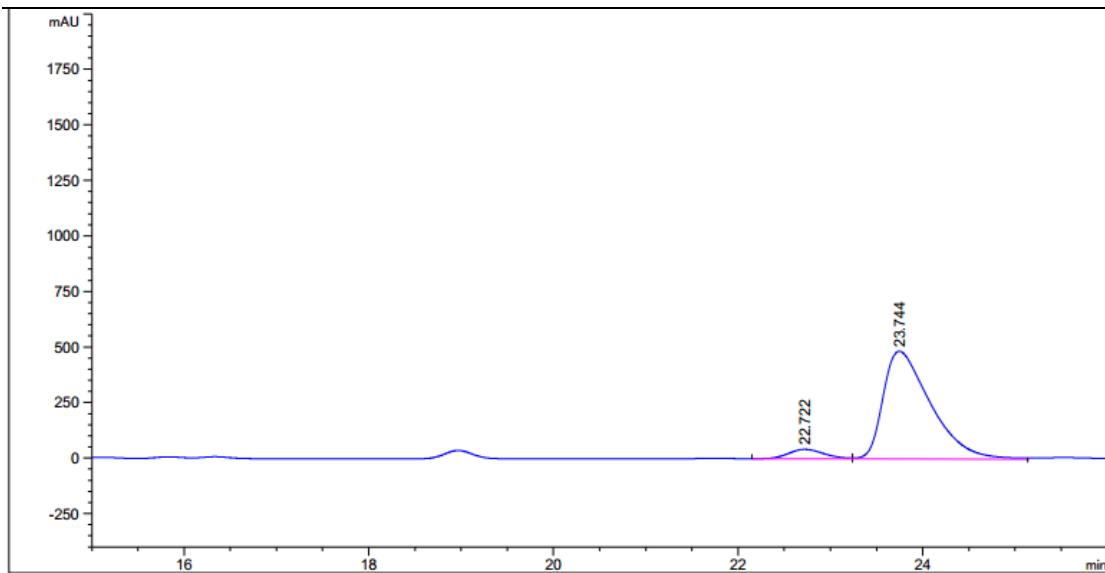
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	15.194	0.2803	2716.46216	147.91949	48.5731
2	15.873	0.3395	2876.06567	141.01596	51.4269



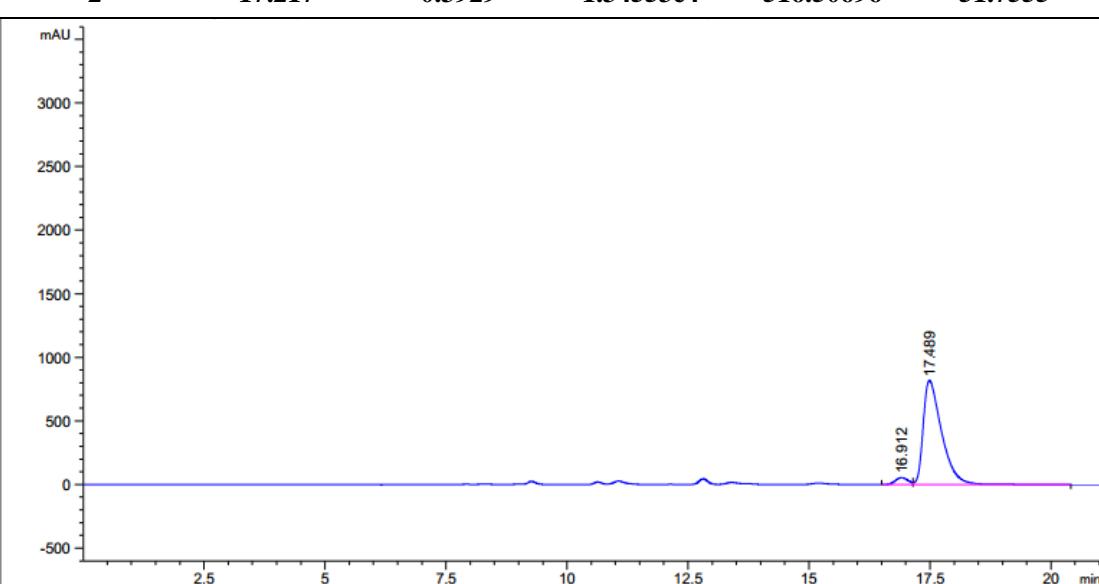
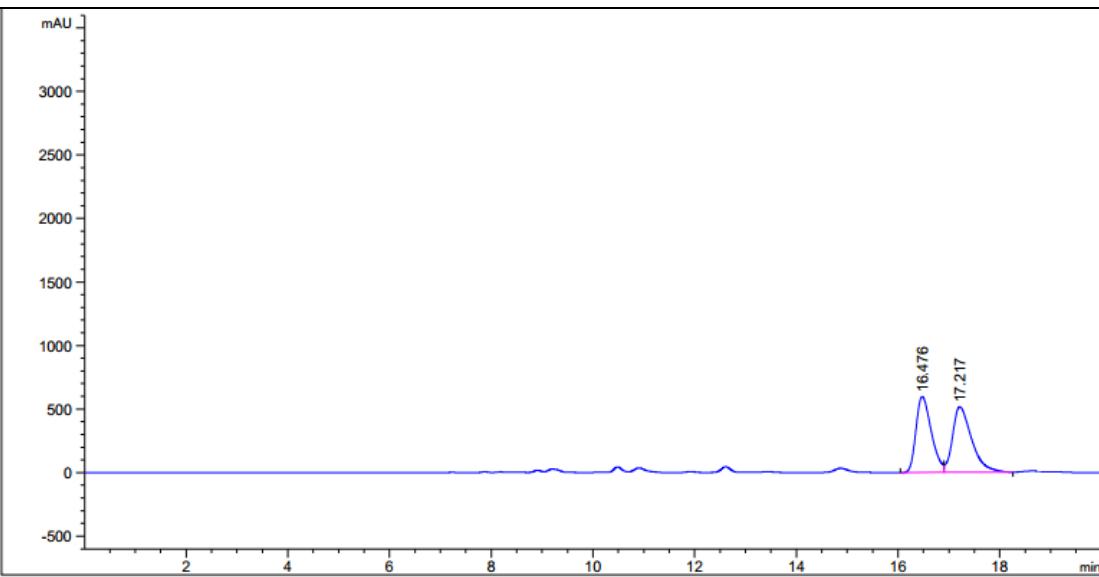
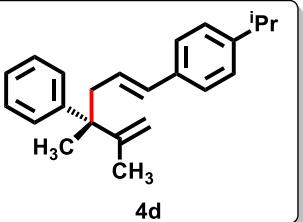
Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	14.593	0.2984	102.99178	5.75167	4.5115
2	15.225	0.3111	2179.85962	116.77763	95.4885

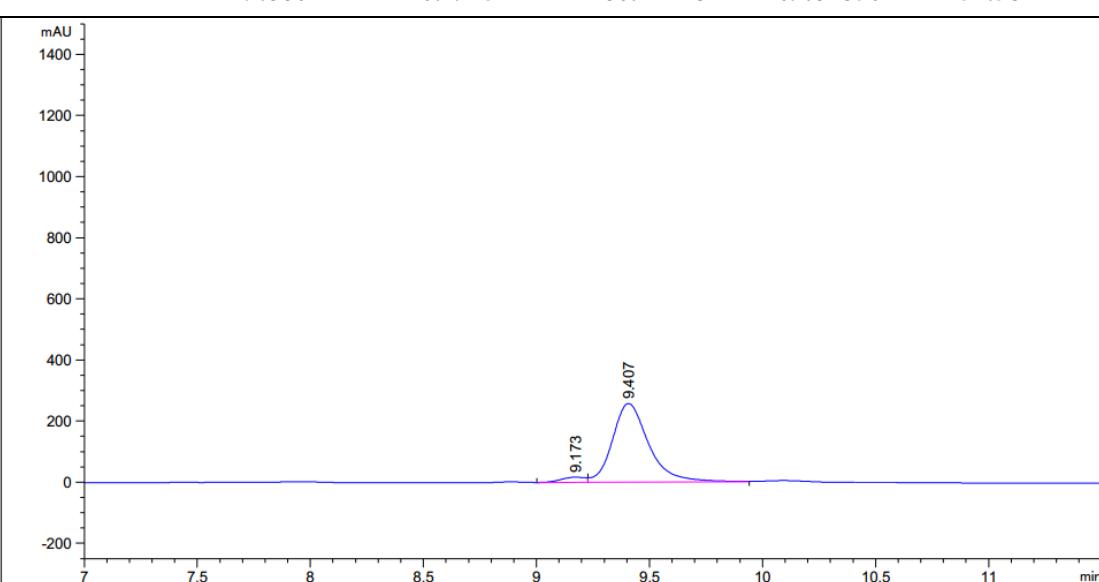
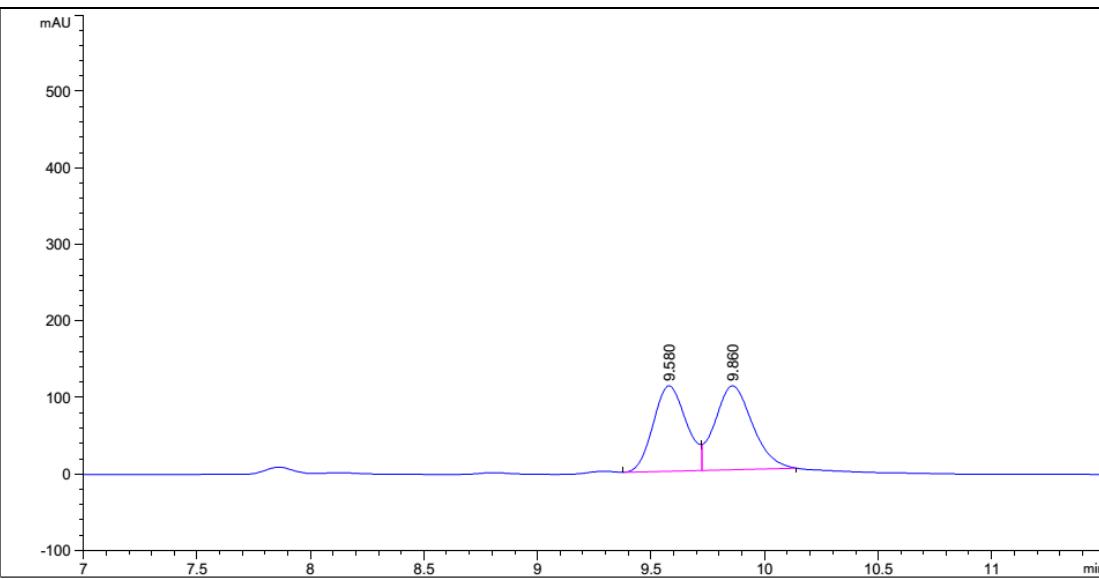
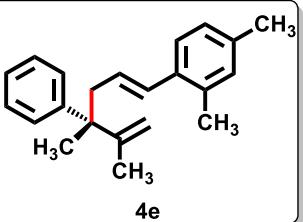


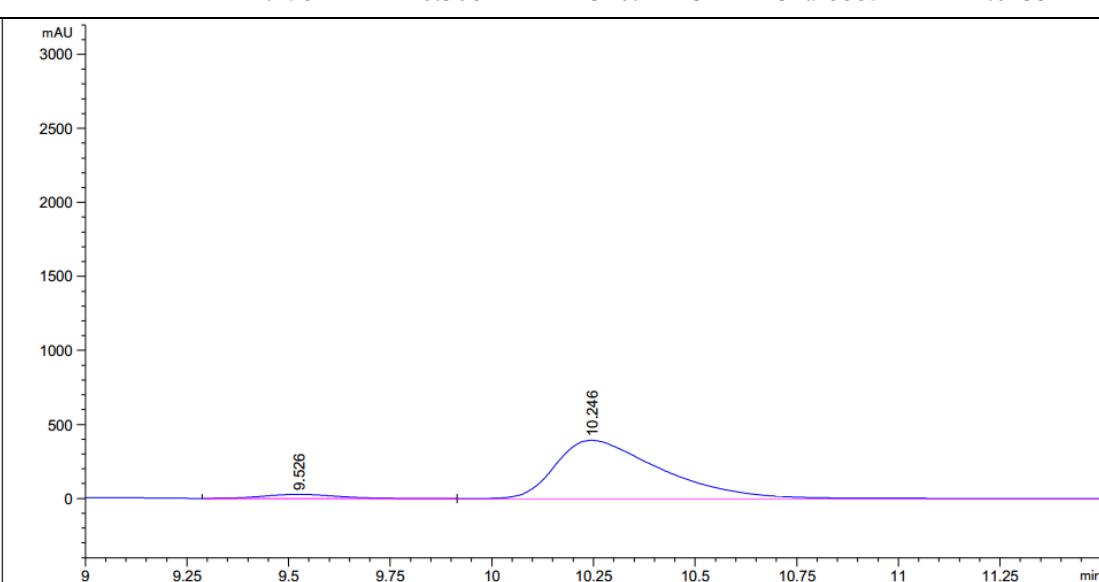
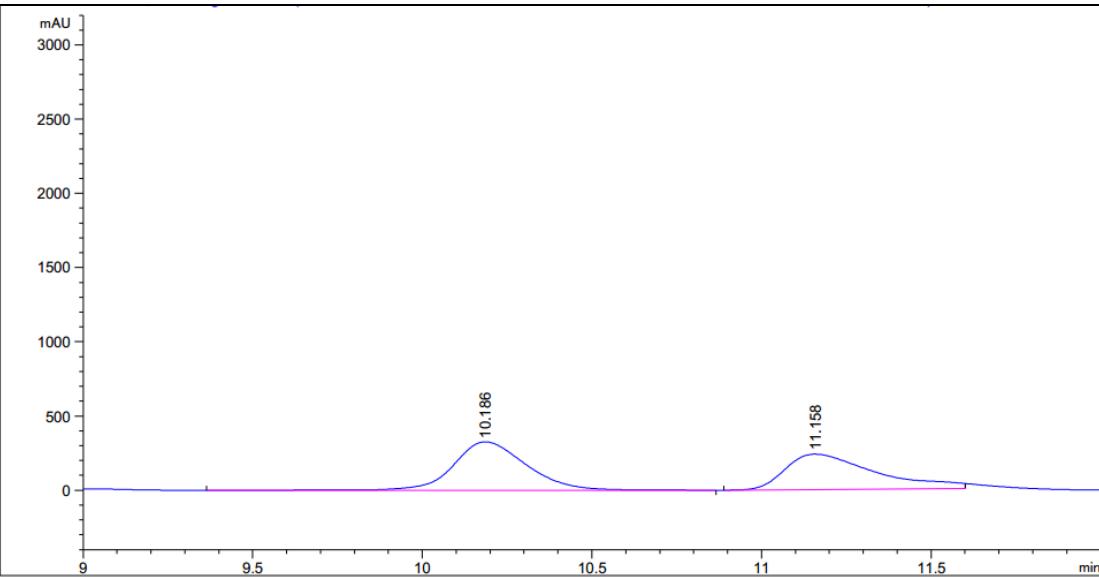
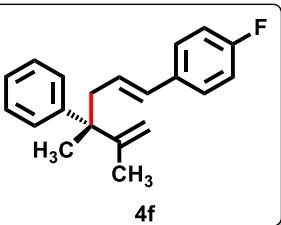
Peak	Ret. Time	Width	Area	Height	Area
#	[min]	[min]	[mAU * s]	[mAU]	%
1	22.150	0.4355	2884.14697	110.32850	46.8122
2	23.176	0.5051	3276.95410	107.97476	53.1878

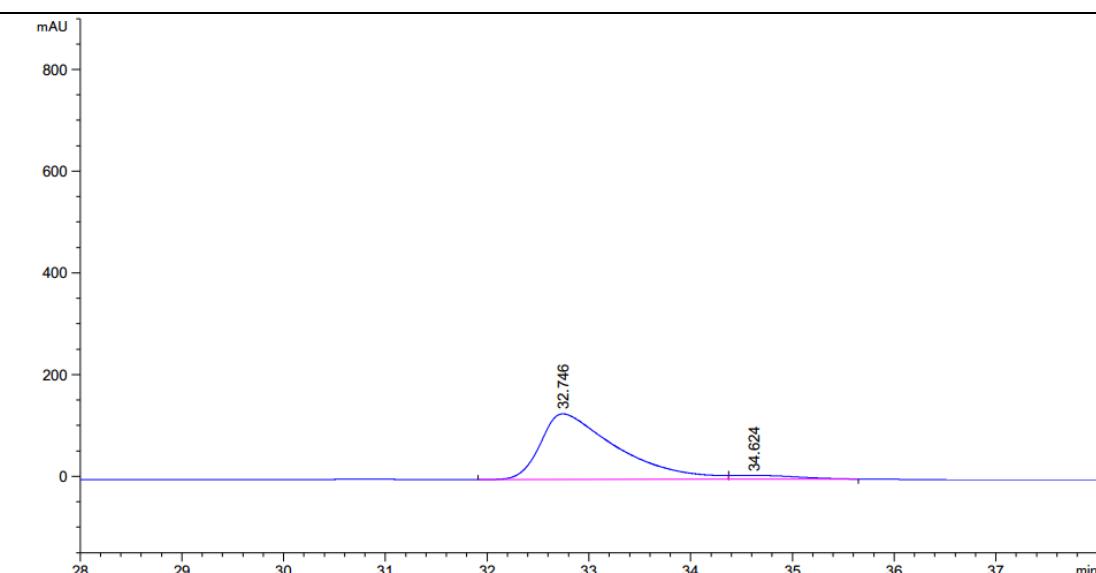
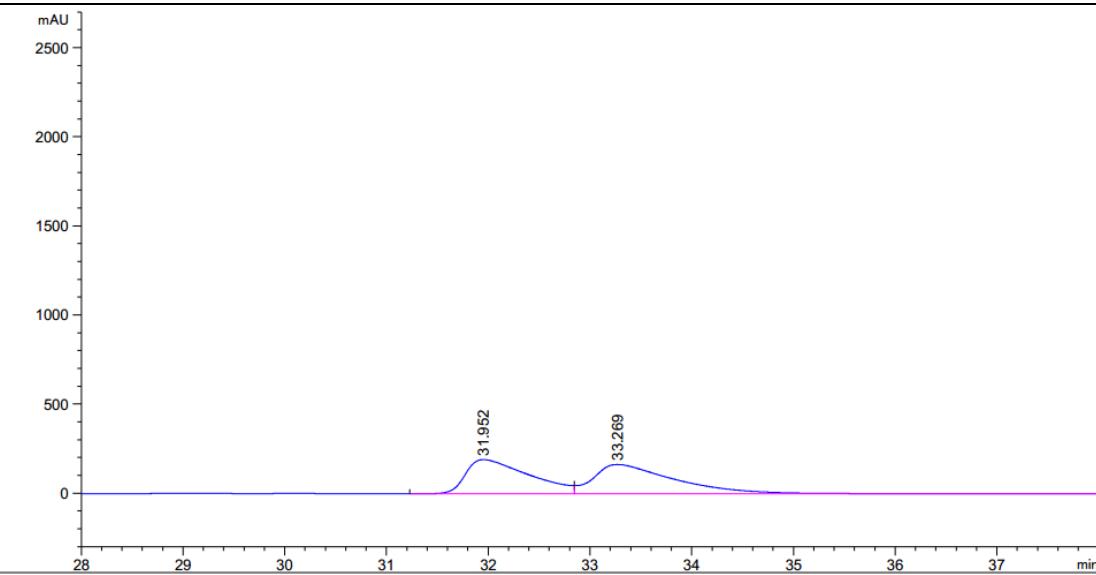
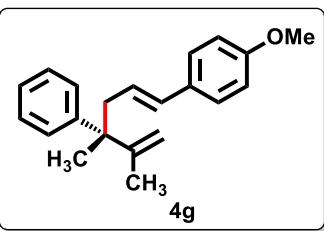


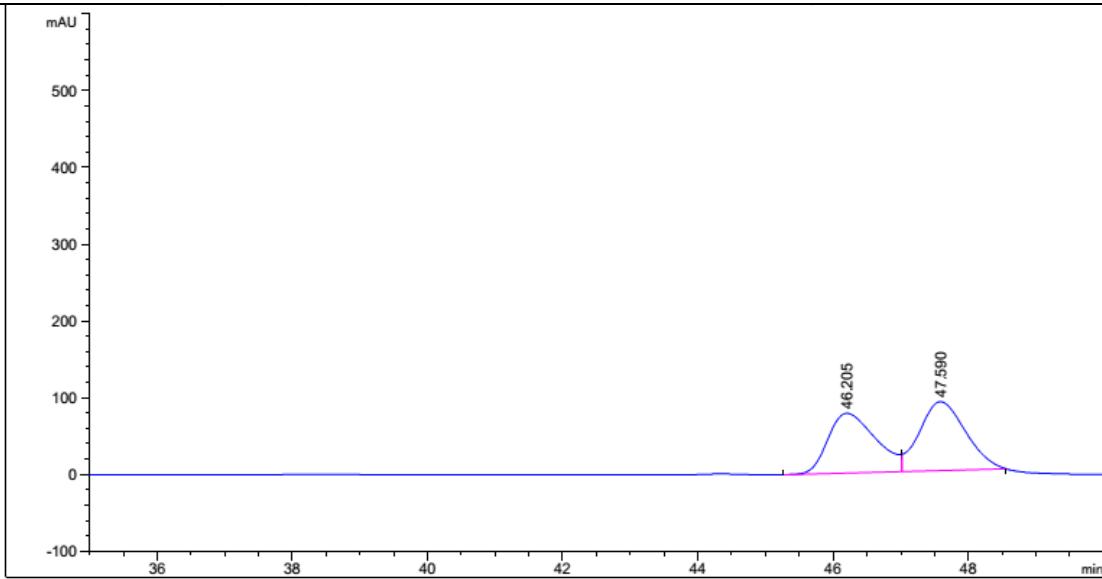
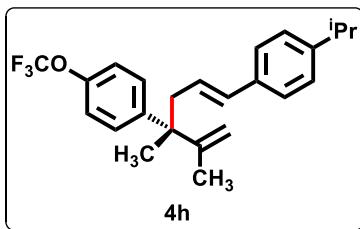
Peak	Ret. Time	Width	Area	Height	Area
#	[min]	[min]	[mAU * s]	[mAU]	%
1	22.722	0.4449	1150.42603	42.73675	6.2408
2	23.744	0.5930	1.72836e <sup>4</sup>	484.93158	93.7592



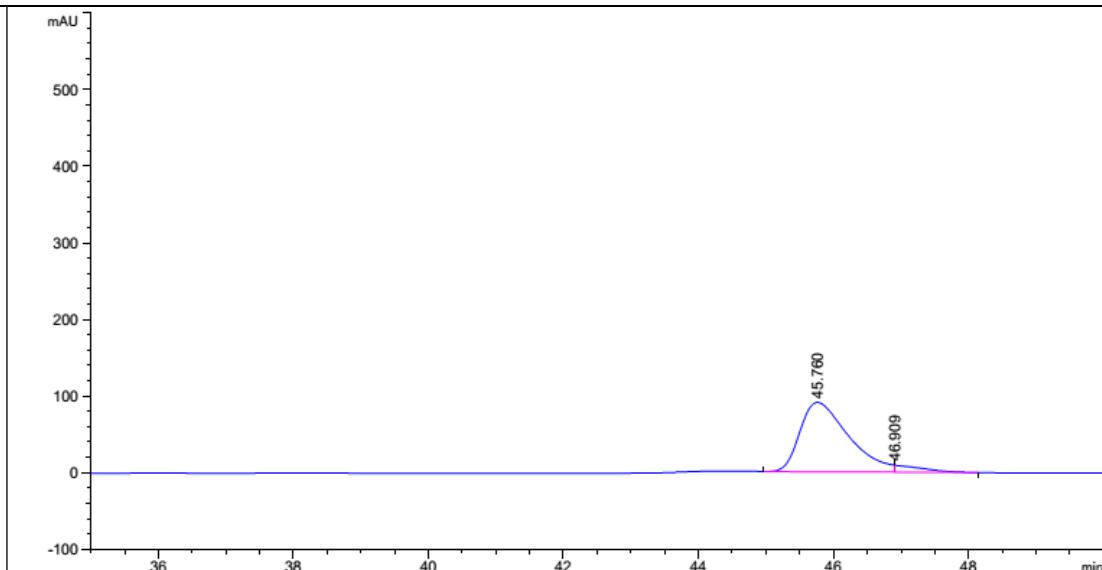




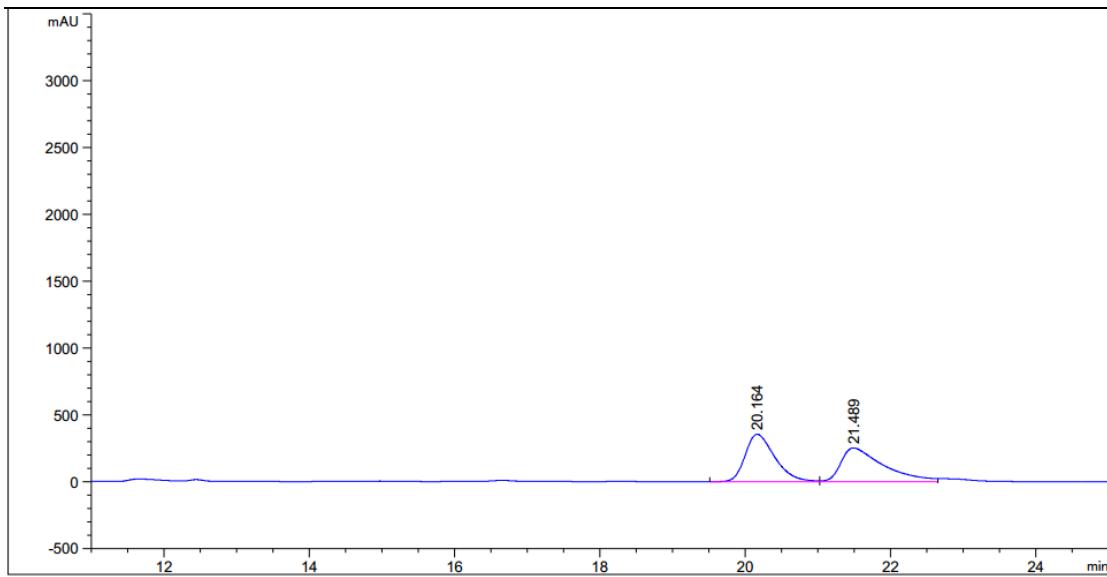
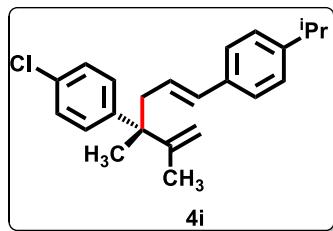




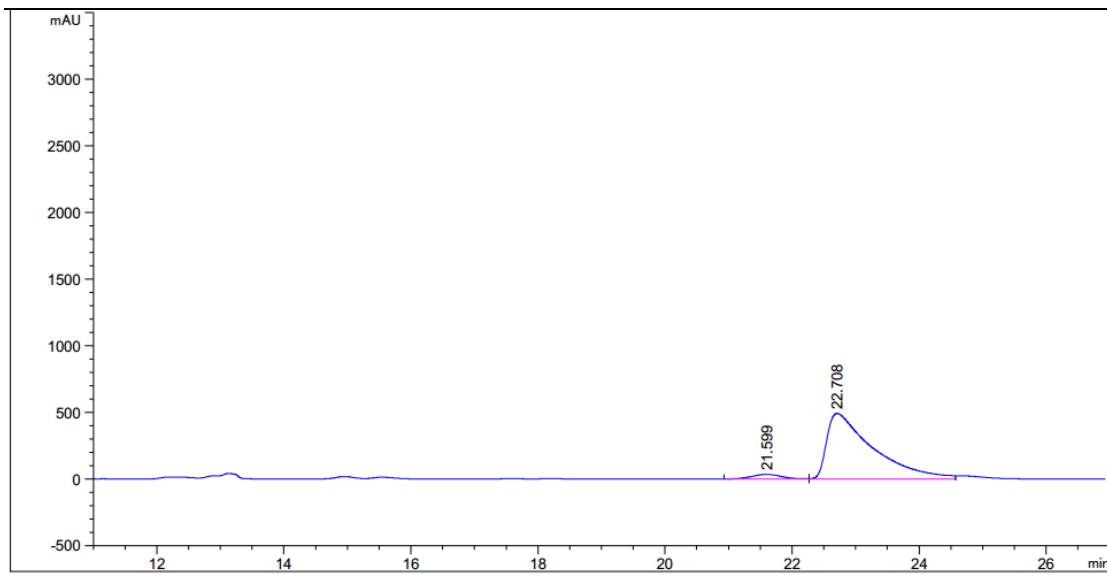
Peak	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	46.205	0.8161	3815.18262	77.83292	47.1953
2	47.590	0.7906	4268.63574	89.79787	52.8047



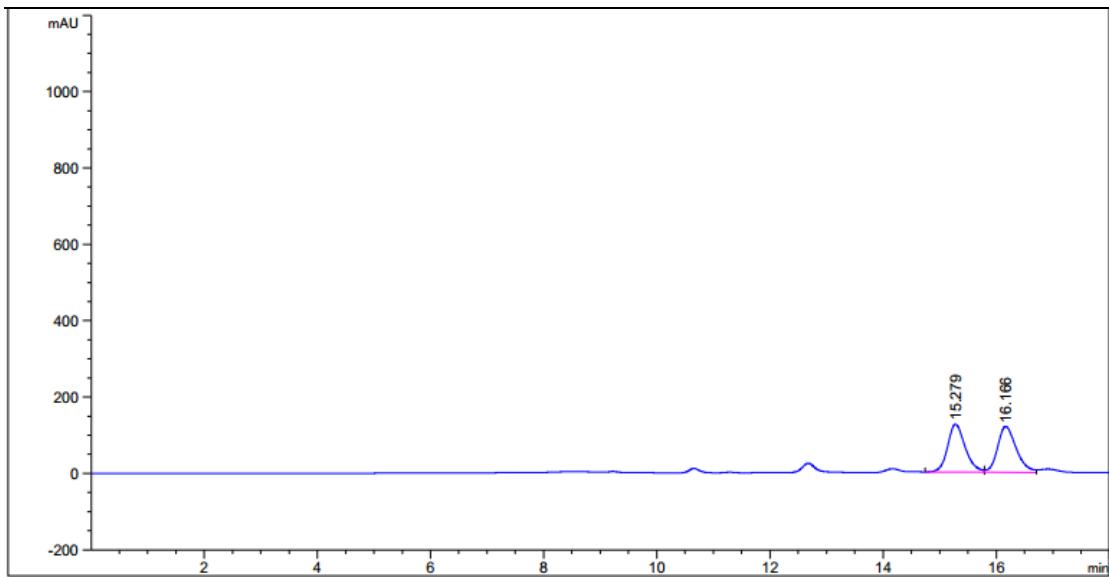
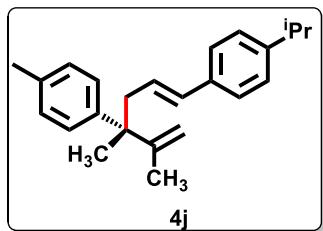
Peak	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	45.760	0.8318	4524.51367	90.58230	94.8985
2	46.909	0.4474	243.22765	9.06024	5.1015



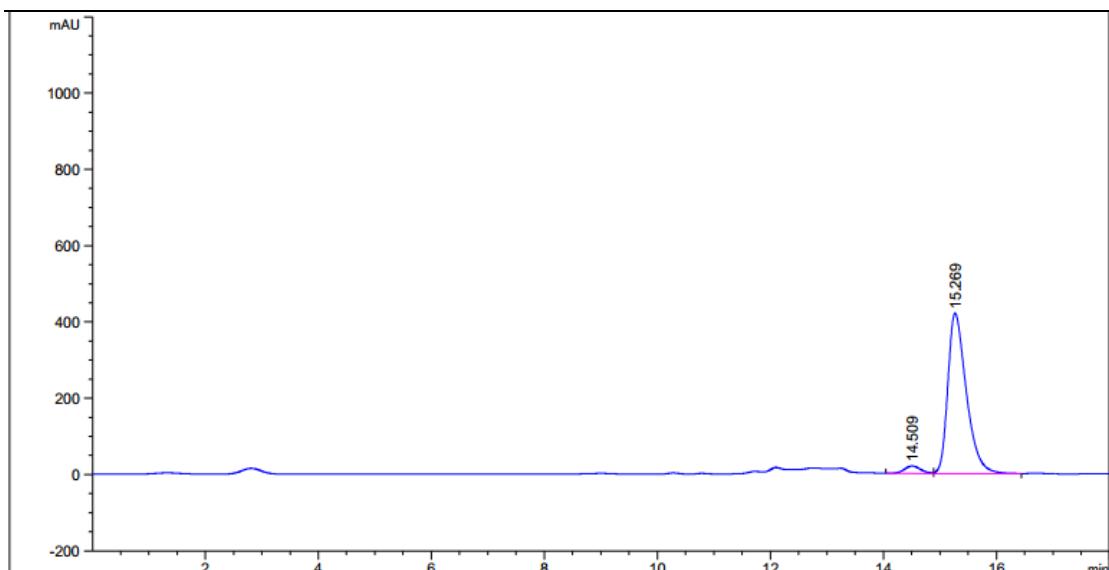
Peak	Ret. Time	Width	Area	Height	Area
#	[min]	[min]	[mAU * s]	[mAU]	%
1	<b>20.164</b>	<b>0.4295</b>	<b>9996.97949</b>	<b>353.93567</b>	<b>49.3547</b>
2	<b>21.489</b>	<b>0.6784</b>	<b>1.02584e<sup>4</sup></b>	<b>251.77444</b>	<b>50.6453</b>



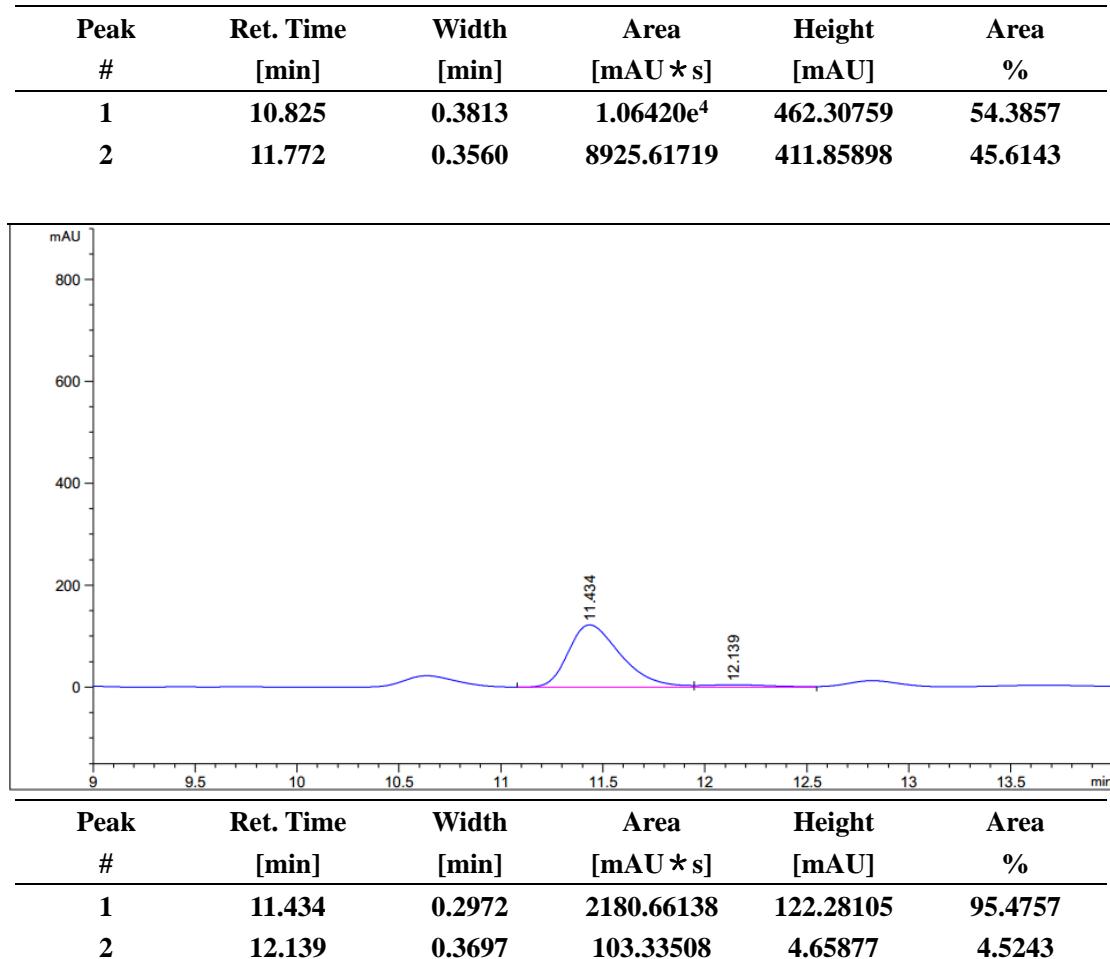
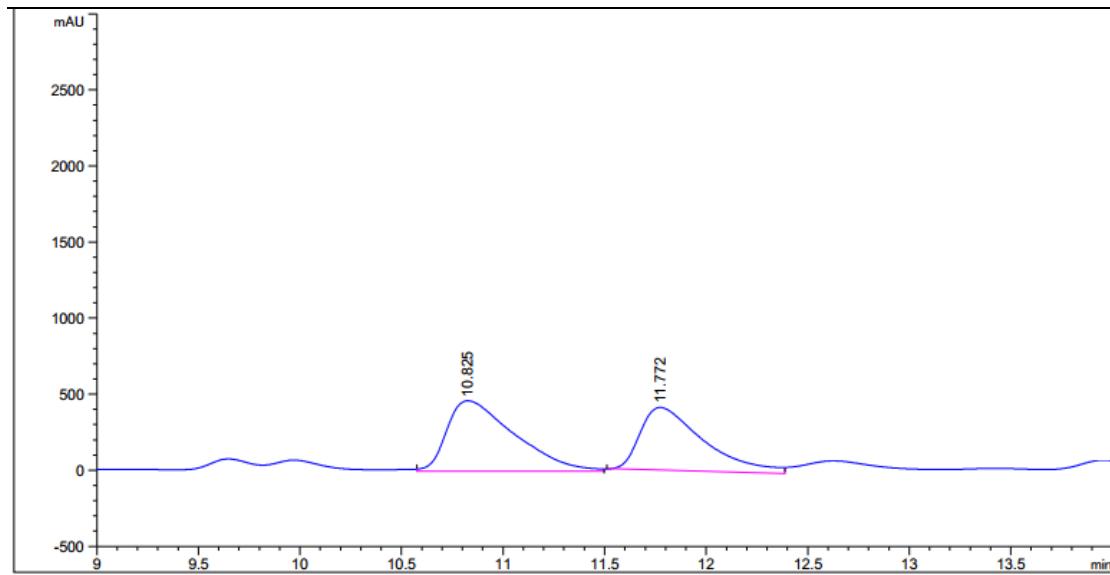
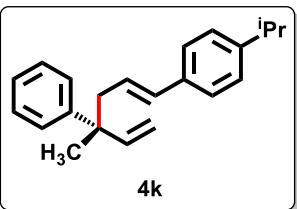
Peak	Ret. Time	Width	Area	Height	Area
#	[min]	[min]	[mAU * s]	[mAU]	%
1	<b>21.599</b>	<b>0.5378</b>	<b>1130.94580</b>	<b>35.04936</b>	<b>4.3566</b>
2	<b>22.708</b>	<b>0.8403</b>	<b>2.48287e<sup>4</sup></b>	<b>492.13495</b>	<b>95.6434</b>

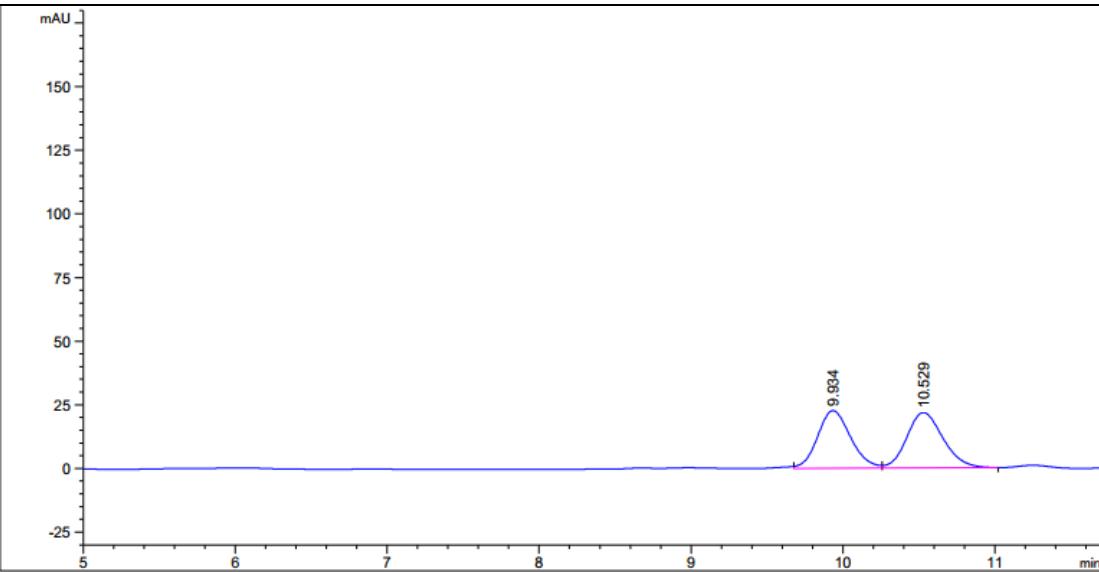
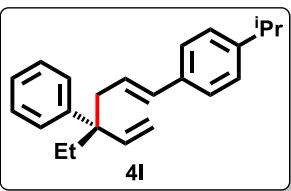


Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	15.279	0.3267	2705.96973	125.40205	49.5810
2	16.166	0.3811	2751.70728	120.09173	50.4190

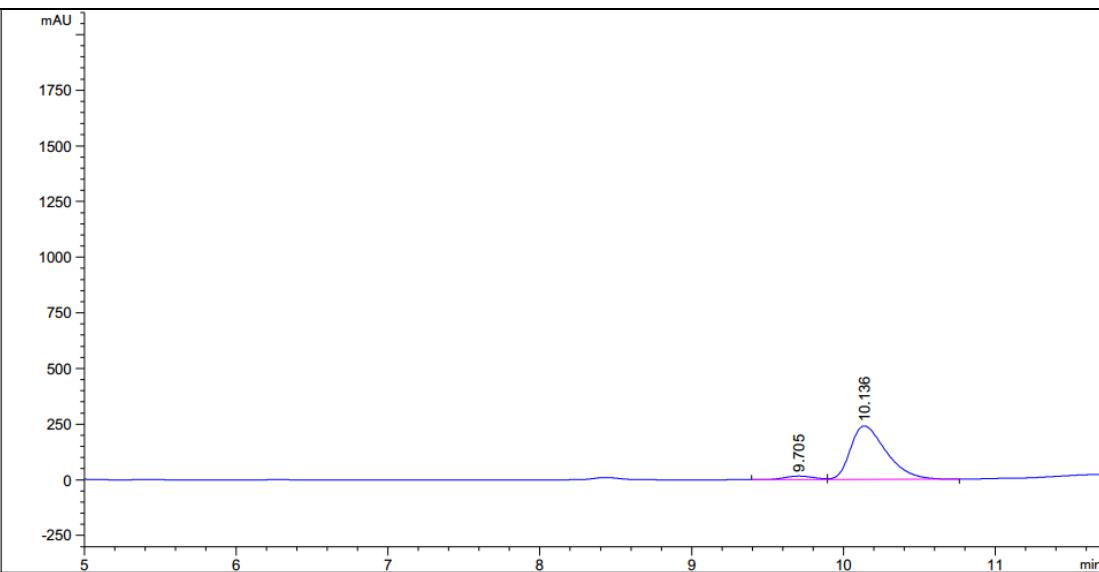


Peak #	Ret. Time [min]	Width [min]	Area [mAU * s]	Height [mAU]	Area %
1	14.509	0.3305	393.37875	19.55937	3.9673
2	15.269	0.3772	9522.09766	420.32910	96.0327





Peak #	Ret. Time [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.934	0.2512	342.01526	22.69213	48.6985
2	10.529	0.2550	360.29626	21.78042	51.3015



Peak #	Ret. Time [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.705	0.2237	216.42914	16.12771	5.2019
2	10.136	0.2730	3944.17310	240.76036	94.7981

