

## Supporting Information

### **Ir(ppy)<sub>3</sub> catalyzed, visible light mediated reaction $\alpha$ -chloro cinnamates with enol acetates – an apparent halogen paradox**

Thomas Föll, Julia Rehbein, Oliver Reiser\*

Institut für Organische Chemie, Universität Regensburg, Universitätsstr. 31, 93053  
Regensburg, Germany

To whom correspondence should be addressed

oliver.reiser@chemie.uni-regensburg.de

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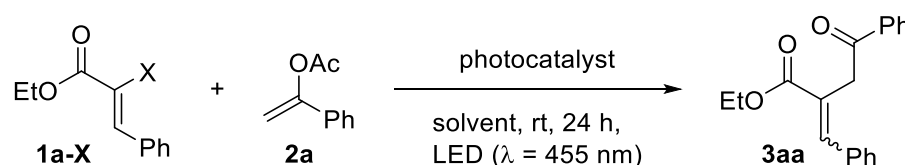
## 1. General information

All chemicals were used as received or purified according to Purification of Common Laboratory Chemicals.<sup>[1]</sup> Glassware was dried in an oven at 110 °C or flame dried and cooled under a dry atmosphere prior to use. All reactions were performed using Schlenk techniques. The blue light irradiation in batch processes was performed using a CREE XLamp XP-E D5-15 LED ( $\lambda = 450\text{-}465$  nm). Analytical thin layer chromatography was performed on Merck TLC aluminium sheets silica gel 60 F 254. Reactions were monitored by TLC and visualized by a short wave UV lamp and stained with a solution of potassium permanganate or vanillin. Column flash chromatography was performed using Merck flash silica gel 60 (0.040-0.063 mm). The melting points were measured on an OptiMelt MPA 100 (uncorrected). IR spectroscopy measurements were performed on an Agilent Gary 630 FTIR spectrometer equipped with a Diamond Single Reflection Accessory. Optical Rotation was measured in a Perkin Elmer Polarimeter or an ElmerAnton Paar MCP500 at 589 nm wavelength (sodium-*d*-line) in the specific solvent. X-ray measurements were performed by the crystallographic department of the University of Regensburg on Agilent Technologies SuperNova, Agilent Technologies Gemini R Ultra or Stoe IPDSI. Analytical HPLC was carried out on a Varian 920-LC with DAD. Chiralpak AS-H, Phenomenex Lux Cellulose-1 and 2 served as chiral stationary phase, and mixtures of *n*-heptane and *i*-PrOH were used for elution. NMR spectra were recorded on

Bruker Avance 300 and Bruker Avance 400 spectrometers. Chemical shifts for  $^1\text{H}$ -NMR were reported as  $\delta$ , parts per million, relative to the signal of  $\text{CHCl}_3$  at 7.26 ppm. Chemical shifts for  $^{13}\text{C}$ -NMR were reported as  $\delta$ , parts per million, relative to the center line signal of the  $\text{CDCl}_3$  triplet at 77 ppm. Coupling constants  $J$  are given in Hertz (Hz). The following notations indicate the multiplicity of the signals: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, and m = multiplet. Mass spectra were recorded at the Central Analytical Laboratory at the Department of Chemistry of the University of Regensburg on a Varian MAT 311A, Finnigan MAT 95, Thermoquest Finnigan TSQ 7000 or Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS. The yields reported are referred to the isolated compounds unless otherwise stated. *fac*-Ir(ppy) $_3$  was prepared as described in the literature.<sup>[2]</sup> (*Z*)- $\alpha$ -halo cinnamates **1a-F** and **1b** were prepared via titanium mediated olefination according to literature.<sup>[3]</sup> The same procedure developed by Jothi *et al.*<sup>[3]</sup> was applied for the preparation of **1a-Cl**, **1a-Br**, **1e-1s** and are in agreement with literature reference.<sup>[4-9]</sup> **1c** and **1d** were prepared via ester hydrolysis and esterification of **1b**. **1t**<sup>[10]</sup> and **1u**<sup>[11]</sup> were prepared according to literature. Enol acetates **2a-2m** were synthesized according to literature procedure<sup>[12]</sup> and are in agreement with literature reference.<sup>[13-18]</sup>

## 2. Optimization of the photochemical transformation

SI-Table 1. Optimization of the photochemical transformation<sup>a</sup>



entry	photocatalyst	$E_{M^+/M}^\circ$ (V vs. SCE)	X	solvent	yield (%) <sup>b</sup>
1	<i>fac</i> -Ir(ppy) <sub>3</sub>	-1.73	Br	benzene	-
2	<i>fac</i> -Ir(ppy) <sub>3</sub>		Br	chloroform	-
3	<i>fac</i> -Ir(ppy) <sub>3</sub>		Br	DMSO	14
4	<i>fac</i> -Ir(ppy) <sub>3</sub>		Br	DMF	16
5	<i>fac</i> -Ir(ppy) <sub>3</sub>		Br	MeCN	8
6 <sup>c</sup>	<i>fac</i> -Ir(ppy) <sub>3</sub>		Br	MeCN	10
7	<i>fac</i> -Ir(ppy) <sub>3</sub>		Cl	benzene	-
8	<i>fac</i> -Ir(ppy) <sub>3</sub>		Cl	chloroform	-
9	<i>fac</i> -Ir(ppy) <sub>3</sub>		Cl	DMSO	18
10	<i>fac</i> -Ir(ppy) <sub>3</sub>		Cl	DMF	43
11	<i>fac</i> -Ir(ppy) <sub>3</sub>		Cl	MeCN	58
12 <sup>c</sup>	<i>fac</i> -Ir(ppy) <sub>3</sub>		Cl	MeCN	31
13 <sup>d</sup>	<i>fac</i> -Ir(ppy) <sub>3</sub>		Cl	MeCN	98
14 <sup>e</sup>	<i>fac</i> -Ir(ppy) <sub>3</sub>		Cl	MeCN	15
15	Ir(ppy) <sub>2</sub> (dtb-bpy)PF <sub>6</sub>	-0.96	Cl	MeCN	-
16	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (dtb-bpy)PF <sub>6</sub>	-0.89	Cl	MeCN	-
17	Ru(bpy) <sub>3</sub> Cl <sub>2</sub>	-0.81	Cl	MeCN	-
18 <sup>f</sup>	Cu(dap) <sub>2</sub> Cl	-1.43	Cl	MeCN	-
19 <sup>g</sup>	-		Cl	MeCN	-
20 <sup>h</sup>	<i>fac</i> -Ir(ppy) <sub>3</sub>		Cl	MeCN	-

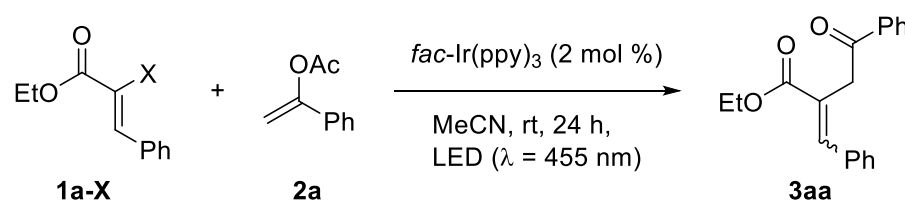
<sup>a</sup>Standard reaction conditions: **1a-X** (0.5 mmol, 1.0 equiv), **2a** (2.5 mmol, 5.0 equiv), photocatalyst (1 mol %), solvent (c = 0.1 M), N<sub>2</sub>-atmosphere, rt, 24 h, blue LED ( $\lambda$  = 455 nm). <sup>b</sup>Isolated yield after purification via column chromatography. *E/Z* ratio of approximately 1:1 in all cases. <sup>c</sup>2 equiv of H<sub>2</sub>O were added. <sup>d</sup>2 mol % catalyst. <sup>e</sup>under O<sub>2</sub>-atmosphere. <sup>f</sup>green LED ( $\lambda$  = 530 nm) was used. <sup>g</sup>no photocatalyst. <sup>h</sup>no light.

### 3. Further control experiments and mechanistic discussion

All following control experiments were performed using optimized reaction conditions for the activation of **1a-Cl** (SI-Table 1, entry 13 or Table 1 entry 5 in the manuscript).

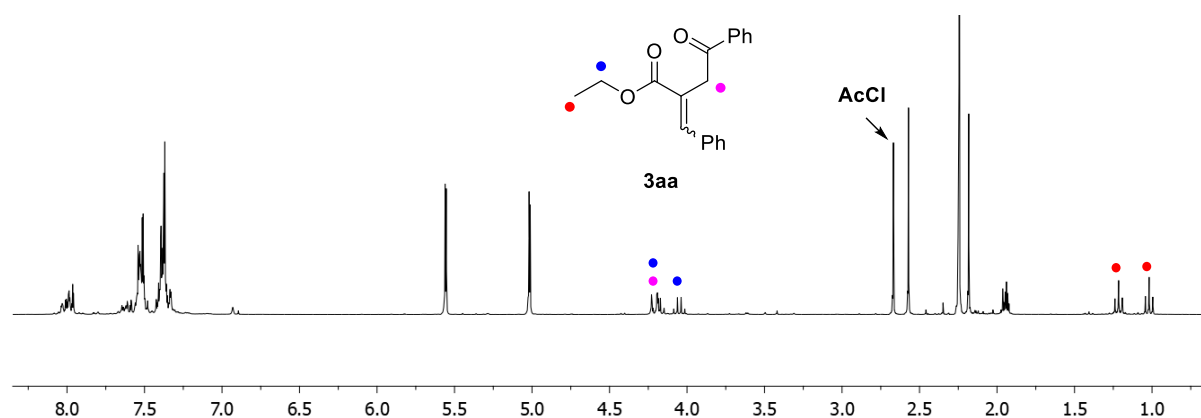
The direct comparison of **1a-Cl** and **1a-Br** revealed an unexpected trend regarding the yield of **3aa**. While full conversion for **1a-Cl** was observed, only poor consumption of **1a-Br** was detected under exact same reaction conditions (SI-Table 2, SI Figure 1 and 2).

SI-Table 2. Direct comparison of **1a-Cl** and **1a-Br**<sup>a</sup>

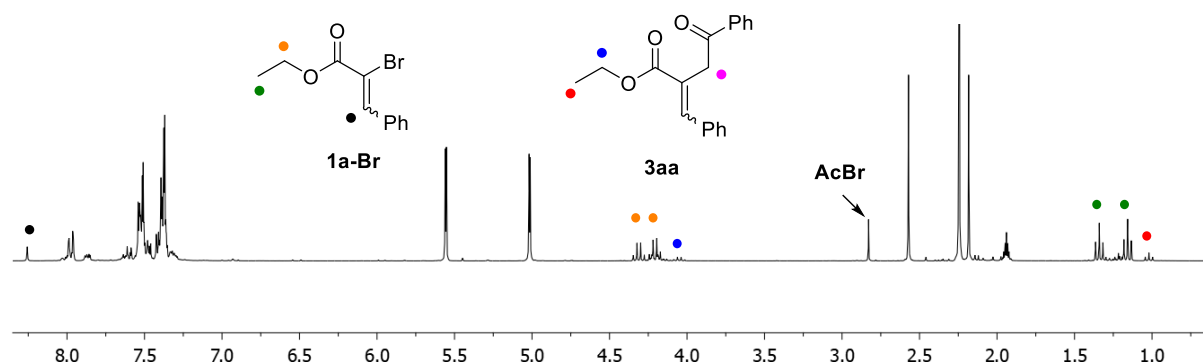
				
entry	X	BDE vinyl-X (kcal mol <sup>-1</sup> )	E <sup>o</sup> <sub>RX/RX<sup>•-</sup></sub>	conv. (%) <sup>c</sup> / yield (%) <sup>c</sup>
1	Cl	91.7	-1.64 V	100 / 98
2	Br	79.4	-1.54 V	23 / 23

<sup>a</sup>Reactions were performed using **1a-X** (0.5 mmol), **2a** (2.5 mmol), *fac*-Ir(ppy)<sub>3</sub> (2 mol %) in 5 mL MeCN. <sup>b</sup>Reduction potentials were measured in MeCN vs. SCE. <sup>c</sup>Conversion and yield were determined by <sup>1</sup>H-NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

SI-Figure 1. Crude reaction of **1a-Cl** in CD<sub>3</sub>CN (*cf.* entry 1, SI-Table 2).



SI-Figure 2. Crude reaction of **1a-Br** in CD<sub>3</sub>CN (*cf.* entry 2, SI-Table 2)



However, performing the reaction with equimolar amounts of **1a-Cl** and **1a-Br** revealed an approximately 3 times higher conversion of **1a-Br** compared to **1a-Cl** (SI-Table 3). Still, the overall conversion of **1a-X** (**1a-Cl** and **1a-Br** in a 1:1 ratio) was only 38% compared to 100% for pure **1a-Cl** and 23% for pure **1a-Br** (SI Table 2). Further analysis showed that the overall conversion of 38% reflects 18% conversion of **1a-Cl** and 56% conversion of **1a-Br** (Please note that in this experiment (SI-Table 3) the amount of catalyst employed is twice as high with respect to the “poisonous” **1a-Br** than in (SI Table 2, entry 2). These experiments indicated that electron transfer to form [**1a-Br**]<sup>-</sup> and subsequent dissociation into the vinyl radical bromide anion is more facile than for **1a-Cl**.

SI-Table 3. Control experiment using equimolar amounts of **1a-Cl** and **1a-Br**<sup>a</sup>

entry	conv. <b>1a-Cl</b> (%)	conv. <b>1a-Br</b> (%)	overall conv. (%)	yield of <b>3aa</b> (%)
1	18	58	38	30

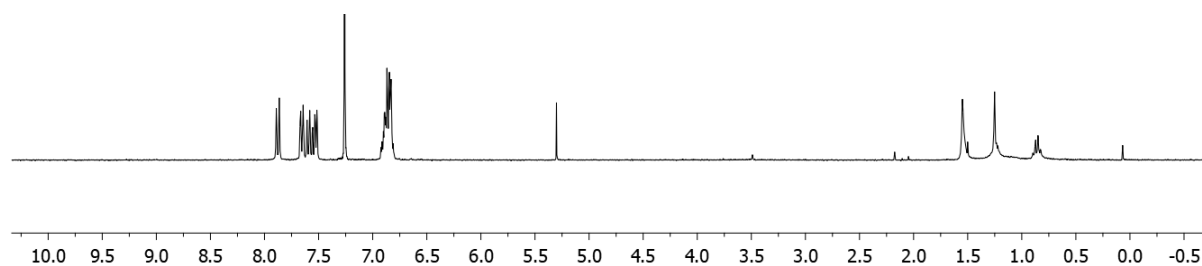
<sup>a</sup>Reactions were performed using **1a-Cl** (0.25 mmol), **1a-Br** (0.25 mmol), **2a** (2.5 mmol), *fac*-Ir(ppy)<sub>3</sub> (2 mol % based on the total amount of 0.5 mmol **1a**) in 5 mL MeCN.

Although the reaction with **1a-Br** proceeded much faster compared to **1a-Cl**, the overall conversion still remained low. We therefore considered deactivation of the catalyst might be the reason for the low conversion whenever **1a-Br** was present. As the only difference in the

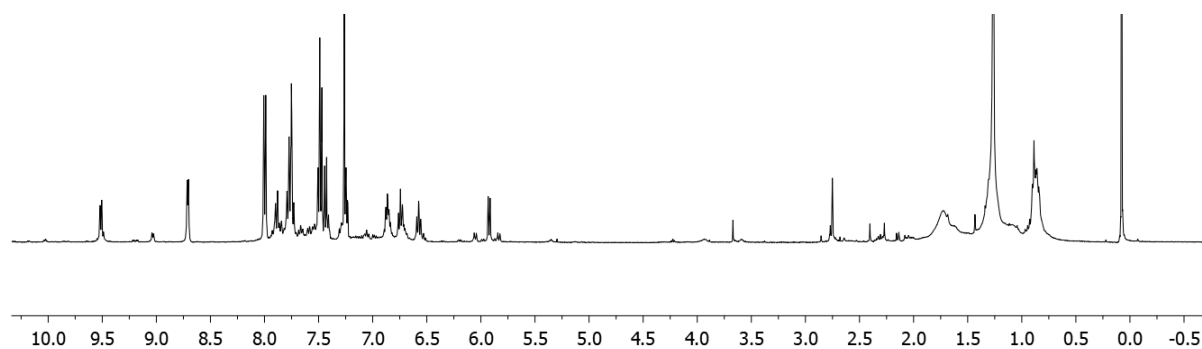
reaction mechanism between **1a-Cl** and **1a-Br** is the formation of acetyl chloride (AcCl) and acetyl bromide (AcBr) as byproduct we hypothesized that acetyl bromide might deactivate the catalyst. The formation of both, AcCl and AcBr in the course of the reaction has been verified by  $^1\text{H-NMR}$  analysis of the crude reaction mixture when the reaction was performed in  $\text{CD}_3\text{CN}$  (SI-Figure 1 and 2).

Indeed, when 0.5 equivalents (reflecting a conversion of 50% of a given reaction) of AcBr were added to the reaction with **1a-Cl** as additive, only 22% of product **3aa** was formed (instead of 98% without AcBr). This indicates that deactivation of the catalyst is indeed occurring but is not instantaneous. Performing the same experiment in the absence of substrates also revealed that *fac*- $\text{Ir}(\text{ppy})_3$  is not stable in the presence of AcBr (SI-Figure 3 and 4).

SI-Figure 3.  $^1\text{H-NMR}$  of *fac*- $\text{Ir}(\text{ppy})_3$  in  $\text{CDCl}_3$

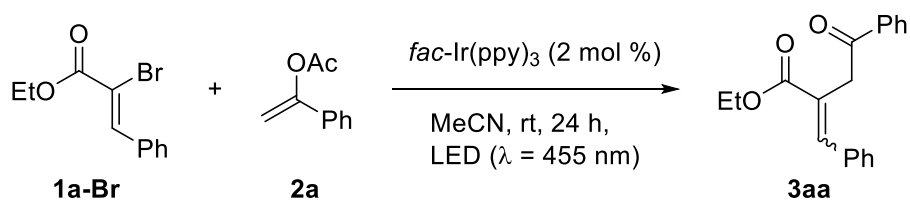


SI-Figure 4.  $^1\text{H-NMR}$  of *fac*- $\text{Ir}(\text{ppy})_3$  after irradiation for 24 h in the presence of AcBr



All efforts to annihilate the formation of AcBr by adding additives to the reaction mixture of **1a-Br** were not successful (SI-Table 4). Neither stoichiometric amounts of  $\text{H}_2\text{O}$  (entry 1) nor an excess of  $\text{H}_2\text{O}$  (entry 2) did improve the yield of **3aa**. The addition of non-redox active inorganic bases to the reaction mixture also did not show a beneficial effect (entry 3 and 4).

SI-Table 4. Control experiments with additives<sup>a</sup>



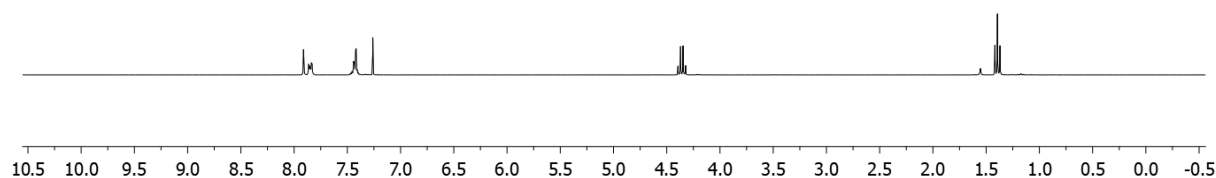
entry	catalyst (2 mol %)	additive (equiv)	solvent	yield (%) <sup>b</sup>
1	<i>fac</i> -Ir(ppy) <sub>3</sub>	H <sub>2</sub> O (2)	MeCN	31
2	<i>fac</i> -Ir(ppy) <sub>3</sub>	-	MeCN/H <sub>2</sub> O 4:1	12
3	<i>fac</i> -Ir(ppy) <sub>3</sub>	K <sub>2</sub> HPO <sub>4</sub> (2)	MeCN	20
4	<i>fac</i> -Ir(ppy) <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub> (2)	MeCN	27

<sup>a</sup>Reactions were performed using optimized reaction conditions: **1a-Br** (0.5 mmol), **2a** (2.5 mmol), *fac*-Ir(ppy)<sub>3</sub> (2 mol %) in 5 mL MeCN. <sup>b</sup>Yield determined by <sup>1</sup>H-analysis using 1,3,5-trimethoxybenzene as internal standard.

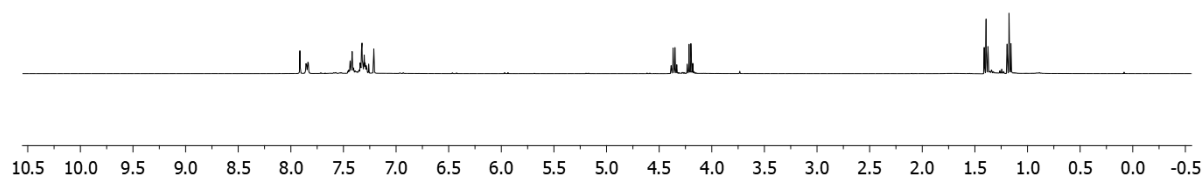
#### 4. Some comments regarding the *E/Z* distribution of product **3**

In most cases, an *E/Z* distribution of product **3** of nearly 1:1 was observed. In order to check if photoisomerization of starting material **1** or photoisomerization of product **3** is possible, we conducted following control experiments. Starting material **1a-Cl** (pure (*Z*)-isomer), (*E*)-**3aa**, and (*Z*)-**3aa** were irradiated with blue LED ( $\lambda = 455$  nm) in the presence of *fac*-Ir(ppy)<sub>3</sub> in MeCN (SI-Figure 5-10). Starting material **1a-Cl** as well as both photoproducts (*E*)-**3aa** and (*Z*)-**3aa** showed an *E/Z* distribution of approximately 1:1 after irradiation in the presence of *fac*-Ir(ppy)<sub>3</sub>. Therefore, the *E/Z* ratio of 1:1 observed in products **3** can be ultimately rationalized by its isomerization.

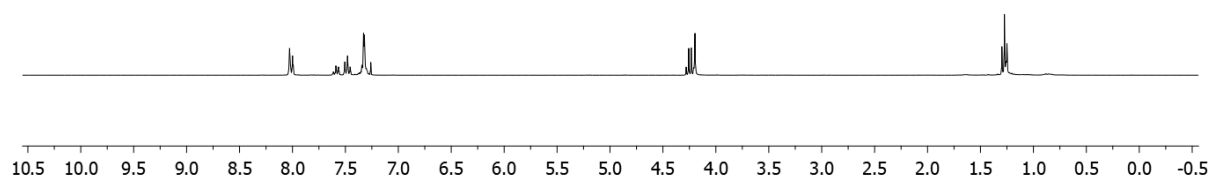
SI-Figure 5. <sup>1</sup>H-NMR of **1a-Cl** before irradiation



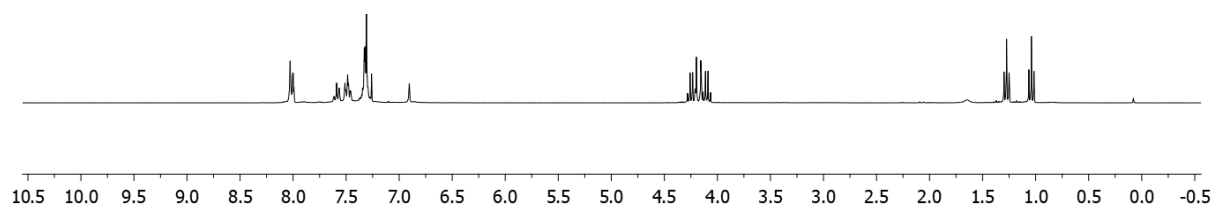
SI-Figure 6. <sup>1</sup>H-NMR of **1a-Cl** after irradiation



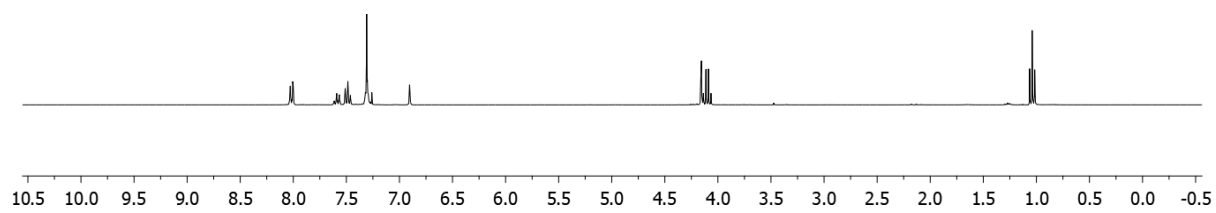
SI-Figure 7. <sup>1</sup>H-NMR of (*E*)-**3aa** before irradiation



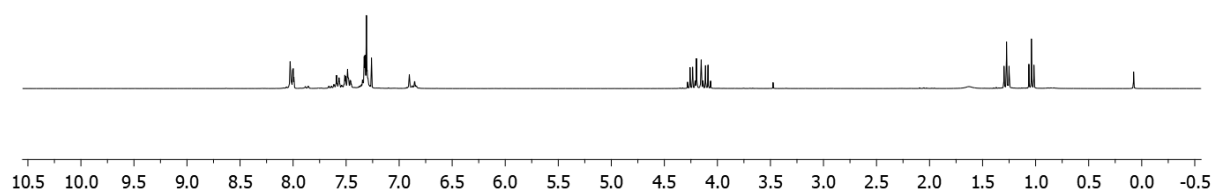
SI-Figure 8. <sup>1</sup>H-NMR of (*E*)-**3aa** after irradiation



**SI-Figure 9.  $^1\text{H-NMR}$  of (Z)-3aa before irradiation**

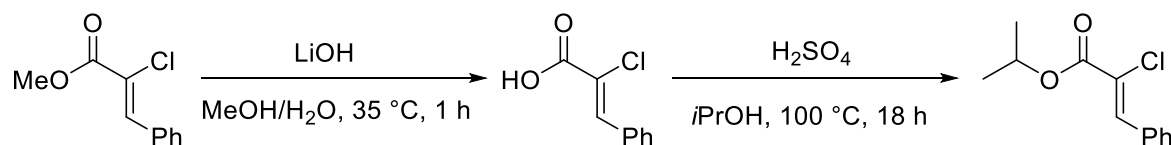


**SI-Figure 10.  $^1\text{H-NMR}$  of (Z)-3aa after irradiation**



## 5. Synthesis of $\alpha$ -halo cinnamates (**1c**, **1d**, **1i**, **1j**, **1k**, **1m**, **1p**)

### *iso*-propyl (*Z*)-2-chloro-3-phenylacrylate (**1c**)

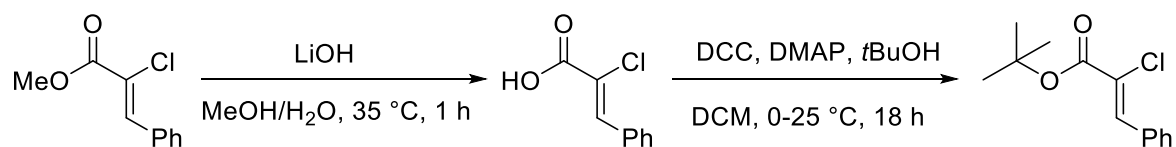


Methyl (*Z*)-2-chloro-3-phenylacrylate (**1b**, 1.00 g, 5.09 mmol, 1.00 equiv) and LiOH (244 mg, 10.2 mmol, 2.00 equiv) was dissolved in a mixture of MeOH (5 mL) and H<sub>2</sub>O (1 mL). The reaction mixture was heated to 35 °C for 1 h. Subsequently, methanol was evaporated and the mixture was diluted with H<sub>2</sub>O (20 mL) and washed with DCM (2 x 20 mL). The aqueous phase was acidified and washed with EA (3 x 20 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed *in vacuo* and (*Z*)-2-chloro-3-phenylacrylic acid (816 mg, 4.47 mmol, 88%) could be used without further purification.

A 100 mL flask was charged with (*Z*)-2-chloro-3-phenylacrylic acid (704 mg, 3.86 mmol, 1.00 equiv), *i*PrOH (25.0 mL, 325 mmol, 84.0 equiv) and conc. H<sub>2</sub>SO<sub>4</sub> (200  $\mu$ L, 3.75 mmol, 0.97 equiv). The reaction was heated to 100 °C and stirred overnight. The mixture was allowed to cool to room temperature, quenched with sat. NaHCO<sub>3</sub> (15 mL) and washed with DCM (3 x 25 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed *in vacuo* and the residue was purified by column chromatography on SiO<sub>2</sub> (hexanes / EA, 15:1) to obtain pure *iso*-propyl (*Z*)-2-chloro-3-phenylacrylate as colorless oil (592 mg, 2.63 mmol, 68%).

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.48; **IR** (neat): 3060, 3030, 2981, 2937, 1714, 1617, 1490, 1446, 1375, 1263, 1200, 1103, 1021, 916, 861, 831, 767, 689 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.88 (s, 1H), 7.87 – 7.82 (m, 2H), 7.45 – 7.40 (m, 3H), 5.18 (sept,  $J$  = 6.3 Hz, 1H), 1.37 (d,  $J$  = 6.3 Hz, 6H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  162.9, 136.6, 133.1, 130.6, 130.1, 128.5, 122.7, 70.4, 21.8; **HRMS** (ESI)  $m/z$  calculated for C<sub>12</sub>H<sub>14</sub>ClO<sub>2</sub> ([M+H]<sup>+</sup>) 225.0677, found 225.0677.

### *tert*-butyl (*Z*)-2-chloro-3-phenylacrylate (**1d**)

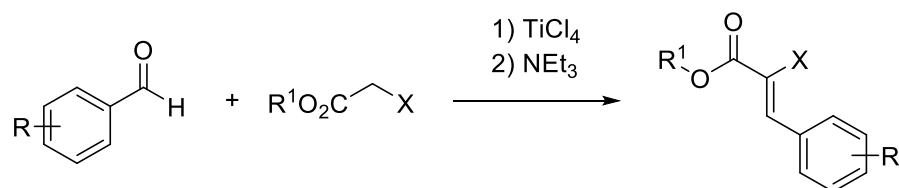


Methyl (*Z*)-2-chloro-3-phenylacrylate (**1b**, 1.00 g, 5.09 mmol, 1.00 equiv) and LiOH (244 mg, 10.2 mmol, 2.00 equiv) was dissolved in a mixture of MeOH (5 mL) and H<sub>2</sub>O (1 mL). The reaction mixture was heated to 35 °C for 1 h. Subsequently, methanol was evaporated and the mixture was diluted with H<sub>2</sub>O (20 mL) and washed with DCM (2 x 20 mL). The aqueous phase was acidified and washed with EA (3 x 20 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed *in vacuo* and (*Z*)-2-chloro-3-phenylacrylic acid (816 mg, 4.47 mmol, 88%) could be used without further purification.

(*Z*)-2-chloro-3-phenylacrylic acid (465 mg, 2.55 mmol, 1.00 equiv), 4-DMAP (31.1 mg, 255 μmol, 0.10 equiv), and *t*-BuOH (189 mg, 2.55 mmol, 1.00 equiv) was dissolved in DCM (10 mL). Subsequently, DCC (578 mg, 2.80 mmol, 1.10 equiv) was added at 0 °C. The reaction was stirred for additional 5 min at 0 °C. After stirring overnight at room temperature the reaction mixture was filtered, diluted with DCM (40 mL) and washed with HCl (0.5 M, 2 x 20 mL) and sat. NaHCO<sub>3</sub> (20 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed *in vacuo* and the residue was purified by column chromatography on SiO<sub>2</sub> (hexanes / EA, 8:1) to obtain pure *tert*-butyl (*Z*)-2-chloro-3-phenylacrylate as yellow oil (453 mg, 1.90 mmol, 75%).

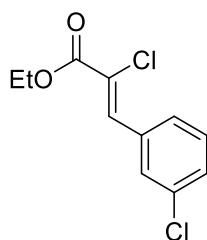
**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.55; **IR** (neat): 3056, 2981, 2933, 1710, 1617, 1490, 1446, 1394, 1367, 1282, 1252, 1203, 1151, 1077, 1043, 1013, 924, 842, 767, 609 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.83 – 7.80 (m, 3H), 7.45 – 7.39 (m, 3H), 1.58 (s, 9H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>): δ 162.3, 135.9, 133.2, 130.5, 129.9, 128.5, 123.8, 83.0, 28.0; **HRMS** (EI) *m/z* calculated for C<sub>13</sub>H<sub>15</sub>ClO<sub>2</sub> ([M]<sup>+</sup>) 238.0751, found 238.0754.

**General procedure (GP-A) for the synthesis of (Z)- $\alpha$ -halo cinnamates via titanium mediated olefination<sup>[3]</sup>**



A flame dried two-neck-flask equipped with a magnetic stir bar and a dropping funnel was charged with aromatic aldehyde (10.0 mmol, 1.00 equiv),  $\alpha$ -halo acetate (13.0 mmol, 1.30 equiv) and dry DCM (15 mL) under  $N_2$  atmosphere. Subsequently,  $TiCl_4$  (14.0 mmol, 1.40 equiv) diluted with dry DCM (14 mL) was added dropwise over a period of 10 min. After stirring for additional 30 min at room temperature,  $NEt_3$  (6.93 mL, 50.0 mmol, 5.00 equiv) was cautiously added in drops within 10 min. The resulting brown mixture was then stirred overnight. Upon completion of the reaction, the mixture was diluted with DCM (20 mL) and washed with  $HCl_{aq}$  (1.0 M, 15 mL),  $H_2O$  (15 mL) and brine (15 mL). The combined organic layers were dried over  $Na_2SO_4$ , the solvent was removed *in vacuo* and the residue was purified by column chromatography on  $SiO_2$  (hexanes / EA, 15:1) to obtain the pure product.

**ethyl (Z)-2-chloro-3-(3-chlorophenyl)acrylate (1i)**

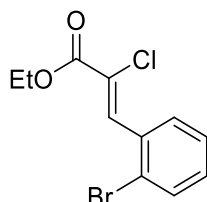


Following general procedure **GP-A** using 3-chlorobenzaldehyde (1.12 mL, 10.0 mmol, 1.00 equiv), ethyl chloroacetate (1.39 mL, 13.0 mmol, 1.30 equiv),  $TiCl_4$  (1.54 mL, 14.0 mmol, 1.40 equiv),  $NEt_3$  (6.93 mL, 50.0 mmol, 5.00 equiv) gave ethyl (Z)-2-chloro-3-(3-chlorophenyl)acrylate (887 mg, 3.62 mmol, 36%) as a yellowish oil after purification on  $SiO_2$  (hexanes / EA, 15:1).

$R_f$  (hexanes / EA, 10:1) = 0.35; **IR** (neat): 3063, 2981, 1718, 1617, 1565, 1476, 1412, 1367, 1241, 1196, 1095, 1039, 998, 902, 861, 782, 682  $cm^{-1}$ ;  **$^1H$ -NMR** (300 MHz,  $CDCl_3$ ):  $\delta$  7.87 – 7.82 (m, 2H), 7.71 – 7.66 (m, 1H), 7.39 – 7.35 (m, 2H), 4.36 (q,  $J$  = 7.1 Hz, 2H), 1.39 (t,  $J$  =

7.1 Hz, 3H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  163.1, 135.4, 134.7, 134.5, 130.2, 130.1, 129.8, 128.7, 123.7, 62.8, 14.2; **HRMS** (EI)  $m/z$  calculated for  $\text{C}_{11}\text{H}_{10}\text{Cl}_2\text{O}_2$  ( $[\text{M}]^+$ ) 244.0052, found 244.0050.

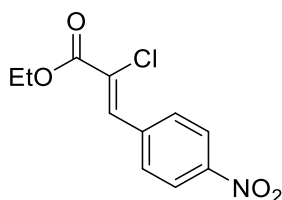
### ethyl (*Z*)-3-(2-bromophenyl)-2-chloroacrylate (**1j**)



Following general procedure **GP-A** using 2-bromobenzaldehyde (1.16 mL, 10.0 mmol, 1.00 equiv), ethyl chloroacetate (1.39 mL, 13.0 mmol, 1.30 equiv),  $\text{TiCl}_4$  (1.54 mL, 14.0 mmol, 1.40 equiv),  $\text{NEt}_3$  (6.93 mL, 50.0 mmol, 5.00 equiv) gave ethyl (*Z*)-3-(2-bromophenyl)-2-chloroacrylate (1.87 g, 6.64 mmol, 65%) as a colorless oil after purification on  $\text{SiO}_2$  (hexanes / EA, 15:1).

**R<sub>f</sub>** (hexanes / EA, 10:1) = 0.41; **IR** (neat): 3056, 2981, 2907, 1722, 1621, 1584, 1464, 1435, 1367, 1237, 1200, 1118, 1039, 998, 849, 760, 719  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.09 (s, 1H), 7.89 (dd,  $J = 7.8, 1.6$  Hz, 1H), 7.64 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.38 (td,  $J = 7.5, 1.0$  Hz, 1H), 7.25 (td,  $J = 7.7, 1.6$  Hz, 1H), 4.38 (q,  $J = 7.1$  Hz, 2H), 1.40 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.9, 136.3, 133.4, 132.9, 130.9, 130.9, 127.1, 124.9, 124.9, 62.8, 14.2; **HRMS** (EI)  $m/z$  calculated for  $\text{C}_{11}\text{H}_{10}\text{O}_2\text{ClBr}$  ( $[\text{M}]^+$ ) 287.9547, found 287.9551.

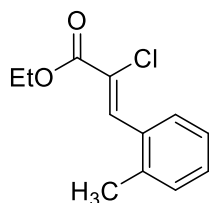
### ethyl (*Z*)-2-chloro-3-(4-nitrophenyl)acrylate (**1k**)



Following general procedure **GP-A** using 4-nitrobenzaldehyde (1.51 g, 10.0 mmol, 1.00 equiv), ethyl chloroacetate (1.39 mL, 13.0 mmol, 1.30 equiv),  $\text{TiCl}_4$  (1.54 mL, 14.0 mmol, 1.40 equiv),  $\text{NEt}_3$  (6.93 mL, 50.0 mmol, 5.00 equiv) gave ethyl (*Z*)-2-chloro-3-(4-nitrophenyl)acrylate (1.02 g, 3.99 mmol, 40%) as an orange solid after purification on  $\text{SiO}_2$  (hexanes / EA, 15:1).

**R<sub>f</sub>** (hexanes / EA, 10:1) = 0.18; **IR** (neat): 3127, 3093, 3026, 2944, 2903, 2851, 1710, 1617, 1509, 1345, 1263, 1200, 1110, 1032, 924, 853, 760, 682 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ 8.31 – 8.25 (m, 2H), 7.99 – 7.93 (m, 3H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 162.6, 148.0, 139.1, 134.3, 131.1, 126.1, 123.7, 63.1, 14.2; **HRMS** (EI) *m/z* calculated for C<sub>11</sub>H<sub>10</sub>NO<sub>4</sub>Cl ([M]<sup>+</sup>) 255.0293, found 255.0295.

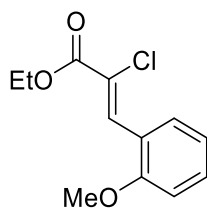
**ethyl (Z)-2-chloro-3-(o-tolyl)acrylate (1m)**



Following general procedure **GP-A** using 2-methylbenzaldehyde (1.16 mL, 10.0 mmol, 1.00 equiv), ethyl chloroacetate (1.39 mL, 13.0 mmol, 1.30 equiv), TiCl<sub>4</sub> (1.54 mL, 14.0 mmol, 1.40 equiv), NEt<sub>3</sub> (6.93 mL, 50.0 mmol, 5.00 equiv) gave ethyl (Z)-2-chloro-3-(o-tolyl)acrylate (1.83 g, 8.14 mmol, 82%) as colorless oil after purification on SiO<sub>2</sub> (hexanes / EA, 15:1).

**R<sub>f</sub>** (hexanes / EA, 10:1) = 0.47; **IR** (neat): 3063, 2981, 1718, 1617, 1483, 1367, 1237, 1039, 1095, 998, 883, 863, 805, 764, 663 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ 8.05 (s, 1H), 7.79 – 7.73 (m, 1H), 7.31 – 7.22 (m, 3H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 163.3, 137.5, 136.2, 132.3, 130.2, 129.5, 129.0, 125.7, 123.9, 62.6, 20.0, 14.2; **HRMS** (EI) *m/z* calculated for C<sub>12</sub>H<sub>13</sub>O<sub>2</sub>Cl ([M]<sup>+</sup>) 224.0599, found 224.0598.

**ethyl (Z)-2-chloro-3-(2-methoxyphenyl)acrylate (1p)**

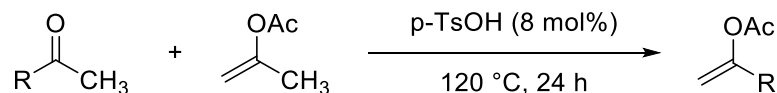


Following general procedure **GP-A** using 2-methoxybenzaldehyde (1.20 mL, 10.0 mmol, 1.00 equiv), ethyl chloroacetate (1.39 mL, 13.0 mmol, 1.30 equiv),  $\text{TiCl}_4$  (1.54 mL, 14.0 mmol, 1.40 equiv),  $\text{NEt}_3$  (6.93 mL, 50.0 mmol, 5.00 equiv) gave ethyl (*Z*)-2-chloro-3-(2-methoxyphenyl)acrylate (1.66 g, 6.90 mmol, 69%) as yellowish oil after purification on  $\text{SiO}_2$  (hexanes / EA, 15:1).

**R<sub>f</sub>** (hexanes / EA, 10:1) = 0.30; **IR** (neat): 3056, 2981, 2940, 2840, 1714, 1599, 1483, 1394, 1367, 1233, 1192, 1110, 1025, 883, 849, 797, 752, 674  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.24 (s, 1H), 8.08 (dd,  $J = 7.8, 1.5$  Hz, 1H), 7.42 – 7.35 (m, 1H), 7.04 – 6.99 (m, 1H), 6.94 – 6.91 (d,  $J = 8.3$  Hz, 1H), 4.36 (q,  $J = 7.1$  Hz, 2H), 3.88 (s, 3H), 1.39 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  163.6, 158.0, 132.1, 131.5, 130.2, 122.5, 122.0, 120.2, 110.5, 62.5, 55.6, 14.3; **HRMS** (EI)  $m/z$  calculated for  $\text{C}_{12}\text{H}_{13}\text{O}_3\text{Cl}$  ( $[\text{M}]^+$ ) 240.0547, found 240.0553.

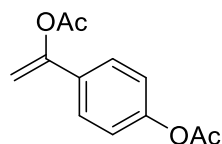
## 6. Synthesis of enol acetates (2c, 2e)

### General procedure (GP-B) for the synthesis of enol acetates<sup>[12]</sup>



A 100 mL flask equipped with a magnetic stir bar, a reflux condenser and a drying tube was charged with ketone (50.0 mmol, 1.00 equiv), isopropenyl acetate (250 mmol, 5.00 equiv) and p-TsOH·H<sub>2</sub>O (4.00 mmol, 0.08 equiv). The reaction mixture was heated to 120 °C. After 24 h the reaction mixture was allowed to cool to room temperature and the remaining isopropenyl acetate was subsequently evaporated under reduced pressure. The residue was redissolved in Et<sub>2</sub>O (100 mL) and the resulting solution was washed with H<sub>2</sub>O (3 x 50 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated *in vacuo* to give a dark red oil. The pure product was obtained by distillation under reduced pressure or by purification on SiO<sub>2</sub> (DCM / hexanes).

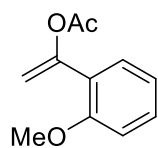
### 1-(4-acetoxyphenyl)vinyl acetate (2c)



Following general procedure **GP-B** using 1-(4-hydroxyphenyl)ethan-1-one (2.72 g, 20.0 mmol, 1.00 equiv), isopropenyl acetate (13.1 mL, 120 mmol, 6.00 equiv) and p-TsOH·H<sub>2</sub>O (304 mg, 1.60 mmol, 0.08 equiv) gave 1-(4-acetoxyphenyl)vinyl acetate (2.01 g, 9.13 mmol, 46%) as a white solid after purification on SiO<sub>2</sub> (DCM / hexanes, 1:1).

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.28; **IR** (neat): 3049, 2926, 2855, 1755, 1643, 1602, 1505, 1367, 1267, 1189, 1088, 1043, 1013, 961, 909, 887, 849, 812 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>): δ 7.50 – 7.45 (m, 2H), 7.11 – 7.06 (m, 2H), 5.45 (d, *J* = 2.3 Hz, 1H), 5.03 (d, *J* = 2.3 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 169.3, 169.0, 152.1, 151.1, 132.1, 126.1, 121.7, 102.4, 21.2, 21.0; **HRMS** (EI) *m/z* calculated for C<sub>12</sub>H<sub>12</sub>O<sub>4</sub> ([M]<sup>+</sup>) 220.0730, found 220.0735.

## 1-(2-methoxyphenyl)vinyl acetate (2e)

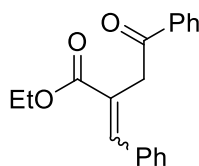


Following general procedure **GP-B** using 1-(2-methoxyphenyl)ethan-1-one (7.51 g, 50.0 mmol, 1.00 equiv), isopropenyl acetate (27.2 mL, 250 mmol, 5.00 equiv) and p-TsOH·H<sub>2</sub>O (761 mg, 4.00 mmol, 0.08 equiv) gave 1-(2-methoxyphenyl)vinyl acetate (5.60 g, 29.1 mmol, 58%) as a colorless oil after purification on SiO<sub>2</sub> (DCM / hexanes, 1:1).

**R<sub>f</sub>** (DCM) = 0.54; **IR** (neat): 3004, 2940, 2840, 1755, 1636, 1599, 1490, 1461, 1435, 1367, 1282, 1244, 1192, 1125, 1073, 1017, 961, 887, 812, 752, 704 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.35 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.32 – 7.27 (m, 1H), 6.96 – 6.91 (m, 2H), 5.59 (d, *J* = 1.3 Hz, 1H), 5.15 (d, *J* = 1.3 Hz, 1H), 3.87 (s, 3H), 2.21 (s, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>): δ 169.1, 157.0, 150.3, 123.0, 128.5, 123.4, 120.5, 111.3, 106.6, 55.6, 21.0; **HRMS** (EI) *m/z* calculated for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub> ([M]<sup>+</sup>) 192.0781, found 192.0785.



### ethyl 2-benzylidene-4-oxo-4-phenylbutanoate (**3aa**)

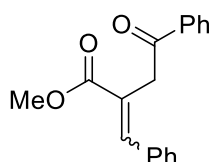


Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-phenylacrylate (**1a-Cl**, 105 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3aa** (68.2 mg, 231  $\mu\text{mol}$ , 46%) and (*Z*)-**3aa** (76.9 mg, 260  $\mu\text{mol}$ , 52%) as colorless oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 12:1). *E/Z* = 47:53.

**R<sub>f</sub>** (hexanes / EA, 10:1) = 0.30 (*E* Isomer), 0.27 (*Z* Isomer); **IR** (neat): 3060, 3026, 2981, 2937, 2903, 1684, 1595, 1448, 1401, 1334, 1211, 1125, 1021, 991, 924, 842, 745, 693  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  8.04 – 7.98 (m, 3H), 7.63 – 7.55 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.40 – 7.27 (m, 5H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.20 (d, *J* = 0.4 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  197.5, 167.5, 142.0, 136.7, 135.3, 133.3, 128.8, 128.7, 128.7, 128.6, 128.3, 127.4, 61.2, 38.1, 14.2; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  8.03 – 8.00 (m, 2H), 7.63 – 7.55 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.32 – 7.27 (m, 5H), 6.90 (s, 1H), 4.16 (d, *J* = 1.2 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 1.04 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  197.1, 168.1, 139.4, 136.4, 135.9, 133.4, 128.7, 128.6, 128.3, 128.1, 127.9, 127.9, 60.8, 45.0, 13.6; **HRMS** (ESI) *m/z* calculated for C<sub>19</sub>H<sub>19</sub>O<sub>3</sub> ([M+H]<sup>+</sup>) 295.1329, found 295.1331.

Analytical data for (*E*)-**3aa** is in agreement with literature reference.<sup>[19]</sup>

### methyl 2-benzylidene-4-oxo-4-phenylbutanoate (**3ba**)



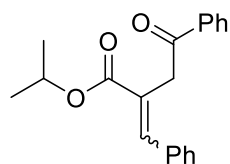
Following general procedure **GP-C** using methyl (*Z*)-2-chloro-3-phenylacrylate (**1b**, 98.3 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3ba** (55.4 mg, 197  $\mu\text{mol}$ , 40%) and (*Z*)-

**3ba** (67.6 mg, 241  $\mu\text{mol}$ , 48%) as yellowish oils as separated *E* and *Z* isomers after purification on  $\text{SiO}_2$  (hexanes / EA, 20:1 to 8:1). *E/Z* = 45:55.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.28 (*E* Isomer), 0.21 (*Z* Isomer); **IR** (neat): 3060, 3026, 2952, 1710, 1595, 1435, 1397, 1334, 1211, 1125, 998, 924, 834, 745, 689  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (400 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  8.04 – 7.99 (m, 3H), 7.61 – 7.57 (m, 1H), 7.51 – 7.46 (m, 2H), 7.36 – 7.28 (m, 5H), 4.20 (s, 2H), 3.79 (s, 3H); **<sup>13</sup>C-NMR** (101 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  197.4, 168.0, 142.3, 136.7, 135.3, 133.3, 128.8, 128.8, 128.7, 128.6, 128.3, 127.1, 52.3, 38.1; **<sup>1</sup>H-NMR** (400 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  8.03 – 7.99 (m, 2H), 7.61 – 7.57 (m, 1H), 7.51 – 7.46 (m, 2H), 7.34 – 7.28 (m, 5H), 6.89 (s, 1H), 4.16 (d,  $J$  = 1.0 Hz, 2H), 3.63 (s, 3H); **<sup>13</sup>C-NMR** (101 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  197.0, 168.6, 139.5, 136.4, 135.8, 133.4, 128.7, 128.6, 128.3, 128.2, 128.0, 127.4, 51.7, 45.1; **HRMS** (ESI)  $m/z$  calculated for  $\text{C}_{18}\text{H}_{17}\text{O}_3$  ( $[\text{M}+\text{H}]^+$ ) 281.1172, found 281.1176.

Analytical data for (*E*)-**3ba** is in agreement with literature reference.<sup>[20]</sup>

### *iso*-propyl 2-benzylidene-4-oxo-4-phenylbutanoate (**3ca**)

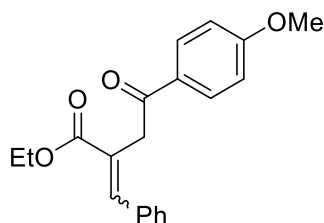


Following general procedure **GP-C** using *iso*-propyl (*Z*)-2-chloro-3-phenylacrylate (**1c**, 112 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*- $\text{Ir}(\text{ppy})_3$  (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3ca** (58.8 mg, 189  $\mu\text{mol}$ , 38%) and (*Z*)-**3ca** (66.3 mg, 214  $\mu\text{mol}$ , 43%) as colorless oils as separated *E* and *Z* isomers after purification on  $\text{SiO}_2$  (hexanes / EA, 20:1 to 8:1). *E/Z* = 47:53.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.35 (*E* Isomer), 0.31 (*Z* Isomer); **IR** (neat): 3060, 3026, 2981, 2937, 1684, 1595, 1494, 1446, 1375, 1334, 1311, 1289, 1211, 1133, 1103, 995, 838, 745, 693  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (400 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  8.01 – 8.00 (m, 3H), 7.58 (t,  $J$  = 7.4 Hz, 1H), 7.47 (t,  $J$  = 7.6 Hz, 2H), 7.37 – 7.28 (m, 5H), 5.11 (sept,  $J$  = 6.2 Hz, 1H), 4.18 (s, 2H), 1.25 (d,  $J$  = 6.3 Hz, 6H); **<sup>13</sup>C-NMR** (101 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  197.6, 166.9, 141.7, 136.9, 135.5, 133.2, 128.8, 128.7, 128.7, 128.6, 128.3, 127.9, 68.6, 38.0, 21.8; **<sup>1</sup>H-NMR** (400 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  8.02 (d,  $J$  = 7.6 Hz, 2H), 7.59 (t,  $J$  = 7.4 Hz, 1H), 7.48 (t,  $J$  = 7.6 Hz, 2H), 7.32 – 7.27 (m, 5H), 6.88 (s, 1H), 4.99 (sept,  $J$  = 6.2 Hz, 1H), 4.14 (s, 2H), 1.05 (d,  $J$  = 6.3 Hz, 6H);

$^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  197.1, 167.5, 138.9, 136.6, 136.1, 133.3, 128.7, 128.7, 128.5, 128.3, 127.9, 127.9, 68.4, 45.1, 21.3; **HRMS** (ESI)  $m/z$  calculated for  $\text{C}_{20}\text{H}_{21}\text{O}_3$  ( $[\text{M}+\text{H}]^+$ ) 309.1485, found 309.1489.

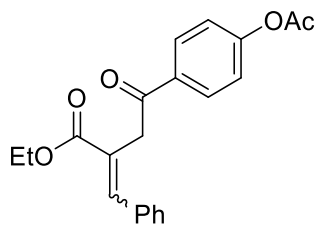
**ethyl 2-benzylidene-4-(4-methoxyphenyl)-4-oxobutanoate (3ab)**



Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-phenylacrylate (**1a-Cl**, 63.2 mg, 300  $\mu\text{mol}$ , 1.00 equiv), 1-(4-methoxyphenyl)vinyl acetate (**2b**, 288 mg, 1.50 mmol, 5.00 equiv) and *fac*- $\text{Ir}(\text{ppy})_3$  (3.93 mg, 6.00  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3ab** (40.7 mg, 126  $\mu\text{mol}$ , 42%) and (*Z*)-**3ab** (47.8 mg, 147  $\mu\text{mol}$ , 49%) as yellowish oils as separated *E* and *Z* isomers after purification on  $\text{SiO}_2$  (hexanes / EA, 20:1 to 6:1). *E/Z* = 46:54.

$R_f$  (hexanes / EA, 10:1) = 0.12 (*E* Isomer), 0.10 (*Z* Isomer); **IR** (neat): 3056, 2978, 2937, 2840, 1708, 1677, 1599, 1509, 1446, 1420, 1371, 1319, 1259, 1218, 1170, 1092, 1025, 931, 831, 760, 704  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  8.01 – 7.97 (m, 3H), 7.33 – 7.29 (m, 5H), 6.97 – 6.91 (m, 2H), 4.24 (q,  $J = 7.1$  Hz, 2H), 4.15 (s, 2H), 3.88 (s, 3H), 1.27 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  196.0, 167.6, 163.6, 141.8, 135.4, 130.6, 129.8, 128.8, 128.7, 128.6, 127.6, 113.8, 61.1, 55.5, 37.7, 14.2;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  8.02 – 7.98 (m, 2H), 7.32 – 7.28 (m, 5H), 6.97 – 6.93 (m, 2H), 6.88 (s, 1H), 4.14 – 4.06 (m, 4H), 3.87 (s, 3H), 1.03 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  195.6, 168.3, 163.7, 139.0, 136.0, 130.6, 129.5, 128.6, 128.2, 128.0, 127.9, 113.8, 60.8, 55.5, 44.7, 13.6; **HRMS** (ESI)  $m/z$  calculated for  $\text{C}_{20}\text{H}_{21}\text{O}_4$  ( $[\text{M}+\text{H}]^+$ ) 325.1434, found 325.1439.

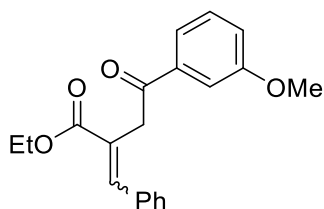
**ethyl 4-(4-acetoxyphenyl)-2-benzylidene-4-oxobutanoate (3ac)**



Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-phenylacrylate (**1a-Cl**, 105 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-(4-acetoxyphenyl)vinyl acetate (**2c**, 551 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3ac** (82.1 mg, 234  $\mu\text{mol}$ , 47%) and (*Z*)-**3ac** (88.9 mg, 252  $\mu\text{mol}$ , 50%) as yellowish oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 6:1). *E/Z* = 48:52.

**R<sub>f</sub>** (hexanes / EA, 4:1) = 0.18 (*E* Isomer), 0.16 (*Z* Isomer); **IR** (neat): 3060, 3026, 2981, 2907, 1759, 1684, 1599, 1502, 1408, 1371, 1334, 1189, 1162, 1125, 995, 909, 849, 745, 697 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  8.06 – 8.01 (m, 3H), 7.35 – 7.28 (m, 5H), 7.22 – 7.18 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.17 (s, 2H), 2.33 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  196.2, 168.9, 167.4, 154.5, 142.1, 135.3, 134.3, 129.9, 128.8, 128.8, 128.7, 127.2, 121.9, 61.2, 38.1, 21.2, 14.2; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  8.08 – 8.03 (m, 2H), 7.33 – 7.28 (m, 5H), 7.25 – 7.21 (m, 2H), 6.90 (s, 1H), 4.14 – 4.06 (m, 4H), 2.34 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  195.8, 168.8, 168.0, 154.5, 139.6, 135.9, 134.1, 130.0, 128.7, 128.1, 127.9, 127.7, 121.9, 60.8, 44.9, 21.2, 13.6; **HRMS** (ESI) *m/z* calculated for C<sub>21</sub>H<sub>21</sub>O<sub>5</sub> ([*M*+*H*]<sup>+</sup>) 353.1384, found 353.1386.

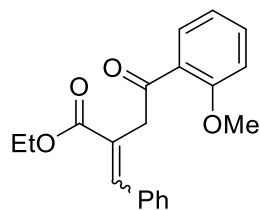
### ethyl 2-benzylidene-4-(3-methoxyphenyl)-4-oxobutanoate (**3ad**)



Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-phenylacrylate (**1a-Cl**, 105 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-(3-methoxyphenyl)vinyl acetate (**2d**, 481 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3ad** (64.4 mg, 199  $\mu\text{mol}$ , 40%) and (*Z*)-**3ad** (75.6 mg, 234  $\mu\text{mol}$ , 47%) as slightly yellow oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 12:1). *E/Z* = 46:54.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.21 (*E* Isomer), 0.17 (*Z* Isomer); **IR** (neat): 3060, 2981, 2836, 1684, 1580, 1487, 1431, 1371, 1319, 1252, 1192, 1092, 1021, 981, 864, 782, 693 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *E* Isomer): δ 8.02 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.40 – 7.28 (m, 6H), 7.15 – 7.11 (m, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.18 (s, 2H), 3.85 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *E* Isomer): δ 197.3, 167.5, 159.9, 142.0, 138.1, 135.4, 129.7, 128.8, 128.8, 128.6, 127.4, 120.9, 119.8, 112.5, 61.1, 55.5, 38.2, 14.2; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *Z* Isomer): δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.33 – 7.28 (m, 5H), 7.13 (dd, *J* = 7.9, 2.3 Hz, 1H), 6.90 (s, 1H), 4.14 (d, *J* = 0.8 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *Z* Isomer): δ 196.9, 168.1, 159.9, 139.3, 137.8, 136.0, 129.7, 128.6, 128.1, 127.9, 121.0, 120.0, 112.4, 60.8, 55.5, 45.1, 13.6; **HRMS** (APCI) *m/z* calculated for C<sub>20</sub>H<sub>21</sub>O<sub>4</sub> ([M+H]<sup>+</sup>) 325.1434, found 325.1440.

#### ethyl 2-benzylidene-4-(2-methoxyphenyl)-4-oxobutanoate (**3ae**)

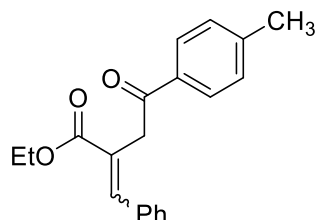


Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-phenylacrylate (**1a-Cl**, 105 mg, 500 μmol, 1.00 equiv), 1-(2-methoxyphenyl)vinyl acetate (**2e**, 481 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0 μmol, 0.02 equiv) gave (*E*)-**3ae** (63.5 mg, 196 μmol, 39%) and (*Z*)-**3ae** (74.5 mg, 231 μmol, 46%) as slightly yellow oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 12:1). *E/Z* = 46:54.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.21 (*E* Isomer), 0.17 (*Z* Isomer); **IR** (neat): 3060, 2981, 2940, 2840, 1703, 1669, 1595, 1483, 1371, 1323, 1244, 1177, 1088, 1021, 998, 909, 823, 756, 693 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *E* Isomer): δ 7.95 (s, 1H), 7.75 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.37 – 7.32 (m, 5H), 7.04 – 6.93 (m, 2H), 4.28 – 4.19 (m, 4H), 3.83 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *E* Isomer): δ 199.5, 167.7, 158.6, 141.3, 135.5, 133.6, 130.6, 129.0, 128.6, 128.5, 128.0, 128.0, 120.7, 111.5, 61.0, 55.5, 43.3, 14.2; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *Z* Isomer): δ 7.78 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.33 – 7.28 (m, 5H), 7.04 – 6.96 (m, 2H), 6.84 (s, 1H), 4.16 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *Z* Isomer): δ 198.8, 168.4, 158.8, 138.5,

136.2, 133.9, 130.8, 128.9, 128.6, 127.9, 127.4, 120.8, 111.5, 60.6, 55.5, 50.4, 13.7; **HRMS** (APCI)  $m/z$  calculated for  $C_{20}H_{21}O_4$  ( $[M+H]^+$ ) 325.1434, found 325.1435.

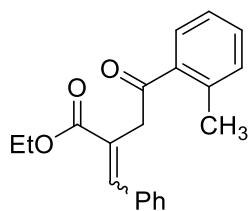
### ethyl 2-benzylidene-4-oxo-4-(p-tolyl)butanoate (**3af**)



Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-phenylacrylate (**1a-Cl**, 105 mg, 500  $\mu$ mol, 1.00 equiv), 1-(*p*-tolyl)vinyl acetate (**2f**, 441 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu$ mol, 0.02 equiv) gave (*E*)-**3af** (56.8 mg, 184  $\mu$ mol, 37%) and (*Z*)-**3af** (75.2 mg, 243  $\mu$ mol, 48%) as slightly yellow oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 10:1). *E/Z* = 43:57.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.32 (*E* Isomer), 0.28 (*Z* Isomer); **IR** (neat): 3056, 3030, 2981, 2922, 1681, 1606, 1446, 1408, 1371, 1326, 1263, 1177, 1092, 1021, 909, 812, 790, 730, 700  $cm^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  8.02 (s, 1H), 7.94 – 7.89 (m, 2H), 7.34 – 7.26 (m, 7H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.18 (s, 2H), 2.42 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  197.1, 167.5, 144.1, 141.9, 135.4, 134.2, 129.3, 128.8, 128.7, 128.6, 128.4, 127.5, 61.1, 37.9, 21.7, 14.2; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  7.91 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.25 (m, 7H), 6.88 (s, 1H), 4.13 – 4.07 (m, 4H), 2.42 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  196.7, 168.1, 144.2, 139.1, 136.0, 134.0, 129.4, 128.6, 128.4, 128.1, 128.0, 127.9, 60.7, 44.9, 21.7, 13.6; **HRMS** (ESI)  $m/z$  calculated for  $C_{20}H_{21}O_3$  ( $[M+H]^+$ ) 309.1485, found 309.1488.

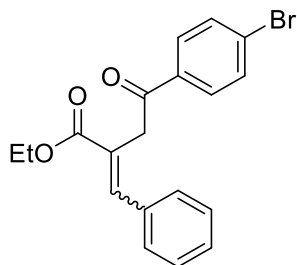
### ethyl 2-benzylidene-4-oxo-4-(o-tolyl)butanoate (**3ag**)



Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-phenylacrylate (**1a-Cl**, 105 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-(*o*-tolyl)vinyl acetate (**2g**, 441 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3ag** (35.5 mg, 115  $\mu\text{mol}$ , 23%) and (*Z*)-**3ag** (40.1 mg, 129.9  $\mu\text{mol}$ , 26%) as slightly yellow oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 12:1). *E/Z* = 47:53.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.38 (*E* Isomer), 0.30 (*Z* Isomer); **IR** (neat): 3060, 3026, 2981, 2929, 2903, 1684, 1602, 1446, 1401, 1323, 1289, 1237, 1207, 1121, 1021, 984, 842, 752, 697  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  8.02 (s, 1H), 7.70 – 7.67 (m, 1H), 7.41 – 7.32 (m, 6H), 7.28 – 7.25 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.12 (s, 2H), 2.51 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  201.4, 167.5, 142.0, 138.2, 137.8, 135.4, 131.9, 131.4, 128.8, 128.7, 128.6, 128.5, 127.5, 125.7, 61.2, 41.0, 21.1, 14.3; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  7.75 (d, *J* = 7.7 Hz, 1H), 7.39 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33 – 7.25 (m, 7H), 6.91 (s, 1H), 4.13 – 4.05 (m, 4H), 2.52 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  200.7, 168.0, 139.7, 138.6, 137.3, 135.9, 132.0, 131.6, 128.7, 128.7, 128.1, 128.0, 127.9, 125.7, 60.8, 47.9, 21.3, 13.7; **HRMS** (ESI) *m/z* calculated for C<sub>20</sub>H<sub>21</sub>O<sub>3</sub> ([M+H]<sup>+</sup>) 309.1485, found 309.1487.

#### ethyl 2-benzylidene-4-(4-bromophenyl)-4-oxobutanoate (**3ah**)

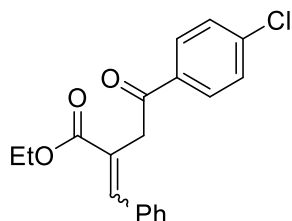


Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-phenylacrylate (**1a-Cl**, 63.2 mg, 300  $\mu\text{mol}$ , 1.00 equiv), 1-(4-bromophenyl)vinyl acetate (**2h**, 362 mg, 1.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (3.93 mg, 6.00  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3ah** (35.2 mg, 94.1  $\mu\text{mol}$ , 32%) and

(*Z*)-**3ah** (28.8 mg, 77.0  $\mu\text{mol}$ , 26%) as slightly yellow oils as separated *E* and *Z* isomers after purification on  $\text{SiO}_2$  (hexanes / EA, 20:1 to 12:1). *E/Z* = 55:45.

**R<sub>f</sub>** (hexanes / EA, 10:1) = 0.30 (*E* Isomer), 0.27 (*Z* Isomer); **IR** (neat): 3060, 3026, 2981, 2929, 1684, 1584, 1483, 1384, 1371, 1319, 1263, 1192, 1092, 995, 935, 812, 764, 700  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  8.02 (s, 1H), 7.91 – 7.82 (m, 2H), 7.65 – 7.59 (m, 2H), 7.38 – 7.27 (m, 5H), 4.24 (q,  $J = 7.1$  Hz, 2H), 4.14 (s, 2H), 1.27 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  196.6, 167.3, 142.2, 135.4, 135.2, 132.0, 129.8, 128.8, 128.7, 128.7, 128.5, 127.1, 61.2, 37.9, 14.2; **<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  7.91 – 7.84 (m, 2H), 7.66 – 7.59 (m, 2H), 7.34 – 7.27 (m, 5H), 6.91 (s, 1H), 4.15 – 4.03 (m, 4H), 1.03 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  196.1, 167.9, 139.7, 135.8, 135.2, 132.0, 129.8, 128.6, 128.6, 128.2, 127.9, 127.5, 60.8, 44.9, 13.6; **HRMS** (ESI)  $m/z$  calculated for  $\text{C}_{19}\text{H}_{18}\text{BrO}_3$  ( $[\text{M}+\text{H}]^+$ ) 373.0434, found 373.0441.

#### ethyl 2-benzylidene-4-(4-chlorophenyl)-4-oxobutanoate (**3ai**)

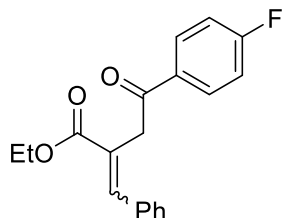


Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-phenylacrylate (**1a-Cl**, 63.2 mg, 300  $\mu\text{mol}$ , 1.00 equiv), 1-(4-chlorophenyl)vinyl acetate (**2i**, 295 mg, 1.50 mmol, 5.00 equiv) and *fac*- $\text{Ir}(\text{ppy})_3$  (3.93 mg, 6.00  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3ai** (34.8 mg, 106  $\mu\text{mol}$ , 35%) and (*Z*)-**3ai** (26.2 mg, 80.0  $\mu\text{mol}$ , 27%) as slightly yellow oils as separated *E* and *Z* isomers after purification on  $\text{SiO}_2$  (hexanes / EA, 20:1 to 12:1). *E/Z* = 57:43.

**R<sub>f</sub>** (hexanes / EA, 10:1) = 0.30 (*E* Isomer), 0.26 (*Z* Isomer); **IR** (neat): 3080, 3026, 2981, 2937, 2903, 1684, 1587, 1490, 1401, 1334, 1207, 1125, 1092, 991, 838, 749, 697  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  8.02 (s, 1H), 7.98 – 7.91 (m, 2H), 7.49 – 7.42 (m, 2H), 7.37 – 7.27 (m, 5H), 4.24 (q,  $J = 7.1$  Hz, 2H), 4.14 (s, 2H), 1.28 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  196.4, 167.4, 142.2, 139.7, 135.2, 135.0, 129.7, 129.0, 128.8, 128.7, 128.7, 127.1, 61.2, 38.0, 14.2; **<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  8.00 – 7.90 (m, 2H), 7.51 – 7.41 (m, 2H), 7.33 – 7.27 (m, 5H), 6.91 (s, 1H), 4.14 – 4.04 (m, 4H), 1.03 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  195.9, 168.0, 139.8, 139.7, 135.8, 134.7, 129.7, 129.0,

128.6, 128.2, 127.9, 127.5, 60.9, 44.9, 13.6; **HRMS** (ESI)  $m/z$  calculated for  $C_{19}H_{18}ClO_3$  ( $[M+H]^+$ ) 329.0939, found 329.0941.

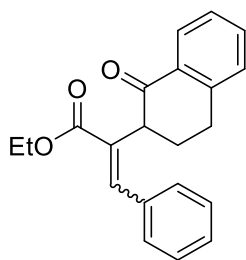
**ethyl 2-benzylidene-4-(4-fluorophenyl)-4-oxobutanoate (3aj)**



Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-phenylacrylate (**1a-Cl**, 63.2 mg, 300  $\mu$ mol, 1.00 equiv), 1-(4-fluorophenyl)vinyl acetate (**2j**, 90.0 mg, 500  $\mu$ mol, 1.67 equiv) and *fac*-Ir(ppy)<sub>3</sub> (3.93 mg, 6.00  $\mu$ mol, 0.02 equiv) gave (*E*)-**3aj** (36.3 mg, 116  $\mu$ mol, 39%) and (*Z*)-**3aj** (37.8 mg, 121  $\mu$ mol, 40%) as slightly yellow oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 15:1). *E/Z* = 49:51.

**R<sub>f</sub>** (hexanes / EA, 10:1) = 0.30 (*E* Isomer), 0.26 (*Z* Isomer); **IR** (neat): 3060, 3026, 2981, 2933, 1684, 1595, 1505, 1408, 1334, 1211, 1155, 1125, 1021, 998, 842, 738, 697  $cm^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  8.08 – 7.99 (m, 3H), 7.37 – 7.29 (m, 5H), 7.19 – 7.10 (m, 2H), 4.24 (q,  $J$  = 7.1 Hz, 2H), 4.15 (s, 2H), 1.28 (t,  $J$  = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  196.0, 167.6, 167.4, 164.2, 142.2, 135.3, 133.2, 133.1, 131.0, 130.9, 128.8, 128.8, 128.6, 127.2, 115.9, 115.6, 61.2, 37.9, 14.2; **<sup>19</sup>F-NMR** (282 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  -105.45; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  8.08 – 8.02 (m, 2H), 7.33 – 7.27 (m, 5H), 7.20 – 7.11 (m, 2H), 6.91 (s, 1H), 4.13 – 4.06 (m, 4H), 1.03 (t,  $J$  = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  195.5, 168.0, 167.6, 164.2, 139.6, 135.9, 132.9, 132.8, 131.0, 130.9, 128.6, 128.1, 127.9, 127.6, 116.0, 115.7, 60.8, 44.9, 13.6; **<sup>19</sup>F-NMR** (282 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  -105.22; **HRMS** (ESI)  $m/z$  calculated for  $C_{19}H_{18}FO_3$  ( $[M+H]^+$ ) 313.1234, found 313.1243.

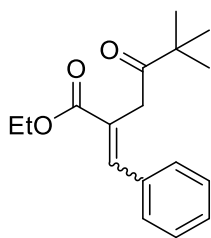
**ethyl 2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)-3-phenylacrylate (3ak)**



Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-phenylacrylate (**1a-Cl**, 105 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 3,4-dihydronaphthalen-1-yl acetate (**2k**, 471 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3ak** (15.4 mg, 48.0  $\mu\text{mol}$ , 10%) and (*Z*)-**3ak** (23.1 mg, 72.0  $\mu\text{mol}$ , 14%) as slightly yellow oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 9:1). *E/Z* = 40:60.

**R<sub>f</sub>** (hexanes / EA, 10:1) = 0.17 (*E* Isomer), 0.10 (*Z* Isomer); **IR** (neat): 3060, 3026, 2937, 2981, 2877, 1707, 1681, 1636, 1599, 1453, 1367, 1271, 1222, 1200, 1125, 902, 745, 700  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  8.08 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.98 (s, 1H), 7.46 (td,  $J = 7.5, 1.5$  Hz, 1H), 7.41 – 7.28 (m, 6H), 7.23 – 7.18 (m, 1H), 4.20 (qd,  $J = 7.1, 1.6$  Hz, 2H), 3.88 (dd,  $J = 12.9, 4.8$  Hz, 1H), 3.02 – 2.91 (m, 2H), 2.71 (ddd,  $J = 25.2, 12.7, 5.3$  Hz, 1H), 2.18 – 2.07 (m, 1H), 1.21 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  197.4, 166.6, 143.7, 142.0, 135.5, 133.3, 133.0, 132.5, 128.6, 128.6, 128.5, 127.6, 126.7, 60.9, 48.5, 29.4, 29.2, 14.10; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  8.07 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.49 (td,  $J = 7.5, 1.5$  Hz, 1H), 7.33 – 7.26 (m, 7H), 6.82 (s, 1H), 4.10 (qd,  $J = 7.1, 0.7$  Hz, 2H), 3.74 (ddd,  $J = 12.5, 4.6, 1.1$  Hz, 1H), 3.18 – 3.03 (m, 2H), 2.62 – 2.31 (m, 2H), 1.02 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  197.0, 168.6, 143.9, 136.8, 136.2, 133.5, 133.3, 132.4, 128.7, 128.5, 127.9, 127.7, 126.8, 60.7, 54.2, 29.5, 29.4, 13.6; **HRMS** (ESI) *m/z* calculated for C<sub>21</sub>H<sub>20</sub>O<sub>3</sub>Na ([M+Na]<sup>+</sup>) 343.1305, found 343.1305.

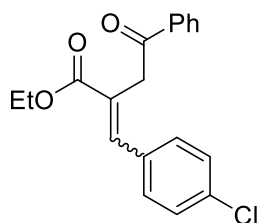
**ethyl 2-benzylidene-5,5-dimethyl-4-oxohexanoate (3al)**



Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-phenylacrylate (**1a-Cl**, 105 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 3,3-dimethylbut-1-en-2-yl acetate (**2l**, 356 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3al** (11.1 mg, 40.3  $\mu\text{mol}$ , 8%) and (*Z*)-**3al** (11.1 mg, 40.3  $\mu\text{mol}$ , 8%) as colorless oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 12:1). *E/Z* = 50:50.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.35 (*E* Isomer), 0.28 (*Z* Isomer); **IR** (neat): 3056, 3026, 2970, 2873, 1703, 1476, 1397, 1323, 1237, 1207, 1125, 1062, 1025, 935, 846, 816, 738, 697  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  7.95 (s, 1H), 7.38 – 7.31 (m, 3H), 7.24 – 7.21 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.21 (s, 9H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  213.1, 167.5, 141.9, 135.5, 128.6, 128.5, 127.7, 61.0, 44.5, 36.5, 26.8, 14.3; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  7.31 – 7.27 (m, 5H), 6.79 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.68 (d, *J* = 0.9 Hz, 2H), 1.21 (s, 9H), 1.04 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  212.8, 168.0, 139.3, 136.1, 128.6, 128.2, 127.9, 127.8, 60.6, 44.2, 43.4, 26.5, 13.7; **HRMS** (APCI) *m/z* calculated for C<sub>17</sub>H<sub>23</sub>O<sub>3</sub> ([*M*+*H*]<sup>+</sup>) 275.1642, found 275.1645.

#### ethyl 2-(4-chlorobenzylidene)-4-oxo-4-phenylbutanoate (**3ea**)

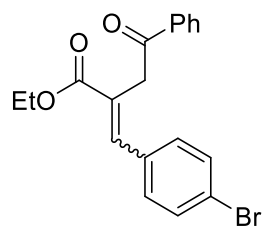


Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-(4-chlorophenyl)acrylate (**1e**, 123 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3ea** (58.1 mg, 177  $\mu\text{mol}$ , 36%) and (*Z*)-**3ea** (73.9 mg, 226  $\mu\text{mol}$ , 45%) as slightly yellow oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 8:1). *E/Z* = 44:56.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.24 (*E* Isomer), 0.20 (*Z* Isomer); **IR** (neat): 3056, 2974, 2907, 1707, 1677, 1591, 1487, 1379, 1341, 1297, 1241, 1125, 998, 849, 749, 685 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *E* Isomer): δ 8.03 – 7.98 (m, 2H), 7.96 (s, 1H), 7.62 – 7.57 (m, 1H), 7.51 – 7.46 (m, 2H), 7.33 – 7.23 (m, 4H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.15 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *E* Isomer): δ 197.4, 167.2, 140.8, 136.6, 134.8, 133.8, 133.4, 130.1, 128.9, 128.7, 128.3, 128.0, 61.3, 37.9, 14.2; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *Z* Isomer): δ 8.01 – 7.98 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 – 7.46 (m, 2H), 7.30 – 7.24 (m, 4H), 6.83 (s, 1H), 4.14 – 4.07 (m, 4H), 1.07 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *Z* Isomer): δ 196.9, 167.6, 138.3, 136.4, 134.4, 133.9, 133.4, 130.1, 128.7, 128.5, 128.3, 128.1, 60.9, 45.0, 13.7; **HRMS** (ESI) *m/z* calculated for C<sub>19</sub>H<sub>18</sub>ClO<sub>3</sub> ([M+H]<sup>+</sup>) 329.0939, found 329.0944.

Analytical data for (*E*)-**3ea** is in agreement with literature reference.<sup>[21]</sup>

#### ethyl 2-(4-bromobenzylidene)-4-oxo-4-phenylbutanoate (**3fa**)



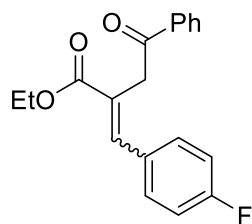
Following general procedure **GP-C** using ethyl (*Z*)-3-(4-bromophenyl)-2-chloroacrylate (**1f**, 145 mg, 500 μmol, 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0 μmol, 0.02 equiv) gave (*E*)-**3fa** (72.2 mg, 193 μmol, 39%) and (*Z*)-**3fa** (84.8 mg, 226 μmol, 45%) as slightly yellow oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 8:1). *E/Z* = 46:54.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.26 (*E* Isomer), 0.20 (*Z* Isomer); **IR** (neat): 3056, 2967, 2907, 1707, 1677, 1580, 1483, 1375, 1341, 1297, 1237, 1125, 1103, 998, 924, 846, 812, 749, 689 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *E* Isomer): δ 8.03 – 7.98 (m, 2H), 7.94 (s, 1H), 7.63 – 7.57 (m, 1H), 7.52 – 7.45 (m, 4H), 7.21 – 7.15 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.15 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *E* Isomer): δ 197.4, 167.2, 140.8, 136.6, 134.2, 133.4, 131.8, 130.3, 128.7, 128.3, 128.1, 123.0, 61.3, 37.9, 14.2; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *Z* Isomer): δ 8.04 – 7.97 (m, 2H), 7.62 – 7.56 (m, 1H), 7.52 – 7.41 (m, 4H), 7.23 – 7.14 (m, 2H), 6.81 (s, 1H), 4.16 – 4.06 (m, 4H), 1.07 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *Z* Isomer): δ 195.8, 166.5, 137.3, 135.3, 133.8, 132.4, 123.0, 129.3, 127.7, 127.5, 127.2, 121.1,

59.9, 43.9, 12.7; **HRMS** (ESI)  $m/z$  calculated for  $C_{19}H_{18}BrO_3$  ( $[M+H]^+$ ) 373.0434, found 373.0438.

Analytical data for (*E*)-**3fa** is in agreement with literature reference.<sup>[21]</sup>

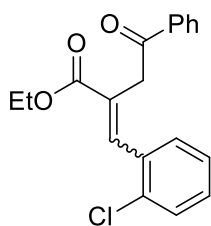
### ethyl 2-(4-fluorobenzylidene)-4-oxo-4-phenylbutanoate (**3ga**)



Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-(4-fluorophenyl)acrylate (**1g**, 114 mg, 500  $\mu$ mol, 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu$ mol, 0.02 equiv) gave (*E*)-**3ga** (66.3 mg, 212  $\mu$ mol, 42%) and (*Z*)-**3ga** (58.8 mg, 188  $\mu$ mol, 38%) as colorless oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 8:1). *E/Z* = 53:47.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.32 (*E* Isomer), 0.20 (*Z* Isomer); **IR** (neat): 3063, 2981, 2907, 1684, 1599, 1505, 1446, 1379, 1334, 1304, 1211, 1159, 1125, 991, 842, 752, 689  $cm^{-1}$ ; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  8.02 – 7.99 (m, 2H), 7.98 (s, 1H), 7.61 – 7.58 (m, 1H), 7.50 – 7.47 (m, 2H), 7.32 – 7.29 (m, 2H), 7.06 – 7.00 (m, 2H), 4.24 (q,  $J = 7.1$  Hz, 2H), 4.16 (s, 2H), 1.26 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  197.5, 167.3, 162.9 (d,  $J = 249.5$  Hz), 140.9, 136.7, 133.4, 131.4 (d,  $J = 3.4$  Hz), 130.7 (d,  $J = 8.3$  Hz), 128.7, 128.3, 127.4 (d,  $J = 1.0$  Hz), 115.7 (d,  $J = 21.6$  Hz), 61.2, 37.9, 14.2; **<sup>19</sup>F-NMR** (376 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  -112.39; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  8.00 (d,  $J = 7.7$  Hz, 2H), 7.59 (t,  $J = 7.3$  Hz, 1H), 7.49 (t,  $J = 7.5$  Hz, 2H), 7.34 – 7.28 (m, 2H), 7.00 (t,  $J = 8.6$  Hz, 2H), 6.85 (s, 1H), 4.17 – 4.07 (m, 4H), 1.07 (t,  $J = 7.1$  Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  197.0, 167.7, 162.5 (d,  $J = 248.0$  Hz), 138.6, 136.5, 133.4, 131.9 (d,  $J = 3.4$  Hz), 130.6 (d,  $J = 8.2$  Hz), 128.7, 128.3, 127.8 (d,  $J = 0.9$  Hz), 114.9 (d,  $J = 21.6$  Hz), 60.8, 45.0, 13.7; **<sup>19</sup>F-NMR** (376 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  -113.76; **HRMS** (APCI)  $m/z$  calculated for  $C_{19}H_{18}FO_3$  ( $[M+H]^+$ ) 313.1234, found 313.1242.

### ethyl 2-(2-chlorobenzylidene)-4-oxo-4-phenylbutanoate (**3ha**)

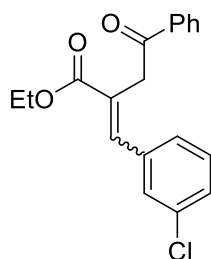


Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-(2-chlorophenyl)acrylate (**1h**, 123 mg, 500  $\mu$ mol, 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu$ mol, 0.02 equiv) gave (*E*)-**3ha** (49.6 mg, 151  $\mu$ mol, 30%) and (*Z*)-**3ha** (74.4 mg, 226  $\mu$ mol, 46%) as colorless oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 8:1). *E/Z* = 40:60.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.29 (*E* Isomer), 0.20 (*Z* Isomer); **IR** (neat): 3063, 2981, 2907, 1684, 1595, 1379, 1334, 1211, 1114, 1054, 1021, 991, 838, 752, 689 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  8.05 (s, 1H), 7.97 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.29 – 7.25 (m, 2H), 7.20 – 7.17 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  197.5, 166.9, 139.2, 136.6, 134.1, 134.0, 133.3, 130.0, 129.8, 129.6, 129.2, 128.7, 128.3, 126.9, 61.3, 38.2, 14.2; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  8.04 – 8.01 (m, 2H), 7.61 – 7.57 (m, 1H), 7.51 – 7.47 (m, 2H), 7.38 – 7.31 (m, 2H), 7.25 – 7.18 (m, 2H), 6.98 (s, 1H), 4.18 (d, *J* = 0.9 Hz, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 0.96 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  196.9, 167.1, 137.3, 136.5, 135.2, 133.4, 132.9, 130.4, 129.8, 129.1, 129.0, 128.7, 128.3, 126.1, 60.8, 44.4, 13.6; **HRMS** (APCI) *m/z* calculated for C<sub>19</sub>H<sub>18</sub>ClO<sub>3</sub> ([*M*+*H*]<sup>+</sup>) 329.0939, found 329.0945.

Analytical data for (*E*)-**3ha** is in agreement with literature reference.<sup>[21]</sup>

#### ethyl 2-(3-chlorobenzylidene)-4-oxo-4-phenylbutanoate (**3ia**)



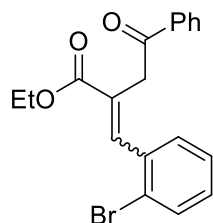
Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-(3-chlorophenyl)acrylate (**1i**, 123 mg, 500  $\mu$ mol, 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and

*fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0 μmol, 0.02 equiv) gave (*E*)-**3ia** (70.6 mg, 215 μmol, 43%) and (*Z*)-**3ia** (76.4 mg, 232 μmol, 46%) as colorless oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 8:1). *E/Z* = 48:52.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.29 (*E* Isomer), 0.22 (*Z* Isomer); **IR** (neat): 3063, 2981, 2933, 1684, 1643, 1595, 1476, 1391, 1326, 1263, 1192, 1021, 1000, 924, 790, 685 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *E* Isomer): δ 8.01 – 7.99 (m, 2H), 7.94 (s, 1H), 7.62 – 7.57 (m, 1H), 7.50 – 7.47 (m, 2H), 7.31 – 7.26 (m, 3H), 7.20 – 7.18 (m, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.15 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *E* Isomer): δ 197.3, 167.1, 140.5, 137.2, 136.6, 134.6, 133.4, 129.9, 128.8, 128.7, 128.7, 128.3, 126.7, 61.3, 37.8, 14.2; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *Z* Isomer): δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.25 (m, 3H), 7.20 – 7.16 (m, 1H), 6.84 (s, 1H), 4.15 (s, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.06 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz, CDCl<sub>3</sub>, *Z* Isomer): δ 196.9, 167.6, 137.8, 137.7, 136.4, 133.8, 133.5, 129.3, 129.2, 128.8, 128.7, 128.3, 128.0, 126.8, 61.0, 44.9, 13.6; **HRMS** (APCI) *m/z* calculated for C<sub>19</sub>H<sub>18</sub>ClO<sub>3</sub> ([*M*+*H*]<sup>+</sup>) 329.0939, found 329.0940.

Analytical data for (*E*)-**3ia** is in agreement with literature reference.<sup>[21]</sup>

### ethyl 2-(2-bromobenzylidene)-4-oxo-4-phenylbutanoate (**3ja**)



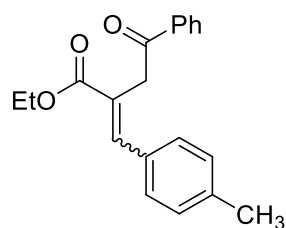
Following general procedure **GP-C** using ethyl (*Z*)-3-(2-bromophenyl)-2-chloroacrylate (**1j**, 145 mg, 500 μmol, 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0 μmol, 0.02 equiv) gave (*E*)-**3ja** (31.9 mg, 85.4 μmol, 17%) and (*Z*)-**3ja** (59.2 mg, 159 μmol, 32%) as colorless oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 8:1). *E/Z* = 35:65.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.27 (*E* Isomer), 0.22 (*Z* Isomer); **IR** (neat): 3060, 2981, 2903, 1684, 1595, 1446, 1401, 1375, 1334, 1274, 1241, 1211, 1110, 1021, 991, 838, 749, 600 cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>, *E* Isomer): δ 7.99 – 7.96 (m, 3H), 7.63 – 7.55 (m, 2H), 7.48 – 7.45 (m, 2H), 7.29 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 2H), 1.28

(t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  197.5, 166.9, 141.3, 136.6, 135.9, 133.4, 132.8, 130.1, 129.8, 128.9, 128.7, 128.3, 127.5, 124.0, 61.3, 38.2, 14.2;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  8.05 – 8.02 (m, 2H), 7.62 – 7.55 (m, 2H), 7.49 (t,  $J = 7.6$  Hz, 2H), 7.31 (dd,  $J = 7.6, 1.5$  Hz, 1H), 7.28 – 7.23 (m, 1H), 7.16 (td,  $J = 7.7, 1.7$  Hz, 1H), 6.94 (s, 1H), 4.18 (d,  $J = 0.8$  Hz, 2H), 4.02 (q,  $J = 7.1$  Hz, 2H), 0.95 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  196.9, 167.0, 139.5, 137.2, 136.5, 133.4, 132.1, 130.5, 129.5, 129.3, 128.7, 128.4, 126.7, 122.8, 60.8, 44.3, 13.6; **HRMS** (APCI)  $m/z$  calculated for  $\text{C}_{19}\text{H}_{18}\text{BrO}_3$  ( $[\text{M}+\text{H}]^+$ ) 373.0434, found 373.0438.

Analytical data for (*E*)-**3ja** is in agreement with literature reference.<sup>[21]</sup>

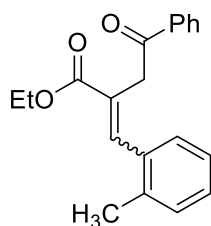
### ethyl 2-(4-methylbenzylidene)-4-oxo-4-phenylbutanoate (**3la**)



Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-(*p*-tolyl)acrylate (**11**, 112 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*- $\text{Ir}(\text{ppy})_3$  (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3la** (28.2 mg, 91.7  $\mu\text{mol}$ , 18%) and (*Z*)-**3la** (31.8 mg, 103  $\mu\text{mol}$ , 21%) as yellowish oils as separated *E* and *Z* isomers after purification on  $\text{SiO}_2$  (hexanes / EA, 20:1 to 8:1).  $E/Z = 47:53$ .

$R_f$  (hexanes / EA, 10:1) = 0.20 (*E* Isomer), 0.13 (*Z* Isomer); **IR** (neat): 3056, 3026, 2981, 2922, 1684, 1599, 1513, 1446, 1371, 1326, 1267, 1211, 1177, 1088, 1021, 916, 849, 812, 756, 689  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  8.04 – 7.99 (m, 3H), 7.61 – 7.56 (m, 1H), 7.51 – 7.43 (m, 2H), 7.27 – 7.12 (m, 4H), 4.25 – 4.21 (m, 4H), 2.34 (s, 3H), 1.27 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  197.6, 167.6, 142.1, 138.9, 136.8, 133.2, 132.4, 129.3, 128.9, 128.7, 128.3, 126.5, 61.1, 38.1, 21.4, 14.2;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  8.06 – 8.00 (m, 2H), 7.61 – 7.55 (m, 1H), 7.51 – 7.45 (m, 2H), 7.24 – 7.11 (m, 4H), 6.85 (s, 1H), 4.17 – 4.07 (m, 4H), 2.35 (s, 3H), 1.08 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  197.2, 168.2, 139.5, 138.1, 136.5, 133.3, 132.9, 128.8, 128.7, 128.6, 128.3, 126.9, 60.7, 45.2, 21.4, 13.7; **HRMS** (ESI)  $m/z$  calculated for  $\text{C}_{20}\text{H}_{20}\text{NaO}_3$  ( $[\text{M}+\text{Na}]^+$ ) 331.1305, found 331.1305.

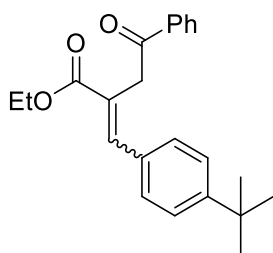
**ethyl 2-(2-methylbenzylidene)-4-oxo-4-phenylbutanoate (3ma)**



Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-(*o*-tolyl)acrylate (**1m**, 112 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave ethyl 2-(2-methylbenzylidene)-4-oxo-4-phenylbutanoate (46.3 mg, 150  $\mu\text{mol}$ , 30%) as yellowish oil as a mixture of *E/Z* = 45:55 after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 8:1).

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.30 (*E* Isomer), 0.24 (*Z* Isomer); **IR** (neat): 3063, 2981, 1684, 1599, 1446, 1371, 1330, 1263, 1215, 1120, 1092, 1021, 998, 916, 846, 745, 689  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  8.05 – 8.02 (m, 3H), 7.62 – 7.54 (m, 1H), 7.52 – 7.43 (m, 2H), 7.23 – 7.11 (m, 4H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.17 (s, 2H), 2.32 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  7.96 – 7.94 (m, 2H), 7.62 – 7.56 (m, 1H), 7.52 – 7.43 (m, 2H), 7.23 – 7.11 (m, 4H), 6.99 (s, 1H), 4.06 (s, 2H), 3.99 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 0.91 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, both Isomers):  $\delta$  197.6, 197.2, 167.6, 167.3, 141.5, 140.1, 136.9, 136.7, 136.5, 136.3, 135.7, 134.7, 133.3, 133.2, 130.1, 129.5, 128.7, 128.6, 128.6, 128.3, 128.2(4), 128.2(1), 128.0, 127.9, 127.8, 125.9, 125.2, 61.1, 60.6, 44.3, 38.0, 20.0, 19.9, 14.2, 13.5; **HRMS** (ESI) *m/z* calculated for C<sub>20</sub>H<sub>21</sub>O<sub>3</sub> ([M+H]<sup>+</sup>) 309.1485, found 309.1487.

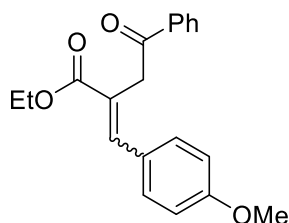
**ethyl 2-(4-(*tert*-butyl)benzylidene)-4-oxo-4-phenylbutanoate (3na)**



Following general procedure **GP-C** using ethyl (*Z*)-3-(4-(*tert*-butyl)phenyl)-2-chloroacrylate (**1n**, 133 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3na** (35.0 mg, 99.8  $\mu\text{mol}$ , 20%) and (*Z*)-**3na** (38.0 mg, 108  $\mu\text{mol}$ , 22%) as yellowish oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 8:1). *E/Z* = 48:52.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.32 (*E* Isomer), 0.24 (*Z* Isomer); **IR** (neat): 3060, 3026, 2959, 2907, 2870, 1688, 1599, 1509, 1449, 1379, 1334, 1267, 1211, 1110, 1021, 991, 842, 752, 689cm<sup>-1</sup>; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  8.05 – 8.00 (m, 3H), 7.62 – 7.56 (m, 1H), 7.51 – 7.46 (m, 2H), 7.39 – 7.35 (m, 2H), 7.28 – 7.24 (m, 2H), 4.28 – 4.20 (m, 4H), 1.33 – 1.23 (m, 12H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  197.5, 167.6, 152.1, 142.0, 136.8, 133.2, 132.4, 128.8, 128.7, 128.3, 126.5, 125.6, 61.1, 38.2, 34.8, 31.2, 14.2; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  8.04 – 7.99 (m, 2H), 7.61 – 7.55 (m, 1H), 7.51 – 7.45 (m, 2H), 7.36 – 7.26 (m, 4H), 6.87 (s, 1H), 4.16 – 4.08 (m, 4H), 1.32 (s, 9H), 1.05 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  197.2, 168.1, 151.3, 139.5, 136.5, 133.3, 132.9, 128.7, 128.6, 128.3, 127.0, 124.8, 60.7, 45.2, 34.7, 31.3, 13.6; **HRMS** (ESI) *m/z* calculated for C<sub>23</sub>H<sub>27</sub>O<sub>3</sub> ([*M*+*H*]<sup>+</sup>) 351.1955, found 351.1964.

#### ethyl 2-(4-methoxybenzylidene)-4-oxo-4-phenylbutanoate (**3oa**)



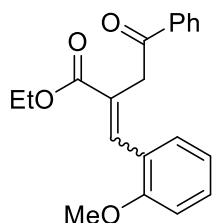
Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-(4-methoxyphenyl)acrylate (**1o**, 120 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3oa** (25.6 mg, 79.0  $\mu\text{mol}$ , 16%) and (*Z*)-

**3oa** (20.1 mg, 62.0  $\mu\text{mol}$ , 12%) as yellowish oils as separated *E* and *Z* isomers after purification on  $\text{SiO}_2$  (hexanes / EA, 20:1 to 8:1). *E/Z* = 56:44.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.20 (*E* Isomer), 0.16 (*Z* Isomer); **IR** (neat): 3083, 2981, 2937, 2840, 1688, 1606, 1513, 1446, 1371, 1304, 1256, 1215, 1174, 1092, 1028, 916, 834, 760, 693  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  8.03 – 8.01 (m, 3H), 7.61 – 7.57 (m, 1H), 7.51 – 7.47 (m, 2H), 7.29 – 7.26 (m, 2H), 6.88 – 6.85 (m, 2H), 4.26 – 4.20 (m, 4H), 3.80 (s, 3H), 1.27 (t,  $J$  = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  197.6, 167.7, 160.1, 141.8, 136.9, 133.2, 130.6, 128.7, 128.3, 127.8, 125.4, 114.1, 61.0, 55.3, 38.1, 14.2; **<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  8.02 – 8.00 (m, 2H), 7.60 – 7.57 (m, 1H), 7.50 – 7.46 (m, 2H), 7.33 – 7.30 (m, 2H), 6.85 – 6.81 (m, 3H), 4.16 – 4.11 (m, 4H), 3.82 (s, 3H), 1.10 (t,  $J$  = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (101 MHz,  $\text{CDCl}_3$ , *Z* Isomer):  $\delta$  197.3, 168.1, 159.7, 139.4, 136.6, 133.3, 130.4, 128.7, 128.3, 128.2, 125.7, 113.3, 60.7, 55.3, 45.3, 13.8; **HRMS** (ESI)  $m/z$  calculated for  $\text{C}_{20}\text{H}_{21}\text{O}_4$  ( $[\text{M}+\text{H}]^+$ ) 325.1434, found 325.1433.

Analytical data for (*E*)-**3oa** is in agreement with literature reference.<sup>[22]</sup>

### ethyl 2-(2-methoxybenzylidene)-4-oxo-4-phenylbutanoate (**3pa**)



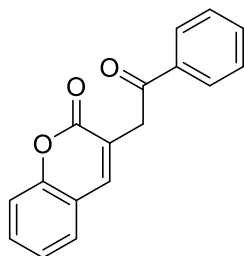
Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-(2-methoxyphenyl)acrylate (**1p**, 120 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*- $\text{Ir}(\text{ppy})_3$  (6.55 mg, 10.0  $\mu\text{mol}$ , 0.02 equiv) gave (*E*)-**3pa** (23.7 mg, 72.9  $\mu\text{mol}$ , 15%) and (*Z*)-**3pa** (40.3 mg, 124  $\mu\text{mol}$ , 25%) as yellowish oil as separated *E* and *Z* isomer after purification on  $\text{SiO}_2$  (hexanes / EA, 20:1 to 6:1). *E/Z* = 37:63.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.18 (*E* Isomer), 0.10 (*Z* Isomer); **IR** (neat): 3063, 2981, 2903, 2840, 1684, 1599, 1487, 1326, 1300, 1287, 1211, 1092, 1021, 946, 916, 846, 790, 752, 689  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ , *E* Isomer):  $\delta$  8.08 (s, 1H), 8.01 – 7.97 (m, 2H), 7.60 – 7.54 (m, 1H), 7.50 – 7.43 (m, 2H), 7.34 – 7.27 (m, 1H), 7.21 – 7.17 (m, 1H), 6.92 – 6.84 (m, 2H), 4.24 (q,  $J$  = 7.1 Hz, 2H), 4.13 (s, 2H), 3.82 (s, 3H), 1.28 (t,  $J$  = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz,

CDCl<sub>3</sub>, *E* Isomer):  $\delta$  197.8, 167.5, 157.5, 138.3, 136.9, 133.1, 130.4, 129.5, 128.6, 128.2, 127.5, 124.4, 120.5, 110.6, 61.0, 55.5, 38.5, 14.2; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  8.05 – 8.00 (m, 2H), 7.62 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 7.31 – 7.23 (m, 2H), 6.97 (s, 1H), 6.93 – 6.83 (m, 2H), 4.17 (d, *J* = 1.1 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  196.2, 167.0, 155.8, 135.5, 134.7, 132.2, 129.2, 128.5, 127.9, 127.6, 127.3, 126.8, 126.74, 124.1, 118.9, 109.2, 59.5, 54.3, 44.0, 12.6; HRMS (EI) *m/z* calculated for C<sub>20</sub>H<sub>20</sub>O<sub>4</sub> ([M]<sup>+</sup>) 324.1356, found 324.1350.

Analytical data for (*E*)-**3pa** is in agreement with literature reference.<sup>[19]</sup>

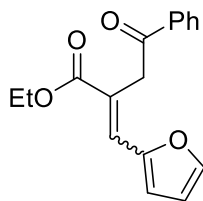
### 3-(2-oxo-2-phenylethyl)-2*H*-chromen-2-one (3qa)



Following general procedure **GP-C** using 3-chloro-2*H*-chromen-2-one (90.3 mg, 500  $\mu$ mol, 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (6.55 mg, 10.0  $\mu$ mol, 0.02 equiv) gave 3-(2-oxo-2-phenylethyl)-2*H*-chromen-2-one (34.1 mg, 129  $\mu$ mol, 26%) as white solid after purification on SiO<sub>2</sub> (hexanes / EA, 10:1 to 6:1).

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.10; **mp**: 128 °C; **IR** (neat): 3071, 2926, 2855, 1710, 1606, 1449, 1401, 1375, 1334, 1252, 1181, 1073, 991, 957, 924, 827, 752, 685 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.07 – 8.03 (m, 2H), 7.68 (s, 1H), 7.62 – 7.56 (m, 1H), 7.53 – 7.44 (m, 4H), 7.35 – 7.23 (m, 2H), 4.26 (d, *J* = 0.7 Hz, 2H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  196.0, 161.6, 153.5, 142.1, 136.3, 133.7, 133.6, 131.3, 130.2, 128.8, 128.5, 127.6, 124.5, 123.1, 119.3, 116.6, 39.6; HRMS (APCI) *m/z* calculated for C<sub>17</sub>H<sub>13</sub>O<sub>3</sub> ([M+H]<sup>+</sup>) 265.0859, found 265.0862.

### ethyl 2-(furan-2-ylmethylene)-4-oxo-4-phenylbutanoate (3ra)



Following general procedure **GP-C** using ethyl (*Z*)-2-chloro-3-(furan-2-yl)acrylate (**1r**, 100 mg, 500  $\mu\text{mol}$ , 1.00 equiv), 1-phenylvinyl acetate (**2a**, 405 mg, 2.50 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (3.27 mg, 5.00  $\mu\text{mol}$ , 0.01 equiv) gave (*E*)-**3ra** (3.25 mg, 11.4  $\mu\text{mol}$ , 2.6%) and (*Z*)-**3ra** (1.75 mg, 6.16  $\mu\text{mol}$ , 1.4%) as dark yellow oils as separated *E* and *Z* isomers after purification on SiO<sub>2</sub> (hexanes / EA, 20:1 to 8:1). *E/Z* = 65:35.

**R<sub>f</sub>** (hexanes / EA, 6:1) = 0.24 (*E* Isomer), 0.20 (*Z* Isomer); **IR** (neat): 3063, 3123, 2981, 2933, 1688, 1640, 1599, 1476, 1371, 1328, 1263, 1196, 1088, 1021, 916, 883, 797, 745, 689  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  8.08 – 8.04 (m, 2H), 7.66 (s, 1H), 7.63 – 7.57 (m, 1H), 7.53 – 7.47 (m, 2H), 7.38 (d, *J* = 1.7 Hz, 1H), 6.60 (d, *J* = 3.4 Hz, 1H), 6.43 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.53 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *E* Isomer):  $\delta$  197.15, 150.31, 143.35, 133.29, 128.68, 128.42, 128.25, 122.27, 115.10, 112.26, 60.77, 45.11, 14.10; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  8.01 – 7.98 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 – 7.43 (m, 4H), 6.69 (s, 1H), 6.47 – 6.46 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.10 (s, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, *Z* Isomer):  $\delta$  195.92, 166.71, 150.21, 143.67, 135.98, 131.98, 127.55, 127.19, 126.72, 121.39, 115.38, 110.98, 60.10, 37.24, 13.21; **HRMS** (ESI) *m/z* calculated for C<sub>17</sub>H<sub>17</sub>O<sub>4</sub> ([M+H]<sup>+</sup>) 285.1121, found 285.1126.

Analytical data for (*E*)-**3ra** is in agreement with literature reference.<sup>[22]</sup>

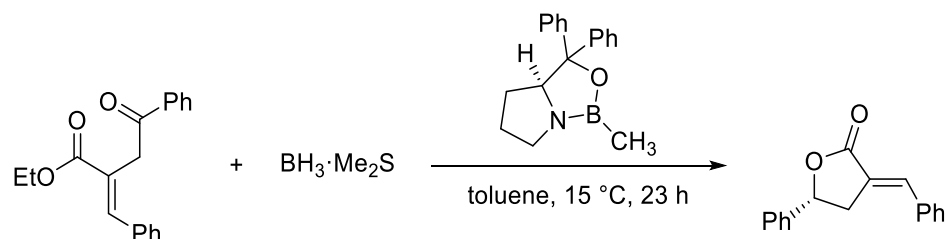
## 8. Photochemical reaction setup for big scale synthesis of **3aa**



A 200 mL flame dried Schlenk tube equipped with a magnetic stir bar was charged with  $\alpha$ -chloro ethyl cinnamate (**1a**, 4.21 g, 20.0 mmol, 1.00 equiv), 1-phenylvinyl acetate (**2a**, 16.2 g, 100 mmol, 5.00 equiv) and *fac*-Ir(ppy)<sub>3</sub> (65.5 mg, 100  $\mu$ mol, 0.5 mol%). The tube was evacuated, backfilled with N<sub>2</sub> (3x) and subsequently completely filled with freshly degassed dry MeCN (~180 mL). The reaction mixture was magnetically stirred for roughly 15 min under N<sub>2</sub> atmosphere until a homogeneous solution was observed. The tube was sealed with the photoapparatus, which was completely immersed in the reaction mixture. The photoapparatus consisted of a hollow glass cylinder containing a water-cooled metal block wrapped with 30 high power LEDs ( $\lambda = 455$  nm). After irradiation for 48 h, the solvent was evaporated under reduced pressure and 1-phenylvinyl acetate was removed by distillation. The resulting residue was subsequently purified by column chromatography on SiO<sub>2</sub> (hexanes / EA, 20:1 to 12:1) to obtain the separated *E* and *Z* isomers of (*E*)-**3aa** (1.73 g, 5.86 mmol, 29%) and (*Z*)-**3aa** (1.87 g, 6.34 mmol, 32%). *E/Z* = 48:52.

## 9. Enantioselective synthesis of $\alpha$ -alkylidene- $\gamma$ -aryl- $\gamma$ -butyrolactone (**5**)

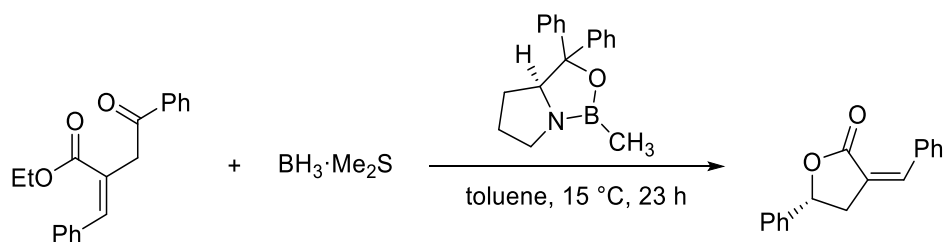
### (*R,E*)-3-benzylidene-5-phenyldihydrofuran-2(3*H*)-one (*R,E*-**5**)



A flame dried 10 mL Schlenk flask equipped with a magnetic stir bar was charged with (*S*)-(-)-2-Methyl-CBS-oxazaborolidine (10.4 mg, 37.4  $\mu\text{mol}$ , 10 mol%) and ethyl (*E*)-2-benzylidene-4-oxo-4-phenylbutanoate ((*E*)-**3aa**, 110 mg, 374  $\mu\text{mol}$ , 1.00 equiv), sealed with a septum and subsequently evacuated and backfilled with  $\text{N}_2$  (3x). Toluene (2 mL) was added and the solution was cooled to -15 °C.  $\text{BH}_3 \cdot \text{Me}_2\text{S}$  (2 M in THF, 243  $\mu\text{L}$ , 486  $\mu\text{mol}$ , 1.30 equiv) was added and the reaction mixture was magnetically stirred for 23 h at -15 °C. Subsequently, MeOH (1 mL) was added and the mixture was acidified with HCl (1 M) to pH 1-2. After stirring for additional 30 minutes, the reaction mixture was diluted with  $\text{H}_2\text{O}$  (15 mL) and washed with DCM (3 x 15 mL). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and evaporated under reduced pressure. The residue was dissolved in DCM (3 mL) and TFA (46.9 mg, 411  $\mu\text{mol}$ , 1.10 equiv) was added. After 2 h full lactonization was observed and the reaction was quenched with sat.  $\text{NaHCO}_3$  (10 mL) and washed with DCM (3 x 30 mL). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and evaporated under reduced pressure. The residue was purified by column chromatography on  $\text{SiO}_2$  (hexanes / EA, 6:1) to obtain (*R,E*)-3-benzylidene-5-phenyldihydrofuran-2(3*H*)-one as white solid (48.8 mg, 195  $\mu\text{mol}$ , 52%).

**R<sub>f</sub>** (hexanes / EA, 4:1) = 0.28; **mp**: 85 °C; **IR** (neat): 3090, 3056, 3030, 2970, 1729, 1647, 1494, 1319, 1226, 1189, 1066, 1021, 984, 764, 685  $\text{cm}^{-1}$ ; **<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64 (t,  $J$  = 2.9 Hz, 1H), 7.52 – 7.31 (m, 10H), 5.61 (dd,  $J$  = 8.3, 6.0 Hz, 1H), 3.70 (ddd,  $J$  = 17.6, 8.3, 2.7 Hz, 1H), 3.16 (ddd,  $J$  = 17.6, 6.0, 3.1 Hz, 1H); **<sup>13</sup>C-NMR** (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.0, 140.3, 137.0, 134.6, 130.1, 130.0, 129.0, 128.9, 128.6, 125.4, 124.1, 78.2, 36.6; **HRMS** (EI)  $m/z$  calculated for  $\text{C}_{17}\text{H}_{14}\text{O}_2$  ( $[\text{M}]^+$ ) 250.0988, found 250.0992; **Chiral HPLC** performed on Chiralpak AS-H (*n*-heptane / *i*-PrOH = 70:30,  $\lambda$  = 215 nm, 0.5 mL/min).  $t_r$  (minor) = 40.0 min,  $t_r$  (major) = 28.8 min; enantiomeric excess: 79%;  $[\alpha]_{\text{D}}^{20}$ : -15.4 ( $c$  = 1.00,  $\text{CHCl}_3$ ).

### (*R,Z*)-3-benzylidene-5-phenyldihydrofuran-2(3*H*)-one (*R,Z*-**5**)



A flame dried 25 mL Schlenk flask equipped with a magnetic stir bar was charged with (*S*)-(-)-2-Methyl-CBS-oxazaborolidine (27.7 mg, 100  $\mu$ mol, 10 mol%) and ethyl (*Z*)-2-benzylidene-4-oxo-4-phenylbutanoate ((*Z*)-**3aa**, 294 mg, 1.00 mmol, 1.00 equiv), sealed with a septum and subsequently evacuated and backfilled with  $N_2$  (3x). Toluene (6 mL) was added and the solution was cooled to  $-15$   $^{\circ}C$ .  $BH_3 \cdot Me_2S$  (2 M in THF, 650  $\mu$ L, 1.30 mmol, 1.30 equiv) was added and the reaction mixture was magnetically stirred for 23 h at  $-15$   $^{\circ}C$ . Subsequently, MeOH (3 mL) was added and the mixture was acidified with HCl (1 M) to pH 1-2. After stirring for additional 30 minutes, the reaction mixture was diluted with  $H_2O$  (40 mL) and washed with DCM (3 x 40 mL). The combined organic layers were dried over  $Na_2SO_4$  and evaporated under reduced pressure. The residue was dissolved in DCM (8 mL) and TFA (125 mg, 1.10 mmol, 1.10 equiv) was added. After 2 h full lactonization was observed and the reaction was quenched with sat.  $NaHCO_3$  (20 mL) and washed with DCM (3 x 20 mL). The combined organic layers were dried over  $Na_2SO_4$  and evaporated under reduced pressure. The residue was purified by column chromatography on  $SiO_2$  (hexanes / EA, 8:1) to obtain (*R,Z*)-3-benzylidene-5-phenyldihydrofuran-2(3*H*)-one as white solid (175 mg, 700  $\mu$ mol, 70%).

**R<sub>f</sub>** (hexanes / EA, 4:1) = 0.30; **mp**: 123  $^{\circ}C$ ; IR (neat): 3034, 2922, 1751, 1654, 1494, 1349, 1215, 1170, 1099, 1023, 928, 730, 693  $cm^{-1}$ ; **<sup>1</sup>H-NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  7.87 (d,  $J$  = 7.3 Hz, 2H), 7.44 – 7.33 (m, 8H), 7.01 (s, 1H), 5.57 (t,  $J$  = 7.3 Hz, 1H), 3.52 (dd,  $J$  = 16.6, 7.1 Hz, 1H), 3.12 (dd,  $J$  = 16.6, 7.1 Hz, 1H); **<sup>13</sup>C-NMR** (101 MHz,  $CDCl_3$ ):  $\delta$  168.3, 139.9, 139.8, 133.6, 130.7, 129.7, 128.9, 128.6, 128.2, 125.5, 124.4, 77.9, 40.3; **HRMS** (ESI)  $m/z$  calculated for  $C_{17}H_{14}O_2$  ( $[M]^+$ ) 250.0988, found 250.0993. **Chiral HPLC** performed on Phenomenex Lux Cellulose-1 (*n*-heptane / *i*-PrOH = 98:2,  $\lambda$  = 215 nm, 0.5 mL/min).  $t_r$  (minor) = 77.5 min,  $t_r$  (major) = 72.9 min; enantiomeric excess: 89%;  **$[\alpha]_D^{20}$** : +78.4 ( $c$  = 1.00,  $CHCl_3$ ).

## 10. Reduction potentials of $\alpha$ -halo cinnamates

Cyclic voltammetry measurements were carried out on an Autolab PGSTAT 302N set-up at 20 °C in MeCN, containing tetrabutyl ammonium tetrafluoroborate as supporting electrolyte. A conventional undivided electrochemical cell equipped with a glassy carbon working electrode, platinum wire as the counter electrode and silver wire as the reference electrode was used. The solvent was degassed by vigorous nitrogen bubbling prior to the measurement. Redox potentials were referenced against ferrocene as an internal standard. All values are reported in reference to the SCE electrode.

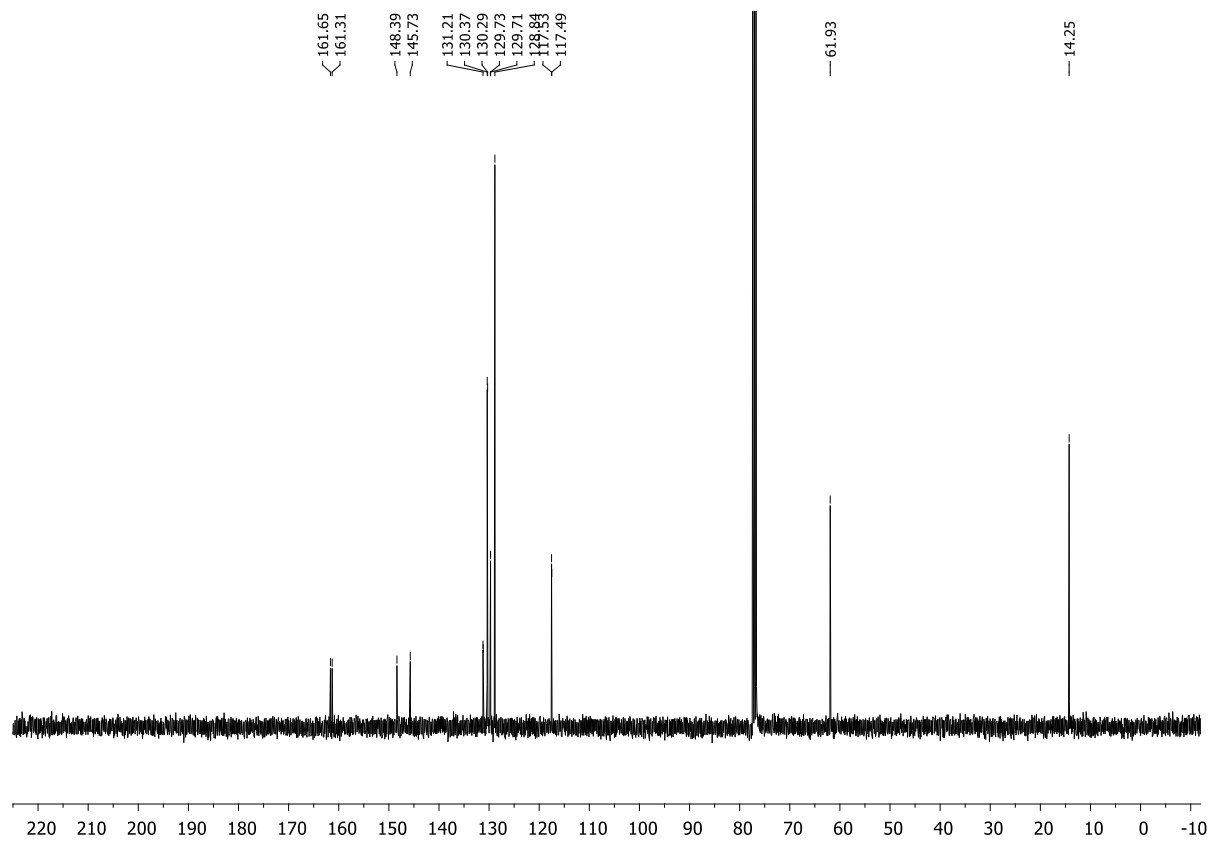
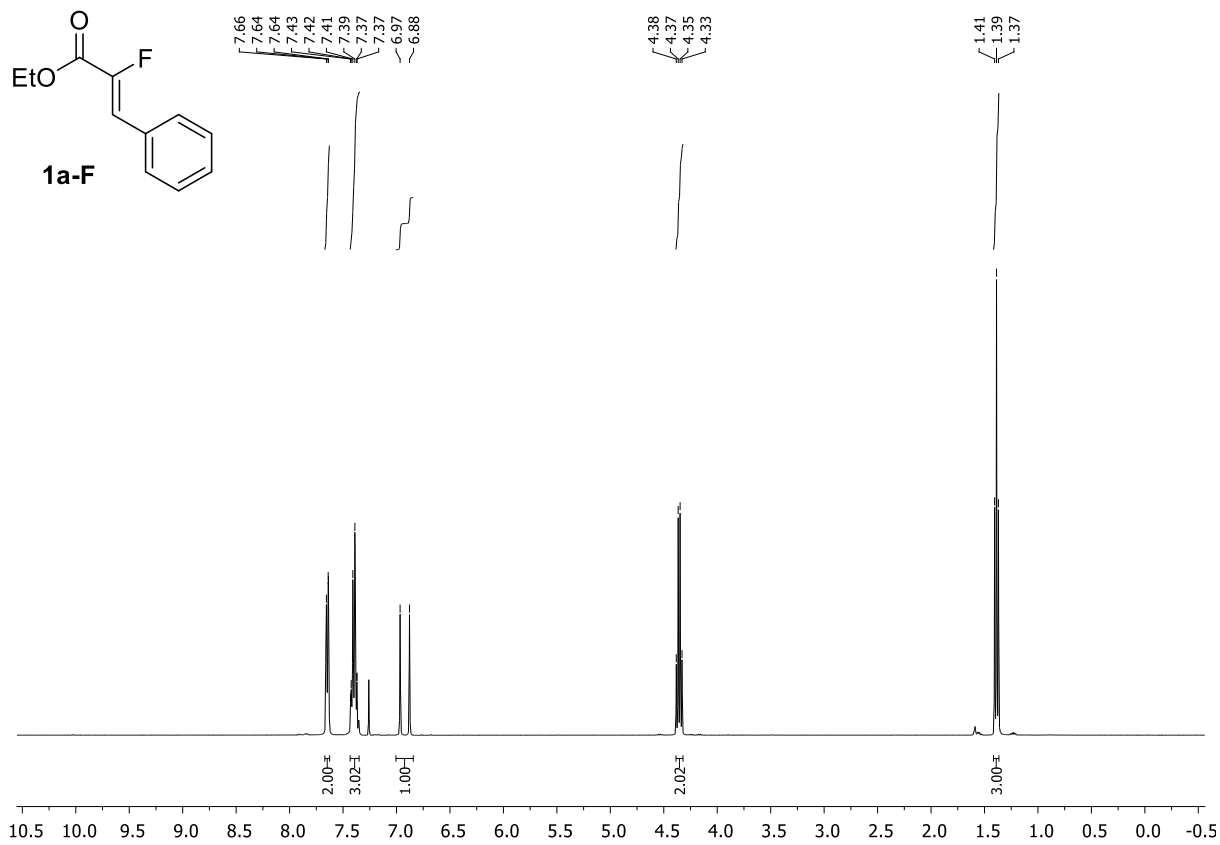
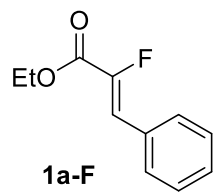
Entry	Compound	Reduction potential vs. SCE [V] in MeCN
1	<b>1a-F</b>	-1.93
2	<b>1a-Cl</b>	-1.64
3	<b>1a-Br</b>	-1.54
4	<b>1b</b>	-1.66
5	<b>1c</b>	-1.66
6	<b>1d</b>	-1.71
7	<b>1e</b>	-1.54
8	<b>1f</b>	-1.56
9	<b>1g</b>	-1.67
10	<b>1h</b>	-1.56
11	<b>1i</b>	-1.56
12	<b>1j</b>	-1.55
13	<b>1k</b>	-1.01
14	<b>1l</b>	-1.67
15	<b>1m</b>	-1.65
16	<b>1n</b>	-1.71
17	<b>1o</b>	-1.73
18	<b>1p</b>	-1.70
19	<b>1q</b>	-1.60
20	<b>1r</b>	n.d.

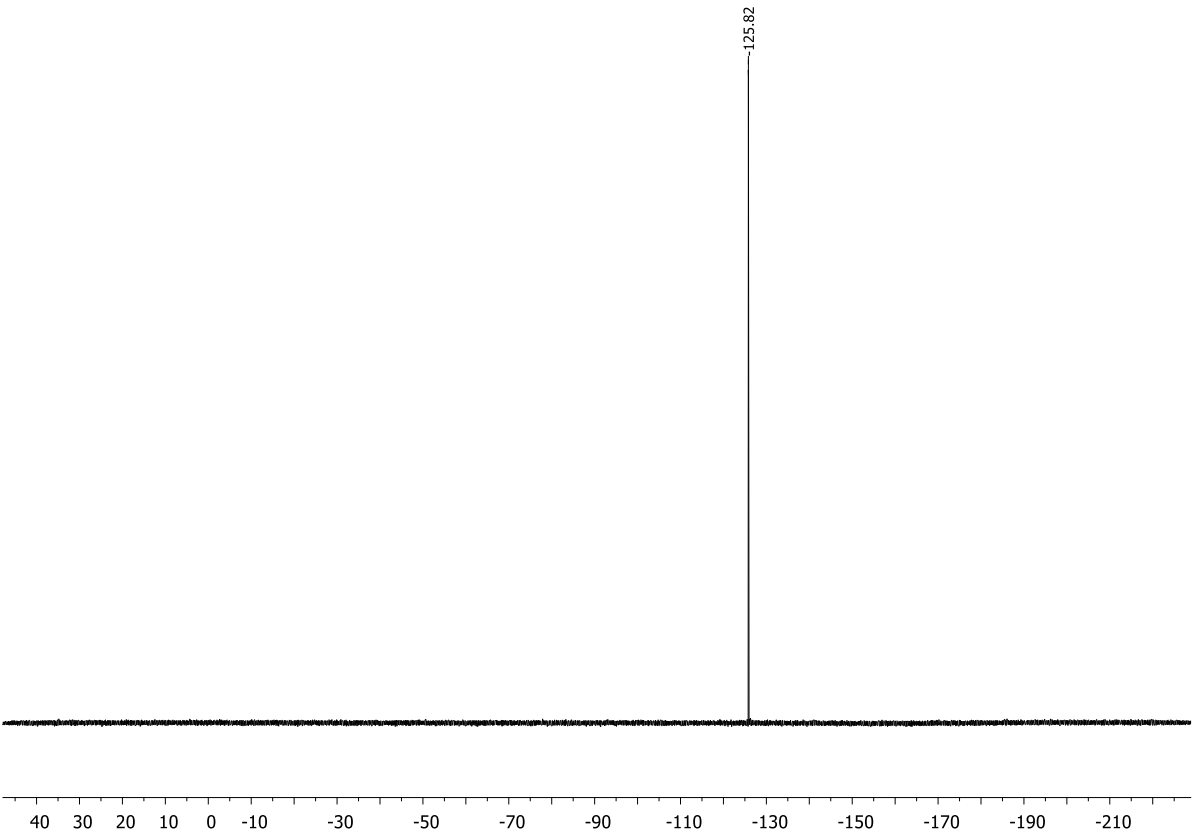
21	<b>1s</b>	n.d.
22	<b>1t</b>	n.d.
23	<b>1u</b>	-2.09

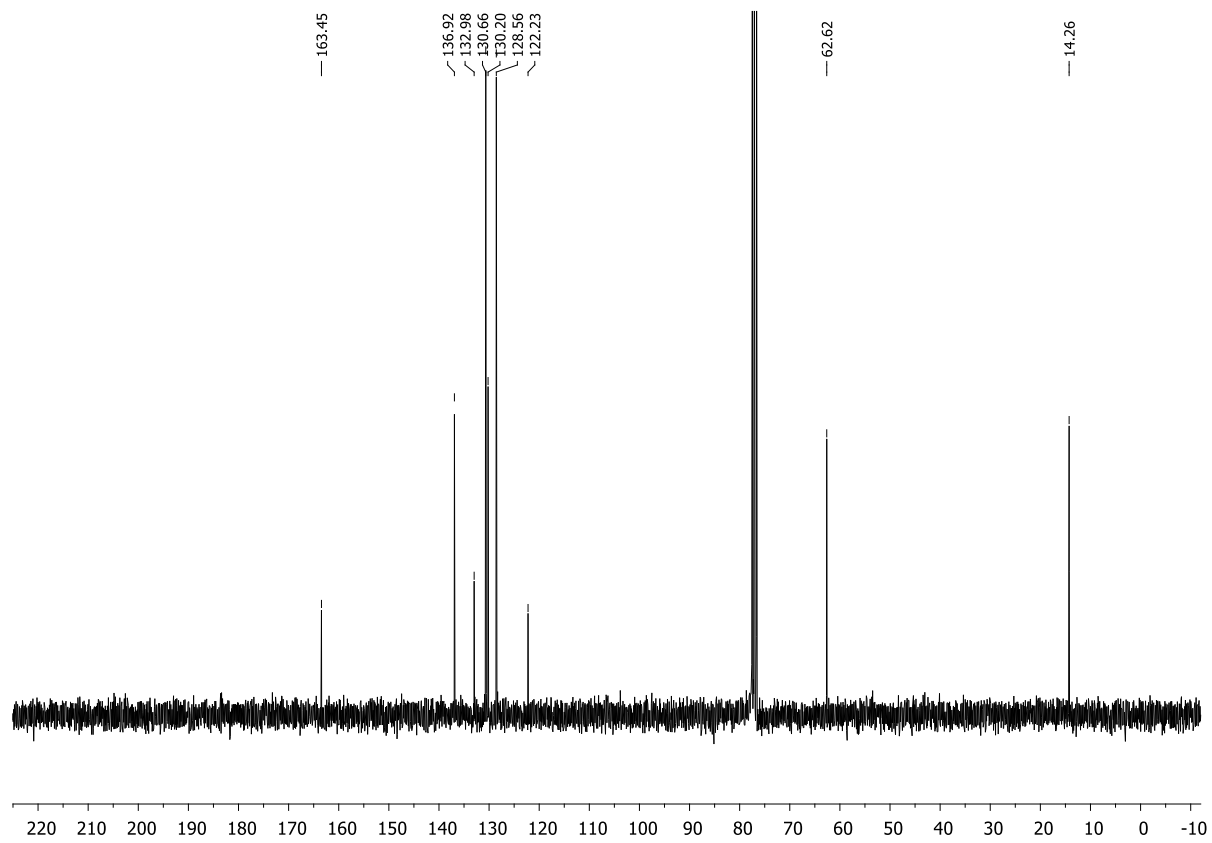
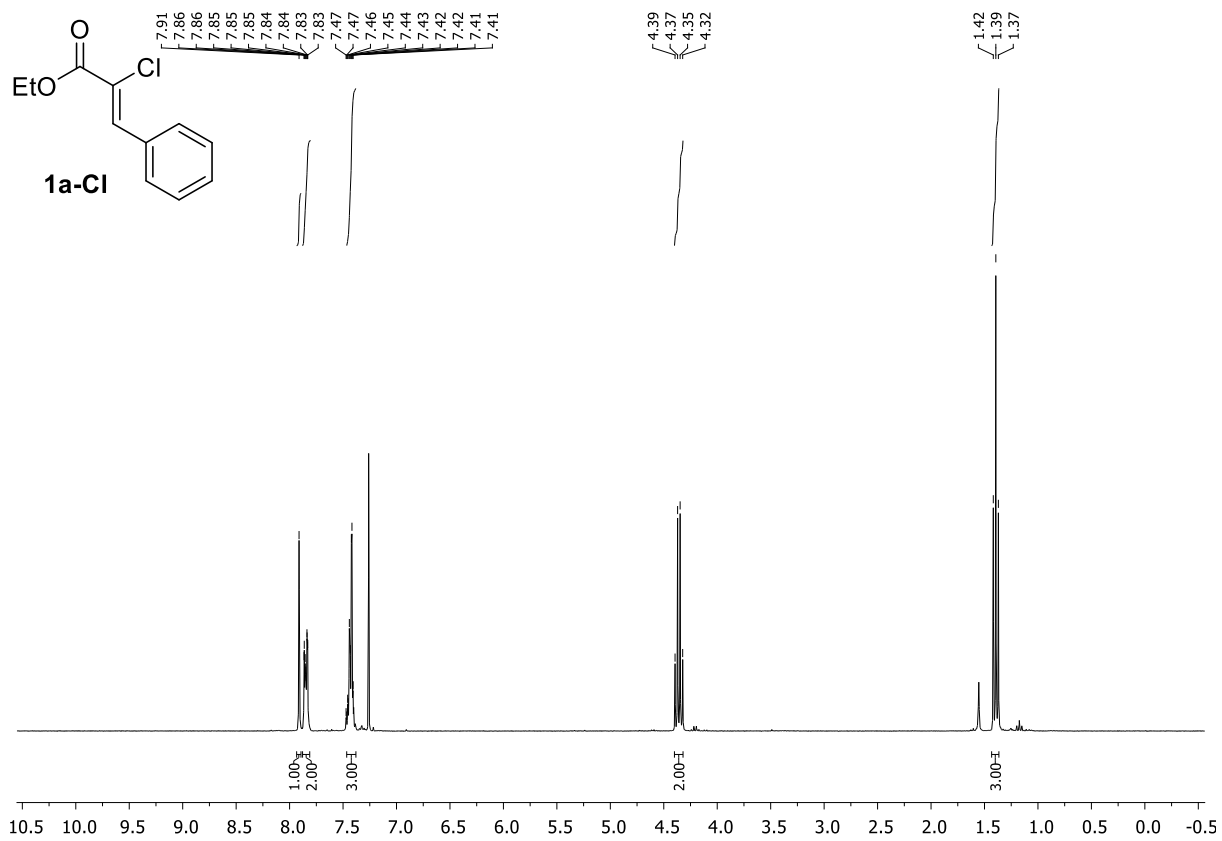
## 11. NMR spectra of all compounds

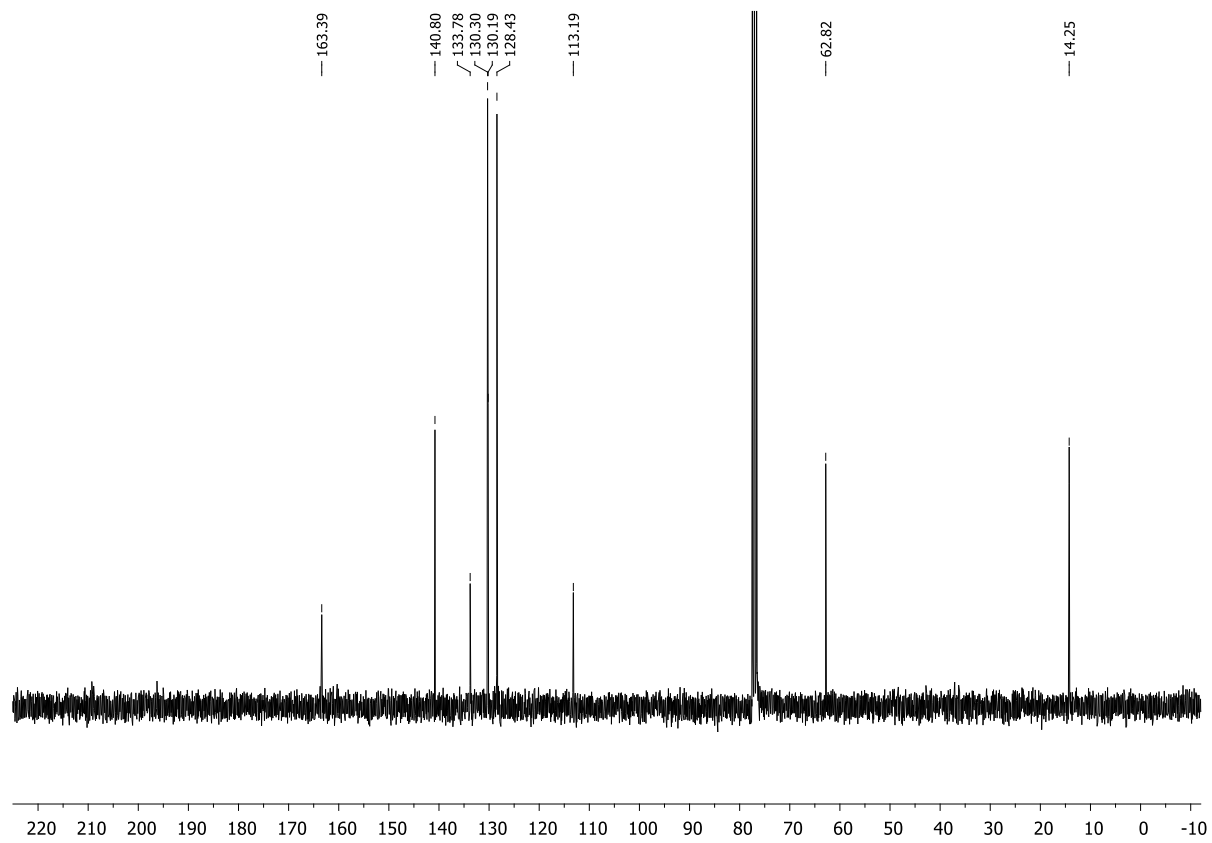
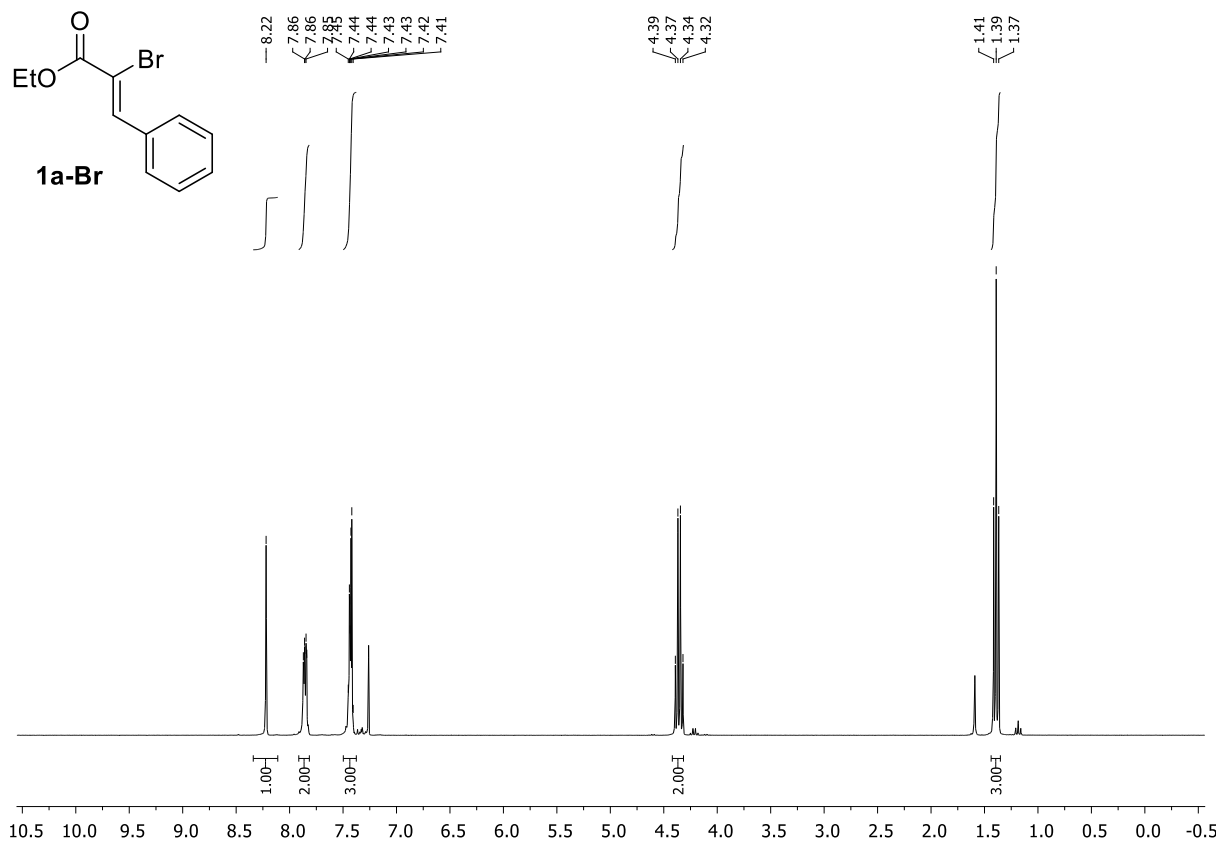
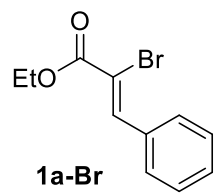
The upper images show the  $^1\text{H}$ -NMR spectra whereas the lower images describe the  $^{13}\text{C}$ -NMR spectra.

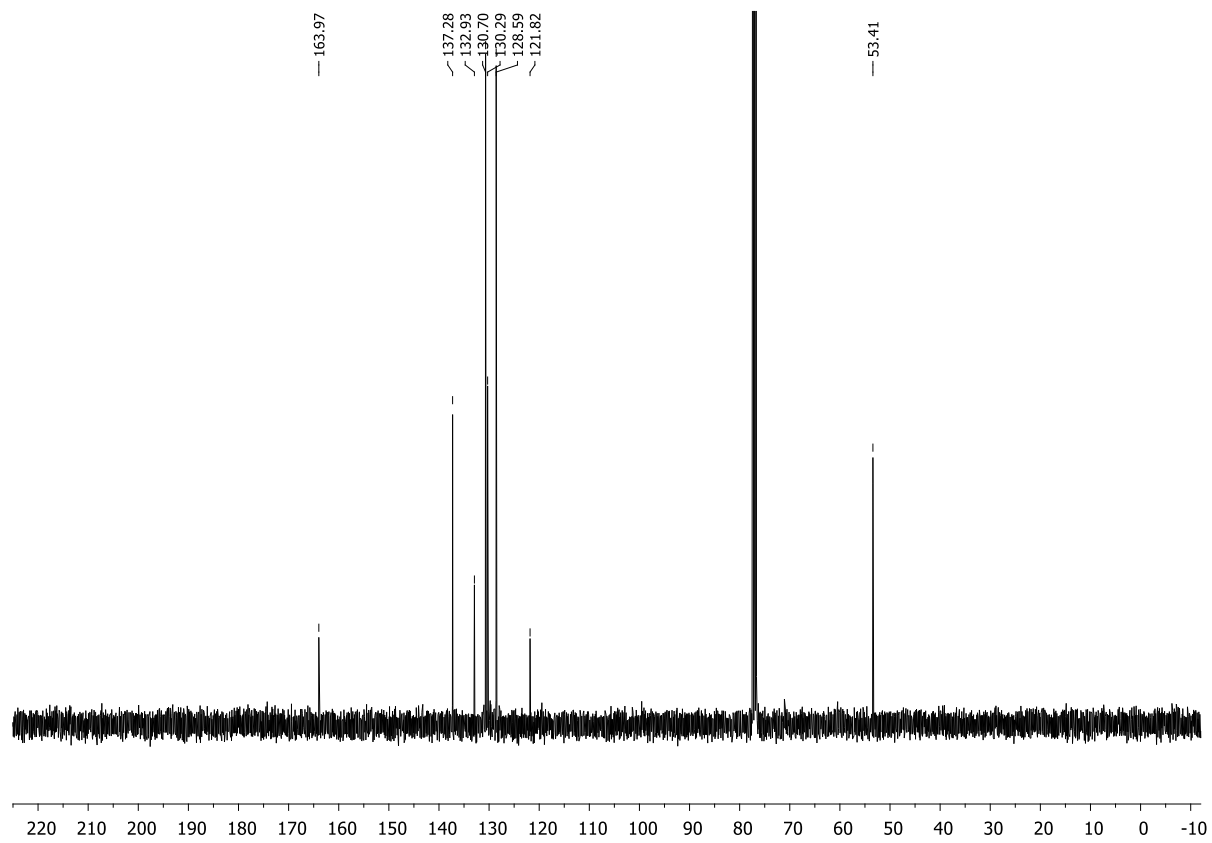
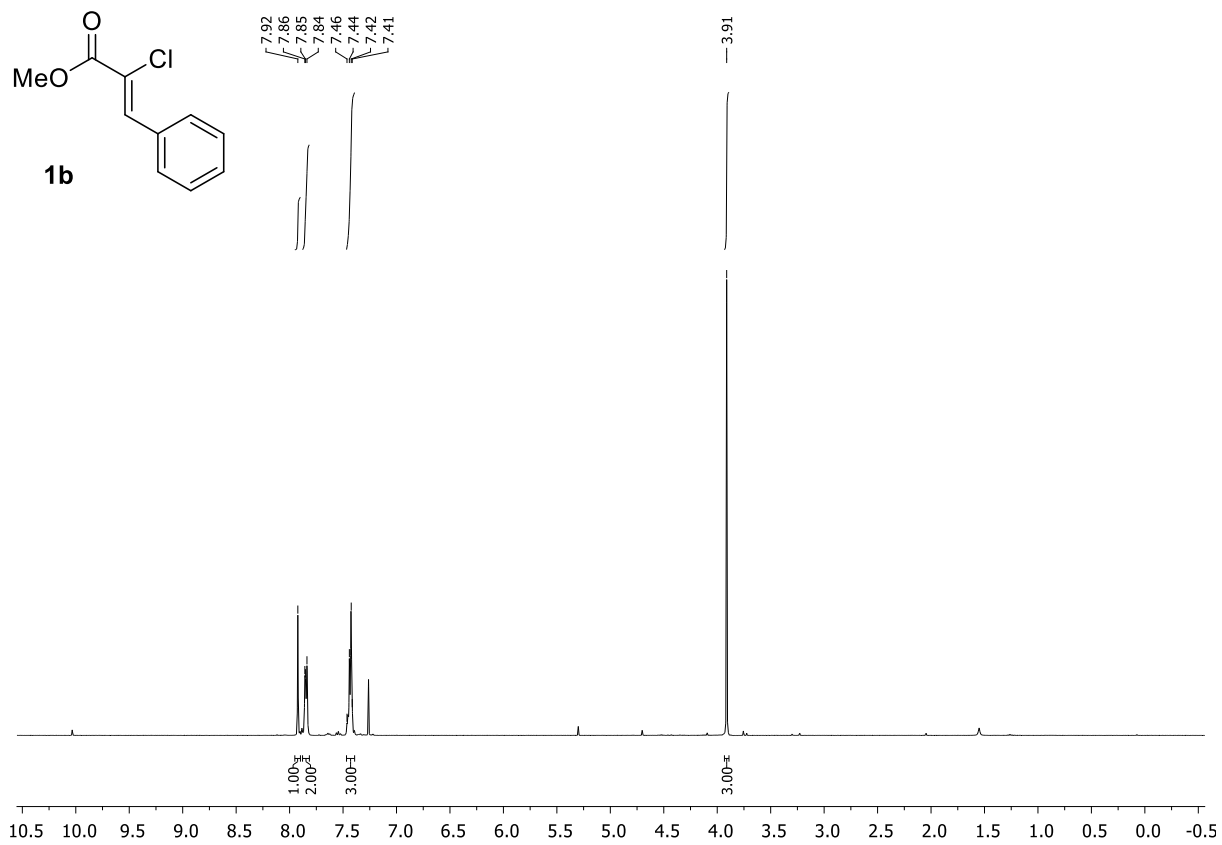
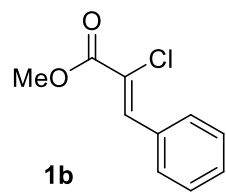
All compounds were dissolved in  $\text{CDCl}_3$  unless otherwise stated.

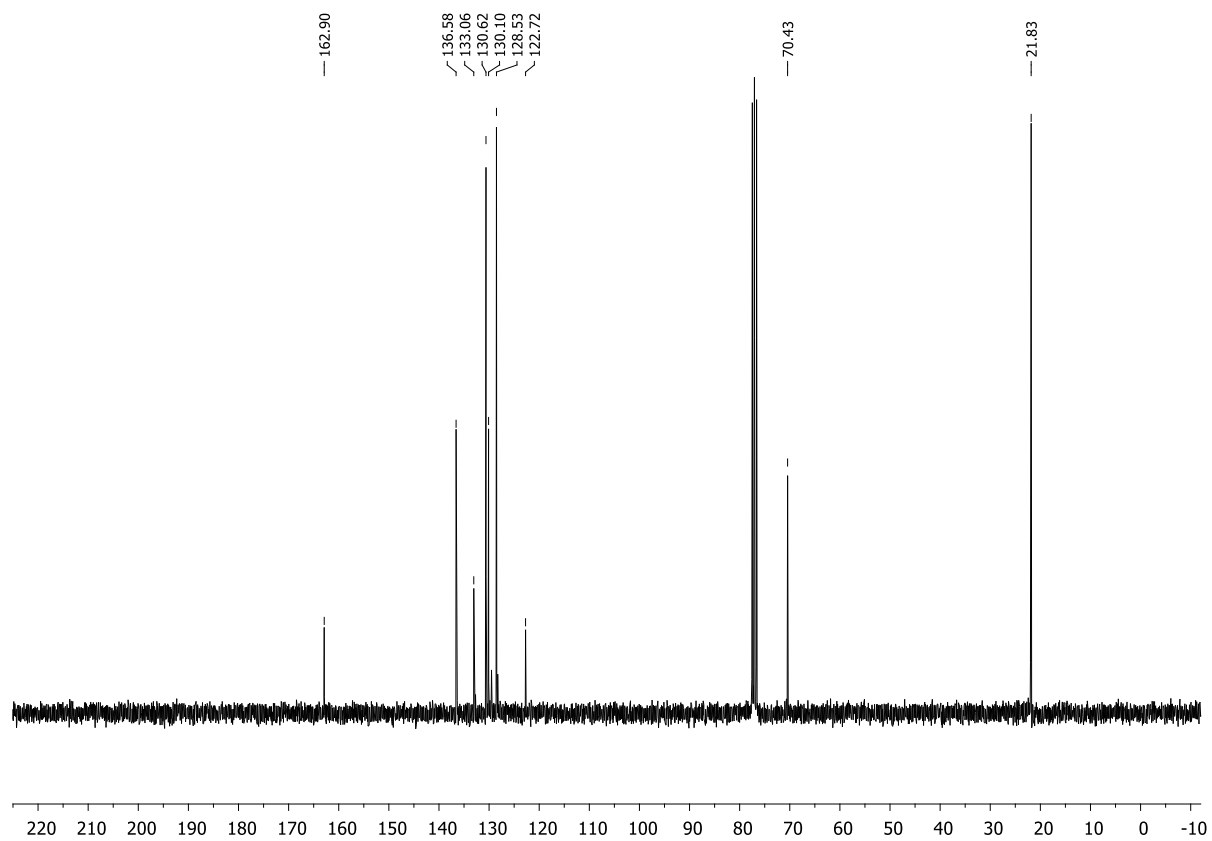
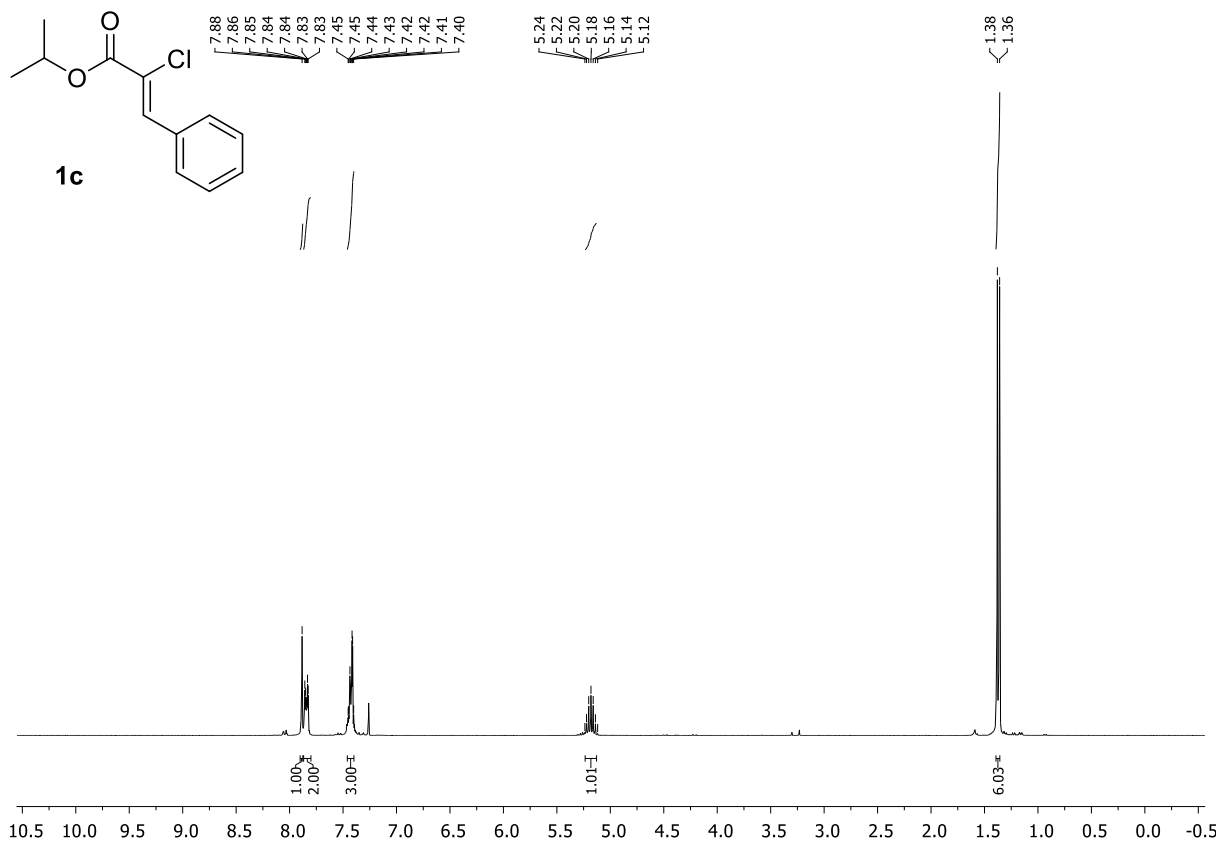


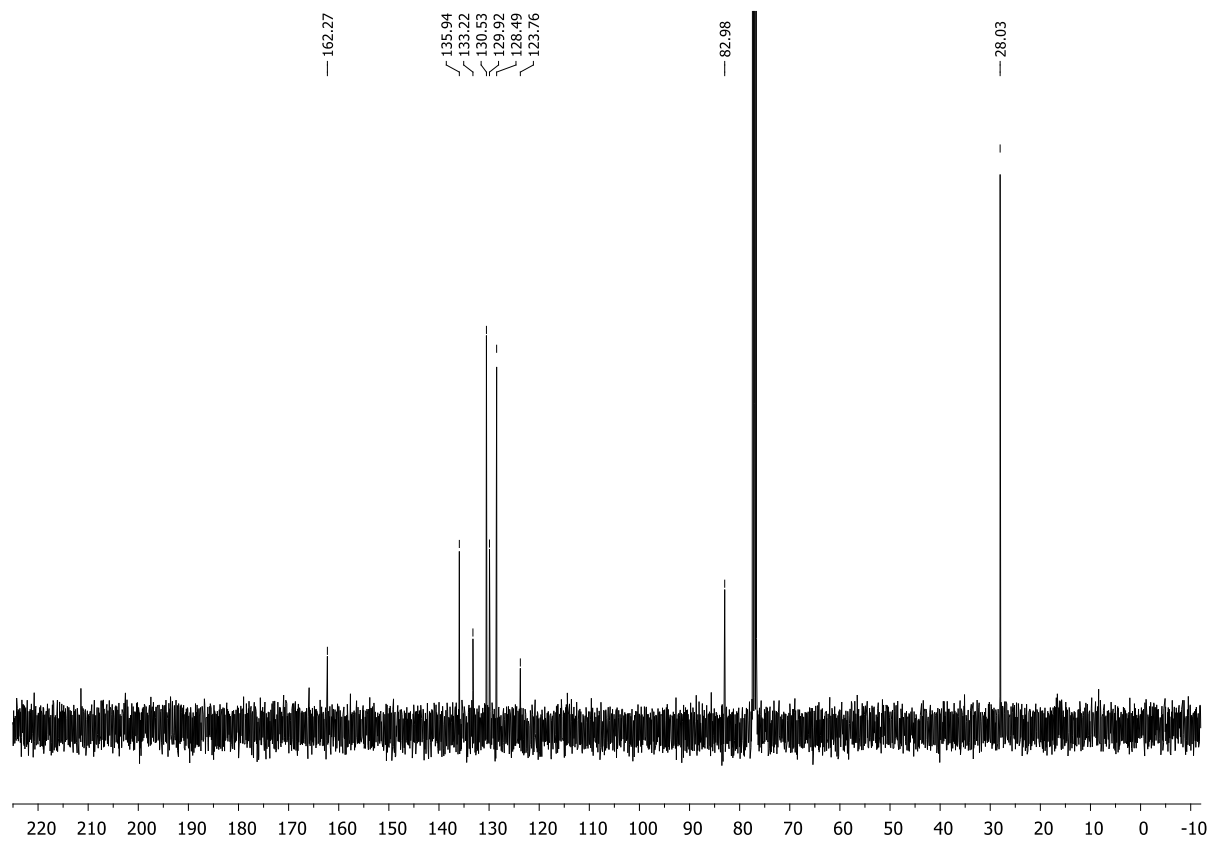
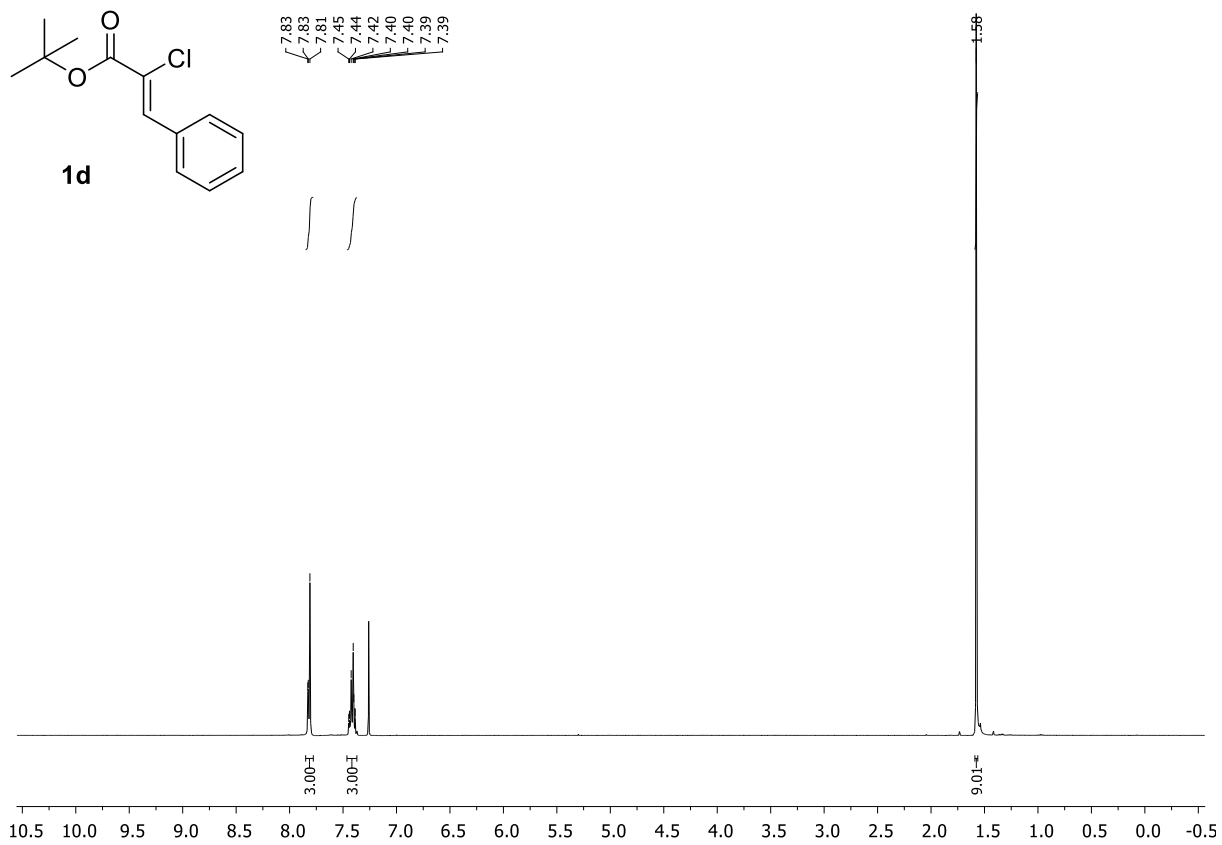


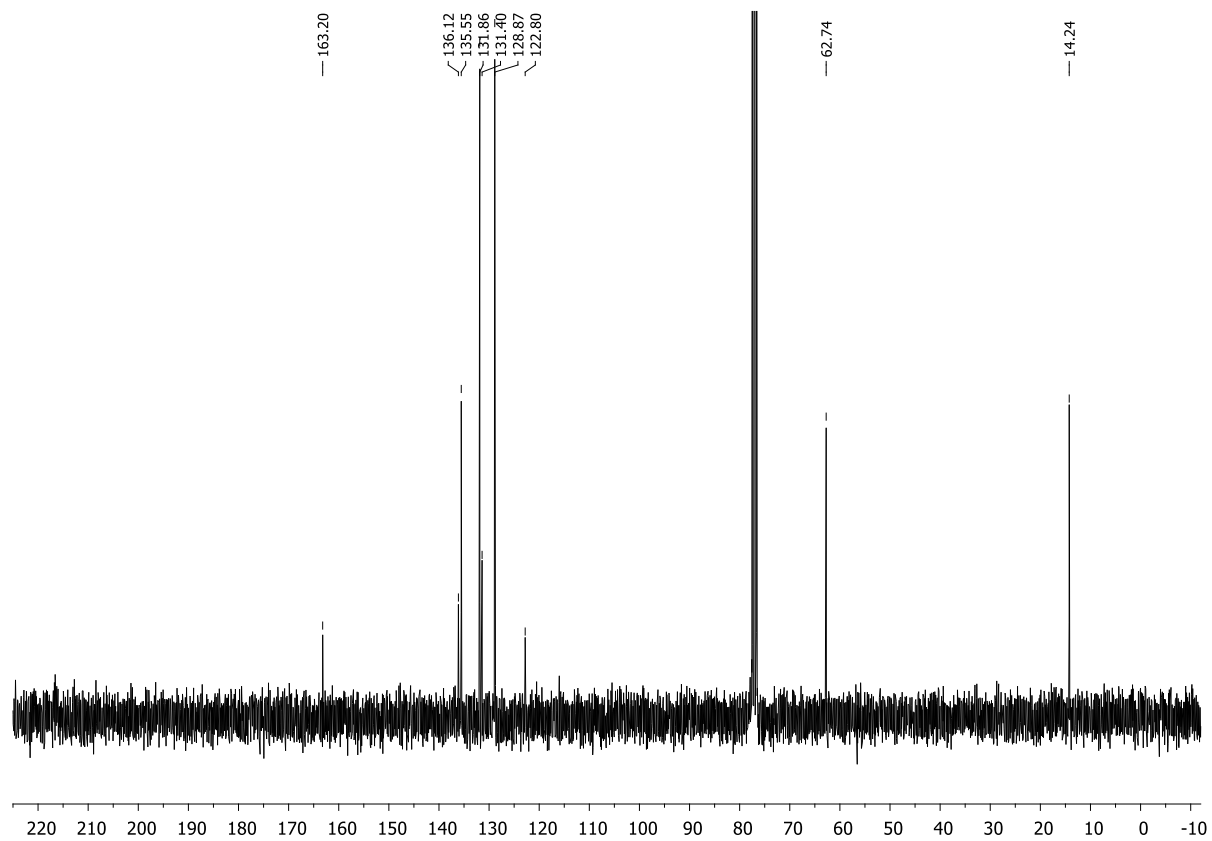
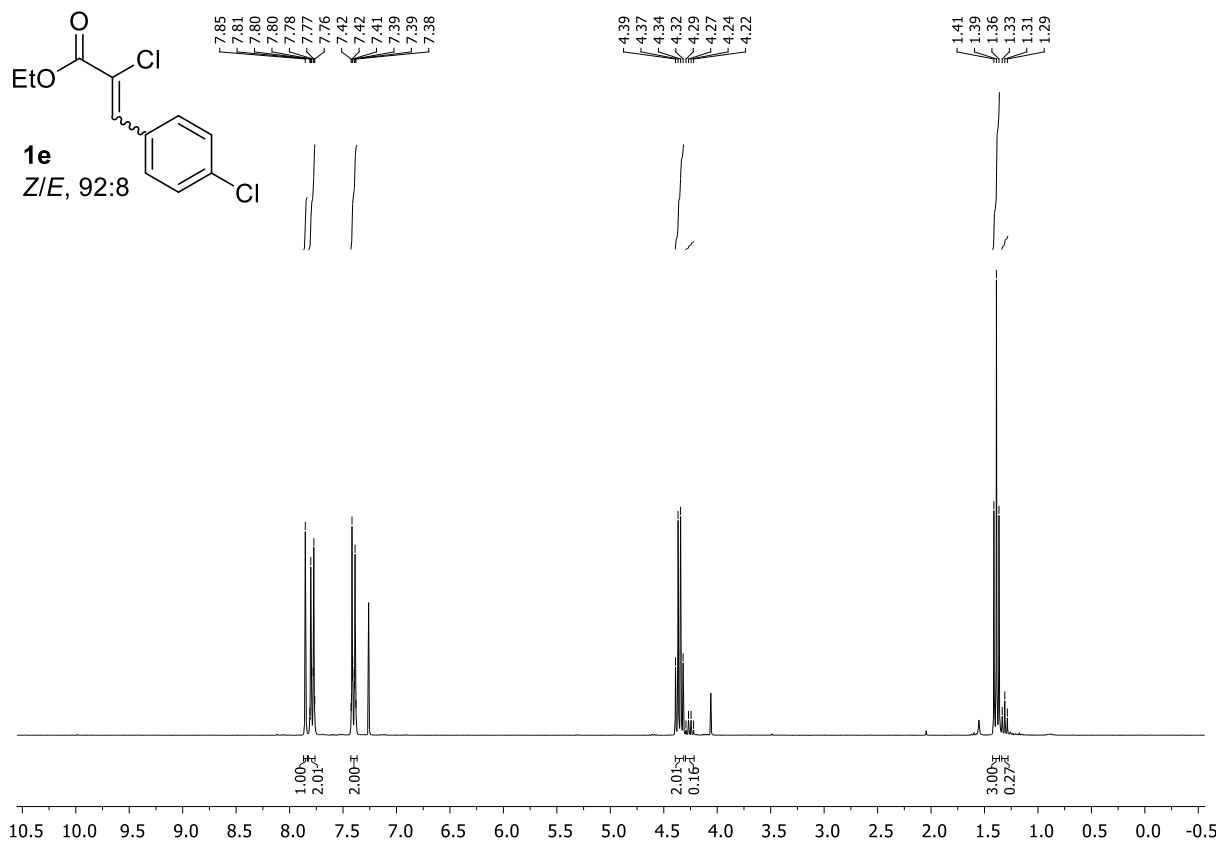


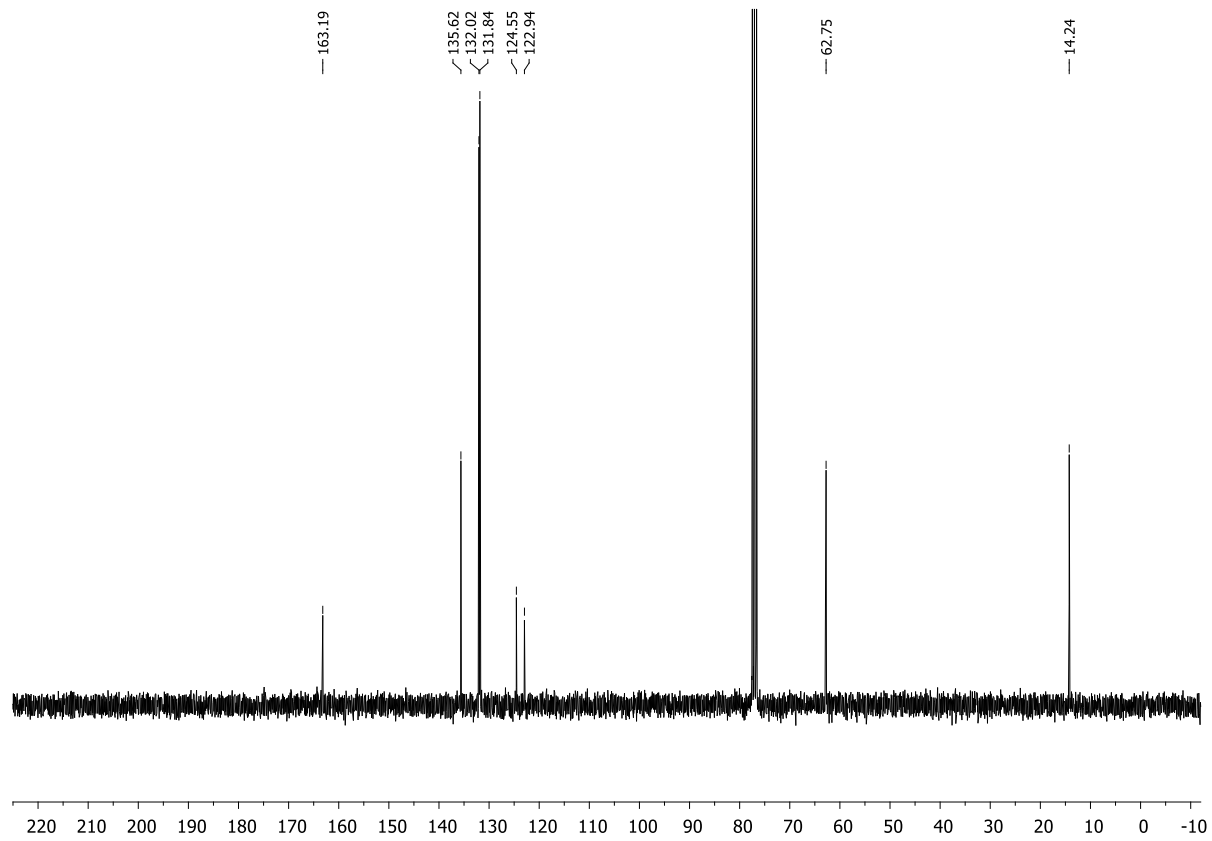
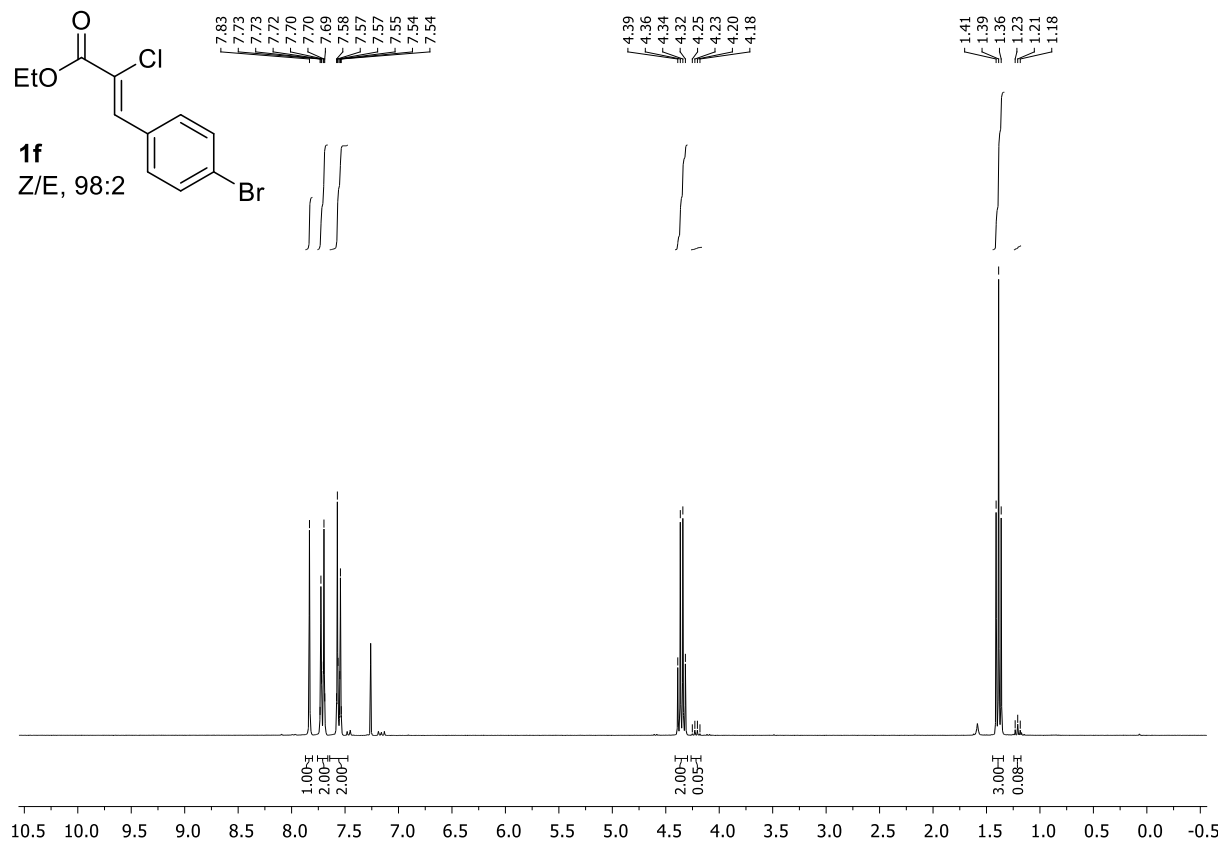


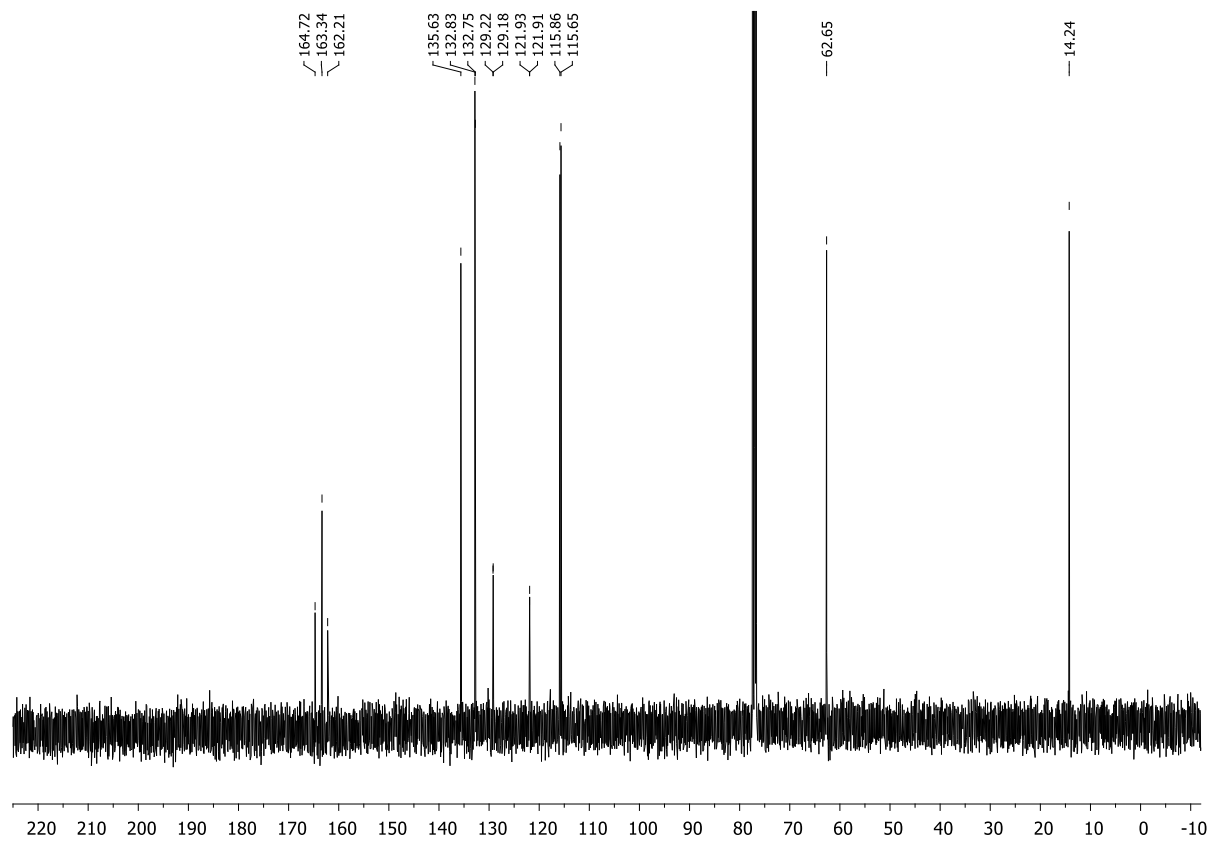
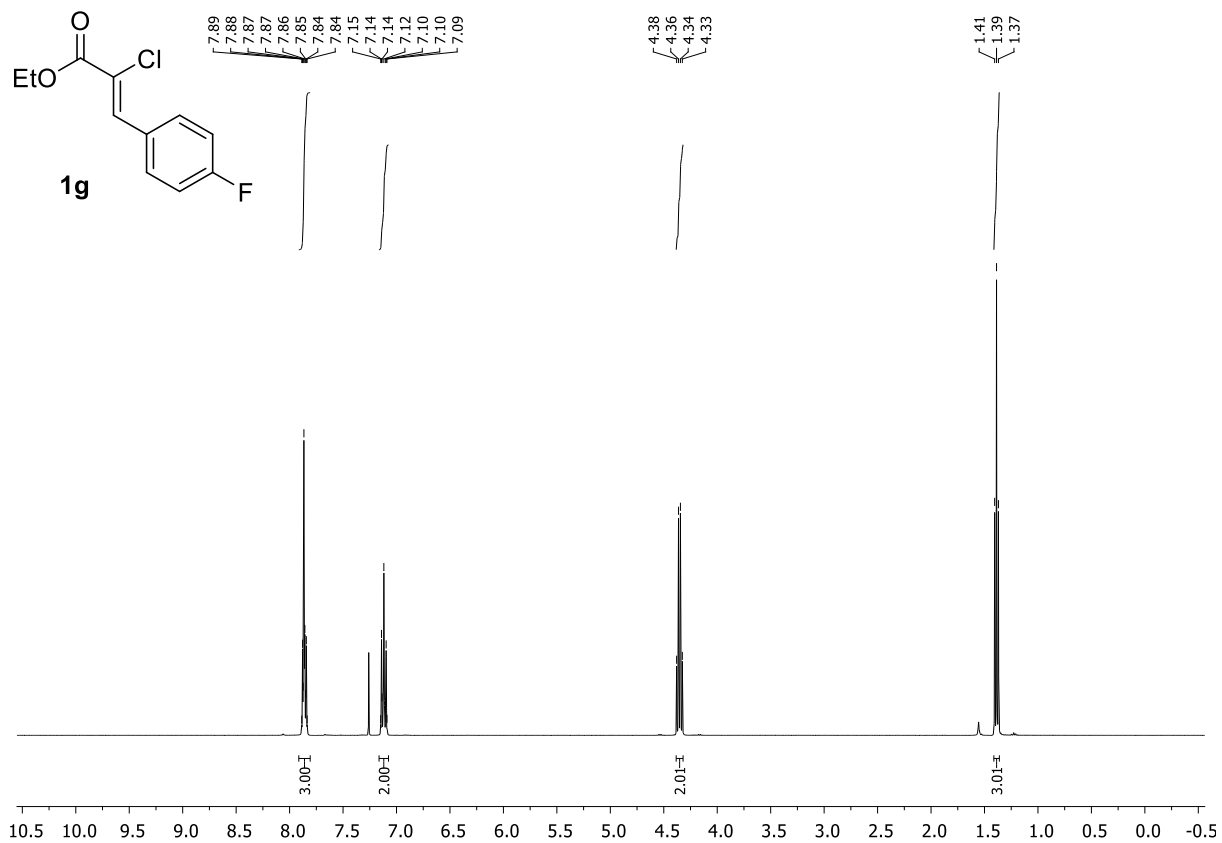


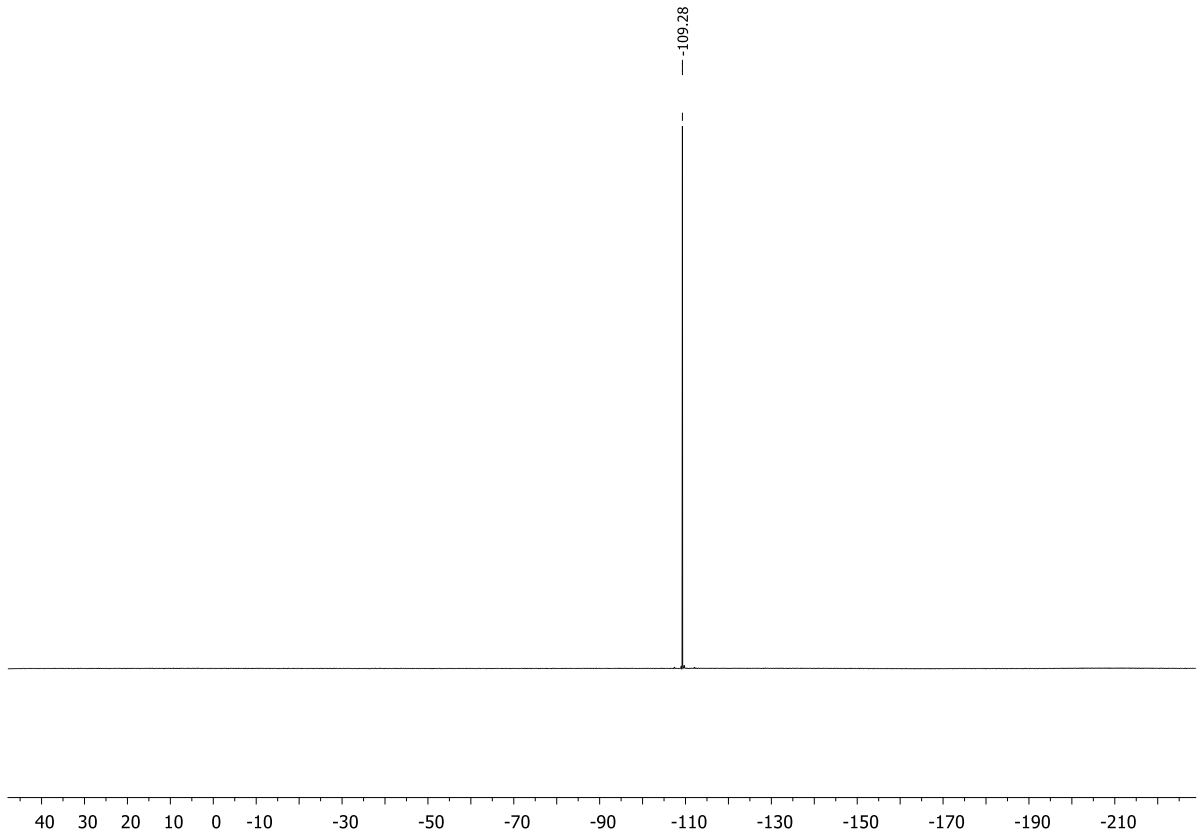


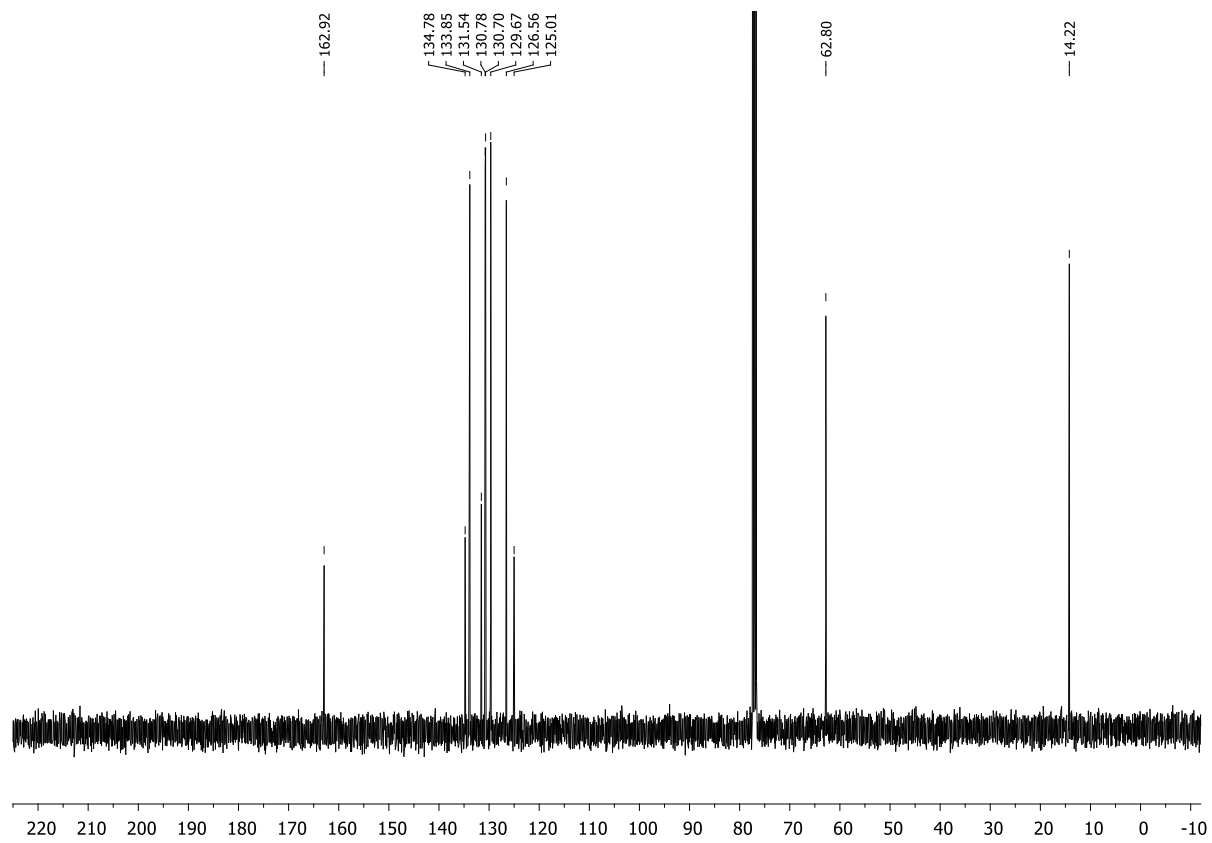
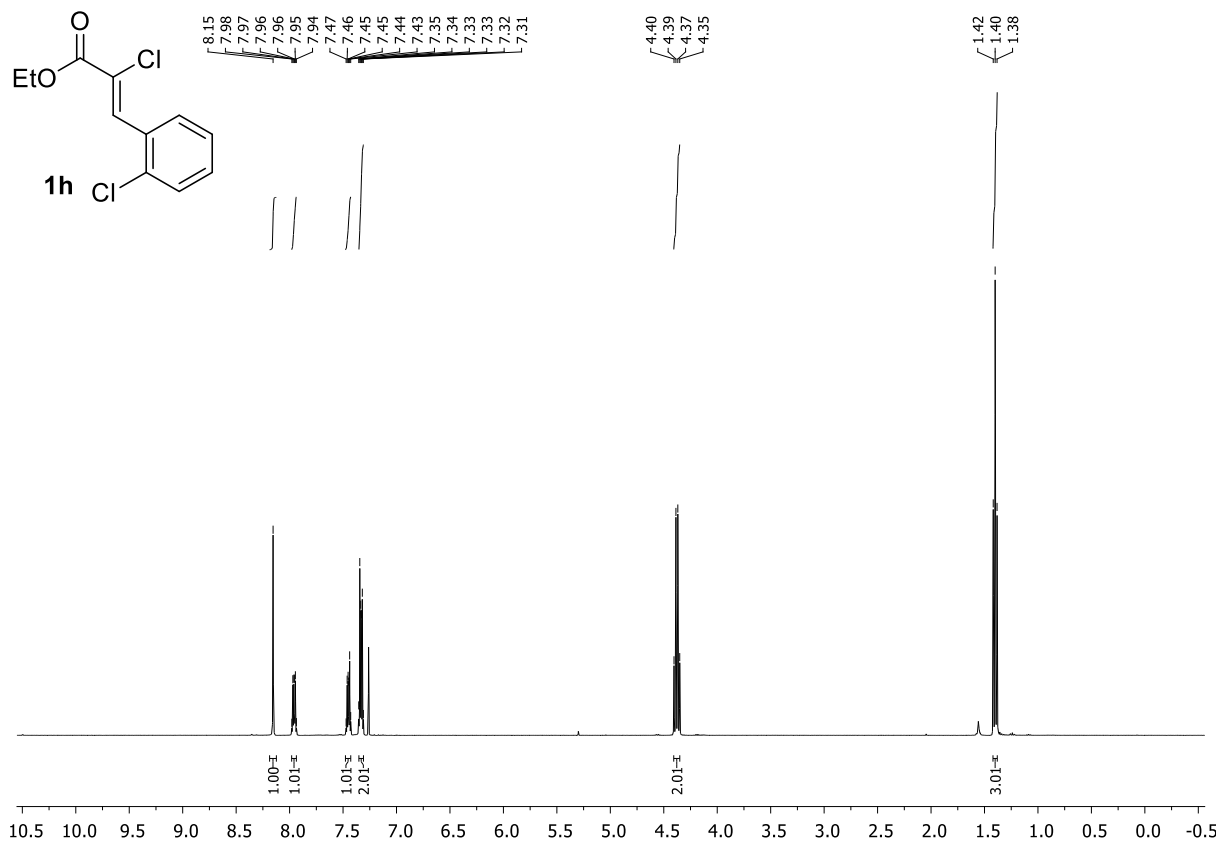




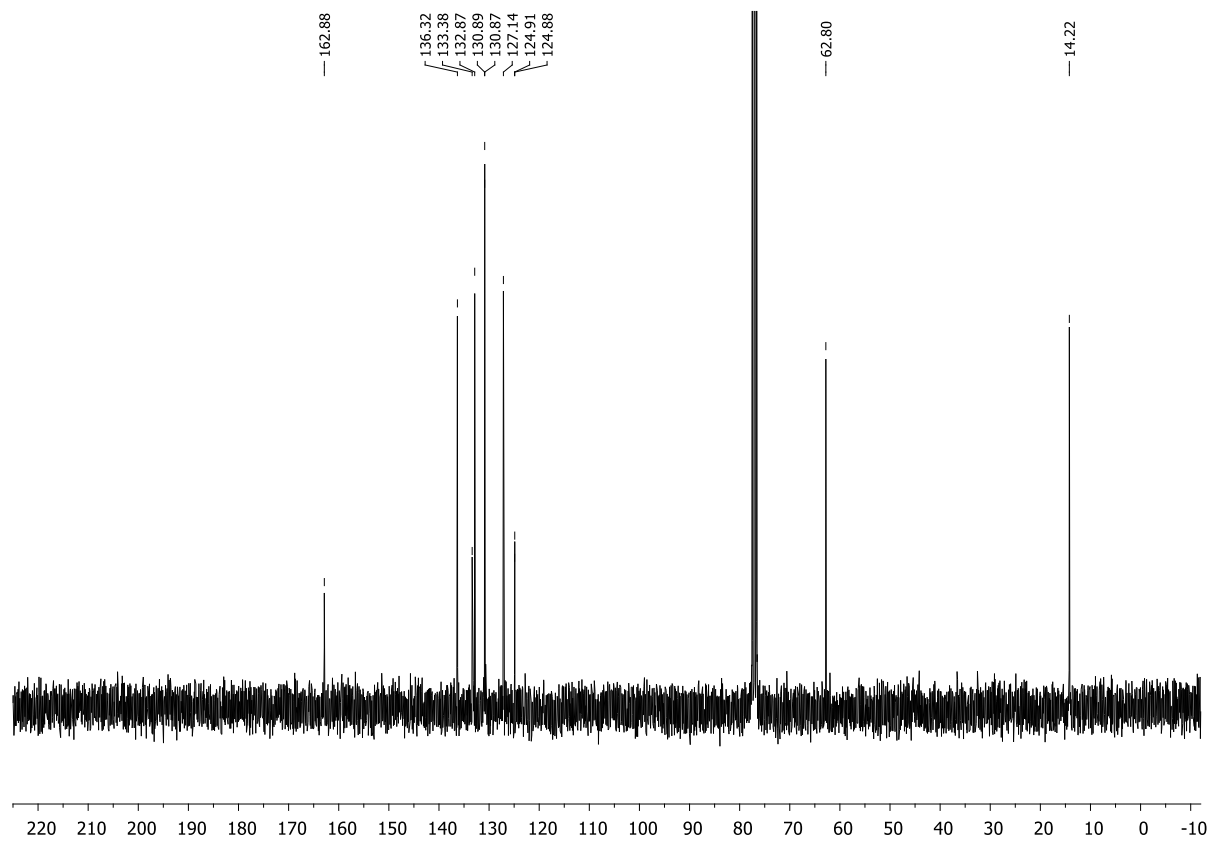
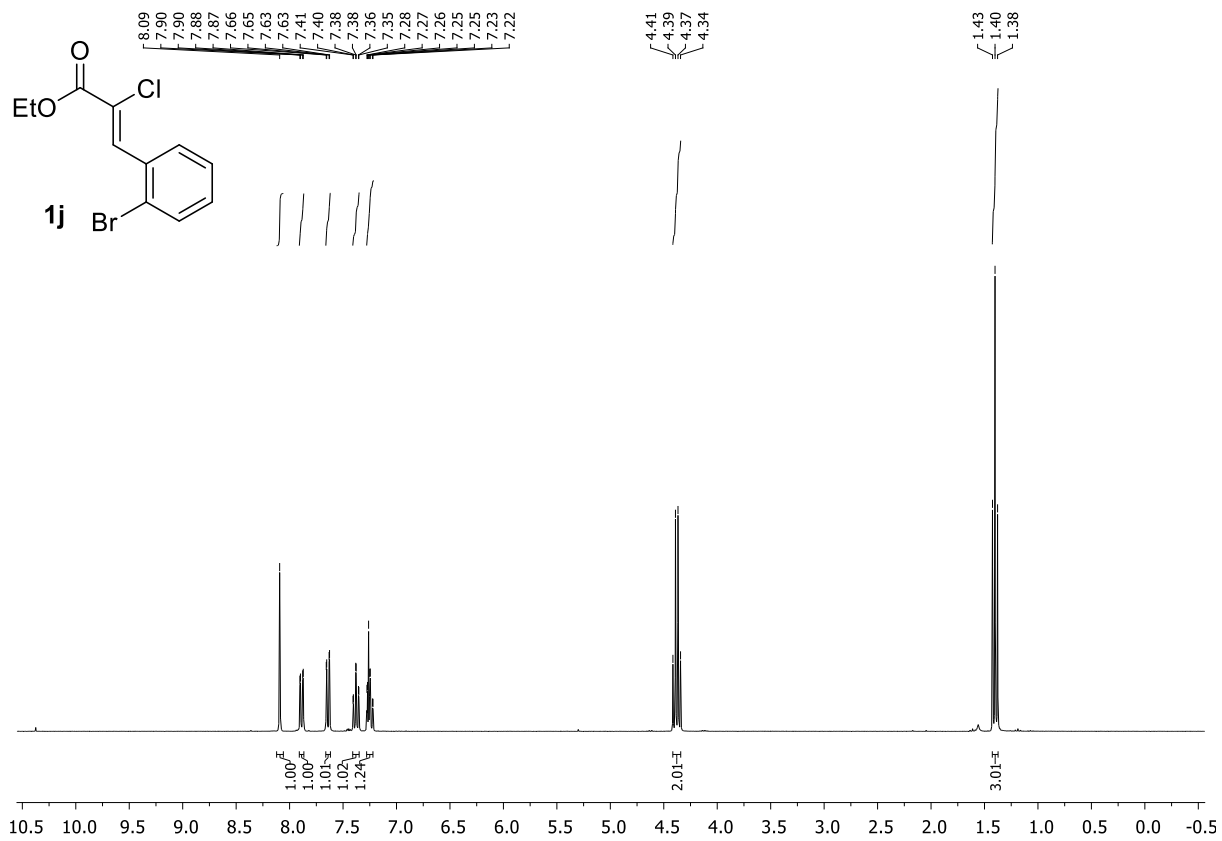


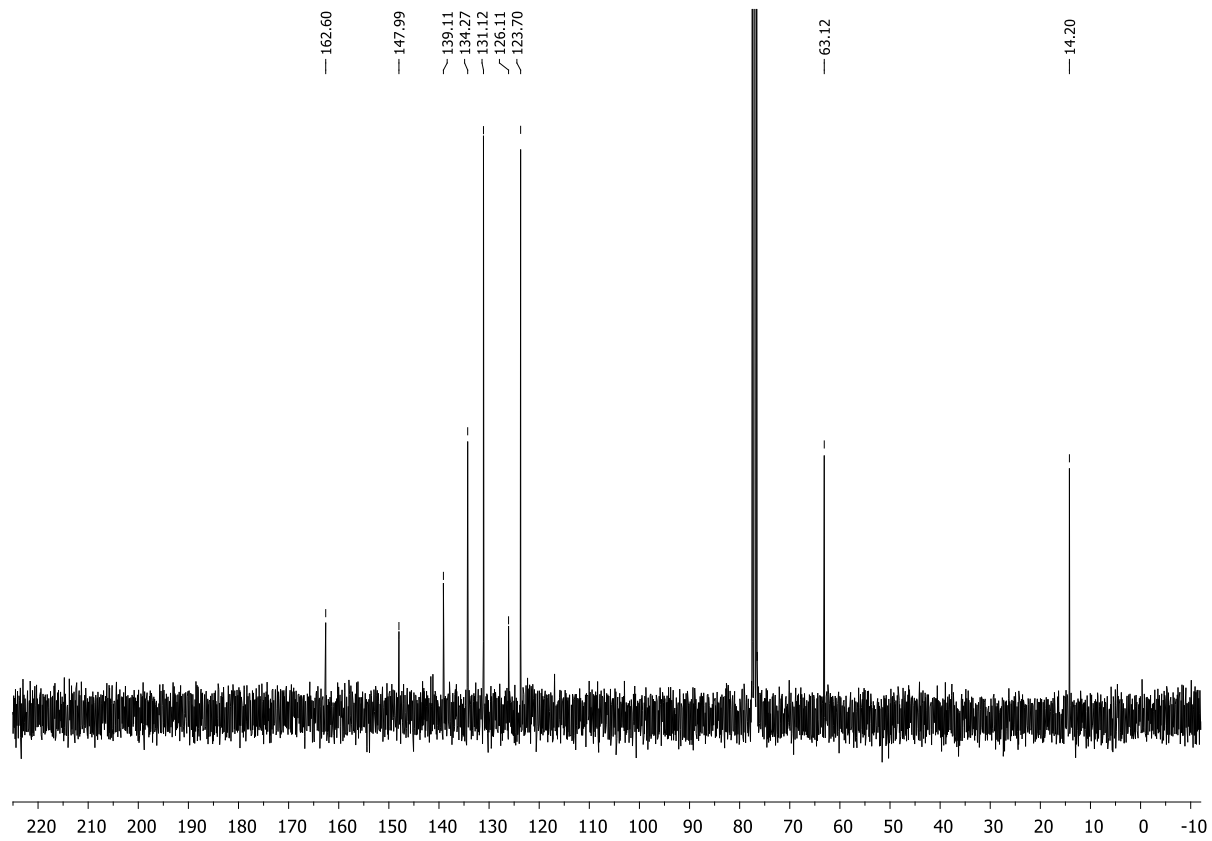
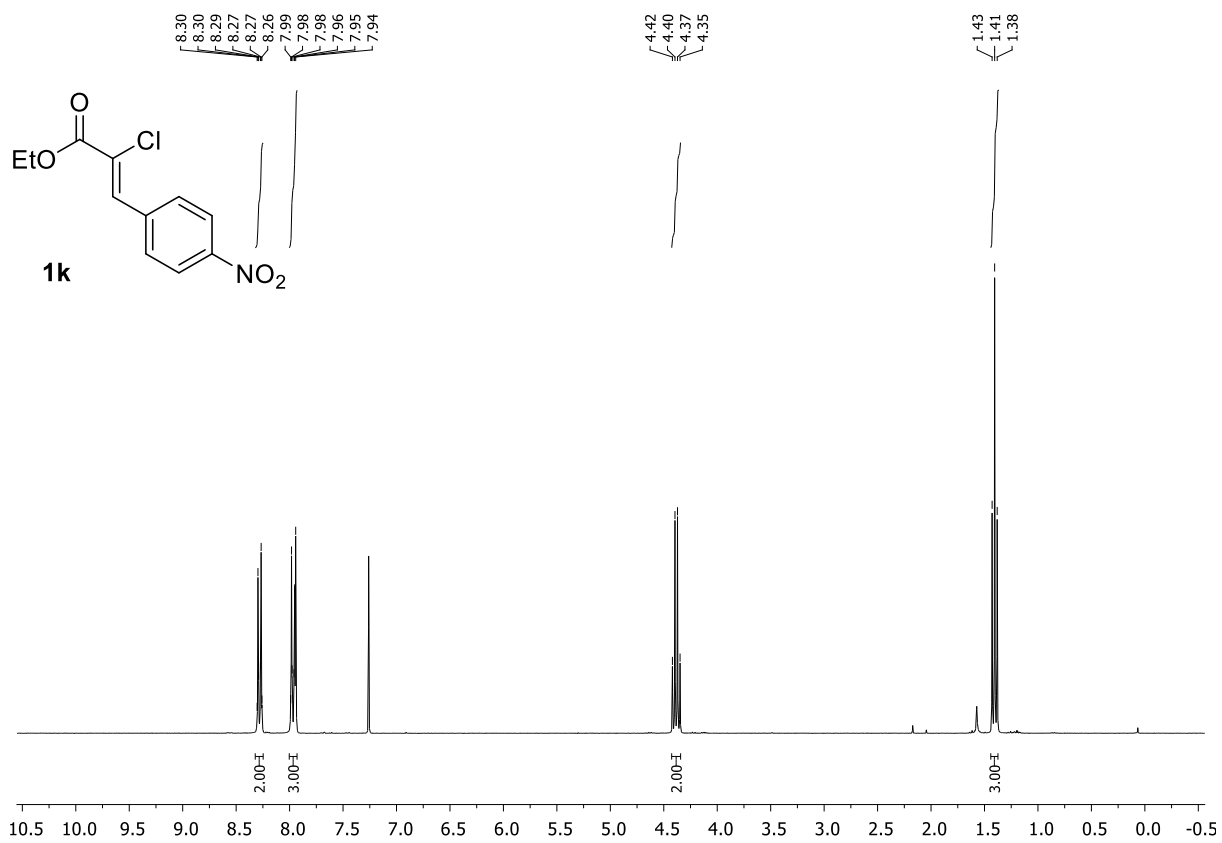


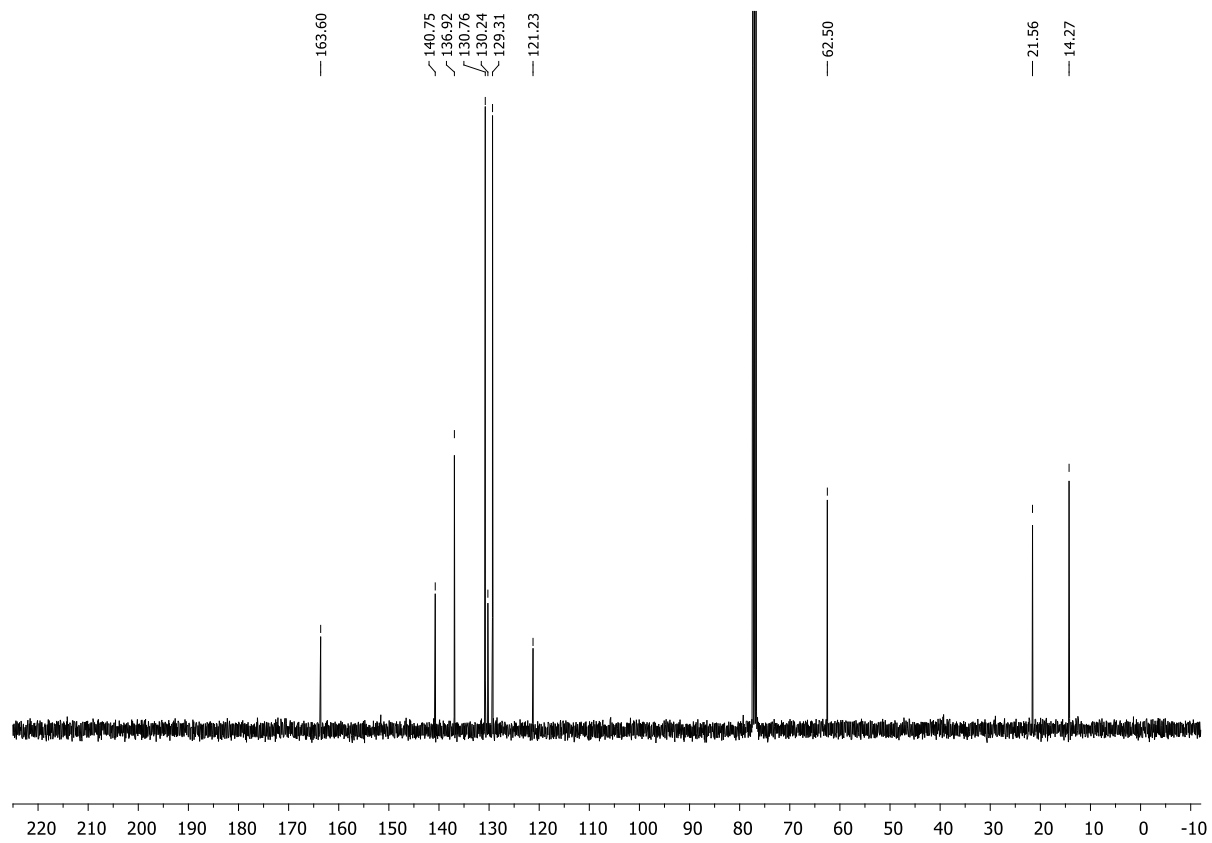
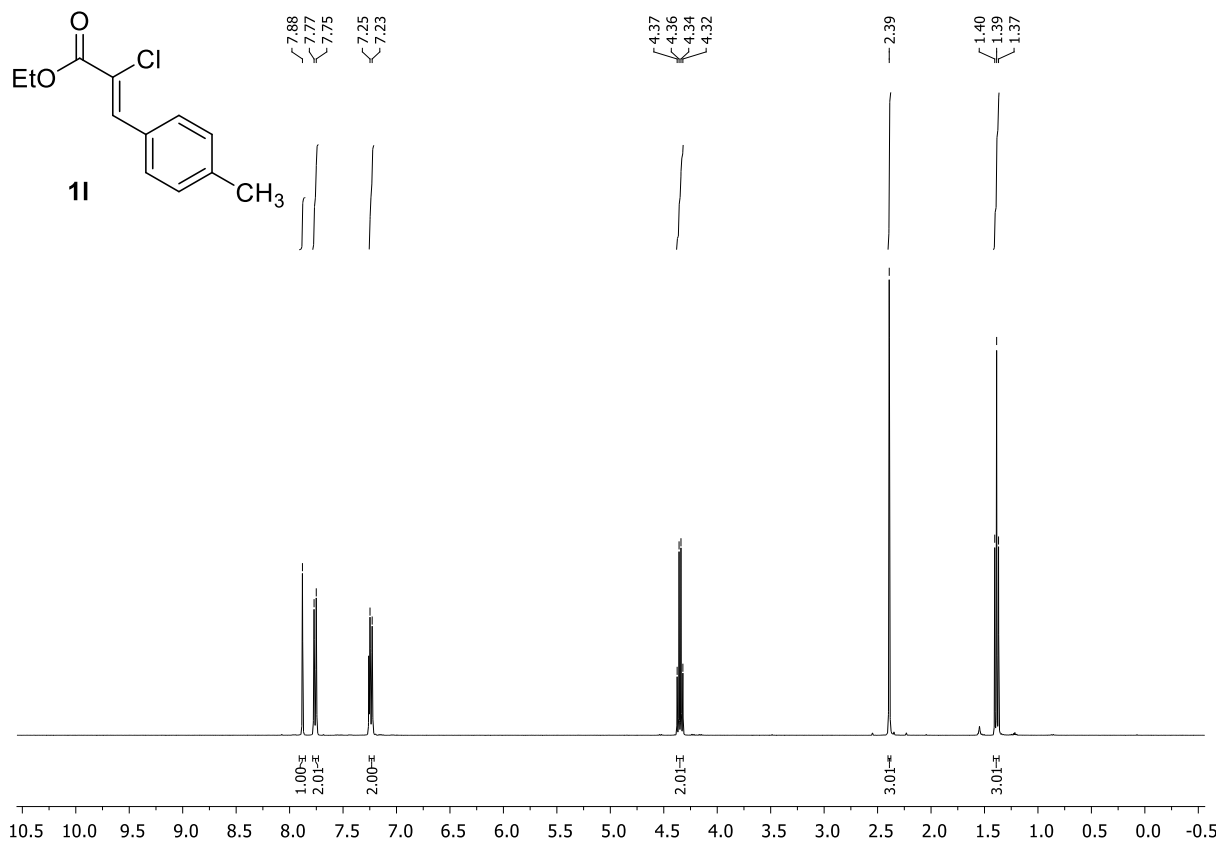


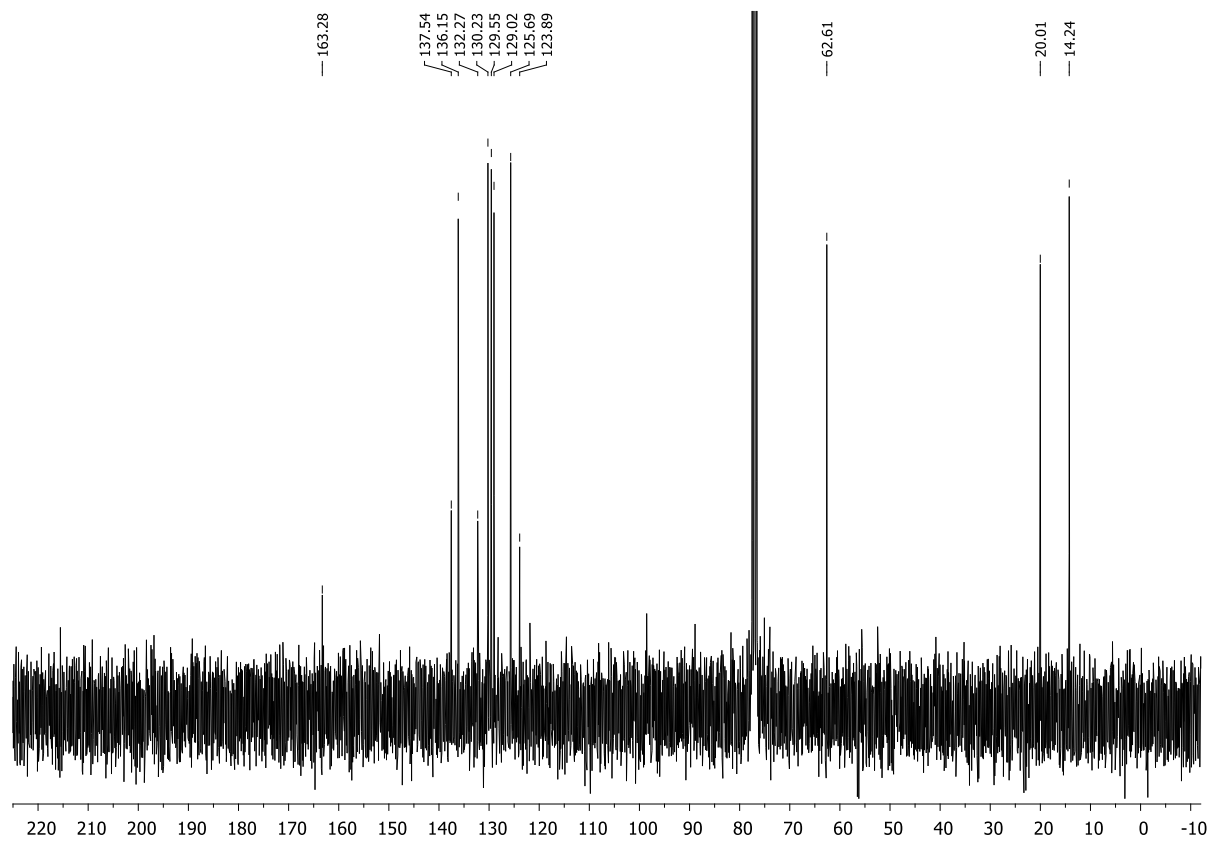
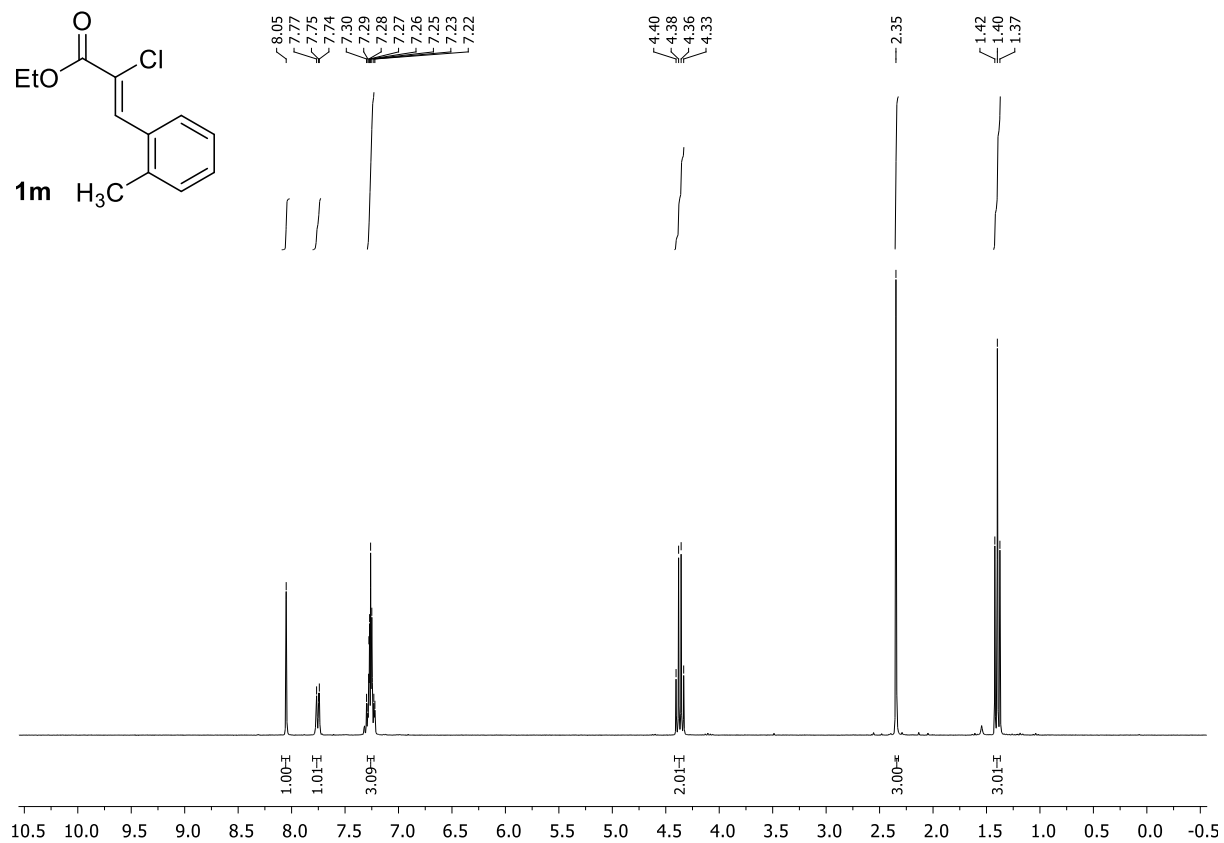
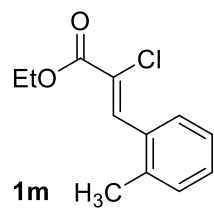


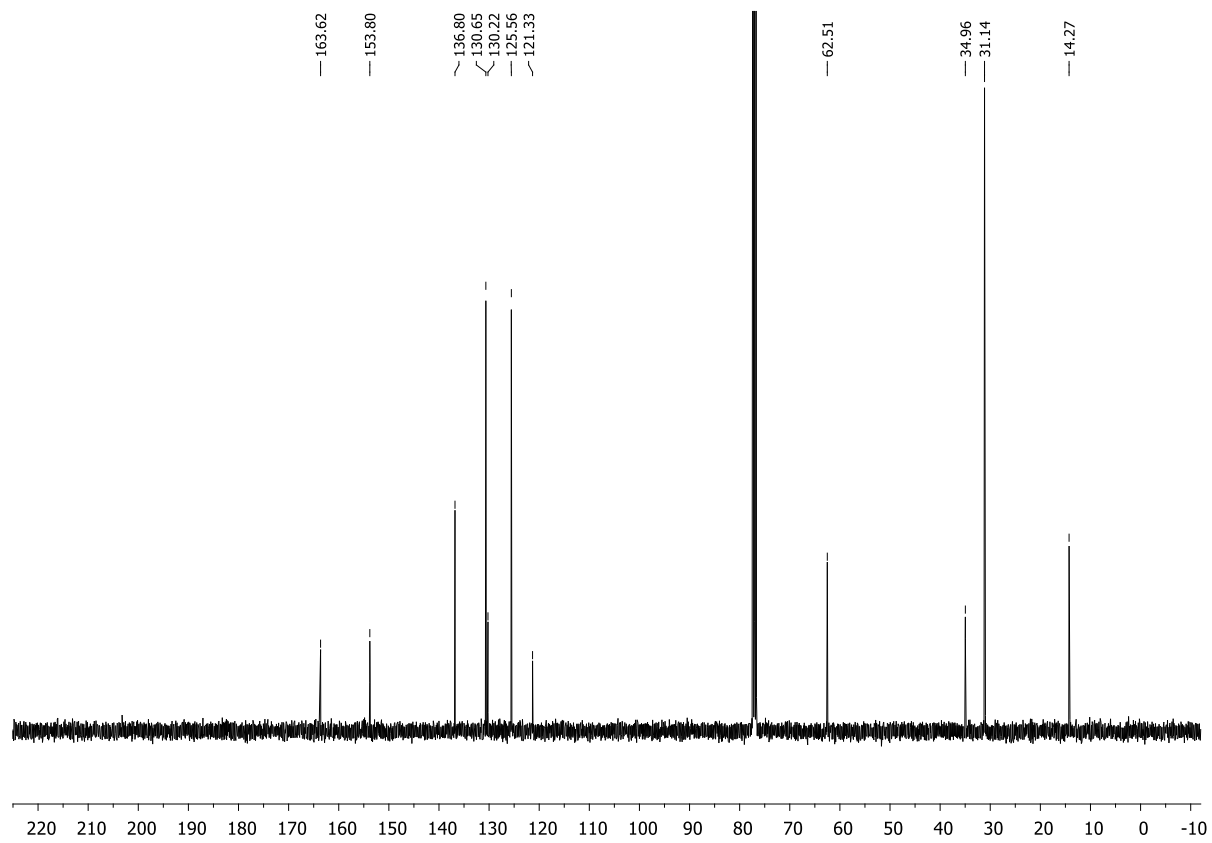
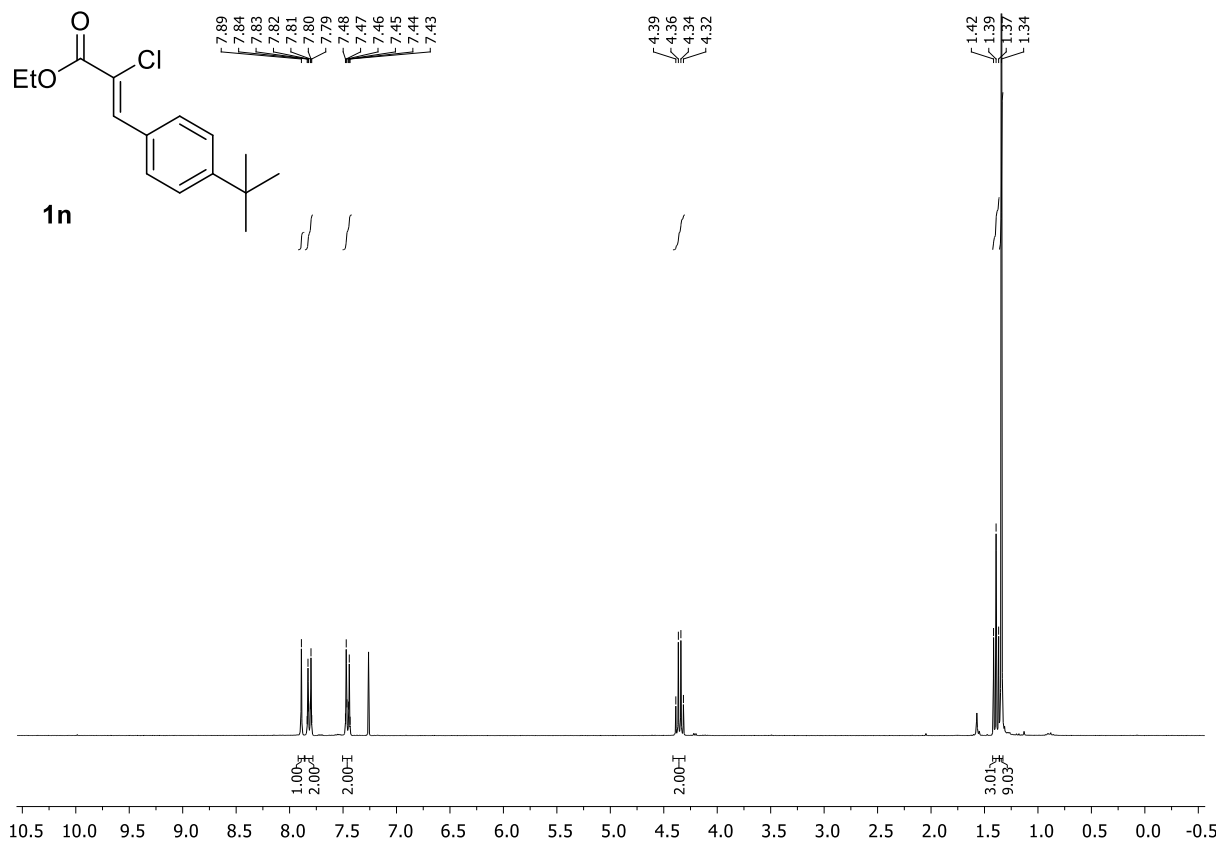


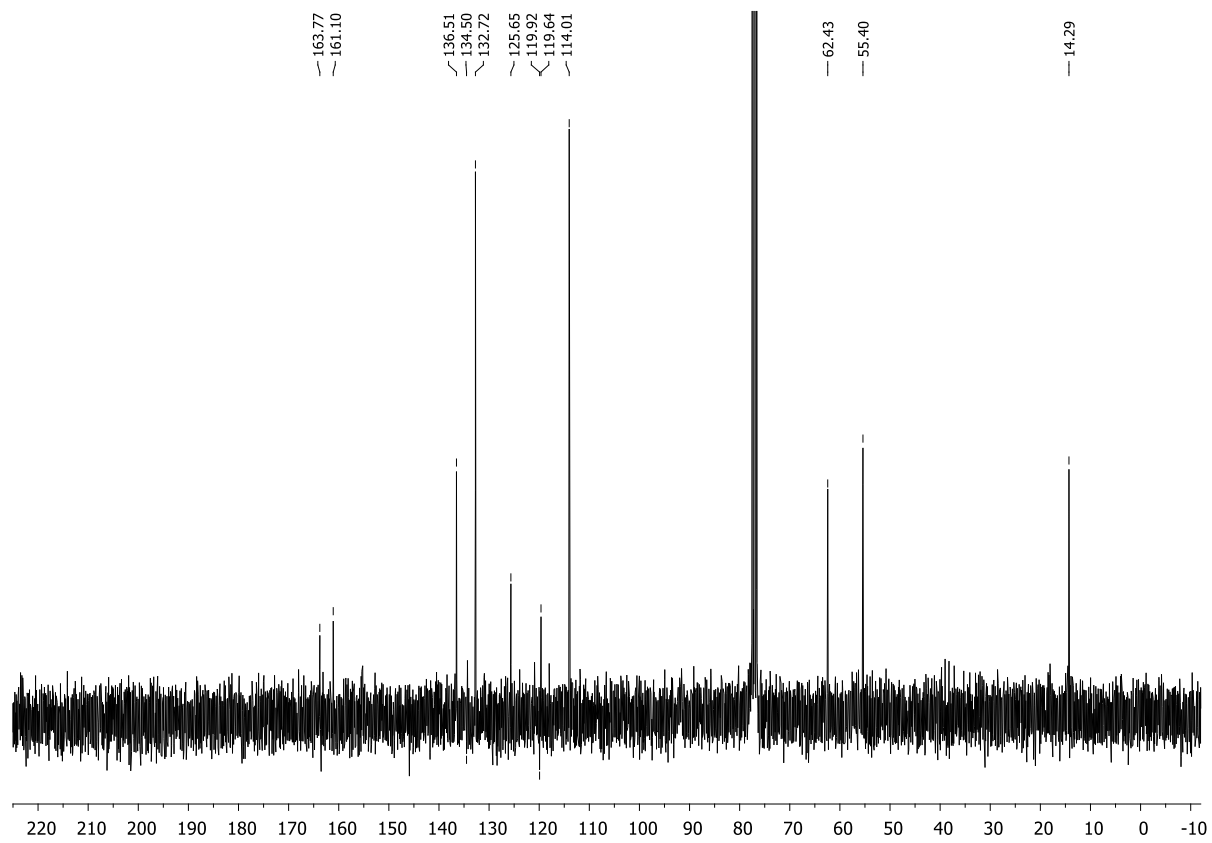
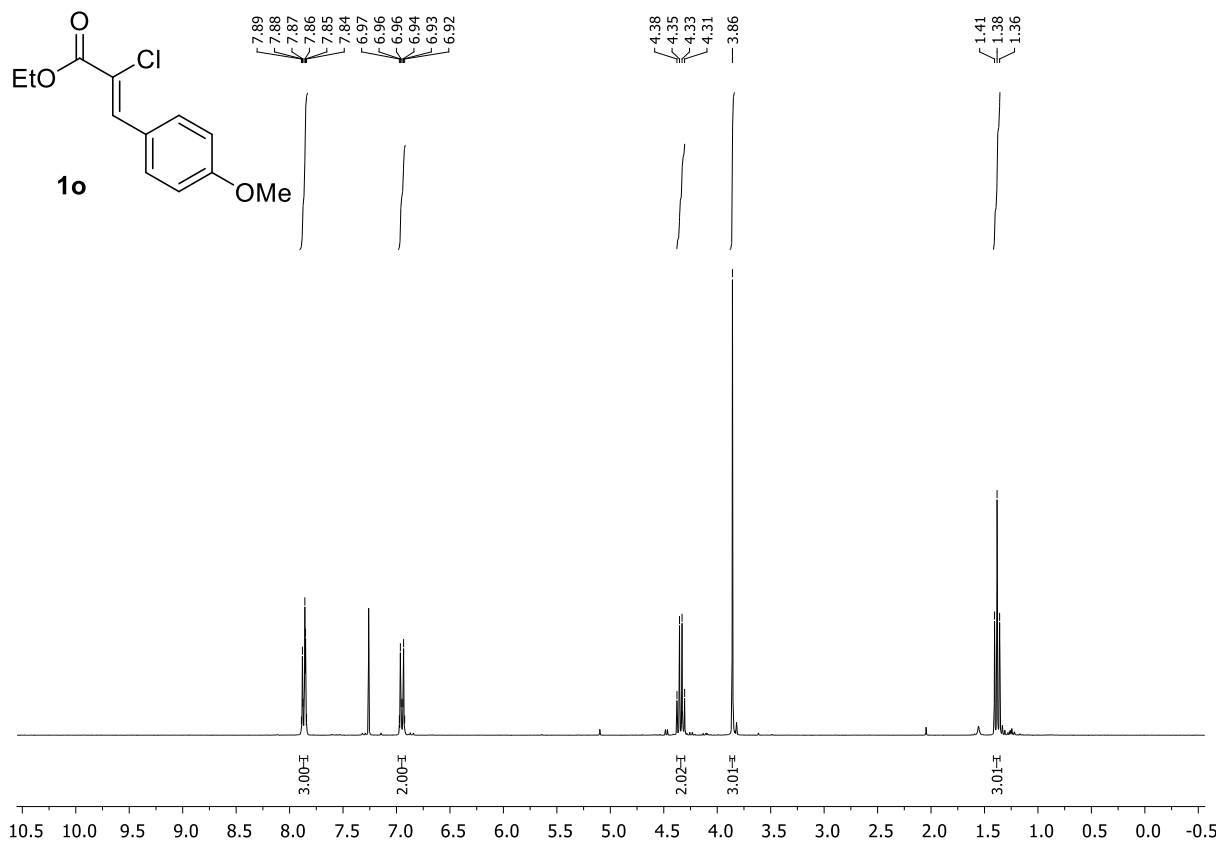


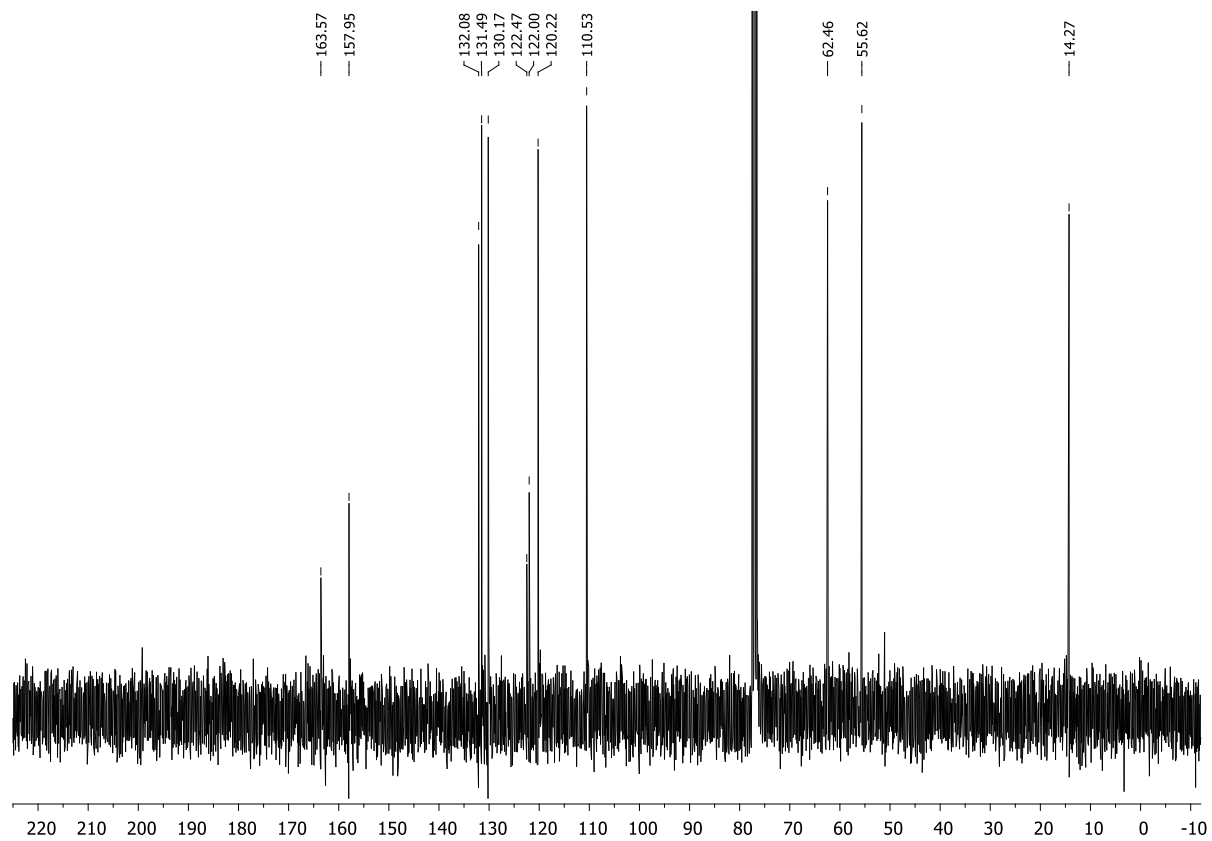
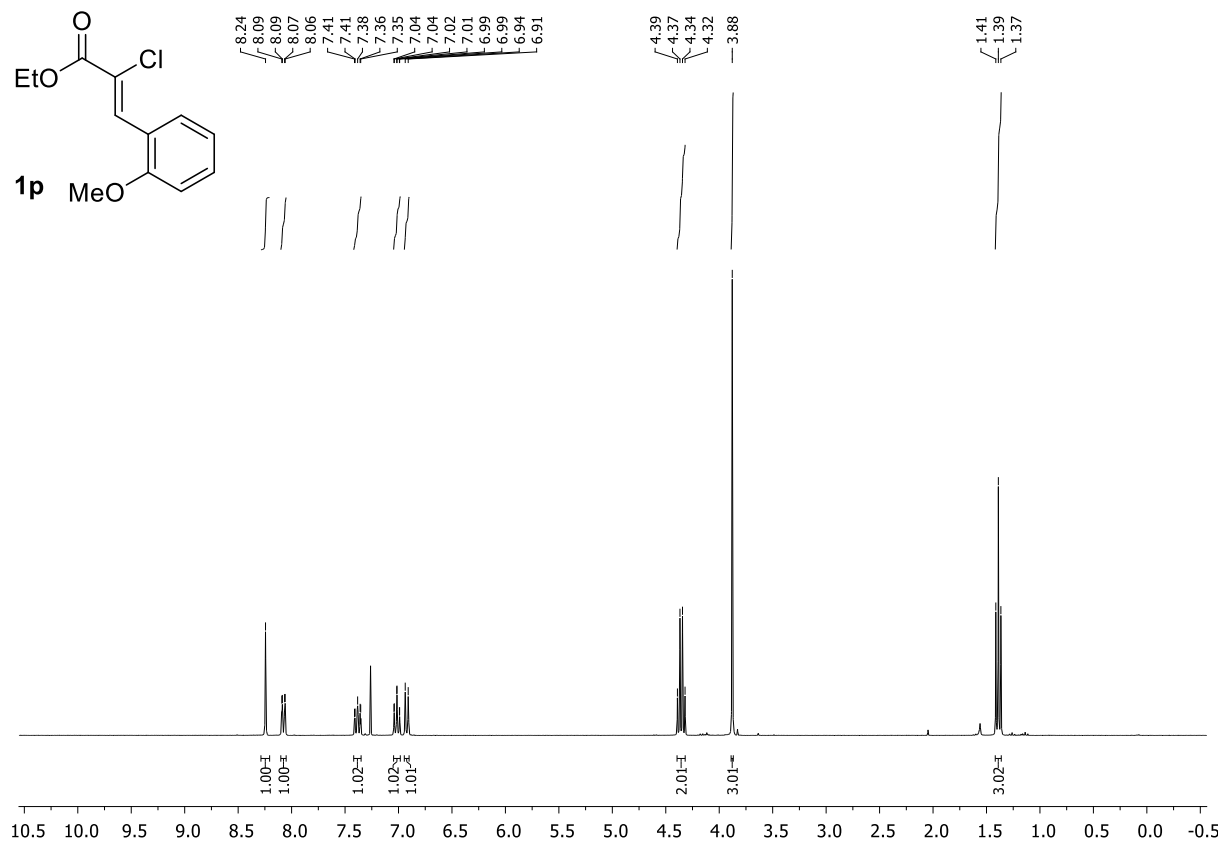
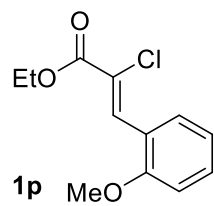


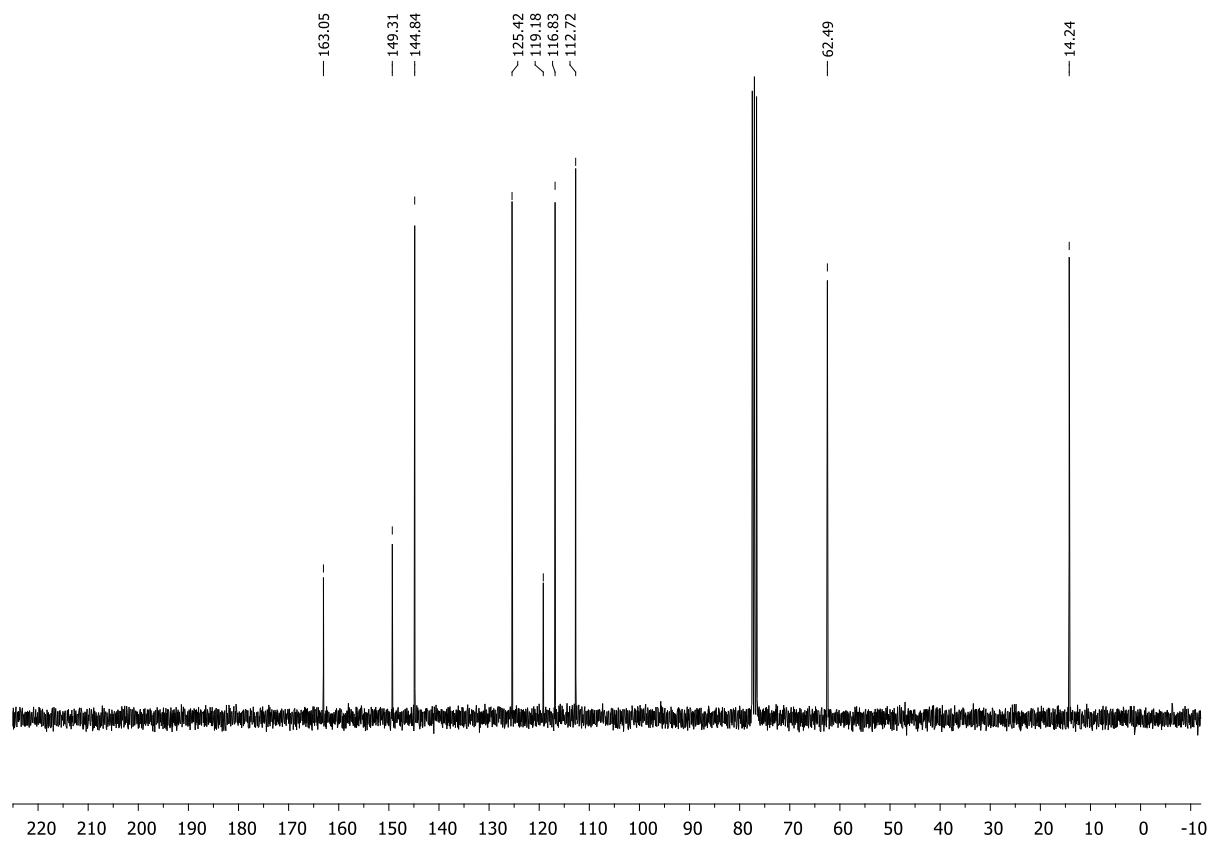
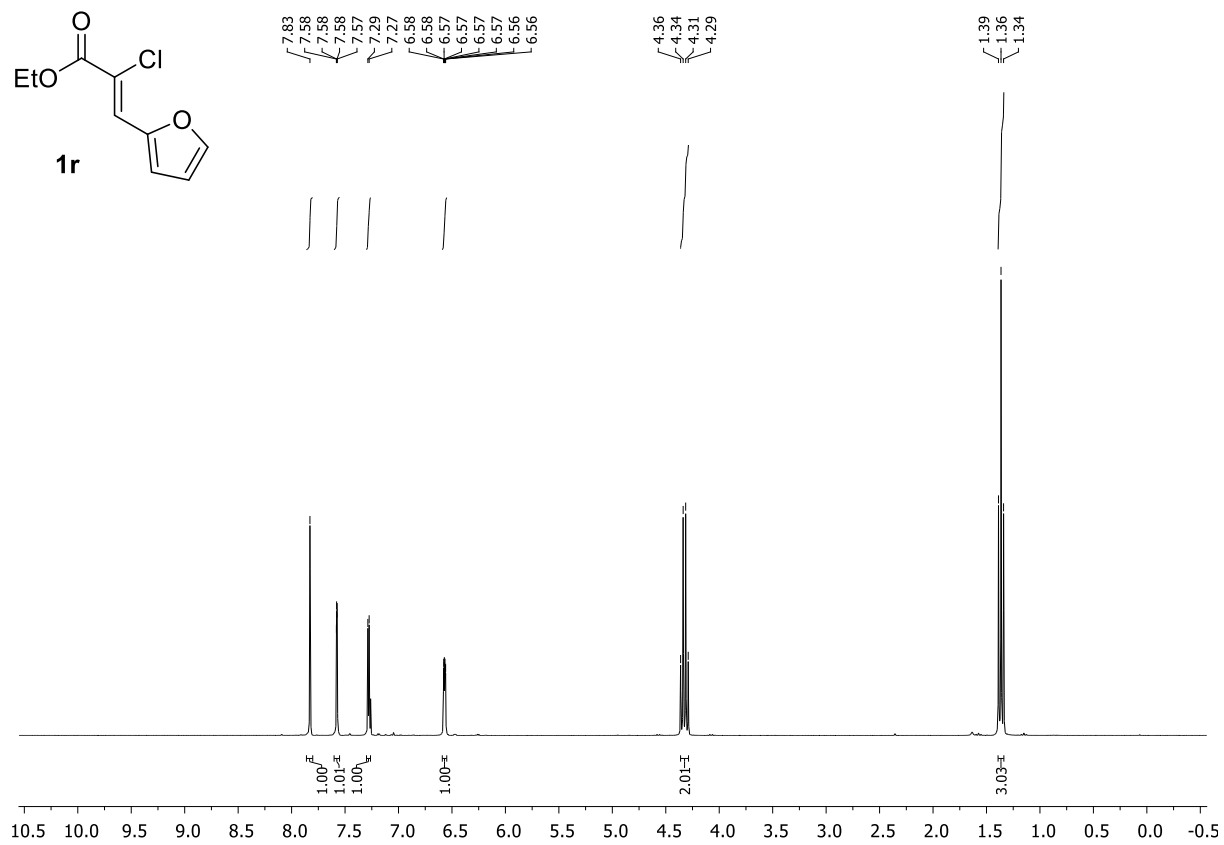
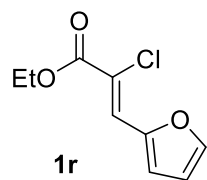


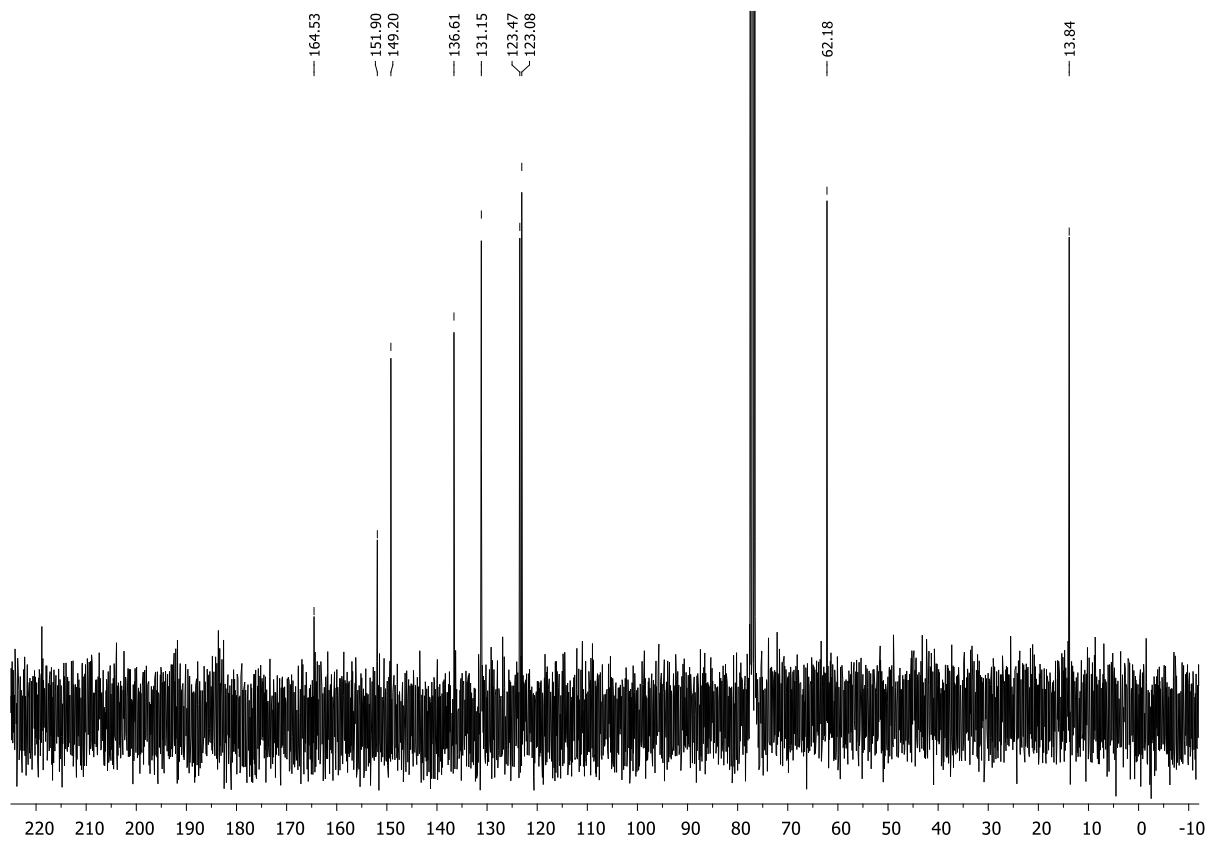
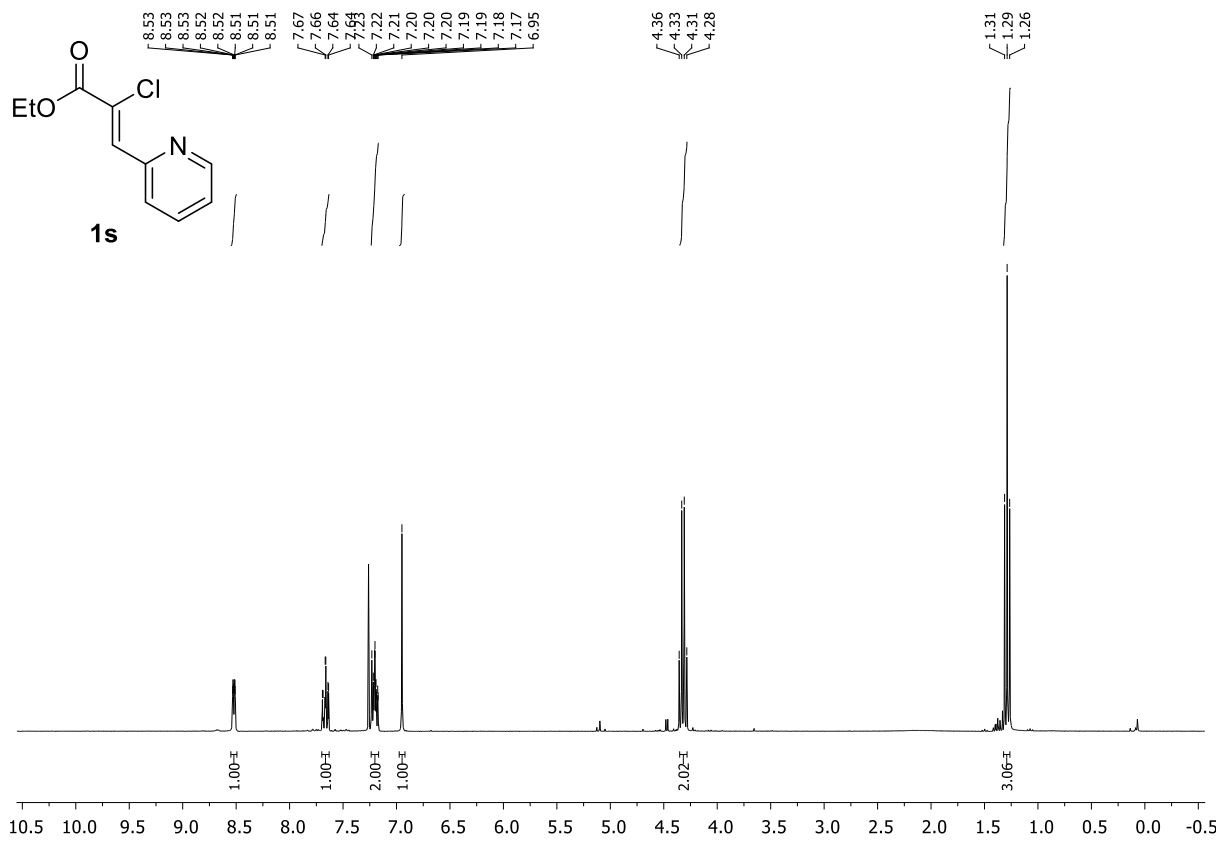


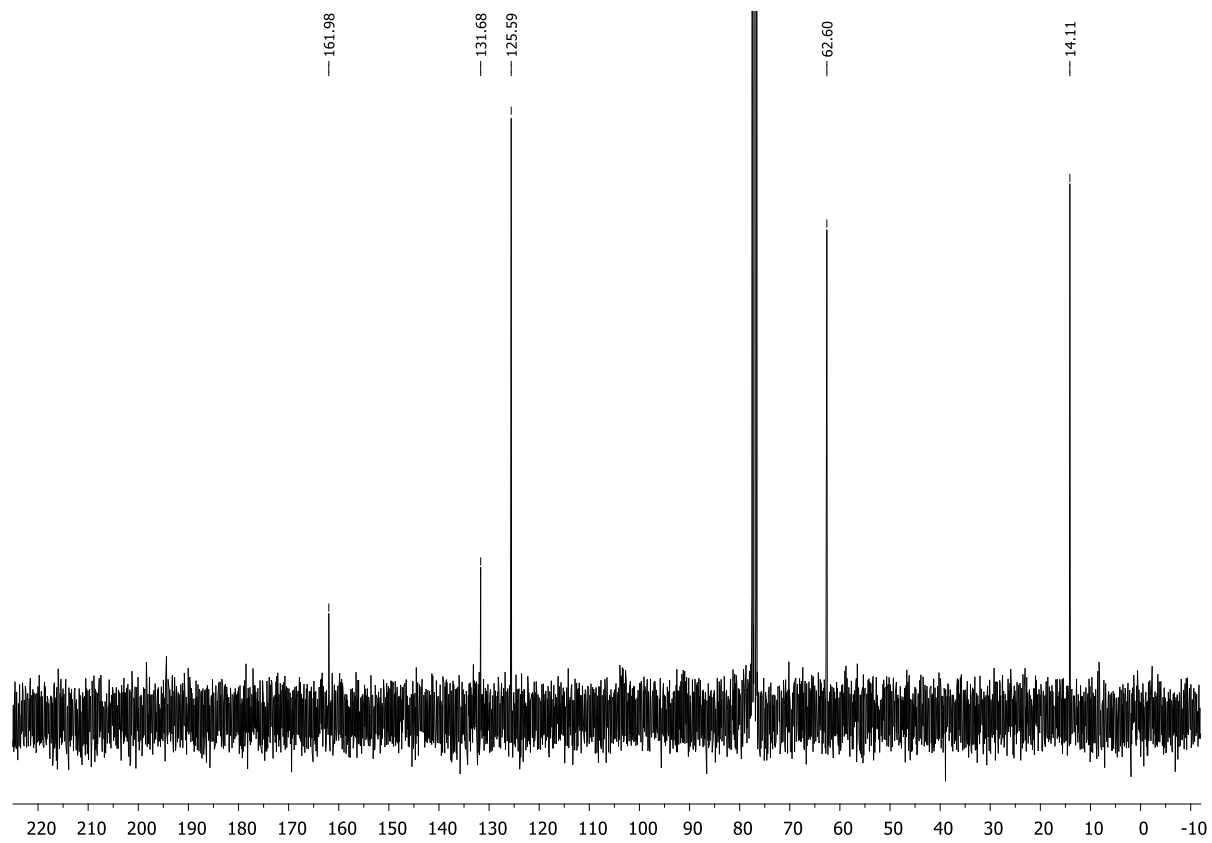
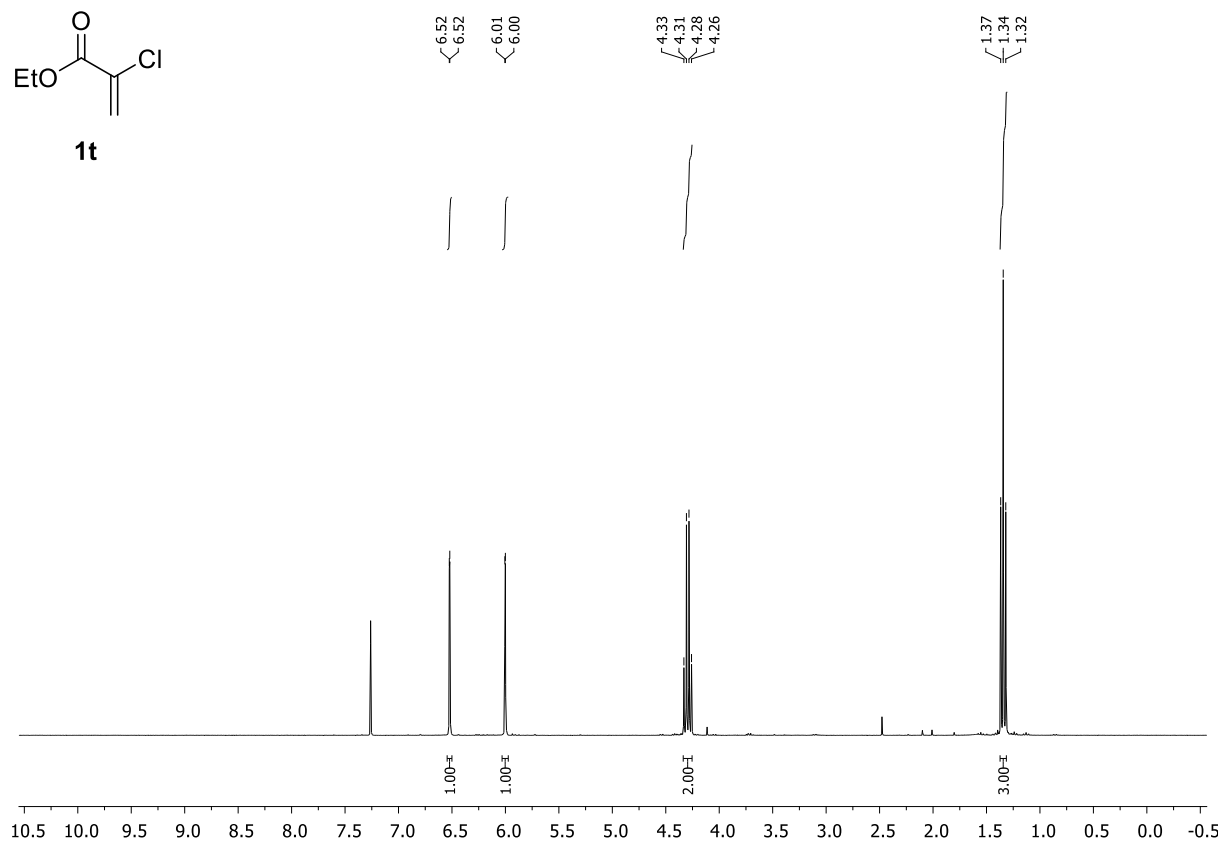
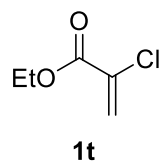


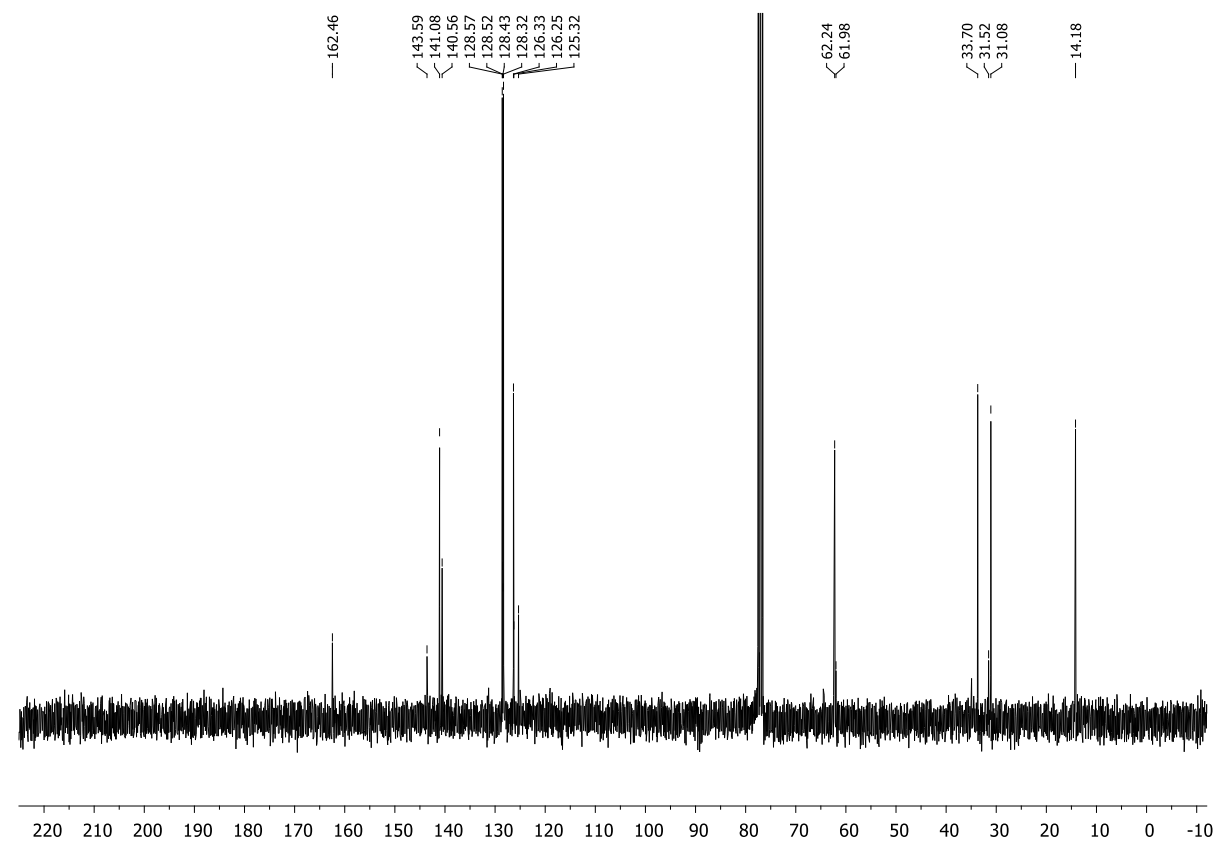
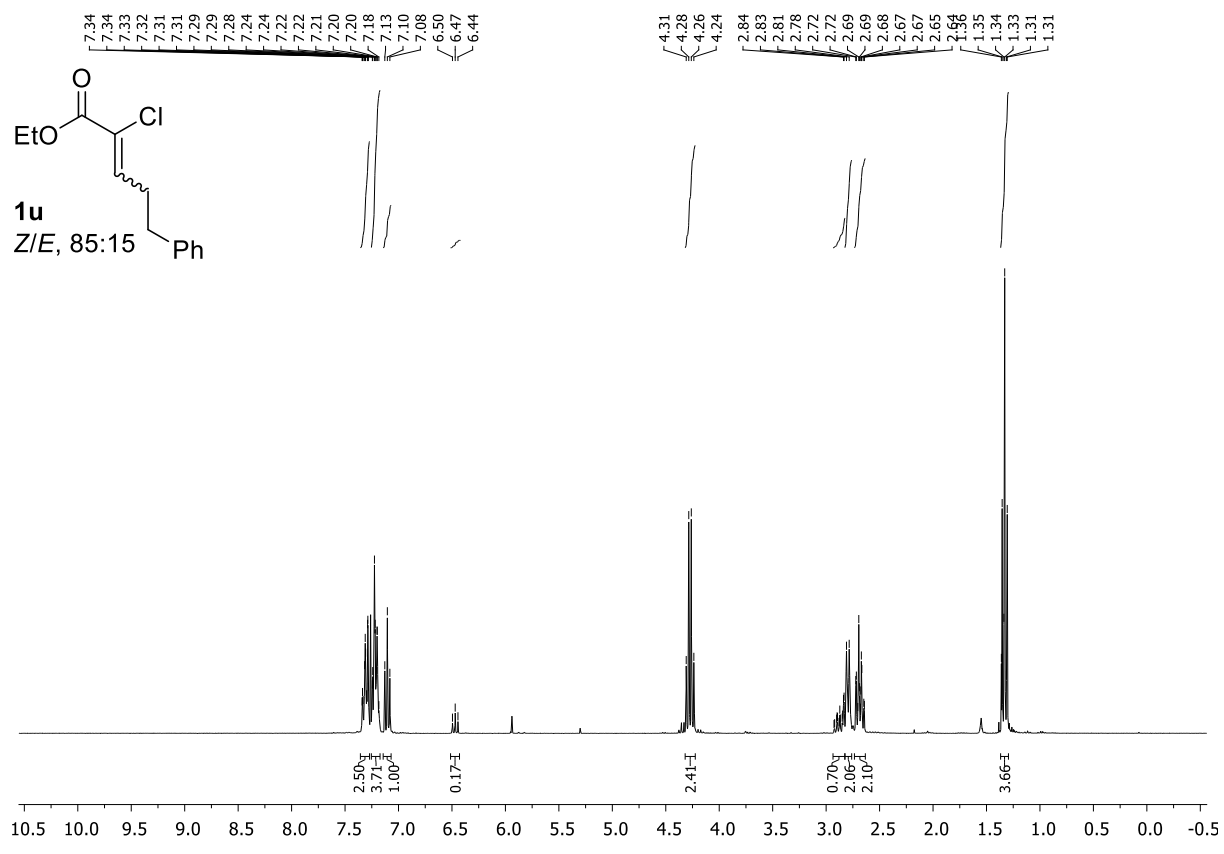


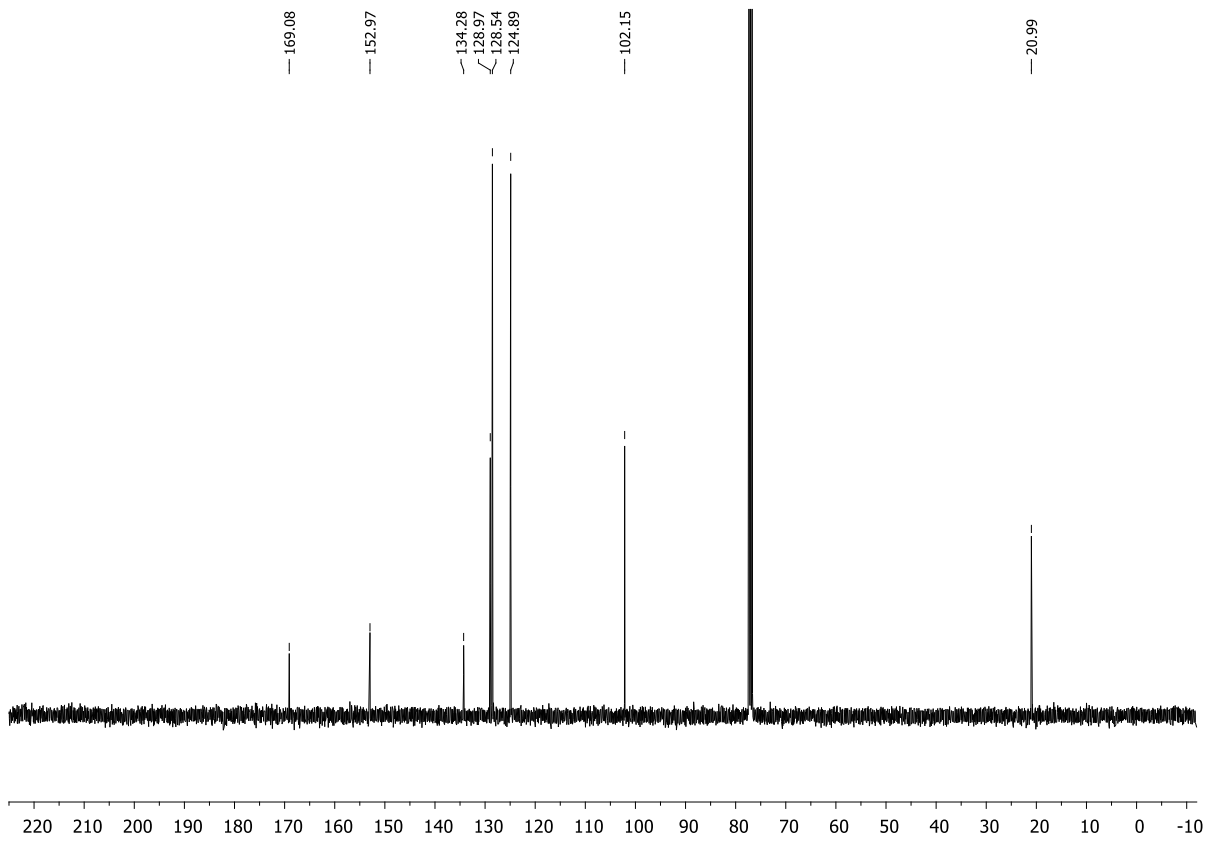
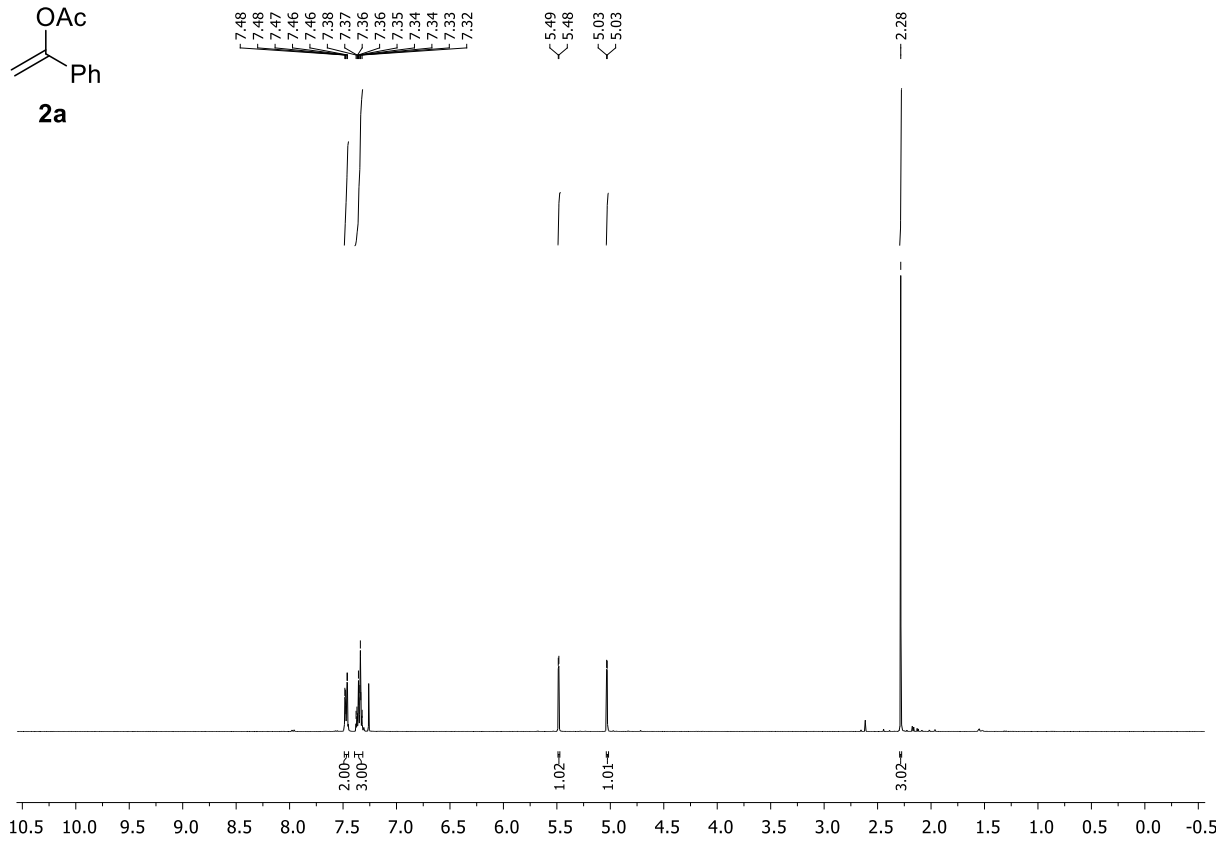
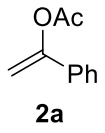


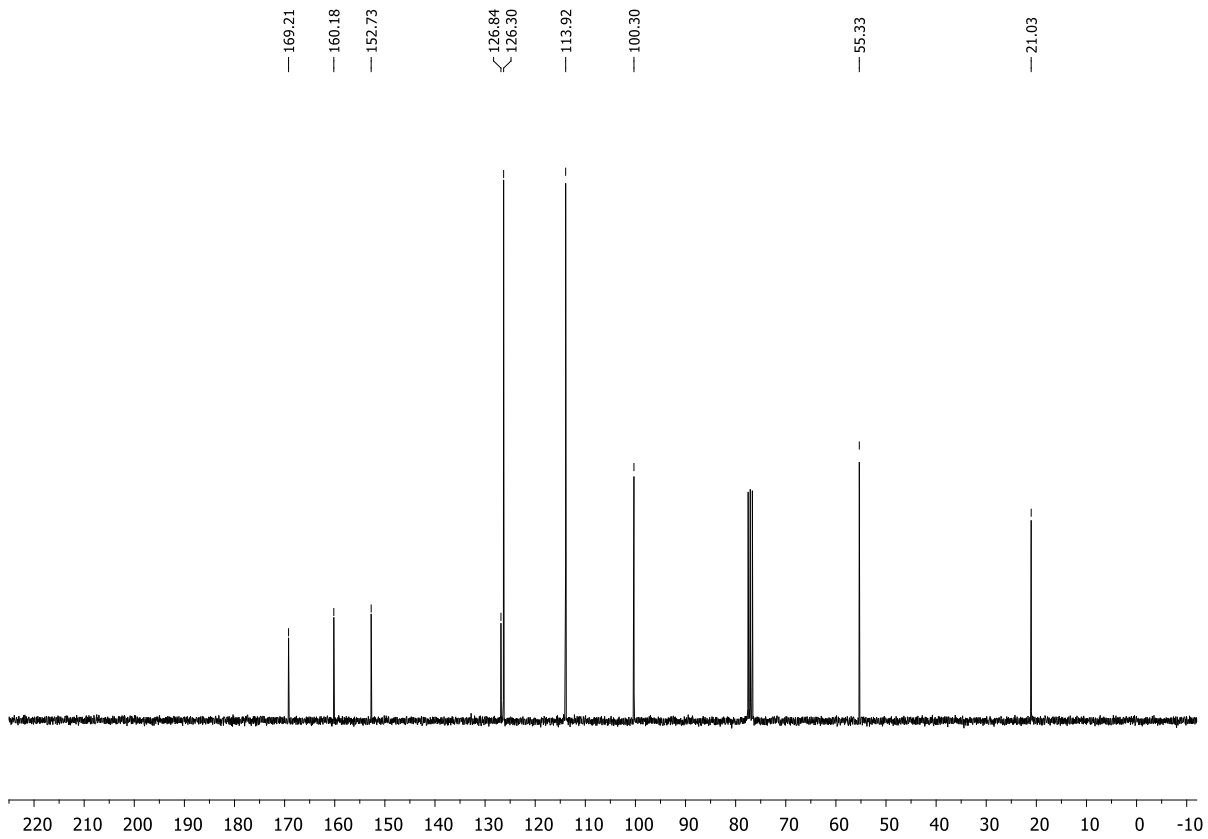
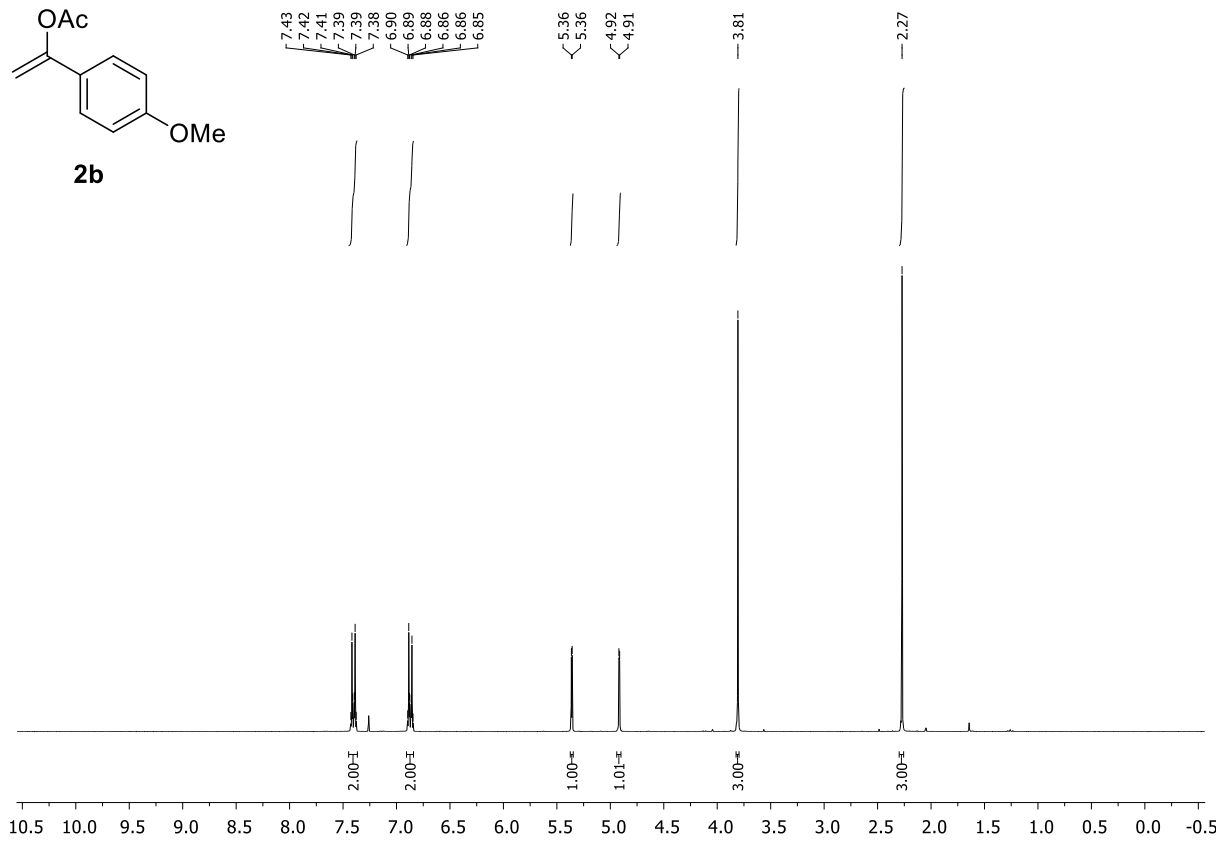
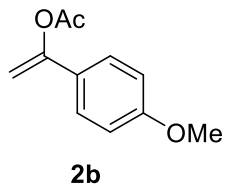


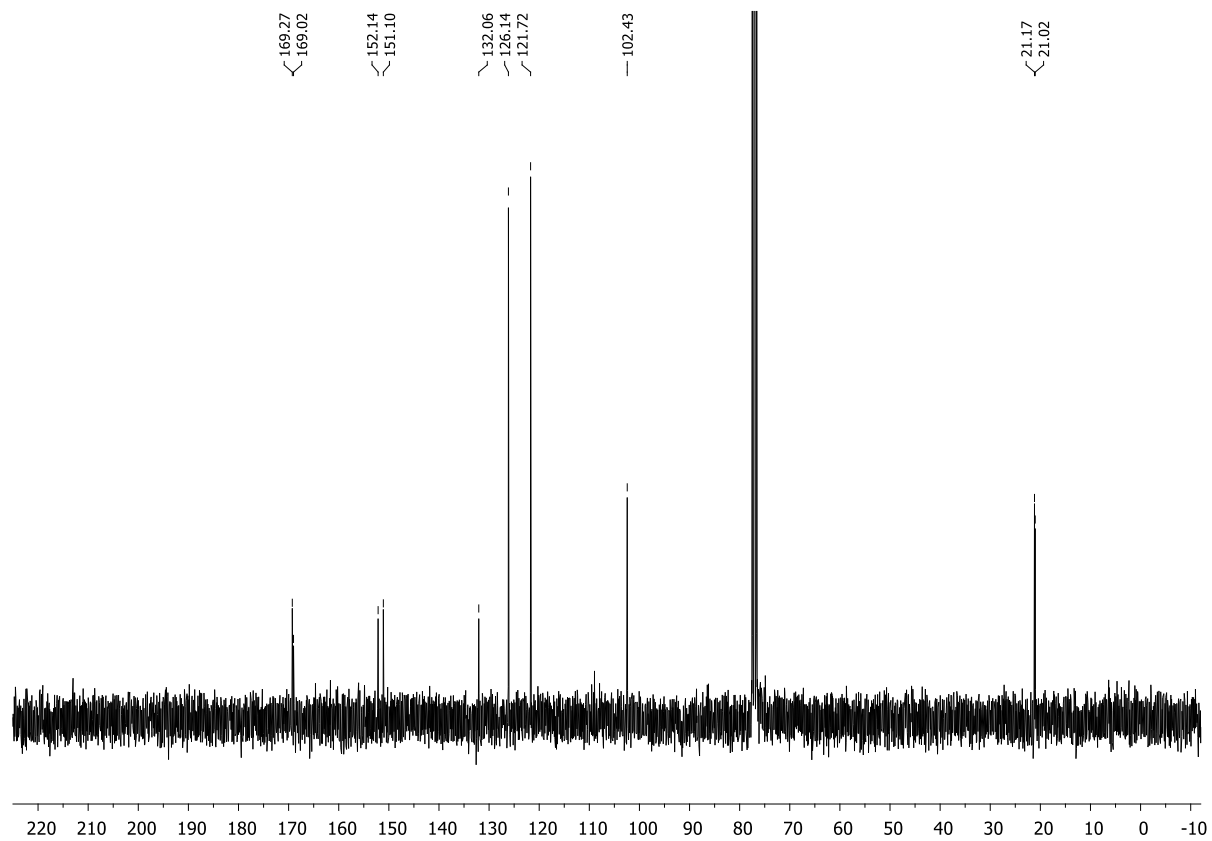
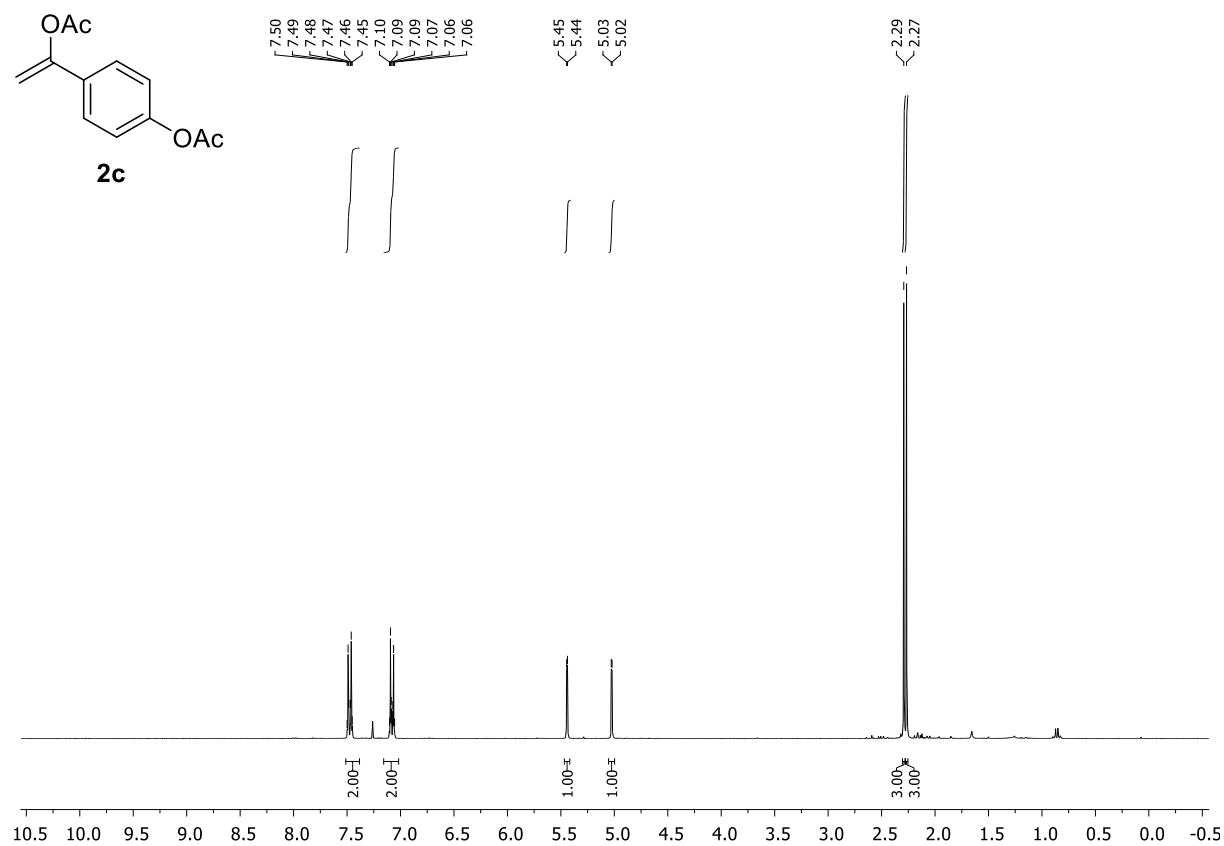
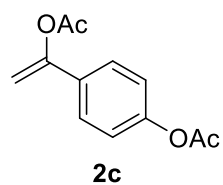


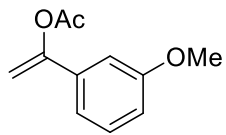




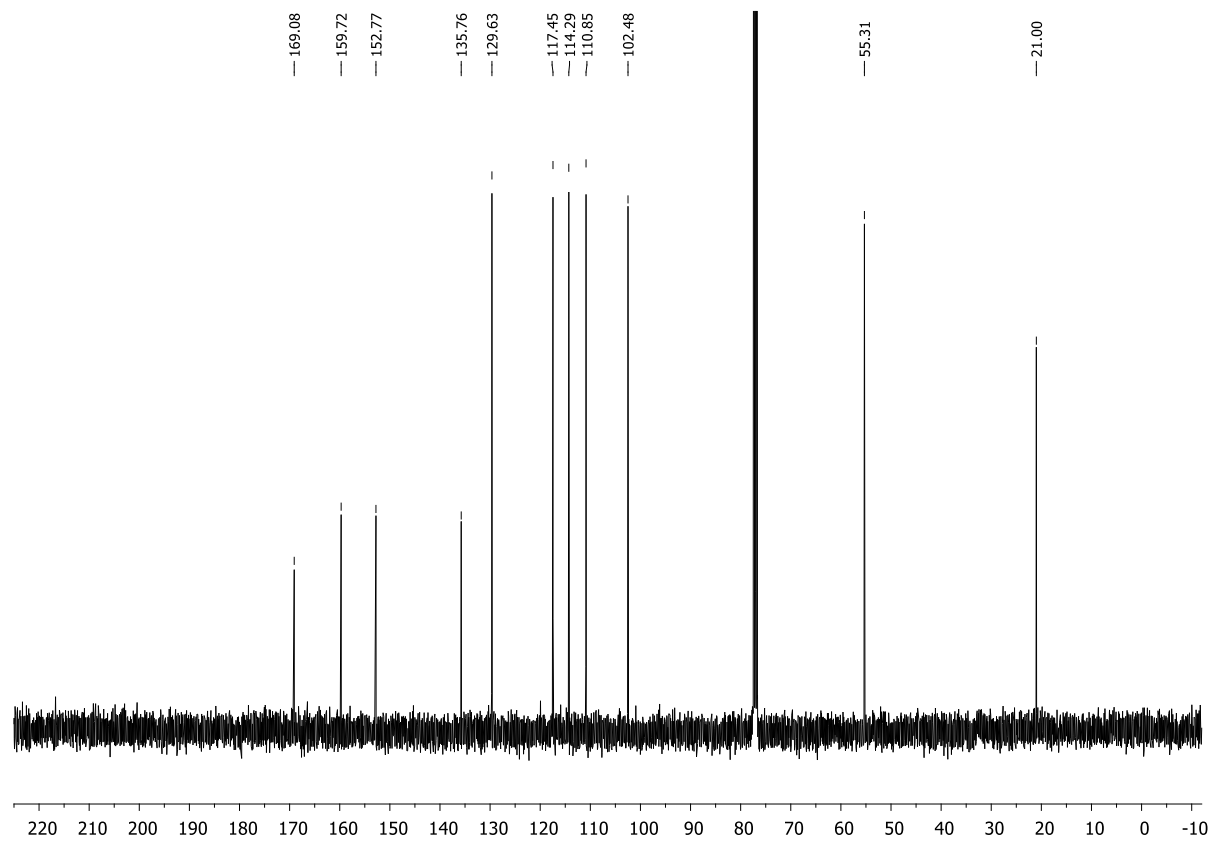
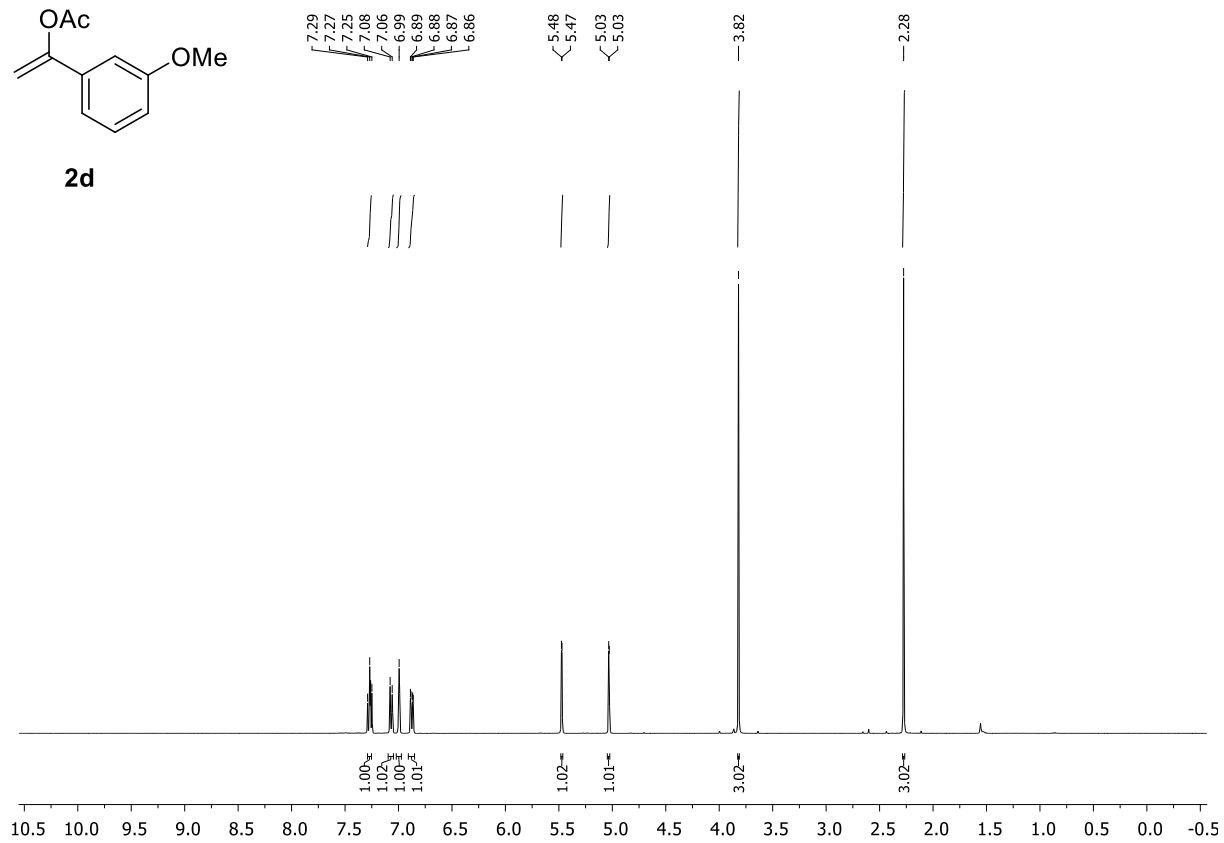


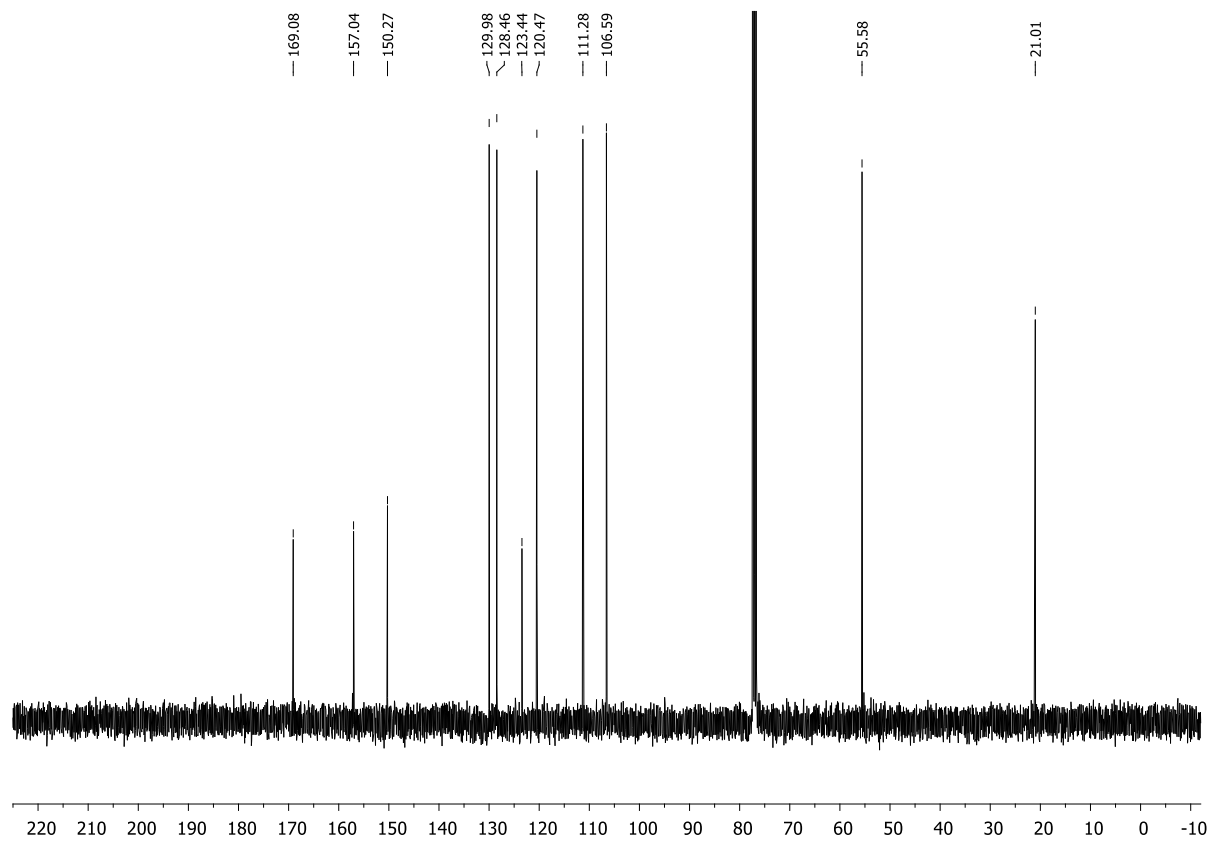
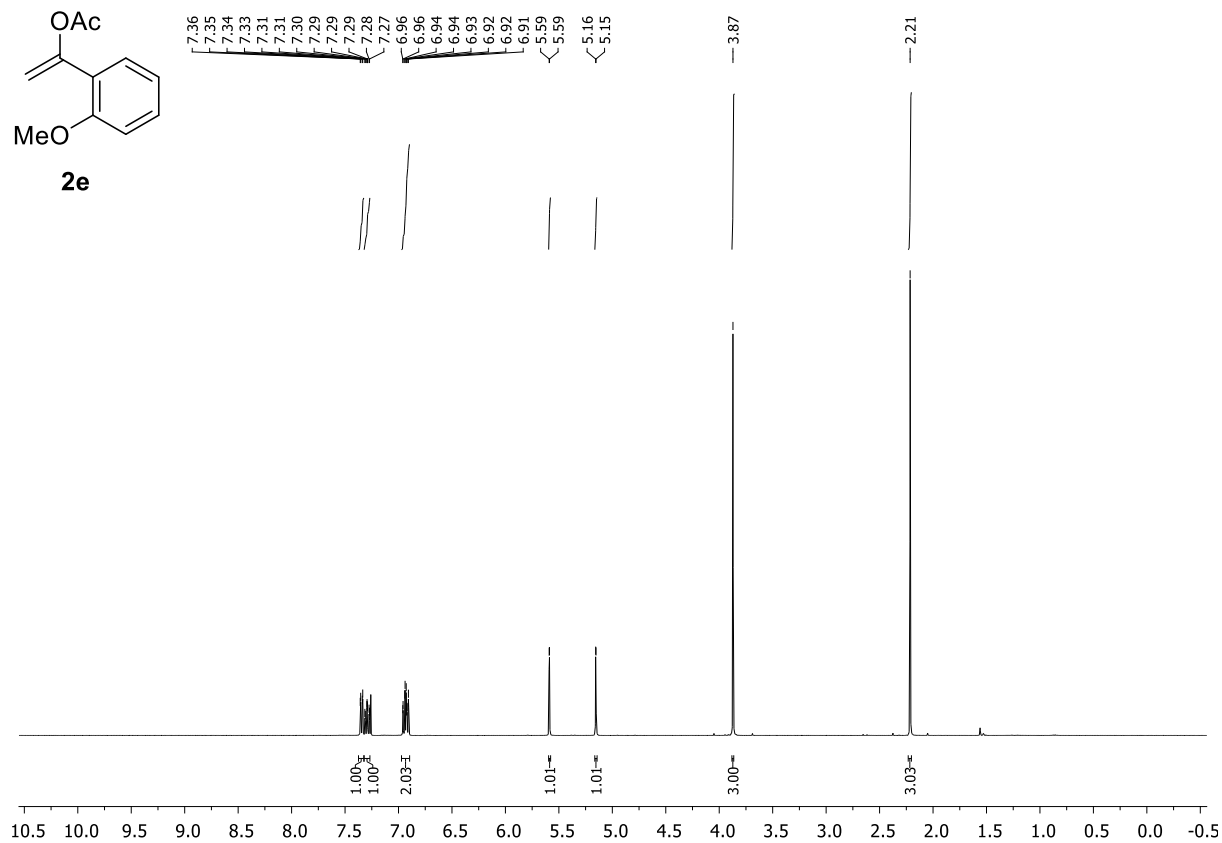
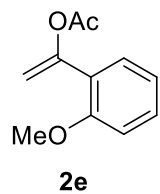


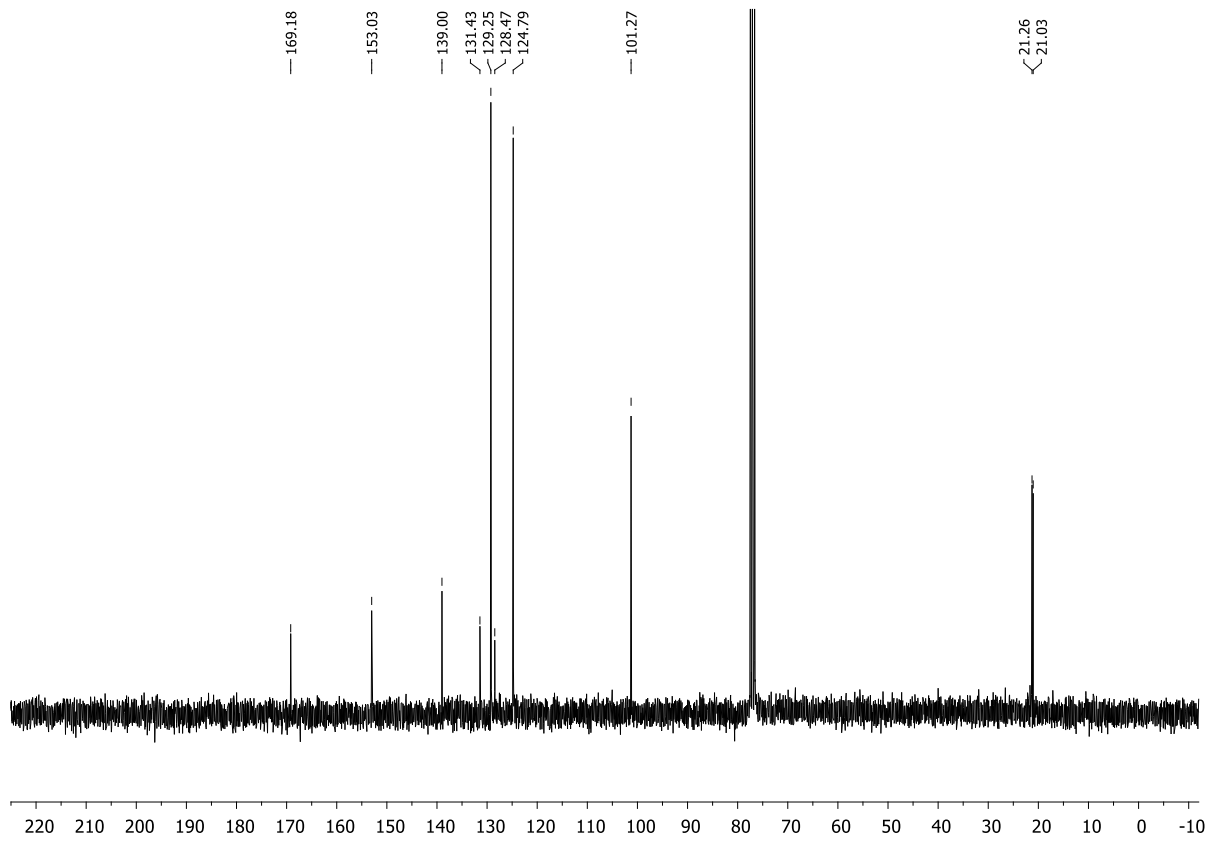
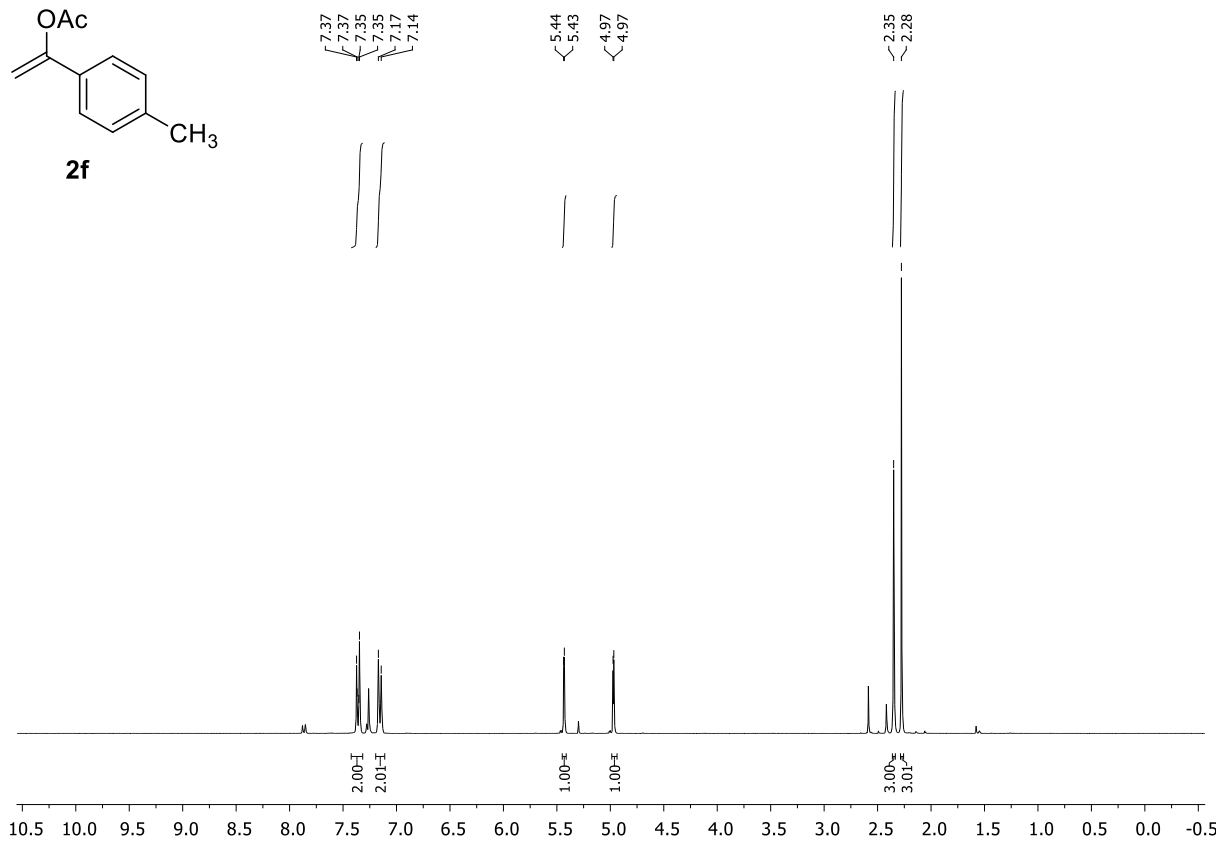
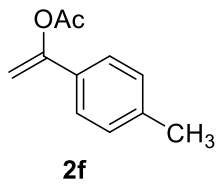


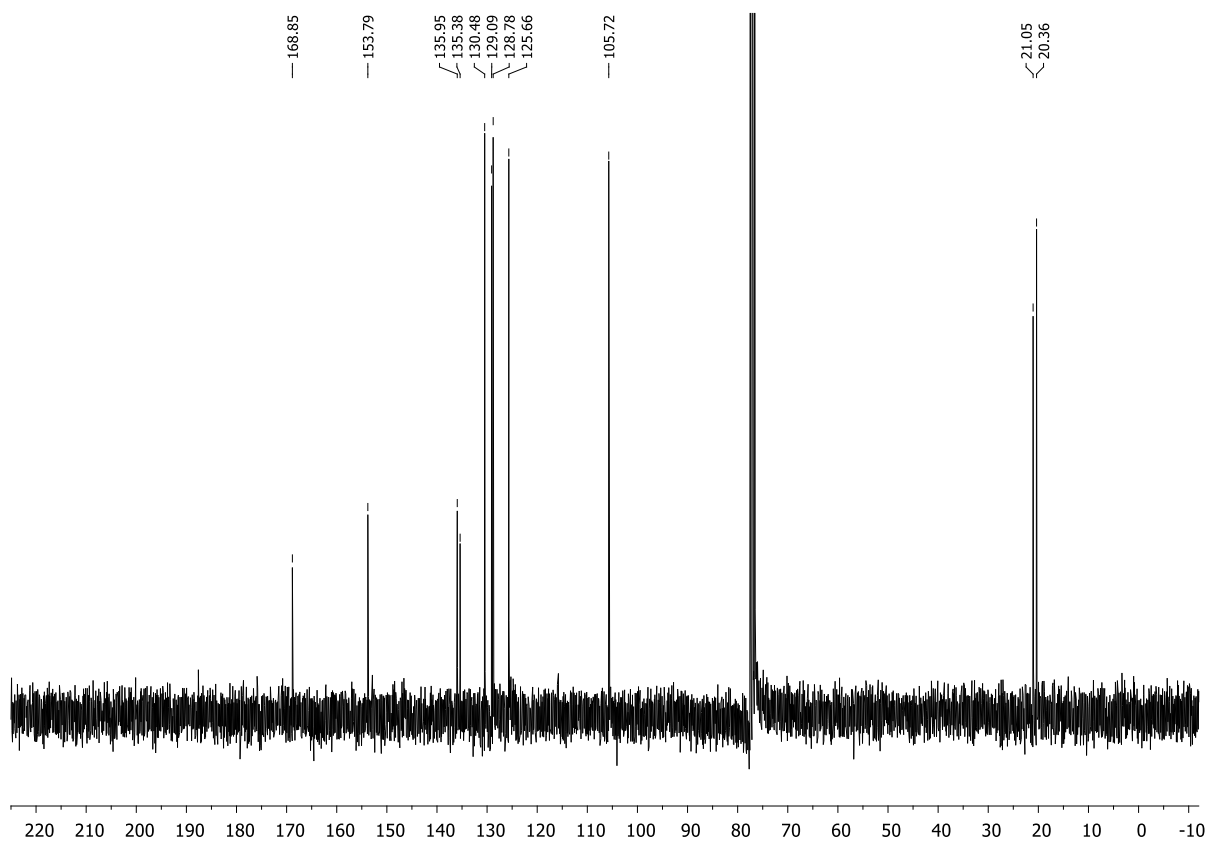
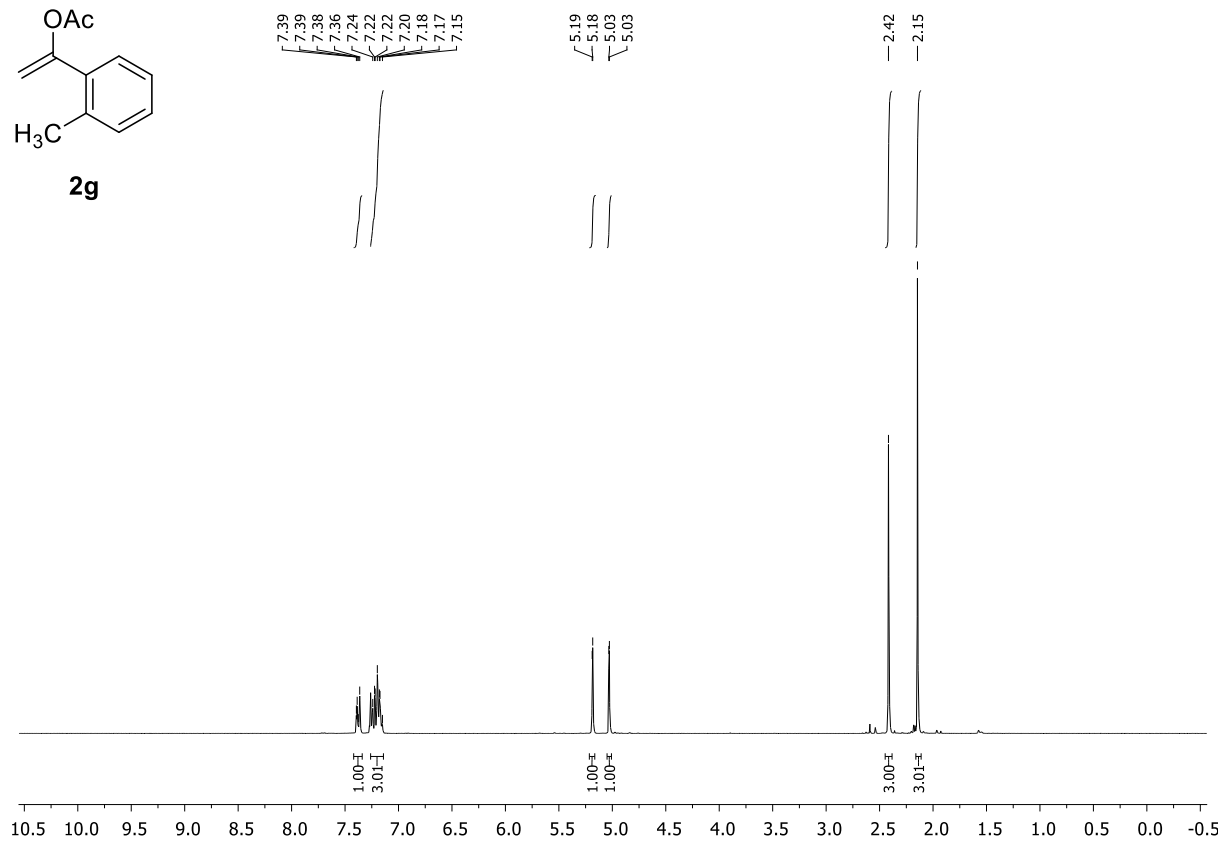
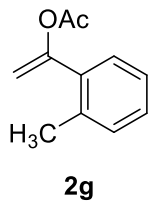


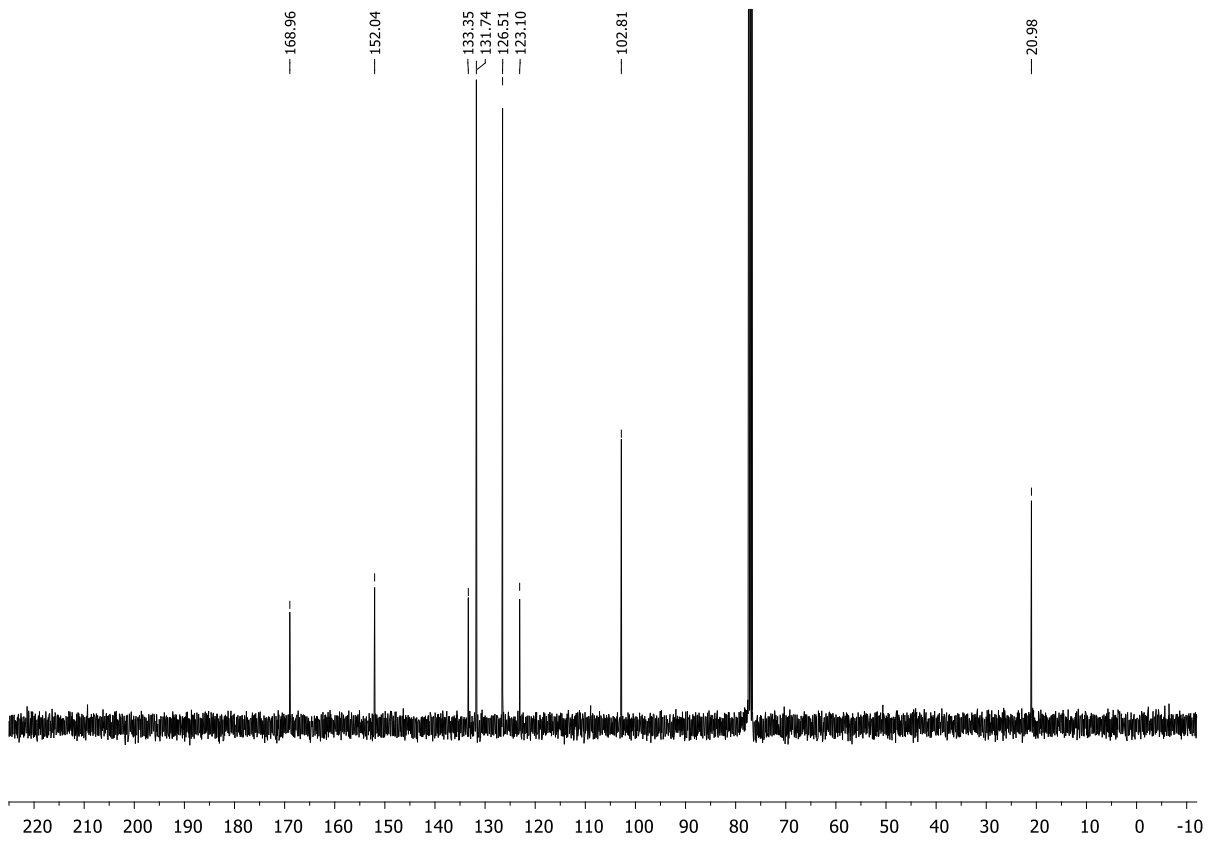
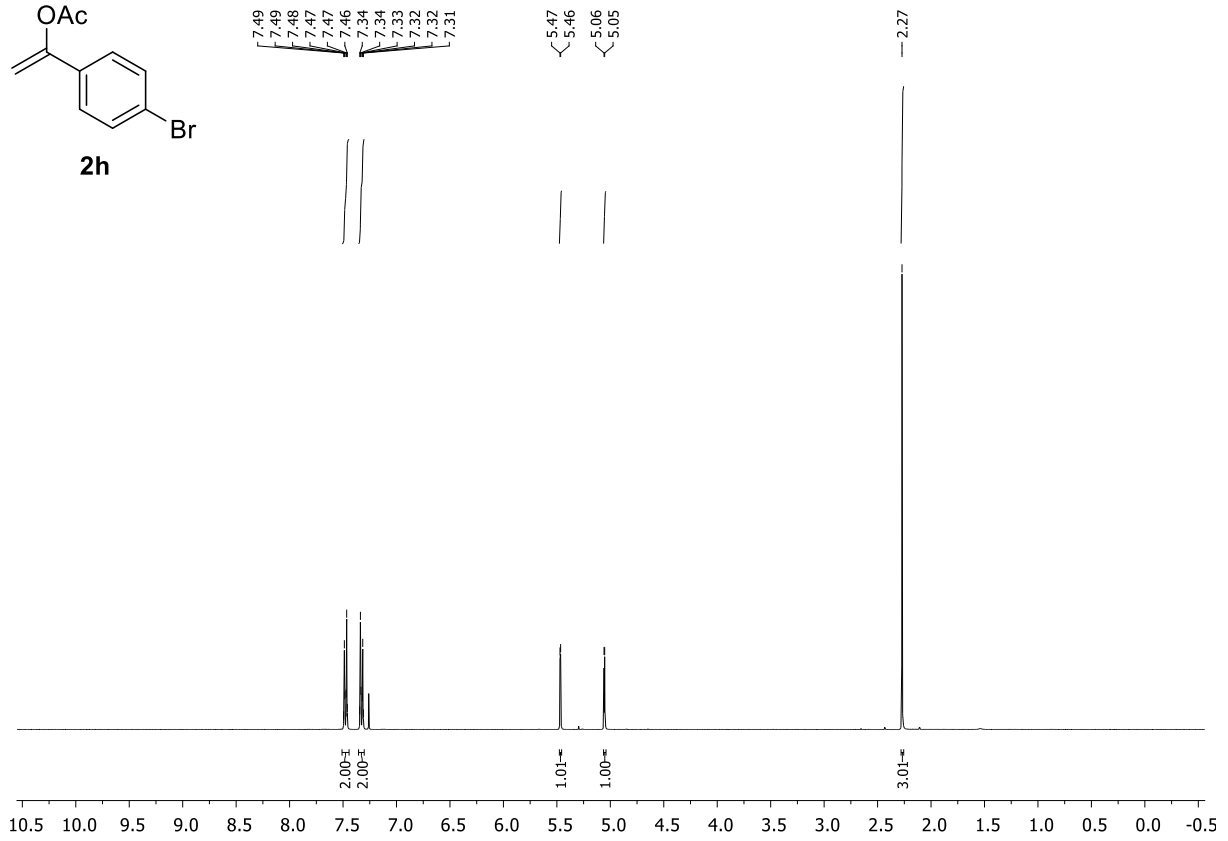
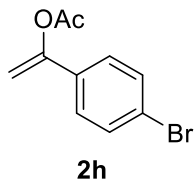
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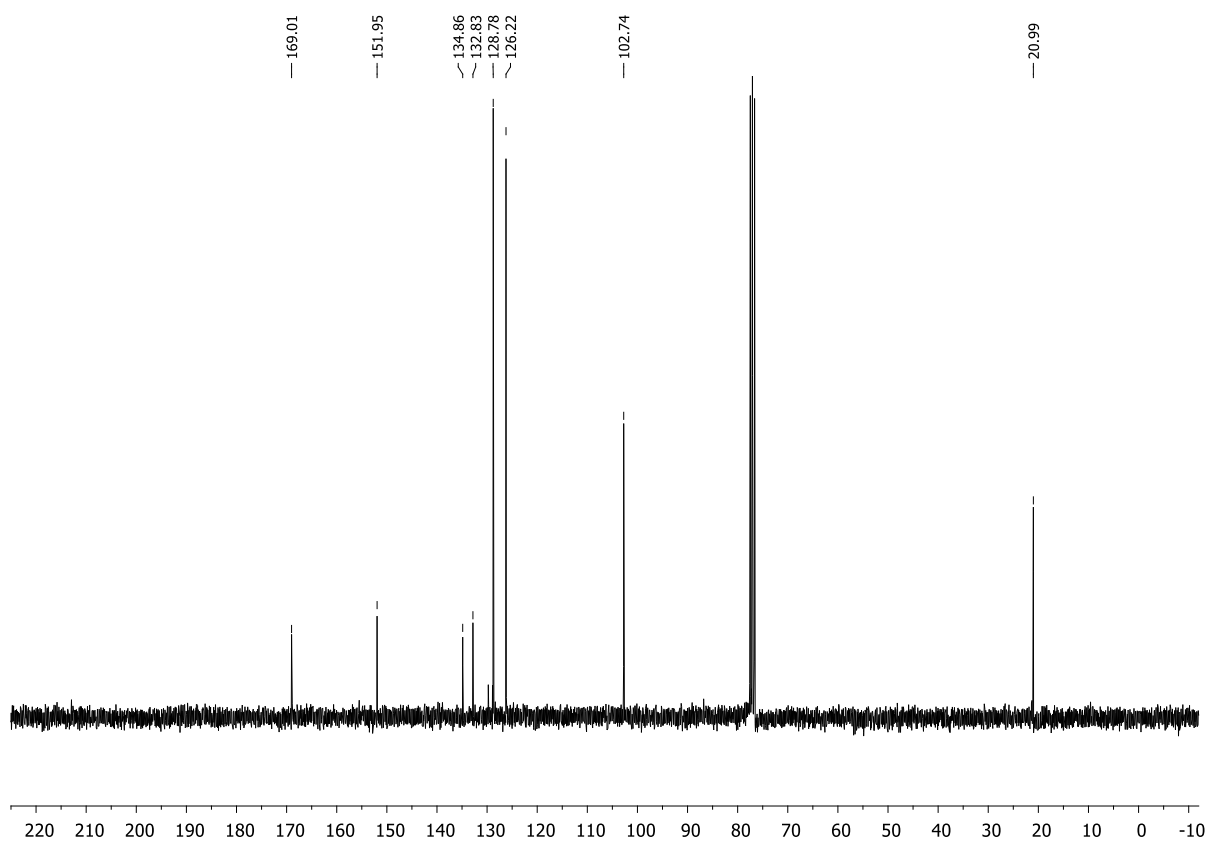
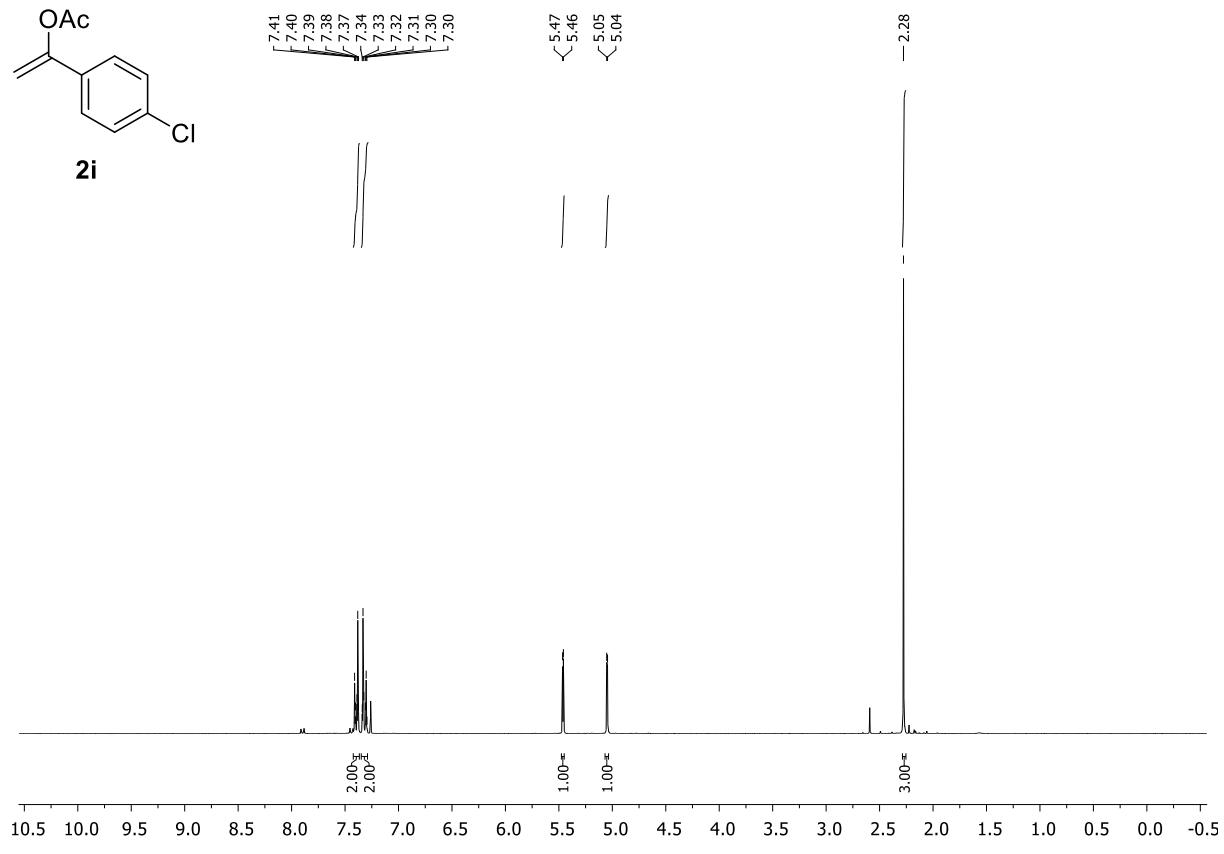
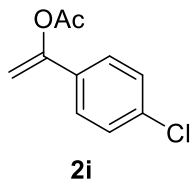


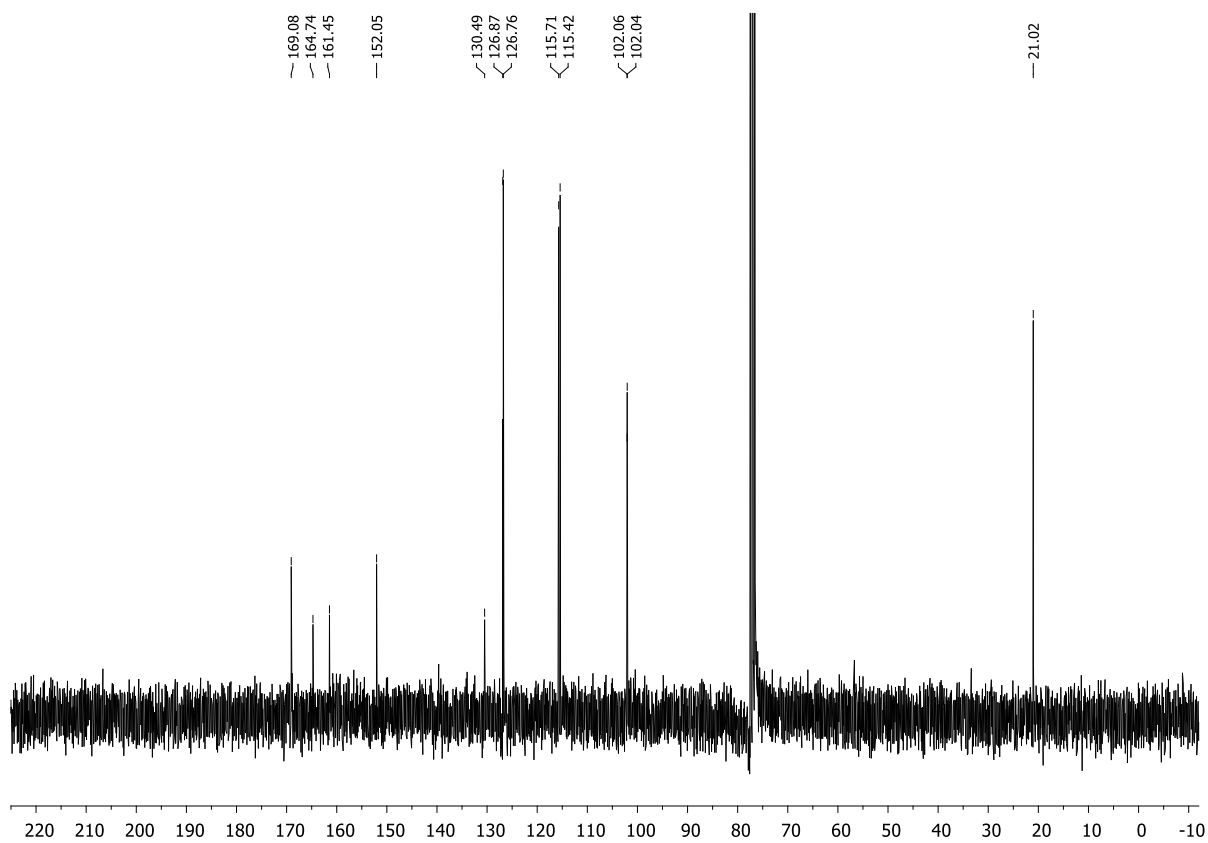
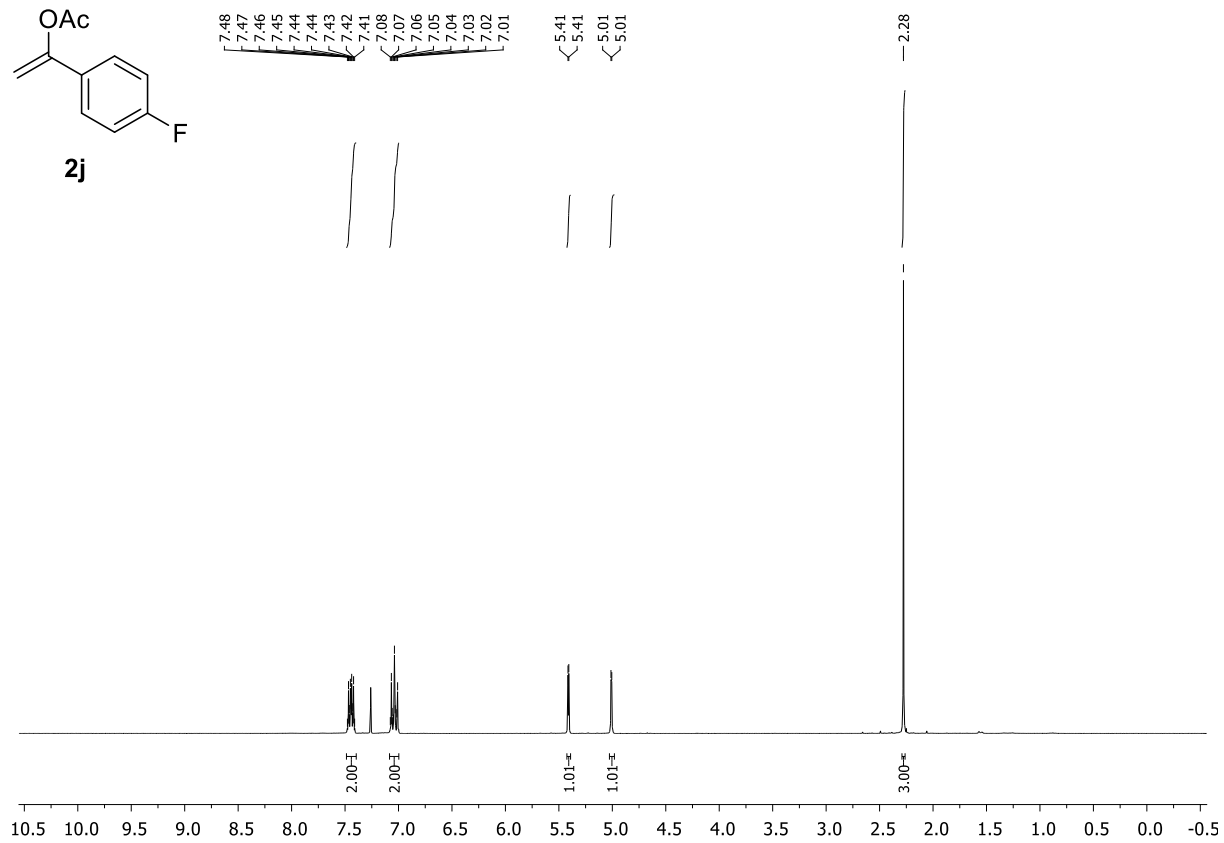
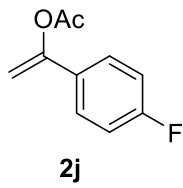


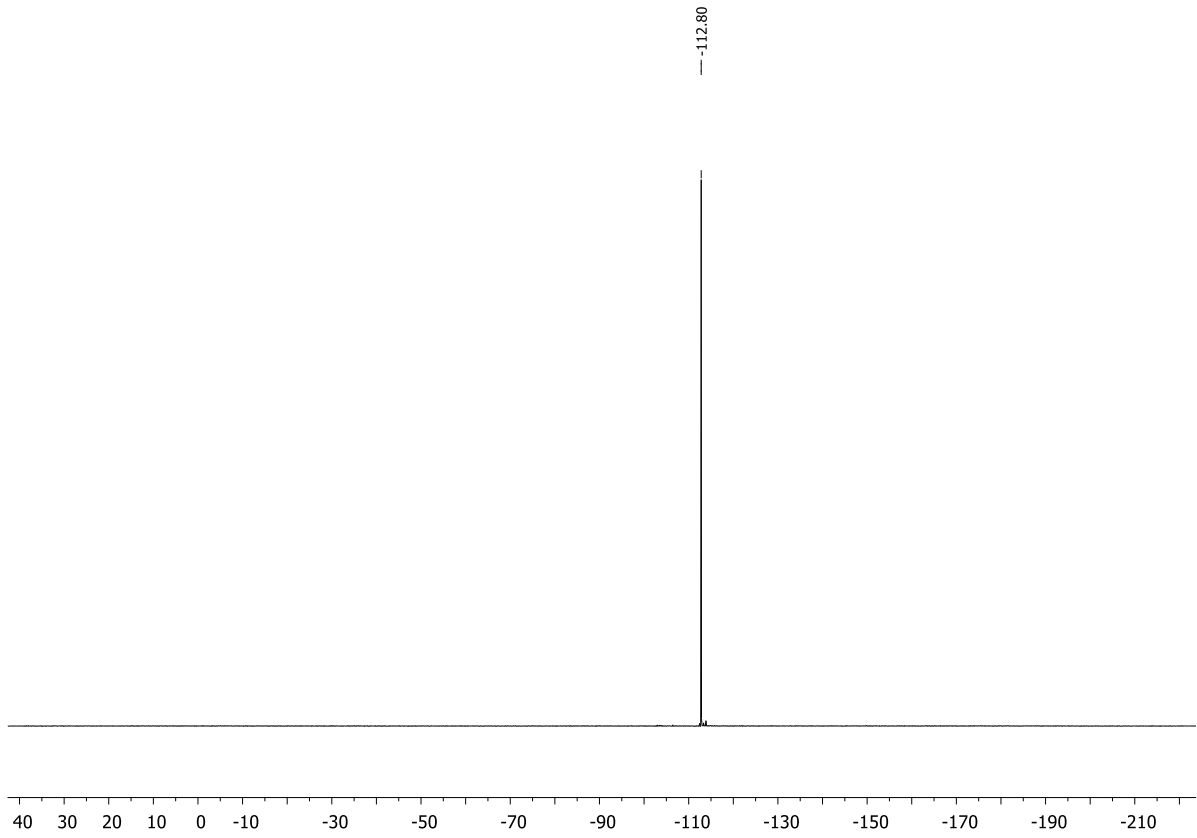


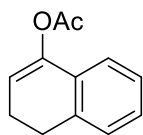




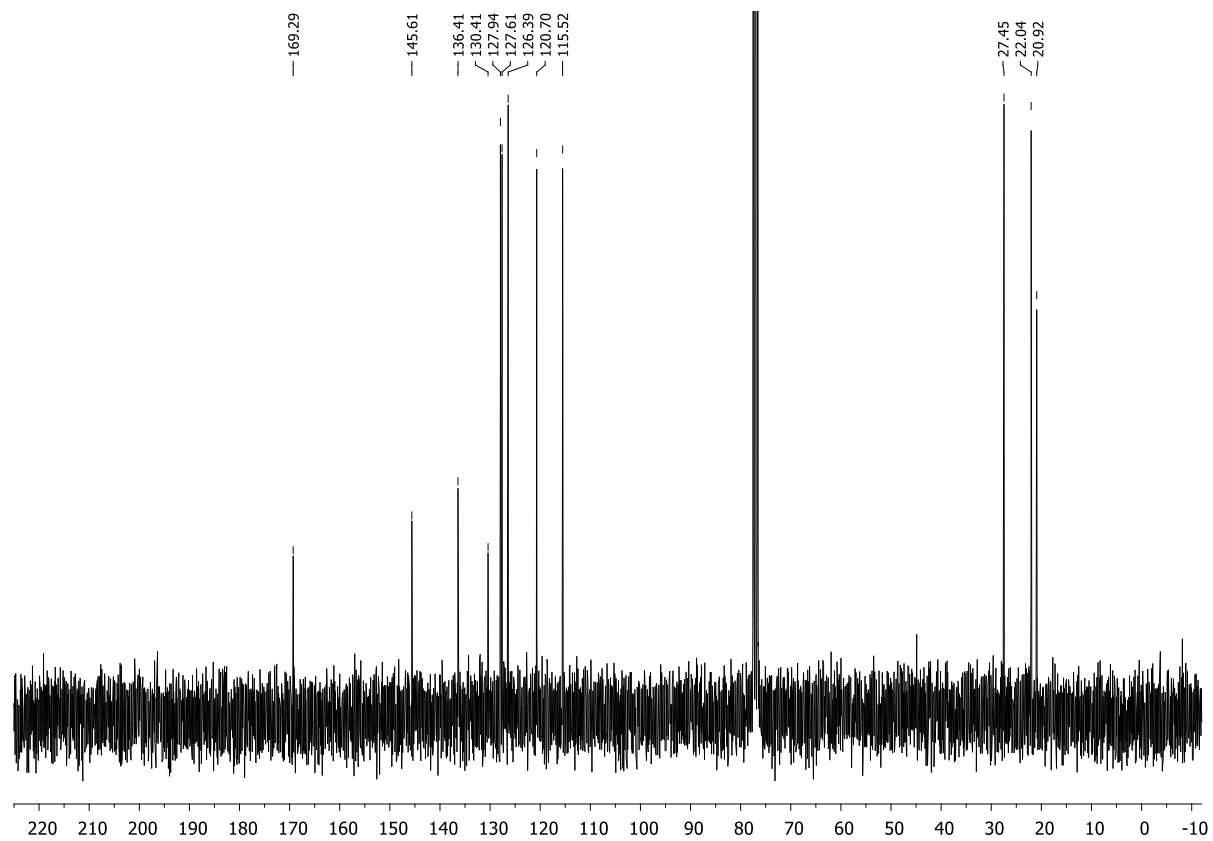
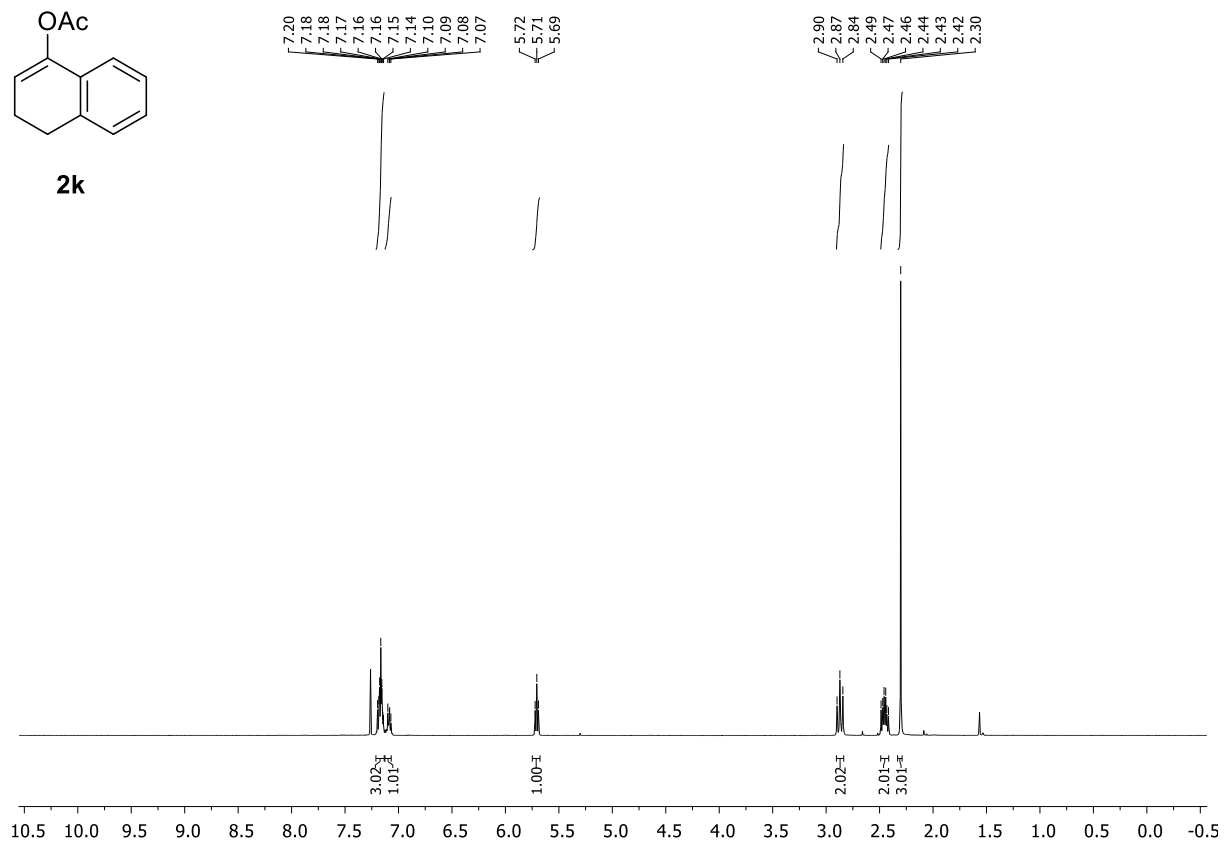


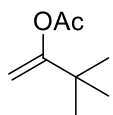




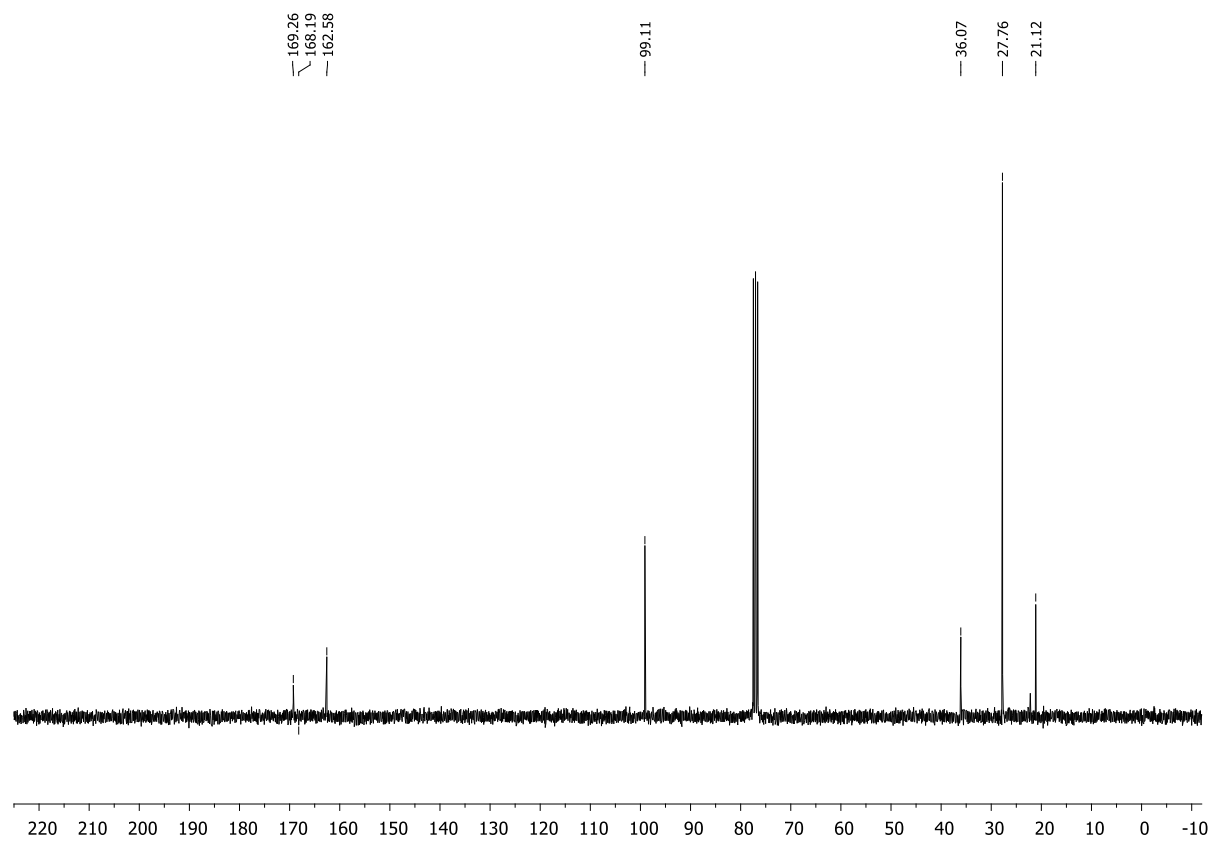
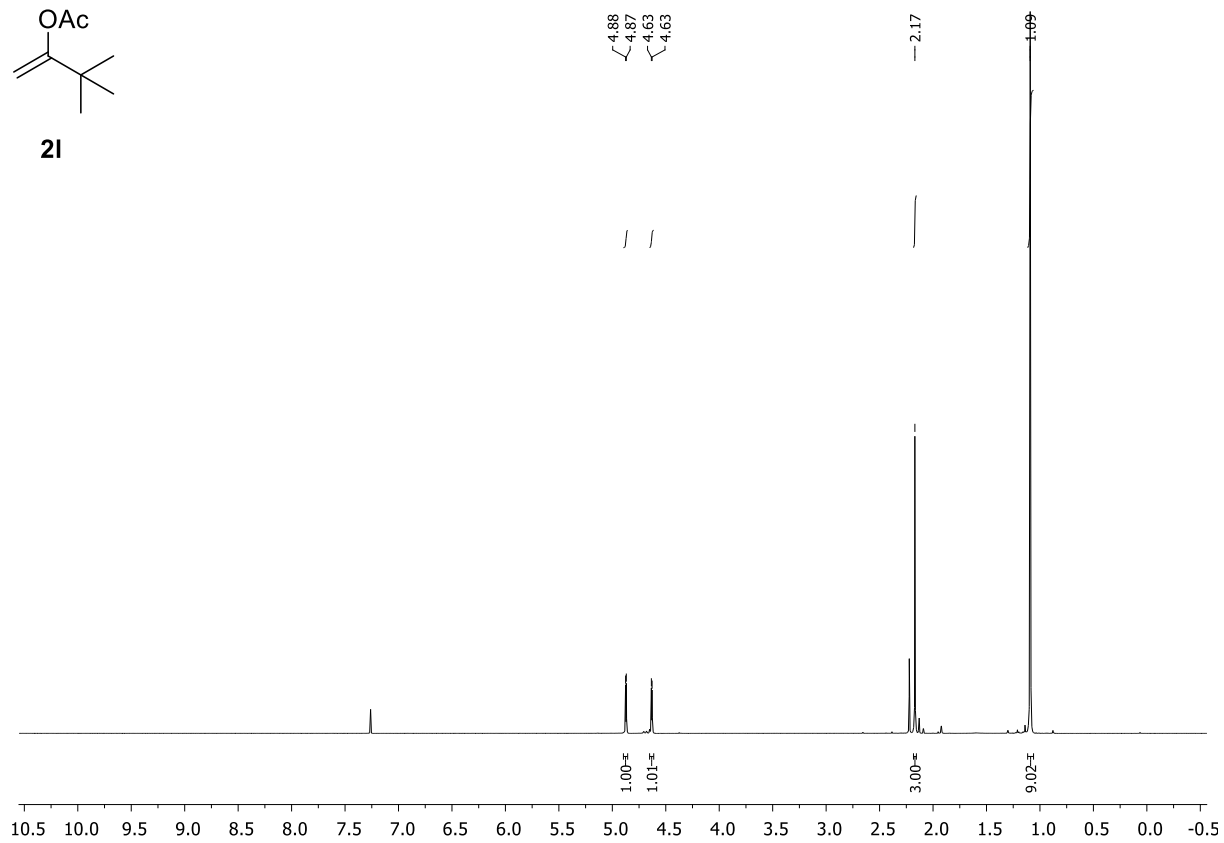


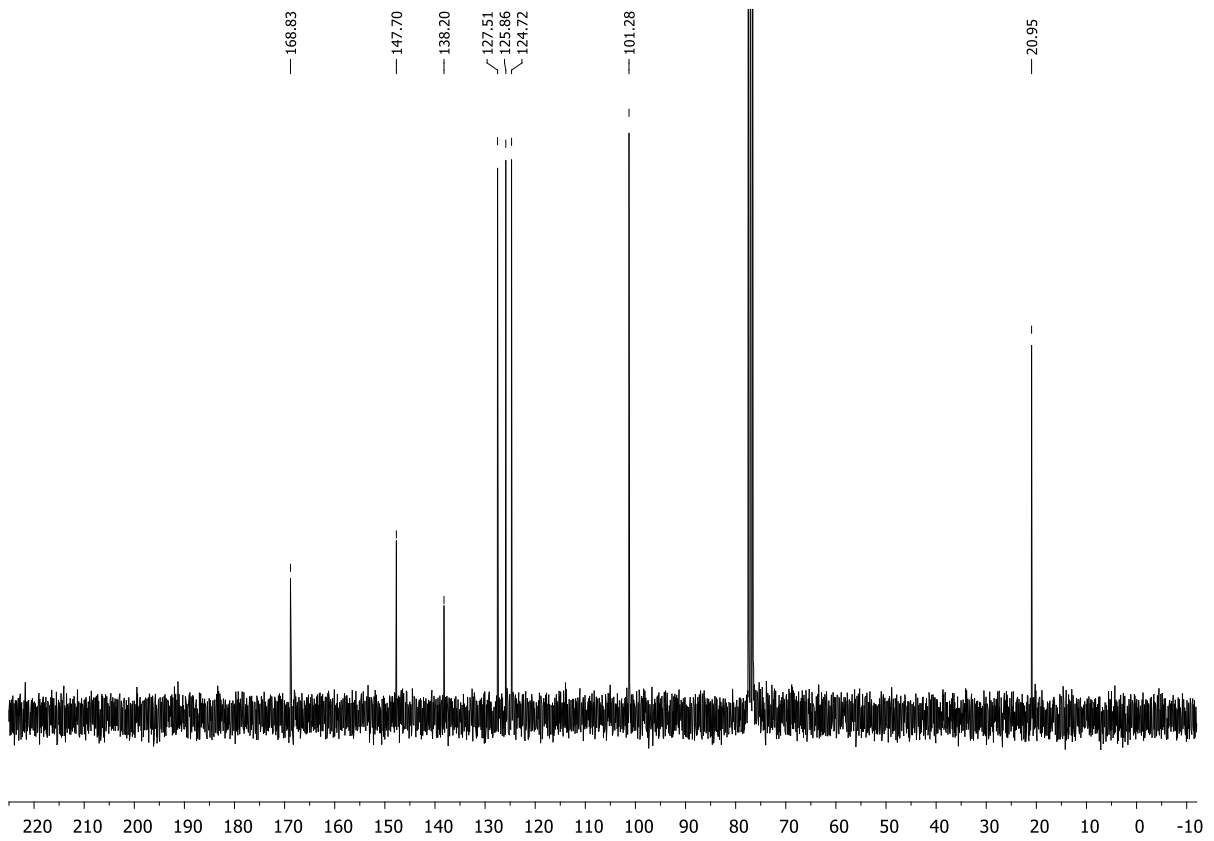
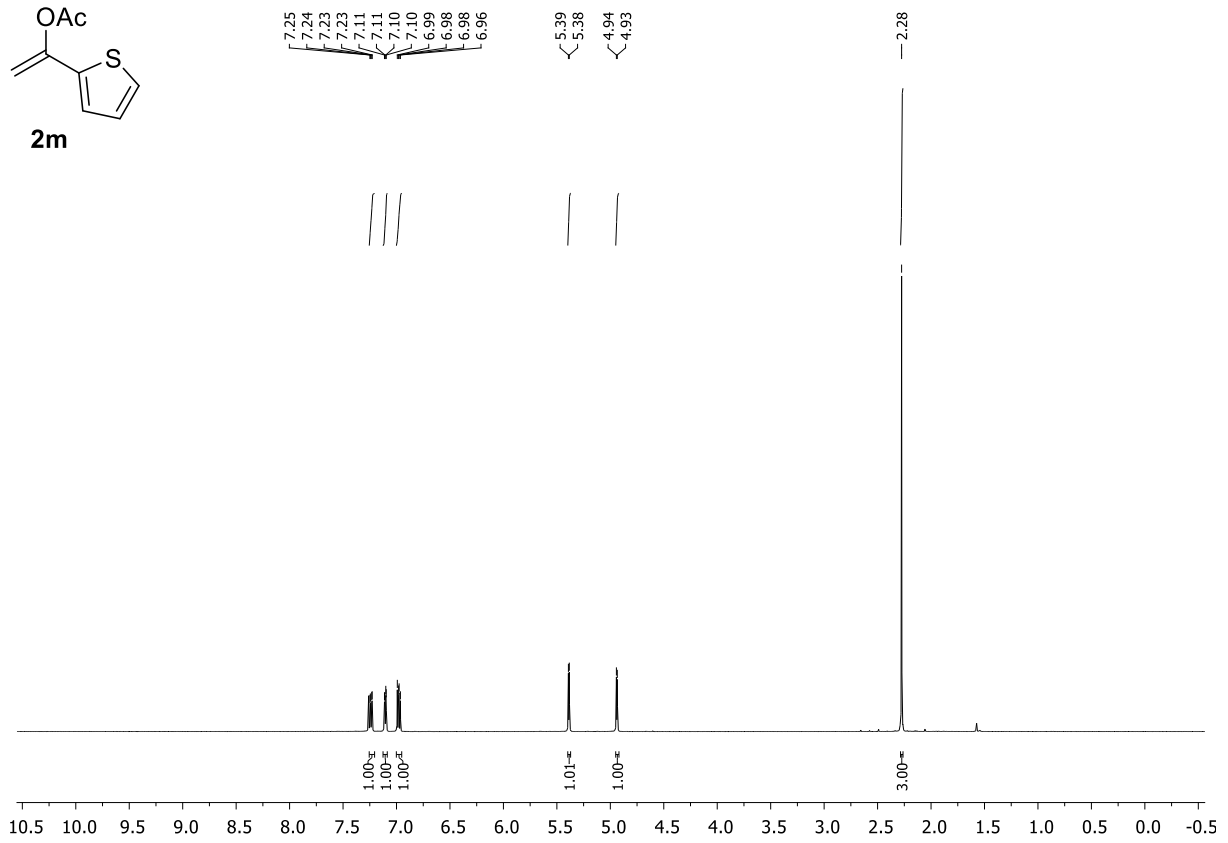
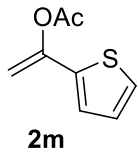
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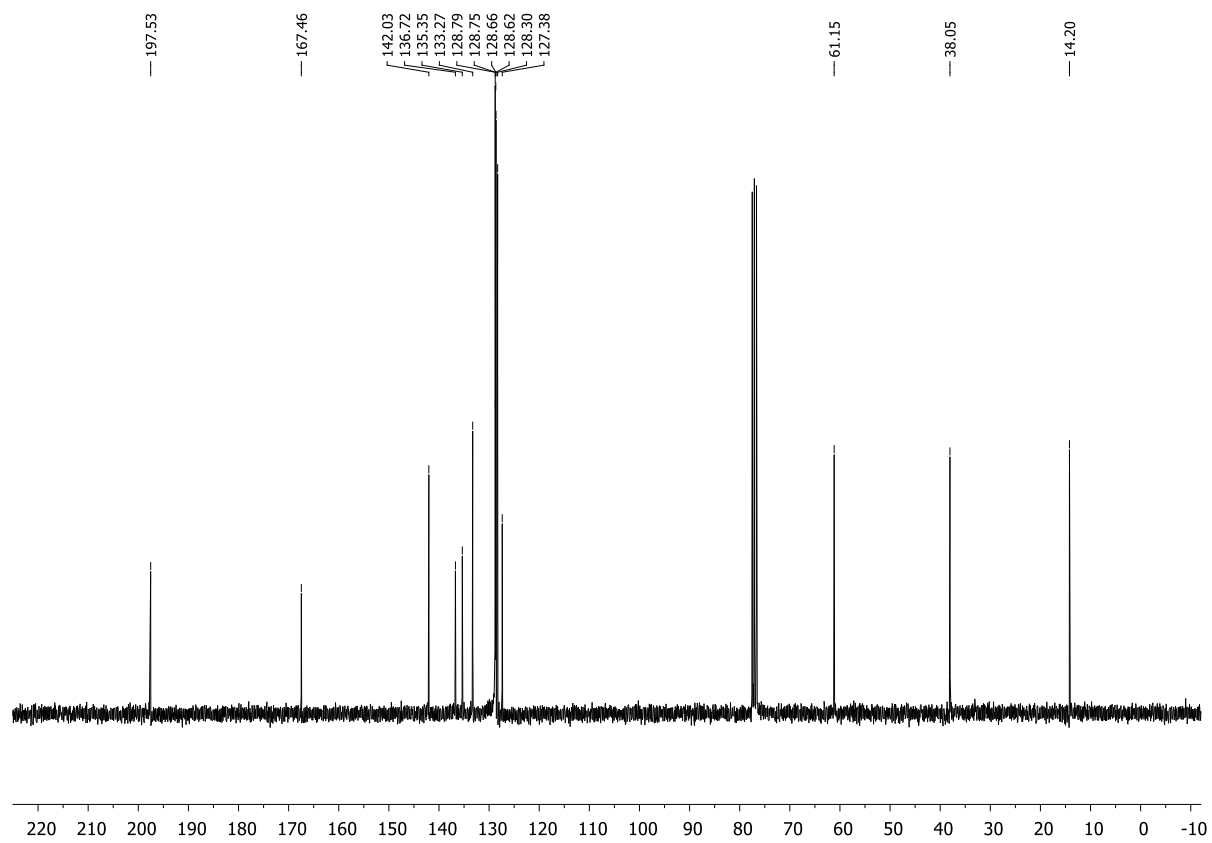
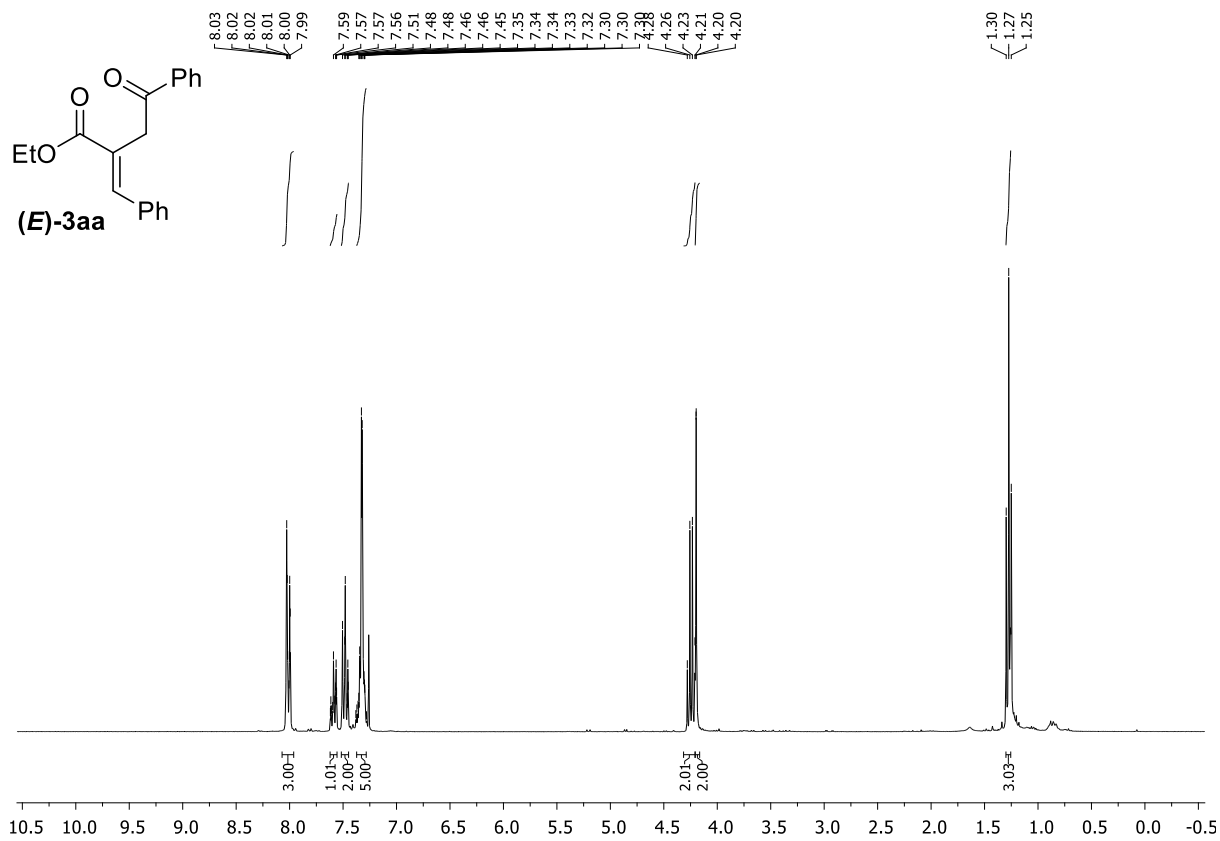


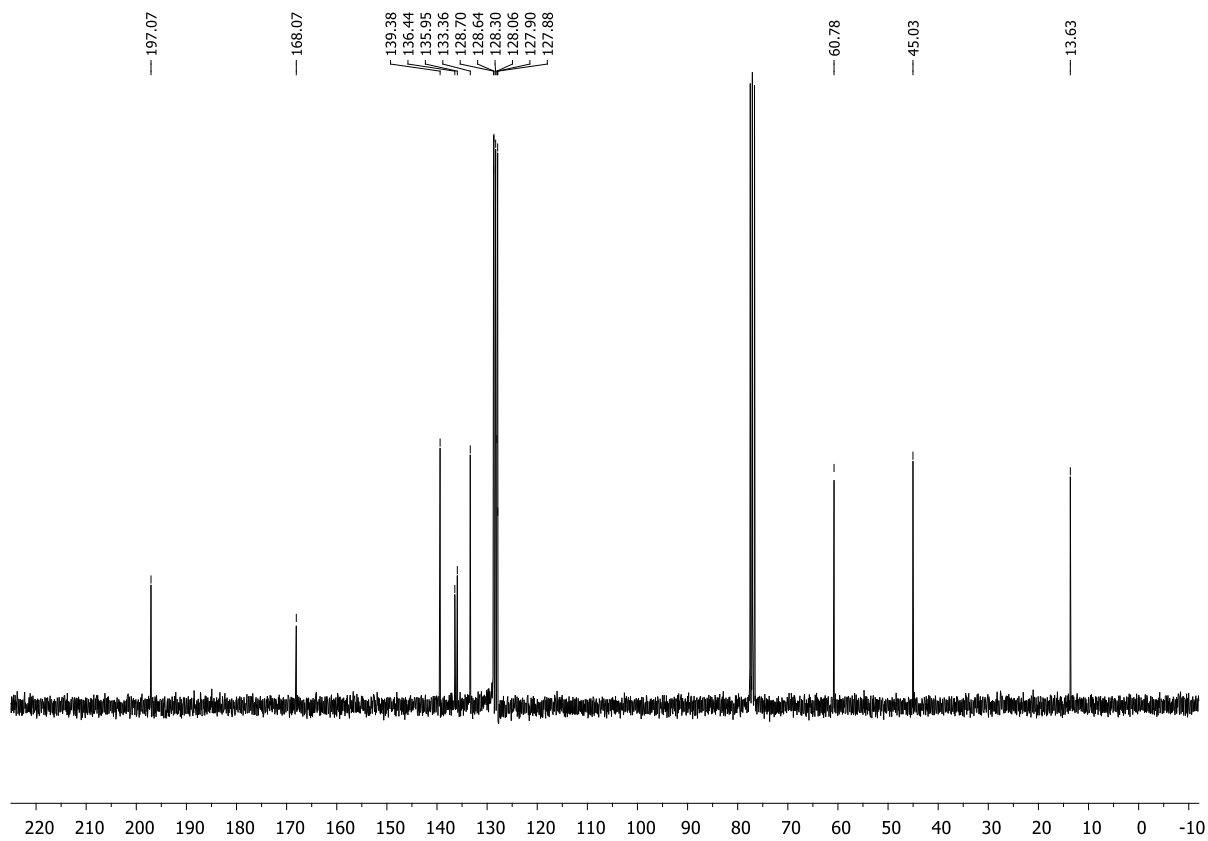
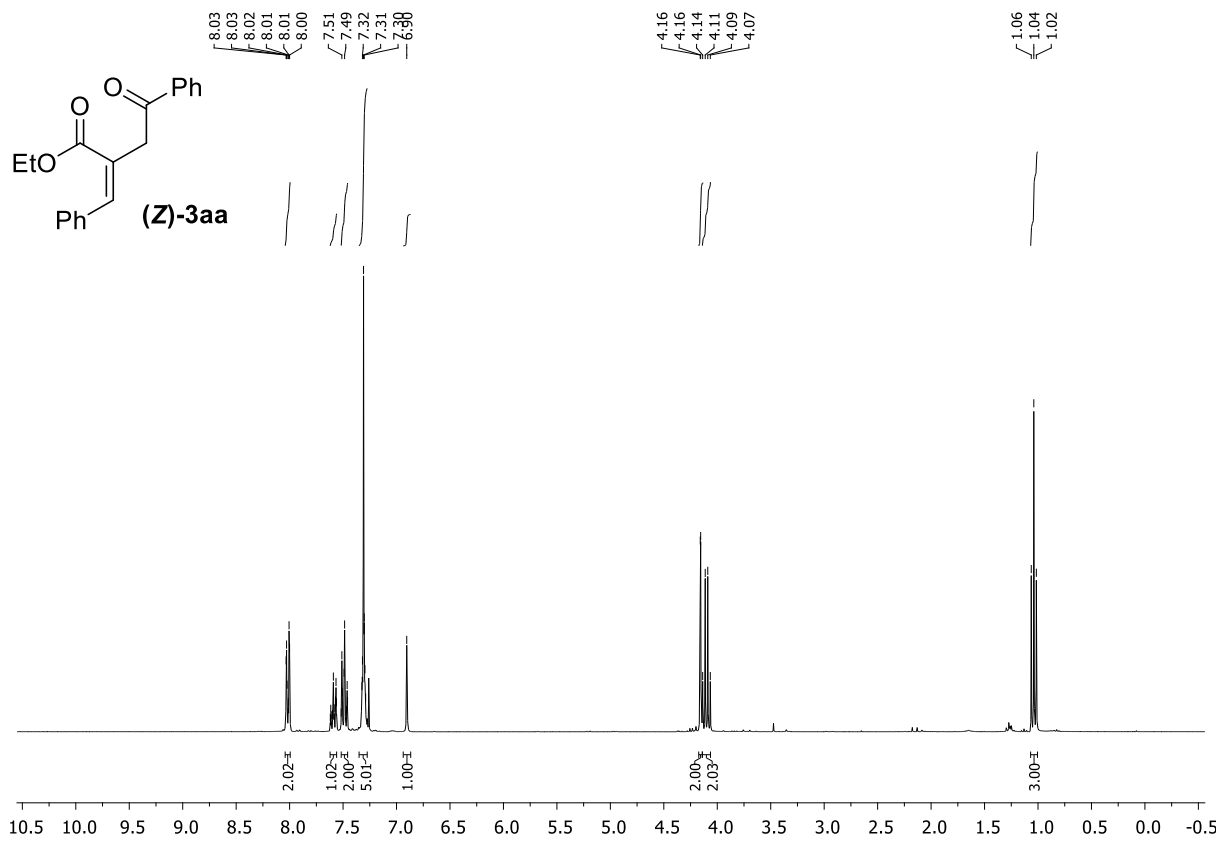


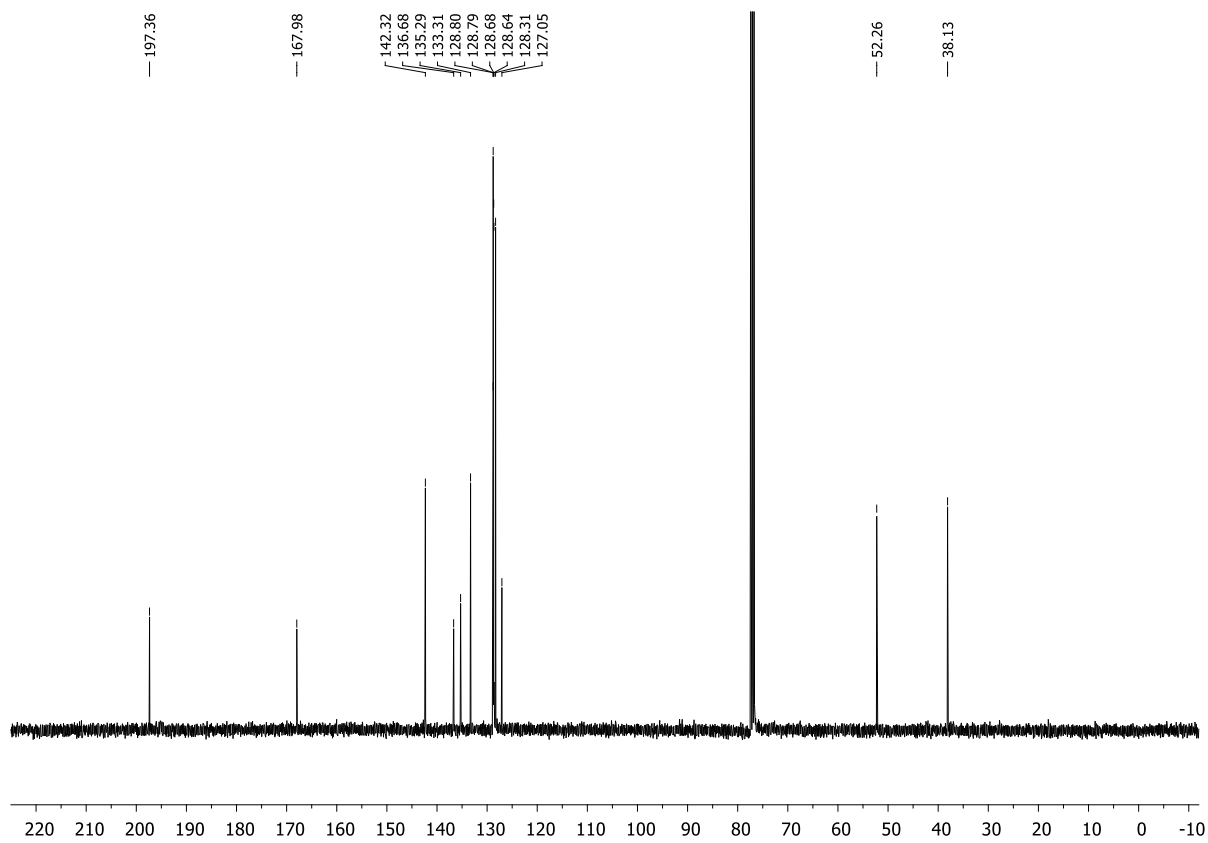
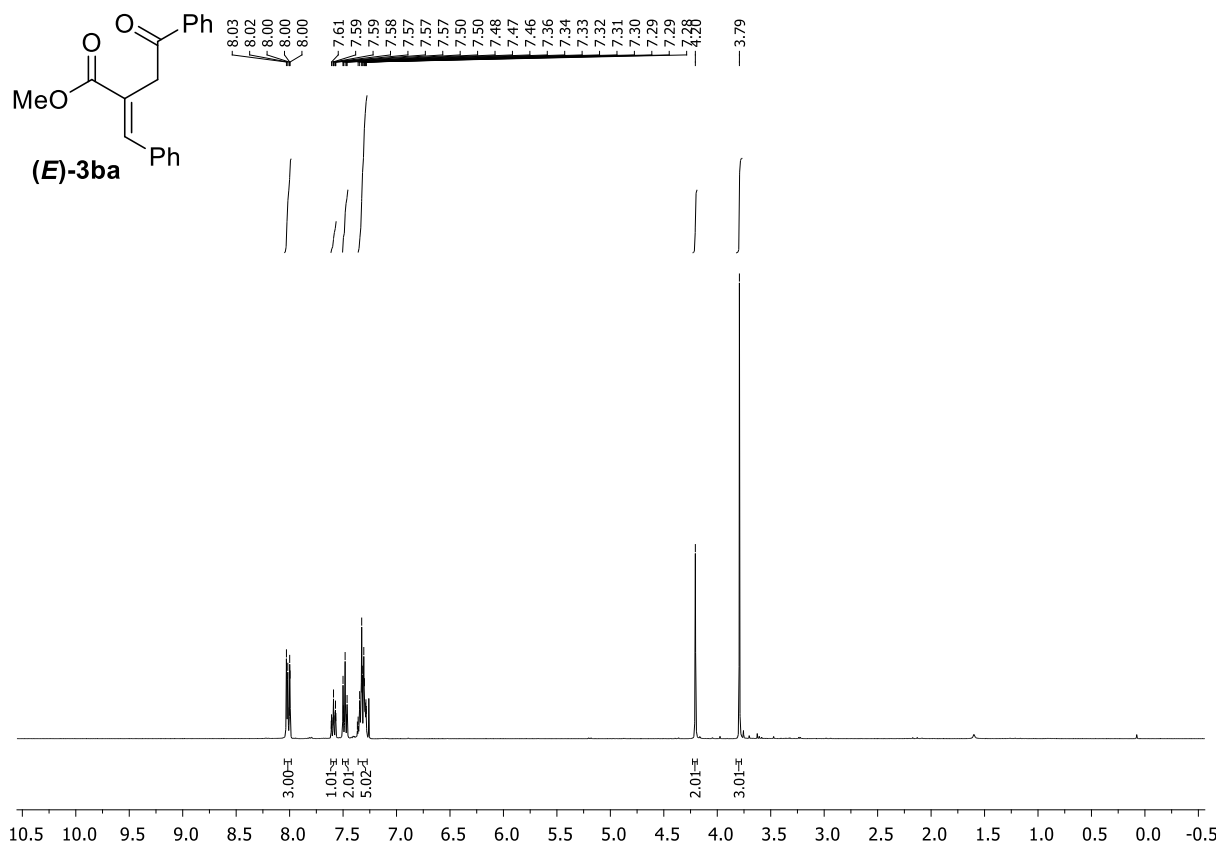
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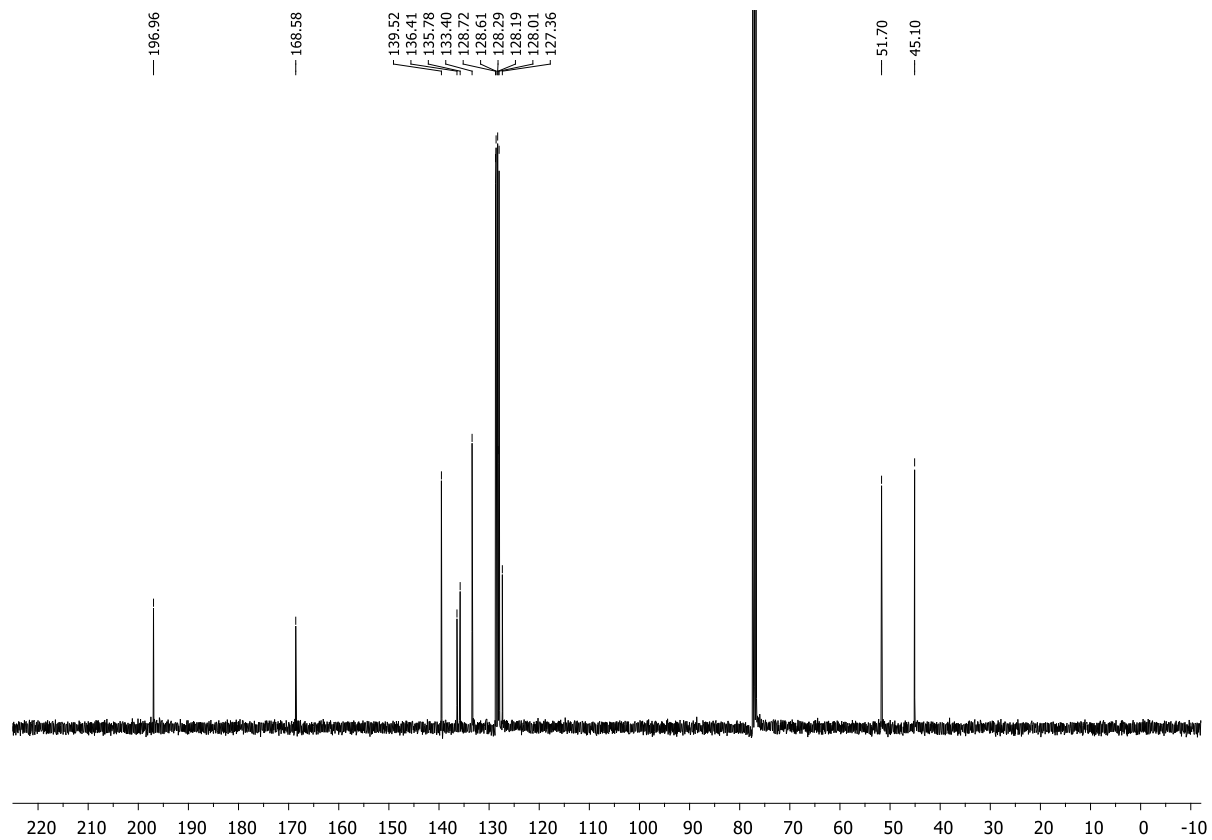
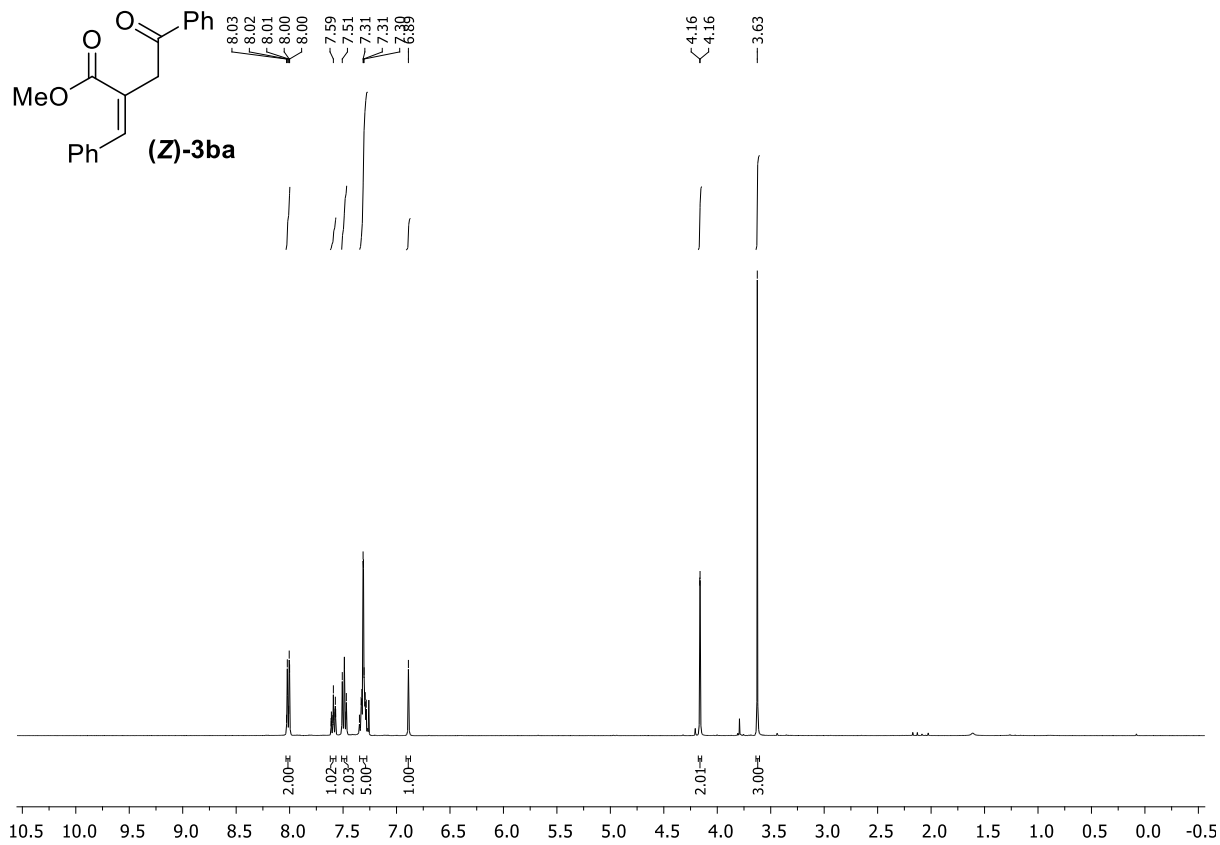


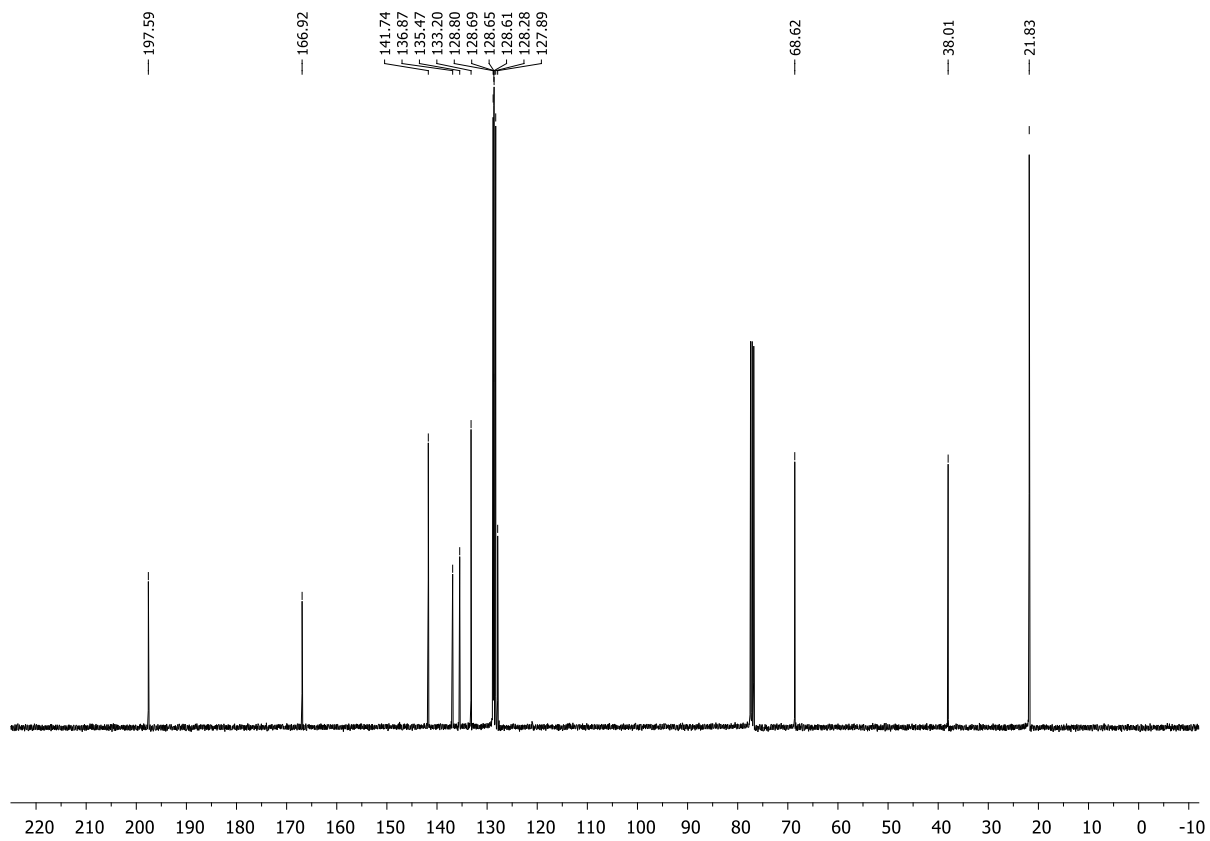
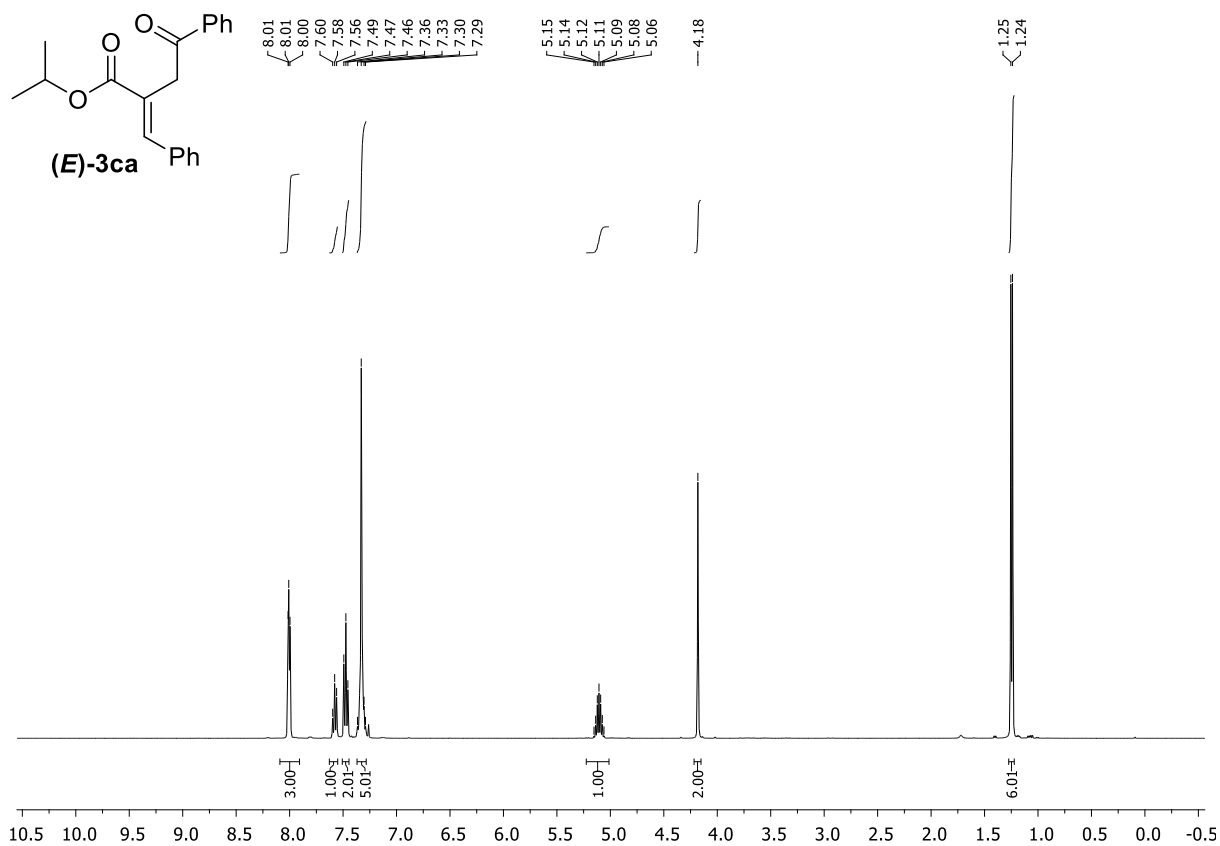


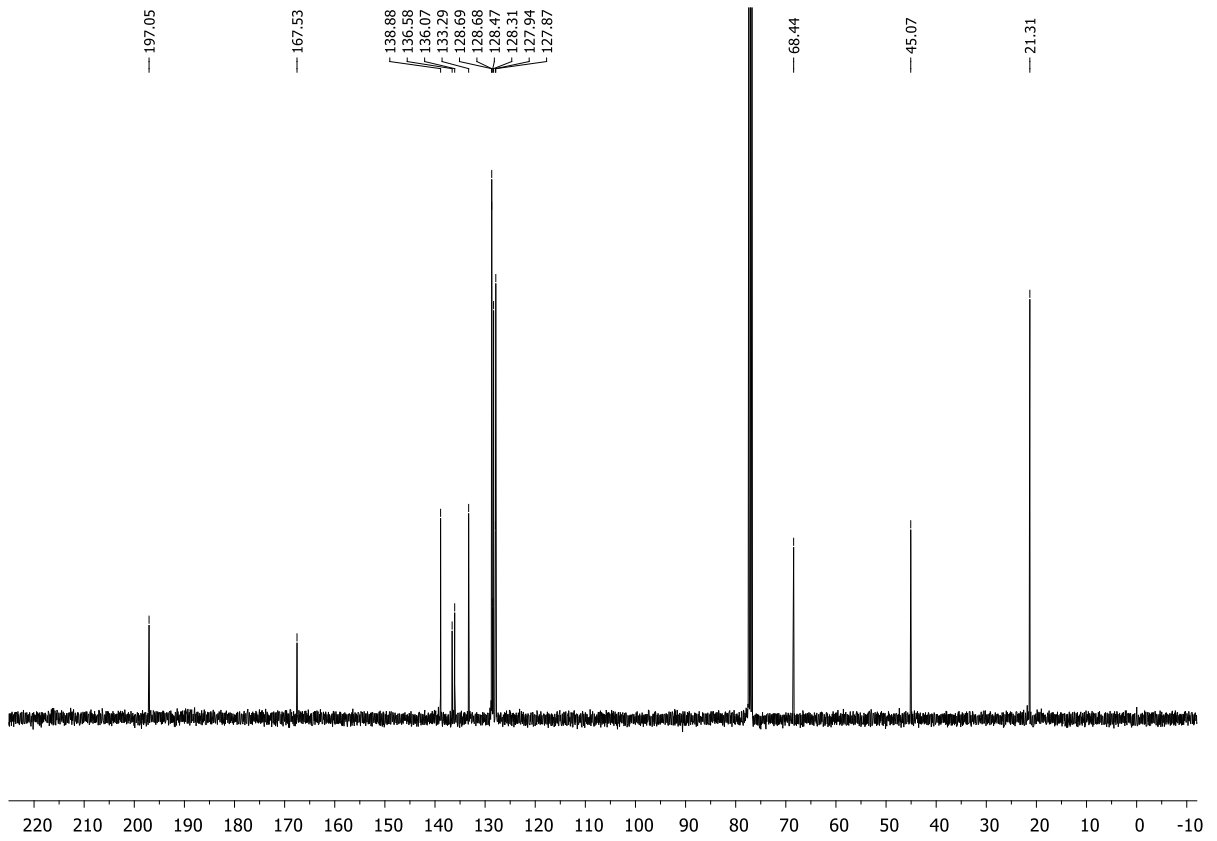
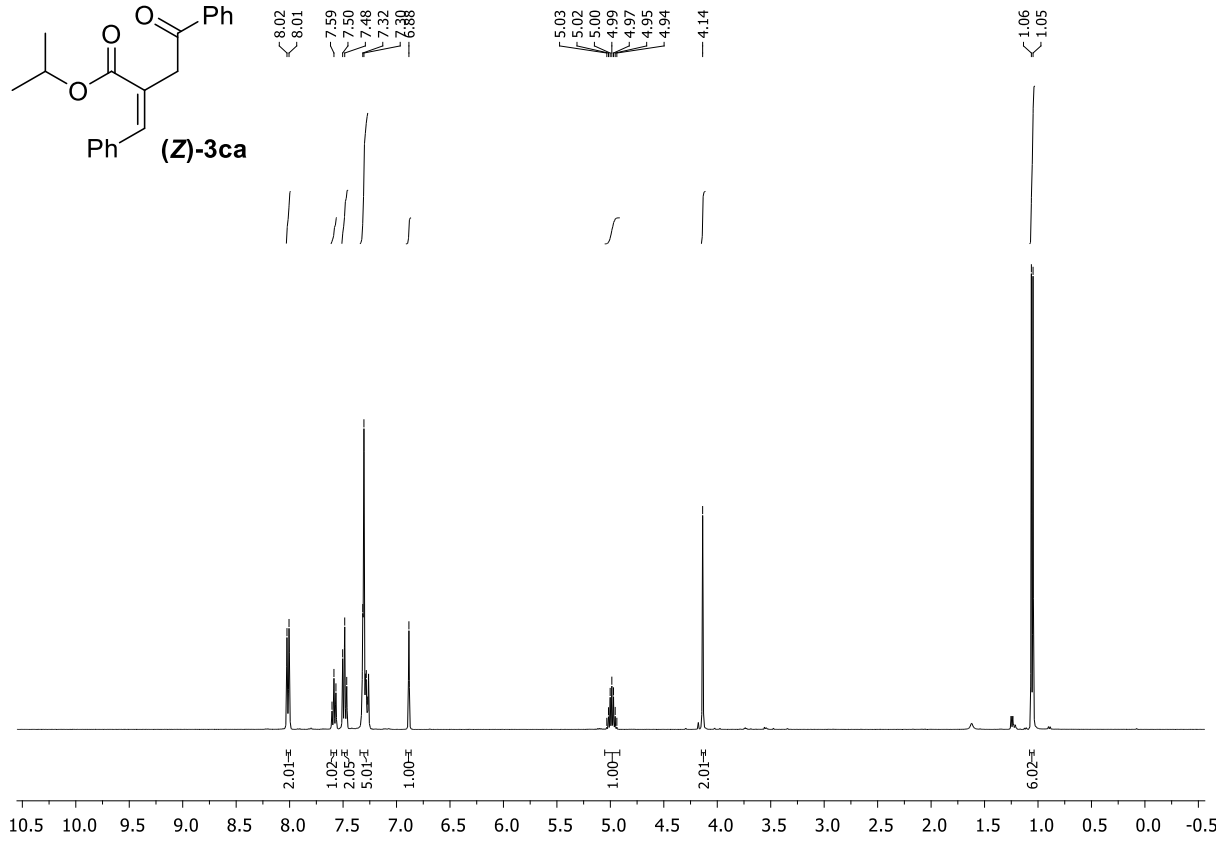
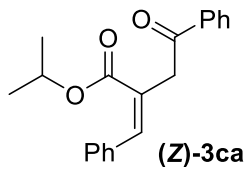


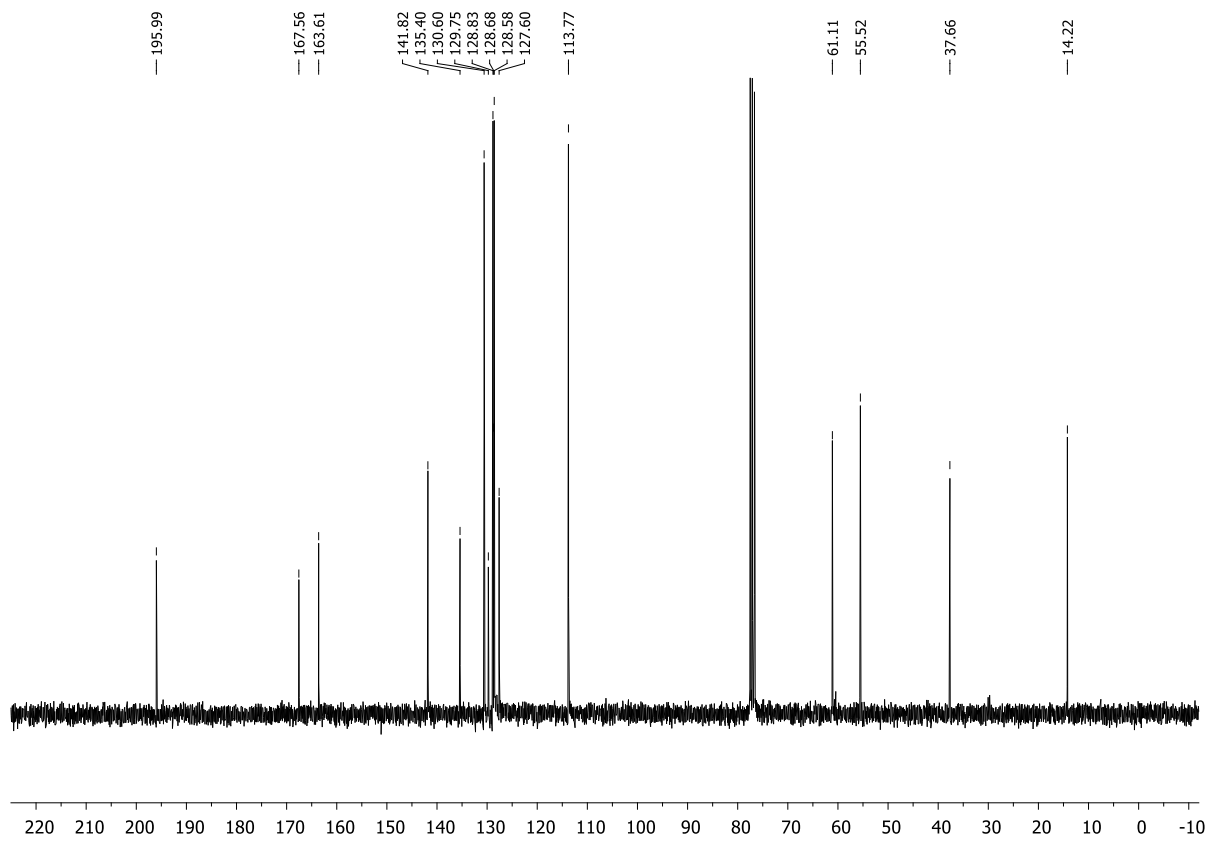
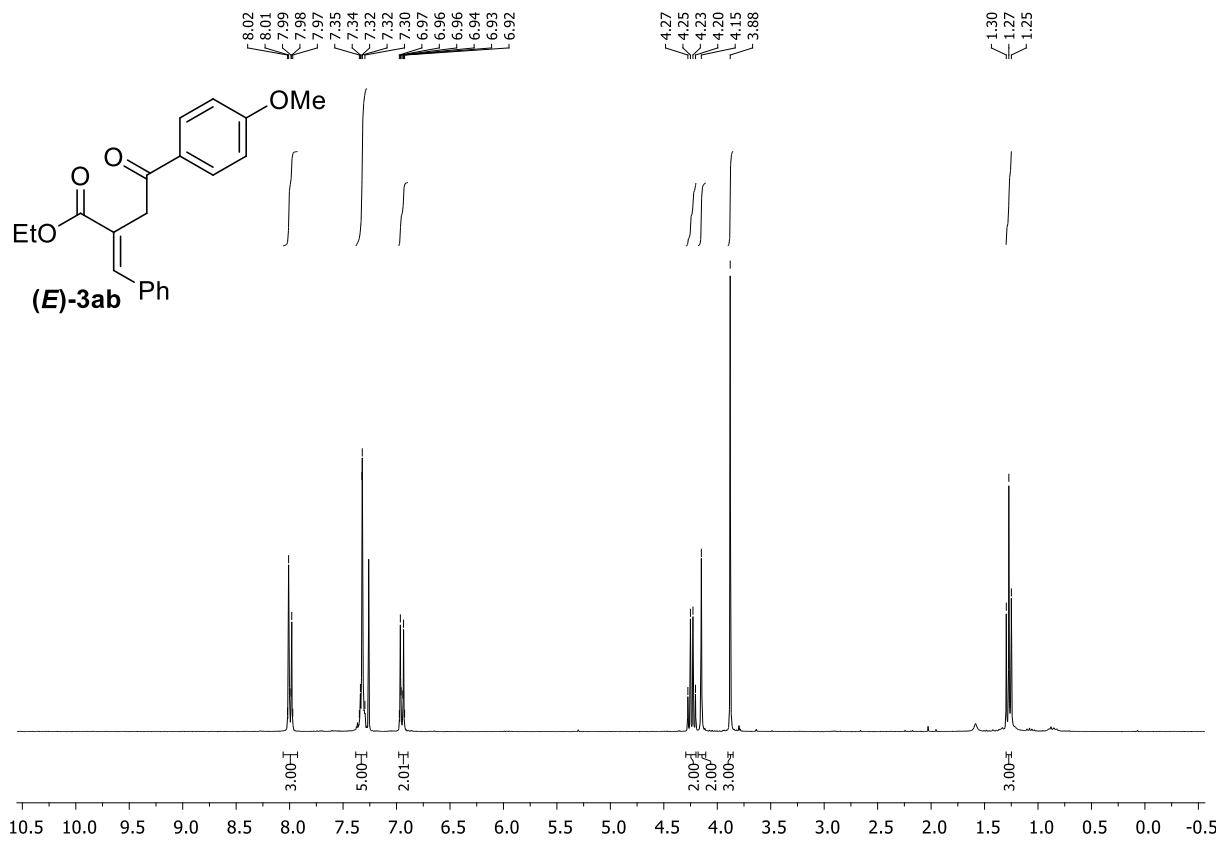


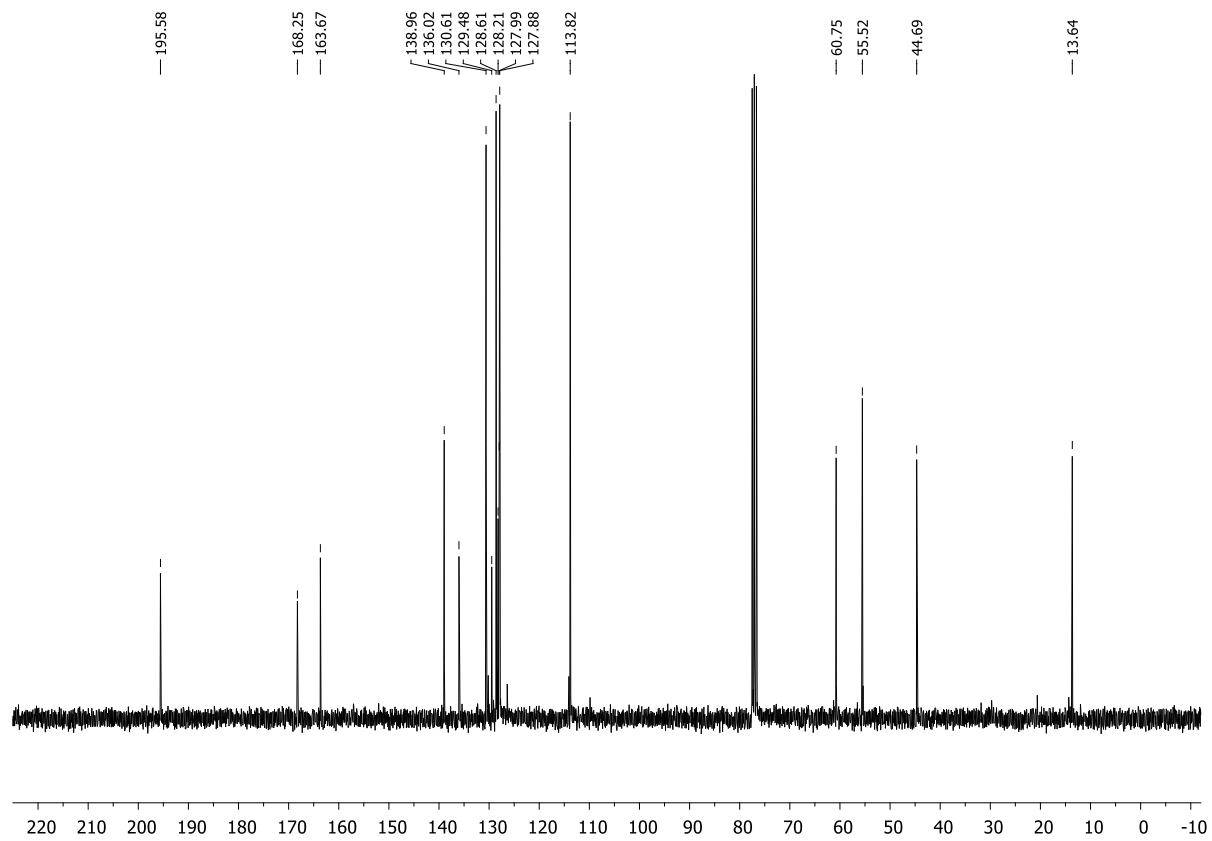
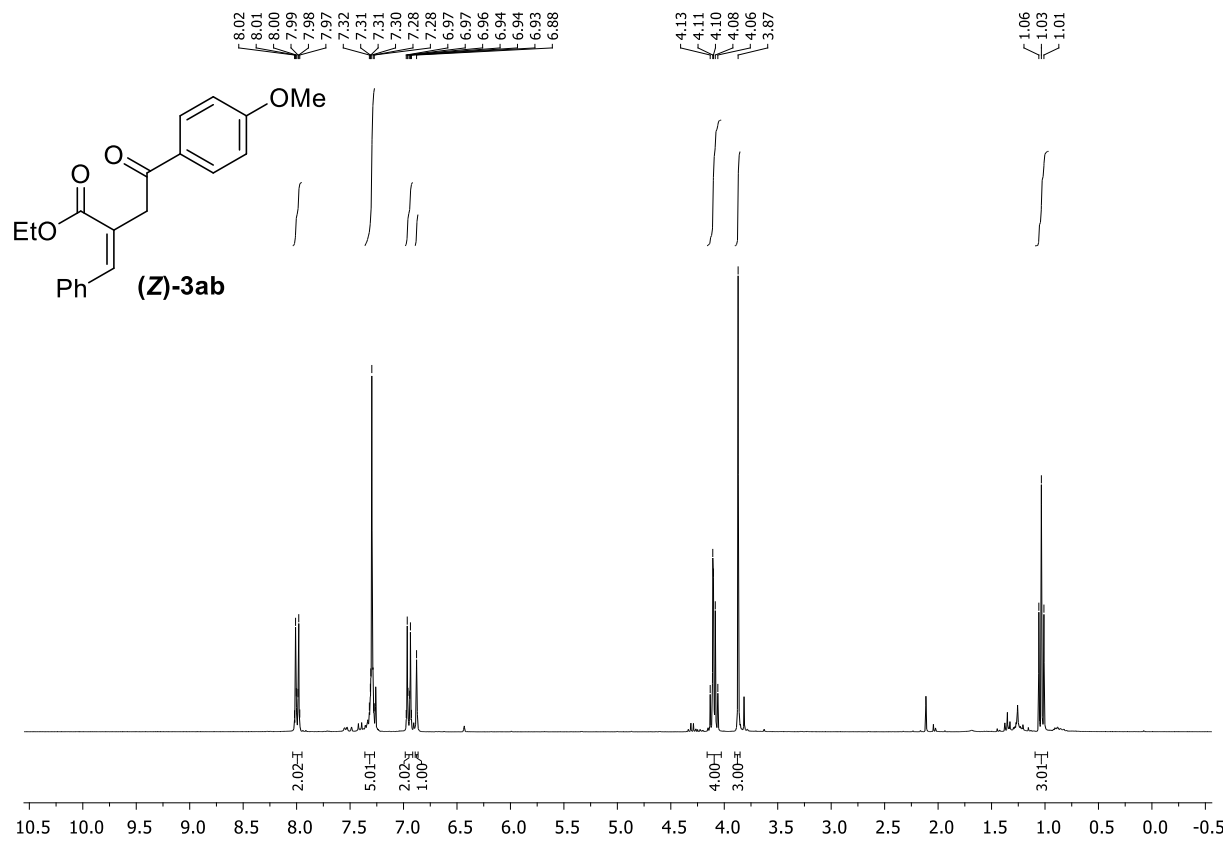


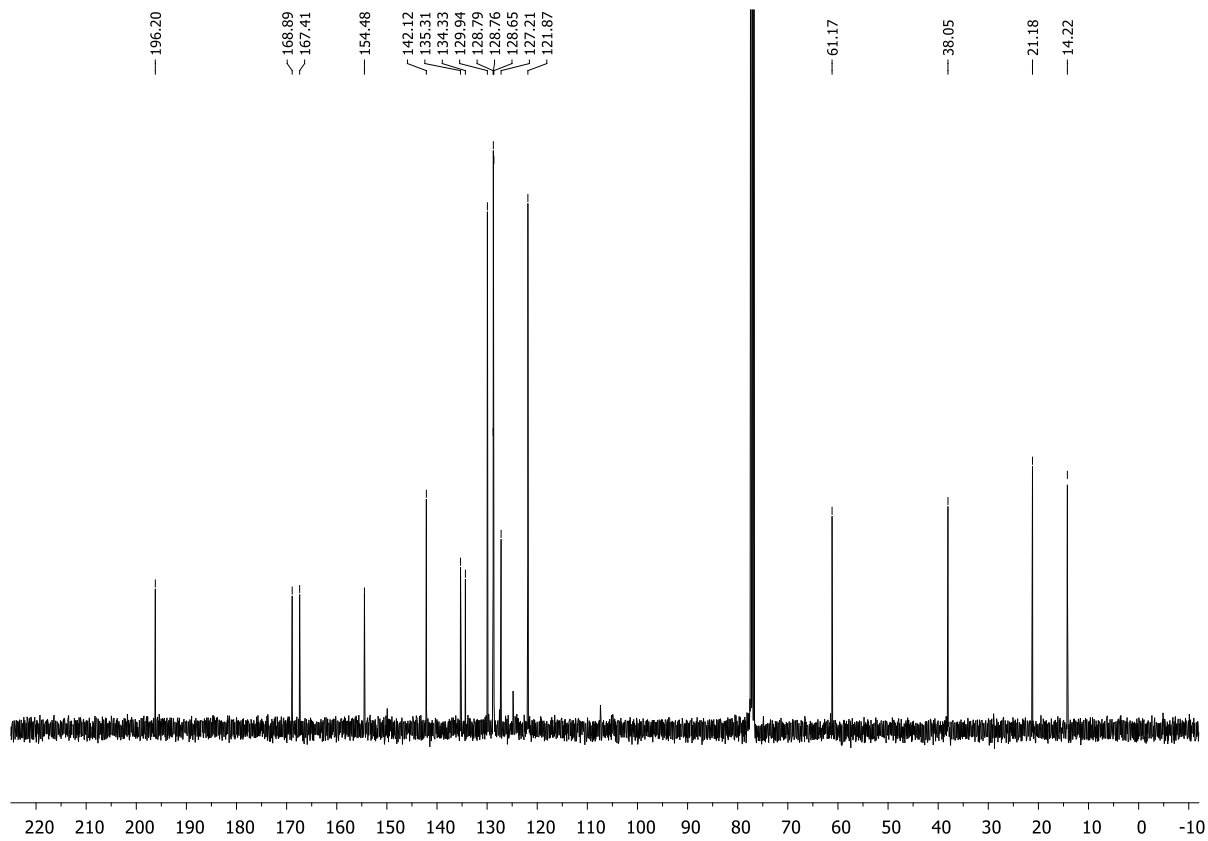
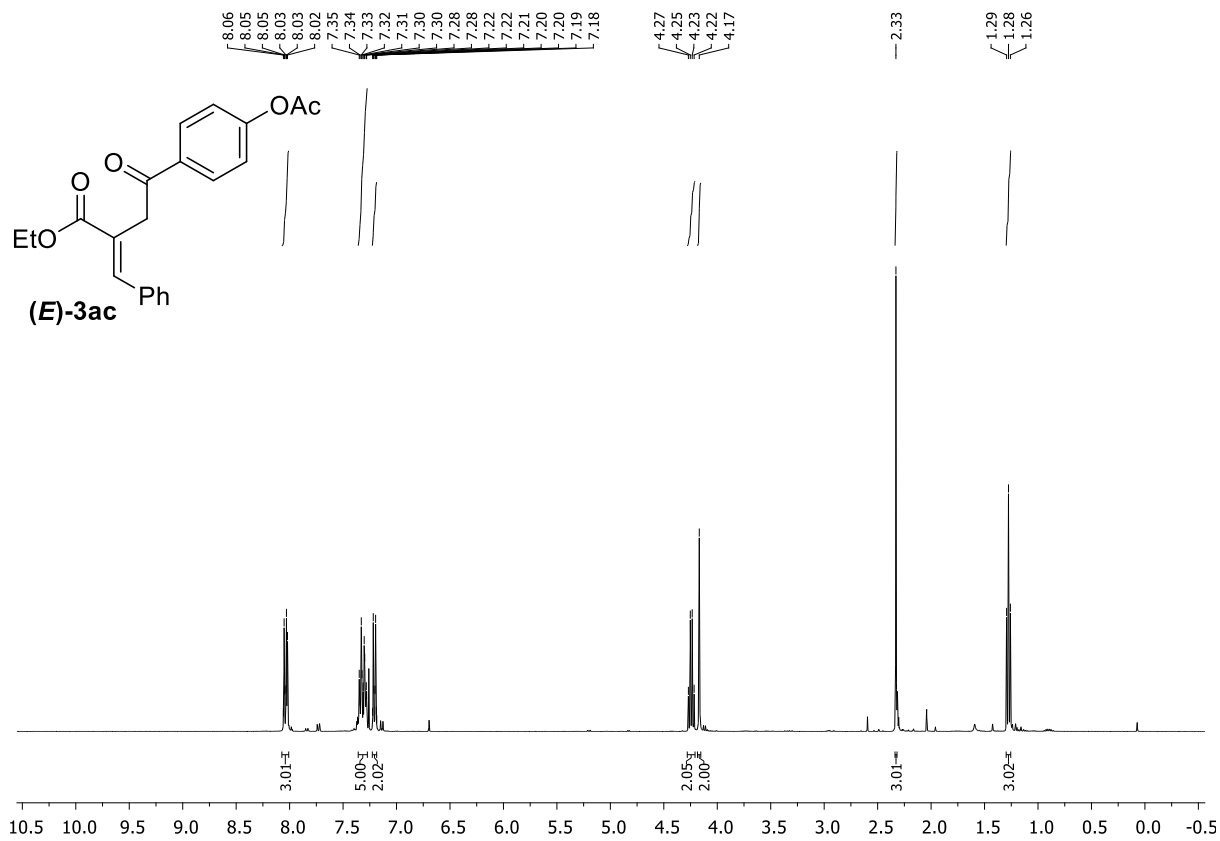


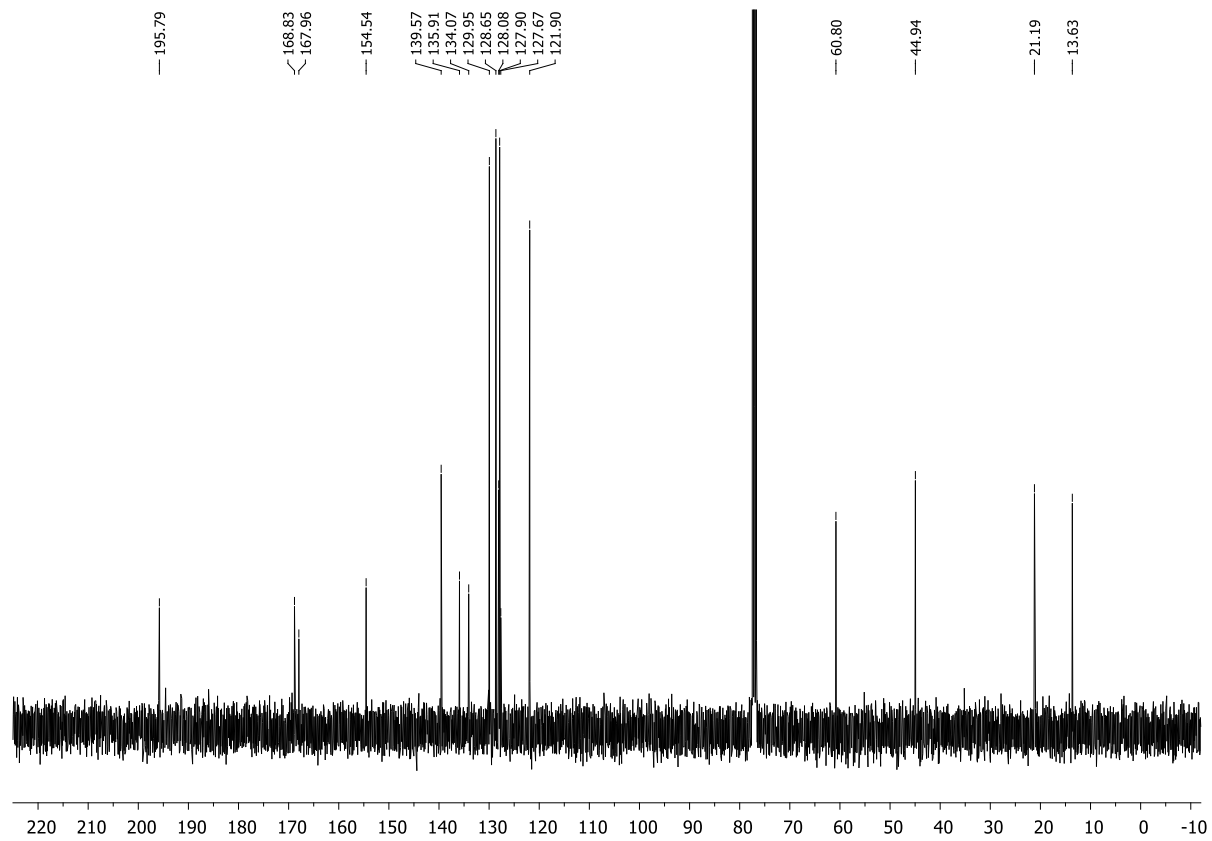
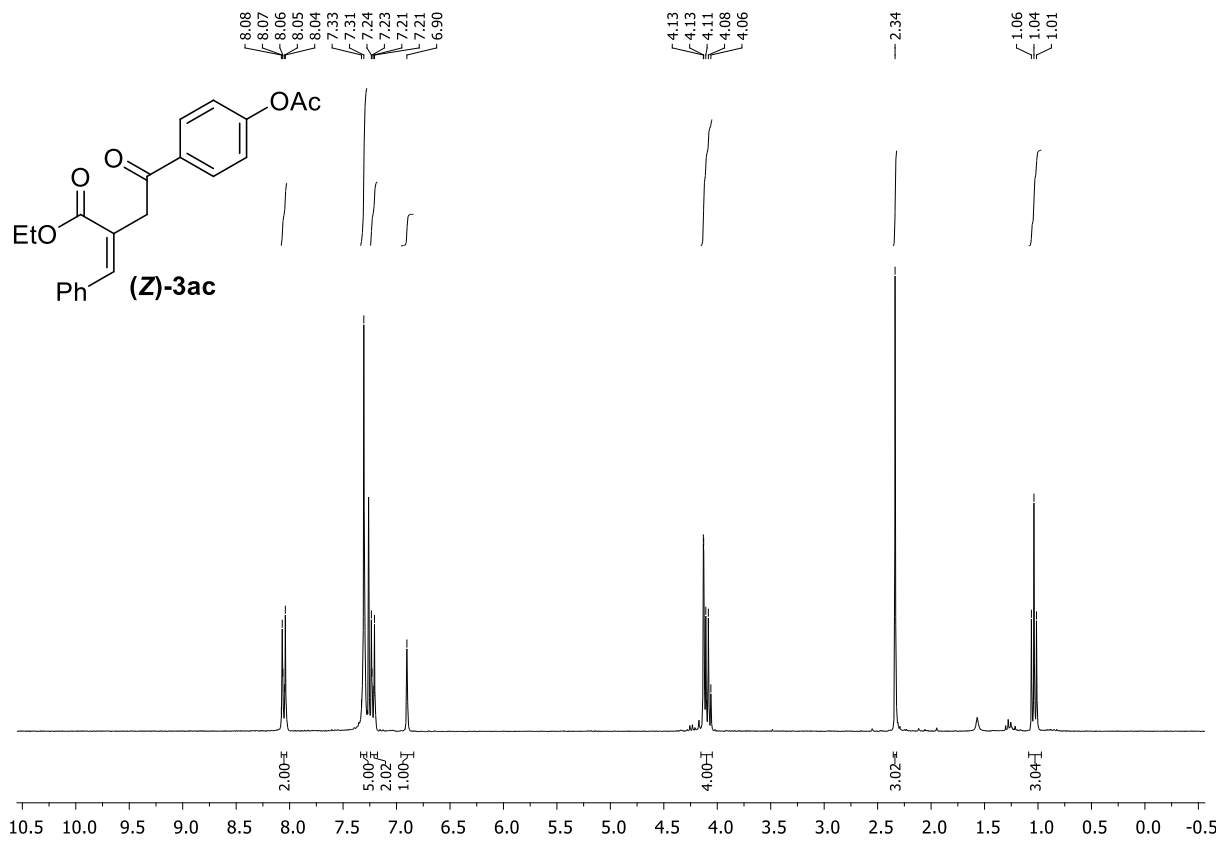


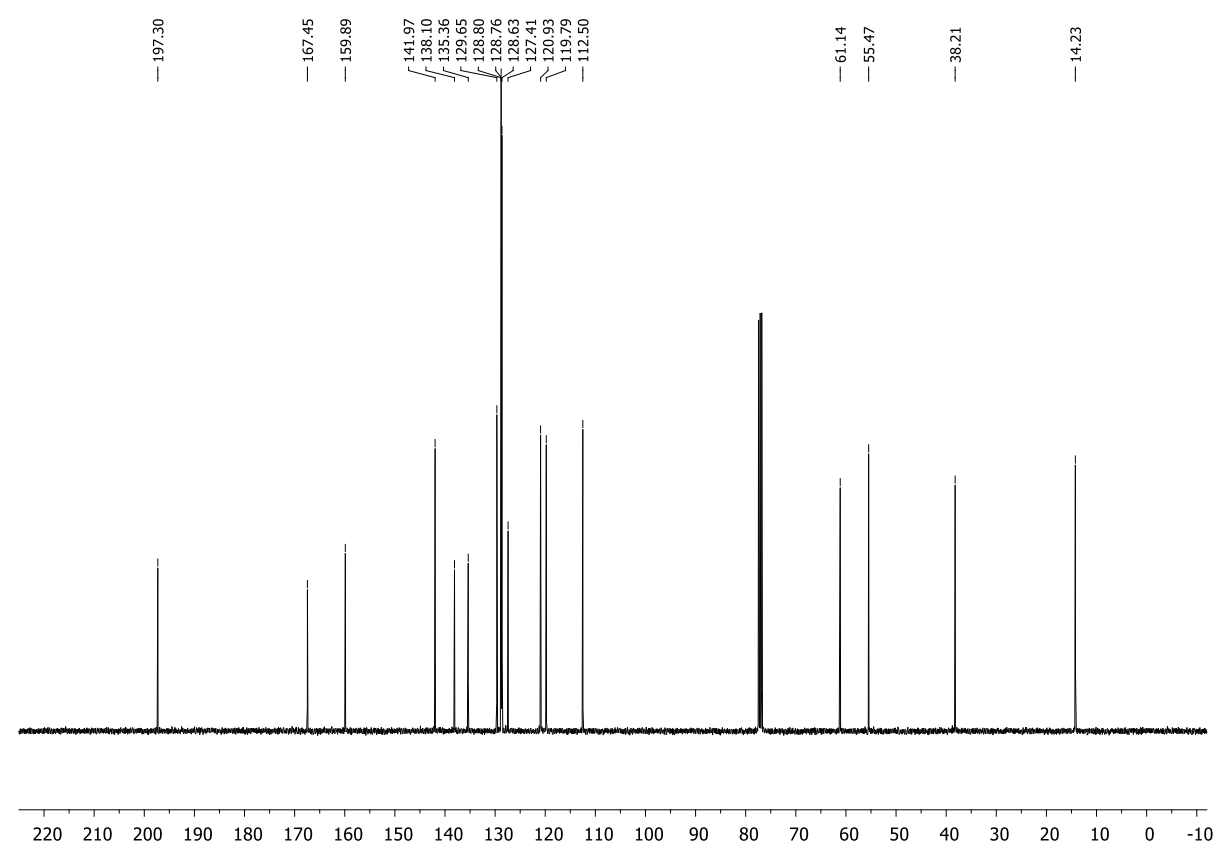
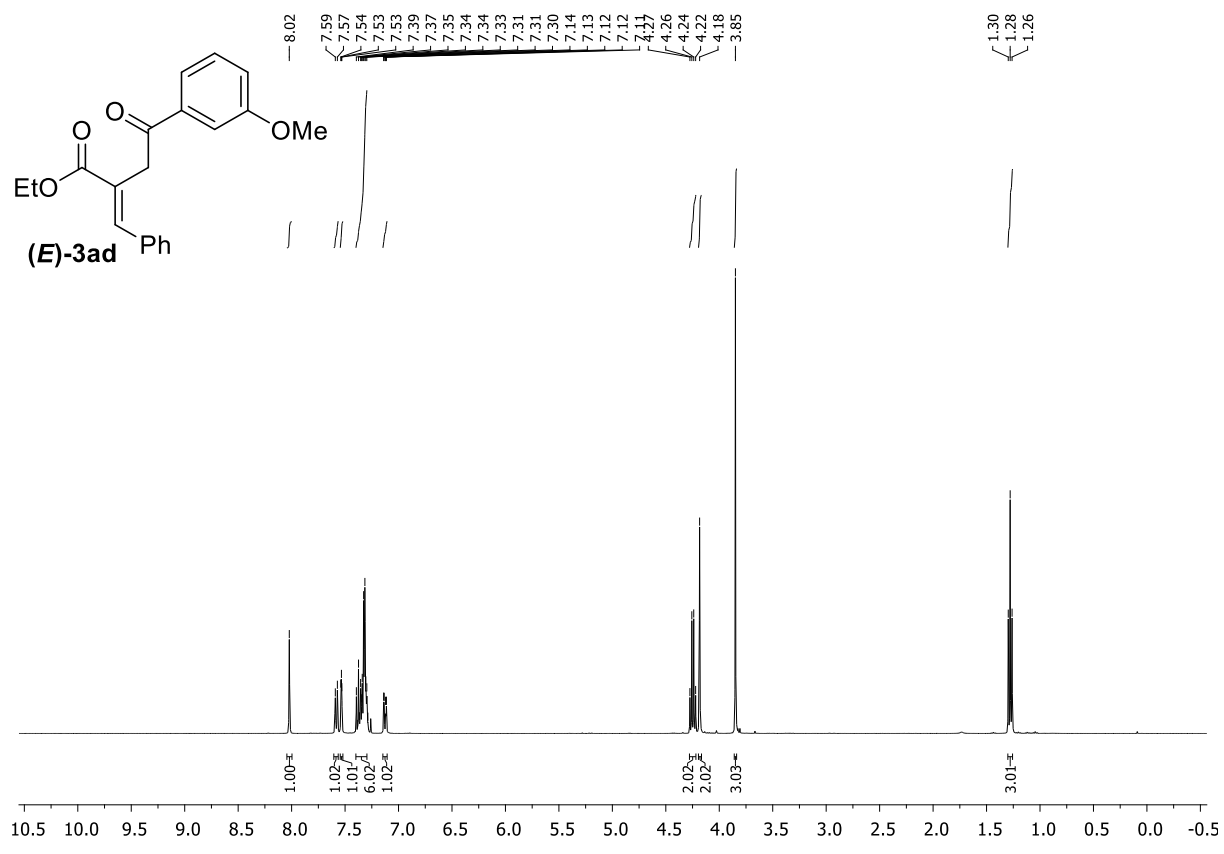


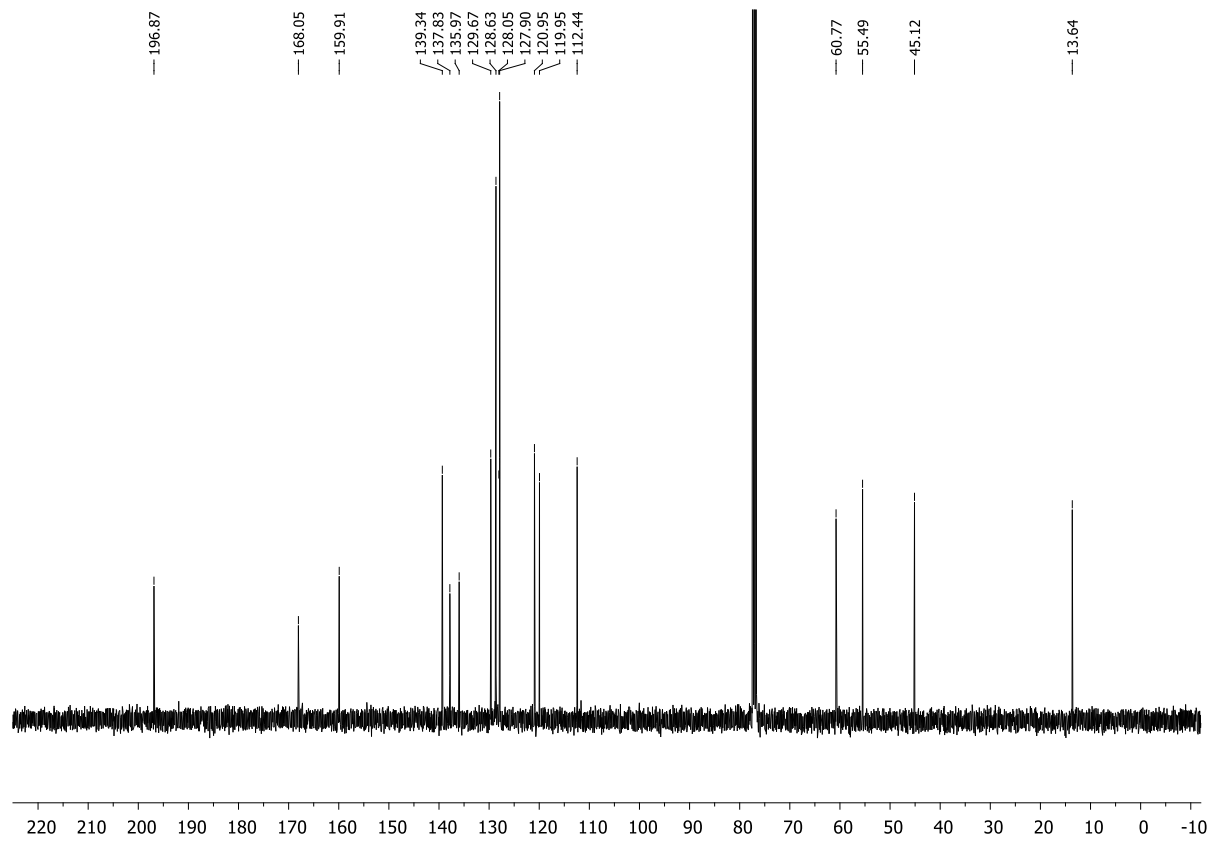
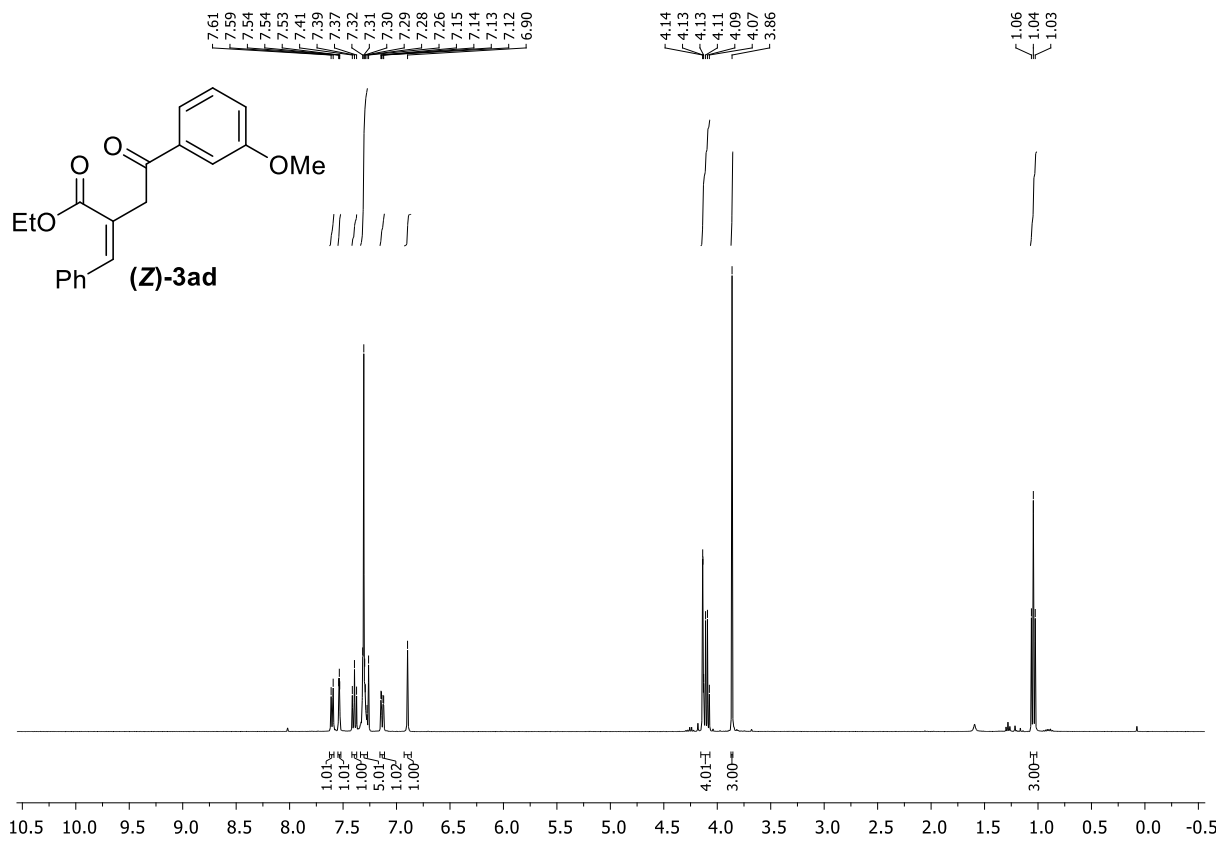


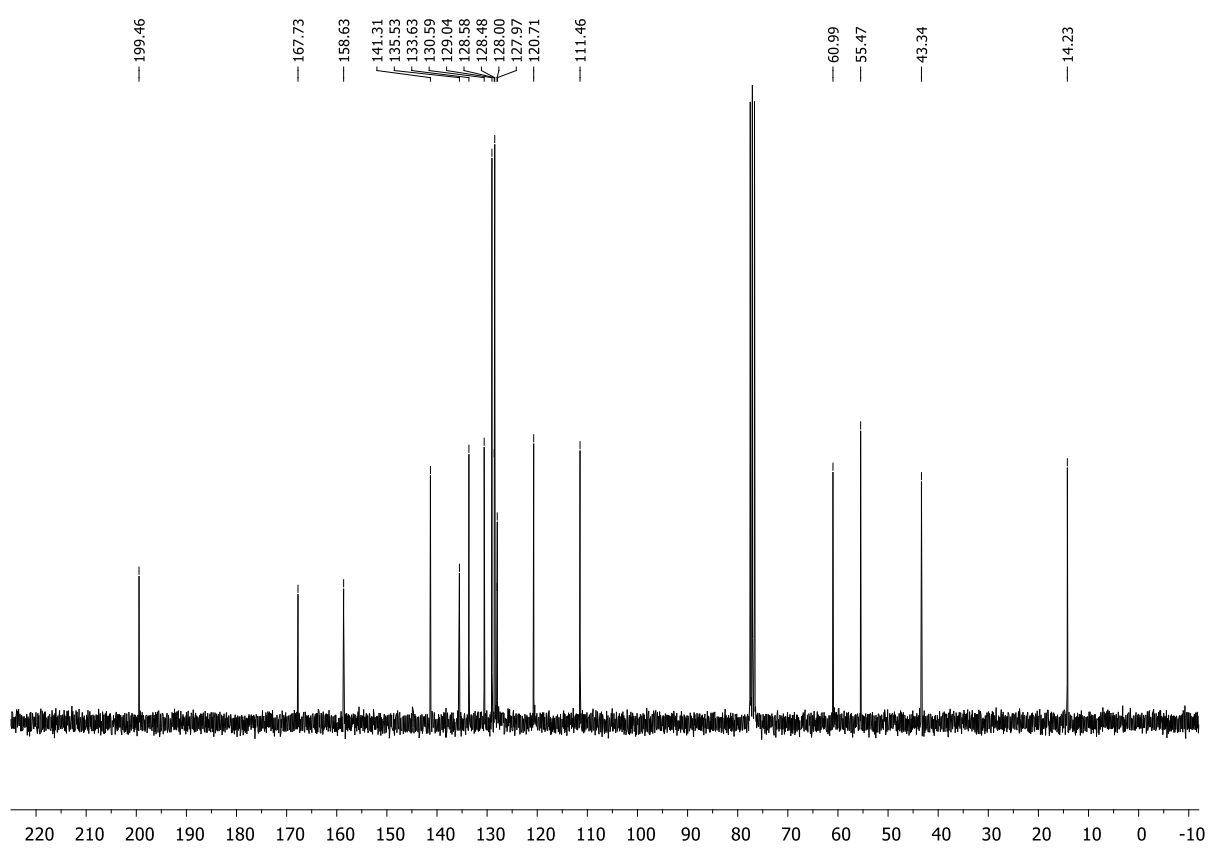
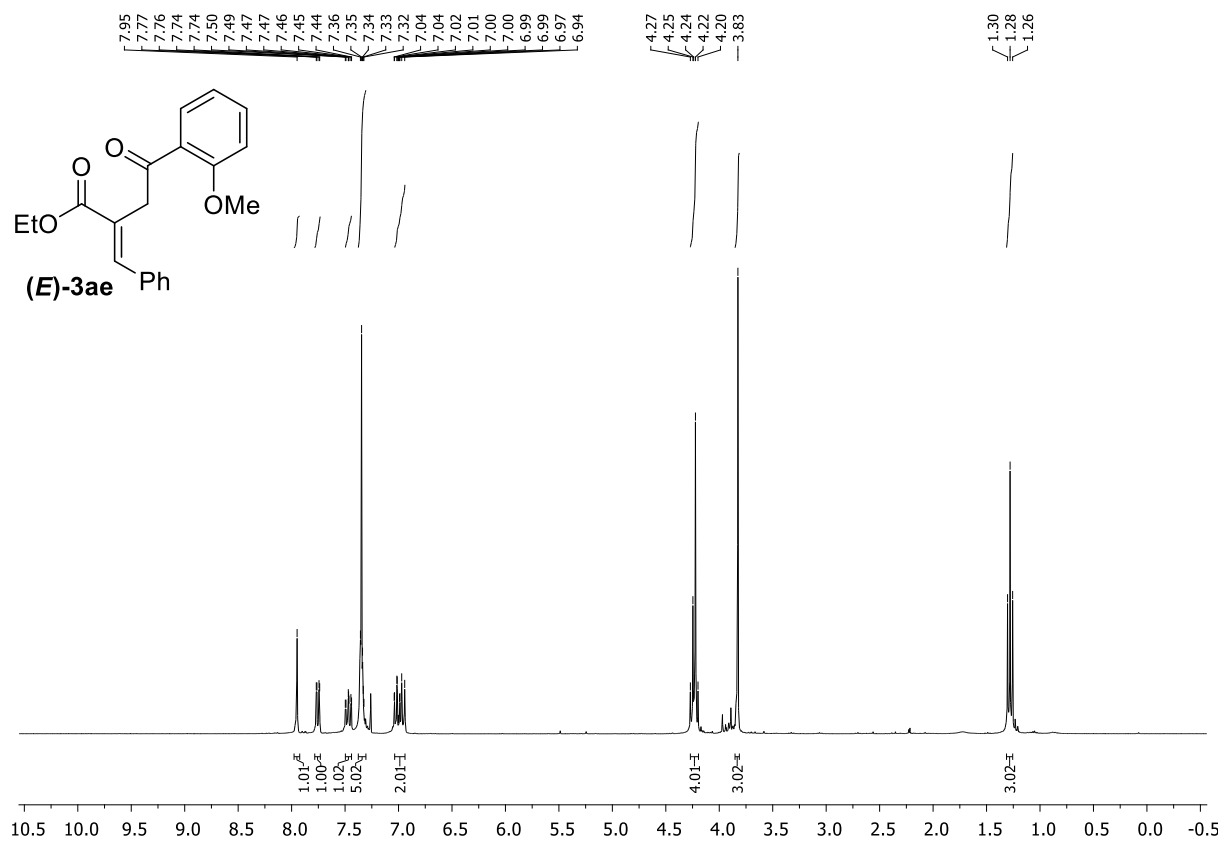


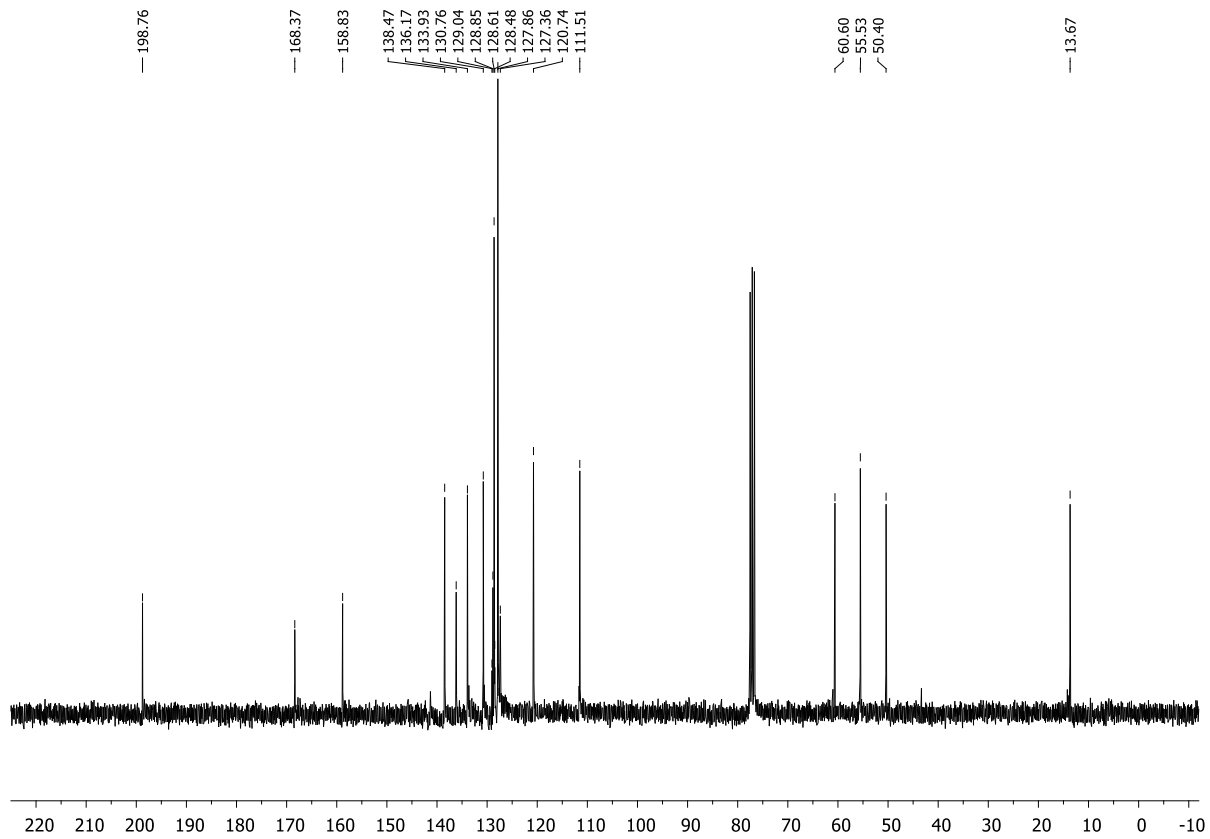
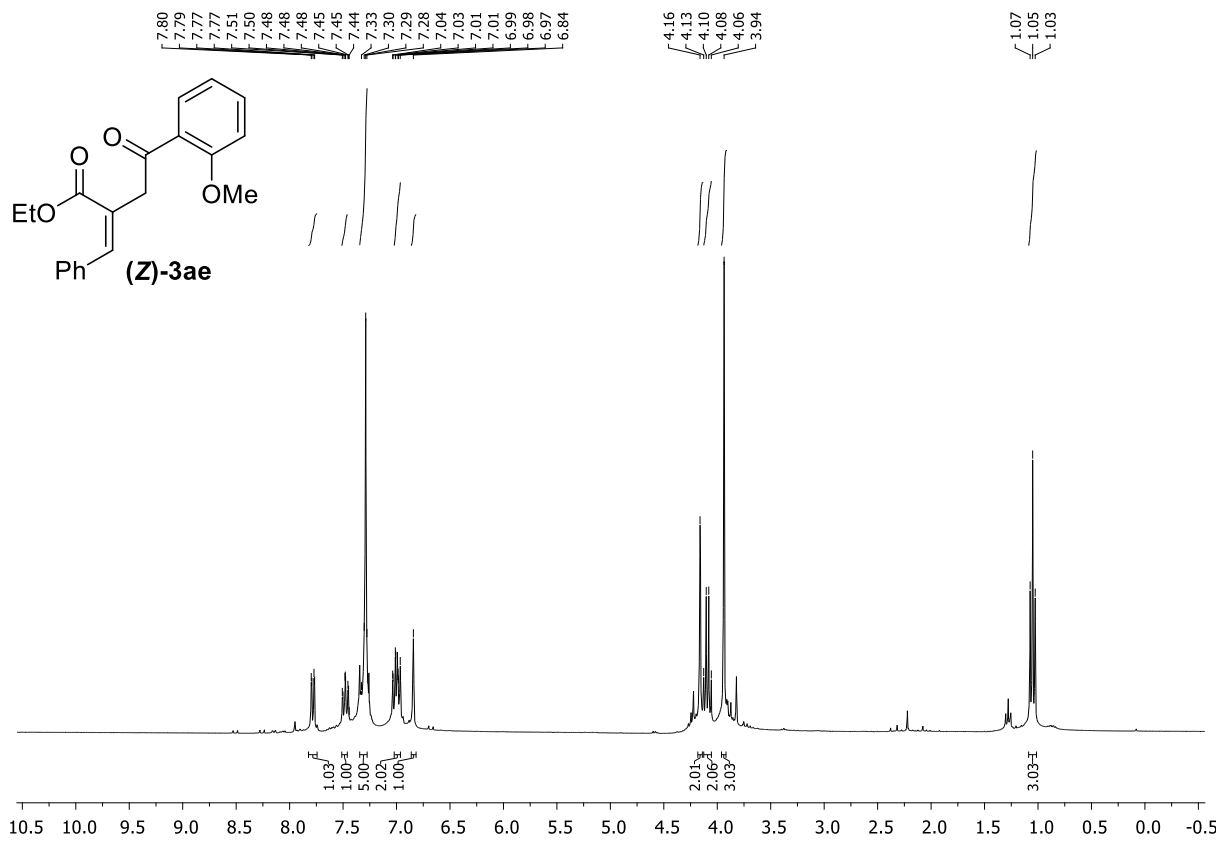


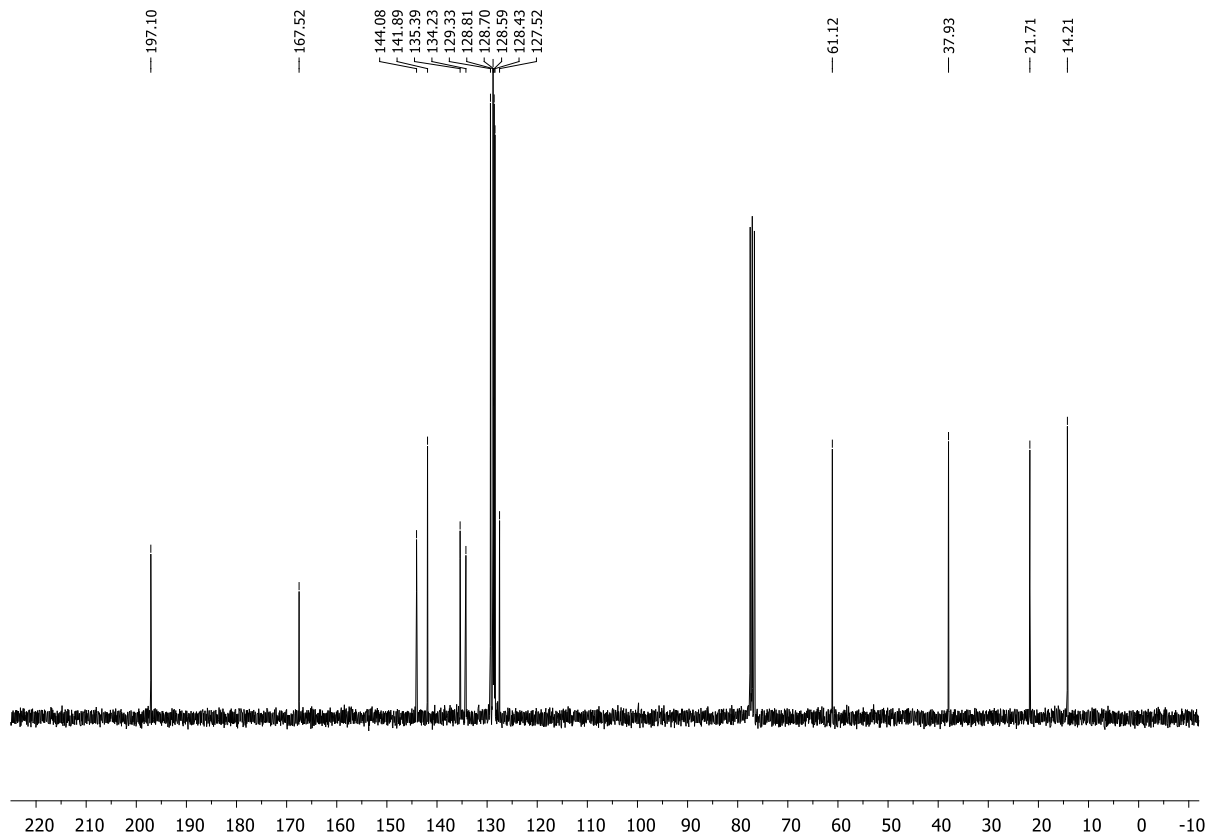
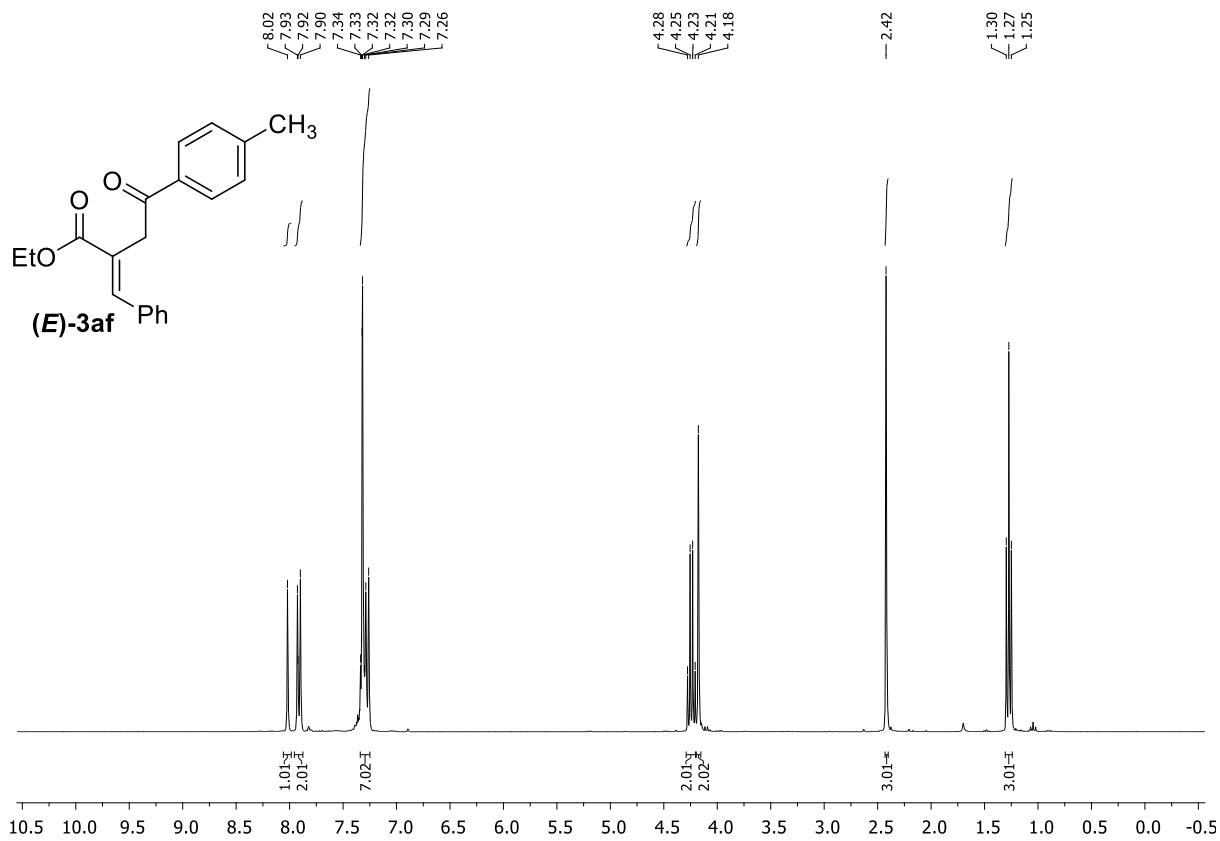


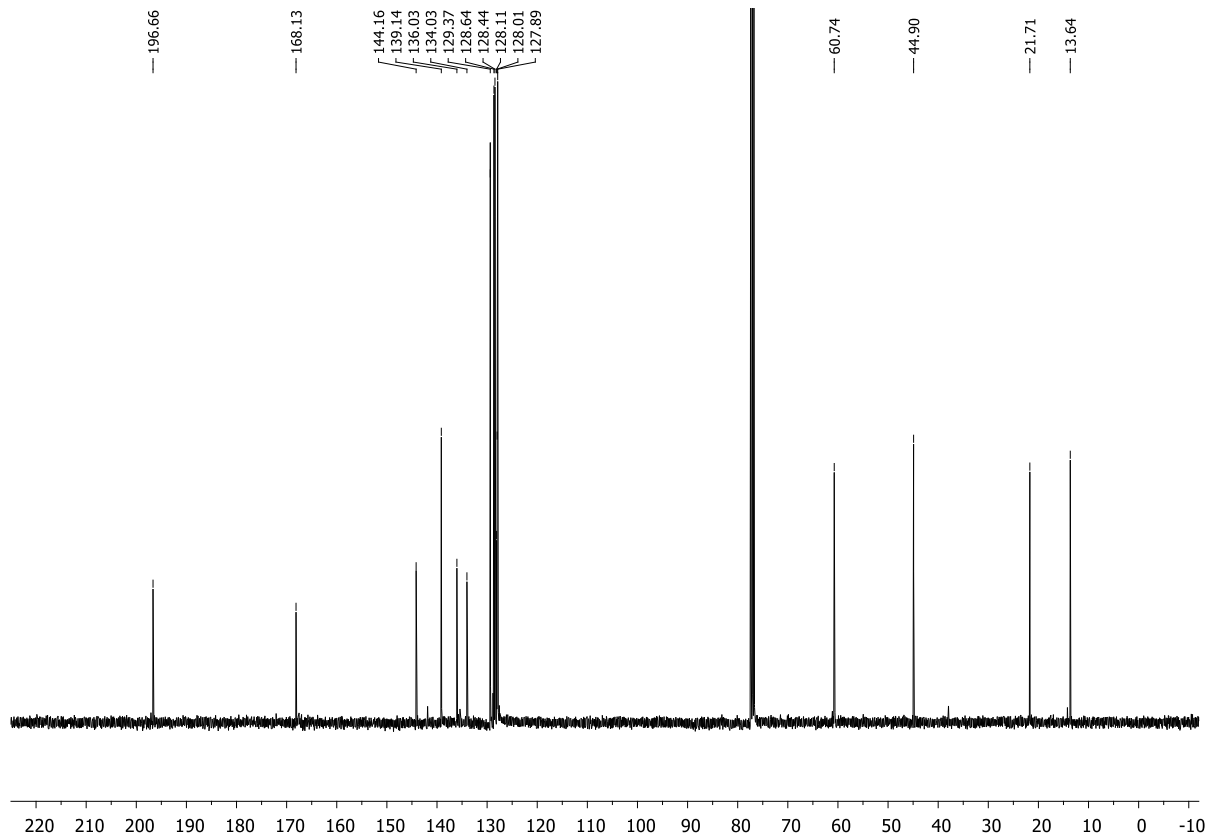
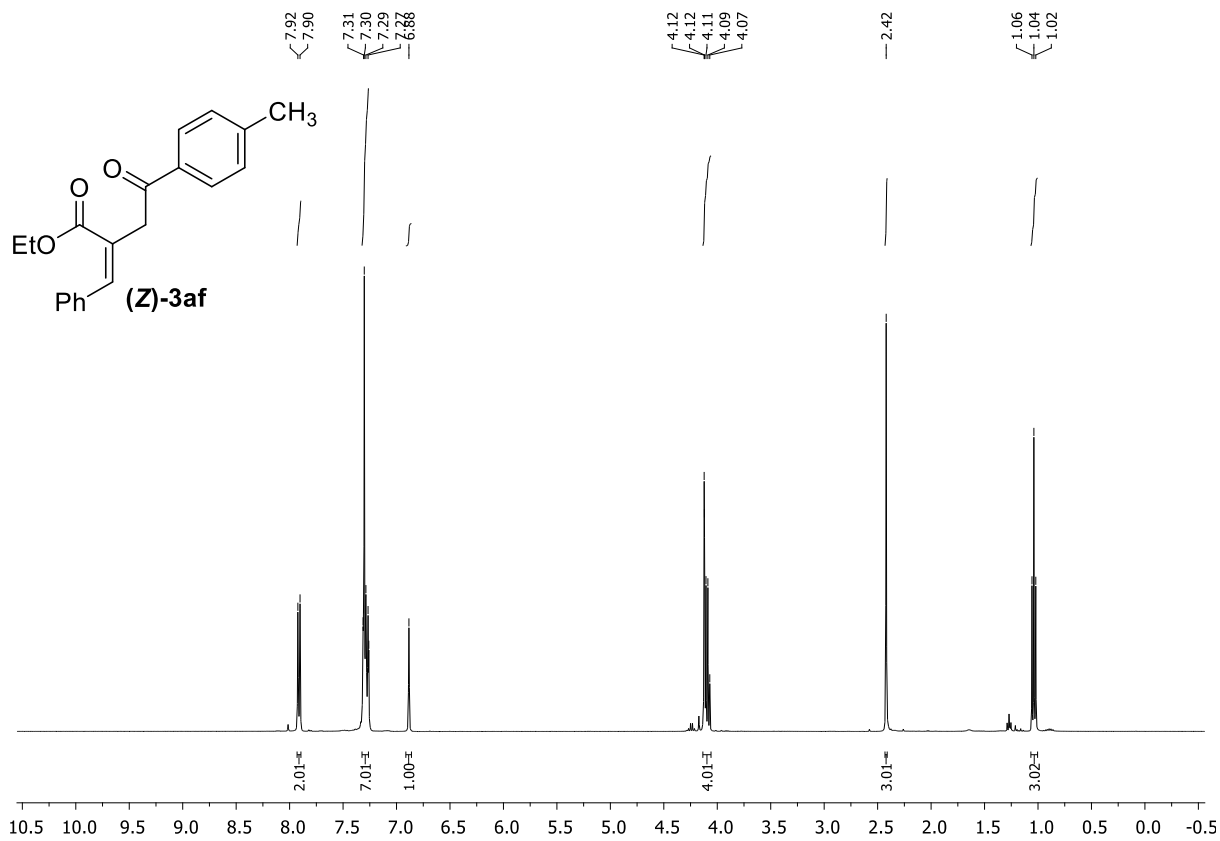


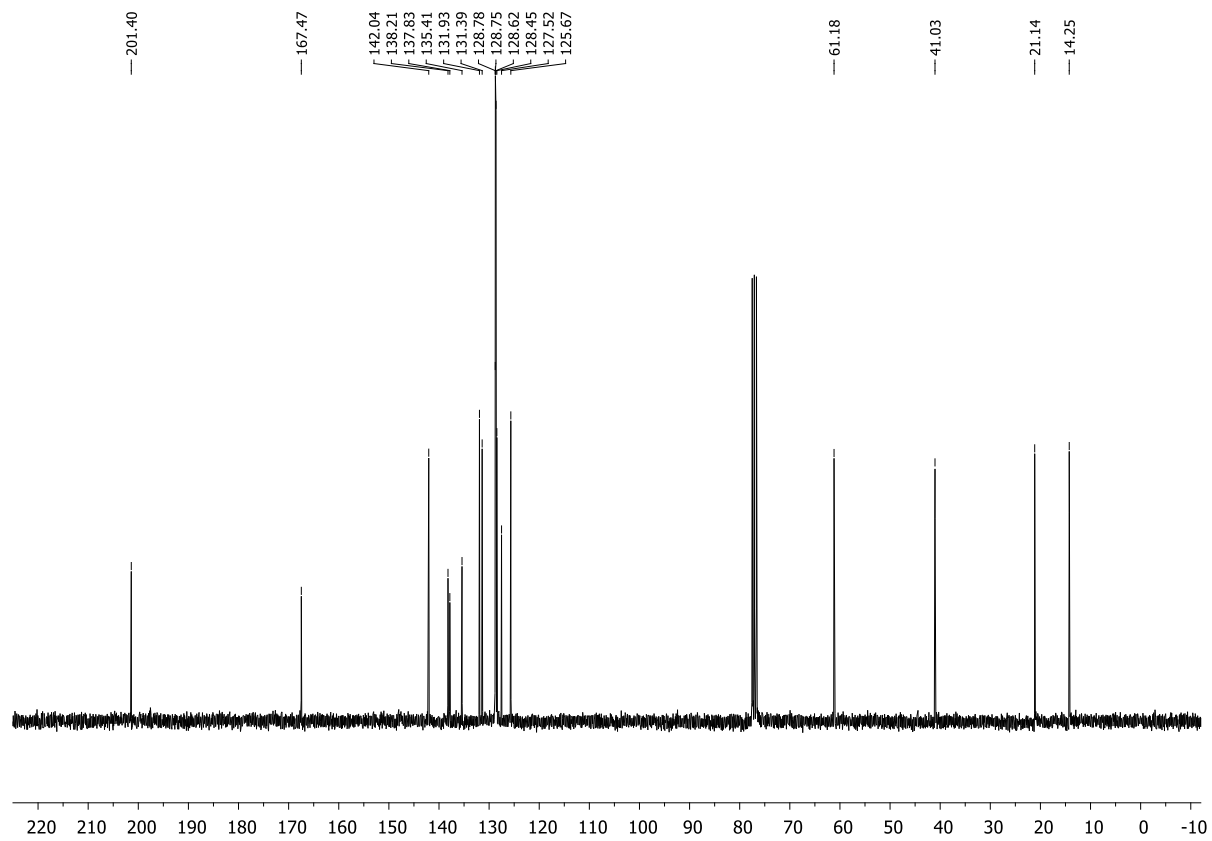
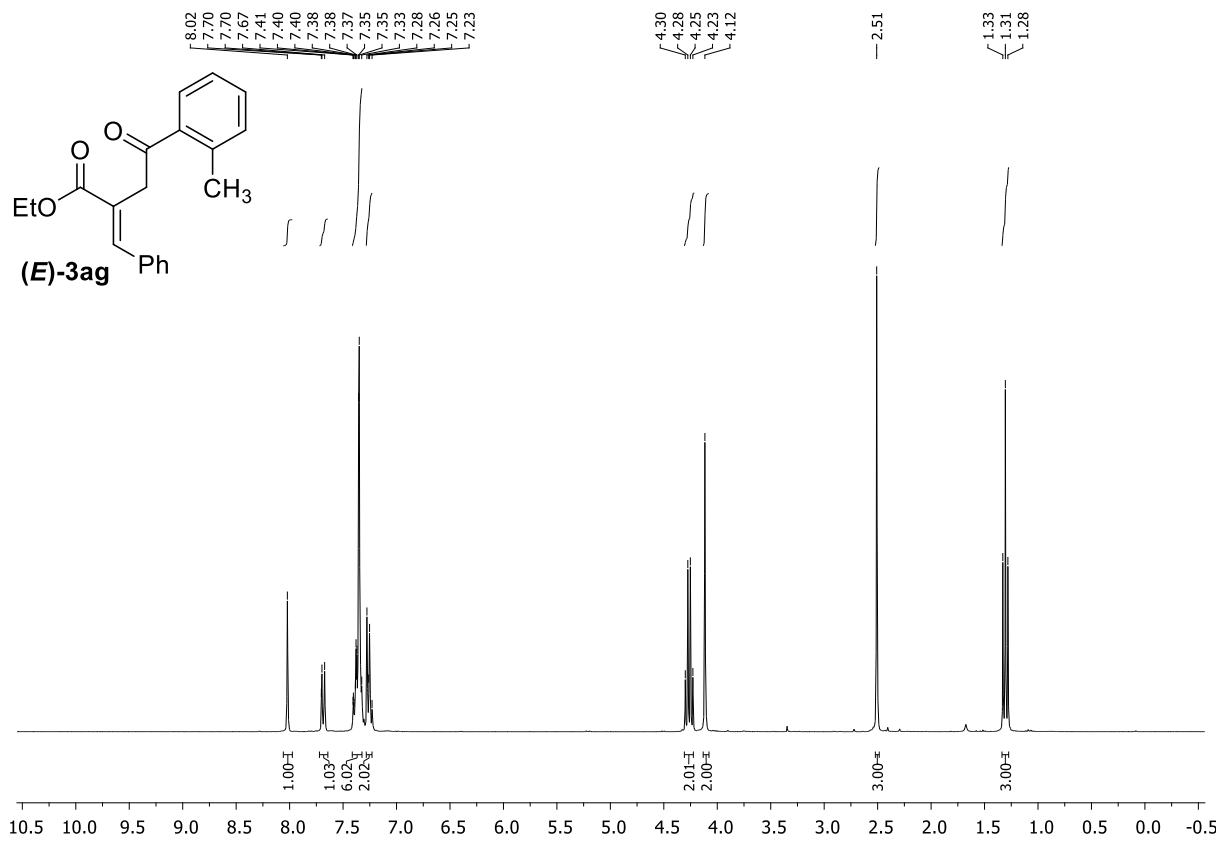


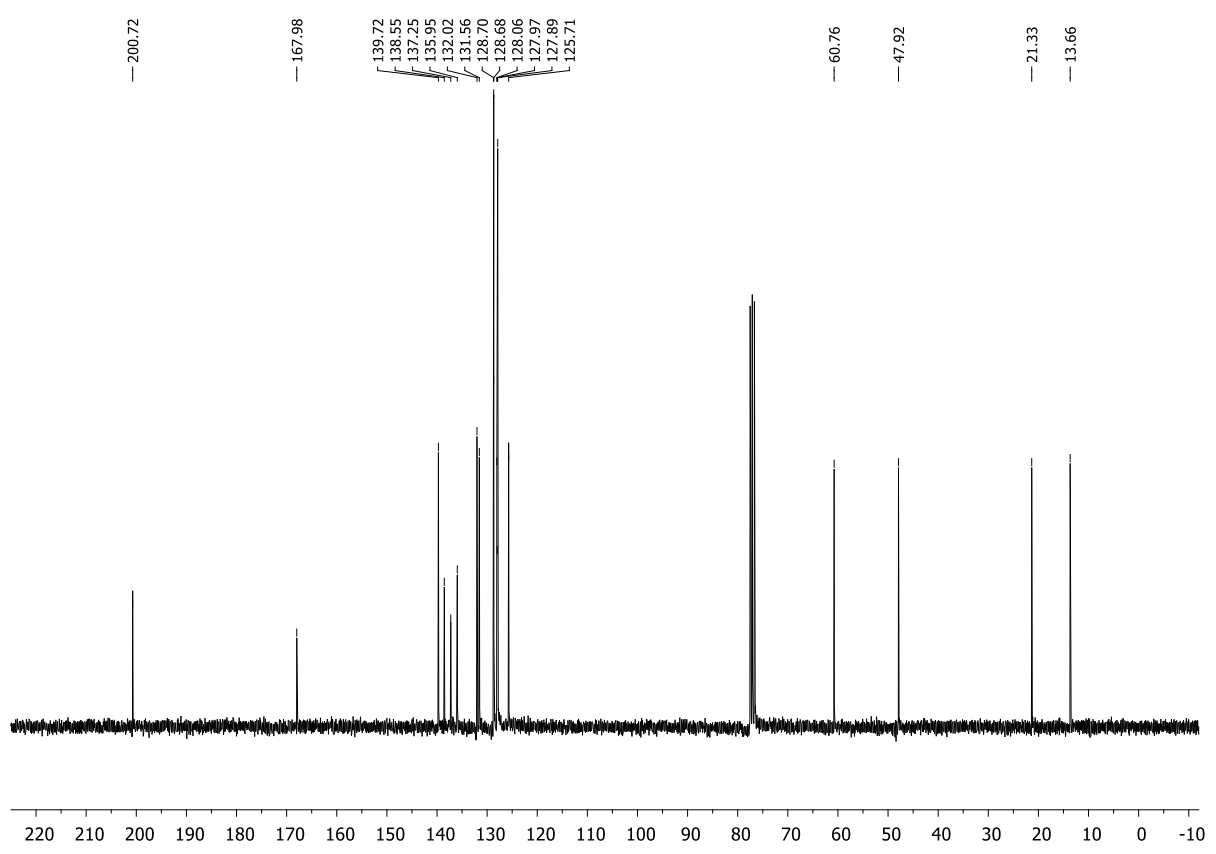
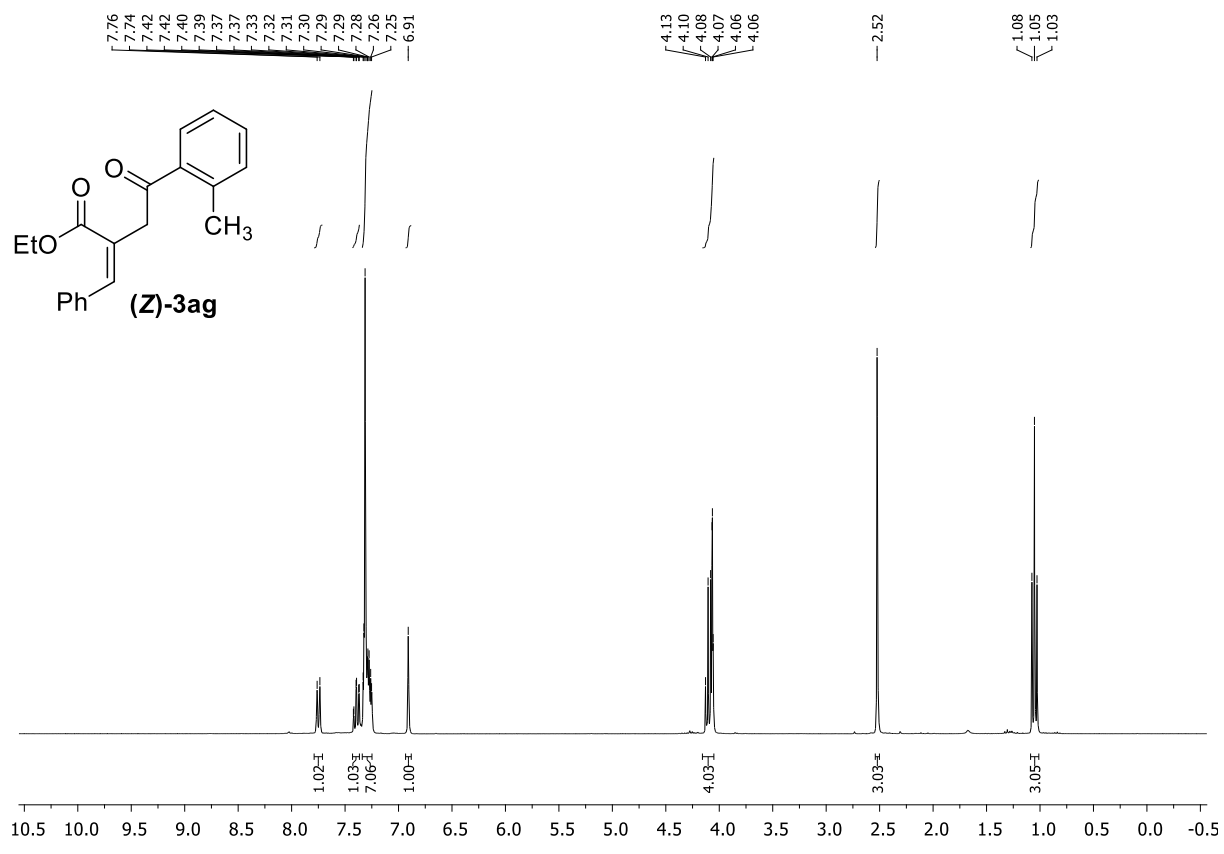


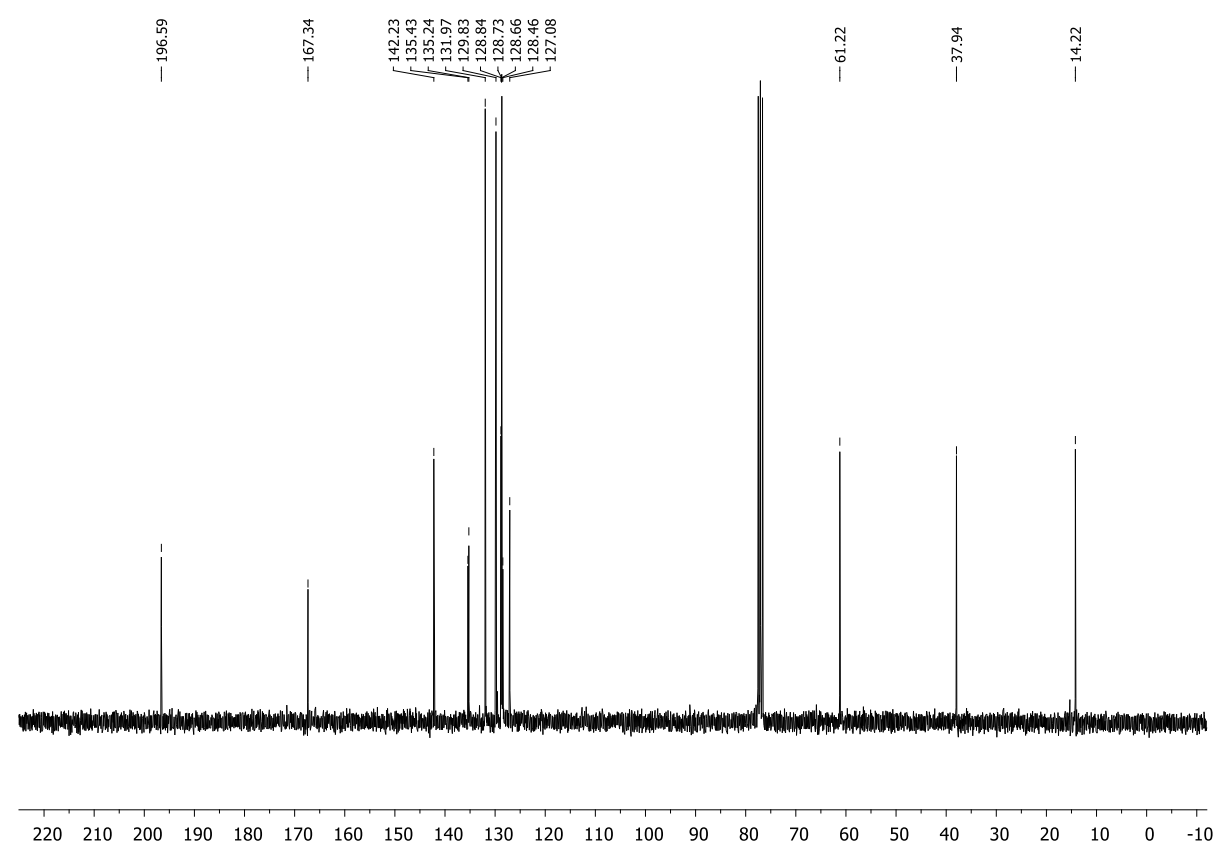
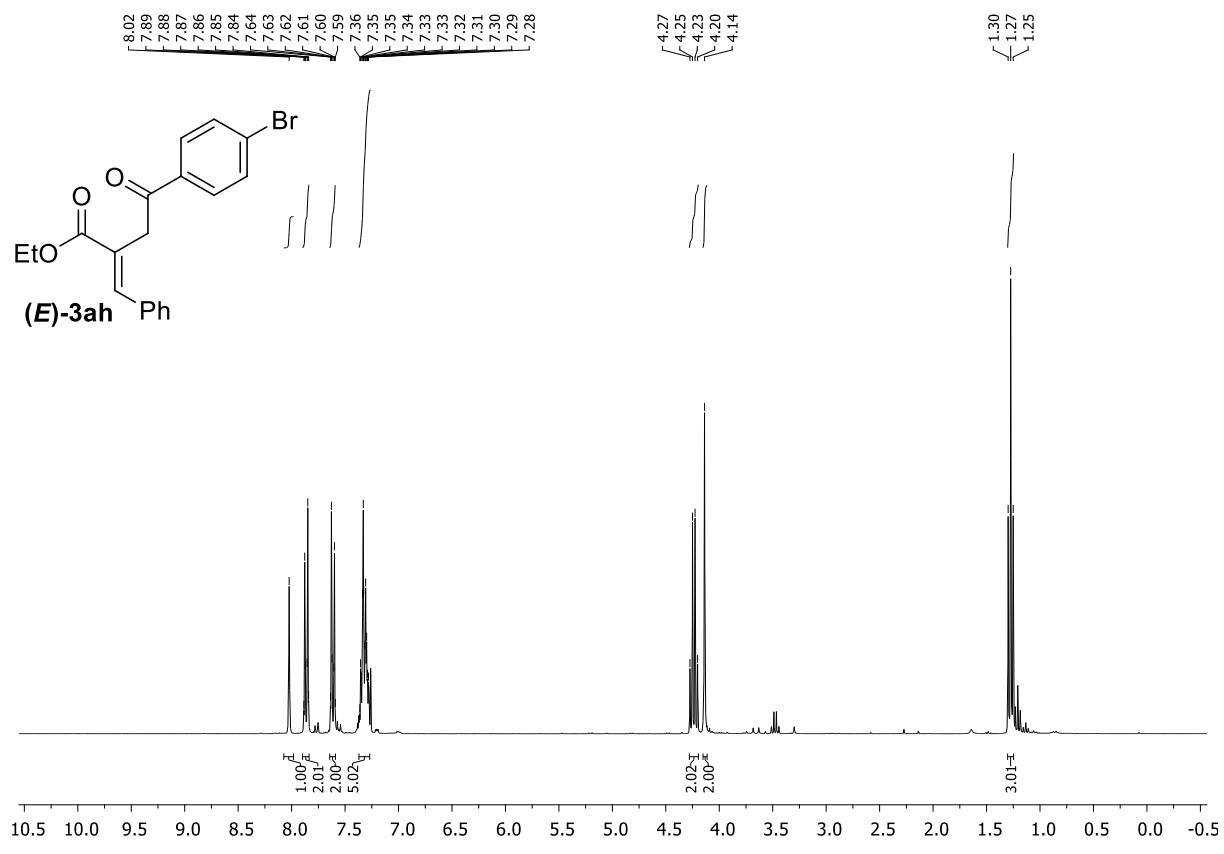


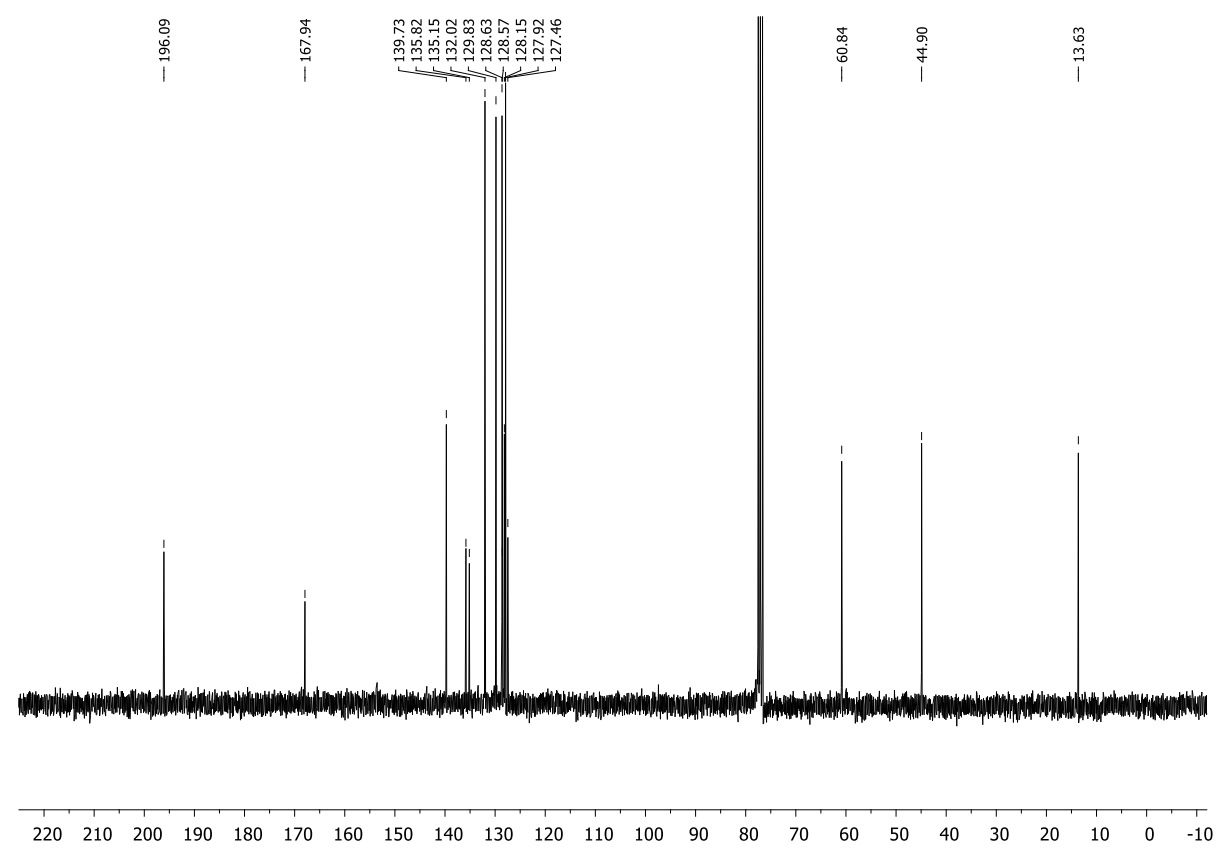
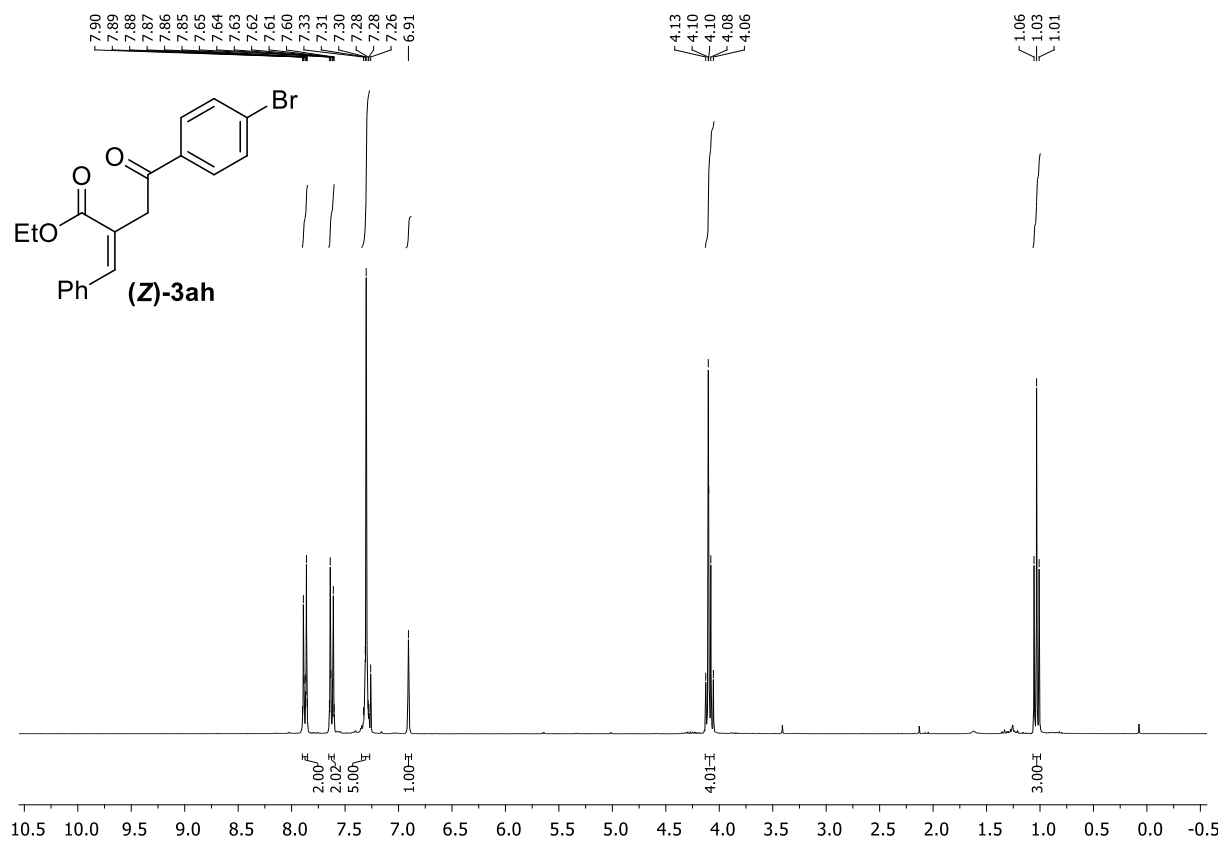


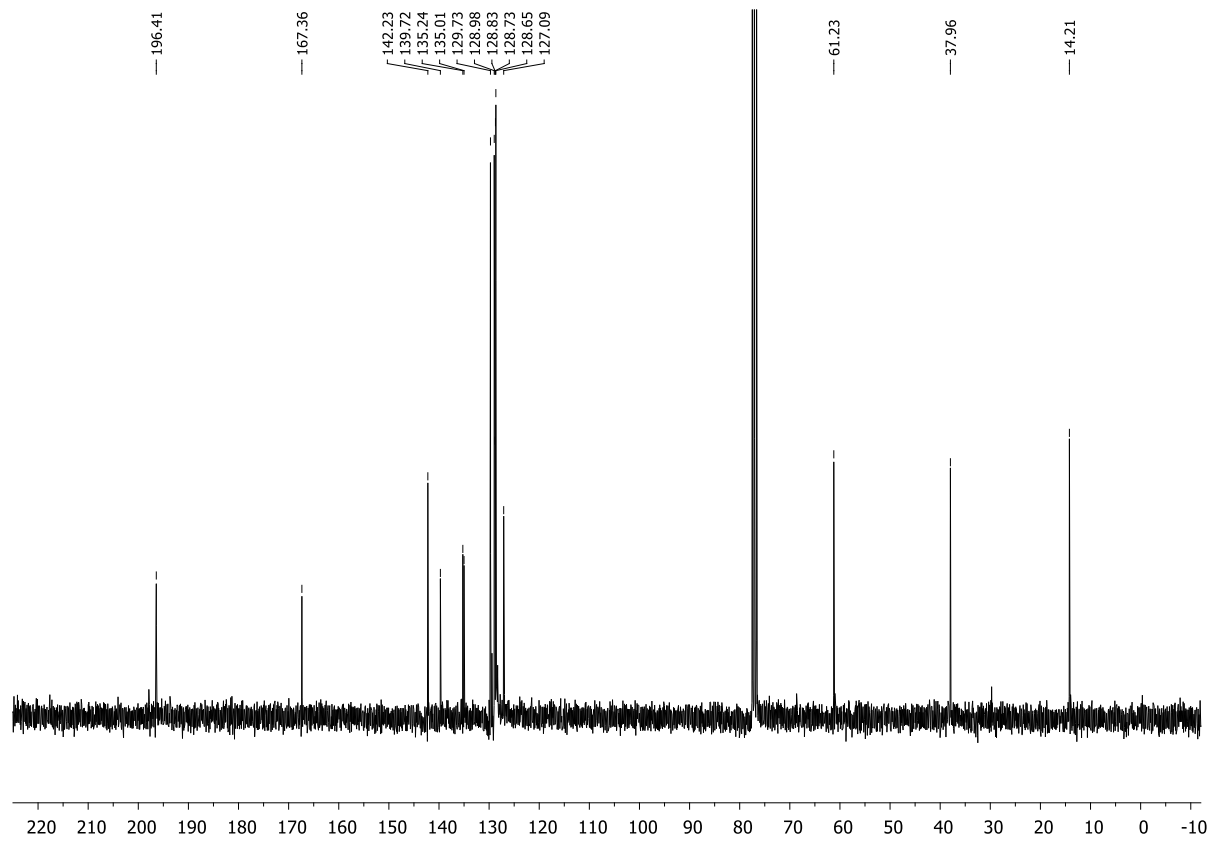
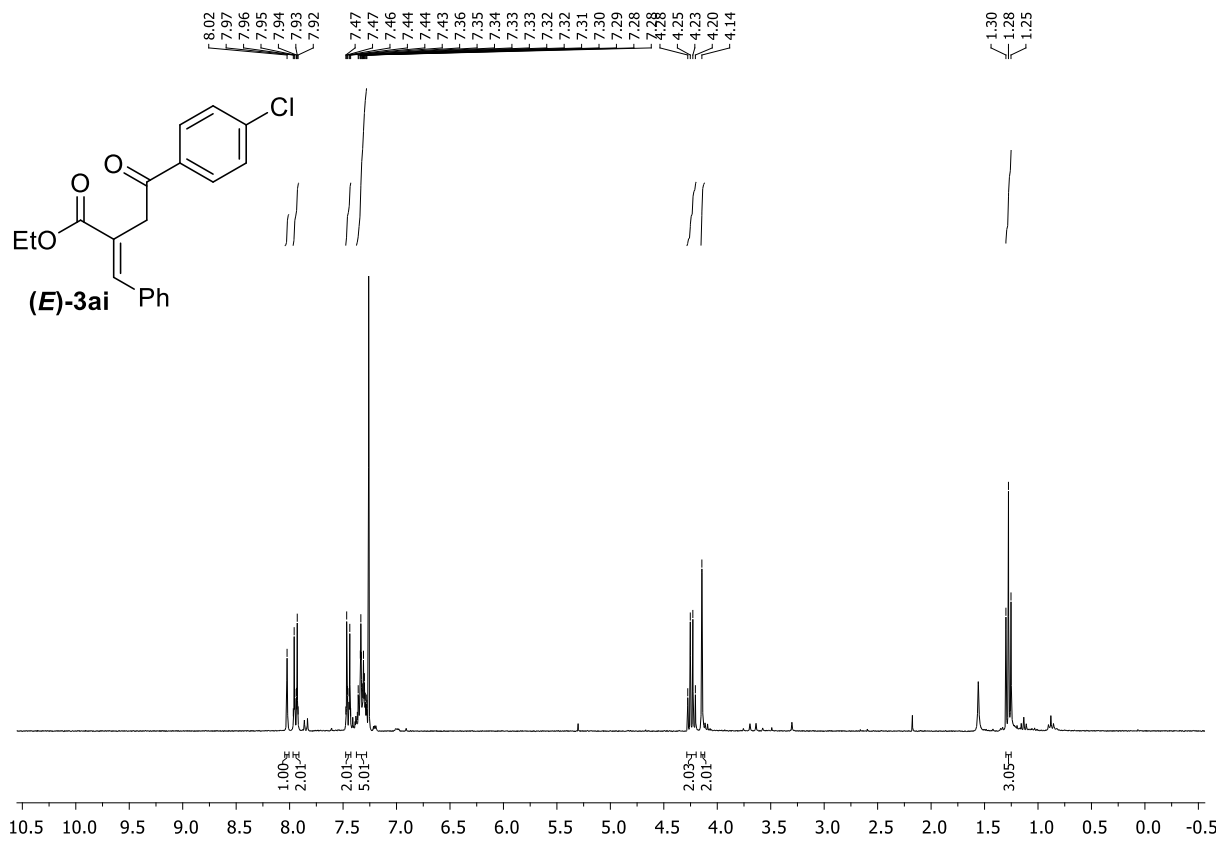


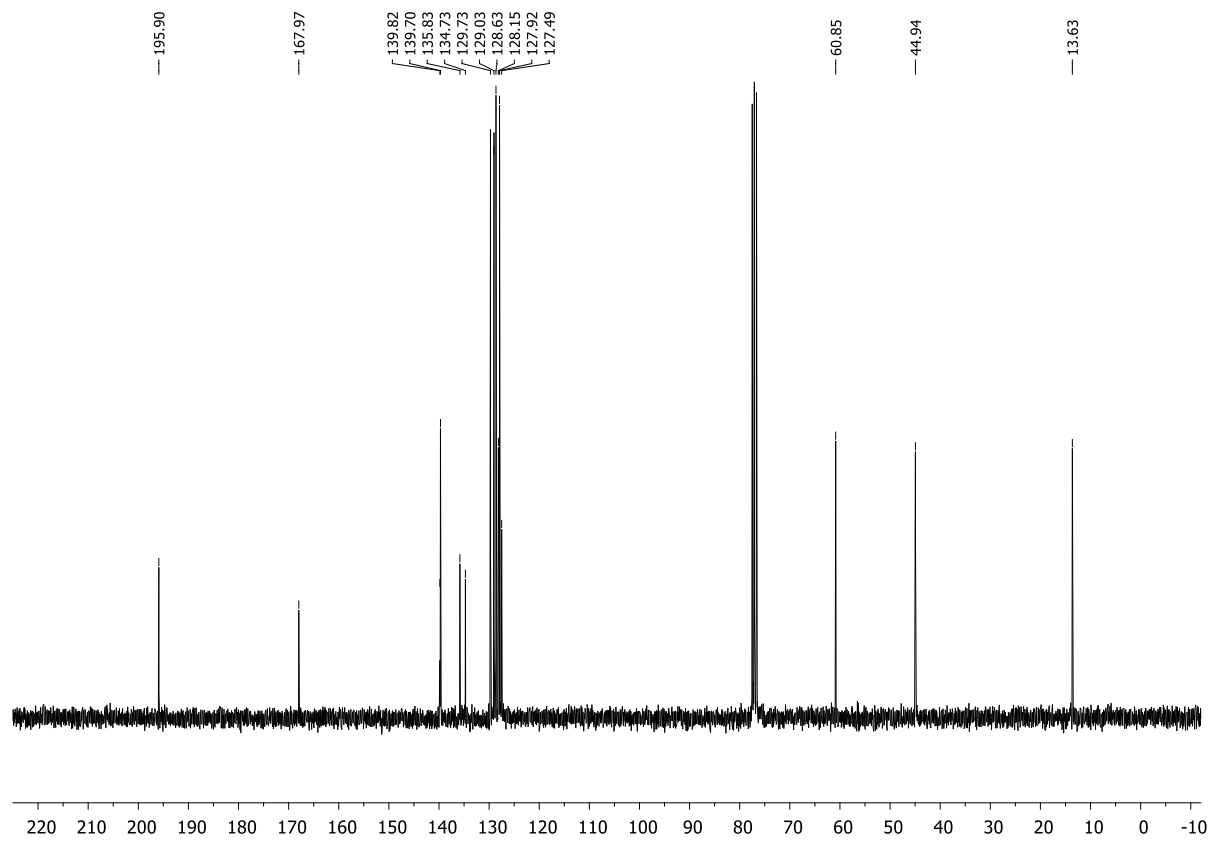
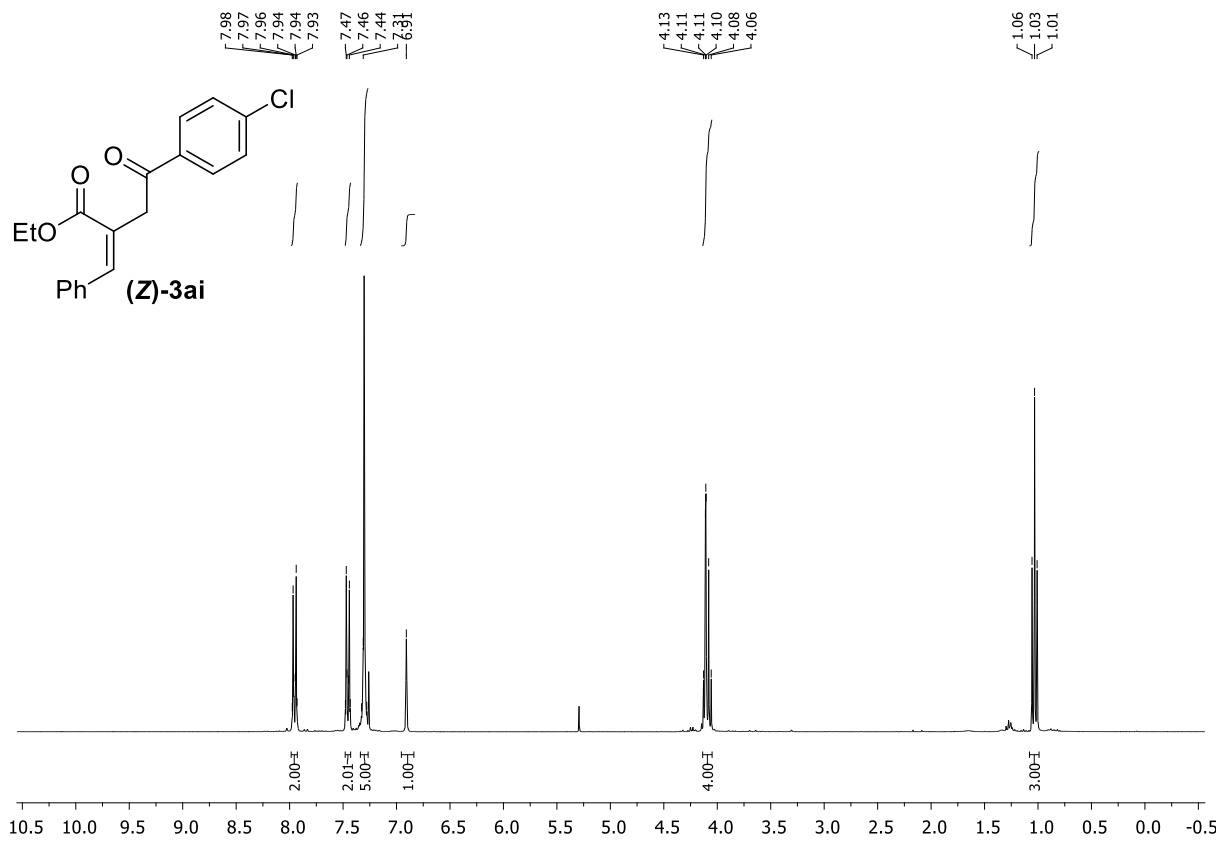


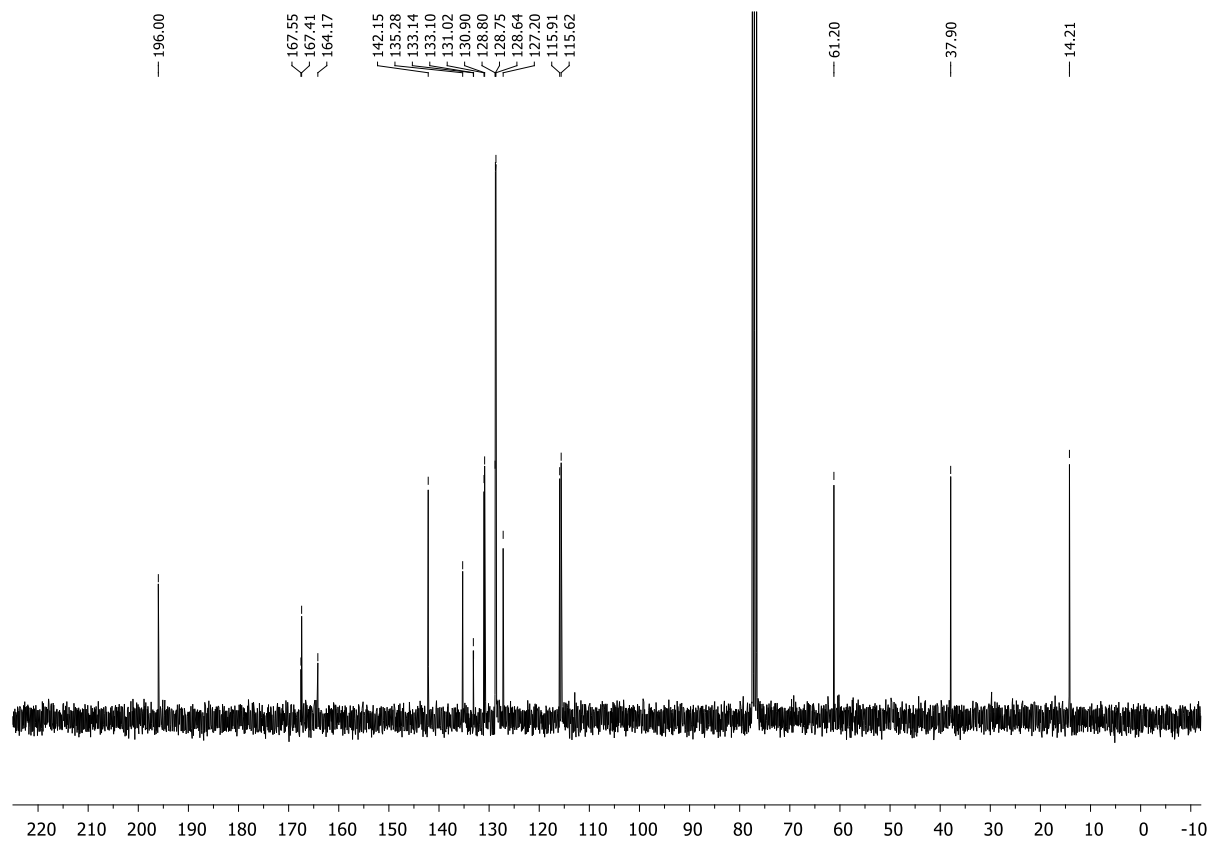
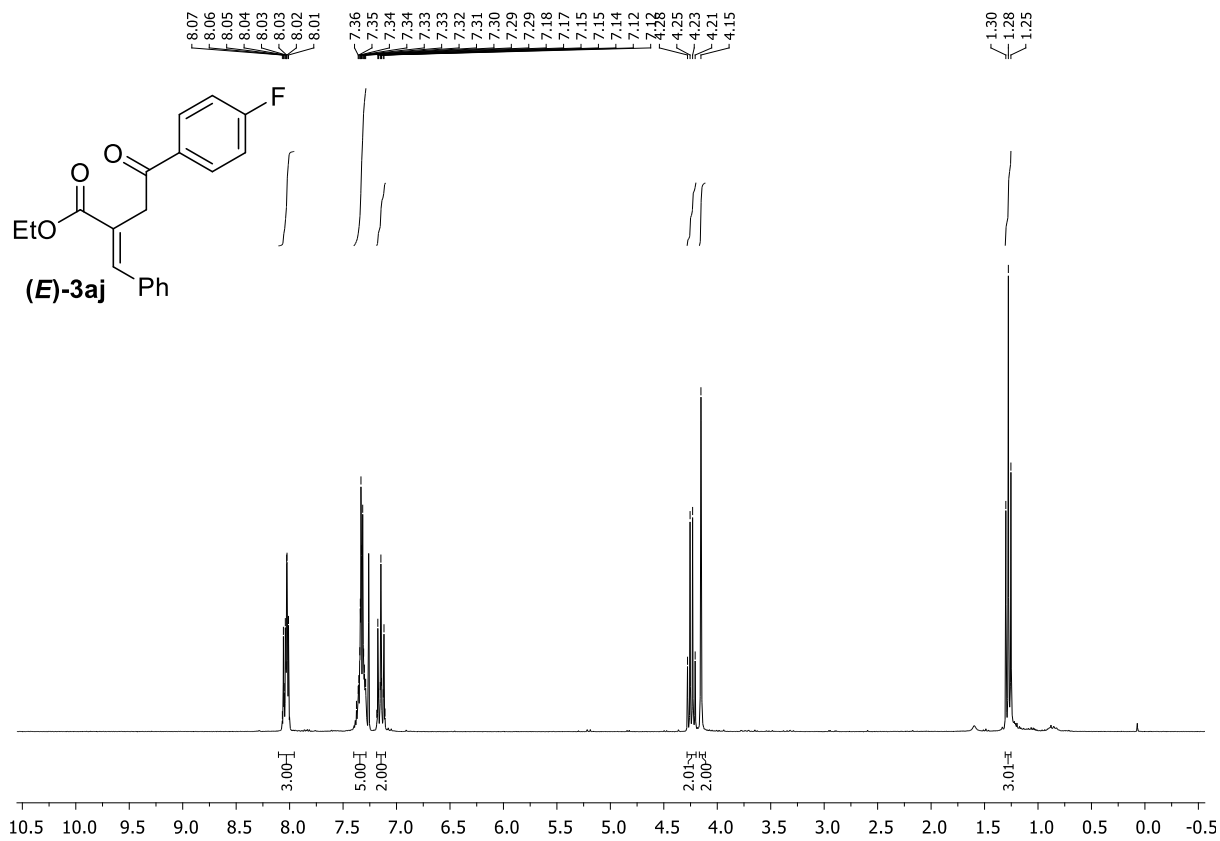


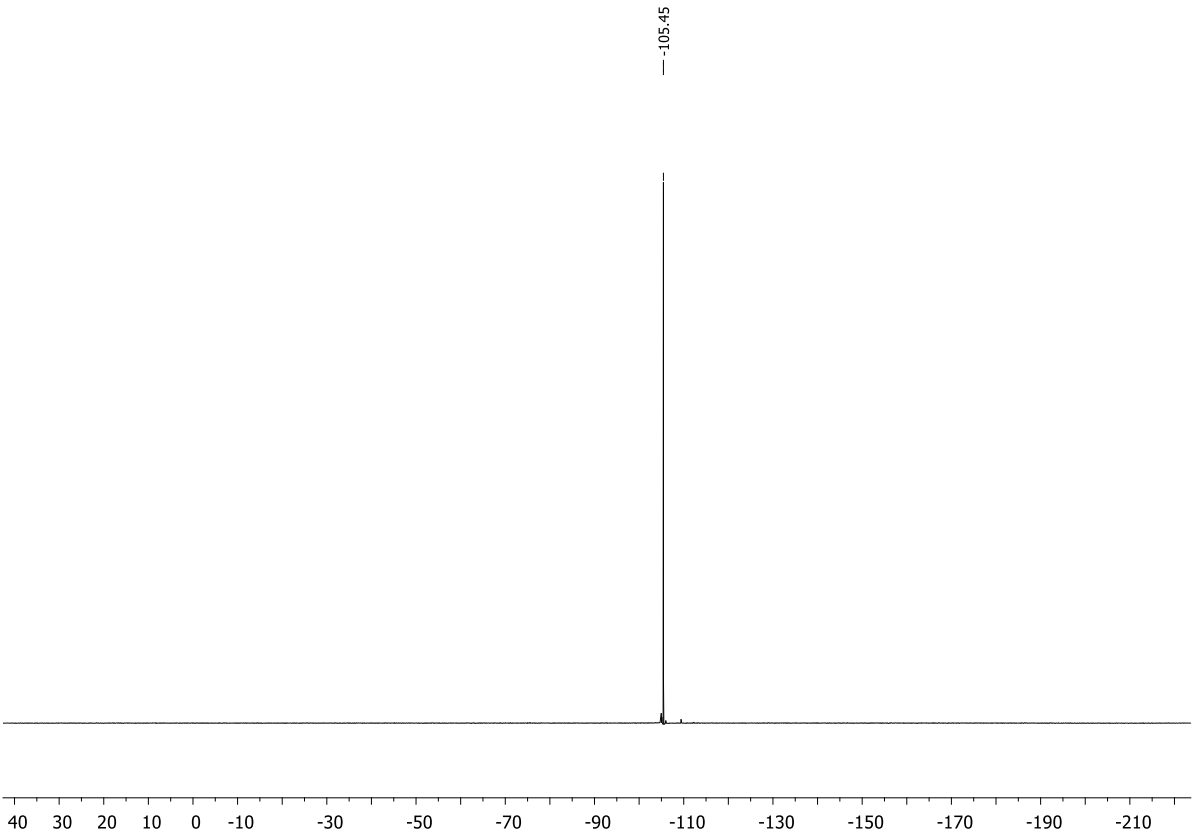


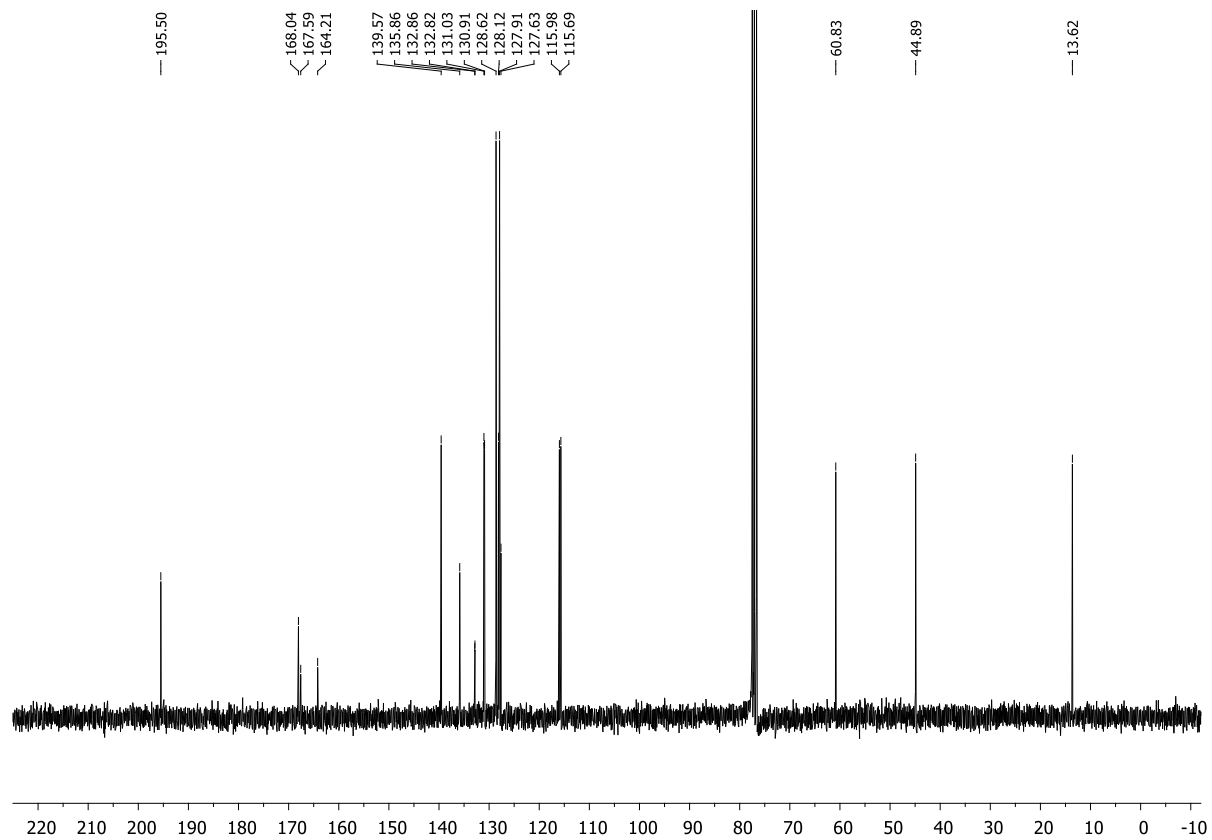
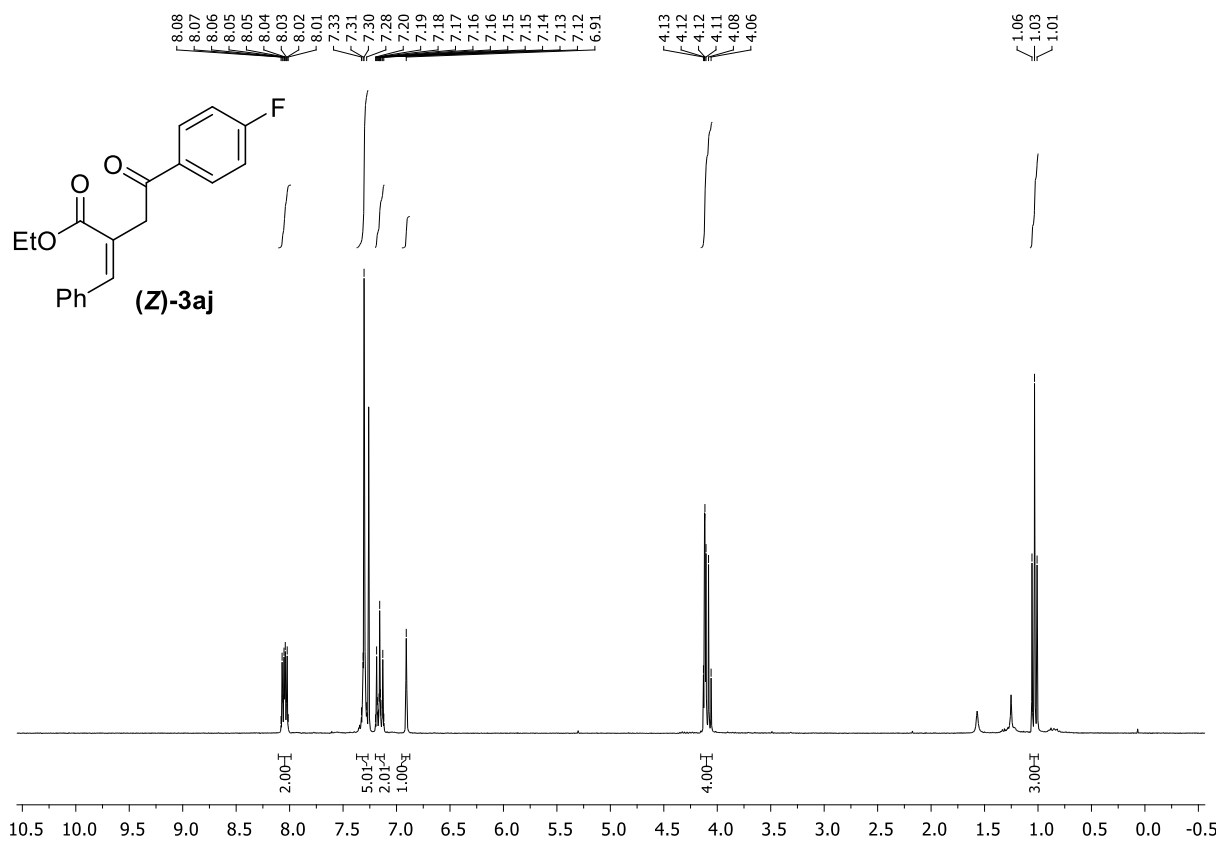


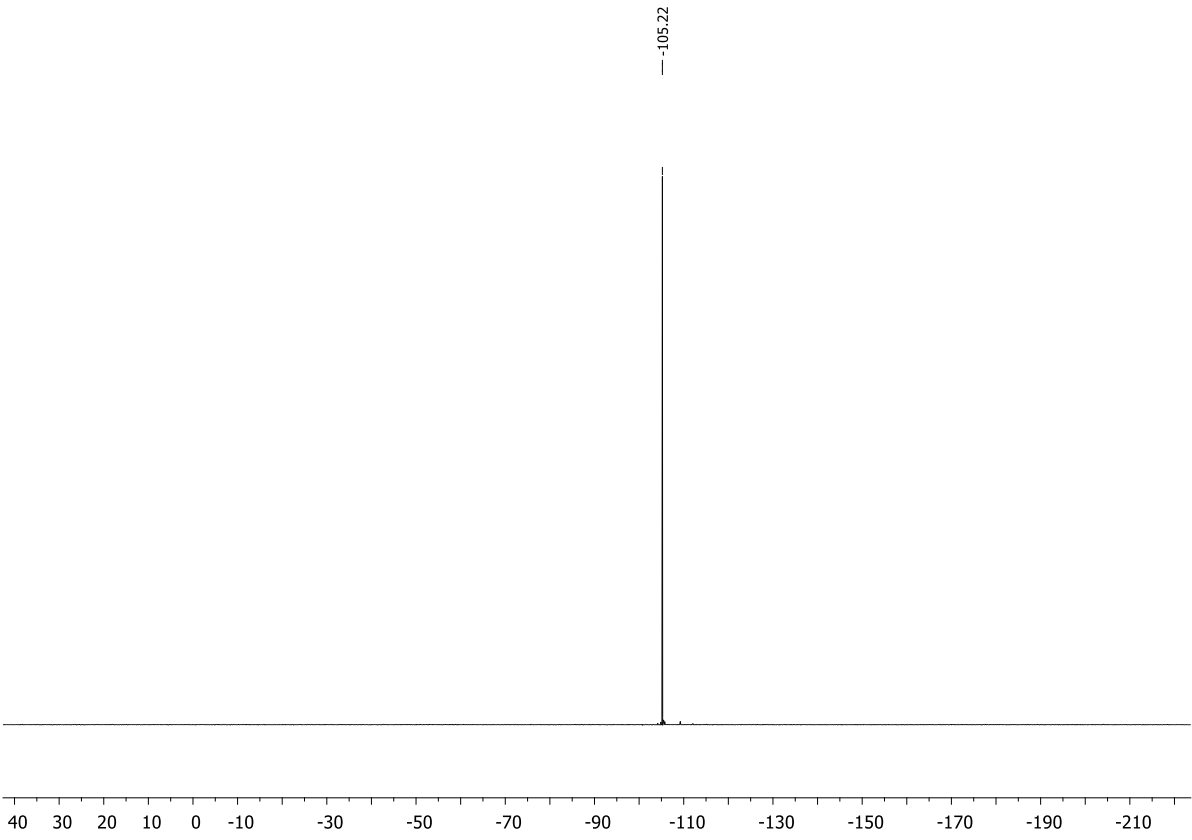


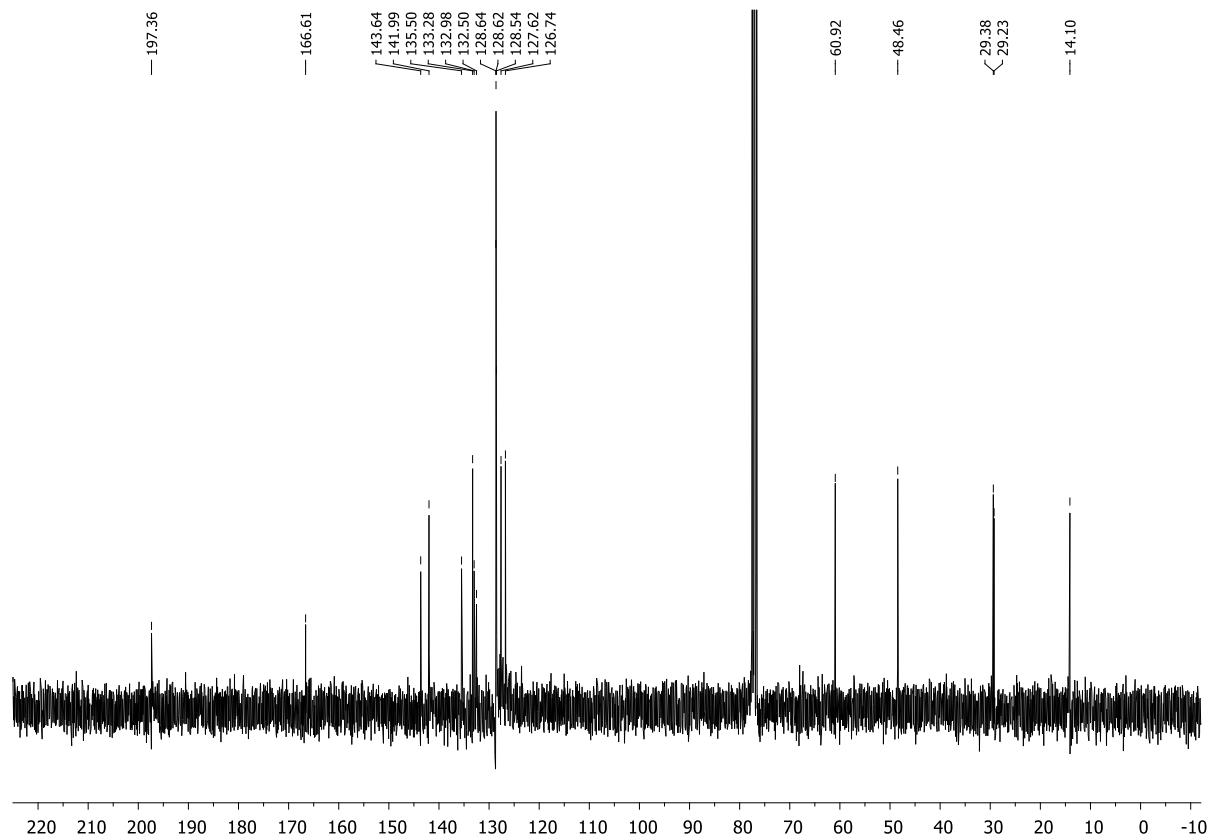
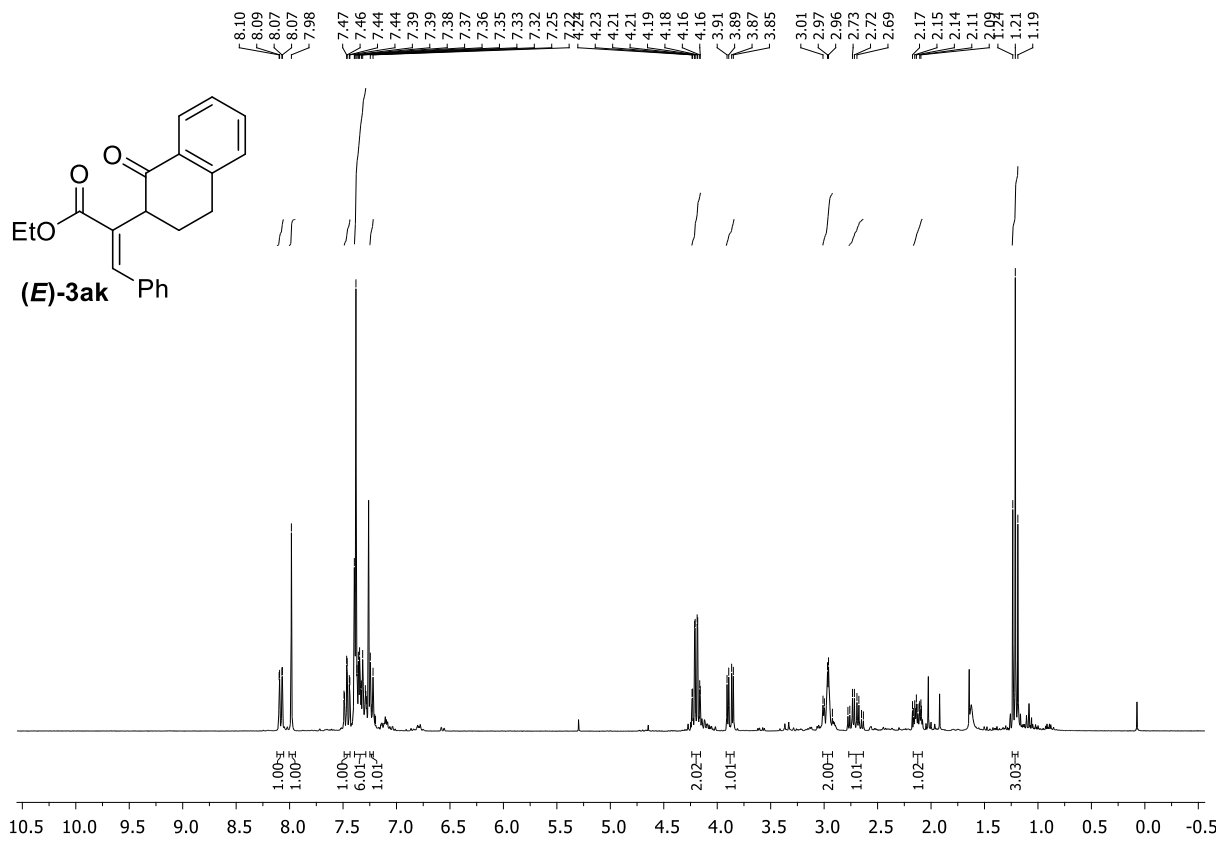


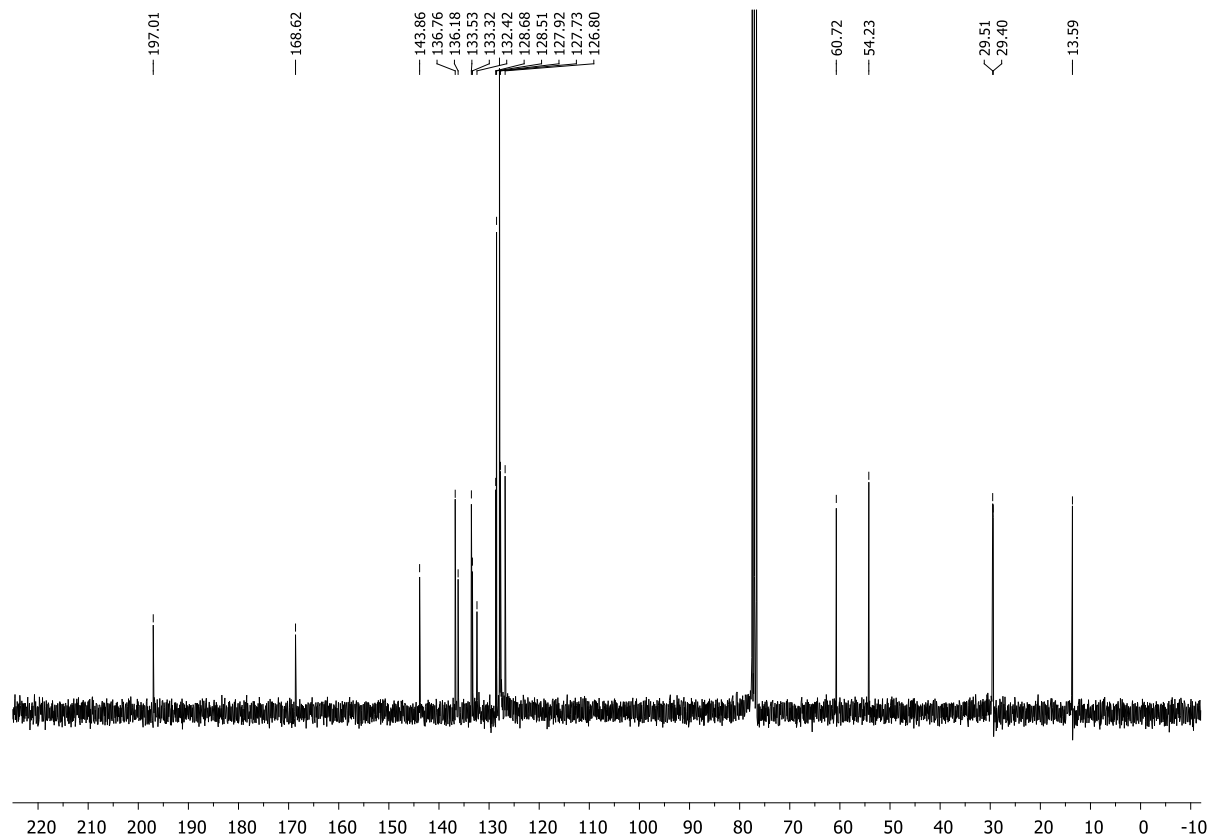
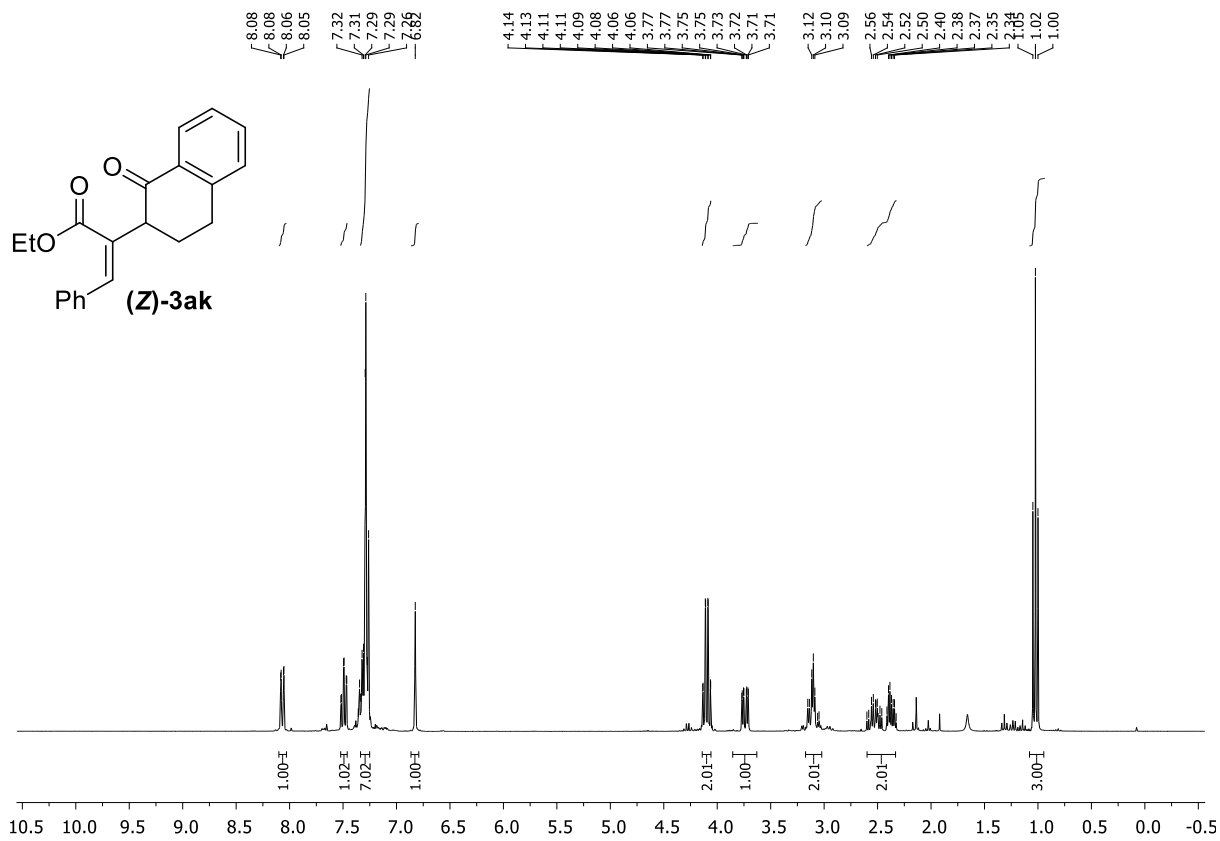


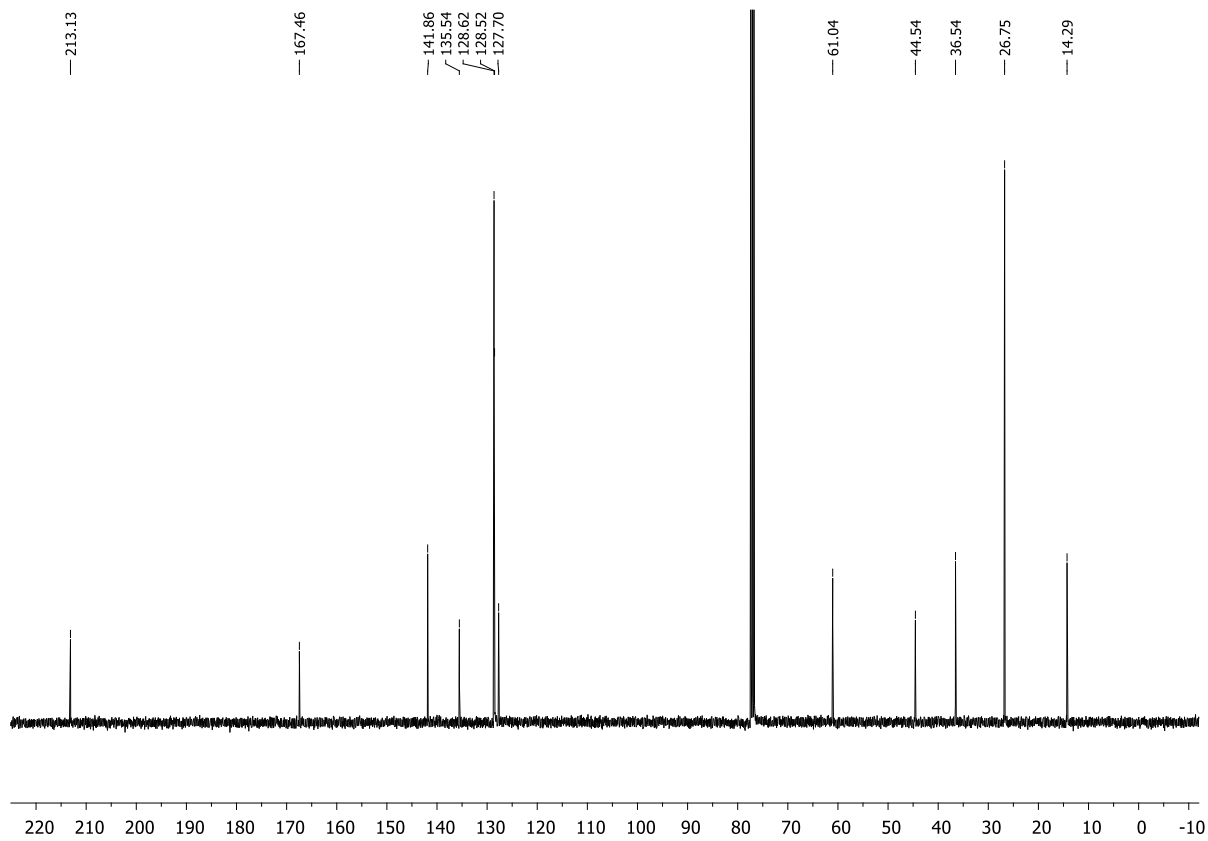
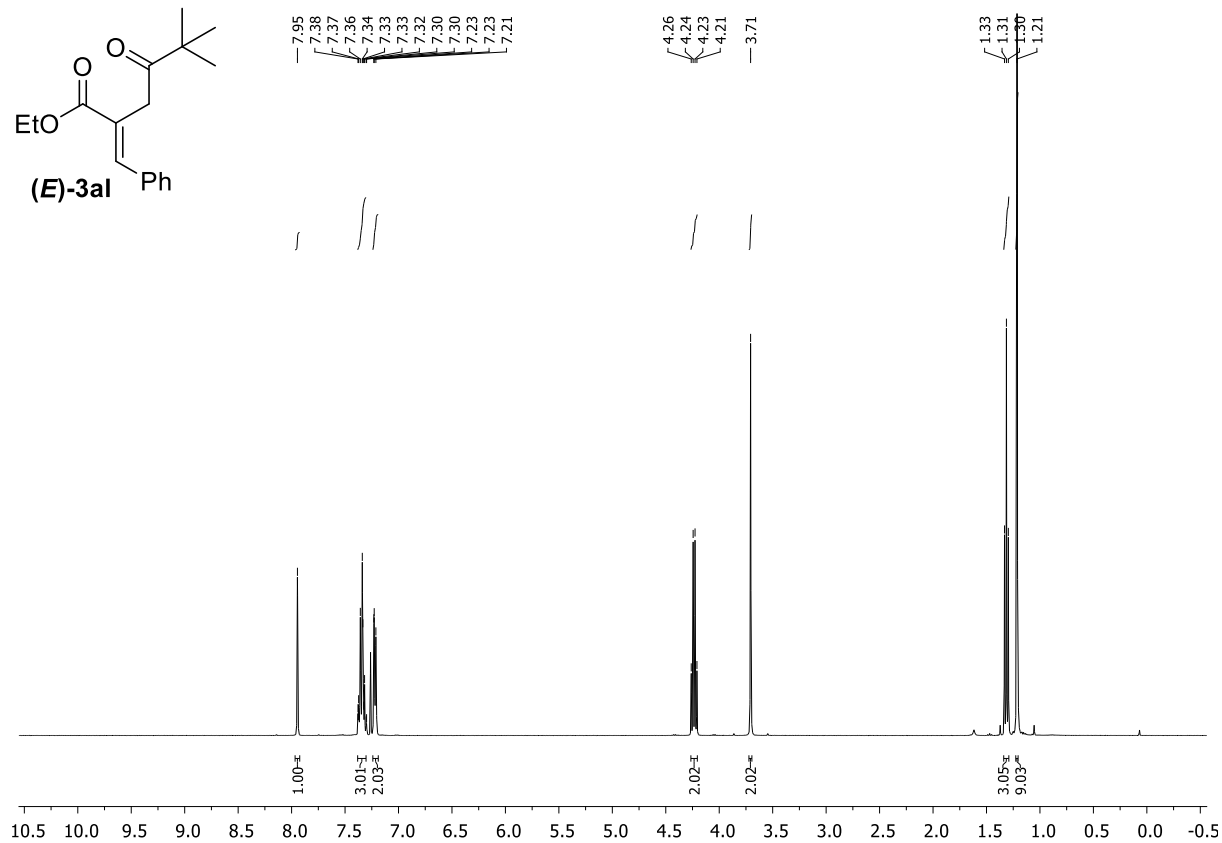
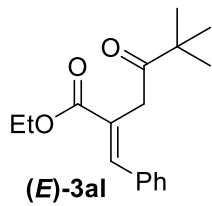


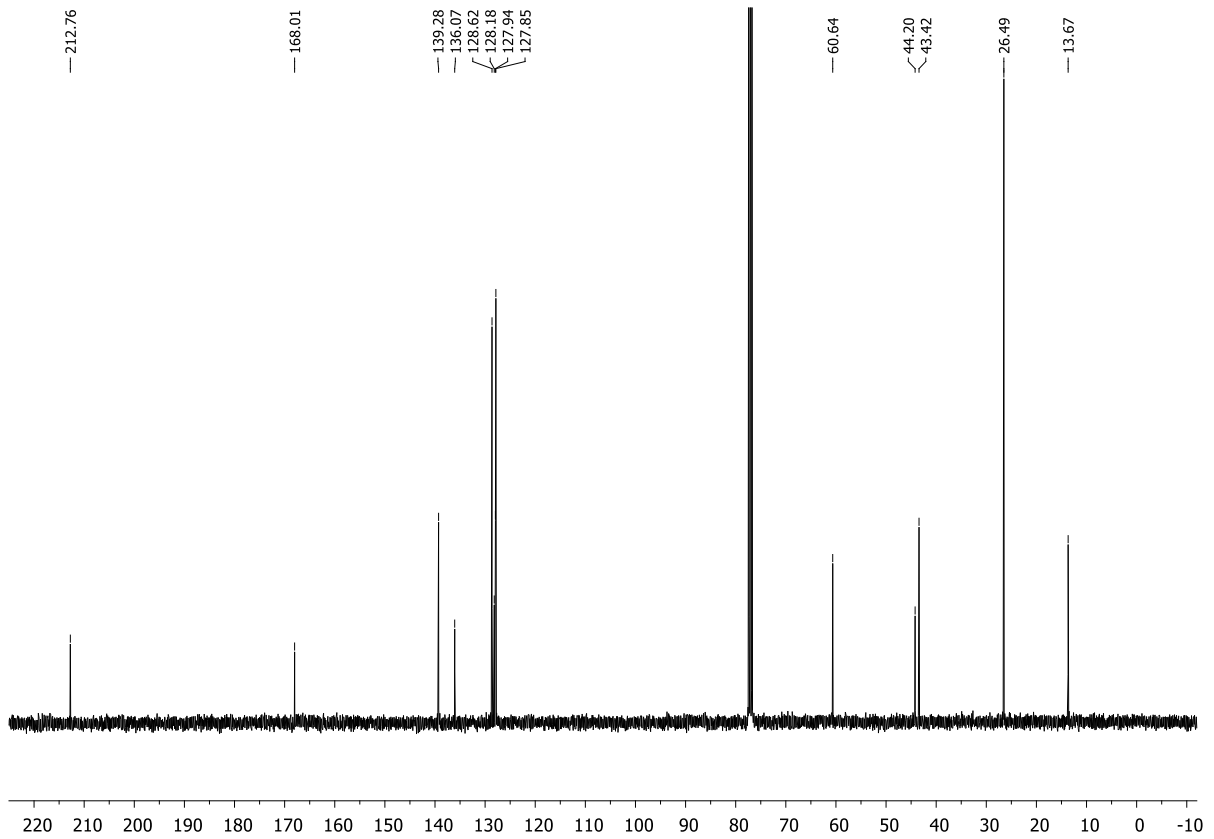
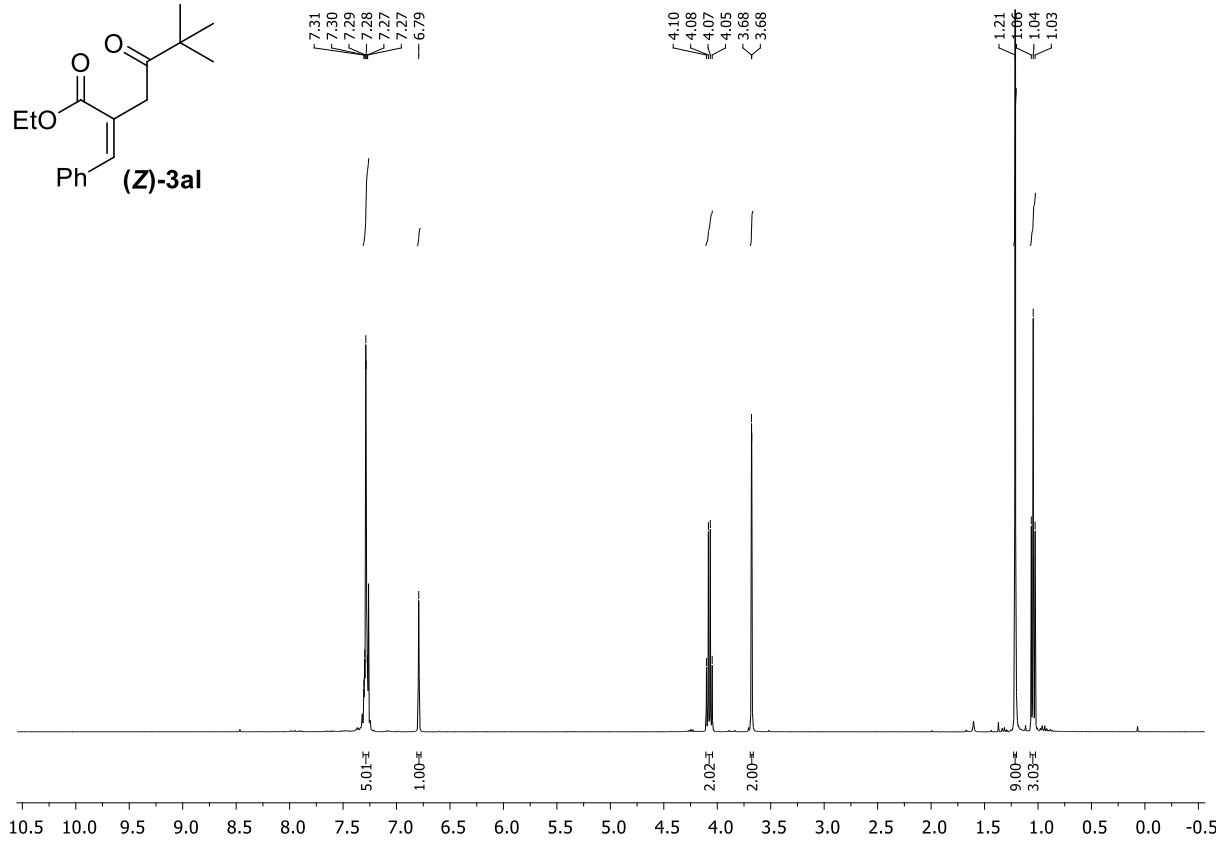
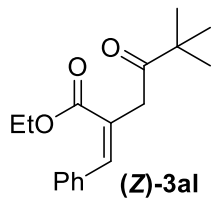


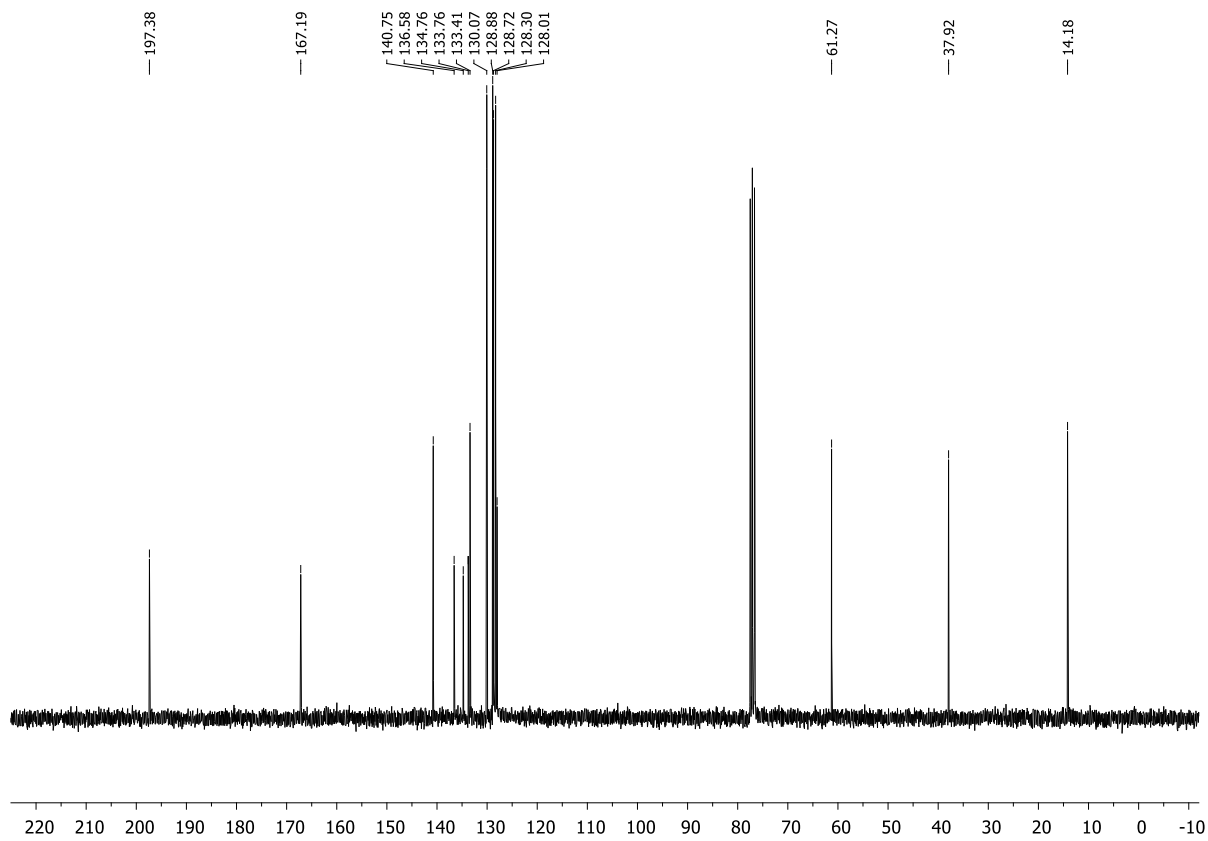
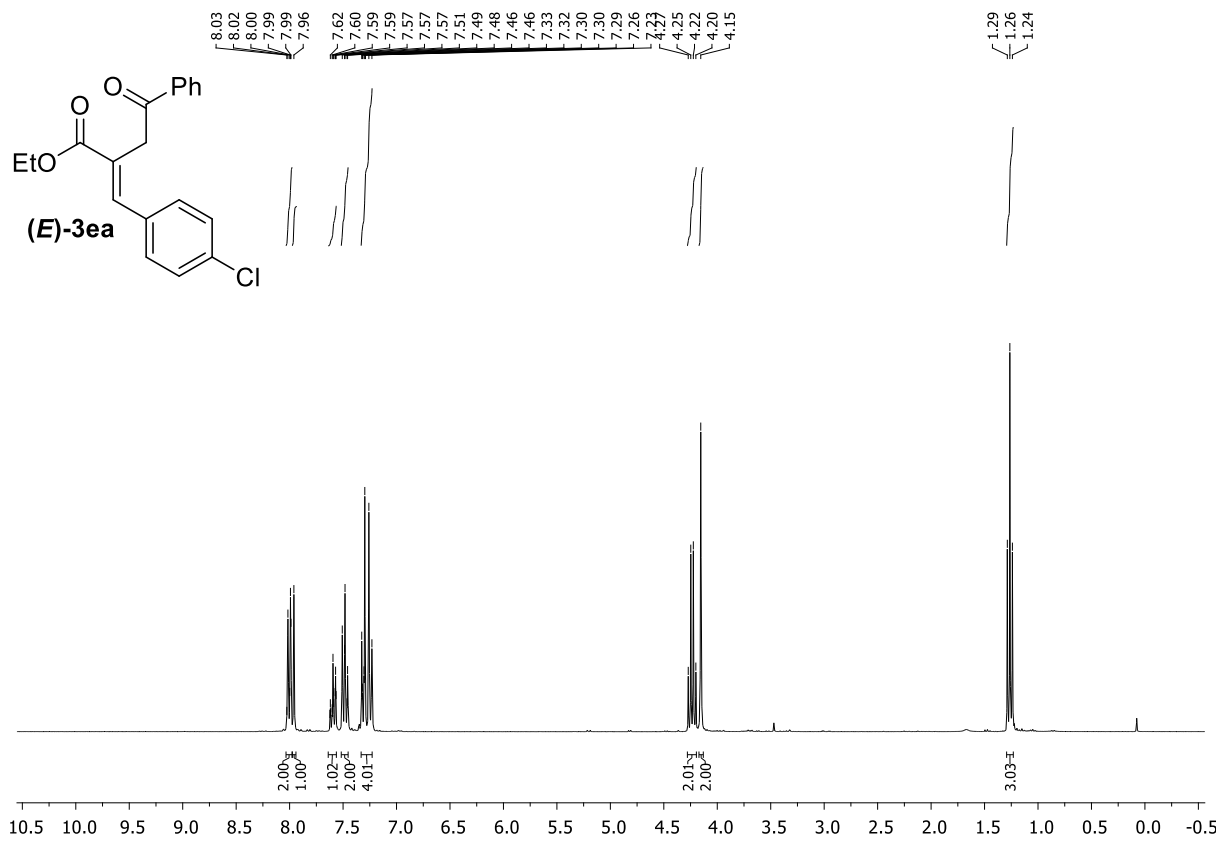


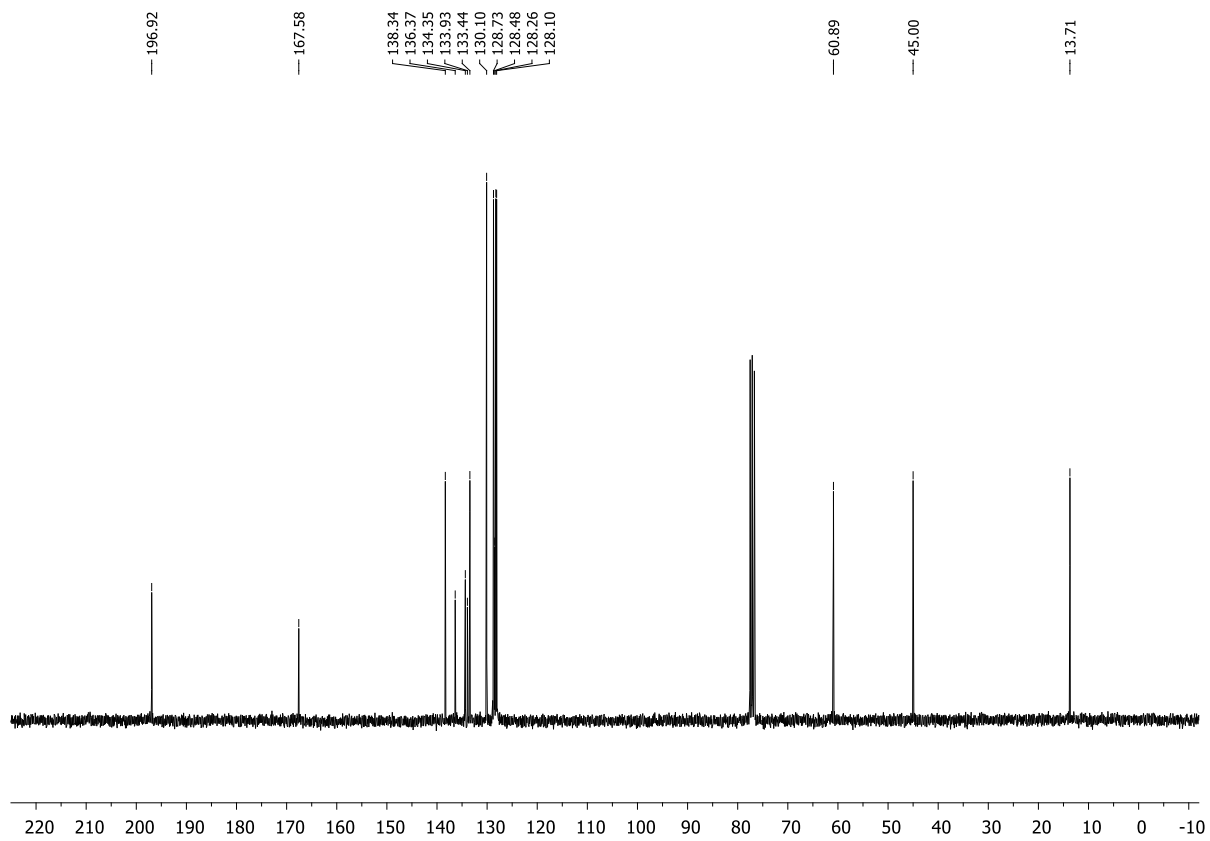
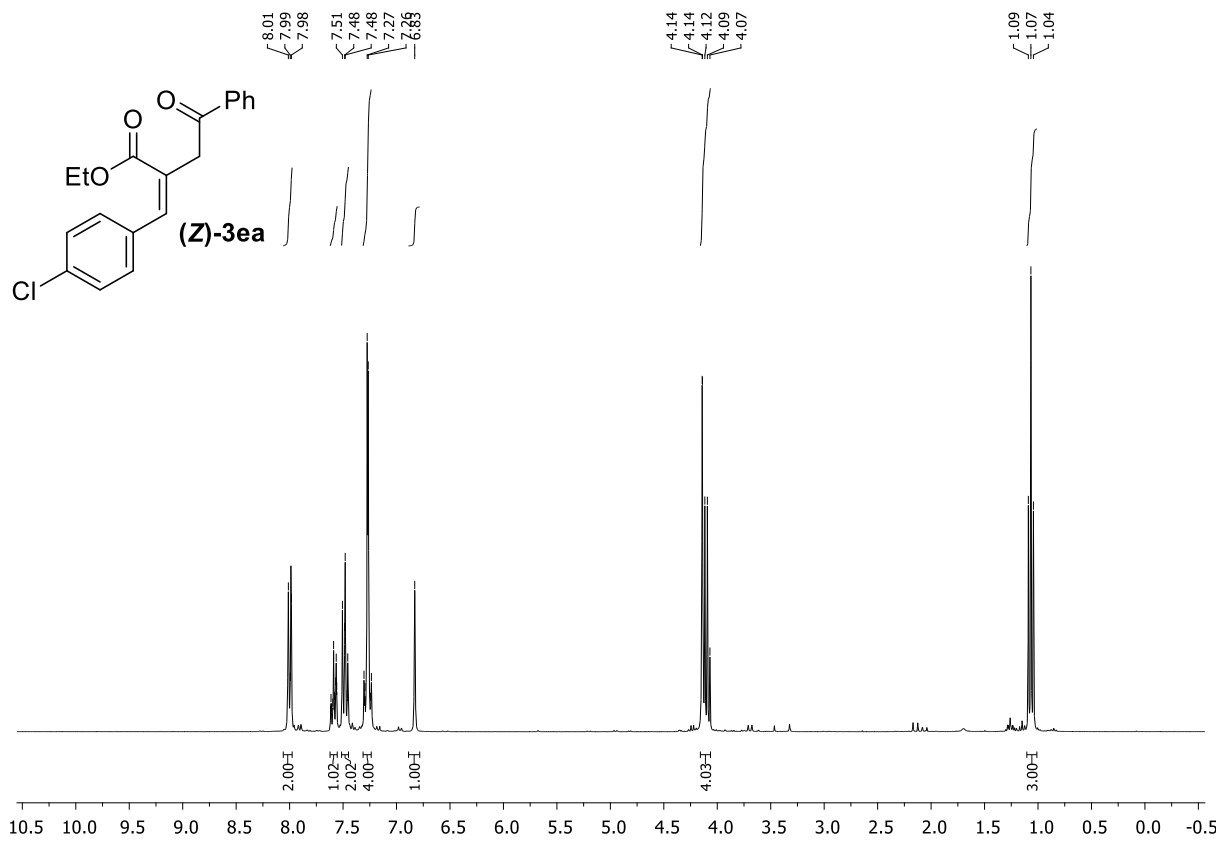


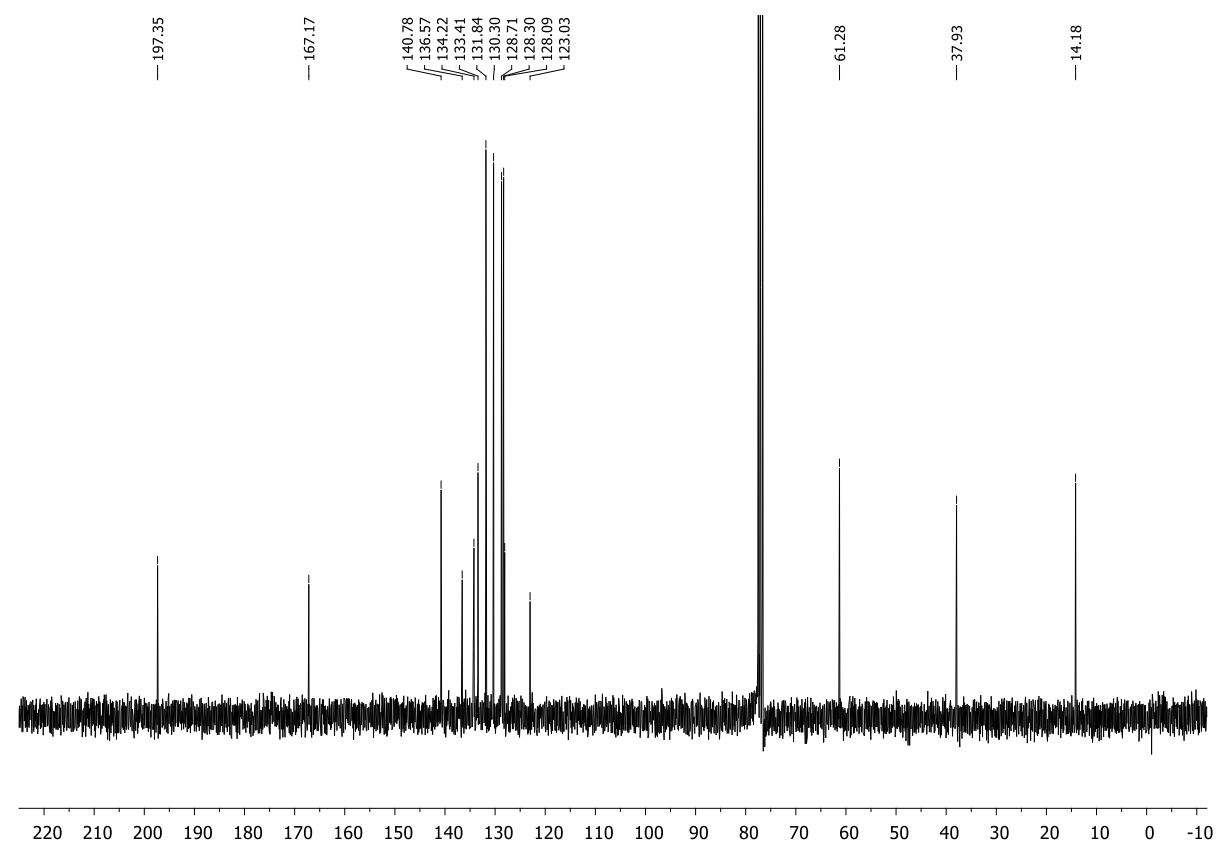
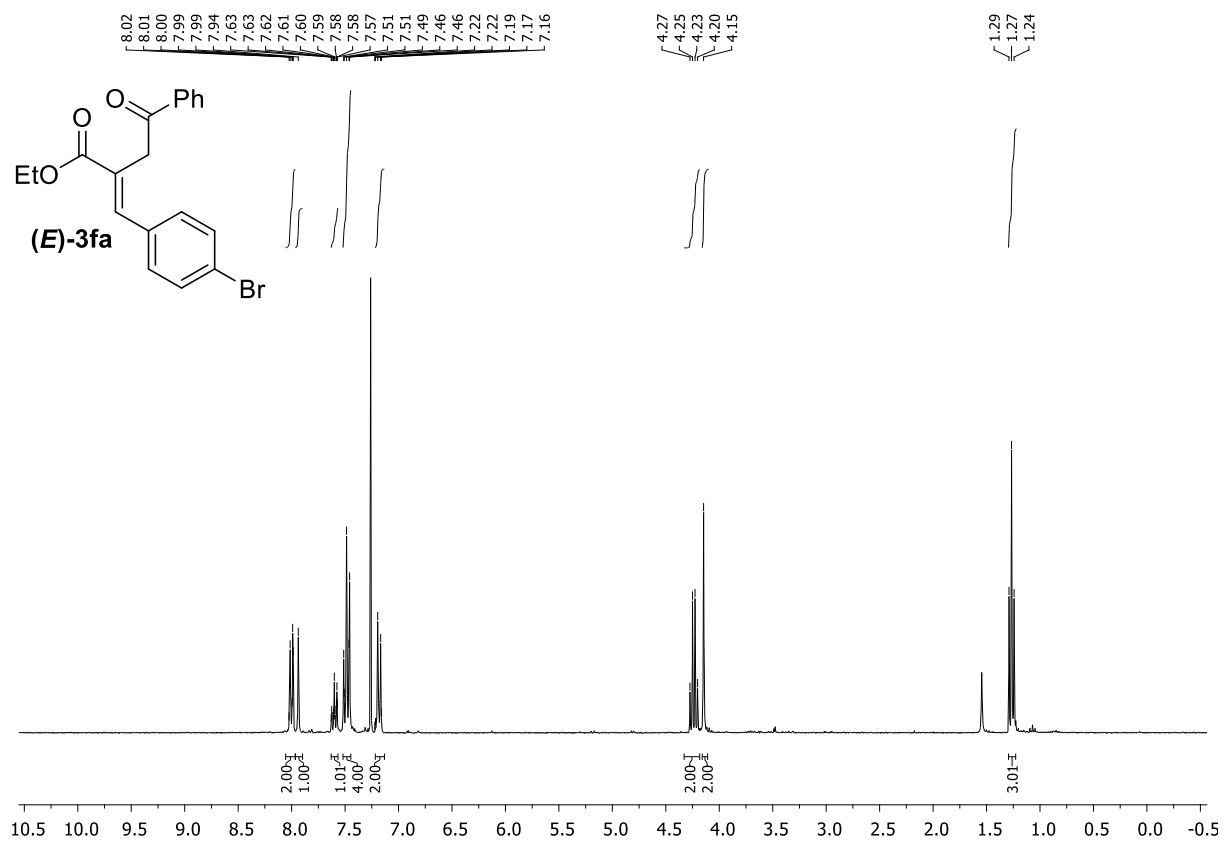


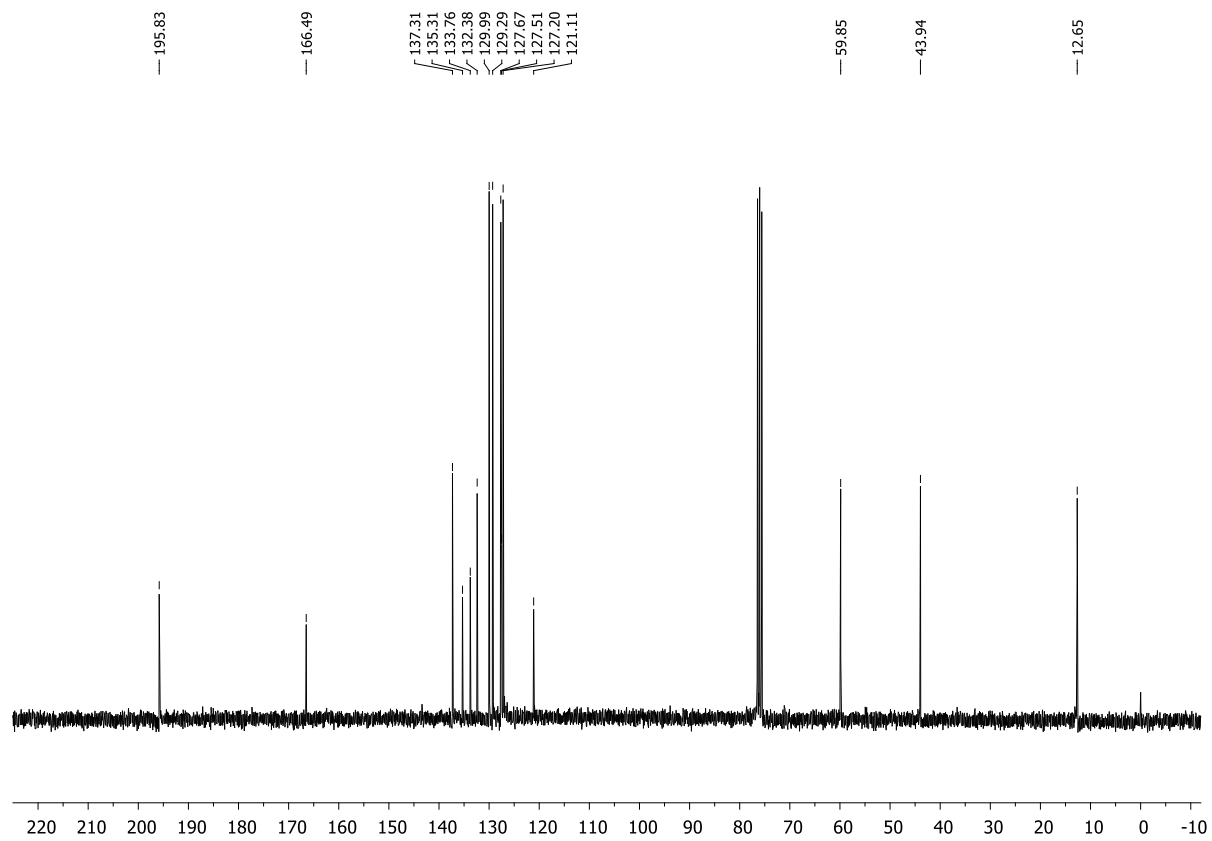
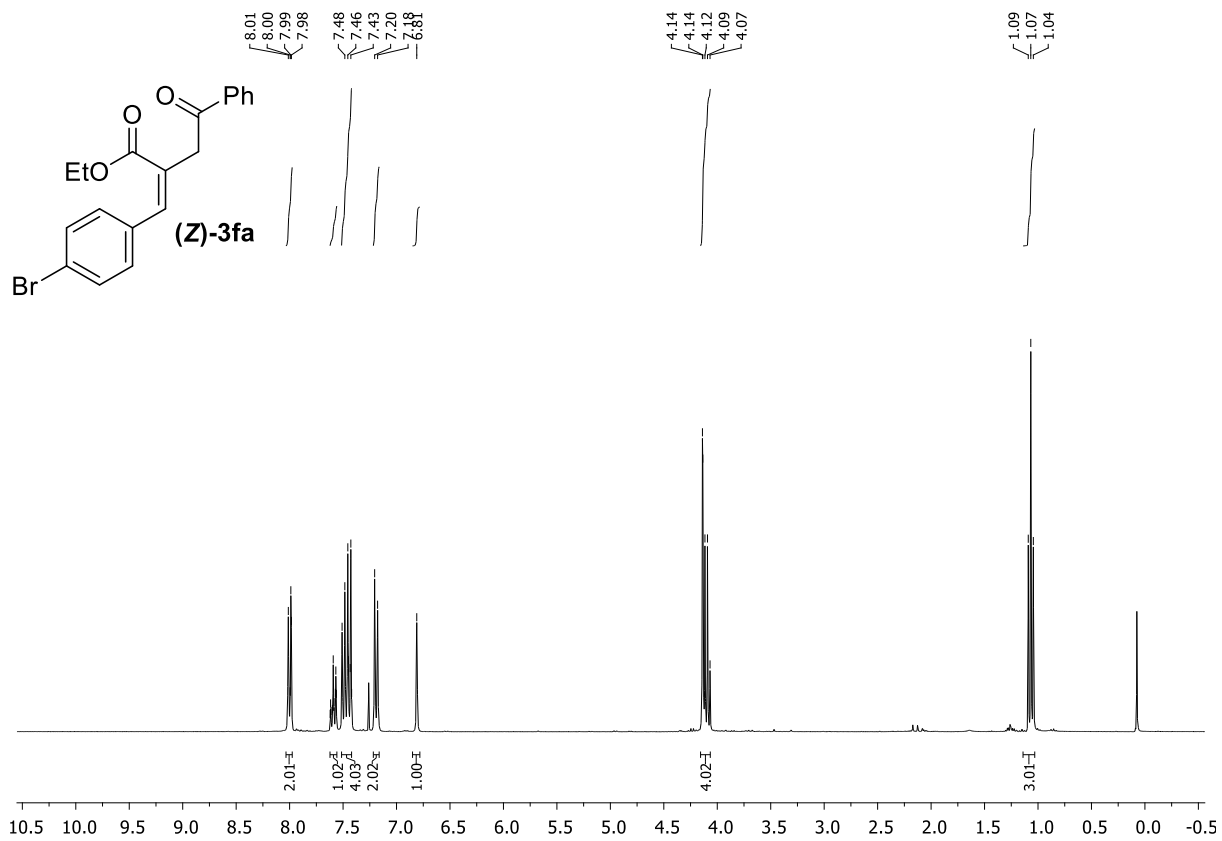


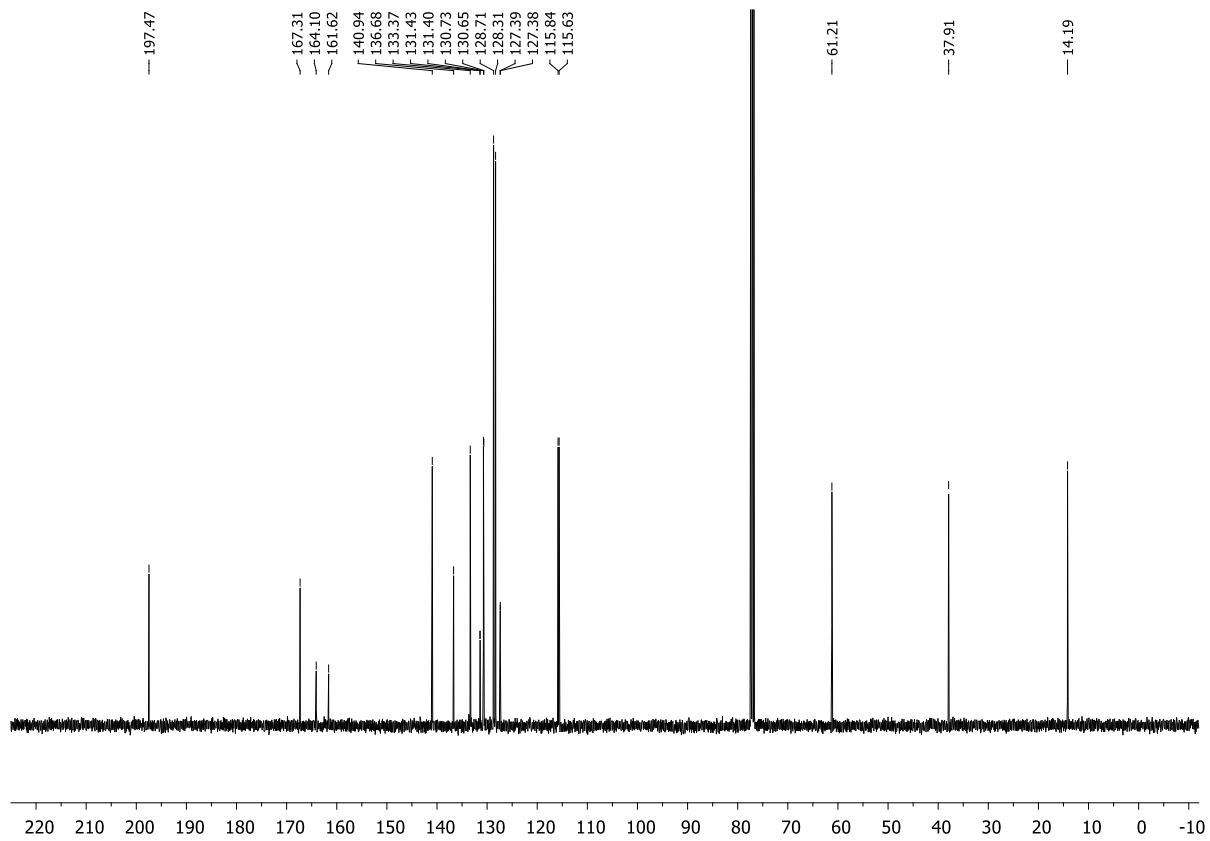
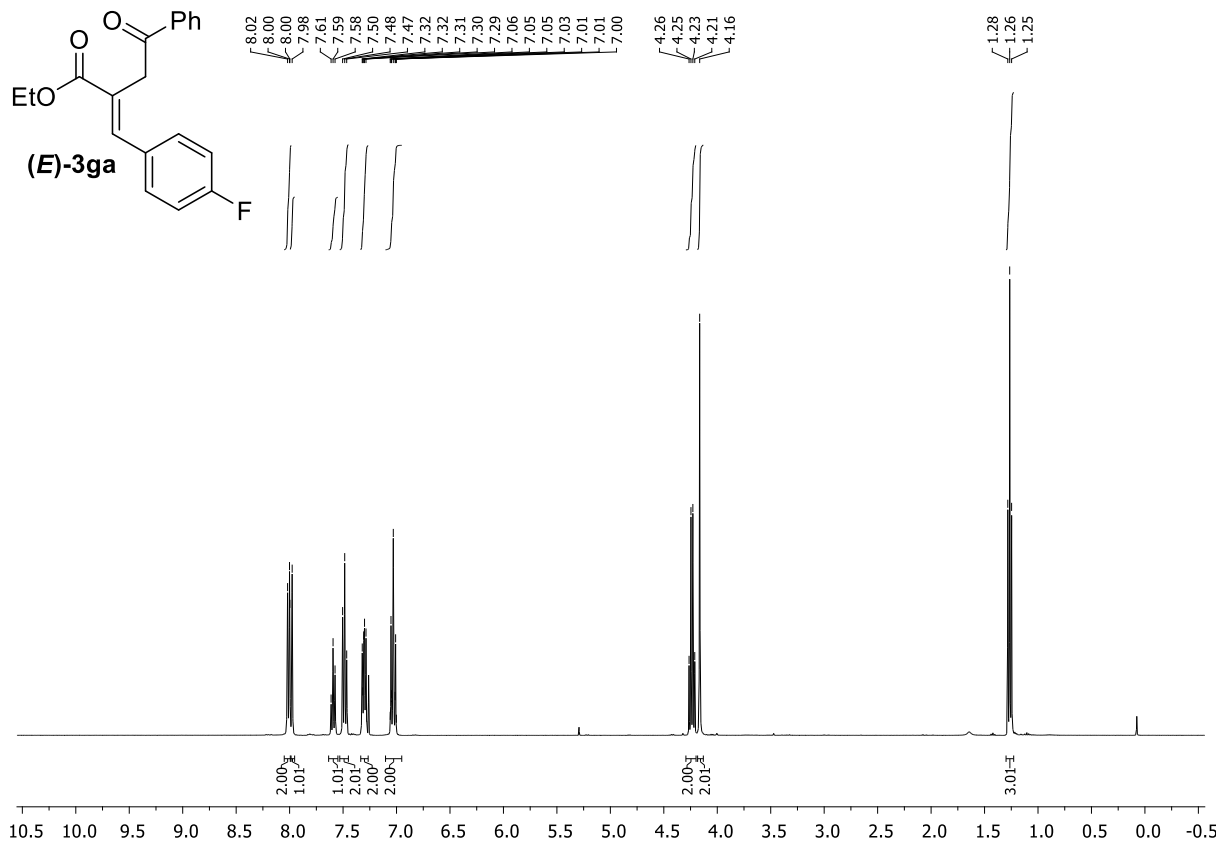


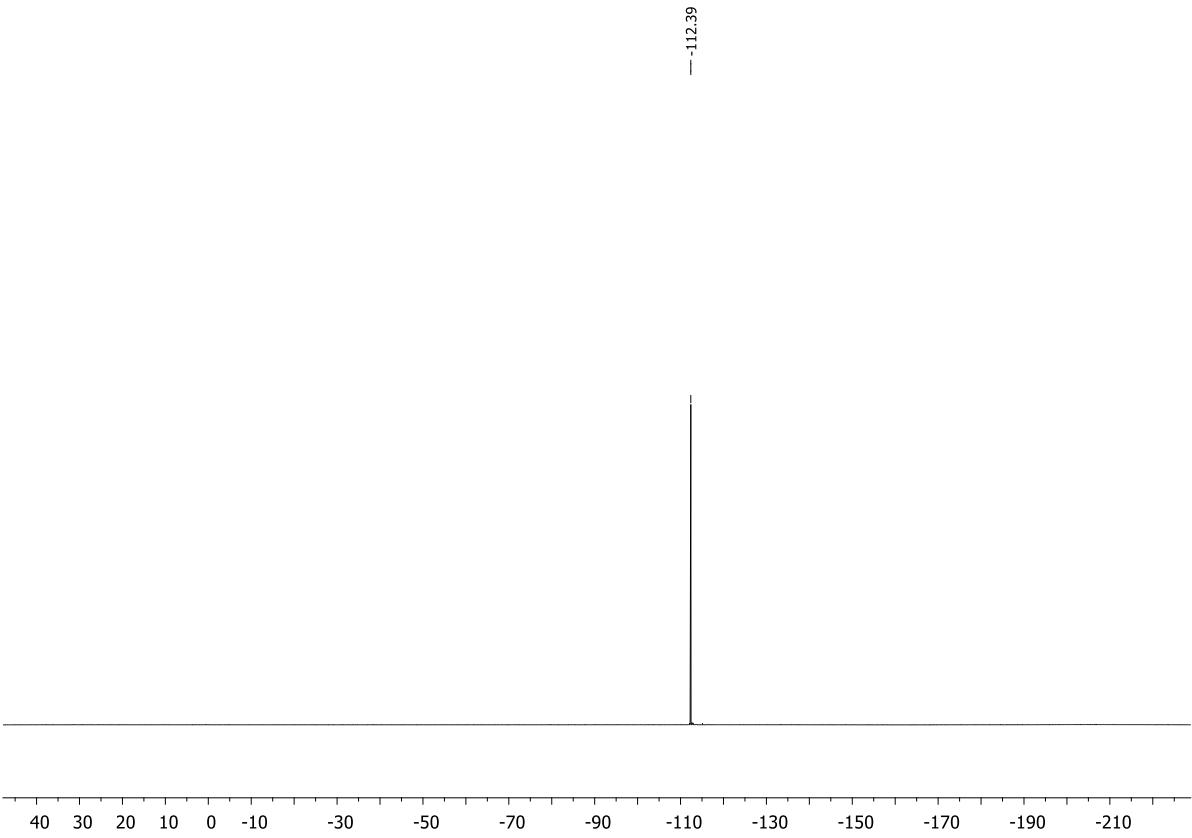


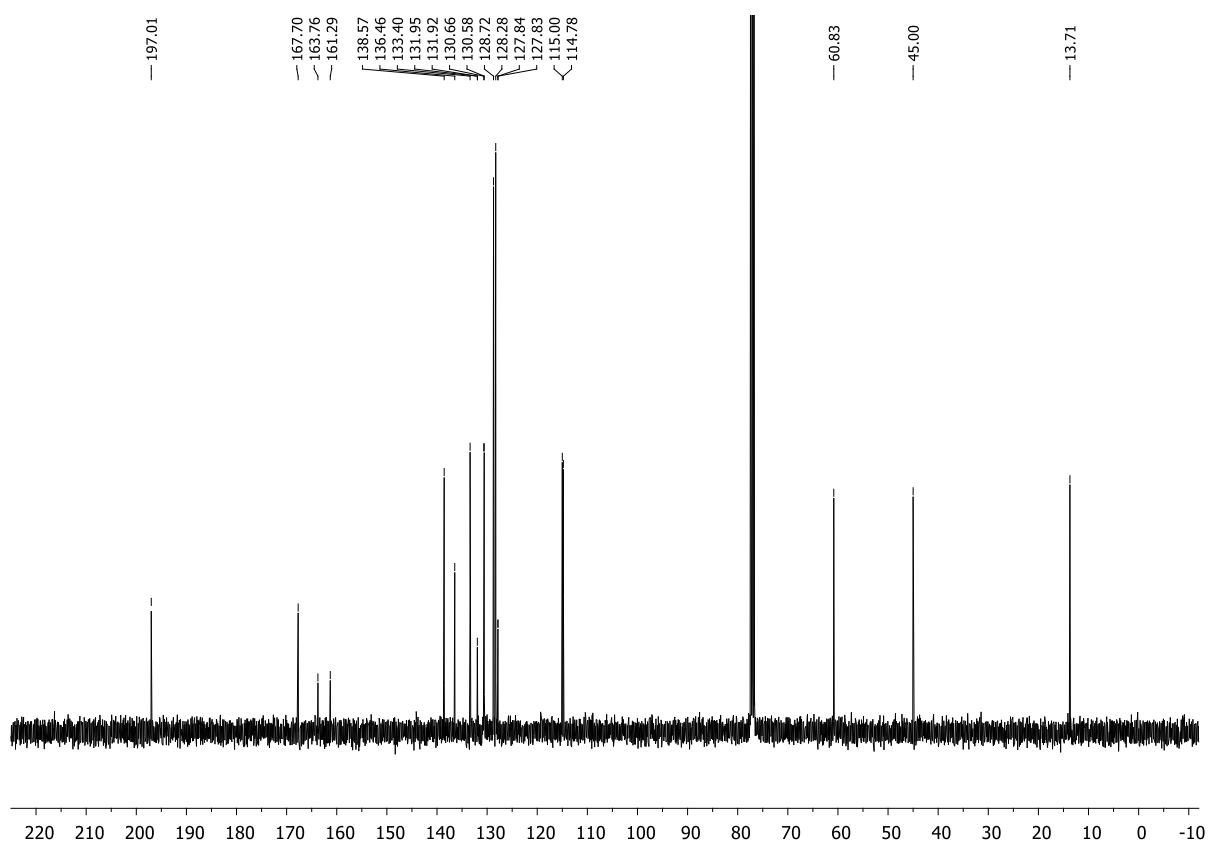
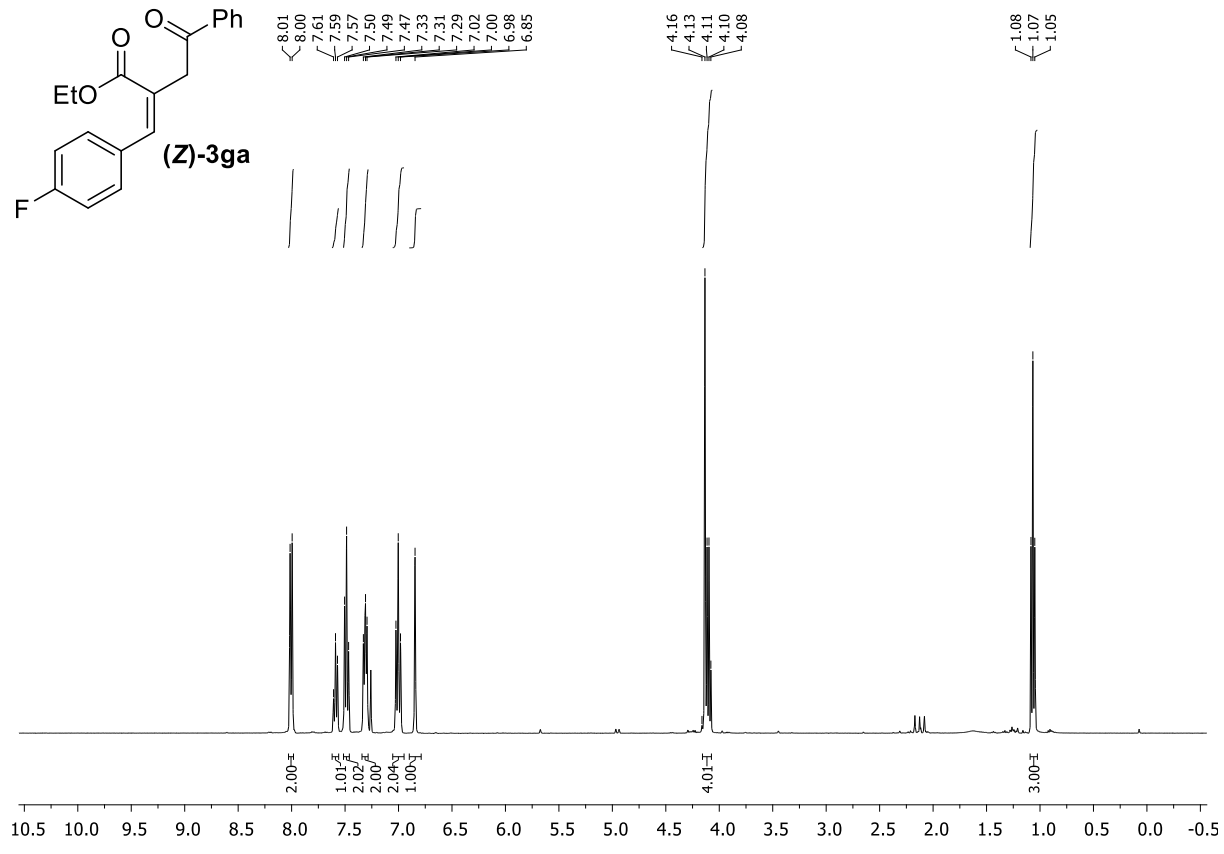
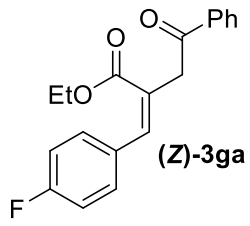


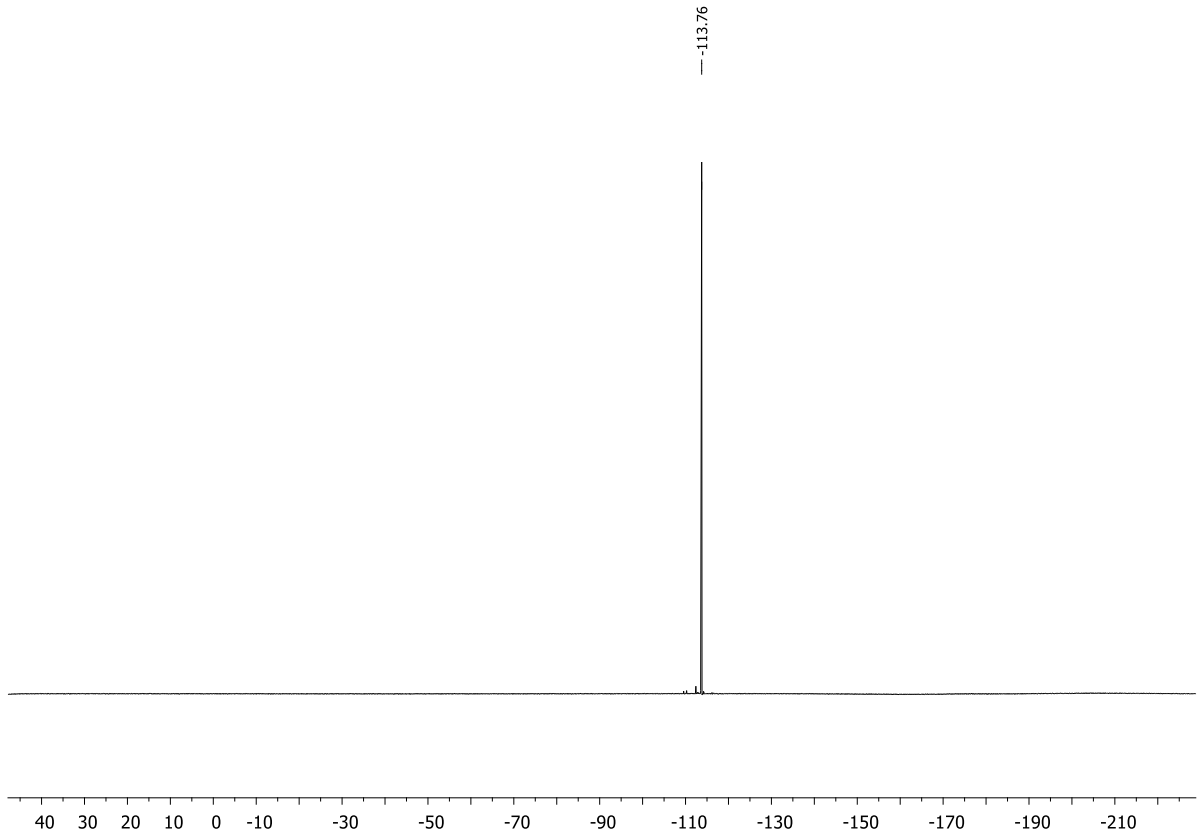


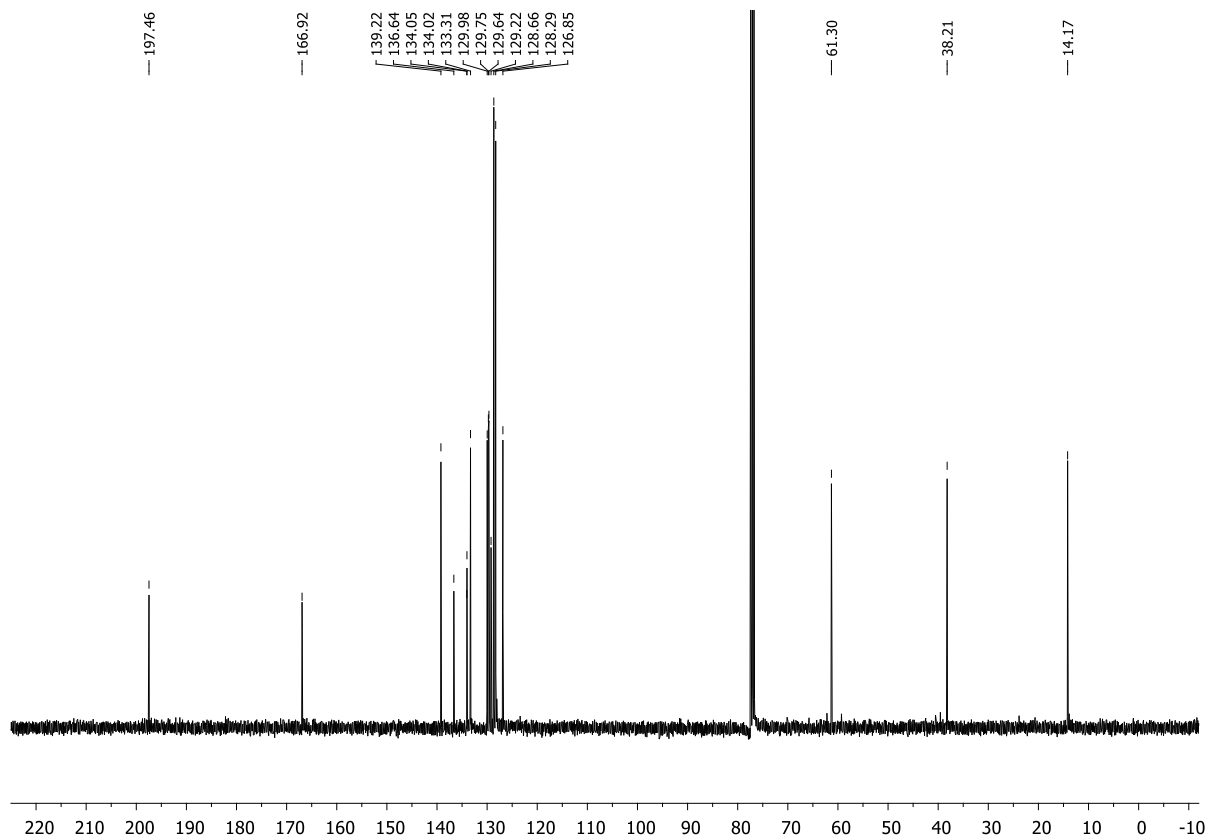
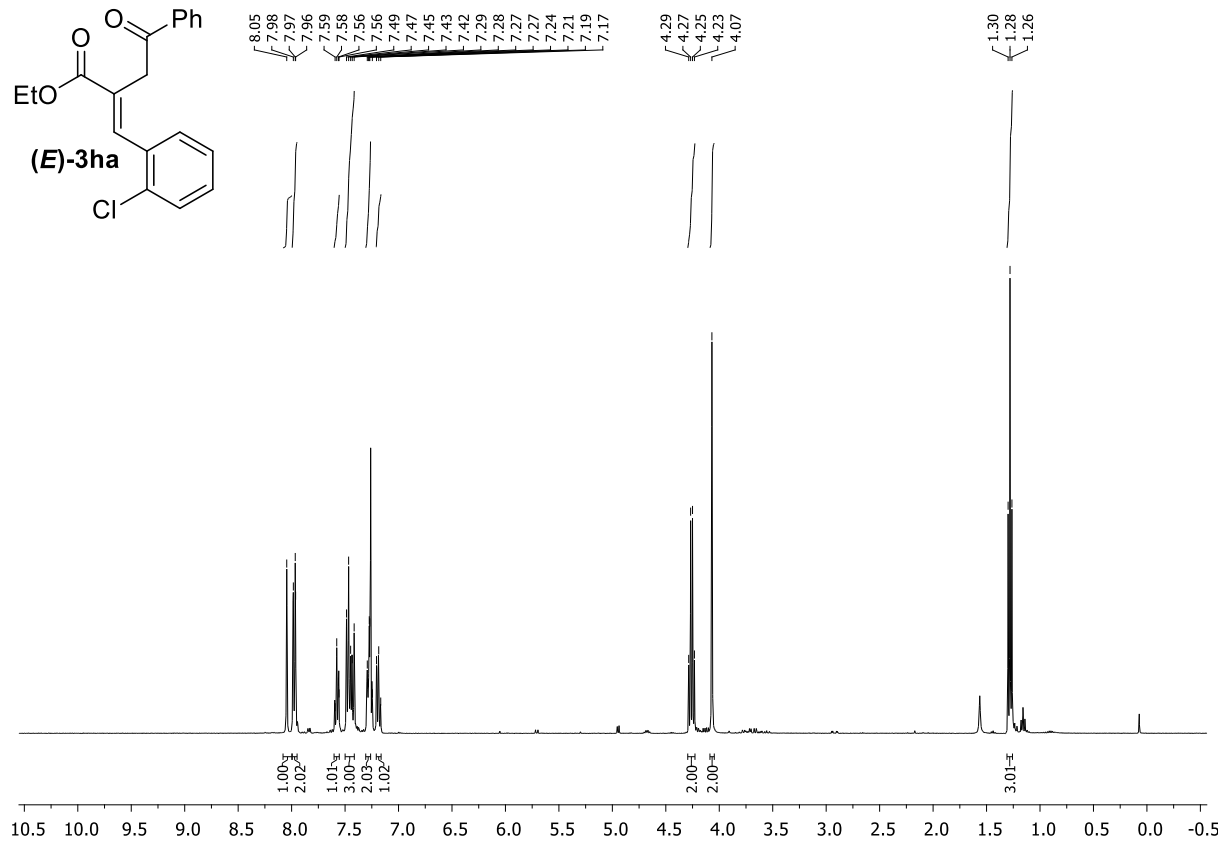
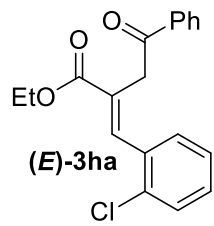


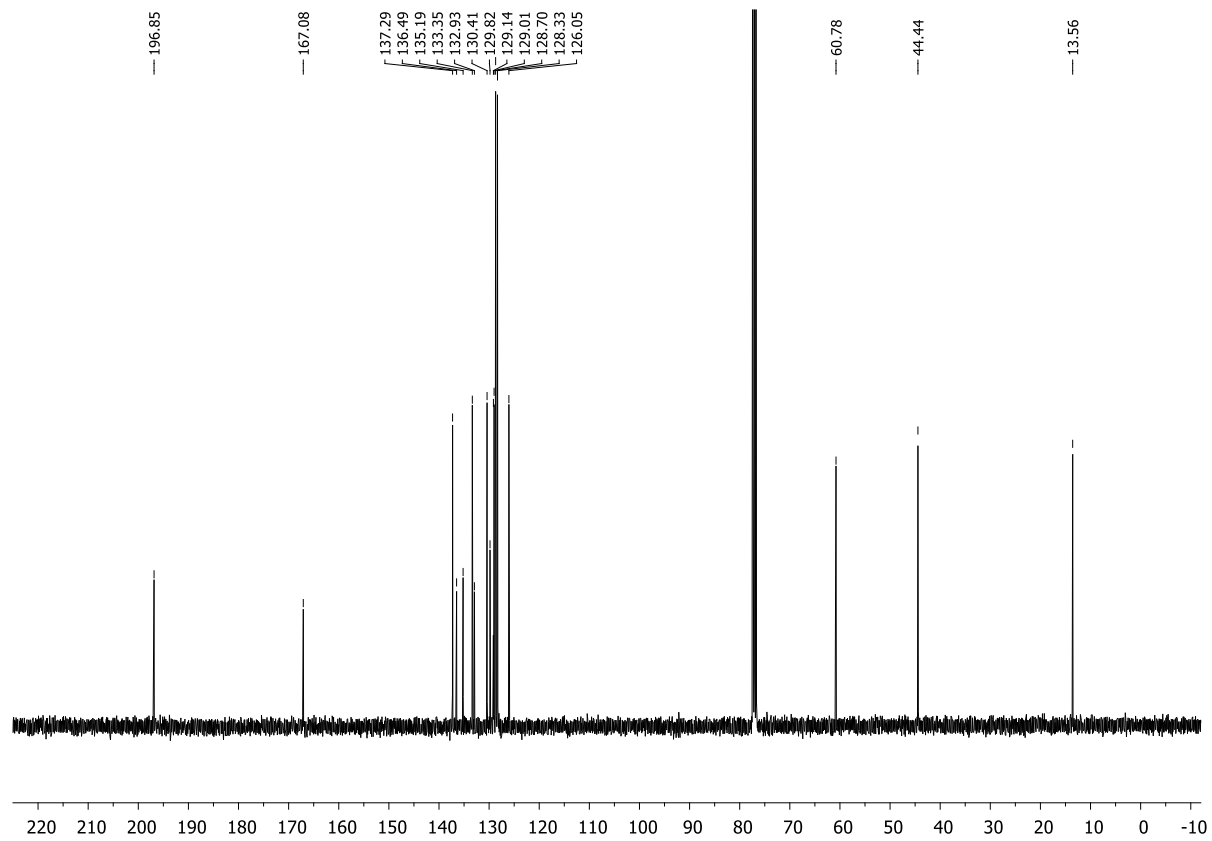
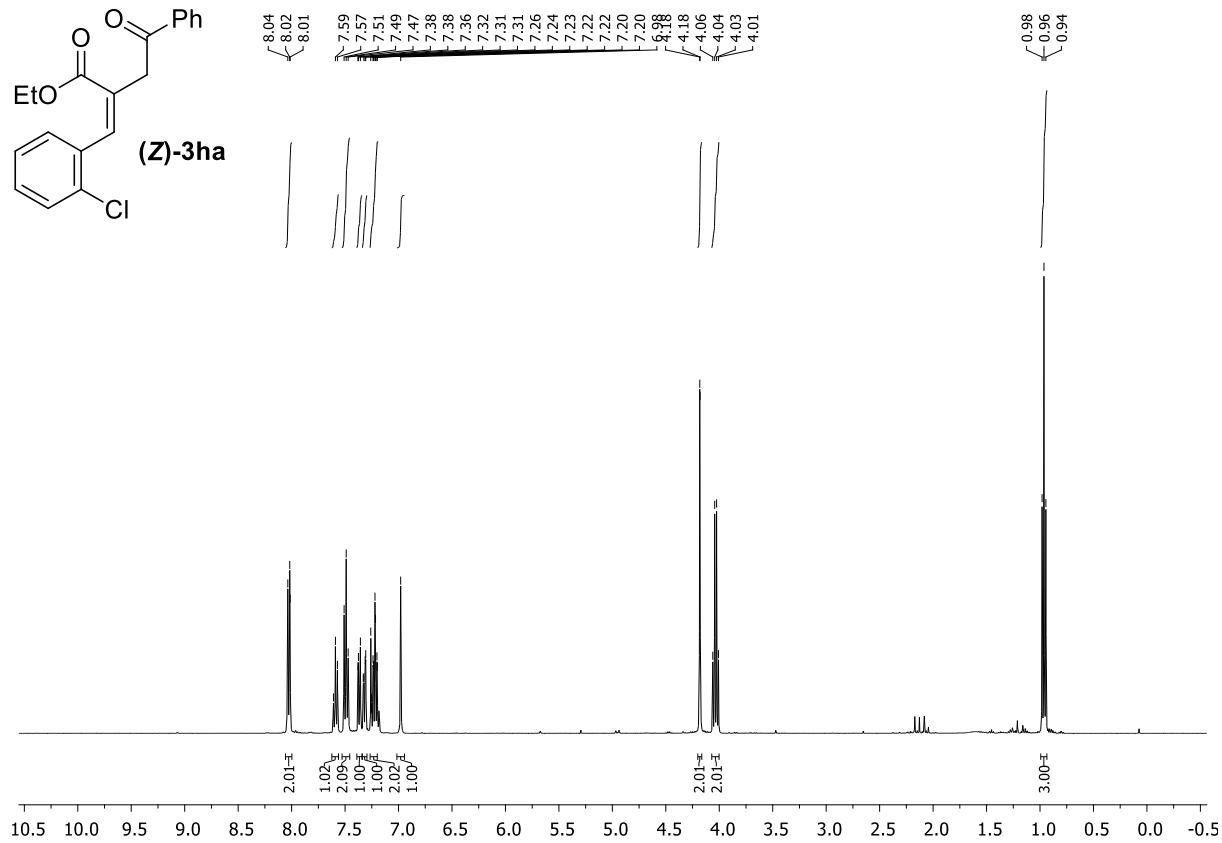
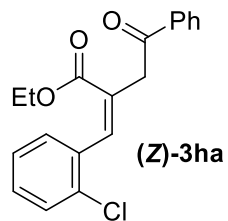


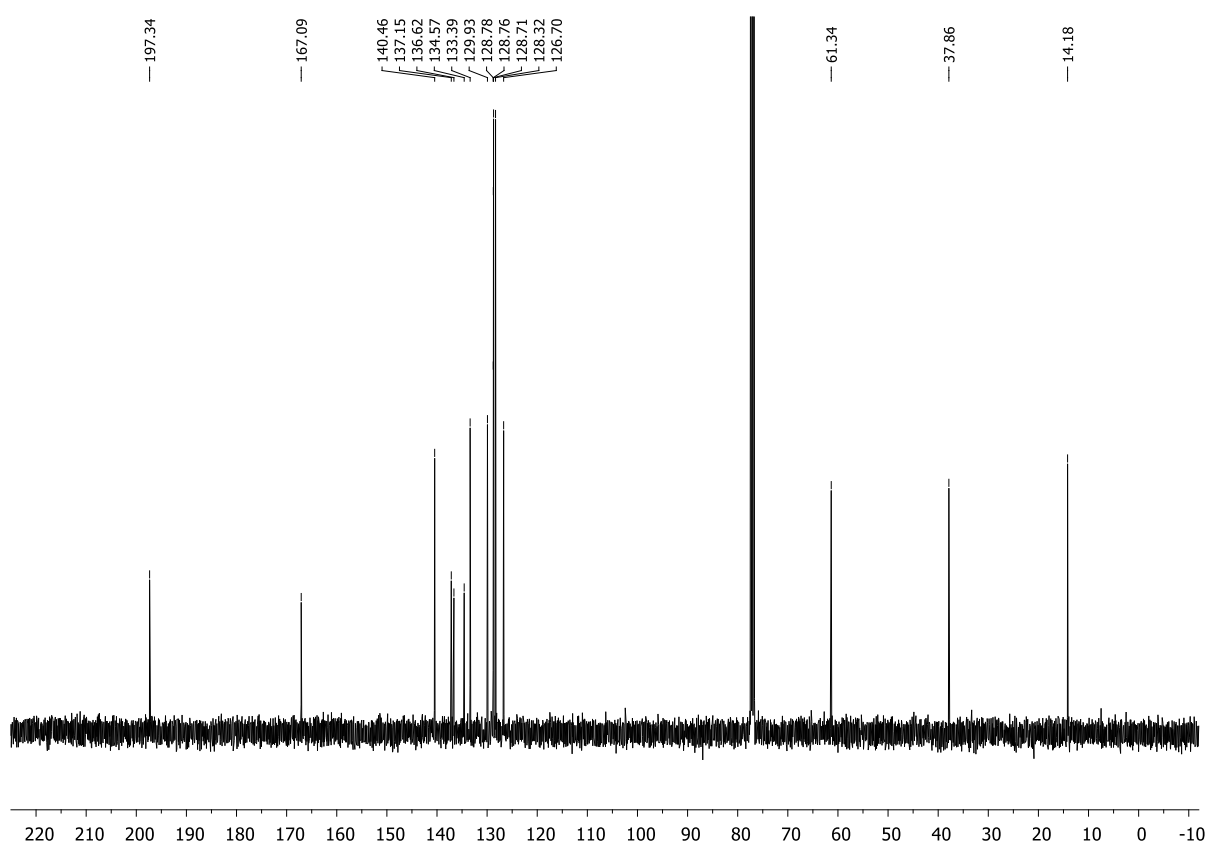
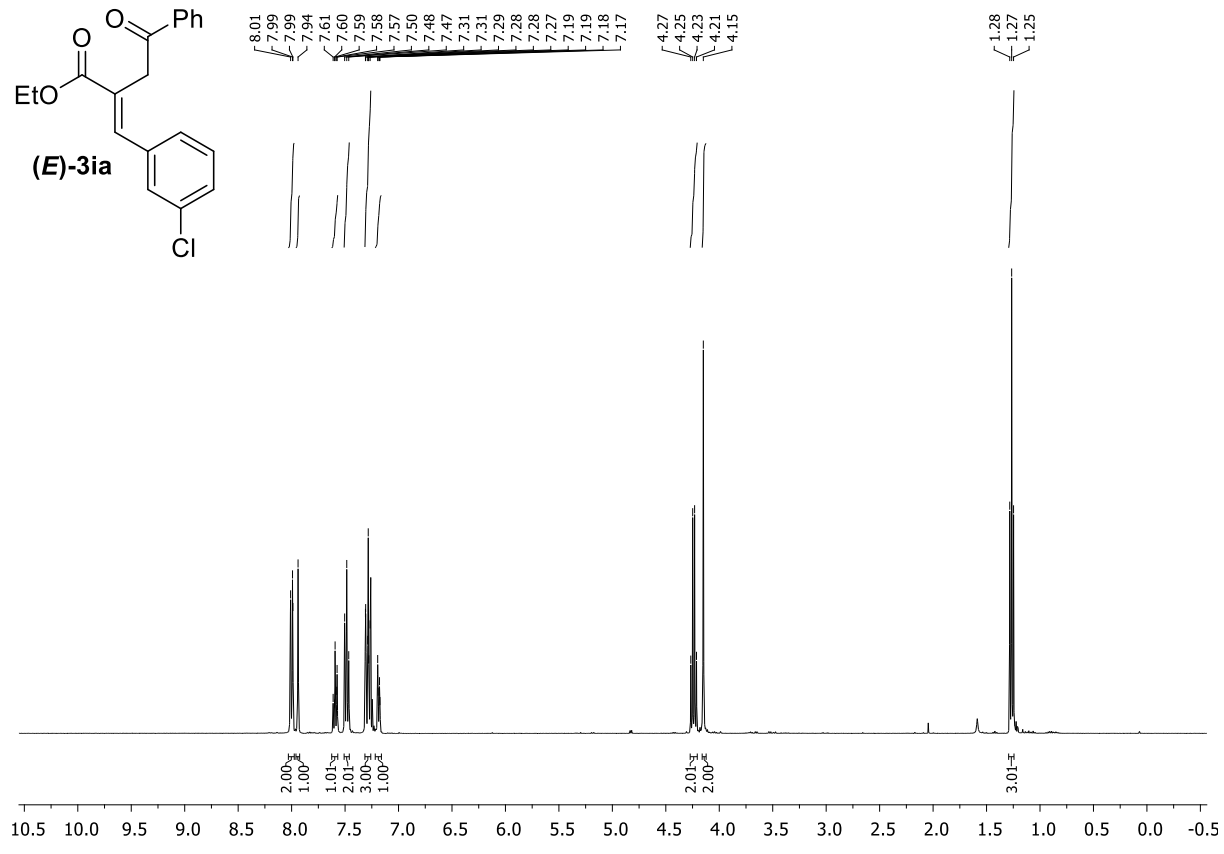
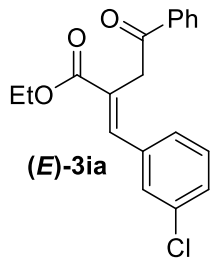


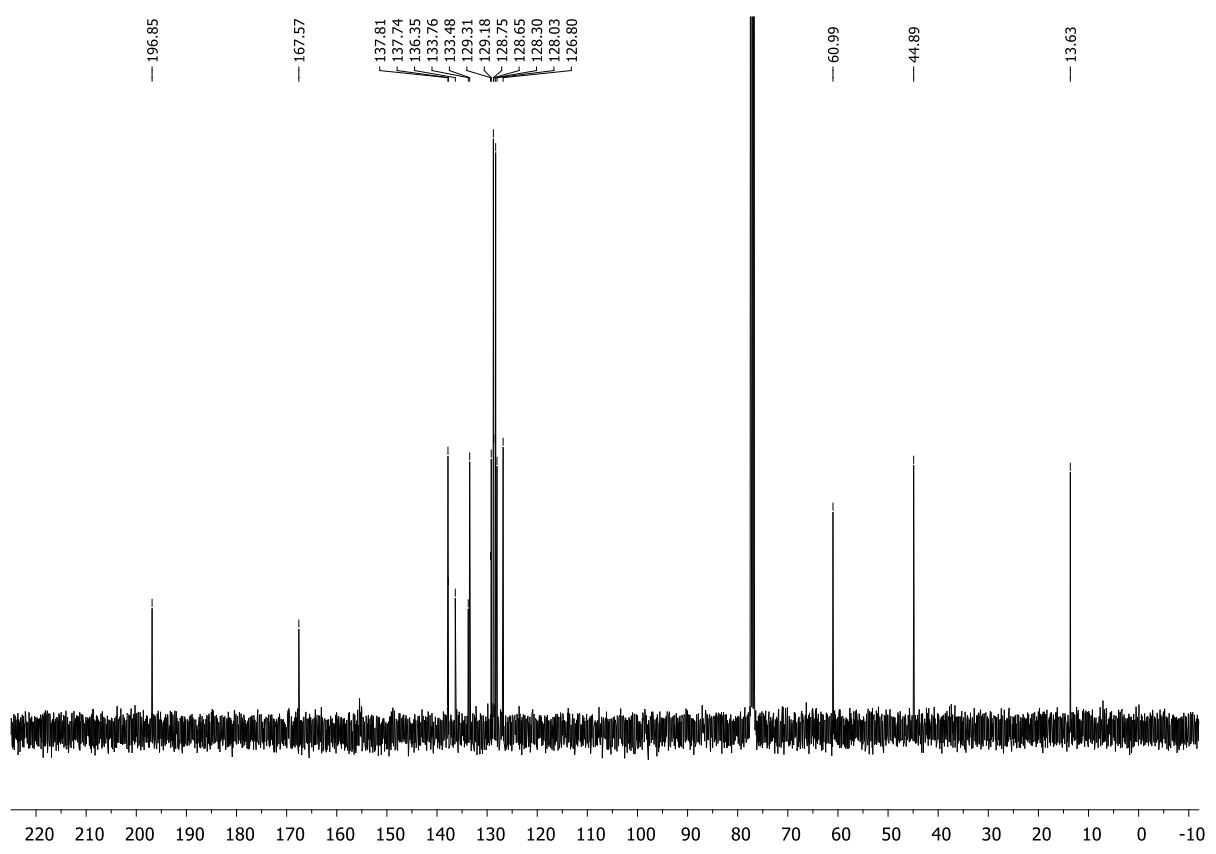
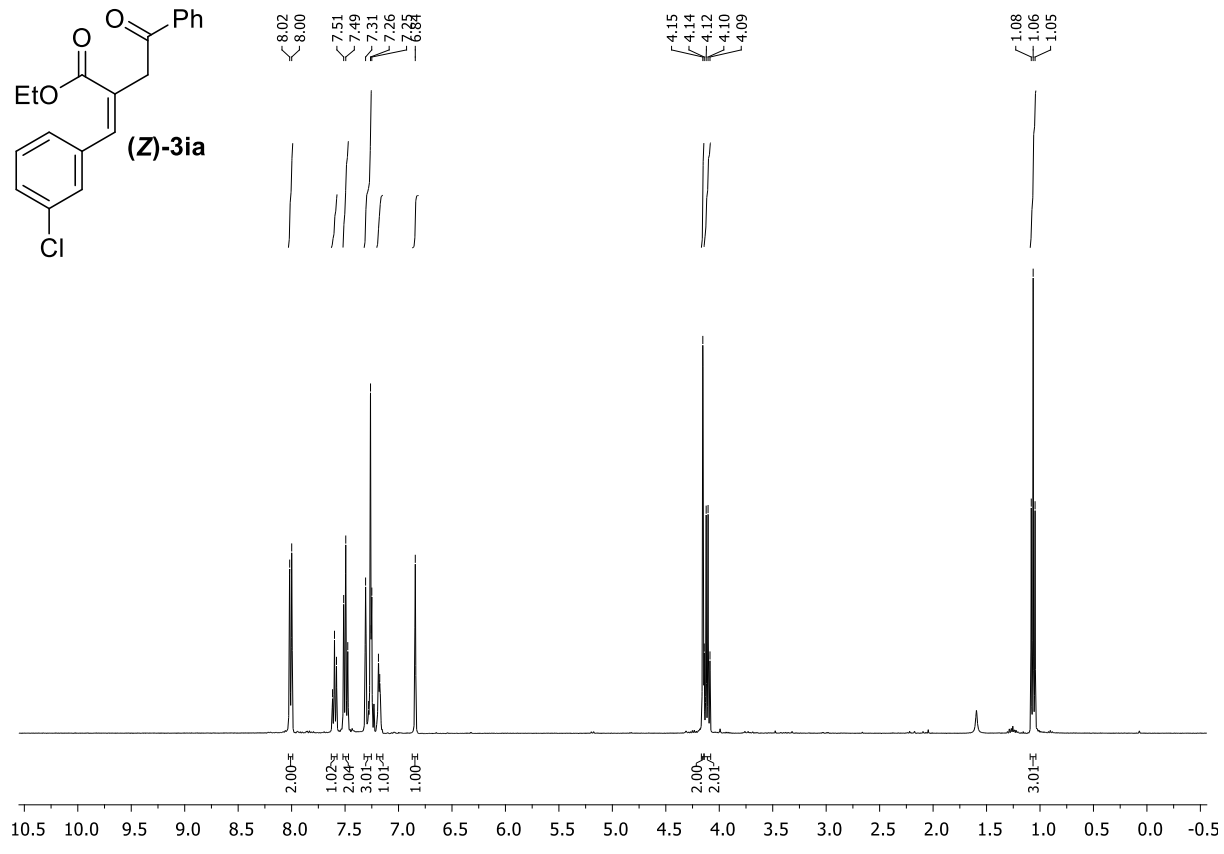
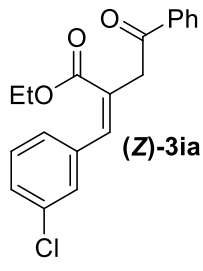


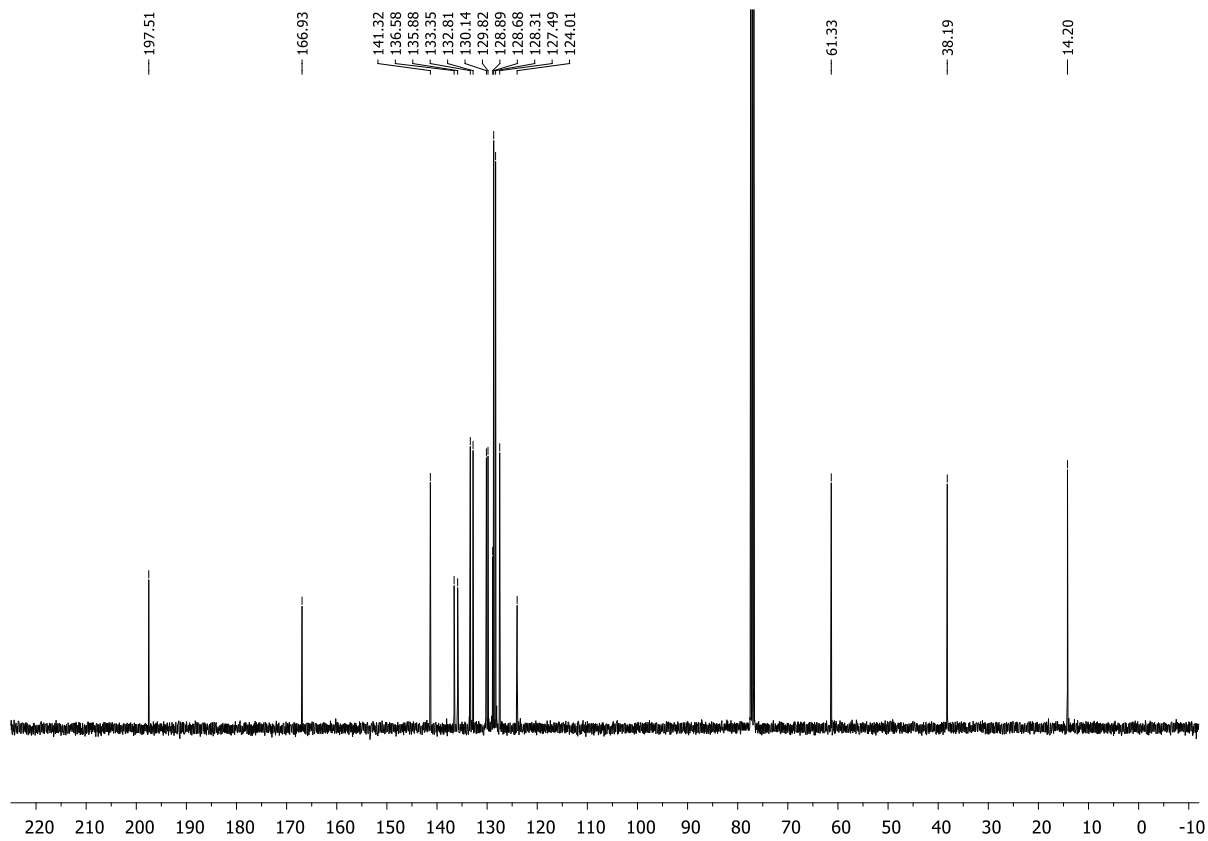
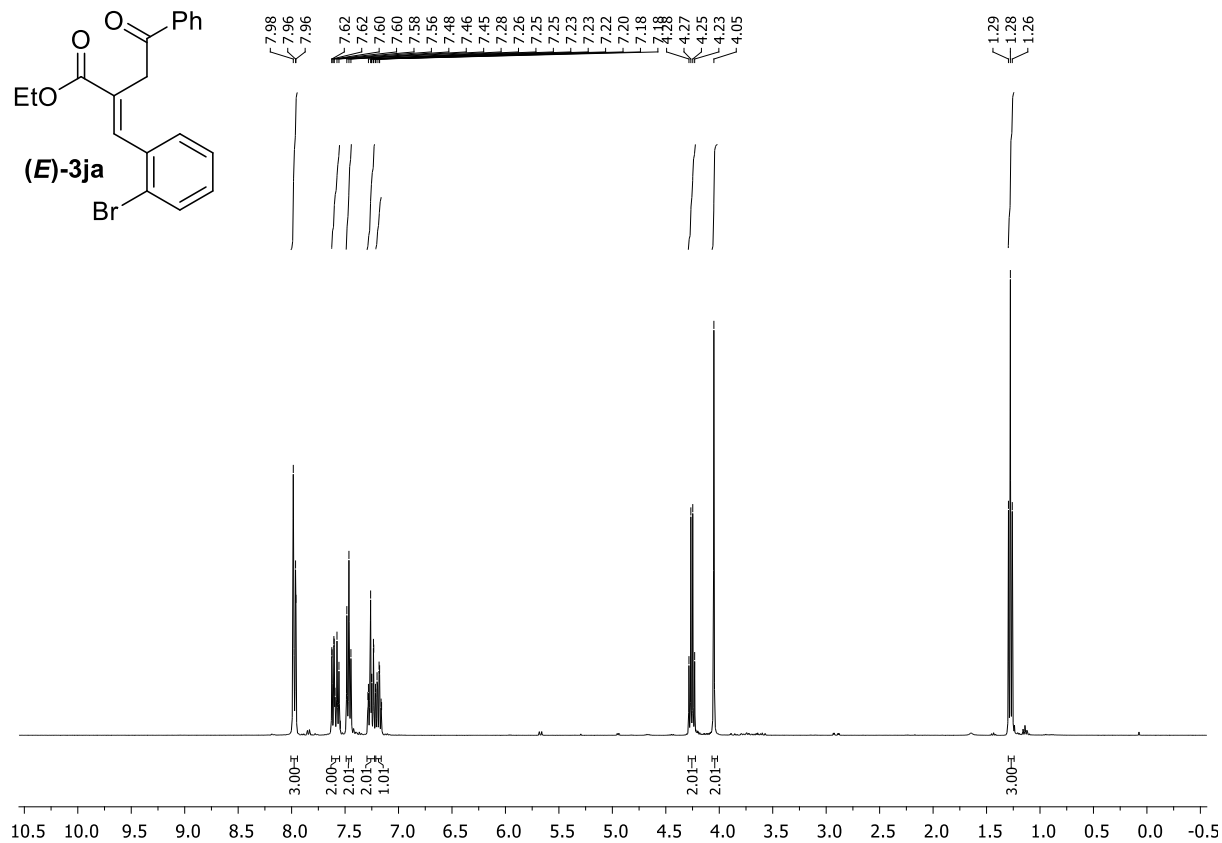
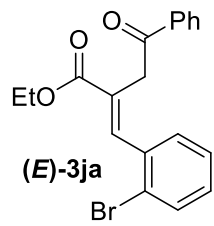


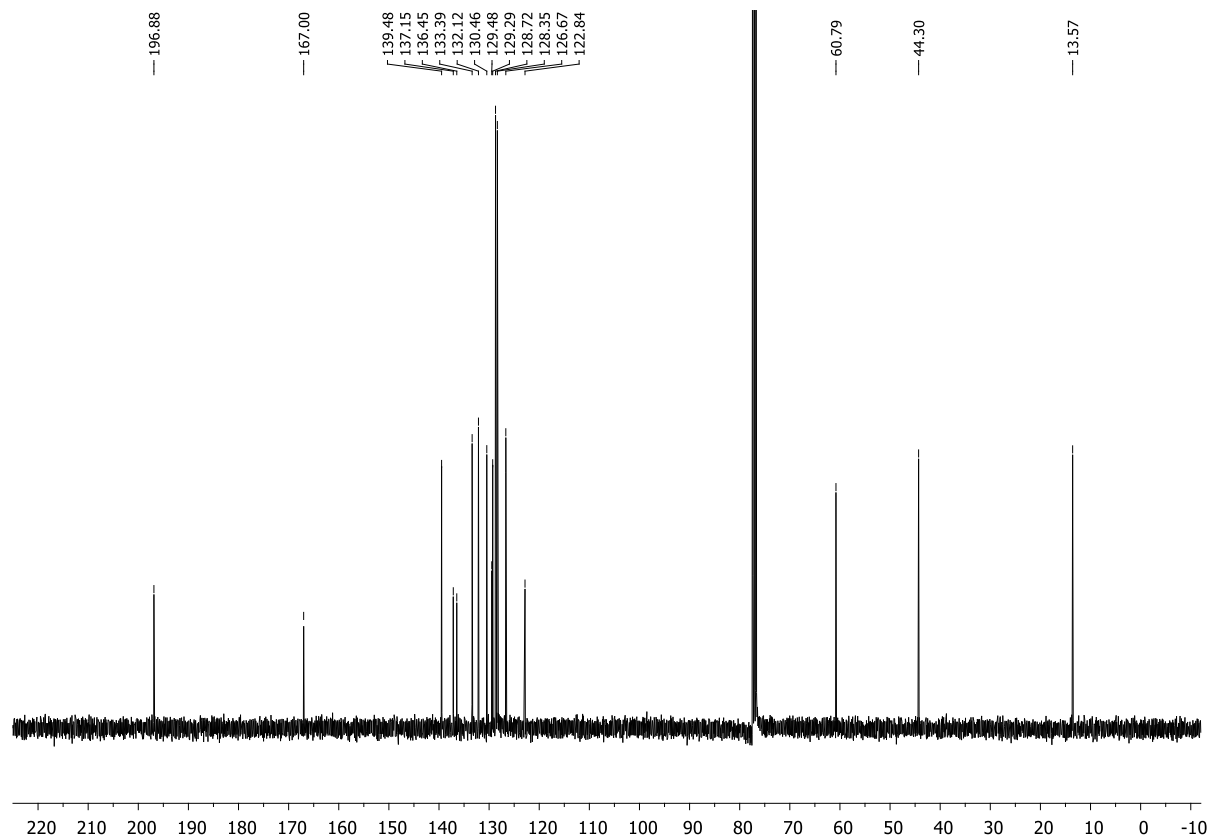
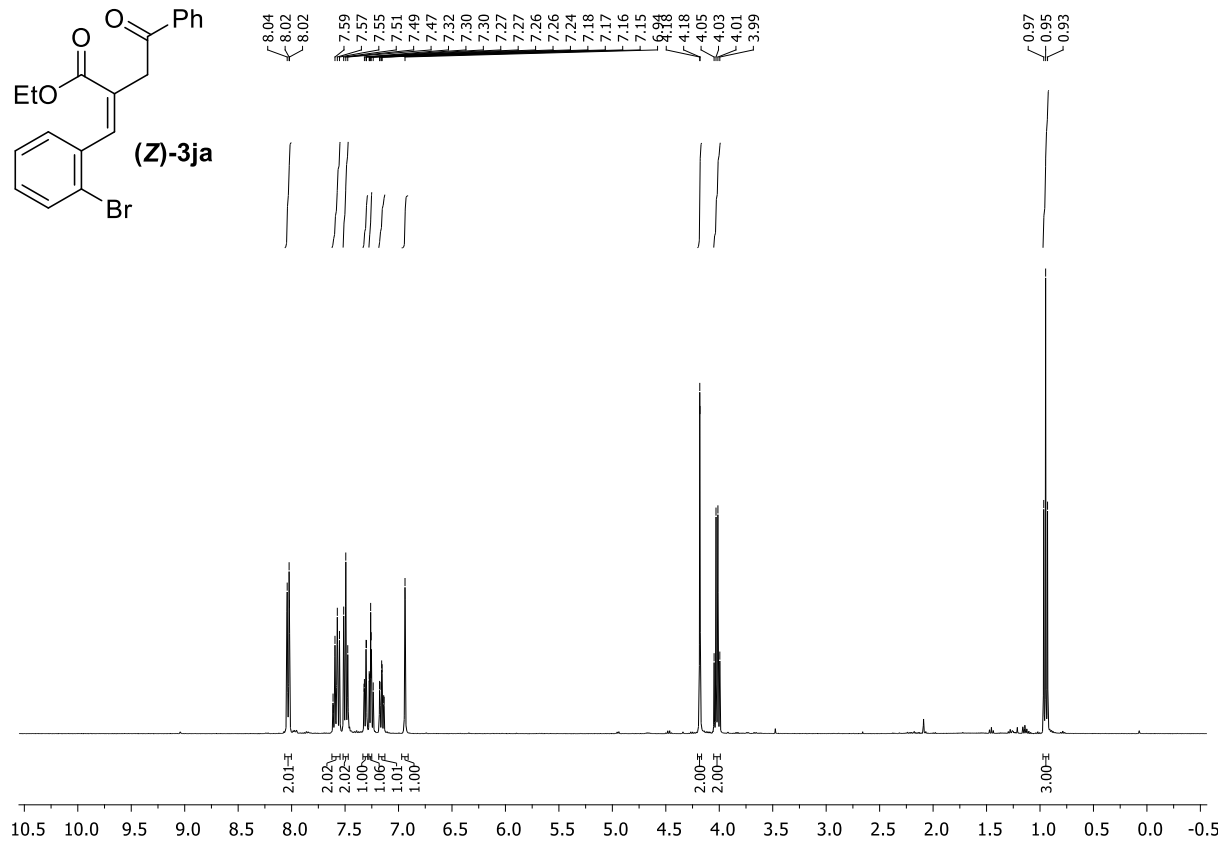
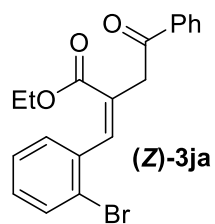


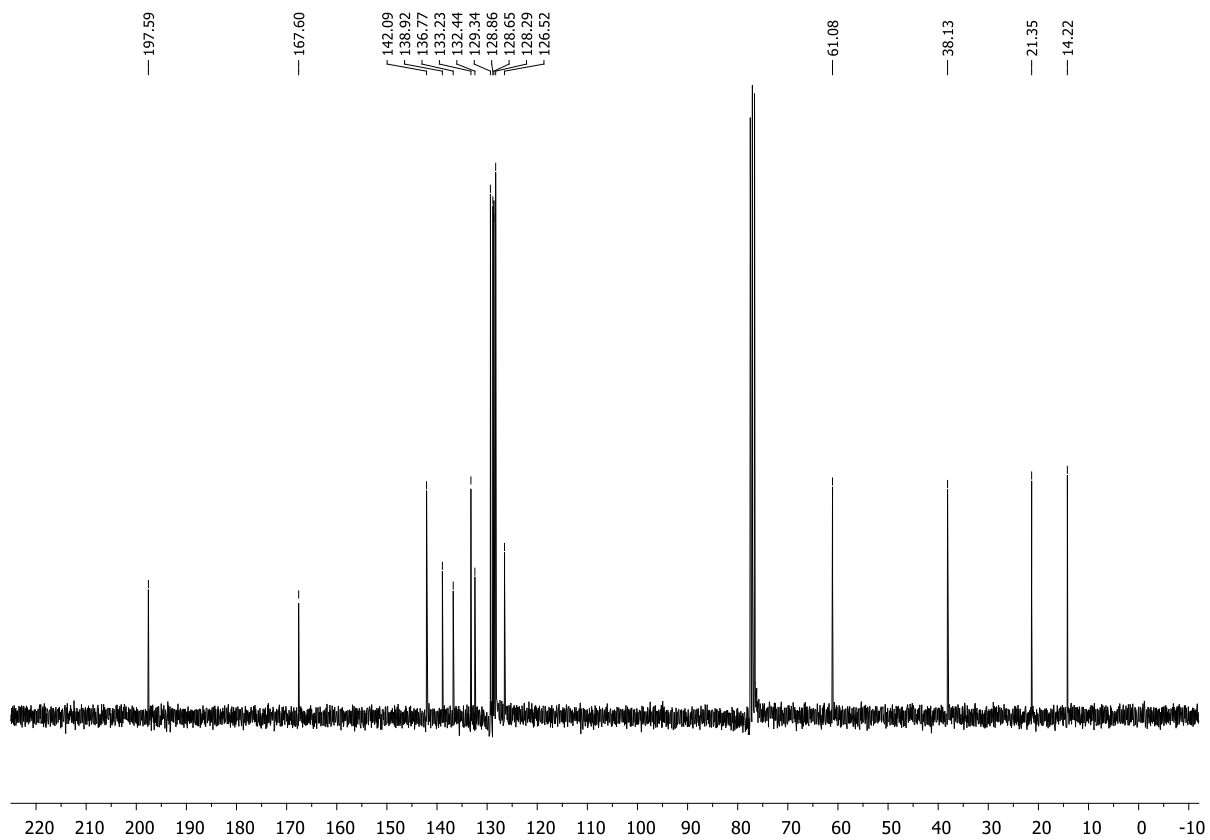
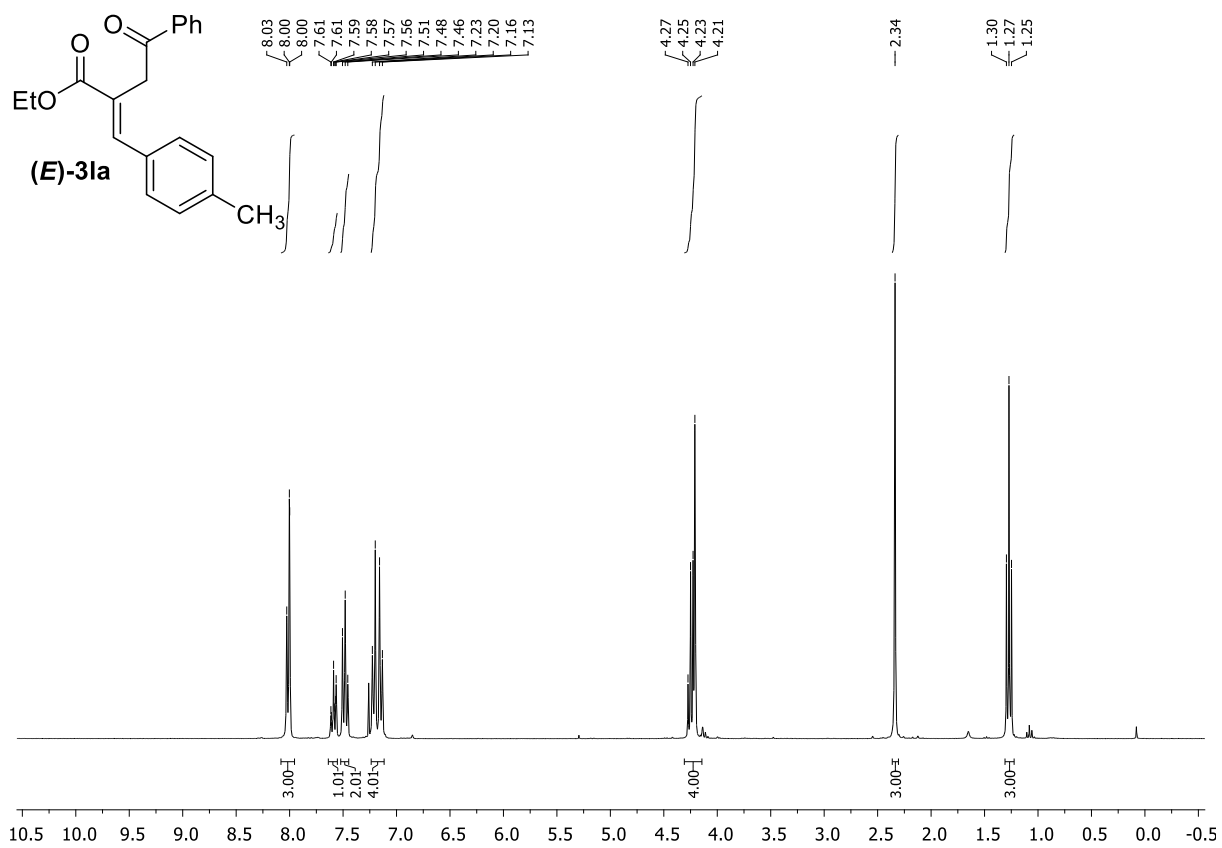


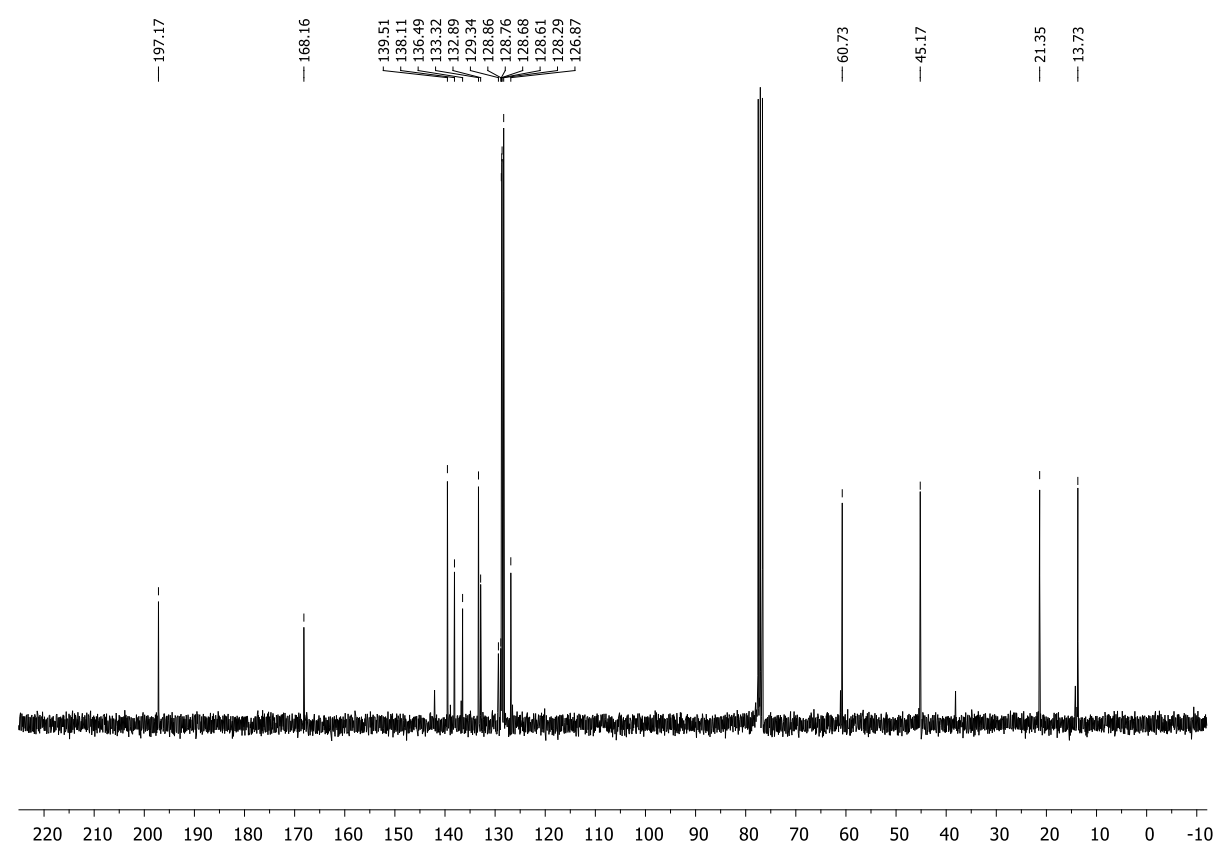
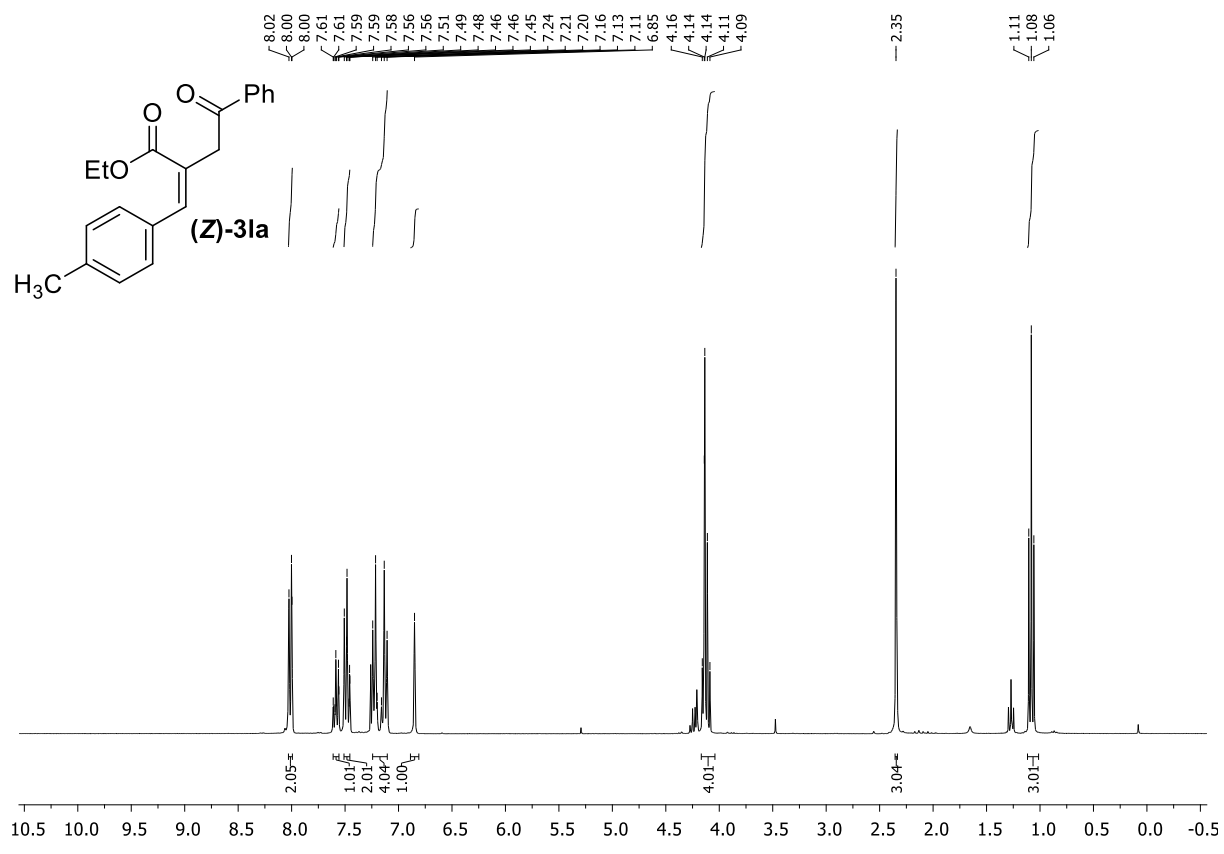


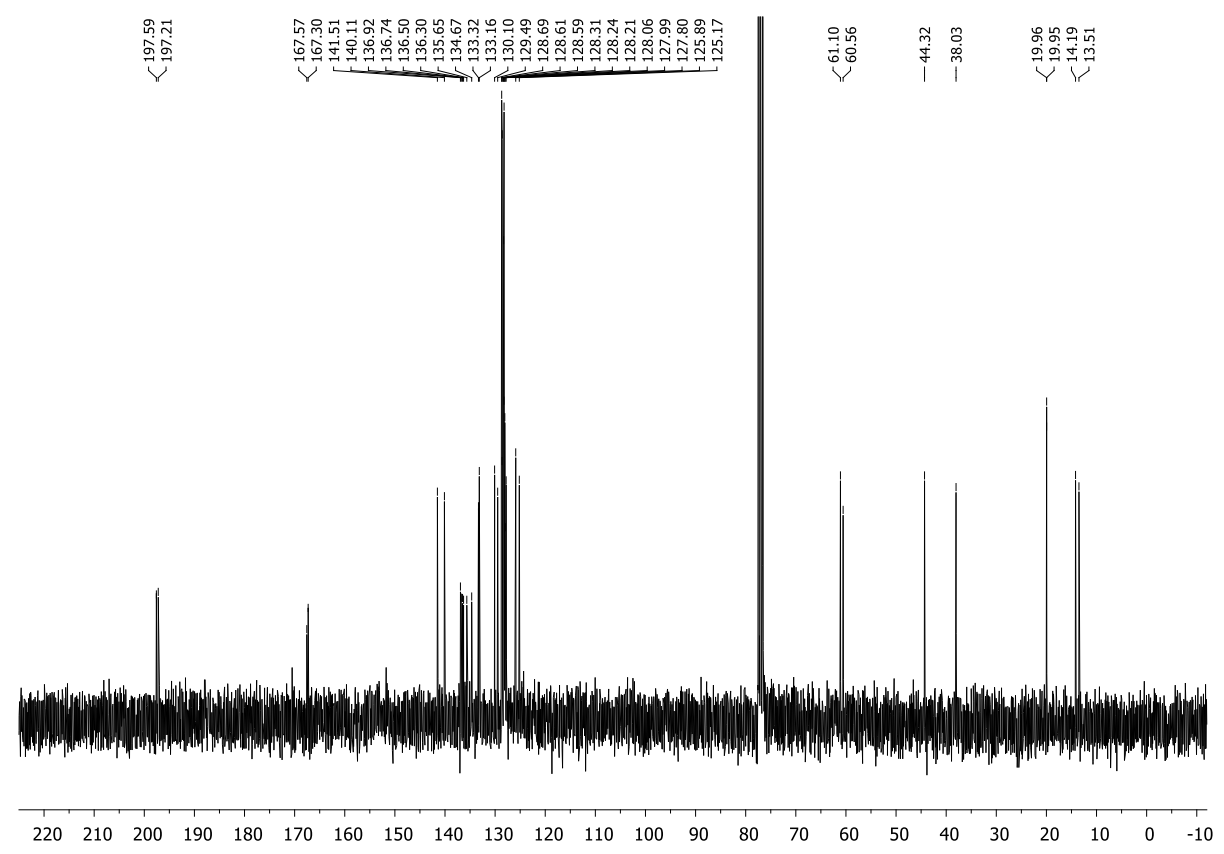
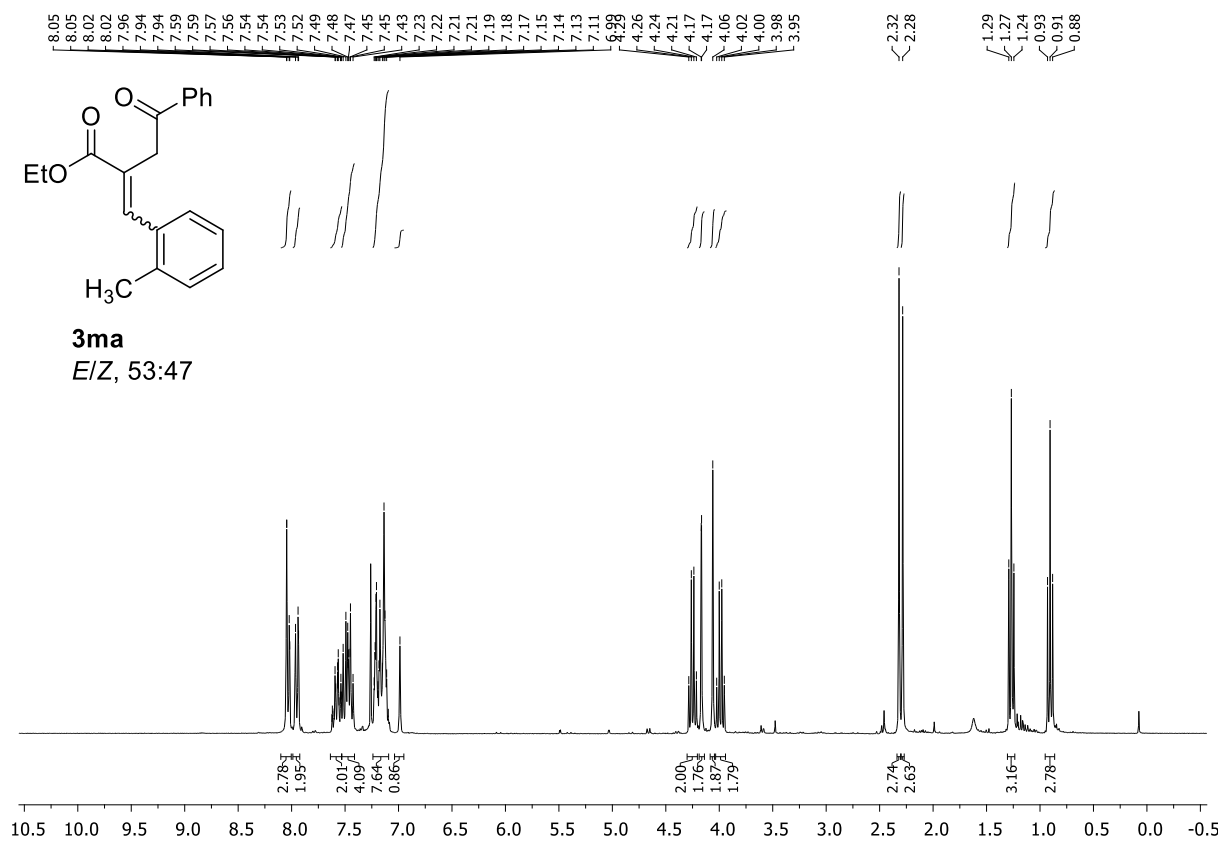


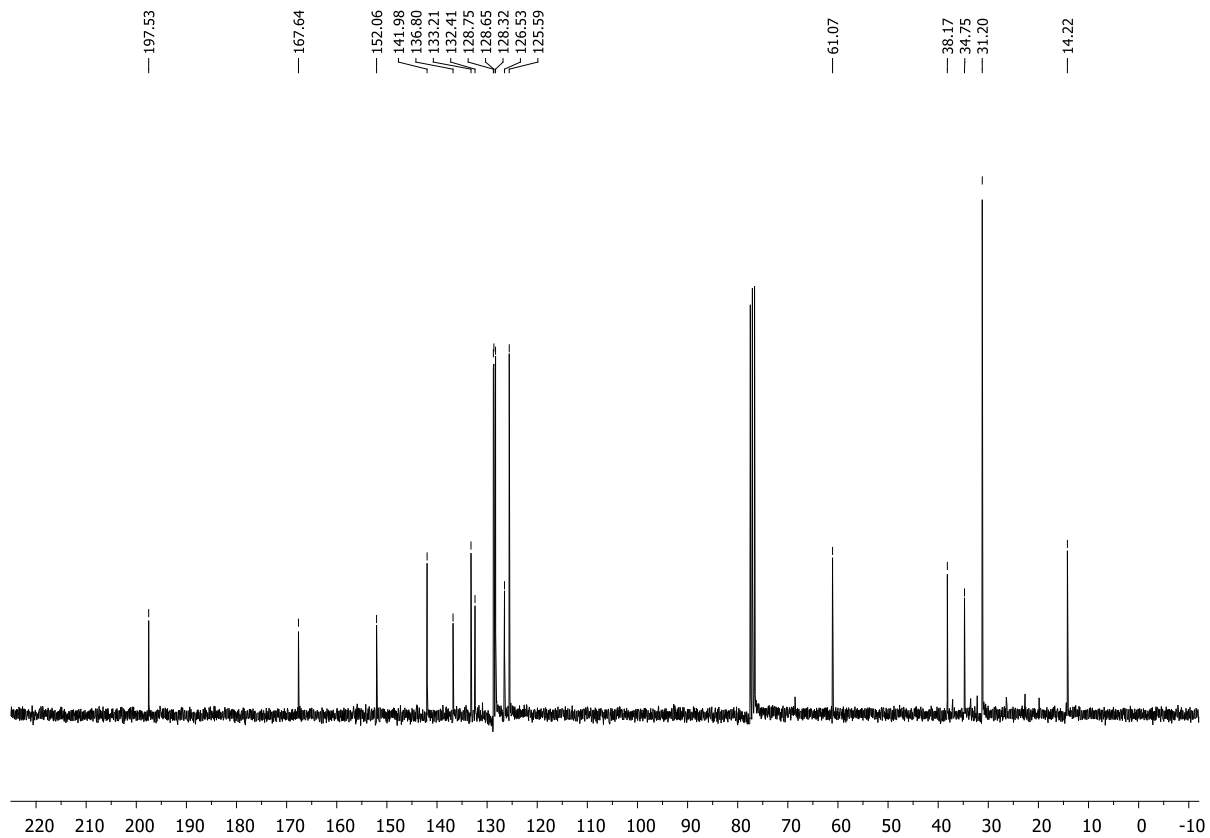
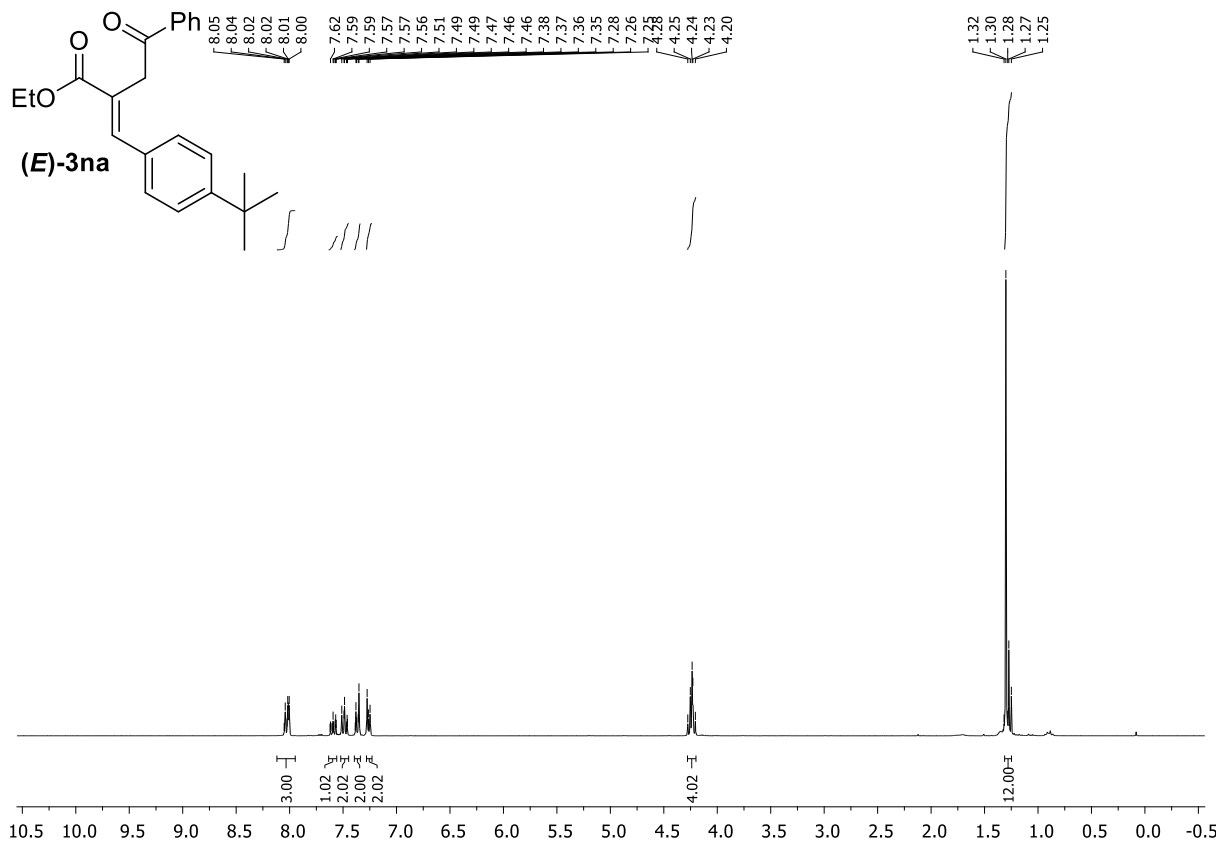


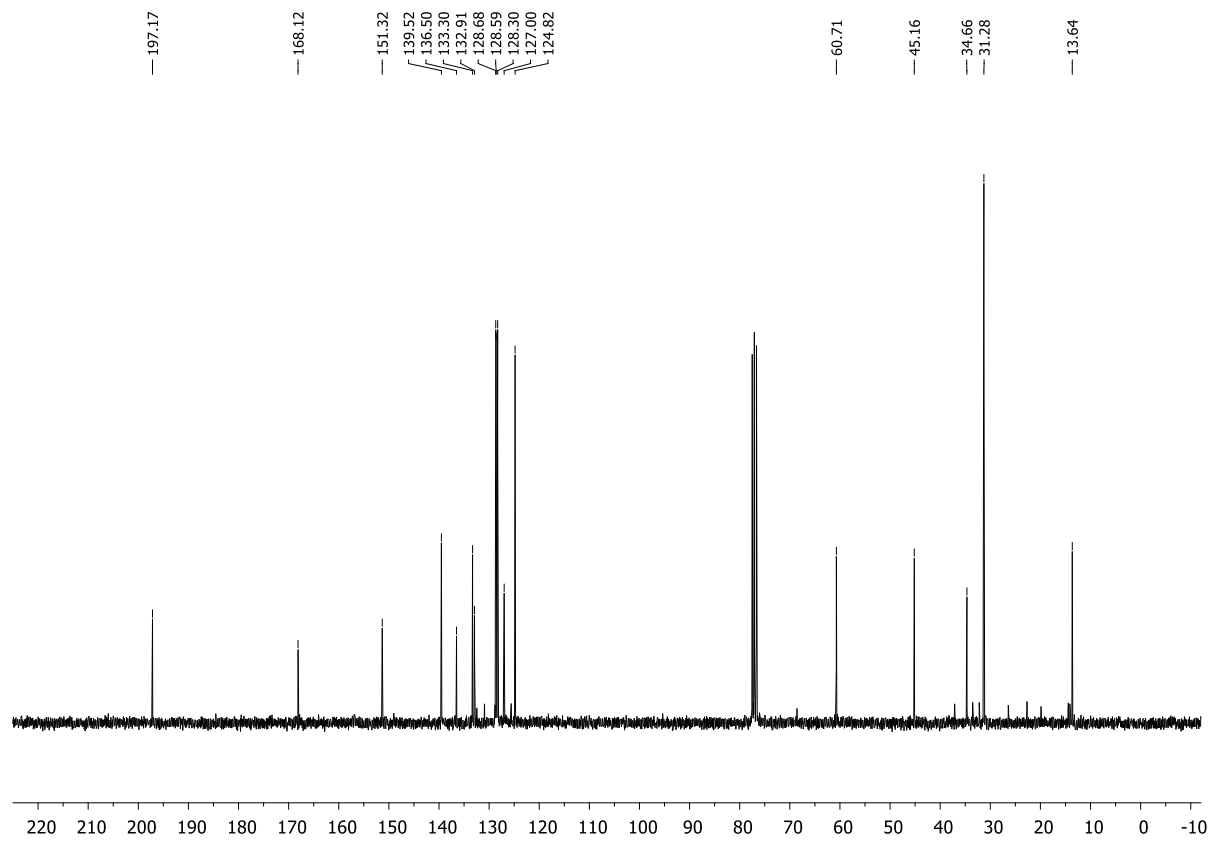
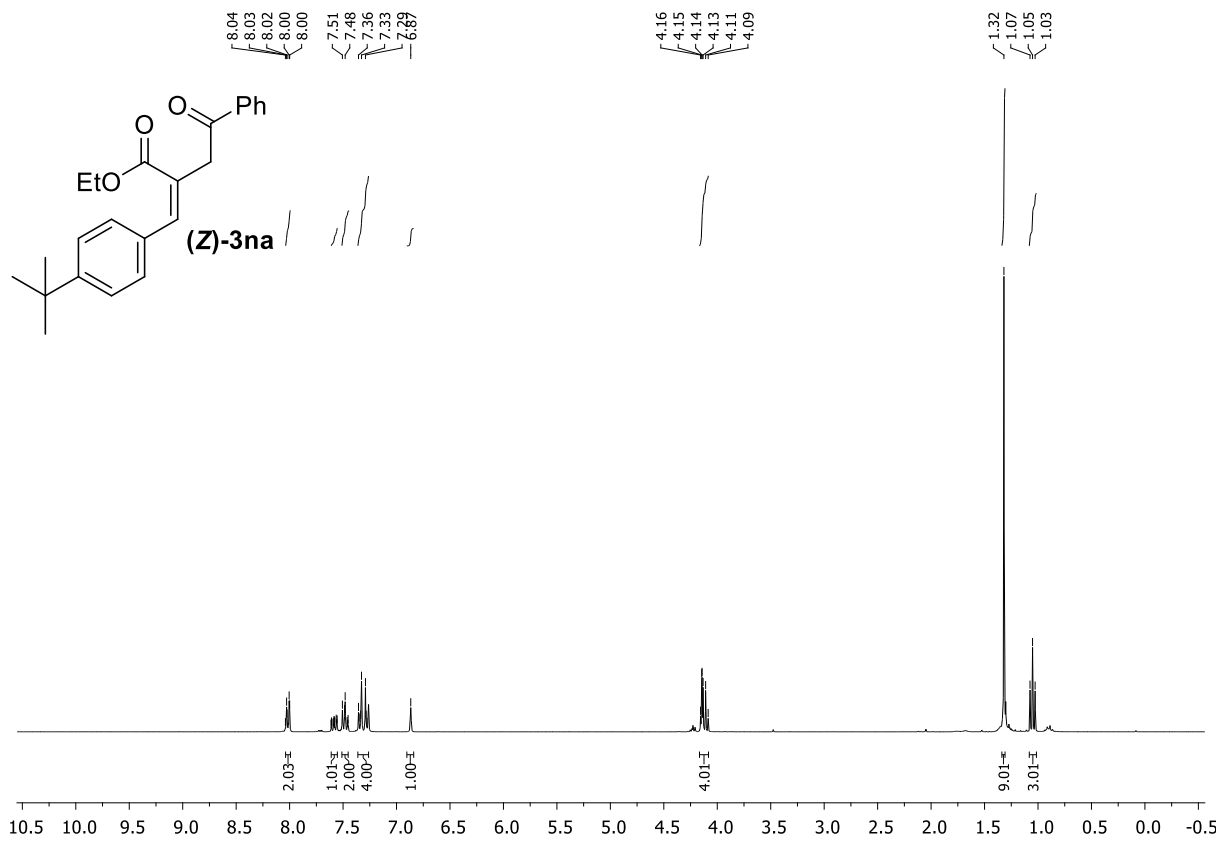


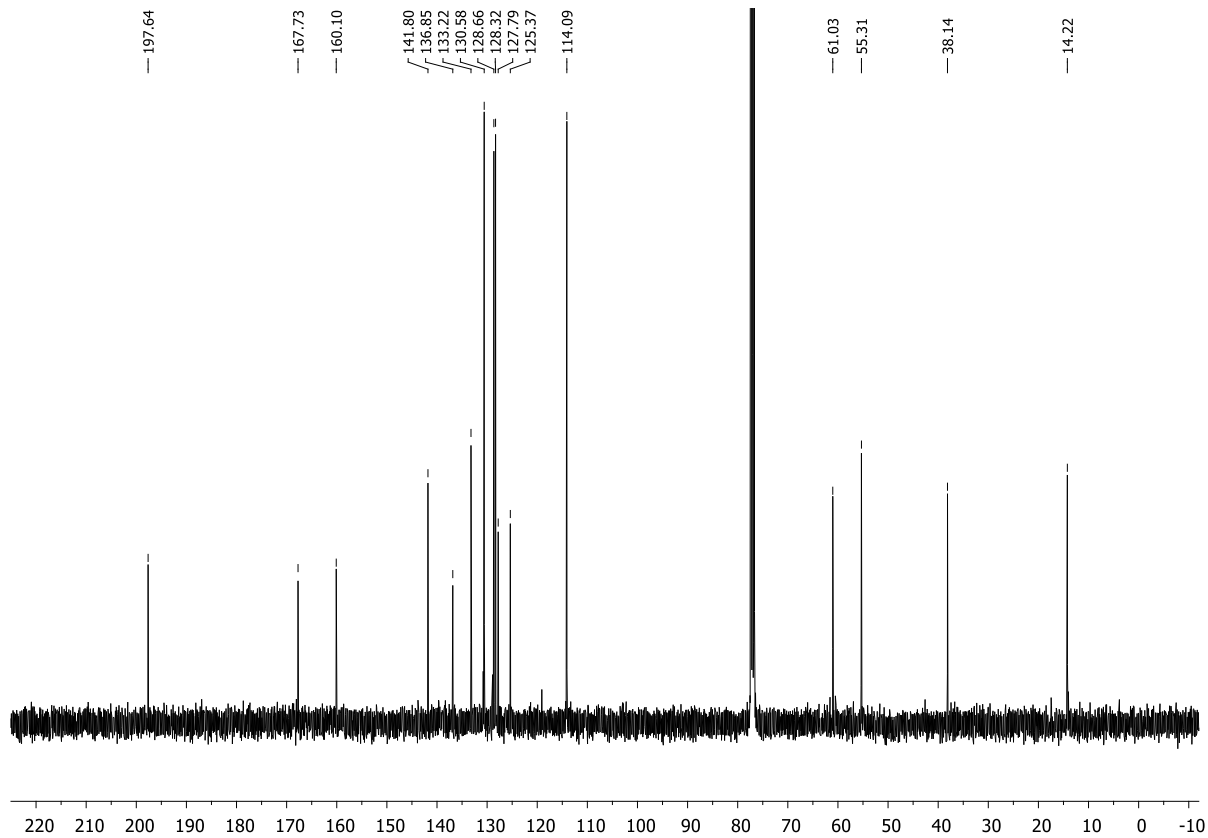
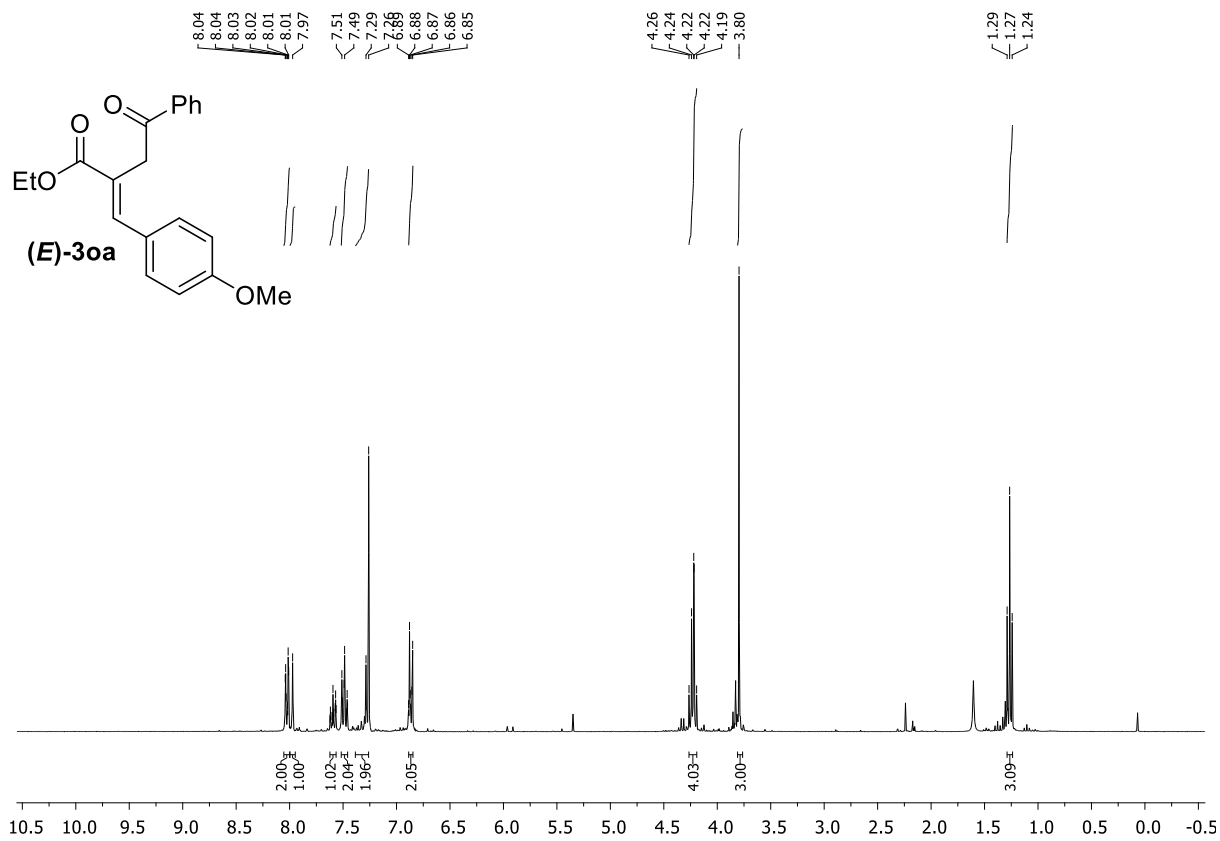


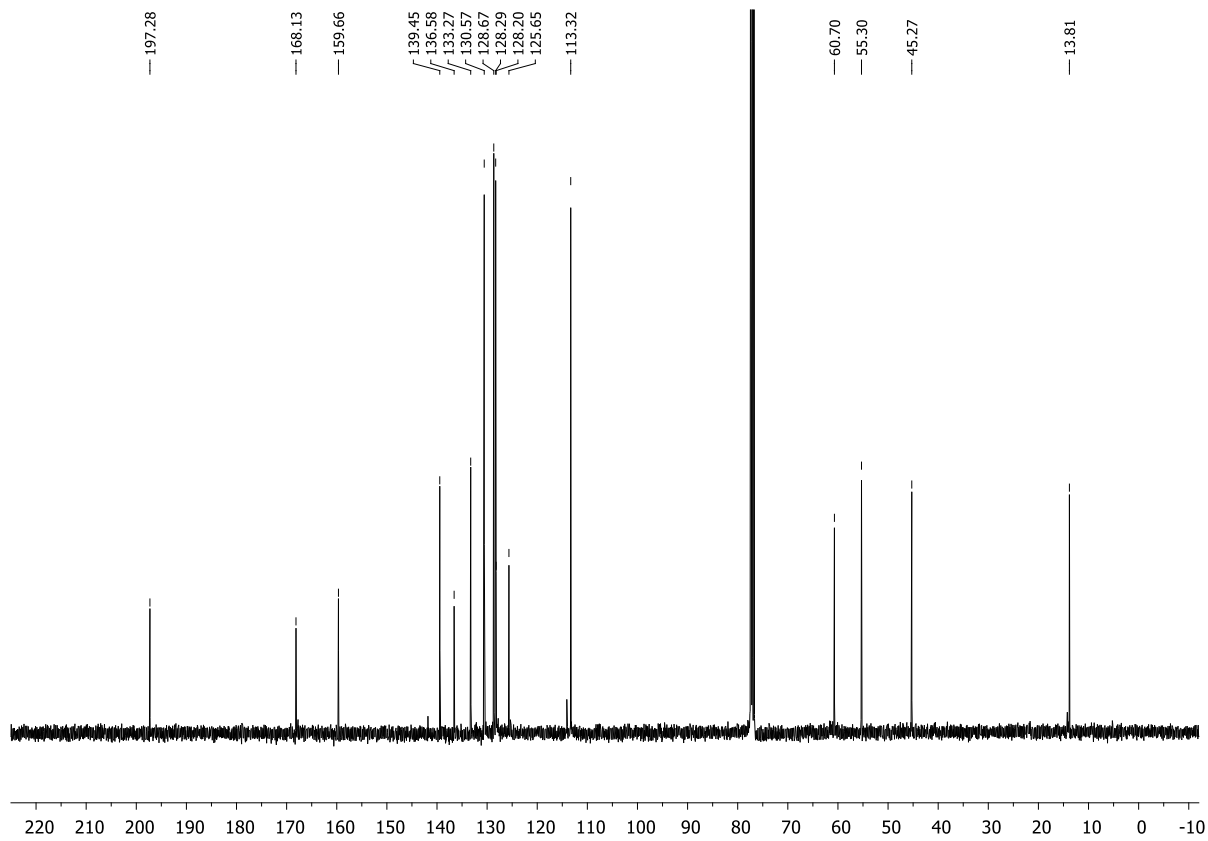
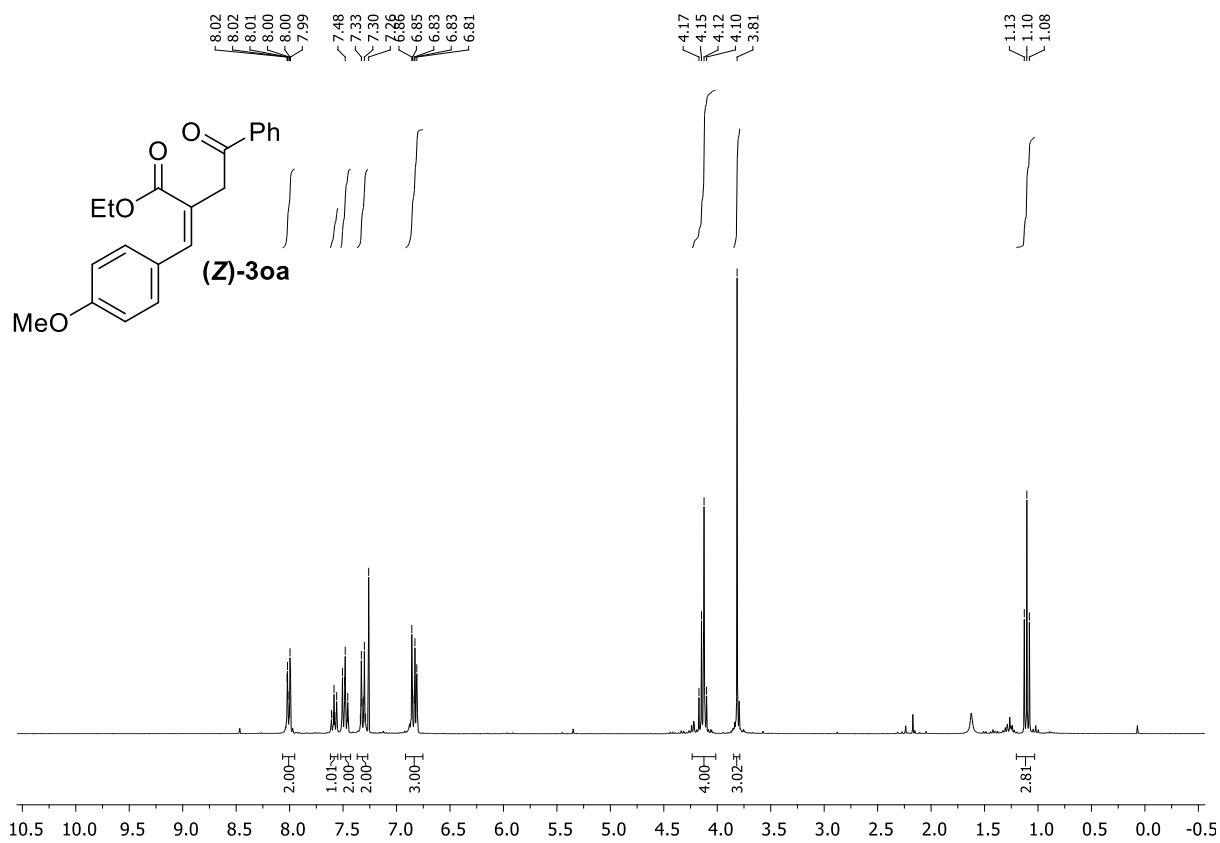


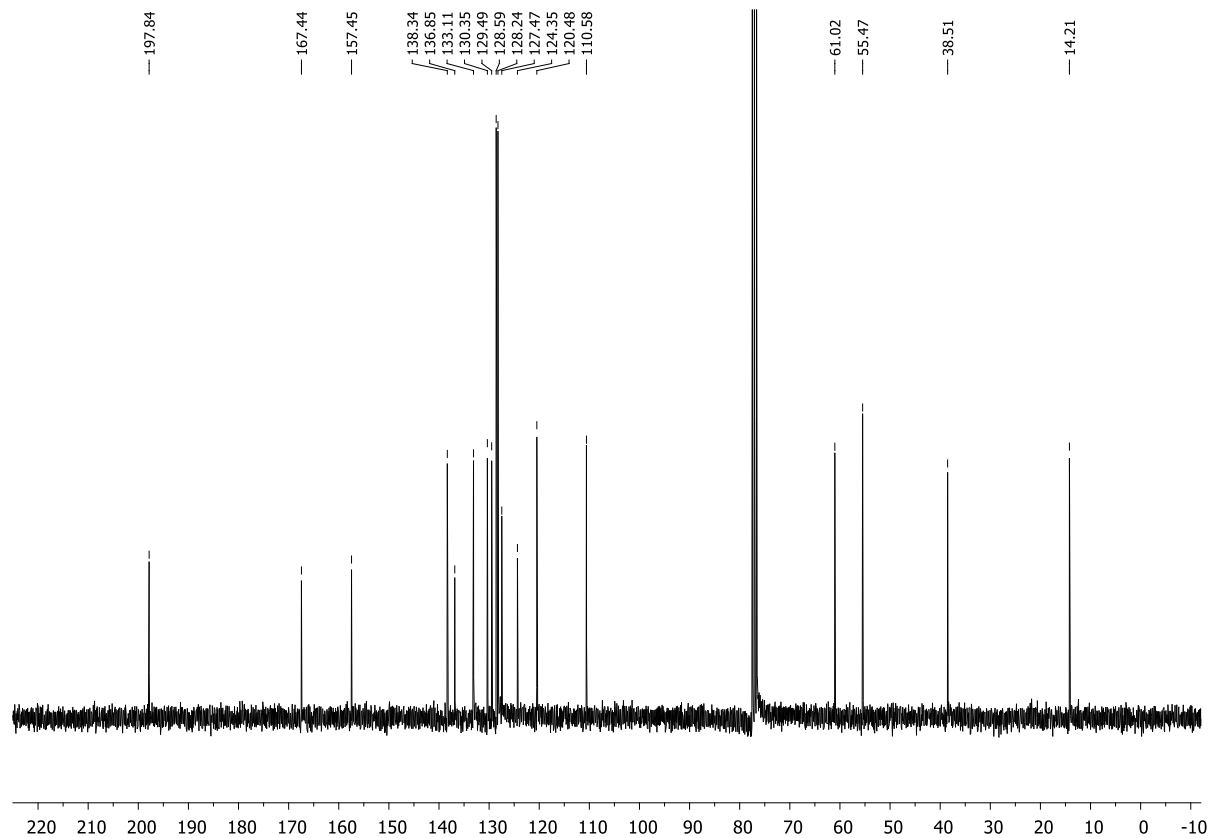
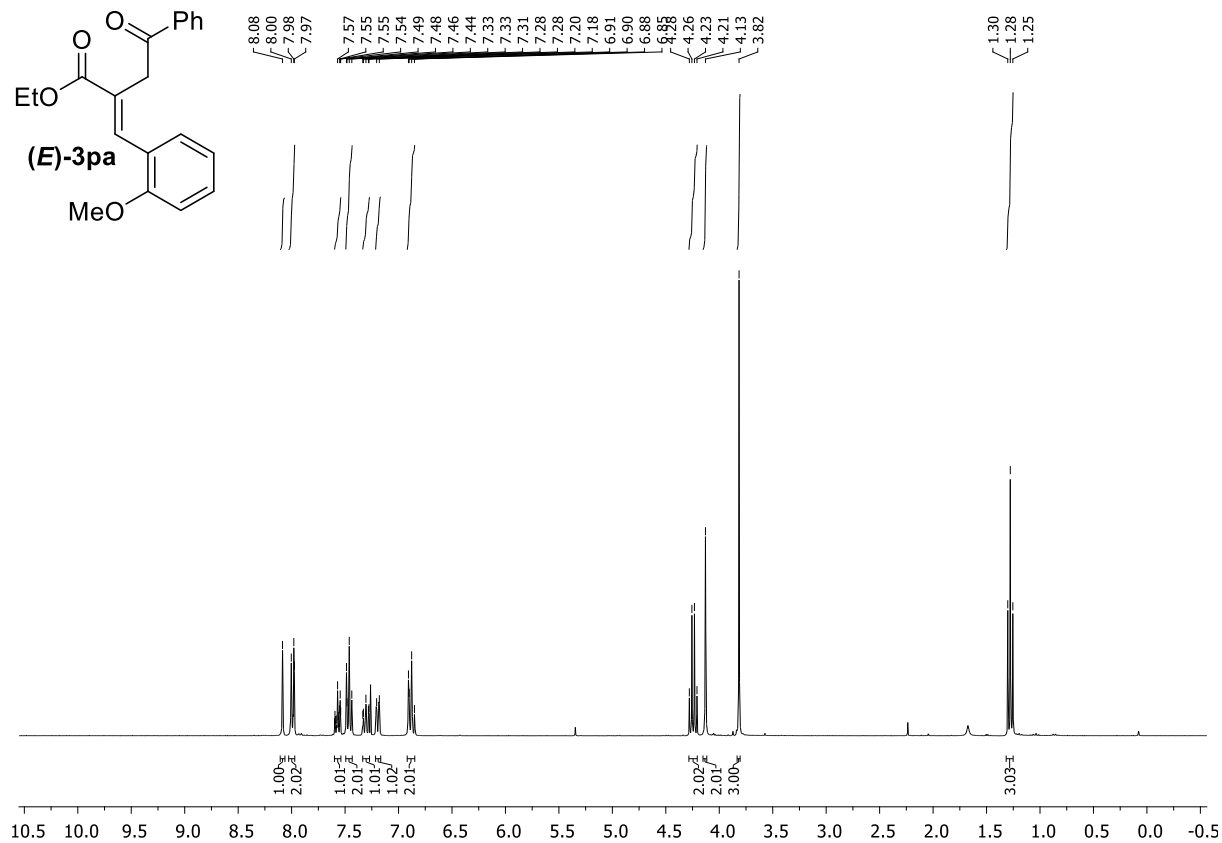
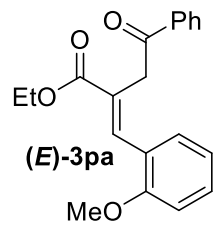


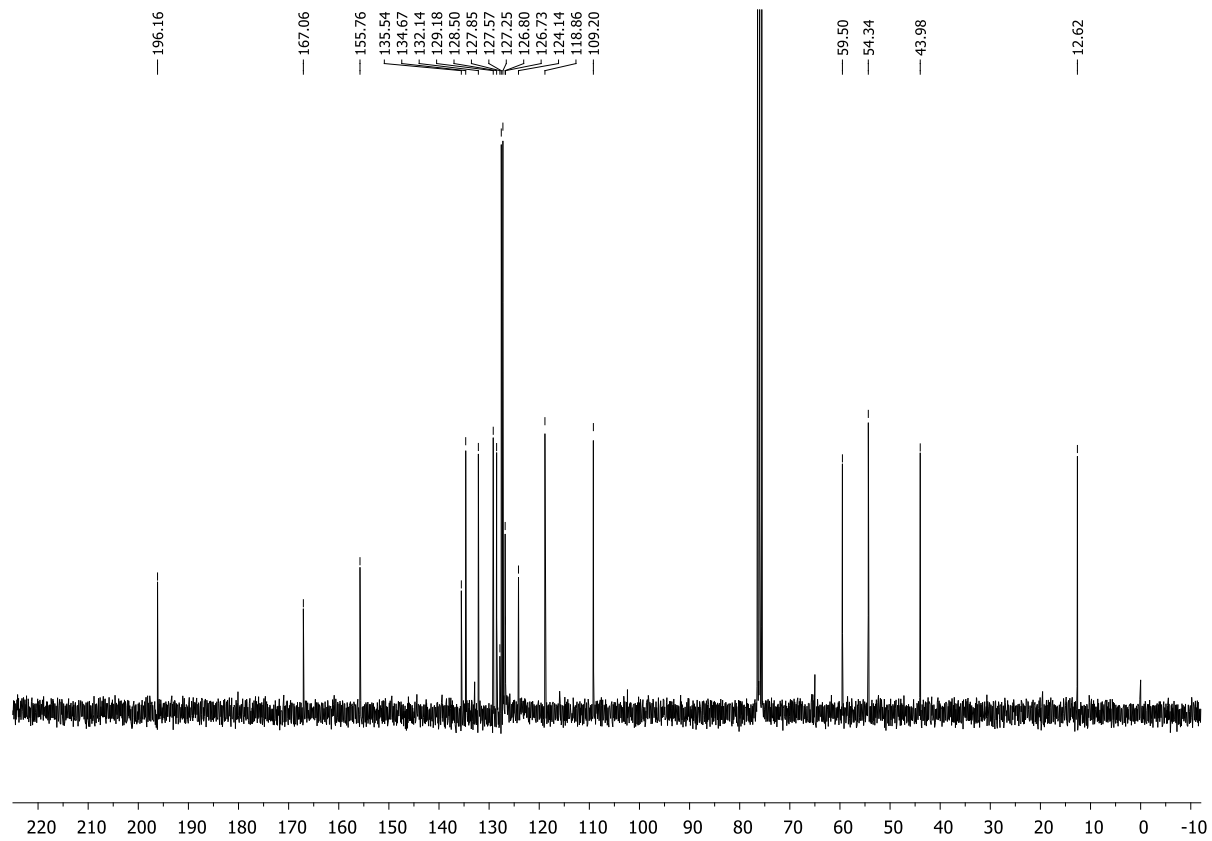
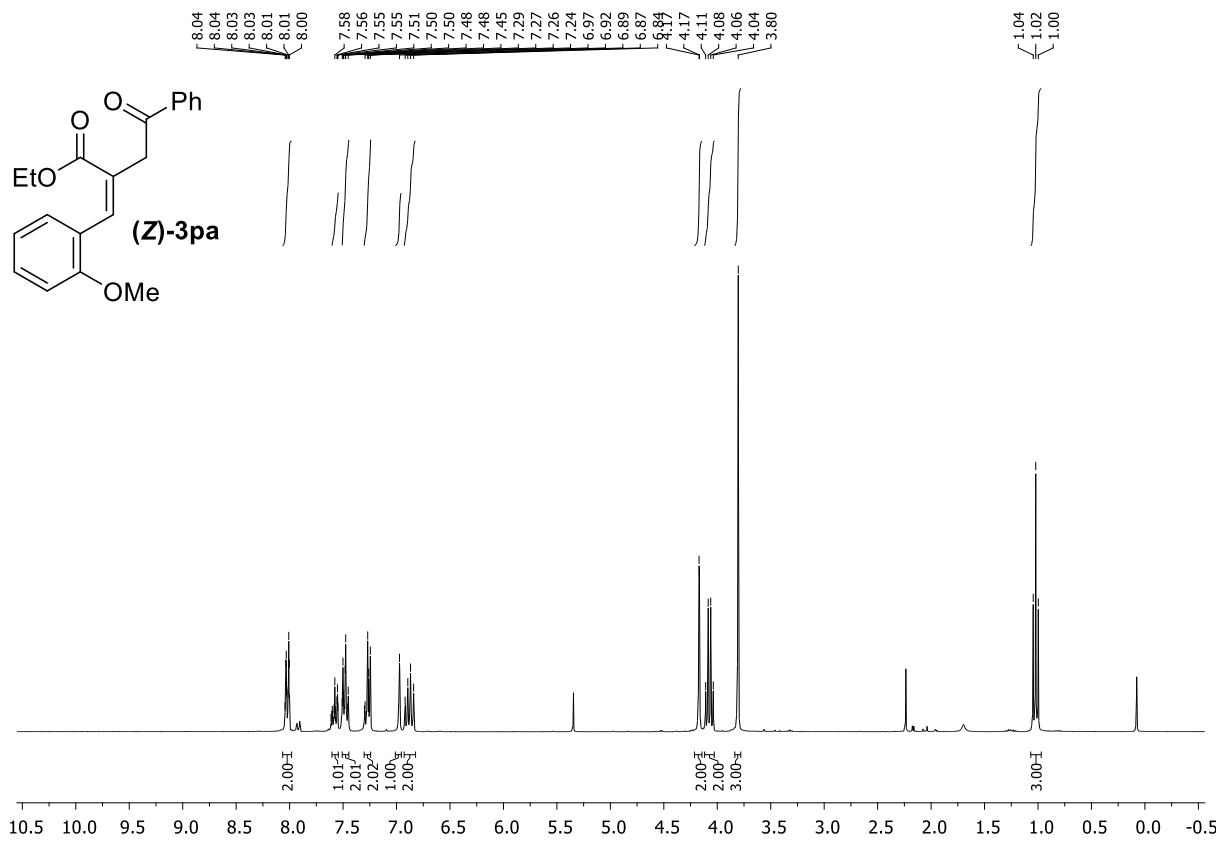


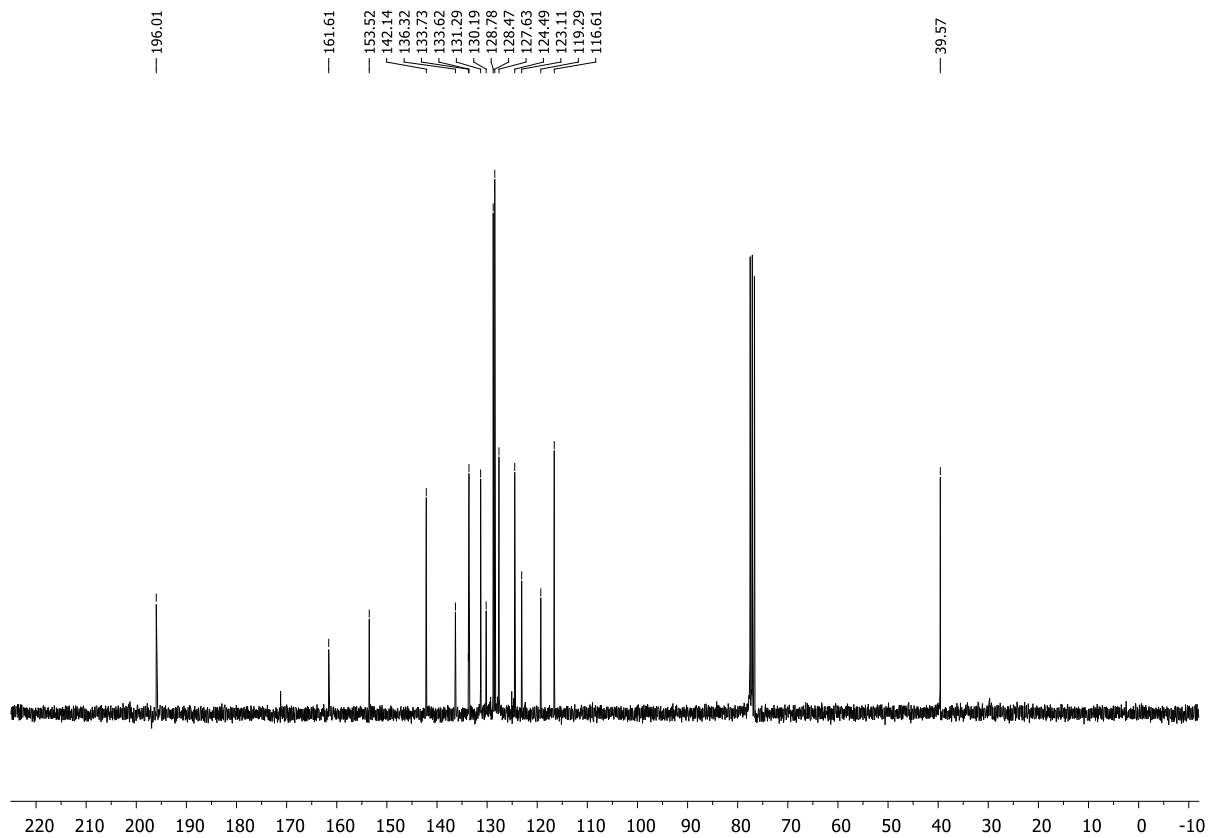
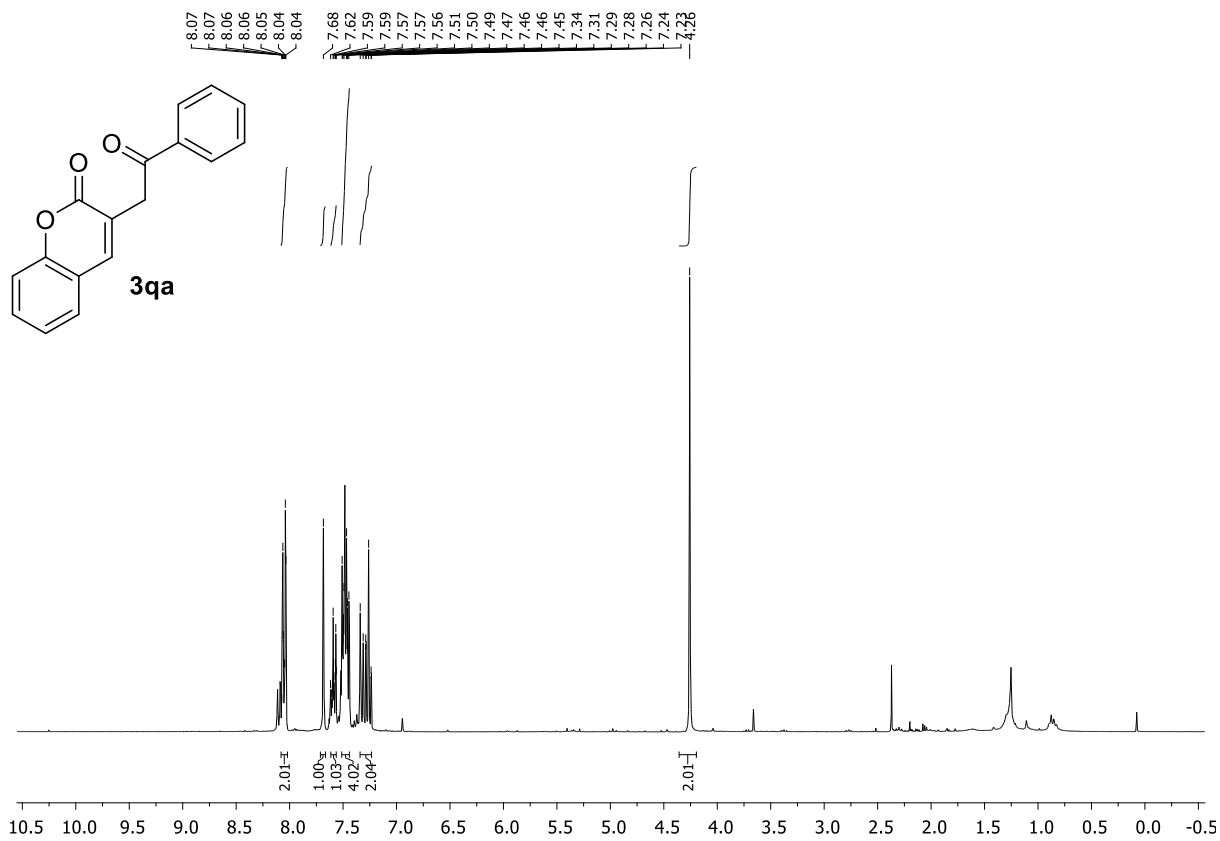


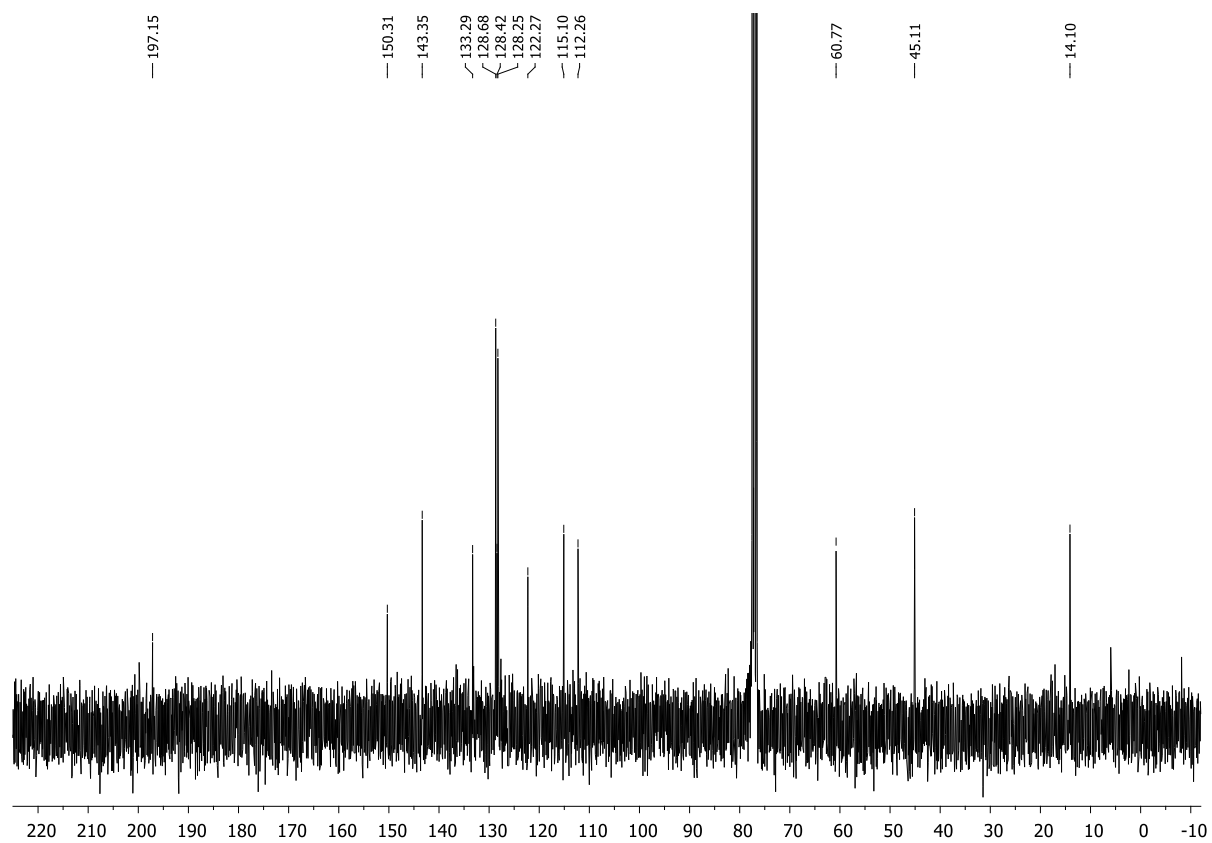
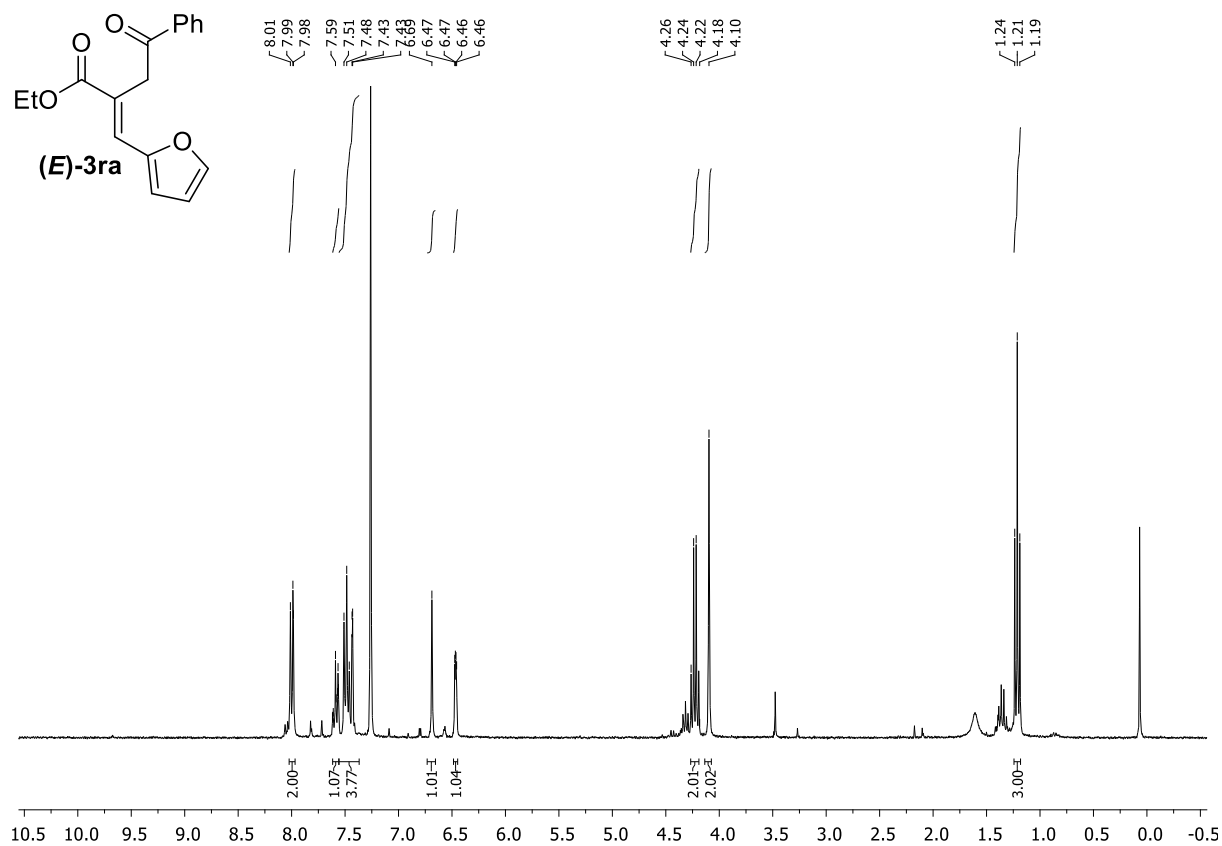
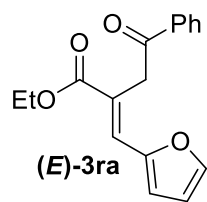


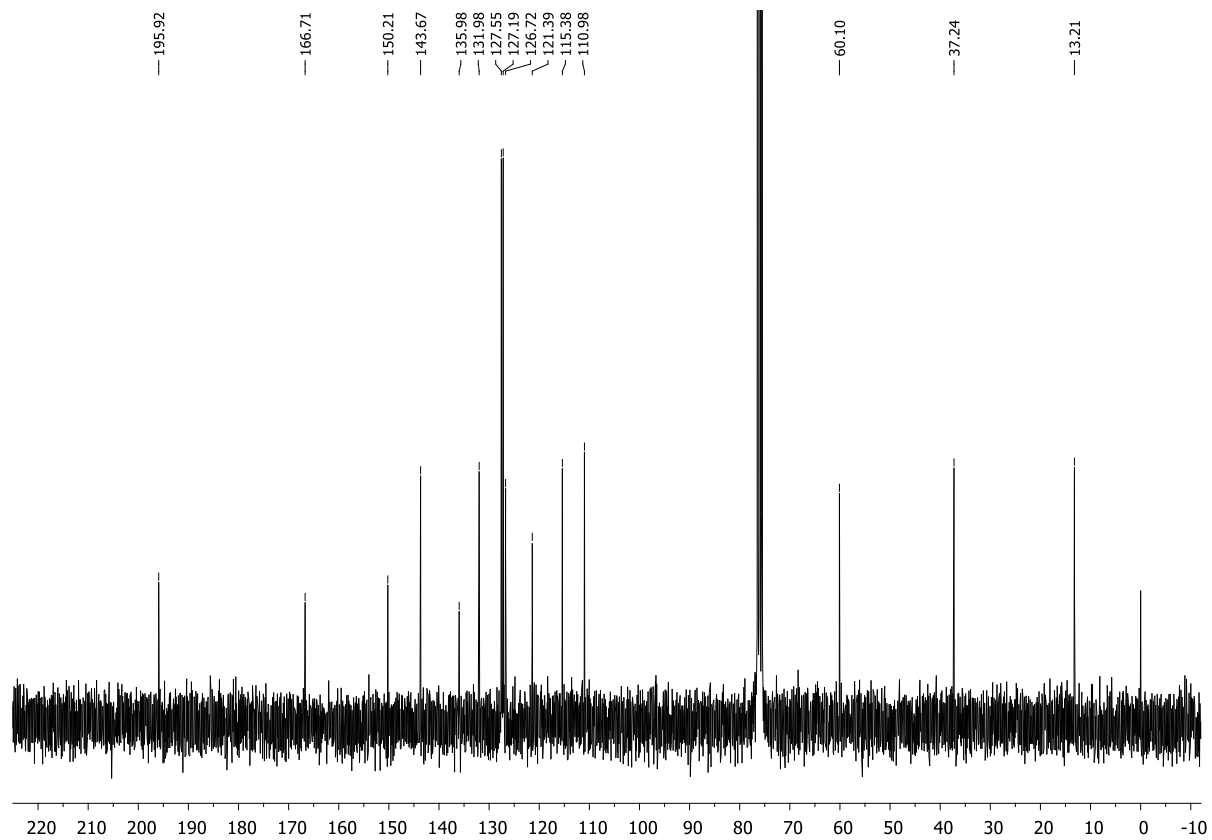
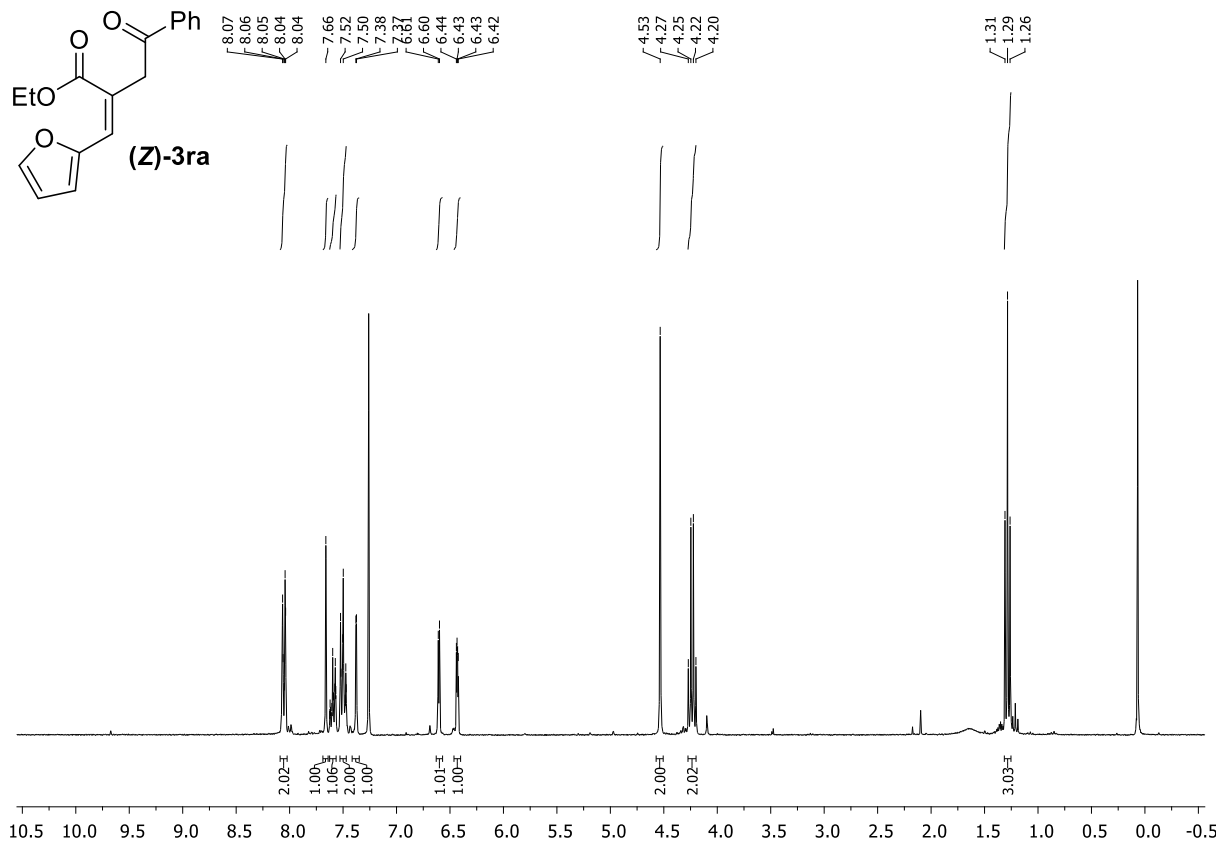


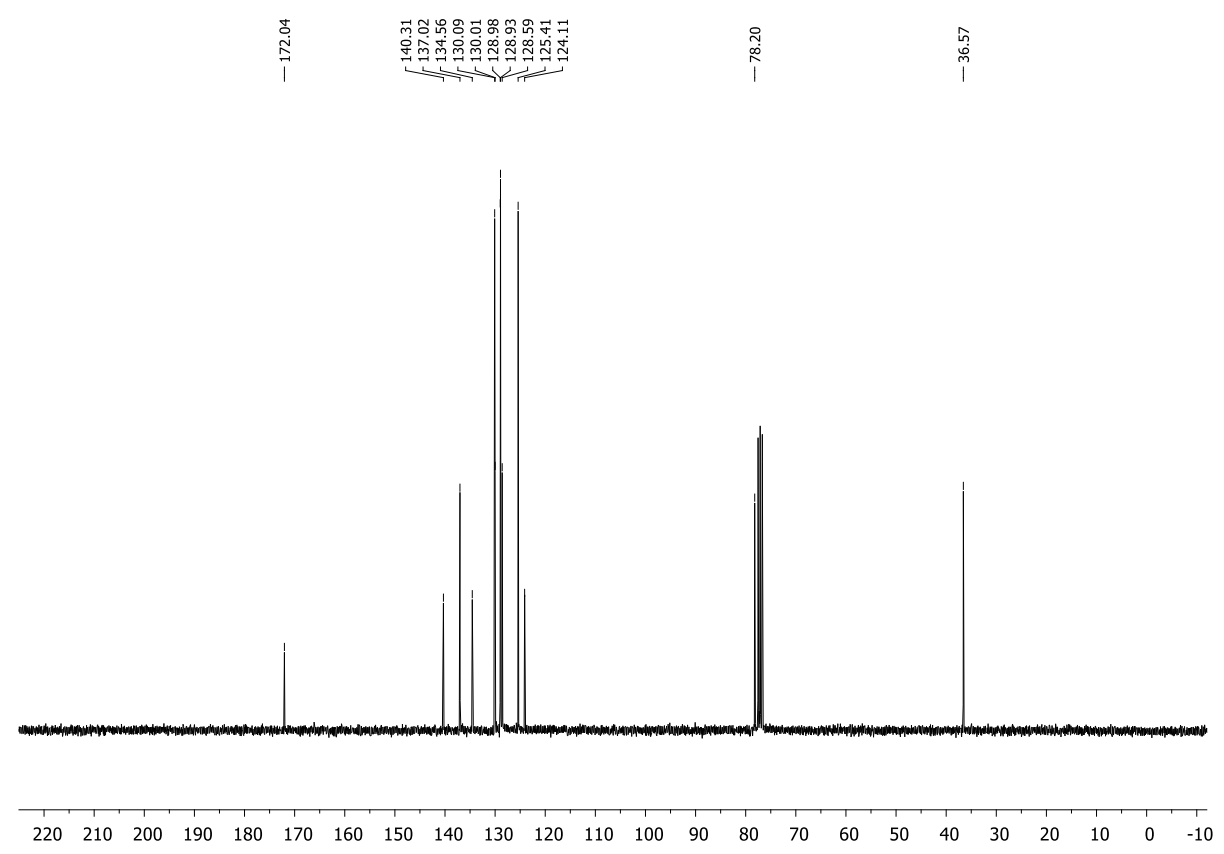
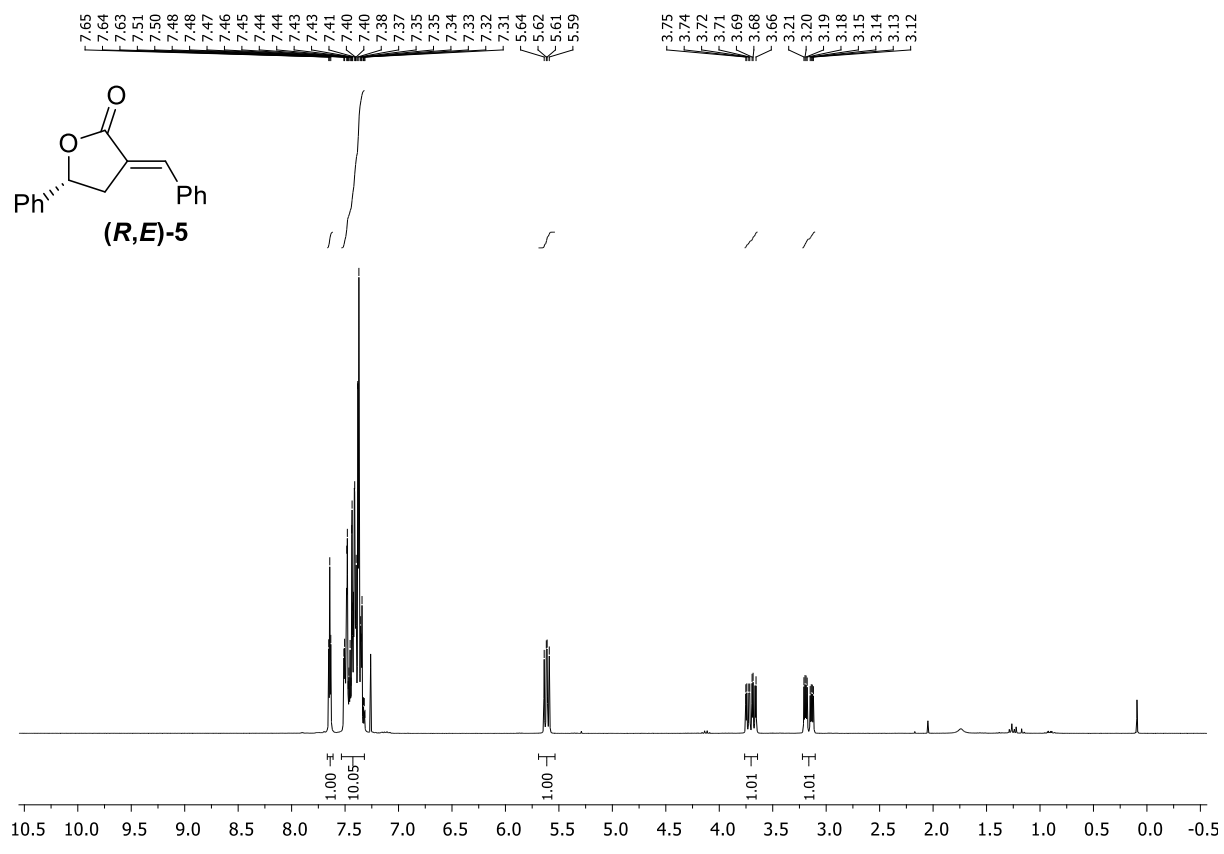


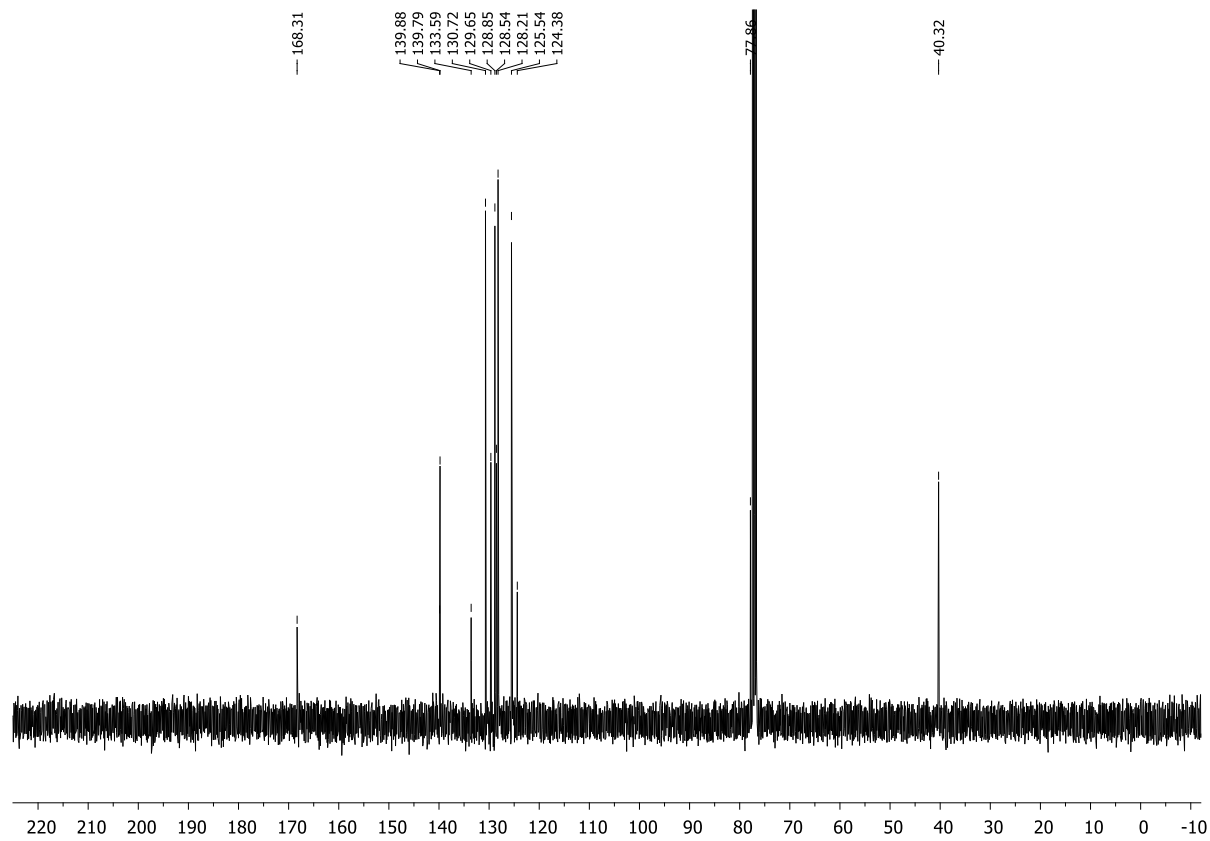
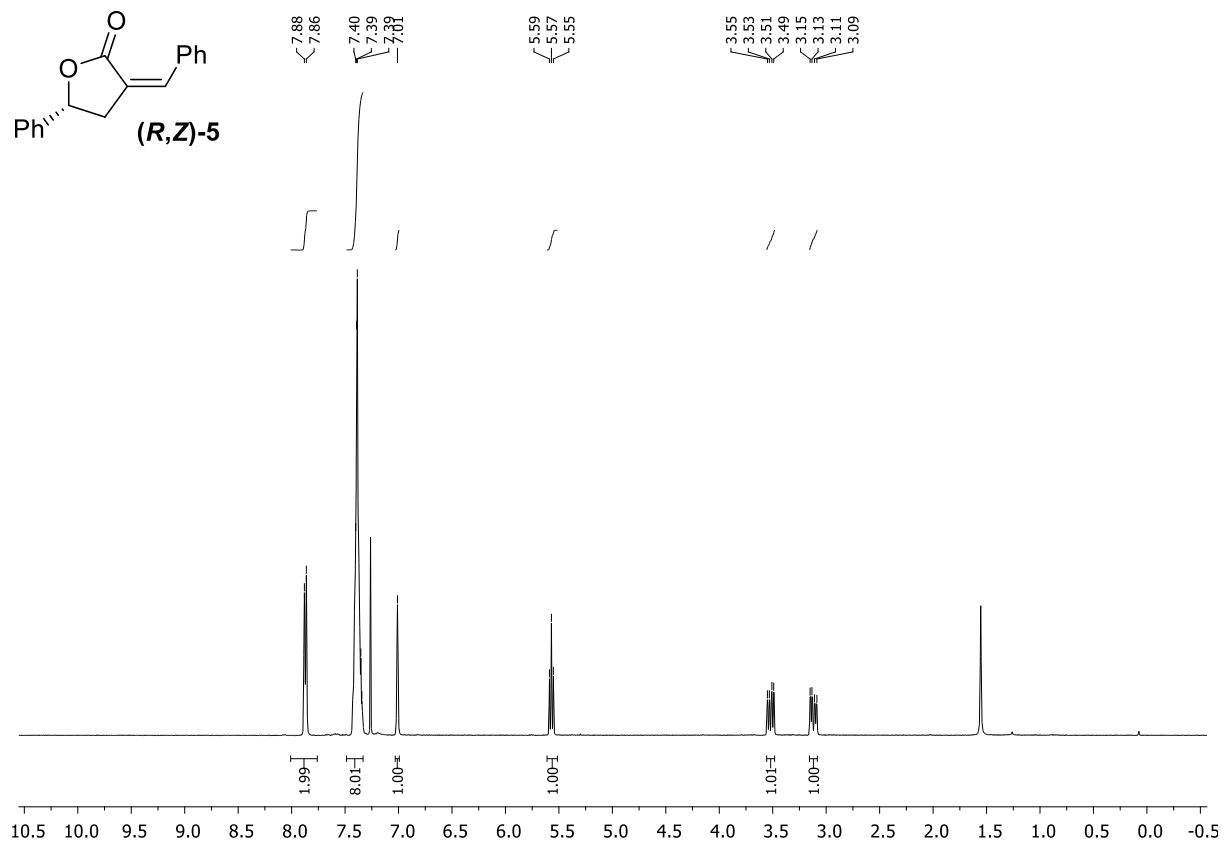
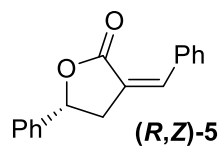






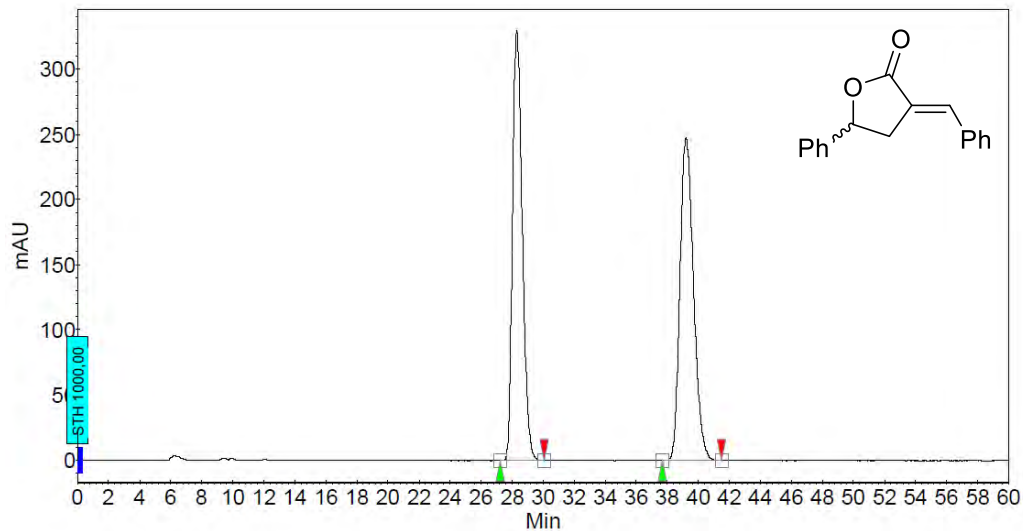






## 12. Chiral HPLC chromatograms

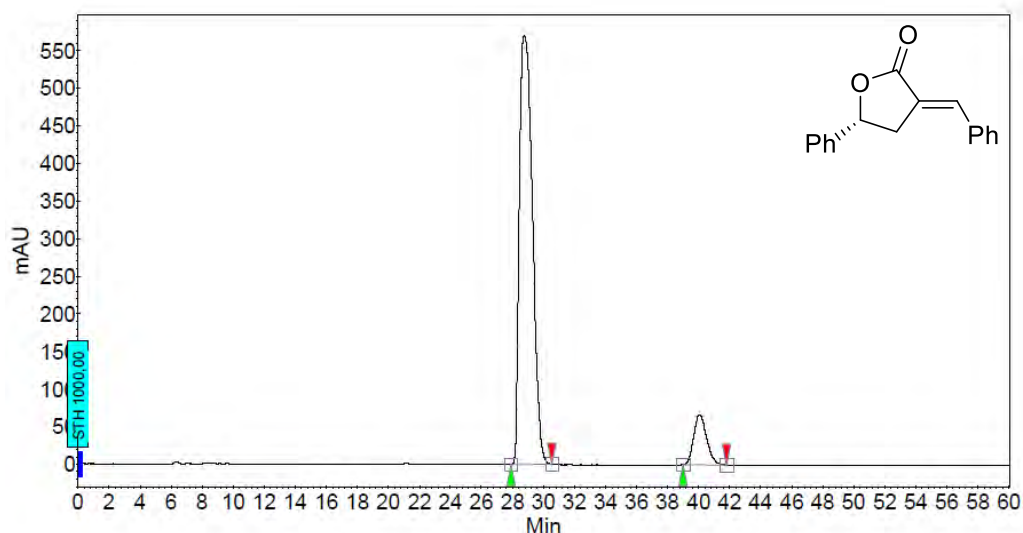
### (*E*)-3-benzylidene-5-phenyldihydrofuran-2(3*H*)-one ((*E*)-5)



#### Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	28.30	49.08	330.0	241.4	49.082
2	UNKNOWN	39.21	50.92	247.6	250.4	50.918
Total			100.00	577.6	491.8	100.000

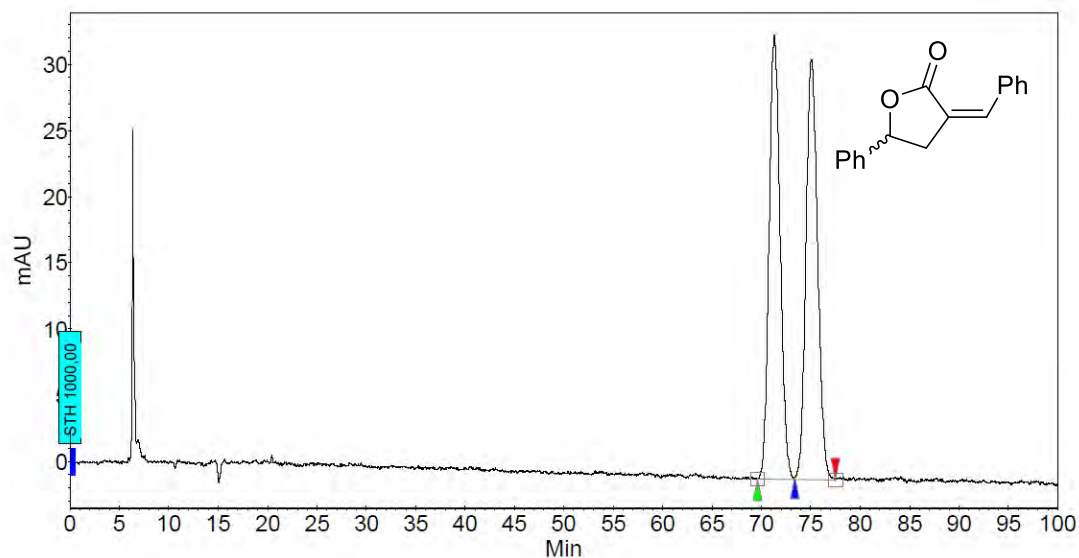
### (*R,E*)-3-benzylidene-5-phenyldihydrofuran-2(3*H*)-one ((*R,E*)-5)



#### Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	28.79	89.53	570.1	556.5	89.528
2	UNKNOWN	40.06	10.47	67.1	65.1	10.472
Total			100.00	637.2	621.6	100.000

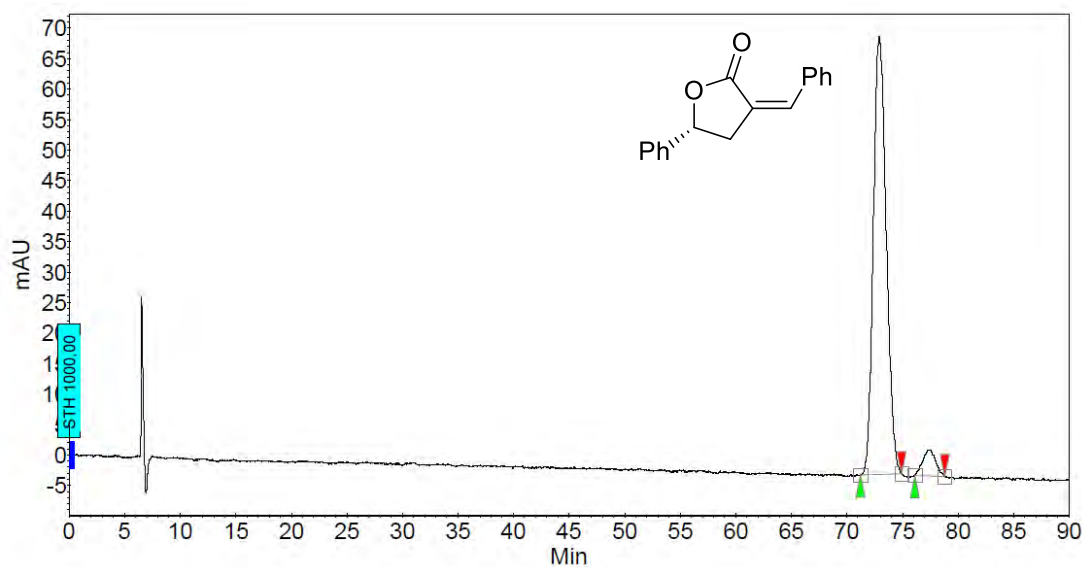
**(Z)-3-benzylidene-5-phenyldihydrofuran-2(3H)-one ((Z)-5)**



**Peak Results :**

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	71.31	50.09	33.6	43.6	50.093
2	UNKNOWN	75.06	49.91	31.7	43.5	49.907
Total			100.00	65.4	87.1	100.000

**(R,Z)-3-benzylidene-5-phenyldihydrofuran-2(3H)-one ((R,Z)-5)**

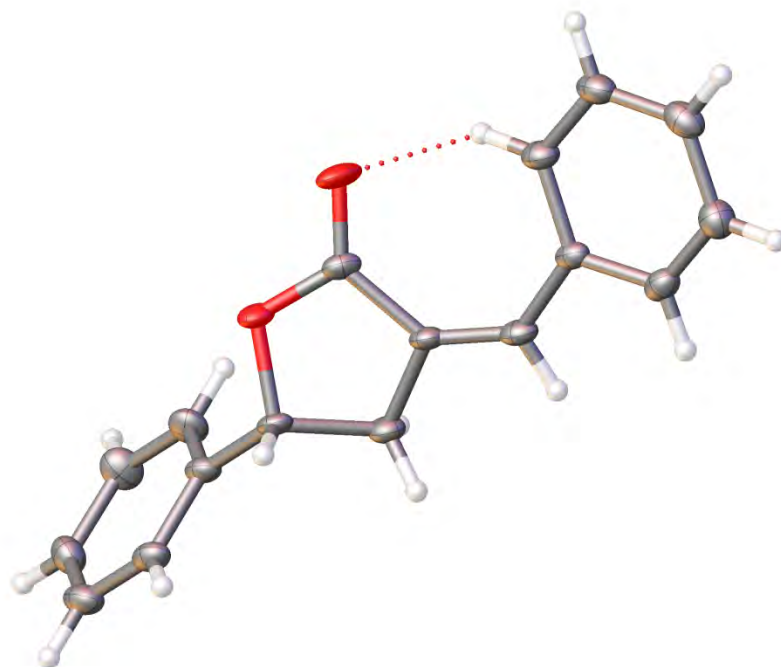


**Peak Results :**

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	72.90	94.42	71.8	97.1	94.421
2	UNKNOWN	77.46	5.58	4.3	5.7	5.579
Total			100.00	76.1	102.9	100.000

### 13. X-ray crystallography data

#### *(R,Z)*-3-benzylidene-5-phenyldihydrofuran-2(3*H*)-one (*(R,Z)*-5)



**Table 1.** Crystal data and structure refinement for *(R,Z)*-5.

Empirical formula	C <sub>17</sub> H <sub>14</sub> O <sub>2</sub>
Formula weight	250.28
Temperature /K	123.01(10)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	5.9605(4)
b/Å	9.7758(9)
c/Å	22.163(2)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1291.39(19)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.287
μ/mm <sup>-1</sup>	0.665
F(000)	528.0
Crystal size/mm <sup>3</sup>	0.22×0.09×0.06
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	3.989 to 74.300
Index ranges	-7 ≤ h ≤ 7, -11 ≤ k ≤ 12, -26 ≤ l ≤ 27

Reflections collected	5343
Independent reflections	2556 [ $R_{\text{int}} = 0.0804$ , $R_{\text{sigma}} = 0.0868$ ]
Data/restraints/parameters	2556/0/172
Goodness-of-fit on $F^2$	1.058
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0655$ , $wR_2 = 0.1625$
Final R indexes [all data]	$R_1 = 0.0794$ , $wR_2 = 0.1776$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.274/-0.412
Flack parameter	-0.4(3)

**Table 2.** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for (**R,Z**)-**5**.  $U_{eq}$  is defined as 1/3 of the trace of the orthogonalised  $U_{ij}$  tensor.

Atom	x	y	z	$U_{eq}$
O1	5017(4)	7652(3)	3606.4(12)	23.5(6)
O2	2178(5)	6297(3)	3361.3(14)	31.1(7)
C5	4078(6)	6400(4)	3554.6(16)	21.2(8)
C1	7965(6)	8784(4)	4174.1(17)	21.3(7)
C7	4409(6)	3011(4)	3349.5(16)	20.0(8)
C2	7354(6)	7535(4)	3809.0(15)	19.4(7)
C4	5684(6)	5351(4)	3779.4(16)	19.7(7)
C3	7399(6)	6159(4)	4130.3(17)	23.7(8)
C8	2266(7)	3290(4)	3106.8(17)	24.3(8)
C6	5789(6)	3995(4)	3684.7(16)	22.0(8)
C12	5299(7)	1703(4)	3269.6(17)	23.9(8)
C17	9962(6)	9460(4)	4049.7(16)	23.6(8)
C13	6554(6)	9263(4)	4629.1(19)	27.0(8)
C10	2051(7)	1002(4)	2703.1(17)	28.4(9)
C15	9130(7)	11106(4)	4820.7(18)	27.8(9)
C9	1119(7)	2285(4)	2788.2(18)	27.3(8)
C16	10545(7)	10624(5)	4372(2)	29.8(9)
C11	4168(7)	715(5)	2947.7(18)	28.7(9)
C14	7138(8)	10413(5)	4949.6(19)	31.6(10)

**Table 3.** Anisotropic Displacement Parameters ( $\times 10^4$ ) for (**R,Z**)-**5**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^*U_{11} + \dots + 2hka^*b^*U_{12}]$ .

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
O1	15.2(12)	26.2(13)	29.3(14)	-1.1(10)	-9.8(10)	2.0(11)
O2	15.5(13)	36.2(16)	41.4(17)	-8.8(13)	-11.2(11)	8.6(12)
C5	13.9(16)	29.5(19)	20.1(17)	-3.0(14)	-1.2(12)	3.9(15)
C1	12.6(15)	29.2(18)	22.2(17)	5.3(14)	0.2(13)	-0.7(15)
C7	14.3(16)	27.0(18)	18.7(16)	6.4(13)	0.2(12)	0.6(15)
C2	9.7(15)	27.6(17)	20.9(16)	2.4(13)	-1.4(11)	2.1(14)
C4	11.3(15)	26.3(17)	21.6(17)	2.2(13)	-3.0(11)	0.6(14)
C3	16.3(17)	29.2(18)	25.6(18)	2.2(14)	-6.0(13)	0.2(15)
C8	17.7(17)	31.7(19)	23.5(18)	4.3(14)	-3.9(14)	-0.7(16)
C6	14.3(16)	32(2)	19.9(17)	3.7(14)	-3.6(12)	0.8(15)
C12	19.0(17)	28.7(18)	24.1(19)	6.9(14)	2.9(13)	4.1(15)
C17	15.4(16)	32.4(19)	23.1(18)	6.5(14)	3.0(13)	0.9(16)
C13	19.8(18)	32(2)	29(2)	2.4(17)	9.4(14)	-2.9(16)
C10	29(2)	34(2)	21.5(19)	1.5(15)	-0.6(15)	-10.1(18)
C15	30(2)	24.7(18)	29(2)	3.2(15)	-0.2(15)	-6.1(17)
C9	20.0(17)	35(2)	26.5(19)	6.3(16)	-3.2(14)	-5.7(17)
C16	19.0(18)	37(2)	33(2)	8.5(16)	-2.1(14)	-5.4(18)
C11	31(2)	26.9(19)	28(2)	0.9(15)	0.1(15)	-1.6(18)

**Table 3.** Anisotropic Displacement Parameters ( $\times 10^4$ ) for (*R,Z*)-**5**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^2U_{11}+\dots+2hka*b*U_{12}]$ .

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
C14	32(2)	36(2)	27(2)	-2.9(15)	8.3(16)	-3(2)

**Table 4.** Bond Lengths for (*R,Z*)-**5**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C5	1.350(5)	O2	C5	1.215(5)
O1	C2	1.468(4)	C5	C4	1.489(5)
C1	C2	1.510(5)	C8	C9	1.390(6)
C1	C17	1.388(5)	C12	C11	1.377(6)
C1	C13	1.394(5)	C17	C16	1.388(6)
C7	C8	1.413(5)	C13	C14	1.374(6)
C7	C6	1.467(5)	C10	C9	1.384(6)
C7	C12	1.396(6)	C10	C11	1.402(6)
C2	C3	1.522(5)	C15	C16	1.386(6)
C4	C3	1.508(5)	C15	C14	1.397(6)
C4	C6	1.344(6)			

**Table 5.** Bond Angles for (*R,Z*)-**5**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	O1	C2	110.4(3)	C6	C4	C5	131.1(3)
O1	C5	C4	109.2(3)	C6	C4	C3	124.4(3)
O2	C5	O1	119.5(4)	C4	C3	C2	102.1(3)
O2	C5	C4	131.3(4)	C9	C8	C7	120.1(4)
C17	C1	C2	119.0(3)	C4	C6	C7	134.4(4)
C17	C1	C13	120.1(4)	C11	C12	C7	121.5(4)
C13	C1	C2	120.9(3)	C16	C17	C1	120.2(4)
C8	C7	C6	125.0(4)	C14	C13	C1	119.7(4)
C12	C7	C8	118.2(4)	C9	C10	C11	119.4(4)
C12	C7	C6	116.9(3)	C16	C15	C14	119.9(4)
O1	C2	C1	109.3(3)	C10	C9	C8	120.8(4)
O1	C2	C3	103.2(3)	C15	C16	C17	119.7(4)
C1	C2	C3	117.4(3)	C12	C11	C10	120.0(4)
C5	C4	C3	104.4(3)	C13	C14	C15	120.4(4)

**Table 6.** Hydrogen Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{Å}^2 \times 10^3$ ) for (*R,Z*)-**5**.

Atom	x	y	z	$U_{eq}$
H2	8333.3	7488.5	3454.39	23
H3A	8871.6	5739.72	4106.5	28
H3B	6970.3	6249.5	4550.62	28
H8	1621.21	4147.74	3160.29	29
H6	7010.25	3588.5	3874.4	26
H12	6687.53	1493.65	3437.57	29
H17	10910.18	9131.6	3749.62	28
H13	5223.1	8806.87	4715.44	32
H10	1279.92	337.89	2485.91	34
H15	9507.56	11889.98	5035.59	33
H9	-292.18	2475.96	2630.17	33
H16	11879.77	11078.09	4288.02	36
H11	4808.77	-143.26	2892.48	34
H14	6200.17	10732.07	5254.06	38

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## 15. Computational Details and Further Analysis Based on Computed Data

### Computational Details

Computations were conducted using the Gaussian09.E01 suit of programs.<sup>1</sup> Structures were fully optimized at B3LYP/6-311+G\*\* (closed shell species) and uB3LYP/6-311+G\*\* (open-shell species) in gas phase<sup>2,3</sup> and in solvent modeled by PCM<sup>4</sup> with the solvent being benzene, dichloromethane, acetonitrile, dimethylformamide and water. Choice of the solvents was guided by a steady increase of their dielectric constants to check for an increase of stabilization of the charged intermediates and potential impact on the driving forces associated to the key elemental steps.

All structures were confirmed as ground states by frequency analysis (zero imaginary frequencies). Thermodynamic data derived of the vibrational analysis (298 K) include zero-point energy and remained unscaled.

### Results

With the help of direct computation of the driving forces and relative stabilities of  $[\mathbf{1b-X}]^-$  for the two key elemental steps (SI-Scheme 1) we tried to elucidate which of these steps is responsible for the observed differences in reactivity of  $\mathbf{1b-X}$ . Since we were not interested in absolute values but relative stabilities in dependence of X we used as an indicator for the relative driving forces of the radical anion formation for X = Br vs. X = Cl the relative stabilities of the radical anions referenced to their closed-shell counterparts. This procedure is possible since the same catalyst was used for both substrates and hence can be taken out of the equation.

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<sup>1</sup> Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

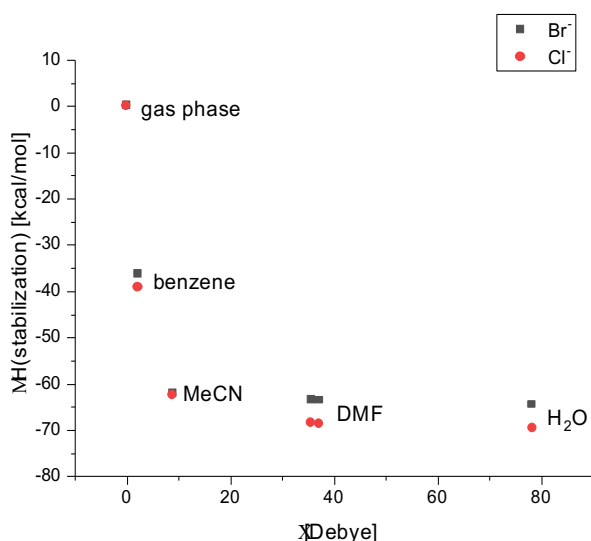
<sup>2</sup> B3LYP: Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

<sup>3</sup> Pople basis set: (a) A. D. McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72* 5639. (b) Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

<sup>4</sup> PCM as implemented in Gaussian: Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105* 2999. And citation therein.

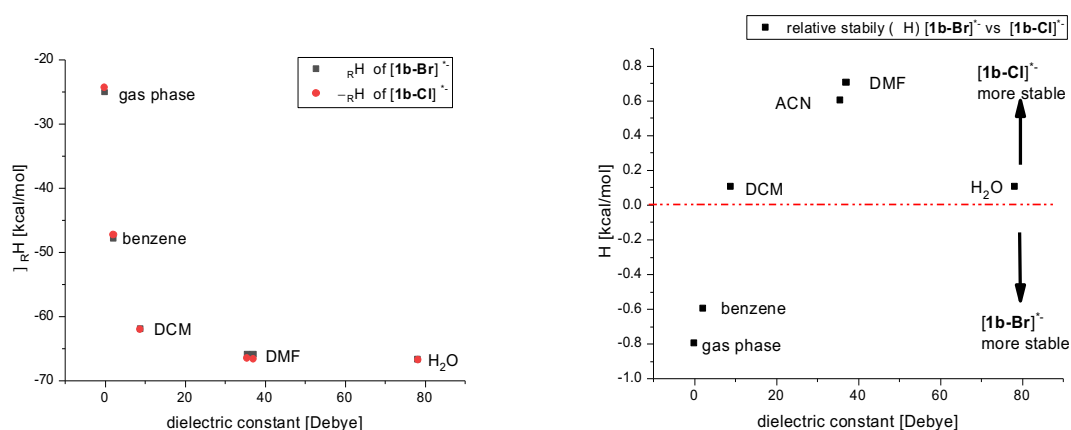


In addition, we tried to elucidate the experimentally observed solvent effect in more detail. As mentioned above, the formation of the radical anion already requires a certain polarity to be favorable. The trend in SI-Figure 11 indicates that as expected the anions are more stabilized the more dielectric the self-consistent reaction field is. Interestingly, the comparison of the relative stabilization of bromide vs. chloride anion shows, that the generally better stabilization of chloride is lost in the series gas phase, benzene, DCM to MeCN and then reemerges again when the solvents become more dielectric.



**SI-Figure 11.** The relative stabilization energies (H-values) of X<sup>-</sup> showing a trend of convergence to a similar stabilization from gas phase to MeCN and then of showing increasingly better stabilization of the bromide ion over the chloride ion in increasing dielectric solvents (DMF, water).

Since this trend also only indicated a threshold of necessary polarity but did not provide information on why MeCN was identified to be the best solvent, we also looked at the stability of the [1b-X]<sup>•-</sup> in the various solvents (SI-Figure 12). Apparently, the relative stability of the radical anions does not follow the continuous trend as the halogen anions do. Rather, the relative stabilization of [1b-Cl]<sup>•-</sup> compared to [1b-Br]<sup>•-</sup> peaks in MeCN and DMF.



**SI-Figure 12.** Reaction enthalpies (left) and relative stabilization of [1b-X]<sup>•-</sup>.

With the combination of all three contributions, i.e. solvent dependent driving force of the radical anion formation, stability of X<sup>-</sup> and of the radical anion [1b-X]<sup>•-</sup>, the experimentally observed trend in solvent-dependent reactivity of 1b-X can be rationalized.

## Optimized xyz-coordinates and thermodynamic data of the respective structures

### Gas phase data

#### Bromide anion

##### Xyz

n.a. (single atom)

##### Thermodynamic data

Zero-point correction= 0.000000 (Hartree/Particle)  
Thermal correction to Energy= 0.001416  
Thermal correction to Enthalpy= 0.002360  
Thermal correction to Gibbs Free Energy= -0.016176  
Sum of electronic and zero-point Energies= -2574.237796  
Sum of electronic and thermal Energies= -2574.236379  
Sum of electronic and thermal Enthalpies= -2574.235435  
Sum of electronic and thermal Free Energies= -2574.253971

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	0.889	2.981	39.012

#### Chloride anion

##### Xyz

n.a. (single atom)

##### Thermodynamic data

Zero-point correction= 0.000000 (Hartree/Particle)  
Thermal correction to Energy= 0.001416  
Thermal correction to Enthalpy= 0.002360  
Thermal correction to Gibbs Free Energy= -0.015023  
Sum of electronic and zero-point Energies= -460.303727  
Sum of electronic and thermal Energies= -460.302311  
Sum of electronic and thermal Enthalpies= -460.301367  
Sum of electronic and thermal Free Energies= -460.318750

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	0.889	2.981	36.586

## 1b-Br

### XYZ

22

XYZ file generated by gabedit : coordinates in Angstrom

C	3.6098060000	2.5007290000	-0.0002690000
O	2.3051620000	1.8918540000	-0.0003370000
C	2.2941510000	0.5380270000	-0.0000310000
C	0.9028690000	-0.0121930000	-0.0000940000
O	3.3000550000	-0.1269500000	0.0002340000
Br	0.8795180000	-1.9209780000	0.0002160000
C	-0.1803730000	0.7888570000	-0.0001930000
C	-1.6257030000	0.5768320000	-0.0001050000
C	-2.4233970000	1.7400830000	0.0005400000
C	-3.8102120000	1.6688040000	0.0006350000
C	-4.4412670000	0.4255490000	0.0000310000
C	-3.6706730000	-0.7366130000	-0.0006780000
C	-2.2817590000	-0.6688530000	-0.0007250000
H	3.4265140000	3.5729860000	-0.0006350000
H	4.1682490000	2.2049310000	-0.8892210000
H	4.1678970000	2.2054790000	0.8890890000
H	0.0933190000	1.8398500000	-0.0002100000
H	-1.9384160000	2.7105050000	0.0009610000
H	-4.3976400000	2.5798160000	0.0011290000
H	-5.5235550000	0.3625780000	0.0000450000
H	-4.1548750000	-1.7066330000	-0.0012310000
H	-1.7070000000	-1.5818620000	-0.0013130000

### Thermodynamic data

Zero-point correction=	0.166152 (Hartree/Particle)
Thermal correction to Energy=	0.178653
Thermal correction to Enthalpy=	0.179598
Thermal correction to Gibbs Free Energy=	0.124026
Sum of electronic and zero-point Energies=	-3111.046774
Sum of electronic and thermal Energies=	-3111.034272
Sum of electronic and thermal Enthalpies=	-3111.033328
Sum of electronic and thermal Free Energies=	-3111.088900

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	112.107	44.615	116.960

HOMO energy: 0.01156 eV

## [1b-Br]<sup>-</sup>

XYZ

22

XYZ file generated by gabedit : coordinates in Angstrom

C	3.6093040000	2.4909410000	-0.0029730000
O	2.3085630000	1.9256640000	-0.0031570000
C	2.2803200000	0.5185140000	-0.0009790000
C	0.9443920000	0.0145690000	-0.0000390000
O	3.3431410000	-0.1039250000	0.0001860000
Br	0.8962540000	-1.9272330000	0.0019830000
C	-0.2095740000	0.8114020000	0.0018000000
C	-1.6137670000	0.5894080000	0.0005140000
C	-2.4687570000	1.7425550000	0.0054410000
C	-3.8471850000	1.6497450000	0.0044170000
C	-4.4866830000	0.3973980000	-0.0016450000
C	-3.6786880000	-0.7489670000	-0.0067000000
C	-2.2946510000	-0.6712220000	-0.0057720000
H	3.4616860000	3.5731860000	-0.0047170000
H	4.1803930000	2.1914900000	-0.8874250000
H	4.1789970000	2.1941600000	0.8832870000
H	0.0618480000	1.8631430000	0.0045050000
H	-2.0025510000	2.7240900000	0.0101960000
H	-4.4408750000	2.5605440000	0.0083370000
H	-5.5686240000	0.3209250000	-0.0024160000
H	-4.1448140000	-1.7314070000	-0.0117090000
H	-1.7168570000	-1.5829350000	-0.0100800000

## Thermodynamic data

Zero-point correction=	0.162024 (Hartree/Particle)
Thermal correction to Energy=	0.174982
Thermal correction to Enthalpy=	0.175926
Thermal correction to Gibbs Free Energy=	0.118857
Sum of electronic and zero-point Energies=	-3111.087462
Sum of electronic and thermal Energies=	-3111.074504
Sum of electronic and thermal Enthalpies=	-3111.073560
Sum of electronic and thermal Free Energies=	-3111.130629

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	109.803	46.352	120.112

## 1b-Cl

XYZ

22

XYZ file generated by gabedit : coordinates in Angstrom

C	-3.9457530000	-1.8236210000	-0.0001130000
O	-2.5913950000	-1.3348310000	-0.0002870000
C	-2.4585260000	0.0114900000	-0.0000920000
C	-1.0238340000	0.4338790000	-0.0001250000
O	-3.3966180000	0.7688510000	0.0002430000
Cl	-0.8363850000	2.1710950000	0.0003800000
C	-0.0100940000	-0.4529980000	-0.0003000000
C	1.4452580000	-0.3332790000	-0.0001730000
C	2.1711370000	-1.5422590000	0.0003510000
C	3.5598440000	-1.5541580000	0.0005180000
C	4.2646690000	-0.3512170000	0.0001060000

C	3.5654670000	0.8552720000	-0.0004920000
C	2.1749820000	0.8713220000	-0.0006140000
H	-3.8601930000	-2.9080060000	0.0000300000
H	-4.4749610000	-1.4788420000	-0.8892740000
H	-4.4748410000	-1.4785800000	0.8890130000
H	-0.3598420000	-1.4800530000	-0.0003790000
H	1.6283920000	-2.4816180000	0.0006900000
H	4.0915990000	-2.4987630000	0.0010080000
H	5.3487570000	-0.3535830000	0.0002740000
H	4.1072140000	1.7943690000	-0.0008100000
H	1.6576210000	1.8177270000	-0.0010690000

### Thermodynamic data

Zero-point correction=	0.166995 (Hartree/Particle)
Thermal correction to Energy=	0.179179
Thermal correction to Enthalpy=	0.180123
Thermal correction to Gibbs Free Energy=	0.126421
Sum of electronic and zero-point Energies=	-997.127227
Sum of electronic and thermal Energies=	-997.115044
Sum of electronic and thermal Enthalpies=	-997.114100
Sum of electronic and thermal Free Energies=	-997.167802

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	112.436	44.083	113.026

LUMO energy = 0.08446 eV

### [1b-Cl]<sup>-</sup>

#### Xyz

22

XYZ file generated by gabedit : coordinates in Angstrom

C	-3.9464660000	-1.8126340000	-0.0005200000
O	-2.6002820000	-1.3672670000	-0.0010160000
C	-2.4450090000	0.0310510000	-0.0002710000
C	-1.0704690000	0.4143720000	0.0000930000
O	-3.4452790000	0.7508040000	0.0001560000
Cl	-0.8507540000	2.1839570000	0.0009690000
C	0.0123790000	-0.4753110000	0.0003020000
C	1.4277750000	-0.3444310000	-0.0000300000
C	2.2103610000	-1.5478140000	0.0011830000
C	3.5919720000	-1.5394420000	0.0010610000
C	4.3075620000	-0.3288090000	-0.0002980000
C	3.5712460000	0.8651640000	-0.0014870000
C	2.1851680000	0.8726090000	-0.0013680000
H	-3.8977120000	-2.9038360000	-0.0008420000
H	-4.4882770000	-1.4640430000	-0.8854690000
H	-4.4874690000	-1.4645170000	0.8851090000
H	-0.3331410000	-1.5041060000	0.0007550000
H	1.6845310000	-2.4988540000	0.0022330000
H	4.1287600000	-2.4849530000	0.0019780000
H	5.3921340000	-0.3189750000	-0.0003830000
H	4.0969820000	1.8171170000	-0.0025930000
H	1.6643750000	1.8180770000	-0.0023790000

### Thermodynamic data

Zero-point correction= 0.162833 (Hartree/Particle)  
Thermal correction to Energy= 0.175439  
Thermal correction to Enthalpy= 0.176383  
Thermal correction to Gibbs Free Energy= 0.121557  
Sum of electronic and zero-point Energies= -997.166584  
Sum of electronic and thermal Energies= -997.153978  
Sum of electronic and thermal Enthalpies= -997.153034  
Sum of electronic and thermal Free Energies= -997.207860

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	110.090	45.830	115.390

## 6

### Xyz

21

XYZ file generated by gabedit : coordinates in Angstrom

C	-4.5085270000	-0.7903670000	-0.0040330000
O	-3.0684040000	-0.7378740000	-0.0060330000
C	-2.5241890000	0.5060880000	0.0015530000
C	-1.0728570000	0.4598160000	-0.0004030000
O	-3.1796260000	1.5235680000	0.0088300000
C	-0.1135180000	-0.4509650000	0.0023790000
C	1.3332620000	-0.2184100000	0.0010200000
C	2.2077830000	-1.3152260000	0.0038970000
C	3.5869540000	-1.1251260000	0.0025850000
C	4.1122750000	0.1652230000	-0.0016210000
C	3.2510030000	1.2657940000	-0.0044640000
C	1.8757150000	1.0782330000	-0.0031570000
H	-4.7579190000	-1.8492200000	-0.0110210000
H	-4.9092850000	-0.2945030000	-0.8891640000
H	-4.9064140000	-0.3069150000	0.8892320000
H	-0.4298660000	-1.4997530000	0.0057480000
H	1.8006610000	-2.3209630000	0.0071530000
H	4.2499960000	-1.9827530000	0.0048240000
H	5.1858620000	0.3155820000	-0.0026670000
H	3.6569620000	2.2710450000	-0.0076990000
H	1.2068420000	1.9315700000	-0.0053140000

### Thermodynamic data

Zero-point correction= 0.162403 (Hartree/Particle)  
Thermal correction to Energy= 0.173756  
Thermal correction to Enthalpy= 0.174700  
Thermal correction to Gibbs Free Energy= 0.122270  
Sum of electronic and zero-point Energies= -536.829295  
Sum of electronic and thermal Energies= -536.817942  
Sum of electronic and thermal Enthalpies= -536.816998  
Sum of electronic and thermal Free Energies= -536.869429

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	109.034	40.581	110.350

## PCM data: Water

### [1b-Br]<sup>-</sup> in water

#### Xyz-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	-3.6576160000	2.4481230000	0.2594510000
O	-2.3449890000	1.8808830000	0.2025880000
C	-2.2849260000	0.4981890000	0.0677430000
C	-0.9409230000	0.0339280000	-0.0049080000
O	-3.3331710000	-0.1655020000	0.0396020000
Br	-0.8307710000	-1.9200430000	-0.1711380000
C	0.1868600000	0.8521210000	-0.1825700000
C	1.5928140000	0.6317530000	-0.0497930000
C	2.4818240000	1.6634630000	-0.4834020000
C	3.8577790000	1.5443780000	-0.3795770000
C	4.4382260000	0.3885940000	0.1659460000
C	3.5919190000	-0.6330500000	0.6129950000
C	2.2099870000	-0.5241490000	0.5150060000
H	-3.5073810000	3.5226690000	0.3578210000
H	-4.2154970000	2.0722720000	1.1198870000
H	-4.2230510000	2.2355630000	-0.6506190000
H	-0.0811730000	1.8711670000	-0.4506670000
H	2.0563740000	2.5667370000	-0.9108280000
H	4.4904700000	2.3558960000	-0.7256660000
H	5.5149170000	0.2926410000	0.2454340000
H	4.0187680000	-1.5287900000	1.0543590000
H	1.5931990000	-1.3298000000	0.8872460000

#### Thermodynamic data

Zero-point correction=	0.162286 (Hartree/Particle)
Thermal correction to Energy=	0.175141
Thermal correction to Enthalpy=	0.176085
Thermal correction to Gibbs Free Energy=	0.120102
Sum of electronic and zero-point Energies=	-3111.163650
Sum of electronic and thermal Energies=	-3111.150795
Sum of electronic and thermal Enthalpies=	-3111.149851
Sum of electronic and thermal Free Energies=	-3111.205834

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	109.903	46.243	117.827

### 1b-Br in water

#### Xyz-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	-3.6132990000	2.5101240000	0.0004040000
O	-2.3117200000	1.8822370000	0.0003980000
C	-2.2958840000	0.5390150000	0.0000150000
C	-0.9063890000	-0.0102120000	0.0000210000
O	-3.3025240000	-0.1368170000	-0.0002800000
Br	-0.8736530000	-1.9241500000	-0.0003300000
C	0.1789510000	0.7889690000	0.0001570000
C	1.6237290000	0.5774000000	0.0001610000

C	2.4179050000	1.7441740000	-0.0005300000
C	3.8055600000	1.6749320000	-0.0005990000
C	4.4392750000	0.4321770000	0.0000800000
C	3.6716720000	-0.7333710000	0.0008320000
C	2.2821970000	-0.6682830000	0.0008650000
H	-3.4139480000	3.5785200000	0.0007910000
H	-4.1703210000	2.2237600000	0.8923700000
H	-4.1700410000	2.2243560000	-0.8919290000
H	-0.0924250000	1.8405660000	0.0002090000
H	1.9316240000	2.7135410000	-0.0010310000
H	4.3910030000	2.5869200000	-0.0011650000
H	5.5215180000	0.3716020000	0.0000460000
H	4.1584490000	-1.7018680000	0.0014050000
H	1.7136380000	-1.5850680000	0.0014830000

### Thermodynamic data

Zero-point correction=	0.165862 (Hartree/Particle)
Thermal correction to Energy=	0.177505
Thermal correction to Enthalpy=	0.178450
Thermal correction to Gibbs Free Energy=	0.125908
Sum of electronic and zero-point Energies=	-3111.056088
Sum of electronic and thermal Energies=	-3111.044444
Sum of electronic and thermal Enthalpies=	-3111.043500
Sum of electronic and thermal Free Energies=	-3111.096042

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	111.386	42.721	110.584

### [1b-Cl]<sup>-</sup> in water

#### Xyz-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	3.9682460000	-1.8164430000	0.0005550000
O	2.6159240000	-1.3503240000	0.0002630000
C	2.4465210000	0.0293920000	-0.0001150000
C	1.0729370000	0.4054450000	-0.0001980000
O	3.4382430000	0.7781180000	-0.0000580000
Cl	0.8398760000	2.1782480000	-0.0003960000
C	-0.0133450000	-0.4856780000	-0.0005030000
C	-1.4327420000	-0.3488590000	-0.0001770000
C	-2.2126660000	-1.5520190000	-0.0012050000
C	-3.5959270000	-1.5404530000	-0.0009220000
C	-4.3055520000	-0.3275450000	0.0004070000
C	-3.5728280000	0.8659100000	0.0014630000
C	-2.1836270000	0.8693940000	0.0011900000
H	3.9025640000	-2.9039040000	0.0007860000
H	4.5057170000	-1.4787460000	0.8895770000
H	4.5059740000	-1.4791340000	-0.8884560000
H	0.3275860000	-1.5159670000	-0.0010500000
H	-1.6903910000	-2.5044220000	-0.0022480000
H	-4.1352700000	-2.4828470000	-0.0017480000
H	-5.3892590000	-0.3162600000	0.0006260000
H	-4.0977100000	1.8168590000	0.0025440000
H	-1.6665330000	1.8169760000	0.0020800000

**Thermodynamic data**

Zero-point correction= 0.163049 (Hartree/Particle)  
 Thermal correction to Energy= 0.175662  
 Thermal correction to Enthalpy= 0.176607  
 Thermal correction to Gibbs Free Energy= 0.121256  
 Sum of electronic and zero-point Energies= -997.243364  
 Sum of electronic and thermal Energies= -997.230751  
 Sum of electronic and thermal Enthalpies= -997.229806  
 Sum of electronic and thermal Free Energies= -997.285157

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	110.230	45.762	116.494

**1b-Cl in water****XYZ-matrix**

22

XYZ file generated by gabedit : coordinates in Angstrom

C	3.9484290000	-1.8336620000	0.0000530000
O	2.5954510000	-1.3255090000	0.0001050000
C	2.4584750000	0.0095290000	0.0000390000
C	1.0261080000	0.4312350000	0.0000470000
O	3.3959680000	0.7784620000	-0.0000570000
Cl	0.8330790000	2.1738760000	-0.0000050000
C	0.0094710000	-0.4529250000	0.0000440000
C	-1.4451780000	-0.3327680000	0.0000150000
C	-2.1680770000	-1.5446560000	-0.0004250000
C	-3.5575020000	-1.5576750000	-0.0004980000
C	-4.2640460000	-0.3548390000	-0.0001030000
C	-3.5672080000	0.8543650000	0.0003670000
C	-2.1763160000	0.8722340000	0.0004210000
H	3.8463210000	-2.9156130000	0.0000810000
H	4.4770990000	-1.4983890000	0.8922220000
H	4.4770210000	-1.4984260000	-0.8921750000
H	0.3563750000	-1.4809580000	0.0000220000
H	-1.6247090000	-2.4832520000	-0.0007180000
H	-4.0877790000	-2.5028280000	-0.0008540000
H	-5.3479570000	-0.3587610000	-0.0001490000
H	-4.1108620000	1.7921200000	0.0006980000
H	-1.6641460000	1.8215760000	0.0008060000

**Thermodynamic data**

Zero-point correction= 0.166797 (Hartree/Particle)  
 Thermal correction to Energy= 0.179003  
 Thermal correction to Enthalpy= 0.179948  
 Thermal correction to Gibbs Free Energy= 0.125950  
 Sum of electronic and zero-point Energies= -997.136522  
 Sum of electronic and thermal Energies= -997.124316  
 Sum of electronic and thermal Enthalpies= -997.123372  
 Sum of electronic and thermal Free Energies= -997.177370

	E (Thermal)	CV	S
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	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	112.326	44.151	113.648

## 6 water

### Xyz-matrix

21

XYZ file generated by gabedit : coordinates in Angstrom

C	-4.5196920000	-0.7925630000	-0.0032390000
O	-3.0739100000	-0.7293110000	-0.0050790000
C	-2.5227780000	0.5002150000	0.0009690000
C	-1.0737750000	0.4567170000	-0.0004920000
O	-3.1717820000	1.5308720000	0.0068980000
C	-0.1112010000	-0.4528120000	0.0020340000
C	1.3345520000	-0.2182870000	0.0009030000
C	2.2076890000	-1.3177550000	0.0034520000
C	3.5874910000	-1.1273050000	0.0024260000
C	4.1134460000	0.1639880000	-0.0011410000
C	3.2531120000	1.2666720000	-0.0036760000
C	1.8770770000	1.0795640000	-0.0026740000
H	-4.7587060000	-1.8527860000	-0.0086050000
H	-4.9198970000	-0.3051500000	-0.8922820000
H	-4.9172260000	-0.3147810000	0.8922120000
H	-0.4229730000	-1.5027320000	0.0050710000
H	1.8004160000	-2.3229860000	0.0062370000
H	4.2500010000	-1.9850550000	0.0044080000
H	5.1869650000	0.3137680000	-0.0019340000
H	3.6602060000	2.2712580000	-0.0064210000
H	1.2112220000	1.9353790000	-0.0046110000

### Thermodynamic data

Zero-point correction=	0.162243 (Hartree/Particle)
Thermal correction to Energy=	0.173605
Thermal correction to Enthalpy=	0.174549
Thermal correction to Gibbs Free Energy=	0.121875
Sum of electronic and zero-point Energies=	-536.838361
Sum of electronic and thermal Energies=	-536.826999
Sum of electronic and thermal Enthalpies=	-536.826055
Sum of electronic and thermal Free Energies=	-536.878728

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	108.939	40.610	110.861

## Bromide anion in water

### Xyz-matrix

n.a.

### Thermodynamic data

Zero-point correction=	0.000000 (Hartree/Particle)
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.016176
Sum of electronic and zero-point Energies=	-2574.340735
Sum of electronic and thermal Energies=	-2574.339319

Sum of electronic and thermal Enthalpies= -2574.338375  
Sum of electronic and thermal Free Energies= -2574.356911

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	0.889	2.981	39.012

## Chloride anion in water

### XYZ-matrix

n.a.

### Thermodynamic data

Zero-point correction= 0.000000 (Hartree/Particle)  
Thermal correction to Energy= 0.001416  
Thermal correction to Enthalpy= 0.002360  
Thermal correction to Gibbs Free Energy= -0.015023  
Sum of electronic and zero-point Energies= -460.414794  
Sum of electronic and thermal Energies= -460.413378  
Sum of electronic and thermal Enthalpies= -460.412434  
Sum of electronic and thermal Free Energies= -460.429817

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	0.889	2.981	36.586

## PCM data: acetonitrile (MeCN)

### 1b-Br in MeCN

#### XYZ-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	-3.6132990000	2.5101240000	0.0004040000
O	-2.3117200000	1.8822370000	0.0003980000
C	-2.2958840000	0.5390150000	0.0000150000
C	-0.9063890000	-0.0102120000	0.0000210000
O	-3.3025240000	-0.1368170000	-0.0002800000
Br	-0.8736530000	-1.9241500000	-0.0003300000
C	0.1789510000	0.7889690000	0.0001570000
C	1.6237290000	0.5774000000	0.0001610000
C	2.4179050000	1.7441740000	-0.0005300000
C	3.8055600000	1.6749320000	-0.0005990000
C	4.4392750000	0.4321770000	0.0000800000
C	3.6716720000	-0.7333710000	0.0008320000
C	2.2821970000	-0.6682830000	0.0008650000
H	-3.4139480000	3.5785200000	0.0007910000
H	-4.1703210000	2.2237590000	0.8923700000
H	-4.1700410000	2.2243550000	-0.8919290000
H	-0.0924250000	1.8405660000	0.0002090000
H	1.9316240000	2.7135410000	-0.0010310000
H	4.3910030000	2.5869200000	-0.0011650000
H	5.5215180000	0.3716030000	0.0000460000
H	4.1584490000	-1.7018680000	0.0014050000
H	1.7136380000	-1.5850680000	0.0014830000

### Thermodynamic data

Zero-point correction= 0.165865 (Hartree/Particle)  
Thermal correction to Energy= 0.177509  
Thermal correction to Enthalpy= 0.178453  
Thermal correction to Gibbs Free Energy= 0.125910  
Sum of electronic and zero-point Energies= -3111.055834  
Sum of electronic and thermal Energies= -3111.044190  
Sum of electronic and thermal Enthalpies= -3111.043246  
Sum of electronic and thermal Free Energies= -3111.095788

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	111.389	42.720	110.586

### 1b-Cl in MeCN

#### XYZ-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	3.9484290000	-1.8336620000	0.0000530000
O	2.5954510000	-1.3255090000	0.0001050000
C	2.4584750000	0.0095290000	0.0000390000
C	1.0261080000	0.4312350000	0.0000470000
O	3.3959680000	0.7784620000	-0.0000570000
Cl	0.8330790000	2.1738760000	-0.0000050000
C	0.0094710000	-0.4529250000	0.0000440000
C	-1.4451780000	-0.3327680000	0.0000150000
C	-2.1680770000	-1.5446560000	-0.0004250000
C	-3.5575020000	-1.5576750000	-0.0004980000
C	-4.2640460000	-0.3548390000	-0.0001030000
C	-3.5672080000	0.8543650000	0.0003670000
C	-2.1763160000	0.8722340000	0.0004210000
H	3.8463210000	-2.9156130000	0.0000810000
H	4.4770990000	-1.4983890000	0.8922220000
H	4.4770210000	-1.4984260000	-0.8921750000
H	0.3563750000	-1.4809580000	0.0000220000
H	-1.6247090000	-2.4832520000	-0.0007180000
H	-4.0877790000	-2.5028280000	-0.0008540000
H	-5.3479570000	-0.3587610000	-0.0001490000
H	-4.1108620000	1.7921200000	0.0006980000
H	-1.6641460000	1.8215760000	0.0008060000

### Thermodynamic data

Zero-point correction= 0.166802 (Hartree/Particle)  
Thermal correction to Energy= 0.179010  
Thermal correction to Enthalpy= 0.179954  
Thermal correction to Gibbs Free Energy= 0.125965  
Sum of electronic and zero-point Energies= -997.136262  
Sum of electronic and thermal Energies= -997.124055  
Sum of electronic and thermal Enthalpies= -997.123110  
Sum of electronic and thermal Free Energies= -997.177099

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	112.330	44.151	113.629

## [1b-Br]<sup>-</sup> in MeCN

### XYZ-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	-3.6585060000	2.4469220000	0.2580780000
O	-2.3456870000	1.8809750000	0.2007340000
C	-2.2852430000	0.4977570000	0.0666110000
C	-0.9409850000	0.0336630000	-0.0043930000
O	-3.3332230000	-0.1657840000	0.0373900000
Br	-0.8308640000	-1.9195850000	-0.1698840000
C	0.1870130000	0.8521590000	-0.1788550000
C	1.5929210000	0.6317240000	-0.0481390000
C	2.4813130000	1.6653020000	-0.4788820000
C	3.8573790000	1.5462500000	-0.3772980000
C	4.4389940000	0.3886620000	0.1631820000
C	3.5933740000	-0.6348170000	0.6075220000
C	2.2113880000	-0.5260690000	0.5116700000
H	-3.5092500000	3.5216550000	0.3565500000
H	-4.2159480000	2.0704120000	1.1185810000
H	-4.2242640000	2.2339150000	-0.6517420000
H	-0.0814300000	1.8720730000	-0.4430660000
H	2.0550810000	2.5699830000	-0.9025600000
H	4.4893480000	2.3592680000	-0.7212880000
H	5.5158330000	0.2926890000	0.2408990000
H	4.0210060000	-1.5321010000	1.0450470000
H	1.5952390000	-1.3332540000	0.8815510000

### Thermodynamic data

Zero-point correction=	0.162310
(Hartree/Particle)	
Thermal correction to Energy=	0.175152
Thermal correction to Enthalpy=	0.176096
Thermal correction to Gibbs Free Energy=	0.120192
Sum of electronic and zero-point Energies=	-3111.162189
Sum of electronic and thermal Energies=	-3111.149347
Sum of electronic and thermal Enthalpies=	-3111.148402
Sum of electronic and thermal Free Energies=	-3111.204307

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	109.910	46.231	117.660

## [1b-Cl]<sup>-</sup> in MeCN

### XYZ-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	3.9682260000	-1.8159360000	0.0005090000
O	2.6157350000	-1.3509300000	0.0003510000
C	2.4463310000	0.0289210000	0.0000790000
C	1.0728150000	0.4053860000	-0.0001160000
O	3.4382010000	0.7771380000	-0.0000670000
Cl	0.8408780000	2.1782840000	-0.0005380000
C	-0.0136370000	-0.4853220000	-0.0004140000
C	-1.4329500000	-0.3485520000	-0.0001430000

C	-2.2129120000	-1.5516900000	-0.0011810000
C	-3.5961280000	-1.5402800000	-0.0009330000
C	-4.3059270000	-0.3274680000	0.0003740000
C	-3.5731270000	0.8659490000	0.0014410000
C	-2.1839880000	0.8695560000	0.0011980000
H	3.9032740000	-2.9035070000	0.0006520000
H	4.5056000000	-1.4777360000	0.8894340000
H	4.5057410000	-1.4779730000	-0.8884180000
H	0.3271580000	-1.5156430000	-0.0008850000
H	-1.6905250000	-2.5040480000	-0.0022000000
H	-4.1353570000	-2.4827910000	-0.0017620000
H	-5.3896740000	-0.3162320000	0.0005700000
H	-4.0979900000	1.8169540000	0.0025050000
H	-1.6668540000	1.8170920000	0.0020960000

### Thermodynamic data

Zero-point correction=	0.162996 (Hartree/Particle)
Thermal correction to Energy=	0.174708
Thermal correction to Enthalpy=	0.175652
Thermal correction to Gibbs Free Energy=	0.123649
Sum of electronic and zero-point Energies=	-997.241968
Sum of electronic and thermal Energies=	-997.230256
Sum of electronic and thermal Enthalpies=	-997.229312
Sum of electronic and thermal Free Energies=	-997.281315

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	109.631	43.784	109.451

### 6 in MeCN

#### XYZ-matrix

21

XYZ file generated by gabedit : coordinates in Angstrom

C	-4.5194350000	-0.7925600000	-0.0029920000
O	-3.0737190000	-0.7293940000	-0.0054210000
C	-2.5225700000	0.5001640000	0.0007540000
C	-1.0737910000	0.4569330000	-0.0009430000
O	-3.1719680000	1.5307340000	0.0074090000
C	-0.1112370000	-0.4526610000	0.0015060000
C	1.3344580000	-0.2181280000	0.0006940000
C	2.2075340000	-1.3176230000	0.0035020000
C	3.5873550000	-1.1273110000	0.0027120000
C	4.1133580000	0.1638410000	-0.0008160000
C	3.2530960000	1.2665350000	-0.0035670000
C	1.8770600000	1.0795710000	-0.0028150000
H	-4.7588140000	-1.8528080000	-0.0086000000
H	-4.9198490000	-0.3049490000	-0.8917660000
H	-4.9164180000	-0.3151610000	0.8928450000
H	-0.4230130000	-1.5025440000	0.0049130000
H	1.8001870000	-2.3228010000	0.0062540000
H	4.2498760000	-1.9850670000	0.0048580000
H	5.1869010000	0.3135330000	-0.0014040000
H	3.6603290000	2.2710520000	-0.0062850000
H	1.2113320000	1.9354480000	-0.0049300000

### Thermodynamic data

Zero-point correction= 0.162258 (Hartree/Particle)  
Thermal correction to Energy= 0.173616  
Thermal correction to Enthalpy= 0.174560  
Thermal correction to Gibbs Free Energy= 0.121945  
Sum of electronic and zero-point Energies= -536.838113  
Sum of electronic and thermal Energies= -536.826755  
Sum of electronic and thermal Enthalpies= -536.825810  
Sum of electronic and thermal Free Energies= -536.878426

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	108.946	40.606	110.738

### Bromide anion in MeCN

#### XYZ-matrix

n.a.

#### Thermodynamic data

Zero-point correction= 0.000000 (Hartree/Particle)  
Thermal correction to Energy= 0.001416  
Thermal correction to Enthalpy= 0.002360  
Thermal correction to Gibbs Free Energy= -0.016176  
Sum of electronic and zero-point Energies= -2574.339121  
Sum of electronic and thermal Energies= -2574.337705  
Sum of electronic and thermal Enthalpies= -2574.336761  
Sum of electronic and thermal Free Energies= -2574.355297

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	0.889	2.981	39.012

### Chloride anion in MeCN

#### XYZ-matrix

n.a.

#### Thermodynamic data

Zero-point correction= 0.000000 (Hartree/Particle)  
Thermal correction to Energy= 0.001416  
Thermal correction to Enthalpy= 0.002360  
Thermal correction to Gibbs Free Energy= -0.015023  
Sum of electronic and zero-point Energies= -460.413061  
Sum of electronic and thermal Energies= -460.411645  
Sum of electronic and thermal Enthalpies= -460.410701  
Sum of electronic and thermal Free Energies= -460.428084

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	0.889	2.981	36.586

### PCM data: benzene

#### 1b-Br in benzene

#### XYZ-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	-3.6124310000	2.5044040000	0.0003230000
O	-2.3087110000	1.8873400000	0.0003550000
C	-2.2951610000	0.5379080000	0.0000520000
C	-0.9042240000	-0.0112650000	0.0000430000
O	-3.3007960000	-0.1323590000	-0.0002530000
Br	-0.8764780000	-1.9221250000	-0.0002700000
C	0.1796700000	0.7892840000	0.0001540000
C	1.6248280000	0.5776280000	0.0001380000
C	2.4211750000	1.7422090000	-0.0005190000
C	3.8083820000	1.6714390000	-0.0005980000
C	4.4402810000	0.4282710000	0.0000330000
C	3.6707260000	-0.7351800000	0.0007440000
C	2.2816130000	-0.6681760000	0.0007900000
H	-3.4221550000	3.5750090000	0.0006470000
H	-4.1701680000	2.2127830000	0.8906100000
H	-4.1698930000	2.2132750000	-0.8902970000
H	-0.0931560000	1.8404510000	0.0002070000
H	1.9360150000	2.7123950000	-0.0009860000
H	4.3951690000	2.5827320000	-0.0011360000
H	5.5225370000	0.3660730000	-0.0000100000
H	4.1558010000	-1.7046480000	0.0012750000
H	1.7094750000	-1.5826830000	0.0013670000

### Thermodynamic data

Zero-point correction=	0.166006 (Hartree/Particle)
Thermal correction to Energy=	0.178559
Thermal correction to Enthalpy=	0.179503
Thermal correction to Gibbs Free Energy=	0.123289
Sum of electronic and zero-point Energies=	-3111.050727
Sum of electronic and thermal Energies=	-3111.038174
Sum of electronic and thermal Enthalpies=	-3111.037230
Sum of electronic and thermal Free Energies=	-3111.093445

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	112.048	44.665	118.314

### [1b-Br]<sup>-</sup> in benzene

#### Xyz-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	-3.6205540000	2.4828180000	0.1584550000
O	-2.3180720000	1.9104340000	0.1005740000
C	-2.2825060000	0.5129250000	0.0300190000
C	-0.9448240000	0.0183400000	-0.0007590000
O	-3.3417750000	-0.1228370000	0.0083890000
Br	-0.8772030000	-1.9253620000	-0.0927960000
C	0.2024260000	0.8222210000	-0.0836440000
C	1.6073390000	0.6000610000	-0.0206260000
C	2.4693220000	1.7216650000	-0.2527680000
C	3.8475680000	1.6227290000	-0.2056670000
C	4.4722220000	0.3965180000	0.0790030000
C	3.6563280000	-0.7172200000	0.3193600000
C	2.2720700000	-0.6319600000	0.2748610000
H	-3.4662900000	3.5621990000	0.1946030000

H	-4.1615670000	2.1557400000	1.0507860000
H	-4.2145610000	2.2213930000	-0.7211190000
H	-0.0677540000	1.8666820000	-0.2107960000
H	2.0119570000	2.6814760000	-0.4759740000
H	4.4507200000	2.5069180000	-0.3926010000
H	5.5528440000	0.3155510000	0.1149840000
H	4.1135750000	-1.6753570000	0.5515860000
H	1.6856020000	-1.5163040000	0.4753010000

### Thermodynamic data

Zero-point correction=	0.162310
(Hartree/Particle)	
Thermal correction to Energy=	0.175174
Thermal correction to Enthalpy=	0.176119
Thermal correction to Gibbs Free Energy=	0.120057
Sum of electronic and zero-point Energies=	-3111.127506
Sum of electronic and thermal Energies=	-3111.114642
Sum of electronic and thermal Enthalpies=	-3111.113698
Sum of electronic and thermal Free Energies=	-3111.169759

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	109.924	46.232	117.992

### 1b-Cl in benzene

#### XYZ-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	3.9475570000	-1.8277380000	-0.0004020000
O	2.5933320000	-1.3312620000	0.0000780000
C	2.4583560000	0.0105940000	0.0005420000
C	1.0244500000	0.4327630000	0.0003350000
O	3.3958880000	0.7728550000	0.0000930000
Cl	0.8359890000	2.1720380000	0.0001810000
C	0.0093990000	-0.4529710000	0.0002440000
C	-1.4456700000	-0.3330230000	0.0000390000
C	-2.1702550000	-1.5431970000	-0.0002620000
C	-3.5592980000	-1.5555000000	-0.0004860000
C	-4.2647470000	-0.3525160000	-0.0003960000
C	-3.5664970000	0.8551470000	-0.0000790000
C	-2.1758290000	0.8718600000	0.0001330000
H	3.8553380000	-2.9110960000	-0.0007340000
H	4.4765540000	-1.4870530000	0.8900360000
H	4.4761450000	-1.4864750000	-0.8908630000
H	0.3576860000	-1.4804500000	0.0003280000
H	-1.6272550000	-2.4822340000	-0.0003260000
H	-4.0904960000	-2.5002800000	-0.0007260000
H	-5.3487550000	-0.3554480000	-0.0005640000
H	-4.1090250000	1.7936660000	0.0000060000
H	-1.6605680000	1.8194650000	0.0003850000

### Thermodynamic data

Zero-point correction=	0.166937 (Hartree/Particle)
Thermal correction to Energy=	0.179129
Thermal correction to Enthalpy=	0.180074

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Thermal correction to Gibbs Free Energy= 0.126219  
 Sum of electronic and zero-point Energies= -997.131116  
 Sum of electronic and thermal Energies= -997.118924  
 Sum of electronic and thermal Enthalpies= -997.117979  
 Sum of electronic and thermal Free Energies= -997.171834

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	112.405	44.109	113.347

### [1b-Cl]<sup>-</sup> in benzene

#### Xyz-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	3.9567210000	-1.8103810000	0.0975860000
O	2.6076100000	-1.3592840000	0.0430690000
C	2.4445500000	0.0298520000	0.0080970000
C	1.0705100000	0.4082410000	-0.0278500000
O	3.4396480000	0.7636500000	0.0137860000
Cl	0.8439710000	2.1778680000	-0.0970730000
C	-0.0129220000	-0.4824320000	-0.0521260000
C	-1.4293820000	-0.3473830000	-0.0197230000
C	-2.2150970000	-1.5424740000	-0.1279510000
C	-3.5970230000	-1.5308250000	-0.0933320000
C	-4.3045370000	-0.3251460000	0.0531020000
C	-3.5653080000	0.8604620000	0.1641320000
C	-2.1783440000	0.8641390000	0.1294580000
H	3.9019840000	-2.8992890000	0.1320430000
H	4.4690250000	-1.4359080000	0.9881470000
H	4.5227790000	-1.4956640000	-0.7835990000
H	0.3288240000	-1.5114550000	-0.0960040000
H	-1.6946810000	-2.4893050000	-0.2424670000
H	-4.1385120000	-2.4688400000	-0.1805060000
H	-5.3883080000	-0.3131450000	0.0813240000
H	-4.0863510000	1.8067660000	0.2835910000
H	-1.6553440000	1.8038420000	0.2245160000

#### Thermodynamic data

Zero-point correction=	0.163101
(Hartree/Particle)	
Thermal correction to Energy=	0.175606
Thermal correction to Enthalpy=	0.176550
Thermal correction to Gibbs Free Energy=	0.121875
Sum of electronic and zero-point Energies=	-997.206988
Sum of electronic and thermal Energies=	-997.194484
Sum of electronic and thermal Enthalpies=	-997.193540
Sum of electronic and thermal Free Energies=	-997.248214

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	110.194	45.741	115.072

### 6 in benzene

#### Xyz-matrix

21

XYZ file generated by gabedit : coordinates in Angstrom

C	-4.5139410000	-0.7906990000	-0.0023530000
O	-3.0711620000	-0.7343050000	-0.0040460000
C	-2.5236110000	0.5032660000	0.0008800000
C	-1.0732340000	0.4578920000	-0.0006070000
O	-3.1760960000	1.5264430000	0.0058250000
C	-0.1122440000	-0.4520050000	0.0014170000
C	1.3340440000	-0.2184100000	0.0005780000
C	2.2080630000	-1.3162530000	0.0024830000
C	3.5874420000	-1.1259050000	0.0017240000
C	4.1128020000	0.1649390000	-0.0009250000
C	3.2518240000	1.2662630000	-0.0028010000
C	1.8762490000	1.0787960000	-0.0020640000
H	-4.7593270000	-1.8500420000	-0.0065530000
H	-4.9138100000	-0.2997150000	-0.8900990000
H	-4.9114430000	-0.3073000000	0.8906060000
H	-0.4260100000	-1.5015110000	0.0038700000
H	1.8009910000	-2.3218950000	0.0045470000
H	4.2504270000	-1.9834900000	0.0032010000
H	5.1863700000	0.3151770000	-0.0015030000
H	3.6580390000	2.2713380000	-0.0048230000
H	1.2084680000	1.9330240000	-0.0034740000

### Thermodynamic data

Zero-point correction=	0.162378 (Hartree/Particle)
Thermal correction to Energy=	0.173722
Thermal correction to Enthalpy=	0.174667
Thermal correction to Gibbs Free Energy=	0.122246
Sum of electronic and zero-point Energies=	-536.833219
Sum of electronic and thermal Energies=	-536.821874
Sum of electronic and thermal Enthalpies=	-536.820930
Sum of electronic and thermal Free Energies=	-536.873351

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	109.012	40.576	110.329

### Bromide anion in benzene

#### Xyz-matrix

n.a.

### Thermodynamic data

Zero-point correction=	0.000000 (Hartree/Particle)
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.016176
Sum of electronic and zero-point Energies=	-2574.295737
Sum of electronic and thermal Energies=	-2574.294321
Sum of electronic and thermal Enthalpies=	-2574.293377
Sum of electronic and thermal Free Energies=	-2574.311913

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	0.889	2.981	39.012

## Chloride anion in benzene

### XYZ-matrix

n.a.

### Thermodynamic data

Zero-point correction= 0.000000 (Hartree/Particle)  
Thermal correction to Energy= 0.001416  
Thermal correction to Enthalpy= 0.002360  
Thermal correction to Gibbs Free Energy= -0.015023  
Sum of electronic and zero-point Energies= -460.366405  
Sum of electronic and thermal Energies= -460.364988  
Sum of electronic and thermal Enthalpies= -460.364044  
Sum of electronic and thermal Free Energies= -460.381427

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	0.889	2.981	36.586

## PCM data: DMF

### 1b-Br in DMF

#### xyz-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	-3.6132990000	2.5101240000	0.0004040000
O	-2.3117200000	1.8822370000	0.0003980000
C	-2.2958840000	0.5390150000	0.0000150000
C	-0.9063890000	-0.0102120000	0.0000210000
O	-3.3025240000	-0.1368170000	-0.0002800000
Br	-0.8736530000	-1.9241500000	-0.0003300000
C	0.1789510000	0.7889690000	0.0001570000
C	1.6237290000	0.5774000000	0.0001610000
C	2.4179050000	1.7441740000	-0.0005300000
C	3.8055600000	1.6749320000	-0.0005990000
C	4.4392750000	0.4321770000	0.0000800000
C	3.6716720000	-0.7333710000	0.0008320000
C	2.2821970000	-0.6682830000	0.0008650000
H	-3.4139480000	3.5785200000	0.0007910000
H	-4.1703210000	2.2237590000	0.8923700000
H	-4.1700410000	2.2243550000	-0.8919290000
H	-0.0924250000	1.8405660000	0.0002090000
H	1.9316240000	2.7135410000	-0.0010310000
H	4.3910030000	2.5869200000	-0.0011650000
H	5.5215180000	0.3716030000	0.0000460000
H	4.1584490000	-1.7018680000	0.0014050000
H	1.7136380000	-1.5850680000	0.0014830000

### Thermodynamic data

Zero-point correction= 0.165864 (Hartree/Particle)  
Thermal correction to Energy= 0.177509  
Thermal correction to Enthalpy= 0.178453  
Thermal correction to Gibbs Free Energy= 0.125910  
Sum of electronic and zero-point Energies= -3111.055853  
Sum of electronic and thermal Energies= -3111.044209  
Sum of electronic and thermal Enthalpies= -3111.043265

Sum of electronic and thermal Free Energies= -3111.095807

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	111.388	42.720	110.585

### 1b-Cl in DMF

#### xyz-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	3.9484290000	-1.8336620000	0.0000530000
O	2.5954510000	-1.3255090000	0.0001050000
C	2.4584750000	0.0095290000	0.0000390000
C	1.0261080000	0.4312350000	0.0000470000
O	3.3959680000	0.7784620000	-0.0000570000
Cl	0.8330790000	2.1738760000	-0.0000050000
C	0.0094710000	-0.4529250000	0.0000440000
C	-1.4451780000	-0.3327680000	0.0000150000
C	-2.1680770000	-1.5446560000	-0.0004250000
C	-3.5575020000	-1.5576750000	-0.0004980000
C	-4.2640460000	-0.3548390000	-0.0001030000
C	-3.5672080000	0.8543650000	0.0003670000
C	-2.1763160000	0.8722340000	0.0004210000
H	3.8463210000	-2.9156130000	0.0000810000
H	4.4770990000	-1.4983890000	0.8922220000
H	4.4770210000	-1.4984260000	-0.8921750000
H	0.3563750000	-1.4809580000	0.0000220000
H	-1.6247090000	-2.4832520000	-0.0007180000
H	-4.0877790000	-2.5028280000	-0.0008540000
H	-5.3479570000	-0.3587610000	-0.0001490000
H	-4.1108620000	1.7921200000	0.0006980000
H	-1.6641460000	1.8215760000	0.0008060000

### Thermodynamic data

Zero-point correction= 0.166802 (Hartree/Particle)  
Thermal correction to Energy= 0.179009  
Thermal correction to Enthalpy= 0.179954  
Thermal correction to Gibbs Free Energy= 0.125964  
Sum of electronic and zero-point Energies= -997.136282  
Sum of electronic and thermal Energies= -997.124074  
Sum of electronic and thermal Enthalpies= -997.123130  
Sum of electronic and thermal Free Energies= -997.177119

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	112.330	44.151	113.630

### [1b-Br]<sup>-</sup> in DMF

#### Xyz-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	-3.6585060000	2.4469220000	0.2580780000
O	-2.3456870000	1.8809750000	0.2007340000
C	-2.2852430000	0.4977570000	0.0666110000
C	-0.9409850000	0.0336630000	-0.0043930000

O	-3.3332230000	-0.1657840000	0.0373900000
Br	-0.8308640000	-1.9195850000	-0.1698840000
C	0.1870130000	0.8521590000	-0.1788550000
C	1.5929210000	0.6317240000	-0.0481390000
C	2.4813130000	1.6653020000	-0.4788820000
C	3.8573790000	1.5462500000	-0.3772980000
C	4.4389940000	0.3886620000	0.1631820000
C	3.5933740000	-0.6348170000	0.6075220000
C	2.2113880000	-0.5260690000	0.5116700000
H	-3.5092500000	3.5216550000	0.3565500000
H	-4.2159480000	2.0704120000	1.1185810000
H	-4.2242640000	2.2339150000	-0.6517420000
H	-0.0814300000	1.8720730000	-0.4430660000
H	2.0550810000	2.5699830000	-0.9025600000
H	4.4893480000	2.3592680000	-0.7212880000
H	5.5158330000	0.2926890000	0.2408990000
H	4.0210060000	-1.5321010000	1.0450470000
H	1.5952390000	-1.3332540000	0.8815510000

### Thermodynamic data

Zero-point correction=	0.162309 (Hartree/Particle)
Thermal correction to Energy=	0.175152
Thermal correction to Enthalpy=	0.176096
Thermal correction to Gibbs Free Energy=	0.120187
Sum of electronic and zero-point Energies=	-3111.162298
Sum of electronic and thermal Energies=	-3111.149455
Sum of electronic and thermal Enthalpies=	-3111.148511
Sum of electronic and thermal Free Energies=	-3111.204419

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	109.909	46.232	117.669

### [1b-Cl]<sup>-</sup> in DMF

#### XYZ-matrix

22

XYZ file generated by gabedit : coordinates in Angstrom

C	3.9682260000	-1.8159360000	0.0005090000
O	2.6157350000	-1.3509300000	0.0003510000
C	2.4463310000	0.0289210000	0.0000790000
C	1.0728150000	0.4053860000	-0.0001160000
O	3.4382010000	0.7771380000	-0.0000670000
Cl	0.8408780000	2.1782840000	-0.0005380000
C	-0.0136370000	-0.4853220000	-0.0004140000
C	-1.4329500000	-0.3485520000	-0.0001430000
C	-2.2129120000	-1.5516900000	-0.0011810000
C	-3.5961280000	-1.5402800000	-0.0009330000
C	-4.3059270000	-0.3274680000	0.0003740000
C	-3.5731270000	0.8659490000	0.0014410000
C	-2.1839880000	0.8695560000	0.0011980000
H	3.9032740000	-2.9035070000	0.0006520000
H	4.5056000000	-1.4777360000	0.8894340000
H	4.5057410000	-1.4779730000	-0.8884180000
H	0.3271580000	-1.5156430000	-0.0008850000
H	-1.6905250000	-2.5040480000	-0.0022000000
H	-4.1353570000	-2.4827910000	-0.0017620000

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H	-5.3896740000	-0.3162320000	0.0005700000
H	-4.0979900000	1.8169540000	0.0025050000
H	-1.6668540000	1.8170920000	0.0020960000

### Thermodynamic data

Zero-point correction= 0.163000 (Hartree/Particle)  
 Thermal correction to Energy= 0.174710  
 Thermal correction to Enthalpy= 0.175654  
 Thermal correction to Gibbs Free Energy= 0.123658  
 Sum of electronic and zero-point Energies= -997.242073  
 Sum of electronic and thermal Energies= -997.230363  
 Sum of electronic and thermal Enthalpies= -997.229419  
 Sum of electronic and thermal Free Energies= -997.281415

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	109.632	43.782	109.435

### 6 in DMF

#### Xyz-matrix

21

XYZ file generated by gabedit : coordinates in Angstrom

C	-4.5194350000	-0.7925600000	-0.0029920000
O	-3.0737190000	-0.7293940000	-0.0054210000
C	-2.5225700000	0.5001640000	0.0007540000
C	-1.0737910000	0.4569330000	-0.0009430000
O	-3.1719680000	1.5307340000	0.0074090000
C	-0.1112370000	-0.4526610000	0.0015060000
C	1.3344580000	-0.2181280000	0.0006940000
C	2.2075340000	-1.3176230000	0.0035020000
C	3.5873550000	-1.1273110000	0.0027120000
C	4.1133580000	0.1638410000	-0.0008160000
C	3.2530960000	1.2665350000	-0.0035670000
C	1.8770600000	1.0795710000	-0.0028150000
H	-4.7588140000	-1.8528080000	-0.0086000000
H	-4.9198490000	-0.3049490000	-0.8917660000
H	-4.9164180000	-0.3151610000	0.8928450000
H	-0.4230130000	-1.5025440000	0.0049130000
H	1.8001870000	-2.3228010000	0.0062540000
H	4.2498760000	-1.9850670000	0.0048580000
H	5.1869010000	0.3135330000	-0.0014040000
H	3.6603290000	2.2710520000	-0.0062850000
H	1.2113320000	1.9354480000	-0.0049300000

### Thermodynamic data

Zero-point correction= 0.162237 (Hartree/Particle)  
 Thermal correction to Energy= 0.173599  
 Thermal correction to Enthalpy= 0.174543  
 Thermal correction to Gibbs Free Energy= 0.121873  
 Sum of electronic and zero-point Energies= -536.838151  
 Sum of electronic and thermal Energies= -536.826789  
 Sum of electronic and thermal Enthalpies= -536.825845  
 Sum of electronic and thermal Free Energies= -536.878516

	E (Thermal)	CV	S
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	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	108.935	40.610	110.855

### Chloride anion in DMF

#### XYZ-matrix

n.a.

#### Thermodynamic data

Zero-point correction=	0.000000 (Hartree/Particle)
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.015023
Sum of electronic and zero-point Energies=	-460.413192
Sum of electronic and thermal Energies=	-460.411776
Sum of electronic and thermal Enthalpies=	-460.410832
Sum of electronic and thermal Free Energies=	-460.428215

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	0.889	2.981	36.586

### Bromide anion in DMF

#### XYZ-matrix

n.a.

#### Thermodynamic data

Zero-point correction=	0.000000 (Hartree/Particle)
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.016176
Sum of electronic and zero-point Energies=	-2574.339243
Sum of electronic and thermal Energies=	-2574.337827
Sum of electronic and thermal Enthalpies=	-2574.336883
Sum of electronic and thermal Free Energies=	-2574.355419

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	0.889	2.981	39.012

### PCM data: DCM

### Bromide anion in DCM

#### XYZ

n.a. (single atom)

#### Thermodynamic data

Zero-point correction=	0.000000
(Hartree/Particle)	
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.016176
Sum of electronic and zero-point Energies=	-2574.336924
Sum of electronic and thermal Energies=	-2574.335508
Sum of electronic and thermal Enthalpies=	-2574.334564
Sum of electronic and thermal Free Energies=	-2574.353100

E (Thermal)	CV	S
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	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	0.889	2.981	39.012

## Chloride anion in DCM

### XYZ

n.a. (single atom)

### Thermodynamic data

Zero-point correction= (Hartree/Particle)	0.000000
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.015023
Sum of electronic and zero-point Energies=	-460.403535
Sum of electronic and thermal Energies=	-460.402119
Sum of electronic and thermal Enthalpies=	-460.401175
Sum of electronic and thermal Free Energies=	-460.418558

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	0.889	2.981	36.586

## 1b-Br in DCM

### XYZ

22

XYZ file generated by gabedit : coordinates in Angstrom

C	-3.6121380000	2.5097590000	0.0001710000
O	-2.3102420000	1.8837740000	0.0004680000
C	-2.2955010000	0.5391840000	0.0003530000
C	-0.9059470000	-0.0106070000	0.0002010000
O	-3.3019920000	-0.1351990000	-0.0002800000
Br	-0.8750900000	-1.9237580000	-0.0003290000
C	0.1792700000	0.7885370000	0.0003230000
C	1.6241750000	0.5770280000	0.0002060000
C	2.4188360000	1.7432600000	-0.0004360000
C	3.8063630000	1.6738140000	-0.0006110000
C	4.4397460000	0.4310840000	-0.0000850000
C	3.6717410000	-0.7339330000	0.0006170000
C	2.2823700000	-0.6685080000	0.0007540000
H	-3.4144700000	3.5786630000	0.0003770000
H	-4.1695380000	2.2224360000	0.8916410000
H	-4.1690150000	2.2226880000	-0.8917080000
H	-0.0924070000	1.8400900000	0.0004880000
H	1.9327660000	2.7128150000	-0.0008180000
H	4.3920430000	2.5857070000	-0.0011360000
H	5.5220080000	0.3701930000	-0.0001990000
H	4.1581860000	-1.7026290000	0.0010710000
H	1.7129640000	-1.5847370000	0.0013280000

### Thermodynamic data

Zero-point correction= (Hartree/Particle)	0.165890
Thermal correction to Energy=	0.177537
Thermal correction to Enthalpy=	0.178481
Thermal correction to Gibbs Free Energy=	0.125930
Sum of electronic and zero-point Energies=	-3111.054538

Sum of electronic and thermal Energies= -3111.042891  
 Sum of electronic and thermal Enthalpies= -3111.041947  
 Sum of electronic and thermal Free Energies= -3111.094498

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	111.406	42.710	110.604

### 1b-Cl in DCM

XYZ

22

XYZ file generated by gabedit : coordinates in Angstrom

C	3.9487360000	-1.8317710000	0.0000790000
O	2.5952580000	-1.3269080000	0.0001210000
C	2.4582620000	0.0097760000	0.0000450000
C	1.0256060000	0.4312090000	0.0000310000
O	3.3952920000	0.7776270000	-0.0000560000
Cl	0.8337400000	2.1730590000	-0.0000670000
C	0.0093800000	-0.4532730000	0.0000530000
C	-1.4453200000	-0.3330210000	0.0000260000
C	-2.1688520000	-1.5443240000	-0.0004220000
C	-3.5581700000	-1.5569390000	-0.0004940000
C	-4.2641890000	-0.3539690000	-0.0000850000
C	-3.5667550000	0.8546900000	0.0003990000
C	-2.1759300000	0.8720190000	0.0004480000
H	3.8495470000	-2.9141750000	0.0000880000
H	4.4773390000	-1.4949330000	0.8917860000
H	4.4772840000	-1.4949410000	-0.8916630000
H	0.3566420000	-1.4811880000	0.0000590000
H	-1.6257140000	-2.4831100000	-0.0007260000
H	-4.0888810000	-2.5018900000	-0.0008600000
H	-5.3481310000	-0.3574300000	-0.0001290000
H	-4.1099590000	1.7927250000	0.0007420000
H	-1.6627310000	1.8208030000	0.0008430000

### Thermodynamic data

Zero-point correction= 0.166839  
 (Hartree/Particle)  
 Thermal correction to Energy= 0.179051  
 Thermal correction to Enthalpy= 0.179995  
 Thermal correction to Gibbs Free Energy= 0.125946  
 Sum of electronic and zero-point Energies= -997.134939  
 Sum of electronic and thermal Energies= -997.122727  
 Sum of electronic and thermal Enthalpies= -997.121782  
 Sum of electronic and thermal Free Energies= -997.175832

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	112.356	44.141	113.757

### [1b-Br]<sup>-</sup> in DCM

XYZ

22

XYZ file generated by gabedit : coordinates in Angstrom

C	-3.6592150000	2.4442620000	0.2523430000
O	-2.3464490000	1.8826570000	0.1925200000

C	-2.2860290000	0.4970550000	0.0616720000
C	-0.9411280000	0.0322780000	-0.0028240000
O	-3.3336080000	-0.1643540000	0.0286810000
Br	-0.8329130000	-1.9184660000	-0.1639410000
C	0.1879730000	0.8511090000	-0.1649850000
C	1.5935180000	0.6306390000	-0.0421310000
C	2.4795120000	1.6725660000	-0.4591880000
C	3.8558250000	1.5541490000	-0.3662320000
C	4.4425010000	0.3888270000	0.1522600000
C	3.5996260000	-0.6429000000	0.5833230000
C	2.2175150000	-0.5352840000	0.4955840000
H	-3.5130980000	3.5199240000	0.3491980000
H	-4.2143150000	2.0670950000	1.1144370000
H	-4.2278780000	2.2281490000	-0.6551720000
H	-0.0817430000	1.8745510000	-0.4134970000
H	2.0499020000	2.5832460000	-0.8664590000
H	4.4847380000	2.3740030000	-0.7000660000
H	5.5199370000	0.2931530000	0.2231330000
H	4.0303170000	-1.5470010000	1.0039110000
H	1.6039700000	-1.3494420000	0.8539260000

### Thermodynamic data

Zero-point correction=	0.162394
(Hartree/Particle)	
Thermal correction to Energy=	0.175191
Thermal correction to Enthalpy=	0.176135
Thermal correction to Gibbs Free Energy=	0.120452
Sum of electronic and zero-point Energies=	-3111.154440
Sum of electronic and thermal Energies=	-3111.141643
Sum of electronic and thermal Enthalpies=	-3111.140699
Sum of electronic and thermal Free Energies=	-3111.196381

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	109.934	46.186	117.193

### [1b-Cl]<sup>-</sup> in DCM

XYZ

22

XYZ file generated by gabedit : coordinates in Angstrom

C	3.9661480000	-1.8122390000	0.0806710000
O	2.6143150000	-1.3520010000	0.0425790000
C	2.4455990000	0.0296970000	0.0080110000
C	1.0716890000	0.4047640000	-0.0215130000
O	3.4374310000	0.7752780000	0.0075710000
Cl	0.8393530000	2.1758590000	-0.0833380000
C	-0.0130910000	-0.4868280000	-0.0434570000
C	-1.4314840000	-0.3495970000	-0.0151700000
C	-2.2153830000	-1.5464130000	-0.1088500000
C	-3.5981710000	-1.5332590000	-0.0812000000
C	-4.3043810000	-0.3247640000	0.0430210000
C	-3.5673350000	0.8623650000	0.1400410000
C	-2.1789100000	0.8642370000	0.1125660000
H	3.9045470000	-2.9000230000	0.1050350000
H	4.4854100000	-1.4510790000	0.9716880000
H	4.5222030000	-1.4932600000	-0.8041530000

H	0.3275130000	-1.5164730000	-0.0822150000
H	-1.6956870000	-2.4953540000	-0.2059300000
H	-4.1401420000	-2.4713570000	-0.1567630000
H	-5.3879810000	-0.3120290000	0.0650820000
H	-4.0889170000	1.8098670000	0.2419640000
H	-1.6580020000	1.8061100000	0.1961400000

### Thermodynamic data

Zero-point correction= (Hartree/Particle)	0.163108
Thermal correction to Energy=	0.175657
Thermal correction to Enthalpy=	0.176601
Thermal correction to Gibbs Free Energy=	0.121755
Sum of electronic and zero-point Energies=	-997.234161
Sum of electronic and thermal Energies=	-997.221612
Sum of electronic and thermal Enthalpies=	-997.220668
Sum of electronic and thermal Free Energies=	-997.275514

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	110.226	45.747	115.433

### 6 in DCM

#### XYZ

21

XYZ file generated by gabedit : coordinates in Angstrom

C	-4.5182650000	-0.7918130000	-0.0025700000
O	-3.0731930000	-0.7306650000	-0.0051450000
C	-2.5227120000	0.5007700000	0.0003980000
C	-1.0736310000	0.4569970000	-0.0012360000
O	-3.1728400000	1.5295930000	0.0068020000
C	-0.1114260000	-0.4526370000	0.0012200000
C	1.3343840000	-0.2182460000	0.0006030000
C	2.2077650000	-1.3172690000	0.0033440000
C	3.5874530000	-1.1268730000	0.0027480000
C	4.1131860000	0.1642240000	-0.0005170000
C	3.2526790000	1.2665000000	-0.0031940000
C	1.8767800000	1.0793340000	-0.0026350000
H	-4.7594220000	-1.8517990000	-0.0075620000
H	-4.9185510000	-0.3034130000	-0.8910720000
H	-4.9149950000	-0.3126100000	0.8925160000
H	-0.4235820000	-1.5024570000	0.0045090000
H	1.8005590000	-2.3226020000	0.0058890000
H	4.2501780000	-1.9845270000	0.0048400000
H	5.1867320000	0.3141260000	-0.0009510000
H	3.6595870000	2.2711860000	-0.0057020000
H	1.2104810000	1.9347420000	-0.0046860000

### Thermodynamic data

Zero-point correction= (Hartree/Particle)	0.162305
Thermal correction to Energy=	0.173655
Thermal correction to Enthalpy=	0.174599
Thermal correction to Gibbs Free Energy=	0.122087
Sum of electronic and zero-point Energies=	-536.836876
Sum of electronic and thermal Energies=	-536.825526

Sum of electronic and thermal Enthalpies= -536.824582  
Sum of electronic and thermal Free Energies= -536.877095

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	108.970	40.591	110.522