

# Supporting Information

## Palladium-Catalyzed Intermolecular [3 + 2] Carbocyclization of Alkynols and Propiolates: An Efficient Entry to Halo-Cyclopentadienes

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## A. Optimization of Reaction Conditions

**Table 1.** Condition screening<sup>a</sup>

Entry	[Pd]	Additive	Ligand	Yield <sup>b</sup> (%)
1	PdCl <sub>2</sub>	LiBr	-	70
2	<b>Pd(OAc)<sub>2</sub></b>	<b>LiBr</b>	-	<b>86 (83)</b>
3	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	LiBr	-	trace
4	Pd(PPh <sub>3</sub> ) <sub>4</sub>	LiBr	-	trace
5	Pd <sub>2</sub> (dba) <sub>3</sub>	LiBr	-	36
6	Pd/C	LiBr	-	18
7 <sup>c</sup>	Pd(OAc) <sub>2</sub>	LiBr	PPh <sub>3</sub>	n.d.
8 <sup>c</sup>	Pd(OAc) <sub>2</sub>	LiBr	1,10-Phen	n.d.
9	Pd(OAc) <sub>2</sub>	TBAB	-	21
10	Pd(OAc) <sub>2</sub>	NBS	-	8
11 <sup>d</sup>	Pd(OAc) <sub>2</sub>	LiBr	-	81
12 <sup>d</sup>	Pd <sub>2</sub> (dba) <sub>3</sub>	LiBr	-	35

<sup>a</sup> Reaction conditions: unless otherwise noted, all reactions were performed with **1a** (0.5 mmol), **2a** (0.5 mmol), Pd-catalyst (5 mol %), additive (1 mmol) in CH<sub>3</sub>CN/HOAc (2 ml, v/v = 1:1) as solvent at 60 °C for 8h. <sup>b</sup> Determined by GC using dodecane as the internal standard. Data in parentheses is the yield of isolated product. n.d. = not detected. <sup>c</sup> 10 mol % ligands were added in the reaction system. <sup>d</sup> The reactions were performed under N<sub>2</sub> atmosphere.

Our initial investigations of this Pd-catalyzed intermolecular carbocyclization focused on the reaction of 2-methylbut-3-yn-2-ol (**1a**) with ethyl propiolate (**2a**) in the presence of PdCl<sub>2</sub> and LiBr in MeCN at 60 °C. Experimental results showed that the acidic solvent system played an important role in the success of this transformation and CH<sub>3</sub>CN/HOAc (v/v = 1:1) was proved to be the most suitable solvent (see Table 2 for details). Among the palladium catalysts tested, both Pd<sup>0</sup> and Pd<sup>II</sup> catalysts could promote this transformation and Pd(OAc)<sub>2</sub> gave the best result (entries 1-6). Further investigation on the influence of ligand revealed that the presence of nitrogen or phosphine ligands would inhibit this chemical process (entries 7-8). Other bromine sources such as NBS, TBAB were examined and LiBr gave the best result (entries 2, 9 and 10). In addition, this reaction could perform smoothly under N<sub>2</sub> atmosphere (entries 11-12).

**Table 2.** Influence of the solvents<sup>a</sup>

Entry	[Pd]	Solvent	Yield (%)
1	Pd(OAc) <sub>2</sub>	Toluene	-
2	Pd(OAc) <sub>2</sub>	THF	-
3	Pd(OAc) <sub>2</sub>	DMF	-
4	Pd(OAc) <sub>2</sub>	DMSO	-
5	Pd(OAc) <sub>2</sub>	Dioxane	-
6	Pd(OAc) <sub>2</sub>	MeCN	trace
7	Pd(OAc) <sub>2</sub>	HOAc	-
8	<b>Pd(OAc)<sub>2</sub></b>	<b>HOAc/CH<sub>3</sub>CN = 1:1</b>	<b>86</b>
9	Pd(OAc) <sub>2</sub>	HCOOH/CH <sub>3</sub> CN	78
10	Pd(OAc) <sub>2</sub>	<i>n</i> -C <sub>4</sub> H <sub>7</sub> OOH/CH <sub>3</sub> CN	65
11 <sup>b</sup>	Pd(OAc) <sub>2</sub>	CH <sub>3</sub> CN	31
12	Pd(OAc) <sub>2</sub>	HOAc/THF	80
13	Pd(OAc) <sub>2</sub>	HOAc/Dioxane	66
14	Pd(OAc) <sub>2</sub>	HOAc/DMF	trace

<sup>a</sup> Reaction conditions: unless otherwise noted, all reactions were performed with **1a** (0.5 mmol), **2a** (0.5 mmol), Pd(OAc)<sub>2</sub> (5 mol %), LiBr (1 mmol) at 60 °C for 8 h. Determined by GC using dodecane as the internal standard. <sup>b</sup> 0.1 mmol BF<sub>3</sub>·OEt<sub>2</sub> was added to the reaction system.

## B. Experimental Procedures

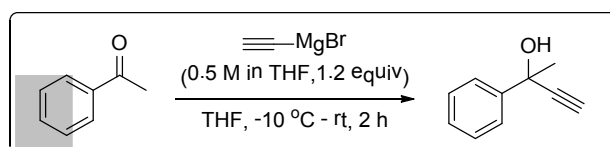
### I. General Methods

<sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> at 400 MHz and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> at 100 MHz respectively, and the chemical shifts (δ) were referenced to TMS. GC-MS was obtained using electron ionization. HRMS was carried out on a MAT 95XP (Thermo). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF<sub>254</sub>), and visualization was effected at 254 nm.

### II. General Procedure for Synthesis of the Substrates

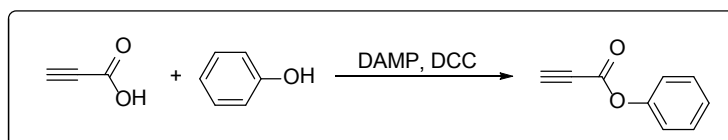
Alkynols **1a-f**, **1h** and **1i** were purchased from Aldrich. **1g**, **1j-l** were synthesized according to the reported method.<sup>1</sup> Apart from **2a**, **2b** which were purchased from Aldrich, other propiolates were synthesized according to the reported method.<sup>2</sup>

#### Preparation of 2-Phenylbut-3-yn-2-ol<sup>1</sup>



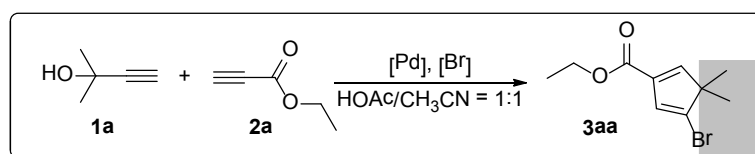
To a solution of acetophenone (2.00 g, 16.64 mmol) in 30 mL anhydrous THF was added ethynylmagnesium bromide (0.50 M solution in THF 40 mL, 19.97 mmol) at -10 °C. The resulting solution was stirred at -10 °C for 10 min and warmed to room temperature and stirred for 2 h after completion of reaction. The resulting solution was quenched with aqueous NH<sub>4</sub>Cl solution (50 mL). The THF was evaporated and the residue was diluted with water (100 mL) and extracted with ether (100 mL × 3) and dried over anhydrous MgSO<sub>4</sub>. After the solvent was evaporated, the crude product was purified by column chromatography (hexanes/ethyl acetate = 4/1) to give 2-phenylbut-3-yn-2-ol as a yellow oil (1.70 g, 70 % yield).

#### Preparation of Phenyl Propiolate<sup>2</sup>



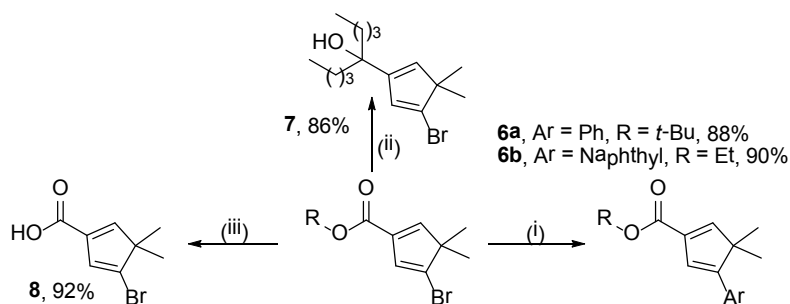
The arylalcohol (5 mmol) and propionic acid (1.0-1.1 equiv) were dissolved in dichloromethane (5 mL). When the mixture was cooled to 0 °C, a solution of DCC (1.0 equiv.) and DAMP (0.1 equiv), dissolved in dichloromethane (5 mL), was added dropwise, that the temperature of the reaction mixture remained under 5 °C. The mixture was stirred for 4 h. The precipitate was filtered off and the solution was washed with H<sub>2</sub>O. The organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub> and the volatile parts were removed under reduced pressure. The product was purified by flash column chromatography.

### III. General Procedure for Synthesis of Halo-Cyclopentadiene



Alkynol (0.5 mmol), propiolate (0.5 mmol), Pd-catalyst (5 mol %), LiBr (1 mmol) in CH<sub>3</sub>CN/HOAc (2 mL, v/v = 1:1) were added to a tube equipped with magnetic stirrer bar. The mixture was stirred at 60 °C (oil bath temperature) for the desired reaction time. After the reaction was finished (monitored by TLC), the mixture was cooled to room temperature and quenched with aqueous Na<sub>2</sub>CO<sub>3</sub>, and the crude product was extracted with ethyl acetate. The organic extracts were concentrated in vacuum, and the resulting residue was purified by column chromatography on silica gel with light petroleum ether/ethyl acetate as eluent to afford the desired product.

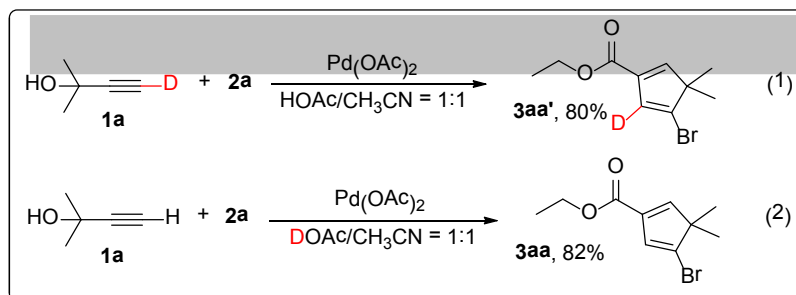
### IV. General Procedure for the Further Transformations



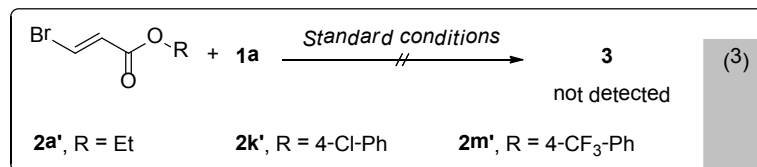
(i) Pd(OAc)<sub>2</sub> (5 mol %), Xphos (10 mol %), PhB(OH)<sub>2</sub> (2.0 equiv), K<sub>3</sub>PO<sub>4</sub> (3.0 equiv), toluene, 110 °C, 10 h. (ii) *n*-BuLi (1.2 equiv), THF, -20 °C, 2 h. (iii) KOH aqueous solution, rt, 3 h.

## V. Control Experiments

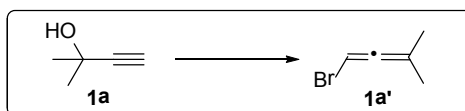
Two deuterated experiments were carried out to distinguish whether there is proton transfer in this cycloaddition process. As depicted in [eq. (1)], deuterium product **3aa'** was obtained exclusively in 80% isolated yield and the deuterium atom (98% examined by <sup>1</sup>H NMR spectroscopy) was still present. However, when deuterated acetic acid was used as the solvent [eq. (2)], there was no deuterium in the product, which indicated that the terminal alkyne hydrogen of alkyne and propiolate remained at the original position.



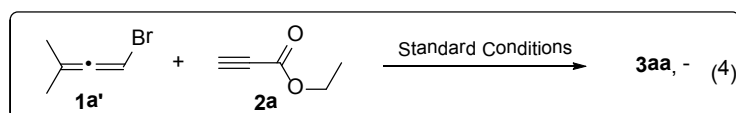
Furthermore, the possibility of byproducts (*E*)-3-bromoacrylate (**2'**) detected in the reaction system as an intermediate was excluded for **2'** could not be transformed to the desired cyclopentadiene products when treated with **1a** under the standard conditions [eq. (3)].



1-Bromo-3-methylbuta-1,2-diene (**1a'**) was prepared according to the reported work.<sup>3</sup>



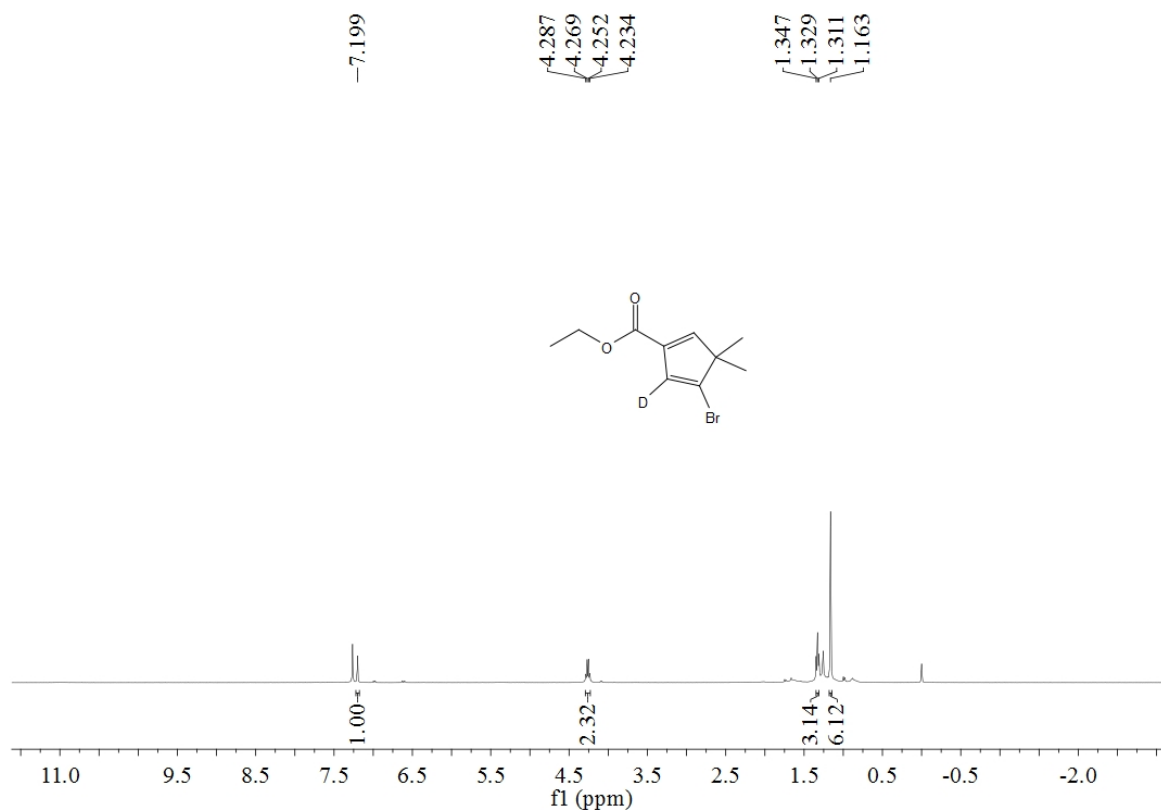
A 100 mL round-bottom flask was charged with copper(I) bromide (6.2 g, 24 mmol), copper metal powder (316 mg, 5.0 mmol), and hydrobromic acid (48%, 25 mL). To this mixture was added dropwise, 2-methyl-3-butyn-2-ol (12 mL, 10.4 g, 124 mmol) dissolved in 30 mL of pentane over 30 minutes. The reaction was then stirred for 3 hours at 40 °C. The biphasic mixture was transferred to a separatory funnel and the organic layer was collected. The aqueous layer was extracted with pentane (3 x 50 mL). The combined organic phases were washed with aqueous concentrated hydrobromic acid (3 x 5 mL) and water (2 x 10 mL), dried over MgSO<sub>4</sub>, and eluted through a plug of silica, which afforded allenyl bromide (10 g, ~50%) after gentle evaporation of volatiles. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 5.84-5.80 (m, 1H), 1.86 (d, *J* = 2.1 Hz, 6H). Spectra data are in accordance with those previously reported.<sup>3</sup>



When **1a'** was treated with **2a** under the standard conditions [eq. (4)], the reaction system became complicated and no desired product **3aa** was detected by GC-MS, which could exclude that compound **1a'** was the possible intermediate for this transformation.

Entry	[Pd]	Atmosphere	Yield (%)
1	Pd <sub>2</sub> (dba) <sub>3</sub>	N <sub>2</sub>	36
2	Pd <sub>2</sub> (dba) <sub>3</sub>	O <sub>2</sub>	38

Control experiments showed that both the Pd<sup>0</sup> and Pd<sup>II</sup> catalysts could afford the desired products, and even in N<sub>2</sub> atmosphere Pd<sub>2</sub>(dba)<sub>3</sub> could afford the desired products without significant influence on the yield (36% compared to 38%). Thus, the active catalyst for this transformation might be Pd<sup>0</sup>.

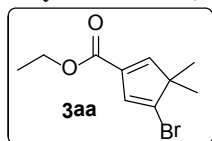


## References

1. Y. Wang, K. Zheng and R. Hong, *J. Am. Chem. Soc.*, 2012, **134**, 4096.
2. H. Wegner, S. Ahles and M. Neuburger, *Chem. Eur. J.*, 2008, **14**, 11310.
3. G. Barretta-Uccello, F. Balzano, A. M. Caporusso and P. Salvadori, *J. Org. Chem.*, 1994, **59**, 836.

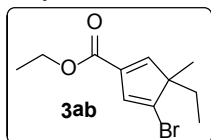
## C. Characterization Data for Compounds 3aa-5e

### Ethyl 4-Bromo-3,3-dimethylcyclopenta-1,4-dienecarboxylate (**3aa**)



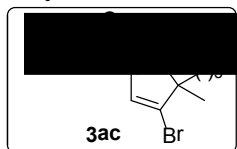
Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.20 (s, 1H), 6.59 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.16 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.4, 153.0, 137.3, 134.9, 127.0, 60.6, 55.7, 21.2, 14.2. IR (KBr, cm<sup>-1</sup>): 2979, 1721, 1245, 1192, 753; ESI-HRMS calcd for C<sub>10</sub>H<sub>13</sub>BrO<sub>2</sub> (M + H)<sup>+</sup> 245.0172; found, 245.0166.

#### Ethyl 4-Bromo-3-ethyl-3-methylcyclopenta-1,3-dienecarboxylate (3ab)



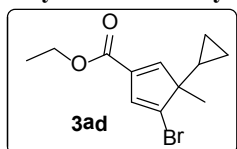
Yellow oil,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (d,  $J = 1.2$  Hz, 1H), 6.64 (d,  $J = 1.1$  Hz, 1H), 4.26 (q,  $J = 7.1$  Hz, 2H), 1.73 (td,  $J = 14.4, 7.2$  Hz, 1H), 1.58 (td,  $J = 14.8, 7.2$  Hz, 1H), 1.33 (t,  $J = 7.1$  Hz, 3H), 1.12 (s, 3H), 0.65 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 151.7, 136.1, 135.8, 128.2, 60.6, 59.9, 28.5, 20.3, 14.2, 8.7. IR (KBr,  $\text{cm}^{-1}$ ): 2976, 2360, 1726, 1258, 1187, 740; ESI-HRMS calcd for  $\text{C}_{11}\text{H}_{15}\text{BrO}_2$  ( $\text{M} + \text{Na}$ ) $^+$  281.0148; found, 281.0139.

#### Ethyl 4-Bromo-3-hexyl-3-methylcyclopenta-1,3-dienecarboxylate (3ac)



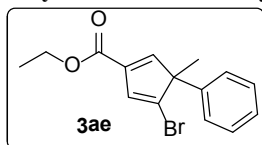
Yellow oil,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 (d,  $J = 1.6$  Hz, 1H), 6.62 (d,  $J = 1.5$  Hz, 1H), 4.26 (q,  $J = 7.1$  Hz, 2H), 1.70 – 1.60 (m, 1H), 1.57 – 1.48 (m, 1H), 1.33 (t,  $J = 7.1$  Hz, 3H), 1.28 – 1.18 (m, 6H), 1.14 (s, 3H), 0.99 (d,  $J = 6.9$  Hz, 2H), 0.85 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 152.0, 136.1, 135.8, 127.9, 60.6, 59.6, 35.6, 31.5, 29.6, 24.2, 22.5, 20.7, 14.2, 14.0. IR (KBr,  $\text{cm}^{-1}$ ): 2989, 1722, 1258, 1184, 756; ESI-HRMS calcd for  $\text{C}_{15}\text{H}_{23}\text{BrO}_2$  ( $\text{M} + \text{H}$ ) $^+$  315.0954; found, 315.0952.

#### Ethyl 4-Bromo-3-cyclopropyl-3-methylcyclopenta-1,3-dienecarboxylate (3ad)



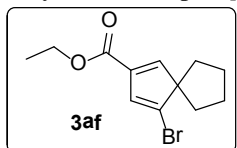
Yellow oil,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.93 (d,  $J = 1.7$  Hz, 1H), 6.60 (d,  $J = 1.7$  Hz, 1H), 4.29 – 4.23 (m, 2H), 1.34 (t,  $J = 7.1$  Hz, 3H), 1.17 (s, 3H), 1.01 – 0.91 (m, 1H), 0.55 (tt,  $J = 9.0, 5.4$  Hz, 1H), 0.46 (dq,  $J = 10.6, 5.4$  Hz, 1H), 0.31 (tt,  $J = 9.1, 5.3$  Hz, 1H), 0.02 (dq,  $J = 10.9, 5.4$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 149.6, 137.2, 136.8, 127.1, 60.7, 58.8, 18.5, 16.0, 14.2, 2.2, 0.2. IR (KBr,  $\text{cm}^{-1}$ ): 2988, 2027, 1763, 1243, 1108, 618; ESI-HRMS calcd for  $\text{C}_{12}\text{H}_{15}\text{BrO}_2$  ( $\text{M} + \text{H}$ ) $^+$  271.0328; found, 271.0325.

#### Ethyl 4-Bromo-3-methyl-3-phenylcyclopenta-1,4-dienecarboxylate (3ae)



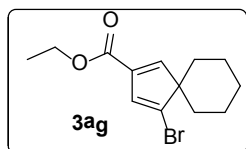
Yellow oil,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.27 (m, 5H), 7.22 (d,  $J = 1.6$  Hz, 1H), 6.78 (d,  $J = 1.7$  Hz, 1H), 4.31 (q,  $J = 7.1$  Hz, 2H), 1.64 (s, 3H), 1.36 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 153.8, 137.6, 136.4, 135.4, 128.7, 128.3, 128.0, 127.5, 126.2, 62.8, 60.8, 18.9, 14.2. IR (KBr,  $\text{cm}^{-1}$ ): 3058, 2986, 1712, 1240, 1198, 746; ESI-HRMS calcd for  $\text{C}_{15}\text{H}_{15}\text{BrO}_2$  ( $\text{M} + \text{Na}$ ) $^+$  329.0148; found, 329.0139.

#### Ethyl 4-Bromospiro[4.4]nona-1,3-diene-2-carboxylate (3af)



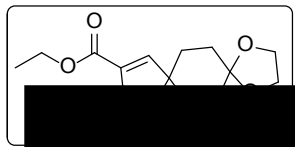
Yellow oil,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 1.7$  Hz, 1H), 6.61 (d,  $J = 1.7$  Hz, 1H), 4.26 (q,  $J = 7.1$  Hz, 2H), 1.99 (ddd,  $J = 11.1, 8.8, 6.3$  Hz, 2H), 1.89 (ddd,  $J = 11.7, 9.3, 6.7$  Hz, 4H), 1.67 – 1.62 (m, 2H), 1.33 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 151.5, 134.7, 134.5, 127.6, 66.3, 60.6, 32.5, 26.0, 14.2. IR (KBr,  $\text{cm}^{-1}$ ): 2989, 1764, 1242, 1056, 740; ESI-HRMS calcd for  $\text{C}_{12}\text{H}_{15}\text{BrO}_2$  ( $\text{M} + \text{H}$ ) $^+$  271.0328; found, 271.0315.

#### Ethyl 4-Bromospiro[4.5]deca-1,3-diene-2-carboxylate (3ag)



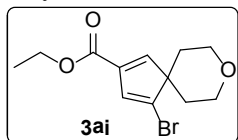
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J = 1.7$  Hz, 1H), 6.65 (d,  $J = 1.7$  Hz, 1H), 4.32 – 4.24 (m, 2H), 1.90 – 1.84 (m, 3H), 1.73 (td,  $J = 13.2, 3.1$  Hz, 2H), 1.63 – 1.50 (m, 3H), 1.35 (t,  $J = 7.1$  Hz, 3H), 1.19 (d,  $J = 12.1$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 149.9, 137.8, 135.8, 127.0, 60.6, 60.0, 31.1, 25.3, 24.2, 14.2. IR (KBr,  $\text{cm}^{-1}$ ): 2935, 2878, 1720, 1224, 741; ESI-HRMS calcd for  $\text{C}_{13}\text{H}_{17}\text{BrO}_2$  ( $\text{M} + \text{H}$ ) $^+$  285.0485; found, 285.0483.

#### Ethyl 4-Bromo- 8,8-ethane-diol-spiro[4.5]deca-1,3-diene-2-carboxylate (3ah)



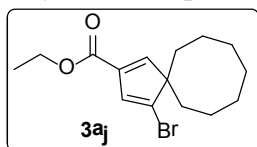
White solid; mp 126-127 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 1.7$  Hz, 1H), 6.66 (d,  $J = 1.7$  Hz, 1H), 4.27 (q,  $J = 7.1$  Hz, 2H), 4.00 (s, 4H), 2.11 (td,  $J = 13.6, 4.1$  Hz, 2H), 1.84 (ddd,  $J = 18.4, 17.7, 8.7$  Hz, 4H), 1.34 (t,  $J = 7.1$  Hz, 3H), 1.27 – 1.16 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 148.5, 136.8, 136.6, 127.6, 107.7, 64.5, 64.4, 60.8, 59.0, 33.2, 29.0, 14.2. IR (KBr,  $\text{cm}^{-1}$ ): 2989, 1764, 1224, 1056, 753; ESI-HRMS calcd for  $\text{C}_{15}\text{H}_{19}\text{BrO}_4$  ( $\text{M} + \text{H}$ ) $^+$  343.0539; found, 343.0534.

#### Ethyl 4-Bromo-8-oxaspiro[4.5]deca-1,3-diene-2-carboxylate (3ai)



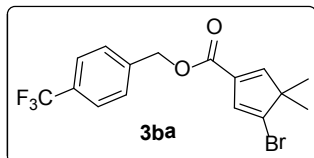
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 1.6$  Hz, 1H), 6.71 (d,  $J = 1.6$  Hz, 1H), 4.30 (q,  $J = 7.1$  Hz, 2H), 4.09 (dd,  $J = 12.0, 4.7$  Hz, 2H), 3.72 (td,  $J = 12.8, 1.8$  Hz, 2H), 2.13 (td,  $J = 13.4, 4.8$  Hz, 2H), 1.36 (t,  $J = 7.1$  Hz, 3H), 1.10 (d,  $J = 14.1$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 147.5, 136.7, 136.3, 127.9, 65.6, 60.8, 57.2, 30.2, 14.2. IR (KBr,  $\text{cm}^{-1}$ ): 2956, 2369, 1720, 1243, 1108, 747; ESI-HRMS calcd for  $\text{C}_{12}\text{H}_{15}\text{BrO}_3$  ( $\text{M} + \text{Na}$ ) $^+$  309.0097; found, 309.0108.

#### Ethyl 4-bromospiro[4.7]dodeca-1,3-diene-2-carboxylate (3aj)



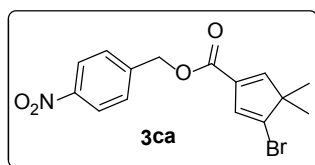
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 1.8$  Hz, 1H), 6.55 (d,  $J = 1.8$  Hz, 1H), 4.26 (q,  $J = 7.1$  Hz, 2H), 1.90 (tt,  $J = 4.9, 4.1$  Hz, 2H), 1.81 (ddd,  $J = 14.2, 8.9, 1.5$  Hz, 2H), 1.76 – 1.66 (m, 4H), 1.66 – 1.60 (m, 4H), 1.44 – 1.37 (m, 2H), 1.33 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.54, 152.71, 137.99, 135.11, 126.66, 61.63, 60.62, 29.38, 28.30, 24.03, 23.89, 14.24. IR (KBr,  $\text{cm}^{-1}$ ): 2935, 2878, 1720, 1224, 741; ESI-HRMS calcd for  $\text{C}_{15}\text{H}_{21}\text{BrO}_2$  ( $\text{M} + \text{H}$ ) $^+$  313.0797; found, 313.0793.

#### 4-(Trifluoromethyl)benzyl 4-Bromo-3,3-dimethylcyclopenta-1,3-dienecarboxylate (3ba)



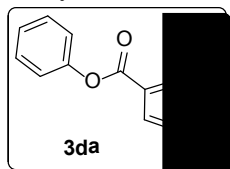
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 8.1$  Hz, 2H), 7.51 (d,  $J = 8.0$  Hz, 2H), 7.27 (d,  $J = 1.6$  Hz, 1H), 6.61 (d,  $J = 1.5$  Hz, 1H), 5.29 (s, 2H), 1.17 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 154.0, 139.8, 137.7, 134.3, 128.2, 126.7, 125.6 (dd,  $J = 7.5, 3.8$  Hz), 65.4, 55.9, 21.1. IR (KBr,  $\text{cm}^{-1}$ ): 2987, 2371, 1724, 1245, 1126, 745; APCI-HRMS calcd for  $\text{C}_{16}\text{H}_{14}\text{BrF}_3\text{O}_2$  ( $\text{M} + \text{H}$ ) $^+$  375.0202; found, 375.0205.

#### 4-Nitrobenzyl 4-Bromo-3,3-dimethylcyclopenta-1,3-dienecarboxylate (3ca)



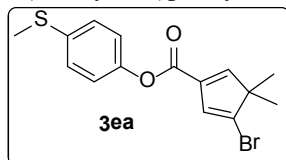
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J = 8.6$  Hz, 2H), 7.58 (d,  $J = 8.6$  Hz, 2H), 7.31 (d,  $J = 1.6$  Hz, 1H), 6.63 (s, 1H), 5.36 (s, 2H), 1.20 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7, 154.2, 147.8, 143.0, 137.8, 134.0, 128.4, 126.5, 123.8, 64.9, 56.0, 21.1. IR (KBr,  $\text{cm}^{-1}$ ): 2964, 2359, 1739, 1530, 1242, 1186, 758; APCI-HRMS calcd for  $\text{C}_{15}\text{H}_{14}\text{BrNO}_4$  ( $\text{M} + \text{H}$ ) $^+$  352.0178; found, 352.0172.

#### Phenyl 4-Bromo-3,3-dimethylcyclopenta-1,3-dienecarboxylate (3da)



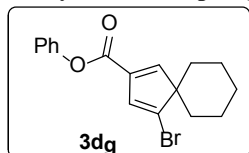
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 1.8$  Hz, 1H), 7.40 – 7.38 (m, 2H), 7.26 – 7.23 (m, 1H), 7.17 – 7.14 (m, 2H), 6.71 (d,  $J = 1.7$  Hz, 1H), 1.22 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 154.9, 150.6, 137.6, 134.3, 129.4, 126.8, 125.9, 121.5, 56.1, 21.1. IR (KBr,  $\text{cm}^{-1}$ ): 2973, 2861, 1762, 1243, 746; ESI-HRMS calcd for  $\text{C}_{14}\text{H}_{13}\text{BrO}_2$  ( $\text{M} + \text{Na}$ ) $^+$  314.9991; found, 314.9985.

#### 4-(Methylthio)phenyl 4-Bromo-3,3-dimethylcyclopenta-1,4-dienecarboxylate (3ea)



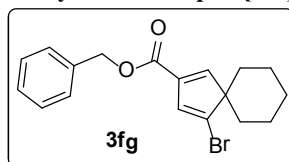
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (s, 1H), 7.29 (d,  $J = 8.4$  Hz, 2H), 7.09 (d,  $J = 8.4$  Hz, 2H), 6.69 (s, 1H), 2.48 (s, 3H), 1.22 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 155.0, 148.2, 137.8, 135.8, 134.1, 128.0, 126.7, 122.0, 56.1, 21.1, 16.4. IR (KBr,  $\text{cm}^{-1}$ ): 2972, 1738, 1247, 1086, 746; APCI-HRMS calcd for  $\text{C}_{15}\text{H}_{15}\text{BrO}_2\text{S}$  ( $\text{M} + \text{H}$ ) $^+$  339.0049; found, 339.0051.

#### Phenyl 4-Bromospiro[4.5]deca-1,3-diene-1-carboxylate (3dg)



White solid; mp 116–117 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 1.7$  Hz, 1H), 7.43 – 7.37 (m, 2H), 7.26 (d,  $J = 6.4$  Hz, 1H), 7.17 – 7.14 (m, 2H), 6.75 (d,  $J = 1.7$  Hz, 1H), 1.89 (dd,  $J = 9.3, 4.9$  Hz, 3H), 1.78 (td,  $J = 13.2, 3.4$  Hz, 2H), 1.65 – 1.51 (m, 2H), 1.41 – 1.30 (m, 1H), 1.28 – 1.23 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.8, 152.0, 150.6, 138.2, 135.2, 129.4, 126.8, 125.9, 121.6, 60.4, 31.1, 25.3, 24.2. IR (KBr,  $\text{cm}^{-1}$ ): 2984, 2360, 1738, 1242, 766; APCI-HRMS calcd for  $\text{C}_{17}\text{H}_{17}\text{BrO}_2$  ( $\text{M} + \text{H}$ ) $^+$  333.0485; found, 333.0479.

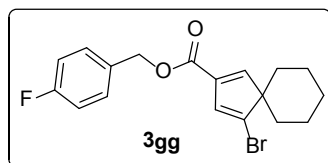
#### Benzyl 4-Bromospiro[4.5]deca-1,3-diene-2-carboxylate (3fg)



Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 1.6$  Hz, 1H), 7.43 – 7.30 (m, 5H), 6.65 (d,  $J = 1.6$  Hz, 1H), 5.25 (s, 2H), 1.83 (d,  $J = 11.0$  Hz, 3H), 1.71 (td,  $J = 13.2, 3.1$  Hz, 2H), 1.53 (ddd,  $J = 16.2, 9.4, 2.9$  Hz, 2H), 1.36 – 1.24 (m, 1H), 1.17 (d,  $J = 12.3$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 150.5, 137.9, 135.8, 135.5, 128.6, 128.3, 126.9, 66.4, 60.1, 31.0, 25.3, 24.2. IR (KBr,  $\text{cm}^{-1}$ ): 2965, 2342, 1721, 1248, 1173, 749, 698; APCI-HRMS calcd for  $\text{C}_{18}\text{H}_{19}\text{BrO}_2$  ( $\text{M} + \text{H}$ ) $^+$  347.0641; found, 347.0640.

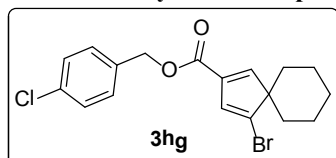
#### 4-(Trifluoromethyl)benzyl-4-Bromo-5,5-dimethylcyclopenta-1,3-diene-2-carboxylate (3gg)





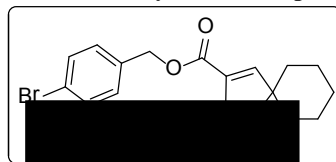
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (s, 1H), 7.41 – 7.37 (m, 2H), 7.06 (t,  $J = 8.2$  Hz, 2H), 6.63 (s, 1H), 5.21 (s, 2H), 1.84 (d,  $J = 10.9$  Hz, 3H), 1.71 (dd,  $J = 21.3, 8.0$  Hz, 2H), 1.53 (dd,  $J = 26.6, 13.0$  Hz, 2H), 1.33 (dd,  $J = 18.1, 8.9$  Hz, 1H), 1.17 (d,  $J = 12.8$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 162.4 (d,  $J = 176.8$  Hz), 150.6, 138.0, 135.4, 131.7 (d,  $J = 3.3$  Hz), 130.3 (d,  $J = 8.3$  Hz), 126.8, 115.5 (d,  $J = 21.5$  Hz), 65.7, 60.2, 31.0, 25.3, 24.2. IR (KBr,  $\text{cm}^{-1}$ ): 2986, 2359, 1722, 1240, 827, 747; APCI-HRMS calcd for  $\text{C}_{18}\text{H}_{18}\text{BrFO}_2$  ( $\text{M} + \text{H}$ ) $^+$  365.0546; found, 365.0550.

#### 4-Chlorobenzyl 4-Bromospiro[4.5]deca-1,3-diene-2-carboxylate (3hg)



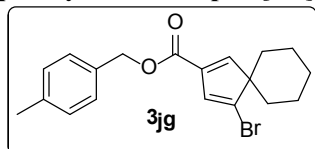
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 1.5$  Hz, 1H), 7.37 – 7.32 (m, 4H), 6.63 (d,  $J = 1.5$  Hz, 1H), 5.21 (s, 2H), 1.84 (d,  $J = 11.0$  Hz, 3H), 1.72 (td,  $J = 13.3, 3.0$  Hz, 2H), 1.53 (td,  $J = 13.0, 3.1$  Hz, 2H), 1.35 – 1.25 (m, 1H), 1.17 (d,  $J = 12.6$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 150.8, 138.0, 135.3, 134.3, 134.2, 129.7, 128.8, 126.8, 65.6, 60.2, 31.0, 25.3, 24.2. IR (KBr,  $\text{cm}^{-1}$ ): 2967, 2359, 1739, 1247, 745; ESI-HRMS calcd for  $\text{C}_{18}\text{H}_{18}\text{BrClO}_2$  ( $\text{M} + \text{Na}$ ) $^+$  403.0071; found, 403.0065.

#### 4-Bromobenzyl 4-Bromospiro[4.5]deca-1,3-diene-2-carboxylate (3ig)



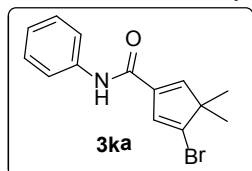
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 1.6$  Hz, 1), 7.50 (d,  $J = 8.4$  Hz, 2H), 7.28 (d,  $J = 8.4$  Hz, 2H), 6.63 (d,  $J = 1.6$  Hz, 1H), 5.19 (s, 2H), 1.84 (d,  $J = 11.0$  Hz, 3H), 1.72 (td,  $J = 13.2, 3.1$  Hz, 2H), 1.60 – 1.47 (m, 2), 1.36 – 1.24 (m, 1H), 1.17 (d,  $J = 12.6$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 150.8, 138.0, 135.3, 134.8, 131.7, 130.0, 126.8, 122.4, 65.6, 60.2, 31.0, 25.3, 24.2. IR (KBr,  $\text{cm}^{-1}$ ): 2932, 2359, 1727, 1246, 810; ESI-HRMS calcd for  $\text{C}_{18}\text{H}_{18}\text{Br}_2\text{O}_2$  ( $\text{M} + \text{Na}$ ) $^+$  446.9566; found, 446.9562.

#### *p*-Tolyl 4-Bromospiro[4.5]deca-1,3-diene-2-carboxylate (3jg)



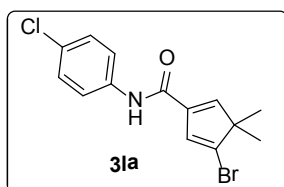
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (s, 1H), 7.30 (d,  $J = 7.8$  Hz, 2H), 7.18 (d,  $J = 7.7$  Hz, 2H), 6.64 (s, 1H), 5.20 (s, 2H), 2.36 (s, 3H), 1.83 (d,  $J = 10.6$  Hz, 3H), 1.75 – 1.66 (m, 2H), 1.52 (dd,  $J = 26.6, 13.0$  Hz, 2H), 1.35 – 1.25 (m, 1H), 1.17 (d,  $J = 12.9$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 150.4, 138.2, 137.8, 135.6, 132.8, 129.2, 128.5, 127.0, 66.4, 60.1, 31.0, 25.3, 24.2, 21.2. IR (KBr,  $\text{cm}^{-1}$ ): 2969, 2342, 1720, 1248, 1173, 749, 688; APCI-HRMS calcd for  $\text{C}_{19}\text{H}_{21}\text{BrO}_2$  ( $\text{M} + \text{H}$ ) $^+$  361.0798; found, 361.0809.

#### 4-Bromo-3,3-dimethyl-*N*-phenylcyclopenta-1,3-dienecarboxamide (3ka)



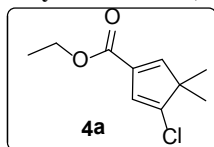
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J = 7.7$  Hz, 2H), 7.36 (t,  $J = 7.9$  Hz, 2H), 7.15 (t,  $J = 7.4$  Hz, 1H), 7.02 (d,  $J = 1.8$  Hz, 1H), 6.69 (d,  $J = 1.8$  Hz, 1H), 1.22 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.5, 147.2, 138.5, 138.3, 137.5, 129.1, 126.6, 124.6, 120.1, 55.9, 21.4. IR (KBr,  $\text{cm}^{-1}$ ): 3256, 2987, 2359, 1699, 1273, 746; APCI-HRMS calcd for  $\text{C}_{14}\text{H}_{14}\text{BrNO}$  ( $\text{M} + \text{H}$ ) $^+$  292.0331; found, 292.0335.

#### 4-Bromo-*N*-(4-chlorophenyl)-3,3-dimethylcyclopenta-1,3-dienecarboxamide (3la)



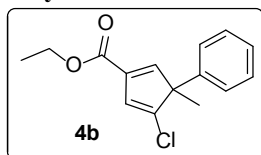
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 8.7$  Hz, 3H), 7.30 (d,  $J = 8.8$  Hz, 2H), 6.99 (d,  $J = 1.7$  Hz, 1H), 6.65 (d,  $J = 1.7$  Hz, 1H), 1.20 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4, 147.5, 138.5, 138.3, 136.1, 129.6, 129.1, 126.5, 121.3, 56.0, 21.4. IR (KBr,  $\text{cm}^{-1}$ ): 3258, 2988, 2359, 1699, 1273, 746; APCI-HRMS calcd for  $\text{C}_{14}\text{H}_{13}\text{BrClNO}$  ( $\text{M} + \text{H}$ ) $^+$  325.9942; found, 325.9940.

#### Ethyl 4-Chloro-3,3-dimethylcyclopenta-1,3-dienecarboxylate (4a)



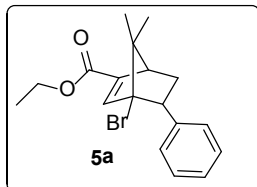
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.07 (d,  $J = 1.8$  Hz, 1H), 6.40 (d,  $J = 1.7$  Hz, 1H), 4.26 (q,  $J = 7.1$  Hz, 2H), 1.33 (t,  $J = 7.1$  Hz, 3H), 1.19 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 151.7, 146.9, 133.9, 122.6, 60.6, 54.6, 20.7, 14.2. IR (KBr,  $\text{cm}^{-1}$ ): 2989, 2309, 1726, 1258, 1192, 786; APCI-HRMS calcd for  $\text{C}_{10}\text{H}_{13}\text{ClO}_2$  ( $\text{M} + \text{Na}$ ) $^+$  223.0496; found, 223.0504.

#### Ethyl 4-Bromo-3-methyl-3-phenylcyclopenta-1,3-dienecarboxylate (4b)



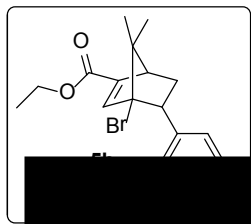
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.25 (m, 4H), 7.20 (d,  $J = 1.4$  Hz, 1H), 7.18 (s, 1H), 6.55 (d,  $J = 1.6$  Hz, 1H), 4.27 (q,  $J = 7.1$  Hz, 2H), 1.63 (s, 3H), 1.33 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 152.2, 147.2, 136.5, 134.6, 128.8, 127.5, 126.2, 124.4, 61.7, 60.8, 18.7, 14.2. IR (KBr,  $\text{cm}^{-1}$ ): 2986, 2362, 1738, 1243, 764; APCI-HRMS calcd for  $\text{C}_{15}\text{H}_{15}\text{ClO}_2$  ( $\text{M} + \text{H}$ ) $^+$  263.0833; found, 263.0839.

#### Ethyl 4-Bromo-7,7-dimethyl-5-phenylbicyclo[2.2.1]hept-2-ene-2-carboxylate (5a)



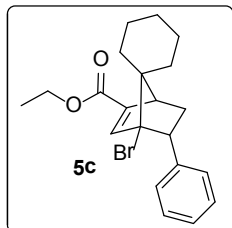
Light yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.24 (m, 3H), 7.12 – 7.08 (m, 2H), 6.48 (s, 1H), 4.35 – 4.25 (m, 2H), 3.63 (dd,  $J = 9.1, 4.6$  Hz, 1H), 2.99 (d,  $J = 3.6$  Hz, 1H), 2.60 (ddd,  $J = 13.0, 9.1, 3.9$  Hz, 1H), 1.67 (dd,  $J = 12.9, 4.6$  Hz, 1H), 1.34 (t,  $J = 7.0$  Hz, 3H), 1.14 (s, 3H), 1.02 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 145.8, 140.1, 139.6, 129.59, 127.8, 127.0, 77.6, 63.2, 60.7, 50.9, 48.5, 34.0, 20.6, 19.6, 14.3. IR (KBr,  $\text{cm}^{-1}$ ): 2979, 2356, 1712, 1598, 1255, 1080, 748; ESI-HRMS calcd for  $\text{C}_{18}\text{H}_{21}\text{BrO}_2$  ( $\text{M} + \text{H}$ ) $^+$  349.0798; found, 349.0798.

#### Ethyl 4-Bromo-5-(4-bromophenyl)-7,7-dimethylbicyclo[2.2.1]hept-2-ene-2-carboxylate (5b)



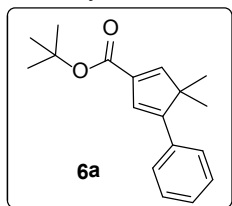
Light yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 8.1$  Hz, 2H), 6.97 (d,  $J = 8.1$  Hz, 2H), 6.43 (s, 1H), 4.34 – 4.24 (m, 2H), 3.58 (dd,  $J = 9.0, 4.4$  Hz, 1H), 2.99 (d,  $J = 2.8$  Hz, 1H), 2.63 – 2.55 (m, 1H), 1.63 – 1.59 (m, 1H), 1.33 (t,  $J = 7.1$  Hz, 3H), 1.12 (s, 3H), 1.01 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.7, 145.4, 140.4, 138.7, 131.1, 130.9, 121.1, 77.2, 63.4, 60.8, 50.4, 48.5, 33.9, 20.5, 19.6, 14.3. IR (KBr,  $\text{cm}^{-1}$ ): 2982, 2362, 1710, 1600, 1254, 1081, 740; ESI-HRMS calcd for  $\text{C}_{18}\text{H}_{20}\text{Br}_2\text{O}_2$  ( $\text{M} + \text{Na}$ ) $^+$  448.9722; found, 448.9720.

### Ethyl 1-Bromo-6-phenylspiro[bicyclo[2.2.1]hept[2]ene-7,1'-cyclohexane]-3-carboxylate (5c)



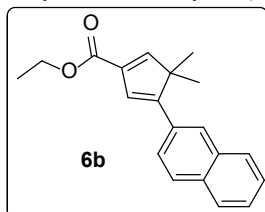
Light yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 – 7.22 (m, 3H), 7.13 – 7.06 (m, 2H), 6.47 (s, 1H), 4.36 – 4.23 (m, 2H), 3.65 (dd,  $J = 9.1, 4.4$  Hz, 1H), 3.33 (d,  $J = 3.4$  Hz, 1H), 2.51 (ddd,  $J = 12.9, 9.2, 3.8$  Hz, 1H), 1.86 – 1.60 (m, 7H), 1.34 (t,  $J = 7.1$  Hz, 3H), 1.31 – 1.12 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 145.9, 139.6, 139.2, 129.6, 127.7, 127.0, 77.9, 67.4, 60.6, 50.4, 43.3, 33.2, 28.5, 28.3, 26.5, 24.1, 23.2, 14.3. IR (KBr,  $\text{cm}^{-1}$ ): 2928, 2858, 2355, 1712, 1597, 1246, 1080, 748; ESI-HRMS calcd for  $\text{C}_{21}\text{H}_{25}\text{BrO}_2$  ( $\text{M} + \text{Na}$ ) $^+$  389.1111; found, 389.1107.

### tert-Butyl 3,3-dimethyl-4-phenylcyclopenta-1,3-dienecarboxylate (6a)



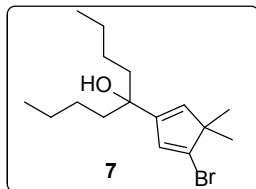
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J = 7.6$  Hz, 2H), 7.35 (t,  $J = 7.6$  Hz, 2H), 7.25 (dd,  $J = 8.4, 6.2$  Hz, 1H), 7.03 (d,  $J = 1.3$  Hz, 1H), 6.80 (d,  $J = 1.2$  Hz, 1H), 1.56 (s, 9H), 1.37 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.8, 155.2, 155.0, 135.4, 135.2, 128.4, 127.0, 126.6, 124.2, 80.6, 53.9, 28.2, 22.0. IR (KBr,  $\text{cm}^{-1}$ ): 2988, 2209, 1726, 1248, 1192, 697; ESI-HRMS calcd for  $\text{C}_{18}\text{H}_{22}\text{O}_2$  ( $\text{M} + \text{H}$ ) $^+$  271.1692; found, 271.1697.

### Ethyl 3,3-dimethyl-4-(naphthalen-2-yl)cyclopenta-1,3-dienecarboxylate (6b)



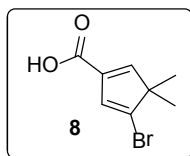
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 – 7.77 (m, 4H), 7.71 (dd,  $J = 8.7, 1.7$  Hz, 1H), 7.49 – 7.41 (m, 2H), 7.18 (d,  $J = 1.6$  Hz, 1H), 7.03 (d,  $J = 1.5$  Hz, 1H), 4.31 (q,  $J = 7.1$  Hz, 2H), 1.47 (s, 6H), 1.37 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 156.3, 154.9, 133.7, 133.4, 132.4, 132.4, 128.2, 128.0, 127.5, 126.2, 125.9, 125.1, 124.9, 124.5, 60.5, 54.1, 22.3, 14.3. IR (KBr,  $\text{cm}^{-1}$ ): 2988, 2210, 1726, 1243, 1192, 680; ESI-HRMS calcd for  $\text{C}_{20}\text{H}_{20}\text{O}_2$  ( $\text{M} + \text{H}$ ) $^+$  293.1536; found, 293.1543.

### 5-(4-Bromo-3,3-dimethylcyclopenta-1,3-dienyl)nonan-5-ol (7)



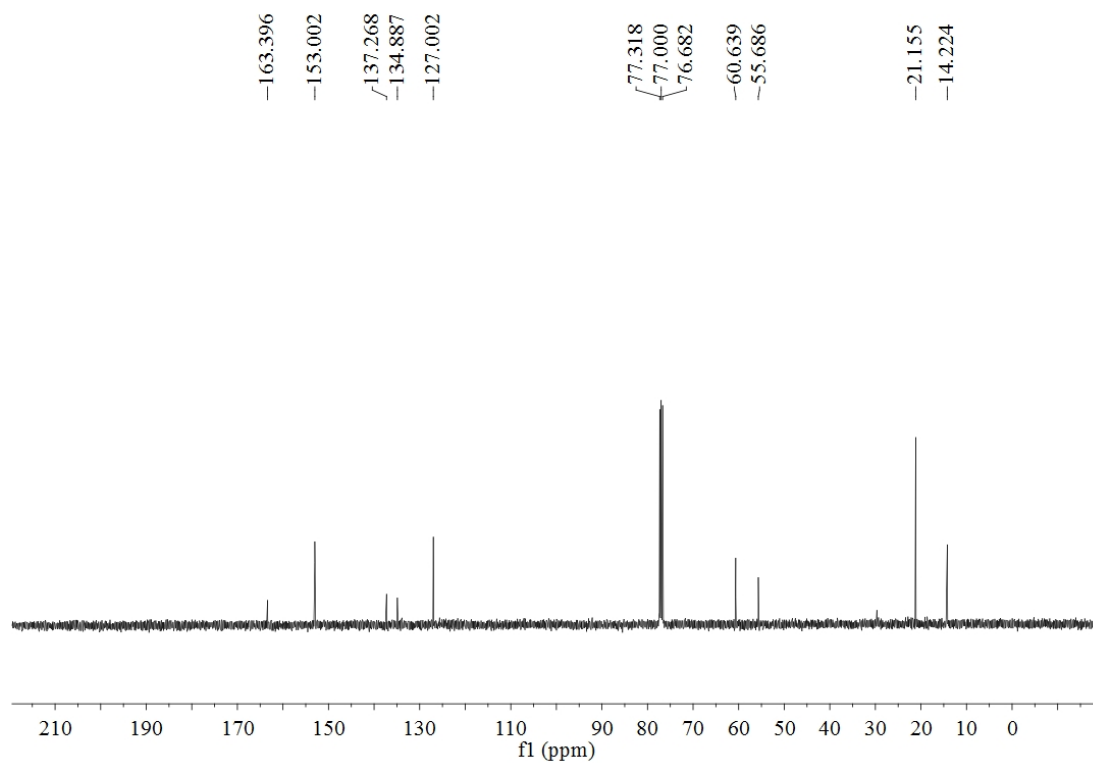
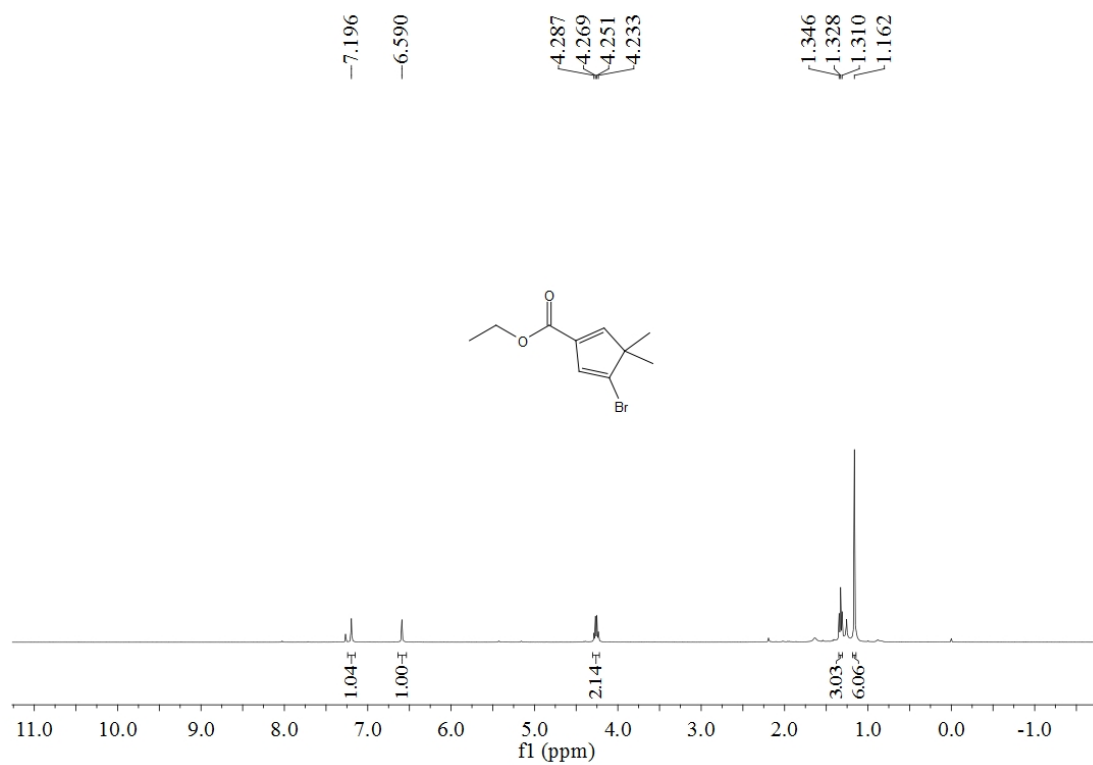
Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.21 (d,  $J = 1.9$  Hz, 1H), 6.13 (d,  $J = 1.9$  Hz, 1H), 1.63 – 1.56 (m, 4H), 1.28 (m, 8H), 1.10 (s, 6H), 0.87 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.9, 138.1, 137.4, 128.3, 74.7, 54.1, 40.1, 25.5, 23.0, 22.1, 14.0. IR (KBr,  $\text{cm}^{-1}$ ): 3380, 2988, 2876, 2309, 1726, 1358, 1192, 797; ESI-HRMS calcd for  $\text{C}_{16}\text{H}_{27}\text{BrO}$  ( $\text{M} + \text{H}$ ) $^+$  315.1318; found, 315.1316.

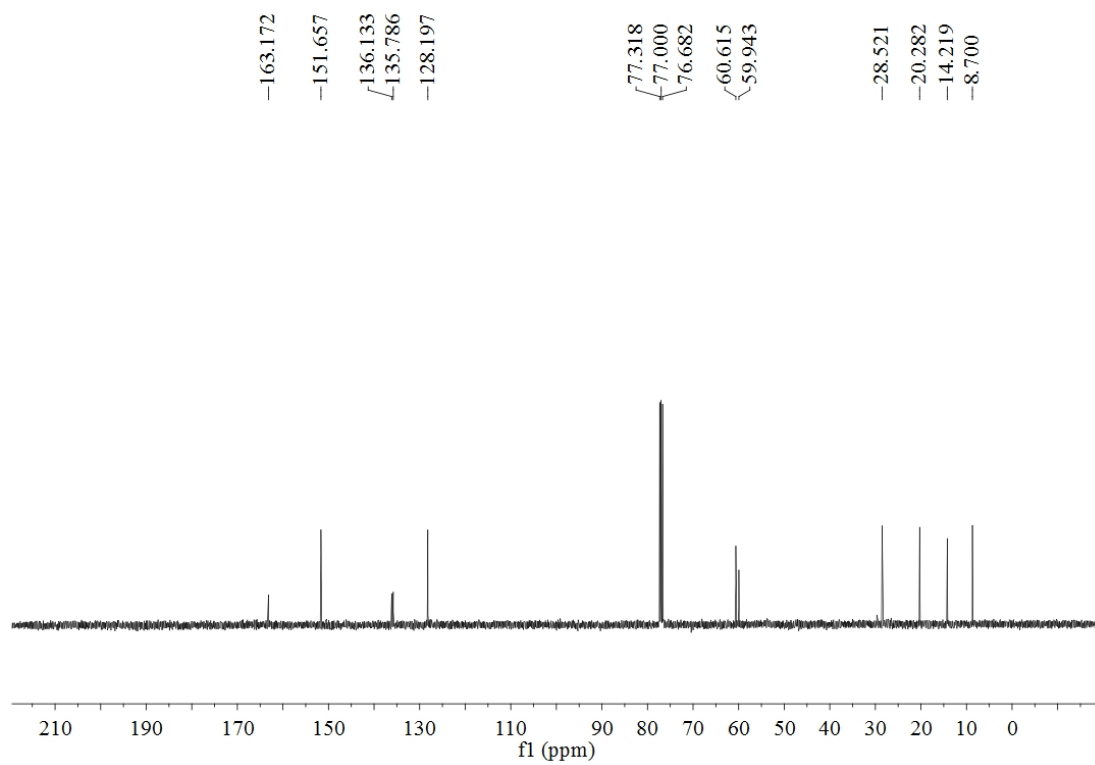
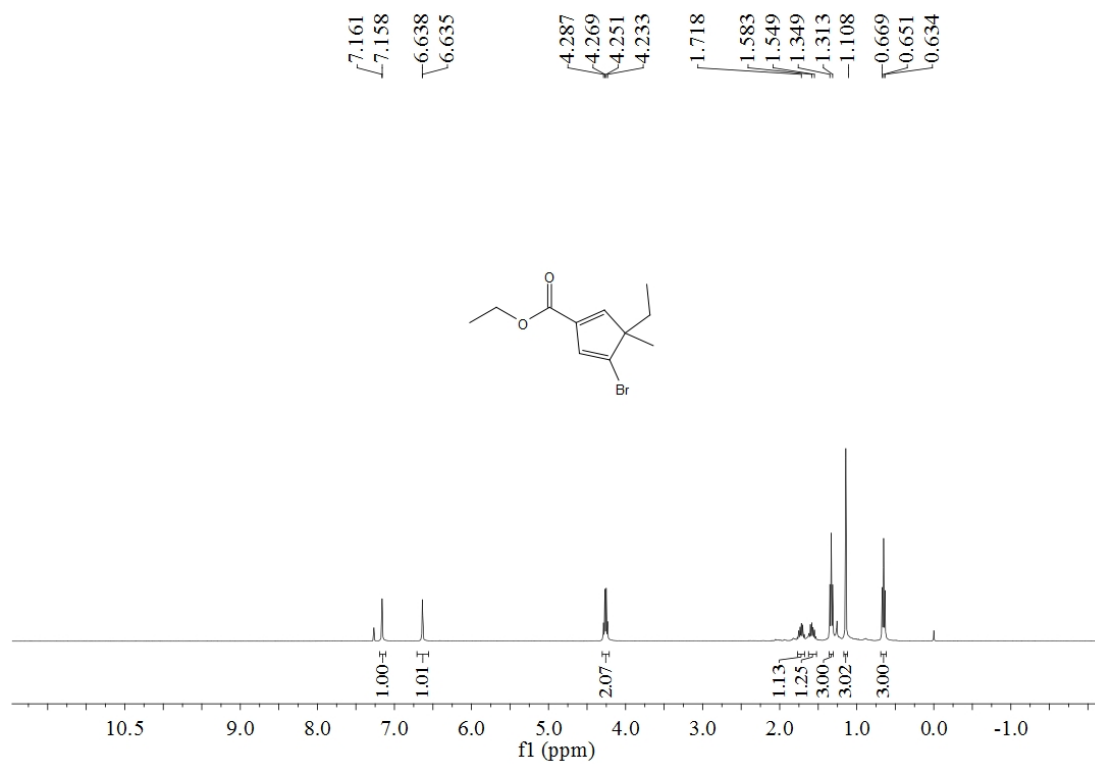
### 4-Bromo-3,3-dimethylcyclopenta-1,3-dienecarboxylic acid (8)

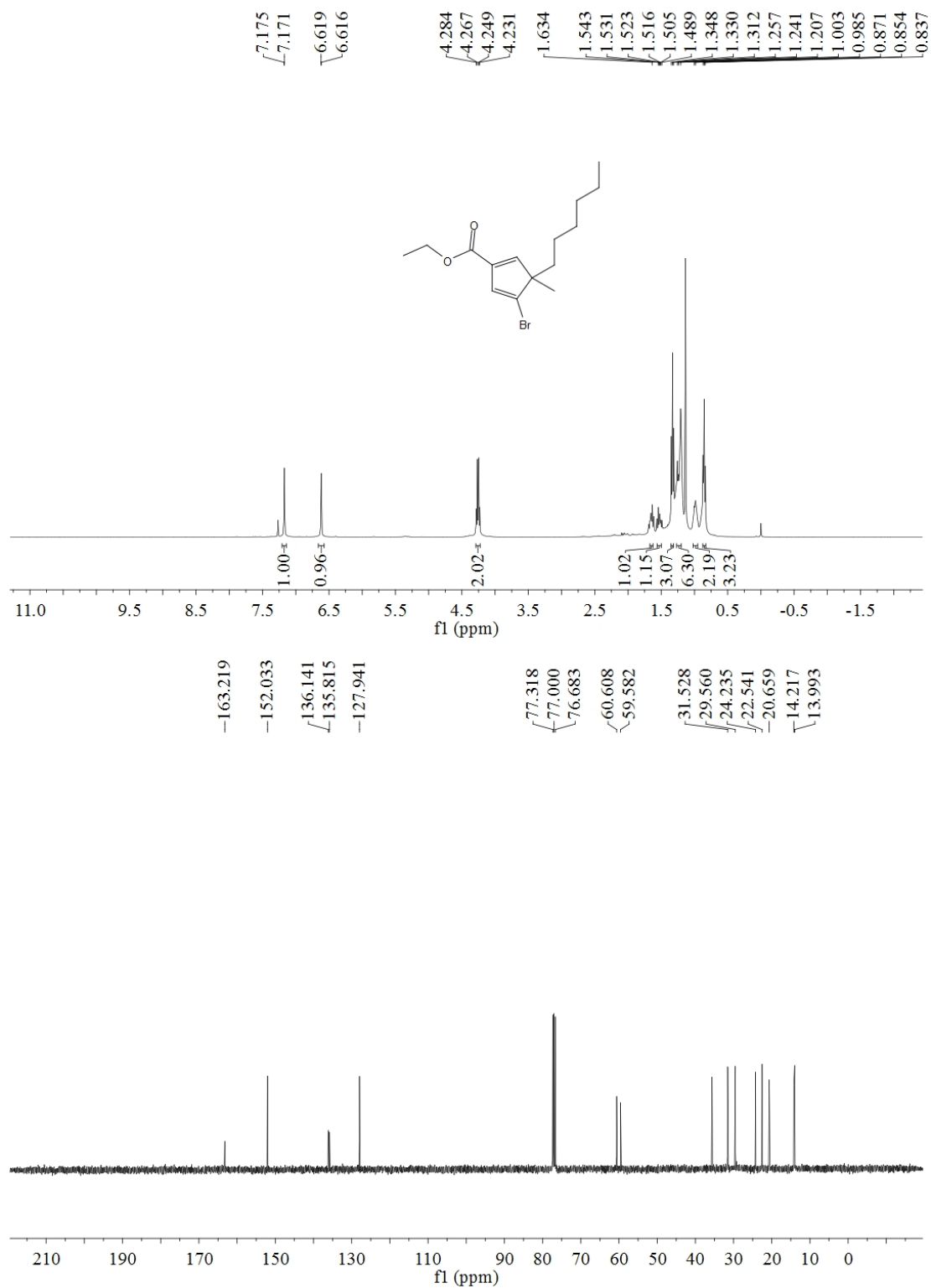


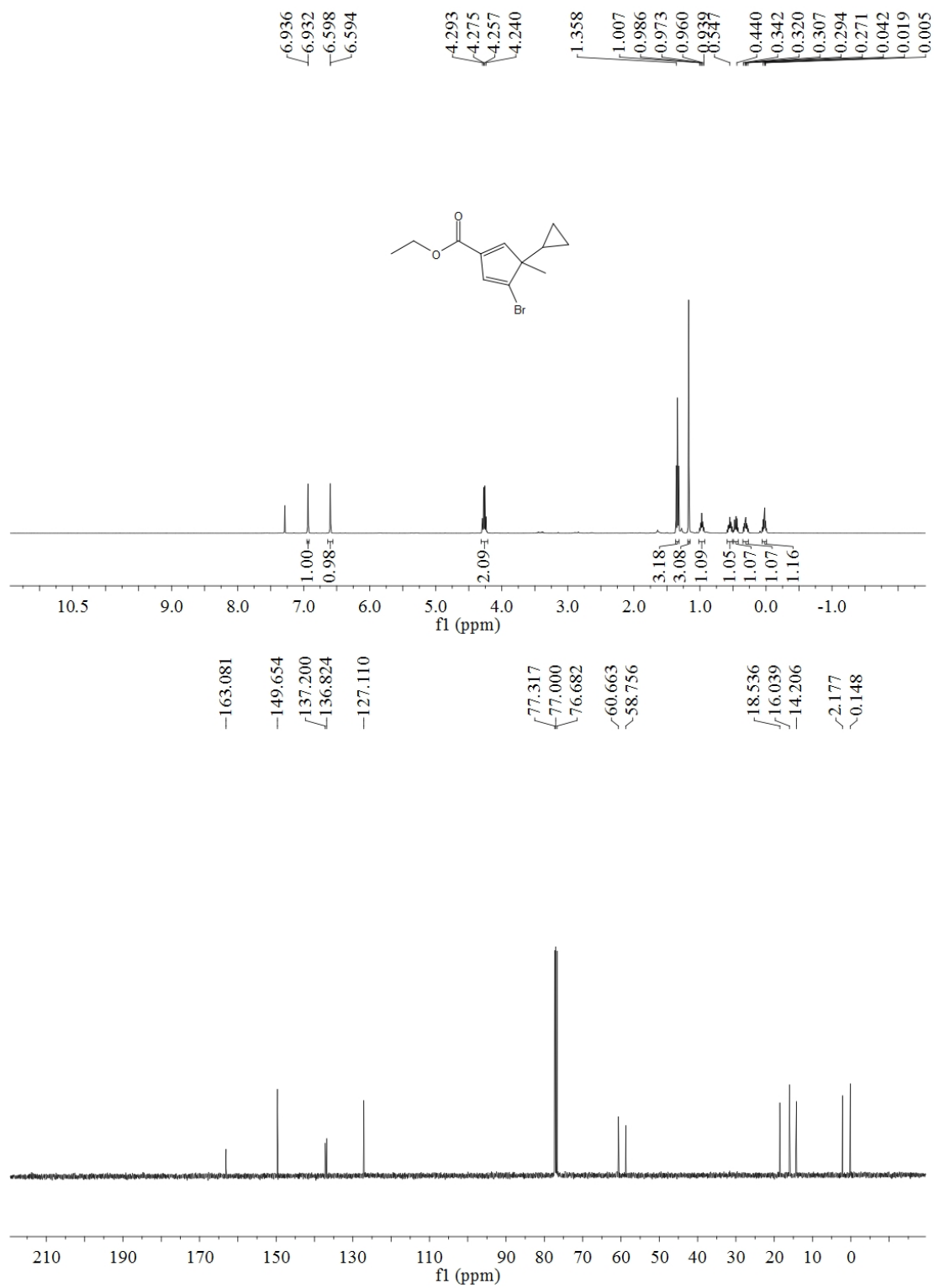
White solid; mp 138-139 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 1.5$  Hz, 1H), 6.62 (d,  $J = 1.5$  Hz, 1H), 1.21 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 155.7, 137.7, 134.2, 126.6, 56.1, 21.1. IR (KBr,  $\text{cm}^{-1}$ ): 2988, 2878, 2310, 1698, 1258, 1192, 796; ESI-HRMS calcd for  $\text{C}_8\text{H}_9\text{BrO}_2$  ( $\text{M} + \text{H}$ ) $^+$  216.9858; found, 216.9864.

## D. NMR Spectra and X-ray Crystallographic Analysis

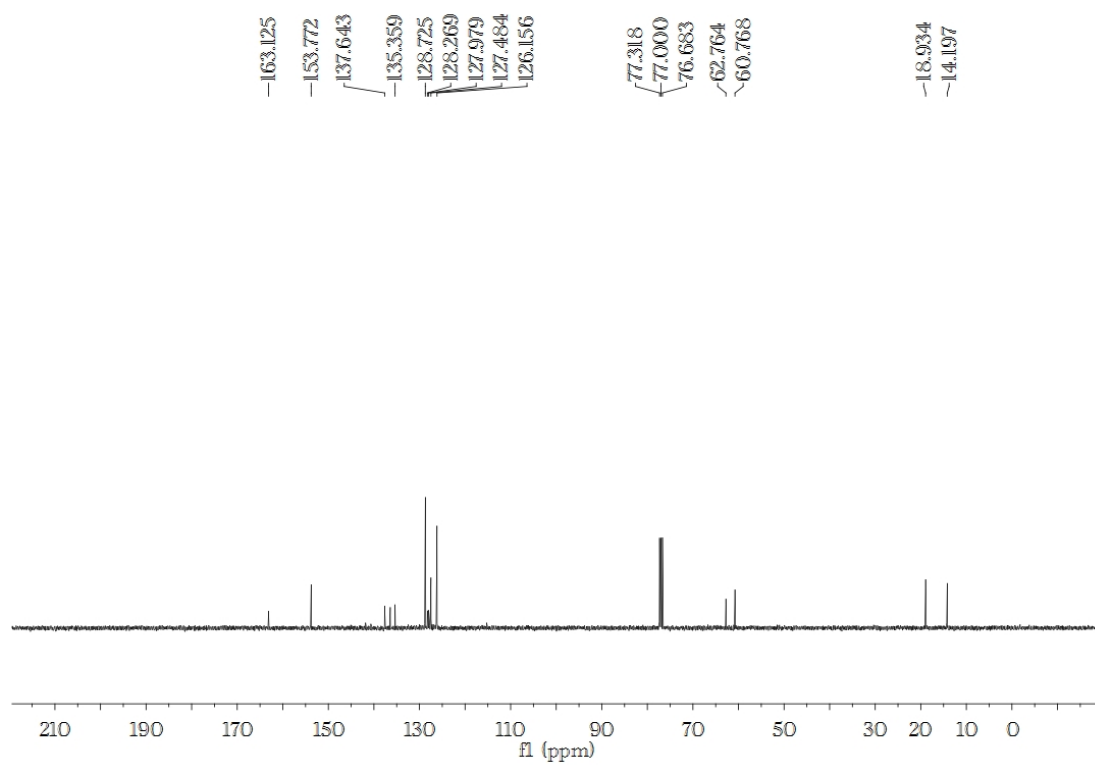
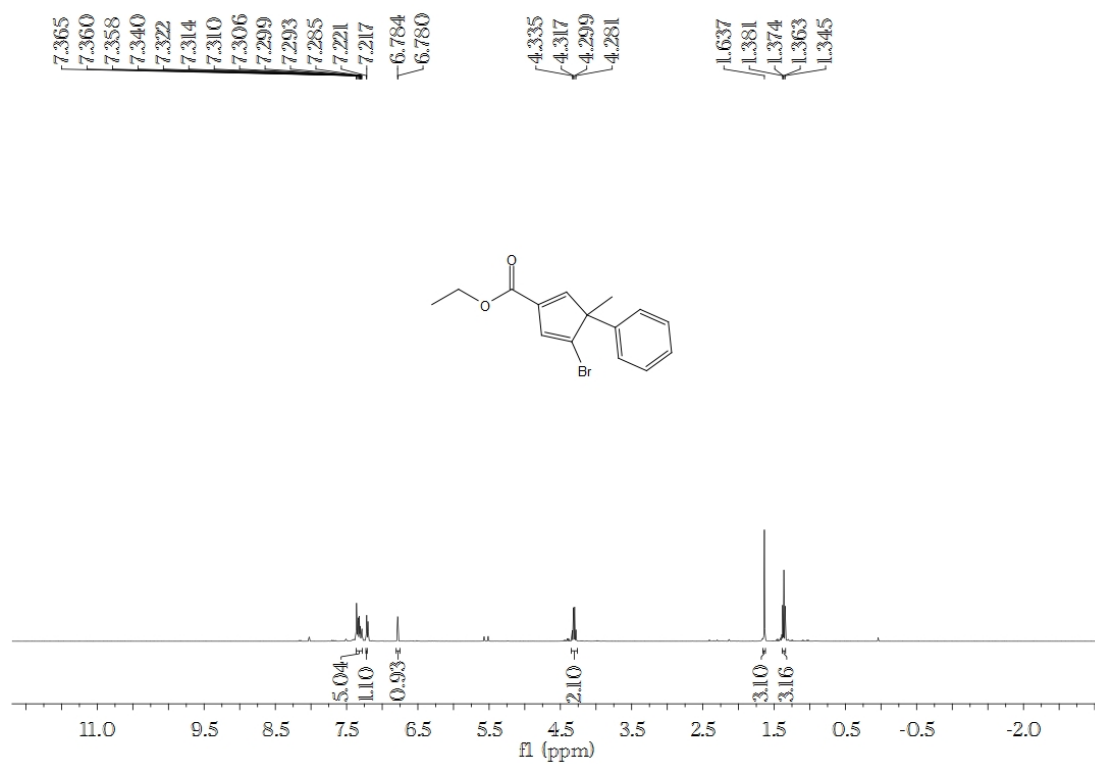


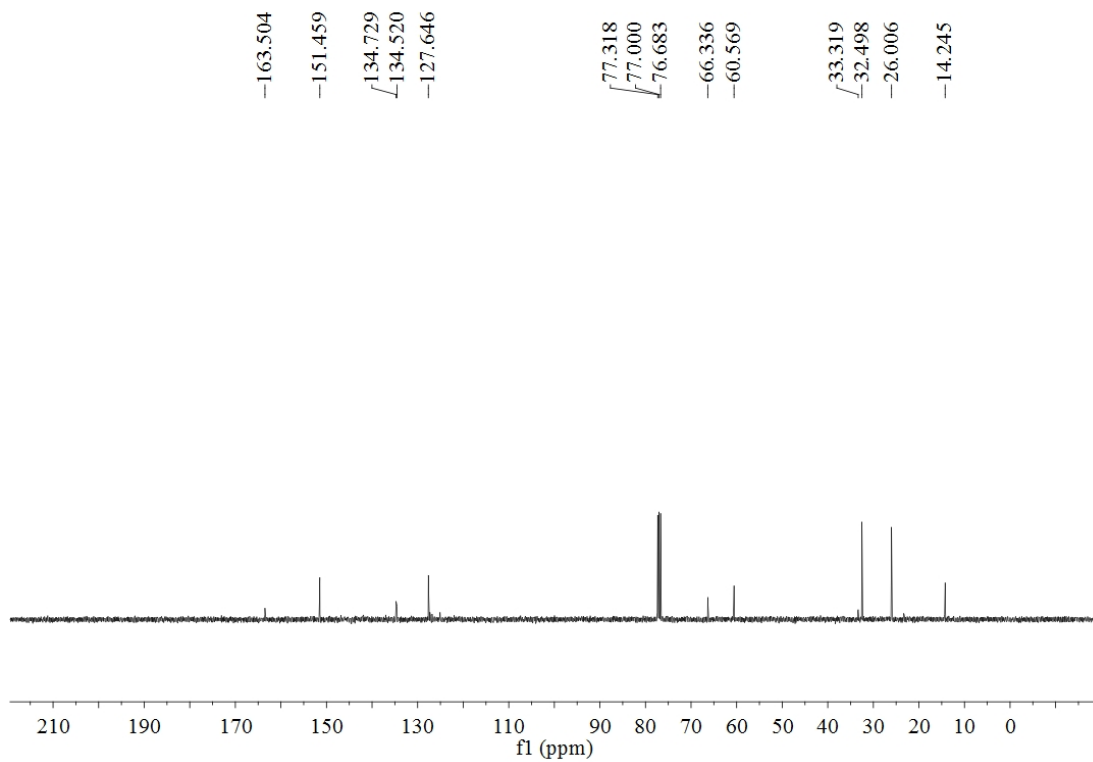
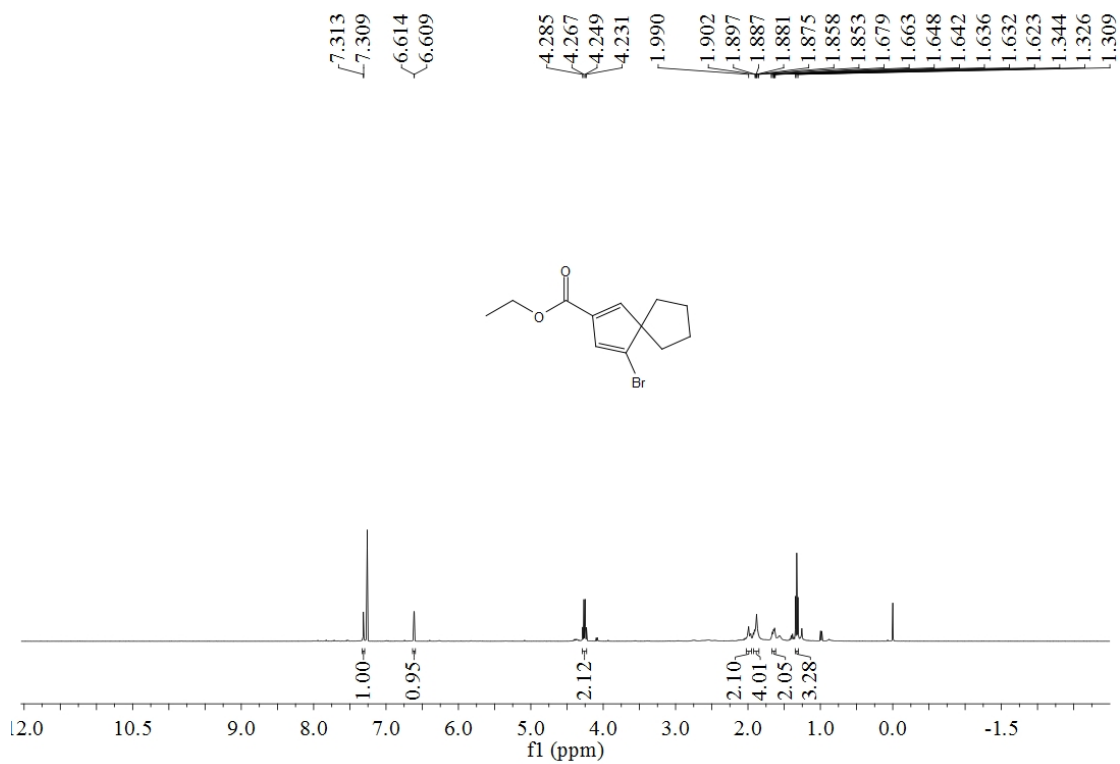


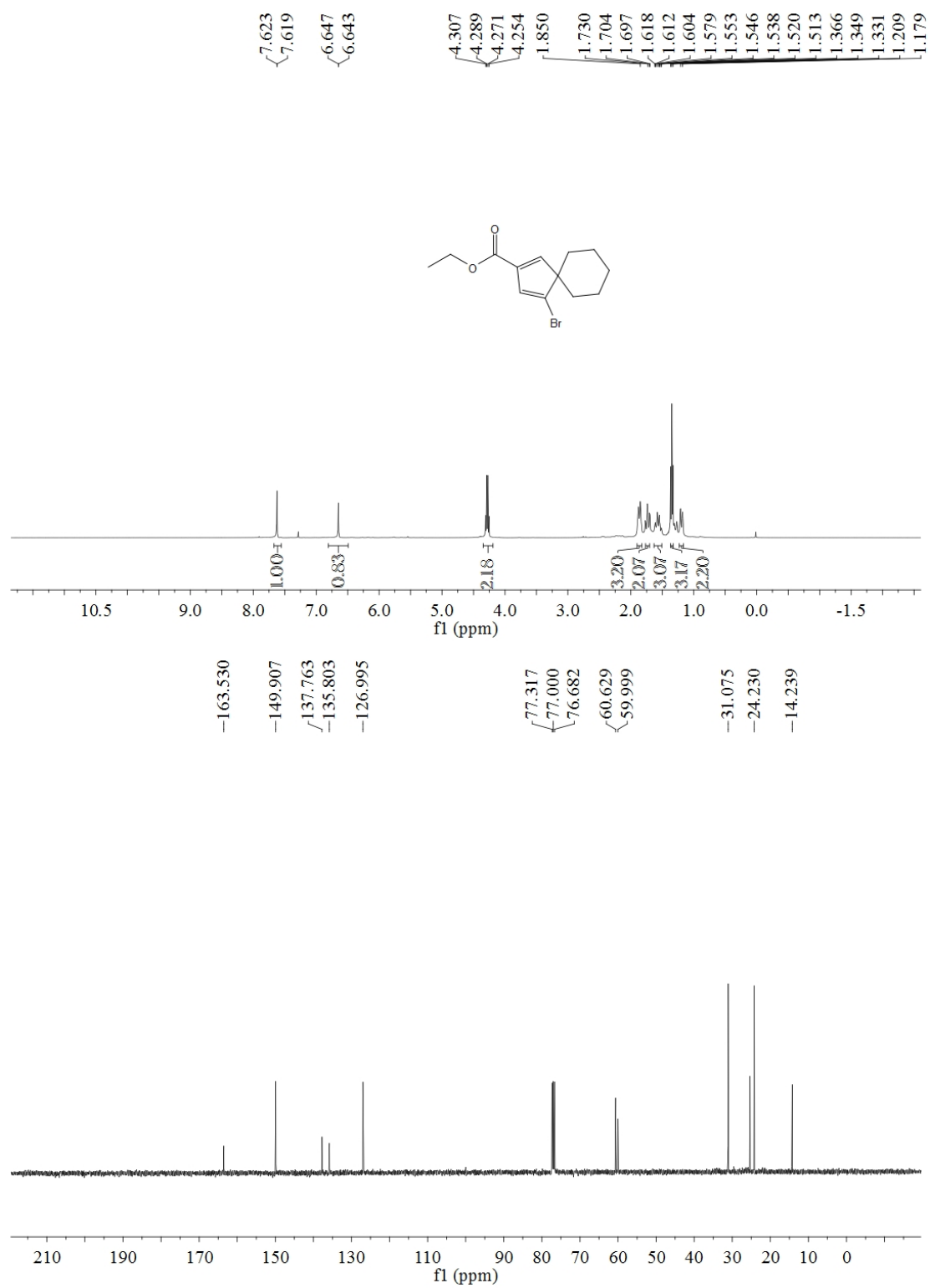


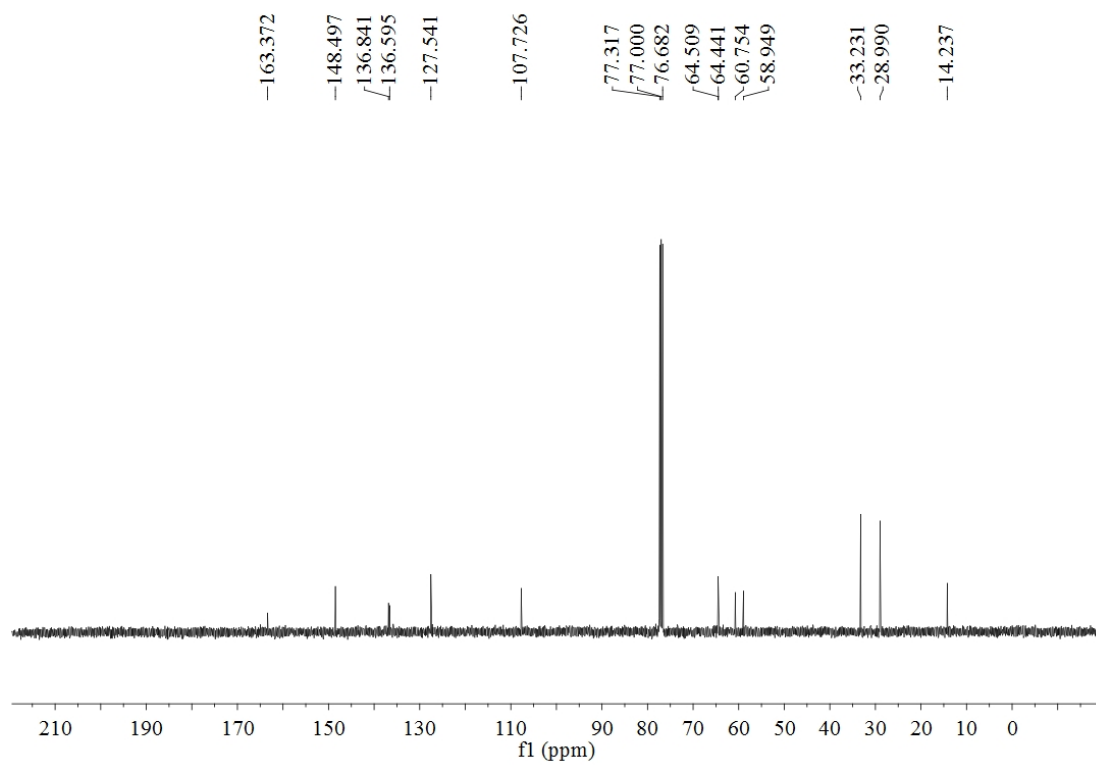
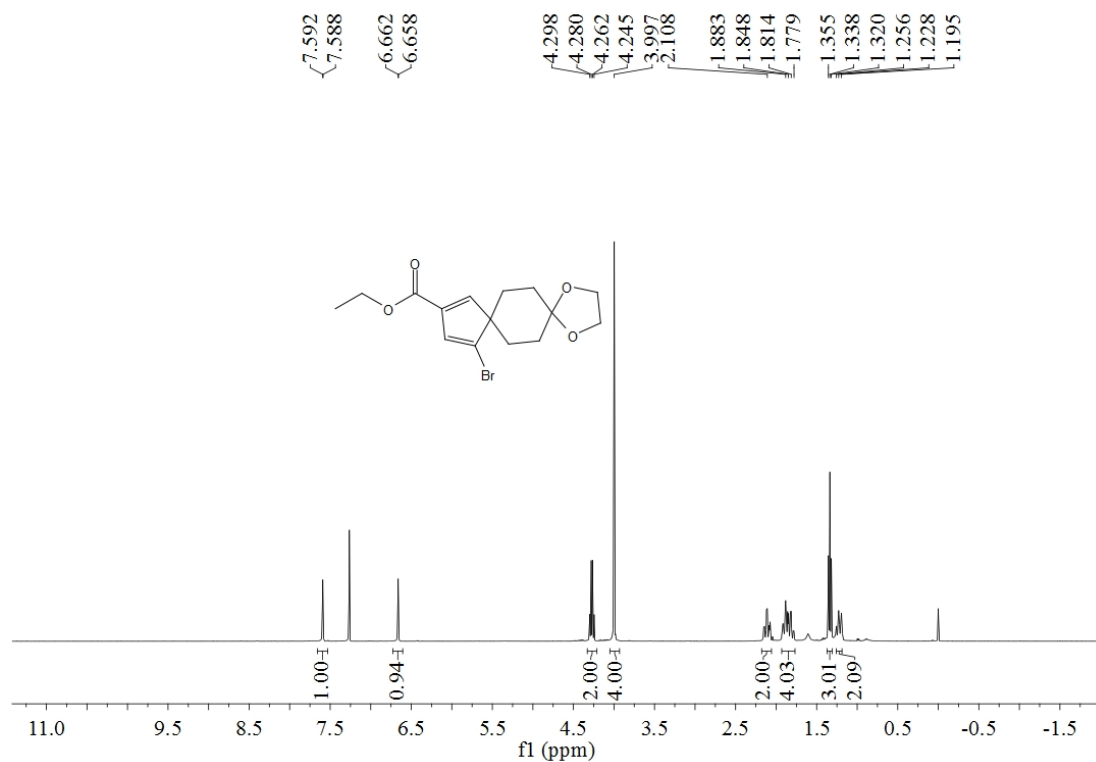


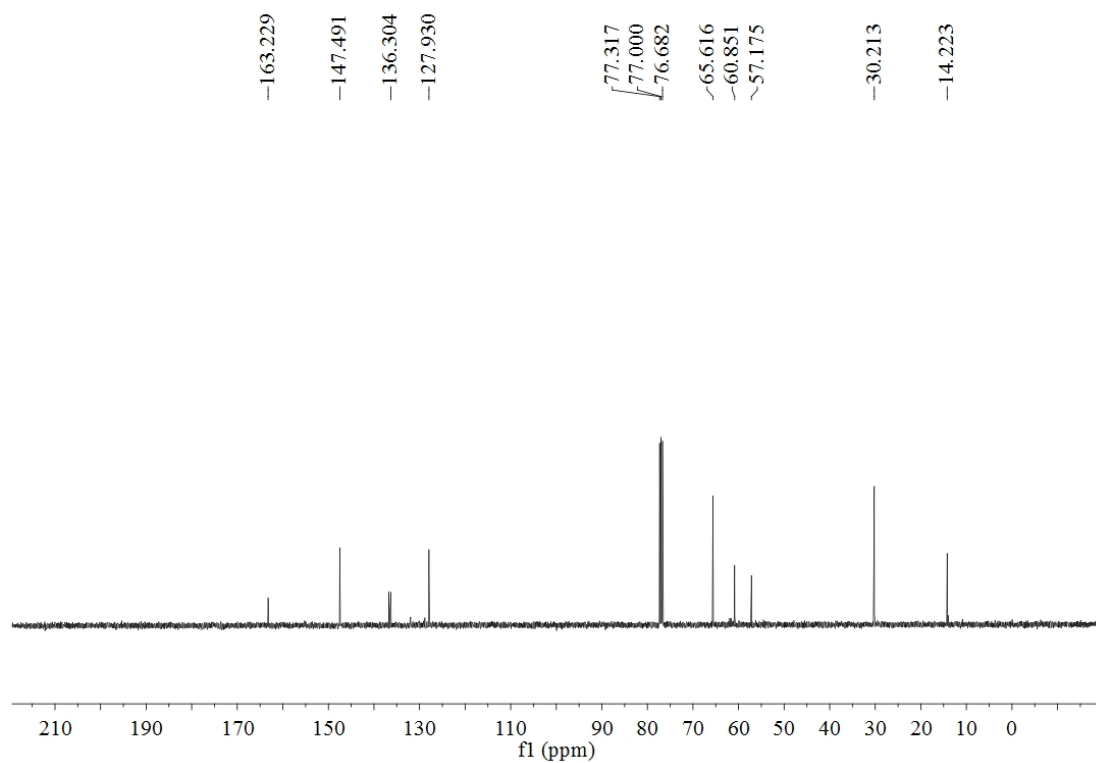
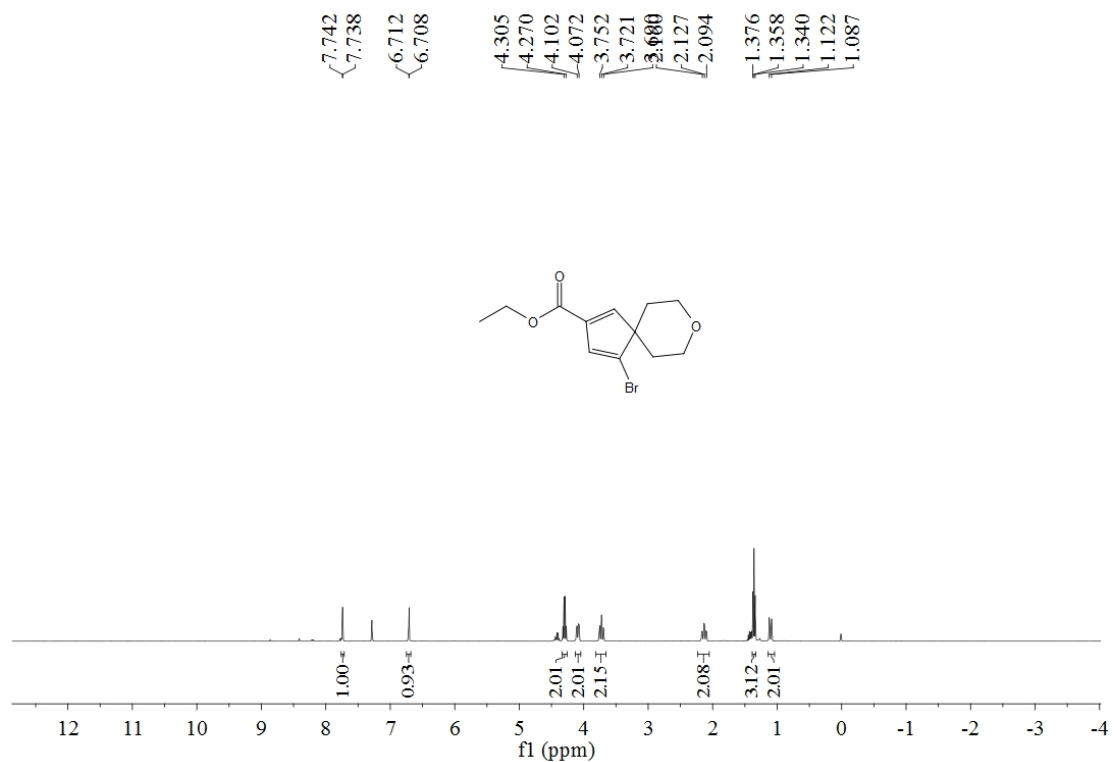


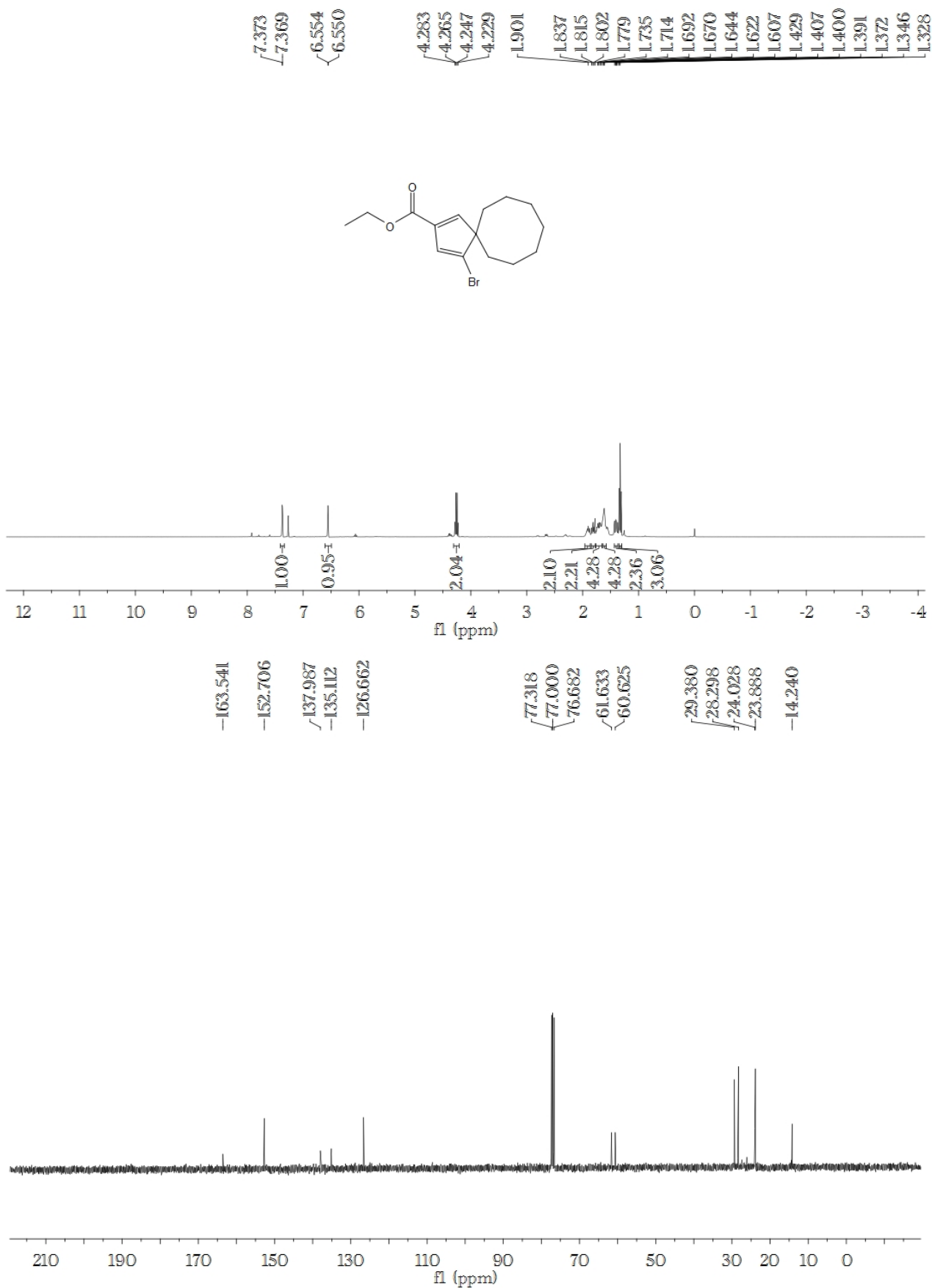


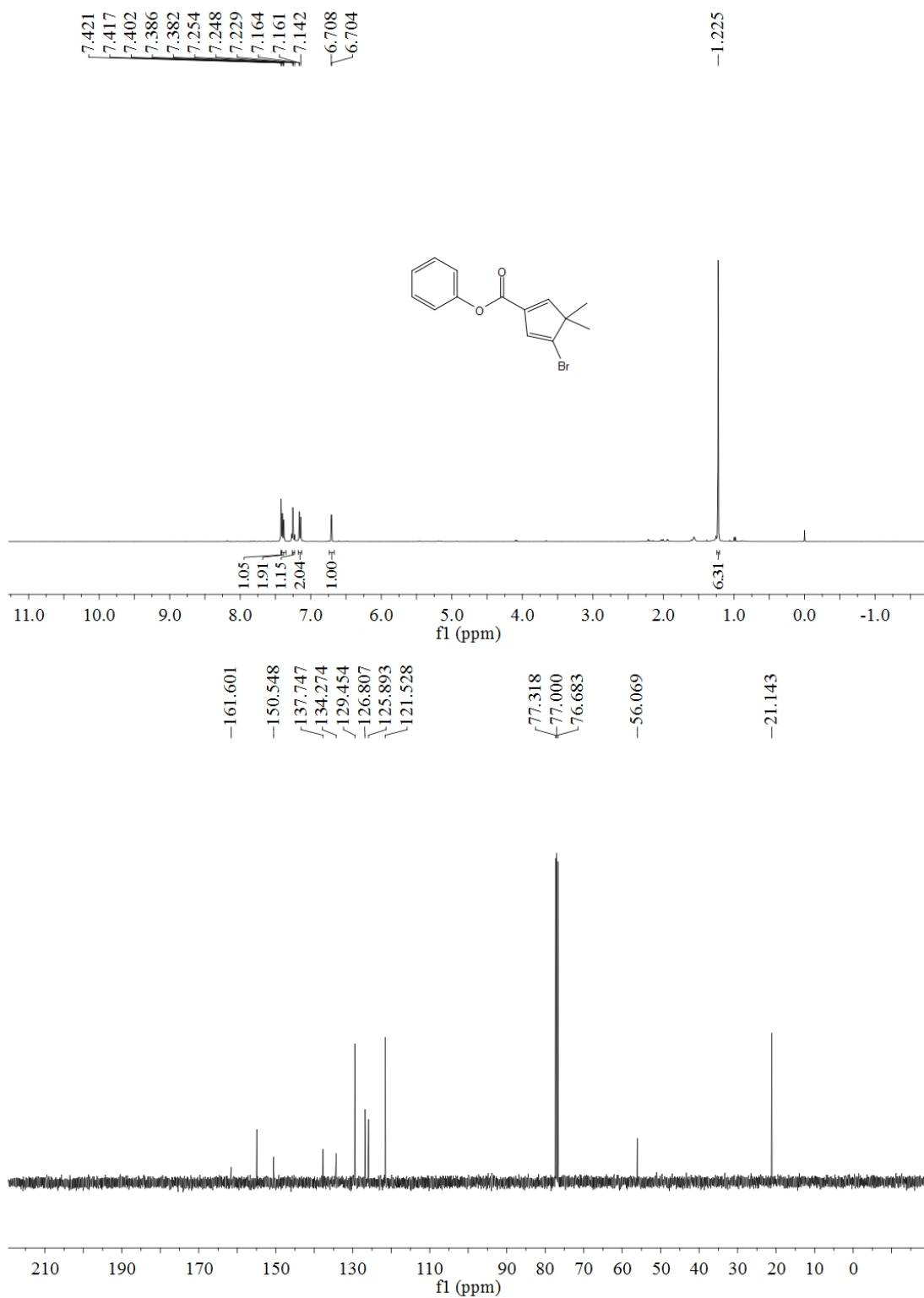


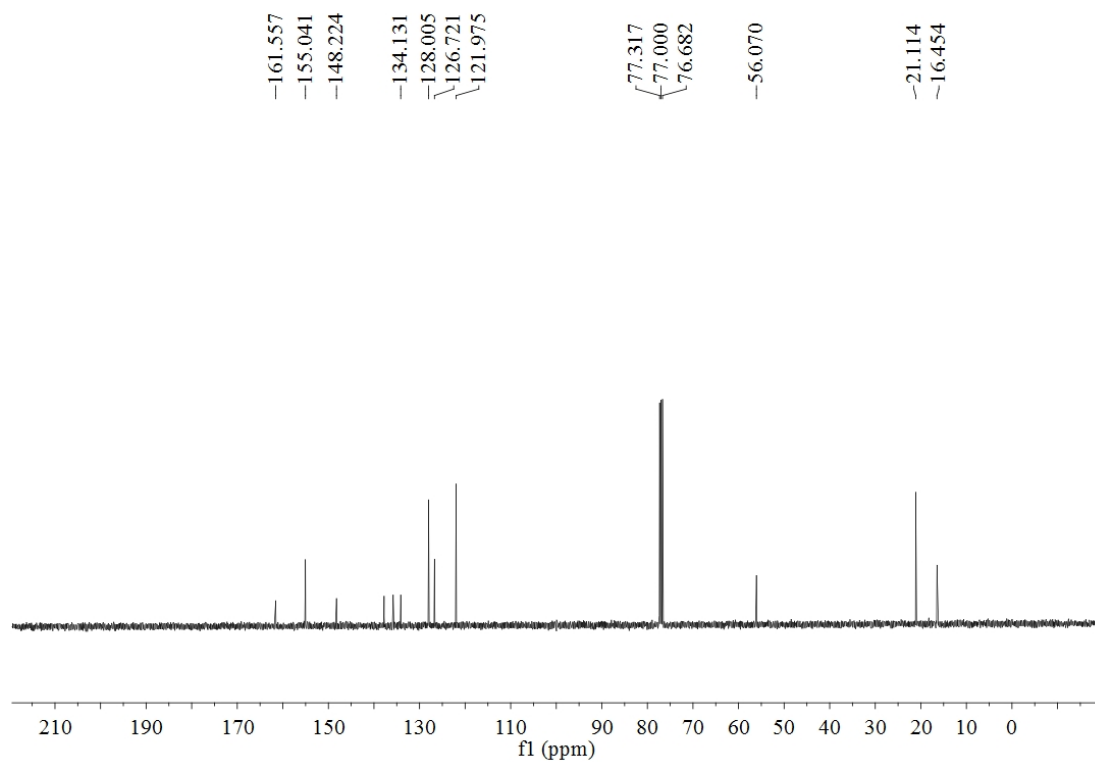
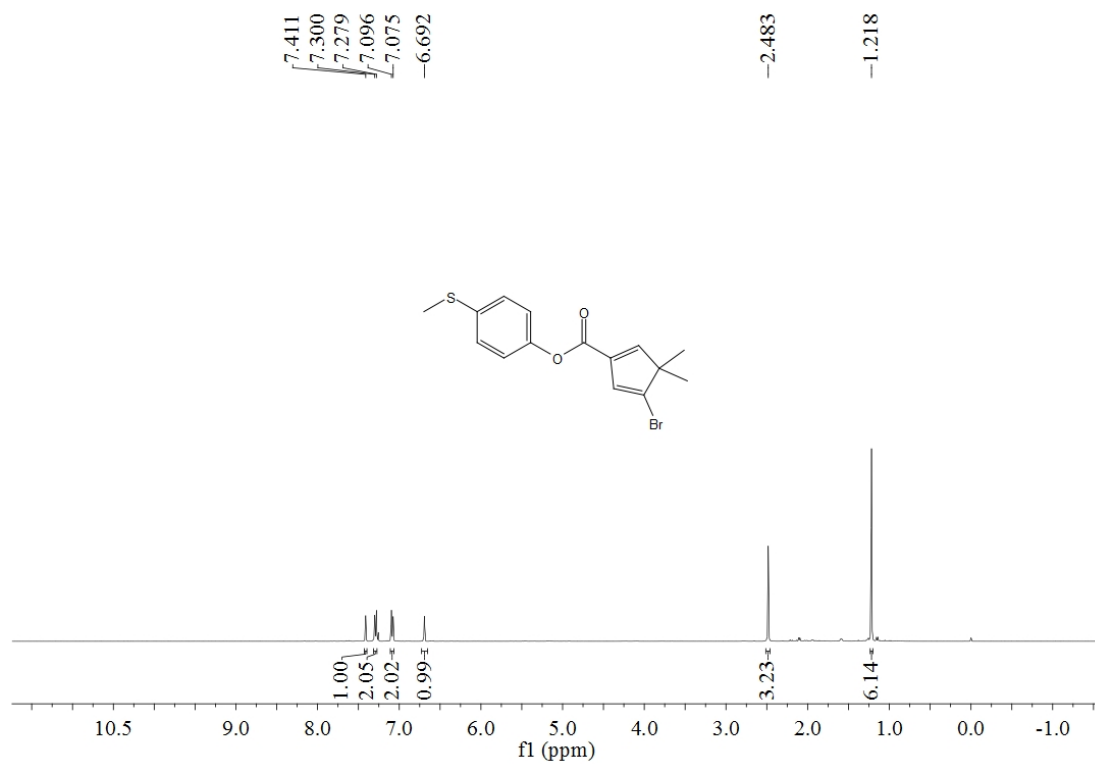




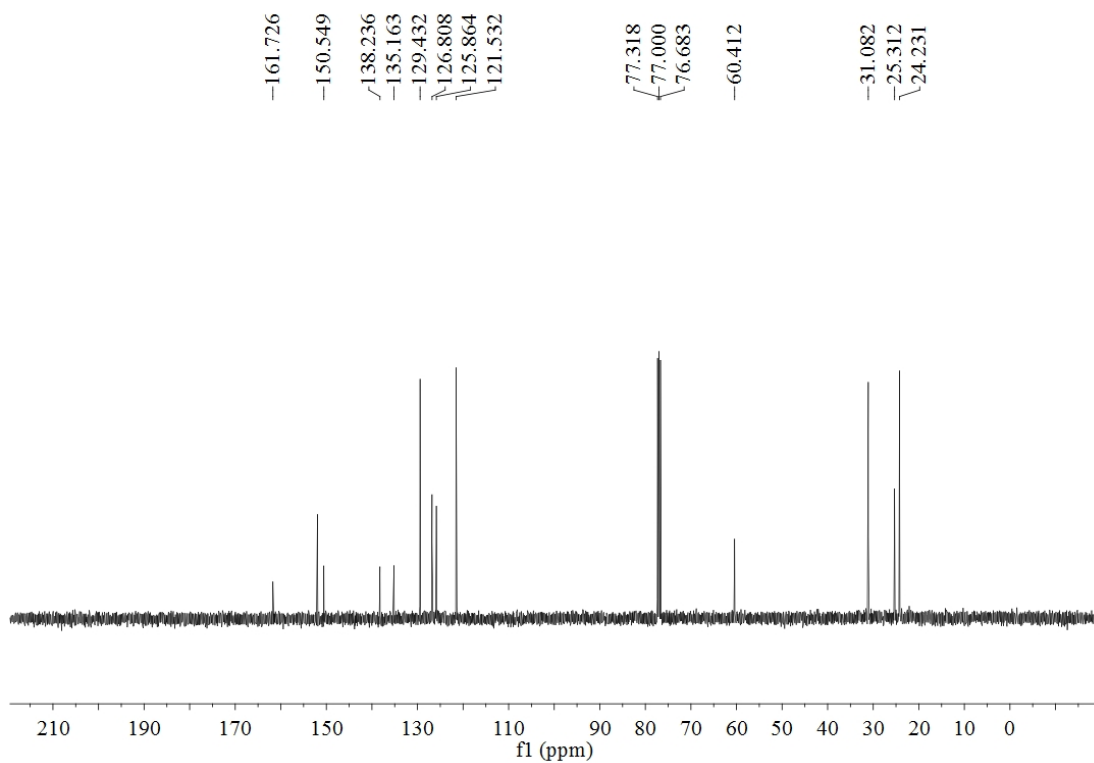
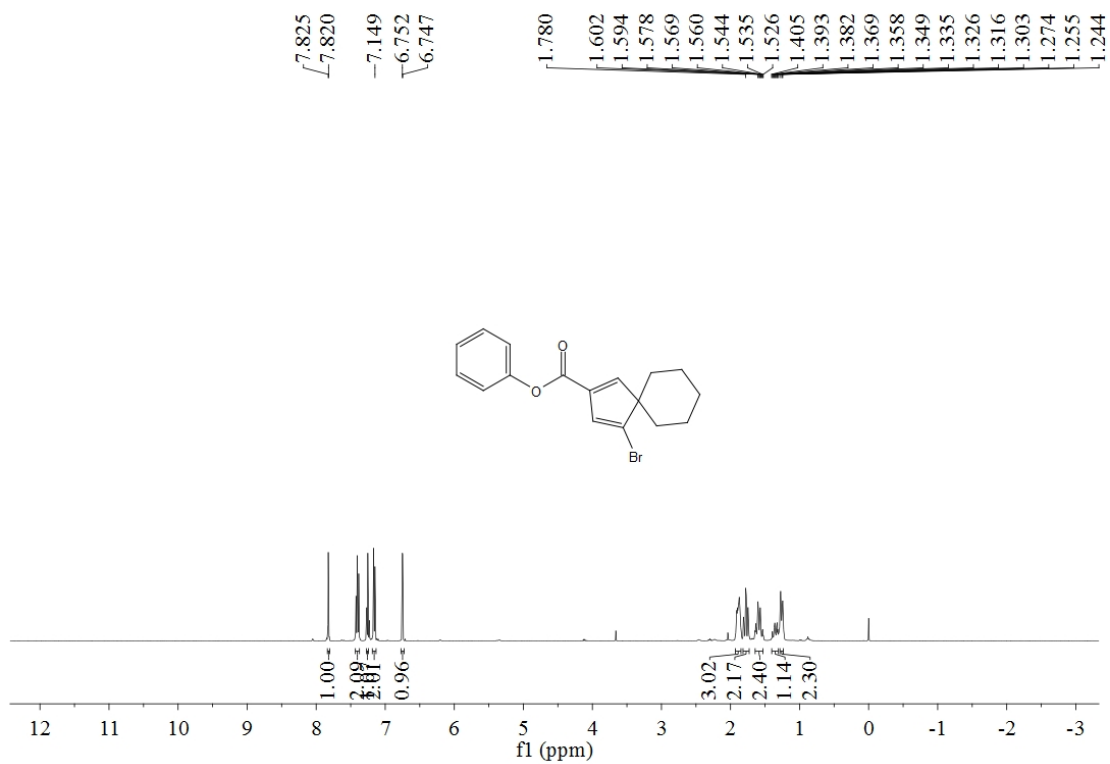


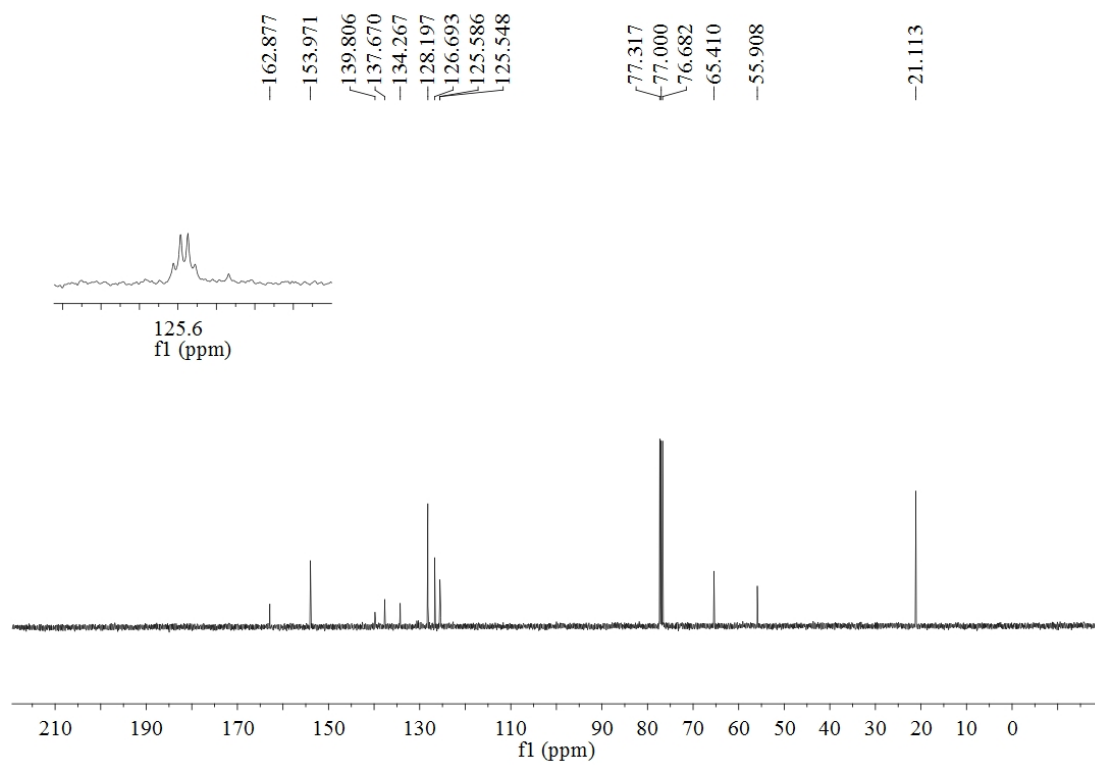
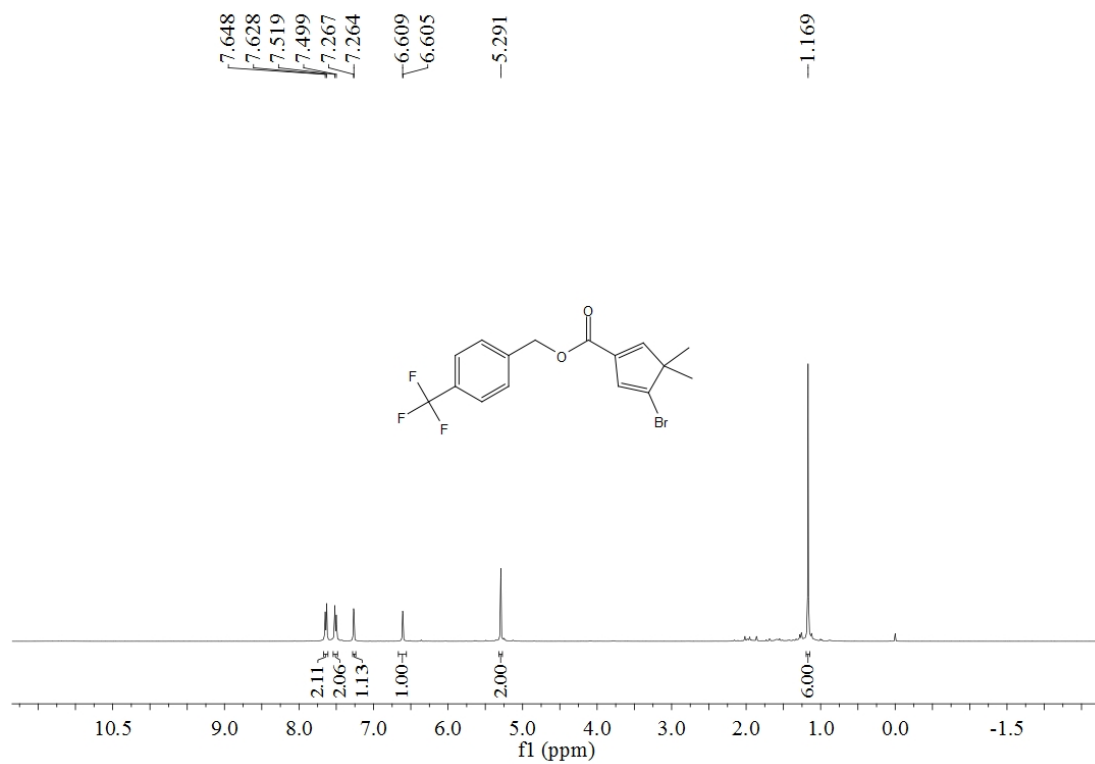


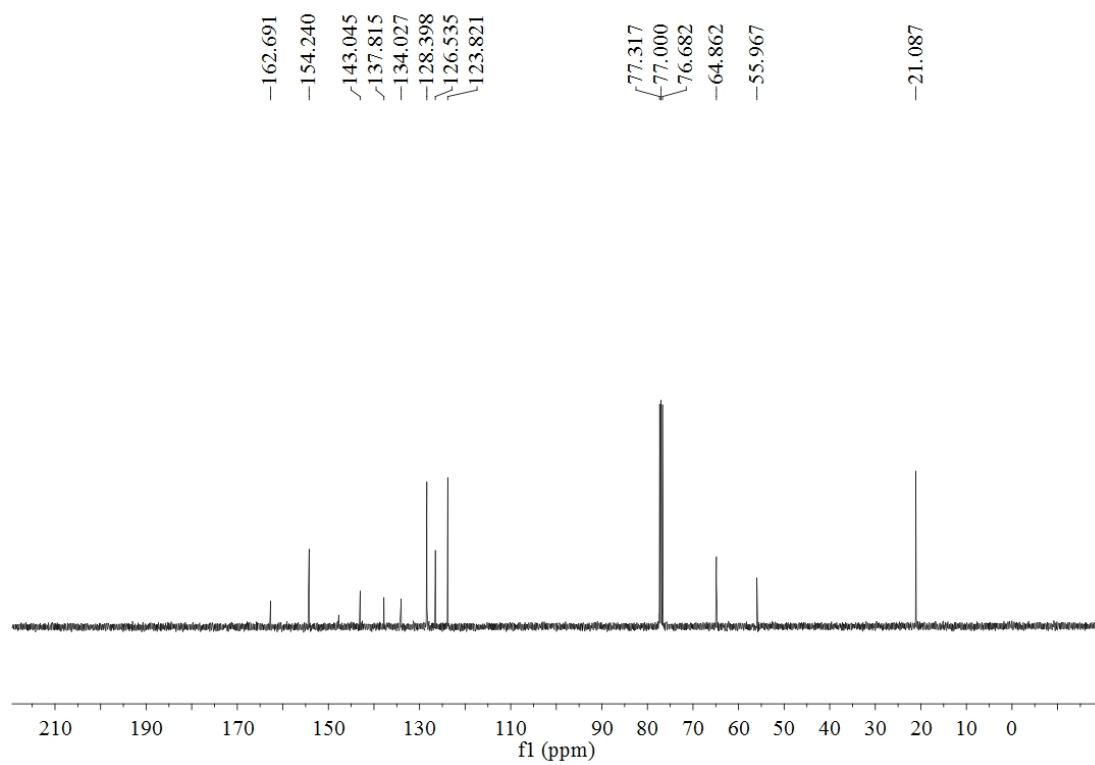
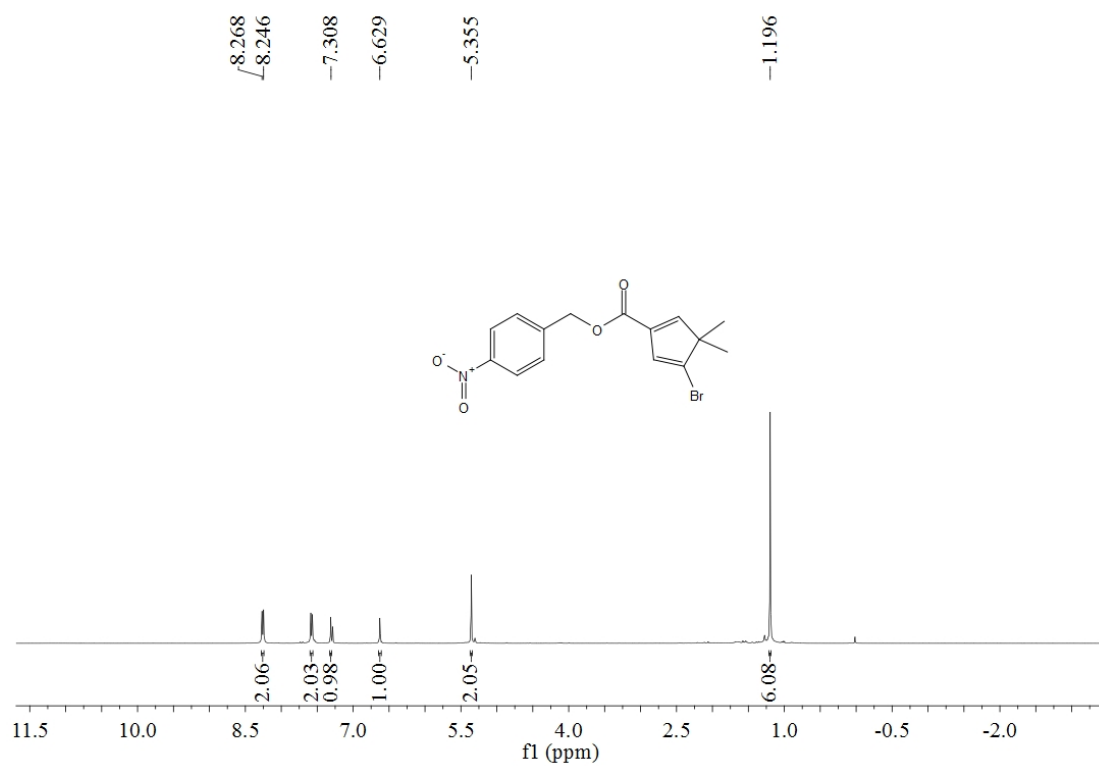


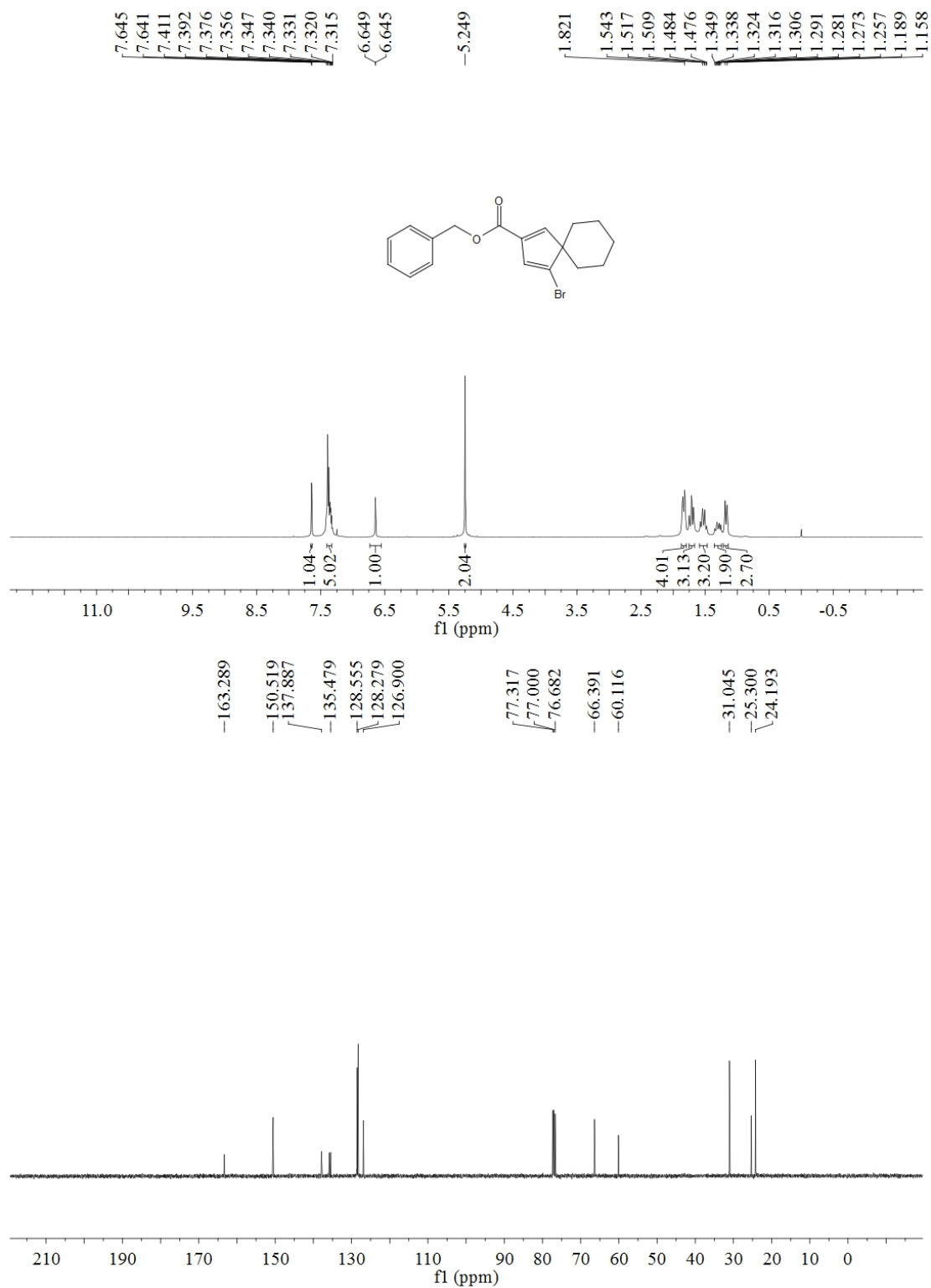


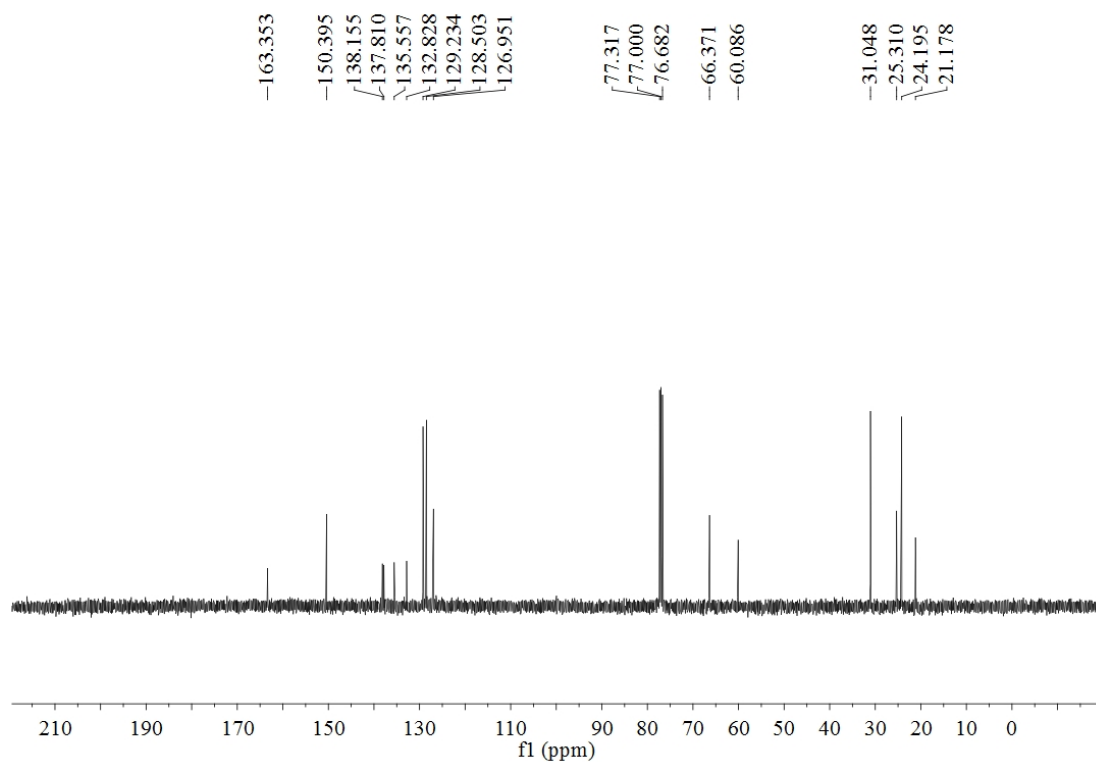
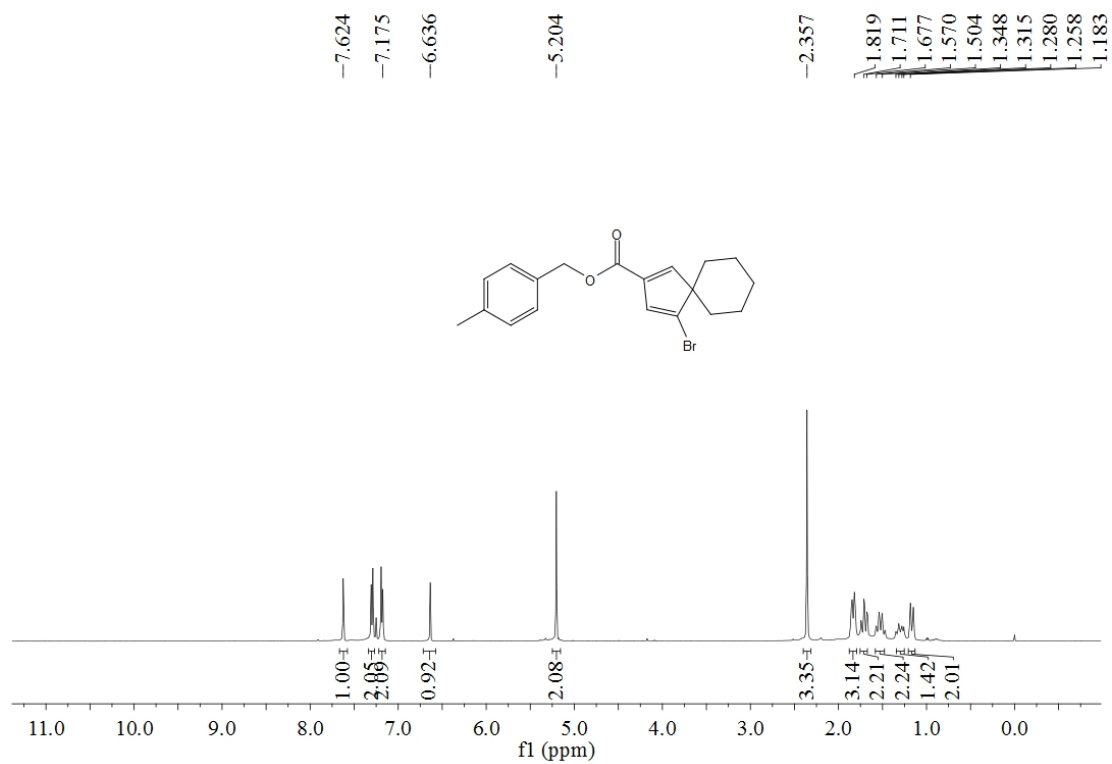


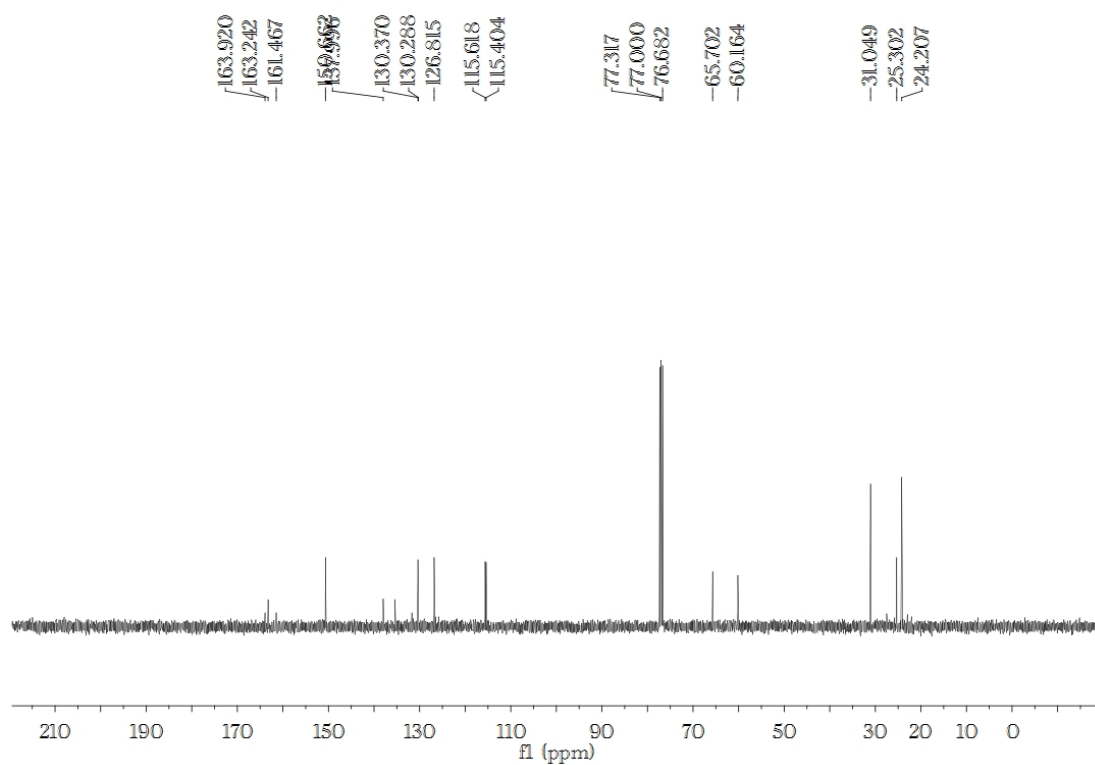
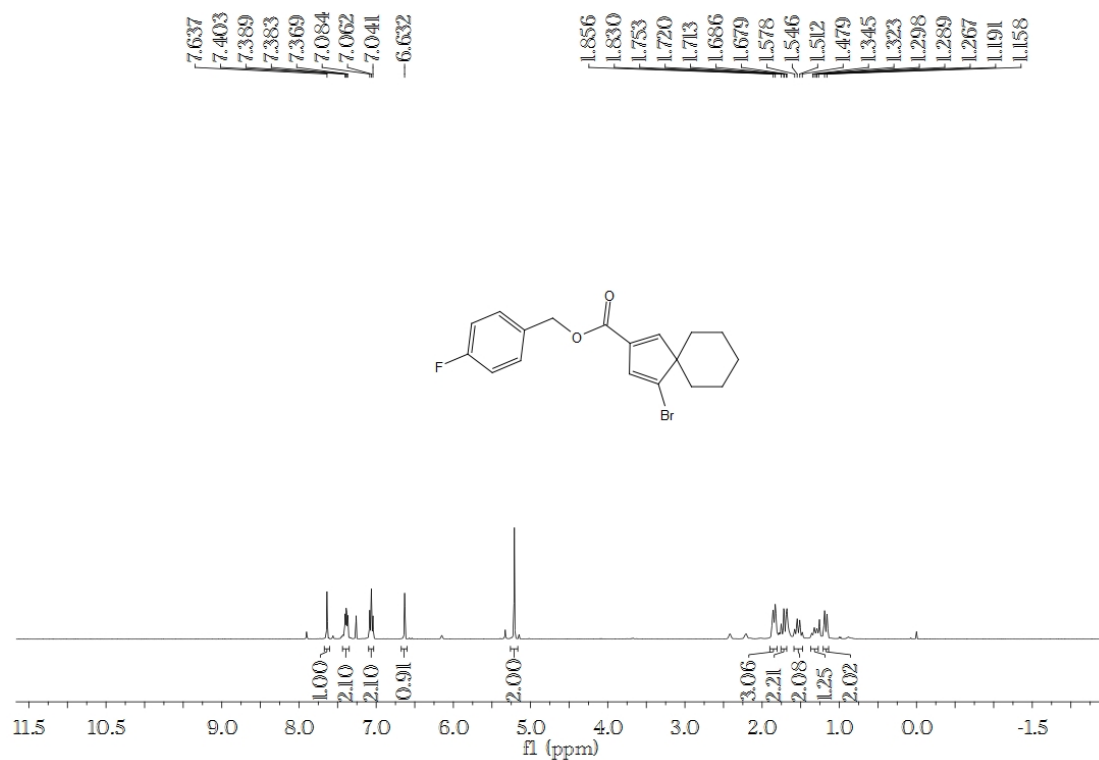


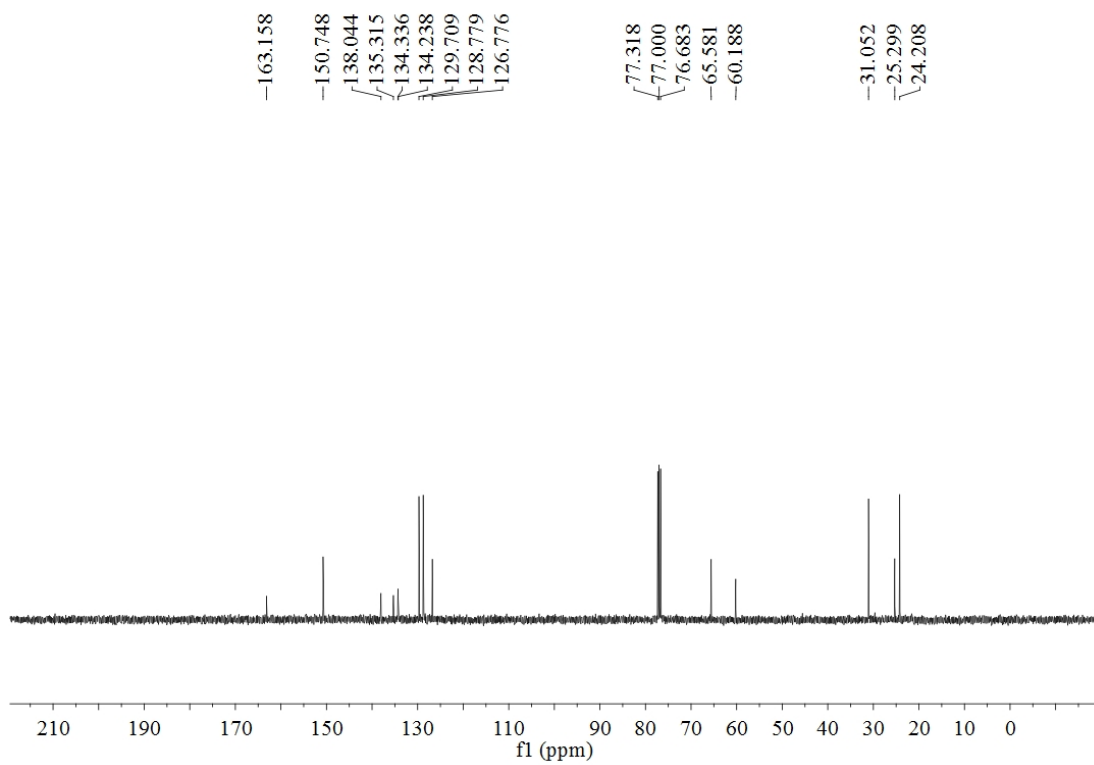
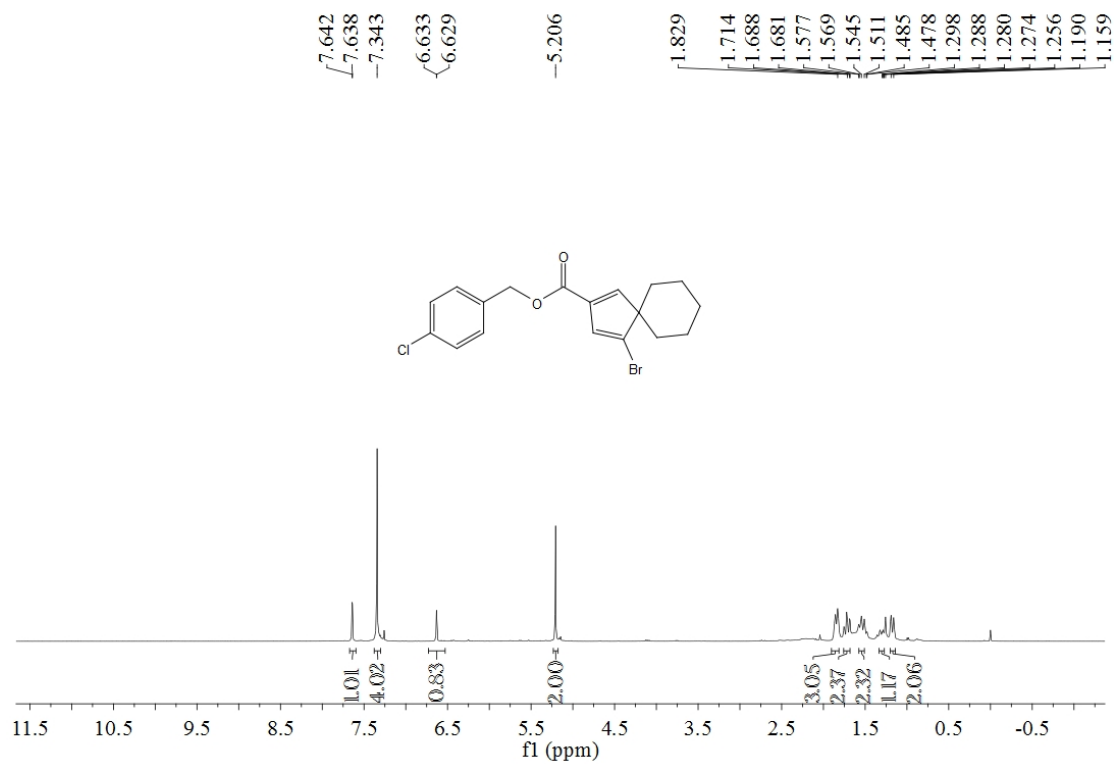


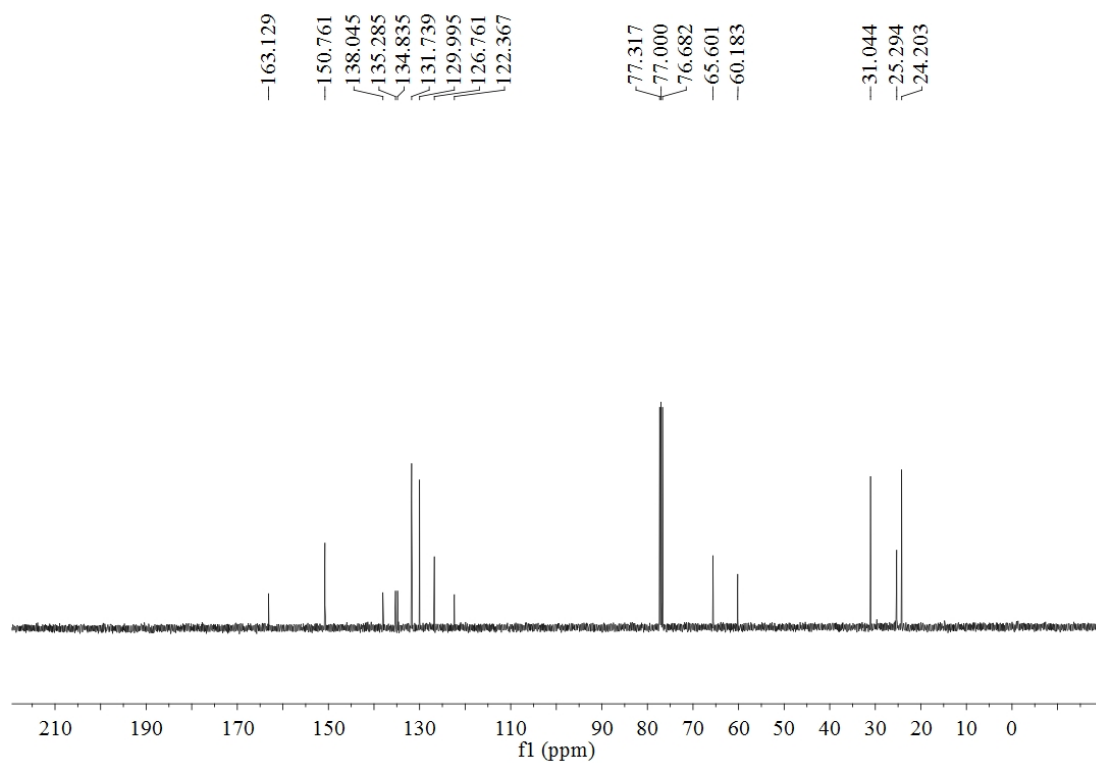
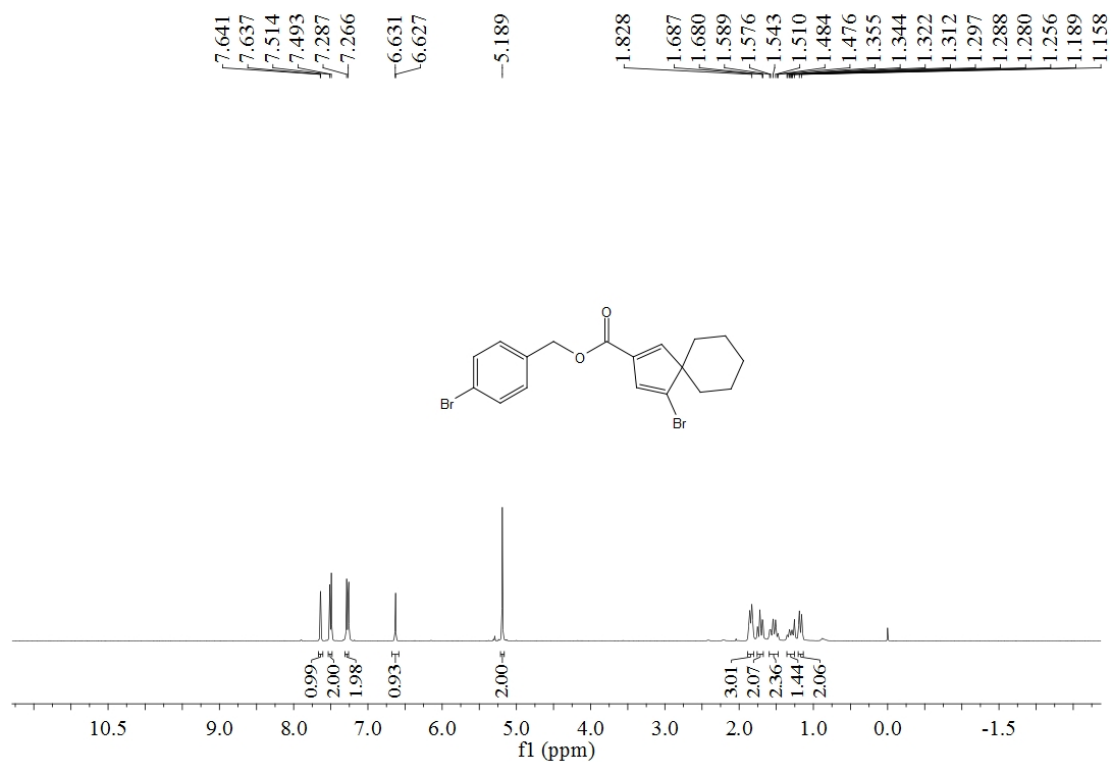




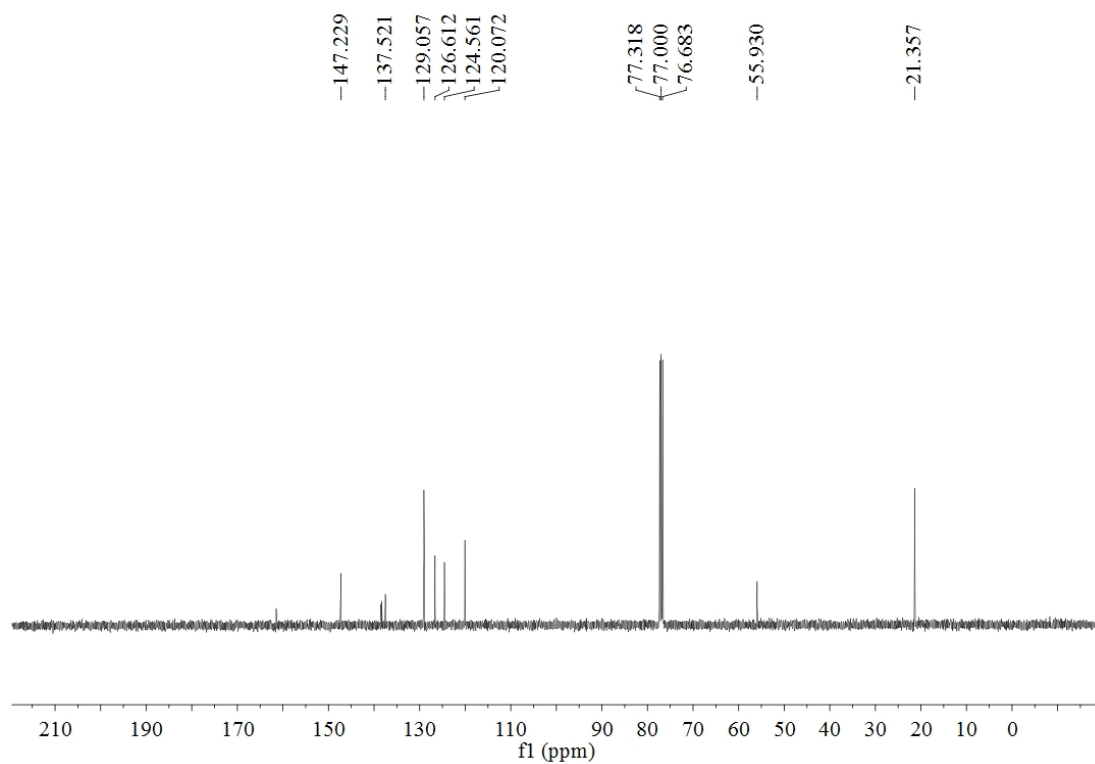
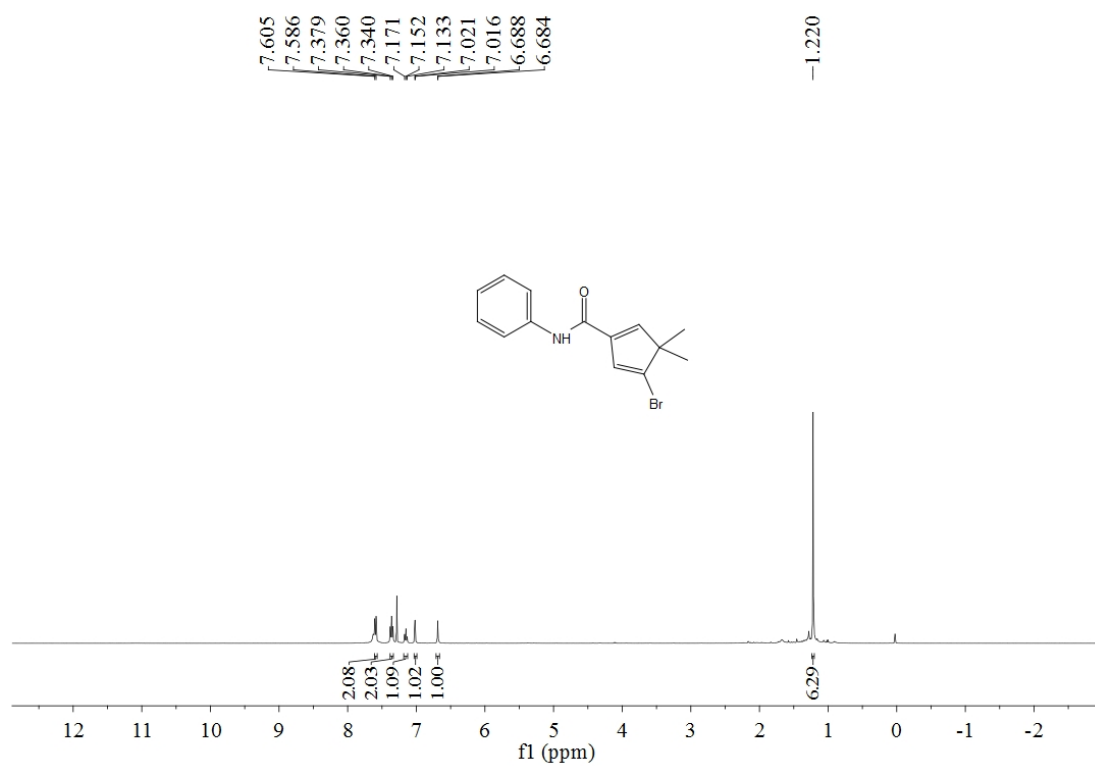


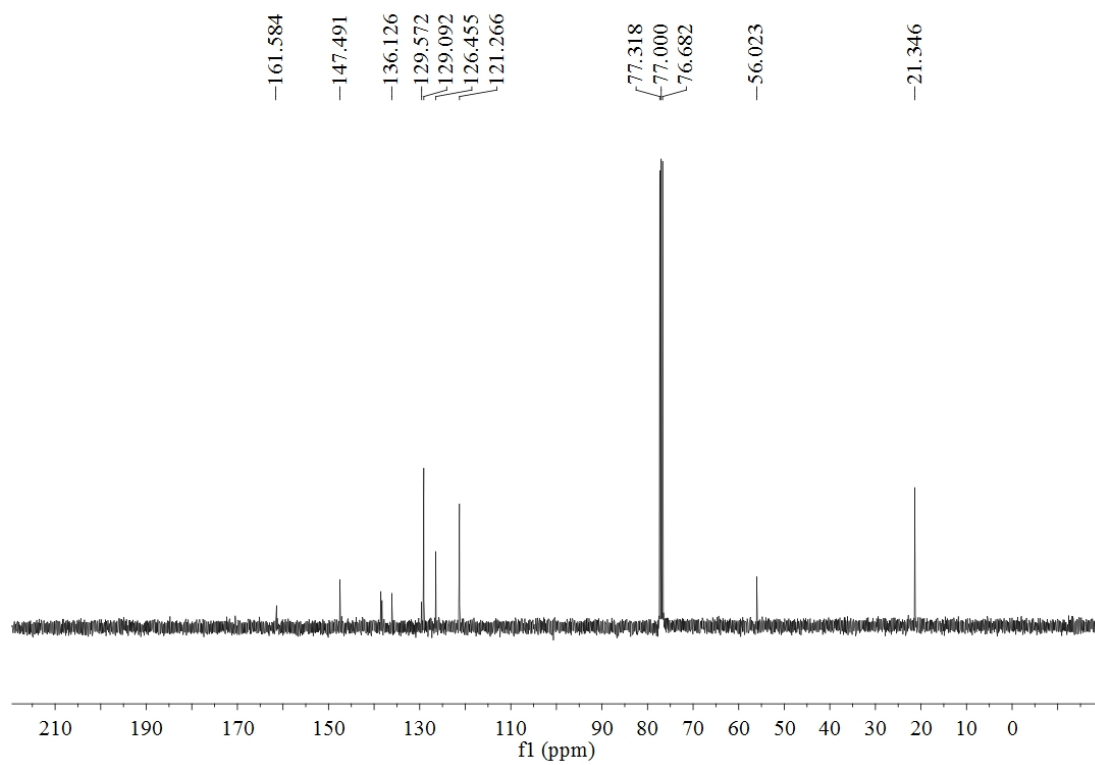
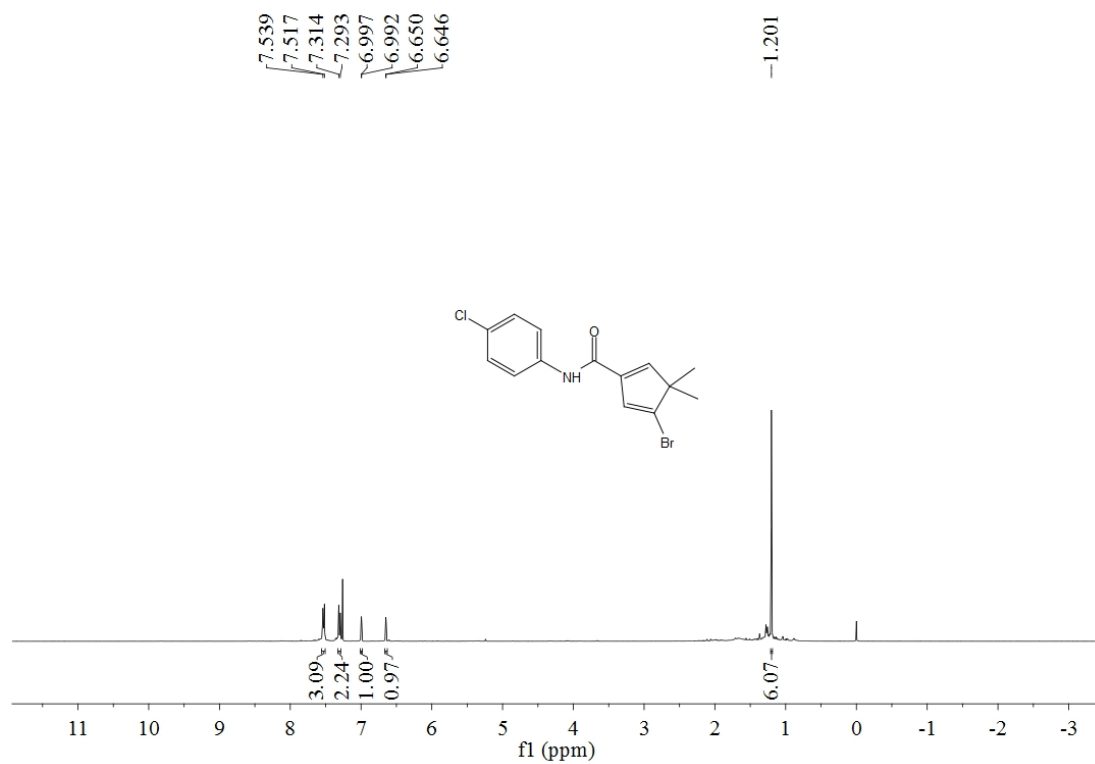


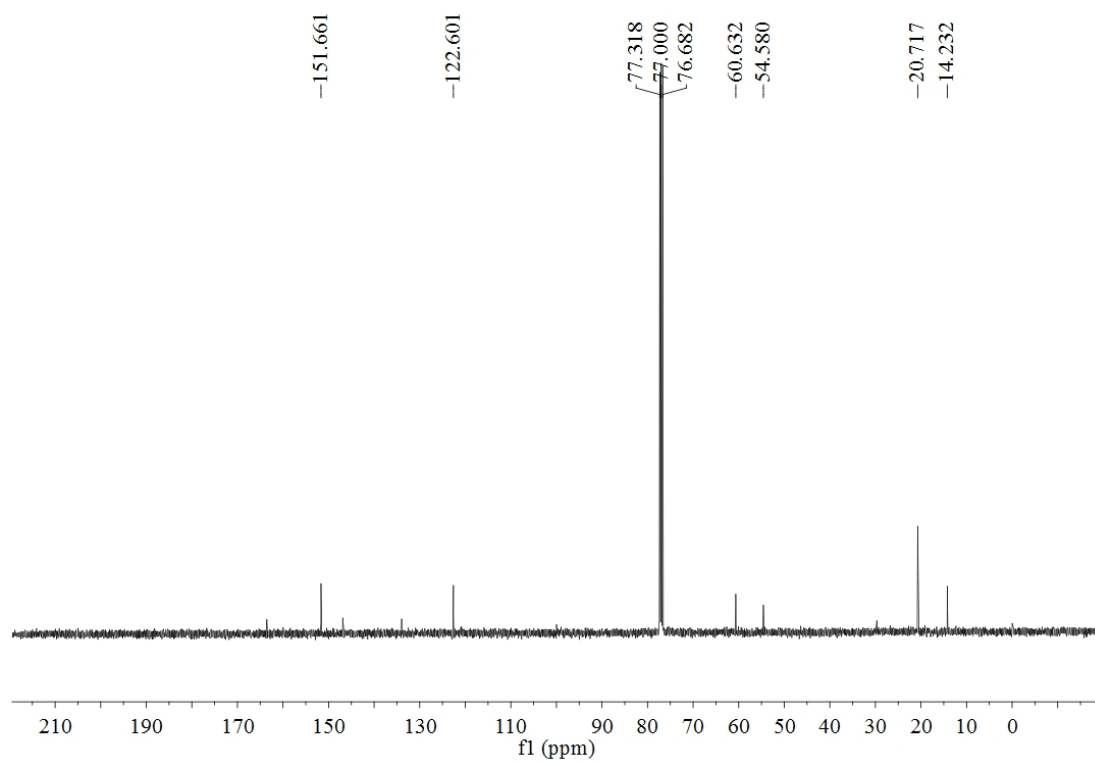
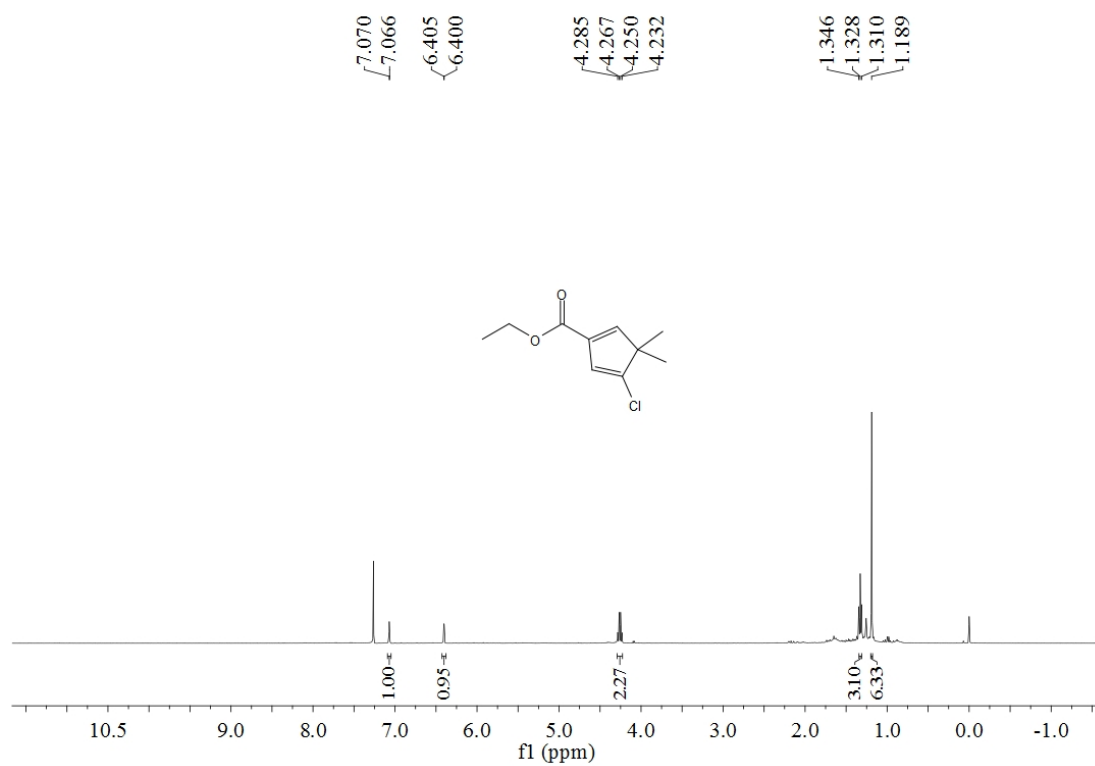


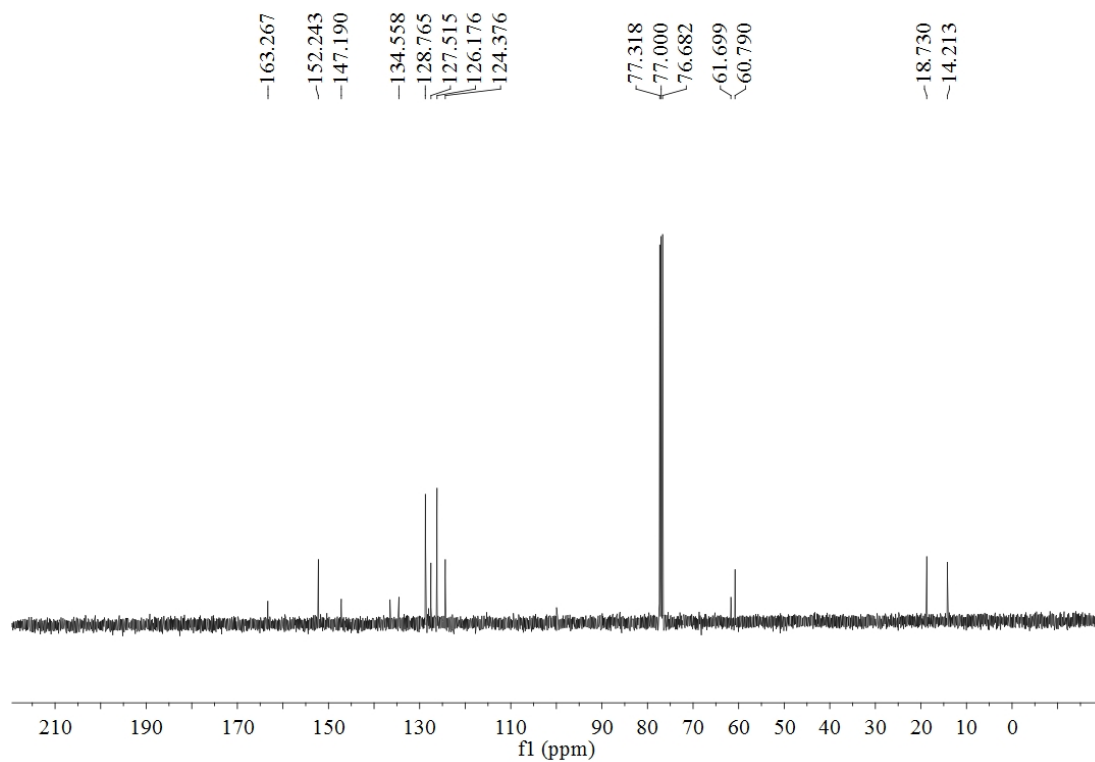
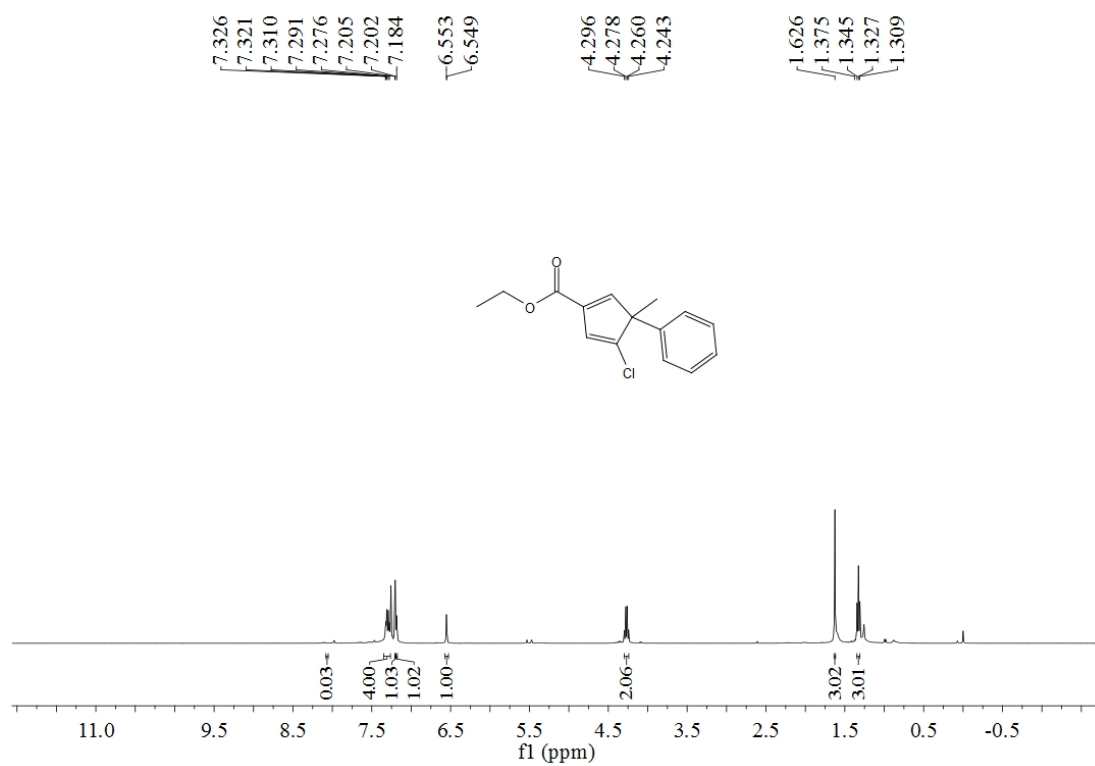


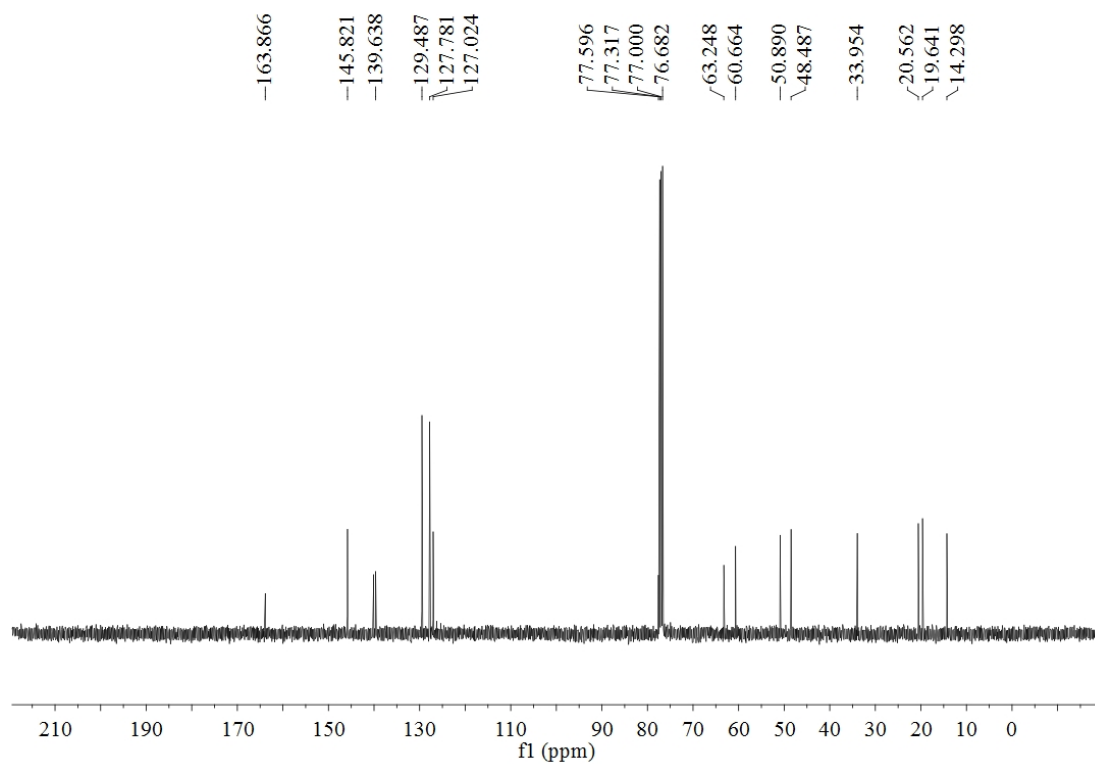
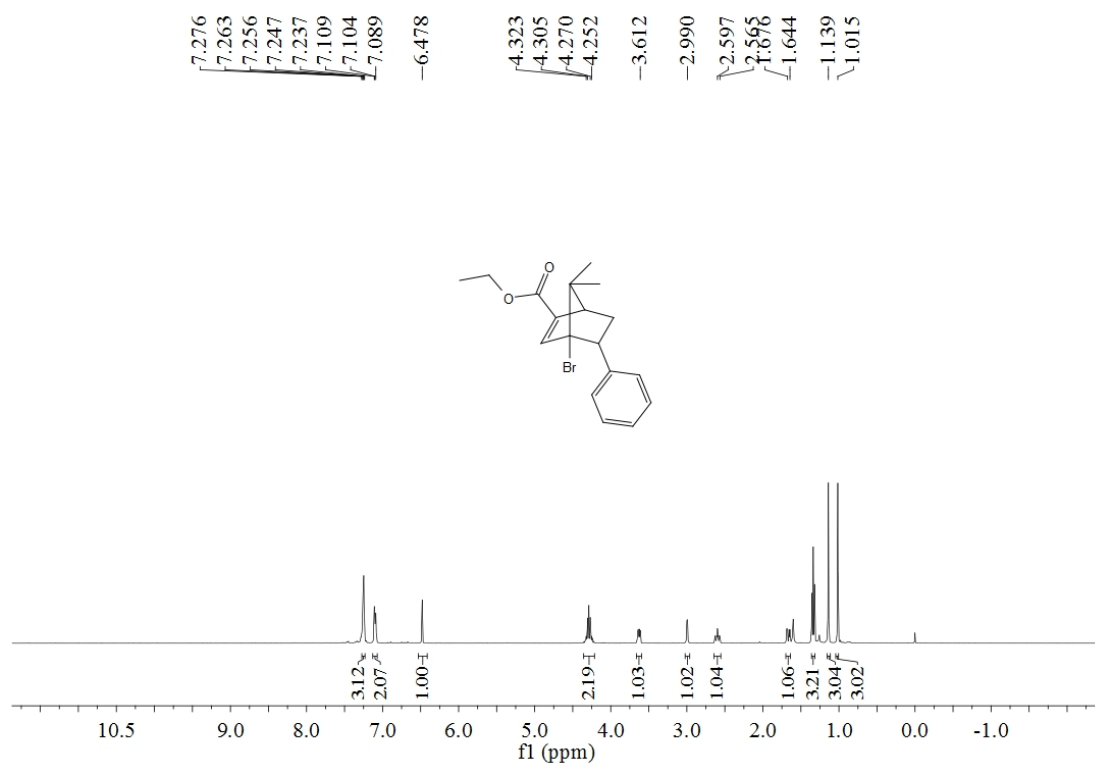


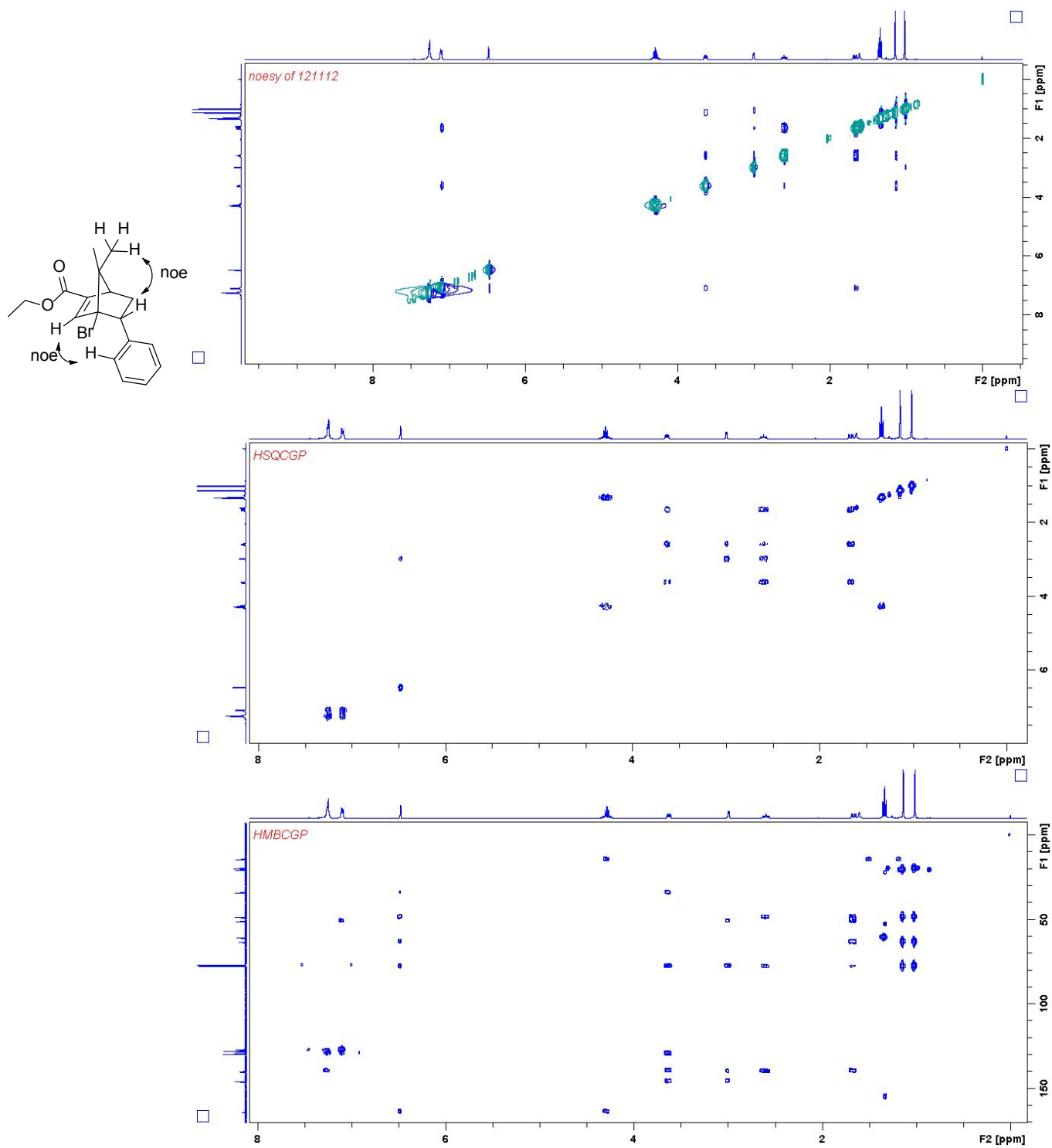


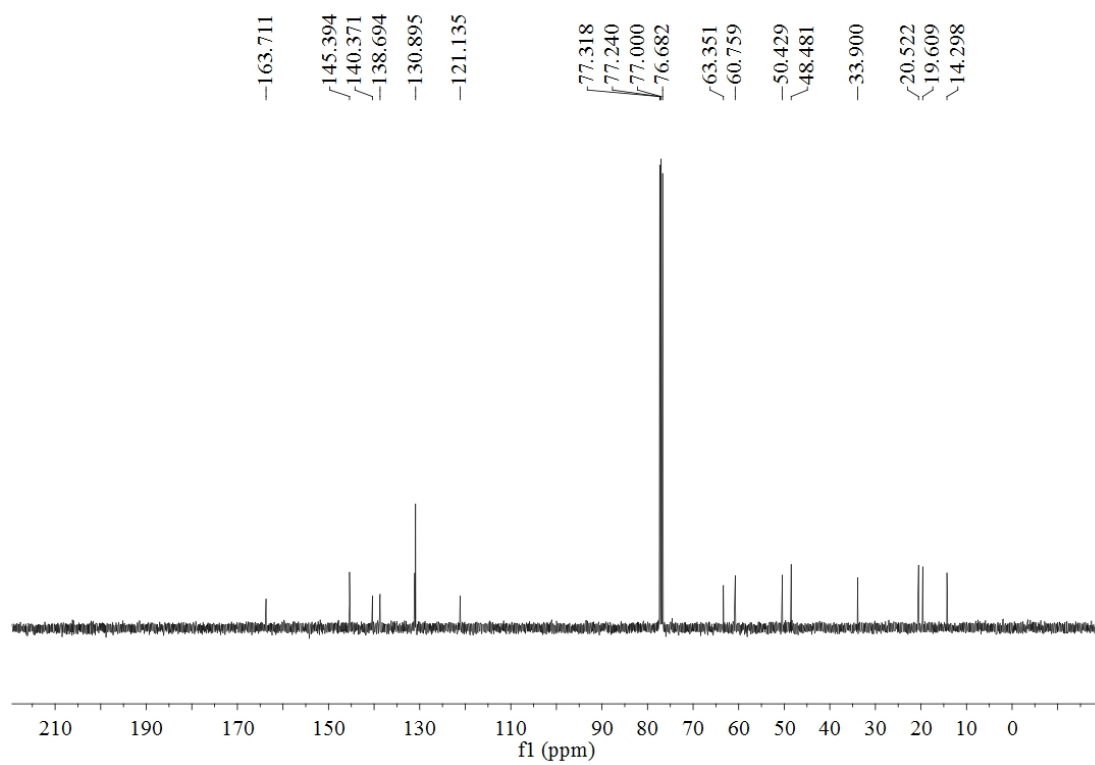
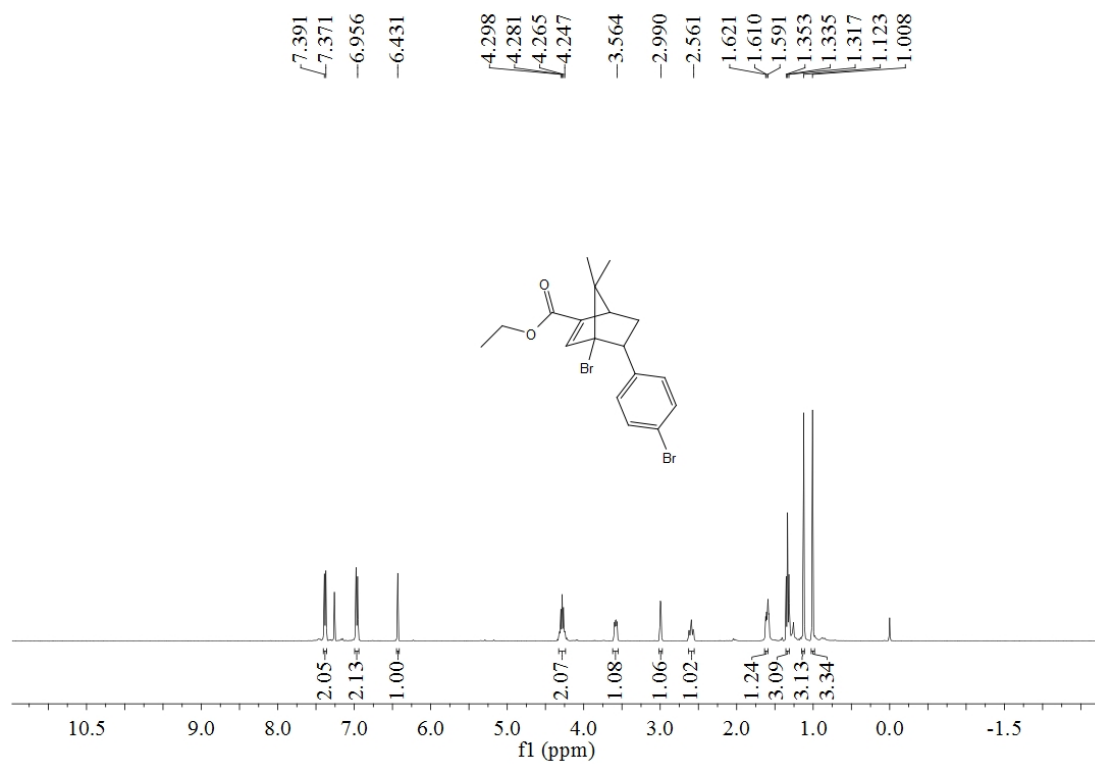


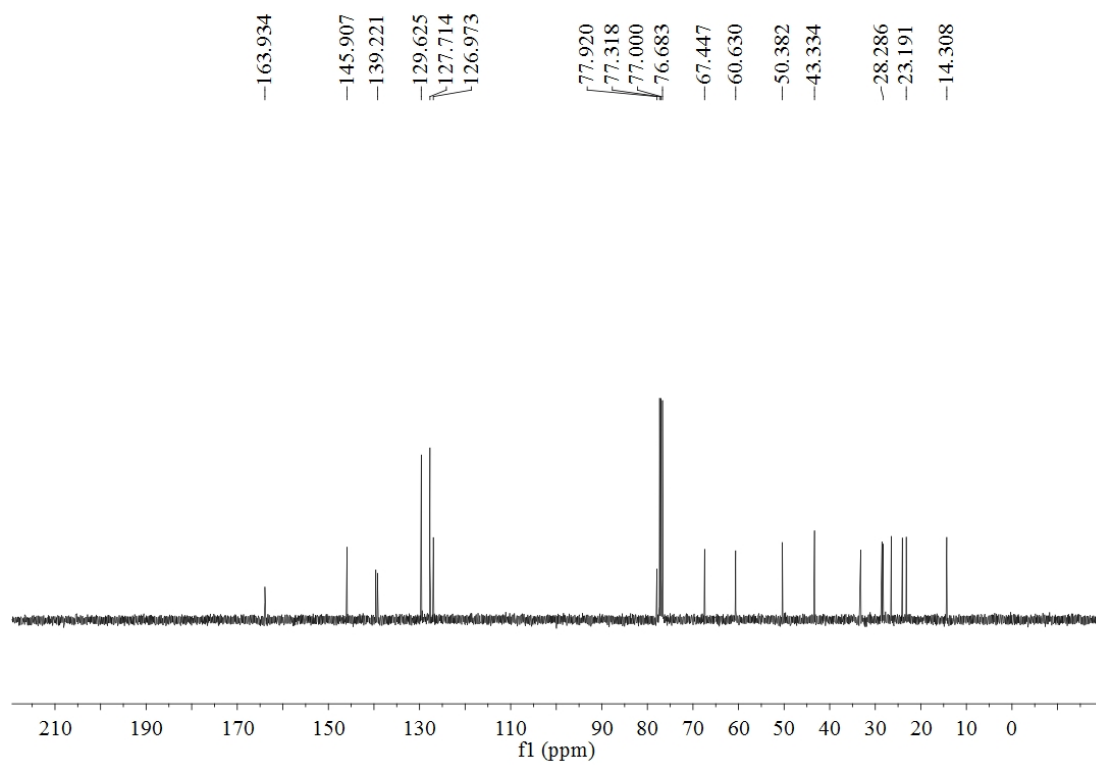
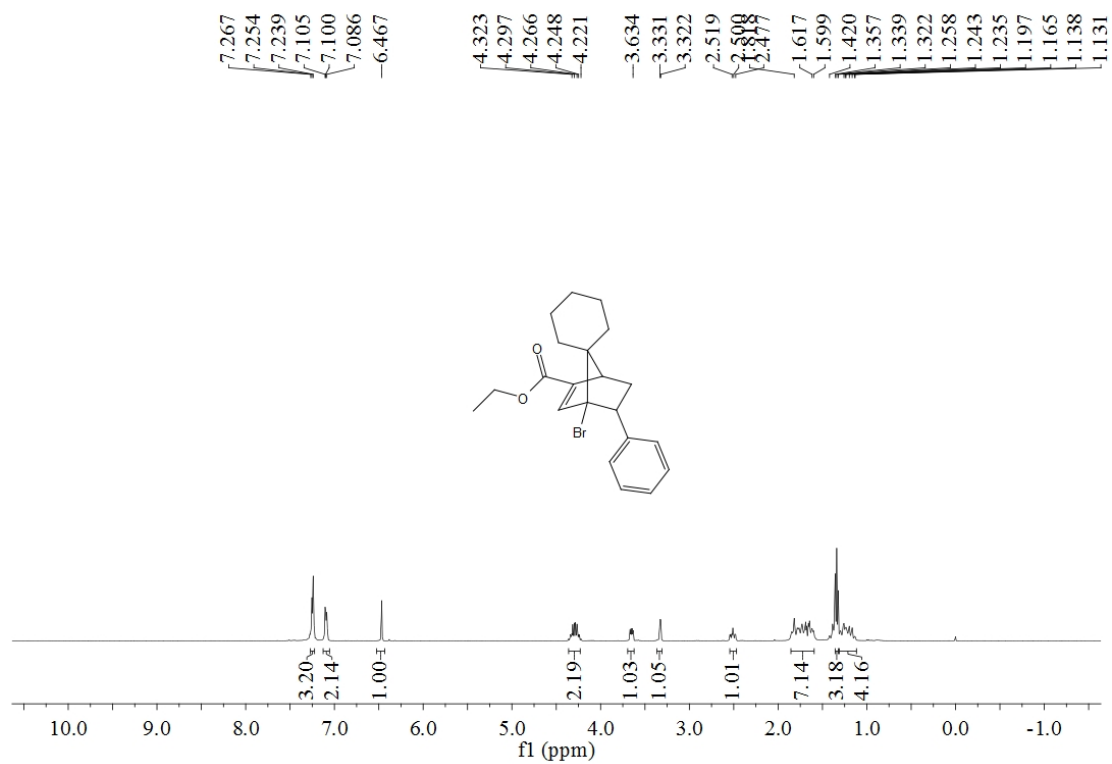




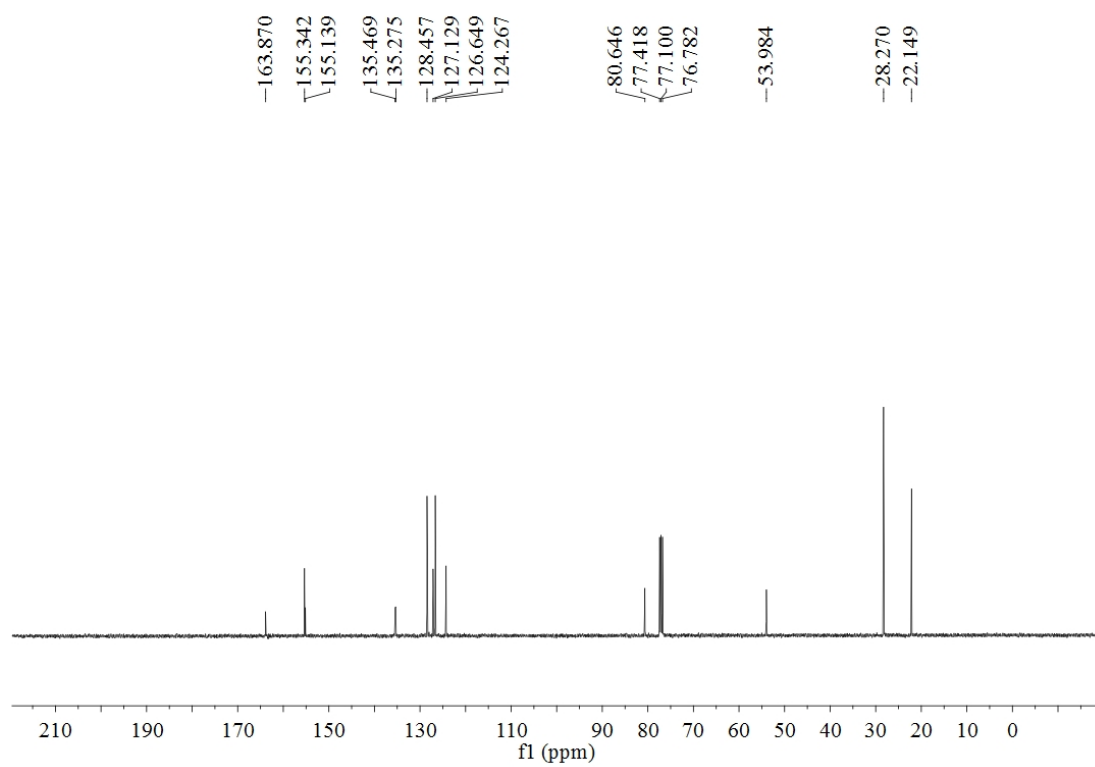
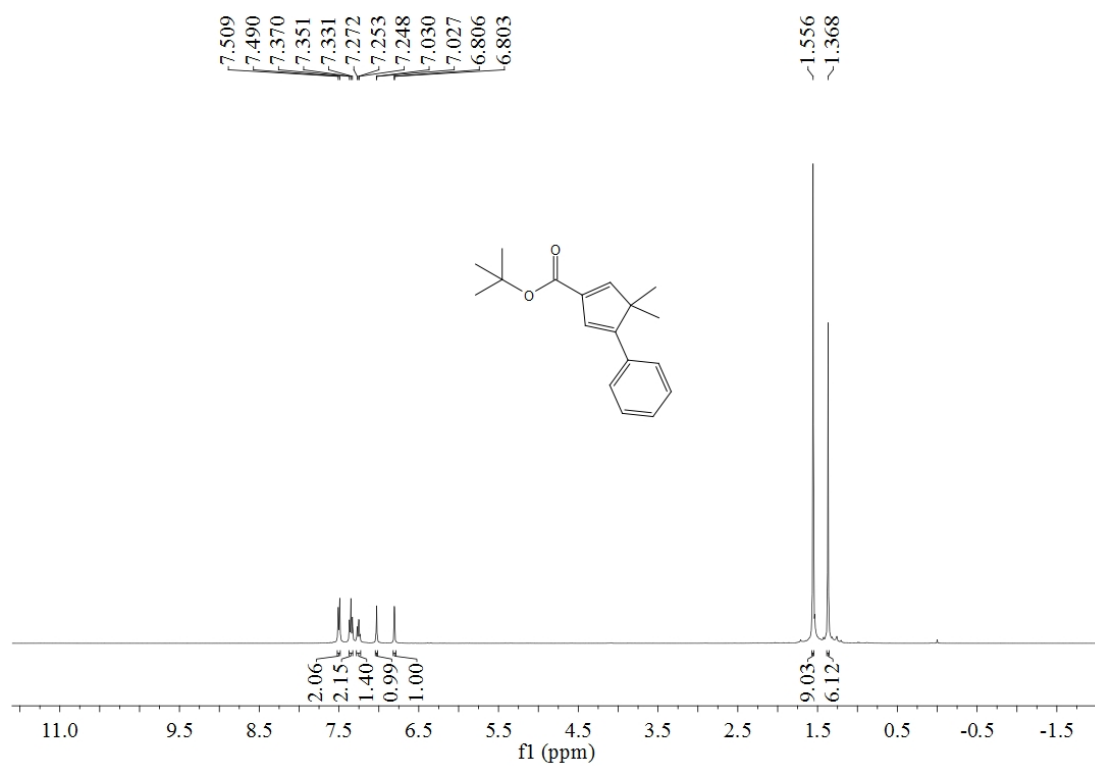


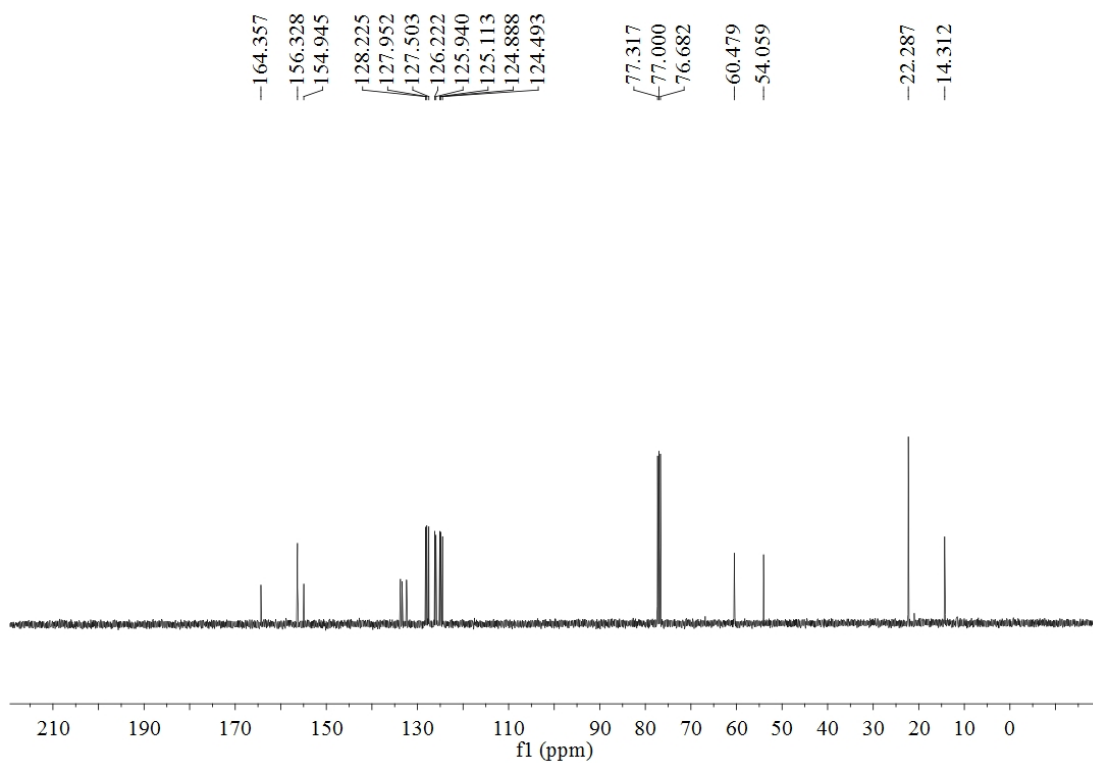
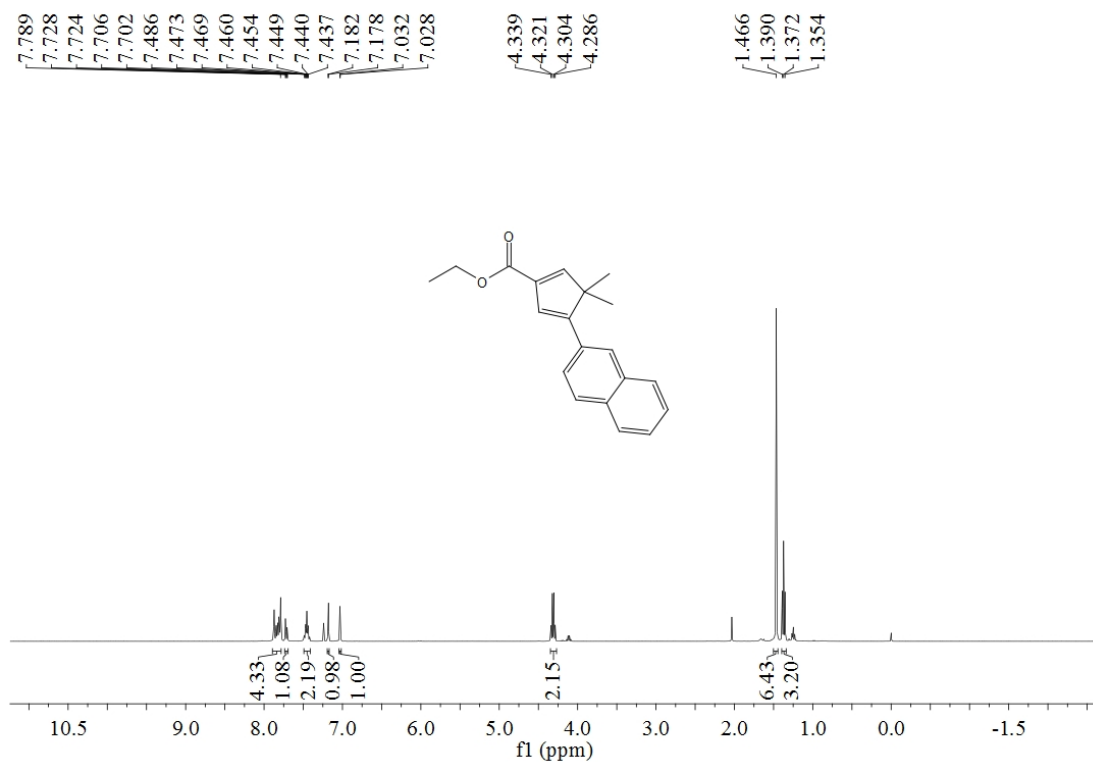


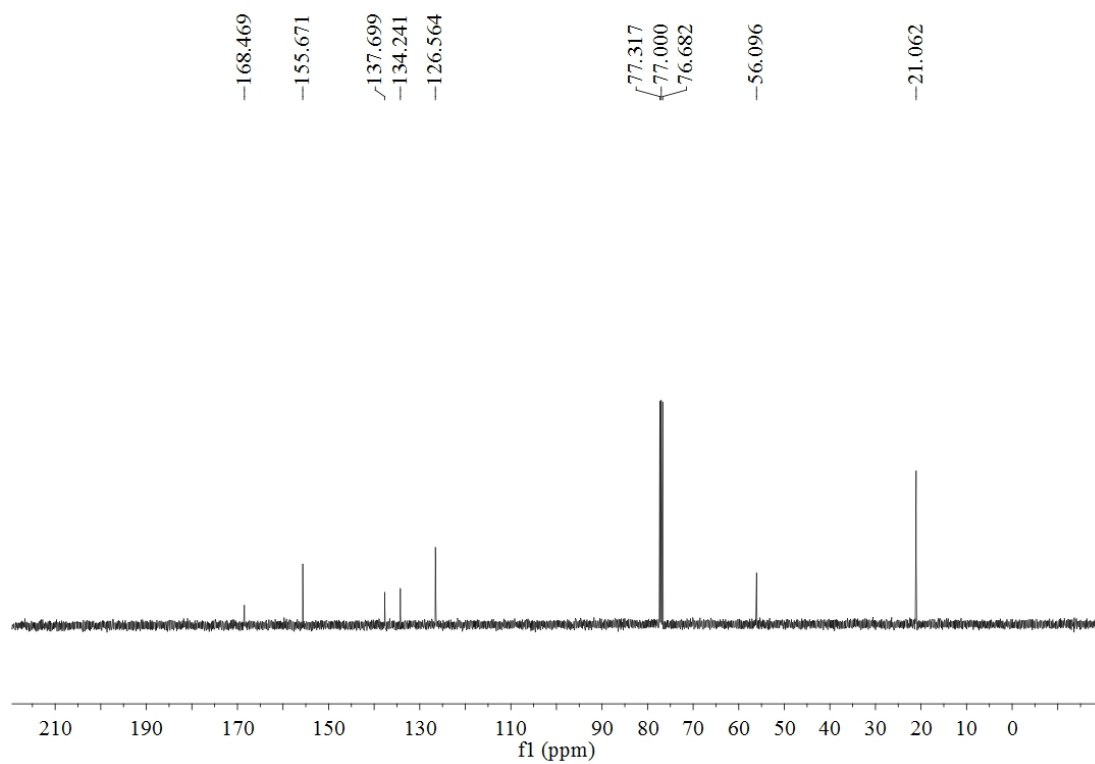
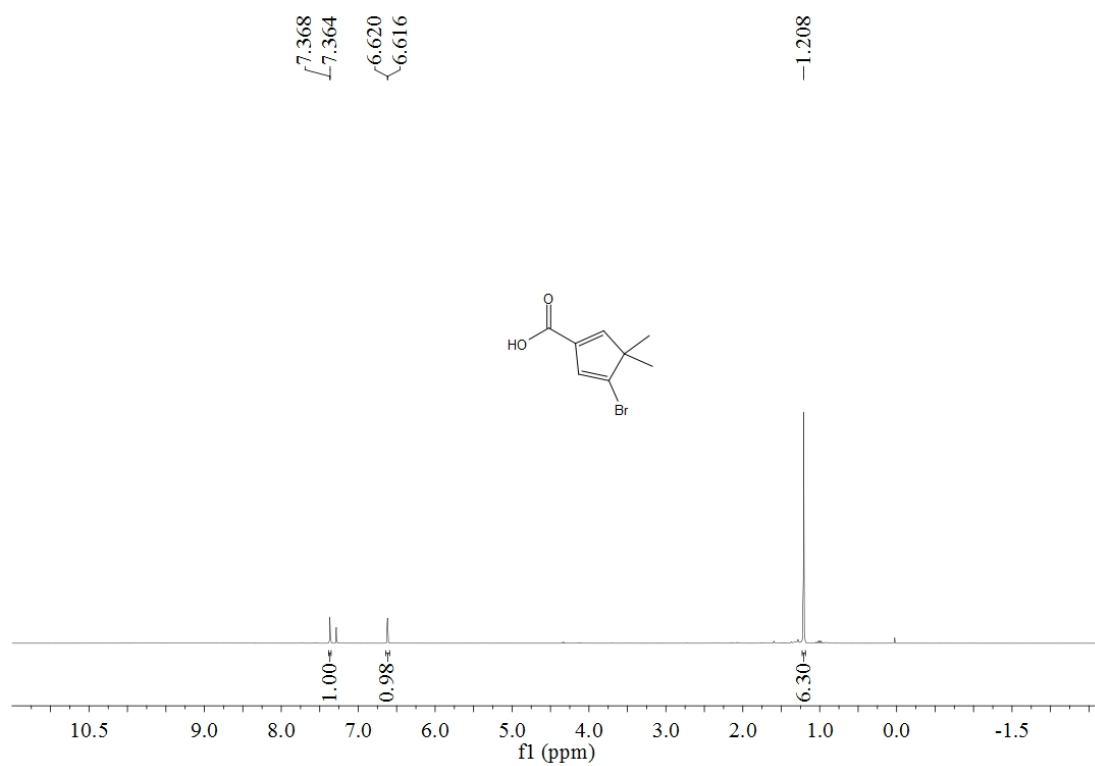


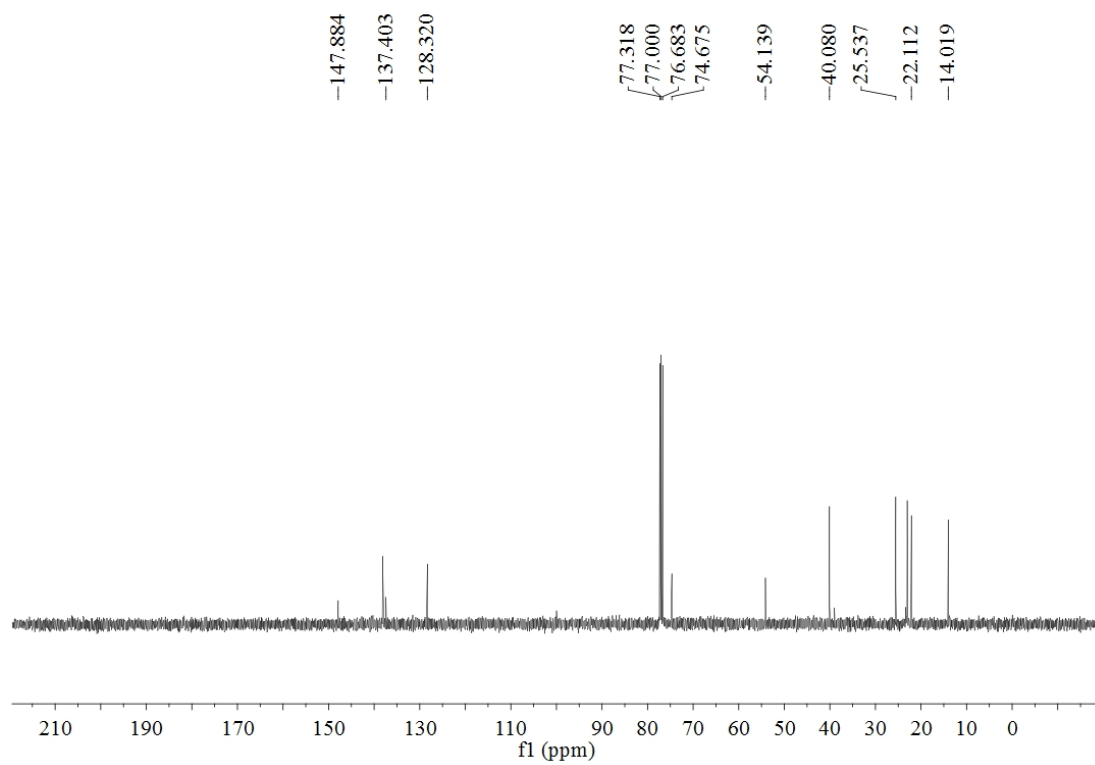
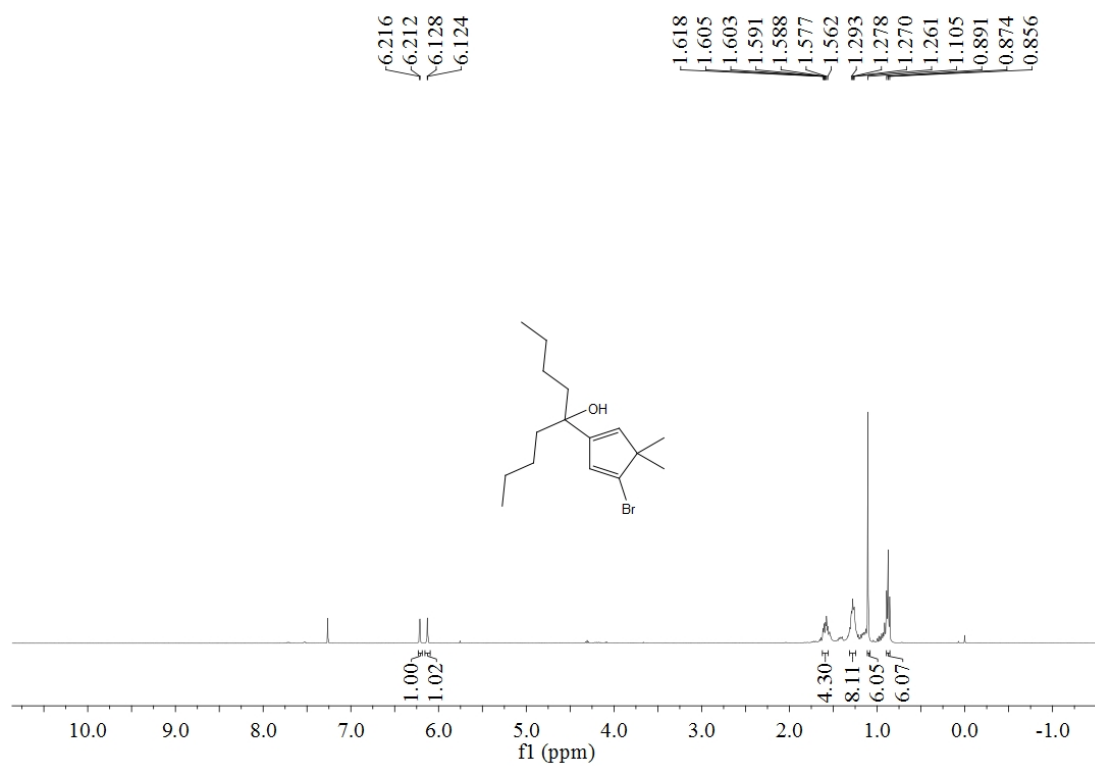


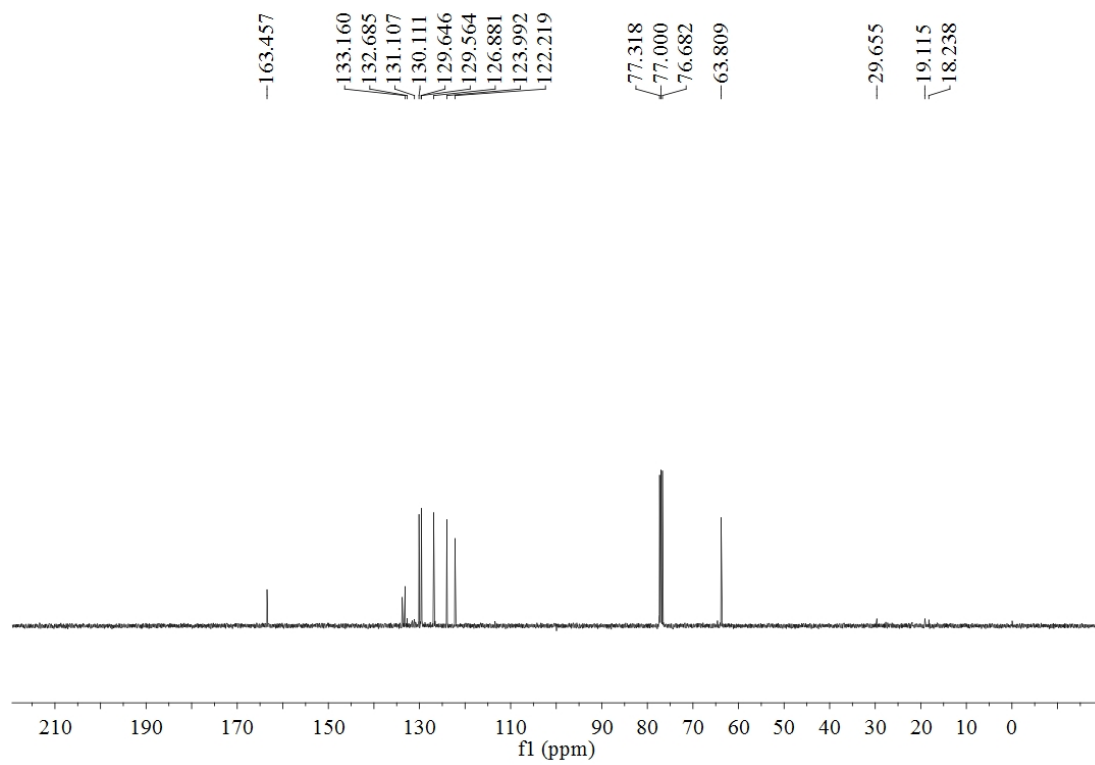
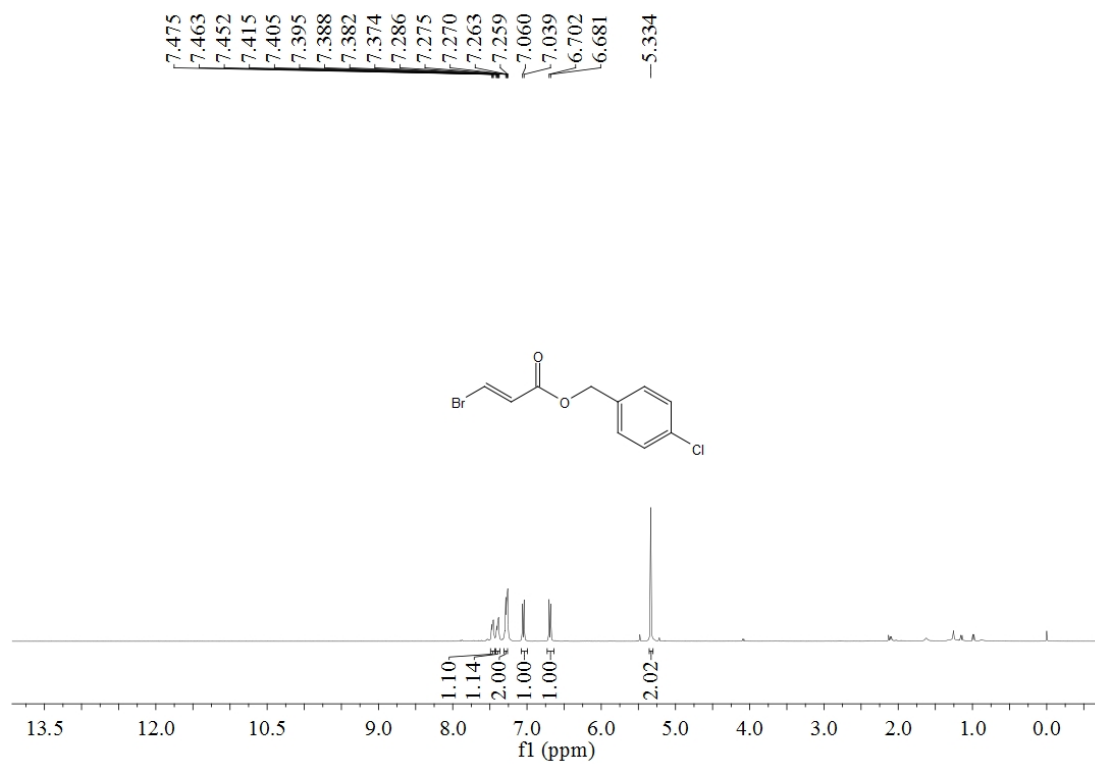


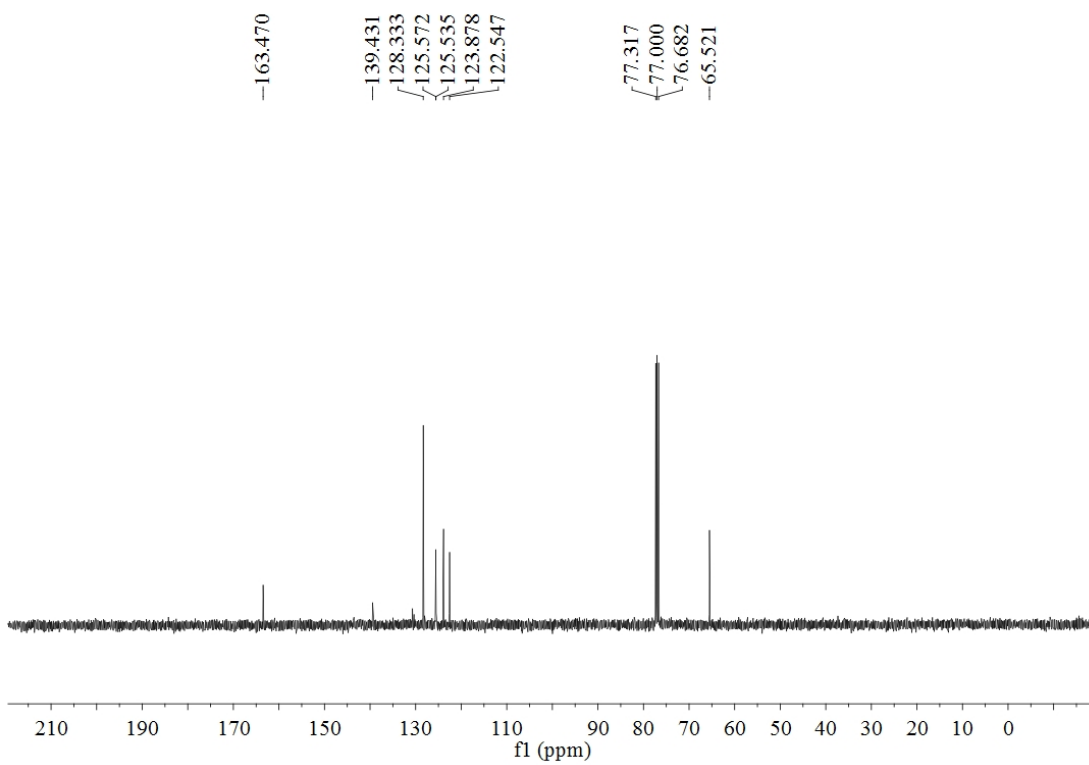
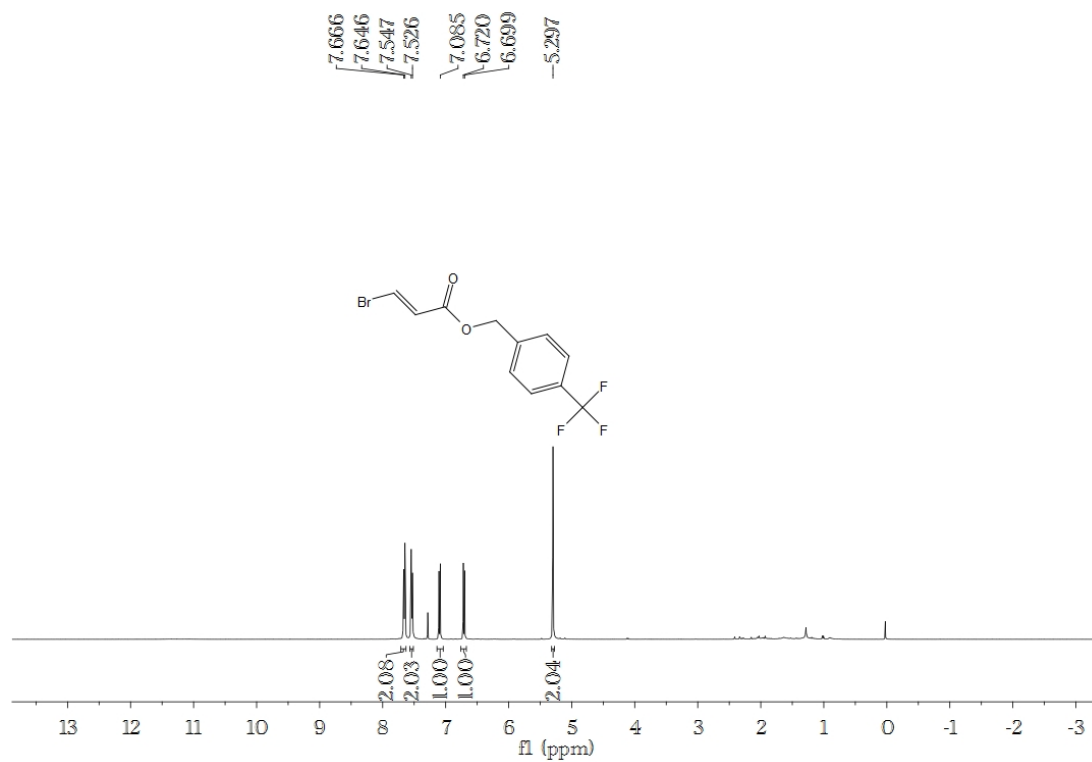




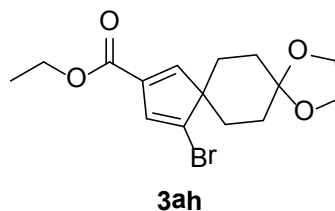
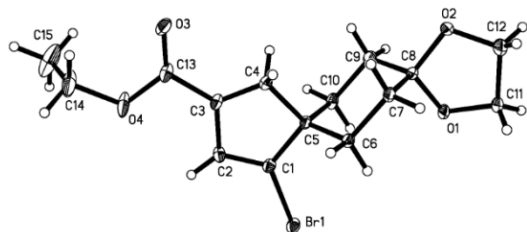








## X-ray Crystallographic Analysis of 3ah and 8



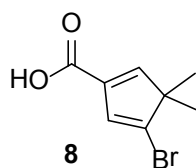
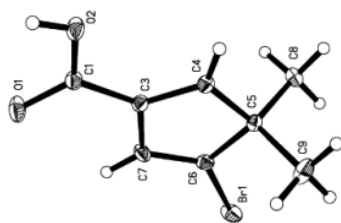
### Summary of Data CCDC 935031

Formula: C<sub>15</sub> H<sub>20</sub> Br<sub>1</sub> O<sub>4</sub>

Unit cell parameters: a 5.76610(10) b 11.1691(2) c 22.7520(5)

alpha 90.00 beta 91.966(2) gamma 90.00

space group P21/n



### Summary of Data CCDC 935030

Formula: C<sub>8</sub> H<sub>9</sub> Br O<sub>2</sub>

Unit cell parameters: a 5.8136(2) b 20.7534(8) c 7.4685(3)

alpha 90.00 beta 103.620(4) gamma 90.00

space group P21/c