

## Supporting information

### Palladium-catalyzed Cross-Coupling Reaction of Alkenylaluminums with 2-Bromobenzo[*b*]furans

Chang Wen, Xin Jiang, Kun Wu, Rui Qiang Luo, Qing Han Li\*

*College of Chemistry and Environmental Protection Engineering, Southwest Minzu University, Chengdu 610041, P. R. China*

e-mail: [lqhchem@163.com](mailto:lqhchem@163.com), [lqhchem@swun.cn](mailto:lqhchem@swun.cn)

---

\* Qing Han Li.  
E-mail address: [lqhchem@163.com](mailto:lqhchem@163.com), [lqhchem@swun.cn](mailto:lqhchem@swun.cn)

## Table of Contents

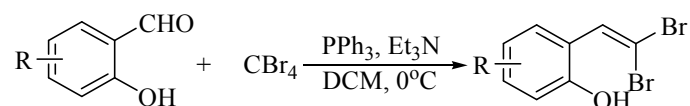
<b>I.</b>	<b>Reagents and General Techniques</b>	S3
<b>II.</b>	<b>Experimental Procedures</b>	S3
<b>III.</b>	<b>References</b>	S8
<b>IV.</b>	<b><sup>1</sup>H and <sup>13</sup>C NMR Spectroscopic Data of Coupling Products</b>	S9
1.	(E)-1-(benzofuran-2-yl)oct-1-en-3-one ( <b>3aa</b> )	S9
2.	(E)-1-(5-methylbenzofuran-2-yl)oct-1-en-3-one ( <b>3ab</b> )	S10
3.	(E)-1-(6-methylbenzofuran-2-yl)oct-1-en-3-one ( <b>3ac</b> )	S11
4.	(E)-1-(6-methoxybenzofuran-2-yl)oct-1-en-3-one ( <b>3ae</b> )	S12
5.	(E)-1-(7-methoxybenzofuran-2-yl)oct-1-en-3-one ( <b>3af</b> )	S13
6.	(E)-1-(5-chlorobenzofuran-2-yl)oct-1-en-3-one ( <b>3ah</b> )	S14
7.	(E)-1-(5-bromobenzofuran-2-yl)oct-1-en-3-one ( <b>3ai</b> )	S15
8.	(E)-1-(5,7-dichlorobenzofuran-2-yl)oct-1-en-3-one ( <b>3ak</b> )	S16
9.	(E)-1-(naphtho[2,1-b]furan-2-yl)oct-1-en-3-one( <b>3am</b> )	S17
10.	(E)-1-(benzofuran-2-yl)dec-1-en-3-one ( <b>3ba</b> )	S18
11.	(E)-1-(7-methoxybenzofuran-2-yl)dec-1-en-3-one ( <b>3bf</b> )	S19
12.	(E)-1-(5-chlorobenzofuran-2-yl)dec-1-en-3-one ( <b>3bh</b> )	S20
13.	(E)-1-(5,7-dichlorobenzofuran-2-yl)dec-1-en-3-one ( <b>3bk</b> )	S21
14.	(E)-2-styrylbenzofuran ( <b>3ca</b> )	S22
15.	(E)-7-methoxy-2-styrylbenzofuran ( <b>3cf</b> )	S23
16.	(E)-5,7-dichloro-2-styrylbenzofuran ( <b>3ck</b> )	S24
17.	(E)-2-(3-phenylprop-1-en-1-yl)benzofuran( <b>3da</b> )	S25
18.	(E)-7-methoxy-2-(3-phenylprop-1-en-1-yl)benzofuran( <b>3df</b> )	S26
<b>V.</b>	<b>Control experiments</b>	S27

## I. Reagents and General Techniques

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Varian 400 MHz spectrometer. The chemical shifts are reported relative to TMS. Analytical thin-layer chromatography (TLC) was performed on silica 60F-254 plates. Flash column chromatography was carried out on silica gel (200-400 mesh). HRMS were recorded on a Bruker Micro TOF spectrometer equipped with an ESI ion source. All reactions were carried out under nitrogen atmosphere. Chemical reagents and solvents were purchased from Adamas-beta, Aldrich and Zhengzhou Spark Technology Co., Ltd. And were used without further purification with the exception of these reagents: THF, Ether and Toluene were distilled from Sodium under Nitrogen. DCE was distilled from Calcium hydride under Nitrogen. Purification of reaction products was carried out by flash chromatography. All synthesis and manipulations were carried out under a dry nitrogen atmosphere.

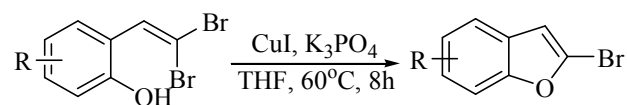
## II. Experimental Procedures

### General procedure for the synthesis of gem-dibromophenols<sup>[1]</sup>



In a round-bottomed flask equipped with a magnetic stirrer was added  $\text{PPh}_3$  (6 equiv) and DCM (1.0 mL per mmol  $\text{PPh}_3$ ). The vessel was cooled to  $0^\circ\text{C}$ , after which a solution of  $\text{CBr}_4$  (3 equiv) in DCM (1.0 mL per mmol  $\text{PPh}_3$ ) was added. After 10 minutes,  $\text{NEt}_3$  (6 equiv) was added dropwise and stirred for an additional 5 minutes, after which a solution of the requisite salicylaldehyde (1 equiv) in DCM (1 mL per mmol salicylaldehyde) was added dropwise over 10 minutes. The internal temperature was maintained below  $10^\circ\text{C}$  over the addition of all reagents. The vessel was stirred for an additional 30 min at  $0^\circ\text{C}$ , after which it was allowed to warm to room temperature and stirred for an additional 1 h. The reaction was quenched by addition of saturated aqueous  $\text{NH}_4\text{Cl}$  solution. The phases were then separated, and the aqueous layer was extracted with DCM. The combined organic layers were concentrated under reduced pressure to approximately 10% of the original volume. The residue was dissolved in  $\text{Et}_2\text{O}$  and filtered over pad of celite. The resulting solution was concentrated by rotary evaporation and purified by flash column chromatography (petroleum ether/ethyl acetate).

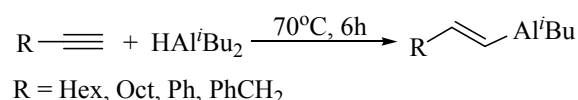
### General procedure for the synthesis of 2-bromobenzofurans<sup>[2]</sup>



In a round-bottomed flask with a magnetic stir bar was added the requisite gem-dibromoolefin (1 equiv),  $\text{CuI}$  (5 mol%), and  $\text{K}_3\text{PO}_4$  (2 equiv), after which THF (1 mL per 0.2

mmol olefin) was added the round-bottomed flask and placed in a pre-heated oil bath at 80°C. The flask was stirred for 6 hours, after which it was removed from the oil bath and allowed to cool to room temperature. The contents were filtered over a pad of silica gel, washing with copious amounts of Et<sub>2</sub>O. The resulting solution was concentrated under reduced pressure to afford spectroscopically pure product (petroleum ether/ethyl acetate).

**General procedures for the preparation dimethyl(2-phenylethynyl)aluminum (C<sub>6</sub>H<sub>13</sub>C=CAI<sup>i</sup>Bu<sub>2</sub>)** [3]



A dry and argon-flushed flask equipped with a magnetic stirrer and condenser was charged with a commercial Diisobutylaluminum Hydride solution (10.0 mL, 1 M in hexane), 1-Octyne (2.0 mL, 10 mmol) was added dropwise via a syringe and the reaction mixture was stirred 6 h at 70°C. The prepared solution can be stored under argon in the dark for several days.

**General producer for cross-coupling of 2-bromobenzo[b]furans with alkenylaluminum reagents**

Under an atmosphere of Argon gas, PdCl<sub>2</sub> (2.6mg, 0.015 mmol), XantPhos (17.4mg, 0.015 mmol), 2-bromobenzo[b]furans (98.0mg, 0.5 mmol) and DCE (3 mL) were mixed in a Schlenk flask. Shortly afterwards, a solution of Alkenylaluminums (0.8 mmol) was added with a syringe pump. At the end of the addition, the reaction mixture stirring was continued for 4 h at 80 °C. After completion the reaction, the mixture was diluted with 1N aqueous HCl solution (10 mL) and extracted with EA (3 × 15 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated *in vacuum*. The residue was subjected to flash column chromatography on silica gel (Hexane gradient) to afford the corresponding products.

(*E*)-1-(benzofuran-2-yl)oct-1-en-3-one (**3aa**)<sup>4</sup>: colourless liquid; yield: 0.099g (82%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.47 (dd, *J* = 7.9, 24.9 Hz, 2H), 7.27-7.17 (m, 2H), 6.56-6.46 (m, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 2.27 (q, *J* = 7.1 Hz, 2H), 1.57-1.49 (m, 2H), 1.41-1.28 (m, 6H), 0.96-0.89 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ: 155.3, 154.6, 134.0, 129.2, 123.9, 122.6, 120.6, 118.6, 110.7, 102.6, 33.0, 31.7, 29.0, 28.9, 22.6, 14.1.

(*E*)-1-(5-methylbenzofuran-2-yl)oct-1-en-3-one (**3ab**): colourless liquid; yield: 0.091g (71%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.31-7.23 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.49-6.24 (m, 3H), 2.40 (s, 3H), 2.27-2.18 (m, 2H), 1.52-1.44 (m, 2H), 1.36-1.24 (m, 6H), 0.88 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ: 155.3, 153.0, 133.7, 132.0, 129.2, 125.1, 120.5, 118.7, 110.2, 102.4, 33.0, 31.8, 29.1, 28.9, 22.6, 21.3, 14.1. HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>21</sub>O<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 257.15361, found 257.15341.

(*E*)-1-(6-methylbenzofuran-2-yl)oct-1-en-3-one (**3ac**): colourless liquid; yield:0.092g (72%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.34 (d, *J* = 7.9 Hz, 1H), 7.22 (s, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.50-6.23 (m, 3H), 2.44 (s, 3H), 2.23 (q, *J* = 6.6, 7.1 Hz, 2H), 1.48 (q, *J* = 6.4, 7.3 Hz, 2H), 1.37-1.26 (m, 6H), 0.92-0.87 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ: 155.0, 154.7, 134.1, 133.2, 126.6, 124.0, 120.0, 118.6, 111.0, 102.5, 33.0, 31.7, 29.0, 28.9, 22.6, 21.7, 14.1. HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>21</sub>O<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 257.15361,found 257.15347.

(*E*)-1-(6-methoxybenzofuran-2-yl)oct-1-en-3-one(**3ae**): brown liquid; yield:0.116g (85%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.32 (d, *J* = 8.5 Hz, 1H), 6.97 (s, 1H), 6.80 (dd, *J* = 2.3, 8.5 Hz, 1H), 6.45-6.21 (m, 3H), 3.82 (s, 3H), 2.21 (q, *J* = 7.5, 8.0 Hz, 2H), 1.47 (p, *J* = 6.9 Hz, 2H), 1.40-1.23 (m, 6H), 0.89 (t, *J* = 6.6 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ: 157.8, 155.6, 154.6, 132.5, 122.5, 120.6, 118.6, 111.4, 102.4, 95.7, 55.7, 33.0, 31.7, 29.1, 28.9, 22.6, 14.0. HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub><sup>+</sup> (M+H)<sup>+</sup> 273.14852,found 273.14813.

(*E*)-1-(7-methoxybenzofuran-2-yl)oct-1-en-3-one(**3af**): brown liquid; yield:0.125g (92%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.09-7.07 (m, 2H), 6.77-6.71 (m, 1H), 6.58-6.48 (m, 1H), 6.44 (s, 1H), 6.30 (d, *J* = 15.8 Hz, 1H), 3.99 (s, 3H), 2.26-2.18 (m, 2H), 1.47 (p, *J* = 7.4 Hz, 2H), 1.37-1.26 (m, 6H), 0.93-0.86 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ: 155.4, 145.0, 143.6, 134.3, 130.8, 123.3, 118.3, 113.1, 106.3, 102.7, 56.0, 33.0, 31.7, 29.0, 28.9, 22.6, 14.1. HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub><sup>+</sup> (M+H)<sup>+</sup> 273.14852,found 273.14838.

(*E*)-1-(5-chlorobenzofuran-2-yl)oct-1-en-3-one (**3ah**): light yellow liquid; yield:0.125g(90%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.41 (d, *J* = 2.1 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.14 (dd, *J* = 2.2, 8.7 Hz, 1H), 6.48 (dt, *J* = 7.0, 15.7 Hz, 1H), 6.35 (s, 1H), 6.26 (d, *J* = 15.8 Hz, 1H), 2.22 (q, *J* = 7.9, 8.7 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 2H), 1.35-1.27 (m, 6H), 0.92-0.87 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ: 156.7, 152.9, 135.1, 130.5, 128.2, 124.0, 120.1, 118.2, 111.6, 102.0, 33.0, 31.7, 28.9, 28.9, 22.6, 14.1. HRMS (ESI) *m/z* calcd for C<sub>16</sub>H<sub>18</sub>ClO<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 277.09898,found 277.09930.

(*E*)-1-(5-bromobenzofuran-2-yl)oct-1-en-3-one(**3ai**): light yellow liquid; yield:0.145g (90%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.57 (d, *J* = 1.9 Hz, 1H), 7.31-7.21 (m, 2H), 6.48 (dt, *J* = 7.0, 15.8 Hz, 1H), 6.35 (s, 1H), 6.26 (d, *J* = 15.8 Hz, 1H), 2.27-2.18 (m, 2H), 1.50-1.43 (m, 2H), 1.33-1.26 (m, 6H), 0.88 (d, *J* = 4.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ: 156.5, 153.3, 135.2, 131.2, 126.7, 123.1, 118.2, 115.7, 112.1, 101.9, 33.0, 31.7, 28.9, 28.9, 22.6, 14.1. HRMS (ESI) *m/z* calcd for C<sub>16</sub>H<sub>18</sub>BrO<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 321.04847,found 321.04877.

(*E*)-1-(5,7-dichlorobenzofuran-2-yl)oct-1-en-3-one(**3ak**): light yellow liquid; yield: 0.145g(93%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 7.32 (s, 1H), 7.20 (s, 1H), 6.63-6.53 (m, 1H), 6.40 (s, 1H), 6.28 (d, *J* = 17.4 Hz, 1H), 2.25 (q, *J* = 7.2 Hz, 2H), 1.49 (p, *J* = 7.1 Hz, 2H), 1.38-1.27 (m, 6H), 0.92-0.86 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ: 157.4, 148.9, 136.5, 131.5, 128.3, 123.8, 118.7, 117.7, 116.6, 102.3, 33.0, 31.7, 28.9, 28.8, 22.6, 14.1.

(*E*)-1-(naphtho[2,1-b]furan-2-yl)oct-1-en-3-one(**3am**):colourless liquid; yield:0.121g (83%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ: 8.05 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.65

(d,  $J = 8.9$  Hz, 1H), 7.60-7.51 (m, 2H), 7.44 (t,  $J = 8.2$  Hz, 1H), 6.92 (s, 1H), 6.54-6.45 (m, 1H), 6.37 (d,  $J = 15.8$  Hz, 1H), 2.25 (q,  $J = 6.7, 7.5$  Hz, 2H), 1.49 (q,  $J = 6.7, 7.2$  Hz, 2H), 1.37-1.27 (m, 6H), 0.92-0.87 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 154.8, 151.9, 144.2, 133.2, 130.3, 128.7, 127.5, 126.1, 124.8, 124.4, 123.5, 118.7, 112.1, 101.7, 33.1, 31.8, 29.1, 29.0, 22.7, 14.2. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{21}\text{O}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  293.15361, found 293.15436.

(*E*)-1-(benzofuran-2-yl)dec-1-en-3-one (**3ba**): light yellow liquid; yield: 0.122g (90%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 7.43 (dd,  $J = 7.6, 25.0$  Hz, 2H), 7.24-7.12 (m, 2H), 6.53-6.42 (m, 2H), 6.30 (d,  $J = 15.8$  Hz, 1H), 2.27-2.18 (m, 2H), 1.52-1.45 (m, 2H), 1.36-1.23 (m, 10H), 0.94-0.86 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 155.3, 154.6, 134.0, 129.2, 123.9, 122.6, 120.6, 118.6, 110.7, 102.6, 33.0, 31.9, 29.5, 29.3, 29.3, 29.1, 22.7, 14.1. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{23}\text{O}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  271.16926, found 271.16974.

(*E*)-1-(7-methoxybenzofuran-2-yl)dec-1-en-3-one (**3bf**): colourless liquid; yield: 0.146g (97%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 7.20-7.16 (m, 2H), 6.84 (dd,  $J = 3.8, 5.1$  Hz, 1H), 6.63 (dt,  $J = 7.0, 15.9$  Hz, 1H), 6.55 (s, 1H), 6.40 (d,  $J = 15.8$  Hz, 1H), 4.10 (s, 3H), 2.32 (q,  $J = 7.2$  Hz, 2H), 1.58 (t,  $J = 7.1$  Hz, 2H), 1.45-1.34 (m, 10H), 1.01-0.95 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 155.4, 145.0, 143.6, 134.3, 130.8, 123.3, 118.3, 113.1, 106.3, 102.7, 56.0, 33.0, 31.9, 29.5, 29.3, 29.2, 29.0, 22.7, 14.1. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{25}\text{O}_3^+$  ( $\text{M}+\text{H}$ ) $^+$  301.17982, found 301.17984.

(*E*)-1-(5-chlorobenzofuran-2-yl)dec-1-en-3-one (**3bh**): light yellow liquid; yield: 0.050g (33%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 7.43 (d,  $J = 2.1$  Hz, 1H), 7.30 (d,  $J = 9.5$  Hz, 1H), 7.16 (dd,  $J = 2.2, 8.7$  Hz, 1H), 6.54-6.45 (m, 1H), 6.38 (s, 1H), 6.28 (d,  $J = 15.8$  Hz, 1H), 2.24 (q,  $J = 7.2$  Hz, 2H), 1.48 (t,  $J = 7.0$  Hz, 2H), 1.32-1.26 (m, 10H), 0.90-0.86 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 156.6, 152.9, 135.1, 130.5, 128.1, 124.0, 120.1, 118.2, 111.6, 102.0, 33.0, 31.9, 29.5, 29.3, 29.3, 29.2, 29.0, 22.7, 14.1.

(*E*)-1-(5,7-dichlorobenzofuran-2-yl)dec-1-en-3-one (**3bk**): white solid; yield: 0.158g (93%), m.p.: 55-56 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 7.29 (d,  $J = 1.9$  Hz, 1H), 7.18 (d,  $J = 1.9$  Hz, 1H), 6.57 (dt,  $J = 7.0, 15.8$  Hz, 1H), 6.37 (s, 1H), 6.26 (d,  $J = 15.8$  Hz, 1H), 2.23 (q,  $J = 7.2$  Hz, 2H), 1.48 (t,  $J = 7.6$  Hz, 2H), 1.31-1.25 (m, 10H), 0.90-0.86 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 157.4, 148.9, 136.4, 131.5, 128.4, 123.8, 118.7, 117.7, 116.6, 102.2, 33.0, 31.9, 29.7, 29.5, 29.3, 28.8, 22.7, 14.1. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{21}\text{Cl}_2\text{O}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  339.09131, found 339.09190.

(*E*)-2-styrylbenzofuran (**3ca**) [4]: white solid; yield: 0.075g (68%), m.p.: 126-127 °C [lit. 4, m.p.: 123-125 °C].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 7.52-7.43 (m, 4H), 7.37-7.14 (m, 6H), 6.96 (d,  $J = 16.2$  Hz, 1H), 6.62 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 155.1, 155.0, 136.6, 130.3, 129.2, 128.8, 128.2, 126.8, 124.7, 123.0, 120.9, 116.5, 111.0, 105.3.

(*E*)-7-methoxy-2-styrylbenzofuran (**3cf**): brown liquid; yield: 0.091g (72%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 7.53 (d,  $J = 7.1$  Hz, 2H), 7.39 (q,  $J = 7.9, 8.4$  Hz, 3H), 7.28 (d,  $J = 7.2$

Hz, 1H), 7.18-7.13 (m, 2H), 7.01 (d,  $J = 16.2$  Hz, 1H), 6.84-6.78 (m, 1H), 6.68 (s, 1H), 4.05 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 155.2, 145.1, 144.0, 136.6, 130.8, 130.4, 128.8, 128.2, 126.7, 123.6, 116.2, 113.3, 106.8, 105.4, 56.1. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{15}\text{O}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  251.10666, found 251.10606.

(*E*)-5,7-dichloro-2-styrylbenzofuran(**3ck**): white solid; yield: 0.088 g (61%), m.p.: 85-87 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 7.50 (d,  $J = 7.0$  Hz, 2H), 7.38-7.28 (m, 5H), 7.22 (d,  $J = 2.6$  Hz, 1H), 6.92 (d,  $J = 16.2$  Hz, 1H), 6.57 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 157.2, 149.2, 136.0, 132.4, 131.4, 128.8, 128.7, 128.6, 126.9, 124.4, 118.9, 116.8, 115.3, 104.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{O}^+$  ( $\text{M}+\text{H}$ ) $^+$  289.01815, found 289.01815.

(*E*)-2-(3-phenylprop-1-en-1-yl)benzofuran(**3da**): light yellow liquid; yield: 0.108 g (92%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 7.55 (d,  $J = 6.7$  Hz, 1H), 7.47 (d,  $J = 8.0$  Hz, 1H), 7.42-7.37 (m, 2H), 7.34-7.21 (m, 5H), 6.71 (dt,  $J = 6.9, 15.4$  Hz, 1H), 6.55 (s, 1H), 6.41 (d,  $J = 15.7$  Hz, 1H), 3.65 (d,  $J = 6.9$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 154.8, 154.6, 139.4, 131.9, 129.0, 128.8, 128.6, 126.4, 124.2, 122.7, 120.7, 119.7, 110.8, 103.5, 39.2. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{15}\text{O}^+$  ( $\text{M}+\text{H}$ ) $^+$  235.11174, found 235.11133.

(*E*)-7-methoxy-2-(3-phenylprop-1-en-1-yl)benzofuran(**3df**): brown liquid; yield: 0.125 g (95%),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 7.34-7.26 (m, 2H), 7.25-7.19 (m, 3H), 7.10-7.05 (m, 2H), 6.76-6.62 (m, 2H), 6.47 (s, 1H), 6.32 (d,  $J = 15.7$  Hz, 1H), 3.95 (s, 3H), 3.54 (d,  $J = 6.9$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 155.0, 145.1, 143.7, 139.4, 132.2, 130.7, 128.9, 128.6, 126.4, 123.4, 119.5, 113.2, 106.6, 103.6, 56.0, 39.2. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{17}\text{O}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  265.12231, found 265.12250.

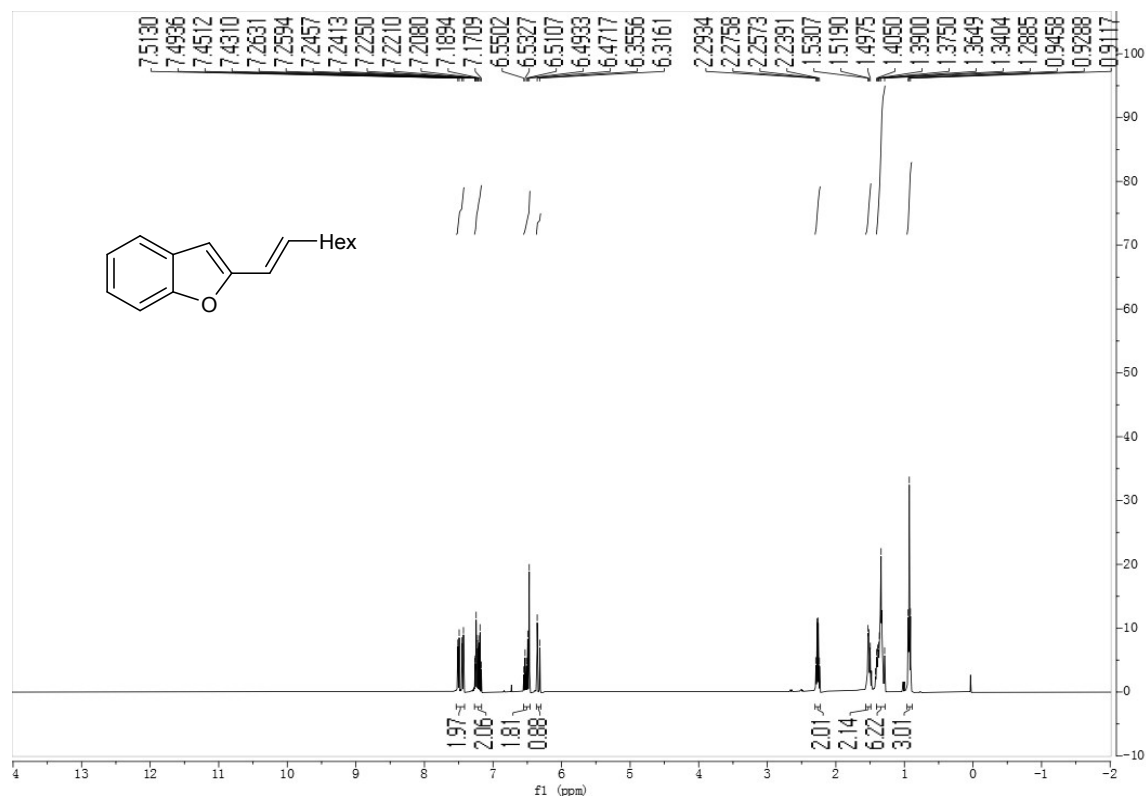
### III. References

- [1] L. Pauli; R. Tannert; R. Scheil, A. Pfaltz, *Chemistry.*, **2015**, *21*, 1482-1487.
- [2] (a) S. G. Newman; V. Aureggi; C. S. Bryan, M. Lautens, *Chem. Commun (Camb).*, **2009**, 5236-5238. (b) Y. Ji; P. Li; X. Zhang, L. Wang, *Org. Biomol. Chem.*, **2013**, *11*, 4095-4101. (c) W. Chen; Y. C. Zhang; L. Zhang; M. Wang, L. Wang, *Chem. Commun.*, **2011**, *47*, 10476-10478.
- [3] I. R. Ramazanov; R. N. Kadikova, U. M. Dzhemilev, *Russ. J. Org. Chem.*, **2013**, *49*, 321-326.
- [4] L. M. Geary, P. G. Hultin, *Eur. J. Org. Chem.*, **2010**, *29*, 5563-5573.

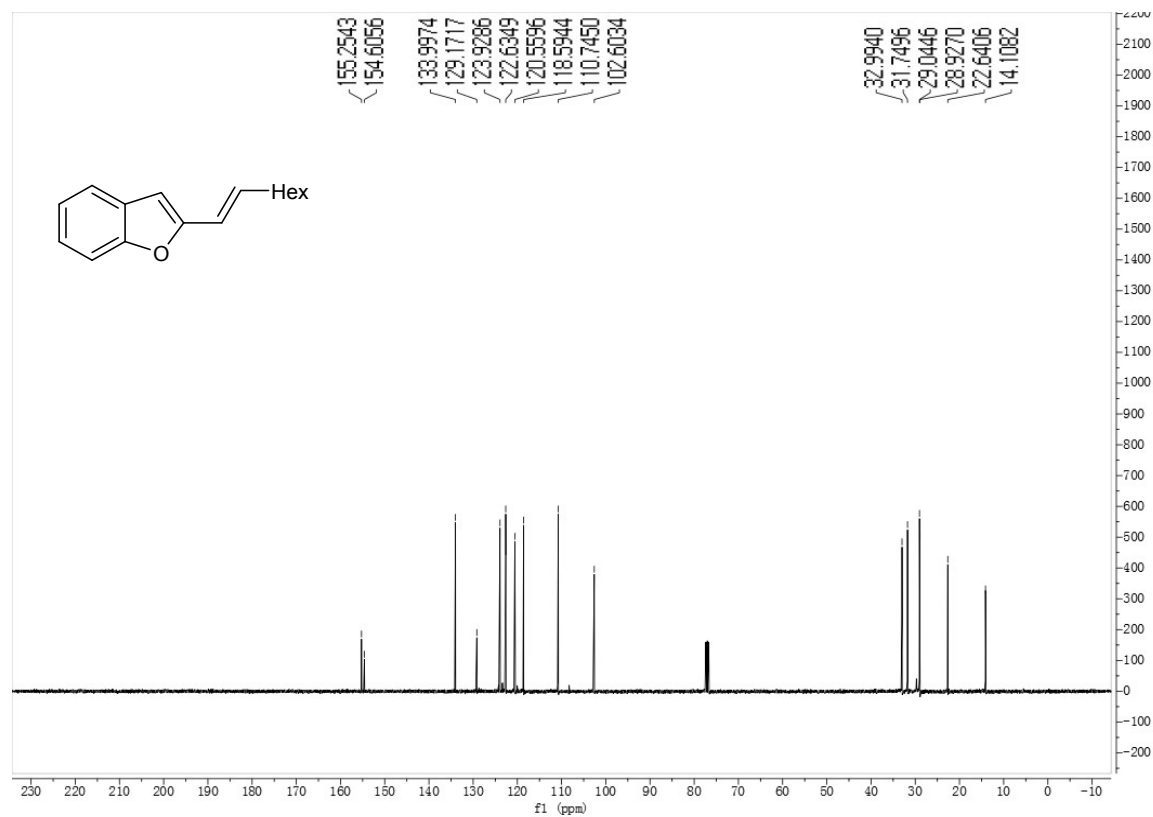


#### IV. <sup>1</sup>H and <sup>13</sup>C NMR and High-Resolution Mass Spectra of Coupling Products

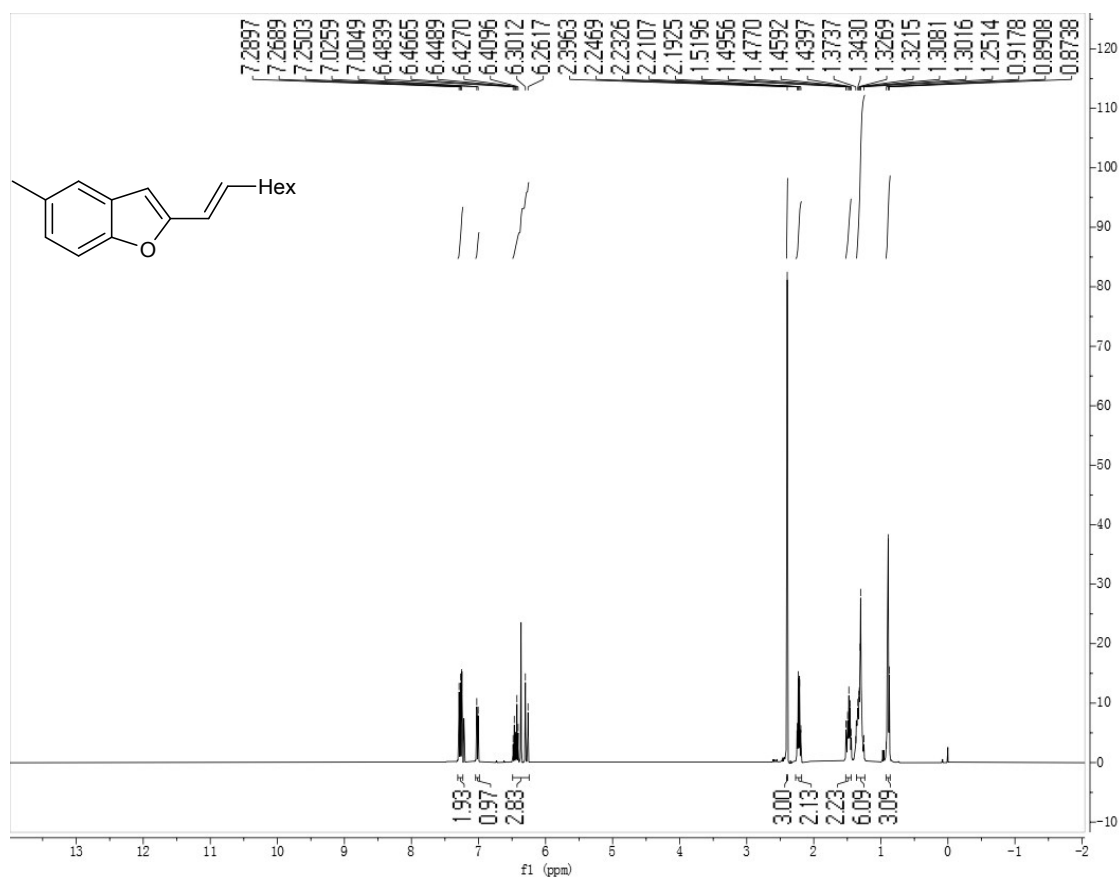
<sup>1</sup>H NMR spectrum of (E)-1-(benzofuran-2-yl)oct-1-en-3-one(3aa)



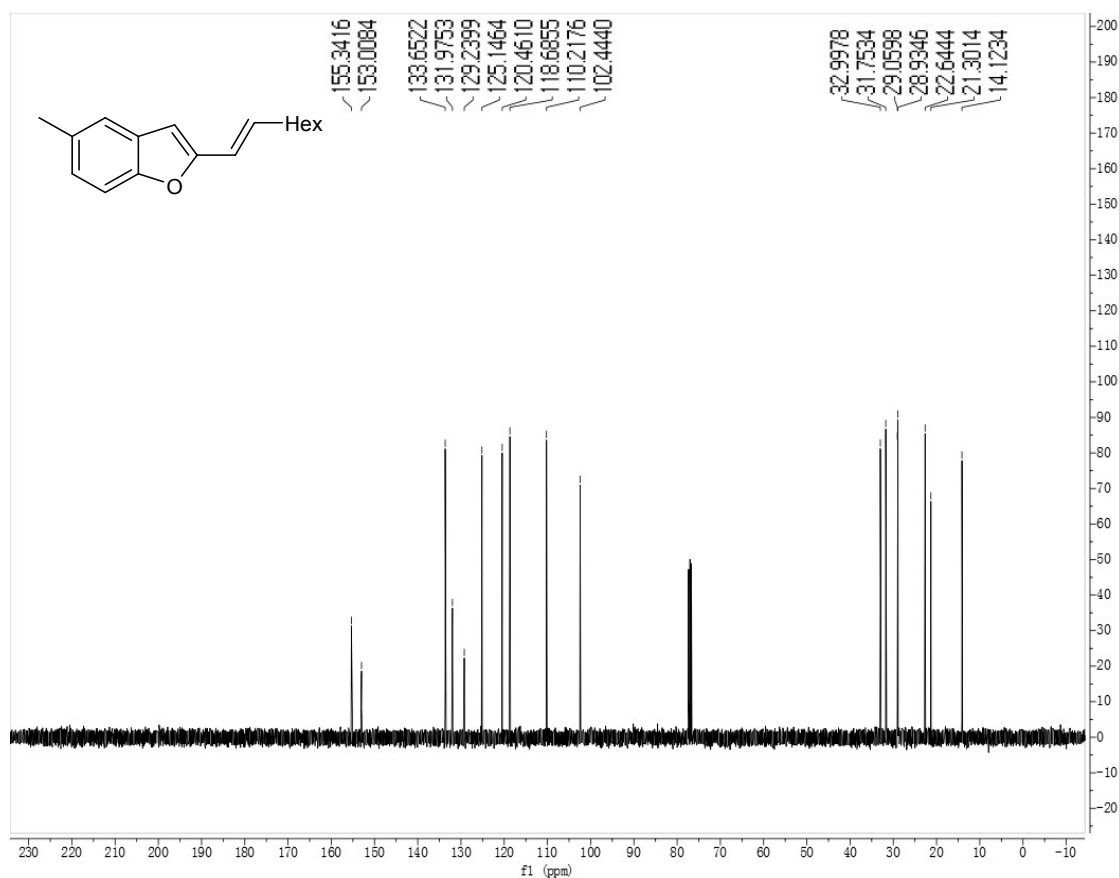
<sup>13</sup>C NMR spectrum of (E)-1-(benzofuran-2-yl)oct-1-en-3-one(3aa)



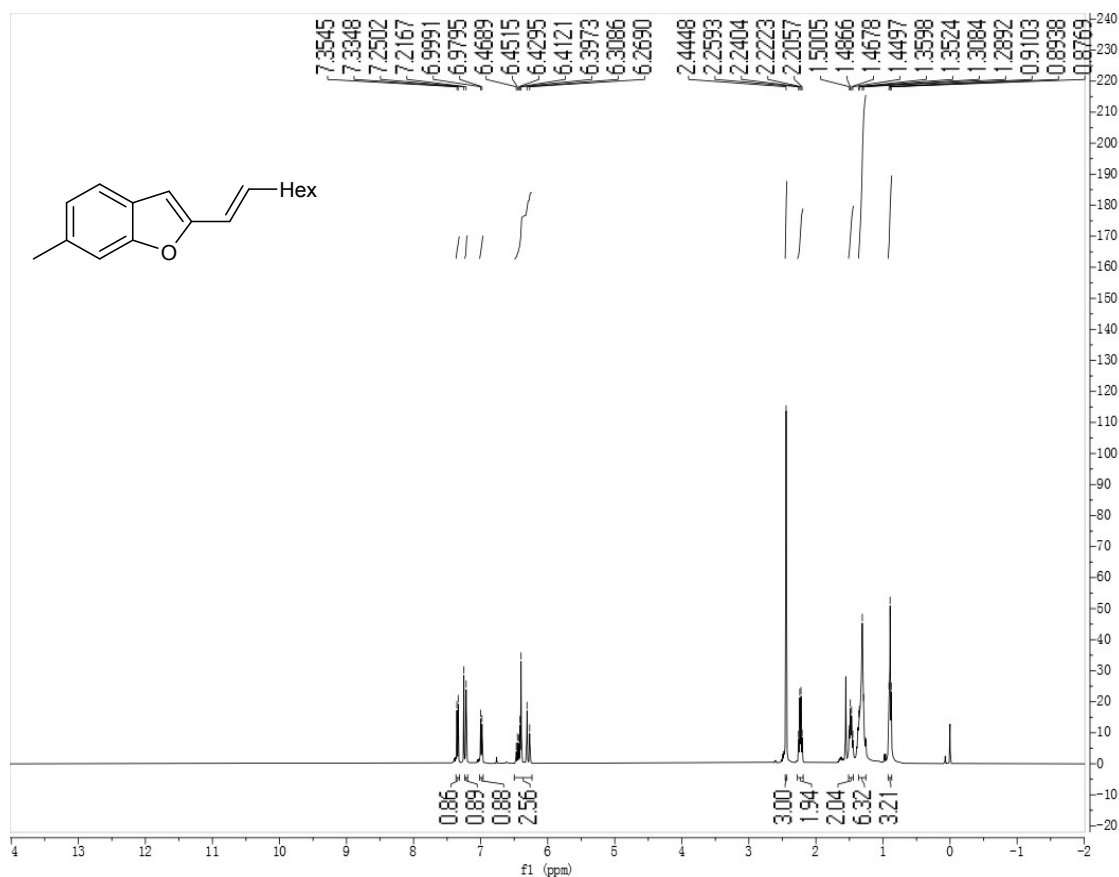
<sup>1</sup>H NMR spectrum of (E)-1-(5-methylbenzofuran-2-yl)oct-1-en-3-one (**3ab**)



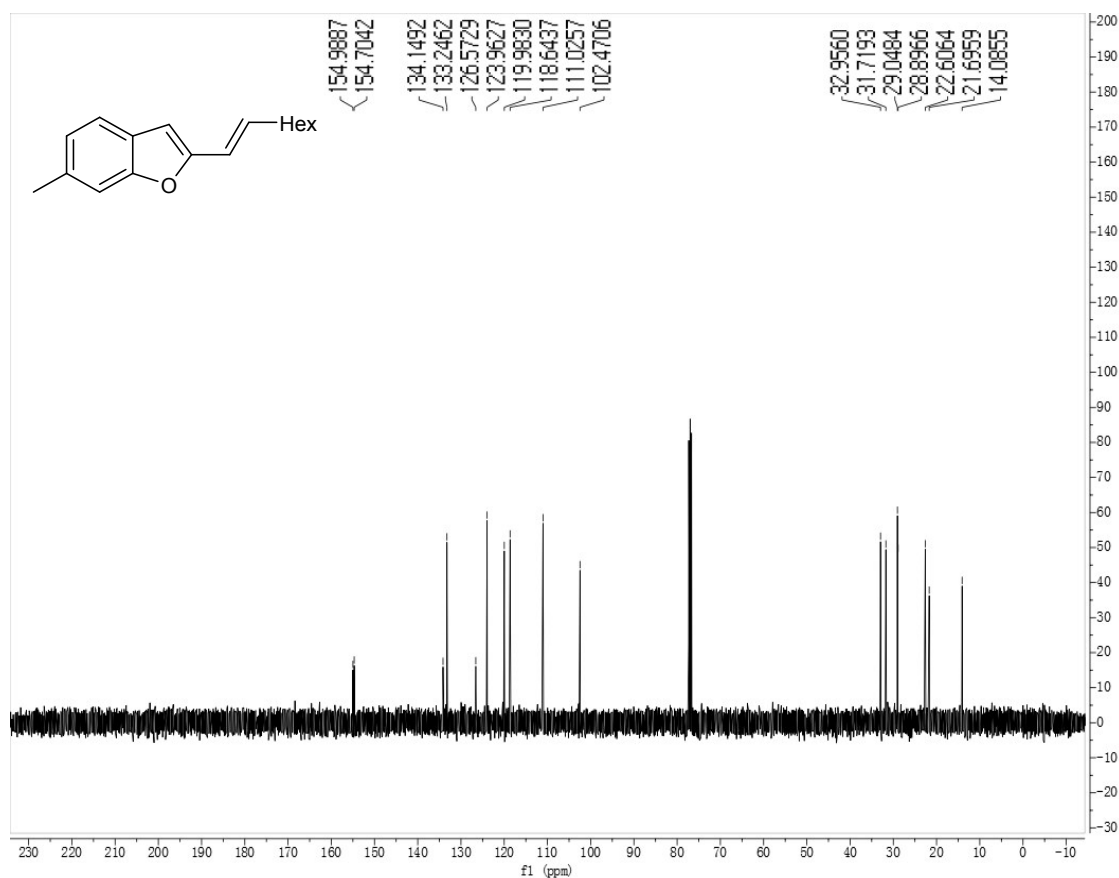
<sup>13</sup>C NMR spectrum of (E)-1-(5-methylbenzofuran-2-yl)oct-1-en-3-one (**3ab**)



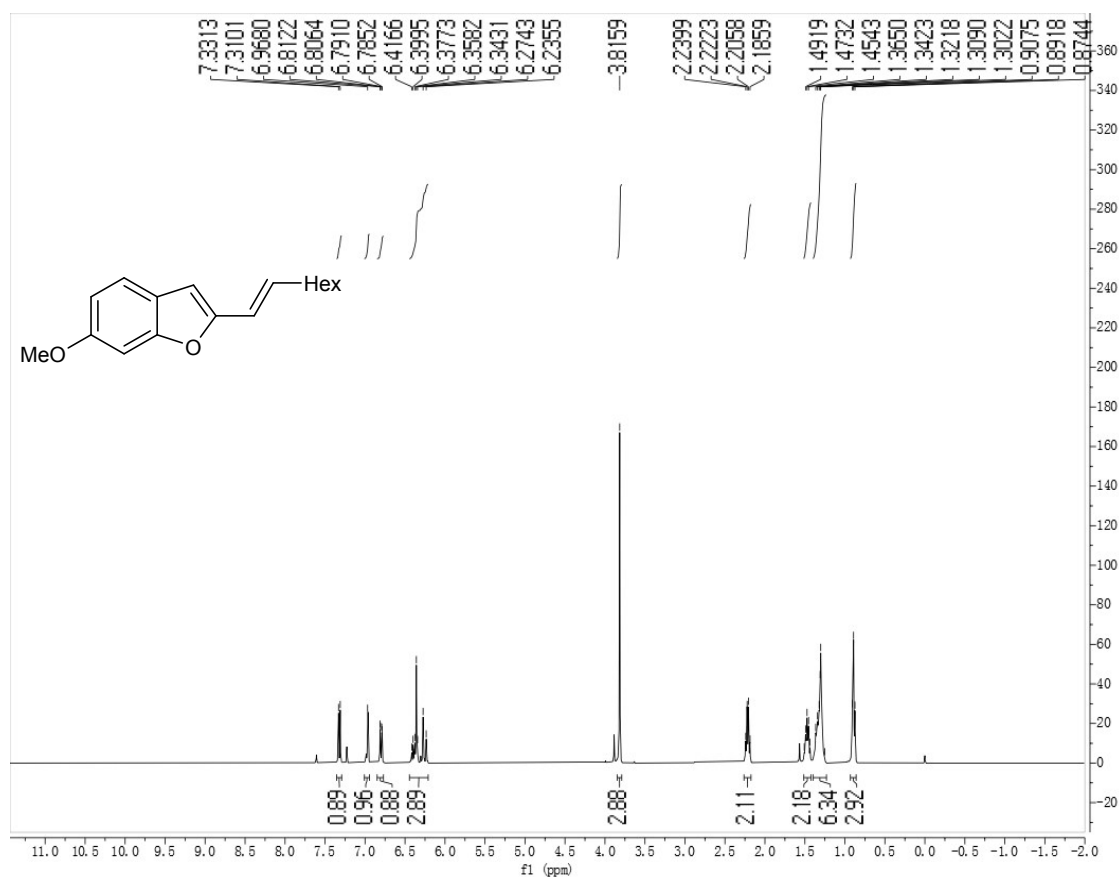
<sup>1</sup>H NMR spectrum of (E)-1-(6-methylbenzofuran-2-yl)oct-1-en-3-one (**3ac**)



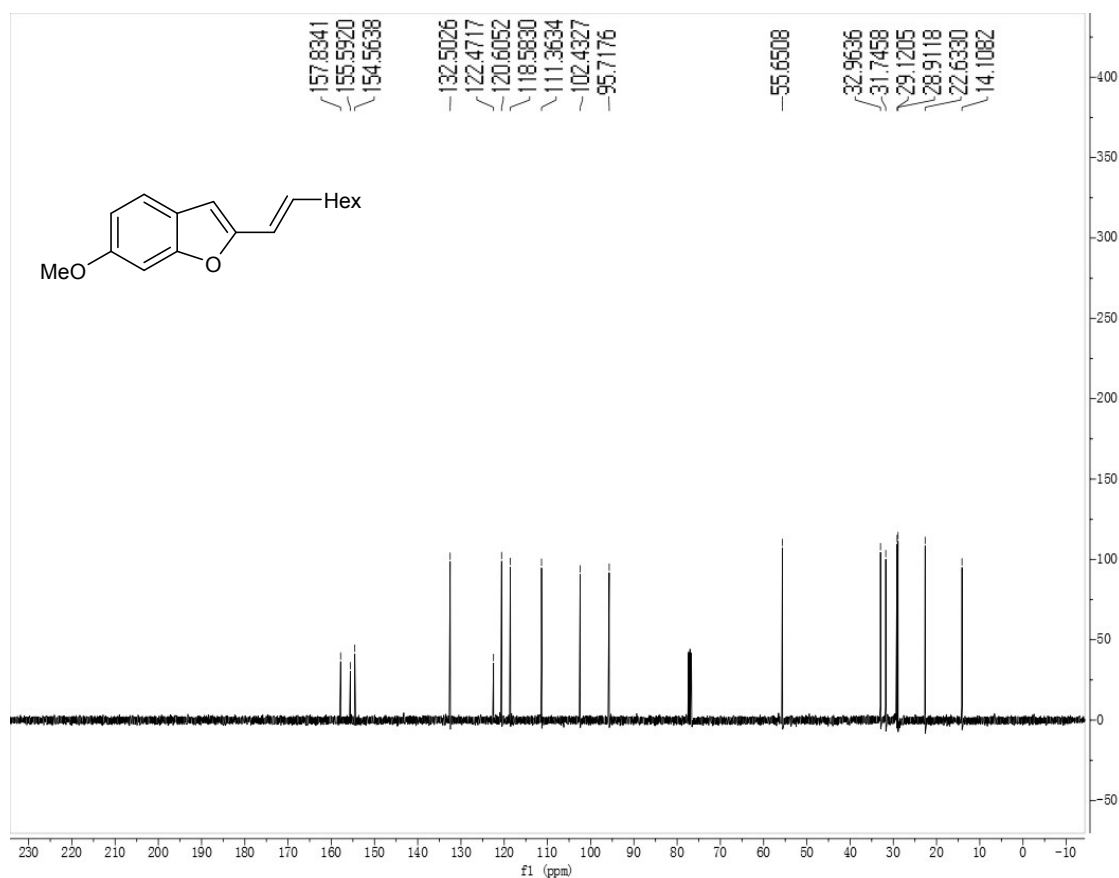
<sup>13</sup>C NMR spectrum of (E)-1-(6-methylbenzofuran-2-yl)oct-1-en-3-one (**3ac**)



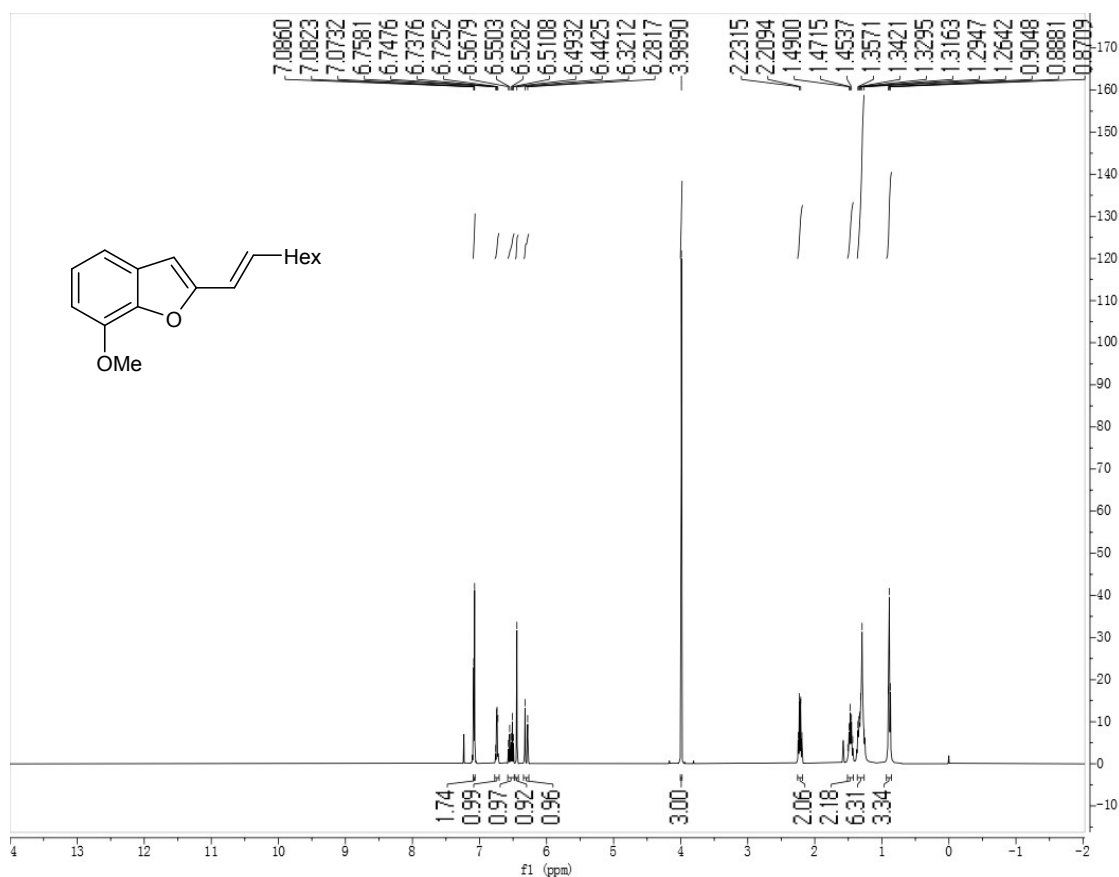
<sup>1</sup>H NMR spectrum of (E)-1-(6-methoxybenzofuran-2-yl)oct-1-en-3-one (**3ae**)



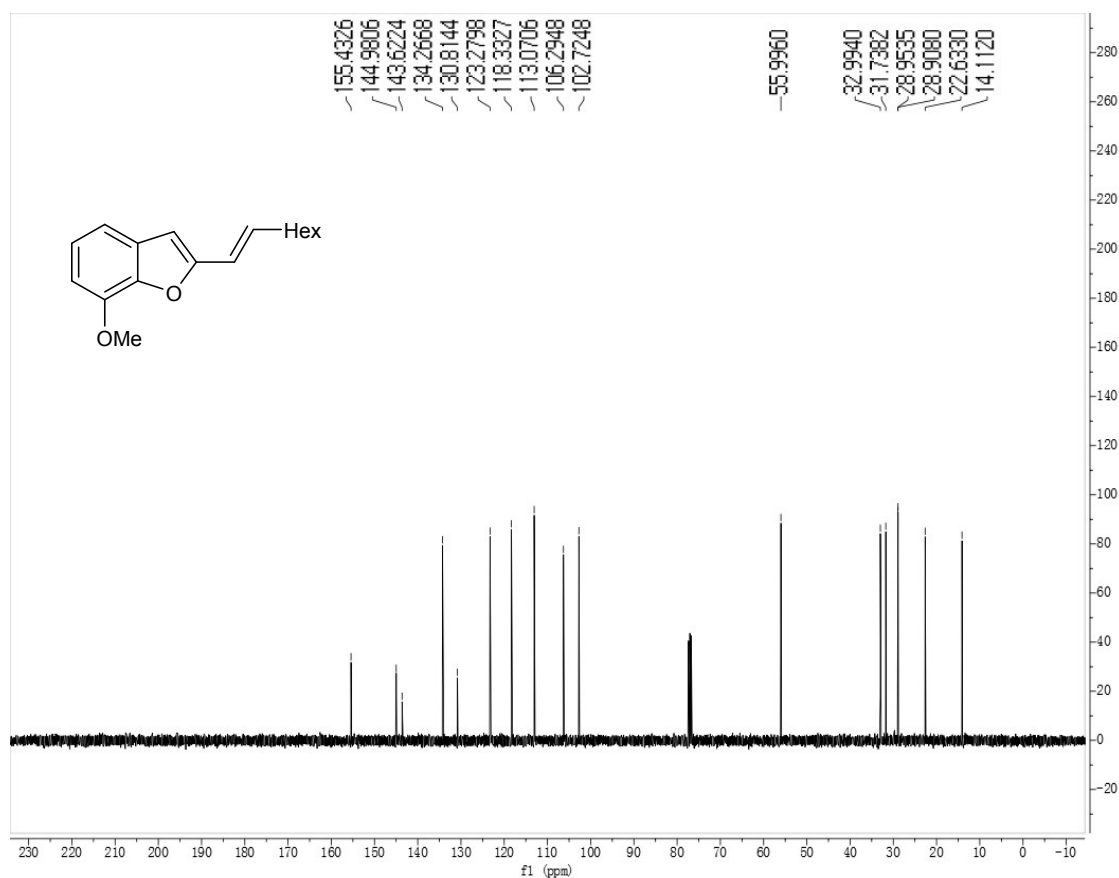
<sup>13</sup>C NMR spectrum of (E)-1-(6-methoxybenzofuran-2-yl)oct-1-en-3-one (**3ae**)



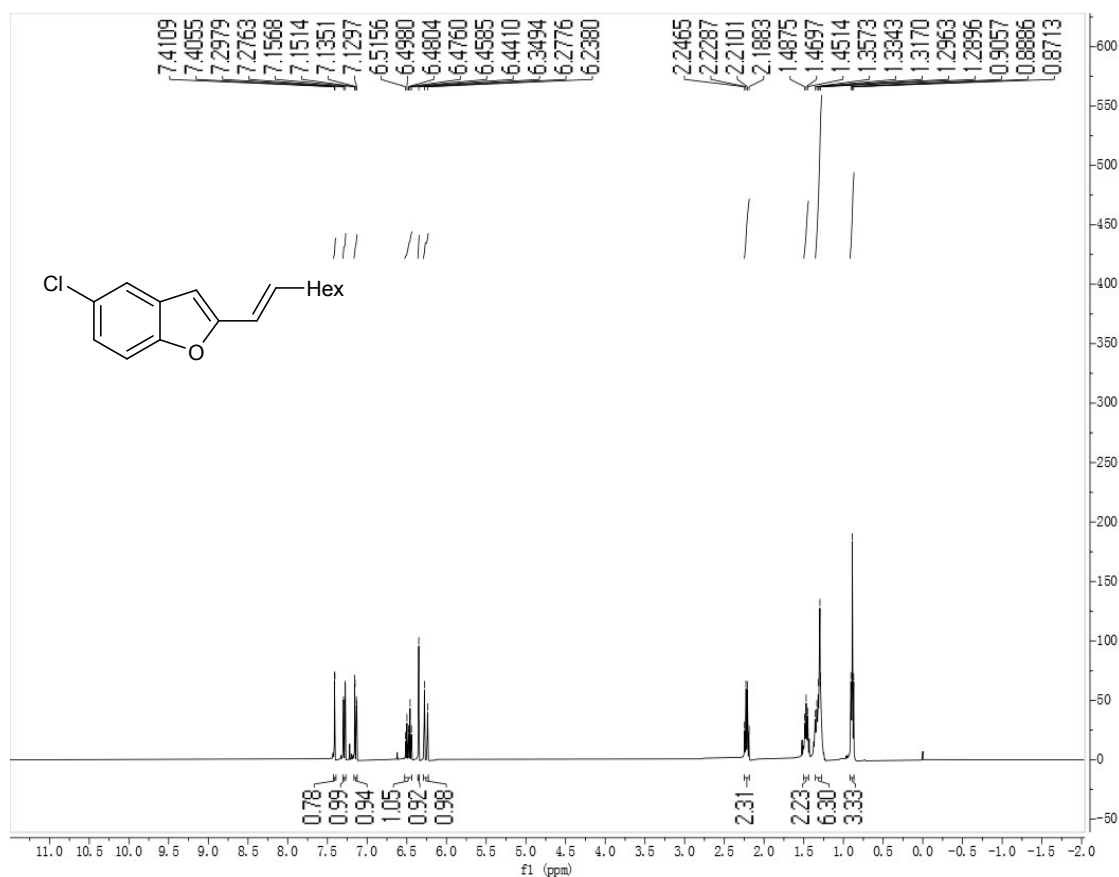
<sup>1</sup>H NMR spectrum of (E)-1-(7-methoxybenzofuran-2-yl)oct-1-en-3-one (**3af**)



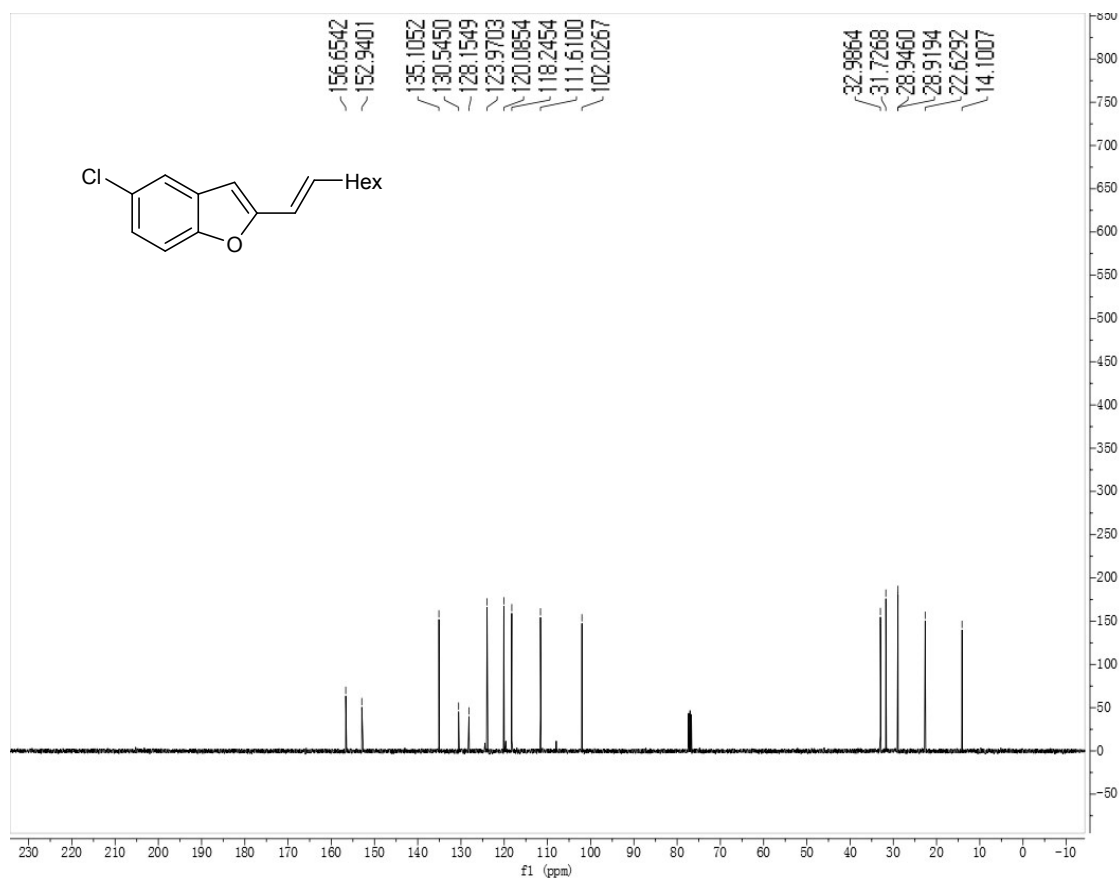
<sup>13</sup>C NMR spectrum of (E)-1-(7-methoxybenzofuran-2-yl)oct-1-en-3-one (**3af**)



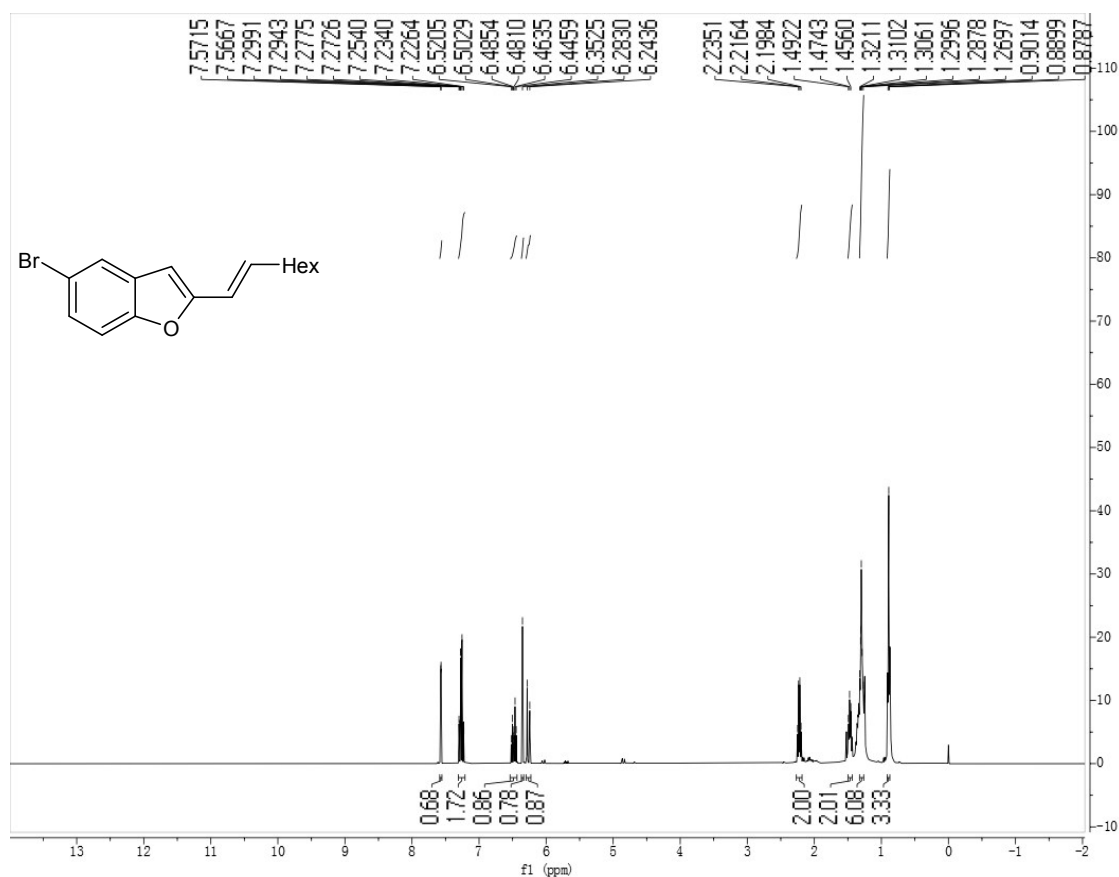
<sup>1</sup>H NMR spectrum of (E)-1-(5-chlorobenzofuran-2-yl)oct-1-en-3-one (**3ah**)



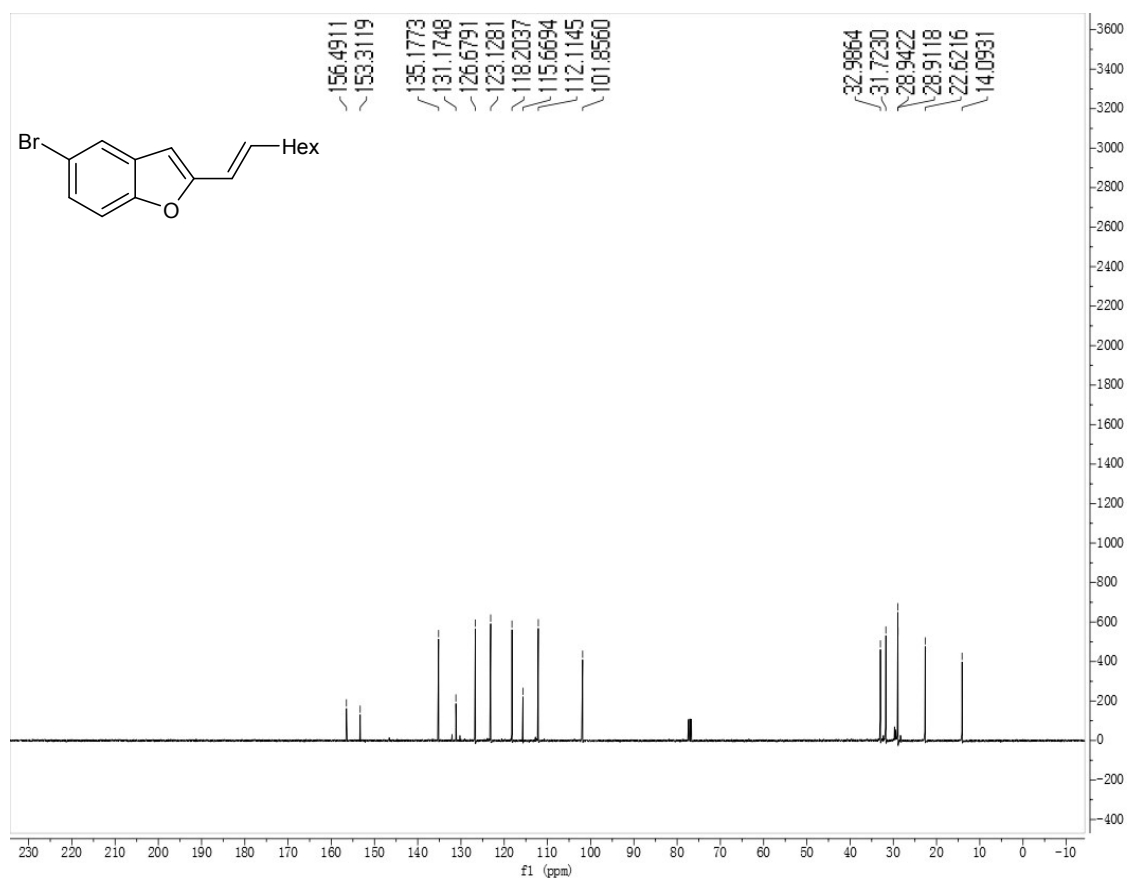
<sup>13</sup>C NMR spectrum of (E)-1-(5-chlorobenzofuran-2-yl)oct-1-en-3-one (**3ah**)



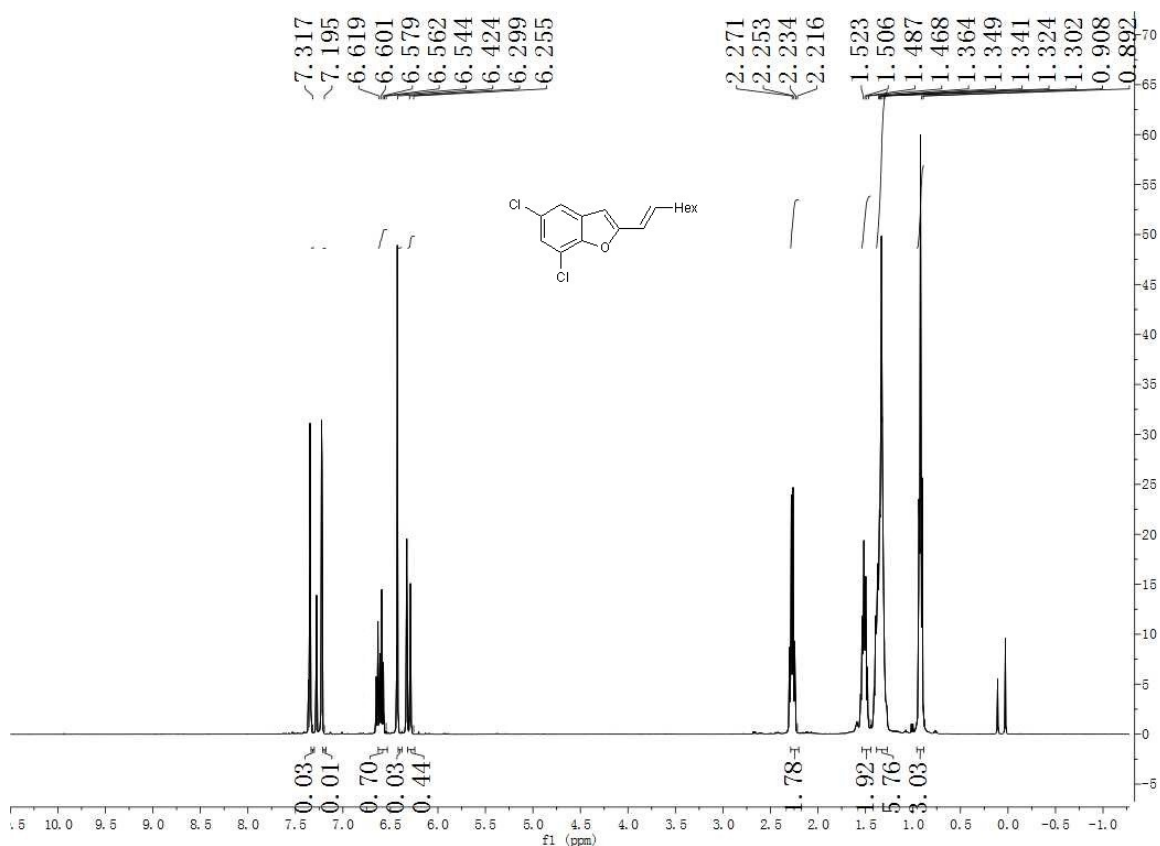
<sup>1</sup>H NMR spectrum of (E)-1-(5-bromobenzofuran-2-yl)oct-1-en-3-one(3ai)



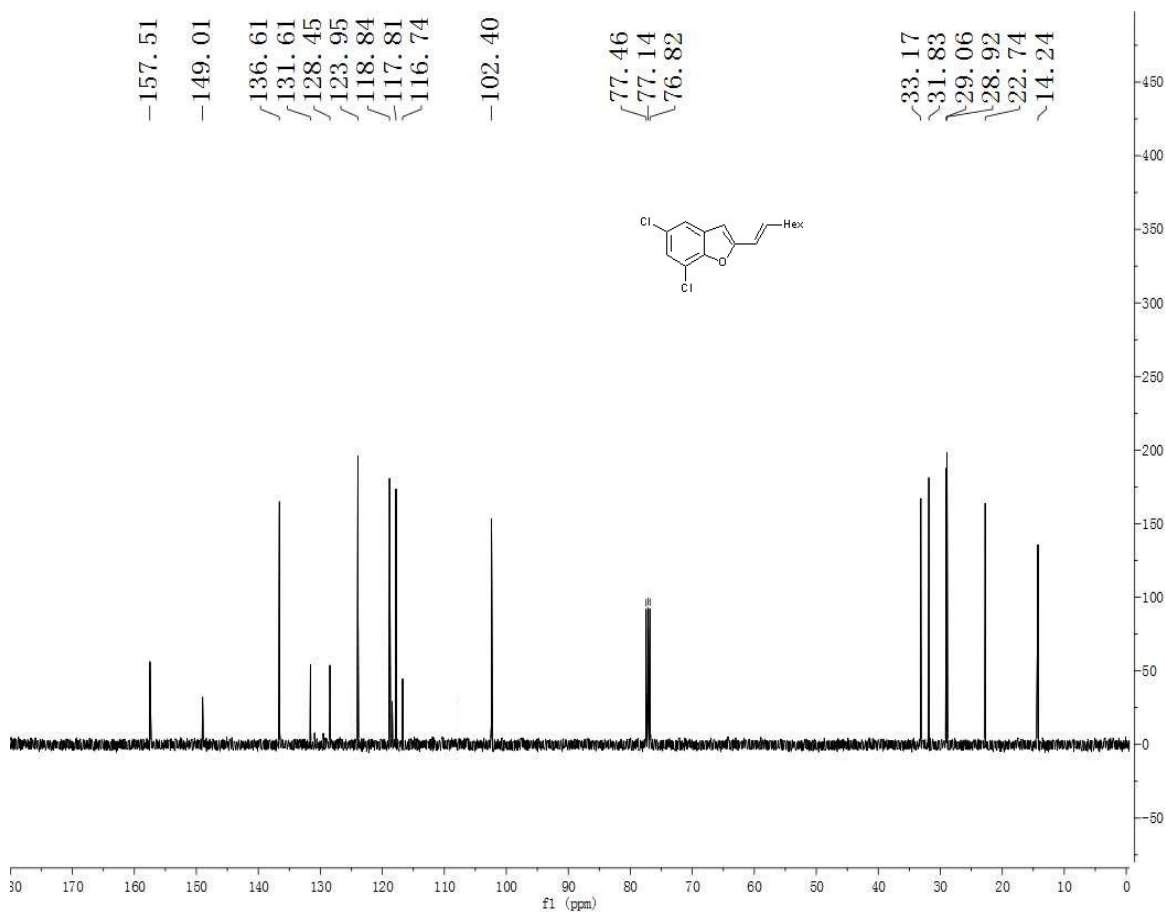
<sup>13</sup>C NMR spectrum of (E)-1-(5-bromobenzofuran-2-yl)oct-1-en-3-one(3ai)



<sup>1</sup>H NMR spectrum of (E)-1-(5,7-dichlorobenzofuran-2-yl)oct-1-en-3-one(**3ak**)

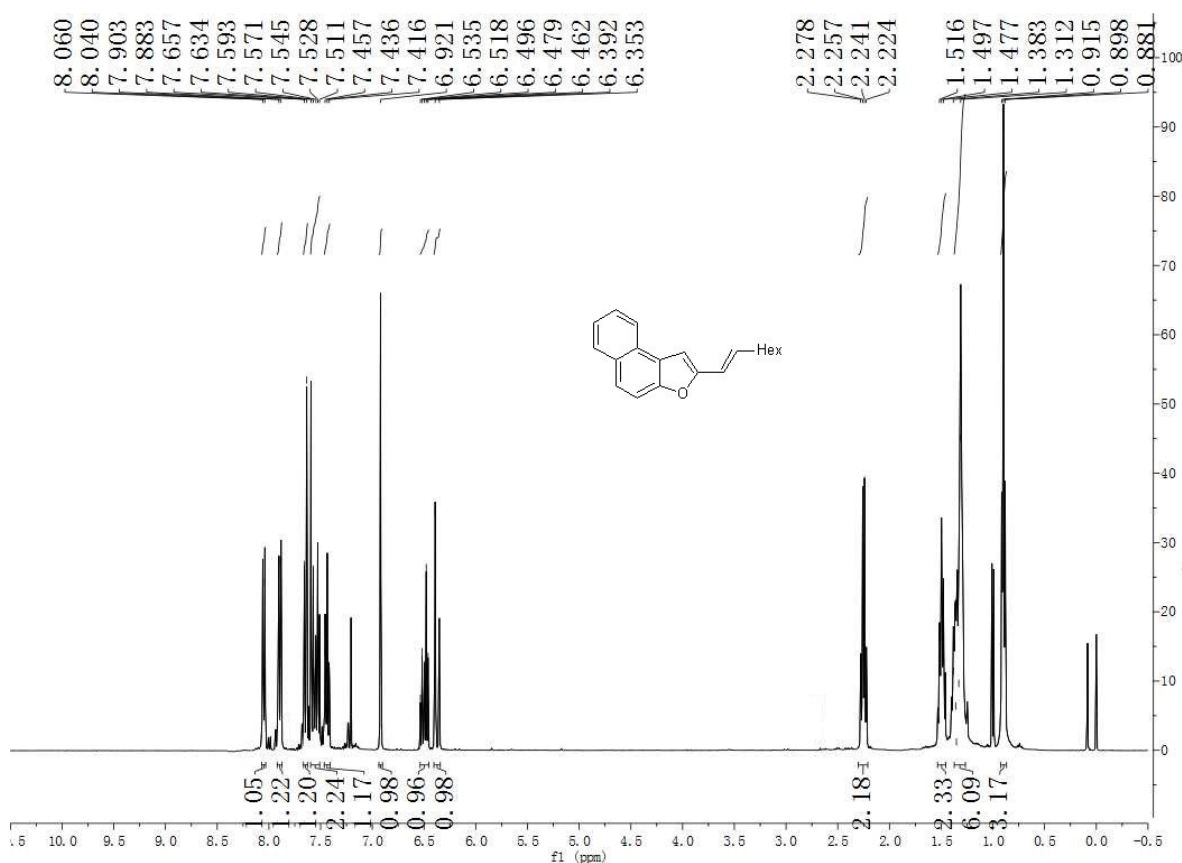


<sup>13</sup>C NMR spectrum of (E)-1-(5,7-dichlorobenzofuran-2-yl)oct-1-en-3-one(**3ak**)

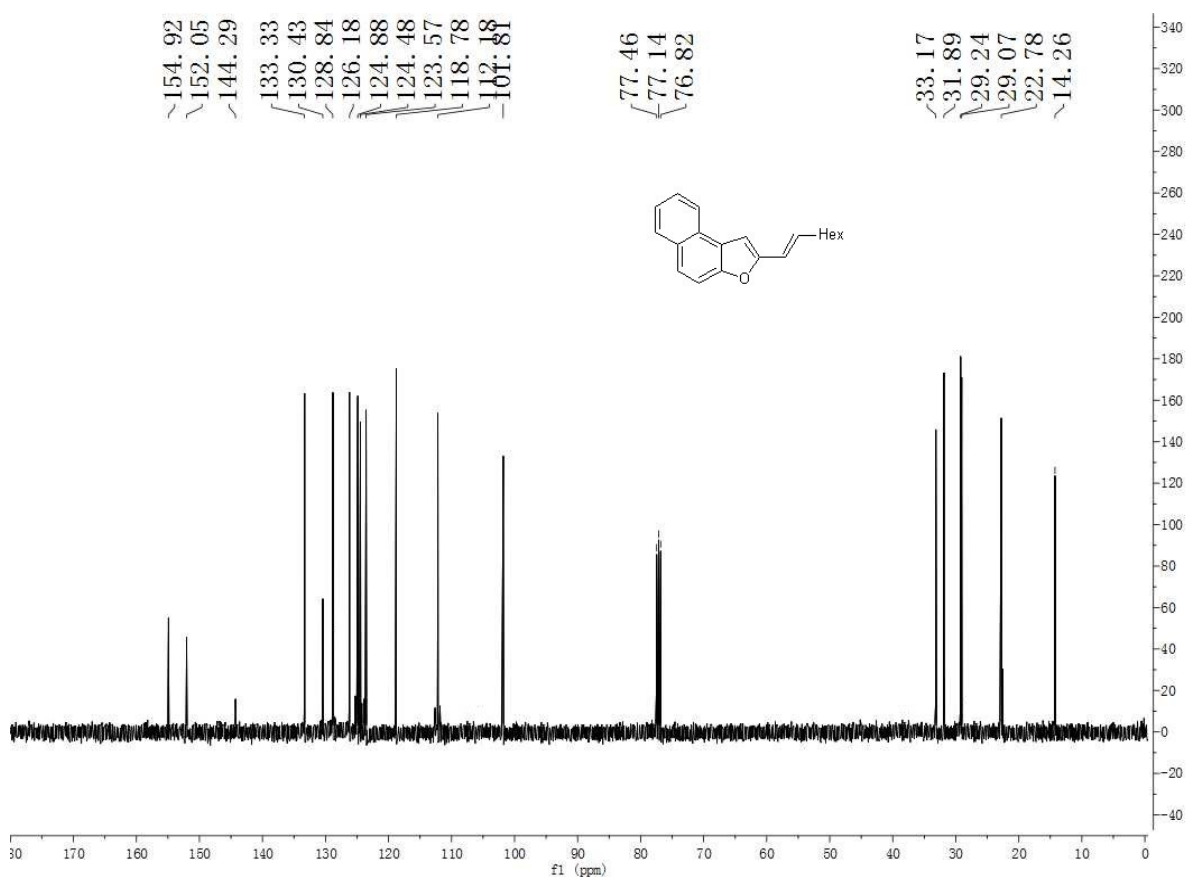




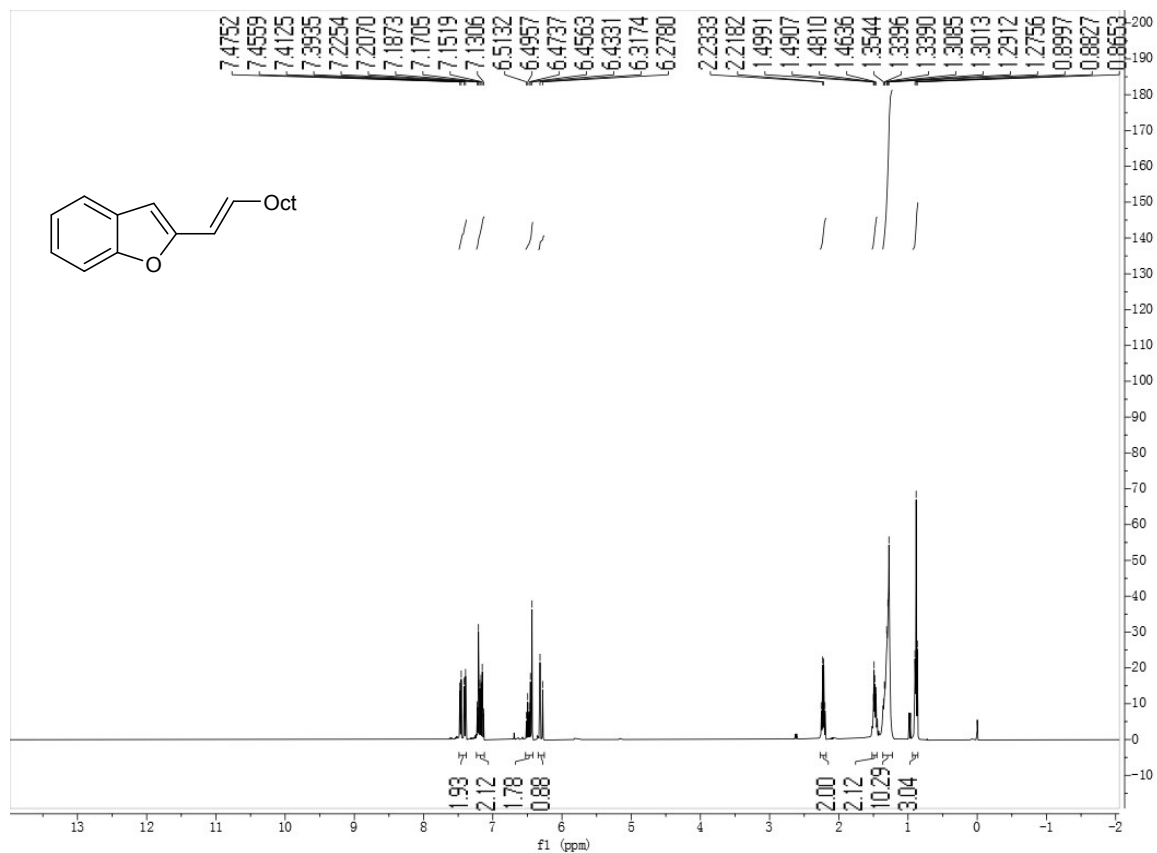
<sup>1</sup>H NMR spectrum of (E)-1-(naphtho[2,1-b]furan-2-yl)oct-1-en-3-one(**3am**)



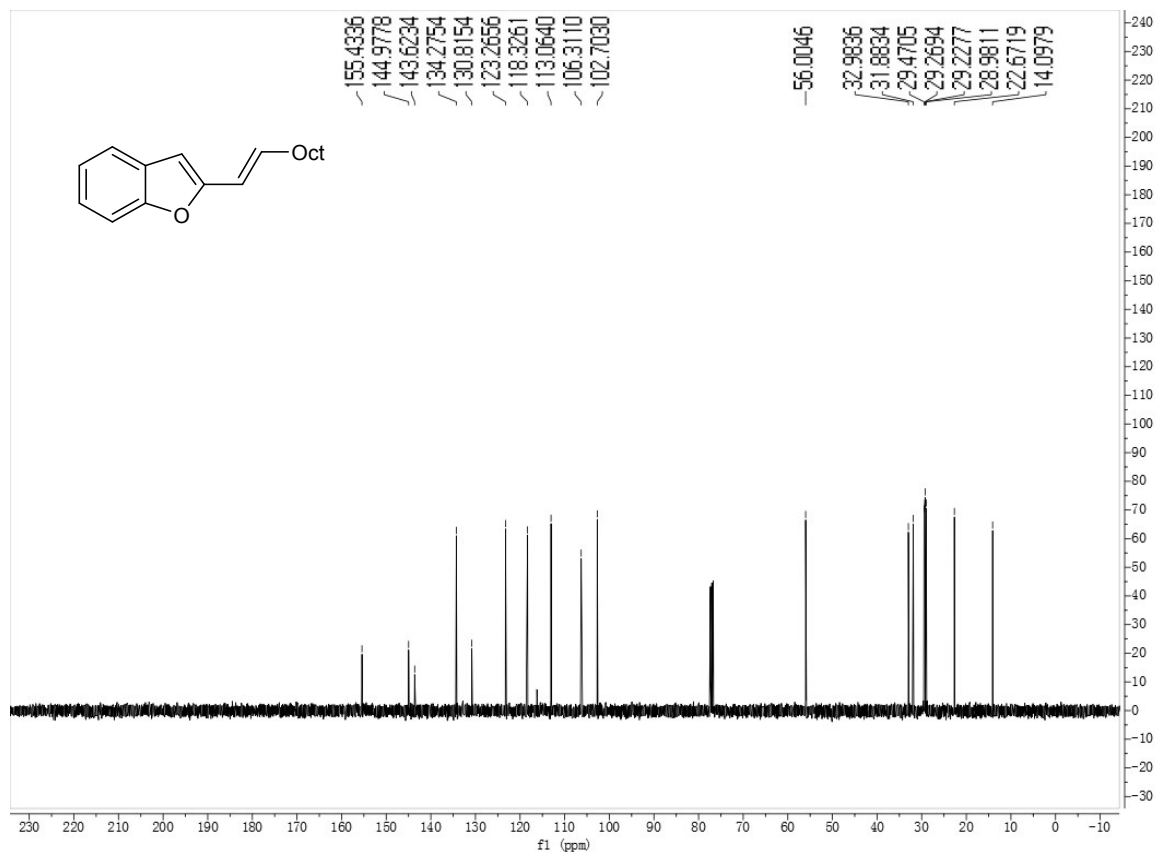
<sup>13</sup>C NMR spectrum of (E)-1-(naphtho[2,1-b]furan-2-yl)oct-1-en-3-one(**3am**)



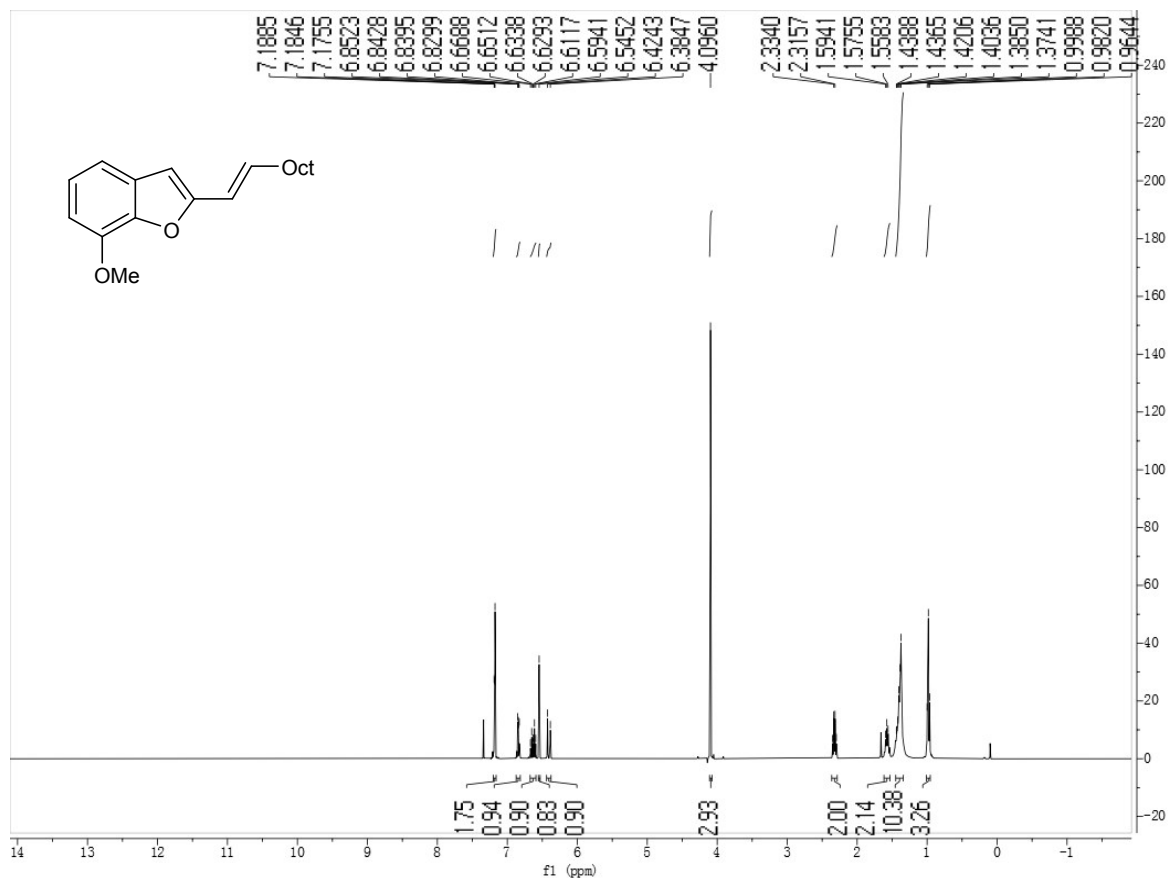
<sup>1</sup>H NMR spectrum of (E)-1-(benzofuran-2-yl)dec-1-en-3-one(**3ba**)



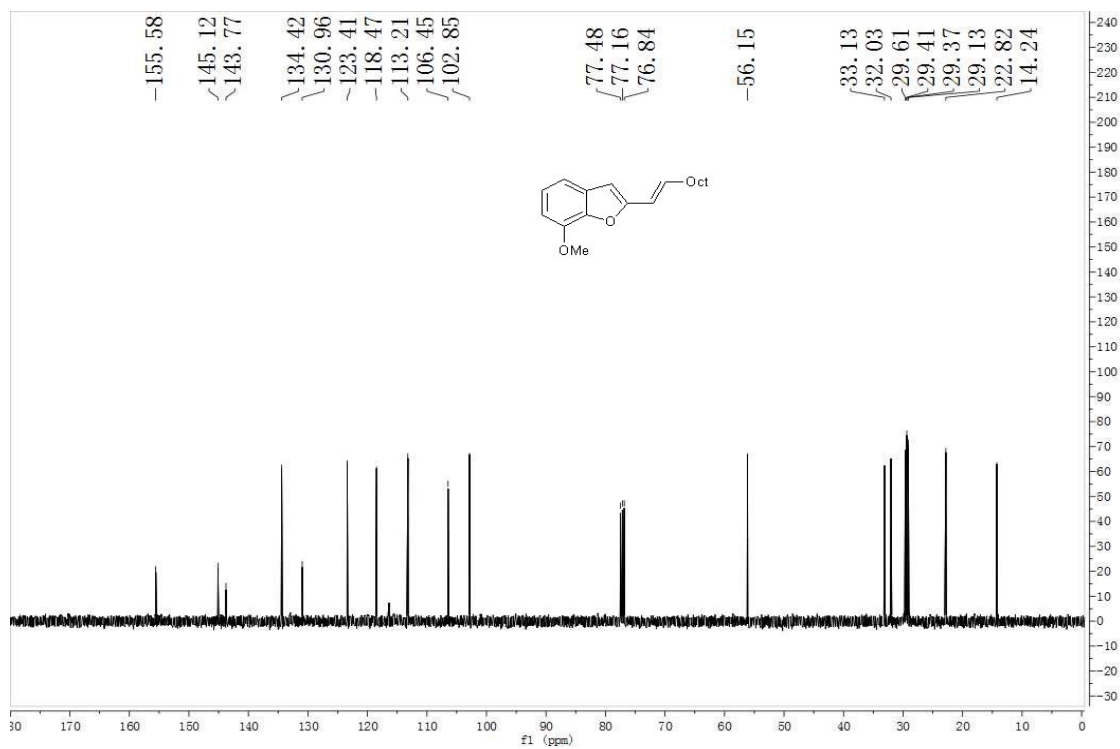
<sup>13</sup>C NMR spectrum of (E)-1-(benzofuran-2-yl)dec-1-en-3-one(**3ba**)



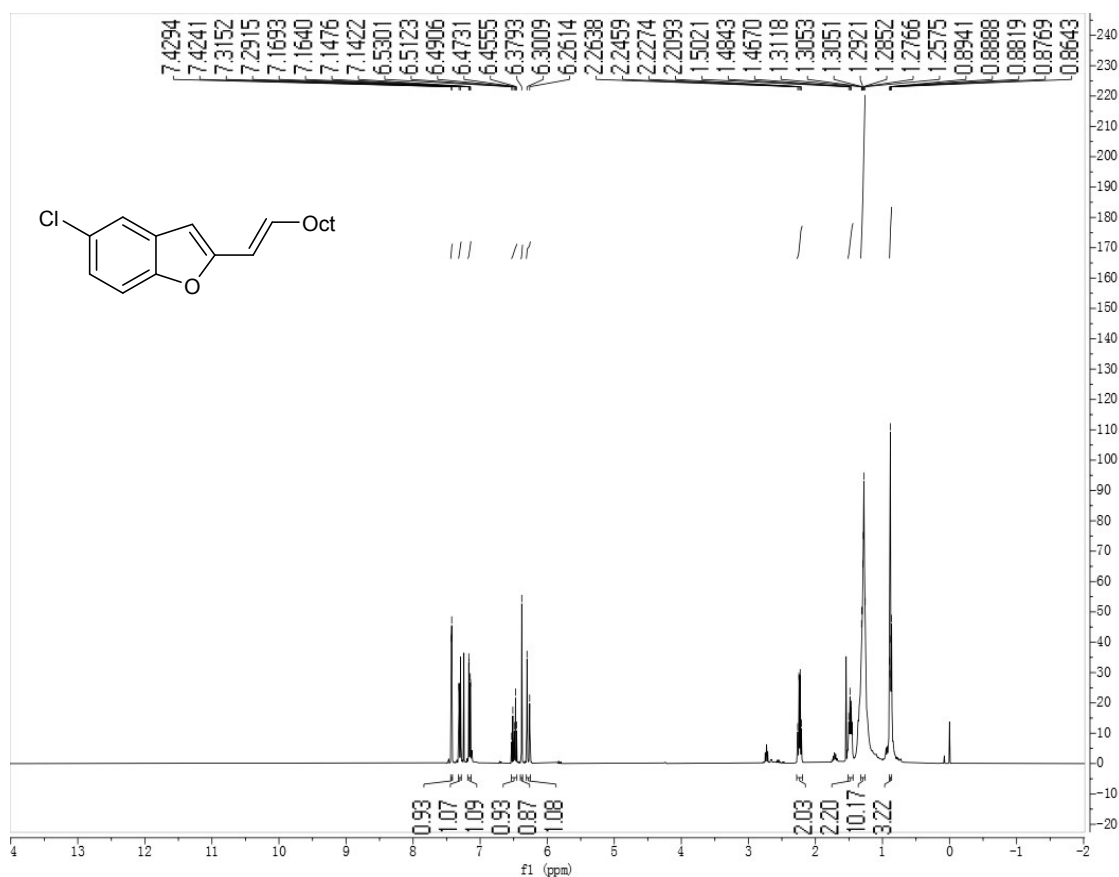
<sup>1</sup>H NMR spectrum of (E)-1-(7-methoxybenzofuran-2-yl)dec-1-en-3-one (**3bf**)



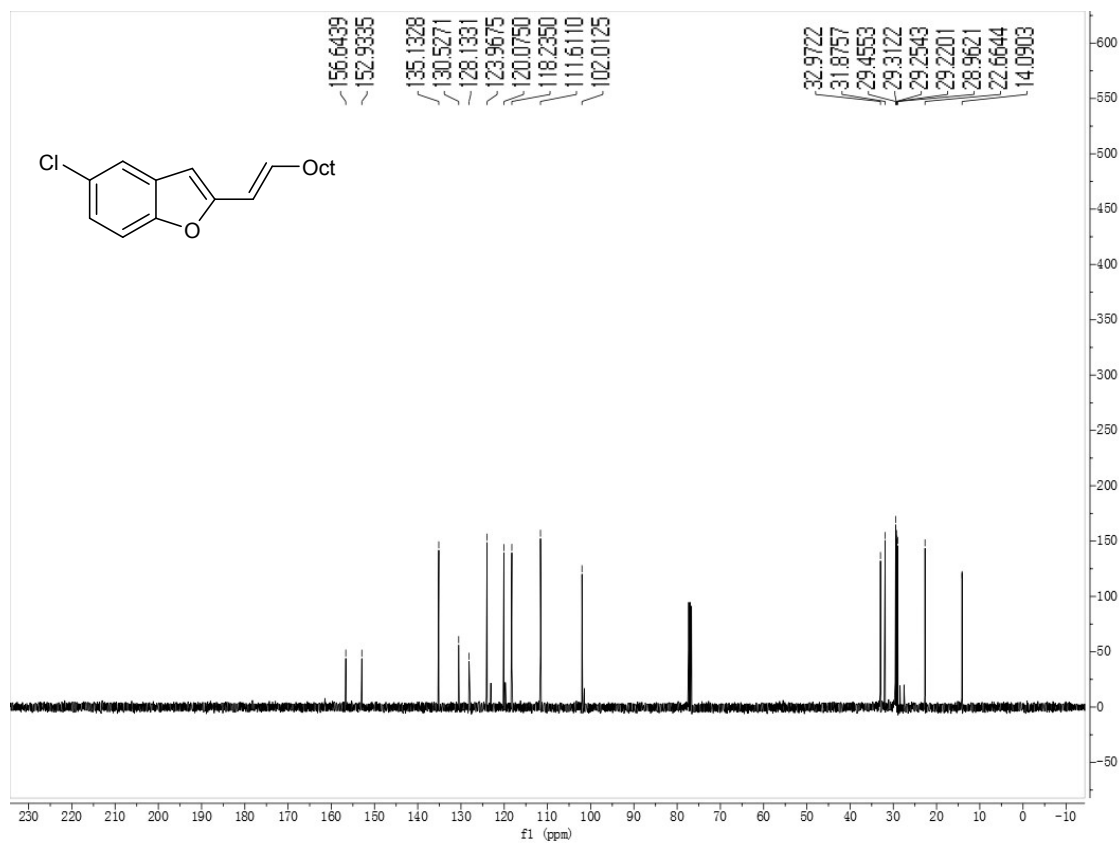
<sup>13</sup>CNMR spectrum of (E)-1-(7-methoxybenzofuran-2-yl)dec-1-en-3-one (**3bf**)



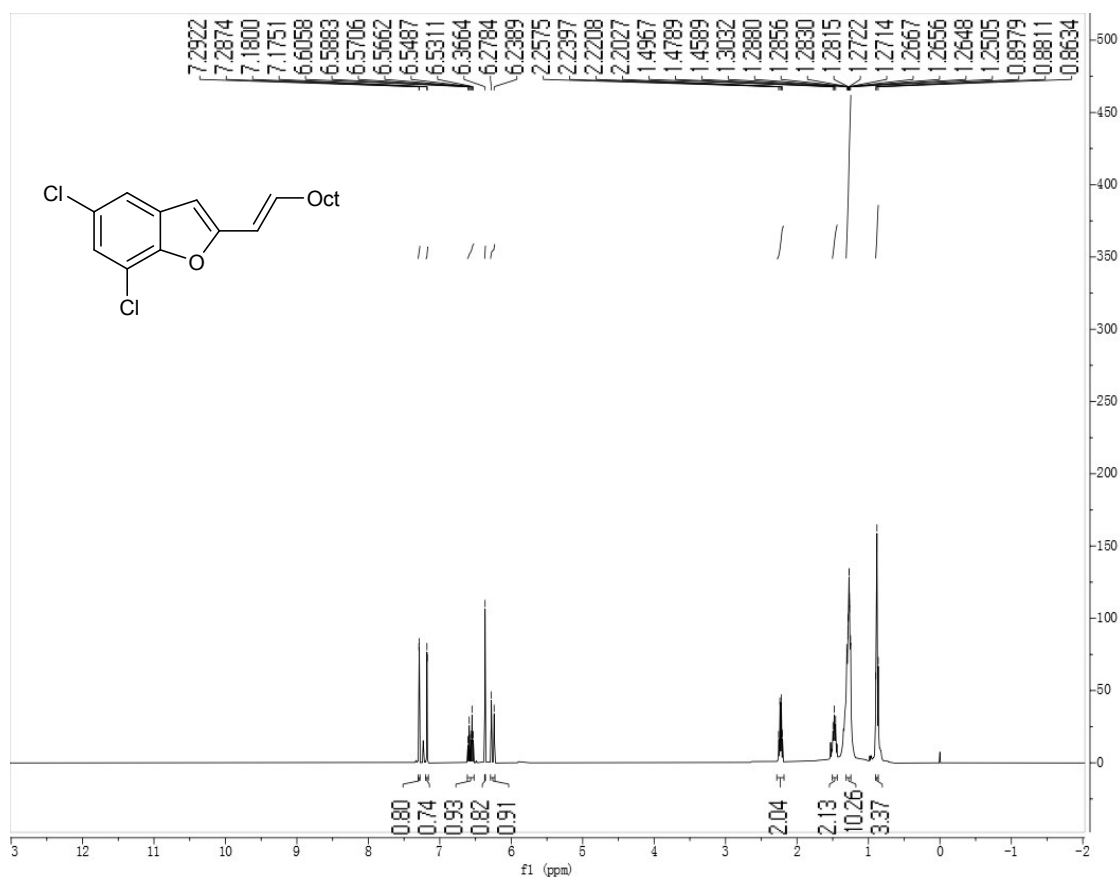
<sup>1</sup>H NMR spectrum of (E)-1-(5-chlorobenzofuran-2-yl)dec-1-en-3-one (**3bh**)



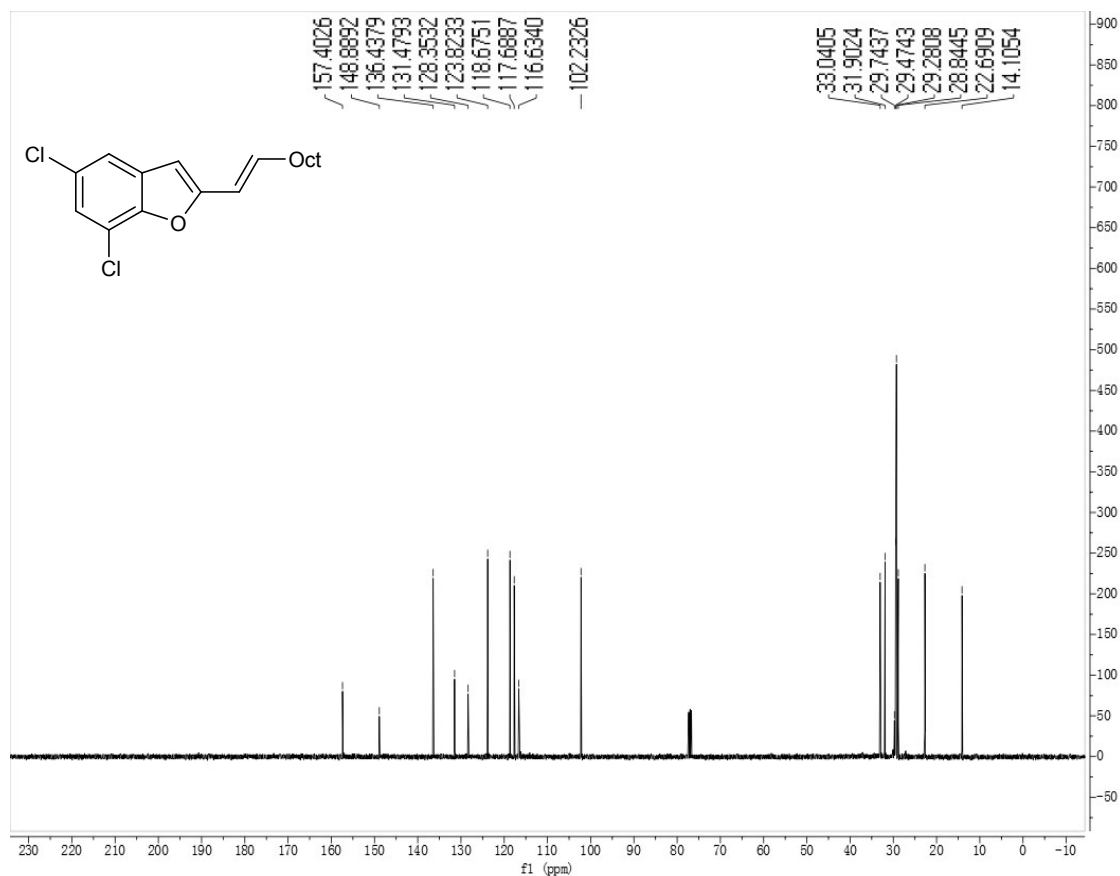
<sup>13</sup>C NMR spectrum of (E)-1-(5-chlorobenzofuran-2-yl)dec-1-en-3-one (**3bh**)



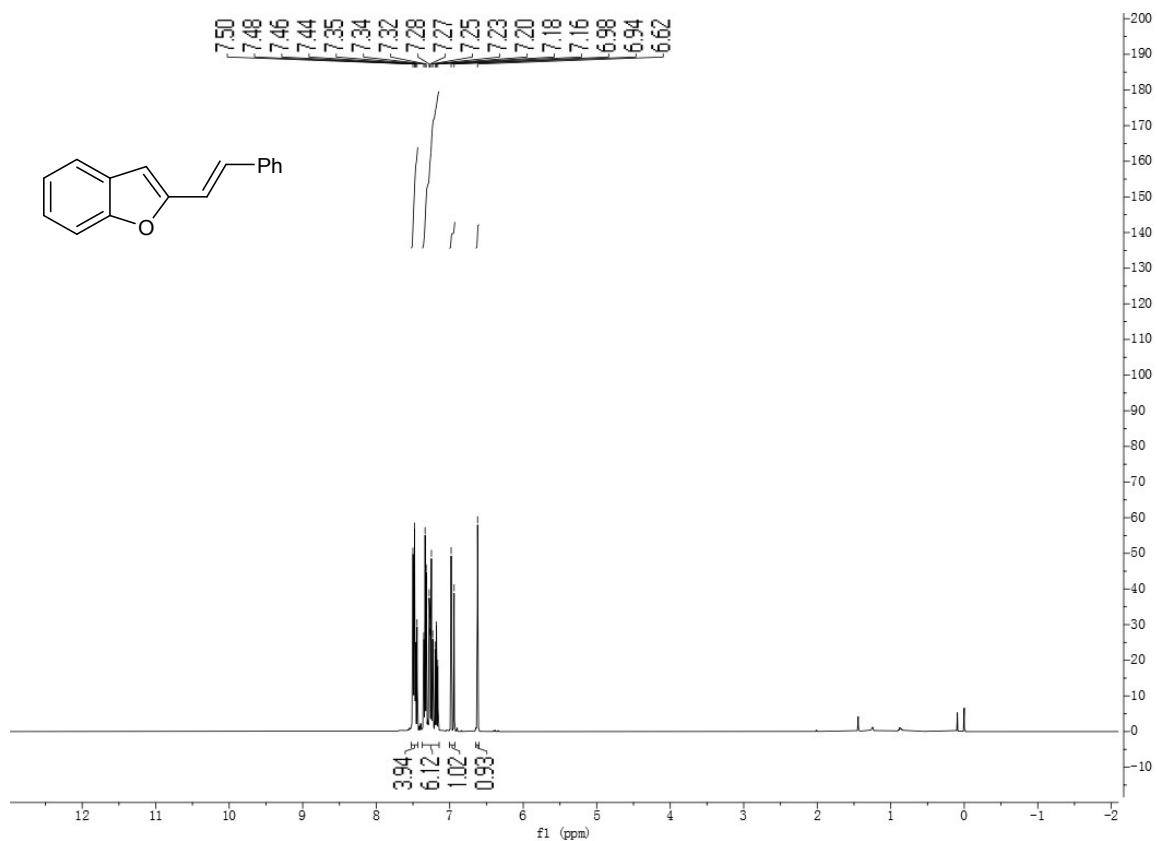
<sup>1</sup>H NMR spectrum of (E)-1-(5,7-dichlorobenzofuran-2-yl)dec-1-en-3-one (**3bk**)



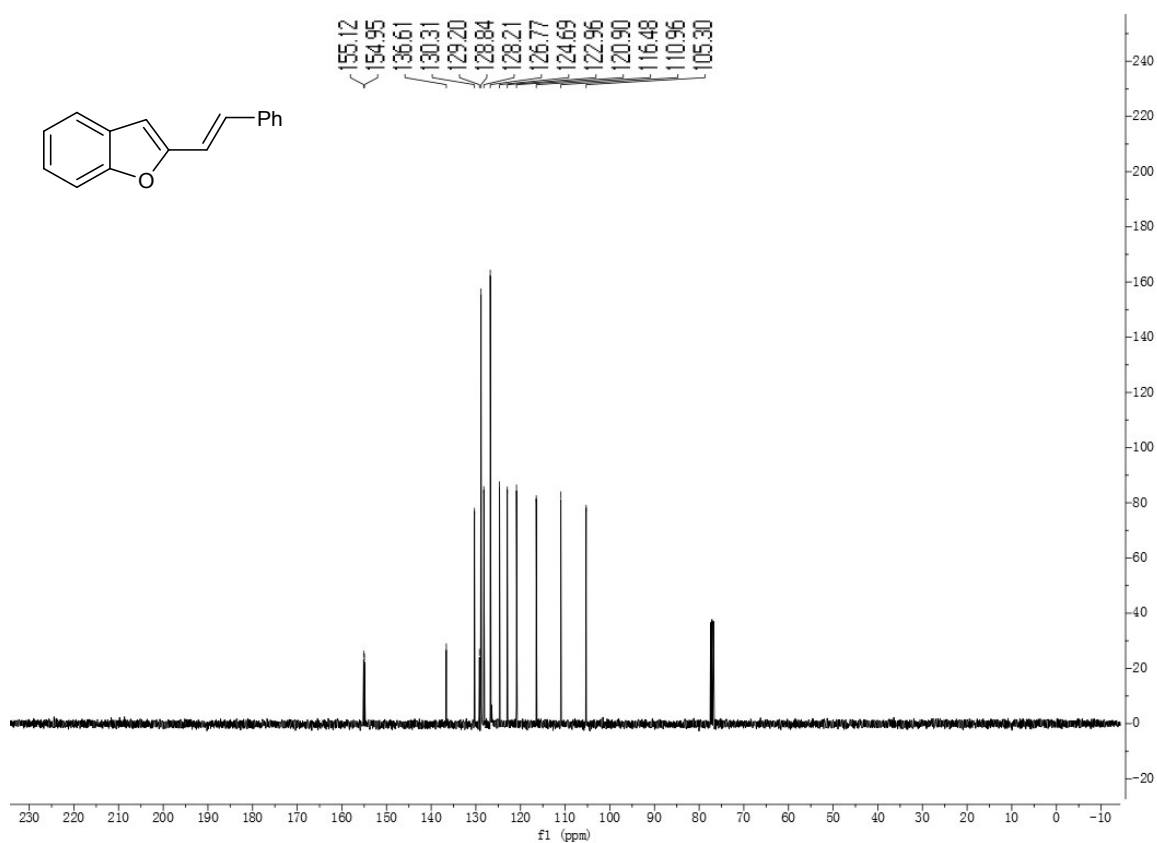
<sup>13</sup>C NMR spectrum of (E)-1-(5,7-dichlorobenzofuran-2-yl)dec-1-en-3-one (**3bk**)



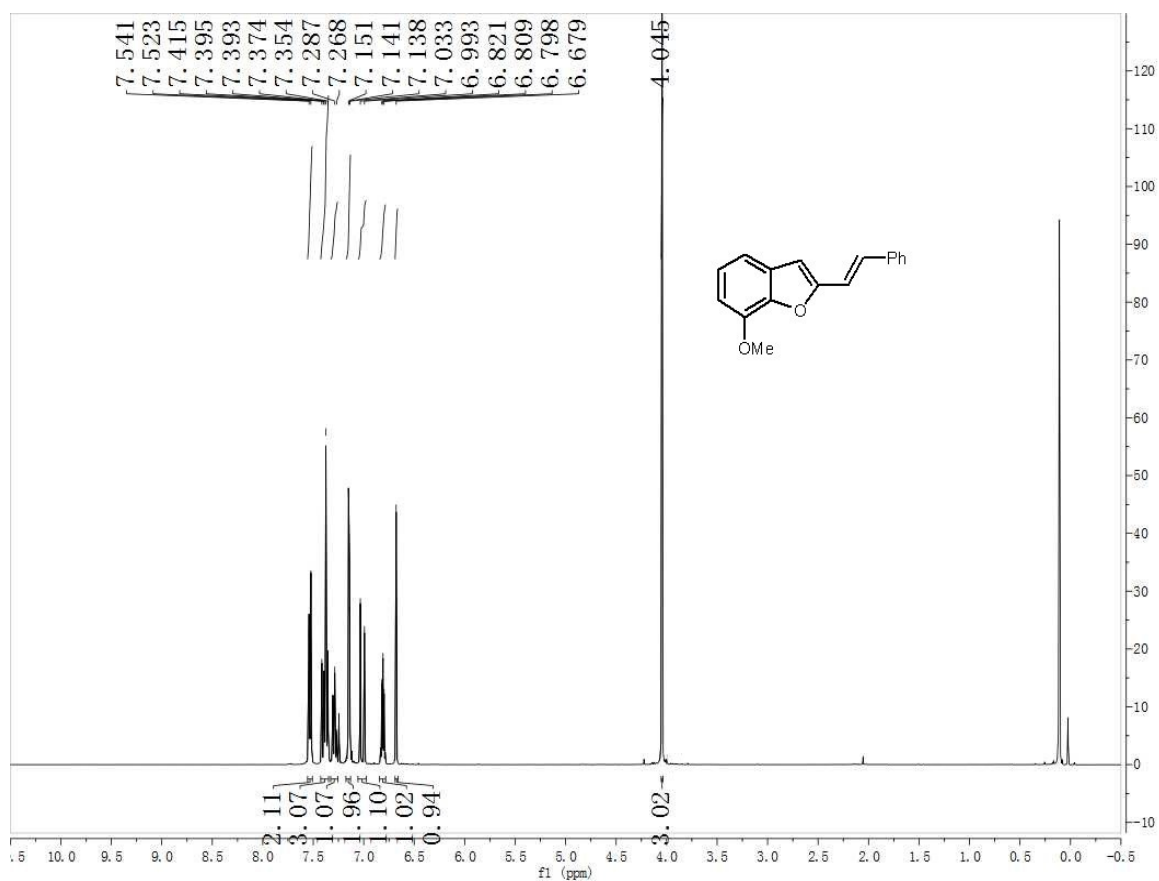
<sup>1</sup>H NMR spectrum of (E)-2-styrylbenzofuran(**3ca**)



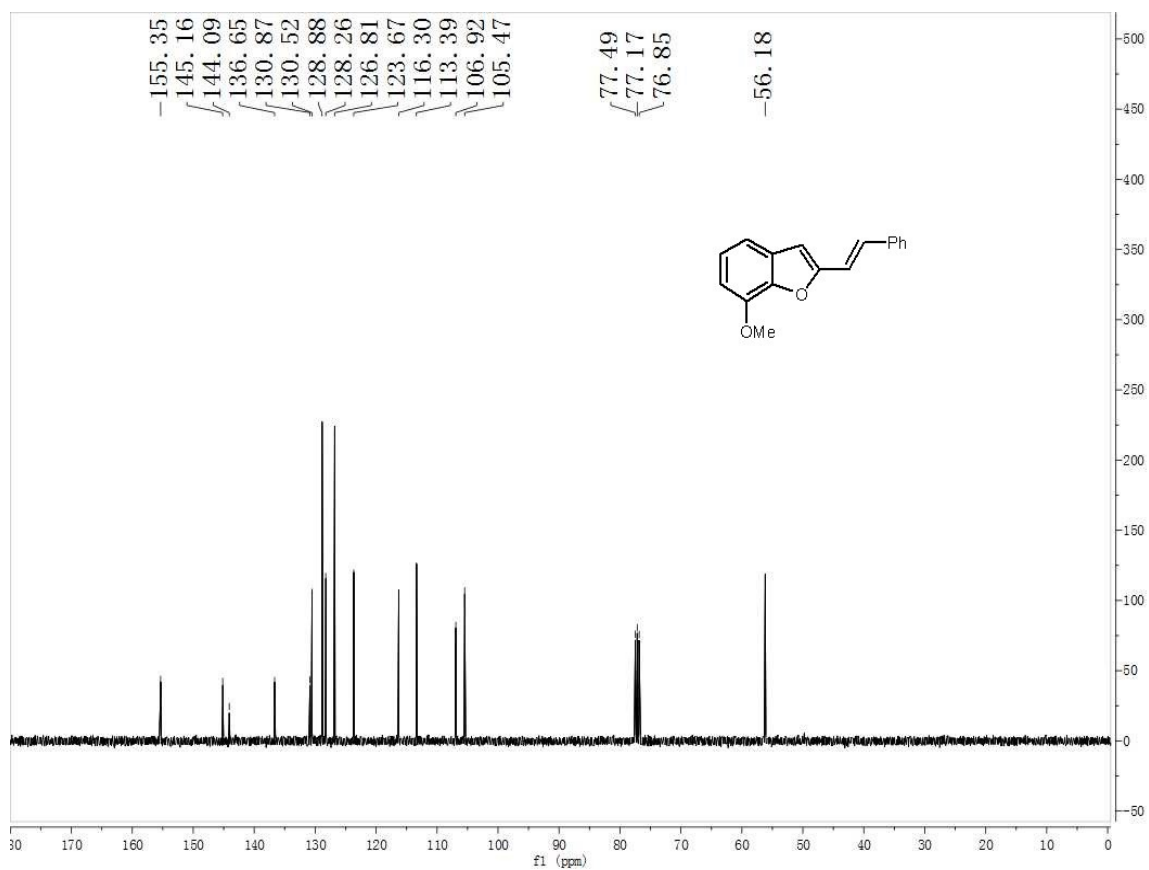
<sup>13</sup>C NMR spectrum of (E)-2-styrylbenzofuran(**3ca**)



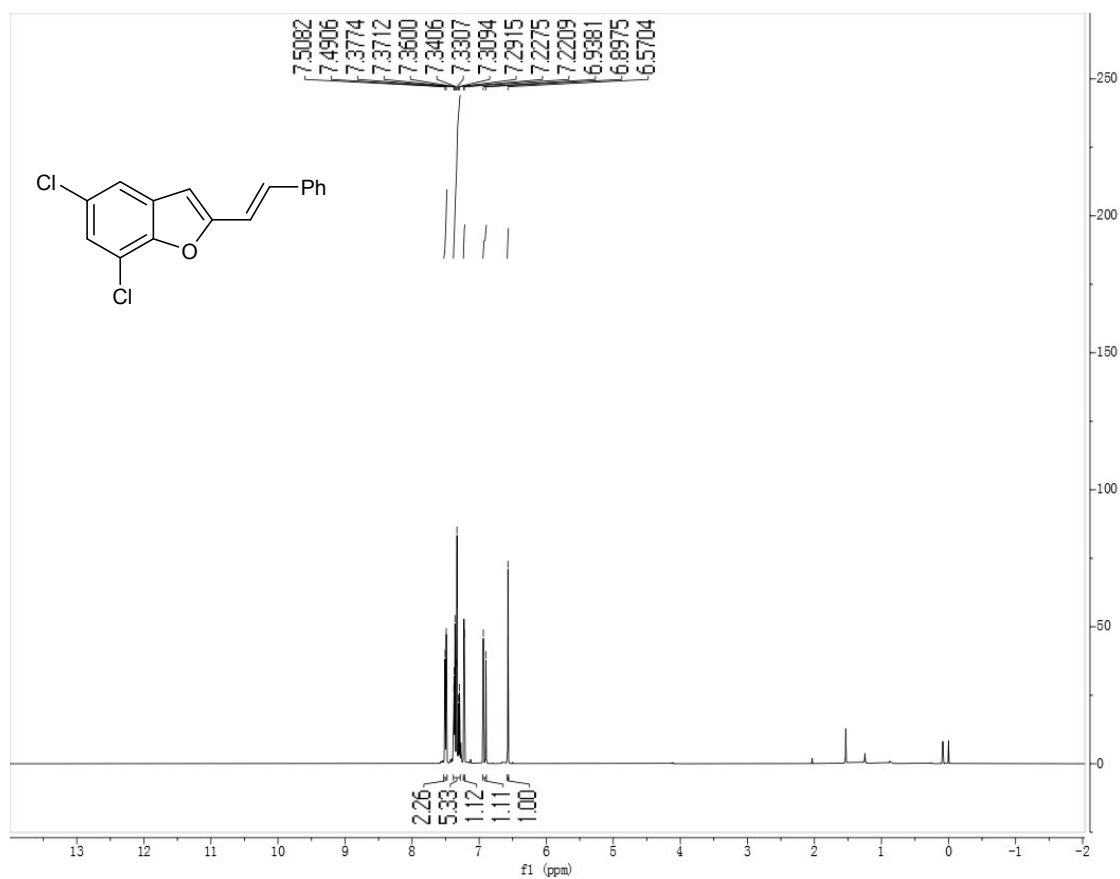
<sup>1</sup>H NMR spectrum of (E)-7-methoxy-2-styrylbenzofuran(**3cf**)



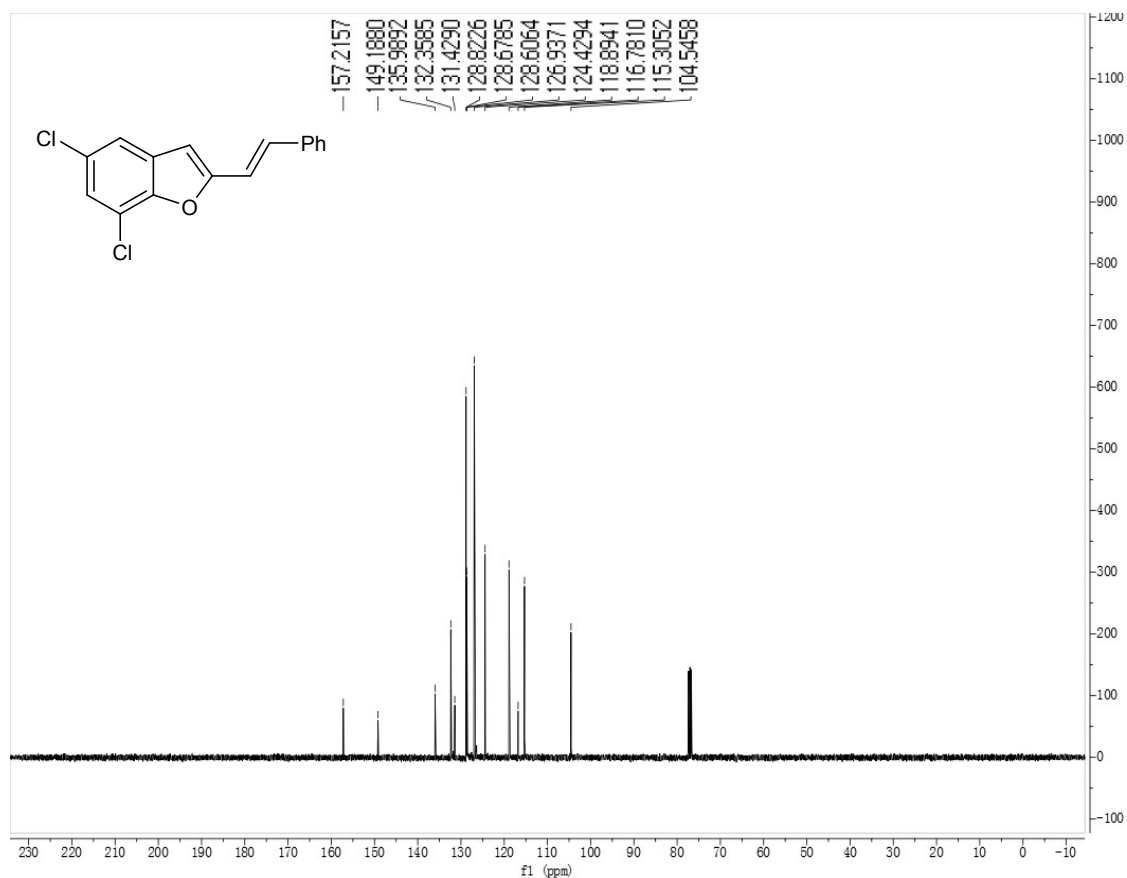
<sup>13</sup>C NMR spectrum of (E)-7-methoxy-2-styrylbenzofuran(**3cf**)



<sup>1</sup>H NMR spectrum of (E)-5,7-dichloro-2-styrylbenzofuran(**3ck**)

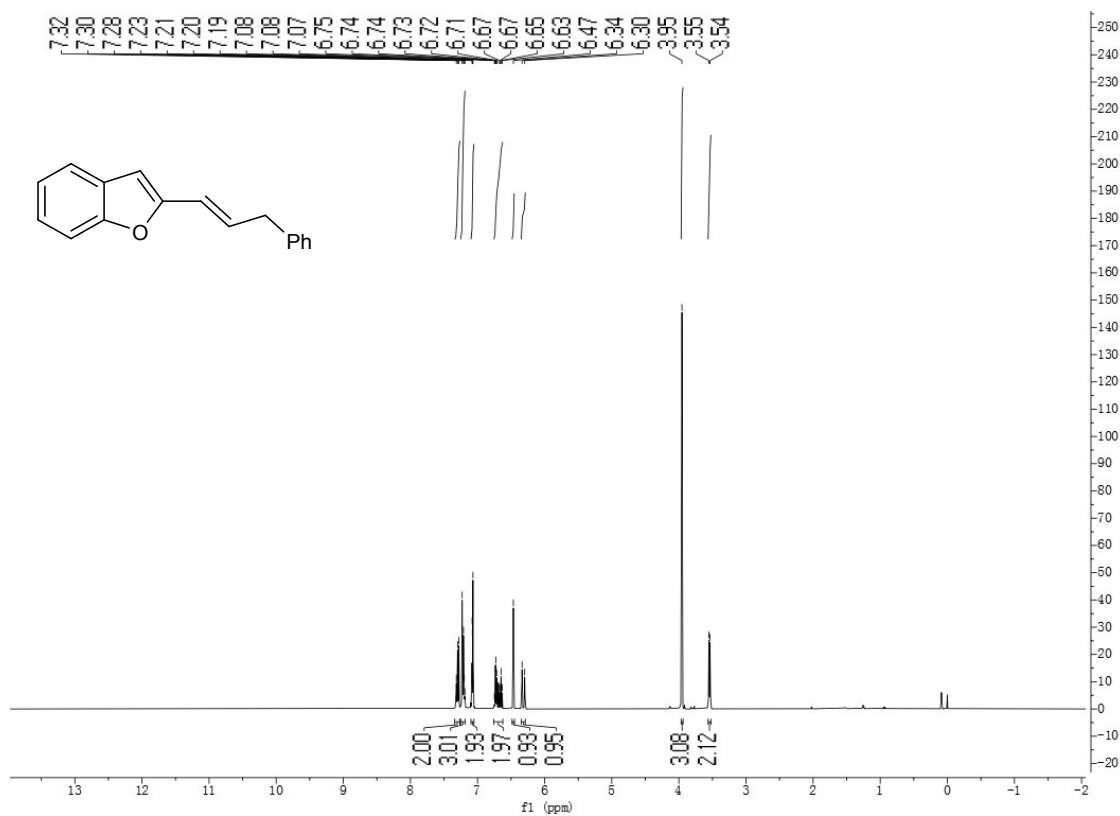


<sup>13</sup>C NMR spectrum of (E)-5,7-dichloro-2-styrylbenzofuran(**3ck**)

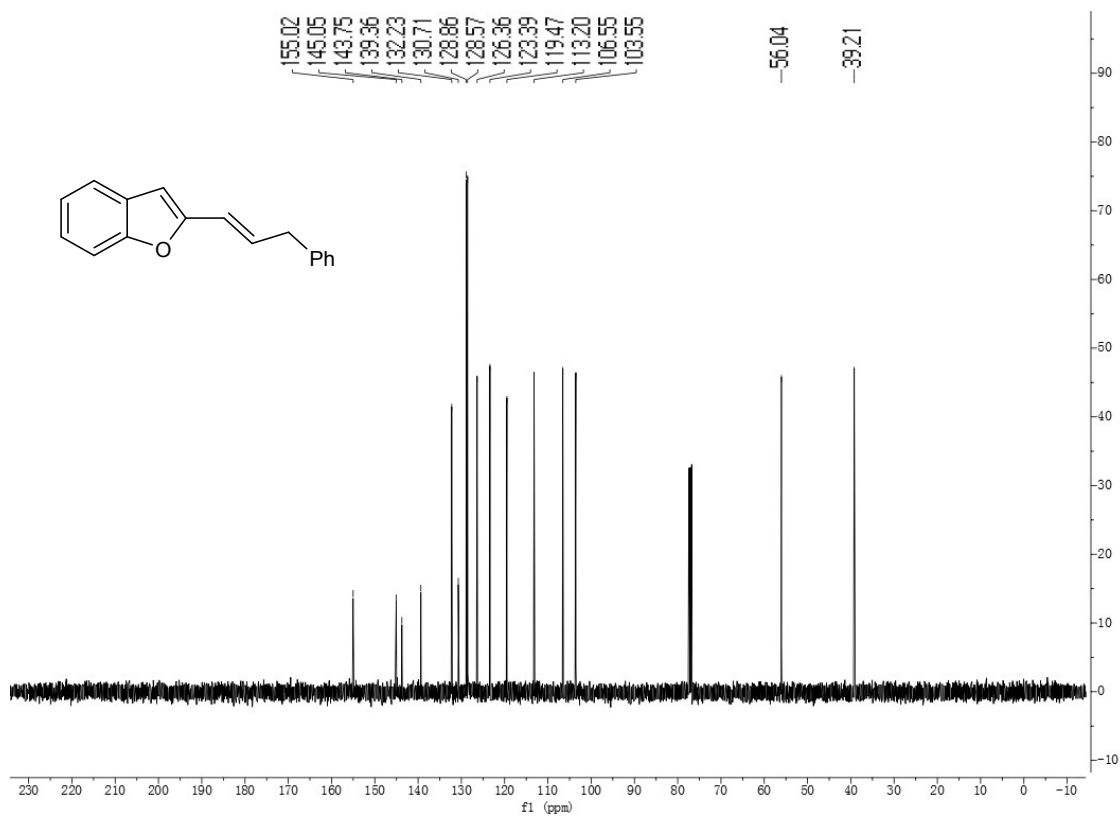




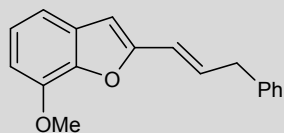
<sup>1</sup>H NMR spectrum of (E)-2-(3-phenylprop-1-en-1-yl)benzofuran(3da)



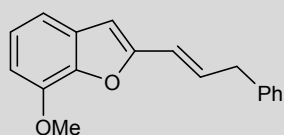
<sup>13</sup>C NMR spectrum of (E)-2-(3-phenylprop-1-en-1-yl)benzofuran(3da)



<sup>1</sup>H NMR spectrum of (E)-7-methoxy-2-(3-phenylprop-1-en-1-yl)benzofuran(**3df**)

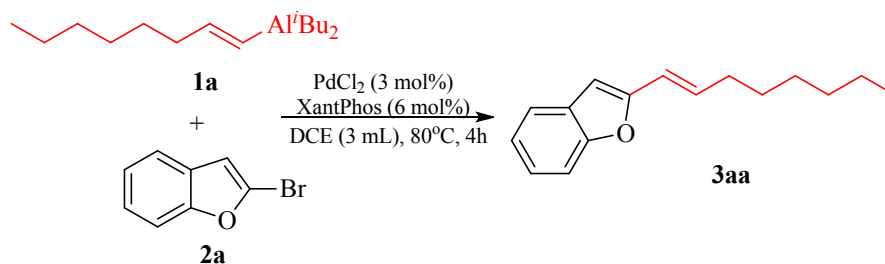


<sup>13</sup>C NMR spectrum of (E)-7-methoxy-2-(3-phenylprop-1-en-1-yl)benzofuran(**3df**)

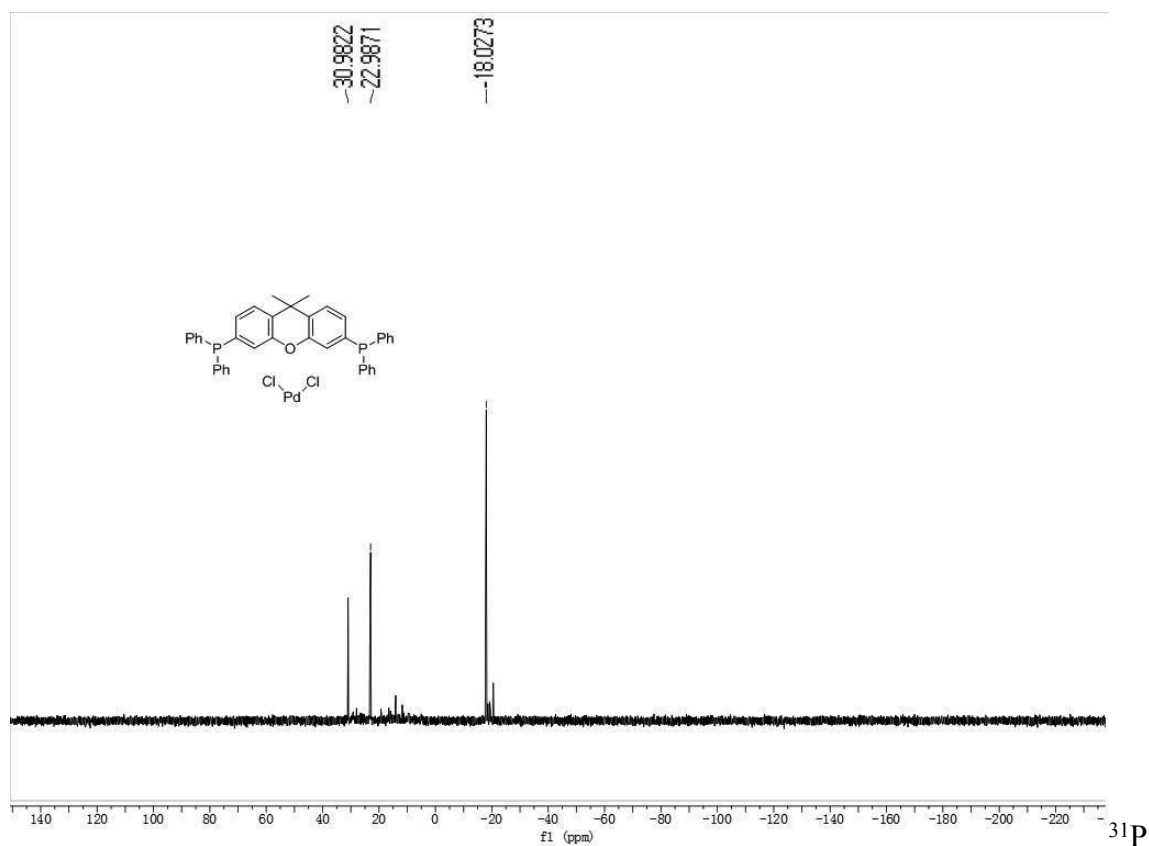


## V. Control experiments

Under a dry nitrogen atmosphere, a mixture of PdCl<sub>2</sub> (0.0026 g, 0.015 mmol) and XantPhos (0.0174 g, 0.03 mmol) in a reaction vessel was added an di-*sec*-butyl(oct-1-enyl)aluminum (**1a**, 0.8 mmol) in 3 mL DCE followed by an addition of 2-bromobenzo[*b*]furan(**2a**, 0.5 mmol). with The resulted solution was stirred at 80 °C for 4 h. The reaction mixture was analyzed by <sup>31</sup>P NMR.



<sup>31</sup>P NMR spectrum of Dichloro[9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene] palladium(II)



NMR spectrum of 4,5-Bis(Diphenylphosphino)-9,9-Dimethylxanthene

