

## Supporting Information

### Phosphinylation/Cyclization of Propynolaldehydes to Isobenzofuranylic Phosphine Oxides Displaying AIE Properties

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## General Information

Column chromatography was carried out on silica gel (200-300 mesh). Reactions were monitored using thin-layer chromatography (TLC) and visualized with UV light at 254 or 365 nm. NMR spectra were recorded on an Agilent Technologies 400 instrument at 400 MHz ( $^1\text{H}$  NMR), 100 MHz ( $^{13}\text{C}$  NMR) and 162 MHz ( $^{31}\text{P}$  NMR) in  $\text{CDCl}_3$ . All products were further characterized by high resolution mass spectra (HRMS) by the ESI technique with a TOF-type analyzer; copies of their  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are provided in the Supporting Information. The X-ray diffraction data for crystallized compounds were collected with  $\text{Mo K}\alpha$  radiation at 296 K using the Bruker D8 venture 400 instrument. Commercial solvents were used without further treatment. The oil bath is used as a heat source.

Absorption spectra were recorded on a YOKU INSTRUMENT TS2023 UV-Vis spectrophotometer. Fluorescence spectra were collected on a HORIBA FLOUROMAX-4 fluorophotometer at 298 K. The lifetimes were measured on an Edinburgh FLS1000 fluorescence spectrophotometer equipped with a continuous xenon lamp (Xe1).

Different IBFPO are highly soluble in DCM, but are hardly dissolved in hexane. The nanoaggregates of the selected IBFPO were prepared by dissolving IBFPO in DCM and then gradually adding hexane as a poor solvent.

And according to the literature, the AIE characteristic of AIEgens is defined as  $\alpha\text{AIE} = I_{\text{agg}} / I_{\text{soln}}$ , where the  $I_{\text{agg}}$  represents PL intensity in aggregation state, and  $I_{\text{soln}}$  represents PL intensity in the pure DCM solution.

Cell imaging tests were carried out on Nikon ECLIPSE Ti2. The OD was detected using BioTek PowerWave XR2.

### Total ROS Detection by DCFH-DA.

The commonly used ROS indicator, 2,7-dichlorodihydrofluorescein diacetate (DCFH-DA), was employed to detect the generation of reactive oxygen species (ROS) in aqueous solutions of **IBFPOs** under white light irradiation ( $100 \text{ mW cm}^{-2}$ ). Briefly, DCFH-DA in 0.5 mL ethanol (1 mM) was added to 2 mL NaOH (10 mM) and placed at room temperature in the dark for 30 min. Then, the ROS indicator (40  $\mu\text{M}$ ) in PBS was

further diluted to a concentration of 5  $\mu\text{M}$  in the sample solution containing **IBFPOs** (10  $\mu\text{M}$ ) for measurement using a PL instrument. The fluorescence emitted by PS-sensitized ROS-triggered conversion of DCFH-DA under white light irradiation was recorded at different time intervals. The PL spectra were measured with excitation at 488 nm and emission collected from 500 to 600 nm. The fluorescence intensity at 525 nm served as an indication of the rate of ROS generation.

#### **Detection of $\text{O}_2^{\cdot-}$ Generation by DHR123.**

The  $\text{O}_2^{\cdot-}$  generation measurements were performed using dihydrorhodamine 123 (DHR123) as an indicator. The stock solution of DHR123 (1 mM) was diluted to 5  $\mu\text{M}$  in the sample solution of **IBFPOs** (10  $\mu\text{M}$ ) in PBS. The fluorescence signal of DHR123 was monitored at different time intervals in a range of 500-600 nm with the excitation wavelength at 488 nm after the solution was irradiated by white light irradiation (100  $\text{mW cm}^{-2}$ ). The fluorescence intensity at 525 nm was recorded to indicate the generation rate of  $\text{O}_2^{\cdot-}$ .

#### **Singlet oxygen ( $^1\text{O}_2$ ) generation.**

For  $^1\text{O}_2$  detection indicated by 9,10-anthracenediyl-bis(methylene)-dimalonic acid (ABDA), the stock solution of ABDA (5 mM) was diluted to 50  $\mu\text{M}$  in the sample solution of **IBFPOs** (10  $\mu\text{M}$ ) in PBS. The absorption spectra of ABDA were monitored in a range of 300-420 nm after the solution was irradiated by white light irradiation (100  $\text{mWcm}^{-2}$ ). The absorbance decrease of ABDA at 378 nm was recorded to indicate the decomposition rates of ABDA.

#### **Cell incubation.**

The cells were incubated in DMEM medium containing fetal bovine serum (10%) and penicillin/streptomycin (1%) at 37°C under a humidified atmosphere containing 5%  $\text{CO}_2$ .

#### **Cell imaging.**



HeLa cells were inoculated in a confocal dish at a concentration of about  $1 \times 10^5$  cells/mL and cultured in a 5% CO<sub>2</sub> humidified incubator at 37°C for 24 h. Then, the culture-medium was removed and new culture-medium containing **IBFPOs** was added and cultured at 37°C with 5% CO<sub>2</sub> 4 h. The AIEgens were excited at a wavelength of 405 nm and their emission spectra were collected within the range of 500-560 nm under confocal fluorescence microscopy.

#### **Co-localization experiments.**

HeLa cells were inoculated in confocal dishes with a concentration of about  $1 \times 10^5$  cells/mL and cultured in a 5% CO<sub>2</sub> humidified incubator at 37°C for 24 h. The culture medium was removed, and a new medium containing **3y** (10 μM) and **3j** (5 μM) was added and cultured at 37°C for 4 h in a humidified atmosphere containing 5% CO<sub>2</sub>. Then, the culture medium was sucked out, cleaned with PBS, and then added to the commercial Nile red tracker to incubate in the cells for 30 minutes. Similarly, the culture medium was removed, and a new medium containing **7a** (10 μM) and **6a** (10 μM) was added and cultured at 37°C for 4 h in a humidified atmosphere containing 5% CO<sub>2</sub>. Then, the culture medium was sucked out, cleaned with PBS, and then added to the commercial BODIPY to incubate in the cells for 30 minutes.

#### **CCK-8 assay.**

HeLa cells were inoculated into 96-well cell culture plates with a density of 8000 cells per well cultured in a 5% CO<sub>2</sub> humidified incubator at 37°C for 24 h. Different concentrations of **IBFPOs** were added to each well, incubated for 1 h, then irradiated with or without white light for 30 min. After the cells were recultured for 1 hour, suck out the medium and add a new medium containing CCK-8 to each well. After 1 h of culture, the optical density of the solution was measured at 450 nm.

HeLa cells were inoculated in 96-well cell culture plates at a density of 8000 cells/well, and incubated at 37°C in a humidified incubator with 5% CO<sub>2</sub> for 24 h. Subsequently, different concentrations of **IBFPOs** were added to each well, incubated for 2 h under normal oxygen conditions, incubated for 10 h under anaerobic conditions, irradiated with or without white light for 30 min. After 24 h incubation, the medium was then

aspirated and replaced with fresh medium containing the CCK-8 reagent. After the cells were recultured for 1 h, the optical density of the solution was measured at the wavelength of 450 nm and the relative cell viability was calculated by the equation:

$$\text{Cell viability (\%)} = (OD_{\text{sample}} - OD_{\text{background}}) / (OD_{\text{control}} - OD_{\text{background}}) \times 100\%$$

**Dead/Live cell co-staining.**

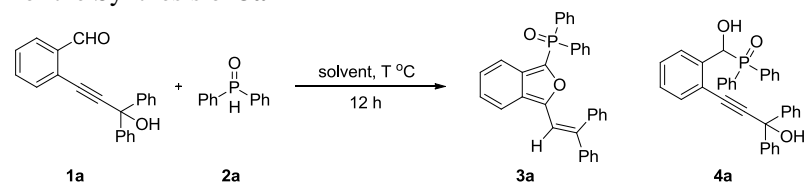
HeLa cells were inoculated in a confocal dish at a concentration of about  $2 \times 10^5$  cells /mL and cultured in a 5% CO<sub>2</sub> humidified incubator at 37°C for 24 h. Different concentrations of **3j** was added to confocal dish, incubated for 1 hour, then irradiated with white light for 30 min. After 24 h incubation, HeLa cells were stained with Calcein AM and Propidium Iodide Detection Kit.

## Experimental Section:

### Optimization of the Reaction Conditions

2-(3-hydroxy-3,3-diphenylprop-1-yn-1-yl)benzaldehyde **1a** and diphenylphosphine oxide **2a** were utilized as model substrates to optimize the reaction conditions (Table S1).

Table S1. Optimization of Tandem Cyclization for the Synthesis of **3a**<sup>a</sup>

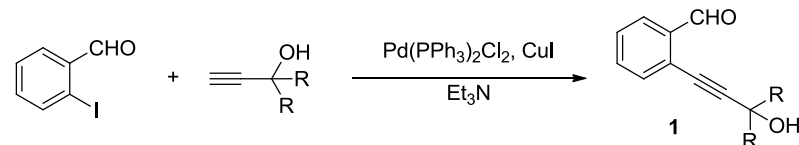


Entry	temperature (°C)	Solvent	Yield <sup>b</sup> (%)	
			<b>3a</b>	<b>4a</b>
1	110	toluene	76	13
2	80	DMF	trace	86
3	65	THF	trace	87
4	80	1,4-Dioxane	trace	85
5	40	DCM	trace	86
6	60	HCCl <sub>3</sub>	28	61
7	80	EtOH	44	45
8	80	CH <sub>3</sub> CN	40	38
9	80	AcOH	83	10
10	80	DCE	90	trace
11 <sup>c</sup>	80	DCE	90	trace
12 <sup>d</sup>	80	DCE	82	10
13 <sup>e</sup>	80	DCE	91	trace
14 <sup>f</sup>	80	DCE	91	trace
15 <sup>g</sup>	80	DCE	59	30
16 <sup>f,h</sup>	60	DCE	52	34
17 <sup>f,i</sup>	100	DCE	82	7

<sup>a</sup>The reaction was conducted with **1a** (0.2 mmol), **2a** (0.6 mmol) in solvent (3 mL), 12 h. <sup>b</sup>Isolated yield based on **1a**. <sup>c</sup>for 18 h. <sup>d</sup>for 6 h. <sup>e</sup>**2a** (0.40 mmol). <sup>f</sup>**2a** (0.30 mmol). <sup>g</sup>**2a** (0.2 mmol). <sup>h</sup>at 60 °C. <sup>i</sup>at 100 °C.

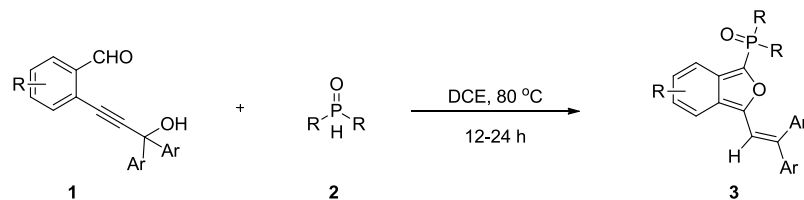
We used 2-(3-hydroxy-3,3-diphenylprop-1-yn-1-yl)benzaldehyde **1a** and diphenylphosphine oxide **2a** as template substrates for condition optimization (Table S1). To our delight, the phosphorylation reaction of **1a** with **2a** occurred successfully in toluene system without metal catalysts at 110°C for 12 h, and produced the cyclic product (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide **3a** in 76% yield, along with the nucleophilic addition byproduct (hydroxy(2-(3-hydroxy-3,3-diphenylprop-1-yn-1-yl)phenyl)methyl)diphenylphosphine oxide **4a** in 13% yield (entry 1). The structure of **3a** was unambiguously confirmed by X-ray crystallographic analysis.<sup>35</sup> In order to improve the conversion from the addition product **4a** to the desired product **3a**, we investigated the effect of solvents on the tandem cyclization. DMF, THF, 1,4-dioxane and DCM gave **4a** in good yield and trace amount of **3a** (entries 2-5). When CHCl<sub>3</sub>, EtOH and CH<sub>3</sub>CN were used, they all yielded the target product **3a**, but their conversion efficiencies were not satisfactory (entries 6-8). Then, we used AcOH and DCE as solvents and their results showed the yield of **3a** was increased to 83% and 90%, respectively (entries 9-10). Next, using DCE as the best solvent, we studied the effect of reaction time on reaction efficiency. It was found that the yield of **3a** was not improved further by prolonging reaction time to 18 h (entry 11). However, shortening the reaction time to 6 h reduces the yield (entry 12). To enhance the utilization of **2a**, reducing the amount of **2a** to 1.5 or 2 equivalents gave a better result (entries 13-14). However, when 1.0 equivalent of **2a** was used, the yield of **3a** was decreased to 59% (entry 15). Additionally, varying the reaction temperature did not help to increase the efficiency of phosphine oxide-triggered tandem cyclization (entries 16-17). Finally, a 1:1.5 equivalent ratio of **1a** and **2a** in DCE at 80 °C for 12 h was the optimal condition (entry 14).

## General Procedure for the Synthesis of *o*-Propargyl Alcohol Benzaldehydes **1v–1y**



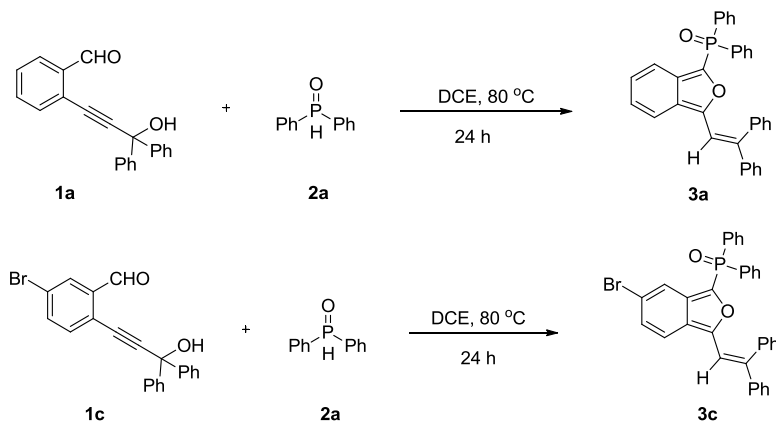
To a solution of 2-iodobenzaldehyde (5 mmol) in triethylamine (Et<sub>3</sub>N) (5 mL) was added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (4 mol %) and CuI (2 mol %). The reaction vial was flushed with Ar, and the reaction mixture was stirred for 5 min. A solution of arylpropargyl alcohol (5 mmol) in Et<sub>3</sub>N (5 mL) was then added dropwise by a syringe over 5 min. The resulting solution was stirred at room temperature overnight. After the completion of reaction, as determined by TLC analysis, the mixture was quenched by adding saturated aqueous ammonium chloride solution (10 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude material was purified by flash column chromatography to afford **1v–1y**.

## Experimental Procedure for Compounds 3a-3y and 3aa-3ah



To a solution of 2-(3-hydroxy-3,3-diarylprop-1-yn-1-yl)benzaldehyde **1** (0.20 mmol, 1 equiv.) and phosphine oxides **2** (0.30 mmol, 1.5 equiv.) in DCE (3.0 mL) at 80°C for 12-24 h. When the reaction was completed, the reaction mixture was evaporated under reduced pressure. The residue was purified by chromatography on silica gel (eluted with dichloromethane/ethyl acetate, 20:1 - 2:1) to afford corresponding (3-(2,2-diarylvinyl)isobenzofuran-1-yl)diarylphosphine oxides **3**.

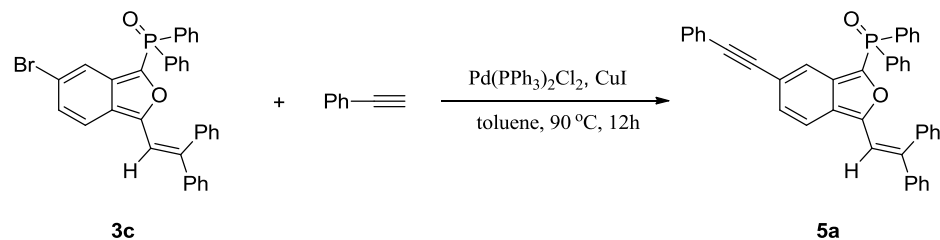
### General Procedure for the Scale-up Reaction of Compound 3



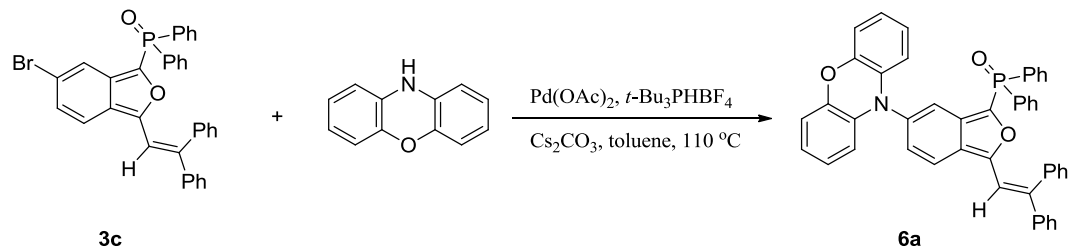
To a solution of 2-(3-hydroxy-3,3-diphenylprop-1-yn-1-yl)benzaldehyde **1a** (5.0 mmol, 1.56 g) and diphenylphosphine oxide **2a** (7.5 mmol, 1.515 g) in DCE (50 mL) at 80°C for 24 h. When the reaction was completed, the reaction mixture was evaporated under reduced pressure. The residue was purified by chromatography on silica gel (eluted with dichloromethane/ethyl acetate, 20:1) to afford a 87% yield of product (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide **3a** (4.37 mmol, 2.17 g).

To a solution of 2-(3-hydroxy-3,3-diphenylprop-1-yn-1-yl)benzaldehyde **1c** (5.0 mmol, 1.95 g) and diphenylphosphine oxide **2a** (7.5 mmol, 1.515 g) in DCE (50 mL) at 80°C for 24 h. When the reaction was completed, the reaction mixture was evaporated under reduced pressure. The residue was purified by chromatography on silica gel (eluted with dichloromethane/ethyl acetate, 20:1) to afford a 77% yield of product **3c** (3.85 mmol, 2.21 g).

### General steps of the derivatization reaction of **3c**



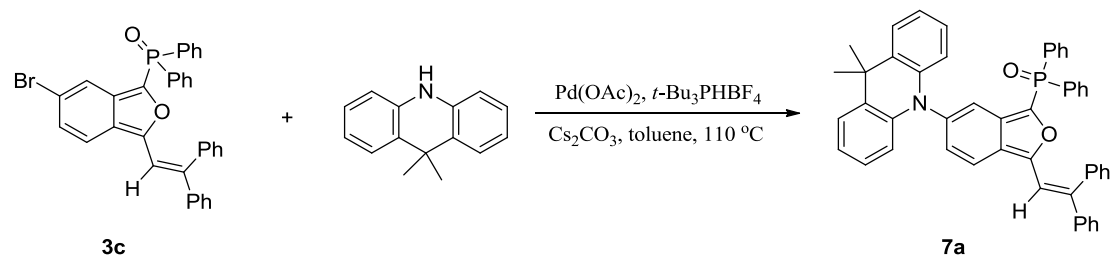
In a 20 mL pressure tube was added **3c** (114.8 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (2.8 mg, 0.004 mmol), CuI (0.9 mg, 0.008 mmol). The tube was filled with argon, then toluene (3 mL) and ethynylbenzene (20.4 mg, 0.2 mmol) was added to the tube, the mixture was heated 90 °C for 12 h. When the reaction was completed after, the reaction mixture was then cooled to room temperature quenched by addition of saturated ammonium chloride solution and extracted with ethyl acetate (3 x 10 mL), washed with water, saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The residue was purified by chromatography on silica gel (eluted with dichloromethane/ethyl acetate, 20:1) to afford the corresponding product **5a** (95 mg, 0.159 mmol) in 80% yield.



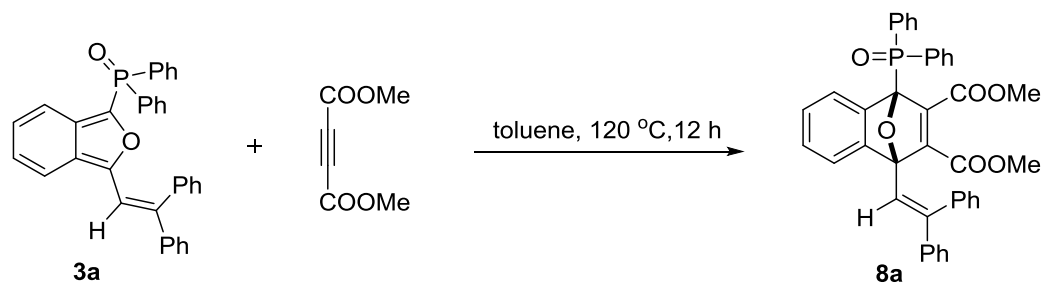
A mixture of **3c** (114.8 mg, 0.2 mmol), phenoxazine (55 mg, 0.3 mmol), cesium carbonate (131 mg, 0.4 mmol), palladium (II) acetate (4.6 mg, 0.02 mmol), *t*-Bu<sub>3</sub>PHBF<sub>4</sub> (12.0 mg, 0.04 mmol) and dry-toluene (5 mL), and heated under an argon atmosphere 110 °C for 8 h. After the mixture was cooled to room temperature, water (3 mL) and EtOAc (3 x 10 mL) were added. The organic layer was separated and washed with brine,



dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluted with dichloromethane/ethyl acetate, 20:1) to afford the corresponding product **6a** as an orange solid (65 mg, 48% yield).

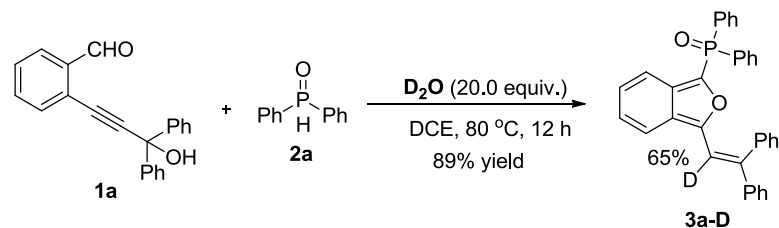


A mixture of **3c** (114.8 mg, 0.2 mmol), 9,9-dimethyl-9,10-dihydroacridine (63 mg, 0.3 mmol), cesium carbonate (131 mg, 0.4 mmol), palladium (II) acetate (4.6 mg, 0.02 mmol),  $t\text{-Bu}_3\text{PHBF}_4$  (12.0 mg, 0.04 mmol) and dry-toluene (5 mL), and heated under an argon atmosphere  $110^\circ\text{C}$  for 8 h.<sup>3</sup> After the mixture was cooled to room temperature, water (3 mL) and EtOAc (3 x 10 mL) were added. The organic layer was separated and washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (eluted with dichloromethane/ethyl acetate, 20:1) to afford the corresponding product **7a** as a yellow solid (106 mg, 75% yield).



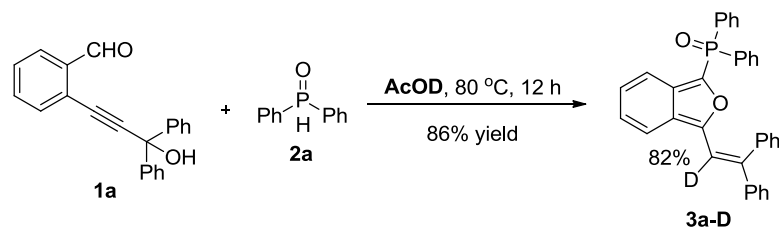
To a solution of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide **3a** (99.2 mg, 0.20 mmol) and dimethyl but-2-ynedioate (28.42 mg, 0.20 mmol) in toluene (3.0 mL) at 120 °C for 12 h. When the reaction was completed, the reaction mixture was evaporated under reduced pressure. The residue was purified by chromatography on silica gel (eluted with dichloromethane/ethylacetate, 10:1) to afford **8a** (97.0 mg, 0.15 mmol) in 76% yield.

## Reaction mechanism synthesis step



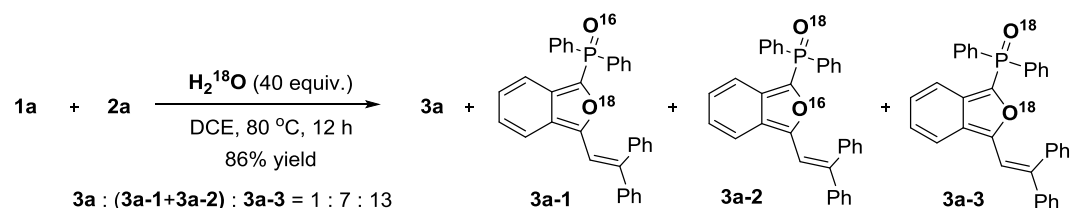
### General Procedure for the Synthesis of **3a-D**.

To a solution of **1a** (0.2 mmol, 62.4 mg) and diphenylphosphine oxide **2a** (0.3 mmol, 60.6 mg) in DCE (3.0 mL) was added  $D_2O$  (4.0 mmol, 80.0 mg) at 80 °C for 12 h. When the reaction was completed, the reaction mixture was evaporated under reduced pressure. The residue was purified by chromatography on silica gel (eluted with dichloromethane/ethyl acetate, 20:1) to afford **3a-D** (89 mg, 0.179 mmol) with an isotopic ratio of 65:35 in 89% yield.



### General Procedure for the Synthesis of **3a-D** in $AcOH$ .

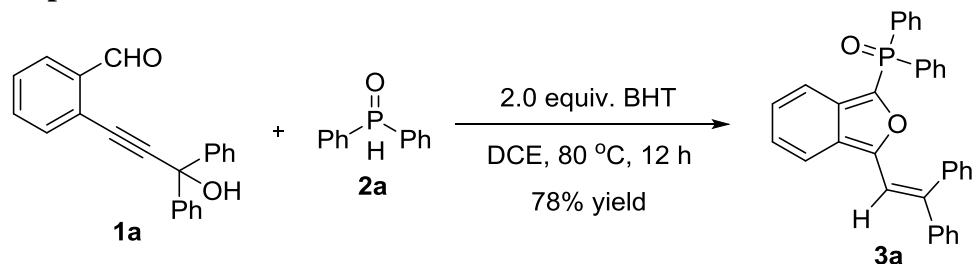
To a solution of **1a** (0.2 mmol, 62.4 mg) in  $AcOD$  (3.0 mL) was added diphenylphosphine oxide **2a** (0.3 mmol, 60.6 mg) at 80 °C for 12 h. When the reaction was completed, the reaction mixture was evaporated under reduced pressure. The residue was purified by chromatography on silica gel (eluted with dichloromethane/ethyl acetate, 20:1) to afford **3a-D** (86 mg, 0.173 mmol) with an isotopic ratio of 82:18 in 86% yield.



### General Procedure of Pudovik Addition/Cyclization/Aromatization with H<sub>2</sub><sup>18</sup>O.

To a solution of **1a** (0.2 mmol, 62.4 mg) and diphenylphosphine oxide **2a** (0.3 mmol, 60.6 mg) in DCE (3.0 mL) was added H<sub>2</sub><sup>18</sup>O (8.0 mmol, 160.0 mg) at 80 °C for 12 h. When the reaction was completed, the reaction mixture was evaporated under reduced pressure. The residue was purified by chromatography on silica gel (eluted with dichloromethane/ethyl acetate, 20:1) to afford the inseparable mixture (**3a** : (**3a-1**+ **3a-2**) : **3a-3** ≈ 1 : 7 : 13) (86 mg) in 86% yield.

### General procedure for inhibition experiments.

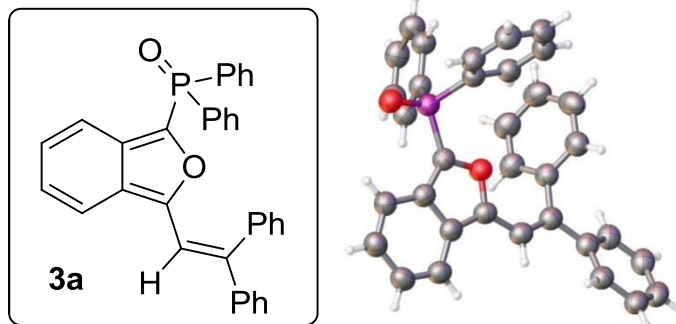


To a solution of **1a** (0.2 mmol, 62.4 mg) and diphenylphosphine oxide **2a** (0.8 mmol, 161.6 mg) and in DCE (5.0 mL) was added 2.0 equivalents 2,6-di-*tert*-butyl-4-methylphenol (BHT) (0.4 mmol, 88.0 mg) at 80 °C for 12 h. When the reaction was completed, the reaction mixture was evaporated under reduced pressure. The residue was purified by chromatography on silica gel (eluted with dichloromethane/ethyl acetate, 20:1) to afford the product **3a** (0.156 mmol, 78 mg,) in 78% yield.

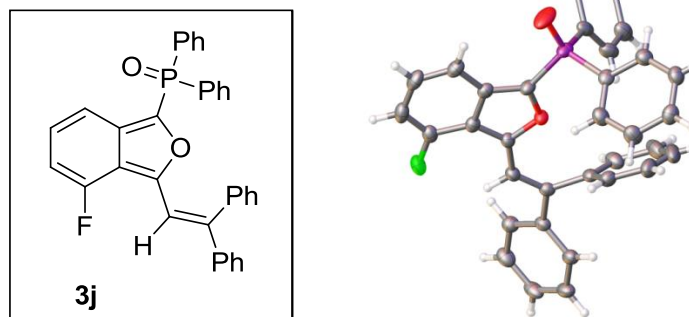
## Crystal Data and Structure Refinement of Compounds **3a** and **3j**

**Table S2.** Crystal data and structure refinement for compounds **3a** and **3j**

Compound	<b>3a</b>	<b>3j</b>
Formula	C <sub>34</sub> H <sub>25</sub> O <sub>2</sub> P	C <sub>34</sub> H <sub>24</sub> FO <sub>2</sub> P
Formula weight	496.51	514.50
Temperature (K)	150	150
Crystal system	Monoclinic	triclinic
Space group	P121/c1	P-1
<i>a</i> (Å)	10.3029(2)	9.3555(5)
<i>b</i> (Å)	26.9879(4)	11.2209(8)
<i>c</i> (Å)	18.4734(3)	14.2183(8)
$\alpha$ (°)	90	68.506(2)
$\beta$ (°)	96.403(10)	85.739(4)
$\gamma$ (°)	90	70.953(2)
<i>V</i> (Å <sup>3</sup> )	5104.55(15)	1311.02(14)
<i>Z</i>	8	2
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.292	1.303
$\mu$ /mm <sup>-1</sup>	1.185	0.142
<i>F</i> (000)	2080.0	536.0
Crystal size/mm <sup>3</sup>	0.39 x 0.35 x 0.25	0.16 × 0.13 × 0.12
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)	MoK $\alpha$ ( $\lambda$ = 0.71073)
<i>R</i> (int)	0.0563	0.0593
Total reflections	61956	15171
Independent reflections	10442	5286
$\theta_{\min} < \theta < \theta_{\max}$	2.911 to 74.661	3.082 to 52.754
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.0797, w <i>R</i> <sub>2</sub> = 0.1848	<i>R</i> <sub>1</sub> = 0.0429, w <i>R</i> <sub>2</sub> = 0.1064
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> (for all data)	<i>R</i> <sub>1</sub> = 0.0887, w <i>R</i> <sub>2</sub> = 0.1984	<i>R</i> <sub>1</sub> = 0.0574, w <i>R</i> <sub>2</sub> = 0.1152
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.051	1.057



**Fig. S1** ORTEP diagram of X-ray crystal structure of compounds **3a** (CCDC No. 2395373). The thermal ellipsoids are shown at 35% probability. Colour code: red, oxygen; white, hydrogen; green, fluorine; orange, phosphorus. The crystal was grown from CH<sub>2</sub>Cl<sub>2</sub> and PE. 20 mg of **3a** was dissolved in CH<sub>2</sub>Cl<sub>2</sub>/PE mixed solvent (1.5/3.0 mL) and the solvent was evaporated slowly in a cold atmosphere.



**Fig. S2** ORTEP diagram of X-ray crystal structure of compounds **3j** (CCDC No. 2395370). The thermal ellipsoids are shown at 35% probability. Colour code: red, oxygen; white, hydrogen; green, fluorine; orange, phosphorus. The crystal was grown from CH<sub>2</sub>Cl<sub>2</sub> and PE. 20 mg of **3j** was dissolved in CH<sub>2</sub>Cl<sub>2</sub>/PE mixed solvent (1.5/3.0 mL) and the solvent was evaporated slowly in a cold atmosphere.

## Analytical Data of Products 1v–1z, 3a-3y, 3aa-3ah, 3a-D, 4a, 5a, 6a, 7a and 8a

### Analytical Data of Products 1v–1z

**2-(3-hydroxy-3,3-di(thiophen-2-yl)prop-1-yn-1-yl)benzaldehyde (1v).** 435 mg, 59%; yellow solid; m. p. 109-111 °C, (SiO<sub>2</sub>) R<sub>f</sub> = 0.4 (PE/EA = 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.50 (s, 1H), 7.94-7.90 (m, 1H), 7.64-7.60 (m, 1H), 7.56 (td, *J* = 7.6, 1.2 Hz, 1H), 7.50-7.44 (m, 1H), 7.31 (dd, *J* = 5.2, 1.2 Hz, 2H), 7.24 (dd, *J* = 3.6, 1.2 Hz, 2H), 6.97 (dd, *J* = 5.2, 3.6 Hz, 2H), 3.74 (s, 1H). <sup>13</sup>C {<sup>1</sup>H}NMR (100 MHz, CDCl<sub>3</sub>) δ 191.5, 148.7, 136.5, 133.9, 133.7, 129.5, 127.7, 126.8, 126.3, 125.7, 125.3, 97.3, 82.0, 70.0. HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>12</sub>O<sub>2</sub>S<sub>2</sub>Na 347.0171; Found: 347.0181.

**2-((9-hydroxy-9H-fluoren-9-yl)ethynyl)benzaldehyde (1w).** 501 mg, 67%; orange solid; m. p. 151 -153 °C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.25 (PE/EA = 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.38 (s, 1H), 7.88 – 7.83 (m, 1H), 7.77 (dd, *J* = 7.6, 0.8 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.40 (dtd, *J* = 20.8, 7.6, 1.2 Hz, 5H), 2.98 (s, 1H). <sup>13</sup>C {<sup>1</sup>H}NMR (101 MHz, CDCl<sub>3</sub>) δ 191.6, 146.8, 139.2, 136.5, 133.8, 130.1, 129.1, 128.9, 127.4, 126.0, 124.4, 120.5, 96.4, 78.7, 75.4. HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>14</sub>O<sub>2</sub>Na 333.0886; Found 333.0894.

**2-((9-hydroxy-10,10-dimethyl-9,10-dihydroanthracen-9-yl)ethynyl)benzaldehyde (1x).** 500 mg, 70%; yellow solid; m. p. 170 - 172 °C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.4 (PE/EA = 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.36 (d, *J* = 0.4 Hz, 1H), 8.14 – 8.09 (m, 2H), 7.90 – 7.86 (m, 1H), 7.65 – 7.61 (m, 2H), 7.56 – 7.49 (m, 2H), 7.47 – 7.38 (m, 5H), 2.84 (s, 1H), 1.77 (s, 3H), 1.69 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 191.6, 142.8, 136.5, 136.4, 133.8, 133.5, 129.2, 129.0, 128.0, 127.4, 127.2, 126.2, 126.2, 100.4, 81.9, 68.2, 38.2, 33.4, 32.8. HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>20</sub>O<sub>2</sub>Na 375.1356; Found: 375.1360.

**2-((5-hydroxy-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl)ethynyl)benzaldehyde (1y).** 400 mg, 69%; white solid; m. p. 156-158 °C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.5 (PE/EA = 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.41 (d, *J* = 0.4 Hz, 1H), 8.07-8.01 (m, 2H), 7.94-7.89 (m, 1H), 7.62-7.53 (m, 2H), 7.49-7.43 (m, 1H), 7.26 – 7.22 (m, 4H), 7.20 – 7.16 (m, 2H), 3.67 – 3.59 (m, 2H), 3.41 – 3.32 (m, 2H), 3.28 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

$\delta$  191.4, 141.1, 138.4, 136.4, 133.9, 133.5, 131.1, 129.1, 128.6, 128.1, 126.4, 126.3, 125.7, 125.1, 99.1, 83.5, 73.6, 32.7. HRMS (ESI)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{24}H_{18}O_2Na$  361.1199; Found: 361.1200.

**2-(3-hydroxy-3-phenylprop-1-yn-1-yl)benzaldehyde (1z).** 340 mg, 72%; yellow oil; (SiO<sub>2</sub>) R<sub>f</sub> = 0.3 (PE/EA = 4:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.46 (s, 1H), 8.00 – 7.76 (m, 1H), 7.63 – 7.49 (m, 4H), 7.46 – 7.31 (m, 4H), 5.74 (s, 1H), 3.16 (s, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  191.8, 140.3, 136.1, 133.9, 133.6, 129.0, 128.9, 128.7, 127.6, 126.7, 125.9, 96.1, 82.2, 65.1. HRMS (ESI)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{16}H_{12}O_2Na$  259.0730; Found: 259.0737.



### Analytical Data of Products 3a-3y and 3aa-3ah.

**(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3a).** 88 mg, 89%; yellow solid; m. p. 196 -198°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.50 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 8.8 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.43 – 7.36 (m, 8H), 7.34 – 7.28 (m, 5H), 7.21 – 7.17 (m, 2H), 7.15 – 7.10 (m, 2H), 7.10 – 7.04 (m, 1H), 7.04 – 6.96 (m, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 150.8 (d, *J* = 5.6Hz), 142.8, 142.3 (d, *J* = 1.4 Hz), 140.4, 136.7, 135.3, 135.2, 135.0, 133.4, 132.3, 131.9 (dd, *J* = 8.9, 6.8 Hz), 130.2, 128.5 (d, *J* = 4.1 Hz), 128.3, 128.2, 128.1, 128.0, 127.8, 127.3 (d, *J* = 1.3 Hz), 125.1, 124.5, 124.4, 120.3, 118.9, 112.4 (d, *J* = 1.7 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 18.0. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>26</sub>O<sub>2</sub>P 497.1665; Found: 497.1665. QY: 51.4%.

**(6-chloro-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3b).** 96 mg, 91%; yellow solid; m. p. 250 - 252°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.7 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00 (s, 1H), 7.56 – 7.49 (m, 2H), 7.44 – 7.34 (m, 9H), 7.34 – 7.27 (m, 5H), 7.20 – 7.11 (m, 3H), 7.08 (s, 1H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.90 (dd, *J* = 9.2, 1.6 Hz, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 151.31 (d, *J* = 5.4 Hz), 143.5, 142.6, 140.2, 139.8, 135.2, 135.1, 133.5, 133.1, 132.1 (d, *J* = 2.8 Hz), 132.0, 131.9, 131.8, 130.1, 128.3 (d, *J* = 19.0 Hz), 128.0 (d, *J* = 2.8 Hz), 126.8, 122.5 (d, *J* = 7.3 Hz), 120.6, 118.7, 112.1. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 18.0. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>25</sub>ClO<sub>2</sub>P 531.1275; Found: 531.1261. QY: 24.9%.

**(6-bromo-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3c).** 99 mg, 86%; yellow solid; m. p. 265 - 267°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.7 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (s, 1H), 7.57 – 7.49 (m, 2H), 7.45 – 7.34 (m, 8H), 7.33 – 7.27 (m, 6H), 7.20 – 7.12 (m, 3H), 7.08 (s, 1H), 7.06 – 6.99 (m, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 151.4 (d, *J* = 5.5 Hz), 143.5 (d, *J* = 1.3 Hz), 142.5, 140.2, 136.23, 135.8, 135.6, 134.85, 133.1, 132.1 (d, *J* = 2.9 Hz), 132.0, 131.8 (d, *J* = 10.8 Hz), 130.1, 129.0, 128.5, 128.4, 128.2, 128.0 (d, *J* = 2.8 Hz), 122.5 (d, *J* = 7.2 Hz), 122.1 (d, *J* = 1.7 Hz), 122.05, 120.6, 112.1 (d, *J* = 1.5 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 18.1. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>25</sub>BrO<sub>2</sub>P 575.0770; Found: 575.0774. QY: 13.0%.

**(3-(2,2-diphenylvinyl)-6-fluoroisobenzofuran-1-yl)diphenylphosphine oxide (3d).** 90 mg, 88%; yellow solid; m. p. 204- 206°C, (SiO<sub>2</sub>) R<sub>f</sub> = 0.7 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.47 (m, 3H), 7.47 – 7.35 (m, 9H), 7.34 – 7.27 (m, 5H), 7.20 – 7.16 (m, 2H), 7.15 – 7.10 (m, 1H), 7.06 – 7.01 (s, 1H), 7.03 (m, 2H), 6.83 – 6.72 (m, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 162.7 (d, *J* = 1.4 Hz), 160.2 (d, *J* = 1.4 Hz), 151.3 (dd, *J* = 5.5, 1.8 Hz) 143.6, 142.6, 140.2, 132.7 (d, *J* = 110.8 Hz), 132.1 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 10.8 Hz), 130.1, 128.51 (d, *J* = 2.4 Hz), 128.4, 128.2, 128.0 (d, *J* = 3.8 Hz), 122.1, 122.0, 121.8, 121.7, 118.0, 117.7, 112.1, 102.3, 102.0. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 17.8. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>25</sub>FO<sub>2</sub>P 515.1571; Found: 515.1566. QY: 24.2%.

**(3-(2,2-diphenylvinyl)-6-methylisobenzofuran-1-yl)diphenylphosphine oxide (3e).** 77 mg, 75%; yellow solid; m. p. 216 - 218°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.6 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 1.2 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.42 – 7.36 (m, 9H), 7.32 – 7.27 (m, 5H), 7.21 – 7.17 (m, 2H), 7.16 – 7.10 (m, 2H), 7.04 – 6.99 (m, 2H), 6.84 (dd, *J* = 9.2, 1.2 Hz, 1H), 2.32 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 150.6 (d, *J* = 5.7 Hz), 142.9, 142.0 (d, *J* = 1.4 Hz), 140.4, 137.2 (d, *J* = 1.2 Hz), 135.9, 135.7, 135.2, 133.8, 133.0 (d, *J* = 110.3 Hz), 131.9 (d, *J* = 1.6 Hz), 131.8, 130.2, 128.5, 128.4 (d, *J* = 5.9 Hz), 128.3, 128.2, 128.1, 127.9, 127.7, 123.6 (d, *J* = 7.6 Hz), 118.6, 117.8, 112.5 (d, *J* = 1.6 Hz), 22.1. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 18.3. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>35</sub>H<sub>28</sub>O<sub>2</sub>P 511.1821; Found: 511.1829. QY: 39.9%.

**(3-(2,2-diphenylvinyl)-6-methoxyisobenzofuran-1-yl)diphenylphosphineoxide (3f).** 65mg, 62%; yellow solid; m. p. 238 - 240°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.4 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 – 7.48 (m, 2H), 7.45 – 7.36 (m, 8H), 7.34 (dd, *J* = 9.6, 0.78 Hz, 1H), 7.31 – 7.28 (m, 5H), 7.21 – 7.17 (m, 2H), 7.15 – 7.09 (m, 2H), 7.07 (s, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.69 (dd, *J* = 9.2, 2 Hz, 2H), 3.81 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 158.7 (d, *J* = 1.2 Hz), 150.7 (d, *J* = 6.0 Hz), 142.8, 142.6 (d, *J* = 1.3 Hz), 140.3, 136.4 (d, *J* = 16.1 Hz), 134.2, 133.2 (d, *J* = 110.2 Hz), 132.8, 131.8 (d, *J* = 1.8 Hz), 131.7, 130.2, 128.4 (d, *J* = 5.2 Hz), 128.3 (d, *J* = 3.1 Hz), 128.0, 127.9, 127.8, 121.7, 121.6 (d, *J* = 7.6 Hz), 120.3, 112.4 (d, *J* = 1.5 Hz), 94.5, 55.5. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 18.4. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>35</sub>H<sub>28</sub>O<sub>3</sub>P 527.1771; Found: 527.1772.

**(3-(2,2-diphenylvinyl)-4-methylisobenzofuran-1-yl)diphenylphosphine oxide (3g).** 54 mg, 53%; yellow solid; m. p. 208 - 210°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.6 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.8 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.40–7.33 (m, 7H), 7.32–7.23 (m, 7H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.97–6.91 (m, 3H), 6.76 (d, *J* = 6.4 Hz, 1H), 2.67 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 151.2 (d, *J* = 5.5 Hz), 143.3, 142.6, 140.6, 136.4, 136.0 (d, *J* = 15.9 Hz), 135.0, 132.7 (d, *J* = 110.5 Hz), 131.9 (d, *J* = 10.8 Hz), 131.8 (d, *J* = 2.5 Hz), 130.1, 130.0, 128.4 (d, *J* = 11.9 Hz), 128.2, 128.1, 128.0, 127.9, 127.6, 127.3, 125.9, 124.6 (d, *J* = 7.3 Hz), 118.3, 114.7 (d, *J* = 1.4 Hz), 21.5. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 18.2. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>35</sub>H<sub>28</sub>O<sub>2</sub>P 511.1821; Found: 511.1833. QY: 22.1%.

**(3-(2,2-diphenylvinyl)-5-methylisobenzofuran-1-yl)diphenylphosphine oxide (3h).** 82 mg, 80%; yellow solid; m. p. 230 - 232°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.6 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 9.0 Hz, 1H), 7.54–7.47 (m, 2H), 7.44–7.36 (m, 8H), 7.34–7.28 (m, 5H), 7.21–7.17 (m, 3H), 7.16–7.11 (m, 2H), 7.05–6.99 (m, 2H), 6.92 (d, *J* = 9.0 Hz, 1H), 2.32 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ ppm 149.8 (d, *J* = 5.6 Hz), 142.9, 141.4 (d, *J* = 1.4 Hz), 140.5, 136.5, 135.1, 134.8, 134.2 (d, *J* = 16.0 Hz), 132.9 (d, *J* = 110.4 Hz), 131.90, 131.9 (d, *J* = 1.6 Hz), 131.8, 130.6, 130.2, 128.4 (d, *J* = 1.7 Hz), 128.3, 128.1, 127.9, 127.7, 124.9 (d, *J* = 7.4 Hz), 119.9, 116.7, 112.6 (d, *J* = 1.6 Hz), 22.2. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 17.9. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>35</sub>H<sub>28</sub>O<sub>2</sub>P 511.1821; Found: 511.1816. QY: 8.0%.

**(3-(2,2-diphenylvinyl)-7-methylisobenzofuran-1-yl)diphenylphosphine oxide (3i).** 65 mg, 64%; yellow solid; m. p. 168 -170°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.6 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52–7.46 (m, 2H), 7.45–7.34 (m, 8H), 7.33–7.26 (m, 5H), 7.25–7.20 (m, 1H), 7.16–7.07 (m, 3H), 7.07–7.01 (m, 3H), 6.91–6.85 (m, 2H), 2.61 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 150.3 (d, *J* = 6.4 Hz), 143.4 (d, *J* = 1.1 Hz), 143.0, 140.1, 138.5, 137.1, 135.1, 134.9, 133.4 (d, *J* = 111.9 Hz), 132.1, 132.0, 131.7 (d, *J* = 2.8 Hz), 130.6, 130.4, 128.4, 128.30, 128.29, 128.26, 127.9, 127.6, 125.4 (d, *J* = 7.1 Hz) 125.1, 116.7, 113.2 (d, *J* = 1.4 Hz), 22.8. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 18.0. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>35</sub>H<sub>28</sub>O<sub>2</sub>P 511.1821; Found: 511.1821. QY: 29.7%.

**(3-(2,2-diphenylvinyl)-4-fluoroisobenzofuran-1-yl)diphenylphosphine oxide (3j).** 74 mg, 72%; yellow solid; m. p. 190 -192°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.7 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.43 – 7.37 (m, 5H), 7.36 – 7.27 (m, 9H), 7.18 – 7.14 (m, 2H), 7.13 – 7.08 (m, 1H), 7.02 – 6.94 (m, 3H), 6.63 (dd, *J* = 11.6, 7.2 Hz, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 157.5, 155.0, 149.6 (dd, *J* = 7.9, 5.7 Hz), 143.5, 142.5, 140.3, 137.1 (dd, *J* = 16.1, 4.5 Hz), 136.9 (dd, *J* = 139.0, 2.4 Hz), 132.9, 132.1 (d, *J* = 2.8 Hz), 131.9, 131.8, 130.0, 128.5, 128.4 (d, *J* = 4.0 Hz), 128.1, 128.0, 127.8, 127.5 (d, *J* = 5.7 Hz), 116.6 (d, *J* = 5.2 Hz), 116.4 (d, *J* = 7.5 Hz), 116.2 (d, *J* = 7.6 Hz), 113.8 (dd, *J* = 6.5, 1.4 Hz), 107.6 (d, *J* = 18.3 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 18.1. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>25</sub>FO<sub>2</sub>P 515.1571; Found: 515.1572. QY: 6.8%.

**(4-chloro-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3k).** 95 mg, 90%; yellow solid; m. p. 196 -198°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.6 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.55 – 7.49 (m, 2H), 7.42– 7.37 (m, 4H), 7.35 – 7.27 (m, 9H), 7.18 – 7.13 (m, 2H), 7.11 – 7.02 (m, 2H), 6.99 – 6.93 (m, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 150.91 (d, *J* = 5.3 Hz), 143.4 (d, *J* = 1.5 Hz), 142.9, 140.5, 136.6 (d, *J* = 15.9 Hz), 136.5 (d, *J* = 138.1 Hz), 132.9, 132.1 (d, *J* = 2.9 Hz), 131.9, 131.8 (d, *J* = 1.9 Hz), 130.0, 128.5 (d, *J* = 1.4 Hz), 128.3 (d, *J* = 2.4 Hz), 128.0 (d, *J* = 4.4 Hz), 127.9, 127.7, 127.1, 126.0, 125.8, 121.50 (d, *J* = 7.3 Hz), 119.5, 113.91 (d, *J* = 1.5 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 18.4. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>25</sub>ClO<sub>2</sub>P 531.1275; Found: 531.1278.

**(3-(2,2-diphenylvinyl)-5-fluoroisobenzofuran-1-yl)diphenylphosphine oxide (3l).** 81 mg, 79%; yellow solid; m. p. 216 - 218°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.7 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (dd, *J* = 9.4, 5.1 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.45 – 7.36 (m, 8H), 7.34 – 7.27 (m, 5H), 7.22 – 7.12 (m, 3H), 7.08 – 7.01 (m, 3H), 6.96 (d, *J* = 9.2 Hz, 1H), 6.89 (td, *J* = 9.2, 2.0 Hz, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 161.3 (d, *J* = 0.8 Hz), 158.8 (d, *J* = 0.7 Hz), 150.5 (d, *J* = 5.5 Hz), 150.4 (d, *J* = 5.4 Hz), 142.6, 142.1, 140.3, 137.5 (d, *J* = 2.2 Hz), 136.2 (d, *J* = 2.2 Hz), 132.9 (d, *J* = 15.8 Hz), 132.5 (d, *J* = 110.8 Hz), 132.10 (*J* = 2.8 Hz), 131.8 (d, *J* = 10.8 Hz), 130.1, 128.5 (d, *J* = 2.3 Hz), 128.4, 128.3,

128.2, 127.9, 127.8, 123.9 (dd,  $J = 10.1, 7.4$  Hz), 123.2 (d,  $J = 9.5$  Hz), 120.1 (dd,  $J = 30.1, 0.9$  Hz), 112.3, 101.1, 100.9.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  18.0. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{25}\text{FO}_2\text{P}$  515.1571; Found: 515.1567.

**(5-chloro-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3m)**. 87 mg, 82%; yellow solid; m. p. 207 - 209°C; ( $\text{SiO}_2$ )  $R_f = 0.7$  (DCM/EA = 20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 9.2$  Hz, 1H), 7.57 – 7.50 (m, 2H), 7.45 – 7.35 (m, 9H), 7.34 – 7.27 (m, 5H), 7.20 – 7.12 (m, 3H), 7.07 – 7.01 (m, 3H), 6.98 (d,  $J = 9.2$  Hz, 1H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.3 (d,  $J = 5.5$  Hz), 143.0 (d,  $J = 1.4$  Hz), 142.5, 140.2, 137.6, 136.9 (d,  $J = 138.6$  Hz), 133.3 (d,  $J = 15.7$  Hz), 133.0, 132.1 (d,  $J = 2.8$  Hz), 131.9, 131.8 (d,  $J = 10.8$  Hz), 130.9, 130.1, 128.9, 128.5 (d,  $J = 1.6$  Hz), 128.4 (d,  $J = 3.8$  Hz), 128.2, 128.0 (d,  $J = 1.9$  Hz), 124.3 (d,  $J = 7.4$  Hz), 122.0, 117.7, 112.2.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.9. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{25}\text{ClO}_2\text{P}$  531.1275; Found: 531.1283.

**(3-(2,2-diphenylvinyl)-5,6-dimethoxyisobenzofuran-1-yl)diphenylphosphineoxide (3n)**. 87 mg, 78%; yellow solid; m. p. 202 - 204°C; ( $\text{SiO}_2$ )  $R_f = 0.3$  (DCM/EA = 20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.48 (m, 2H), 7.47 – 7.36 (m, 8H), 7.34 – 7.28 (m, 5H), 7.23 – 7.19 (m, 2H), 7.15 – 7.10 (m, 2H), 7.08 – 7.02 (m, 2H), 7.00 (s, 1H), 6.48 (s, 1H), 3.88 (s, 3H), 3.83 (s, 3H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.9 (d,  $J = 1.1$  Hz), 150.5, 149.2 (d,  $J = 5.9$  Hz), 143.1, 141.2 (d,  $J = 1.1$  Hz), 140.6, 134.5, 133.2, 133.1 (d,  $J = 110.3$  Hz), 132.7, 131.9 (d,  $J = 2.8$  Hz), 131.8 (d,  $J = 10.7$  Hz), 130.4, 128.4 (d,  $J = 4.5$  Hz), 128.3, 128.2, 128.02, 127.9 (d,  $J = 30.1$  Hz), 120.6 (d,  $J = 7.5$  Hz), 113.3, 96.1, 95.3, 56.1 (d,  $J = 18.6$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  18.3. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{30}\text{O}_4\text{P}$  577.1871; Found: 577.1873.

**(3-(2,2-diphenylvinyl)-5,6-difluoroisobenzofuran-1-yl)diphenylphosphineoxide (3o)**. 79 mg, 74%; yellow solid; m. p. 225 - 227°C; ( $\text{SiO}_2$ )  $R_f = 0.7$  (DCM/EA = 20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (dd,  $J = 10.0, 7.6$  Hz, 1H), 7.59 – 7.49 (m, 2H), 7.46 – 7.36 (m, 8H), 7.35 – 7.27 (m, 5H), 7.21 – 7.14 (m, 3H), 7.10 – 7.01 (m, 3H), 7.00 (s, 1H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.4, 142.4, 140.1, 132.9, 132.2 (d,  $J = 2.8$  Hz), 131.8 (d,  $J = 1.9$  Hz), 131.7, 131.5 (dd,  $J = 15.7, 10.1$  Hz), 130.1, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 120.1, 120.0, 119.9, 112.1,

105.1 (d,  $J = 21.6$  Hz), 103.9 (d,  $J = 21.2$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta = 18.0$ . HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{24}\text{F}_2\text{O}_2\text{P}$  533.1476; Found: 533.1481.

**(3-(2,2-diphenylvinyl)-4,5-dimethylisobenzofuran-1-yl)diphenylphosphine oxide (3p)**. 76 mg, 73%; yellow solid; m. p. 201 - 203°C; ( $\text{SiO}_2$ )  $R_f = 0.6$  (DCM/EA =20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 8.8$  Hz, 1H), 7.52 – 7.47 (m, 2H), 7.41 (s, 1H), 7.40 – 7.34 (m, 6H), 7.34 – 7.26 (m, 7H), 7.15 – 7.11 (m, 2H), 7.05 (t,  $J = 7.4$  Hz, 1H), 6.95 (t,  $J = 7.4$  Hz, 2H), 6.90 (d,  $J = 9.0$  Hz, 1H), 2.60 (s, 3H), 2.31 (s, 3H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5 (d,  $J = 5.5$  Hz), 143.4, 142.3 (d,  $J = 1.4$  Hz), 140.7, 135.4 (d,  $J = 16.1$  Hz), 135.2 (d,  $J = 140.8$  Hz), 133.3, 132.2, 132.0, 131.9, 131.82, 131.78, 130.2, 128.4 (d,  $J = 9.6$  Hz), 128.2, 128.0, 127.9 (d,  $J = 4.6$  Hz), 127.5, 126.0, 125.2 (d,  $J = 7.3$  Hz), 117.5, 115.4 (d,  $J = 1.5$  Hz), 19.7, 16.6.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  18.1. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{30}\text{O}_2\text{P}$  525.1972; Found: 525.1956.

**(3-(2,2-bis(4-methoxyphenyl)vinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3q)**. 63 mg, 57%; yellow solid; m. p. 177 - 179°C; ( $\text{SiO}_2$ )  $R_f = 0.4$  (DCM/EA =20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 8.8$  Hz, 1H), 7.45 – 7.35 (m, 4H), 7.35 – 7.27 (m, 7H), 7.16 (d,  $J = 8.8$  Hz, 2H), 7.04 – 6.93 (m, 3H), 6.92 – 6.84 (m, 2H), 6.76 (d,  $J = 8.8$  Hz, 2H), 3.72 (s, 3H), 3.55 (s, 3H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 159.4, 151.4 (d,  $J = 5.6$  Hz), 142.1, 135.8, 135.4, 135.3 (d,  $J = 16.0$  Hz), 134.0, 133.1 (d,  $J = 110.5$  Hz), 132.7, 131.9 (d,  $J = 2.8$  Hz), 131.8 (d,  $J = 10.8$  Hz), 131.5, 129.4, 128.4, 128.3, 127.3, 124.7, 123.9 (d,  $J = 7.5$  Hz), 120.1, 119.1, 113.8, 113.5, 110.5, 55.4 (d,  $J = 19.2$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.9. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{30}\text{O}_4\text{P}$  557.1876; Found: 557.1880.

**(3-(2,2-di-p-tolylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3r)**. 51 mg, 49%; yellow solid; m. p. 206 - 208°C; ( $\text{SiO}_2$ )  $R_f = 0.6$  (DCM/EA =20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.8$  Hz, 1H), 7.57 – 7.47 (m, 3H), 7.43 – 7.33 (m, 7H), 7.22 (d,  $J = 8.2$  Hz, 2H), 7.12 (d,  $J = 8.1$  Hz, 2H), 7.10 – 7.04 (m, 4H), 7.01 – 6.95 (m, 1H), 6.78 (d,  $J = 7.8$  Hz, 2H), 2.36 (s, 3H), 2.19 (s, 3H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.1 (d,  $J = 5.6$  Hz), 142.5 (d,  $J = 1.4$  Hz), 140.1, 138.3, 137.5, 137.4, 135.8, 135.3, 135.1, 134.4, 133.6, 132.5, 131.9 (d,  $J = 2.8$  Hz),

131.8 (d,  $J = 10.8$  Hz), 130.1, 129.2, 128.7, 128.3, 128.2, 127.9, 127.3, 124.9, 124.2 (d,  $J = 7.5$  Hz), 120.2, 119.0, 111.3 (d,  $J = 1.6$  Hz), 21.3 (d,  $J = 7.1$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  18.2. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{30}\text{O}_2\text{P}$  525.1972; Found: 525.1944.

**(3-(2,2-bis(4-fluorophenyl)vinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3s).** 97 mg, 91%; yellow solid; m. p. 159 -161 °C; ( $\text{SiO}_2$ )  $R_f = 0.5$  (DCM/EA = 20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.4$  Hz, 1H), 7.58 – 7.51 (m, 2H), 7.50 – 7.43 (m, 3H), 7.43 – 7.36 (m, 6H), 7.26 – 7.22 (m, 2H), 7.12 – 7.07 (m, 2H), 7.06 – 6.96 (m, 5H), 6.68 – 6.60 (m, 2H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9 (d,  $J = 53.4$  Hz), 161.7, 161.2, 150.4 (d,  $J = 5.5$  Hz), 140.0, 138.8, 136.0, 135.0, 134.9, 133.2, 132.2 (d,  $J = 2.8$  Hz), 132.1, 131.9, 131.8, 131.7, 129.6 (d,  $J = 8.0$  Hz), 128.5 (d,  $J = 12.7$  Hz), 127.4, 125.3, 124.6 (d,  $J = 7.5$  Hz), 120.3, 118.8, 115.4 (dd,  $J = 31.9, 21.5$  Hz), 112.4.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.7. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{24}\text{F}_2\text{O}_2\text{P}$  533.1476; Found: 533.1499.

**(3-(2,2-bis(4-chlorophenyl)vinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3t).** 82 mg, 82%; yellow solid; m. p. 205 - 207 °C; ( $\text{SiO}_2$ )  $R_f = 0.6$  (DCM/EA = 20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 8.4$  Hz, 1H), 7.58 – 7.49 (m, 3H), 7.47 – 7.34 (m, 8H), 7.30 – 7.25 (m, 2H), 7.19 (d,  $J = 8.4$  Hz, 2H), 7.11 – 7.00 (m, 5H), 6.91 (d,  $J = 8.4$  Hz, 2H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.0 (d,  $J = 5.7$  Hz), 140.8, 139.3, 138.3, 137.5, 135.0 (d,  $J = 15.9$  Hz), 134.4, 133.9, 132.5 (d,  $J = 110.8$  Hz), 132.2 (d,  $J = 2.8$  Hz), 131.8, 131.7, 131.5, 129.1, 128.8, 128.6, 128.5 (d,  $J = 2.7$  Hz), 127.5, 125.6, 125.0 (d,  $J = 7.4$  Hz), 120.4, 118.7, 112.8.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  18.1. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{24}\text{Cl}_2\text{O}_2\text{P}$  565.0885; Found: 565.0892.

**(3-(2,2-bis(4-bromophenyl)vinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3u).** 98 mg, 75%; yellow solid; m. p. 218 - 220 °C; ( $\text{SiO}_2$ )  $R_f = 0.5$  (PE/EA = 20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 8.6$  Hz, 1H), 7.59 – 7.50 (m, 3H), 7.48 – 7.40 (m, 8H), 7.40 – 7.36 (m, 2H), 7.16 – 7.11 (m, 2H), 7.11 – 7.03 (m, 5H), 7.02 – 6.97 (m, 2H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.9 (d,  $J = 5.6$  Hz), 141.2, 140.3, 139.2, 138.7, 136.2, 135.1, 134.9, 133.8, 133.1, 132.2 (d,  $J = 2.8$  Hz), 132.0, 131.9, 131.7 (d,  $J = 1.8$  Hz), 131.7, 131.4, 129.0 (d,  $J = 76.8$  Hz), 128.5, 127.5, 125.7, 125.1 (d,  $J = 7.5$  Hz), 122.4 (d,  $J = 45.1$  Hz), 120.4, 118.6, 112.7.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  18.2. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd

for C<sub>34</sub>H<sub>24</sub>Br<sub>2</sub>O<sub>2</sub>P 652.9875. Found: 652.9867.

**(3-(2,2-di(thiophen-2-yl)vinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3v).** 86 mg, 85%; yellow solid; m. p. 234 - 236 °C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.5(DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (d, *J* = 8.8 Hz, 1H), 7.57 – 7.46 (m, 7H), 7.45 – 7.37 (m, 4H), 7.27 – 7.23 (m, 1H), 7.20 (s, 1H), 7.13 – 7.04 (m, 2H), 7.03 – 6.94 (m, 4H), 6.74 – 6.69 (m, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 149.9 (d, *J* = 5.6 Hz), 147.1, 139.9, 137.7, 136.3, 135.0 (d, *J* = 15.8 Hz), 133.3, 132.2, 132.0 (d, *J* = 2.8 Hz), 131.9 (d, *J* = 10.8 Hz), 128.6, 128.5, 128.3, 128.0, 127.8, 127.4, 127.0 (d, *J* = 37.1 Hz), 126.4, 126.2, 125.4, 125.0 (d, *J* = 7.5 Hz), 120.3, 118.9, 112.6. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 17.9. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>30</sub>H<sub>22</sub>O<sub>2</sub>PS<sub>2</sub> 509.0793; Found: 509.0799. QY: 2.2%.

**(3-((9H-fluoren-9-ylidene)methyl)isobenzofuran-1-yl)diphenylphosphine oxide (3w).** 87 mg, 88%; red solid; m. p. 197 -199 °C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.5(DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 8.0 Hz, 1H), 7.92 (ddd, *J* = 12.8, 8.2, 1.2 Hz, 4H), 7.82 – 7.74 (m, 2H), 7.72 – 7.68 (m, 1H), 7.68 – 7.58 (m, 5H), 7.56 – 7.49 (m, 4H), 7.35 – 7.27 (m, 2H), 7.23 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.17 – 7.11 (m, 2H), 6.66 (td, *J* = 8.0, 1.2 Hz, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 150.0 (d, *J* = 5.6 Hz), 141.2, 140.4, 140.1, 139.3, 139.1, 135.8, 135.0, 134.9, 132.8, 132.7 (d, *J* = 2.8 Hz), 132.0, 131.9, 131.7, 129.1, 128.94, 128.89, 128.6, 127.9, 127.3, 127.2, 127.1, 126.2, 125.8, 120.2, 119.8 (d, *J* = 16.2 Hz), 119.7 (d, *J* = 88.0 Hz), 107.9 (d, *J* = 1.6 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 17.2. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>24</sub>O<sub>2</sub>P 495.1508; Found: 495.1531. QY: 3.7%.

**(3-((10,10-dimethylantracen-9(10H)-ylidene)methyl)isobenzofuran-1-yl)diphenylphosphine oxide (3x).** 85 mg, 79%; yellow solid; m. p. 209 - 211 °C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.5(DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.8 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.57 – 7.49 (m, 10H), 7.40 – 7.34 (m, 4H), 7.33 – 7.28 (m, 2H), 7.17 – 7.09 (m, 2H), 7.08 (s, 1H), 7.02 (dd, *J* = 8.4, 6.4 Hz, 1H), 6.33 (td, *J* = 7.6, 0.8 Hz, 1H), 1.61 (s, 6H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 150.33 (d, *J* = 5.6 Hz), 146.4, 144.5, 139.1, 137.7, 136.5, 135.2, 135.1, 135.0, 134.9, 133.1 (d, *J* = 110.6 Hz), 132.0, 131.9 (d, *J* = 10.7 Hz), 128.5, 128.4 (d, *J* = 12.8 Hz), 128.1, 127.6, 127.4, 126.6, 125.2, 125.1, 124.4 (d, *J* = 7.4 Hz), 123.5,



123.4, 122.7, 120.2, 119.2, 110.1, 40.0, 28.9.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.8. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{37}\text{H}_{30}\text{O}_2\text{P}$  537.1978. Found: 537.1975. QY: 20.6%.

**(3-((10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)methyl)isobenzofuran-1-yl)diphenylphosphine oxide (3y)**. 92 mg, 88%; yellow solid; m. p. 170 - 172°C; ( $\text{SiO}_2$ )  $R_f = 0.5$  (DCM/EA = 20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.8$  Hz, 1H), 7.64 – 7.27 (m, 12H), 7.25 – 7.17 (m, 3H), 7.11 – 7.05 (m, 3H), 7.04 – 6.96 (m, 3H), 6.41 (td,  $J = 7.6, 1.2$  Hz, 1H), 3.48 – 3.26 (m, 2H), 3.06 – 2.77 (m, 2H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.28 (d,  $J = 5.5$  Hz), 144.0, 141.4, 140.7, 138.4, 137.8, 136.4, 135.1, 135.04, 134.97, 131.8, 130.6, 128.3, 128.23 (dd,  $J = 35.9, 1.8$  Hz), 128.0, 127.6, 127.3, 126.4, 126.0, 125.1, 124.3, 124.2, 120.3, 118.8, 115.0 (d,  $J = 1.5$  Hz), 33.8, 32.1.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  18.1. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{28}\text{O}_2\text{P}$  523.1821. Found: 523.1831. QY: 10.7%.

**(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)bis(4-methoxyphenyl)phosphine oxide (3aa)**. 76 mg, 68%; yellow solid; m. p. 168 -170°C; ( $\text{SiO}_2$ )  $R_f = 0.2$  (DCM/EA =20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 8.8$  Hz, 1H), 7.47 – 7.41 (m, 1H), 7.38 – 7.28 (m, 9H), 7.22 – 7.12 (m, 4H), 7.09 – 7.01 (m, 3H), 6.96 (ddd,  $J = 8.6, 6.4, 0.64$  Hz, 1H), 6.91 – 6.86 (m, 4H), 3.85 (s, 6H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5 (d,  $J = 3.0$  Hz), 150.3 (d,  $J = 5.6$  Hz), 142.9, 141.9 (d,  $J = 1.4$  Hz), 140.4, 137.2 (d,  $J = 140.2$  Hz), 134.5, 134.4, 133.7 (d,  $J = 12.2$  Hz), 130.2, 128.4, 128.0 (d,  $J = 10.6$  Hz), 127.9 (d,  $J = 40.2$  Hz), 127.0 (d,  $J = 1.0$  Hz), 125.0 (d,  $J = 3.4$  Hz), 124.4 (d,  $J = 7.3$  Hz), 123.9, 120.4, 118.9, 113.9 (d,  $J = 13.9$  Hz), 112.5 (d,  $J = 1.5$  Hz), 55.5.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.7. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{30}\text{O}_4\text{P}$  557.1876; Found: 557.1846. QY: 14.3%.

**(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)di-p-tolylphosphine oxide (3ab)**. 75 mg, 72%; yellow solid; m. p. 248-250°C; ( $\text{SiO}_2$ )  $R_f = 0.6$  (DCM/EA =20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 8.8$  Hz, 1H), 7.44 (d,  $J = 8.8$  Hz, 1H), 7.36 – 7.26 (m, 9H), 7.22 – 7.17 (m, 6H), 7.16 – 7.12 (m, 2H), 7.08 – 7.01 (m, 3H), 6.96 (dd,  $J = 8.6, 6.4$  Hz, 1H), 2.41 (s, 6H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5 (d,  $J = 5.4$  Hz), 142.9, 142.3 (d,  $J = 2.9$  Hz), 142.0 (d,  $J = 1.2$  Hz), 140.4, 136.8 (d,  $J = 139.6$  Hz), 134.7 (d,  $J = 15.8$  Hz), 131.9 (d,  $J = 11.1$  Hz), 130.3, 130.2,

129.2, 129.1, 129.0, 128.4, 128.1, 128.0, 127.9, 127.7, 127.1, 125.0, 124.4 (d,  $J = 7.4$  Hz), 120.36, 118.9, 112.5 (d,  $J = 1.5$  Hz), 21.8 (d,  $J = 1.3$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  18.1. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{30}\text{O}_2\text{P}$  525.1972; Found: 525.1957. QY: 11.4%.

**bis(4-chlorophenyl)(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)phosphine oxide (3ac).** 83 mg, 74%; yellow solid; m. p. 254 - 256°C; ( $\text{SiO}_2$ )  $R_f = 0.6$  (DCM/EA =30:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J = 8.8$  Hz, 1H), 7.52 (d,  $J = 8.8$  Hz, 1H), 7.40 – 7.35 (m, 4H), 7.34 – 7.26 (m, 9H), 7.21 – 7.14 (m, 4H), 7.13 – 7.06 (m, 3H), 7.05 – 6.99 (m, 1H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.2 (d,  $J = 5.8$  Hz), 142.9, 142.6, 140.5, 138.8 (d,  $J = 3.4$  Hz), 135.5, 135.3, 134.0, 133.2, 133.1, 131.0 (d,  $J = 112.4$  Hz), 130.2, 128.9, 128.8, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8 (d,  $J = 1.1$  Hz), 125.3, 124.6 (d,  $J = 7.7$  Hz), 119.9, 119.1, 112.1 (d,  $J = 1.6$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  16.0. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{24}\text{Cl}_2\text{O}_2\text{P}$  565.0885; Found: 565.0854.

**bis(4-bromophenyl)(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)phosphine oxide (3ad).** 104 mg, 80%; yellow solid; m. p. 260 -262°C; ( $\text{SiO}_2$ )  $R_f = 0.6$  (DCM/EA =30:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.8$  Hz, 1H), 7.56 – 7.49 (m, 5H), 7.35 – 7.27 (m, 5H), 7.26 – 7.24 (m, 2H), 7.23 – 7.21 (m, 2H), 7.21 – 7.13 (m, 5H), 7.12 – 7.05 (m, 3H), 7.04 – 6.99 (m, 1H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.3 (d,  $J = 5.8$  Hz), 142.9 (d,  $J = 1.4$  Hz), 142.6, 140.5, 135.4 (d,  $J = 16.5$  Hz), 135.4, 133.8, 133.3, 133.2, 131.9, 131.7, 131.4 (d,  $J = 111.9$  Hz), 130.2, 128.5, 128.4, 128.1, 128.0, 127.9, 127.86 (d,  $J = 1.2$  Hz), 127.4 (d,  $J = 3.5$  Hz), 125.3, 124.5 (d,  $J = 7.7$  Hz), 119.9, 119.1, 112.1.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  16.3. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{24}\text{Br}_2\text{O}_2\text{P}$  652.9875. Found: 652.9844.

**(3,5-dimethylphenyl)(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)(*m*-tolyl)phosphine oxide (3ae).** 88 mg, 80%; yellow solid; m. p. 137 -139°C; ( $\text{SiO}_2$ )  $R_f = 0.5$  (DCM/EA =20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.8$  Hz, 1H), 7.39 (d,  $J = 8.8$  Hz, 1H), 7.35 – 7.28 (m, 5H), 7.20 – 7.07 (m, 9H), 7.05 – 6.98 (m, 2H), 6.97 – 6.89 (m, 3H), 2.31 (s, 12H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.6 (d,  $J = 5.7$  Hz), 142.9, 142.1 (d,  $J = 1.3$  Hz), 140.0, 138.1, 138.0, 137.5, 136.1, 135.0, 134.8, 133.9 (d,  $J = 2.9$  Hz), 133.0, 131.9, 130.0, 129.5 (d,  $J = 10.7$  Hz), 128.5, 128.1 (d,

$J = 11.9$  Hz), 127.4, 127.0 (d,  $J = 1.0$  Hz), 124.9, 124.4, 124.3, 120.4, 119.0, 112.8 (d,  $J = 1.5$  Hz), 21.5.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  19.1. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{38}\text{H}_{34}\text{O}_2\text{P}$  553.2291; Found: 553.2277. QY: 1.9%.

**(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)di(naphthalen-1-yl)phosphine oxide (3af)**. 85 mg, 71%; yellow solid; m. p. 78 - 80°C; ( $\text{SiO}_2$ )  $R_f = 0.5$  (DCM/EA = 30:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.71 (d,  $J = 8.4$  Hz, 2H), 8.06 (d,  $J = 9.2$  Hz, 1H), 7.97 (d,  $J = 8.0$  Hz, 2H), 7.87 (d,  $J = 8.0$  Hz, 2H), 7.50 – 7.45 (m, 1H), 7.43 – 7.35 (m, 3H), 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 5H), 7.19 (dd,  $J = 7.2, 1.2$  Hz, 1H), 7.15 (dd,  $J = 6.8, 0.8$  Hz, 1H), 7.08 – 7.00 (m, 4H), 6.97 – 6.89 (m, 4H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9 (d,  $J = 5.7$  Hz), 142.6, 142.5 (d,  $J = 1.3$  Hz), 140.1, 137.2, 135.8, 135.3, 135.1, 133.9 (dd,  $J = 9.3, 3.9$  Hz), 133.3 (d,  $J = 12.5$  Hz), 133.2 (d,  $J = 3.0$  Hz), 129.7 (d,  $J = 5.5$  Hz), 128.8 (d,  $J = 1.3$  Hz), 128.6, 128.4, 128.2, 127.8, 127.6, 127.5, 127.4, 127.3, 126.5, 125.0, 124.6 (d,  $J = 15.0$  Hz), 124.5 (d,  $J = 8.0$  Hz), 120.4, 119.2, 112.7 (d,  $J = 1.5$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  24.9. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{42}\text{H}_{30}\text{O}_2\text{P}$  597.1978; Found: 597.1954. QY: 9.0%.

**(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)di(naphthalen-2-yl)phosphine oxide (3ag)**. 93 mg, 78%; yellow solid; m. p. 181 - 183°C; ( $\text{SiO}_2$ )  $R_f = 0.5$  (DCM/EA = 20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J = 14.4$  Hz, 2H), 8.02 (d,  $J = 8.8$  Hz, 1H), 7.93 – 7.87 (m, 4H), 7.81 (dd,  $J = 8.4, 2.8$  Hz, 2H), 7.63 – 7.50 (m, 5H), 7.34 – 7.27 (m, 7H), 7.19 – 7.15 (m, 3H), 7.13 – 7.07 (m, 1H), 7.04 – 6.98 (m, 1H), 6.81 – 6.69 (m, 3H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.0 (d,  $J = 5.7$  Hz), 142.7, 142.4 (d,  $J = 1.3$  Hz), 140.2, 136.8, 135.4, 135.2 (d,  $J = 16.0$  Hz), 134.9 (d,  $J = 2.4$  Hz), 133.8 (d,  $J = 10.0$  Hz), 133.8 (d,  $J = 10.0$  Hz), 130.4, 129.9, 129.3, 129.1, 128.4, 128.3, 128.2 (d,  $J = 3.9$  Hz), 128.1, 127.9 (d,  $J = 2.2$  Hz), 127.6, 127.4, 126.9 (d,  $J = 3.8$  Hz), 126.8, 125.1, 124.6, 124.5, 120.3, 119.0, 112.3.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  18.1. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{42}\text{H}_{30}\text{O}_2\text{P}$  597.1978; Found: 597.1961. QY: 6.6%.

**(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diethylphosphine oxide (3ah)**. 67 mg, 83%; oil; ( $\text{SiO}_2$ )  $R_f = 0.1$  (DCM/EA = 5:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 8.4$  Hz, 1H), 7.52 (d,  $J = 8.4$  Hz, 1H), 7.48 – 7.32 (m, 7H), 7.32 – 7.27 (m, 3H), 7.20 (s, 1H), 7.08 – 6.96 (m, 2H), 1.74 – 1.59 (m, 2H), 1.56 – 1.43 (m, 2H), 0.96 (t,  $J = 7.6$  Hz, 3H), 0.92 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.5 (d,  $J = 4.7$

Hz), 142.0, 141.6 (d,  $J = 1.4$  Hz), 141.2, 134.5 (d,  $J = 13.3$  Hz), 130.2, 128.4 (d,  $J = 14.8$  Hz), 128.2, 127.5, 126.9 (d,  $J = 1.1$  Hz), 125.1, 124.4 (d,  $J = 6.7$  Hz), 119.4 (d,  $J = 108.6$  Hz), 112.2 (d,  $J = 1.6$  Hz), 22.9, 22.2, 5.5 (d,  $J = 5.3$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  40.4. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{26}\text{H}_{26}\text{O}_2\text{P}$  401.1665. Found: 401.1641.

### Analytical Data of Products 3a-D

**(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3a-D)**. D: 65%, 89 mg, 89%; yellow solid; m. p. 196-198°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.50 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.45 – 7.36 (m, 8H), 7.35 – 7.27 (m, 5H), 7.22 – 7.17 (m, 2H), 7.15 – 7.11 (m, 1.35 H), 7.07 (dd, *J* = 8.4, 6.4 Hz, 1H), 7.04 – 6.96 (m, 3H). HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>25</sub>DO<sub>2</sub>P 498.1728; Found: 498.1713.

**(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3a-D)**. D: 82%, 86 mg, 86%; yellow solid; m. p. 196-198°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.50 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 8.8 Hz, 1H), 7.55 – 7.46 (m, 3H), 7.43 – 7.36 (m, 8H), 7.33 – 7.29 (m, 5H), 7.21 – 7.16 (m, 2H), 7.15 – 7.11 (m, 1.18 H), 7.07 (dd, *J* = 8.6, 6.6 Hz, 1H), 7.04 – 6.96 (m, 3H).

### Analytical Data of Products 4a, 5a, 6a, 7a and 8a

**(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (4a)**. 93mg, 87%; white solid; m. p. 204 - 206°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.10 (PE/EA = 1:1). <sup>1</sup>H NMR (400 MHz, DMSO) δ 7.79 – 7.66 (m, 6H), 7.64 – 7.56 (m, 3H), 7.55 – 7.47 (m, 3H), 7.42 – 7.28 (m, 6H), 7.28 – 7.15 (m, 6H), 7.01 (s, 1H), 6.66 (dd, *J* = 18.4, 5.6 Hz, 1H), 6.05 (t, *J* = 5.6 Hz, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, DMSO) δ 146.4 (d, *J* = 6.6 Hz), 139.9, 133.1, 132.2, 132.0 (d, *J* = 8.4 Hz), 131.7 (d, *J* = 2.3 Hz), 131.5 (d, *J* = 2.3 Hz), 131.4, 131.02 (d, *J* = 8.7 Hz), 130.2, 128.4 (d, *J* = 3.7 Hz), 128.3 (d, *J* = 11.0 Hz), 128.1 (d, *J* = 11.1 Hz), 128.0 (d, *J* = 4.0 Hz), 127.7, 127.0 (d, *J* = 14.0 Hz), 125.8, 125.6, 121.8, 121.7, 97.7, 83.6, 73.3, 69.7 (d, *J* = 86.9 Hz). <sup>31</sup>P NMR (162 MHz, DMSO) δ 27.6. HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>20</sub>O<sub>3</sub>PNa 537.1590; Found: 537.1577.

**(3-(2,2-diphenylvinyl)-6-(phenylethynyl)isobenzofuran-1-yl)diphenylphosphine oxide (5a)**. 95 mg, 80%; yellow solid; m. p. 237 - 239°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.5 (DCM/EA = 50:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 (s, 1H), 7.55 – 7.50 (m, 4H), 7.46 – 7.41 (m, 4H), 7.41 – 7.38 (m, 5H), 7.35 – 7.30 (m, 8H), 7.20 – 7.17 (m, 2H), 7.14 (dt, *J* = 2.6, 1.6 Hz, 1H), 7.11 (s, 1H), 7.08 – 7.01 (m, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 151.0 (d, *J* = 5.4 Hz), 142.9, 142.7, 140.3, 136.4 (d, *J* = 139.2 Hz), 134.8, 134.6, 133.2, 132.1 (d, *J* = 2.8 Hz), 131.9, 131.8 (d, *J* = 2.8 Hz), 130.2, 128.5, 128.4, 128.1 (d, *J* = 16.8 Hz), 127.9, 127.7, 124.1, 123.3, 123.0 (d, *J* = 7.2 Hz), 122.2, 119.1, 112.3, 90.9, 89.9. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 18.2. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>42</sub>H<sub>30</sub>O<sub>2</sub>P 597.1978; Found: 597.1967. QY: 3.8%.

**(3-(2,2-diphenylvinyl)-6-(10H-phenoxazin-10-yl)isobenzofuran-1-yl)diphenylphosphine oxide (6a)**. 65 mg, 48%; orange solid; m. p. 137-139°C; (SiO<sub>2</sub>) R<sub>f</sub> = 0.5 (DCM/EA = 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (s, 1H), 7.71 – 7.68 (m, 1H), 7.56 – 7.51 (m, 2H), 7.46 – 7.39 (m, 8H), 7.34 – 7.32 (m, 5H), 7.24 – 7.21 (m, 2H), 7.19 – 7.14 (m, 2H), 7.09 – 7.04 (m, 2H), 6.87 (dd, *J* = 9.2, 1.6 Hz, 1H), 6.70 – 6.65 (m, 3H), 6.65 – 6.56 (m, 4H), 6.08 (dd, *J* = 7.6, 1.6 Hz, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 151.3 (d, *J* = 5.4 Hz), 144.2, 143.4, 142.6, 140.2, 137.6, 135.5 (d, *J* = 15.6 Hz), 133.7, 133.0, 132.2 (d, *J* = 2.8 Hz), 131.9 (d, *J* = 10.8 Hz), 130.1, 128.6 (d, *J* = 2.0 Hz), 128.4, 128.2, 128.0, 127.4, 123.4,

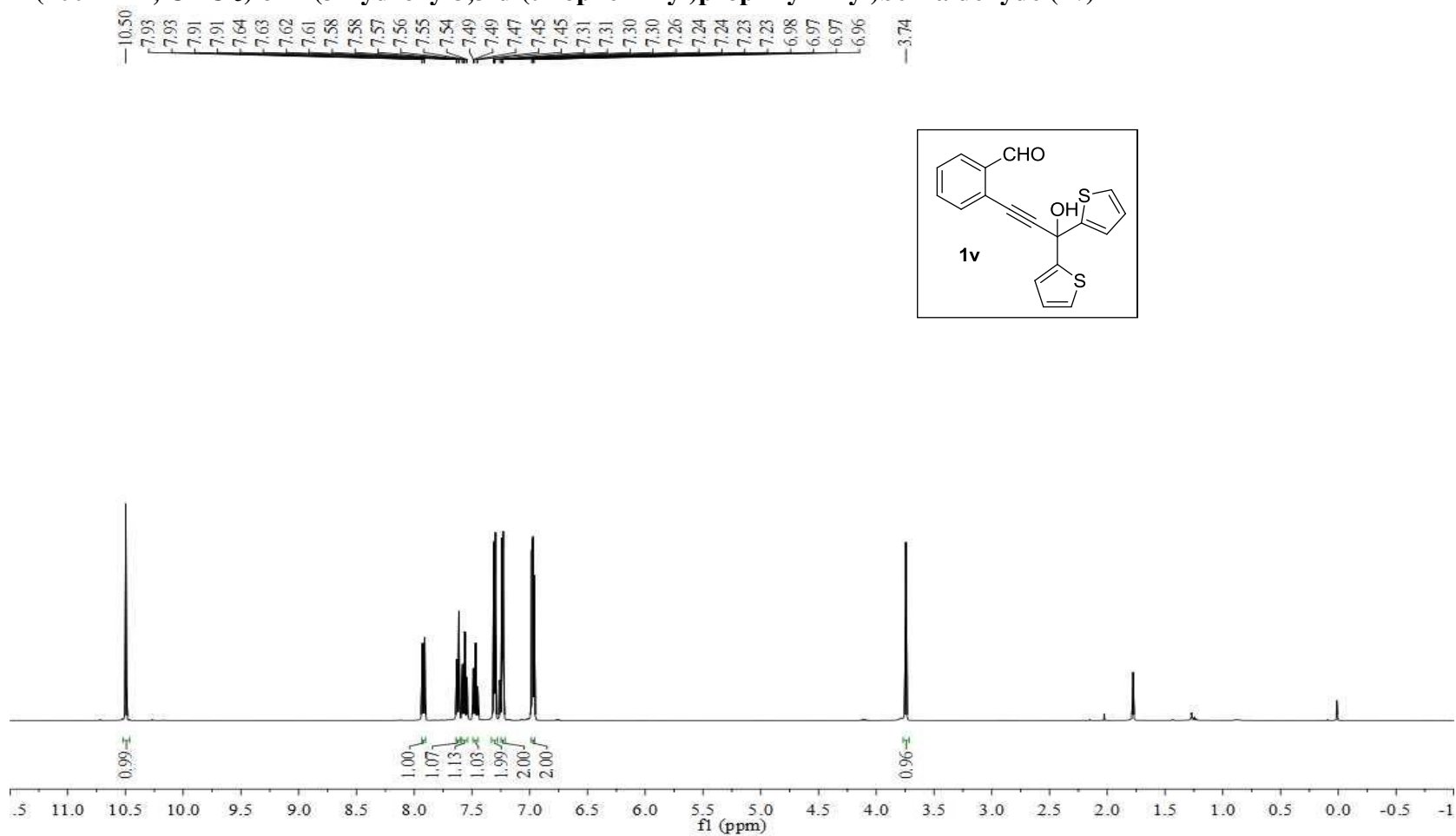
123.0 (d,  $J = 26.0$  Hz), 122.8, 121.6, 115.6, 114.4, 113.9, 112.1.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.6. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{46}\text{H}_{33}\text{NO}_3\text{P}$  678.2193; Found: 678.2188. QY: 3.1%.

**(6-(9,9-dimethylacridin-10(9H)-yl)-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diph-enylphosphine oxide (7a)**. 106 mg, 75%; yellow solid; m. p. 141 - 143 °C; ( $\text{SiO}_2$ )  $R_f = 0.5$  (DCM/EA = 20:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (s, 1H), 7.76 – 7.71 (m, 1H), 7.56 – 7.49 (m, 2H), 7.46 – 7.42 (m, 5H), 7.41 – 7.38 (m, 5H), 7.35 – 7.33 (m, 4H), 7.26 – 7.23 (m, 2H), 7.21 (s, 1H), 7.19 – 7.14 (m, 1H), 7.09 – 7.05 (m, 2H), 7.00 – 6.84 (m, 6H), 6.41 (dd,  $J = 8.0, 1.4$  Hz, 2H), 1.66 (s, 6H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.3 (d,  $J = 5.5$  Hz), 143.2 (d,  $J = 1.3$  Hz), 142.6, 140.6, 140.3, 139.9, 135.9, 133.1, 132.1 (d,  $J = 2.8$  Hz), 132.0, 131.9 (d,  $J = 10.8$  Hz), 130.4, 130.2, 128.8, 128.6, 128.3 (d,  $J = 15.4$  Hz), 128.2 (dd,  $J = 48.6, 2.2$  Hz), 126.5, 125.1, 123.5, 122.8, 122.1, 120.8, 114.4, 112.1, 36.1, 31.0.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  17.8. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{49}\text{H}_{39}\text{NO}_2\text{P}$  704.2713; Found: 704.2700. QY: 8.4%.

**1-(diphenylphosphoryl)-4-(2,2-diphenylvinyl)-1,4-dihydro-1,4-epoxynaphthalene-2,3-dicarboxylate (8a)**. 97 mg, 76 %; oil; ( $\text{SiO}_2$ )  $R_f = 0.5$  (DCM/EA = 10:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 – 7.86 (m, 2H), 7.81 – 7.75 (m, 2H), 7.71 (d,  $J = 6.8$  Hz, 1H), 7.64 – 7.58 (m, 1H), 7.57 – 7.51 (m, 2H), 7.48 – 7.43 (m, 1H), 7.39 – 7.35 (m, 2H), 7.34 – 7.30 (m, 6H), 7.25 – 7.20 (m, 1H), 7.13 – 7.04 (m, 4H), 7.00 – 6.90 (m, 2H), 6.77 (s, 1H), 3.62 (s, 3H), 3.50 (s, 3H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 163.4, 162.4, 153.6, 151.3, 149.4, 148.6, 147.2, 142.8, 138.5, 132.4 (d,  $J = 2.8$  Hz), 132.3, 132.2 (d,  $J = 2.5$  Hz), 132.12 (d,  $J = 2.9$  Hz), 132.0, 131.14 (d,  $J = 26.7$  Hz), 130.8, 130.11 (d,  $J = 27.9$  Hz), 128.5, 128.29 (dd,  $J = 10.9, 2.9$  Hz), 128.1, 127.6, 126.1, 125.9, 123.1, 121.0, 118.1, 92.85 (d,  $J = 9.3$  Hz), 90.8, 89.9, 52.4, 52.1.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta = 23.6$ . HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{40}\text{H}_{32}\text{O}_6\text{P}$  639.1931; Found: 639.1909.

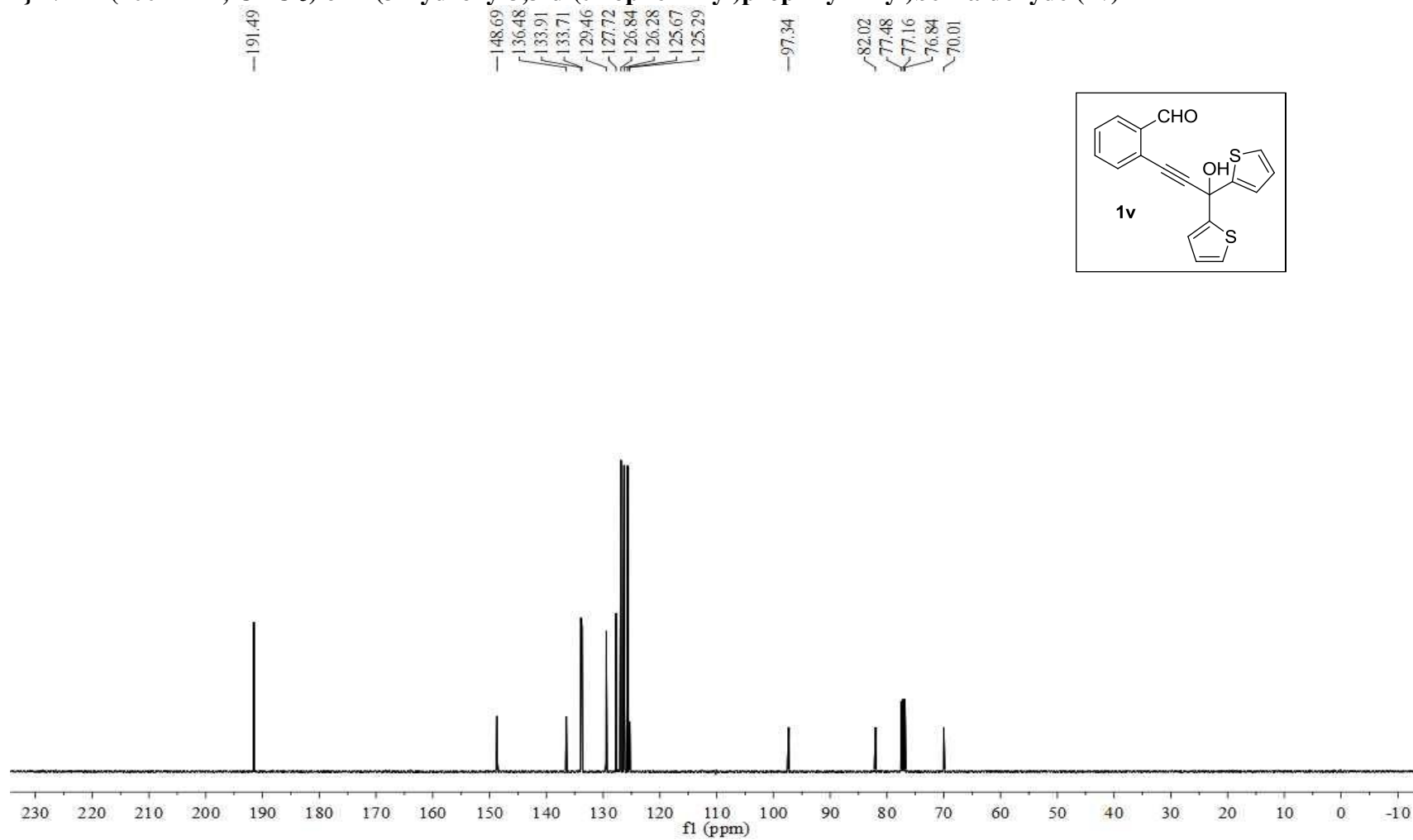
# $^1\text{H}$ , $^{13}\text{C}$ , $^{31}\text{P}$ and $^{19}\text{F}$ NMR Spectra for All Products

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of 2-(3-hydroxy-3,3-di(thiophen-2-yl)prop-1-yn-1-yl)benzaldehyde (**1v**)

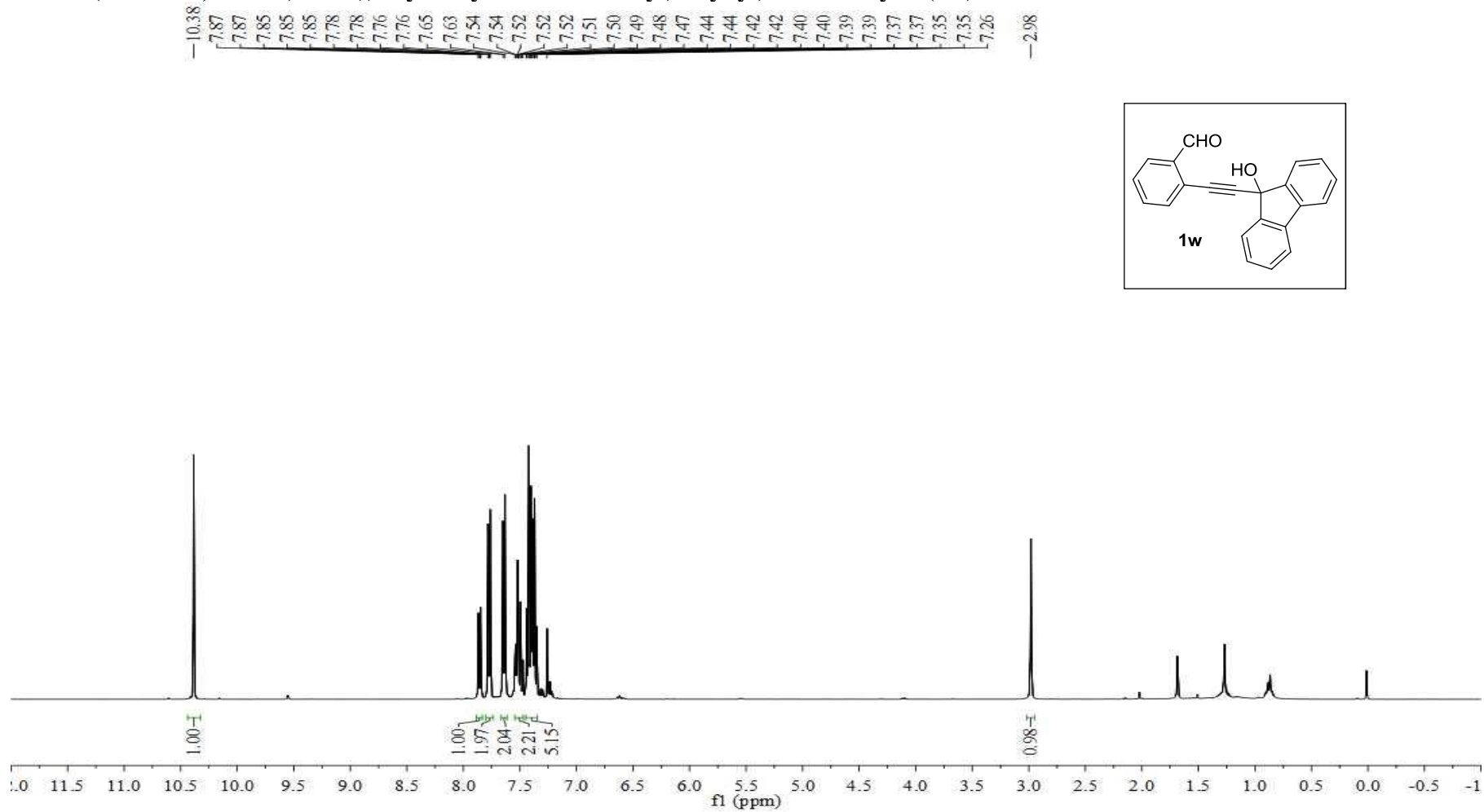




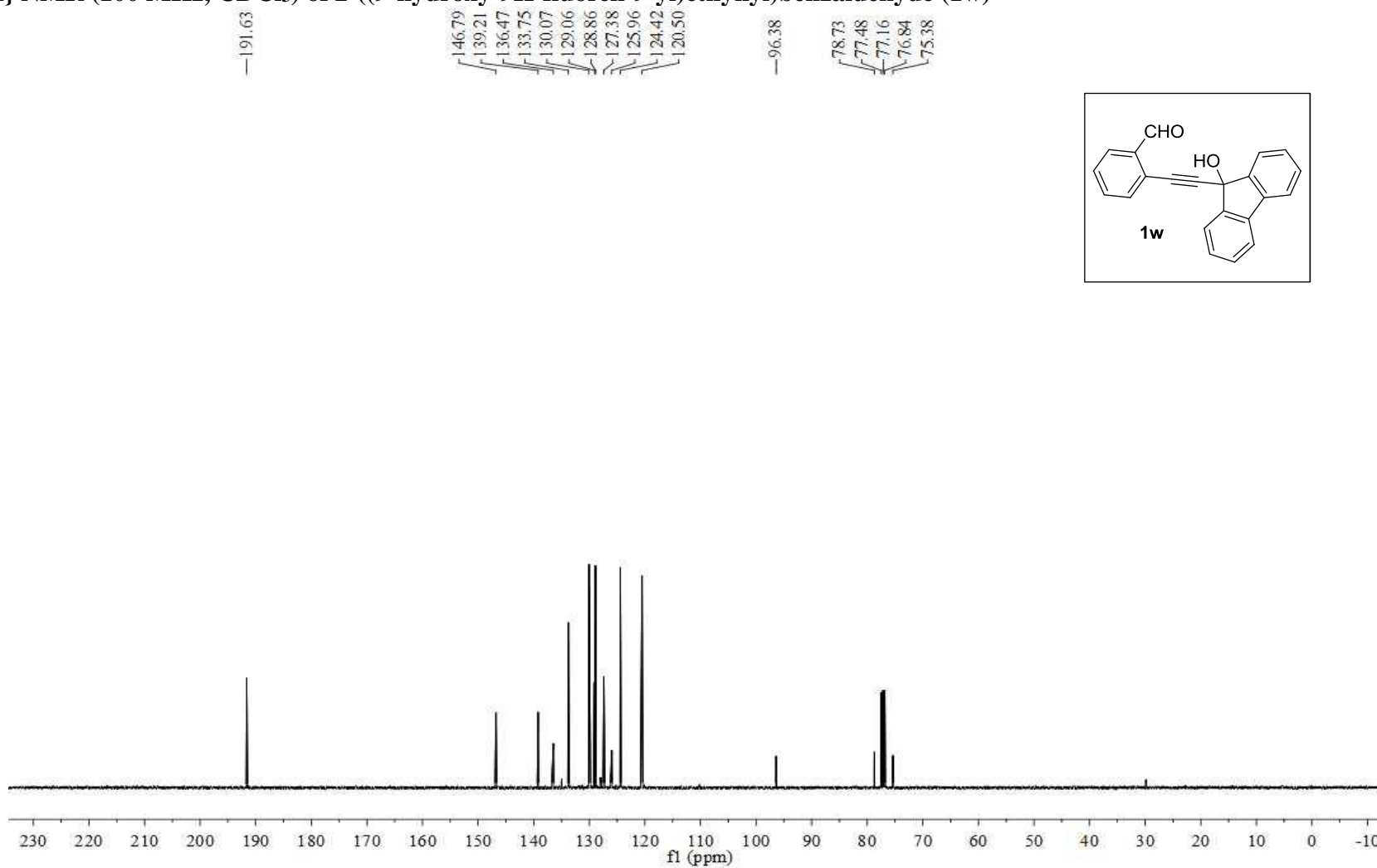
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of 2-(3-hydroxy-3,3-di(thiophen-2-yl)prop-1-yn-1-yl)benzaldehyde (**1v**)



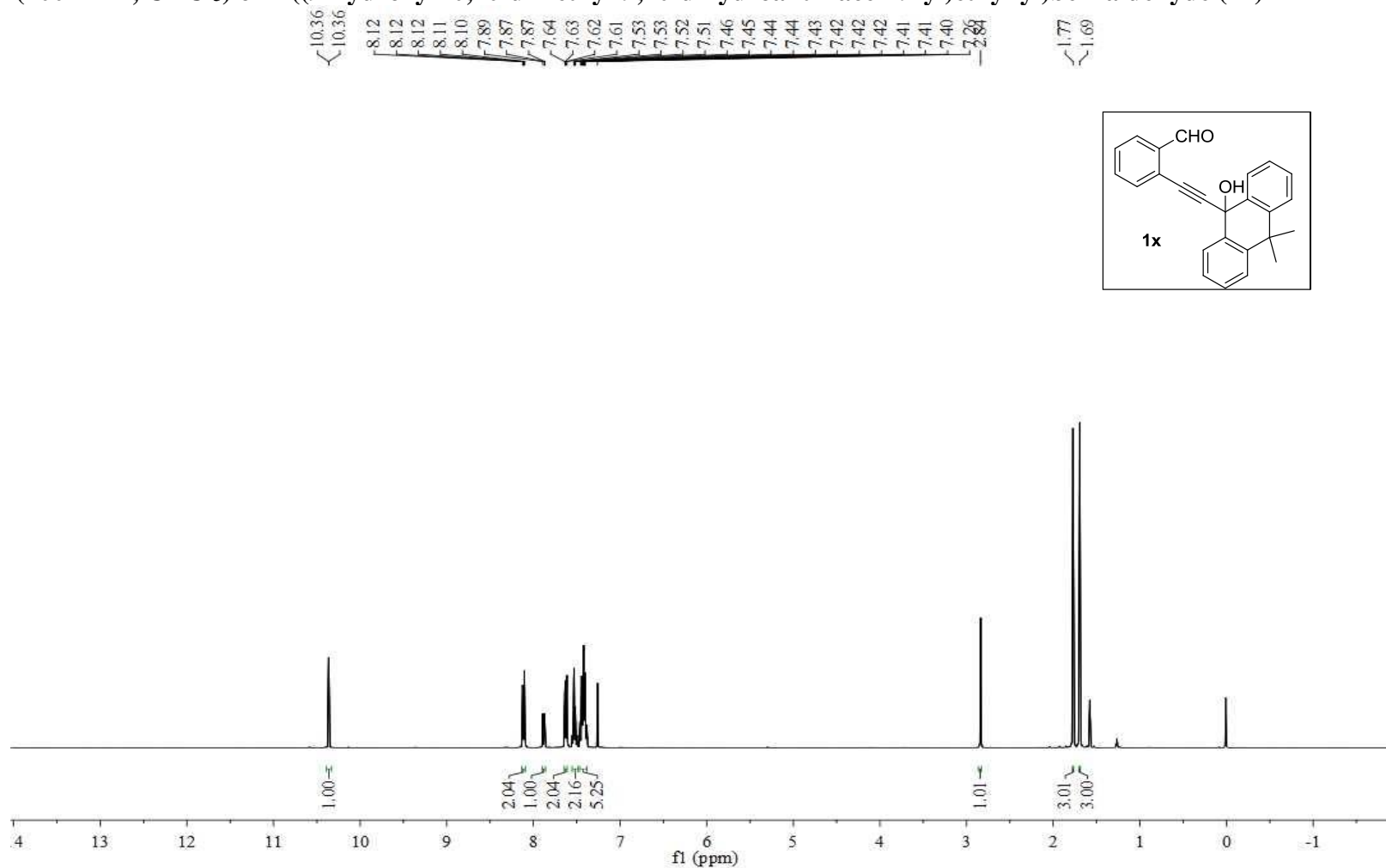
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2-((9-hydroxy-9H-fluoren-9-yl)ethynyl)benzaldehyde (1w)**



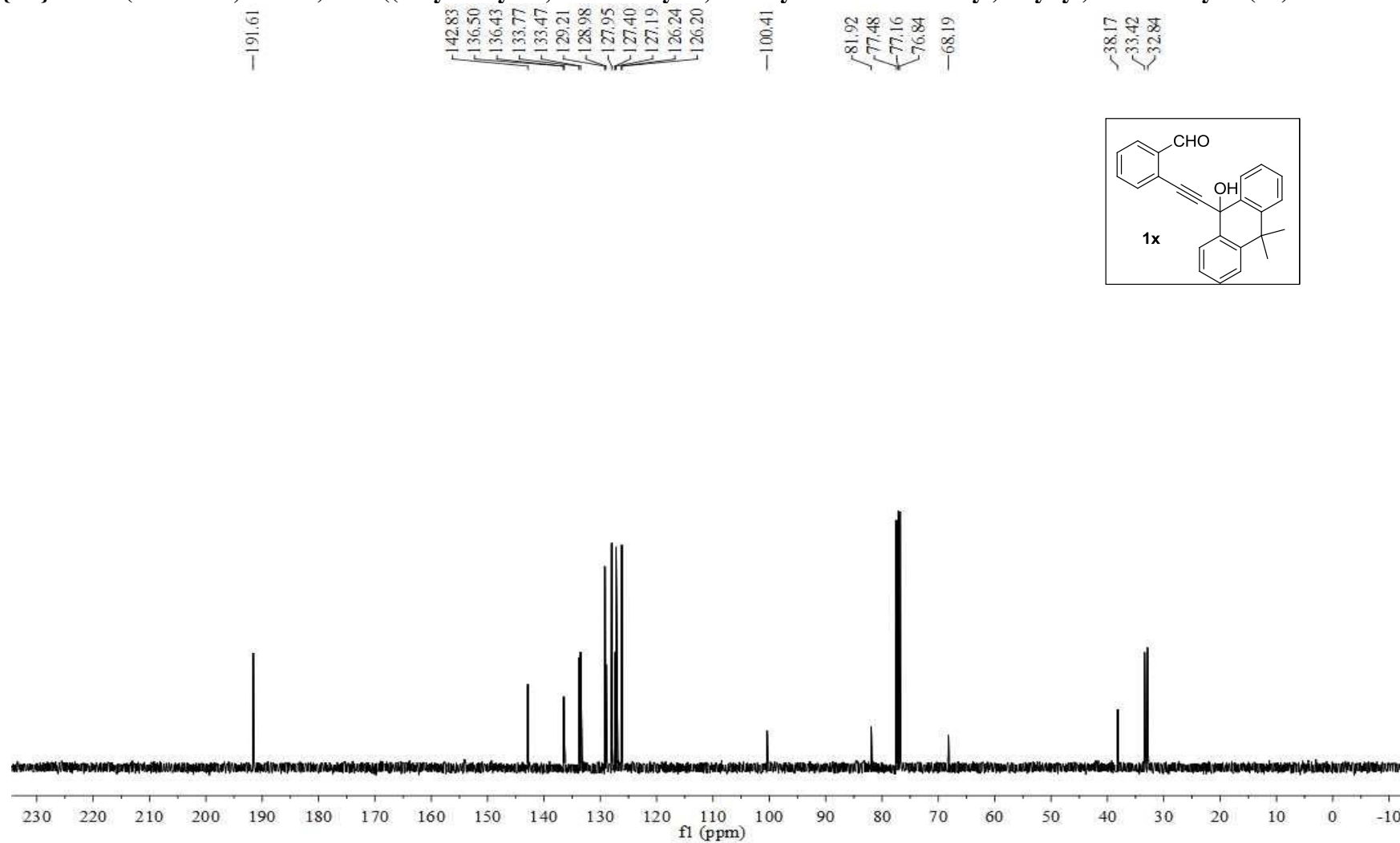
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of 2-((9-hydroxy-9H-fluoren-9-yl)ethynyl)benzaldehyde (**1w**)



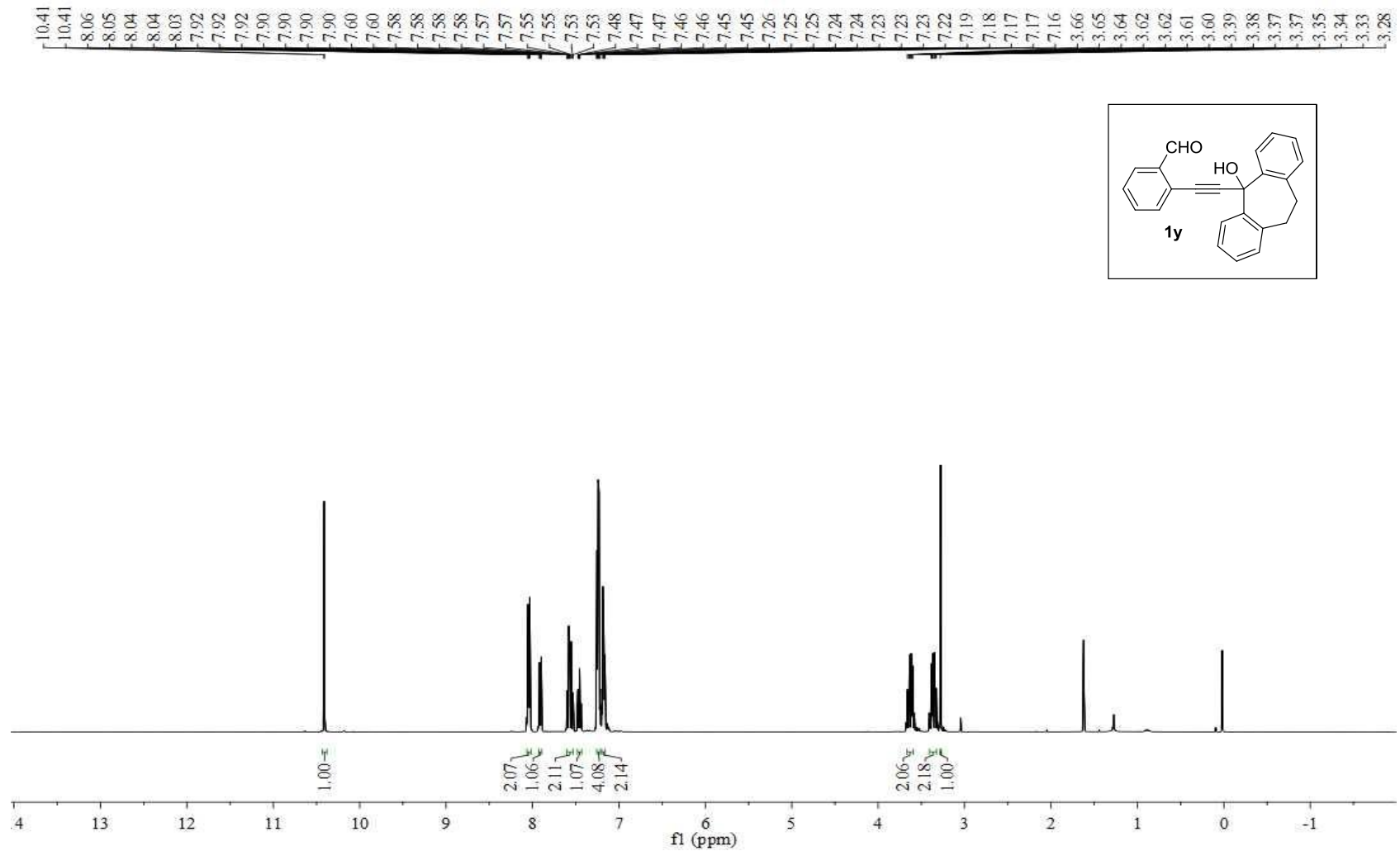
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2-((9-hydroxy-10,10-dimethyl-9,10-dihydroanthracen-9-yl)ethynyl)benzaldehyde (1x)



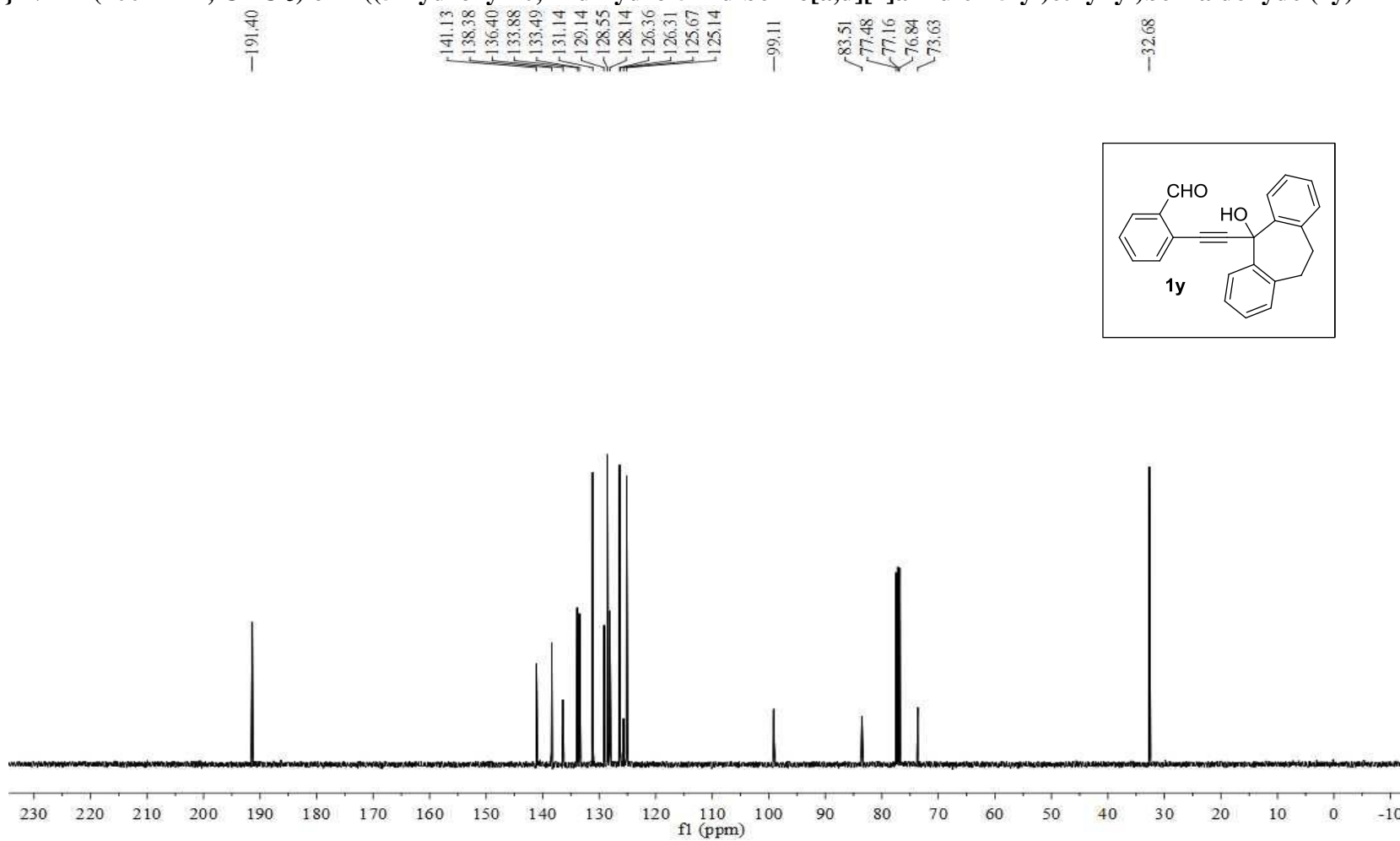
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of 2-((9-hydroxy-10,10-dimethyl-9,10-dihydroanthracen-9-yl)ethynyl)benzaldehyde (**1x**)



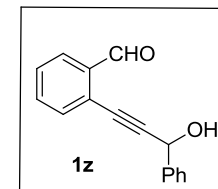
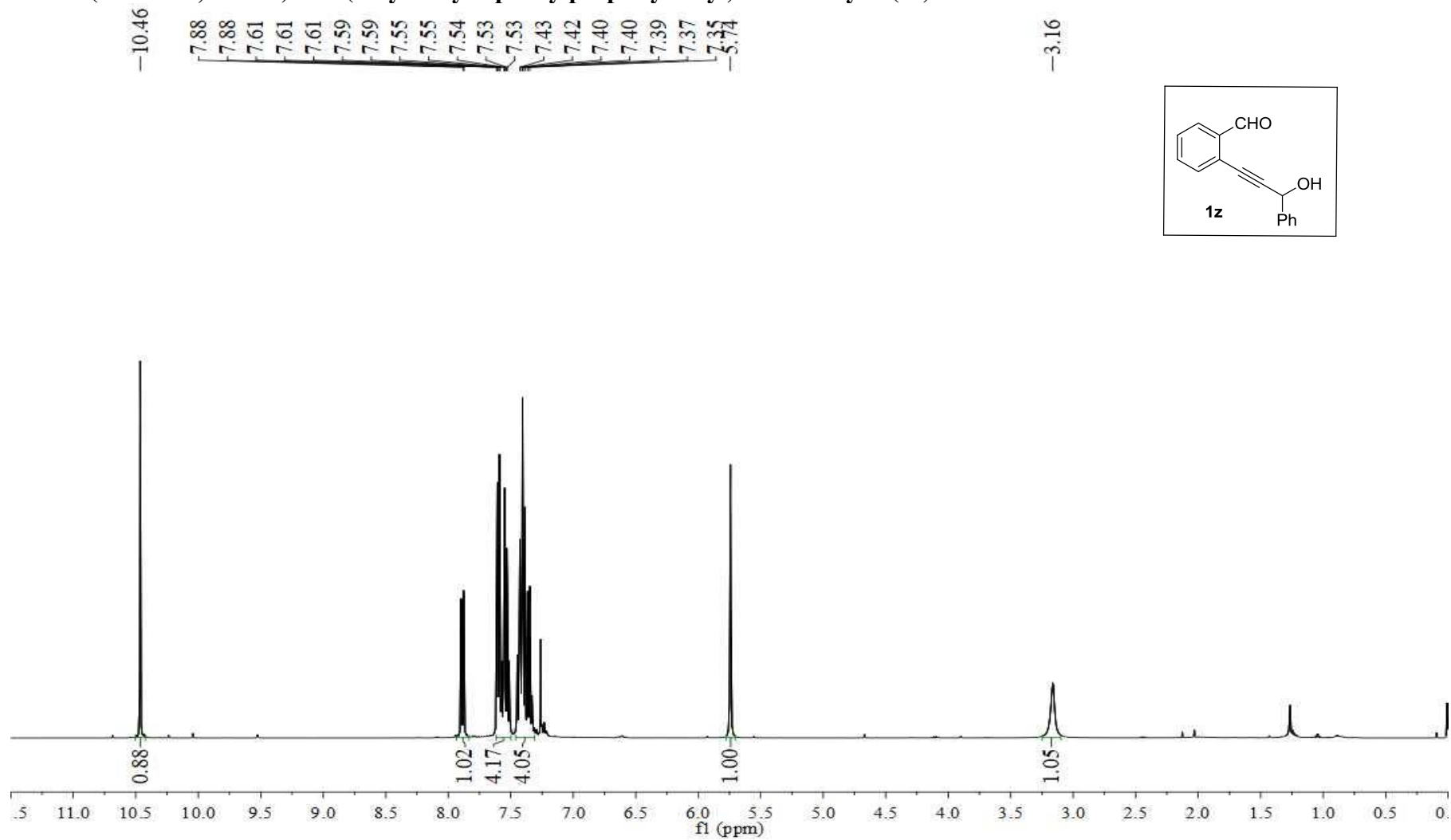
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2-((5-hydroxy-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl)ethynyl)benzaldehyde (1y)**



$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of 2-((5-hydroxy-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl)ethynyl)benzaldehyde (**1y**)

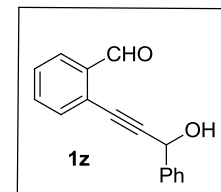
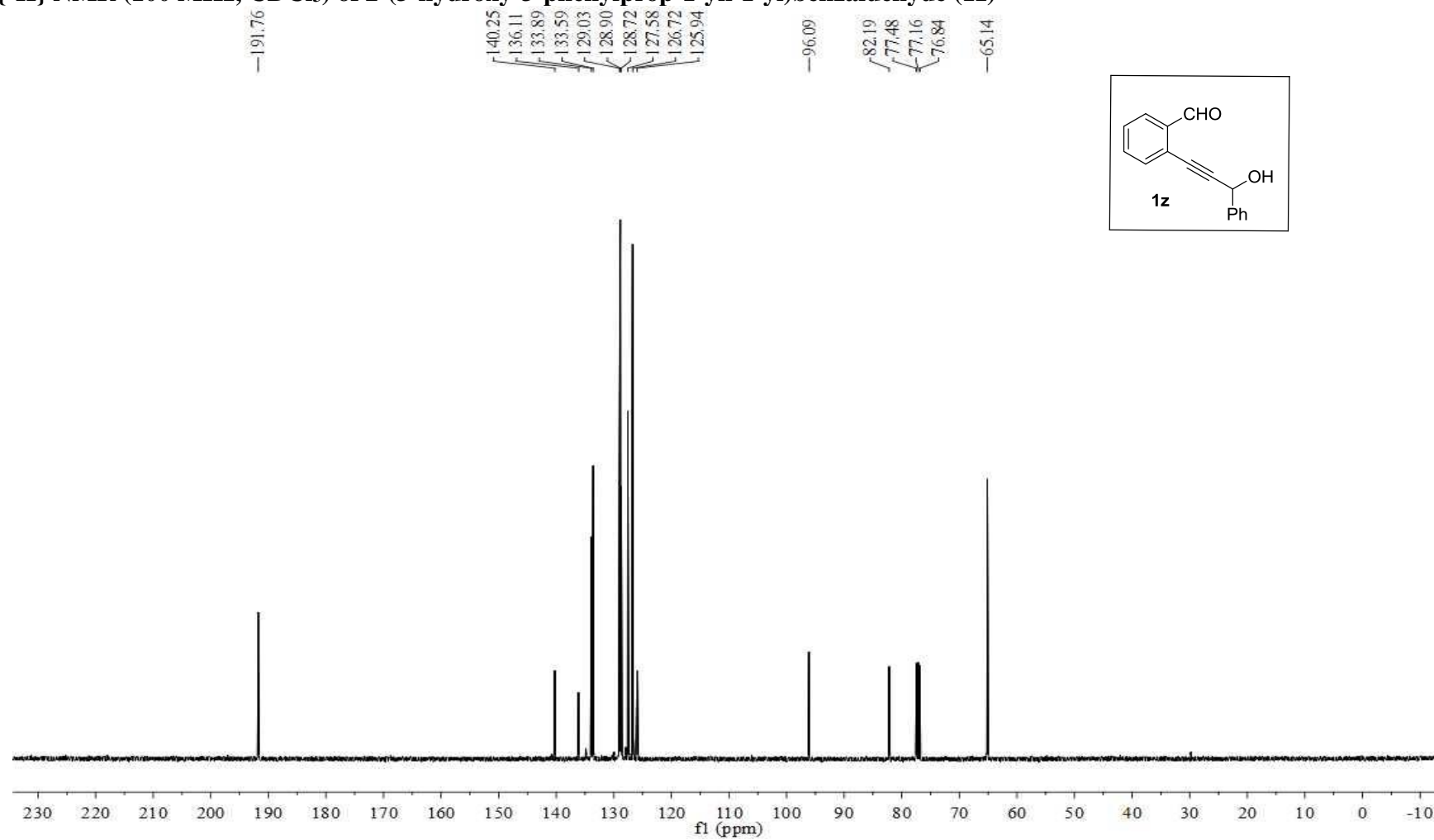


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2-(3-hydroxy-3-phenylprop-1-yn-1-yl)benzaldehyde (1z)**

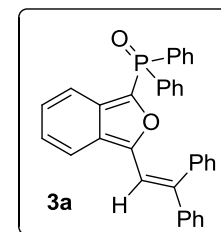
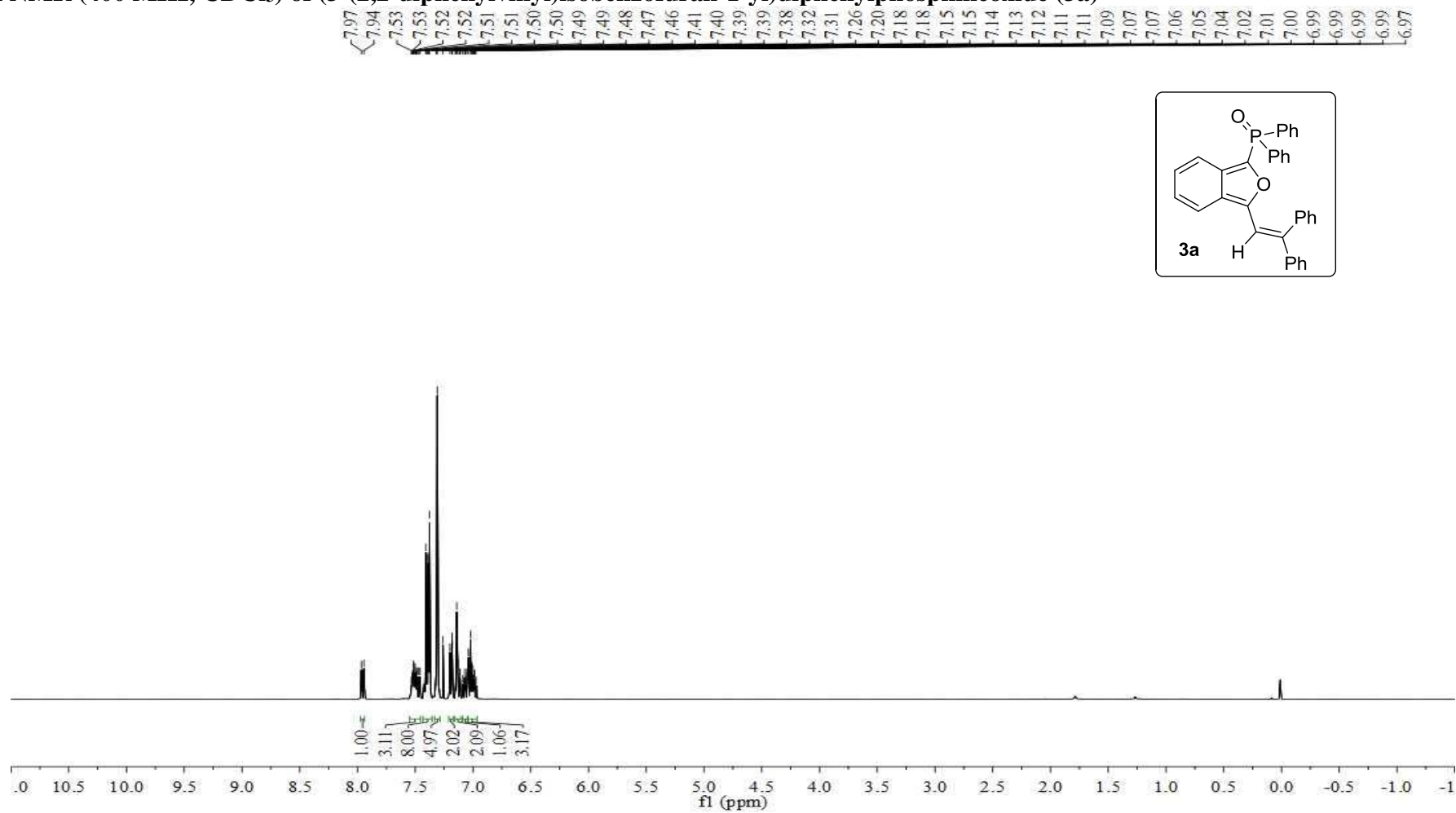




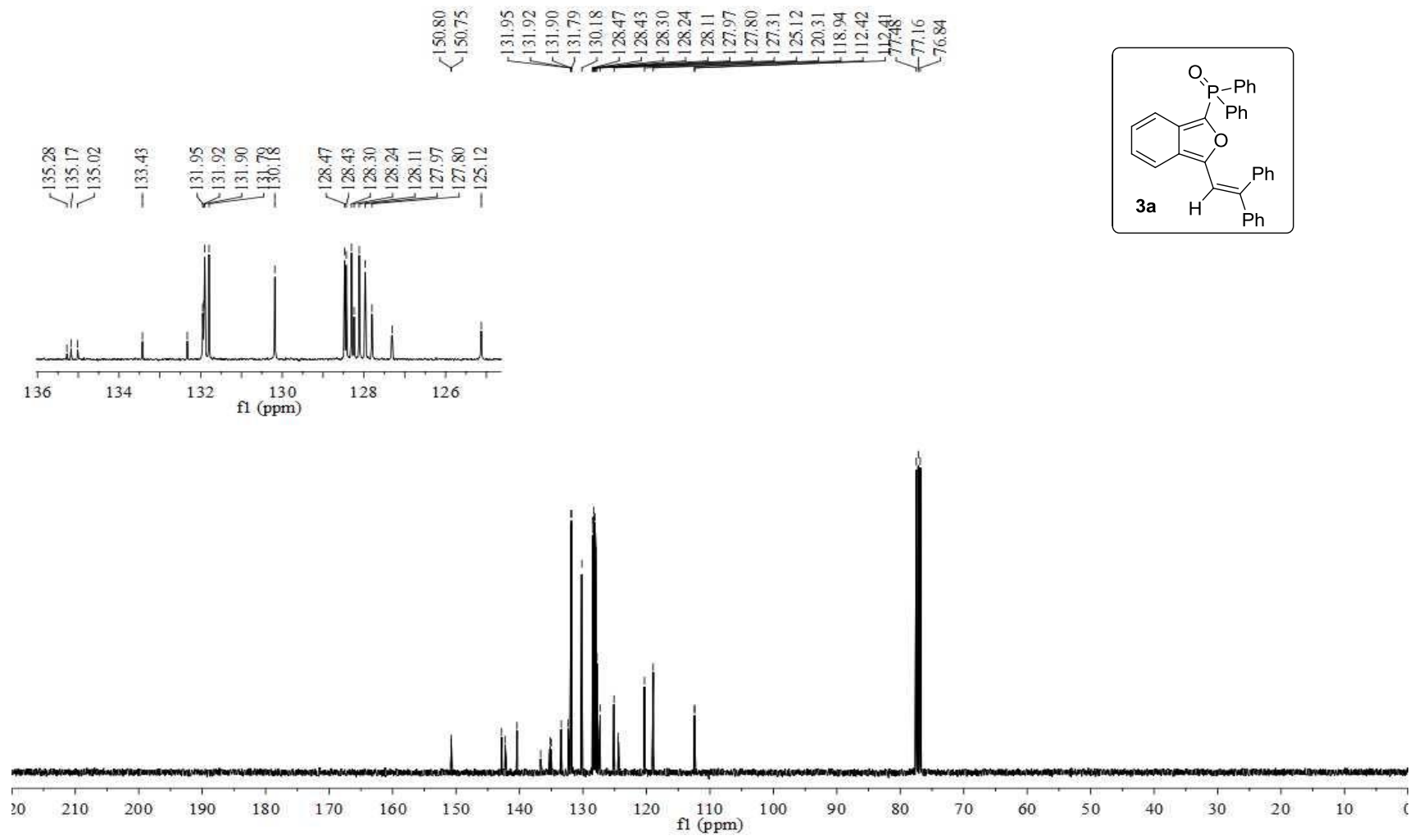
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of 2-(3-hydroxy-3-phenylprop-1-yn-1-yl)benzaldehyde (**1z**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphineoxide (3a)

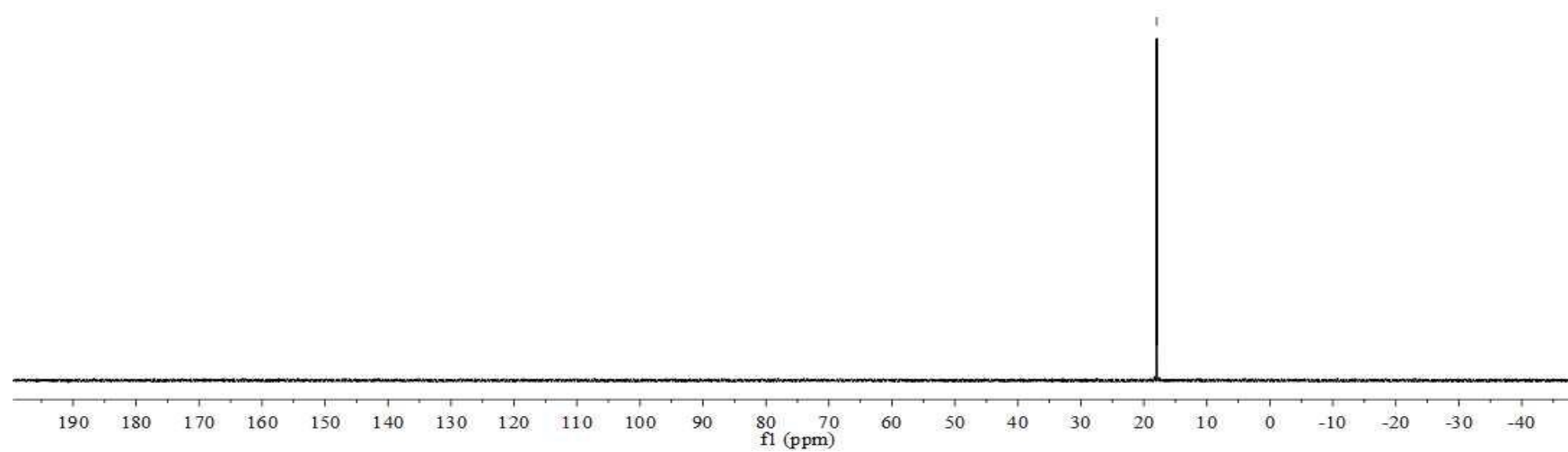
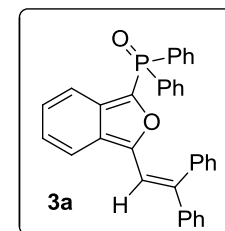


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphineoxide (3a)

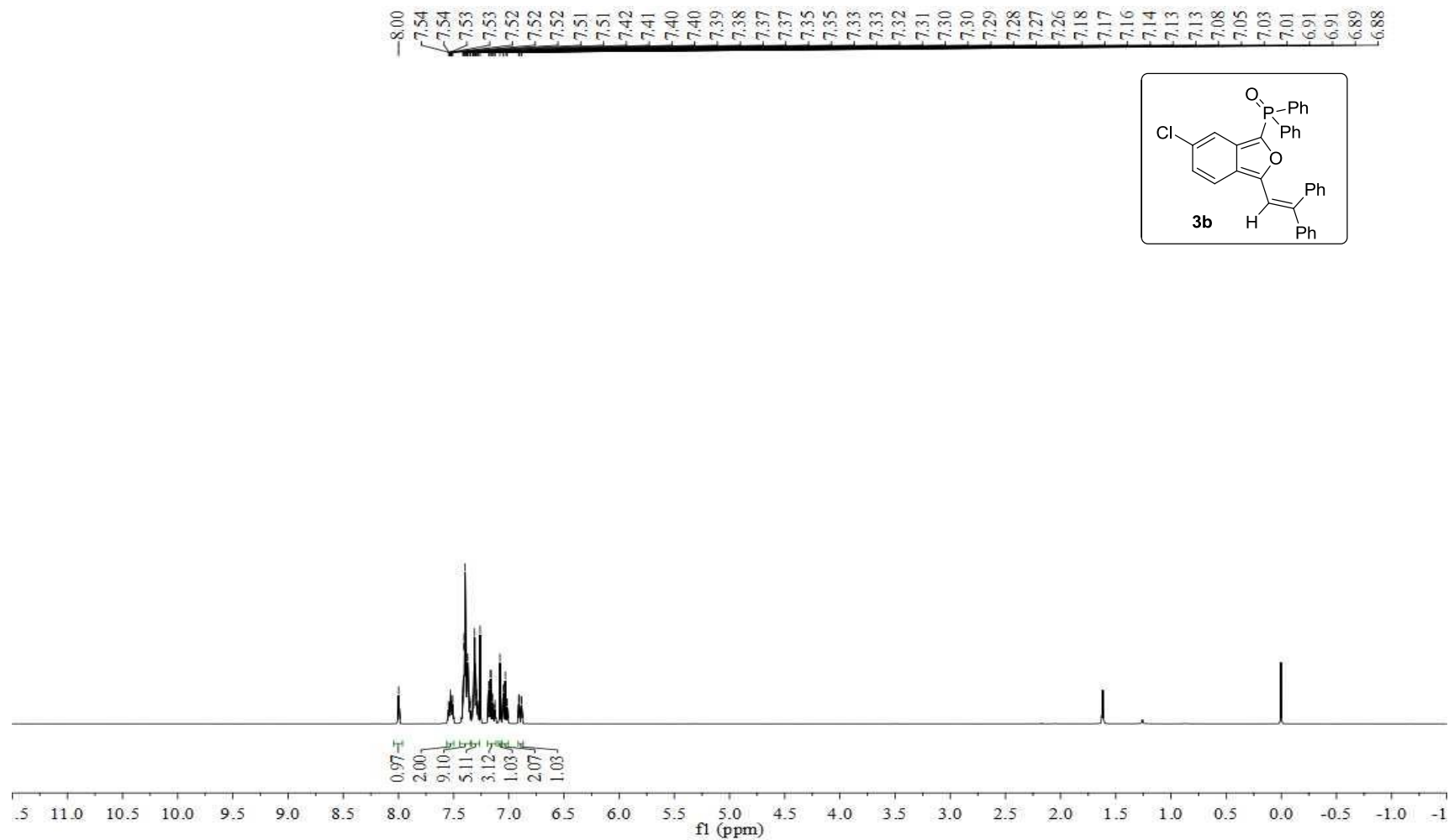


$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphineoxide (3a)

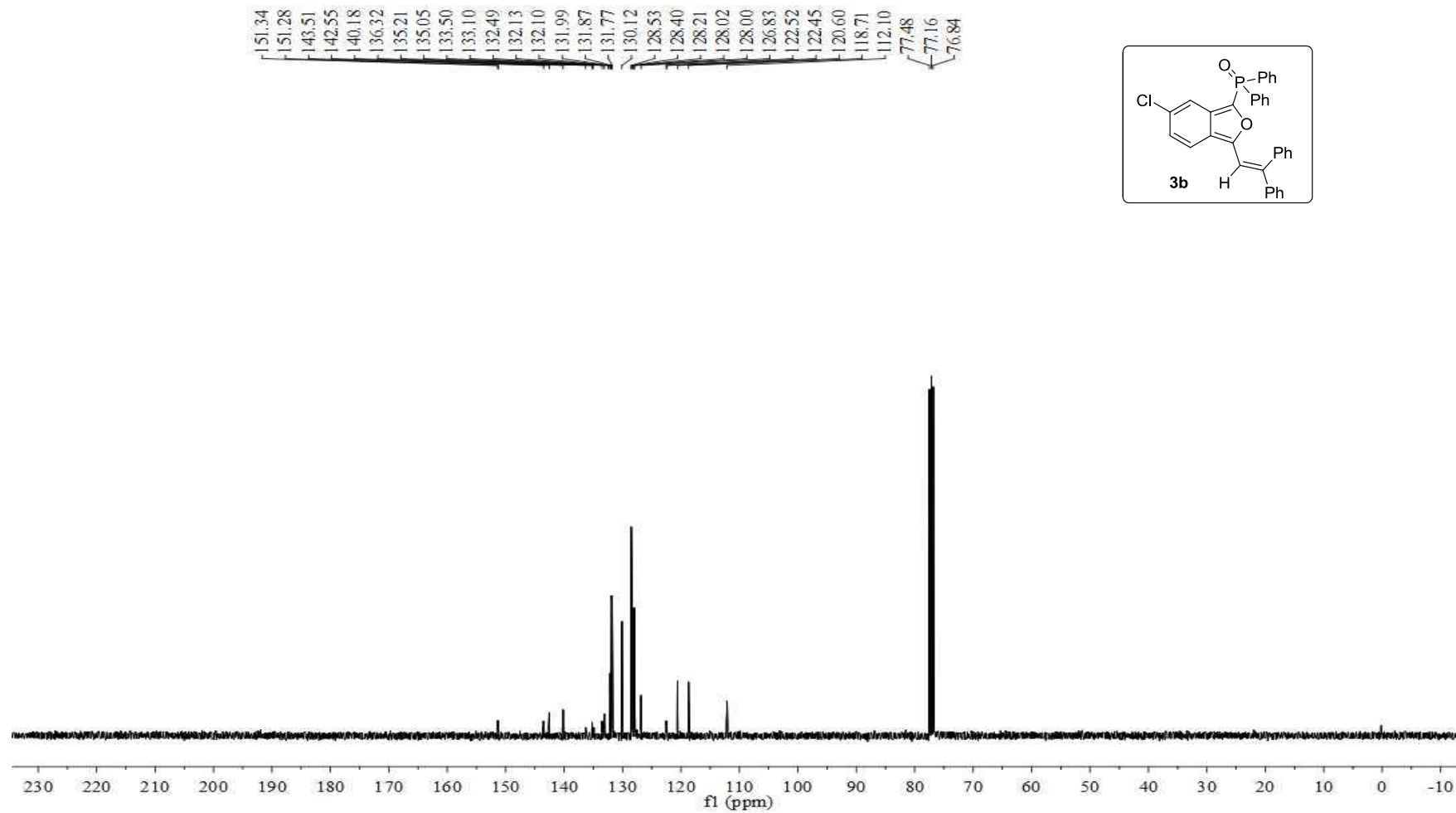
17.96



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (6-chloro-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3b)

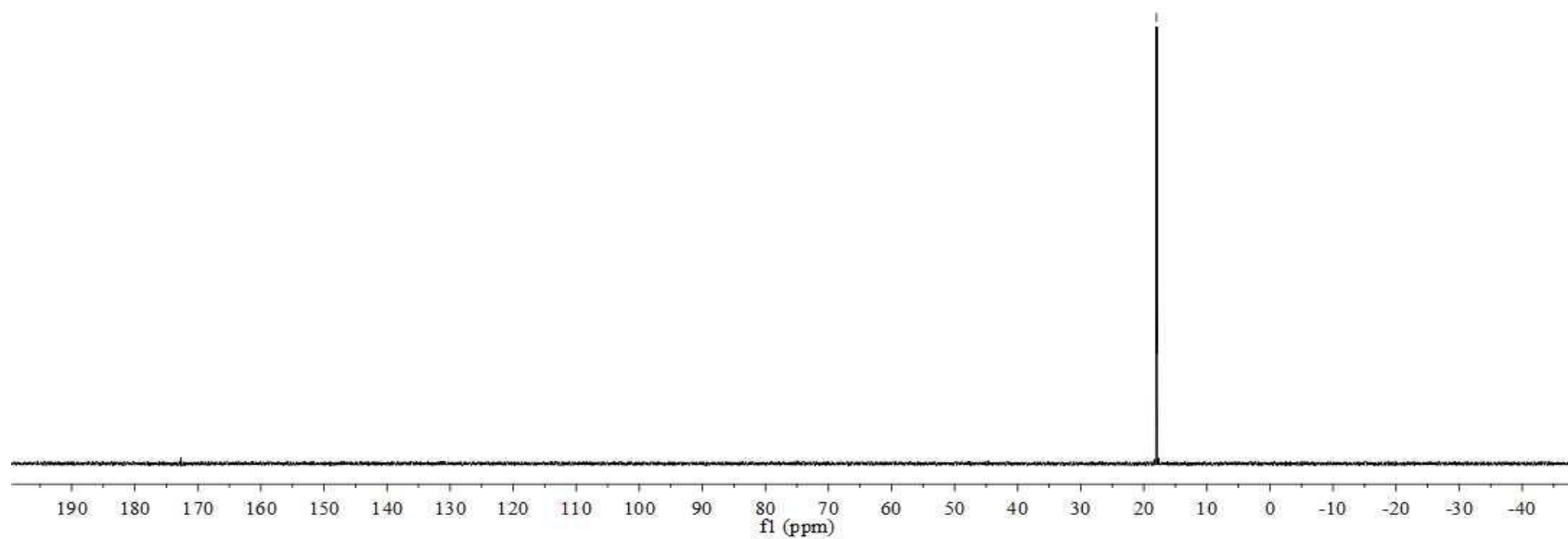
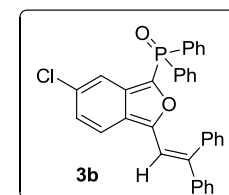


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (6-chloro-3-(2,2-diphenylvinyl) isobenzofuran-1-yl)diphenylphosphine oxide (3b)**



$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (6-chloro-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (**3b**)

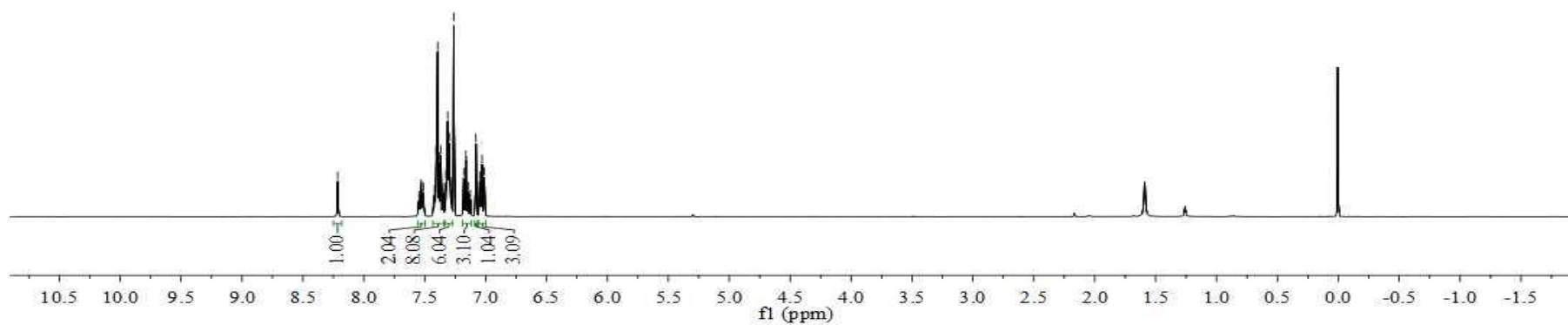
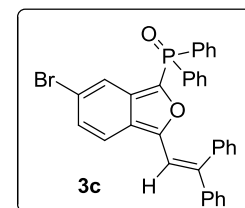
—17.99



S51

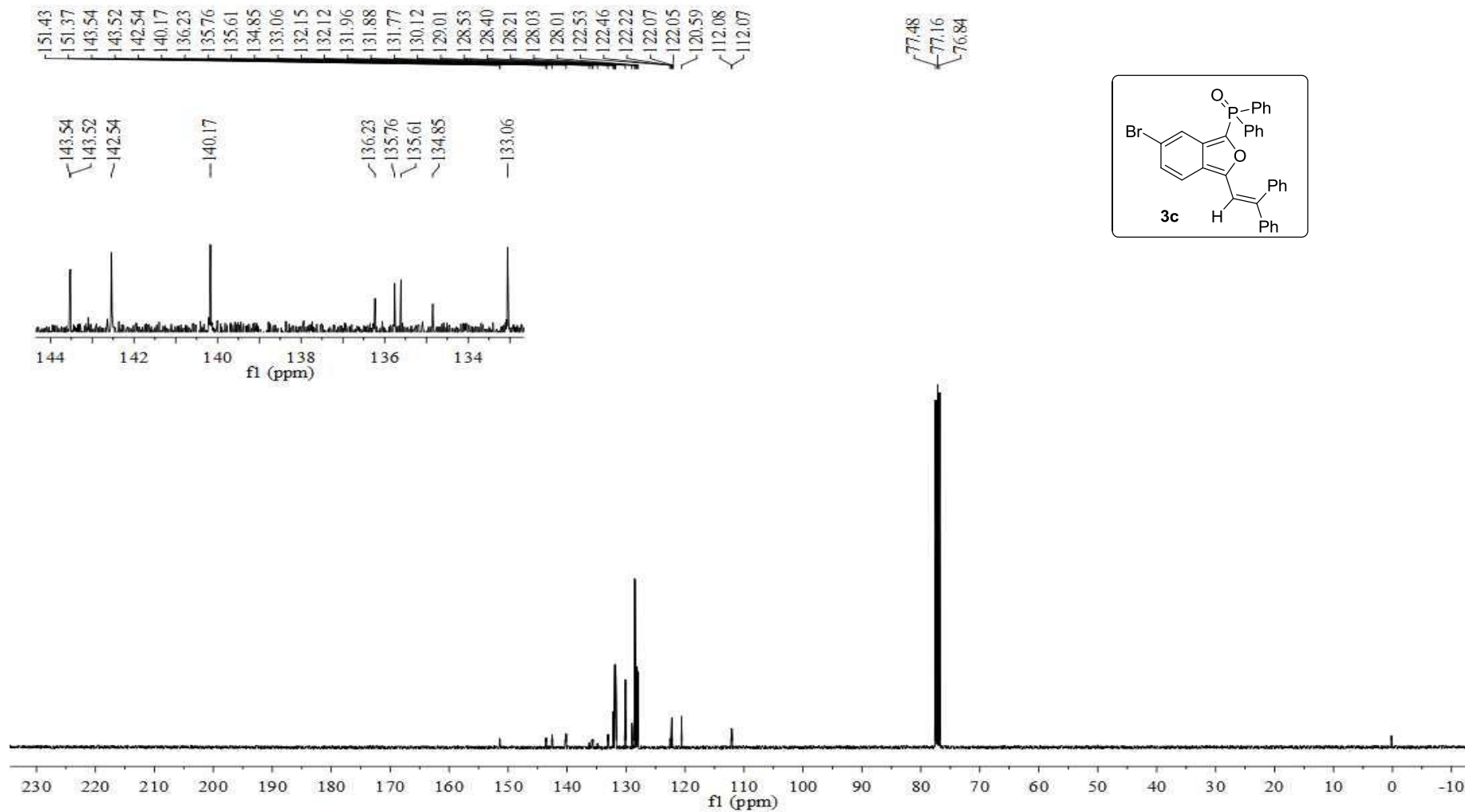
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (6-bromo-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3c)

8.21, 7.56, 7.55, 7.54, 7.53, 7.53, 7.53, 7.53, 7.52, 7.52, 7.51, 7.51, 7.43, 7.43, 7.42, 7.41, 7.41, 7.40, 7.39, 7.39, 7.39, 7.38, 7.37, 7.37, 7.35, 7.35, 7.33, 7.32, 7.32, 7.32, 7.31, 7.30, 7.30, 7.29, 7.28, 7.27, 7.26, 7.18, 7.16, 7.16, 7.15, 7.14, 7.13, 7.13, 7.08, 7.05, 7.04, 7.03, 7.03, 7.02, 7.01



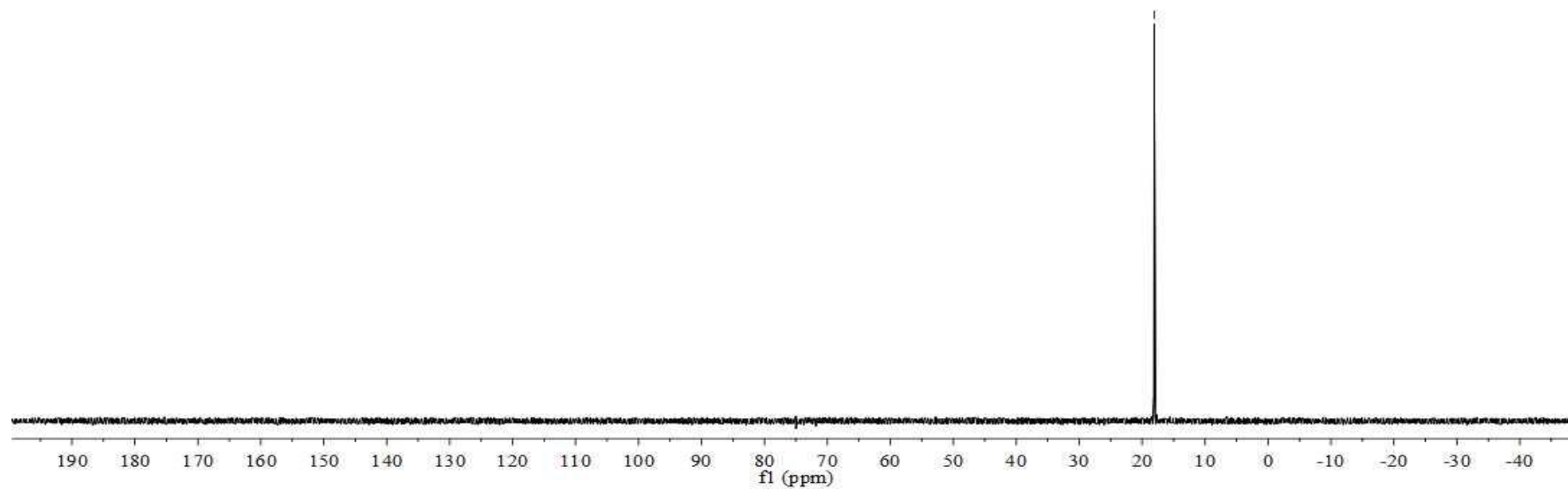
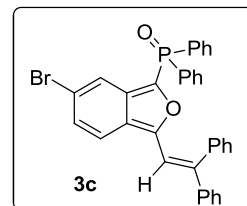


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (6-bromo-3-(2,2-diphenylvinyl) isobenzofuran-1-yl)diphenylphosphine oxide (3c)**



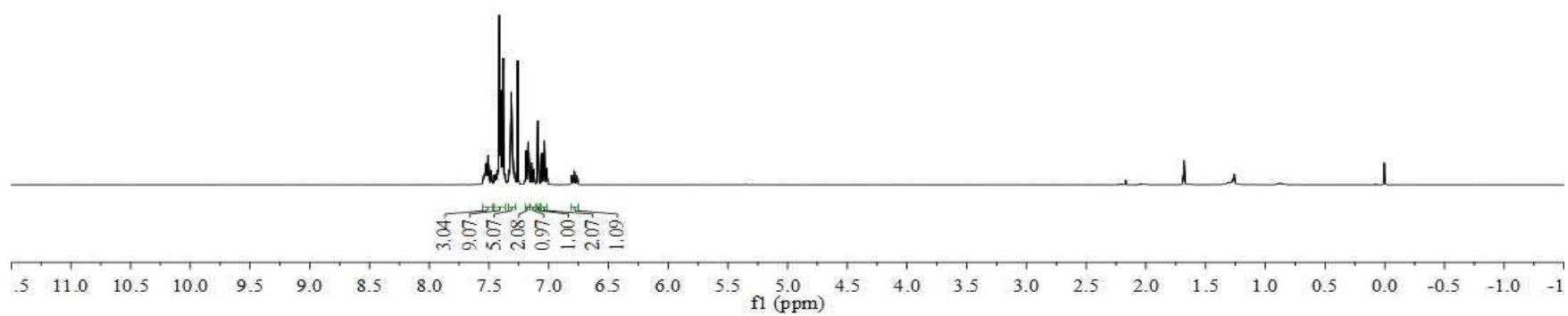
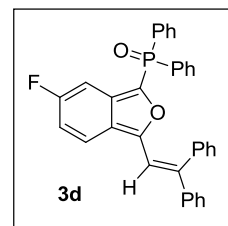
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (6-bromo-3-(2,2-diphenylvinyl) isobenzofuran-1-yl)diphenylphosphine oxide (**3c**)

18.08



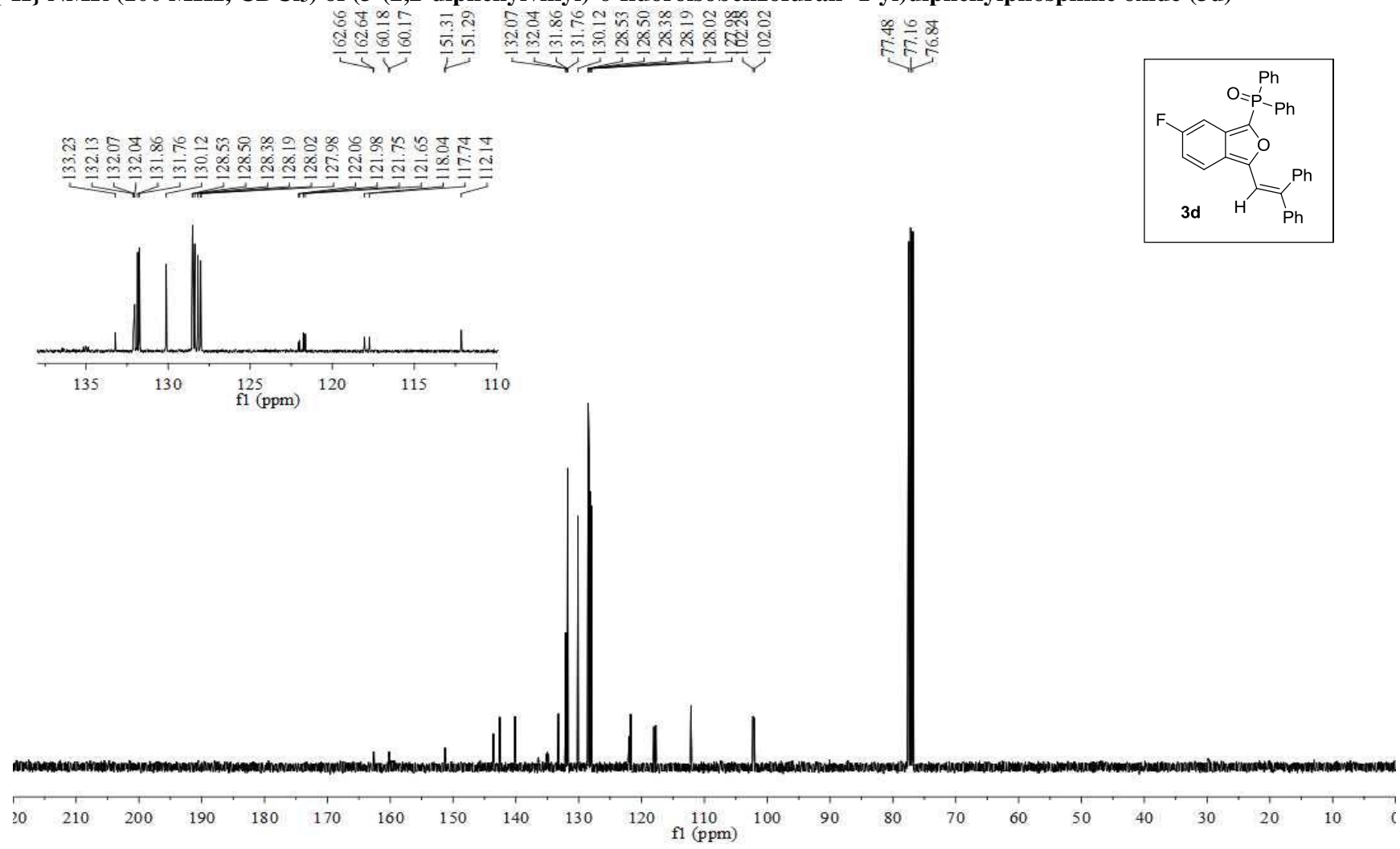
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-6-fluorobenzofuran-1-yl)diphenylphosphine oxide (3d)**

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6.78  
6.76  
6.76



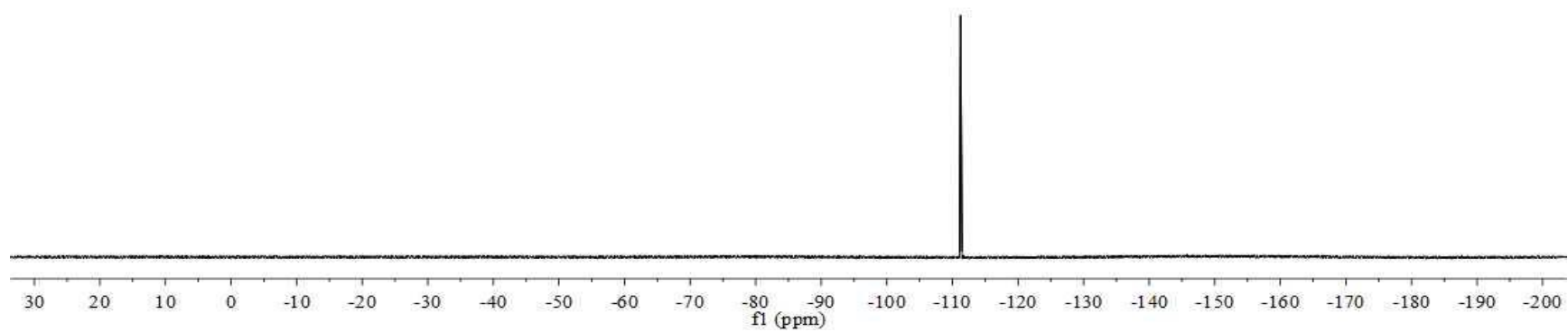
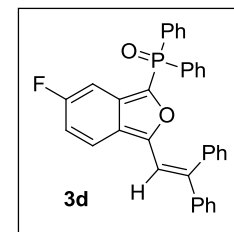
S55

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-6-fluoroisobenzofuran -1-yl)diphenylphosphine oxide (3d)**



$^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-6-fluoroisobenzofuran -1-yl)diphenylphosphine oxide (3d)

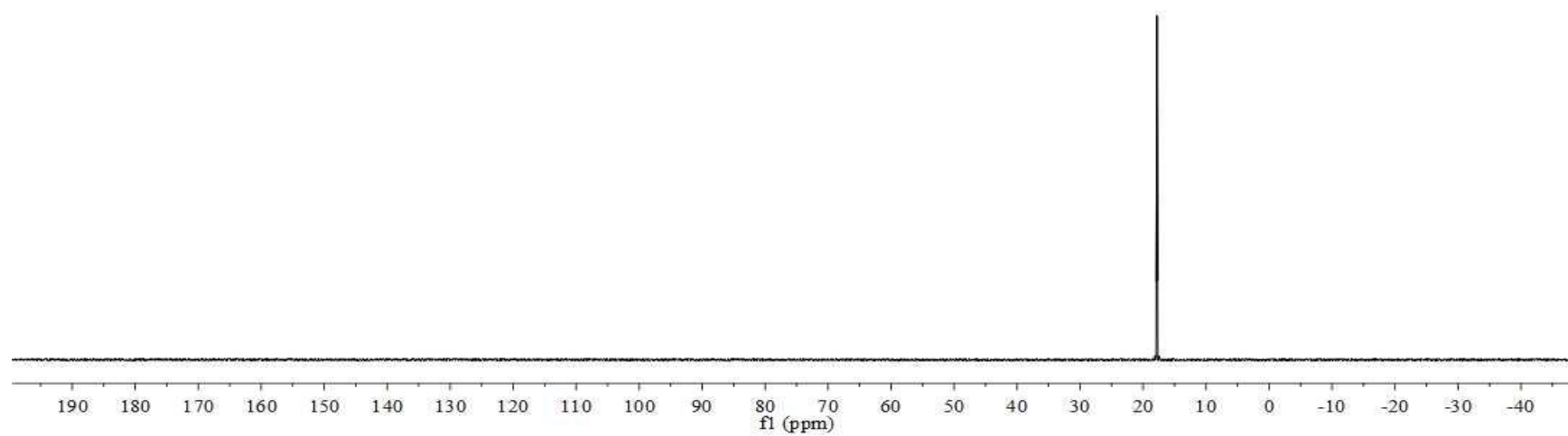
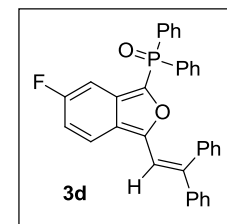
-111.23  
-111.23  
-111.24  
-111.25  
-111.26  
-111.27  
-111.28  
-111.29



S57

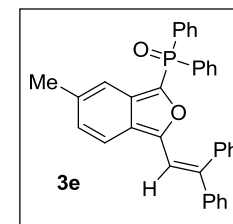
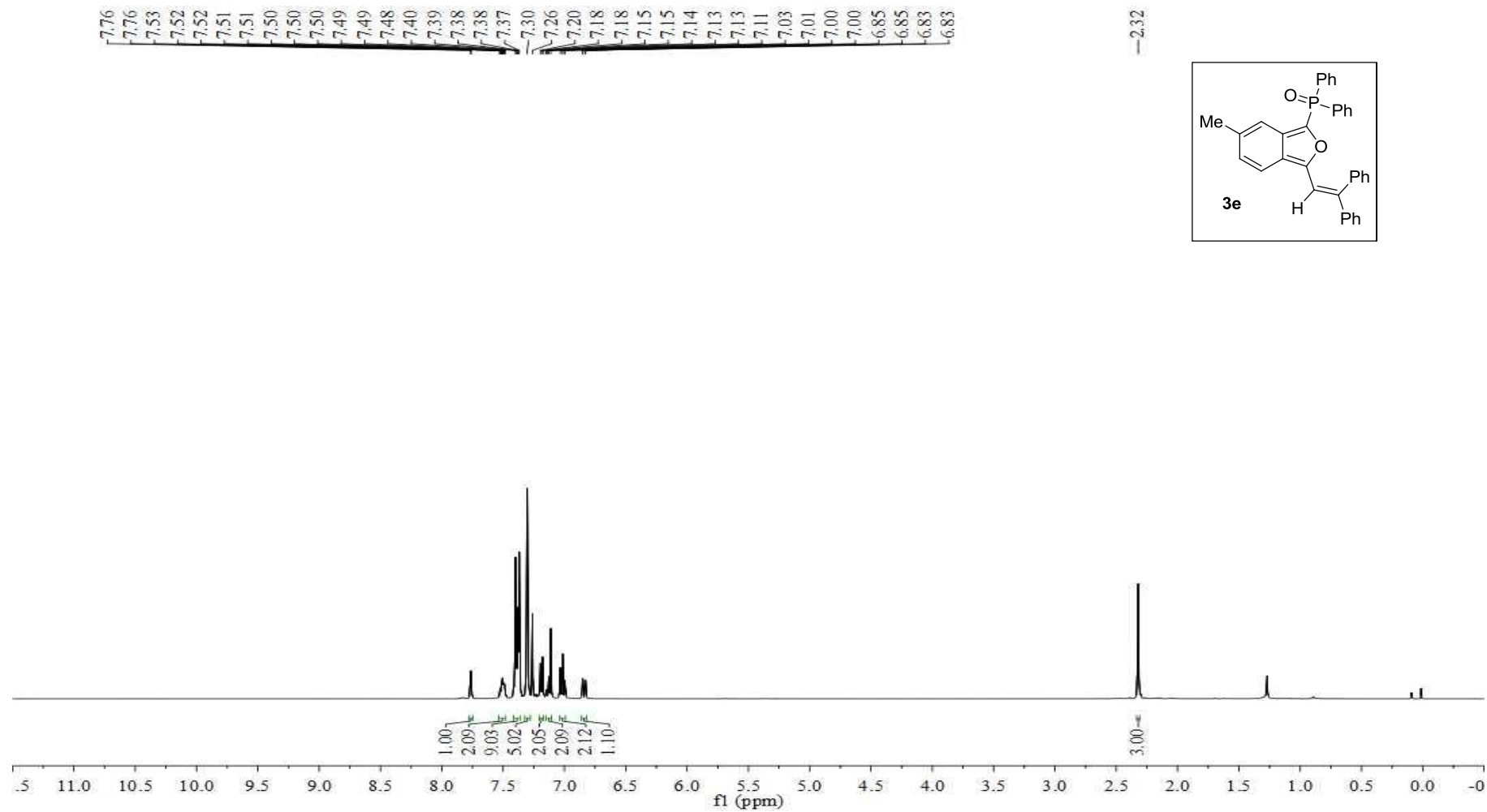
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-6-fluoroisobenzofuran-1-yl)diphenylphosphine oxide (3d)

17.79

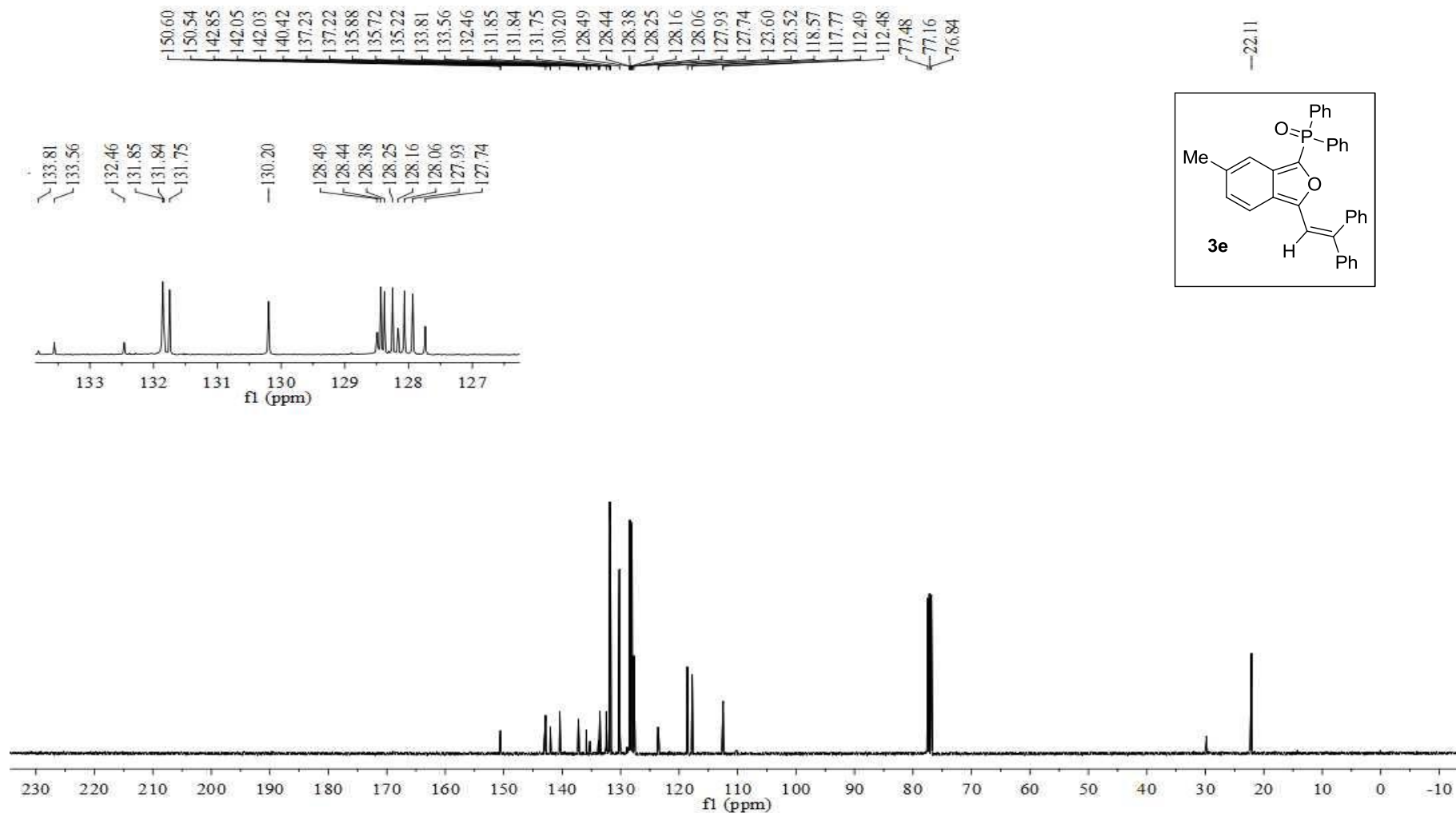


S58

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-6-methylisobenzofuran-1-yl)diphenylphosphine oxide (3e)**

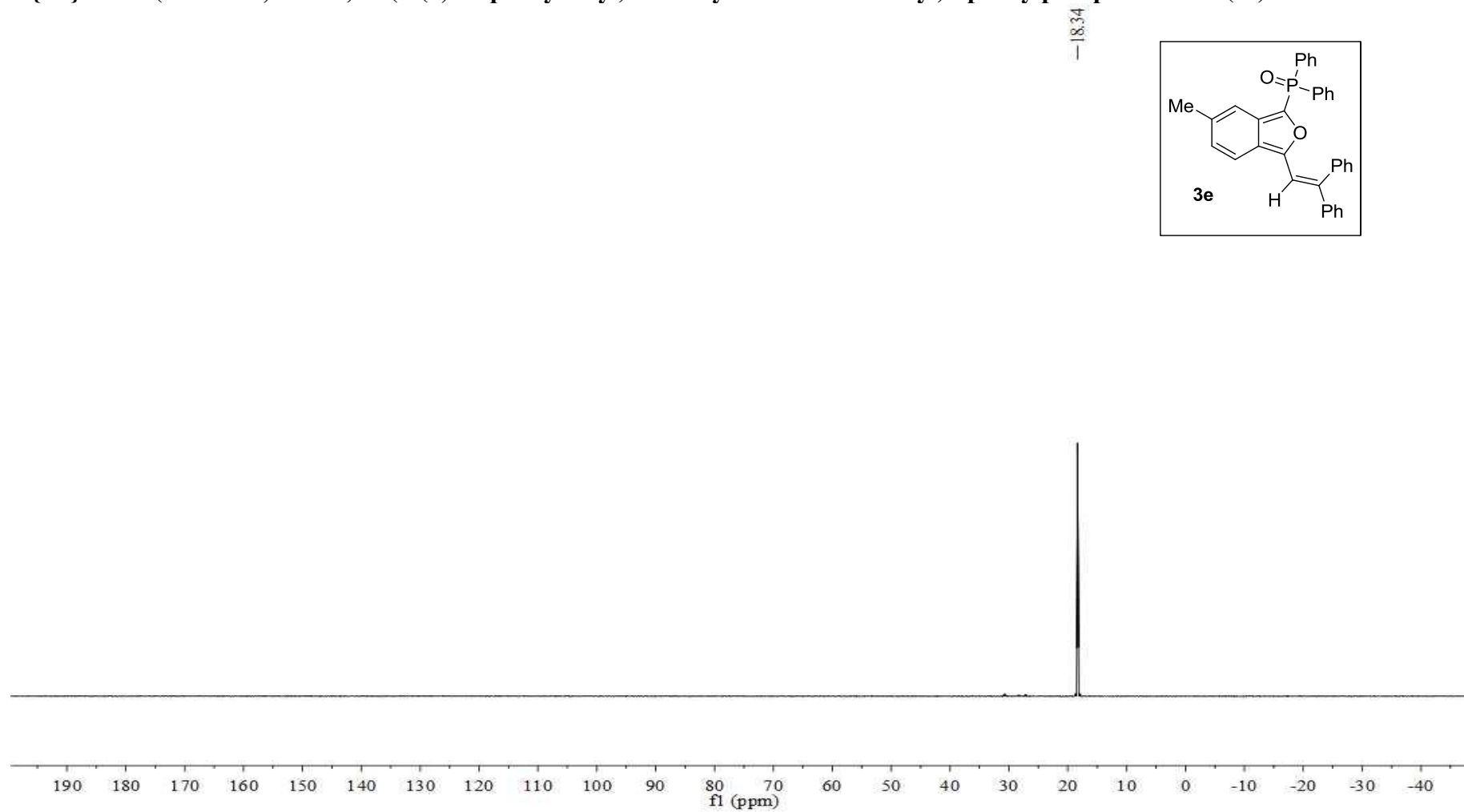


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-6-methylisobenzofuran-1-yl)diphenylphosphine oxide (3e)**

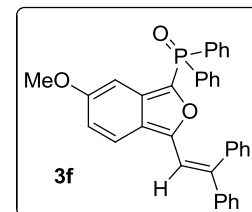
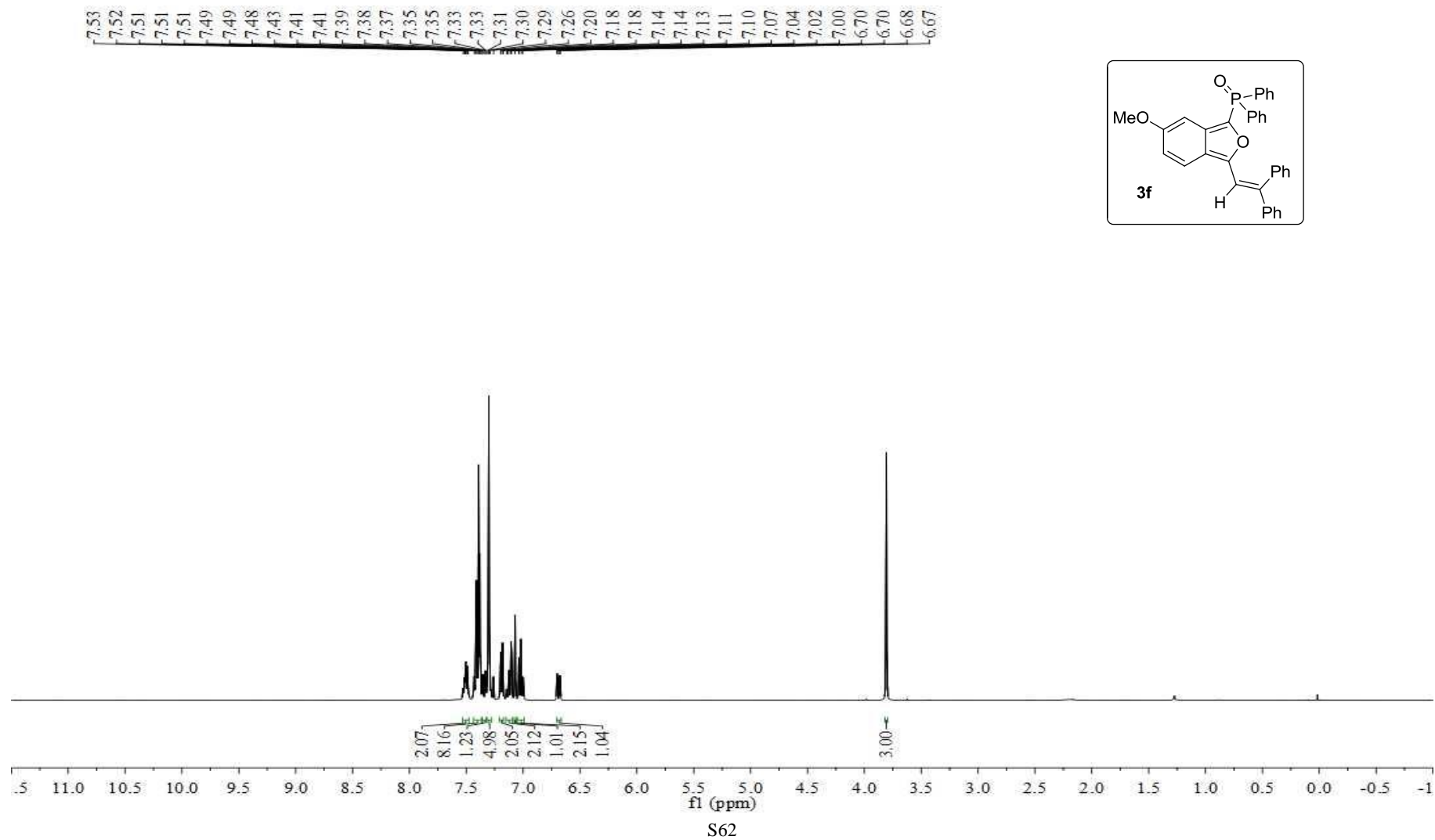




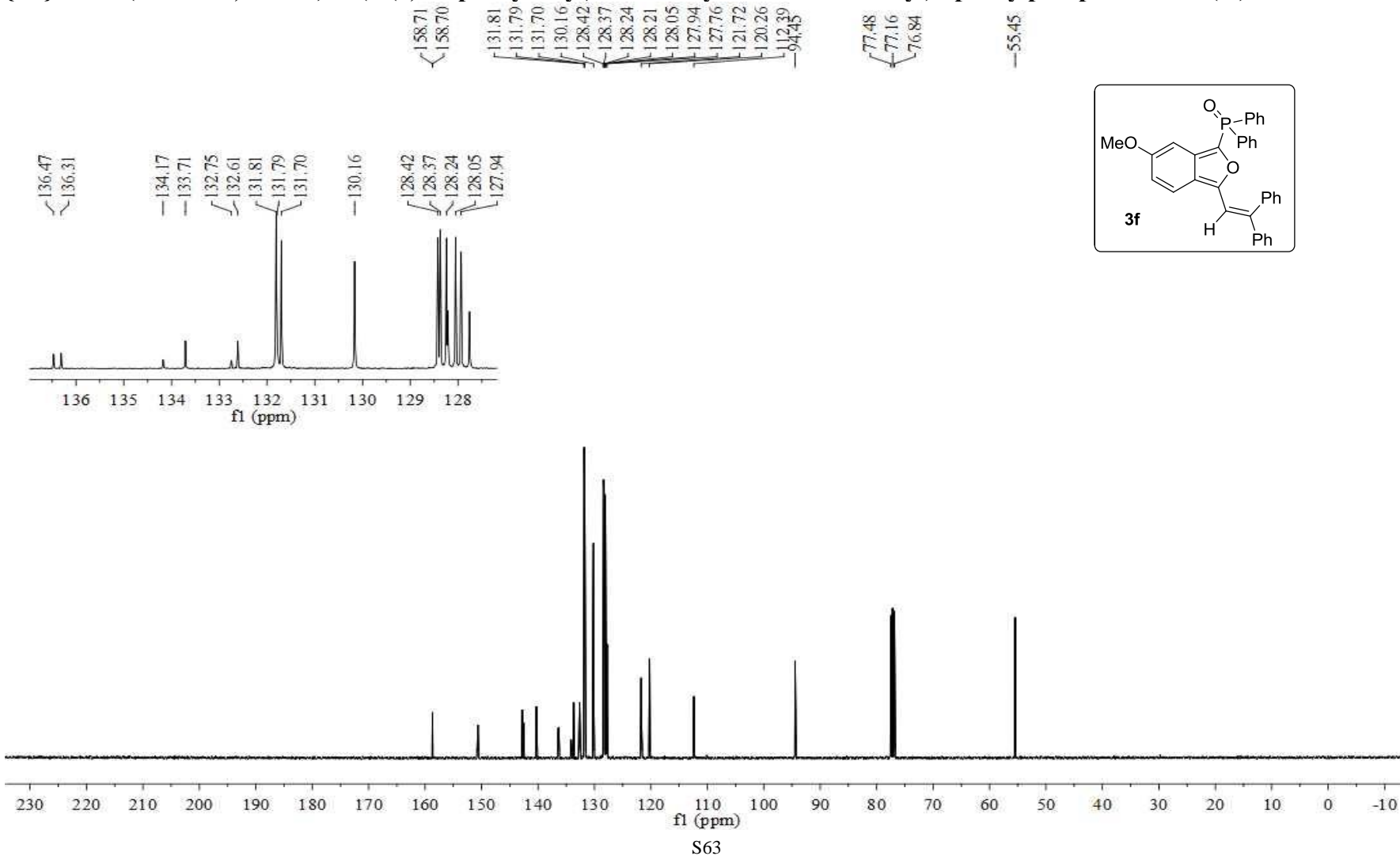
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-6-methylisobenzofuran-1-yl)diphenylphosphine oxide (**3e**)



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-6-methoxyisobenzofuran-1-yl)diphenylphosphine oxide (3f)**

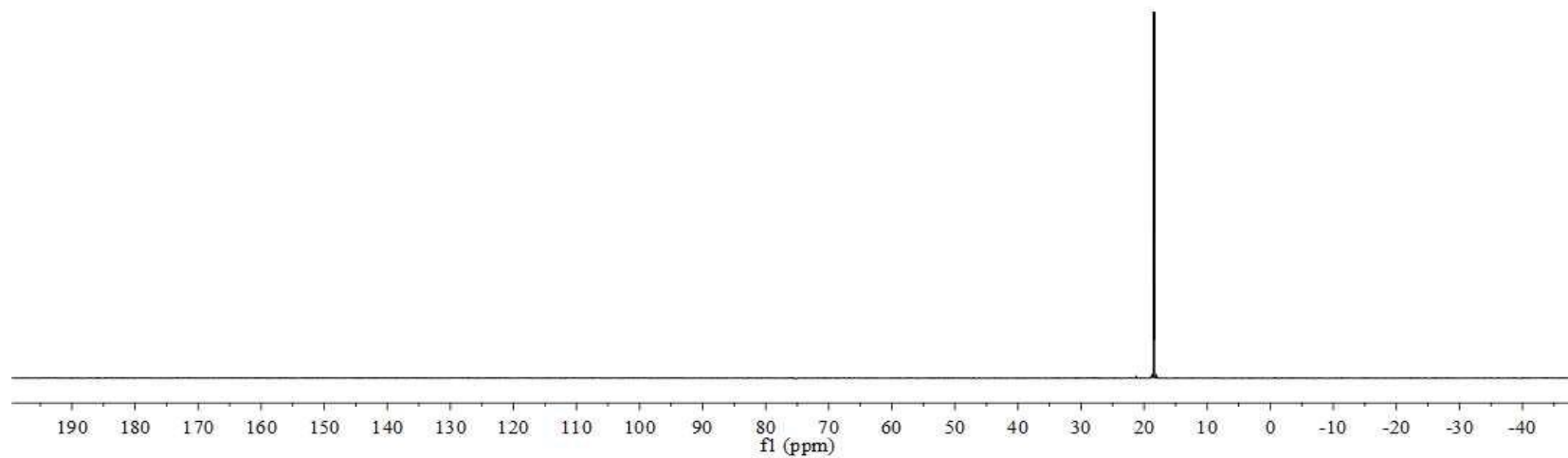
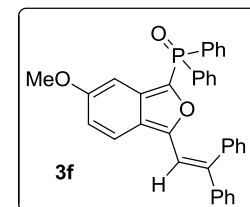


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-6-methoxyisobenzofuran-1-yl)diphenylphosphine oxide (3f)



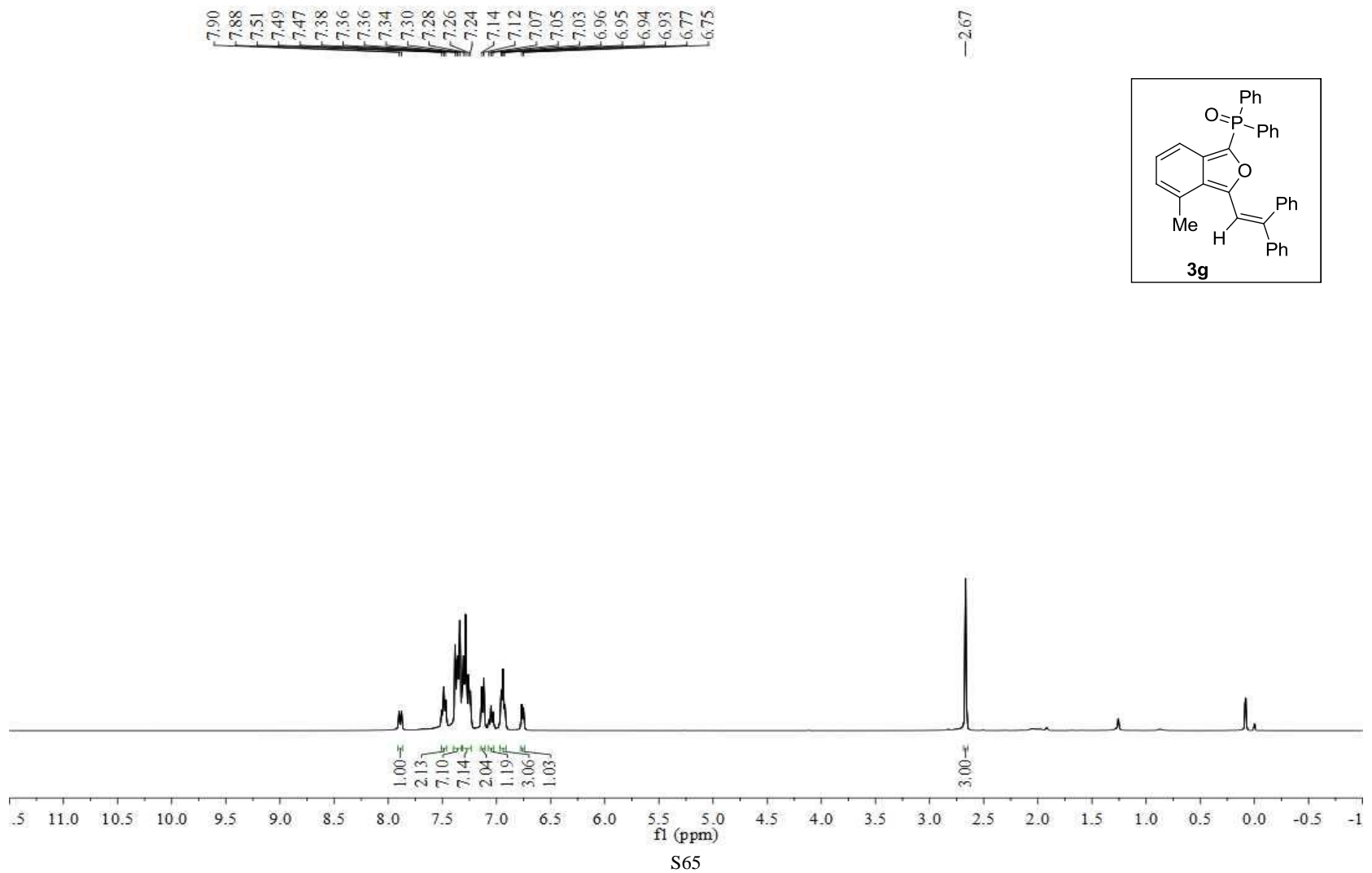
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) (3-(2,2-diphenylvinyl)-6-methoxyisobenzofuran-1-yl)diphenylphosphine oxide (3f)

— 18.42

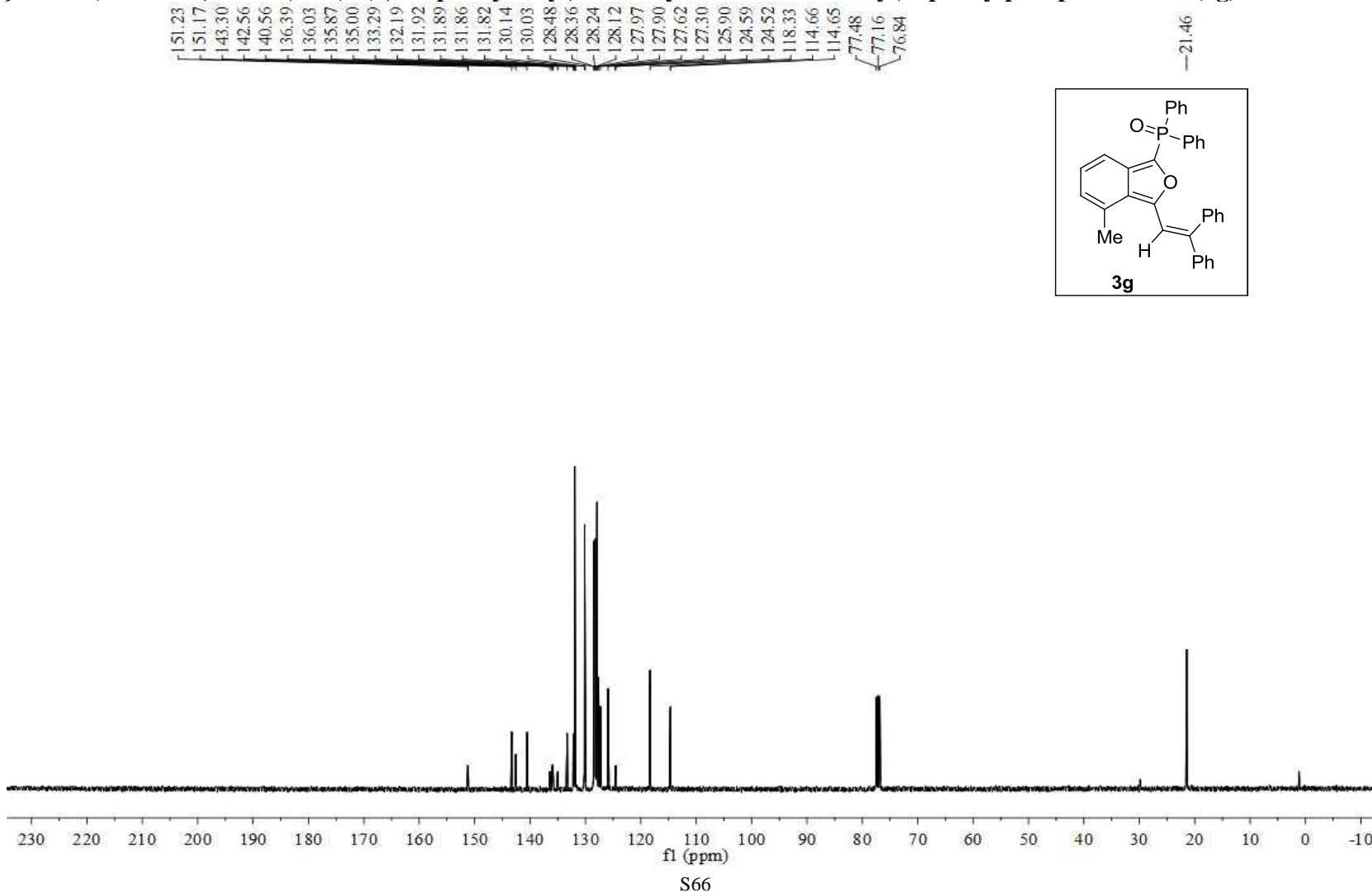


S64

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-4-methylisobenzofuran-1-yl)diphenylphosphine oxide (3g)**

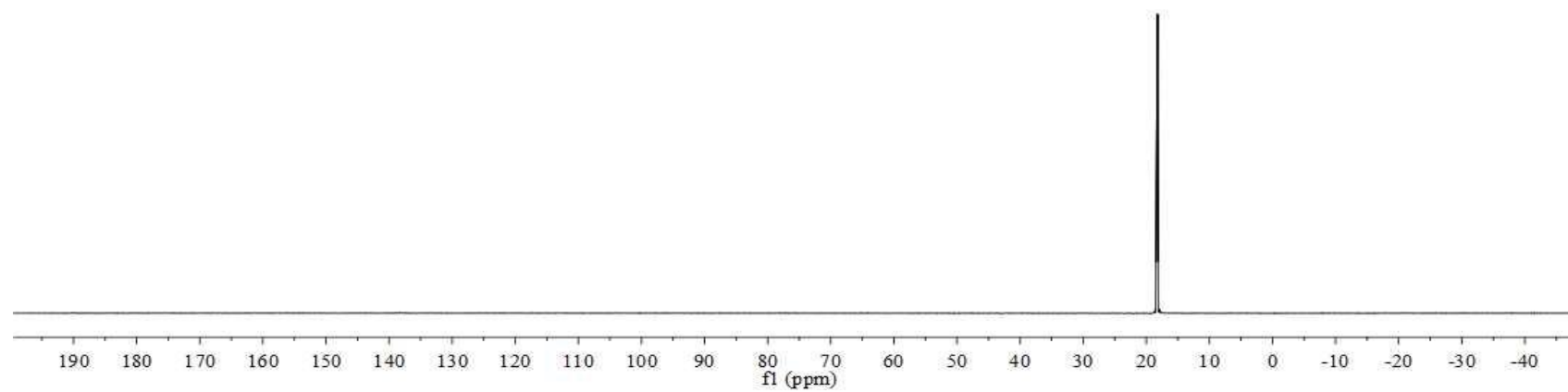
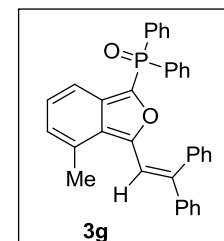


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-4-methylisobenzofuran-1-yl)diphenylphosphine oxide (3g)**



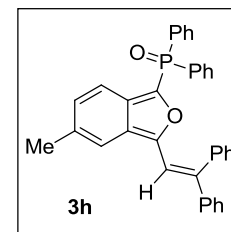
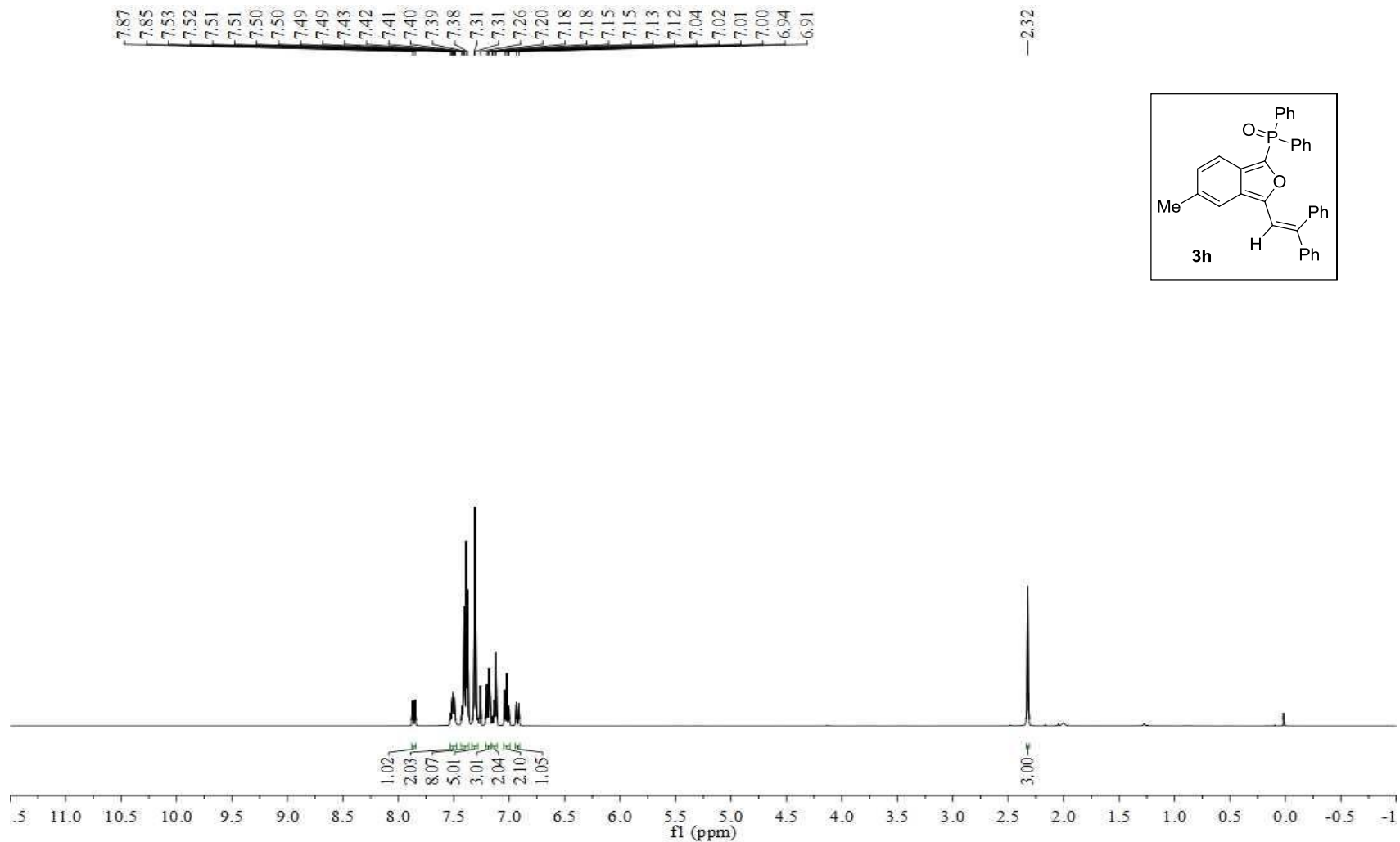
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-4-methylisobenzofuran-1-yl)diphenylphosphine oxide (3g)

18.22



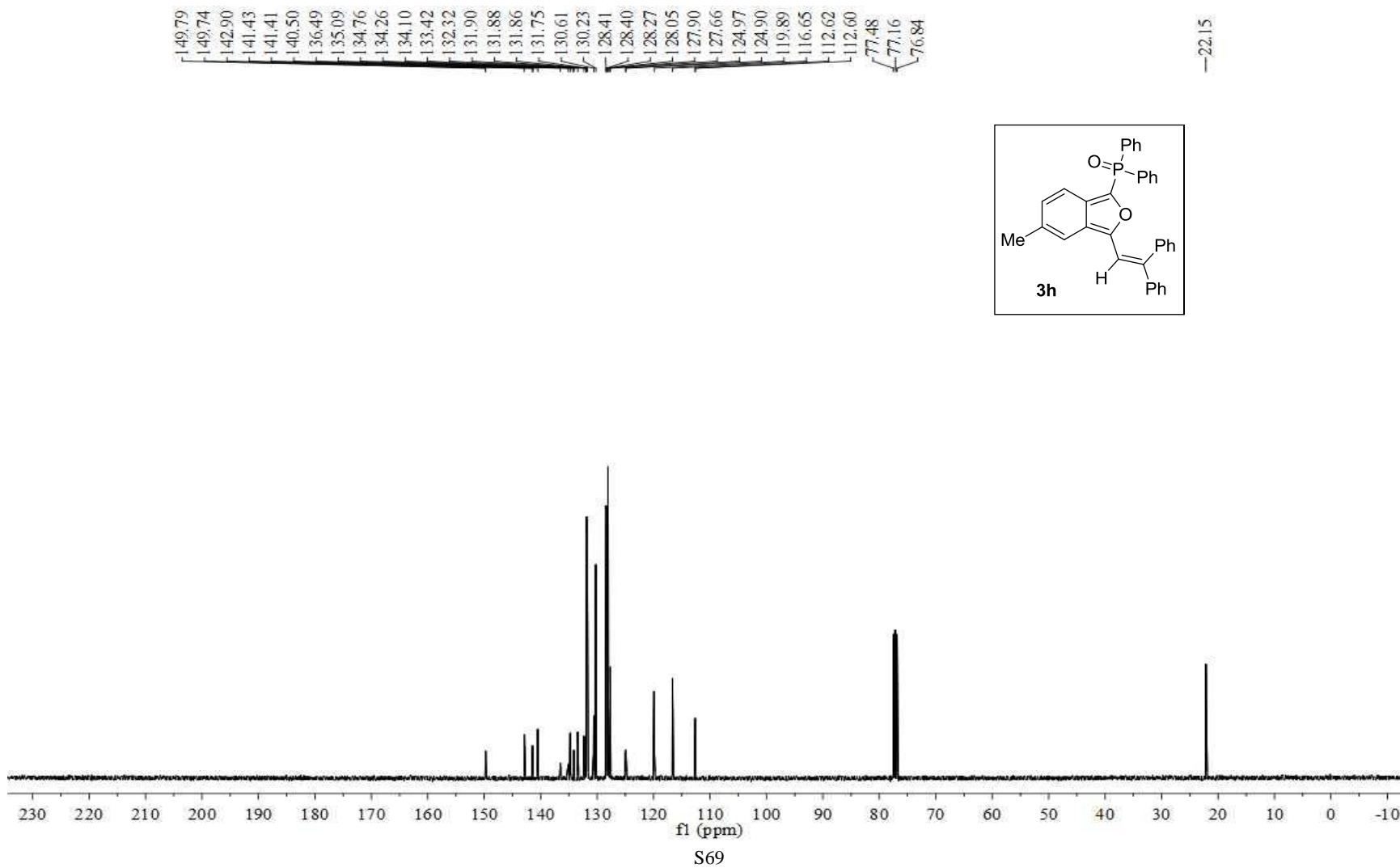
S67

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-5-methylisobenzofuran-1-yl)diphenylphosphine oxide (3h)



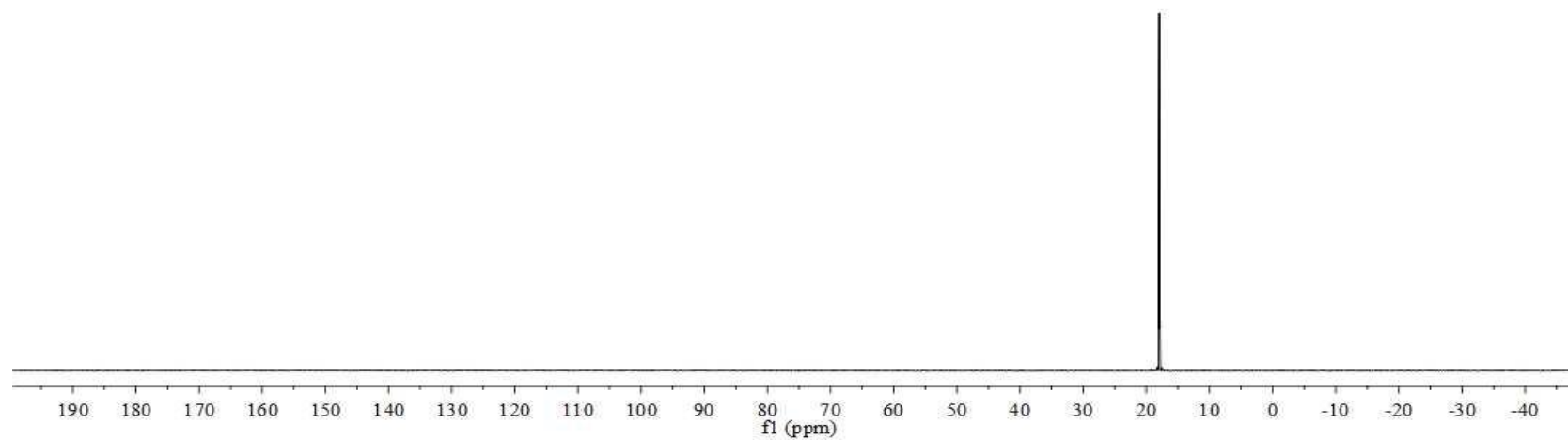
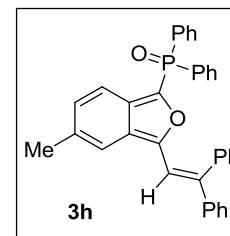


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-5-methylisobenzofuran-1-yl)diphenylphosphine oxide (3h)**



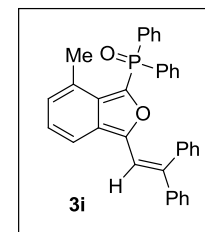
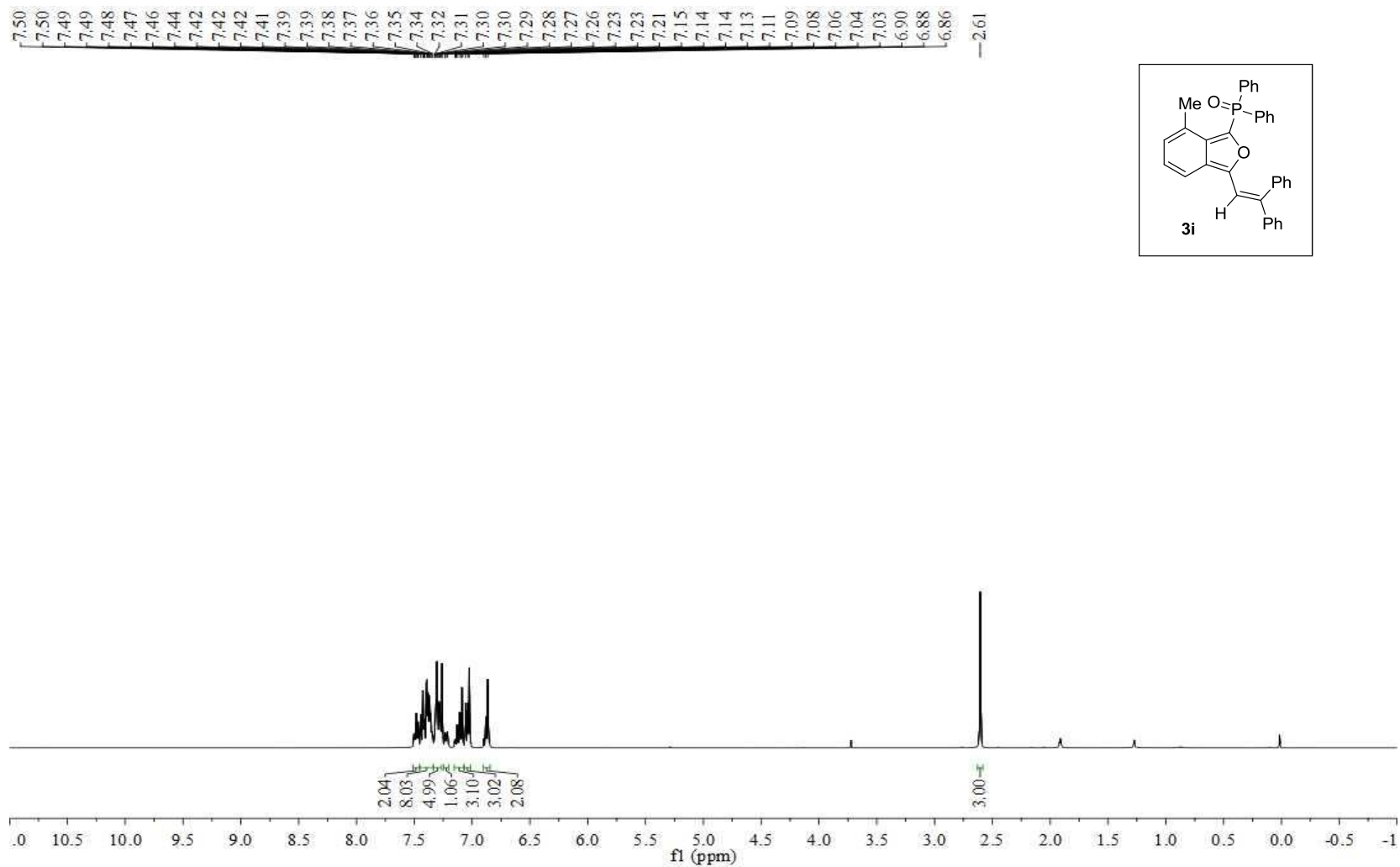
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-5-methylisobenzofuran-1-yl)diphenylphosphine oxide (3h)

17.90

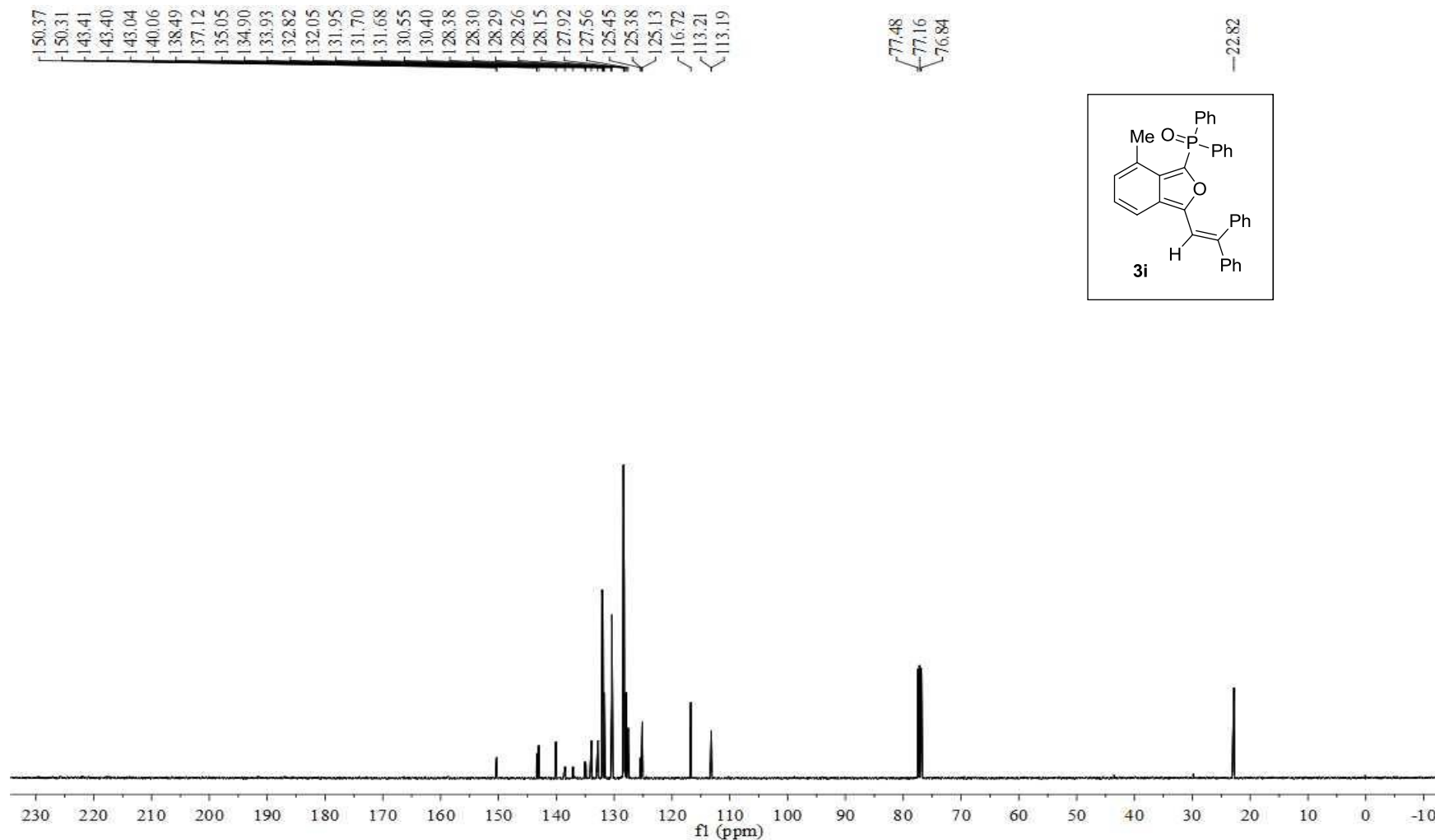


S70

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-7-methylisobenzofuran-1-yl)diphenylphosphine oxide (3i)**

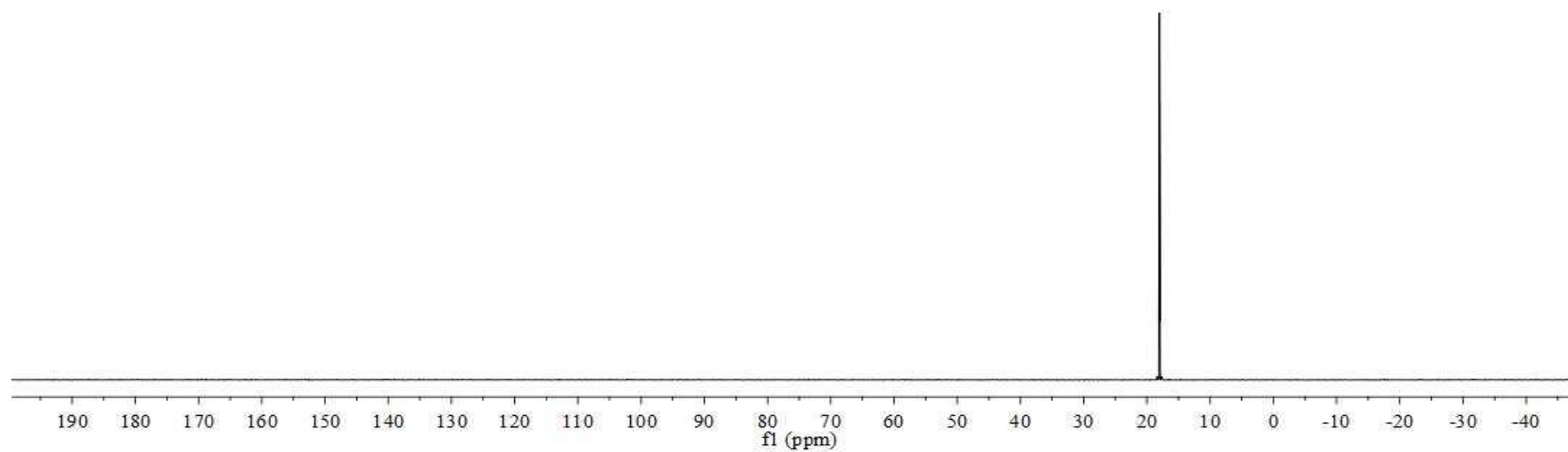
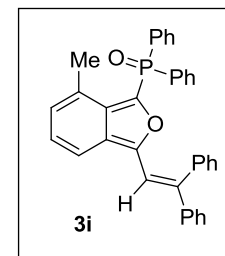


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-7-methylisobenzofuran-1-yl)diphenylphosphine oxide (3i)**



$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-7-methylisobenzofuran-1-yl)diphenylphosphine oxide (**3i**)

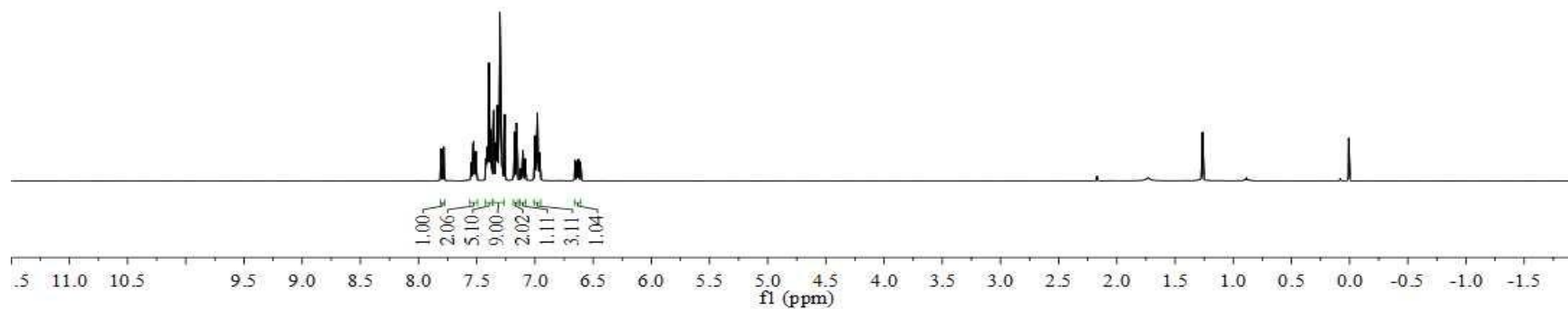
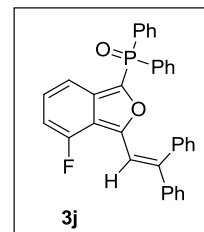
18.03



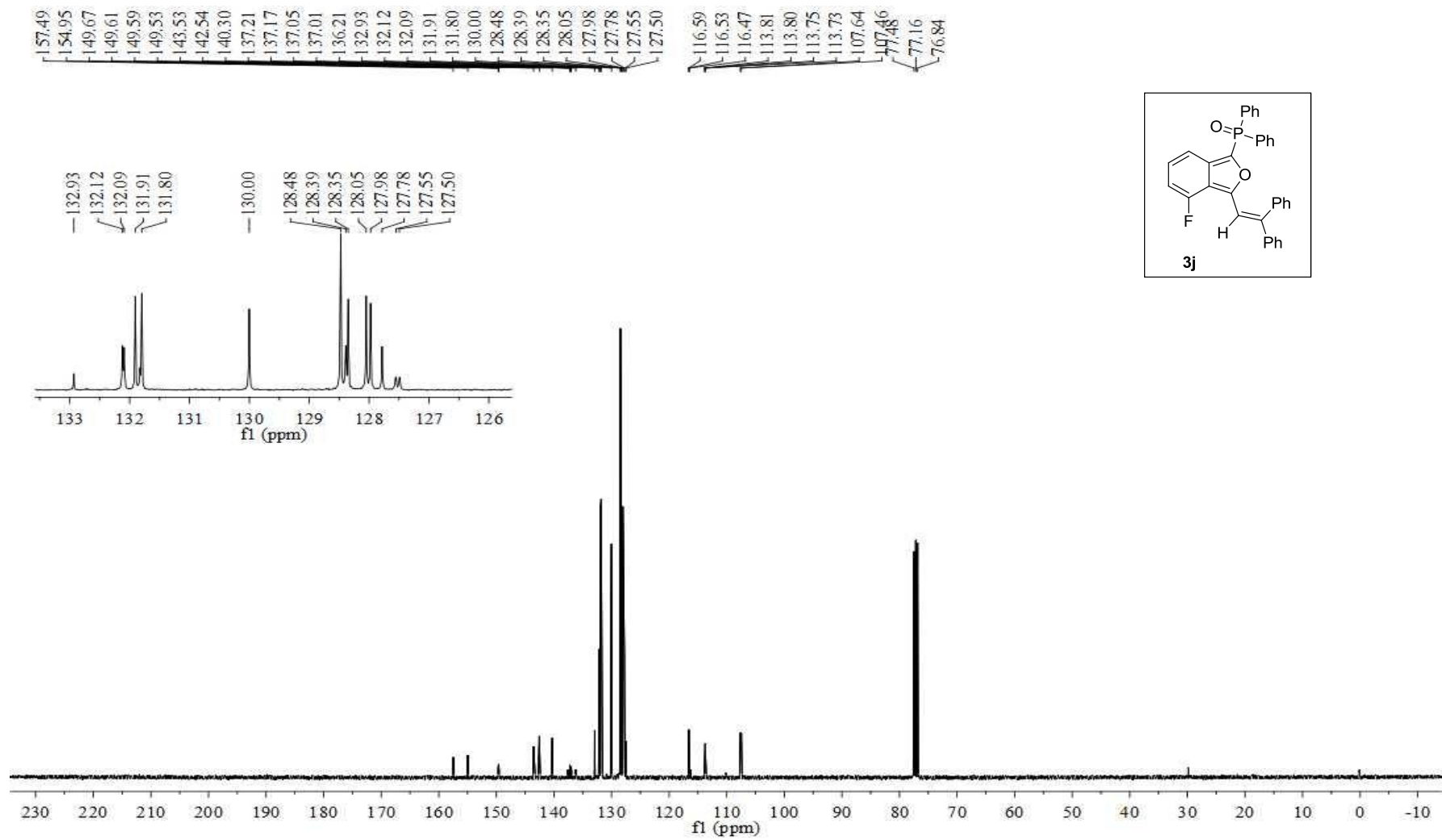
S73

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-4-fluorobenzofuran-1-yl)diphenylphosphine oxide (3j)**

7.81, 7.78, 7.55, 7.54, 7.54, 7.53, 7.53, 7.52, 7.52, 7.51, 7.51, 7.50, 7.42, 7.41, 7.41, 7.41, 7.39, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.34, 7.33, 7.33, 7.32, 7.31, 7.31, 7.30, 7.30, 7.26, 7.17, 7.16, 7.16, 7.15, 7.12, 7.12, 7.12, 7.11, 7.10, 7.10, 7.10, 7.09, 7.08, 7.08, 7.01, 7.00, 7.00, 6.99, 6.99, 6.98, 6.96, 6.96, 6.95, 6.95, 6.66, 6.64, 6.63, 6.61

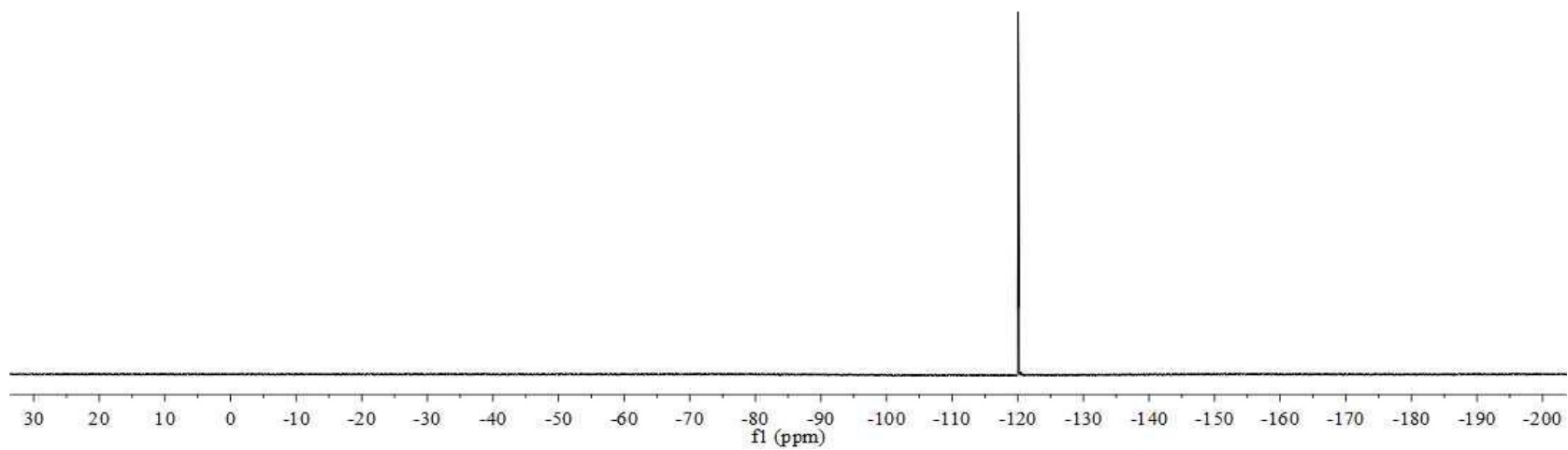
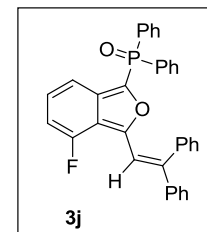


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-4-fluorobenzofuran-1-yl)diphenylphosphine oxide (3j)**



$^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-4-fluoroisobenzofuran-1-yl)diphenylphosphine oxide (**3j**)

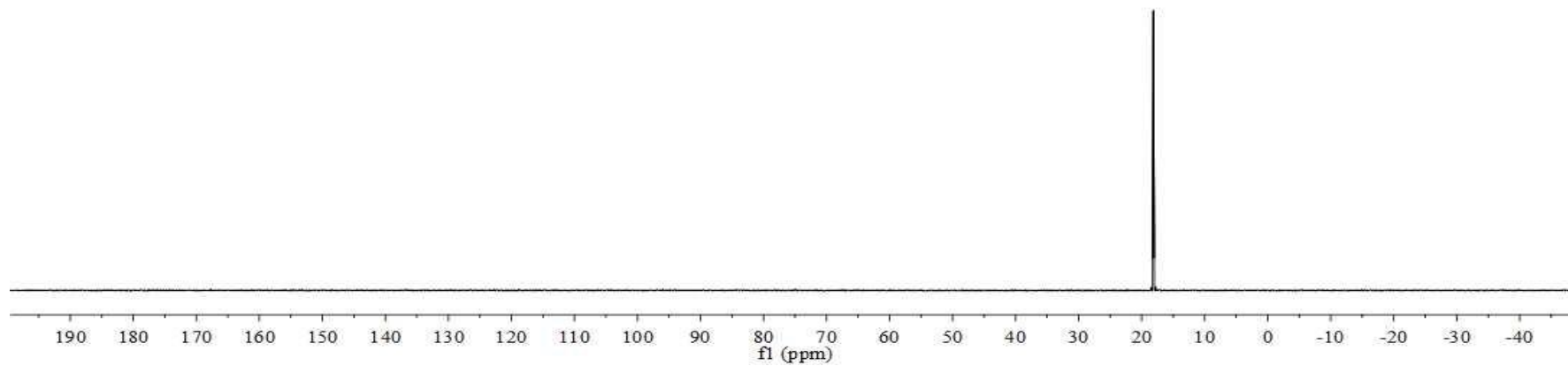
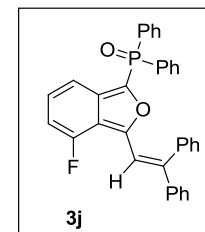
-120.05  
-120.06  
-120.08  
-120.09



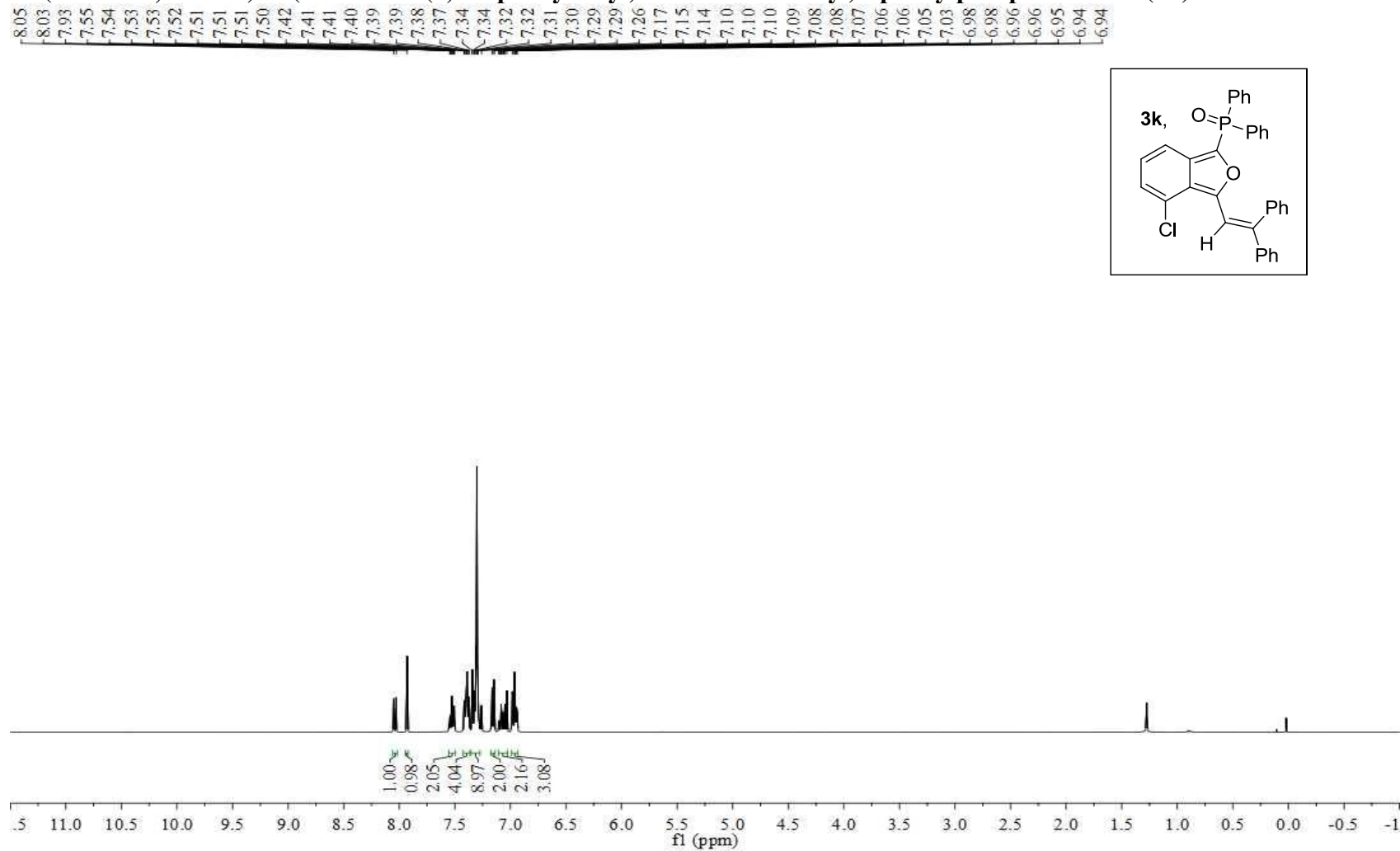


$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-4-fluorobenzofuran-1-yl)diphenylphosphine oxide (**3j**)

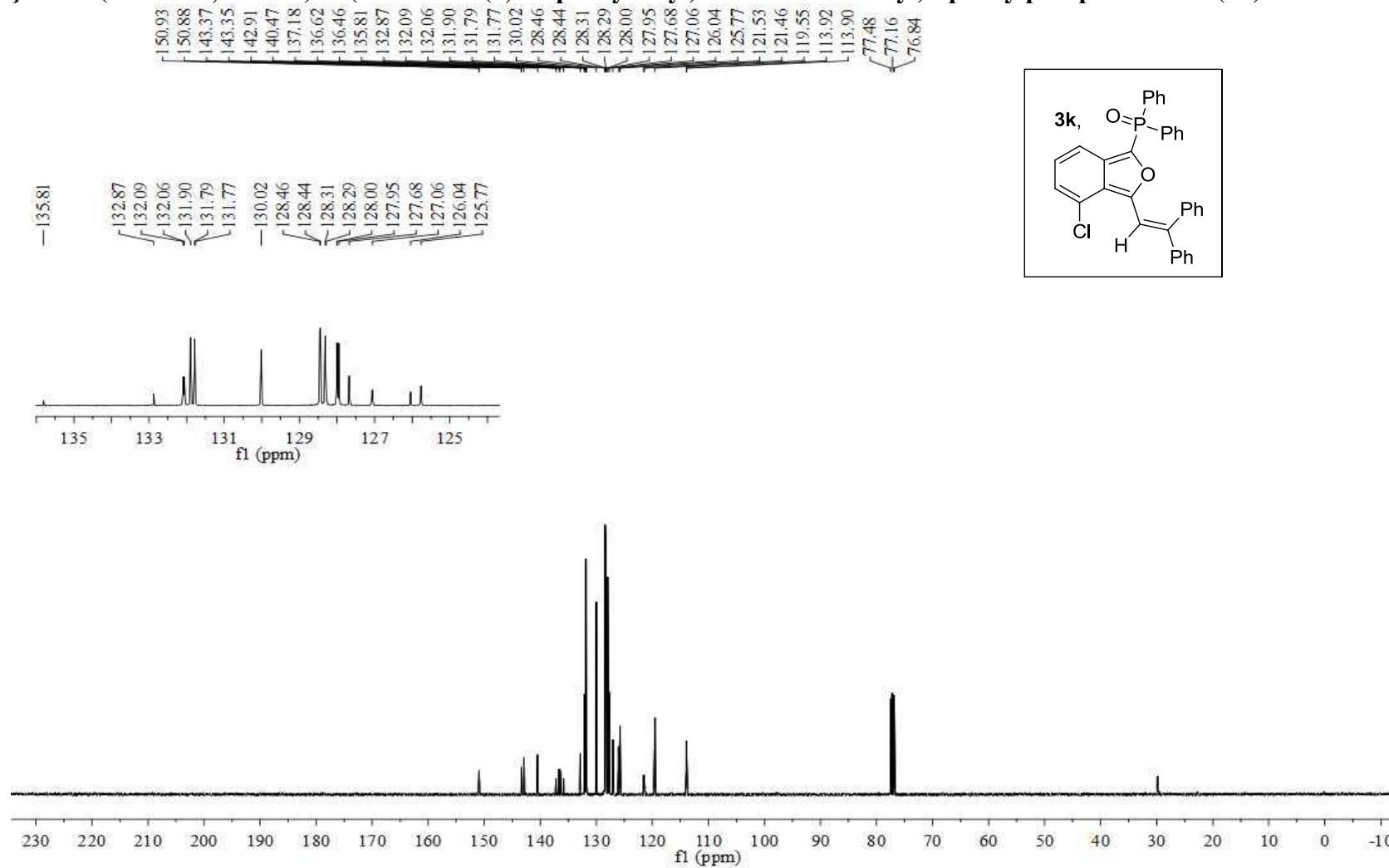
-18.12



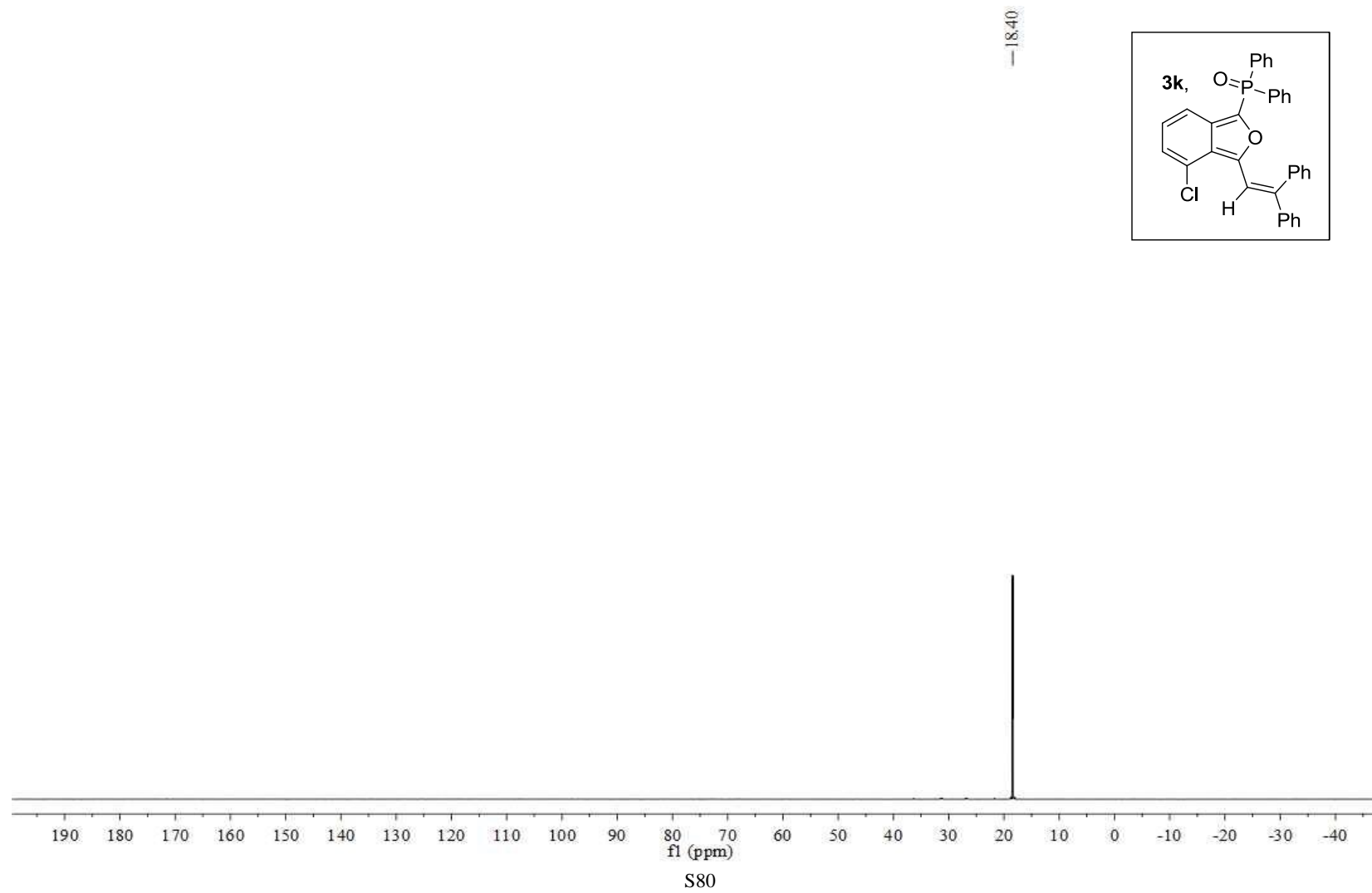
**<sup>1</sup>H NMR (400 MHz, DMSO) of (4-chloro-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3k)**



**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO) of (4-chloro-3-(2,2-diphenylvinyl) isobenzofuran-1-yl)diphenylphosphine oxide (3k)**

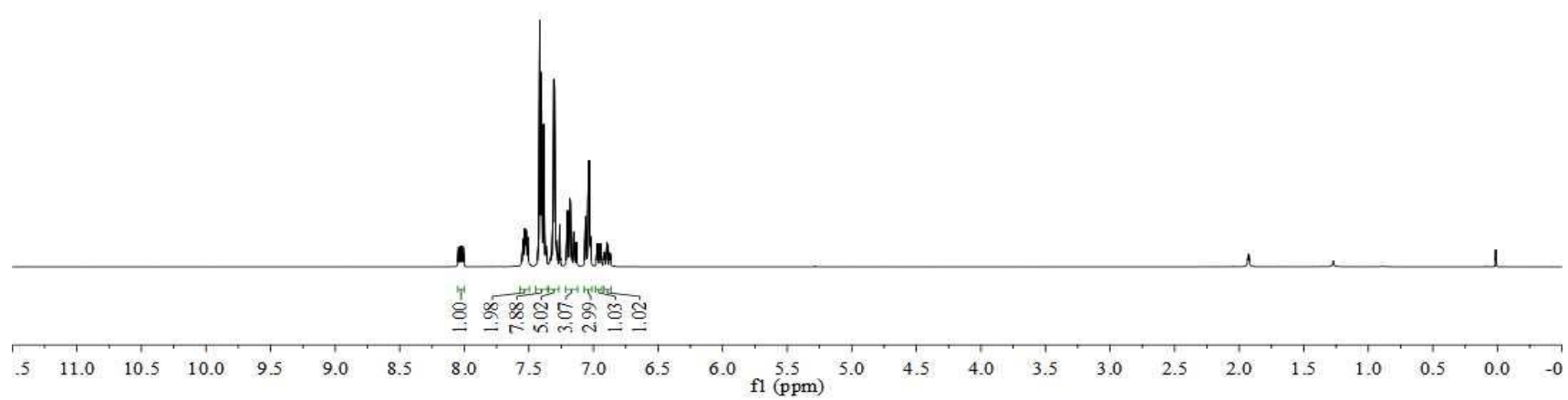
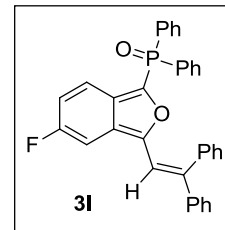


$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (4-chloro-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (**3k**)

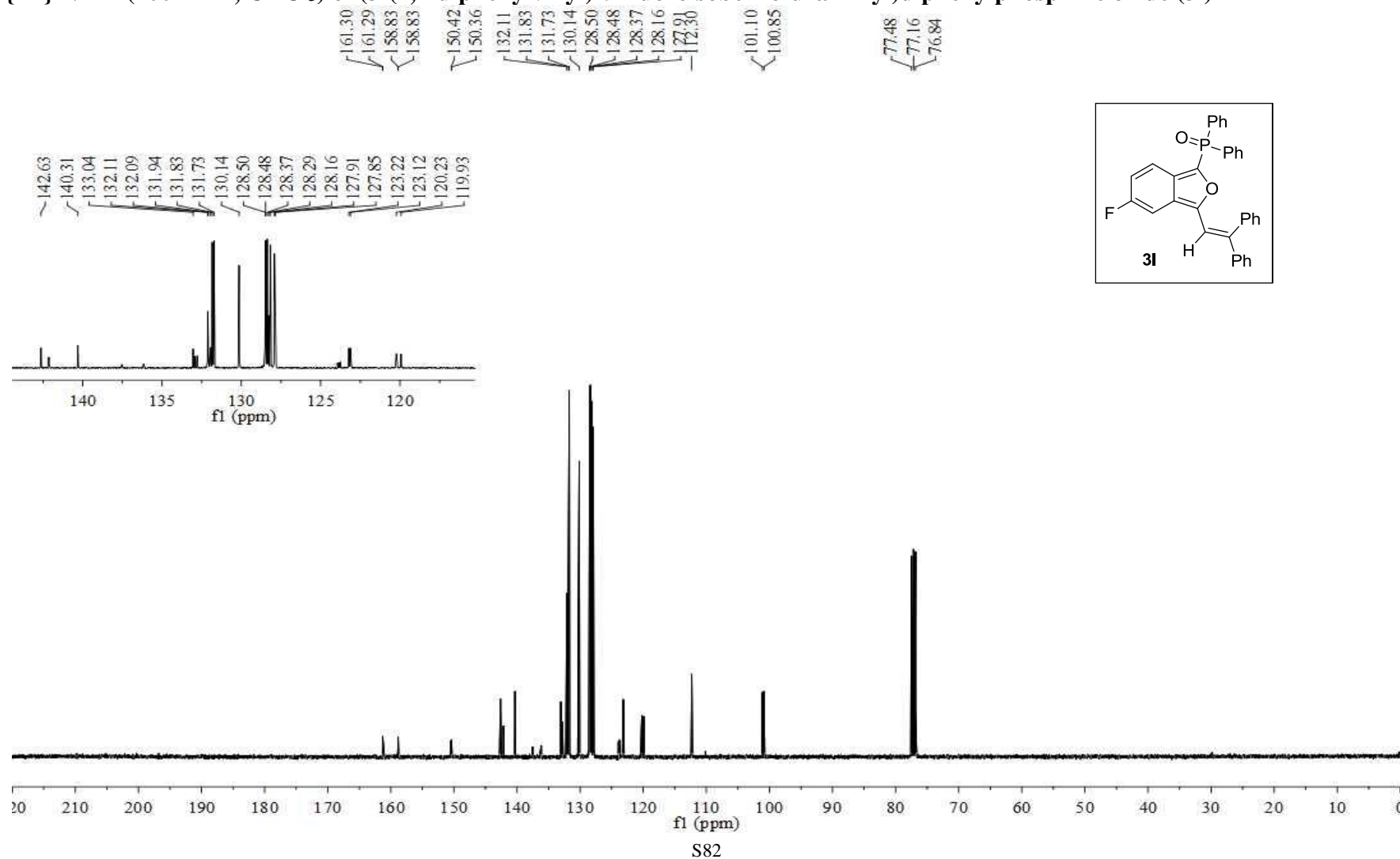


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-5-fluorobenzofuran-1-yl)diphenylphosphine oxide (31)**

8.045  
8.032  
8.022  
8.009  
7.554  
7.550  
7.544  
7.540  
7.532  
7.528  
7.522  
7.518  
7.511  
7.506  
7.415  
7.403  
7.385  
7.383  
7.373  
7.367  
7.362  
7.329  
7.326  
7.314  
7.307  
7.302  
7.290  
7.284  
7.280  
7.260  
7.060  
7.041  
7.037  
7.033  
7.023  
6.969  
6.946  
6.918  
6.913  
6.895  
6.891  
6.873  
6.868

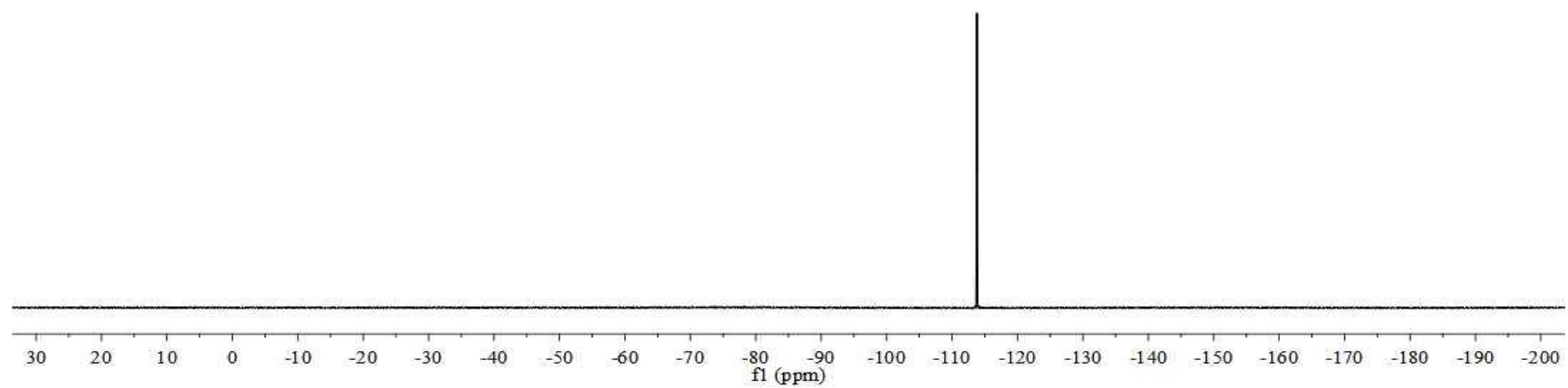
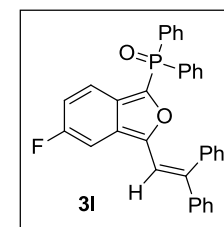


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-5-fluorobenzofuran-1-yl)diphenylphosphine oxide (3I)**



$^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-5-fluoroisobenzofuran-1-yl)diphenylphosphine oxide (3l)

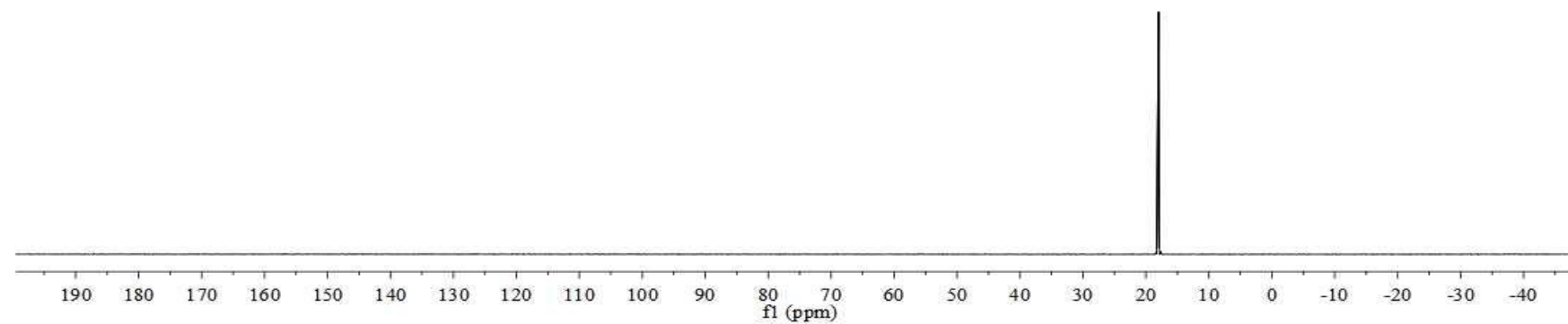
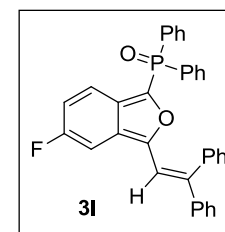
113.76  
113.77  
113.78  
113.79



S83

$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-5-fluorobenzofuran-1-yl)diphenylphosphine oxide (3l)

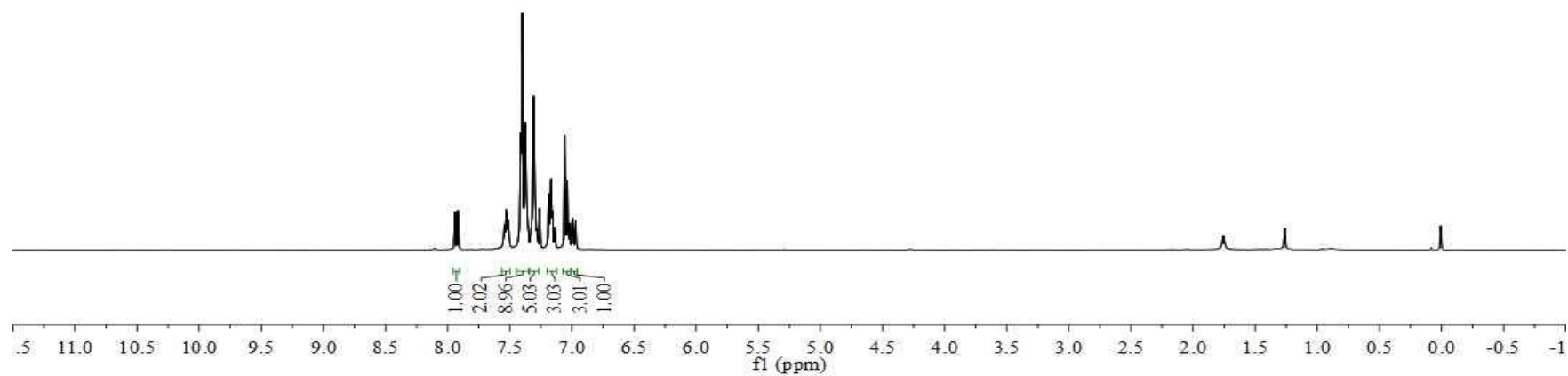
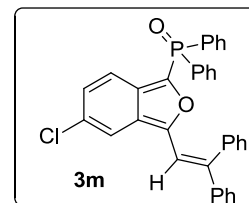
18.00



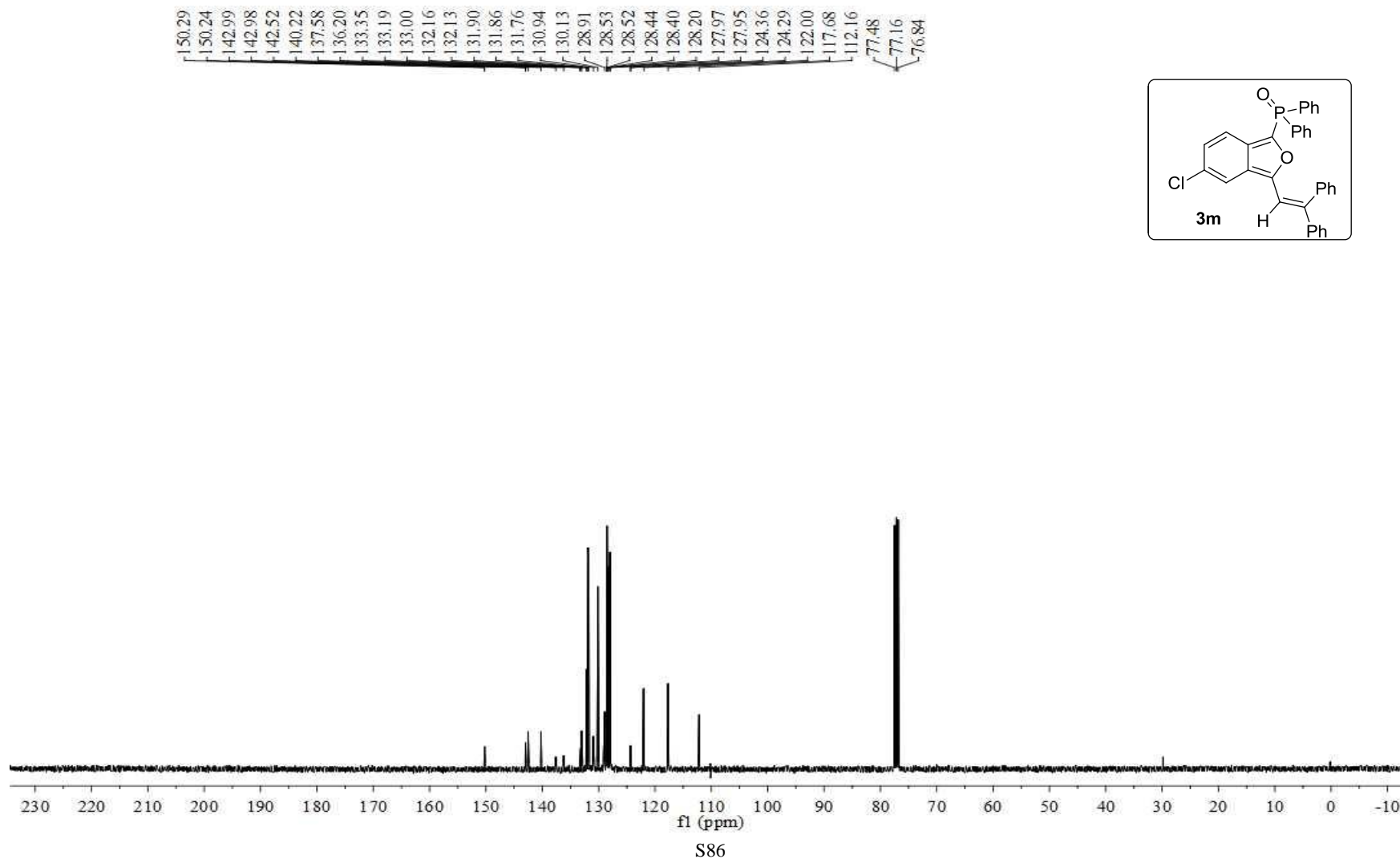
S84



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (5-chloro-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3m)

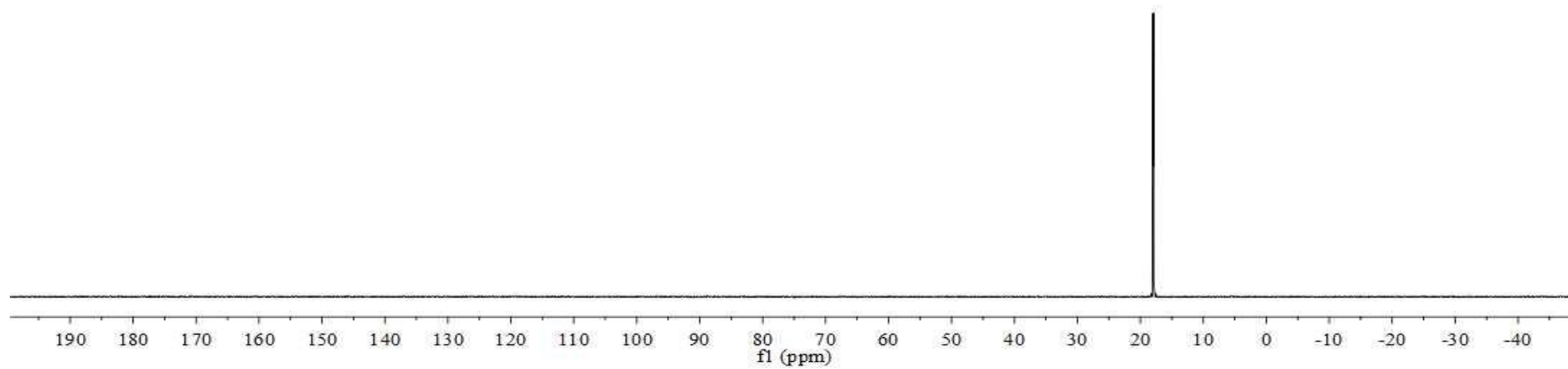
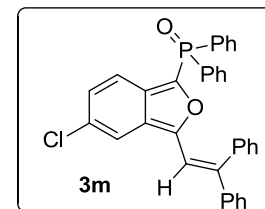


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (5-chloro-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3m)**



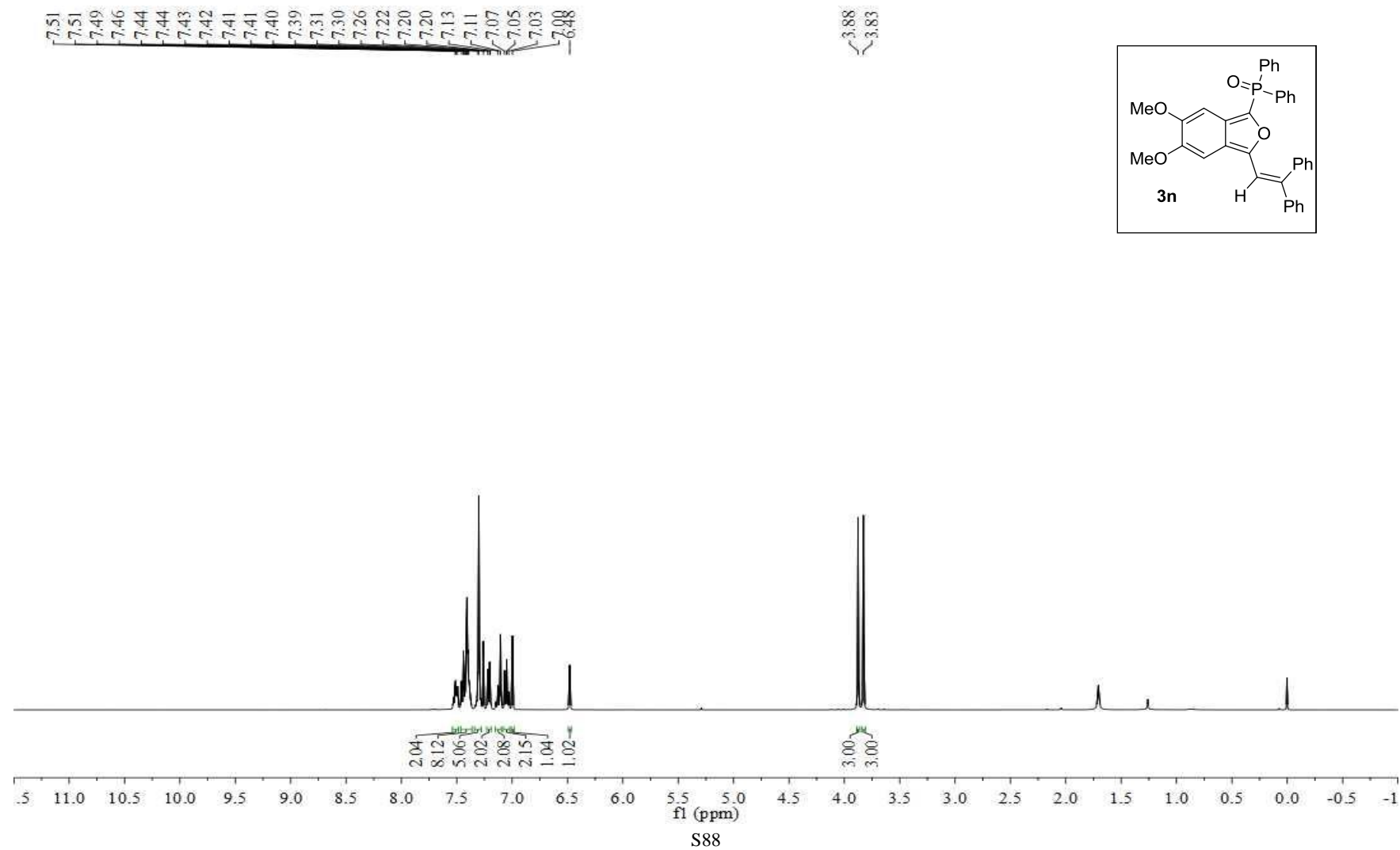
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (5-chloro-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (**3m**)

— 17.93

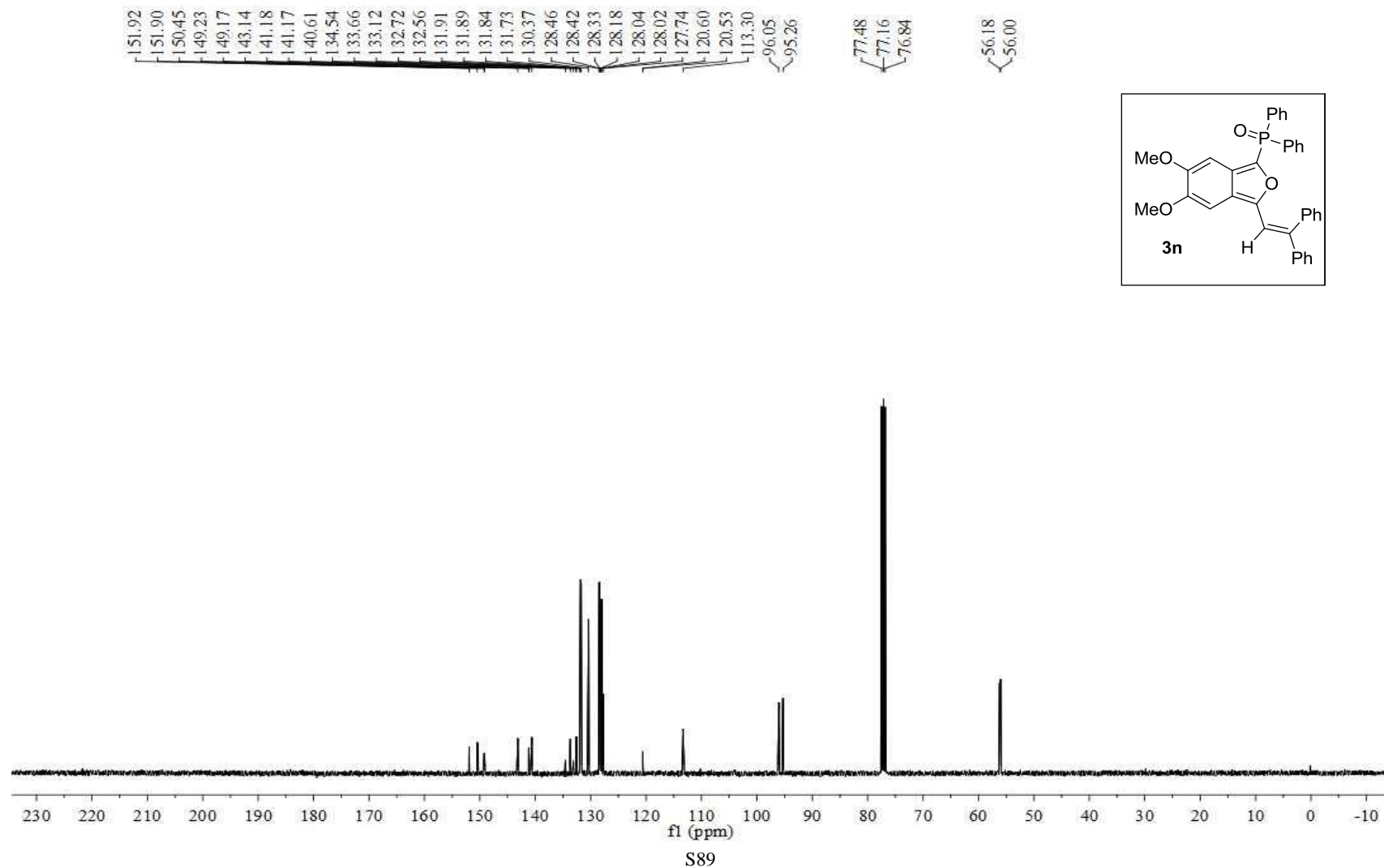


S87

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-5,6-dimethoxyisobenzofuran-1-yl)diphenylphosphine oxide (3n)**

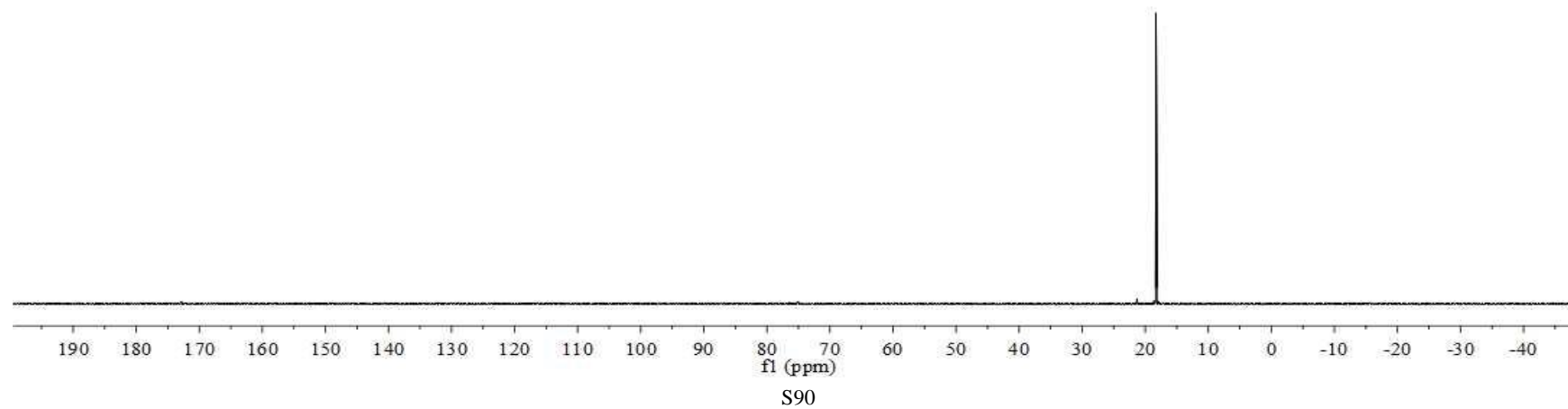
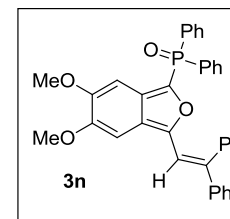


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-5,6-dimethoxyisobenzofuran-1-yl)diphenylphosphine oxide (3n)**

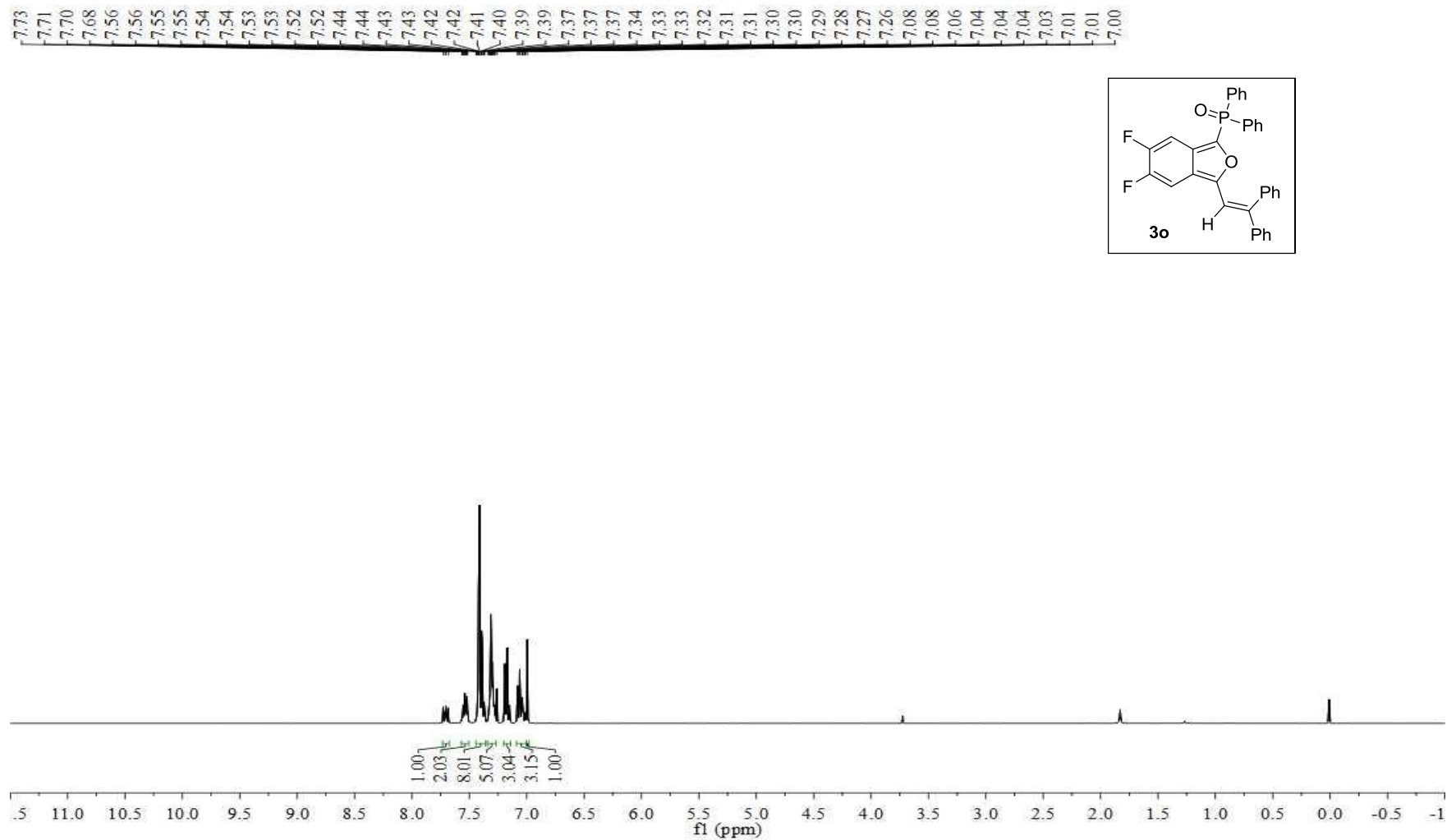


$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-5,6-dimethoxyisobenzofuran-1-yl)diphenylphosphine oxide (3n)

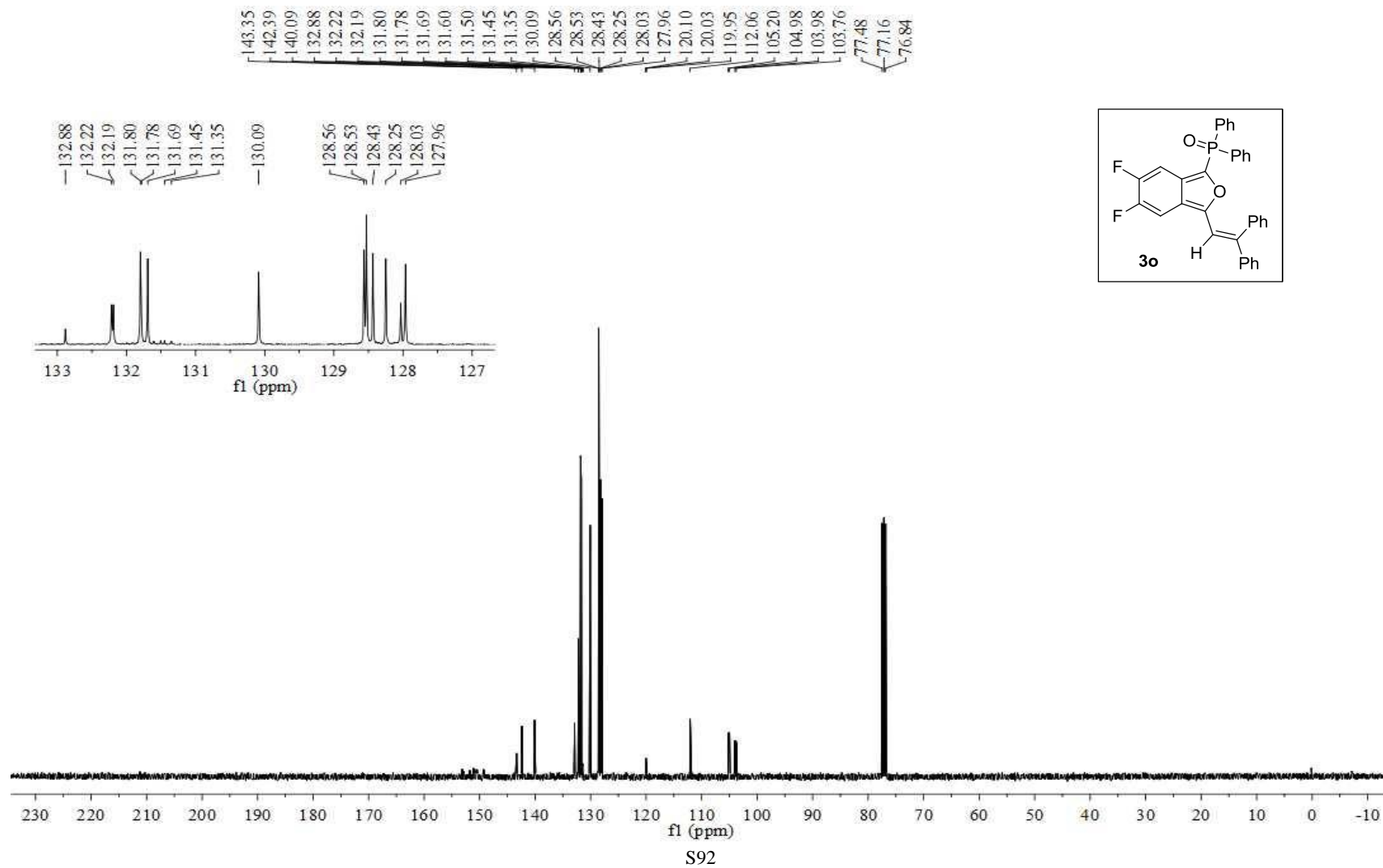
— 18.29



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-5,6-difluorobenzofuran-1-yl)diphenylphosphine oxide (3o)**



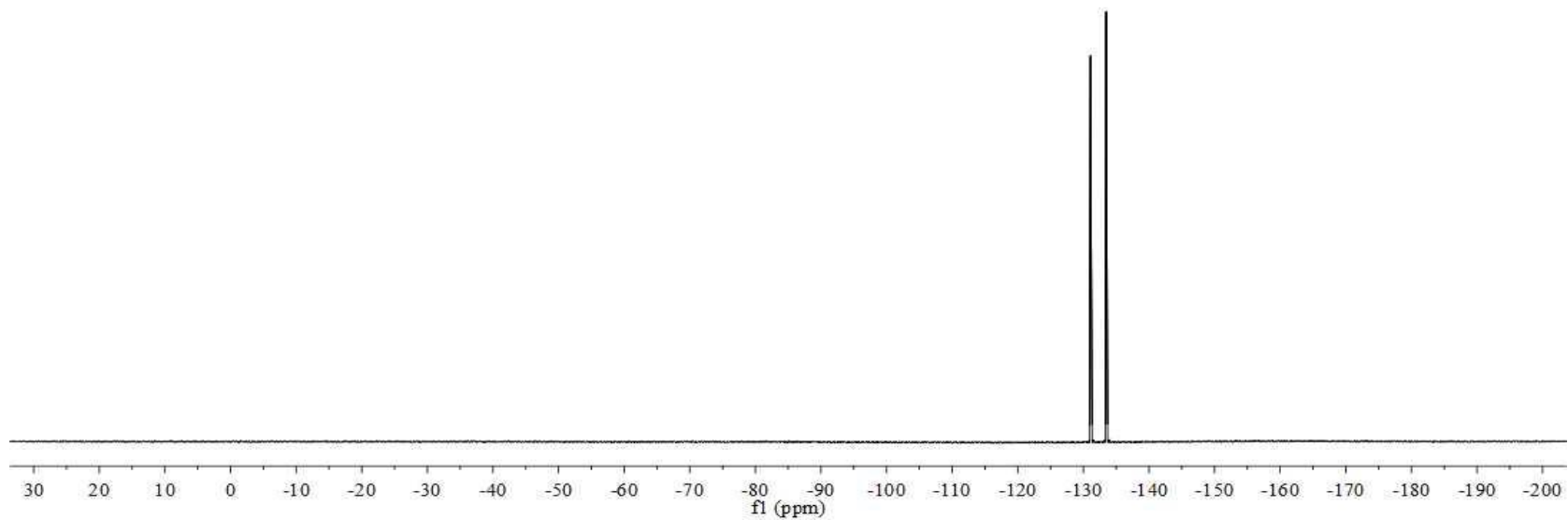
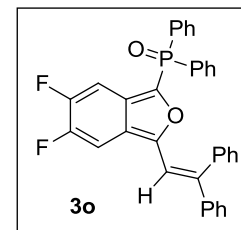
**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-5,6-difluoroisobenzofuran-1-yl)diphenylphosphine oxide (3o)**





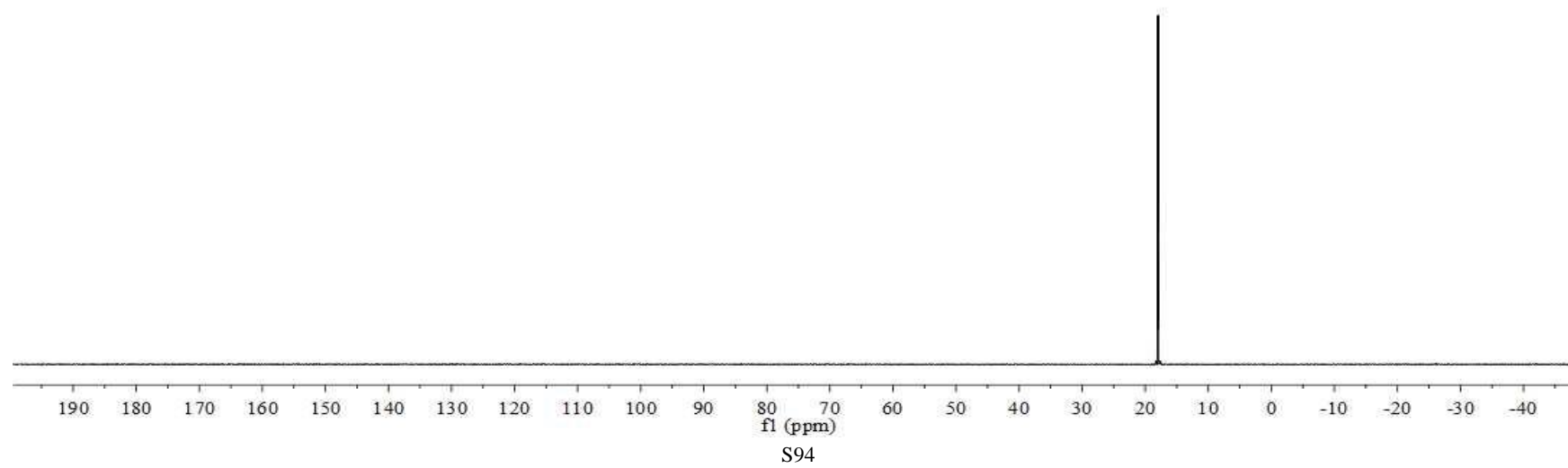
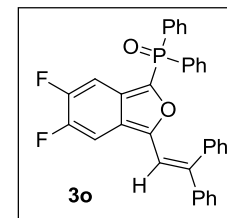
$^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-5,6-difluoroisobenzofuran-1-yl)diphenylphosphine oxide (3o)

-131.06  
-131.07  
-131.09  
-131.11  
-131.13  
-131.14  
-131.15  
-133.45  
-133.47  
-133.48  
-133.50  
-133.51  
-133.52  
-133.54



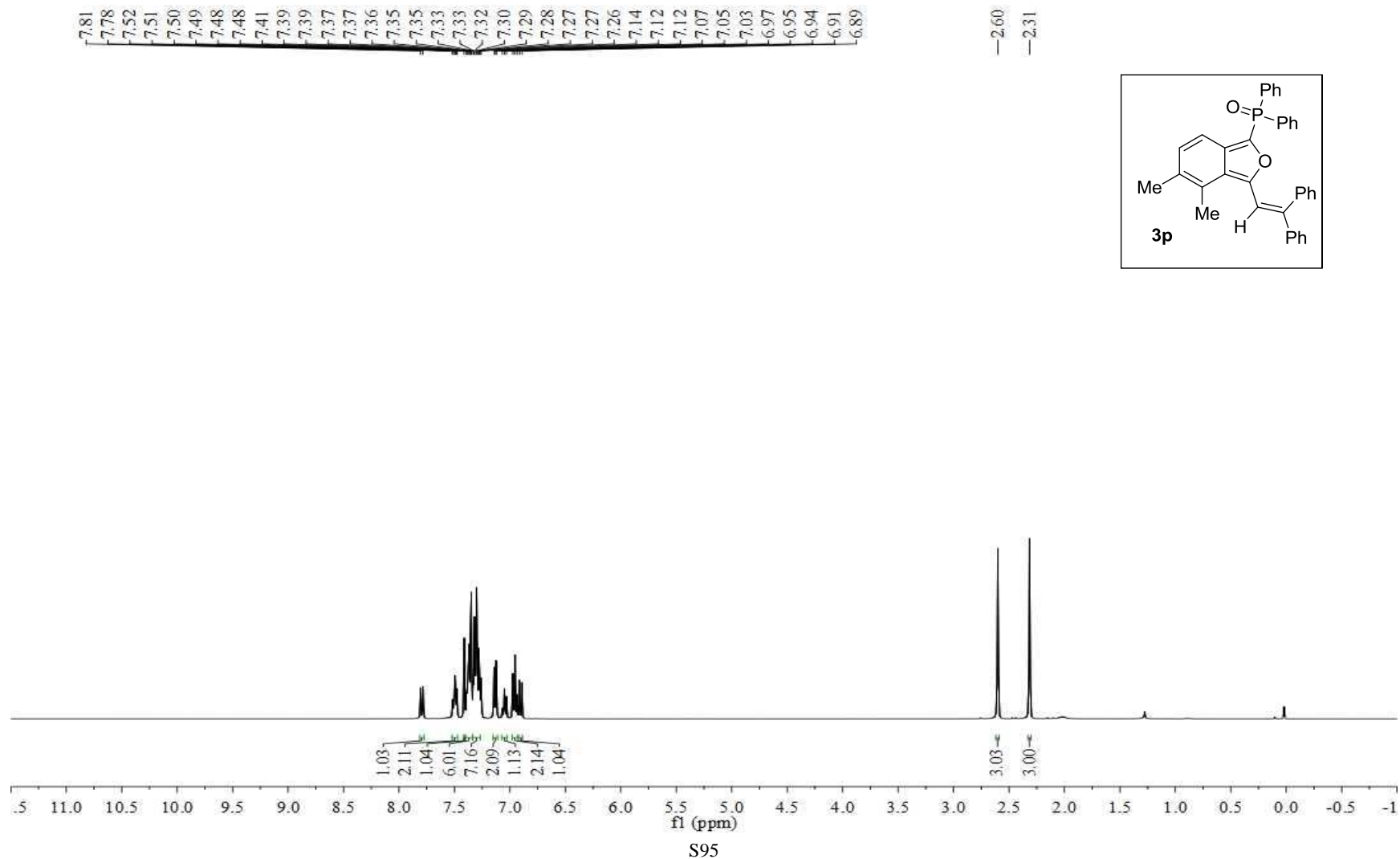
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-5,6-difluoroisobenzofuran-1-yl)diphenylphosphine oxide (3o)

17.95



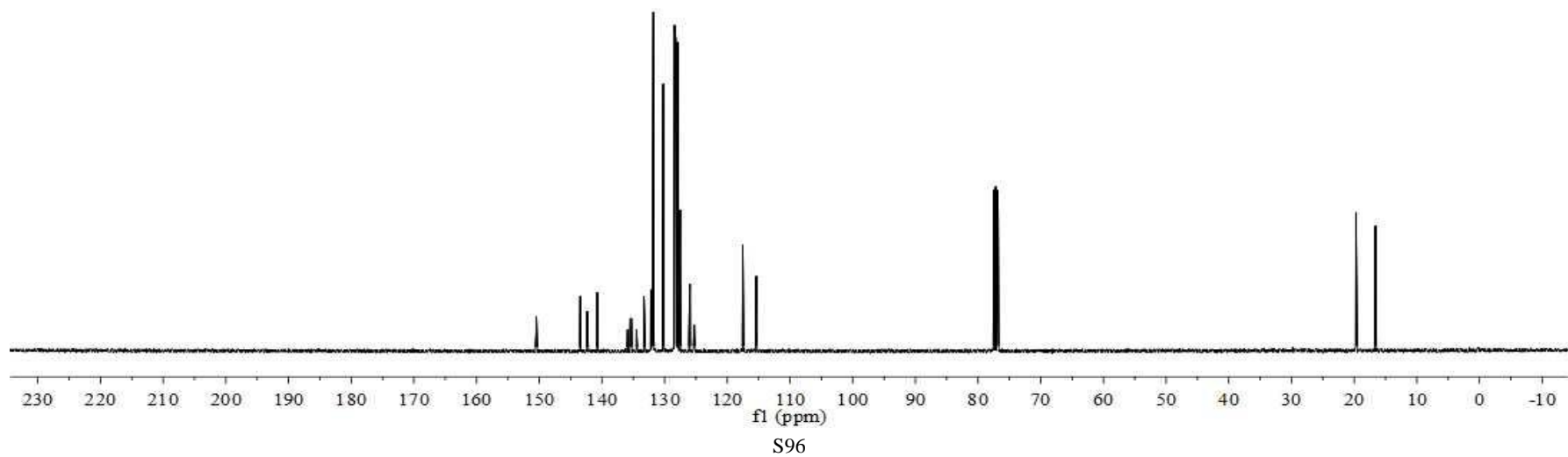
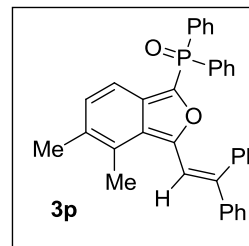
S94

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-4,5-dimethylisobenzofuran-1-yl)diphenylphosphine oxide (3p)**



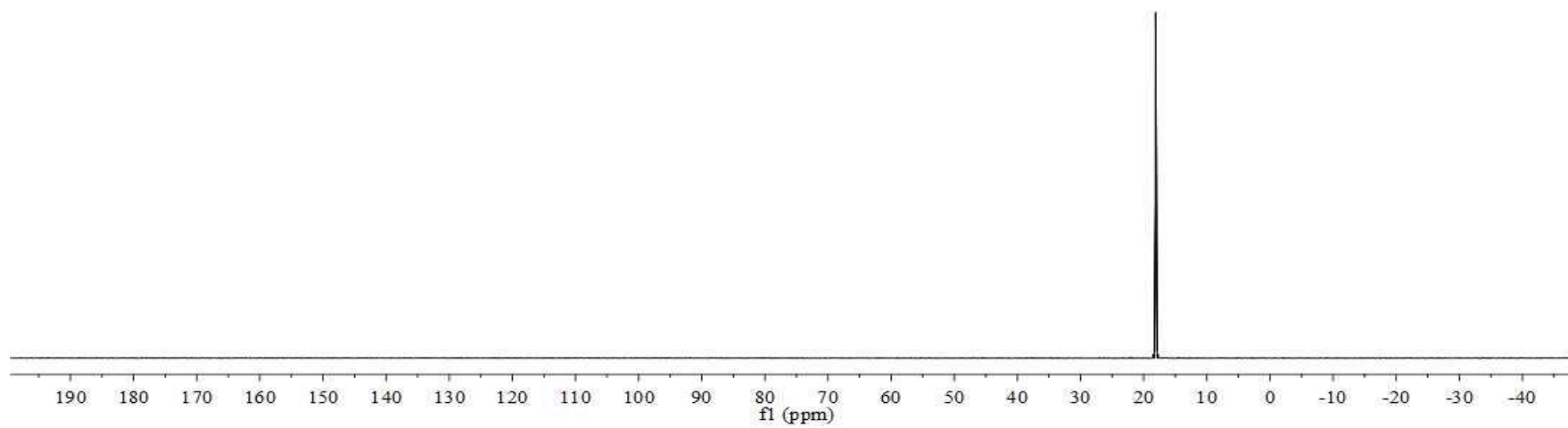
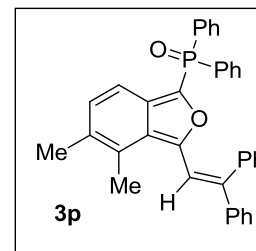
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-4,5-dimethylisobenzofuran-1-yl)diphenylphosphine oxide (3p)

150.51  
150.45  
143.44  
142.34  
142.32  
140.72  
135.90  
135.45  
135.29  
134.50  
133.30  
132.20  
132.02  
131.89  
131.82  
131.78  
130.21  
128.43  
128.34  
128.21  
128.00  
127.97  
127.92  
127.53  
125.96  
125.27  
125.20  
117.54  
115.38  
115.36  
77.48  
77.16  
76.84  
19.71  
16.59



$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-4,5-dimethylisobenzofuran-1-yl)diphenylphosphine oxide (3p)

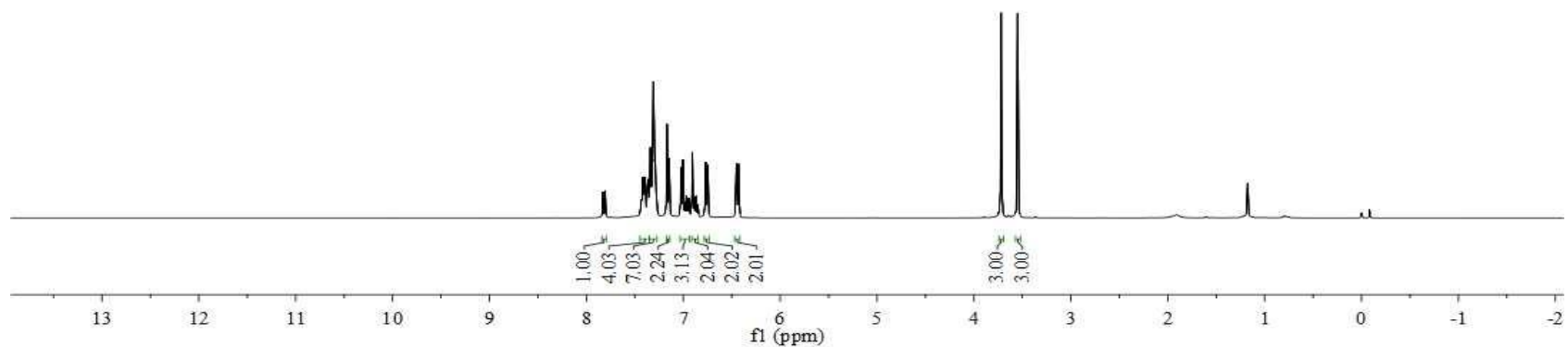
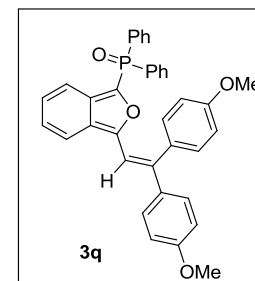
-18.11



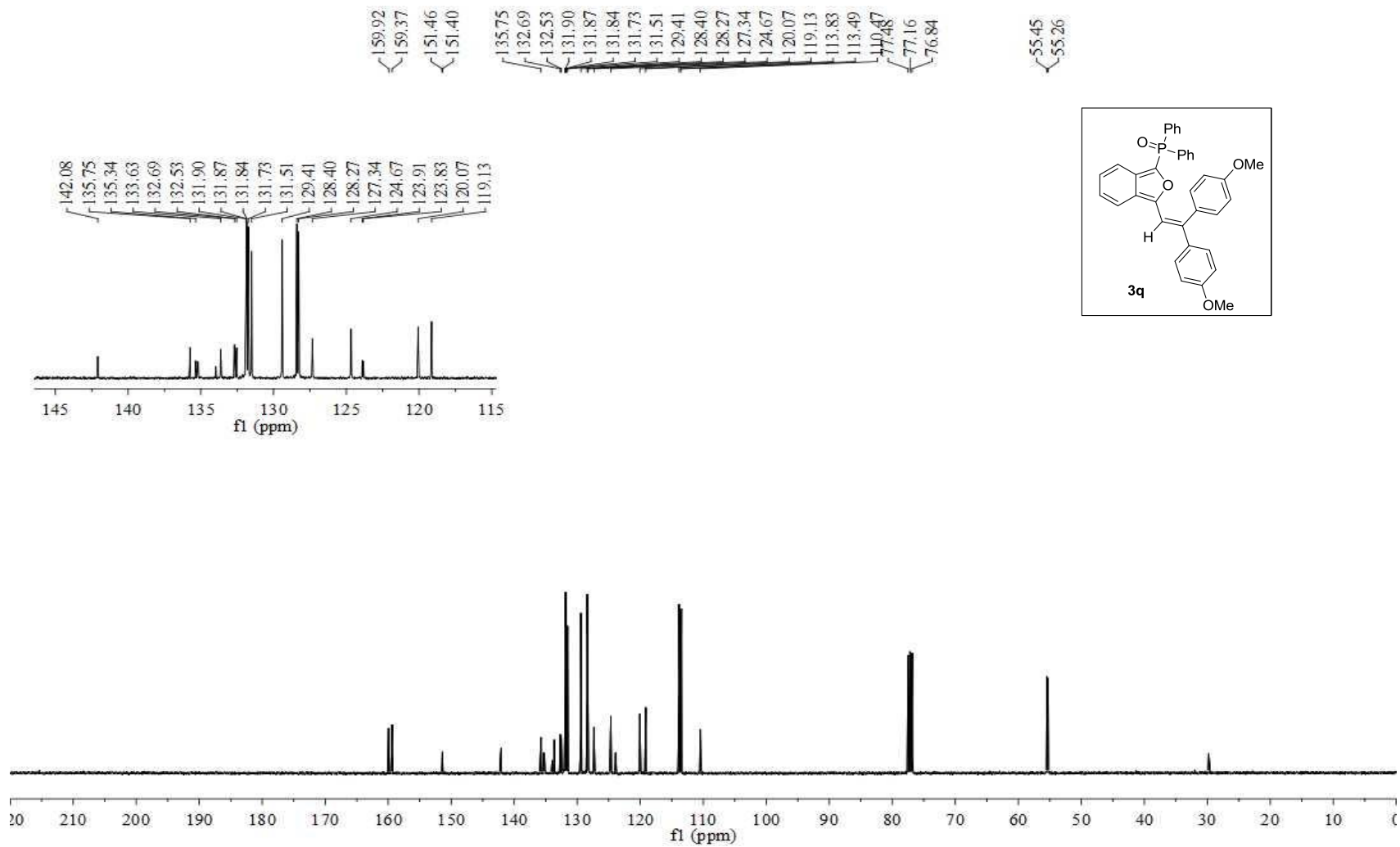
S97

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-bis(4-methoxyphenyl)vinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3q)**

7.83  
7.81  
7.43  
7.42  
7.39  
7.37  
7.36  
7.34  
7.33  
7.33  
7.31  
7.29  
7.17  
7.15  
7.02  
7.00  
6.98  
6.97  
6.94  
6.91  
6.89  
6.87  
6.85  
6.77  
6.75  
6.45  
6.43  
3.72  
3.55

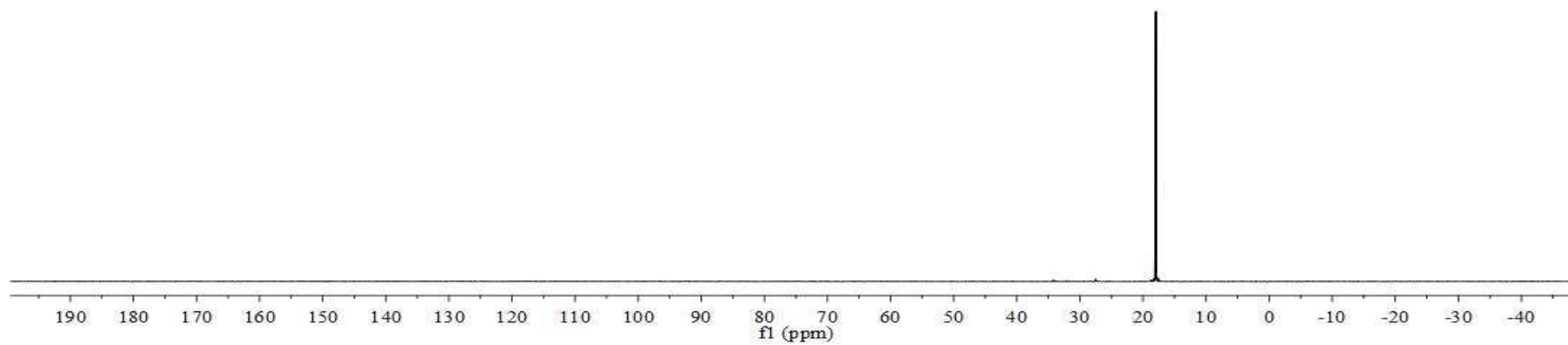
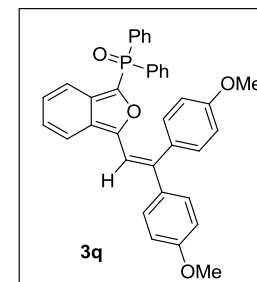


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-bis(4-methoxyphenyl)vinyl) isobenzofuran-1-yl)diphenylphosphine oxide (3q)



$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-bis(4-methoxyphenyl)vinyl)isobenzofuran-1-yl)diphenylphosphine oxide (**3q**)

-17.93

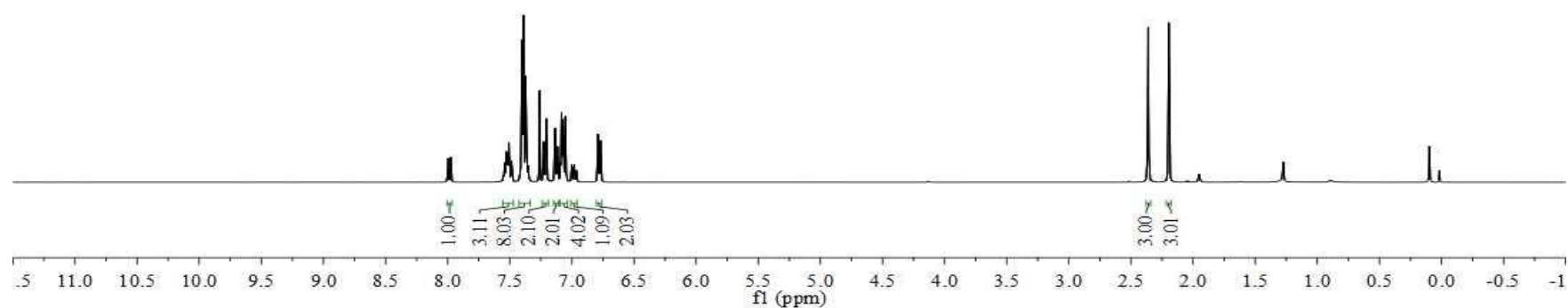
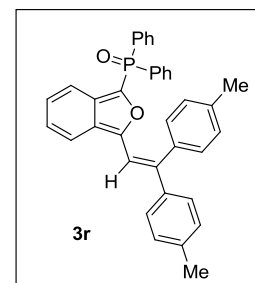


S100



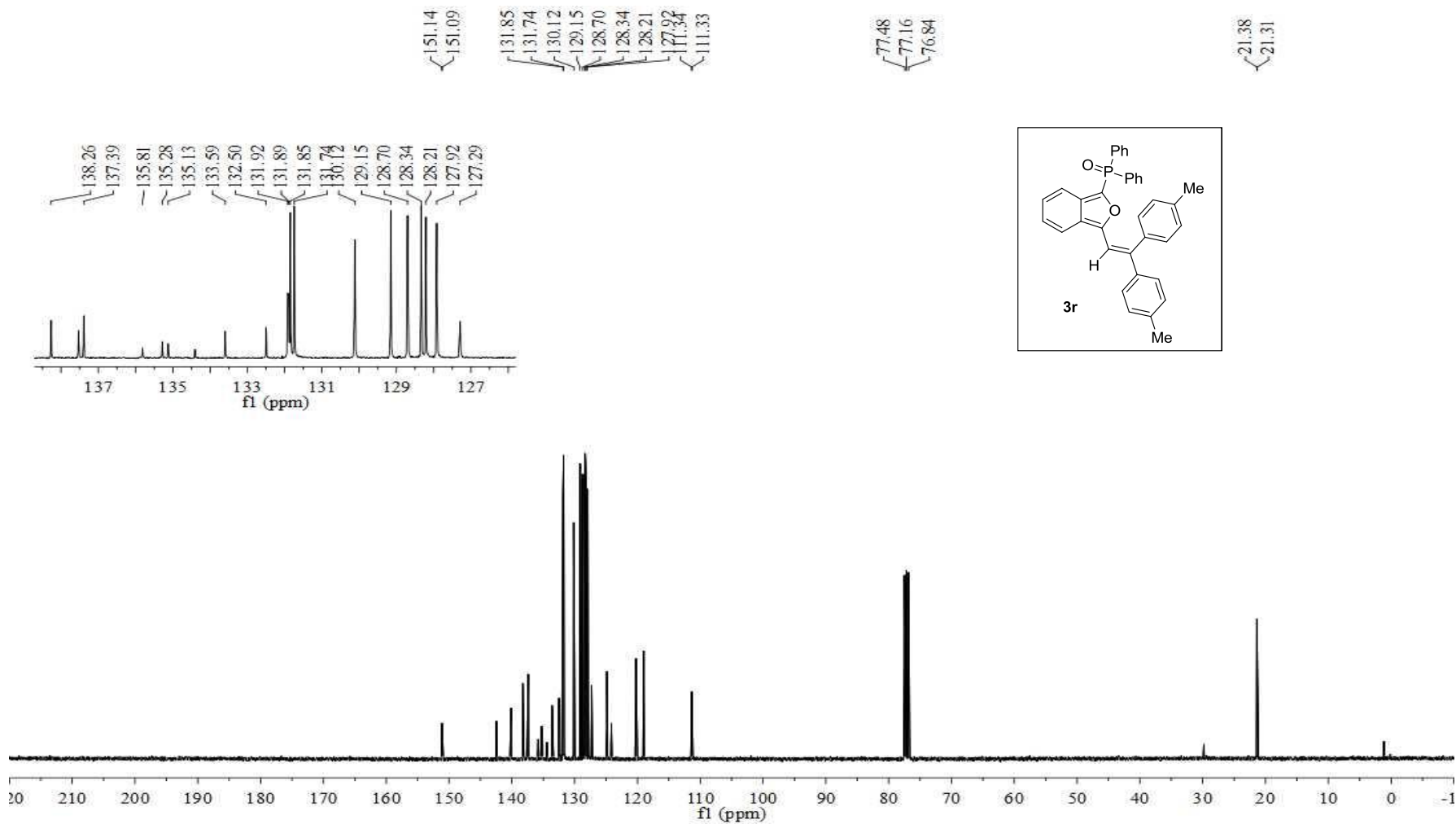
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-di-p-tolylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3r)

8.00  
7.97  
7.54  
7.53  
7.52  
7.52  
7.51  
7.49  
7.40  
7.39  
7.37  
7.37  
7.35  
7.26  
7.23  
7.21  
7.14  
7.11  
7.09  
7.08  
7.07  
7.05  
7.00  
6.99  
6.98  
6.96  
6.79  
6.77  
2.36  
2.19



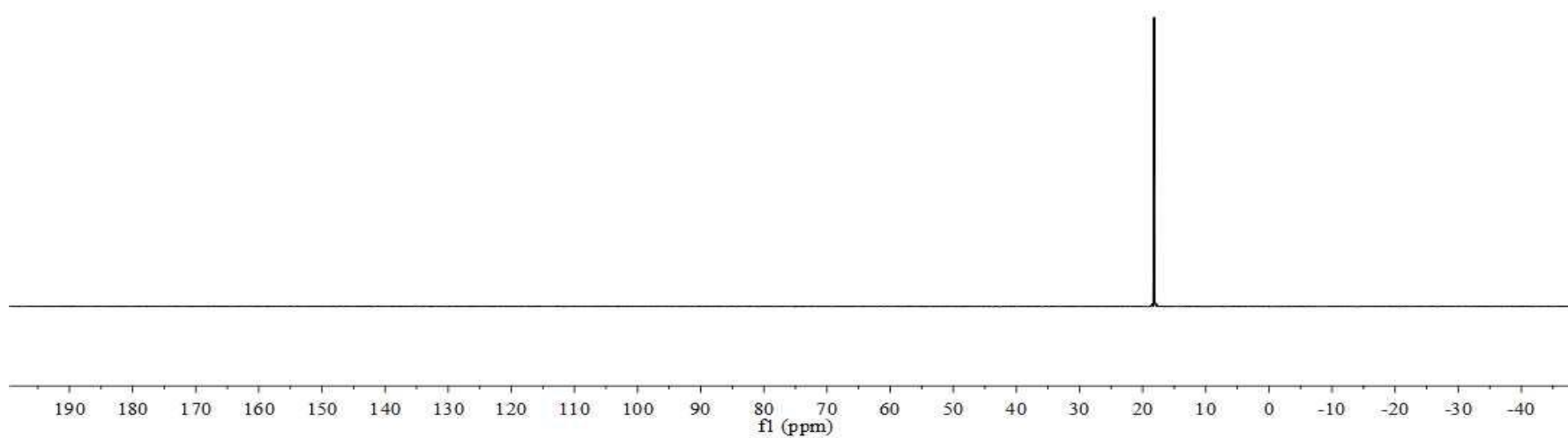
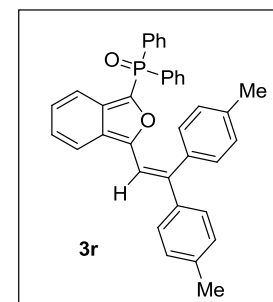
S101

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-di-p-tolylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3r)



$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-di-p-tolylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3r)

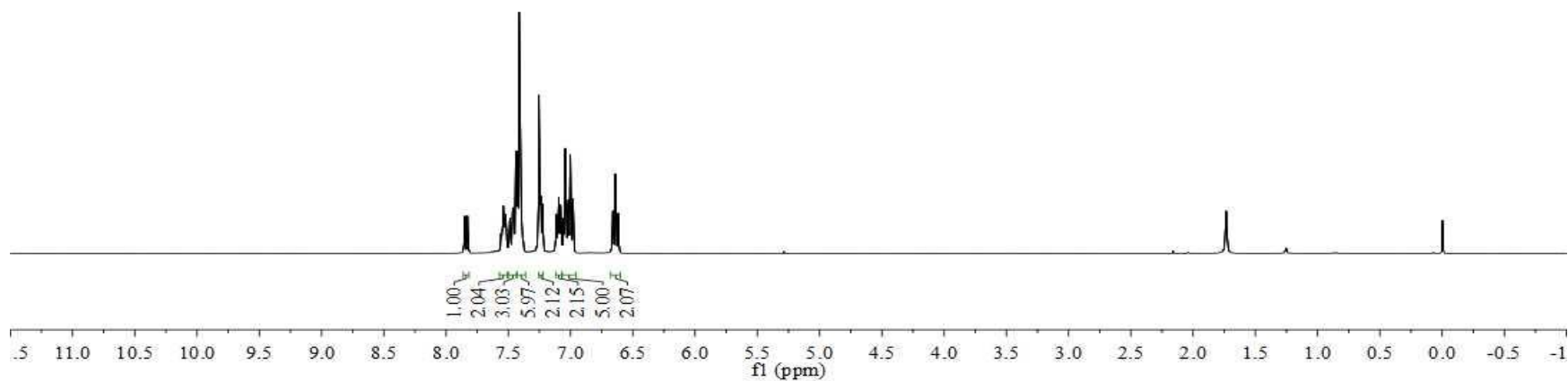
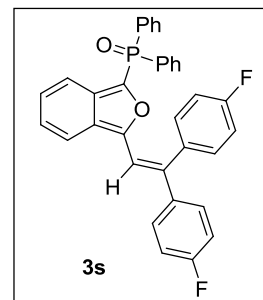
181.7



S103

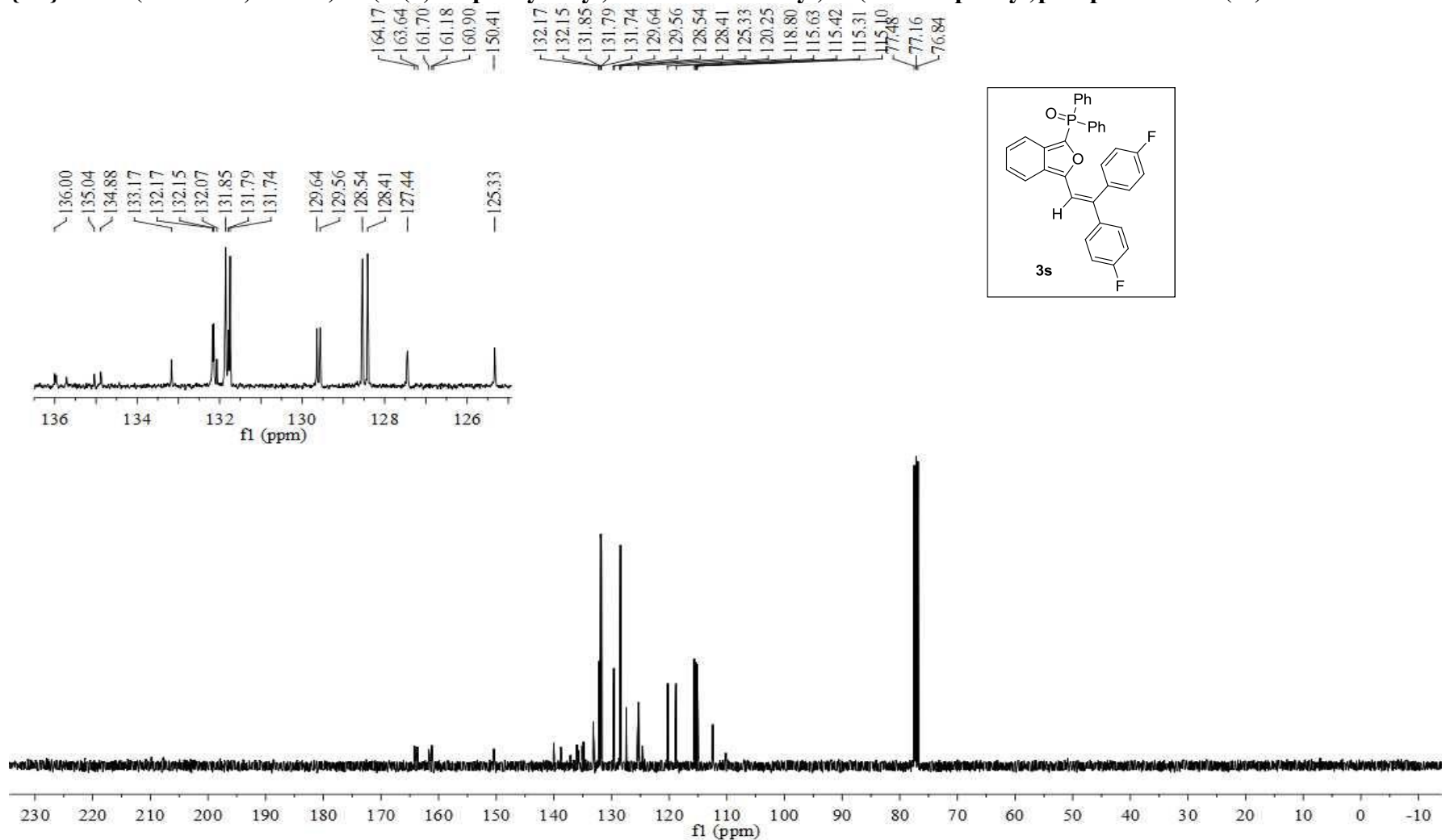
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)bis(4-fluorophenyl)phosphine oxide (3s)**

7.85  
7.83  
7.56  
7.55  
7.54  
7.54  
7.53  
7.52  
7.51  
7.49  
7.46  
7.46  
7.46  
7.44  
7.44  
7.43  
7.41  
7.41  
7.41  
7.40  
7.39  
7.38  
7.26  
7.25  
7.25  
7.24  
7.23  
7.23  
7.12  
7.10  
7.09  
7.09  
7.08  
7.06  
7.04  
7.02  
7.02  
7.00  
6.98  
6.66  
6.64  
6.62



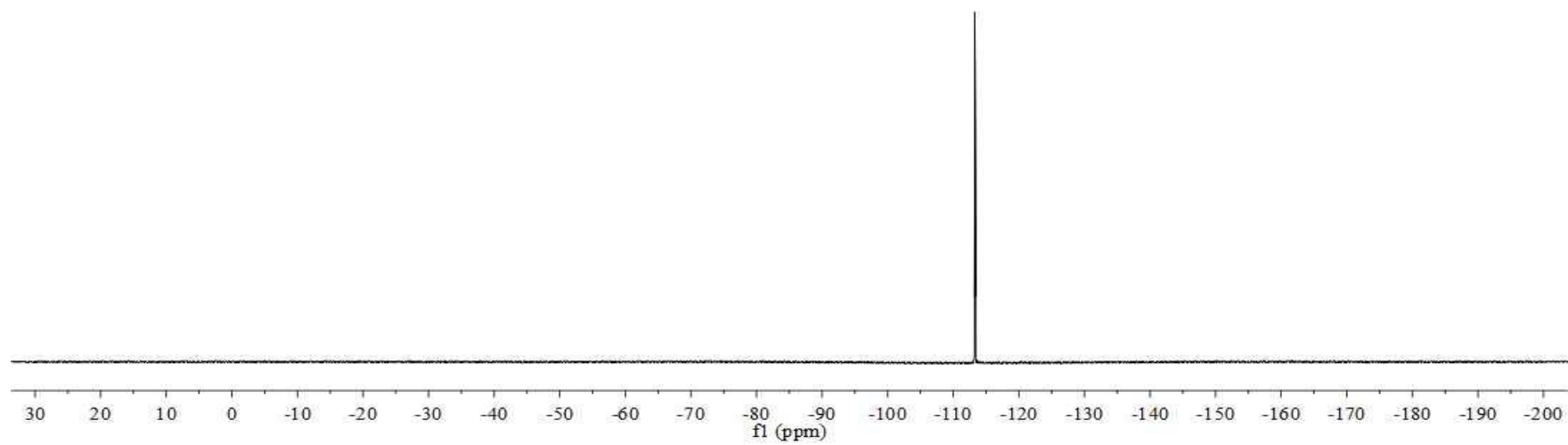
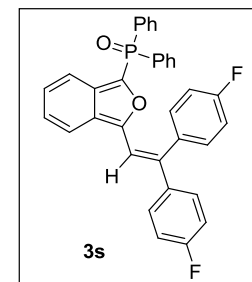
S104

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)bis(4-fluorophenyl)phosphine oxide (3s)**



$^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)bis(4-fluorophenyl)phosphine oxide (**3s**)

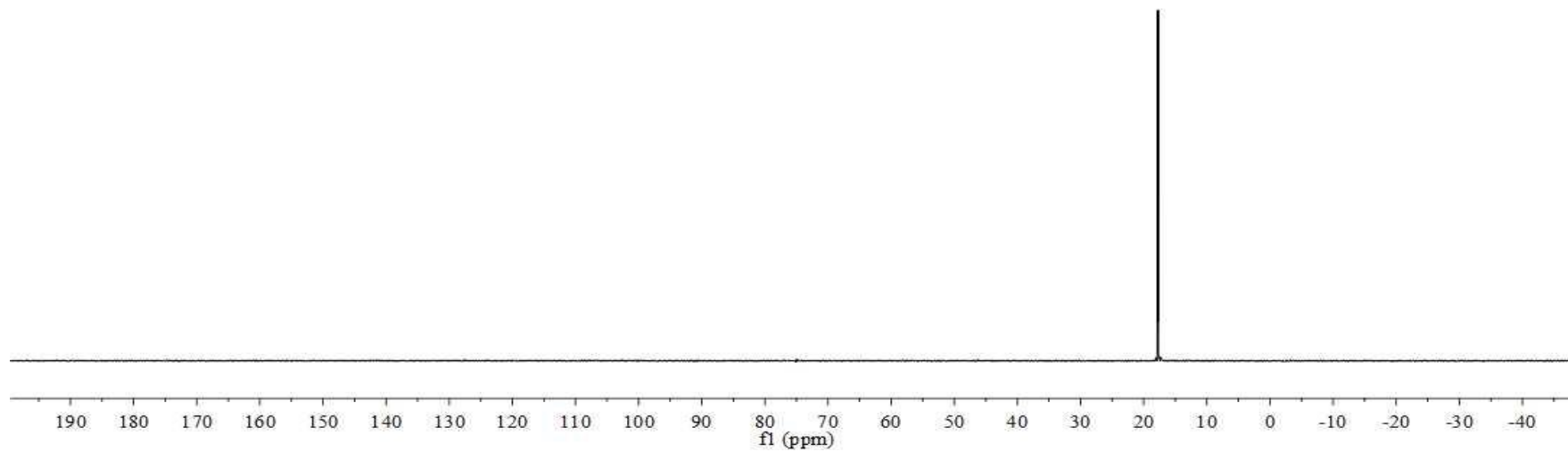
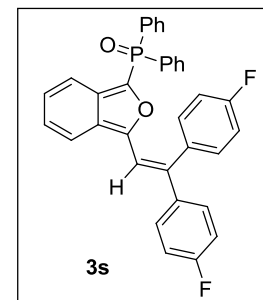
-113.26  
-113.27  
-113.28  
-113.29  
-113.30  
-113.31  
-113.33  
-113.34  
-113.36  
-113.37  
-113.38



S106

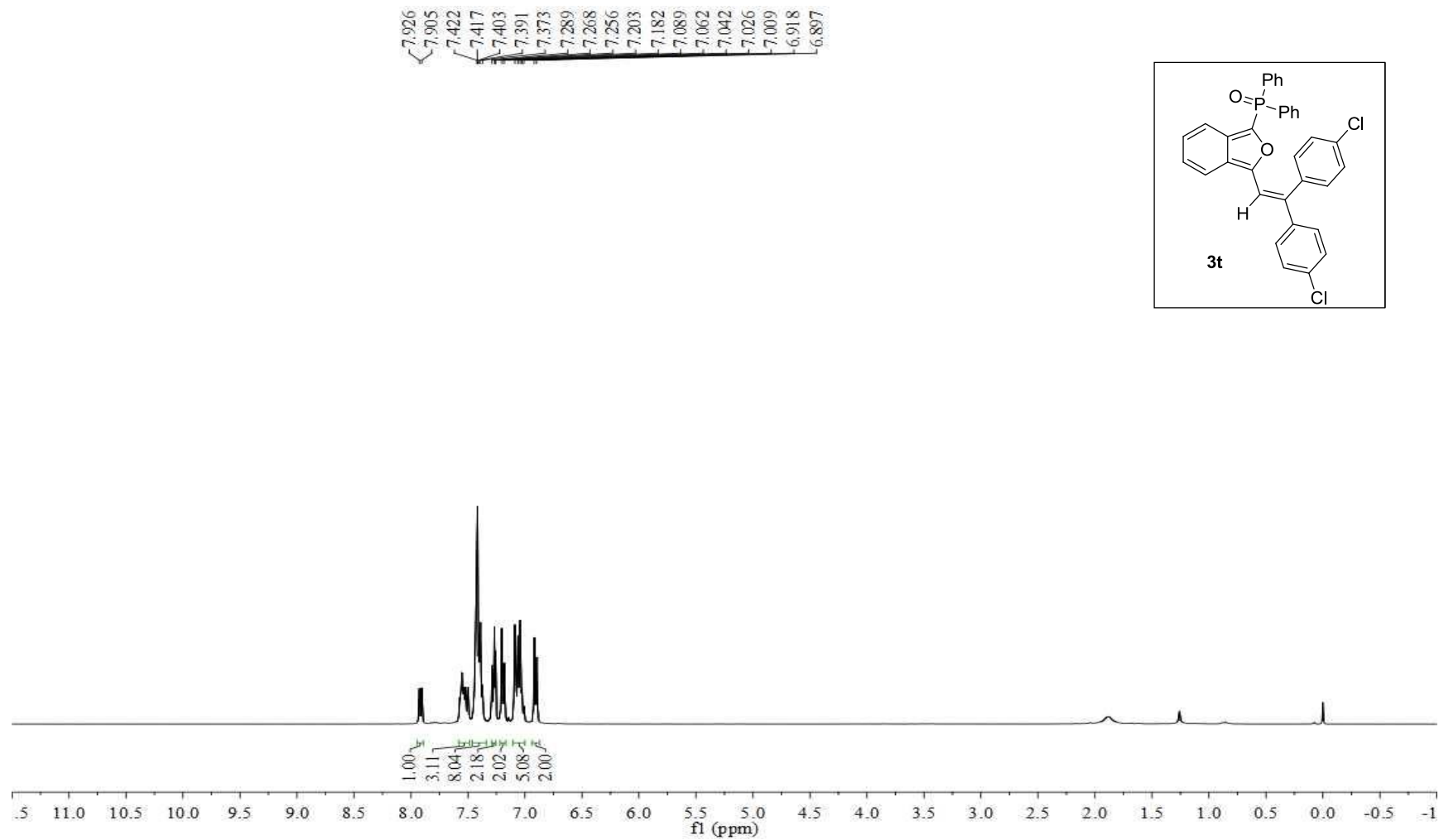
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)bis(4-fluorophenyl)phosphine oxide (**3s**)

17.7



S107

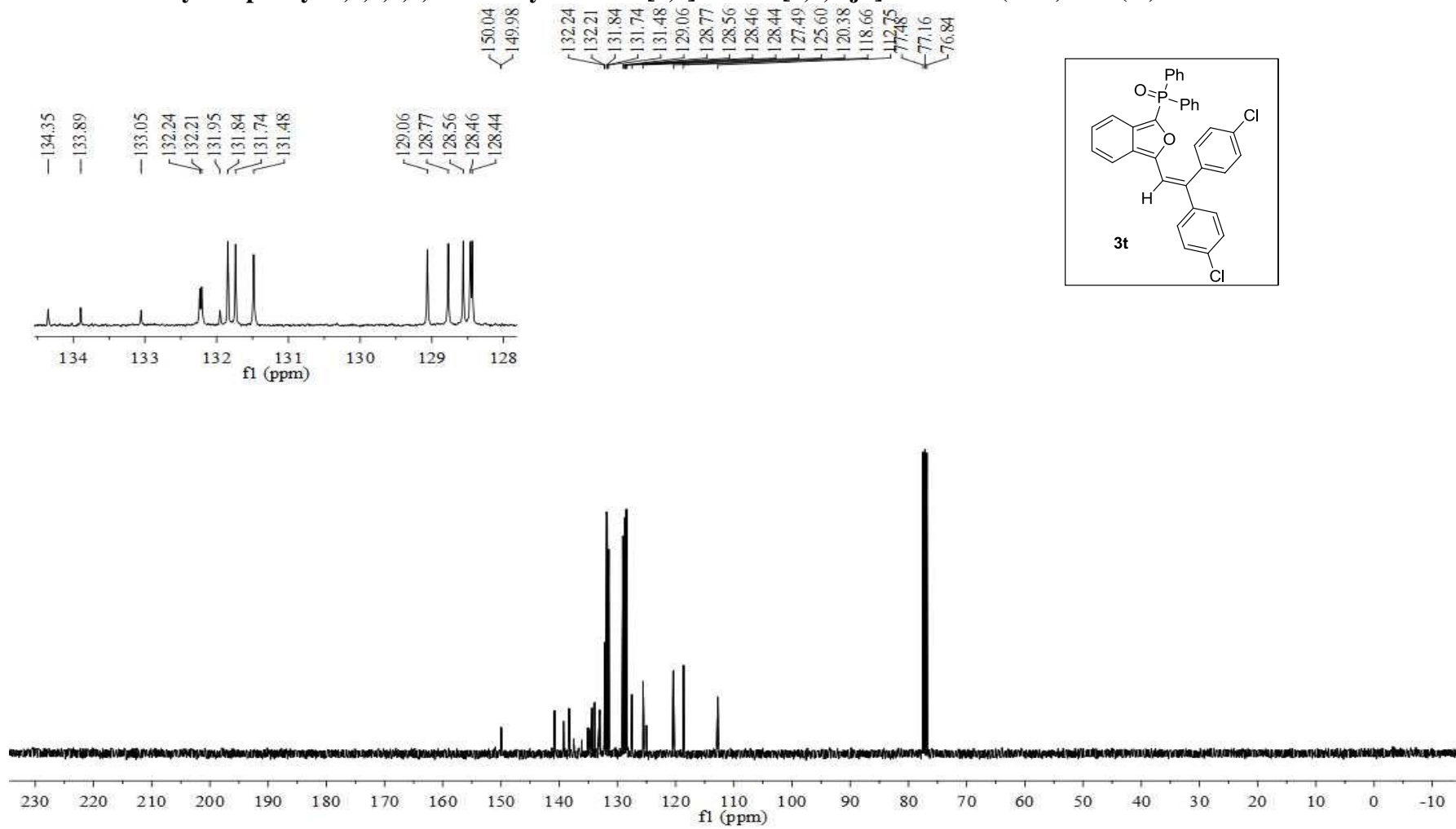
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 10-bromo-12-methyl-14-phenyl-4,5,6,7,8,8a-hexahydrobenzo[1,2]azuleno[5,6,7-jk]fluoren-13(3bH)-one (3t)



S108

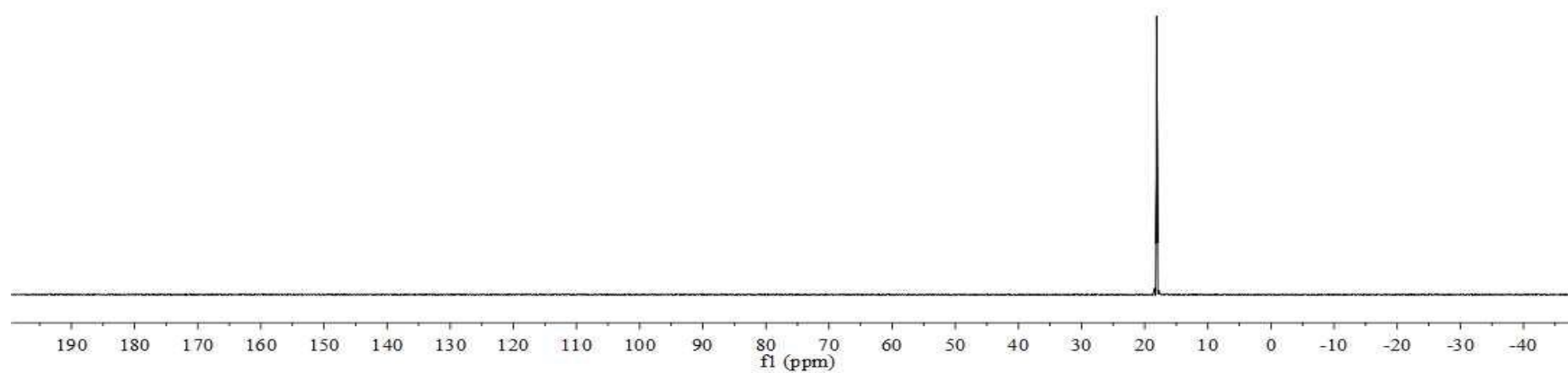
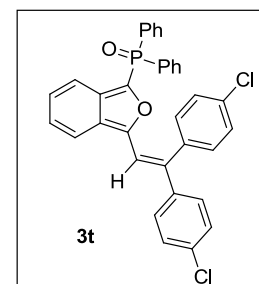


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of  
 10-bromo-12-methyl-14-phenyl-4,5,6,7,8,8a-hexahydrobenzo[1,2]azuleno[5,6,7-jk]fluoren-13(3bH)-one (3t)



$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of  
10-bromo-12-methyl-14-phenyl-4,5,6,7,8,8a-hexahydrobenzo[1,2]azuleno[5,6,7-jk]fluoren-13(3bH)-one (3t)

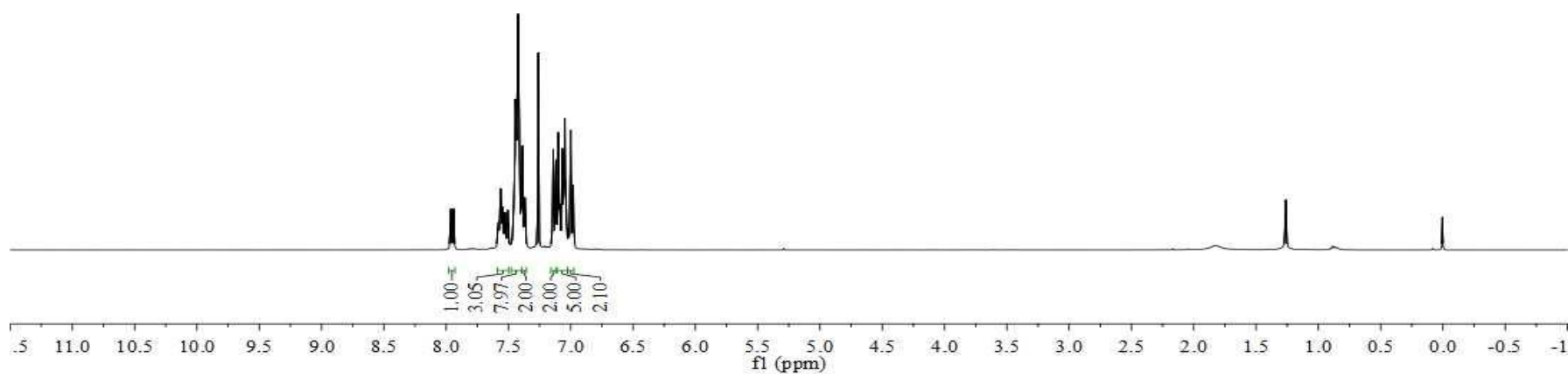
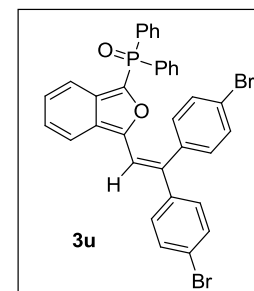
18.11



S110

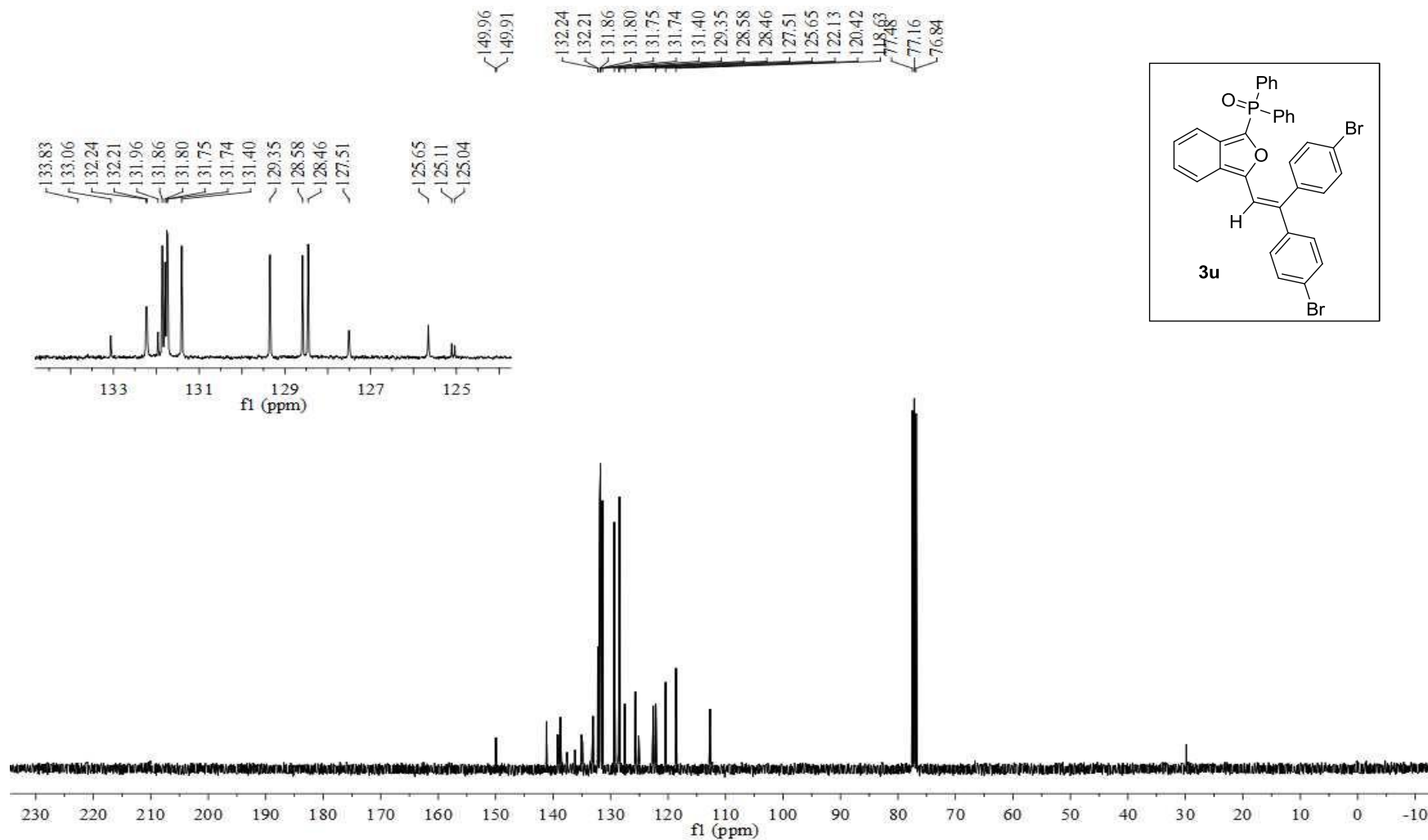
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of bis(4-bromophenyl)(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)phosphine oxide (3u)**

7.96  
7.94  
7.58  
7.56  
7.55  
7.54  
7.53  
7.51  
7.44  
7.43  
7.42  
7.42  
7.40  
7.39  
7.37  
7.26  
7.14  
7.12  
7.10  
7.09  
7.07  
7.05  
7.02  
7.00  
6.98



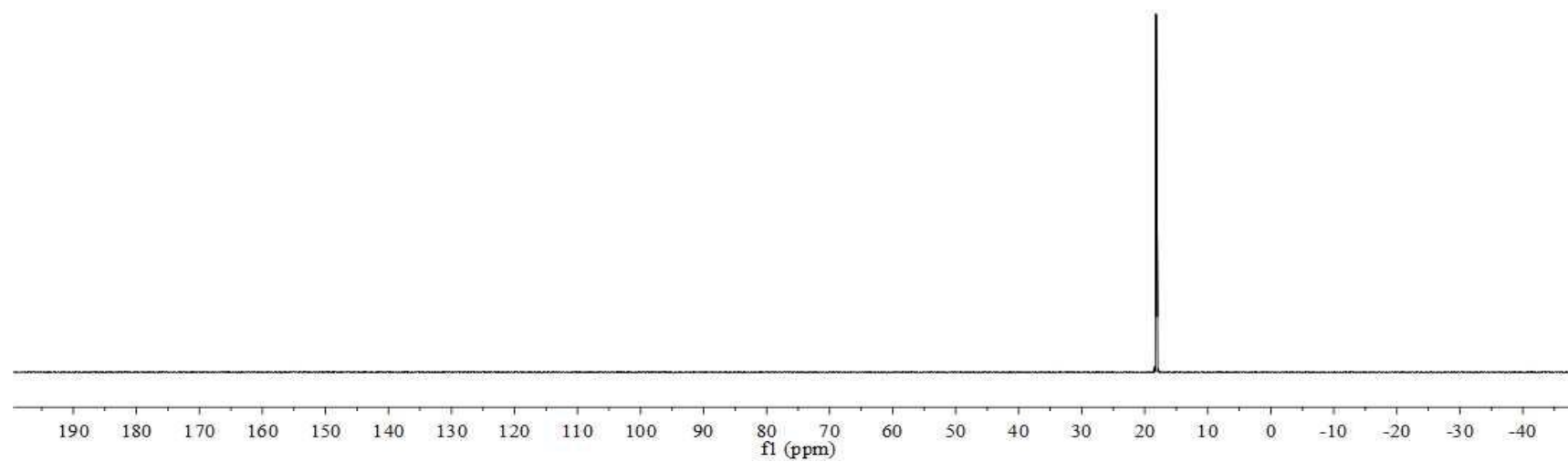
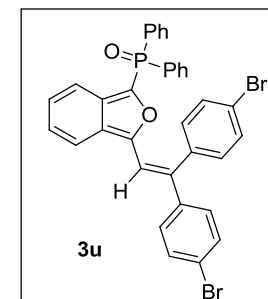
S111

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of bis(4-bromophenyl)(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)phosphine oxide (3u)



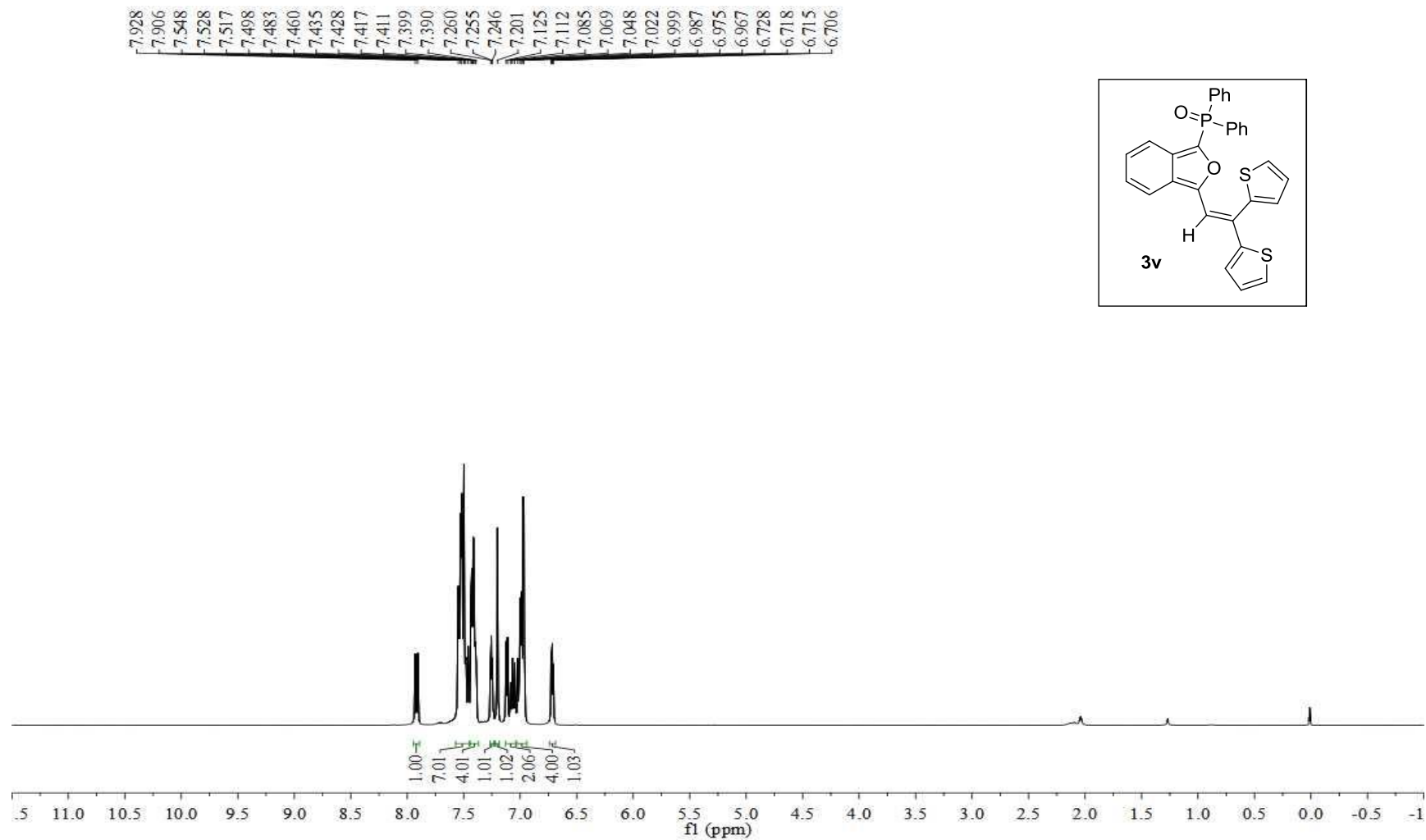
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of bis(4-bromophenyl)(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)phosphine oxide (**3u**)

18.23



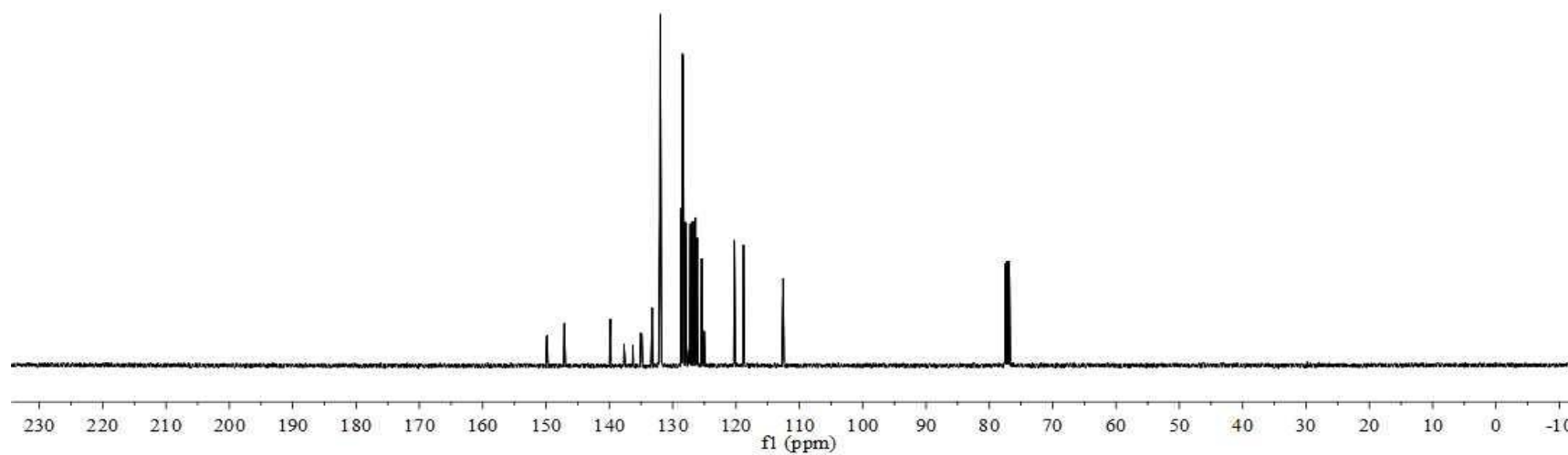
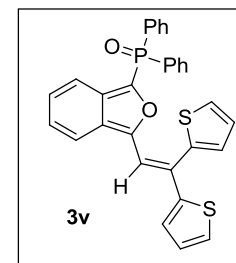
S113

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-di(thiophen-2-yl)vinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3v)**



**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of 3-(2,2-di(thiophen-2-yl)vinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3v)**

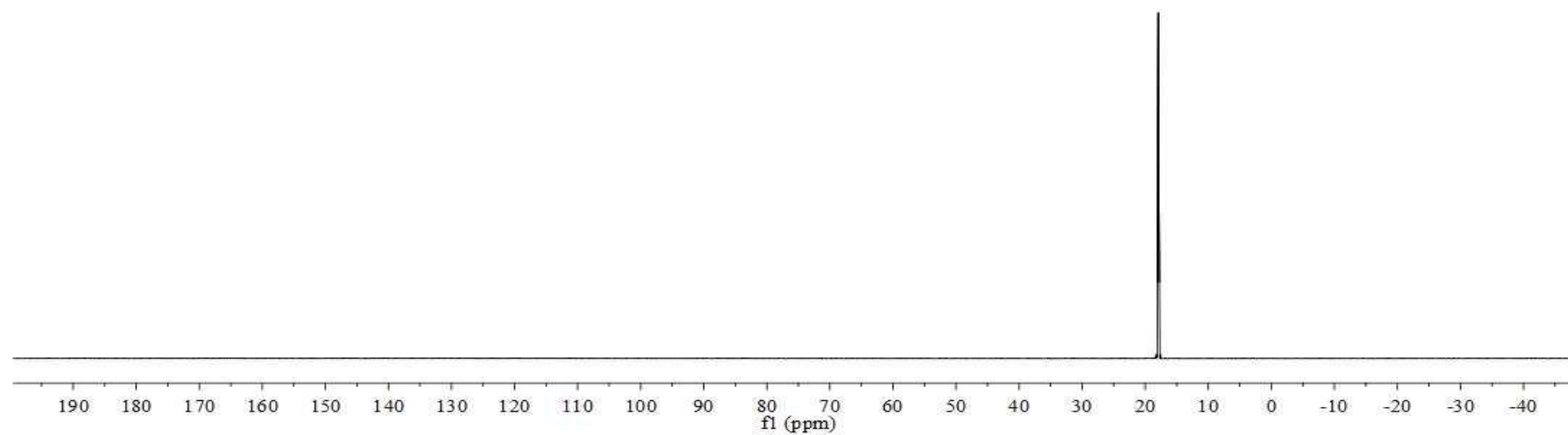
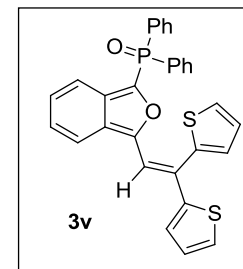
149.88  
149.83  
147.08  
139.87  
137.68  
136.30  
135.03  
134.88  
133.26  
132.15  
132.04  
132.02  
131.97  
131.86  
128.64  
128.45  
128.32  
127.98  
127.84  
127.40  
127.21  
126.84  
126.42  
126.15  
125.40  
125.04  
124.96  
120.26  
118.85  
112.56  
77.48  
77.16  
76.84



S115

$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-di(thiophen-2-yl)vinyl)isobenzofuran-1-yl)diphenylphosphine oxide (3v)

17.89

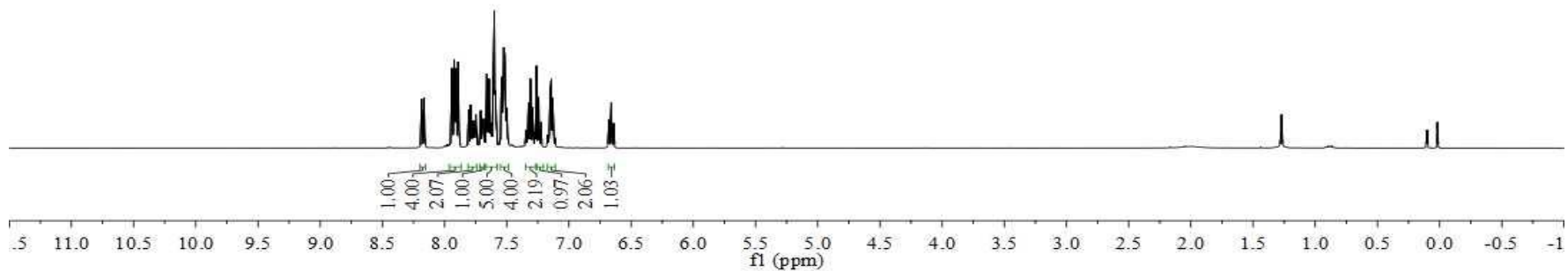
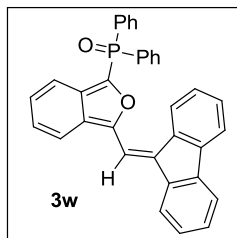


S116



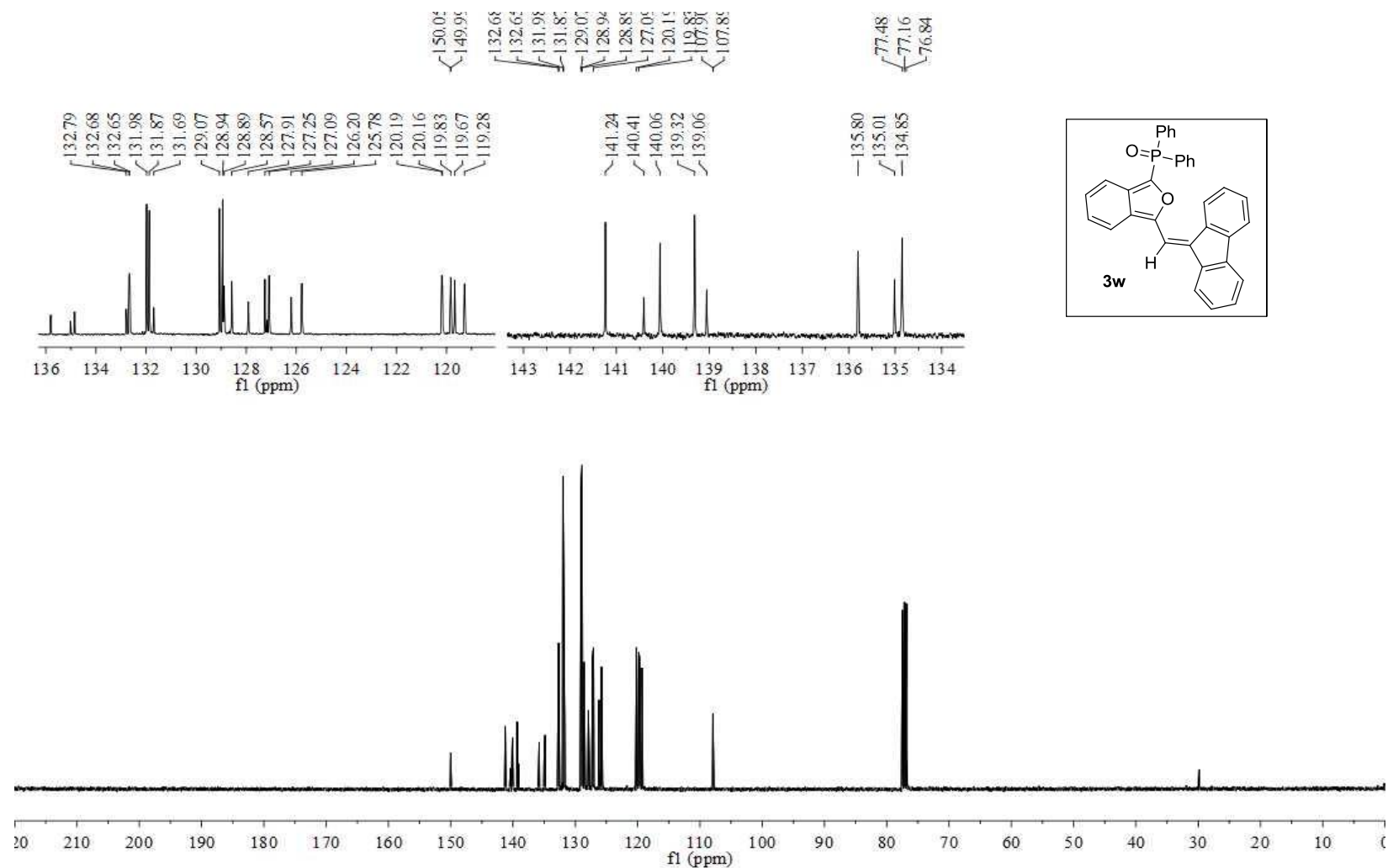
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-((9H-fluoren-9-ylidene)methyl)isobenzofuran-1-yl)diphenylphosphine oxide(3w)**

8.184  
8.164  
7.943  
7.941  
7.923  
7.920  
7.911  
7.908  
7.891  
7.888  
7.806  
7.803  
7.790  
7.787  
7.772  
7.769  
7.765  
7.762  
7.752  
7.748  
7.664  
7.661  
7.649  
7.642  
7.629  
7.625  
7.610  
7.605  
7.600  
7.591  
7.588  
7.543  
7.540  
7.536  
7.524  
7.520  
7.516  
7.506  
7.504  
7.499  
7.328  
7.326  
7.312  
7.307  
7.293  
7.290  
7.260  
7.245  
7.243  
7.227  
7.225  
7.156  
7.151  
7.141  
7.131  
7.127  
6.681  
6.678  
6.661  
6.660  
6.643  
6.640



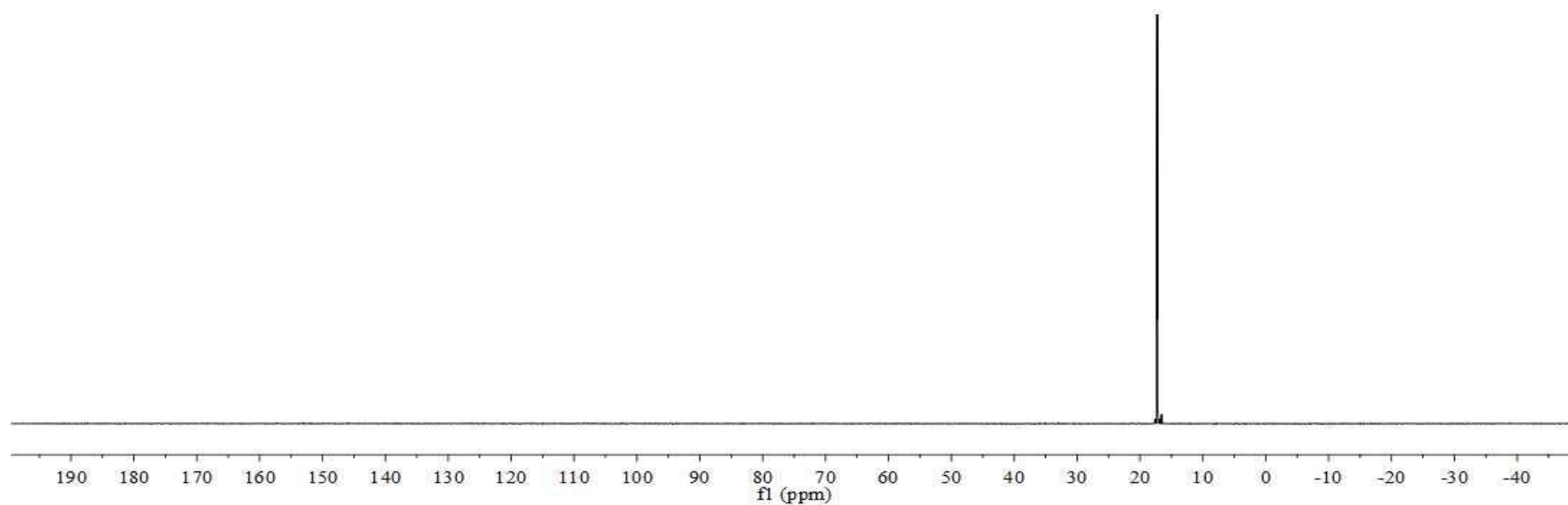
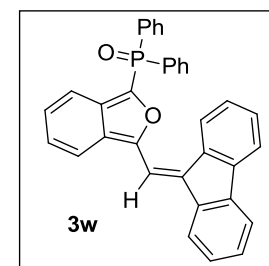
S117

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-((9H-fluoren-9-ylidene)methyl) isobenzofuran-1-yl)diphenylphosphine oxide (3w)**



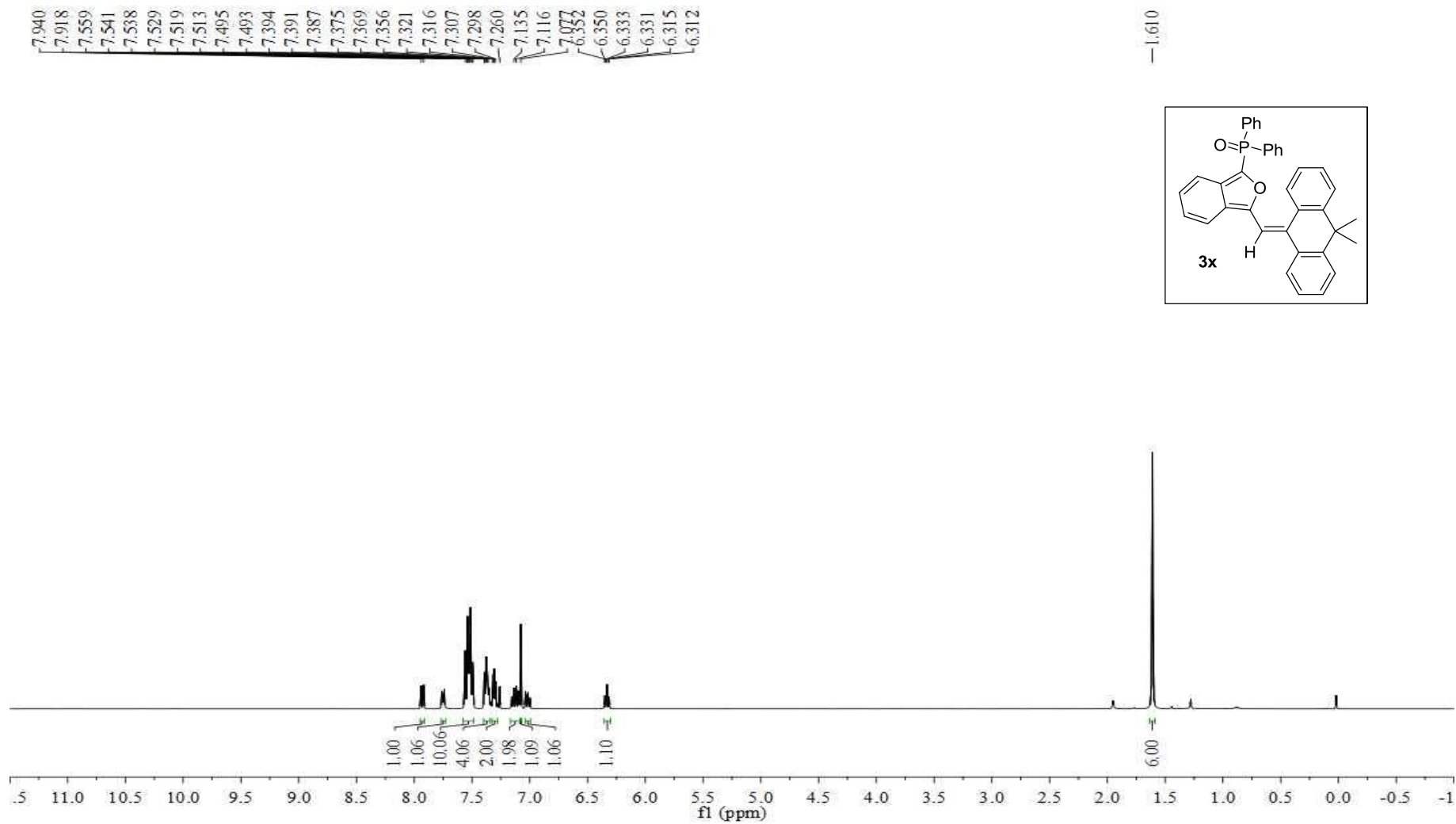
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-((9H-fluoren-9-ylidene)methyl)isobenzofuran-1-yl)diphenylphosphine oxide (**3w**)

17.22

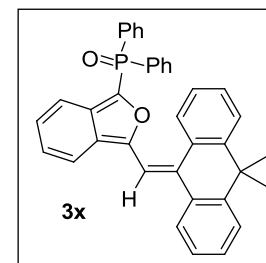
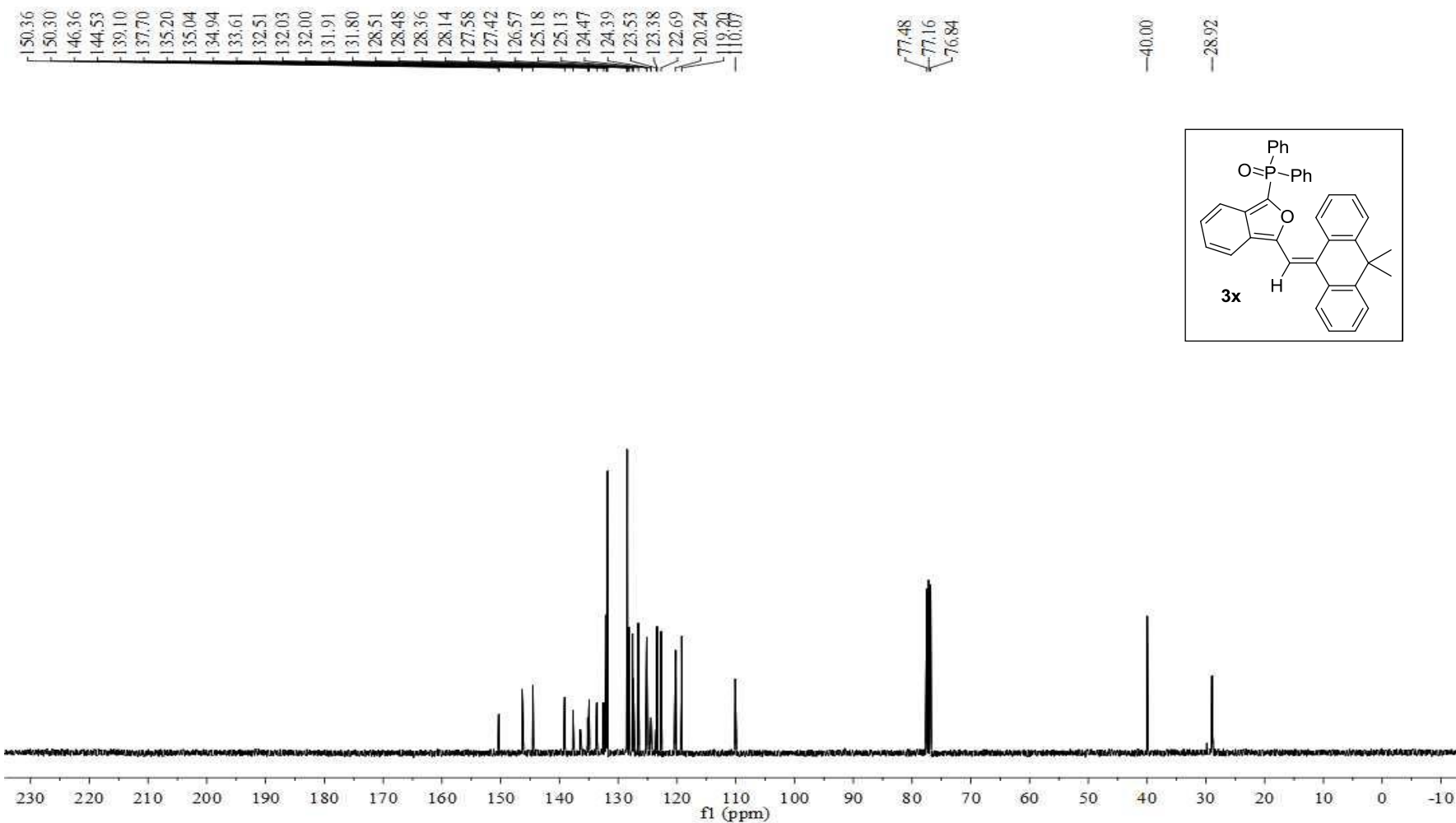


S119

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-((10,10-dimethylantracen-9(10H)-ylidene)methyl)isobenzofuran-1-yl)diphenylphosphine oxide(3x)**

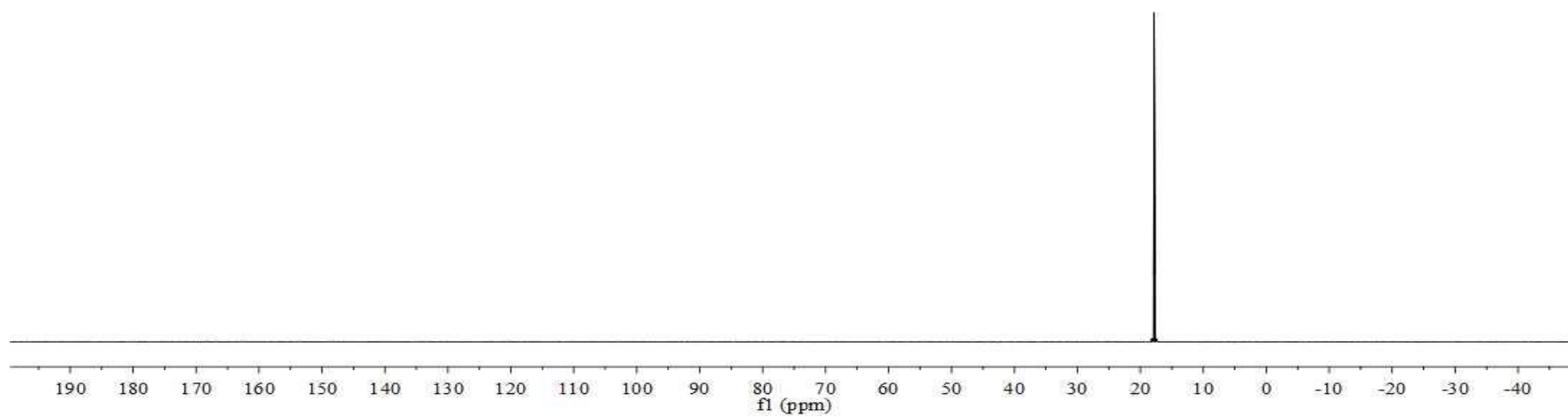
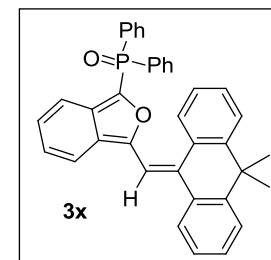


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-((10,10-dimethylantracen-9(10H)-ylidene)methyl)isobenzofuran-1-yl)diphenylphosphine oxide(3x)**



$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-((10,10-dimethylantracen-9(10H)-ylidene)methyl)isobenzofuran-1-yl)diphenylphosphine oxide(3x)

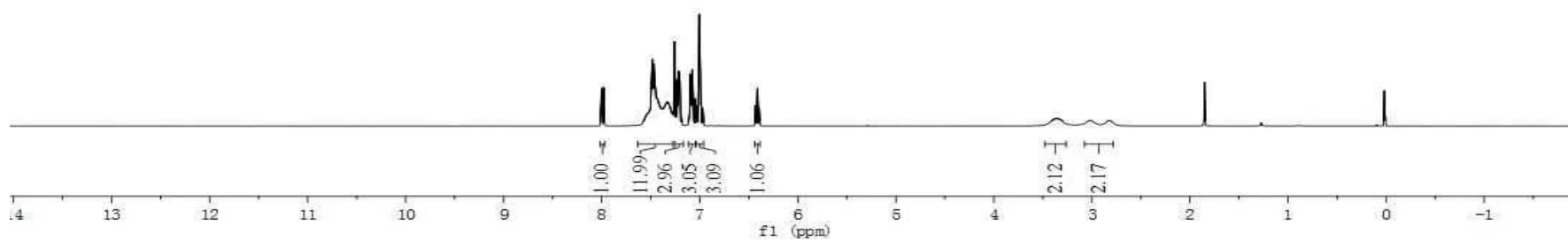
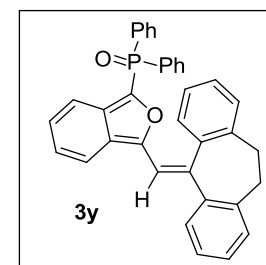
-17.83



S122

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-((10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)methyl)isobenzofuran-1-yl)diphenylphosphine oxide (3y)

8.00  
7.98  
7.49  
7.48  
7.48  
7.47  
7.47  
7.46  
7.46  
7.26  
7.24  
7.23  
7.22  
7.22  
7.21  
7.20  
7.20  
7.10  
7.10  
7.09  
7.08  
7.08  
7.02  
7.01  
7.00  
7.00  
6.99  
6.99  
6.43  
6.43  
6.41  
6.41  
6.39  
6.39  
3.37  
3.02  
2.83

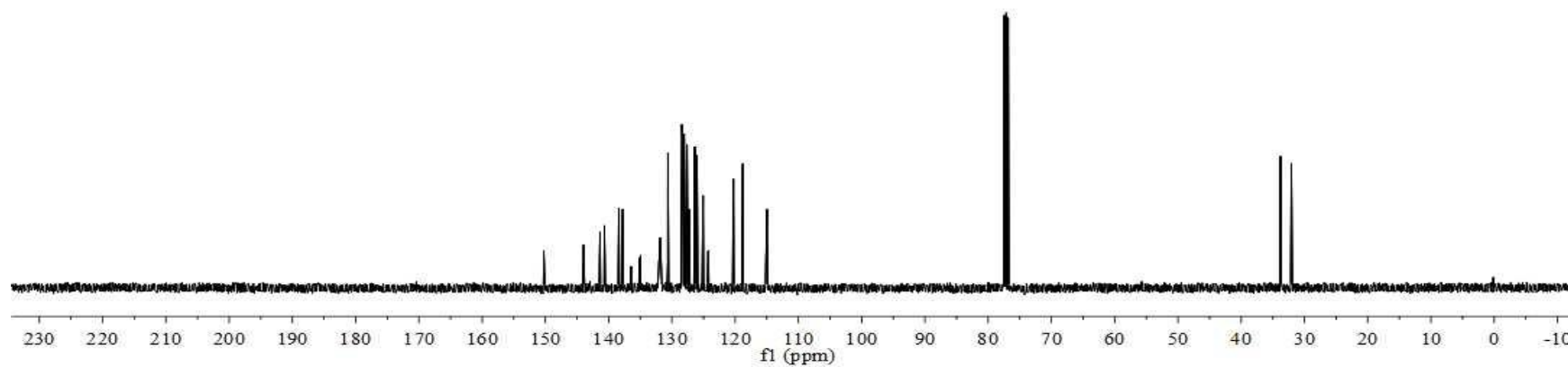
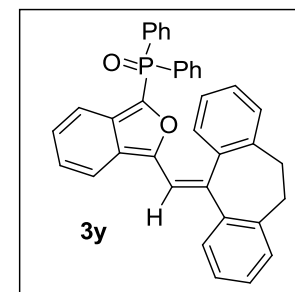


S123

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-((10,11-dihydro-5H-dibenzo[a,d][7]

annulen-5-ylidene)methyl)isobenzofuran-1-yl)diphenylphosphine oxide (3y)

(3-((10,11-dihydro-5H-dibenzo[a,d][7]



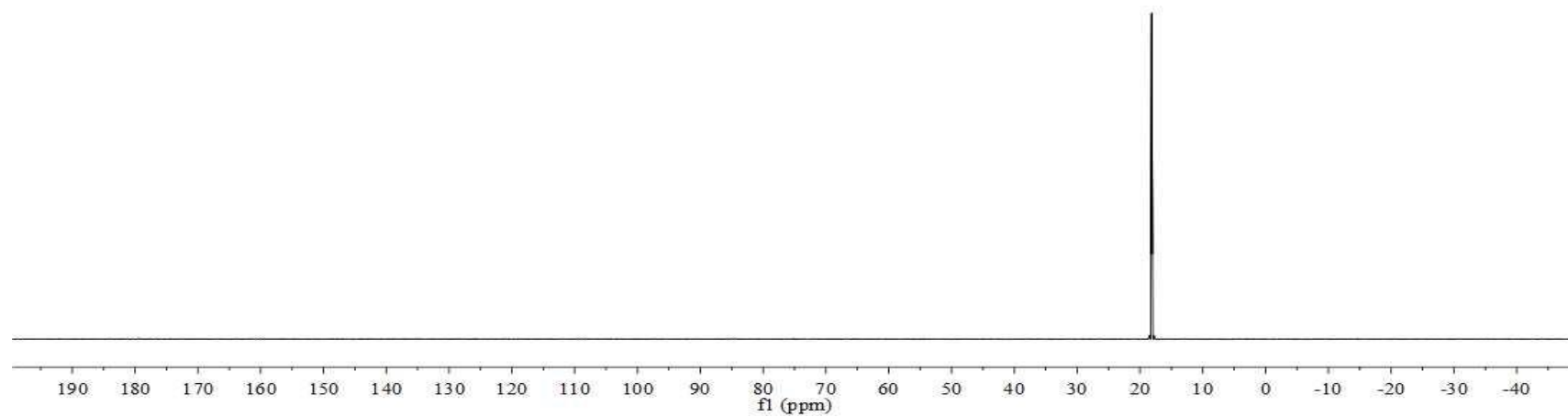
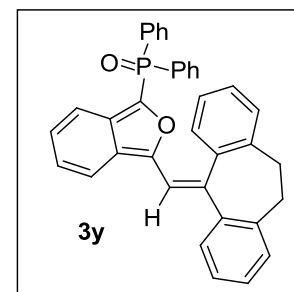
S124



$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )  
annulen-5-ylidene)methyl)isobenzofuran-1-yl)diphenylphosphine oxide (3y)

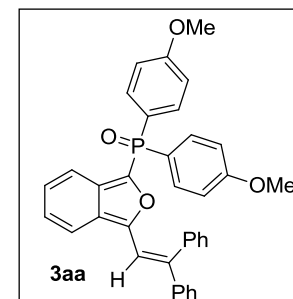
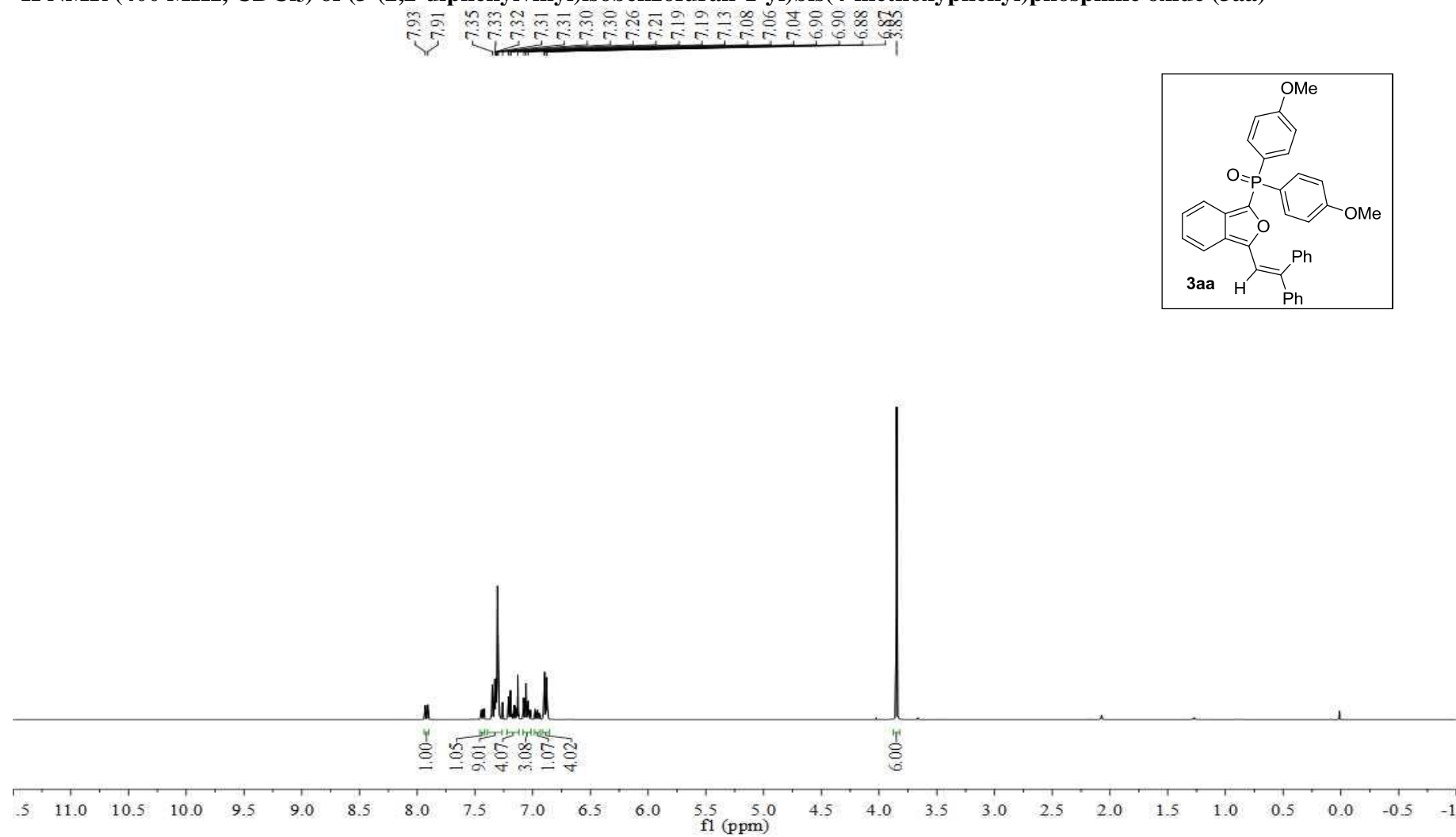
of (3-((10,11-dihydro-5H-dibenzo[a,d][7]

-18.12

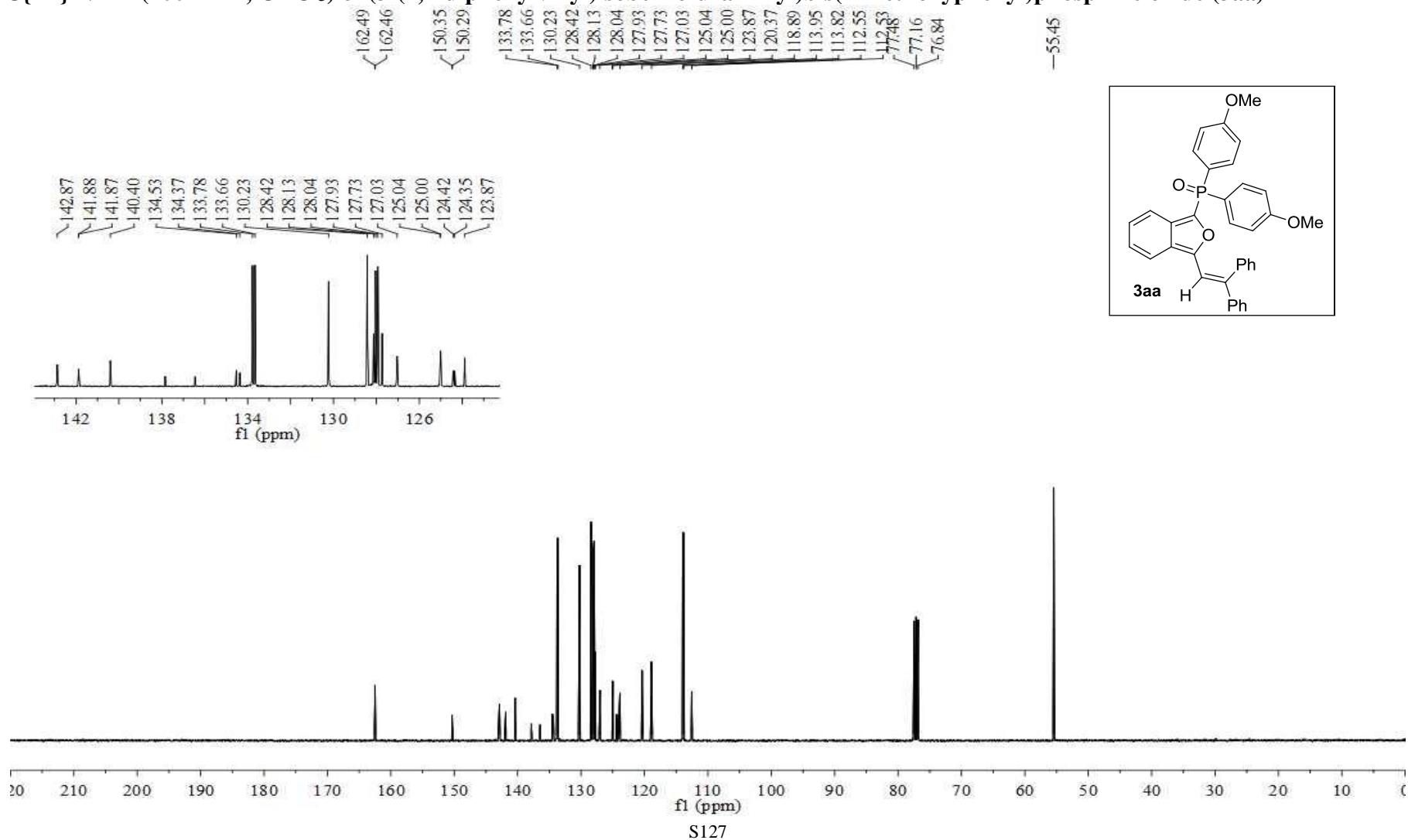


S125

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)bis(4-methoxyphenyl)phosphine oxide (3aa)

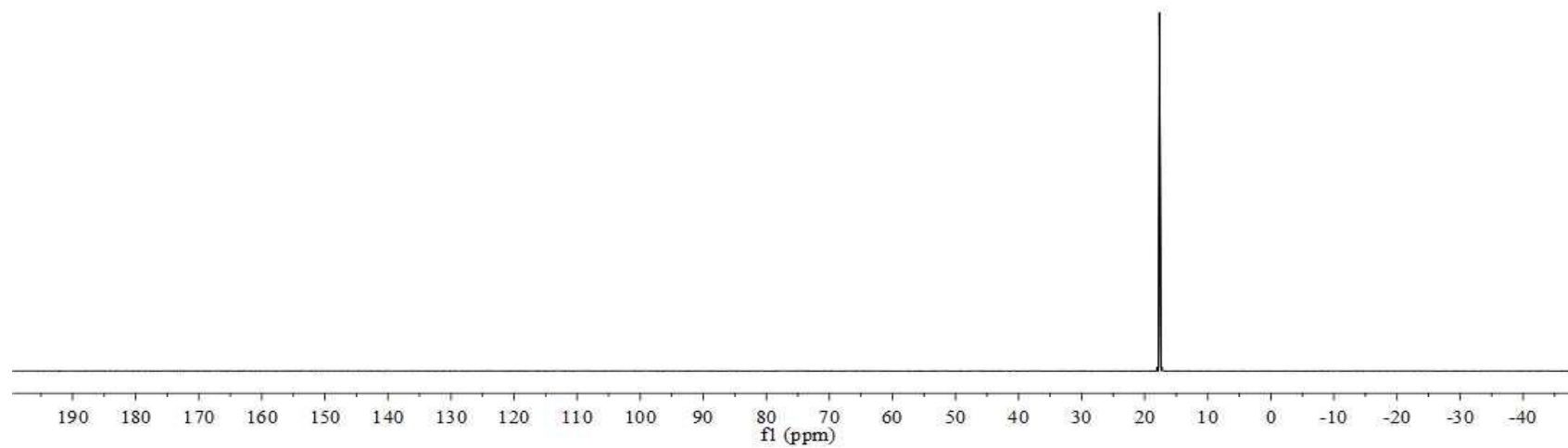
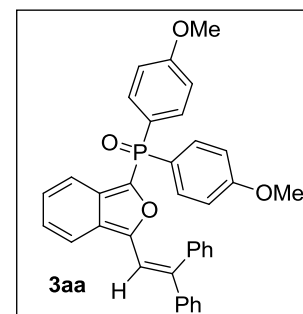


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)bis(4-methoxyphenyl)phosphine oxide (3aa)



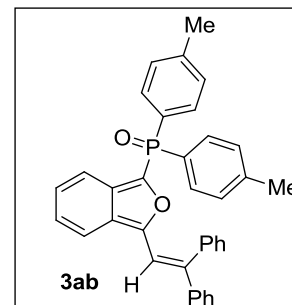
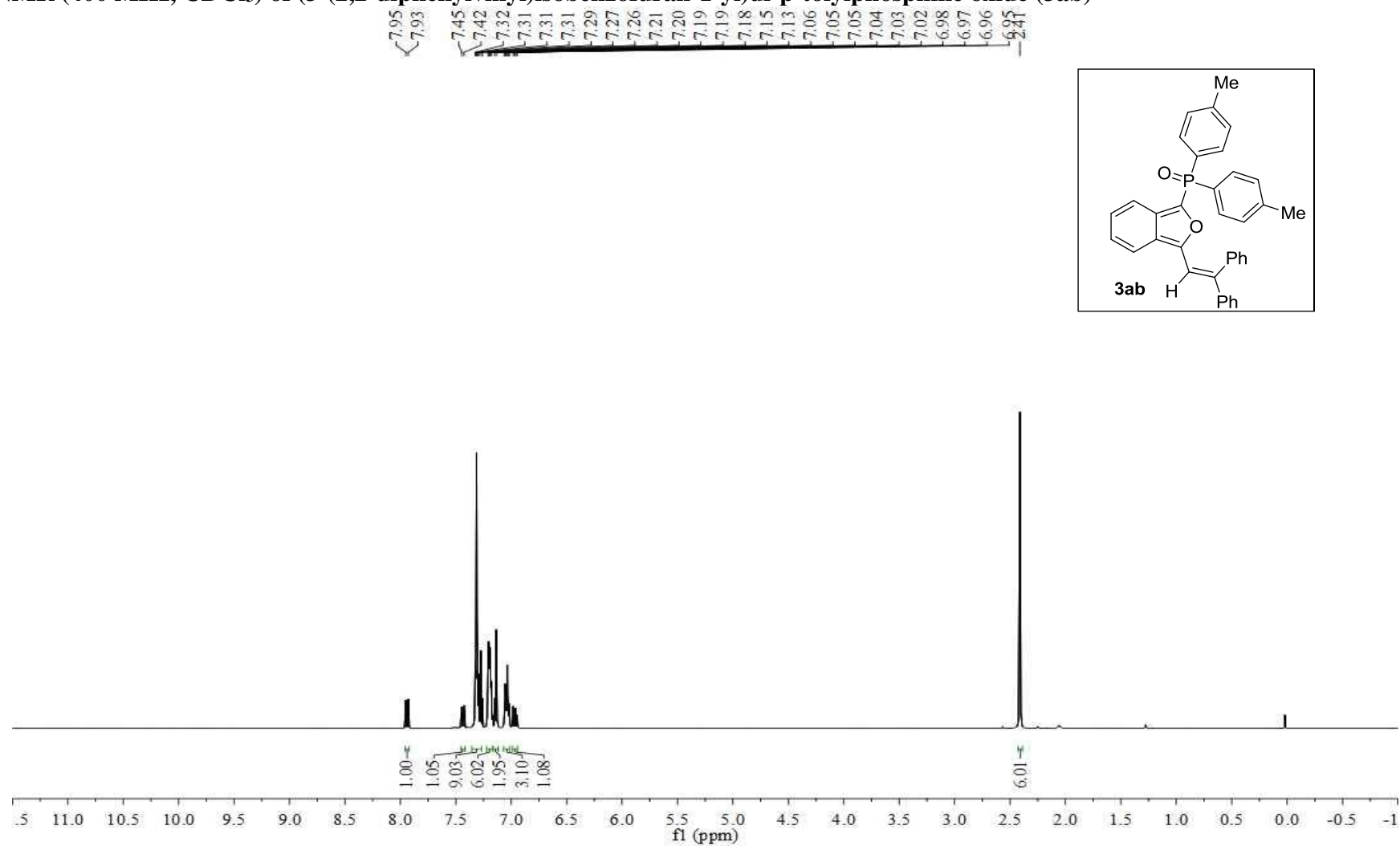
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)bis(4-methoxyphenyl)phosphine oxide (3aa)

—17.65

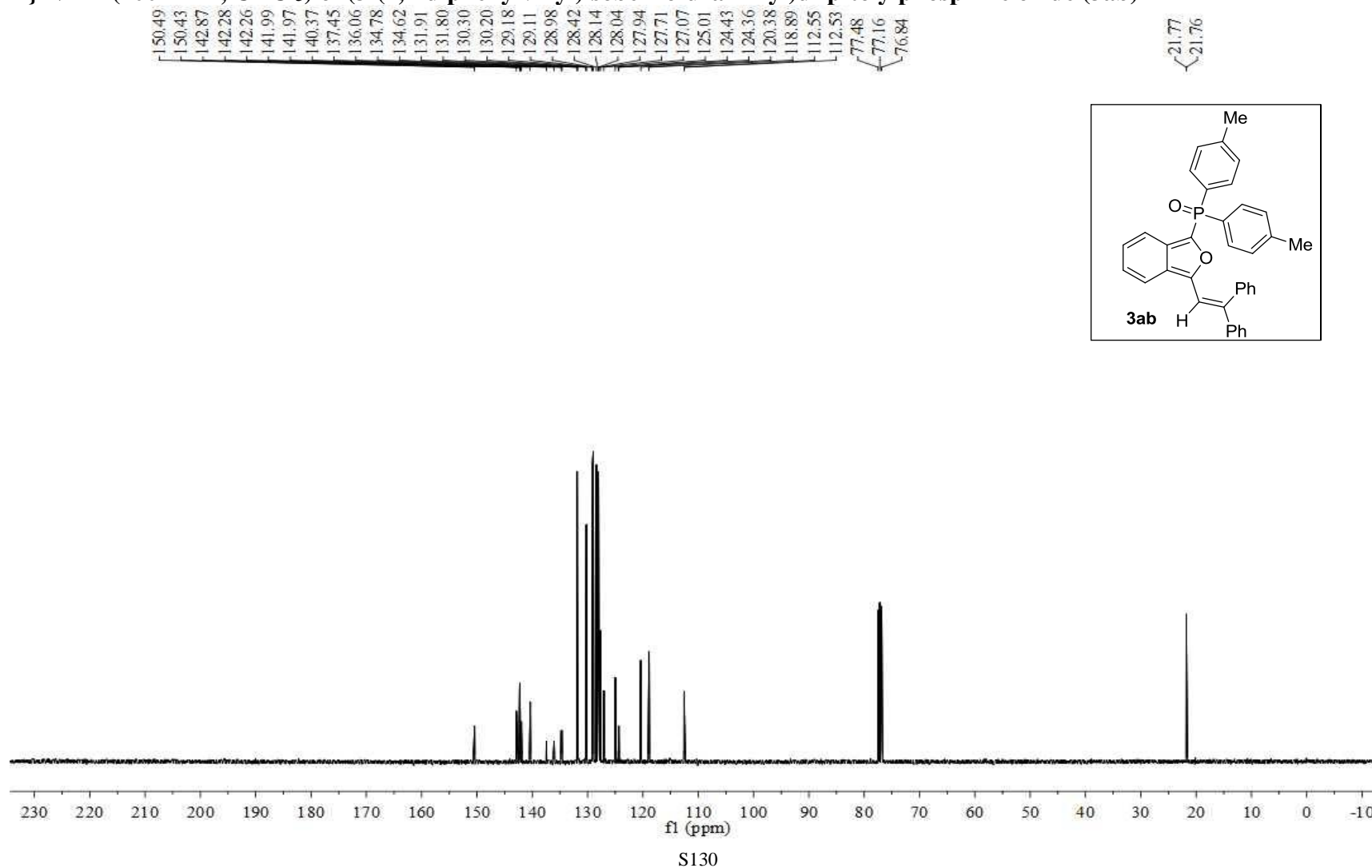


S128

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)di-p-tolylphosphine oxide (3ab)

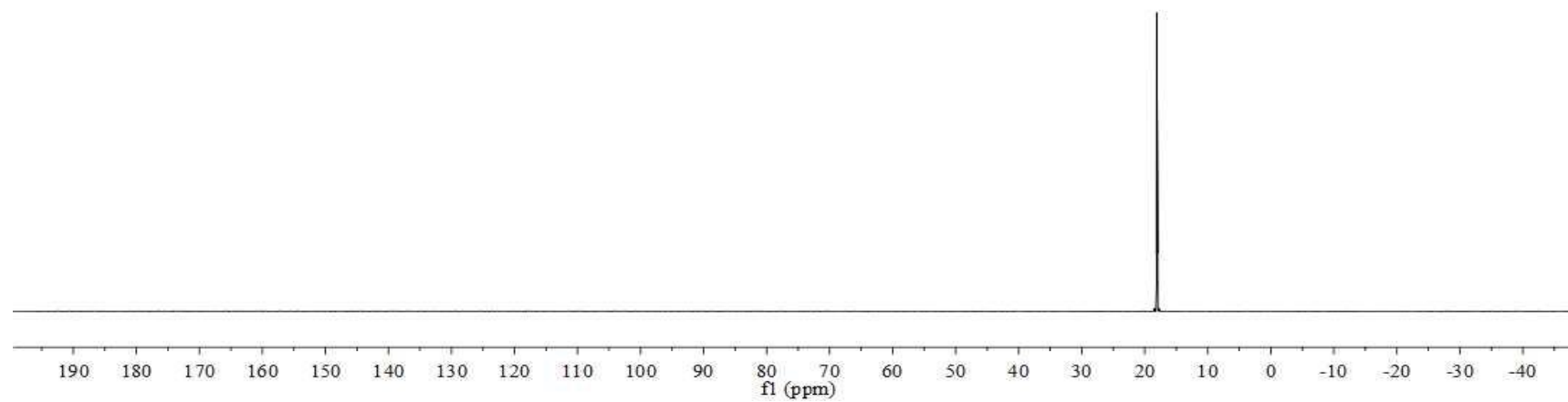
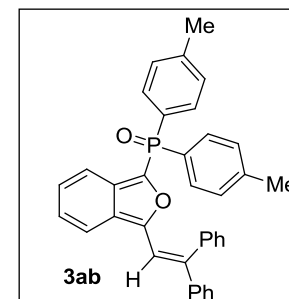


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)di-p-tolylphosphine oxide (3ab)**



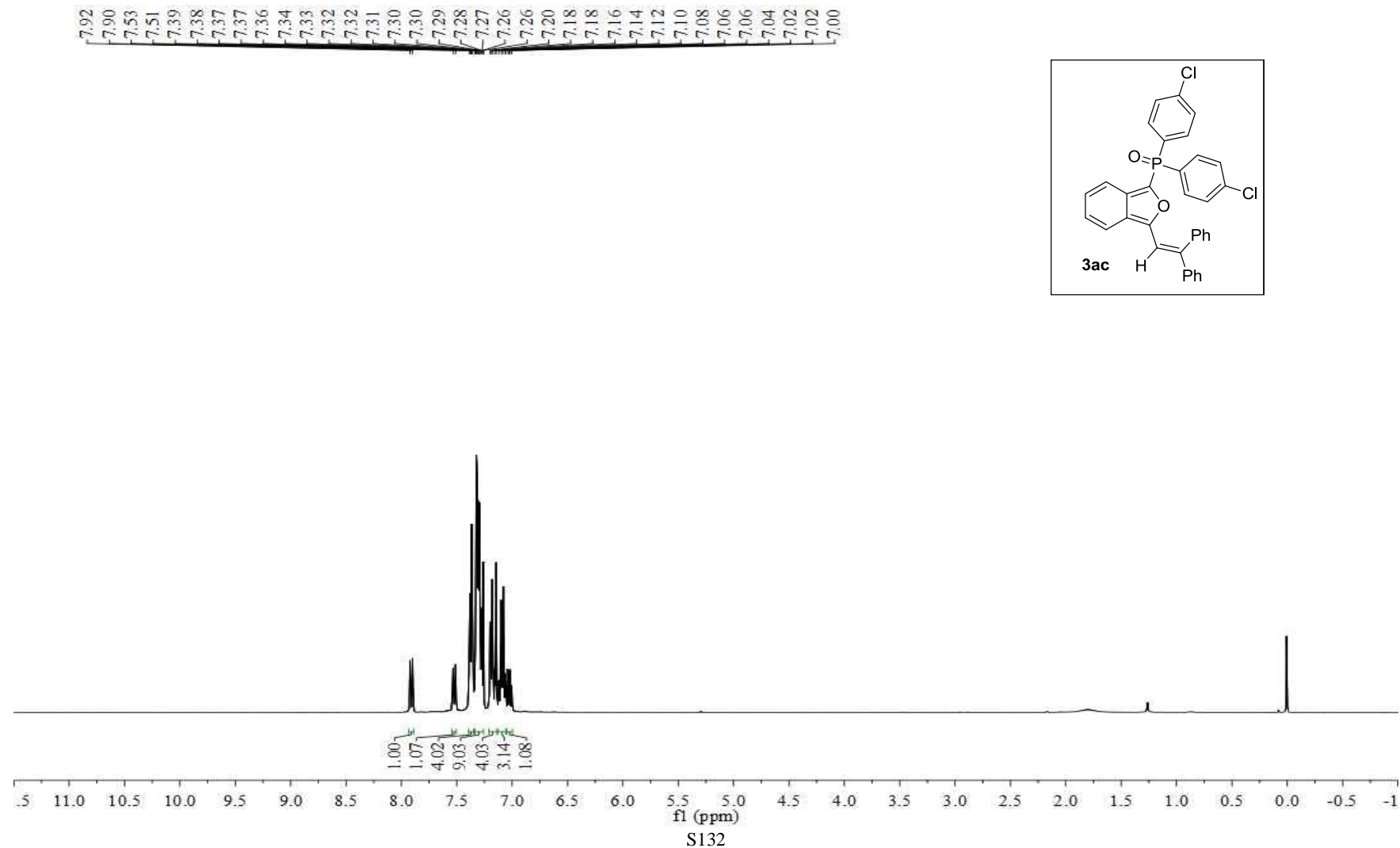
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)di-p-tolylphosphine oxide (3ab)

181.0



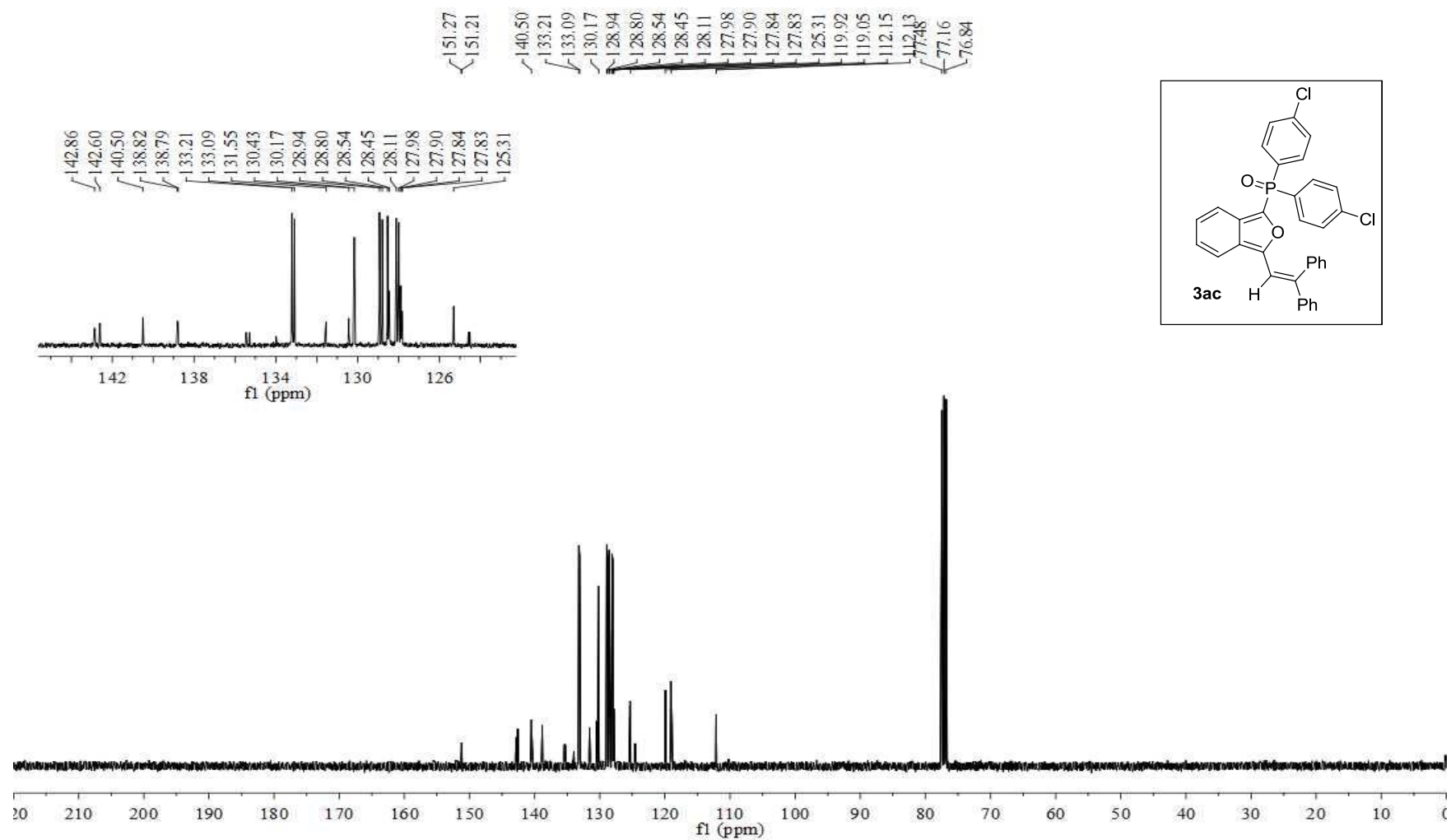
S131

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of bis(4-chlorophenyl)(3-(2,2-diphenylvinyl) isobenzofuran-1-yl)phosphine oxide (3ac)**



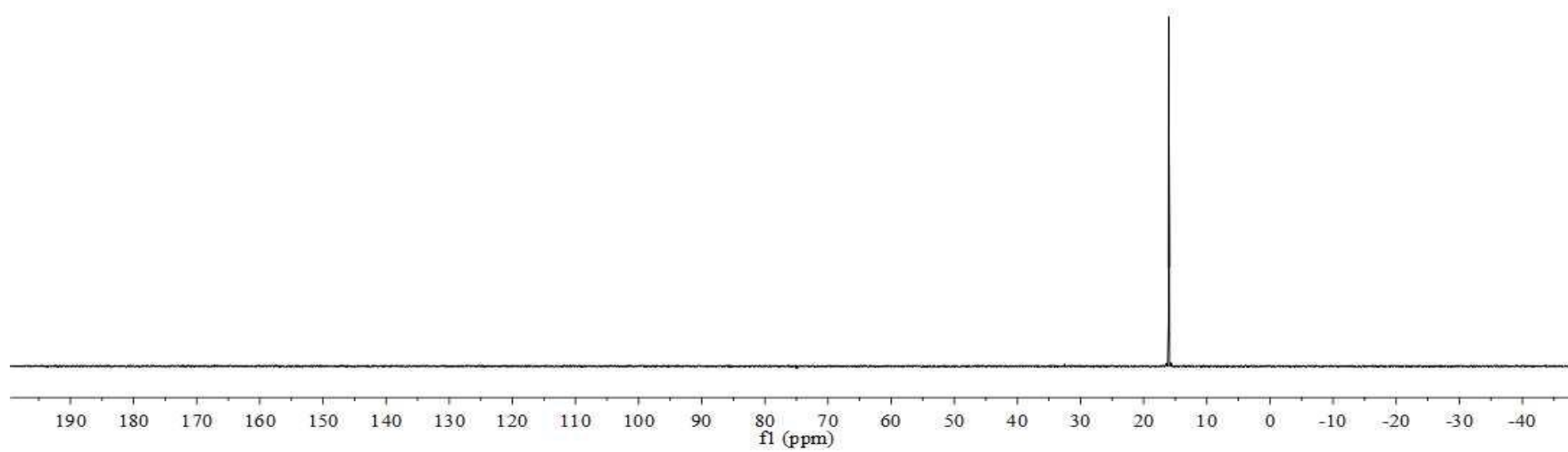
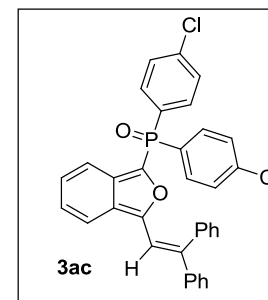


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of bis(4-chlorophenyl)(3-(2,2-diphenylvinyl) isobenzofuran-1-yl)phosphine oxide (**3ac**)



$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of bis(4-chlorophenyl)(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)phosphine oxide (**3ac**)

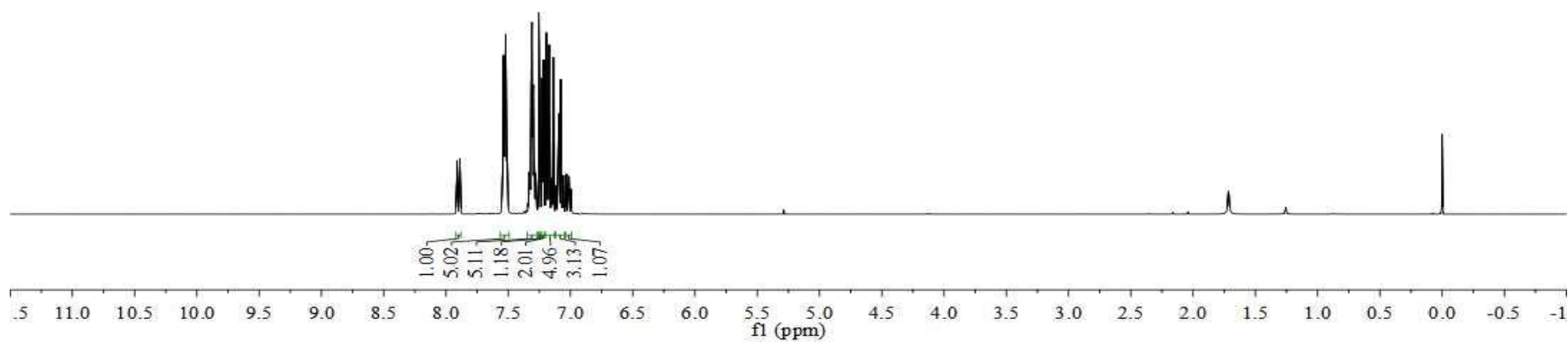
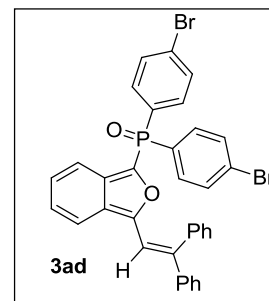
16.04



S134

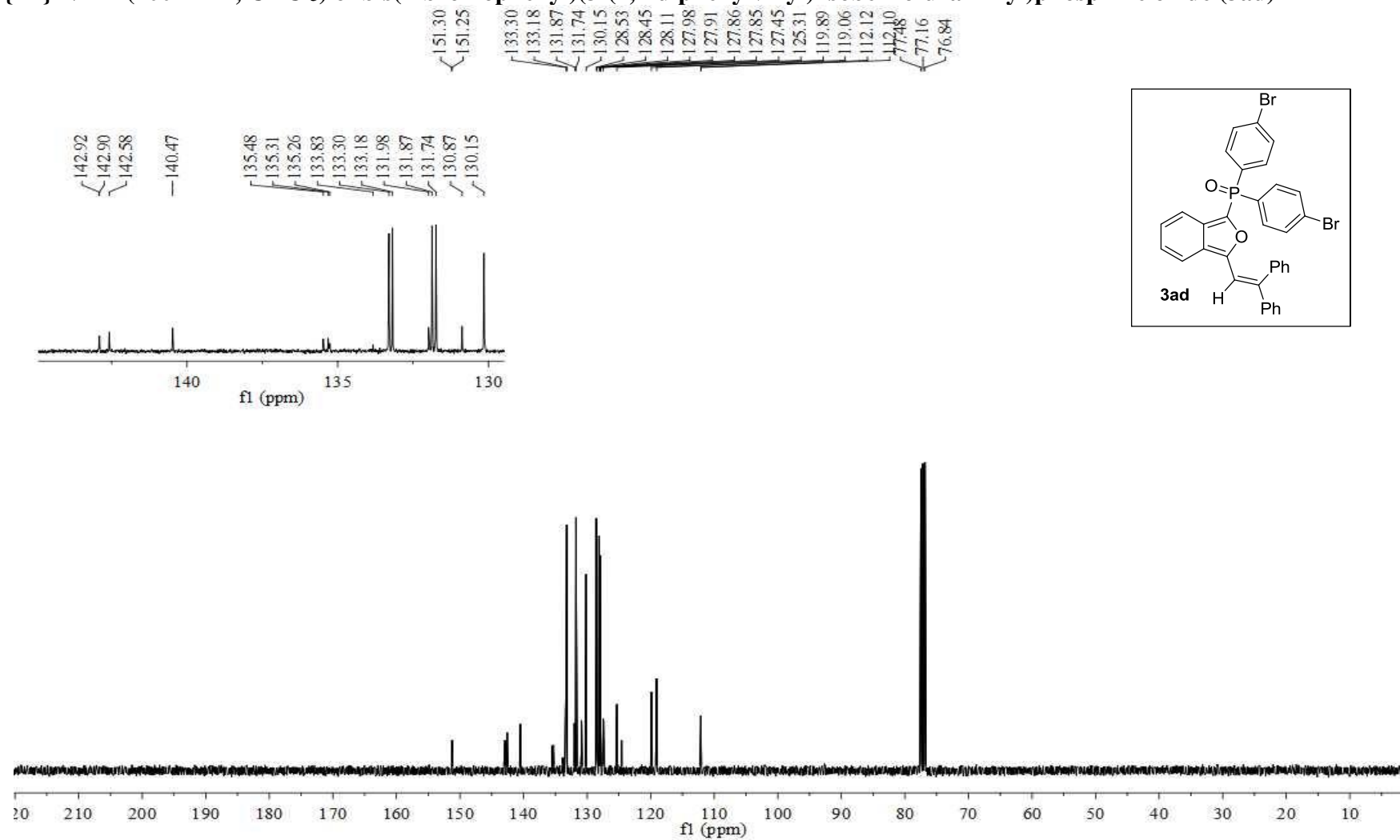
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of bis(4-bromophenyl)(3-(2,2-diphenylvinyl) isobenzofuran-1-yl)phosphine oxide (3ad)**

7.91 7.89 7.55 7.54 7.54 7.53 7.53 7.52 7.52 7.51 7.51 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.25 7.25 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.16 7.15 7.15 7.14 7.14 7.12 7.12 7.10 7.10 7.09 7.09 7.08 7.08 7.06 7.06 7.06 7.06 7.03 7.02 7.02 7.01 7.01 7.01 7.00 7.00



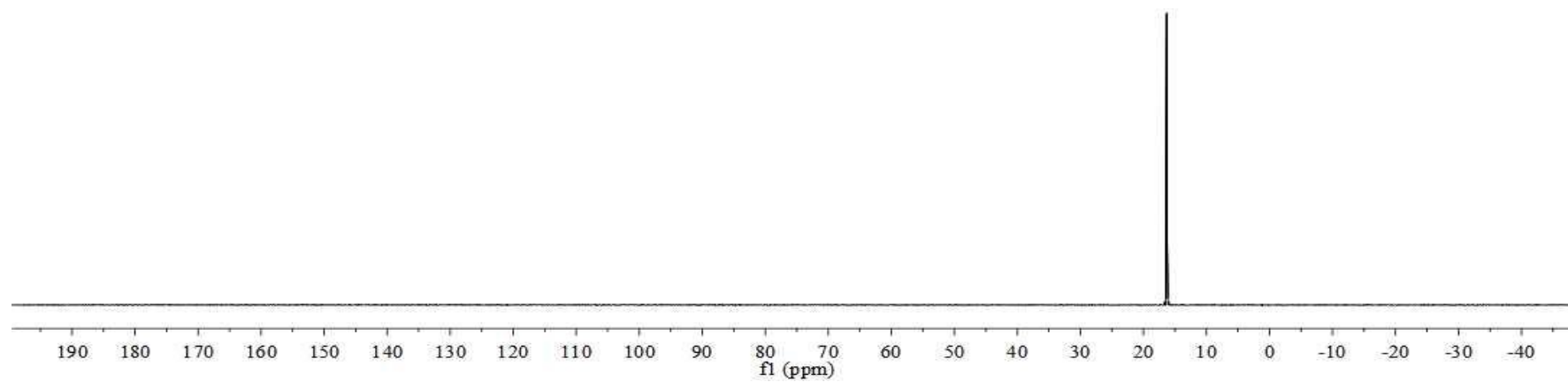
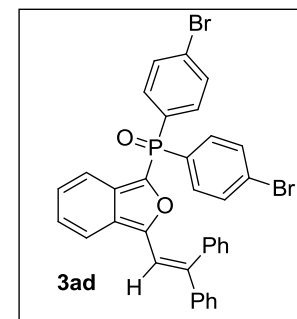
S135

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of bis(4-bromophenyl)(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)phosphine oxide (3ad)**



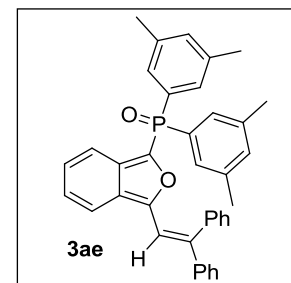
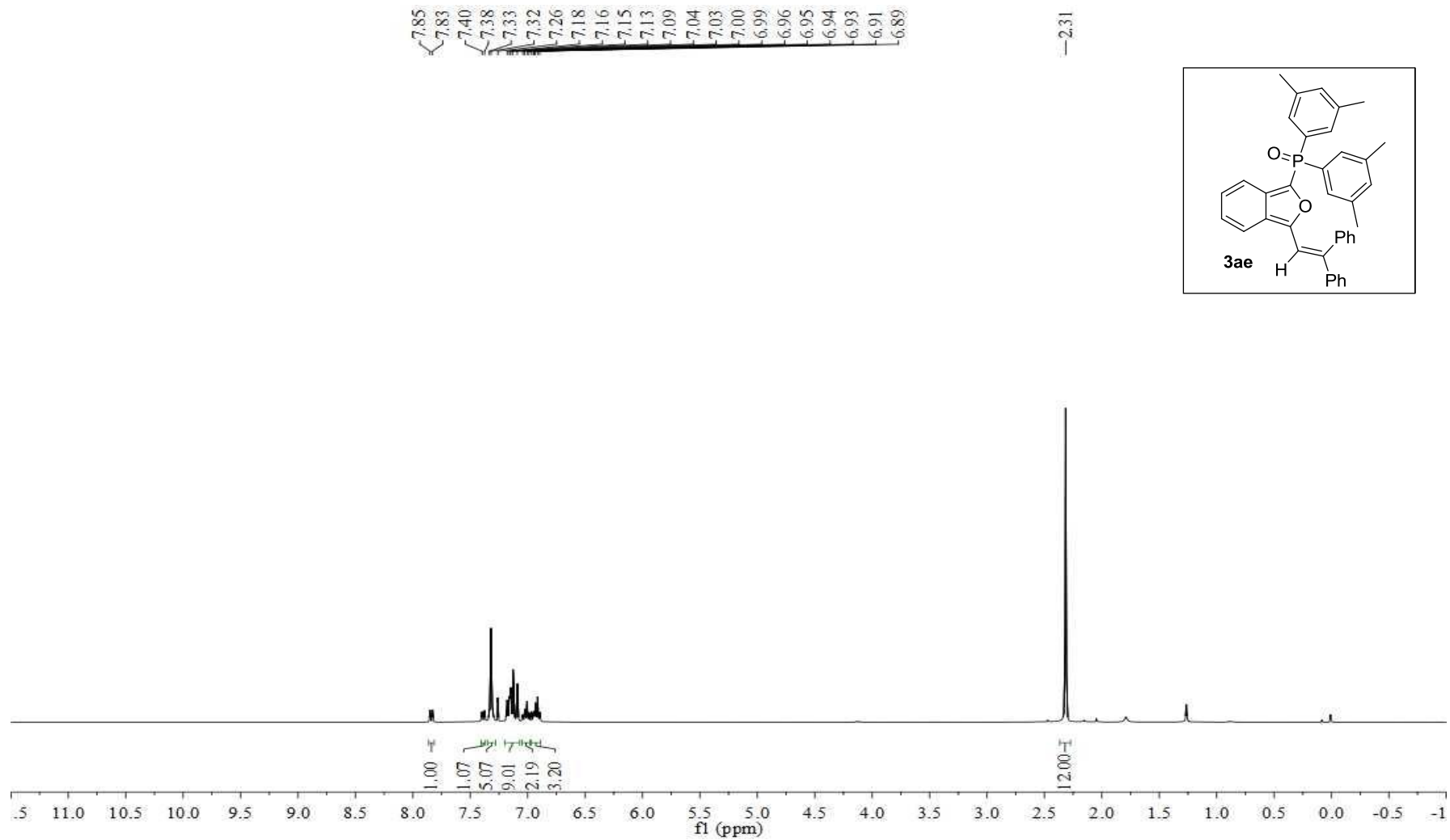
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of bis(4-bromophenyl)(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)phosphine oxide (3ad)

16.29

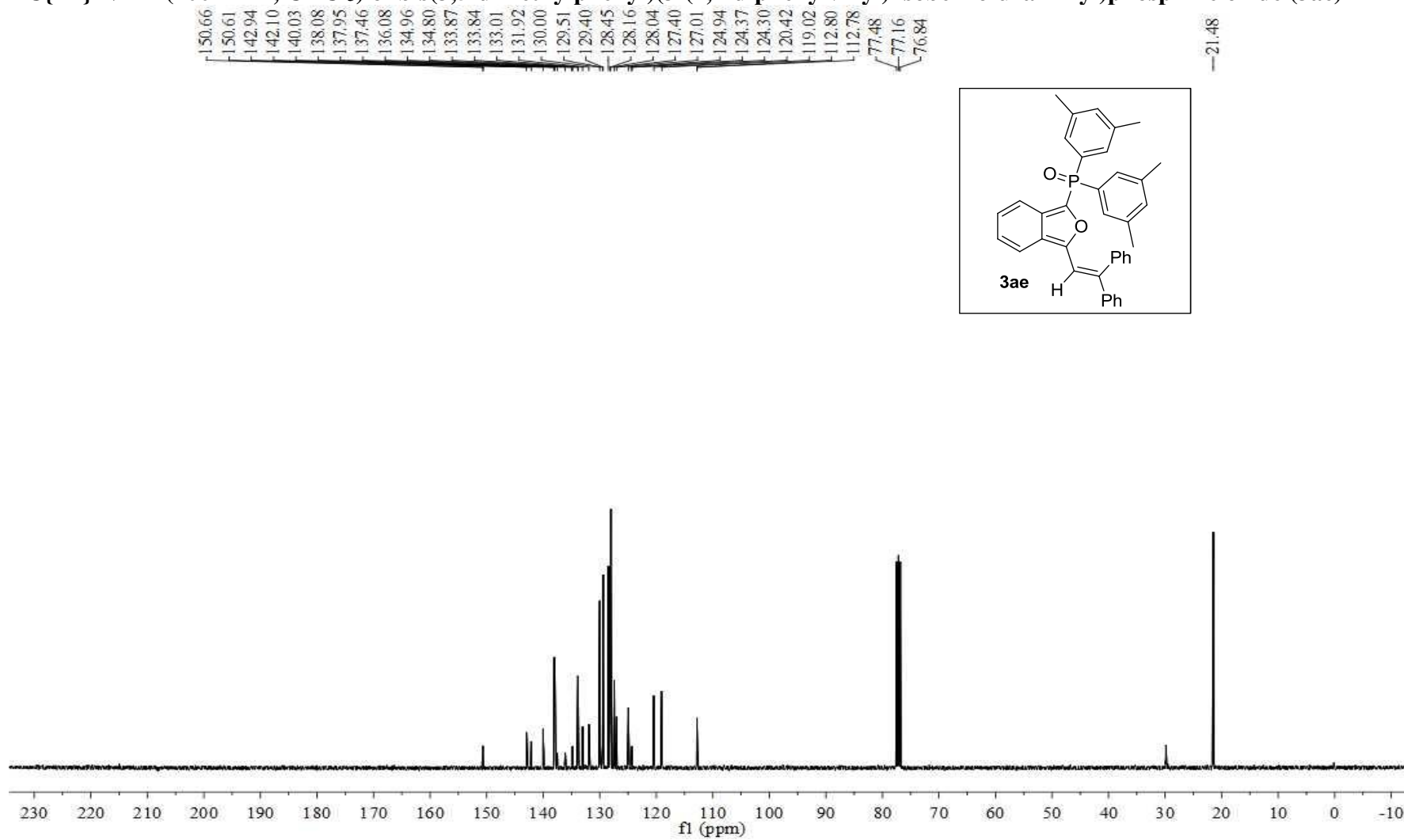


S137

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of bis(3,5-dimethylphenyl)(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)phosphine oxide (3ae)

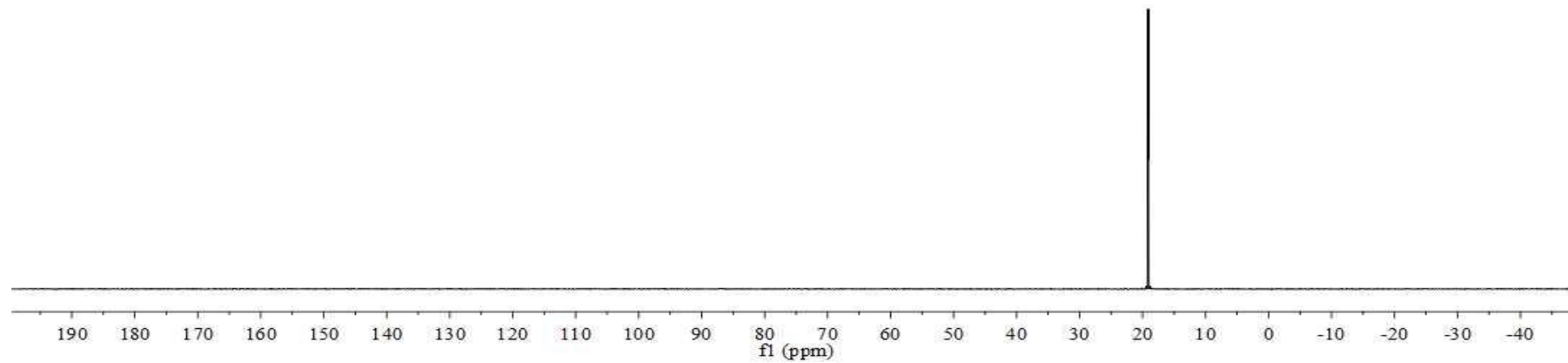
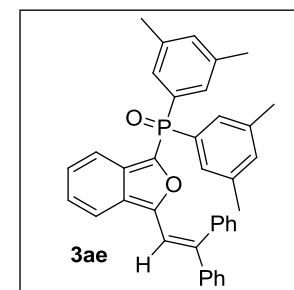


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of bis(3,5-dimethylphenyl)(3-(2,2-diphenylvinyl) isobenzofuran-1-yl)phosphine oxide (3ae)**



$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of bis(3,5-dimethylphenyl)(3-(2,2-diphenylvinyl)isobenzofuran-1-yl)phosphine oxide (3ae)

19.10

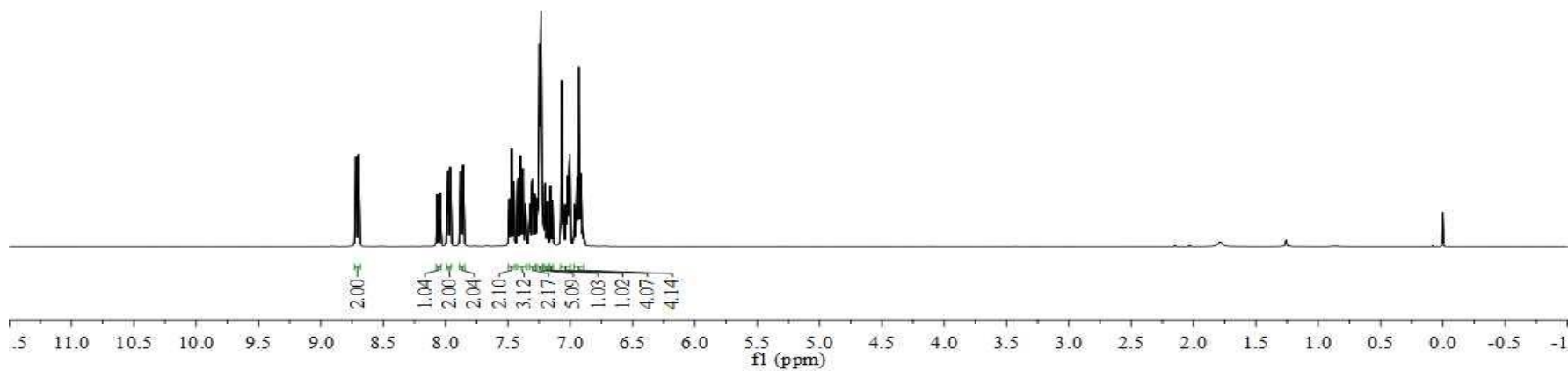
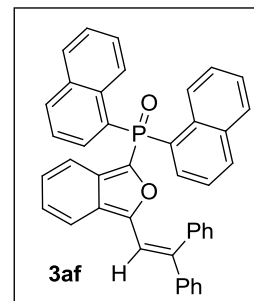


S140

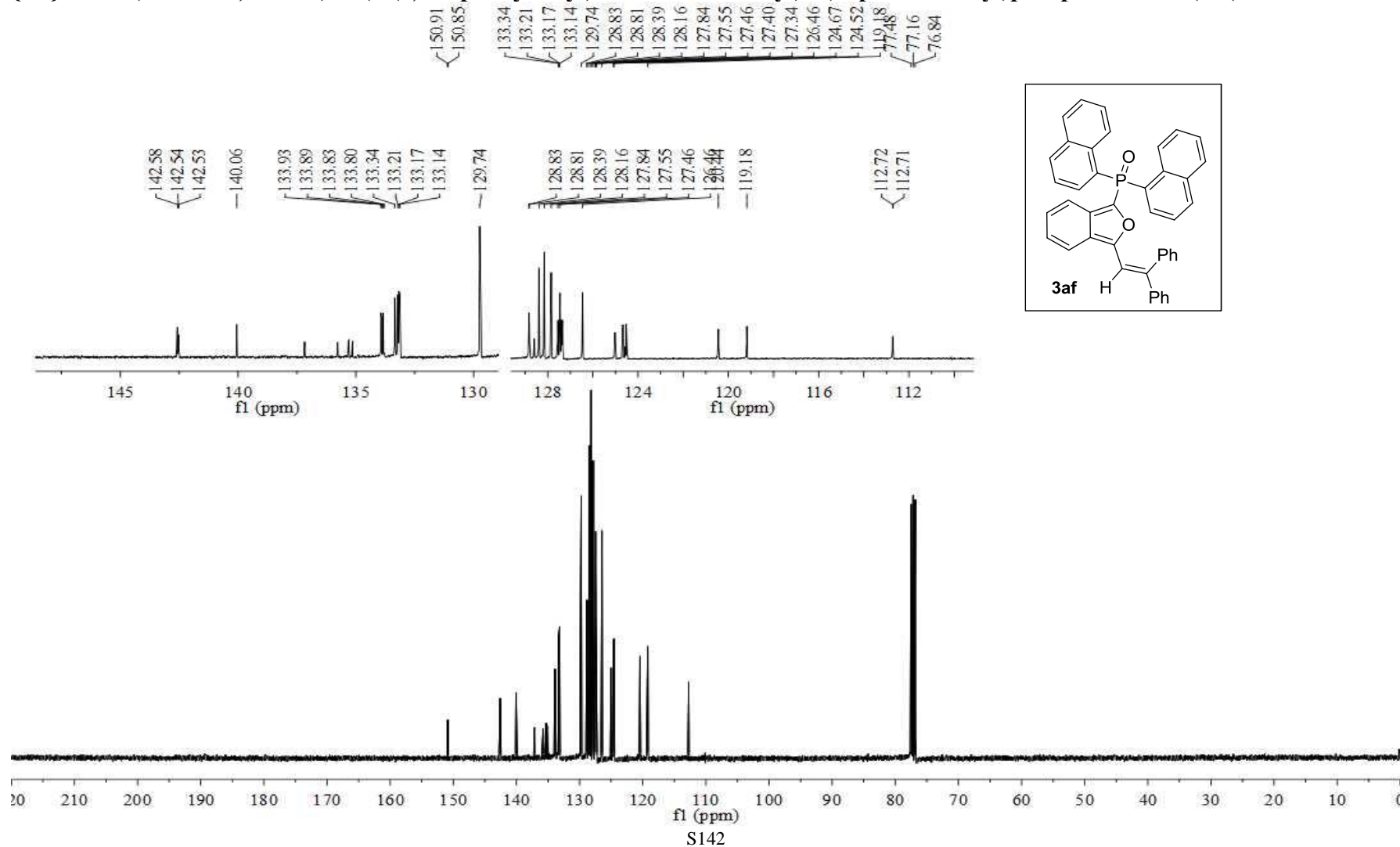


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)di(naphthalen-1-yl)phosphine oxide (3af)**

8.719, 8.698, 8.067, 8.044, 7.982, 7.962, 7.879, 7.859, 7.491, 7.488, 7.471, 7.453, 7.451, 7.422, 7.418, 7.404, 7.401, 7.397, 7.383, 7.380, 7.359, 7.327, 7.321, 7.309, 7.307, 7.303, 7.289, 7.282, 7.265, 7.261, 7.252, 7.247, 7.242, 7.237, 7.233, 7.227, 7.217, 7.211, 7.203, 7.200, 7.185, 7.183, 7.160, 7.158, 7.143, 7.140, 7.067, 7.057, 7.051, 7.035, 7.027, 7.023, 7.014, 7.008, 7.003, 6.967, 6.946, 6.936, 6.931, 6.922, 6.913, 0.000

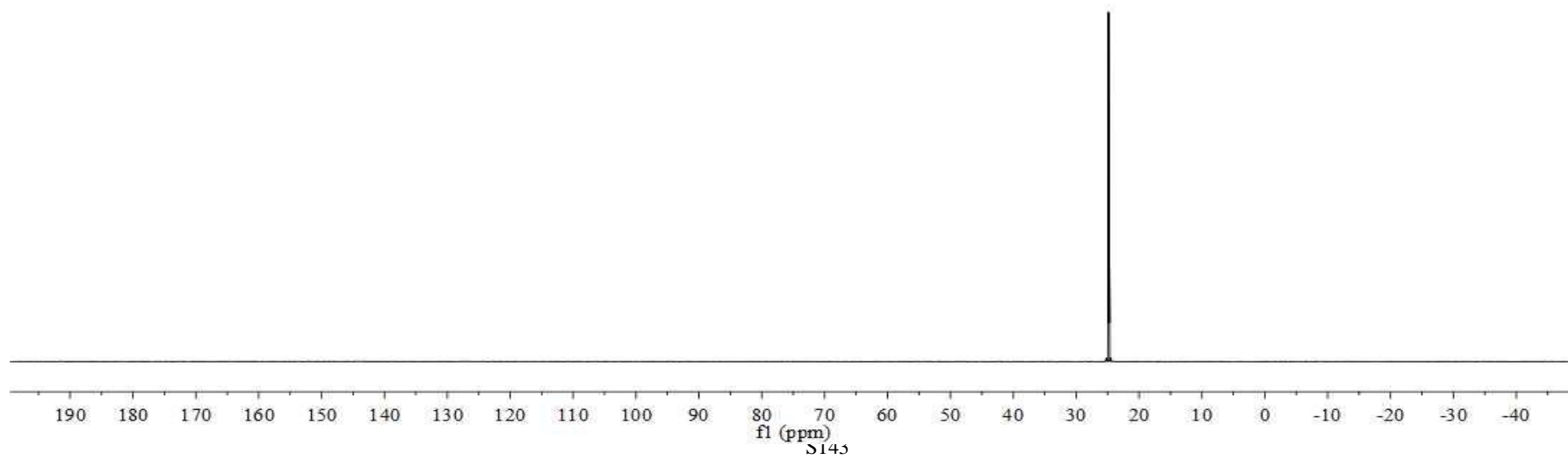
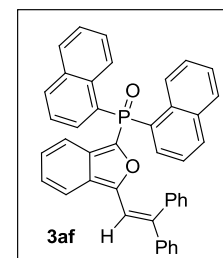


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)di(naphthalen-1-yl)phosphine oxide (3af)



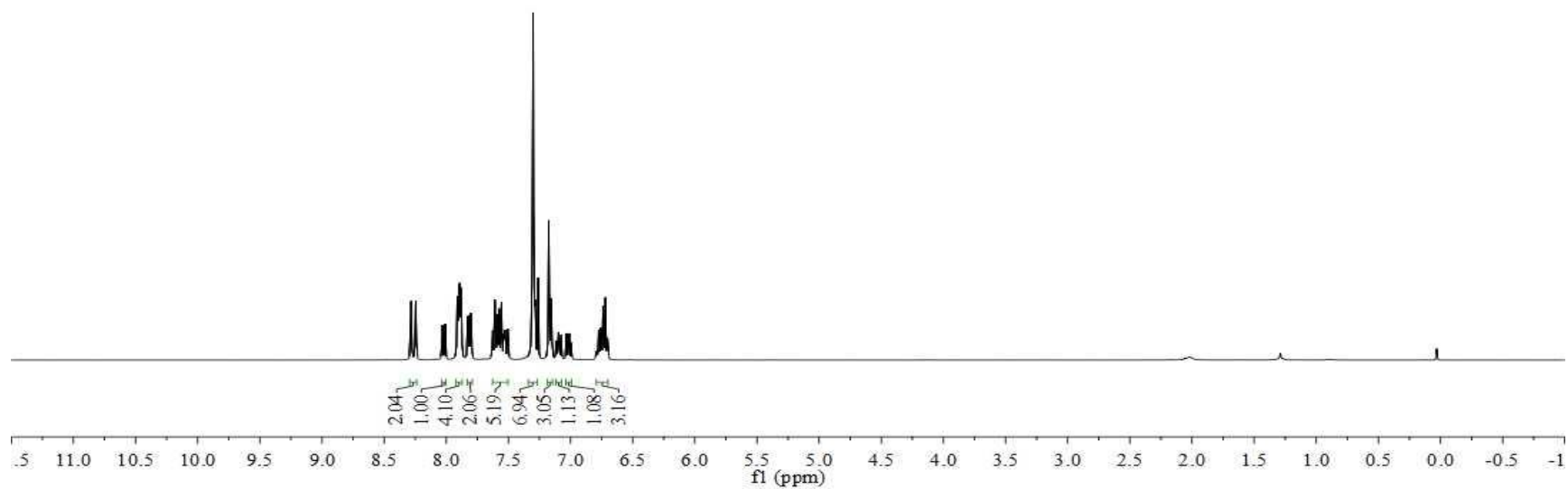
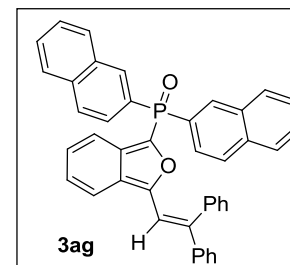
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)di(naphthalen-1-yl)phosphine oxide (3af)

-24.87



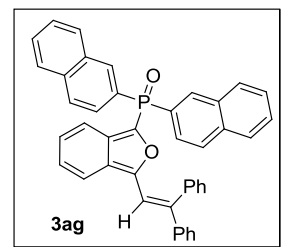
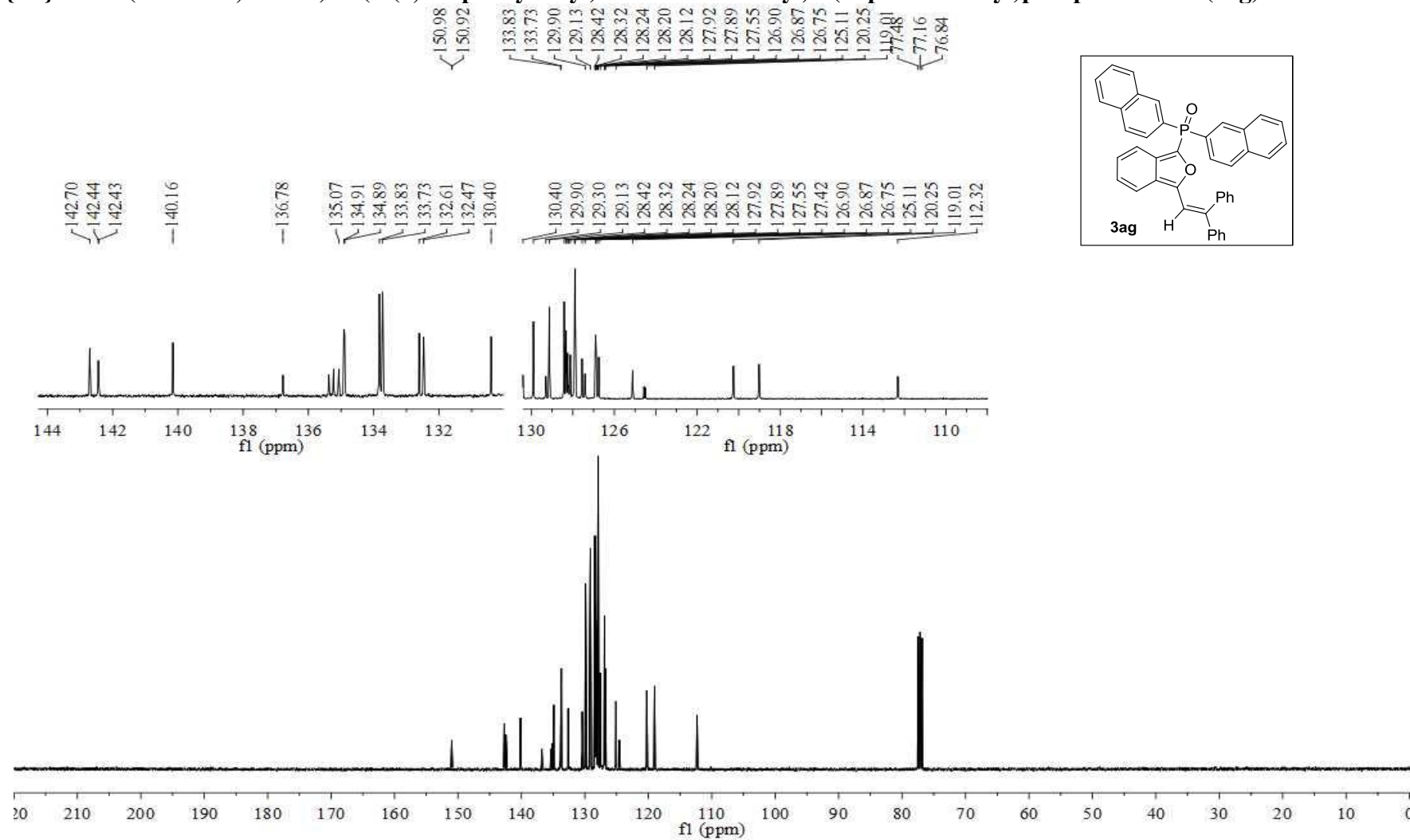
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)di(naphthalen-2-yl)phosphine oxide (3ag)**

8.282, 8.246, 8.030, 8.008, 7.911, 7.899, 7.892, 7.879, 7.827, 7.820, 7.806, 7.799, 7.626, 7.609, 7.589, 7.575, 7.556, 7.537, 7.528, 7.505, 7.301, 7.291, 7.285, 7.260, 7.175, 7.156, 7.153, 7.113, 7.097, 7.075, 7.032, 7.015, 7.010, 6.994, 6.792, 6.781, 6.774, 6.768, 6.756, 6.738, 6.719, 6.702



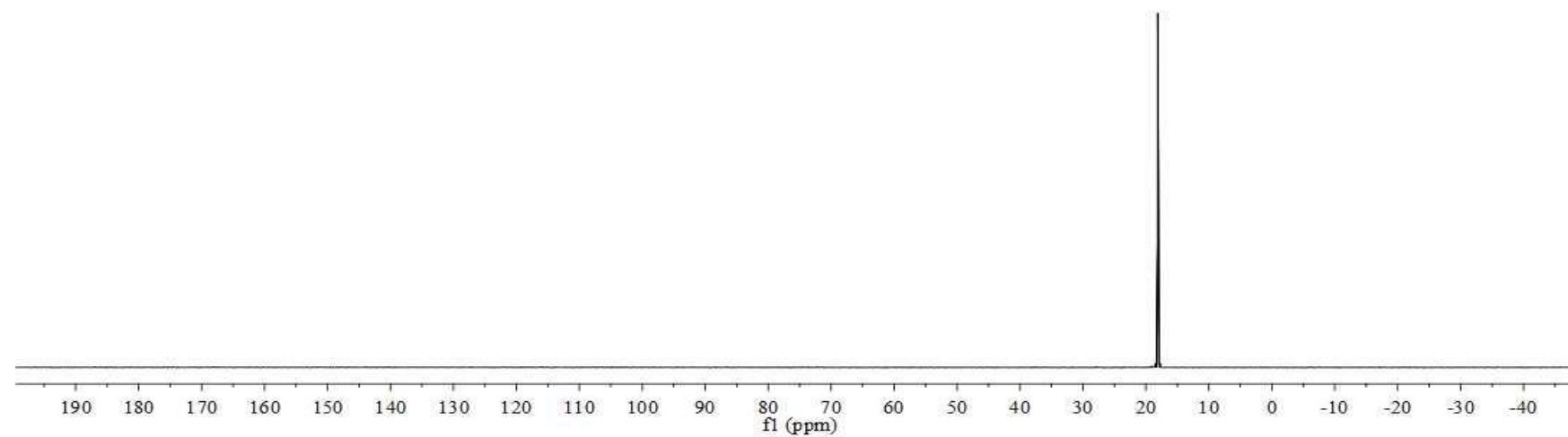
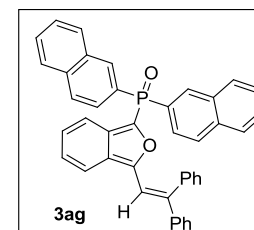
S144

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)di(naphthalen-2-yl)phosphine oxide (3ag)



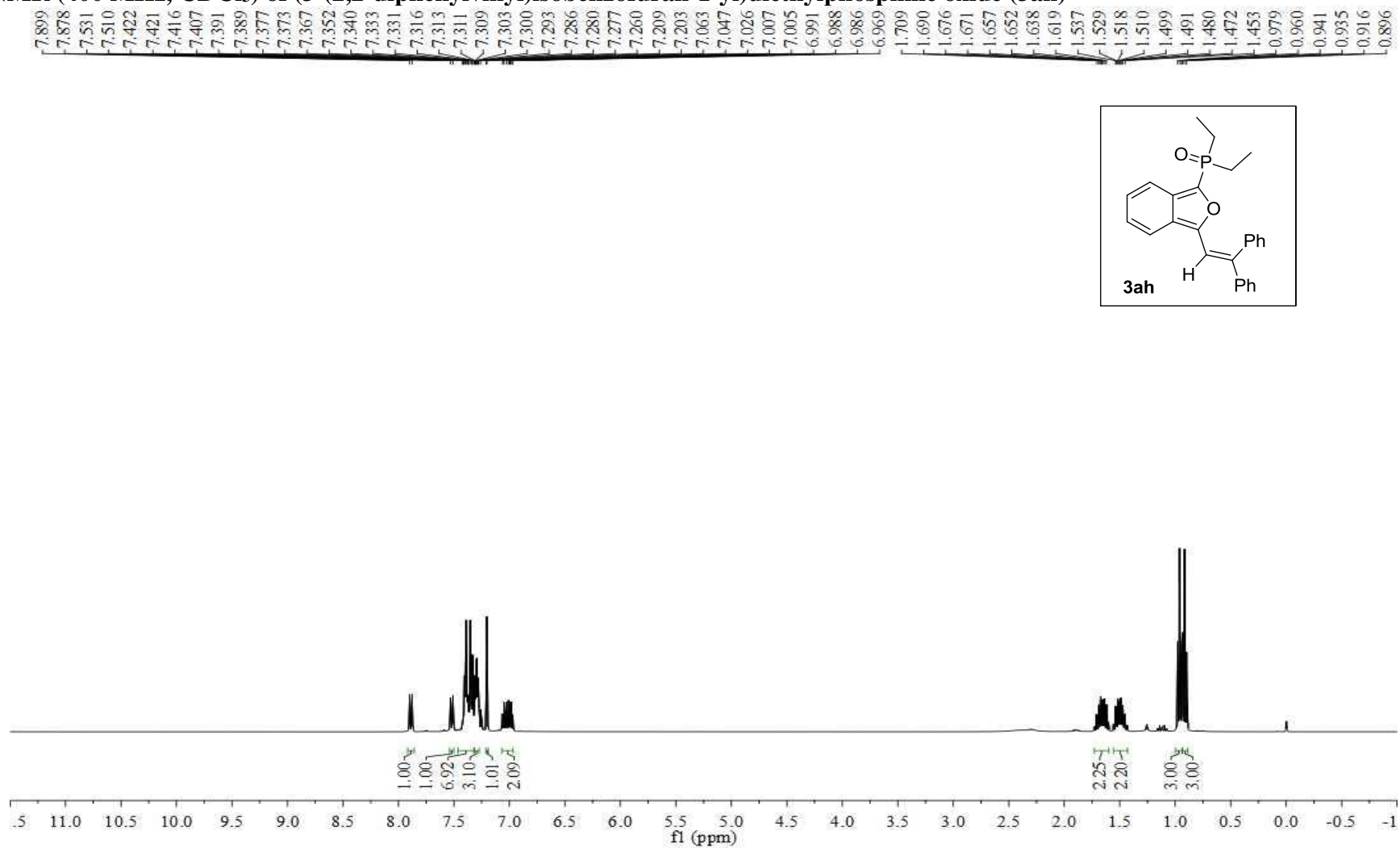
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)di(naphthalen-2-yl)phosphine oxide (3ag)

-18.11



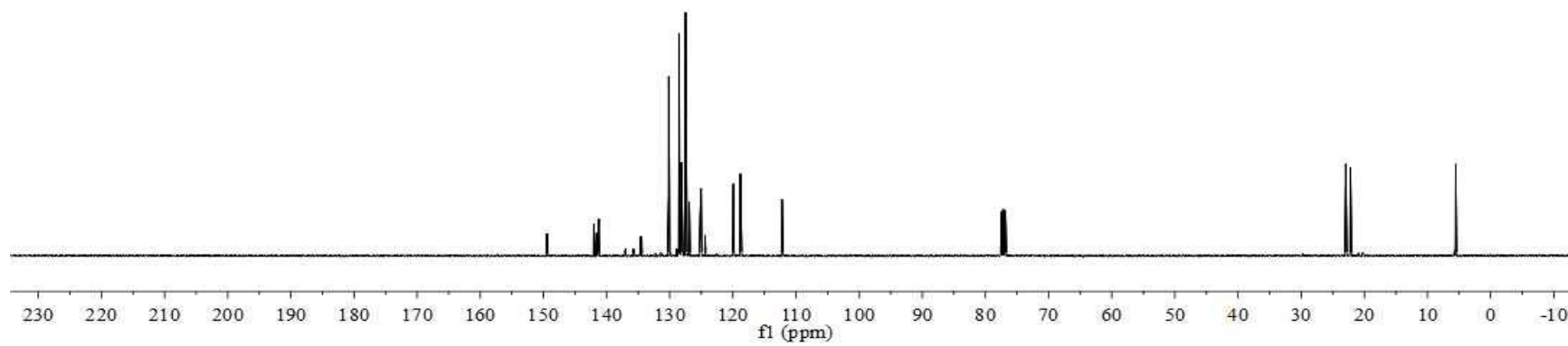
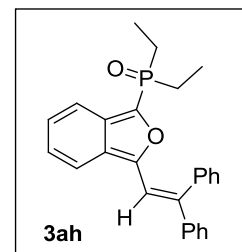
S146

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diethylphosphine oxide (3ah)**



$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diethylphosphine oxide (3ah)

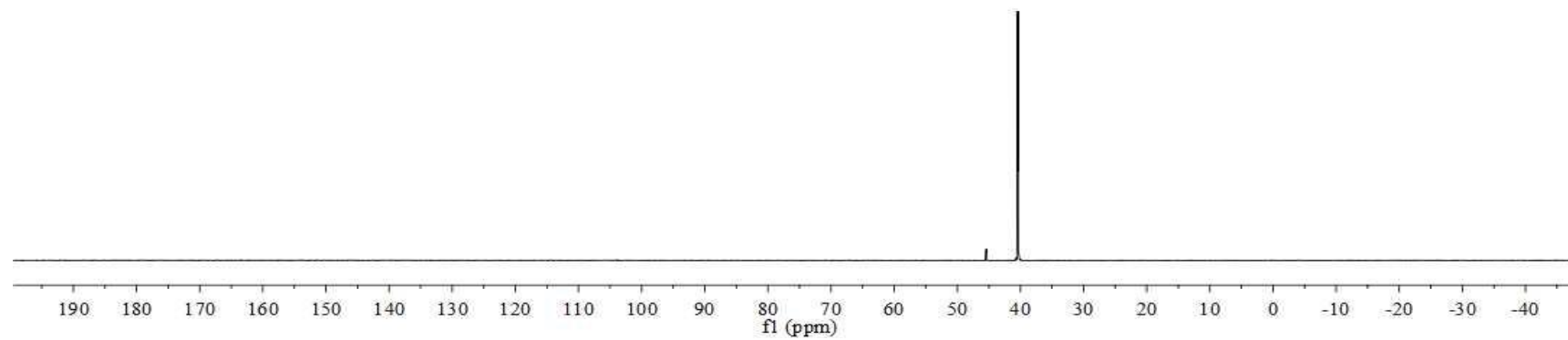
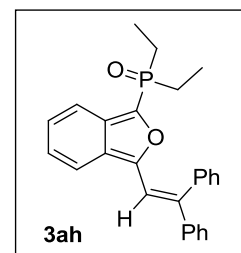
149.47, 149.42, 142.03, 141.60, 141.59, 141.24, 134.58, 134.44, 130.15, 128.51, 128.36, 128.16, 127.52, 126.92, 126.91, 125.05, 124.41, 124.35, 119.90, 118.82, 112.22, 112.21, 77.48, 77.16, 76.84, 22.93, 22.21, 5.54, 5.49





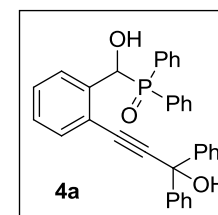
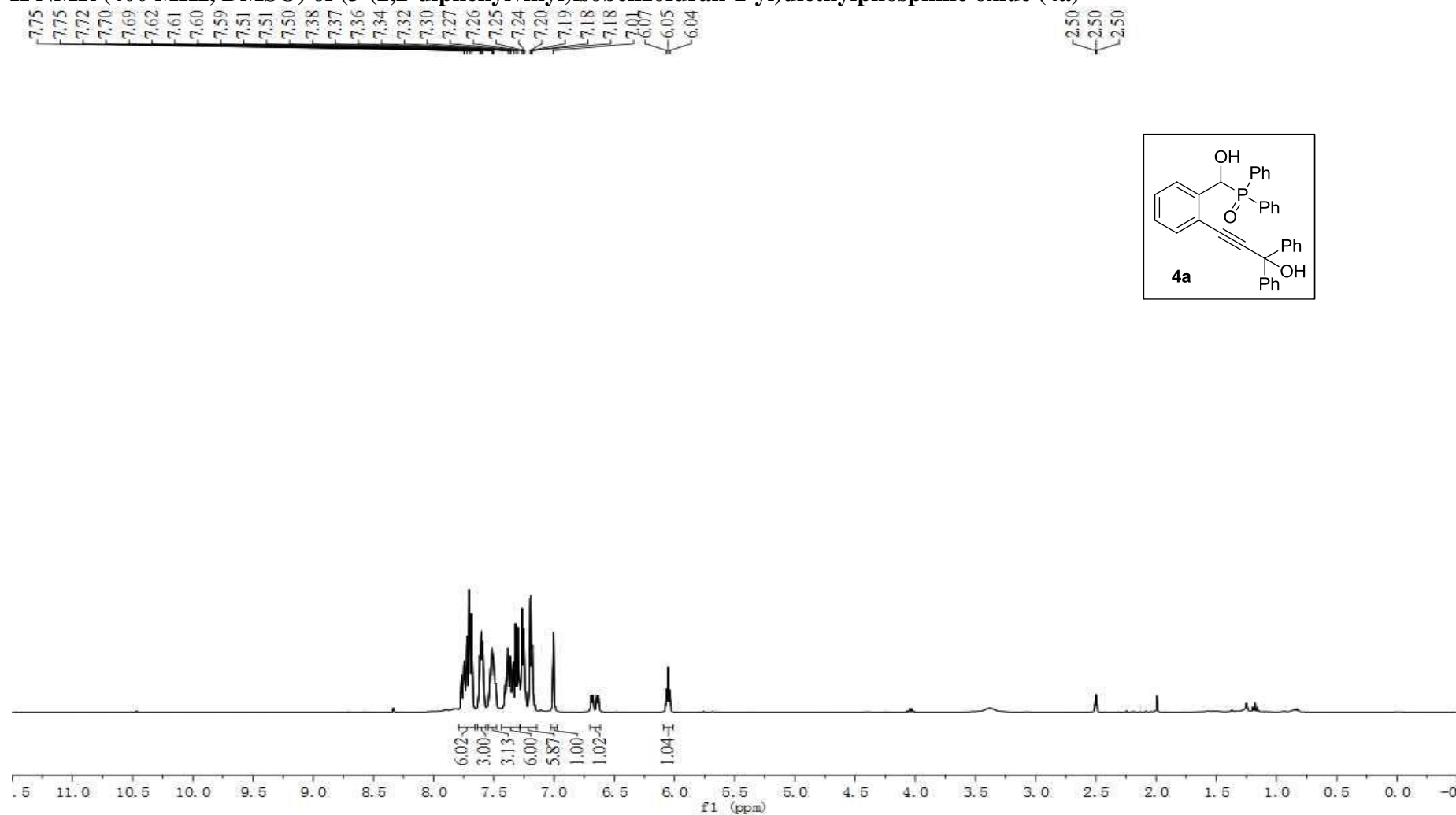
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diethylphosphine oxide (3ah)

40.39



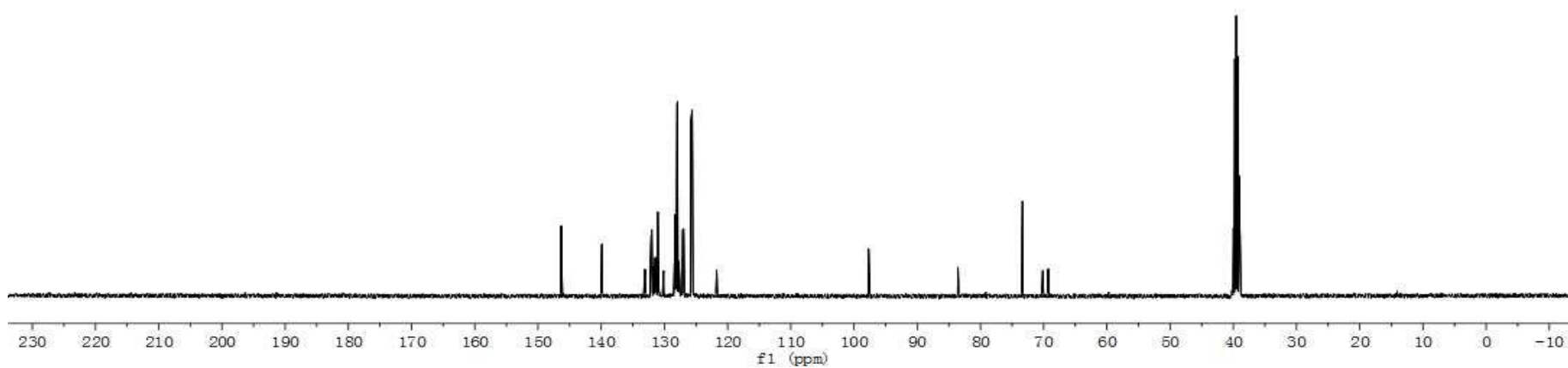
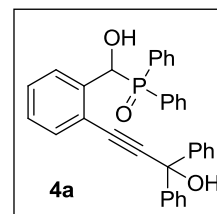
S149

**<sup>1</sup>H NMR (400 MHz, DMSO) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diethylphosphine oxide (4a)**



$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, DMSO) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diethylphosphine oxide (4a)

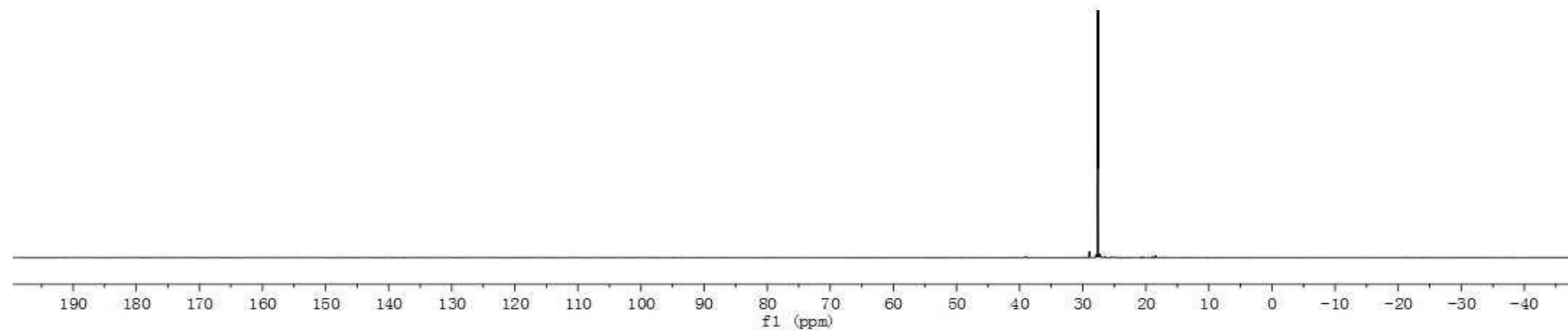
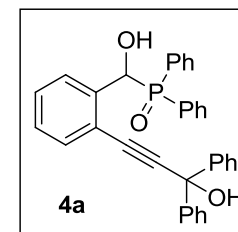
146.39, 146.33, 139.87, 133.09, 132.16, 132.08, 132.00, 131.69, 131.54, 131.43, 131.06, 130.98, 130.15, 128.43, 128.39, 128.30, 128.19, 128.14, 128.03, 127.98, 127.94, 127.72, 127.10, 126.96, 125.82, 125.61, 121.79, 121.73, 97.71, 83.55, 73.33, 70.13, 69.26, 40.15, 39.94, 39.73, 39.52, 39.31, 39.10, 38.89



S151

$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz, DMSO) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diethylphosphine oxide (4a)

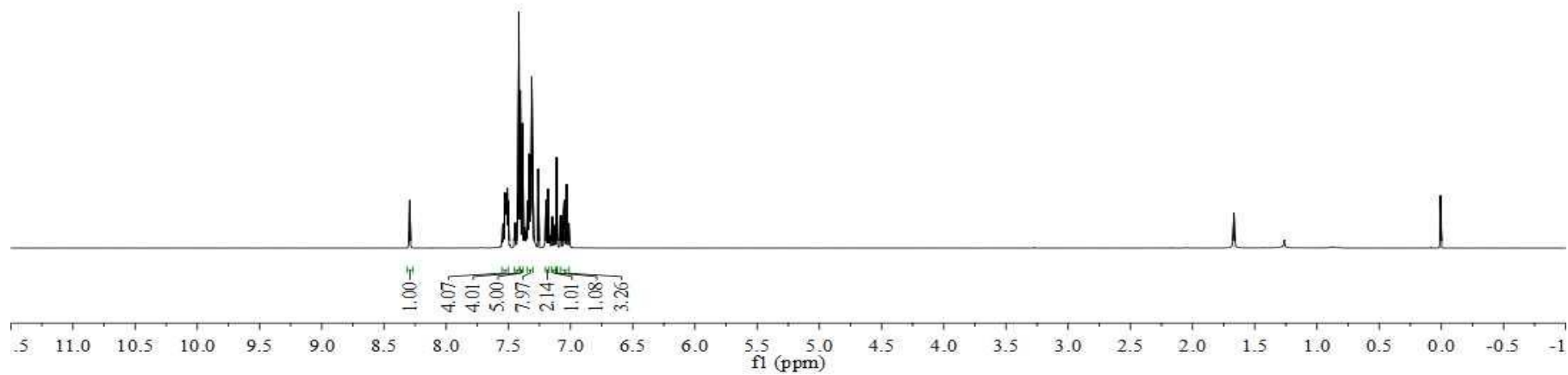
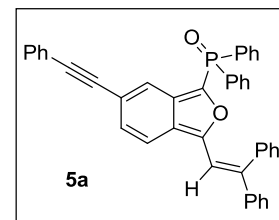
-27.564



S152

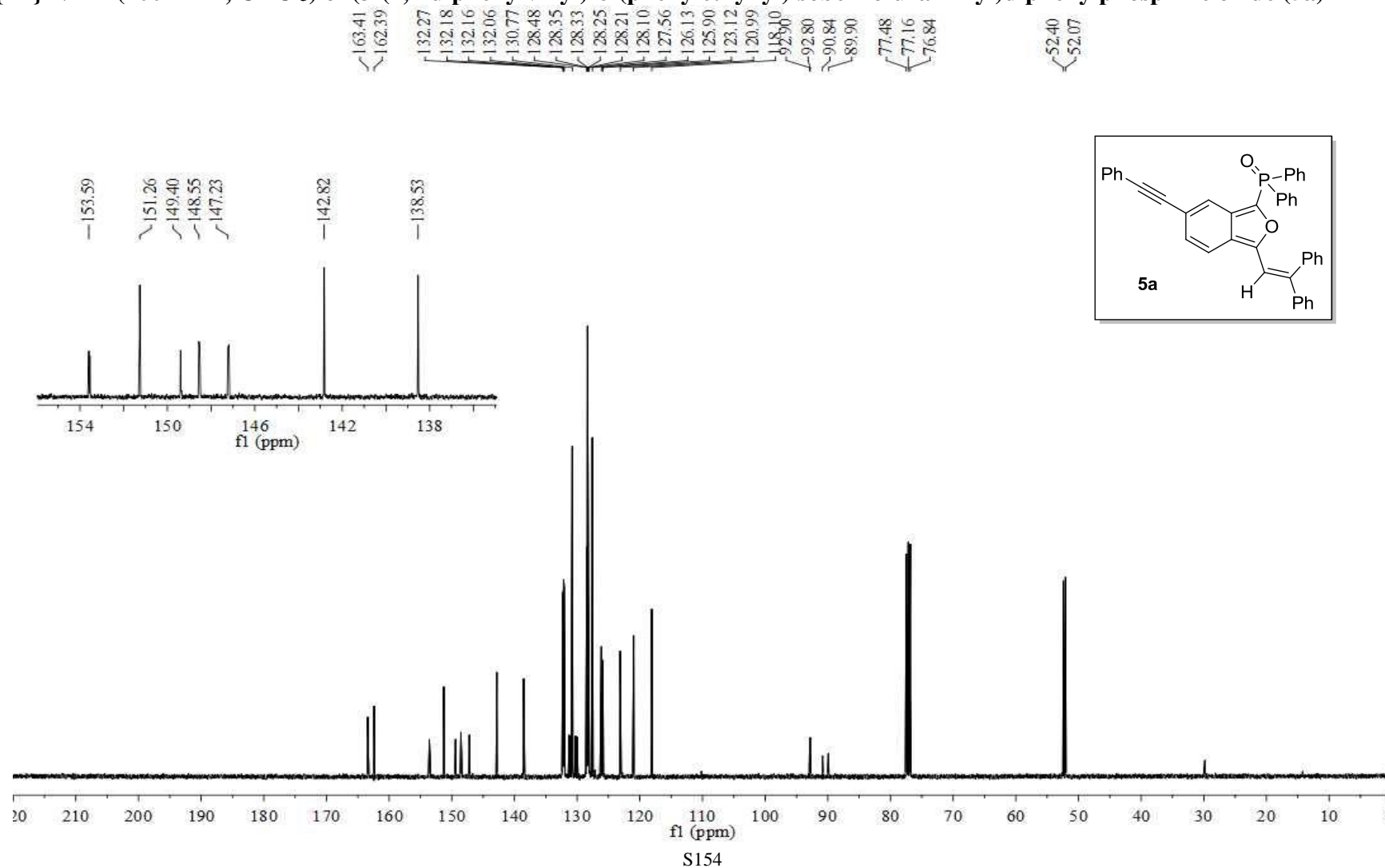
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-6-(phenylethynyl)isobenzofuran-1-yl)diphenylphosphine oxide (5a)**

8.29, 7.54, 7.54, 7.53, 7.53, 7.52, 7.52, 7.52, 7.51, 7.51, 7.50, 7.45, 7.45, 7.44, 7.43, 7.42, 7.42, 7.42, 7.41, 7.40, 7.39, 7.39, 7.38, 7.37, 7.37, 7.36, 7.35, 7.35, 7.34, 7.34, 7.33, 7.33, 7.32, 7.32, 7.31, 7.31, 7.30, 7.29, 7.26, 7.20, 7.19, 7.18, 7.18, 7.17, 7.15, 7.14, 7.13, 7.13, 7.12, 7.11, 7.08, 7.08, 7.06, 7.05, 7.05, 7.03, 7.03, 7.02, 7.01, 1.67, 0.01



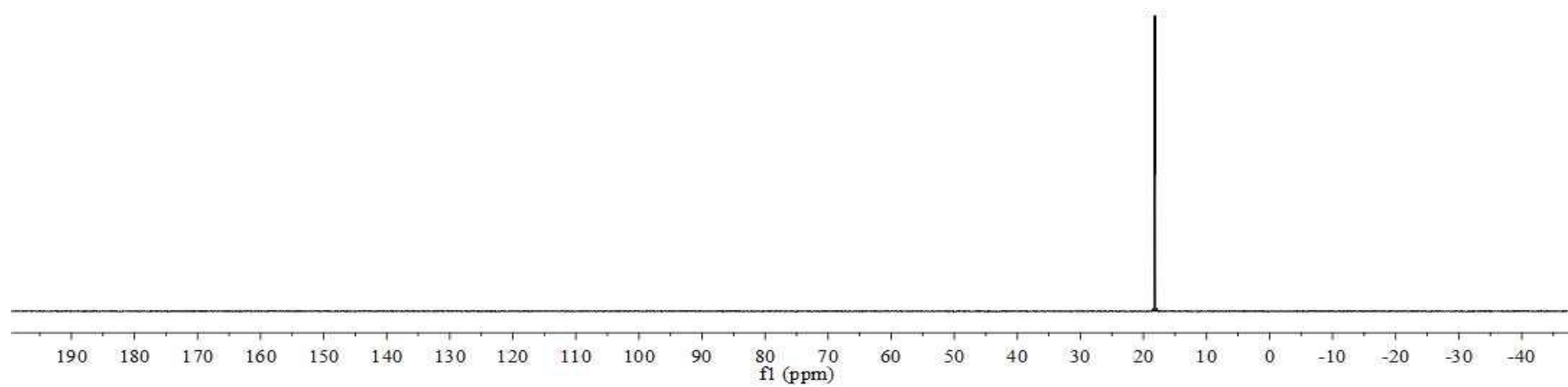
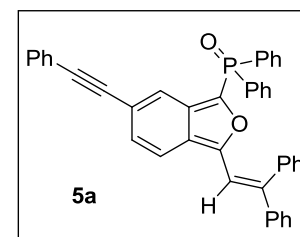
S153

**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of 3-(2,2-diphenylvinyl)-6-(phenylethynyl)isobenzofuran-1-yl)diphenylphosphine oxide (5a)**



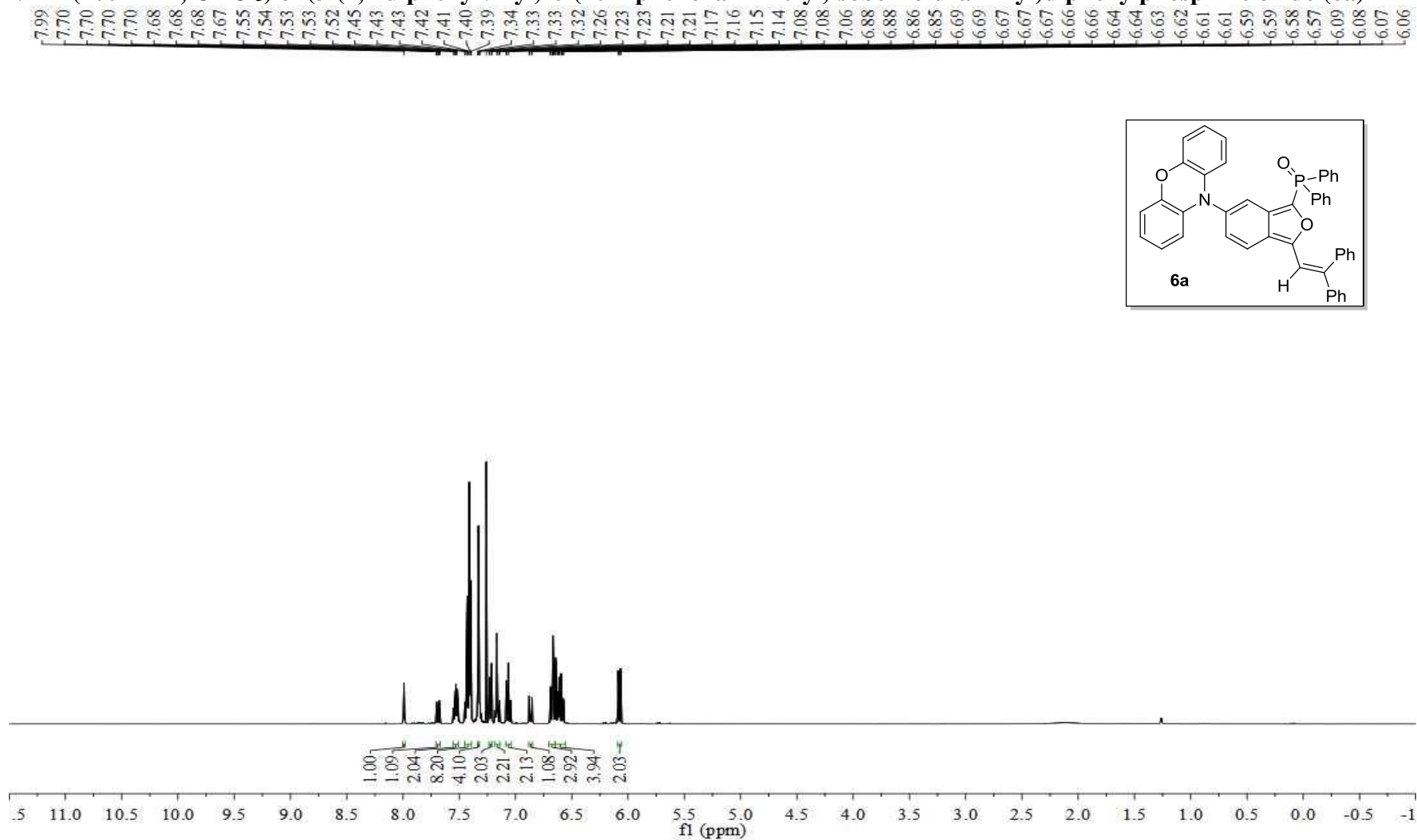
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-6-(phenylethynyl)isobenzofuran-1-yl)diphenylphosphine oxide (5a)

181.8



S155

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)-6-(10H-phenoxazin-10-yl)isobenzofuran-1-yl)diphenylphosphine oxide (6a)**

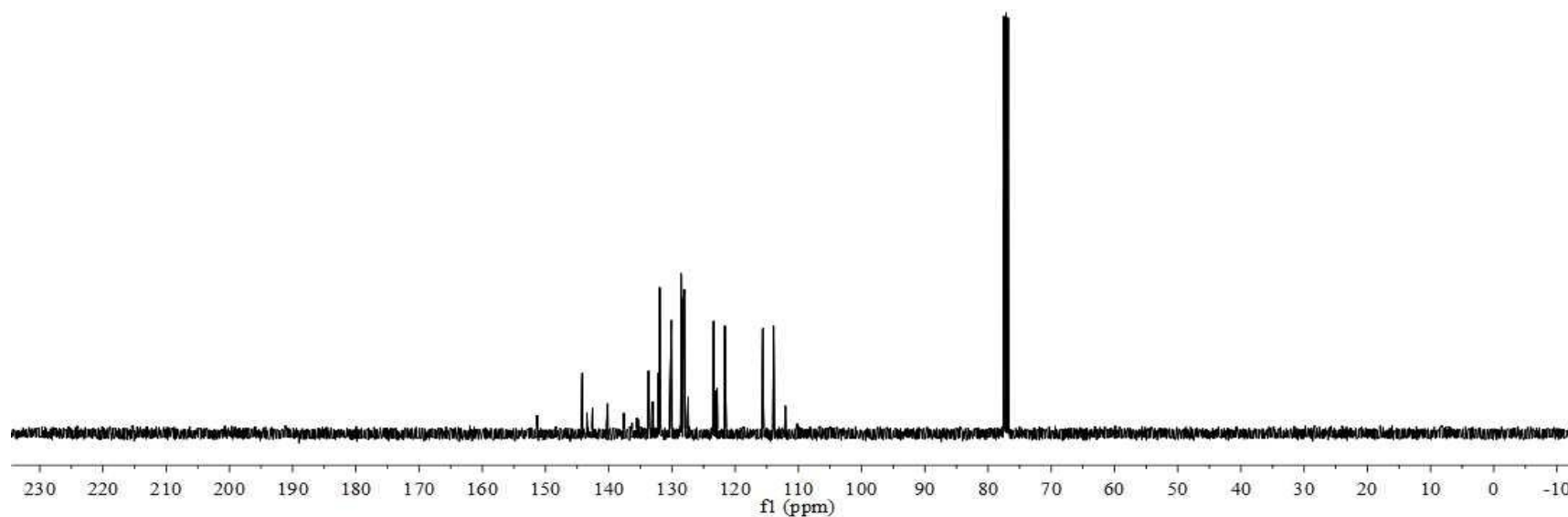
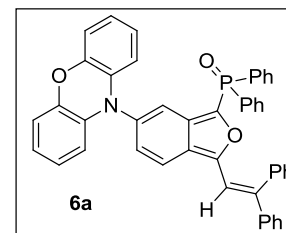


S156



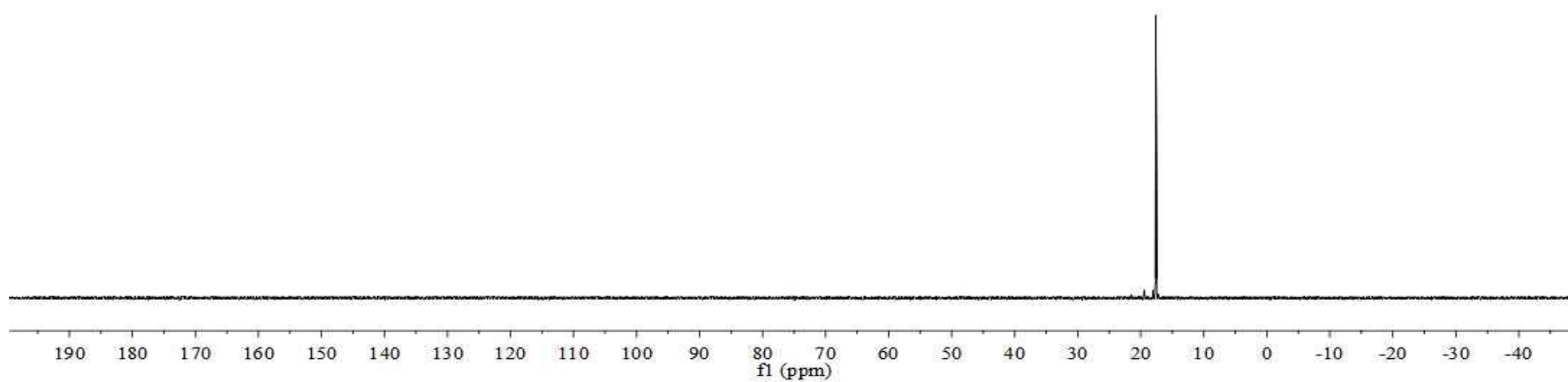
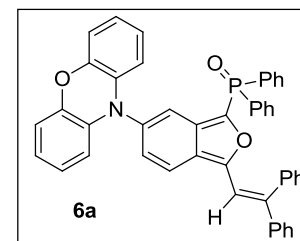
**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-6-(10H-phenoxazin-10-yl)isobenzofuran-1-yl)diphenylphosphine oxide (6a)**

151.34  
151.29  
146.07  
144.18  
143.44  
142.55  
140.20  
137.62  
135.53  
135.37  
133.71  
133.03  
132.16  
132.13  
131.94  
131.84  
130.12  
128.57  
128.55  
128.42  
128.24  
128.01  
127.44  
123.40  
123.28  
123.11  
122.85  
121.64  
115.60  
114.40  
113.92  
112.06  
77.48  
77.16  
76.84



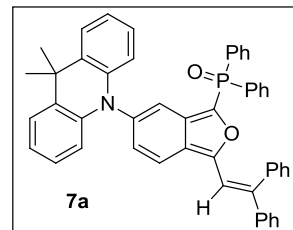
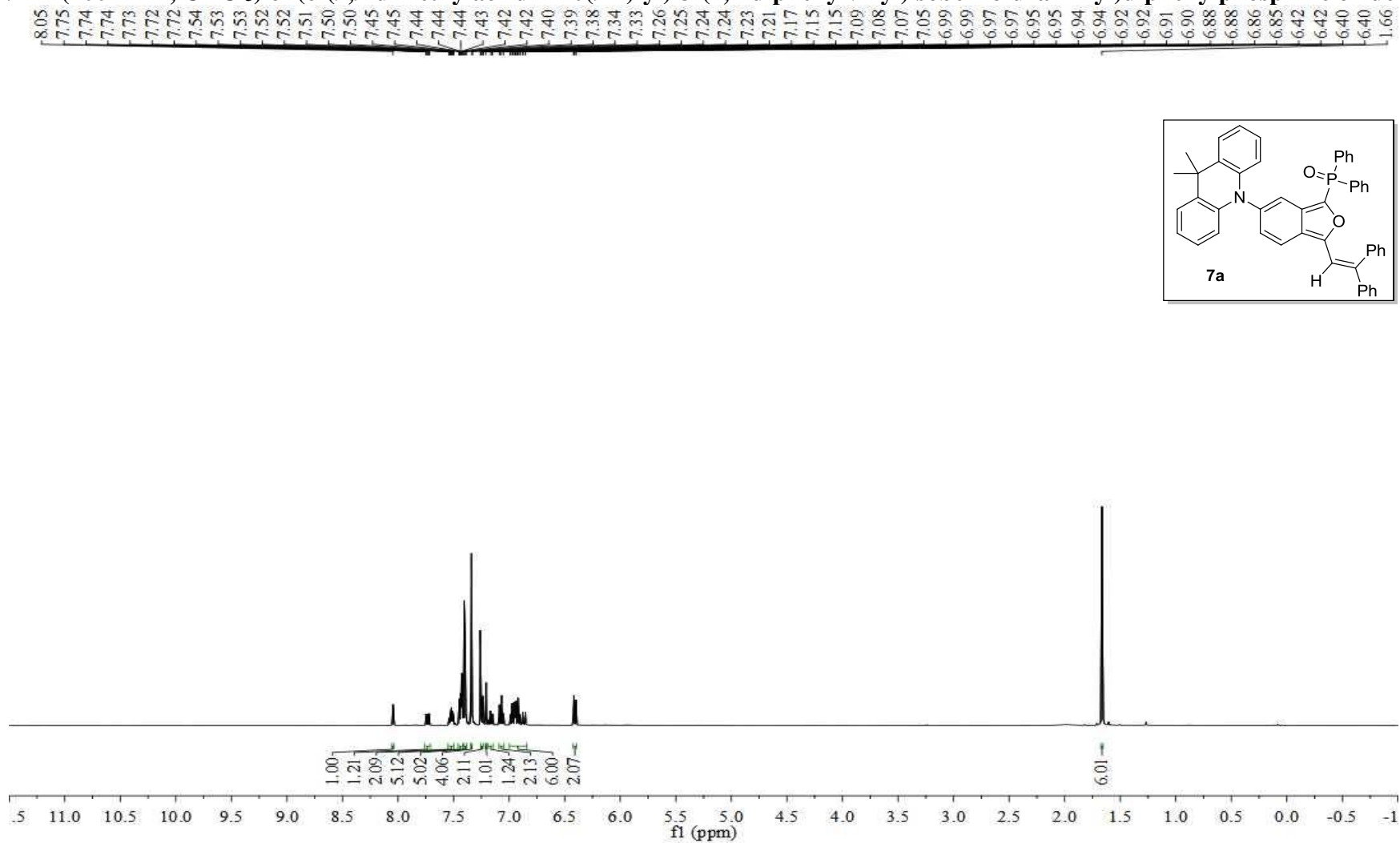
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (3-(2,2-diphenylvinyl)-6-(10H-phenoxazin-10-yl)isobenzofuran-1-yl)diphenylphosphine oxide (6a)

17.62

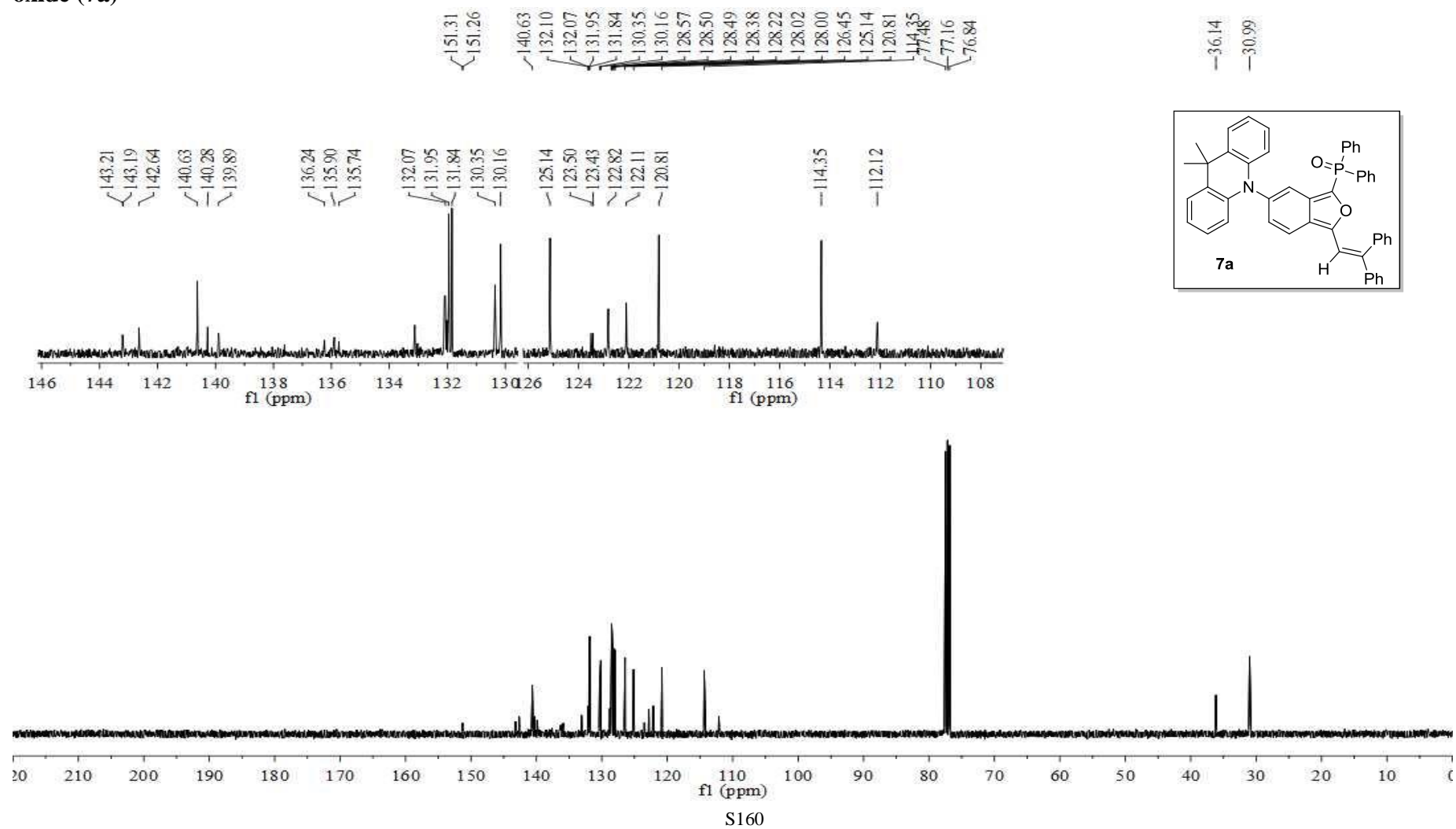


S158

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (6-(9,9-dimethylacridin-10(9H)-yl)-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (7a)**

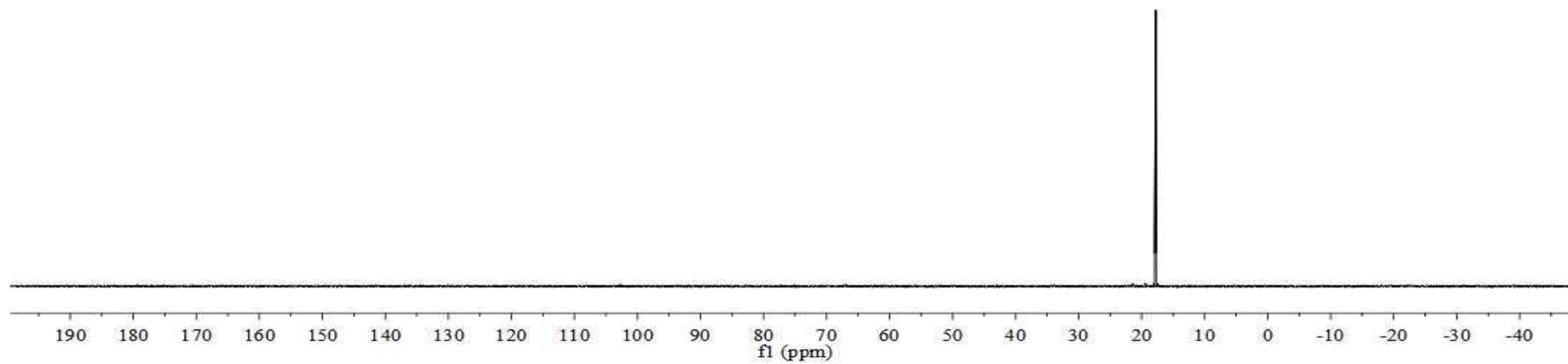
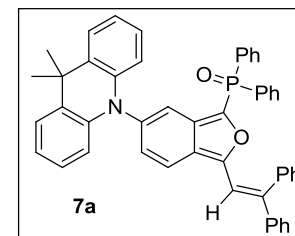


**$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (6-(9,9-dimethylacridin-10(9H)-yl)-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (7a)**



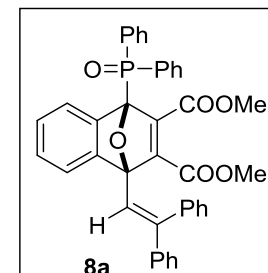
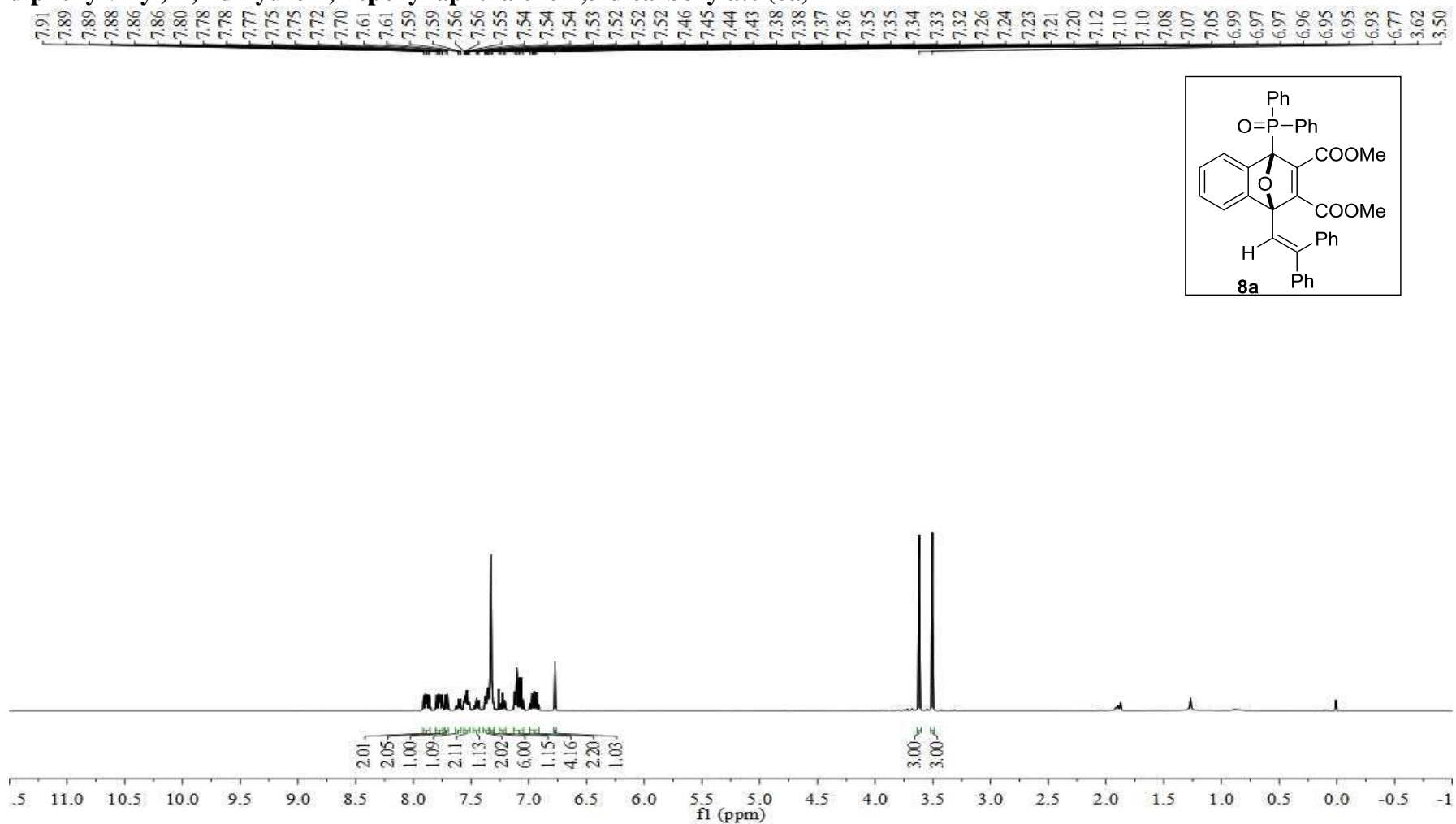
$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of (6-(9,9-dimethylacridin-10(9H)-yl)-3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphine oxide (7a)

—17.78

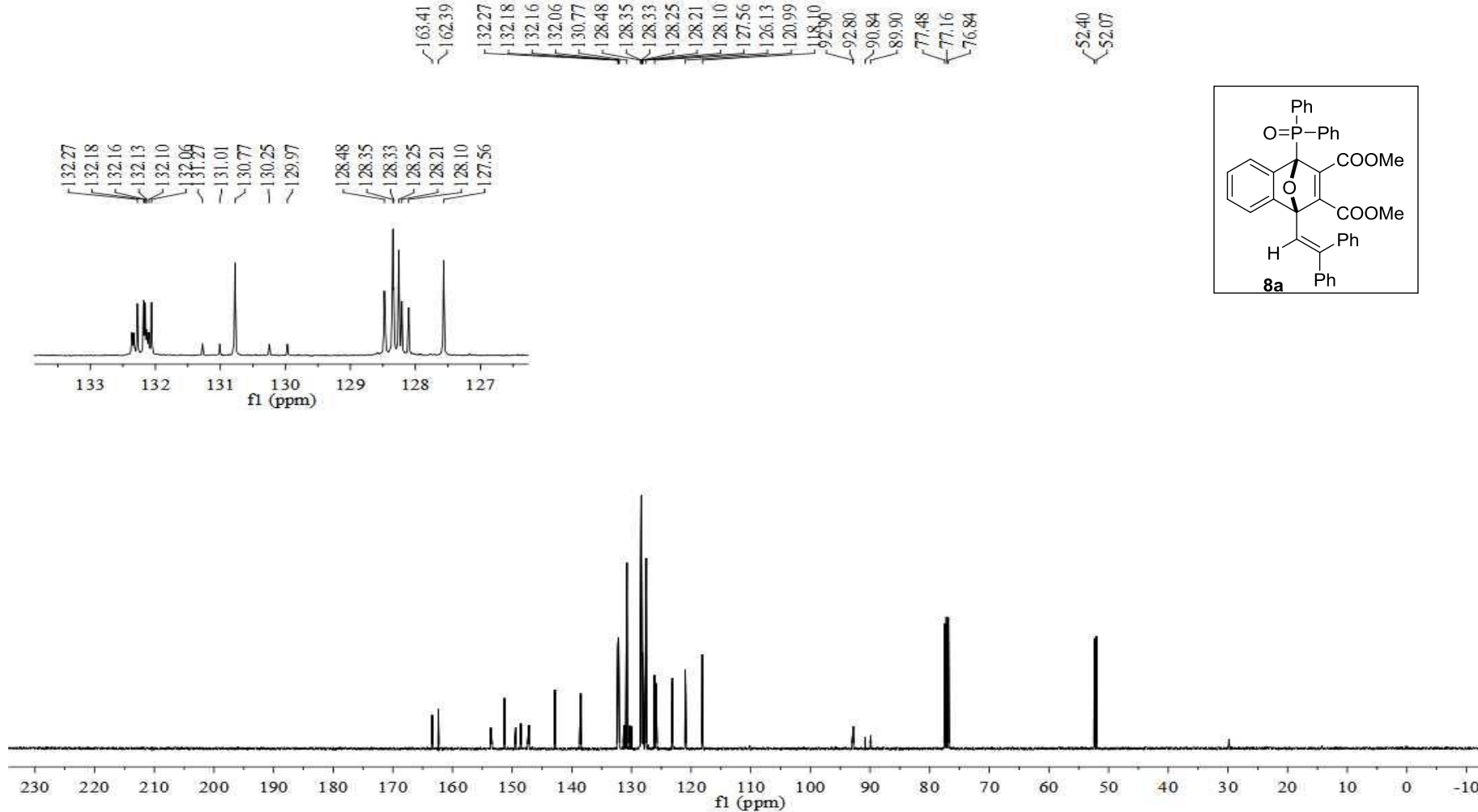


S161

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of dimethyl 1-(diphenylphosphoryl)-4-(2,2-diphenylvinyl)-1,4-dihydro-1,4-epoxynaphthalene-2,3-dicarboxylate (8a)

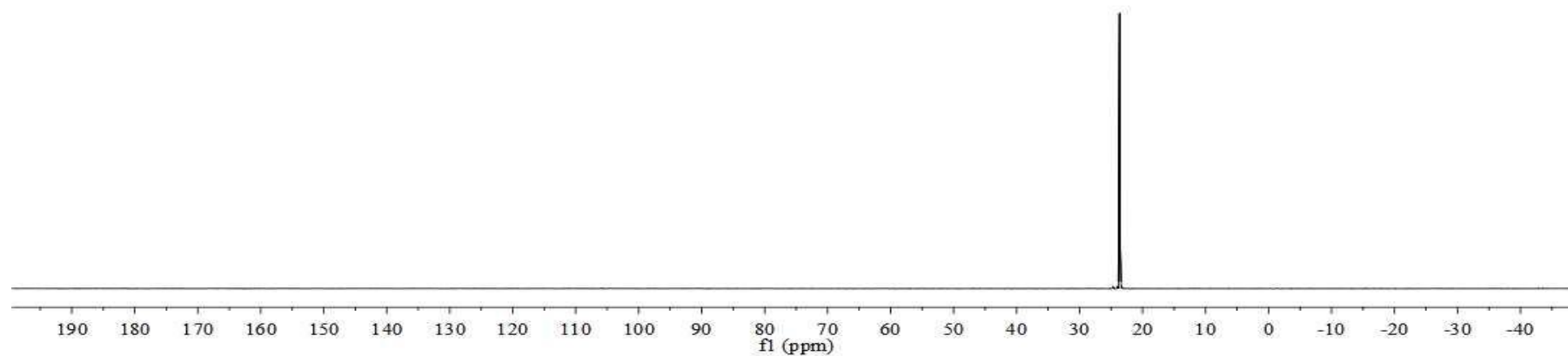
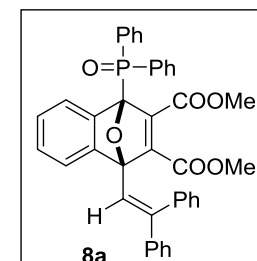


<sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) of dimethyl 1-(diphenylphosphoryl)-4-(2,2-diphenylvinyl)-1,4-dihydro-1,4-epoxynaphthalene-2,3-dicarboxylate (8a)



$^{31}\text{P}$   $\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ) of dimethyl 1-(diphenylphosphoryl)-4-(2,2-

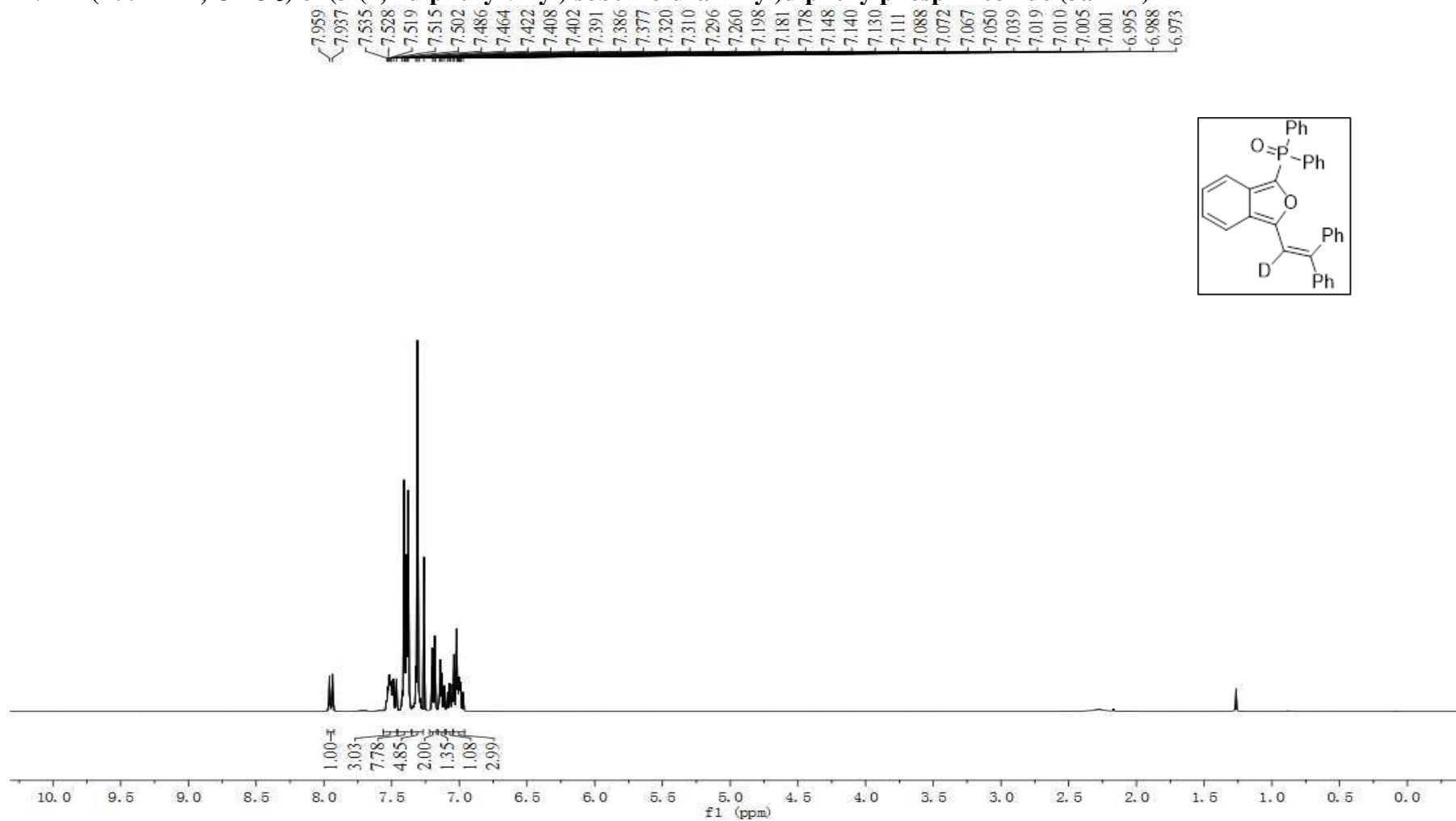
-23.62



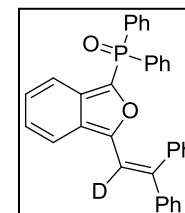
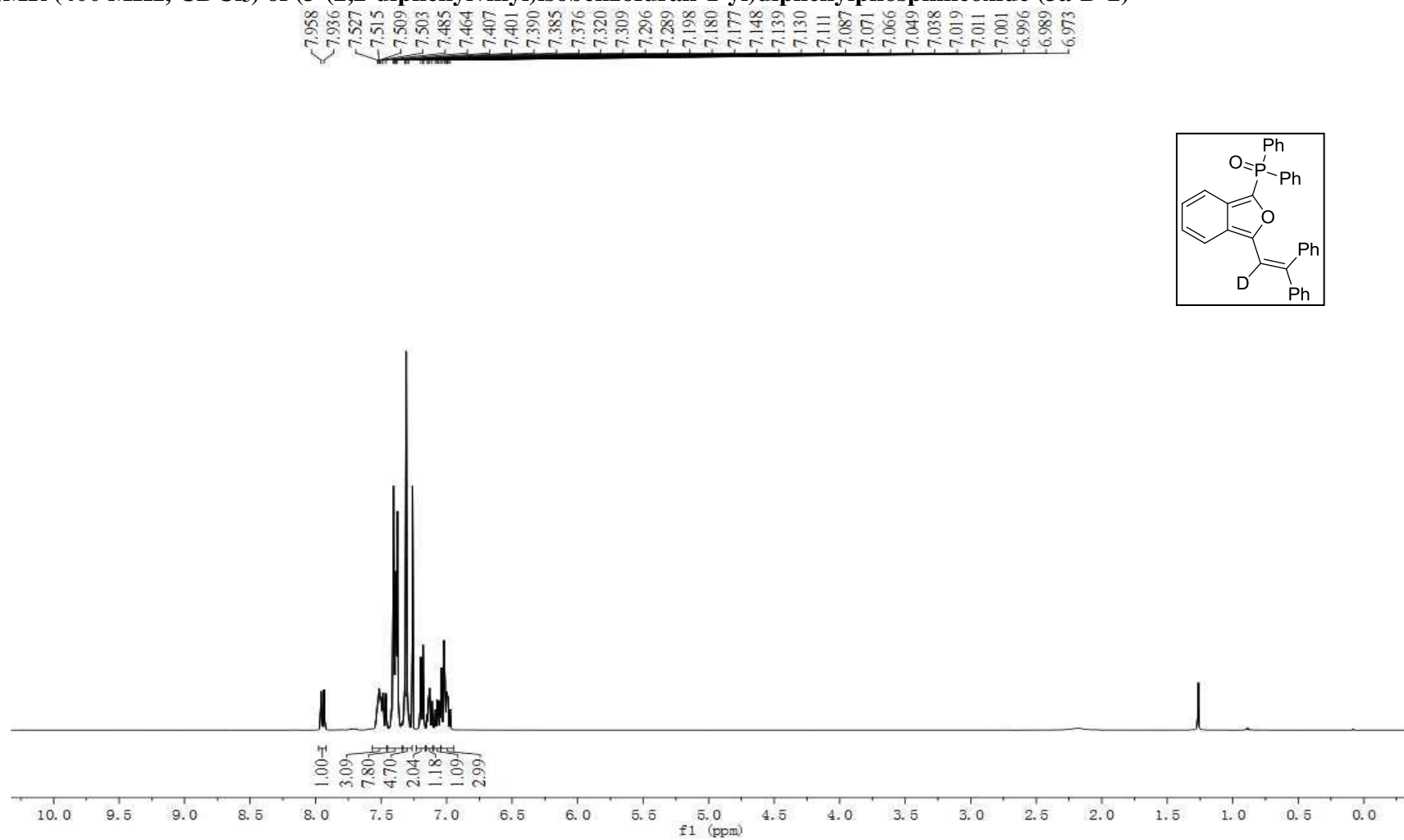
S164



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphineoxide (3a-D-1)**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (3-(2,2-diphenylvinyl)isobenzofuran-1-yl)diphenylphosphineoxide (3a-D-2)**



## Photophysical Properties of IBFPOs

With the positive results in synthesis of **IBFPOs**, we also investigated the AIE performance of **IBFPOs**. the photophysical data of all synthesized compounds are summerized in Table S3 and corresponding spectra are given (Fig. S3-S37).

**Table S3.** Photophysical data of compounds **IBFPOs**

Title compound	Solution(nm)			$\tau F^{[b]}$ (ns)	
	$\lambda_{\text{abs}}^{[a]}$	$\lambda_{\text{em}}^{[a]}$	Stoke's shift	Solid	Solution
<b>3a</b>	412	507	94	5.19	0.28
<b>3b</b>	415	508	92	1.41	0.28
<b>3c</b>	414	507	93	0.39	0.31
<b>3d</b>	412	514	102	2.08	0.39
<b>3e</b>	414	509	95	4.60	0.21
<b>3f</b>	414	514	100	5.56	0.33
<b>3g</b>	415	509	94	5.25	0.18

<b>3h</b>	413	499	86	1.60	0.34
<b>3i</b>	413	510	97	1.74	0.31
<b>3j</b>	413	515	102	2.34	0.26
<b>3k</b>	417	502	85	2.44	0.90
<b>3l</b>	410	486	76	1.40	0.29
<b>3m</b>	414	497	83	0.82	0.24
<b>3n</b>	409	489	80	0.67	0.34
<b>3o</b>	405	495	90	1.08	0.29
<b>3p</b>	418	505	87	1.54	0.30
<b>3q</b>	426	518	92	0.34	1.25
<b>3r</b>	417	515	98	2.46	1.12

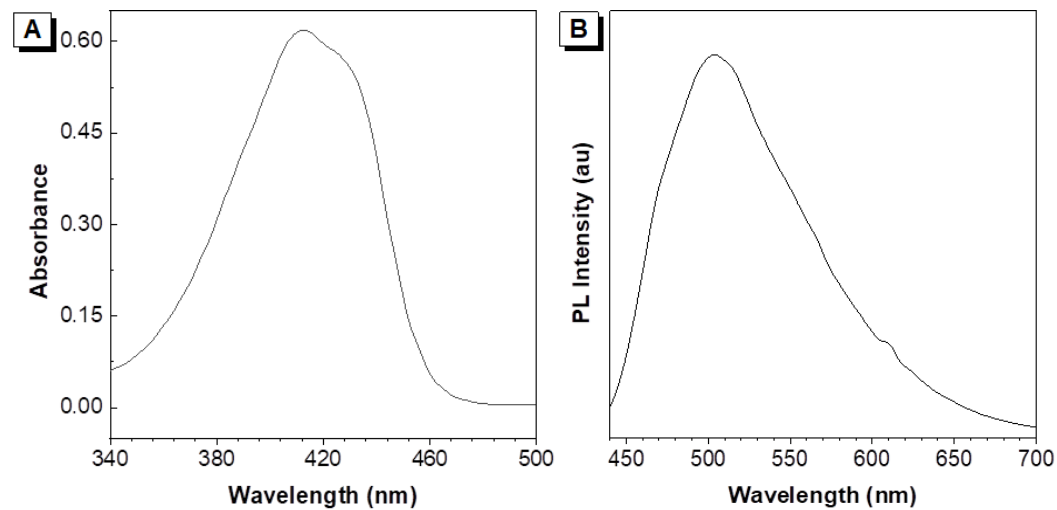
<b>3s</b>	411	505	94	4.83	0.23
<b>3t</b>	414	505	91	1.64	0.38
<b>3u</b>	416	506	90	1.09	0.40
<b>3v</b>	426	490	64	0.60	2.05
<b>3w</b>	442/471	508/544	66/73	0.67	3.95
<b>3x</b>	446	514	68	2.73	1.59
<b>3y</b>	399	464	65	1.61	0.78
<b>3aa</b>	415	503	88	1.91	0.33
<b>3ab</b>	412	501	89	1.49	0.32
<b>3ac</b>	413	509	96	1.02	1.48
<b>3ad</b>	414	511	97	1.48	0.17

<b>3ae</b>	413	502	89	1.39	0.31
<b>3af</b>	412	505	93	2.78	0.24
<b>3ag</b>	413	505	92	0.61	0.28
<b>5a</b>	421	502	81	1.15	0.41
<b>6a</b>	413	643	230	2.32	2.89
<b>7a</b>	414	599	185	13.72	0.16

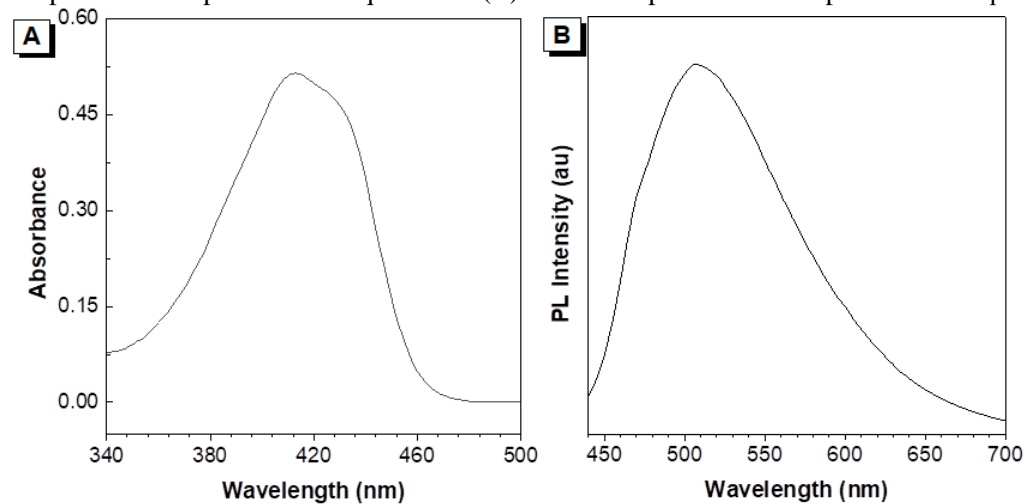
[a]  $\lambda_{\text{obs}}$  and  $\lambda_{\text{em}}$  refer to optimal absorption wavelength and photoluminescence (PL) Peak, respectively. [b]  $\tau_{\text{F}}$  is fluorescence lifetime. [c]  $\Phi_{\text{F}}$  is absolute fluorescence quantum yield.

### Investigation on the Absorption and Emission Spectra

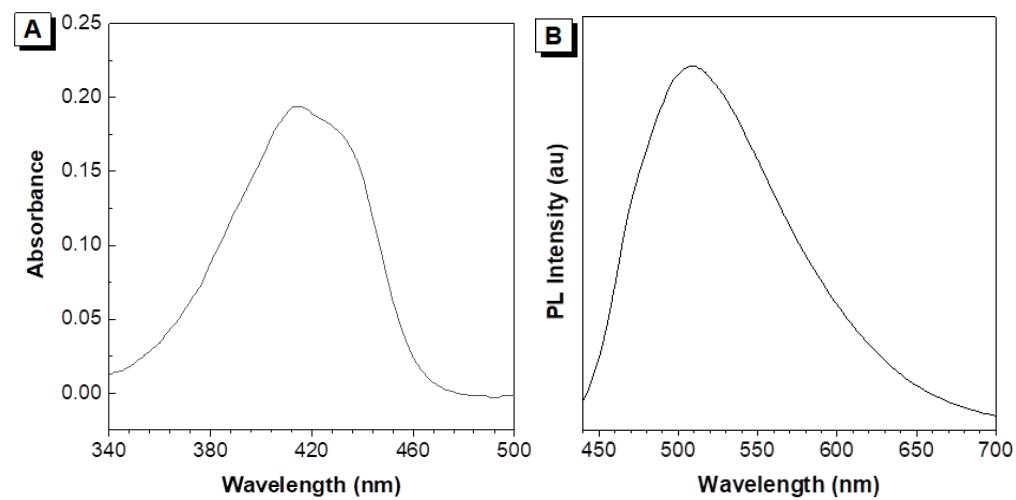
The absorption and emission spectra of all synthesized compounds (Fig. S3-S37) were investigated firstly.



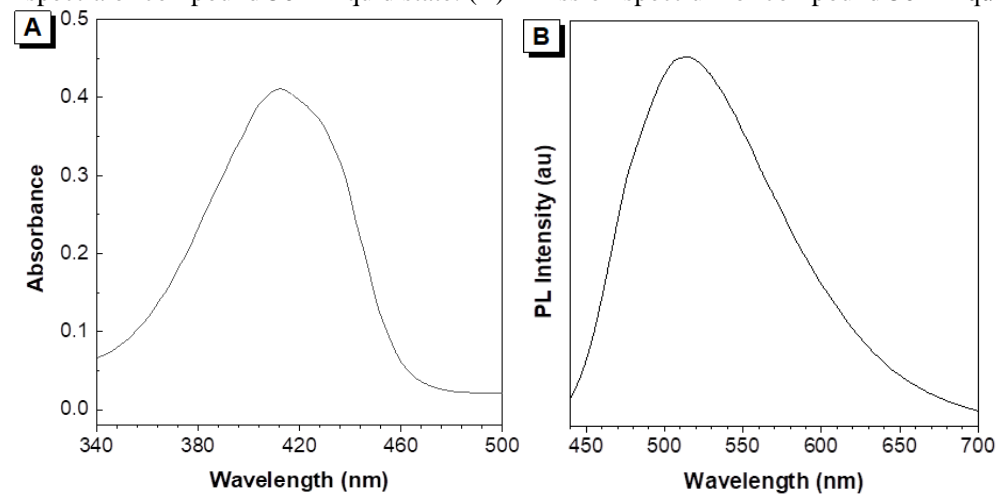
**Fig. S3** (A) Absorption spectra of compound **3a** in liquid state. (B) Emission spectrum of compound **3a** in liquid state ( $\lambda_{\text{ex}} = 412$  nm).



**Fig. S4** (A) Absorption spectra of compound **3b** in liquid state. (B) Emission spectrum of compound **3b** in liquid state ( $\lambda_{\text{ex}} = 415$  nm).

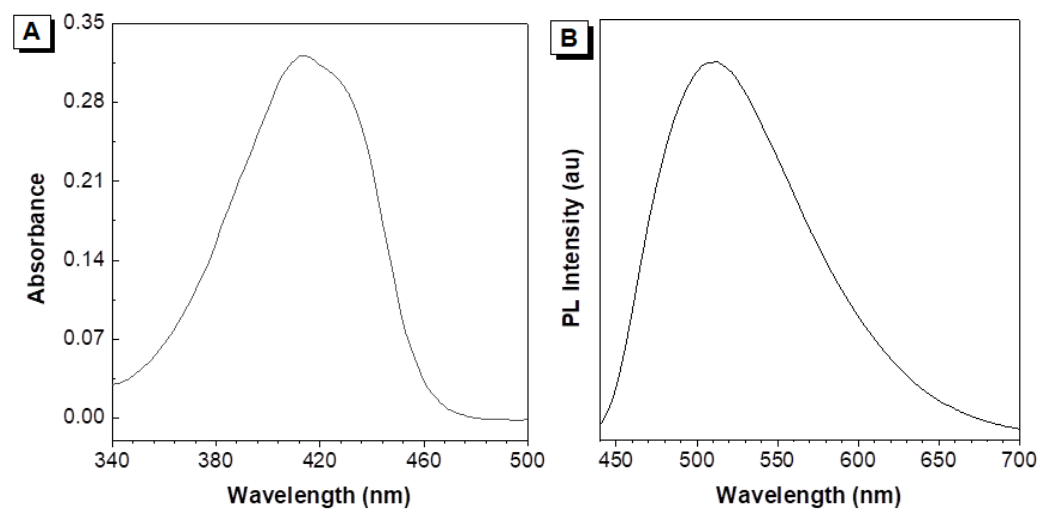


**Fig. S5** (A) Absorption spectra of compound **3c** in liquid state. (B) Emission spectrum of compound **3c** in liquid state ( $\lambda_{\text{ex}} = 414$  nm).

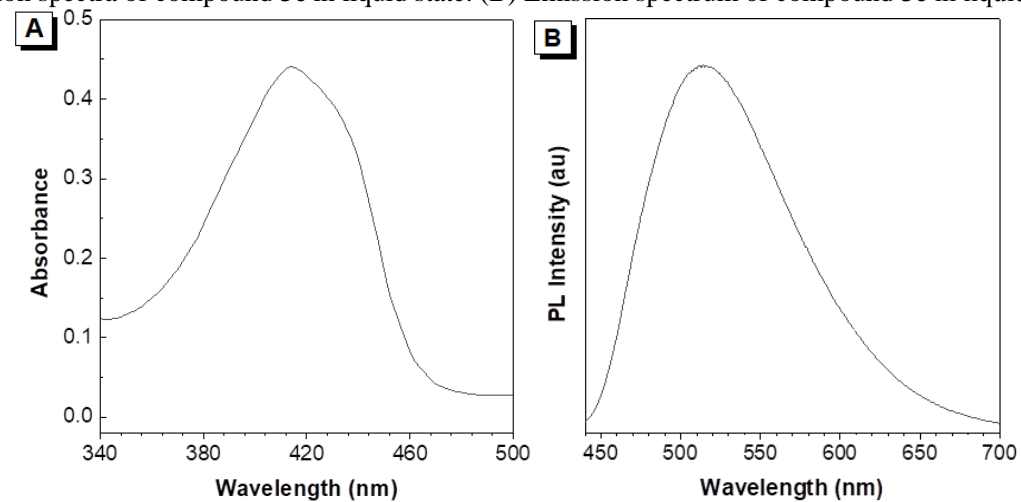


**Fig. S6** (A) Absorption spectra of compound **3d** in liquid state. (B) Emission spectrum of compound **3d** in liquid state ( $\lambda_{\text{ex}} = 412$  nm).

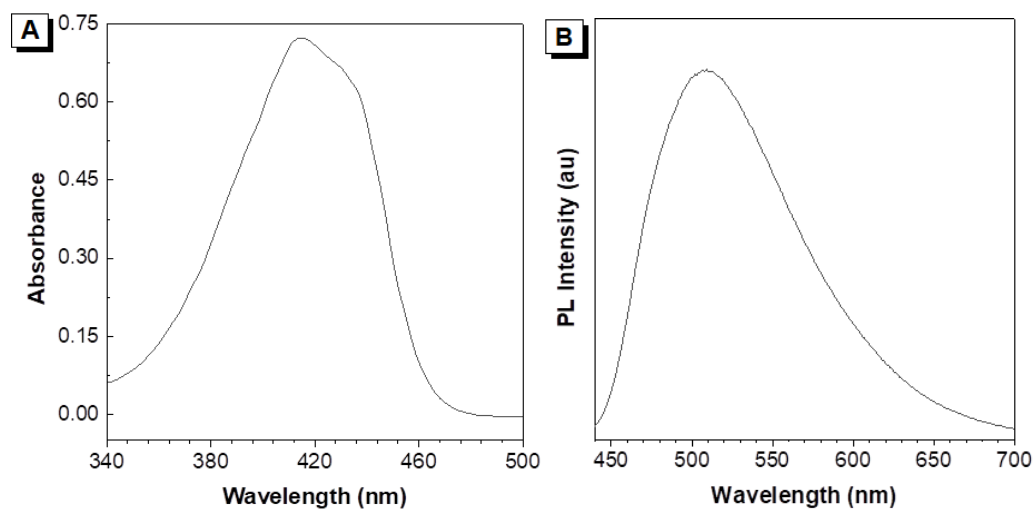




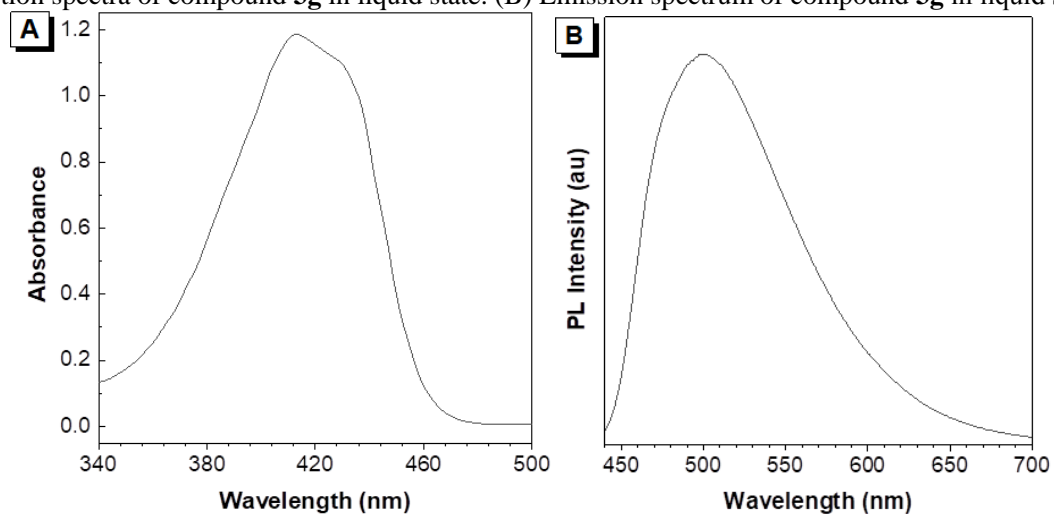
**Fig. S7** (A) Absorption spectra of compound **3e** in liquid state. (B) Emission spectrum of compound **3e** in liquid state ( $\lambda_{\text{ex}} = 414$  nm).



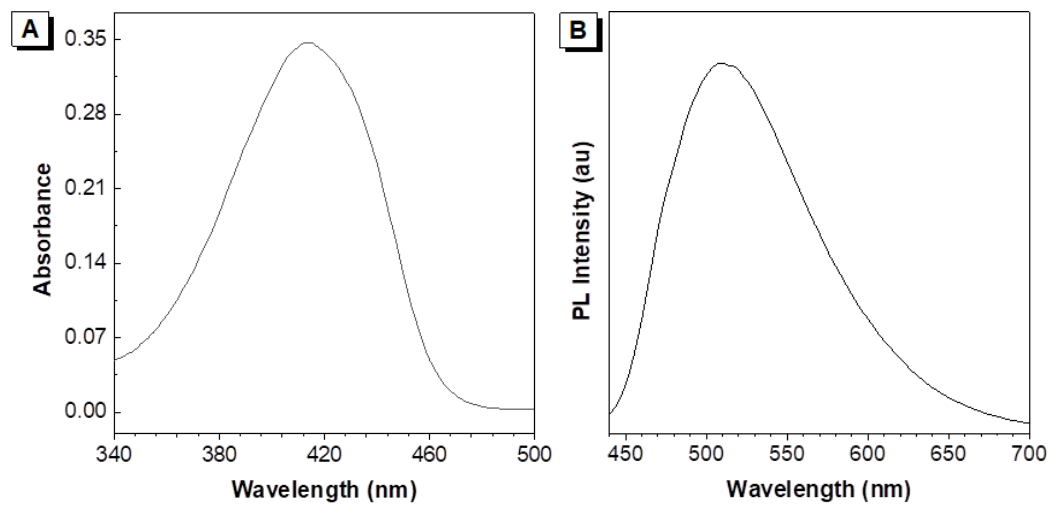
**Fig. S8** (A) Absorption spectra of compound **3f** in liquid state. (B) Emission spectrum of compound **3f** in liquid state ( $\lambda_{\text{ex}} = 414$  nm).



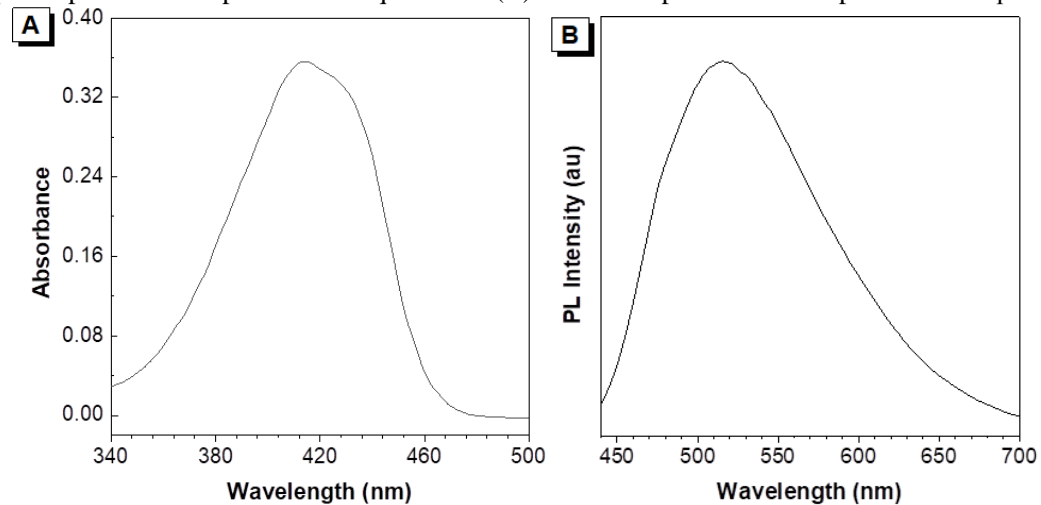
**Fig. S9** (A) Absorption spectra of compound **3g** in liquid state. (B) Emission spectrum of compound **3g** in liquid state ( $\lambda_{\text{ex}} = 415$  nm).



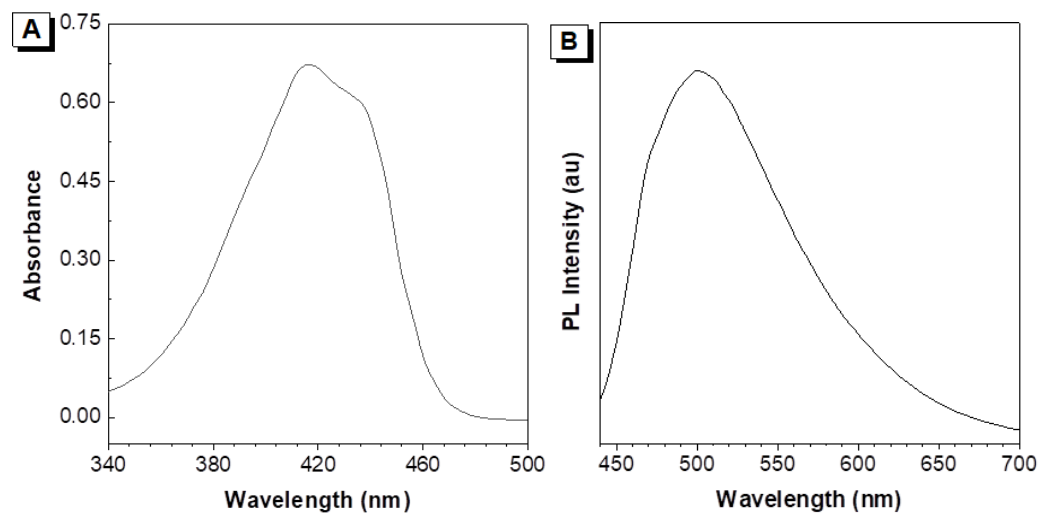
**Fig. S10** (A) Absorption spectra of compound **3h** in liquid state (B) Emission spectrum of compound **3h** in liquid state ( $\lambda_{\text{ex}} = 413$  nm).



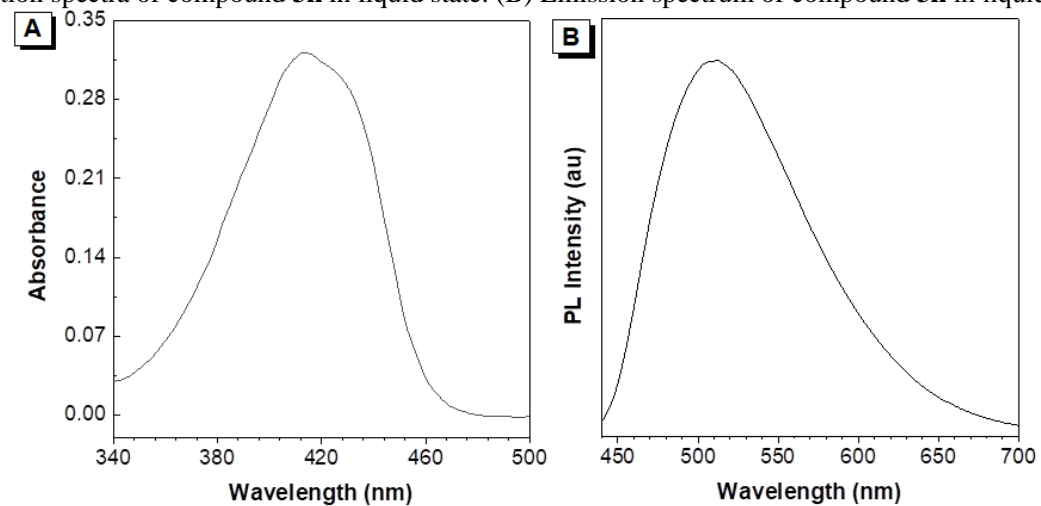
**Fig. S11** (A) Absorption spectra of compound **3i** in liquid state. (B) Emission spectrum of compound **3i** in liquid state ( $\lambda_{\text{ex}} = 413$  nm).



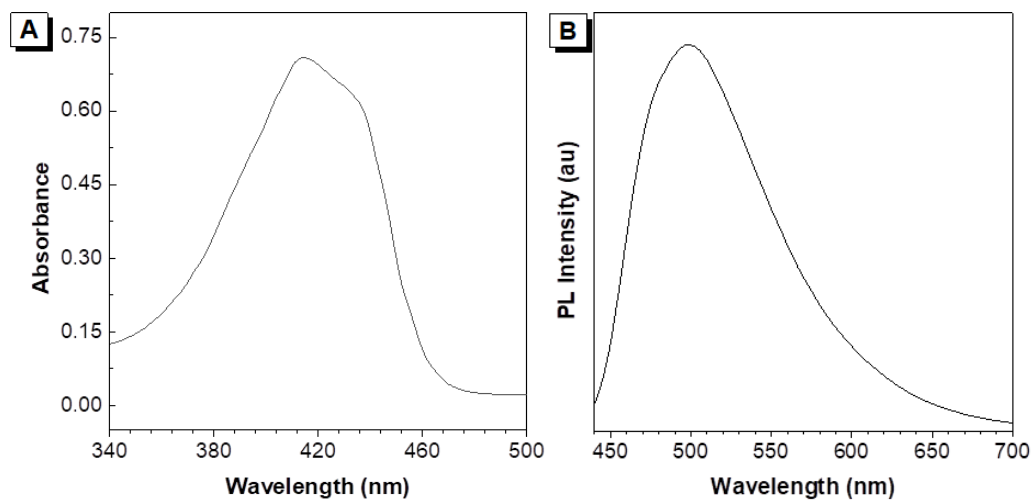
**Fig. S12** (A) Absorption spectra of compound **3j** in liquid state. (B) Emission spectrum of compound **3j** in liquid state ( $\lambda_{\text{ex}} = 413$  nm).



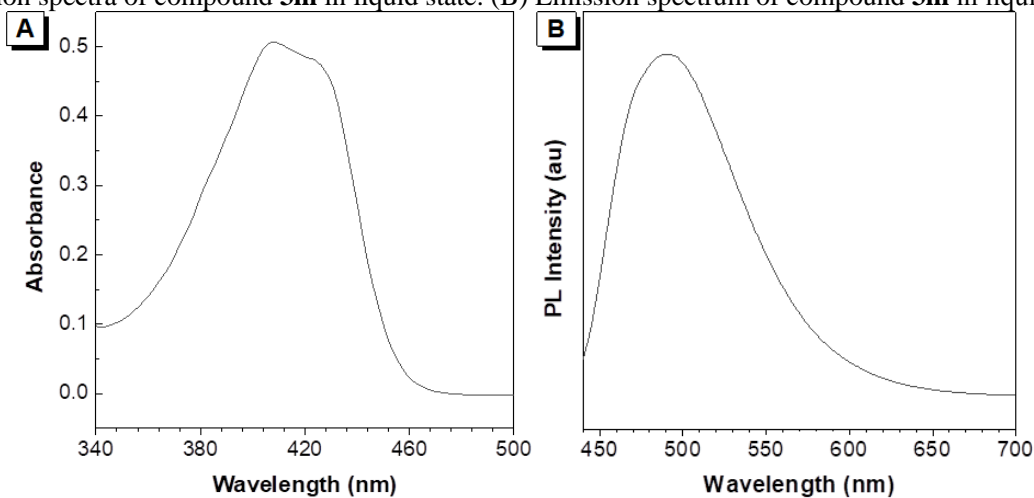
**Fig. S13** (A) Absorption spectra of compound **3k** in liquid state. (B) Emission spectrum of compound **3k** in liquid state ( $\lambda_{\text{ex}} = 417$  nm).



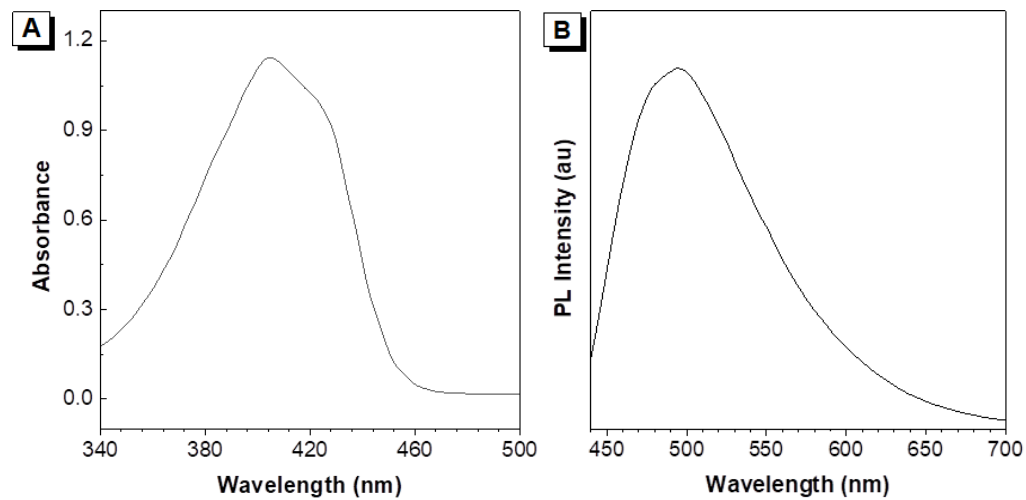
**Fig. S14** (A) Absorption spectra of compound **3l** in liquid state. (B) Emission spectrum of compound **3l** in liquid state ( $\lambda_{\text{ex}} = 410$  nm).



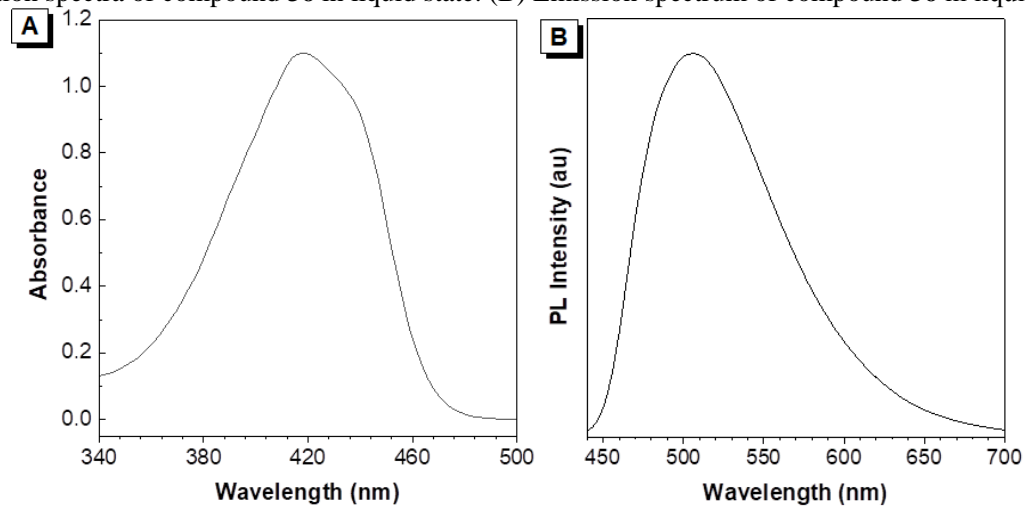
**Fig. S15** (A) Absorption spectra of compound **3m** in liquid state. (B) Emission spectrum of compound **3m** in liquid state ( $\lambda_{\text{ex}} = 414$  nm).



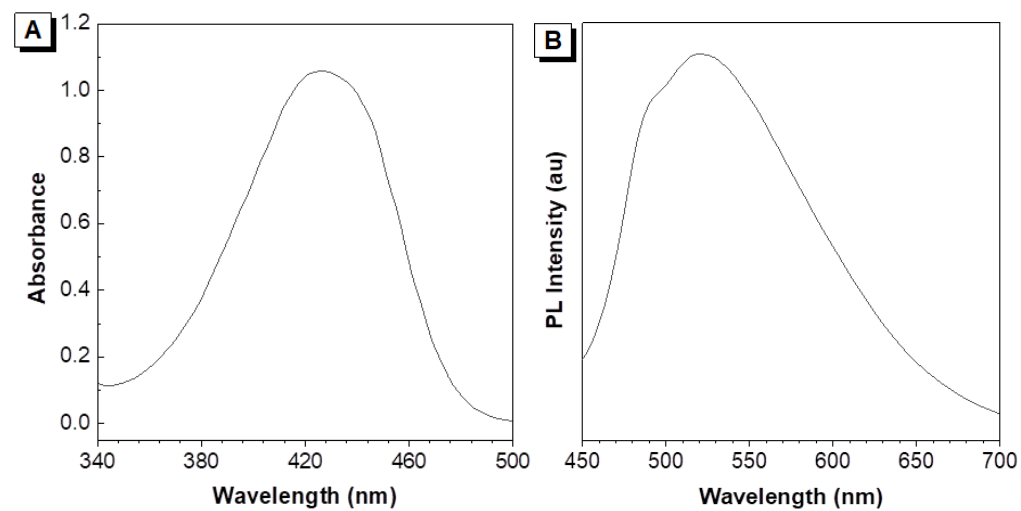
**Fig. S16** (A) Absorption spectra of compound **3n** in liquid state. (B) Emission spectrum of compound **3n** in liquid state ( $\lambda_{\text{ex}} = 409$  nm).



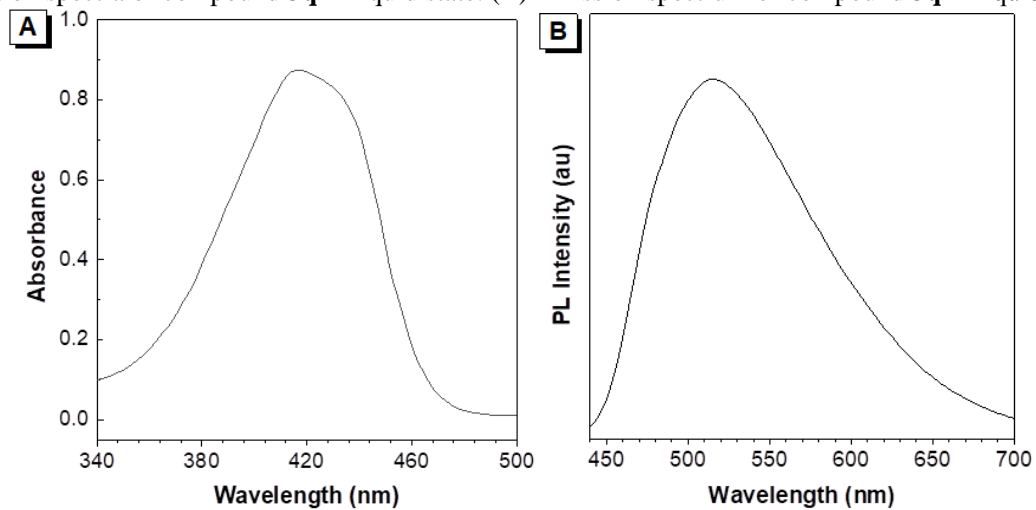
**Fig. S17** (A) Absorption spectra of compound **3o** in liquid state. (B) Emission spectrum of compound **3o** in liquid state ( $\lambda_{\text{ex}} = 405$  nm).



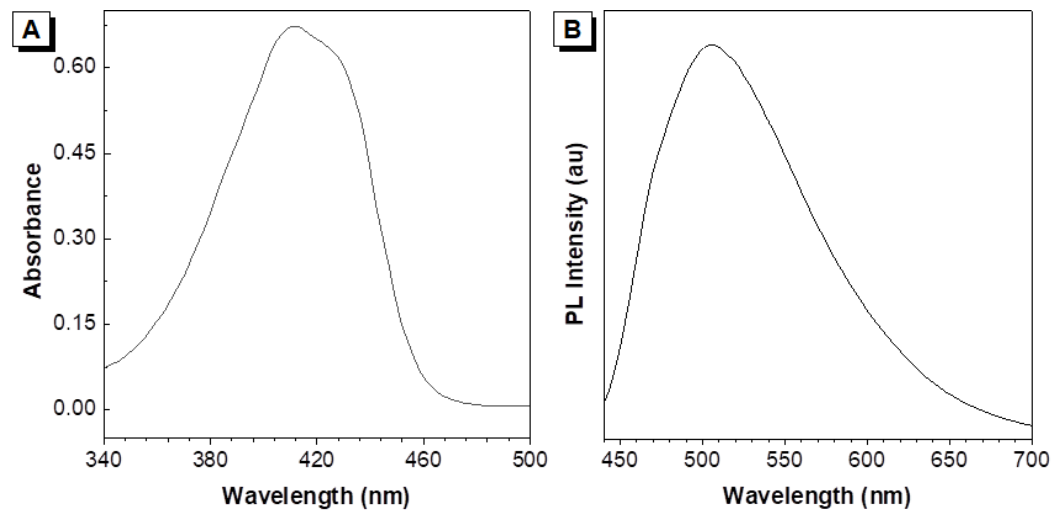
**Fig. S18** (A) Absorption spectra of compound **3p** in liquid state. (B) Emission spectrum of compound **3p** in liquid state ( $\lambda_{\text{ex}} = 418$  nm).



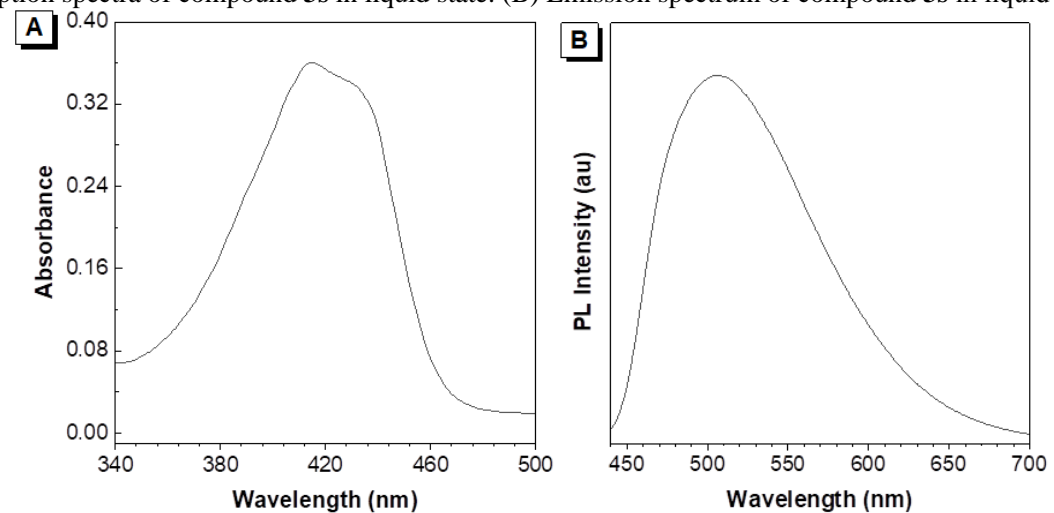
**Fig. S19** (A) Absorption spectra of compound **3q** in liquid state. (B) Emission spectrum of compound **3q** in liquid state ( $\lambda_{\text{ex}} = 426$  nm).



**Fig. S20** (A) Absorption spectra of compound **3r** in liquid state. (B) Emission spectrum of compound **3r** in liquid state ( $\lambda_{\text{ex}} = 417$  nm).

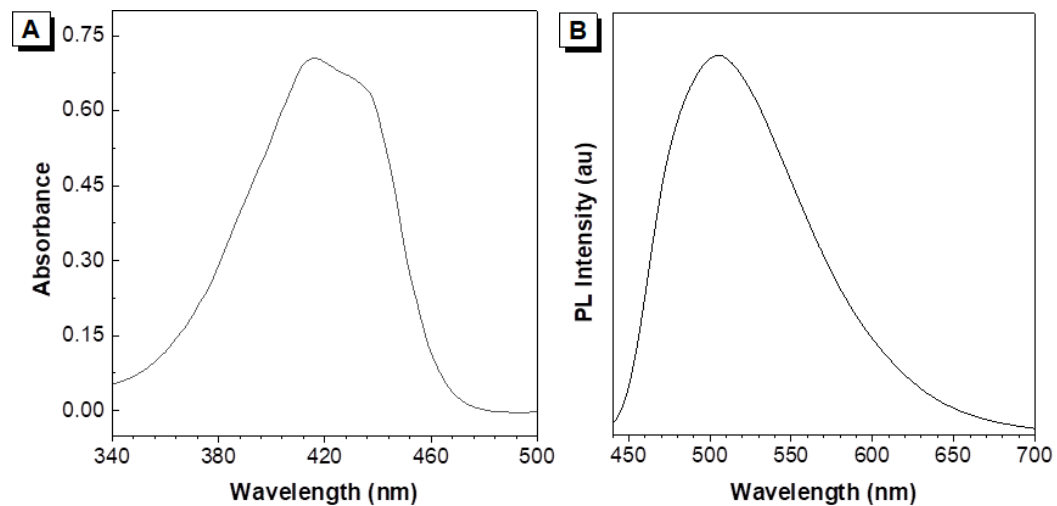


**Fig. S21** (A) Absorption spectra of compound **3s** in liquid state. (B) Emission spectrum of compound **3s** in liquid state ( $\lambda_{\text{ex}} = 411$  nm).

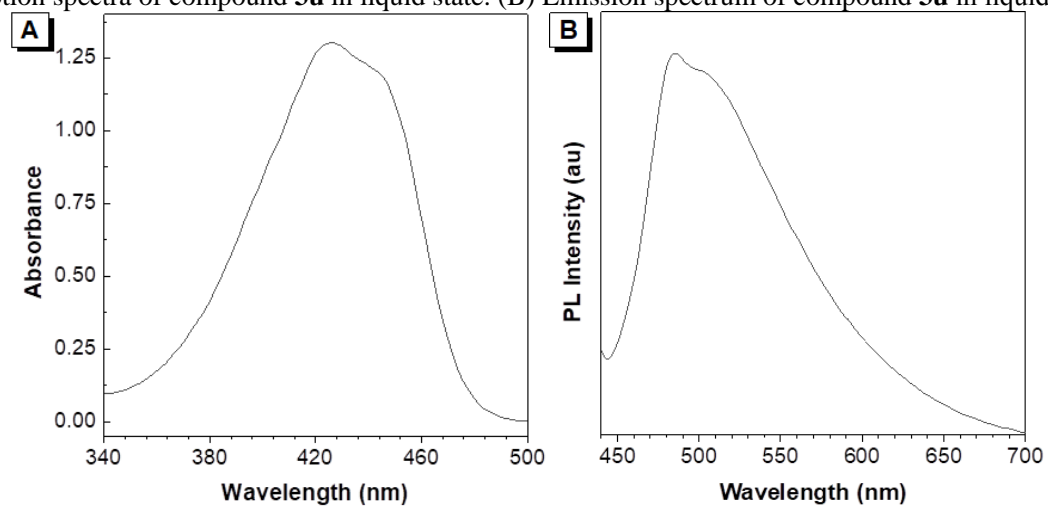


**Fig. S22** (A) Absorption spectra of compound **3t** in liquid state. (B) Emission spectrum of compound **3t** in liquid state ( $\lambda_{\text{ex}} = 414$  nm).

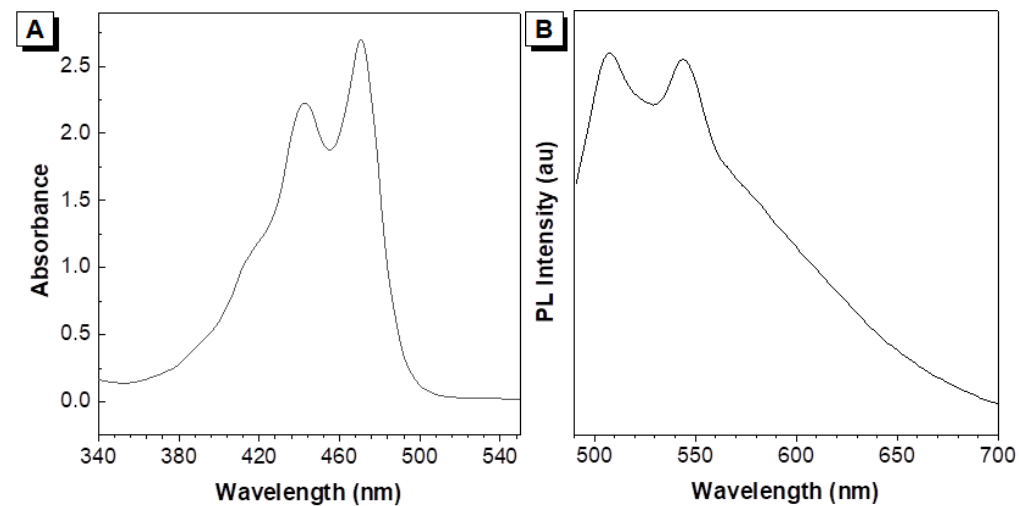




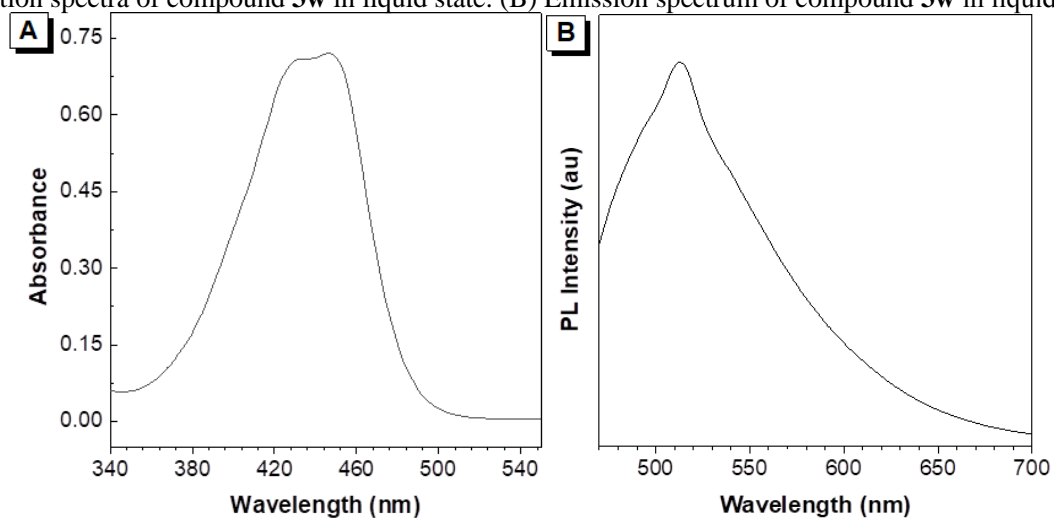
**Fig. S23** (A) Absorption spectra of compound **3u** in liquid state. (B) Emission spectrum of compound **3u** in liquid state ( $\lambda_{\text{ex}} = 416$  nm).



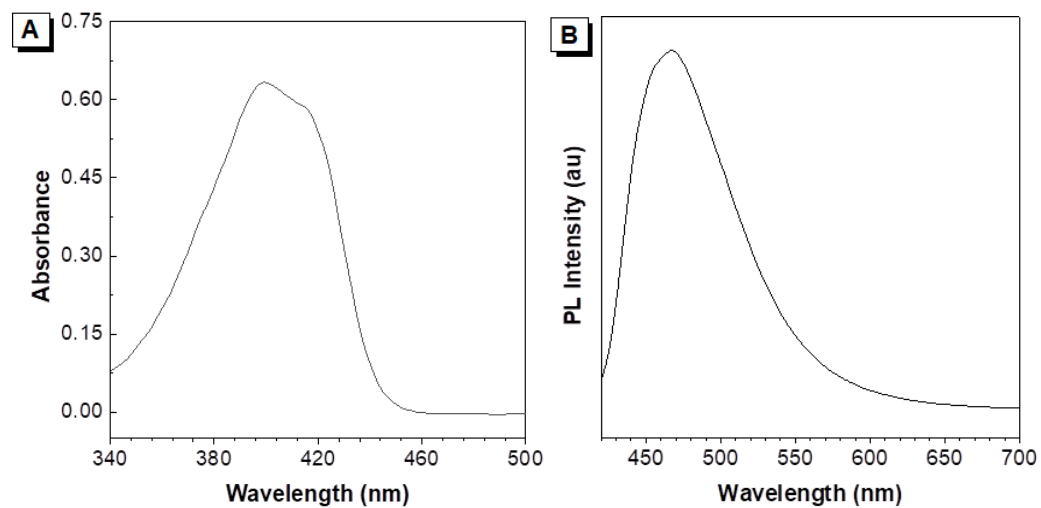
**Fig. S24** (A) Absorption spectra of compound **3v** in liquid state. (B) Emission spectrum of compound **3v** in liquid state ( $\lambda_{\text{ex}} = 426$  nm).



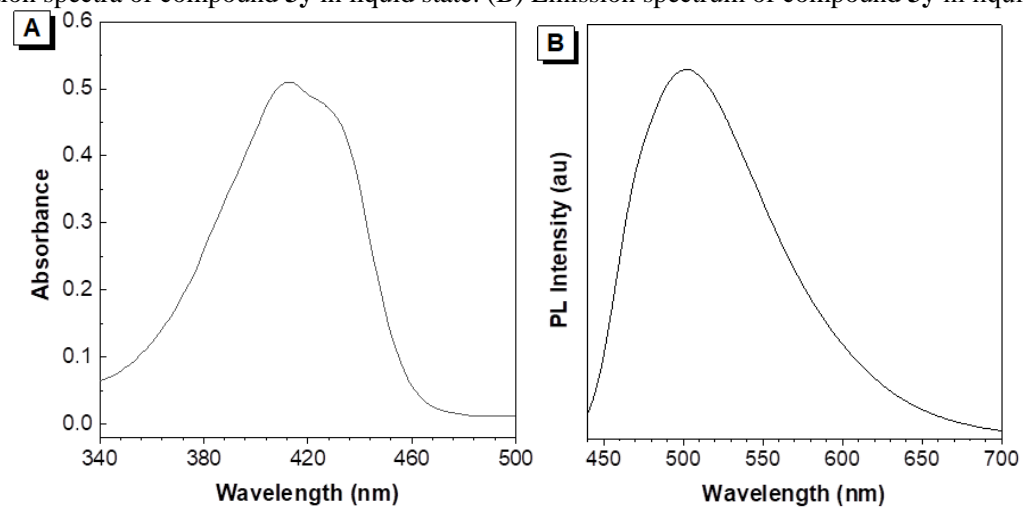
**Fig. S25** (A) Absorption spectra of compound **3w** in liquid state. (B) Emission spectrum of compound **3w** in liquid state ( $\lambda_{\text{ex}} = 442$  nm).



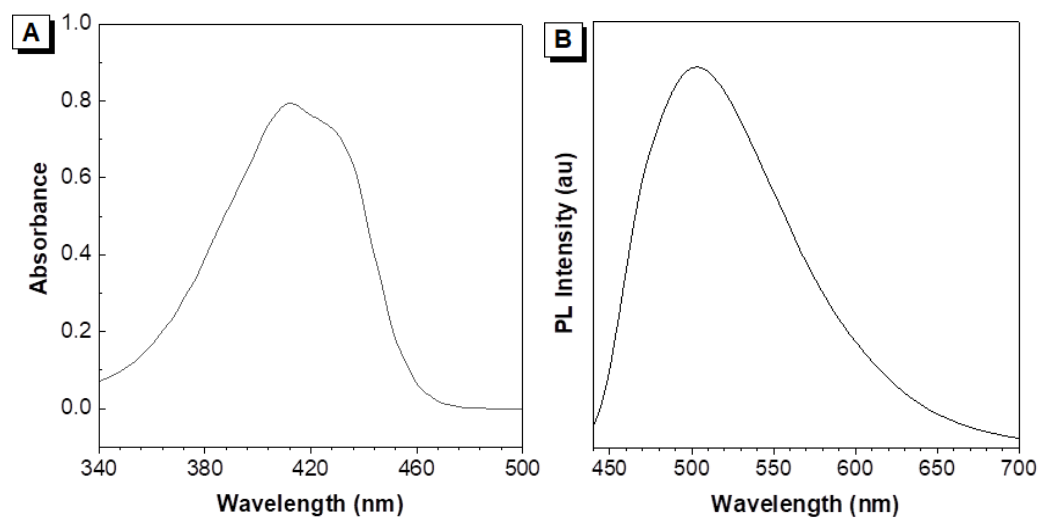
**Fig. S26** (A) Absorption spectra of compound **3x** in liquid state. (B) Emission spectrum of compound **3x** in liquid state ( $\lambda_{\text{ex}} = 446$  nm).



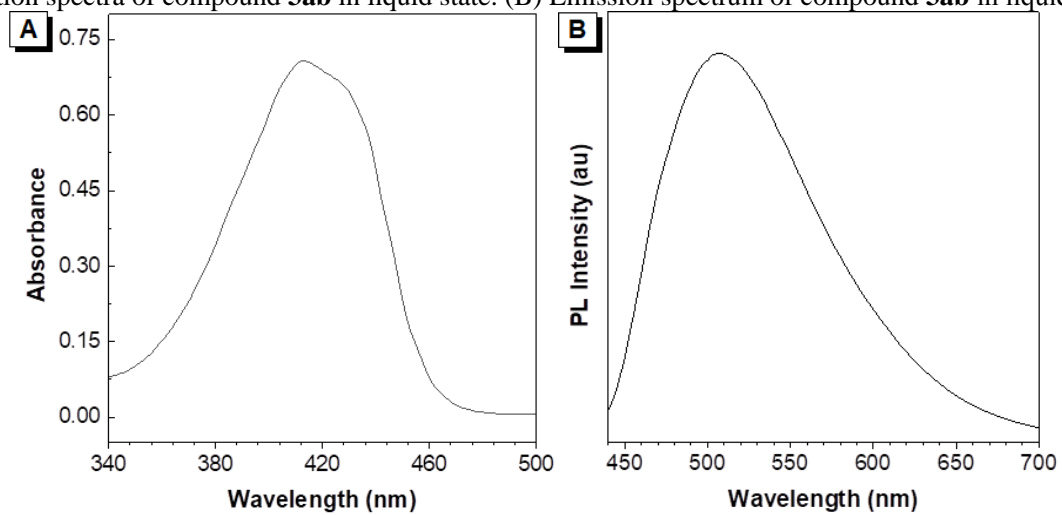
**Fig. S27** (A) Absorption spectra of compound **3y** in liquid state. (B) Emission spectrum of compound **3y** in liquid state ( $\lambda_{\text{ex}} = 399$  nm).



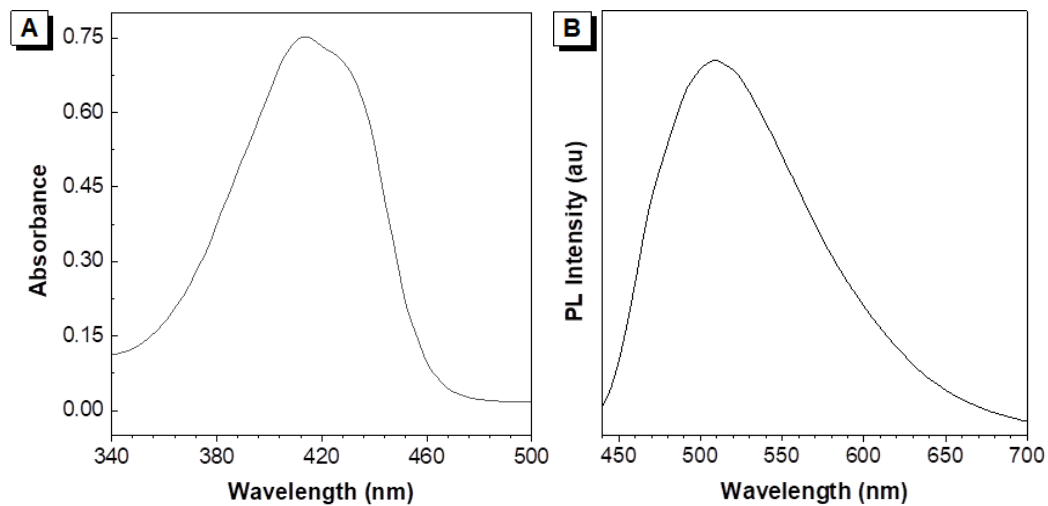
**Fig. S28** (A) Absorption spectra of compound **3aa** in liquid state. (B) Emission spectrum of compound **3aa** in liquid state ( $\lambda_{\text{ex}} = 415$  nm).



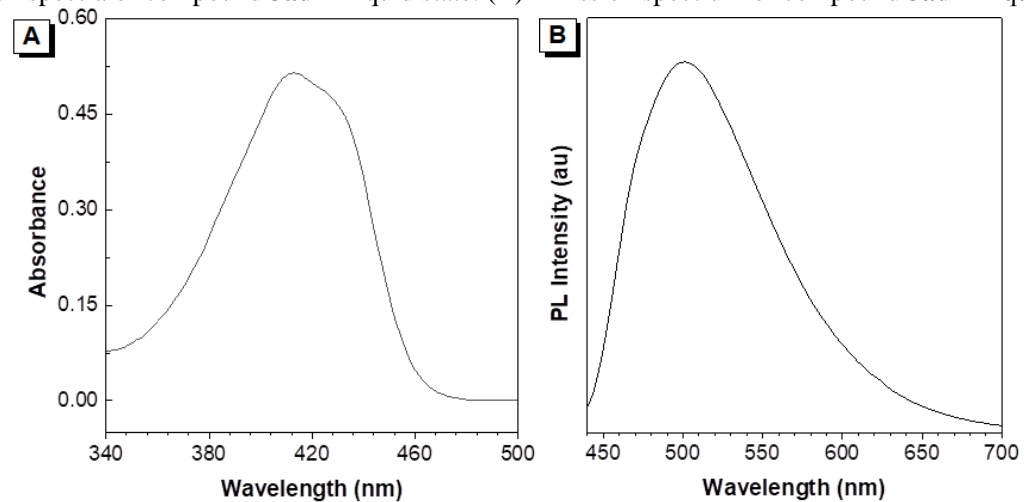
**Fig. S29** (A) Absorption spectra of compound **3ab** in liquid state. (B) Emission spectrum of compound **3ab** in liquid state ( $\lambda_{\text{ex}} = 412$  nm).



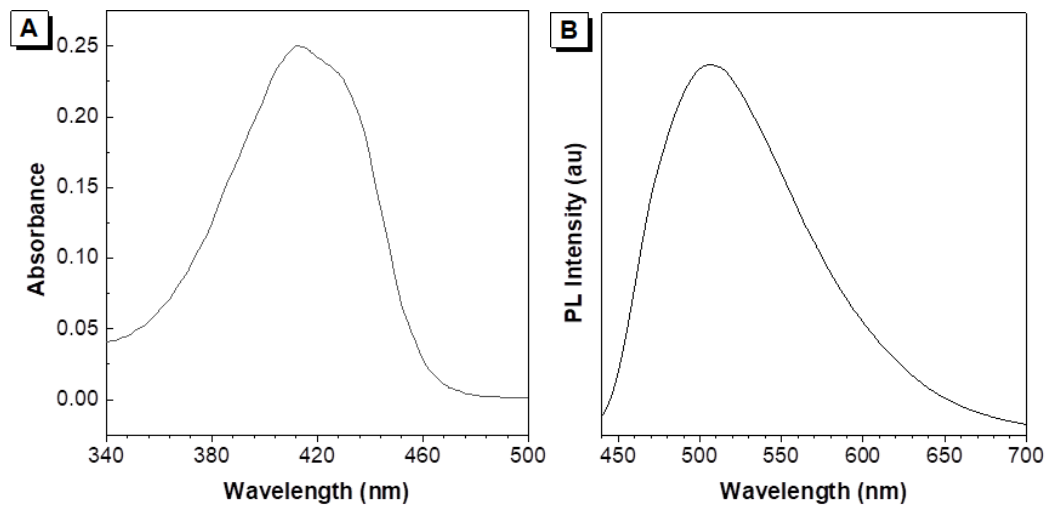
**Fig. S30** (A) Absorption spectra of compound **3ac** in liquid state. (B) Emission spectrum of compound **3ac** in liquid state ( $\lambda_{\text{ex}} = 413$  nm).



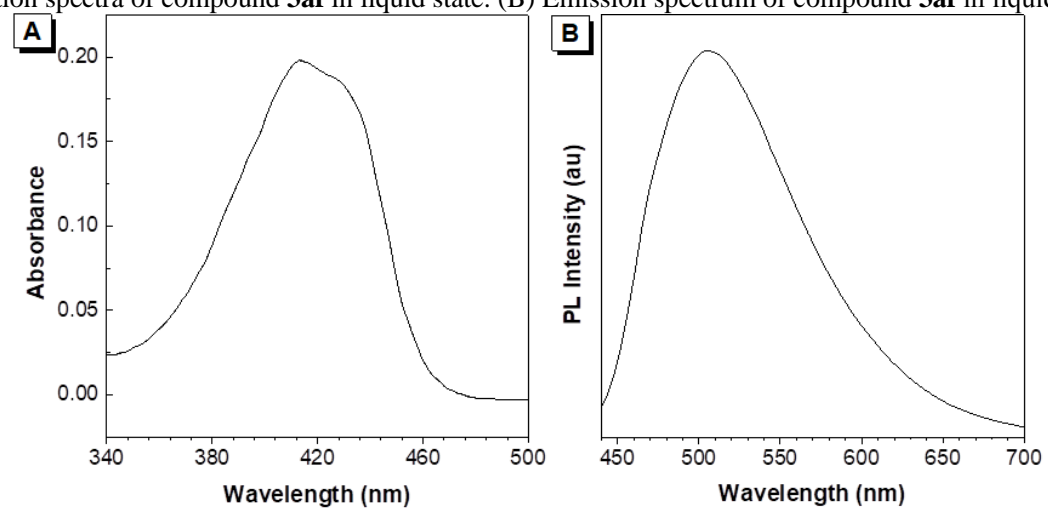
**Fig. S31** (A) Absorption spectra of compound **3ad** in liquid state. (B) Emission spectrum of compound **3ad** in liquid state ( $\lambda_{\text{ex}} = 414$  nm).



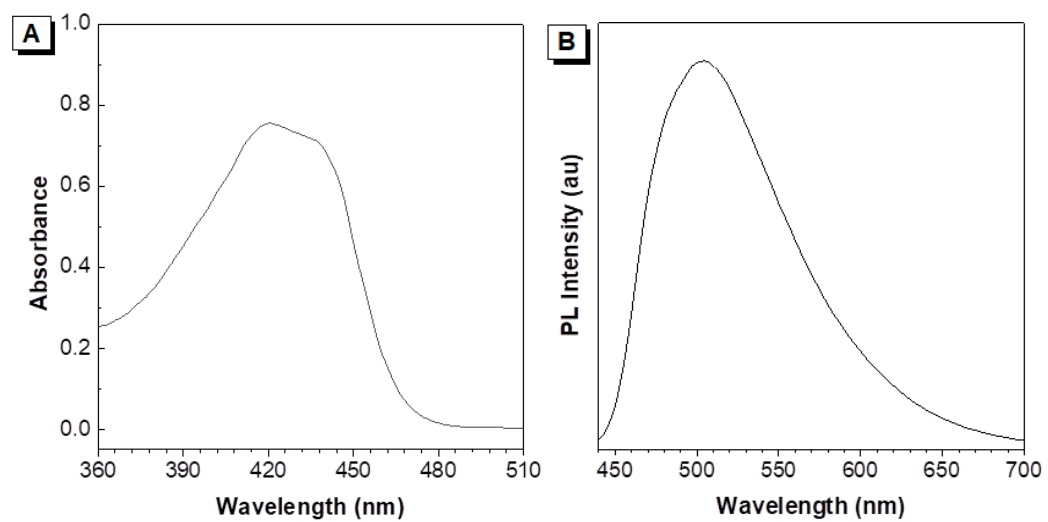
**Fig. S32** (A) Absorption spectra of compound **3ae** in liquid state. (B) Emission spectrum of compound **3ae** in liquid state ( $\lambda_{\text{ex}} = 413$  nm).



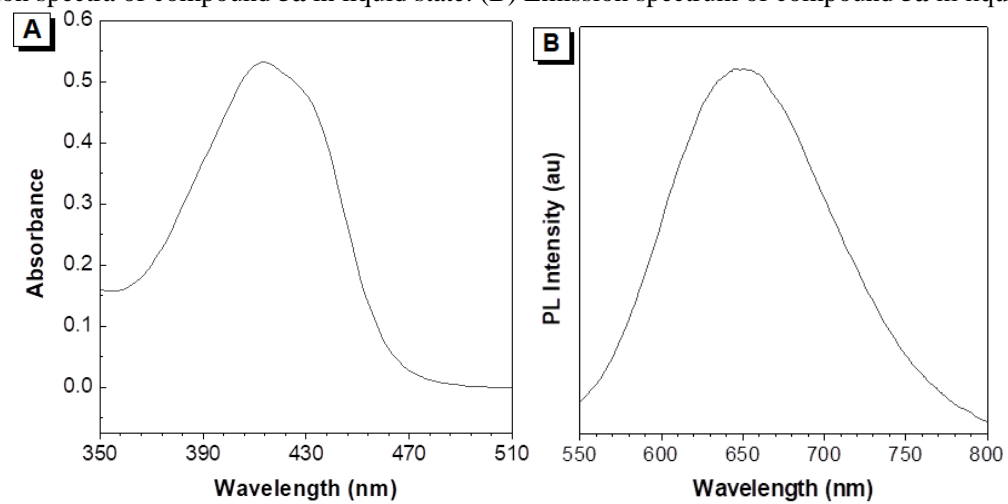
**Fig. S33** (A) Absorption spectra of compound **3af** in liquid state. (B) Emission spectrum of compound **3af** in liquid state ( $\lambda_{\text{ex}} = 412$  nm).



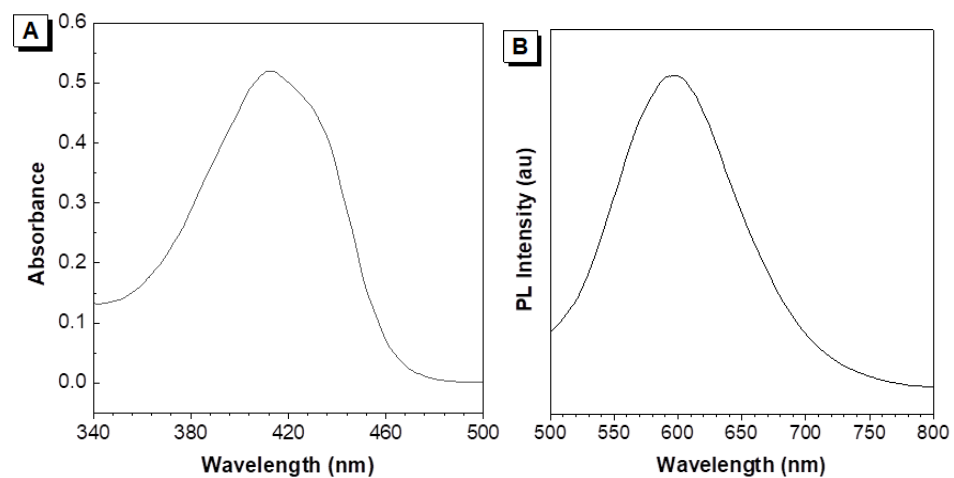
**Fig. S34** (A) Absorption spectra of compound **3ag** in liquid state. (B) Emission spectrum of compound **3ag** in liquid state ( $\lambda_{\text{ex}} = 413$  nm).



**Fig. S35** (A) Absorption spectra of compound **5a** in liquid state. (B) Emission spectrum of compound **5a** in liquid state ( $\lambda_{\text{ex}} = 421$  nm).

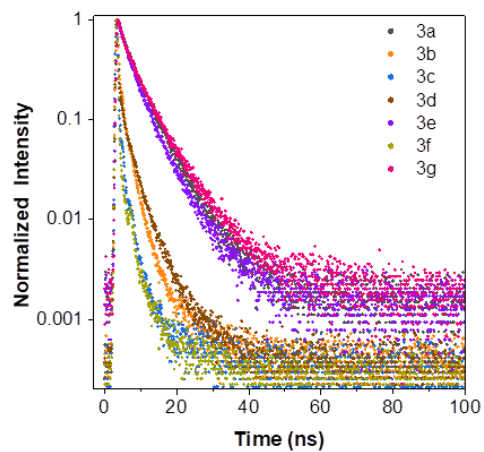


**Fig. S36** (A) Absorption spectra of compound **6a** in liquid state. (B) Emission spectrum of compound **6a** in liquid state ( $\lambda_{\text{ex}} = 413$  nm).



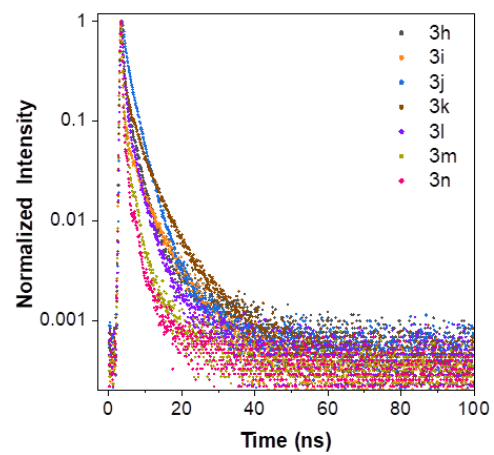
**Fig. S37** (A) Absorption spectra of compound **7a** in liquid state. (B) Emission spectrum of compound **7a** in liquid state ( $\lambda_{\text{ex}} = 414$  nm).

### Investigation on the Fluorescence Lifetime

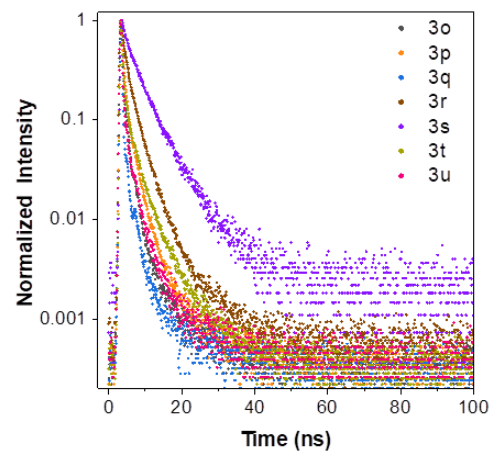


**Fig. S38** Fluorescence decay curves of **3a**, **3b**, **3c**, **3d**, **3e**, **3f** and **3g** (in solid state).

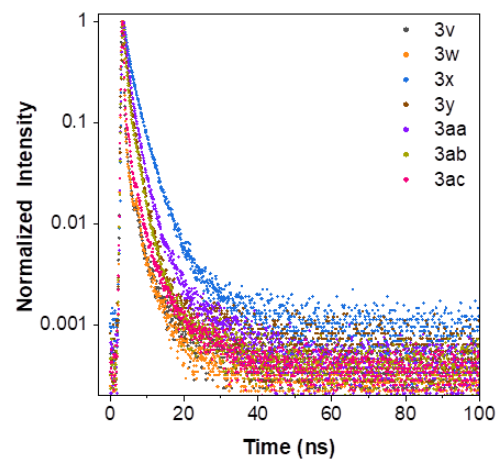




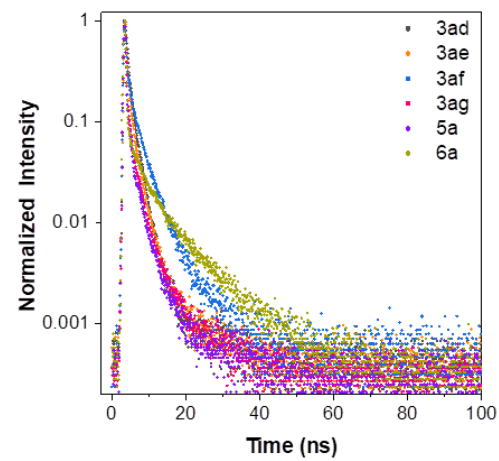
**Fig. S39** Fluorescence decay curves of **3h**, **3i**, **3j**, **3k**, **3l**, **3m** and **3n** (in solid state).



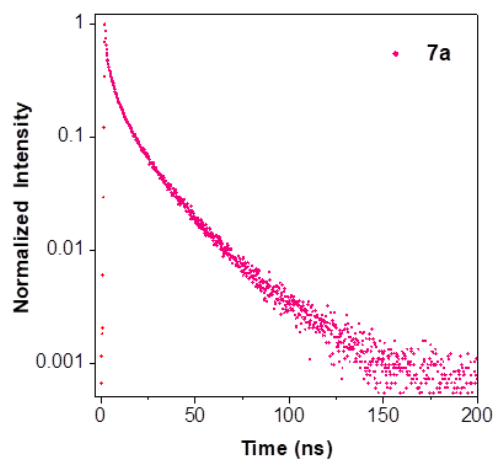
**Fig. S40** Fluorescence decay curves of **3o**, **3p**, **3q**, **3r**, **3s**, **3t** and **3u** (in solid state).



**Fig. S41** Fluorescence decay curves of **3v**, **3w**, **3x**, **3y**, **3aa**, **3ab** and **3ac** (in solid state).



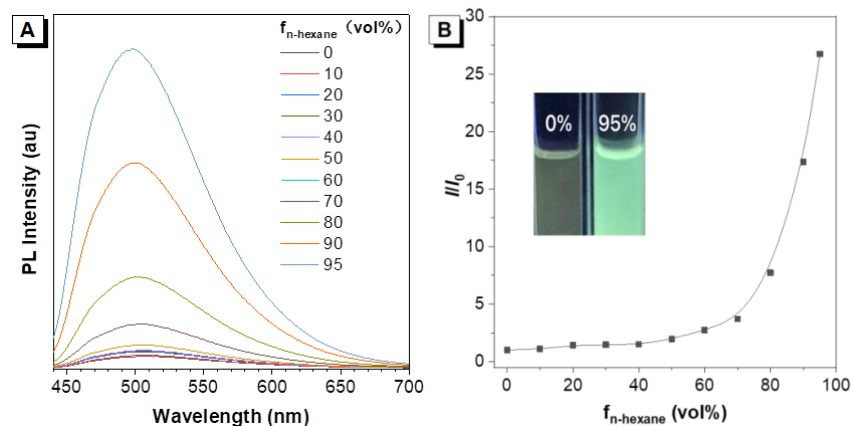
**Fig. S42** Fluorescence decay curves of **3ad**, **3ae**, **3af**, **3ag**, **5a** and **6a** (in solid state).



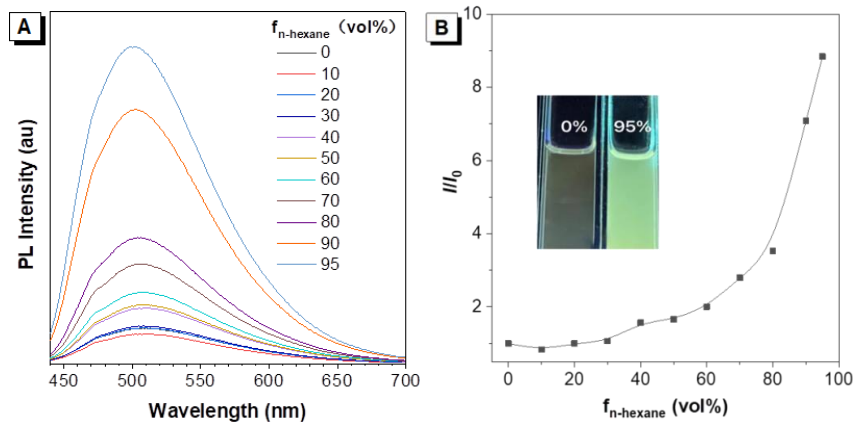
**Fig. S43** Fluorescence decay curves of **7a** (in solid state).

### **Fluorescence properties of some compounds**

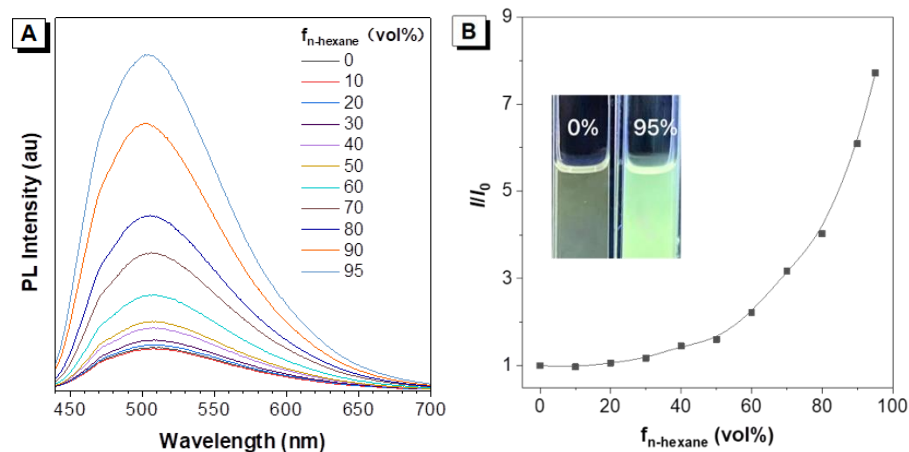
PL spectra of some compounds in good solvents and good/bad solvent mixture with different bad solvent fraction. [compound] =  $1.0 \times 10^{-5}$ M. Fluorescence intensity ratio of  $I/I_0$  in different good/bad solvent mixture.



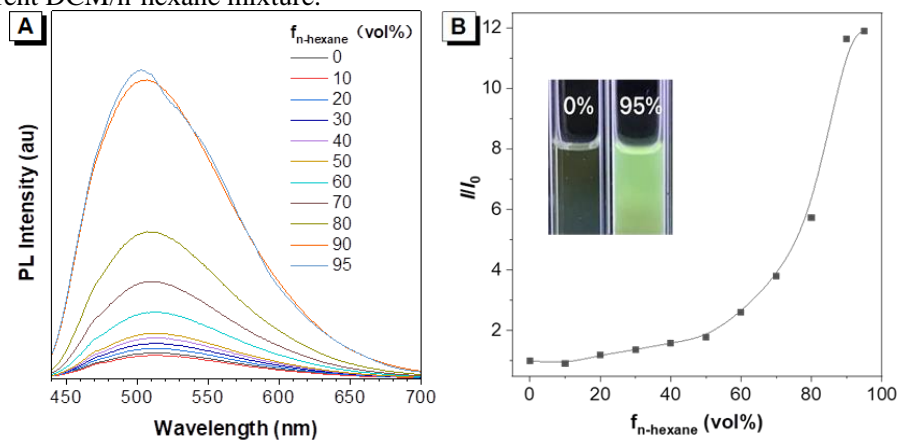
**Fig. S44** (A) PL spectra of **3a** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 412 nm,  $[3a] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



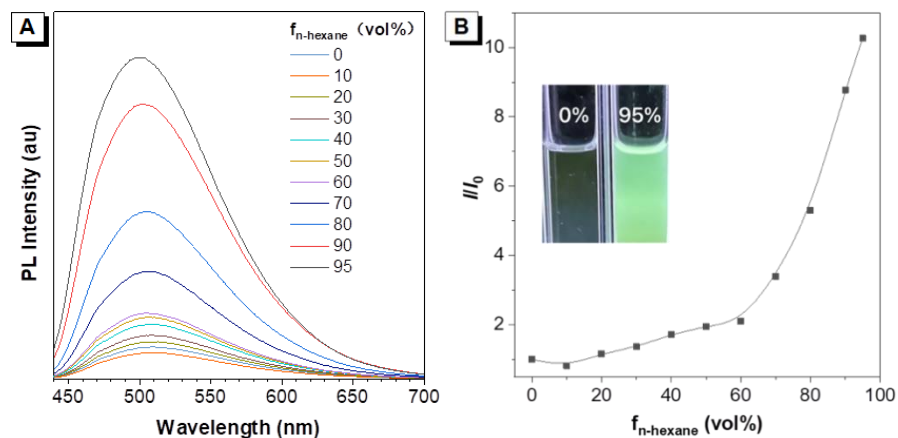
**Fig. S45** (A) PL spectra of **3b** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 415 nm,  $[3b] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



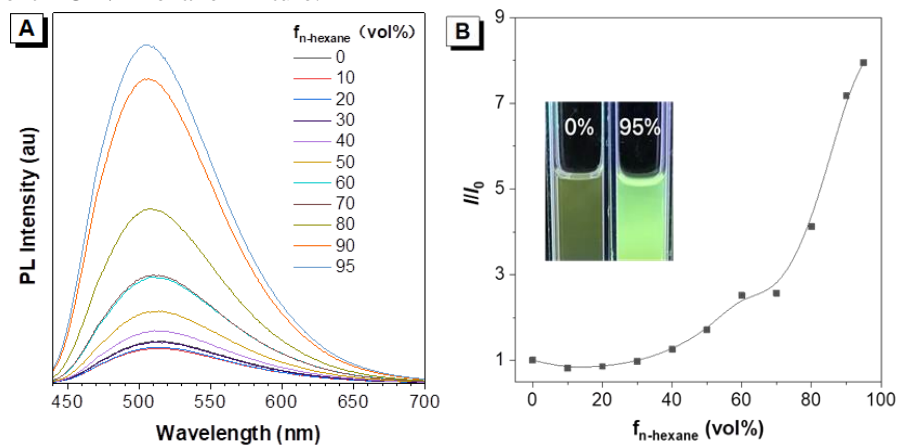
**Fig. S46** (A) PL spectra of **3c** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 414 nm,  $[3c] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



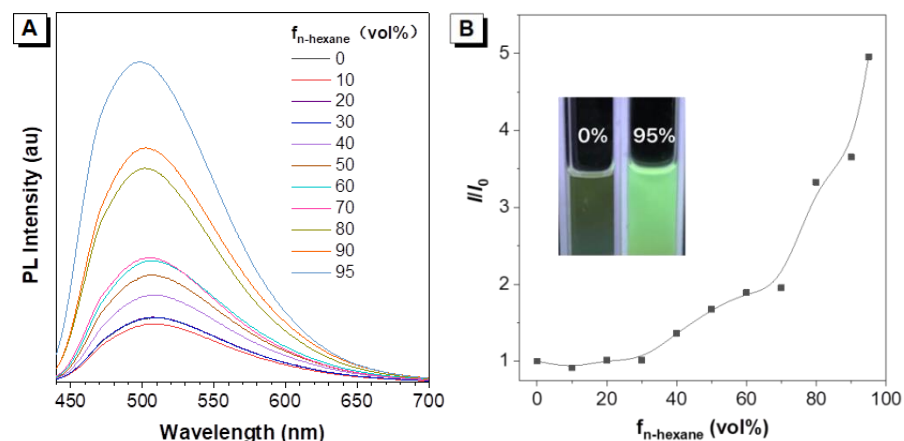
**Fig. S47** (A) PL spectra of **3d** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 412 nm,  $[3d] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



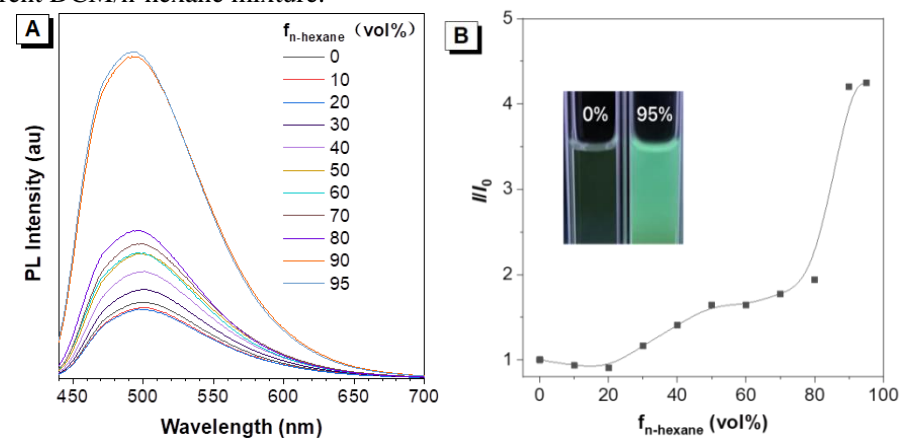
**Fig. S48** (A) PL spectra of **3e** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 414 nm,  $[3e] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



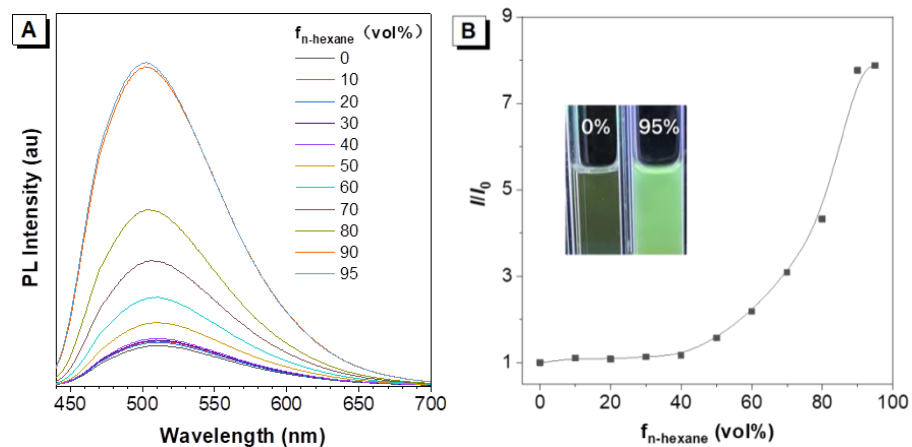
**Fig. S49** (A) PL spectra of **3f** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 414 nm,  $[3f] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



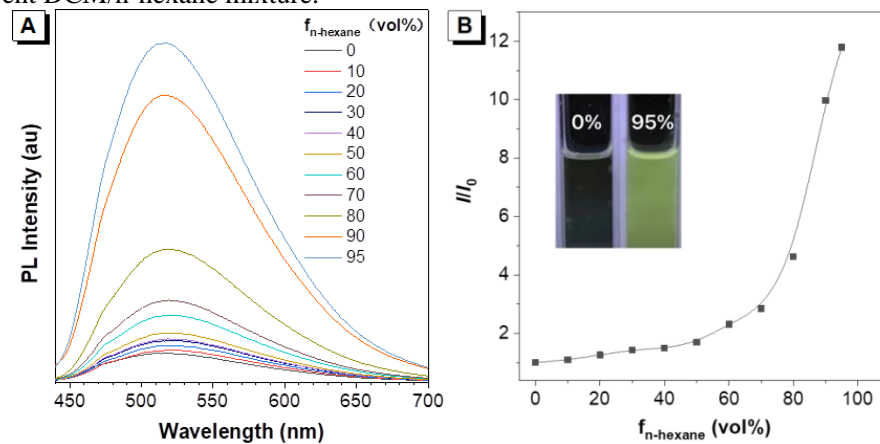
**Fig. S50** (A) PL spectra of **3g** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 415 nm,  $[3g] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



**Fig. S51** (A) PL spectra of **3h** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 413 nm,  $[3h] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.

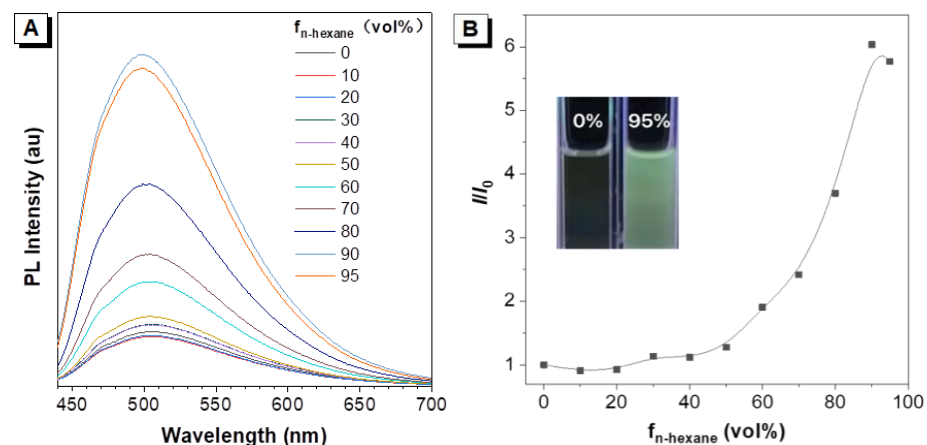


**Fig. S52** (A) PL spectra of **3i** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 413 nm,  $[3i] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.

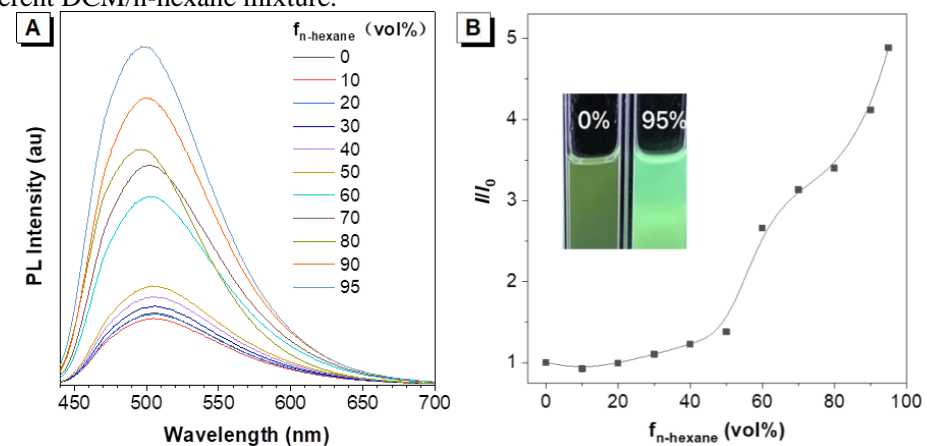


**Fig. S53** (A) PL spectra of **3j** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 413 nm,  $[3j] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.

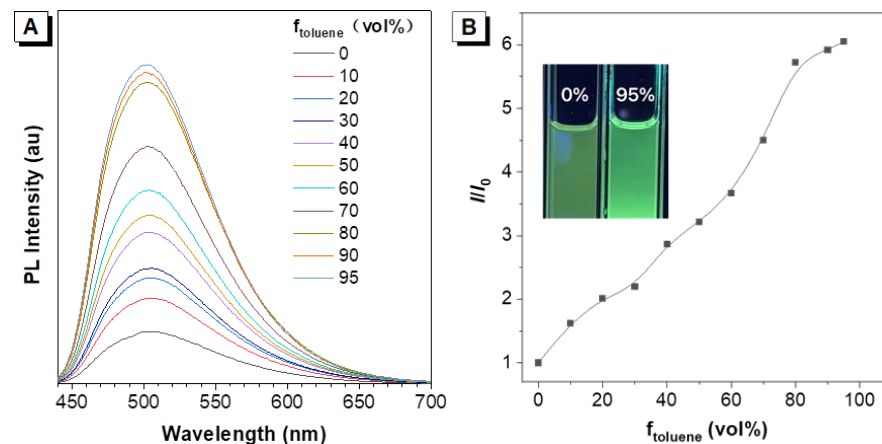




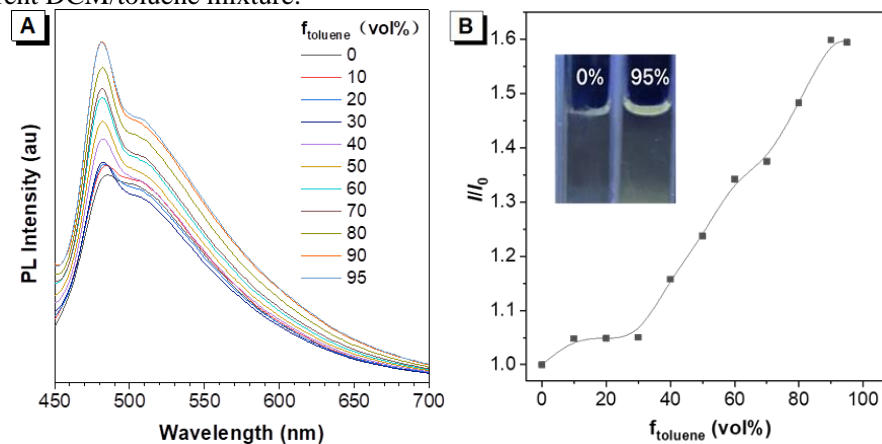
**Fig. S54** (A) PL spectra of **3s** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 411 nm,  $[3s] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



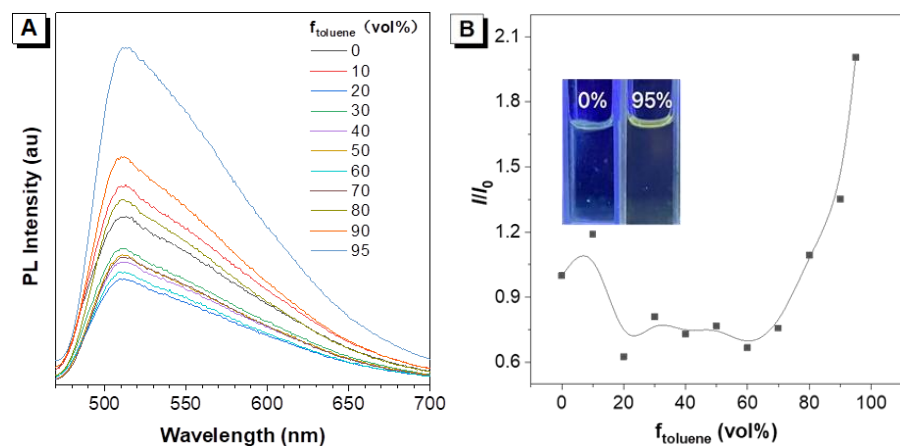
**Fig. S55** (A) PL spectra of **3t** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 414 nm,  $[3t] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



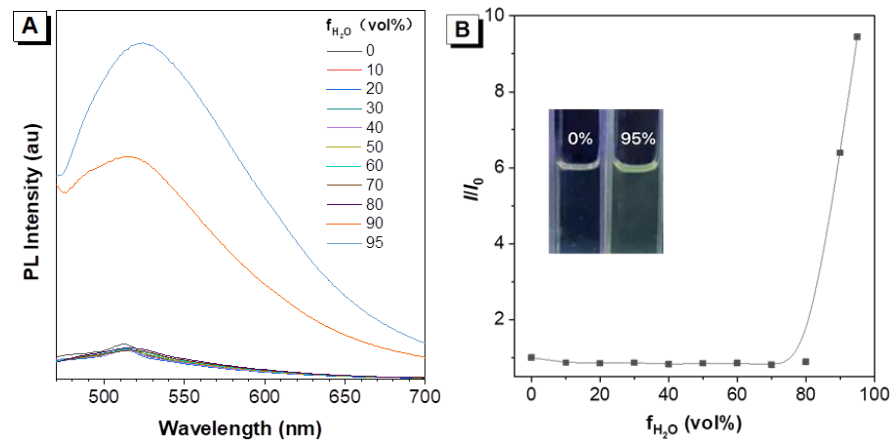
**Fig. S56** (A) PL spectra of **3u** in DCM and DCM/toluene mixture with different toluene fraction. Excitation wavelength: 416 nm,  $[3u] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/toluene mixture.



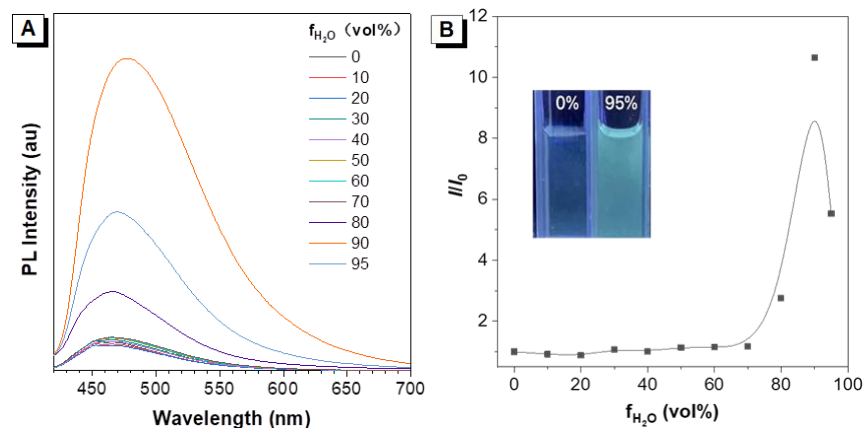
**Fig. S57** (A) PL spectra of **3v** in DCM and DCM/toluene mixture with different toluene fraction. Excitation wavelength: 426 nm,  $[3v] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/toluene mixture.



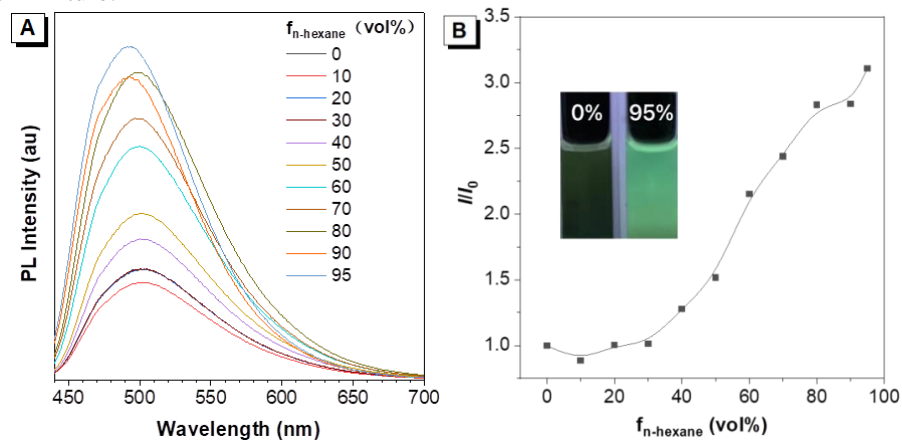
**Fig. S58** (A) PL spectra of **3w** in DCM and DCM/toluene mixture with different toluene fraction. Excitation wavelength: 442 nm,  $[3w] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/toluene mixture.



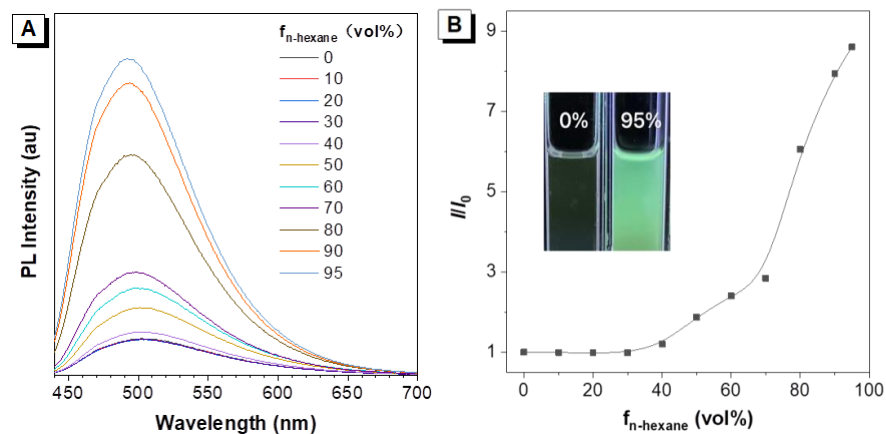
**Fig. S59** (A) PL spectra of **3x** in THF and THF/water mixture with different water fraction. Excitation wavelength: 446 nm,  $[3x] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different THF/water mixture.



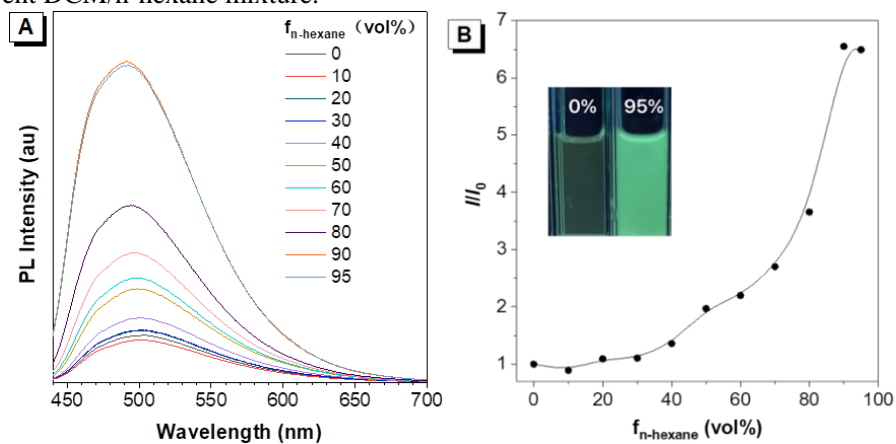
**Fig. S60** (A) PL spectra of **3y** in THF and THF/water mixture with different water fraction. Excitation wavelength: 399 nm,  $[3y] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different THF/water mixture.



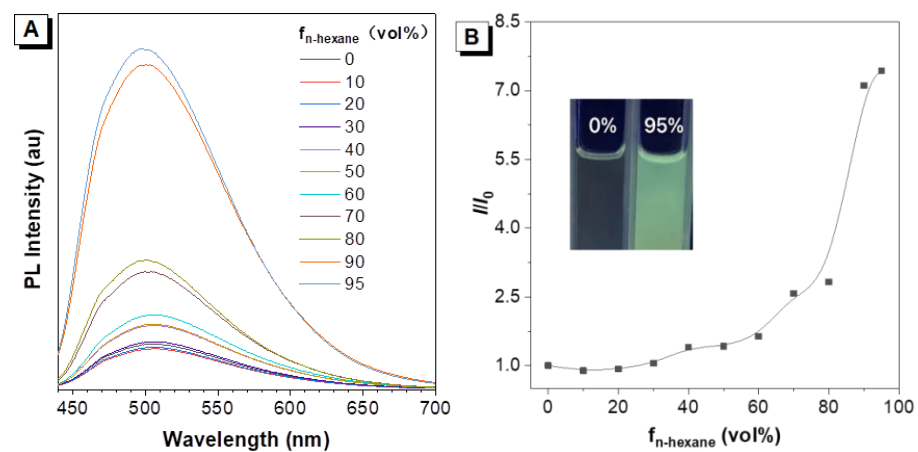
**Fig. S61** (A) PL spectra of **3aa** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 415 nm,  $[3aa] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



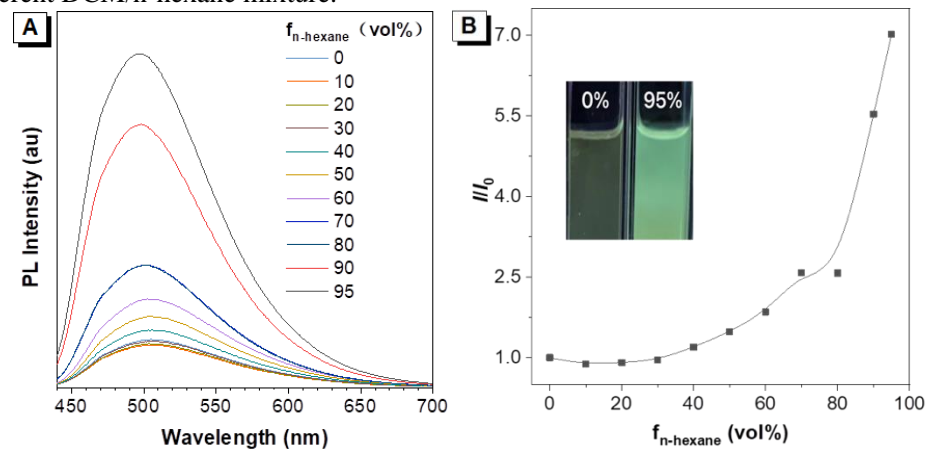
**Fig. S62** (A) PL spectra of **3ab** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 412 nm,  $[\mathbf{3ab}] = 1.0 \times 10^{-5}\text{M}$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



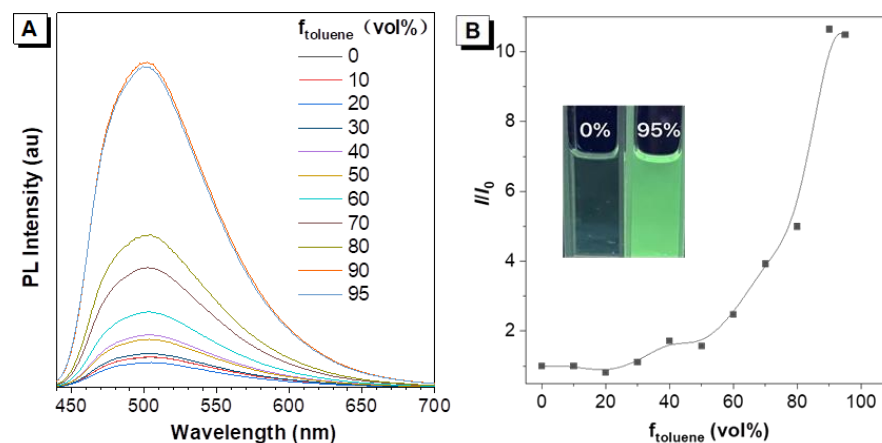
**Fig. S63** (A) PL spectra of **3ae** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 413 nm,  $[\mathbf{3ae}] = 1.0 \times 10^{-5}\text{M}$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



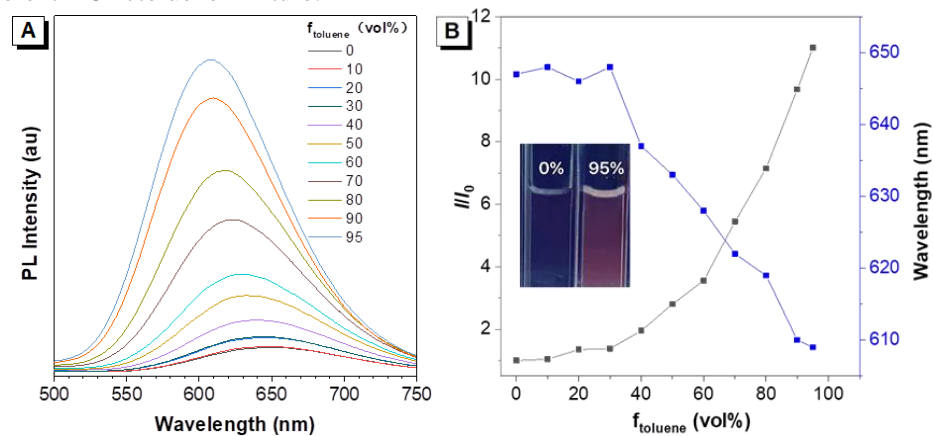
**Fig. S64** (A) PL spectra of **3af** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 412 nm,  $[3af] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



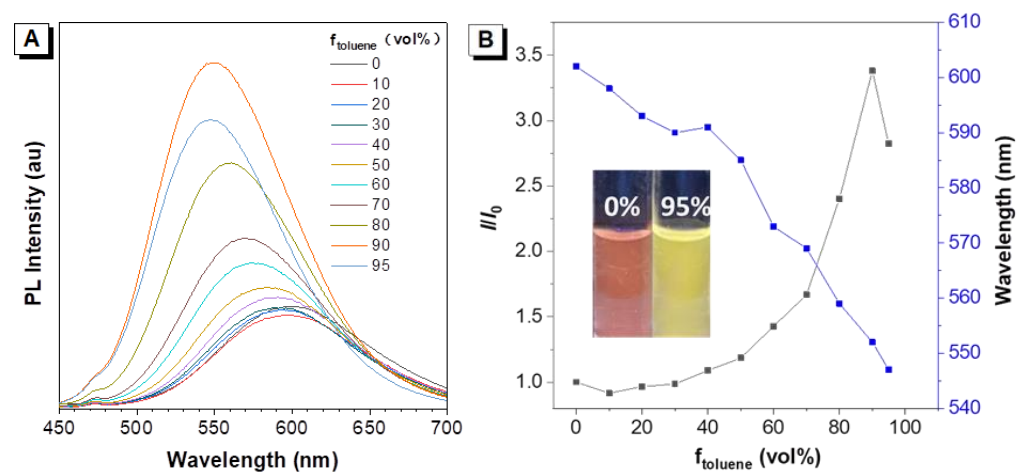
**Fig. S65** (A) PL spectra of **3ag** in DCM and DCM/n-hexane mixture with different n-hexane fraction. Excitation wavelength: 413 nm,  $[3ag] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/n-hexane mixture.



**Fig. S66** (A) PL spectra of **5a** in DCM and DCM/toluene mixture with different toluene fraction. Excitation wavelength: 421 nm,  $[5a] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/toluene mixture.



**Fig. S67** (A) PL spectra of **6a** in DCM and DCM/toluene mixture with different toluene fraction. Excitation wavelength: 413 nm,  $[6a] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  and Wavelength (nm) in different DCM/toluene mixture.

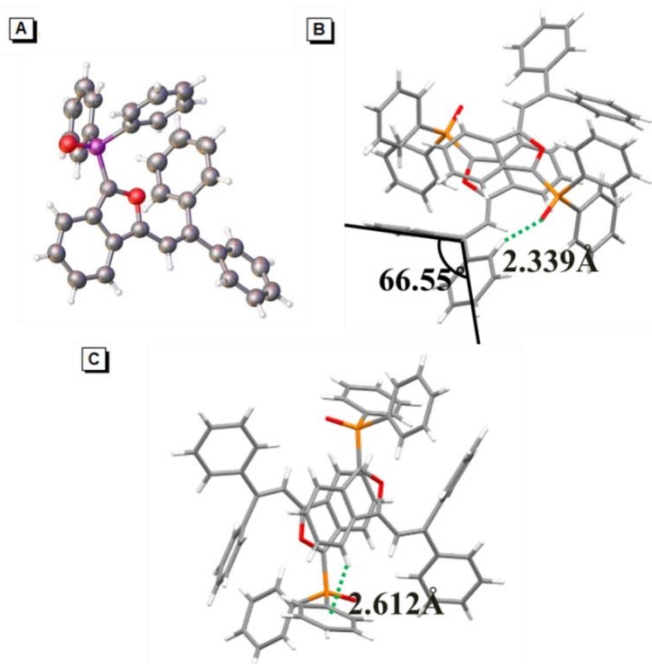


**Fig. S68** (A) PL spectra of **7a** in DCM and DCM/toluene mixture with different toluene fraction. Excitation wavelength: 414 nm,  $[7a] = 1.0 \times 10^{-5}M$ . (B) Fluorescence intensity ratio of  $I/I_0$  in different DCM/toluene mixture.



## Analysis on the Results of Crystalline Structure

The determination and analysis on the single-crystal structure are useful for revealing AIE mechanism. we studied the molecular and packing structure of **3a** and **3j** (Fig. 4 in the main text, and Fig. S69). The dihedral angle between the benzene ring of **3a** and the central double bond is measured at  $66.55^\circ$ , indicating a significantly distorted conformation when packing. Molecular configuration is impeded not only by weak C-H $\cdots$  $\pi$  interactions among molecules but also by hydrogen bonding that restricts intramolecular rotation (Fig. S69), which in turn activates luminescence in AIEgens. In summary, the origin of luminescence in aggregated or solid states can be ascribed to this distorted conformation.

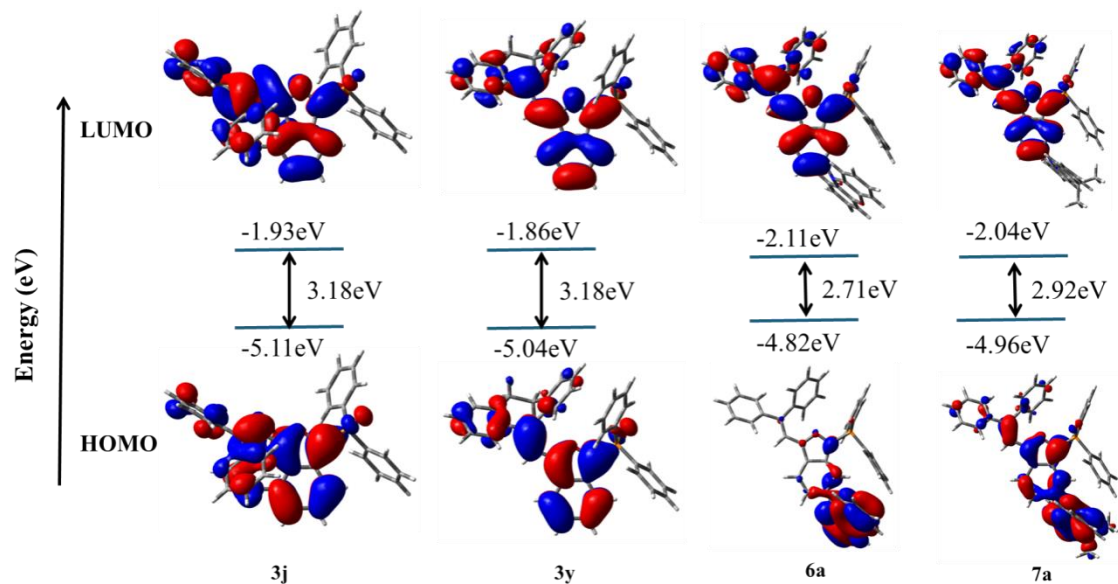


**Fig. S69** (A) Molecular conformation of **3a**. (B) and (C) Side view of packing structure of **3a** crystal.

## More Discussion on Theoretical Calculation

The optimized structure of **3j**, **3y**, **6a** and **7a** were calculated to further comprehend the relationship between optical performance and electronic structure.

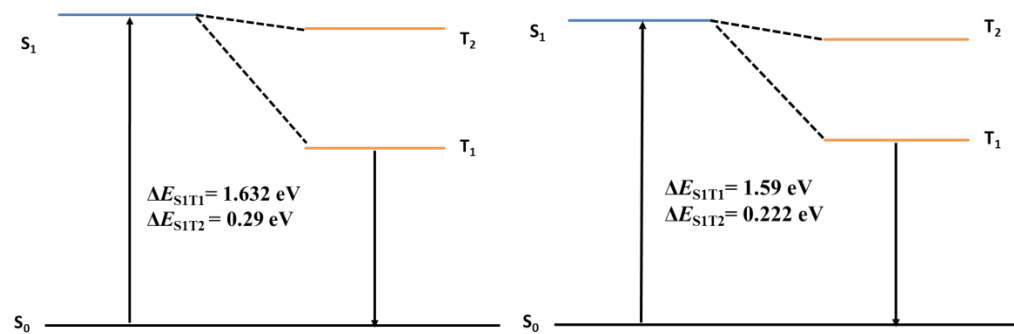
It can be observed in Fig. S70 that, compounds **3j** and **3y** have similar HOMO and LUMO energy levels. And their electron cloud is distributed on the whole molecule, indicating that these two compounds have good molecular conjugation. Therefore, they have similar optical characteristic.



**Fig. S70** Frontier molecular orbitals and energy levels of compounds **3j**, **3y**, **6a** and **7a**.

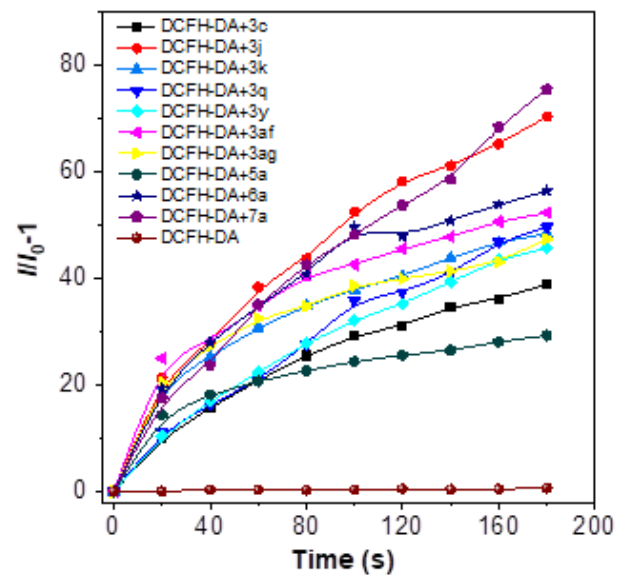
## EST

The energy gap was computed to be 3.18 eV (Figure S72). In addition, the lowest energy gap of singlet and triplet states ( $\Delta E_{S1-T2}$ ) of **3y** was computed to be 0.29 eV and **3j** was computed to be 0.222 eV.

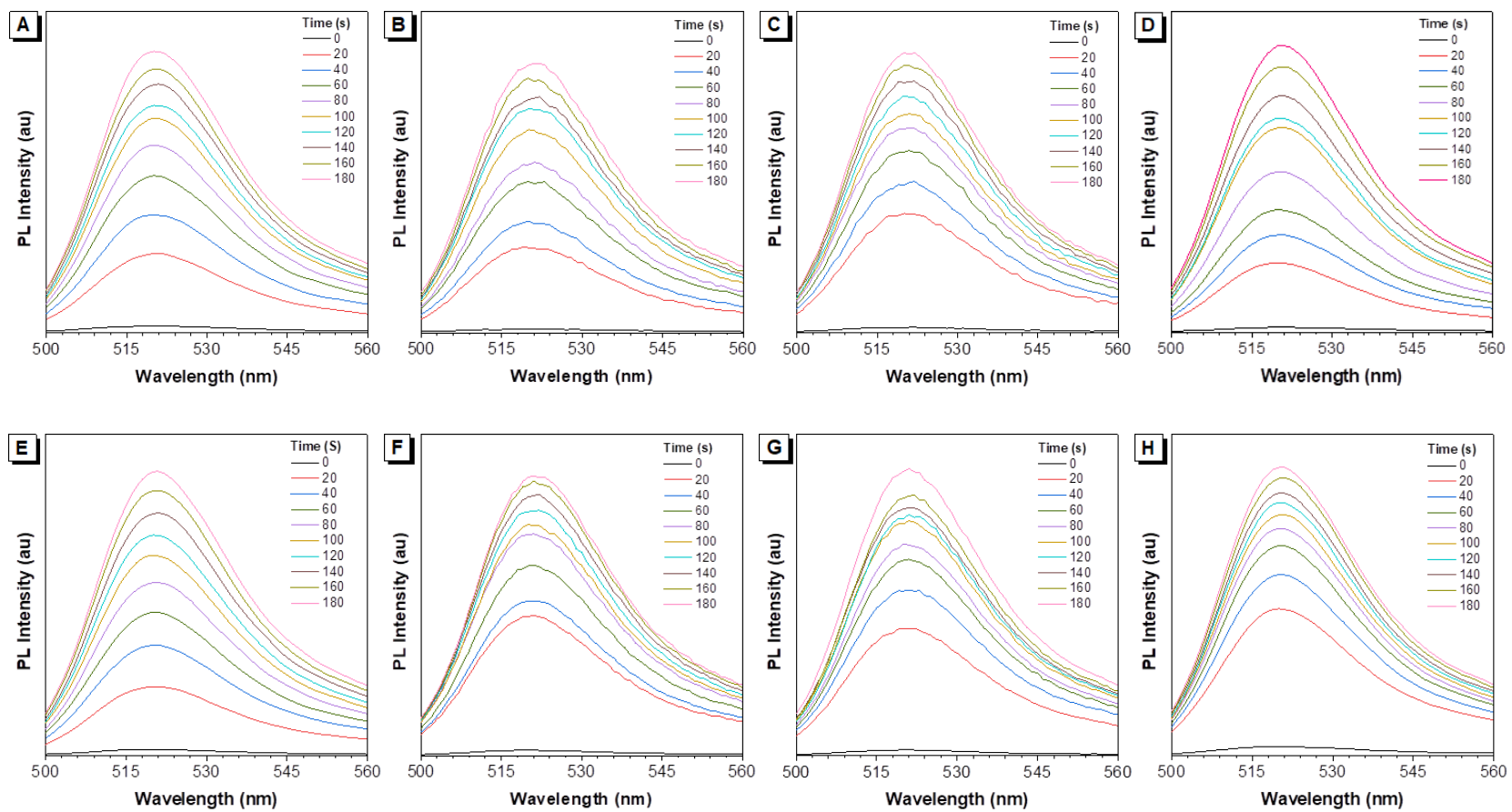


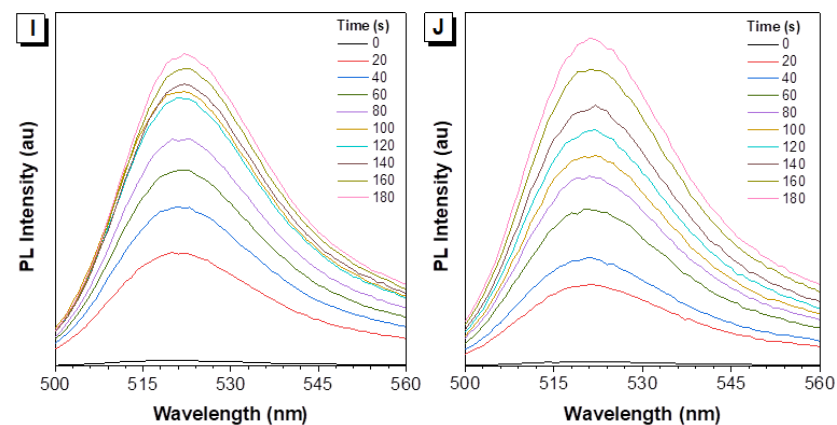
**Fig. S71** Calculated energy level diagram between singlet and triplet states of **3y** and **3j**.

## ROS Detection of IBFPOs

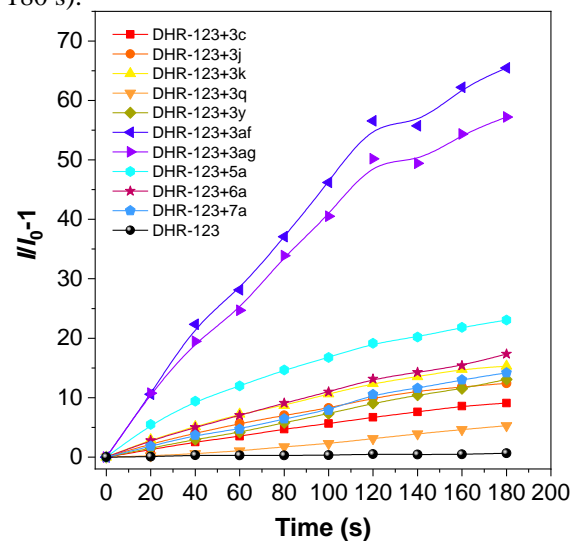


**Fig. S72** Fluorescence intensity ratio of DCFH-DA (10  $\mu$ M) with **3c**, **3j**, **3k**, **3q**, **3y**, **3af**, **3ag**, **5a**, **6a** and **7a** (10  $\mu$ M) ROS detection under white light irradiation for different times.

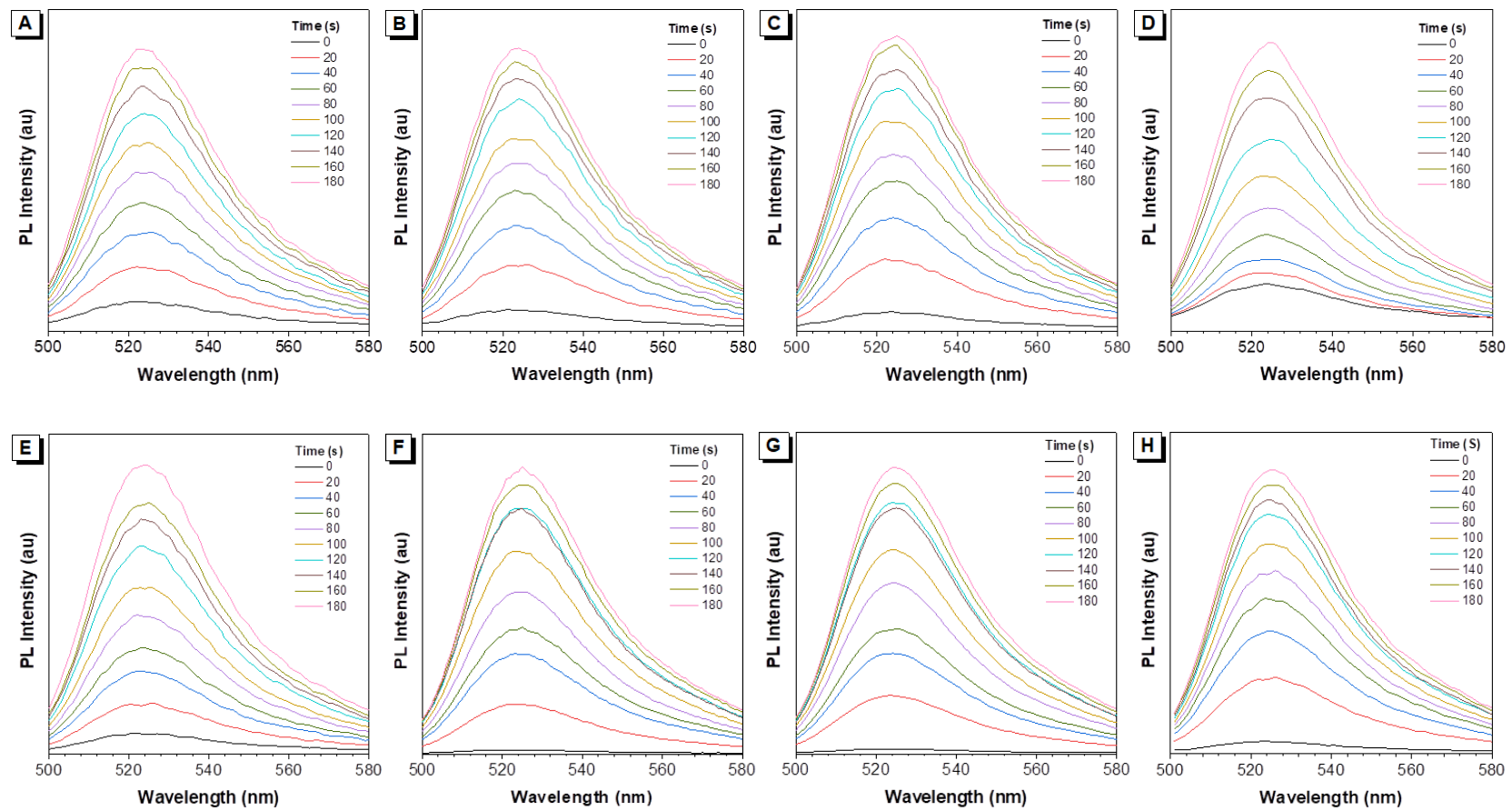


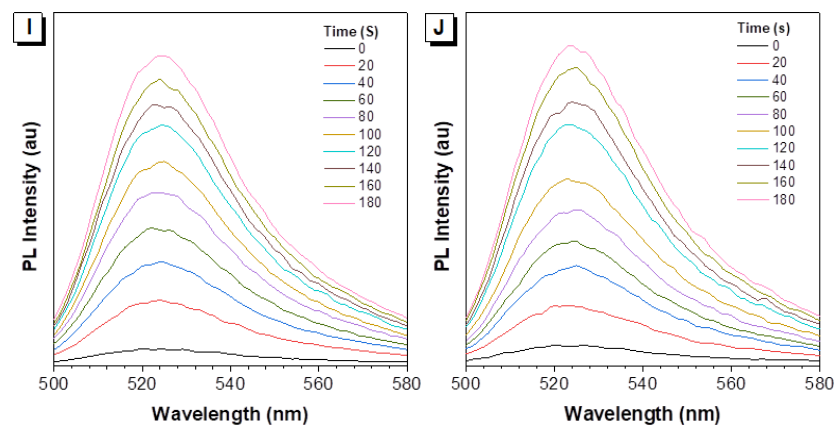


**Fig. S73** PL spectra changes of DCFH-DA (10 μM) in the presence of compounds ( (A) **3c**, (B) **3j**, (C) **3k**, (D) **3q**, (E) **3y**, (F) **3af**, (G) **3ag**, (H) **5a**, (I) **6a**, (J) **7a** (10 μM) ) under white light irradiation for different times (0–180 s).

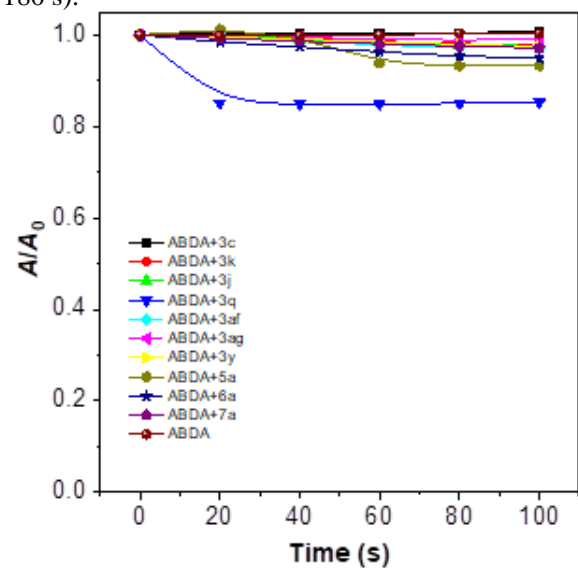


**Fig. S74** Fluorescence intensity ratio of DHR-123 (10 μM) with **3c**, **3j**, **3k**, **3q**, **3y**, **3af**, **3ag**, **5a**, **6a** and **7a** (10 μM) ROS detection under white light irradiation for different times.



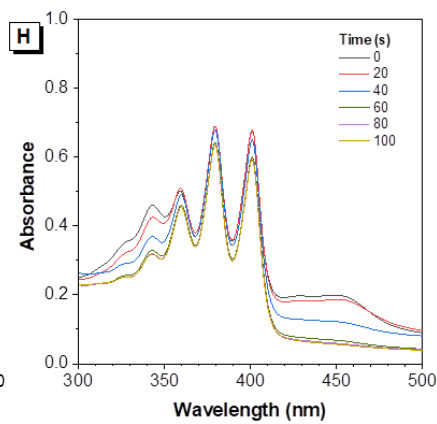
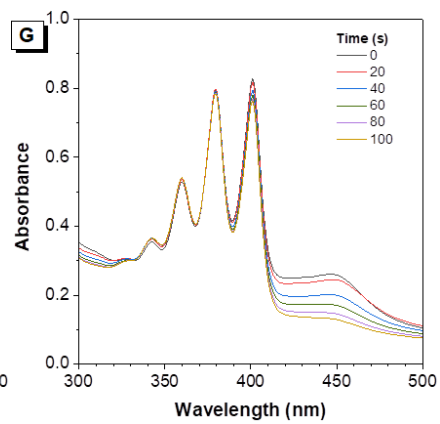
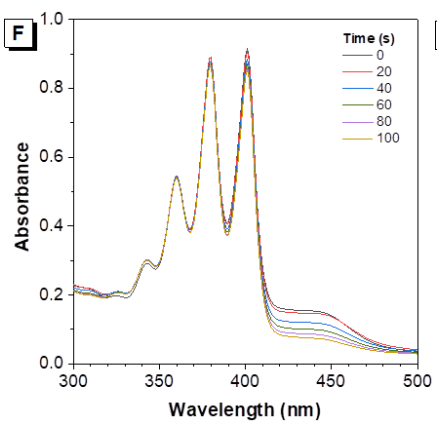
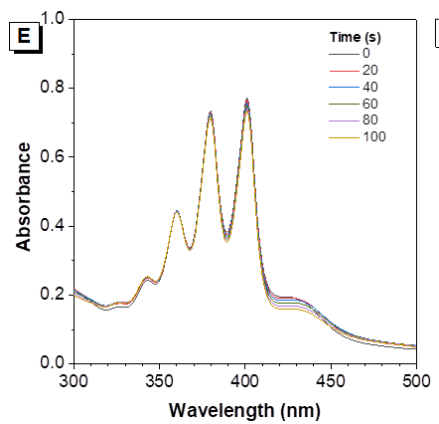
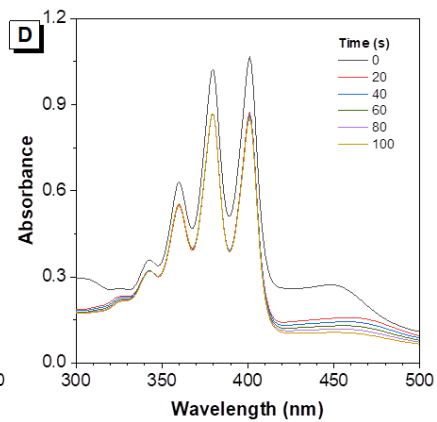
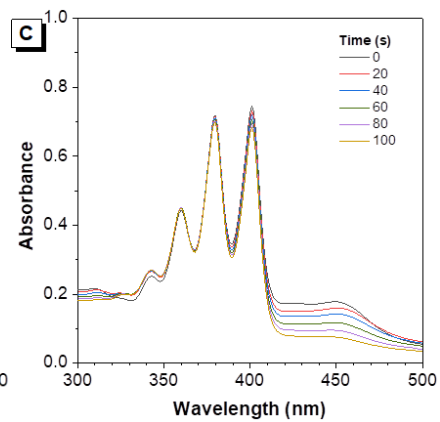
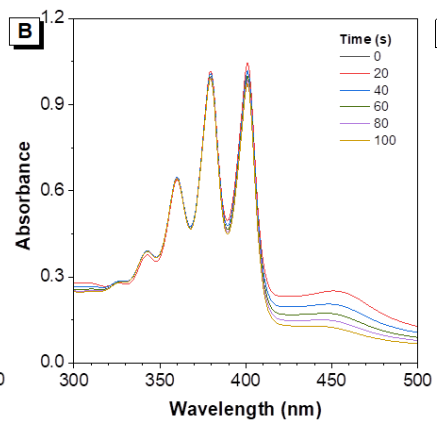
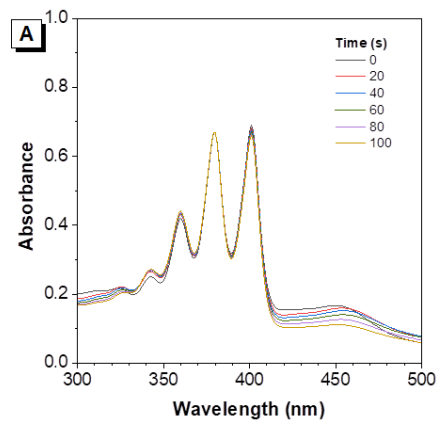


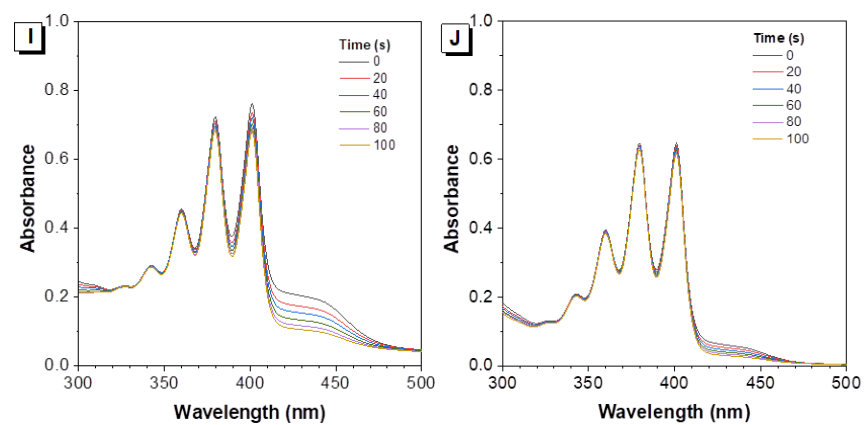
**Fig. S75** PL spectra changes of DHR-123 (10  $\mu\text{M}$ ) in the presence of compounds ( (A) **3c**, (B) **3j**, (C) **3k**, (D) **3q**, (E) **3y**, (F) **3af**, (G) **3ag**, (H) **5a**, (I) **6a**, (J) **7a** (10  $\mu\text{M}$ ) under white light irradiation for different times (0–180 s).



**Fig. S76** Decomposition rates of ABDA (50  $\mu\text{M}$ ) with **3c**, **3j**, **3k**, **3q**, **3y**, **3af**, **3ag**, **5a**, **6a** and **7a** (10  $\mu\text{M}$ ) under white light irradiation for different times.

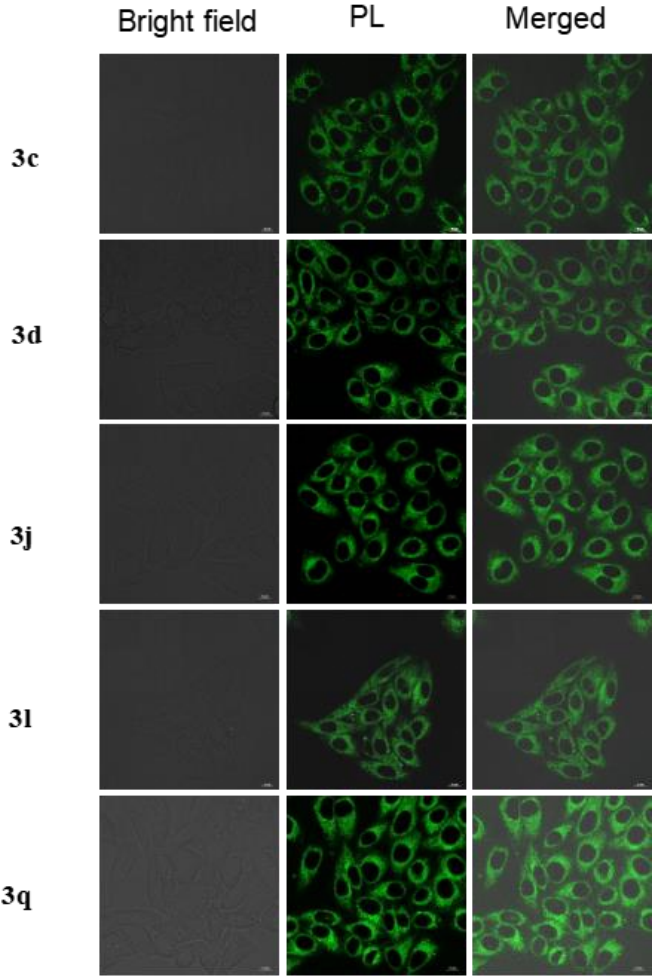


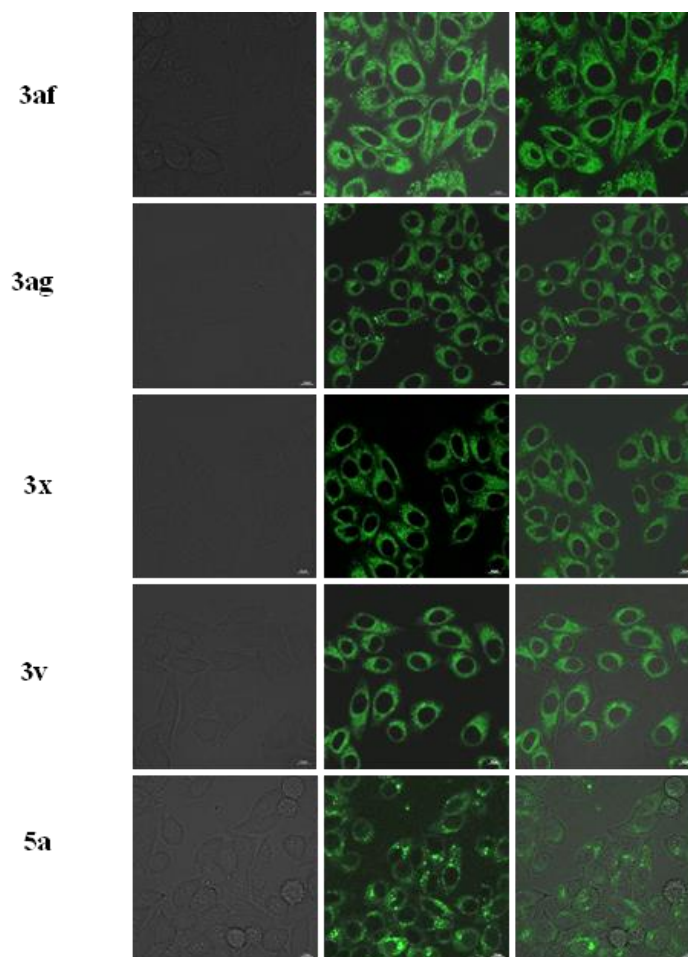




**Fig. S77** Absorbance spectra changes of ABDA (50  $\mu\text{M}$ ) in the presence of compounds ( (A) **3c**, (B) **3j**, (C) **3k**, (D) **3q**, (E) **3y**, (F) **3af**, (G) **3ag**, (H) **5a**, (I) **6a**, (J) **7a** (10  $\mu\text{M}$ ) ) under white light irradiation for different times (0–100 s).

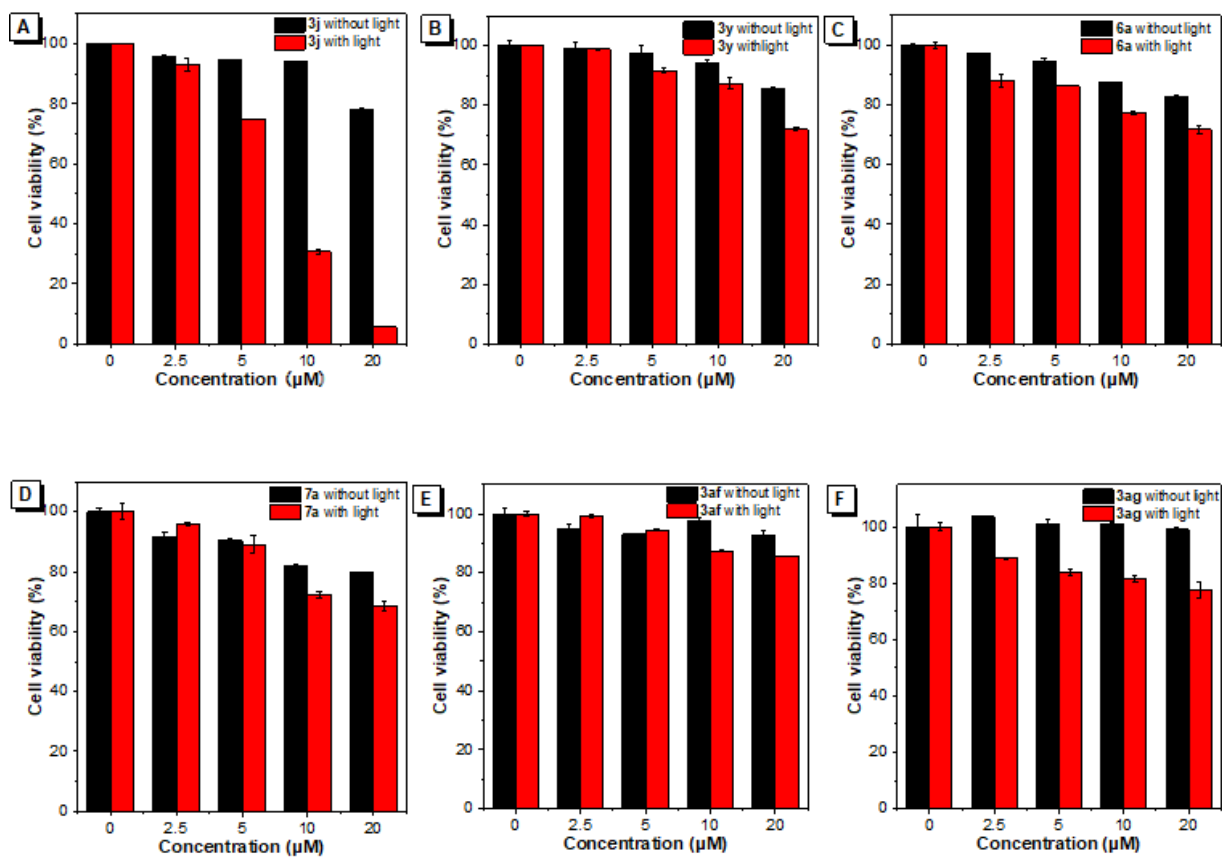
# Cell imaging of IBFPOs





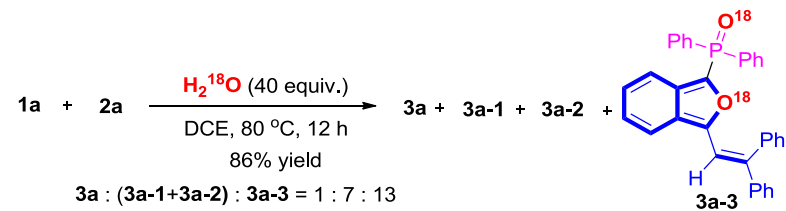
**Fig. S78** Fluorescence images of HeLa cells incubated with **3c** (10  $\mu$ M), **3d** (10  $\mu$ M), **3j** (5  $\mu$ M), **3l** (10  $\mu$ M), **3q** (5  $\mu$ M), **3af** (10  $\mu$ M), **3ag** (10  $\mu$ M), **3x** (10  $\mu$ M), **3v** (10  $\mu$ M) and **5a** (10  $\mu$ M) for 4 h.

## CCK-8 assay of IBFPOs



**Fig. S79** CCK-8 assays of HeLa cells treated with various concentrations of (A) **3j**, (B) **3y**, (C) **6a**, (D) **7a**, (E) **3af** and (F) **3ag** under dark and white light irradiation, respectively.

# H<sub>2</sub>O<sup>18</sup> Experiment:



20230803-3AX-POS #3279 RT: 7.0632 AV: 1 NL: 2.36E8  
T: FTMS + p ESI Full ms [100.0000-1500.0000]

