

## Electronic Supplementary Information

for

### Visible-light-induced denitrogenative phosphorylation of benzotriazinones: a metal- and additive-free method for accessing *ortho*-phosphorylated benzamide derivatives

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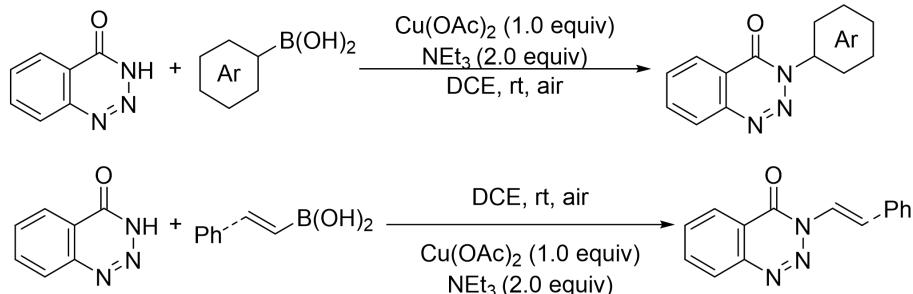
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## 1. General information.

All reactions were carried out under dry argon. all reagents and solvents were obtained from commercial suppliers and used without further purification.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were measured on Bruker AV 500M spectrometers with  $\text{CDCl}_3$  as solvent and tetramethylsilane (TMS) as internal standard for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, 85%  $\text{H}_3\text{PO}_4$  as external standard for  $^{31}\text{P}$  NMR spectra. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets), coupling constants in Hertz (Hz). The products were purified by column chromatography on silica gel 300-400 mesh. The unknown products were further characterized by HRMS (FT-ICR-MS) and an electrospray ionization source in positive-ion mode.

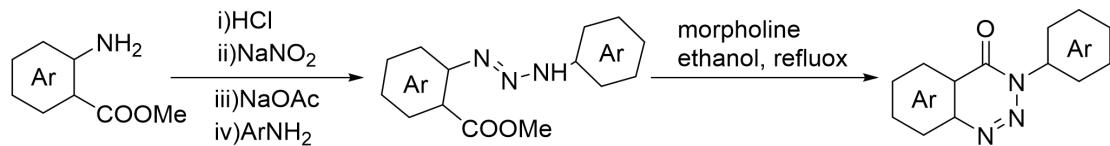
## 2. General preparation of 1,2,3-Benzotriazin-4(3H)-one derivatives.

### Method A: (1a-1c, 1f-1m, 1o-1q, 1s).<sup>1</sup>



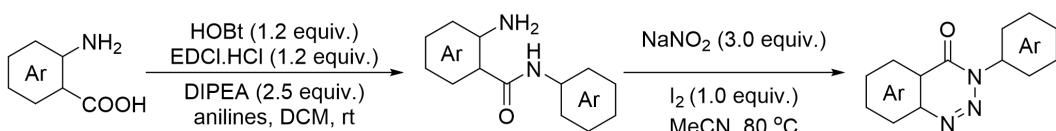
A mixture of the benzo[d][1,2,3]triazin-4(3*H*)-one (5.0 mmol), organoboronic acid (7.5 mmol), anhydrous  $\text{Cu}(\text{OAc})_2$  (5.0 mmol) and  $\text{Et}_3\text{N}$  (10.0 mmol) in DCE (30.0 mL) was stirred at room temperature till the reaction finished (monitored by TLC). The reaction mixture was filtered through celite. The filtrate was collected, concentrated in vacuo, and the residue was purified by chromatography on silica gel using hexane/ethyl acetate to afford the desired product.

### Method B: (1d-1e, 1n, 1r, 1t, 1x).<sup>2</sup>



To a round bottom flask containing methyl anthranilate derivatives (10.0 mmol) were evacuated and purged with argon three times. and then  $\text{HCl(aq)}$  (16.0 mL, 2 M) was added, then stirred at 0 °C for 5 min. A solution of  $\text{NaNO}_2$  (11.7 mmol) in water (5.5 mL) were slowly added within 40 min to the system and then stirred at 0 °C for 30 min. Then, a solution of  $\text{NaOAc}$  (38.6 mmol) in water (12.5 mL) was slowly added within 20 min, followed by addition of corresponding anilines (15.2 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 3 h. The precipitate was collected by filtration, washed with cold water (25.0 ml). The above triazene and morpholine (30.0 mmol) was refluxed in ethanol (75.0 mL) until triazene was completely consumed. The reaction mixture was cooled to -30 °C for crystallization. The product was collected by filtration and washed with cold ethanol to give corresponding products as white solid.

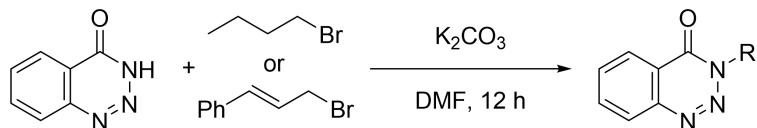
**Method C: (1u-1w, 1y)<sup>3,4</sup>**



To a stirred solution of anthranilic acid derivatives (10.0 mmol) in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) (30.0 mL) was added EDCI • HCl (12.0 mmol), HOBr (12.0 mmol) and aniline derivatives (12.0 mmol) followed by the dropwise addition of DIPEA (25.0 mmol). The reaction mixture was allowed to stir at room temperature until the completion of reaction was monitored by TLC (24 ~ 36 h). After completion, the reaction mixture was diluted with ice water (90.0 mL) followed by the extraction with ethyl acetate (3\*60 mL). The combined organic layer was washed with 1M HCl (100.0 mL) followed by saturated brine solution, dried over  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum. The obtained crude purified by silica gel column chromatograph using petroleum ether/ethyl acetate as the eluent to afford the desired products.

To a stirred solution of 2-amino-N-phenylbenzamide derivative (8 mmol) in MeCN (50.0 mL) were added  $\text{NaNO}_2$  (24.0 mmol) and  $\text{I}_2$  (8.0 mmol) at room temperature and the mixture was then heated at 80 °C for 3 h. then the solvent was removed under vacuum and the residue was diluted with  $\text{H}_2\text{O}$  (200 mL) and extracted with EtOAc (3x80 mL). The combined organic layer was dried over  $\text{Na}_2\text{SO}_4$  and evaporated under reduced pressure. The crude residue was purified by column chromatography over silica gel using petroleum ether/ethyl acetate (4:1, v/v) as the eluent to afford the desired product.

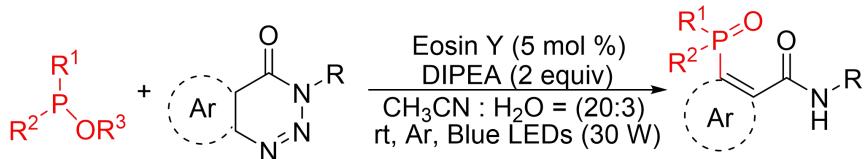
**Method D: (1z).<sup>4</sup>**



A schlenk tube containing 1,2,3-benzotriazin-4(3H)-one (10.0 mmol),  $\text{K}_2\text{CO}_3$  (14.7 mmol) were evacuated and purged with argon three times. Dry DMF (14.7 mL), alkyl bromide (16.2 mmol) were sequentially added to the system at 0 °C. Subsequently, the mixture was stirred at room temperature for 12 h, and then quenched with addition of water (120.0 mL), extracted with ethyl acetate (3\*80 mL). The combined organic layer were washed with brine and dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the residue was purified by flash chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired products.

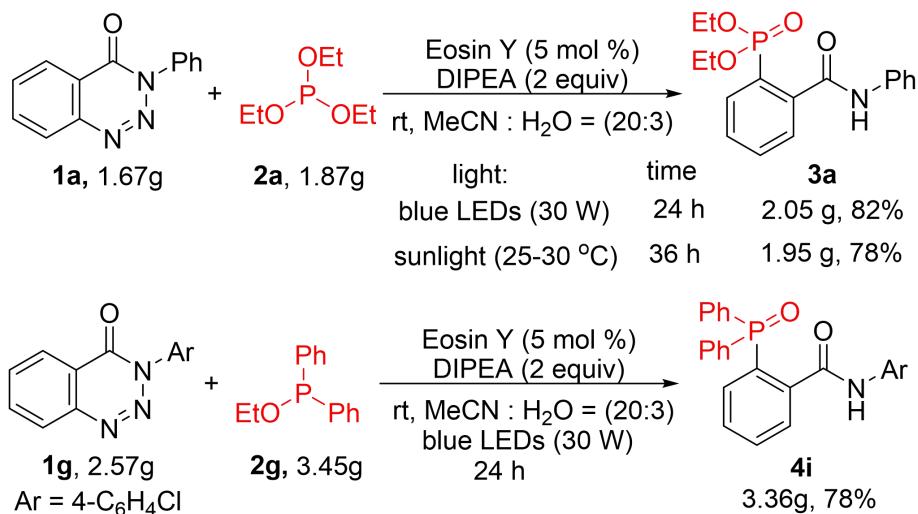
1. K. S. Kumar, R. Adepu, S. Sandra, D. Rambabua, G. R. Krishna, C. M. Reddy, P. Misraa and M. Pal, *Bioorg. Med. Chem. Lett.*, 2012, **22**, 1146-1150.
2. a) Y. Motoshi, M. Masao, M. Tomoya and M. Masahiro, *J. Am. Chem. Soc.*, 2010, **132**, 54- 55; b) A. S. Clark, B. Deans, M. F. G. Stevens, M. J. Tisdale, R. T. Wheelhouse, B. J. Denny and J. A. Hartley, *J. Med. Chem.*, 1995, **38**, 1493-1504; c) V. H. Thorat, N. S. Upadhyay, M. Murakami and C. -H. Cheng, *Adv. Synth. Catal.*, 2018, **360**, 284-289.
3. a) G. C. Senadi, V. S. Kudale and J.-J. Wang, *Green Chem.*, 2019, **21**, 979-985; b) D. S. Barak, S. Mukhopadhyay, D. J. Dahatonde and S. Batra, *Tetrahedron Lett.*, 2019, **60**, 248-251.
4. T. Miura, M. Yamauchi and M. Murakami, *Org. Lett.*, 2008, **10**, 3085-3088.

### 3. General procedure for photoreaction.



Organic-dye-catalyzed denitrogenative phosphorylation of benzotriazinones

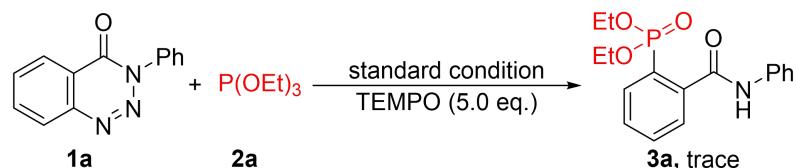
A schlenk tube containing benzotriazinone derivatives (**1**, 0.2 mmol) and eosin Y (0.01 mmol) were evacuated and purged with argon three times. DIPEA (0.4 mmol), phosphorylation reagent (**2**, 0.3 mmol), H<sub>2</sub>O (0.3 mL) and CH<sub>3</sub>CN (2.0 mL) were sequentially added to the system at room temperature. Then the system stirred at room temperature under the irradiation of 30 W blue LEDs for 90 min (or irradiated by sunlight at 25-30 °C for 6 h). Afterwards, the solvent was removed in vacuum, and residues were purified by silica gel column chromatograph using petroleum ether/ethyl acetate as the eluent (2:1) to afford the desired phosphorylation products.



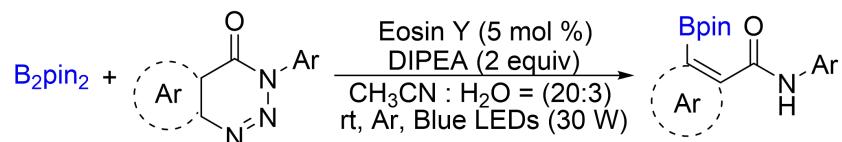
Gram-scale preparation of **3a** and **4i**

A round flask containing benzotriazinone derivatives **1a**, and eosin Y (5 mol %) were evacuated and purged with argon three times. DIPEA (2.0 equiv), phosphorylation reagent **2a** (**2g**) (1.5 equiv) A mixture of H<sub>2</sub>O and CH<sub>3</sub>CN (0.3:2.0) were sequentially added to the system at room temperature. Then the system stirred at room temperature under the irradiation of 30 W blue LEDs for 24 hours (or irradiated by sunlight at 25-30 °C for 36 h). Quenched with addition of potassium carbonate and water (6 mL/1 mmol) to pH = 8.5 and extracted with ethyl acetate (3\*60 mL). The combined organic layer were removed in vacuum, dried over with MgSO<sub>4</sub>. Recrystallization using a petroleum ether/AcOEt mixture as the solvent to afford the desired phosphorylation products.

#### 4. Investigation for reaction mechanism.

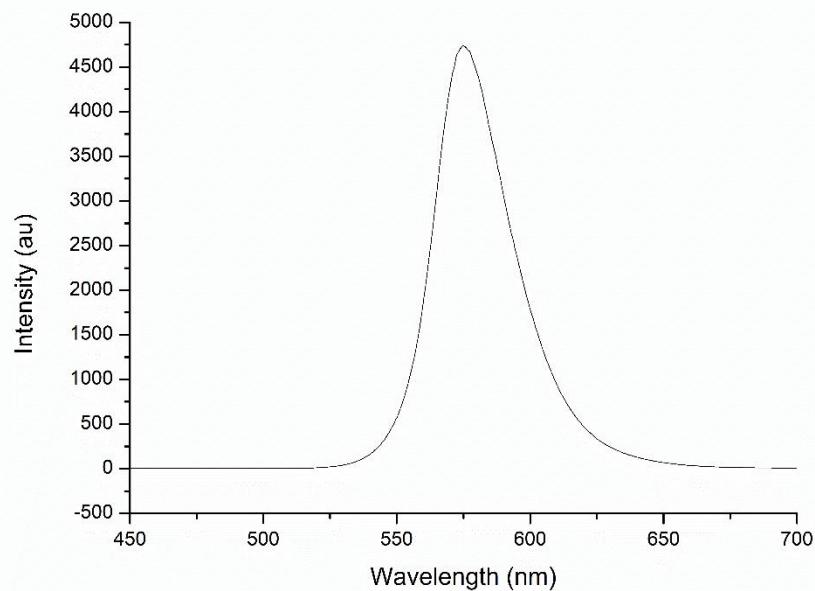


A schlenk tube containing benzotriazinone derivative (**1a**, 0.2 mmol), eosin Y (0.01 mmol) and TEMPO (1.0 mmol) were evacuated and purged with argon three times. DIPEA (0.4 mmol), phosphorylation reagent (**2a**, 0.3 mmol), H<sub>2</sub>O (0.3 mL) and CH<sub>3</sub>CN (2.0 mL) were sequentially added to the system at room temperature. Then the system stirred at room temperature under the irradiation of 30 W blue LEDs for 90 min.

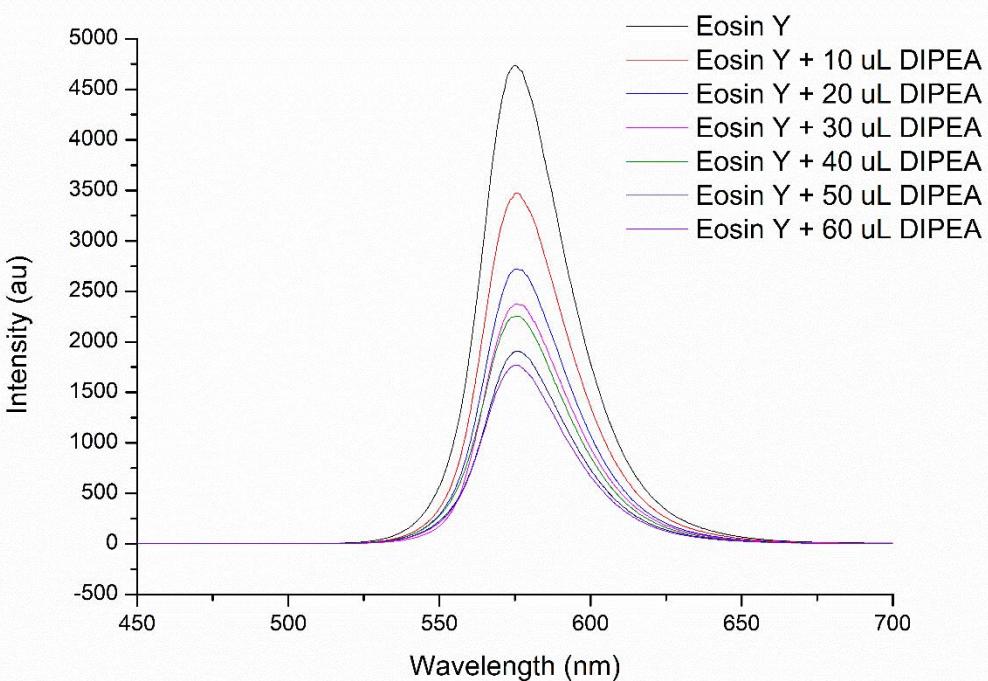


A schlenk tube containing benzotriazinone derivatives (**1**, 0.2 mmol), B<sub>2</sub>pin<sub>2</sub> (**4**, 0.4 mmol) and eosin Y (0.01 mmol) were evacuated and purged with argon three times. DIPEA (0.4 mmol), H<sub>2</sub>O (0.3 mL) and CH<sub>3</sub>CN (2.0 mL) were sequentially added to the system at room temperature. then the system stirred at room temperature under the irradiation of 30 W blue LEDs for 90 min. Remove the solvent under vacuum, residues were purified by silica gel column chromatograph using petroleum ether/ethyl acetate as the eluent (4:1) to afford the desired products.

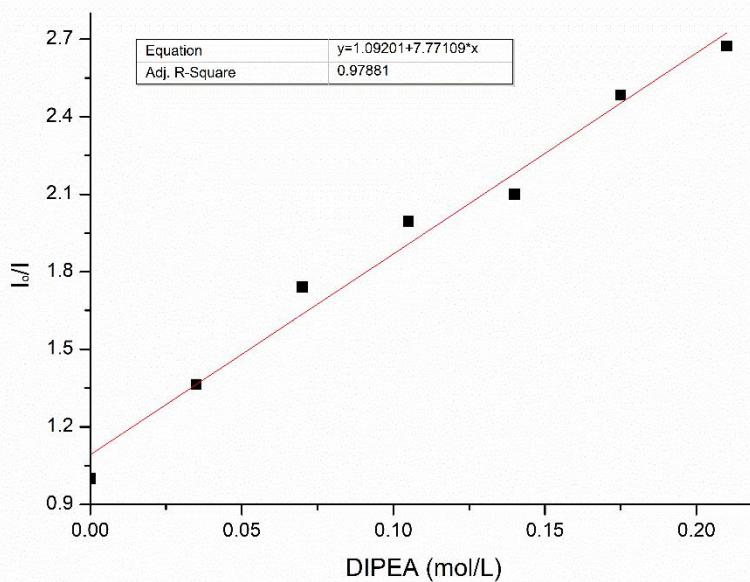
## 5. Luminescence quenching experiments.



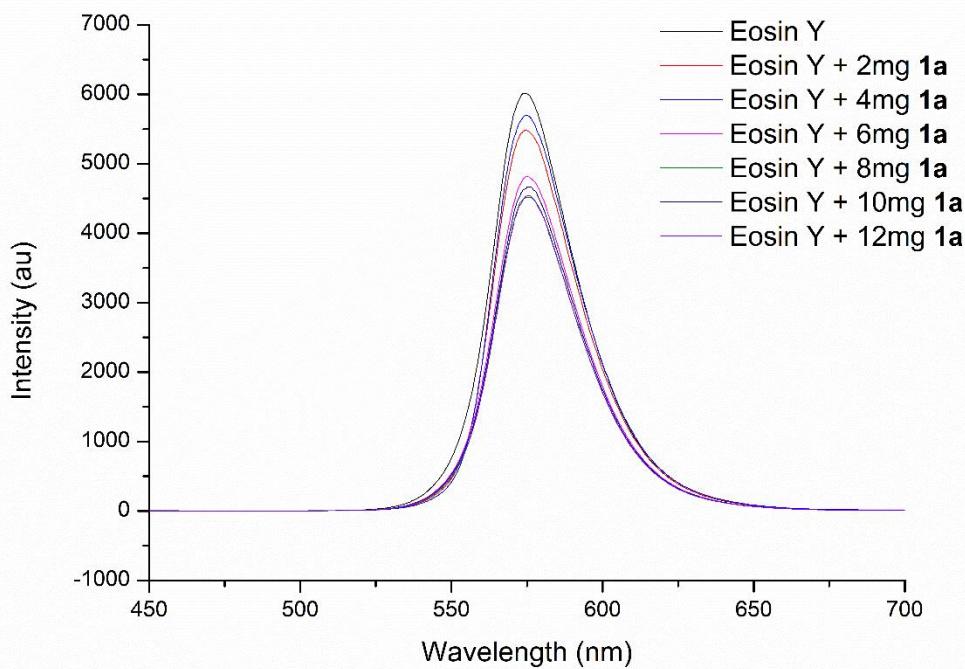
the emission spectra of a  $4.3 \times 10^{-3}$  M solution of eosin Y in degassed CH<sub>3</sub>CN: H<sub>2</sub>O = 20:3 excited at 575 nm;



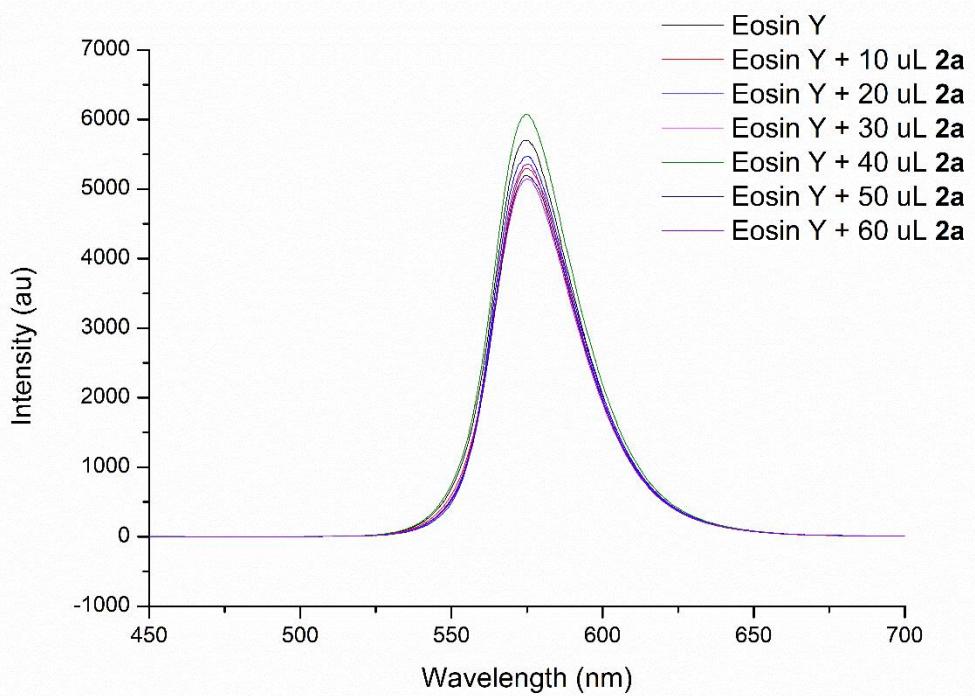
the emission spectra of a  $4.3 \times 10^{-3}$  M solution of eosin Y with various concentrations of DIPEA in degassed CH<sub>3</sub>CN: H<sub>2</sub>O = 20:3 excited at 575 nm;



The Stern–Volmer plot of a  $4.3 \times 10^{-3}$  M solution of eosin Y with various concentrations of DIPEA in degassed  $\text{CH}_3\text{CN}: \text{H}_2\text{O} = 20:3$  excited at 575 nm;



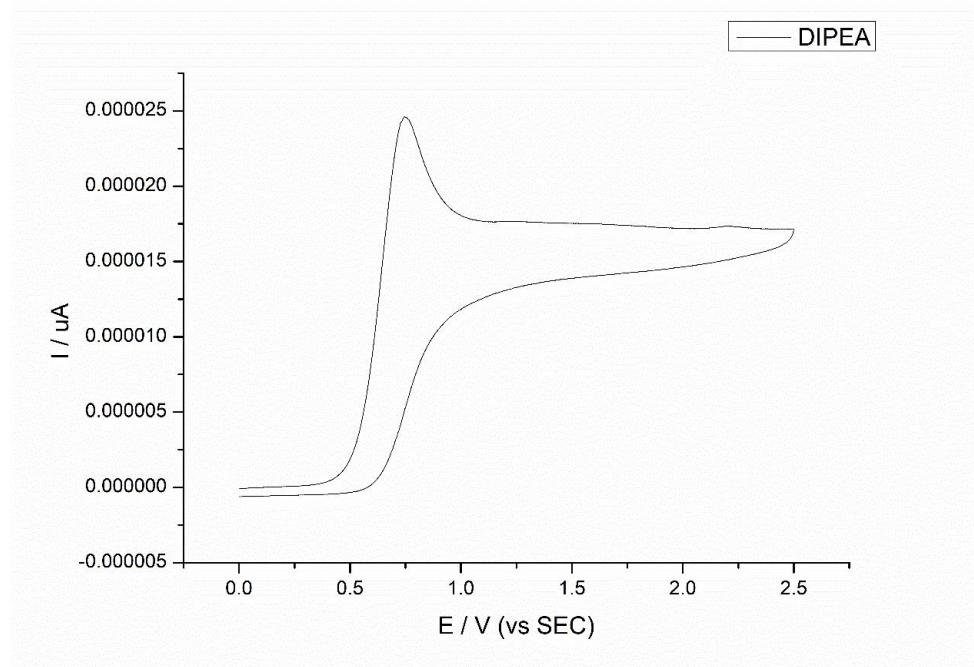
the emission spectra of a  $4.3 \times 10^{-3}$  M solution of eosin Y with various concentrations of **1a** in degassed anhydrous  $\text{CH}_3\text{CN}: \text{H}_2\text{O} = 20:3$  excited at 575 nm;



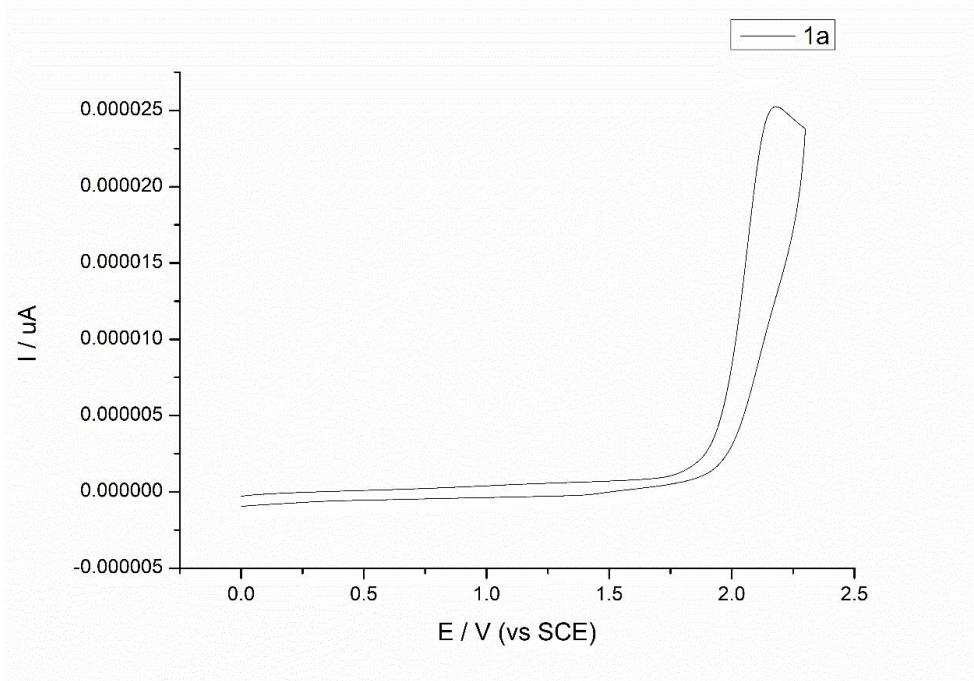
the emission spectra of a  $4.3 \times 10^{-3}$  M solution of eosin Y with various concentrations of **2a** in degassed anhydrous  $\text{CH}_3\text{CN} : \text{H}_2\text{O} = 20:3$  excited at 575 nm.

## 6. Cyclic Voltammetry Studies

The cyclic voltammograms were recorded in an electrolyte of Et<sub>4</sub>NPF<sub>6</sub> (0.1 M) in the indicated solvent (6 mL) using a glassy carbon disk working electrode (diameter, 1 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate was 100 mV/s.



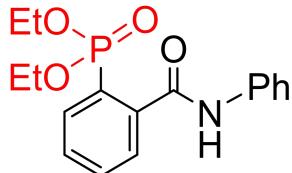
Cyclic voltammogram of DIPEA (10 mM) in MeCN,  $E_{p/2}^{\text{ox}} = 0.63$  V.



Cyclic voltammogram of **1a** (10 mM) in MeCN,  $E_{p/2}^{\text{ox}} = 2.04$  V

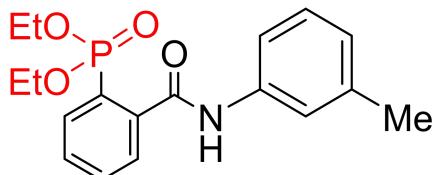
## 7. Characterization for all the products.

### Diethyl (2-(phenylcarbamoyl)phenyl)phosphonate (3a, CAS NO. 41327-48-4)



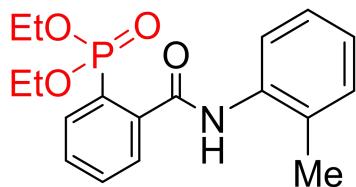
White solid; 60.6 mg, 91% yield; **<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):** δ 9.15 (s, 1H), 7.91-7.86 (m, 2H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.56-7.53 (m, 1H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 4.17-4.12 (m, 4H), 1.28 (t, *J* = 7.3 Hz, 6H); **<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125 MHz):** δ 166.5 (d, *J* = 4.5 Hz), 140.4 (d, *J* = 10.0 Hz), 138.5, 133.0 (d, *J* = 2.2 Hz), 132.8 (d, *J* = 8.9 Hz), 130.8 (d, *J* = 13.2 Hz), 130.3 (d, *J* = 13.8 Hz), 129.2, 125.2 (d, *J* = 187.0 Hz), 124.7, 120.2, 63.5 (d, *J* = 6.7 Hz), 16.4 (d, *J* = 6.7 Hz); **<sup>31</sup>P NMR (CDCl<sub>3</sub>, 202 MHz):** δ 17.78; **IR (film) v<sub>max</sub>:** 2979, 1605, 1679, 1601, 1543, 1441, 1322, 1230, 1142, 1104, 988, 755 cm<sup>-1</sup>; **HRMS:** [M+H]<sup>+</sup> m/z calcd for C<sub>17</sub>H<sub>21</sub>NO<sub>4</sub>P<sup>+</sup> 334.1203, found 334.1205.

### Diethyl (2-(*m*-tolylcarbamoyl)phenyl)phosphonate (3b, new compound)



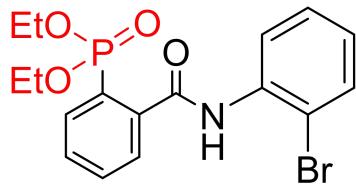
White solid; 60.4 mg, 87% yield; **<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):** δ 9.09 (s, 1H), 7.90-7.85 (m, 2H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.55-7.51 (m, 3H), 7.23 (t, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 4.17-4.13 (m, 4H), 2.35 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H); **<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125 MHz):** δ 166.4 (d, *J* = 5.5 Hz), 140.5 (d, *J* = 10.9 Hz), 139.1, 138.4, 133.0 (d, *J* = 2.6 Hz), 132.7 (d, *J* = 8.3 Hz), 130.8 (d, *J* = 13.2 Hz), 130.2 (d, *J* = 14.3 Hz), 129.0, 125.5, 125.2 (d, *J* = 187.1 Hz), 120.7, 117.2, 63.4 (d, *J* = 6.6 Hz), 21.7, 16.4 (d, *J* = 6.6 Hz); **<sup>31</sup>P NMR (CDCl<sub>3</sub>, 202 MHz):** δ 17.87; **IR (film) v<sub>max</sub>:** 3265, 2982, 1680, 1614, 1511, 1489, 1372, 1025, 970, 780, cm<sup>-1</sup>; **HRMS:** [M+H]<sup>+</sup> m/z calcd for C<sub>18</sub>H<sub>23</sub>NO<sub>4</sub>P<sup>+</sup> 348.1359, found 348.1358.

**Diethyl (2-(*o*-tolylcarbamoyl)phenyl)phosphonate (3c, new compound)**



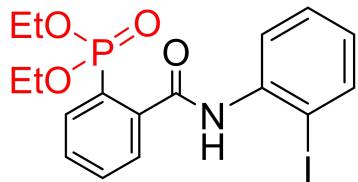
White solid; 59.0 mg, 85% yield;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  8.52 (s, 1H), 8.02 (d,  $J$  = 8.7 Hz, 1H), 7.92 (dd,  $J_1$  = 14.2 Hz,  $J_2$  = 7.6 Hz, 1H), 7.82 (t,  $J$  = 6.2 Hz, 1H), 7.64 (t,  $J$  = 7.6 Hz, 1H), 7.57-7.54 (m, 1H), 7.24 (t,  $J$  = 7.9 Hz, 1H), 7.20 (d,  $J$  = 7.5 Hz, 1H), 7.09 (t,  $J$  = 7.4 Hz, 1H), 4.17-4.13 (m, 4H), 2.31 (s, 3H), 1.30 (t,  $J$  = 7.1 Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  166.8 (d,  $J$  = 4.4 Hz), 140.6 (d,  $J$  = 9.9 Hz), 136.1, 132.97 (d,  $J$  = 3.3 Hz), 132.96 (d,  $J$  = 7.7 Hz), 130.7, 130.20 (d,  $J$  = 13.2 Hz), 130.17, 130.0 (d,  $J$  = 13.6 Hz), 126.8, 125.5, 125.4 (d,  $J$  = 187.1 Hz), 123.1, 63.3 (d,  $J$  = 5.5 Hz), 18.0, 16.4 (d,  $J$  = 6.6 Hz);  **$^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):**  $\delta$  17.57; **IR (film)  $\nu_{\text{max}}$ :** 2983, 1679, 1532, 1488, 1453, 1312, 1024, 981, 752 cm<sup>-1</sup>; **HRMS:** [M+Na]<sup>+</sup> m/z calcd for C<sub>18</sub>H<sub>22</sub>NO<sub>4</sub>PNa<sup>+</sup> 370.1179, found 370.1179.

**Diethyl (2-((2-bromophenyl)carbamoyl)phenyl)phosphonate (3d, CAS NO.: 126391-00-6)**



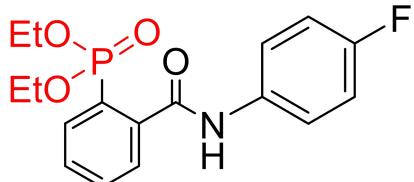
White solid; 67.4 mg, 82% yield;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  8.43 (d,  $J$  = 7.9 Hz, 1H), 8.35 (s, 1H), 8.00 (dd,  $J_1$  = 14.2 Hz,  $J_2$  = 7.6 Hz, 1H), 7.71 (t,  $J$  = 6.7 Hz, 1H), 7.64 (t,  $J$  = 7.6 Hz, 1H), 7.57-7.55 (m, 2H), 7.36 (t,  $J$  = 7.4 Hz, 1H), 7.01 (d,  $J$  = 8.0 Hz, 1H), 4.17-4.11 (m, 4H), 1.28 (t,  $J$  = 6.8 Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  167.1 (d,  $J$  = 5.5 Hz), 140.3 (d,  $J$  = 9.9 Hz), 136.0, 133.7 (d,  $J$  = 8.9 Hz), 132.9 (d,  $J$  = 3.3 Hz), 132.7, 130.3 (d,  $J$  = 13.5 Hz), 129.1 (d,  $J$  = 13.4 Hz), 128.5, 126.0 (d,  $J$  = 187.2 Hz), 125.9, 122.8, 114.4, 63.1 (d,  $J$  = 6.6 Hz), 16.5 (d,  $J$  = 6.6 Hz);  **$^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):**  $\delta$  16.28; **IR (film)  $\nu_{\text{max}}$ :** 2959, 1665, 1588, 1537, 1483, 1432, 1318, 1223, 1167, 1054, 1012, 965, 753 cm<sup>-1</sup>; **HRMS:** [M+Na]<sup>+</sup> m/z calcd for C<sub>17</sub>H<sub>19</sub>BrNO<sub>4</sub>PNa<sup>+</sup> 434.0127, found 434.0127.

**Diethyl (2-((2-iodophenyl)carbamoyl)phenyl)phosphonate (3e, new compound)**



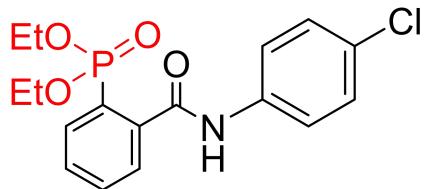
White solid; 74.4 mg, 81% yield;  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  8.27 (d,  $J = 7.9$  Hz, 1H), 8.18 (s, 1H), 8.01 (dd,  $J_1 = 14.0$  Hz,  $J_2 = 7.1$  Hz, 1H), 7.81 (dd,  $J_1 = 8.1$  Hz,  $J_2 = 1.1$  Hz, 1H), 7.75-7.73 (m, 1H), 7.65 (t,  $J = 7.4$  Hz, 1H), 7.59-7.56 (m, 1H), 7.40 (t,  $J = 7.7$  Hz, 1H), 6.91-6.88 (m, 1H), 4.19-4.12 (m, 4H), 1.30 (t,  $J = 7.1$  Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  167.1 (d,  $J = 4.4$  Hz), 140.3 (d,  $J = 9.6$  Hz), 139.2, 138.6, 133.8 (d,  $J = 8.8$  Hz), 132.9 (d,  $J = 3.3$  Hz), 130.3 (d,  $J = 14.3$  Hz), 129.4, 129.0 (d,  $J = 13.3$  Hz), 128.8, 126.1 (d,  $J = 187.2$  Hz), 123.3, 91.1, 63.2 (d,  $J = 6.6$  Hz), 16.5 (d,  $J = 6.6$  Hz);  **$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 202 MHz):**  $\delta$  16.85; **IR (film)  $\nu_{\text{max}}$ :** 2981, 1682, 1583, 1517, 1431, 1300, 1246, 1142, 1019, 970, 753, 1180, 1142, 1075, 960, 752  $\text{cm}^{-1}$ ; **HRMS:**  $[\text{M}+\text{Na}]^+$  m/z calcd for  $\text{C}_{17}\text{H}_{19}\text{INO}_4\text{PNa}^+$  481.9989, found 481.9990.

**Diethyl (2-((4-fluorophenyl)carbamoyl)phenyl)phosphonate (3f, new compound)**



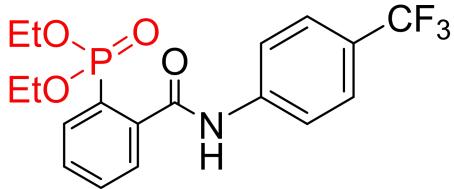
White solid; 56.9 mg, 81% yield;  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  9.32 (s, 1H), 7.87-7.83 (m, 2H), 7.70-7.68 (m, 2H), 7.64-7.62 (m, 1H), 7.55-7.52 (m, 1H), 7.03-7.00 (m, 2H), 4.16-4.10 (m, 4H), 1.28 (t,  $J = 7.3$  Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  166.3 (d,  $J = 5.5$  Hz), 159.6 (d,  $J = 243.2$  Hz), 140.1 (d,  $J = 11.0$  Hz), 134.4 (d,  $J = 2.2$  Hz), 133.0 (d,  $J = 3.3$  Hz), 132.6 (d,  $J = 8.8$  Hz), 130.8 (d,  $J = 13.2$  Hz), 130.3 (d,  $J = 13.3$  Hz), 125.2 (d,  $J = 187.1$  Hz), 121.9 (d,  $J = 7.7$  Hz), 115.8 (d,  $J = 22.1$  Hz), 63.5 (d,  $J = 6.6$  Hz), 16.4 (d,  $J = 6.7$  Hz);  **$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 202 MHz):**  $\delta$  17.80 (d,  $J = 11.4$  Hz); **IR (film)  $\nu_{\text{max}}$ :** 3258, 3065, 2930, 1675, 1616, 1589, 1549, 1509, 1406, 1323, 1158, 1076, 1026, 972, 835, 791, 751  $\text{cm}^{-1}$ ; **HRMS:**  $[\text{M}+\text{Na}]^+$  m/z calcd for  $\text{C}_{17}\text{H}_{19}\text{FNO}_4\text{PNa}^+$  374.0928, found 374.0928.

**Diethyl (2-((4-chlorophenyl)carbamoyl)phenyl)phosphonate (3g, new compound)**



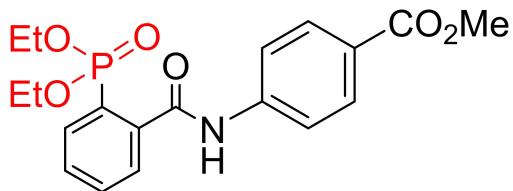
White solid; 58.7 mg, 80% yield;  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  9.44 (s, 1H), 7.87-7.82 (m, 2H), 7.69 (d,  $J$  = 8.8 Hz, 2H), 7.63 (t,  $J$  = 7.6 Hz, 1H), 7.55-7.52 (m, 1H), 7.29 (d,  $J$  = 8.7 Hz, 2H), 4.16-4.11 (m, 4H), 1.28 (t,  $J$  = 7.1 Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  166.4 (d,  $J$  = 4.4 Hz), 140.0 (d,  $J$  = 11.0 Hz), 137.1, 133.0 (d,  $J$  = 3.3 Hz), 132.6 (d,  $J$  = 7.8 Hz), 130.9 (d,  $J$  = 13.2 Hz), 130.4 (d,  $J$  = 13.4 Hz), 129.5, 129.2, 125.2 (d,  $J$  = 187.3 Hz), 121.4, 63.5 (d,  $J$  = 5.5 Hz), 16.4 (d,  $J$  = 6.6 Hz);  **$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 202 MHz):**  $\delta$  17.80; **IR (film)  $\nu_{\text{max}}$ :** 2968, 1680, 1597, 1539, 1493, 1398, 1318, 1233, 1143, 1093, 1025, 970, 829, 652  $\text{cm}^{-1}$ ; **HRMS:**  $[\text{M}+\text{Na}]^+$  m/z calcd for  $\text{C}_{17}\text{H}_{19}\text{ClNO}_4\text{PNa}^+$  390.0632, found 390.0629.

**Diethyl (2-((4-(trifluoromethyl)phenyl)carbamoyl)phenyl)phosphonate (3h, new compound)**



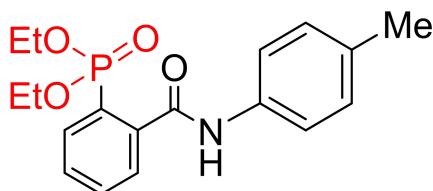
White solid; 62.6 mg, 78% yield;  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  9.77 (s, 1H), 7.87-7.80 (m, 4H), 7.64-7.62 (m, 1H), 7.57-7.52 (m, 3H), 4.16-4.10 (m, 4H), 1.29 (t,  $J$  = 7.0 Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  166.7 (d,  $J$  = 5.4 Hz), 141.6, 139.8 (d,  $J$  = 11.0 Hz), 133.0 (d,  $J$  = 2.1 Hz), 132.6 (d,  $J$  = 8.7 Hz), 130.9 (d,  $J$  = 13.1 Hz), 130.5 (d,  $J$  = 14.5 Hz), 126.4 (q,  $J$  = 3.4 Hz), 126.2 (q,  $J$  = 33.2 Hz), 125.3 (d,  $J$  = 186.8 Hz), 124.4 (q,  $J$  = 271.6 Hz), 119.8, 63.5 (d,  $J$  = 6.5 Hz), 16.4 (d,  $J$  = 6.6 Hz);  **$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 202 MHz):**  $\delta$  17.80 (d,  $J$  = 9.2 Hz); **IR (film)  $\nu_{\text{max}}$ :** 2980, 1682, 1606, 1543, 1409, 1323, 1230, 1113, 1066, 1025, 971, 843, 748  $\text{cm}^{-1}$ ; **HRMS:**  $[\text{M}+\text{Na}]^+$  m/z calcd for  $\text{C}_{18}\text{H}_{19}\text{F}_3\text{NO}_4\text{PNa}^+$  424.0896, found 424.0893.

**Methyl 4-(2-(diethoxyphosphoryl)benzamido)benzoate (3i, new compound)**



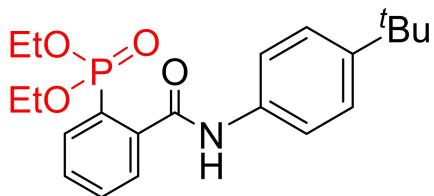
White solid; 66.5 mg, 85% yield;  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  9.64 (s, 1H), 8.00 (d,  $J$  = 8.8 Hz, 2H), 7.89-7.80 (m, 4H), 7.64 (t,  $J$  = 7.8 Hz, 1H), 7.57-7.54 (m, 1H), 4.16-4.11 (m, 4H), 3.89 (s, 3H), 1.28 (t,  $J$  = 7.1 Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  166.9, 166.6 (d,  $J$  = 5.5 Hz), 142.7, 139.9 (d,  $J$  = 10.7 Hz), 133.0 (d,  $J$  = 3.2 Hz), 132.6 (d,  $J$  = 7.7 Hz), 131.01, 130.96 (d,  $J$  = 9.9 Hz), 130.5 (d,  $J$  = 14.0 Hz), 125.9, 125.3 (d,  $J$  = 187.1 Hz), 119.3, 63.5 (d,  $J$  = 6.6 Hz), 52.2, 16.4 (d,  $J$  = 6.6 Hz);  **$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 202 MHz):**  $\delta$  17.84; **IR (film)  $\nu_{\text{max}}$ :** 2974, 1729, 1680, 1602, 1549, 1500, 1442, 1326, 1295, 1251, 1125, 1069, 1022, 970, 759  $\text{cm}^{-1}$ ; **HRMS:**  $[\text{M}+\text{Na}]^+$  m/z calcd for  $\text{C}_{19}\text{H}_{22}\text{NO}_6\text{PNa}^+$  414.1077, found 414.1077.

**Diethyl (2-(*p*-tolylcarbamoyl)phenyl)phosphonate (3j, new compound)**



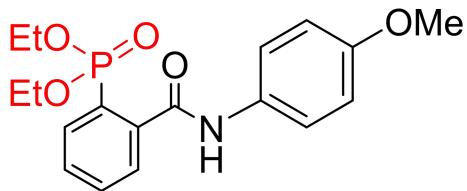
White solid; 62.5 mg, 90% yield;  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  9.06 (s, 1H), 7.92-7.87 (m, 2H), 7.65 (t,  $J$  = 7.8 Hz, 1H), 7.61 (d,  $J$  = 8.3 Hz, 2H), 7.56-7.53 (m, 1H), 7.16 (d,  $J$  = 8.1 Hz, 2H), 4.18-4.13 (m, 4H), 2.33 (s, 3H), 1.30 (t,  $J$  = 7.0 Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  166.3 (d,  $J$  = 4.4 Hz), 140.5 (d,  $J$  = 11.0 Hz), 135.9, 134.3, 133.0 (d,  $J$  = 3.2 Hz), 132.7 (d,  $J$  = 8.9 Hz), 130.9 (d,  $J$  = 13.3 Hz), 130.2 (d,  $J$  = 13.9 Hz), 129.7, 125.2 (d,  $J$  = 187.3 Hz), 120.2, 63.5 (d,  $J$  = 6.6 Hz), 21.2, 16.5 (d,  $J$  = 5.5 Hz);  **$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 202 MHz):**  $\delta$  17.94; **IR (film)  $\nu_{\text{max}}$ :** 2970, 1670, 1603, 1533, 1515, 1405, 1322, 1236, 1142, 1024, 974, 818  $\text{cm}^{-1}$ ; **HRMS:**  $[\text{M}+\text{Na}]^+$  m/z calcd for  $\text{C}_{18}\text{H}_{22}\text{NO}_4\text{PNa}^+$  370.1179, found 370.1180.

**Diethyl (2-((4-(*tert*-butyl)phenyl)carbamoyl)phenyl)phosphonate (3k, new compound)**



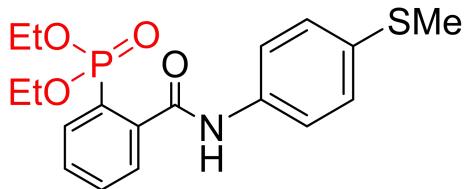
White solid; 66.2 mg, 85% yield;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):** δ 9.06 (s, 1H), 7.91-7.85 (m, 2H), 7.65-7.61 (m, 3H), 7.55-7.52 (m, 1H), 7.37-7.35 (m, 2H), 4.17-4.12 (m, 4H), 1.31 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):** δ 166.3 (d, *J* = 5.5 Hz), 147.6, 140.5 (d, *J* = 11.0 Hz), 135.8, 133.0 (d, *J* = 3.3 Hz), 132.8 (d, *J* = 7.7 Hz), 130.8 (d, *J* = 13.2 Hz), 130.1 (d, *J* = 13.3 Hz), 126.0, 125.2 (d, *J* = 186.7 Hz), 120.0, 63.4 (d, *J* = 6.6 Hz), 34.6, 31.6, 16.4 (d, *J* = 6.6 Hz);  **$^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):** δ 17.33; **IR (film)  $\nu_{\text{max}}$ :** 2960, 1680, 1646, 1602, 1532, 1516, 1404, 1325, 1261, 1021, 834, 754, 648 cm<sup>-1</sup>; **HRMS:** [M+H]<sup>+</sup> m/z calcd for C<sub>21</sub>H<sub>29</sub>NO<sub>4</sub>P<sup>+</sup> 390.1829, found 390.1829.

**Diethyl (2-((4-methoxyphenyl)carbamoyl)phenyl)phosphonate (3l, new compound)**



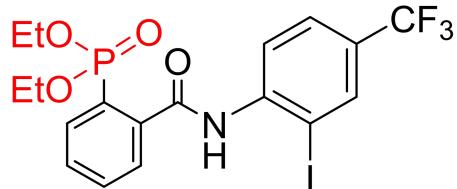
White solid; 62.5 mg, 86% yield;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):** δ 9.05 (s, 1H), 7.91-7.87 (m, 2H), 7.66-7.63 (m, 3H), 7.56-7.53 (m, 1H), 6.91-6.88 (m, 2H), 4.18-4.13 (m, 4H), 3.80 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):** δ 166.2 (d, *J* = 5.5 Hz), 156.7, 140.5 (d, *J* = 9.9 Hz), 133.0 (d, *J* = 2.2 Hz), 132.7 (d, *J* = 7.7 Hz), 131.7, 130.9 (d, *J* = 13.2 Hz), 130.2 (d, *J* = 13.3 Hz), 125.2 (d, *J* = 187.0 Hz), 121.8, 114.4, 63.5 (d, *J* = 6.6 Hz), 55.7, 16.5 (d, *J* = 6.6 Hz);  **$^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):** δ 17.99; **IR (film)  $\nu_{\text{max}}$ :** 3649, 1669, 1510, 1244, 1180, 1142, 1022, 971, 832 cm<sup>-1</sup>; **HRMS:** [M+H]<sup>+</sup> m/z calcd for C<sub>18</sub>H<sub>23</sub>NO<sub>5</sub>P<sup>+</sup> 364.1308, found 364.1306.

**Diethyl (2-((4-(methylthio)phenyl)carbamoyl)phenyl)phosphonate (3m, new compound)**



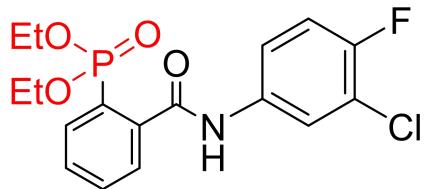
White solid; 62.9 mg, 83% yield;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):** δ 9.25 (s, 1H), 7.87-7.83 (m, 2H), 7.67-7.65 (m, 2H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.54-7.51 (m, 1H), 7.25-7.23 (m, 2H), 4.15-4.10 (m, 4H), 2.46 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):** δ 166.3 (d, *J* = 4.4 Hz), 140.2 (d, *J* = 11.1 Hz), 136.1, 133.8, 133.0 (d, *J* = 3.3 Hz), 132.6 (d, *J* = 8.8 Hz), 130.8 (d, *J* = 13.2 Hz), 130.2 (d, *J* = 13.7 Hz), 128.0, 125.2 (d, *J* = 188.2 Hz), 120.7, 63.4 (d, *J* = 6.6 Hz), 16.8, 16.4 (d, *J* = 6.6 Hz);  **$^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):** δ 17.79; **IR (film)  $\nu_{\text{max}}$ :** 2980, 1670, 1594, 1528, 1496, 1397, 1316, 1232, 1142, 1095, 1022, 972, 819 cm<sup>-1</sup>; **HRMS:** [M+Na]<sup>+</sup> m/z calcd for C<sub>18</sub>H<sub>22</sub>NO<sub>4</sub>PSNa<sup>+</sup> 402.0899, found 402.0896.

**Diethyl (2-((2-iodo-4-(trifluoromethyl)phenyl)carbamoyl)phenyl)phosphonate (3n, new compound)**



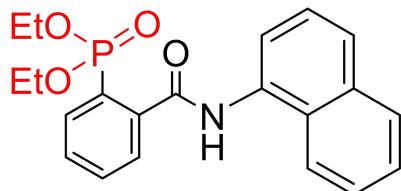
White solid; 79.1 mg, 75% yield;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):** δ 8.46 (d, *J* = 8.4 Hz, 1H), 8.37 (s, 1H), 8.05 (s, 1H), 8.00 (dd, *J*<sub>1</sub> = 14.0 Hz, *J*<sub>2</sub> = 7.6 Hz, 1H), 7.73 (t, *J* = 6.1 Hz, 1H), 7.68-7.64 (m, 2H), 7.61-7.58 (m, 1H), 4.18-4.12 (m, 4H), 1.30 (t, *J* = 7.2 Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):** δ 167.3 (d, *J* = 4.4 Hz), 141.8, 139.8 (d, *J* = 9.9 Hz), 136.2 (q, *J* = 4.4 Hz), 133.7 (d, *J* = 8.8 Hz), 133.0 (d, *J* = 3.2 Hz), 130.6 (d, *J* = 13.2 Hz), 129.0 (d, *J* = 12.1 Hz), 128.1 (q, *J* = 33.3 Hz), 126.6 (q, *J* = 3.3 Hz), 126.2 (d, *J* = 187.0 Hz), 123.1 (q, *J* = 271.7 Hz), 122.3, 89.8, 63.2 (d, *J* = 5.5 Hz), 16.6 (d, *J* = 5.5 Hz);  **$^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):** δ 16.56; **IR (film)  $\nu_{\text{max}}$ :** 3369, 2984, 1689, 1603, 1577, 1521, 1321, 1303, 1245, 1171, 1126, 1023, 970, 750 568 cm<sup>-1</sup>; **HRMS:** [M+H]<sup>+</sup> m/z calcd for C<sub>18</sub>H<sub>19</sub>F<sub>3</sub>INO<sub>4</sub>P<sup>+</sup> 528.0034, found 528.0034.

**Diethyl (2-((3-chloro-4-fluorophenyl)carbamoyl)phenyl)phosphonate (3o, new compound)**



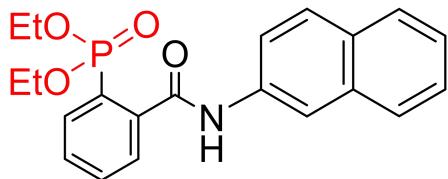
White solid; 60.1 mg, 78% yield;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  9.69 (s, 1H), 7.93 (dd,  $J_1 = 6.7$  Hz,  $J_2 = 2.5$  Hz, 1H), 7.82 (t,  $J = 6.7$  Hz, 1H), 7.78 (dd,  $J_1 = 14.2$  Hz,  $J_2 = 7.7$  Hz, 1H), 7.61 (t,  $J = 7.5$  Hz, 1H), 7.54-7.50 (m, 2H), 7.05 (t,  $J = 8.9$  Hz, 1H), 4.16-4.11 (m, 4H), 1.30 (t,  $J = 7.1$  Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  166.4 (d,  $J = 4.4$  Hz), 154.9 (d,  $J = 246.4$  Hz), 139.8 (d,  $J = 11.0$  Hz), 135.3 (d,  $J = 3.3$  Hz), 132.9 (d,  $J = 2.2$  Hz), 132.6 (d,  $J = 7.8$  Hz), 130.8 (d,  $J = 14.3$  Hz), 130.4 (d,  $J = 14.3$  Hz), 125.3 (d,  $J = 187.1$  Hz), 122.3, 121.1 (d,  $J = 18.8$  Hz), 119.8 (d,  $J = 7.7$  Hz), 116.6 (d,  $J = 22.0$  Hz), 63.5 (d,  $J = 6.6$  Hz), 16.4 (d,  $J = 6.6$  Hz);  **$^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):**  $\delta$  17.64; **IR (film)  $\nu_{\text{max}}$ :** 2960, 1672, 1579, 1514, 1428, 1296, 1250, 1024, 985, 772, 692 cm<sup>-1</sup>; **HRMS:** [M+Na]<sup>+</sup> m/z calcd for C<sub>17</sub>H<sub>18</sub>ClFNO<sub>4</sub>PNa<sup>+</sup> 408.0538, found 408.0536.

**Diethyl (2-(naphthalen-1-ylcarbamoyl)phenyl)phosphonate (3p, new compound)**



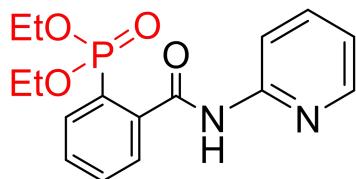
White solid; 62.1 mg, 81% yield;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  9.21 (s, 1H), 8.23 (d,  $J = 7.4$  Hz, 1H), 8.04 (d,  $J = 8.0$  Hz, 1H), 7.98 (dd,  $J_1 = 14.2$  Hz,  $J_2 = 7.7$  Hz, 1H), 7.91 (t,  $J = 6.8$  Hz, 1H), 7.86 (dd,  $J_1 = 6.7$  Hz,  $J_2 = 1.9$  Hz, 1H), 7.72 (d,  $J = 8.8$  Hz, 1H), 7.67 (t,  $J = 7.8$  Hz, 1H), 7.60-7.57 (m, 1H), 7.54-7.46 (m, 3H), 4.18-4.11 (m, 4H), 1.27 (t,  $J = 6.9$  Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  167.4 (d,  $J = 4.4$  Hz), 140.5 (d,  $J = 10.0$  Hz), 134.3, 130.1 (d,  $J = 8.7$  Hz), 130.06 (d,  $J = 3.0$  Hz), 132.97, 130.5 (d,  $J = 13.6$  Hz), 130.2 (d,  $J = 13.9$  Hz), 128.8, 127.3, 126.4, 126.2, 126.0, 125.9, 125.3 (d,  $J = 186.7$  Hz), 121.4, 120.4, 63.4 (d,  $J = 6.4$  Hz), 16.4 (d,  $J = 6.4$  Hz);  **$^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):**  $\delta$  17.87; **IR (film)  $\nu_{\text{max}}$ :** 3253, 3058, 2981, 1679, 1607, 1589, 1550, 1506, 1472, 1394, 1360, 1294, 1233, 1143, 1024, 969, 748 cm<sup>-1</sup>; **HRMS:** [M+H]<sup>+</sup> m/z calcd for C<sub>21</sub>H<sub>23</sub>NO<sub>4</sub>P<sup>+</sup> 384.1359 found 384.1359.

**Diethyl (2-(naphthalen-2-ylcarbamoyl)phenyl)phosphonate (3q, new compound)**



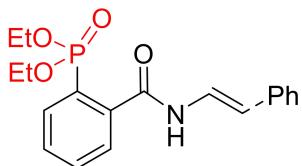
White solid; 56.7 mg, 74% yield;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  9.48 (s, 1H), 8.47 (d,  $J$  = 1.1 Hz, 1H), 7.94 (t,  $J$  = 6.4 Hz, 1H), 7.90 (dd,  $J_1$  = 14.3 Hz,  $J_2$  = 7.7 Hz, 1H), 7.84 (d,  $J$  = 8.1 Hz, 1H), 7.81 (d,  $J$  = 8.8 Hz, 1H), 7.79 (d,  $J$  = 8.2 Hz, 1H), 7.69-7.65 (m, 2H), 7.58-7.55 (m, 1H), 7.46 (t,  $J$  = 7.5 Hz, 1H), 7.40 (t,  $J$  = 7.5 Hz, 1H), 4.19-4.13 (m, 4H), 1.29 (t,  $J$  = 7.1 Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  166.5 (d,  $J$  = 4.4 Hz), 140.3 (d,  $J$  = 10.0 Hz), 136.0, 134.1, 130.0 (d,  $J$  = 3.3 Hz), 132.6 (d,  $J$  = 7.7 Hz), 132.98, 132.97 (d,  $J$  = 13.2 Hz), 130.3 (d,  $J$  = 13.4 Hz), 128.9, 128.1, 127.7, 126.6, 125.3 (d,  $J$  = 187.3 Hz), 125.2, 120.1, 116.9, 63.4 (d,  $J$  = 6.6 Hz), 16.4 (d,  $J$  = 6.6 Hz);  **$^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):**  $\delta$  18.02; **IR (film)  $\nu_{\text{max}}$ :** 3239, 2981, 1674, 1538, 1504, 1395, 1346, 1235, 1142, 1023, 967, 797, 796, 773 cm<sup>-1</sup>; **HRMS:** [M+H]<sup>+</sup> m/z calcd for C<sub>21</sub>H<sub>23</sub>NO<sub>4</sub>P<sup>+</sup> 384.1359 found 384.1359.

**Diethyl (2-(pyridin-2-ylcarbamoyl)phenyl)phosphonate (3r, new compound)**



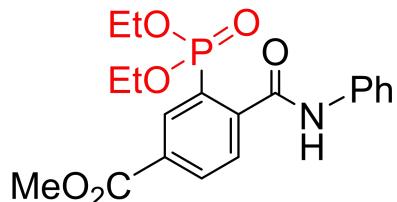
White solid; 54.8 mg, 82% yield;  **$^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):**  $\delta$  9.33 (s, 1H), 8.35 (d,  $J$  = 8.4 Hz, 1H), 8.14-8.12 (m, 1H), 7.99 (dd,  $J_1$  = 14.2 Hz,  $J_2$  = 7.6 Hz, 1H), 7.74-7.71 (m, 2H), 7.62 (t,  $J$  = 7.5 Hz, 1H), 7.58-7.55 (m, 1H), 7.02-6.99 (m, 1H), 4.17-4.10 (m, 4H), 1.26 (t,  $J$  = 7.2 Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):**  $\delta$  167.4 (d,  $J$  = 4.4 Hz), 151.8, 148.2, 140.2 (d,  $J$  = 9.9 Hz), 138.5, 133.7 (d,  $J$  = 9.4 Hz), 132.9 (d,  $J$  = 2.6 Hz), 130.3 (d,  $J$  = 14.1 Hz), 129.4 (d,  $J$  = 13.1 Hz), 125.8 (d,  $J$  = 187.7 Hz), 120.1, 114.3, 63.2 (d,  $J$  = 5.5 Hz), 16.3 (d,  $J$  = 6.6 Hz);  **$^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):**  $\delta$  16.69; **IR (film)  $\nu_{\text{max}}$ :** 2960, 1683, 1579, 1533, 1433, 1308, 1243, 1144, 1022, 967, 781 cm<sup>-1</sup>; **HRMS:** [M+H]<sup>+</sup> m/z calcd for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>P<sup>+</sup> 335.1155, found 335.1155.

**Diethyl (E/Z)-(2-(styrylcarbamoyl)phenyl)phosphonate (3s, new compound)**



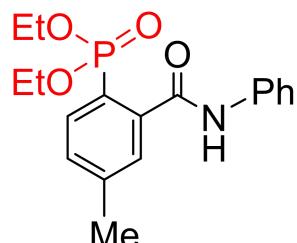
Colorless oil; 53.8 mg, 75% yield;  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  8.61 (d,  $J = 10.7$  Hz, 1H), 7.97-7.94 (m, 1H), 7.70-7.68 (m, 1H), 7.63-7.61 (m, 1H), 7.56-7.53 (m, 1H), 7.34-7.30 (m, 4H), 7.20-7.17 (m, 1H), 7.15-7.11 (m, 1H), 5.87 (d,  $J = 9.7$  Hz, 1H), 4.02-3.97 (m, 4H), 1.81 (t,  $J = 7.1$  Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  166.8 (d,  $J = 4.9$  Hz), 139.3 (d,  $J = 9.1$  Hz), 135.7, 135.6 (d,  $J = 9.4$  Hz), 132.9 (d,  $J = 2.9$  Hz), 130.3 (d,  $J = 13.7$  Hz), 129.8 (d,  $J = 12.8$  Hz), 129.2, 128.2, 127.2, 125.8 (d,  $J = 187.2$  Hz), 122.1, 111.8, 63.2 (d,  $J = 6.6$  Hz), 16.3 (d,  $J = 5.6$  Hz);  **$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 202 MHz):**  $\delta$  16.71; **IR (film)  $\nu_{\text{max}}$ :** 3253, 2977, 2899, 1675, 1598, 1540, 1437, 1389, 1321, 1235, 1022, 985, 754  $\text{cm}^{-1}$ ; **HRMS:**  $[\text{M}+\text{Na}]^+$  m/z calcd for  $\text{C}_{19}\text{H}_{22}\text{NO}_4\text{PNa}^+$  382.1179, found 382.1179.

**Methyl 3-(diethoxyphosphoryl)-4-(phenylcarbamoyl)benzoate (3t, new compound)**



White solid; 67.3 mg, 86% yield;  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  9.27 (s, 1H), 8.53 (dd,  $J_1 = 14.8$  Hz,  $J_2 = 1.3$  Hz, 1H), 8.28 (d,  $J = 8.0$  Hz, 1H), 7.97 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 5.2$  Hz, 1H), 7.73 (d,  $J = 7.8$  Hz, 2H), 7.36 (t,  $J = 7.6$  Hz, 2H), 7.15 (t,  $J = 7.4$  Hz, 1H) 4.22-4.16 (m, 4H), 3.97 (s, 3H), 1.32 (t,  $J = 7.0$  Hz, 6H);  **$^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz):**  $\delta$  165.7 (d,  $J = 1.8$  Hz), 165.5 (d,  $J = 4.6$  Hz), 144.0 (d,  $J = 10.9$  Hz), 138.2, 133.9 (d,  $J = 10.0$  Hz), 133.8 (d,  $J = 2.7$  Hz), 131.7 (d,  $J = 13.6$  Hz), 131.3 (d,  $J = 12.7$  Hz), 129.3, 126.1 (d,  $J = 189.0$  Hz), 125.0, 120.3, 63.8 (d,  $J = 6.4$  Hz), 52.9, 16.5 (d,  $J = 6.4$  Hz);  **$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 202 MHz):**  $\delta$  16.31; **IR (film)  $\nu_{\text{max}}$ :** 2961, 1732, 1701, 1682, 1645, 1545, 1522, 1411, 1331, 1271, 1142, 1022, 970, 762  $\text{cm}^{-1}$ ; **HRMS:**  $[\text{M}+\text{Na}]^+$  m/z calcd for  $\text{C}_{19}\text{H}_{22}\text{NO}_6\text{PNa}^+$  414.1077, found 414.1077.

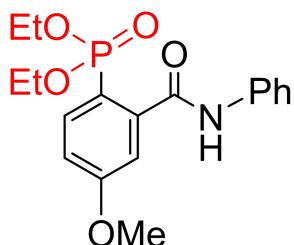
**Diethyl (4-methyl-2-(phenylcarbamoyl)phenyl)phosphonate (3u, new compound)**



White solid; 60.4 mg, 87% yield;  **$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):**  $\delta$  9.17 (s, 1H), 7.77 (dd,  $J_1 = 14.1$

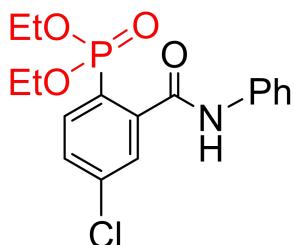
Hz,  $J_2 = 7.8$  Hz, 1H), 7.71 (d,  $J = 8.0$  Hz, 2H), 7.69 (d,  $J = 4.8$  Hz, 1H), 7.34 (t,  $J = 7.0$  Hz, 3H), 7.11 (t,  $J = 7.3$  Hz, 1H), 4.14-4.09 (m, 4H), 2.42 (s, 3H), 1.27 (t,  $J = 7.0$  Hz, 6H);  $^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  166.6 (d,  $J = 5.5$  Hz), 143.8 (d,  $J = 2.2$  Hz), 140.2 (d,  $J = 11.0$  Hz), 138.5, 132.9 (d,  $J = 8.8$  Hz), 131.5 (d,  $J = 13.5$  Hz), 130.8 (d,  $J = 14.3$  Hz), 129.2, 124.6, 121.9 (d,  $J = 189.4$  Hz), 120.1, 63.3 (d,  $J = 6.7$  Hz), 21.6, 16.4 (d,  $J = 6.7$  Hz);  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):  $\delta$  18.60; IR (film)  $\nu_{\text{max}}$ : 3255, 2981, 1679, 1600, 1543, 1500, 1442, 1393, 1324, 1232, 1025, 970, 756, 694 cm<sup>-1</sup>; HRMS: [M+Na]<sup>+</sup> m/z calcd for C<sub>18</sub>H<sub>22</sub>NO<sub>4</sub>PNa<sup>+</sup> 370.1179, found 370.1178.

#### Diethyl (4-methoxy-2-(phenylcarbamoyl)phenyl)phosphonate (3v, new compound)



White solid; 61.7 mg, 85% yield;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  9.28 (s, 1H), 7.81 (dd,  $J_1 = 13.5$  Hz,  $J_2 = 8.6$  Hz, 1H), 7.72 (d,  $J = 7.7$  Hz, 2H), 7.40 (dd,  $J_1 = 4.5$  Hz,  $J_2 = 2.7$  Hz, 1H), 7.34 (t,  $J = 7.6$  Hz, 2H), 7.12 (t,  $J = 7.4$  Hz, 1H), 7.02 (dt,  $J_1 = 8.5$  Hz,  $J_2 = 2.5$  Hz, 1H), 4.14-4.08 (m, 4H), 3.87 (s, 3H), 1.27 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  166.1 (d,  $J = 4.4$  Hz), 163.1 (d,  $J = 3.3$  Hz), 142.4 (d,  $J = 12.1$  Hz), 138.4, 135.0 (d,  $J = 8.8$  Hz), 129.2, 124.6, 120.2, 116.4 (d,  $J = 194.0$  Hz), 116.1 (d,  $J = 15.4$  Hz), 116.0 (d,  $J = 14.3$  Hz), 63.2 (d,  $J = 6.6$  Hz), 55.8, 16.4 (d,  $J = 5.5$  Hz);  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):  $\delta$  18.89; IR (film)  $\nu_{\text{max}}$ : 2972, 1663, 1562, 1501, 1478, 1244, 1170, 1132, 1076, 1016, 965, 825, 782 cm<sup>-1</sup>; HRMS: [M+Na]<sup>+</sup> m/z calcd for C<sub>18</sub>H<sub>22</sub>NO<sub>5</sub>PNa<sup>+</sup> 386.1128, found 386.1124.

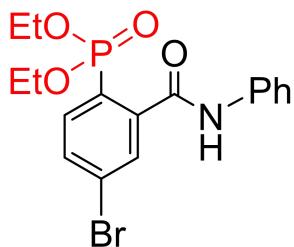
#### Diethyl (4-chloro-2-(phenylcarbamoyl)phenyl)phosphonate (3w, new compound)



White solid; 59.5 mg, 81% yield;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  9.22 (s, 1H), 7.88 (dd,  $J_1 = 4.3$

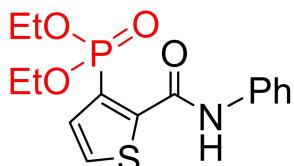
Hz,  $J_2$  = 2.0 Hz, 1H), 7.82 (dd,  $J_1$  = 13.8 Hz,  $J_2$  = 8.3 Hz, 1H), 7.70 (d,  $J$  = 7.9 Hz, 2H), 7.51 (dt,  $J_1$  = 8.2 Hz,  $J_2$  = 2.4 Hz, 1H), 7.35 (t,  $J$  = 8.1 Hz, 2H), 7.14 (t,  $J$  = 7.4 Hz, 1H), 4.14-4.13 (m, 4H), 1.29 (t,  $J$  = 7.1 Hz, 6H);  $^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  164.9 (d,  $J$  = 4.4 Hz), 161.9 (d,  $J$  = 11.0 Hz), 139.7 (d,  $J$  = 3.3 Hz), 138.2, 134.3 (d,  $J$  = 8.8 Hz), 131.1 (d,  $J$  = 13.2 Hz), 130.3 (d,  $J$  = 15.4 Hz), 129.3, 124.9, 123.7 (d,  $J$  = 190.4 Hz), 120.2, 63.7 (d,  $J$  = 6.6 Hz), 16.4 (d,  $J$  = 5.5 Hz);  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):  $\delta$  16.90; IR (film)  $\nu_{\text{max}}$ : 2965, 1672, 1589, 1532, 1481, 1395, 1318, 1225, 1089, 1019, 962, 826, 595 cm<sup>-1</sup>; HRMS: [M+Na]<sup>+</sup> m/z calcd for C<sub>17</sub>H<sub>19</sub>ClNO<sub>4</sub>PNa<sup>+</sup> 390.0632, found 390.0631.

#### Diethyl (4-bromo-2-(phenylcarbamoyl)phenyl)phosphonate (3x, new compound)



White solid; 70.7 mg, 86% yield;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  9.19 (s, 1H), 8.03 (dd,  $J_1$  = 4.5 Hz,  $J_2$  = 1.8 Hz, 1H), 7.74 (dd,  $J_1$  = 13.7 Hz,  $J_2$  = 8.3 Hz, 1H), 7.71-7.67 (m, 3H), 7.35 (t,  $J$  = 7.6 Hz, 2H), 7.14 (t,  $J$  = 7.5 Hz, 1H), 4.17-4.12 (m, 4H), 1.29 (t,  $J$  = 7.0 Hz, 6H);  $^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  164.8 (d,  $J$  = 4.4 Hz), 141.8 (d,  $J$  = 12.1 Hz), 138.2, 134.2 (d,  $J$  = 9.9 Hz), 133.9 (d,  $J$  = 14.3 Hz), 133.3 (d,  $J$  = 14.4 Hz), 129.3, 128.1 (d,  $J$  = 4.4 Hz), 124.9, 124.2 (d,  $J$  = 189.8 Hz), 120.2, 63.7 (d,  $J$  = 6.6 Hz), 16.4 (d,  $J$  = 6.6 Hz);  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):  $\delta$  17.03; IR (film)  $\nu_{\text{max}}$ : 2962, 1680, 1599, 1544, 1500, 1322, 1235, 1067, 1021, 973, 770, 693 cm<sup>-1</sup>; HRMS: [M+Na]<sup>+</sup> m/z calcd for C<sub>17</sub>H<sub>19</sub>BrNO<sub>4</sub>PNa<sup>+</sup> 434.0127, found 434.1027.

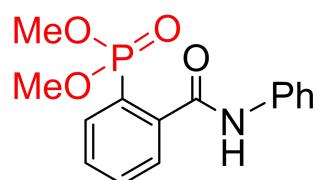
#### Diethyl (2-(phenylcarbamoyl)thiophen-3-yl)phosphonate (3y, new compound)



White solid; 59.0 mg, 87% yield;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  12.12 (s, 1H), 7.80 (dd,  $J_1$  = 8.3 Hz,  $J_2$  = 0.7 Hz, 2H), 7.55 (dd,  $J_1$  = 5.5 Hz,  $J_2$  = 2.2 Hz, 1H), 7.34 (t,  $J$  = 7.6 Hz, 2H), 7.30 (t,  $J$  =

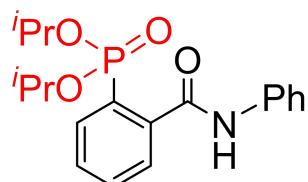
4.8 Hz, 1H), 7.11 (t,  $J$  = 7.3 Hz, 1H), 4.24-4.11 (m, 4H), 1.34 (t,  $J$  = 7.1 Hz, 6H);  $^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  158.7 (d,  $J$  = 3.3 Hz), 151.5 (d,  $J$  = 20.9 Hz), 138.8, 132.8 (d,  $J$  = 13.2 Hz), 130.4 (d,  $J$  = 18.7 Hz), 129.1, 125.3 (d,  $J$  = 187.7 Hz), 124.5, 120.3, 63.5 (d,  $J$  = 5.5 Hz), 16.4 (d,  $J$  = 6.6 Hz);  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):  $\delta$  14.03; IR (film)  $\nu_{\text{max}}$ : 2983, 1772, 1604, 1553, 1492, 1462, 1390, 1285, 1183, 1114, 1019, 997, 754 cm<sup>-1</sup>; HRMS: [M+Na]<sup>+</sup> m/z calcd for C<sub>15</sub>H<sub>18</sub>NO<sub>4</sub>PSNa<sup>+</sup> 362.0586, found 362.0586.

**Dimethyl (2-(phenylcarbamoyl)phenyl)phosphonate (4a, CAS NO.: 460836-90-0)**



White solid; 54.9 mg, 90% yield;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  9.02 (s, 1H), 7.87-7.83 (m, 2H), 7.71 (d,  $J$  = 8.1 Hz, 2H), 7.64 (t,  $J$  = 7.7 Hz, 1H), 7.56-7.53 (m, 1H), 7.34 (t,  $J$  = 7.4 Hz, 2H), 7.13 (t,  $J$  = 7.3 Hz, 1H), 3.77 (t,  $J$  = 11.0 Hz, 6H);  $^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  166.5 (d,  $J$  = 4.4 Hz), 140.6 (d,  $J$  = 10.3 Hz), 138.4, 133.2 (d,  $J$  = 2.4 Hz), 133.0 (d,  $J$  = 7.9 Hz), 130.5 (d,  $J$  = 13.3 Hz), 130.3 (d,  $J$  = 14.1 Hz), 129.3, 124.8, 134.2 (d,  $J$  = 188.0 Hz), 120.3, 53.8 (d,  $J$  = 6.1 Hz);  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):  $\delta$  20.33; IR (film)  $\nu_{\text{max}}$ : 3251, 2960, 1670, 1601, 1544, 1492, 1442, 1324, 1241, 1031, 836, 788, 758 cm<sup>-1</sup>; HRMS: [M+Na]<sup>+</sup> m/z calcd for C<sub>15</sub>H<sub>16</sub>NO<sub>4</sub>PNa<sup>+</sup> 328.0709, found 328.0709.

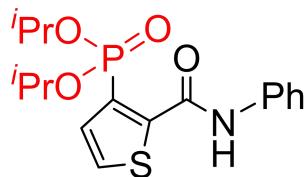
**Diisopropyl (2-(phenylcarbamoyl)phenyl)phosphonate (4b, CAS NO.: 60815-47-6)**



White solid; 62.8 mg, 87% yield;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  9.41 (s, 1H), 7.92-7.84 (m, 2H), 7.71 (d,  $J$  = 8.2 Hz, 2H), 7.58 (t,  $J$  = 7.5 Hz, 1H), 7.50 (t,  $J$  = 8.2 Hz, 1H), 7.31 (t,  $J$  = 7.8 Hz, 2H), 7.08 (t,  $J$  = 7.2 Hz, 1H), 4.77-4.72 (m, 2H), 1.27-1.24 (m, 12H);  $^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  166.3 (d,  $J$  = 5.5 Hz), 140.1 (d,  $J$  = 11.0 Hz), 138.5, 132.63 (d,  $J$  = 3.3 Hz), 132.57 (d,  $J$

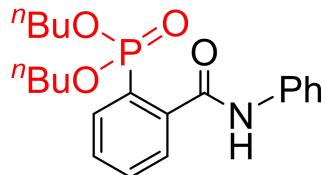
= 9.1 Hz), 130.9 (d,  $J$  = 13.2 Hz), 130.0 (d,  $J$  = 14.1 Hz), 129.0, 126.4 (d,  $J$  = 188.1 Hz), 124.4, 120.1, 72.4 (d,  $J$  = 6.5 Hz), 24.1 (d,  $J$  = 4.3 Hz), 23.9 (d,  $J$  = 4.4 Hz);  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):  $\delta$  15.81; IR (film)  $\nu_{\text{max}}$ : 3261, 3063, 2979, 2934, 1680, 1601, 1544, 1499, 1442, 1386, 1375, 1322, 1230, 1142, 1105, 1072, 995, 756 570 cm<sup>-1</sup>; HRMS: [M+Na]<sup>+</sup> m/z calcd for C<sub>19</sub>H<sub>24</sub>NO<sub>4</sub>PNa<sup>+</sup> 384.1335, found 384.1334.

#### Diiisopropyl (2-(phenylcarbamoyl)thiophen-3-yl)phosphonate (4c, new compound)



White solid; 63.1 mg, 86% yield;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  12.25 (s, 1H), 7.81 (d,  $J$  = 7.7 Hz, 2H), 7.53 (dd,  $J_1$  = 5.1 Hz,  $J_2$  = 2.3 Hz, 1H), 7.35-7.30 (m, 3H), 7.11 (t,  $J$  = 7.4 Hz, 1H), 4.78-4.72 (m, 2H), 1.39 (d,  $J$  = 6.2 Hz, 6H), 1.26 (d,  $J$  = 6.2 Hz, 6H);  $^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  158.9 (d,  $J$  = 3.3 Hz), 150.9 (d,  $J$  = 20.7 Hz), 138.9, 133.1 (d,  $J$  = 12.1 Hz), 130.2 (d,  $J$  = 19.0 Hz), 129.1, 127.0 (d,  $J$  = 189.1 Hz), 124.4, 120.4, 72.7 (d,  $J$  = 5.6 Hz), 24.2 (d,  $J$  = 4.2 Hz), 23.9 (d,  $J$  = 4.4 Hz);  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):  $\delta$  11.53 IR (film)  $\nu_{\text{max}}$ : 2962, 1660, 1627, 1565, 1489, 1447, 1398, 1324, 1270, 1225, 1167, 1020, 976, 844, 758 cm<sup>-1</sup>; HRMS: [M+Na]<sup>+</sup> m/z calcd for C<sub>17</sub>H<sub>22</sub>NO<sub>4</sub>PSNa<sup>+</sup> 390.0899, found 390.0904.

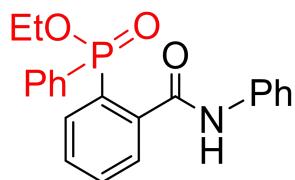
#### Dibutyl (2-(phenylcarbamoyl)phenyl)phosphonate (4d, new compound)



White solid; 63.1 mg, 81% yield;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  9.28 (s, 1H), 7.86-7.83 (m, 2H), 7.72 (d,  $J$  = 8.3 Hz, 2H), 7.60 (t,  $J$  = 7.7 Hz, 1H), 7.51 (t,  $J$  = 7.7 Hz, 1H), 7.33-7.30 (m, 2H), 7.09 (t,  $J$  = 6.6 Hz, 1H), 4.07-4.03 (m, 4H), 1.61-1.56 (m, 4H), 1.32-1.26 (m, 4H), 0.83-0.80 (m, 6H);  $^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  166.3 (d,  $J$  = 5.3 Hz), 140.2 (d,  $J$  = 10.0 Hz), 138.5, 132.9 (d,  $J$  = 2.2 Hz), 132.5 (d,  $J$  = 7.7 Hz), 130.8 (d,  $J$  = 13.6 Hz), 130.1 (d,  $J$  = 13.5 Hz), 129.0, 125.2

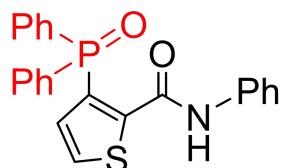
(d,  $J = 188.0$  Hz), 124.5, 120.0, 67.1 (d,  $J = 6.6$  Hz), 32.5 (d,  $J = 6.6$  Hz), 18.8, 13.6;  **$^{31}\text{P}$  NMR** ( $\text{CDCl}_3$ , **202 MHz**):  $\delta$  20.33; **IR (film)  $\nu_{\text{max}}$** : 3254, 3133, 3061, 2961, 2873, 1679, 1602, 1545, 1499, 1465, 1442, 1323, 1228, 1074, 1024, 757, 693, 571  $\text{cm}^{-1}$ ; **HRMS**:  $[\text{M}+\text{Na}]^+$  m/z calcd for  $\text{C}_{21}\text{H}_{28}\text{NO}_4\text{PNa}^+$  412.1648, found 412.1649.

#### Ethyl phenyl(2-(phenylcarbamoyl)phenyl)phosphinate (4f, new compound)



White solid; 65.0 mg, 89% yield;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , **500 MHz**):  $\delta$  9.70 (s, 1H), 7.91-7.89 (m, 1H), 7.72-7.68 (m, 4H), 7.63-7.59 (m, 2H), 7.56-7.53 (m, 1H), 7.49-7.46 (m, 1H), 7.42-7.39 (m, 2H), 7.32 (t,  $J = 7.9$  Hz, 2H), 7.11 (t,  $J = 7.3$  Hz, 1H), 4.14-4.07 (m, 1H), 3.97-3.90 (m, 1H), 1.21 (t,  $J = 7.2$  Hz, 3H);  **$^{13}\text{C}\{\text{H}\}$  NMR** ( $\text{CDCl}_3$ , **125 MHz**):  $\delta$  166.2 (d,  $J = 4.4$  Hz), 140.6 (d,  $J = 10.0$  Hz), 138.5, 133.2 (d,  $J = 2.7$  Hz), 132.8 (d,  $J = 2.2$  Hz), 132.5 (d,  $J = 10.8$  Hz), 132.1 (d,  $J = 10.5$  Hz), 131.2 (d,  $J = 11.2$  Hz), 130.1 (d,  $J = 13.0$  Hz), 129.2 (d,  $J = 134.7$  Hz), 129.1, 128.9 (d,  $J = 13.3$  Hz), 128.8 (d,  $J = 136.8$  Hz), 124.5, 120.0, 62.1 (d,  $J = 5.6$  Hz), 16.4 (d,  $J = 6.6$  Hz);  **$^{31}\text{P}$  NMR** ( $\text{CDCl}_3$ , **202 MHz**):  $\delta$  35.66; **IR (film)  $\nu_{\text{max}}$** : 3121, 2490, 1680, 1649, 1601, 1549, 1440, 1324, 1260, 1142, 1032, 799, 758, 693  $\text{cm}^{-1}$ ; **HRMS**:  $[\text{M}+\text{H}]^+$  m/z calcd for  $\text{C}_{21}\text{H}_{21}\text{NO}_3\text{P}^+$  366.1254, found 366.1256.

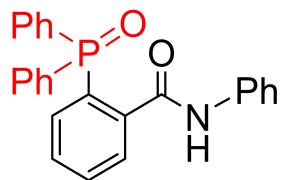
#### 3-(Diphenylphosphoryl)-N-phenylthiophene-2-carboxamide (4g, new compound)



White solid; 69.3 mg, 86% yield;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , **500 MHz**):  $\delta$  12.49 (s, 1H), 7.77 (d,  $J = 7.7$  Hz, 2H), 8.67-8.64 (m, 4H), 7.60-7.58 (m, 2H), 7.51-7.48 (m, 5H), 7.30 (t,  $J = 7.7$  Hz, 2H), 7.08 (t,

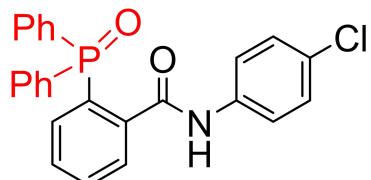
*J* = 7.3 Hz, 1H), 6.70 (t, *J* = 5.2 Hz, 1H);  $^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  159.1 (d, *J* = 2.2 Hz), 152.6 (d, *J* = 11.0 Hz), 138.9, 133.5 (d, *J* = 16.5 Hz), 133.1 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 10.8 Hz), 131.4 (d, *J* = 108.9 Hz), 129.9 (d, *J* = 16.5 Hz), 129.6 (d, *J* = 101.4 Hz), 129.2 (d, *J* = 13.1 Hz), 129.0, 124.4, 120.4;  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):  $\delta$  29.27; IR (film)  $\nu_{\text{max}}$ : 2960, 1716, 1688, 1601, 1533, 1408, 1279, 1260, 1178, 1143, 1112, 1024, 971, 770 cm<sup>-1</sup>; HRMS: [M+H]<sup>+</sup> m/z calcd for C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub>PS<sup>+</sup> 404.0869, found 404.0869.

#### 2-(Diphenylphosphoryl)-N-phenylbenzamide (4h, new compound)



White solid; 66.7 mg, 84% yield;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  10.54 (s, 1H), 8.08-8.06 (m, 1H), 7.68-7.63 (m, 5H), 7.51-7.49 (m, 2H), 7.44-7.39 (m, 7H), 7.21-7.19 (m, 2H), 7.14-7.10 (m, 1H), 7.04-7.01 (m, 1H);  $^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  165.4 (d, *J* = 4.4 Hz), 141.3 (d, *J* = 8.3 Hz), 137.9, 133.2 (d, *J* = 11.9 Hz), 132.8 (d, *J* = 3.3 Hz), 132.4 (d, *J* = 3.3 Hz), 132.3 (d, *J* = 8.9 Hz), 131.6 (d, *J* = 10.2 Hz), 130.5 (d, *J* = 94.8 Hz), 130.1, 129.6 (d, *J* = 98.0 Hz), 128.7 (d, *J* = 12.5 Hz), 128.5, 124.1, 120.1;  $^{31}\text{P}$  NMR (CDCl<sub>3</sub>, 202 MHz):  $\delta$  34.45; IR (film)  $\nu_{\text{max}}$ : 3062, 1670, 1601, 1549, 1499, 1438, 1325, 1180, 1120, 1075, 756, 727, 692, 542 cm<sup>-1</sup>; HRMS: [M+H]<sup>+</sup> m/z calcd for C<sub>25</sub>H<sub>21</sub>NO<sub>2</sub>P<sup>+</sup> 398.1304, found 398.1302.

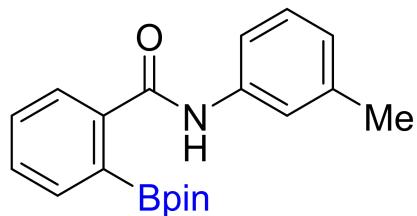
#### N-(4-Chlorophenyl)-2-(diphenylphosphoryl)benzamide (4i, new compound)



White solid; 74.1 mg, 86% yield;  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  10.73 (s, 1H), 8.08 (dd, *J*<sub>1</sub> = 7.9 Hz, *J*<sub>2</sub> = 4.1 Hz, 1H), 7.70-7.67 (m, 1H), 7.66-7.62 (m, 4H), 7.54-7.51 (m, 2H), 7.46-7.40 (m, 7H), 7.19-7.16 (m, 2H), 7.12 (dd, *J*<sub>1</sub> = 14.0 Hz, *J*<sub>2</sub> = 7.3 Hz, 1H);  $^{13}\text{C}\{\text{H}\}$  NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  165.6 (d, *J* = 3.8 Hz), 141.1 (d, *J* = 8.8 Hz), 136.8, 133.5 (d, *J* = 11.8 Hz), 133.0 (d, *J* = 2.2 Hz),

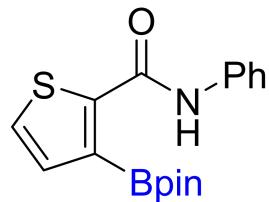
132.7 (d,  $J = 3.2$  Hz), 132.5 (d,  $J = 9.4$  Hz), 131.7 (d,  $J = 9.9$  Hz), 130.5 (d,  $J = 12.1$  Hz), 130.4 (d,  $J = 106.4$  Hz), 129.14, 129.08 (d,  $J = 105.7$  Hz), 128.9 (d,  $J = 12.3$  Hz), 128.7, 121.5;  **$^{31}\text{P}$  NMR** ( $\text{CDCl}_3$ , **202 MHz**):  $\delta$  35.84; **IR (film)  $\nu_{\text{max}}$** : 3061, 1702, 1692, 1653, 1606, 1543, 1458, 1337, 1258, 1152, 1064, 1030, 976, 755  $\text{cm}^{-1}$ ; **HRMS**:  $[\text{M}+\text{H}]^+$  m/z calcd for  $\text{C}_{25}\text{H}_{20}\text{ClNO}_2\text{P}^+$  432.0915, found 432.0912.

**2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(m-tolyl)benzamide (6a, new compound)**



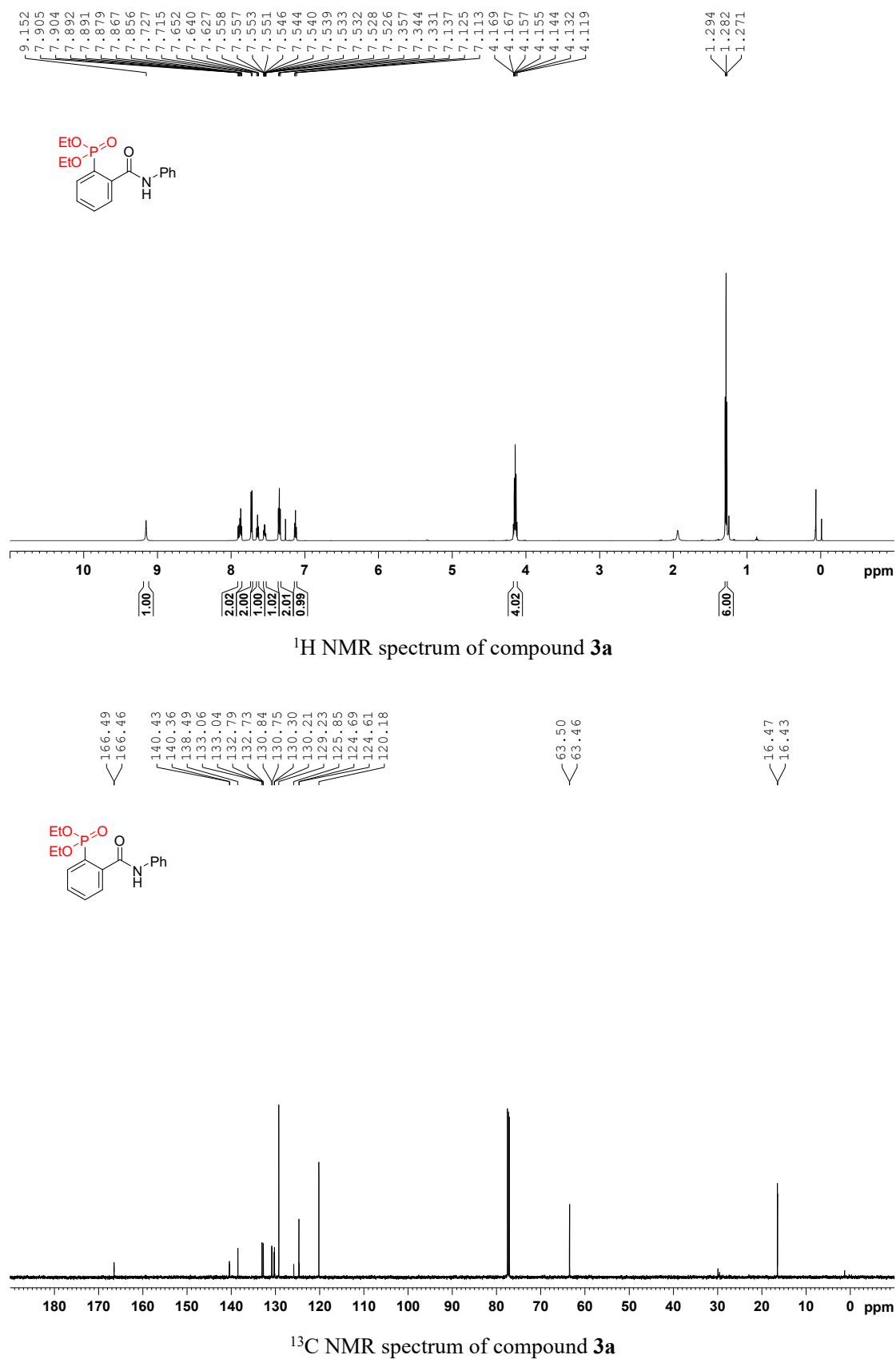
White solid; 47.2 mg, 70% yield;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , **500 MHz**):  $\delta$  7.09 (s, 1H), 7.86 (d,  $J = 7.3$  Hz, 2H), 7.54-7.51 (m, 1H), 7.46 (t,  $J = 8.0$  Hz, 2H), 7.42 (d,  $J = 8.1$  Hz, 1H), 7.24 (t,  $J = 7.8$  Hz, 1H), 6.96 (d,  $J = 7.7$  Hz, 1H), 2.35 (s, 3H), 1.25 (s, 12H);  **$^{13}\text{C}\{\text{H}\}$  NMR** ( $\text{CDCl}_3$ , **125 MHz**):  $\delta$  166.0, 139.2, 135.3, 138.1, 132.0, 129.1, 129.0, 127.2, 125.6, 121.1, 117.5, 83.7, 25.2, 21.7; **IR (film)  $\nu_{\text{max}}$** : 2978, 1748, 1688, 1649, 1612, 1544, 1489 1281, 1124, 1030, 848, 780, 692  $\text{cm}^{-1}$ ; **HRMS**:  $[\text{M}+\text{Na}]^+$  m/z calcd for  $\text{C}_{20}\text{H}_{24}\text{BNO}_3\text{Na}^+$  360.1741, found 360.1740.

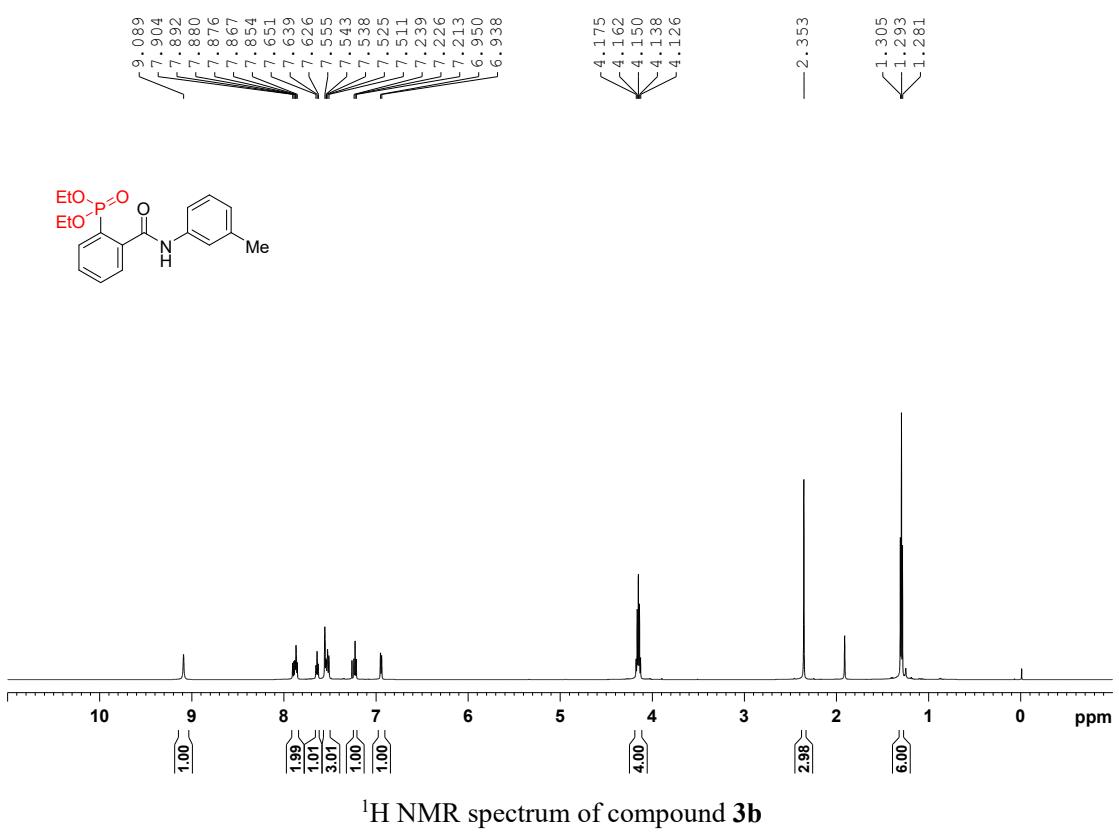
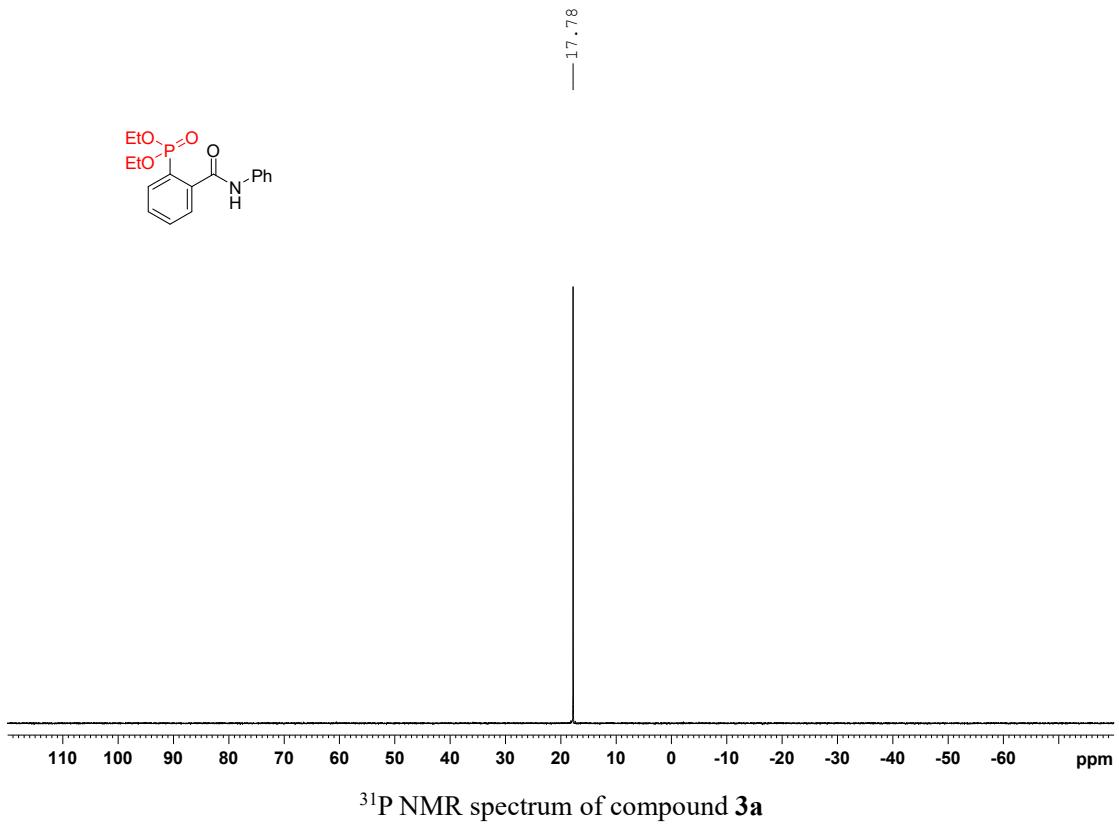
**N-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carboxamide (6b, new compound)**

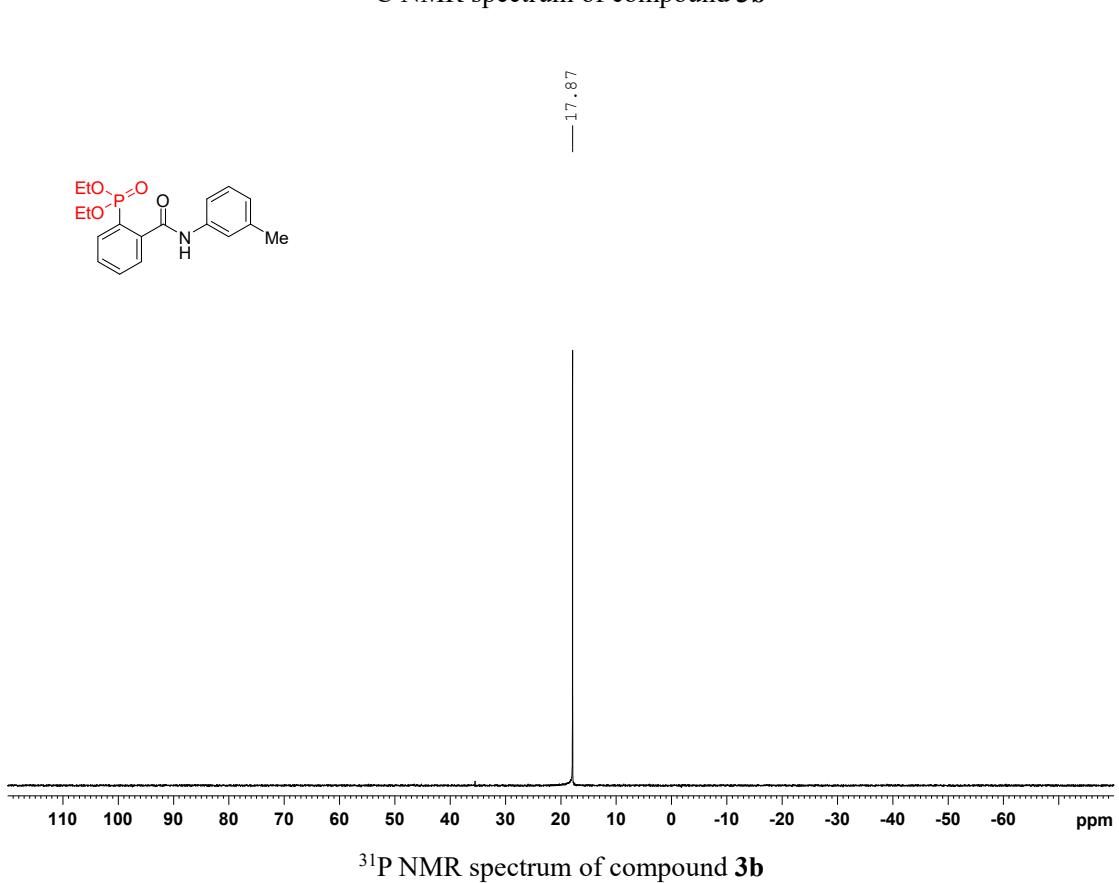
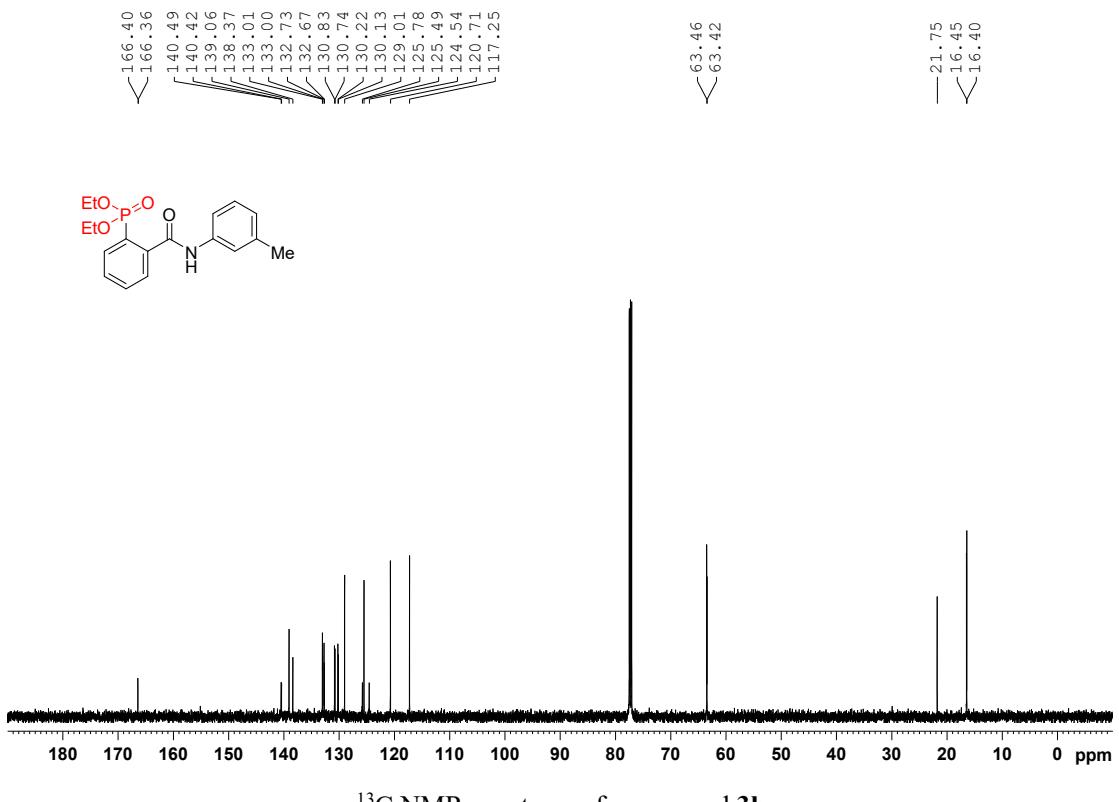


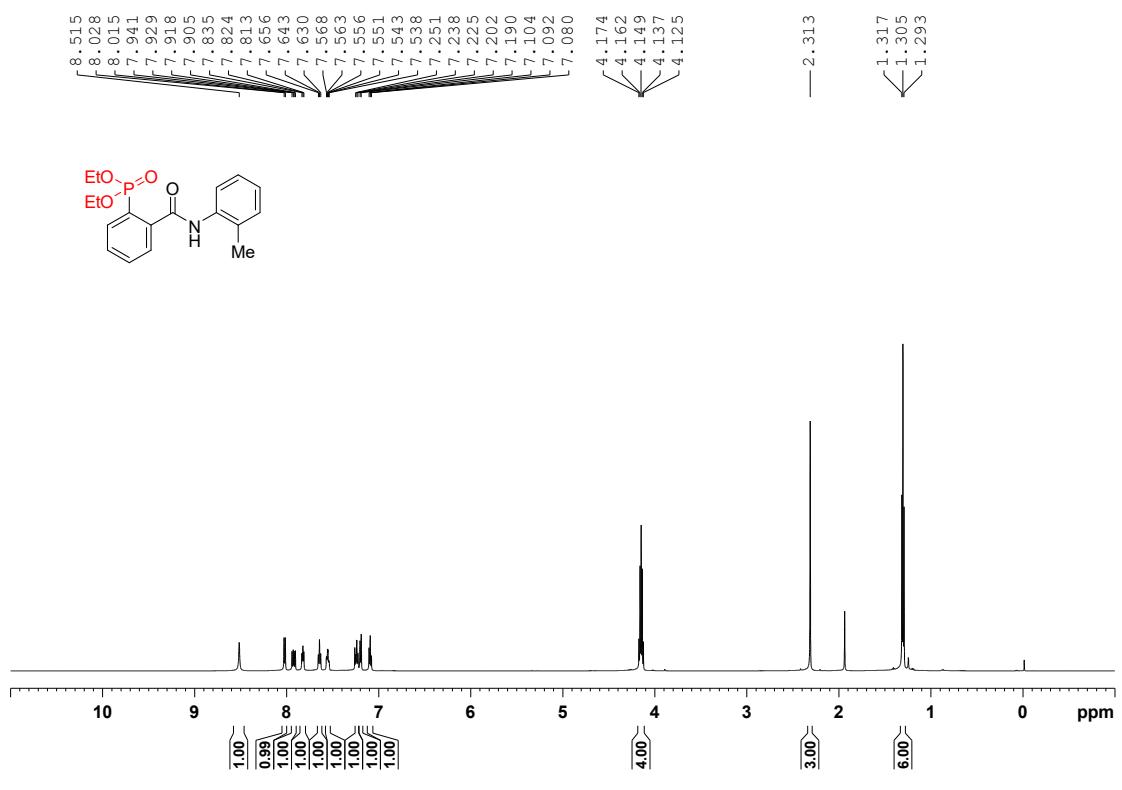
White solid; 42.8 mg, 65% yield;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , **500 MHz**):  $\delta$  10.75 (s, 1H), 7.73-7.71 (m, 2H), 7.51 (s, 2H), 7.38-7.35 (m, 2H), 7.14-7.11 (m, 1H), 1.45 (s, 12H);  **$^{13}\text{C}\{\text{H}\}$  NMR** ( $\text{CDCl}_3$ , **125 MHz**):  $\delta$  160.5, 151.9, 139.1, 136.4, 130.1, 129.3, 124.2, 120.0, 85.6, 25.1; **IR (film)  $\nu_{\text{max}}$** : 2976, 1754, 1744, 1678, 1642, 1609, 1558, 1482, 1280, 1142, 1021, 853, 778  $\text{cm}^{-1}$ ; **HRMS**:  $[\text{M}+\text{H}]^+$  m/z calcd for  $\text{C}_{17}\text{H}_{21}\text{BNO}_3\text{S}^+$  330.1330, found 330.1328.

**8.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  spectrum for all the products.**

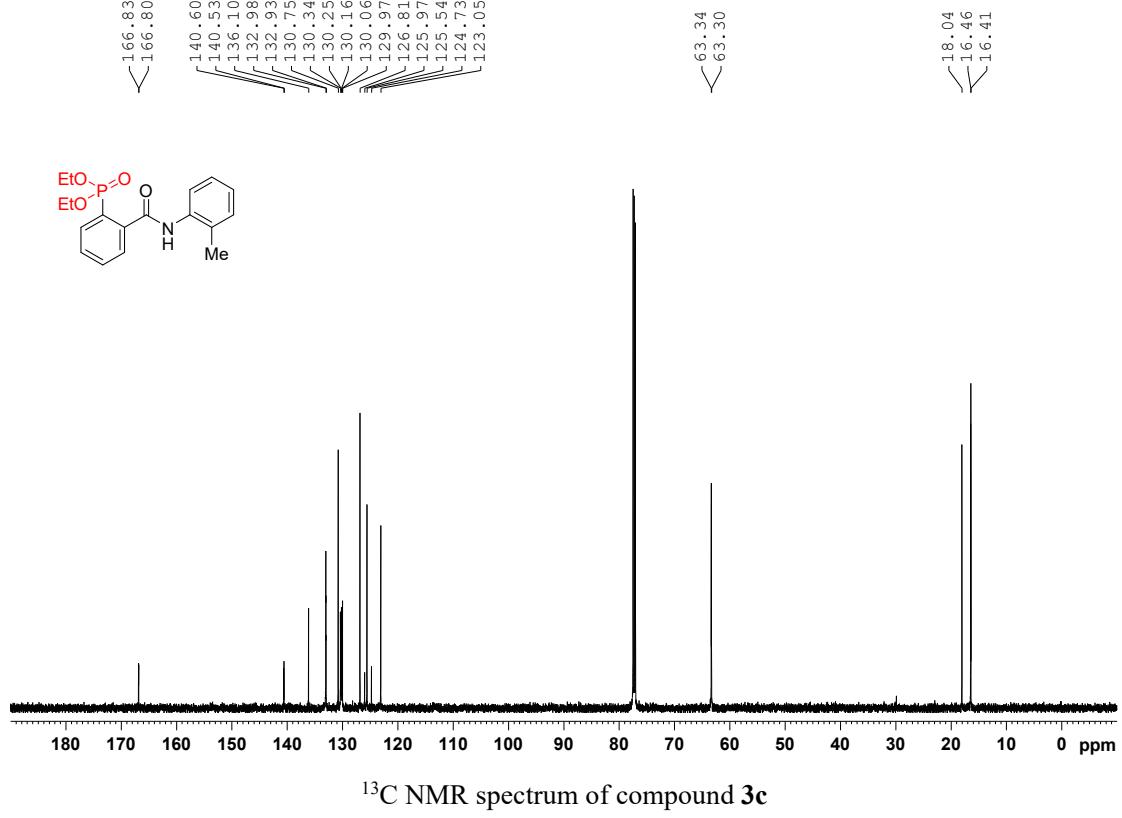




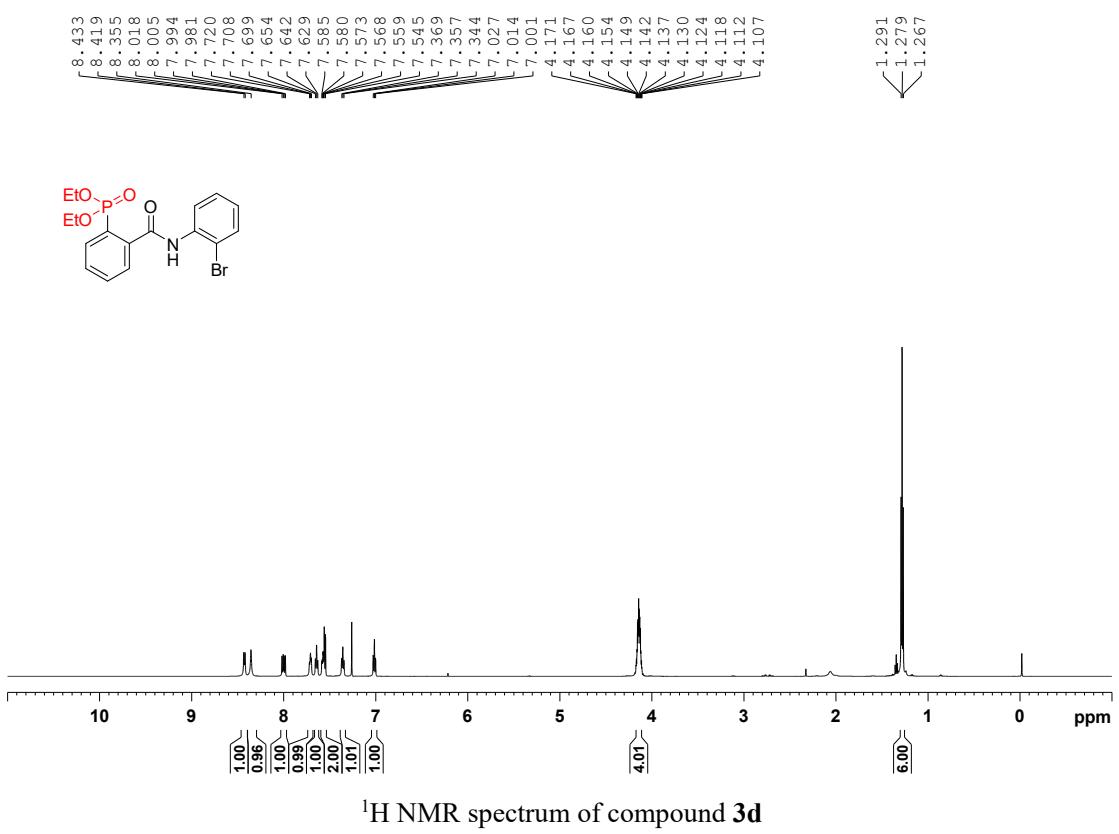
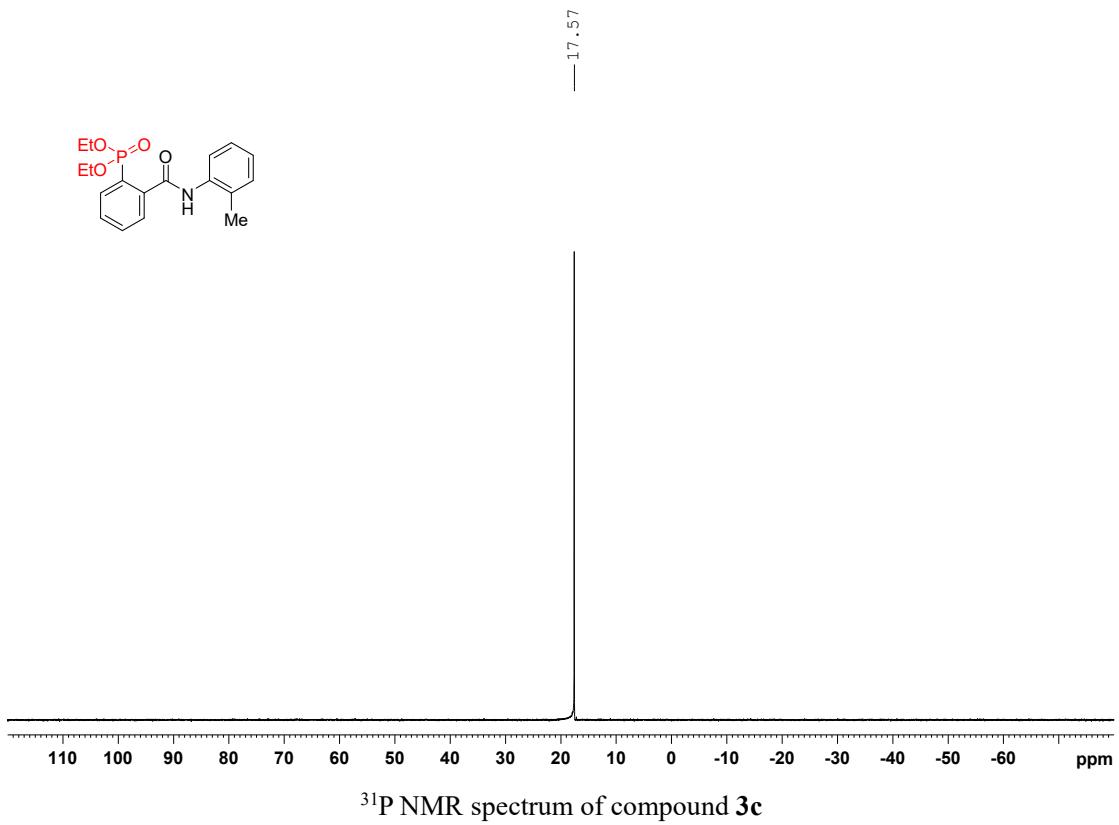


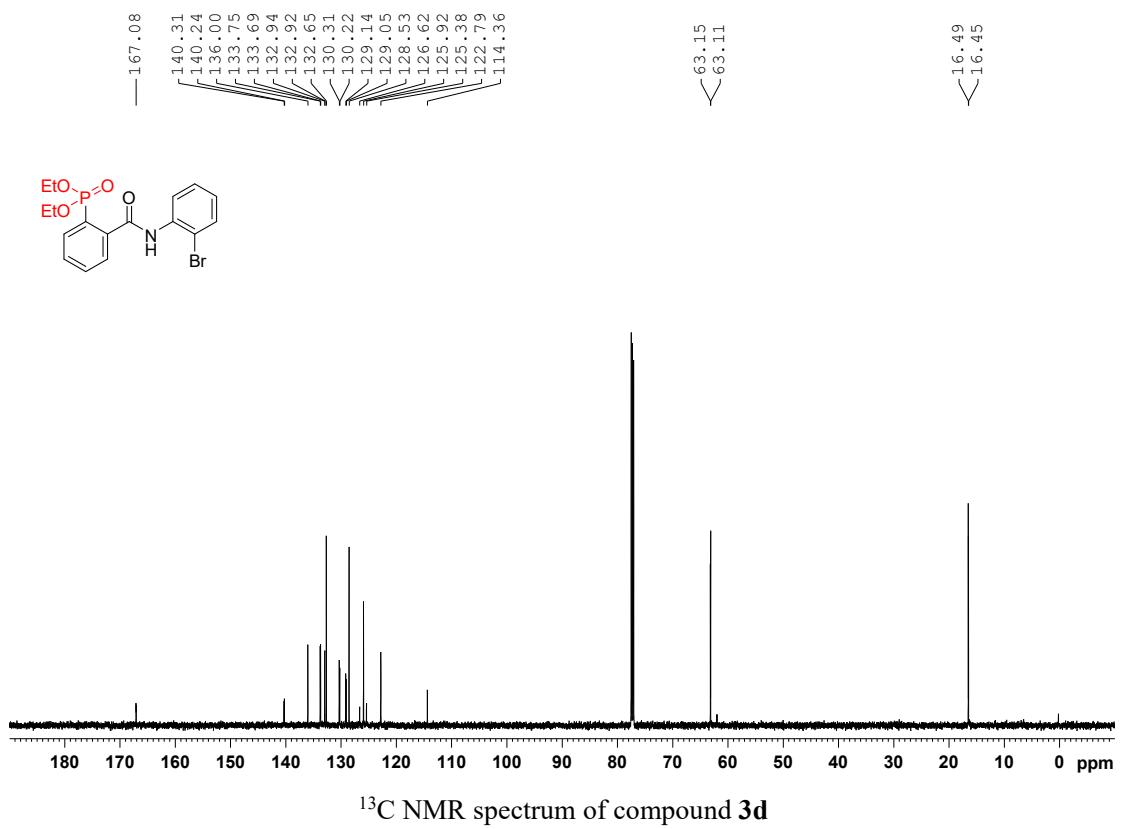


<sup>1</sup>H NMR spectrum of compound 3c

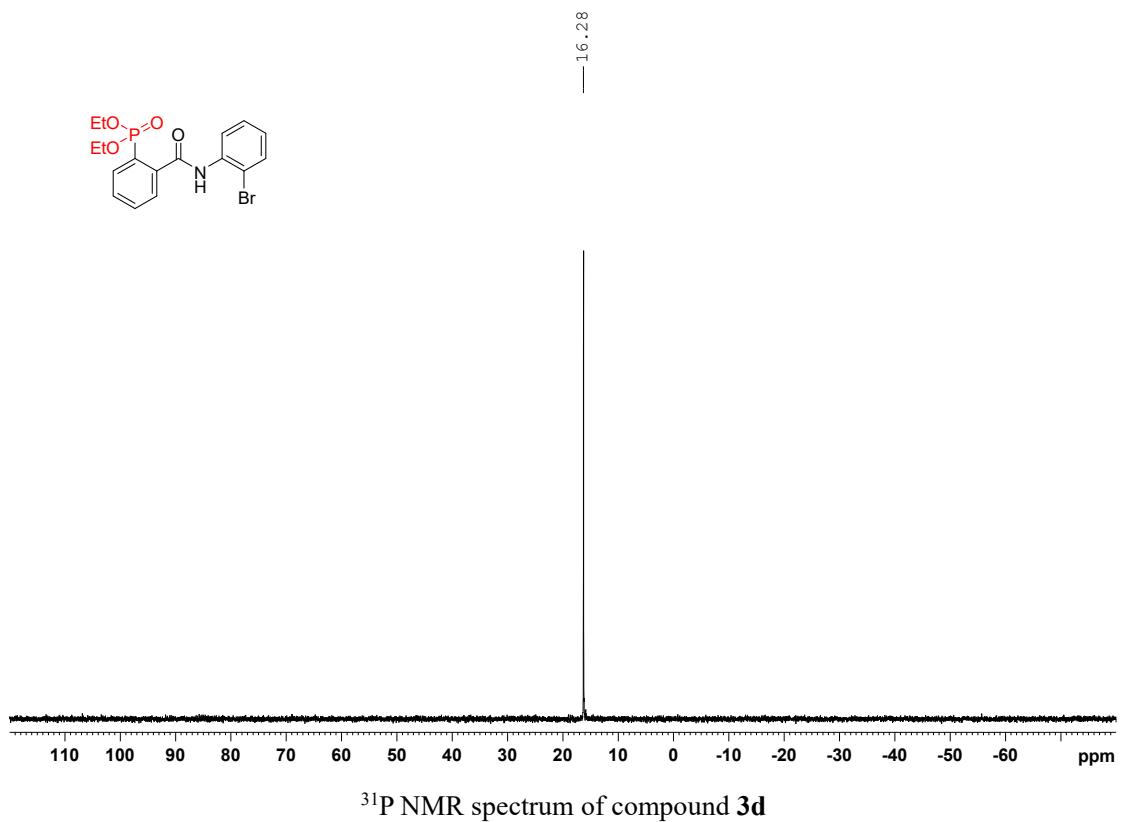


### <sup>13</sup>C NMR spectrum of compound 3c

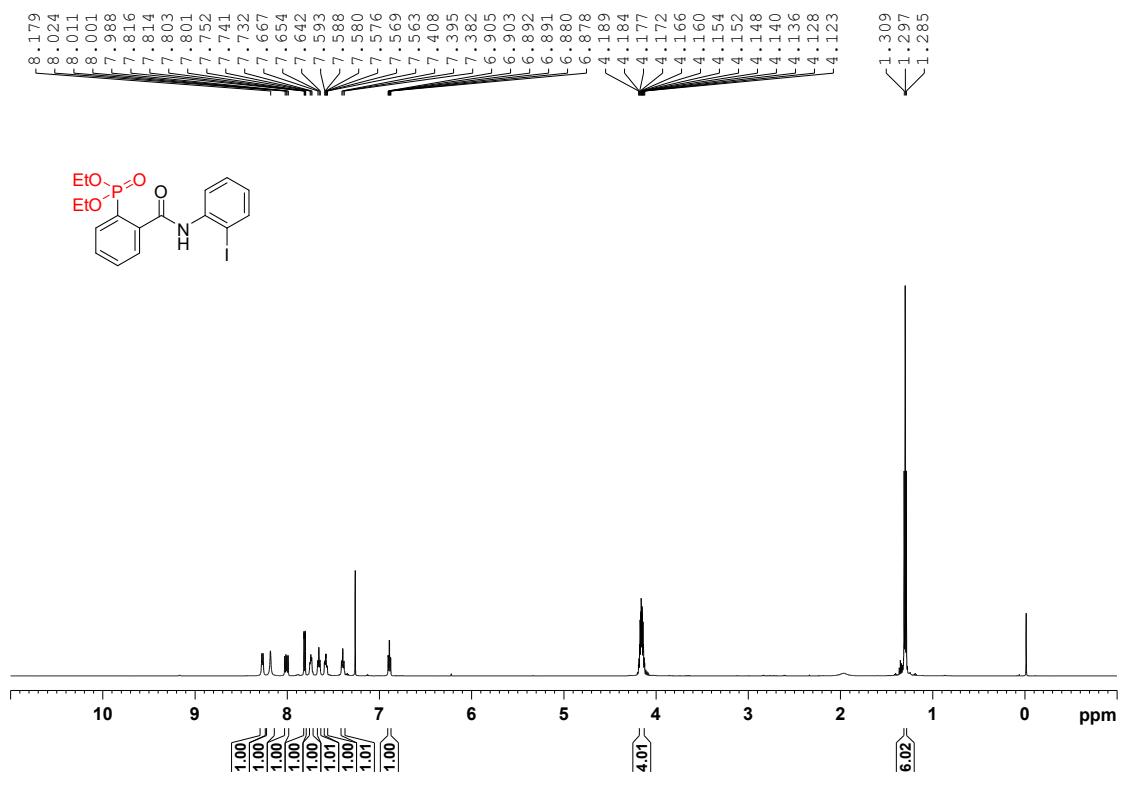




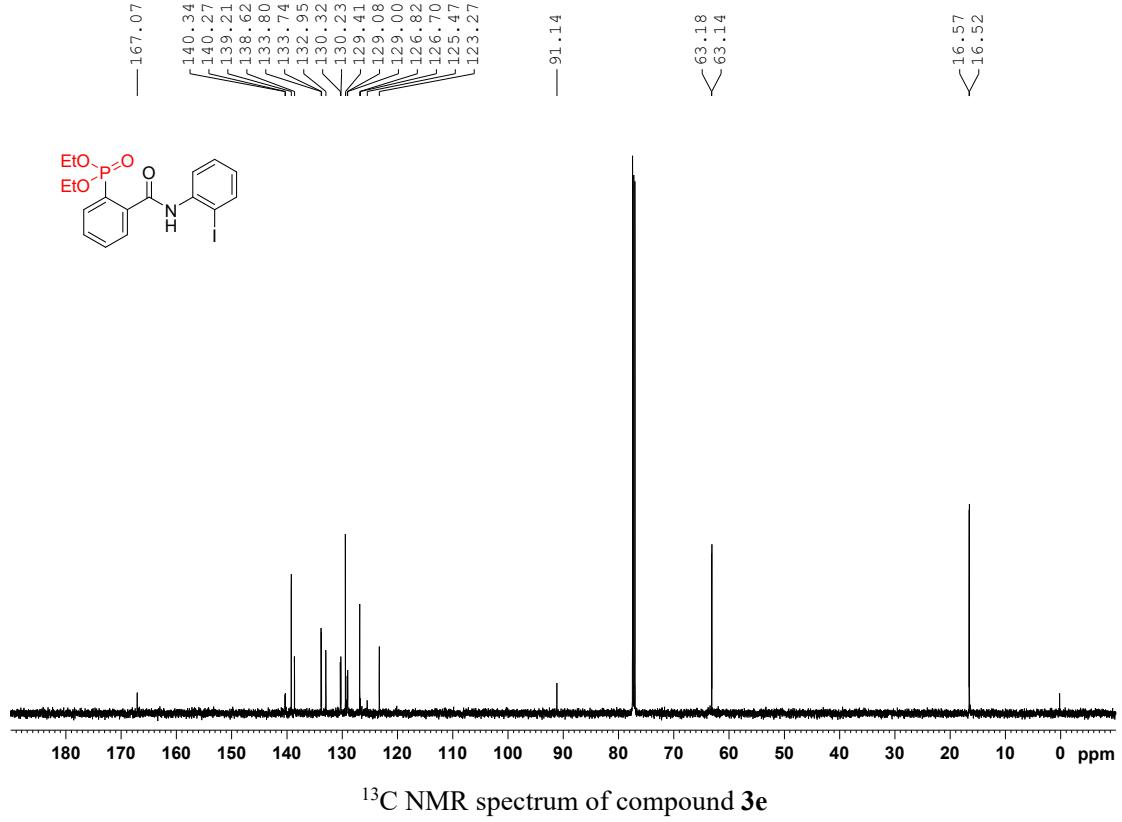
<sup>13</sup>C NMR spectrum of compound 3d



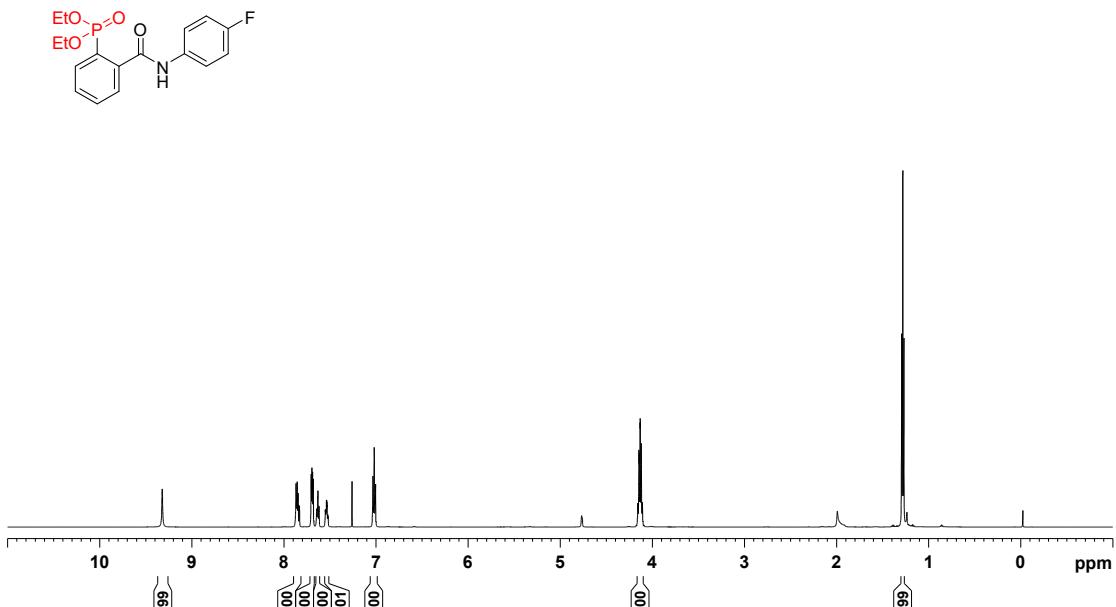
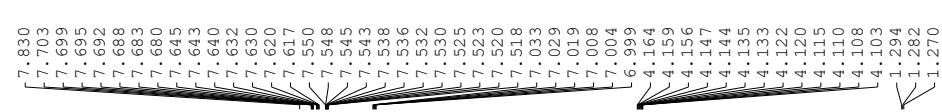
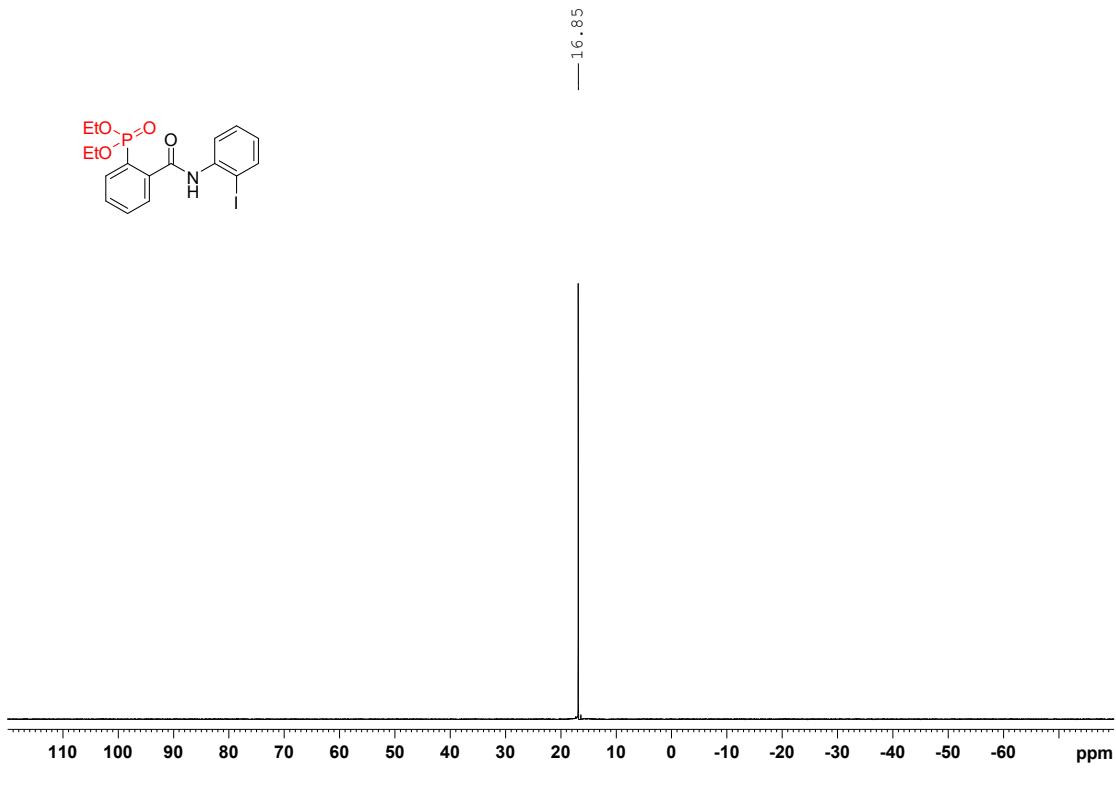
<sup>31</sup>P NMR spectrum of compound 3d

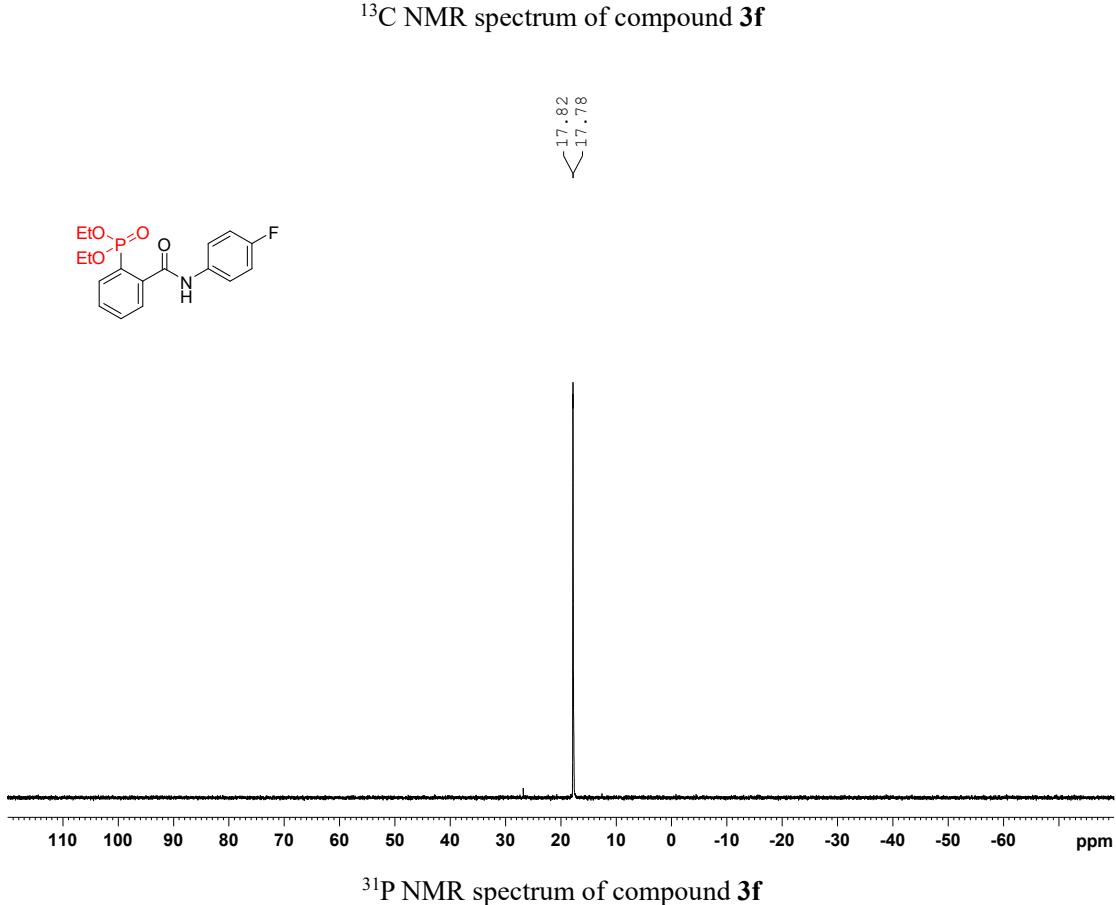
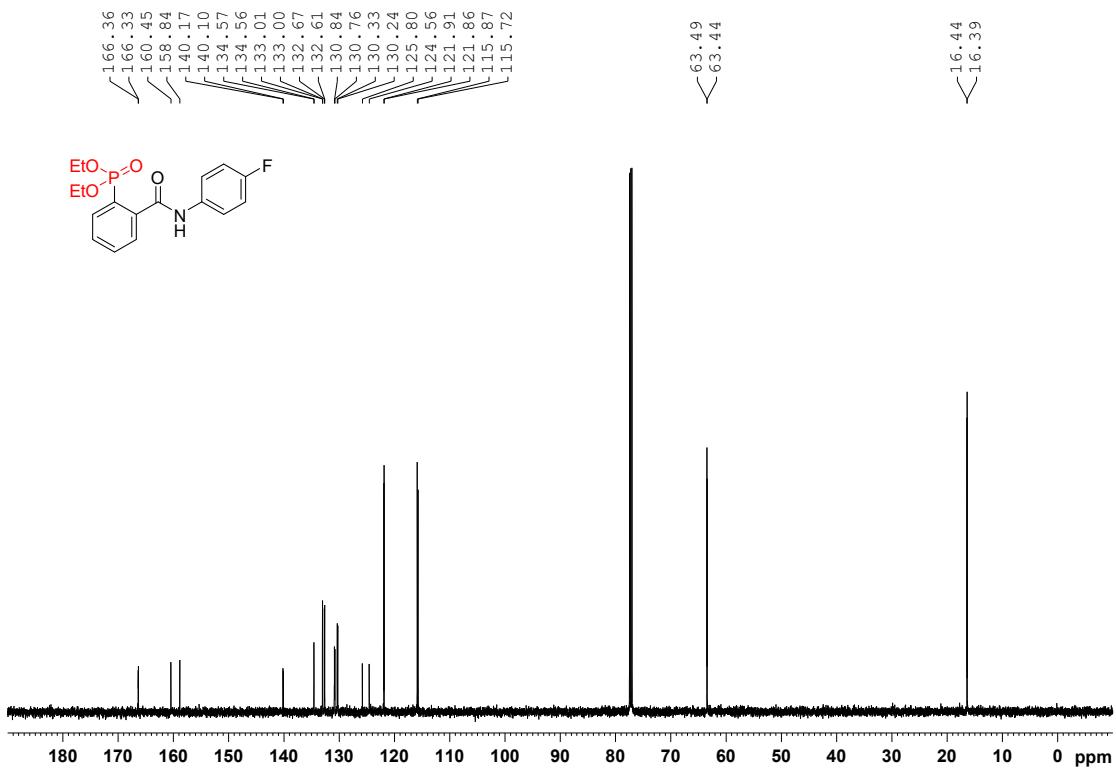


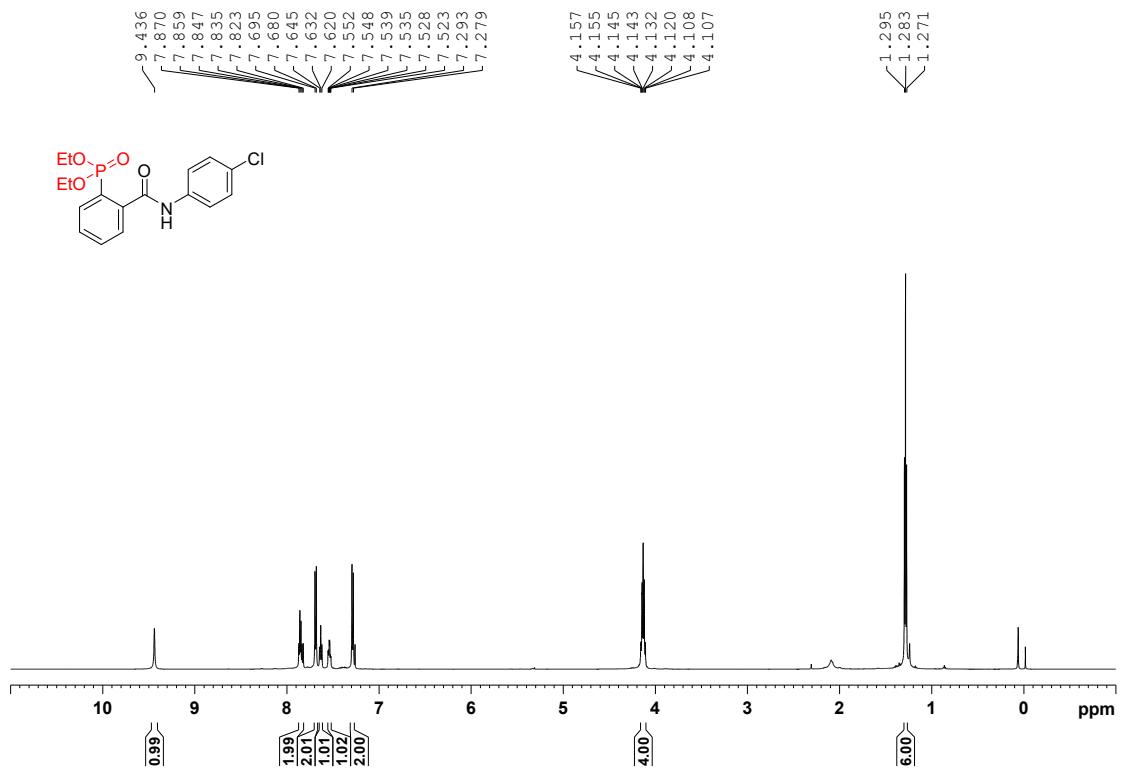
### <sup>1</sup>H NMR spectrum of compound 3e



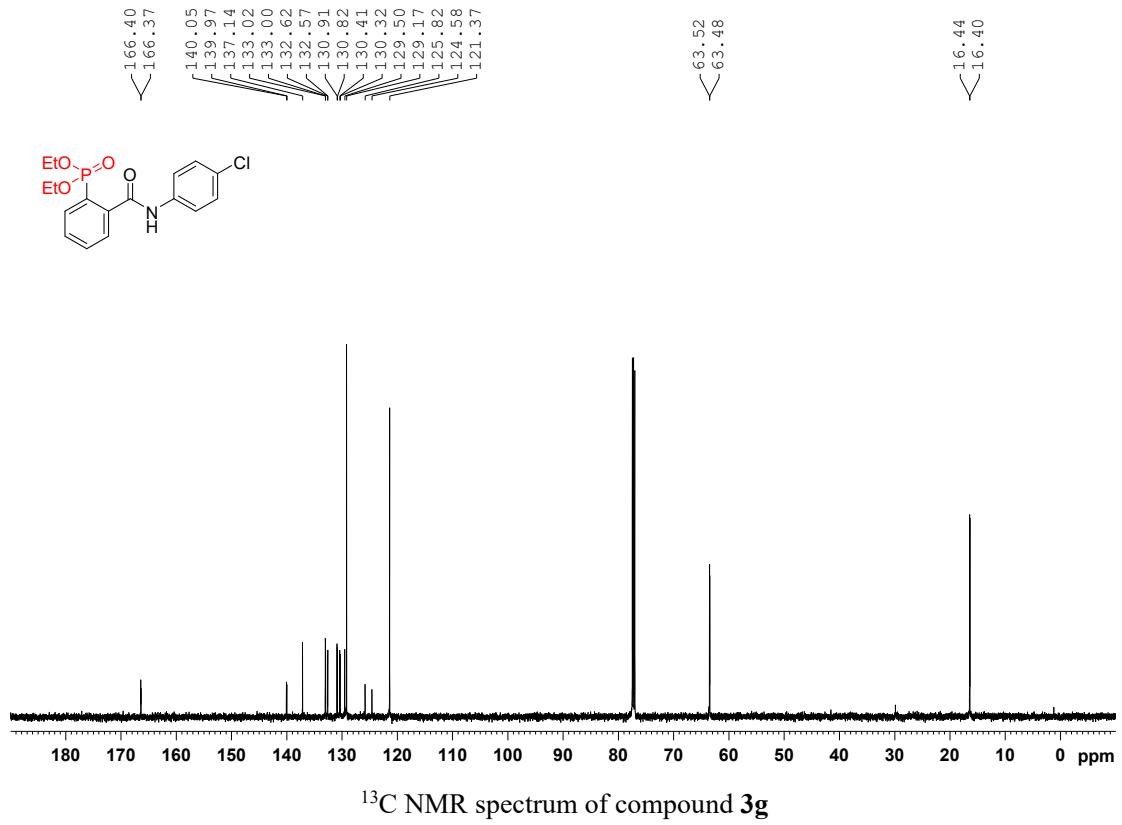
<sup>13</sup>C NMR spectrum of compound **3e**



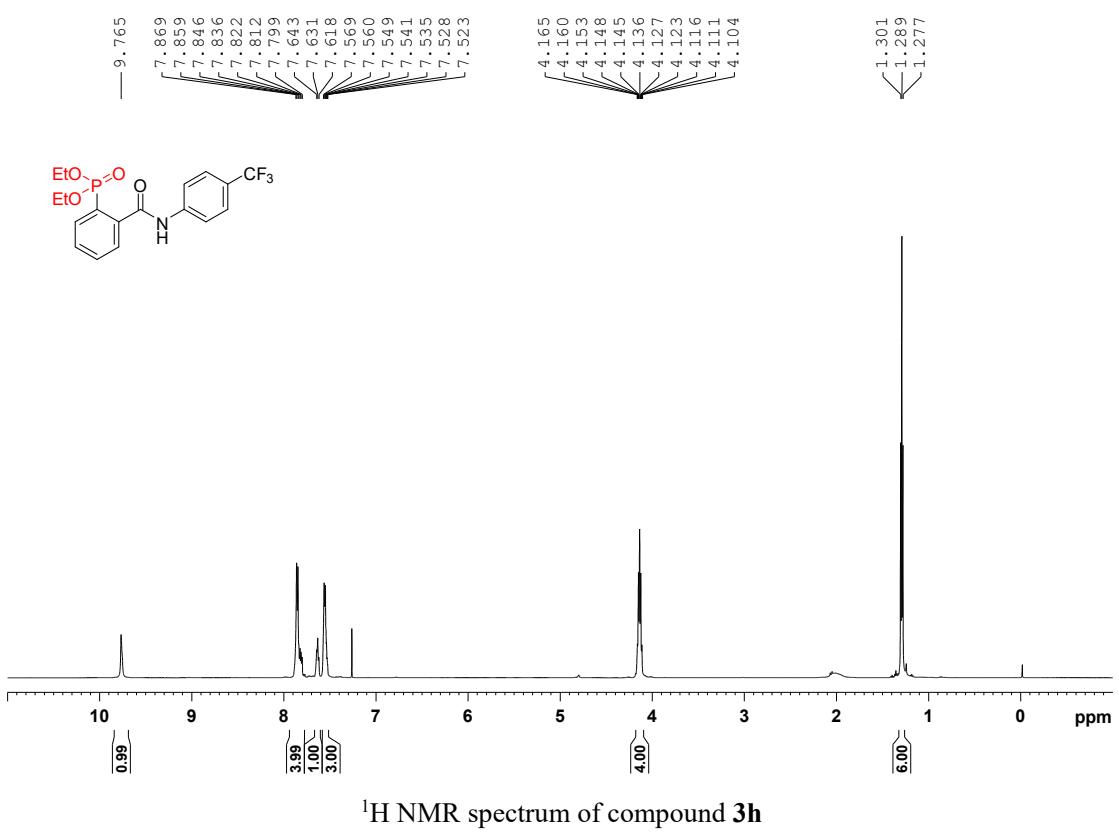
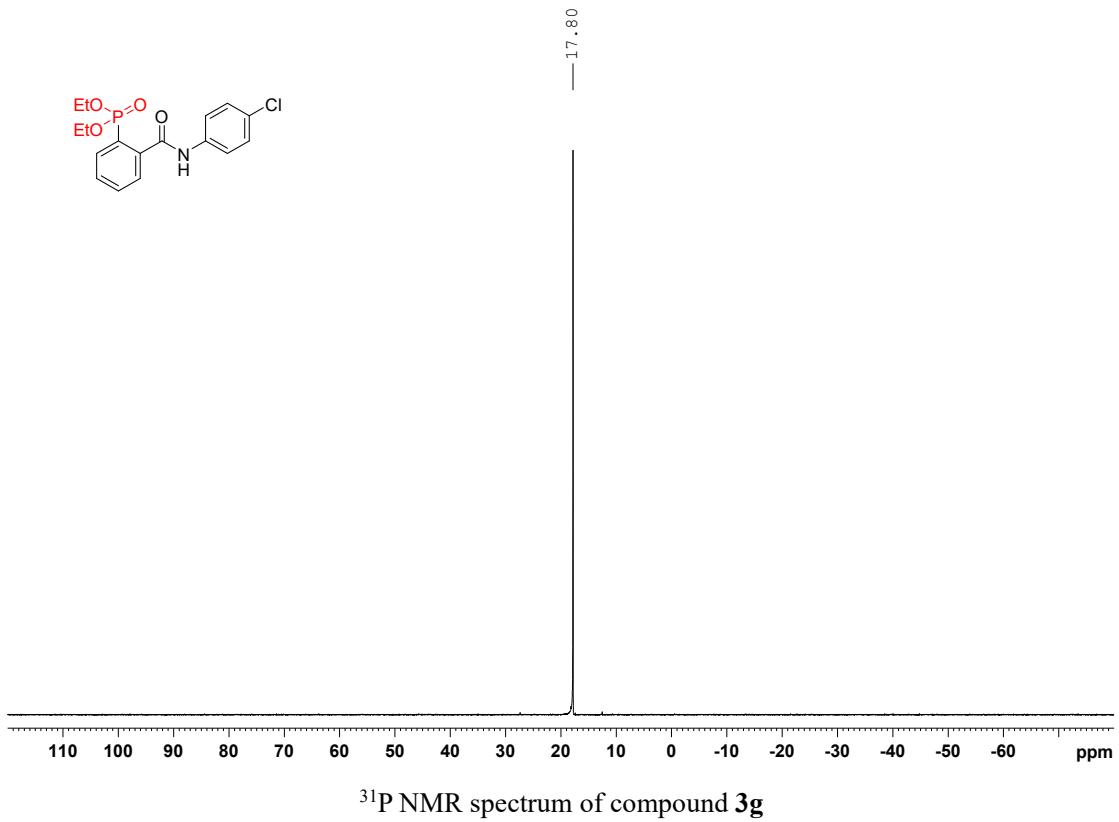


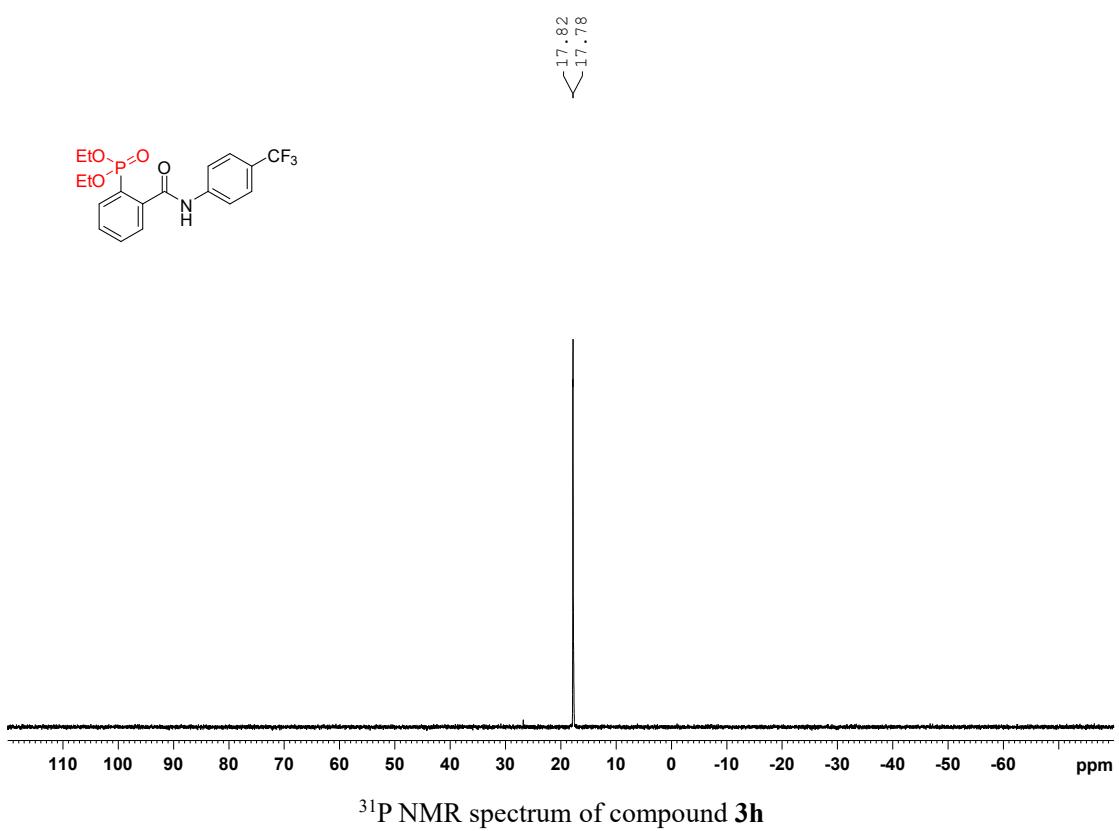
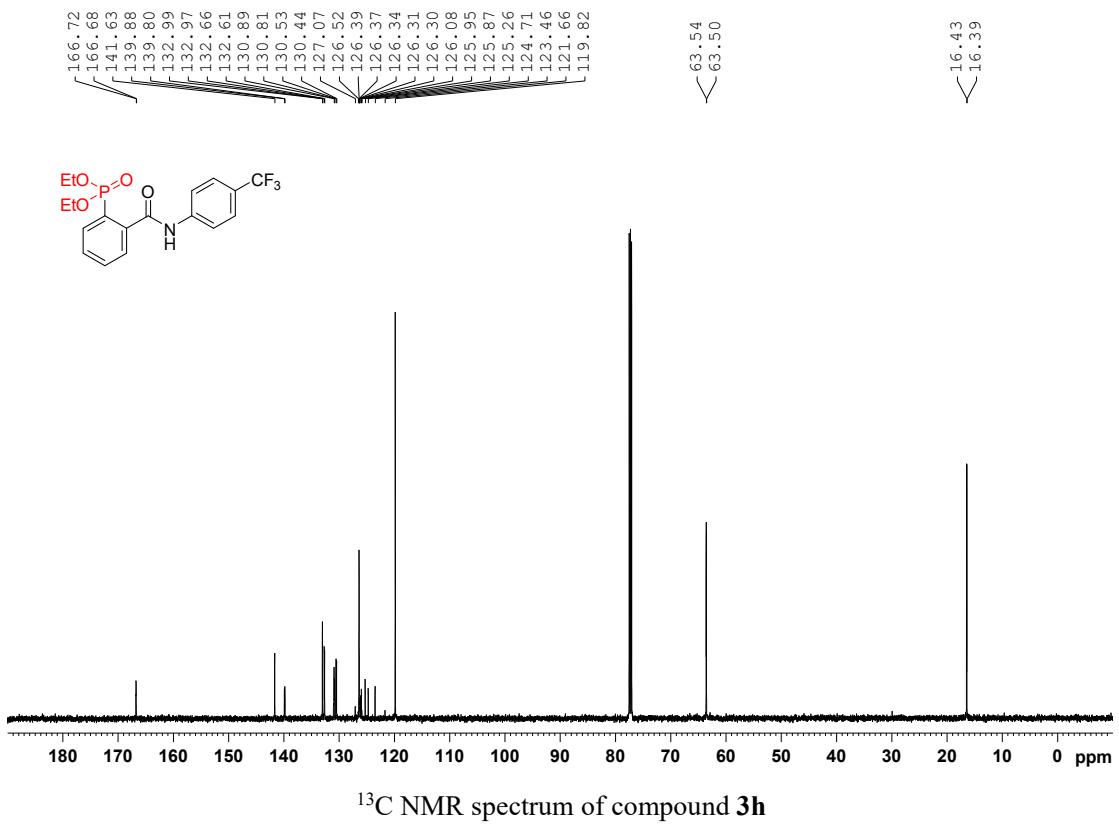


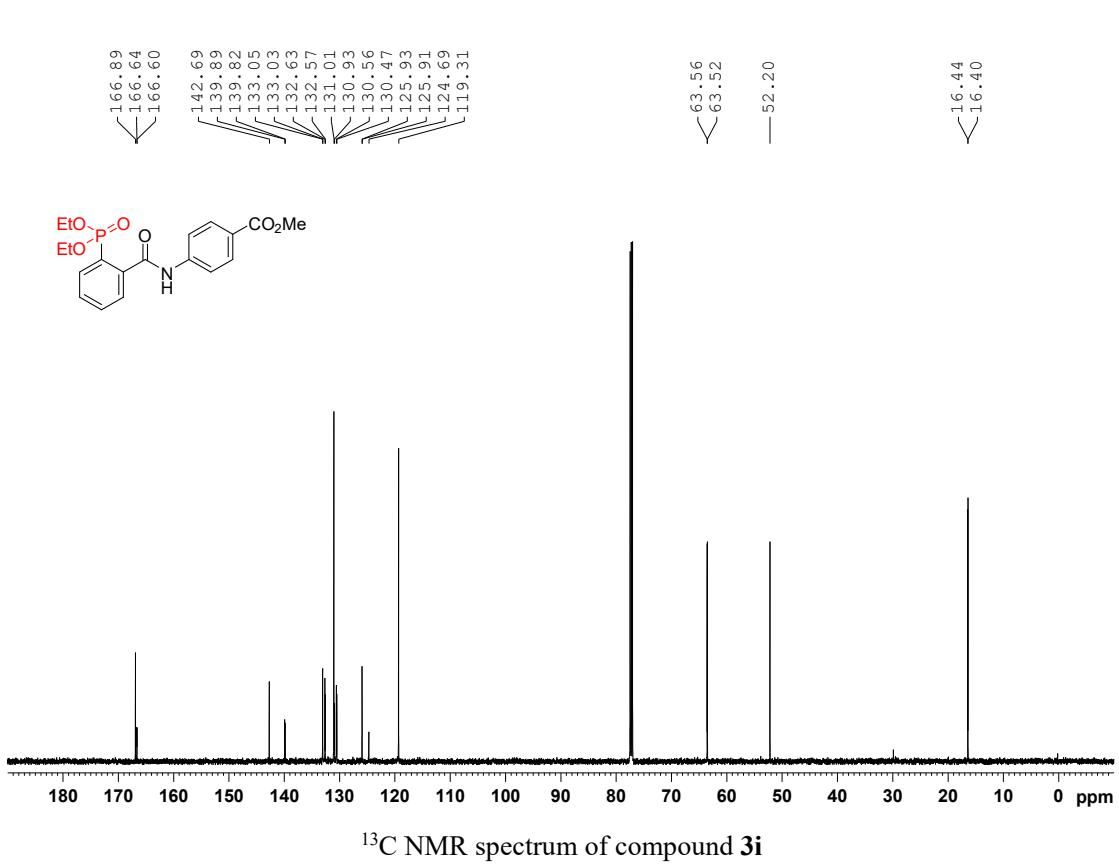
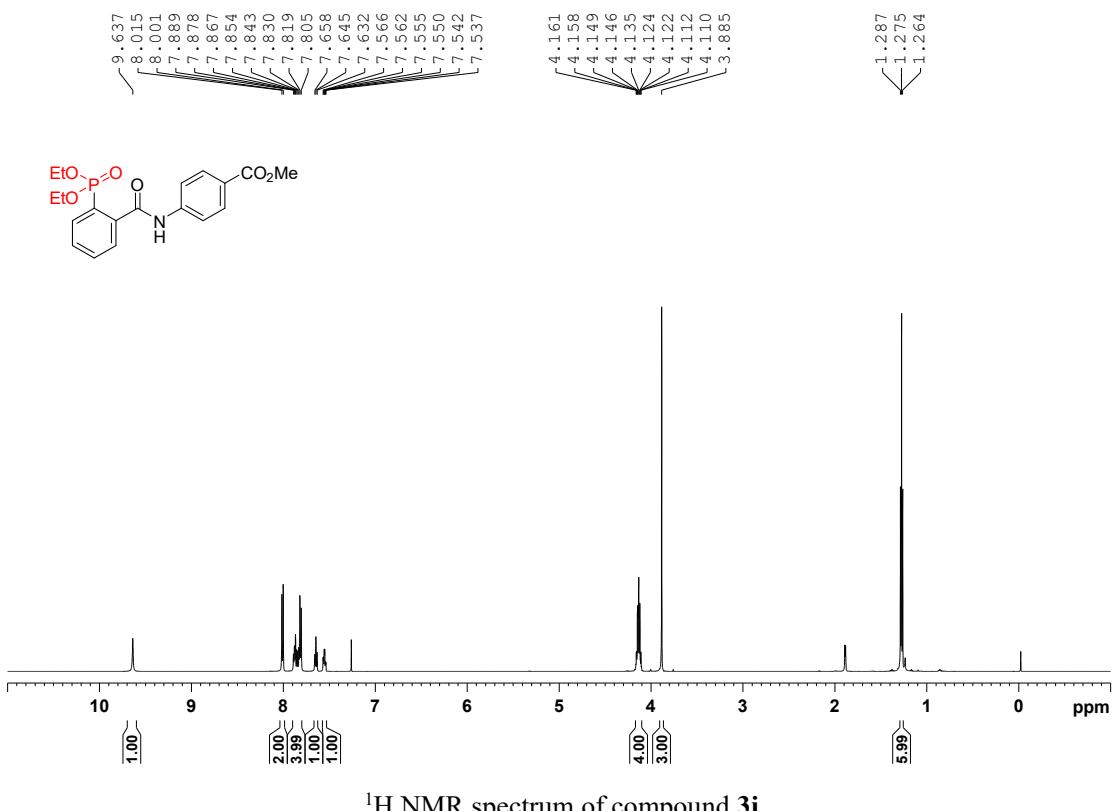
### <sup>1</sup>H NMR spectrum of compound 3g

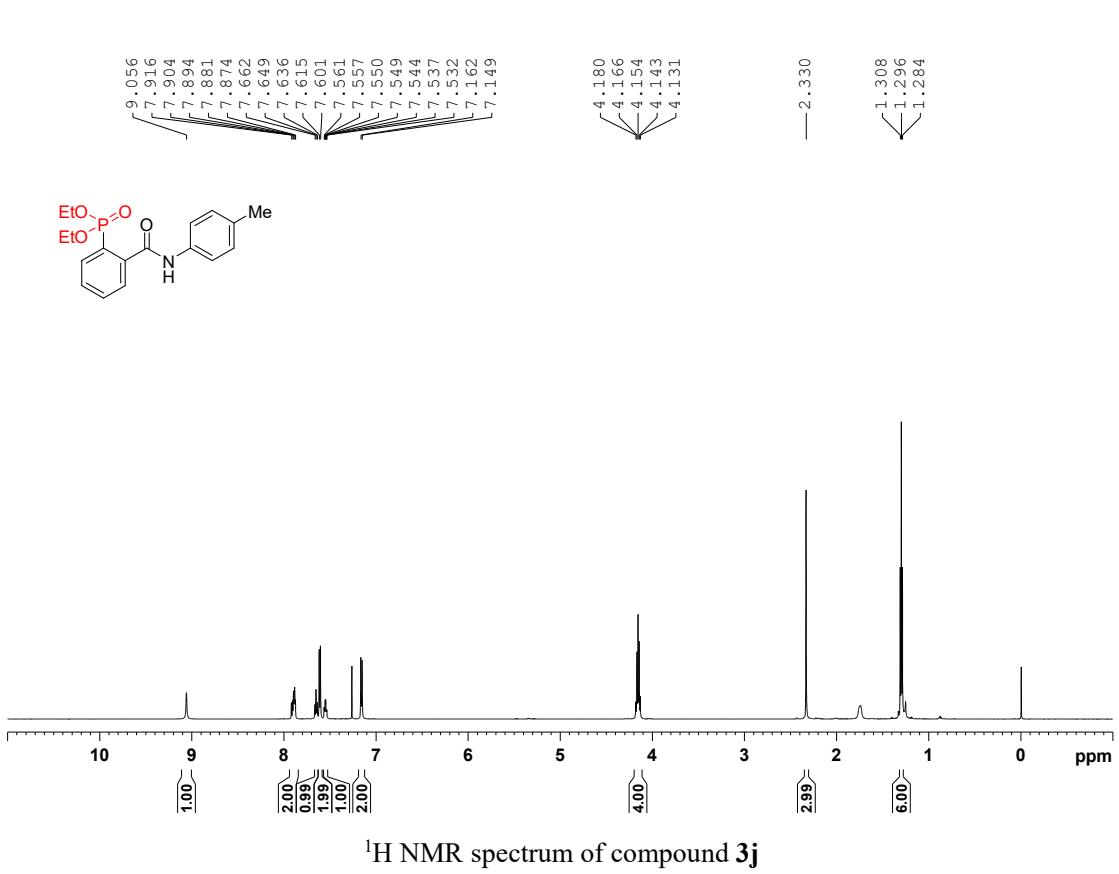
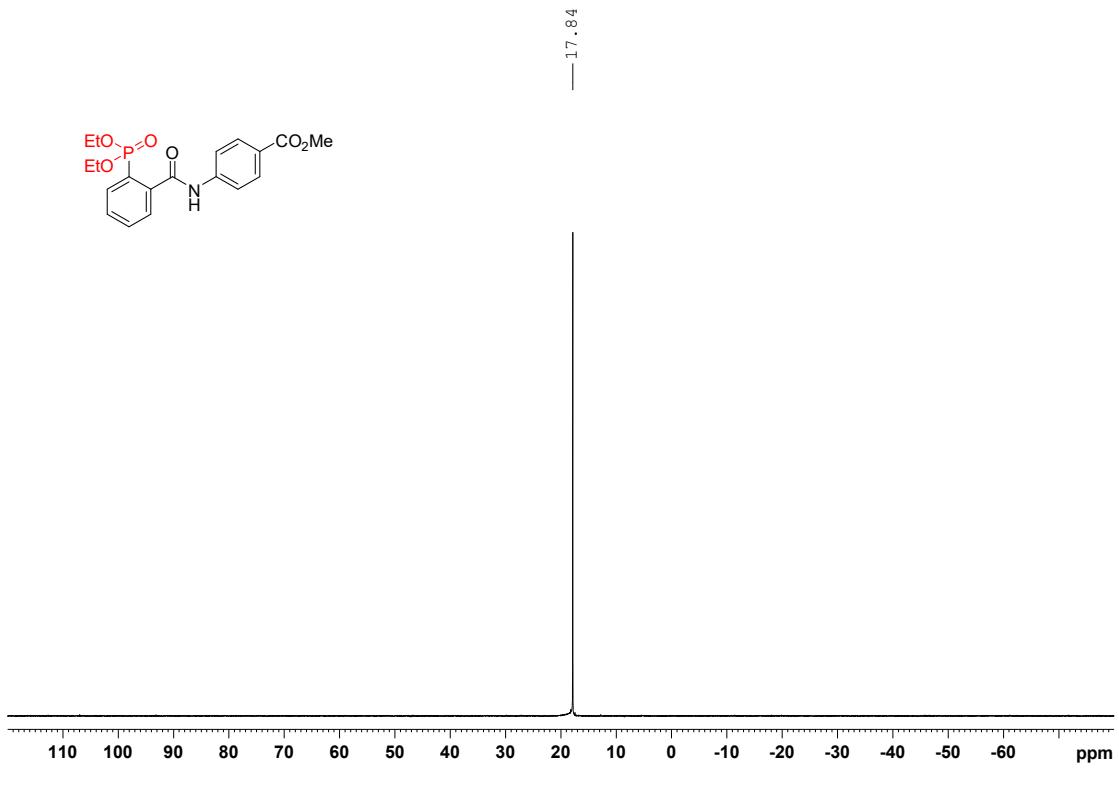


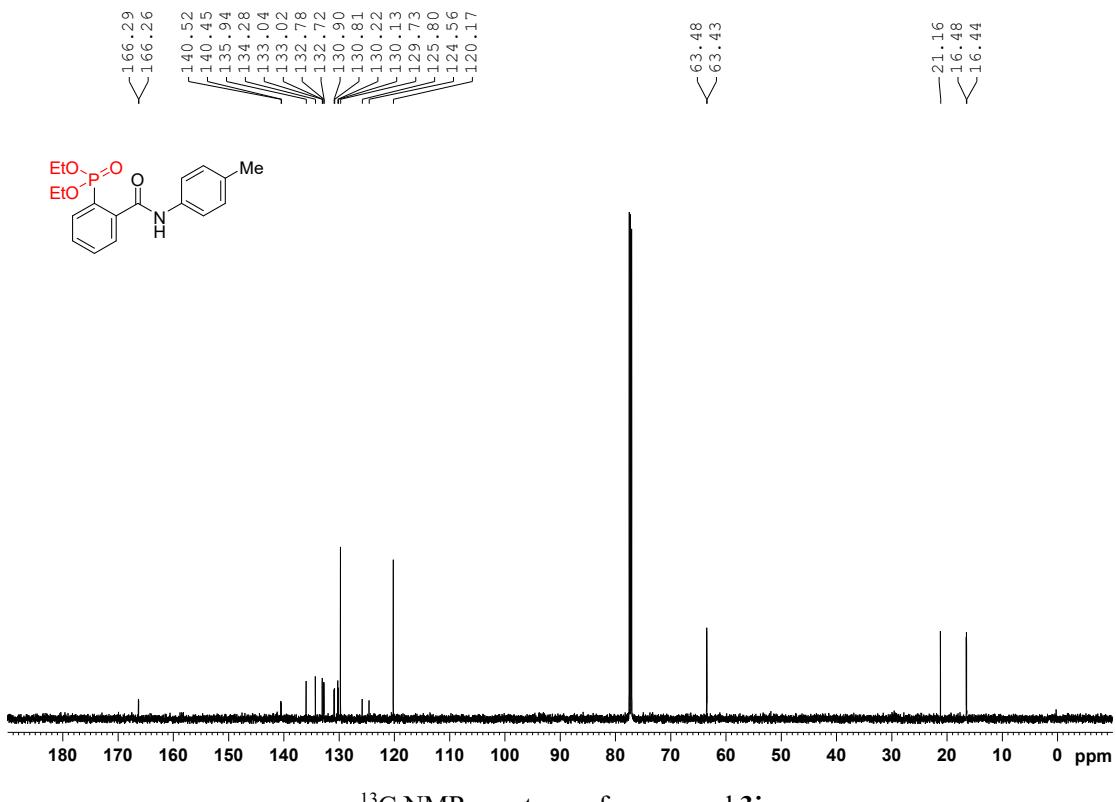
### <sup>13</sup>C NMR spectrum of compound 3g



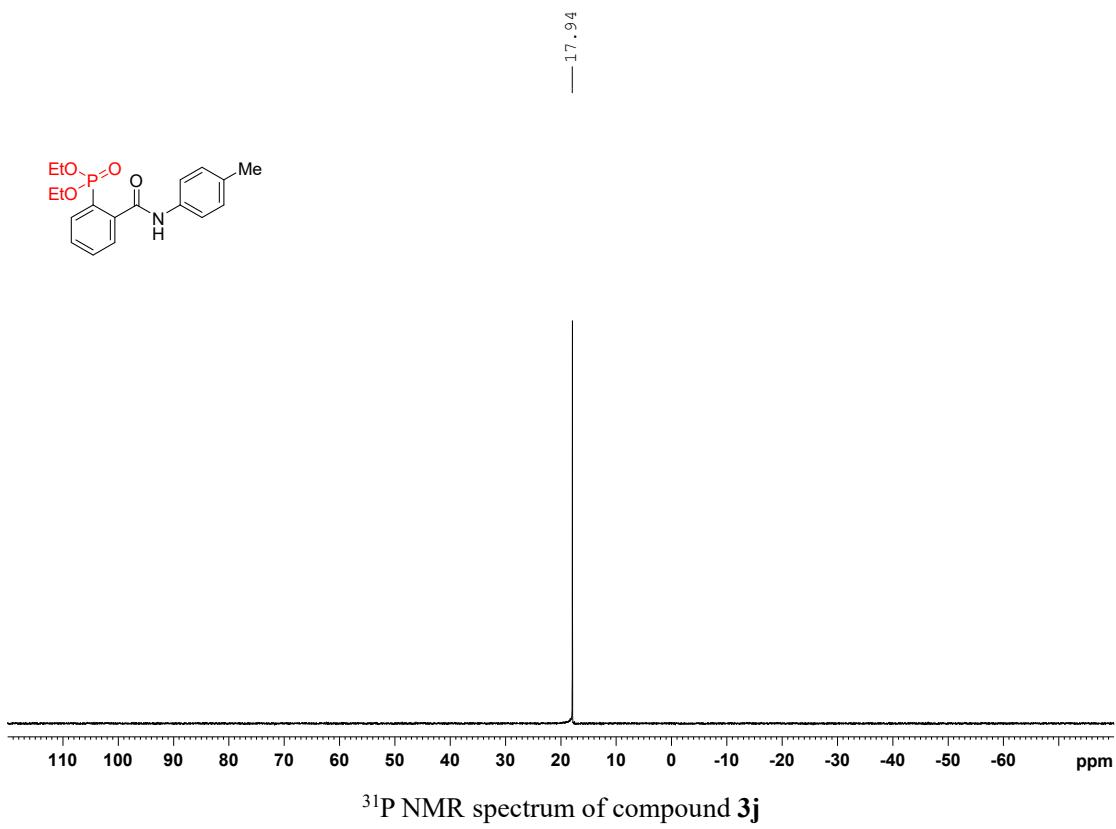




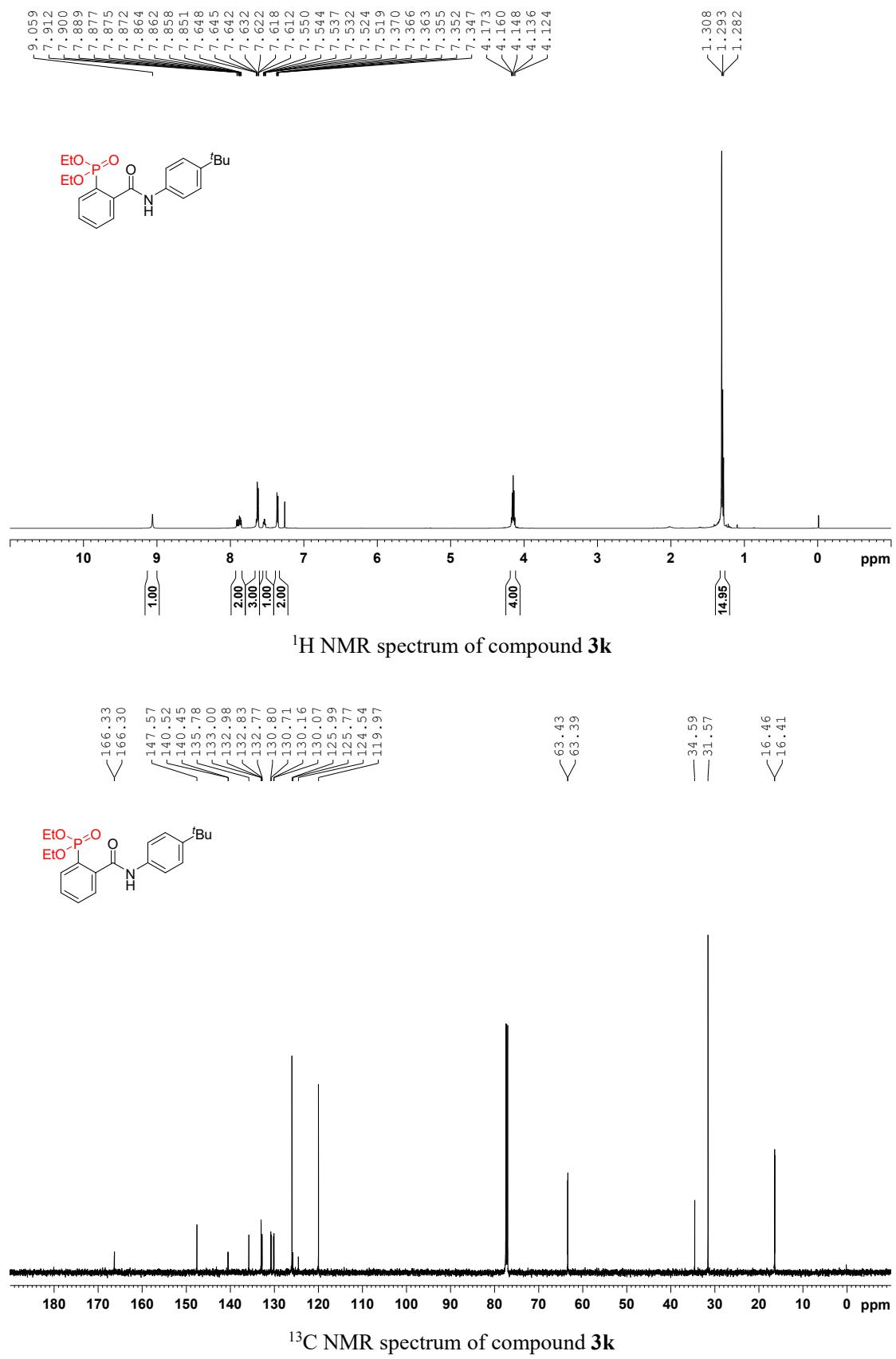


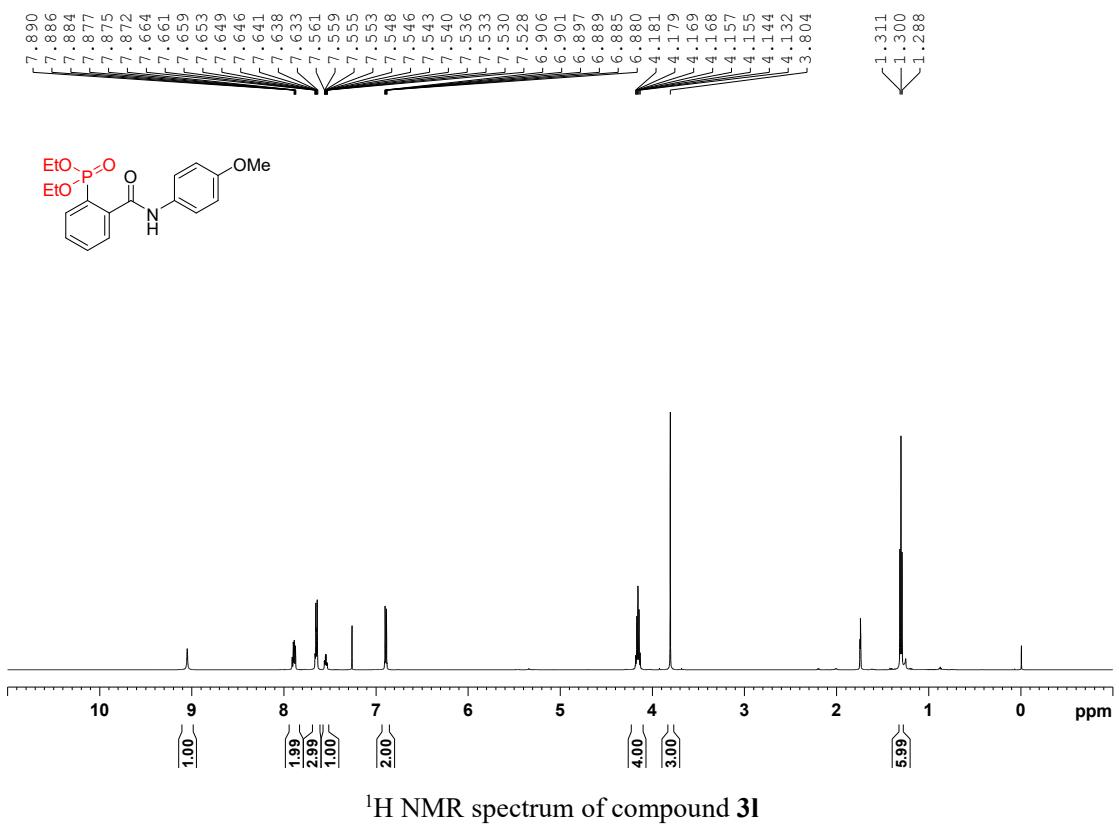
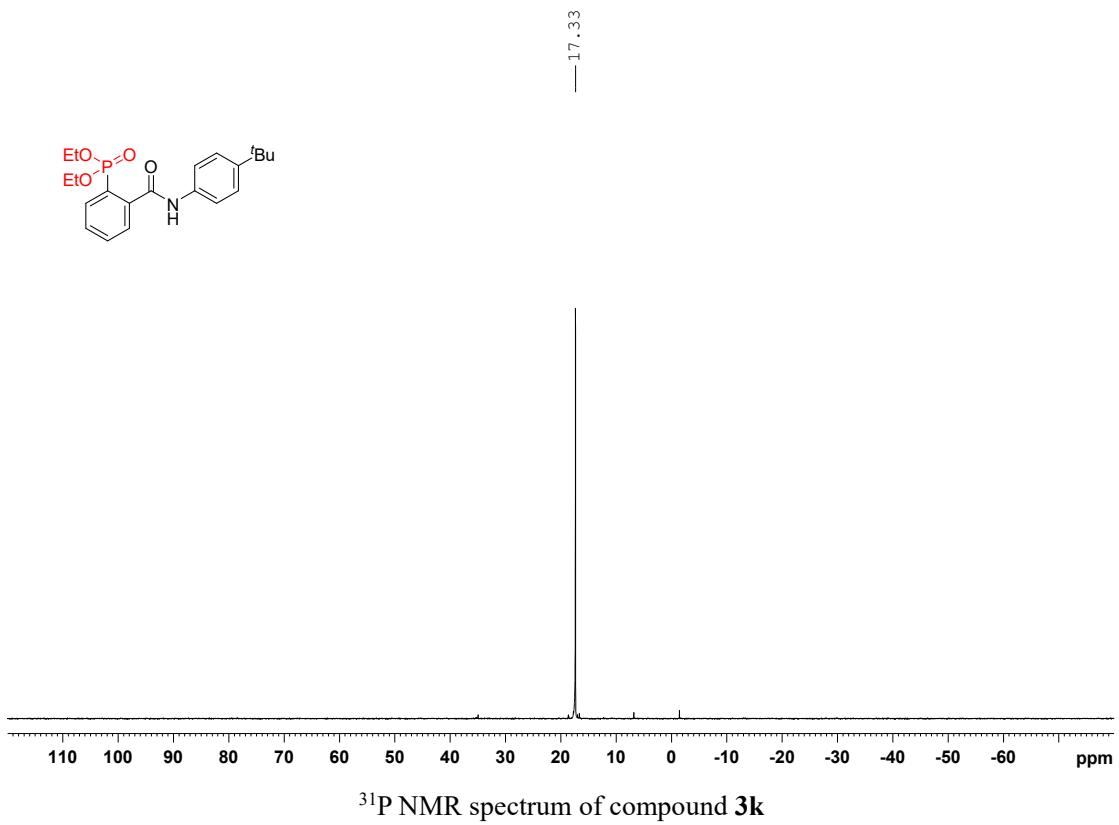


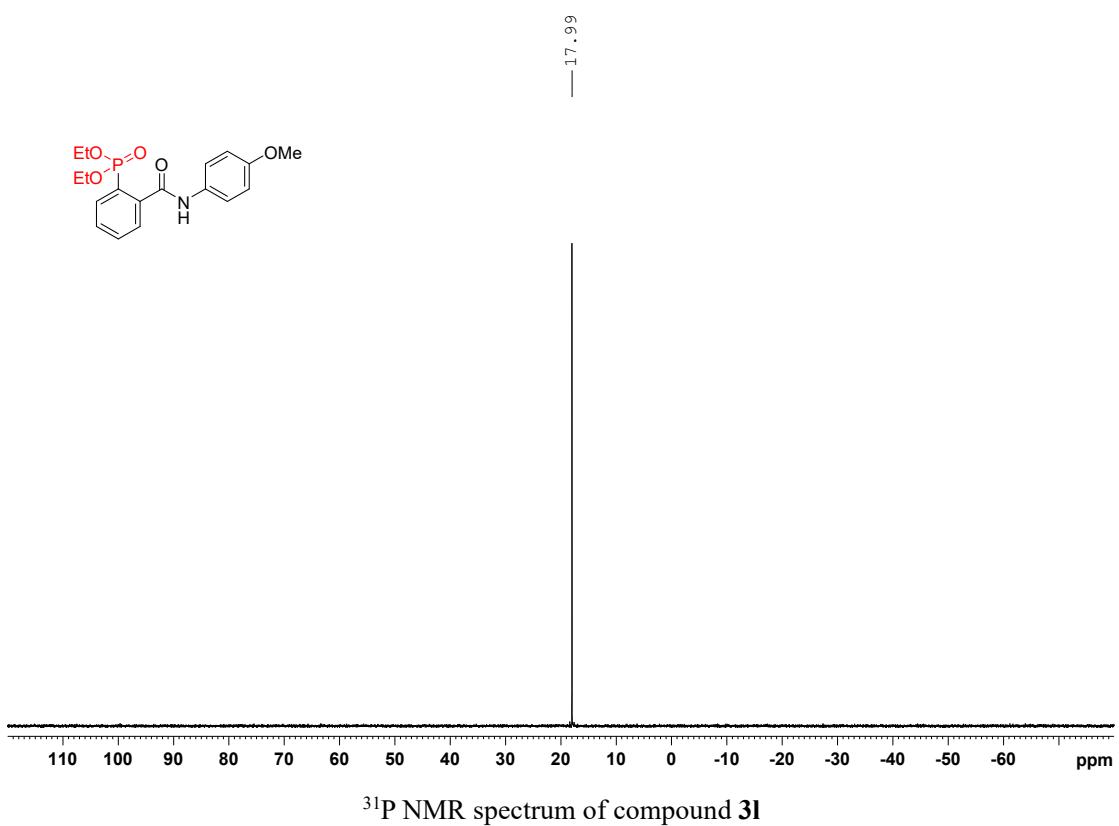
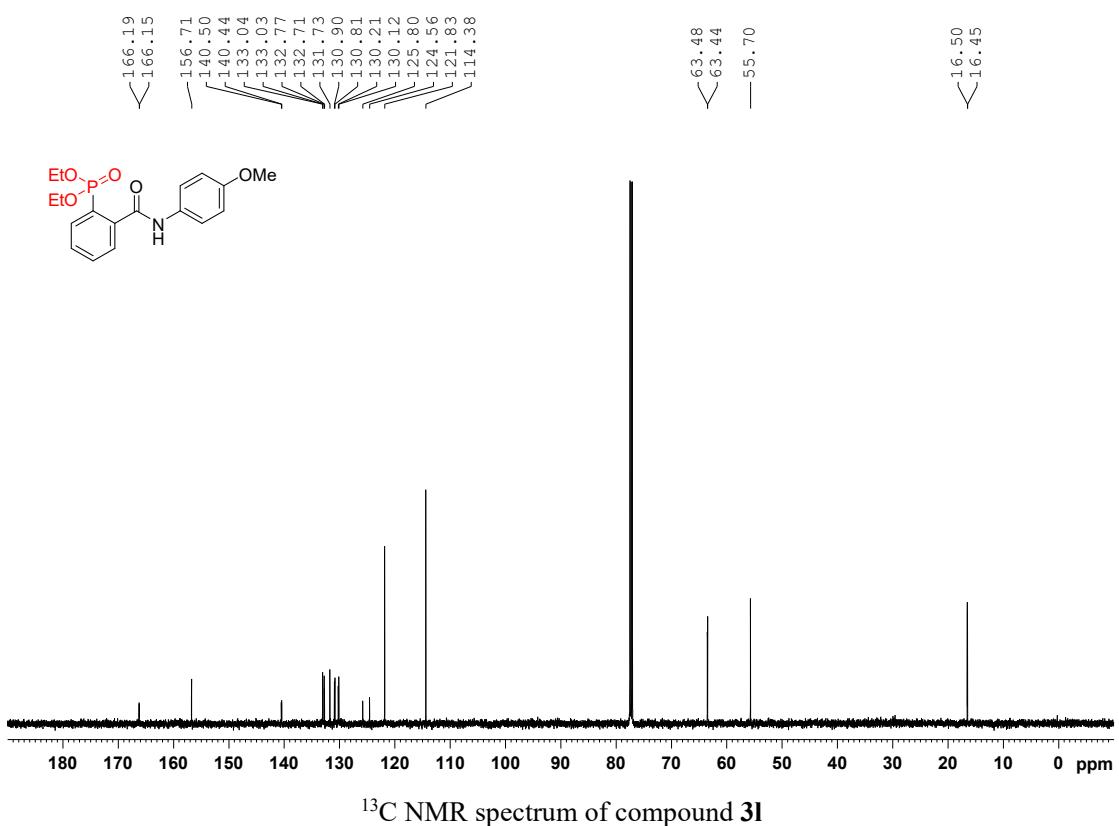
$^{13}\text{C}$  NMR spectrum of compound **3j**

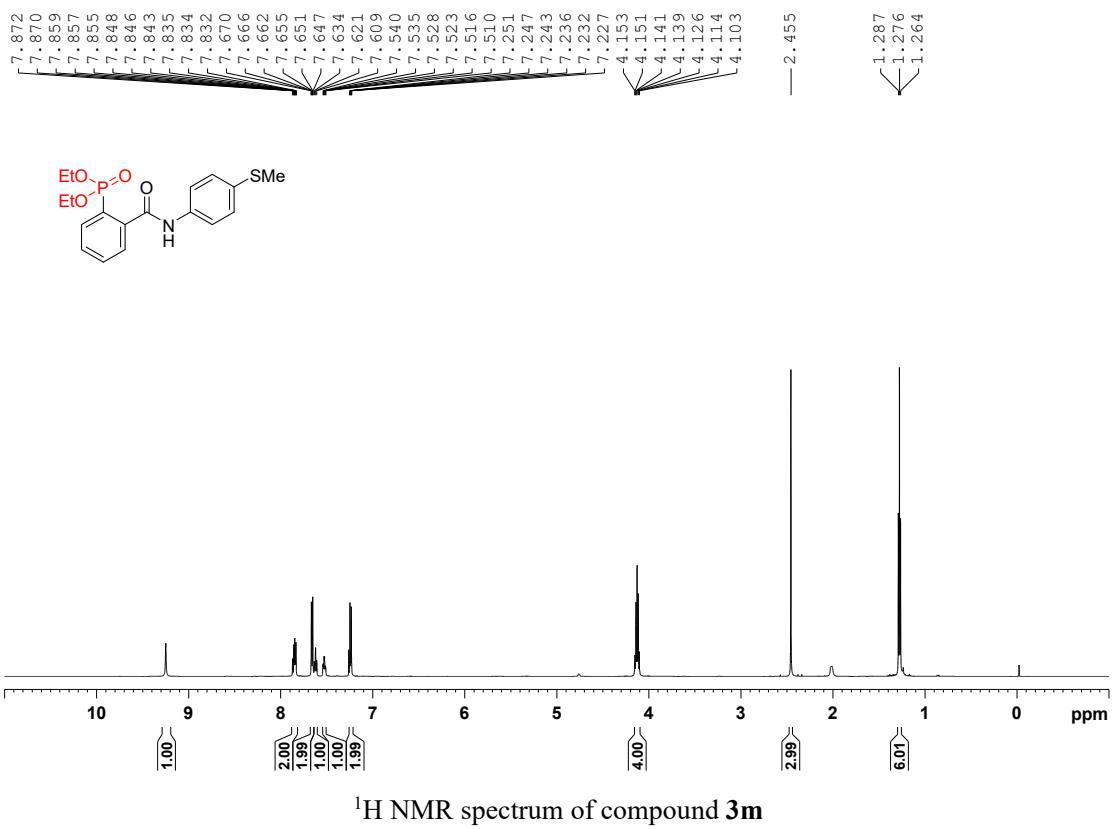


$^{31}\text{P}$  NMR spectrum of compound **3j**

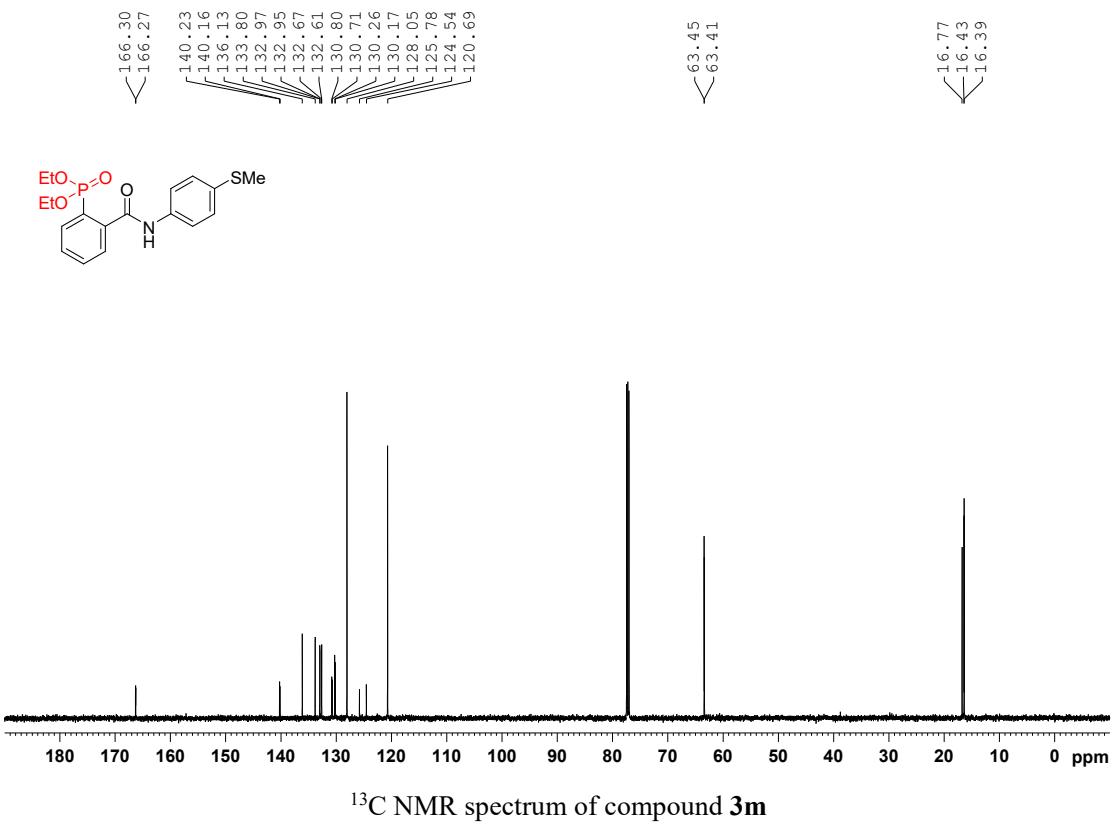




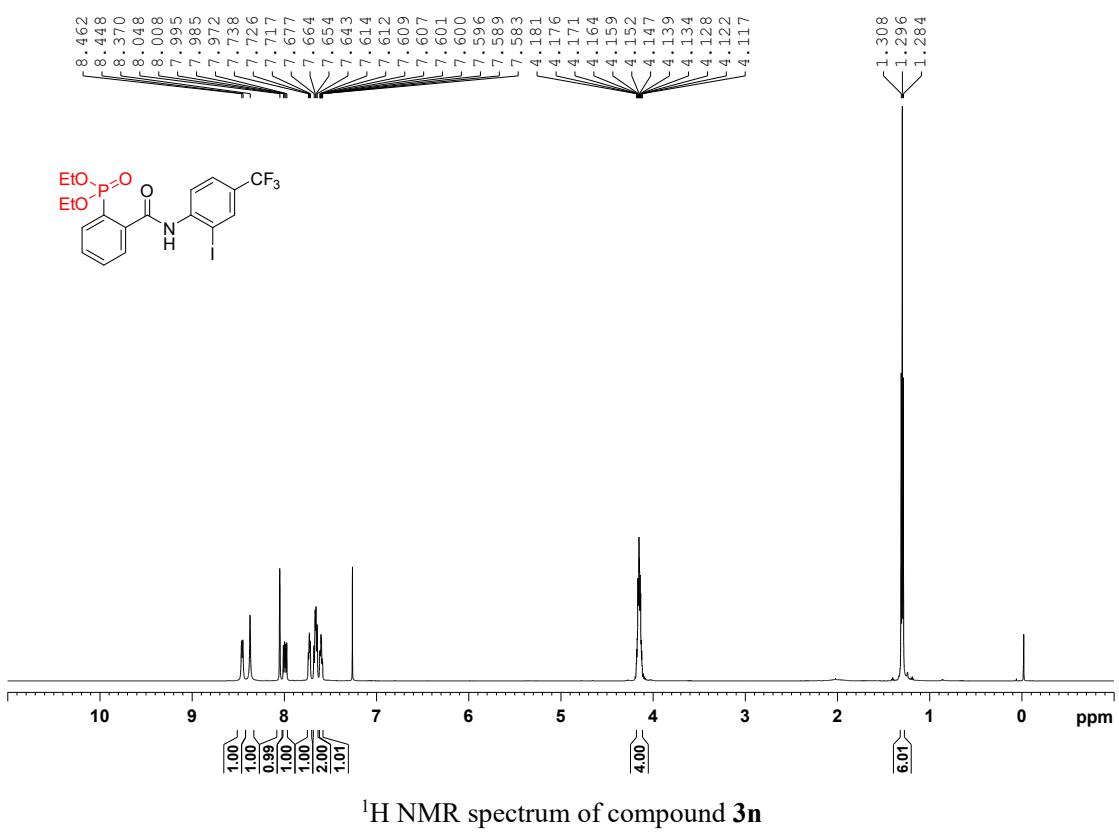
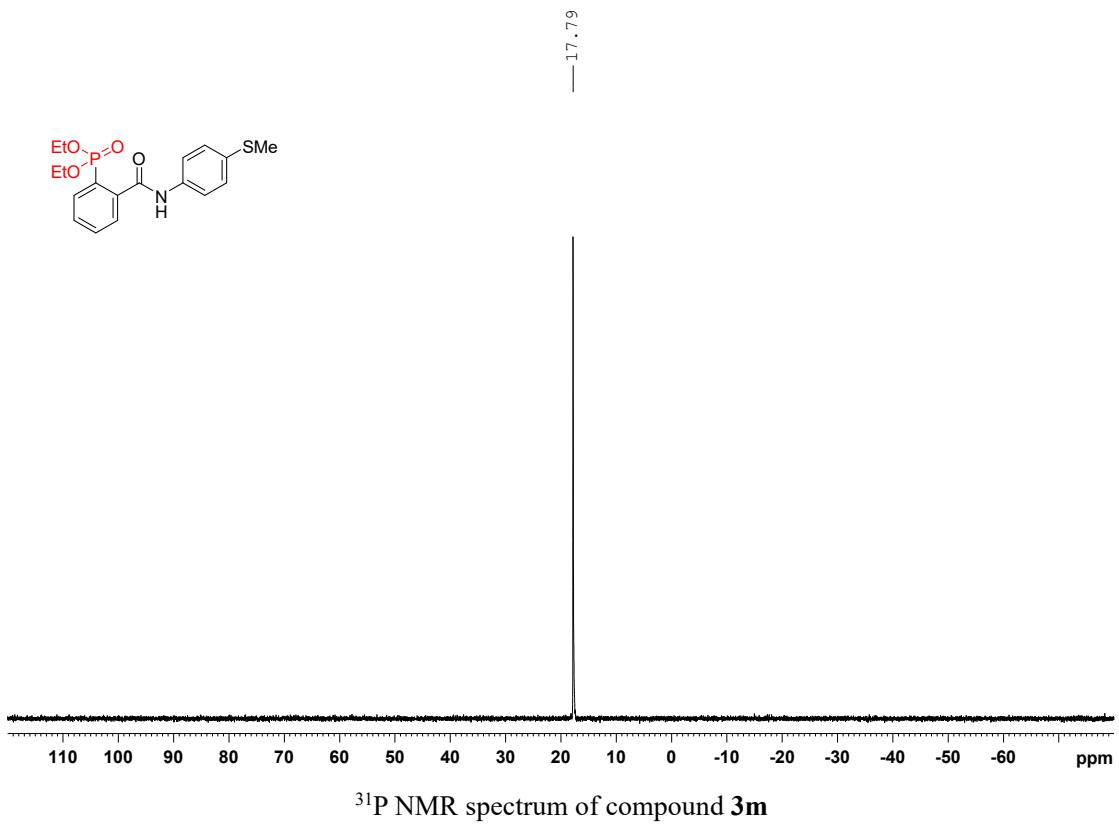


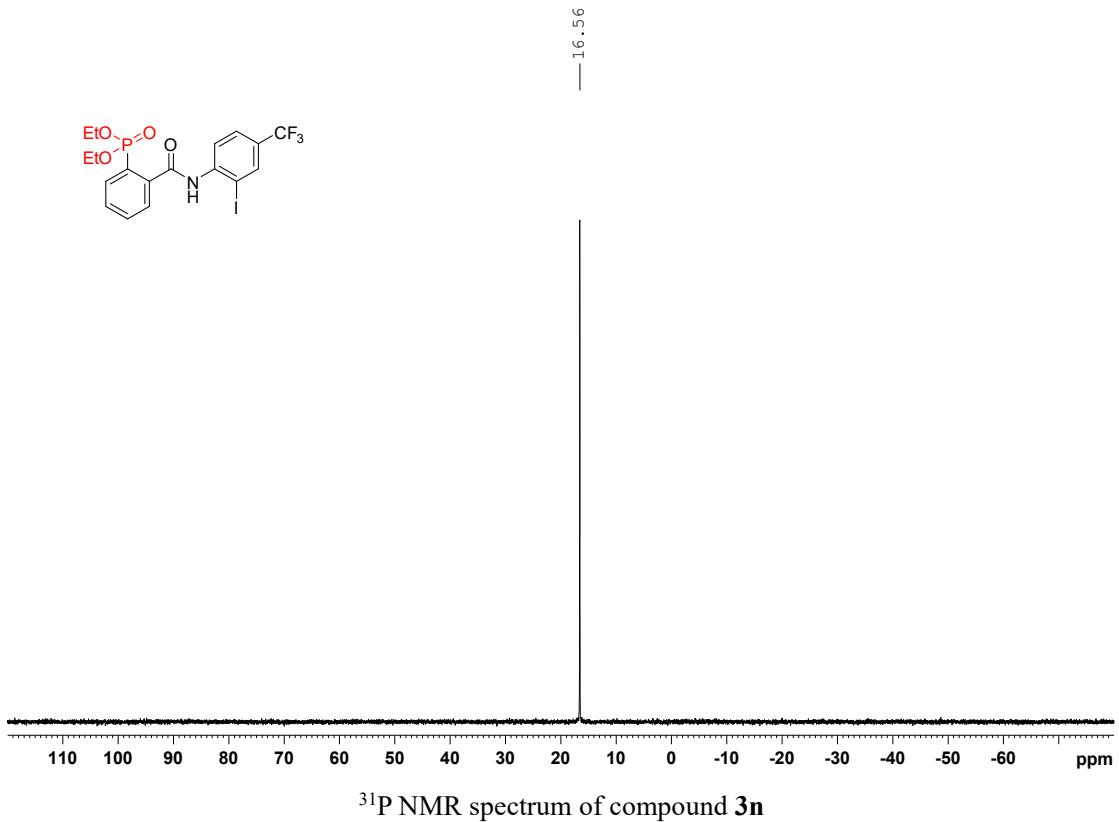
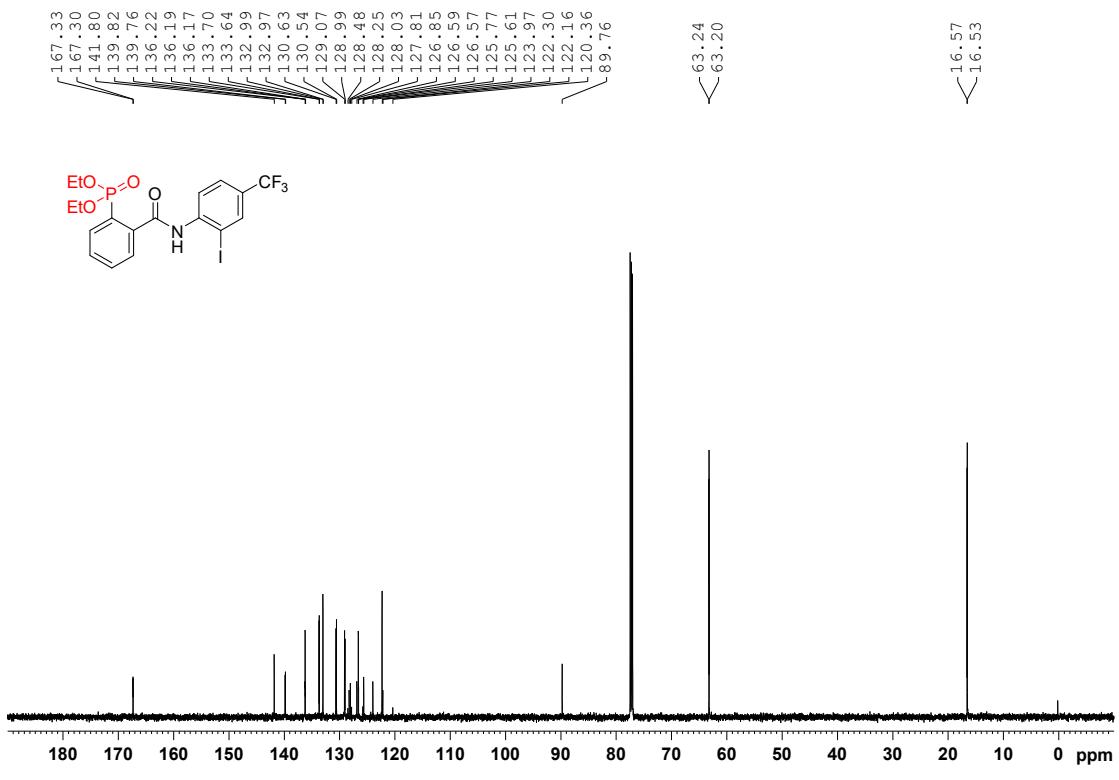


<sup>1</sup>H NMR spectrum of compound **3m**

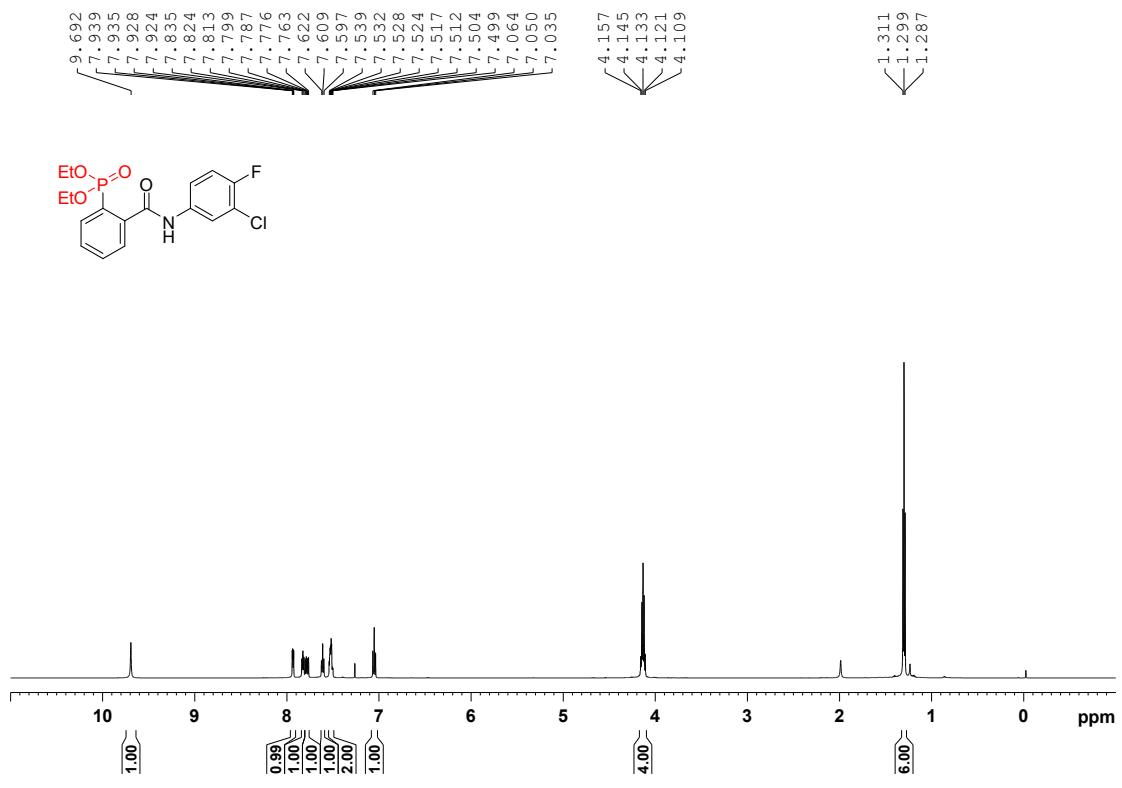


<sup>13</sup>C NMR spectrum of compound **3m**

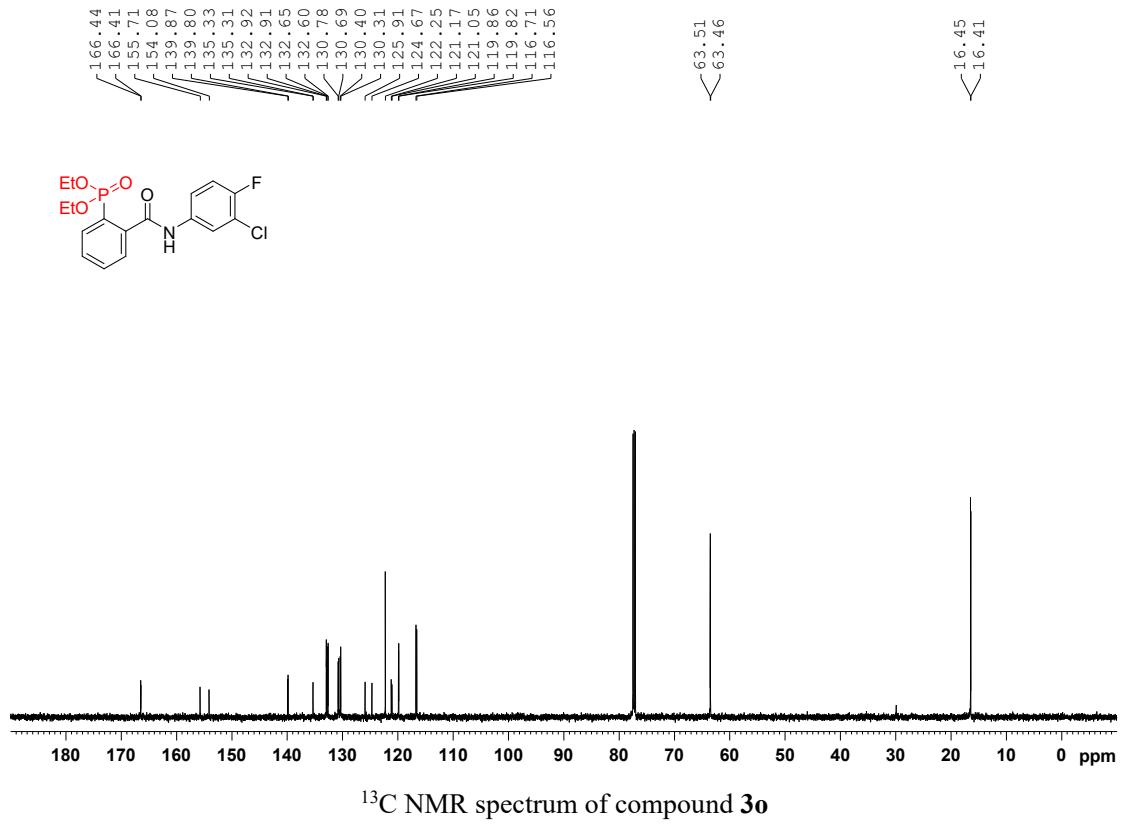




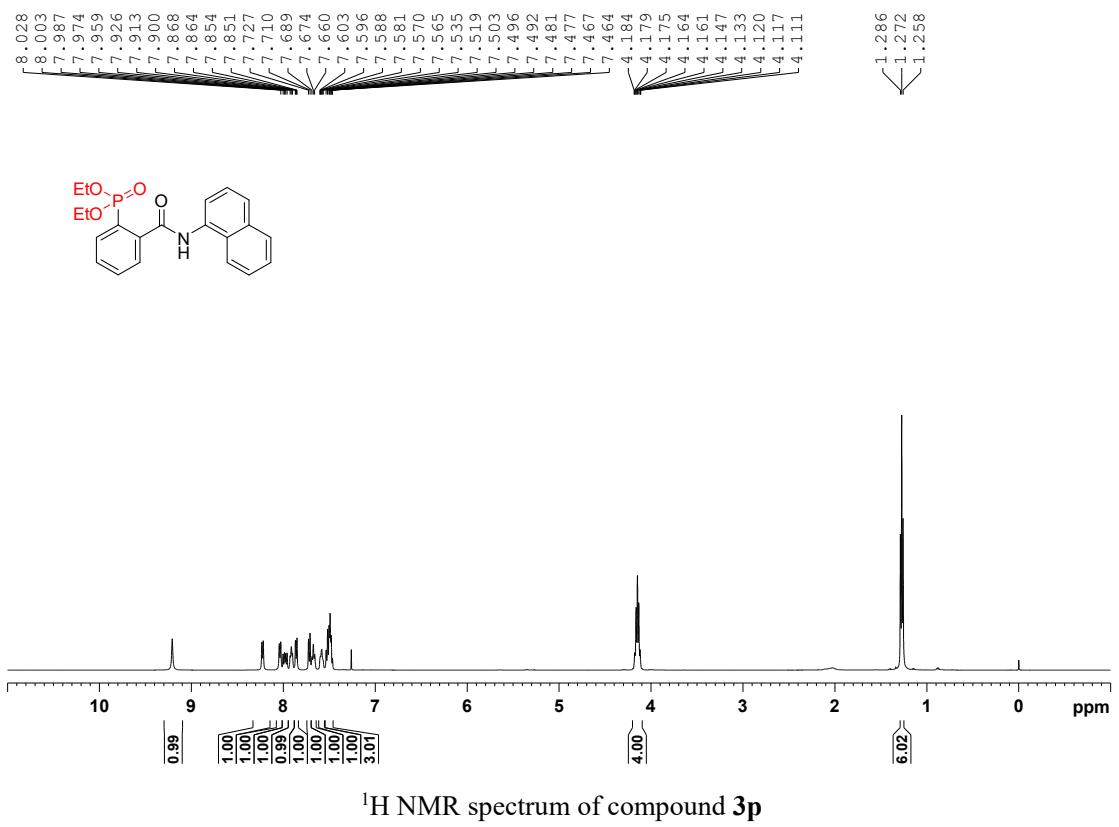
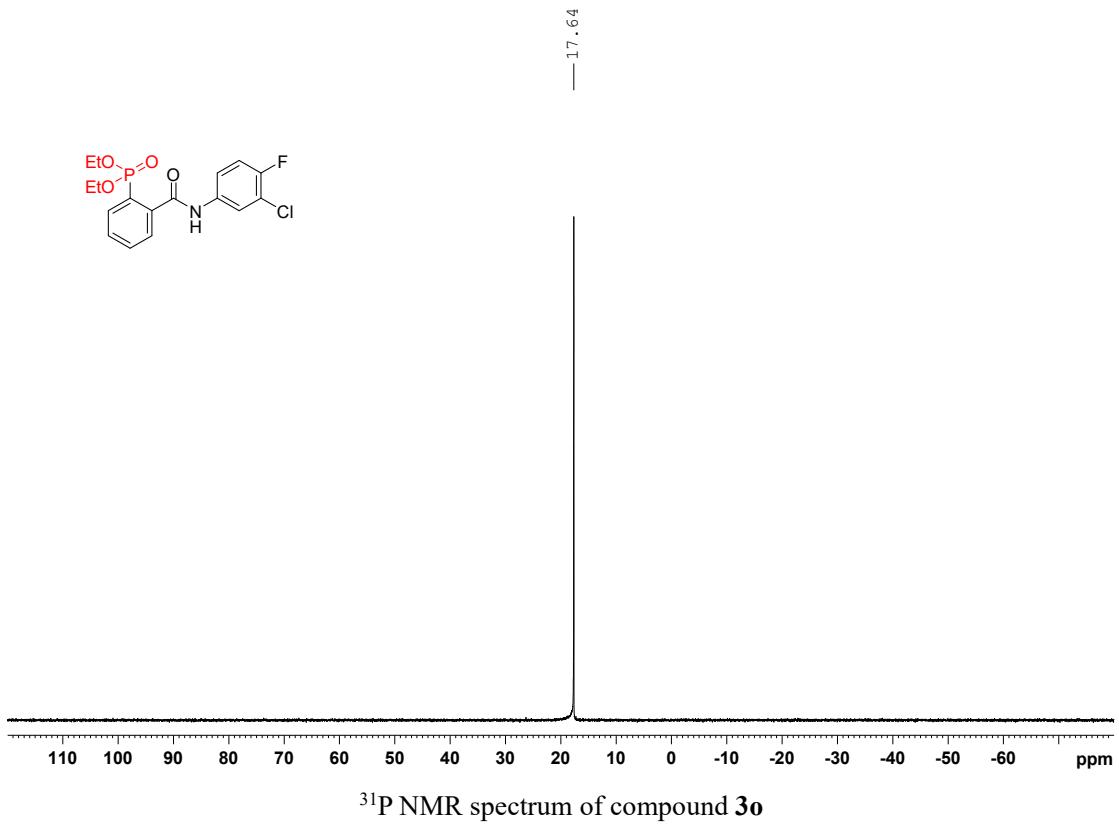
$^{31}\text{P}$  NMR spectrum of compound **3n**

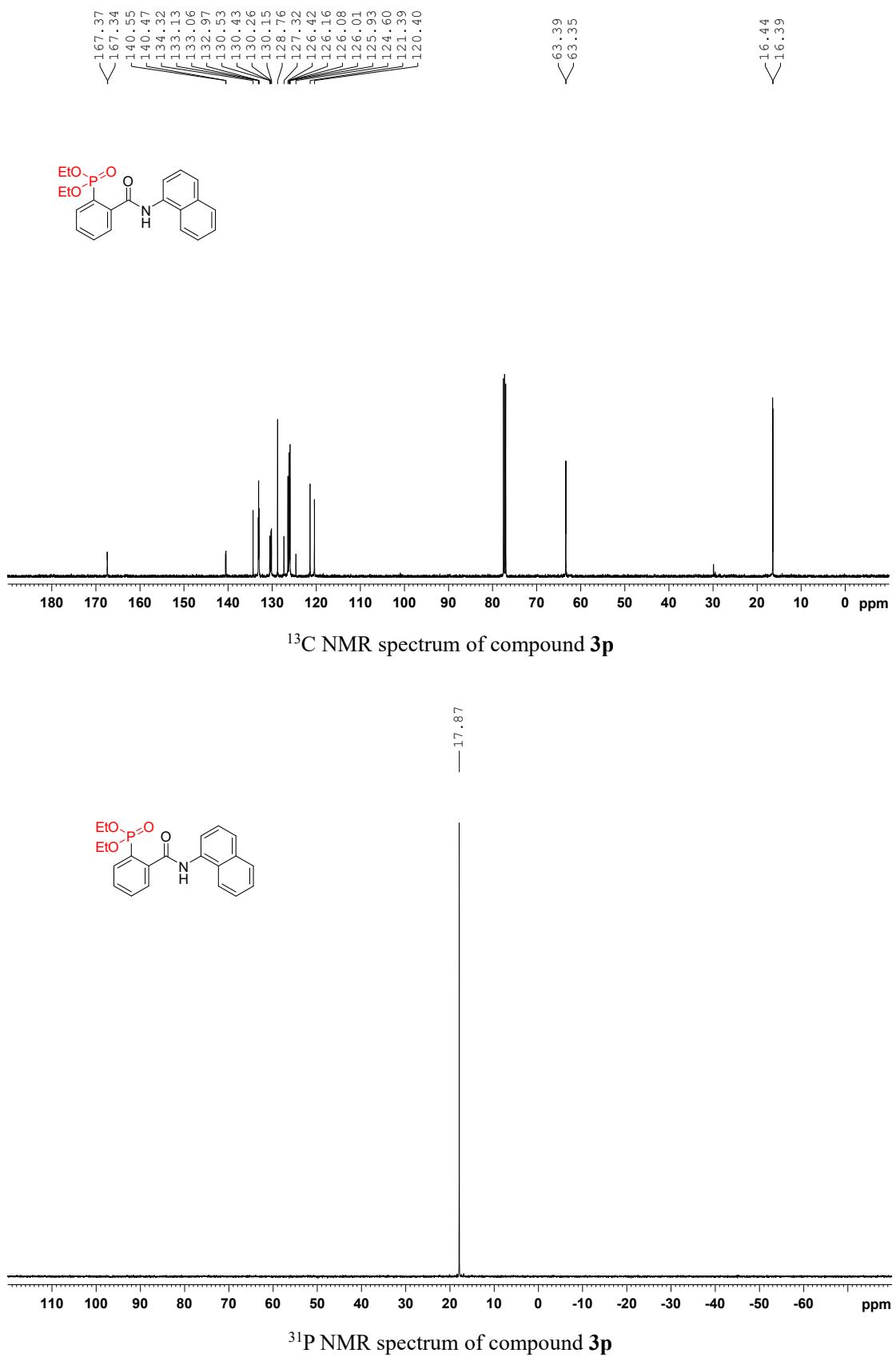


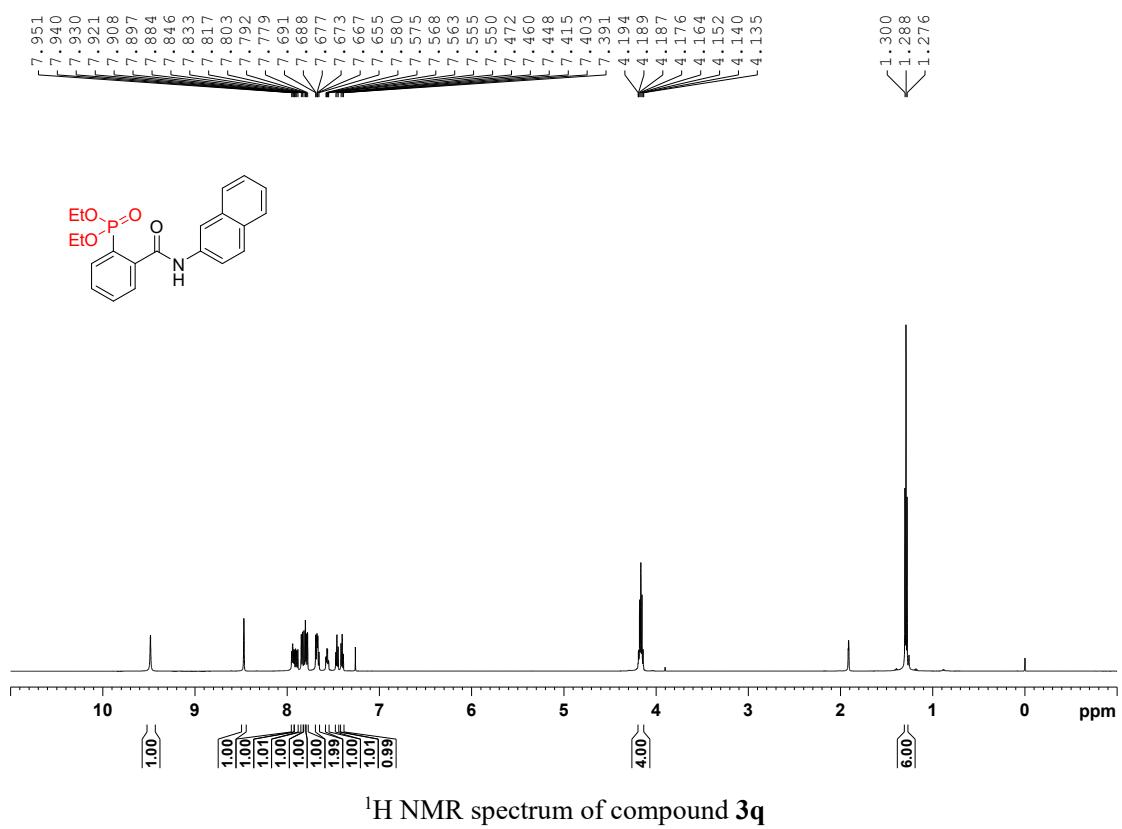
<sup>1</sup>H NMR spectrum of compound **3o**



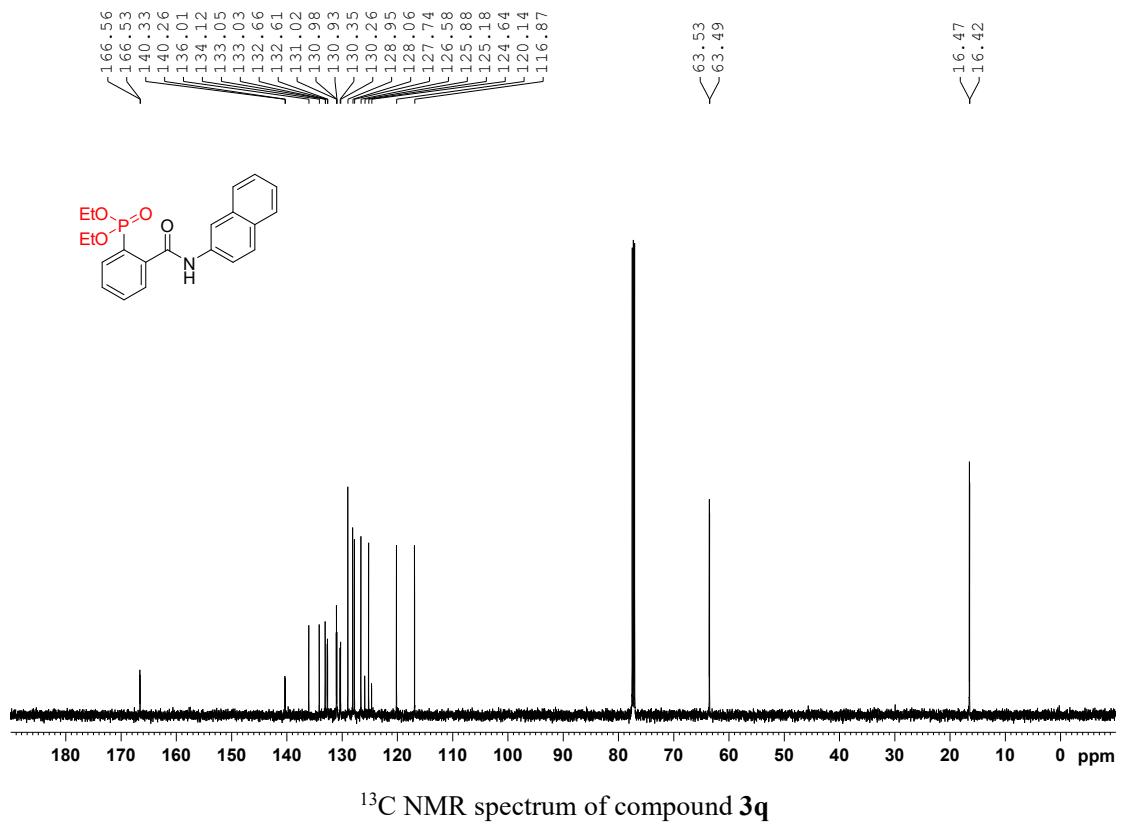
### <sup>13</sup>C NMR spectrum of compound **3o**



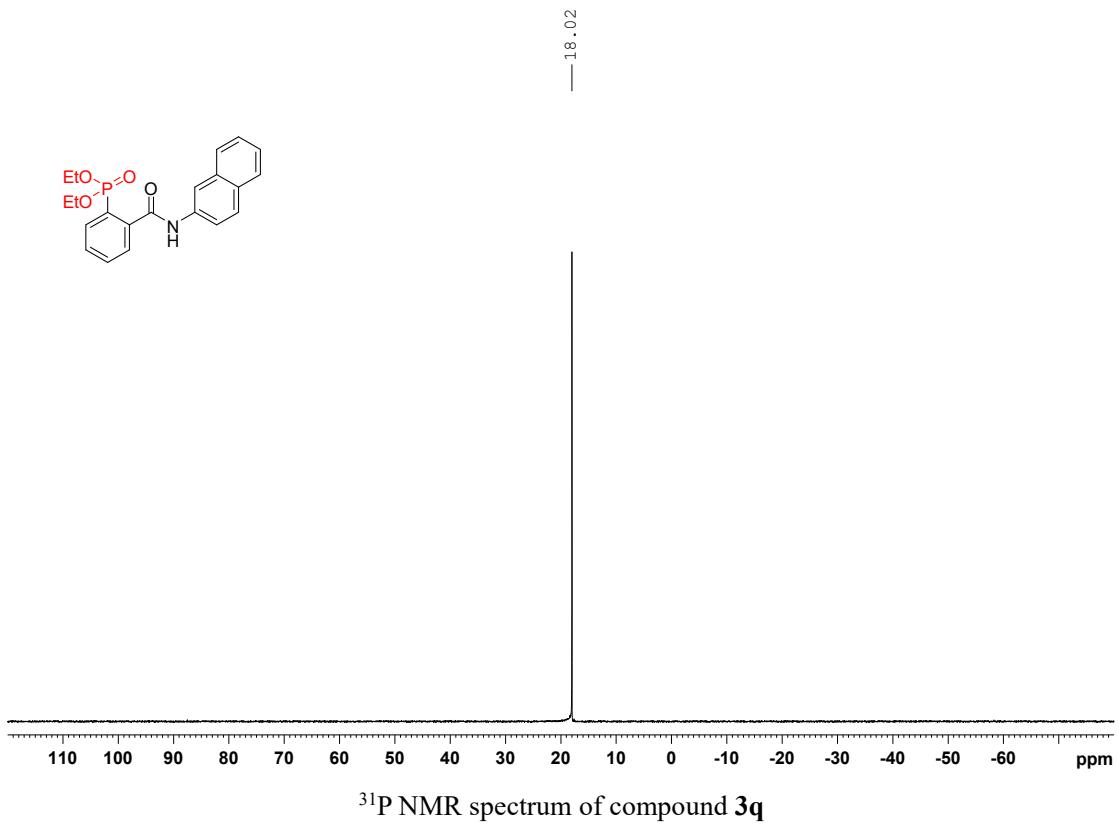




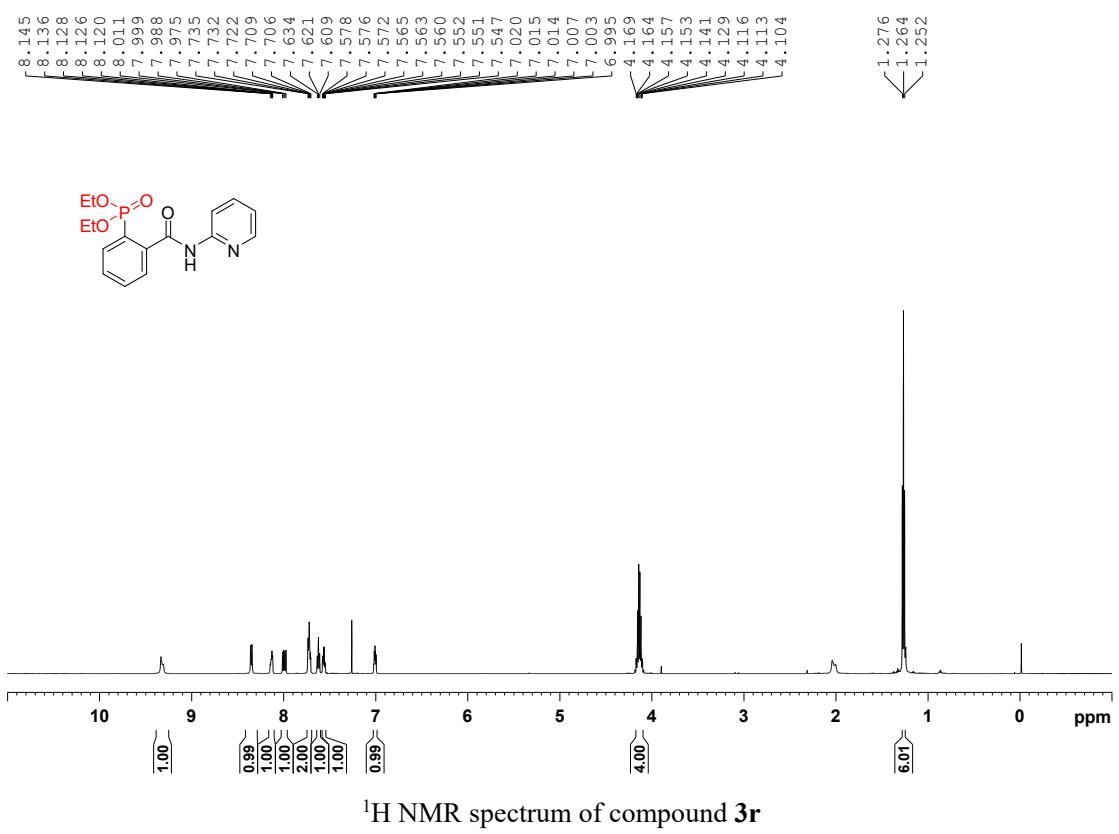
<sup>1</sup>H NMR spectrum of compound **3q**



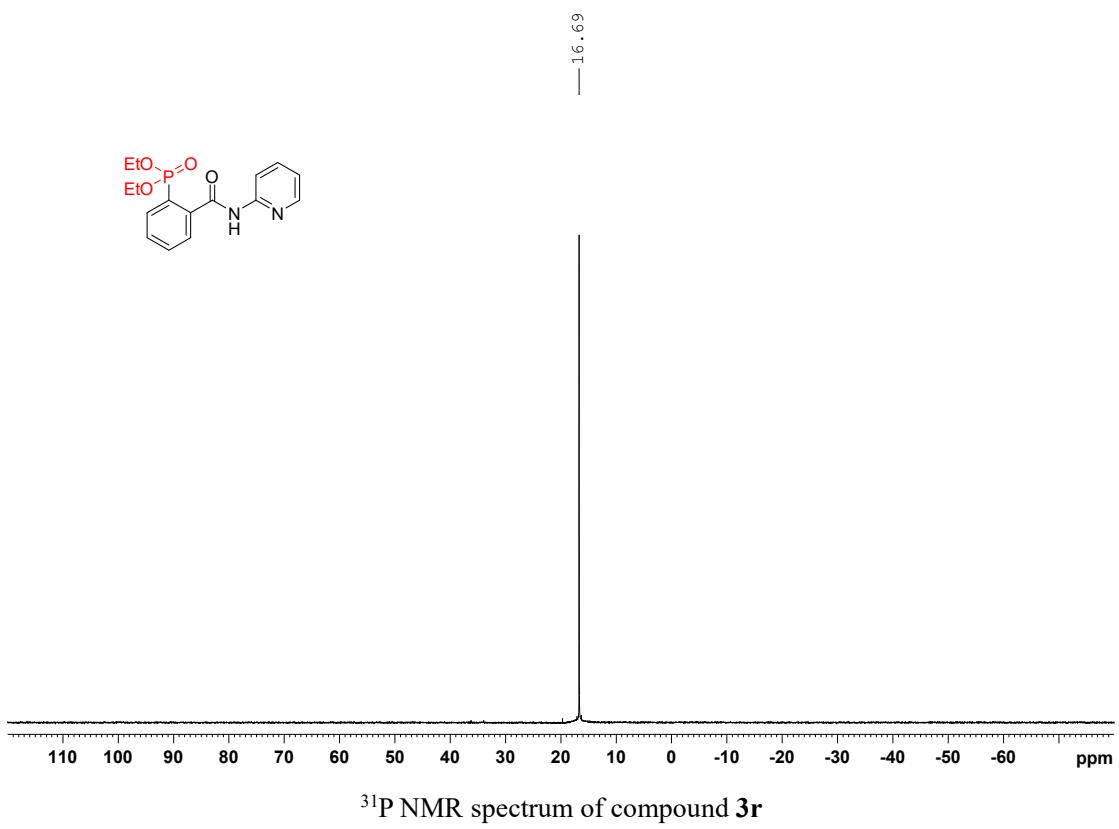
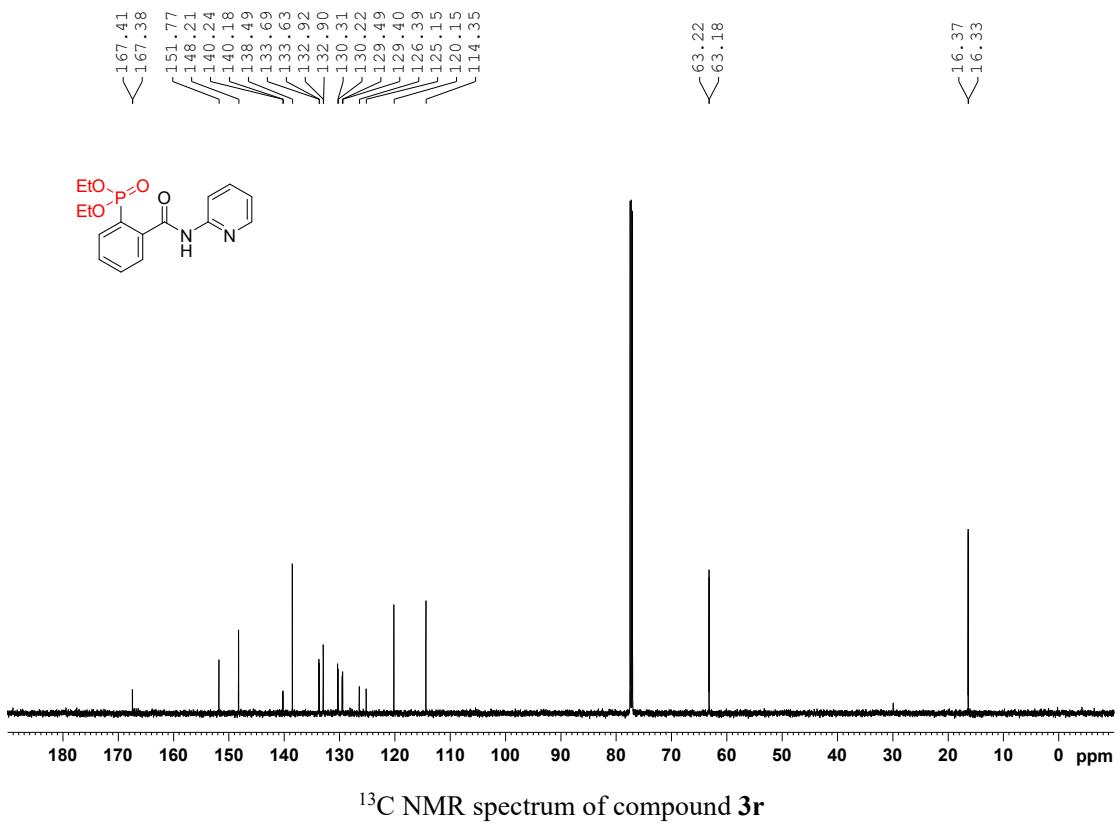
<sup>13</sup>C NMR spectrum of compound 3q

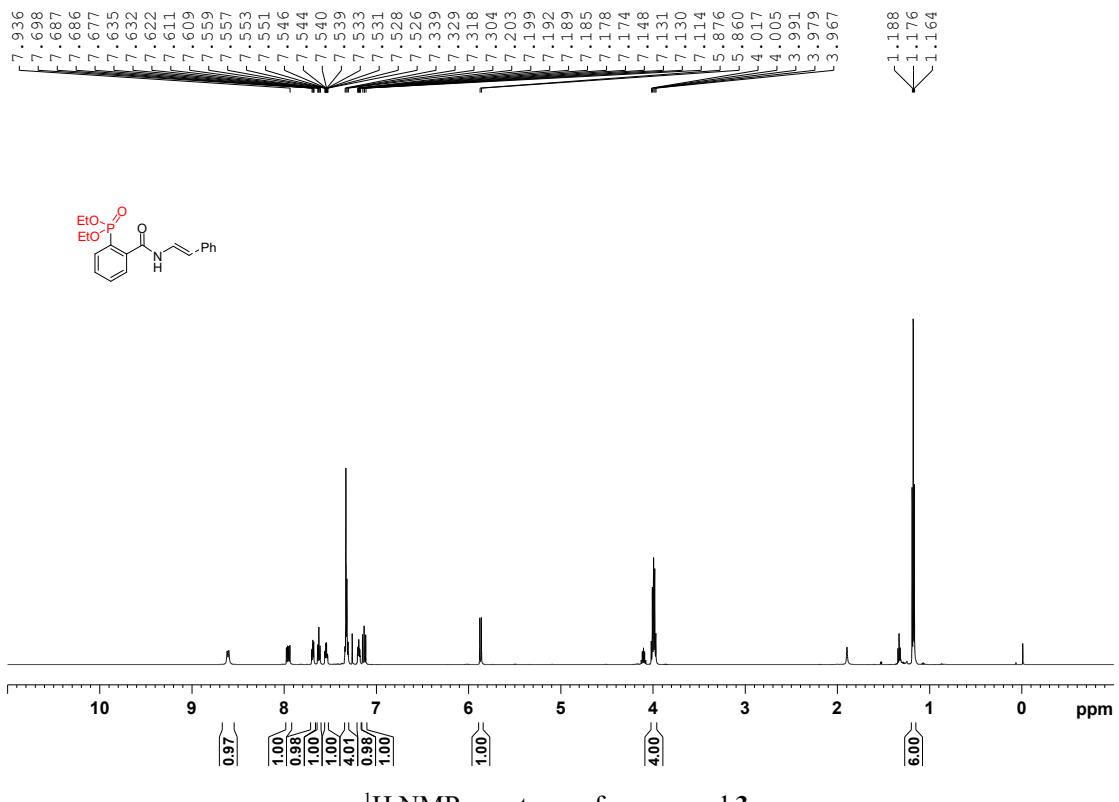


$^{31}\text{P}$  NMR spectrum of compound **3q**

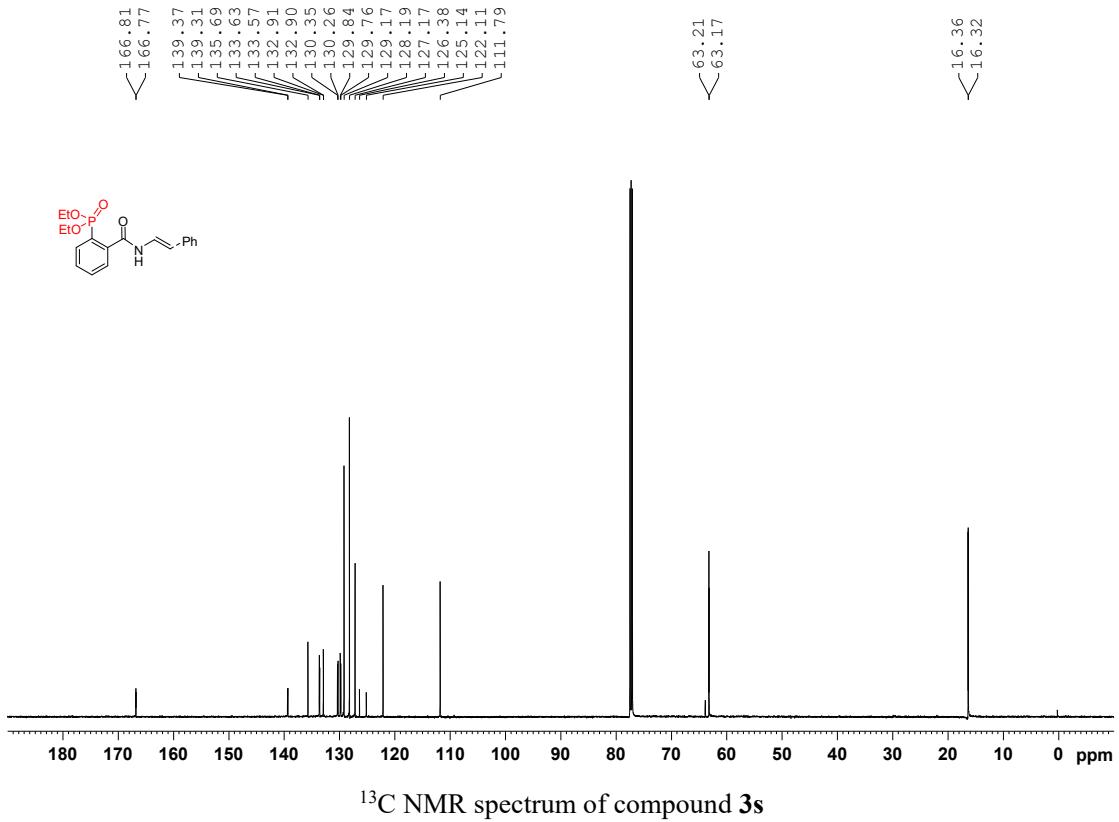


$^1\text{H}$  NMR spectrum of compound **3r**

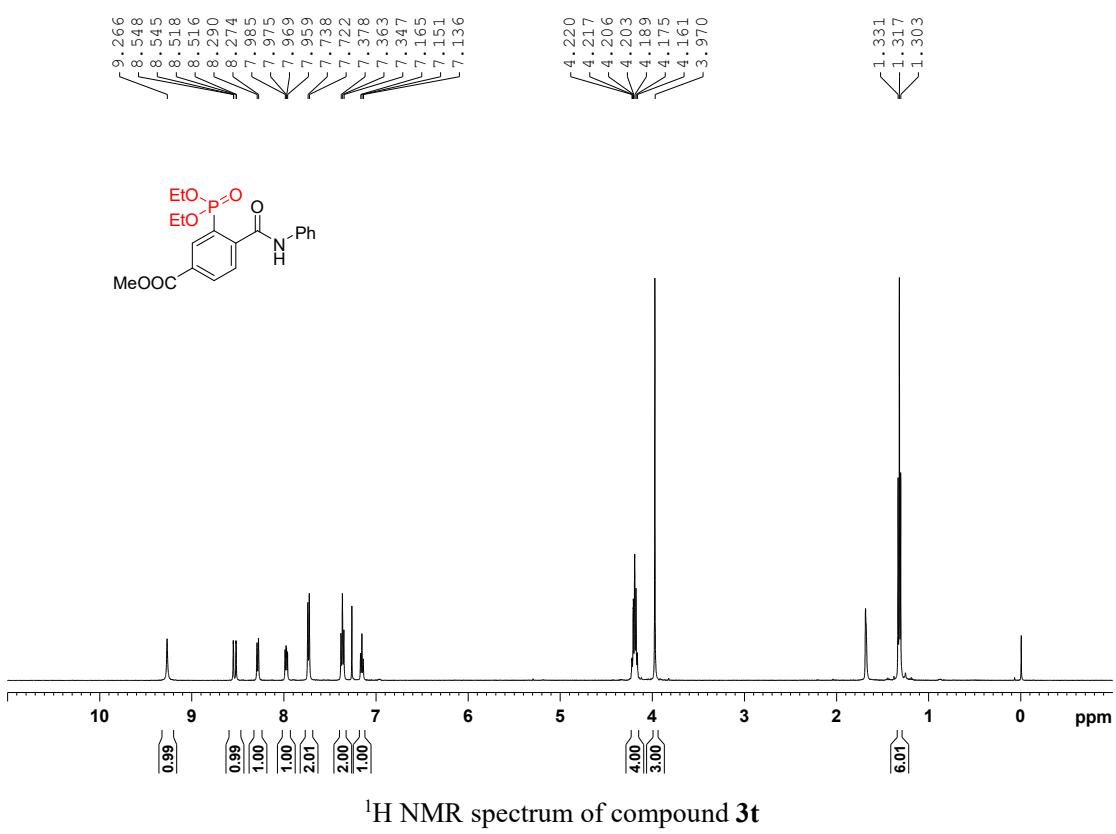
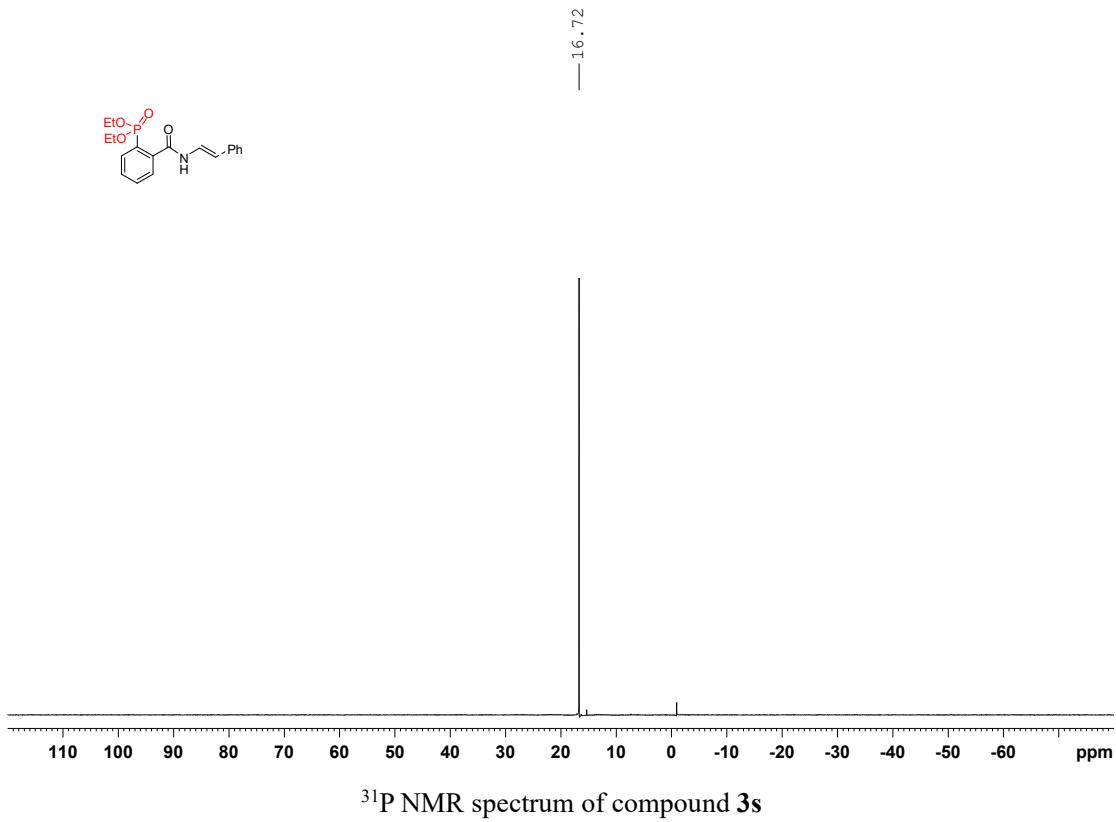


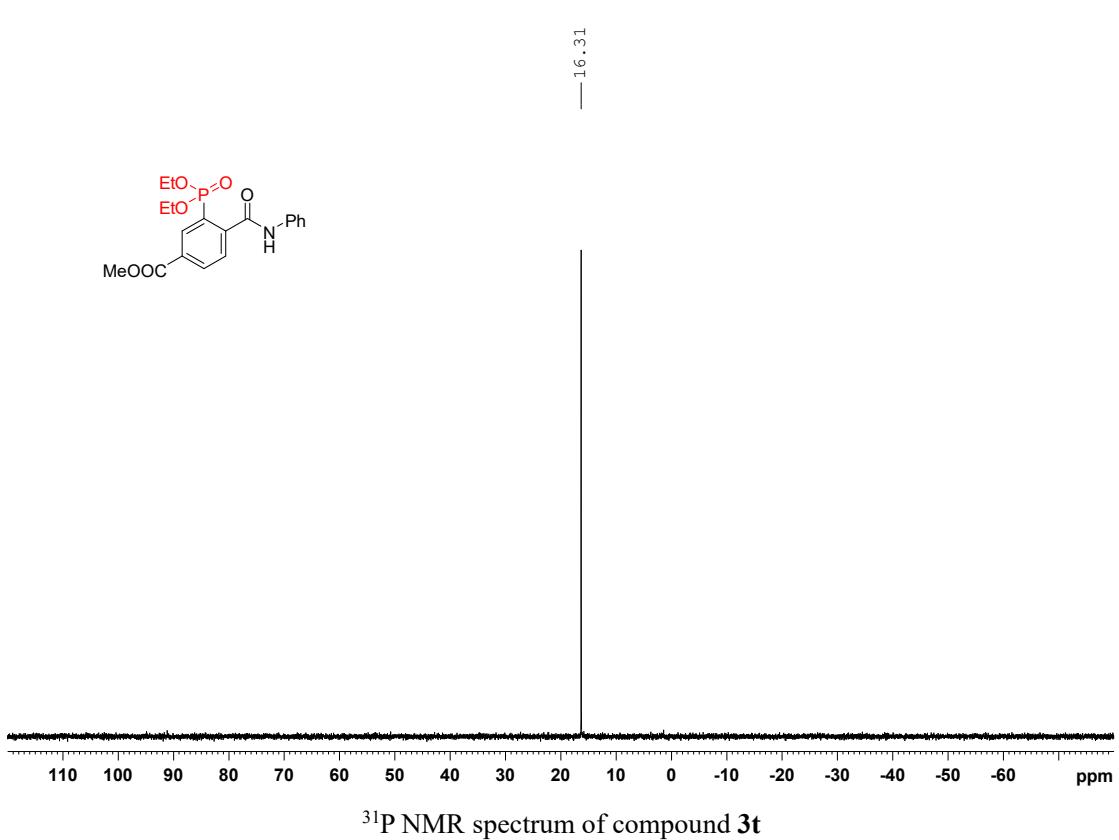
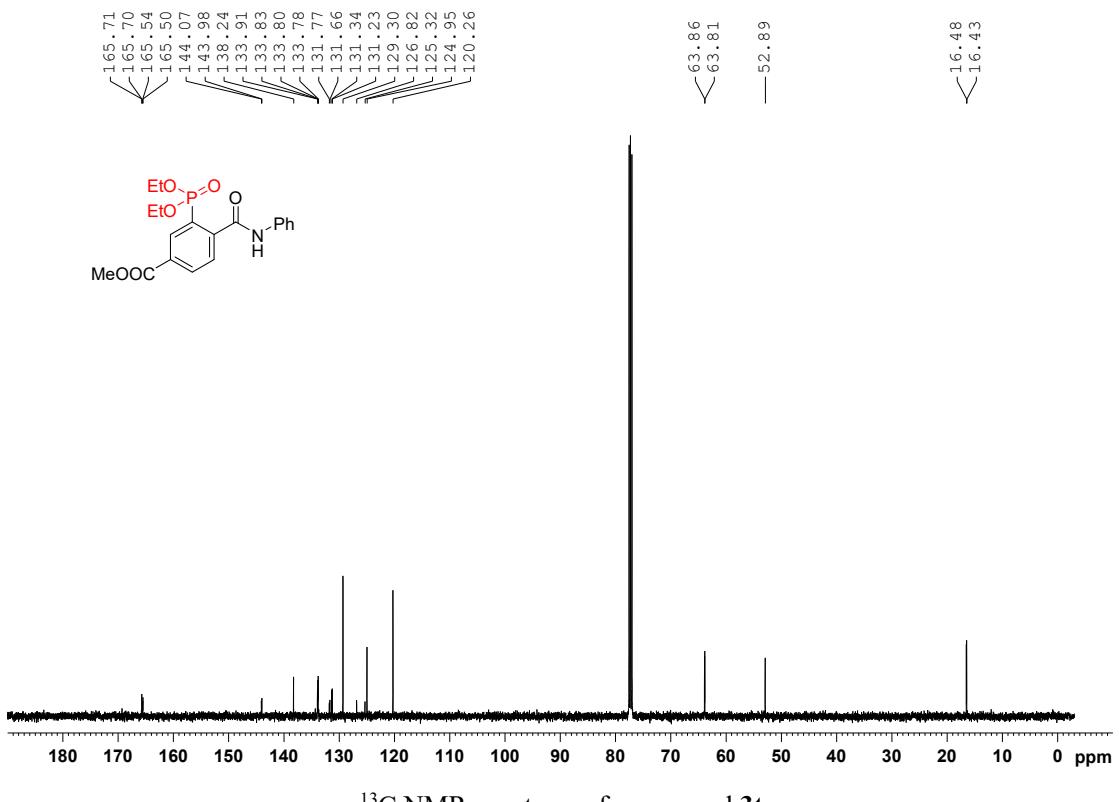


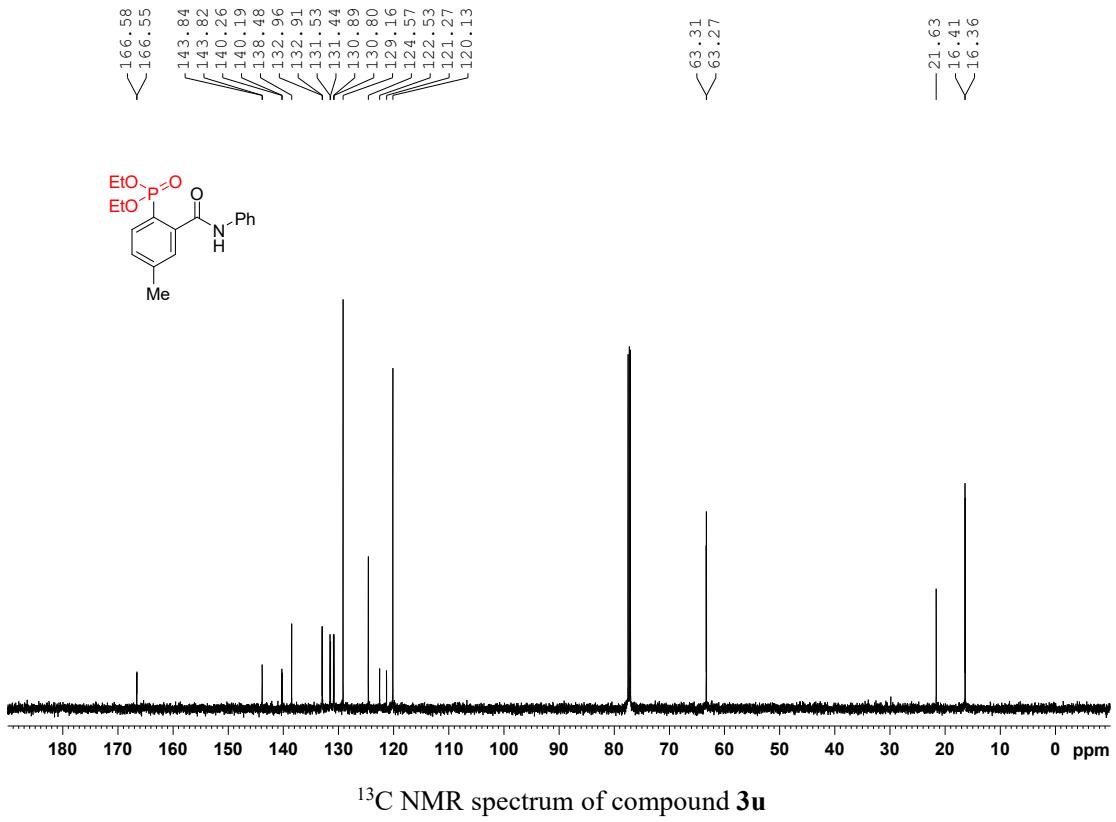
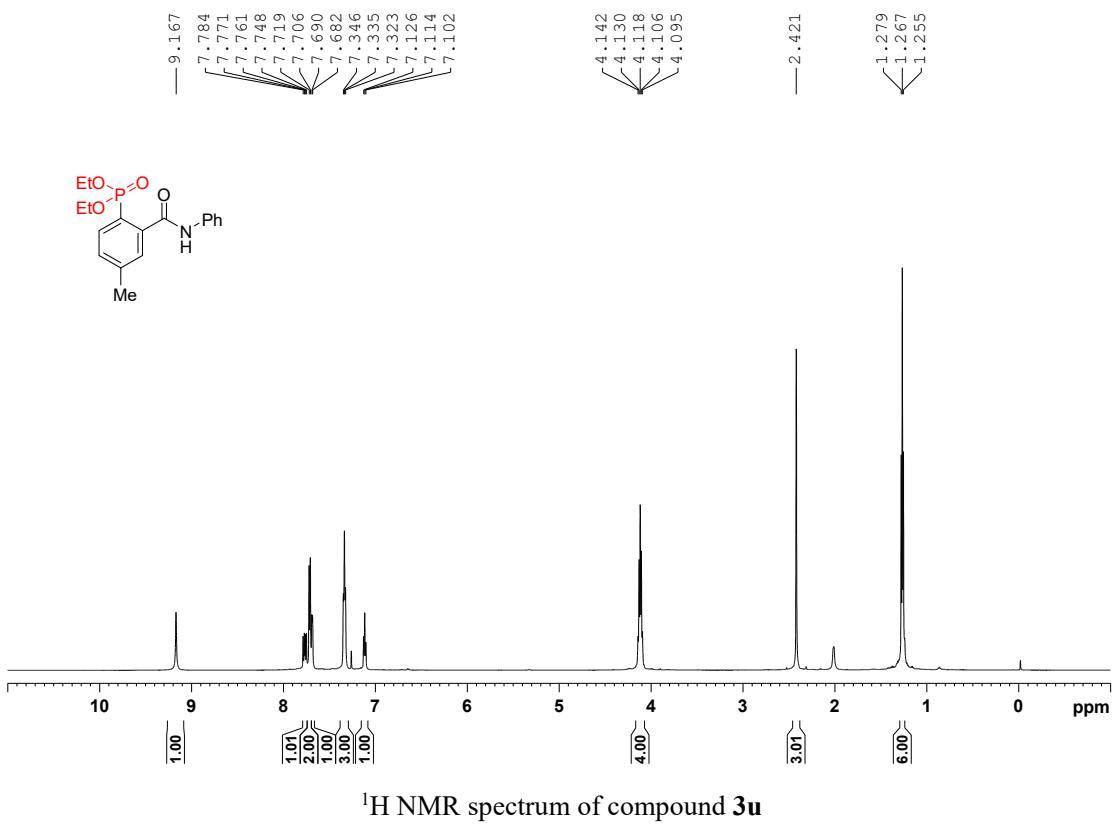
<sup>1</sup>H NMR spectrum of compound 3s

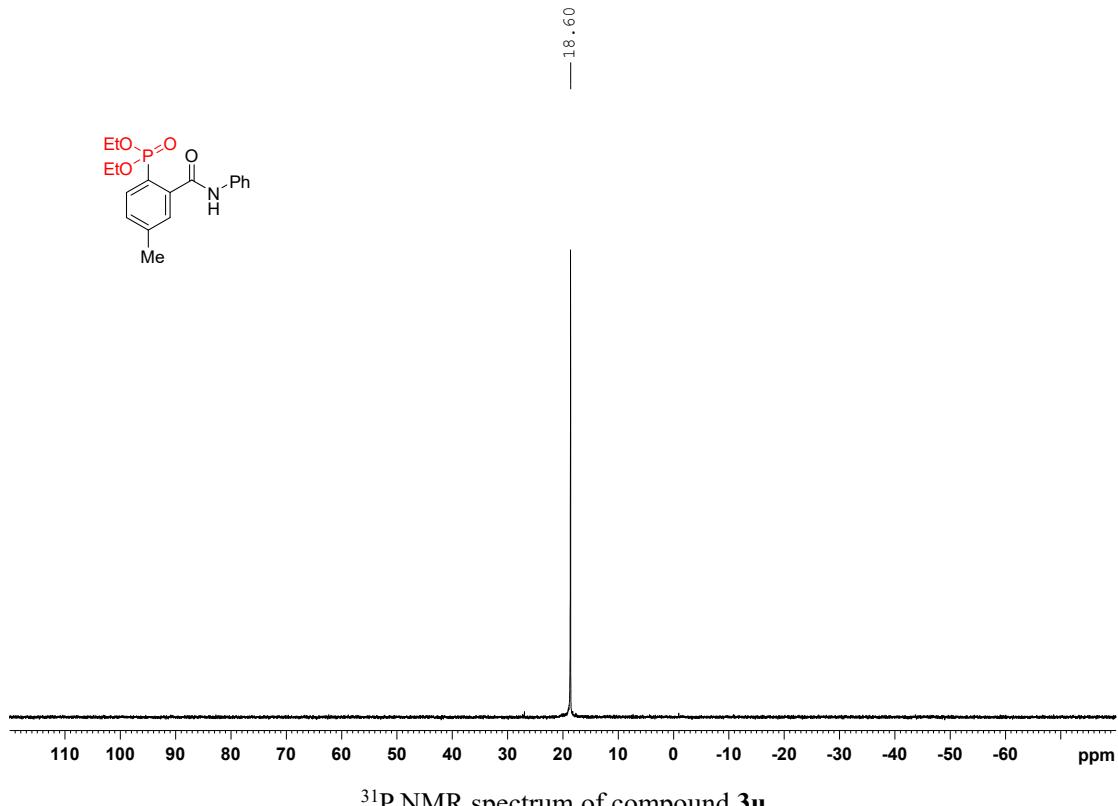
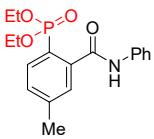


<sup>13</sup>C NMR spectrum of compound 3s

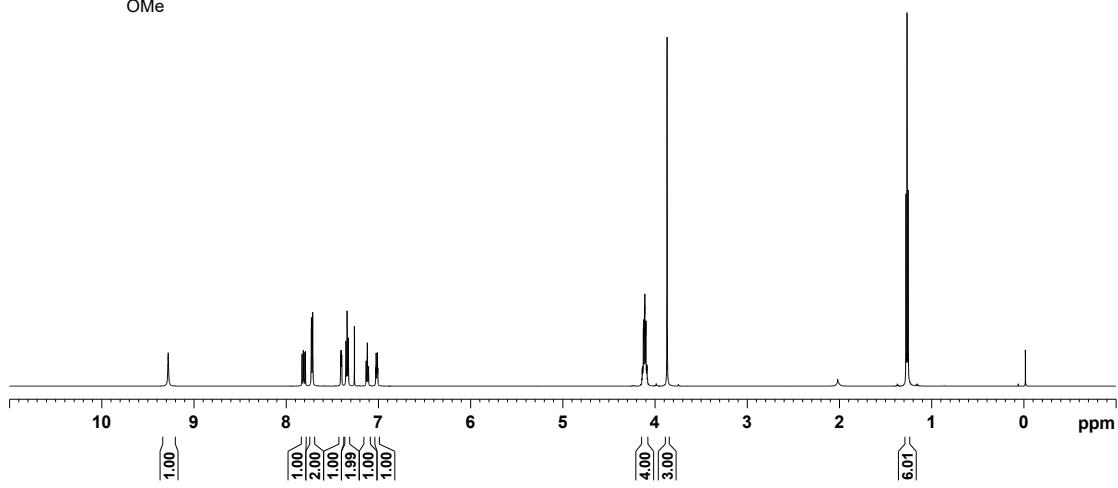
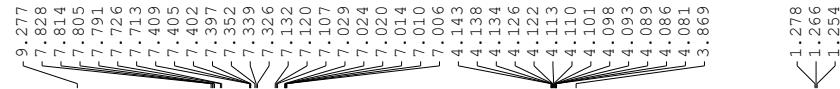




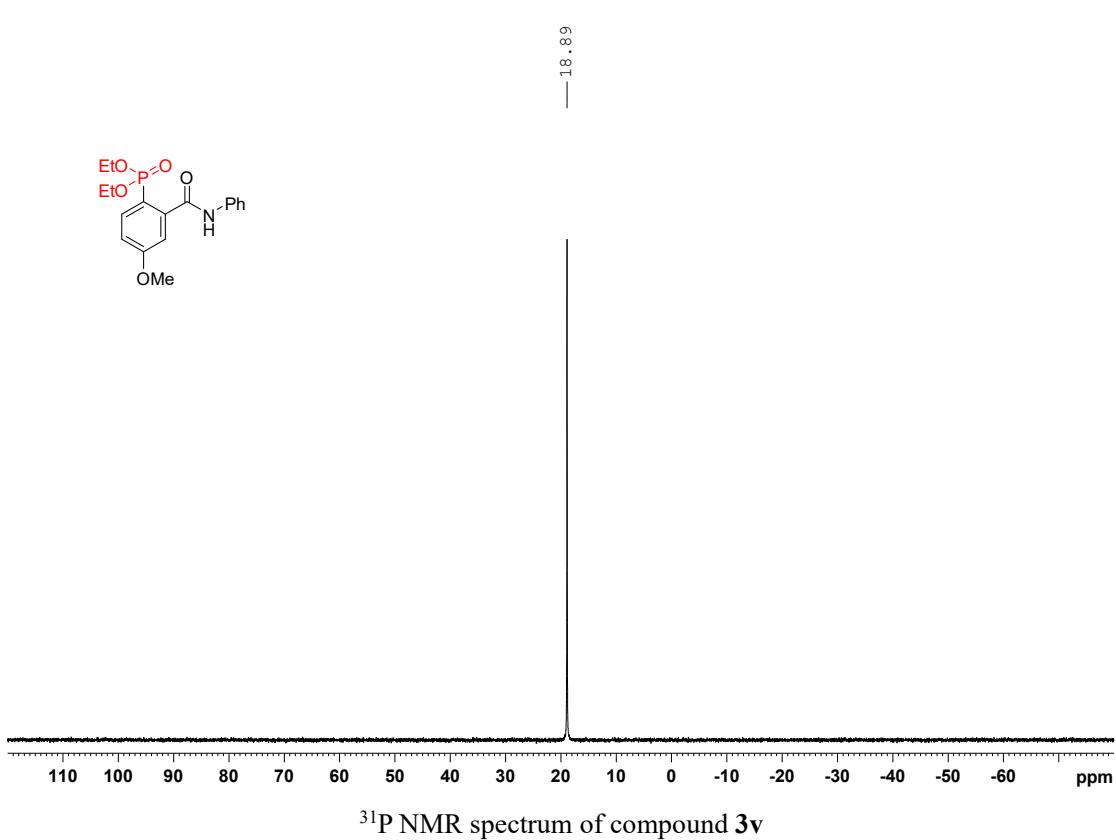
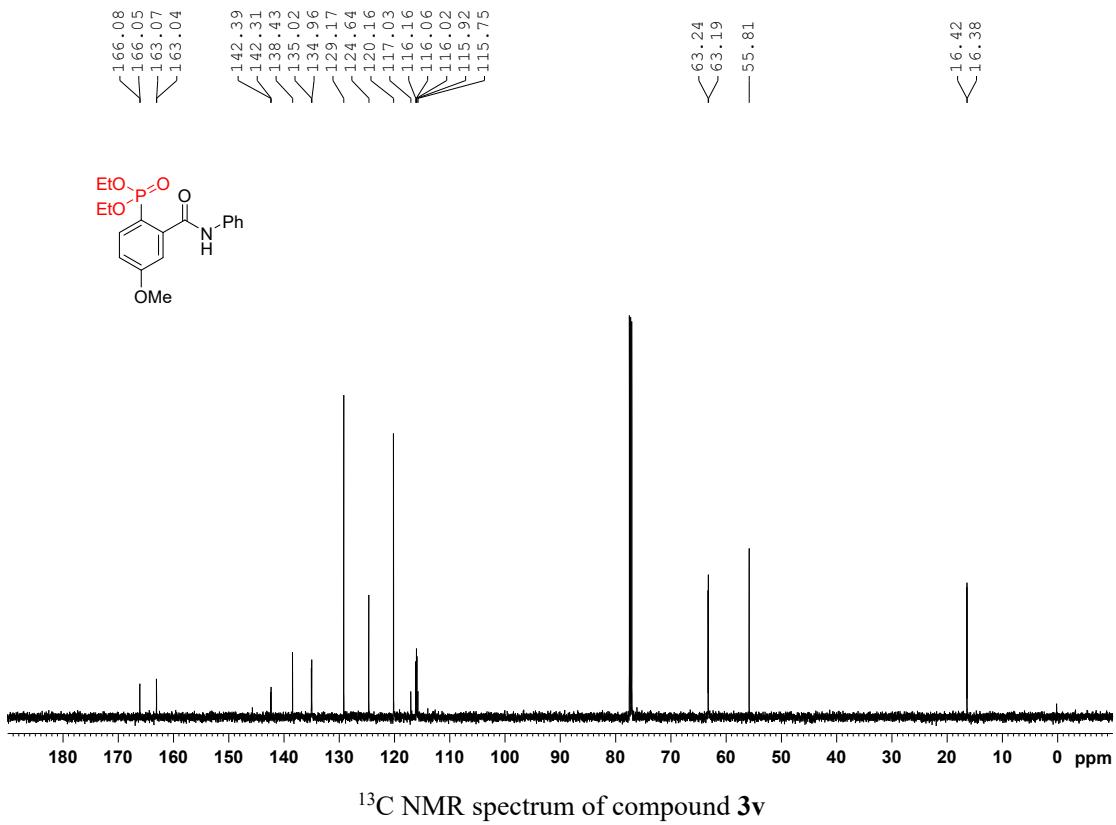


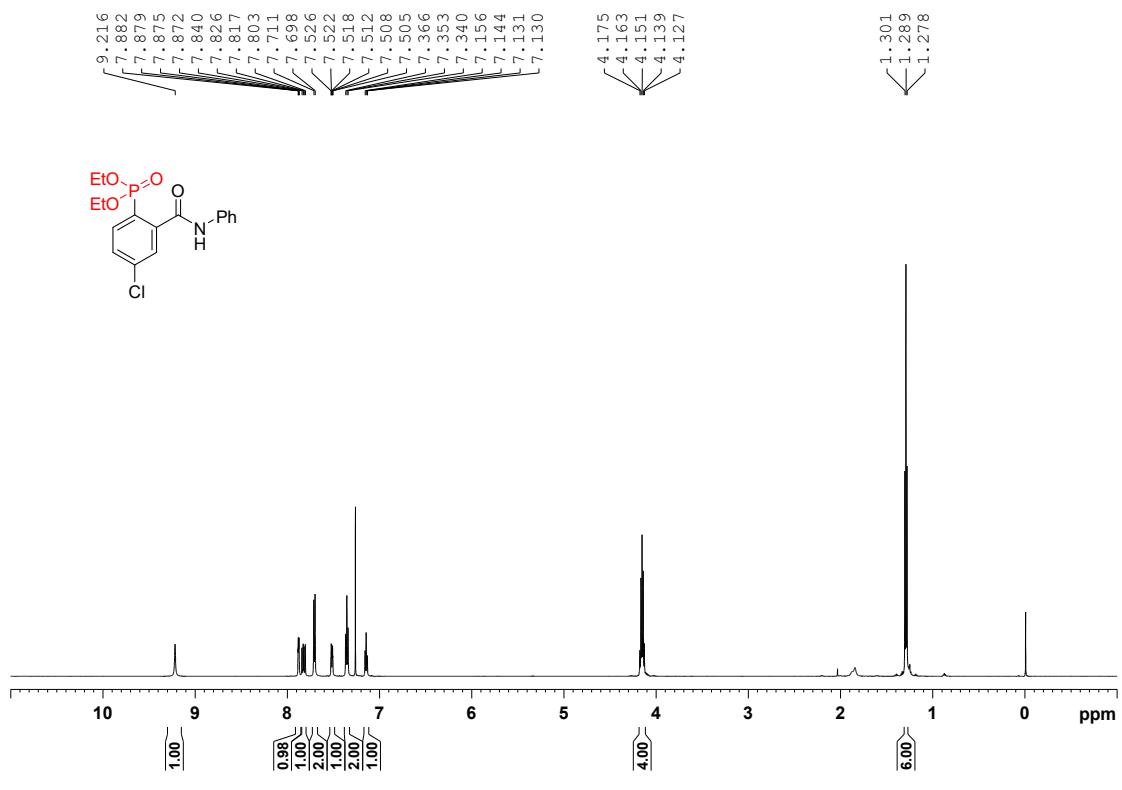


### <sup>31</sup>P NMR spectrum of compound 3u

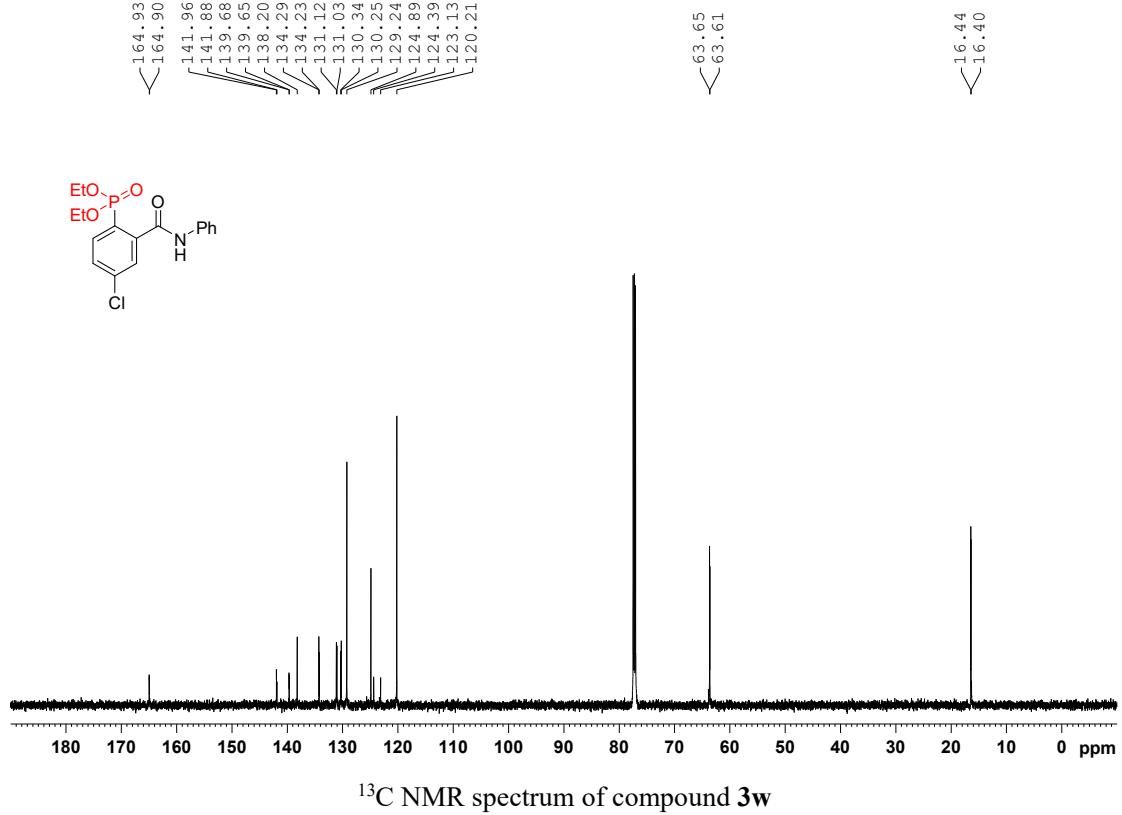


<sup>1</sup>H NMR spectrum of compound **3v**

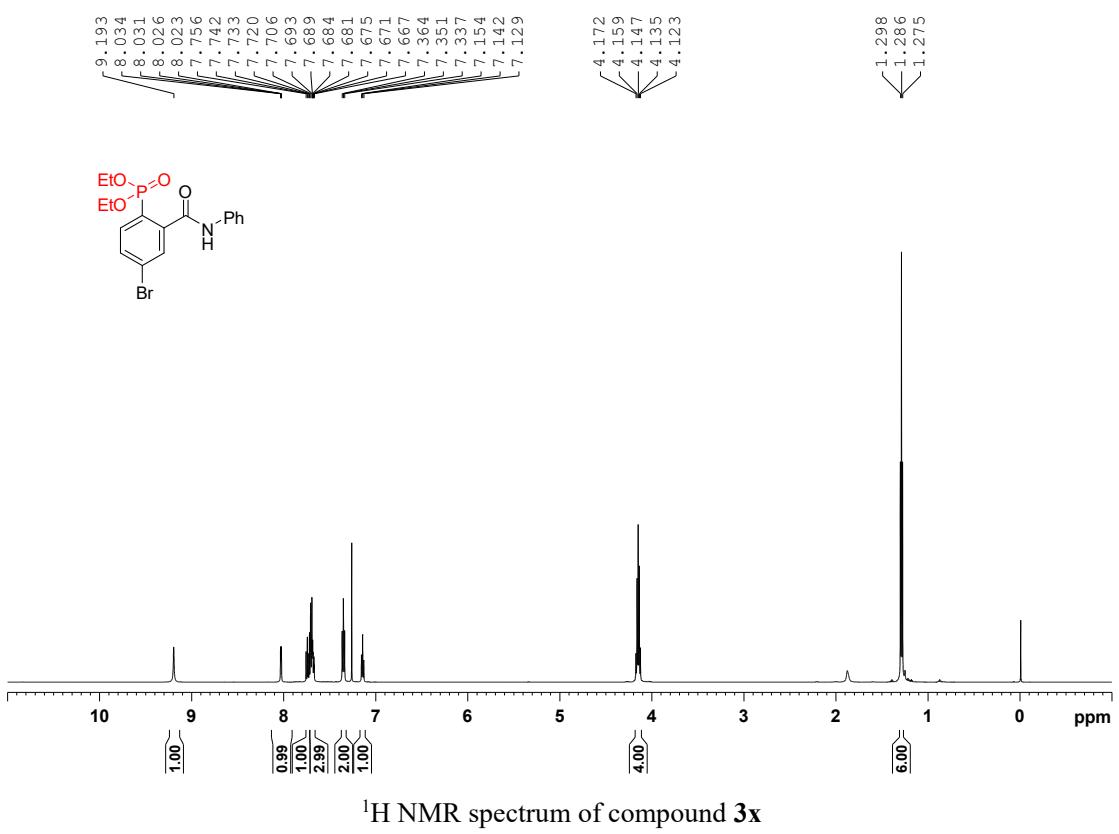
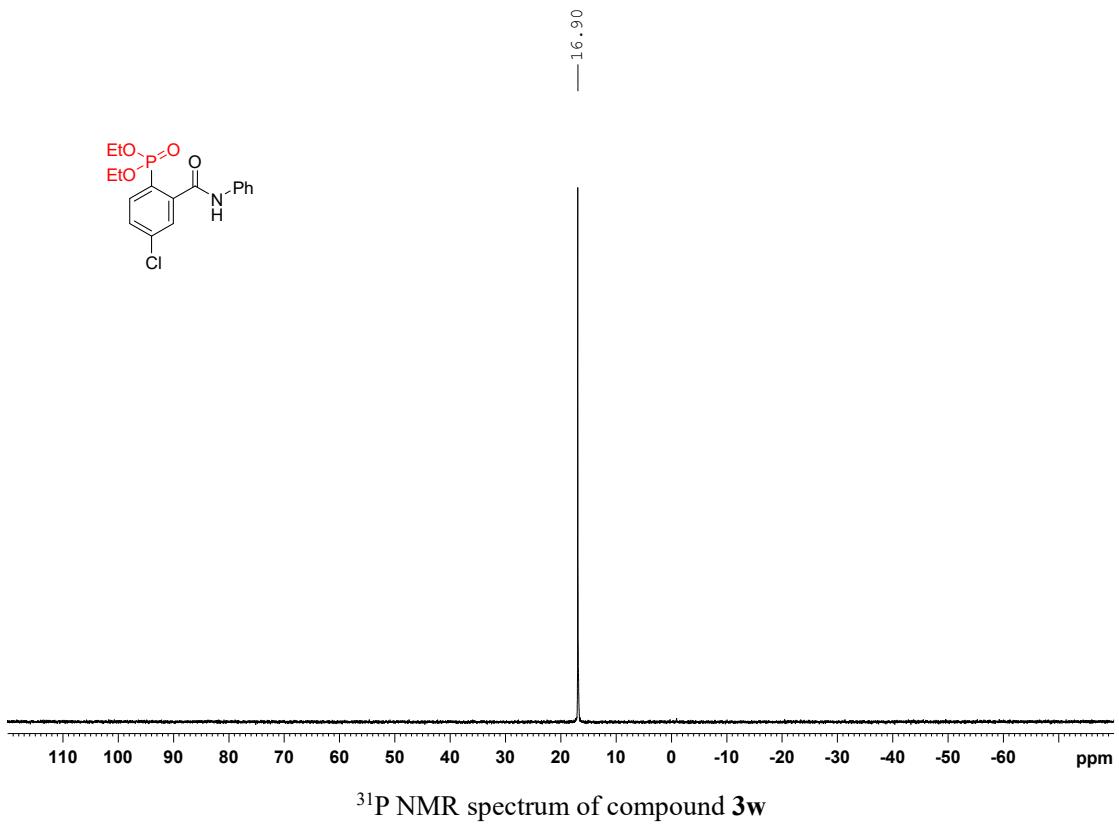


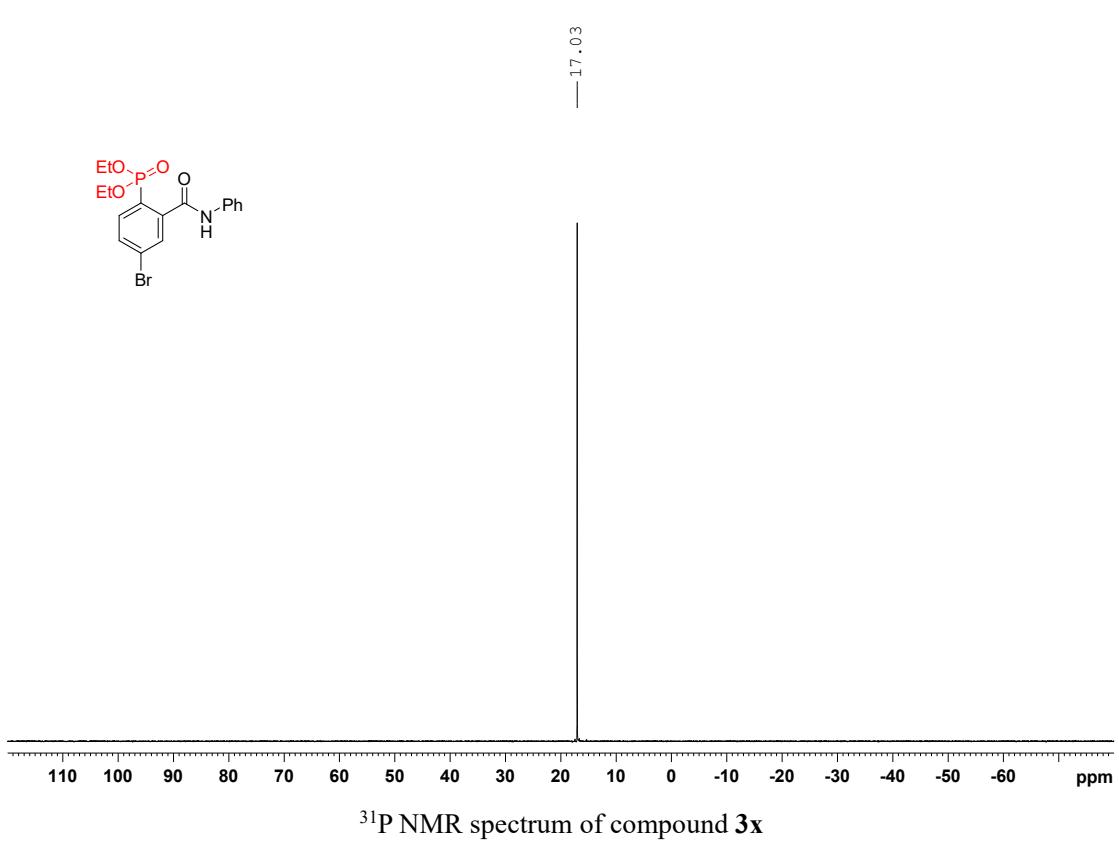
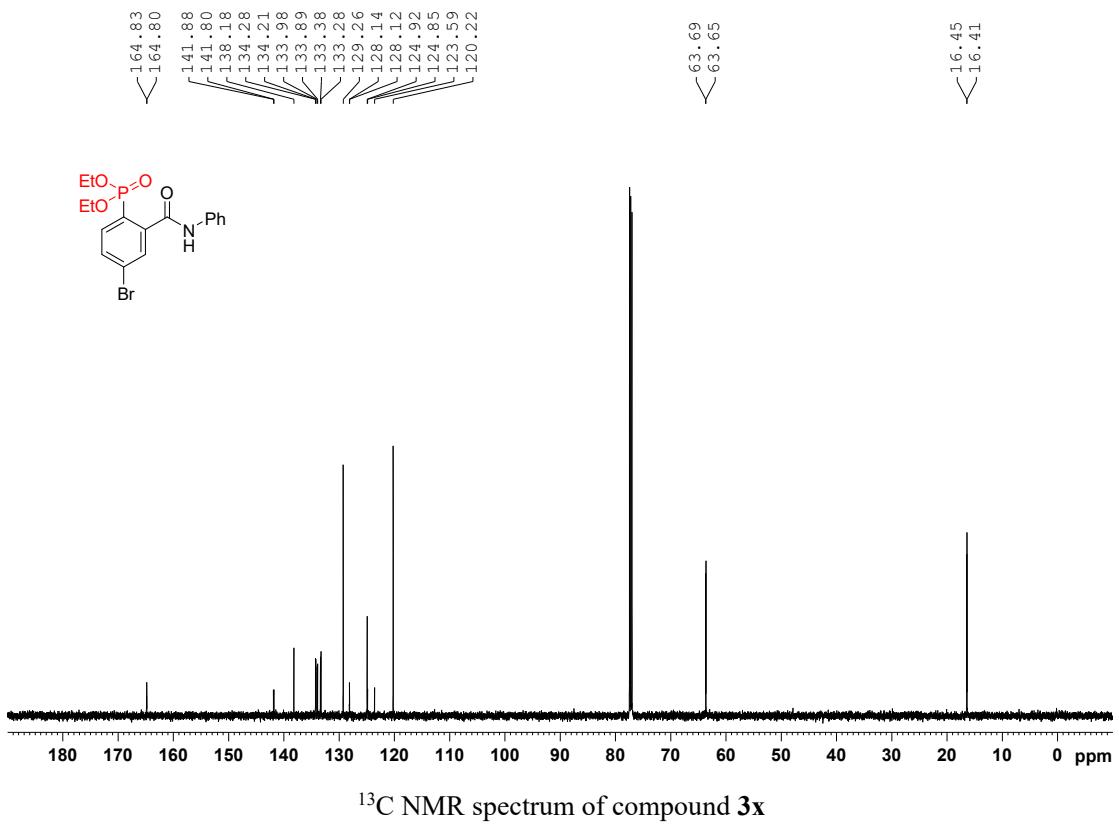


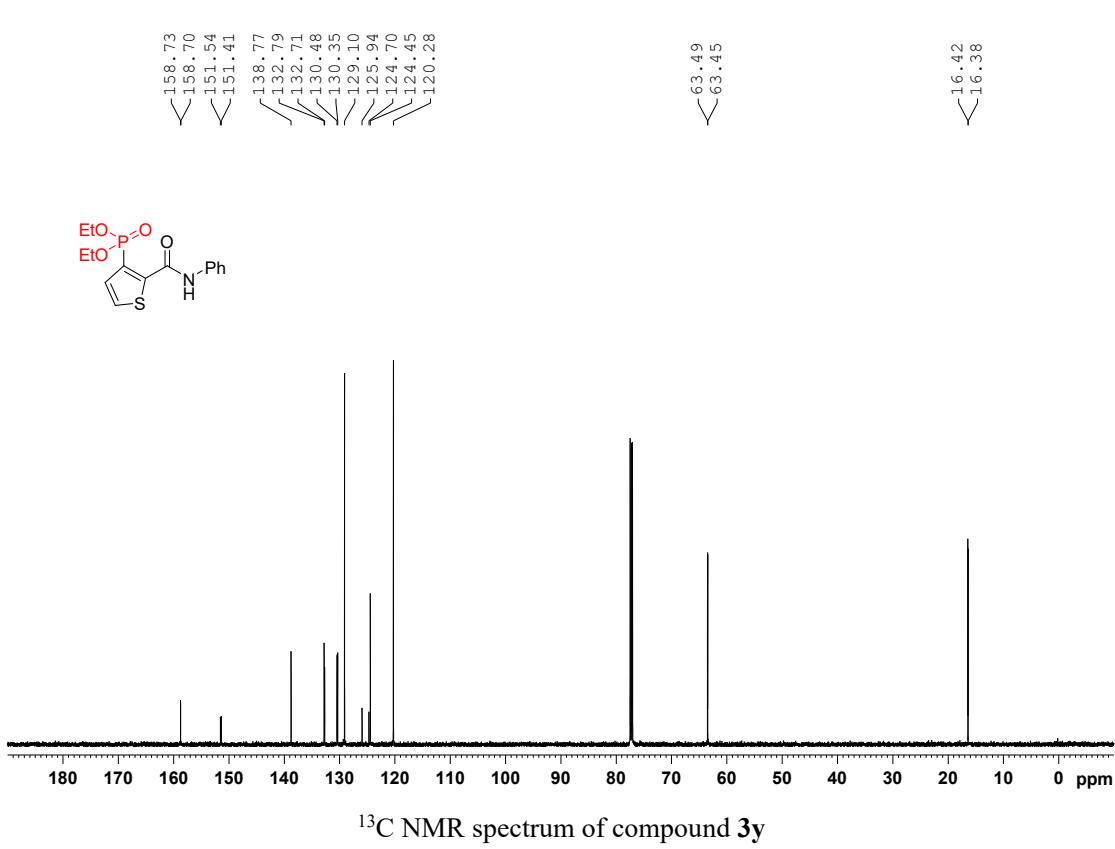
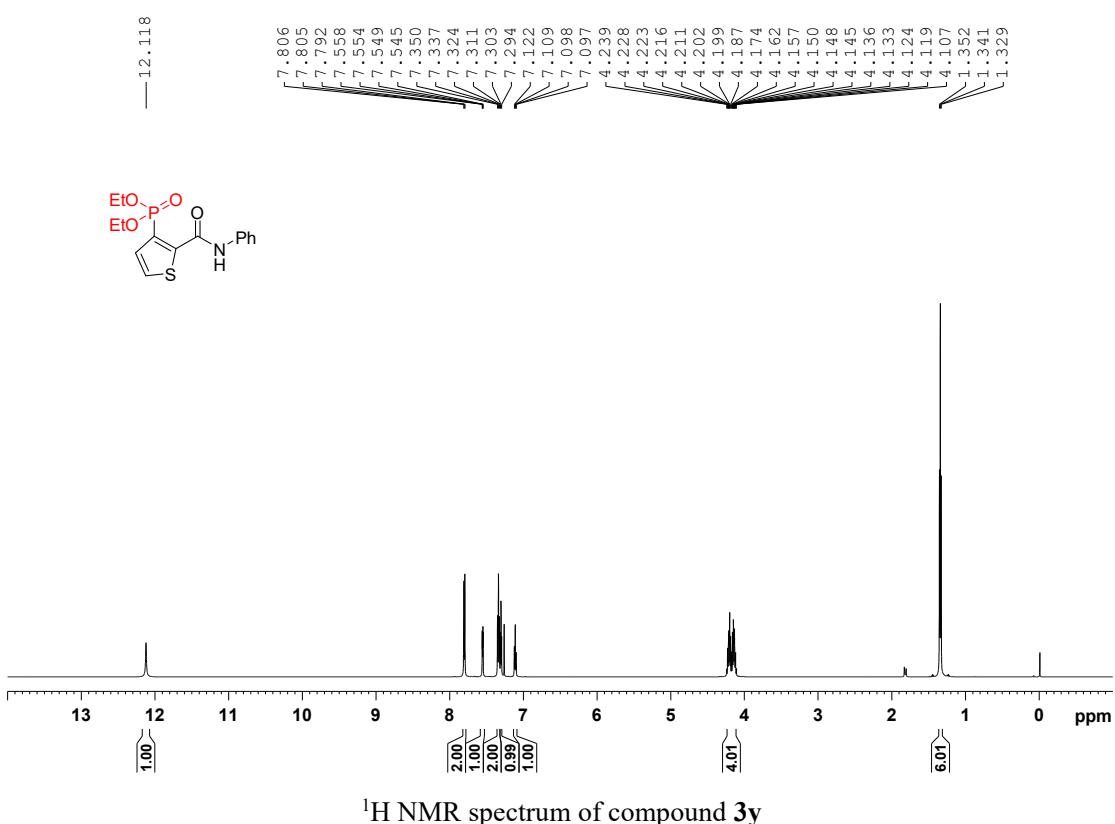
<sup>1</sup>H NMR spectrum of compound 3w

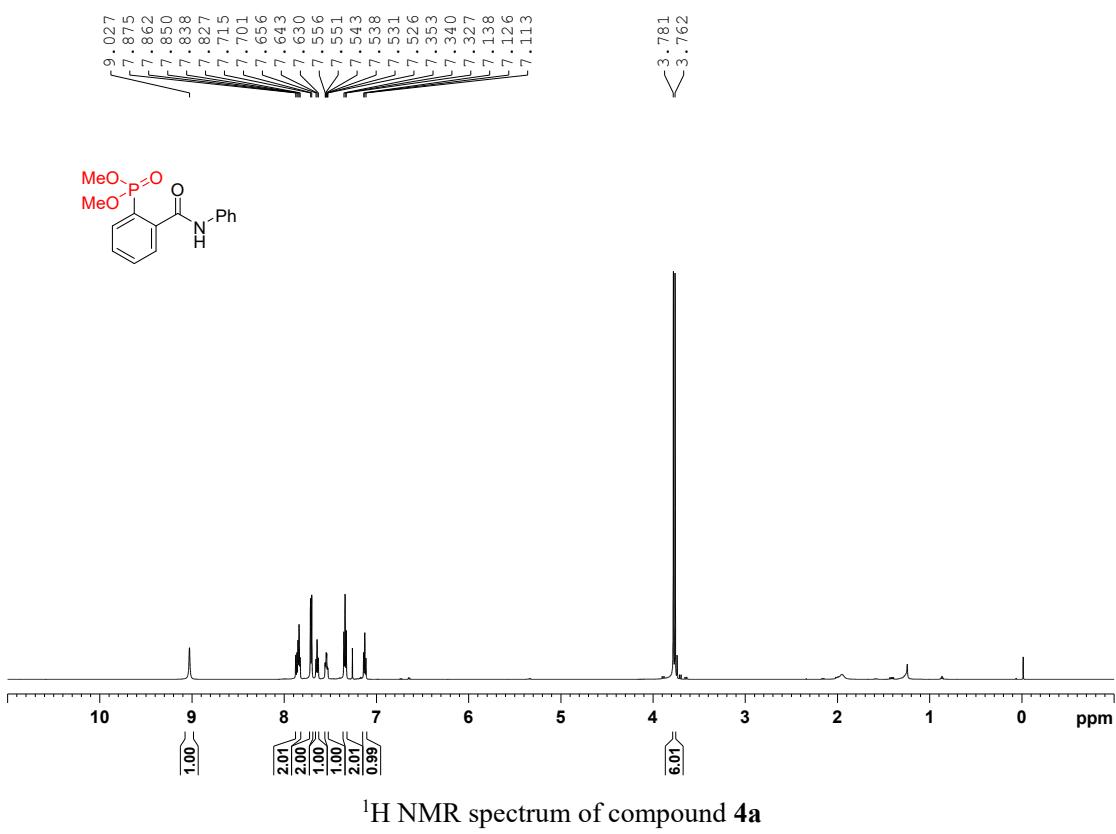
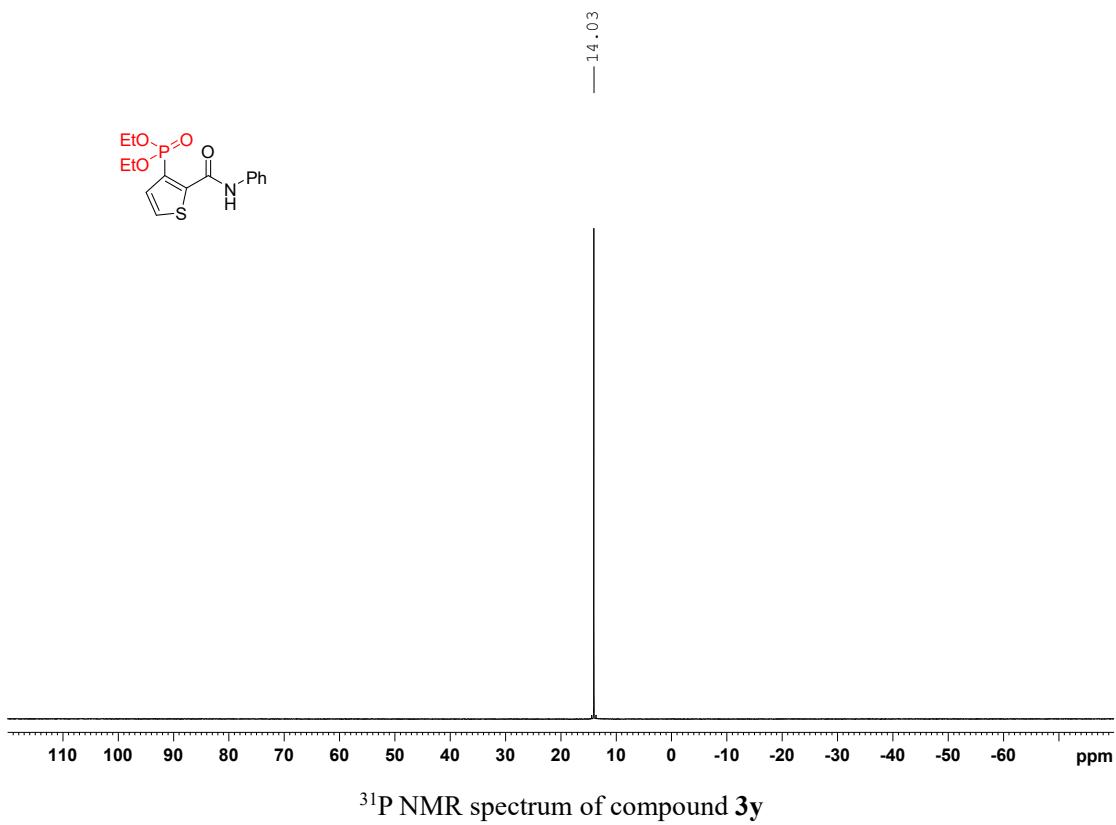


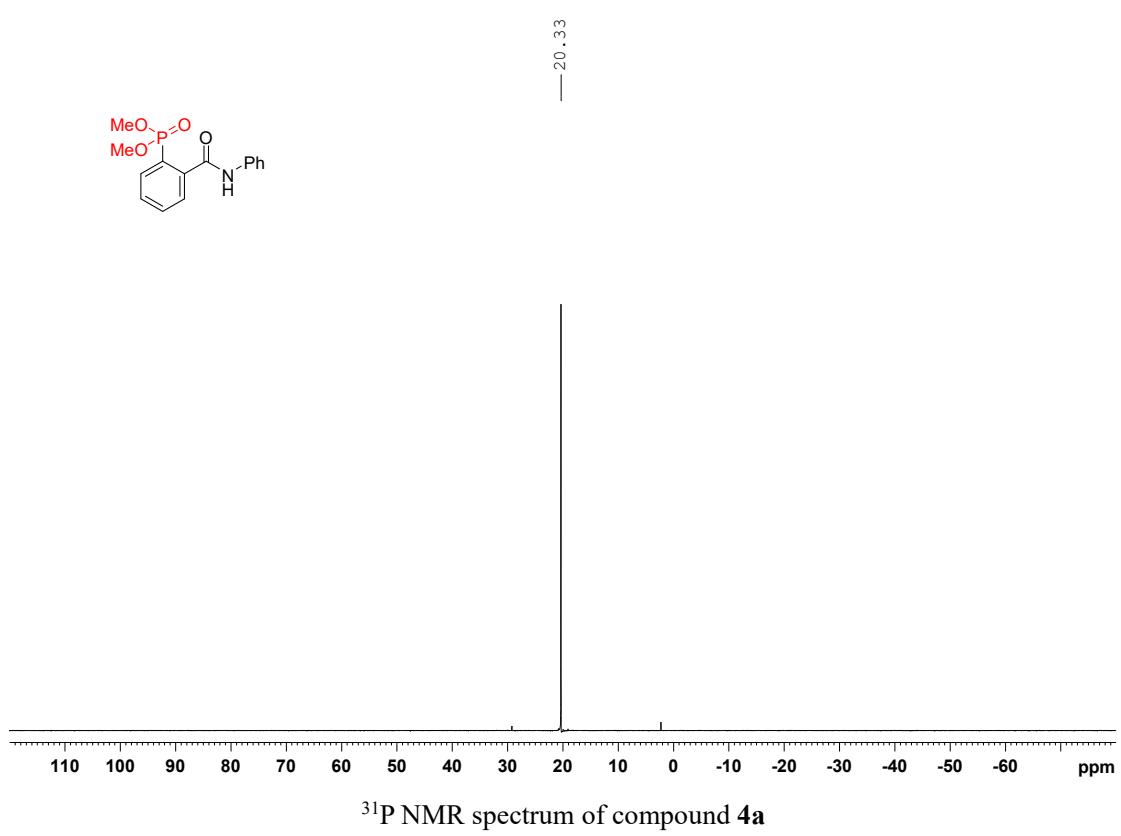
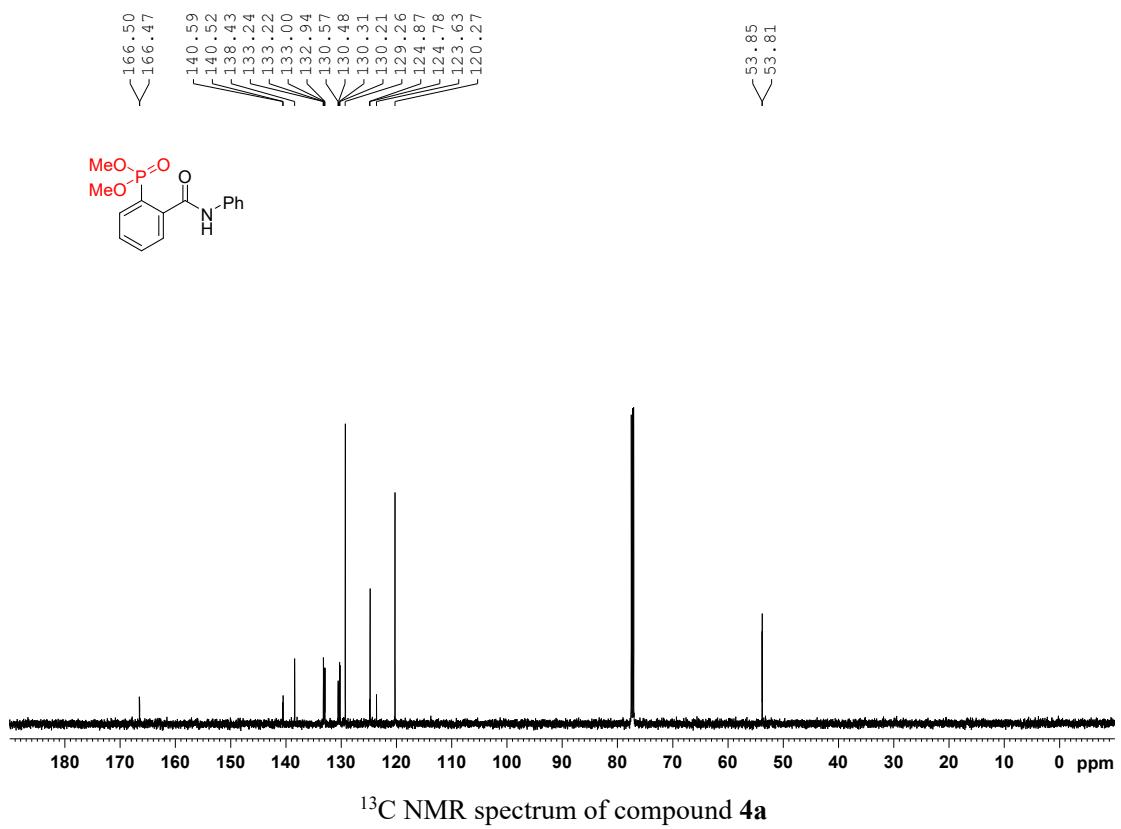
<sup>13</sup>C NMR spectrum of compound 3w

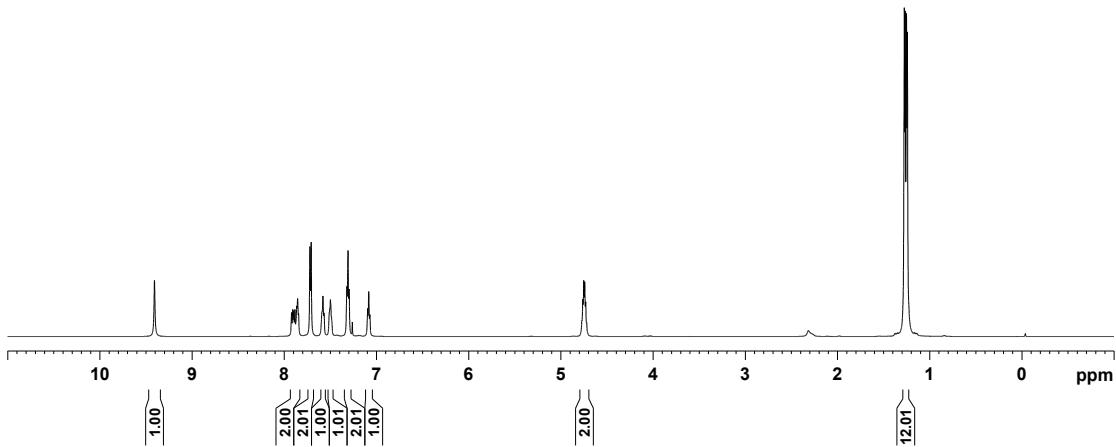
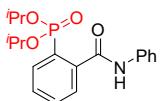
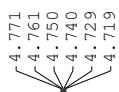
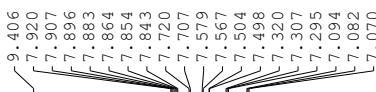




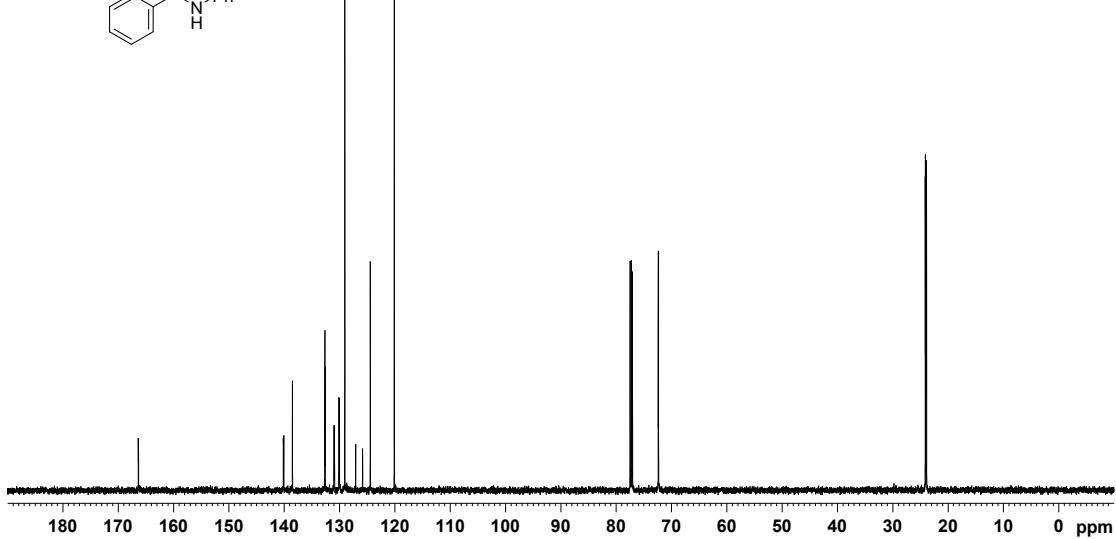
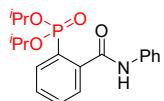




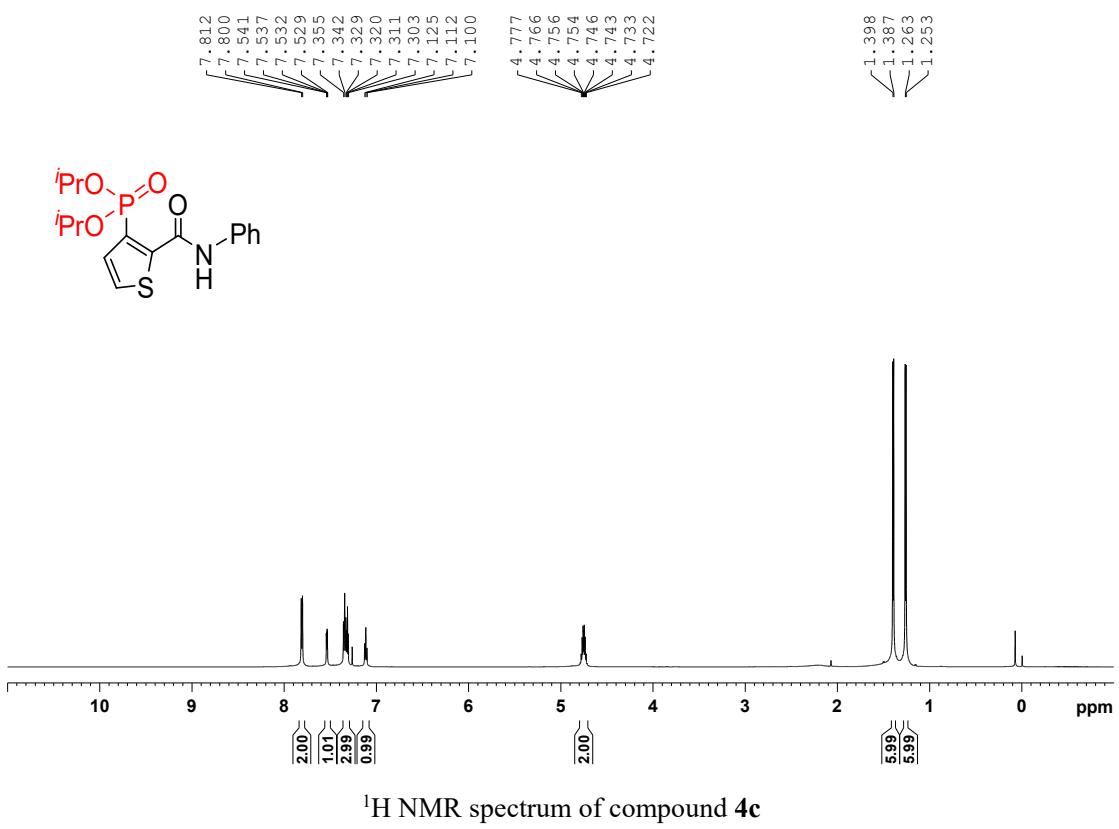
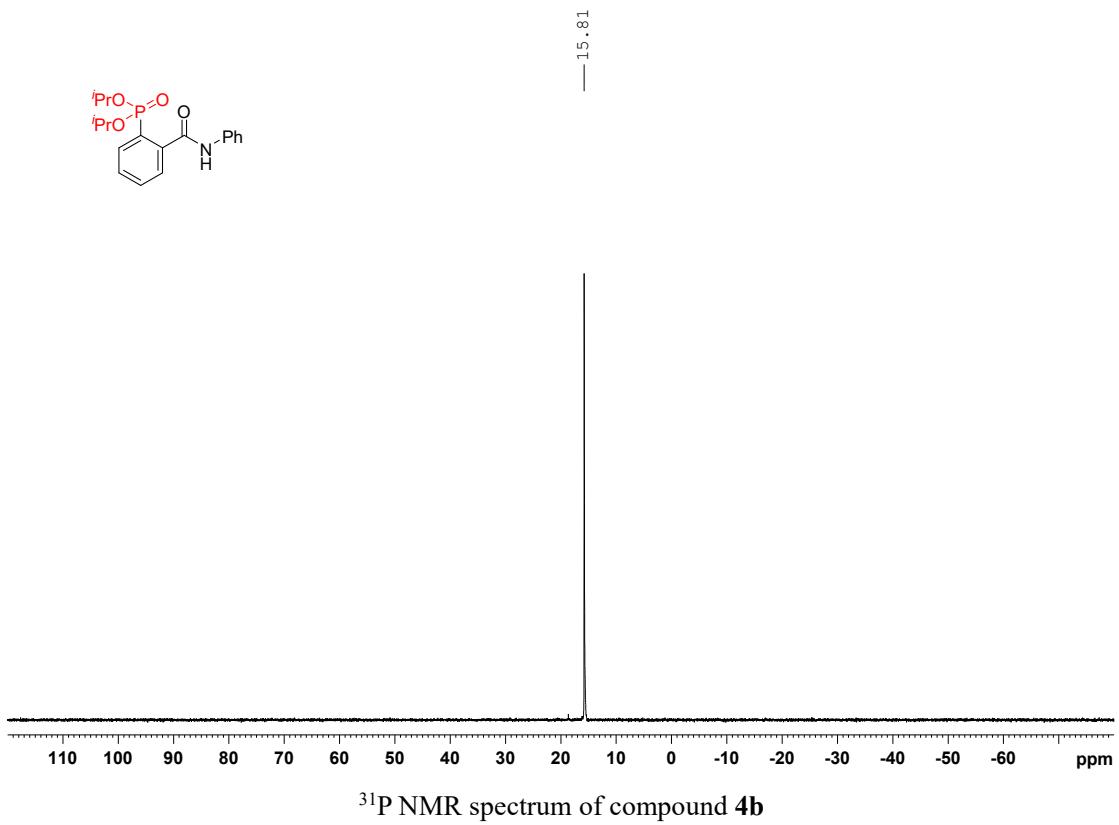


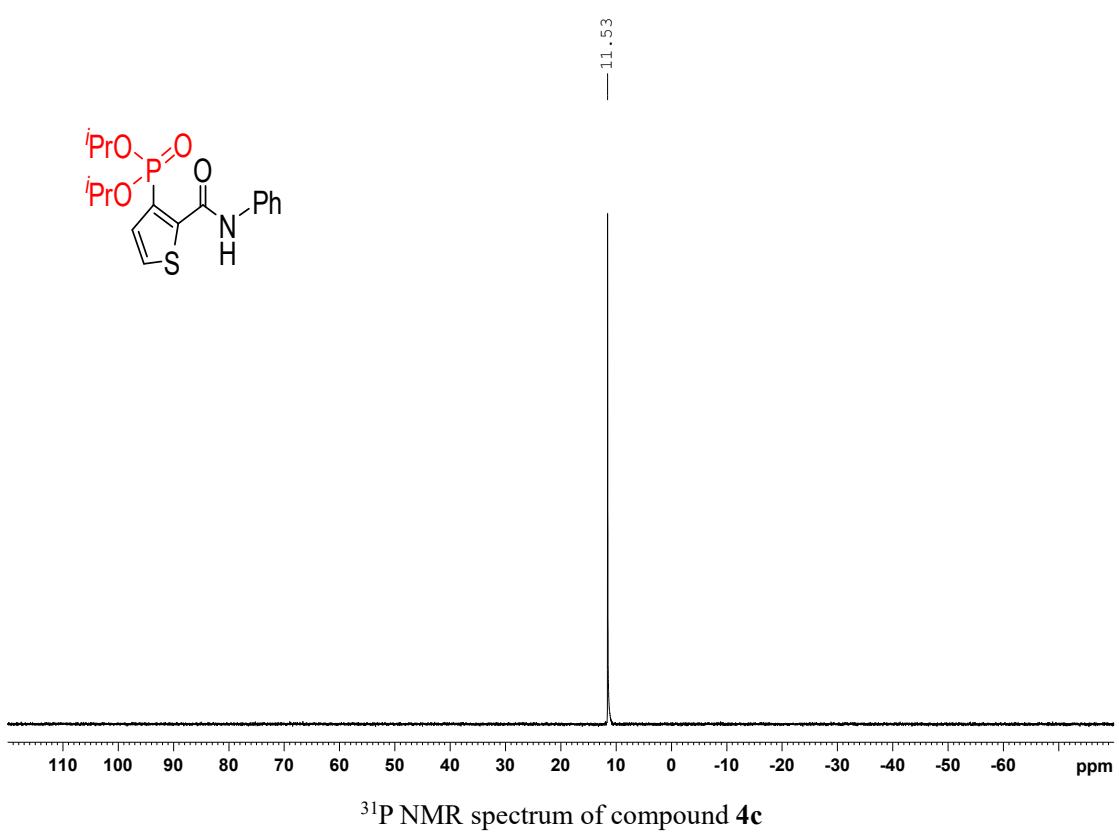
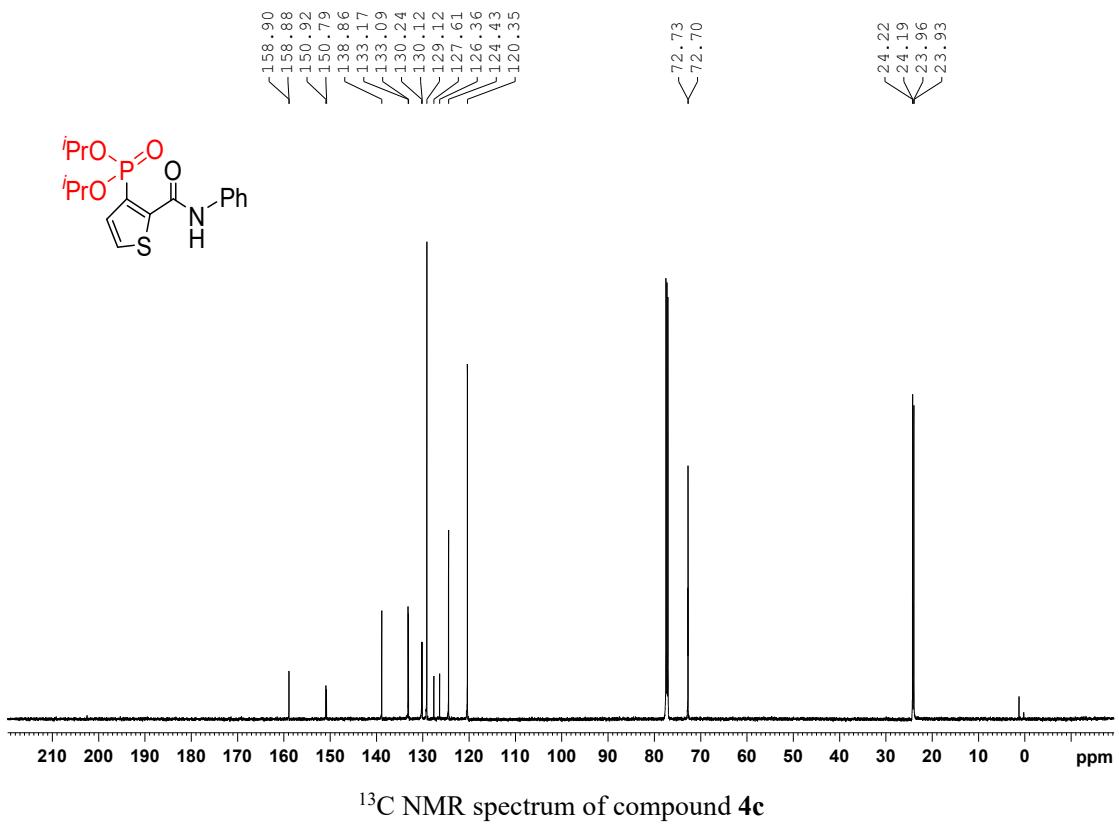


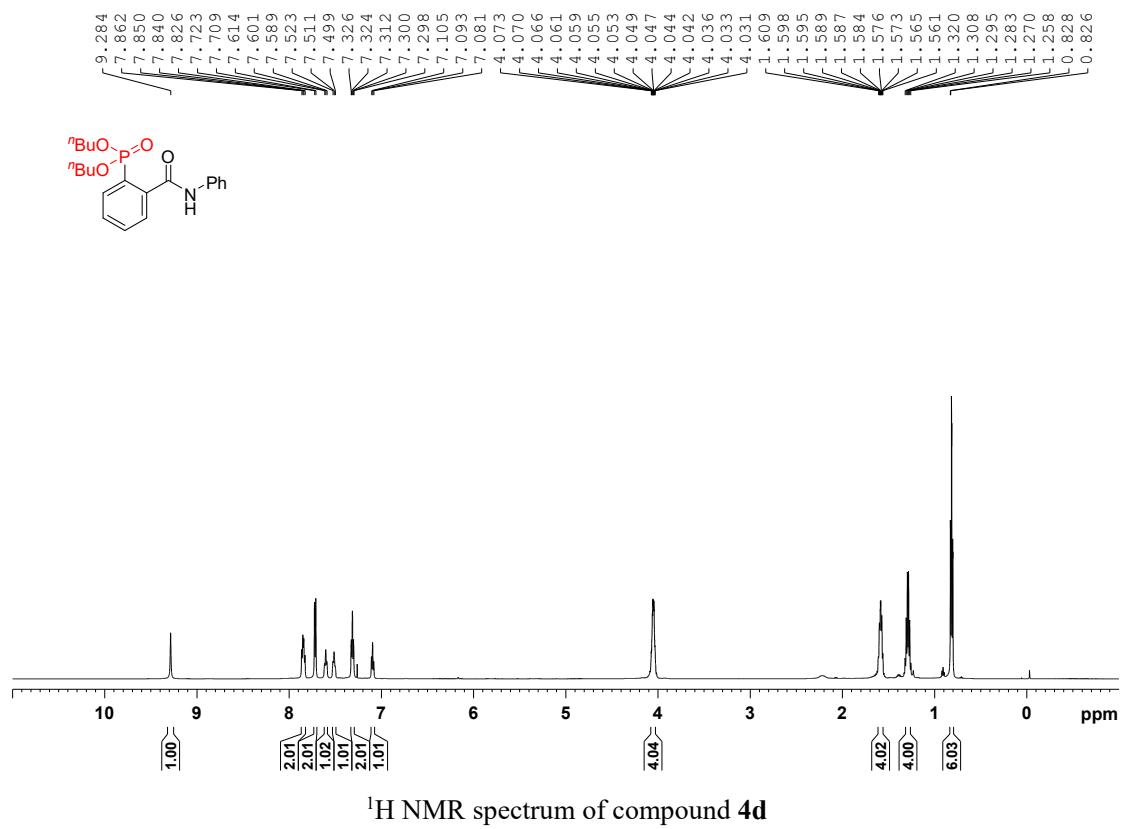
<sup>1</sup>H NMR spectrum of compound 4b



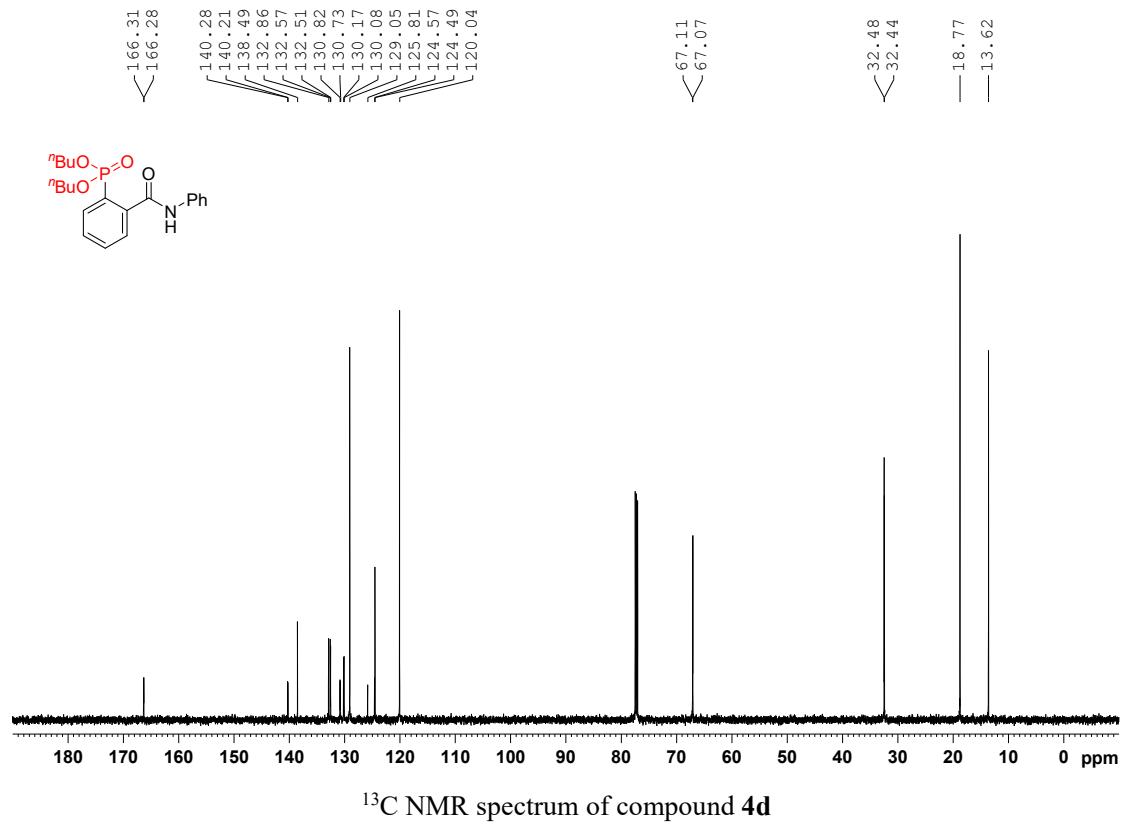
### <sup>13</sup>C NMR spectrum of compound 4b

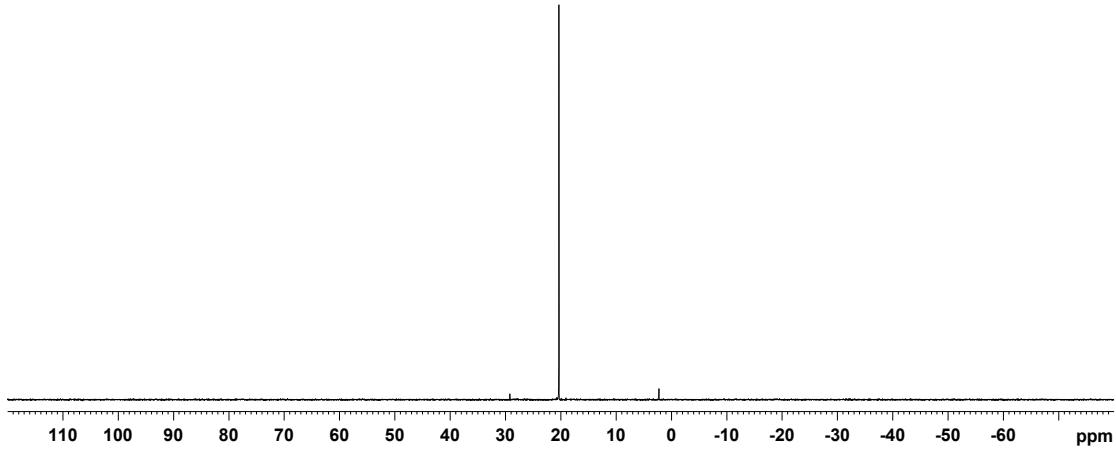
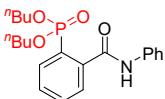




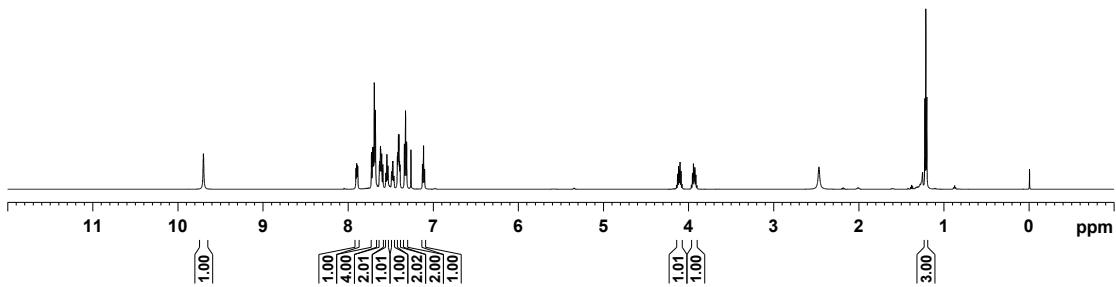
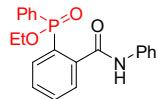


<sup>1</sup>H NMR spectrum of compound **4d**

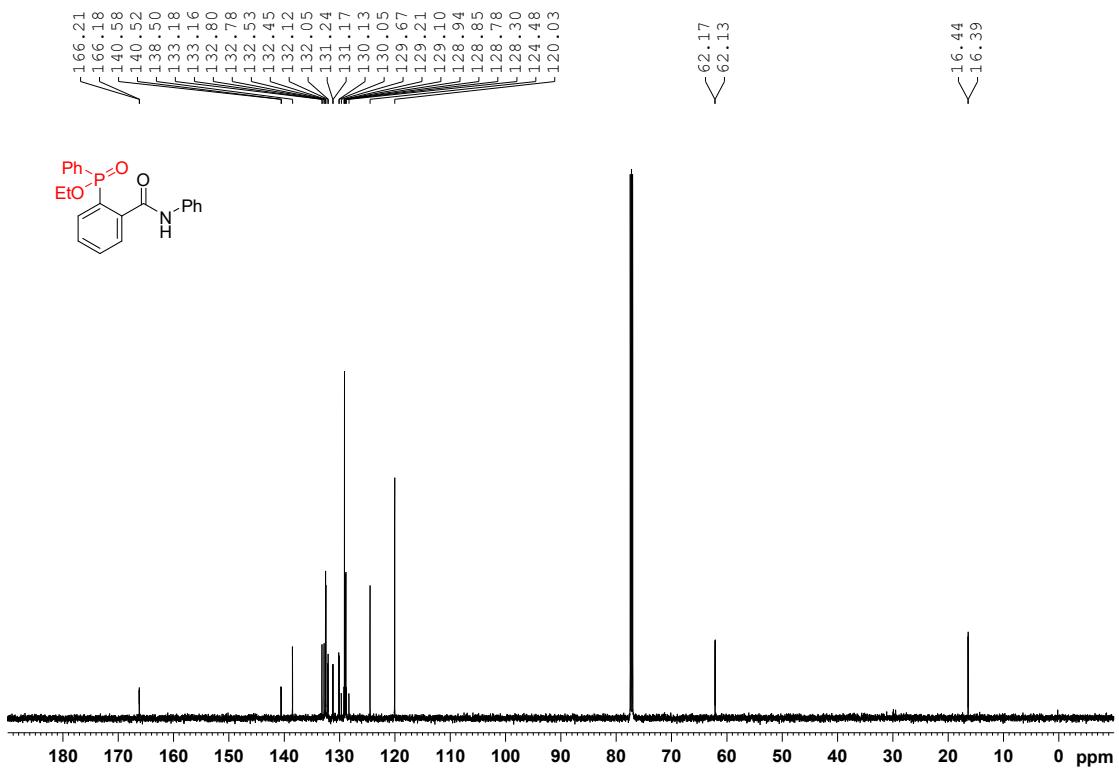


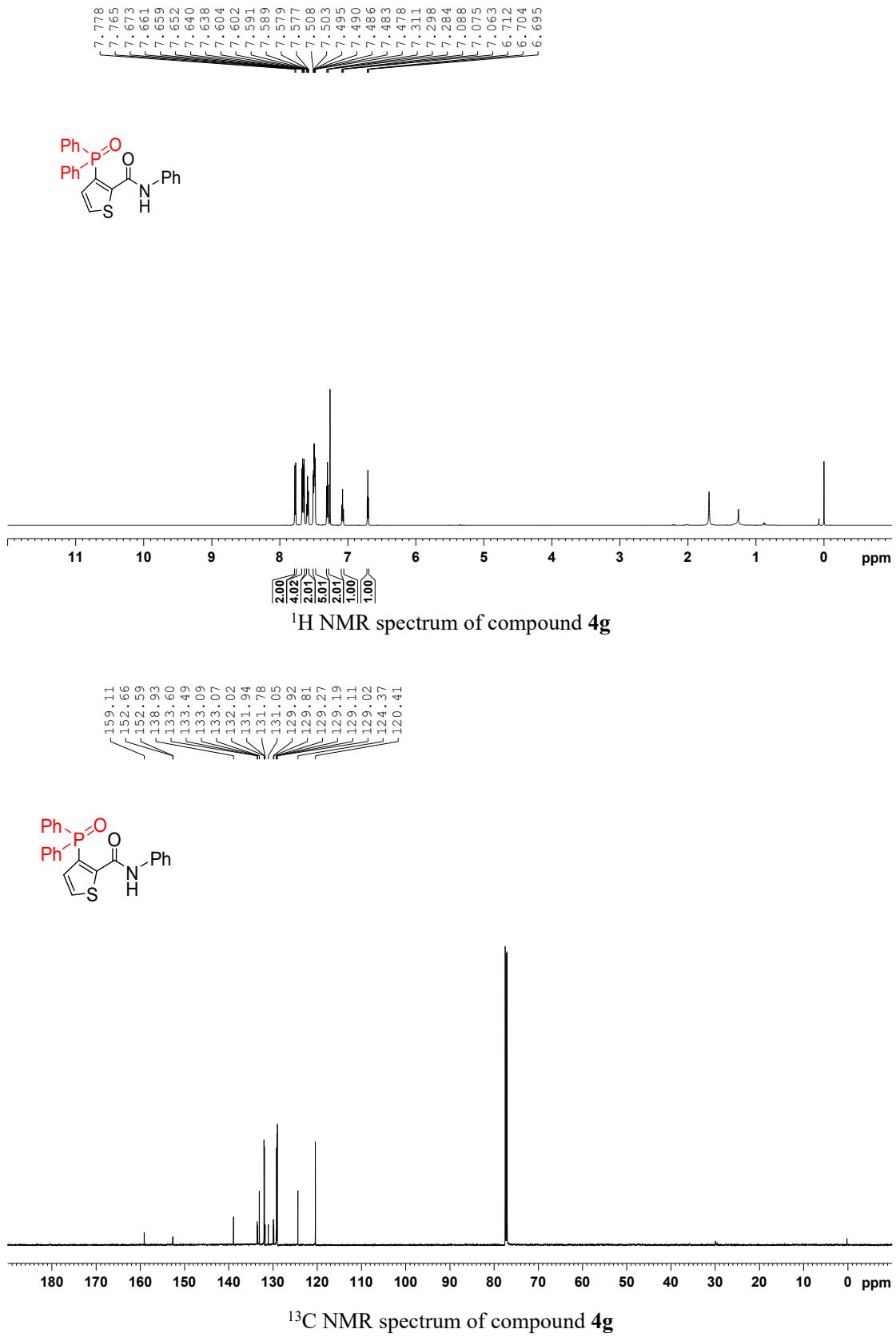


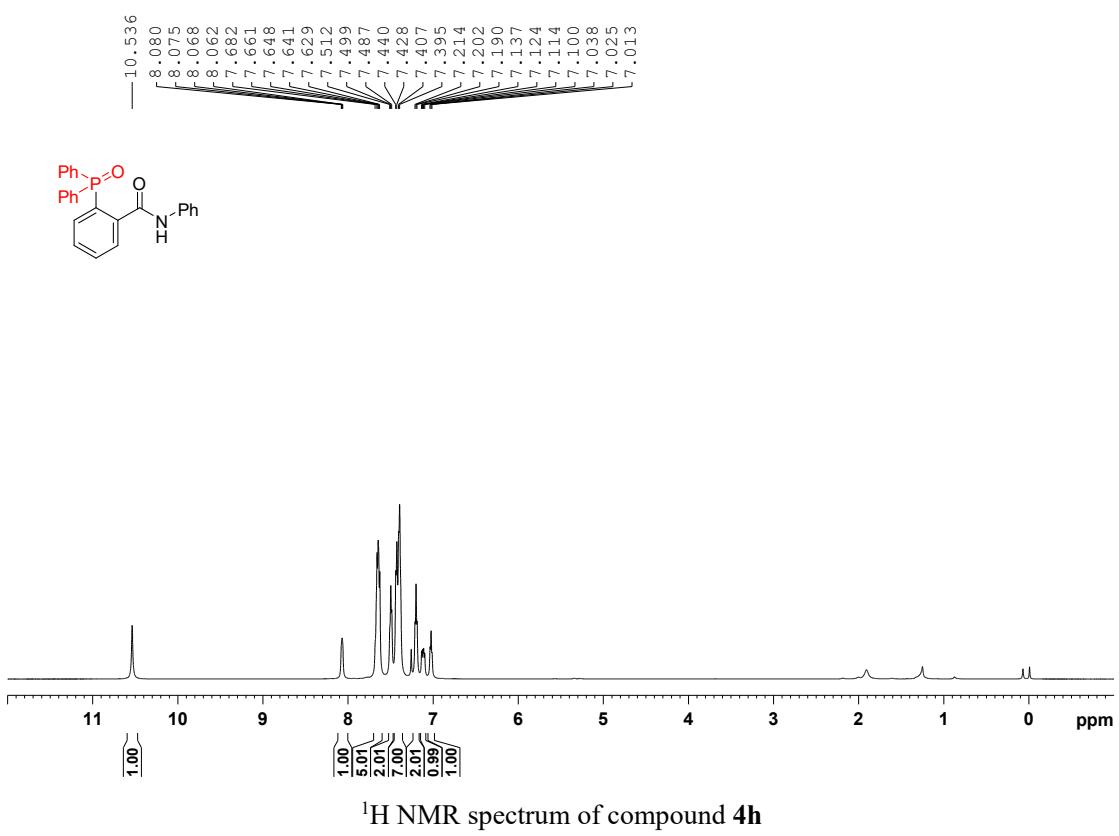
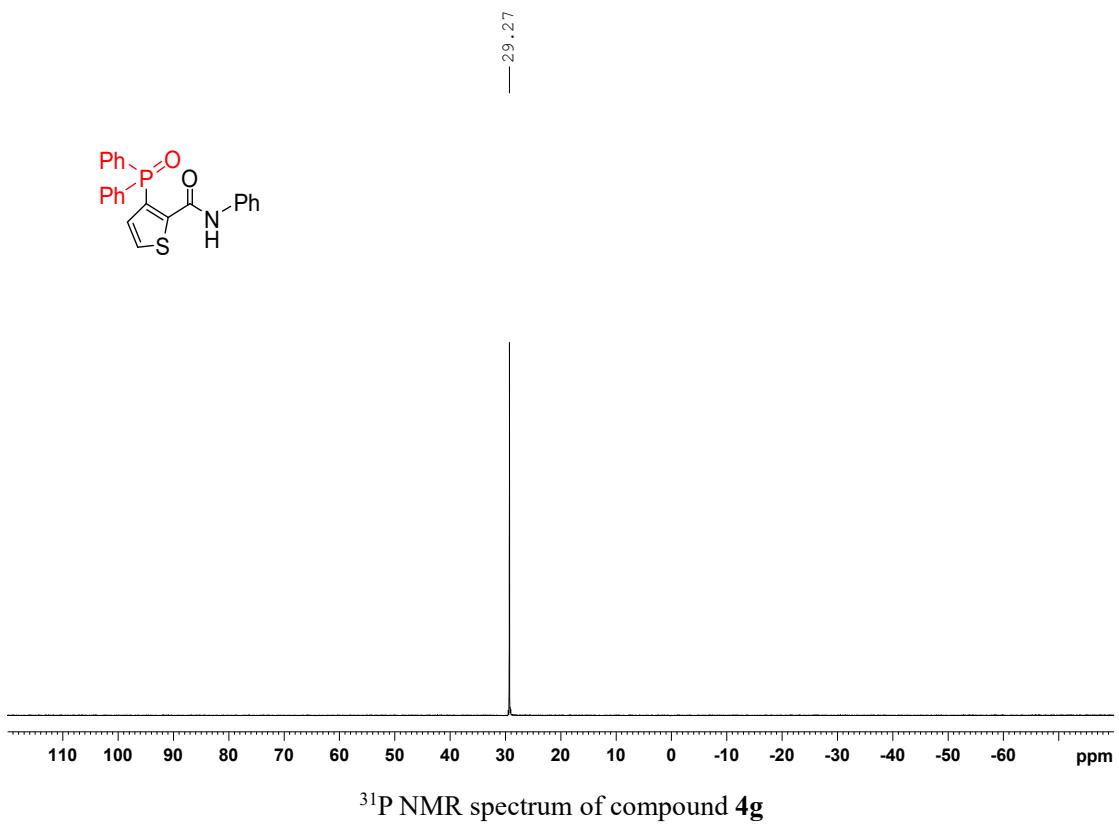
### <sup>31</sup>P NMR spectrum of compound 4d

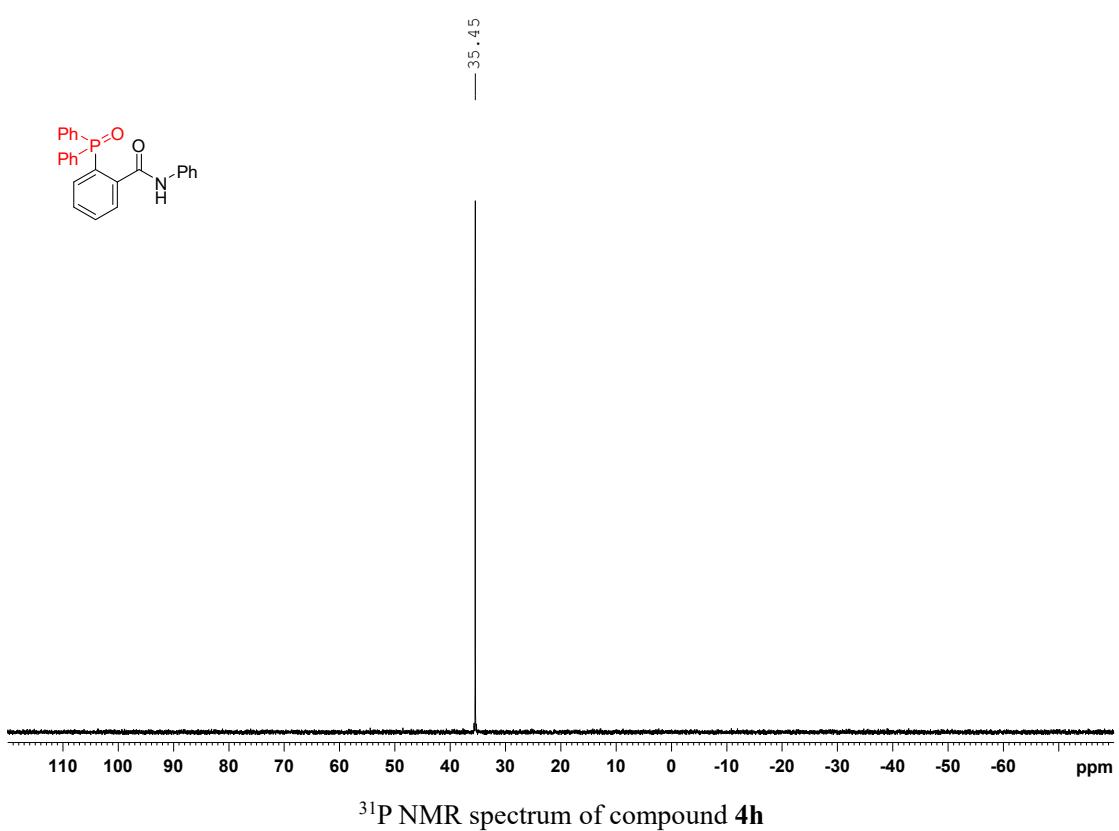
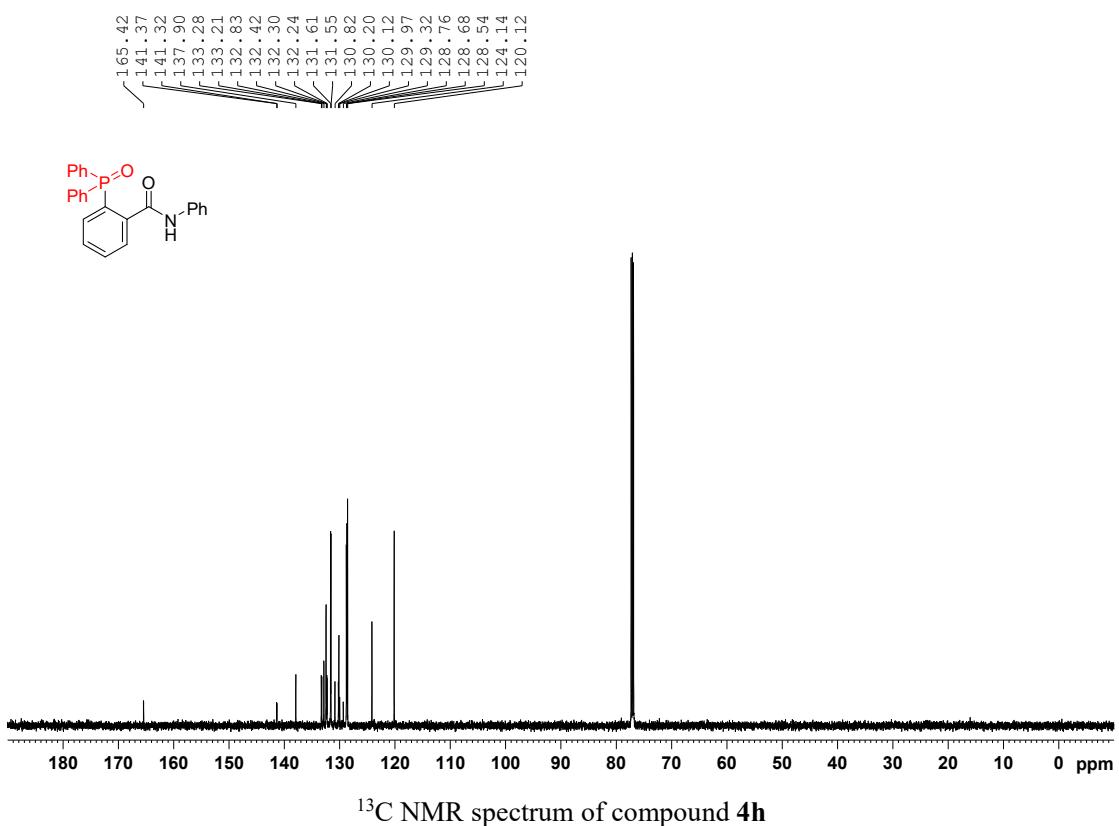


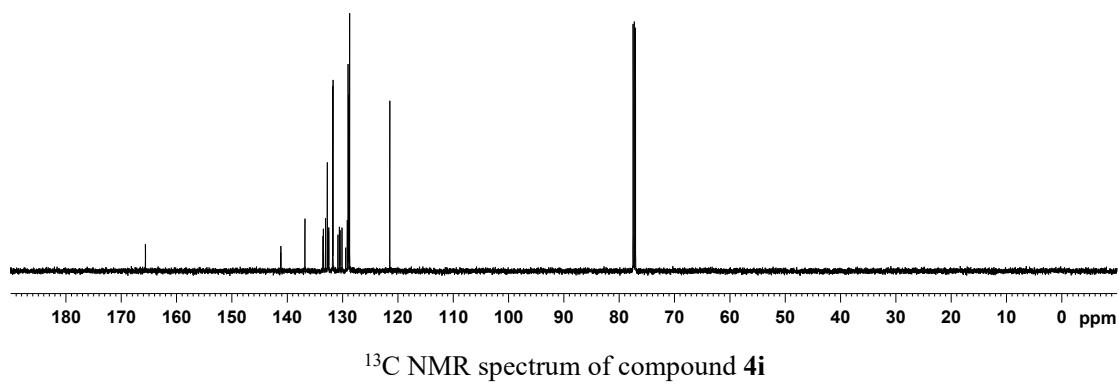
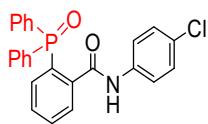
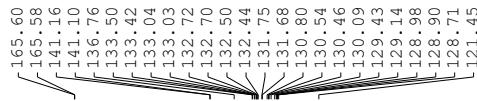
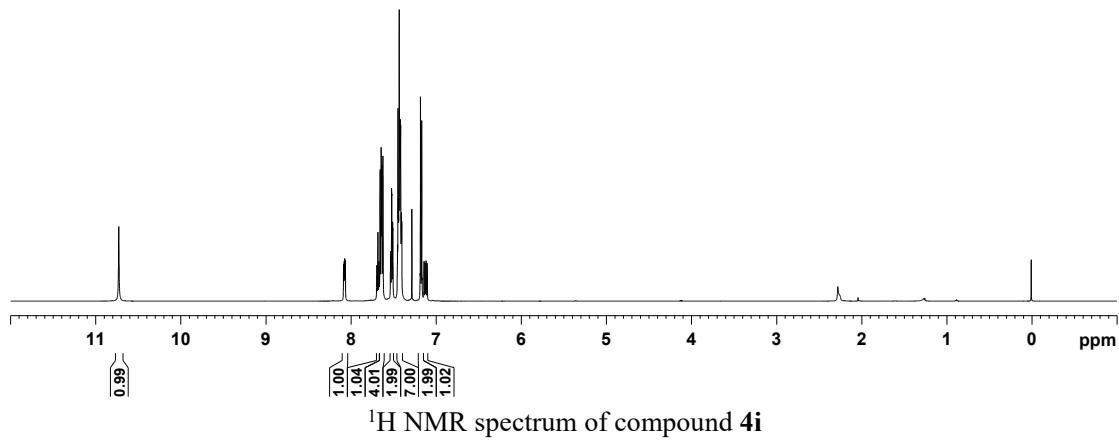
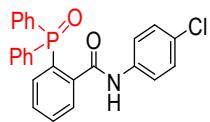
### <sup>1</sup>H NMR spectrum of compound 4f

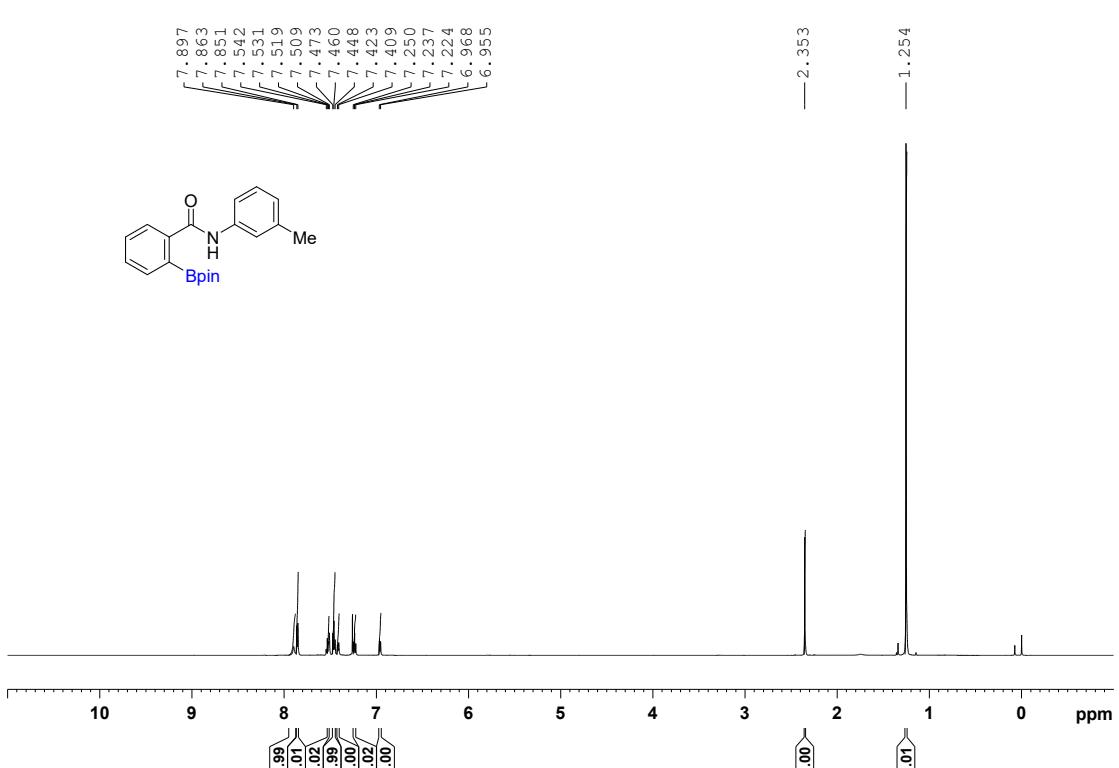
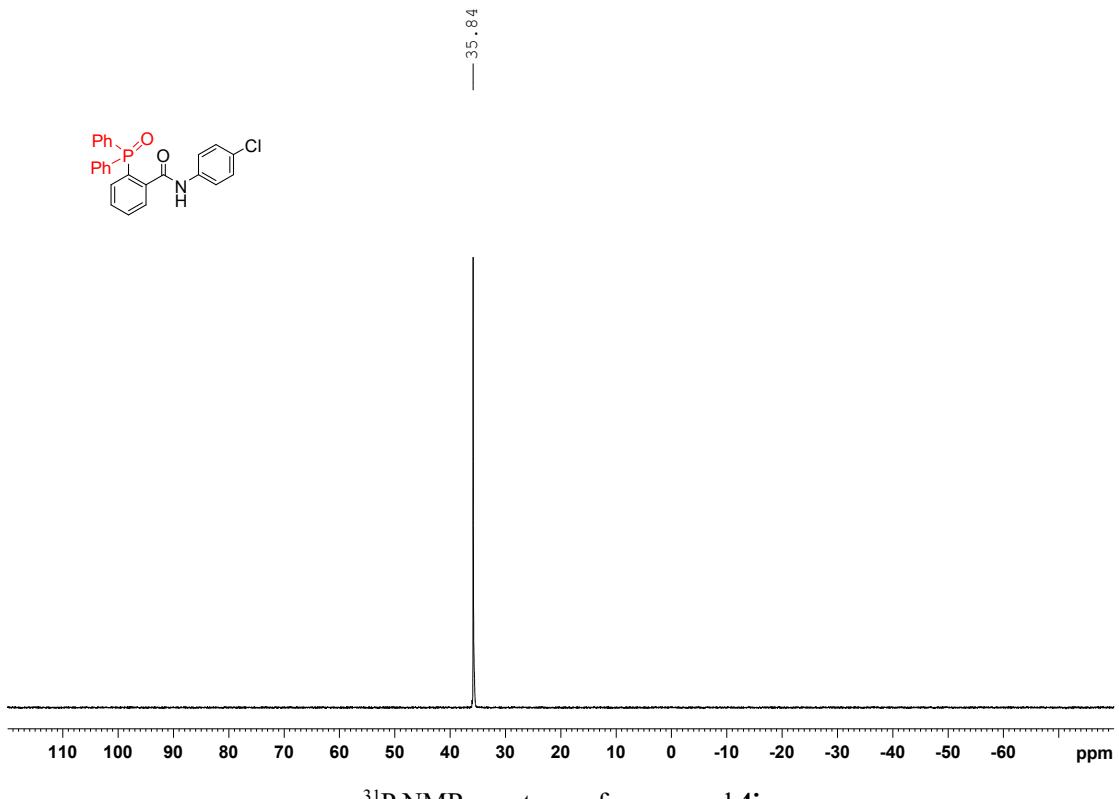




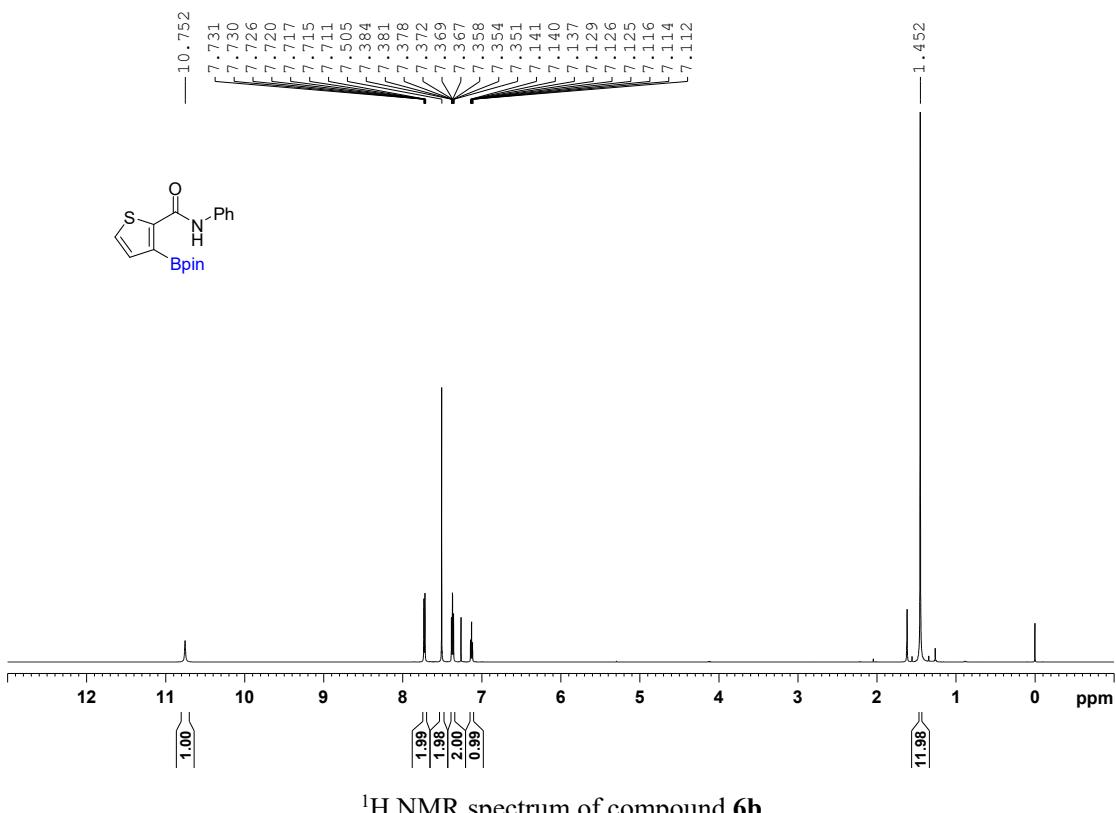
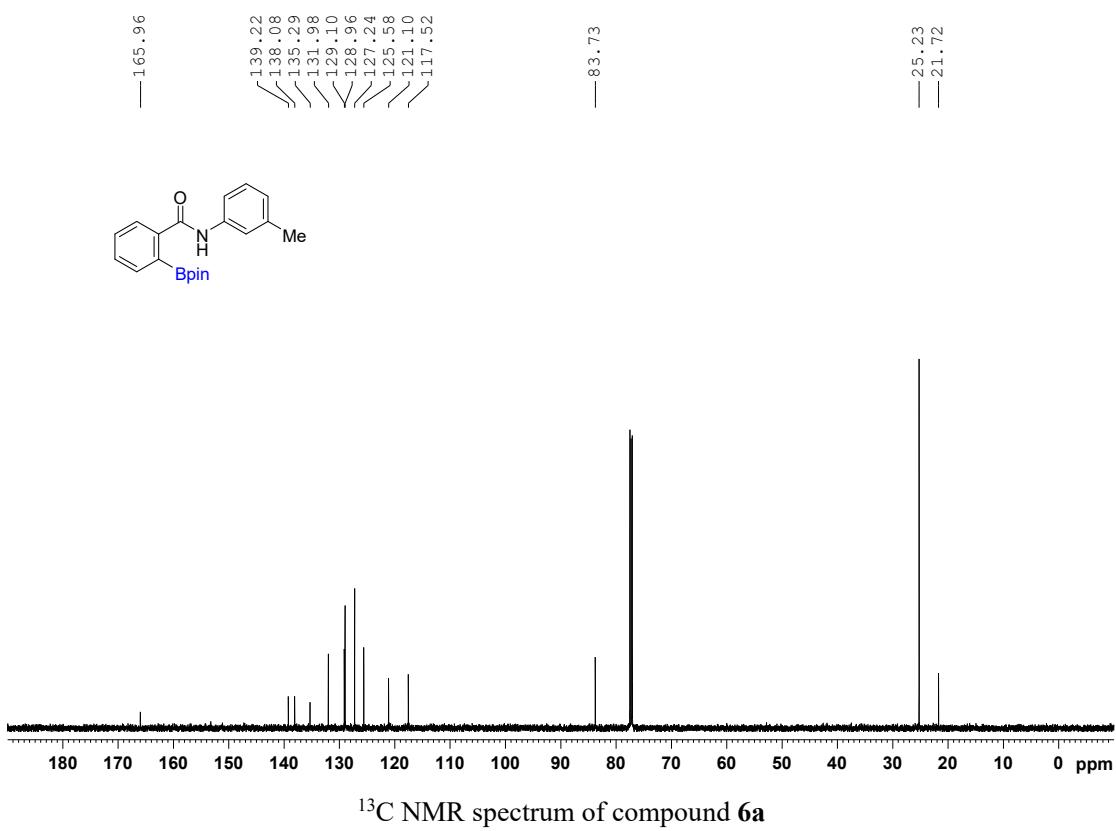




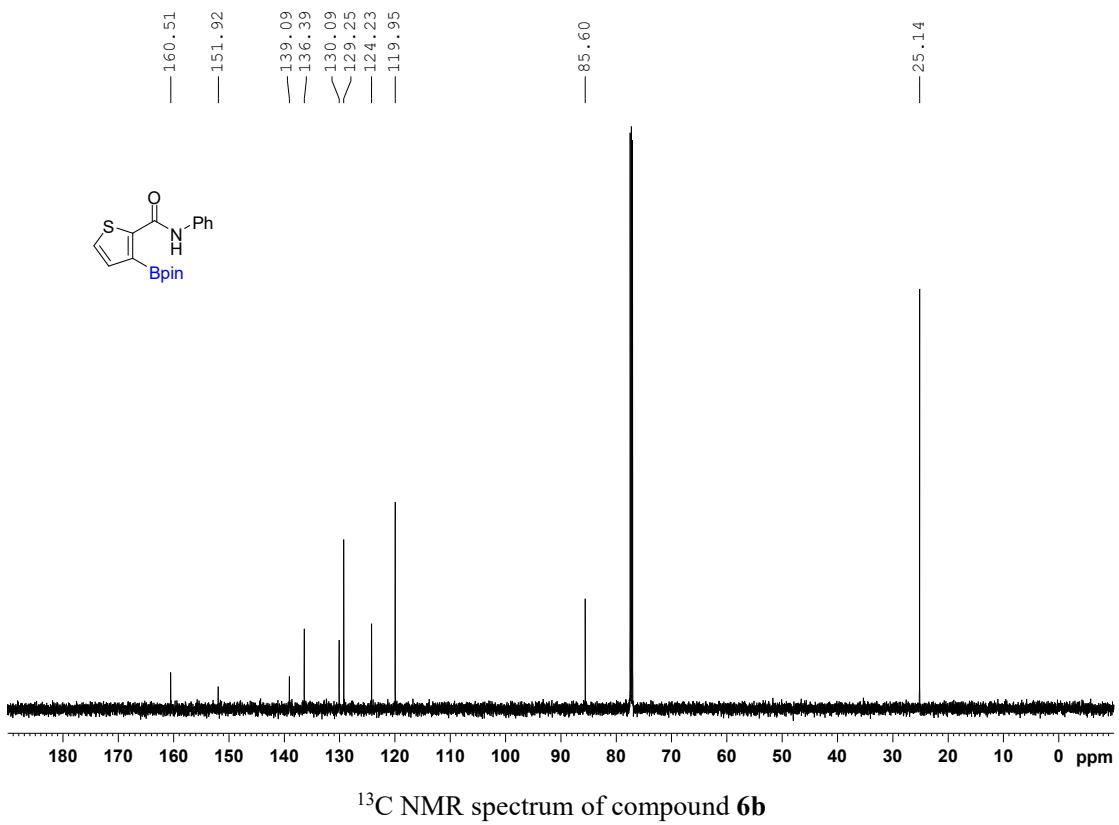




<sup>1</sup>H NMR spectrum of compound 6a



<sup>1</sup>H NMR spectrum of compound **6b**



$^{13}\text{C}$  NMR spectrum of compound **6b**