

# I<sub>2</sub>-mediated Csp<sup>2</sup>-P bond formation via tandem cyclization of o-alkynylphenyl isothiocyanates with organophosphorus esters

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## Support Information

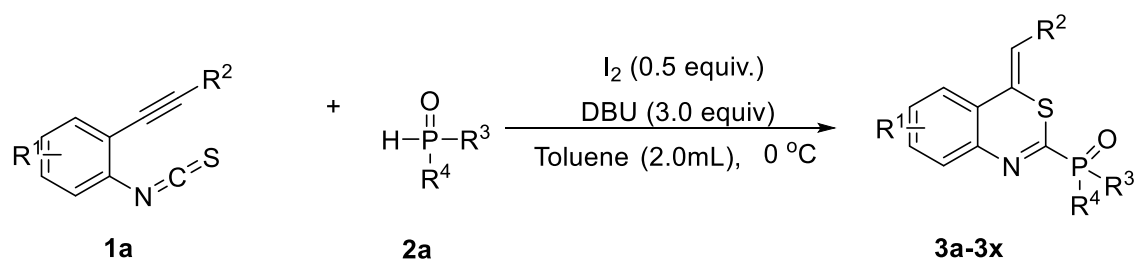
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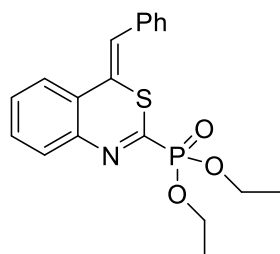
## 1. General Information

All reagents and metal catalysts were obtained from commercial sources without further purification, and commercially available solvents were purified before use. All reactions were performed in reaction tubes. All new compounds were fully characterized. Silica gel plate GF254 were used for thin layer chromatography (TLC) and silica gel H or 300-400 mesh were used for flash column chromatography. Thin layer chromatography plates were visualized by exposure to ultraviolet light. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the  $\delta$  scale. The mass analyzer type used for the HRMS measurements is micro TOF. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise indicated.

## 2. Synthesis and Characterization for Compounds 3a-3u

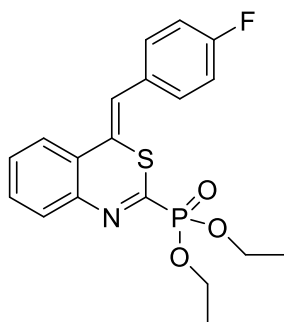


A mixture of *o*-alkynylphenylisothiocyanate **1** (0.20 mmol) and I<sub>2</sub> (0.1 mmol) was added into a tube. Subsequently, DBU (3.0equiv.) and Toluene (2.0 ml) were added. Then, phosphites **2** (0.6 mmol) was added into the tube. Then, the sealed tube was cooled at 0 °C for 12 hours. After completion of reaction as indicated by TLC, the mixture was concentrated and directly purified by flash column chromatography (EtOAc/petroleum ether, 1:2) to give the desired product **3**.



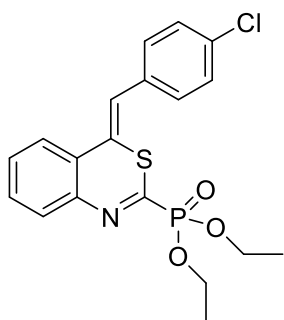
### *diethyl (Z)-(4-benzylidene-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3a)*<sup>[1]</sup>

Yellow oil; (62.7 mg, 84%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (dd, *J* = 5.0, 4.0 Hz, 1H), 7.54-7.50 (m, 1H), 7.47-7.37 (m, 6H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 4.34-4.23 (m, 4H), 1.37 (t, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.6, 141.3, 135.2, 130.7, 130.2, 129.8, 129.2, 128.4, 127.8, 127.0, 124.4, 123.7, 122.5, 64.3, 64.2, 16.3, 16.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 2.78. HRMS calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>3</sub>PS<sup>+</sup> (M+ H<sup>+</sup>): 374.0974; Found: 374.0978.



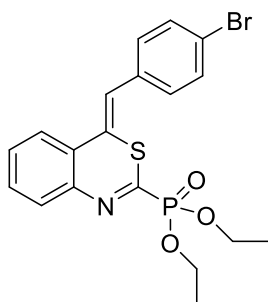
**diethyl (Z)-(4-(4-fluorobenzylidene)-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3b)<sup>[1]</sup>**

Yellow oil; (54.8mg, 70% ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (t, *J* = 3.8 Hz, 1H), 7.52 (t, *J* = 5.4 Hz, 1H), 7.45-7.40 (m, 4H), 7.09 (t, *J* = 8.6 Hz, 2H), 6.96 (s, 1H), 4.31-4.25 (m, 4H), 1.38 (t, *J* = 7.2 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.0 (d, <sup>1</sup>*J*<sub>CF</sub> = 248 Hz), 156.0 (d, <sup>1</sup>*J*<sub>CF</sub> = 238 Hz), 141.4 (d, <sup>2</sup>*J*<sub>CF</sub> = 25 Hz), 131.4, 131.0 (d, <sup>3</sup>*J*<sub>CF</sub> = 8 Hz), 130.8, 130.2, 129.9, 125.7, 124.3, 123.7, 122.3, 115.4 (d, <sup>2</sup>*J*<sub>CF</sub> = 22 Hz), 64.3, 64.3, 16.3, 16.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 2.64. <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, CDCl<sub>3</sub>, 25°C, TMS): δ = -112.7. HRMS calcd for C<sub>19</sub>H<sub>20</sub>FNO<sub>3</sub>PS<sup>+</sup>(M + H<sup>+</sup>): 392.0880; Found: 392.0870.



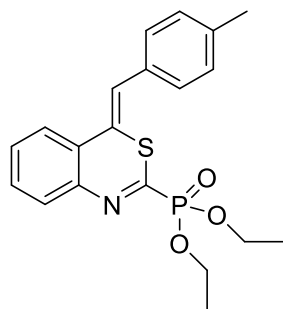
**diethyl(Z)-(4-(4-chlorobenzylidene)-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3c)<sup>[1]</sup>**

Yellow oil; (57.8 mg, 71% ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, *J* = 5.8, 3.2 Hz, 1H), 7.53 (dd, *J* = 6.2, 3.0 Hz, 1H), 7.44 (dd, *J* = 6.2, 2.6 Hz, 2H), 7.37 (s, 4H), 6.94 (d, *J* = 2.0 Hz, 1H), 4.31-4.26 (m, 4H), 1.38 (t, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.5, 141.2, 133.7, 133.4, 130.8, 130.4, 130.3, 130.0, 128.6, 125.4, 124.6, 124.3, 122.1, 64.4, 64.3, 16.3, 16.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 2.64. HRMS calcd for C<sub>19</sub>H<sub>20</sub>ClNO<sub>3</sub>PS<sup>+</sup>(M+ H<sup>+</sup>): 408.0585; Found: 408.0575.



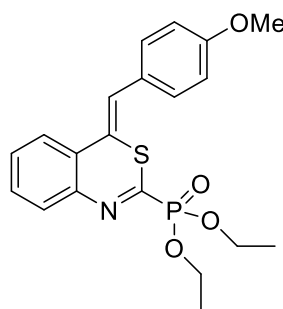
**diethyl (Z)-(4-(4-bromobenzylidene)-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3d)<sup>[1]</sup>**

Yellow oil; (64.9mg, 72%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (t, *J* = 4.0Hz, 1H), 7.52 (t, *J* = 4.0Hz, 1H), 7.45-7.40 (m, 4H), 7.09 (t, *J* = 8.6 Hz, 2H), 6.96 (s, 1H), 4.31-4.26 (m, 4H), 1.37 (t, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.4, 141.2, 134.1, 131.5, 130.9, 130.7, 130.3, 130.1, 125.4, 124.7, 124.3, 122.1, 121.6, 64.4, 64.3, 16.3, 16.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 2.57. HRMS calcd for C<sub>19</sub>H<sub>20</sub>BrNO<sub>3</sub>PS<sup>+</sup>(M+ H<sup>+</sup>): 452.0079; Found: 452.0061.



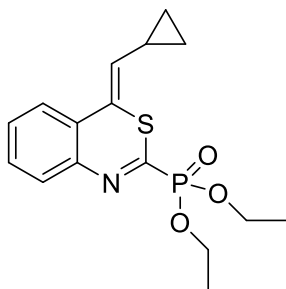
**diethyl (Z)-(4-(4-methylbenzylidene)-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3e)<sup>[1]</sup>**

Yellow oil;(62.7mg, 81%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57(t, *J* = 3.4 Hz, 1H), 7.50 (t, *J* = 5.4Hz, 1H), 7.42 (dd, *J* = 5.8, 3.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.97 (s, 1H), 4.30-4.25 (m, 4H), 2.38 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.6, 141.3, 137.8, 132.5, 130.7, 130.1, 129.7, 129.2, 129.1, 127.5, 127.0, 124.4, 122.7, 64.3, 64.2, 21.4, 16.3, 16.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 2.80. HRMS calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>3</sub>PS<sup>+</sup>(M+ H<sup>+</sup>): 388.1131; Found: 388.1169.



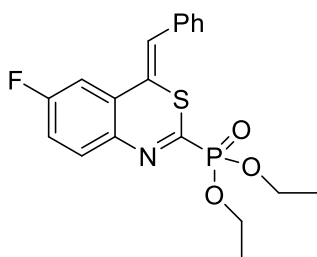
**diethyl (Z)-(4-(4-methoxybenzylidene)-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3f)<sup>[1]</sup>**

Yellow oil; (68.56mg, 85%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 (dd, *J* = 5.8, 3.4 Hz, 1H), 7.49 (dd, *J* = 5.8, 3.6 Hz, 1H), 7.41 (dd, *J* = 9.0, 4.2 Hz, 4H), 6.93 (t, *J* = 6.4Hz, 3H), 4.31-4.25 (m, 4H), 3.84 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.1, 141.5, 141.2, 130.7, 130.0, 129.5, 128.9, 128.1, 126.9, 124.4, 123.0, 121.3, 113.8, 64.3, 64.2, 55.3, 16.3, 16.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 2.80. HRMS calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>4</sub>PS<sup>+</sup>(M+ H<sup>+</sup>): 404.1080; Found: 404.1100.



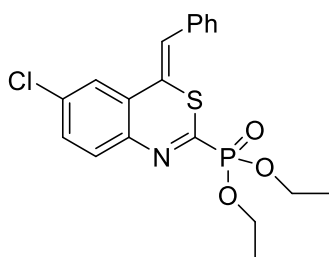
**diethyl (Z)-(4-(cyclopropylmethylene)-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3g)<sup>[1]</sup>**

Yellow oil; (47.2mg, 70% ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (d, *J* = 5.8 Hz, 1H), 7.31 (s, 3H), 5.42 (d, *J* = 9.4 Hz, 1H), 4.36-4.28 (m, 4H), 1.42 (t, *J* = 6.8 Hz, 6H), 0.93 (d, *J* = 7.6 Hz, 2H), 0.55 (d, *J* = 4.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.4, 141.1, 131.6, 130.4, 130.1, 129.0, 123.4, 122.3, 120.6, 64.2, 64.1, 16.4, 16.3, 11.6, 7.8. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 2.83. HRMS calcd for C<sub>16</sub>H<sub>21</sub>NO<sub>3</sub>PS<sup>+</sup>(M+ H<sup>+</sup>): 338.0974; Found: 338.0978.



**diethyl (Z)-(4-benzylidene-6-fluoro-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3h)<sup>[1]</sup>**

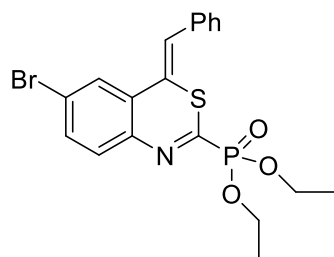
Yellow oil; (57.1 mg, 73% ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52 (dd, *J* = 8.6, 5.8 Hz, 1H), 7.38-7.46 (m, 4H), 7.34-7.27 (m, 2H), 7.13 (td, *J* = 8.4, 2.6 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 4.31-4.25 (m, 4H), 1.37 (t, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.6 (d, <sup>1</sup>*J*<sub>CF</sub> = 250 Hz), 134.9, 132.4 (d, <sup>3</sup>*J*<sub>CF</sub> = 9 Hz), 129.2, 128.5, 128.1, 127.5, 124.4 (d, <sup>3</sup>*J*<sub>CF</sub> = 8 Hz), 123.0, 116.9 (d, <sup>2</sup>*J*<sub>CF</sub> = 22 Hz), 110.8 (d, <sup>2</sup>*J*<sub>CF</sub> = 24 Hz), 64.3, 64.3, 16.3, 16.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 2.71. <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, CDCl<sub>3</sub>, 25°C, TMS): δ = -109.0. HRMS calcd for C<sub>19</sub>H<sub>20</sub>FNO<sub>3</sub>PS<sup>+</sup>(M+ H<sup>+</sup>): 392.0880; Found: 392.0906.



**diethyl (Z)-(4-benzylidene-6-chloro-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3i)<sup>[1]</sup>**

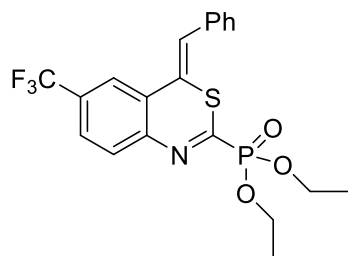
Yellow oil; (71.6 mg, 88% ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 2.0 Hz, 1H),

7.46-7.40 (m, 6H), 7.32 (d,  $J = 7.0$  Hz, 1H), 6.99 (s, 1H), 4.30 -4.25 (m, 4H), 1.37 (t,  $J = 7.0$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 139.9, 136.1, 134.8, 131.4, 129.8, 129.3, 128.5, 128.1, 128.0, 124.3, 124.0, 122.5, 64.4, 64.3, 16.3, 16.3.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  2.51. HRMS calcd for  $\text{C}_{19}\text{H}_{20}\text{ClNO}_3\text{PS}^+(\text{M} + \text{H}^+)$ : 408.0585; Found: 408.0605.



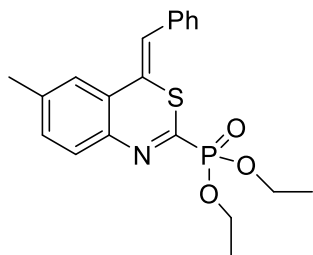
**diethyl (Z)-(4-benzylidene-6-bromo-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3j)<sup>[1]</sup>**

Yellow oil; (83.0 mg, 92%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 2.0$  Hz, 1H), 7.54 (dd,  $J = 8.4, 2.0$  Hz, 1H), 7.45-7.36 (m, 5H), 7.31 (t,  $J = 6.8$  Hz, 1H), 6.98 (d,  $J = 1.8$  Hz, 1H), 4.30-4.25 (m, 4H), 1.37 (t,  $J = 7.0$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.5, 140.3, 138.8, 134.8, 132.8, 131.5, 129.3, 128.4, 128.1, 127.3, 124.3, 124.2, 122.2, 64.4, 64.4, 16.3, 16.2.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  2.52. HRMS calcd for  $\text{C}_{19}\text{H}_{20}\text{BrNO}_3\text{PS}^+(\text{M} + \text{H}^+)$ : 452.0079; Found: 452.0110.



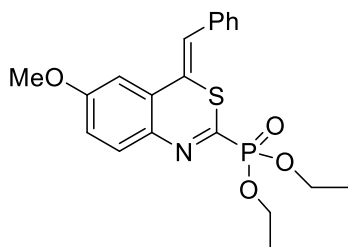
**diethyl (Z)-(4-benzylidene-6-(trifluoromethyl)-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3k)<sup>[1]</sup>**

Yellow oil; (60.9 mg, 69%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (s, 1H), 7.68 (d,  $J = 8.2$  Hz, 1H), 7.61 (d,  $J = 8.2$  Hz, 1H), 7.42 (t,  $J = 6.2$  Hz, 4H), 7.34 (t,  $J = 6.8$  Hz, 1H), 7.04 (s, 1H), 4.32-4.26 (m, 4H), 1.38 (t,  $J = 7.0$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.3, 159.0, 143.8, 134.6, 132.4, 130.4, 129.3, 129.1, 128.5, 128.3, 126.5 (q,  $J_{\text{CF}_3} = 4$  Hz), 125.0, 123.4, 122.2 (q,  $J_{\text{CF}_3} = 4$  Hz), 122.0 (q,  $J_{\text{CF}_3} = 4$  Hz), 64.5, 16.3.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  2.07.  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = -62.7$ . HRMS calcd for  $\text{C}_{20}\text{H}_{20}\text{F}_3\text{NO}_3\text{PS}^+(\text{M} + \text{H}^+)$ : 442.0848; Found: 442.0850.



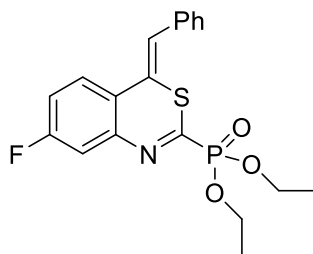
**diethyl (Z)-(4-benzylidene-6-methyl-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3l)<sup>[1]</sup>**

Yellow oil; (69.7mg, 90%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46-7.37 (m, 6H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 4.29-4.24 (m, 4H), 2.43 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.1, 139.4, 139.2, 135.3, 130.7, 130.1, 129.1, 128.3, 127.7, 126.3, 124.6, 123.9, 122.0, 64.2, 64.1, 21.5, 16.3, 16.2. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 3.04. HRMS calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>3</sub>PS<sup>+</sup> (M+ H<sup>+</sup>): 388.1131; Found: 388.1116.



**diethyl (Z)-(4-benzylidene-6-methoxy-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3m)**

Yellow oil; (74.2mg, 92%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.36 (m, 3H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.90 (dd, *J* = 2.8 Hz, 8.8 Hz, 1H), 4.23-4.13 (m, 4H), 3.80 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.3, 153.4, 135.2, 132.0, 129.2, 128.9, 128.4, 127.8, 126.2, 124.1, 123.6, 115.5, 108.7, 64.1, 55.7, 16.3. HRMS calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>4</sub>PS<sup>+</sup> (M+ H<sup>+</sup>): 404.1080; Found: 404.1082.

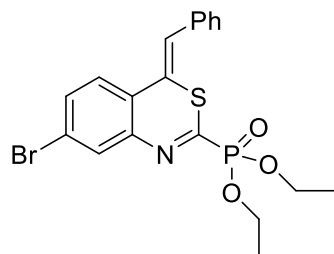


**diethyl (Z)-(4-benzylidene-7-fluoro-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3n)<sup>[1]</sup>**

Yellow oil; (57.9mg, 74%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 (dd, *J* = 8.2, 6.0 Hz, 1H), 7.39 (t, *J* = 6.0 Hz, 4H), 7.31 (dd, *J* = 13.0, 7.0 Hz, 2H), 7.21 (d, *J* = 9.0 Hz, 1H), 7.15 (t, *J* = 9.0 Hz, 1H), 6.94 (s, 1H), 4.31 – 4.25 (m, 4H), 1.38 (t, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.3 (d, <sup>1</sup>J<sub>CF</sub> = 248 Hz), 158.6 (d, <sup>1</sup>J<sub>CF</sub> = 235 Hz), 135.0,

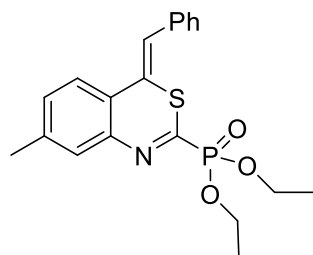


129.1, 128.4, 127.9, 127.5, 127.0, 126.2(d,  $^3J_{CF} = 8$  Hz), 122.8, 118.9, 117.8(d,  $^2J_{CF} = 22$  Hz), 116.2(d,  $^2J_{CF} = 24$  Hz), 64.5, 64.4, 16.3, 16.2.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  2.34.  $^{19}\text{F}$   $\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = -111.6$ . HRMS calcd for  $\text{C}_{19}\text{H}_{20}\text{FNO}_3\text{PS}^+(\text{M} + \text{H}^+)$ : 392.0880; Found: 392.0888.



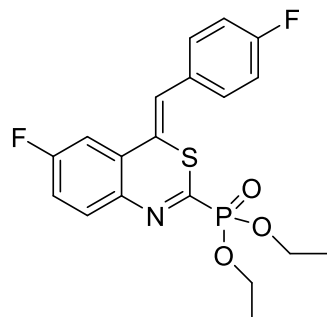
**diethyl (Z)-(4-benzylidene-7-bromo-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3o)<sup>[1]</sup>**

Yellow solid; (81.1mg, 90%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (s, 1H), 7.53 (d,  $J = 9.8$  Hz, 1H), 7.45-7.38(m, 5H), 7.31 (t,  $J = 6.6$  Hz, 1H), 6.98 (s, 1H), 4.30-4.25 (m, 4H), 1.37 (t,  $J = 7.0$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.6, 142.3, 134.9, 133.4, 132.6, 129.2, 128.4, 128.0, 127.5, 125.8, 123.3, 122.7, 121.6, 64.5, 64.4, 16.3, 16.3.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  2.20. HRMS calcd for  $\text{C}_{19}\text{H}_{20}\text{BrNO}_3\text{PS}^+(\text{M} + \text{H}^+)$ : 452.0079; Found: 452.0068.



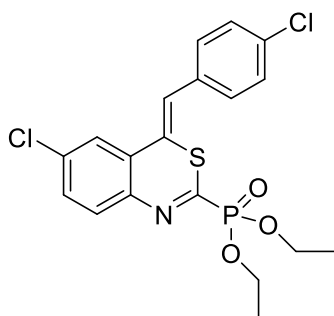
**diethyl (Z)-(4-benzylidene-7-methyl-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3p)<sup>[1]</sup>**

Yellow oil; (61.9 mg, 80%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 8.0$  Hz, 1H), 7.44-7.37(m, 4H), 7.34 (s, 1H), 7.29 (d,  $J = 7.2$  Hz, 1H), 7.24 (d,  $J = 8.0$  Hz, 1H), 6.97 (d,  $J = 2.0$  Hz, 1H), 4.30-4.25 (m, 4H), 2.40 (s, 3H), 1.37 (t,  $J = 7.0$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.3, 141.1, 140.2, 135.4, 131.6, 130.6, 129.1, 128.4, 127.6, 125.6, 124.1, 123.9, 119.6, 64.3, 64.2, 20.9, 16.3, 16.3.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  2.83. HRMS calcd for  $\text{C}_{20}\text{H}_{23}\text{NO}_3\text{PS}^+(\text{M} + \text{H}^+)$ : 388.1131; Found: 388.1129.



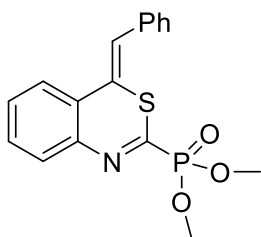
**diethyl (Z)-(6-fluoro-4-(4-fluorobenzylidene)-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3q)<sup>[1]</sup>**

Yellow oil; (58.1 mg, 71% ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52 (dd, *J* = 8.6, 5.8 Hz, 1H), 7.43 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.30-7.26 (m, 1H), 7.15 (dd, *J* = 8.0, 2.6 Hz, 1H), 7.10 (t, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 1.4 Hz, 1H), 4.31 – 4.26 (m, 4H), 1.38 (t, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.6 (d, <sup>1</sup>*J*<sub>CF</sub> = 250 Hz), 162.1 (d, <sup>1</sup>*J*<sub>CF</sub> = 248 Hz), 156.2, 153.8, 137.8 (d, <sup>2</sup>*J*<sub>CF</sub> = 26 Hz), 132.4 (d, <sup>3</sup>*J*<sub>CF</sub> = 9 Hz), 131.0 (d, <sup>3</sup>*J*<sub>CF</sub> = 8 Hz), 126.3, 124.2 (d, <sup>3</sup>*J*<sub>CF</sub> = 8 Hz), 122.9, 117.0 (d, <sup>2</sup>*J*<sub>CF</sub> = 23 Hz), 115.5 (d, <sup>2</sup>*J*<sub>CF</sub> = 22 Hz), 110.7 (d, <sup>2</sup>*J*<sub>CF</sub> = 24 Hz), 64.4, 64.3, 16.3, 16.2. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 2.59. <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = -112.2, -108.9. HRMS calcd for C<sub>19</sub>H<sub>19</sub>F<sub>2</sub>NO<sub>3</sub>PS<sup>+</sup>(M+ H<sup>+</sup>): 410.0786; Found: 410.0794.



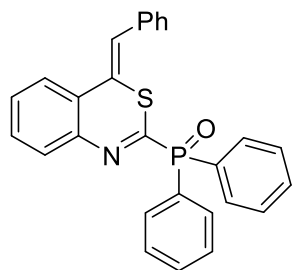
**diethyl (Z)-(6-chloro-4-(4-chlorobenzylidene)-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3r)<sup>[1]</sup>**

Yellow oil; (67.0 mg, 76% ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 2.0 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.29 (s, 4H), 6.85 (d, *J* = 2.0 Hz, 1H), 4.23-4.18 (m, 4H), 1.30 (t, *J* = 7.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.0, 139.8, 136.3, 133.8, 133.3, 131.5, 130.5, 130.0, 128.7, 126.4, 124.2, 123.5, 123.3, 64.4, 64.4, 16.3, 16.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 2.34. HRMS calcd for C<sub>19</sub>H<sub>19</sub>Cl<sub>2</sub>NO<sub>3</sub>PS<sup>+</sup>(M+ H<sup>+</sup>): 442.0195; Found: 442.0201.



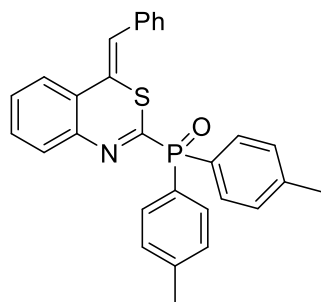
**dimethyl (Z)-(4-benzylidene-4H-benzo[d][1,3]thiazin-2-yl)phosphonate(3s)<sup>[1]</sup>**

Yellow oil; (56.0 mg, 81% ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (t, *J* = 5.4 Hz, 1H), 7.52 (m, *J* = 4.2 Hz, 1H), 7.46 – 7.39 (m, 6H), 7.31 (t, *J* = 6.8 Hz, 1H), 7.02 (d, *J* = 1.8 Hz, 1H), 3.91 (d, *J* = 11.2 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.5, 141.2, 135.1, 130.9, 130.2, 129.9, 129.2, 128.4, 127.9, 127.1, 124.4, 123.4, 122.5, 54.5, 54.4. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 5.00. HRMS calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>3</sub>PS<sup>+</sup>(M+ H<sup>+</sup>): 346.0661; Found: 346.0650.



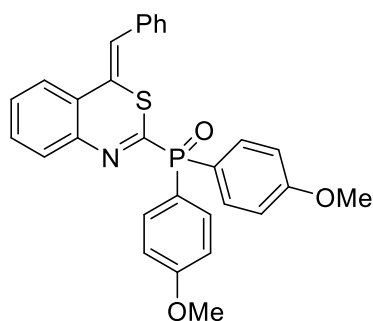
**(Z)-(4-benzylidene-4H-benzo[d][1,3]thiazin-2-yl)diphenylphosphine oxide(3t)<sup>[1]</sup>**

Yellow solid; (69.1 mg, 79%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97- 7.91 (m, 4H), 7.60-7.51 (m, 3H), 7.48-7.42 (m, 6H), 7.40-7.34 (m, 5H), 7.28-7.24 (m, 1H), 6.99 (d, *J* = 1.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.6, 141.4, 135.2, 132.5, 132.3, 132.2, 131.0, 130.7, 130.0, 129.9, 129.8, 129.2, 128.5, 128.5, 128.4, 127.8, 126.8, 124.4, 124.1, 122.0. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 20.62. HRMS calcd for C<sub>27</sub>H<sub>21</sub>NOPS<sup>+</sup>(M+ H<sup>+</sup>): 438.1076; Found: 438.1064.



**(Z)-(4-benzylidene-4H-benzo[d][1,3]thiazin-2-yl)di-p-tolylphosphine oxide(3u)**

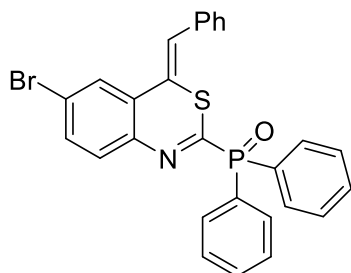
Yellow solid; (89.3mg,96%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.36 (s, 6H), 6.97 (s, 1H), 7.25 (dd, *J* = 4.0 Hz, 5H), 7.33-7.37 (m, 5H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.55-7.58 (m, 1H), 7.79-7.84 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 21.7, 122.0, 124.3, 126.6, 126.8, 127.7, 127.9, 128.4, 129.1, 129.2, 129.3, 129.7, 129.9, 130.5, 135.3, 141.5, 141.7, 143.0, 143.0, 162.2, 163.5. HRMS calcd for C<sub>29</sub>H<sub>25</sub>NOPS<sup>+</sup>(M+ H<sup>+</sup>): 466.1389; Found: 466.1392.



**(Z)-(4-benzylidene-4H-benzo[d][1,3]thiazin-2-yl)bis(4-methoxyphenyl)phosphine oxide (3v)**

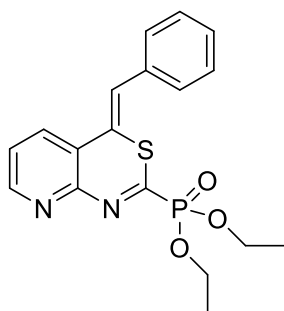
Yellow solid; (98.4mg,99%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.80 (s, 6H), 6.93-6.97 (m, 5H), 7.23-7.27 (m, 1H), 7.33-7.37 (m, 5H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.55-7.58 (m, 1H),

7.81-7.87 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  16.3, 55.7, 64.1, 64.1, 72.0, 108.7, 115.5, 123.6, 124.1, 126.2, 127.8, 128.4, 129.0, 129.0, 129.2, 132.0, 135.2, 151.0, 153.4, 161.3. HRMS calcd for  $\text{C}_{29}\text{H}_{25}\text{NO}_3\text{PS}^+(\text{M} + \text{H}^+)$ : 498.1287; Found: 498.1289.



**(Z)-(4-benzylidene-6-bromo-4H-benzo[d][1,3]thiazin-2-yl)diphenylphosphine oxide(3w)**

Yellow solid; (82.4mg, 80%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (dd,  $J = 12.0, 7.4$  Hz, 4H), 7.71 (d,  $J = 2.0$  Hz, 1H), 7.56 (t,  $J = 7.4$  Hz, 2H), 7.51-7.42(m, 7H), 7.37 (t,  $J = 7.6$  Hz, 2H), 7.29 (d,  $J = 7.2$  Hz, 1H), 7.23 (d,  $J = 8.4$  Hz, 1H), 6.97 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.8, 132.7, 132.6, 132.2, 132.1, 131.3, 130.7, 129.7, 129.3, 128.6, 128.5, 128.5, 128.1, 128.0, 127.2, 124.1, 123.8.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.99. HRMS calcd for  $\text{C}_{27}\text{H}_{20}\text{BrNOPS}^+(\text{M} + \text{H}^+)$ : 516.0181; Found: 516.0183.

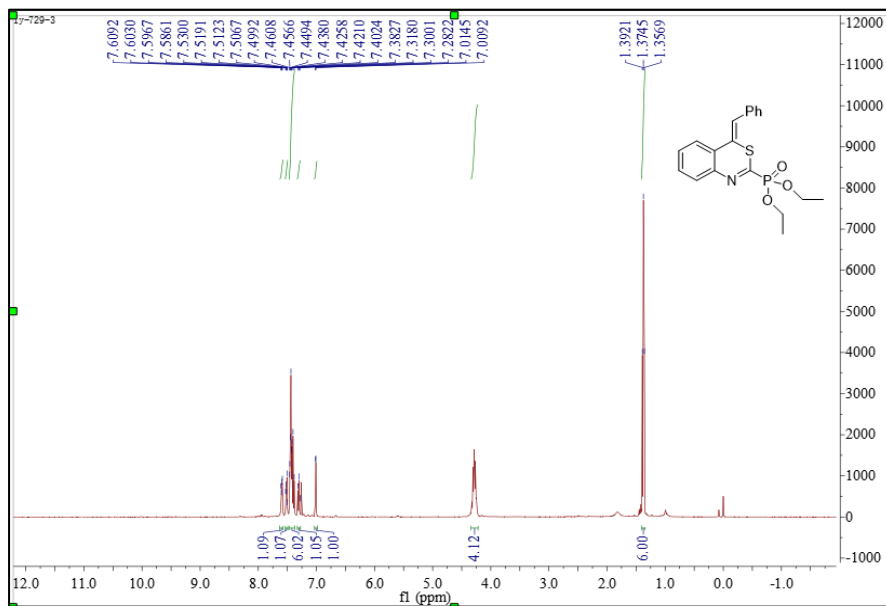


**diethyl (Z)-(4-benzylidene-4H-pyrido[2,3-d][1,3]thiazin-2-yl)phosphonate(3x)<sup>[1]</sup>**

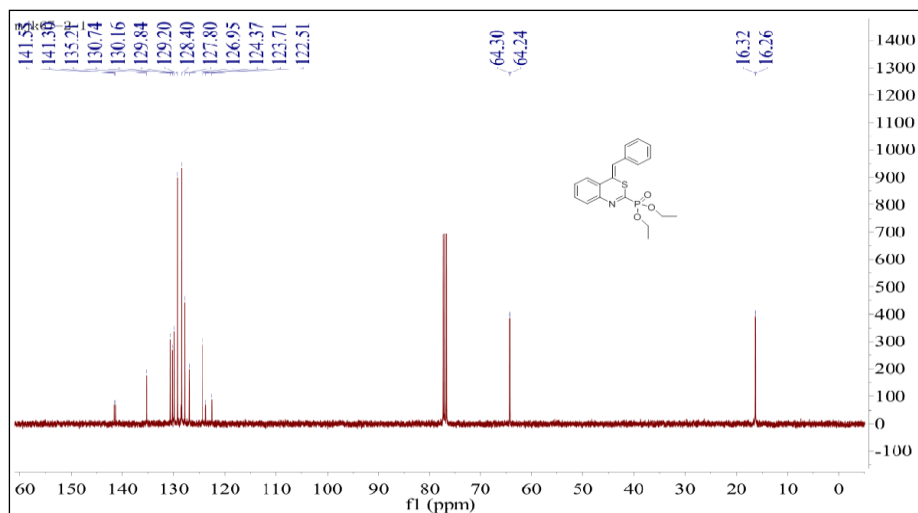
Yellow oil; (35.2mg, 47%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J = 4.0$  Hz, 1H), 7.94 (d,  $J = 7.4$  Hz, 1H), 7.44 -7.38 (m, 5H), 7.34 (d,  $J = 6.2$  Hz, 1H), 6.96 (d,  $J = 1.6$  Hz, 1H), 4.36 -4.31 (m, 4H), 1.38 (t,  $J = 7.0$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.2, 134.6, 133.8, 129.2, 129.2, 128.6, 128.4, 125.4, 123.1, 119.0, 64.9, 64.9, 16.3, 16.3.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  1.15. HRMS calcd for  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_3\text{PS}^+(\text{M} + \text{H}^+)$ : 375.0927; Found: 375.0935.

### 3. Copies of $^1\text{H}$ NMR, $^{13}\text{C}$ NMR $^{31}\text{P}$ NMR Spectra for compounds **3a-3x**

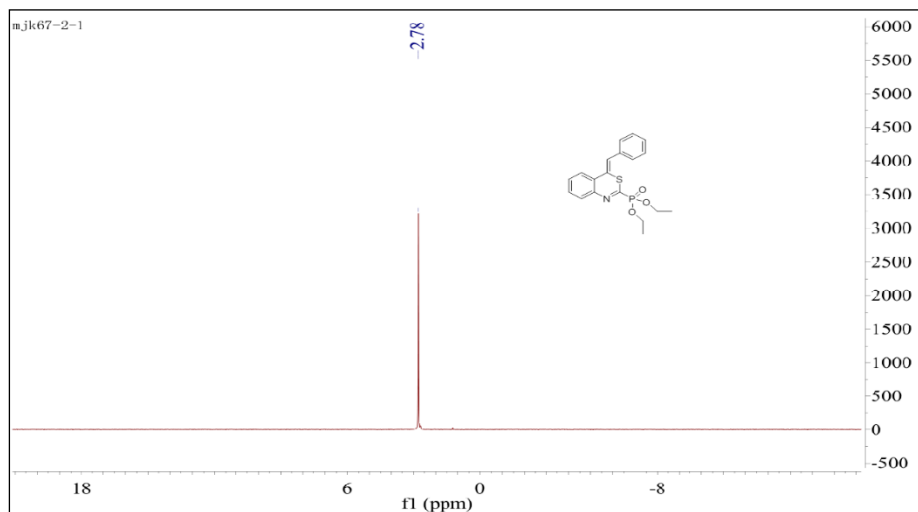
#### $^1\text{H}$ NMR of **3a**



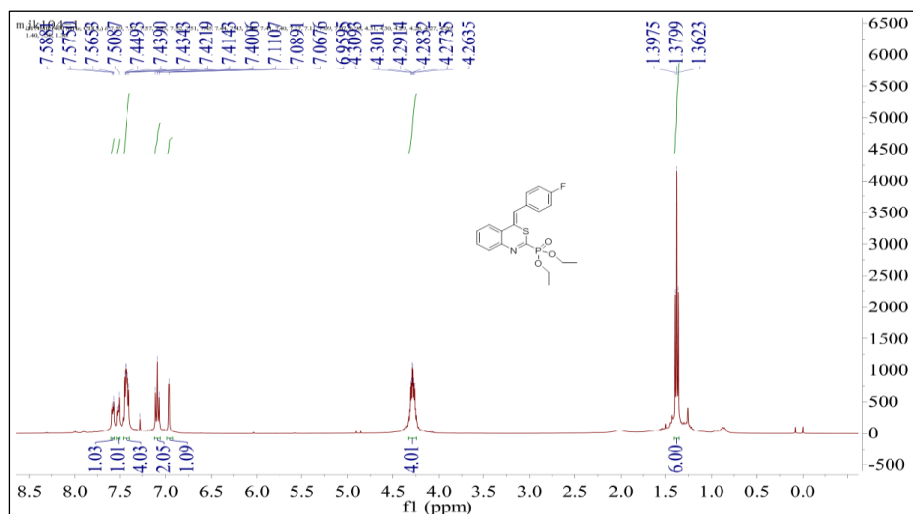
#### $^{13}\text{C}$ NMR of **3a**



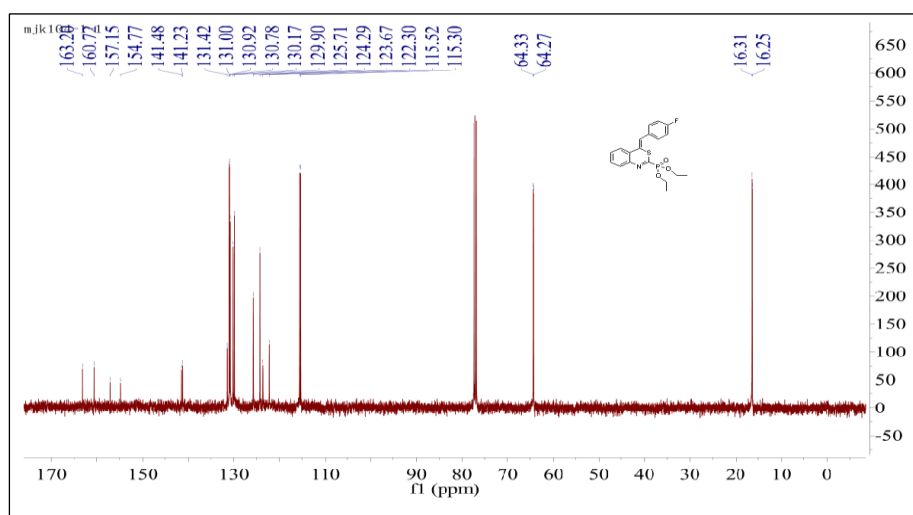
#### $^{31}\text{P}$ NMR of **3a**



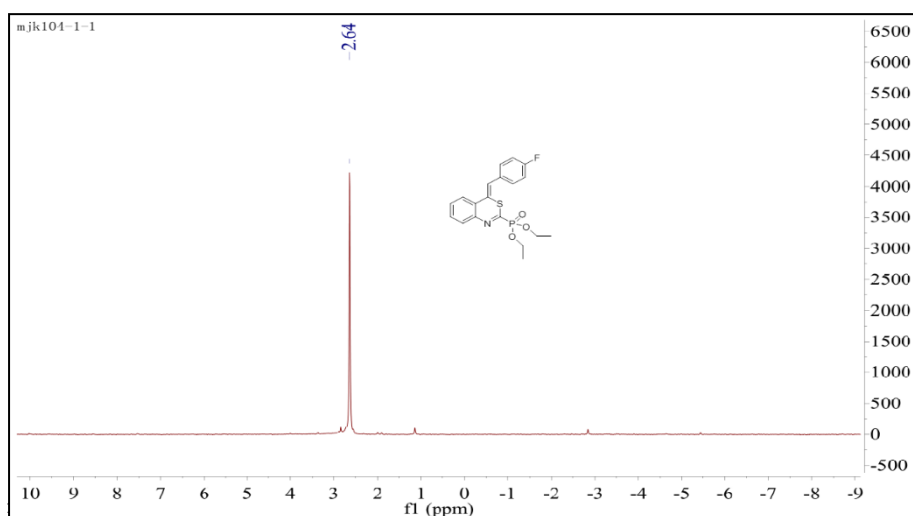
### <sup>1</sup>H NMR of **3b**



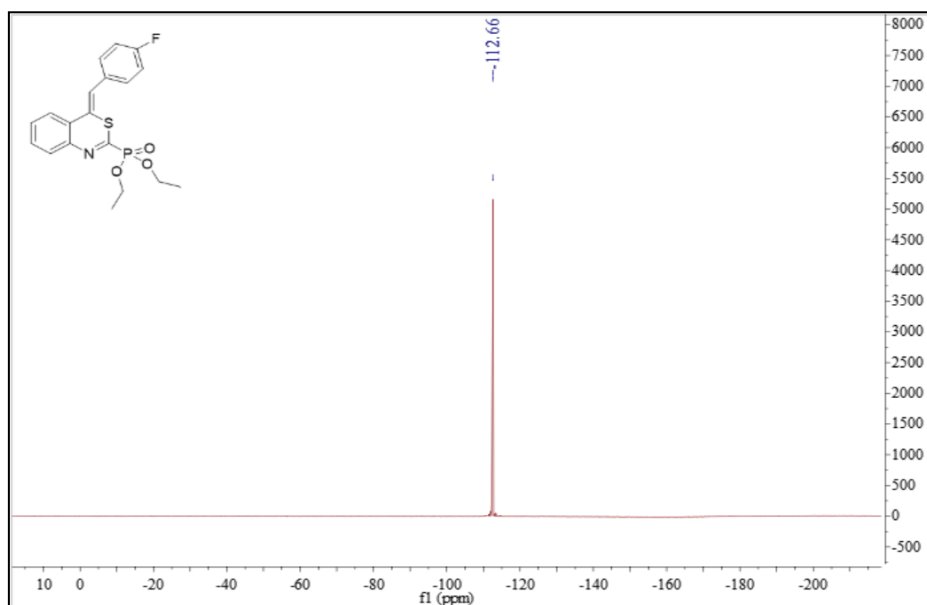
### <sup>13</sup>C NMR of **3b**



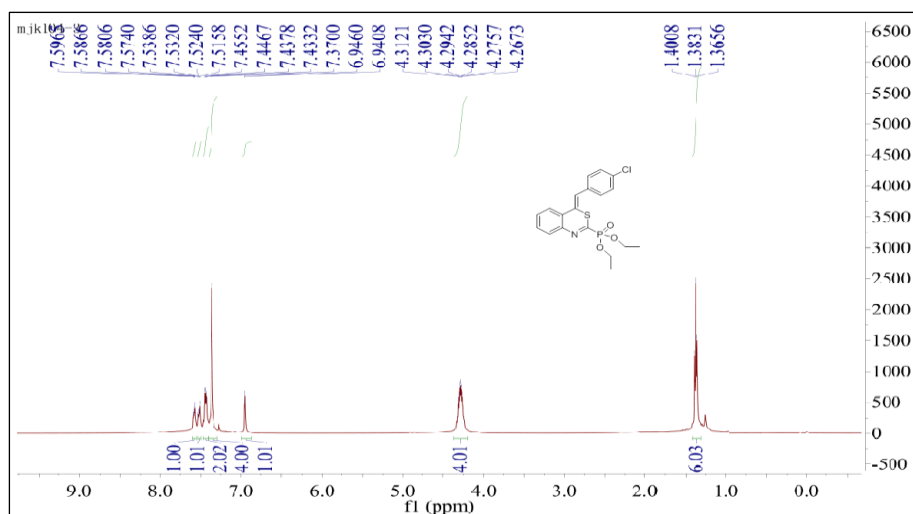
### <sup>31</sup>P NMR of **3b**



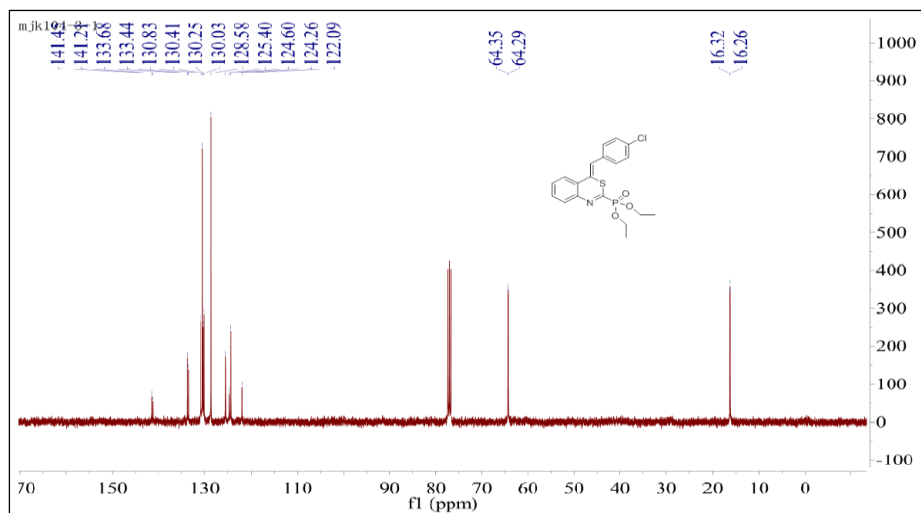
### <sup>19</sup>F NMR of **3b**



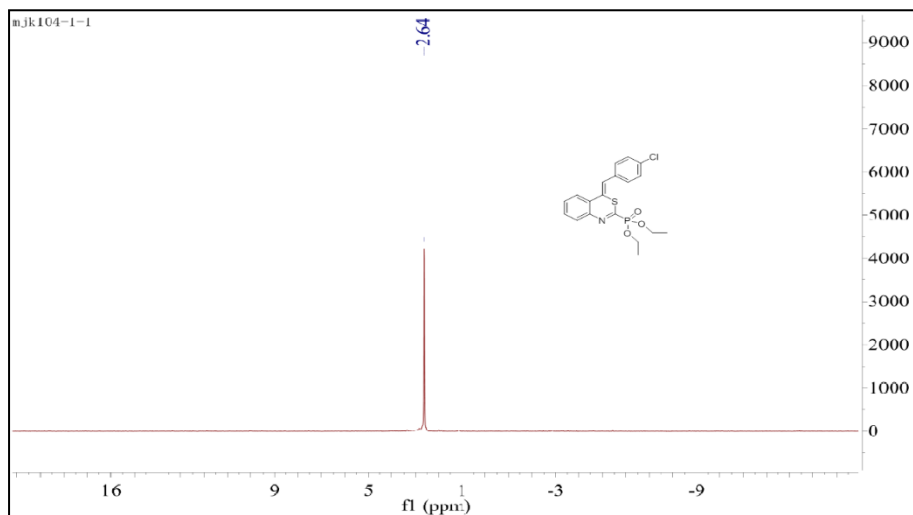
### <sup>1</sup>H NMR of **3c**



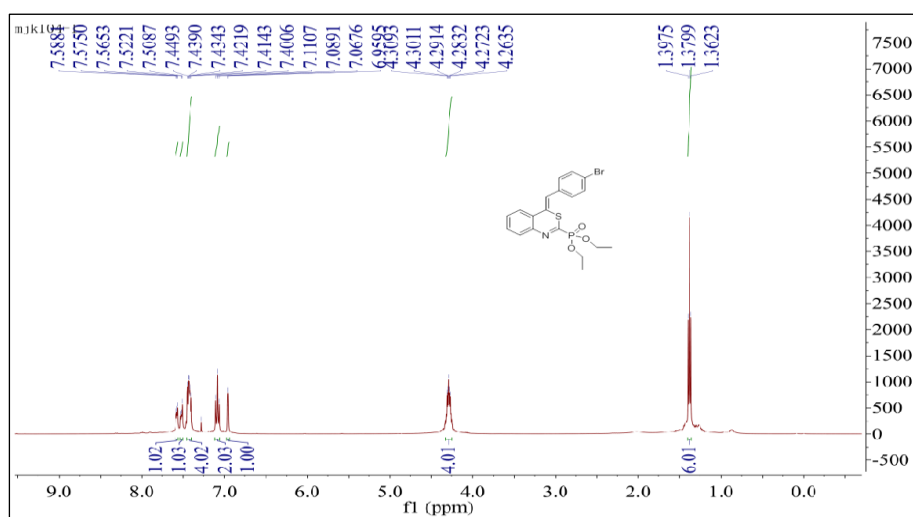
### <sup>13</sup>C NMR of **3c**



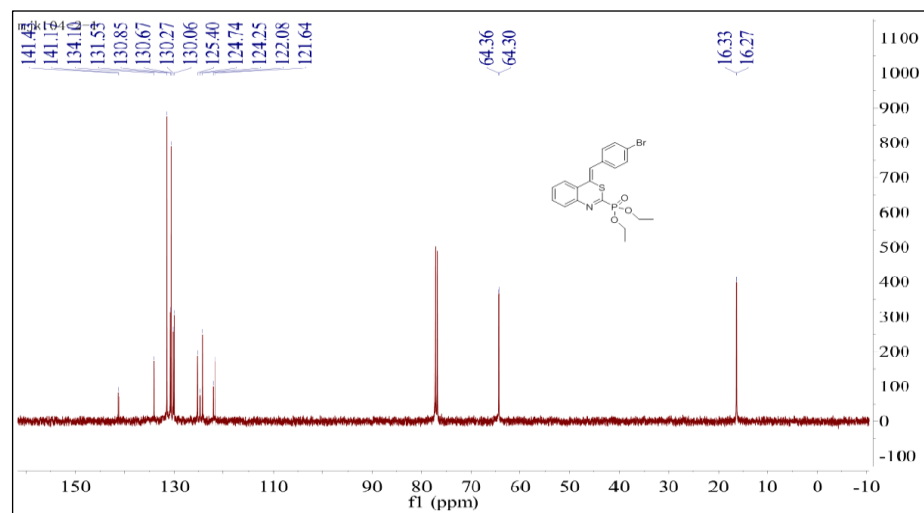
### <sup>31</sup>P NMR of **3c**



### <sup>1</sup>H NMR of **3d**

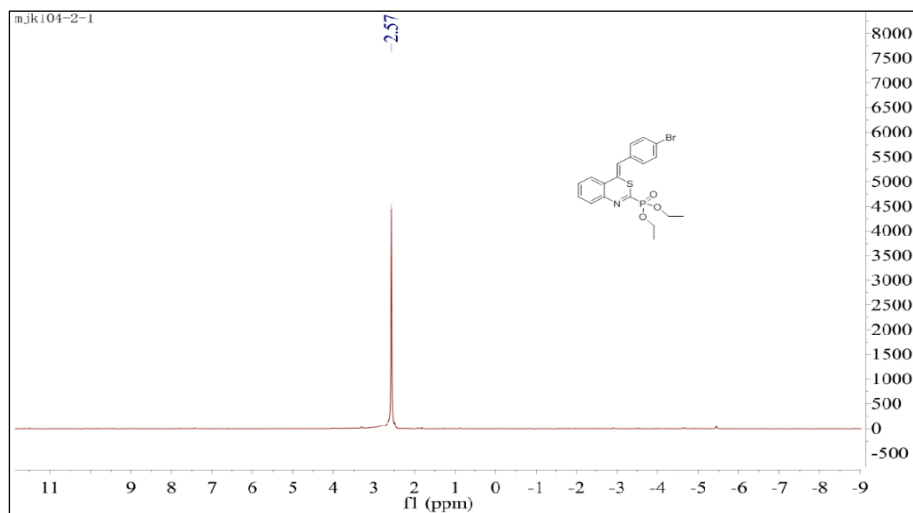


### <sup>13</sup>C NMR of **3d**

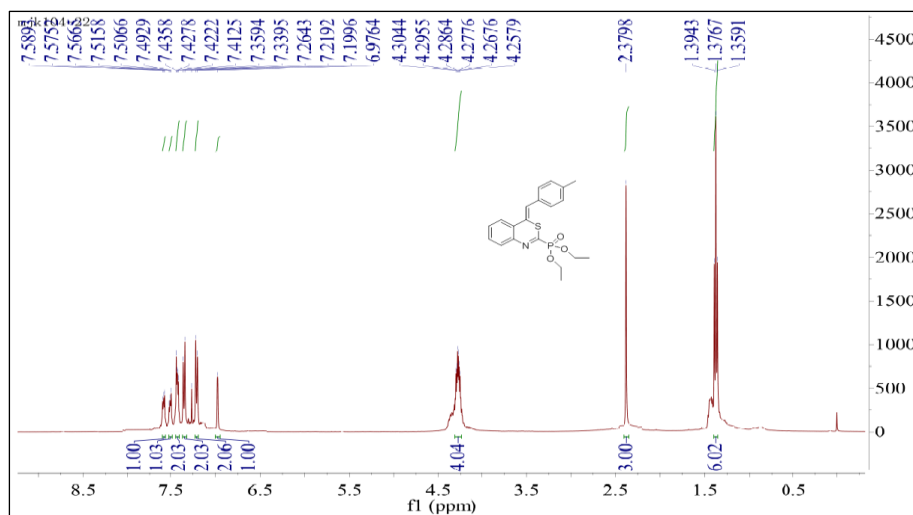




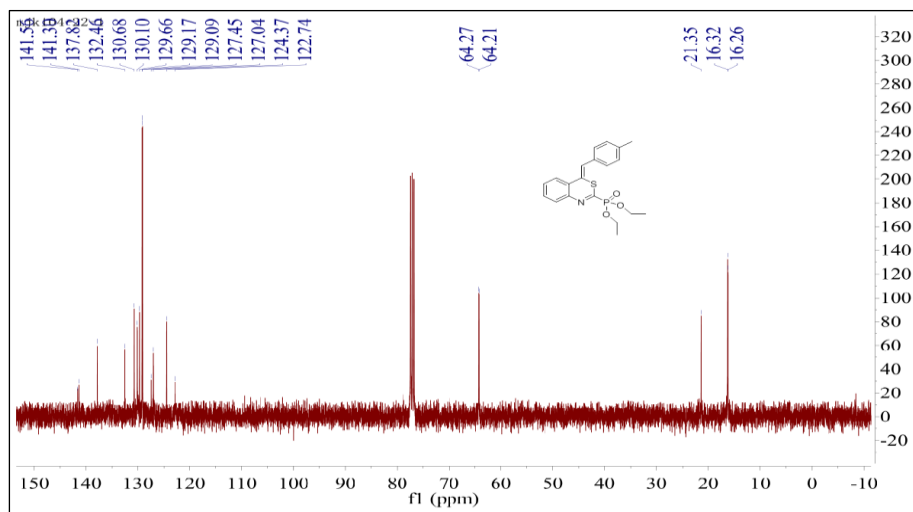
### <sup>31</sup>P NMR of 3d



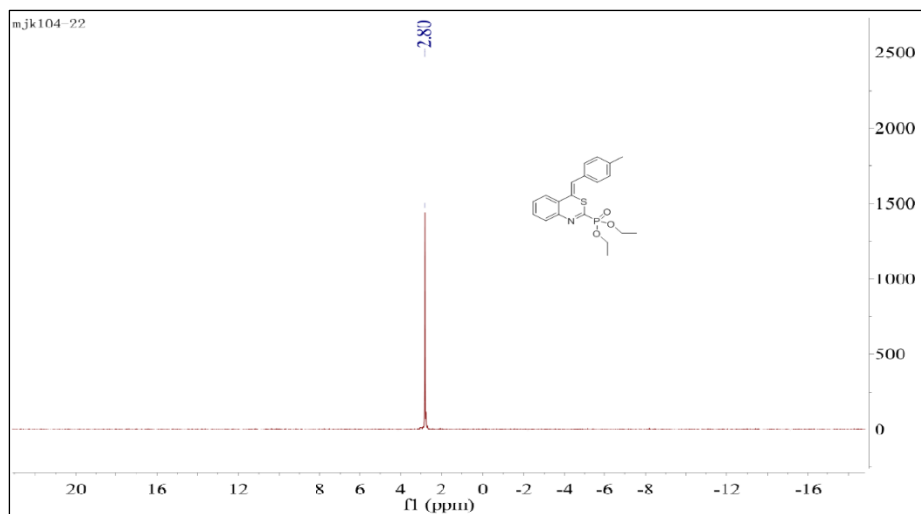
### <sup>1</sup>H NMR of 3e



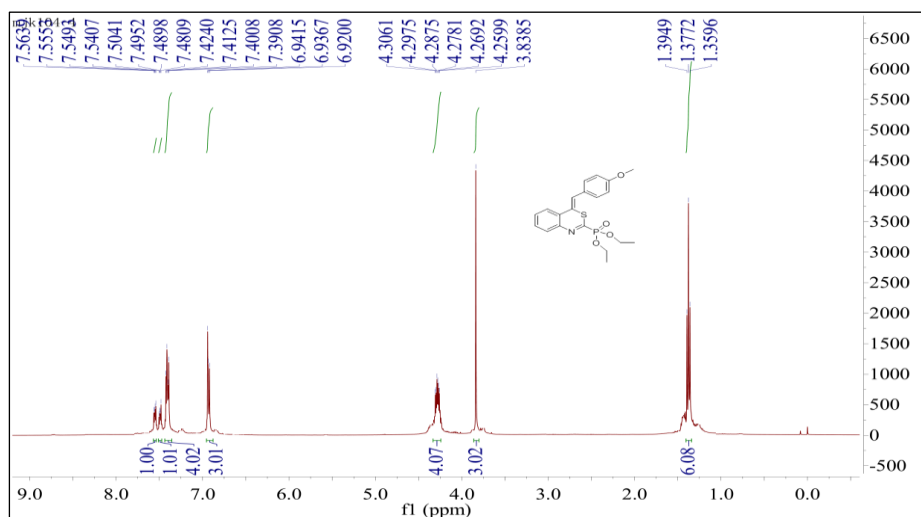
### <sup>13</sup>C NMR of 3e



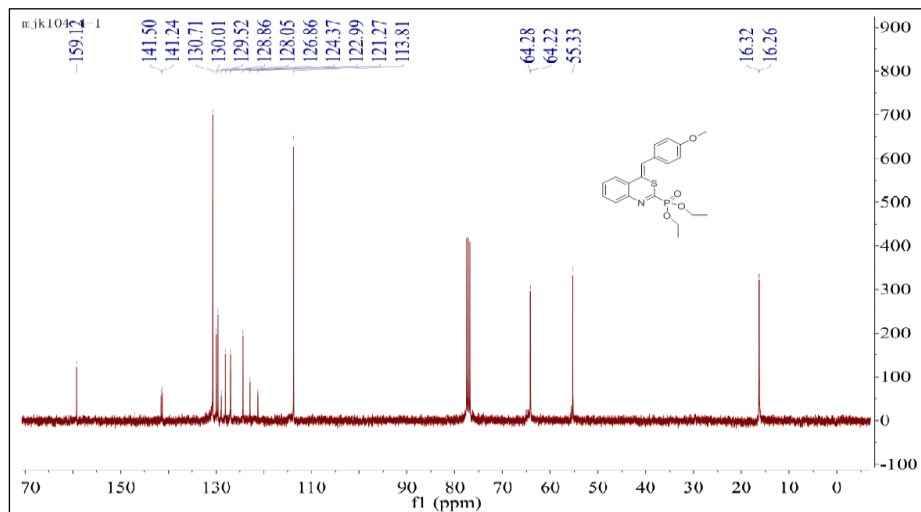
### $^{31}\text{P}$ NMR of **3e**



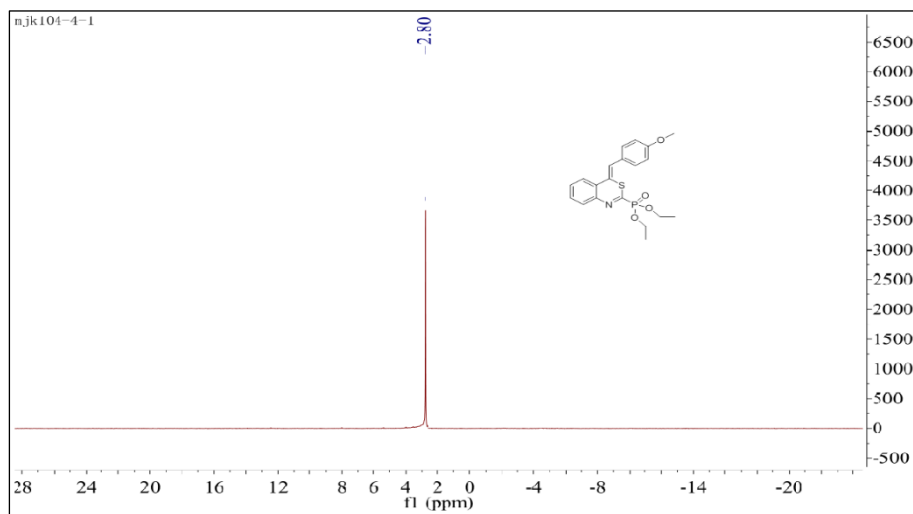
### $^1\text{H}$ NMR of **3f**



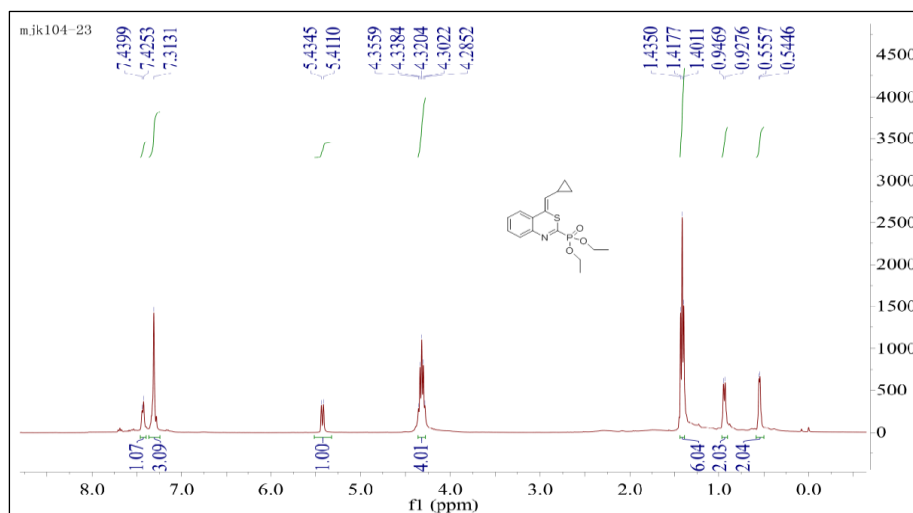
### $^{13}\text{C}$ NMR of **3f**



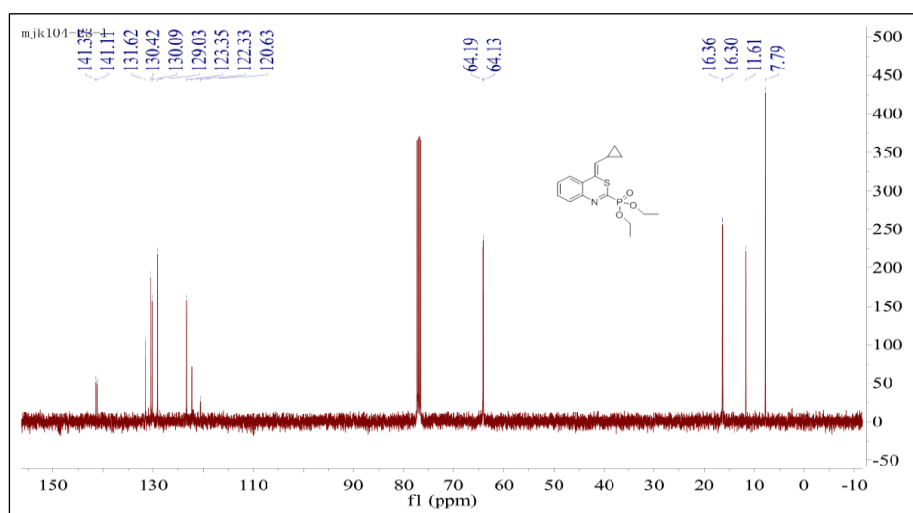
### $^{31}\text{P}$ NMR of **3f**



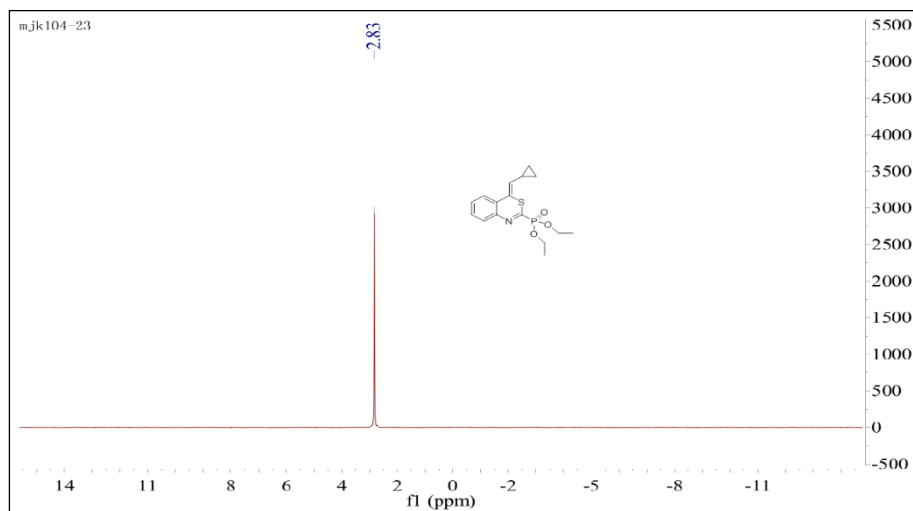
### $^1\text{H}$ NMR of **3g**



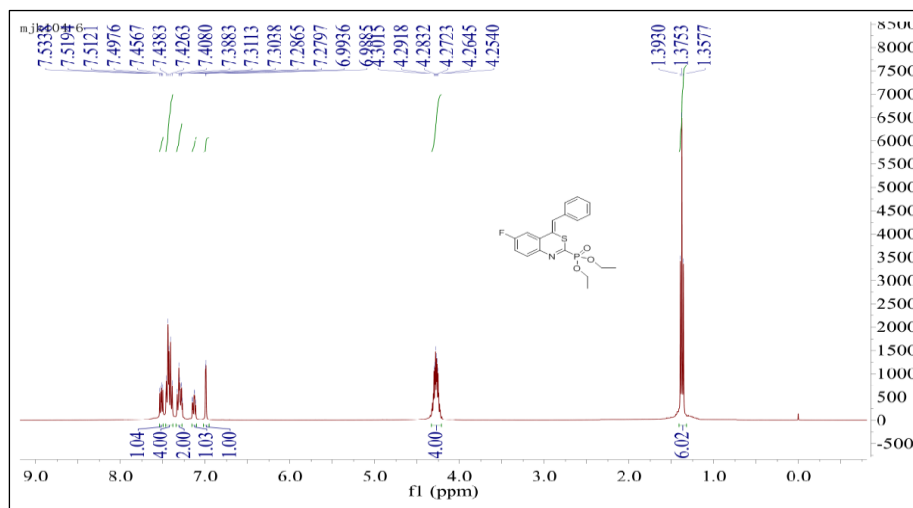
### $^{13}\text{C}$ NMR of **3g**



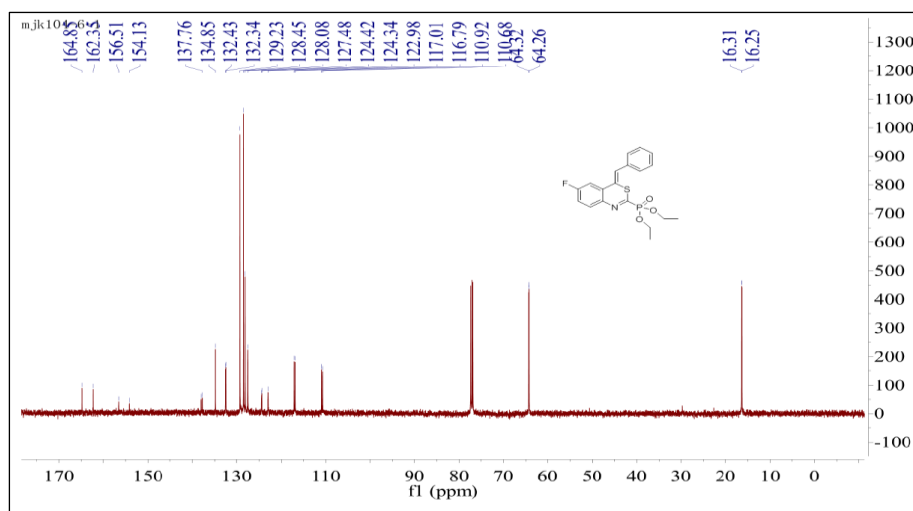
### <sup>31</sup>P NMR of **3g**



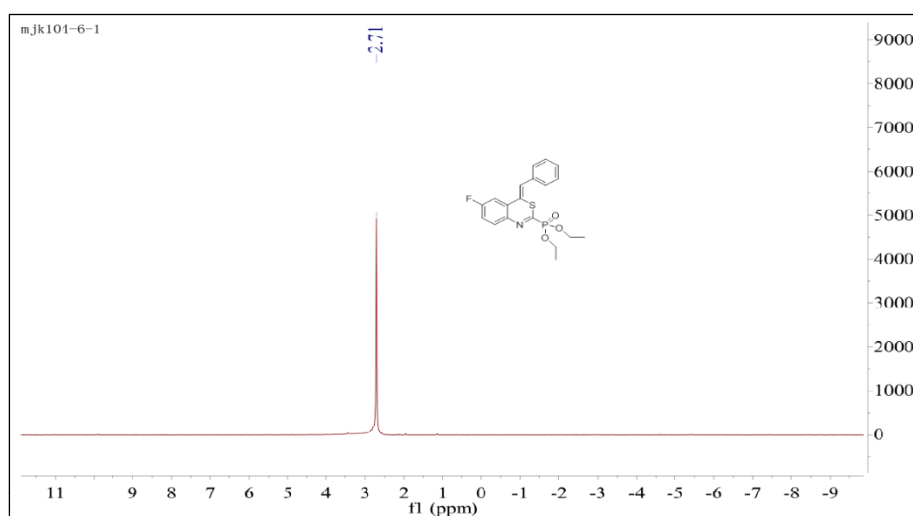
### <sup>1</sup>H NMR of **3h**



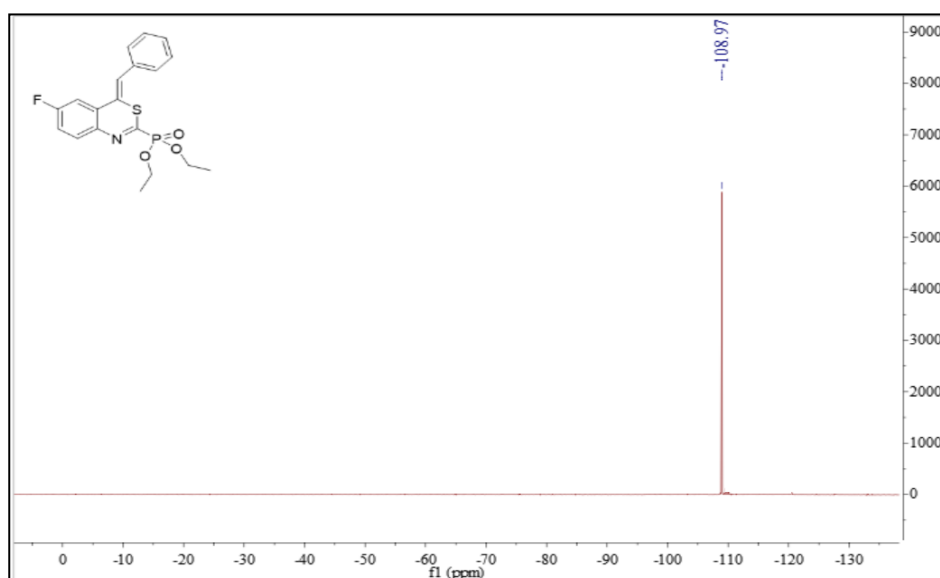
### <sup>13</sup>C NMR of **3h**



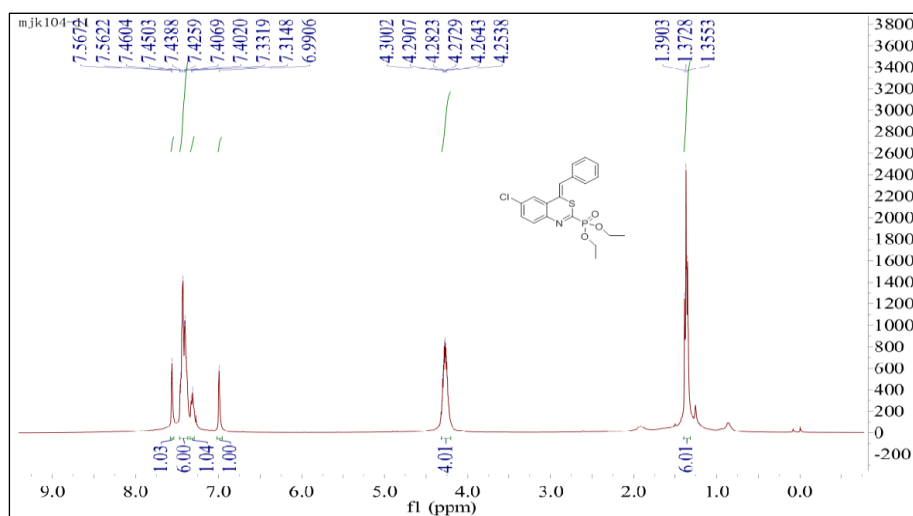
### $^{31}\text{P}$ NMR of **3h**



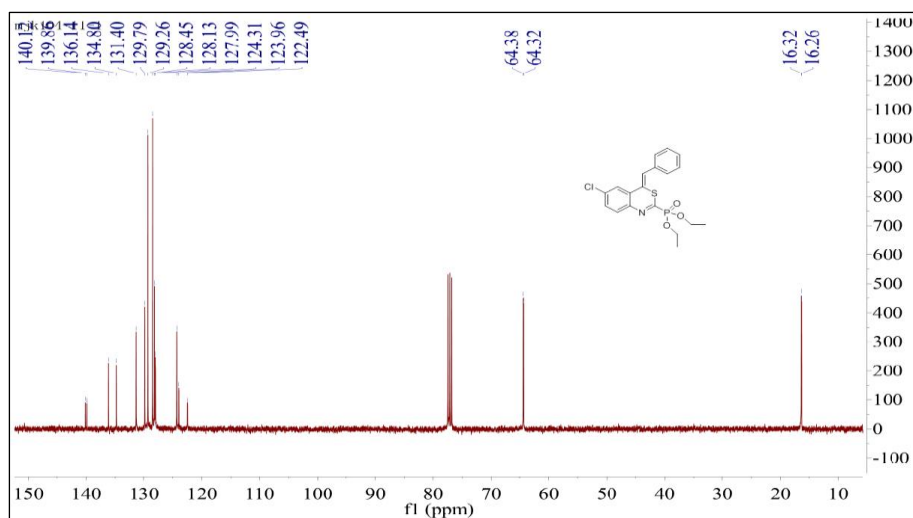
### $^{19}\text{F}$ NMR of **3h**



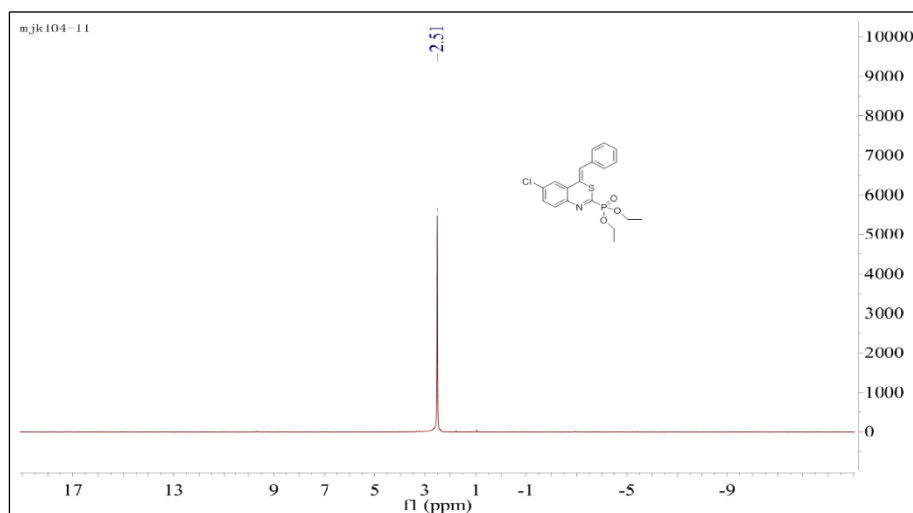
### $^1\text{H}$ NMR of **3i**



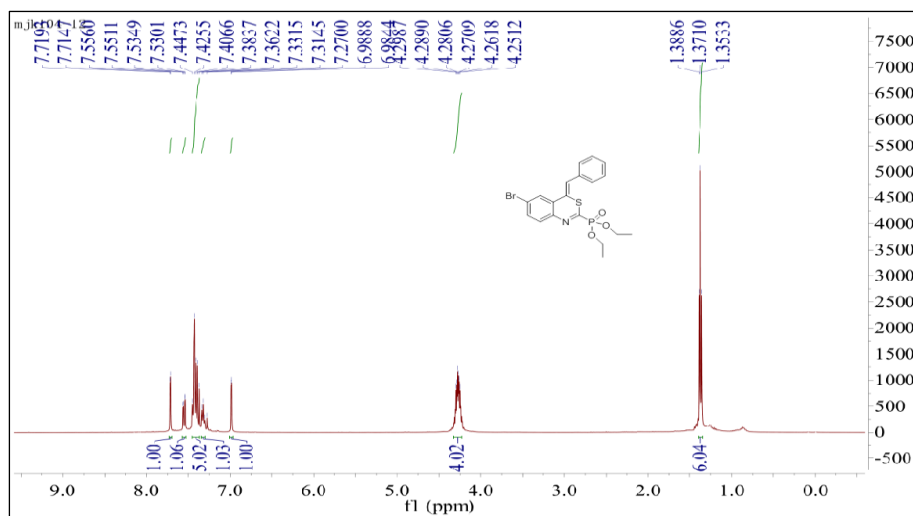
### <sup>13</sup>C NMR of **3i**



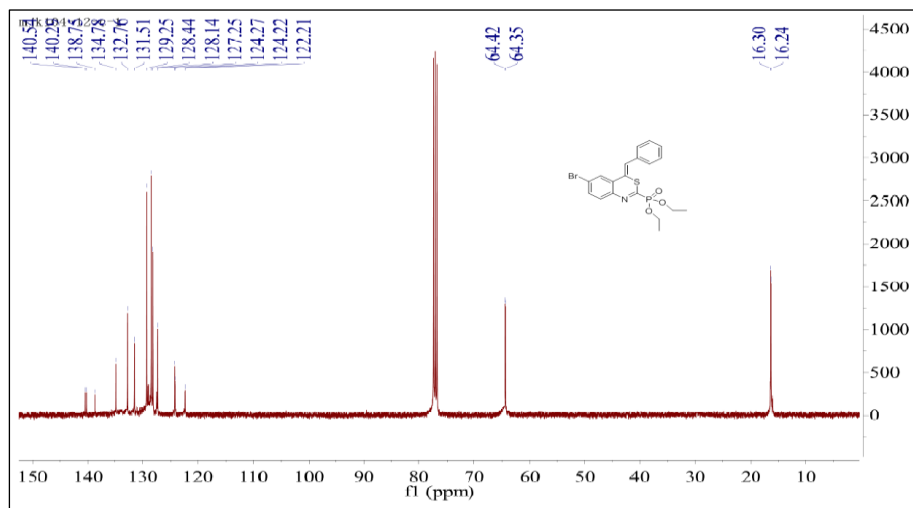
### <sup>31</sup>P NMR of **3i**



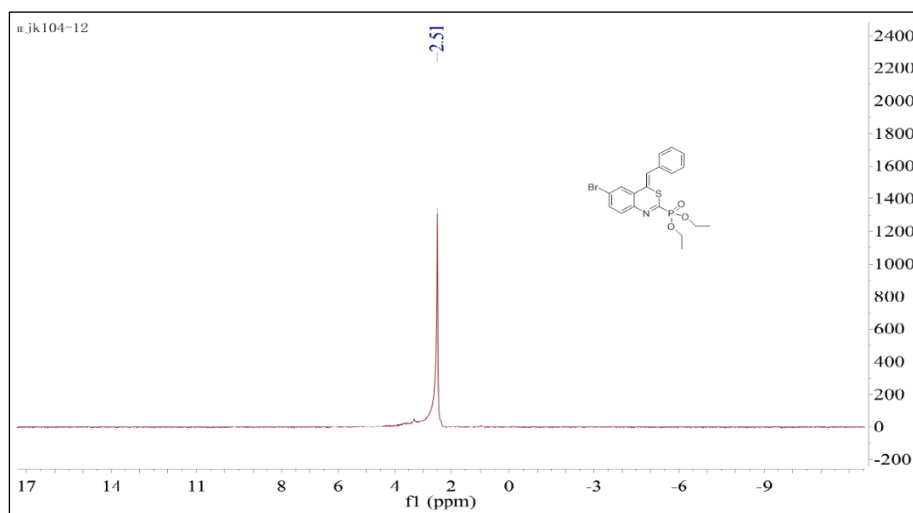
### <sup>1</sup>H NMR of **3j**



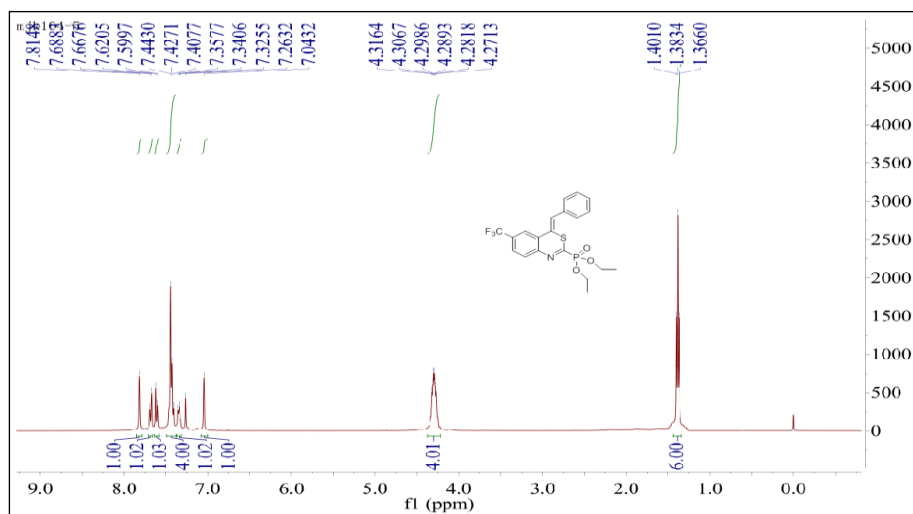
### <sup>13</sup>C NMR of **3j**



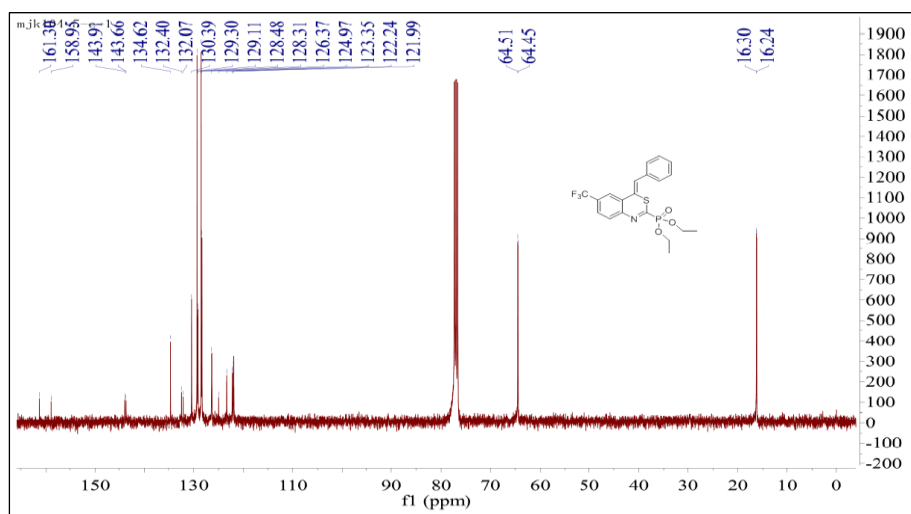
### <sup>31</sup>P NMR of **3j**



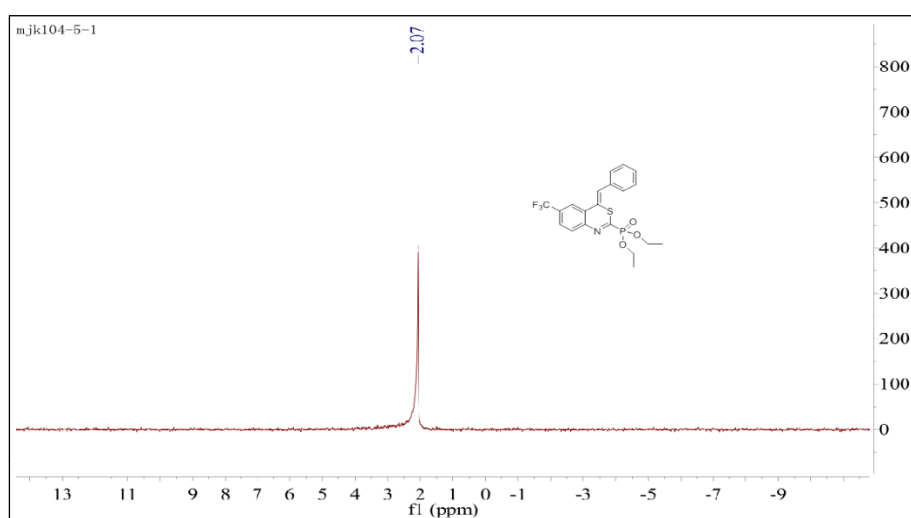
### <sup>1</sup>H NMR of **3k**



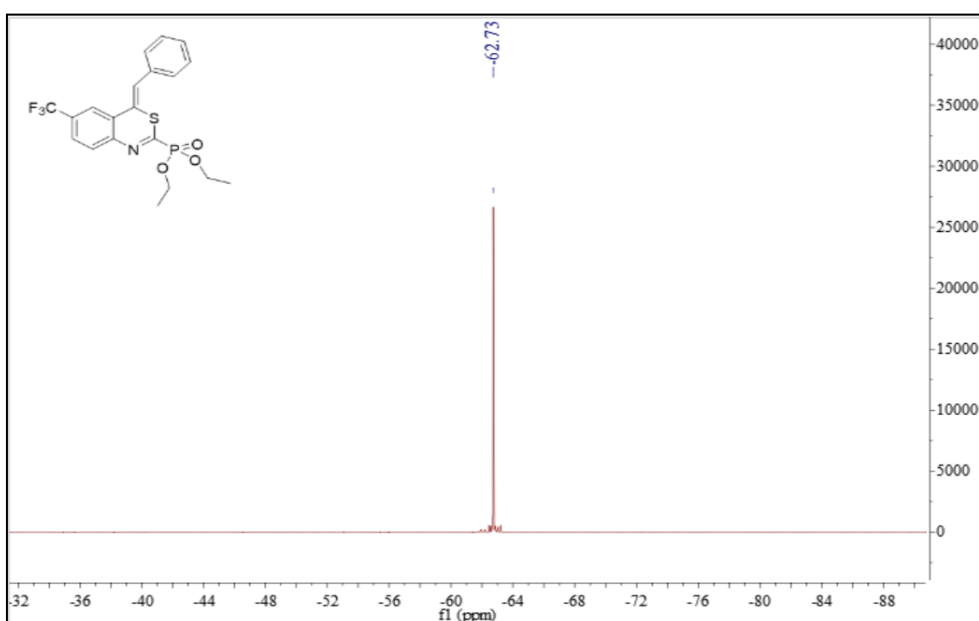
### $^{13}\text{C}$ NMR of **3k**



### $^{31}\text{P}$ NMR of **3k**

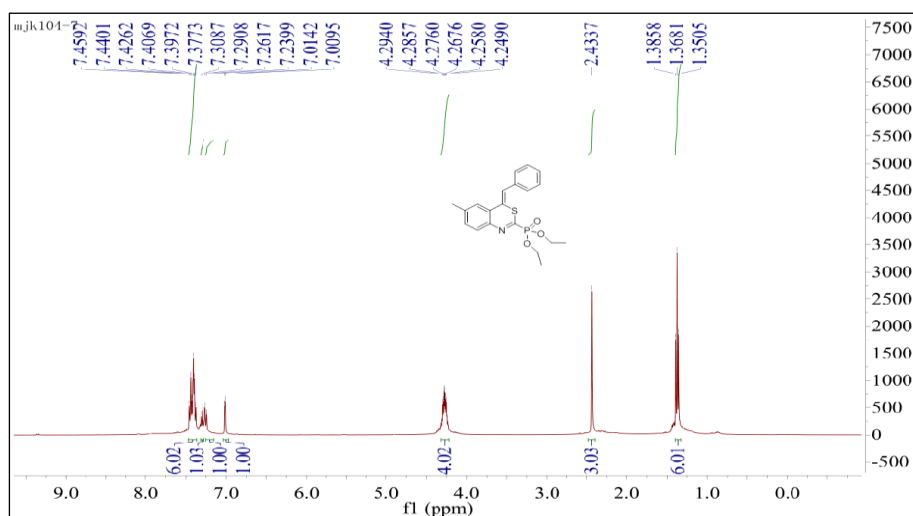


### $^{19}\text{F}$ NMR of **3k**

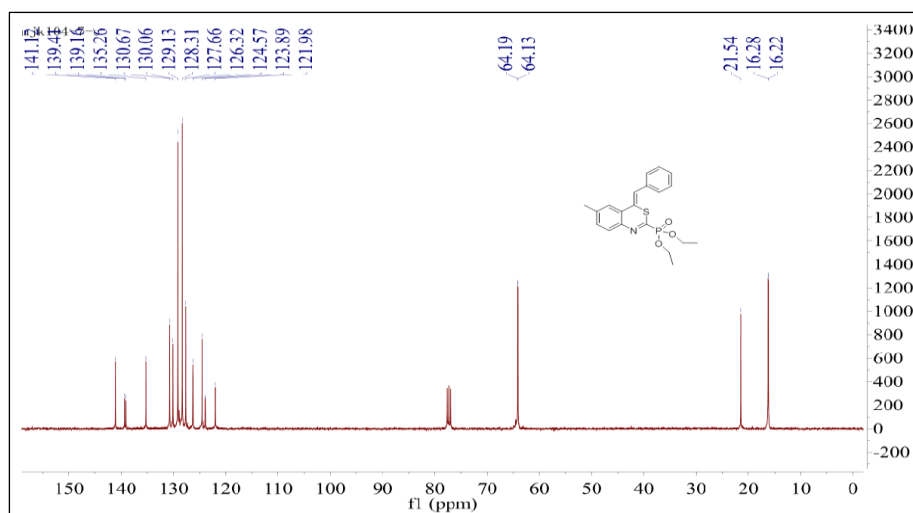




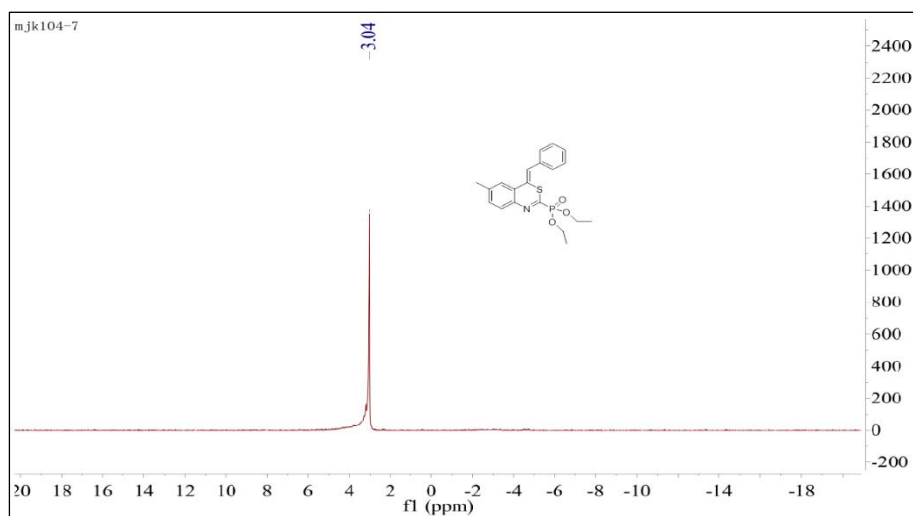
### $^1\text{H}$ NMR of **31**



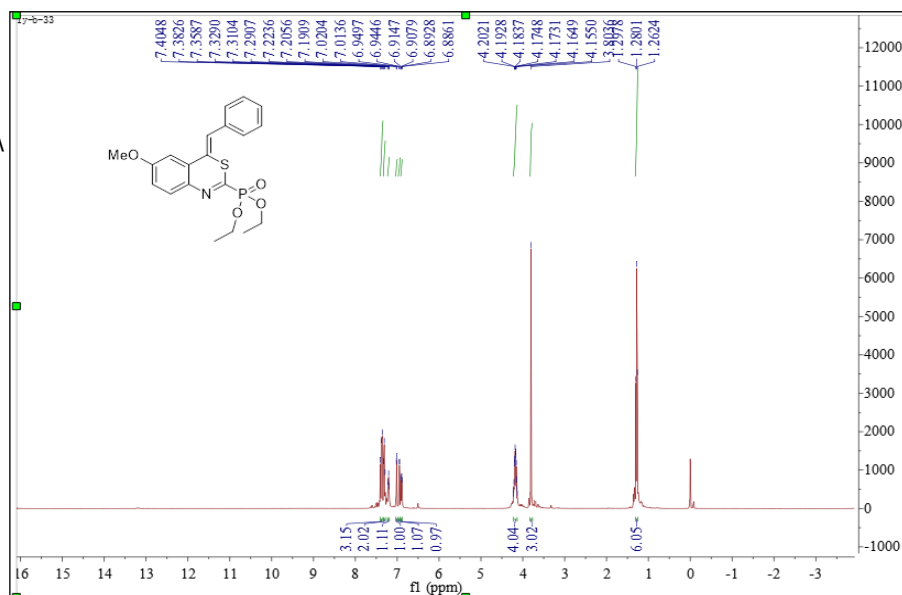
### $^{13}\text{C}$ NMR of **31**



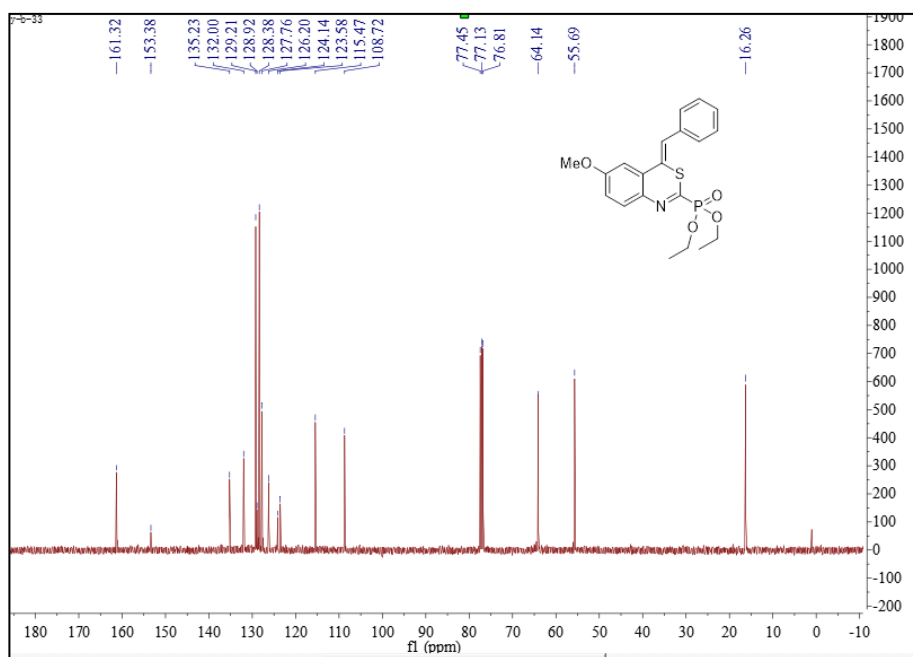
### $^{31}\text{P}$ NMR of **31**



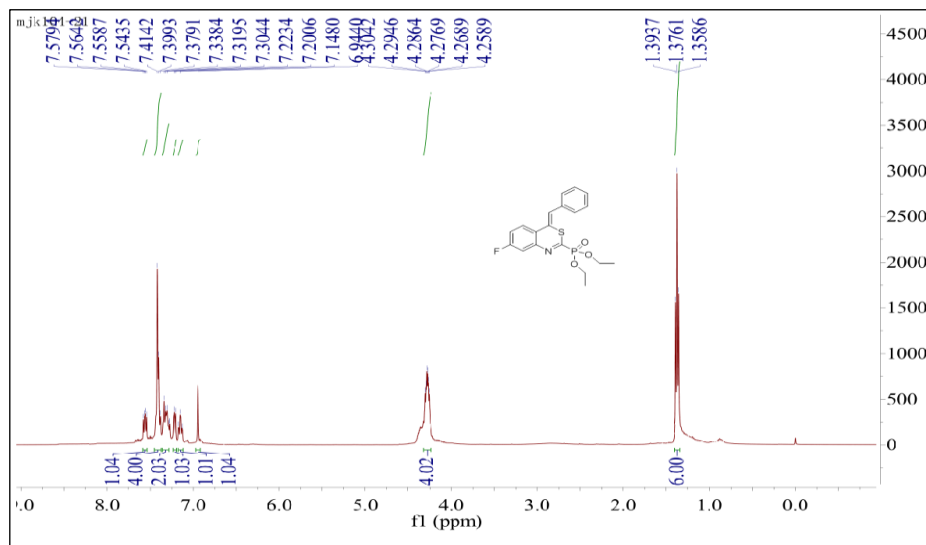
### $^1\text{H}$ NMR of **3m**



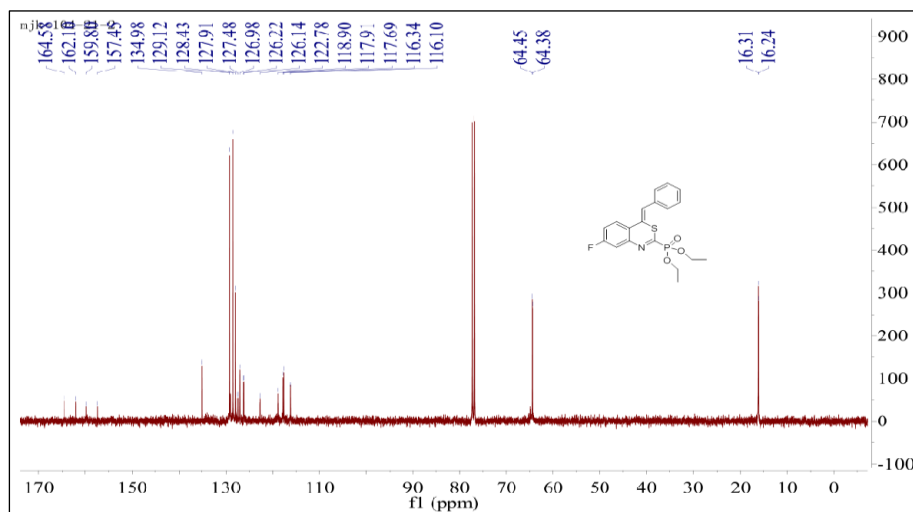
### $^{13}\text{C}$ NMR of **3m**



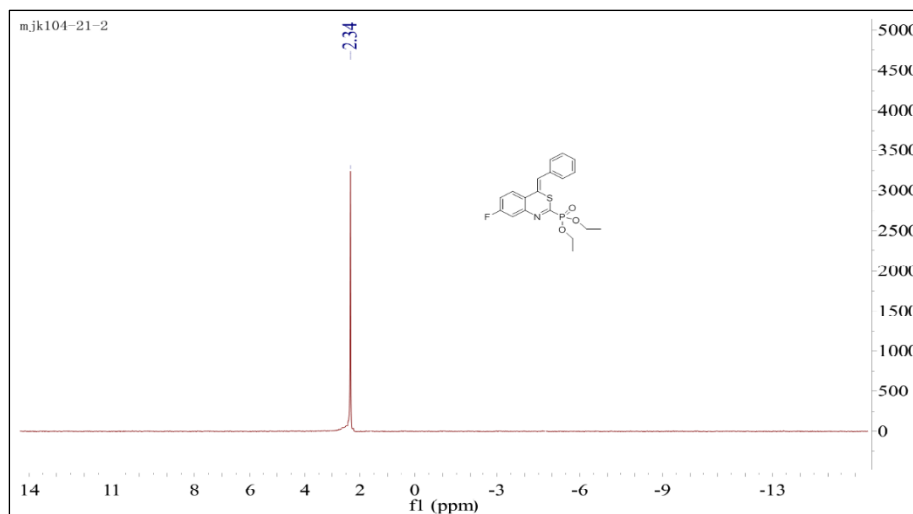
### <sup>1</sup>H NMR of **3n**



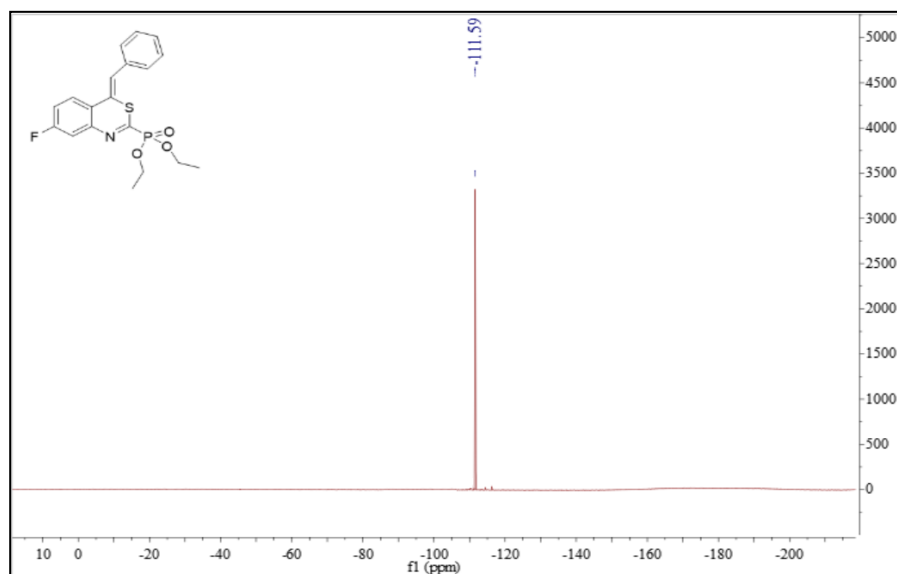
### <sup>13</sup>C NMR of **3n**



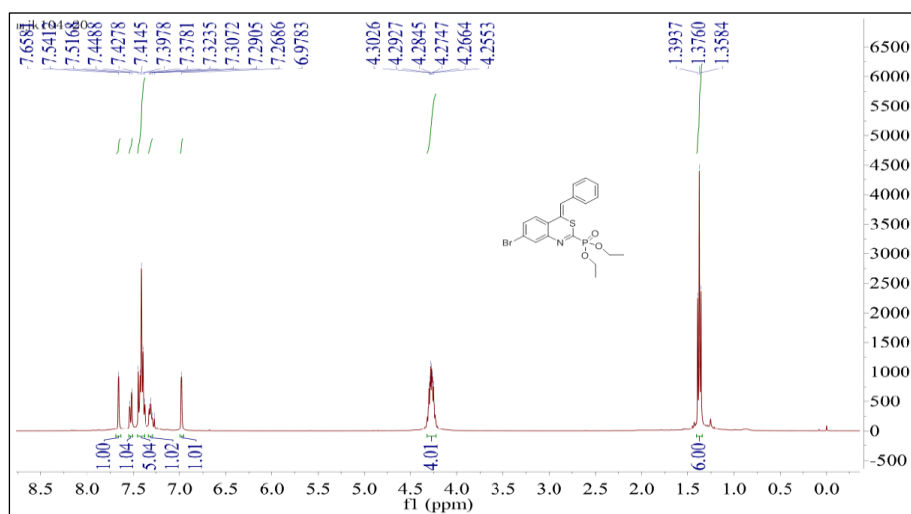
### <sup>31</sup>P NMR of **3n**



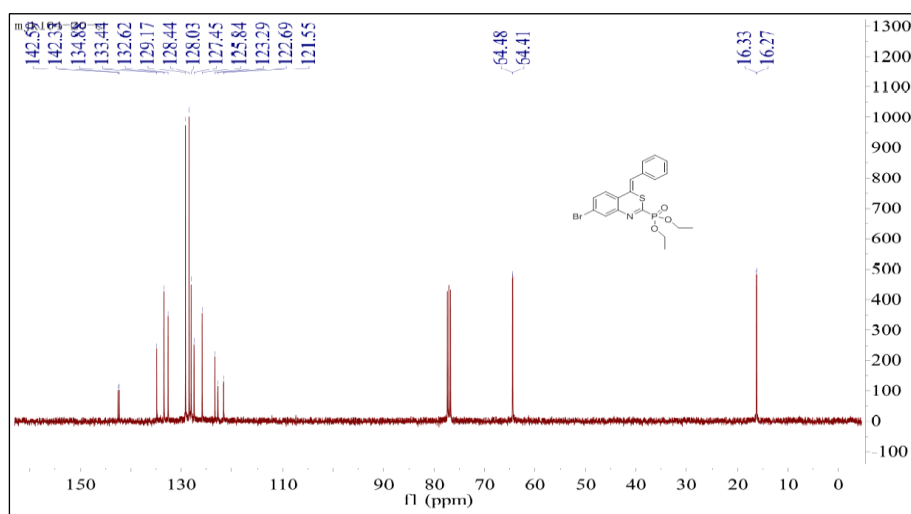
### <sup>19</sup>F NMR of **3n**



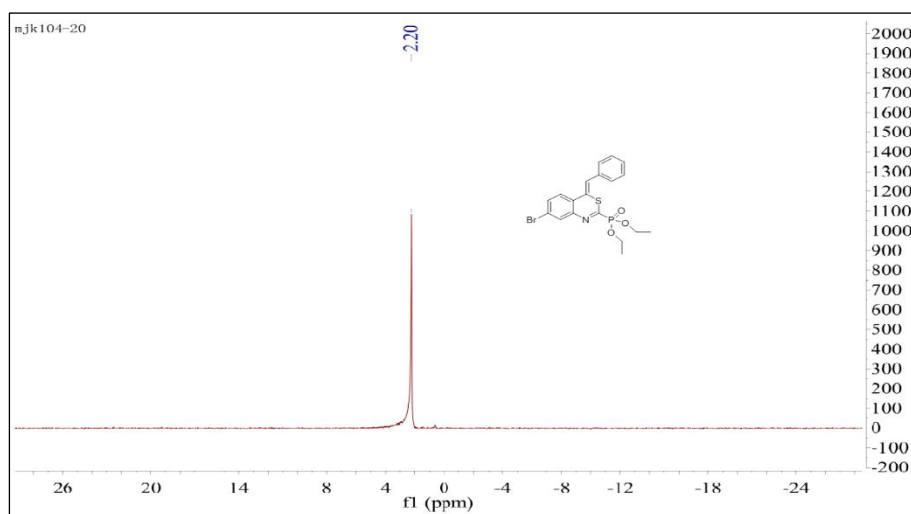
### <sup>1</sup>H NMR of **3o**



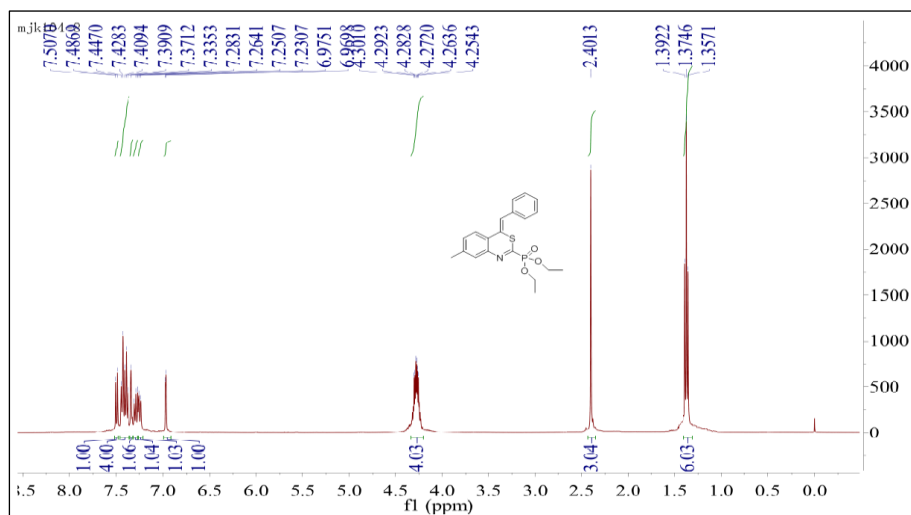
### <sup>13</sup>C NMR of **3o**



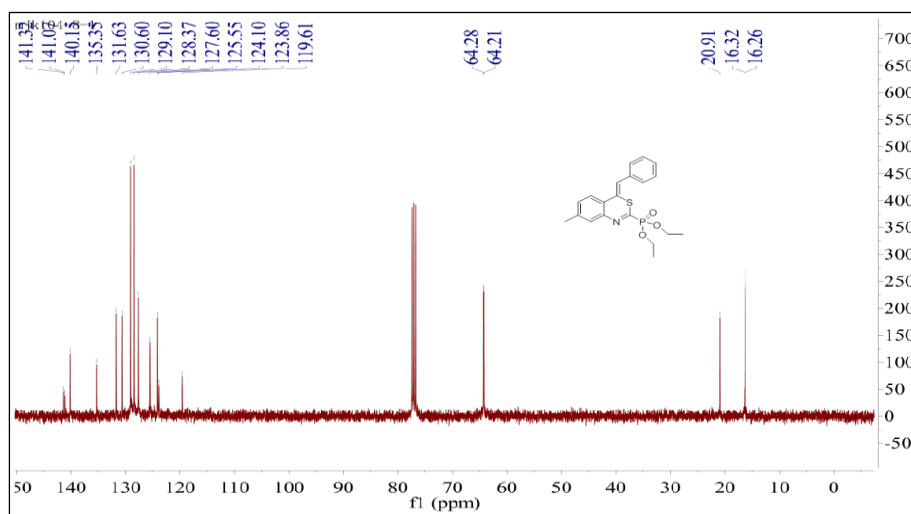
### <sup>31</sup>P NMR of **3o**



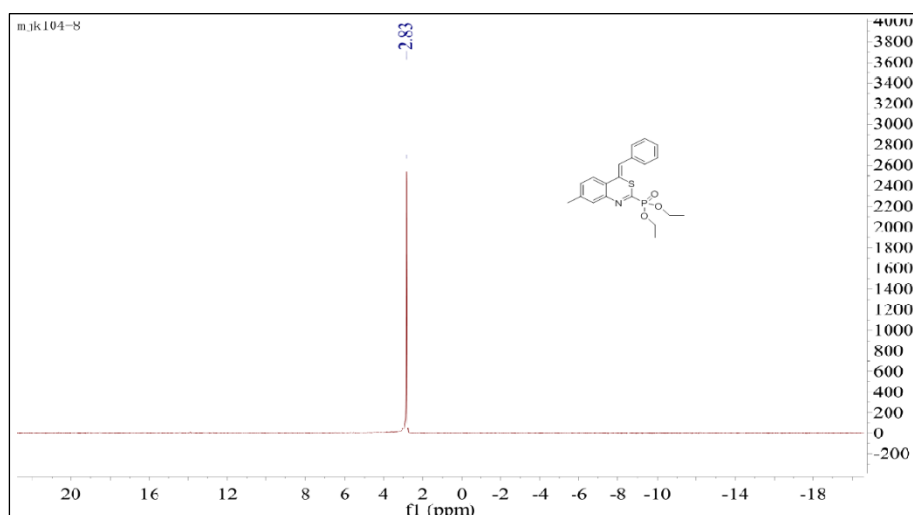
### <sup>1</sup>H NMR of **3p**



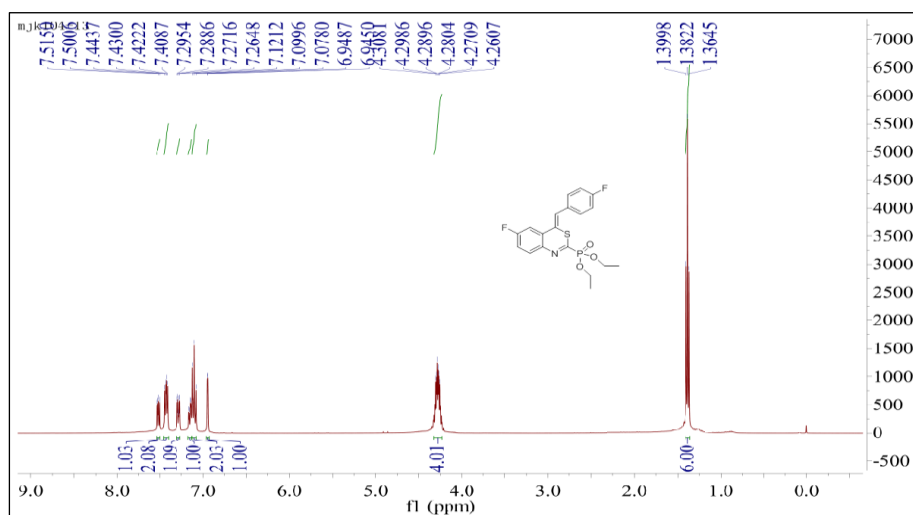
### <sup>13</sup>C NMR of **3p**



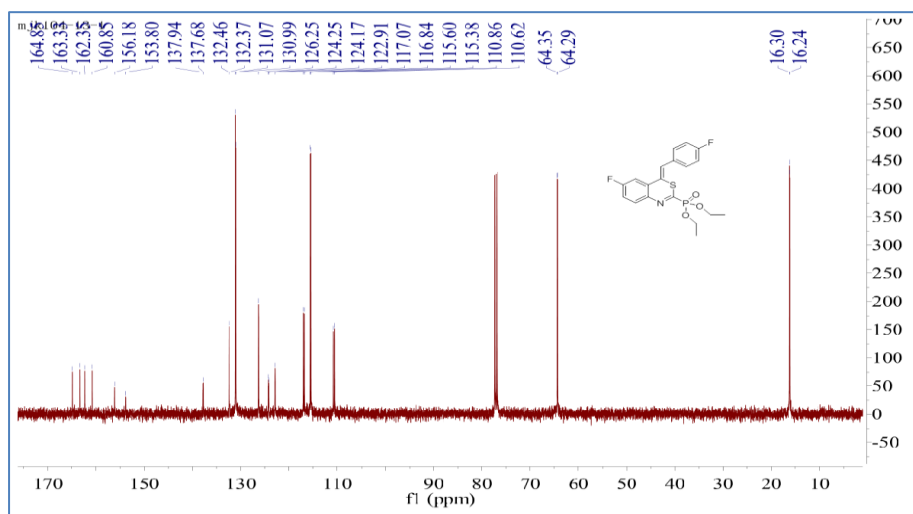
### <sup>31</sup>P NMR of 3p



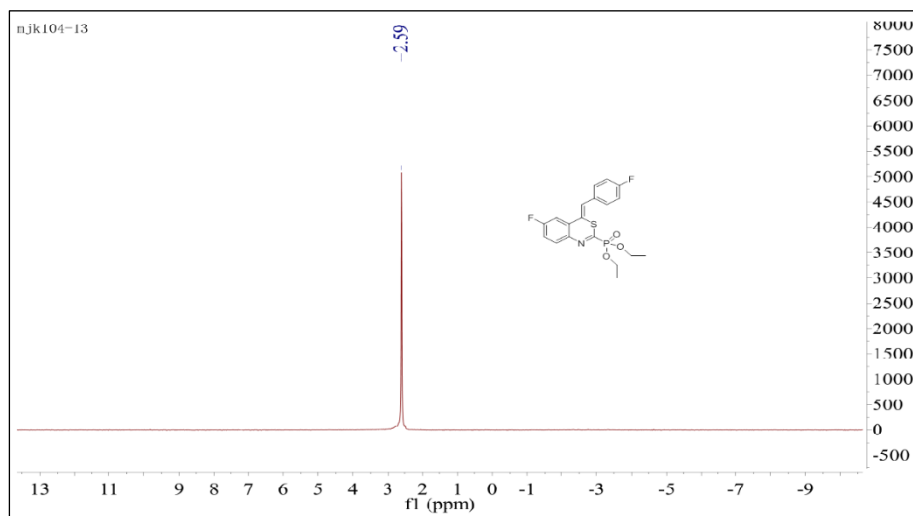
### <sup>1</sup>H NMR of 3q



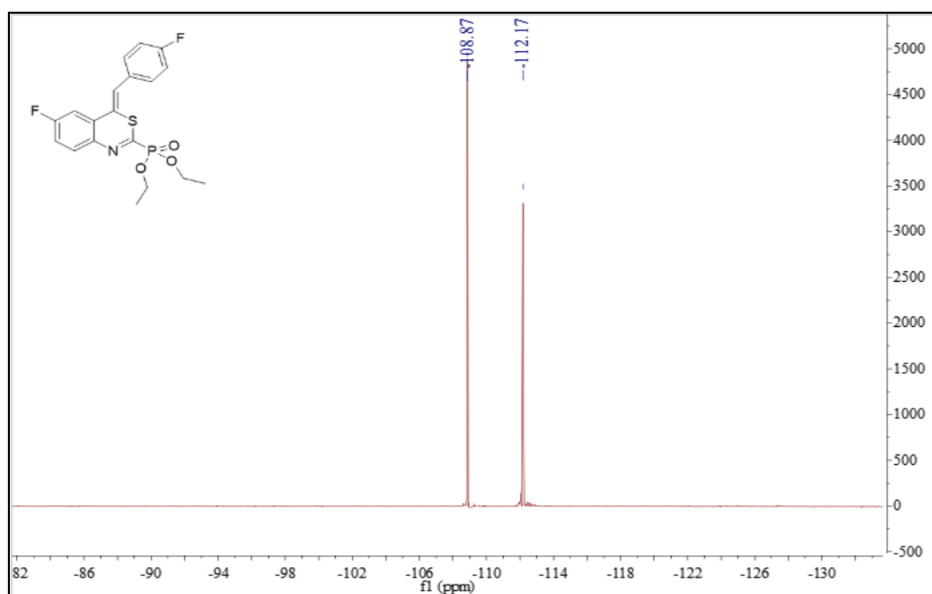
### <sup>13</sup>C NMR of 3q



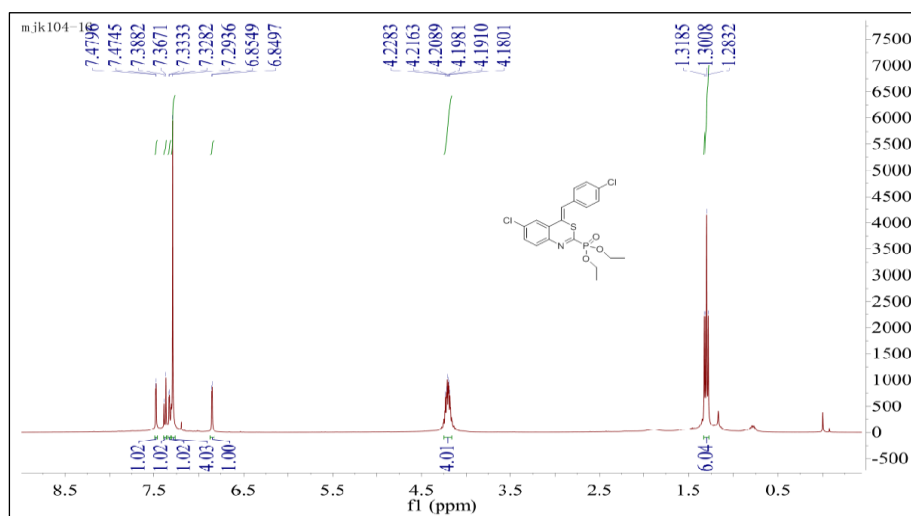
### $^{31}\text{P}$ NMR of **3q**



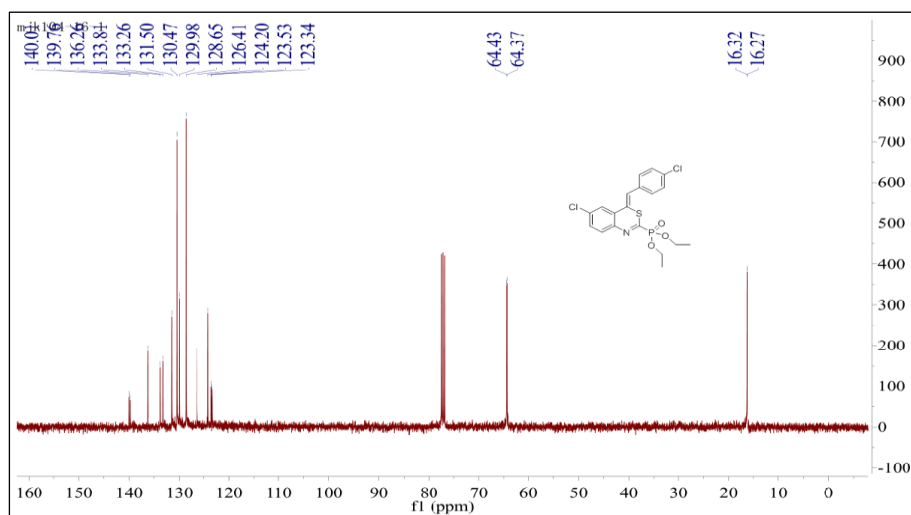
### $^{19}\text{F}$ NMR of **3q**



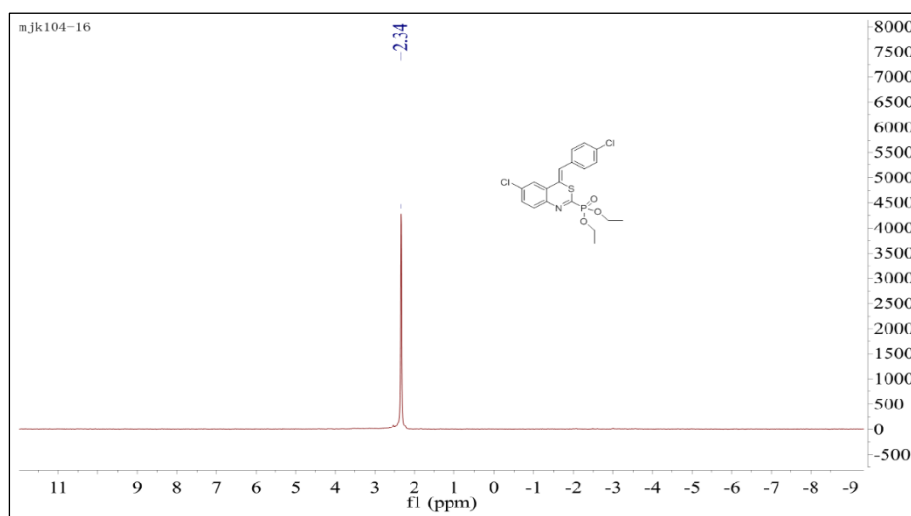
### $^1\text{H}$ NMR of **3r**



### $^{13}\text{C}$ NMR of **3r**

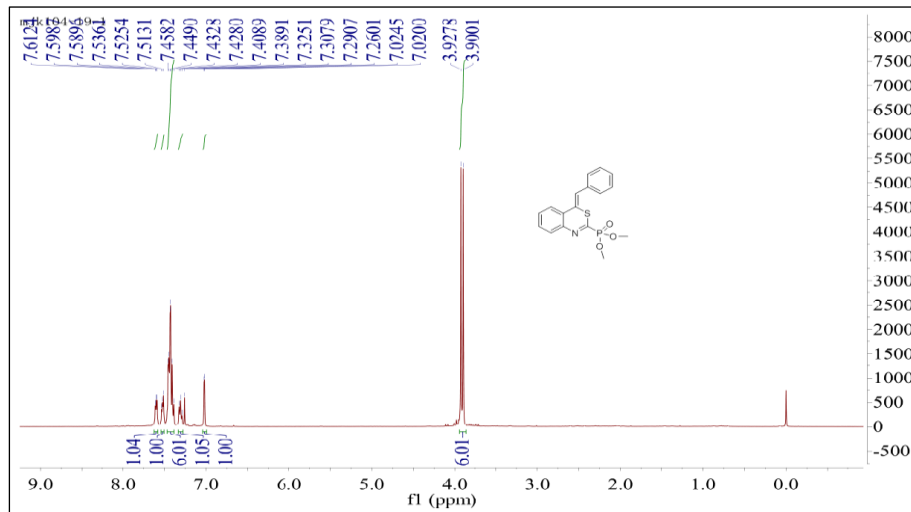


### $^{31}\text{P}$ NMR of **3r**

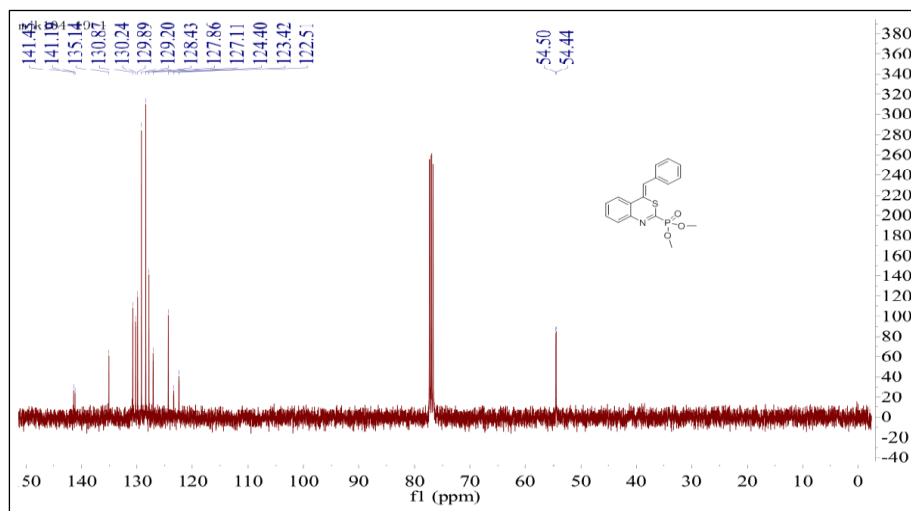




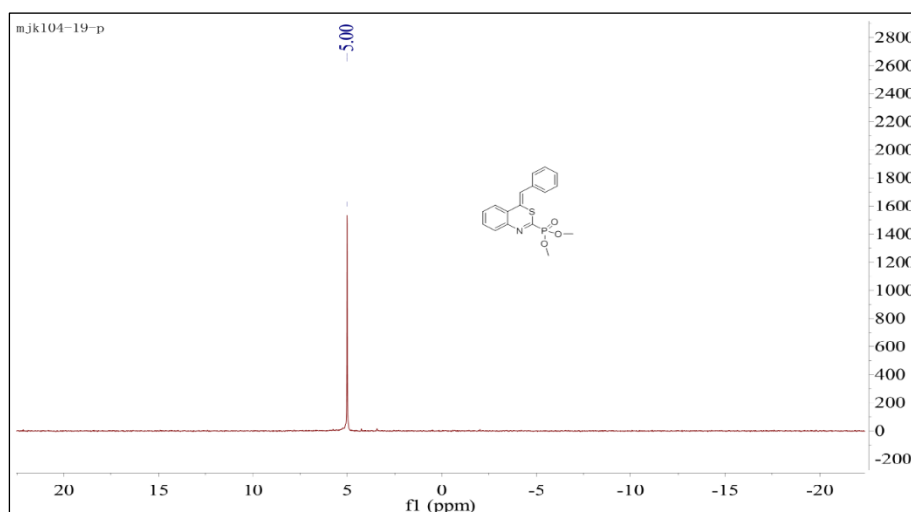
### $^1\text{H}$ NMR of **3s**



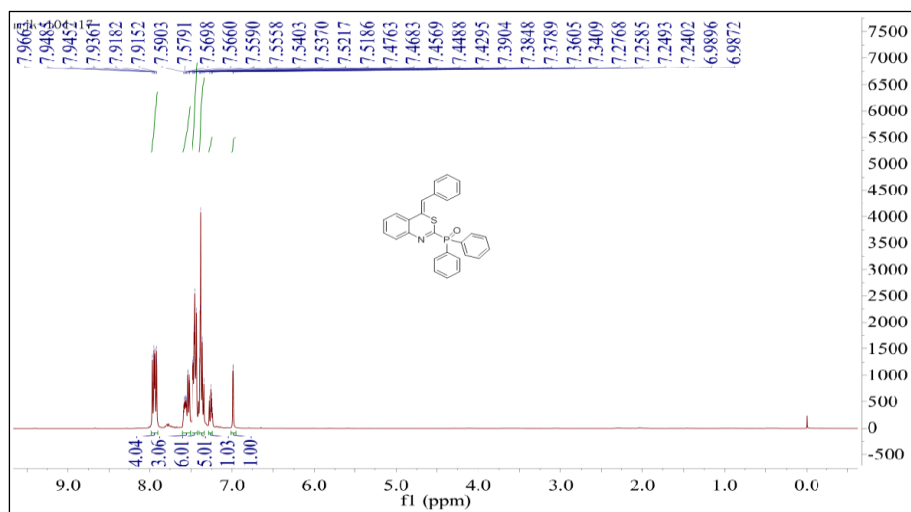
### $^{13}\text{C}$ NMR of **3s**



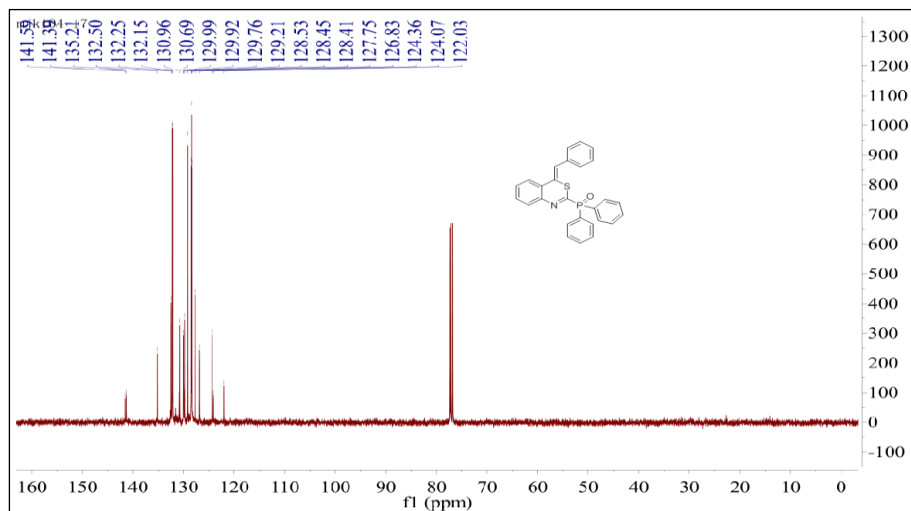
### $^{31}\text{P}$ NMR of **3s**



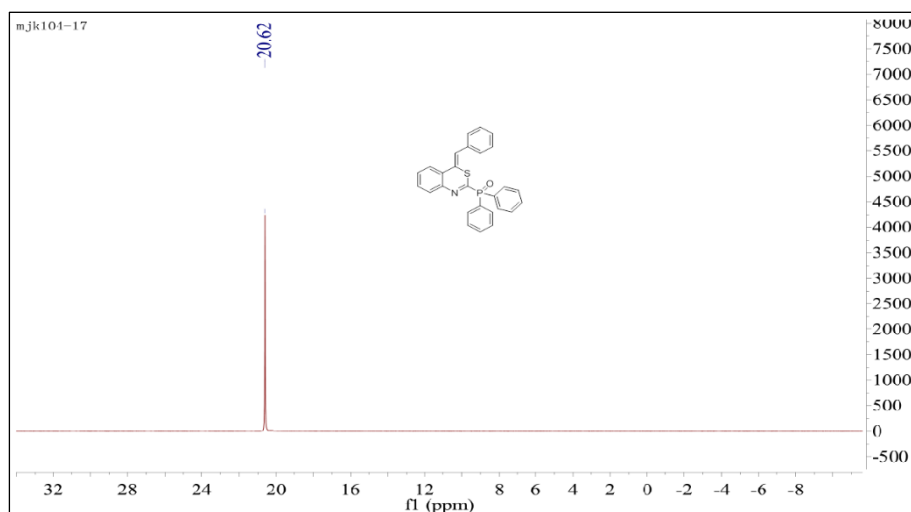
### <sup>1</sup>H NMR of **3t**



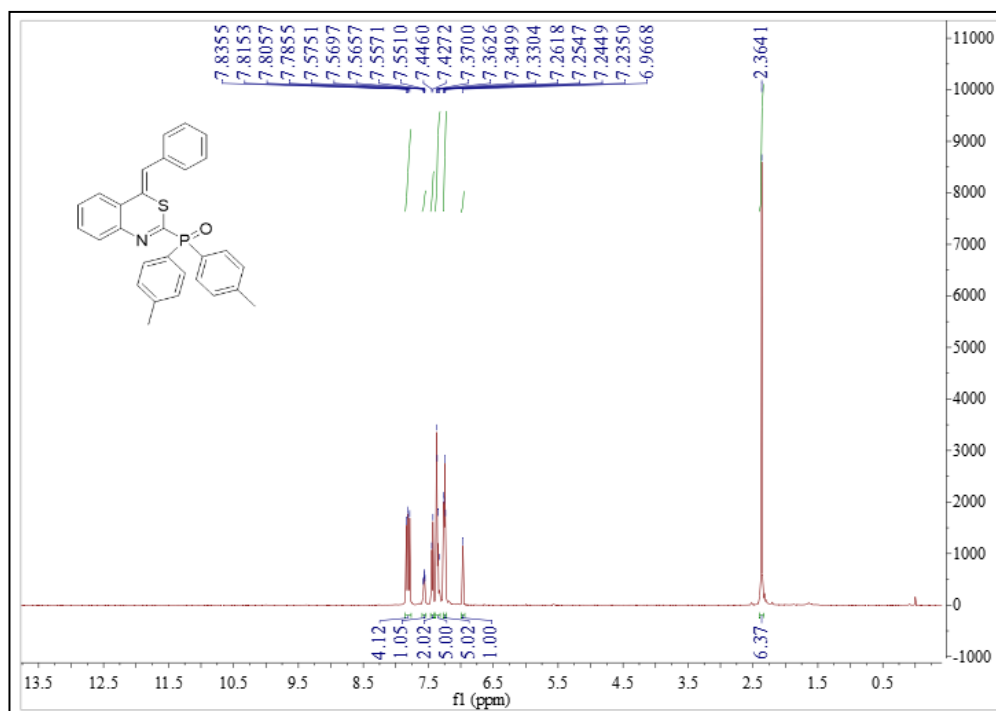
### <sup>13</sup>C NMR of **3t**



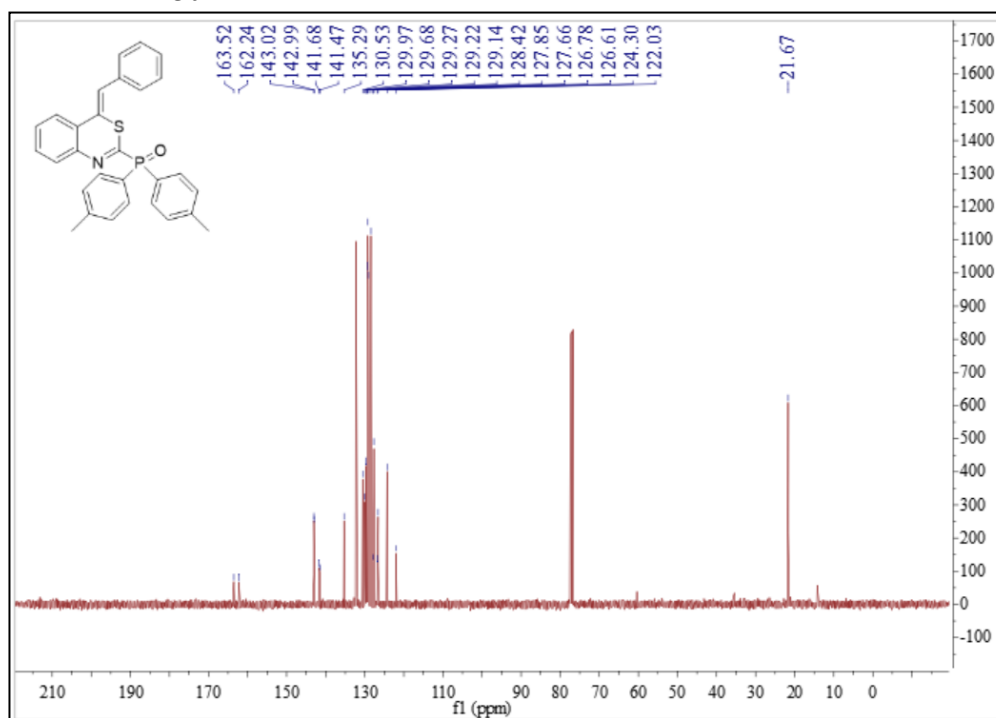
### <sup>31</sup>P NMR of **3t**



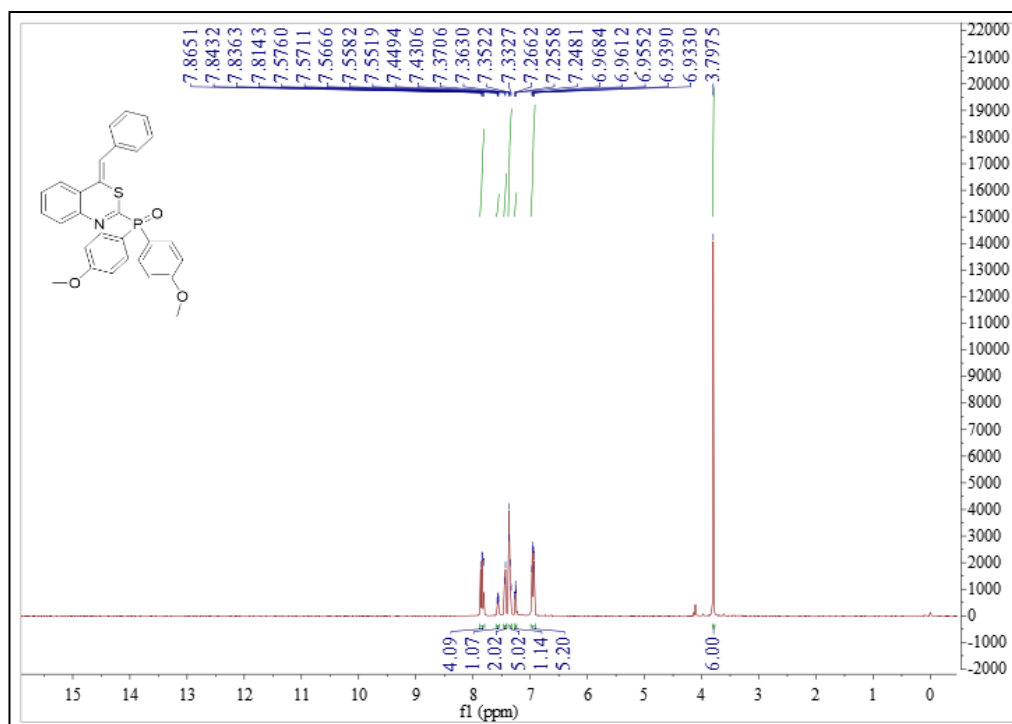
### $^1\text{H}$ NMR of **3u**



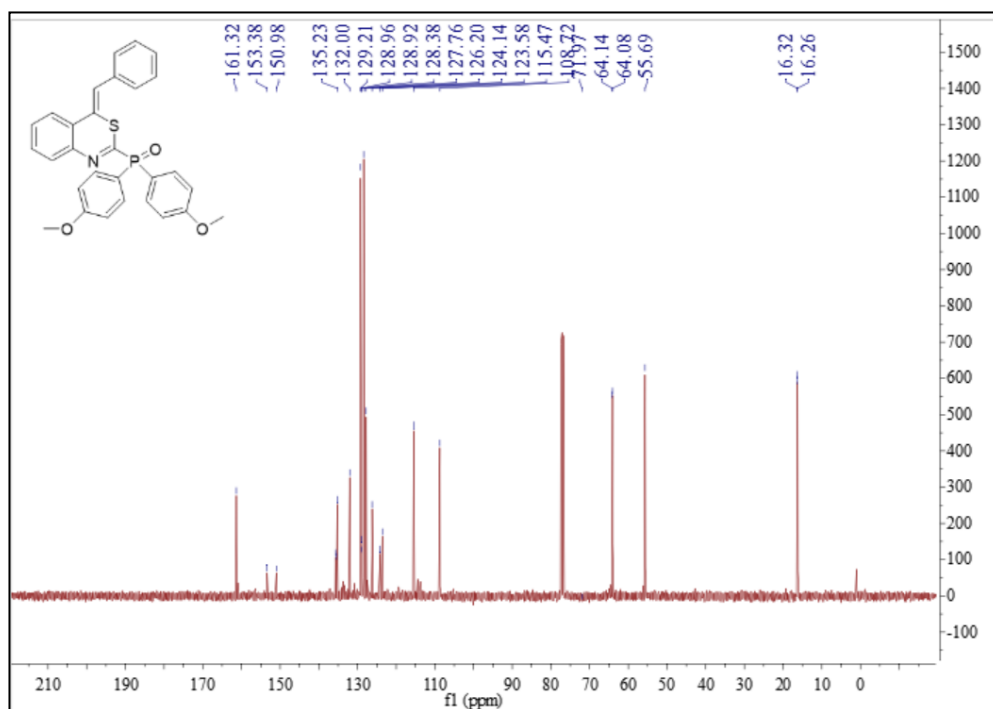
### $^{13}\text{C}$ NMR of **3u**



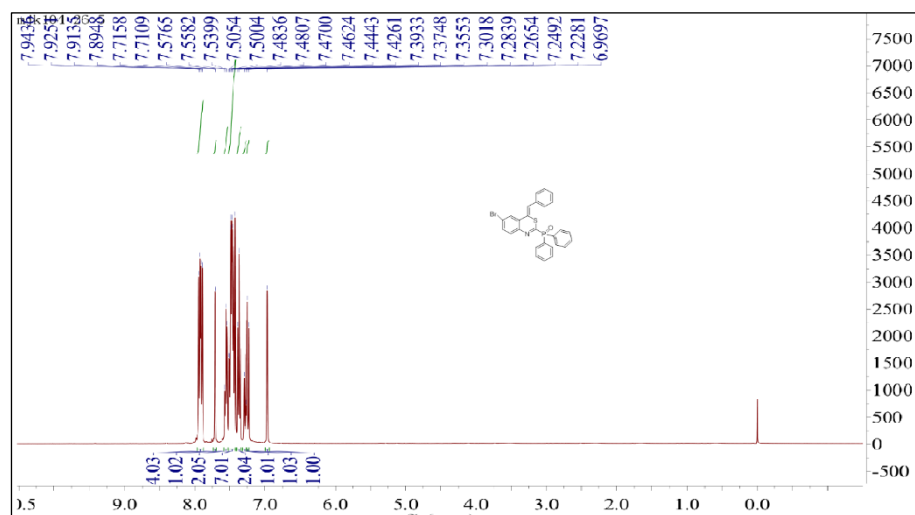
### $^1\text{H}$ NMR of **3v**



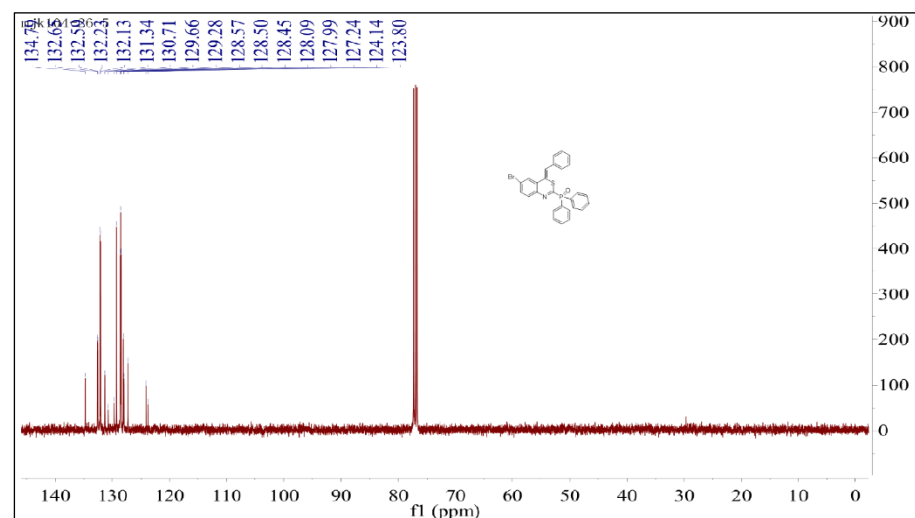
### $^{13}\text{C}$ NMR of **3v**



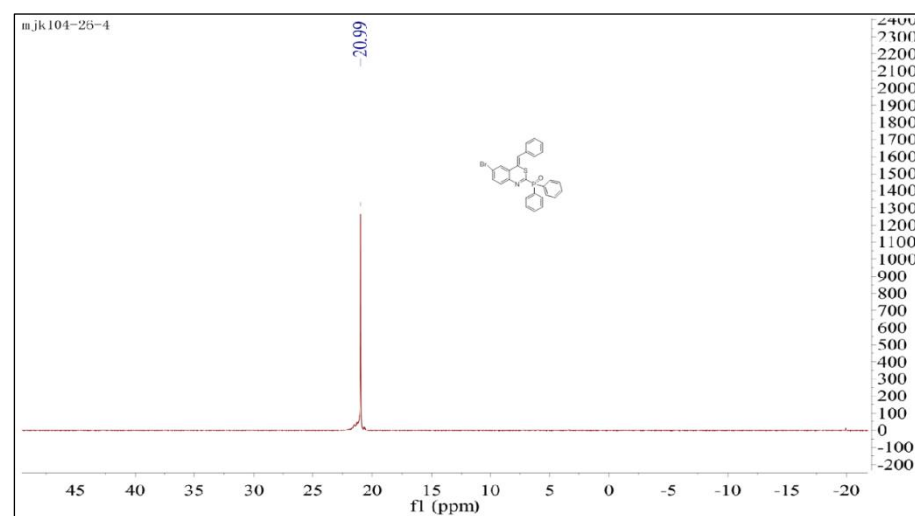
### <sup>1</sup>H NMR of **3w**



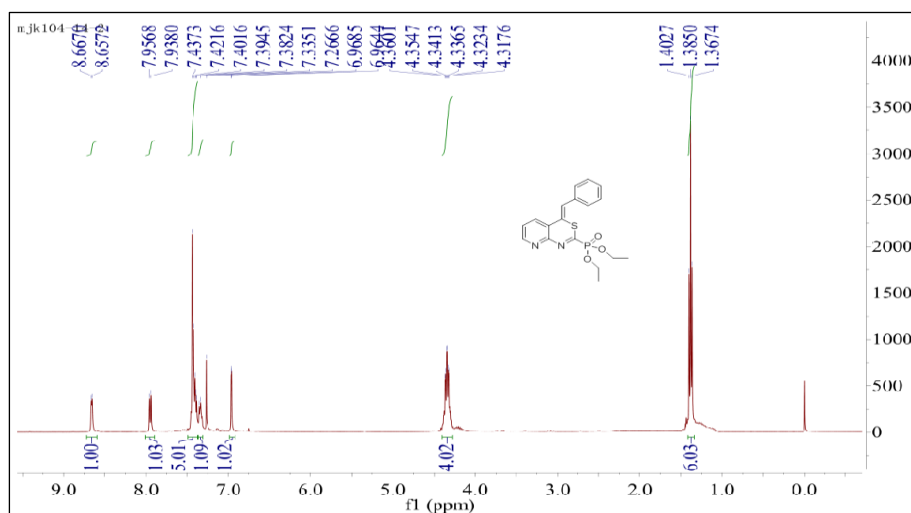
### <sup>13</sup>C NMR of **3w**



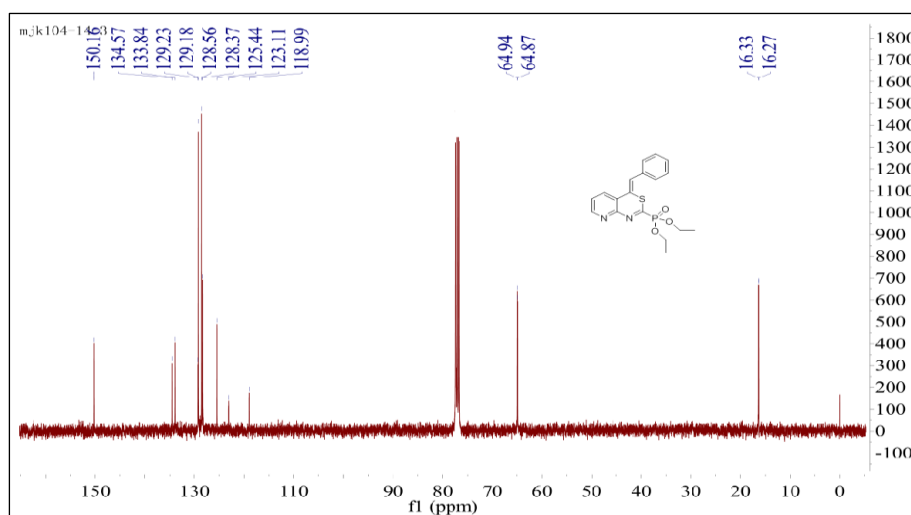
### <sup>31</sup>P NMR of **3w**



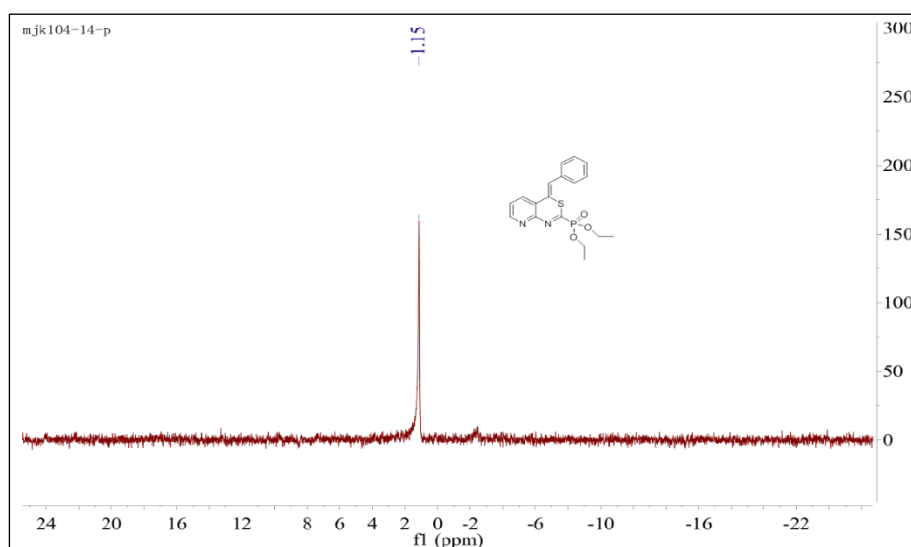
### $^1\text{H}$ NMR of **3x**



### $^{13}\text{C}$ NMR of **3x**



### $^{31}\text{P}$ NMR of **3x**



[1] Y. Liu, S. J. Yao, C. L. Wang, Y. H. Zhang, W. Y. Hao, *RSC Adv.*, 2020, **10**, 32211.