# Electrooxidation-Induced Synthesis 3-Thio/selenophosphorylated Imidazole: A Potent Pesticide with Good Biocompatibility

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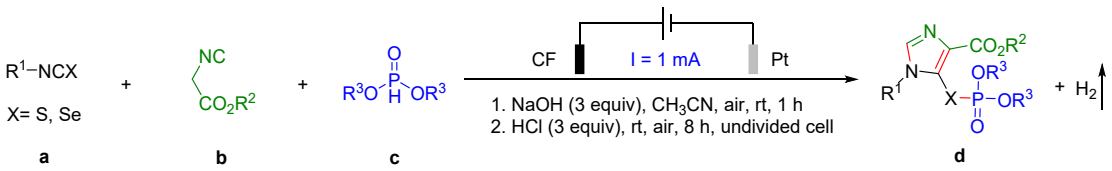
## 1. General information

All glassware was oven dried at 100 °C for hours and cooled down under vacuum. Isoselenocyanatobenzene, isoselenocyanatobenzenes, and phosphite ester derivatives were prepared according to reported procedures.[1] All the reaction prepared using the solvent of $CH_3CN$, DMF, and DMSO (AR, 99.0%) was purchased from Macklin. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B or SS-L303SPD) (made in China), the carbon rods (ϕ = 6 mm), carbon felt (1 x 1 $cm^2$), Pt plates (1 x 1 $cm^2$), and Ni plates (1 x 1 $cm^2$) was purchased from Xuzhou Xinke Instrument and Meter Co. LTD. The thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (b. p. 60-90 °C). $^1H$, $^{13}C$ and $^{19}F$ NMR data were recorded with Bruker Advance III (400 or 500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks (77.00 ppm, chloroform, or 40.0 ppm, DMSO-$d_6$), respectively.

## 2. General procedure electrooxidation-induced synthesis 3-thio/selenophosphorylated imidazoles with $H_2$ evolution

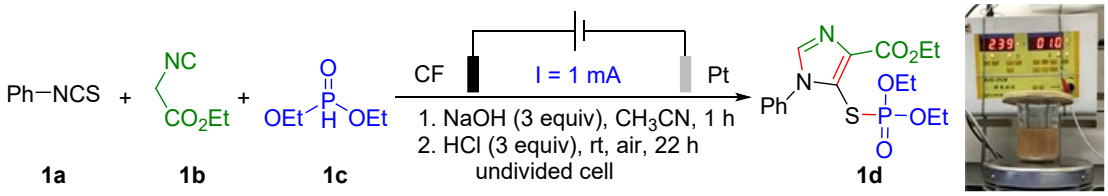



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **a** (0.5 mmol), **b** (0.5 mmol), and NaOH (1.5 mmol, 60.0 mg) were combined. The flask was equipped with a carbon felt (1.0 × 1.0 $cm^2$) as the anode and Pt plates (1.0 × 1.0 $cm^2$) as the cathode. Under the air, $CH_3CN$ (8.0 mL) was slowly injected into the reaction flask. The reaction mixture was stirred 1 h, and **c** (1.0 mmol), HCl (37%, 1.5 mmol) were added and then electrolyzed at a constant current of 1.0 mA under room temperature for

8 h. When the reaction was finished, adjust pH to neutral with HCl, the reaction mixture was concentrated and then extracted with $CH_2Cl_2$ (10 mL × 3). The organic layers were combined, dried over $Na_2SO_4$, and concentrated. The pure product was obtained by flash column chromatography on silica gel.

Note: the resulting products should be stored under an inert atmosphere at 2-8 °C.

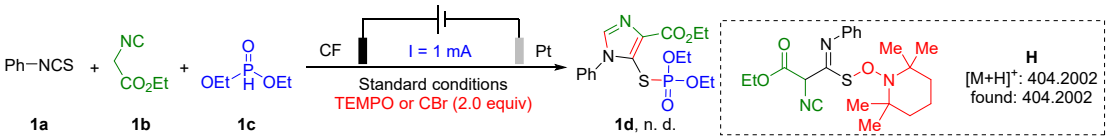
### 3. Large-scale synthesis of 1d




In an oven-dried beaker (500 mL) equipped with a stir bar, **1a** (10.0 mmol, 1.35 g), **1b** (10.0 mmol, 1.01 g), and NaOH (30.0 mmol, 1.2 g) were combined. The beaker was equipped with a carbon felt (2.0 × 2.0 $cm^2$) as the anode and Pt plates (1.0 × 1.0 $cm^2$) as the cathode. Under the air, $CH_3CN$ (160.0 mL) was slowly injected into the reaction system. The reaction mixture was stirred 1 h, and **1c** (20.0 mmol), HCl (37%, 30.0 mmol) were added and then electrolyzed at a constant current of 1.0 mA under room temperature for 22 h. Adjust pH to neutral with HCl, the reaction mixture was concentrated and then extracted with $CH_2Cl_2$ (10 mL × 3). The organic layers were combined, dried over $Na_2SO_4$, and concentrated again. The pure product **1d** was obtained in a yield of 57% (2.19 g) by flash column chromatography on silica gel.

### 4. Preliminary mechanistic studies

#### a) Radical trapping experiments




In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **a** (0.5 mmol), **b** (0.5 mmol), and NaOH (1.5 mmol, 60.0 mg) were combined. The flask was equipped with a carbon felt (1.0 × 1.0 $cm^2$) as the anode and Pt plates (1.0 × 1.0 $cm^2$) as the cathode. Under the air, $CH_3CN$ (8.0 mL) was slowly injected into the reaction flask. The reaction mixture was stirred 1 h, and **c** (1.0 mmol), HCl (37%, 1.5 mmol), TEMPO or $CBr_4$ (1.0 mmol) were added and then electrolyzed at a constant current of 1.0 mA under room temperature for 8 h. When the reaction was finished, the solution was concentrated in a vacuum and not detected the desired product **1d**. The compound **H** can be detected by HRMS.

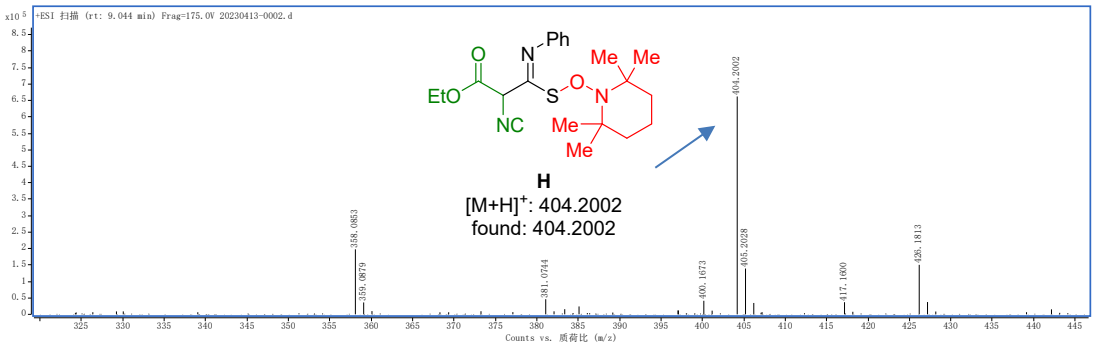



**Figure S1**. The HRMS results of **H**.

**b) HRMS sampling results**

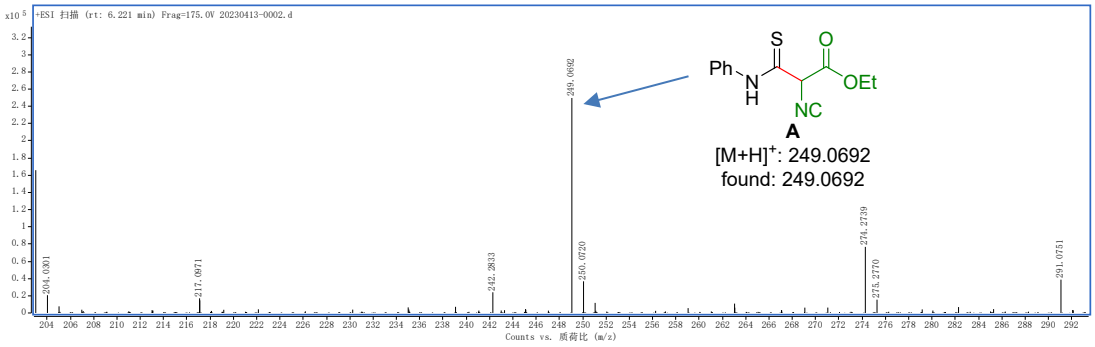



**Figure S2**. The HRMS results of **A**.

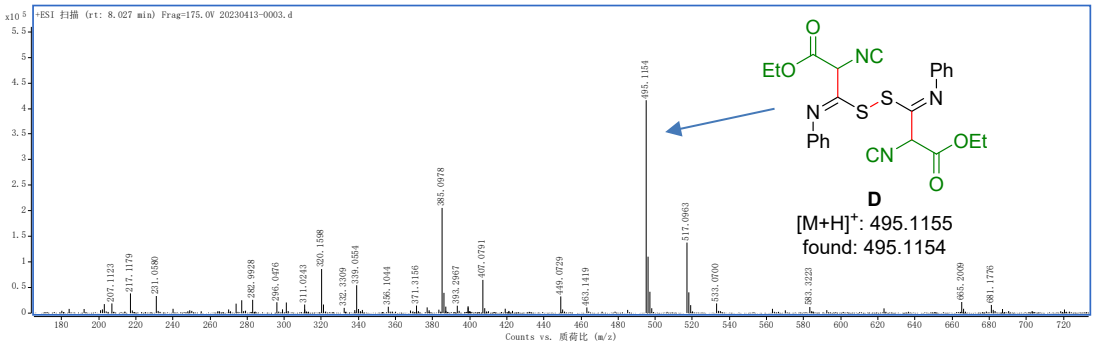



**Figure S3**. The HRMS results of **D**.

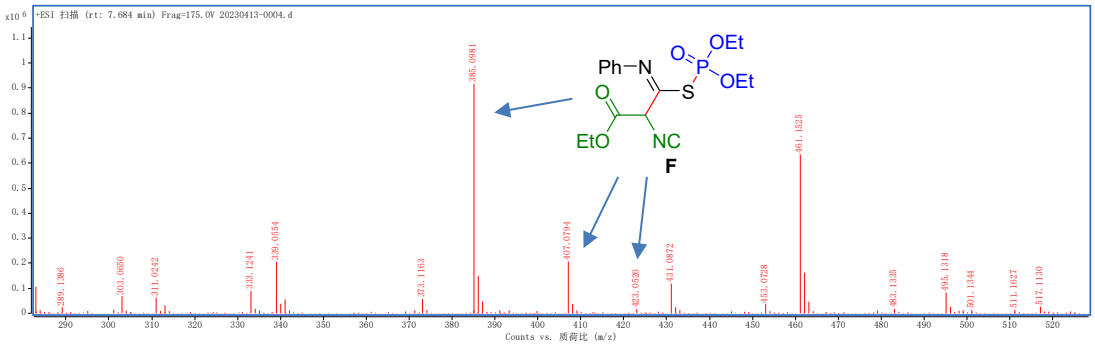



**Figure S4**. The HRMS results of **F**.

**c) CV experiments**

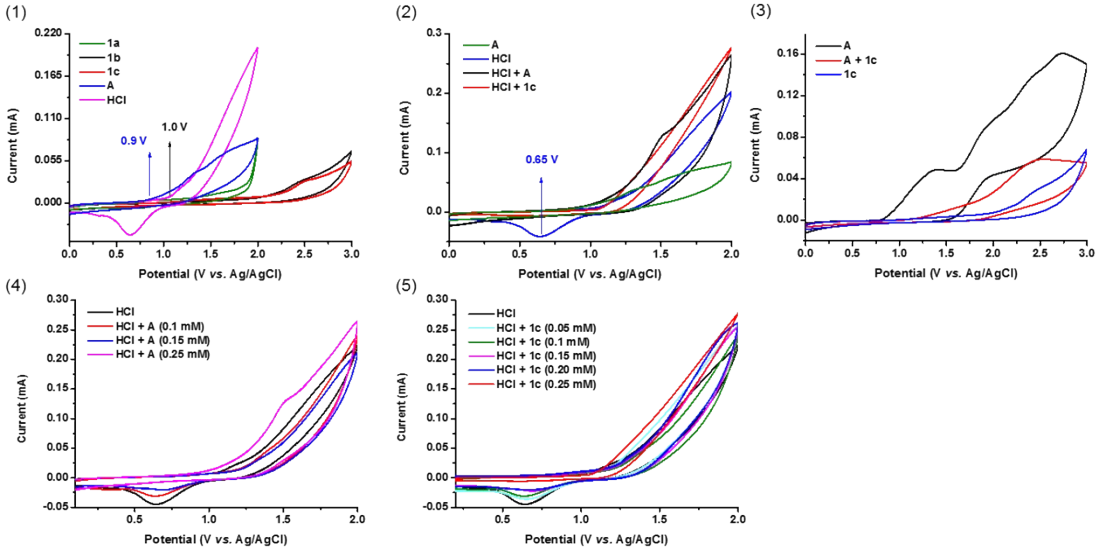
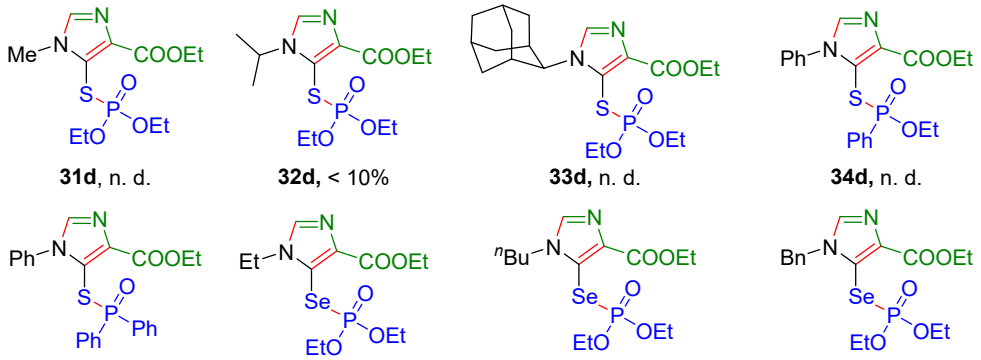


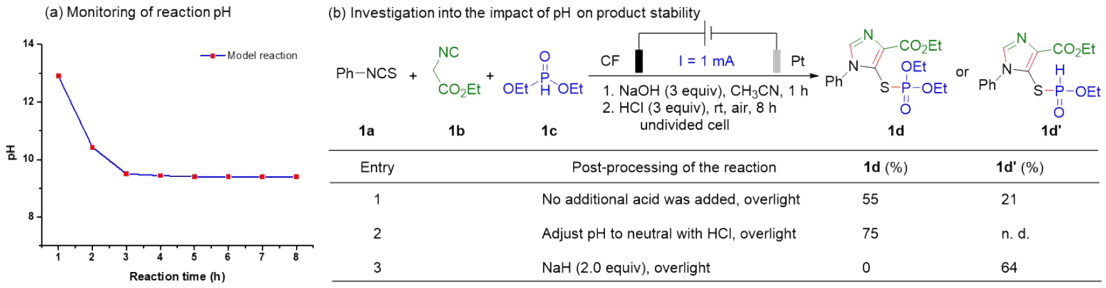

**Figure S5**. Cyclic voltammograms at grass carbon as work electrode, Ag/AgCl as the reference electrode, Pt (1 x 1 cm $^2$) as counter electrode in 0.1 M $^n$Bu$_4$NBF$_4$ in CH$_3$CN, scan rate 100 mV/s. (1), (2) ), (3) **1a** (0.25 mM), **1b** (0.25 mM), **1c, A** (0.25 mM), HCl (0.25 mM). (4), (5) Mixed CV curves of HCl (0.25 mM) and varying concentrations of **1c** or intermediate **A**.




**31d**, n. d. **32d,** < 10% **33d,** n. d. **34d,** n. d.

**35d**, n. d. **36d**, n. d. **37d**, n. d. **38d**, n. d.

**Scheme S1**. Unsuccessful examples.




| Entry | Post-processing of the reaction | **1d** (%) | **1d'** (%) |
|---|---|---|---|
| 1 | No additional acid was added, overlight | 55 | 21 |
| 2 | Adjust pH to neutral with HCl, overlight | 75 | n. d. |
| 3 | NaH (2.0 equiv), overlight | 0 | 64 |

**Scheme S2**. (a) Monitoring of reaction pH. (b) Investigation into the impact of pH on product stability.

## 5. The anti-locust activity of wheat seedlings and aquatic toxicity

**Figure S6**. Cultivation of wheat seedlings. Wheat seedlings were derived from the germination of wheat seeds without any pharmaceutical additives.

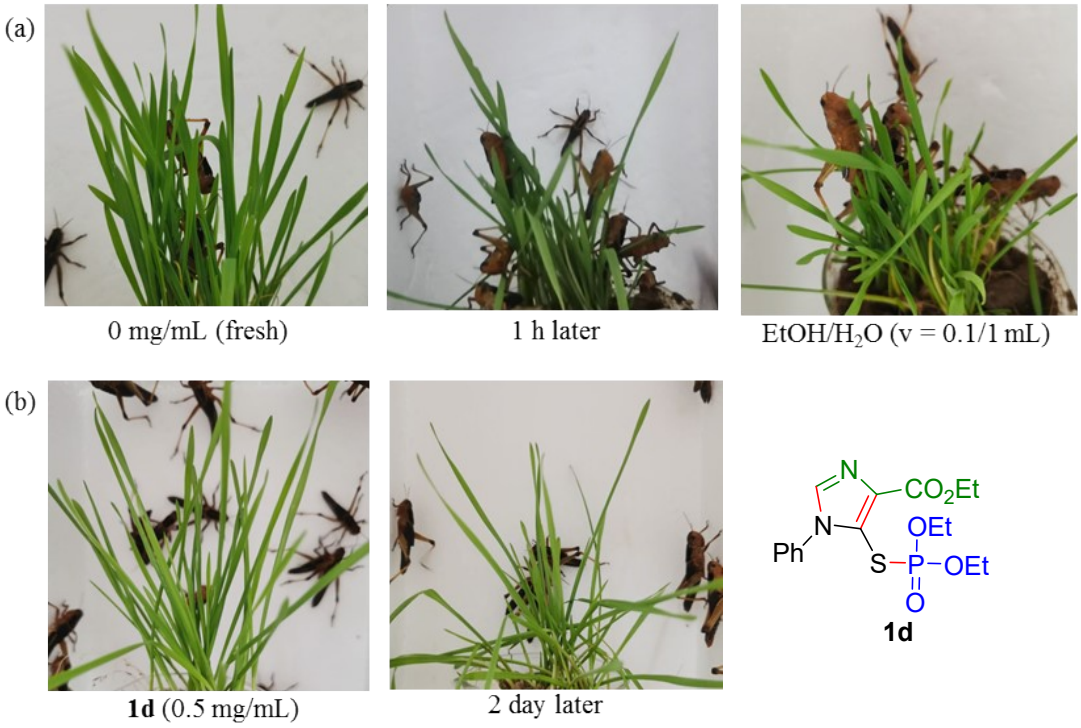
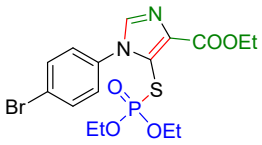



**Figure S7**. Preliminary study on the activity of pesticides. Grasshopper (2-3 cm) was purchased from Feixian affluence grasshopper breeding base in Linyi city, Shandong province, and all the grasshoppers were fed normally in groups for a week before the experiment. All animal experiments were conducted in adherence with the Biomedical Ethics Committee of Qufu Normal University (approval number 2023102).

**Table S1**. Aquatic toxicity, the mortality rate of carp juveniles (2-3 cm) at different trial times

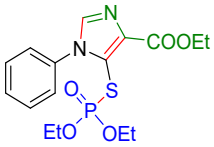
| Sample | Concentration (mg/L) | Mortality rate of carp juvenile at different trial times | | | |
|---|---|---|---|---|---|
| | | 24 h | 48 h | 72 h | 96 h |
| EtOH/$H_2O$ | (v = 0.1/50 mL) | 0 | 0 | 0 | 0 |
|  **6d** | 5 | 0 | 0 | 0 | 0 |
| | 6.5 | 0 | 40 | 80 | 100 |
| | 8.5 | 30 | 70 | 100 | 100 |
| | 10 | 80 | 100 | 100 | 100 |
| | 60 | 100 | 100 | 100 | 100 |

Carp juveniles (2-3 cm) was purchased from Zhizhi fishery aquaculture farm in Weihai, Shandong province, and all the carp juveniles were fed normally in groups for a week before the experiment. Carp juveniles were divided into several groups of 10 in each groups, and the results were the average of 3 parallel experiments. All animal experiments were conducted in adherence with the Biomedical Ethics Committee of Qufu Normal University (approval number 2023102).

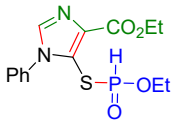
## 6. References

1. (a) Takemoto, Y.; Nanjo, T.; Tsukano, C, *Synlett.* **2014,** *25*, 1473-1477; (b) Zhou, M.; Ji, S.; Wu, Z.; Li, Y.; Zheng, W.; Zhou, H.; Chen, T., *Eur. J. Med. Chem.* **2015,** *96*, 92-7.

## 7. Detail descriptions for products

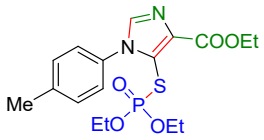


**Ethyl 5-((diethoxyphosphoryl)thio)-1-phenyl-1H-imidazole-4-carboxylate (1d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 75% isolated yield (144.2 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 1.7 Hz, 1H), 7.52 (dd, *J* = 9.1, 6.1 Hz, 3H), 7.47 (dd, *J* = 7.8, 1.5 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.02 – 3.93 (m, 2H), 3.88 – 3.79 (m, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 2.3 Hz), 140.1 (d, *J* = 2.0 Hz), 138.5 (d, *J* = 6.1 Hz), 135.0, 129.3 (d, *J* = 18.5 Hz), 127.4, 120.5 (d, *J* = 8.7 Hz), 64.3 (d, *J* = 6.2 Hz), 60.9, 15.8 (d, *J* = 7.4 Hz), 14.4. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{16}H_{21}N_2O_5PS$: 385.0982; found: 385.0982. IR (film) ν, $cm^{-1}$: 3112, 3068, 2979, 2929, 1718, 1594, 1496, 1463, 1384, 1309, 1249, 1190, 1050, 842, 767, 696.

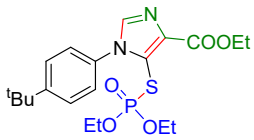


**1d'**

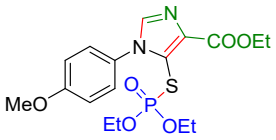
**Ethyl 5-((ethoxyphosphoryl)thio)-1-phenyl-1H-imidazole-4-carboxylate (1d'):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 21% isolated yield (17.8 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.47 (t, *J* = 5.4 Hz, 3H), 7.28 (dd, *J* = 10.8, 5.0 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.70 (q, *J* = 7.4 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.3, 138.8, 136.5, 135.2, 130.5, 129.3, 126.7, 68.2, 60.8, 14.5, 14.4.



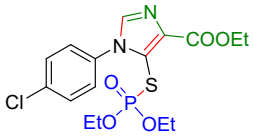
**Ethyl 5-((diethoxyphosphoryl)thio)-1-(p-tolyl)-1H-imidazole-4-carboxylate (2d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 64% isolated yield (127.4 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.5 Hz, 1H), 7.34 – 7.30 (m, 4H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.03 – 3.95 (m, 2H), 3.90 – 3.82 (m, 2H), 2.43 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 2.4 Hz), 140.2 (d, *J* = 2.0 Hz), 139.6, 138.4 (d, *J* = 6.1 Hz), 132.41, 129.7, 127.1, 120.6, 64.2 (d, *J* = 6.3 Hz), 60.9, 21.1, 15.8 (d, *J* = 7.5 Hz), 14.3. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{17}H_{23}N_2O_5PS$: 399.1138; found: 399.1138. IR (film) ν, cm$^{-1}$: 3110, 3072, 2981, 2929, 1720, 1583, 1513, 1479, 1384, 1307, 1251, 1184, 1045, 821, 819.



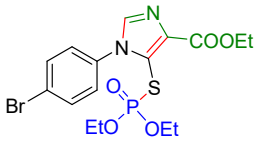
**Ethyl 1-(4-(tert-butyl)phenyl)-5-((diethoxyphosphoryl)thio)-1H-imidazole-4-carboxylate (3d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 60% isolated yield (132.1 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 4.36 (dd, *J* = 14.0, 7.0 Hz, 2H), 3.92 (m, 2H), 3.77 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.29 (s, 9H), 1.10 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.0, 152.7, 140.2, 132.3, 126.9, 126.1, 120.6, 64.1 (d, *J* = 6.0 Hz), 60.8, 34.8, 31.2, 15.8 (d, J = 7.5 Hz), 14.3. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{20}H_{29}N_2O_5PS$: 441.1608; found: 441.1607. IR (film) ν, cm$^{-1}$: 3114, 3056, 2969, 2917, 1724, 1610, 1513, 1469, 1380, 1309, 1251, 1187, 1051, 840, 781.




**Ethyl 5-((diethoxyphosphoryl)thio)-1-(4-methoxyphenyl)-1H-imidazole-4-carboxylate (4d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 55% isolated yield (114.0 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.46 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 8.9 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.07 – 3.97 (m, 2H), 3.97 – 3.89 (m, 2H), 3.88 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.1, 158.4, 139.6 (d, *J* = 2.4 Hz), 136.0, 132.3, 128.8, 115.2 (d, *J* = 3.1 Hz), 114.6, 65.0 (d, *J* = 6.8 Hz), 62.3, 55.7, 15.8 (d, *J* = 7.4 Hz), 14.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{23}N_2O_6PS$: 415.1087; found: 415.1088. IR (film) ν, $cm^{-1}$: 3124, 3079, 2981, 2935, 1727, 1608, 1511, 1496, 1384, 1301, 1253, 1186, 1180, 1041, 840, 838.

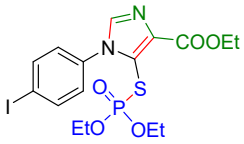



**Ethyl 1-(4-chlorophenyl)-5-((diethoxyphosphoryl)thio)-1H-imidazole-4-carboxylate (5d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 51% isolated yield (106.6 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.5 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.00 – 3.91 (m, 2H), 3.90 – 3.80 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.16 (td, *J* = 7.1, 0.7 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, *J* = 2.6 Hz), 140.0 (d, *J* = 1.6 Hz), 138.7, 135.7, 133.4, 129.5, 129.4, 128.8, 64.5 (d, *J* = 6.5 Hz), 61.0, 15.9 (d, *J* = 7.4 Hz), 14.3. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{16}H_{20}ClN_2O_5PS$: 419.0592; found: 419.0590. IR (film) ν, $cm^{-1}$: 3102, 3072, 2979, 2927, 1720, 1640, 1512, 1465, 1392, 1306, 1253, 1189, 1091, 1045, 835, 806.

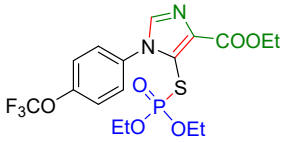



**Ethyl 1-(4-bromophenyl)-5-((diethoxyphosphoryl)thio)-1H-imidazole-4-carboxylate (6d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 49% isolated yield (113.4 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.07 – 3.98 (m, 2H), 3.97 – 3.88 (m, 2H), 1.44 (t, *J* =

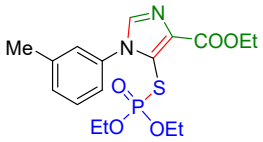
7.1 Hz, 3H), 1.23 (t, $J$ = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.8, 140.0, 138.7 (d, $J$ = 5.8 Hz), 133.9, 132.4, 129.1, 123.6, 120.5 (d, $J$ = 8.7 Hz), 64.5 (d, $J$ = 6.4 Hz), 61.0, 15.9 (d, $J$ = 7.3 Hz), 14.3. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{16}H_{20}BrN_2O_5PS$: 463.0087; found: 463.0086. IR (film) ν, $cm^{-1}$: 3106, 3073, 2983, 2923, 1720, 1643, 1515, 1494, 1398, 1309, 1251, 1186, 1071, 1047, 833, 784.



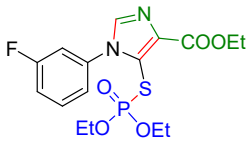

**Ethyl 5-((diethoxyphosphoryl)thio)-1-(4-iodophenyl)-1H-imidazole-4-carboxylate (7d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 48% isolated yield (122.4 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.83 (d, $J$ = 8.4 Hz, 2H), 7.54 – 7.48 (m, 2H), 4.42 (q, $J$ = 7.2 Hz, 2H), 4.01 – 3.91 (m, 2H), 3.88 – 3.78 (m, 2H), 1.43 (t, $J$ = 7.1 Hz, 3H), 1.18 (t, $J$ = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.2, 140.4 (d, $J$ = 10.5 Hz), 138.7, 129.5, 129.4, 129.1, 127.5, 95.5, 64.4 (d, $J$ = 6.3 Hz), 61.2, 16.0 (d, $J$ = 7.5 Hz), 14.4. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{16}H_{20}IN_2O_5PS$: 510.9948; found: 510.9948. IR (film) ν, $cm^{-1}$: 3109, 3075, 2986, 2923, 1720, 1651, 1516, 1496 1399, 1308, 1251, 1185, 1080, 1047, 832, 802.



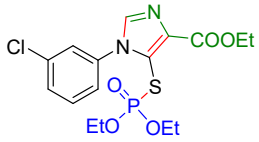

**Ethyl 5-((diethoxyphosphoryl)thio) -1-(4-(trifluoromethoxy)phenyl)-1H-imidazole- 4-carboxylate (8d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 50% isolated yield (117.1 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.55 (d, $J$ = 7.8 Hz, 2H), 7.40 (d, $J$ = 8.5 Hz, 2H), 4.44 (q, $J$ = 6.8 Hz, 2H), 4.04 – 3.96 (m, 2H), 3.94 – 3.85 (m, 2H), 1.44 (td, $J$ = 7.0, 0.8 Hz, 3H), 1.22 (t, $J$ = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.9 (d, $J$ = 2.2 Hz), 149.7 (d, $J$ = 1.8 Hz), 140.1 (d, $J$ = 1.7 Hz), 138.8 (q, $J$ = 6.0 Hz), 133.4, 129.4, 121.7, 120.8 (q, $J$ = 8.9 Hz), 120.4 (q, $J$ = 258.8 Hz), 64.6 (d, $J$ = 6.5 Hz), 61.1, 15.9 (d, $J$ = 7.3 Hz), 14.4i (s). HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{20}F_3N_2O_6PS$: 469.0805; found: 469.0805. IR (film) ν, $cm^{-1}$: 3110, 3062, 2923, 2852, 1716, 1598, 1511, 1463 1378, 1302, 1249, 1205, 1184, 1047, 825, 804.



**Ethyl 5-((diethoxyphosphoryl)thio)-1-(m-tolyl)-1H-imidazole-4-carboxylate (9d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 71% isolated yield (141.3 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.8 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 5.0 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.03 – 3.95 (m, 2H), 3.89 – 3.80 (m, 2H), 2.44 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 2.3 Hz), 140.1 (d, *J* = 1.9 Hz), 139.5, 138.5 (d, *J* = 6.1 Hz), 134.9, 130.0, 129.0, 127.8, 124.3, 120.5 (d, *J* = 8.7 Hz), 64.2 (d, *J* = 6.2 Hz), 60.9, 21.2, 15.9 (d, *J* = 7.5 Hz), 14.4. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{17}H_{23}N_2O_5PS$: 399.1138; found: 399.1138. IR (film) ν, cm$^{-1}$: 3114, 3056, 2978, 2927, 1716, 1619, 1477, 1488, 1386, 1306, 1257, 1197, 1035, 854, 852, 788, 694.

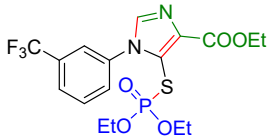



**Ethyl 5-((diethoxyphosphoryl)thio)-1-(3-fluorophenyl)-1H-imidazole-4-carboxylate (10d):** white oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 68% isolated yield (136.8 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.44 (dd, *J* = 14.2, 7.8 Hz, 1H), 7.25 – 7.15 (m, 3H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.02 – 3.92 (m, 2H), 3.91 – 3.79 (m, 2H), 1.38 – 1.34 (m, 3H), 1.15 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.4 (d, *J* = 250.1 Hz), 161.8 (d, *J* = 2.3 Hz), 140.0 (d, *J* = 2.1 Hz), 138.7 (d, *J* = 6.2 Hz), 136.1 (d, *J* = 10.0 Hz), 130.5 (d, *J* = 8.9 Hz), 123.2 (d, *J* = 3.4 Hz), 120.5 (d, *J* = 8.7 Hz), 116.5 (d, *J* = 20.9 Hz), 115.2 (d, *J* = 24.4 Hz), 64.5 (d, *J* = 6.5 Hz), 61.0, 15.8 (d, *J* = 7.3 Hz), 14.3. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{16}H_{20}FN_2O_5PS$: 403.0887; found: 403.0888. IR (film) ν, cm$^{-1}$: 3114, 3045, 2925, 2854, 1716, 1608, 1488, 1460, 1376, 1309, 1201, 1130, 1078, 1035, 860, 852, 780, 650.

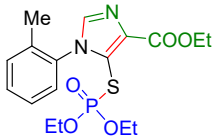



**Ethyl 5-((diethoxyphosphoryl)thio)-1-(m-tolyl)-1H-imidazole-4-carboxylate (11d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 77% isolated yield (161.2 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.49 (s, 1H), 7.44 – 7.39 (m, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.02 – 3.92 (m, 2H), 3.92 – 3.80 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, *J* = 2.2 Hz), 140.0 (d, *J* = 1.9 Hz),

138.7 (d, $J$ = 6.3 Hz), 135.9, 134.9, 130.2, 129.6, 127.6, 125.7, 120.6 (d, $J$ = 8.5 Hz), 76.8, 64.5 (d, $J$ = 6.5 Hz), 61.0, 15.9 (d, $J$ = 7.4 Hz), 14.3. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{16}H_{20}ClN_2O_5PS$: 419.0592; found: 419.0592. IR (film) ν, cm$^{-1}$: 3115, 3077, 2976, 2923, 1720, 1639, 1511, 1492, 1389, 1308, 1253, 1189, 1090, 1044, 878, 840, 785, 693.

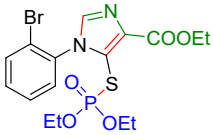



**Ethyl 5-((diethoxyphosphoryl)thio)-1-(3-(trifluoromethyl)phenyl)-1H-imidazole-4-carboxylate (12d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 75% isolated yield (169.5 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, $J$ = 1.6 Hz, 1H), 7.76 (s, 1H), 7.72 (dd, $J$ = 4.4, 3.5 Hz, 1H), 7.63 (d, $J$ = 5.2 Hz, 2H), 4.37 (q, $J$ = 7.1 Hz, 2H), 3.99 – 3.90 (m, 2H), 3.88 – 3.79 (m, 2H), 1.37 (t, $J$ = 7.1 Hz, 3H), 1.14 (td, $J$ = 7.0, 0.6 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.7 (d, $J$ = 2.4 Hz), 140.4, 140.0 (d, $J$ = 2.1 Hz), 135.3 (d, $J$ = 32.0 Hz), 131.8 (qd, $J$ = 33.3, 5.5 Hz), 130.9 (d, $J$ = 25.2 Hz), 130.0 (d, $J$ = 10.3 Hz), 126.3 (dq, $J$ = 34.5, 7.1 Hz), 124.5 (q, $J$ = 3.7 Hz), 123.2 (q, $J$ = 273.6 Hz), 120.6 (d, $J$ = 8.6 Hz), 64.5 (d, $J$ = 6.6 Hz), 61.0, 15.7 (d, $J$ = 7.3 Hz), 14.3. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{17}H_{20}F_3N_2O_5PS$: 453.0855; found: 453.0857. IR (film) ν, cm$^{-1}$: 3112, 3048, 2925, 2854, 1718, 1621, 1498, 1473, 1382, 1322, 1263, 1201, 1178, 1049, 862, 806, 701, 659.

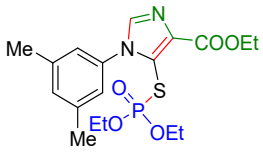



**Ethyl 5-((diethoxyphosphoryl)thio)-1-(o-tolyl)-1H-imidazole-4-carboxylate (13d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 76% isolated yield (151.2 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, $J$ = 1.7 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.28 (dd, $J$ = 14.7, 7.1 Hz, 2H), 4.37 (q, $J$ = 7.1 Hz, 2H), 3.99 – 3.91 (m, 1H), 3.90 – 3.83 (m, 1H), 3.82 – 3.75 (m, 1H), 3.71 – 3.64 (m, 1H), 2.03 (s, 3H), 1.38 (t, $J$ = 7.1 Hz, 3H), 1.16 (t, $J$ = 7.0 Hz, 3H), 1.09 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.0 (d, $J$ = 2.1 Hz), 140.0 (d, $J$ = 1.7 Hz), 138.0 (d, $J$ = 6.2 Hz), 136.0, 133.9, 130.9, 129.9, 129.3, 126.5, 121.2 (d, $J$ = 8.6 Hz), 64.2 (d, $J$ = 22.6 Hz), 60.9, 17.7, 15.8 (d, $J$ = 14.4 Hz), 15.8 14.3. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{17}H_{23}N_2O_5PS$: 399.1138; found: 399.1138. IR (film) ν, cm$^{-1}$: 3110, 3070, 2977, 2929, 1720, 1579, 1500, 1477, 1382, 1305,

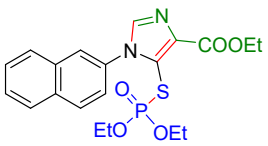
1249, 1187, 1041, 815, 767.




**Ethyl 1-(2-bromophenyl)-5-((diethoxyphosphoryl)thio)-1H-imidazole-4-carboxylate (14d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 70% isolated yield (162.1 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.60 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.44 (td, *J* = 7.7, 1.2 Hz, 1H), 7.36 (td, *J* = 7.8, 1.6 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.17 – 4.01 (m, 2H), 3.82 – 3.62 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, *J* = 2.4 Hz), 139.9 (d, *J* = 2.2 Hz), 138.1 (d, *J* = 6.4 Hz), 134.1, 133.2, 131.3, 131.2, 128.0, 122.8, 121.3 (d, *J* = 8.6 Hz), 64.4 (d, *J* = 67.8 Hz), 64.4 (d, *J* = 67.5 Hz), 60.9, 15.9 (d, *J* = 16.0 Hz), 15.8 (d, *J* = 15.6 Hz), 14.3. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{16}H_{20}BrN_2O_5PS$: 463.0087; found: 463.0087. IR (film) ν, cm$^{-1}$: 3106, 3073, 2983, 2923, 1720, 1643, 1515, 1494, 1398, 1309, 1251, 1186, 1043, 1039, 833, 784.

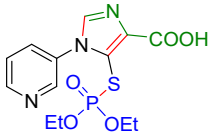



**Ethyl 5-((diethoxyphosphoryl)thio)-1-(3,5-dimethylphenyl)-1H-imidazole-4-carboxylate (15d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 72% isolated yield (148.3 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 1.8 Hz, 1H), 7.05 (s, 1H), 6.98 (s, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.98 – 3.86 (m, 2H), 3.77 -3.79 (m, 2H), 2.31 (s, 6H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 2.3 Hz), 140.1 (d, *J* = 2.1 Hz), 139.1, 138.4 (d, *J* = 6.3 Hz), 134.7, 130.9, 130.8, 124.7, 124.6, 120.4 (d, *J* = 8.8 Hz), 64.1 (d, *J* = 6.1 Hz), 60.8, 21.1, 15.8 (d, *J* = 7.5 Hz), 14.3. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{18}H_{25}N_2O_5PS$: 413.1295; found: 413.1295. IR (film) ν, cm$^{-1}$: 3112, 3031, 2983, 2927, 1720, 1612, 1484, 1382, 1378, 1222, 1184, 1037, 850, 786, 696.

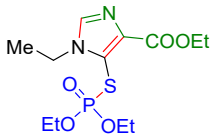



**Ethyl 5-((diethoxyphosphoryl)thio)-1-(naphthalen-2-yl)-1H-imidazole-4-carboxylate (16d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with

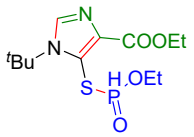
50% isolated yield (108.5 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.63 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.42 (m, 3H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.92 – 3.76 (m, 2H), 3.72 – 3.62 (m, 1H), 3.54 – 3.45 (m, 1H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 2.2 Hz), 141.1 (d, *J* = 11.3 Hz), 138.5, 133.8 (d, *J* = 15.7 Hz), 130.3 (d, *J* = 2.8 Hz), 128.2, 127.9, 127.1, 127.1, 126.9, 125.1, 124.9, 122.3, 121.7, 64.3 (d, *J* = 6.4 Hz), 64.0 (d, *J* = 6.3 Hz), 61.0, 15.7 (d, *J* = 7.6 Hz), 15.6 (d, *J* = 7.2 Hz), 14.4. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{20}H_{23}N_2O_5PS$: 435.1138; found: 435.1138. IR (film) ν, $cm^{-1}$: 3110, 3062, 2981, 2931, 1718, 1598, 1508, 1479, 1369, 1309, 1249, 1189, 1035, 806, 844, 775.



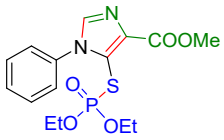

**5-((diethoxyphosphoryl)thio)-1-(pyridin-3-yl)-1H-imidazole-4-carboxylic acid (17d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 61% isolated yield (109.0 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 10.85 (s, 1H), 8.98 (s, 1H), 8.63 (d, *J* = 8.3 Hz, 1H), 8.53 (d, *J* = 4.7 Hz, 1H), 7.91 (s, 1H), 7.37 (dd, *J* = 8.3, 4.8 Hz, 1H), 4.34 – 4.23 (m, 4H), 1.38 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 192.0, 149.0, 147.9, 143.9, 130.4, 129.2, 128.4 (d, *J* = 8.7 Hz), 126.3, 123.3, 65.5 (d, *J* = 6.9 Hz), 16.2 (d, *J* = 6.3 Hz). HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{13}H_{16}N_3O_5PS$: 358.0621; found: 358.0621. IR (film) ν, $cm^{-1}$: 3403, 3081, 3070, 2977, 2929, 1718, 1509, 1479, 1332, 1242, 1230, 1045, 808.



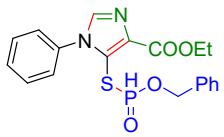

**ethyl 5-((diethoxyphosphoryl)thio)-1-ethyl-1H-imidazole-4-carboxylate (18d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 36% isolated yield (60.5 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 4.45 – 4.35 (m, 4H), 3.72 (q, *J* = 7.0 Hz, 2H), 3.35 – 3.20 (m, 2H), 1.41 (t, *J* = 7.1 Hz, 6H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.9, 133.7, 128.4 (d, *J* = 8.2 Hz), 119.6, 61.4, 60.3, 58.4, 44.1 18.4, 14.5 (d, *J* = 8.3 Hz), 14.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{12}H_{21}N_2O_5PS$: 337.0982; found: 337.0980. IR (film) ν, $cm^{-1}$: 3085, 2975, 2923, 1741, 1546, 1301, 1225, 1187, 1029, 838.



**Ethyl 1-(tert-butyl)-5-((ethoxyphosphoryl)thio)-1H-imidazole-4-carboxylate (19d)**: yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/2) with 42% isolated yield (67.2 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.03 (q, *J* = 7.5 Hz, 2H), 1.77 (s, 9H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.5 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.4, 137.8, 136.0, 130.0, 60.6, 58.7, 31.8, 30.2, 14.4, 13.8. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{12}H_{22}N_2O_4PS$: 321.1032; found: 321.1030. IR (film) ν, $cm^{-1}$: 3084, 2973, 2920, 1741, 1546, 1300, 1227, 1187, 1029, 828.

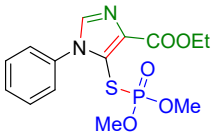


**Methyl 5-((diethoxyphosphoryl)thio)-1-phenyl-1H-imidazole-4-carboxylate (20d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 73% isolated yield (135.2 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.52 (t, *J* = 7.2 Hz, 3H), 7.49 – 7.44 (m, 2H), 3.95 (s, 3H), 3.90 – 3.79 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.3, 149.0, 140.2, 134.9, 129.4, 129.2, 128.4 (d, *J* = 8.2 Hz), 127.4, 64.3 (d, *J* = 6.3 Hz), 51.9, 15.8 (d, *J* = 7.3 Hz). HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{15}H_{19}N_2O_5PS$: 371.0825; found: 371.0826. IR (film) ν, $cm^{-1}$: 3112, 3072, 2979, 2931, 1720, 1596, 1500, 1455, 1396, 1301, 1251, 1197, 1047, 809, 769, 698.

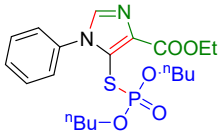


**Ethyl 5-{[(benzyloxy)phosphonoyl]sulfanyl}-1-phenyl-1H-imidazole-4-carboxylate (21d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 81% isolated yield (163.0 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.43 – 7.40 (m, 1H), 7.37 – 7.32 (m, 2H), 7.21 – 7.11 (m, 3H), 6.90 (d, *J* = 7.0 Hz, 2H), 6.75 (d, *J* = 7.2 Hz, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.5, 138.8, 137.3, 137.1, 134.8, 129.8, 129.0, 128.9, 128.8, 128.4, 127.2, 126.8, 74.2, 60.9, 14.4. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{19}H_{19}N_2O_4PS$: 403.0876; found: 403.0876. IR (film) ν, $cm^{-1}$: 3104, 3062, 2983, 2929,

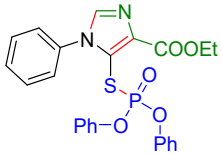
2346, 1708, 1598, 1498, 1455, 1378, 1317, 1249, 1186, 1052, 836, 767, 698.




**Ethyl 5-((dimethoxyphosphoryl)thio)-1-phenyl-1H-imidazole-4-carboxylate (22d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 72% isolated yield (128.3 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.51 – 7.47 (m, 3H), 7.36 (d, *J* = 3.0 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.54 (s, 3H), 3.52 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.3, 140.2, 134.9, 129.4, 129.2, 128.4 (d, *J* = 8.0 Hz), 127.4, 120.7 (d, *J* = 8.8 Hz), 64.3 (d, *J* = 6.4 Hz), 51.9, 15.8 (d, *J* = 7.5 Hz). HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{14}H_{17}N_2O_5PS$: 357.0669; found: 357.0669. IR (film) ν, $cm^{-1}$: 3112, 3041, 2979, 2927, 1702, 1592, 1498, 1463, 1380, 1307, 1251, 1193, 1054, 854, 773, 698.

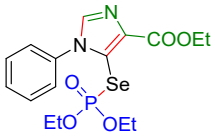



**Ethyl 5-((dibutoxyphosphoryl)thio)-1-phenyl-1H-imidazole-4-carboxylate (23d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 75% isolated yield (165.1 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.54 – 7.49 (m, 3H), 7.48 – 7.44 (m, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.66 – 3.60 (m, 2H), 3.53 – 3.46 (m, 2H), 1.85 – 1.75 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 12H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.8, 140.1, 138.3 (d, *J* = 5.5 Hz), 135.0 (d, *J* = 4.0 Hz), 129.4, 129.2, 127.5, 120.7 (d, *J* = 5.6 Hz), 73.7 (d, *J* = 7.0 Hz), 60.9, 28.8 (d, *J* = 7.4 Hz), 18.5, 18.5, 14.3. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{20}H_{29}N_2O_5PS$: 441.1608; found: 441.1606. IR (film) ν, $cm^{-1}$: 3110, 3066, 2962, 2935, 1720, 1596, 1500, 1471, 1382, 1307, 1187, 1027, 875, 765, 696.

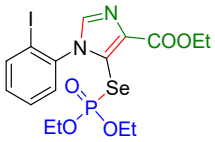



**Ethyl 5-((diphenoxyphosphoryl)thio)-1-phenyl-1H-imidazole-4-carboxylate (24d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 56% isolated yield (134.4 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.42 – 7.37 (m, 3H), 7.35 – 7.32 (m, 2H), 7.30 – 7.27 (m, 4H), 7.23 – 7.17 (m, 3H), 7.02 (d, *J* = 8.2 Hz, 3H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* =

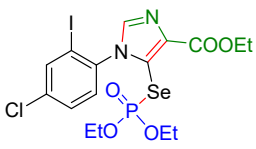
7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 160.9, 150.1 (d, *J* = 9.4 Hz), 144.7, 140.8 (d, *J* = 1.6 Hz), 134.5, 130.4, 129.7, 129.4 (d, *J* = 2.4 Hz), 129.2, 128.4, 127.1, 125.6, 120.2 (d, *J* = 5.0 Hz), 61.1, 14.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{24}H_{21}N_2O_5PS$: 481.0982; found: 481.0982. IR (film) ν, $cm^{-1}$: 3102, 3064, 2923, 2852, 1720, 1594, 1492, 1454, 1378, 1245, 1205, 1313, 1083, 842, 763, 692.




**Ethyl 5-((diethoxyphosphoryl)selanyl)-1-phenyl-1H-imidazole-4-carboxylate (25d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 52% isolated yield (112.1 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.53 (d, *J* = 7.1 Hz, 3H), 7.45 (dd, *J* = 7.7, 1.8 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.02 – 3.94 (m, 2H), 3.86 – 3.78 (m, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, *J* = 2.1 Hz), 140.7 (d, *J* = 0.8 Hz), 138.9 (d, *J* = 5.0 Hz), 135.7, 129.4, 129.2, 127.5, 116.7 (d, *J* = 10.9 Hz), 64.0 (d, *J* = 5.8 Hz), 61.0 (s), 15.8 (d, *J* = 7.6 Hz), 14.3. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{16}H_{21}N_2O_5PSe$: 433.0426; found: 433.0426. IR (film) ν, $cm^{-1}$: 3112, 3064, 2981, 2927, 1716, 1637, 1598, 1496, 1390, 1249, 1184, 1041, 815, 767, 696.

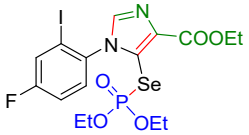



**Ethyl 5-((diethoxyphosphoryl)selanyl)-1-(2-iodophenyl)-1H-imidazole-4-carboxylate (26d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 59% isolated yield (164.6 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 1.4 Hz, 1H), 7.75 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.20 (m, 2H), 4.47 – 4.40 (m, 2H), 4.20 – 4.08 (m, 2H), 3.90 – 3.74 (m, 2H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 175.3, 140.4, 139.5, 138.5 (d, *J* = 10.7 Hz), 131.4 (d, *J* = 9.8 Hz), 130.7, 130.2, 129.3, 129.0, 98.8 (d, *J* = 48.1 Hz), 64.3 (dd, *J* = 54.1, 6.2 Hz), 61.1, 15.9 (dd, *J* = 15.3, 7.5 Hz), 14.4. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{16}H_{20}IN_2O_5PSe$: 558.9392; found: 558.9393. IR (film) ν, $cm^{-1}$: 3110, 3075, 2981, 2923, 1716, 1621, 1510, 1492, 1389, 1241, 1185, 1083, 1040, 809, 800.

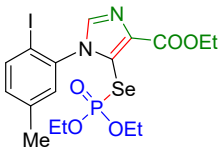



**Ethyl 1-(4-chloro-2-iodophenyl)-5-((diethoxyphosphoryl)selanyl)-1H-imidazole-4-**

**carboxylate (27d):** rufous oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 38% isolated yield (112.5 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.2 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 9.5 Hz, 1H), 7.53 – 7.49 (m, 1H), 4.48 – 4.30 (m, 2H), 4.25 (q, *J* = 6.9 Hz, 2H), 4.22 – 4.15 (m, 1H), 3.97 – 3.75 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.4, 140.2, 138.7 (d, *J* = 4.1 Hz), 137.3, 136.6 (d, *J* = 4.0 Hz), 130.8, 129.4, 129.0, 120.8, 99.2 (d, *J* = 46.3 Hz), 64.4 (dd, *J* = 54.3, 6.3 Hz), 61.0, 60.3, 15.8 (d, *J* = 7.8 Hz), 14.4. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{16}H_{19}ClIN_2O_5PSe$: 592.9003; found: 592.9004. IR (film) ν, cm$^{-1}$: 3110, 3070, 2983, 2923, 1716, 1631, 1521, 1496, 1398, 1249, 1184, 1091, 1086, 1041, 817, 769, 696.

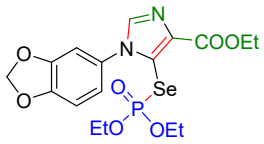



**Ethyl 5-((diethoxyphosphoryl)selanyl)-1-(4-fluoro-2-iodophenyl)-1H-imidazole-4-carboxylate (28d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 41% isolated yield (118.1 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 1.5 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.24 – 7.18 (m, 1H), 4.44 – 4.37 (m, 2H), 4.20 – 4.03 (m, 2H), 3.96 – 3.74 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 174.4, 162.4 (d, *J* = 250.8 Hz), 161.6 (dd, *J* = 82.4, 3.3 Hz), 140.4, 138.9 (d, *J* = 5.4 Hz), 134.8 (dd, *J* = 11.1, 3.4 Hz), 131.7 (d, *J* = 8.9 Hz), 126.3 (dd, *J* = 25.0, 4.7 Hz), 116.0 (dd, *J* = 53.0, 22.3 Hz), 98.9 (dd, *J* = 50.9, 8.8 Hz), 64.4 (dd, *J* = 57.5, 6.4 Hz), 61.0, 15.8 (d, *J* = 7.5 Hz), 14.3. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{16}H_{19}FIN_2O_5PSe$: 576.9298; found: 576.9298. IR (film) ν, cm$^{-1}$: 3100, 3054, 2925, 2857, 1710, 1631, 1581, 1490, 1372, 1261, 1201, 1092, 1060, 1054, 863, 784, 669.




**Ethyl 5-((diethoxyphosphoryl)selanyl)-1-(2-iodo-5-methylphenyl)-1H-imidazole-4-carboxylate (29d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 2/1) with 60% isolated yield (171.6 mg). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.66 (s, 1H), 7.42 (s, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.20 – 4.07 (m, 2H), 3.90 – 3.73 (m, 2H), 2.38 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz,

3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.6, 140.1, 139.5 (d, *J* = 3.5 Hz), 139.0, 138.3 (d, *J* = 13.5 Hz), 132.2 (d, *J* = 11.5 Hz), 131.2, 130.7, 130.3, 94.3 (d, *J* = 49.2 Hz), 64.1 (dd, *J* = 63.3, 6.0 Hz), 60.9, 20.7, 15.8 (dd, *J* = 17.9, 7.4 Hz), 14.4. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{22}IN_2O_5PSe$: 572.9549; found: 572.9549. IR (film) ν, $cm^{-1}$: 3118, 3054, 2977, 2923, 1716, 1589, 1508, 1479, 1378, 1241, 1178, 1092, 1033, 813, 705, 659.

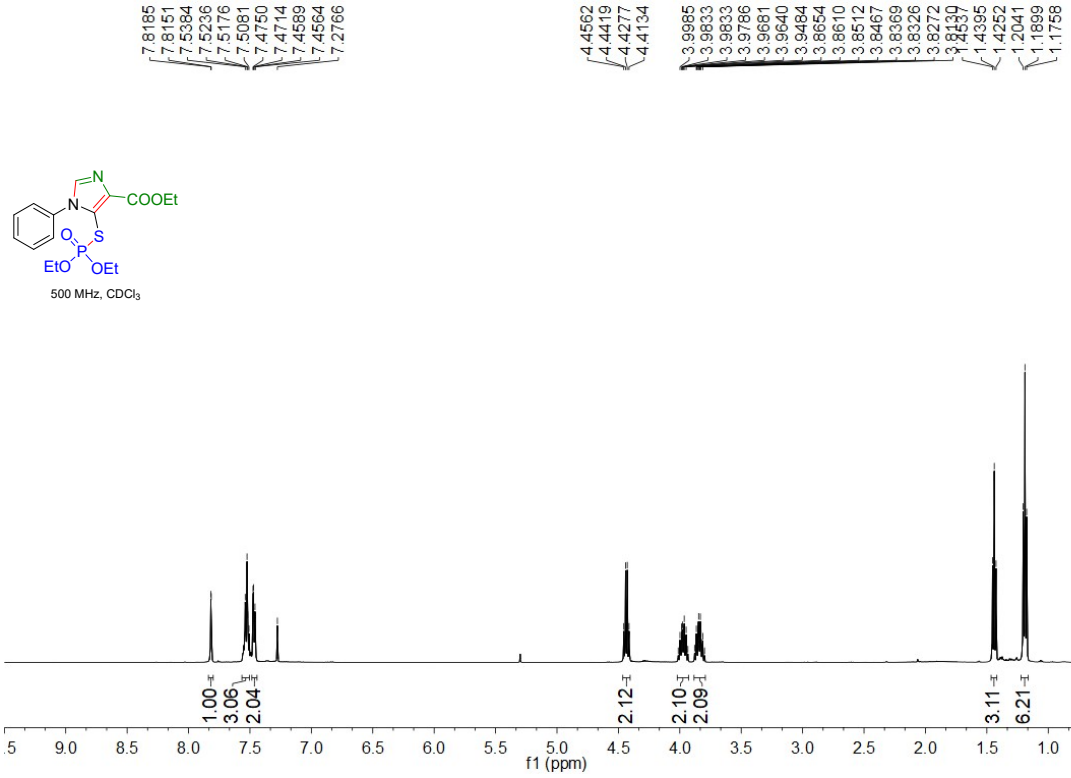



**Ethyl 1-(benzo[d][1,3]dioxol-5-yl)-5-((diethoxyphosphoryl)selanyl)-1H-imidazole-4-carboxylate (30d):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 59% isolated yield (140.4 mg). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 6.94 (s, 1H), 6.88 (s, 2H), 6.06 (s, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.14 – 4.01 (m, 2H), 4.00 – 3.91 (m, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.1, 148.5, 147.9, 140.9, 129.4, 129.2, 127.4, 121.3, 108.8, 108.0, 102.1, 64.2 (d, *J* = 6.3 Hz), 60.9, 15.8 (d, *J* = 7.5 Hz), 14.3. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{21}N_2O_7PSe$: 477.0324; found: 477.0324. IR (film) ν, $cm^{-1}$: 3112, 3054, 2979, 2919, 1712, 1612, 1488, 1452, 1378, 1243, 1218, 1182, 1037, 815, 705, 659.

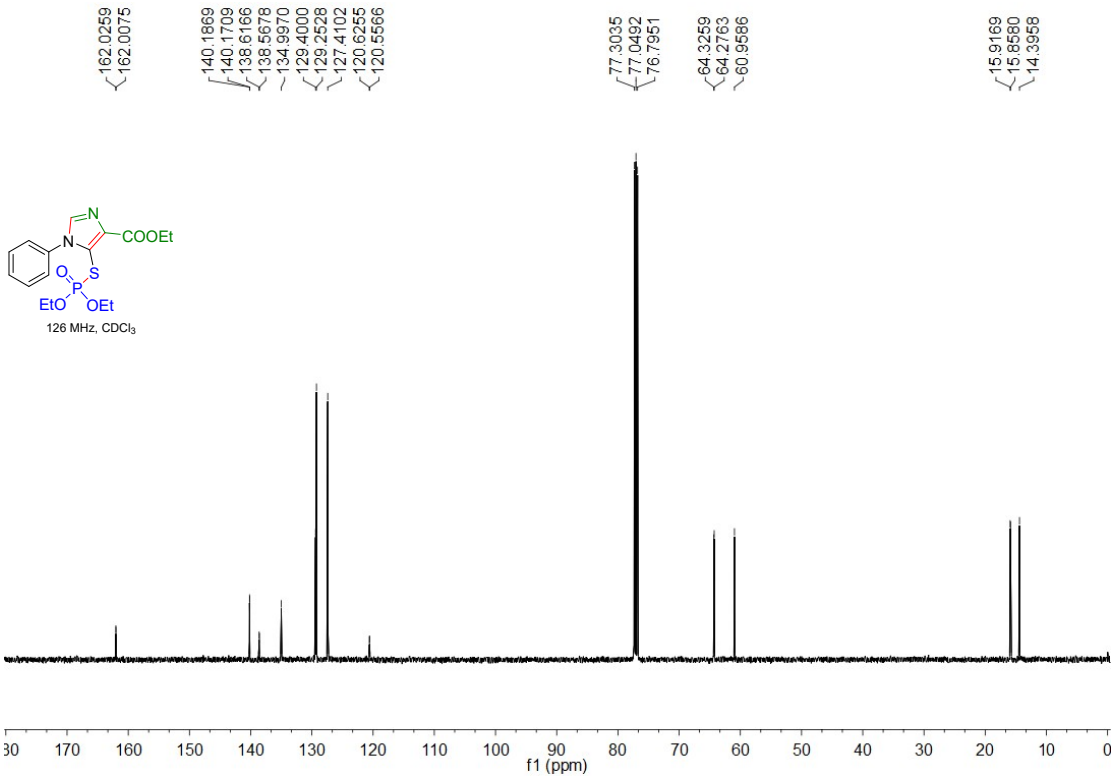
## 8. Copies of product NMR Spectra

**1d**

### $^{1}$H NMR

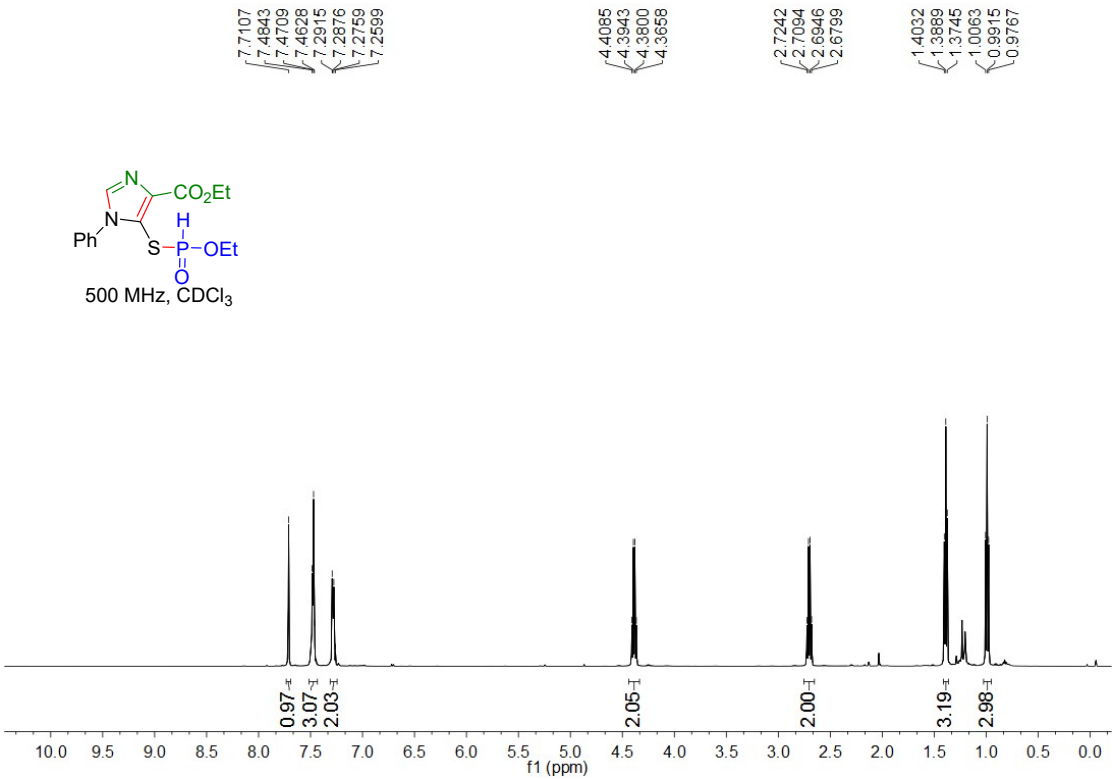



### $^{13}$C NMR

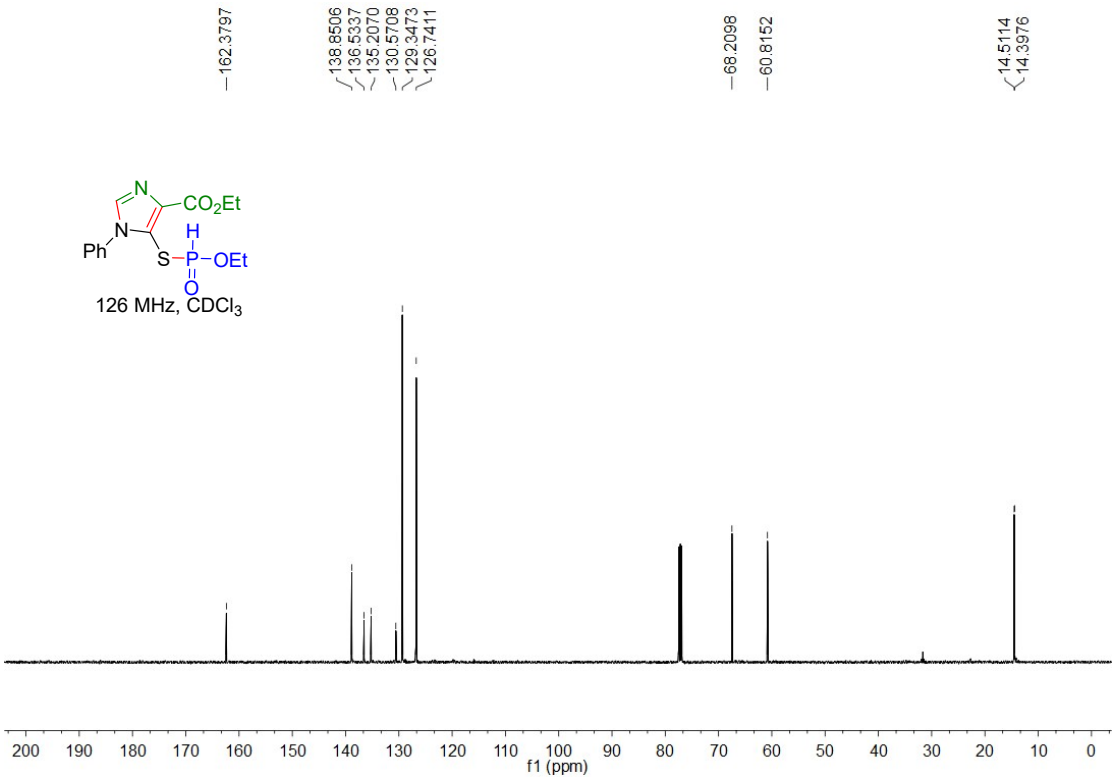


**1d'**

**$^{1}$H NMR**

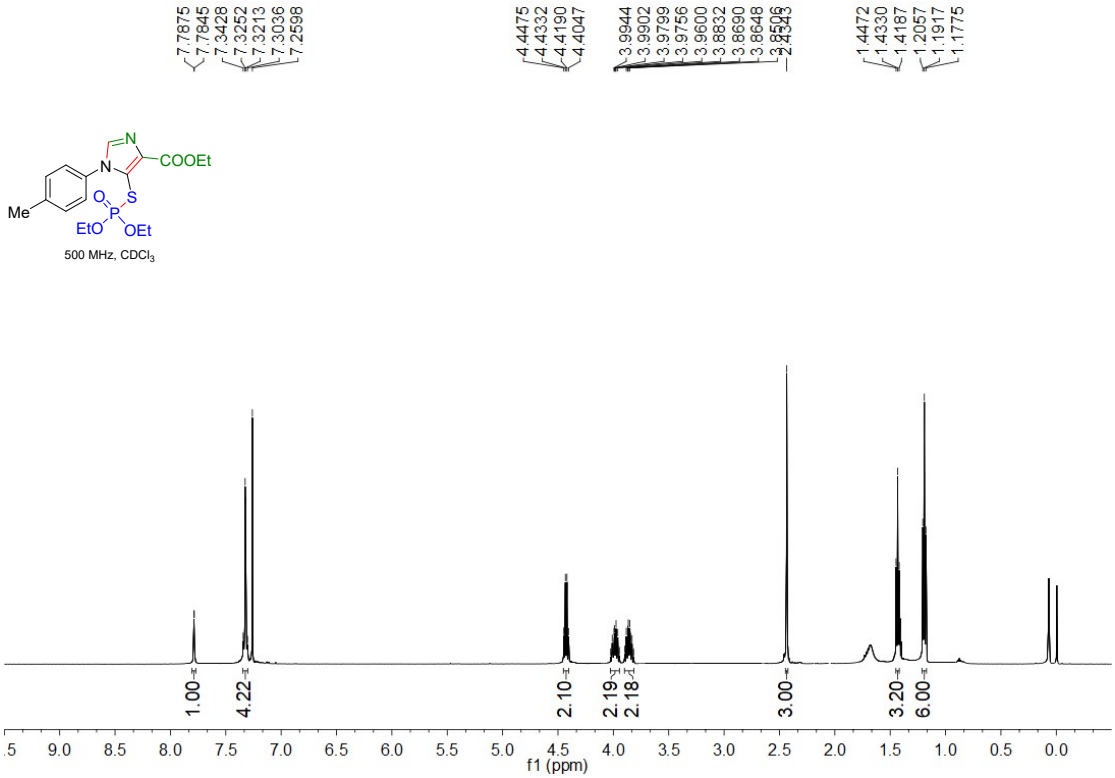



**$^{13}$C NMR**

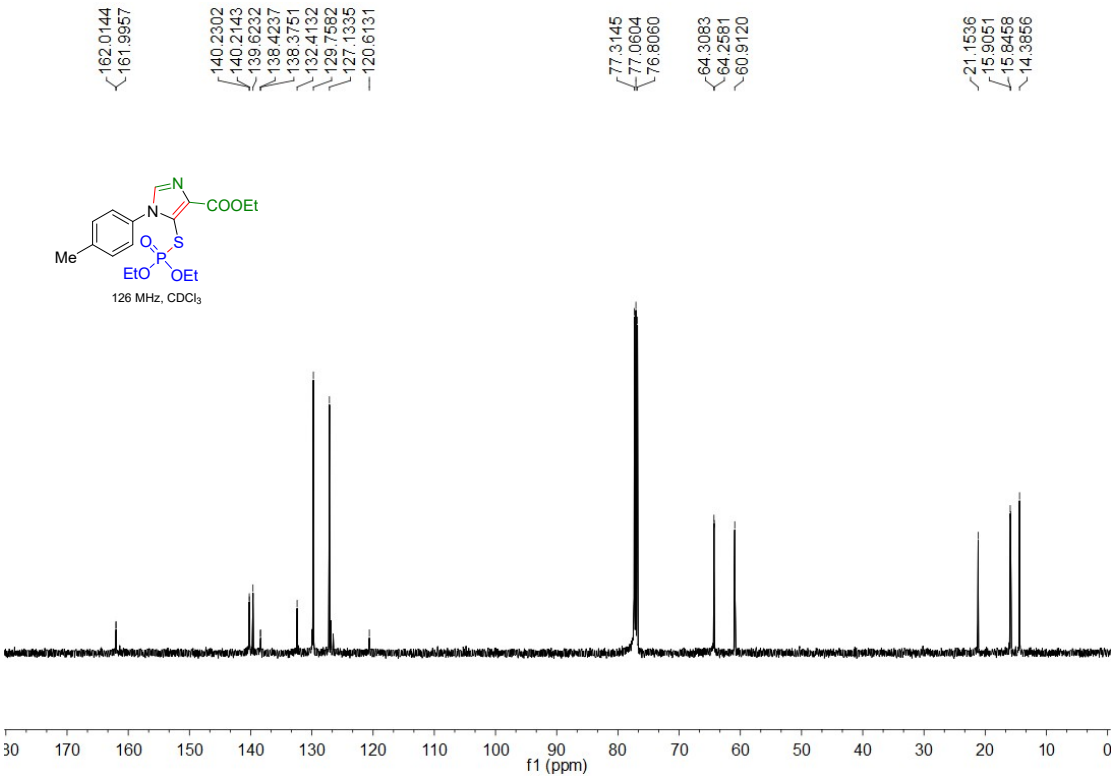


**2d**

**$^{1}$H NMR**

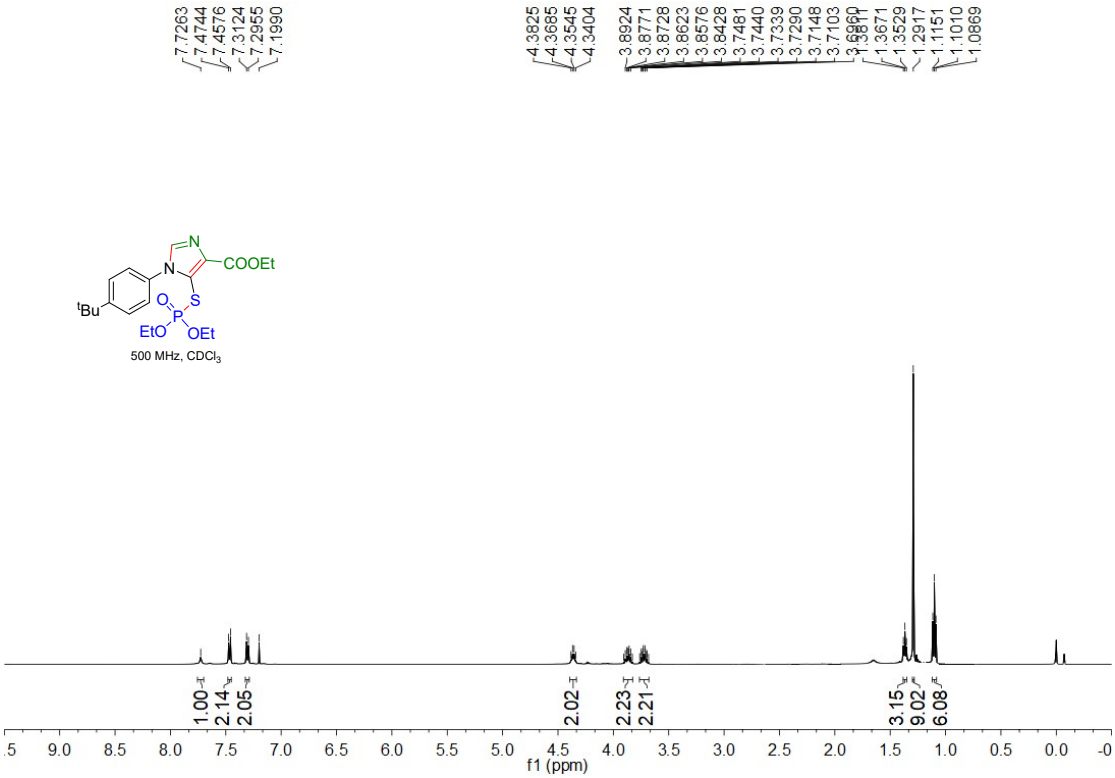



**$^{13}$C NMR**

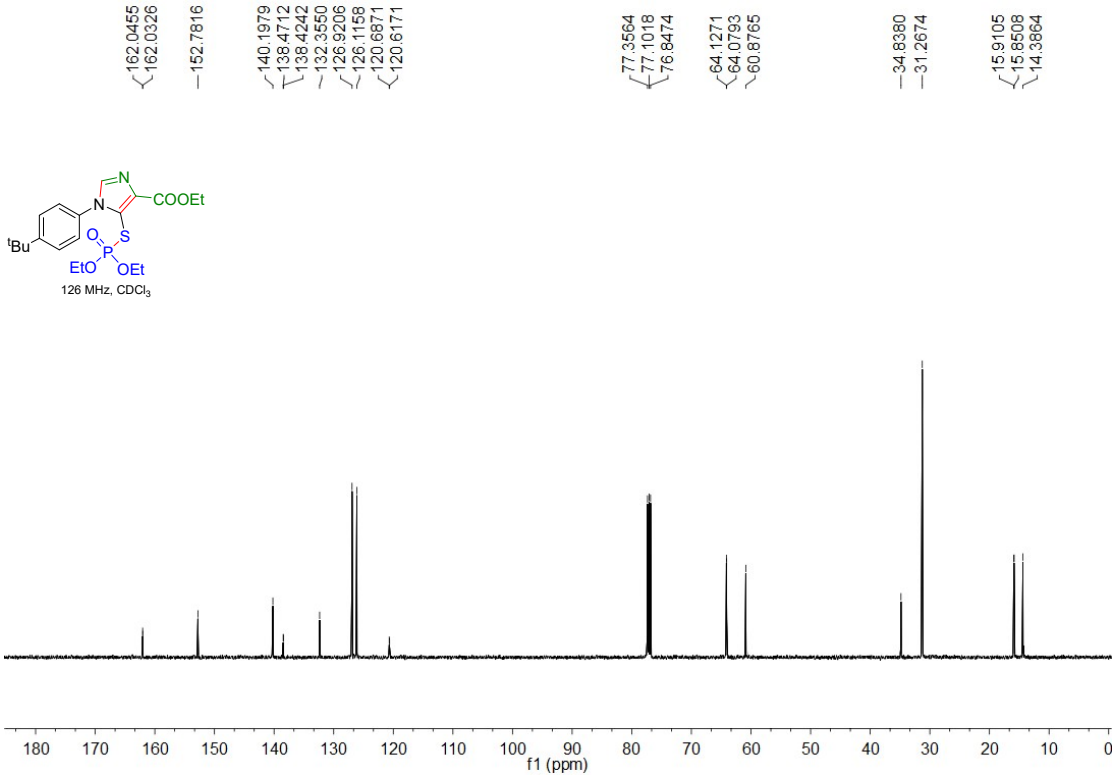


**3d**

**$^{1}$H NMR**

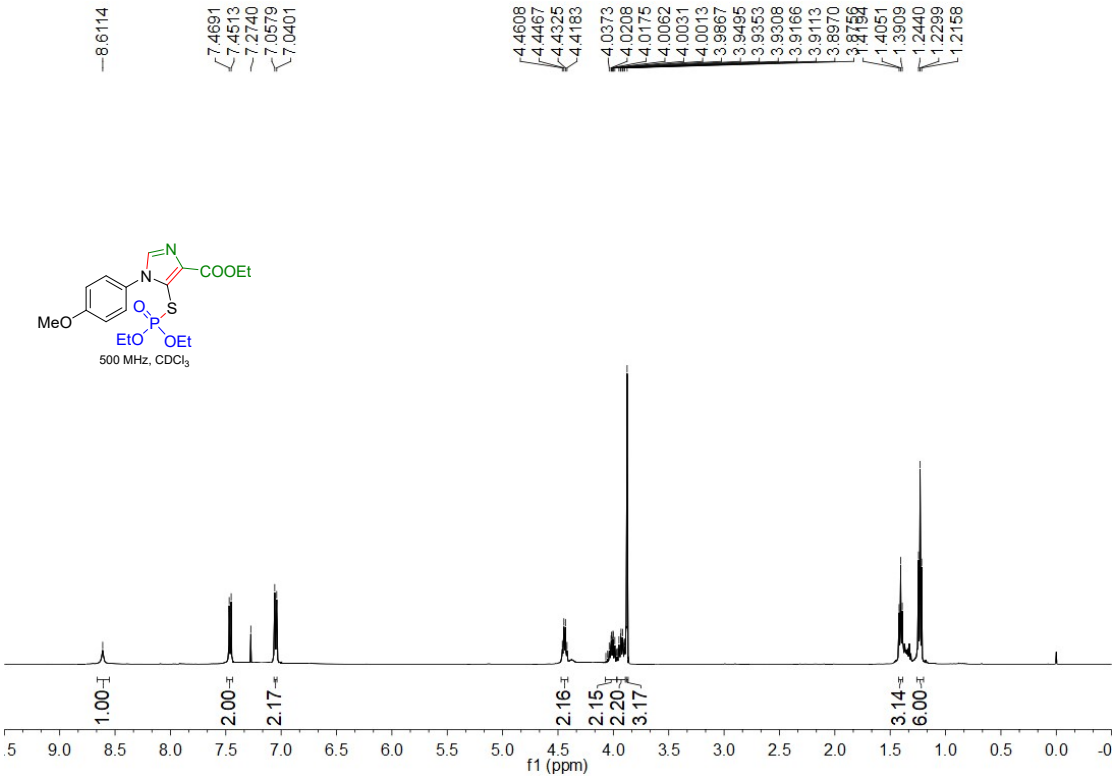



**$^{13}$C NMR**

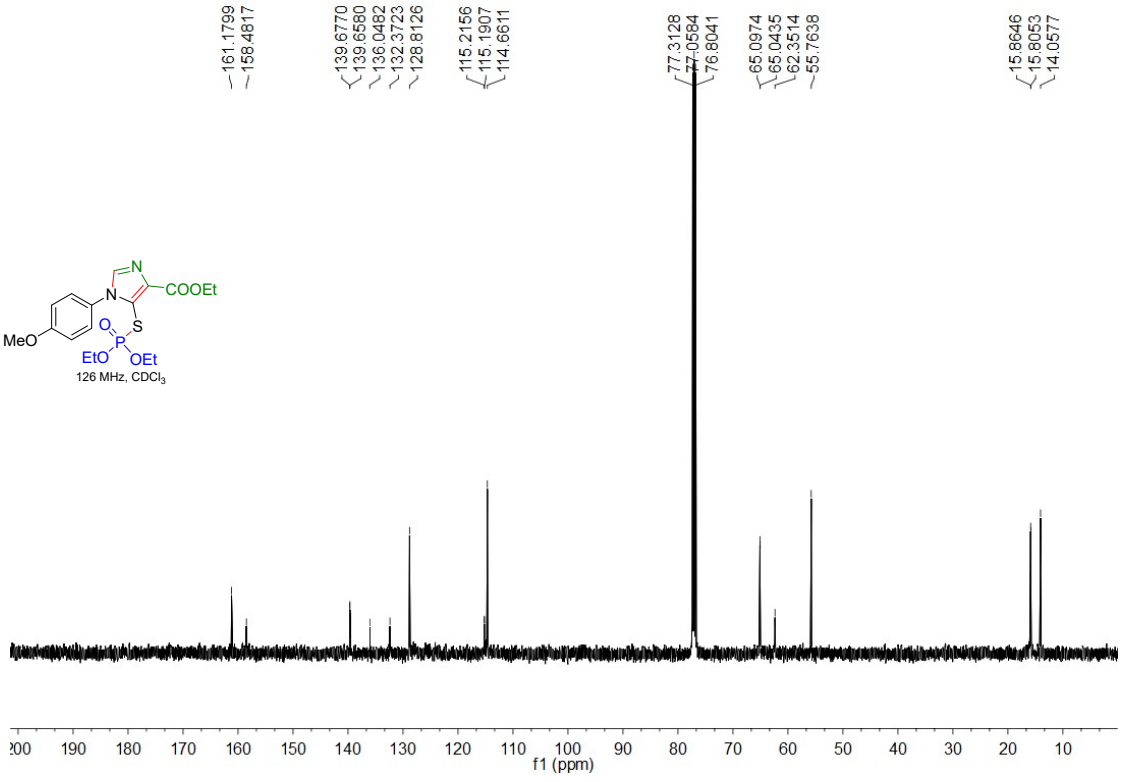


**4d**

**$^{1}$H NMR**

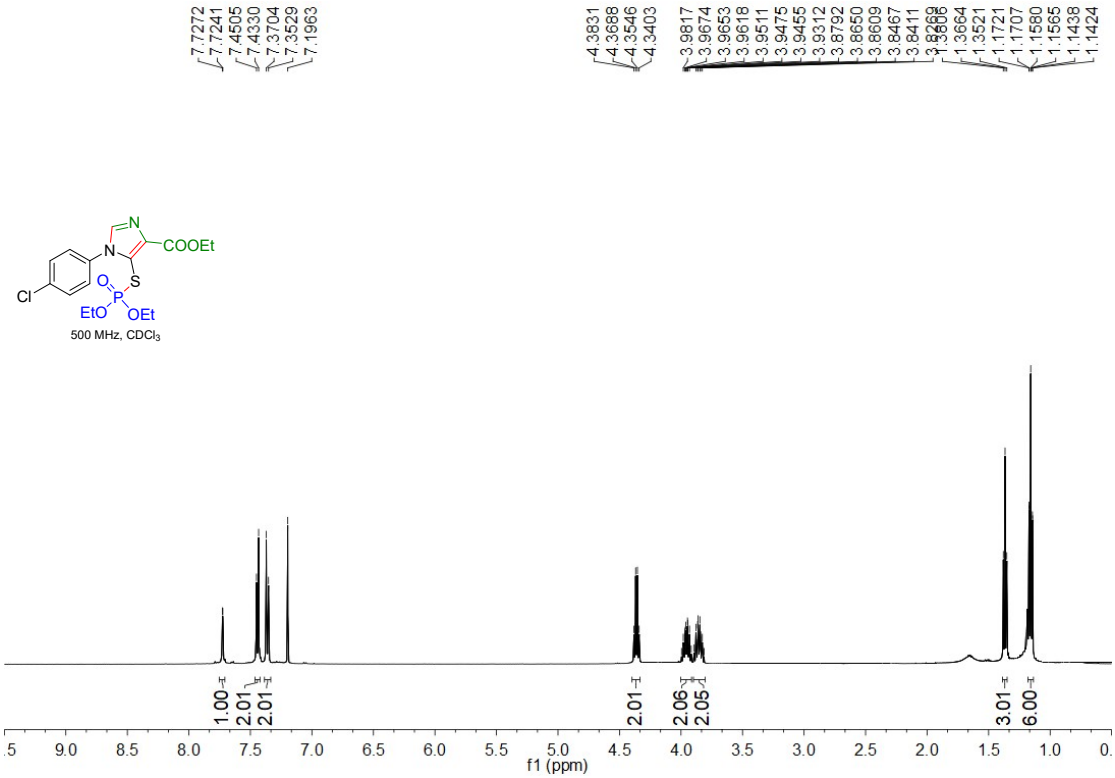



**$^{13}$C NMR**

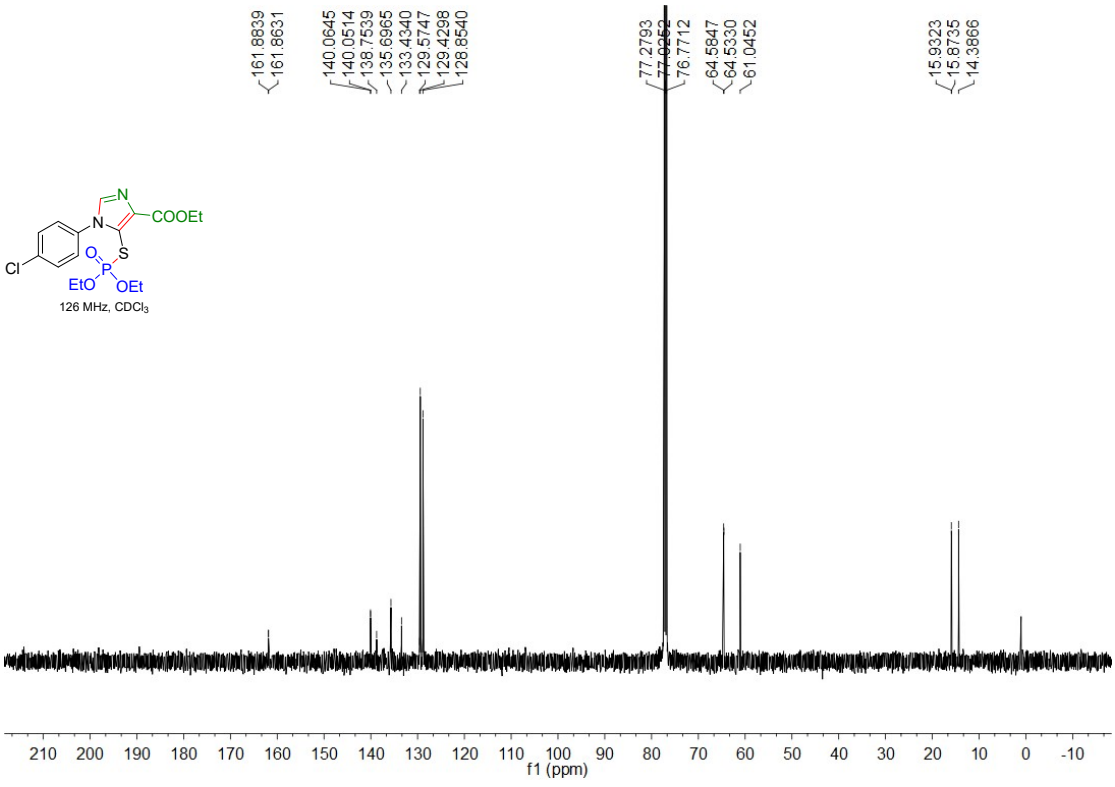


**5d**

**$^{1}$H NMR**

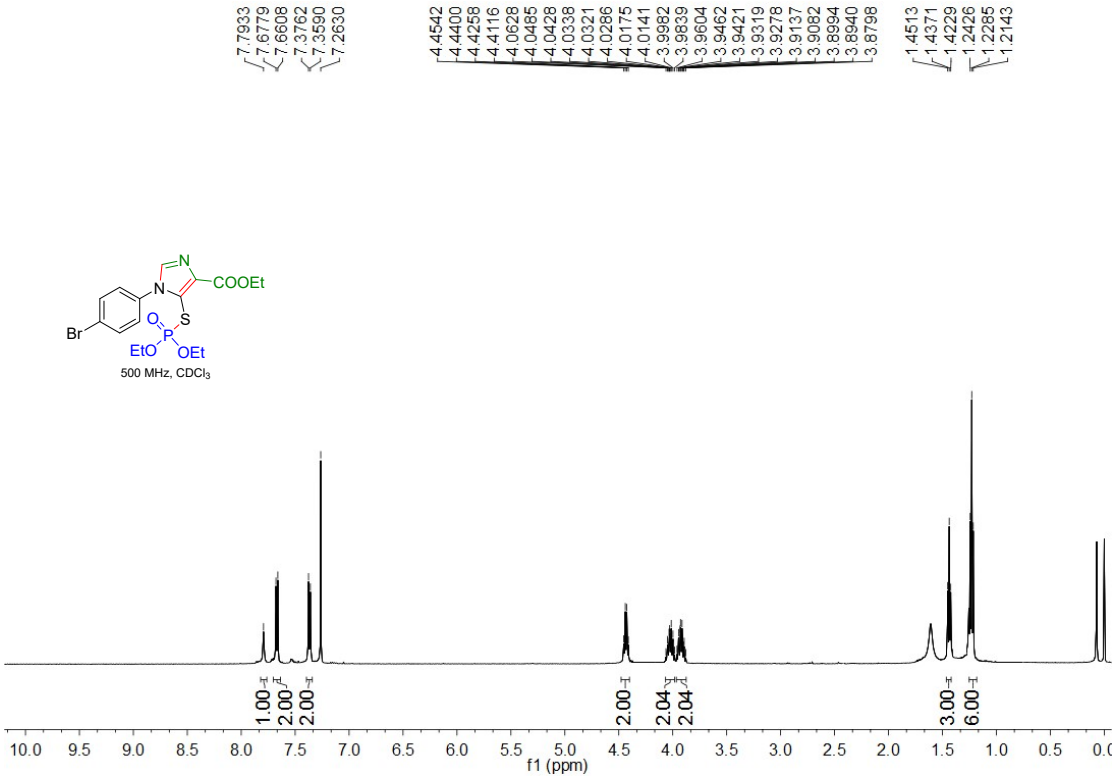



**$^{13}$C NMR**

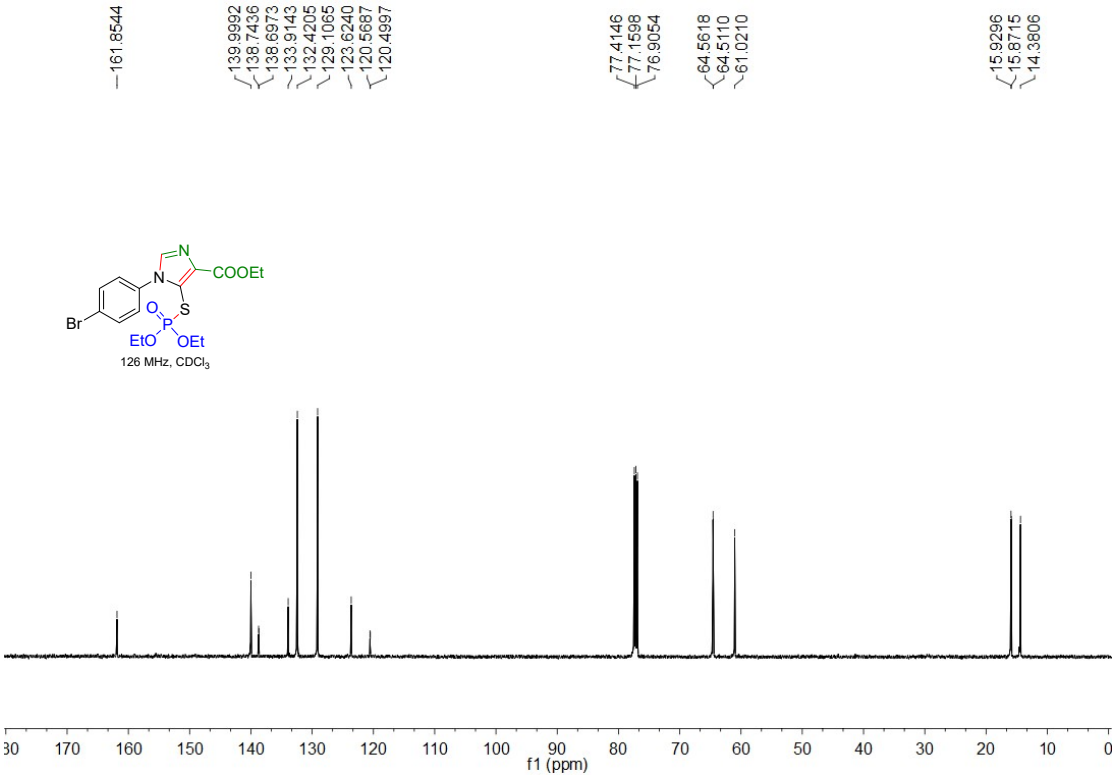


**6d**

**$^{1}$H NMR**

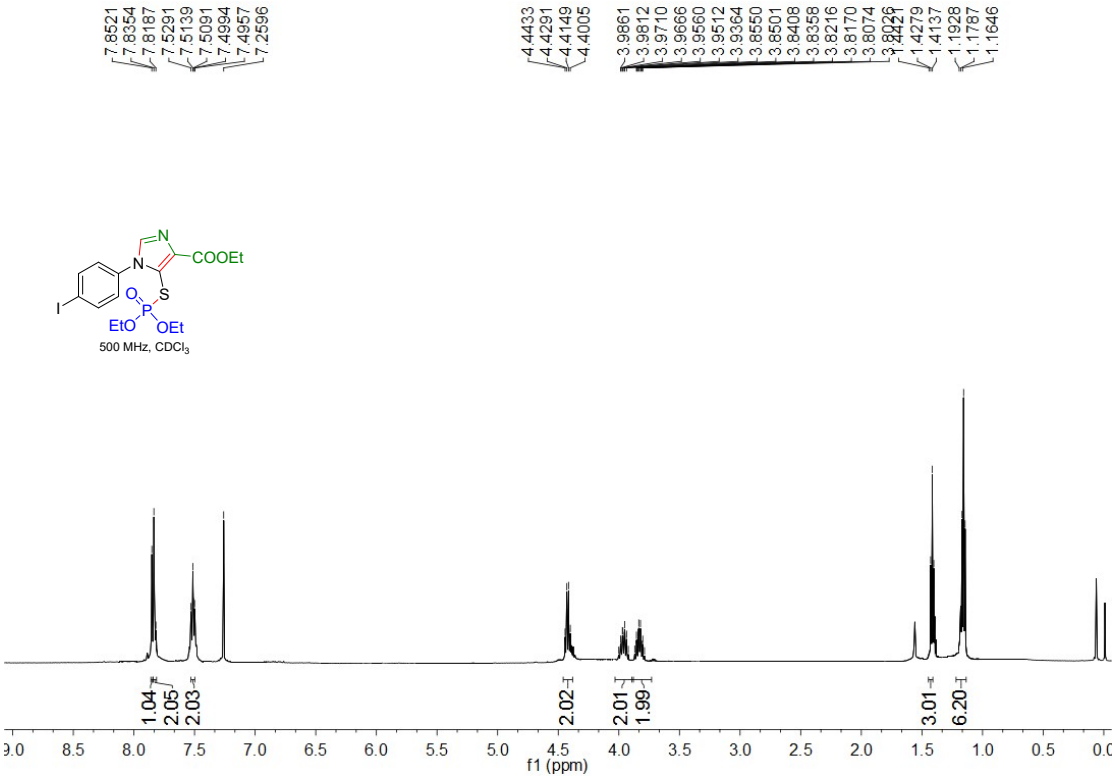



**$^{13}$C NMR**

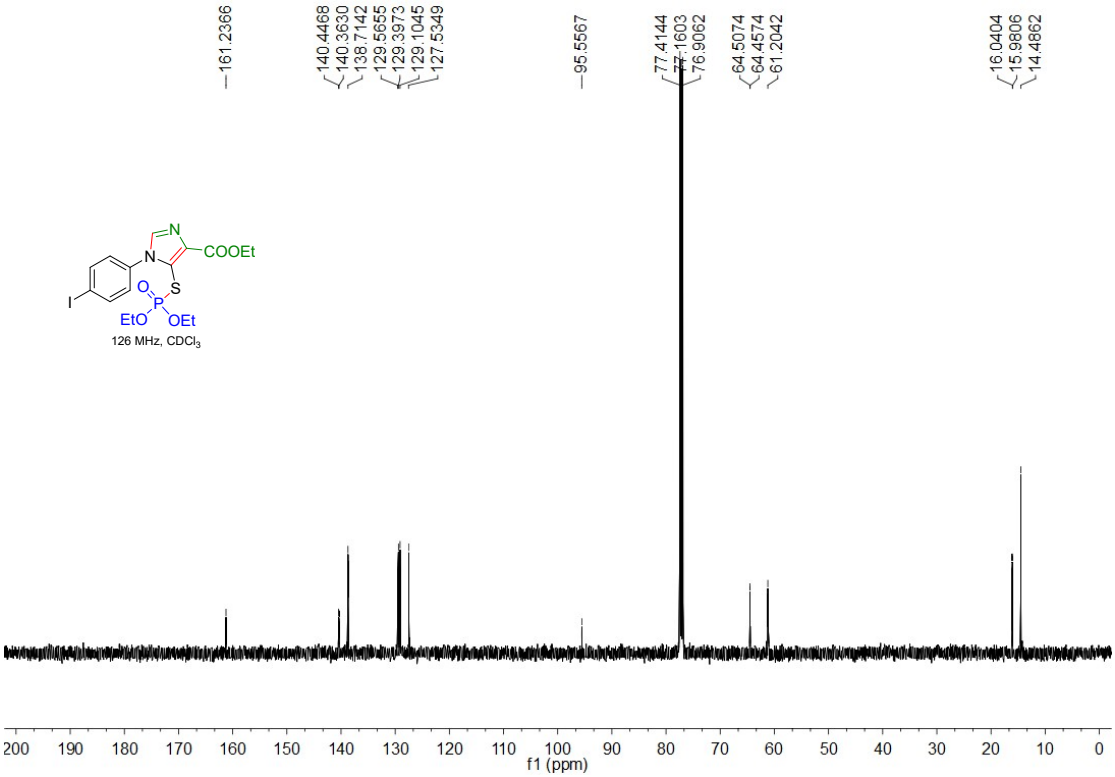


**7d**

**$^{1}$H NMR**

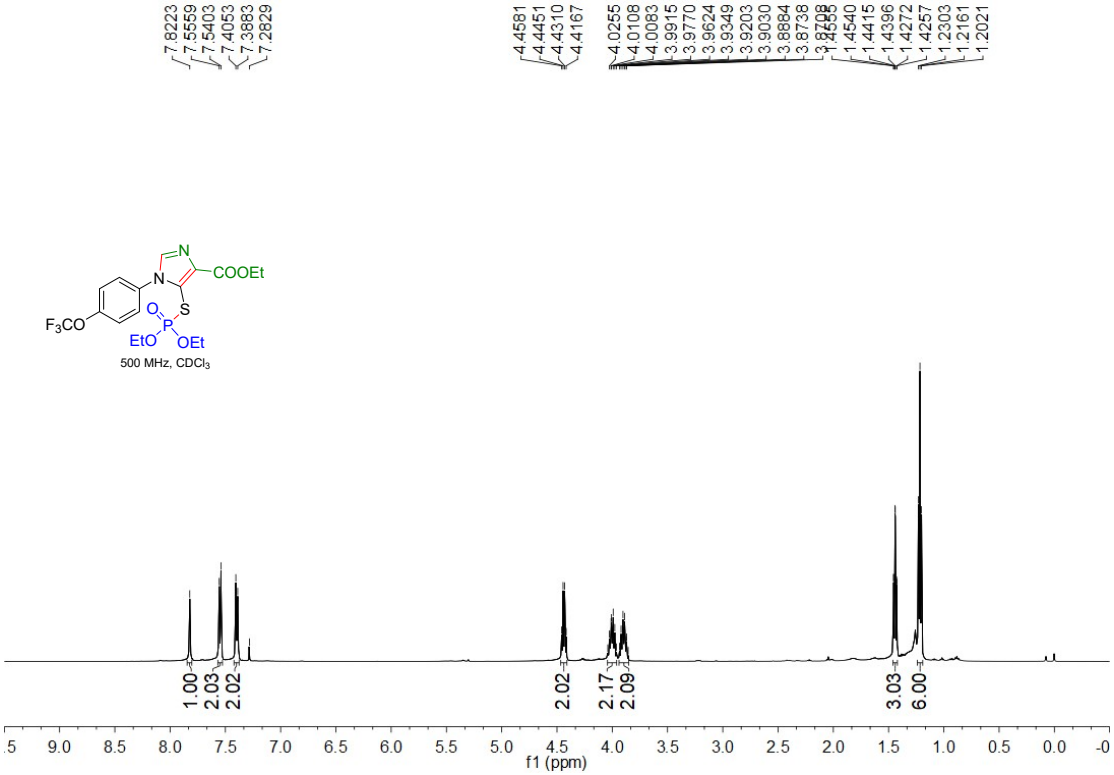



**$^{13}$C NMR**

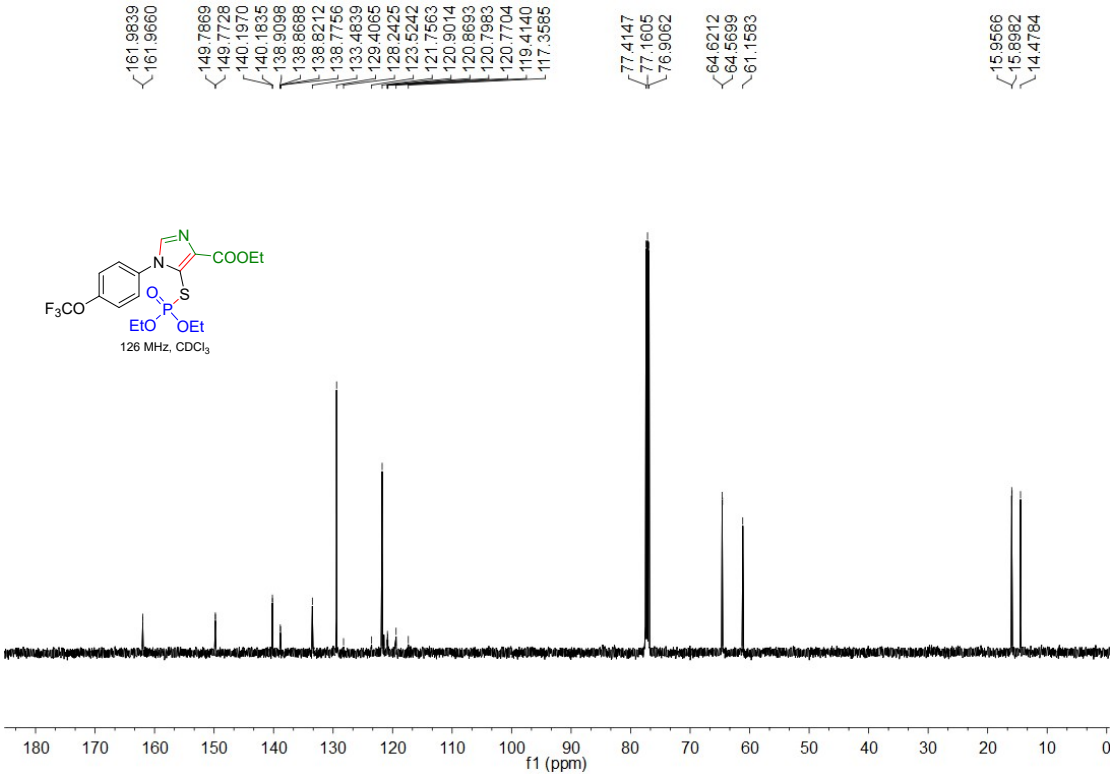


**8d**

**$^{1}$H NMR**

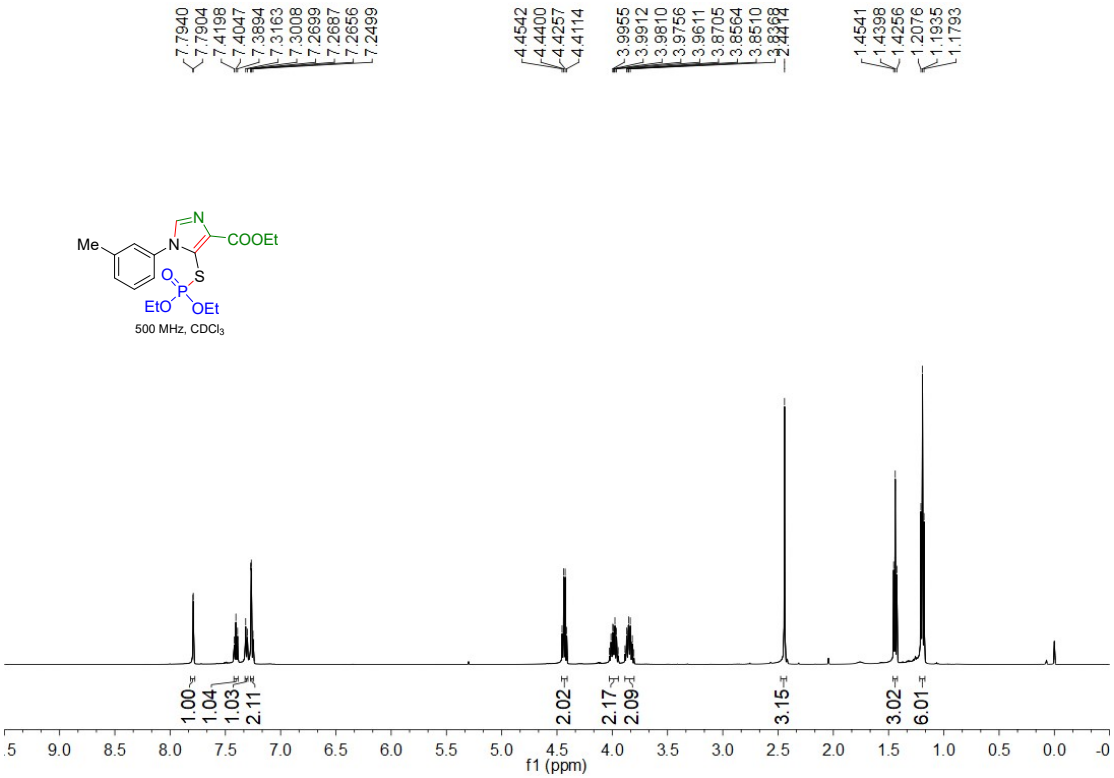



**$^{13}$C NMR**

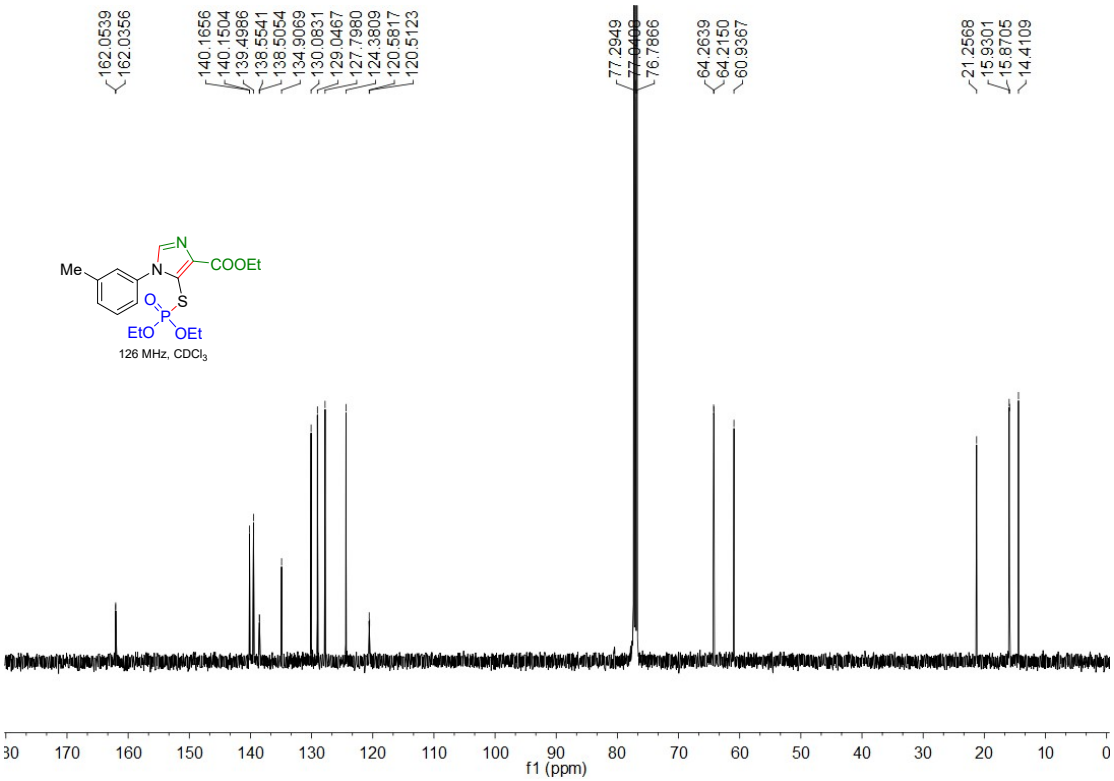


**9d**

**$^{1}$H NMR**

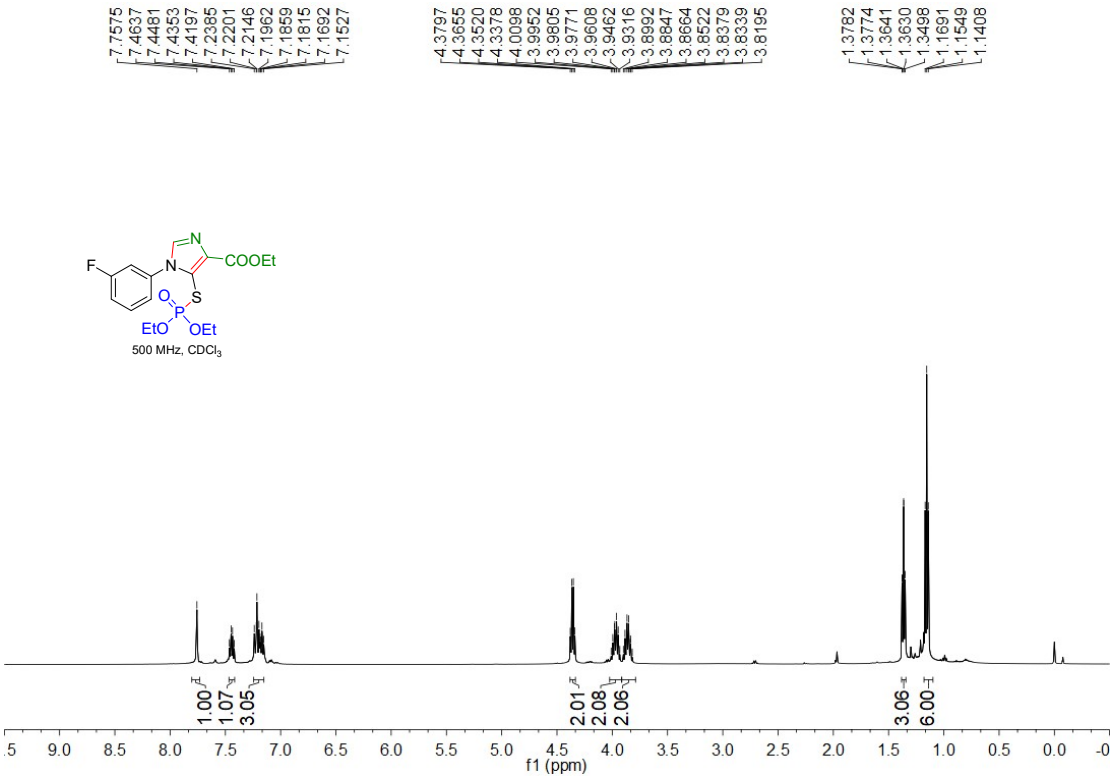



**$^{13}$C NMR**

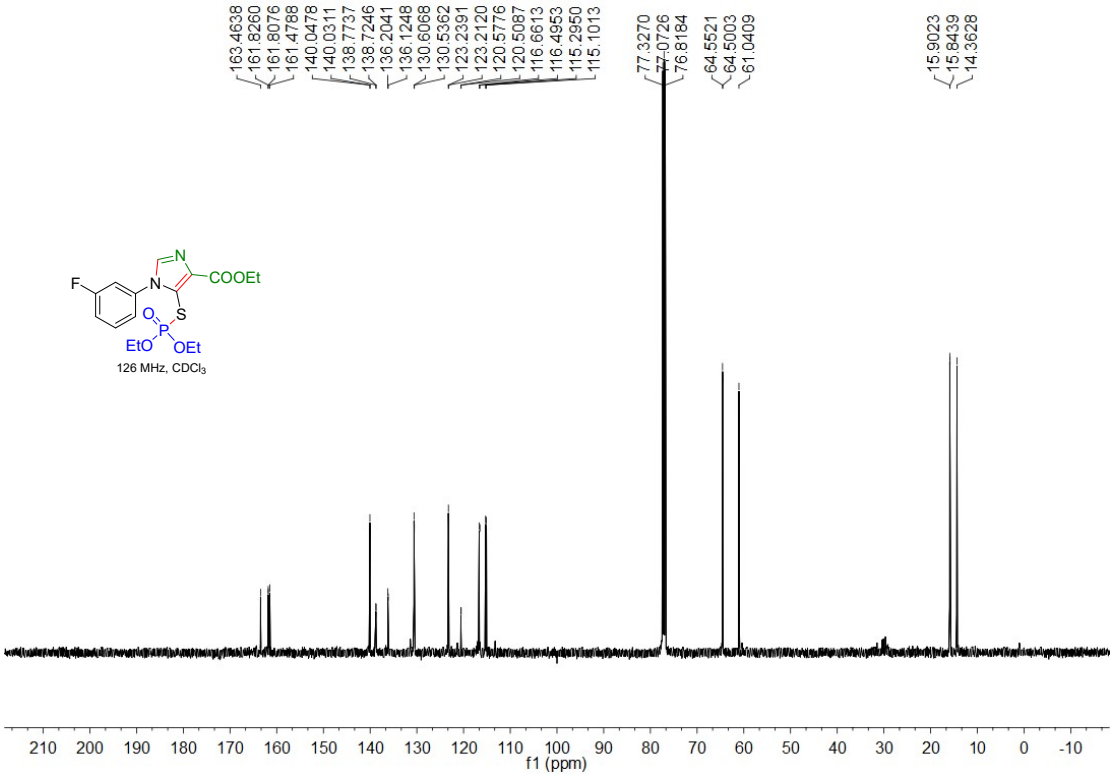


**10d**

**$^{1}$H NMR**

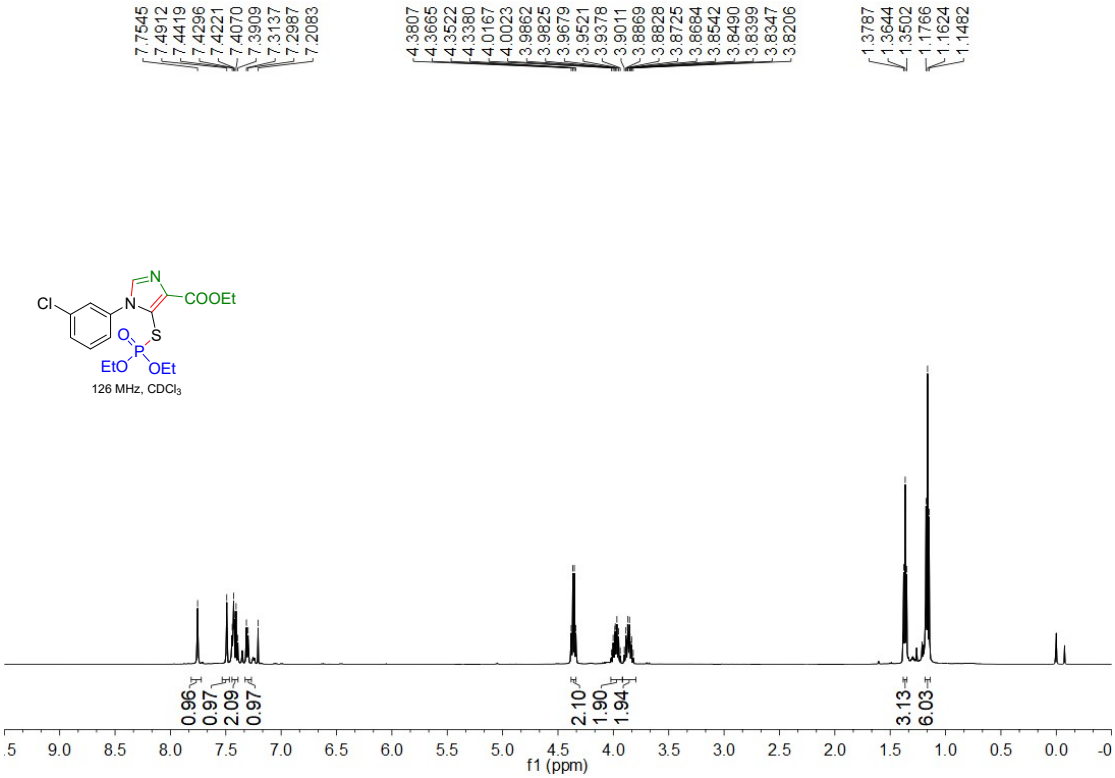



**$^{13}$C NMR**

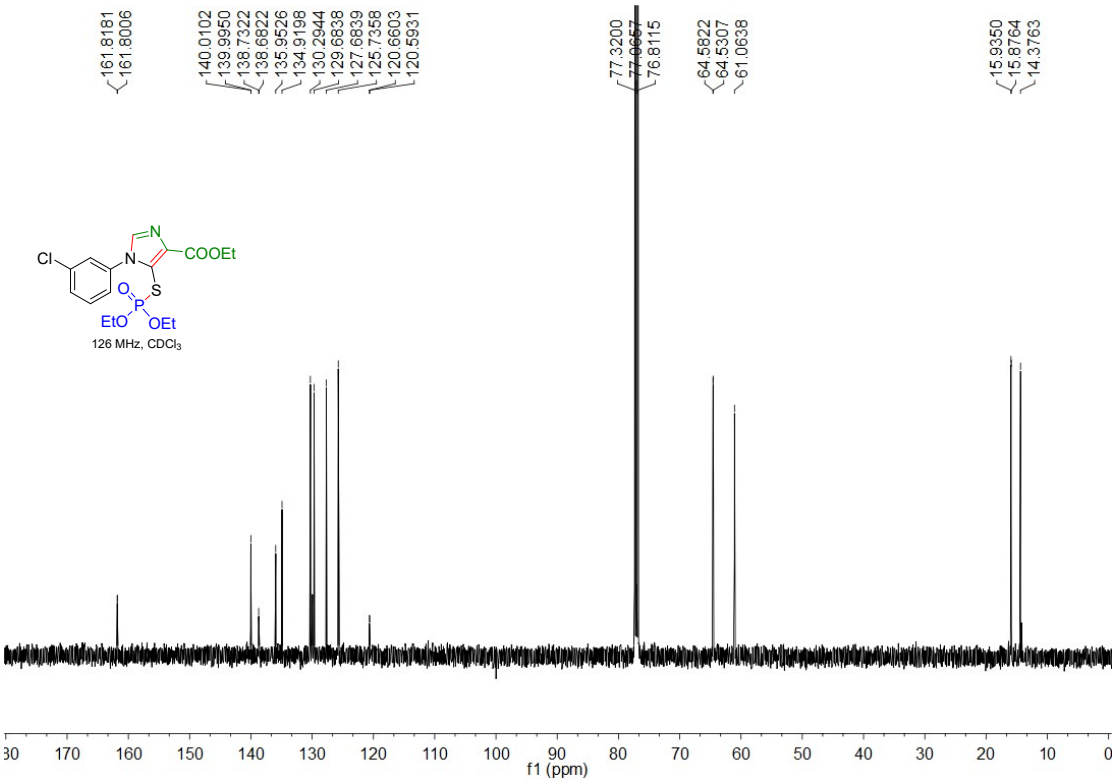


**11d**

**$^{1}$H NMR**

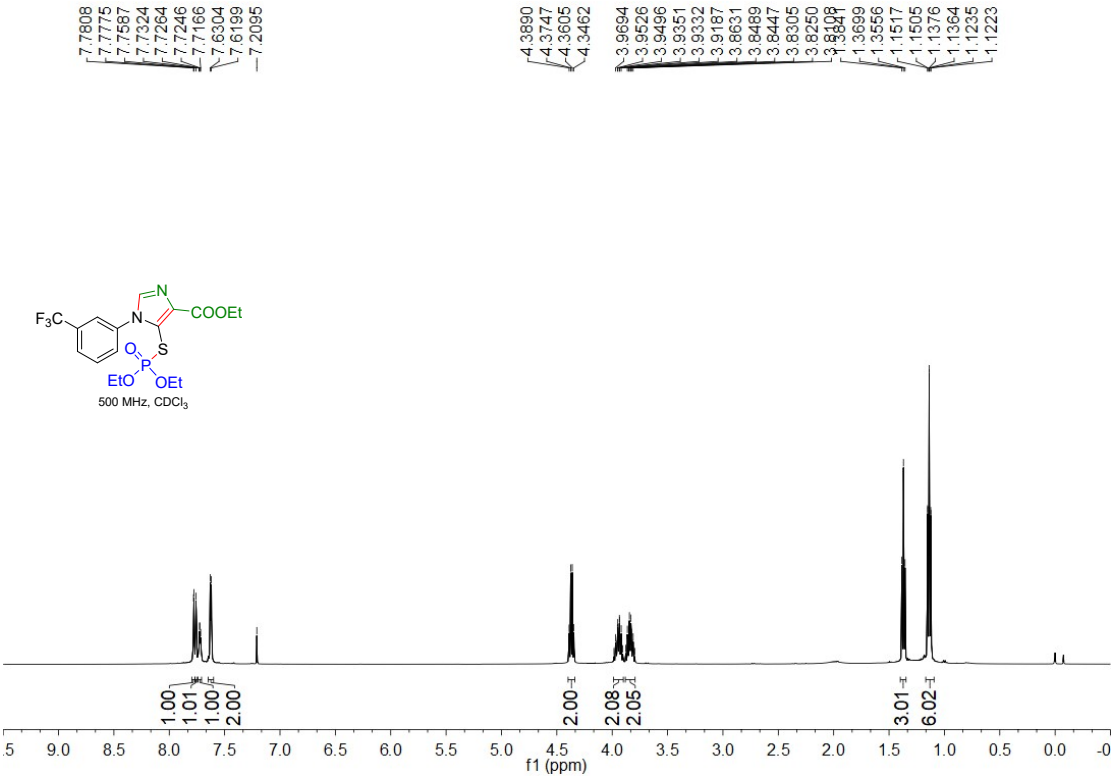



**$^{13}$C NMR**

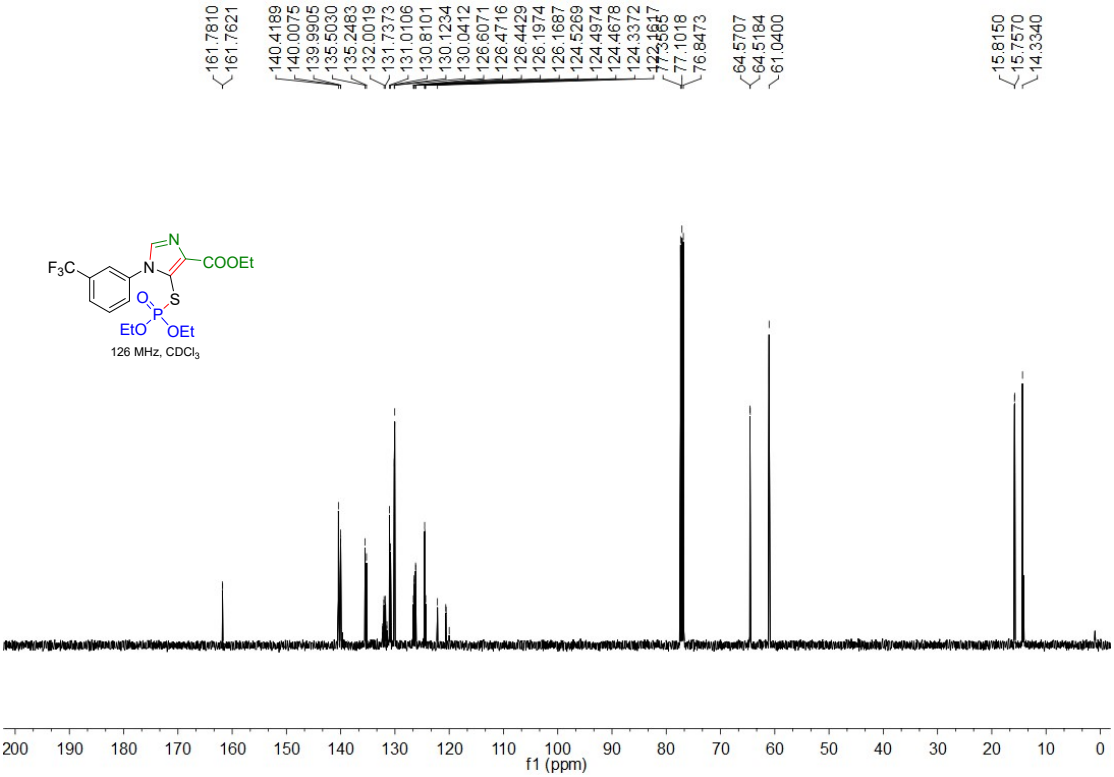


**12d**

**$^{1}$H NMR**

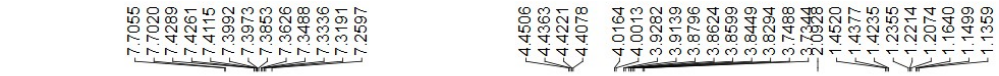


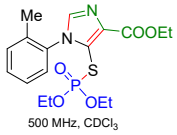

**$^{13}$C NMR**



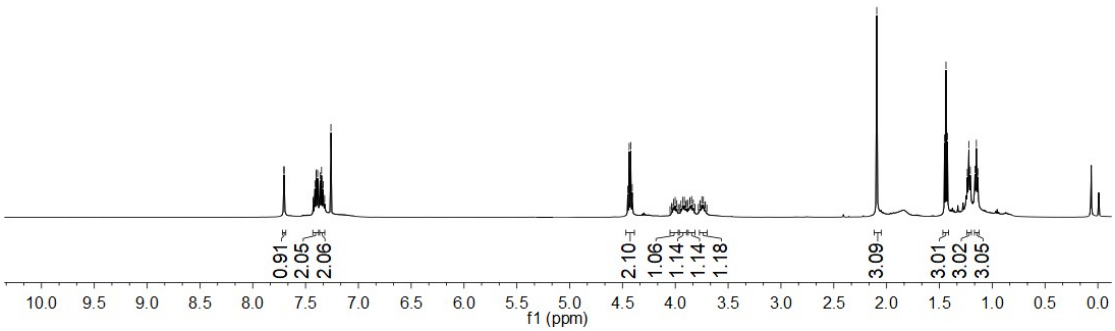
**13d**

**$^{1}$H NMR**

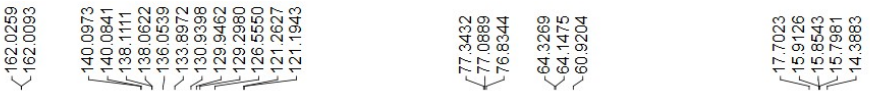


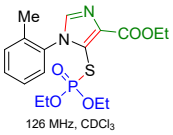




500 MHz, $CDCl_3$

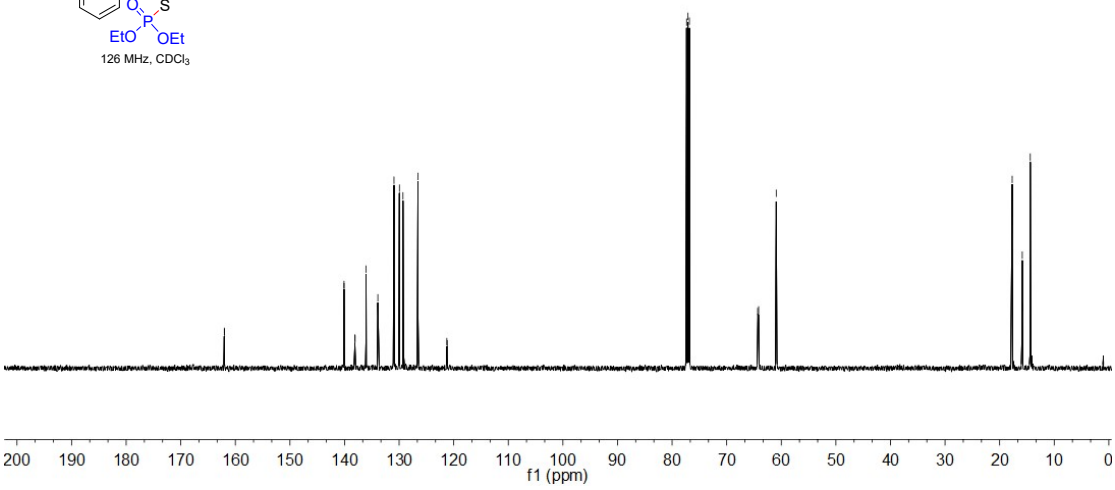



**$^{13}$C NMR**



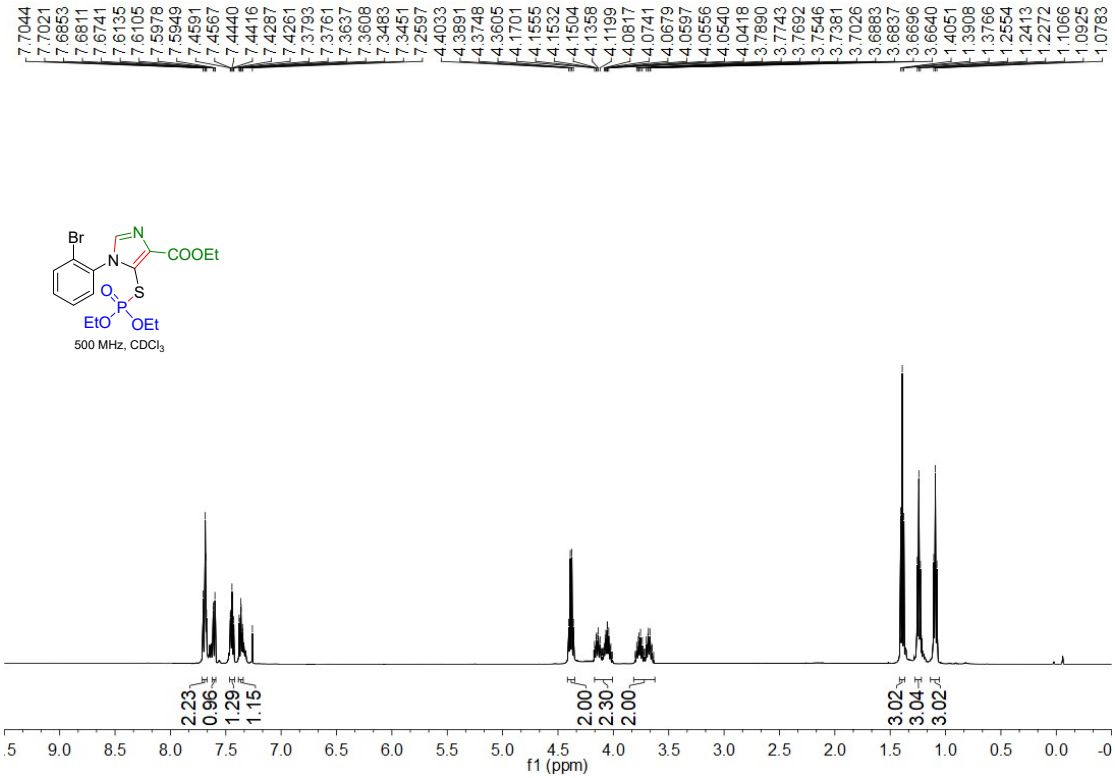




126 MHz, $CDCl_3$

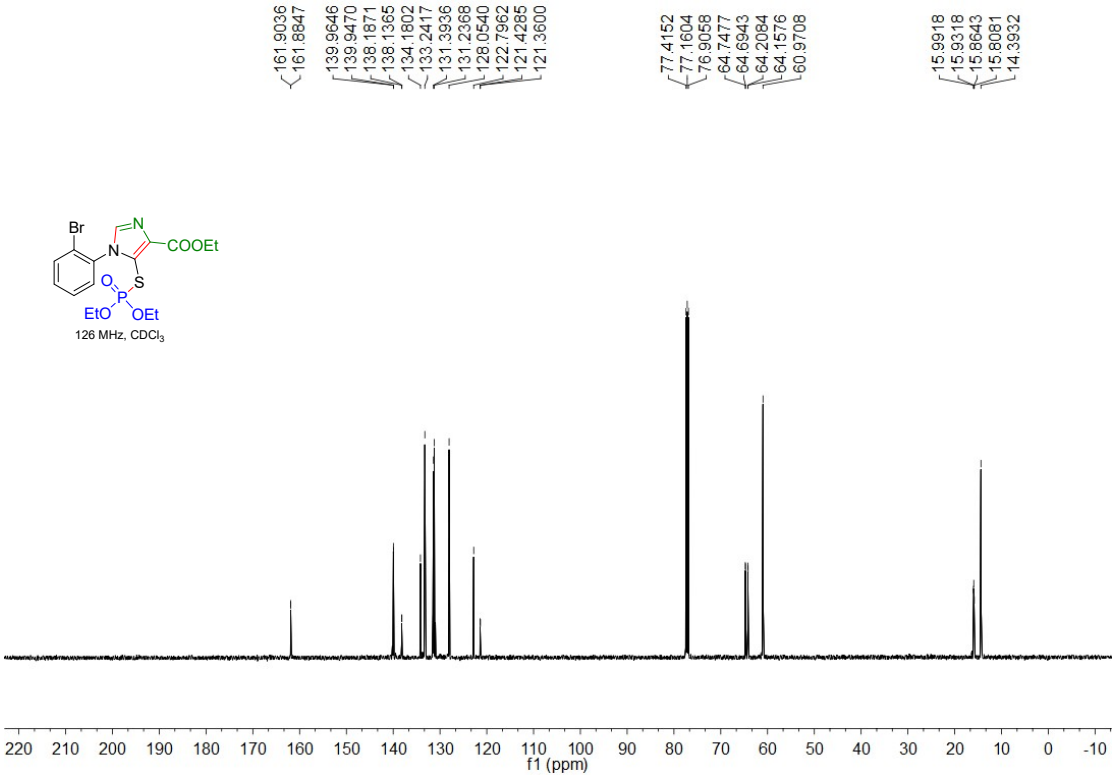


**14d**

**$^{1}$H NMR**

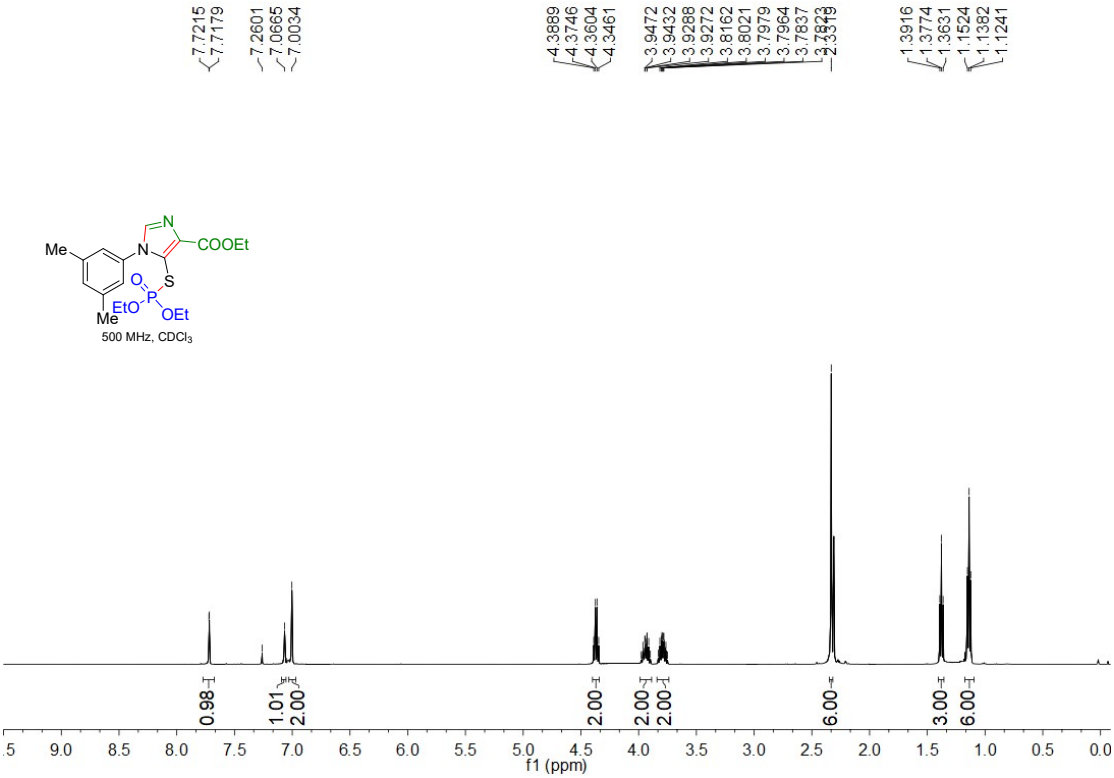



**$^{13}$C NMR**

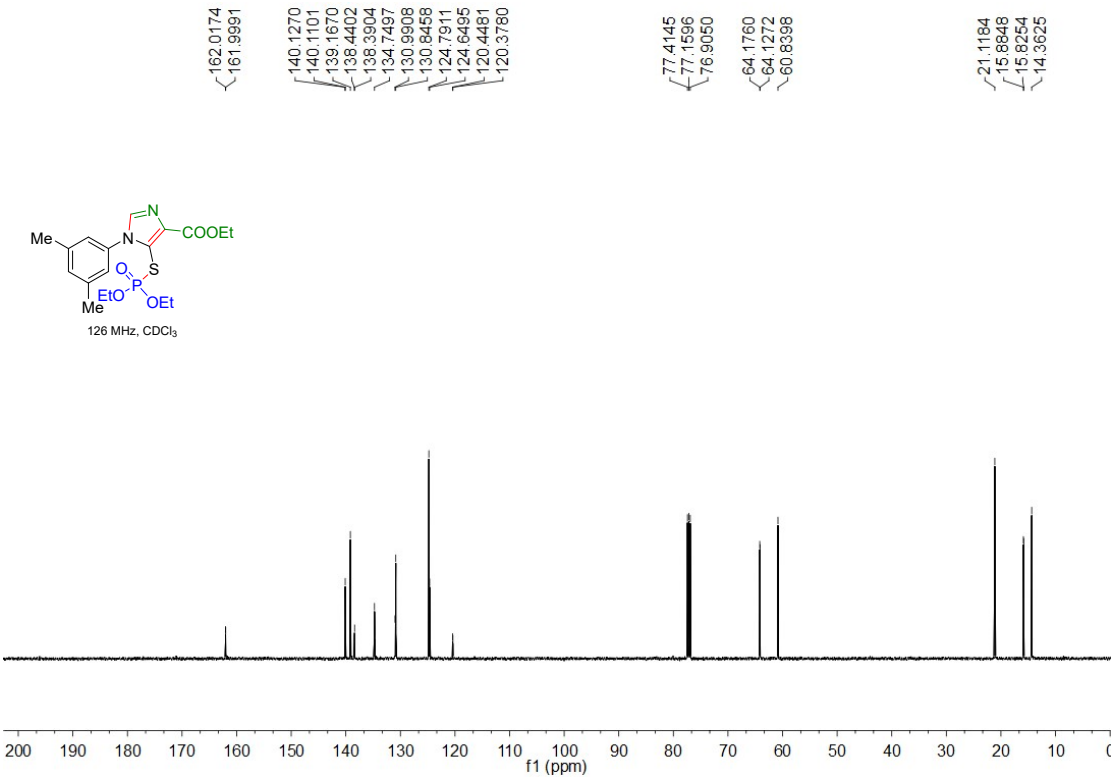


## 15d

**$^{1}$H NMR**

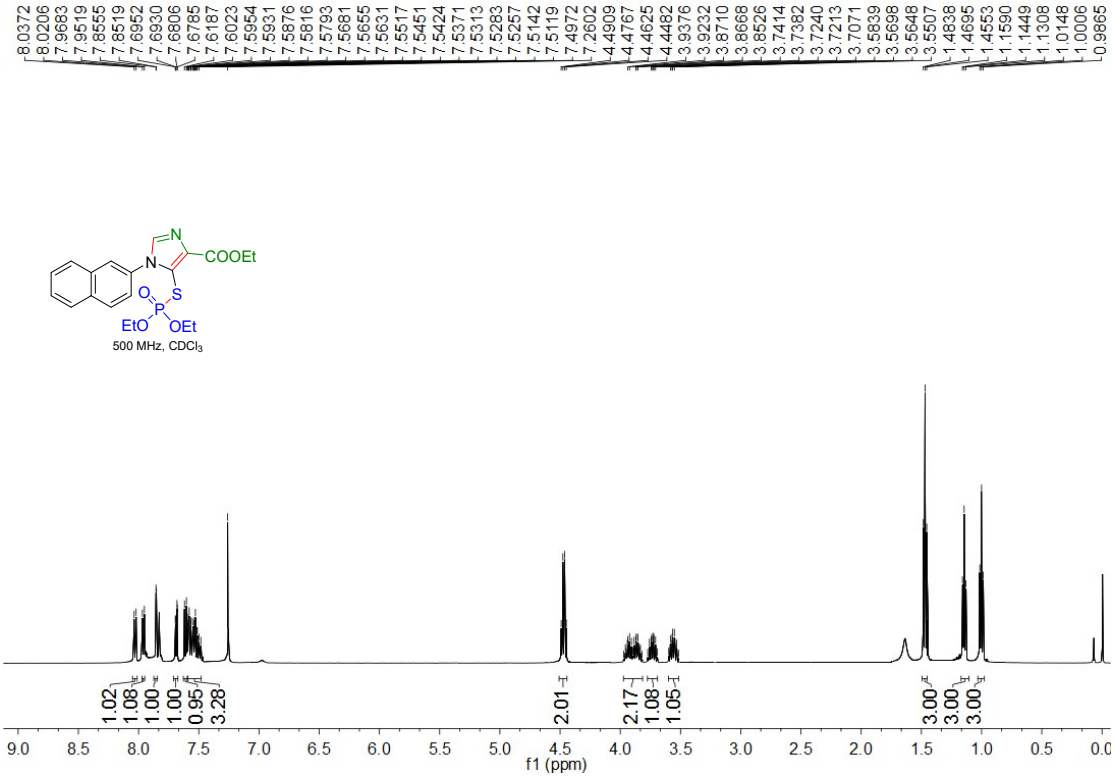



**$^{13}$C NMR**

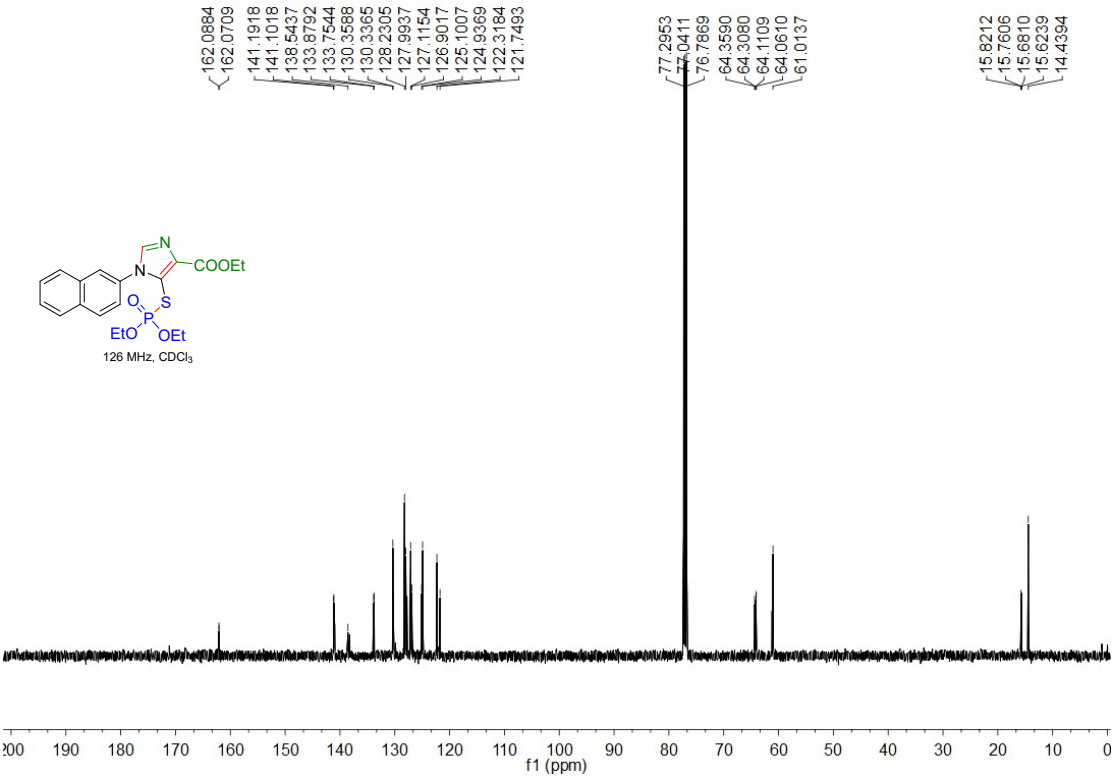


## 16d

**$^{1}$H NMR**

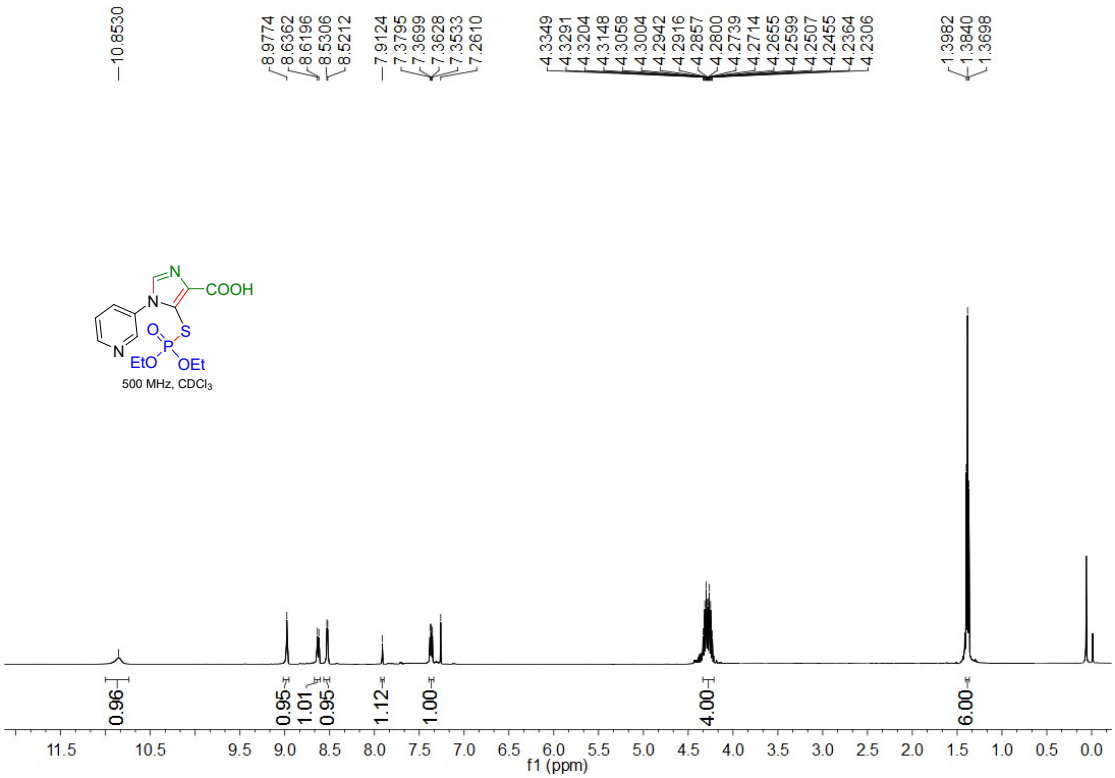



**$^{13}$C NMR**

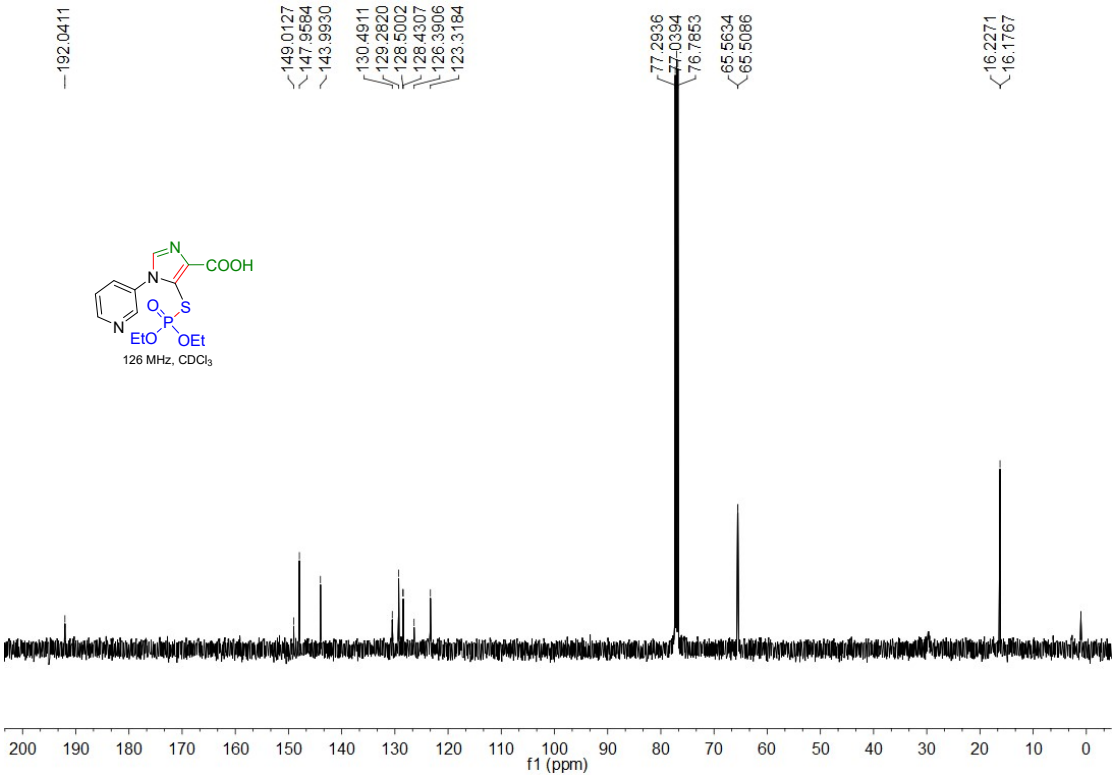


**17d**

**$^{1}$H NMR**

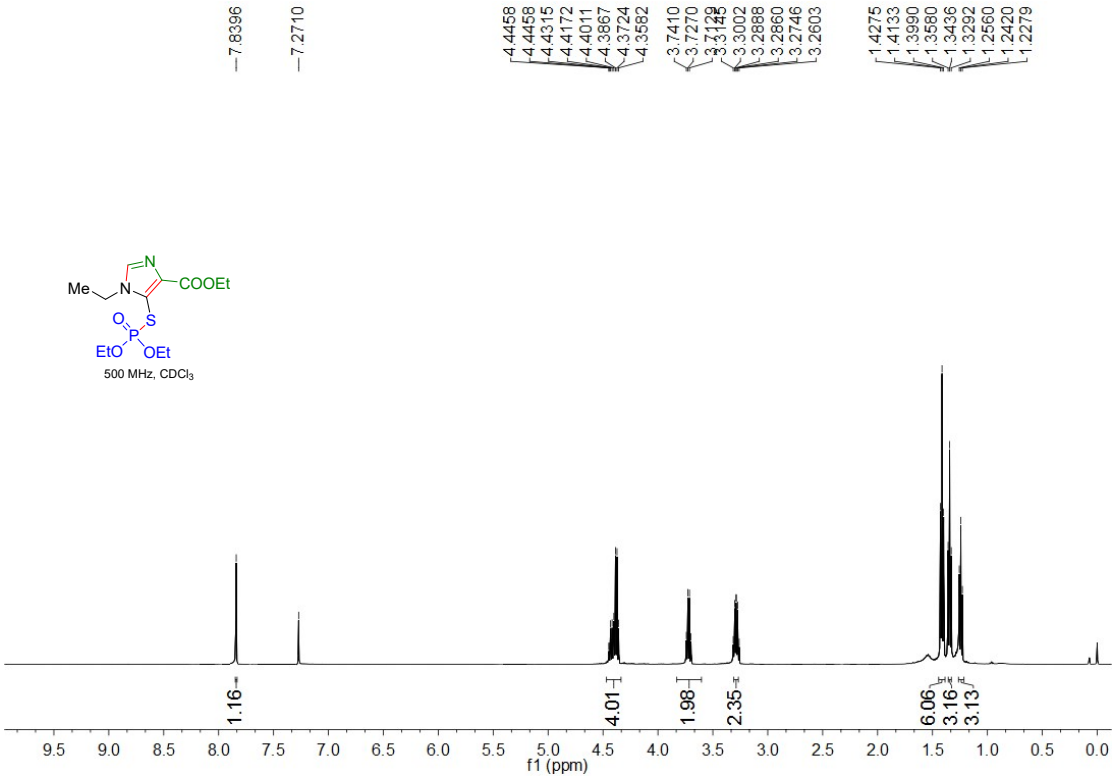



**$^{13}$C NMR**

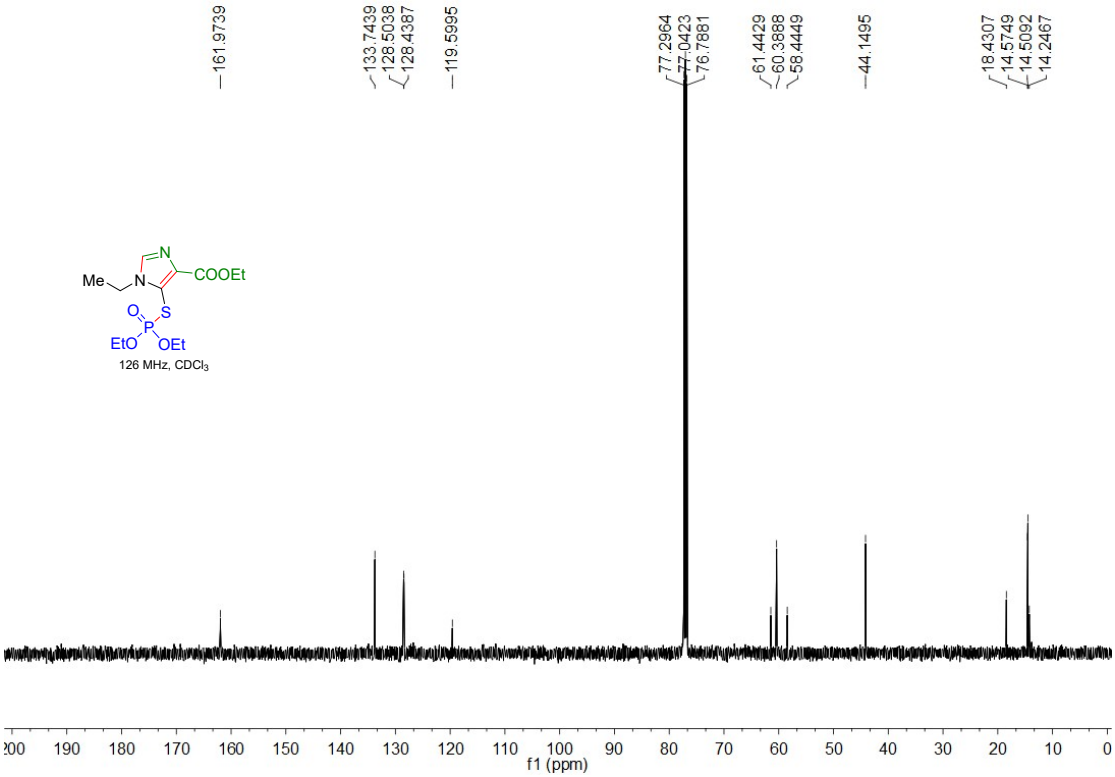


**18d**

**$^{1}$H NMR**

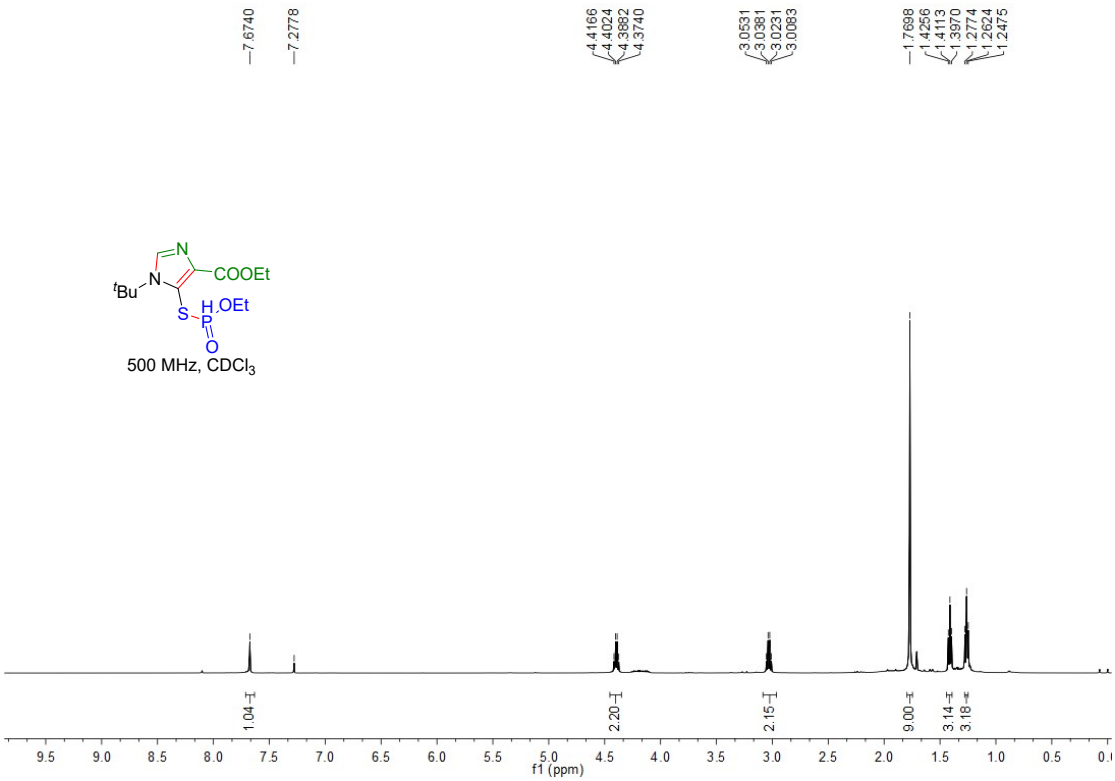



**$^{13}$C NMR**

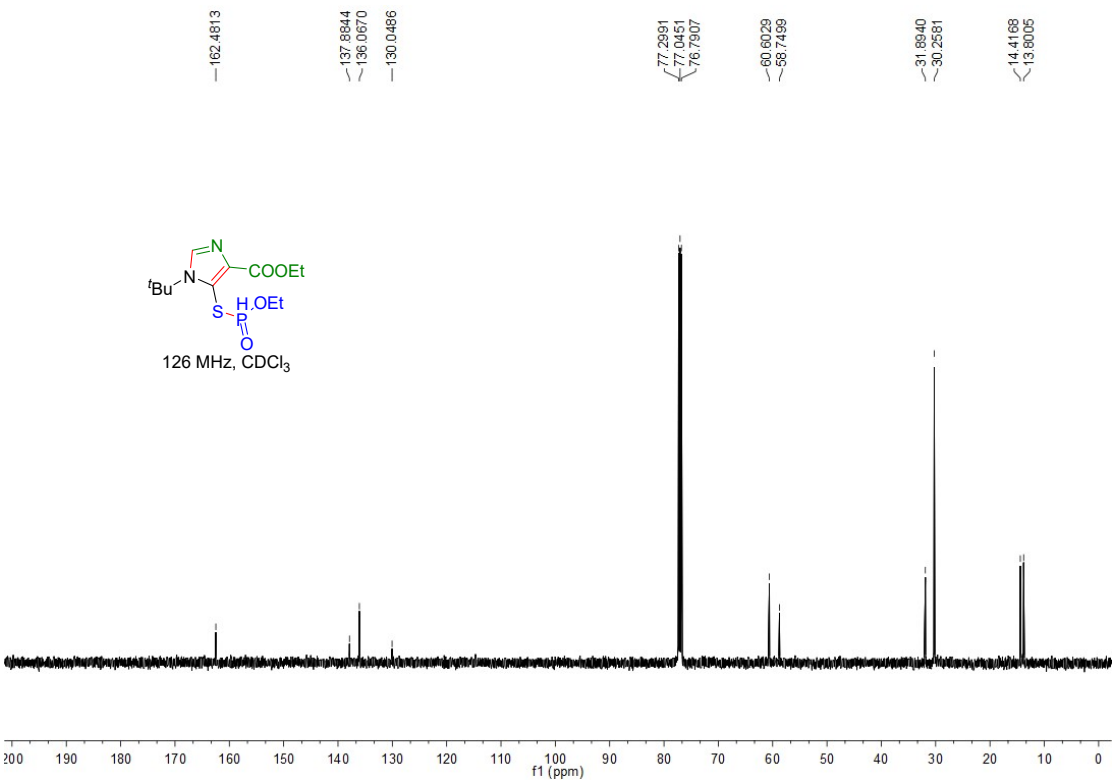


**19d**

**$^{1}$H NMR**

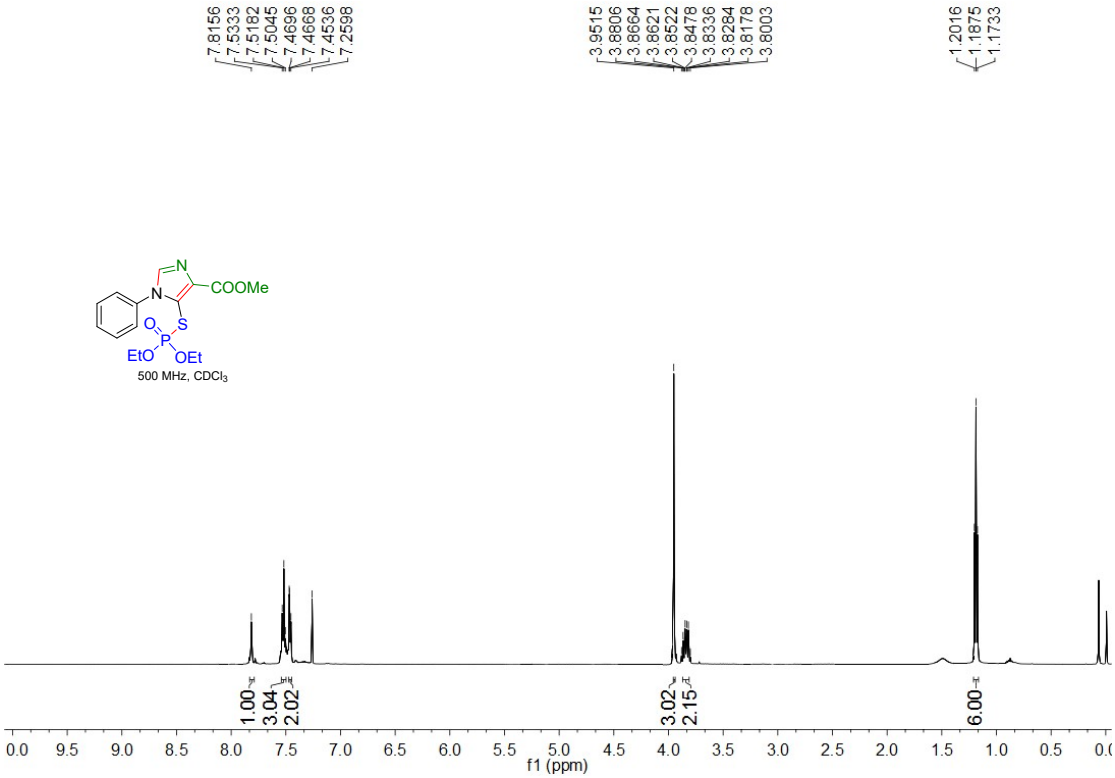



**$^{13}$C NMR**

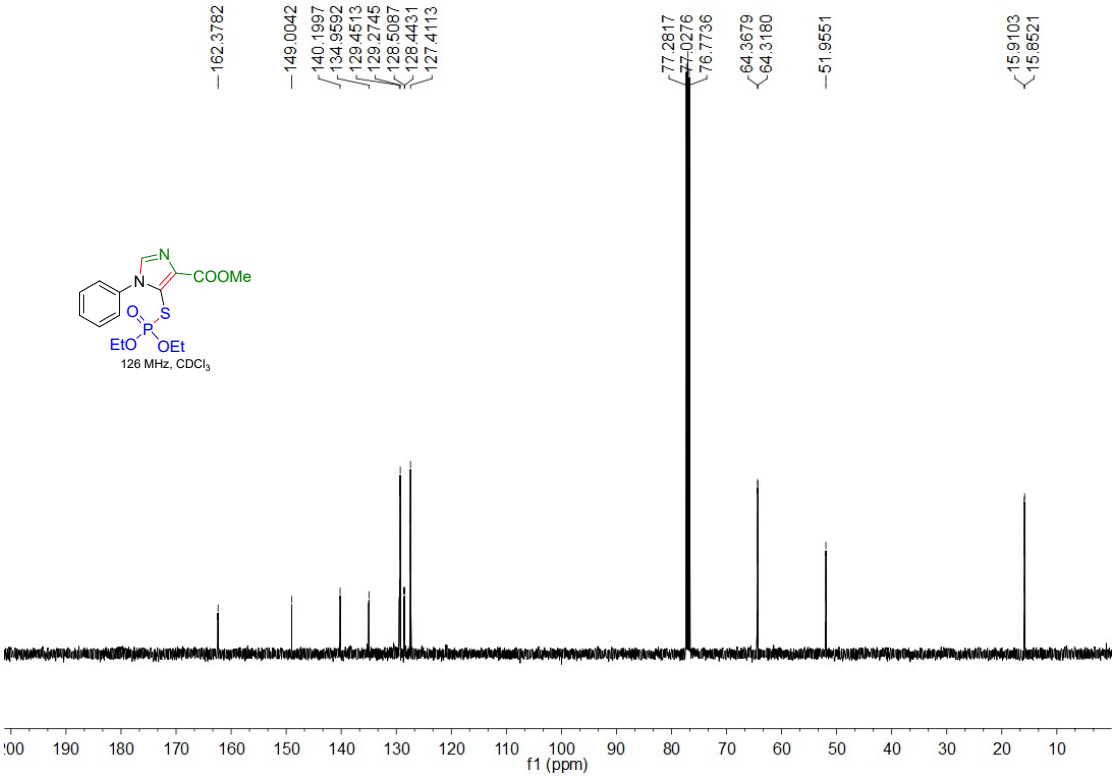


**20d**

**$^{1}$H NMR**

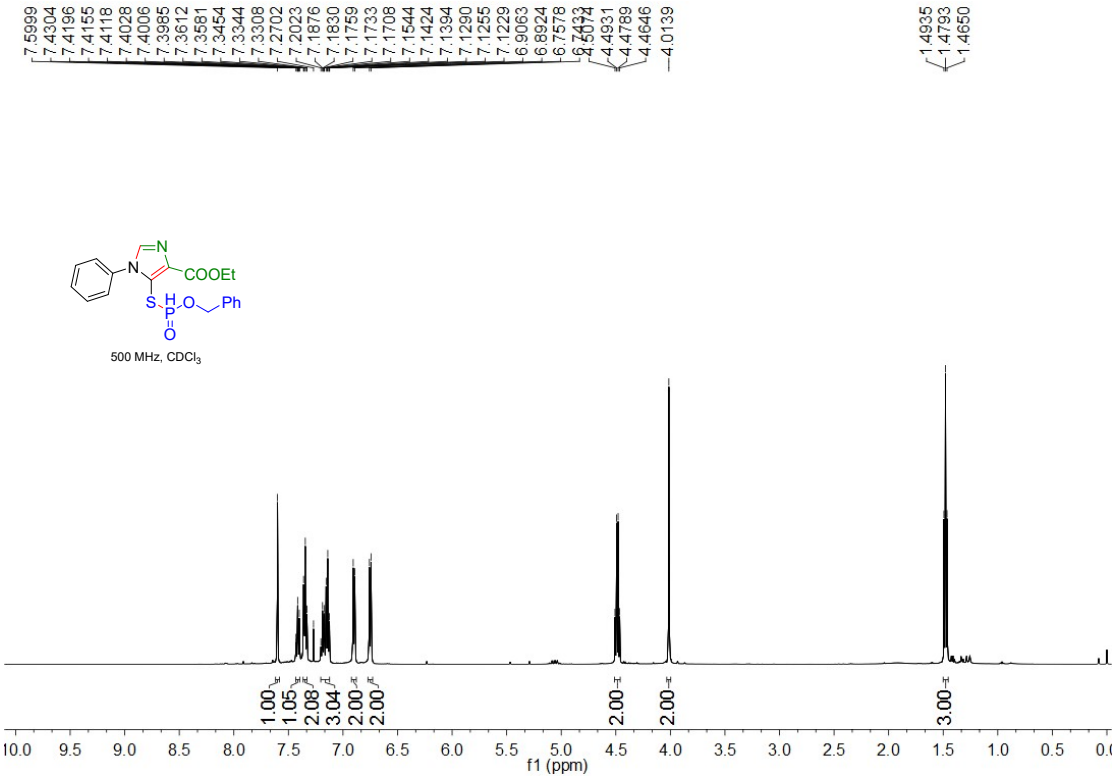



**$^{13}$C NMR**

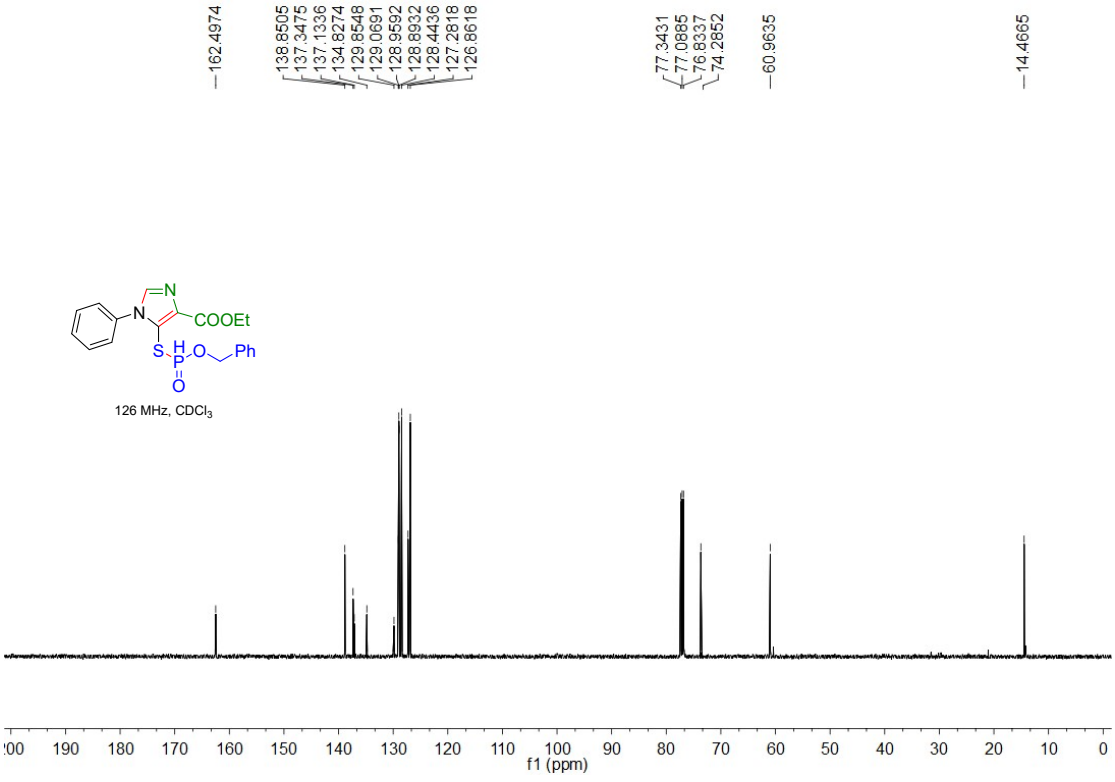


**21d**

**$^{1}$H NMR**

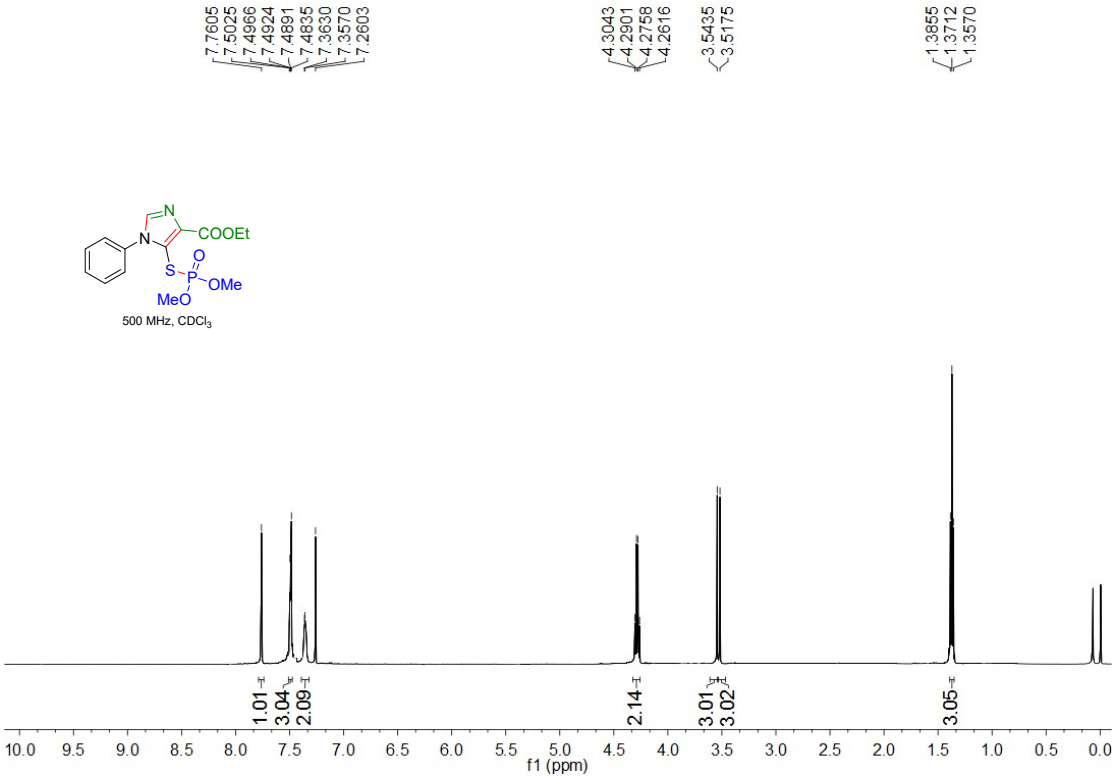



**$^{13}$C NMR**

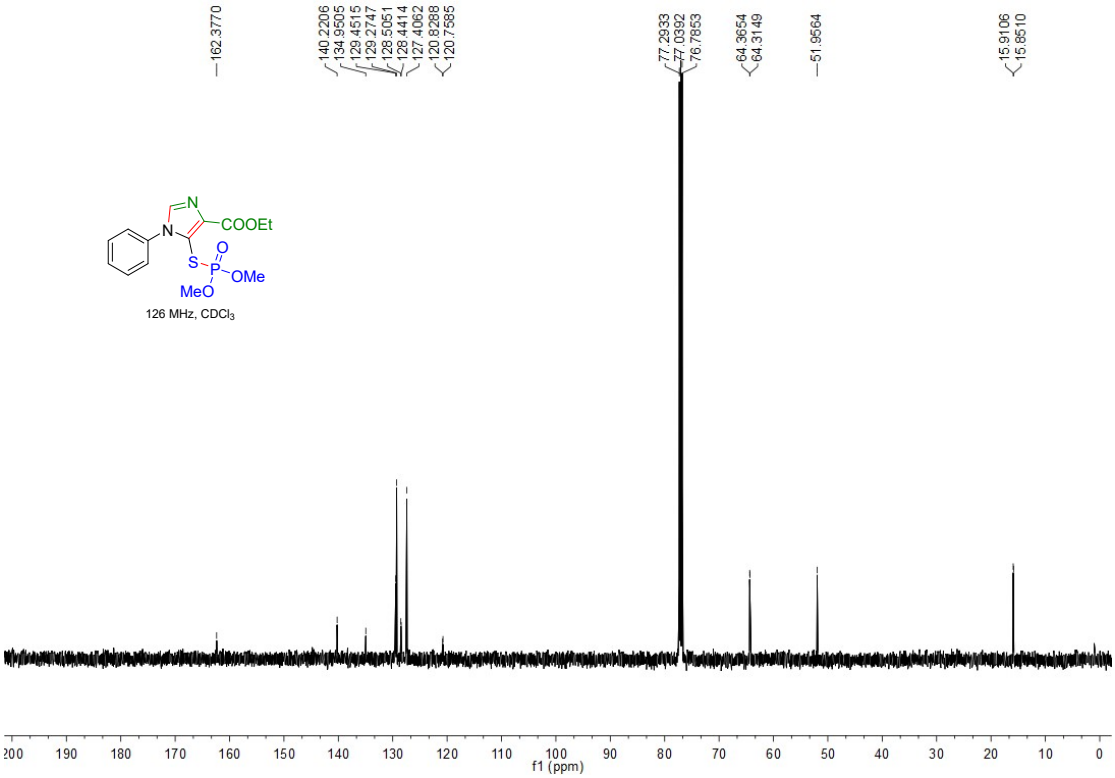


**22d**

**$^{1}$H NMR**

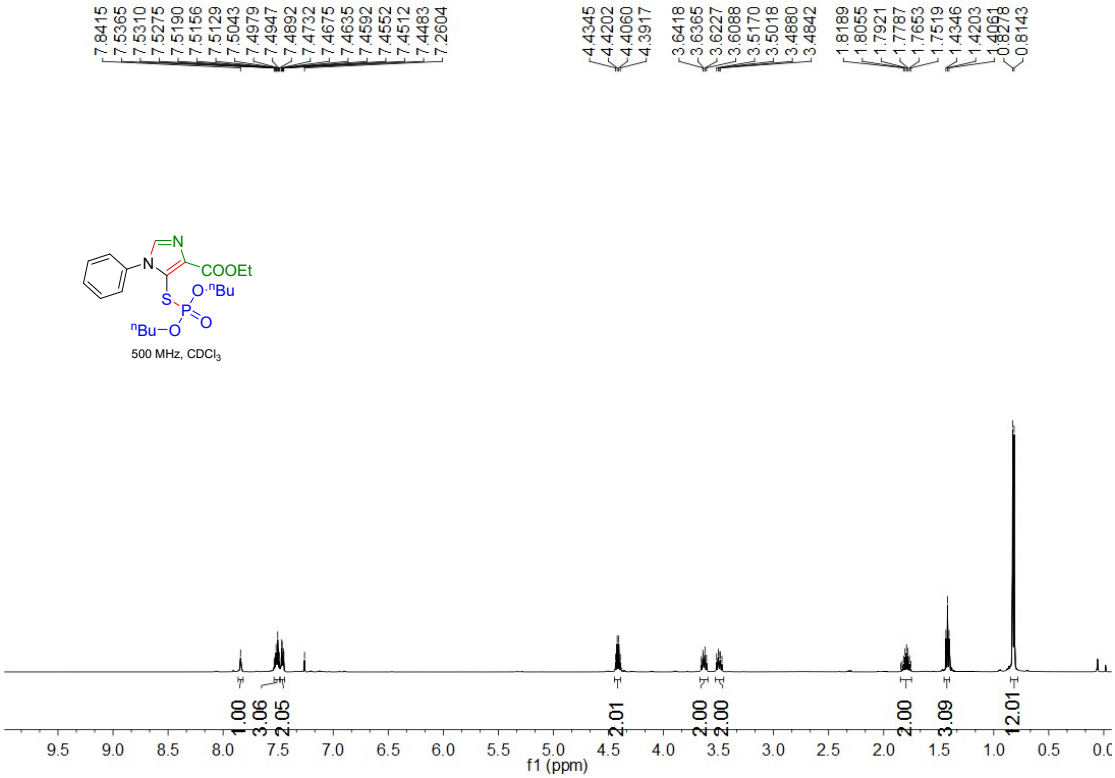



**$^{13}$C NMR**

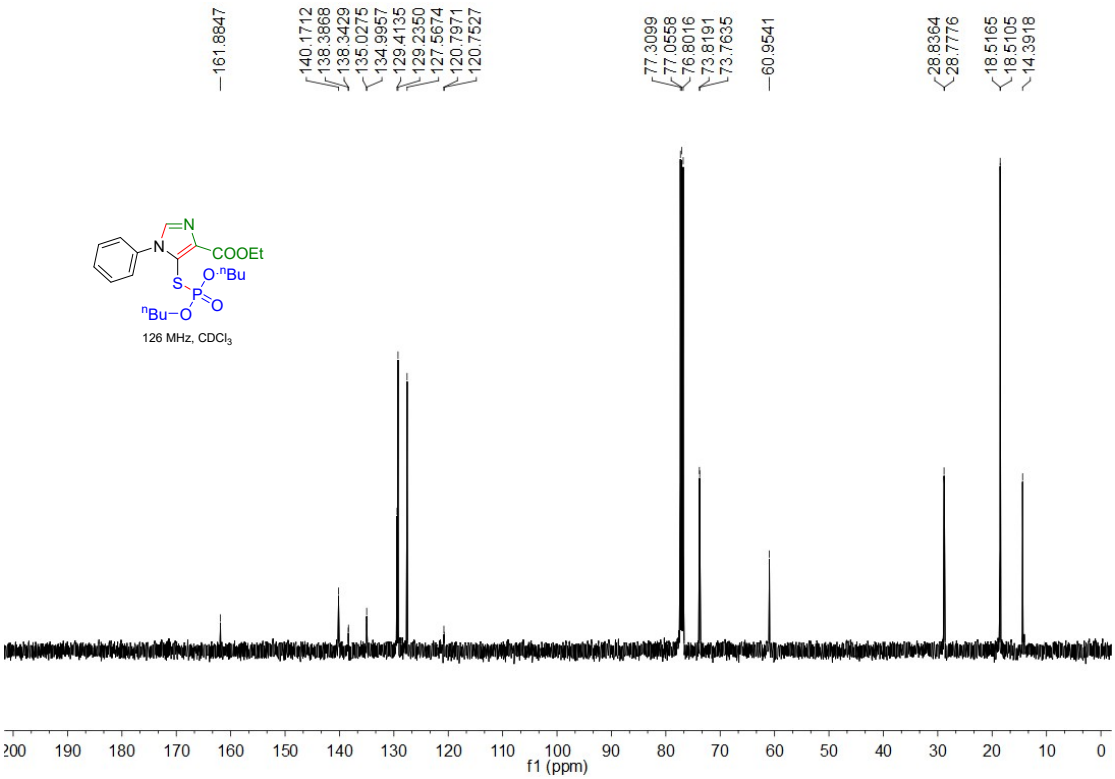


**23d**

**$^{1}$H NMR**

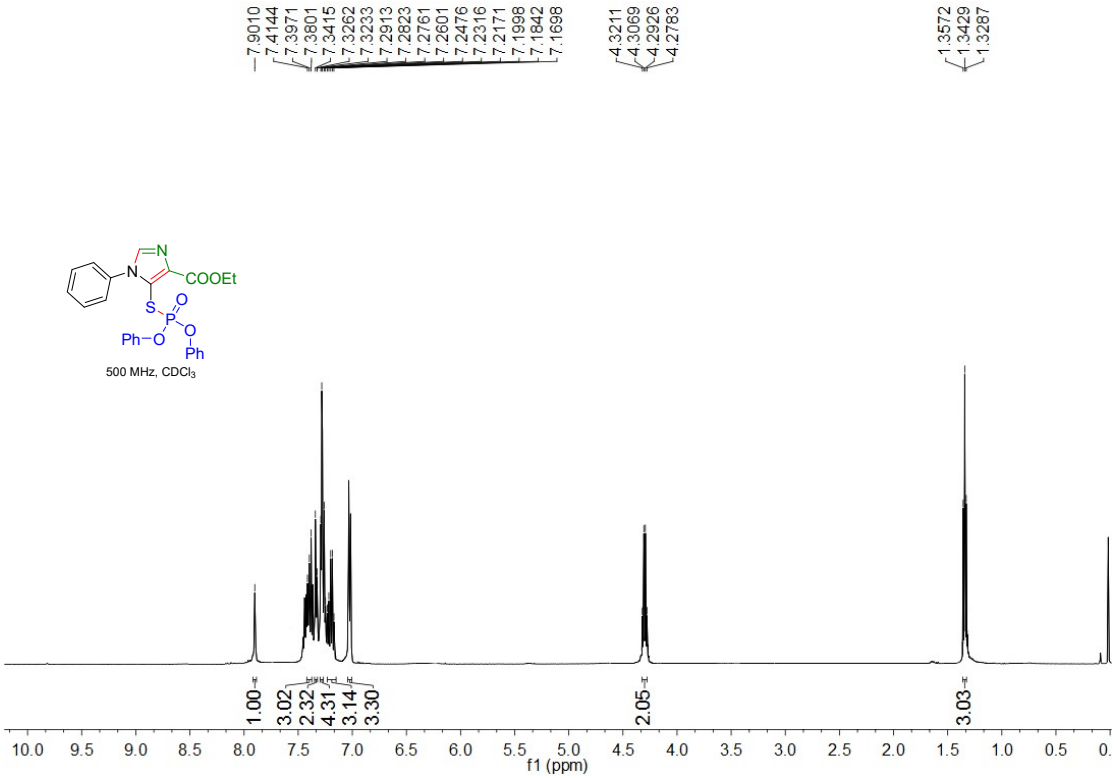



**$^{13}$C NMR**

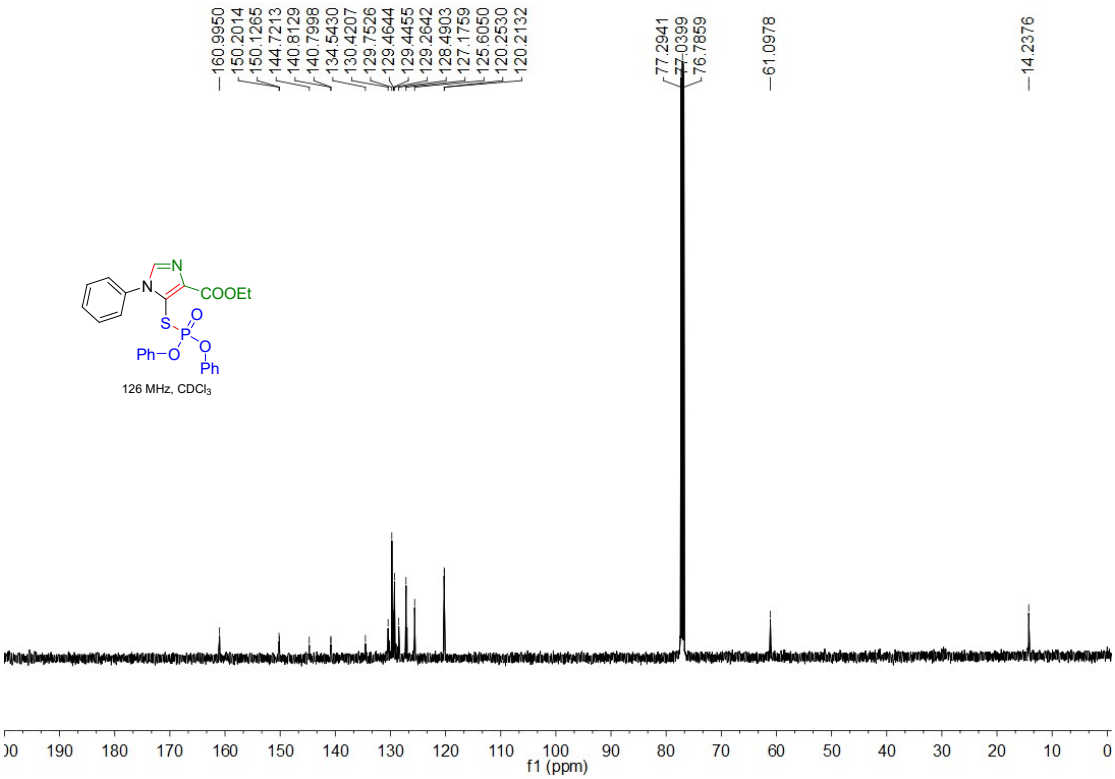


**24d**

**$^{1}$H NMR**

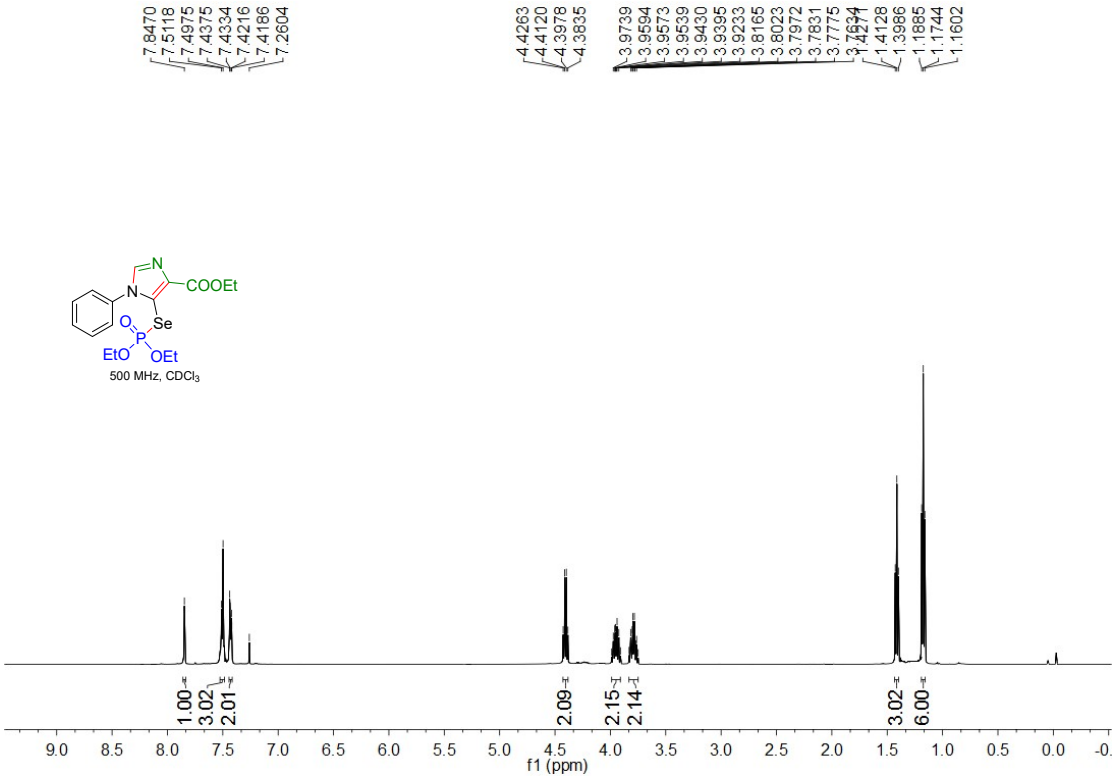



**$^{13}$C NMR**

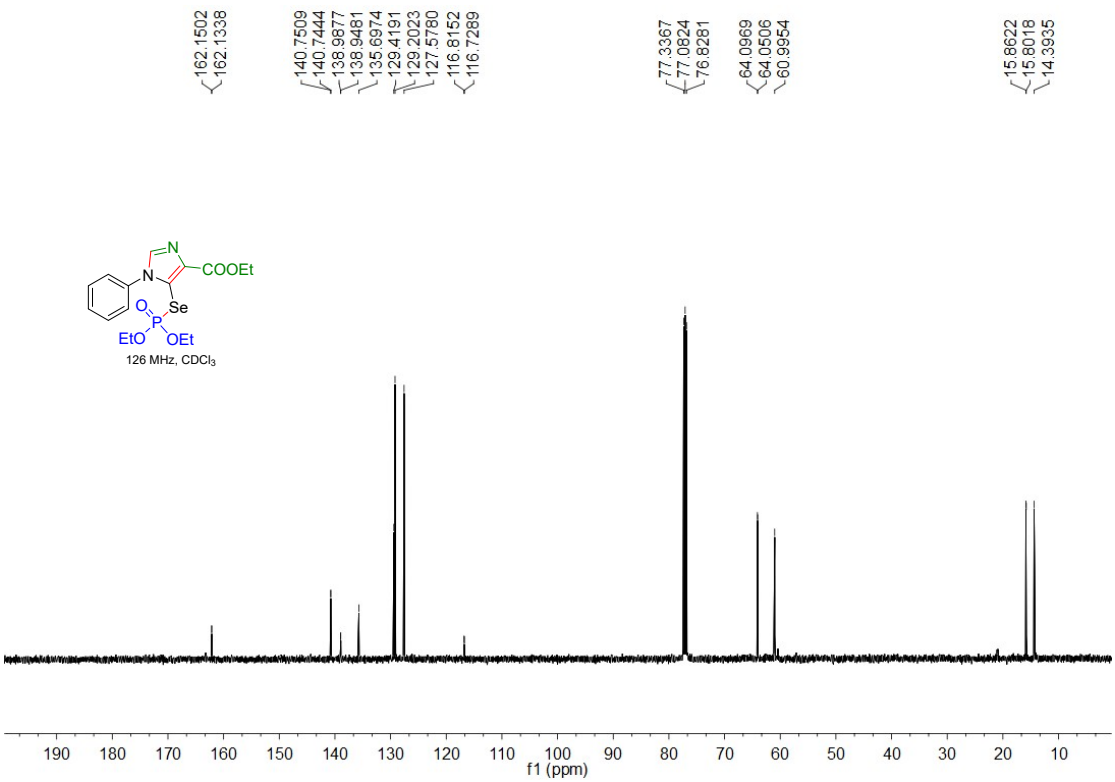


**25d**

**$^{1}$H NMR**

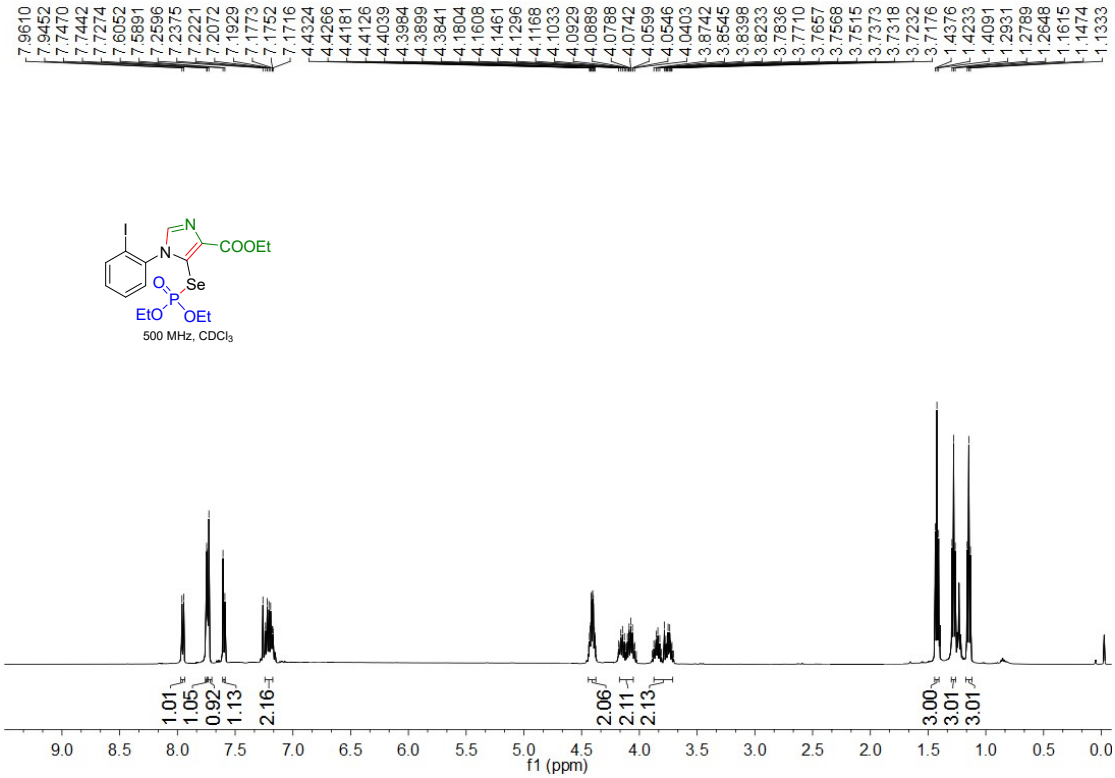



**$^{13}$C NMR**

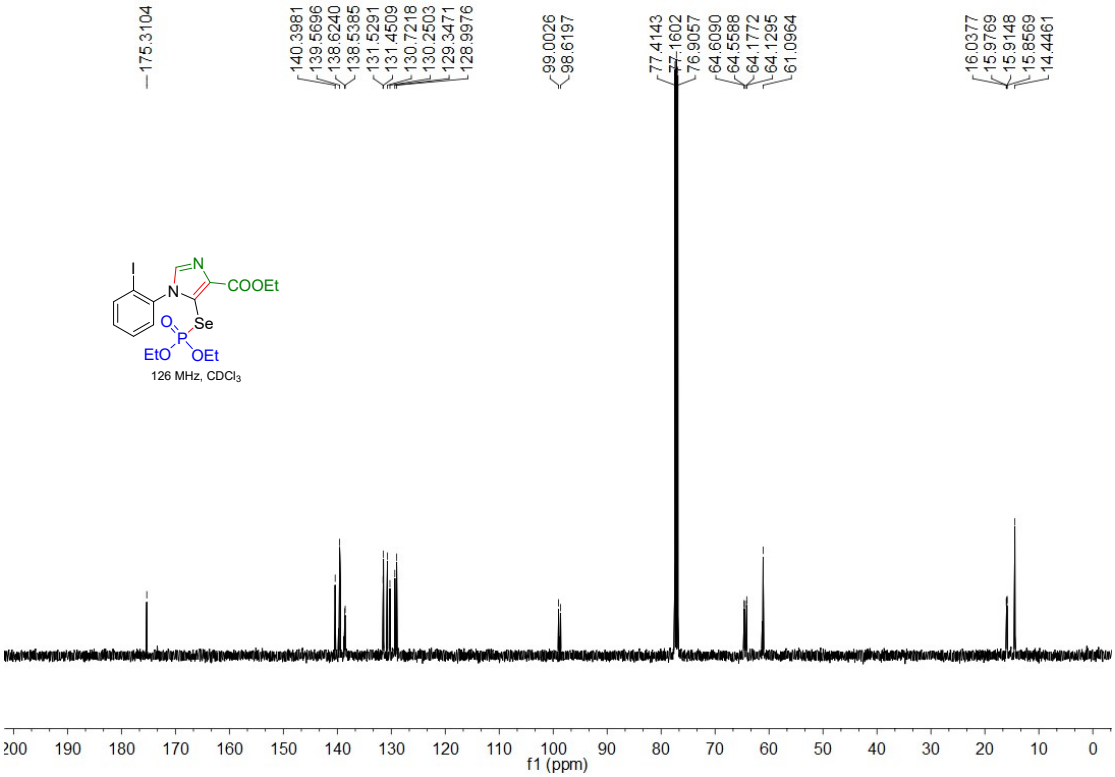


**26d**

**$^{1}$H NMR**

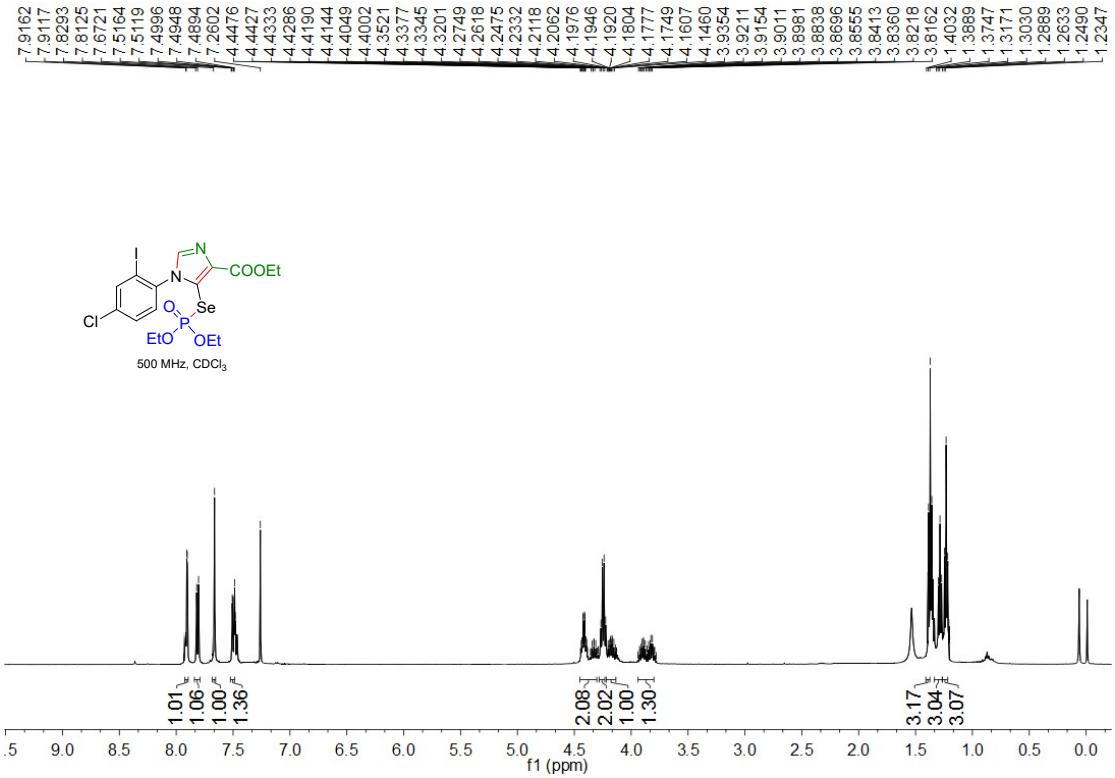



**$^{13}$C NMR**

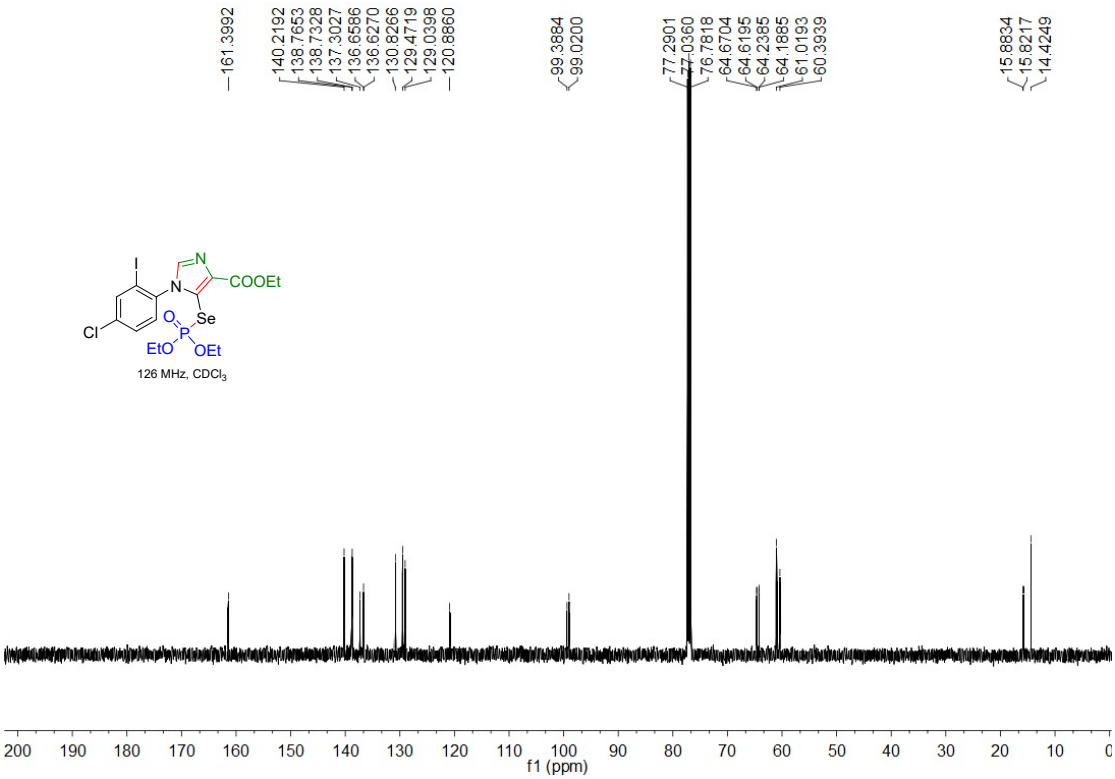


**27d**

**$^{1}$H NMR**

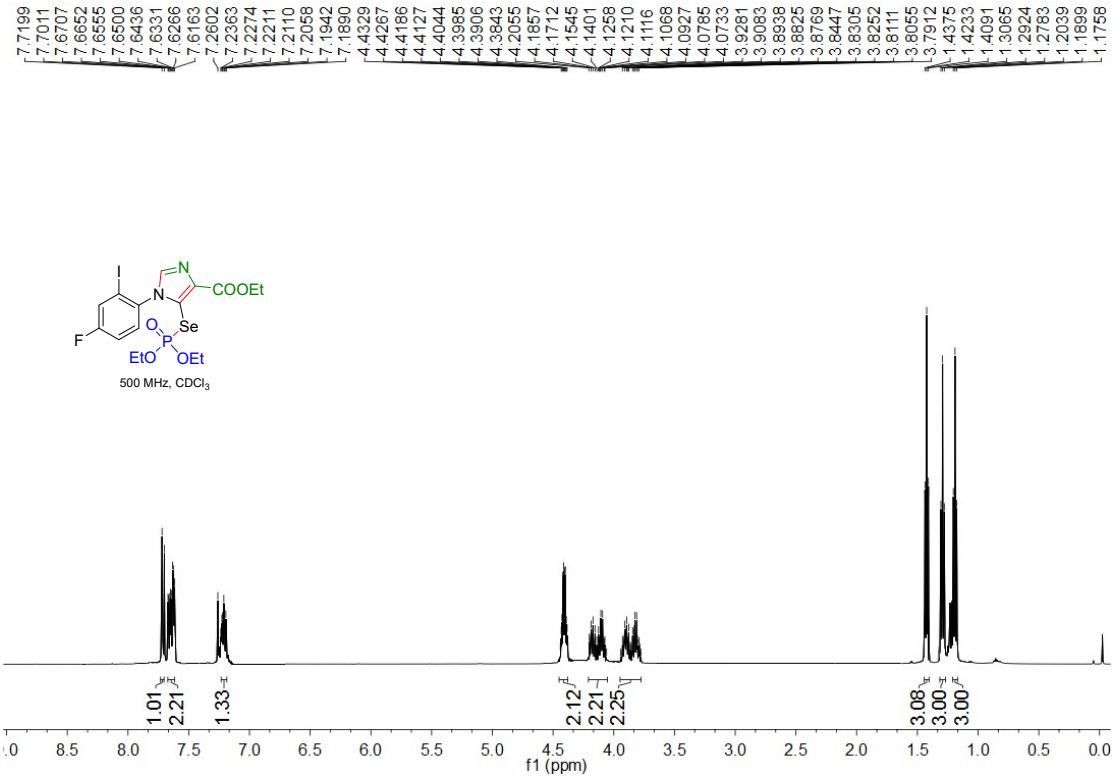



**$^{13}$C NMR**

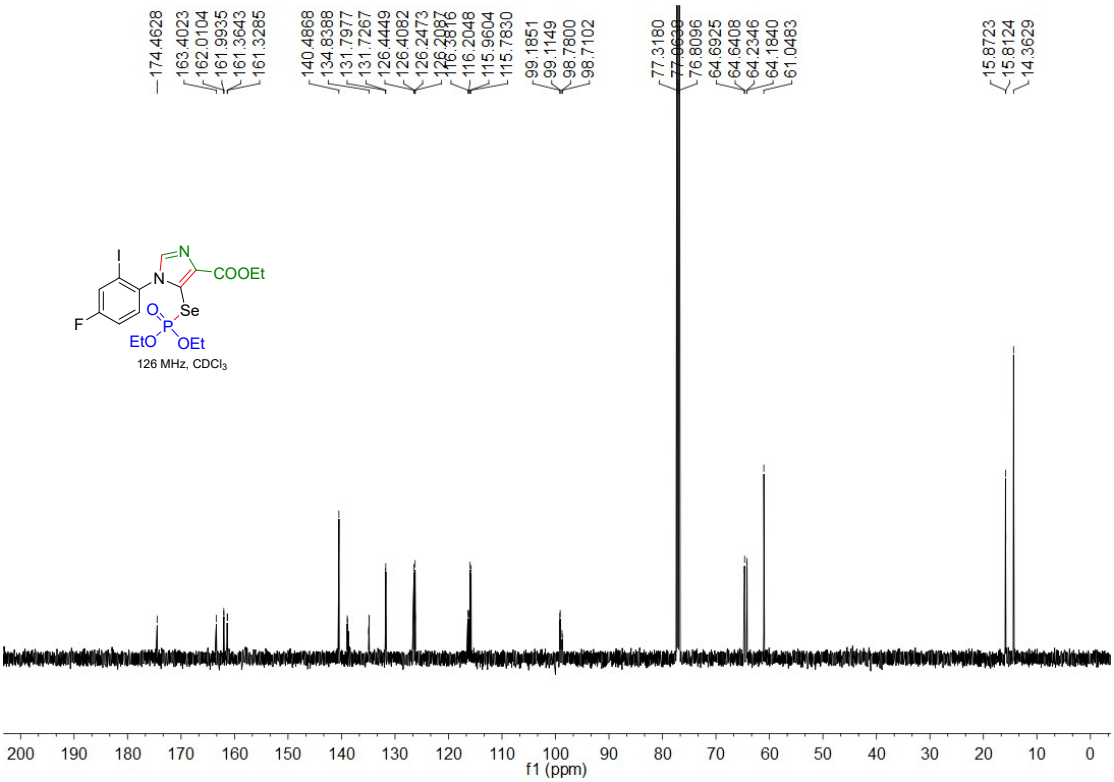


**28d**

**$^{1}$H NMR**

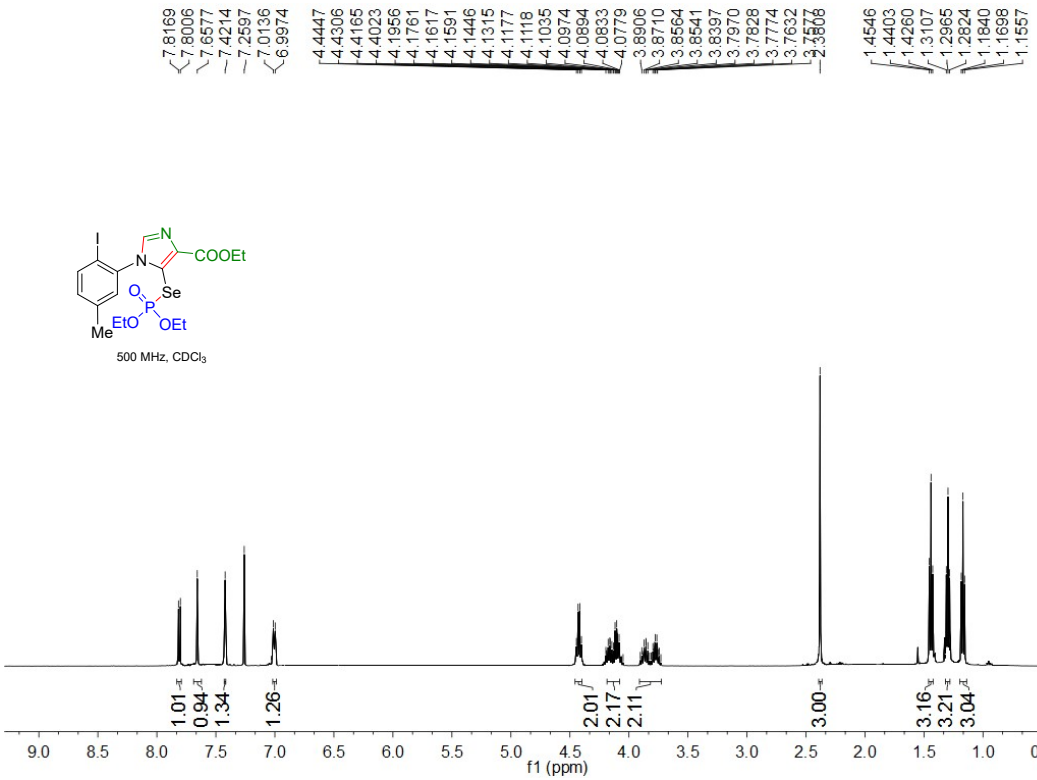



**$^{13}$C NMR**

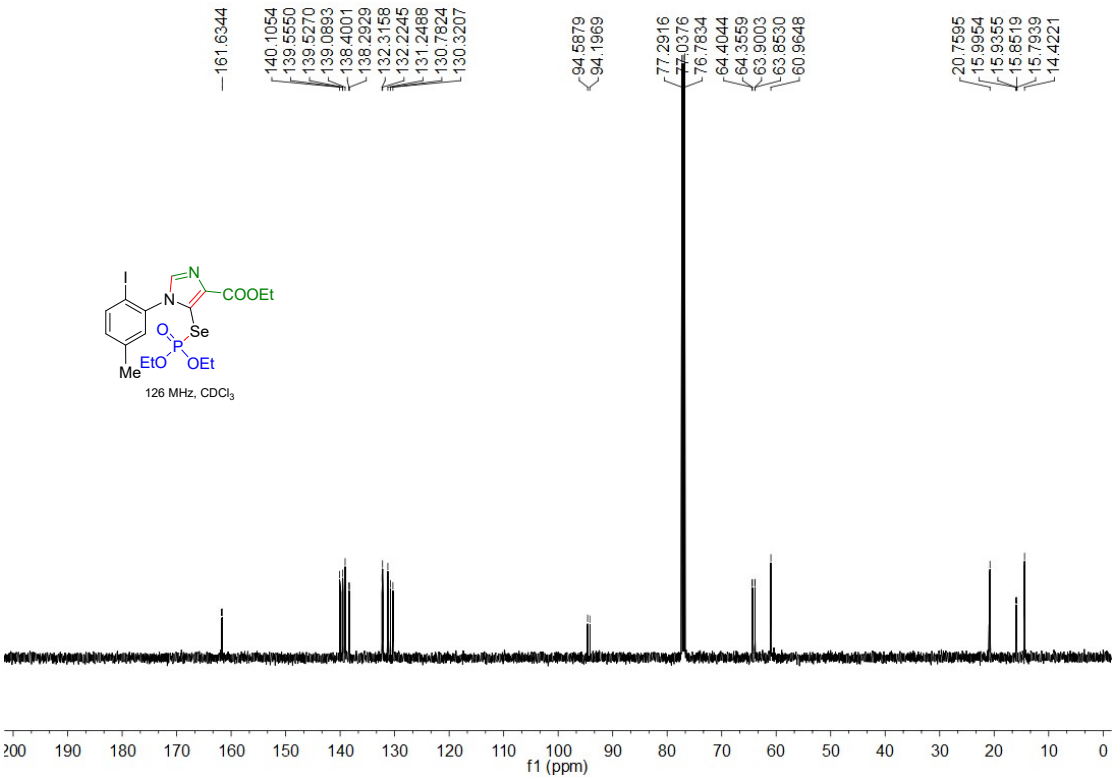


**29d**

**$^{1}$H NMR**

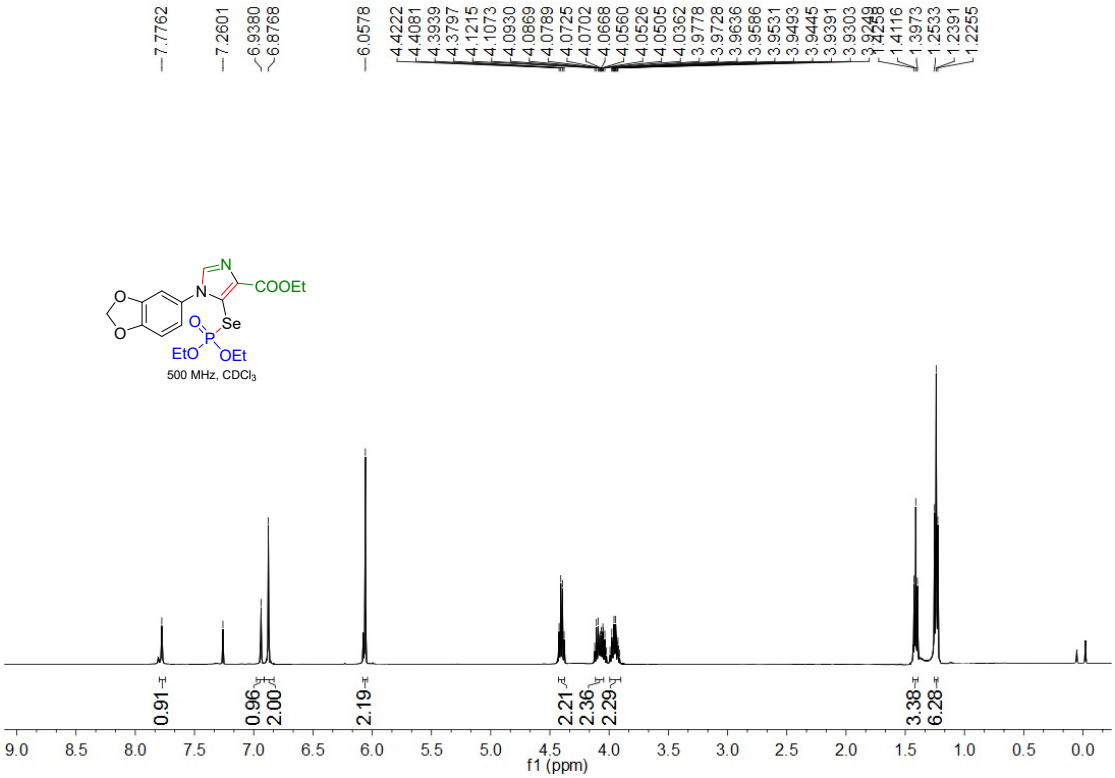



**$^{13}$C NMR**



**30d**

**$^{1}$H NMR**




**$^{13}$C NMR**