Electronic Supplementary Material (ESI) for Chemical Communications

Electrocatalytic three-component reaction for the synthesis of phosphoroselenoates

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1. Materials and equipment

Unless otherwise special indicated, all the reagents were purchased from commercial supplies unless otherwise stated. And all the solvents were used as received without further purification. The instrument for electrolysis was dual display potentiostat (UDP8305M) (made in China, UNI-T, **Figure S1**). Thin layer chromatography (TLC) employed glass 0.20-0.25 mm silica gel plates (GF254). Flash chromatography columns were packed with 200- 300 mesh silica gel in petroleum (bp. 60-90 ℃). Gradient flash chromatography was conducted eluting with PE (petroleum)/EA (ethyl acetate), they are listed as volume/volume ratios. Melting points were measured on a capillary melting point apparatus and were uncorrected. NMR spectra were recorded on a Bruker Avance III spectrometer operating. Chemical shifts were reported in ppm downfield. Coupling constants were quoted in Hz (*J*). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and the time-of-flight (TOF) mass analyzer, accurate masses are reported for the molecular ion + hydrogen ($[M+H]^+$). Mass spectra (MS) were measured using electron ionization (EI) method by GC-MS.

Figure S1：Experimental setup

2. Experimental Procedure

2.1 General Procedure A

A 15-mL undivided three-necked bottle was equipped with a platinum plate (with a length of 10 mm, a width of 10 mm, and a thickness of 0.2 mm) cathode and carbon rod (Ø 6 mm) anode which was connected to a DC regulated power supply. (Hetero)arenes **1** (0.3 mmol), elemental selenium (0.45 mmol), dialkyl phosphite **2**

(0.75 mmol) and Et_3N (0.6 mmol) dissolved in 4 mL MeCN, and KI (0.36 mmol) dissolved in 4 mL H_2O were added to the cell and electrolyzed at a constant current of 9 mA (~8 mA/cm^2). The electrolysis was terminated when the starting materials were consumed as determined by TLC (~6 h, **Figure S2**). After electrolysis, the reaction mixture was diluted in 50 mL ethyl acetate, washed with a saturated solution of brine (2 × 15 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (PE/EA) to afford the desired product **3**.

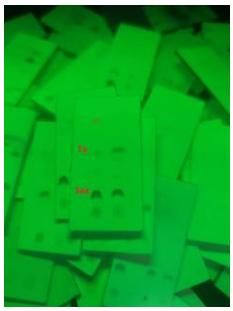
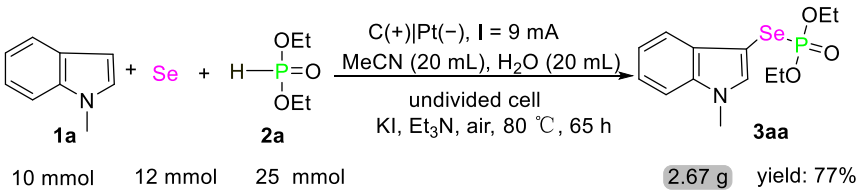


Figure S2：Reaction monitored by TLC

2.2 General Procedure B

A 15-mL undivided three-necked bottle was equipped with a platinum plate (with a length of 10 mm, a width of 10 mm, and a thickness of 0.2 mm) cathode and carbon rod (Ø 6 mm) anode which was connected to a DC regulated power supply. (Hetero)arenes **1** (0.3 mmol), elemental selenium (0.45 mmol), dialkyl phosphite **2** (0.75 mmol) and Et_3N (0.6 mmol) dissolved in 4 mL MeCN, and KI (0.36 mmol) dissolved in 4 mL H_2O were added to the cell and electrolyzed at a constant current of 16 mA (~14 mA/cm^2). The electrolysis was terminated when the starting materials were consumed as determined by TLC (~6 h). After electrolysis, the reaction mixture was diluted in 50 mL ethyl acetate, washed with a saturated solution of brine (2 × 15 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (PE/EA) to afford the desired product **3**.

2.3 Scale-up Reaction Procedure



A 250-mL undivided three-necked bottle was equipped with a platinum plate (with a length of 10 mm, a width of 10 mm, and a thickness of 0.2 mm) cathode and carbon rod (Ø 6 mm) anode which was connected to a DC regulated power supply. 1-Methylindole **1a** (10 mmol), elemental selenium (12 mmol), diethyl phosphite **2a** (25 mmol) and Et_3N (20 mmol) dissolved in 20 mL MeCN, and KI (12 mmol) dissolved in 20 mL H_2O were added to the cell and electrolyzed at a constant current of 9 mA (~8 mA/cm^2). The electrolysis was terminated when the starting materials were consumed as determined by TLC (65 h). After electrolysis, the reaction mixture was diluted in 150 mL ethyl acetate, washed with a saturated solution of brine (2 × 30 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (eluent: PE/EA = 4:1) to afford the desired product **3aa** (2.67 g, **Figure S3**).

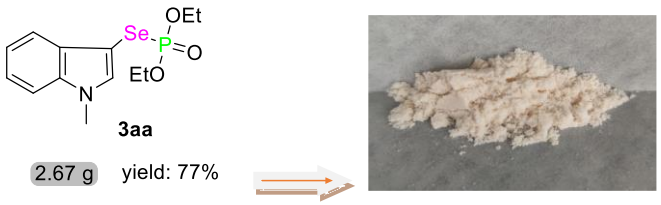
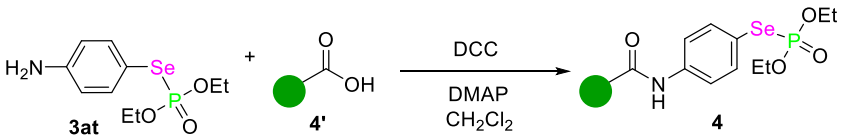


Figure S3：Product 3aa

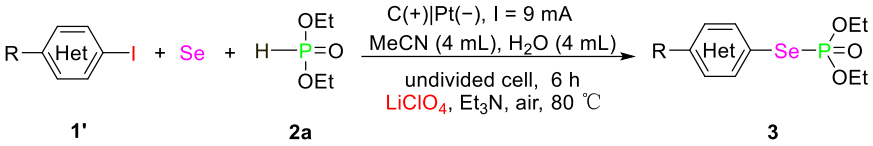
2.4 General Procedure for the Synthesis of 4aa–4ad



A 25-mL three-necked bottle was charged with phenylamine **3at** (0.5 mmol, 0.154 g), 4-dimethylaminopyridine (DMAP) (0.55 mmol, 0.067 g), N,N'-dicyclohexyl-carbodiimide (DCC) (0.55 mmol, 0.113 g,) and acid **4'** (0.5 mmol) in CH_2Cl_2 (4.0 mL) at 0 ℃ for 4 h. Then the reaction mixture was stirred at room temperature for 10 h. The electrolysis was terminated when the starting materials were consumed as determined by TLC. The reaction mixture was diluted in 50 mL ethyl acetate, washed

with a solution of HCl (0.5 M, 10 mL). saturated solution of brine (10 mL), saturated solution of $NaHCO_3$(10.0 mL), brine (10 mL). dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (PE/EA) to afford the desired product **4**.

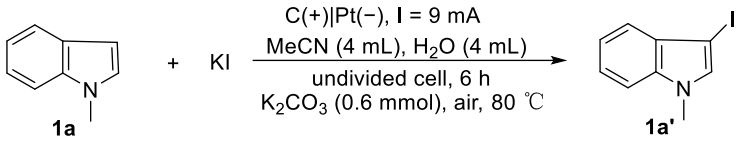
2.5 Synthesis of 3at, 3ax and 3ay from aryl iodides



1' **2a** **3**

A 15-mL undivided three-necked bottle was equipped with a platinum plate (with a length of 10 mm, a width of 10 mm, and a thickness of 0.2 mm) cathode and carbon rod (Ø 6 mm) anode which was connected to a DC regulated power supply. Aryl iodides **1** (0.3 mmol), elemental selenium (0.45 mmol), dialkyl phosphite **2** (0.75 mmol) and Et_3N (0.6 mmol) dissolved in 4 mL MeCN, and $LiClO_4$ (0.36 mmol) dissolved in 4 mL H_2O were added to the cell and electrolyzed at a constant current of 9 mA (~8 mA/cm^2). The reaction mixture was stirred at 80 ^oC for 6 h. After electrolysis, the reaction mixture was diluted in 50 mL ethyl acetate, washed with a saturated solution of brine (2 × 15 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (PE/EA) to afford the desired product **3**.

2.6 Synthesis of 3-iodo-1-methyl-1H-indole (1a')



0.3 mmol 0.36 mmol 68.6 mg

A 15-mL undivided three-necked bottle was equipped with a platinum plate (with a length of 10 mm, a width of 10 mm, and a thickness of 0.2 mm) cathode and carbon rod (Ø 6 mm) anode which was connected to a DC regulated power supply. 1-methylindole **1a** (0.3 mmol), KI (0.36 mmol) dissolved in 4 mL MeCN. Then 4 mL H_2O were added to the cell and electrolyzed at a constant current of 9 mA (~8 mA/cm^2). The electrolysis was terminated when the starting materials were

consumed as determined by TLC (~6 h). After electrolysis, the reaction mixture was diluted in 50 mL ethyl acetate, washed with a saturated solution of brine (2 × 15 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (eluent: PE/EA = 40:1) to afford the product **1a'**.

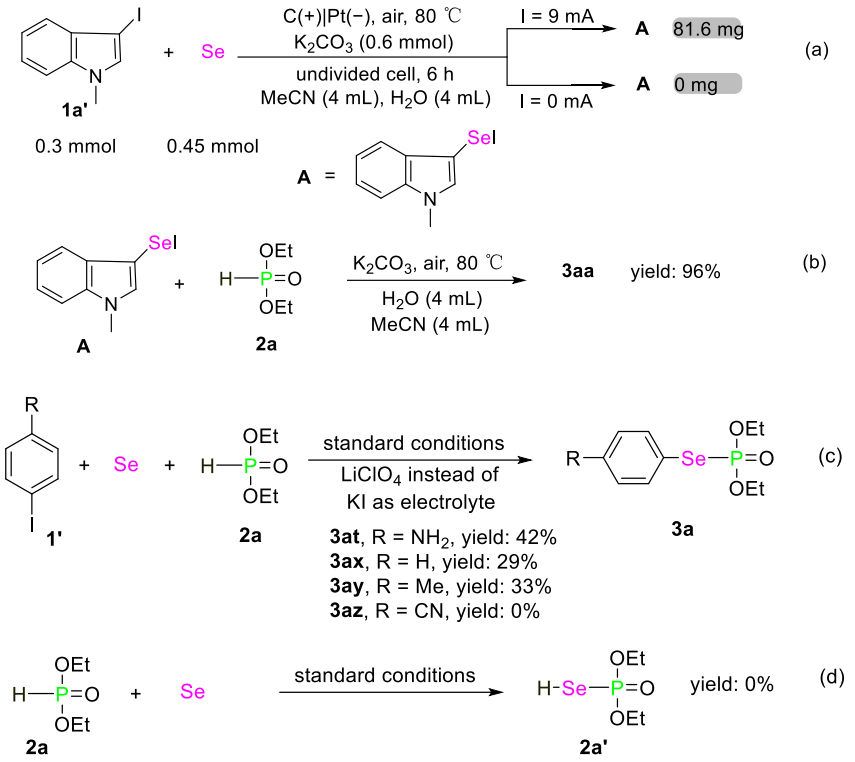
2.7 Synthesis of 1-methyl-1H-indol-3-yl hypoiodoselenoite (A)

A 15-mL undivided three-necked bottle was equipped with a platinum plate (with a length of 10 mm, a width of 10 mm, and a thickness of 0.2 mm) cathode and carbon rod (Ø 6 mm) anode which was connected to a DC regulated power supply. 3-Iodo-1-methyl-1H-indole **1a'** (0.3 mmol) and elemental selenium (0.45 mmol) dissolved in 4 mL MeCN, and $LiClO_4$ (0.36 mmol) dissolved in 4 mL H_2O were added to the cell and electrolyzed at a constant current of 9 mA (~8 mA/cm^2). The electrolysis was terminated when the starting materials were consumed as determined by TLC (~4 h). After electrolysis, the reaction mixture was diluted in 50 mL ethyl acetate, washed with a saturated solution of brine (2 × 15 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (eluent: PE/EA = 10:1) to afford the products desired product **A**.

2.8 Free radical trapping experiment

A 15-mL undivided three-necked bottle was equipped with a platinum plate (with a length of 10 mm, a width of 10 mm, and a thickness of 0.2 mm) cathode and carbon rod (Ø 6 mm) anode which was connected to a DC regulated power supply. 1-Methylindole **1a** (0.3 mmol), elemental selenium (0.45 mmol), diethyl phosphite **2a** (0.75 mmol), 2,2,6,6-tetramethyl-1-piperidinyloxy (0.9 mmol) and Et_3N (0.6 mmol) dissolved in 4 mL MeCN, and KI (0.36 mmol) dissolved in 4 mL H_2O were added to the cell and electrolyzed at a constant current of 9 mA (~8 mA/cm^2). The electrolysis was terminated when the starting materials were consumed as determined by TLC (~6 h, **Figure S2**). After electrolysis, the reaction mixture was diluted in 50 mL ethyl acetate, washed with a saturated solution of brine (2 × 15 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (PE/EA) to afford the desired product **3aa**.

2.9 Control experiments



Scheme S1 Control experiments

3. Cyclic Voltammetry Experiments

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 5 mL of CH_3CN and 5 mL of H_2O containing 0.1 M $LiClO_4$ were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s, ranging from 0 V to 2.0 V.

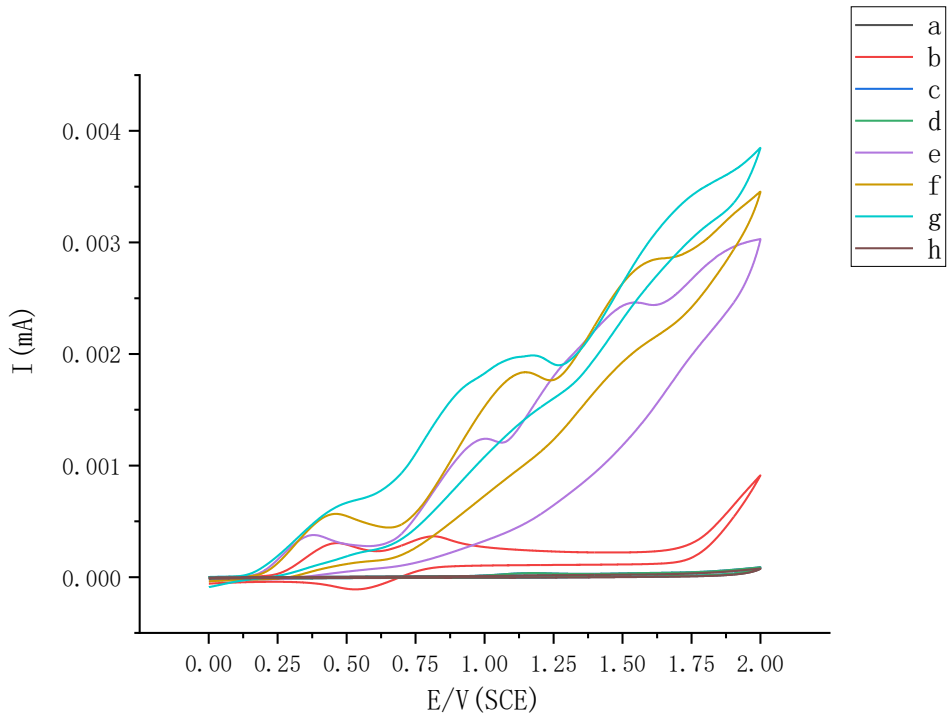
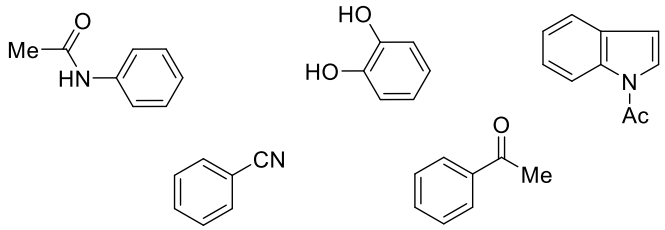
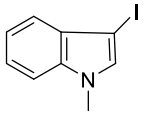


Figure S4. Cyclic voltammograms of 0.1 mol L^{-1} of $LiClO_4$ in 5 mL of CH_3CN and 5 mL of H_2O solution containing different compounds: (a) blank experiment; (b) KI (12 mmol L^{-1}), (c) **1a** (10 mmol L^{-1}), (d) **2a** (30 mmol L^{-1}), (e) **1a** (10 mmol L^{-1}), KI (12 mmol L^{-1}), (f) **1a** (10 mmol L^{-1}), KI (12 mmol L^{-1}), Se (15 mmol L^{-1}), (g) **1a** (10 mmol L^{-1}), KI (12 mmol L^{-1}), Se (15 mmol L^{-1}), **2a** (30 mmol L^{-1}), K_2CO_3 (15 mmol L^{-1}), (h) **Se** (15 mmol L^{-1}), with a GC disk working electrode, Pt counter electrode, and SCE reference electrode at 0.1 V/s scan rate.

4. Unsucessful substrates

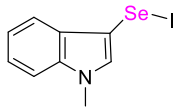


5. Analytical data

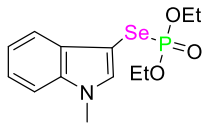


3-iodo-1-methyl-1H-indole (1a'): Overall Yield: 89% (68.6 mg). Nature: white solid. mp: 58−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (dd, J = 0.8 Hz, J = 7.6 Hz,

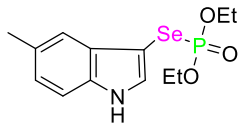
1H), 7.23-7.15 (m, 3H), 7.03 (s, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.6, 132.6, 130.2, 122.5, 121.0, 120.1, 109.3, 54.6, 33.0.



1-methyl-1H-indol-3-yl hypoiodoselenoite (A): Overall Yield: 81% (81.6 mg). Nature: yellow oil. IR (neat cm^{-1}): 741, 1005, 1237, 1502, 2917; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (t, J = 4.2 Hz, 1H), 7.17-7.11 (m, 3H), 7.10-7.06 (m, 2H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.0, 133.6, 130.2, 121.9, 120.3, 119.7, 109.2, 99.5, 32.8; HRMS m/z (ESI) calcd for $C_9H_{12}IN_2Se$ $(M+NH_4)^+$ 354.9205, found 354.9203.

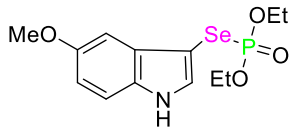


O,O-diethyl Se-1-methyl-1H-indol-3-yl phosphoroselenoate (3aa): General Procedure A. Overall Yield: 81% (90.3 mg). Nature: white solid. mp: 94−96 °C. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.29-7.25 (m, 2H), 7.23-7.19 (m, 1H), 4.22-4.10 (m, 4H), 3.81 (s, 3H), 1.27 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.0, 135.1 (d, $J_{C\text{-}P}$ = 4.6 Hz), 130.4 (d, $J_{C\text{-}P}$ = 1.4 Hz), 122.3, 120.3, 119.9, 109.6, 89.7 (d, $J_{C\text{-}P}$ = 8.8 Hz), 63.6 (d, $J_{C\text{-}P}$ = 5.7 Hz), 33.1, 15.9 (d, $J_{C\text{-}P}$ = 7.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.4. HRMS m/z (ESI) calcd for $C_{13}H_{19}NO_3PSe$ $(M+H)^+$ 348.0262, found 348.0266.

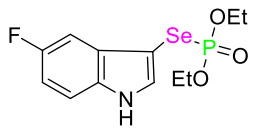


O,O-diethyl Se-(5-methyl-1H-indol-3-yl) phosphoroselenoate (3ab): General Procedure A. Overall Yield: 91% (94.4 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.32 (s, 1H), 7.42 (s, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.13 (t, J = 3.0 Hz, 1H), 6.99 (dd, J = 0.8 Hz, J = 1.2 Hz, 1H), 4.23-4.13 (m, 4H), 2.46 (s, 3H), 1.30 (td, J = 0.4 Hz, J = 0.4 Hz, J = 0.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$)

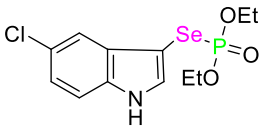
δ: 134.3, 131.5 (d, $J_{C\text{-}P}$ = 5.0 Hz), 129.9, 129.7, 124.0, 119.0, 111.4, 89.8 (d, $J_{C\text{-}P}$ = 8.5 Hz), 63.9 (d, $J_{C\text{-}P}$ = 6.1 Hz), 21.4, 15.9 (d, $J_{C\text{-}P}$ = 7.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.8. HRMS m/z (ESI) calcd for $C_{13}H_{19}NO_3PSe$ $(M+H)^+$ 348.0262, found 348.0260.



O,O-diethyl Se-(5-methoxy-1H-indol-3-yl) phosphoroselenoate (3ac): General Procedure A. Overall Yield: 91% (92.3 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.60 (s, 1H), 7.10 (t, J = 2.8 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H), 6.96 (t, J = 8.0 Hz, 1H), 4.28-4.18 (m, 4H), 3.92 (s, 3H), 1.30 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.7, 137.9, 130.4 (d, $J_{C\text{-}P}$ = 5.1 Hz), 123.0, 118.4 (d, $J_{C\text{-}P}$ = 2.1 Hz), 105.2, 100.3, 88.1 (d, $J_{C\text{-}P}$ = 8.7 Hz), 63.7 (d, $J_{C\text{-}P}$ = 5.7 Hz), 54.9, 15.9 (d, $J_{C\text{-}P}$ = 7.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.7. HRMS m/z (ESI) calcd for $C_{13}H_{19}NO_4PSe$ $(M+H)^+$ 364.0211, found 364.0215.

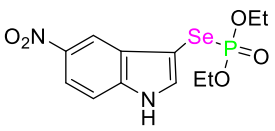


O,O-diethyl Se-(5-fluoro-1H-indol-3-yl) phosphoroselenoate (3ad): General Procedure A. Overall Yield: 66% (69.3 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.86 (s, 1H), 7.25 (t, J = 4.8 Hz, 1H), 7.09 (s, 1H), 7.07 (dd, J = 4.4 Hz, J = 4.4 Hz, 1H), 6.82 (td, J = 2.0 Hz, J = 2.0 Hz, J = 2.4 Hz, 1H), 4.29-4.17 (m, 4H), 1.38 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.6 (d, $J_{C\text{-}F}$ = 234.1 Hz), 133.5, 133.4, 132.6, 130.3, 130.2, 112.7, 112.6, 110.8, 110.6, 104.1, 103.9, 89.66, 89.62, 89.58, 89.53, 64.1 (d, $J_{C\text{-}P}$ = 6.6 Hz), 16.0 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.8. HRMS m/z (ESI) calcd for $C_{12}H_{16}FNO_3PSe$ $(M+H)^+$ 352.0012, found 352.0018.



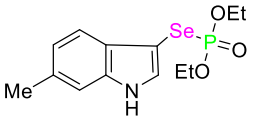
O,O-diethyl Se-(5-chloro-1H-indol-3-yl) phosphoroselenoate (3ae): General Procedure A. Overall Yield: 62% (68.1 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.1 (s, 1H), 7.54 (s, 1H), 7.03 (t, J = 2.8 Hz, 1H), 6.98 (t, J = 9.4 Hz, 2H), 4.31-4.19 (m, 4H), 1.40 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.6, 133.2 (d, $J_{C\text{-}P}$ = 5.0 Hz), 130.7 (d, $J_{C\text{-}P}$ = 1.1 Hz), 126.1, 122.4, 118.5, 112.9, 89.0 (d, $J_{C\text{-}P}$ = 8.5 Hz), 64.2 (d, $J_{C\text{-}P}$ = 6.8 Hz), 16.0 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.8. HRMS m/z (ESI) calcd for $C_{12}H_{16}ClNO_3PSe$ $(M+H)^+$ 367.9716, found 367.9713.

O,O-diethyl Se-(5-bromo-1H-indol-3-yl) phosphoroselenoate (3af): General Procedure A. Overall Yield: 77% (94.9 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.0 (s, 1H), 7.69 (d, J = 1.6 Hz, 1H), 7.09 (dd, J = 1.6 Hz, J = 2.0 Hz, 1H), 7.02 (t, J = 3.0 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 4.31-4.19 (m, 4H), 1.41 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.8, 133.0 (d, $J_{C\text{-}P}$ = 5.1 Hz), 131.2 (d, $J_{C\text{-}P}$ = 1.1 Hz), 124.9, 121.5, 113.7, 113.3, 88.8 (d, $J_{C\text{-}P}$ = 8.3 Hz), 64.3 (d, $J_{C\text{-}P}$ = 6.7 Hz), 16.0 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.8. HRMS m/z (ESI) calcd for $C_{12}H_{16}BrNO_3PSe$ $(M+H)^+$ 411.9211, found 411.9214.

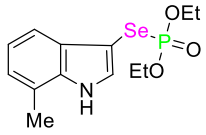


O,O-diethyl Se-(5-nitro-1H-indol-3-yl) phosphoroselenoate (3ag): General Procedure A. Overall Yield: 64% (72.4 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1).

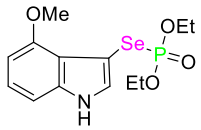
^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.5 (s, 1H), 8.53 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 6.97 (dd, J = 2.8 Hz, J = 2.8 Hz, 1H), 4.40-4.27 (m, 4H), 1.40 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.2, 139.2, 135.1 (d, $J_{C\text{-}P}$ = 5.5 Hz), 129.1, 117.5, 116.3, 111.8, 92.4 (d, $J_{C\text{-}P}$ = 8.5 Hz), 64.7 (d, $J_{C\text{-}P}$ = 6.9 Hz), 16.0 (d, $J_{C\text{-}P}$ = 7.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.2. HRMS m/z (ESI) calcd for $C_{12}H_{16}N_2O_5PSe$ $(M+H)^+$ 378.9957, found 378.9961.



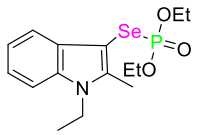
O,O-diethyl Se-(6-methyl-1H-indol-3-yl) phosphoroselenoate (3ah): General Procedure A. Overall Yield: 84% (87.2 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.50 (s, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.07 (d, J = 2.8 Hz, J = 2.8 Hz , 1H), 6.97 (d, J = 3.4 Hz, 1H), 4.24-4.14 (m, 4H), 2.37 (s, 3H), 1.33 (d, J =7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.5, 131.9, 131.1 (d, $J_{C\text{-}P}$ = 5.1 Hz), 127.5, 122.0, 118.8, 111.6, 89.7 (d, $J_{C\text{-}P}$ = 8.5 Hz), 63.9 (d, $J_{C\text{-}P}$ = 6.2 Hz), 21.5, 16.0 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.0. HRMS m/z (ESI) calcd for $C_{13}H_{19}NO_3PSe$ $(M+H)^+$ 348.0262, found 348.0258.



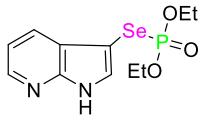
O,O-diethyl Se-(7-methyl-1H-indol-3-yl) phosphoroselenoate (3ai): General Procedure A. Overall Yield: 68% (70.6 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.33 (s, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 3.0 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 4.23-4.15 (m, 4H), 2.25 (s, 3H), 1.33 (t, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.6, 131.5 (d, $J_{C\text{-}P}$ = 5.0 Hz), 129.3 (d, $J_{C\text{-}P}$ = 1.2 Hz), 122.9, 121.2, 120.6, 117.0, 90.9 (d, $J_{C\text{-}P}$ = 8.5 Hz), 63.8 (d, $J_{C\text{-}P}$ = 6.2 Hz), 16.2, 16.0 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.8. HRMS m/z (ESI) calcd for $C_{13}H_{19}NO_3PSe$ $(M+H)^+$ 348.0262, found 348.0267.



O,O-diethyl Se-(4-methoxy-1H-indol-3-yl) phosphoroselenoate (3aj): General Procedure A. Overall Yield: 75% (81.4 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.60 (s, 1H), 7.10 (t, J = 2.8 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H),6.51 (t, J = 7.6 Hz, 1H), 4.28-4.18 (m, 4H), 3.92 (s, 3H), 1.30 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.7, 137.9, 130.4 (d, $J_{C\text{-}P}$ = 5.1 Hz), 123.0, 118.4 (d, $J_{C\text{-}P}$ = 2.1 Hz), 105.2, 100.3, 88.1 (d, $J_{C\text{-}P}$ = 8.7 Hz), 63.7 (d, $J_{C\text{-}P}$ = 5.7 Hz), 54.9, 15.9 (d, $J_{C\text{-}P}$ = 7.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 20.0. HRMS m/z (ESI) calcd for $C_{13}H_{19}NO_4PSe$ $(M+H)^+$ 364.0211, found 364.0214.

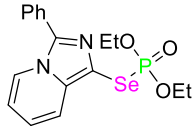


O,O-diethyl Se-(1-ethyl-2-methyl-1H-indol-3-yl) phosphoroselenoate **(3ak)**: General Procedure A. Overall Yield: 91% (94.7 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (dd, J = 2.0 Hz, J = 1.2 Hz, 1H), 7.28-7.25 (m, 1H), 7.20-7.13 (m, 2H), 4.19-4.07 (m, 6H), 2.59 (d, J = 2.8 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.6 (d, $J_{C\text{-}P}$ = 4.9 Hz), 135.8, 130.5, 121.4, 120.1, 119.4, 109.0, 89.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 63.5 (d, $J_{C\text{-}P}$ = 6.2 Hz), 38.7, 15.9 (d, $J_{C\text{-}P}$ = 7.2 Hz), 15.0, 11.8 (d, $J_{C\text{-}P}$ = 1.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.3. HRMS m/z (ESI) calcd for $C_{15}H_{23}NO_3PSe$ $(M+H)^+$ 376.0576, found 376.0571.

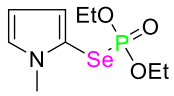


O,O-diethyl Se-(1H-pyrrolo[2,3-b]pyridin-3-yl) phosphoroselenoate (3al): General Procedure A. Overall Yield: 65% (64.9 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA =

2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.3 (br.s, 1H), 8.33 (t, J = 2.4 Hz, 1H), 8.07 (dd, J = 1.2 Hz, J = 1.2 Hz, 1H), 7.58 (d, J = 3.6 Hz, 1H), 7.20 (dd, J = 4.8 Hz, J = 5.2 Hz, 1H), 4.20-4.09 (m, 4H), 1.27 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.1, 142.4, 132.5 (d, $J_{C\text{-}P}$ = 5.4 Hz), 129.1, 123.2, 116.5, 90.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 63.9 (d, $J_{C\text{-}P}$ = 6.3 Hz), 15.9 (d, $J_{C\text{-}P}$ = 7.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.5. HRMS m/z (ESI) calcd for $C_{11}H_{16}N_2O_3PSe$ $(M+H)^+$ 335.0058, found 335.0061.

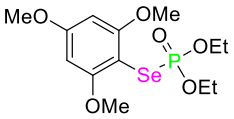


O,O-diethyl Se-(3-phenylimidazo[1,5-a]pyridin-1-yl) phosphoroselenoate (3am): General Procedure A. Overall Yield: 81% (99.4 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (d, J = 7.2 Hz, 1H), 7.76 (t, J = 4.4 Hz, 2H), 7.64 (d, J = 9.2 Hz, 1H), 7.53 (dd, J = 1.6 Hz, J = 7.6 Hz, 2H), 7.46 (dd, J = 5.2 Hz, J = 7.6 Hz, 1H), 6.91 (dd, J = 6.4 Hz, J = 6.8 Hz, 1H), 6.66 (m, 1H), 4.34-4.26 (m, 4H), 1.34 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.6, 135.7 (d, $J_{C\text{-}P}$ = 4.3 Hz), 129.4, 129.0 (d, $J_{C\text{-}P}$ = 4.0 Hz), 128.0, 121.9, 121.0 (d, $J_{C\text{-}P}$ = 1.9 Hz), 118.8 (d, $J_{C\text{-}P}$ = 2.3 Hz), 113.7, 110.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 63.9 (d, $J_{C\text{-}P}$ = 5.3 Hz), 15.9 (d, $J_{C\text{-}P}$ = 7.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.7. HRMS m/z (ESI) calcd for $C_{17}H_{20}N_2O_3PSe$ $(M+H)^+$ 411.0371, found 411.0377.

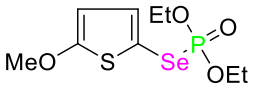


O,O-diethyl Se-(1-methyl-1H-pyrrol-2-yl) phosphoroselenoate (3an): General Procedure A. Overall Yield: 63% (55.9 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.84 (dd, J = 3.2 Hz, J = 3.2 Hz, 1H), 6.44-6.42 (m, 1H), 6.15 (dd, J = 3.2 Hz, J = 3.2 Hz, 1H), 4.17-4.10 (m, 4H), 1.33 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 126.3 (d, $J_{C\text{-}P}$ = 4.1 Hz), 120.4 (d, $J_{C\text{-}P}$ = 5.5 Hz), 109.0 (d, $J_{C\text{-}P}$ = 7.0 Hz), 107.0 (d, $J_{C\text{-}P}$ = 9.5 Hz), 64.1 (d, $J_{C\text{-}P}$ = 6.8 Hz), 35.8, 16.0 (d,

$J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 15.8. HRMS m/z (ESI) calcd for $C_9H_{17}NO_3PSe$ $(M+H)^+$ 298.0106, found 298.0101.



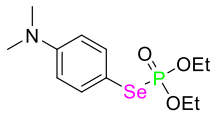
O,O-diethyl Se-(2,4,6-trimethoxyphenyl) phosphoroselenoate (3ao): General Procedure A. Overall Yield: 76% (87.3 mg). Nature: white soild. mp: 102−104 °C. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.14 (s, 2H), 4.29-4.12 (m, 4H), 3.84 (s, 6H), 3.82 (m, 3H), 1.31 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.1, 161.7 (d, $J_{C\text{-}P}$ = 3.5 Hz), 92.8, 90.9 (d, $J_{C\text{-}P}$ = 2.2Hz), 63.1 (d, $J_{C\text{-}P}$ = 4.5 Hz), 56.0, 55.3, 15.9 (d, $J_{C\text{-}P}$ = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.5. HRMS m/z (ESI) calcd for $C_{13}H_{22}O_6PSe$ $(M+H)^+$ 385.0314, found 385.0310.



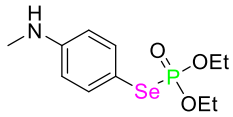
O,O-diethyl Se-(5-methoxythiophen-2-yl) phosphoroselenoate (3ap): General Procedure A. Overall Yield: 65% (64.1 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.93 (t, J = 4.0 Hz, 1H), 6.11 (d, J = 3.6 Hz, 1H), 4.26-4.16 (m, 4H), 3.87 (s, 3H), 1.37 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.8 (d, $J_{C\text{-}P}$ = 3.4 Hz), 136.0 (d, $J_{C\text{-}P}$ = 6.3 Hz), 105.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 101.1 (d, $J_{C\text{-}P}$ = 9.9 Hz), 64.0 (d, $J_{C\text{-}P}$ = 6.6 Hz), 60.1, 15.9 (d, $J_{C\text{-}P}$ = 7.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.0. HRMS m/z (ESI) calcd for $C_9H_{16}O_4PSSe$ $(M+H)^+$ 330.9667, found 330.9674.

O,O-diethyl Se-(4-hydroxyphenyl) hosphoroselenoate (3aq): General Procedure B. Overall Yield: 38% (35.2 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.37 (s, 1H), 7.38-7.35 (m, 2H), 6.59 (d, J = 8.8 Hz, 2H),

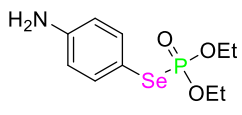
4.24-4.13 (m, 4H), 1.36 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 137.7 (d, $J_{C\text{-}P}$ = 4.0 Hz), 117.2 (d, $J_{C\text{-}P}$ = 2.5 Hz), 110.5 (d, $J_{C\text{-}P}$ = 8.3 Hz), 64.3 (d, $J_{C\text{-}P}$ = 6.6 Hz), 16.0 (d, $J_{C\text{-}P}$ = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.5. HRMS m/z (ESI) calcd for $C_{10}H_{16}O_4PSe$ $(M+H)^+$ 310.9946, found 310.9940.



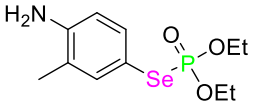
O,O-diethyl Se-(4-(dimethylamino)phenyl) phosphoroselenoate **(3ar)**: General Procedure A. Overall Yield: 84% (84.7 mg). Nature: white soild. mp: 135−137 °C. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (dd, J = 2.0 Hz, J = 1.6 Hz, 2H), 6.62 (d, J = 8.8 Hz, 2H), 4.22-4.11 (m, 4H), 2.95 (s, 3H), 1.32 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.7 (d, $J_{C\text{-}P}$ = 1.5 Hz), 137.0 (d, $J_{C\text{-}P}$ = 3.6 Hz), 113.0 (d, $J_{C\text{-}P}$ = 2.2 Hz), 107.5 (d, $J_{C\text{-}P}$ = 8.3 Hz), 63.5 (d, $J_{C\text{-}P}$ = 5.9 Hz), 40.2, 16.0 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.3. HRMS m/z (ESI) calcd for $C_{12}H_{21}NO_3PSe$ $(M+H)^+$ 338.0412, found 338.0412.



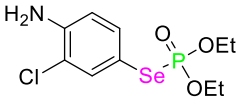
O,O-diethyl Se-(4-(methylamino)phenyl) phosphoroselenoate **(3as)**: General Procedure B. Overall Yield: 84% (73.4 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (dd, J = 2.0 Hz, J = 2.0 Hz, 2H), 6.50 (d, J = 8.8 Hz, 2H), 4.16-4.10 (m, 4H), 2.77 (s, 3H), 1.30 (td, J = 0.4 Hz, J = 0.8 Hz, J = 0.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.9 (d, $J_{C\text{-}P}$ = 2.1 Hz), 137.0 (d, $J_{C\text{-}P}$ = 3.8 Hz), 113.0 (d, $J_{C\text{-}P}$ = 2.1 Hz), 108.0 (d, $J_{C\text{-}P}$ = 8.6 Hz), 63.4 (d, $J_{C\text{-}P}$ = 5.8 Hz), 30.1, 15.8 (d, $J_{C\text{-}P}$ = 7.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.0. HRMS m/z (ESI) calcd for $C_{11}H_{19}NO_3PSe$ $(M+H)^+$ 324.0262, found 324.0266.



O,O-diethyl Se-(4-aminophenyl) phosphoroselenoate **(3at)**: General Procedure B. Overall Yield: 72% (66.5 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (dd, J = 2.0 Hz, J = 2.0 Hz, 2H), 6.55 (t, J = 8.4 Hz, 2H), 4.17-4.06 (m, 4H), 3.91 (br.s, 2H), 1.28 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6 (d, $J_{C\text{-}P}$ = 2.5 Hz), 137.1 (d, $J_{C\text{-}P}$ = 4.1 Hz), 115.7 (d, $J_{C\text{-}P}$ = 2.2 Hz), 109.4 (d, $J_{C\text{-}P}$ = 8.7 Hz), 63.5 (d, $J_{C\text{-}P}$ = 5.9 Hz), 15.8 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.9. HRMS m/z (ESI) calcd for $C_{10}H_{17}NO_3PSe$ $(M+H)^+$ 310.0106, found 310.0111.

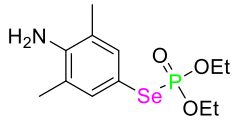


O,O-diethyl Se-(4-amino-3-methylphenyl) phosphoroselenoate **(3au)**: General Procedure B. Overall Yield: 72% (66.5 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (s, 1H), 7.25 (d, J = 7.2 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 4.12-4.10 (m, 4H), 3.60 (s, 2H), 2.10 (s, 3H), 1.32 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.7 (d, $J_{C\text{-}P}$ = 2.5 Hz), 137.9 (d, $J_{C\text{-}P}$ = 1.8 Hz), 134.8 (d, $J_{C\text{-}P}$ = 3.9 Hz), 123.2 (d, $J_{C\text{-}P}$ = 2.1 Hz), 115.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 109.5 (d, $J_{C\text{-}P}$ = 8.6 Hz), 63.5 (d, $J_{C\text{-}P}$ = 5.9 Hz), 17.0, 15.8 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.0. HRMS m/z (ESI) calcd for $C_{11}H_{19}NO_3PSe$ $(M+H)^+$ 324.0262, found 324.0259.

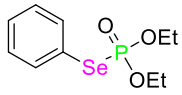


O,O-diethyl Se-(4-amino-3-chlorophenyl) phosphoroselenoate (3av): General Procedure B. Overall Yield: 51% (52.3 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (t, J = 1.8 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H), 5.73 (s, 2H), 4.11-4.04 (m, 4H), 1.23 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.8 (d, $J_{C\text{-}P}$ = 1.8 Hz), 137.0 (d, $J_{C\text{-}P}$ = 1.8 Hz), 135.5

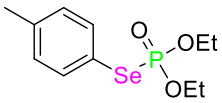
(d, J_{C-P} = 6.6 Hz), 117.1 (d, J_{C-P} = 3.6Hz), 115.9 (d, J_{C-P} = 1.9 Hz), 106.7 (d, J_{C-P} = 1.8 Hz), 63.4 (d, J_{C-P} = 5.8 Hz), 15.7 (d, J_{C-P} = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.2. HRMS m/z (ESI) calcd for $C_{10}H_{16}ClNO_3PSe$ $(M+H)^+$ 343.9716, found 343.9723.



O,O-diethyl Se-(4-amino-3,5-dimethylphenyl) phosphoroselenoate (3aw): General Procedure B. Overall Yield: 76% (76.6 mg). Nature: white soild. mp: 133−135 °C. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15 (d, J = 1.2 Hz, 2H), 4.19-4.09 (m, 4H), 3.71 (br.s, 2H), 2.10 (s, 6H), 1.30 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.9 (d, J_{C-P} = 2.8 Hz), 135.8 (d, J_{C-P} = 3.9 Hz), 122.4 (d, J_{C-P} = 2.3 Hz), 108.8 (d, J_{C-P} = 8.7 Hz), 63.4 (d, J_{C-P} = 5.8 Hz), 17.3, 15.8 (d, J_{C-P} = 7.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 19.2. HRMS m/z (ESI) calcd for $C_{12}H_{21}NO_3PSe$ $(M+H)^+$ 338.0412, found 338.0419.

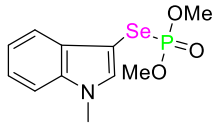


O,O-diethyl Se-phenyl phosphoroselenoate (3ax): Overall Yield: 29% (25.5 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64-7.61 (m, 2H), 7.38-7.26 (m, 3H), 4.25-4.09 (m, 4H), 1.32 (t, J = 7.2 Hz, 6H)； ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.5 (d, J_{C-P} = 5.2 Hz), 128.4 (d, J_{C-P} = 2.2 Hz), 127.7 (d, J_{C-P} = 2.3 Hz), 122.6 (d, J_{C-P} = 8.1 Hz), 62.6 (d, J_{C-P} = 6.8 Hz), 14.9 (d, J_{C-P} = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.2. HRMS m/z (ESI) calcd for $C_{10}H_{16}O_3PSe$ $(M+H)^+$ 294.9997, found 294.9999.

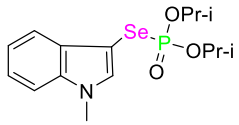


O,O-diethyl Se-(p-tolyl) phosphoroselenoate (3ay): Overall Yield: 33% (30.4 mg). Nature: yellow oil. Purification of the product was performed by silica gel

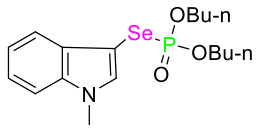
column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, J = 5.2 Hz, 2H), 7.07 (d, J = 6.4 Hz, 2H), 4.19-4.06 (m, 4H), 2.31 (s, 3H), 1.32 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8 (d, $J_{C\text{-}P}$ = 3.4 Hz), 134.9 (d, $J_{C\text{-}P}$ = 2.6 Hz), 129.9 (d, $J_{C\text{-}P}$ = 2.3 Hz), 119.6 (d, $J_{C\text{-}P}$ = 7.1 Hz), 63.5 (d, $J_{C\text{-}P}$ = 8.0 Hz), 21.4, 15.9 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.8. HRMS m/z (ESI) calcd for $C_{11}H_{18}O_3PSe$ $(M+H)^+$ 309.0153, found 309.0157.



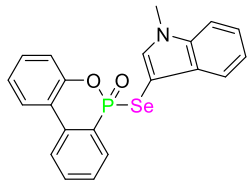
O,O-dimethyl Se-(1-methyl-1H-indol-3-yl) phosphoroselenoate (3ba): Overall Yield: 66% (62.9 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.30-7.20 (m, 3H), 3.82 (d, J = 1.2 Hz, 3H), 3.78 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.0, 135.2 (d, $J_{C\text{-}P}$ = 4.6 Hz), 130.4, 122.4, 120.5, 119.8, 109.7, 89.2 (d, $J_{C\text{-}P}$ = 8.7 Hz), 5^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.0, 3.9 (d, $J_{C\text{-}P}$ = 5.4 Hz), 33.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.0. HRMS m/z (ESI) calcd for $C_{11}H_{15}NO_3PSe$ $(M+H)^+$ 319.9949, found 319.9957.



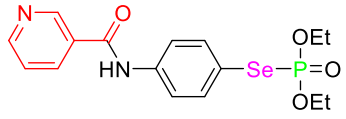
O,O-diisopropyl Se-(1-methyl-1H-indol-3-yl) phosphoroselenoate (3ca): Overall Yield: 91% (102.1 mg). Nature: colorless oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, J = 7.6 Hz, 1H), 7.32-7.24 (m, 3H), 7.23-7.18 (m, 1H), 4.77-4.72 (m, 2H), 3.80 (s, 3H), 1.28 (d, J = 6.0 Hz, 6H), 1.21 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.9, 135.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 130.4 (d, $J_{C\text{-}P}$ = 1.6 Hz), 122.2, 120.2 (d, $J_{C\text{-}P}$ = 10.3 Hz), 109.4, 90.2 (d, $J_{C\text{-}P}$ = 8.8 Hz), 72.9 (d, $J_{C\text{-}P}$ = 6.8 Hz), 33.1, 23.8 (d, $J_{C\text{-}P}$ = 3.6 Hz), 23.5 (d, $J_{C\text{-}P}$ = 6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 15.4. HRMS m/z (ESI) calcd for $C_{15}H_{23}NO_3PSe$ $(M+H)^+$ 376.0575, found 376.0582.



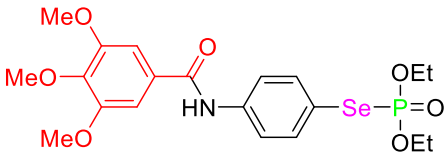
O,O-dibutyl Se-(1-methyl-1H-indol-3-yl) phosphoroselenoate (3da): Overall Yield: 90% (108.5 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.28-7.24 (m, 2H), 7.22 (t, J = 4.0 Hz, 1H), 4.13-4.02 (m, 4H), 3.81 (s, 3H), 1.58-1.52 (m, 4H), 1.33-1.25 (m, 4H), 0.88 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.0, 135.1 (d, $J_{C\text{-}P}$ = 4.7 Hz), 130.5 (d, $J_{C\text{-}P}$ = 11.6 Hz), 122.3, 120.3, 120.0, 109.5, 89.7 (d, $J_{C\text{-}P}$ = 8.8 Hz), 67.4 (d, $J_{C\text{-}P}$ = 6.2 Hz), 33.1, 32.0 (d, $J_{C\text{-}P}$ = 7.3 Hz), 18.6, 13.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.4. HRMS m/z (ESI) calcd for $C_{17}H_{27}NO_3PSe$ $(M+H)^+$ 404.0888, found 404.0882.



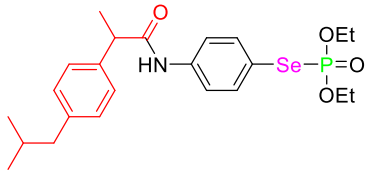
6-((1-methyl-1H-indol-3-yl)selanyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (3ea): Overall Yield: 62% (78.8 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (dd, J = 7.2 Hz, J = 7.2 Hz, 1H), 7.50 (t, J = 3.6 Hz, 2H), 7.45-7.43 (m, 1H), 7.35 (dd, J = 1.6 Hz, J = 1.6 Hz, 1H), 7.11-7.00 (m, 5H), 6.98-6.87 (m, 2H), 6.60 (d, J = 3.2 Hz, 1H), 3.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.7 (d, $J_{C\text{-}P}$ = 10.1 Hz), 136.5, 136.1(d, $J_{C\text{-}P}$ = 4.1 Hz), 136.0 (d, $J_{C\text{-}P}$ = 7.2 Hz), 133.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.2 (d, $J_{C\text{-}P}$ = 11.4 Hz), 129.9, 129.7, 128.5 (d, $J_{C\text{-}P}$ = 14.7 Hz), 126.9, 125.8, 123.9, 123.5, 122.4 (d, $J_{C\text{-}P}$ = 9.8 Hz), 121.9 (d, $J_{C\text{-}P}$ = 10.9 Hz), 120.2, 119.4 (d, $J_{C\text{-}P}$ = 8.6 Hz), 108.9, 87.8 (d, $J_{C\text{-}P}$ = 7.0 Hz), 32.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 30.9. HRMS m/z (ESI) calcd for $C_{21}H_{17}NO_2PSe$ $(M+H)^+$ 426.0157, found 426.0153.



O,O-diethyl Se-(4-(nicotinamido)phenyl) phosphoroselenoate (4aa): Overall Yield: 92% (192 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.46 (brs, 1H), 9.14 (d, J = 1.6 Hz, 1H), 8.70 (d, J = 3.6 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 2.0 Hz, 2H), 7.53 (dd, J = 2.0 Hz, J = 1.6 Hz, 2H), 7.38 (dd, J = 4.8 Hz, J = 4.8 Hz, 1H), 4.16-4.07 (m, 4H), 1.30 (d, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.4, 152.1, 148.7, 139.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 136.4 (d, $J_{C\text{-}P}$ = 4.4 Hz), 135.6, 130.7, 123.2, 121.4 (d, $J_{C\text{-}P}$ = 2.1 Hz), 117.2 (d, $J_{C\text{-}P}$ = 8.4 Hz), 64.2 (d, $J_{C\text{-}P}$ = 6.6 Hz), 15.9 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.9. HRMS m/z (ESI) calcd for $C_{16}H_{20}N_2O_4PSe$ $(M+H)^+$ 415.0320, found 415.0329.

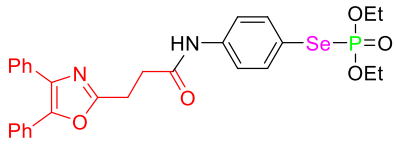


O,O-diethyl Se-(4-(3,4,5-trimethoxybenzamido)phenyl) phosphoroselenoate **(4ab)**: Overall Yield: 87% (219 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (brs, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.56 (t, J = 4.4 Hz, 2H), 7.12 (s, 2H), 4.16-4.07 (m, 4H), 3.89 (s, 6H), 3.88 (s, 3H), 1.30 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.8, 153.1, 141.1, 139.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 136.4 (d, $J_{C\text{-}P}$ = 4.4 Hz), 130.1, 121.1 (d, $J_{C\text{-}P}$ = 1.9 Hz), 117.4 (d, $J_{C\text{-}P}$ = 8.5 Hz), 104.8, 64.0 (d, $J_{C\text{-}P}$ = 6.2 Hz), 60.8, 56.3, 15.9 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 17.8. HRMS m/z (ESI) calcd for $C_{20}H_{27}NO_7PSe$ $(M+H)^+$ 504.0685, found 504.0693.



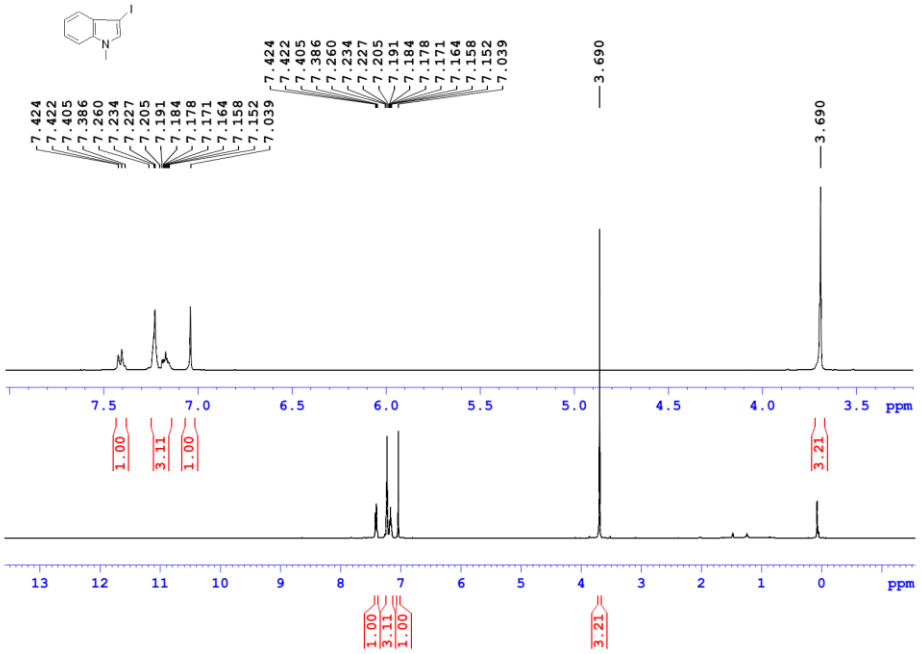
O,O-diethyl Se-(4-(2-(4-isobutylphenyl)propanamido)phenyl) phosphoroselenoate **(4ac)**: Overall Yield: 74% (184 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (brs, 1H), 7.41 (dd, J = 2.0 Hz, J = 1.6 Hz, 2H), 7.35 (d, J

= 8.8 Hz, 2H), 7.20 (t, *J* = 4.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.13-4.03 (m, 4H), 3.67 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H), 2.38 (d, *J* = 7.2 Hz, 2H), 1.80-1.74 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 6H), 0.83 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.9, 140.8, 139.2, 138.0, 136.4 (d, $J_{C\text{-}P}$ = 4.4 Hz), 129.6, 127.2, 120.4, 116.9 (d, $J_{C\text{-}P}$ = 8.5 Hz), 63.9 (d, $J_{C\text{-}P}$ = 6.2 Hz), 47.3, 44.9, 30.1, 22.3, 18.5, 15.9 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.0. HRMS m/z (ESI) calcd for $C_{23}H_{33}NO_4PSe$ $(M+H)^+$ 498.1307, found 498.1316.

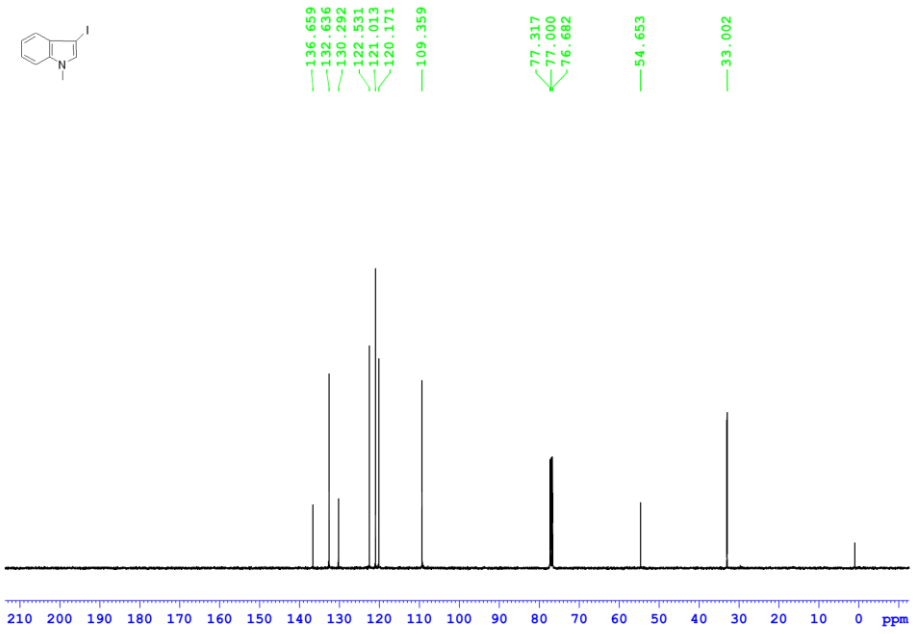


O,O-diethyl Se-(4-(3-(4,5-diphenyloxazol-2-yl)propanamido)phenyl) phosphoroselenoate **(4ad)**: Overall Yield: 79% (231 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.05 (brs, 1H), 7.63-7.61 (m, 2H), 7.56-7.54 (m, 2H), 7.52 (dd, *J* = 1.6 Hz, *J* = 2.0 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.39-7.32 (m, 6H), 4.18-4.11 (m, 4H), 3.28 (t, *J* = 7.0 Hz, 2H), 2.97 (t, *J* = 7.0 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 162.4, 145.6, 139.2, 136.5 (d, $J_{C\text{-}P}$ = 4.4 Hz), 134.7, 132.1, 128.6 (d, $J_{C\text{-}P}$ = 4.9 Hz), 128.2, 128.1, 127.8, 127.6, 126.4, 125.9, 120.4, 117.1 (d, $J_{C\text{-}P}$ = 8.8 Hz), 63.9 (d, $J_{C\text{-}P}$ = 6.3 Hz), 34.0 23.9, 15.9 (d, $J_{C\text{-}P}$ = 7.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 18.0. HRMS m/z (ESI) calcd for $C_{28}H_{30}N_2O_5PSe$ $(M+H)^+$ 585.1052, found 585.1049.

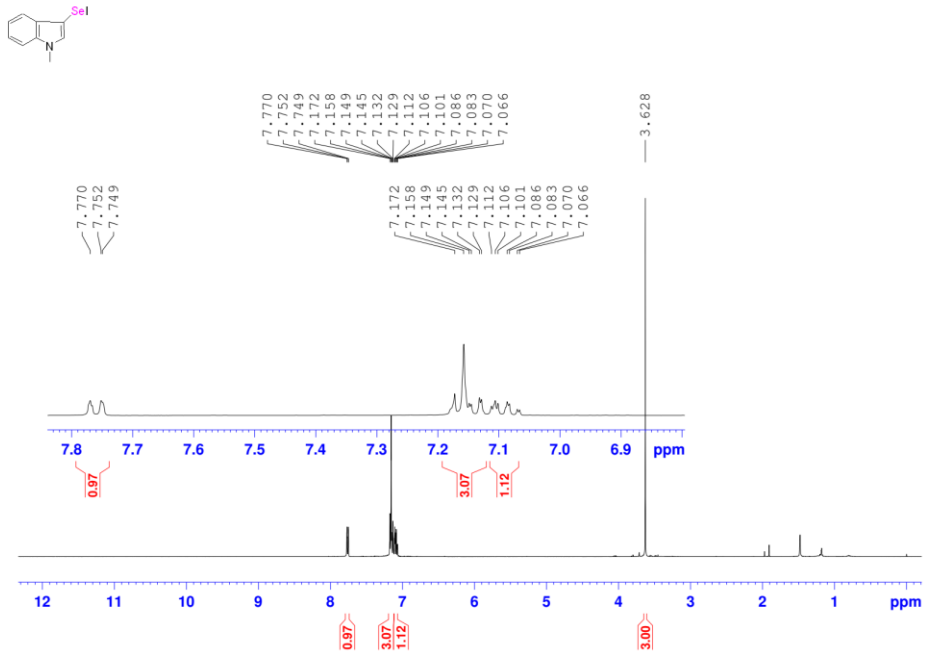
6. Spectra



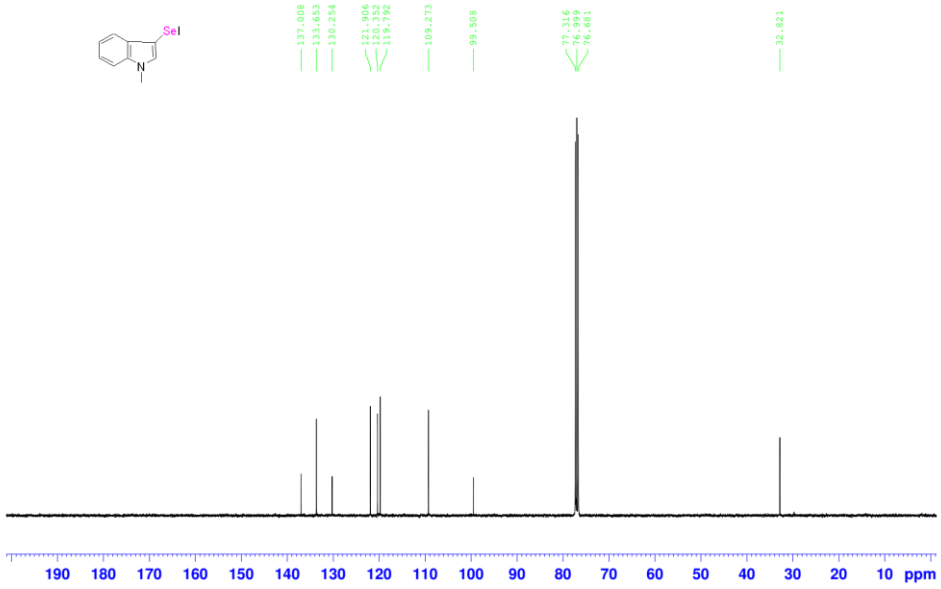
^{1}H NMR Spectrum of **1a'**



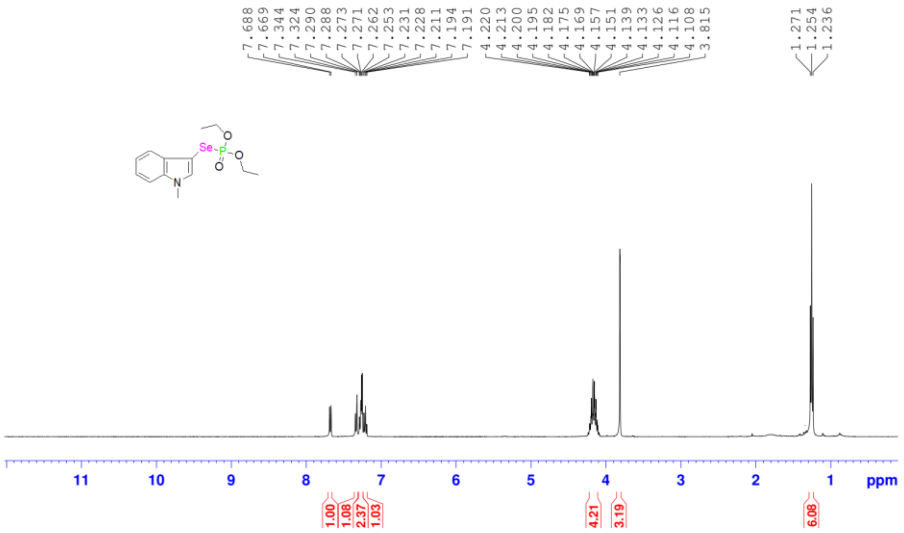
^{13}C NMR Spectrum of **1a'**



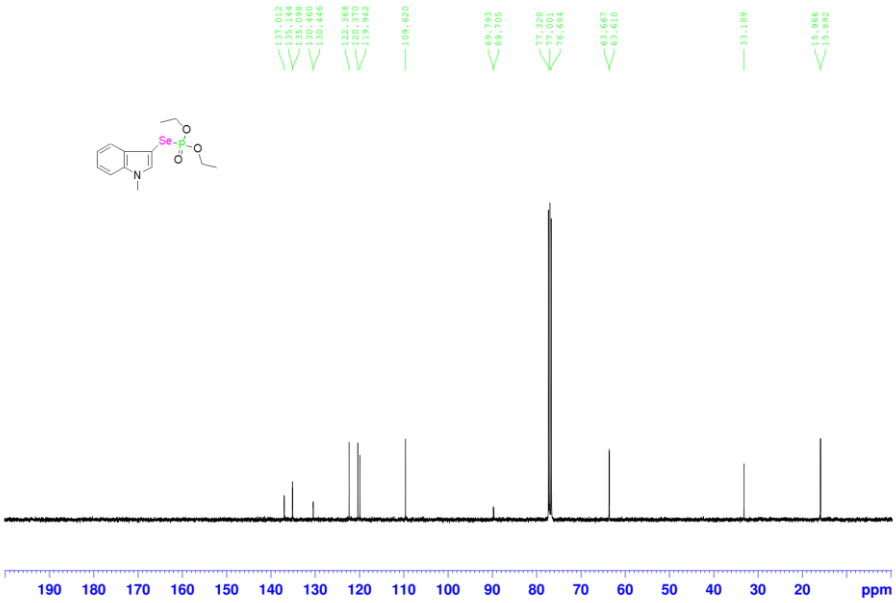
^{1}H NMR Spectrum of **compound A**



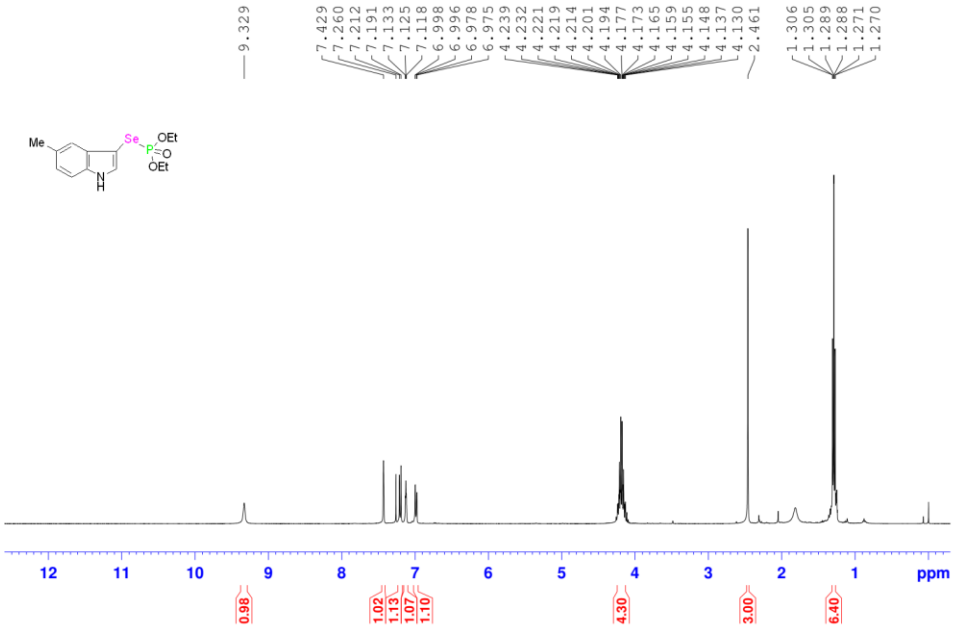
^{13}C NMR Spectrum of **compound A**



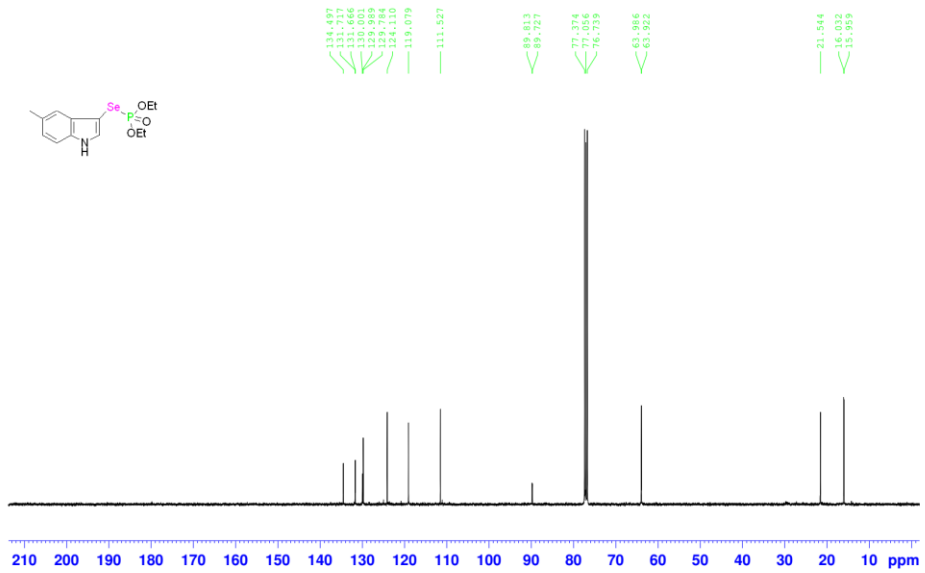
^{1}H NMR Spectrum of **3aa**



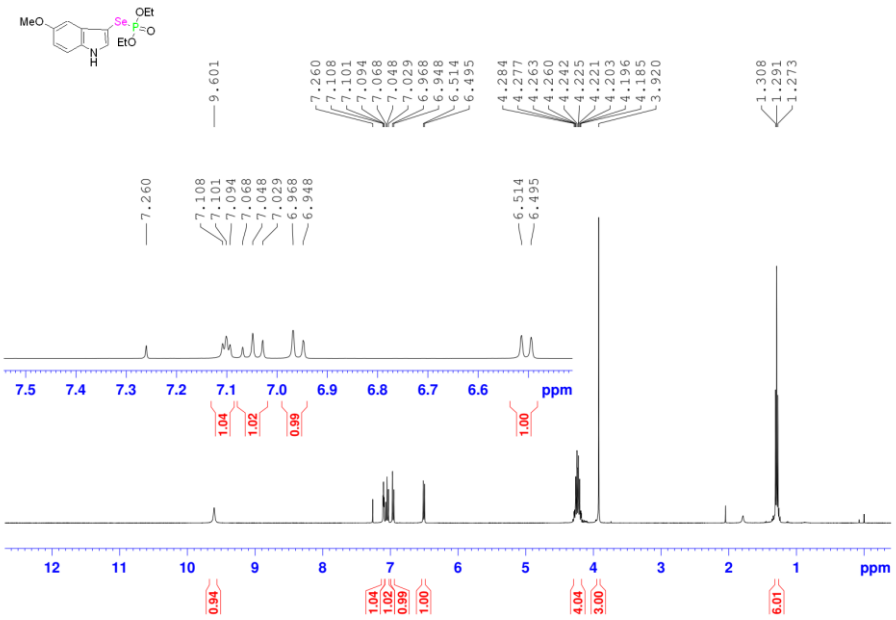
^{13}C NMR Spectrum of **3aa**



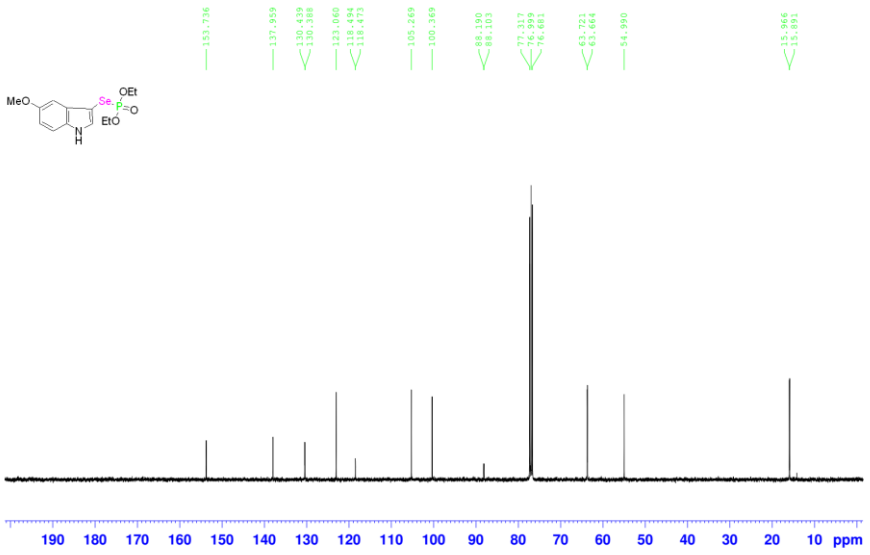
^{1}H NMR Spectrum of **3ab**



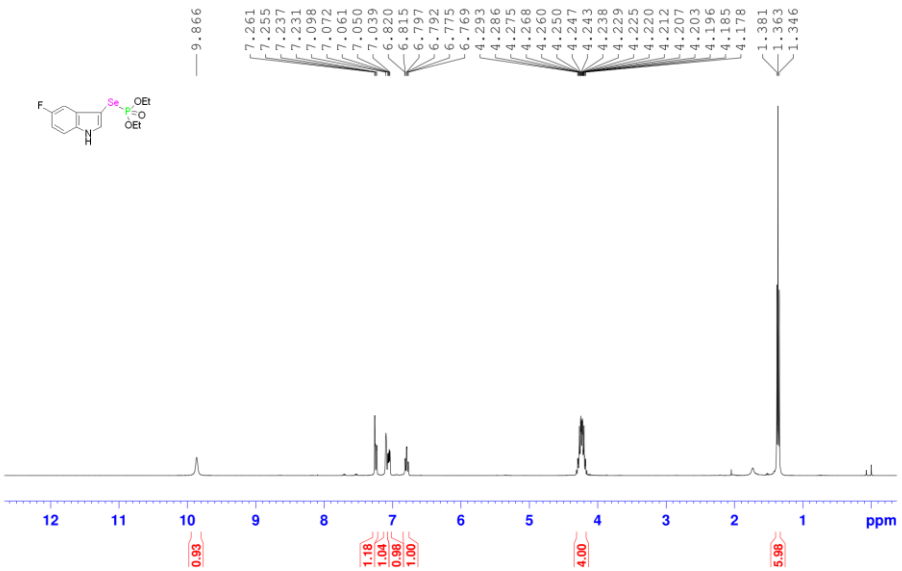
^{13}C NMR Spectrum of **3ab**



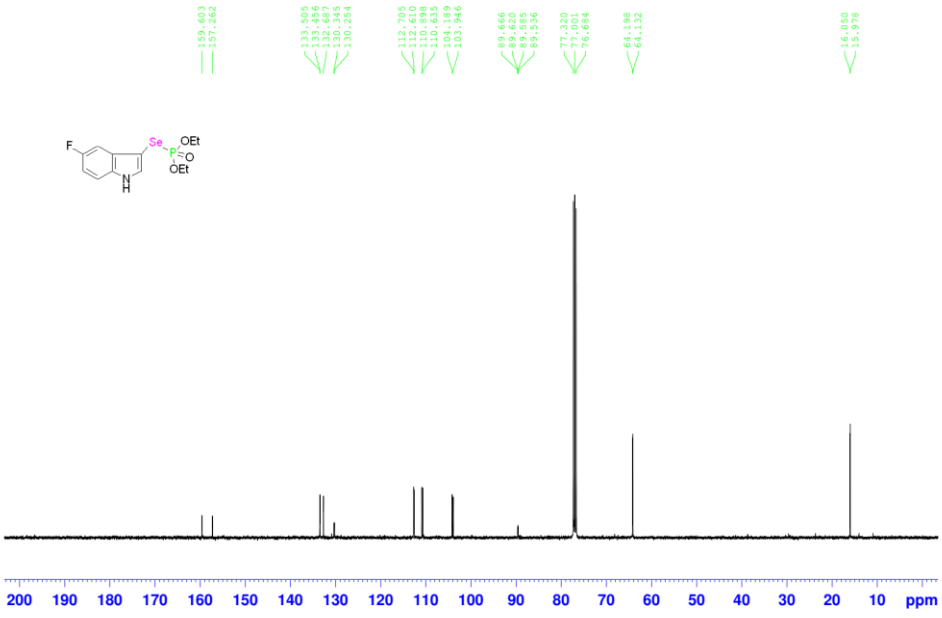
^{1}H NMR Spectrum of **3ac**



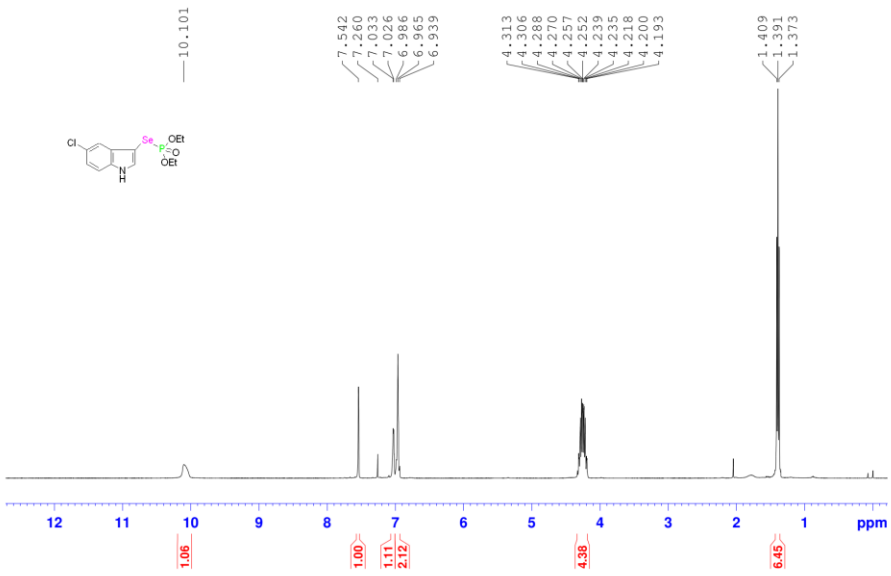
^{13}C NMR Spectrum of **3ac**



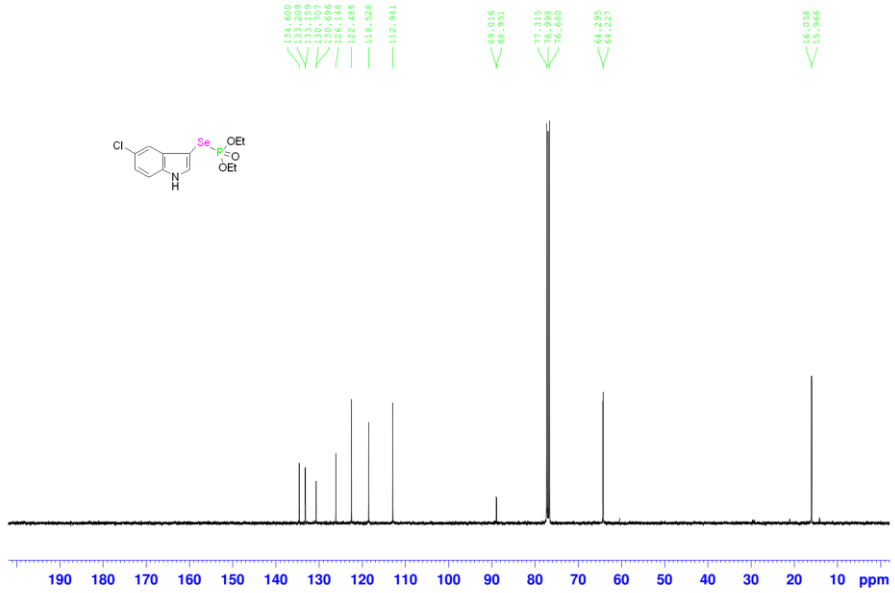
^{1}H NMR Spectrum of **3ad**



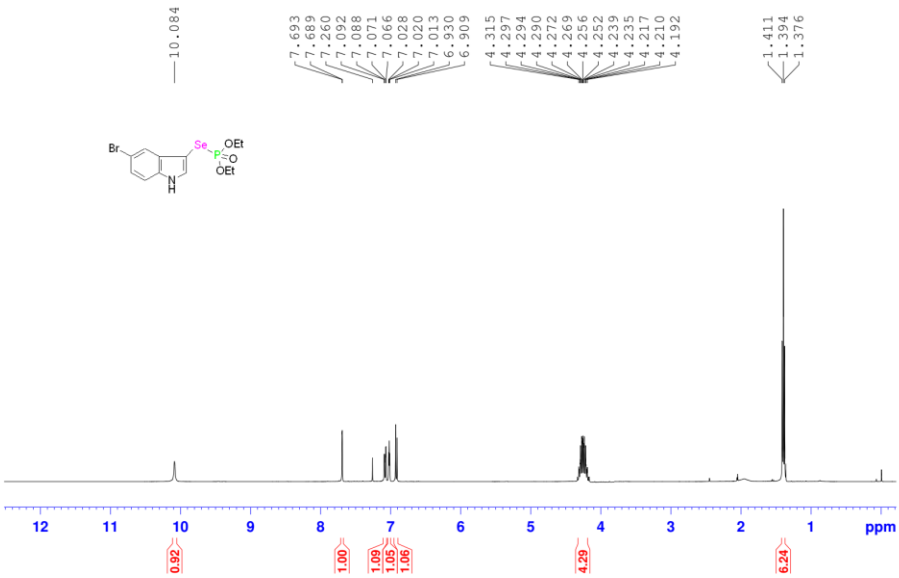
^{13}C NMR Spectrum of **3ad**



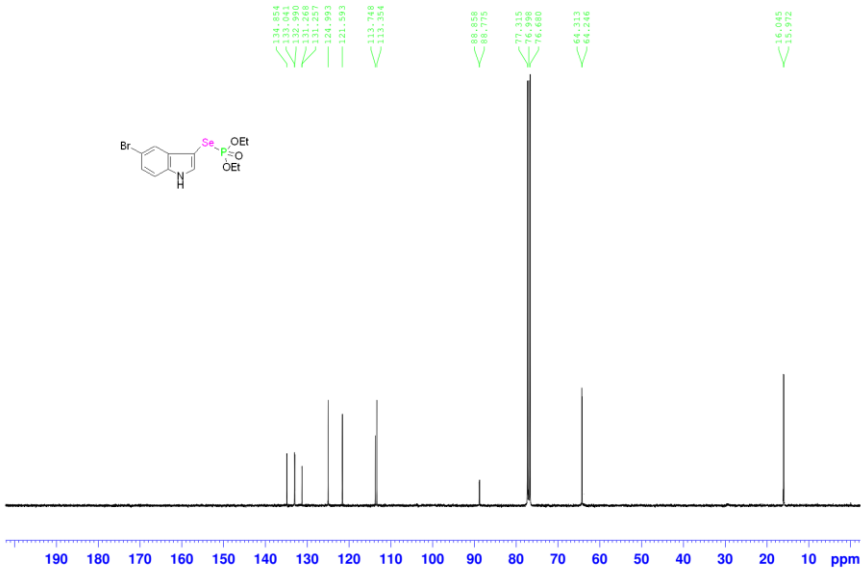
^{1}H NMR Spectrum of **3ae**



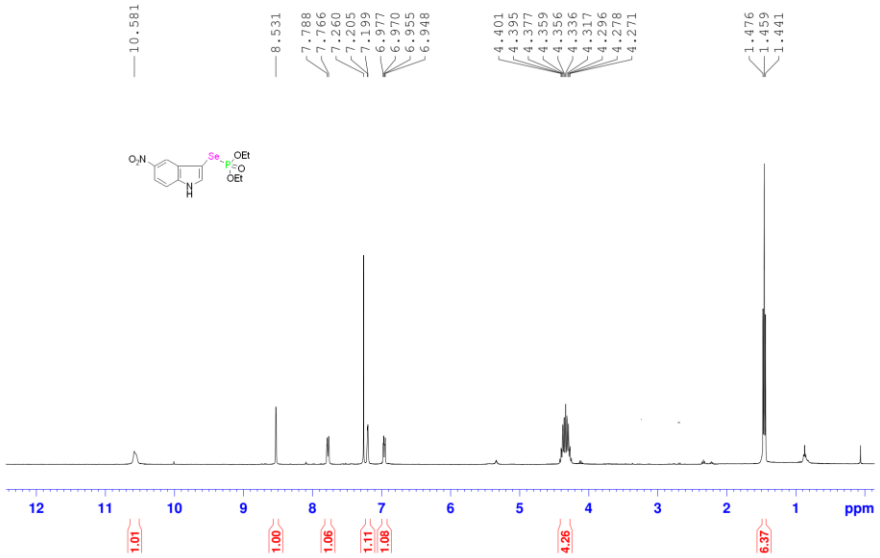
^{13}C NMR Spectrum of **3ae**



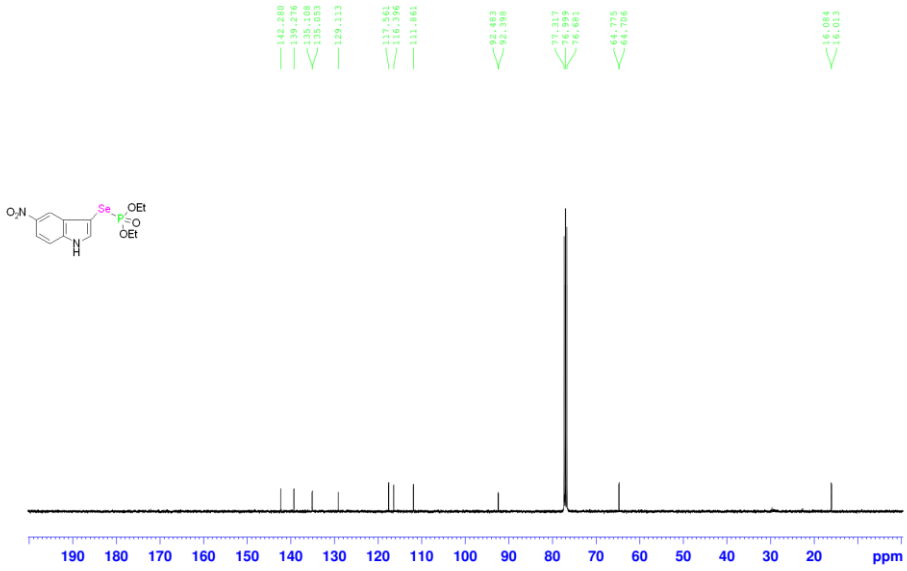
^{1}H NMR Spectrum of **3af**



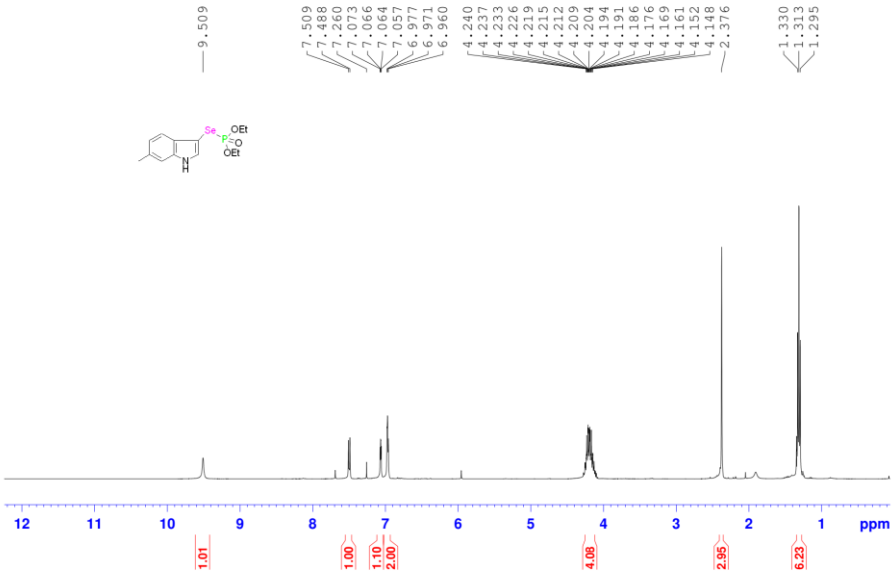
^{13}C NMR Spectrum of **3af**



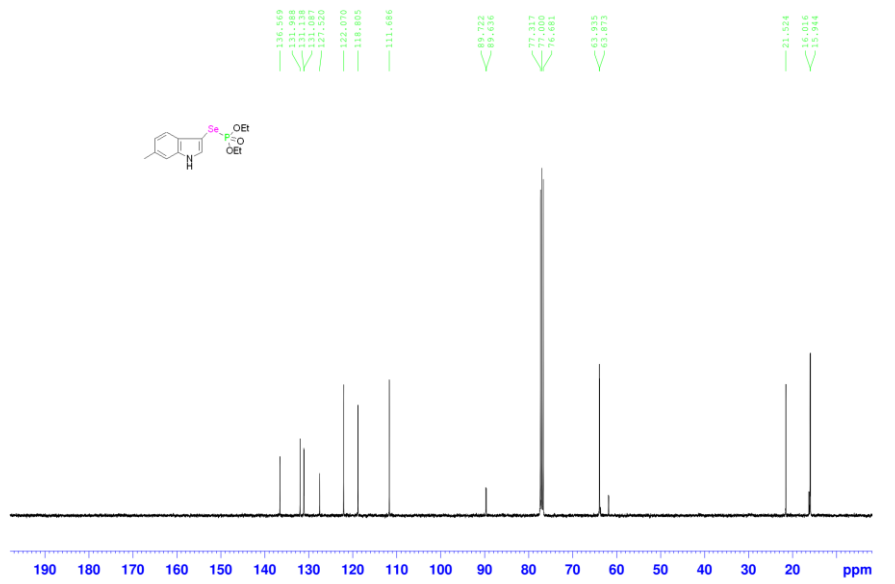
^{1}H NMR Spectrum of **3ag**



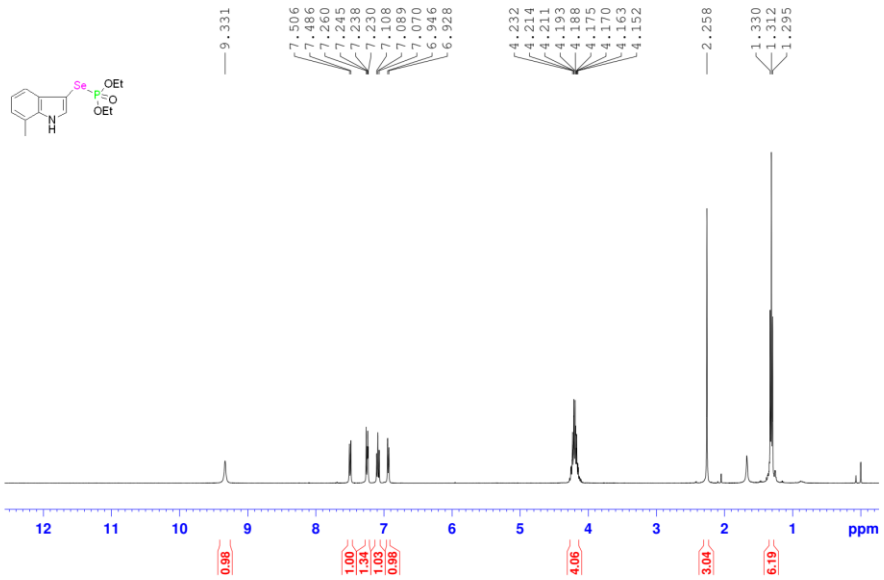
^{13}C NMR Spectrum of **3ag**



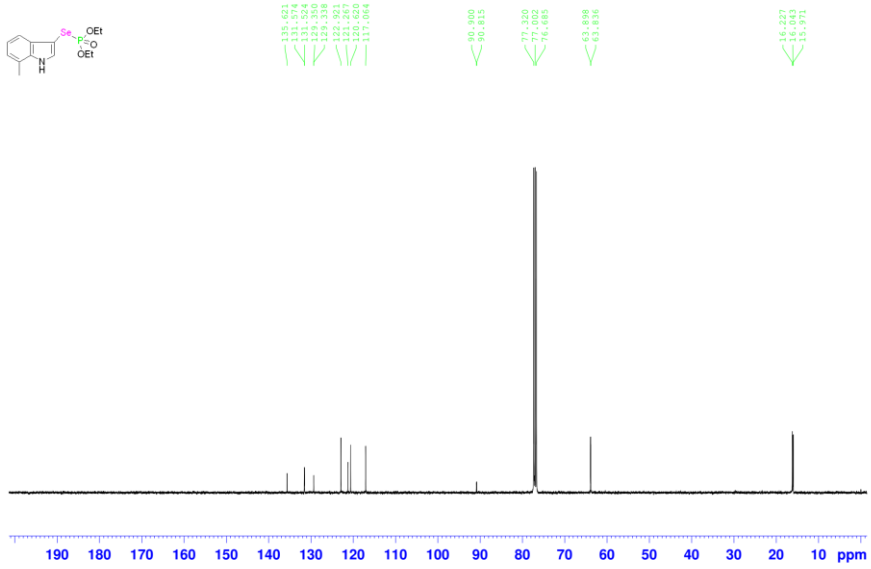
^{1}H NMR Spectrum of **3ah**



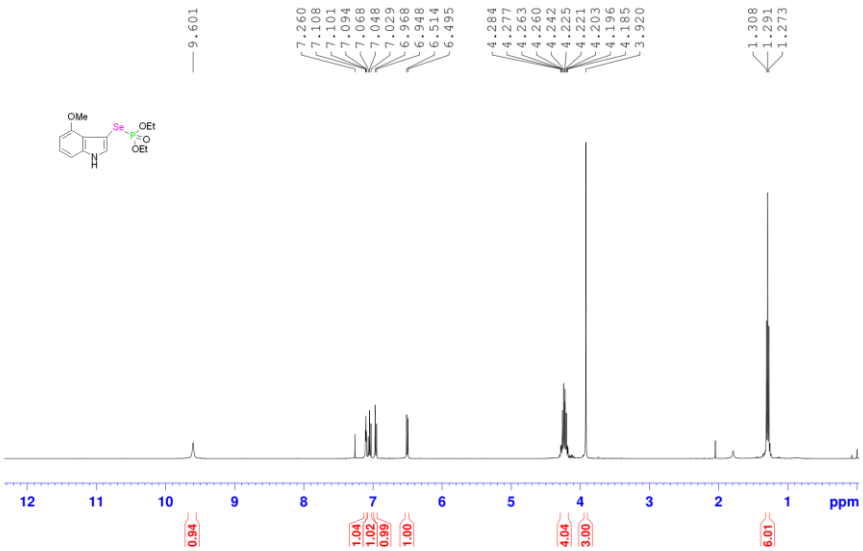
^{13}C NMR Spectrum of **3ah**



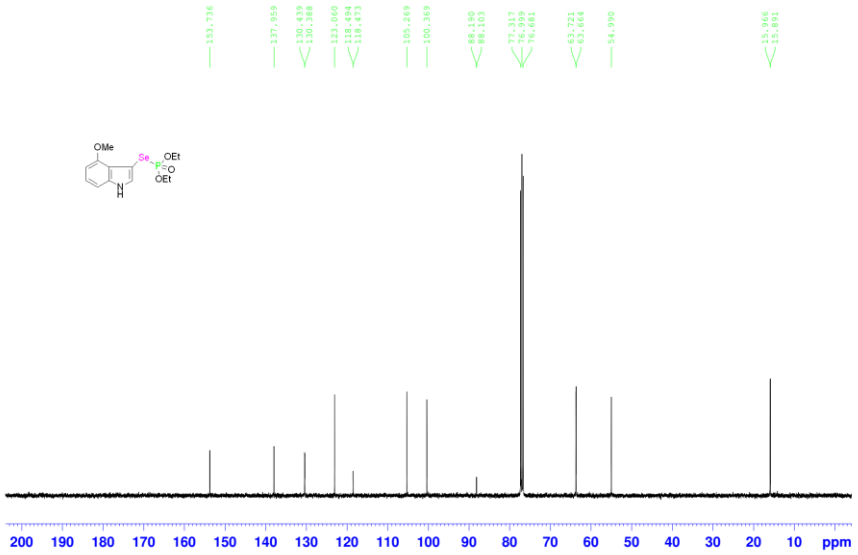
^{1}H NMR Spectrum of **3ai**



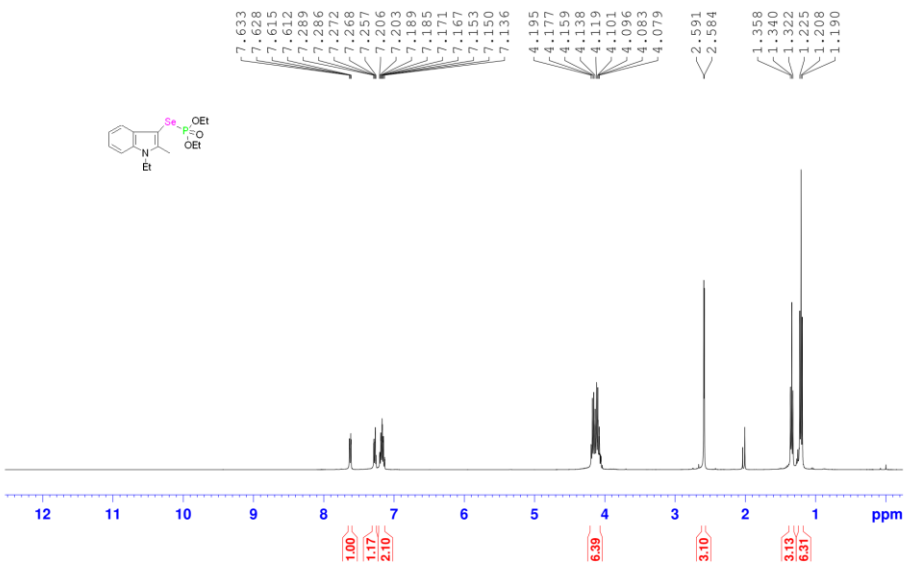
^{13}C NMR Spectrum of **3ai**



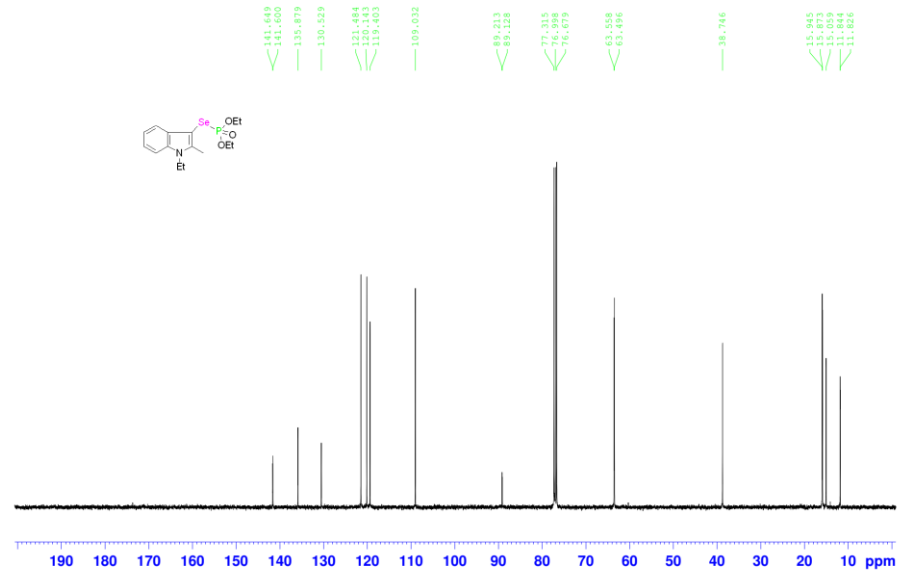
^{1}H NMR Spectrum of **3aj**



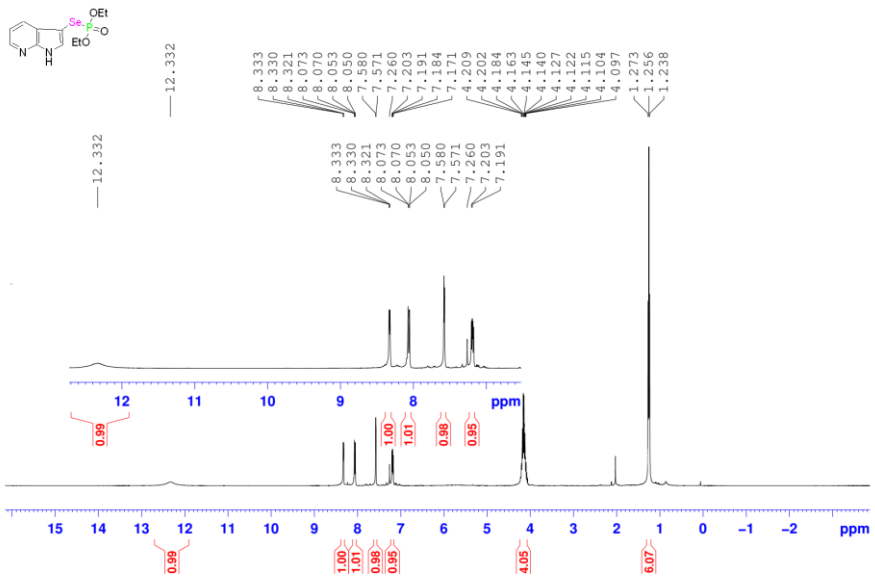
^{13}C NMR Spectrum of **3aj**



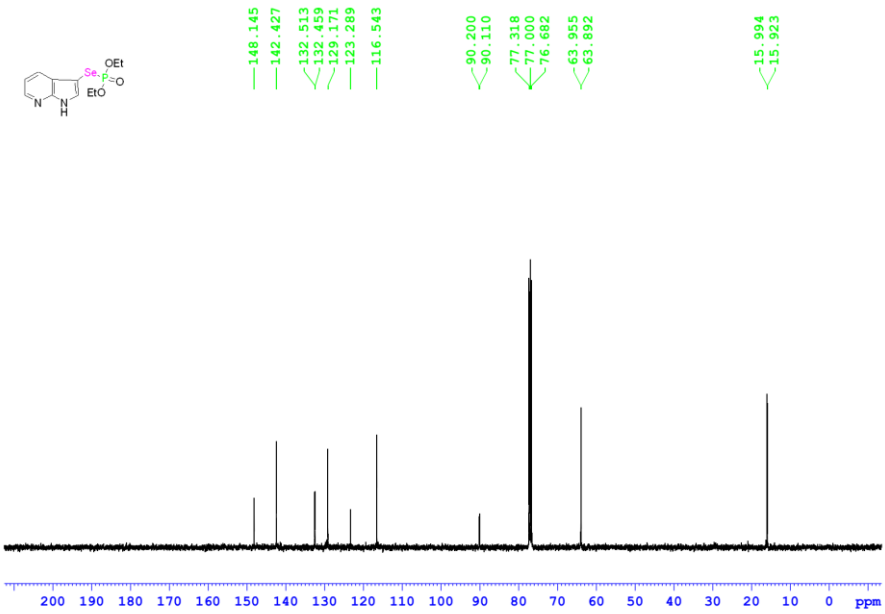
^{1}H NMR Spectrum of **3ak**



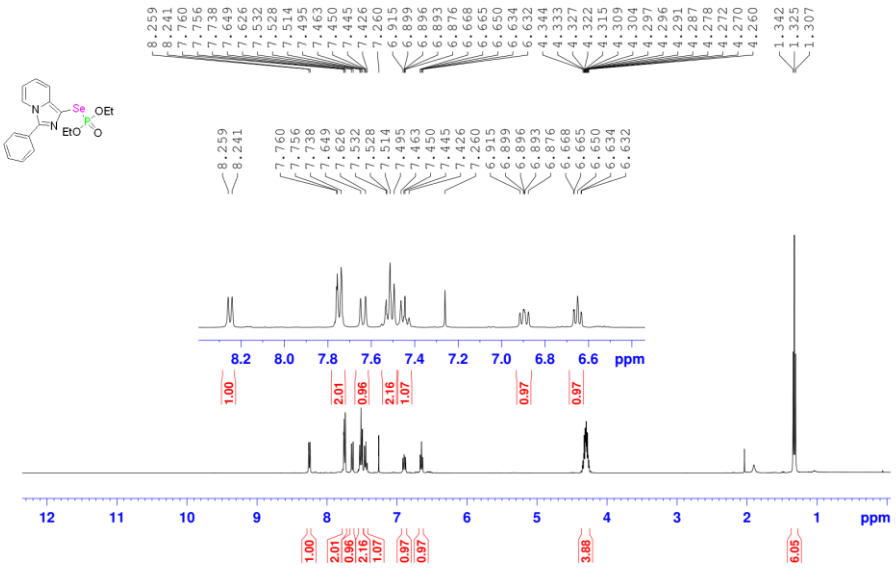
^{13}C NMR Spectrum of **3ak**



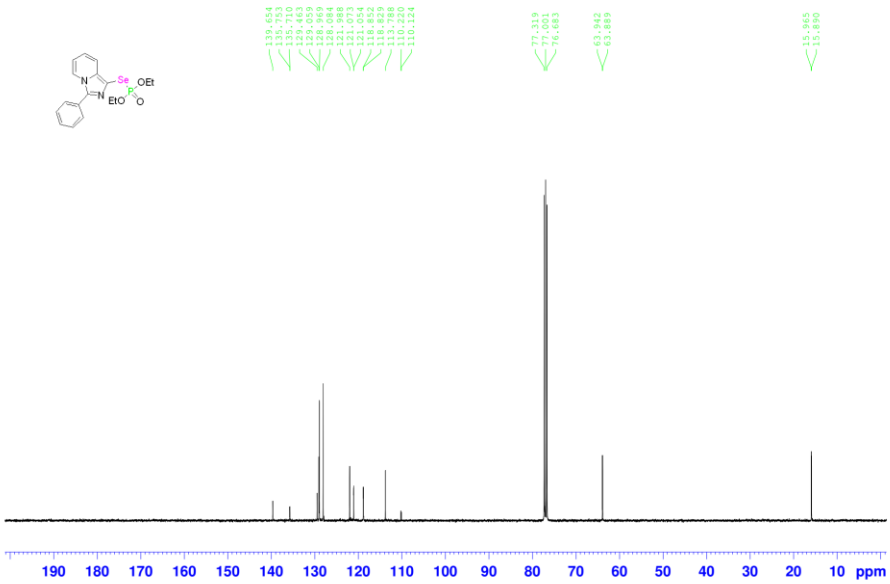
^{1}H NMR Spectrum of **3al**



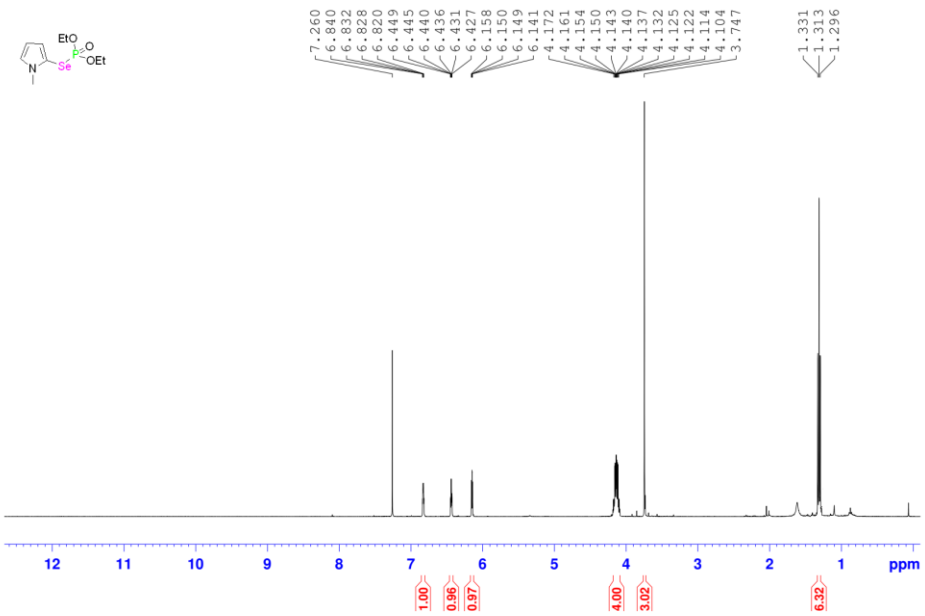
^{13}C NMR Spectrum of **3al**



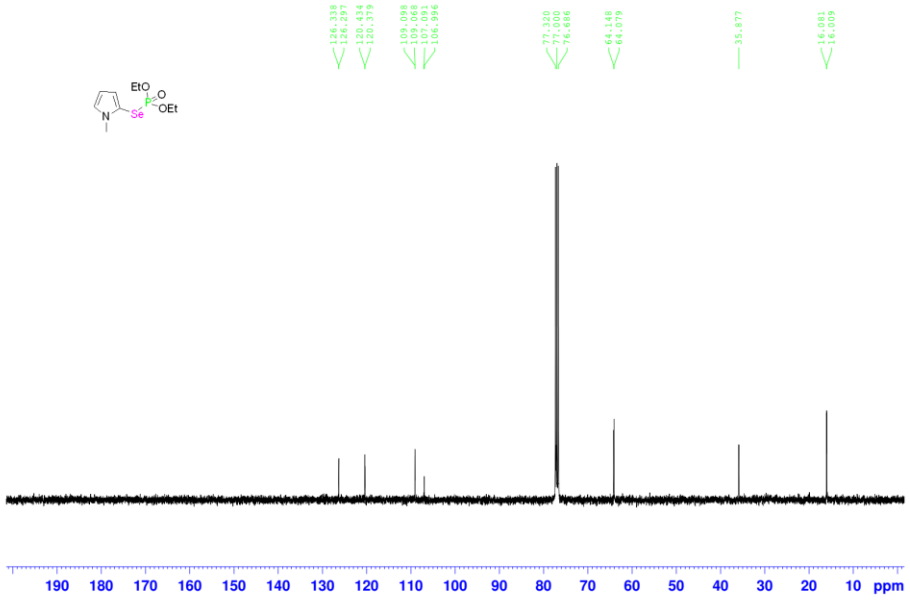
^{1}H NMR Spectrum of **3am**



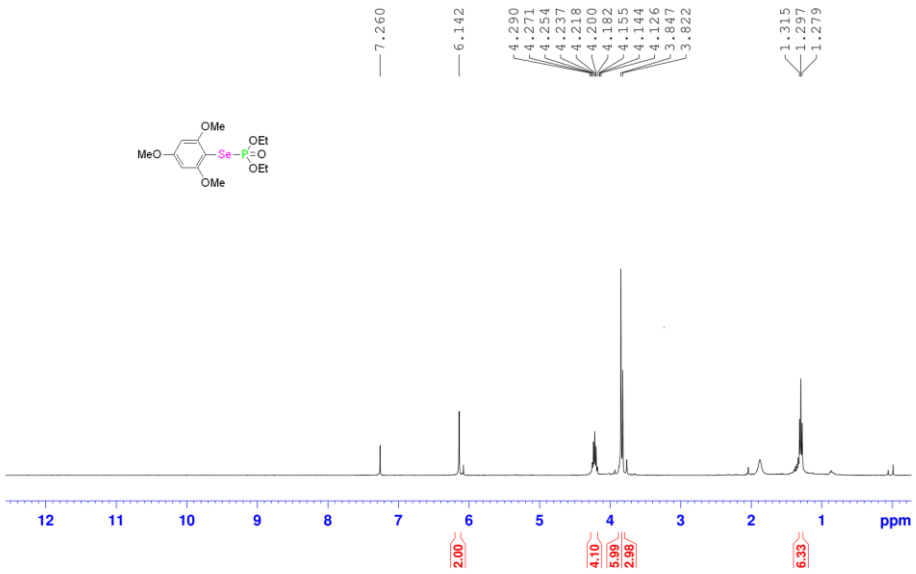
^{13}C NMR Spectrum of **3am**



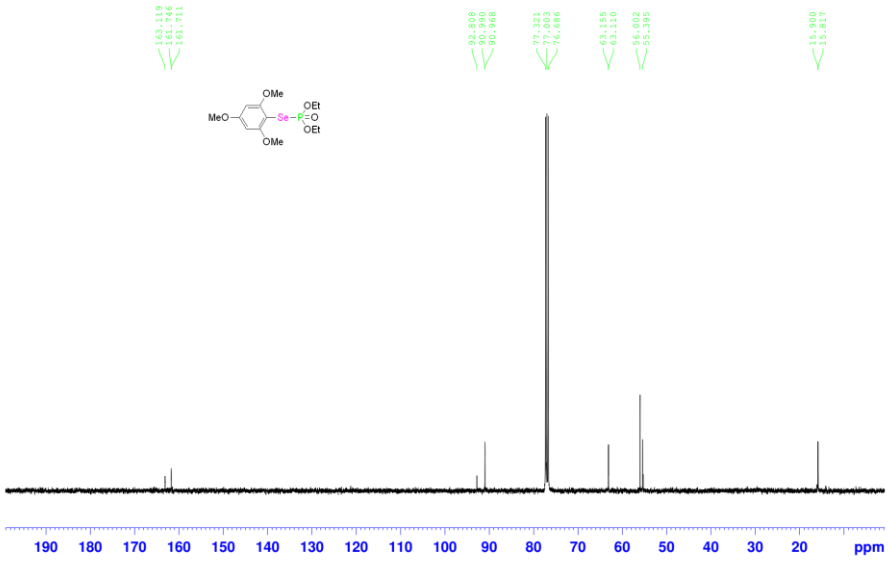
^{1}H NMR Spectrum of **3an**



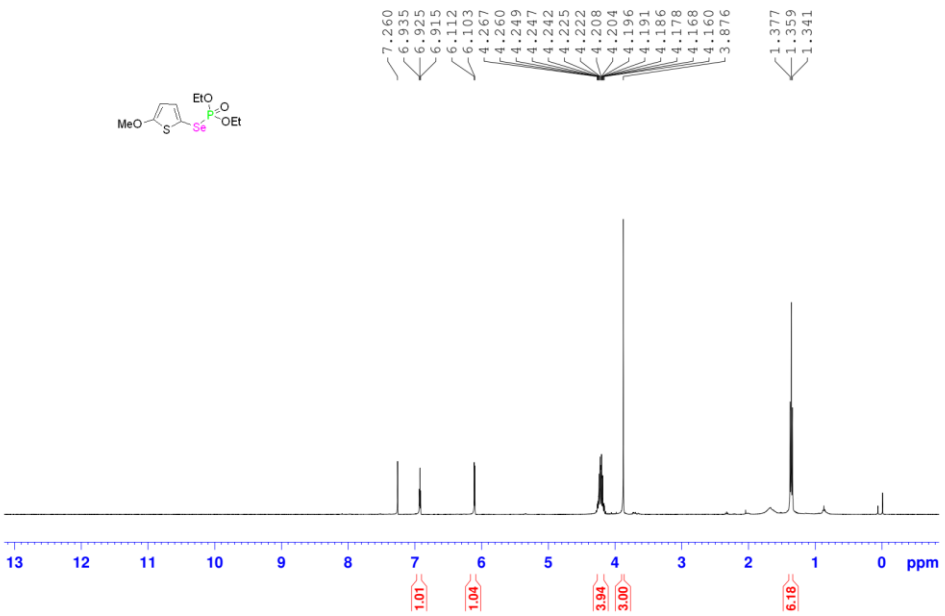
^{13}C NMR Spectrum of **3an**



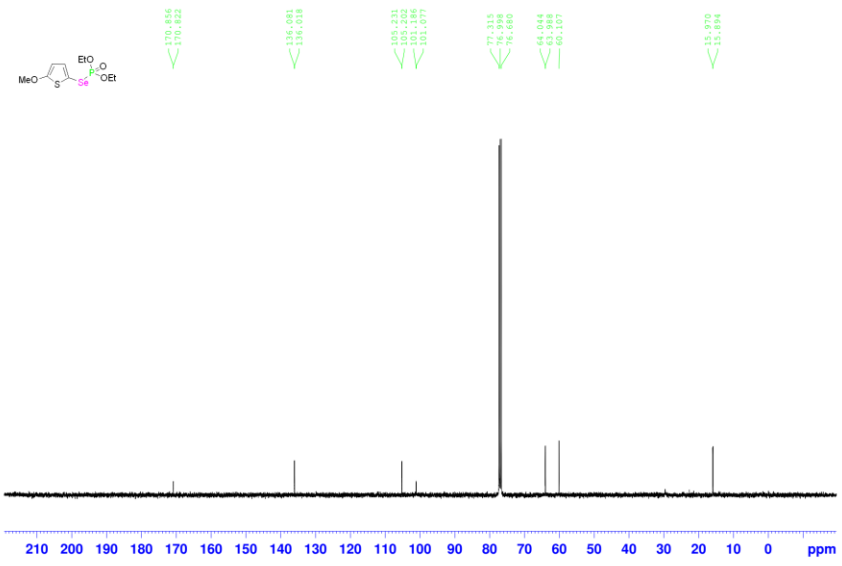
^{1}H NMR Spectrum of **3ao**



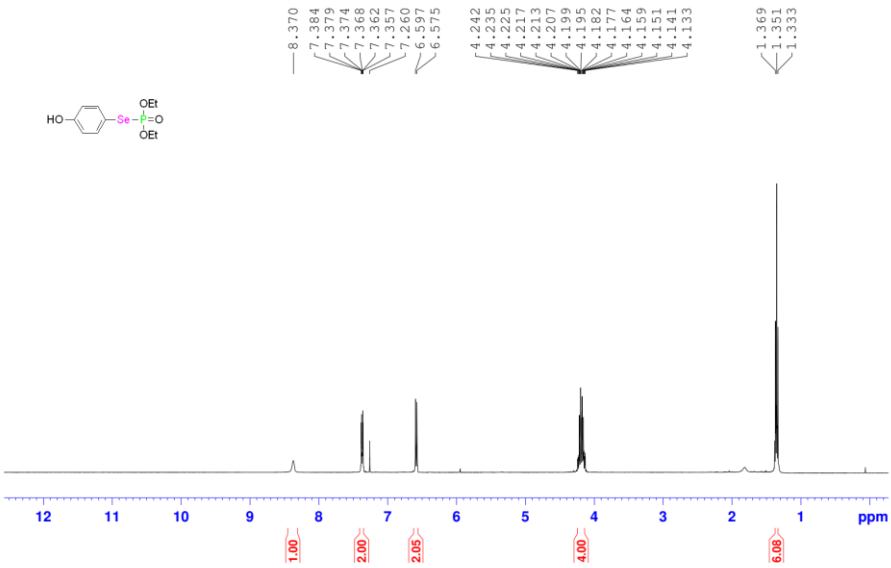
^{13}C NMR Spectrum of **3ao**



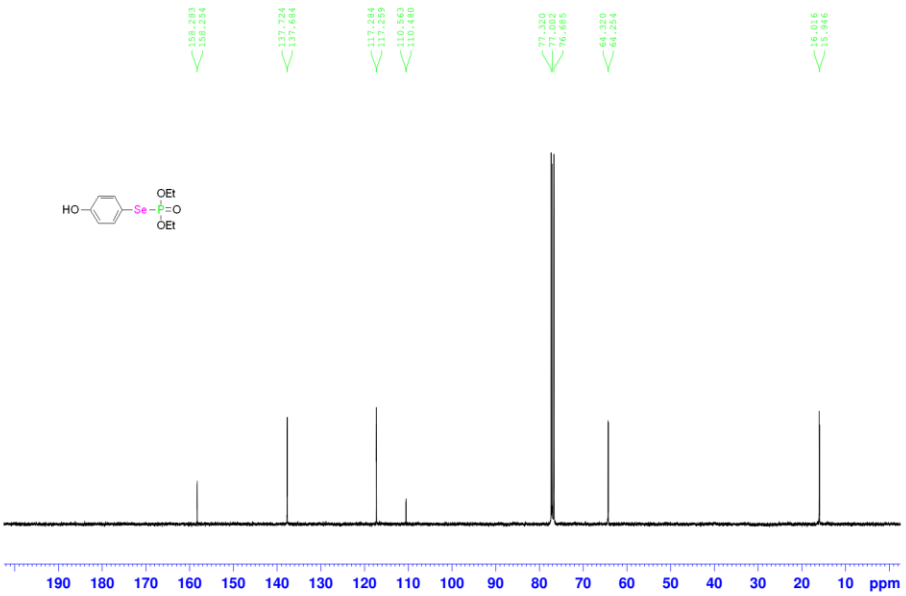
^{1}H NMR Spectrum of **3ap**



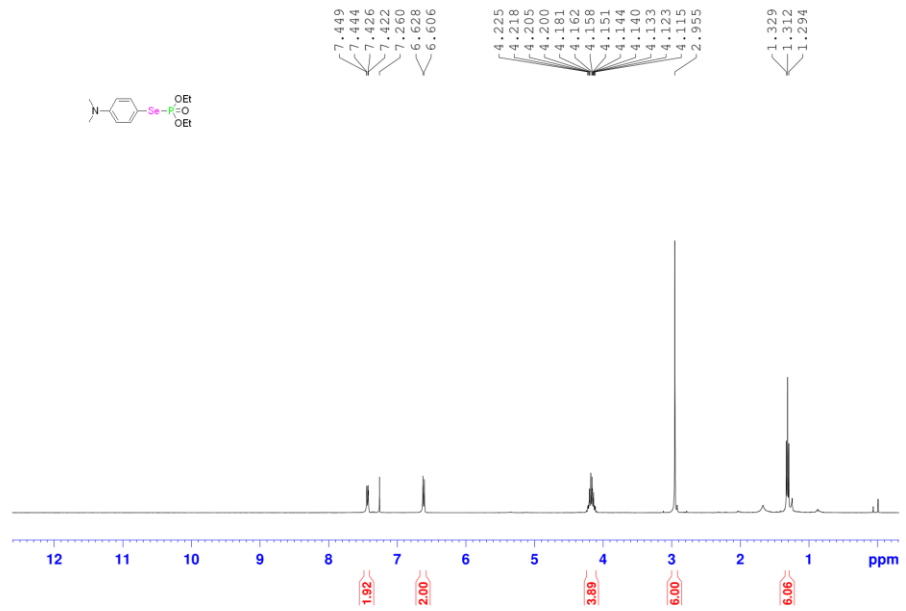
^{13}C NMR Spectrum of **3ap**



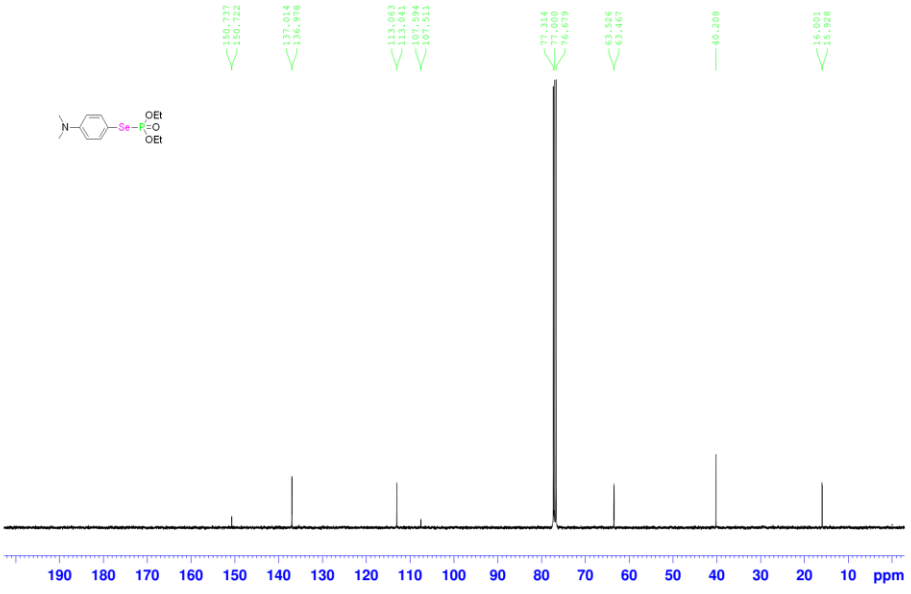
^{1}H NMR Spectrum of **3aq**



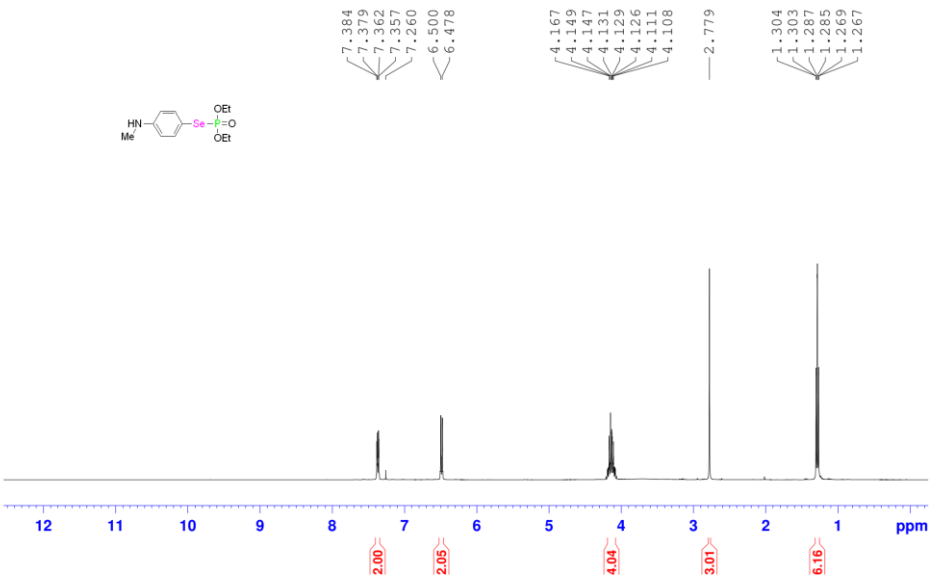
^{13}C NMR Spectrum of **3aq**



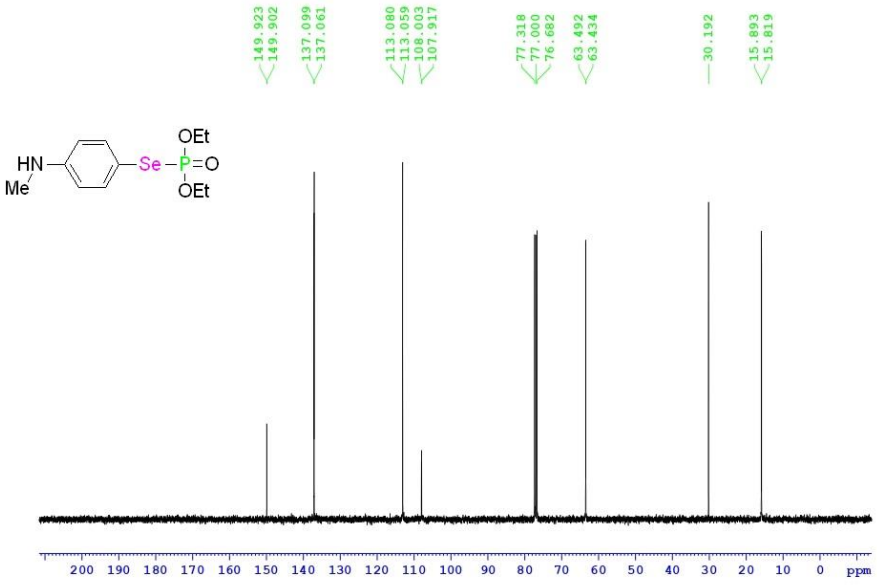
^{1}H NMR Spectrum of **3ar**



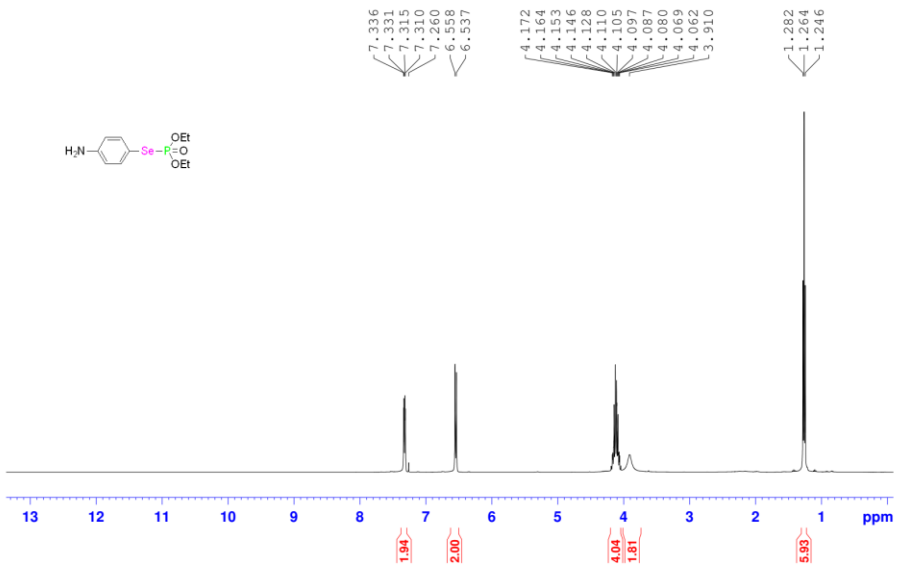
^{13}C NMR Spectrum of **3ar**



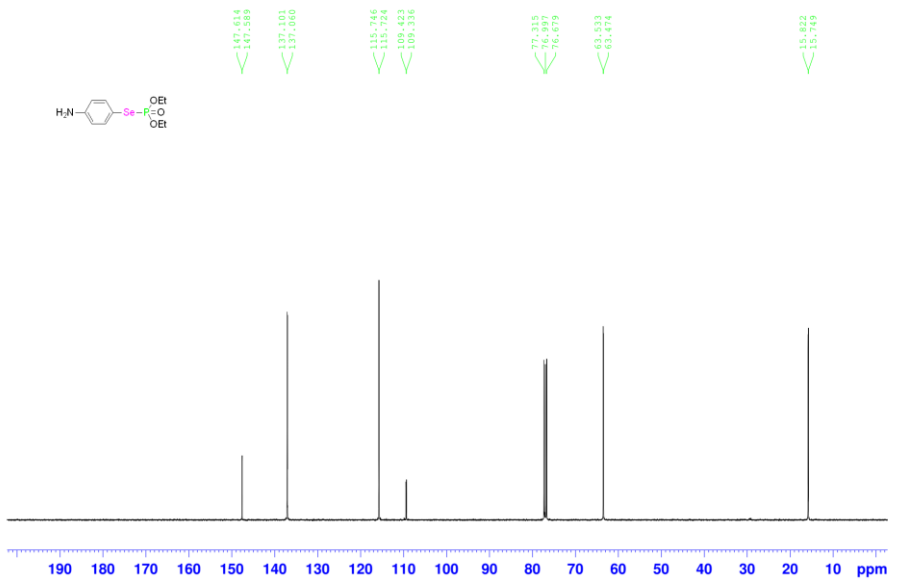
^{1}H NMR Spectrum of **3as**



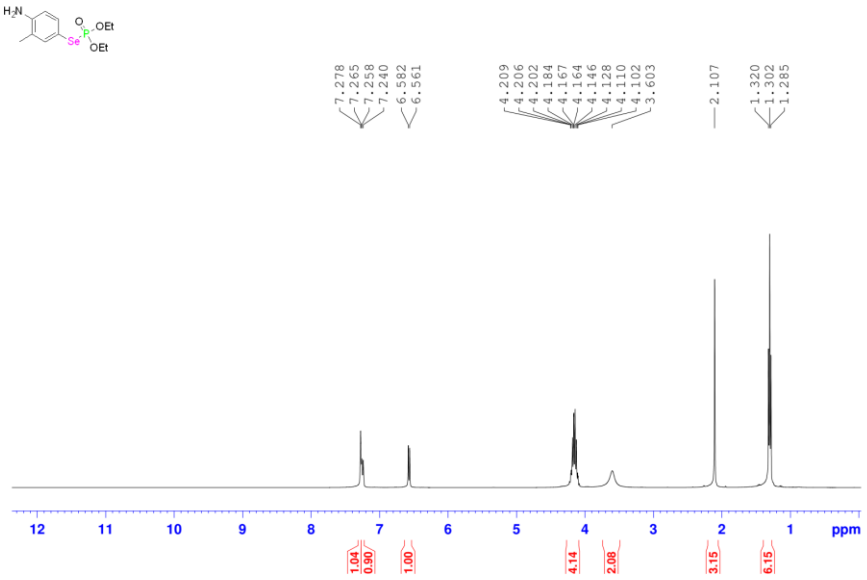
^{13}C NMR Spectrum of **3as**



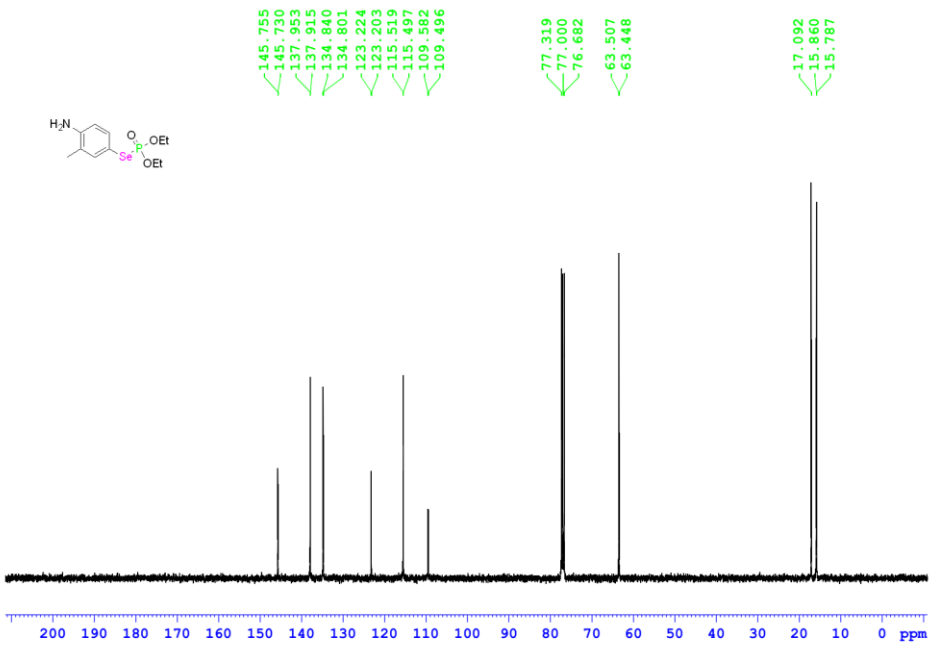
^{1}H NMR Spectrum of **3at**



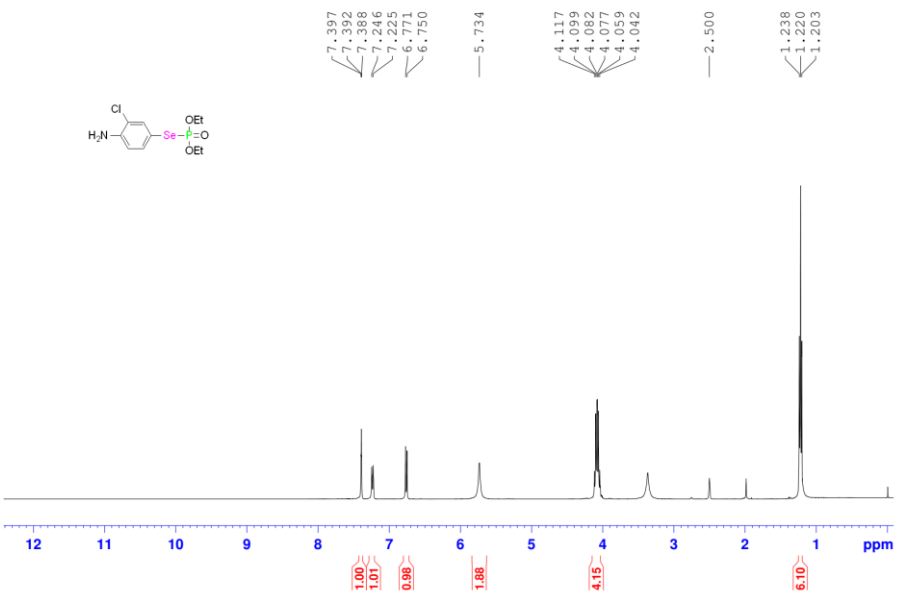
^{13}C NMR Spectrum of **3at**



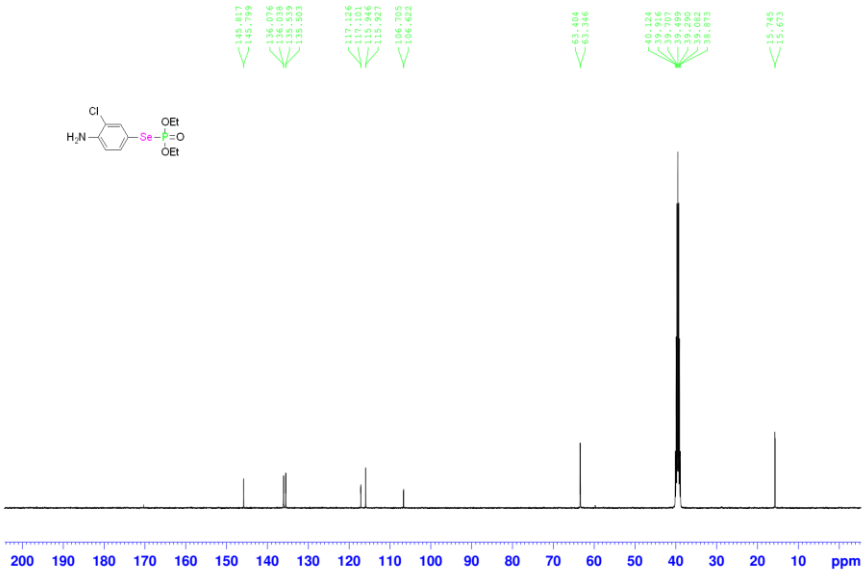
^{1}H NMR Spectrum of **3au**



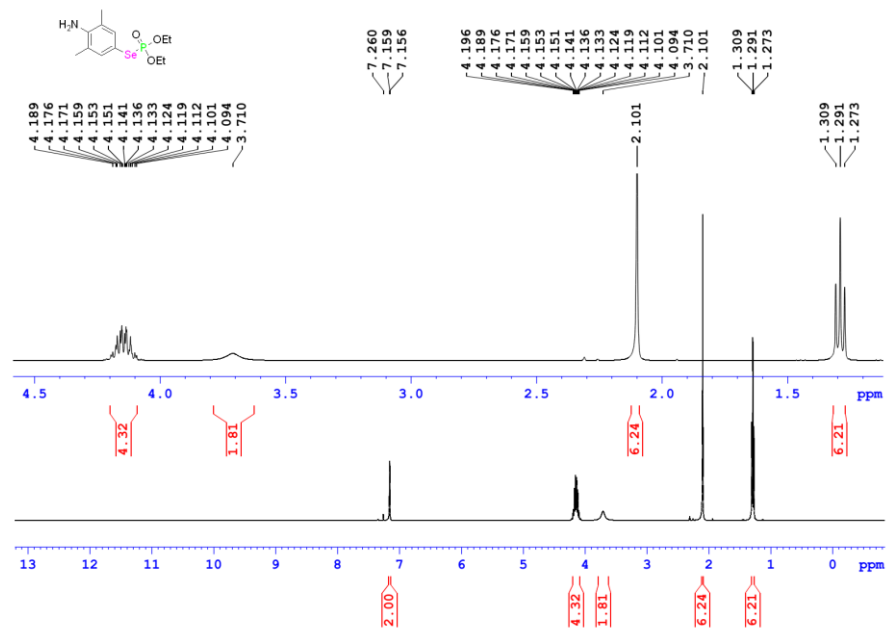
^{13}C NMR Spectrum of **3au**



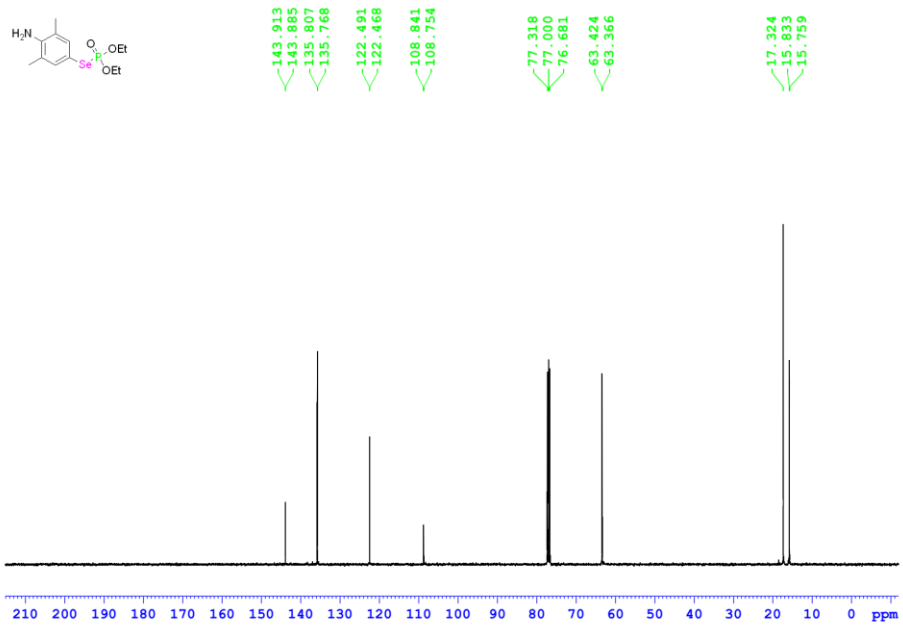
^{1}H NMR Spectrum of **3av**



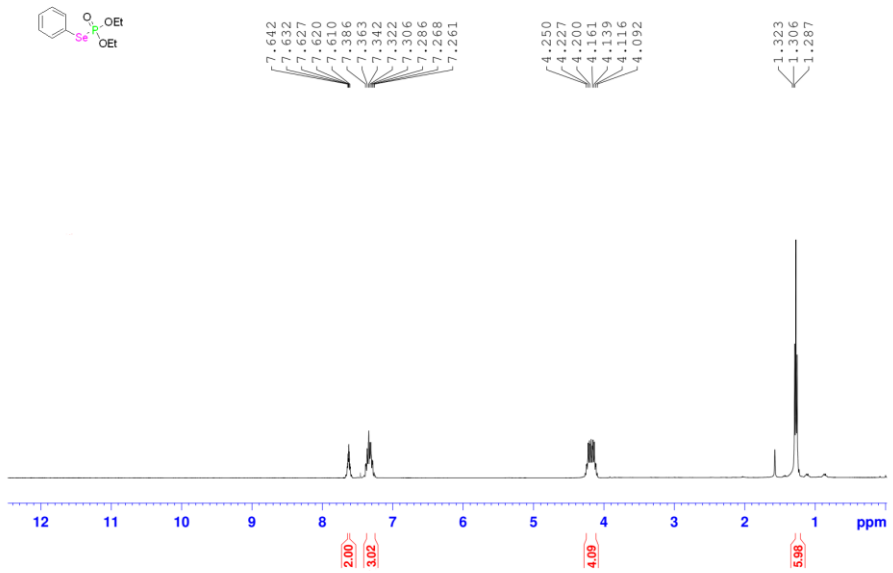
^{13}C NMR Spectrum of **3av**



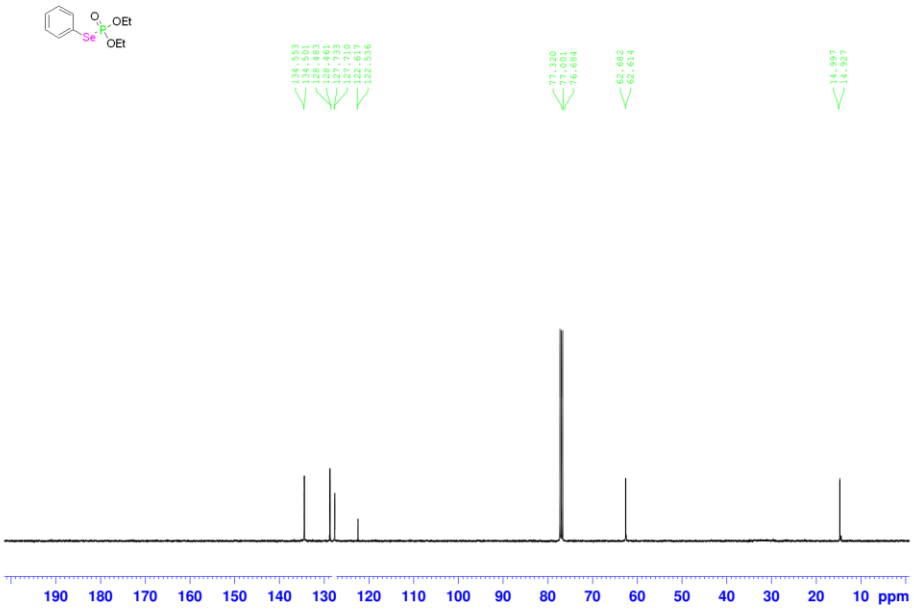
^{1}H NMR Spectrum of **3aw**



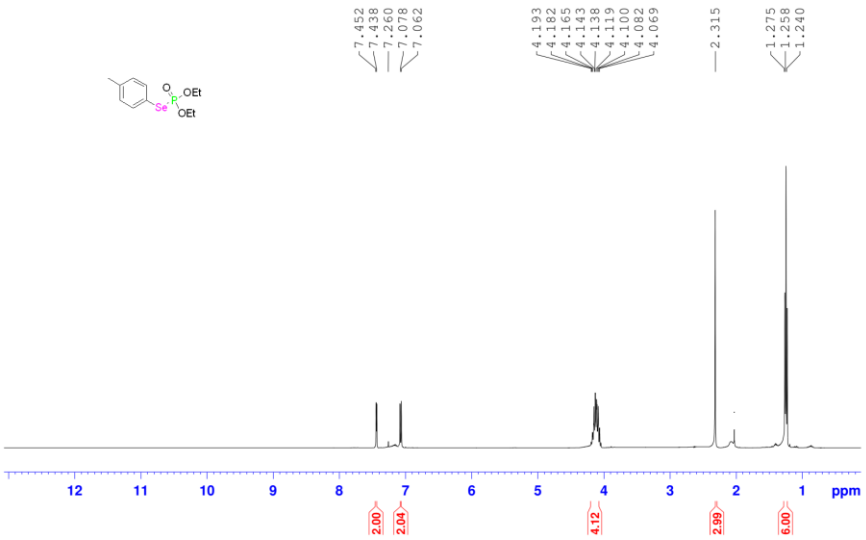
^{13}C NMR Spectrum of **3aw**



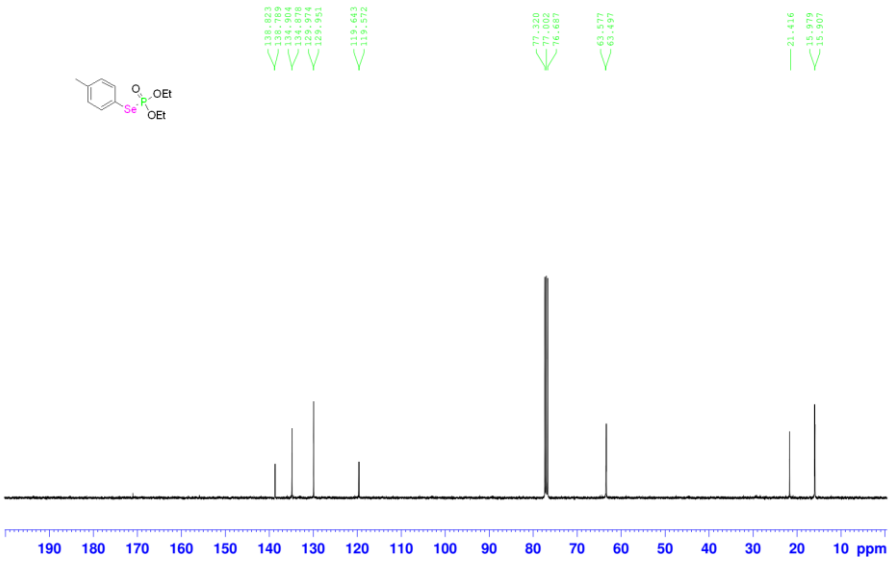
^{1}H NMR Spectrum of **3ax**



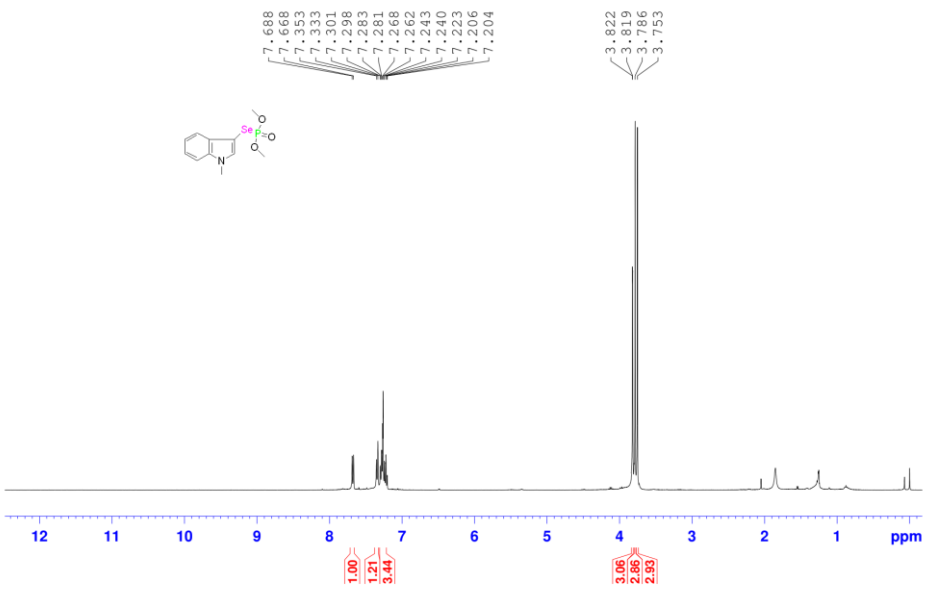
^{13}C NMR Spectrum of **3ax**



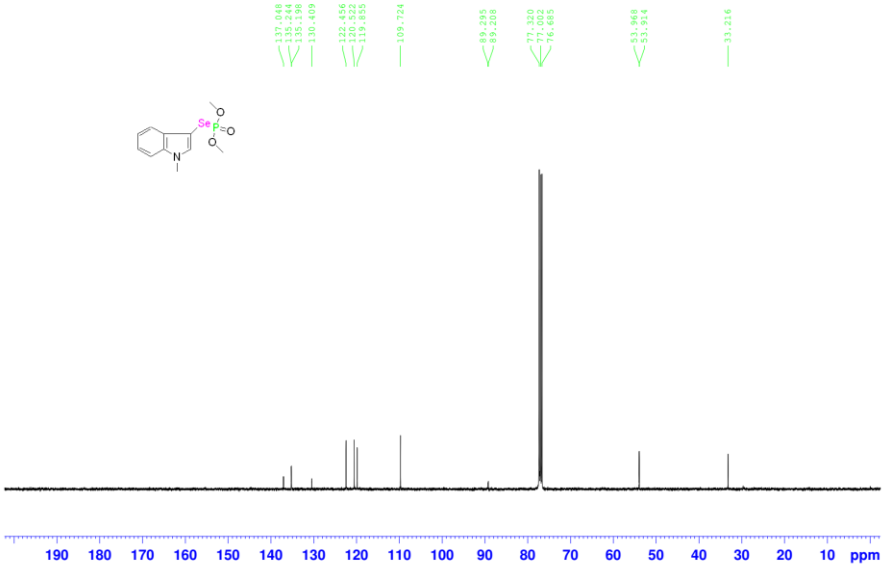
^{1}H NMR Spectrum of **3ay**



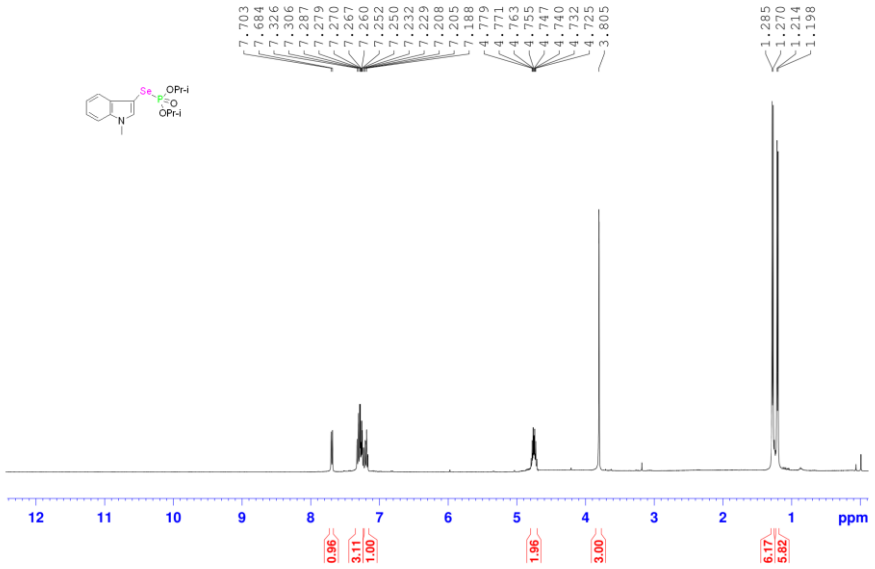
^{13}C NMR Spectrum of **3ay**



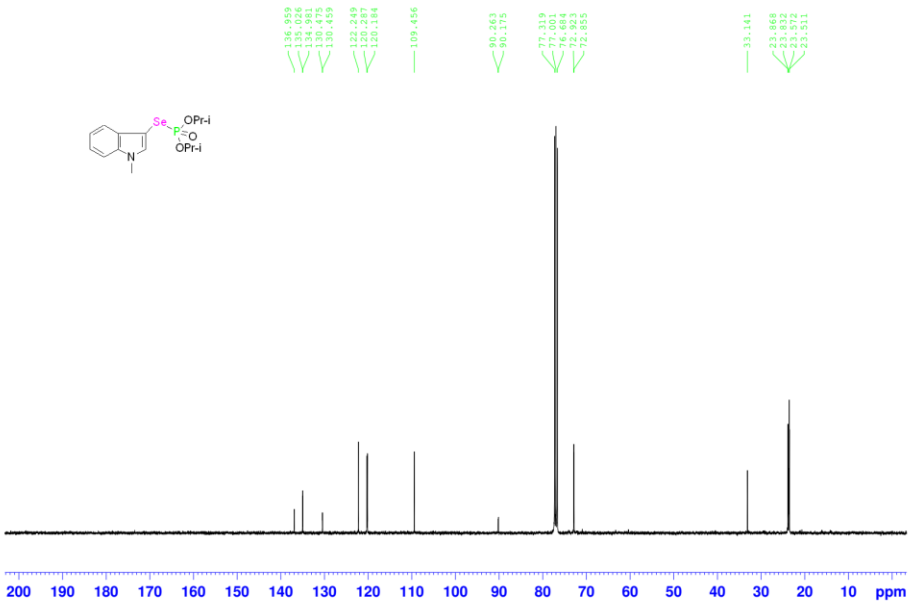
^{1}H NMR Spectrum of **3ba**



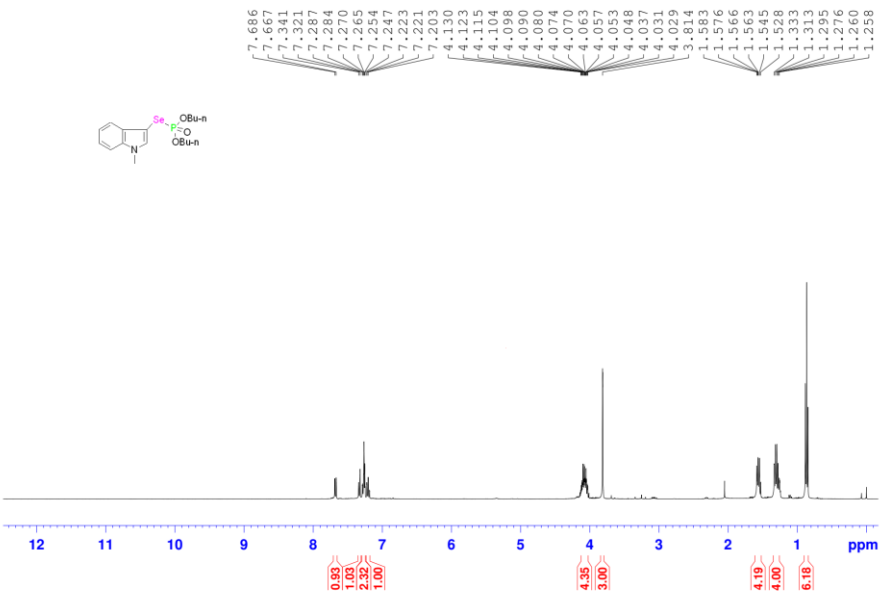
^{13}C NMR Spectrum of **3ba**



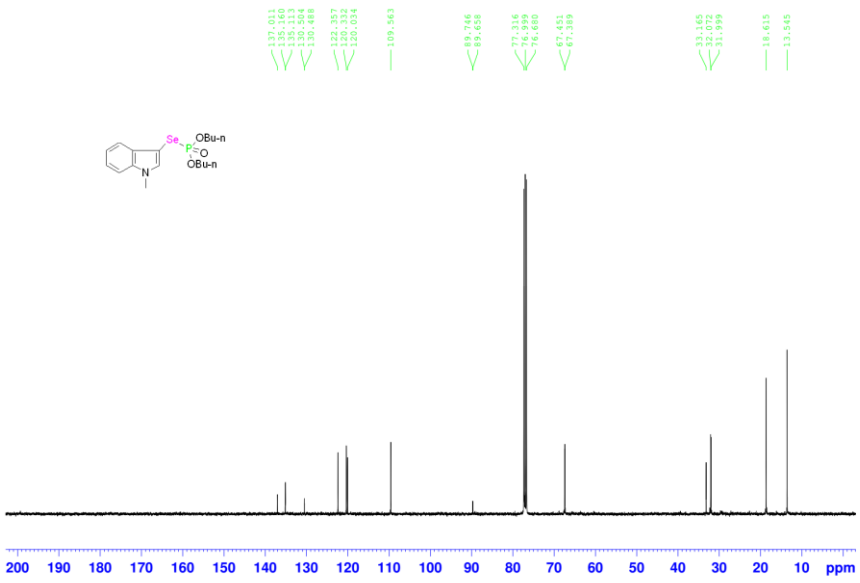
^{1}H NMR Spectrum of **3ca**



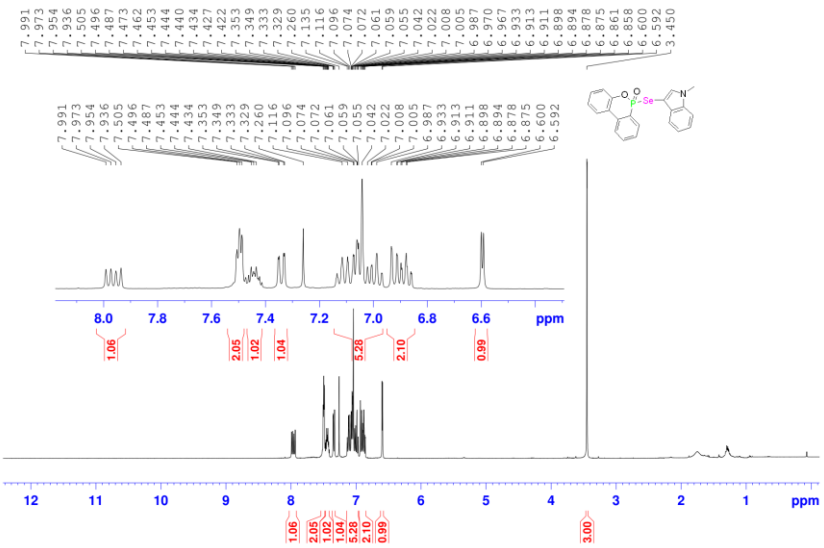
^{13}C NMR Spectrum of **3ca**



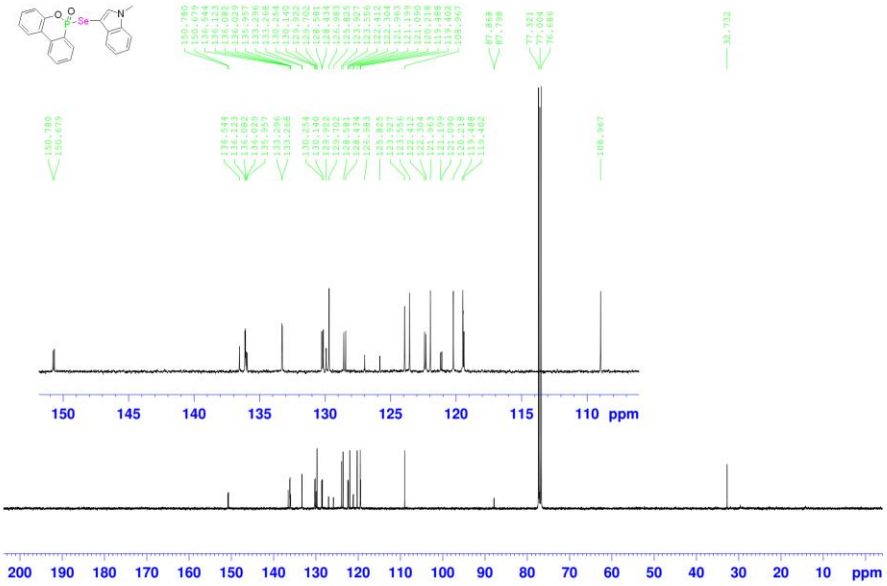
^{1}H NMR Spectrum of **3da**



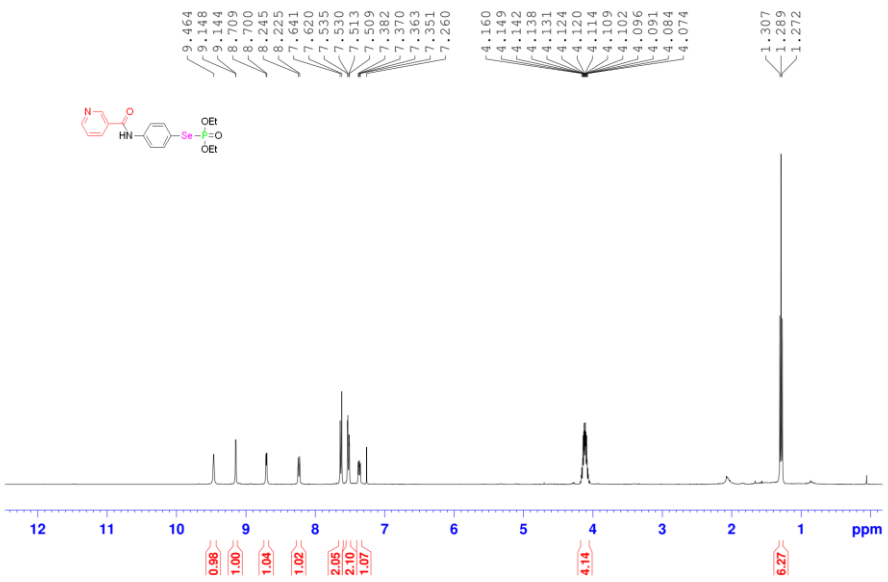
^{13}C NMR Spectrum of **3da**



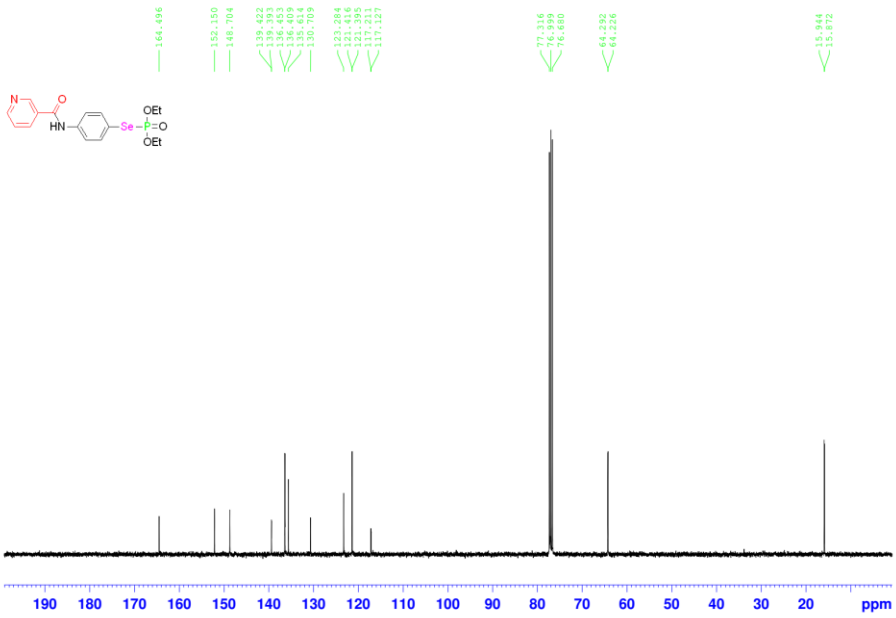
^{1}H NMR Spectrum of **3ea**



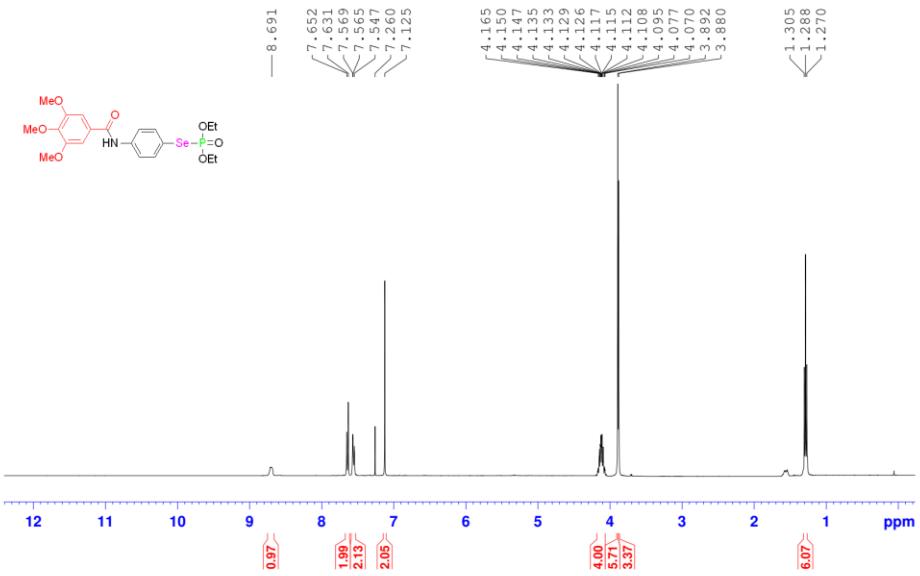
^{13}C NMR Spectrum of **3ea**



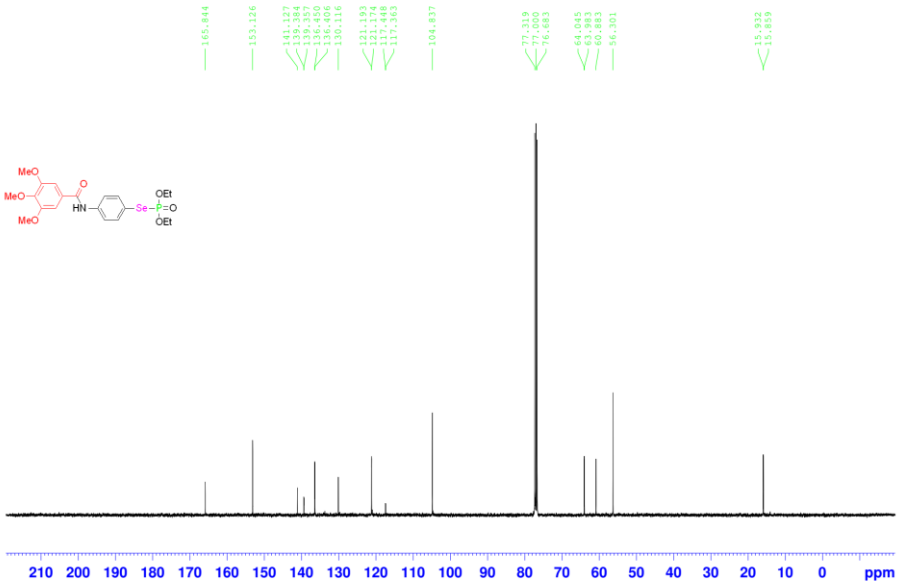
^{1}H NMR Spectrum of **4aa**



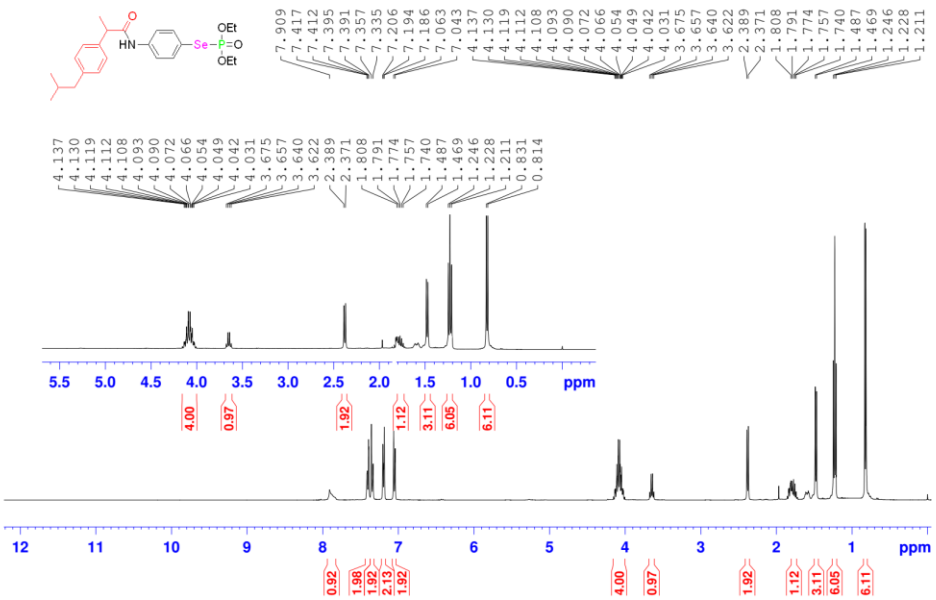
^{13}C NMR Spectrum of **4aa**



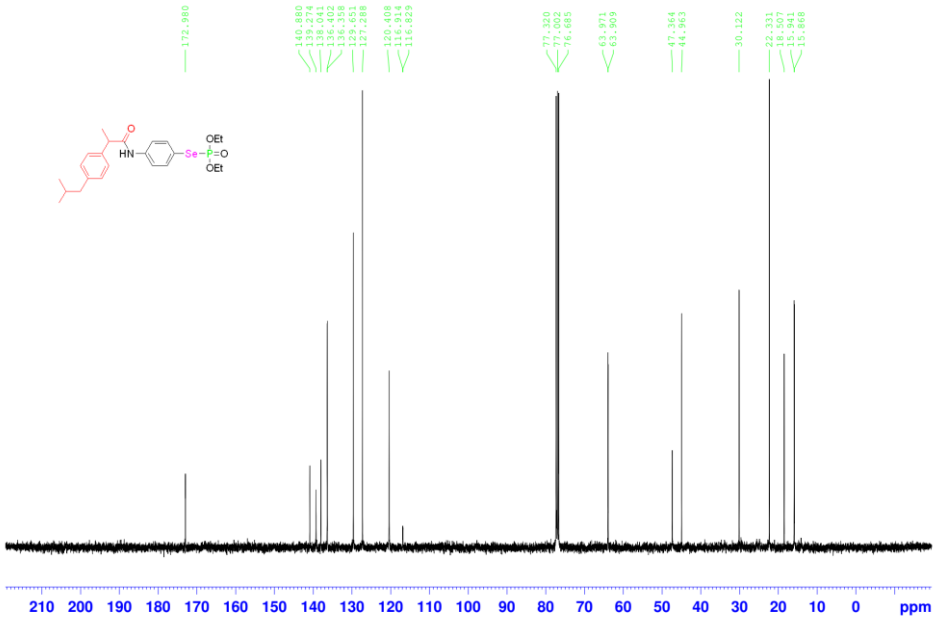
^{1}H NMR Spectrum of 4**ab**



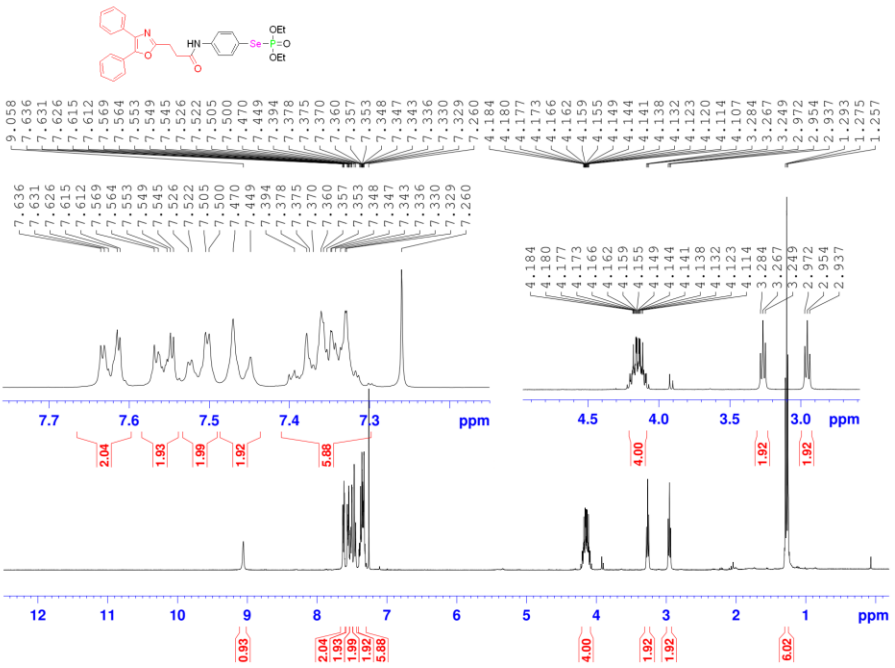
^{13}C NMR Spectrum of **4ab**



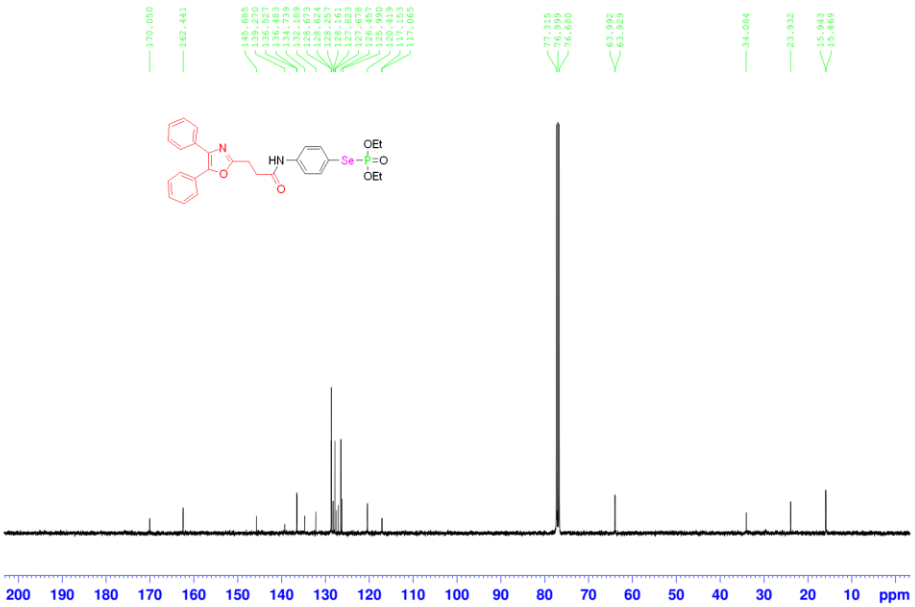
^{1}H NMR Spectrum of **4ac**



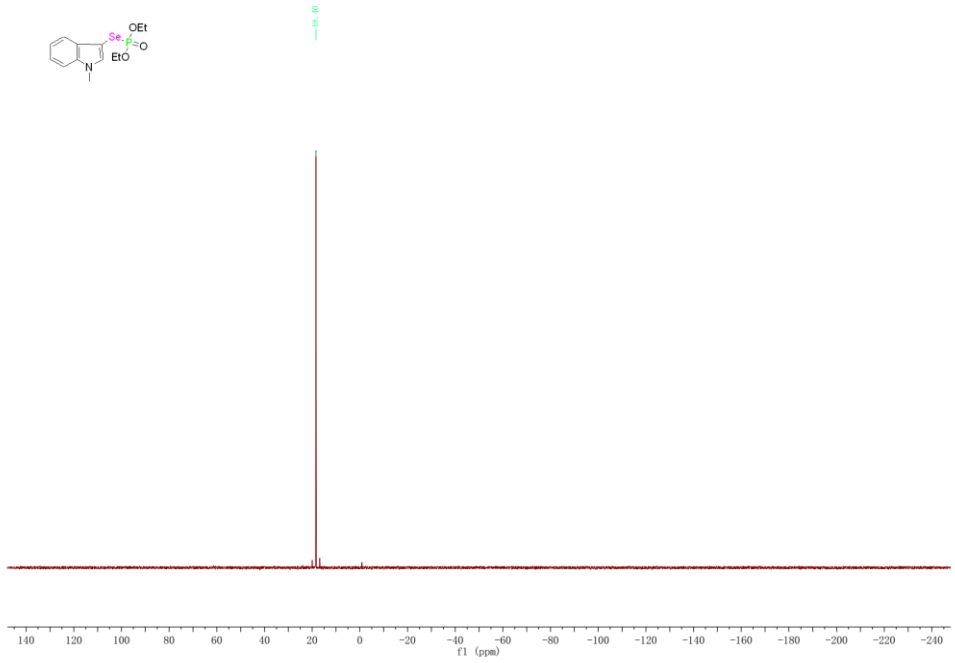
^{13}C NMR Spectrum of **4ac**



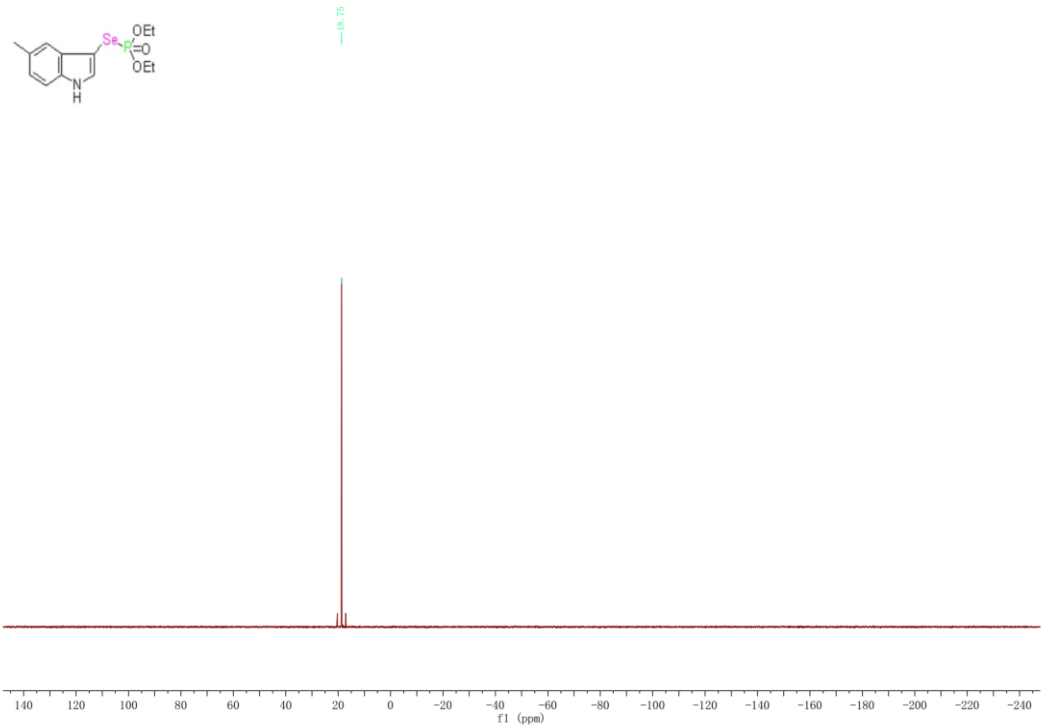
^{1}H NMR Spectrum of **4ad**



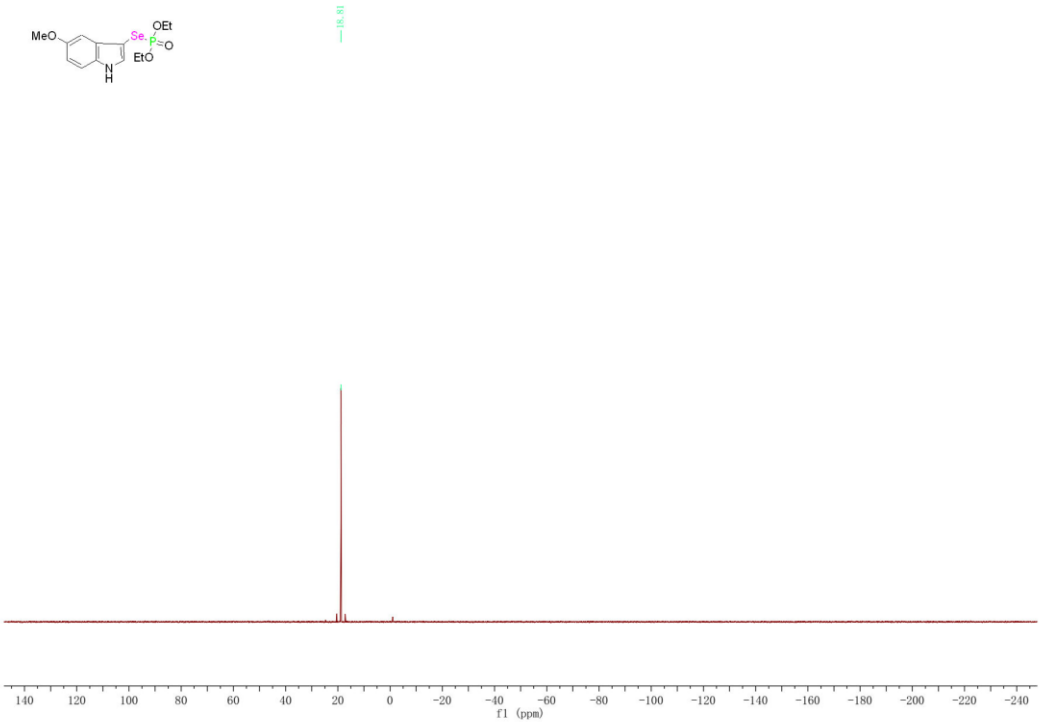
^{13}C NMR Spectrum of **4ad**



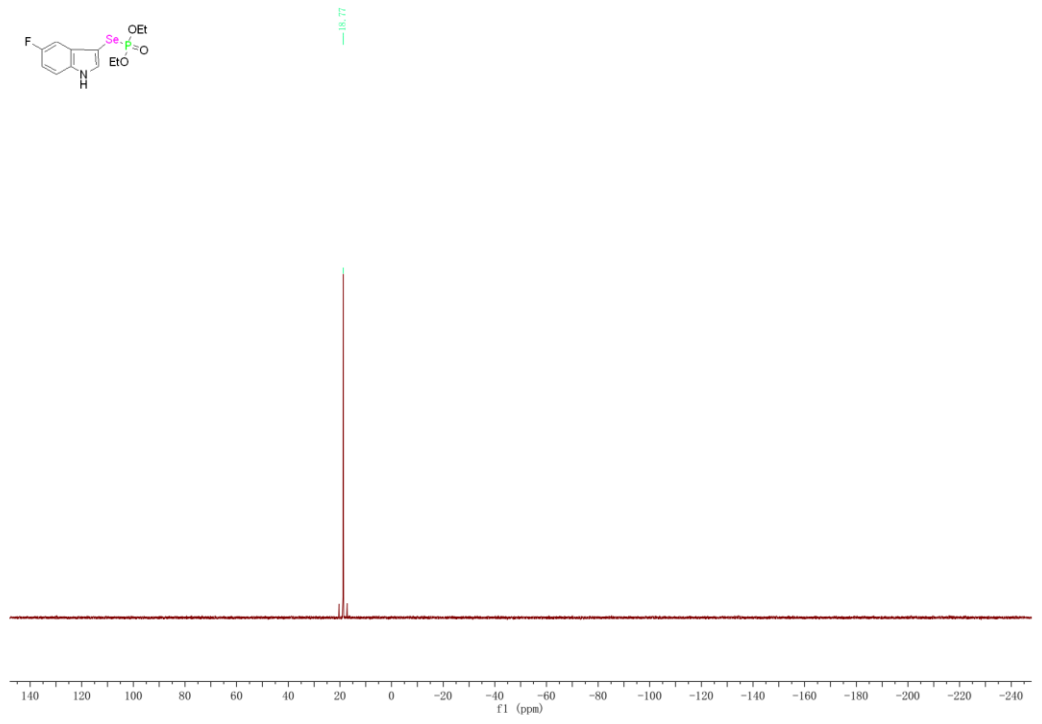
^{31}P NMR Spectrum of **3aa**



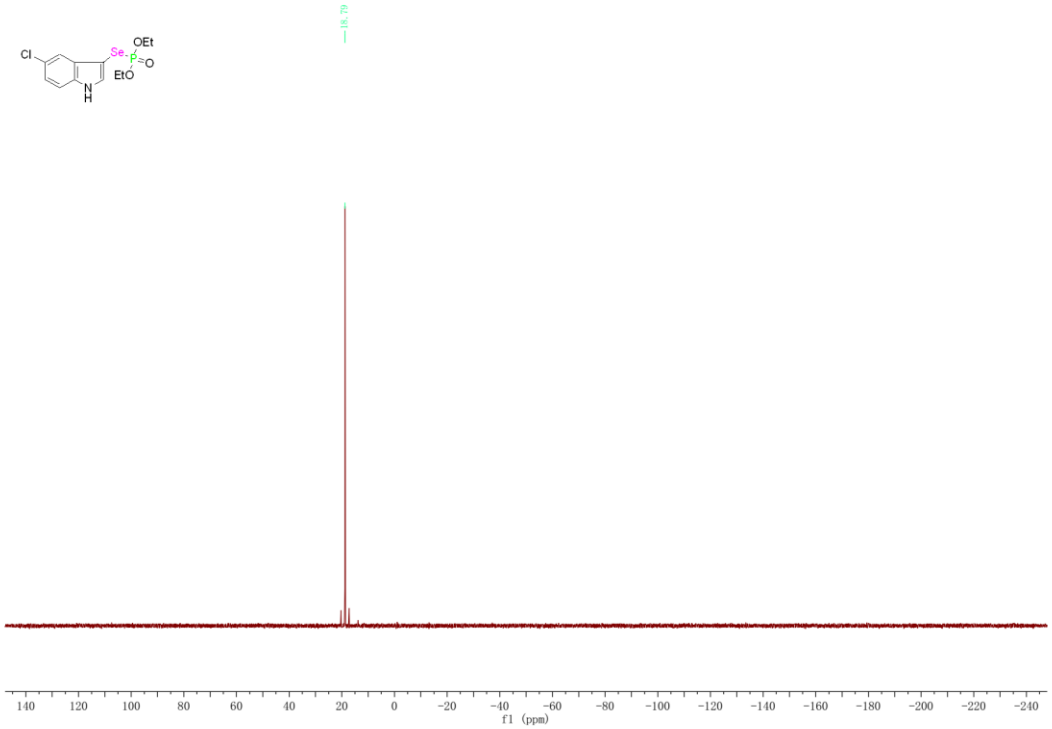
^{31}P NMR Spectrum of **3ab**



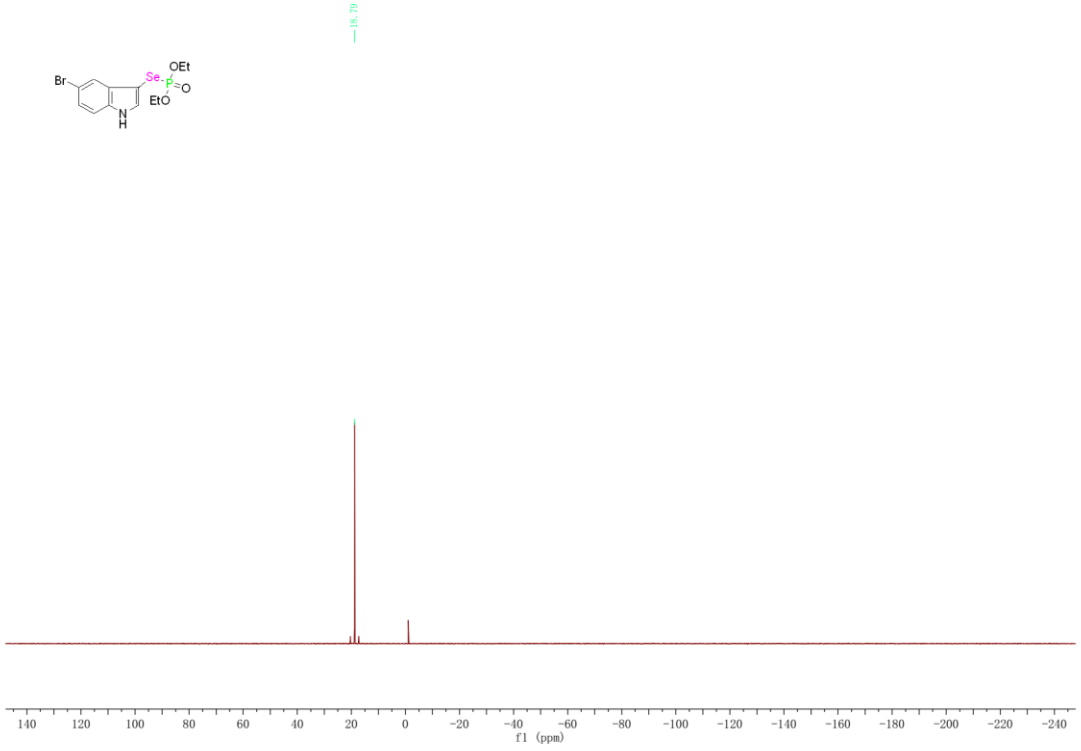
^{31}P NMR Spectrum of **3ac**



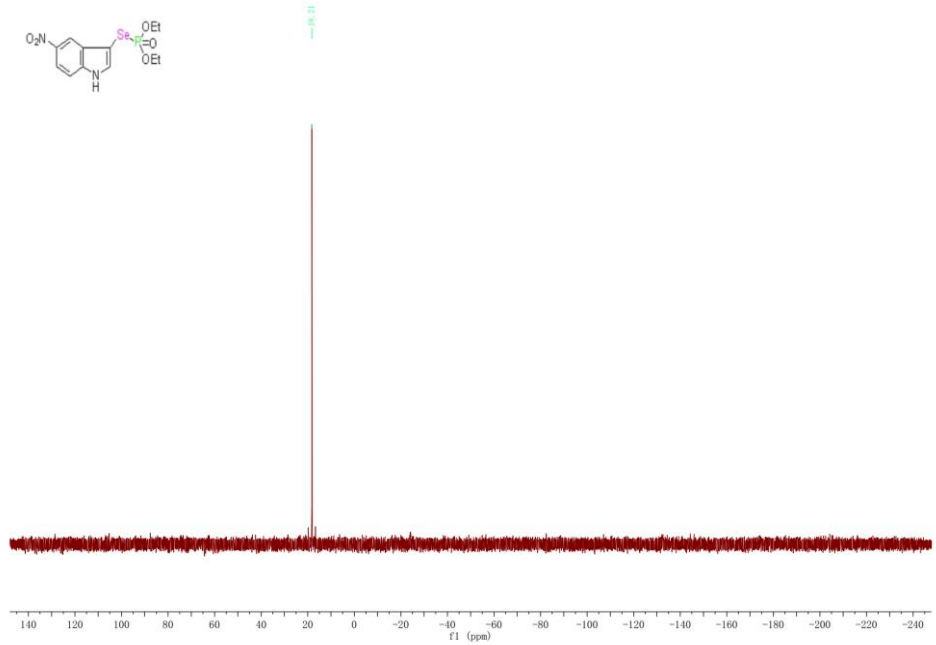
^{31}P NMR Spectrum of **3ad**



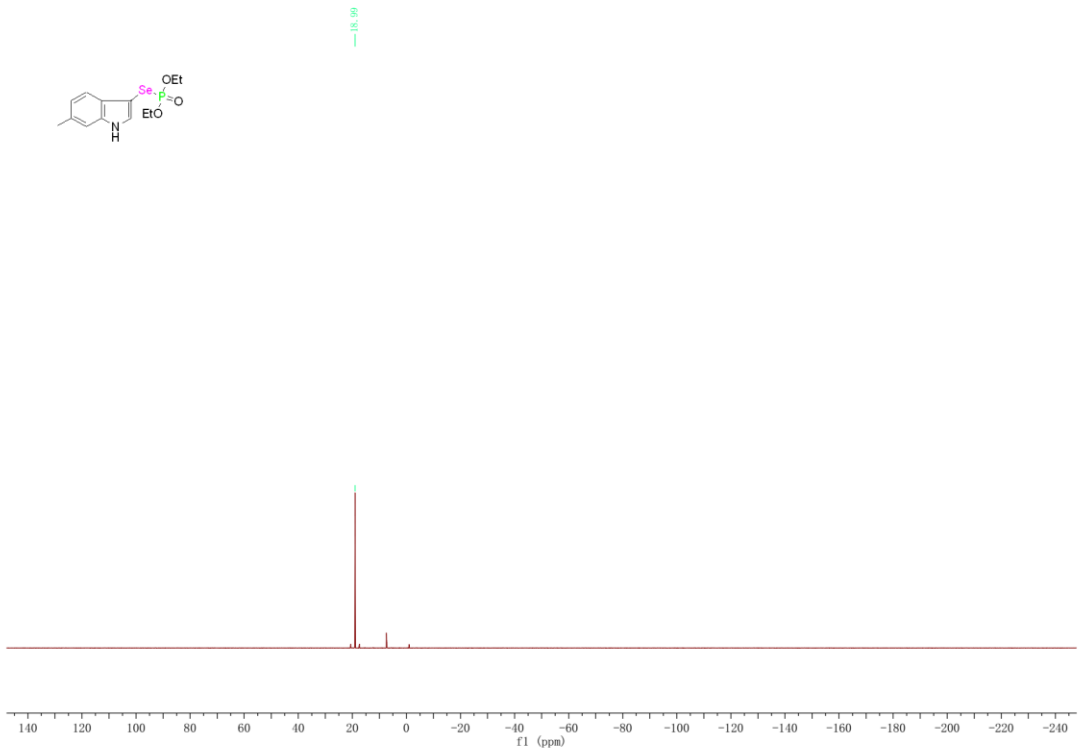
^{31}P NMR Spectrum of **3ae**



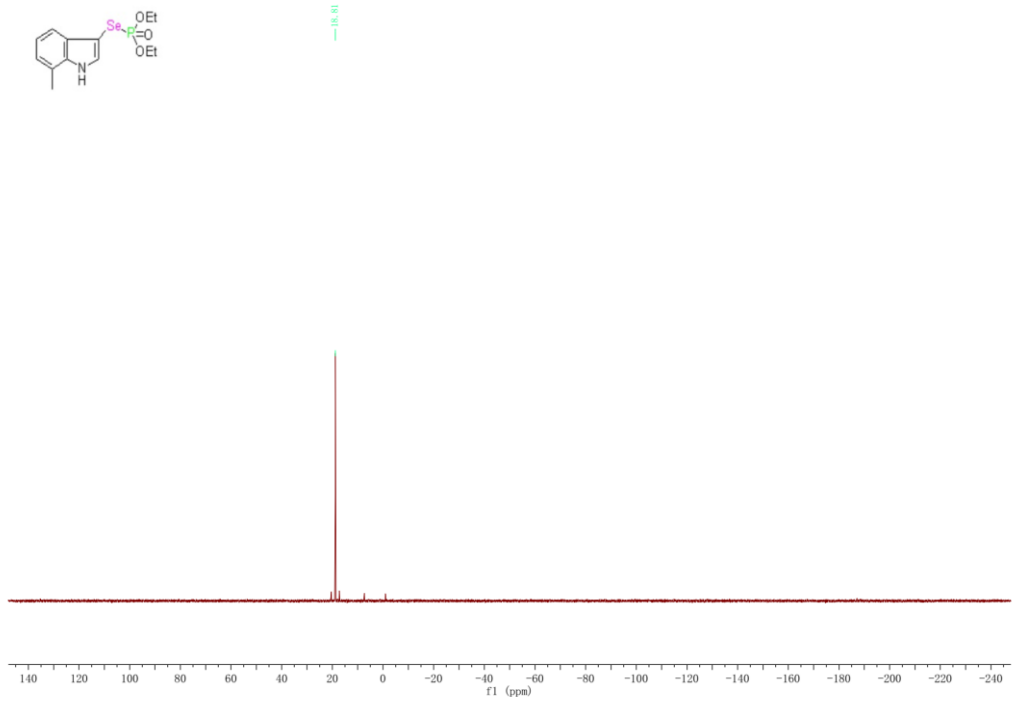
^{31}P NMR Spectrum of **3af**



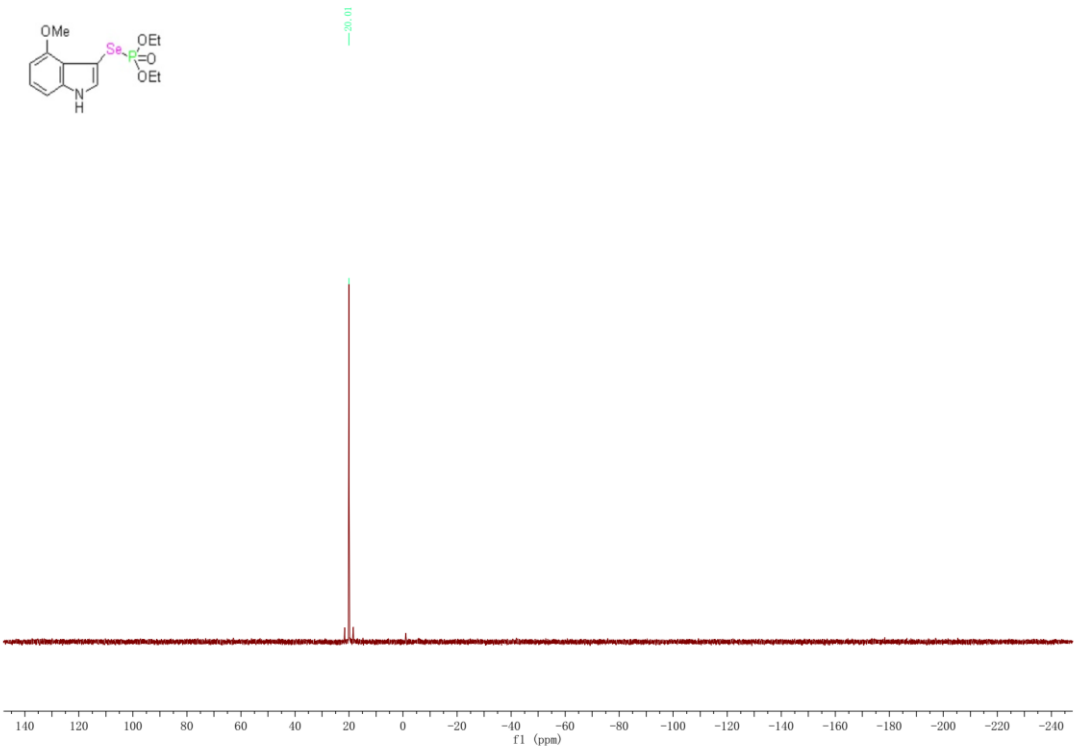
^{31}P NMR Spectrum of **3ag**



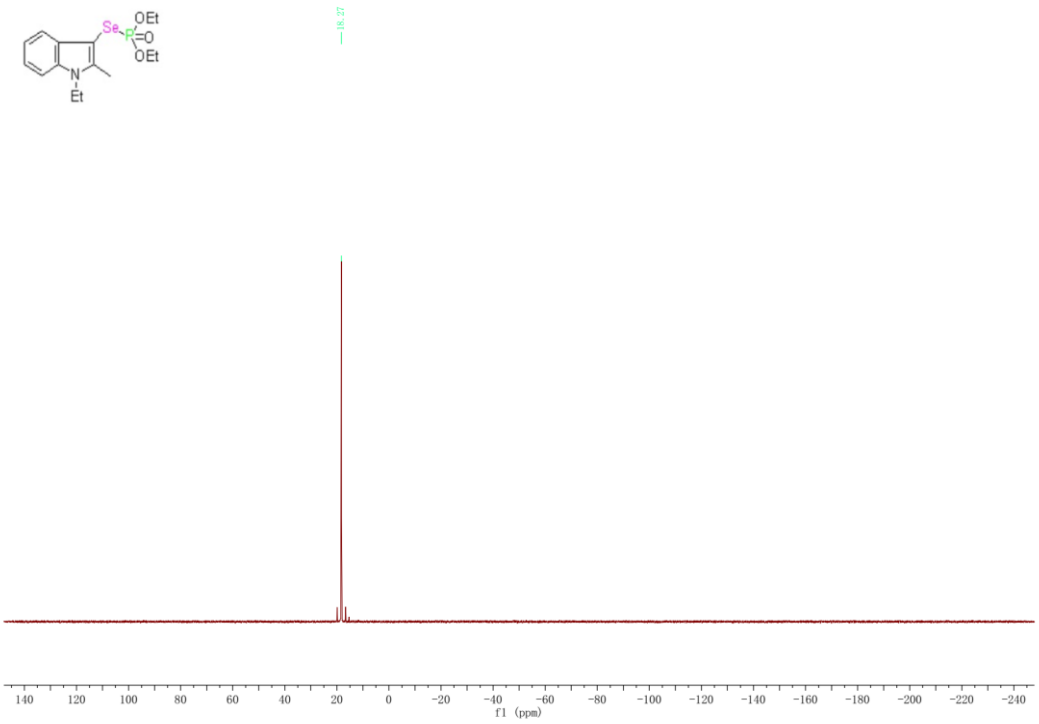
^{31}P NMR Spectrum of **3ah**



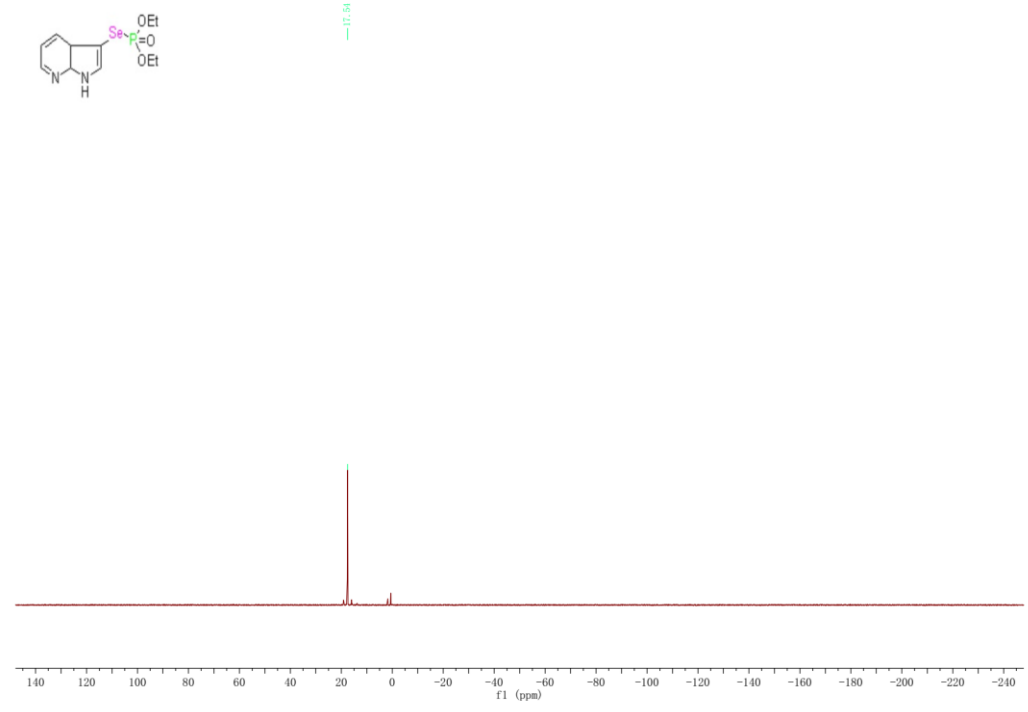
^{31}P NMR Spectrum of **3ai**



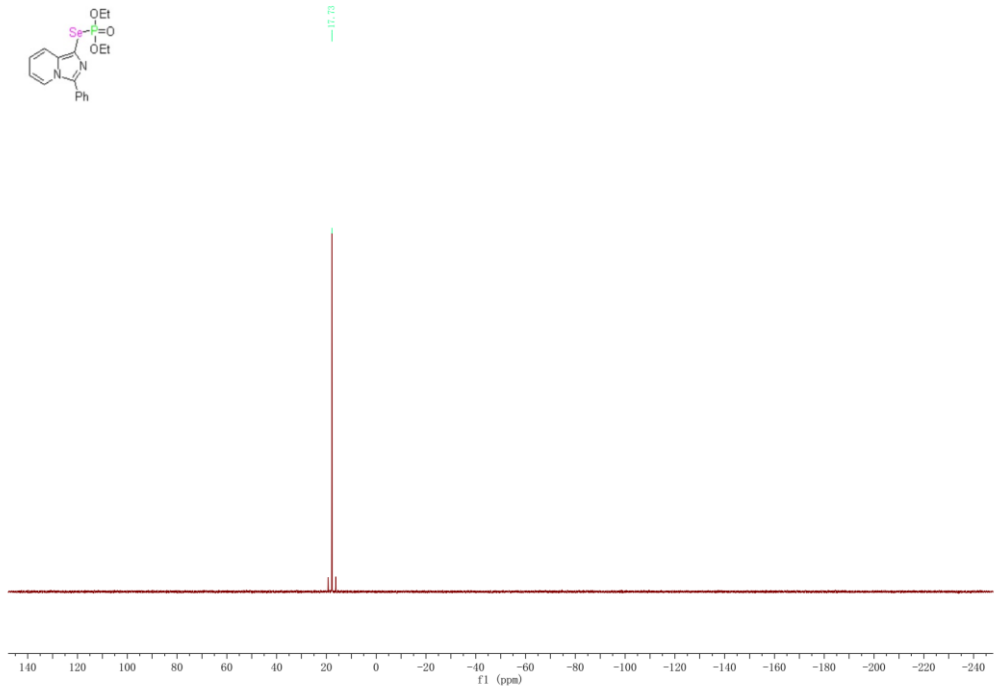
^{31}P NMR Spectrum of **3aj**



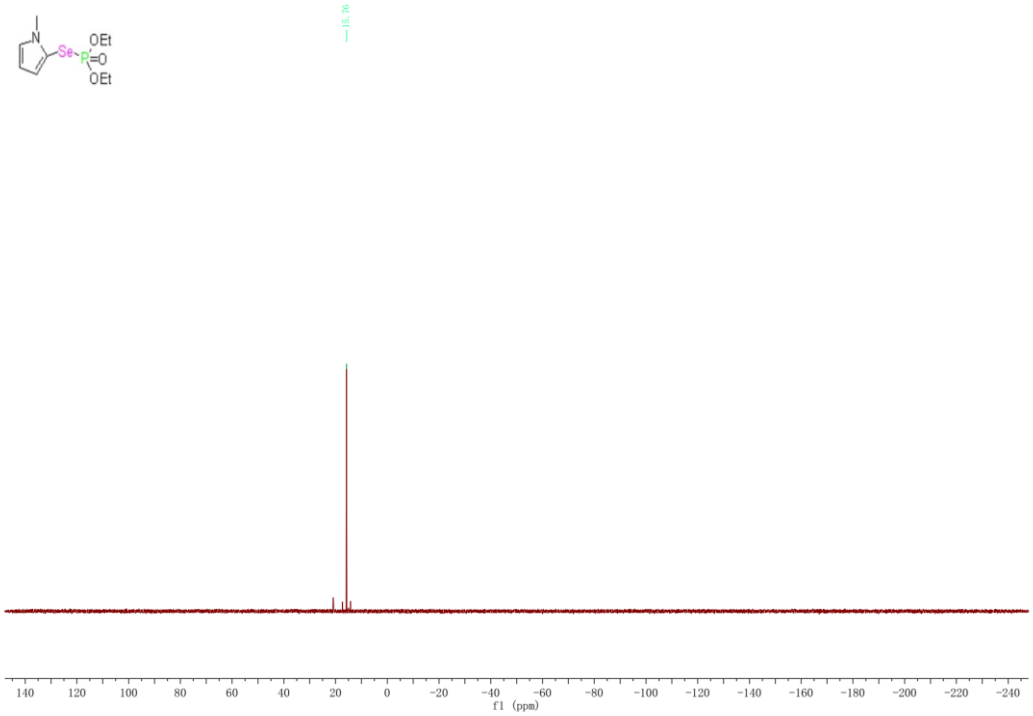
^{31}P NMR Spectrum of **3ak**



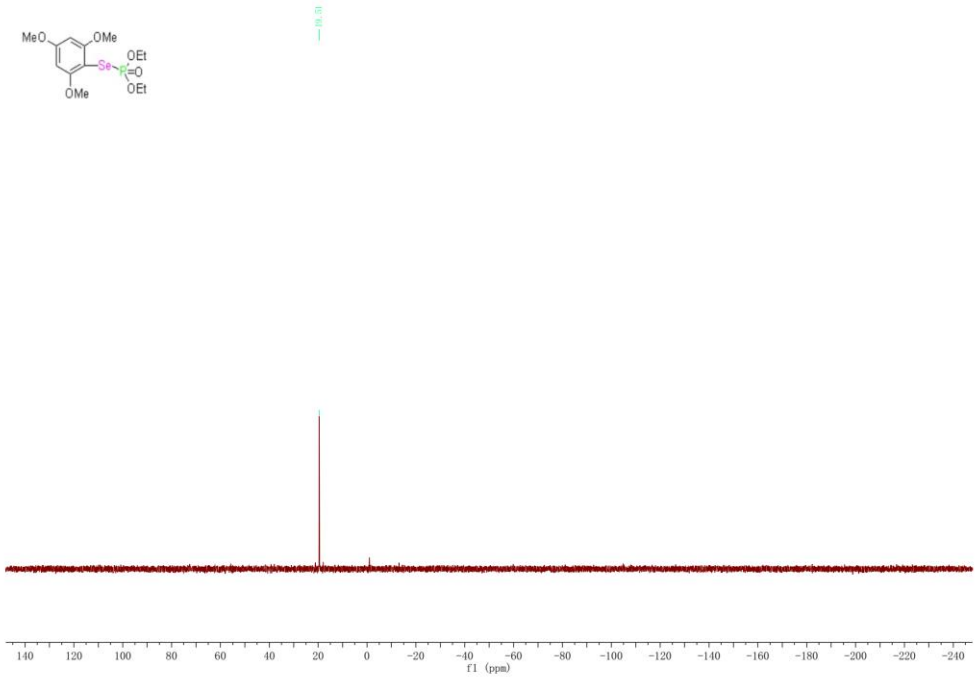
^{31}P NMR Spectrum of **3al**



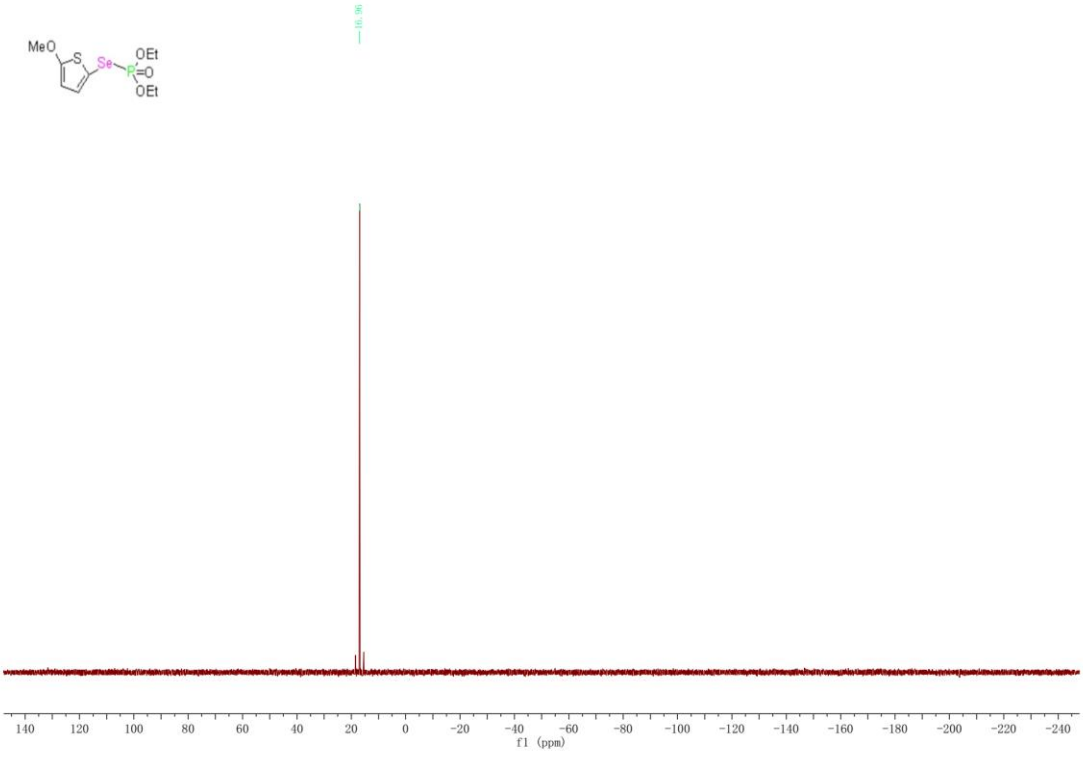
^{31}P NMR Spectrum of **3am**



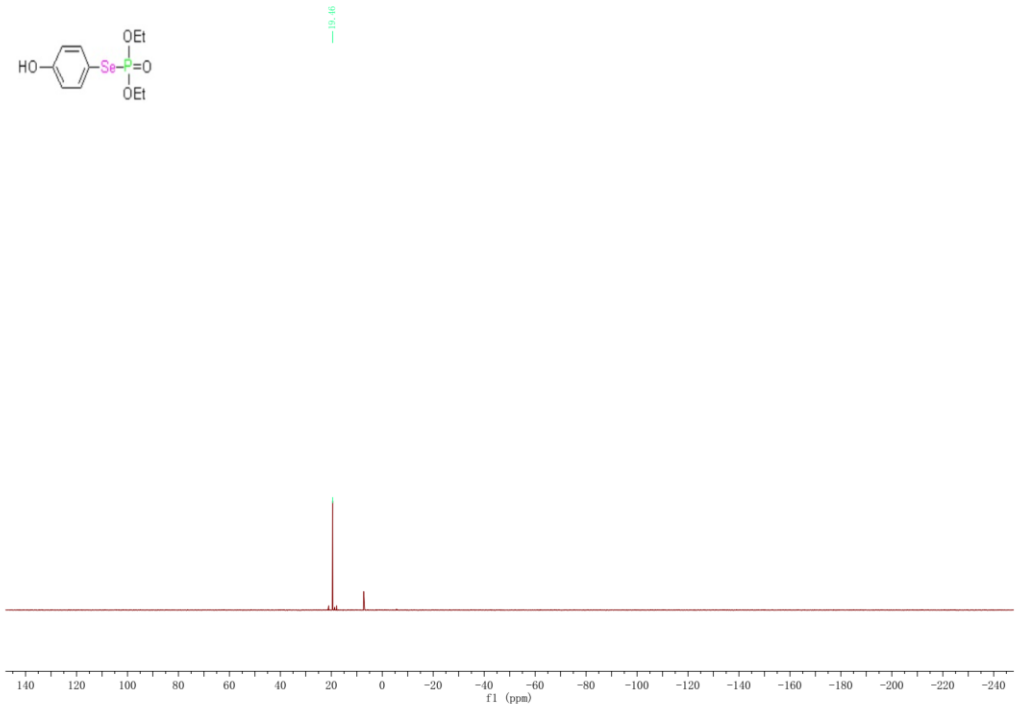
^{31}P NMR Spectrum of **3an**



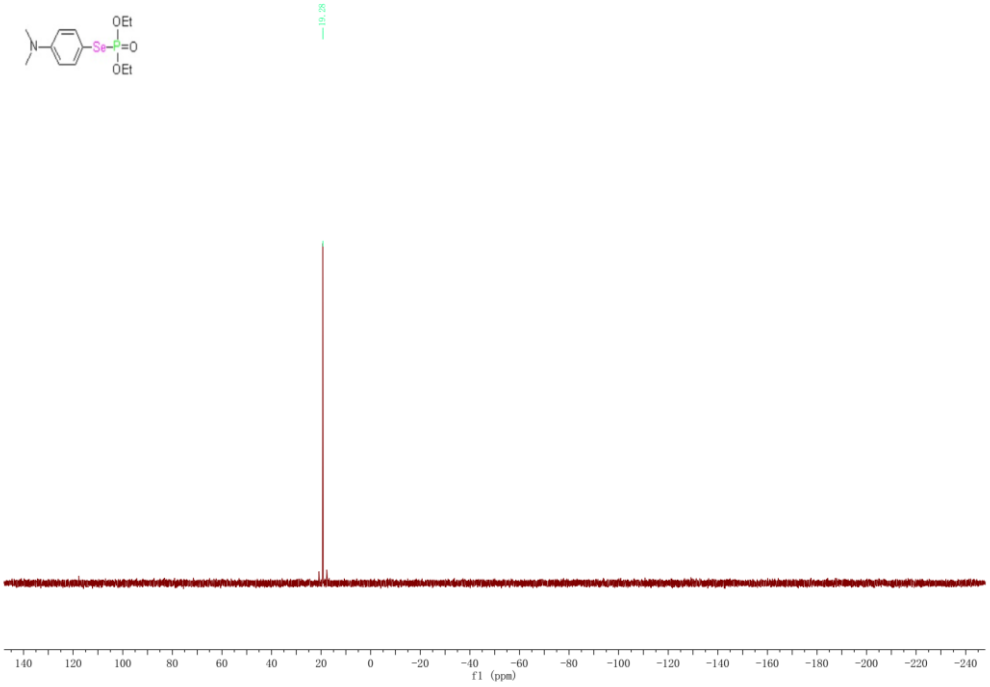
^{31}P NMR Spectrum of **3ao**



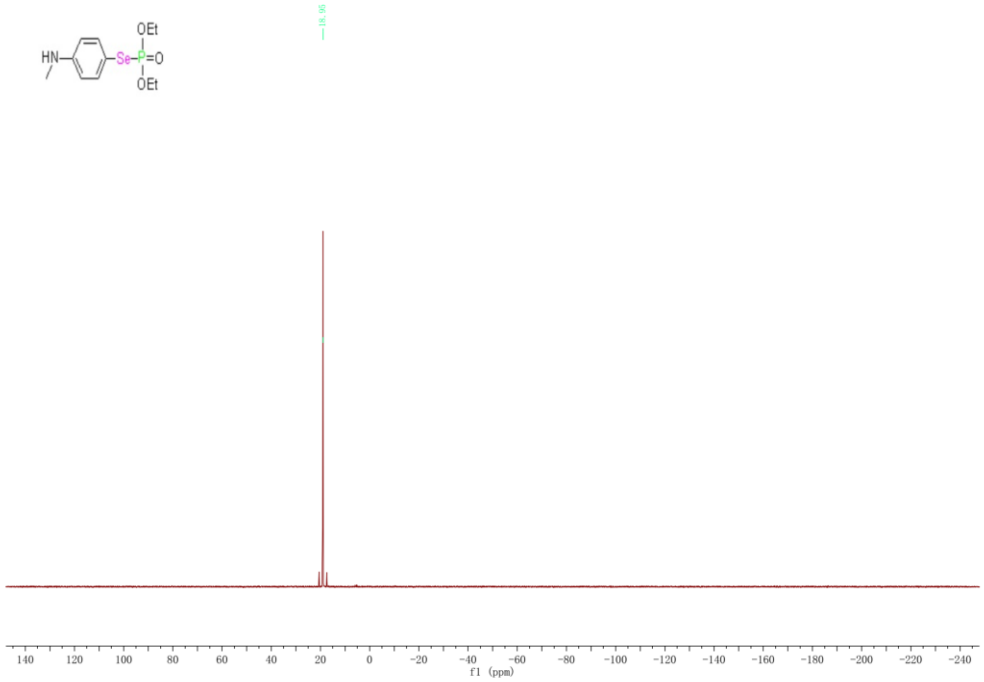
^{31}P NMR Spectrum of **3ap**



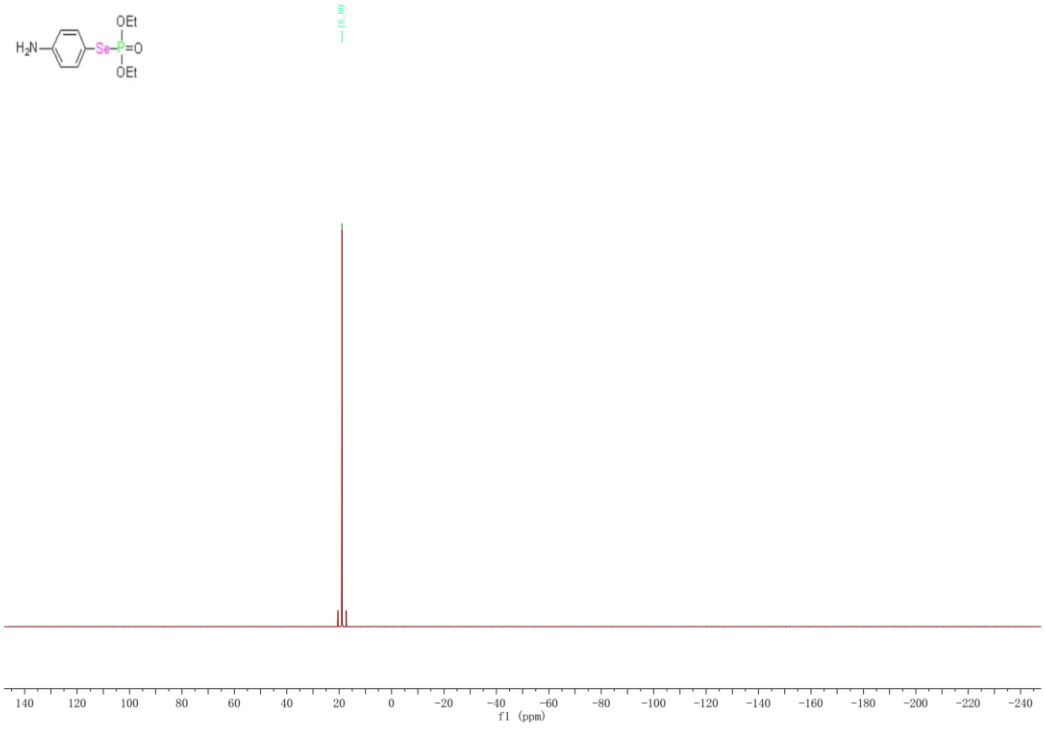
^{31}P NMR Spectrum of **3aq**



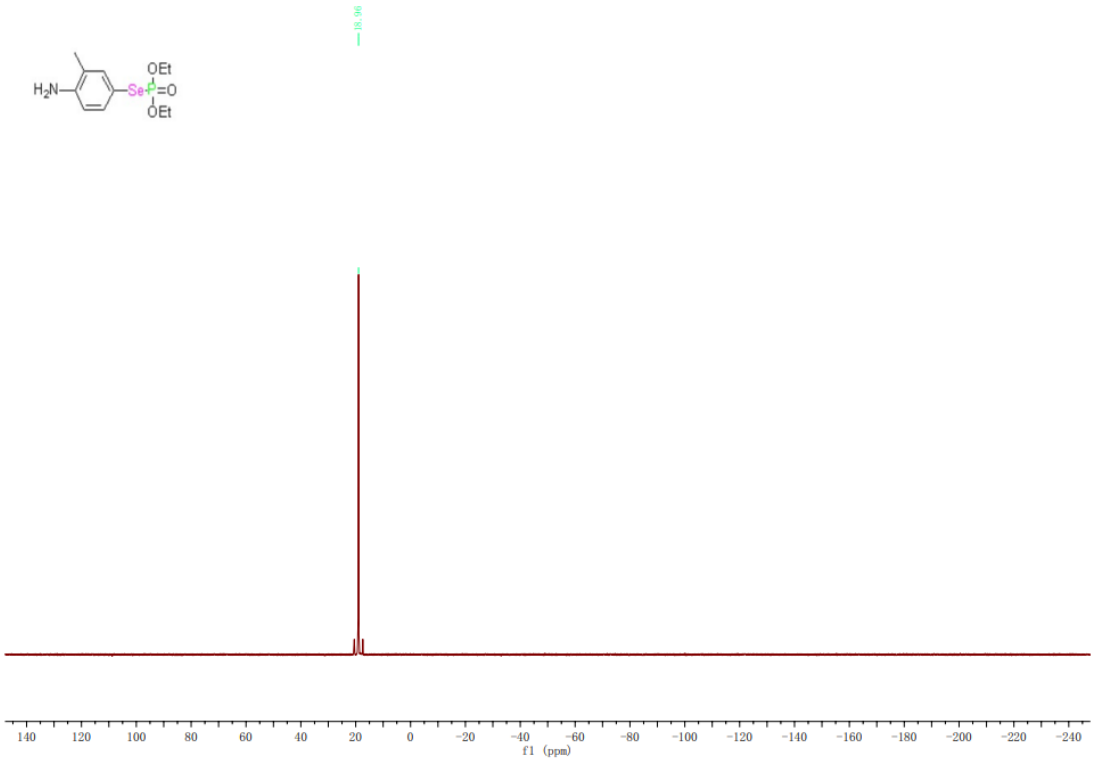
^{31}P NMR Spectrum of **3ar**



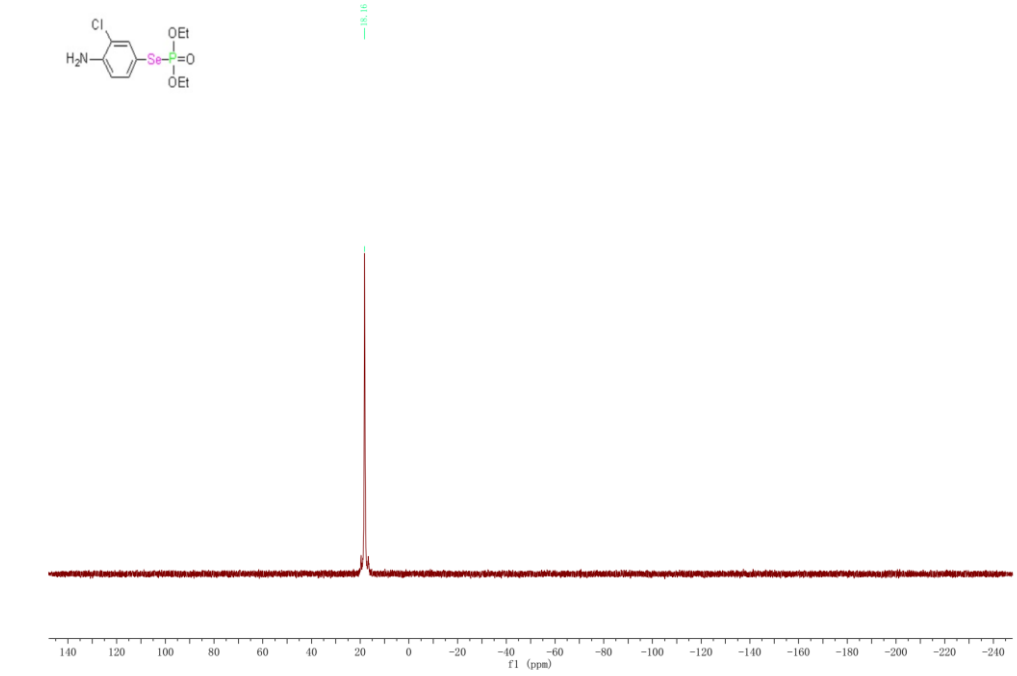
^{31}P NMR Spectrum of **3as**



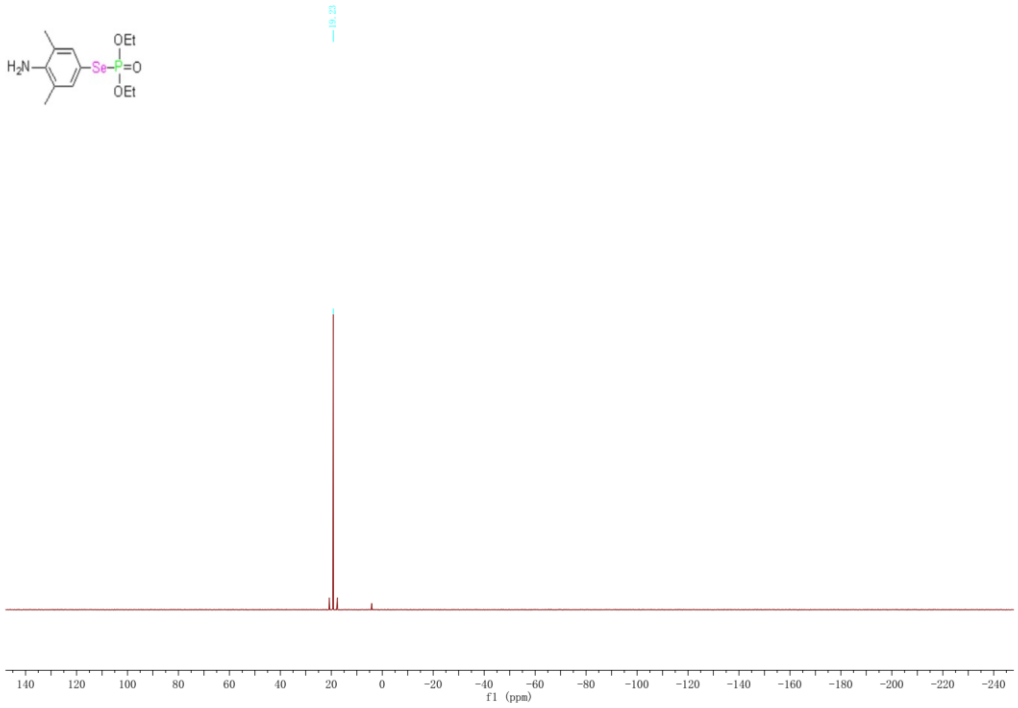
^{31}P NMR Spectrum of **3at**



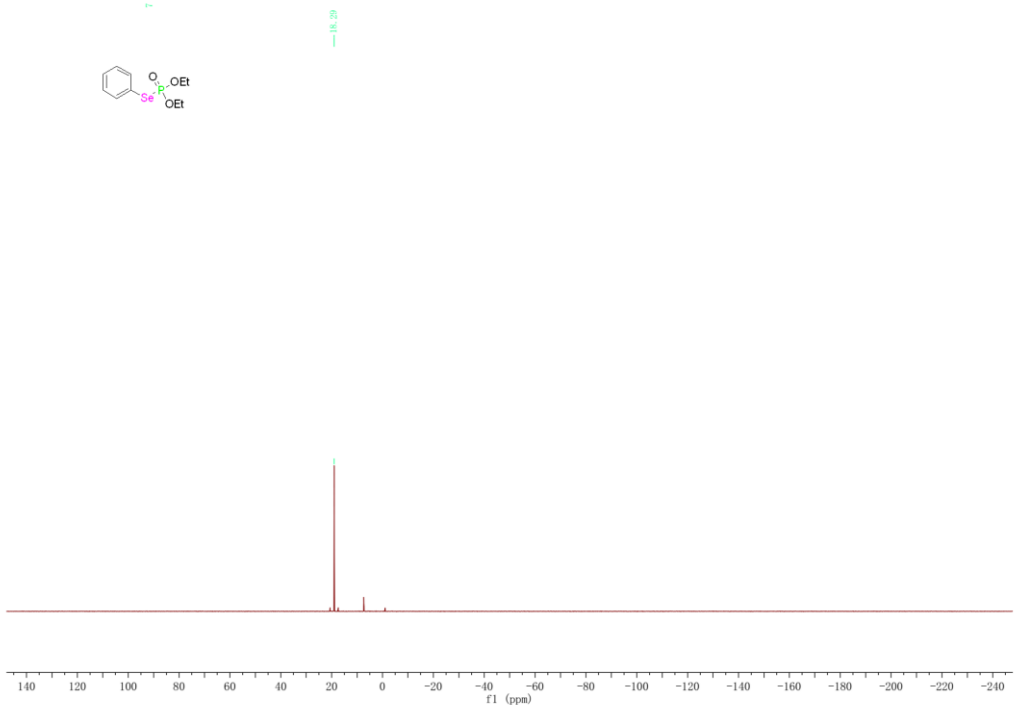
^{31}P NMR Spectrum of **3au**



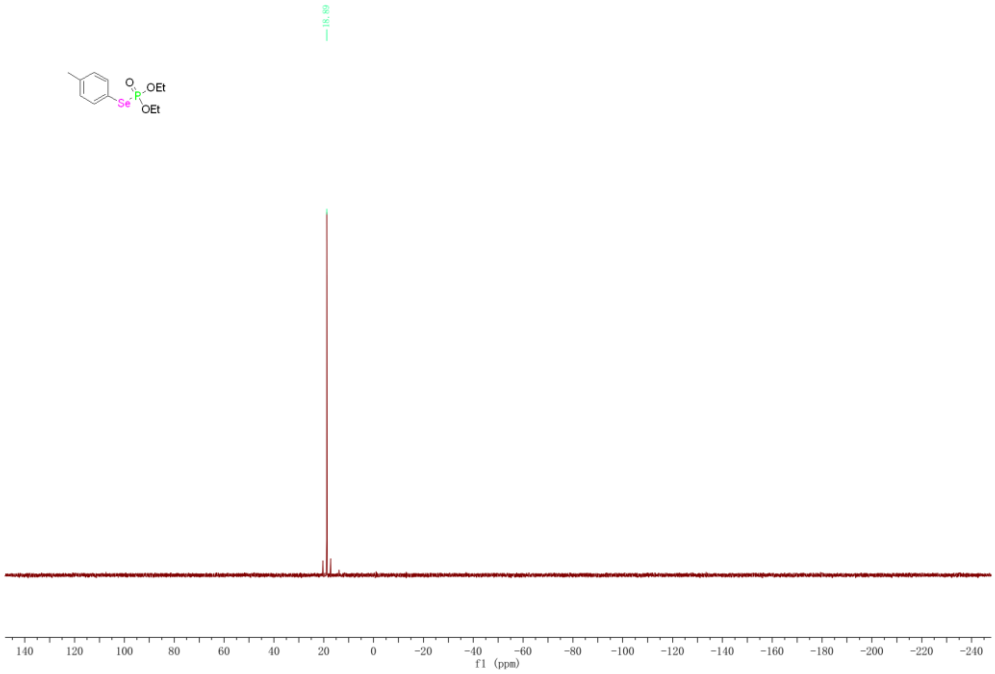
^{31}P NMR Spectrum of **3av**



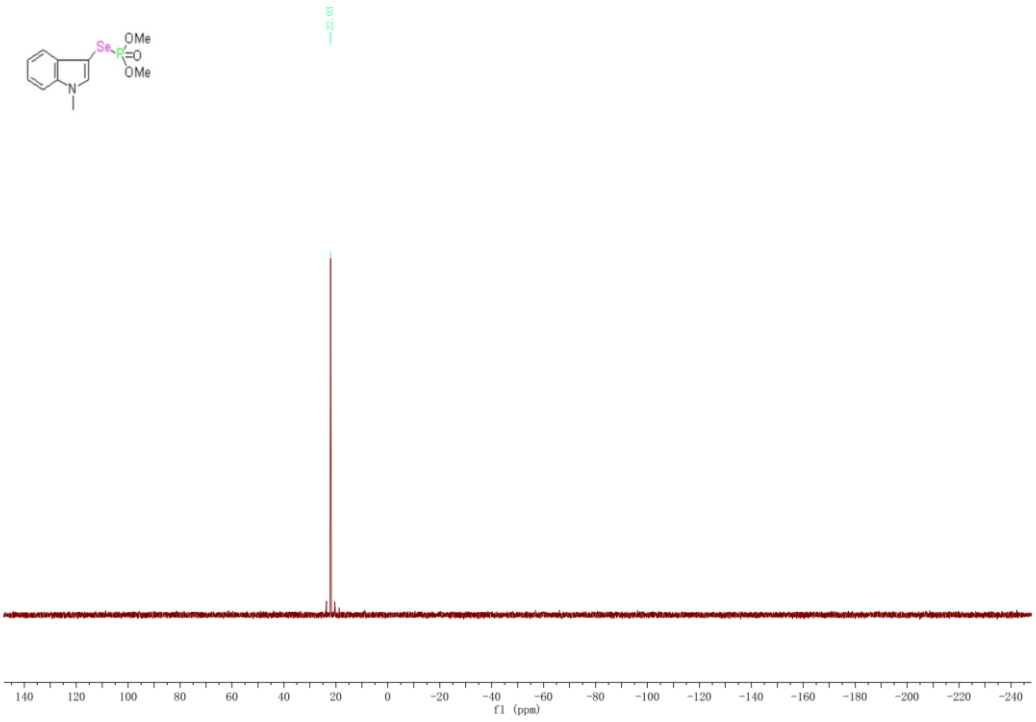
^{31}P NMR Spectrum of **3aw**



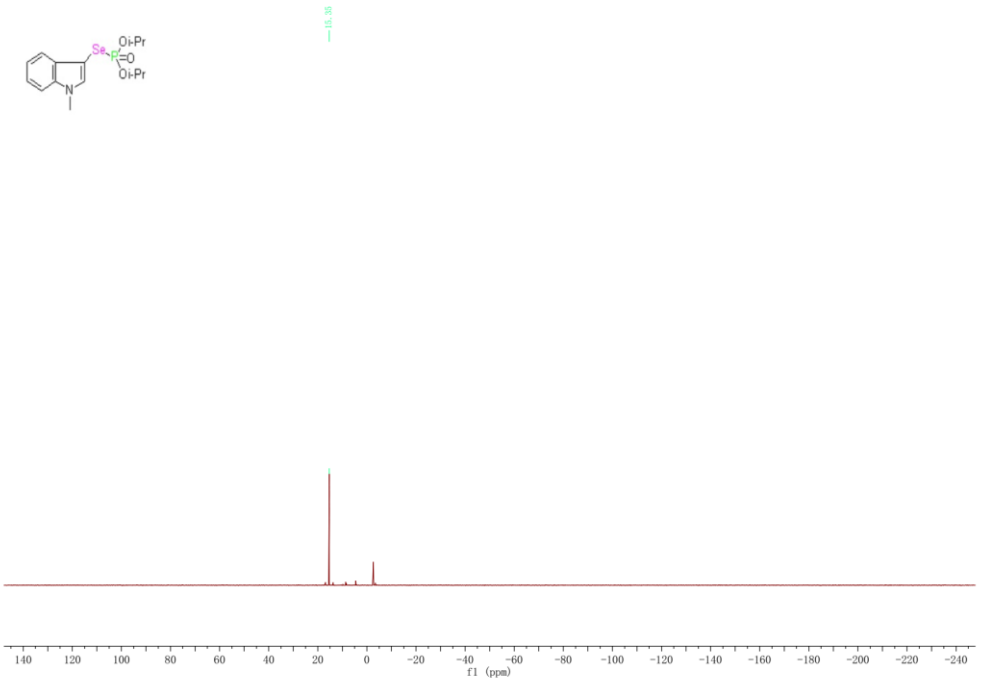
^{31}P NMR Spectrum of **3ax**



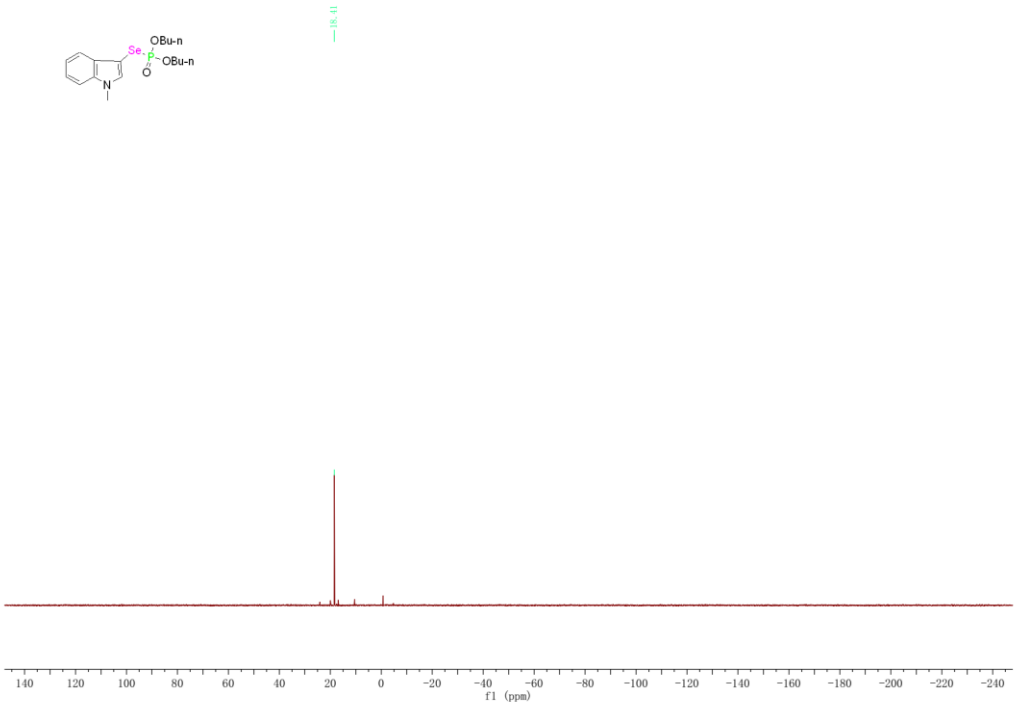
^{31}P NMR Spectrum of **3ay**



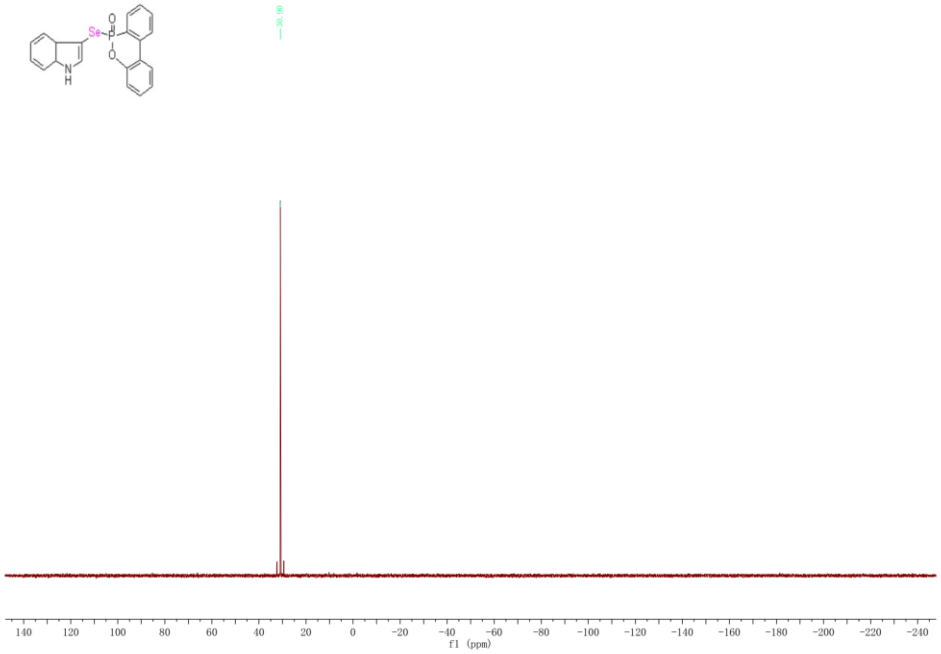
^{31}P NMR Spectrum of **3ba**



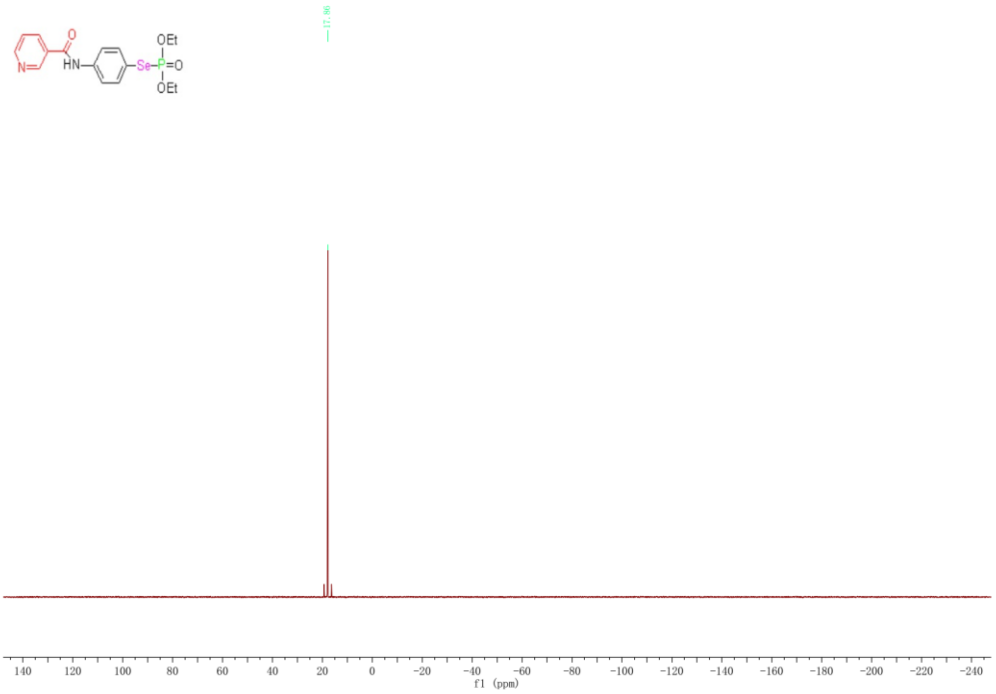
^{31}P NMR Spectrum of **3ca**



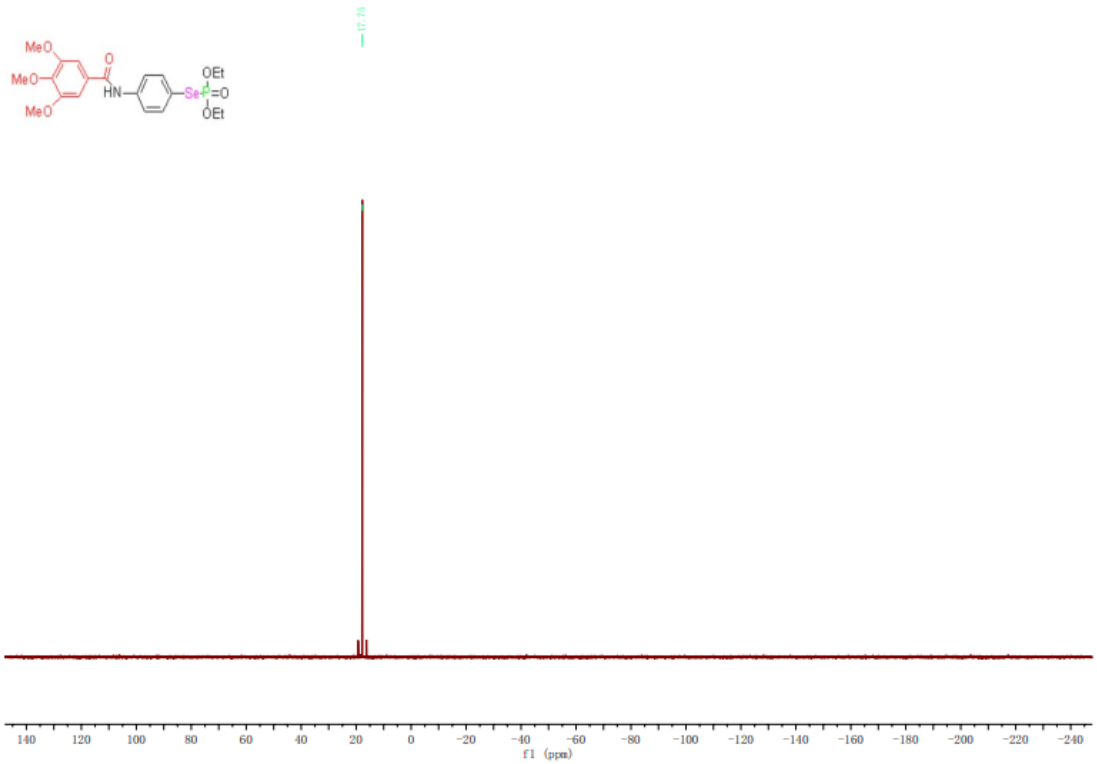
^{31}P NMR Spectrum of **3da**



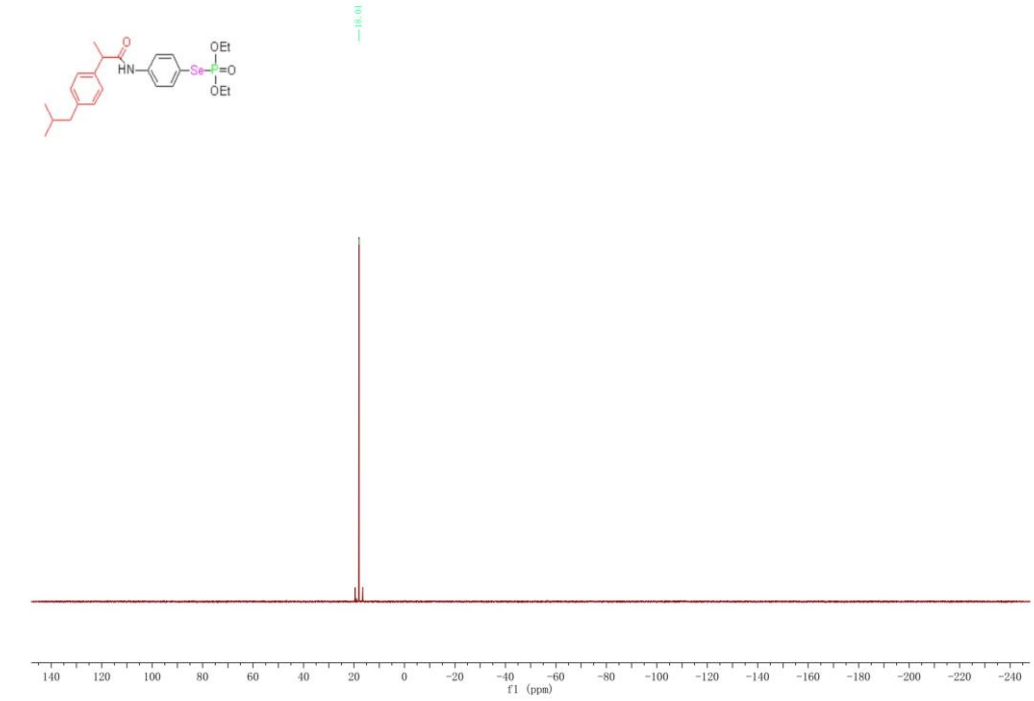
^{31}P NMR Spectrum of **3ea**



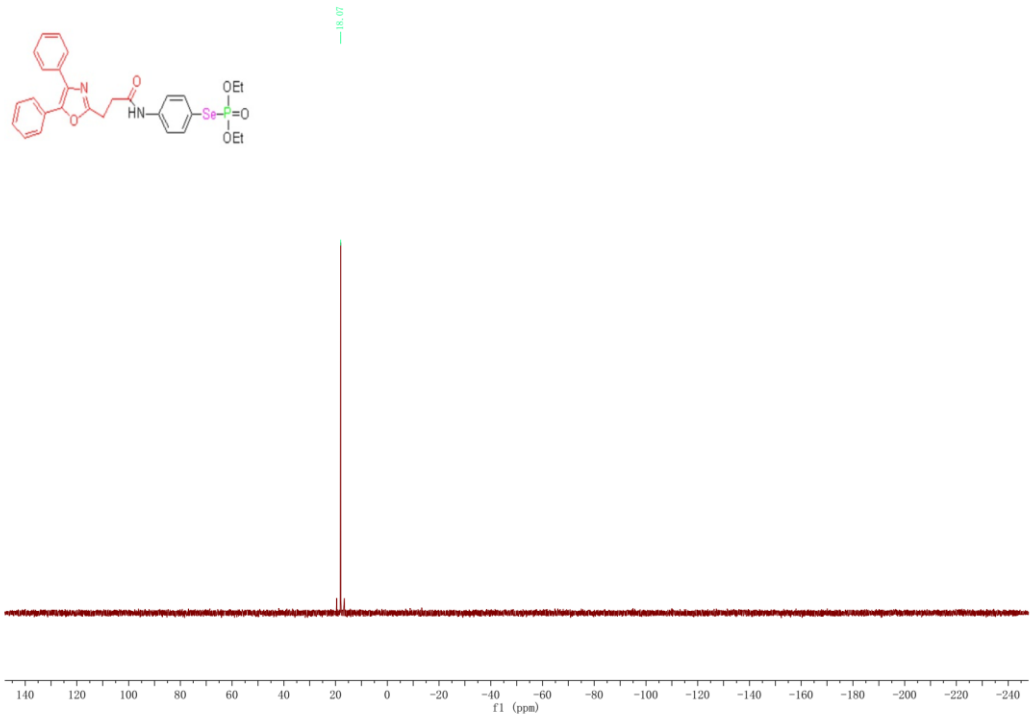
^{31}P NMR Spectrum of **4aa**



^{31}P NMR Spectrum of **4ab**



^{31}P NMR Spectrum of **4ac**



^{31}P NMR Spectrum of **4ad**