Supporting Information

Selective C2 and C3 Phosphorylmethylation of Indoles with a Phosphorylmethyl Dibenzothiophenium Reagent

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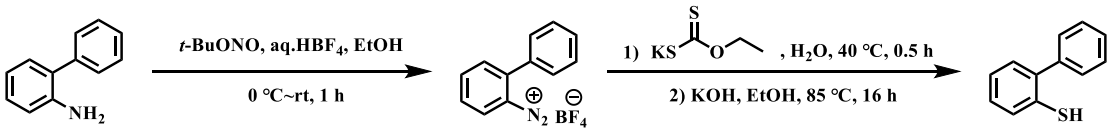
1. General Information

Unless otherwise noted, all reactions were carried out in a pre-dried, sealed Schlenk reaction tube under nitrogen atmosphere. All reactions were monitored by TLC with silica gel-coated plates. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded with a JEOL AL-600, AL-400 spectrometer. Coupling constants (J) are quoted in Hz. The following abbreviations were used to show the multiplicities: s: singlet, d: doublet, t: triplet, q: quadruplet, dd: doublet of doublet, m: multiplet. The residual solvent signals were used as references (DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.5 ppm. $CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). HRMS data were recorded on a high-resolution mass spectrometer in EI or ESI mode. UV-vis absorption spectra were recorded on an UV 2700. Melting points were reported for new compounds.

Starting Materials: Unless stated otherwise, all commercially available compounds were used as supplied without further purification or prepared according to published procedures. Solvents were purified by means of a solvent purification system.

Photochemistry: All photoredox-catalyzed reactions with blue light were carried out using a photoreactor equipped with a blue LED module (25 W Power LED blau 450 nm, purchased from GreeThink), consisting out of 50 LED-chips. The power of the LED was adjusted using a linear regulator.

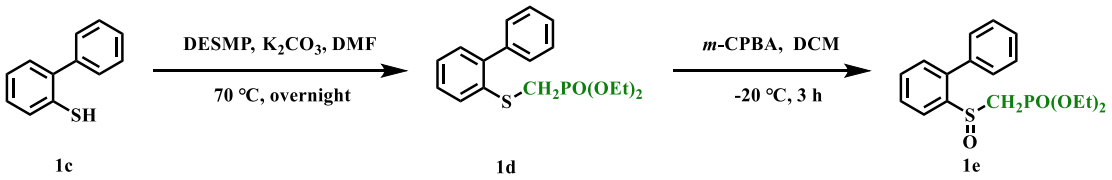
2. Preparation of the Reagent I.



1a 1b 1c

To a solution of 2-Aminodiphenyl 1a (40 mmol, 6.77 g, 1.0 equiv.) in absolute EtOH (20 mL, 3.3 M) was added HBF_4 (12.8 mL, 48% in water) at room temperature. After being stirred for 5 minutes, the mixture was cooled to 0 °C and tert-butyl nitrite (10.8 mL, 2.0 equiv.) was added dropwise. After being stirred at 0 °C for 1 h, Et_2O (80 mL) was added to the reaction mixture. The resulting solid was filtered, washed with Et_2O (3 x 20 mL), and to give the corresponding product 1b in 97% yields. Dissolved diazonium salts 1b in water and cooled to 0 °C. The cold diazonium solution was added slowly to a solution of potassium ethyl xanthate (7.74 g, 48 mmol, 1.25 equiv.) in water (100 mL) at 45 °C. The reaction mixture was stirred for an additional 30 minutes at 45 °C and then cooled to room temperature. The reaction mixture was extracted with diethyl ether (3 x 50 mL). The combined organic extracts were washed with 10 % NaOH solution (100 mL), water (3 x 50 mL), brine (100 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure.

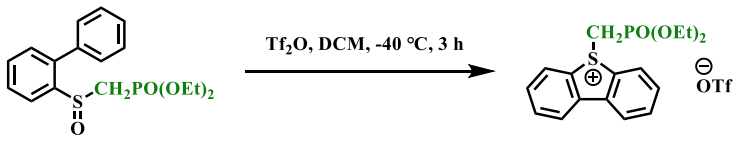
The resulting crude aryl xanthate product was dissolved in ethanol (100 mL) and heated to reflux. Potassium hydroxide pellets (8.67 g, 154.5 mmol, 4 equiv.) were added and refluxing continued overnight. The solution was cooled to room temperature and the ethanol was evaporated under reduced pressure. The residue was dissolved in water and washed with ethyl acetate (100 mL). The aqueous layer was acidified with 2 N HCl and extracted with ethyl acetate (3 x 50 mL). The organic extracts were washed with water (100 mL), brine (100 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure to afford 5.3 g (71 %) of crude product (overall, 3 steps). The crude thiol was used directly in the next step without further purification[1].



1c 1d 1e

The crude thiol 1c (5.3 g, 28 mmol) and K_2CO_3 (7.84 g, 56 mmol, 2 equiv.) were dissolved in DMF (80 mL), the mixture of which was stirred at 70 °C overnight. After concentration of the reaction, the residue was washed with a large amount of H_2O (300 mL) and extracted with ethyl acetate. The resulting organic phase was then dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified via flash column chromatography on silica gel (petroleum ether: ethyl acetate = 2:1) to get 9.408 g of 1d as a colorless oil (98 %). **diethyl (([1,1'-biphenyl]-2-ylthio)methyl)phosphonate (1d)** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.17 (m, 8H), 4.10 – 3.89 (m, 4H), 2.91 (d, *J* = 14.1 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.07, 140.44, 134.00 (d, *J* = 5.7 Hz), 130.56, 130.11, 129.48, 128.17, 128.12, 126.93, 62.71 (d, *J* = 6.4 Hz), 28.99, 27.52, 16.42, 16.35. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 23.71. HRMS (EI) m/z: calcd for $C_{17}H_{21}O_3PS$: 337.1882, found $[M]^+$: 337.1880.

To a solution of above oil 1d in DCM (80 mL) was added *m*-CPBA (85 % purity) (5.97 g, 29.4 mmol, 1.05 equiv.) in portions at -20 °C. The resulting suspension was stirred for 3 h at -20 °C, allowing full conversion of 1d into the product 1e. DCM (200 mL) was added and the solution was washed with 10% (w/w) aqueous solution of $Na_2S_2O_3$ (2 x 100 mL), 5% (w/w) aqueous solution of $NaHCO_3$ (2 x 100 mL), brine (2 x 100 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude was purified via flash column chromatography on silica gel (petroleum ether: ethyl acetate = 2 : 1) to get 9.73 g of 1e as a colorless oil (98 %). **diethyl (([1,1'-biphenyl]-2-ylsulfinyl)methyl)phosphonate (1e)** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 6.6 Hz, 1H), 7.51 – 7.40 (m, 2H), 7.28 – 7.23 (m, 6H), 4.09 – 3.49 (m, 4H), 2.80 (p, *J* = 14.4, 14.0 Hz, 2H), 1.16 – 1.05 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.76 (d, *J* = 10.8 Hz), 139.63, 137.47, 131.24, 130.60, 129.10 (d, *J* = 23.9 Hz), 128.63 (d, *J* = 28.8 Hz), 123.96, 62.66 (dd, *J* = 17.7, 6.1 Hz), 52.08, 50.70, 16.30, 16.22. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 17.50. HRMS (EI) m/z: calcd for $C_{17}H_{21}O_4PS$: 353.1171, found $[M]^+$: 353.1176.



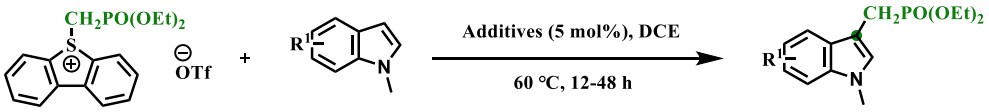
1e I

To a solution of the above sulfoxide 1e in DCM (80 mL) was added Tf_2O (4.8 mL, 28 mmol, 1.0 equiv.) dropwise at -40 °C. The mixture was stirred at the same temperature for 2~3 h, and then the solvent was removed under reduced pressure. The resulting brown oil was dissolved in a minimum of DCM (10 mL). Then, Et_2O (200 mL) was added and the crude product was stirred vigorous under ether for about 1 h. Then the solid was collected by filtration and dried under vacuum as a white powder (13 g, 98 %). ***S*-([diethoxyphosphoryl]methyl) dibenzothiophene salt (I)** Melting Point: 123-125 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 8.2 Hz, 2H), 8.10 (d, *J* = 7.8 Hz, 2H), 7.84 (t, *J* = 7.7 Hz, 2H), 7.69 (t, *J* = 7.8 Hz, 2H), 4.42 (d, *J* = 12.9 Hz, 2H), 4.14 – 4.02 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.66, 134.53, 131.22, 130.09,

128.28 (d, J = 3.6 Hz), 123.78, 64.48 (d, J = 6.3 Hz), 43.34, 41.95, 16.21, 16.15. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -78.13. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 11.63. HRMS (EI) m/z: calcd for $C_{18}H_{20}F_3O_6PS_2$: 484.4410, found $[M]^+$: 484.4400.

3. The optimization of the metal catalyzed phosphorylmethylation of Indoles C3 reaction conditions

Additives screening



I 2'r 4r

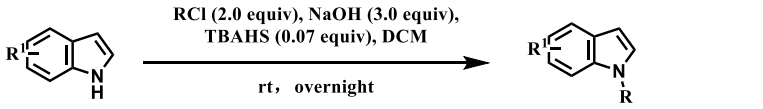
A mixture of indole 2 (0.2 mmol, 1.0 equiv.), reagent I (106.5 mg, 0.22 mmol, 1.1 equiv.) and Additives (5 mol %) in DCE (2.0 mL) was stirred at 60 ºC overnight. The course of the reaction was monitored with thin layer chromatography (TLC). The reaction mixture was then cooled to the room temperature and 10 μL of *n*-dodecane was added as an internal standard and the reaction mixture was diluted with EtOAc. The crude reaction mixture was filtered through a plug of silica then subjected to GC-MS analysis.

Table S1. Additives screening

Entry	Additives	Yield/%
1	$Cu(OTf)_2$	58
2	CuBr	10
3	CuOTf	42
4	$ZnCl_2$	0
5	/	0
6	LiBr	0
7	$Ni(OTf)_2$	27
8	$La(OTf)_3$	trace
9	$In(OTf)_3$	10
10	$BF_3{\cdot}Et_2O$	0
11	$MgCl_2$	0

4. Preparation of N-substituted Indoles Substrates.

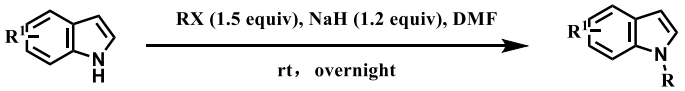
4.1 General procedure for synthesis of protected indoles 2 and 2' (GP-1[2]).



(R=Cbz, Fmoc)

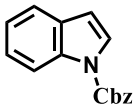
Indole (5.0 mmol, 1.0 equiv.), NaOH (600 mg, 15 mmol), tetrabutylammonium bisulfate (TBAHS) (85 mg, 0.35 mmol) were suspended in DCM (25 mL) and stirred at room temperature for 1 hour, after which the mixture was cooled to 0 ºC and R-Cl (R= Cbz, Fmoc) (10 mmol) was added dropwise. The mixture was stirred for 16 hours at room temperature, then partitioned between DCM and saturated aqueous NH_4Cl. The aqueous layer was extracted with DCM (2 x 30 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue was purified by silica chromatography using the indicated eluent.

4.2 General procedure for synthesis of protected indoles 2 and 2'(GP-2[3]).

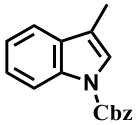


(RX = BnBr, Cbz-Cl)

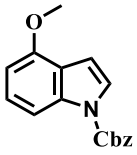
To a stirred suspension of NaH (60 % dispersion in mineral oil; 240 mg, 6.0 mmol, 1.2 equiv.) in DMF (5 mL) was added dropwise a solution of an indole (5.0 mmol, 1.0 equiv.) in DMF (5 mL) at 0 °C, and the mixture was stirred at room temperature for 1 h. To the mixture was added dropwise BnBr or Cbz-Cl (7.5 mmol, 1.5 equiv.) at 0 °C, and the resulting mixture was stirred at room temperature overnight. The reaction was quenched with water and the aqueous layer was extracted with ethyl acetate (2 x 30 mL). The combined organic layer was dried over Na_2SO_4 and evaporated to leave a residue, which was purified by column chromatography using the indicated eluent.



benzyl 1*H*-indole-1-carboxylate (2a) was prepared using 1*H*-indole and benzyl carbonochloridate according to the GP-2 as a colourless solid (0.89 g, 71 %). Spectroscopic data are in accordance with the reported in the literature[4].



benzyl 3-methyl-1*H*-indole-1-carboxylate (2b) was prepared using 3-methyl-1*H*-indole and benzyl carbonochloridate according to the GP-2 as a yellow solid (0.90 g, 68 %). Spectroscopic data are in accordance with the reported in the literature[5].

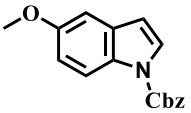


benzyl 4-methoxy-1*H*-indole-1-carboxylate (2c) was prepared using 3-methyl-1*H*-indole and benzyl carbonochloridate according to the GP-2 as a white solid (1.25 g, 89 %). Melting Point: 92-

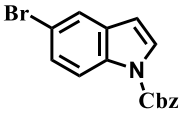
93 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.59 (d, *J* = 3.7 Hz, 1H), 7.47 (d, *J* = 6.6 Hz, 2H), 7.44 – 7.33 (m, 3H), 7.02 (d, *J* = 2.6 Hz, 1H), 6.92 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.51 (d, *J* = 3.8 Hz, 1H), 5.43 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.21, 135.25, 131.45, 128.86, 128.80, 128.53, 126.25, 115.96, 113.29, 108.16, 103.74, 68.71, 55.76. HRMS (EI) m/z: calcd for $C_{17}H_{15}NO_3$: 282.0443, found $[M]^+$: 282.0440.

benzyl 4-nitro-1*H*-indole-1-carboxylate (2d) was prepared using 4-nitro-1*H*-indole and benzyl carbonochloridate according to the GP-2 as a yellow solid (1.21 g, 82 %). Melting Point: 112-114 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 8.3 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 3.7 Hz, 1H), 7.51 (d, *J* = 6.4 Hz, 2H), 7.43 (q, *J* = 7.4, 6.8 Hz, 3H), 7.36 (t, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 3.8 Hz, 1H), 5.48 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.28, 140.56, 137.01, 134.57, 129.45, 129.18, 129.00, 128.82, 128.68, 128.63, 125.04, 123.99, 121.56, 119.93, 107.45, 69.59. HRMS (EI) m/z: calcd for $C_{16}H_{12}N_2O_4$: 297.0143, found $[M]^+$: 297.0145.

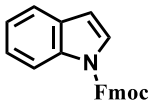
benzyl 4-chloro-1*H*-indole-1-carboxylate (2e) was prepared using 4-chloro-1*H*-indole and benzyl carbonochloridate according to the GP-1 as a pink solid (0.89 g, 63 %). Melting Point: 53-55 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.66 (d, *J* = 3.7 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.45 – 7.35 (m, 3H), 7.27 – 7.20 (m, 2H), 6.71 (d, *J* = 3.8 Hz, 1H), 5.45 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.72, 136.07, 134.91, 129.35, 128.97, 128.92, 128.64, 126.31, 126.18, 125.34, 122.97, 113.83, 106.39, 69.12. HRMS (EI) m/z: calcd for $C_{16}H_{12}ClNO_2$: 286.4593, found $[M]^+$: 286.4589.



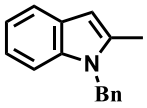
benzyl 5-methoxy-1*H*-indole-1-carboxylate (2f) was prepared using 5-methoxy-1*H*-indole and benzyl carbonochloridate according to the GP-1 as a white solid (0.87 g, 62 %). Melting Point: 71-73 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.61 (d, *J* = 3.7 Hz, 1H), 7.48 (d, *J* = 6.3 Hz, 2H), 7.46 – 7.33 (m, 3H), 7.03 (d, *J* = 2.6 Hz, 1H), 6.94 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.52 (d, *J* = 3.6 Hz, 1H), 5.44 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.24, 135.29, 131.48, 128.87, 128.80, 128.54, 126.27, 115.97, 113.31, 108.18, 103.76, 68.71, 55.76. HRMS (EI) m/z: calcd for $C_{17}H_{15}NO_3$: 282.0433, found $[M]^+$: 282.0431.



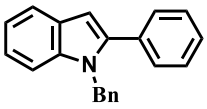
benzyl 5-bromo-1*H*-indole-1-carboxylate (2g) was prepared using 5-bromo-1*H*-indole and benzyl carbonochloridate according to the GP-2 as a white solid (1.40 g, 85 %). Melting Point: 76-78 ºC. Spectroscopic data are in accordance with the reported in the literature[6].



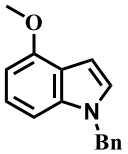
(9H-fluoren-9-yl)methyl 1*H*-indole-1-carboxylate (2j) was prepared using 1*H*-indole and (9H-fluoren-9-yl)methyl carbonochloridate according to the GP-1 as a yellow solid (0.85 g, 47 %). Spectroscopic data are in accordance with the reported in the literature[7].



1-benzyl-2-methyl-1*H*-indole (2'b) was prepared using 2-methyl-1*H*-indole and (bromomethyl)benzene according to the GP-2 as a colourless oil (630 mg, 57 %). Spectroscopic data are in accordance with the reported in the literature[8].

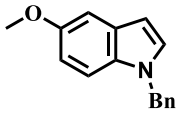


1-benzyl-2-phenyl-1*H*-indole (2'c) was prepared using 2-phenyl-1*H*-indole and (bromomethyl)benzene according to the GP-2 as a white solid (523 mg, 37 %). Spectroscopic data are in accordance with the reported in the literature[5].

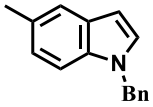


1-benzyl-4-methoxy-1*H*-indole (2'd) was prepared using 4-methoxy-1*H*-indole and (bromomethyl)benzene according to the GP-2 as a white solid (0.86 g, 73 %). Melting Point: 90-92 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.21 (m, 3H), 7.12 – 7.05 (m, 3H), 7.02 (q, *J* = 3.3 Hz, 1H), 6.89 (t, *J* = 7.2 Hz, 1H), 6.64 (s, 2H), 6.51 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.54, 137.90, 137.68, 128.82, 127.64, 126.88, 126.83, 122.62, 119.30, 103.28, 99.51, 99.05, 55.40, 50.36. HRMS (EI) m/z: calcd for $C_{16}H_{15}NO$: 238.0343, found $[M]^{+}$: 238.0347.

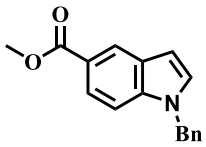
1-benzyl-4-nitro-1*H*-indole (2'e) was prepared using 4-nitro-1*H*-indole and (bromomethyl)benzene according to the GP-2 as a yellow solid (1.04 g, 83 %). Spectroscopic data are in accordance with the reported in the literature[9].



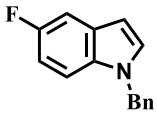
1-benzyl-5-methoxy-1*H*-indole (2'f) was prepared using 5-methoxy-1*H*-indole and (bromomethyl)benzene according to the GP-2 as a white solid (0.84 mg, 71 %). Spectroscopic data are in accordance with the reported in the literature[10].



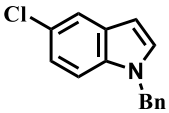
methyl 1-benzyl-1*H*-indole-5-carboxylate (2'g) was prepared using 5-fluoro-1*H*-indole and (bromomethyl)benzene according to the GP-2 as a white solid (0.74 g, 67 %). Spectroscopic data are in accordance with the reported in the literature[11].



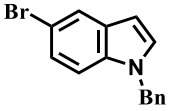
1-benzyl-5-methoxy-1*H*-indole (2'h) was prepared using 5-methoxy-1*H*-indole and (bromomethyl)benzene according to the GP-2 as a white solid (1.10 mg, 83 %). Spectroscopic data are in accordance with the reported in the literature[12].



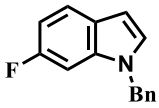
1-benzyl-5-fluoro-1*H*-indole (2'i) was prepared using 5-fluoro-1*H*-indole and (bromomethyl)benzene according to the GP-2 as a yellow oil (0.85 g, 76 %). Spectroscopic data are in accordance with the reported in the literature[11].



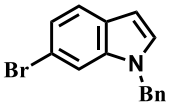
1-benzyl-5-chloro-1*H*-indole (2'j) was prepared using 5-chloro-1*H*-indole and (bromomethyl)benzene according to the GP-2 as a white solid (0.72 g, 60 %). Spectroscopic data are in accordance with the reported in the literature[11].



1-benzyl-5-bromo-1*H*-indole (2'k) was prepared using 5-bromo-1*H*-indole and (bromomethyl)benzene according to the GP-2 as a white solid (1.28 g, 90 %). Spectroscopic data are in accordance with the reported in the literature[13].

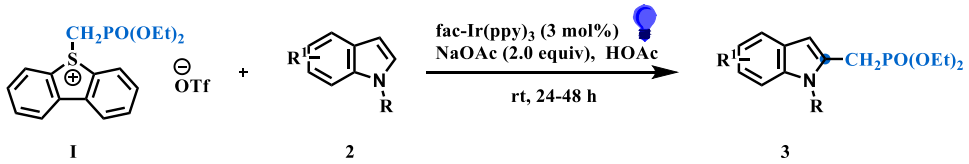


1-benzyl-6-fluoro-1*H*-indole (2'm) was prepared using 6-fluoro-1*H*-indole and (bromomethyl)benzene according to the GP-2 as a white solid (0.63 g, 56 %). Melting Point: 89-91 ºC. Spectroscopic data are in accordance with the reported in the literature[14].



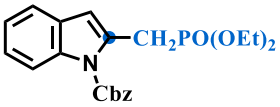
1-benzyl-6-bromo-1*H*-indole (2'n) was prepared using 6-bromo-1*H*-indole and (bromomethyl)benzene according to the GP-2 as a white solid (1.13 g, 79 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.3 Hz, 1H), 7.44 (s, 1H), 7.35 – 7.27 (m, 3H), 7.22 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.10 (q, *J* = 4.0, 3.1 Hz, 3H), 6.53 (d, *J* = 3.2 Hz, 1H), 5.28 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.25, 137.04, 128.98, 127.91, 127.64, 126.81, 122.96, 122.29, 115.47, 112.74, 102.08, 50.20. HRMS (EI) m/z: calcd for $C_{15}H_{12}BrN$: 286.9043, found $[M]^+$: 286.9042.

5. General Procedure for the Preparation of 3.

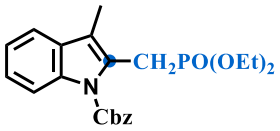


I 2 3

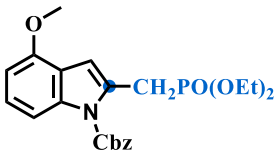
The mixture of indole 2 (0.2 mmol, 1.0 equiv.), reagent I (96.8 mg, 0.2 mmol, 1 equiv.), NaOAc (16.4 mg, 0.4 mmol, 2.0 equiv.), and the photocatalyst fac-Ir(ppy)$_3$, (2 mg, 3 mol%) in HOAc (2.0 mL) was stirred under irradiation of blue LEDs overnight at room temperature. Then another portion sulfonium salt (96.8 mg, 0.2 mmol, 1 equiv.) was added to the reaction solution and the mixture was stirred for 12-24 h under blue light. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (dichloromethane: methanol = 20 : 1) to afford the desired product 3.



benzyl 2-((diethoxyphosphoryl)methyl)-1*H*-indole-1-carboxylate (3a) was prepared using benzyl 1*H*-indole-1-carboxylate and reagent I according to the general procedure as a yellow oil (35 mg, 44 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.31 (m, 4H), 7.21 (p, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 4.4 Hz, 1H), 5.47 (s, 2H), 4.01 (m, 4H), 3.77 (d, *J* = 21.6 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.91, 136.67, 134.92, 131.07 (d, *J* = 10.2 Hz), 129.11 (d, *J* = 3.7 Hz), 128.91 (d, *J* = 4.4 Hz), 124.25, 123.19, 120.35, 115.71, 111.07 (d, *J* = 8.8 Hz), 69.10, 62.31 (d, *J* = 6.7 Hz), 28.52, 27.11, 16.46 (d, *J* = 5.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.83. HRMS (EI) m/z: calcd for: $C_{21}H_{24}NO_5P$: 402.1311, found $[M]^+$: 402.1302.

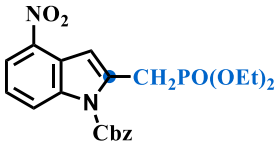


benzyl 2-((diethoxyphosphoryl)methyl)-3-methyl-1*H*-indole-1-carboxylate (3b) was prepared using benzyl 3-methyl-1*H*-indole-1-carboxylate and reagent I according to the general procedure as a yellow oil (149 mg, 36 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.00 (m, 1H), 7.54 – 7.48 (m, 2H), 7.47 – 7.29 (m, 4H), 7.26 – 7.17 (m, 2H), 5.46 (s, 2H), 4.04 – 3.86 (m, 4H), 3.81 (d, *J* = 21.9 Hz, 2H), 2.23 (d, *J* = 4.6 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.99, 136.06, 135.14, 130.42 (d, *J* = 4.0 Hz), 128.95 – 128.63 (m), 126.52 (d, *J* = 14.2 Hz), 124.38, 122.84, 118.45, 117.71 (d, *J* = 10.7 Hz), 115.66, 68.88, 62.10 (d, *J* = 6.7 Hz), 26.29, 24.87, 9.01. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.29. HRMS (EI) m/z: calcd for: $C_{22}H_{26}NO_5P$: 416.1581, found $[M]^+$: 416.1571.

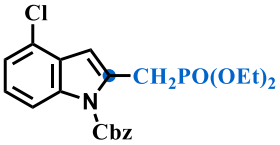


benzyl 2-((diethoxyphosphoryl)methyl)-4-methoxy-1*H*-indole-1-carboxylat (3c) was prepared using benzyl 3-methyl-1*H*-indole-1-carboxylate and reagent I according to the general procedure as

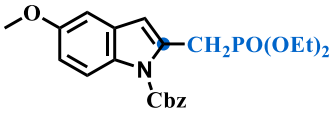
a yellow oil (44 mg, 51 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.6 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.46 – 7.33 (m, 3H), 7.15 (t, *J* = 8.2 Hz, 1H), 6.72 (d, *J* = 4.6 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 5.46 (s, 2H), 4.00 (m, *J* = 7.2, 3.1 Hz, 4H), 3.90 (s, 2H), 3.75 (d, *J* = 21.5 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.48, 151.99, 137.98, 134.93, 129.36 (d, *J* = 11.2 Hz), 128.89 (d, *J* = 7.6 Hz), 125.03, 119.40, 108.80, 107.97 (d, *J* = 9.4 Hz), 103.50, 69.12, 62.30 (d, *J* = 6.7 Hz), 55.50, 28.61, 27.20, 16.45 (d, *J* = 6.1 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.80. HRMS (EI) m/z: calcd for: $C_{22}H_{26}NO_6P$: 432.8894, found $[M]^+$: 432.8890.



benzyl 2-((diethoxyphosphoryl)methyl)-4-nitro-1*H*-indole-1-carboxylate (3d) was prepared using benzyl 4-nitro-1*H*-indole-1-carboxylate and reagent I according to the general procedure as a yellow oil (30 mg, 34 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.46 – 7.38 (m, 3H), 7.38 – 7.28 (m, 2H), 5.50 (s, 2H), 4.09 – 3.96 (m, 4H), 3.80 (d, *J* = 22.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.21, 139.82, 138.57, 136.09 (d, *J* = 11.6 Hz), 134.23, 129.21 (d, *J* = 5.4 Hz), 123.46, 121.81, 120.01, 109.82 (d, *J* = 9.2 Hz), 70.04, 62.56 (d, *J* = 6.7 Hz), 29.02, 27.62, 16.44 (d, *J* = 6.0 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 23.36. HRMS (EI) m/z: calcd for: $C_{21}H_{23}N_2O_7P$: 447.1281, found $[M]^+$: 447.1287.

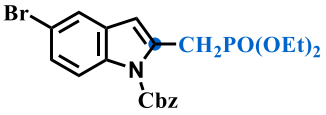


benzyl 4-chloro-2-((diethoxyphosphoryl)methyl)-1*H*-indole-1-carboxylate (3e) was prepared using benzyl 4-chloro-1*H*-indole-1-carboxylate and reagent I according to the general procedure as a yellow oil (31 mg, 36 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.46 – 7.34 (m, 3H), 7.17 (dt, *J* = 16.0, 7.8 Hz, 2H), 6.72 (d, *J* = 4.4 Hz, 1H), 5.48 (s, 2H), 4.11 – 3.96 (m, 4H), 3.78 (d, *J* = 21.8 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.60, 137.38, 132.04 (d, *J* = 11.0 Hz), 128.97 (d, *J* = 9.8 Hz), 127.82, 125.52, 124.84, 122.95, 114.22, 108.87 (d, *J* = 9.2 Hz), 69.46, 62.39 (d, *J* = 6.7 Hz), 28.71, 27.30, 16.45 (d, *J* = 5.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.21. HRMS (EI) m/z: calcd for: $C_{21}H_{23}ClNO_5P$: 436.5731, found $[M]^+$: 436.5726.

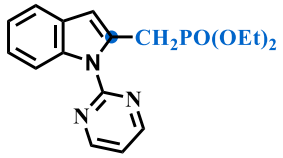


benzyl 2-((diethoxyphosphoryl)methyl)-5-methoxy-1*H*-indole-1-carboxylate (3f) was prepared using benzyl 5-methoxy-1*H*-indole-1-carboxylate and reagent I according to the general procedure as a yellow oil (31 mg, 36 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 9.1 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.46 – 7.32 (m, 3H), 6.93 (d, *J* = 2.6 Hz, 1H), 6.83 (dd, *J* = 9.5, 2.7 Hz, 1H), 6.56 (d, *J* = 4.3 Hz, 1H), 5.45 (s, 2H), 4.09 – 3.93 (m, 4H), 3.81 (s, 3H), 3.76 (d, *J* = 21.6 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.16, 151.81, 134.98, 131.73 (d, *J* = 9.9 Hz), 131.26, 129.96 (d, *J* = 3.6 Hz), 128.88, 116.54, 112.79, 111.00 (d, *J* = 8.7 Hz), 102.90, 68.99, 62.29 (d, *J* = 6.7 Hz), 55.70, 28.53, 27.12, 16.46 (d, *J* = 5.9 Hz). ^{31}P NMR (162 MHz,

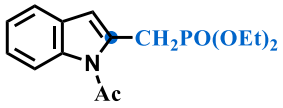
Chloroform-*d*) δ 24.85. HRMS (EI) m/z: calcd for: $C_{22}H_{26}BrNO_6P$: 433.1571, found $[M]^+$: 433.1566.



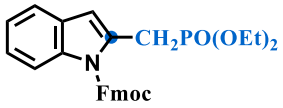
benzyl 5-bromo-2-((diethoxyphosphoryl)methyl)-1*H*-indole-1-carboxylate (3g) was prepared using benzyl 5-bromo-1*H*-indole-1-carboxylate and reagent I according to the general procedure as a yellow oil (32 mg, 33 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 1.9 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.45 – 7.35 (m, 3H), 7.31 (dd, *J* = 9.0, 2.1 Hz, 1H), 6.55 (d, *J* = 4.4 Hz, 2H), 5.46 (s, 4H), 4.00 (pd, *J* = 7.1, 2.7 Hz, 4H), 3.74 (d, *J* = 22.0 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.55, 135.40, 134.64, 132.54 (d, *J* = 10.2 Hz), 130.78, 129.11 – 128.74 (m), 127.03, 122.89, 117.15, 116.49, 110.07 (d, *J* = 8.8 Hz), 69.40, 62.37 (d, *J* = 6.7 Hz), 28.56, 27.16, 16.46 (d, *J* = 6.0 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.34. HRMS (EI) m/z: calcd for: $C_{21}H_{23}BrNO_5P$: 481.0271, found $[M]^+$: 481.0274.



diethyl ((1-(pyrimidin-2-yl)-1*H*-indol-2-yl)methyl)phosphonate (3h) was prepared using 1-(pyrimidin-2-yl)-1*H*-indole and reagent I according to the general procedure as a yellow oil (40 mg, 58 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 4.9 Hz, 2H), 8.25 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.27 – 7.11 (m, 3H), 6.68 (d, *J* = 4.2 Hz, 1H), 4.08 (d, *J* = 21.5 Hz, 2H), 4.00 – 3.81 (m, 4H), 1.11 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.20, 137.25, 130.81, 130.71, 128.90, 123.23, 122.06, 120.17, 117.37, 113.96, 109.09, 109.00, 62.07 (d, *J* = 6.8 Hz), 28.14, 26.74, 16.36 (d, *J* = 5.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.29. HRMS (EI) m/z: calcd for: $C_{17}H_{20}N_3O_3P$: 346.0712, found $[M]^+$: 346.0710.

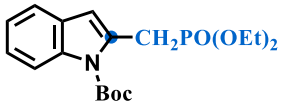


diethyl ((1-acetyl-1*H*-indol-2-yl)methyl)phosphonate (3i) was prepared using 1-(1*H*-indol-1-yl)ethan-1-one and reagent I according to the general procedure as a yellow oil (20 mg, 33 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 6.9 Hz, 1H), 7.30 – 7.19 (m, 2H), 6.64 (d, *J* = 4.5 Hz, 1H), 4.06 (p, *J* = 7.3 Hz, 4H), 3.81 (d, *J* = 21.6 Hz, 2H), 2.80 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.03, 136.14, 131.97, 131.87, 129.62 (d), 123.98, 123.03, 120.94, 114.13, 111.39 (d, *J* = 8.9 Hz), 62.31 (d, *J* = 6.5 Hz), 29.77, 28.64, 27.67, 27.24, 16.46 (d, *J* = 6.4 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.99. HRMS (EI) m/z: calcd for: $C_{15}H_{20}NO_4P$: 310.0341, found $[M]^+$: 310.0337.

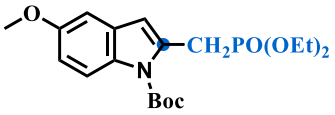


(9H-fluoren-9-yl)methyl 2-((diethoxyphosphoryl)methyl)-1*H*-indole-1-carboxylate (3j) was prepared using (9*H*-fluoren-9-yl)methyl 1*H*-indole-1-carboxylate and reagent I according to the general procedure as a yellow oil (49 mg, 50 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.42 (td, *J* = 7.6, 5.1 Hz, 4H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 4.1 Hz, 1H), 4.94 (d, *J* = 5.4 Hz, 2H), 4.45

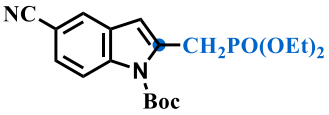
(t, *J* = 5.5 Hz, 1H), 4.10 – 3.92 (m, 4H), 3.73 (d, *J* = 21.6 Hz, 2H), 1.20 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.11, 143.40, 141.65, 136.24, 131.24 (d, *J* = 9.5 Hz), 129.00, 128.13, 127.48, 124.80, 124.14, 123.08, 120.36, 120.26, 115.63, 111.14 (d, *J* = 8.8 Hz), 68.54, 62.31 (d, *J* = 7.0 Hz), 46.93, 28.12, 26.71, 16.47 (d, *J* = 5.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.89. HRMS (EI) m/z: calcd for: $C_{28}H_{28}NO_5P$: 490.2402, found $[M]^+$: 490.2401.



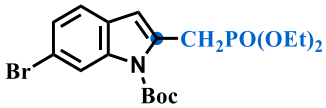
tert-butyl 2-((diethoxyphosphoryl)methyl)-5-methoxy-1*H*-indole-1-carboxylate (3k) was prepared using tert-butyl 1*H*-indole-1-carboxylate and reagent I according to the general procedure as a yellow oil (62 mg, 84 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.13 (m, 2H), 6.61 (d, *J* = 4.3 Hz, 1H), 4.13 – 3.91 (m, 4H), 3.80 (d, *J* = 21.8 Hz, 2H), 1.68 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.55, 136.76, 131.03 (d, *J* = 10.2 Hz), 125.51, 123.89, 122.80, 120.23, 115.63, 110.38 (d, *J* = 9.0 Hz), 84.41, 62.29 (d, *J* = 6.8 Hz), 28.58, 28.25, 27.18, 16.47 (d, *J* = 6.1 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.18. HRMS (EI) m/z: calcd for: $C_{18}H_{26}NO_5P$: 368.1141, found $[M]^+$: 368.1135.



tert-butyl 2-((diethoxyphosphoryl)methyl)-5-methoxy-1*H*-indole-1-carboxylate (3l) was prepared using tert-butyl 5-methoxy-1*H*-indole-1-carboxylate and reagent I according to the general procedure as a orange oil (30 mg, 38 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 9.1 Hz, 1H), 6.92 (d, *J* = 2.6 Hz, 1H), 6.84 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.54 (d, *J* = 4.2 Hz, 1H), 4.12 – 3.97 (m, 4H), 3.81 (s, 3H), 3.78 (d, *J* = 21.6 Hz, 2H), 1.67 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.91, 150.47, 132.88 – 130.58 (m), 129.74 (d, *J* = 3.6 Hz), 116.44, 112.58, 110.28 (d, *J* = 8.7 Hz), 102.70, 84.24, 62.27 (d, *J* = 6.7 Hz), 55.70, 28.61, 28.25, 27.20, 16.47 (d, *J* = 6.3 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 25.13. HRMS (EI) m/z: calcd for: $C_{19}H_{28}NO_6P$: 397.1404, found $[M]^+$: 398.1405.



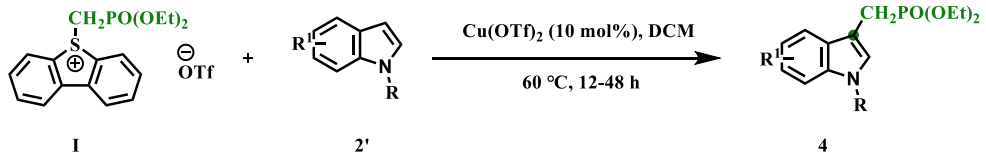
tert-butyl 5-cyano-2-((diethoxyphosphoryl)methyl)-1*H*-indole-1-carboxylate (3m) was prepared using tert-butyl 5-cyano-1*H*-indole-1-carboxylate and reagent I according to the general procedure as a yellow oil (37 mg, 47 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.8 Hz, 1H), 7.78 (s, 1H), 7.47 (dd, *J* = 8.7, 1.7 Hz, 1H), 6.64 (d, *J* = 4.2 Hz, 1H), 4.23 – 3.95 (m, 4H), 3.78 (d, *J* = 21.9 Hz, 2H), 1.69 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.79, 138.65, 133.87 (d, *J* = 10.3 Hz), 128.87, 126.99, 119.83, 116.39, 109.60 (d, *J* = 8.7 Hz), 106.18, 85.79, 62.43 (d, *J* = 6.6 Hz), 29.76, 28.69, 28.15, 27.28, 16.47 (d, *J* = 5.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.24. HRMS (EI) m/z: calcd for: $C_{19}H_{25}N_2O_5P$: 393.1241, found $[M]^+$: 393.1243.



tert-butyl 6-bromo-2-((diethoxyphosphoryl)methyl)-1*H*-indole-1-carboxylate (3n) was

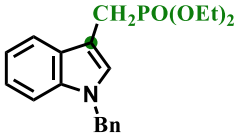
prepared using tert-butyl 6-bromo-1*H*-indole-1-carboxylate and reagent I according to the general procedure as a brown oil (46 mg, 51 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (s, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 6.56 (d, *J* = 4.3 Hz, 1H), 4.04 (m, 4H), 3.76 (d, *J* = 21.7 Hz, 2H), 1.68 (s, 2H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.08, 137.45, 131.69 (d), 127.70, 126.03, 121.22, 118.88, 117.60, 109.99 (d, *J* = 8.8 Hz), 85.10, 62.34 (d, *J* = 6.6 Hz), 28.65, 28.16, 27.24, 16.48 (d, *J* = 5.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.64. HRMS (EI) m/z: calcd for: $C_{18}H_{25}BrNO_5P$: 447.0102, found $[M]^+$: 447.0105.

6. General Procedure for the Preparation of 4.

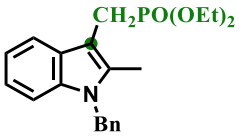


I 2' 4

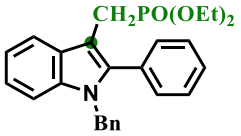
A mixture of indole 2 (0.2 mmol, 1.0 equiv.), reagent I (106.5 mg, 0.22 mmol, 1.1 equiv.) and $Cu(OTf)_2$ (7.2 mg, 10 mol%) in DCM (2.0 mL) was stirred at 60 ºC overnight. The course of the reaction was monitored with thin layer chromatography (TLC). The reaction mixture was then cooled to the room temperature and quenched with water and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and evaporated to leave a residue, which was purified by flash chromatography (dichloromethane: methanol = 20 : 1).



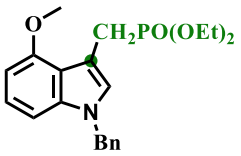
diethyl ((1-benzyl-1*H*-indol-3-yl)methyl)phosphonate (4a) was prepared using 1-benzyl-1*H*-indole and reagent I according to the general procedure as a brown solid (51 mg, 72 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.32 – 7.22 (m, 4H), 7.20 – 7.06 (m, 5H), 5.28 (s, 2H), 4.09 – 3.90 (m, 4H), 3.30 (d, *J* = 20.4 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.58, 136.47, 128.81, 128.34 (d, *J* = 6.1 Hz), 127.70, 127.60 (d, *J* = 6.9 Hz), 126.90, 122.02, 119.44, 119.25, 109.79, 104.47 (d, *J* = 9.6 Hz), 62.11 (d, *J* = 6.7 Hz), 50.12, 23.83, 22.40, 16.48 (d, *J* = 5.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.06. HRMS (EI) m/z: calcd for: $C_{20}H_{24}NO_3P$: 358.1221, found $[M]^+$: 358.1220.



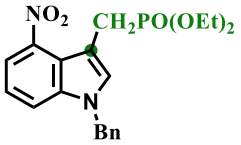
diethyl ((1-benzyl-2-methyl-1*H*-indol-3-yl)methyl)phosphonate (4b) was prepared using 1-benzyl-2-methyl-1*H*-indole and reagent I according to the general procedure as a yellow oil (27 mg, 36 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dt, *J* = 7.2, 3.6 Hz, 1H), 7.27 – 7.16 (m, 4H), 7.11 (dt, *J* = 5.9, 3.4 Hz, 2H), 7.01 – 6.85 (m, 2H), 5.30 (s, 2H), 4.05 – 3.86 (m, 4H), 3.29 (d, *J* = 19.5 Hz, 2H), 2.35 (d, *J* = 3.5 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.94, 136.53, 134.74 (d, *J* = 7.8 Hz), 128.83, 127.98, 127.37, 126.06, 121.20, 119.48, 118.53, 109.11, 101.32 (d, *J* = 10.4 Hz), 62.00 (d, *J* = 6.8 Hz), 46.72, 23.93, 22.49, 16.52 (d, *J* = 5.8 Hz), 10.67. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.96. HRMS (EI) m/z: calcd for: $C_{21}H_{26}NO_3P$: 372.1490, found $[M]^+$: 372.1495.



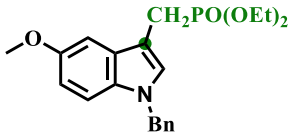
diethyl ((1-benzyl-2-phenyl-1*H*-indol-3-yl)methyl)phosphonate (4c) was prepared using 1-benzyl-2-phenyl-1*H*-indole and reagent I according to the general procedure as a yellow oil (59 mg, 68 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 6.9, 2.6 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.46 – 7.36 (m, 3H), 7.27 – 7.12 (m, 6H), 6.92 (dd, *J* = 7.4, 2.0 Hz, 2H), 5.23 (s, 2H), 4.06 – 3.86 (m, 4H), 3.29 (d, *J* = 20.3 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.67 (d, *J* = 9.6 Hz), 138.26, 131.22, 130.87, 128.82 – 128.53 (m), 128.04, 127.21, 126.16, 122.31, 120.37, 119.90, 110.38, 103.48 (d, *J* = 9.7 Hz), 61.92 (d, *J* = 6.7 Hz), 47.85, 24.56, 23.12, 16.53 (d, *J* = 6.1 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.10. HRMS (EI) m/z: calcd for: $C_{26}H_{28}FNO_3P$: 434.2201, found $[M]^+$: 434.2203.



diethyl ((1-benzyl-4-methoxy-1*H*-indol-3-yl)methyl)phosphonate (4d) was prepared using 1-benzyl-4-methoxy-1*H*-indole and reagent I according to the general procedure as a brown oil (39 mg, 50 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.16 (m, 3H), 7.12 (d, *J* = 3.3 Hz, 1H), 7.10 – 7.00 (m, 3H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.23 (s, 2H), 4.12 – 4.00 (m, 4H), 3.90 (s, 3H), 3.65 (d, *J* = 20.3 Hz, 2H), 1.20 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.95, 137.90, 128.77, 127.63, 126.85, 126.50 (d, *J* = 6.3 Hz), 122.67, 118.05 (d, *J* = 7.9 Hz), 104.52 (d, *J* = 9.0 Hz), 103.33, 99.61, 61.91 (d, *J* = 6.7 Hz), 55.16, 50.26, 24.37, 22.97, 16.47 (d, *J* = 5.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 29.14. HRMS (EI) m/z: calcd for: $C_{21}H_{26}NO_4P$: 388.1481, found $[M]^+$: 388.1476.

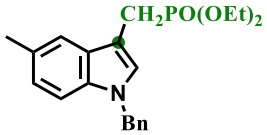


diethyl ((1-benzyl-4-nitro-1*H*-indol-3-yl)methyl)phosphonate (4e) was prepared using 1-benzyl-4-nitro-1*H*-indole and reagent I according to the general procedure as a brown solid (19 mg, 23 %). Melting Point: 112-114 ºC. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 3.5 Hz, 1H), 7.34 – 7.23 (m,3H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 7.3, 2.2 Hz, 2H), 5.33 (s, 2H), 4.04 – 3.86 (m, 4H), 3.53 (d, *J* = 20.3 Hz, 2H), 1.16 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.64, 139.06, 136.21, 132.85 (d, *J* = 7.8 Hz), 129.08, 128.22, 126.83, 120.67, 119.88 (d, *J* = 5.2 Hz), 118.08, 115.82, 104.57 (d, *J* = 10.6 Hz), 62.05 (d, *J* = 7.0 Hz), 50.63, 25.57, 24.14, 16.33 (d, *J* = 6.2 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.12. HRMS (EI) m/z: calcd for: $C_{20}H_{23}N_2O_5P$: 403.1194, found $[M]^+$: 403.1191.

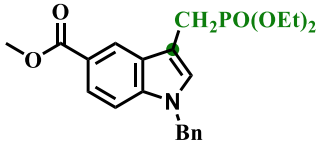


diethyl ((1-benzyl-5-methoxy-1*H*-indol-3-yl)methyl)phosphonate (4f) was prepared using 1-

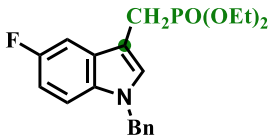
methyl-1*H*-indole and reagent I according to the general procedure as a orange oil (39 mg, 50 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (qt, *J* = 6.0, 3.5 Hz, 3H), 7.16 – 7.05 (m, 5H), 6.81 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.23 (s, 2H), 4.09 – 3.90 (m, 1H), 3.85 (s, 3H), 3.26 (d, *J* = 20.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.17, 137.65, 131.76, 128.80, 128.67 (d, *J* = 6.5 Hz), 128.20 (d, *J* = 7.5 Hz), 127.69, 126.83, 112.40, 110.65, 103.87 (d, *J* = 8.8 Hz), 100.96, 62.12 (d, *J* = 6.7 Hz), 55.95, 50.31, 29.78, 23.96, 22.53, 16.52 (d, *J* = 5.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.18. HRMS (EI) m/z: calcd for: $C_{21}H_{26}NO_4P$: 388.1481, found $[M]^+$: 388.1484.



diethyl ((1-benzyl-5-methyl-1*H*-indol-3-yl)methyl)phosphonate (4g) was prepared using 1-benzyl-5-methyl-1*H*-indole and reagent I according to the general procedure as a brown oil (30 mg, 40 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (s, 1H), 7.29 – 7.20 (m, 3H), 7.15 – 7.11 (m,2H), 7.14 – 7.01 (m, 2H), 6.98 (d, *J* = 8.2 Hz, 1H), 5.25 (s, 2H), 4.09 – 3.90 (m, 4H), 3.27 (d, *J* = 20.1 Hz, 2H), 2.44 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.74, 134.89, 128.72 (d, *J* = 12.9 Hz), 128.56 (d, *J* = 6.7 Hz), 127.68 (d, *J* = 8.4 Hz), 126.85, 123.65, 118.93, 109.51, 103.79 (d, *J* = 9.0 Hz), 62.11 (d, *J* = 6.9 Hz), 50.15, 23.82, 22.40, 21.55, 16.48 (d, *J* = 6.4 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.20. HRMS (EI) m/z: calcd for: $C_{21}H_{26}NO_3P$: 372.1493, found $[M]^+$: 372.1489.

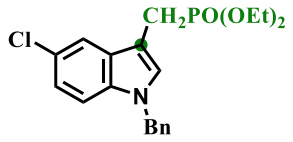


methyl 1-benzyl-3-((diethoxyphosphoryl)methyl)-1*H*-indole-5-carboxylate (4h) was prepared using methyl 1-benzyl-1*H*-indole-5-carboxylate and reagent I according to the general procedure as a yellow oil (59 mg, 61 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.28 – 7.19 (m, 5H), 7.08 (d, *J* = 6.4 Hz, 2H), 5.28 (s, 2H), 4.09 – 3.92 (m, 4H), 3.90 (s, 1H), 3.30 (d, *J* = 20.3 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.15, 138.93, 136.90, 128.98 (d, *J* = 9.0 Hz), 126.91, 123.44, 122.44, 121.57, 109.52, 106.42 (d, *J* = 9.0 Hz), 62.19 (d, *J* = 6.7 Hz), 51.92, 50.31, 23.77, 22.34, 16.45 (d, *J* = 5.7 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.47. HRMS (EI) m/z: calcd for: $C_{22}H_{26}NO_5P$: 416.1579, found $[M]^+$: 416.1583.

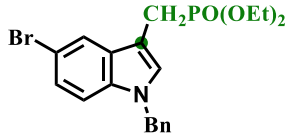


diethyl ((1-benzyl-5-fluoro-1*H*-indol-3-yl)methyl)phosphonate (4i) was prepared using 1-benzyl-5-fluoro-1*H*-indole and reagent I according to the general procedure as a yellow oil (42 mg, 56 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.23 (m, 4H), 7.20 (d, *J* = 3.4 Hz, 1H), 7.13 (dd, *J* = 8.9, 4.3 Hz, 1H), 7.10 – 7.04 (m, 1H), 6.89 (td, *J* = 9.1, 2.6 Hz, 1H), 5.25 (s, 2H), 4.00 (m, *J* = 7.1 Hz, 4H), 3.22 (d, *J* = 20.2 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.14, 156.80, 137.25, 133.05, 129.28 (d, *J* = 7.4 Hz), 128.88, 128.66 (dd, *J* = 9.6, 5.9 Hz), 127.84, 126.84, 110.56 (d, *J* = 8.6 Hz), 110.33, 104.52 (dd), 104.28 (d, *J* = 24.0 Hz), 62.15 (d, *J* =

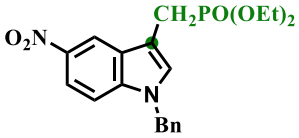
6.6 Hz), 50.43, 23.91, 22.48, 16.48 (d, J = 5.8 Hz). ^{19}F NMR (377 MHz, Chloroform-*d*) δ -124.72. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.78. HRMS (EI) m/z: calcd for: $C_{20}H_{23}FNO_3P$: 376.1125, found $[M]^+$: 376.1122.



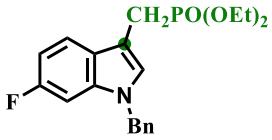
diethyl ((1-benzyl-5-chloro-1*H*-indol-3-yl)methyl)phosphonate (4j) was prepared using 1-benzyl-5-chloro-1*H*-indole and reagent I according to the general procedure as a yellow oil (47 mg, 66 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, J = 2.0 Hz, 1H), 7.26 (q, J = 6.5 Hz, 3H), 7.18 (d, J = 3.6 Hz, 1H), 7.13 (d, J = 8.6 Hz, 1H), 7.11 – 7.04 (m, 3H), 5.23 (s, 2H), 4.09 – 3.91 (m, 4H), 3.22 (d, J = 20.2 Hz, 2H), 1.21 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.09, 134.87, 129.32 (d, J = 6.0 Hz), 128.98 (d, J = 7.7 Hz), 128.90, 127.89, 126.84, 125.37, 122.35, 118.93, 110.93, 104.33 (d, J = 9.3 Hz), 62.17 (d, J = 6.8 Hz), 50.34, 23.83, 22.40, 16.48 (d, J = 5.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.56. HRMS (EI) m/z: calcd for: $C_{20}H_{23}ClNO_3P$: 392.5648, found $[M]^+$: 392.5645.



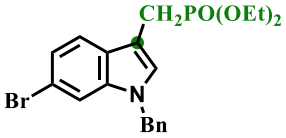
diethyl ((1-benzyl-5-bromo-1*H*-indol-3-yl)methyl)phosphonate (4k) was prepared using 5-bromo-1-methyl-1*H*-indole and reagent I according to the general procedure as a yellow oil (47 mg, 65 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, J = 1.9 Hz, 1H), 7.33 – 7.18 (m, 4H), 7.16 (d, J = 3.6 Hz, 1H), 7.09 (d, J = 8.7 Hz, 1H), 7.07 – 7.03 (m, 2H), 5.23 (s, 2H), 4.00 (m, 4H), 3.22 (d, J = 20.2 Hz, 2H), 1.21 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.04, 135.14, 129.95 (d, J = 5.9 Hz), 128.85 (d, J = 10.7 Hz), 127.91, 126.83, 124.89, 122.05, 112.89, 111.37, 104.26 (d, J = 8.9 Hz), 62.20 (d, J = 6.8 Hz), 50.33, 23.83, 22.40, 16.48 (d, J = 5.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.53. HRMS (EI) m/z: calcd for: $C_{20}H_{23}BrNO_3P$: 437.0183, found $[M]^+$: 437.0180.



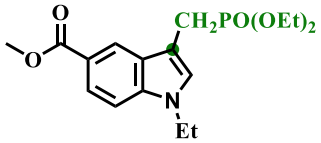
diethyl ((1-benzyl-5-nitro-1*H*-indol-3-yl)methyl)phosphonate (4l) was prepared using 1-benzyl-5-nitro-1*H*-indole and reagent I according to the general procedure as a brown oil (40 mg, 52 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (qt, J = 6.0, 3.5 Hz, 3H), 7.16 – 7.05 (m, 5H), 6.81 (dd, J = 8.8, 2.4 Hz, 1H), 5.23 (s, 2H), 4.09 – 3.90 (m, 1H), 3.85 (s, 3H), 3.26 (d, J = 20.1 Hz, 2H), 1.20 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.17, 137.65, 131.76, 128.80, 128.67 (d, J = 6.5 Hz), 128.20 (d, J = 7.5 Hz), 127.69, 126.83, 112.40, 110.65, 103.87 (d, J = 8.8 Hz), 100.96, 62.12 (d, J = 6.7 Hz), 55.95, 50.31, 29.78, 23.96, 22.53, 16.52 (d, J = 5.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.18. HRMS (EI) m/z: calcd for: $C_{20}H_{23}N_2O_5P$: 403.1190, found $[M]^+$: 403.1186.



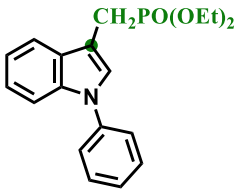
diethyl ((1-benzyl-6-fluoro-1*H*-indol-3-yl)methyl)phosphonate (4m) was prepared using 1-benzyl-6-fluoro-1*H*-indole and reagent I according to the general procedure as a yellow oil (50 mg, 67 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 8.6, 5.2 Hz, 1H), 7.33 – 7.17 (m, 3H), 7.12 (d, *J* = 3.6 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.87 (ddd, *J* = 17.4, 9.3, 2.3 Hz, 2H), 5.19 (s, 2H), 4.08 – 3.89 (m, 4H), 3.25 (d, *J* = 20.3 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.26, 158.90, 137.06, 136.50 (d, *J* = 12.2 Hz), 128.90, 127.96 (d, *J* = 4.1 Hz), 127.87, 126.89, 124.85 (d, *J* = 6.0 Hz), 120.25 (d, *J* = 10.0 Hz), 108.25 (d, *J* = 24.7 Hz), 104.83 (d, *J* = 9.0 Hz), 96.25 (d, *J* = 26.1 Hz), 62.16 (d, *J* = 6.7 Hz), 50.29, 23.92, 22.49, 16.48 (d, *J* = 5.9 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.43. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.77. HRMS (EI) m/z: calcd for: $C_{20}H_{23}FNO_3P$: 376.1127, found $[M]^+$: 376.1125.



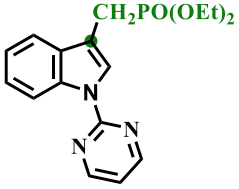
diethyl ((1-benzyl-6-bromo-1*H*-indol-3-yl)methyl)phosphonate (4n) was prepared using 1-benzyl-6-bromo-1*H*-indole and reagent I according to the general procedure as a offwhite solid (61 mg, 70 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.6 Hz, 1H), 7.40 (d, *J* = 1.8 Hz, 1H), 7.31 – 7.23 (m, 3H), 7.21 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.11 (d, *J* = 3.6 Hz, 1H), 7.07 (dd, *J* = 7.5, 2.0 Hz, 2H), 5.21 (s, 2H), 4.13 – 3.79 (m, 4H), 3.24 (d, *J* = 20.3 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.28, 136.96, 128.94, 128.19 (d, *J* = 7.7 Hz), 127.94, 127.17 (d, *J* = 5.9 Hz), 126.85, 122.79, 120.71, 115.81, 112.75, 105.00 (d, *J* = 9.5 Hz), 62.18 (d, *J* = 6.7 Hz), 50.14, 23.85, 22.42, 16.50 (d, *J* = 5.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.63. HRMS (EI) m/z: calcd for: $C_{20}H_{23}BrNO_3P$: 435.7922, found $[M]^{+\cdot}$ 435.7918.



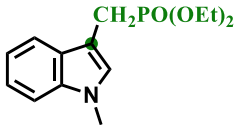
methyl 3-((diethoxyphosphoryl)methyl)-1-ethyl-1*H*-indole-5-carboxylate (4o) was prepared using methyl 1-ethyl-1*H*-indole-5-carboxylate and reagent I according to the general procedure as a yellow oil (52 mg, 74 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 1.6 Hz, 1H), 7.88 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.20 (d, *J* = 3.5 Hz, 1H), 4.12 (q, *J* = 7.3 Hz, 2H), 4.06 – 3.94 (m, 4H), 3.90 (s, 3H), 3.28 (d, *J* = 20.4 Hz, 2H), 1.42 (t, *J* = 7.3 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.25, 138.34, 127.80 (dd, *J* = 13.9, 7.0 Hz), 123.06, 122.39, 121.17, 109.05, 105.72 (d, *J* = 9.1 Hz), 62.14 (d, *J* = 6.6 Hz), 51.87, 41.23, 23.72, 22.29, 16.43 (d, *J* = 5.9 Hz), 15.47. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.63. HRMS (EI) m/z: calcd for: $C_{17}H_{24}NO_5P$: 354.0870, found $[M]^+$: 354.0871.



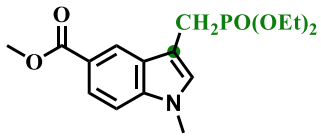
diethyl ((1-phenyl-1*H*-indol-3-yl)methyl)phosphonate (4p) was prepared using 1-phenyl-1*H*-indole and reagent I according to the general procedure as a purple solid (38 mg, 55 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.57 – 7.42 (m, 5H), 7.39 (d, *J* = 3.6 Hz, 1H), 7.33 (dq, *J* = 5.7, 3.0 Hz, 1H), 7.27 – 7.12 (m, 2H), 4.14 – 3.96 (m, 4H), 3.35 (d, *J* = 20.3 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.68, 135.92, 129.69, 129.03 (d), 127.20 (d, *J* = 7.7 Hz), 126.47, 124.31, 122.71, 120.30, 119.41, 110.65, 106.52 (d, *J* = 9.5 Hz), 62.18 (d, *J* = 6.7 Hz), 23.81, 22.38, 16.53 (d, *J* = 5.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.87. HRMS (EI) m/z: calcd for: $C_{19}H_{22}NO_3P$: 344.0950, found $[M]^+$: 344.0949. Spectroscopic data are in accordance with the reported in the literature[15].



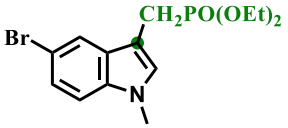
diethyl ((1-(pyrimidin-2-yl)-1*H*-indol-3-yl)methyl)phosphonate (4q) was prepared using 1-(pyrimidin-2-yl)-1*H*-indole and reagent I according to the general procedure as a colourless oil (13 mg, 19 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.77 (d, *J* = 8.3 Hz, 1H), 8.67 (d, *J* = 4.9 Hz, 2H), 8.27 (d, *J* = 4.1 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.26 (t, 1H), 7.01 (t, *J* = 4.7 Hz, 1H), 4.13 – 3.96 (m, 4H), 3.31 (d, *J* = 20.7 Hz, 2H), 1.24 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.18, 157.68, 135.53, 130.99 (d, *J* = 5.8 Hz), 124.96 (d, *J* = 8.6 Hz), 124.04, 122.08, 119.22, 116.33, 116.14, 62.26 (d, *J* = 6.7 Hz), 24.09, 22.66, 16.49 (d, *J* = 5.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.18. HRMS (EI) m/z: calcd for: $C_{17}H_{20}N_3O_3P$: 346.0711, found $[M]^+$: 346.0708.



diethyl ((1-methyl-1*H*-indol-3-yl)methyl)phosphonate (4r) was prepared using 1-methyl-1*H*-indole and reagent I according to the general procedure as a brown oil (40 mg, 72 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.21 (t, 1H), 7.10 (dd, *J* = 10.4, 5.2 Hz, 2H), 4.09 – 3.90 (m, 4H), 3.74 (s, 3H), 3.28 (d, *J* = 20.2 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.85, 128.22 (d, *J* = 7.0 Hz), 128.06 (d, *J* = 6.6 Hz), 121.76, 119.09 (d, *J* = 7.9 Hz), 109.29, 62.09 (d, *J* = 6.7 Hz), 32.83, 23.72, 22.29, 16.49 (d, *J* = 5.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.31. HRMS (EI) m/z: calcd for: $C_{14}H_{20}NO_3P$: 282.0241, found $[M]^+$: 282.0240. Spectroscopic data are in accordance with the reported in the literature[15].



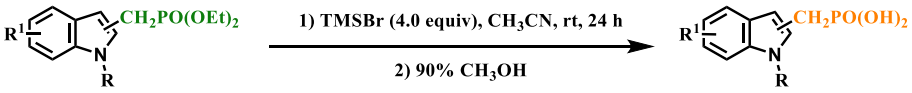
methyl 3-((diethoxyphosphoryl)methyl)-1-methyl-1*H*-indole-5-carboxylate (4s) was prepared using methyl 1-methyl-1*H*-indole-5-carboxylate and reagent I according to the general procedure as a brown oil (40 mg, 58 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 1.7 Hz, 1H), 7.89 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.25 (d, *J* = 8.7 Hz, 1H), 7.13 (d, *J* = 3.6 Hz, 1H), 4.08 – 3.94 (m, 4H), 3.90 (s, 3H), 3.74 (s, 3H), 3.27 (d, *J* = 20.3 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.25, 139.27, 129.62 (d, *J* = 7.5 Hz), 127.58 (d, *J* = 6.5 Hz), 123.18, 122.27, 121.21, 109.03, 105.60 (d, *J* = 9.0 Hz), 62.15 (d, *J* = 6.7 Hz), 51.87, 33.04, 29.76, 23.66, 22.22, 16.43 (d, *J* = 5.8 Hz). δ 27.65. HRMS (EI) m/z: calcd for: $C_{16}H_{22}NO_5P$: 3340.0601, found $[M]^+$: 340.0605.



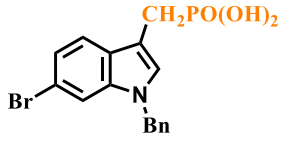
diethyl ((5-bromo-1-methyl-1*H*-indol-3-yl)methyl)phosphonate (4t) was prepared using 5-bromo-1-methyl-1*H*-indole and reagent I according to the general procedure as a colourless oil (26 mg, 36 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 2.1 Hz, 1H), 7.26 (dd, *J* = 9.2, 1.6 Hz, 1H), 7.12 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.06 (d, *J* = 3.4 Hz, 1H), 4.01-3.90 (m, 4H), 3.71 (s, 3H), 3.19 (d, *J* = 20.1 Hz, 2H), 1.26 – 1.18 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.55, 129.63 (d, *J* = 5.8 Hz), 129.41 (d, *J* = 7.6 Hz), 124.60, 121.84, 112.61, 110.84, 103.42 (d, *J* = 9.2 Hz), 62.15 (d, *J* = 6.9 Hz), 33.02, 29.77, 23.74, 22.31, 16.48 (d, *J* = 5.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 27.72. HRMS (EI) m/z: calcd for: $C_{14}H_{19}BrNO_3P$: 360.9200, found $[M]^+$: 340.9201.

7. Functional Group Transformation.

7.1 Hydrolysis of products 3 or 4[16].

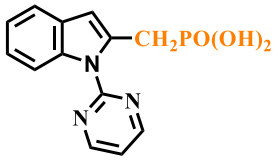


Trimethylsilylbromide (104 μL, 0.8 mmol, 4.0 equiv) was added dropwise to the phosphonate ester 3 or 4 (0.2 mmol, 1.0 equiv.) in CH_3CN (2.0 mL) and the mixture stirred overnight at room temperature under N_2. At the end of the reaction, removed the large excesses of bromotrimethylsilane and ACN by evaporation under low pressure. Added a mixture of methanol and water (9: 1, 10 mL) to the residue. Removed the solvents again and dry the solid product under vacuum to obtain the phosphonic acid.



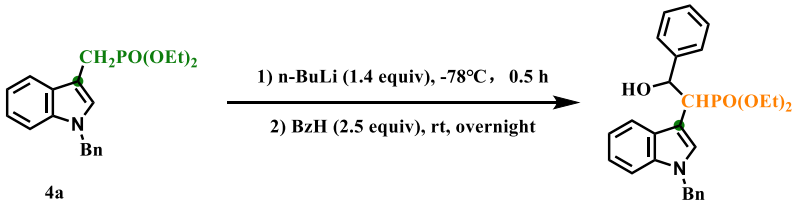
((1-benzyl-6-bromo-1*H*-indol-3-yl)methyl)phosphonic acid (5n) was prepared using diethyl ((1-benzyl-6-bromo-1*H*-indol-3-yl)methyl)phosphonate according to the general procedure as a brown solid (59 mg, 68 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 3.2 Hz, 1H), 7.34 – 7.15 (m, 5H), 7.12 (d, *J* = 8.4 Hz, 1H), 5.39 (s, 2H), 3.04 (d, *J* = 20.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.56, 137.14, 129.18, 129.11, 127.95, 127.72 (d, *J* = 5.8 Hz), 127.59, 121.93, 114.65, 113.07, 107.29 (d, *J* = 8.7 Hz), 49.42, 25.92, 24.54. ^{31}P NMR (162 MHz, DMSO-d_6) δ 22.93. HRMS (EI) m/z: calcd for: $C_{16}H_{15}BrNO_3P$: 380.9104, found $[M]^+$:

380.9107.



((1-(pyrimidin-2-yl)-1*H*-indol-2-yl)methyl)phosphonic acid (5h) was prepared using diethyl ((1-benzyl-6-bromo-1*H*-indol-3-yl)methyl)phosphonate according to the general procedure as a brown solid (48 mg, 83 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.94 (s, 2H), 8.88 (s, 2H), 8.04 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 6.7 Hz, 1H), 7.38 (s, 1H), 7.14 – 7.09 (m, 2H), 6.63 (s, 1H), 3.79 (d, J = 21.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.26, 157.85, 136.99, 133.53 (d, J = 9.3 Hz), 128.88, 122.80, 120.20, 118.74, 113.80, 107.79 (d, J = 8.0 Hz), 29.60, 28.27. ^{31}P NMR (162 MHz, DMSO-d_6) δ 20.66. HRMS (EI) m/z: calcd for: $C_{13}H_{12}N_3O_3P$: 289.9630, found $[M]^+$: 289.9629.

7.2. Synthesis of diethyl (1-(1-benzyl-1*H*-indol-3-yl)-2-hydroxy-2-phenylethyl)phosphonate[17].



A solution of n-BuLi (2.5 M, 1.4 equiv.) in THF was added dropwise into a Schlenk tube equipped with a magnetic stir bar containing a solution of 4a (71.5 mg, 0.2 mmol) in dry THF (2 mL) at -78˚C under N_2. The solution was stirred at this temperature for 30 min until a bright yellow color appeared. Benzaldehyde (51 µL, 0.25 mmol) was then added and the cooling bath was removed. The reaction was continued at room temperature with stirring overnight. Then the solution was acidified by 2 M HCl, stirred for 30 minutes and extracted with CH_2Cl_2 (3 x 25 mL). The resulting organic phase was then dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified via flash column chromatography on silica gel (Petroleum ether : Ethyl Acetate = 3:1) to get 6a as a colourless oil (80 mg, 87 %). **diethyl (1-(1-benzyl-1*H*-indol-3-yl)-2-hydroxy-2-phenylethyl)phosphonate (6a)** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, J = 2.8 Hz, 1H), 7.28 – 7.14 (m, 8H), 7.13 – 7.03 (m, 4H), 6.99 (dd, J = 7.1, 2.5 Hz, 2H), 6.94 (t, J = 7.4 Hz, 1H), 5.55 (dd, J = 7.7, 2.7 Hz, 1H), 5.30 (s, 2H), 4.37 – 4.25 (m, 1H), 4.24 – 4.05 (m, 2H), 3.85 – 3.68 (m, 2H), 3.42 – 3.27 (m, 1H), 1.36 (t, J = 7.1 Hz, 3H), 0.82 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.40 (d, J = 14.6 Hz), 137.73, 135.80, 129.33 (d, J = 5.8 Hz), 129.05 (d, J = 7.2 Hz), 128.76, 127.79, 127.64, 127.17, 126.64, 126.13, 121.75, 119.35, 118.69, 109.63, 104.07 (d, J = 5.3 Hz), 72.06, 63.70 (d, J = 6.8 Hz), 62.02 (d, J = 7.4 Hz), 50.13, 43.18, 41.81, 16.55 (d, J = 5.8 Hz), 16.16 (d, J = 5.7 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.42. HRMS (EI) m/z: calcd for: $C_{27}H_{30}NO_4P$: 464.2164, found $[M]^+$: 464.2161.

8. Mechanistic Investigations.

8.1 UV-vis absorption spectra.

UV-vis absorption spectra UV-visible absorption spectra were recorded on an UV-2700 spectrophotometer, equipped with a temperature control unit at 25 °C. The samples were measured in Starna Fluorometer Microquartz cuvettes (volume: 1.8 ml, path length: 10 mm) equipped with a PTFE-stopper. The spectra were aquired from 210 to 530 nm using 1.0 nm steps. All measurements were performed in MeCN at the following concentrations: N-Boc indole (3k) and reagent I (1/100 of the reaction concentration); fac-Ir(ppy)$_3$ (0.1 mM, 1/10 of the reaction concentration).

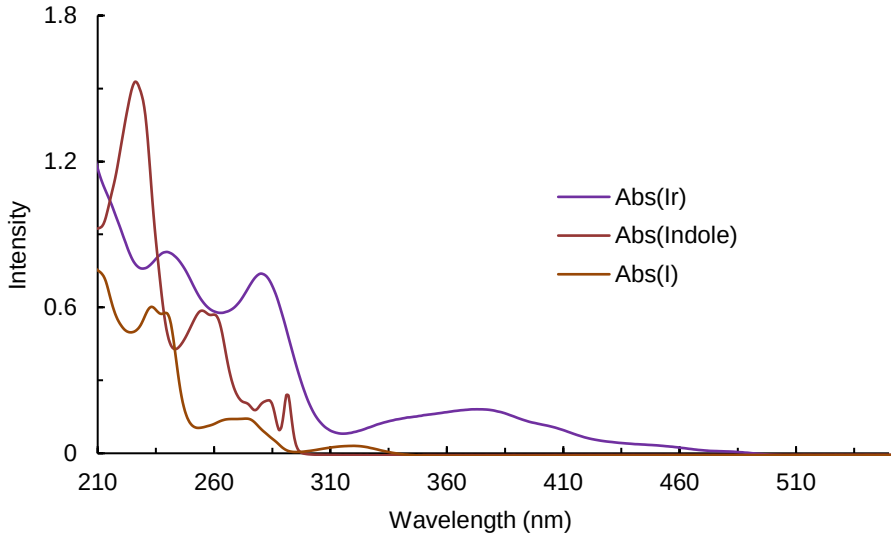
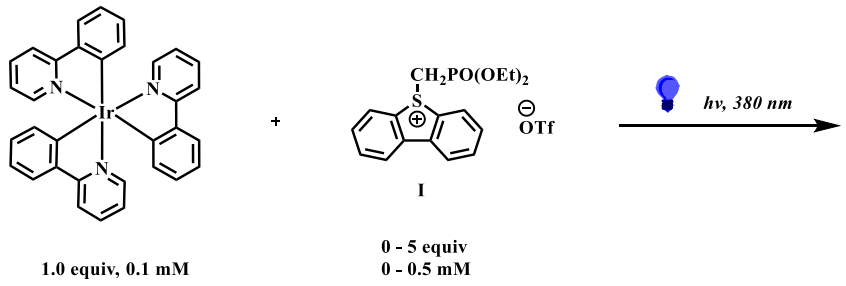


Figure S1. UV-vis absorption spectrum.

8.2 Stern-Volmer luminescence quenching experiments.

Fluorescence quenching studies were performed using a Hitachi F-4600 spectro fluorometer. In each experiment, fac-Ir(ppy)$_3$ and various concentrations of reagent I were combined in MeCN in Starna Fluorometer Microquartz cuvettes (volume: 1.8 ml, path length: 10 mm) equipped with a PTFE-stopper. The emission quenching of the fac-Ir(ppy)$_3$ was achieved using a concentration of 0.1 mM under excitation at 380 nm. The emission intensity was observed at 520 nm. Plots were constructed according to the Stern-Volmer equation $I_0/I = 1 + kq\tau 0[Q]$.



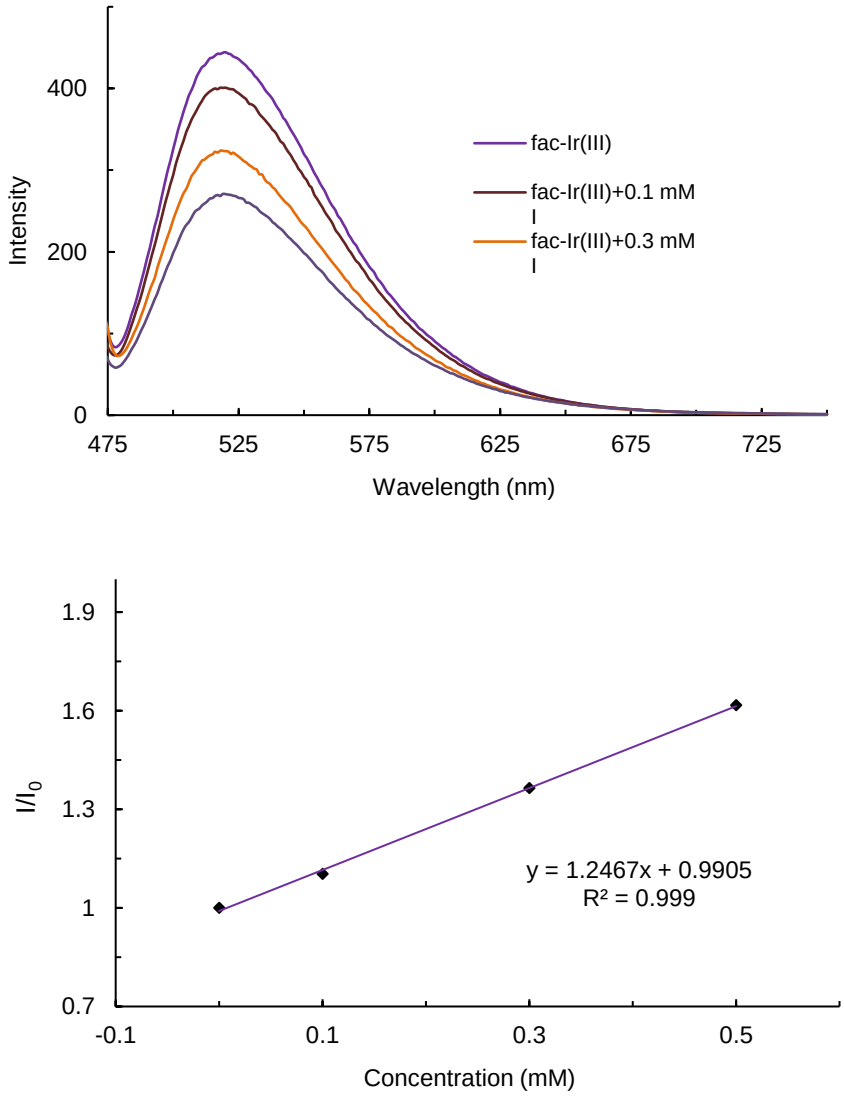
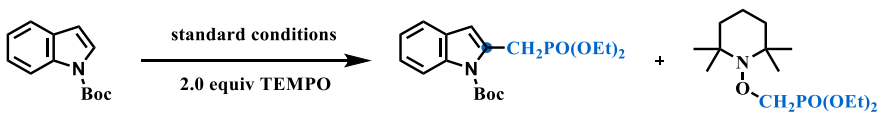


Figure S2. Stern-Volmer luminescence quenching experiments of reagent I.

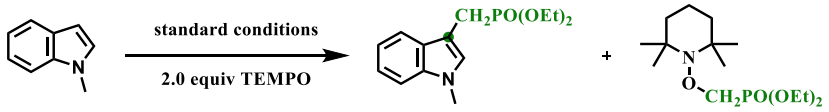
8.3 Radical trap experiment.



2k **not detected** **[M+H]$^+$308.1959**

The mixture of indole 3k (0.2 mmol, 1.0 equiv.), reagent I (96.8 mg, 0.2 mmol, 1 equiv.), NaOAc (16.4 mg, 0.4 mmol, 2.0 equiv.), the photocatalyst fac-Ir(ppy)$_3$, (2 mg, 3 mol%) and 2, 2, 6, 6-tetramethylpiperidinyl-1-oxide (TEMPO, 62.4 mg, 0.40 mmol, 2.0 equiv.) in HOAc (2.0 mL) was stirred under irradiation of blue LEDs overnight at room temperature. Then another portion sulfonium salt (96.8 mg, 0.2 mmol, 1.0 equiv.) was added to the reaction solution and the mixture was stirred for 12-24 h under blue light. The progress of the reaction was monitored by TLC. After completion of the reaction, 10 μL of n-dodecane was added as an internal standard and the reaction

mixture was diluted with EtOAc. The crude reaction mixture was diluted with EtOAc and filtered through a plug of silica then subjected to LC-HRMS analysis. HRMS (EI) m/z: calcd for: $C_{14}H_{30}NO_4P$: 308.1985, found $[M]^+$: 308.1959**.**



2'r **4r, 54%** **0%**

A mixture of indole 2'r (0.2 mmol, 1.0 equiv.), reagent I (106.5 mg, 0.22 mmol, 1.1 equiv.), $Cu(OTf)_2$ (7.2 mg, 10 mol %) and TEMPO (62.4 mg, 0.40 mmol, 2.0 equiv.) in DCM (2.0 mL) was stirred at 60 ºC overnight. The course of the reaction was monitored with thin layer chromatography (TLC). The reaction mixture was then cooled to the room temperature and 10 µL of *n*-dodecane was added as an internal standard and the reaction mixture was diluted with EtOAc. 4r was obtained in 54 % yield.

8.4 *In situ* ^{1}H-NMR experiments.

All experiments were carried out in NMR tubes. Two portions of the reagents I (24 mg, 0.05 mmol) in CD_2Cl_2 were loaded into two NMR tubes separately and the ^{1}H-NMR spectras were collected. Subsequently, $Cu(OTf)_2$ (2 mg, 10 mol%) and $ZnCl_2$ (0.6 mg, 10 mol%) were added into the above NMR tubes separately. Then the ^{1}H-NMR spectras were collected.

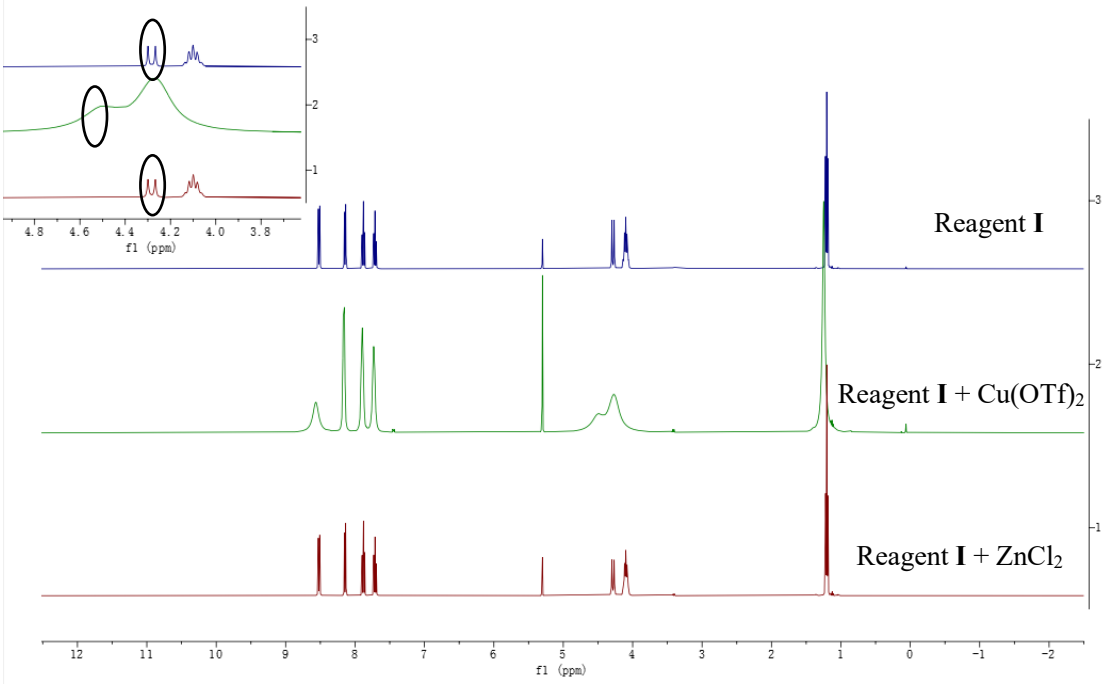


Figure S3. *In situ* ^{1}H-NMR experiments.

9. X-Ray Crystal Structures.

Crystal Structure of $[C_{17}H_{20}O_3PS][CF_3SO_3]$

The low temperature (170±2°K) single-crystal X-ray experiments were performed on a Rigaku diffractometer with Cu K_α radiation. Unit cell was obtained and refined by 13311 reflections with $3.8° < \theta < 66.4°$. No decay was observed in data collection. Raw intensities were corrected for Lorentz and polarization effects, and for absorption by empirical method. Direct phase determination yielded the positions of all non-hydrogen atoms. All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms of carbons were generated geometrically with C-H bonds of 0.95-0.99 according to criteria described in the SHELXTL manual (Bruker, 1997). They were included in the refinement with $U_{iso}(H) = 1.2U_{eq}$ or $1.5U_{eq}$ (for methyl C) of their parent atoms. The final full-matric least-square refinement on F^2 converged with $R1 = 0.0613$ and $wR2 = 0.1643$ for 3476 observed reflections [$I \geq 2\sigma(I)$]. The final difference electron density map shows no features. Details of crystal parameters, data collection and structure refinement are given in Table 1.

Data collection was controlled by CrysAlisPro, Agilent Technologies, Version 1.171.36.32 (Oxford, 2013). Computations were performed using the SHELXTL NT ver. 5.10 program package (Bruker, 1997) on an IBM PC 586 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1989). Crystal drawings were produced with XP (Bruker, 1997).

References

Bruker. (1997) SHELXTL. Structure Determination Programs, Version 5.10, Bruker AXS Inc.,6300 Enterprise Lane, Madison, WI 53719-1173, USA.

International Tables for X-ray Crystallography: (1989) Vol. C (Kluwer Academic Publishers, Dordrecht) Tables 4.2.6.8 and 6.1.1.4.

Oxford. (2013) CrysAlisPro, Agilent Technologies, Version 1.171.36.32, Oxford Diffraction Ltd., 68 Milton Park, Abingdon, Oxfordshire, OX14 4RX, UK.

Table S2. Details of Data Collection, Processing and Structure Refinement

Sample code	**Reagent I**
Molecular formula	$[C_{17}H_{20}O_3PS][CF_3SO_3]$
Molecular weight	484.43
Color and habit	colorless needle
Crystal size	0.05 × 0.20 × 0.20 mm
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell parameters	a = 11.3092(2) α = 90.00° b = 10.0133(2) β = 90.7760(10)° c = 18.3326(3) γ = 90.00° V = 2075.84(6) $Å^3$ Z = 4 $F(000)$ = 1000
Density (calcd)	1.550 g/cm^3
Diffractometer	XtaLAB AFC11 (RINC): quarter-chi single
Radiation	Cu K_α, λ = 1.54178
Temperature	170±2K
Scan type	ω-scan
Data collection range	$-13 < h < 13$, $-10 < k < 11$, $-21 < l < 21$; θ_{max} = 66.6°
Reflections measured	Total: 16158 Unique (n): 3536 Observed [I ≥ 2σ(I)]: 3476
Absorption coefficient	3.617 mm^{-1}
Minimum and maximum transmission	0.064, 1.000
No. of variables, p	273
Weighting scheme	$w = \frac{1}{\sigma^2(F_o^2) + (0.0983P)^2 + 3.4060P}$ $P = (F_o^2 + 2F_c^2)/3$
$R1 = \frac{\Sigma\|\|F_o\|-\|F_c\|\|}{\Sigma\|F_o\|}$ (for all reflections)	0.0618 0.0613 (for observed data)
$wR2 = \sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{\Sigma w(F_o^2)^2}}$ (for all reflections)	0.1647 0.1643 (for observed data)
Goof = S = $\sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{n - p}}$	1.051
Largest and mean Δ/σ	0.000, 0.000
Residual extrema in final difference map	-0.504 to 0.658 e^{-3}

Table S3. Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

Atoms	*x*	*y*	*z*	$U_{eq.}$
S(1)	0.10736(6)	-0.00005(6)	0.13675(3)	0.0229(2)
S(2)	0.62833(9)	0.63470(10)	0.16870(5)	0.0491(3)
P(1)	0.29739(6)	0.20403(7)	0.19818(4)	0.0220(2)
F(1)	0.5570(3)	0.4096(3)	0.2226(2)	0.0854(9)
F(2)	0.7149(4)	0.3944(4)	0.1653(3)	0.140(2)
F(3)	0.7129(4)	0.4812(5)	0.2698(2)	0.1307(17)
O(1)	0.3091(2)	0.2895(2)	0.26271(12)	0.0348(5)
O(2)	0.26454(17)	0.2722(2)	0.12451(11)	0.0290(5)
O(3)	0.40960(18)	0.1188(2)	0.18078(11)	0.0308(5)
O(4)	0.5623(7)	0.6087(5)	0.1055(3)	0.155(3)
O(5)	0.5645(4)	0.7013(4)	0.2235(2)	0.0934(14)
O(6)	0.7422(4)	0.6861(4)	0.1571(3)	0.1186(19)
C(1)	0.0487(2)	0.1253(3)	0.07807(15)	0.0243(6)
C(2)	-0.0479(3)	0.2053(3)	0.09371(17)	0.0300(6)
C(3)	-0.0827(3)	0.2960(3)	0.04057(18)	0.0361(7)
C(4)	-0.0242(3)	0.3029(3)	-0.02557(18)	0.0373(7)
C(5)	0.0717(3)	0.2200(3)	-0.04052(16)	0.0307(7)
C(6)	0.1089(2)	0.1296(3)	0.01226(15)	0.0247(6)
C(7)	0.2080(2)	0.0352(3)	0.01025(15)	0.0250(6)
C(8)	0.2210(2)	-0.0399(3)	0.07386(14)	0.0238(6)
C(9)	0.3065(3)	-0.1368(3)	0.08432(16)	0.0291(6)
C(10)	0.3843(3)	-0.1577(3)	0.02755(18)	0.0354(7)
C(11)	0.3745(3)	-0.0833(3)	-0.03645(17)	0.0360(7)
C(12)	0.2877(3)	0.0123(3)	-0.04608(16)	0.0311(7)
C(13)	0.1745(2)	0.0923(3)	0.21191(14)	0.0238(6)
C(14)	0.3483(3)	0.3429(4)	0.0777(2)	0.0394(8)
C(15)	0.2968(5)	0.4715(4)	0.0549(3)	0.0634(12)
C(16)	0.5015(3)	0.0918(5)	0.2369(2)	0.0532(10)
C(17)	0.4661(5)	-0.0128(4)	0.2885(2)	0.0604(11)
C(18)	0.6550(3)	0.4715(5)	0.2055(2)	0.0524(10)

*$U_{eq.}$ defined as one third of the trace of the orthogonalized **U** tensor.

Table S4. Bond lengths (Å) and bond angles (°)

S(1)-C(1)	1.776(3)	C(1)-C(2)	1.387(4)
S(1)-C(8)	1.784(3)	C(1)-C(6)	1.394(4)
S(1)-C(13)	1.817(3)	C(2)-C(3)	1.385(4)
S(2)-O(4)	1.394(5)	C(3)-C(4)	1.391(5)
S(2)-O(6)	1.406(4)	C(4)-C(5)	1.396(5)
S(2)-O(5)	1.412(3)	C(5)-C(6)	1.386(4)
S(2)-C(18)	1.792(4)	C(6)-C(7)	1.467(4)
P(1)-O(1)	1.465(2)	C(7)-C(8)	1.394(4)
P(1)-O(2)	1.554(2)	C(7)-C(12)	1.398(4)
P(1)-O(3)	1.566(2)	C(8)-C(9)	1.381(4)
P(1)-C(13)	1.804(3)	C(9)-C(10)	1.388(4)
F(1)-C(18)	1.311(5)	C(10)-C(11)	1.393(5)
F(2)-C(18)	1.270(5)	C(11)-C(12)	1.381(5)
F(3)-C(18)	1.343(5)	C(14)-C(15)	1.472(5)
O(2)-C(14)	1.469(4)	C(16)-C(17)	1.470(6)
O(3)-C(16)	1.478(4)		

C(1)-S(1)-C(8)	91.90(13)	C(6)-C(5)-C(4)	118.8(3)
C(1)-S(1)-C(13)	104.40(13)	C(5)-C(6)-C(1)	118.5(3)
C(8)-S(1)-C(13)	107.84(13)	C(5)-C(6)-C(7)	128.9(3)
O(4)-S(2)-O(6)	115.1(4)	C(1)-C(6)-C(7)	112.6(2)
O(4)-S(2)-O(5)	114.0(4)	C(8)-C(7)-C(12)	117.9(3)
O(6)-S(2)-O(5)	114.4(3)	C(8)-C(7)-C(6)	113.5(2)
O(4)-S(2)-C(18)	103.2(3)	C(12)-C(7)-C(6)	128.6(3)
O(6)-S(2)-C(18)	104.0(2)	C(9)-C(8)-C(7)	124.1(3)
O(5)-S(2)-C(18)	104.3(2)	C(9)-C(8)-S(1)	125.2(2)
O(1)-P(1)-O(2)	117.61(13)	C(7)-C(8)-S(1)	110.6(2)
O(1)-P(1)-O(3)	114.72(13)	C(8)-C(9)-C(10)	116.9(3)
O(2)-P(1)-O(3)	104.32(11)	C(9)-C(10)-C(11)	120.4(3)
O(1)-P(1)-C(13)	108.13(13)	C(12)-C(11)-C(10)	121.8(3)
O(2)-P(1)-C(13)	102.60(12)	C(11)-C(12)-C(7)	118.9(3)
O(3)-P(1)-C(13)	108.55(13)	P(1)-C(13)-S(1)	121.63(15)
C(14)-O(2)-P(1)	124.85(19)	O(2)-C(14)-C(15)	109.4(3)
C(16)-O(3)-P(1)	121.5(2)	C(17)-C(16)-O(3)	112.5(3)
C(2)-C(1)-C(6)	123.8(3)	F(2)-C(18)-F(1)	108.1(4)
C(2)-C(1)-S(1)	124.9(2)	F(2)-C(18)-F(3)	107.2(5)
C(6)-C(1)-S(1)	111.3(2)	F(1)-C(18)-F(3)	103.2(4)
C(3)-C(2)-C(1)	116.8(3)	F(2)-C(18)-S(2)	115.1(3)
C(2)-C(3)-C(4)	120.8(3)	F(1)-C(18)-S(2)	112.5(3)
C(3)-C(4)-C(5)	121.4(3)	F(3)-C(18)-S(2)	110.0(4)

Table S5. Anisotropic thermal parameters* (Å^2)

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	0.0294(4)	0.0201(4)	0.0193(4)	-0.0006(2)	0.0028(3)	-0.0031(2)
S(2)	0.0555(6)	0.0504(6)	0.0417(5)	0.0037(4)	0.0133(4)	-0.0018(4)
P(1)	0.0268(4)	0.0183(4)	0.0209(4)	-0.0007(2)	-0.0003(3)	0.0006(2)
F(1)	0.0715(17)	0.0577(16)	0.128(3)	0.0095(17)	0.0318(17)	-0.0161(14)
F(2)	0.171(4)	0.082(2)	0.170(4)	0.028(3)	0.117(3)	0.060(3)
F(3)	0.147(4)	0.143(4)	0.100(3)	0.049(3)	-0.066(3)	-0.021(3)
O(1)	0.0414(12)	0.0304(12)	0.0324(11)	-0.0119(9)	0.0002(9)	-0.0047(9)
O(2)	0.0276(10)	0.0286(11)	0.0307(11)	0.0106(8)	-0.0020(8)	-0.0041(8)
O(3)	0.0311(11)	0.0313(11)	0.0299(11)	0.0026(8)	0.0032(8)	0.0085(8)
O(4)	0.252(7)	0.102(3)	0.106(4)	0.013(3)	-0.108(4)	0.026(4)
O(5)	0.107(3)	0.064(2)	0.111(3)	-0.018(2)	0.069(2)	-0.014(2)
O(6)	0.092(3)	0.087(3)	0.180(5)	0.030(3)	0.085(3)	-0.015(2)
C(1)	0.0277(14)	0.0232(14)	0.0218(13)	0.0006(10)	-0.0016(11)	-0.0032(11)
C(2)	0.0303(15)	0.0299(16)	0.0299(15)	-0.0034(12)	-0.0003(12)	-0.0006(12)
C(3)	0.0314(15)	0.0393(18)	0.0373(17)	-0.0017(14)	-0.0038(13)	0.0058(13)
C(4)	0.0413(17)	0.0363(18)	0.0342(17)	0.0081(13)	-0.0090(14)	0.0016(14)
C(5)	0.0350(15)	0.0330(16)	0.0240(14)	0.0034(12)	-0.0031(12)	-0.0041(12)
C(6)	0.0279(14)	0.0246(14)	0.0215(13)	-0.0028(11)	-0.0012(11)	-0.0069(11)
C(7)	0.0299(14)	0.0238(14)	0.0213(13)	-0.0031(11)	-0.0002(11)	-0.0056(11)
C(8)	0.0301(14)	0.0212(13)	0.0201(13)	-0.0042(10)	0.0052(10)	-0.0033(11)
C(9)	0.0391(16)	0.0219(14)	0.0264(14)	-0.0007(11)	0.0025(12)	-0.0006(12)
C(10)	0.0371(16)	0.0304(16)	0.0387(17)	-0.0046(13)	0.0054(13)	0.0036(13)
C(11)	0.0379(16)	0.0409(18)	0.0294(15)	-0.0058(13)	0.0118(13)	0.0000(14)
C(12)	0.0372(16)	0.0355(17)	0.0207(14)	-0.0008(11)	0.0046(12)	-0.0061(12)
C(13)	0.0338(14)	0.0207(13)	0.0170(12)	-0.0014(10)	0.0026(10)	-0.0020(11)
C(14)	0.0354(16)	0.0397(18)	0.0433(18)	0.0167(15)	0.0063(14)	-0.0019(14)
C(15)	0.081(3)	0.039(2)	0.070(3)	0.026(2)	0.015(2)	0.003(2)
C(16)	0.0355(17)	0.068(3)	0.057(2)	0.026(2)	-0.0013(16)	0.0084(17)
C(17)	0.081(3)	0.051(2)	0.049(2)	0.0149(18)	-0.011(2)	0.002(2)
C(18)	0.0367(18)	0.062(2)	0.059(2)	0.009(2)	0.0056(17)	0.0008(17)

*The exponent takes the form: $-2\pi^2\Sigma\Sigma U_{ij}h_ih_j\mathbf{a}_i^*\mathbf{a}_j^*$

Table S6. Coordinates and isotropic temperature factors* (Å^2) for H atoms

Atoms	*x*	*y*	*z*	$U_{eq.}$
H(2)	-0.0881	0.1982	0.1387	0.036
H(3)	-0.1473	0.3541	0.0494	0.043
H(4)	-0.0500	0.3655	-0.0613	0.045
H(5)	0.1107	0.2254	-0.0860	0.037
H(9)	0.3118	-0.1867	0.1283	0.035
H(10)	0.4447	-0.2232	0.0324	0.042
H(11)	0.4290	-0.0988	-0.0745	0.043
H(12)	0.2821	0.0616	-0.0902	0.037
H(13A)	0.1109	0.1454	0.2345	0.029
H(13B)	0.2005	0.0257	0.2487	0.029
H(14A)	0.3655	0.2880	0.0342	0.047
H(14B)	0.4234	0.3583	0.1047	0.047
H(15A)	0.2185	0.4564	0.0328	0.095
H(15B)	0.3483	0.5141	0.0191	0.095
H(15C)	0.2892	0.5298	0.0975	0.095
H(16A)	0.5752	0.0640	0.2127	0.064
H(16B)	0.5184	0.1751	0.2642	0.064
H(17A)	0.3944	0.0153	0.3137	0.091
H(17B)	0.5299	-0.0274	0.3243	0.091
H(17C)	0.4504	-0.0959	0.2619	0.091

*The exponent takes the form: $-8\pi^2 U\sin^2\theta/\lambda^2$

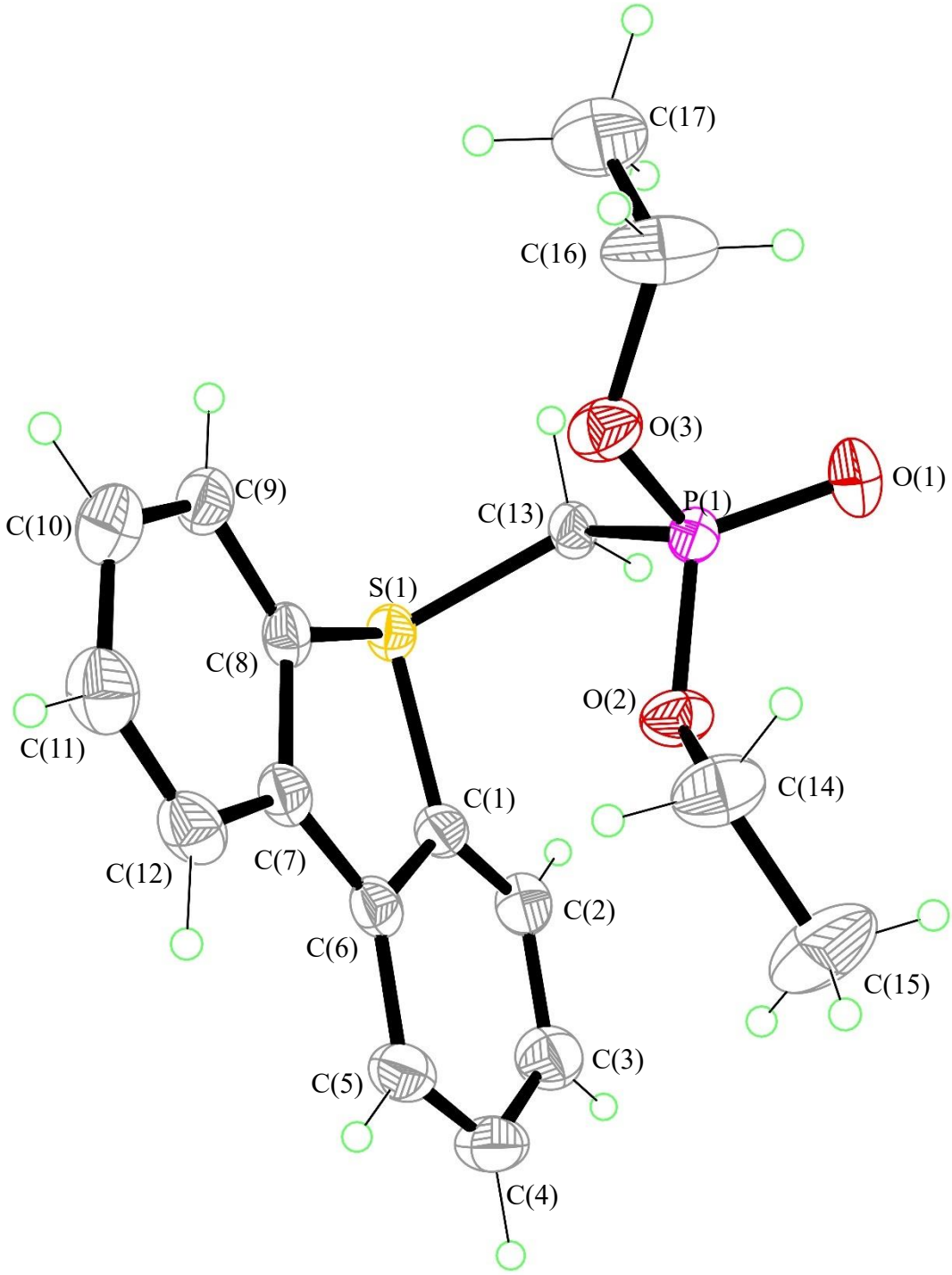


Figure S4 ORTEP drawing of $[C_{16}H_{20}O_3PS]^+$ with 50% probability ellipsoids, showing the atomic numbering scheme.

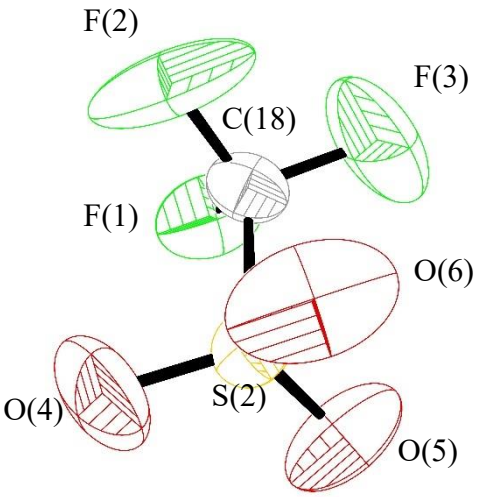


Figure S5 ORTEP drawing of $[CF_3SO_3]^-$ with 50% probability ellipsoids, showing the atomic numbering scheme.

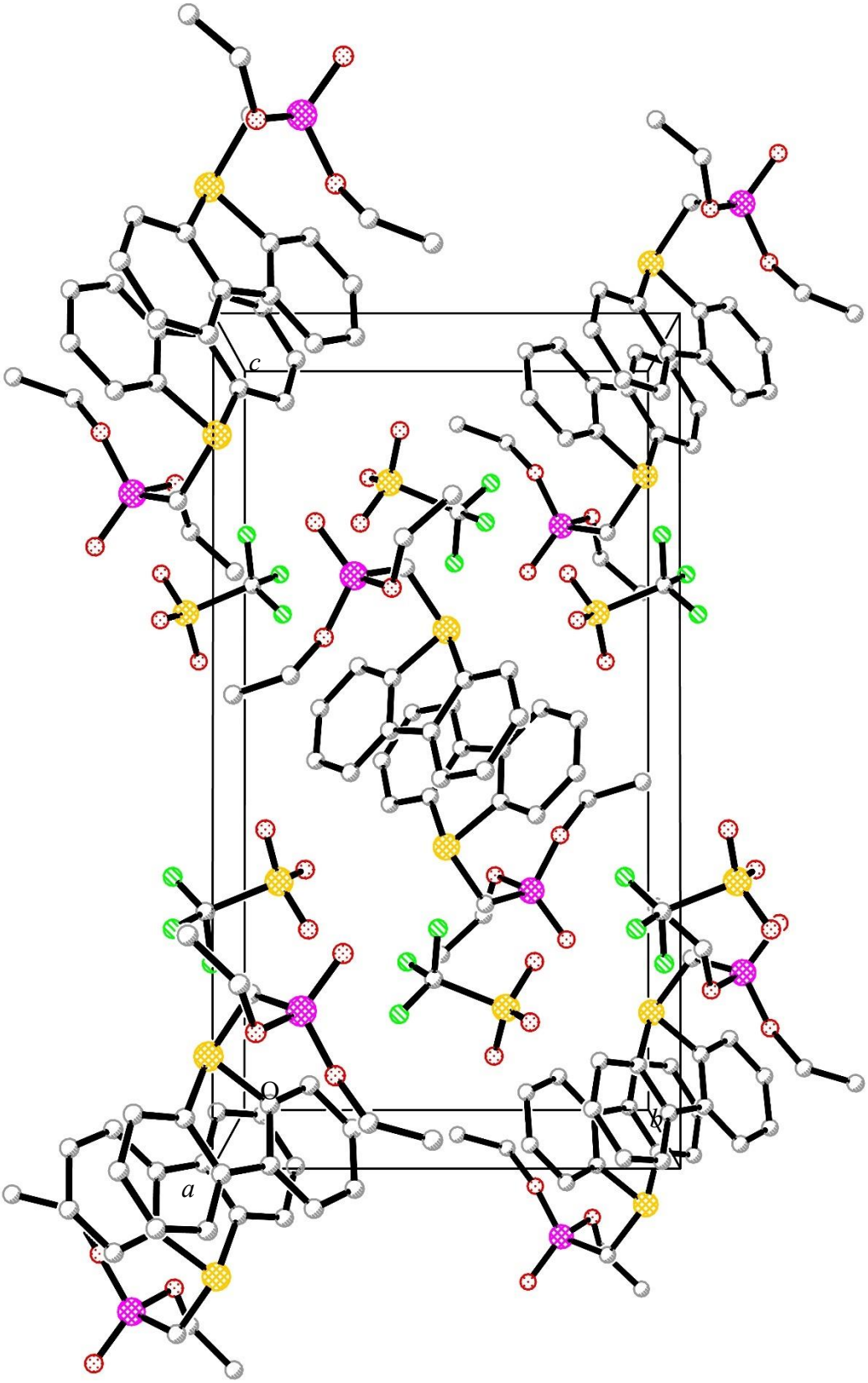


Figure S6 A packing view along the *a* direction

Crystal Structure of $C_{20}H_{23}BrNO_3P$

The low temperature (100±2°K) single-crystal X-ray experiments were performed on a Rigaku diffractometer with Cu K_α radiation. Unit cell was obtained and refined by 14895 reflections with $4.1° < \theta < 73.8°$. No decay was observed in data collection. Raw intensities were corrected for Lorentz and polarization effects, and for absorption by empirical method. Direct phase determination yielded the positions of all non-hydrogen atoms. All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms of carbons were generated geometrically with C-H bonds of 0.95-0.99 according to criteria described in the SHELXTL manual (Bruker, 1997). They were included in the refinement with $U_{iso}(H) = 1.2U_{eq}$ or $1.5U_{eq}$ (for methyl C) of their parent atoms. The final full-matric least-square refinement on F^2 converged with $R1 = 0.0339$ and $wR2 = 0.0914$ for 3696 observed reflections [$I \geq 2\sigma(I)$]. The final difference electron density map shows no features. Details of crystal parameters, data collection and structure refinement are given in Table 1.

Data collection was controlled by CrysAlisPro, Agilent Technologies, Version 1.171.36.32 (Oxford, 2013). Computations were performed using the SHELXTL NT ver. 5.10 program package (Bruker, 1997) on an IBM PC 586 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1989). Crystal drawings were produced with XP (Bruker, 1997).

References

Bruker. (1997) SHELXTL. Structure Determination Programs, Version 5.10, Bruker AXS Inc.,6300 Enterprise Lane, Madison, WI 53719-1173, USA.

International Tables for X-ray Crystallography: (1989) Vol. C (Kluwer Academic Publishers, Dordrecht) Tables 4.2.6.8 and 6.1.1.4.

Oxford. (2013) CrysAlisPro, Agilent Technologies, Version 1.171.36.32, Oxford Diffraction Ltd., 68 Milton Park, Abingdon, Oxfordshire, OX14 4RX, UK.

Table S7. Details of Data Collection, Processing and Structure Refinement

Sample code	**4n**
Molecular formula	$C_{20}H_{23}BrNO_3P$
Molecular weight	436.27
Color and habit	colorless plate
Crystal size	0.03 × 0.20 × 0.30 mm
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell parameters	a = 9.23480(10) α = 108.8050(10)° b = 10.7943(2) β = 95.4870(10)° c = 11.6518(2) γ = 113.088(2)° V = 987.00(3) ^{3} Z = 2 F(000) = 448
Density (calcd)	1.481 g/cm^3
Diffractometer	ROD, Synergy Custom system, HyPix-Arc 150
Radiation	Cu K$_\alpha$, λ = 1.54178
Temperature	100±2K
Scan type	ω-scan
Data collection range	-11 < h < 11, -13 < k < 13, -13 < l < 14; θ_{max} = 73.9°
Reflections measured	Total: 17978 Unique (n): 3776 Observed [I ≥ 2σ(I)]: 3696
Absorption coefficient	3.799 mm^{-1}
Minimum and maximum transmission	0.571, 1.000
No. of variables, p	237
Weighting scheme	$w = \frac{1}{\sigma^2(F_o^2) + (0.0499P)^2 + 0.8846P}$ $P = (F_o^2 + 2F_c^2)/3$
$R1 = \frac{\Sigma\|\|F_o\|-\|F_c\|\|}{\Sigma\|F_o\|}$ (for all reflections)	0.0343 0.0339 (for observed data)
$wR2 = \sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{\Sigma w(F_o^2)^2}}$ (for all reflections)	0.0918 0.0914 (for observed data)
Goof = S = $\sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{n - p}}$	1.070
Largest and mean Δ/σ	0.000, 0.000
Residual extrema in final difference map	-0.778 to 0.544 e^{-3}

Table S8. Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

Atoms	*x*	*y*	*z*	$U_{eq.}$
Br(1)	-0.06235(3)	0.03115(2)	0.20883(2)	0.02766(10)
P(1)	0.86751(7)	0.46121(6)	0.25932(5)	0.02057(13)
O(1)	0.72984(19)	0.43877(18)	0.16717(14)	0.0263(3)
O(2)	1.00922(19)	0.44041(18)	0.20145(14)	0.0262(3)
O(3)	0.96259(19)	0.61879(16)	0.36789(14)	0.0236(3)
N(1)	0.5211(2)	0.37227(19)	0.53589(16)	0.0199(4)
C(1)	0.6771(3)	0.4042(2)	0.5226(2)	0.0207(4)
C(2)	0.6736(3)	0.3403(2)	0.3992(2)	0.0207(4)
C(3)	0.5056(3)	0.2631(2)	0.3315(2)	0.0197(4)
C(4)	0.4243(3)	0.1785(2)	0.2042(2)	0.0213(4)
C(5)	0.2565(3)	0.1129(2)	0.1691(2)	0.0241(4)
C(6)	0.1694(3)	0.1333(2)	0.2604(2)	0.0234(4)
C(7)	0.2437(3)	0.2194(2)	0.3862(2)	0.0206(4)
C(8)	0.4138(3)	0.2834(2)	0.41995(19)	0.0199(4)
C(9)	0.8162(3)	0.3451(2)	0.3452(2)	0.0221(4)
C(10)	0.9703(3)	0.3381(3)	0.0720(2)	0.0305(5)
C(11)	1.1285(3)	0.3587(3)	0.0378(2)	0.0357(6)
C(12)	1.0314(3)	0.7454(3)	0.3331(2)	0.0318(5)
C(13)	1.1403(3)	0.8770(3)	0.4487(2)	0.0329(5)
C(14)	0.4793(3)	0.4100(2)	0.65550(19)	0.0226(4)
C(15)	0.4776(3)	0.3092(2)	0.72182(19)	0.0202(4)
C(16)	0.4440(3)	0.3388(2)	0.8391(2)	0.0220(4)
C(17)	0.4505(3)	0.2549(3)	0.9063(2)	0.0262(5)
C(18)	0.4884(3)	0.1394(3)	0.8557(2)	0.0285(5)
C(19)	0.5183(3)	0.1074(3)	0.7380(2)	0.0306(5)
C(20)	0.5127(3)	0.1918(2)	0.6709(2)	0.0257(5)

*$U_{eq.}$ defined as one third of the trace of the orthogonalized **U** tensor.

Table S9. Bond lengths (Å) and bond angles (°)

Br(1)-C(6)	1.906(2)	C(3)-C(8)	1.413(3)
P(1)-O(1)	1.4688(16)	C(4)-C(5)	1.379(3)
P(1)-O(3)	1.5792(16)	C(5)-C(6)	1.407(3)
P(1)-O(2)	1.5872(16)	C(6)-C(7)	1.383(3)
P(1)-C(9)	1.798(2)	C(7)-C(8)	1.399(3)
O(2)-C(10)	1.461(3)	C(10)-C(11)	1.502(3)
O(3)-C(12)	1.470(3)	C(12)-C(13)	1.493(3)
N(1)-C(8)	1.375(3)	C(14)-C(15)	1.520(3)
N(1)-C(1)	1.380(3)	C(15)-C(20)	1.393(3)
N(1)-C(14)	1.455(3)	C(15)-C(16)	1.393(3)
C(1)-C(2)	1.370(3)	C(16)-C(17)	1.389(3)
C(2)-C(3)	1.433(3)	C(17)-C(18)	1.390(3)
C(2)-C(9)	1.503(3)	C(18)-C(19)	1.384(3)
C(3)-C(4)	1.405(3)	C(19)-C(20)	1.390(3)

O(1)-P(1)-O(3)	116.19(9)	C(7)-C(6)-C(5)	123.2(2)
O(1)-P(1)-O(2)	114.07(9)	C(7)-C(6)-Br(1)	118.46(17)
O(3)-P(1)-O(2)	102.02(9)	C(5)-C(6)-Br(1)	118.25(16)
O(1)-P(1)-C(9)	115.13(10)	C(6)-C(7)-C(8)	115.99(19)
O(3)-P(1)-C(9)	102.18(9)	N(1)-C(8)-C(7)	129.72(19)
O(2)-P(1)-C(9)	105.60(9)	N(1)-C(8)-C(3)	107.81(19)
C(10)-O(2)-P(1)	119.62(15)	C(7)-C(8)-C(3)	122.47(19)
C(12)-O(3)-P(1)	118.22(13)	C(2)-C(9)-P(1)	113.73(14)
C(8)-N(1)-C(1)	108.40(17)	O(2)-C(10)-C(11)	107.5(2)
C(8)-N(1)-C(14)	126.39(19)	O(3)-C(12)-C(13)	108.34(18)
C(1)-N(1)-C(14)	124.67(18)	N(1)-C(14)-C(15)	113.91(17)
C(2)-C(1)-N(1)	110.30(19)	C(20)-C(15)-C(16)	119.38(19)
C(1)-C(2)-C(3)	106.33(19)	C(20)-C(15)-C(14)	122.19(19)
C(1)-C(2)-C(9)	127.3(2)	C(16)-C(15)-C(14)	118.41(19)
C(3)-C(2)-C(9)	126.37(19)	C(17)-C(16)-C(15)	120.4(2)
C(4)-C(3)-C(8)	119.2(2)	C(16)-C(17)-C(18)	119.8(2)
C(4)-C(3)-C(2)	133.6(2)	C(19)-C(18)-C(17)	120.0(2)
C(8)-C(3)-C(2)	107.13(18)	C(18)-C(19)-C(20)	120.2(2)
C(5)-C(4)-C(3)	119.2(2)	C(19)-C(20)-C(15)	120.1(2)
C(4)-C(5)-C(6)	119.8(2)		

Table S10. Anisotropic thermal parameters* (Å^2)

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	0.02424(15)	0.02680(15)	0.02637(15)	0.00844(10)	0.00320(10)	0.00844(11)
P(1)	0.0228(3)	0.0225(3)	0.0179(2)	0.0094(2)	0.0072(2)	0.0098(2)
O(1)	0.0264(8)	0.0325(8)	0.0233(7)	0.0149(7)	0.0061(7)	0.0134(7)
O(2)	0.0255(8)	0.0309(8)	0.0195(7)	0.0068(6)	0.0080(6)	0.0119(7)
O(3)	0.0300(8)	0.0211(7)	0.0195(7)	0.0100(6)	0.0085(6)	0.0091(6)
N(1)	0.0254(9)	0.0201(8)	0.0159(8)	0.0092(7)	0.0057(7)	0.0101(7)
C(1)	0.0251(11)	0.0182(9)	0.0195(9)	0.0097(8)	0.0041(8)	0.0089(8)
C(2)	0.0263(11)	0.0174(9)	0.0215(10)	0.0114(8)	0.0069(9)	0.0095(8)
C(3)	0.0250(11)	0.0180(9)	0.0199(10)	0.0111(8)	0.0078(8)	0.0101(8)
C(4)	0.0302(11)	0.0195(10)	0.0182(9)	0.0090(8)	0.0089(9)	0.0129(9)
C(5)	0.0319(12)	0.0206(10)	0.0200(10)	0.0090(8)	0.0054(9)	0.0113(9)
C(6)	0.0254(11)	0.0199(10)	0.0245(10)	0.0104(8)	0.0048(9)	0.0089(9)
C(7)	0.0251(11)	0.0194(10)	0.0204(10)	0.0108(8)	0.0087(8)	0.0099(8)
C(8)	0.0277(11)	0.0161(9)	0.0184(9)	0.0098(8)	0.0068(8)	0.0098(8)
C(9)	0.0237(11)	0.0225(10)	0.0220(10)	0.0095(8)	0.0070(9)	0.0112(9)
C(10)	0.0367(13)	0.0292(12)	0.0208(11)	0.0059(9)	0.0101(10)	0.0127(10)
C(11)	0.0434(15)	0.0465(15)	0.0269(12)	0.0146(11)	0.0164(11)	0.0275(13)
C(12)	0.0411(14)	0.0246(11)	0.0279(11)	0.0164(10)	0.0089(10)	0.0080(10)
C(13)	0.0384(14)	0.0227(11)	0.0328(12)	0.0118(10)	0.0109(11)	0.0080(10)
C(14)	0.0309(12)	0.0224(10)	0.0177(9)	0.0100(8)	0.0089(9)	0.0128(9)
C(15)	0.0211(10)	0.0192(10)	0.0189(9)	0.0090(8)	0.0040(8)	0.0067(8)
C(16)	0.0238(11)	0.0219(10)	0.0201(10)	0.0090(8)	0.0067(8)	0.0092(9)
C(17)	0.0299(12)	0.0293(11)	0.0197(10)	0.0128(9)	0.0080(9)	0.0104(10)
C(18)	0.0341(13)	0.0285(11)	0.0289(11)	0.0195(10)	0.0086(10)	0.0130(10)
C(19)	0.0423(14)	0.0251(11)	0.0333(12)	0.0162(10)	0.0141(11)	0.0187(11)
C(20)	0.0350(12)	0.0237(11)	0.0217(10)	0.0114(9)	0.0122(9)	0.0132(10)

*The exponent takes the form: $-2\pi^2\Sigma\Sigma U_{ij}h_ih_j\mathbf{a}_i^*\mathbf{a}_j^*$

Table S11. Coordinates and isotropic temperature factors* (Å^2) for H atoms

Atoms	*x*	*y*	*z*	$U_{eq.}$
H(1)	0.7731	0.4623	0.5894	0.025
H(4)	0.4842	0.1666	0.1430	0.026
H(5)	0.1999	0.0542	0.0835	0.029
H(7)	0.1828	0.2341	0.4461	0.025
H(9A)	0.7912	0.2444	0.2887	0.027
H(9B)	0.9120	0.3801	0.4143	0.027
H(10A)	0.9036	0.3581	0.0154	0.037
H(10B)	0.9080	0.2361	0.0644	0.037
H(11A)	1.1868	0.4586	0.0422	0.054
H(11B)	1.1066	0.2885	-0.0476	0.054
H(11C)	1.1951	0.3423	0.0964	0.054
H(12A)	0.9429	0.7614	0.2956	0.038
H(12B)	1.0941	0.7275	0.2707	0.038
H(13A)	1.0754	0.8998	0.5065	0.049
H(13B)	1.1955	0.9606	0.4261	0.049
H(13C)	1.2217	0.8570	0.4894	0.049
H(14A)	0.3704	0.4071	0.6412	0.027
H(14B)	0.5586	0.5116	0.7111	0.027
H(16)	0.4166	0.4169	0.8732	0.026
H(17)	0.4290	0.2763	0.9867	0.031
H(18)	0.4939	0.0825	0.9019	0.034
H(19)	0.5426	0.0275	0.7030	0.037
H(20)	0.5330	0.1693	0.5901	0.031

*The exponent takes the form: $-8\pi^2 U\sin^2\theta/\lambda^2$

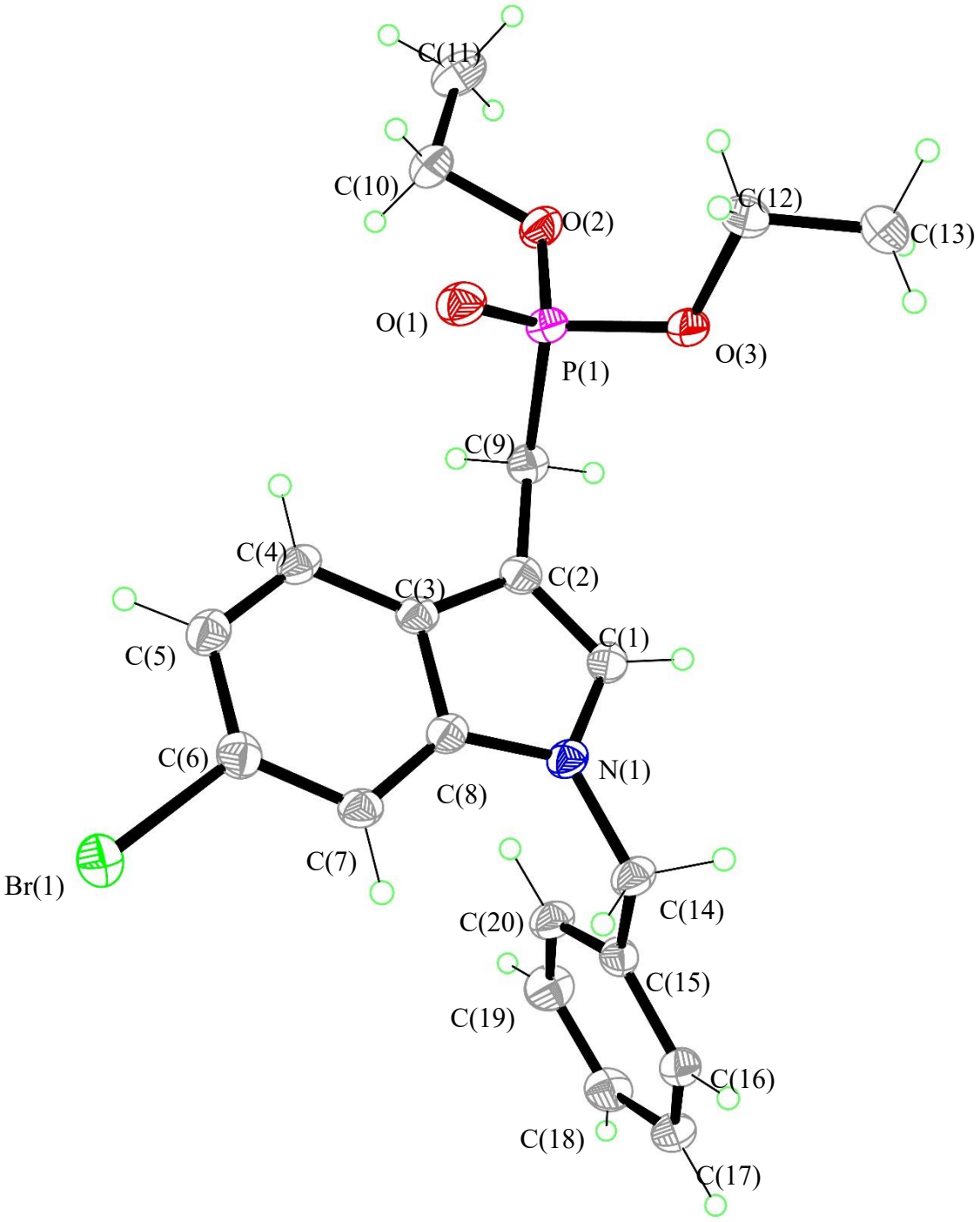


Figure S7 ORTEP drawing of $C_{20}H_{23}BrNO_3P$ with 50% probability ellipsoids, showing the atomic numbering scheme.

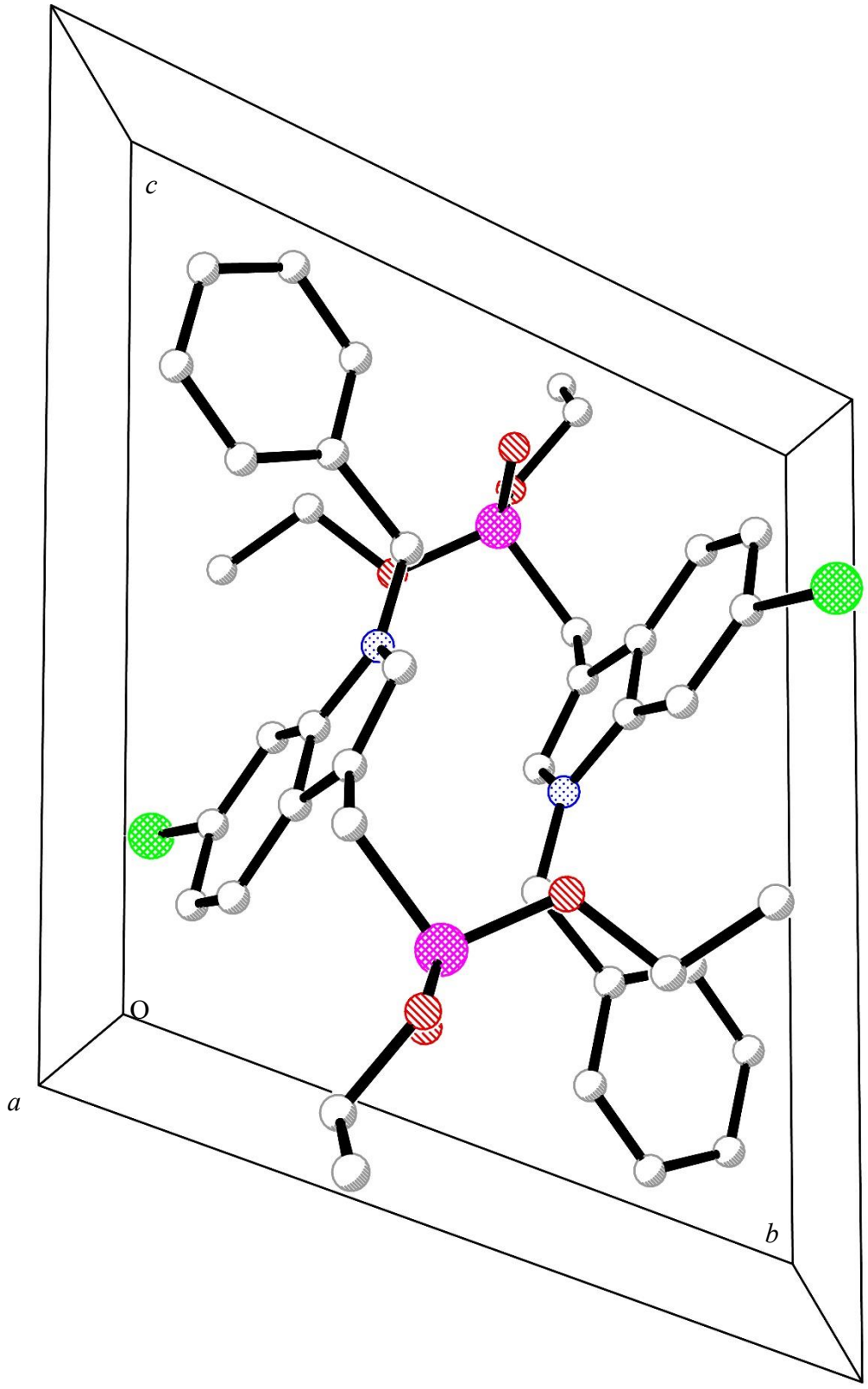
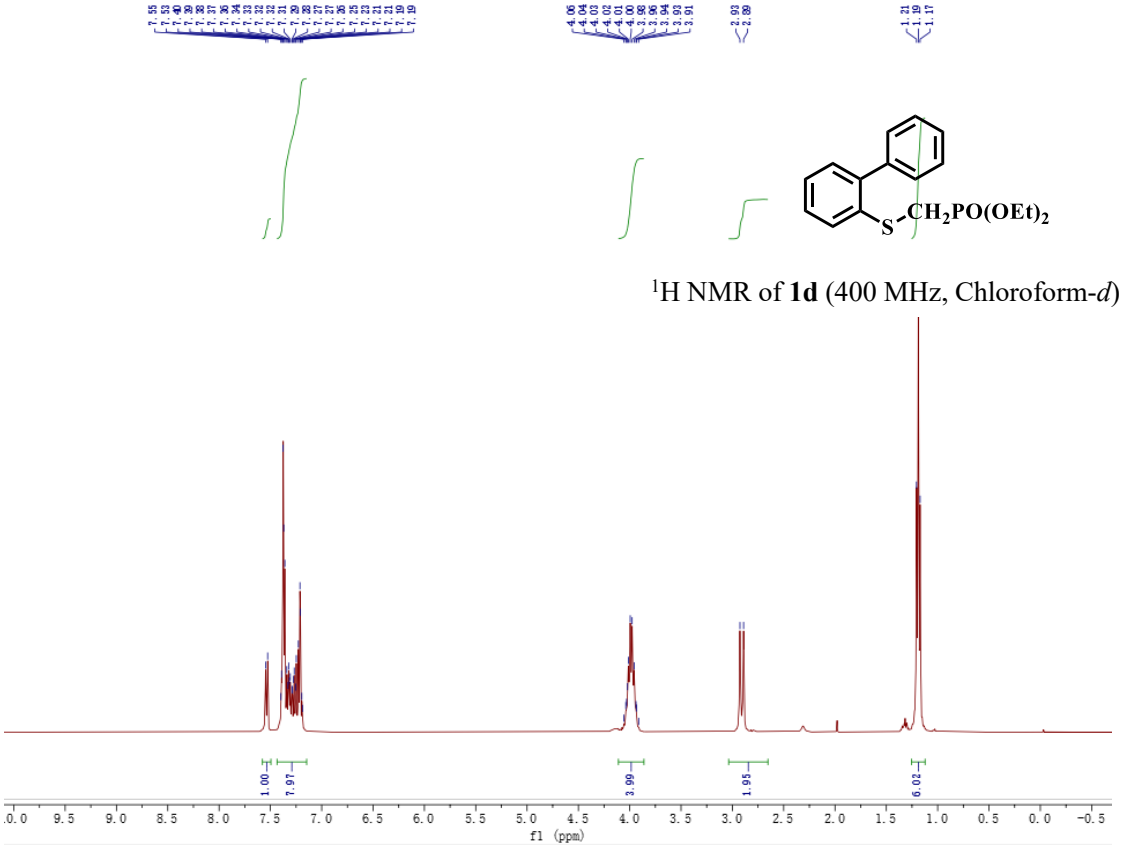
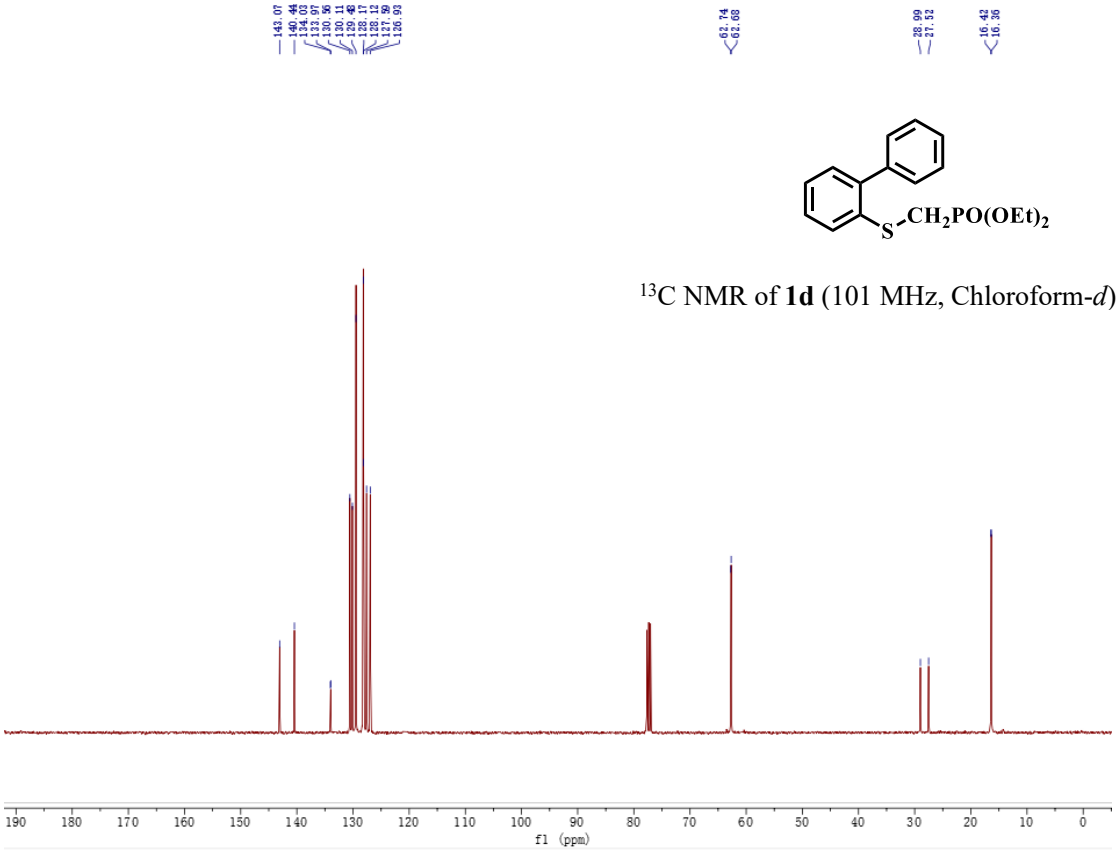


Figure S8 A packing view along the *a* direction

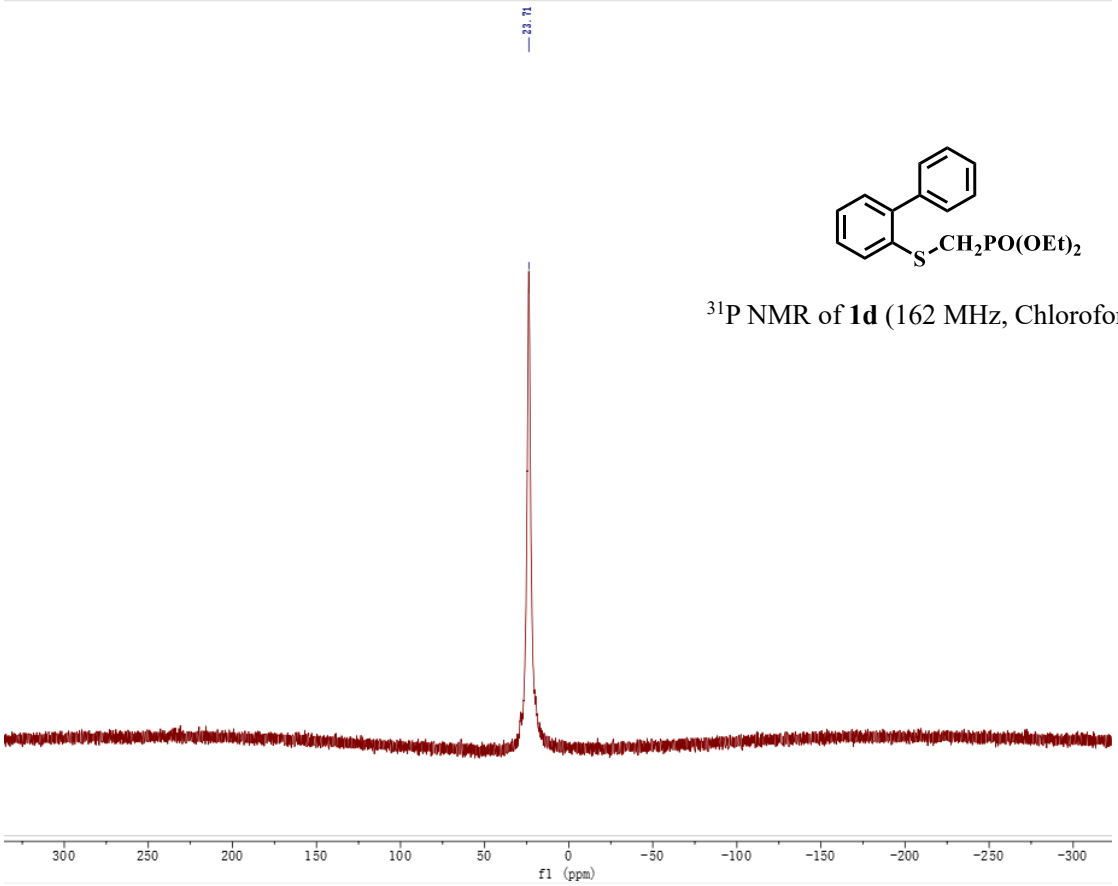
10. NMR Spectra.



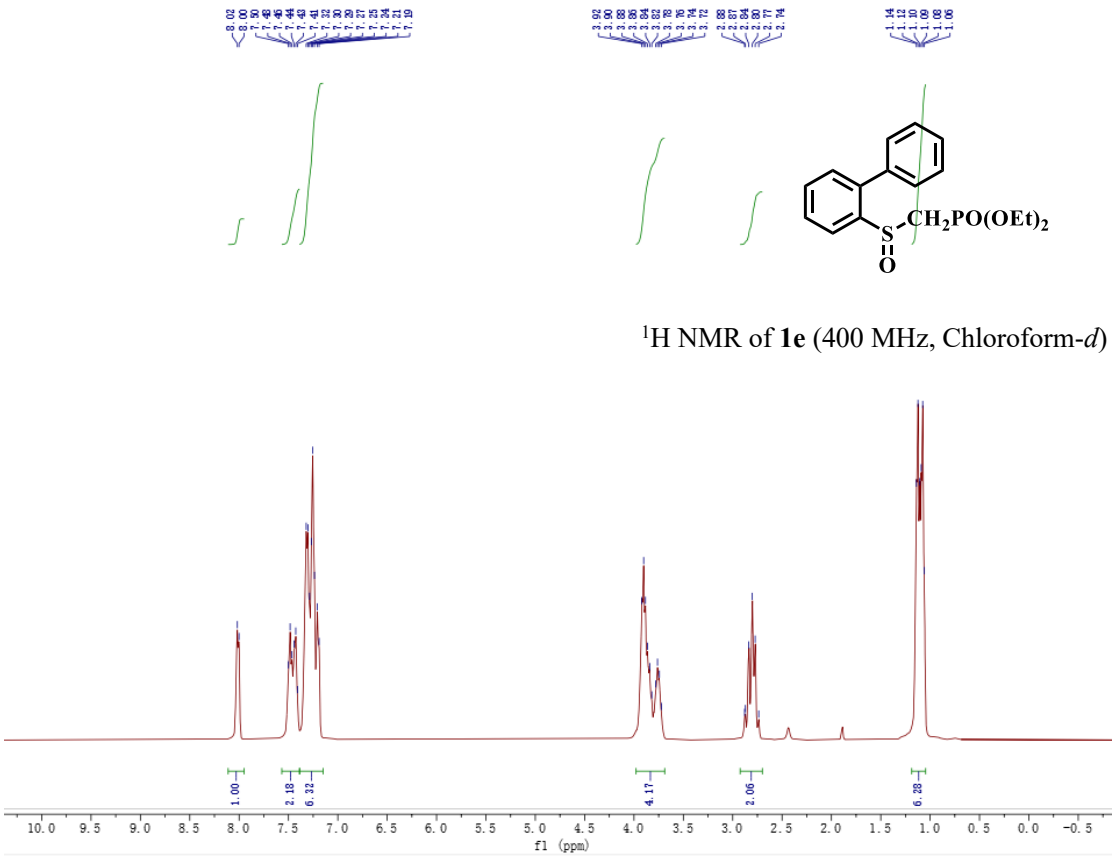
^{1}H NMR of **1d** (400 MHz, Chloroform-*d*)



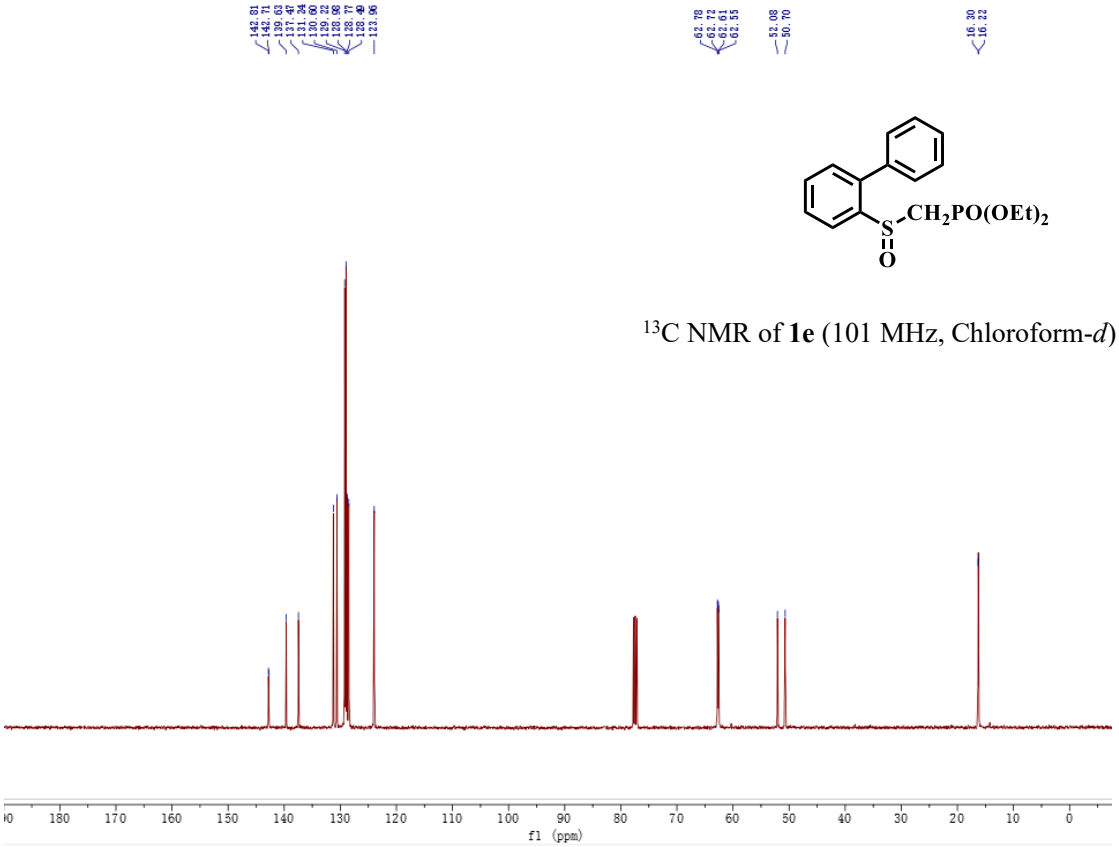
^{13}C NMR of **1d** (101 MHz, Chloroform-*d*)



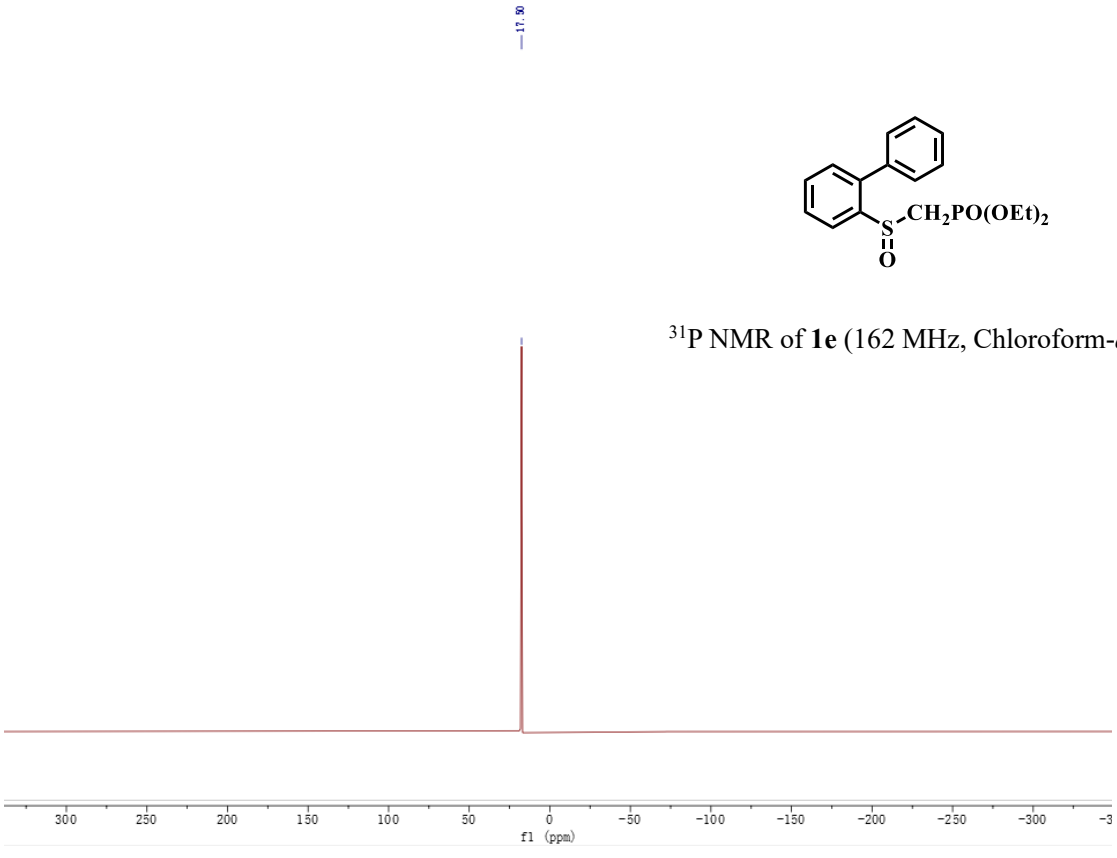
^{31}P NMR of **1d** (162 MHz, Chloroform-*d*)



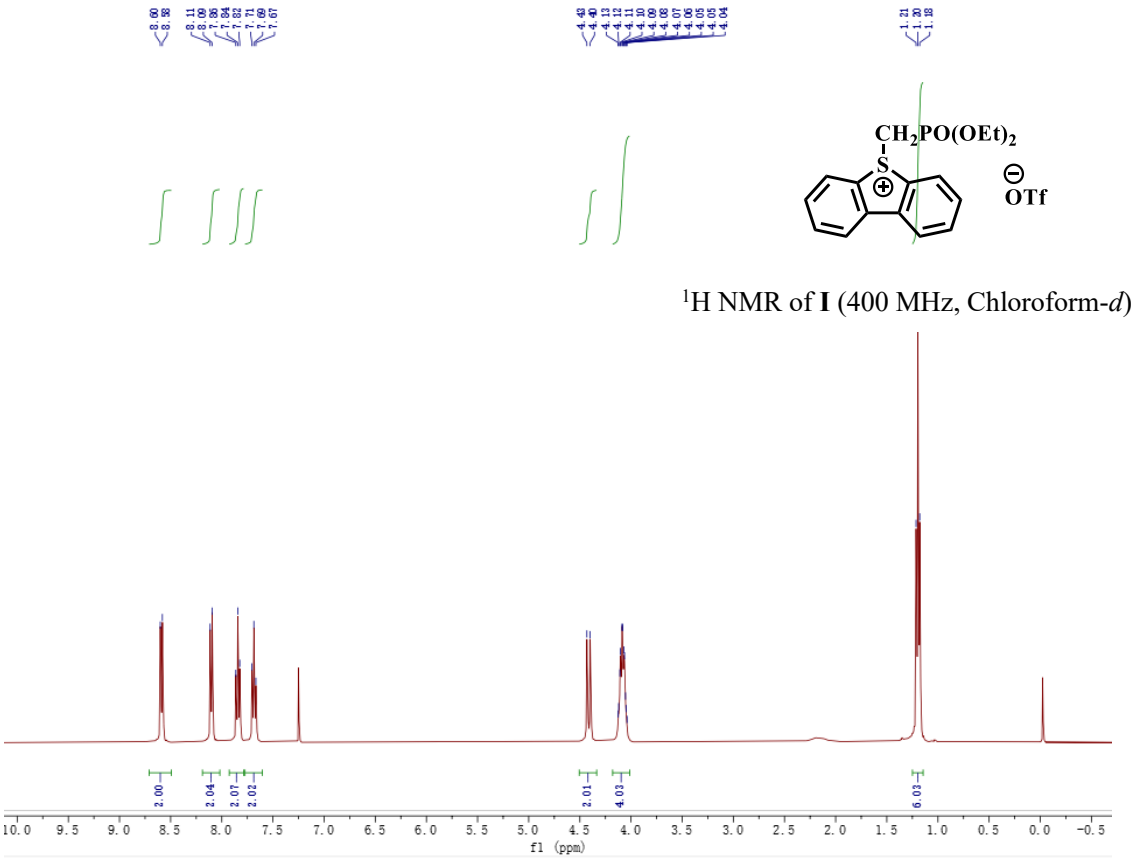
^{1}H NMR of **1e** (400 MHz, Chloroform-*d*)



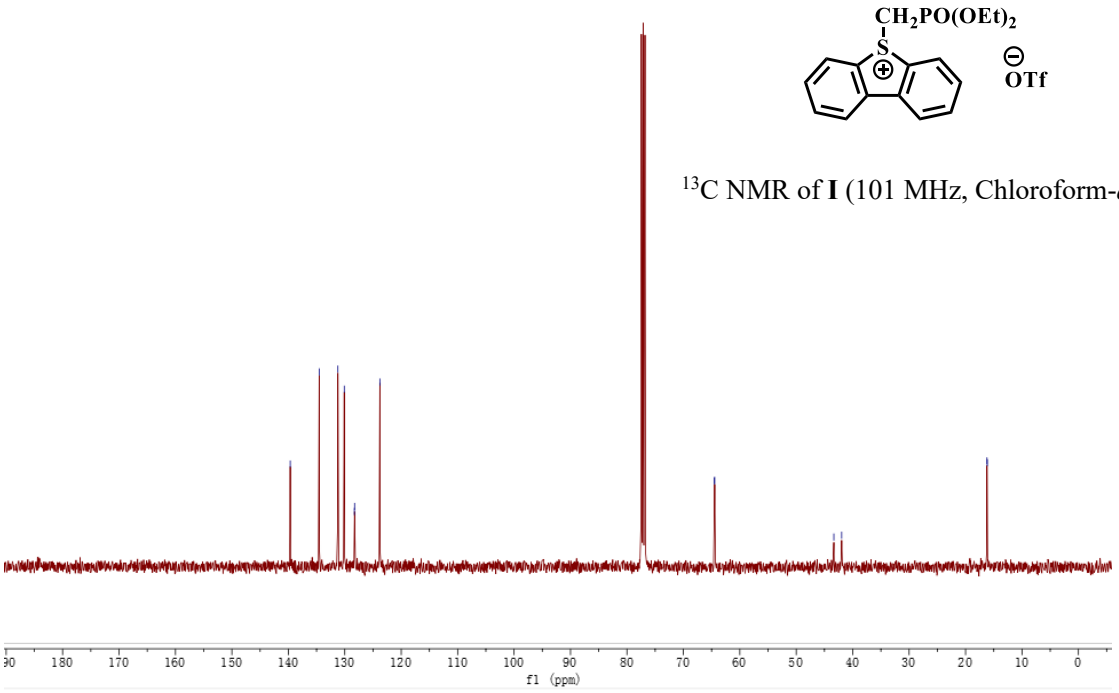
^{13}C NMR of **1e** (101 MHz, Chloroform-*d*)



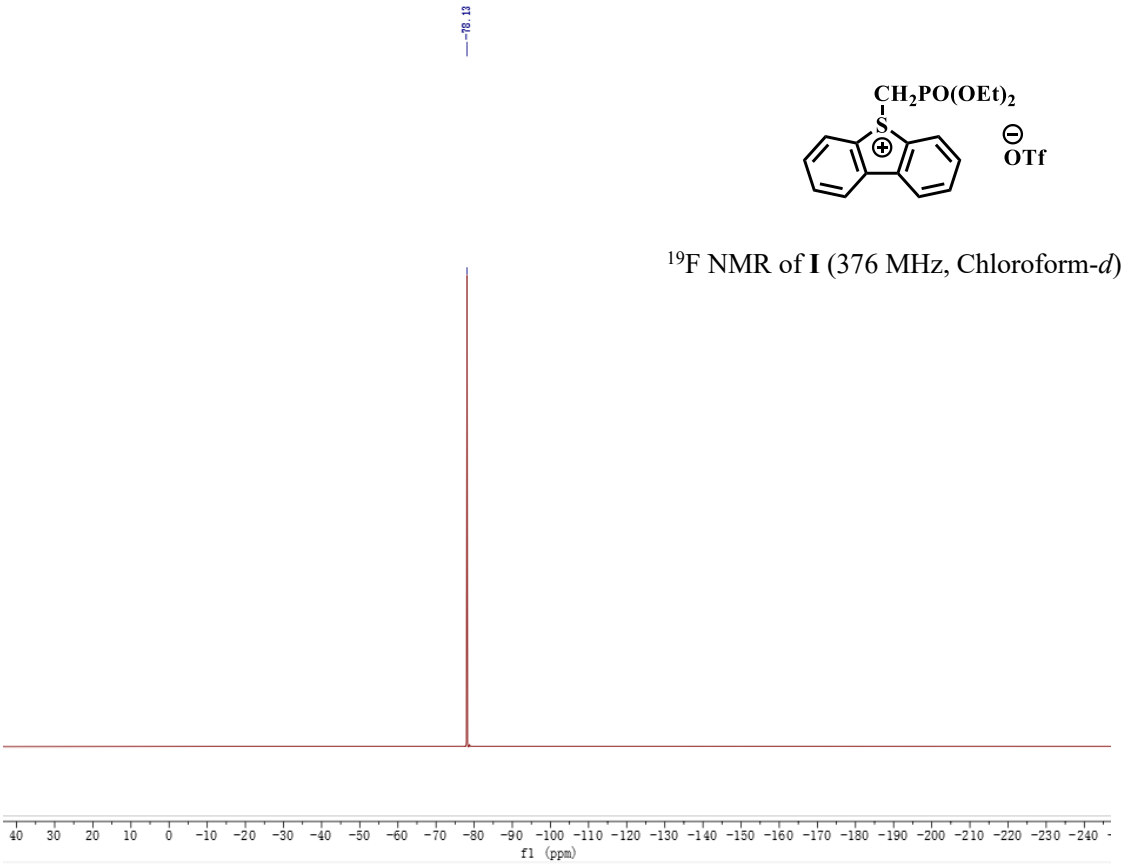
^{31}P NMR of **1e** (162 MHz, Chloroform-*d*)



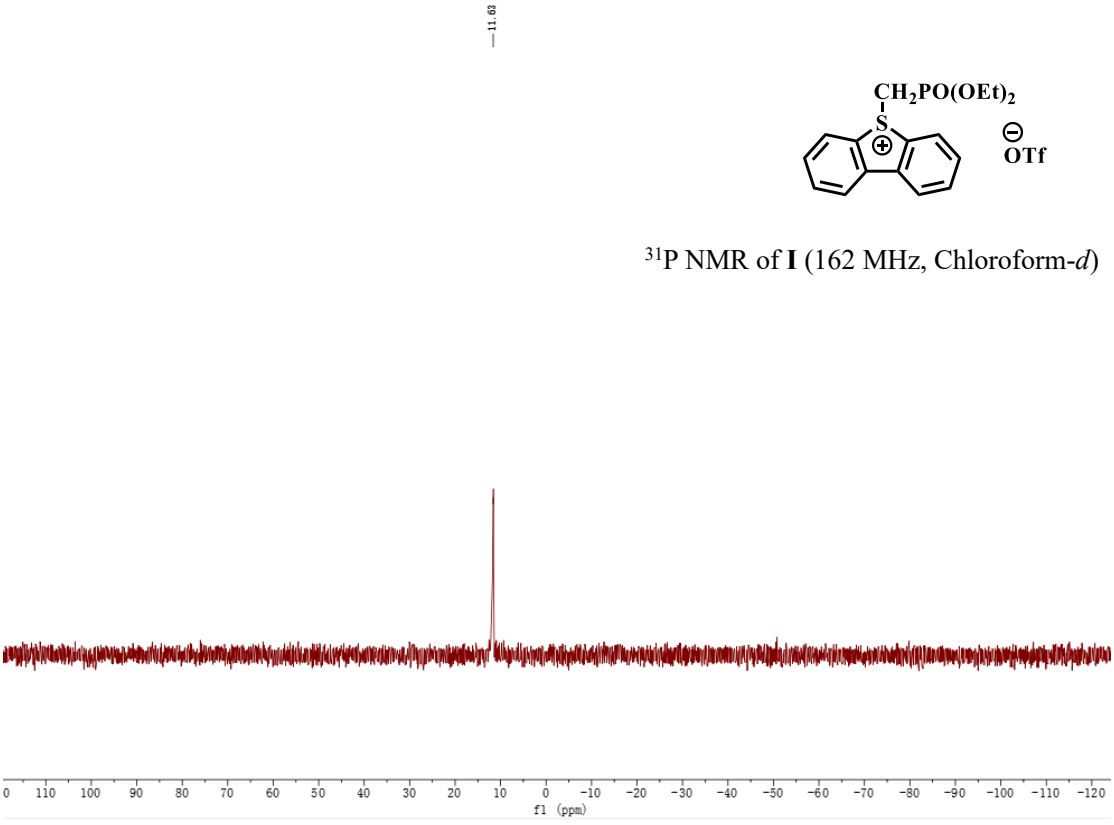
^{1}H NMR of **I** (400 MHz, Chloroform-*d*)



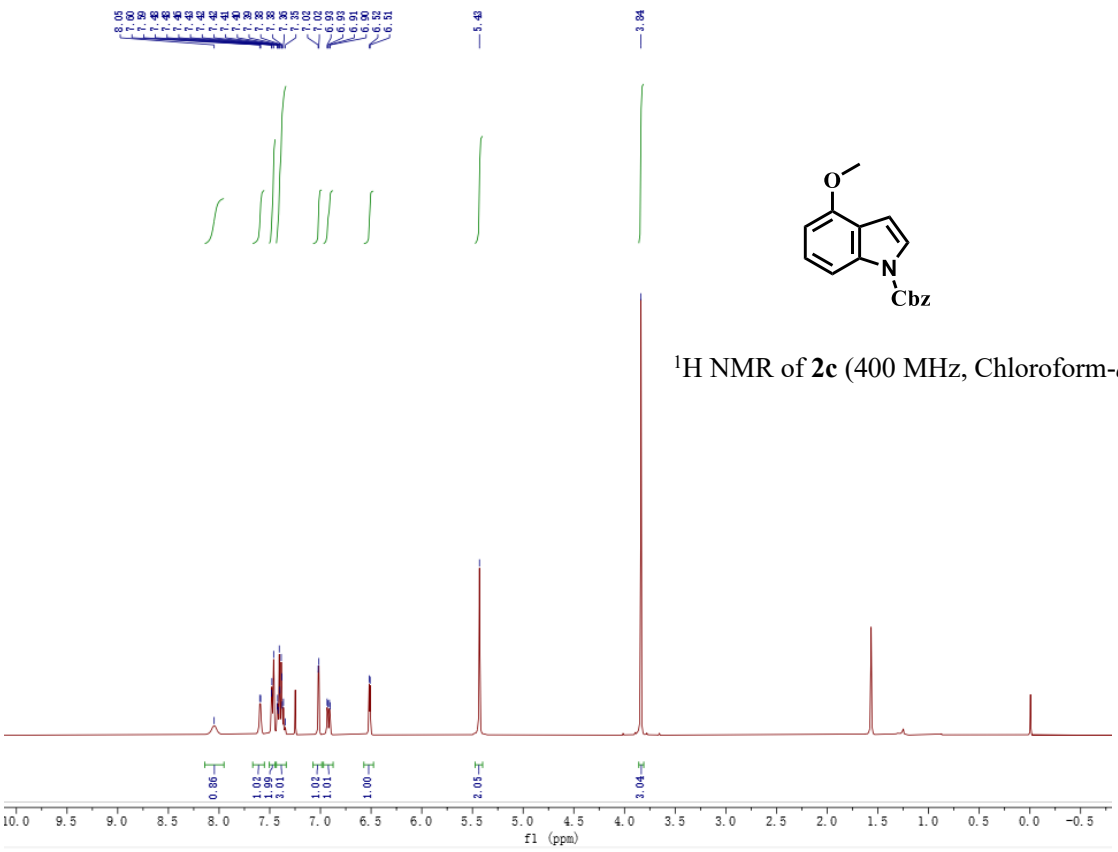
^{13}C NMR of **I** (101 MHz, Chloroform-*d*)



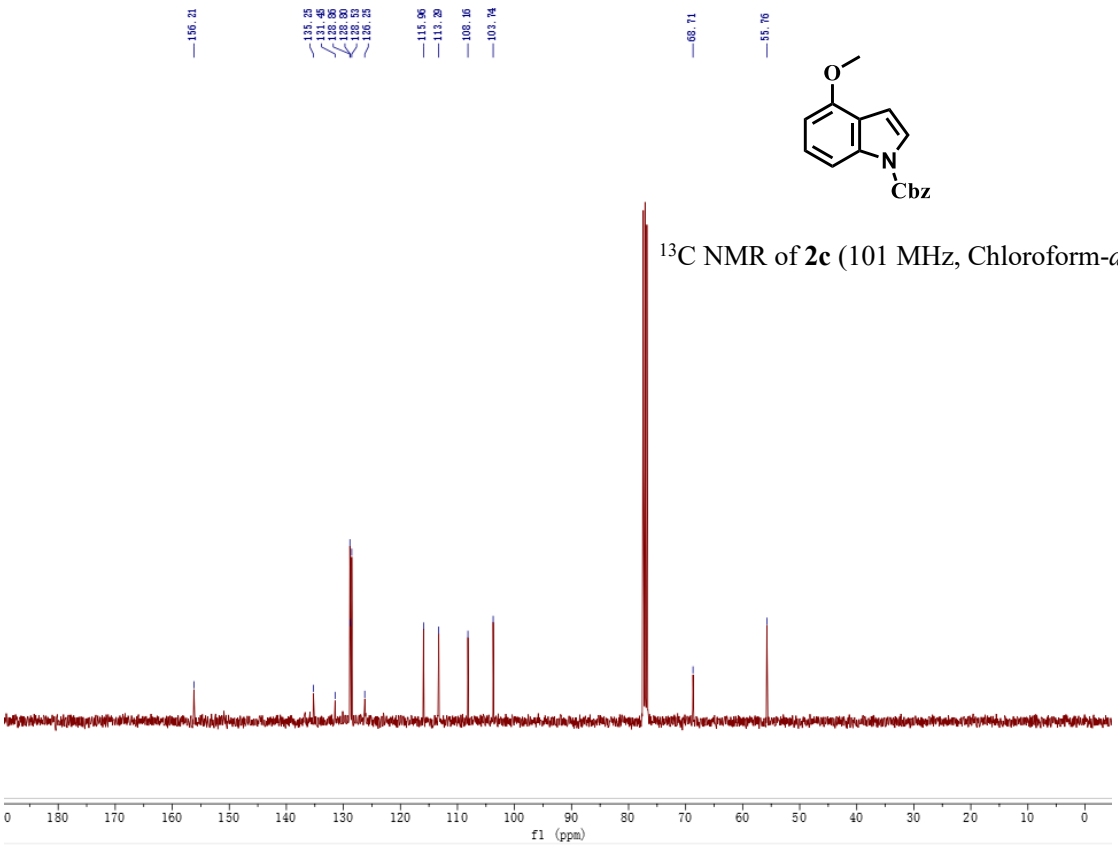
^{19}F NMR of **I** (376 MHz, Chloroform-*d*)



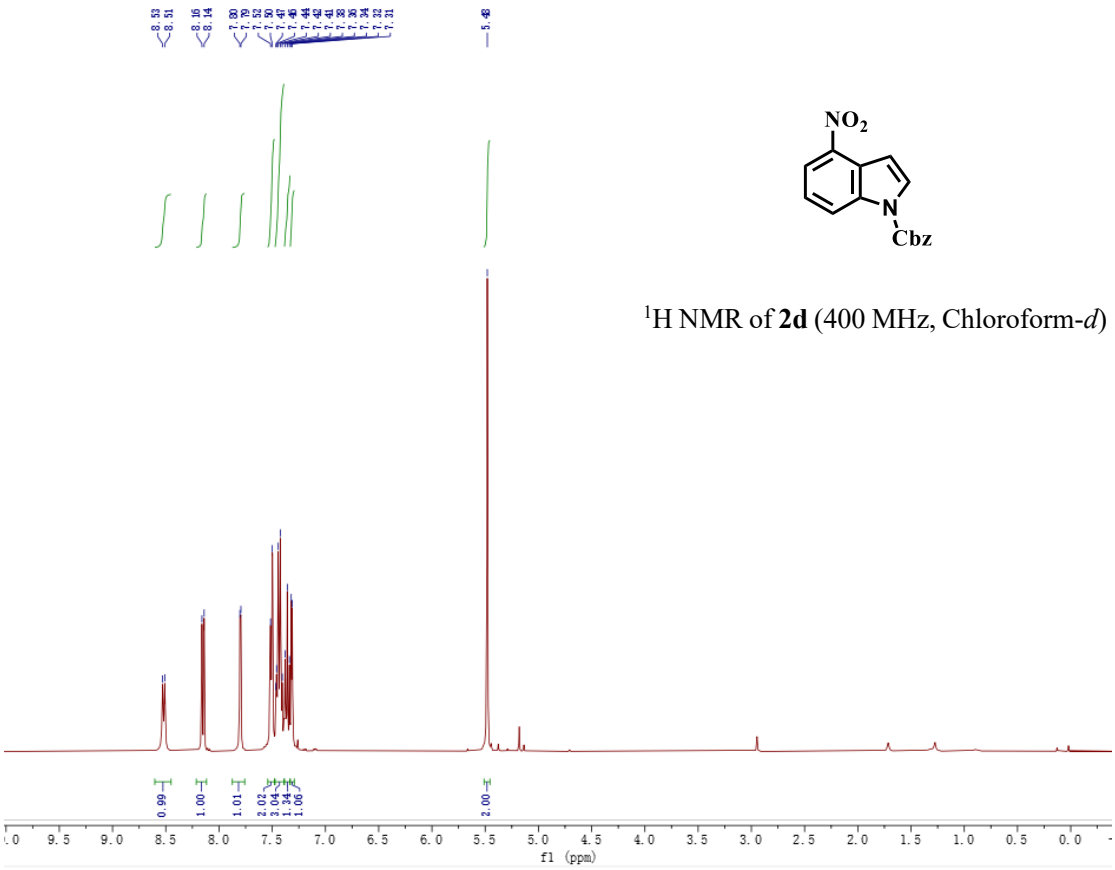
^{31}P NMR of **I** (162 MHz, Chloroform-*d*)



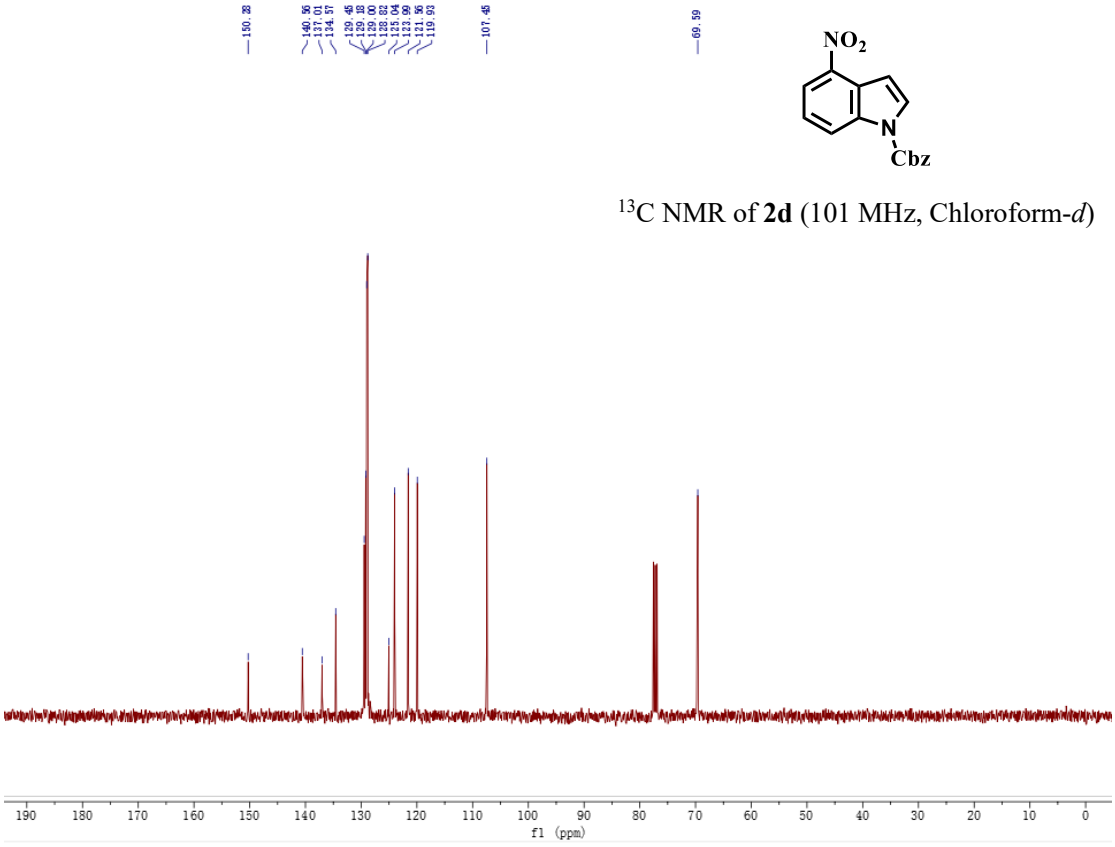
^{1}H NMR of **2c** (400 MHz, Chloroform-*d*)



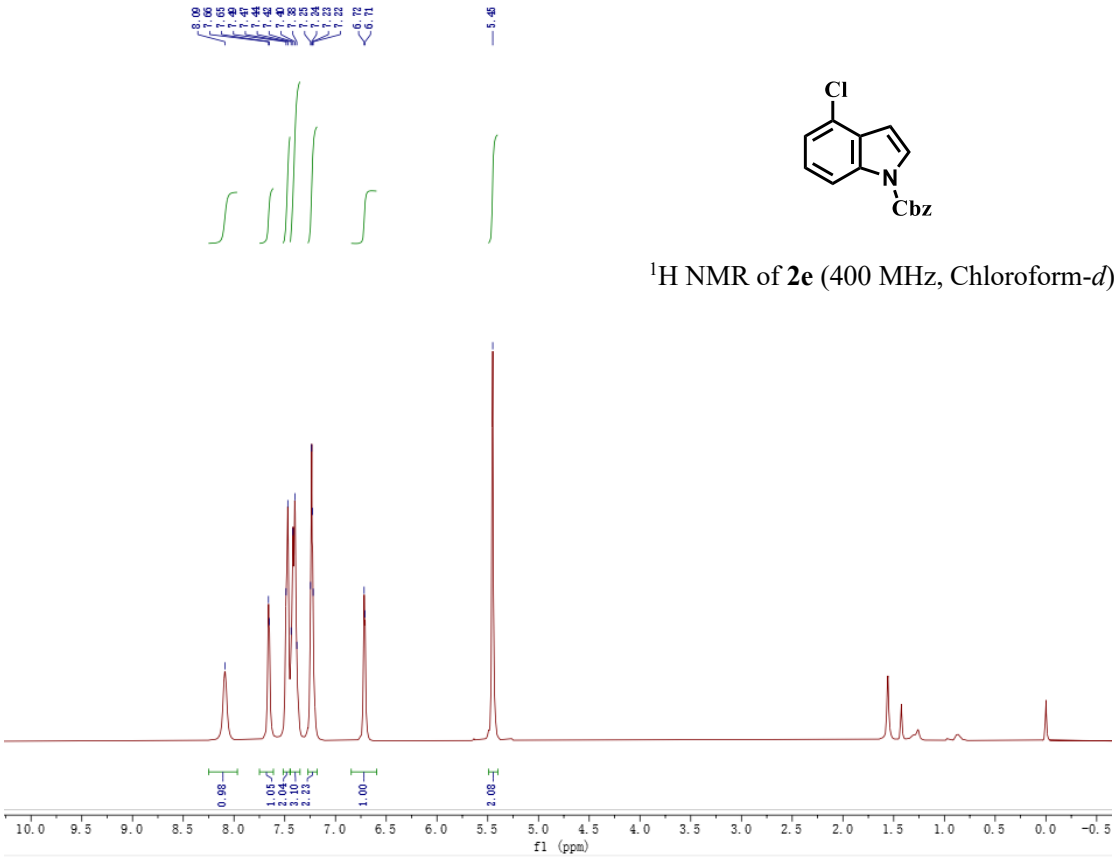
^{13}C NMR of **2c** (101 MHz, Chloroform-*d*)



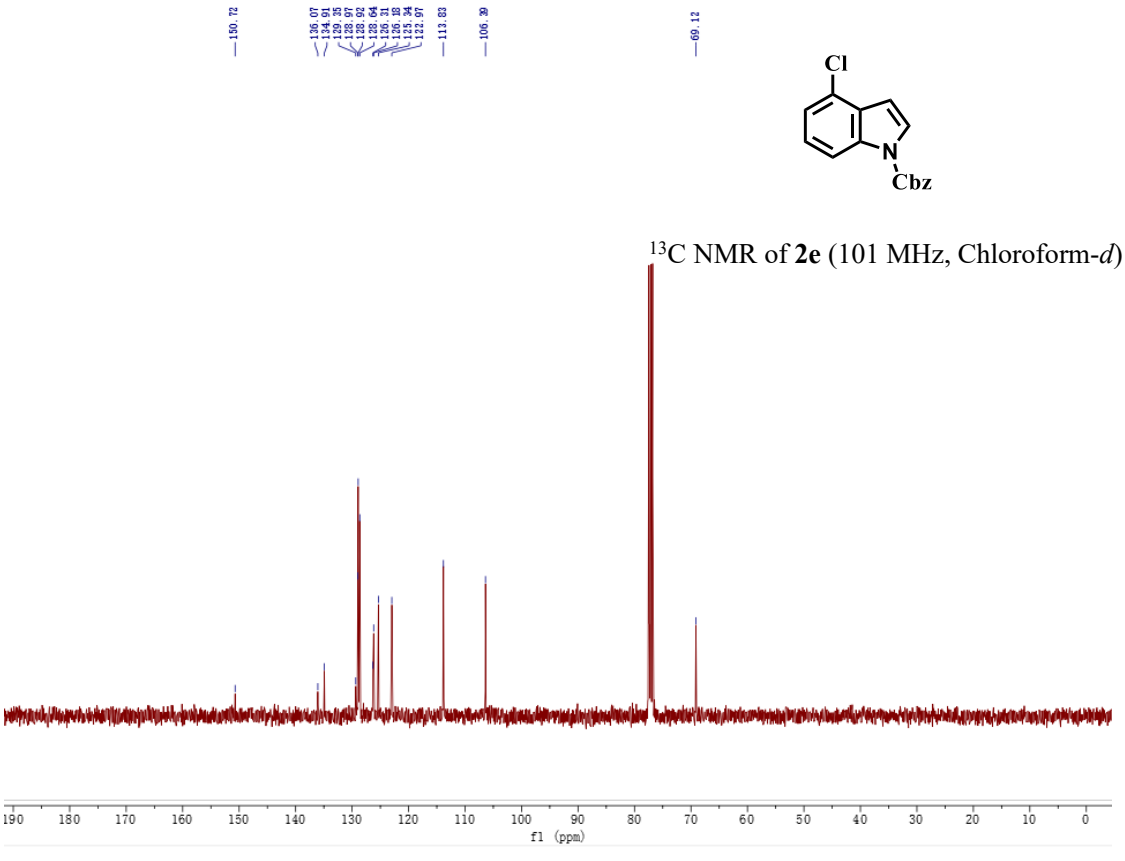
^{1}H NMR of **2d** (400 MHz, Chloroform-*d*)



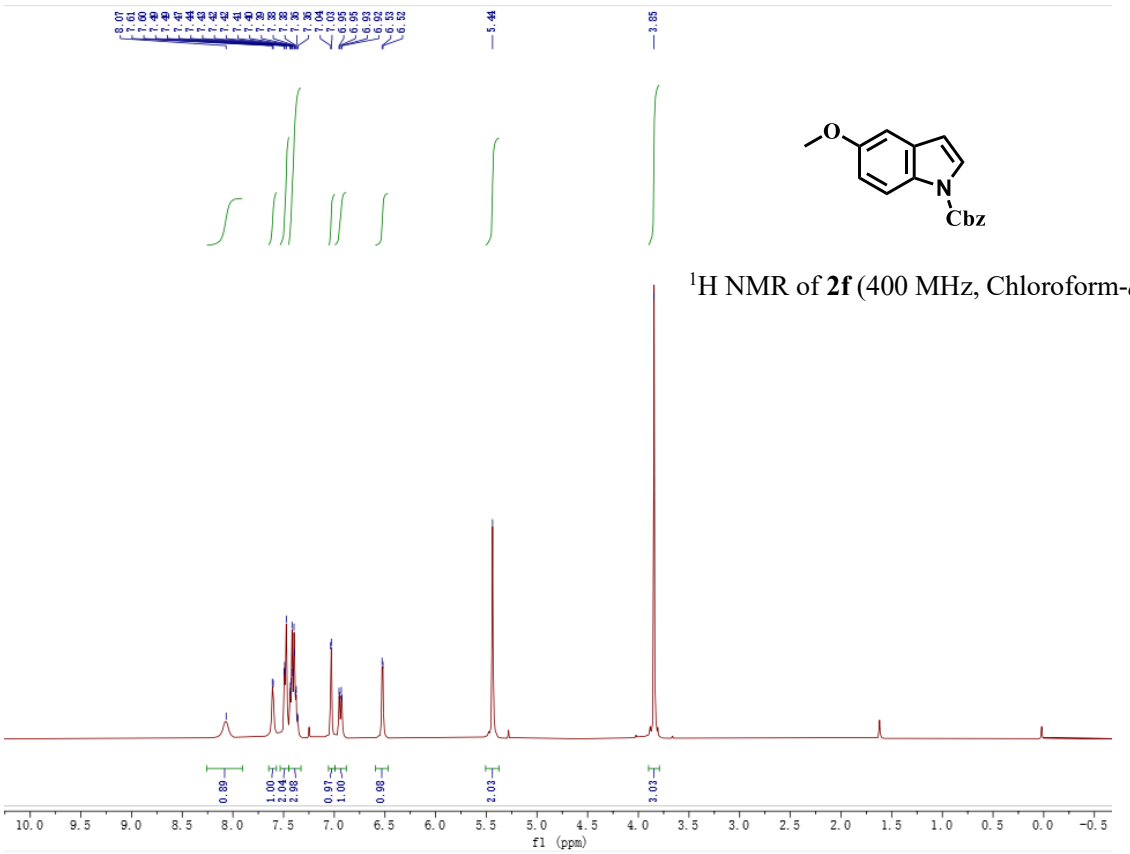
^{13}C NMR of **2d** (101 MHz, Chloroform-*d*)



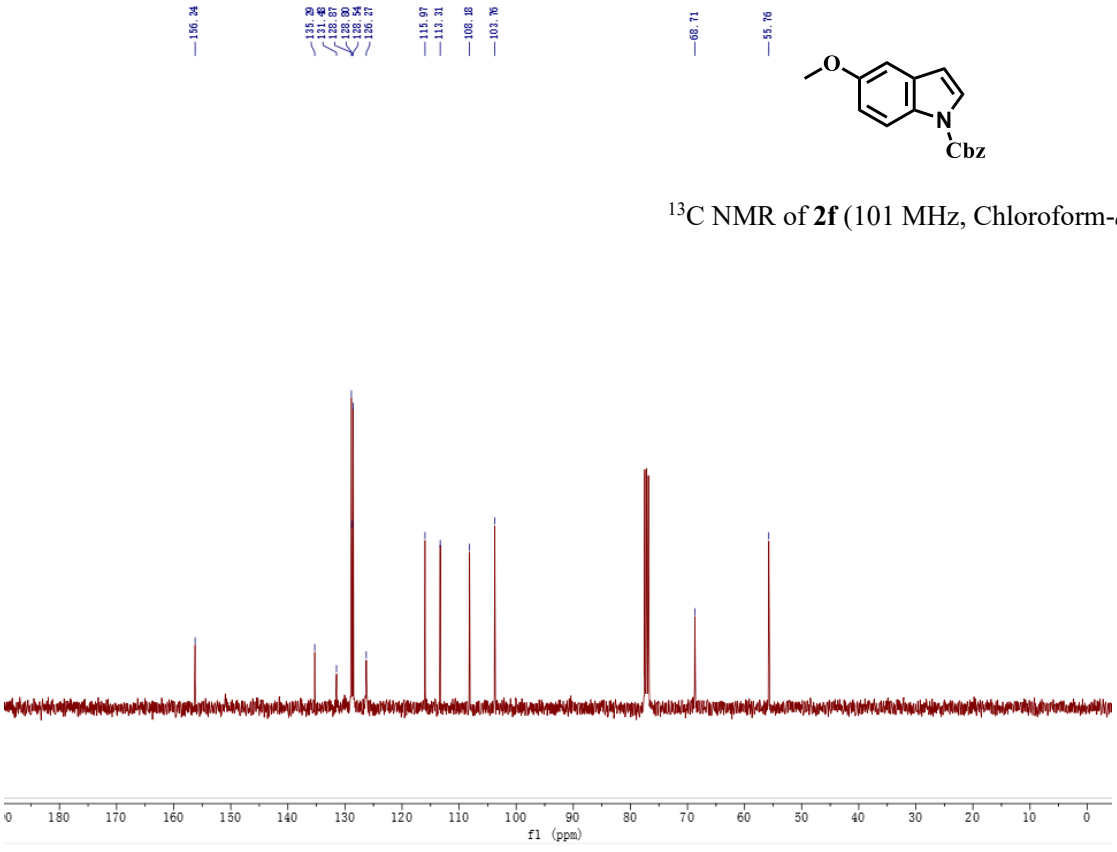
^{1}H NMR of **2e** (400 MHz, Chloroform-*d*)



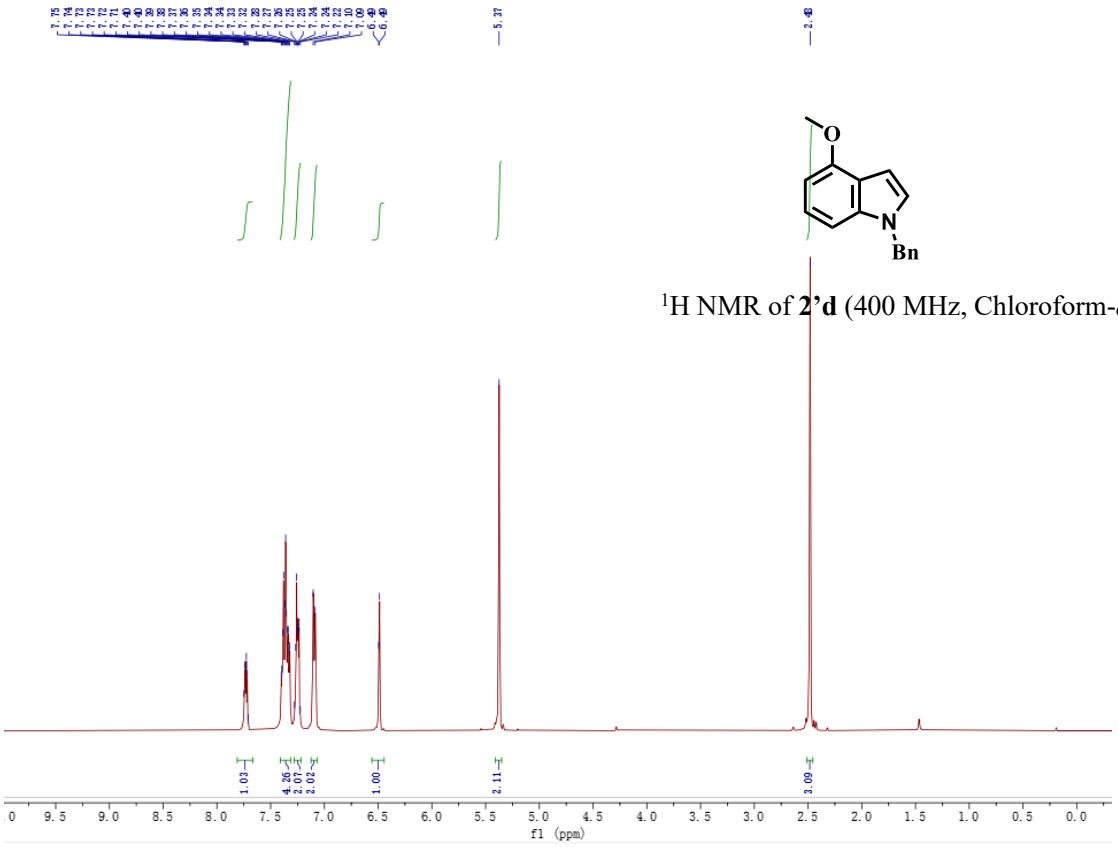
^{13}C NMR of **2e** (101 MHz, Chloroform-*d*)



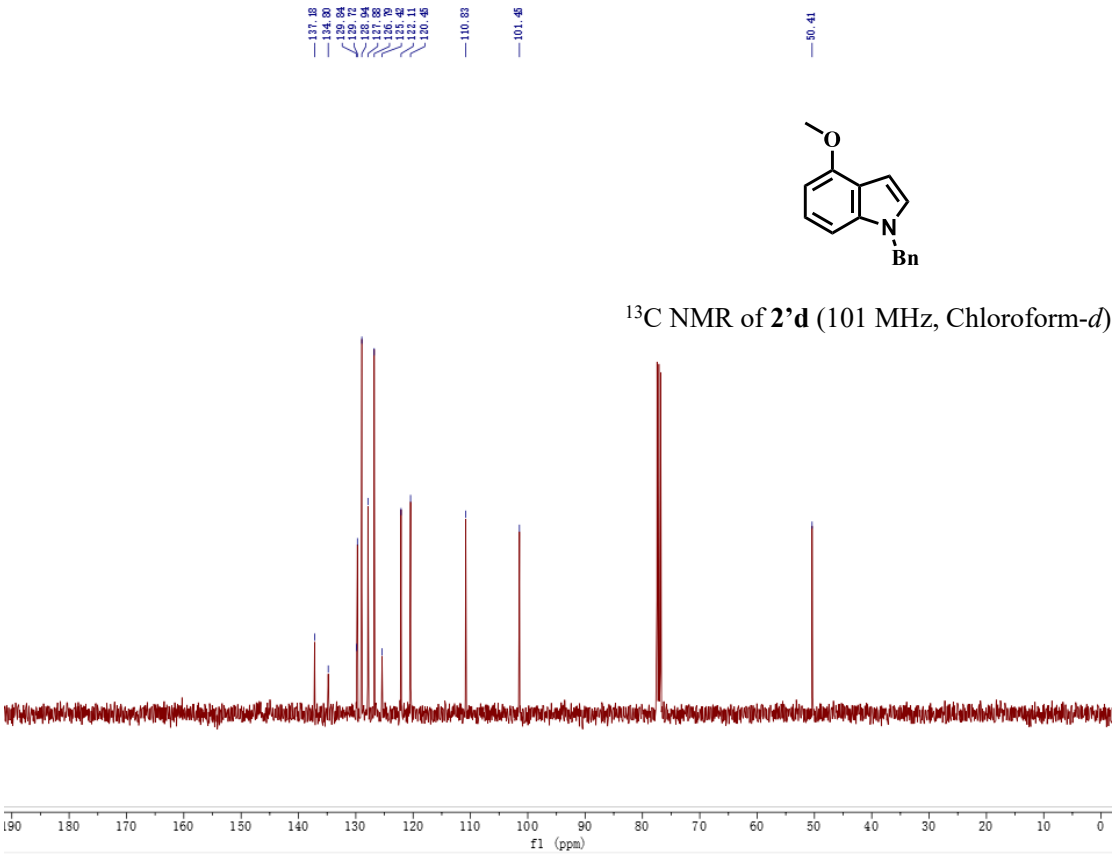
^{1}H NMR of **2f** (400 MHz, Chloroform-*d*)



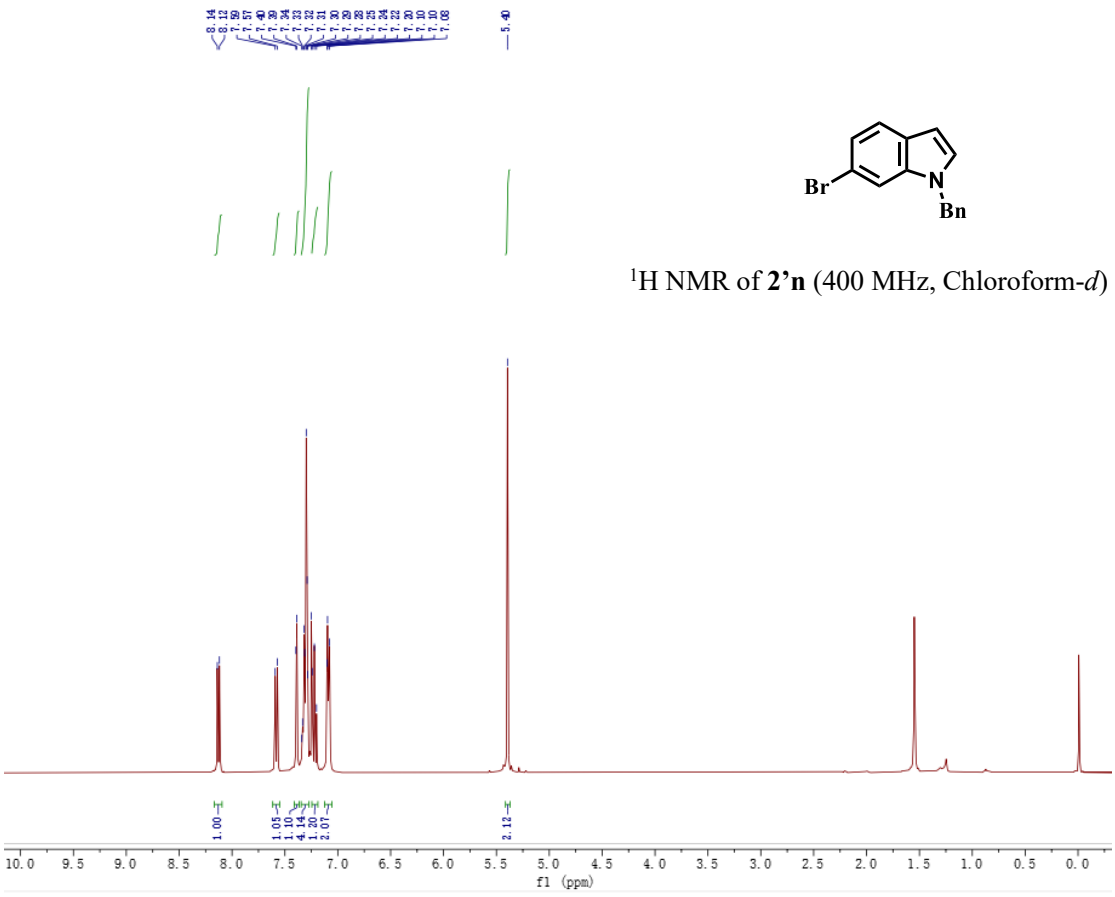
^{13}C NMR of **2f** (101 MHz, Chloroform-*d*)



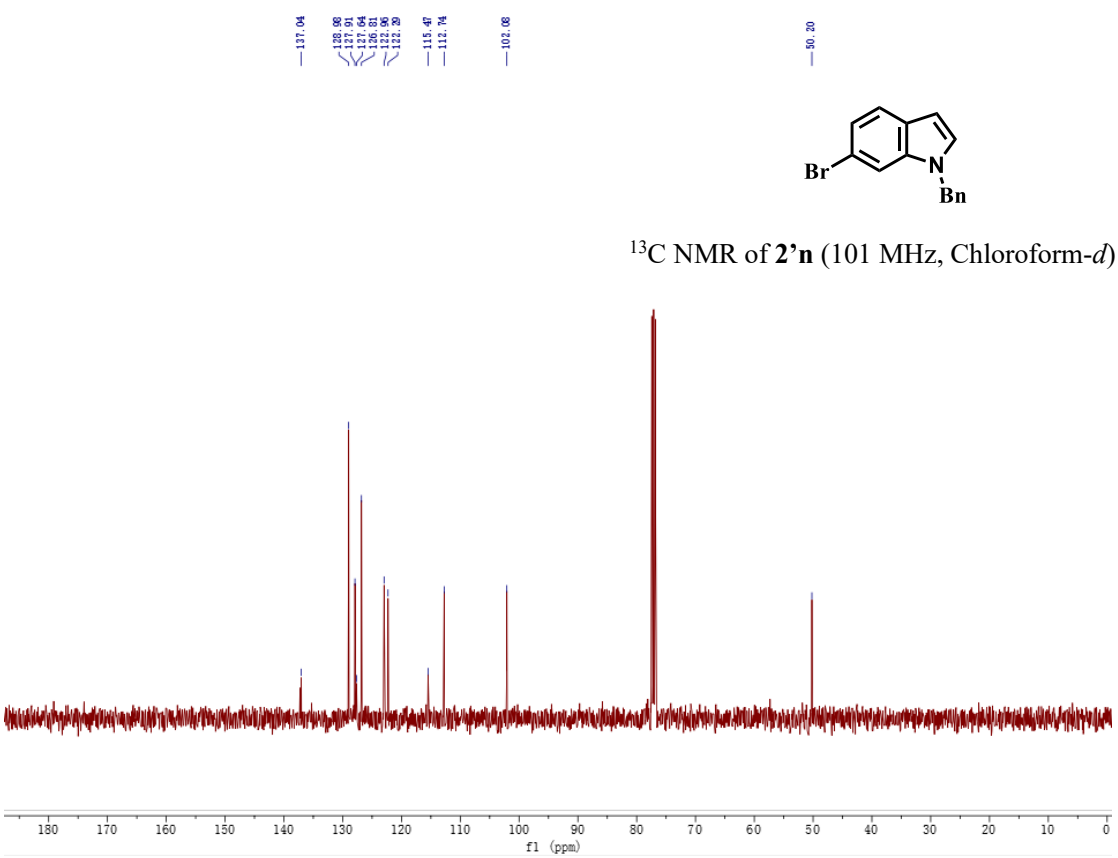
^{1}H NMR of **2'd** (400 MHz, Chloroform-*d*)



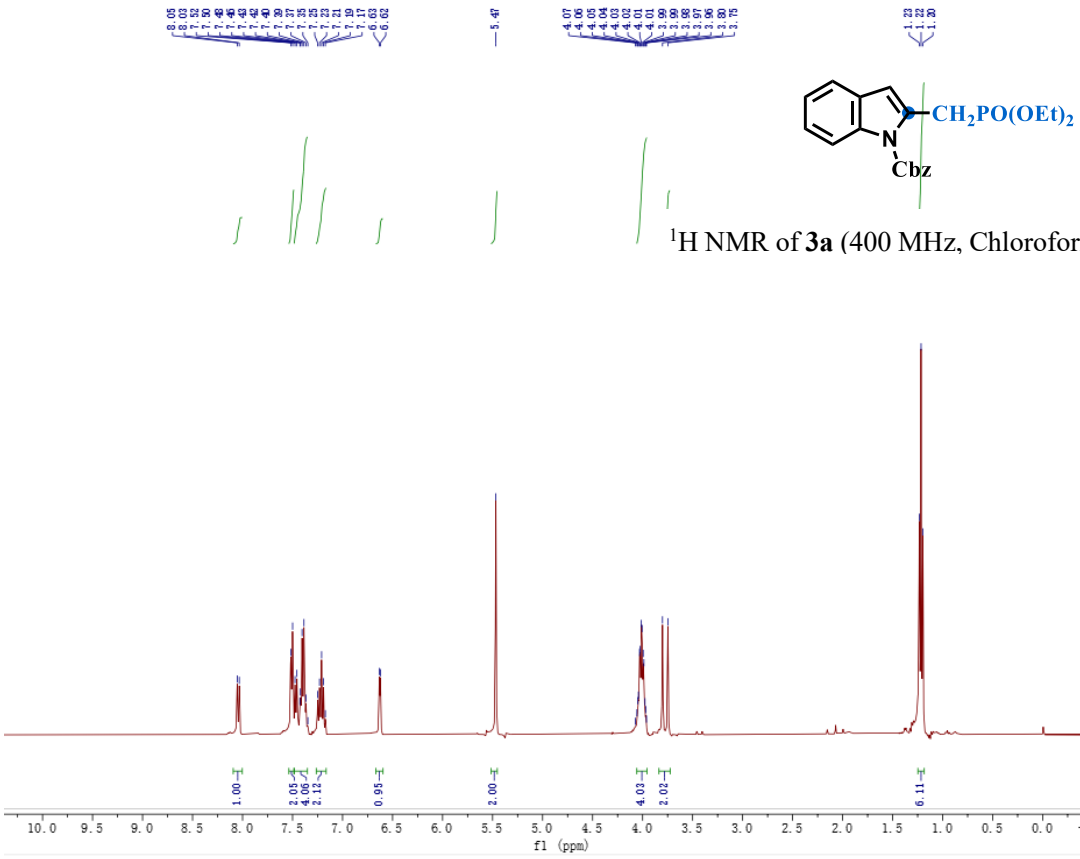
^{13}C NMR of **2'd** (101 MHz, Chloroform-*d*)



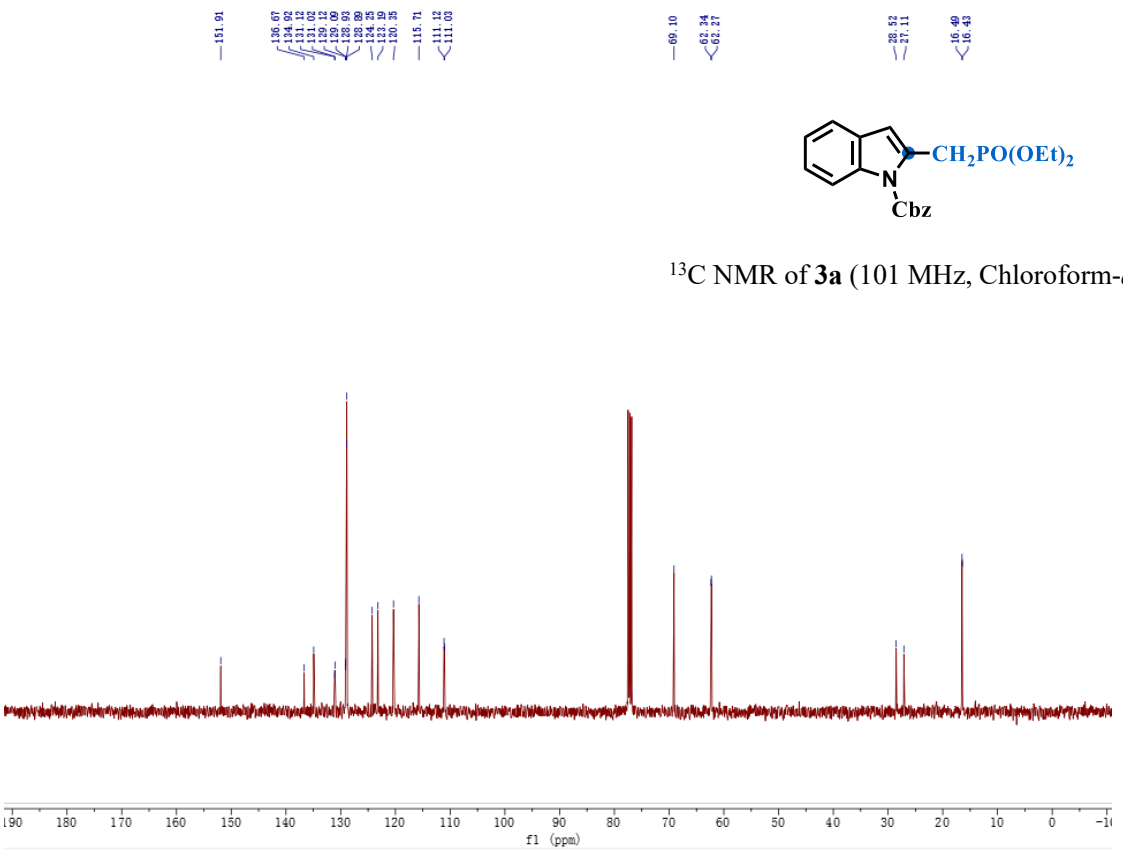
^{1}H NMR of **2'n** (400 MHz, Chloroform-*d*)



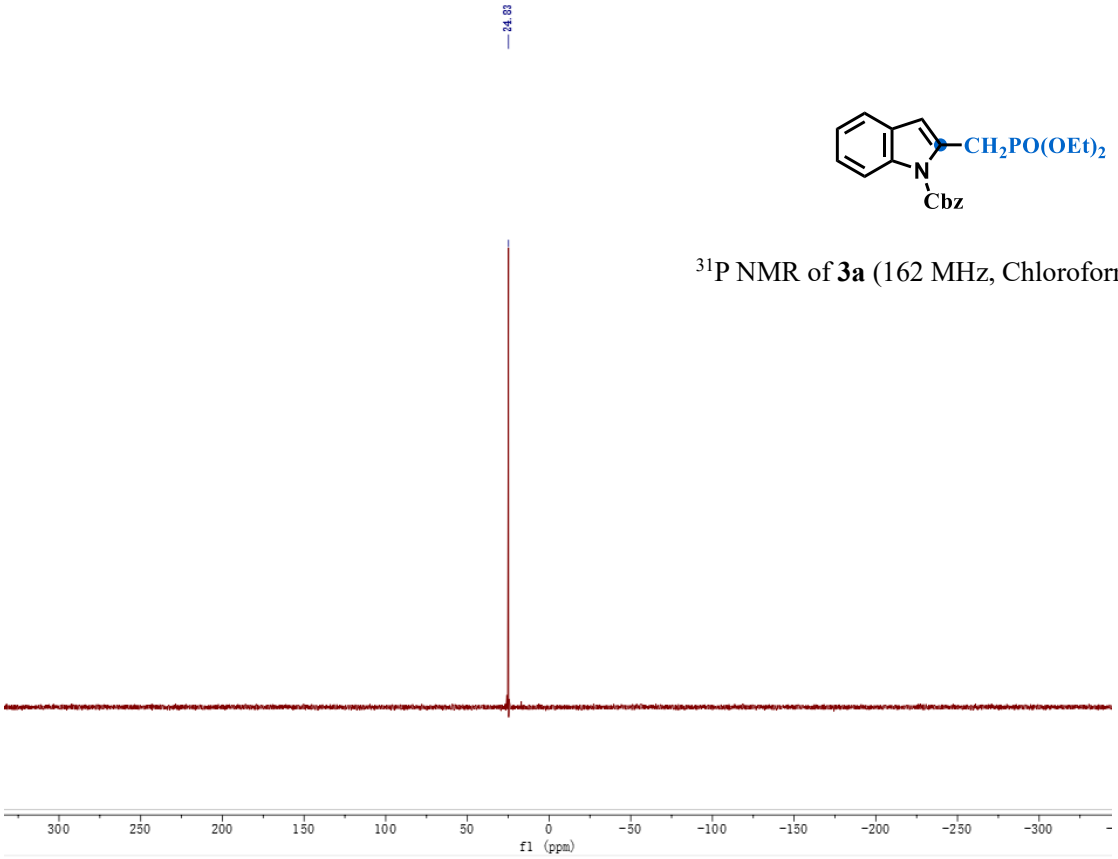
^{13}C NMR of **2'n** (101 MHz, Chloroform-*d*)



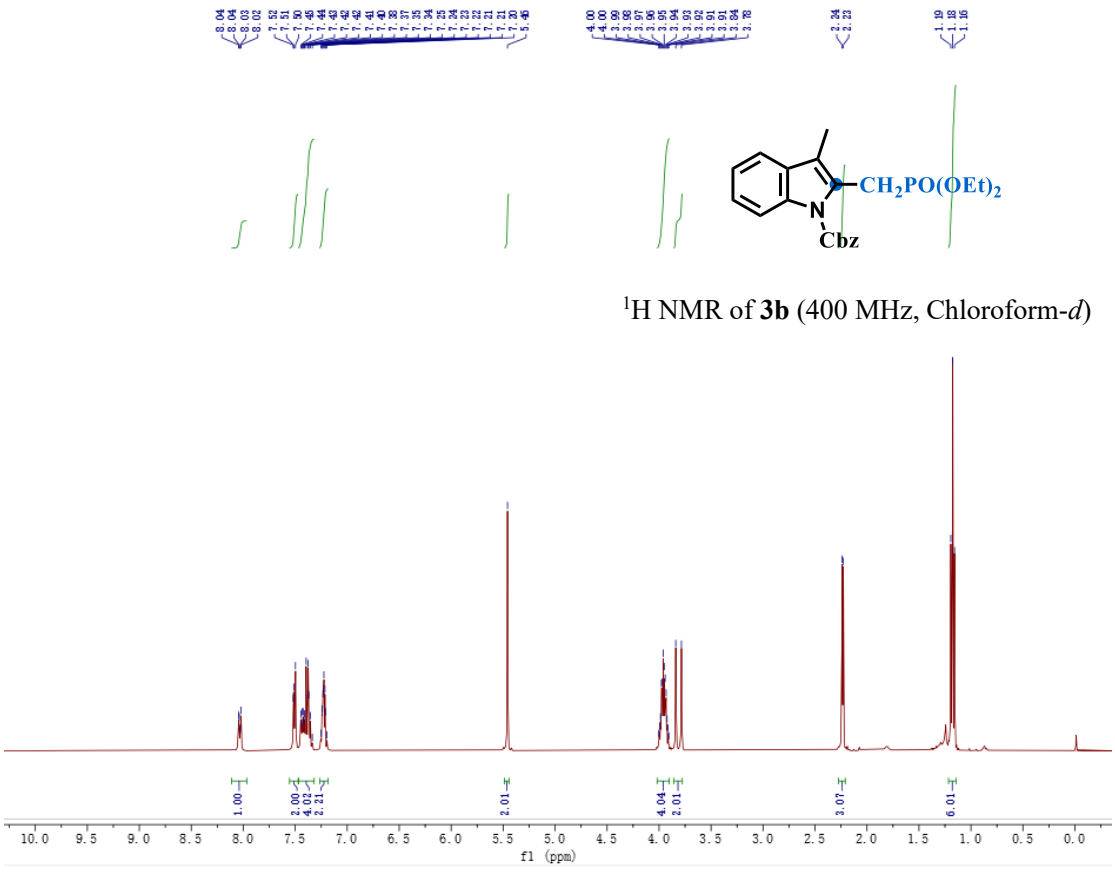
^{1}H NMR of **3a** (400 MHz, Chloroform-*d*)



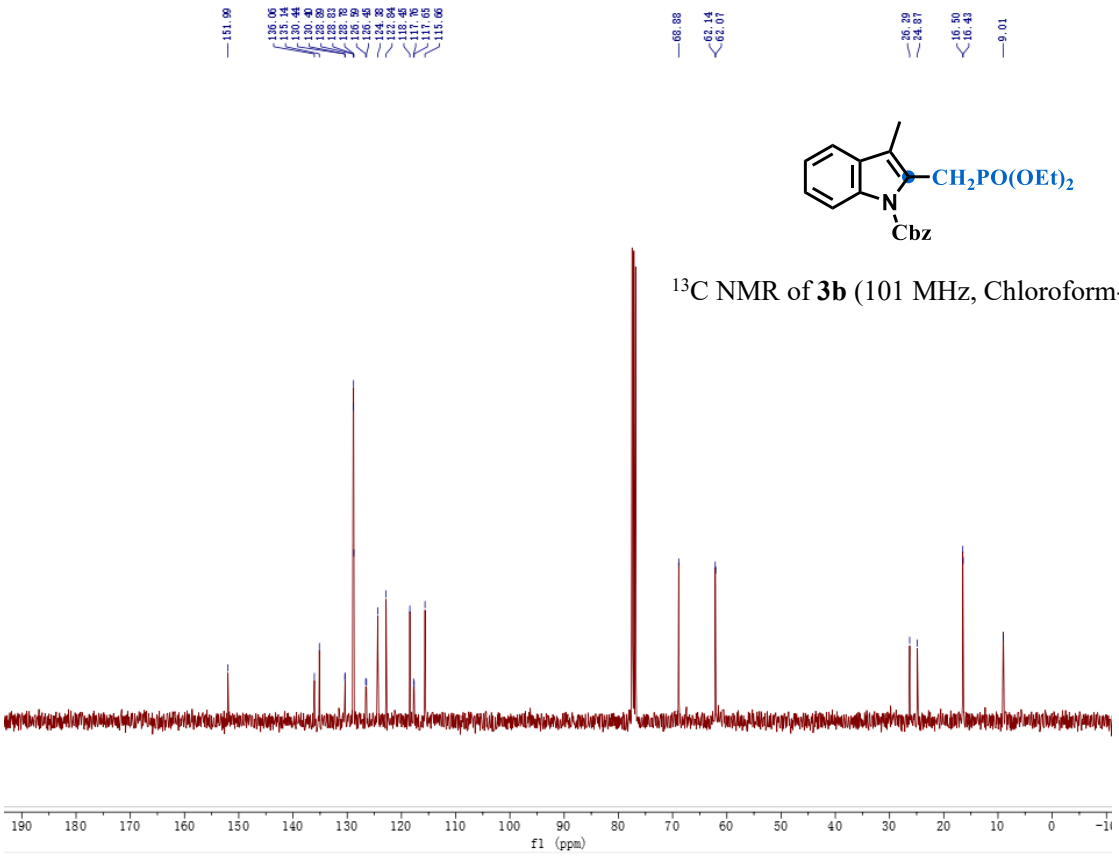
^{13}C NMR of **3a** (101 MHz, Chloroform-*d*)



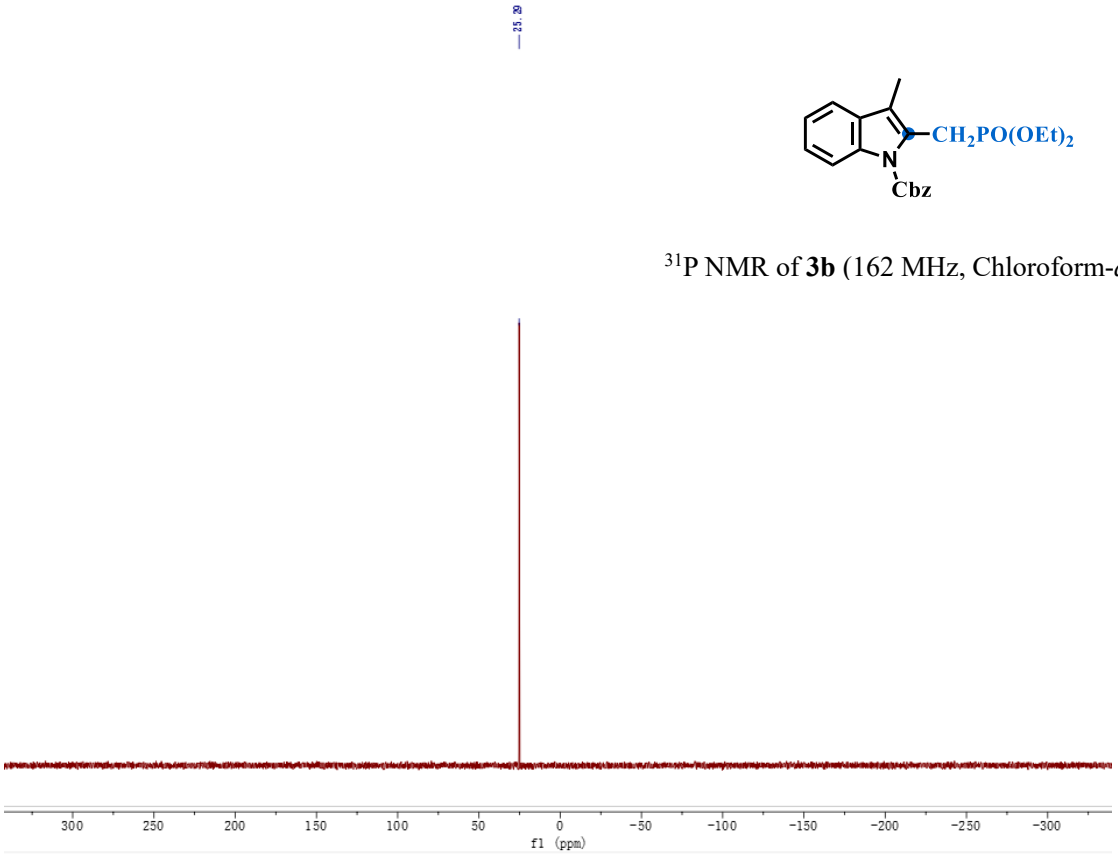
^{31}P NMR of **3a** (162 MHz, Chloroform-*d*)



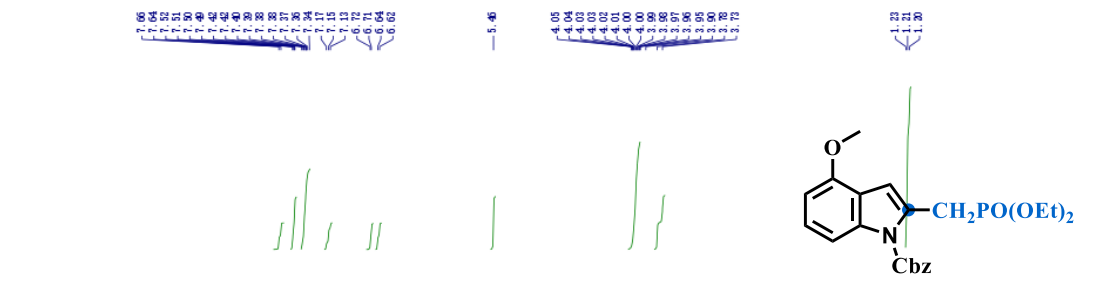
^{1}H NMR of **3b** (400 MHz, Chloroform-*d*)



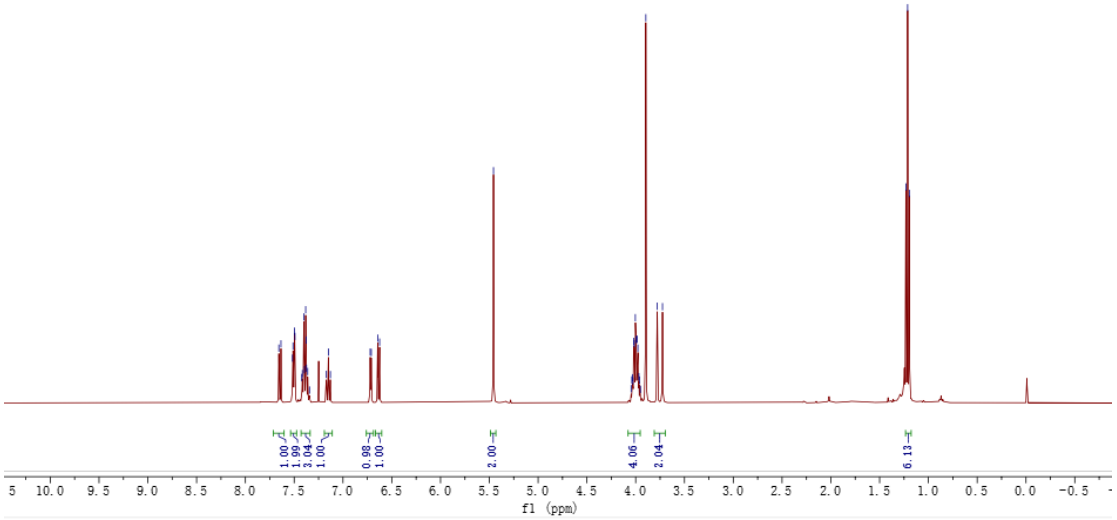
^{13}C NMR of **3b** (101 MHz, Chloroform-*d*)

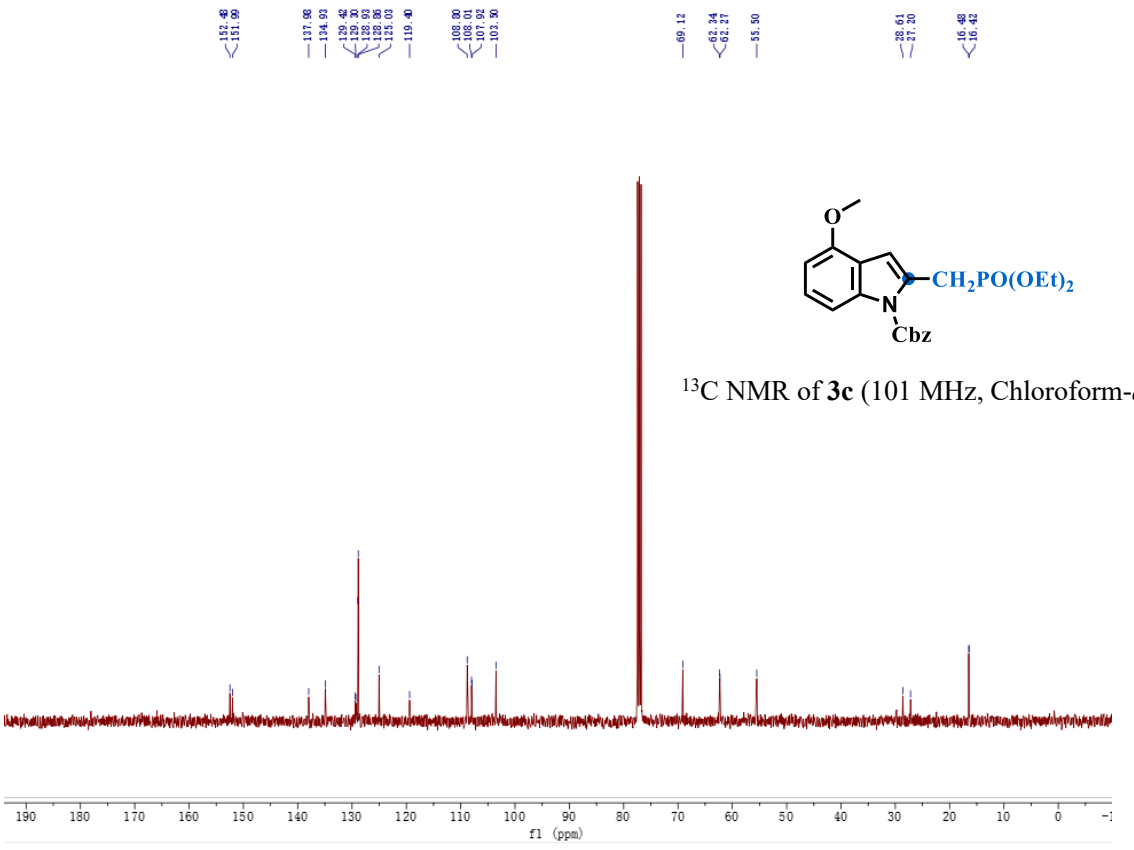


^{31}P NMR of **3b** (162 MHz, Chloroform-*d*)

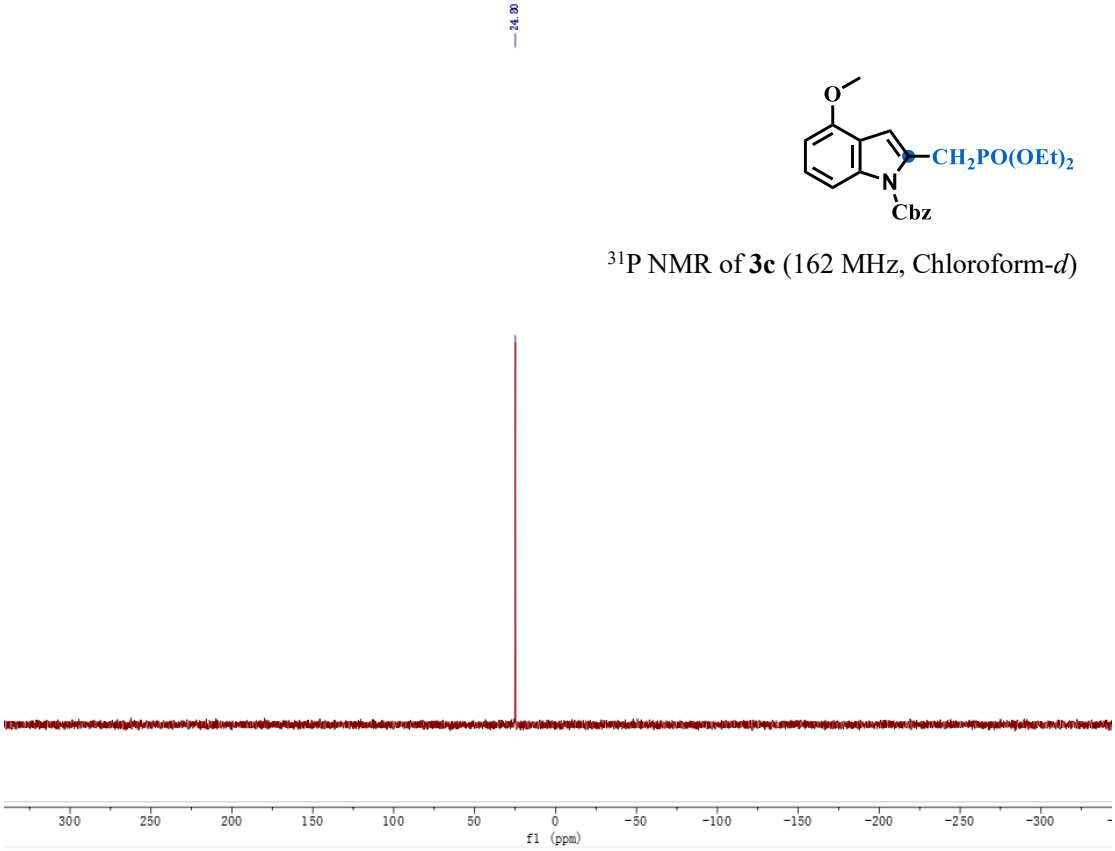


^{1}H NMR of **3c** (400 MHz, Chloroform-*d*)

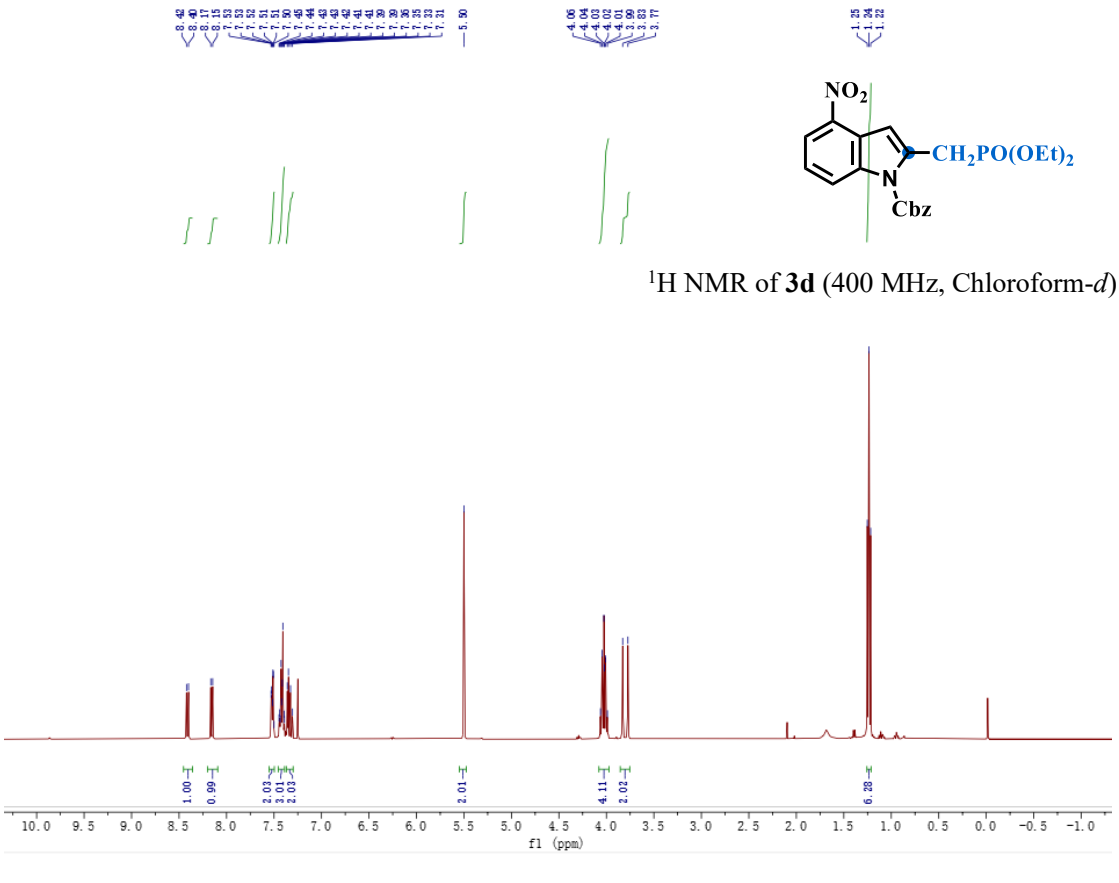




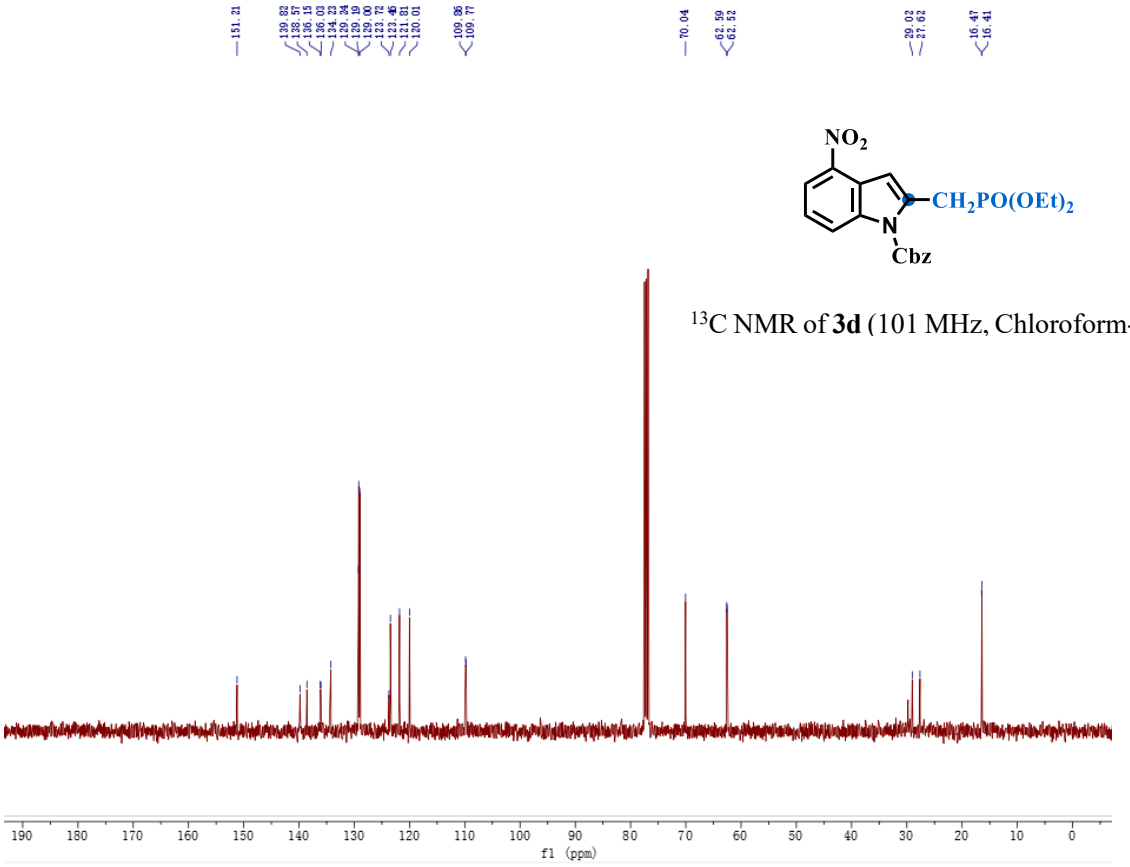
^{13}C NMR of **3c** (101 MHz, Chloroform-*d*)



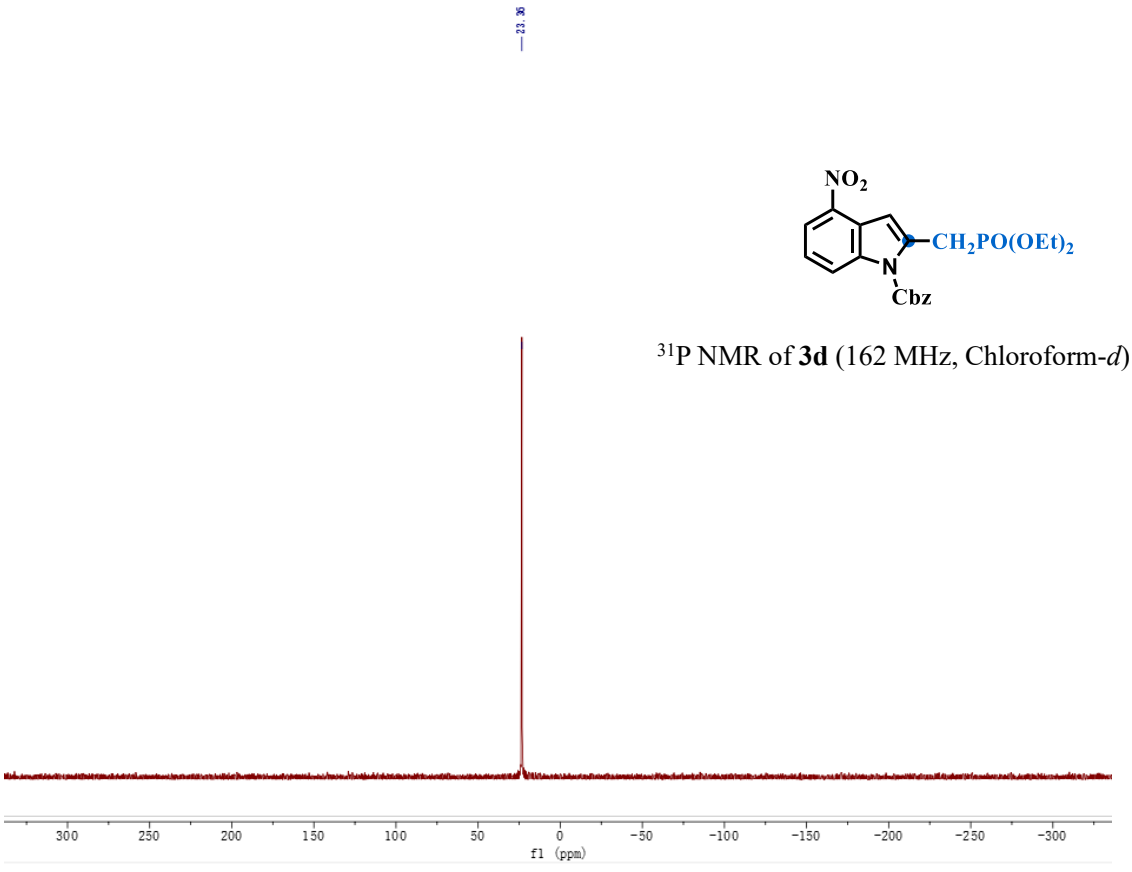
^{31}P NMR of **3c** (162 MHz, Chloroform-*d*)



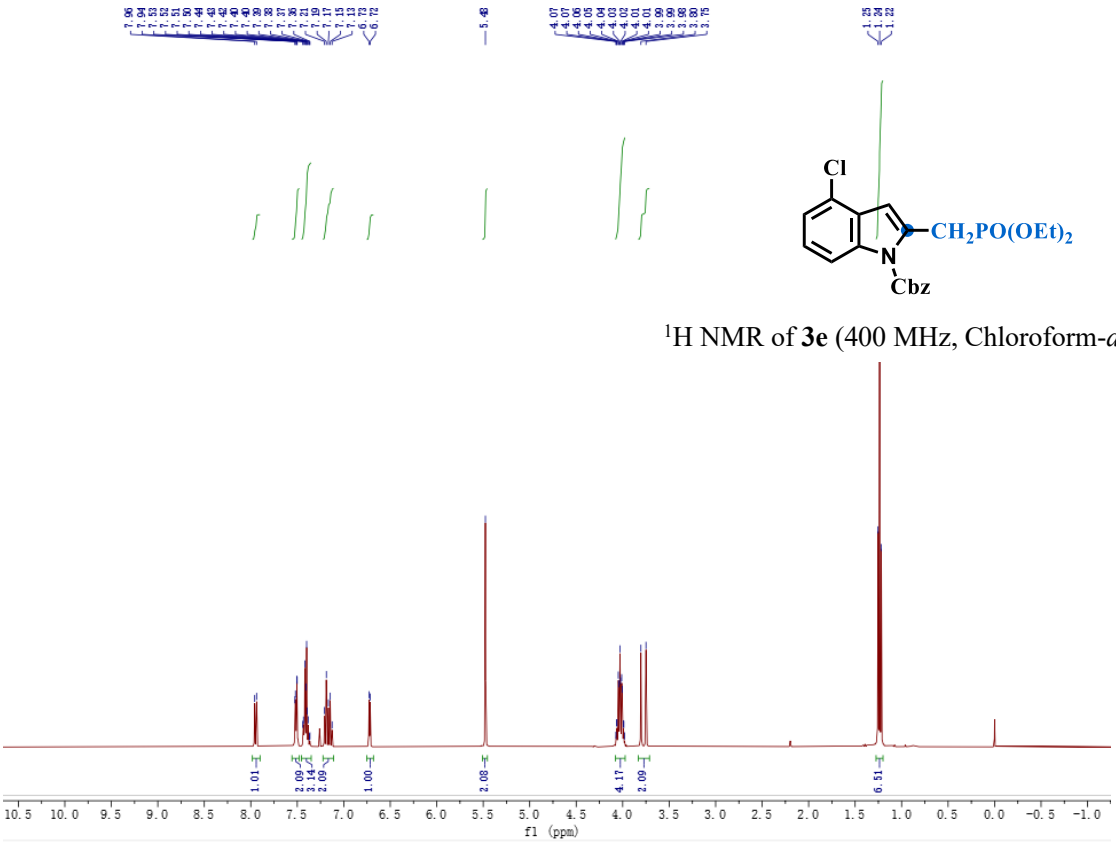
^{1}H NMR of **3d** (400 MHz, Chloroform-*d*)



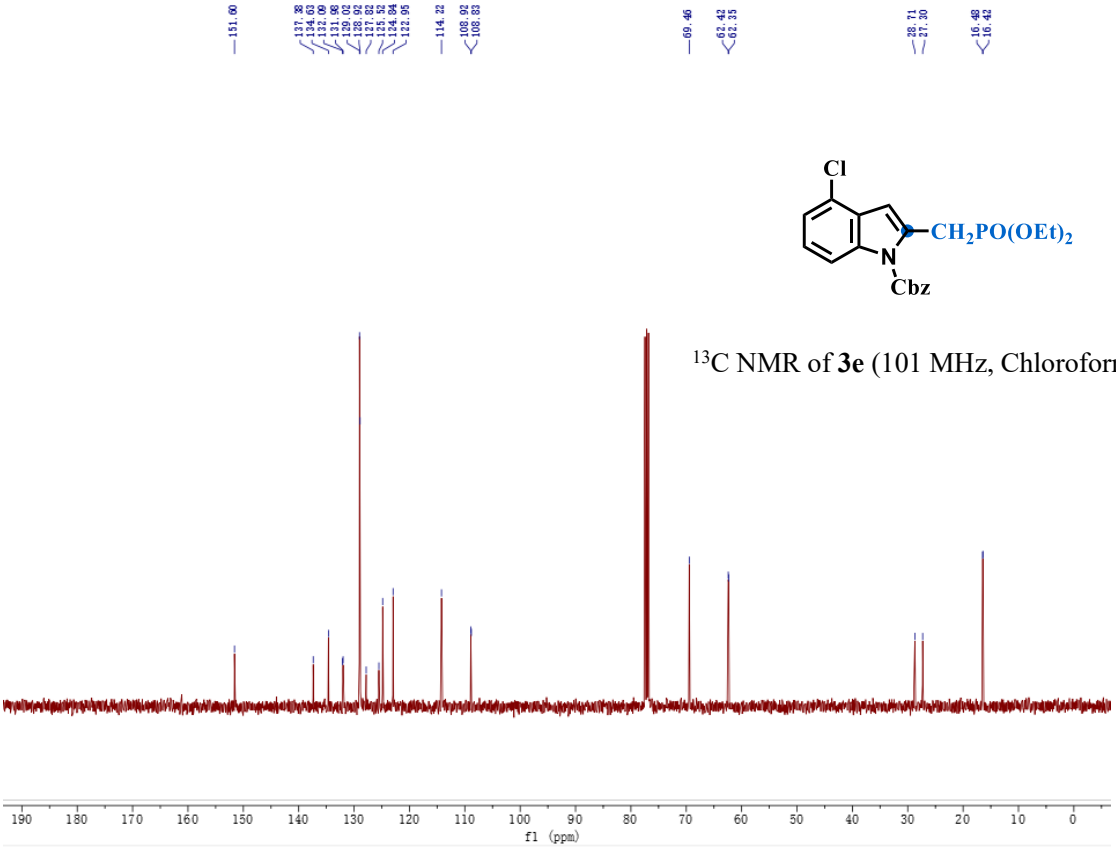
^{13}C NMR of **3d** (101 MHz, Chloroform-*d*)



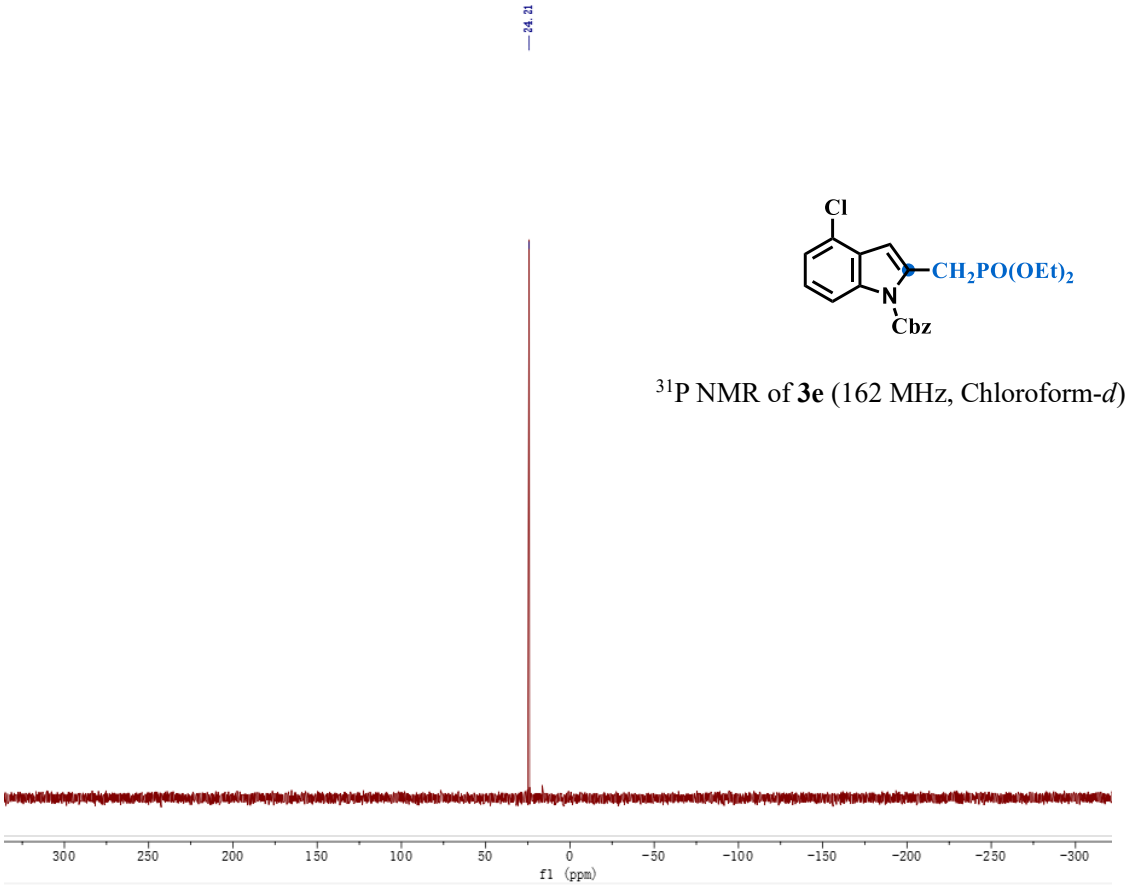
^{31}P NMR of **3d** (162 MHz, Chloroform-*d*)



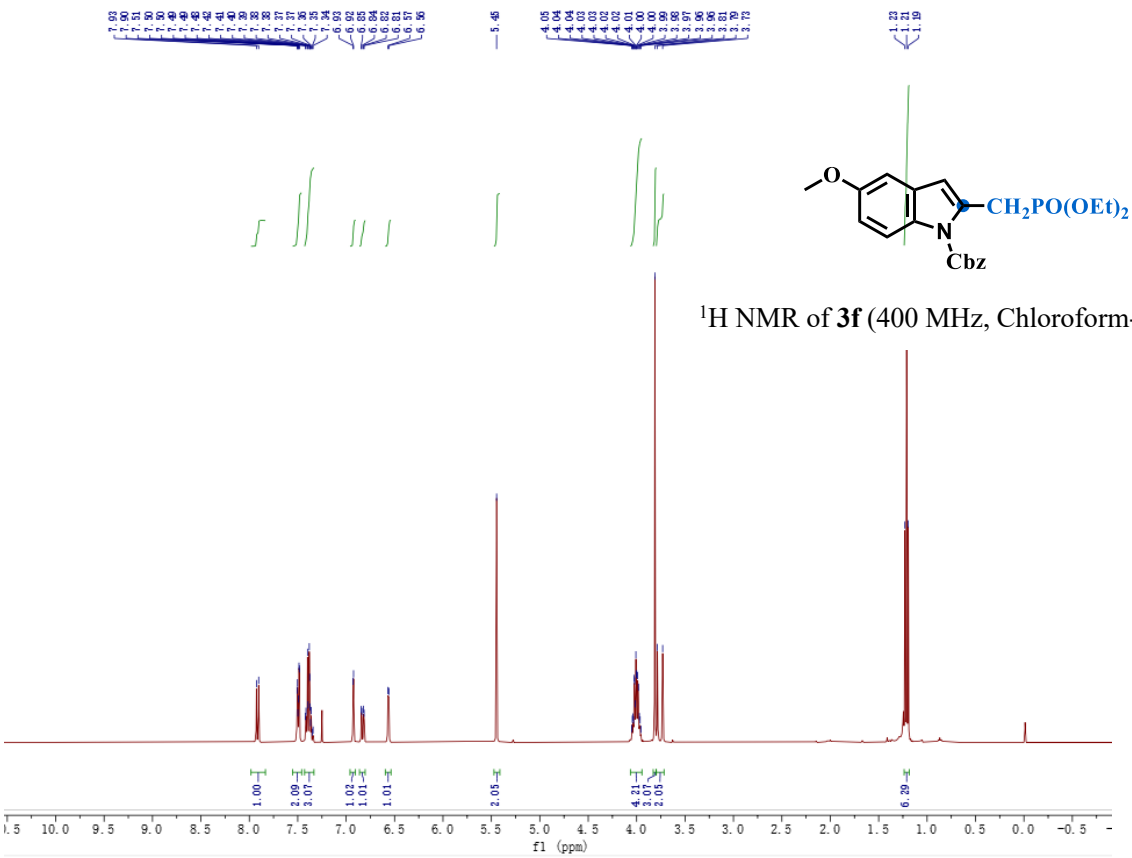
^{1}H NMR of **3e** (400 MHz, Chloroform-*d*)



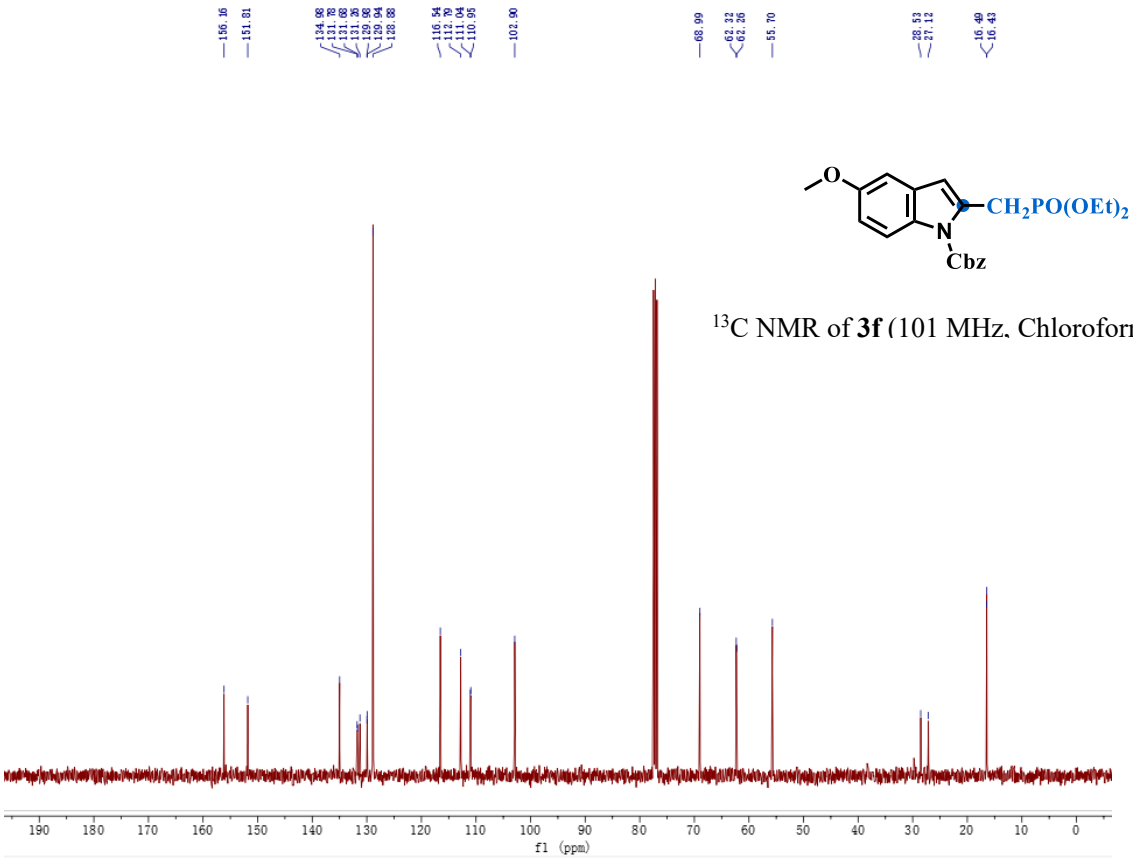
^{13}C NMR of **3e** (101 MHz, Chloroform-*d*)



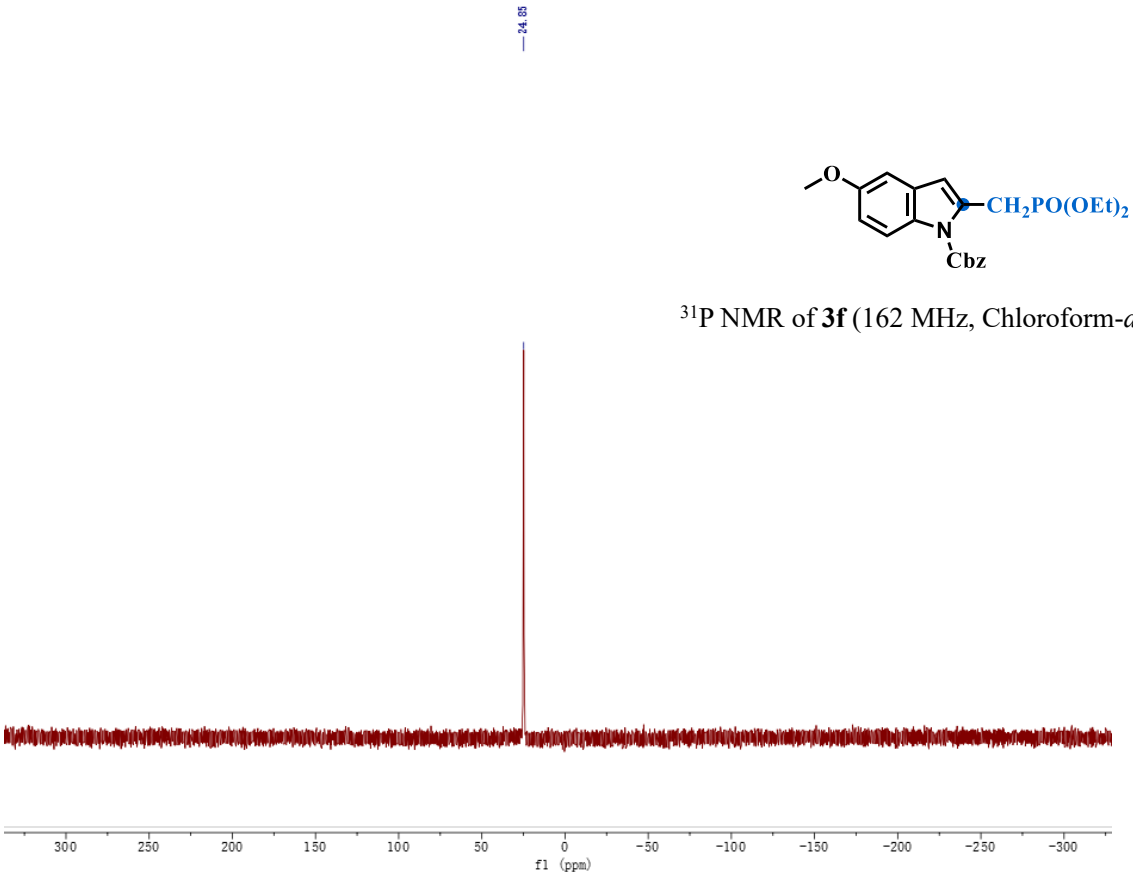
^{31}P NMR of **3e** (162 MHz, Chloroform-*d*)



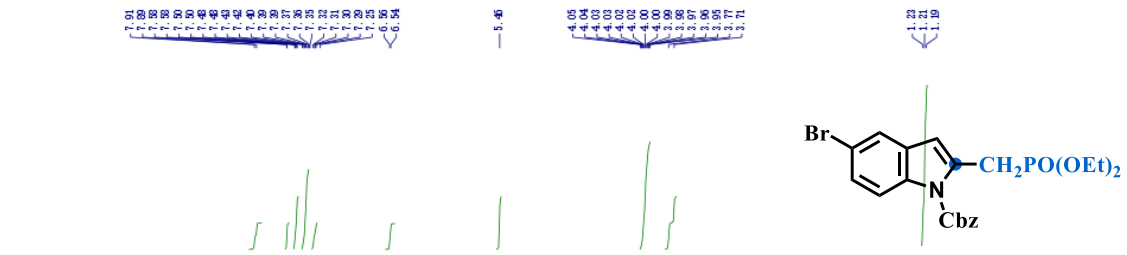
^{1}H NMR of **3f** (400 MHz, Chloroform-*d*)



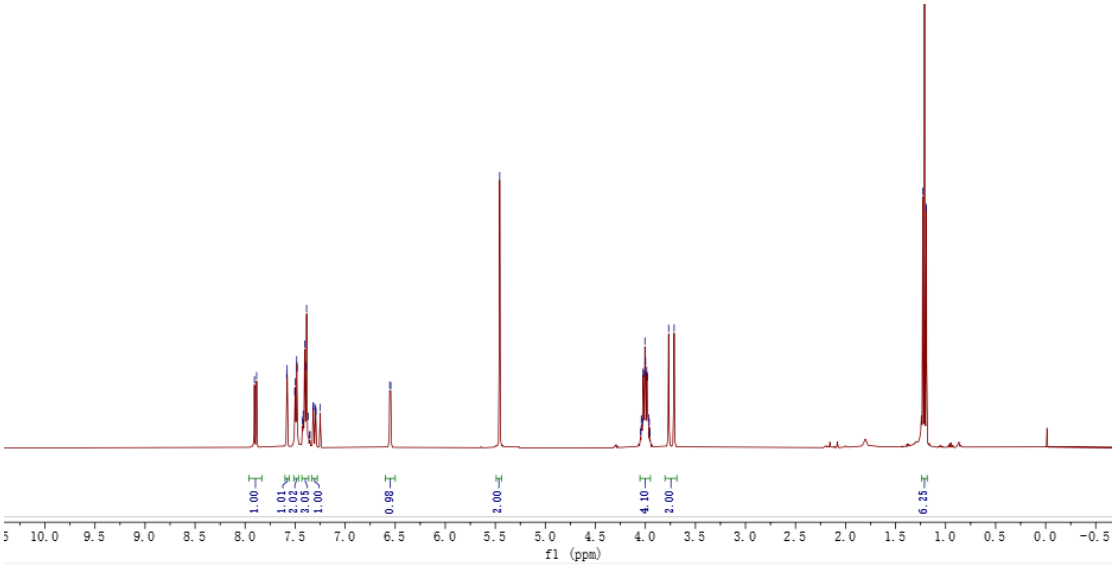
^{13}C NMR of **3f** (101 MHz, Chloroform-*d*)

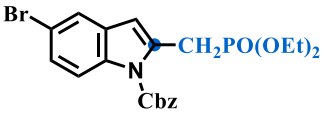


^{31}P NMR of **3f** (162 MHz, Chloroform-*d*)

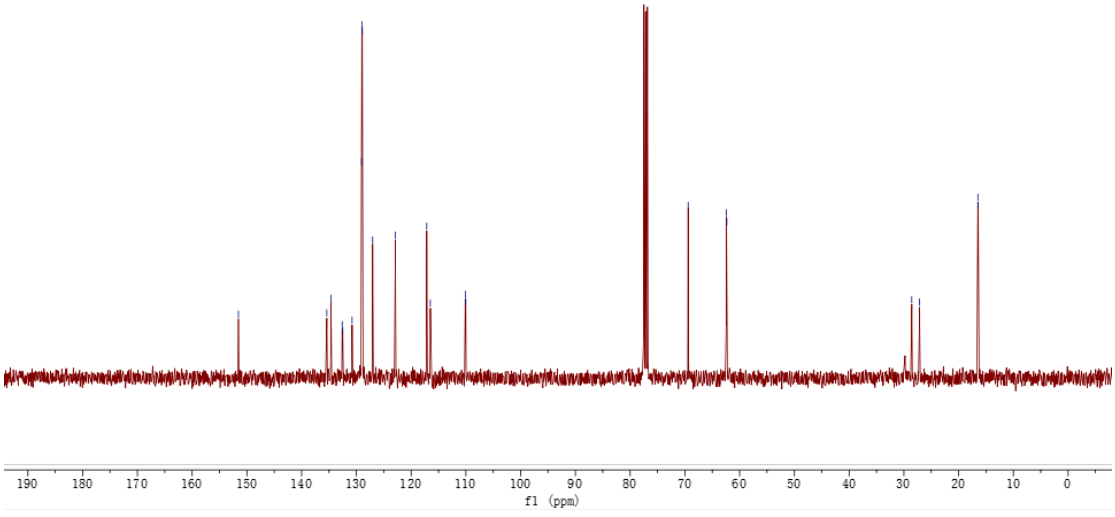


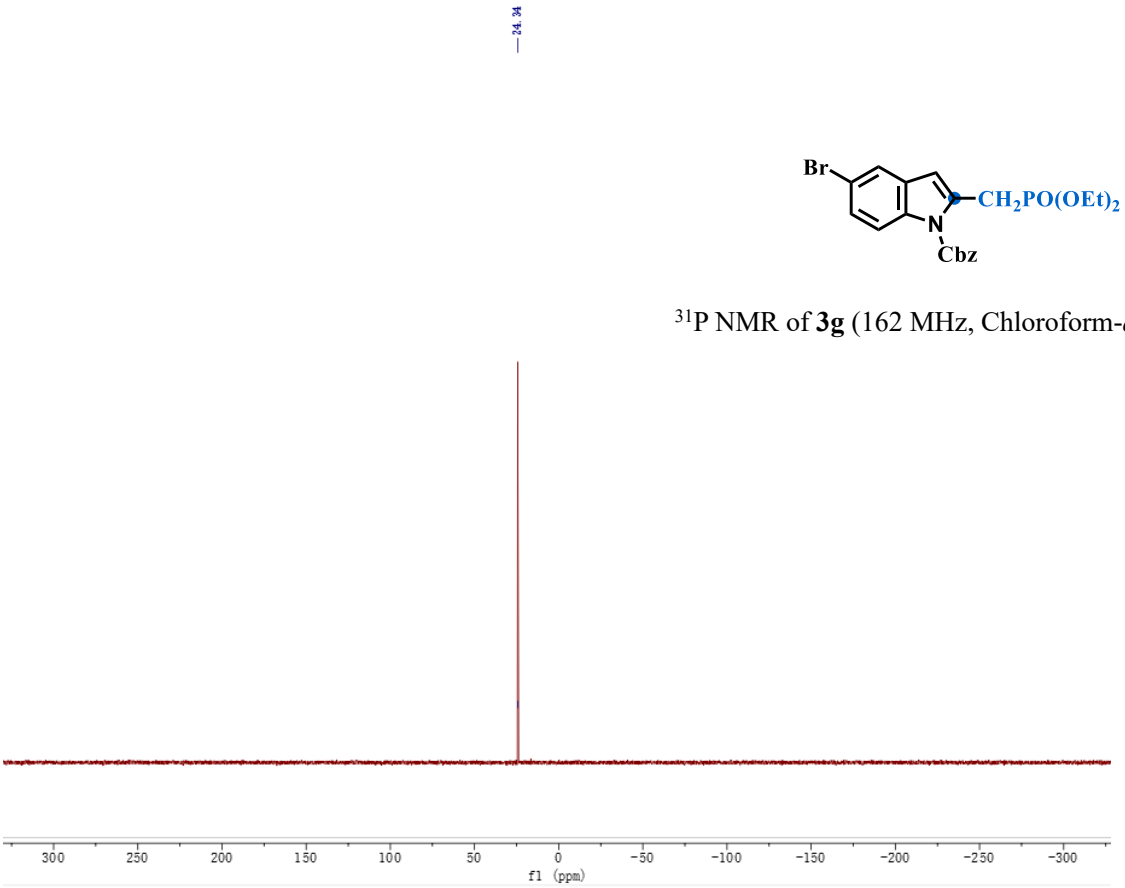
^{1}H NMR of **3g** (400 MHz, Chloroform-*d*)



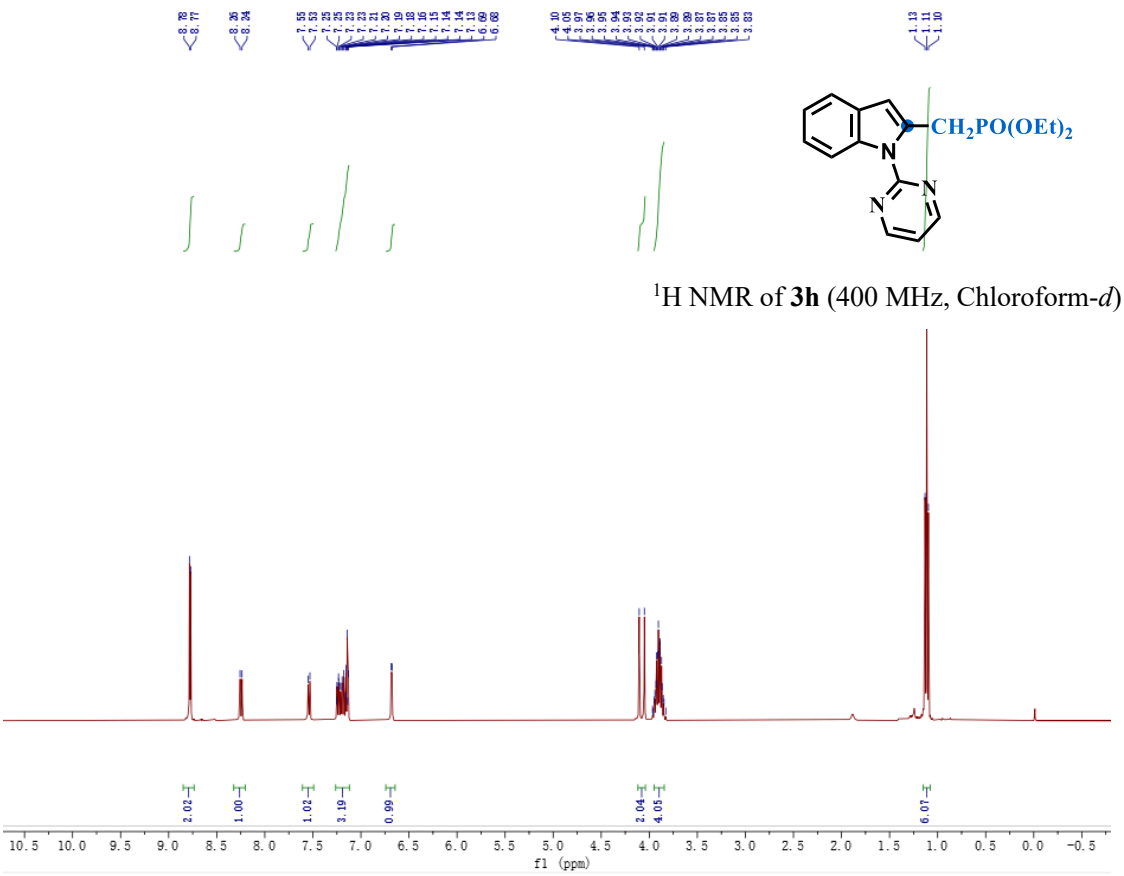


^{13}C NMR of **3g** (101 MHz, Chloroform-*d*)

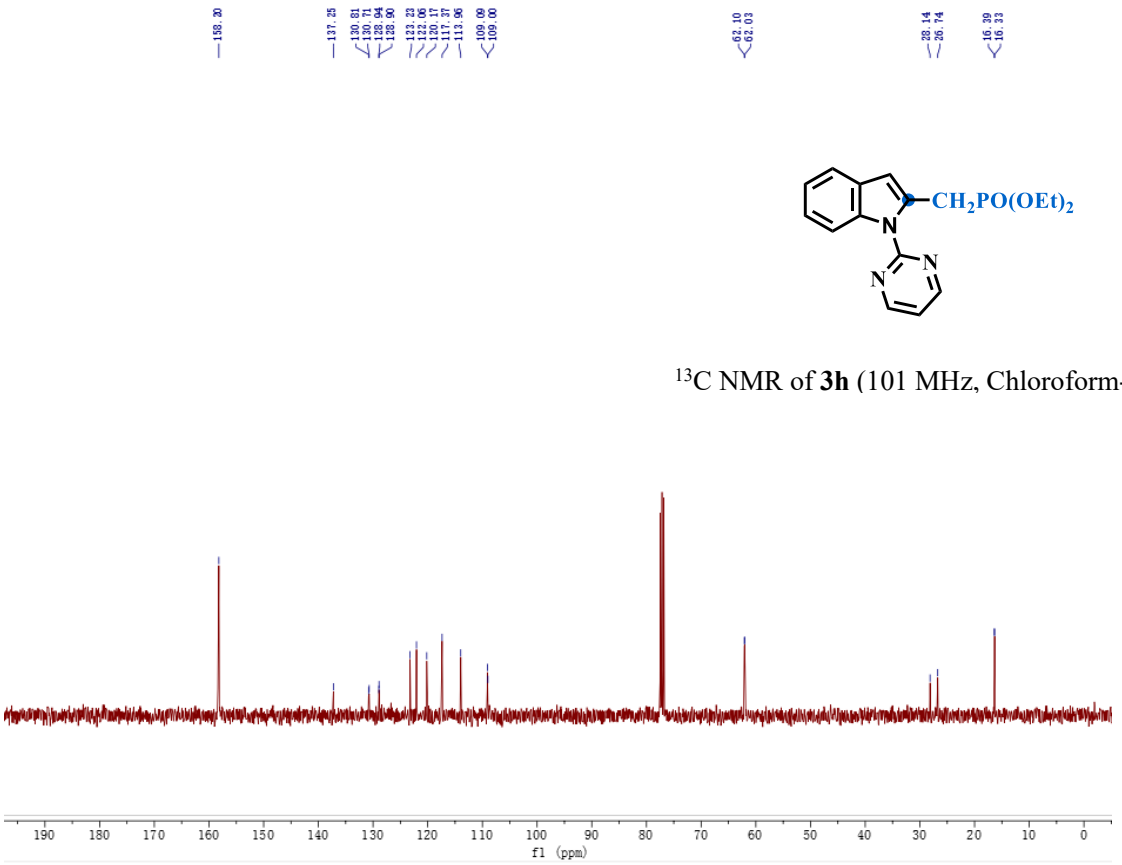




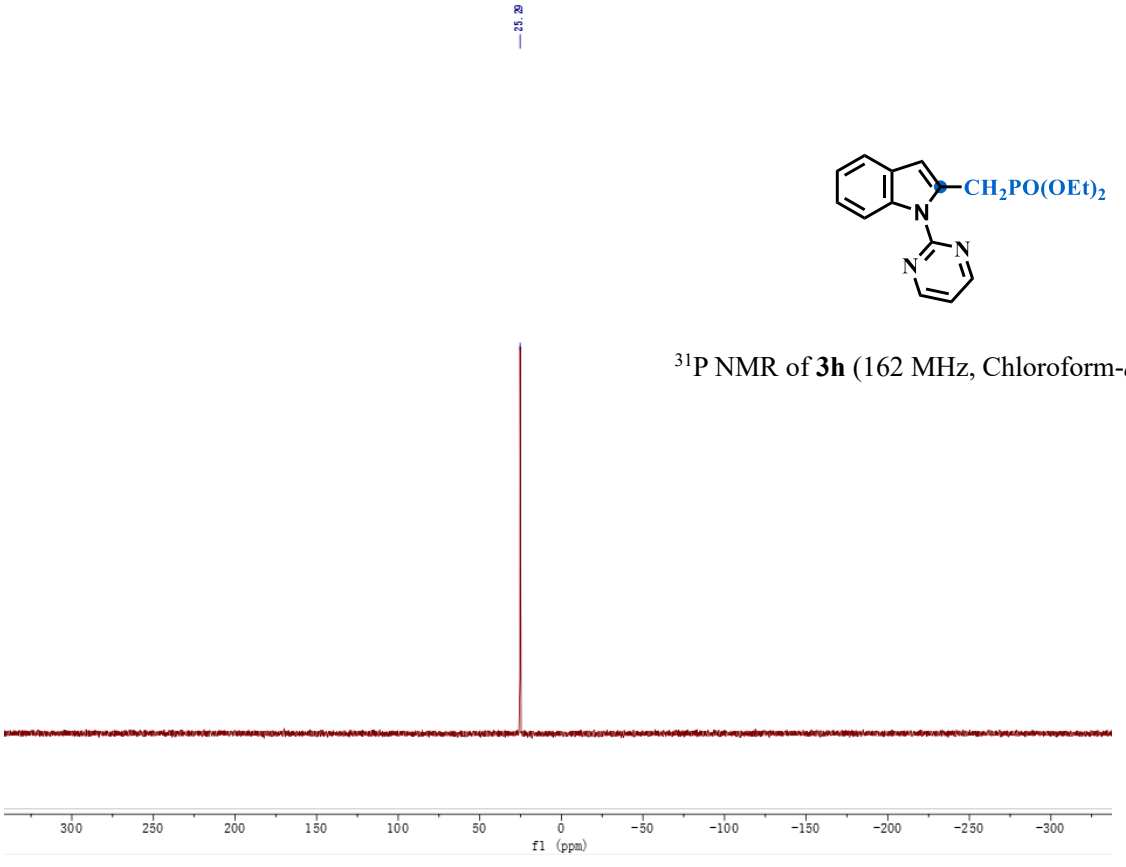
^{31}P NMR of **3g** (162 MHz, Chloroform-*d*)



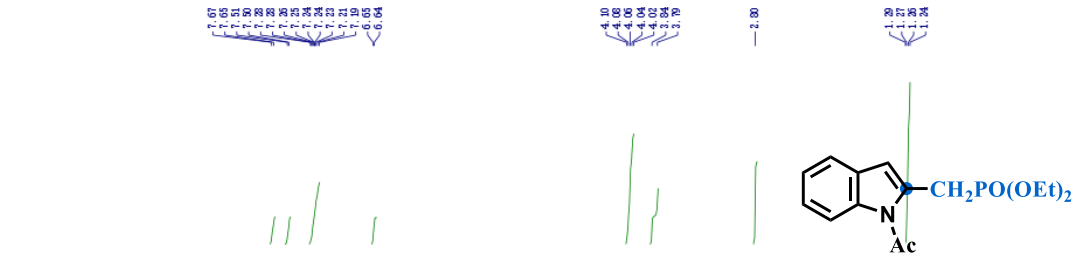
^{1}H NMR of **3h** (400 MHz, Chloroform-*d*)



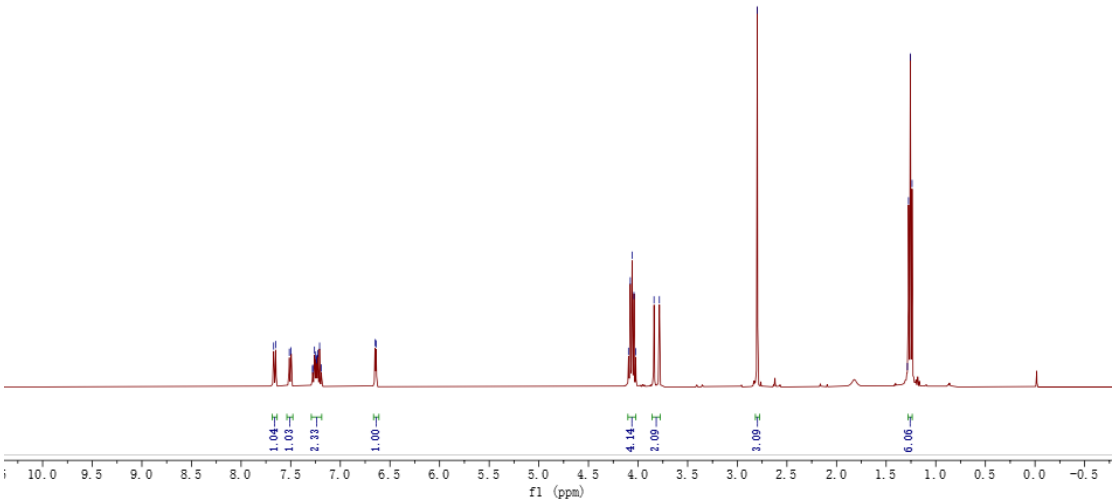
^{13}C NMR of **3h** (101 MHz, Chloroform-*d*)

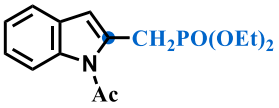


^{31}P NMR of **3h** (162 MHz, Chloroform-*d*)

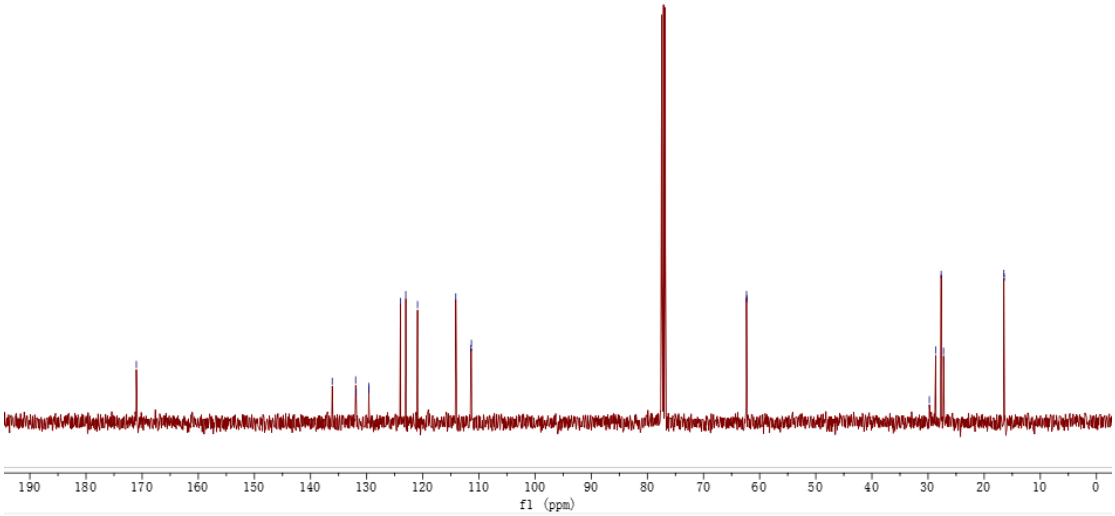


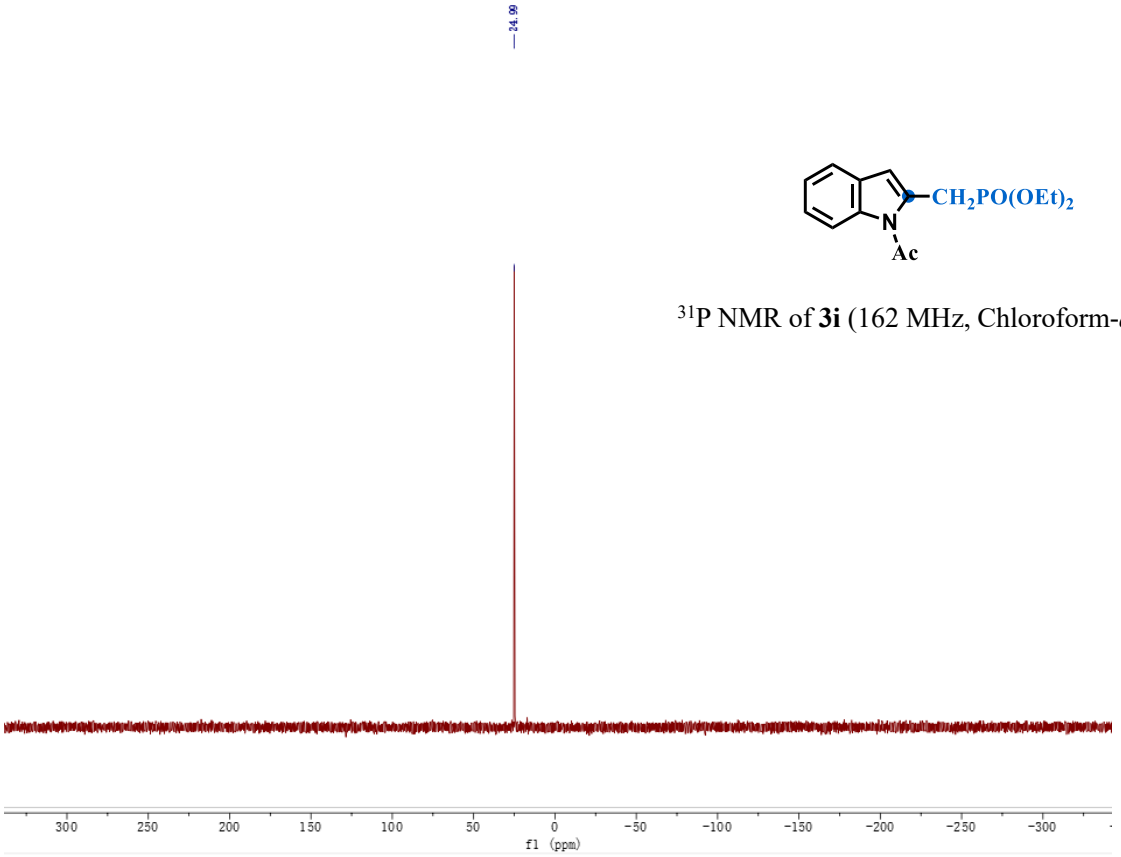
^{1}H NMR of **3i** (400 MHz, Chloroform-*d*)



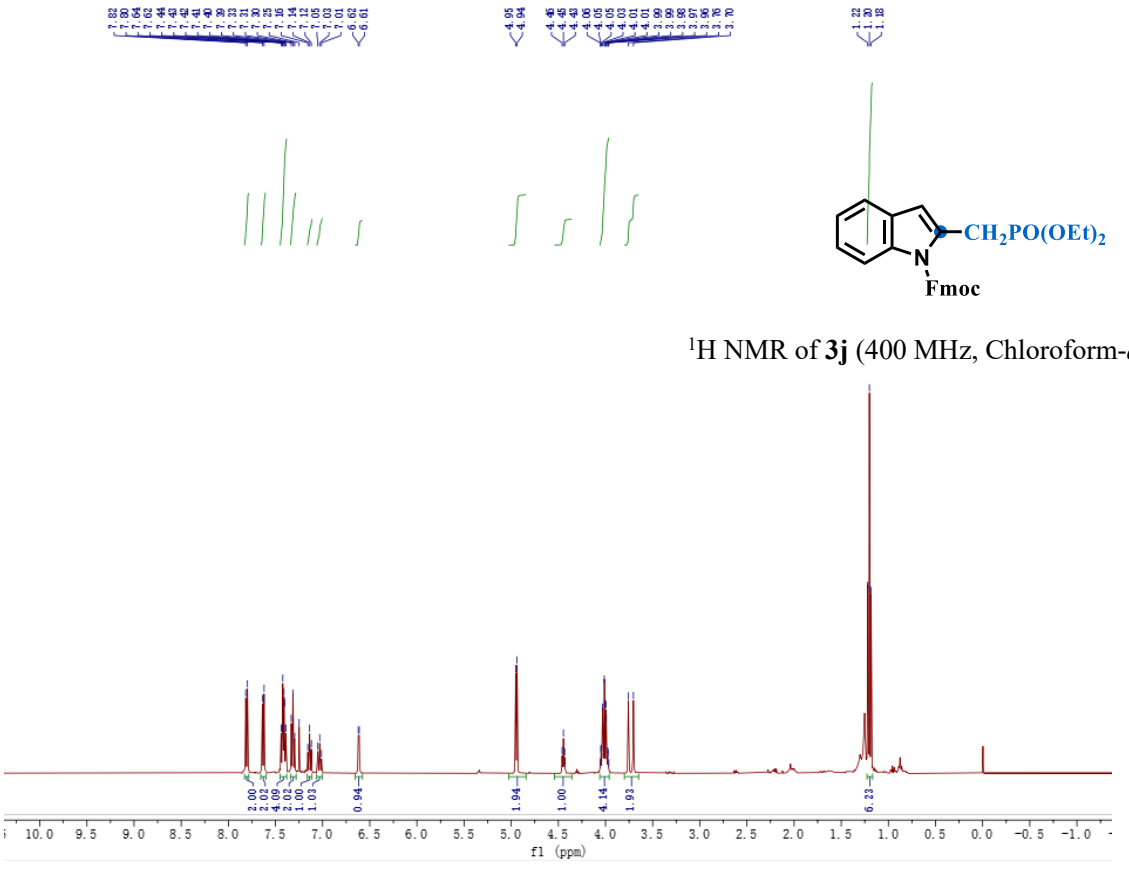


^{13}C NMR of **3i** (101 MHz, Chloroform-*d*)

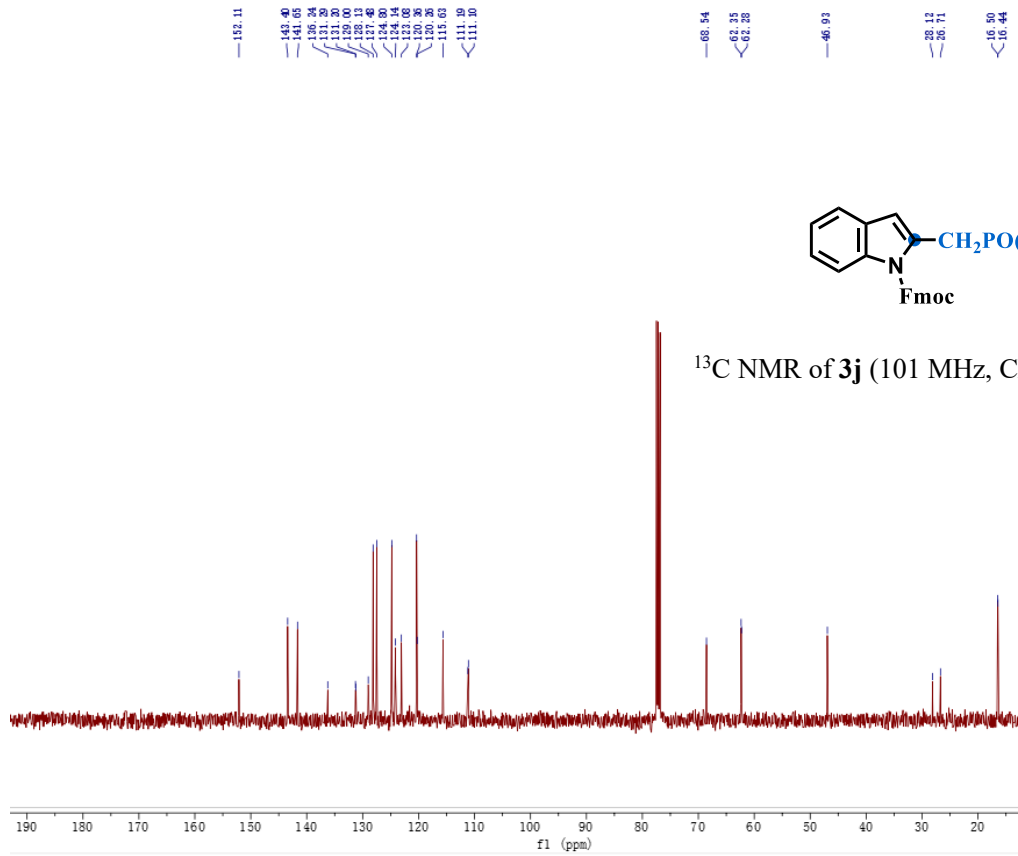




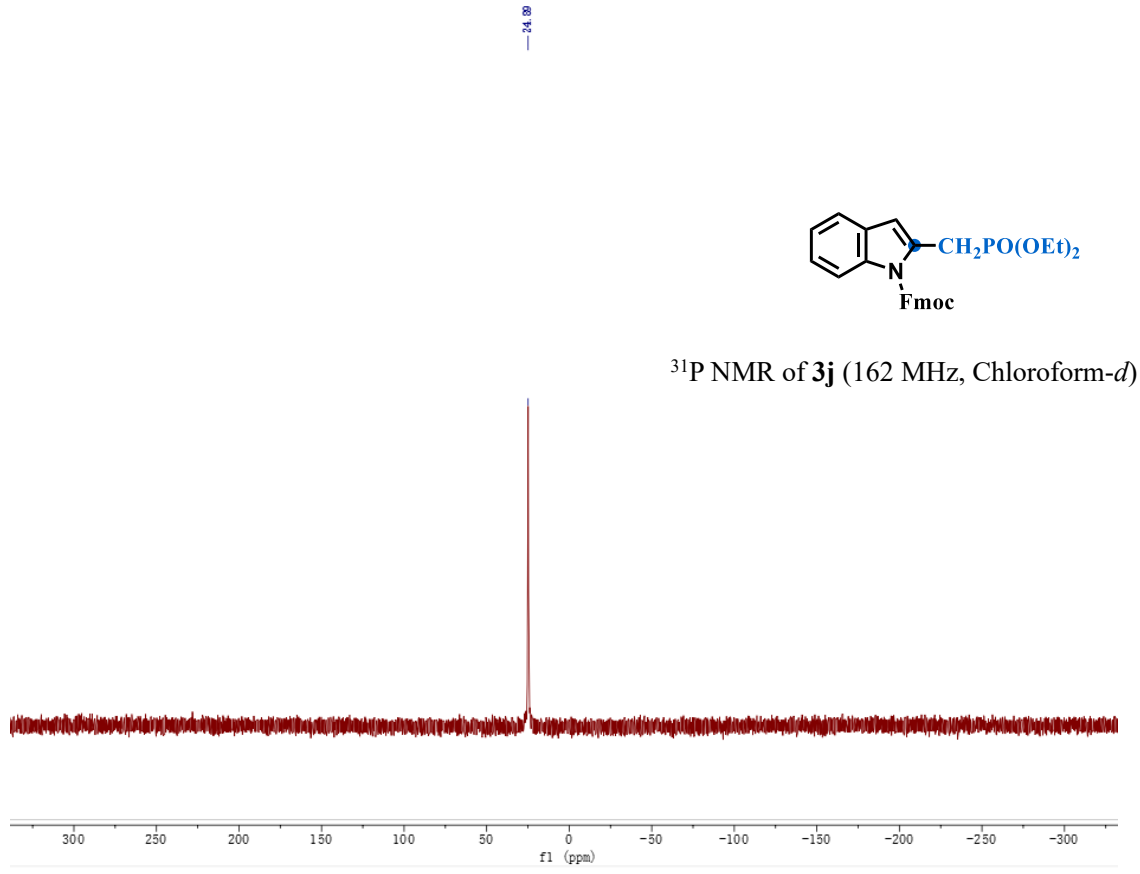
^{31}P NMR of **3i** (162 MHz, Chloroform-*d*)



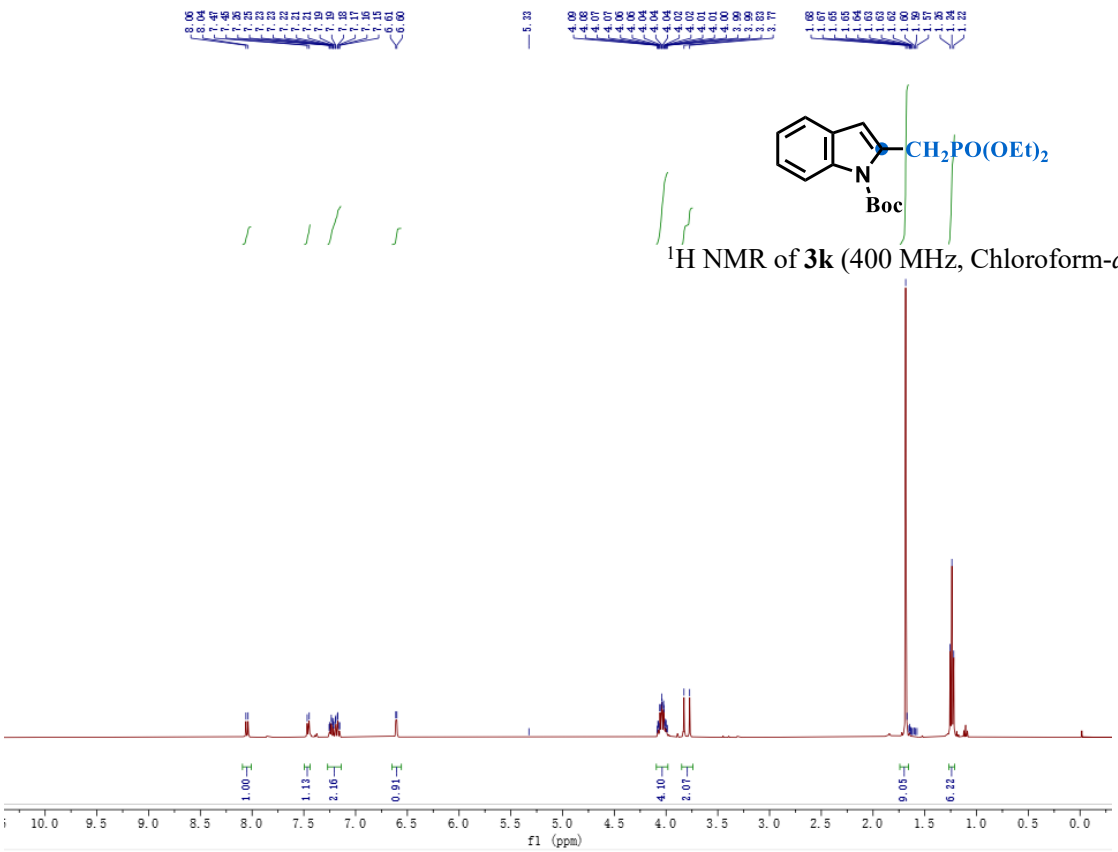
^{1}H NMR of **3j** (400 MHz, Chloroform-*d*)



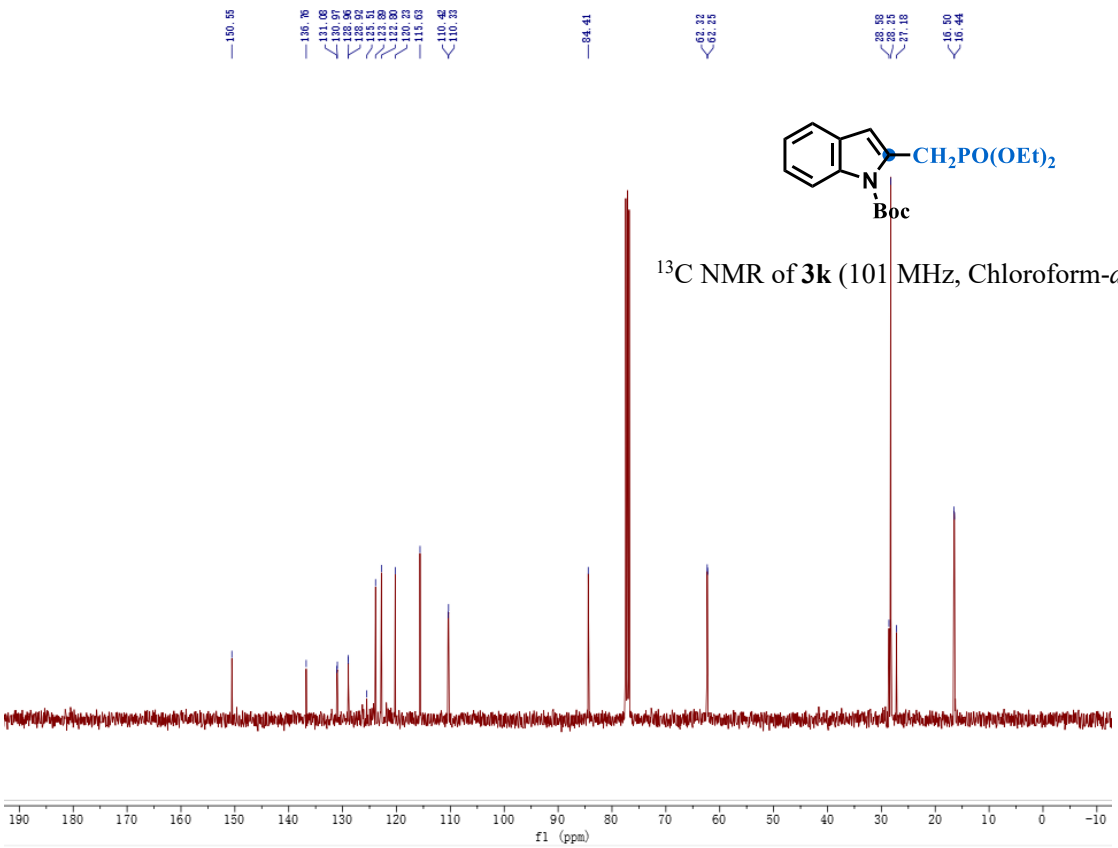
^{13}C NMR of **3j** (101 MHz, Chloroform-*d*)



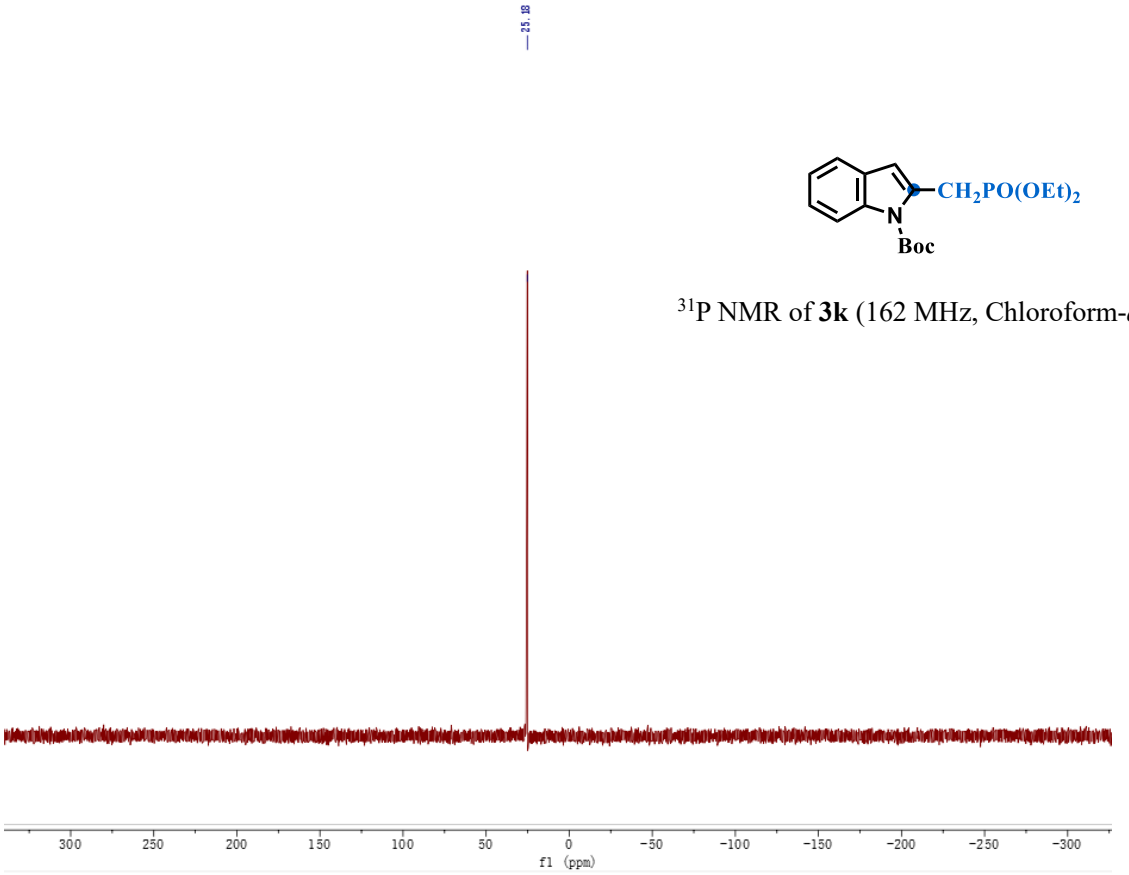
^{31}P NMR of **3j** (162 MHz, Chloroform-*d*)



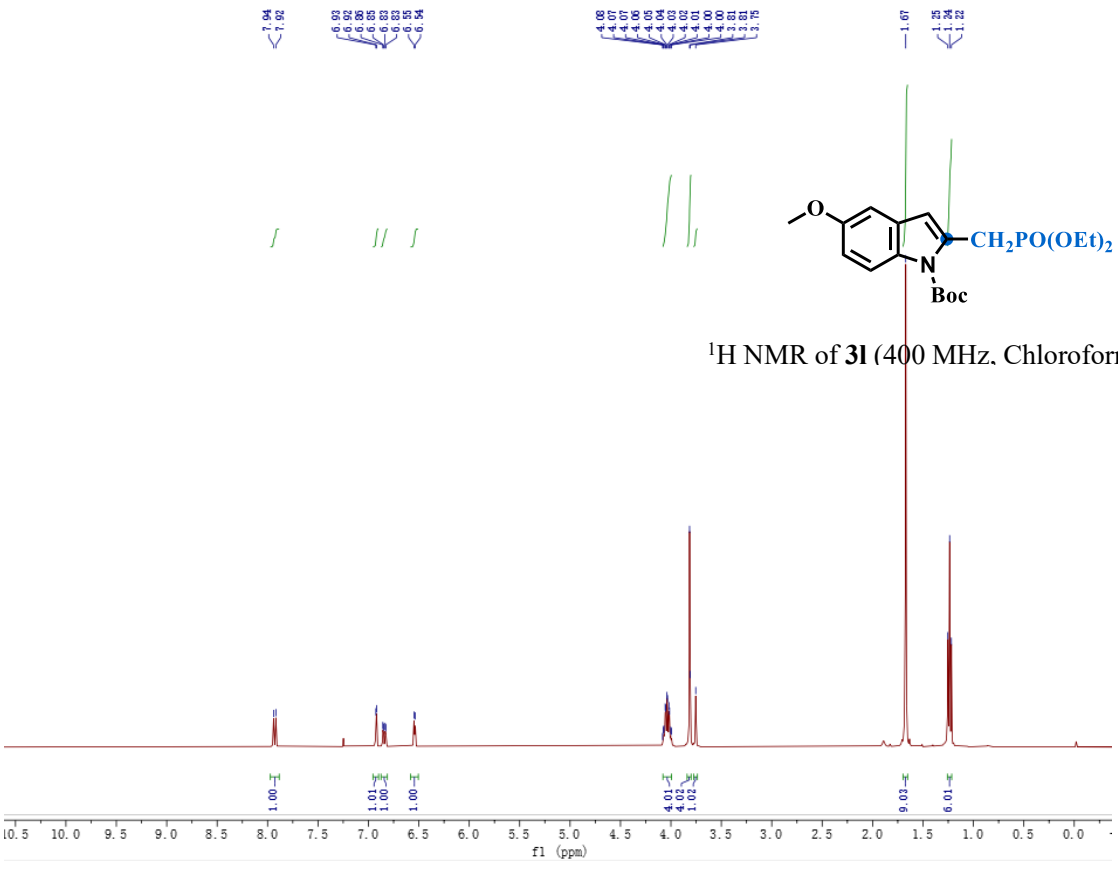
^{1}H NMR of **3k** (400 MHz, Chloroform-*d*)



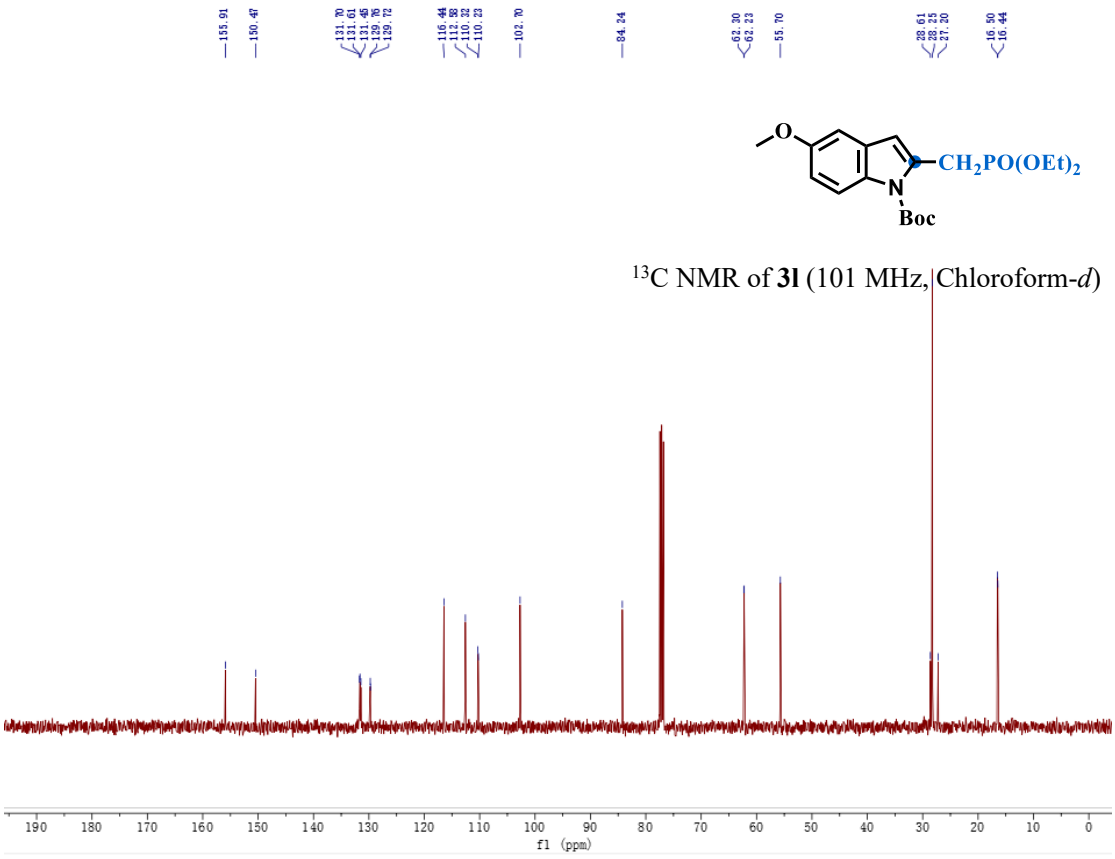
^{13}C NMR of **3k** (101 MHz, Chloroform-*d*)



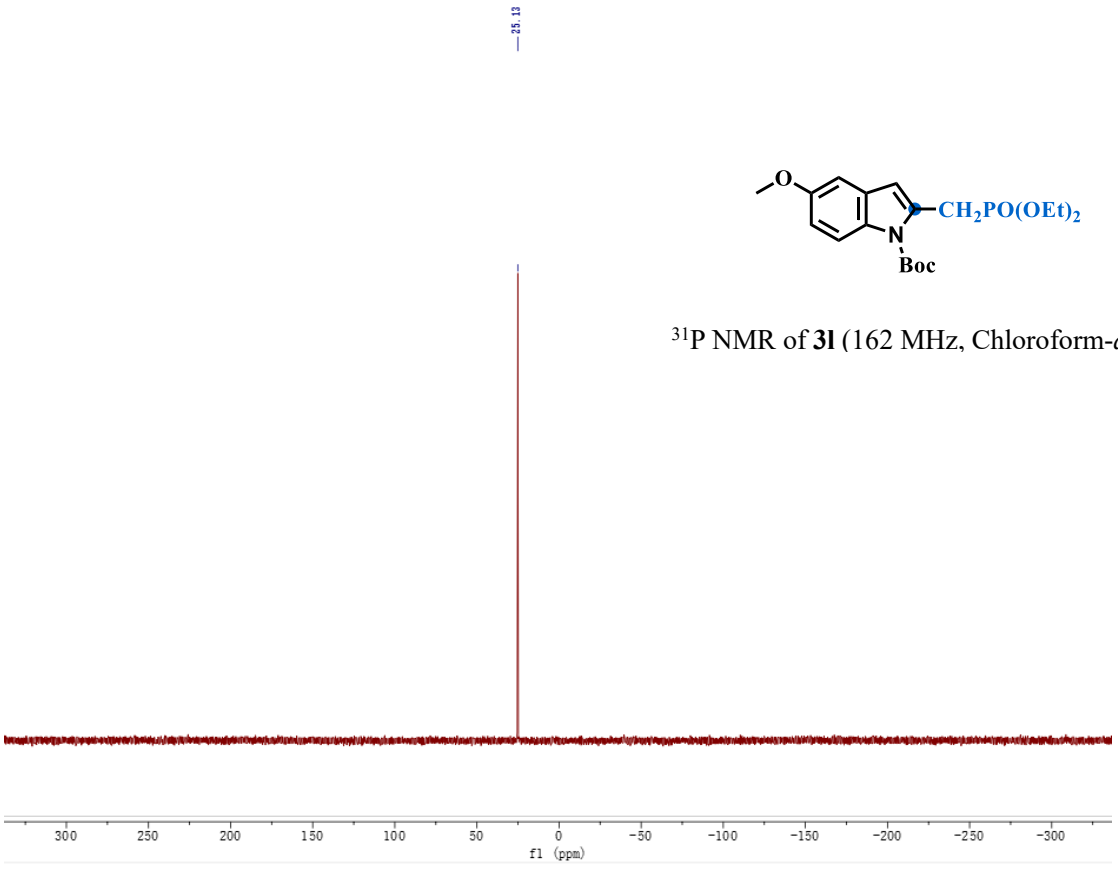
^{31}P NMR of **3k** (162 MHz, Chloroform-*d*)



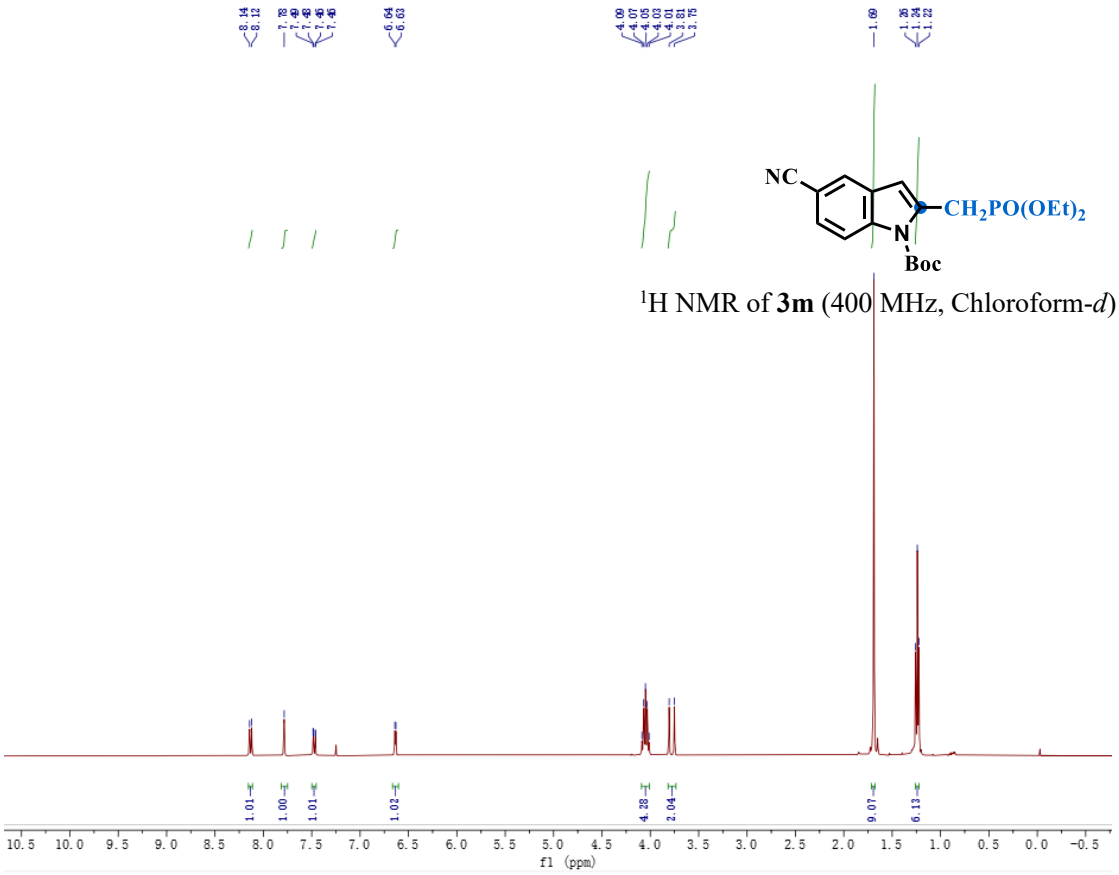
^{1}H NMR of **3l** (400 MHz, Chloroform-*d*)



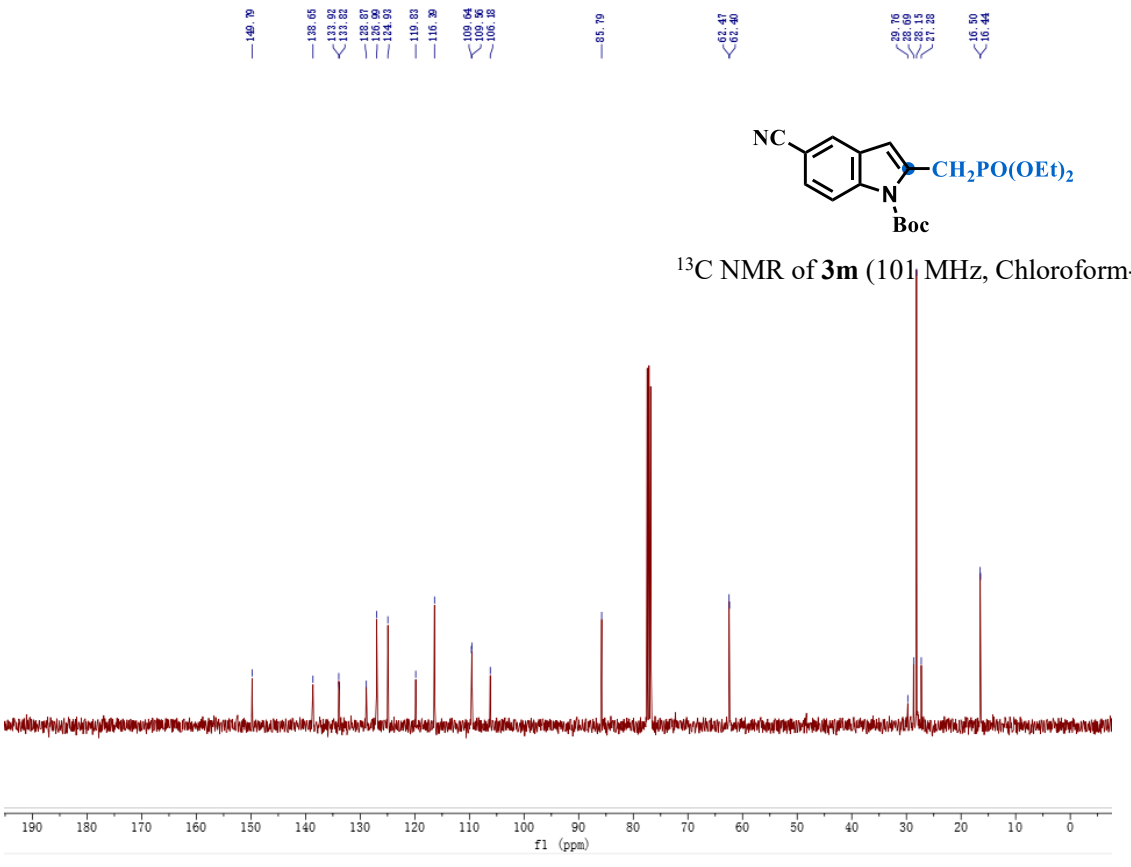
^{13}C NMR of **3l** (101 MHz, Chloroform-*d*)



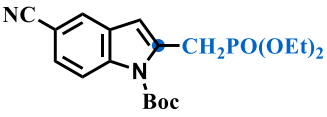
^{31}P NMR of **3l** (162 MHz, Chloroform-*d*)



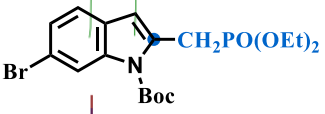
^{1}H NMR of **3m** (400 MHz, Chloroform-*d*)



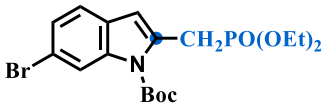
^{13}C NMR of **3m** (101 MHz, Chloroform-*d*)



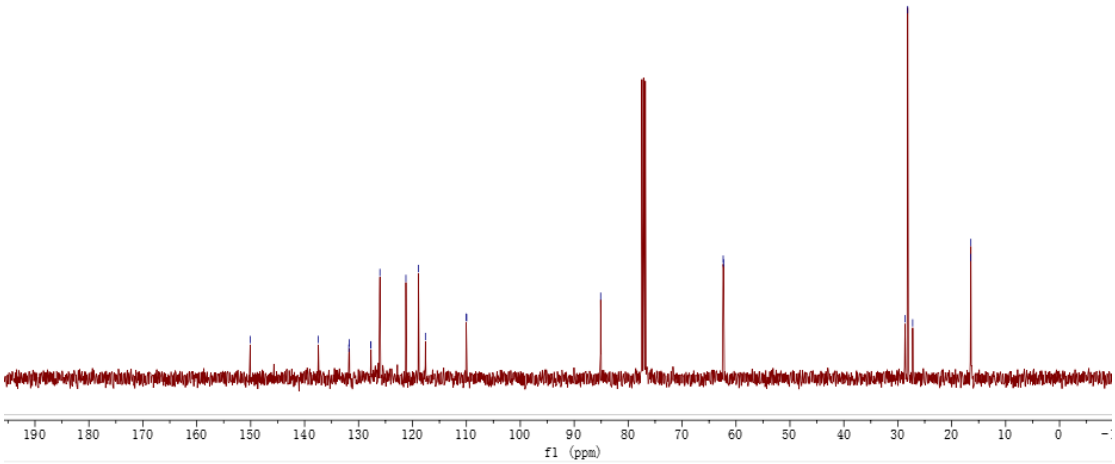
^{31}P NMR of **3m** (162 MHz, Chloroform-*d*)

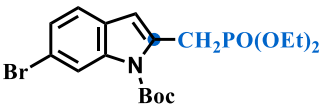


^{1}H NMR of **3n** (400 MHz, Chloroform-*d*)

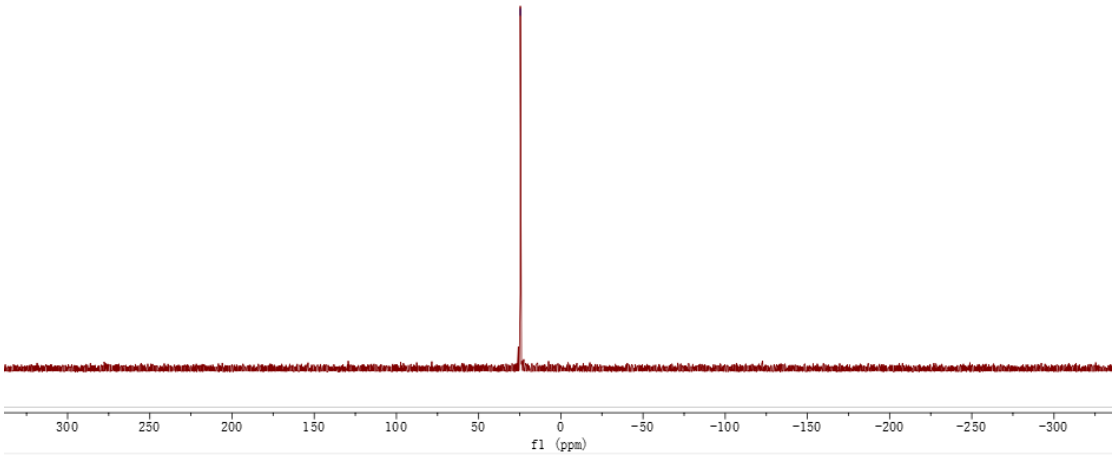


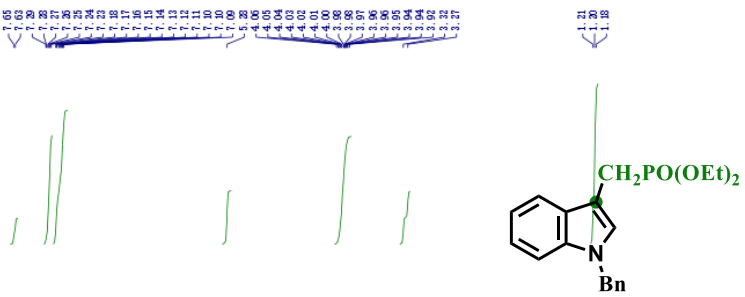
^{13}C NMR of **3n** (101 MHz, Chloroform-*d*)



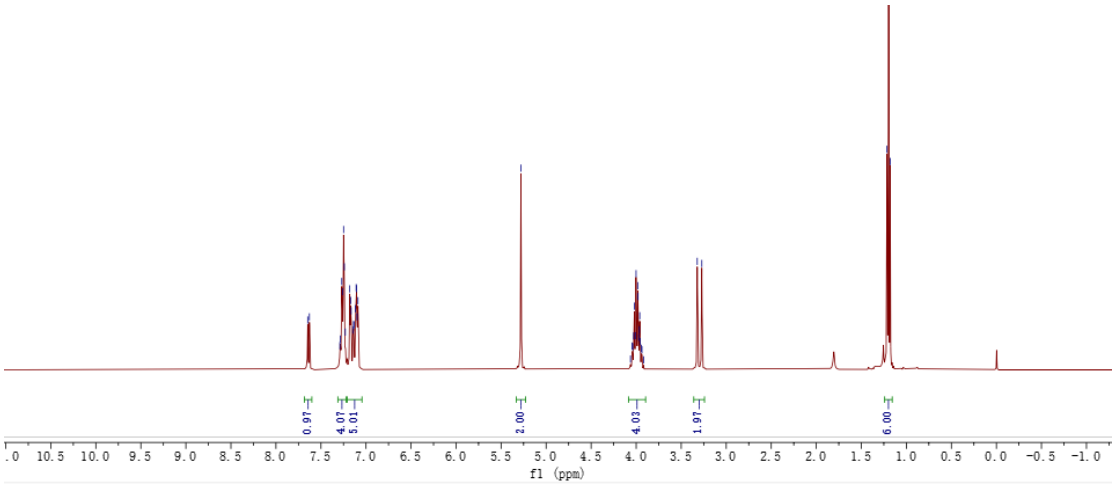


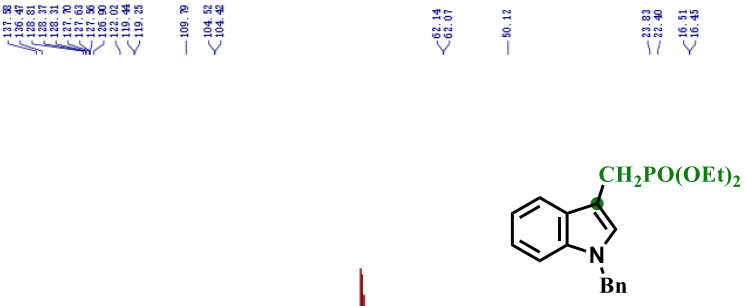
^{31}P NMR of **3n** (162 MHz, Chloroform-*d*)



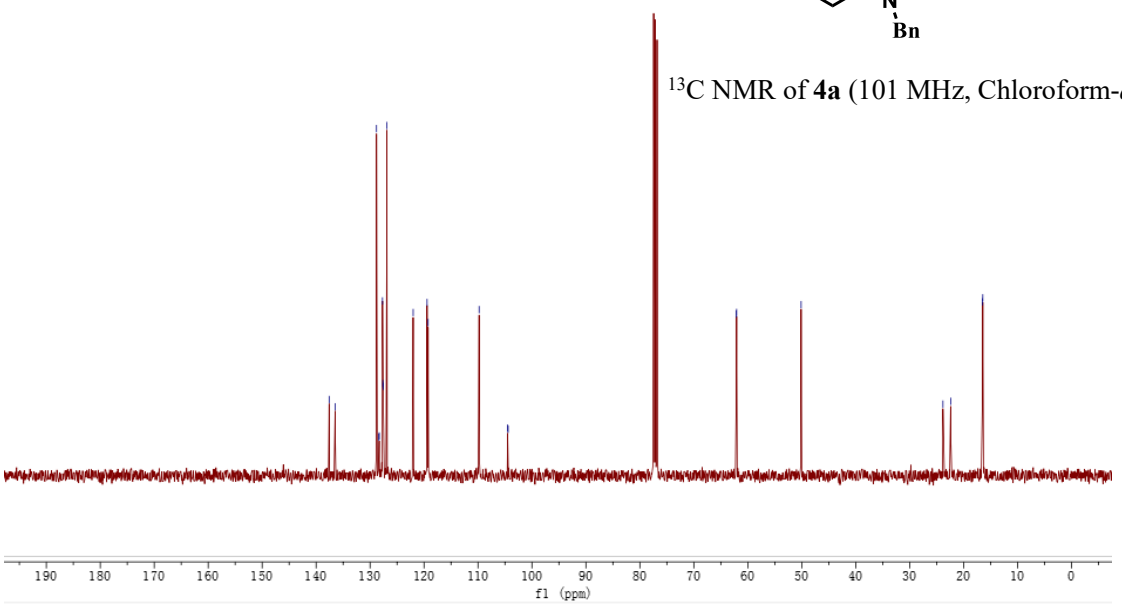


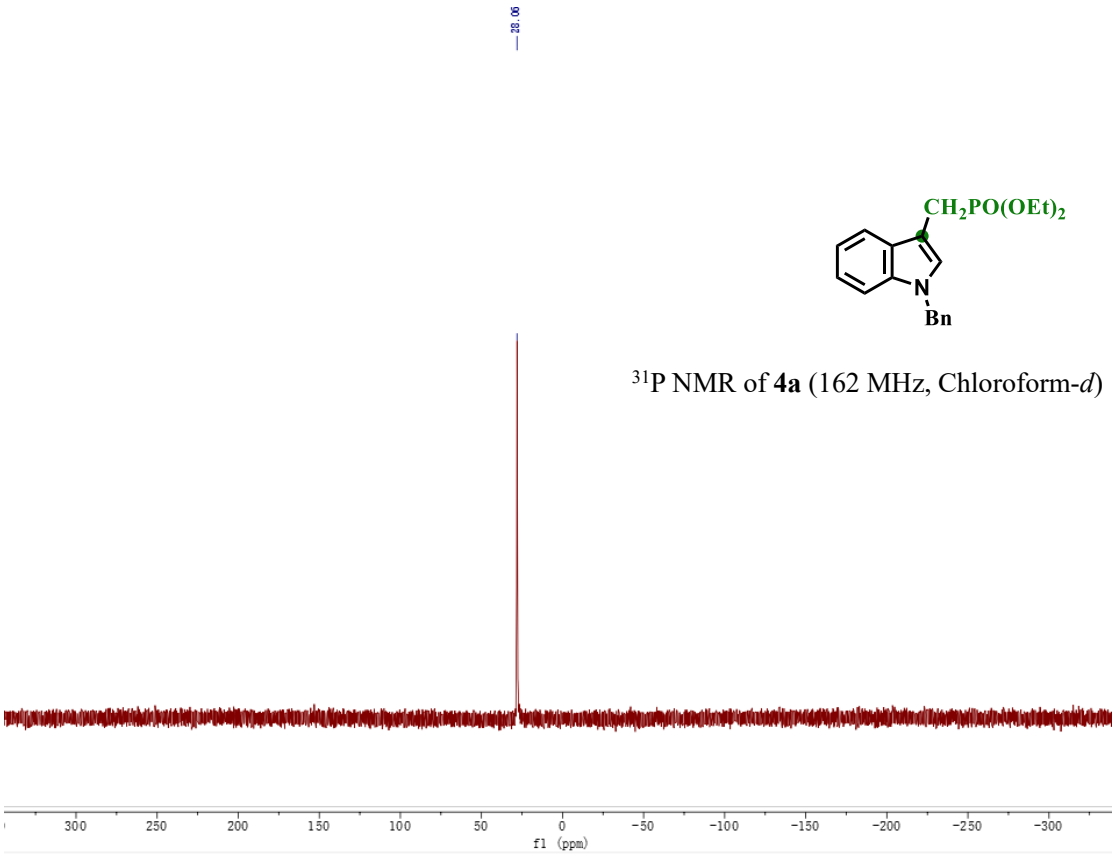
^{1}H NMR of **4a** (400 MHz, Chloroform-*d*)



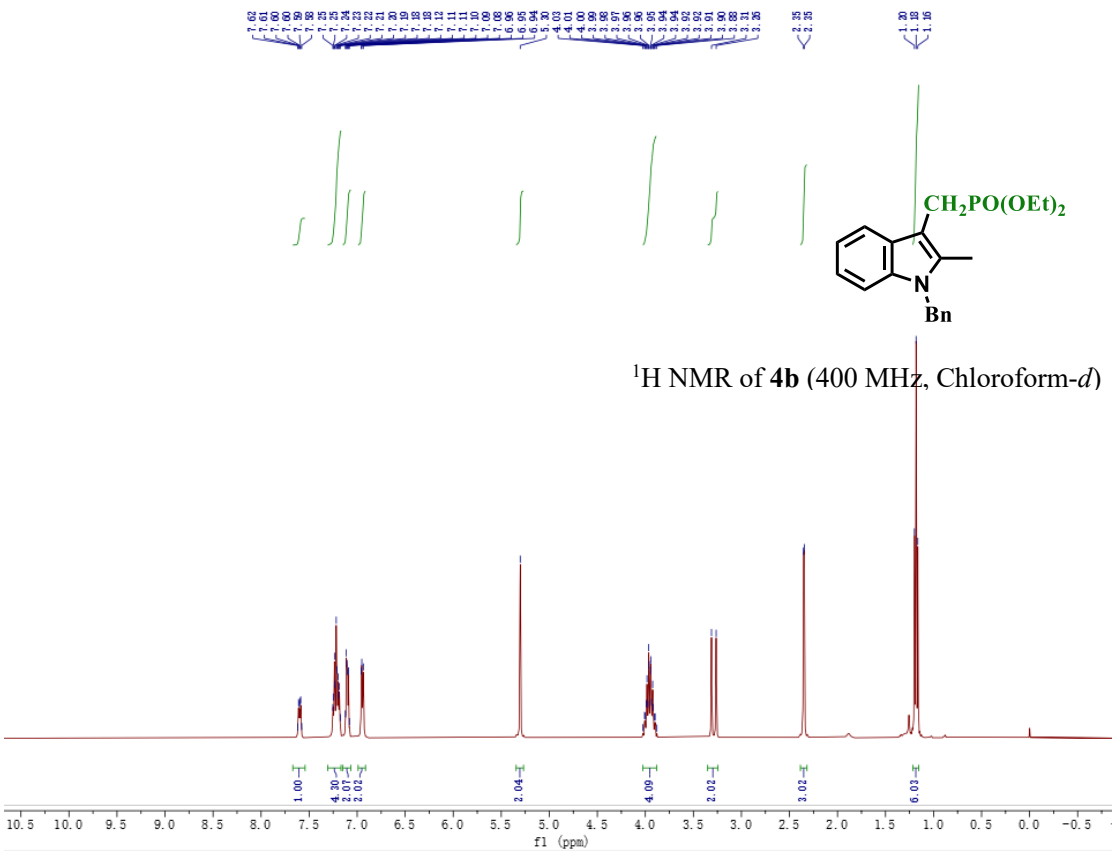


^{13}C NMR of **4a** (101 MHz, Chloroform-*d*)

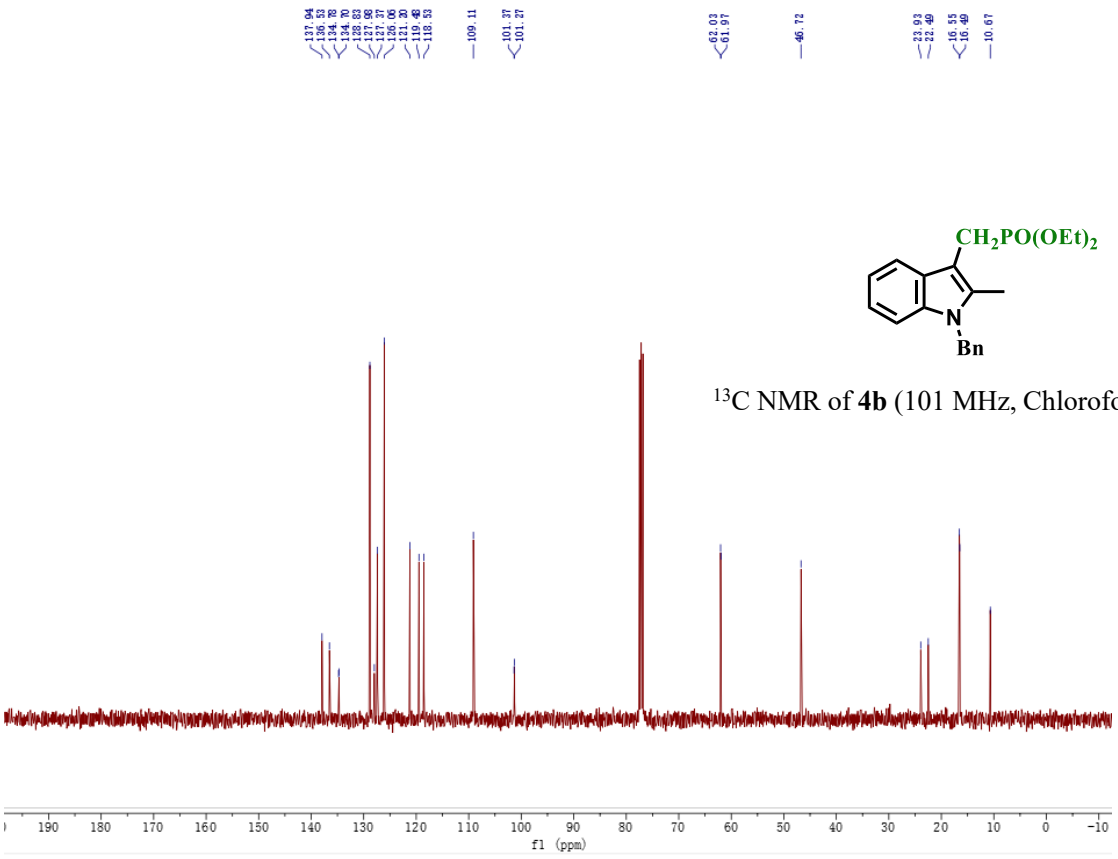




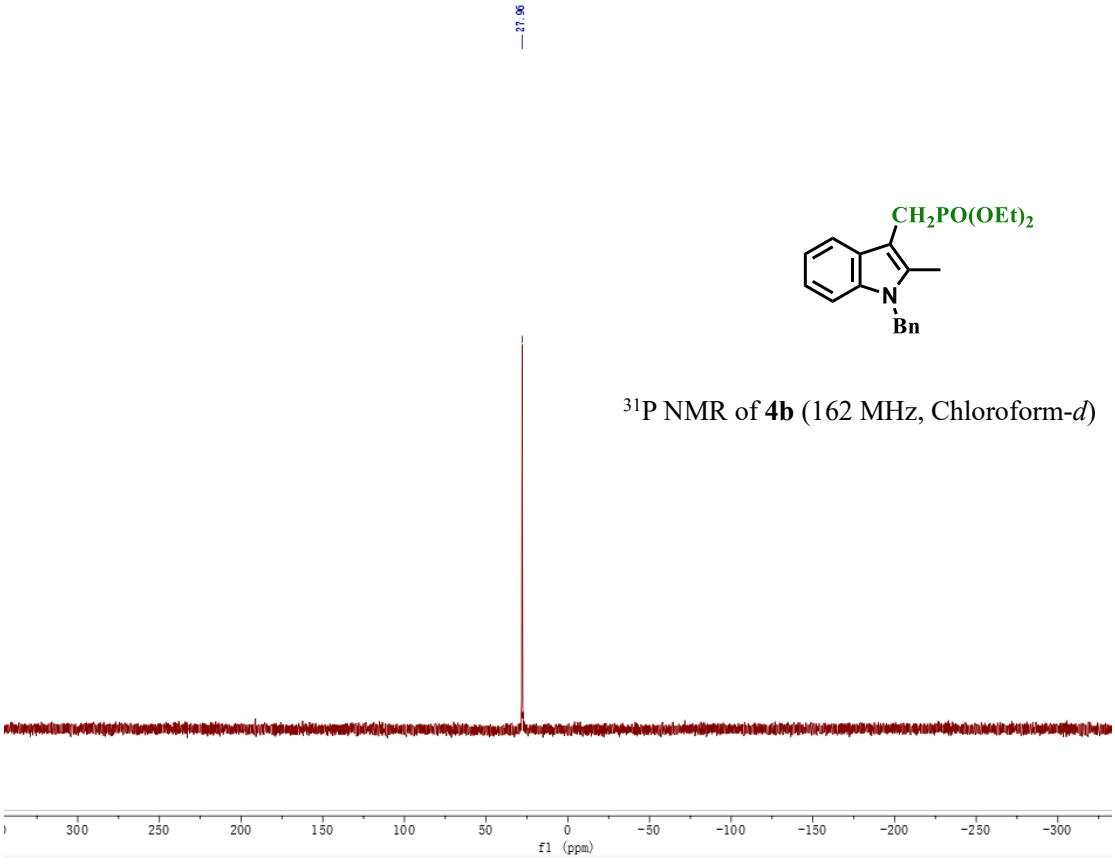
^{31}P NMR of **4a** (162 MHz, Chloroform-*d*)



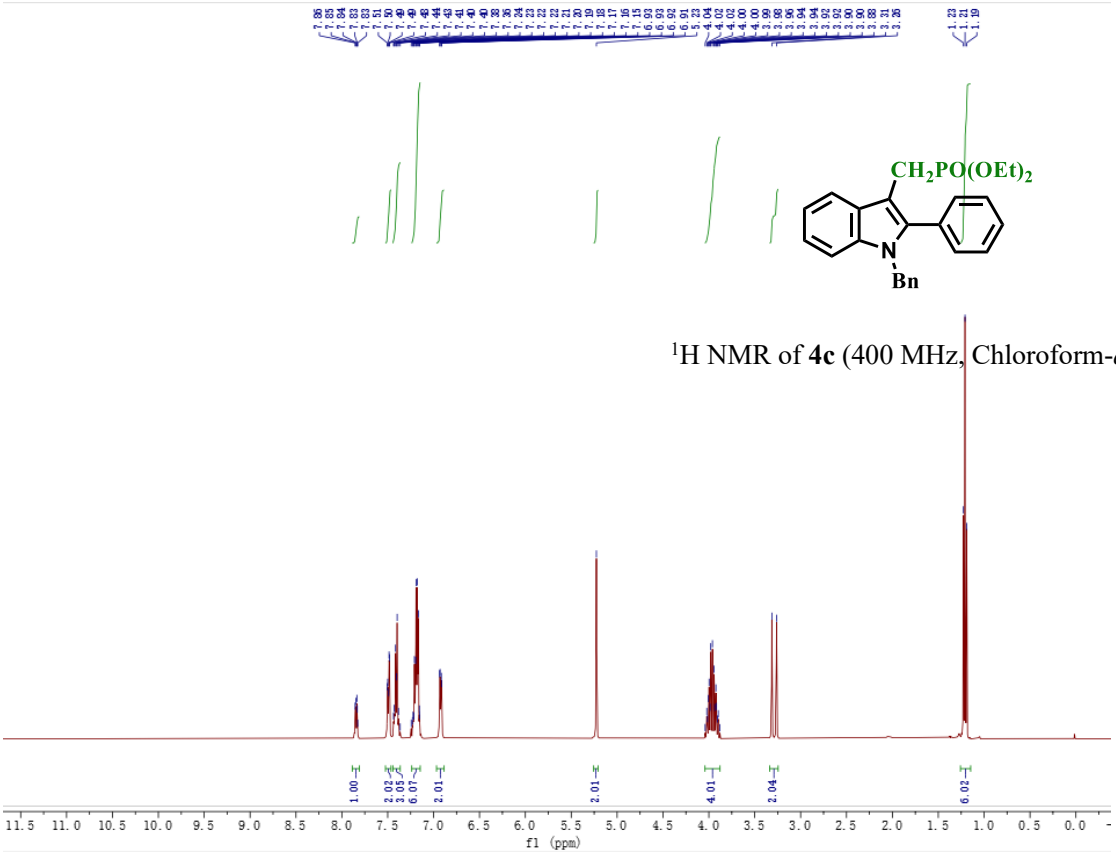
^{1}H NMR of **4b** (400 MHz, Chloroform-*d*)



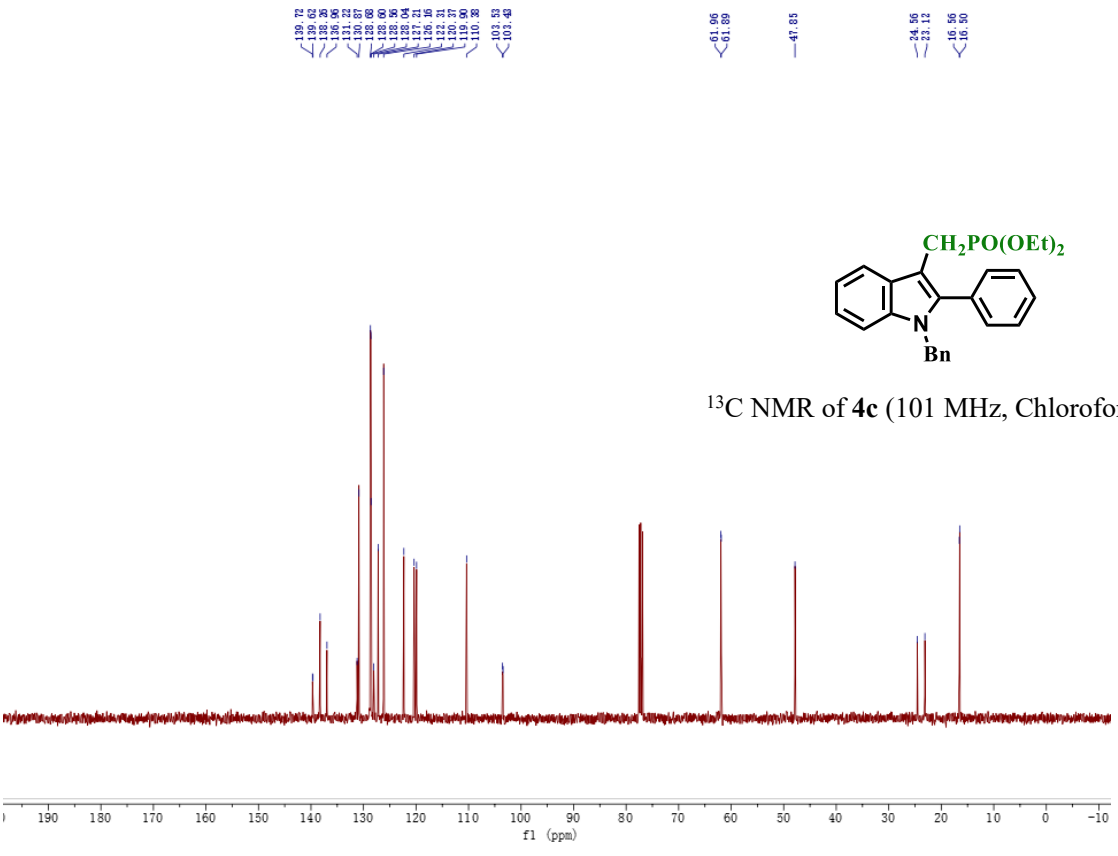
^{13}C NMR of **4b** (101 MHz, Chloroform-*d*)



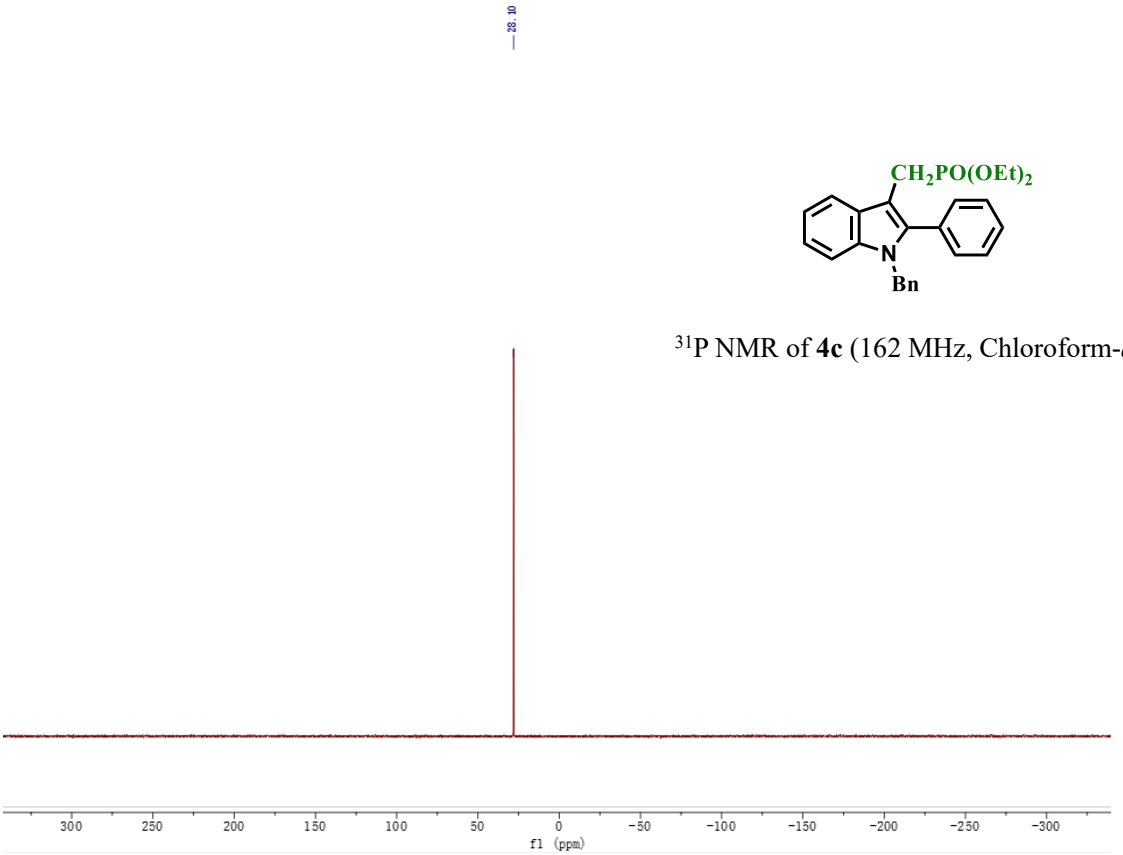
^{31}P NMR of **4b** (162 MHz, Chloroform-*d*)



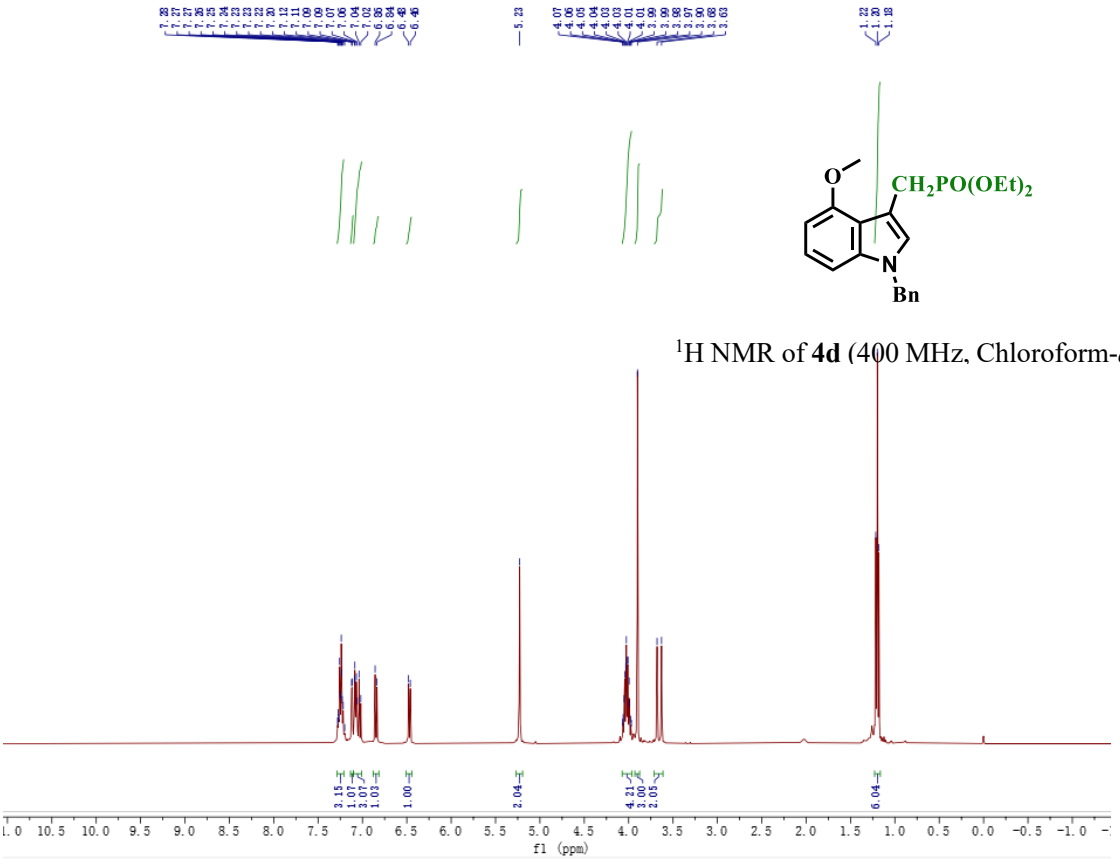
^{1}H NMR of **4c** (400 MHz, Chloroform-*d*)



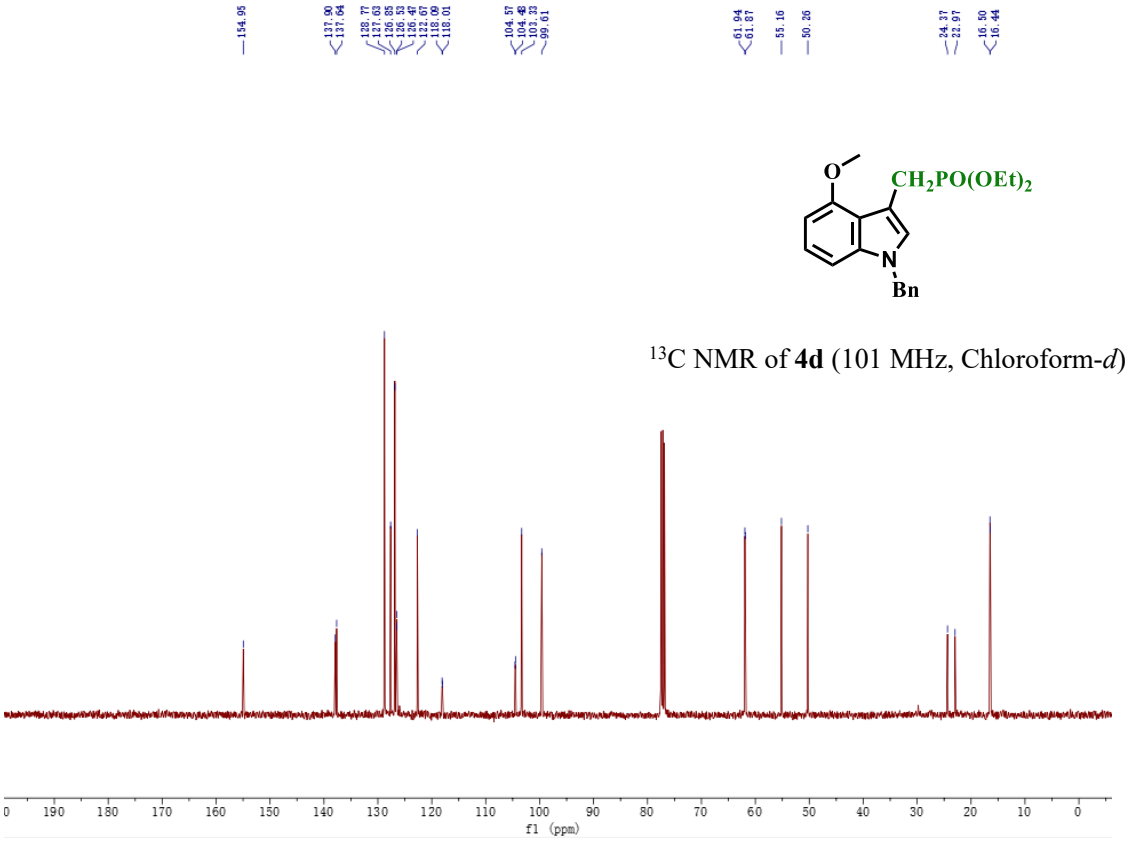
^{13}C NMR of **4c** (101 MHz, Chloroform-*d*)



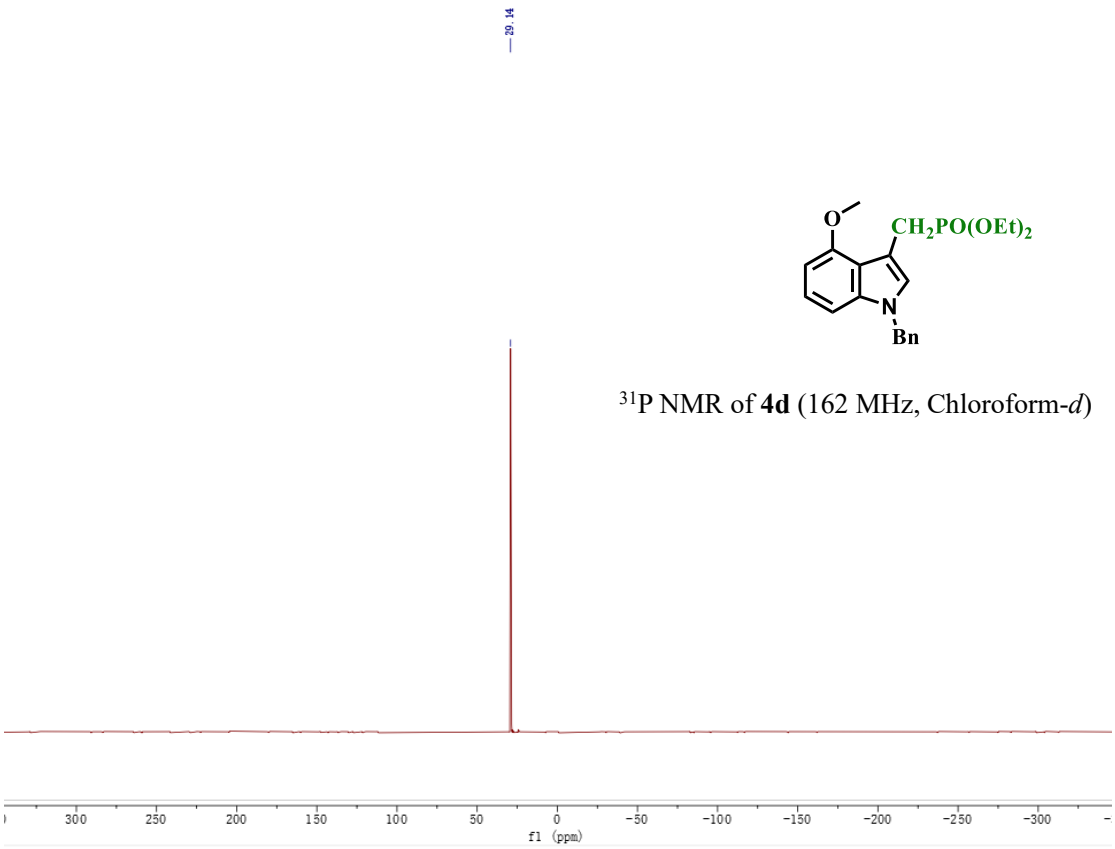
^{31}P NMR of **4c** (162 MHz, Chloroform-*d*)



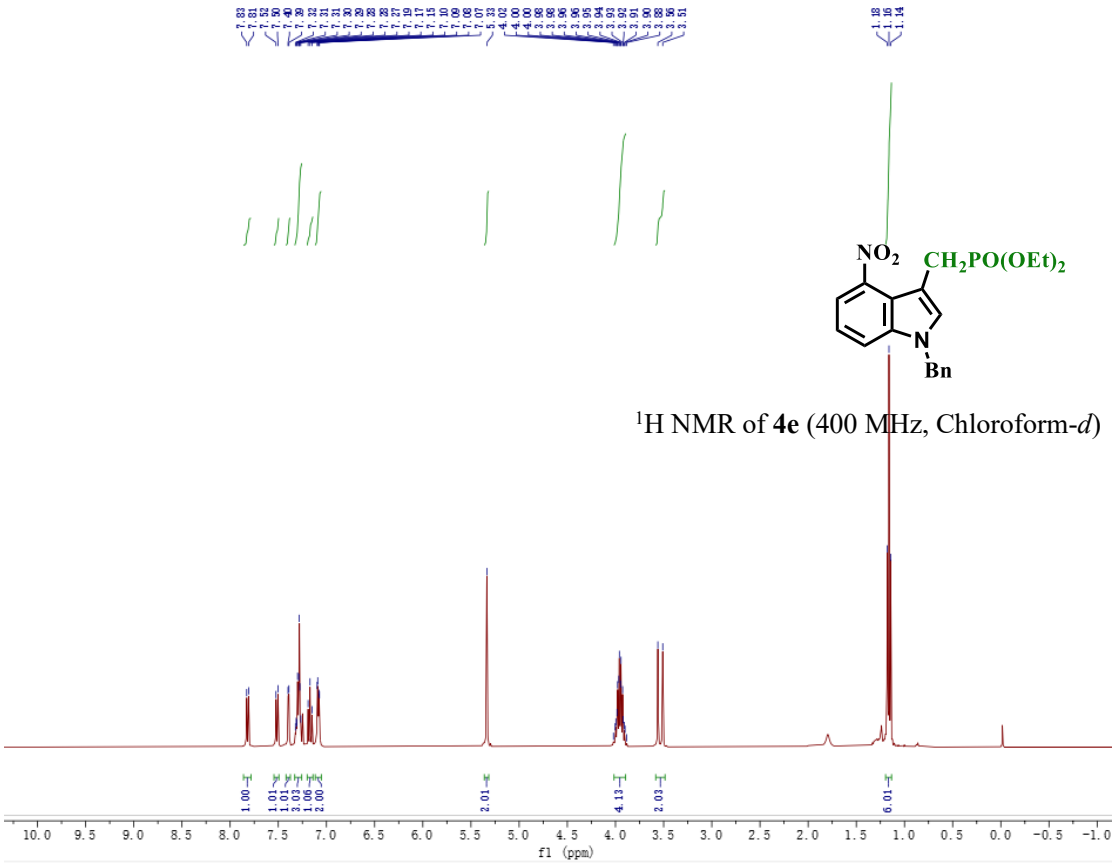
^{1}H NMR of **4d** (400 MHz, Chloroform-*d*)



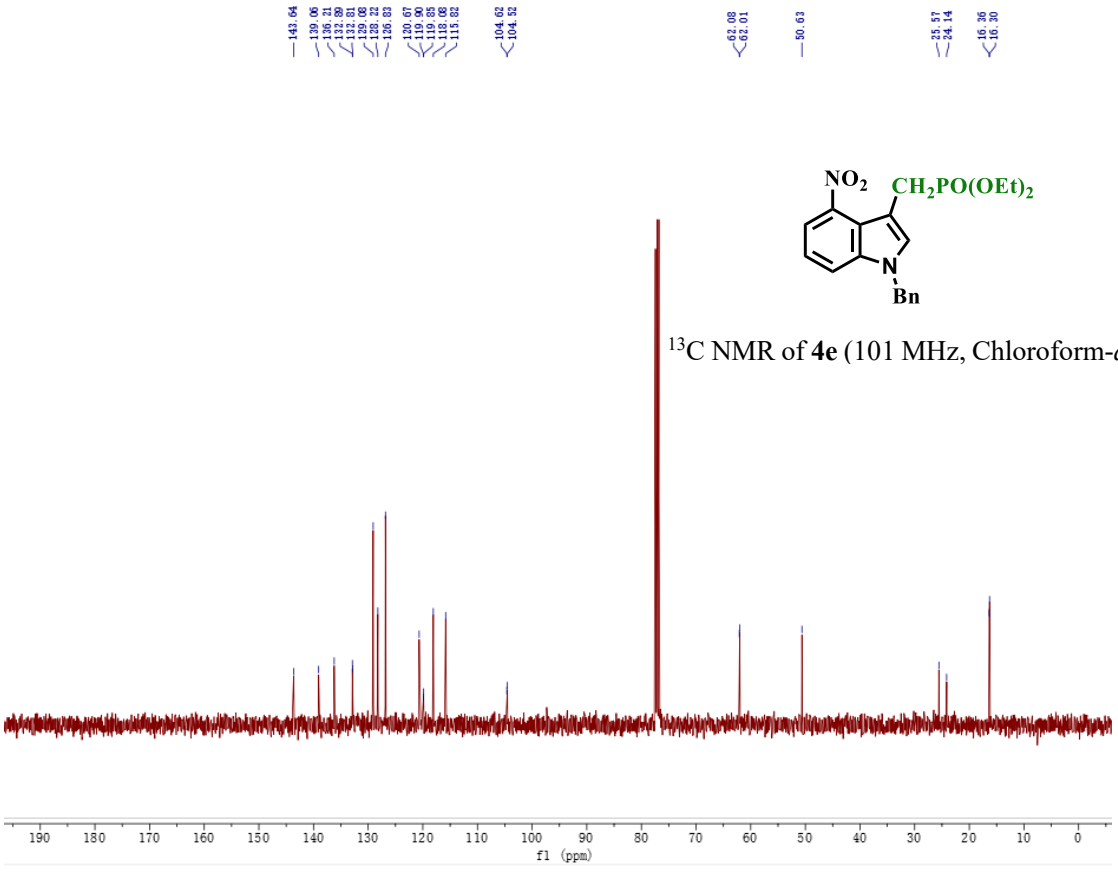
^{13}C NMR of **4d** (101 MHz, Chloroform-*d*)



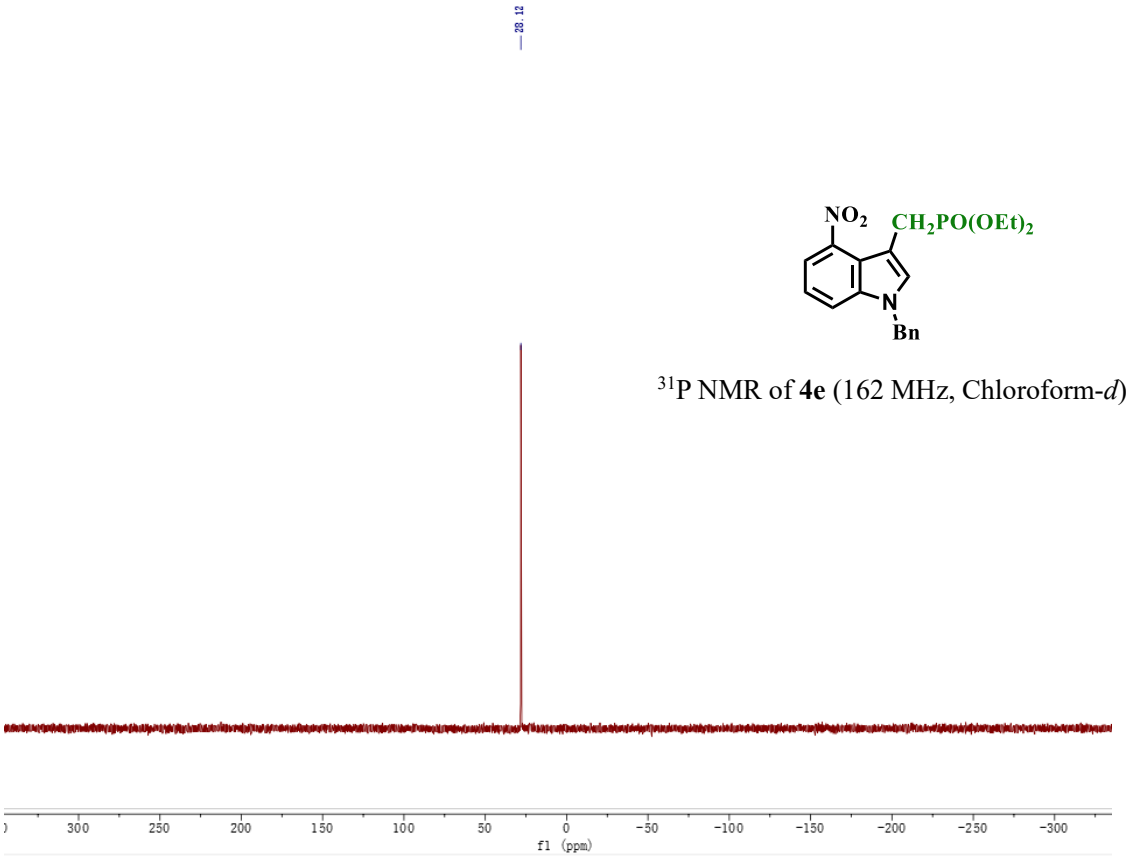
^{31}P NMR of **4d** (162 MHz, Chloroform-*d*)



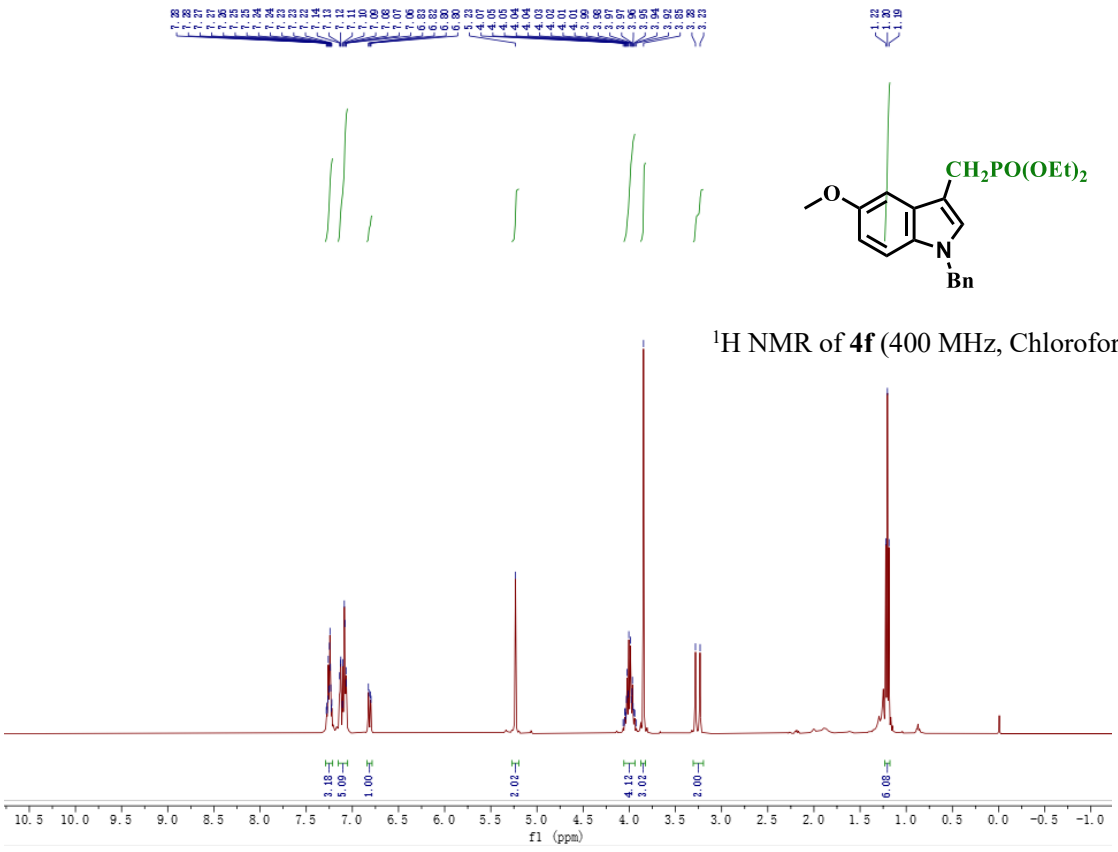
^{1}H NMR of **4e** (400 MHz, Chloroform-*d*)



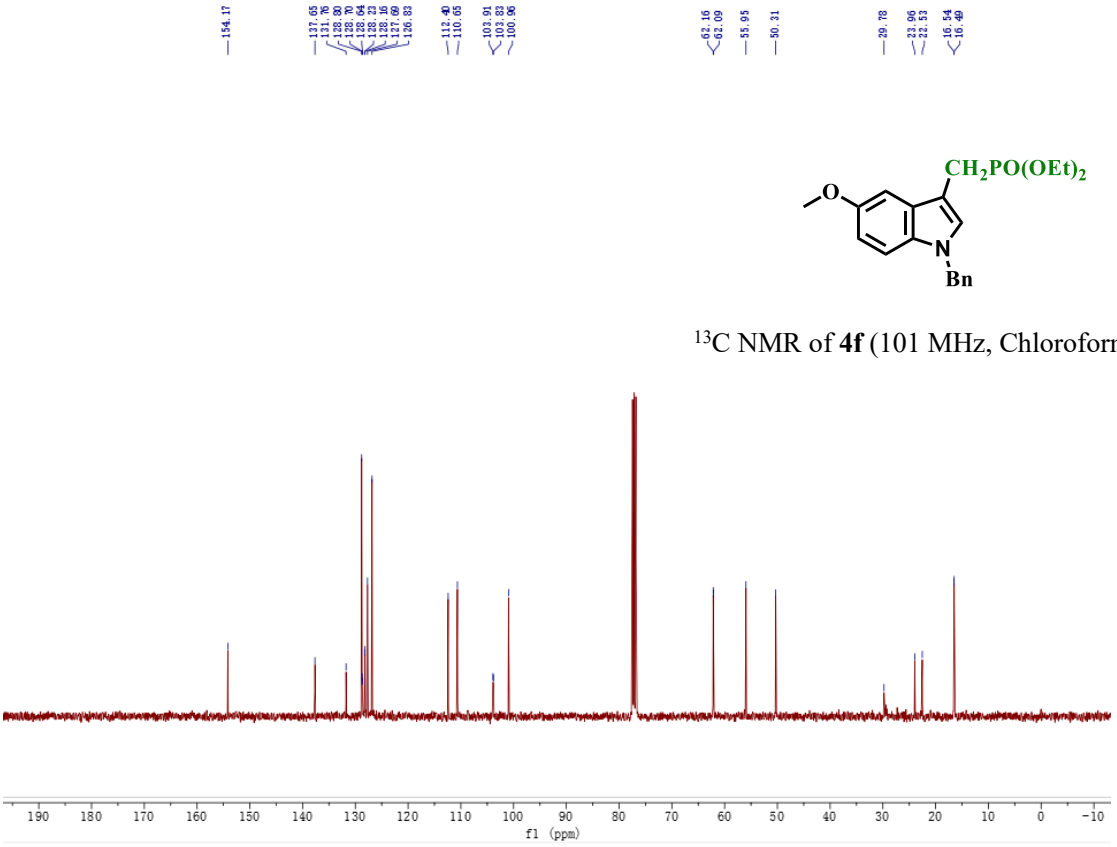
^{13}C NMR of **4e** (101 MHz, Chloroform-*d*)



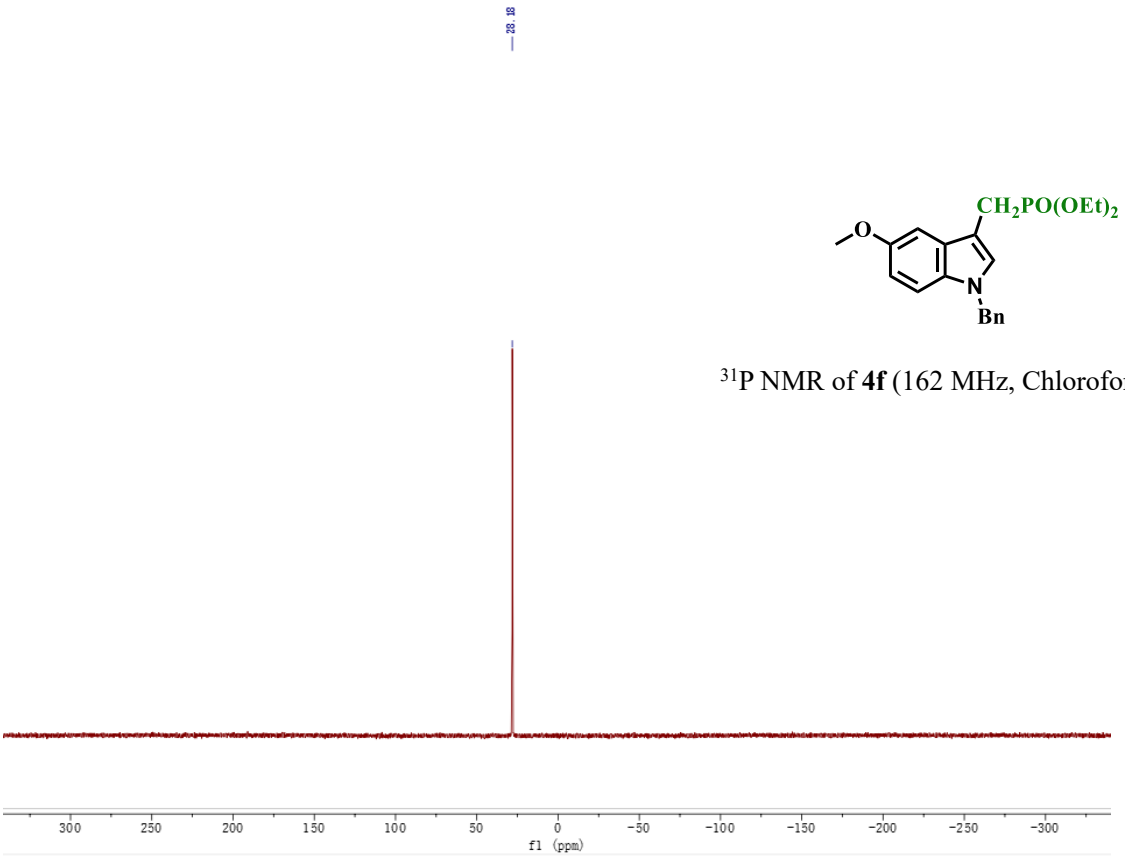
^{31}P NMR of **4e** (162 MHz, Chloroform-*d*)



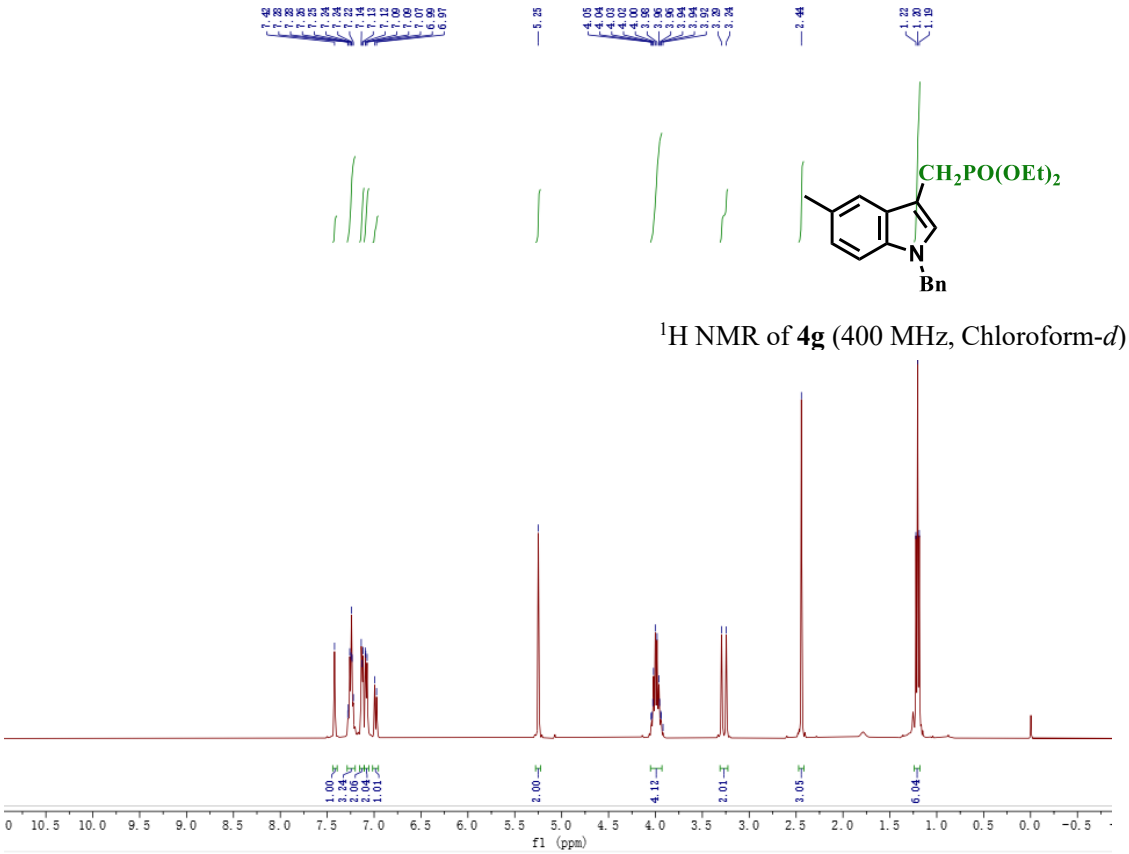
^{1}H NMR of **4f** (400 MHz, Chloroform-*d*)



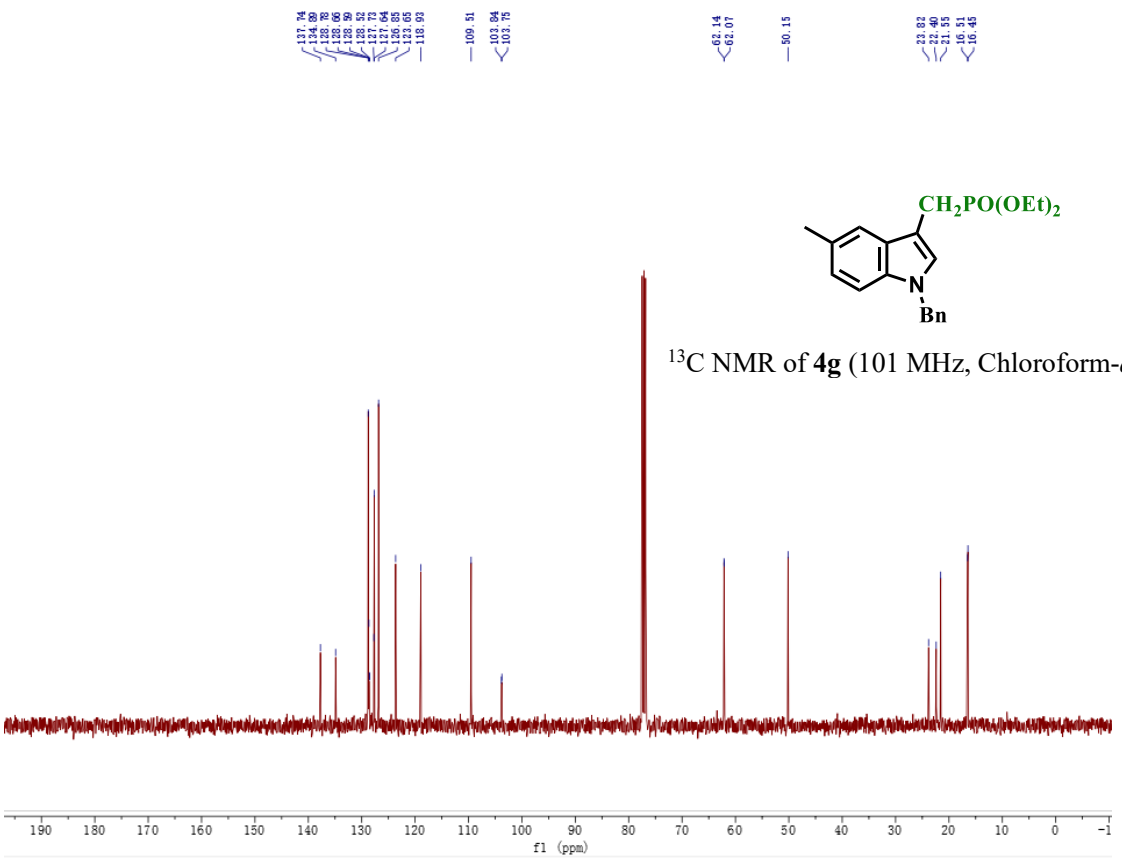
^{13}C NMR of **4f** (101 MHz, Chloroform-*d*)



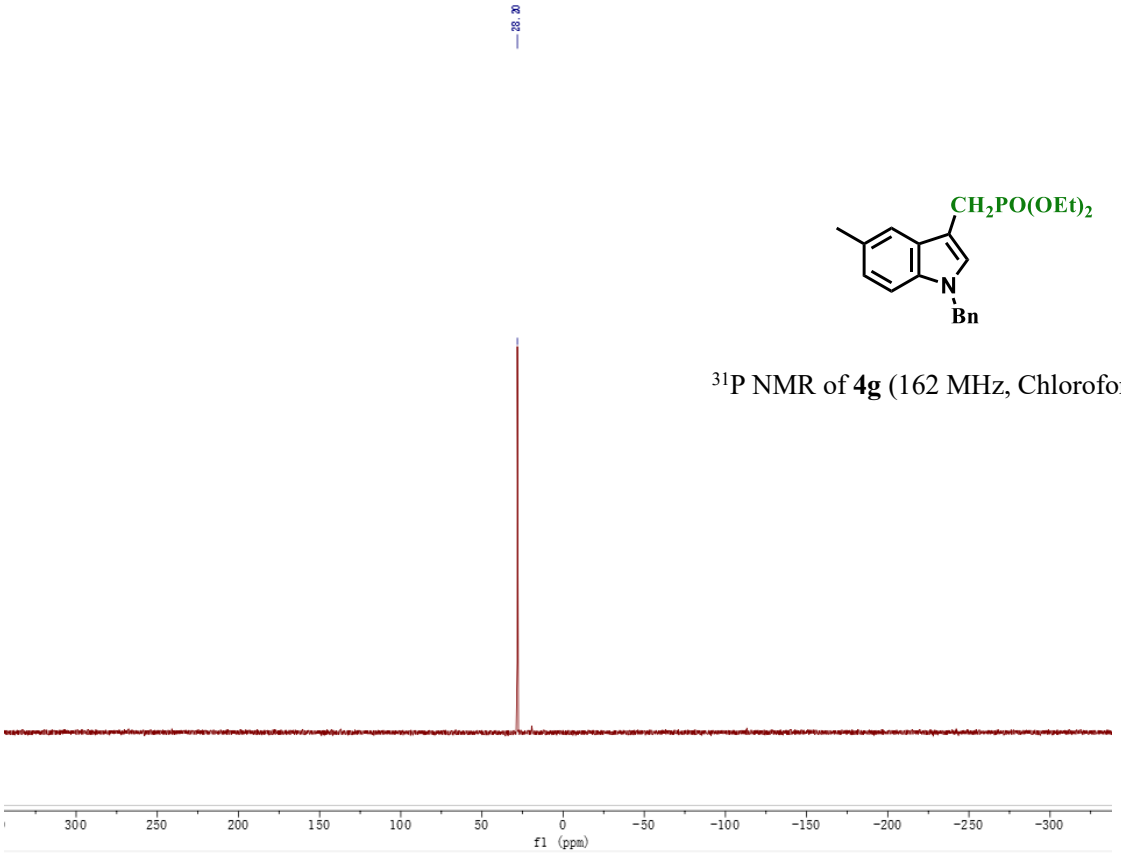
^{31}P NMR of **4f** (162 MHz, Chloroform-*d*)



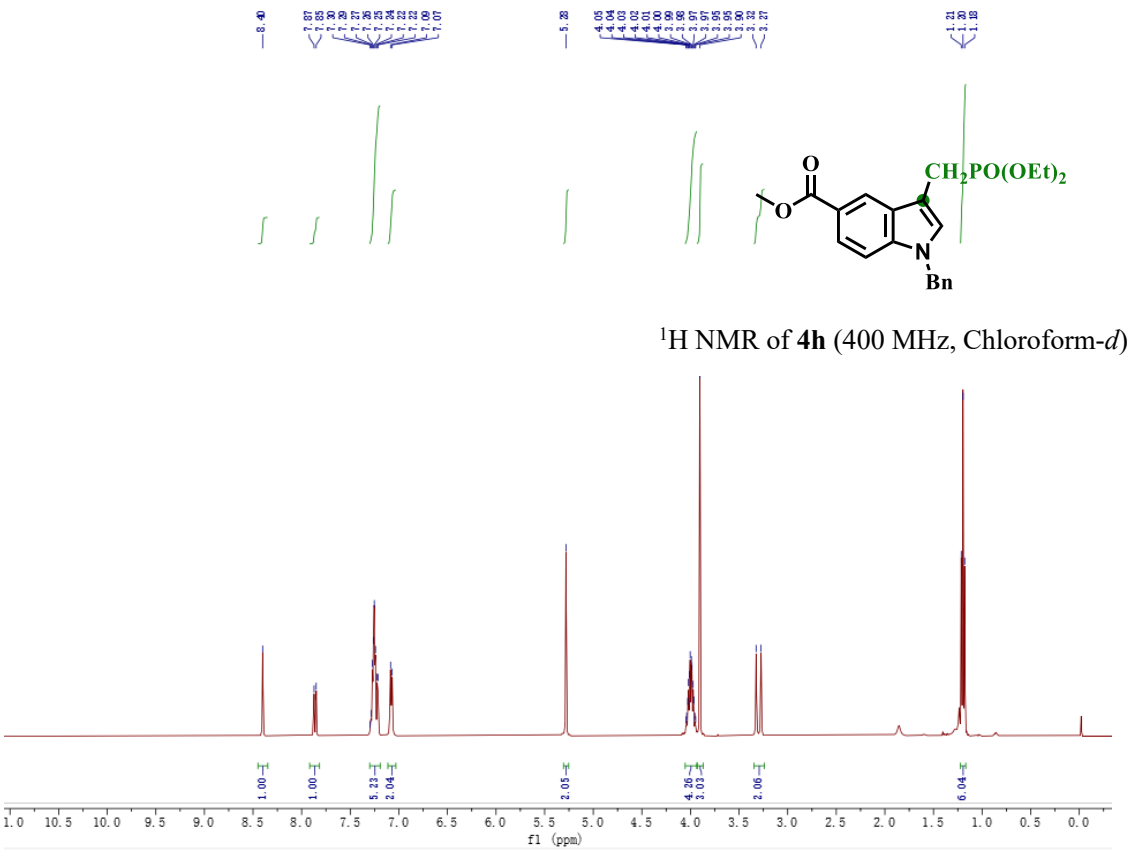
^{1}H NMR of **4g** (400 MHz, Chloroform-*d*)



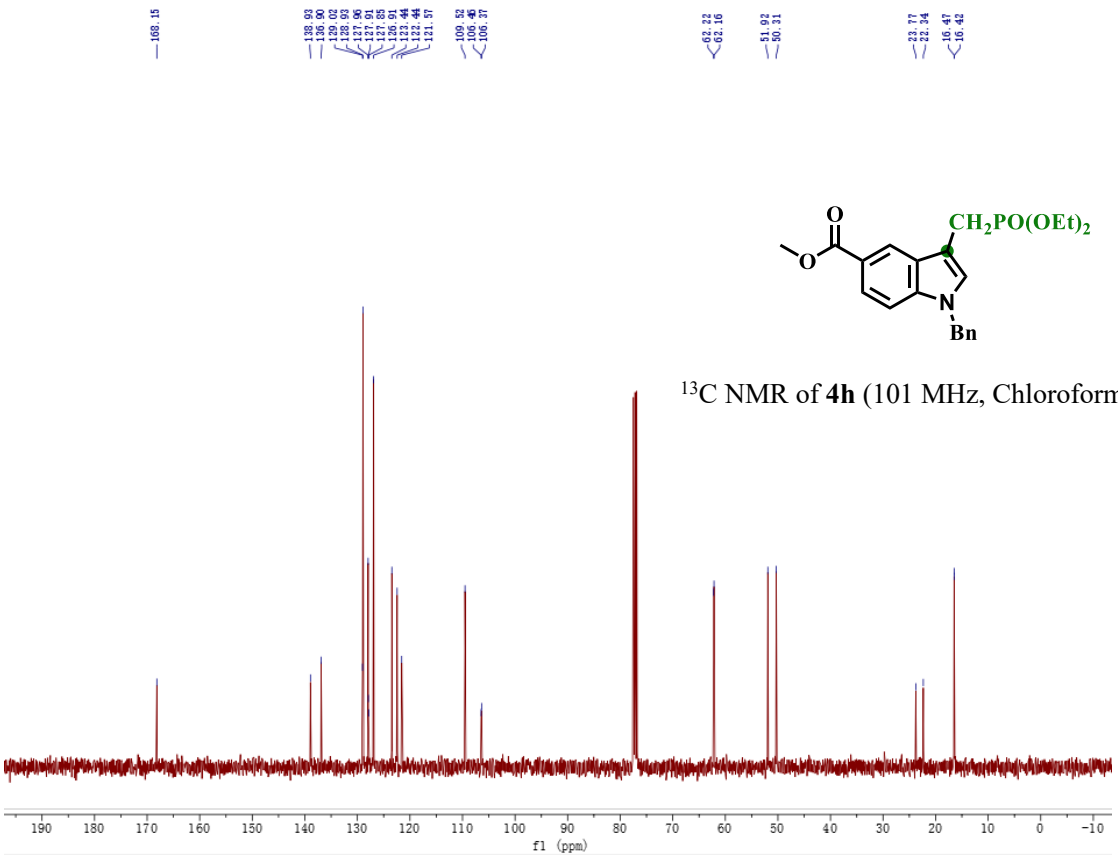
^{13}C NMR of **4g** (101 MHz, Chloroform-*d*)



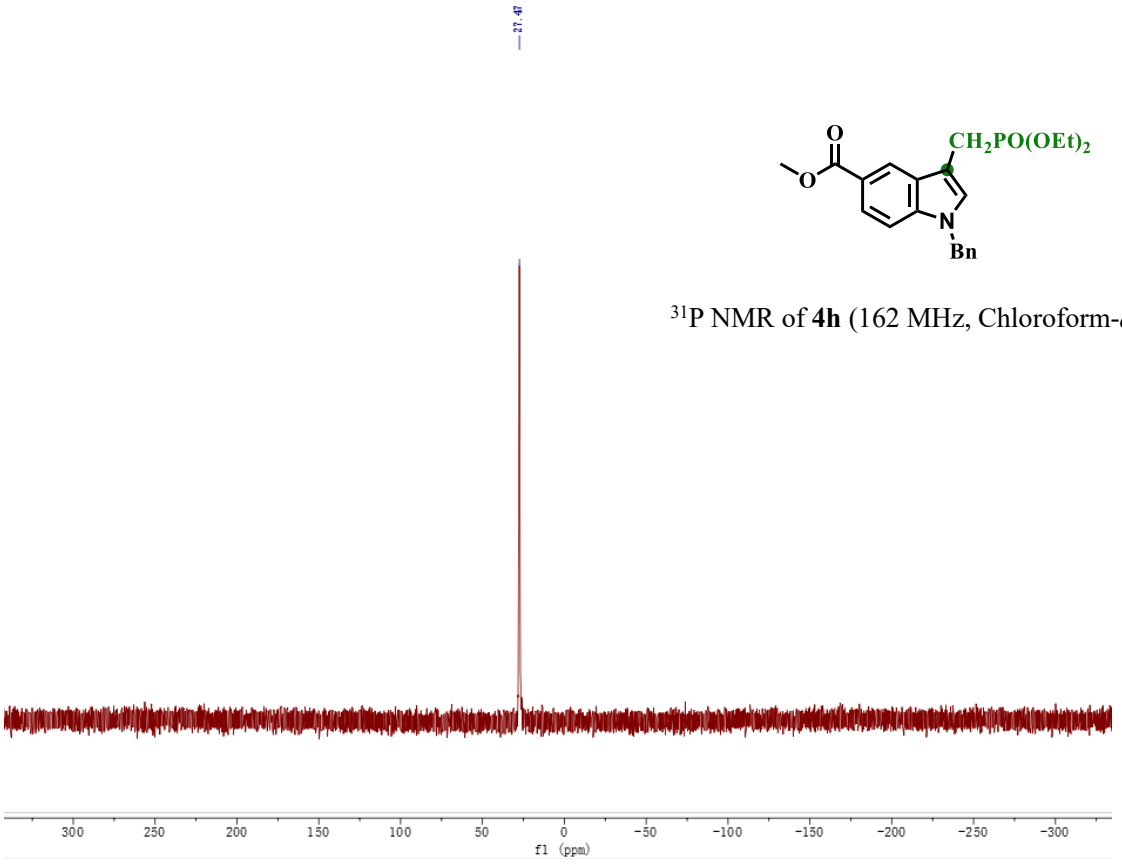
^{31}P NMR of **4g** (162 MHz, Chloroform-*d*)



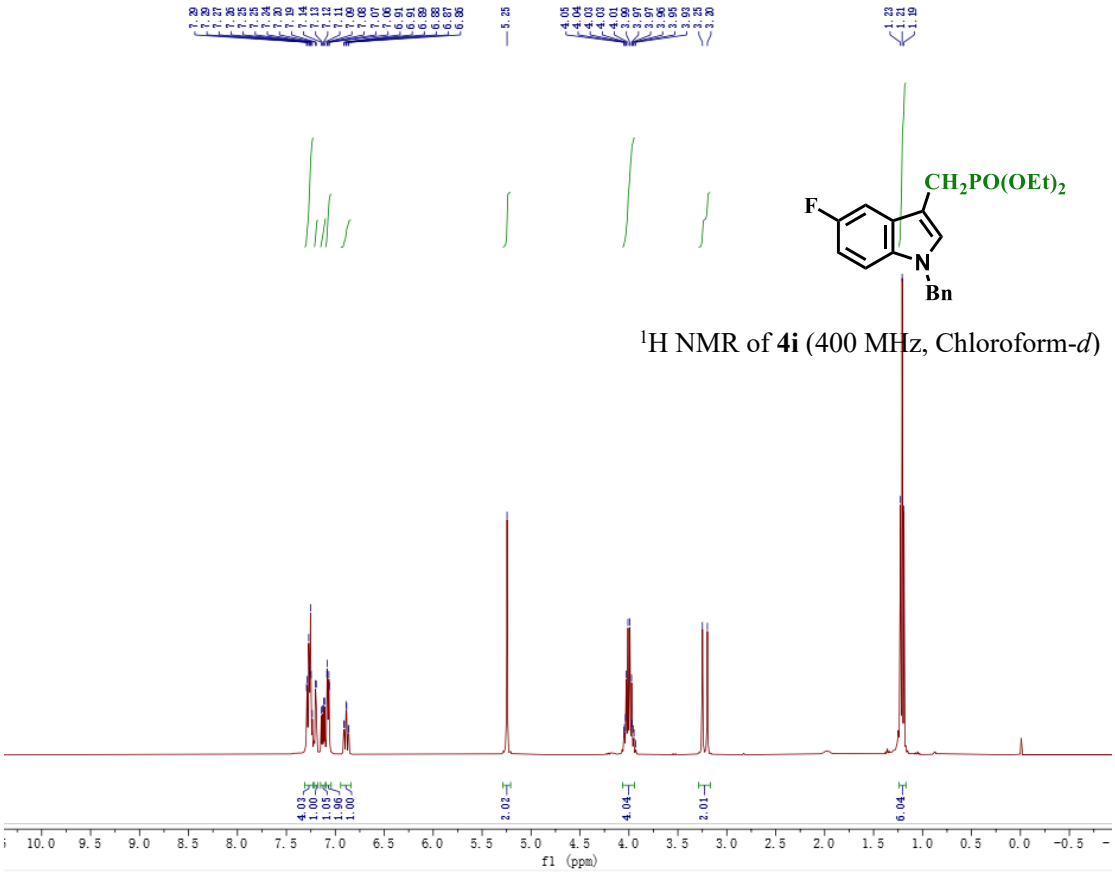
^{1}H NMR of **4h** (400 MHz, Chloroform-*d*)



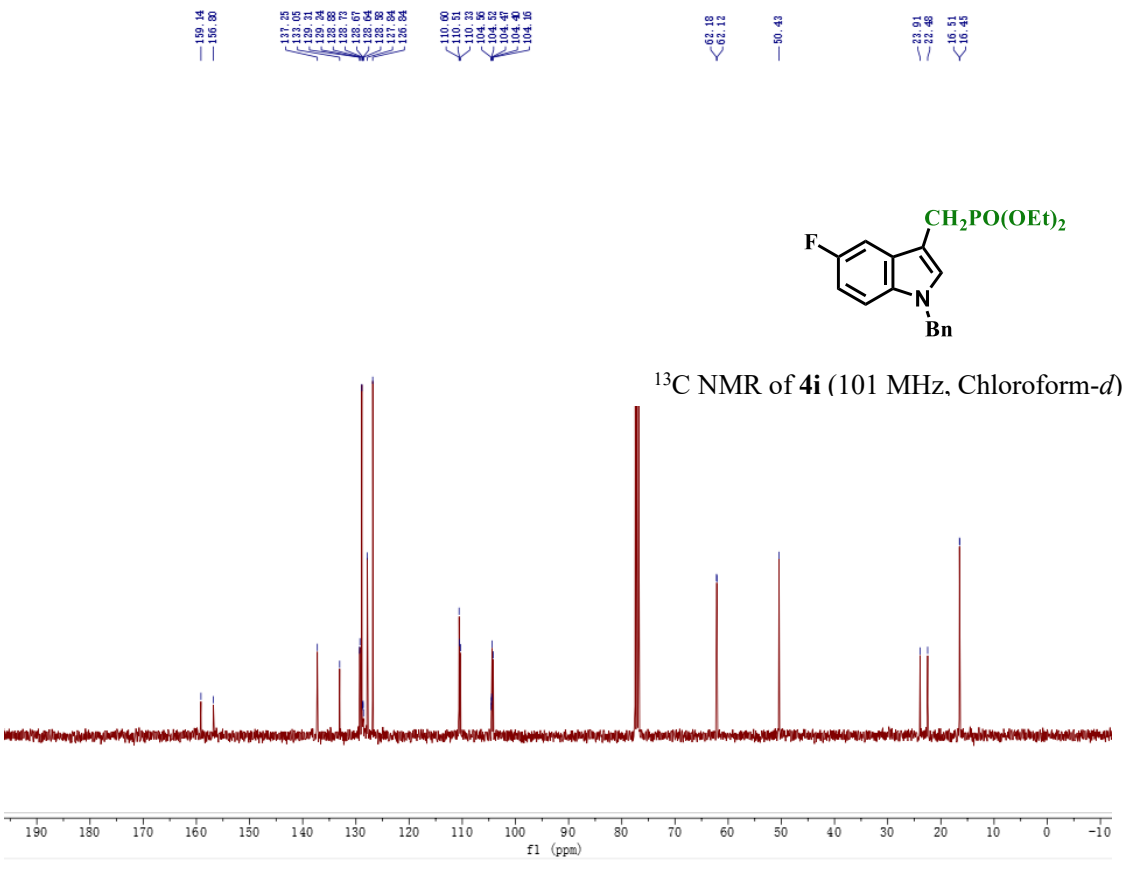
^{13}C NMR of **4h** (101 MHz, Chloroform-*d*)



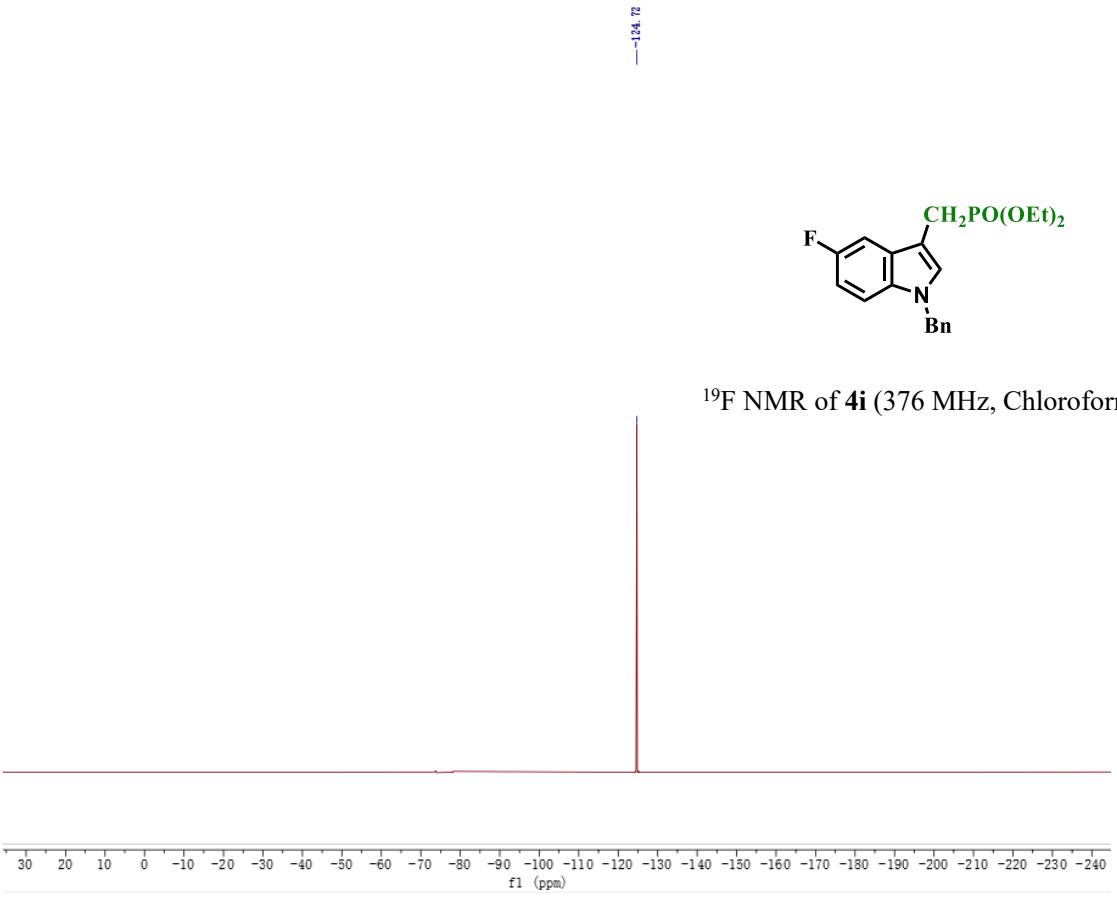
^{31}P NMR of **4h** (162 MHz, Chloroform-*d*)



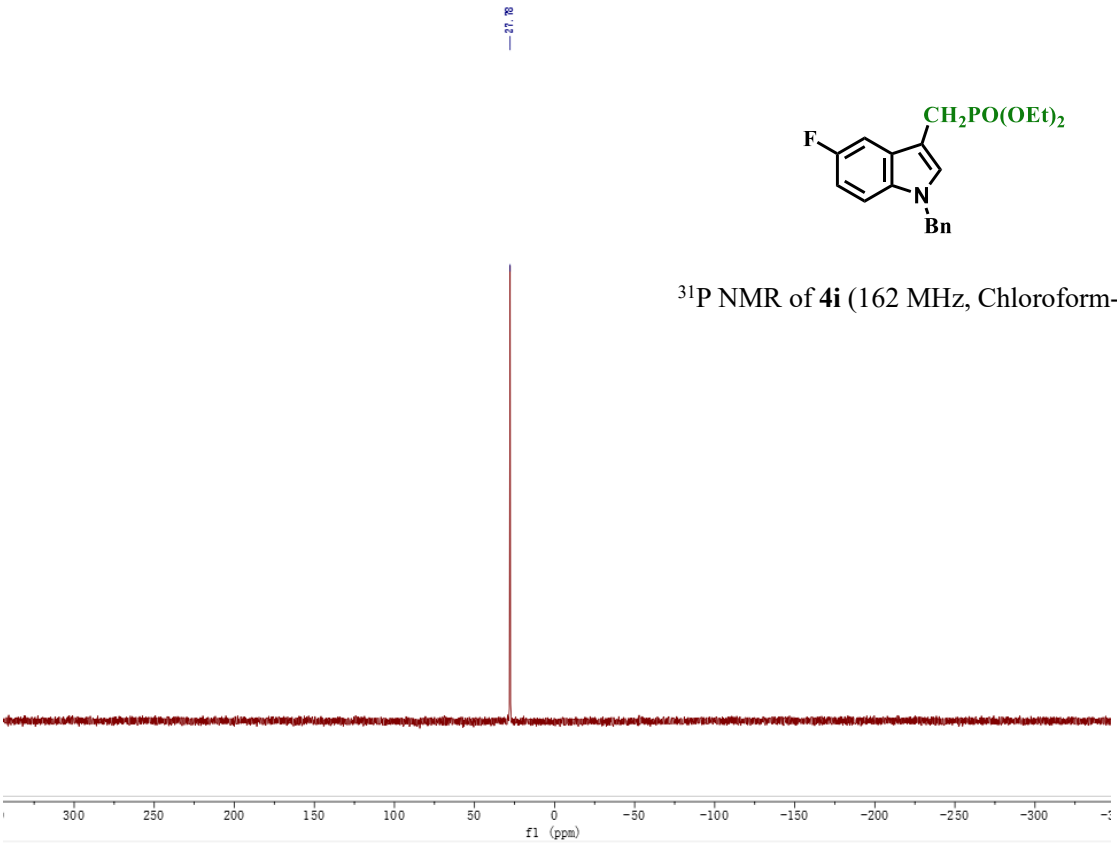
^{1}H NMR of **4i** (400 MHz, Chloroform-*d*)



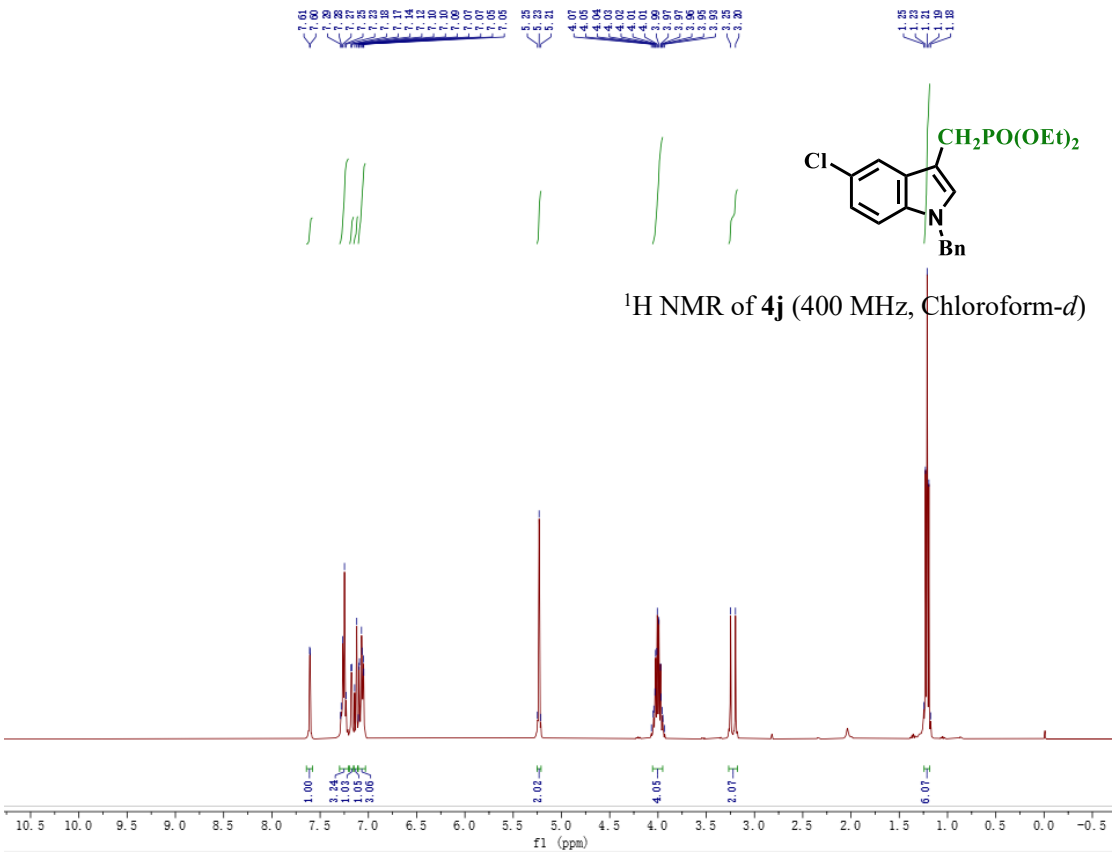
^{13}C NMR of **4i** (101 MHz, Chloroform-*d*)



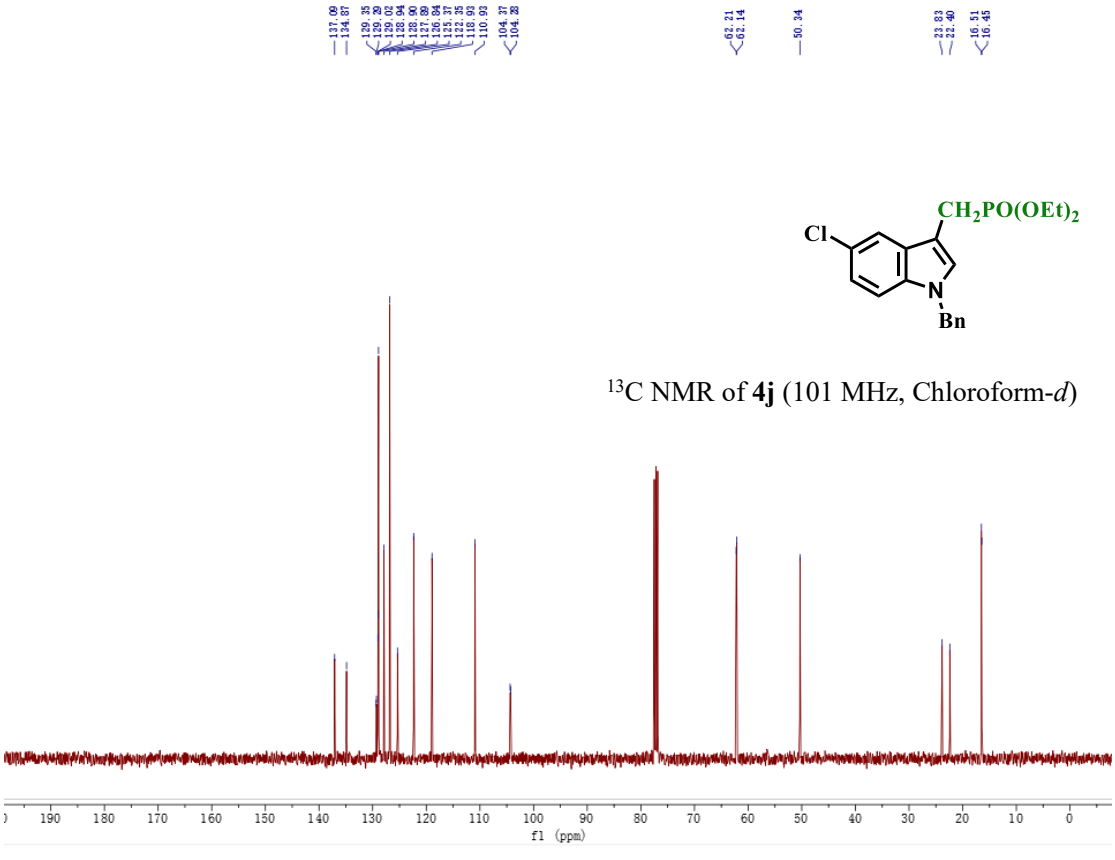
^{19}F NMR of **4i** (376 MHz, Chloroform-*d*)



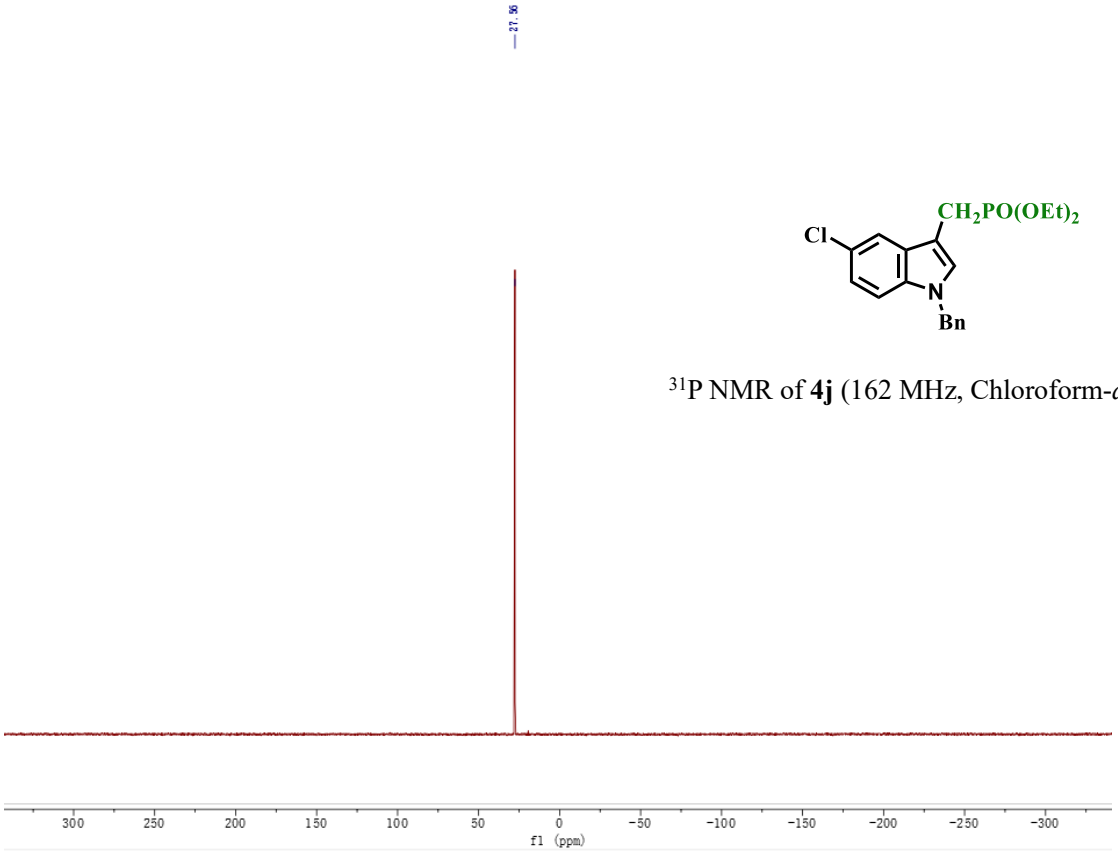
^{31}P NMR of **4i** (162 MHz, Chloroform-*d*)



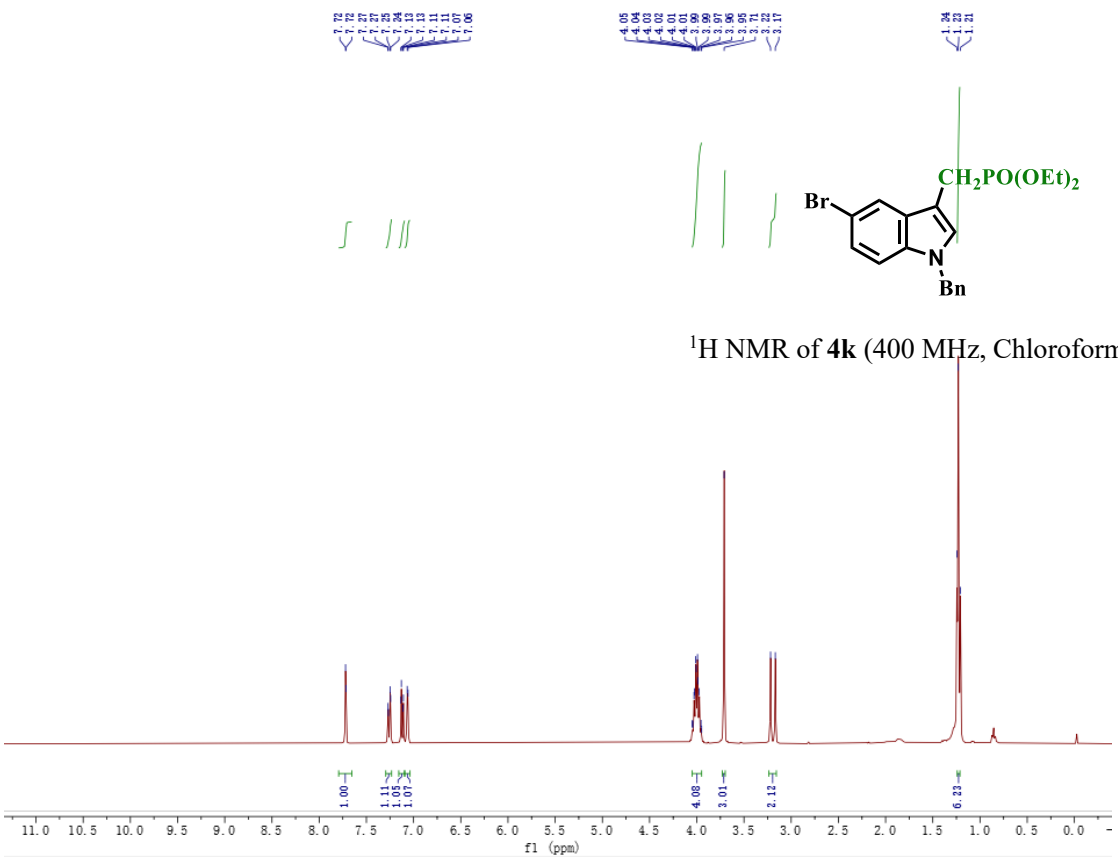
^{1}H NMR of **4j** (400 MHz, Chloroform-*d*)



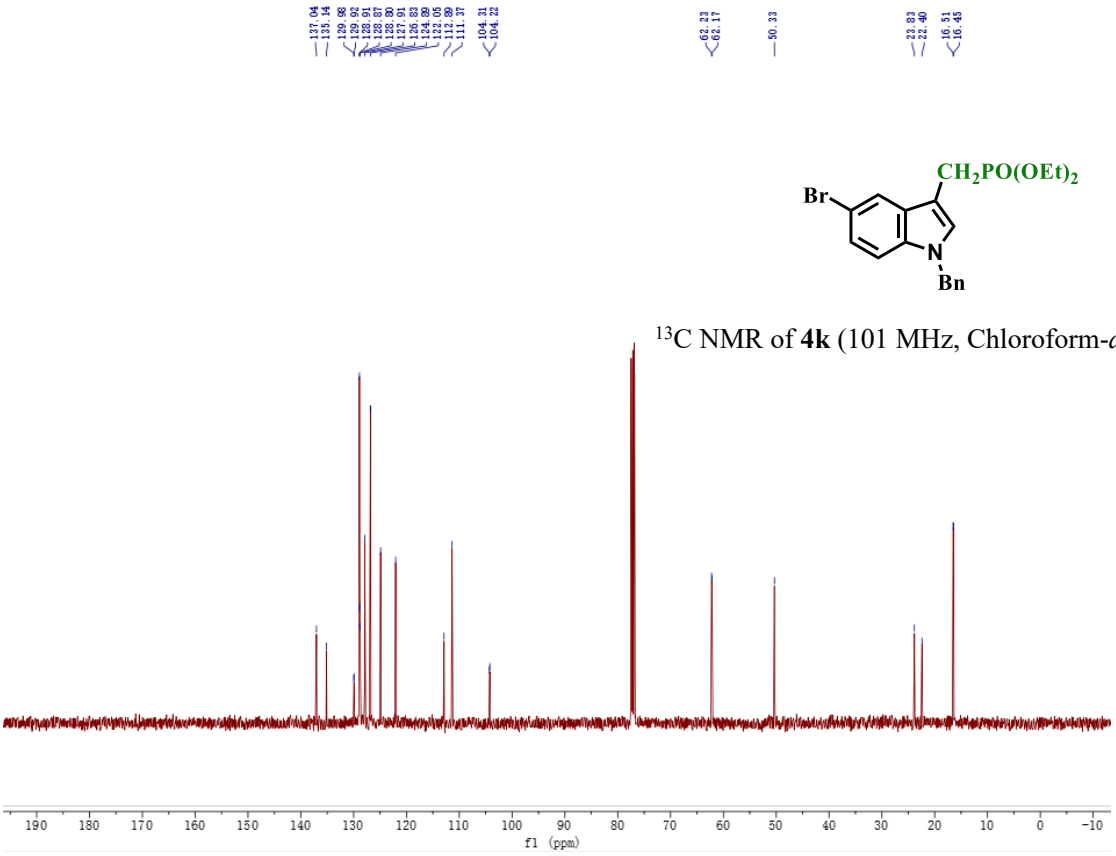
^{13}C NMR of **4j** (101 MHz, Chloroform-*d*)



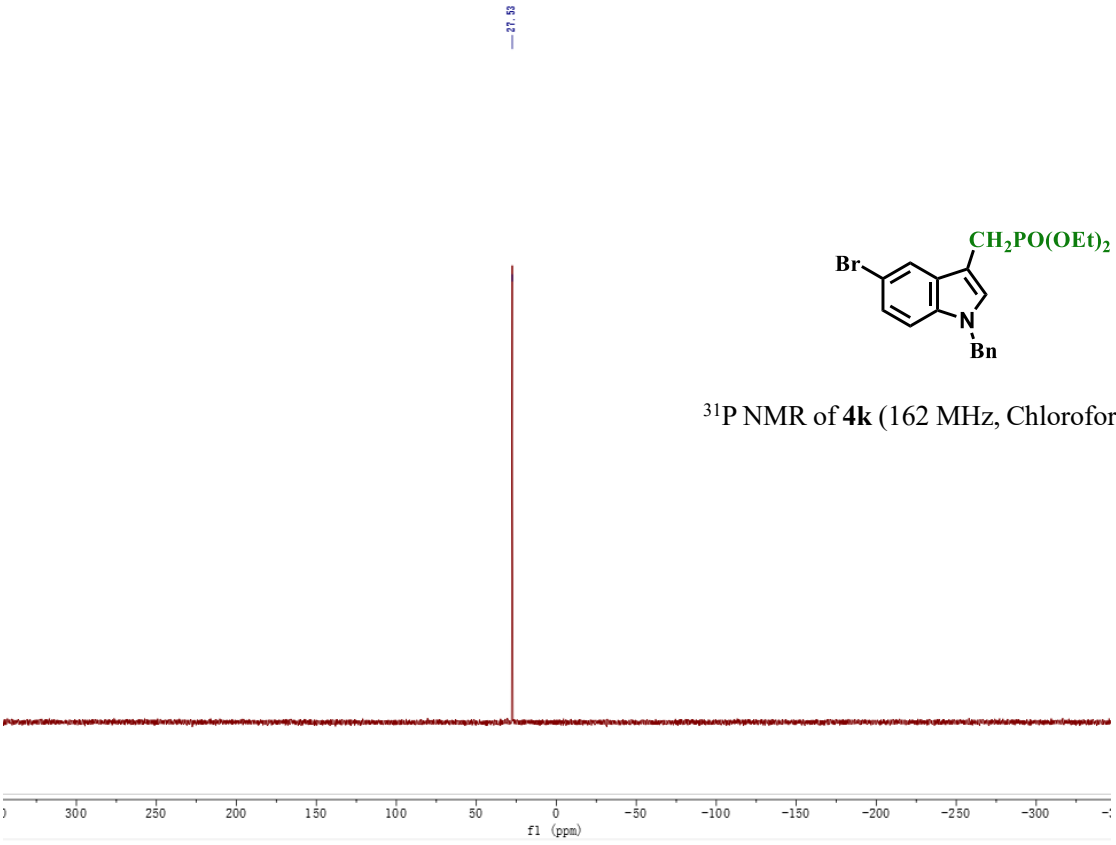
^{31}P NMR of **4j** (162 MHz, Chloroform-*d*)



^{1}H NMR of **4k** (400 MHz, Chloroform-*d*)

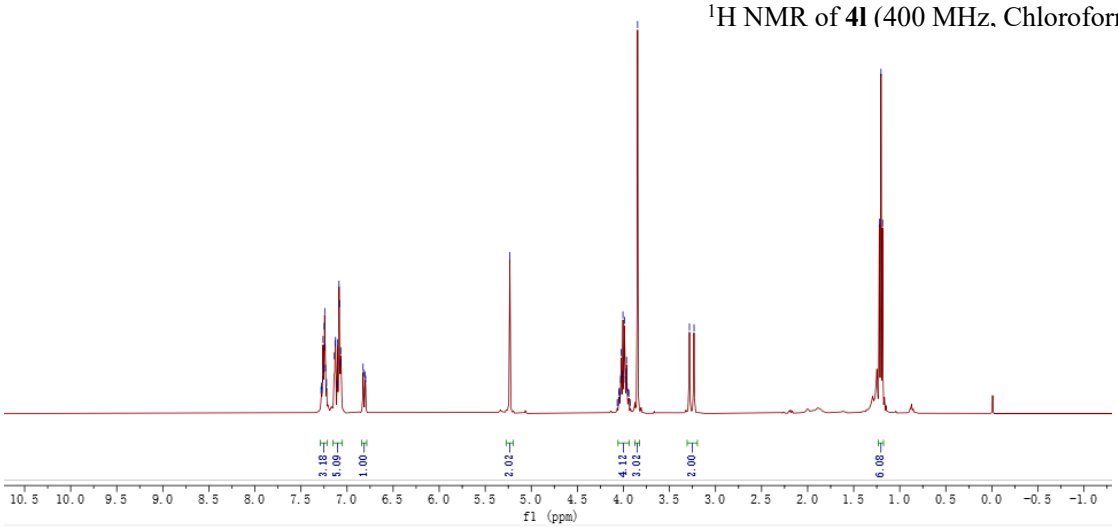


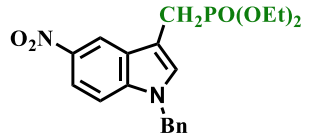
^{13}C NMR of **4k** (101 MHz, Chloroform-*d*)



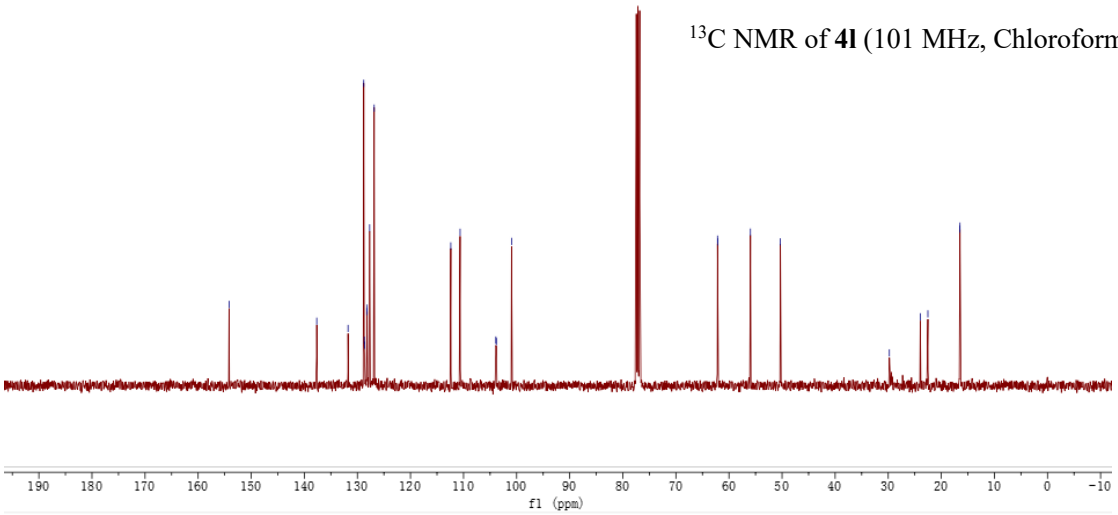
^{31}P NMR of **4k** (162 MHz, Chloroform-*d*)

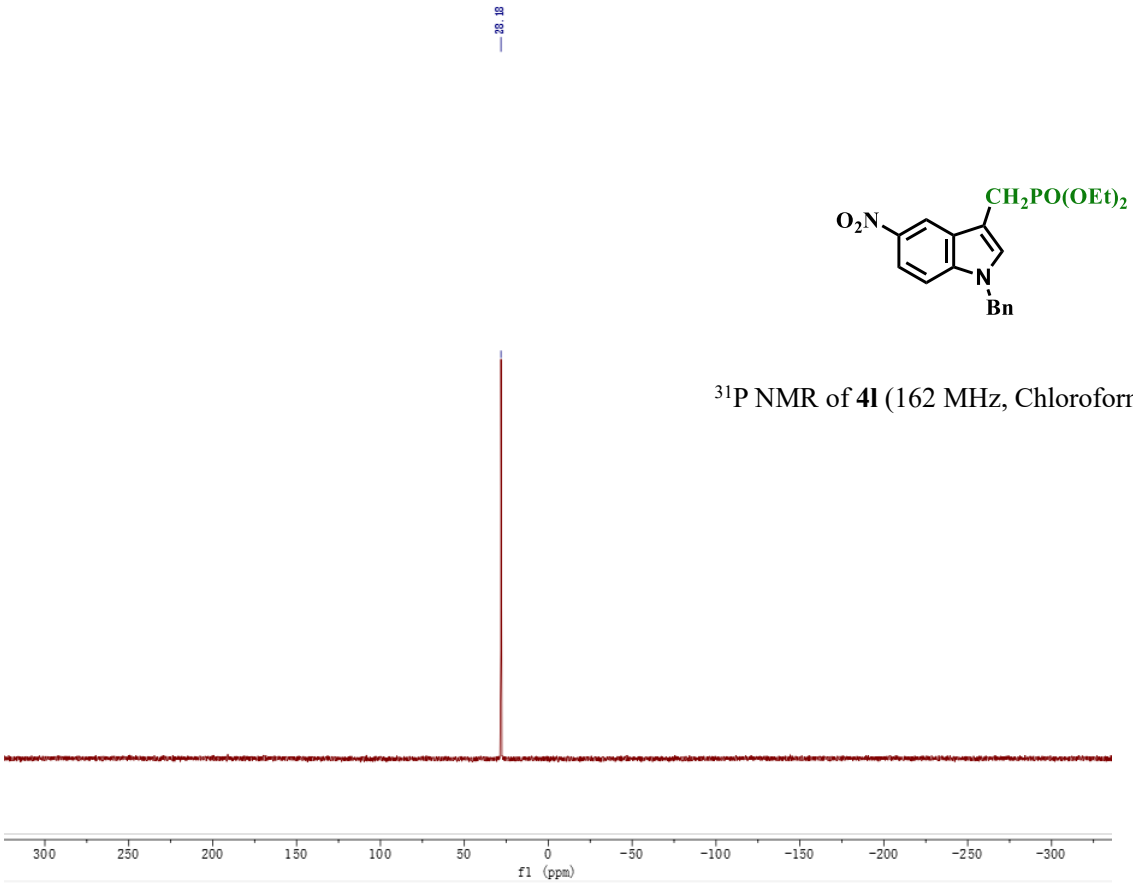
^{1}H NMR of **4l** (400 MHz, Chloroform-*d*)



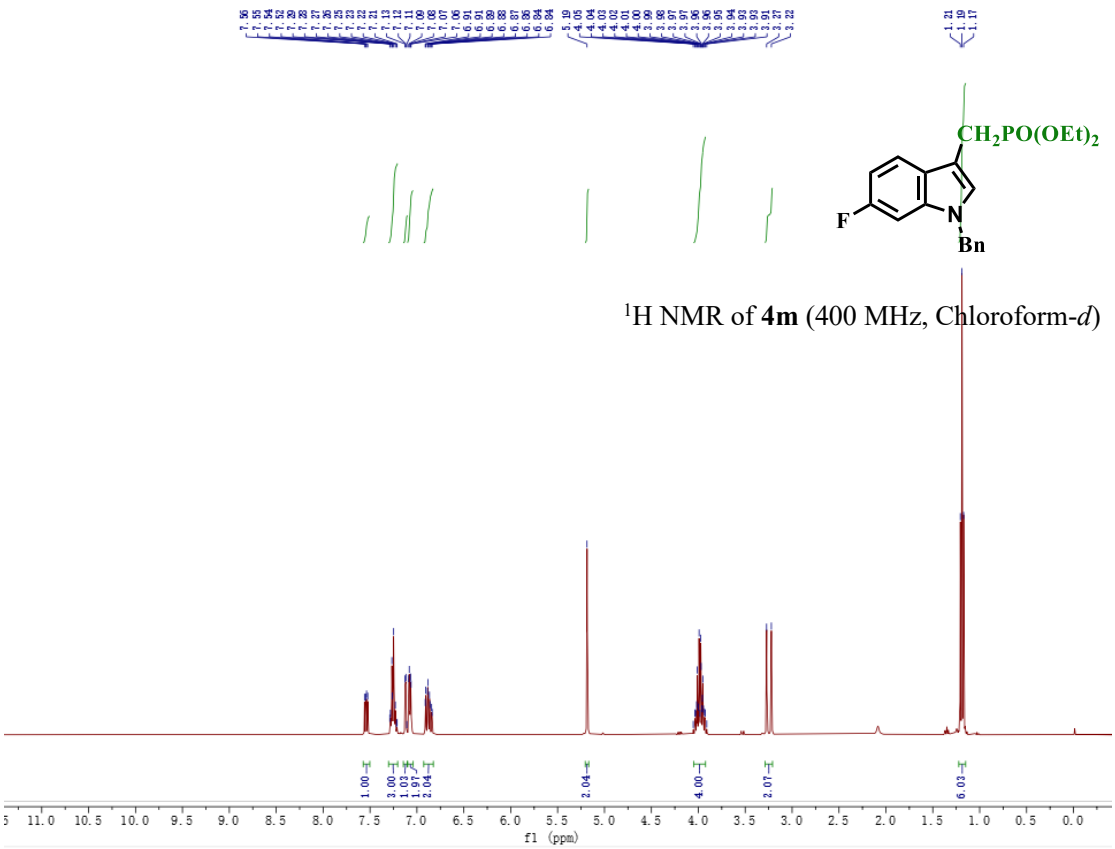


^{13}C NMR of **4l** (101 MHz, Chloroform-*d*)

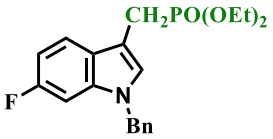




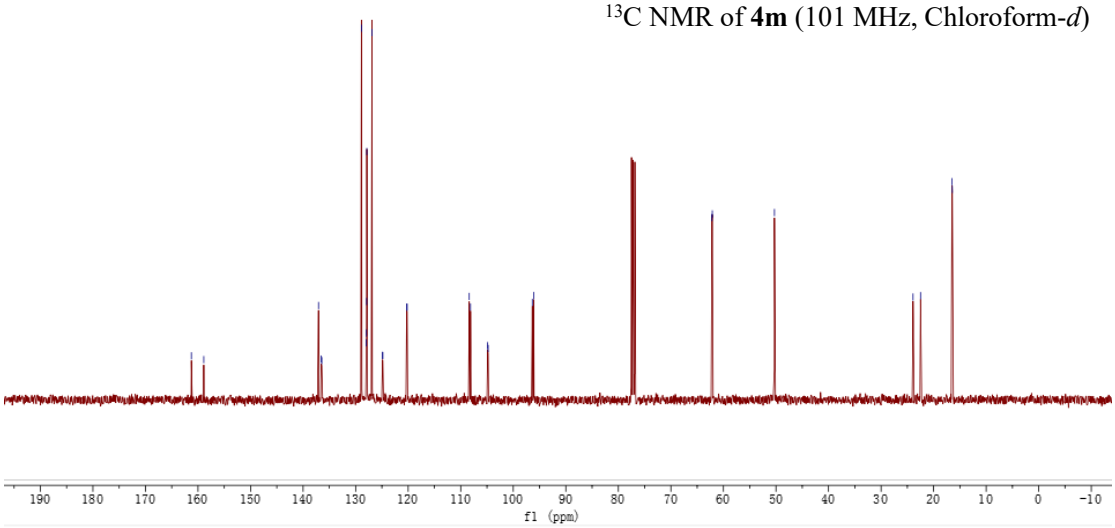
^{31}P NMR of **4l** (162 MHz, Chloroform-*d*)

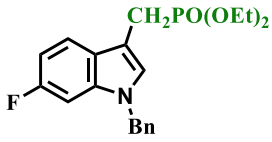


^{1}H NMR of **4m** (400 MHz, Chloroform-*d*)

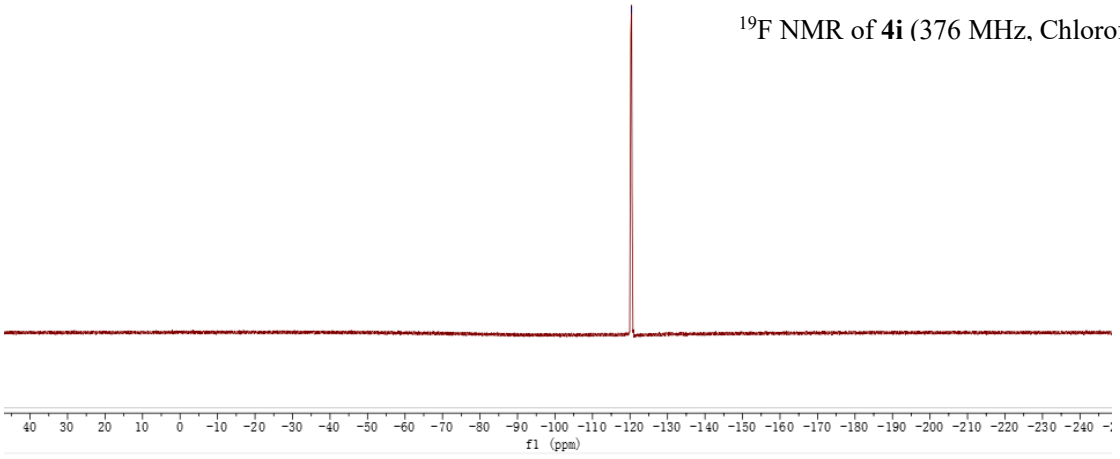


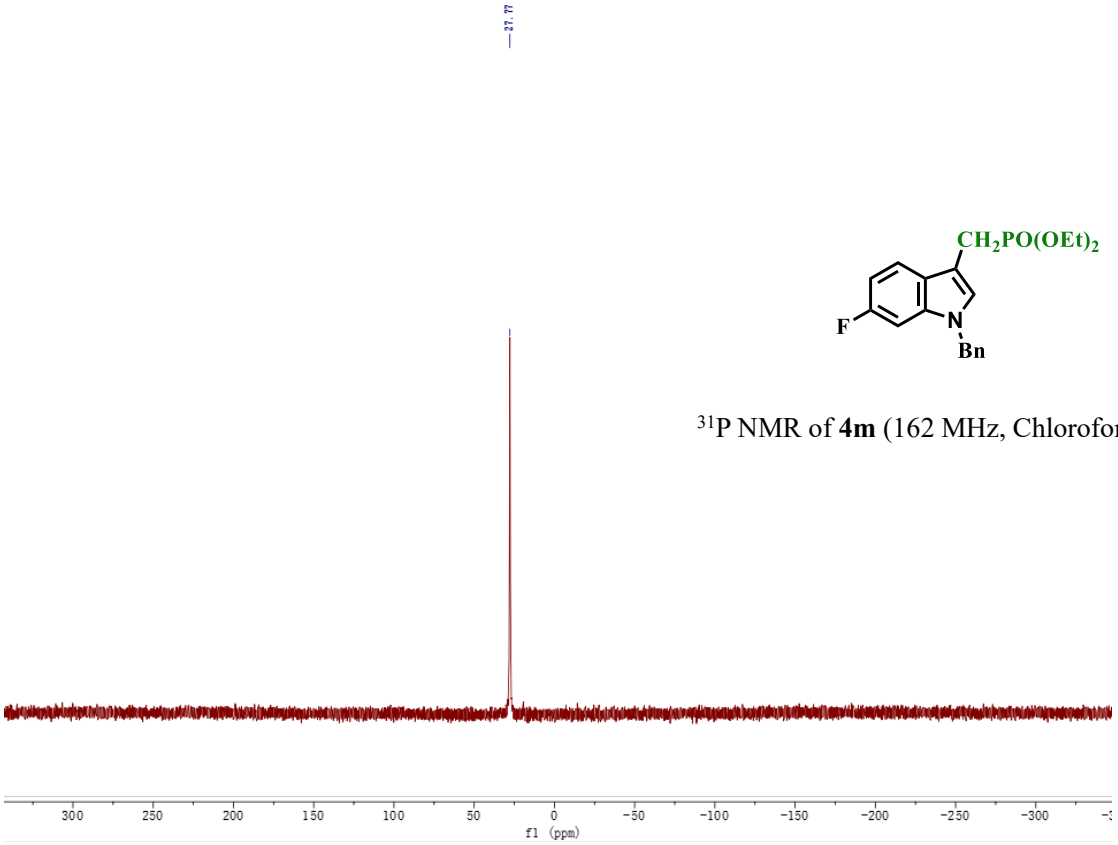
^{13}C NMR of **4m** (101 MHz, Chloroform-*d*)



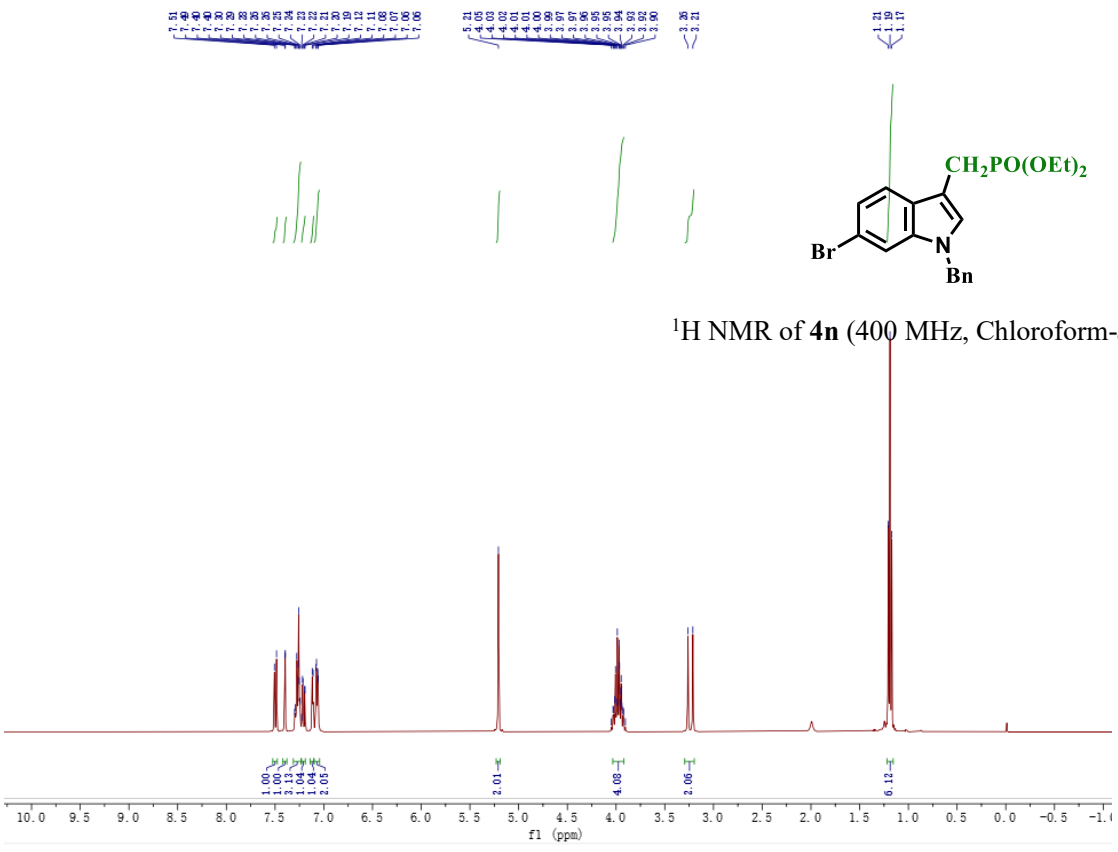


^{19}F NMR of **4i** (376 MHz, Chloroform-*d*)

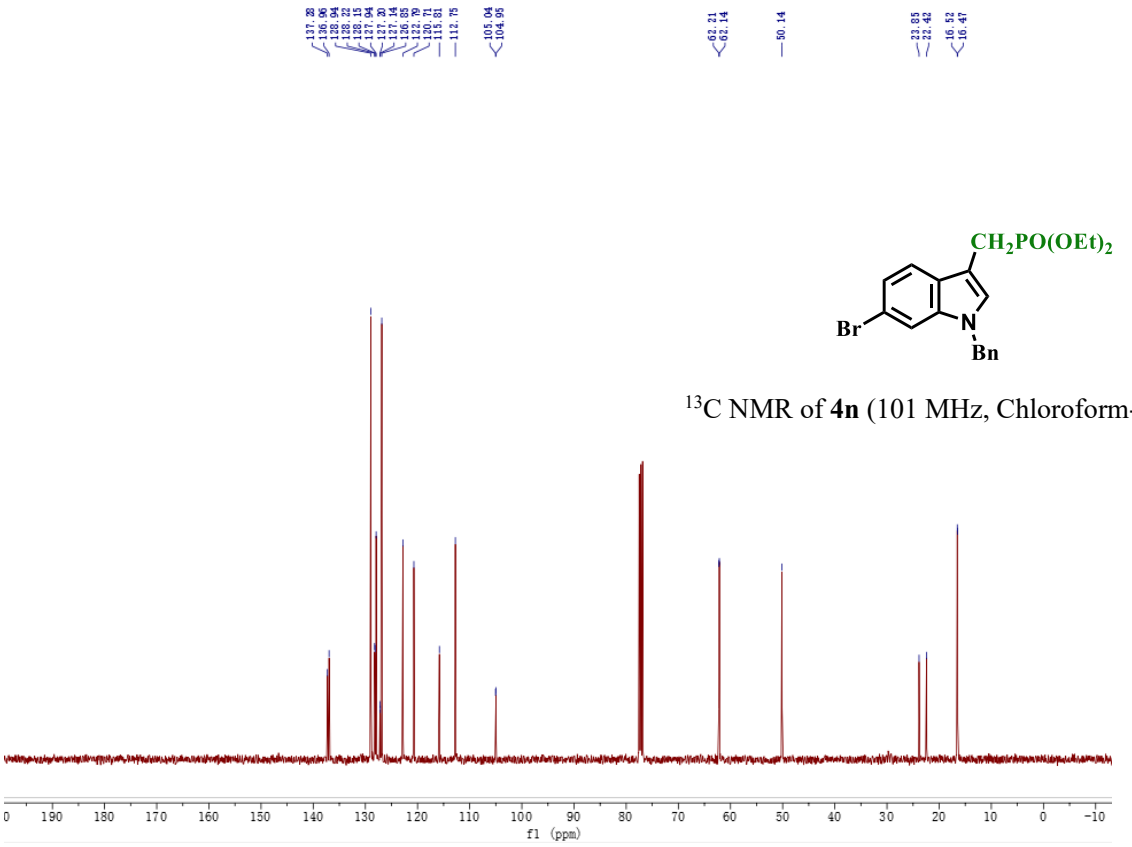




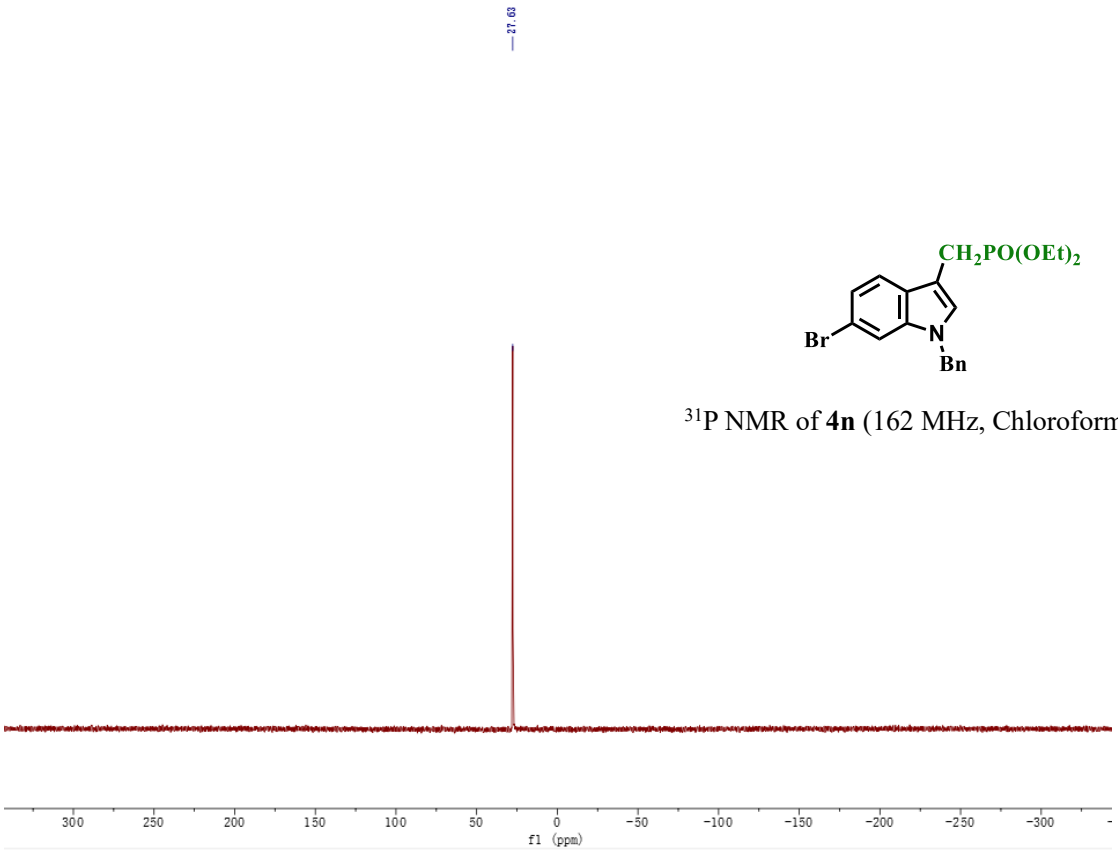
^{31}P NMR of **4m** (162 MHz, Chloroform-*d*)



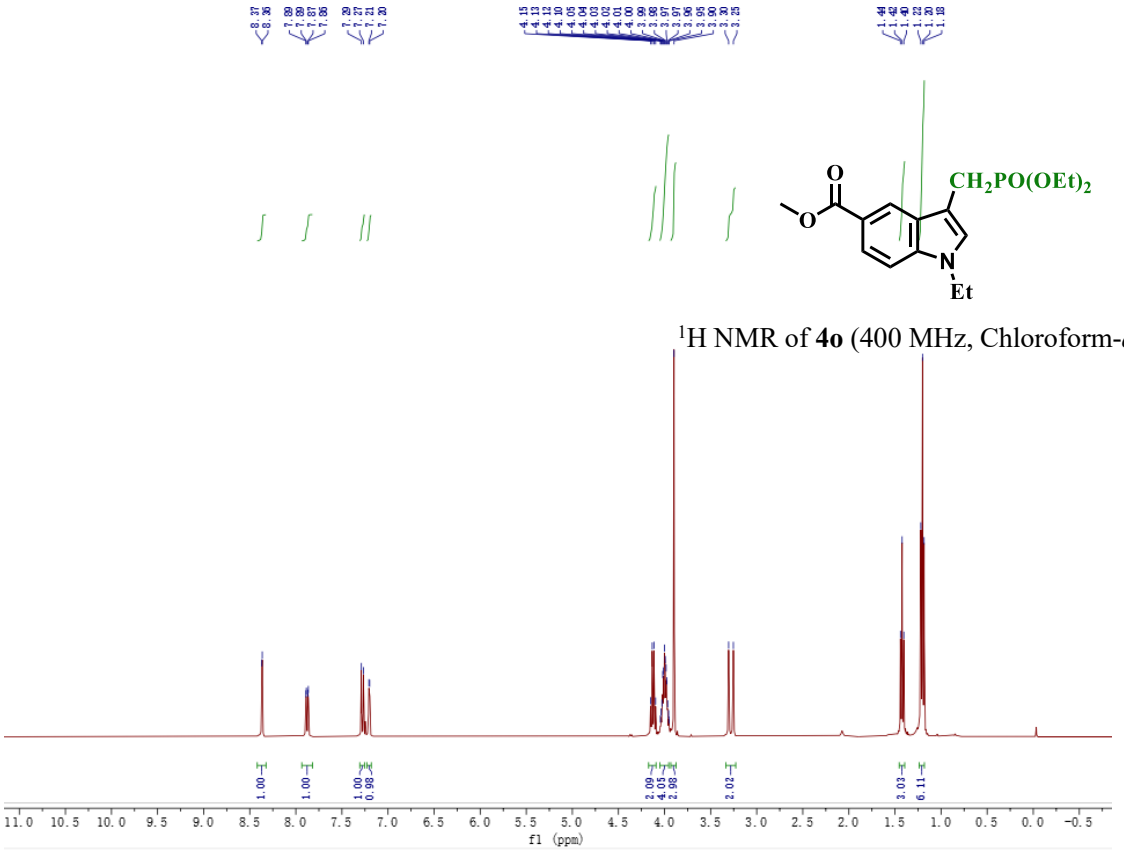
^{1}H NMR of **4n** (400 MHz, Chloroform-*d*)



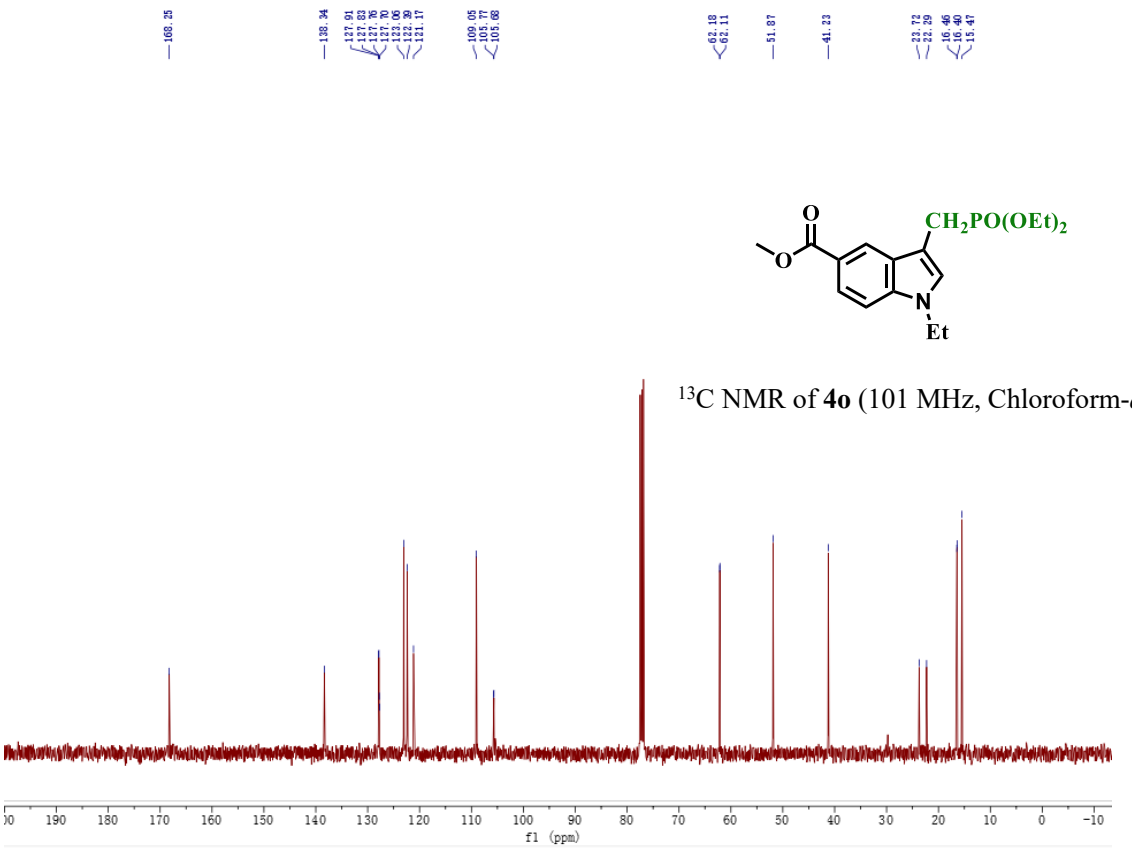
^{13}C NMR of **4n** (101 MHz, Chloroform-*d*)



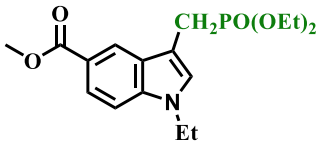
^{31}P NMR of **4n** (162 MHz, Chloroform-*d*)



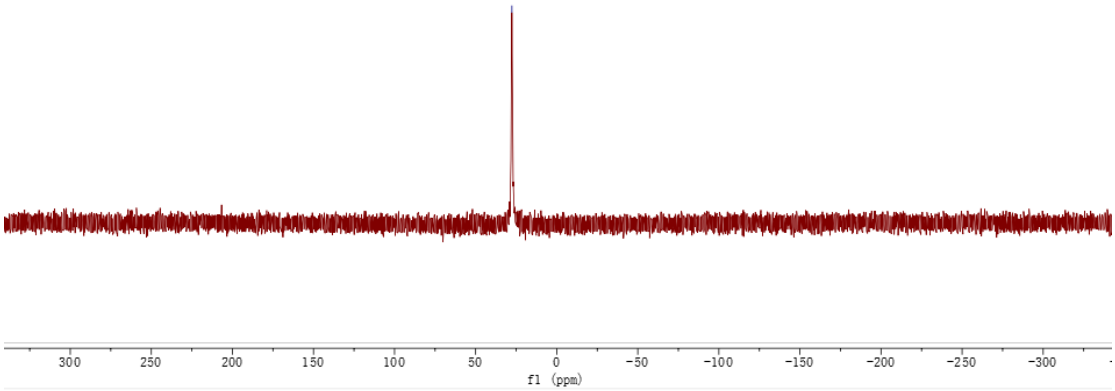
^{1}H NMR of **4o** (400 MHz, Chloroform-*d*)

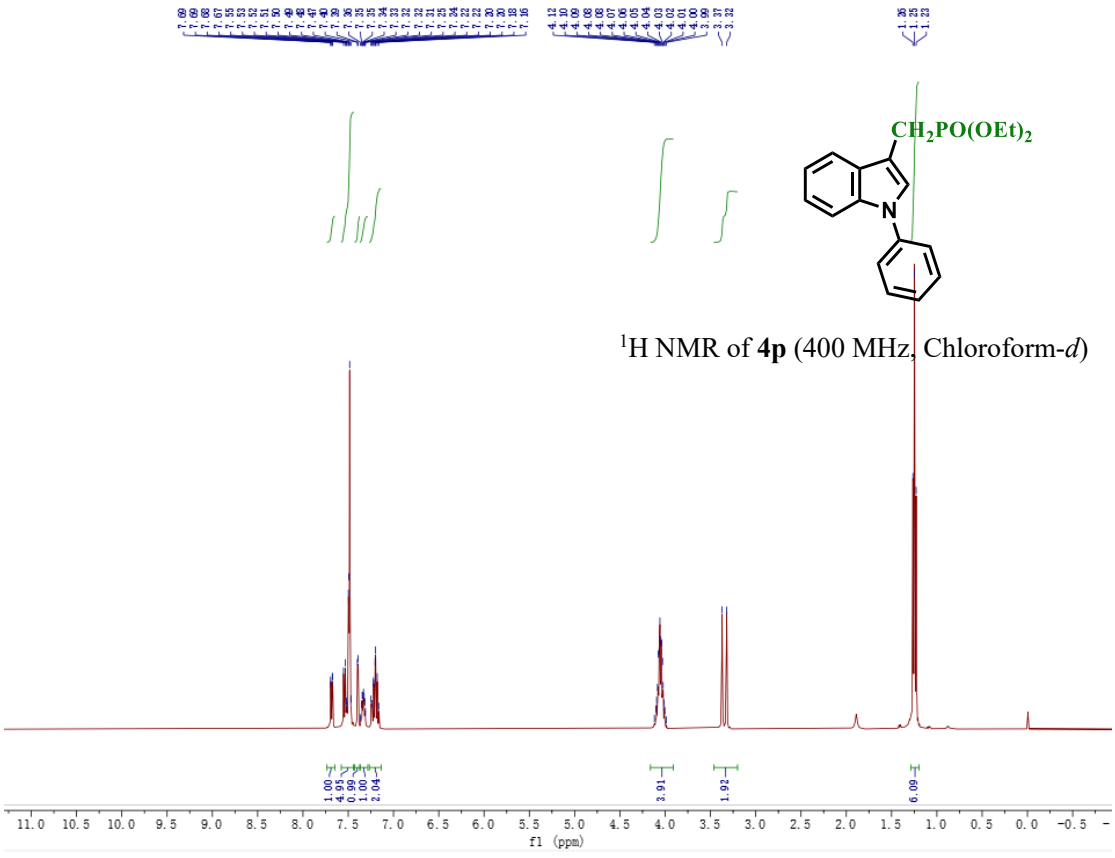


^{13}C NMR of **4o** (101 MHz, Chloroform-*d*)

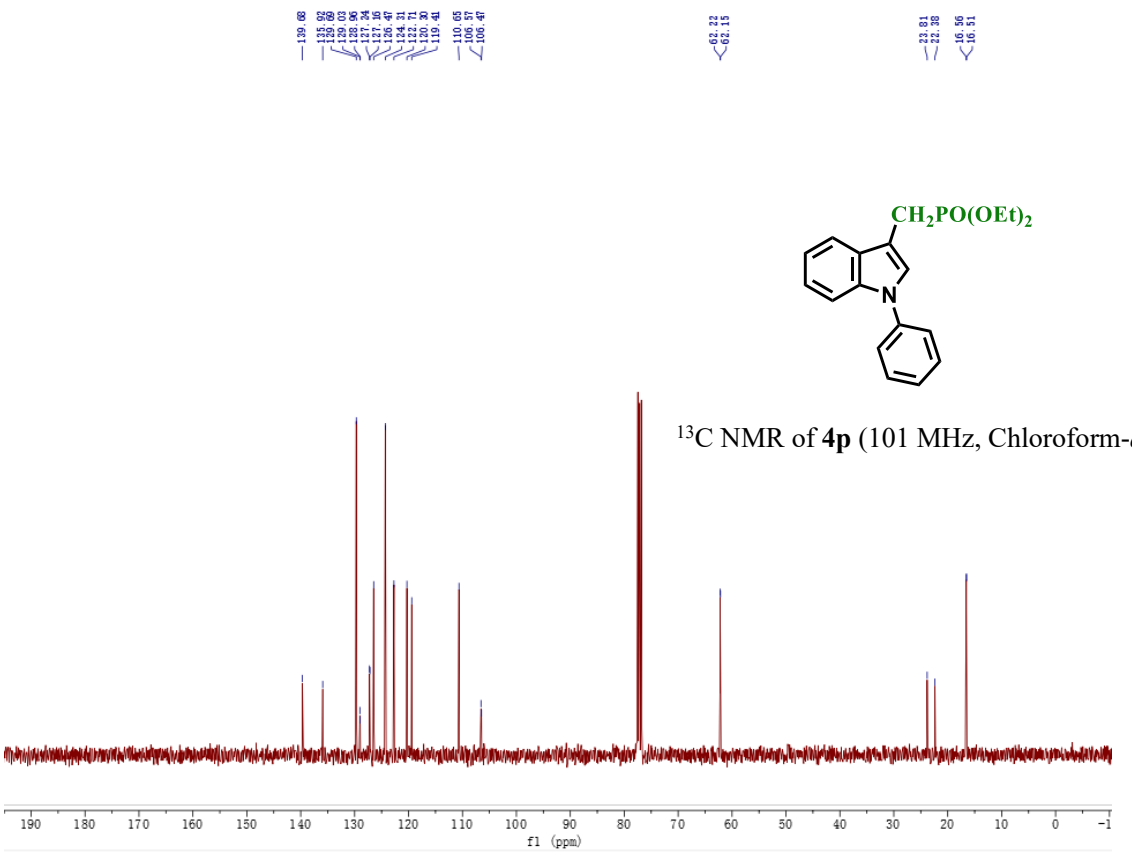


^{31}P NMR of **4o** (162 MHz, Chloroform-*d*)

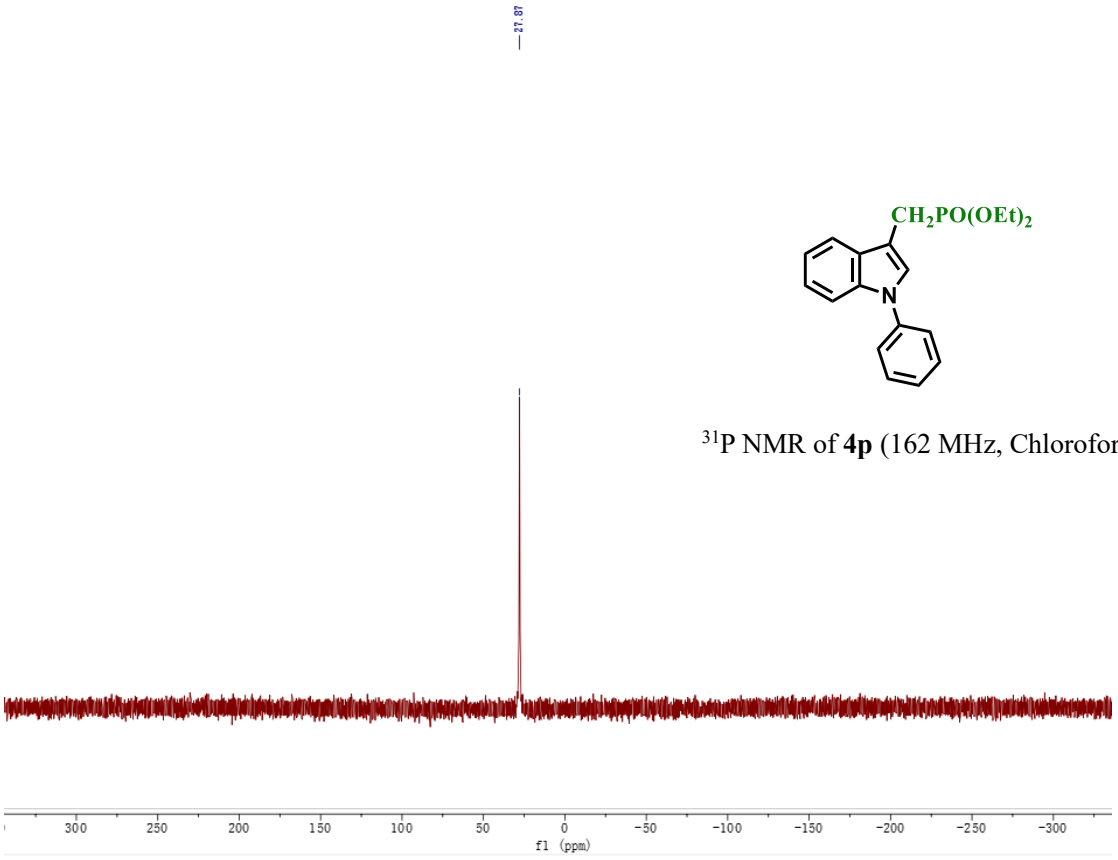




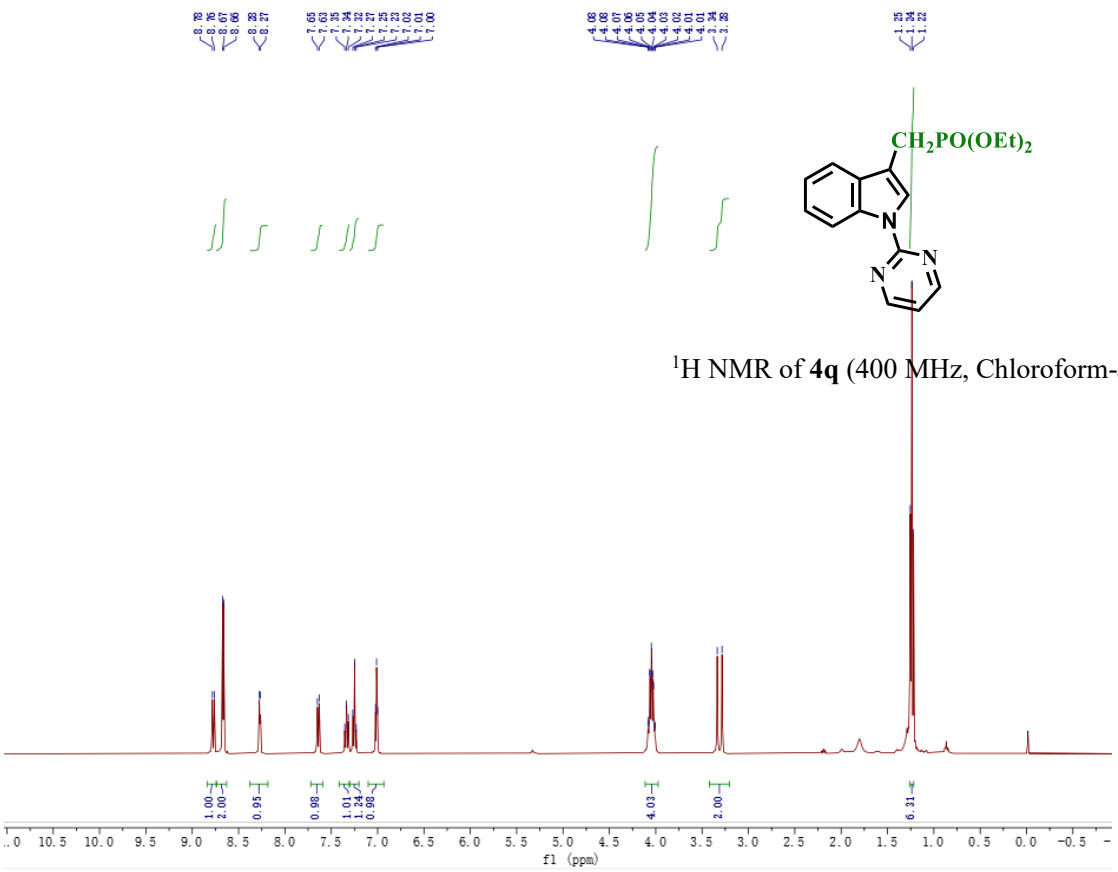
^{1}H NMR of **4p** (400 MHz, Chloroform-*d*)



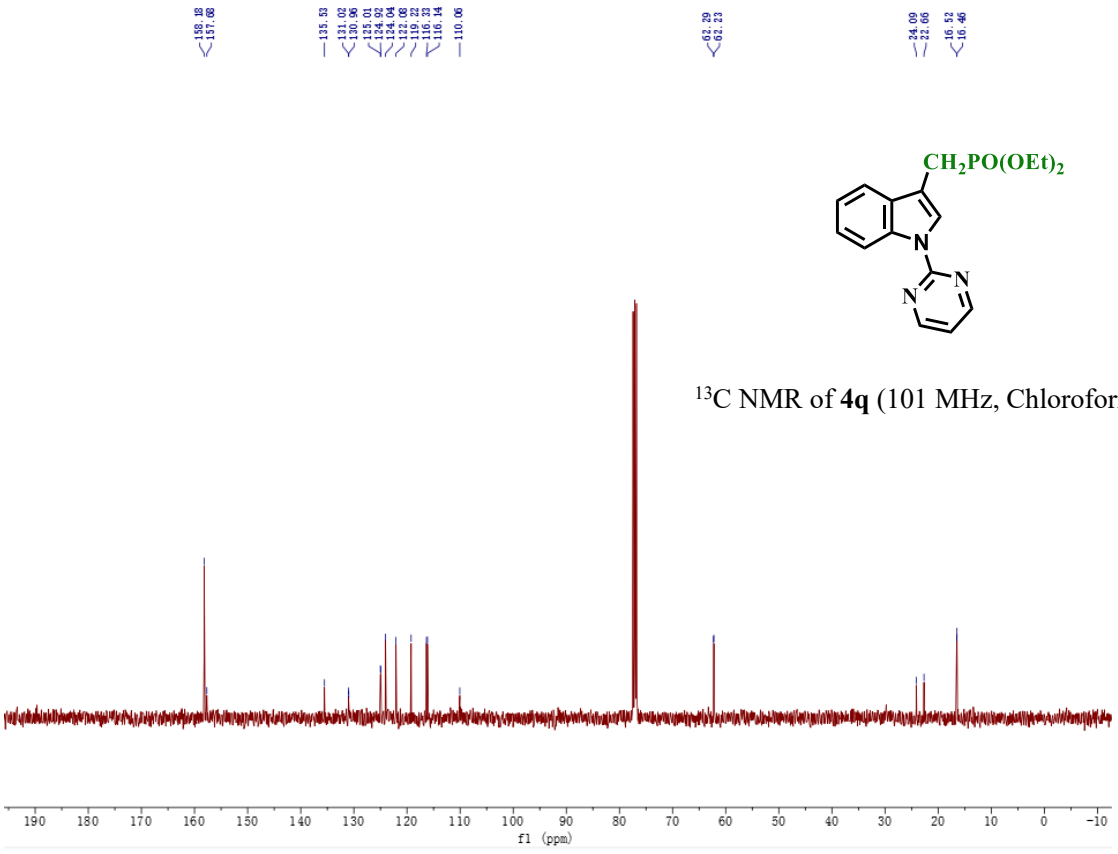
^{13}C NMR of **4p** (101 MHz, Chloroform-*d*)



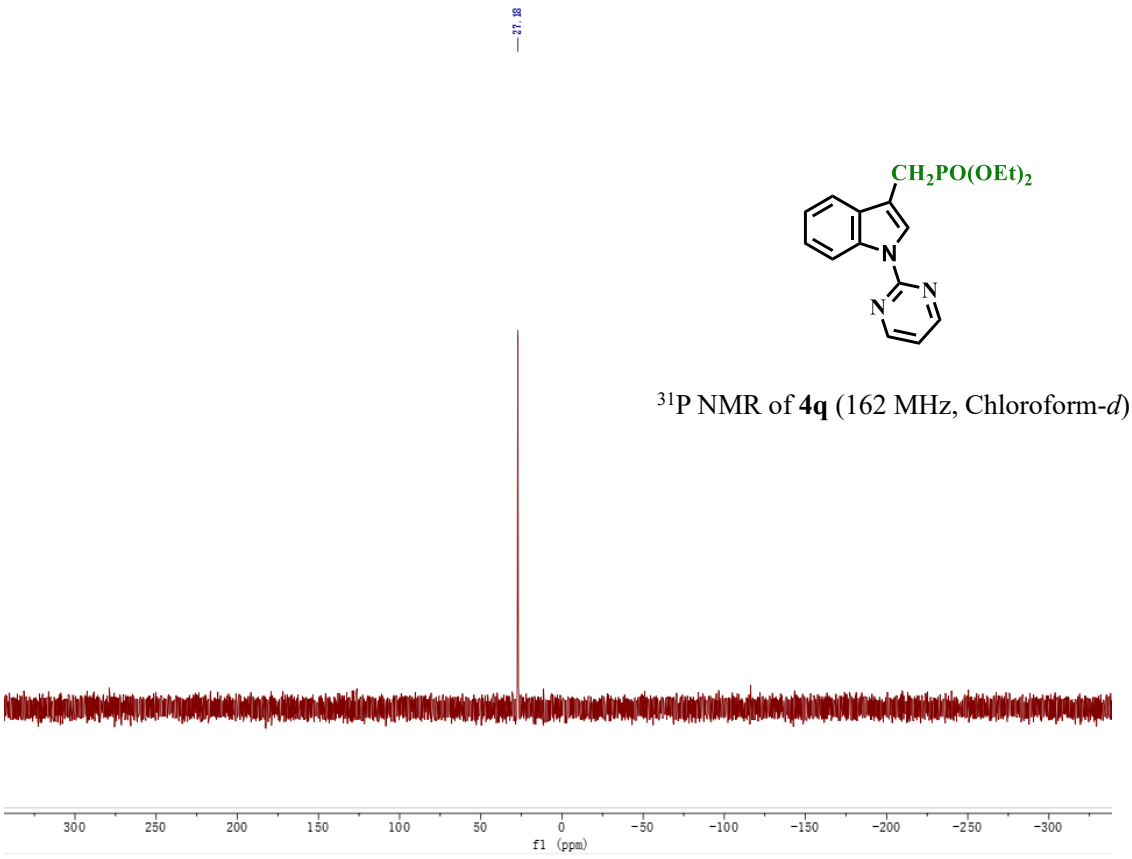
^{31}P NMR of **4p** (162 MHz, Chloroform-*d*)



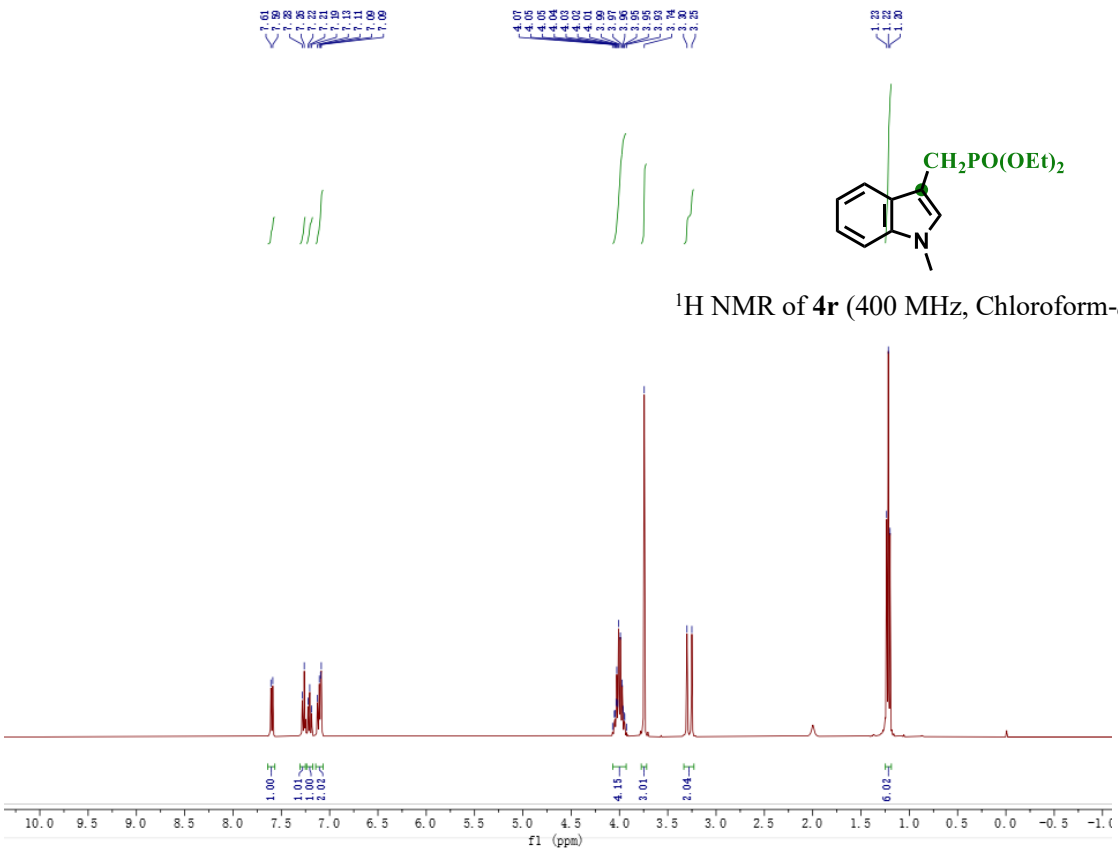
^{1}H NMR of **4q** (400 MHz, Chloroform-*d*)



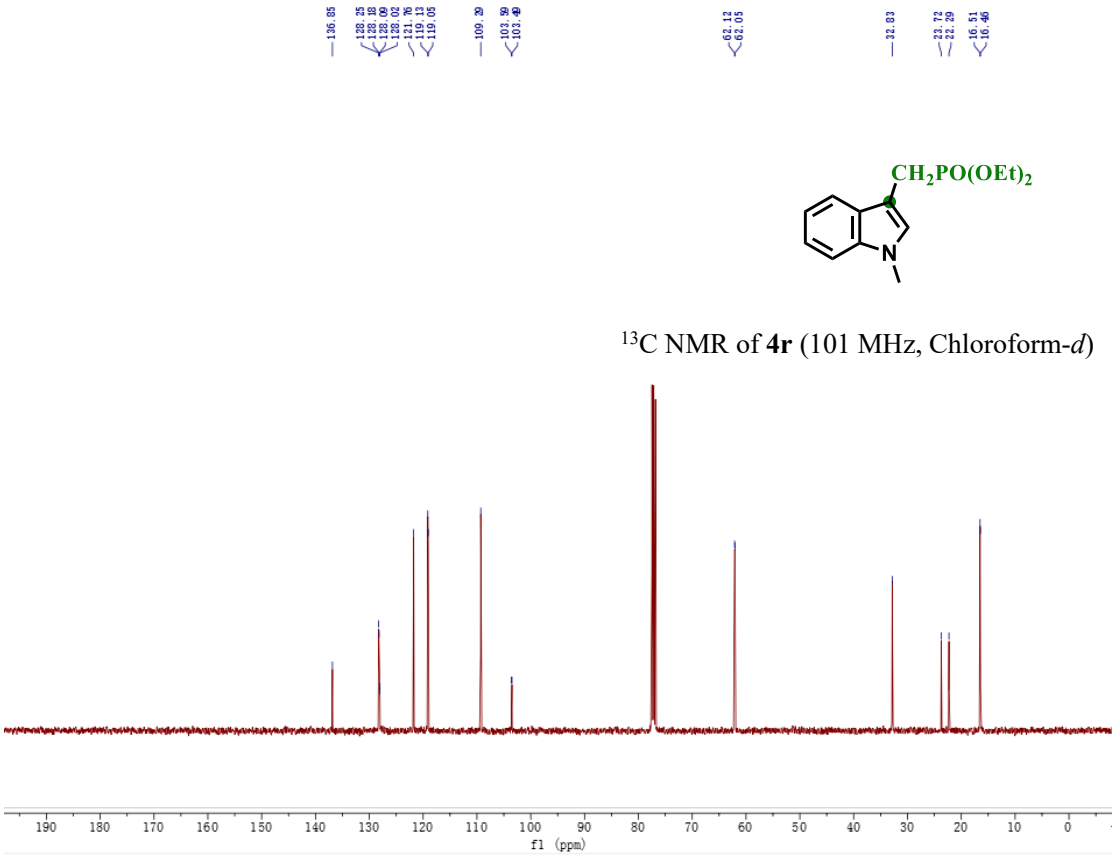
^{13}C NMR of **4q** (101 MHz, Chloroform-*d*)



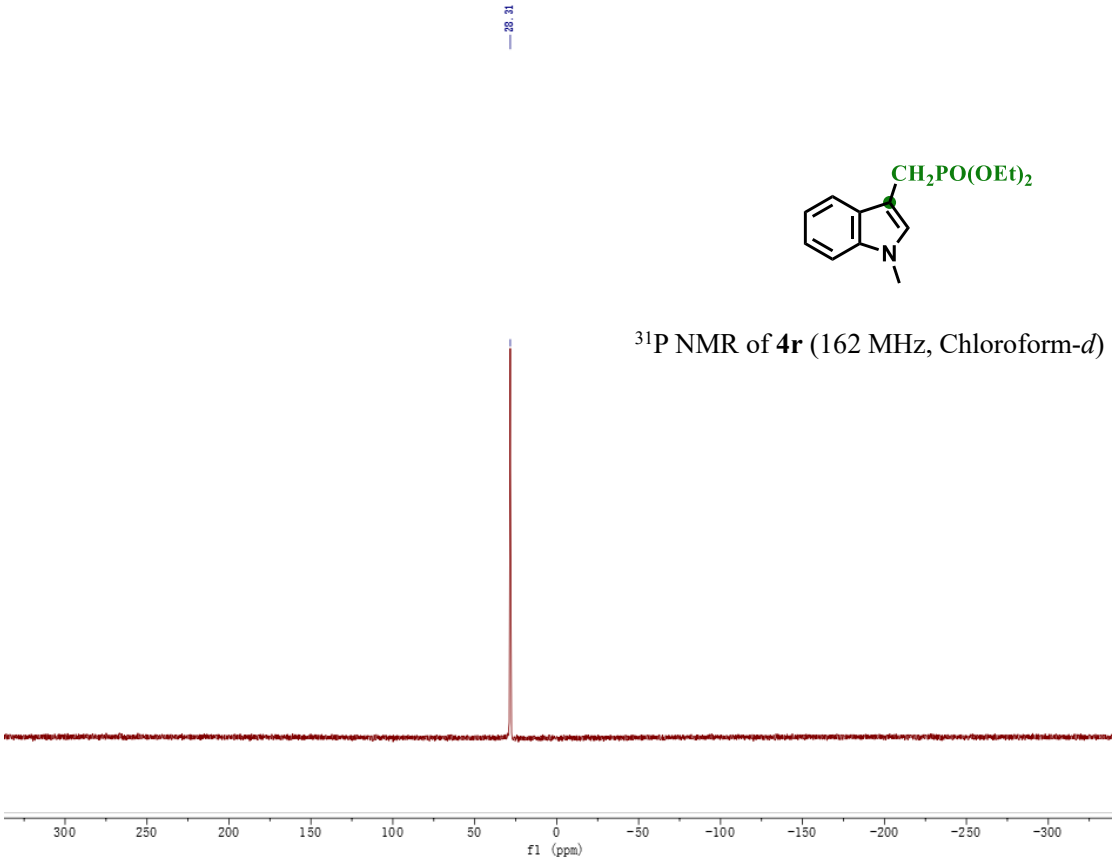
^{31}P NMR of **4q** (162 MHz, Chloroform-*d*)



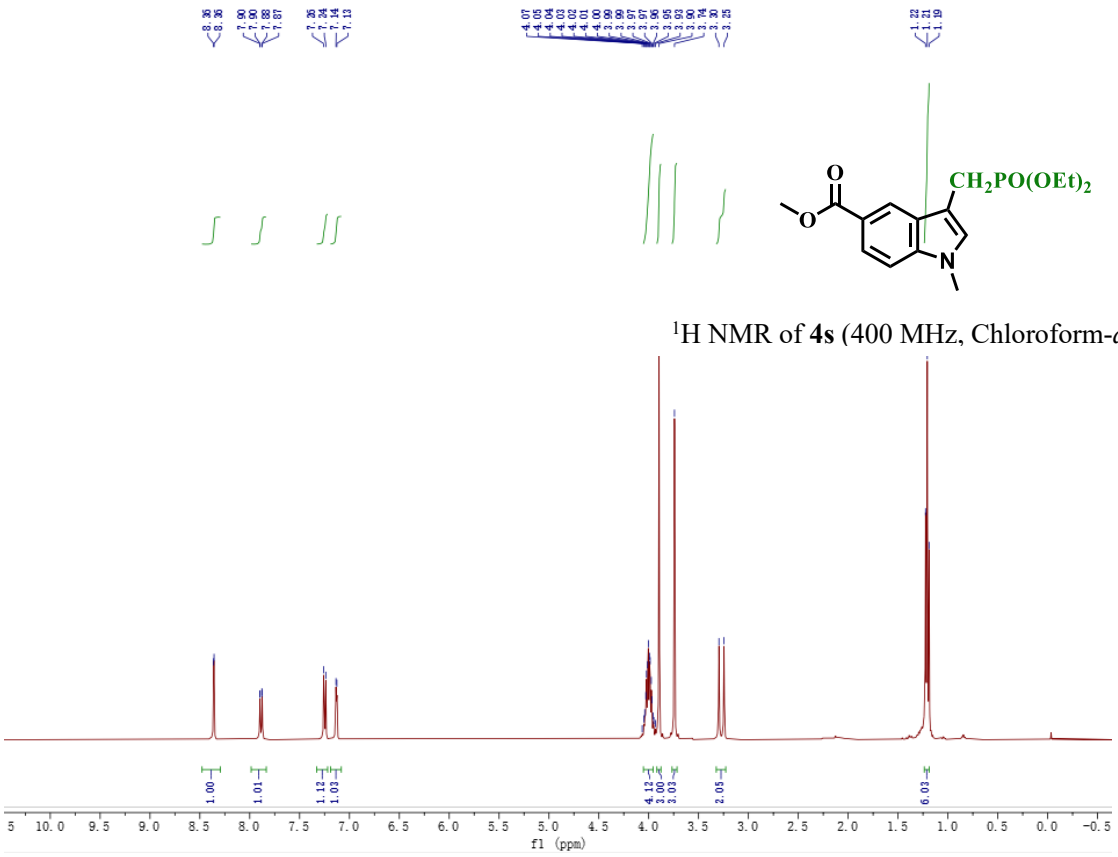
^{1}H NMR of **4r** (400 MHz, Chloroform-*d*)



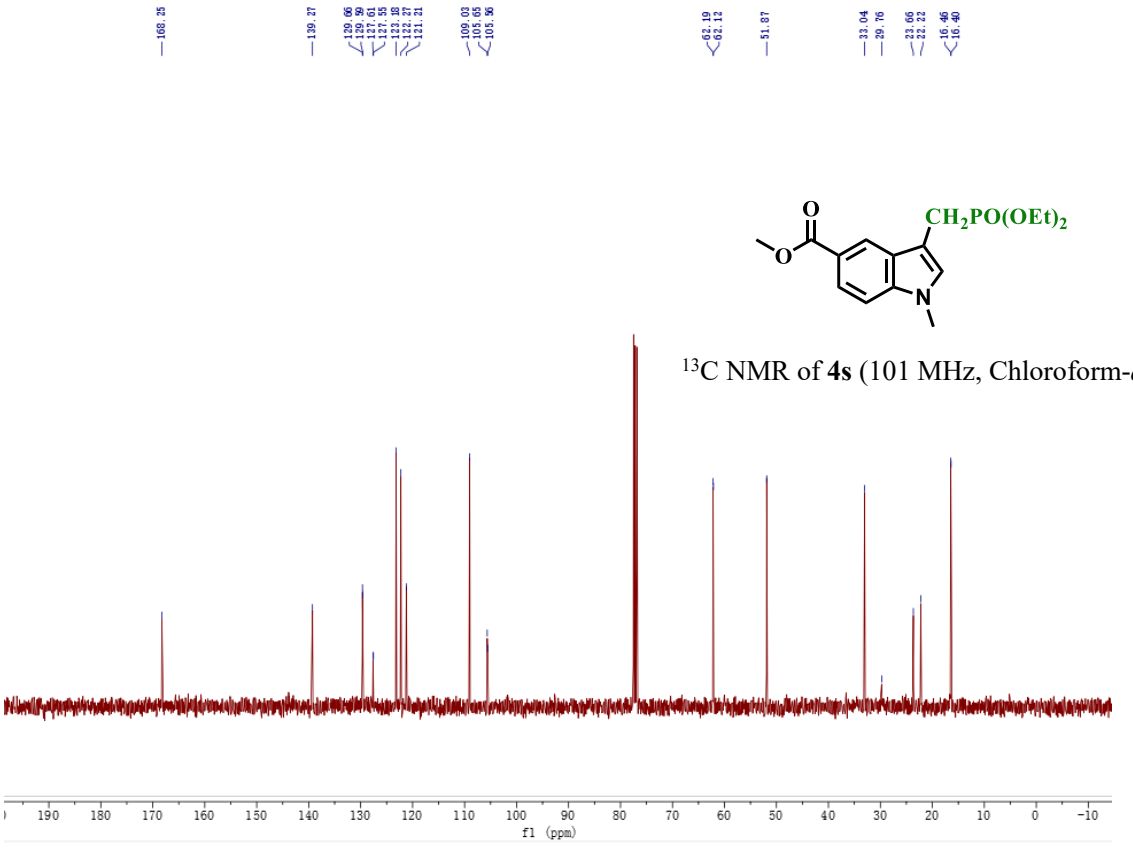
^{13}C NMR of **4r** (101 MHz, Chloroform-*d*)



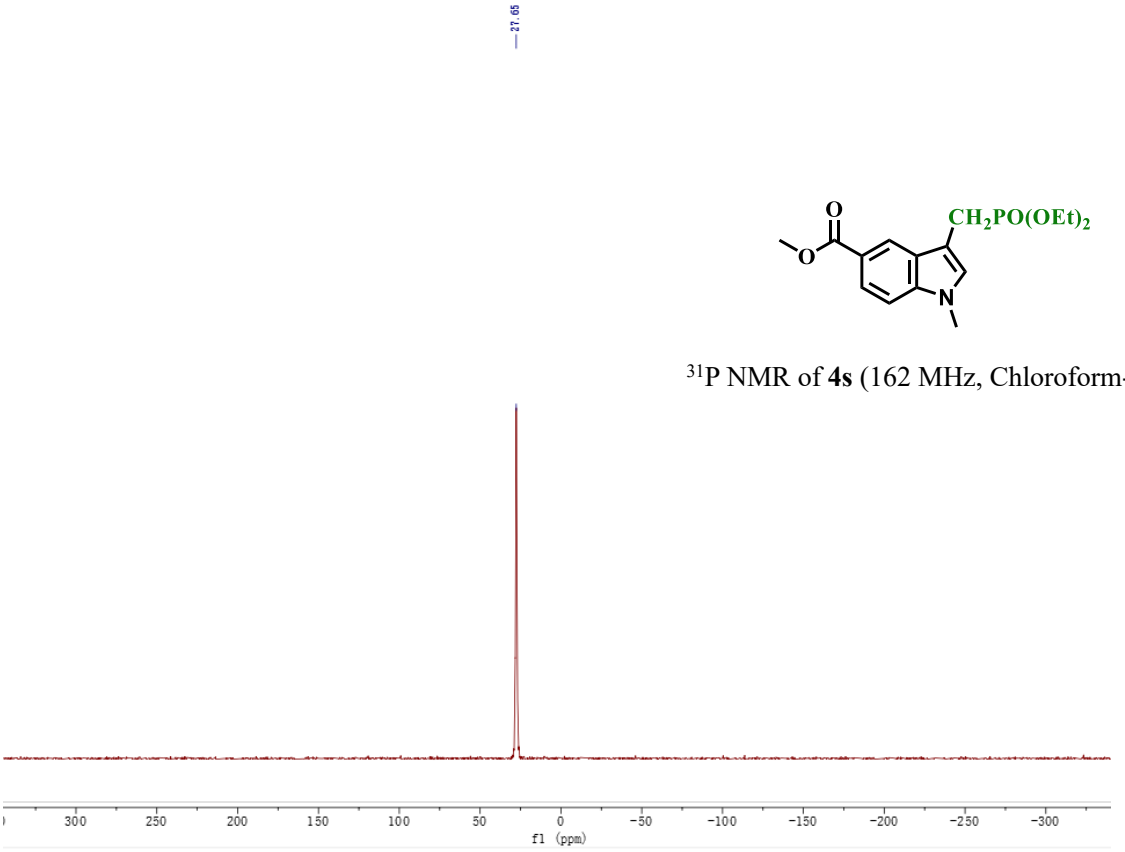
^{31}P NMR of **4r** (162 MHz, Chloroform-*d*)



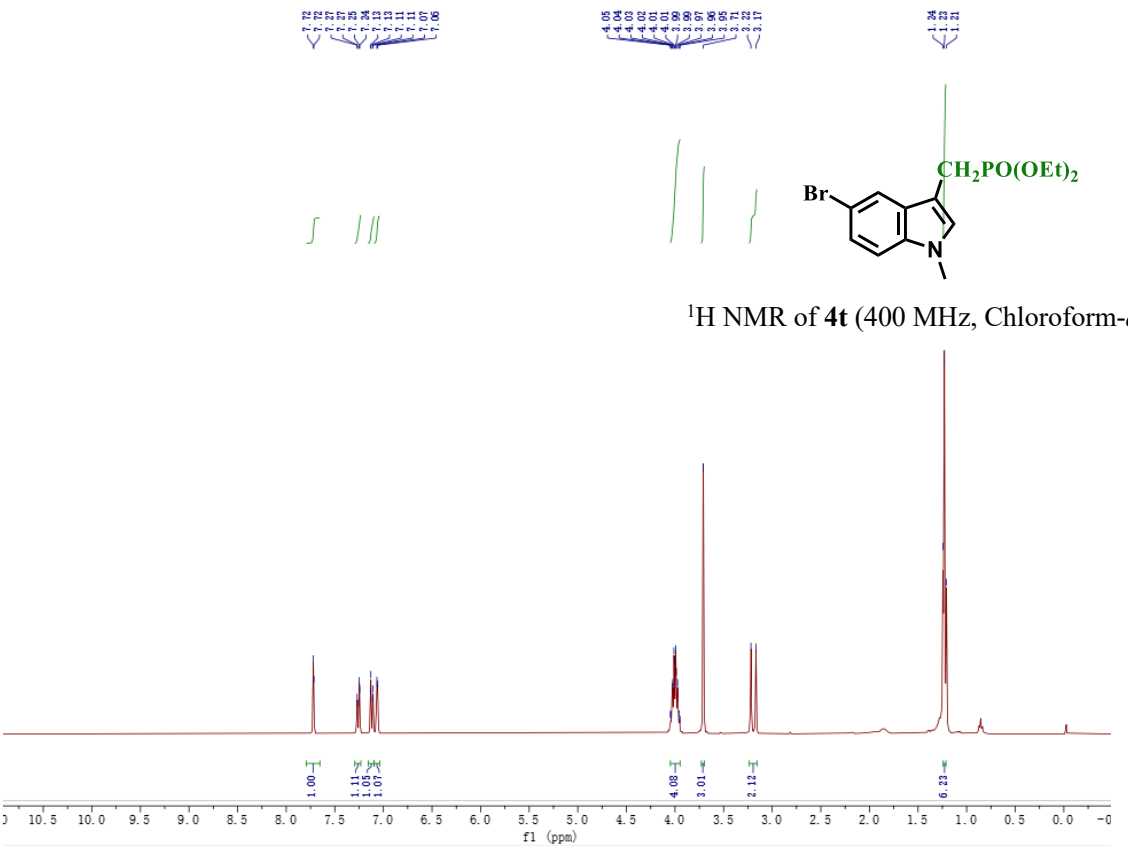
^{1}H NMR of **4s** (400 MHz, Chloroform-*d*)



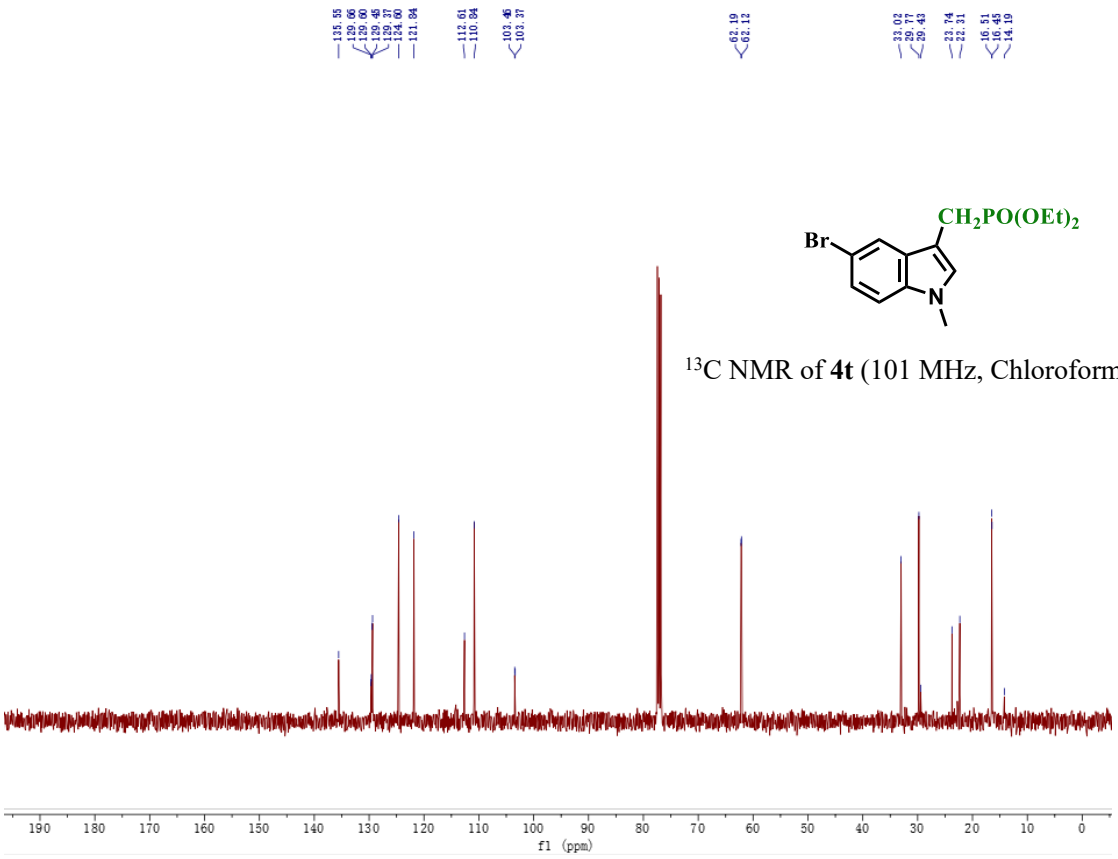
^{13}C NMR of **4s** (101 MHz, Chloroform-*d*)



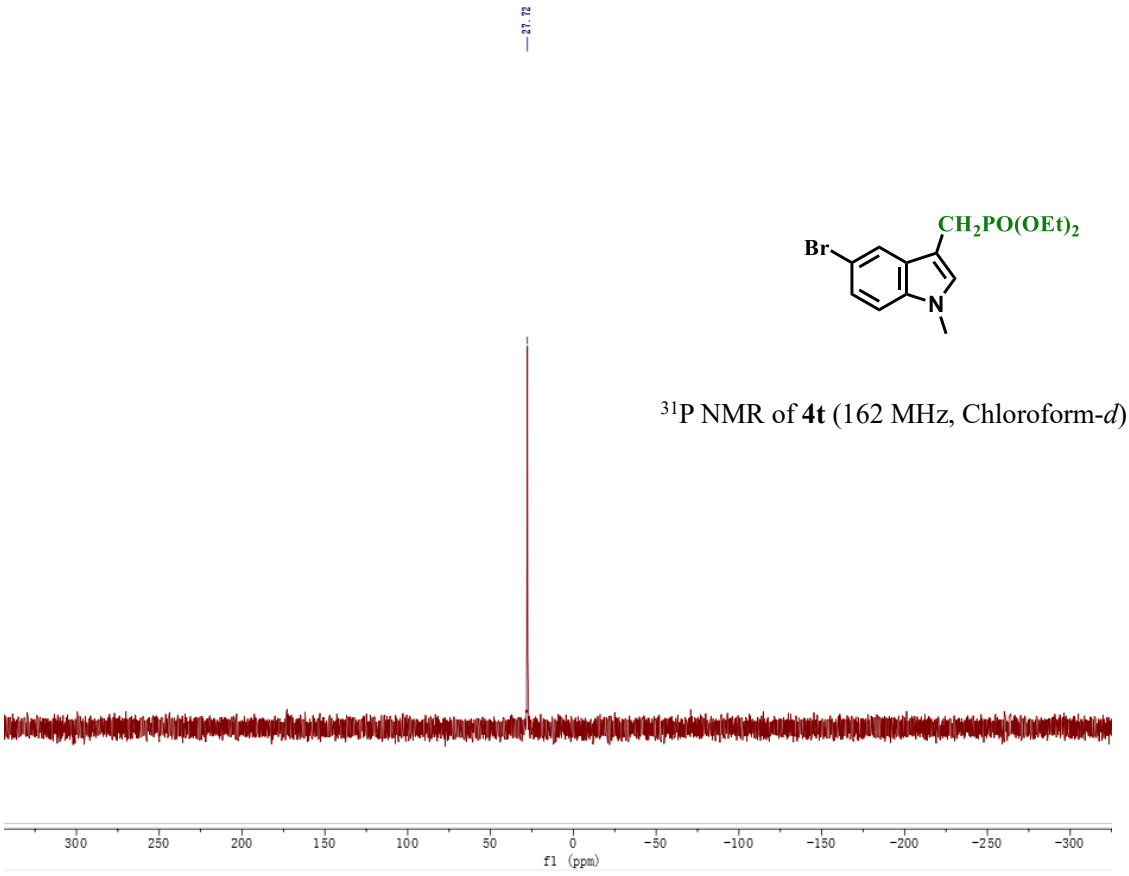
^{31}P NMR of **4s** (162 MHz, Chloroform-*d*)



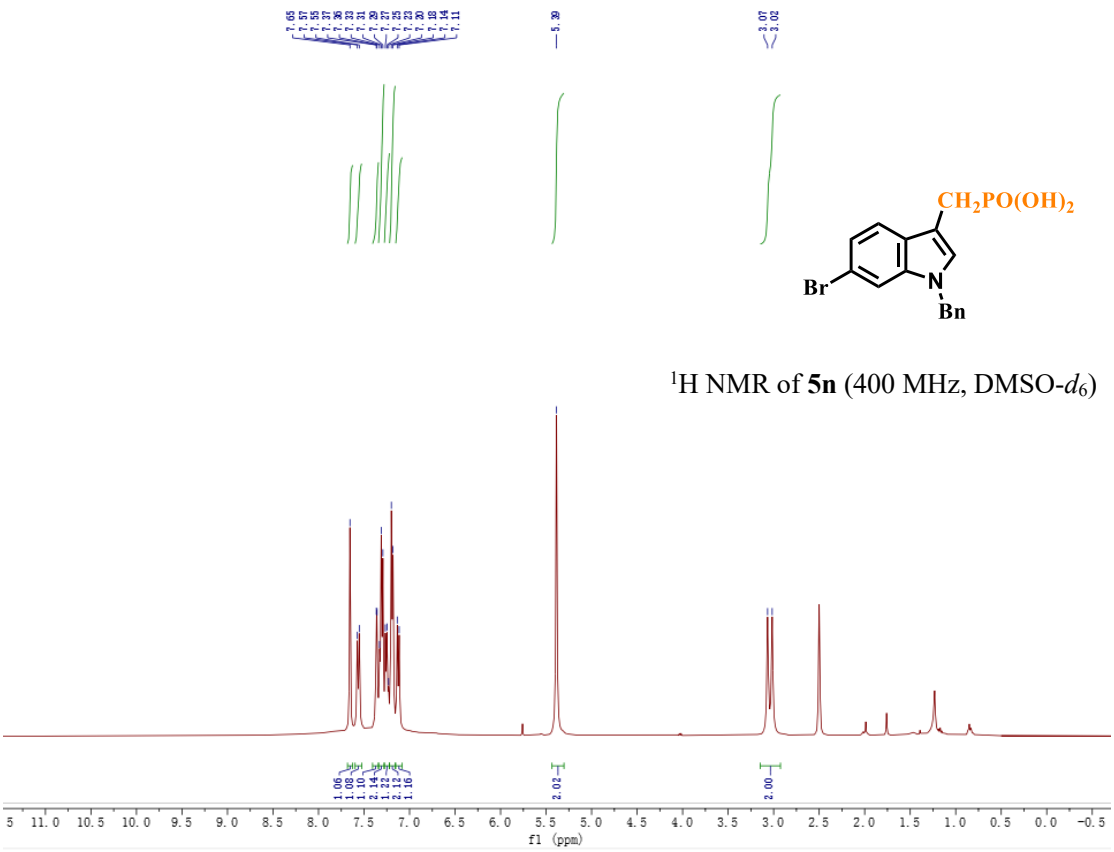
^{1}H NMR of **4t** (400 MHz, Chloroform-*d*)



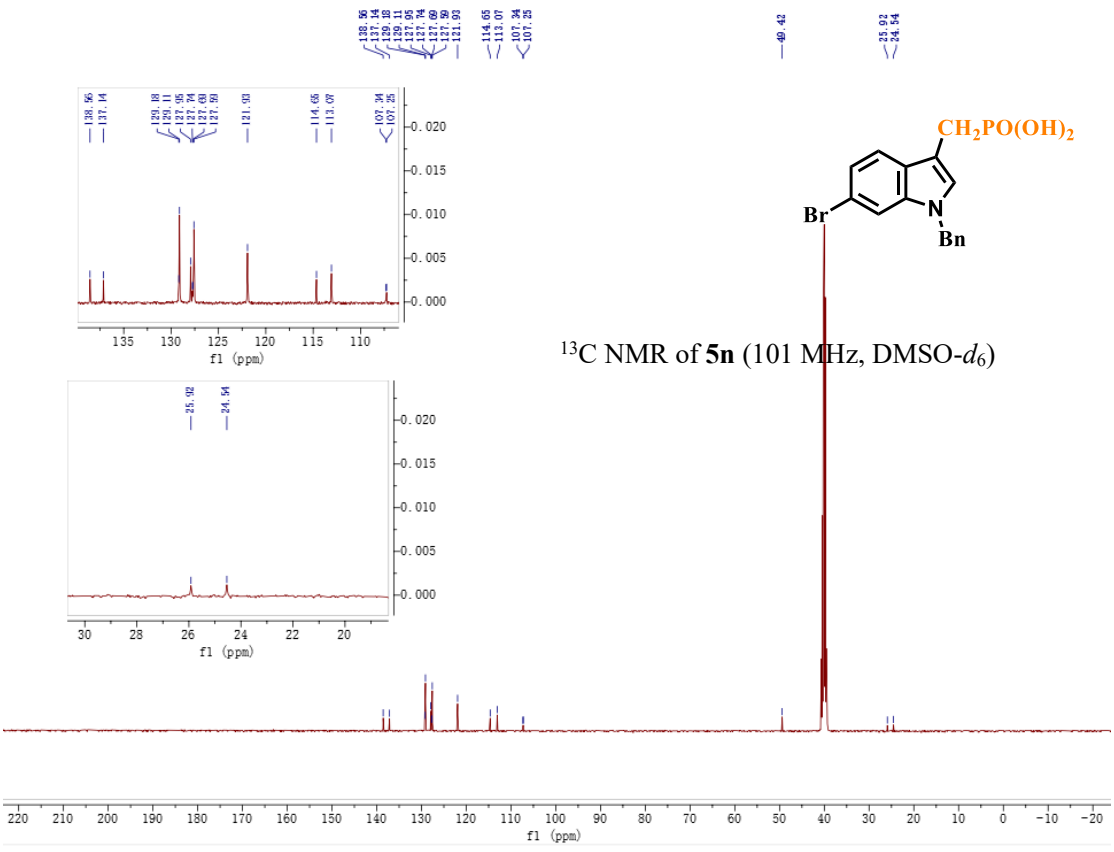
^{13}C NMR of **4t** (101 MHz, Chloroform-*d*)



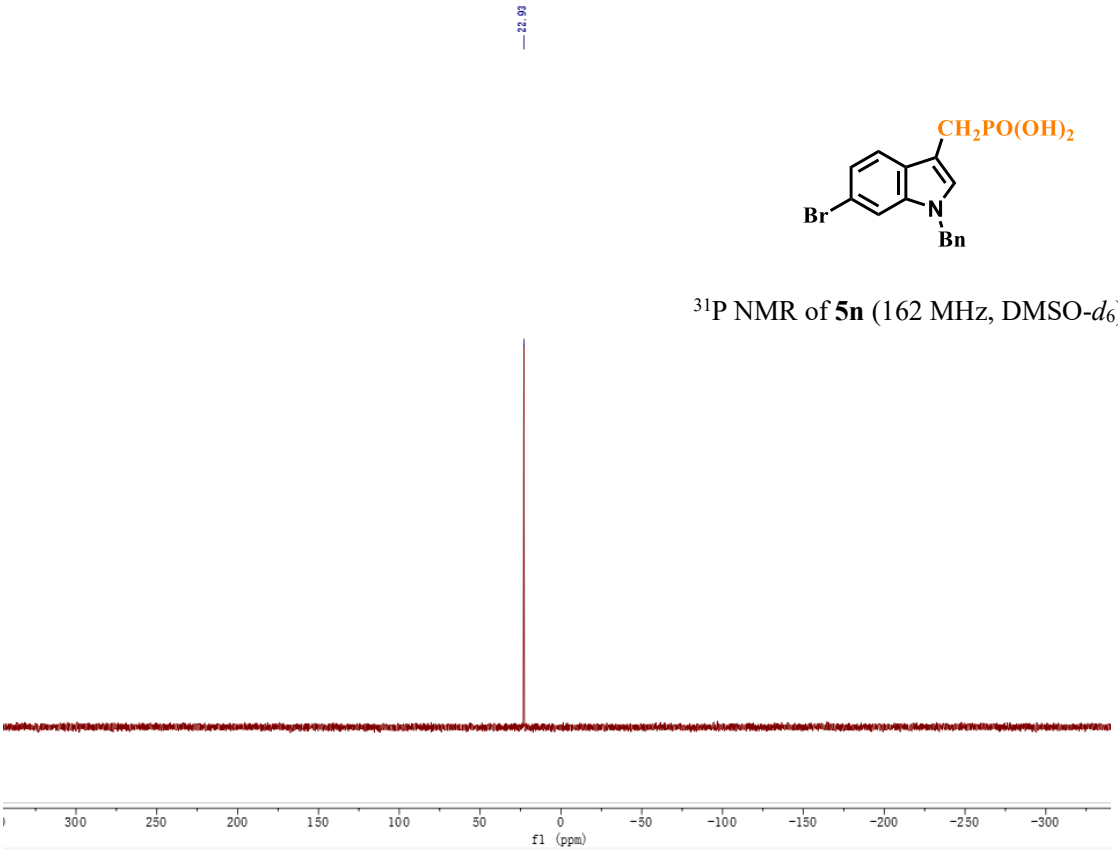
^{31}P NMR of **4t** (162 MHz, Chloroform-*d*)



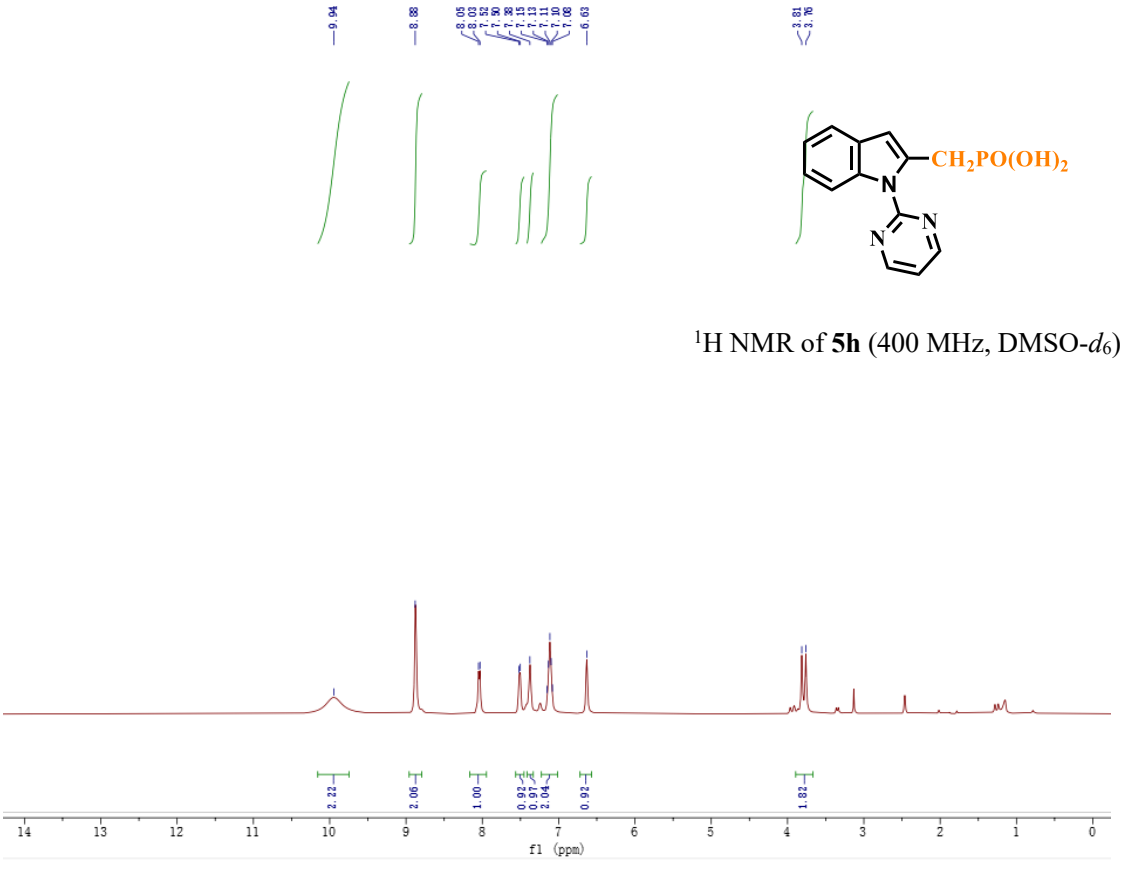
^{1}H NMR of **5n** (400 MHz, DMSO-d_6)



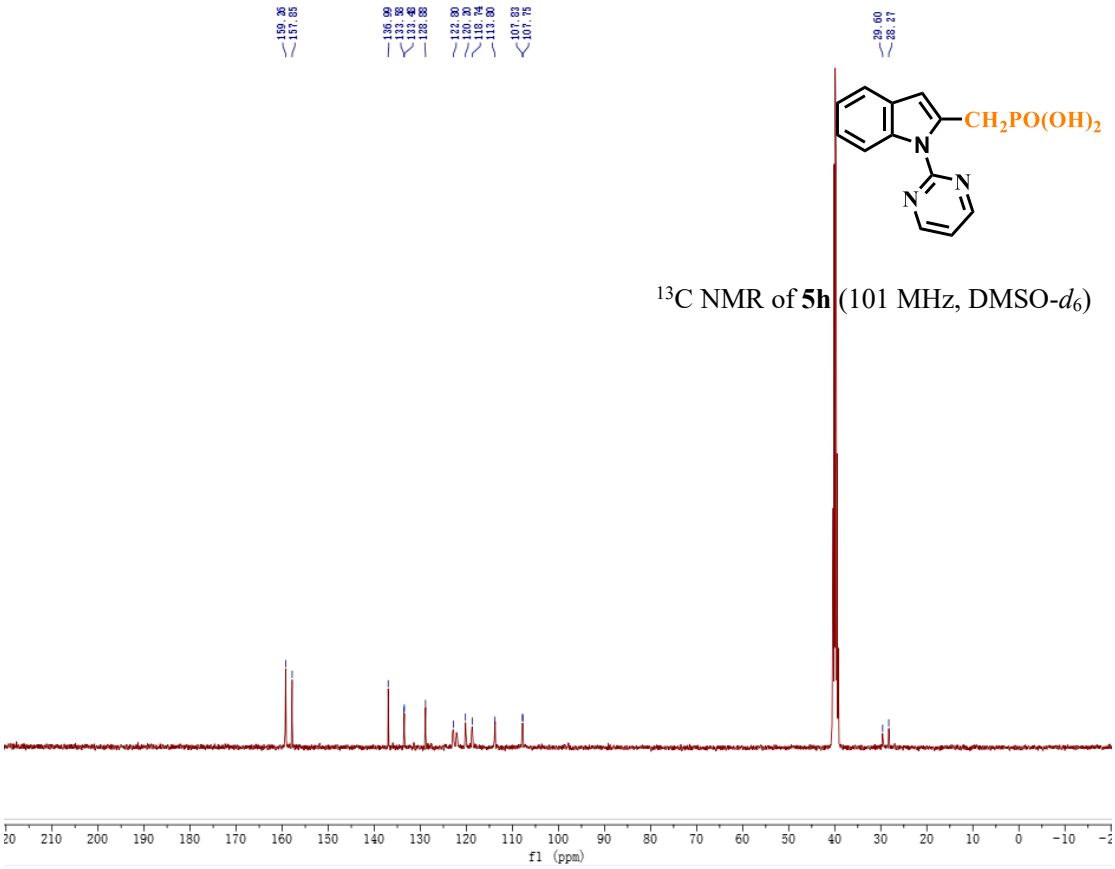
^{13}C NMR of **5n** (101 MHz, DMSO-d_6)



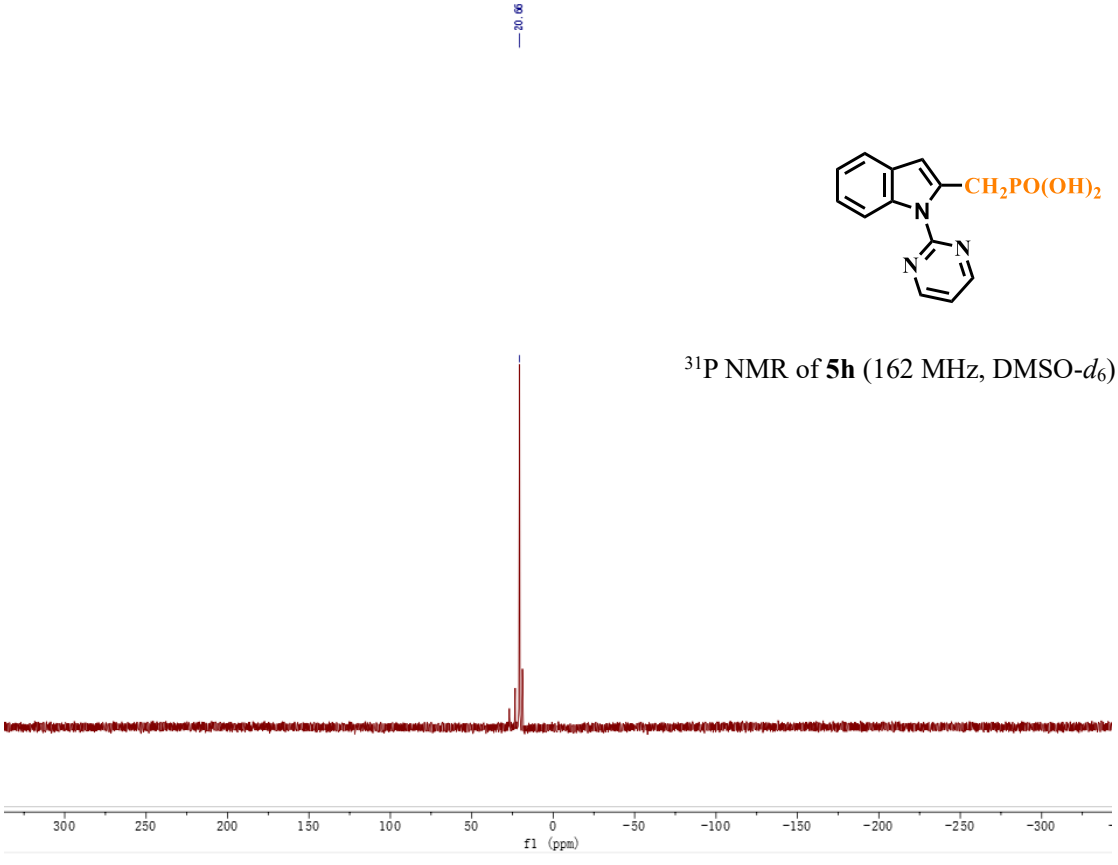
^{31}P NMR of **5n** (162 MHz, DMSO-d_6)



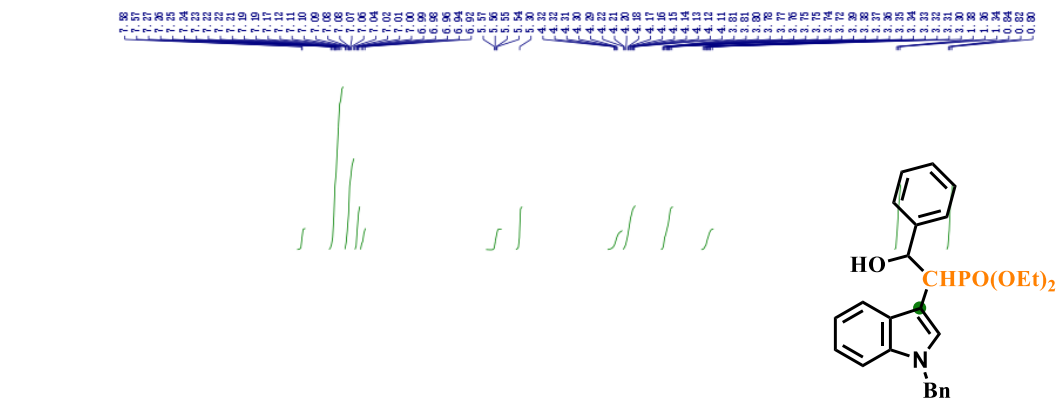
^{1}H NMR of **5h** (400 MHz, DMSO-d_6)



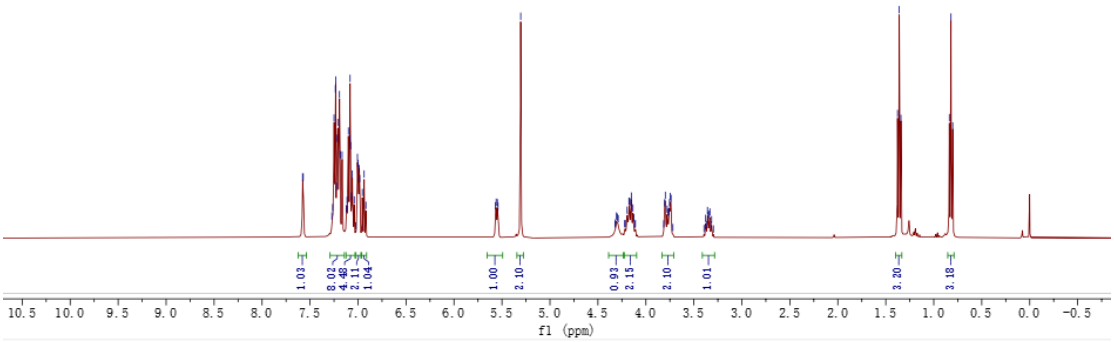
^{13}C NMR of **5h** (101 MHz, DMSO-d_6)

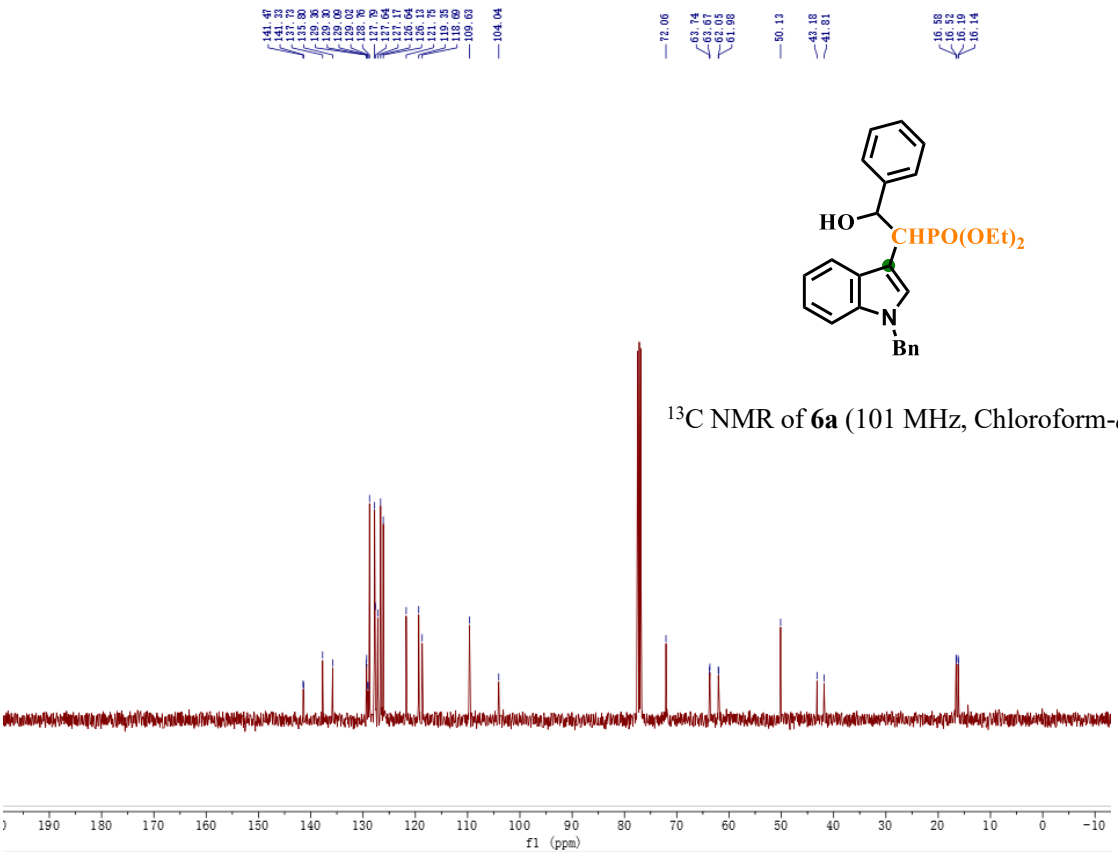


^{31}P NMR of **5h** (162 MHz, DMSO-d_6)

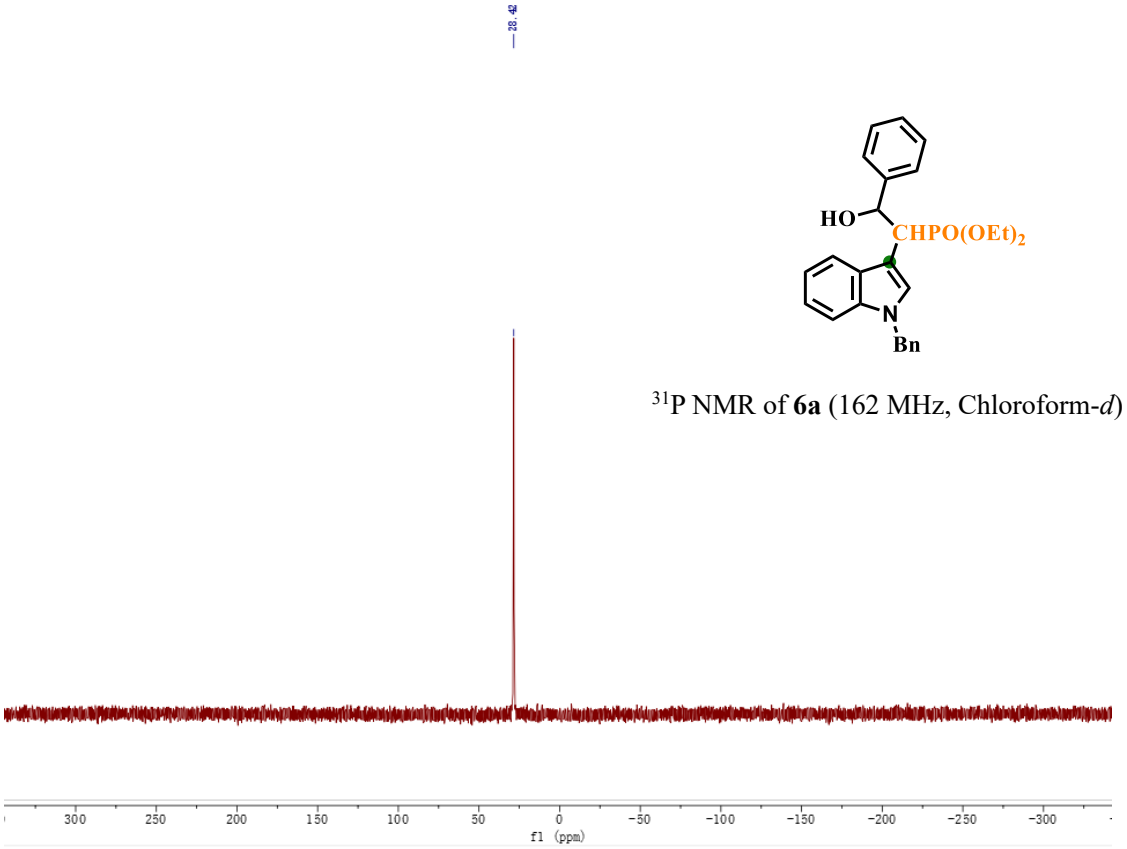


^{1}H NMR of **6a** (400 MHz, Chloroform-*d*)





^{13}C NMR of **6a** (101 MHz, Chloroform-*d*)



^{31}P NMR of **6a** (162 MHz, Chloroform-*d*)

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