Copper-catalyzed decarboxylative cyclization via tandem C–P and C–N bond formation: access to 2-phosphorylmethyl indoles

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1. General Information

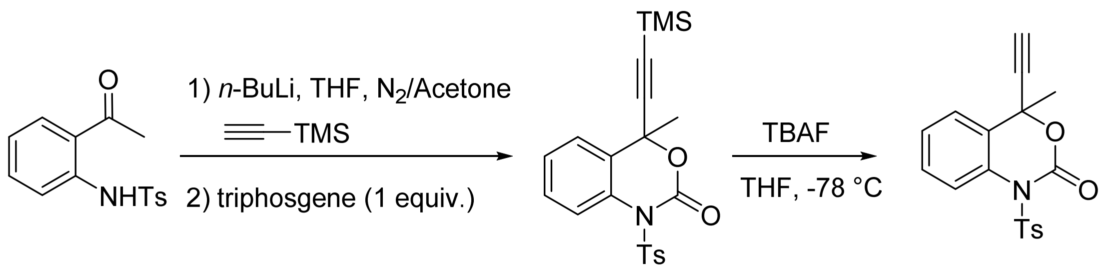
Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Mercury 100 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). ^{31}P NMR spectra were recorded on Varian Mercury 162 MHz spectrophotometers. HRMS was recorded on Bruker ultrafleXtreme MALDITOF/TOF mass spectrometer.

2. Preparation and Spectral Data of Substrates

2.1 General procedure for the preparation of substrates 1l-t and 2f-j.

Substrates(**1l-t and 2f-j**) were prepared according to the reported procedures[1,2,3]. Ligands were synthesized according to the literature[4] or commercially available.

Synthesis of substrate 1t



Procedure: Under argon atmosphere, an oven dried 250 mL three-necked flask, equipped with a magnetic stirring bar, was charged with trimethylsilylacetylene (3.1 mL, 22 mmol) and anhydrous THF (100 mL). To this solution was added *n*-BuLi (8.8 mL, 2.5 M in hexane, 22 mmol) dropwise over 15 min at 0 °C, stirring for 30 min. Then the solution was cooled to -94 °C (liquid N_2/Acetone bath), and the *N*-(2-acetylphenyl)-4-methylbenzenesulfonamide[5] (2.89 g, 10 mmol) was added. The reaction was stirred for 0.5 h at the same temperature. After this interval, a solution of triphosgen (2.96 g, 10 mmol) in anhydrous THF (50 mL) was added dropwise over a period of 0.5 h. The yellow solution was maintained at -94 °C for 1 h, and the reaction was then carefully quenched by dropwise addition of H_2O over a period of 15 min. The resulting yellow solution was allowed to warm to room temperature. The organic phase was separated, and aqueous phases were extracted with EtOAc (50 mL×3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was used directly without further purification.

The trimethylsilanylethynyl-benzoxazinanone from previous step was charged into a dry 100 mL flask along with anhydrous THF (50 mL). The flask was then cooled to -94 ºC and TBAF (10.0 mL, 10.0 mmol, 1.0 M solution in THF) was added dropwise. The resulting solution was stirred for 5 min at -94 °C (liquid N_2/Acetone bath). The reaction was quenched with H_2O. The resulting red solution was allowed to warm to room temperature. The organic phase was separated, and aqueous phases were extracted with EtOAc (30 mL×3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash silica gel chromatography (PE/EtOAc/DCM = 20:1:1) to give the product as white solid (2.21 g, 65% yield over two steps).

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[3] (a) J. Ke, Y. Tang, H. Yi, Y. Li, Y. Cheng, C. Liu and A. Lei, *Angew. Chem., Int. Ed.,* 2015, **54**, 1-5; (b) R. Shen, B. Luo, J. Yang, L. Zhang and L.-B. Han, *Chem. Commun..*, 2016, **52**, 6451-6454.

[4] Y.-Y. Zhu, C. Cui, N. Li, B.-W. Wang, Z.-M. Wang and S. Gao, *Eur. J. Inorg. Chem.,* 2013, **17**, 3101-3111.

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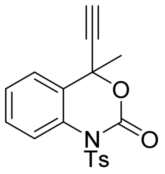
2.2 Spectral data of the substrate 1t

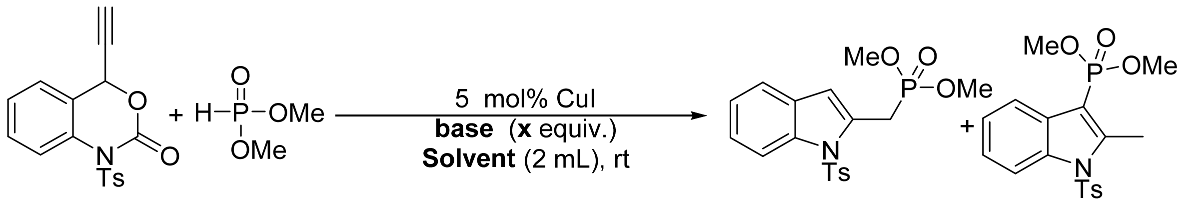
4-Ethynyl-4-methyl-1-tosyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (1t)



Yield of **1t** : 65% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.14 (d, *J* = 1.8 Hz, 1H), 8.12 (d, *J* = 1.8 Hz, 1H), 7.66 (dd, *J* = 8.3 Hz, 1.0 Hz, 1H), 7.45 (m, 1H), 7.42 – 7.38 (m, 2H), 7.37 (s, 1H), 7.30 (m, 1H), 2.69 (s, 1H), 2.46 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 148.4, 145.8, 135.4, 133.4, 129.6, 129.5, 129.5, 129.3, 126.3, 123.4, 121.2, 81.0, 76.1, 75.5, 26.2, 21.8. **M.P.**: 164 – 166 °C. **HRMS (ESI)** for $C_{18}H_{15}NO_4S$ $[M + Na]^+$: calcd 364.0614, found 364.0609.

3. Optimization of the Reaction Conditions

3.1 The effect of solvent, base and the loading of base [a]

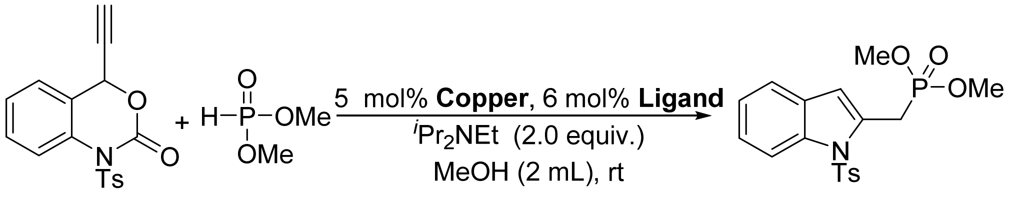


1a 2a 3a 3a'

Entry	Solvent	Base	Base(x equiv.)	Yield of 3a (%)[b]
1	THF	$^{i}Pr_2NEt$	2.0	69
2	MTBE	$^{i}Pr_2NEt$	2.0	52
3	CH_3CN	$^{i}Pr_2NEt$	2.0	43
4	CF_3CH_2OH	$^{i}Pr_2NEt$	2.0	Trace
5	EtOH	$^{i}Pr_2NEt$	2.0	79
6	**MeOH**	**$^{i}Pr_2NEt$**	2.0	**89**[c]
7	^{i}PrOH	$^{i}Pr_2NEt$	2.0	41
8	MeOH/DCM	$^{i}Pr_2NEt$	2.0	65
9	MeOH/THF	$^{i}Pr_2NEt$	2.0	69
10	MeOH	Et_3N	2.0	72[c]
11	MeOH	DBU	2.0	50[c]
12	MeOH	DABCO	2.0	23
13	MeOH	Cs_2CO_3	2.0	19
14	MeOH	K_3PO_4	2.0	48
15	MeOH	$^{i}Pr_2NEt$	0	N.R.
16	MeOH	$^{i}Pr_2NEt$	0.1	Trace
17	MeOH	$^{i}Pr_2NEt$	1.0	73[c]
18	MeOH	$^{i}Pr_2NEt$	1.5	77[c]

[a] Reaction Conditions: 1a (0.2 mmol), 2a (0.5 mmol), CuI (5 mol%) in 2 mL of solvent at rt for 1h. [b] Isolated yields. [c] a trace of 3a' (<10% yield) was determined by ^{1}H NMR. MTBE: methyl tert-butyl ether.

3.2 The effect of Ligand , copper and the loading of 2a[a]



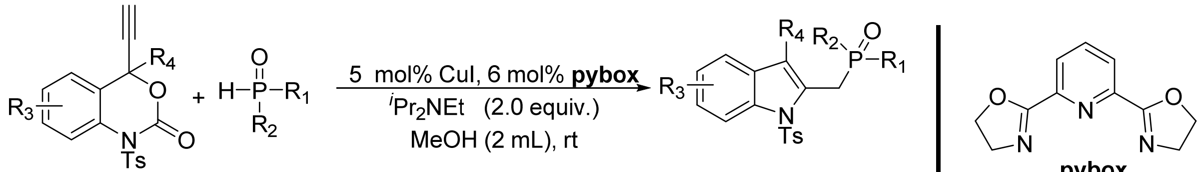
1a **2a** **3a**

Entry	Copper	Ligand	2a (equiv.)	Yield (3a %)[b]
1	CuI	dppe	2.5	77
2	CuI	dppb	2.5	79
3	CuI	dppp	2.5	89
4	CuI	PPh_3	2.5	79
5	**CuI**	**pybox**	**2.5**	**96**
6	CuF_2	pybox	2.5	90
7	$CuCl_2$	pybox	2.5	83
8	$Cu(acac)_2$	pybox	2.5	94
9	$Cu(OAc)_2$	pybox	2.5	96
10	$Cu(CH_3CN)_4BF_4$	pybox	2.5	96
11	**CuI**	**pybox**	**2.0**	**96**
12	CuI	pybox	1.5	88
13	CuI	pybox	1.2	87

[a] Reaction Conditions: **1a** (0.2 mmol), **2a** (x mmol), Copper salt (5 mol%), Ligand (6 mol%), $^{i}Pr_2NEt$ (2.0 equiv.) in 2 mL of MeOH at rt for 1h. [b] Isolated yields.

4. General Procedure and Spectral Data of the Products

4.1 General procedure for the synthesis of 3

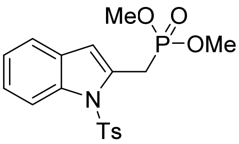


1:0.2 mmol **2:0.4 mmol** **3** **pybox**

Procedure: Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with CuI (0.01 mmol, 5 mol %), **pybox** (0.012 mmol, 6 mol%) and anhydrous MeOH (2 mL). The resulting solution was stirred for 5 min at room temperature. Then, $^{i}Pr_2NEt$ (0.4 mmol, 2.0 equiv.) and **2** (0.4 mmol, 2.0 equiv.) were added, the resulting solution was stirred for 10 min at rt. Then ethynyl benzoxazinanone **1** (0.2 mmol, 1.0 equiv.) was added. The resulting solution was stirred until complete conversion of ethynyl benzoxazinanones (monitored by TLC). The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 5/1 to 1/1) to give product **3**.

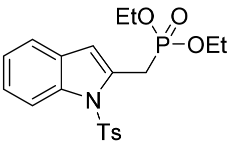
4.2 Spectral data of the desired products 3a-3t and 3a'

Dimethyl ((1-tosyl-1H-indol-2-yl)methyl)phosphonate (3a)



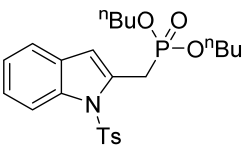
Yield of **3a** : 96% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.13 – 8.07 (m, 1H), 7.66 – 7.60 (m, 2H), 7.47 – 7.41 (m, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.23 (dd, *J* = 7.5 Hz, 1.1 Hz, 1H), 7.20 (s, 1H), 7.17 (s, 1H), 6.84 – 6.78 (m, 1H), 3.82 (d, *J* = 1.0 Hz, 1H), 3.78 (s, 3H), 3.77 (d, *J* = 1.0 Hz, 1H), 3.76 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.8, 136.7, 135.2, 130.5 (d, *J* = 4.0 Hz), 129.7, 129.3 (d, *J* = 1.0 Hz), 126.2, 124.3, 123.6, 120.5, 114.8, 112.4 (d, *J* = 5.0 Hz), 52.9 (d, *J* = 5.0 Hz), 25.1 (d, *J* = 94.0 Hz), 21.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 26.40. **HRMS (ESI)** for $C_{18}H_{20}NO_5PS$ $[M + H]^+$: calcd 394.0873, found 394.0866.

Diethyl ((1-tosyl-1H-indol-2-yl)methyl)phosphonate (3b)



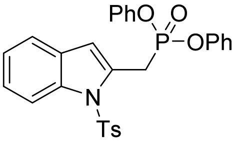
Yield of **3b** : 84% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.18 (s, 1H), 7.16 (s, 1H), 6.83 (d, *J* = 3.6 Hz, 1H), 4.13 (m, 4H), 3.80 (s, 1H), 3.75 (s, 1H), 2.31 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.9, 136.9, 135.5, 131.0 (d, *J* = 5.0 Hz), 129.8, 129.5 (d, *J* = 3.0 Hz), 126.3, 124.4, 123.7, 120.6, 114.9, 112.4 (d, *J* = 6.0 Hz), 62.4 (d, *J* = 6.0 Hz), 26.0 (d, *J* = 142.0 Hz), 21.4, 16.3 (d, *J* = 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 23.82. **HRMS (ESI)** for $C_{20}H_{24}NO_5PS$ $[M + Na]^+$: calcd 444.1005, found 444.0998.

Dibutyl ((1-tosyl-1H-indol-2-yl)methyl)phosphonate (3c)



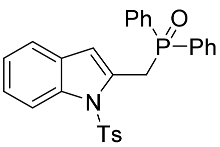
Yield of **3c** : 65% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 4.4 Hz, 1H), 7.22 (d, *J* =7.5 Hz, 1H), 7.18 (s, 1H), 7.16 (s, 1H), 6.83 (t, *J* = 2.4 Hz, 1H), 4.07 (dd, *J* = 6.9 Hz, 1.7 Hz, 2H), 4.03 (dd, *J* = 6.9 Hz, 1.8 Hz, 2H), 3.79 (s, 1H), 3.74 (s, 1H), 2.32 (d, *J* = 1.9 Hz, 3H), 1.61 (m, 4H), 1.35 (m, 4H), 0.89 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.0, 137.0, 135.6, 131.1, 129.9, 129.7, 126.4, 124.5, 123.8, 120.7, 115.0, 112.6 (d, *J* = 7.0 Hz), 66.2 (d, *J* = 7.0 Hz), 32.5 (d, *J* = 7.0 Hz), 26.0 (d, *J* = 142.0 Hz), 21.6, 18.7, 13.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 23.87. **HRMS (ESI)** for $C_{24}H_{32}NO_5PS$ $[M + Na]^+$: calcd 500.1631, found 500.1627.

Diphenyl ((1-tosyl-1H-indol-2-yl)methyl)phosphonate (3d)



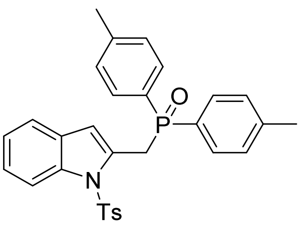
Yield of **3d** : 93% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 8.3 Hz, 1H), 7.62 (s, 1H), 7.61 – 7.59 (m, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.29 (s, 1H), 7.27 (s, 2H), 7.24 (d, *J* = 6.9 Hz, 2H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.17 – 7.13 (m, 4H), 7.13 – 7.09 (m, 4H), 6.97 (d, *J* = 3.5 Hz, 1H), 4.15 (s, 1H), 4.10 (s, 1H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 150.3 (d, *J* = 9.0 Hz), 145.1, 137.1, 135.6, 129.9, 129.8, 129.7 (d, *J* = 4.0 Hz), 129.5 (d, *J* = 3.0 Hz), 126.4, 125.4, 124.8, 123.9, 120.9, 120.6 (d, *J* = 5.0 Hz), 115.1, 113.1 (d, *J* = 6.0 Hz), 26.4 (d, *J* = 144.0 Hz), 21.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 16.93. **HRMS (ESI)** for $C_{28}H_{24}NO_5PS$ $[M + Na]^+$: calcd 540.1005, found 540.1002.

Diphenyl((1-tosyl-1H-indol-2-yl)methyl)phosphine oxide (3e)



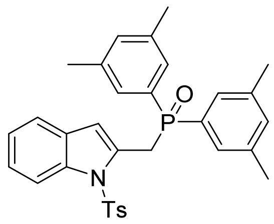
Yield of **3e** : 94% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.3 Hz, 1H), 7.81 (s, 1H), 7.78 (d, *J* = 4.2 Hz, 2H), 7.76 (s, 1H), 7.55 (s, 1H), 7.52 (d, *J* = 6.7 Hz 2H), 7.50 (s, 1H), 7.45 (m, 4H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.13 (s, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 4.27 (s, 1H), 4.24 (s, 1H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.0, 136.8, 135.4, 132.6, 132.1 (d, *J* = 3.0 Hz), 131.6, 131.1, 131.0, 129.9, 128.7 (d, *J* = 12.0 Hz), 126.3, 124.5, 123.8, 120.9, 114.9, 113.5 (d, *J* = 6.0 Hz), 30.0 (d, *J* = 68.0 Hz), 21.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 28.82. **M.P.**: 176 – 178 °C. **HRMS (ESI)** for $C_{28}H_{24}NO_3PS$ $[M + H]^+$: calcd 486.1287, found 486.1283.

Di-p-tolyl((1-tosyl-1H-indol-2-yl)methyl)phosphine oxide (3f)



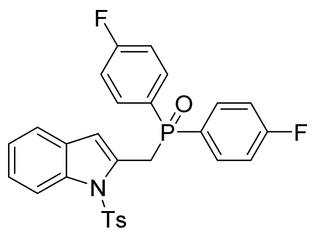
Yield of **3f** : 96% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 8.3 Hz, 1H), 7.67 (s, 1H), 7.65 (d, *J* = 3.6 Hz, 2H), 7.63 (s, 1H), 7.54 (s, 1H), 7.52 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.25 (s, 2H), 7.23 (s, 3H), 7.15 (t, *J* = 10.8 Hz, 3H), 7.02 (s, 1H), 4.21 (s, 1H), 4.18 (s, 1H), 2.37 (s, 6H), 2.32 (d, *J* = 3.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.0, 142.7, 136.8, 135.4, 131.7 (d, *J* = 10.0 Hz), 131.1 (d, *J* = 9.0 Hz), 129.9, 129.8, 129.6, 129.4, 126.3, 124.4, 123.8, 120.9, 114.9, 113.7, 30.0 (d, *J* = 67.0 Hz), 29.3, 21.6 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 29.42. **M.P.**: 193 – 194 °C. **HRMS (ESI)** for $C_{30}H_{28}NO_3PS$ $[M + Na]^+$: calcd 536.1420, found 536.1417.

Bis(3,5-dimethylphenyl)((1-tosyl-1H-indol-2-yl)methyl)phosphine oxide (3g)



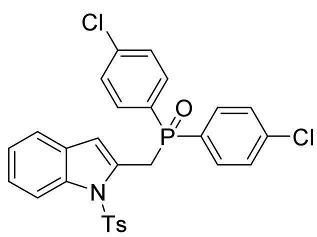
Yield of **3g** : 93% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 2.1 Hz, 1H), 7.53 (s, 1H), 7.41 (s, 2H), 7.37 (d, *J* = 7.4 Hz, 3H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 17.4 Hz, 2H), 7.12 (s, 3H), 7.00 (s, 1H), 4.21 (d, *J* = 13.6 Hz, 2H), 2.31 (s, 15H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.9, 138.4 (d, *J* = 13.0 Hz), 136.8, 135.5, 133.8 (d, *J* = 3.0 Hz), 132.4, 131.4 (d, *J* = 5.0 Hz), 129.9 (d, *J* = 2.0 Hz), 129.9, 128.5 (d, *J* = 9.0 Hz), 126.3, 124.3, 123.7, 120.9, 114.9, 113.5 (d, *J* = 6.0 Hz), 30.0 (d, *J* = 67.0 Hz), 21.6, 21.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 29.40. **M.P.**: 172 – 174 °C. **HRMS (ESI)** for $C_{32}H_{32}NO_3PS$ $[M + Na]^+$: calcd 564.1733, found 564.1737.

Bis(4-fluorophenyl)((1-tosyl-1H-indol-2-yl)methyl)phosphine oxide (3h)



Yield of **3h** : 96% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.3 Hz, 1H), 7.78 (m, 4H), 7.52 (d, *J* = 1.9 Hz, 1H), 7.51 (d, *J* = 1.9 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.18 – 7.13 (m, 3H), 7.12 (d, *J* = 2.3 Hz, 3H), 7.10 (d, *J* = 2.2 Hz, 1H), 7.02 (d, *J* = 3.0 Hz, 1H), 4.36 (s, 1H), 4.33 (s, 1H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 166.5 (d, *J* = 4.0 Hz), 164.0 (d, *J* = 3.0 Hz), 145.2, 136.9, 135.2, 133.7 (dd, *J* = 10.0 Hz, 8.0 Hz), 129.9, 129.6 (d, *J* = 2.0 Hz), 126.2, 124.7, 124.0, 120.9, 116.4 (d, *J* = 13.0 Hz), 116.2 (d, *J* = 13.0 Hz), 115.0, 114.0 (d, *J* = 6.0 Hz), 30.5 (d, *J* = 68.0 Hz), 21.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 27.55. **HRMS (ESI)** for $C_{28}H_{22}F_2NO_3PS$ $[M + H]^+$: calcd 522.1099, found 522.1110.

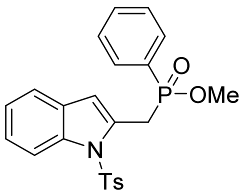
Bis(4-chlorophenyl)((1-tosyl-1H-indol-2-yl)methyl)phosphine oxide (3i)



Yield of **3i** : 99% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.04 – 7.99 (m, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.71 (t, *J* = 2.3 Hz, 2H), 7.69 (d, *J* = 1.9 Hz, 1H), 7.52 (d, *J* = 1.9 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.44 (d, *J* = 2.4 Hz, 2H), 7.42 (d, *J* = 2.3 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.26 – 7.22 (m, 1H), 7.18 (m, 1H), 7.15 (s, 1H), 7.13 (s, 1H), 6.99 (d, *J* = 2.7 Hz, 1H), 4.29 – 4.25 (m, 1H), 4.25 – 4.21 (m, 1H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.1, 138.9 (d, *J* = 4.0 Hz), 136.0 (d, *J* = 155.0 Hz), 132.3 (d, *J* = 11.0 Hz), 130.6, 130.1 (d, *J* = 5.0 Hz), 129.9, 129.5 (d, *J* = 2.0 Hz), 129.2, 129.1, 126.1, 124.7, 123.9, 120.8, 114.9, 113.6 (d, *J* = 6.0 Hz), 30.0 (d, *J* = 68.0 Hz), 21.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 27.55. **M.P.**: 170 – 172 °C. **HRMS (ESI)** for $C_{28}H_{22}Cl_2NO_3PS$ [M +

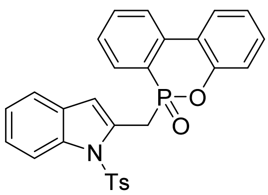
H]$^+$: calcd 554.0508, found 554.0502.

Methyl phenyl((1-tosyl-1H-indol-2-yl)methyl)phosphinate (3j)



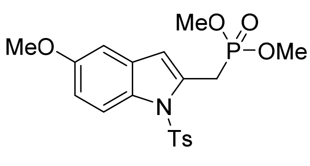
Yield of **3j** : 72% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 8.2 Hz, 1H), 7.77 (dd, *J* = 11.9 Hz, 7.6 Hz, 2H), 7.55 (m, 3H), 7.44 (m, 3H), 7.20 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 3.3 Hz, 1H), 3.98 (d, *J* = 6.9 Hz, 1H), 3.93 (d, *J* = 5.5 Hz, 1H), 3.67 (dd, *J* = 11.1 Hz, 1.9 Hz, 3H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.8, 136.8, 135.5, 132.6 (d, *J* = 2.0 Hz), 132.0 (d, *J* = 9.0 Hz), 130.6 (d, *J* = 5.0 Hz), 129.8, 129.7, 129.5 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 12.0 Hz), 126.2, 124.3, 123.7, 120.6, 114.9, 112.7 (d, *J* = 7.0 Hz), 51.6 (d, *J* = 7.0 Hz), 29.7 (d, *J* = 98.0 Hz), 21.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 39.52. **HRMS (ESI)** for $C_{23}H_{22}NO_4PS$ [M + H]$^+$: calcd 440.1080, found 440.1085.

(6-((1-Tosyl-1H-indol-2-yl)methyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (3k)



Yield of **3k** : 98% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.96 – 7.88 (m, 2H), 7.88 – 7.81 (m, 1H), 7.71 (dd, *J* = 8.0 Hz, 1.5, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.47 (s, 1H), 7.45 (d, *J* = 2.6 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.19 – 7.17 (m, 1H), 7.17 – 7.13 (m, 1H), 7.12 – 7.07 (m, 1H), 7.06 (s, 1H), 7.04 (s, 1H), 6.66 (d, *J* = 3.7 Hz, 1H), 4.13 (t, *J* = 17.1 Hz, 1H), 3.98 (t, *J* = 16.7 Hz, 1H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 149.3 (d, *J* = 8.0 Hz), 144.8, 136.7, 136.1 (d, *J* = 7.0 Hz), 135.0, 133.5, 130.6 (d, *J* = 10.0 Hz), 130.3, 129.6, 129.4, 129.3 (d, *J* = 5.0 Hz), 128.3 (d, *J* = 13.0 Hz), 126.1, 124.8, 124.3 (d, *J* = 6.0 Hz), 124.0, 123.6, 123.5 (d, *J* = 10.0 Hz), 122.7, 121.8 (d, *J* = 11 Hz), 120.5, 120.1 (d, *J* = 6.0 Hz), 114.8, 113.5 (d, *J* = 7.0 Hz), 29.8 (d, *J* = 92.0 Hz), 21.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 32.28. **M.P.**: 170 – 171 ºC. **HRMS (ESI)** for $C_{28}H_{22}NO_4PS$ [M + H]$^+$: calcd 500.1080, found 500.1073.

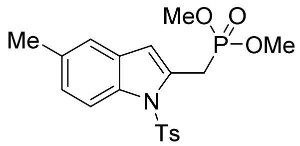
Dimethyl ((5-methoxy-1-tosyl-1H-indol-2-yl)methyl)phosphonate) (3l)



Yield of **3l** : 84% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 9.8 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.93 – 6.85 (m, 2H), 6.74 (d, *J* = 3.6 Hz, 1H), 3.79 (d, *J* = 3.6 Hz, 4H), 3.77 (s, 3H), 3.74 (s, 4H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 156.7, 144.9, 135.3, 131.6, 131.4 (d, *J* = 7.0 Hz), 130.6 (d, *J* = 3.0 Hz), 129.8, 126.3, 116.0, 113.4, 113.0 (d, *J* = 7.0 Hz), 103.1, 55.6, 53.1 (d, *J* = 7.0 Hz), 25.4 (d, *J* = 142.0 Hz), 21.5. **^{31}P NMR**

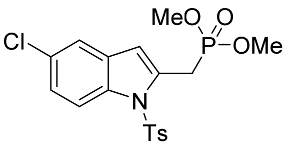
(162 MHz, $CDCl_3$) δ = 26.37. **HRMS (ESI)** for $C_{19}H_{22}NO_6PS$ $[M + Na]^+$: calcd 446.0798, found 446.0801.

Dimethyl ((5-methyl-1-tosyl-1H-indol-2-yl)methyl)phosphonate (3m)



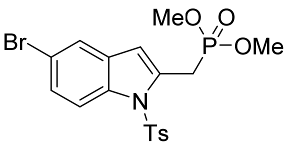
Yield of **3m** : 99% colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 1.7 Hz, 1H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.21 (d, *J* = 1.7 Hz, 1H), 7.18 (s, 1H), 7.16 (s, 1H), 7.11 – 7.07 (m, 1H), 6.75 – 6.72 (m, 1H), 3.81 – 3.79 (m, 1H), 3.77 (s, 3H), 3.74 (s, 4H), 2.38 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.8, 135.5, 135.1, 133.4, 130.6, 130.6, 129.7, 126.3, 125.8, 120.5, 114.7, 112.5 (d, *J* = 7.0 Hz), 53.0 (d, *J* = 6.0 Hz), 25.2 (d, *J* = 142.0 Hz), 21.4, 21.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 26.42. **HRMS (ESI)** for $C_{19}H_{22}NO_5PS$ $[M + Na]^+$: calcd 430.0849, found 430.0854.

Dimethyl ((5-chloro-1-tosyl-1H-indol-2-yl)methyl)phosphonate (3n)



Yield of **3n** : 97% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.22 (d, *J* = 4.2 Hz, 2H), 7.19 (s, 1H), 6.76 (d, *J* = 3.6 Hz, 1H), 3.82 (s, 1H), 3.79 (s, 3H), 3.76 (s, 4H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.6, 135.6, 135.5, 132.5 (d, *J* = 6.0 Hz), 131.0 (d, *J* = 3.0 Hz), 130.3, 129.9, 126.7, 125.0, 120.5, 116.4, 112.2 (d, *J* = 7.0 Hz), 53.6 (d, *J* = 6.0 Hz), 25.6 (d, *J* = 142.0 Hz), 21.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 25.99. **HRMS (ESI)** for $C_{18}H_{19}ClNO_5PS$ $[M + Na]^+$: calcd 450.0302, found 450.0302.

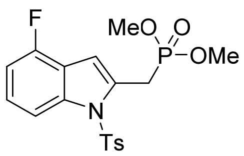
Dimethyl ((5-bromo-1-tosyl-1H-indol-2-yl)methyl)phosphonate (3o)



Yield of **3o** : 99% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.0 (d, *J* = 8.9 Hz, 1H), 7.6 (s, 1H), 7.6 (s, 1H), 7.6 (s, 1H), 7.4 (d, *J* = 8.9 Hz, 1H), 7.2 (s, 1H), 7.2 (s, 1H), 6.7 (d, *J* = 3.5 Hz, 1H), 3.8 (s, 1H), 3.8 (s, 3H), 3.8 (s, 4H), 2.3 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.8, 135.5, 135.1, 133.4, 130.6, 130.6, 129.7, 126.3, 125.8, 120.5, 114.7, 112.5 (d, *J* = 7.0 Hz), 53.0 (d, *J* = 6.0 Hz), 25.2 (d, *J* = 142.0 Hz), 21.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 25.94. **HRMS (ESI)** for $C_{18}H_{19}BrNO_5PS$ $[M + Na]^+$: calcd493.9797, found 493.9798.

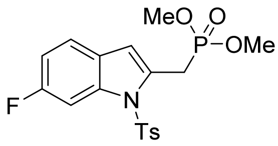
Dimethyl ((4-fluoro-1-tosyl-1H-indol-2-yl)methyl)phosphonate (3p)

Yield of **3p** : 97% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 8.4 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 3H), 6.95 – 6.84 (m, 2H), 3.81 (s, 1H), 3.80 (d, *J* =



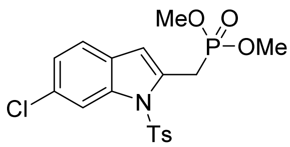
1.1 Hz, 3H), 3.78 – 3.75 (m, 4H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 155.2 (d, *J* = 248.0 Hz), 145.3, 138.9 (d, *J* = 9.0 Hz), 135.3, 131.0 (d, *J* = 6.0 Hz), 129.9, 126.4, 125.2 (d, *J* = 8.0 Hz), 118.5 (dd, *J* = 3.0 Hz), 111.0 (d, *J* = 4.0 Hz), 109.1 (d, *J* = 19.0 Hz), 107.6 (d, *J* = 7.0 Hz), 53.1 (d, *J* = 6.0 Hz), 25.3 (d, *J* = 142.0 Hz), 21.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 25.93. **HRMS (ESI)** for $C_{18}H_{19}FNO_5PS$ $[M + Na]^+$: calcd 434.0598, found 434.0604.

Dimethyl ((6-fluoro-1-tosyl-1H-indol-2-yl)methyl)phosphonate (3q)



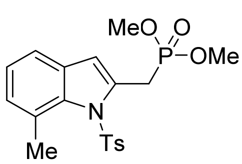
Yield of **3q** : 93% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.85 (dd, *J* = 10.4 Hz, 2.3 Hz, 1H), 7.65 (s, 1H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.36 (dd, *J* = 8.6 Hz, 5.4 Hz, 1H), 7.22 (s, 1H), 7.20 (s, 1H), 6.97 (m, 1H), 6.78 (d, *J* = 3.6 Hz, 1H), 3.78 (s, 4H), 3.75 (s, 3H), 3.73 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 160.8 (d, *J* = 240.0 Hz), 145.3, 137.1 (d, *J* = 13.0 Hz), 135.3, 131.1 – 131.0 (m), 130.0, 126.4, 126.0 – 125.2 (m), 121.3 (d, *J* = 10.0 Hz), 112.3, 112.2 – 112.0 (m), 102.6 (d, *J* = 29.0 Hz), 53.1 (d, *J* = 7.0 Hz), 25.3 (d, *J* = 142.0 Hz), 21.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 26.24. **HRMS (ESI)** for $C_{18}H_{19}FNO_5PS$ $[M + Na]^+$: calcd 434.0598, found 434.0602.

Dimethyl ((6-chloro-1-tosyl-1H-indol-2-yl)methyl)phosphonate (3r)



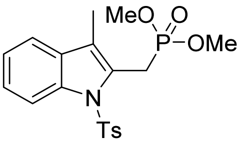
Yield of **3r** : 93% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.15 (s, 1H), 7.65 (s, 1H), 7.63 (d, *J* = 1.4 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.25 (d, *J* = 15.1 Hz, 1H), 7.22 – 7.18 (m, 2H), 6.78 (d, *J* = 3.5 Hz, 1H), 3.78 (d, *J* = 1.4 Hz, 4H), 3.75 (d, *J* = 1.3 Hz, 3H), 3.72 (s, 1H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 145.3, 137.2, 135.3, 131.4 (d, *J* = 6.0 Hz), 130.5, 130.0, 127.9 (d, *J* = 3.0 Hz), 126.4, 124.5, 121.3, 115.1, 112.0 (d, *J* = 7.0 Hz), 53.1 (d, *J* = 6.0 Hz), 25.2 (d, *J* = 142.0 Hz), 21.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 26.04. **HRMS (ESI)** for $C_{18}H_{19}ClNO_5PS$ $[M + Na]^+$: calcd 450.0302, found 450.0297.

Dimethyl ((7-methyl-1-tosyl-1H-indol-2-yl)methyl)phosphonate (3s)



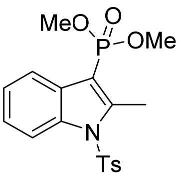
Yield of **3s** : 99% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.84 (s, 1H), 7.53 (s, 1H), 7.51 (s, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.10 (s, 1H), 7.08 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 3.6 Hz, 1H), 3.70 (s, 1H), 3.69 – 3.66 (m, 3H), 3.65 (s, 4H), 2.37 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.8, 137.3, 135.5, 134.5, 129.8, 129.7, 127.1 (d, *J* = 3.0 Hz), 126.2, 125.2, 120.1, 115.1, 112.5 (d, J = 7.0 Hz), 53.0 (d, J = 6.0 Hz), 25.2 (d, J = 141.0 Hz), 21.9, 21.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 26.51. **HRMS (ESI)** for $C_{19}H_{22}NO_5PS$ $[M + Na]^+$: calcd 430.0849, found 430.0849.

Dimethyl ((3-methyl-1-tosyl-1H-indol-2-yl)methyl)phosphonate (3t)



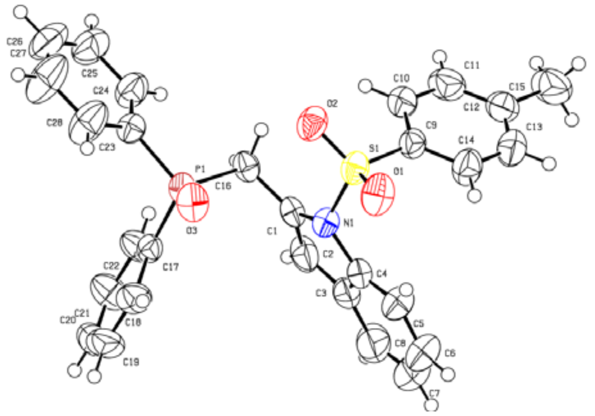
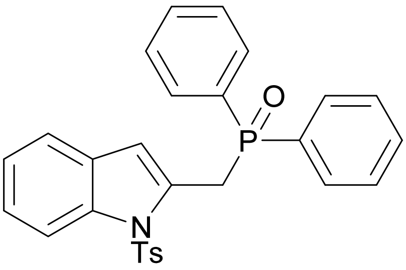
Yield of **3t** : 40% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.09 (d, J = 8.1 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.38 (dd, J = 6.9 Hz, 1.7 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.26 – 7.20 (m, 1H), 7.14 (s, 1H), 7.12 (s, 1H), 3.86 (s, 1H), 3.81 (s, 1H), 3.76 (d, J = 1.3 Hz, 3H), 3.73 (d, J = 1.3 Hz, 3H), 2.30 (s, 3H), 2.21 (dd, J = 4.8 Hz, 1.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 144.8, 137.3, 135.5, 134.5, 129.8, 129.7, 127.1 (d, J = 3.0 Hz), 126.2, 125.2, 120.1, 115.1, 112.5 (d, J = 7.0 Hz), 53.0 (d, J = 6.0 Hz), 25.2 (d, J = 141.0 Hz), 21.9, 21.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 26.51. **HRMS (ESI)** for $C_{19}H_{22}NO_5PS$ $[M + Na]^+$: calcd 430.0849, found 430.0848.

Dimethyl (2-methyl-1-tosyl-1H-indol-3-yl)phosphonate (3a')



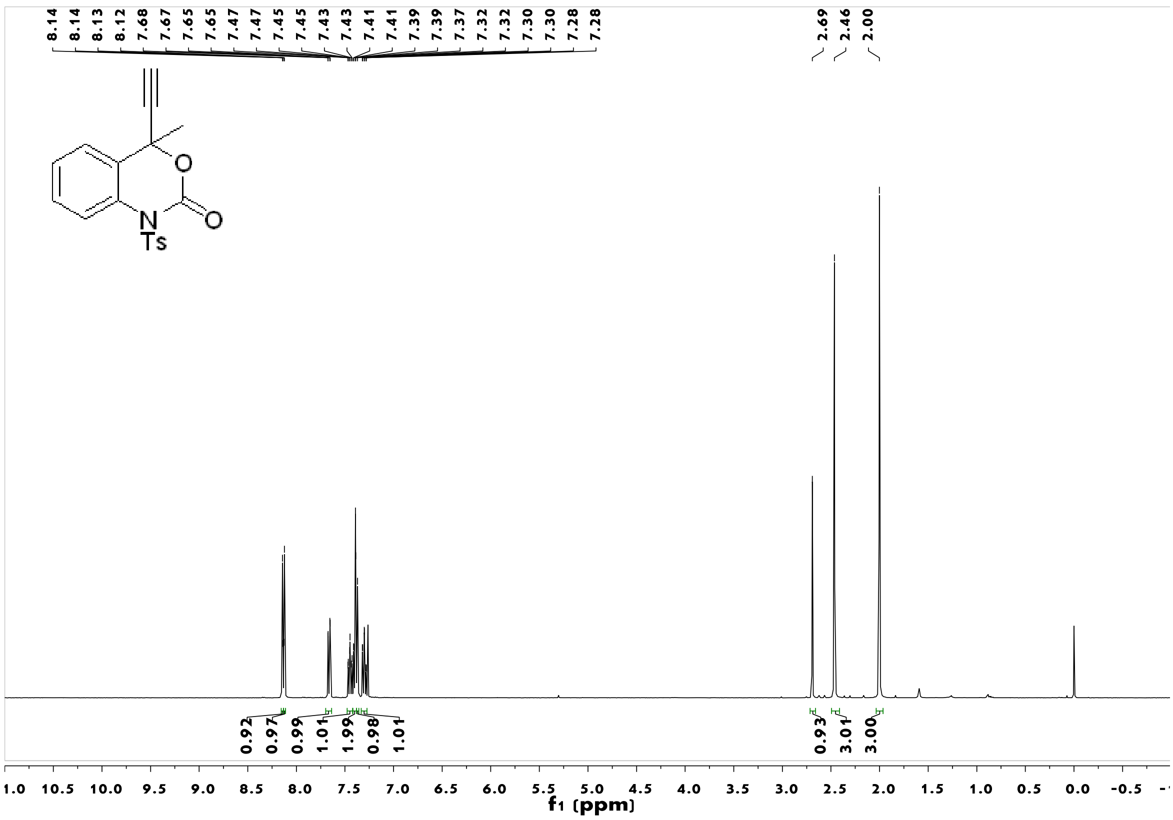
Yield of **3a'** : a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.23 (m, 1H), 7.77 (dd, J = 7.8 Hz, 1.4 Hz, 1H), 7.74 (s, 1H), 7.72 (s, 1H), 7.34 (m, 1H), 7.30 (m, 1H), 7.27 (s, 1H), 7.25 (s, 1H), 3.74 (d, J = 0.7 Hz, 3H), 3.71 (d, J = 0.7 Hz, 3H), 2.94 (d, J = 2.2 Hz, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 147.0 (d, J = 28.0 Hz), 145.6, 136.5 (d, J = 13.0 Hz), 135.8, 130.1, 128.8 (d, J = 12.0 Hz), 126.7, 124.9, 124.2, 120.9, 114.4, 105.0 (d, J = 210.0 Hz), 52.3 (d, J = 5.0 Hz), 21.6, 14.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 18.18. **HRMS (ESI)** for $C_{18}H_{20}NO_5PS$ $[M + H]^+$: calcd 394.0873, found 394.0877.

5.X-ray Crystal Structure Determination of 3e.

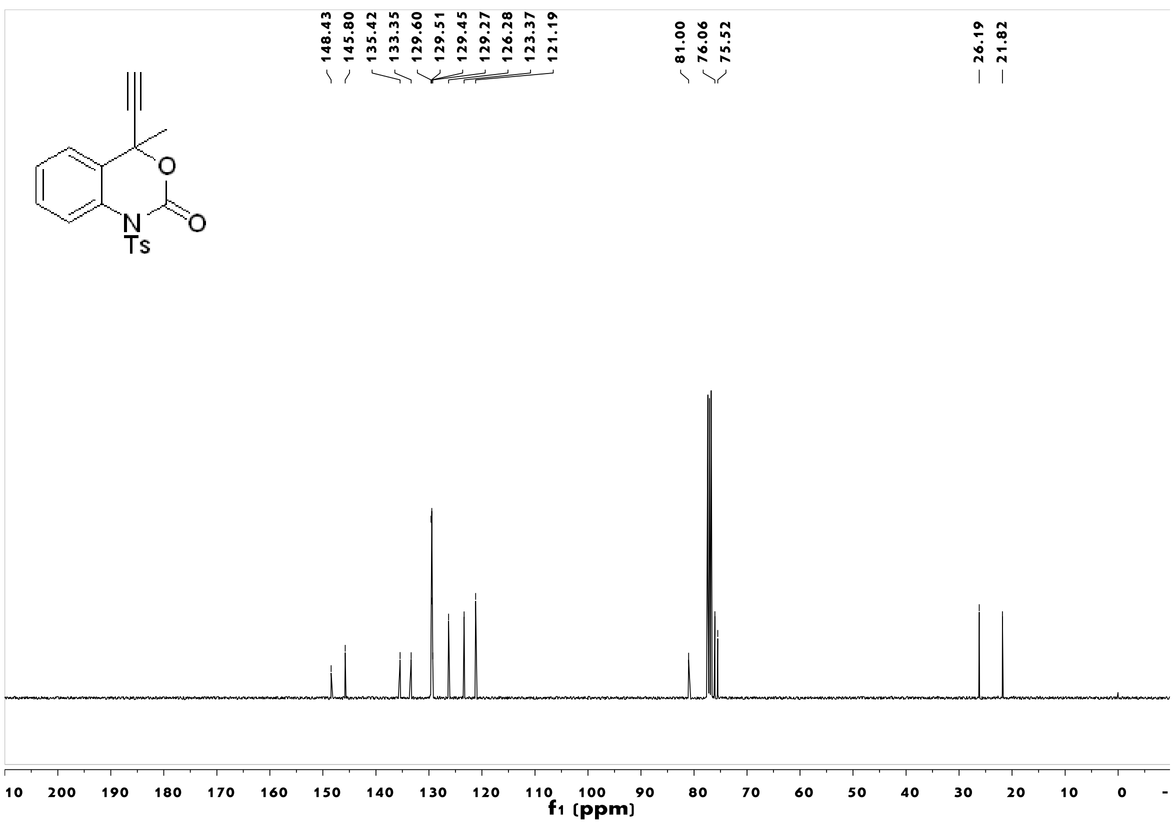
3e		

6.Copies of ^{1}H NMR, ^{13}C NMR and ^{31}P NMR Spectra.

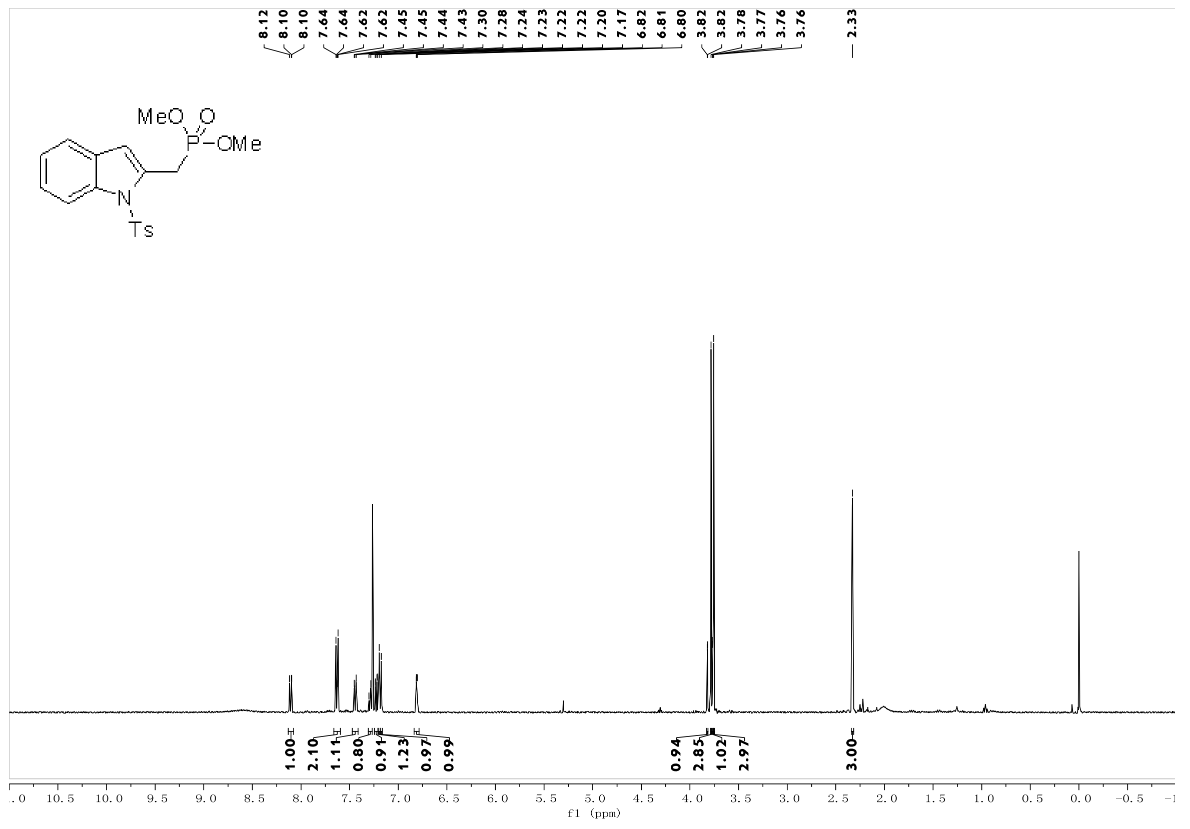
^{1}H NMR Spectrum of **1t**



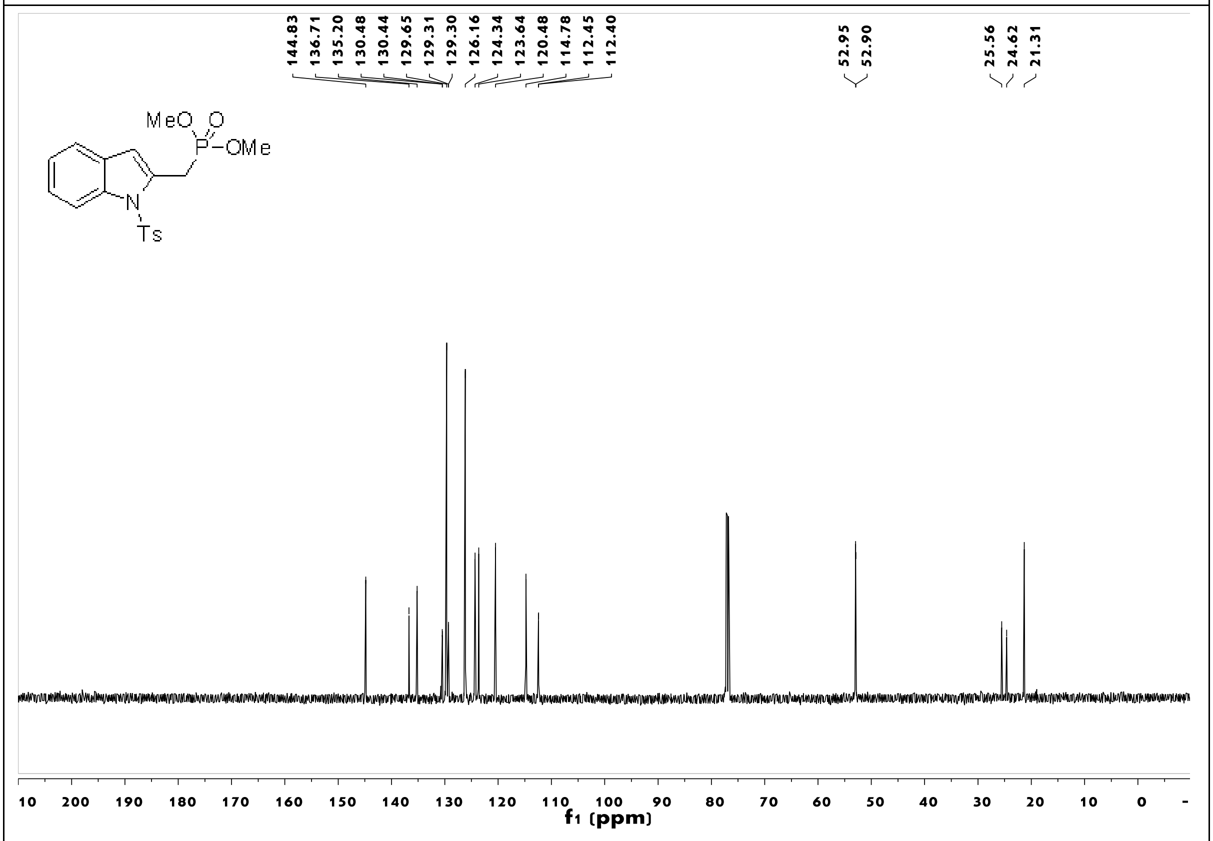
^{13}C NMR Spectrum of **1t**



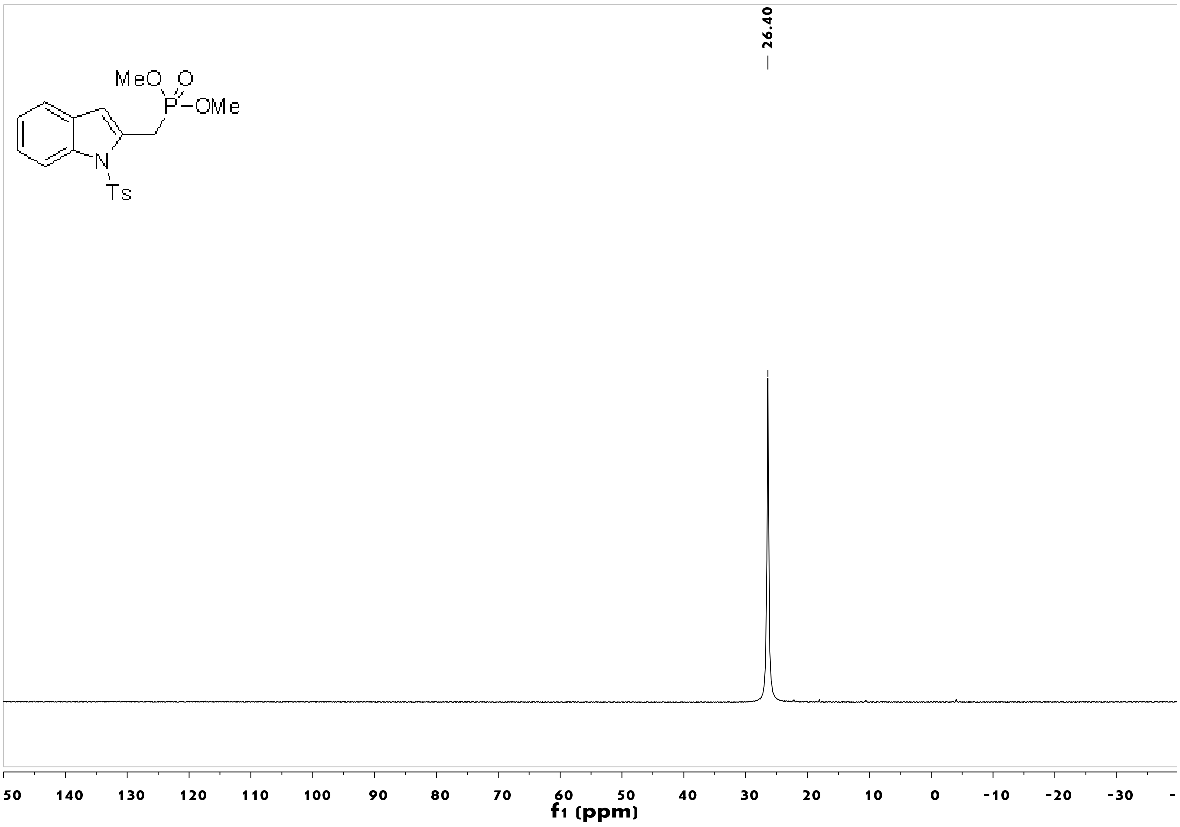
^{1}H NMR Spectrum of **3a**



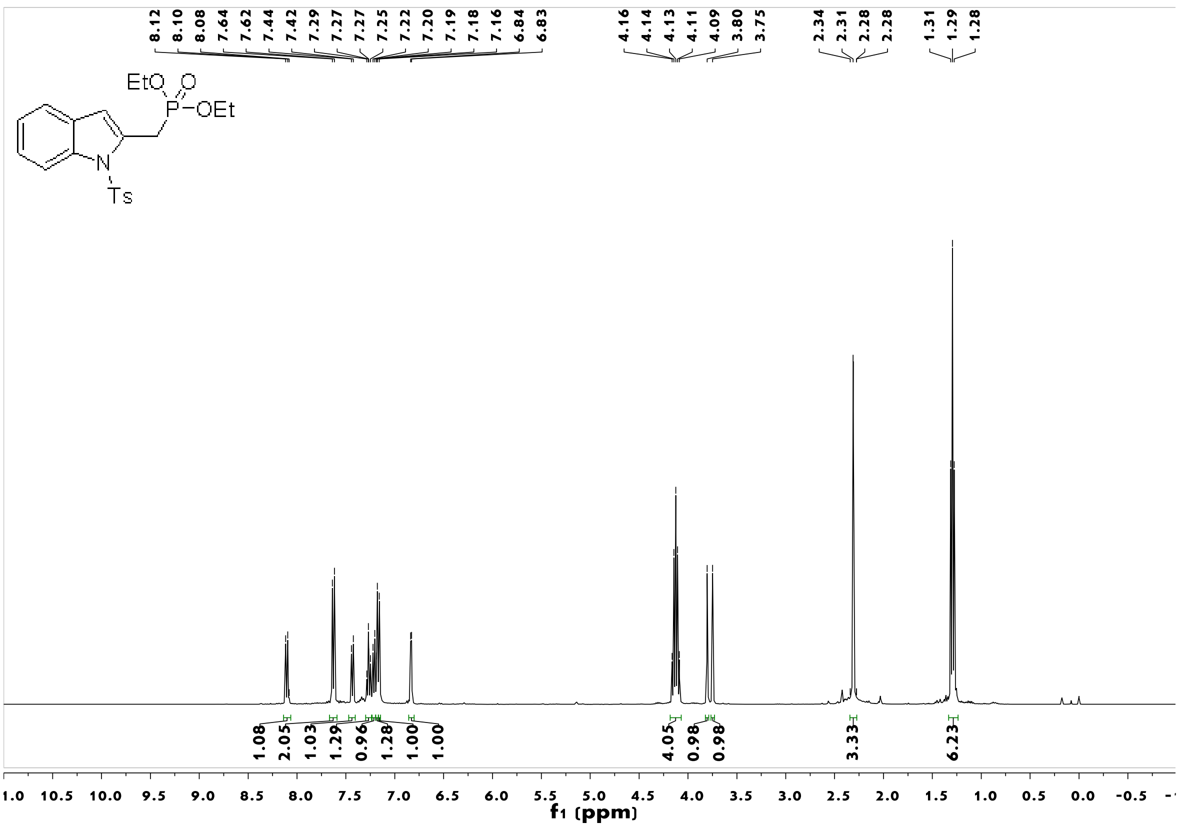
^{13}C NMR Spectrum of **3a**



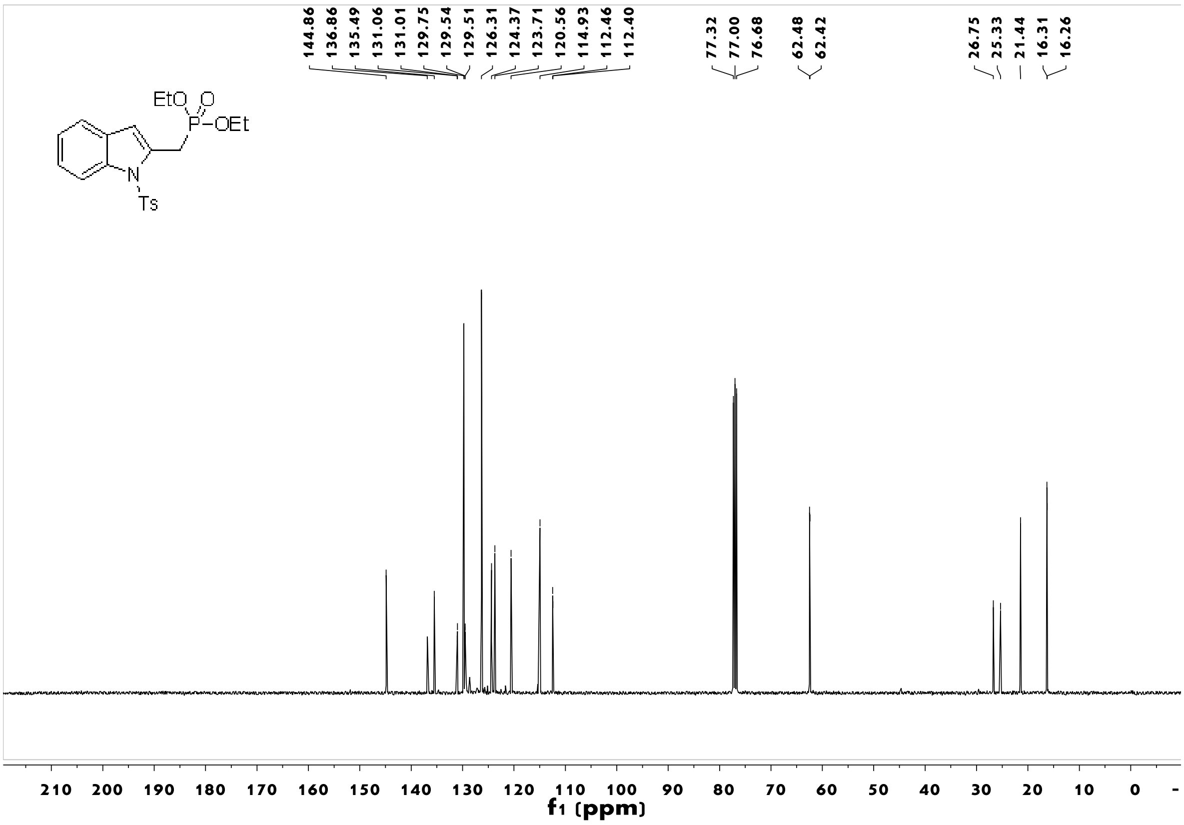
^{31}P NMR Spectrum of **3a**



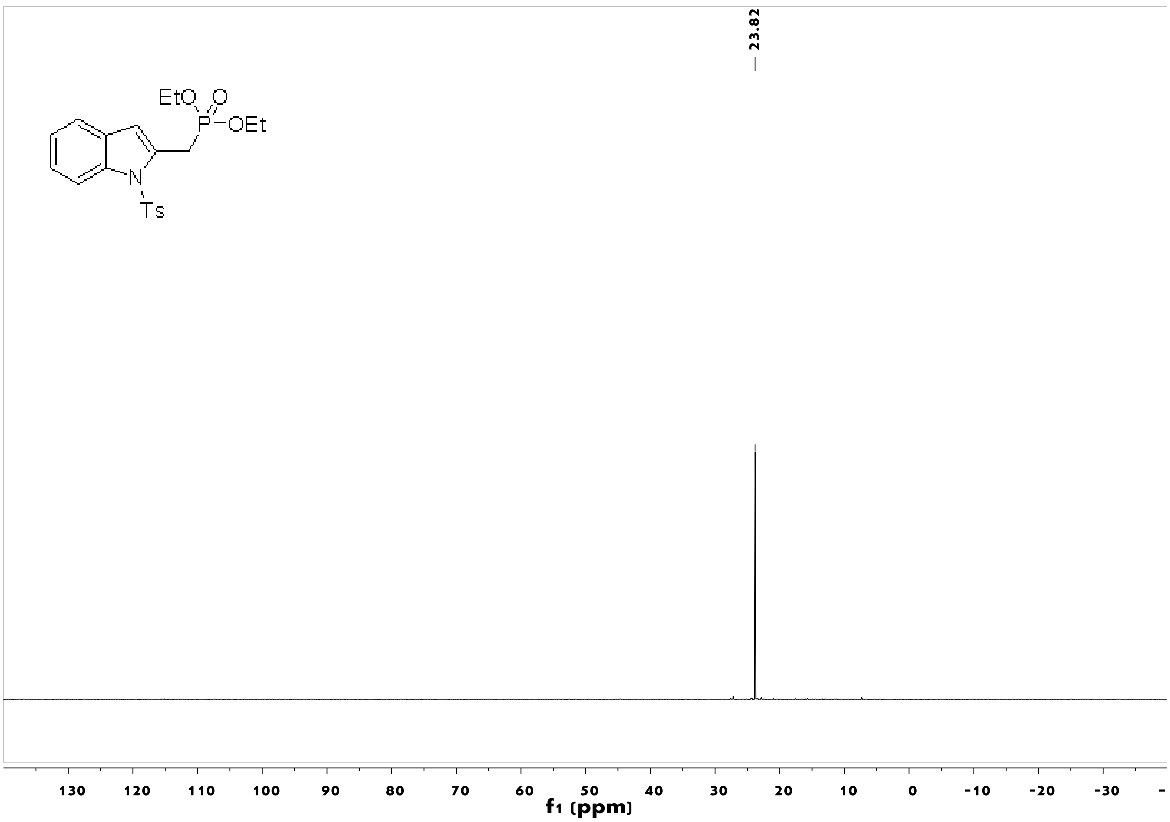
^{1}H NMR Spectrum of **3b**



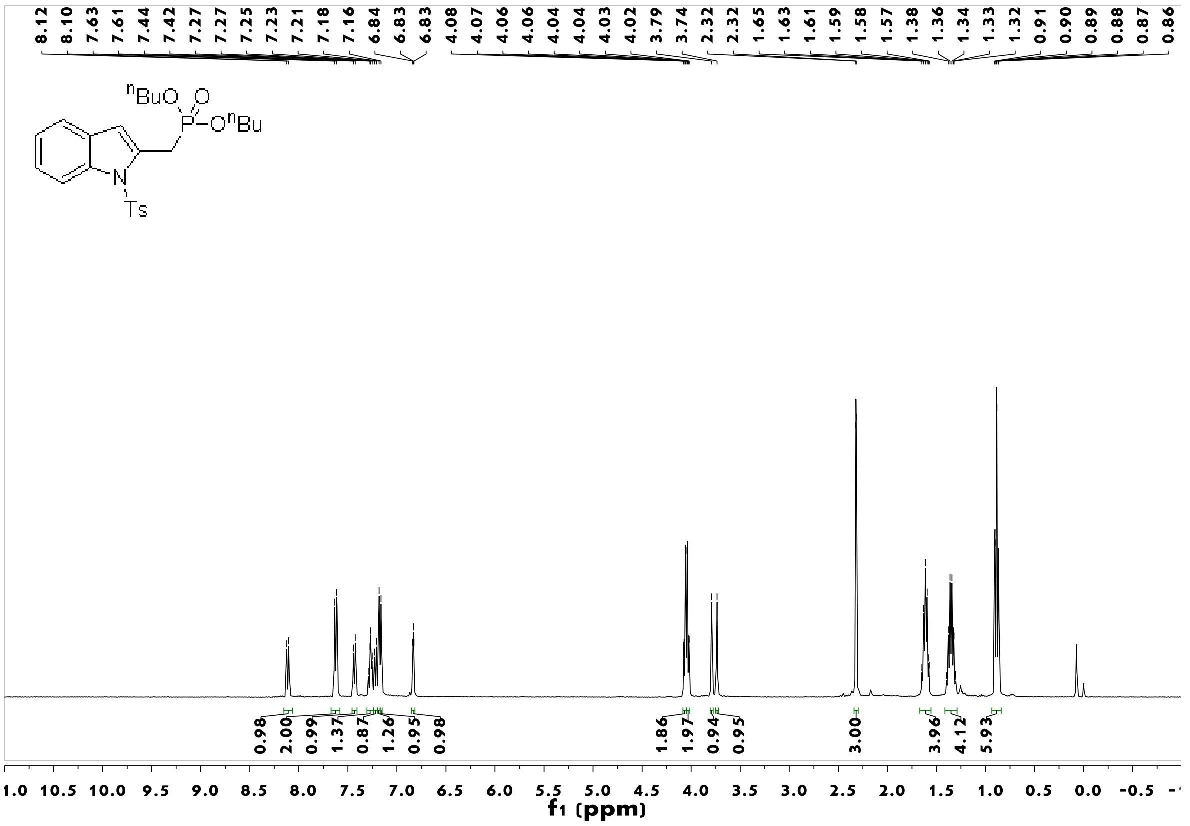
^{13}C NMR Spectrum of **3b**



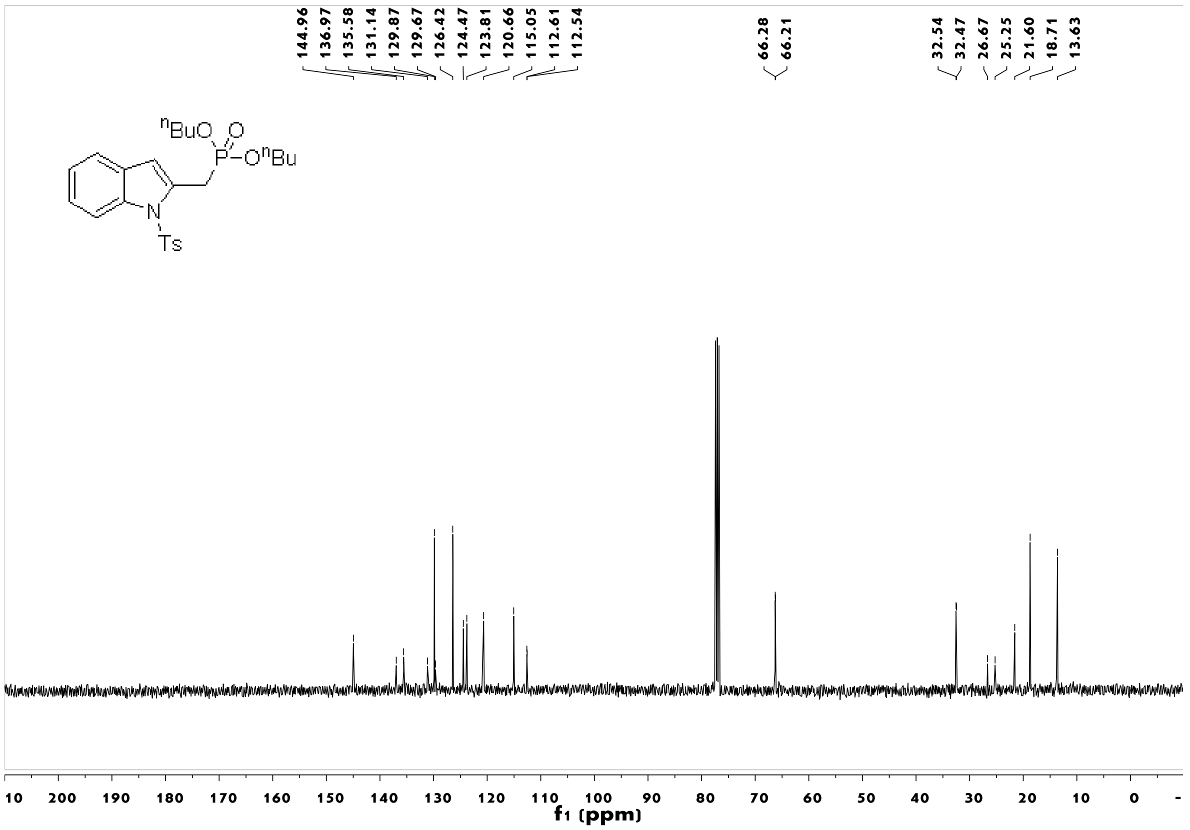
^{31}P NMR Spectrum of **3b**



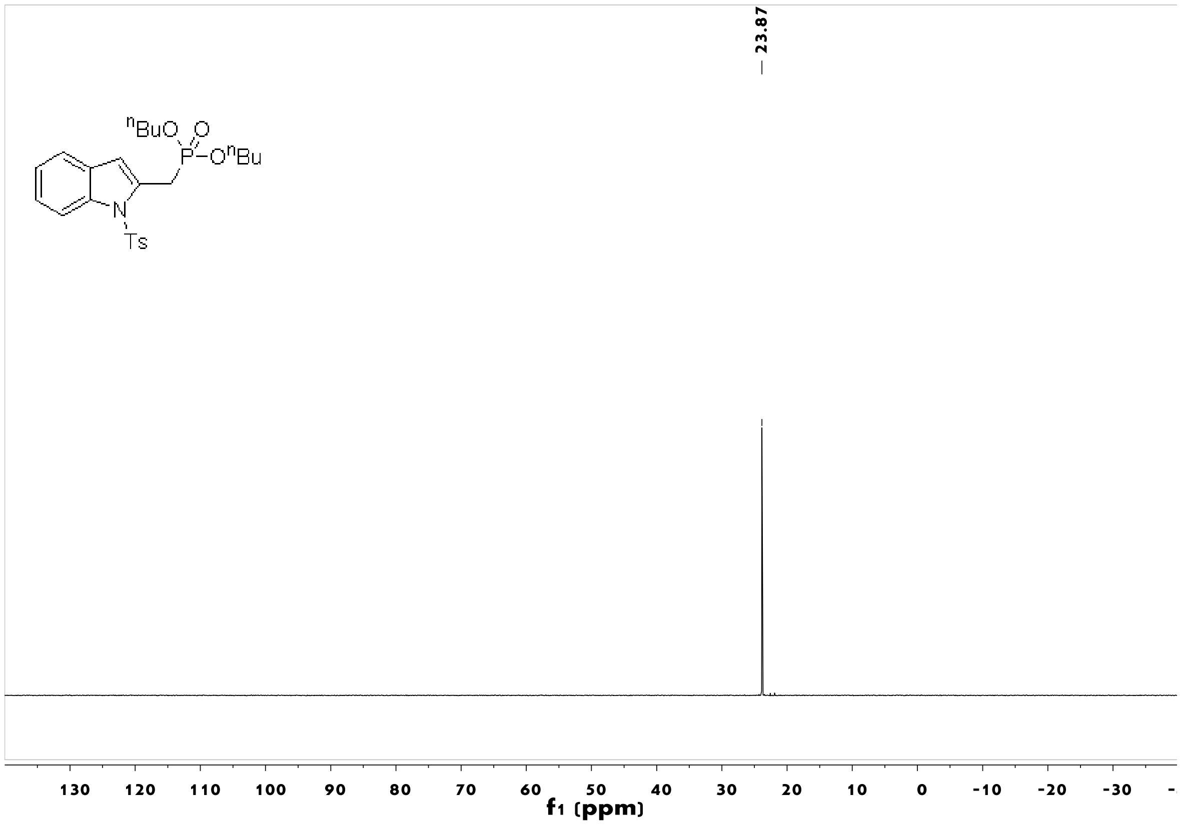
^{1}H NMR Spectrum of **3c**



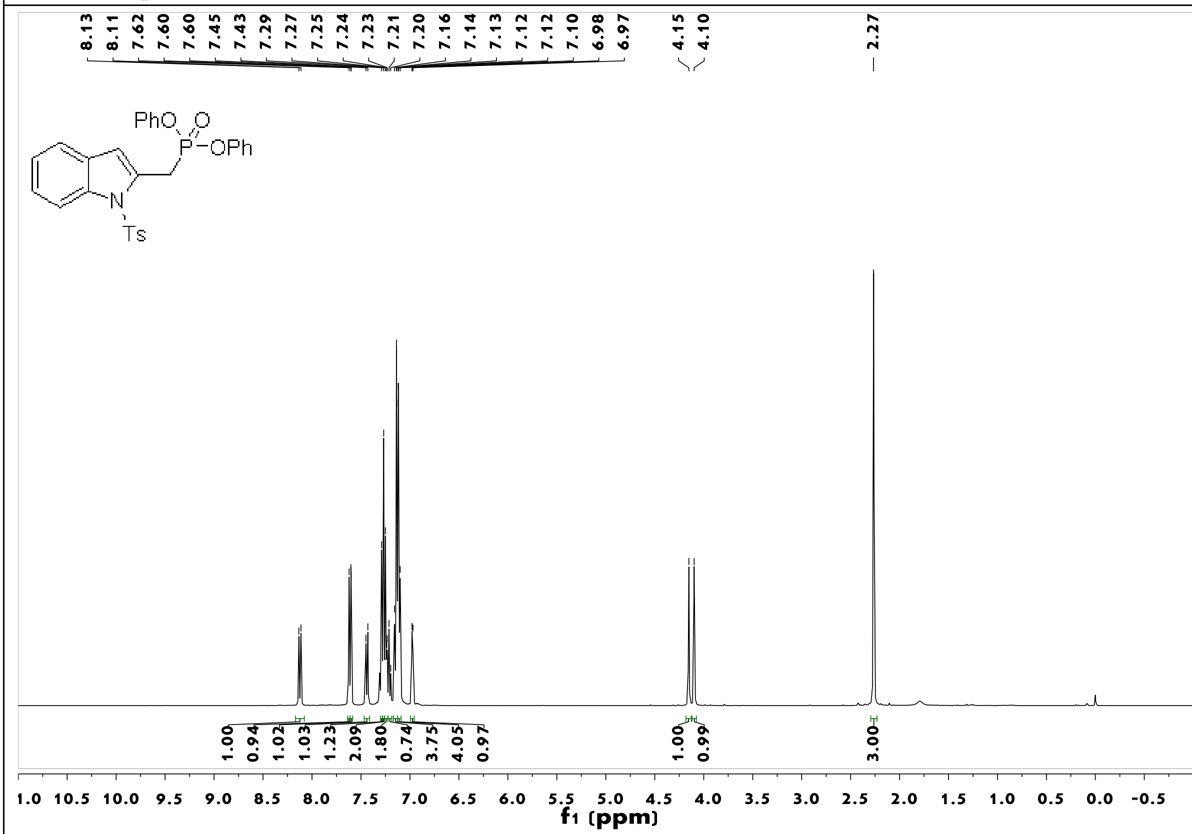
^{13}C NMR Spectrum of **3c**



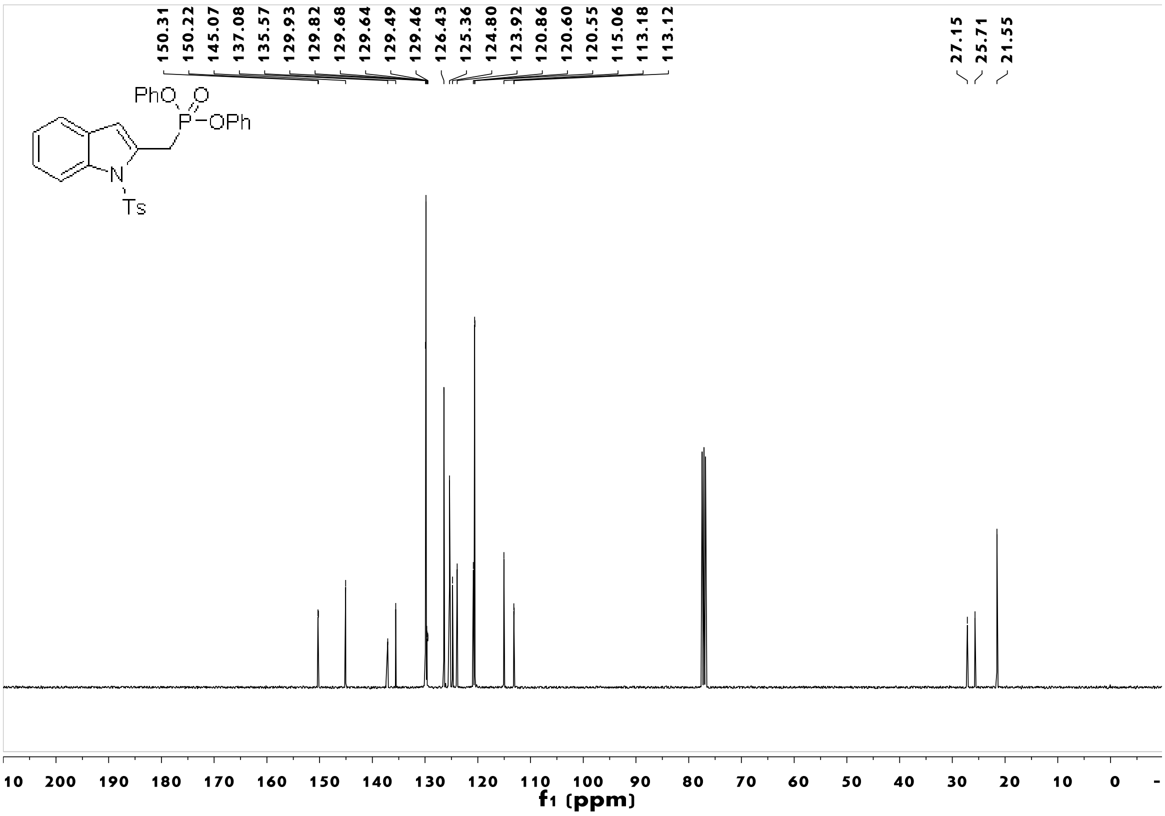
^{31}P NMR Spectrum of **3c**



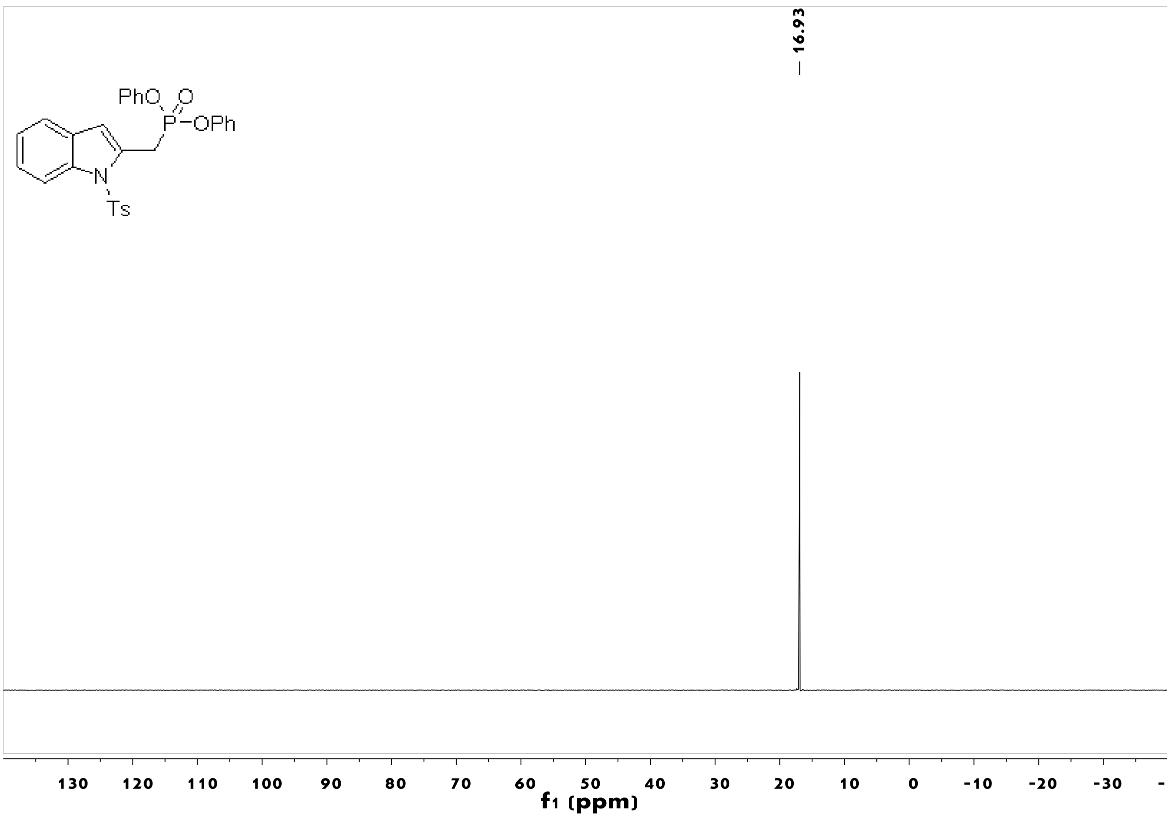
^{1}H NMR Spectrum of **3d**



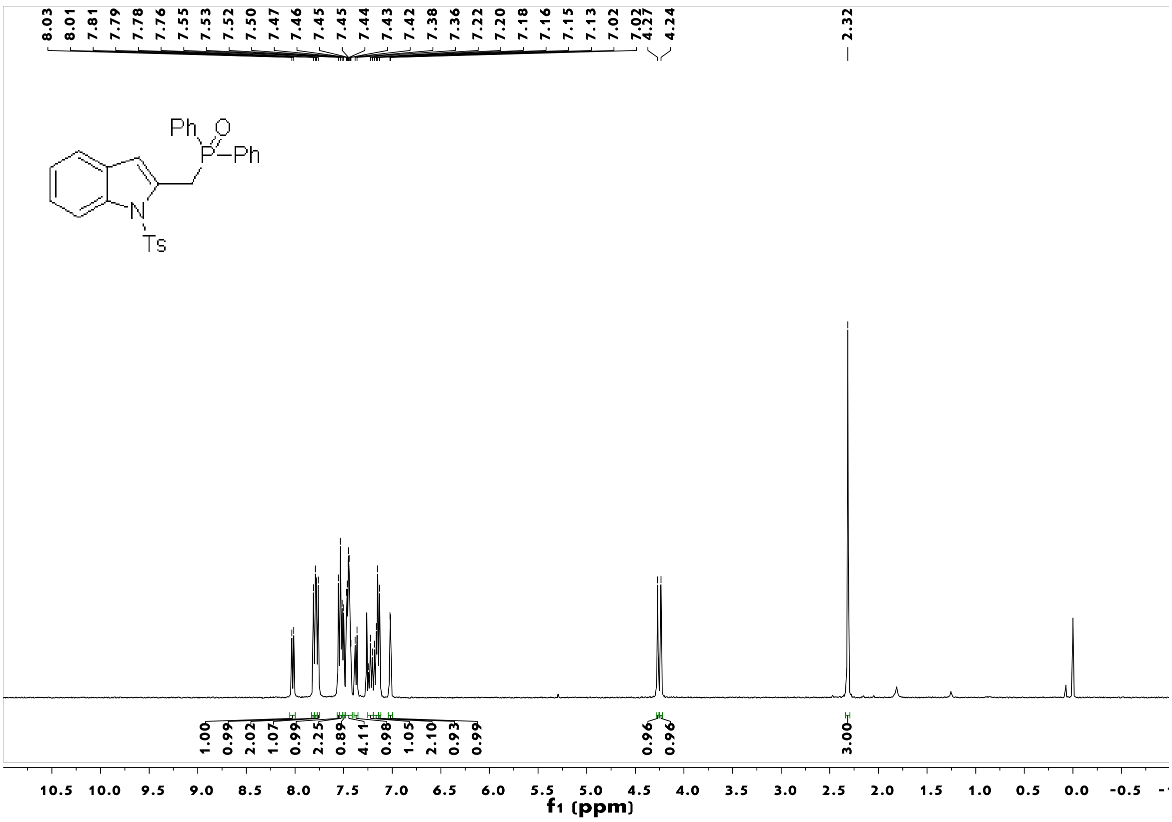
^{13}C NMR Spectrum of **3d**



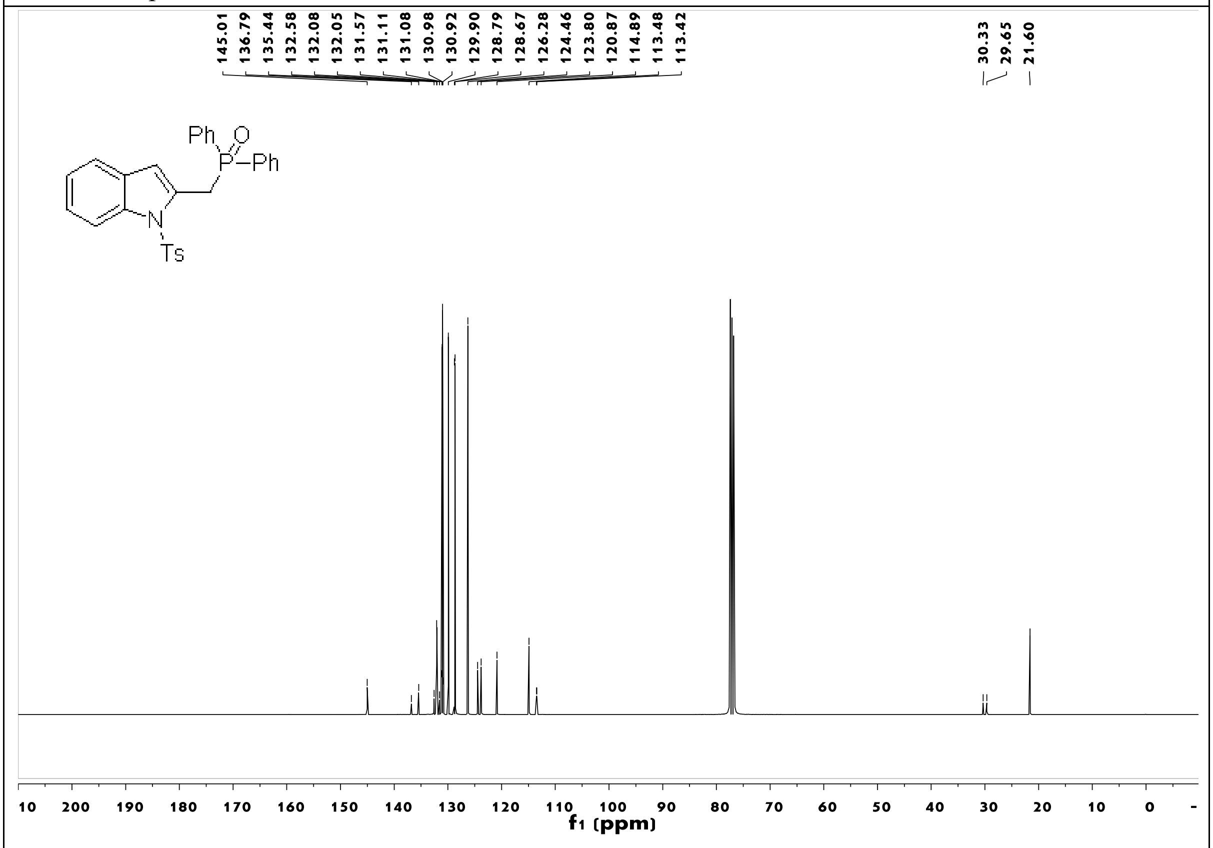
^{31}P NMR Spectrum of **3d**



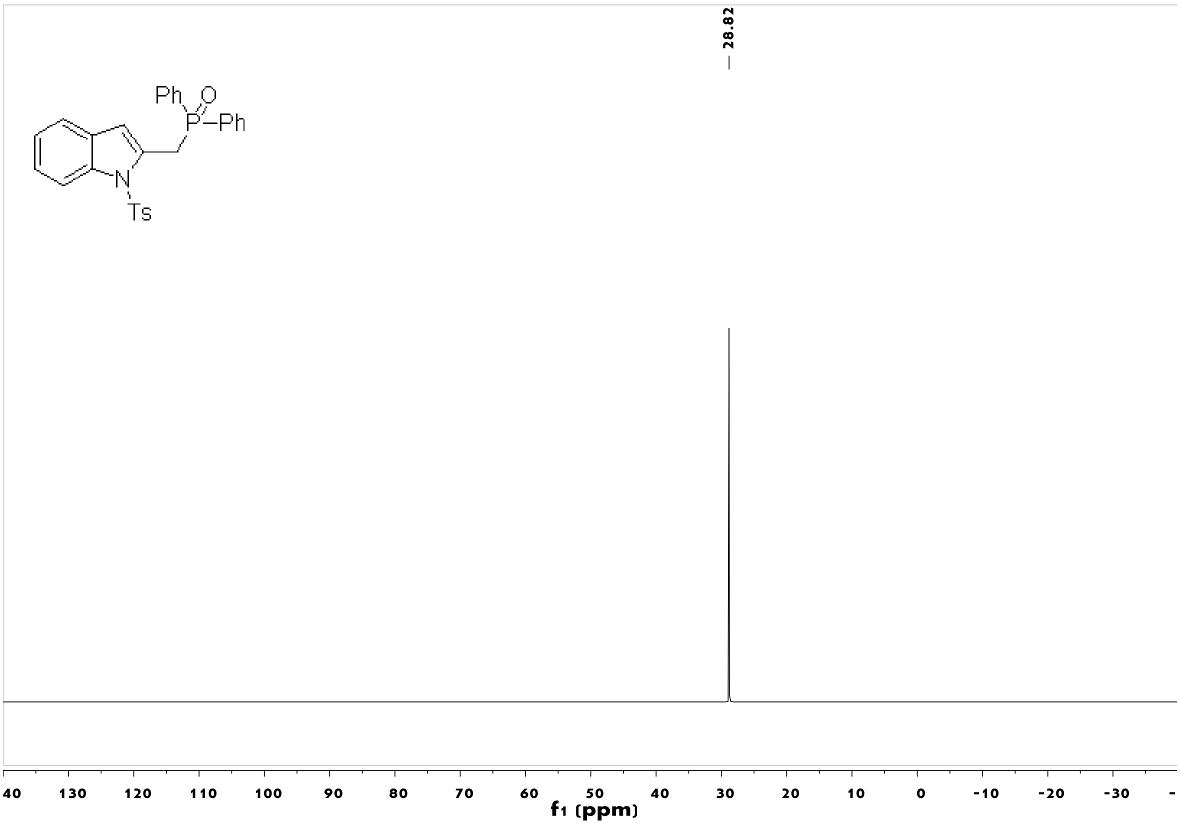
[1]H NMR Spectrum of **3e**



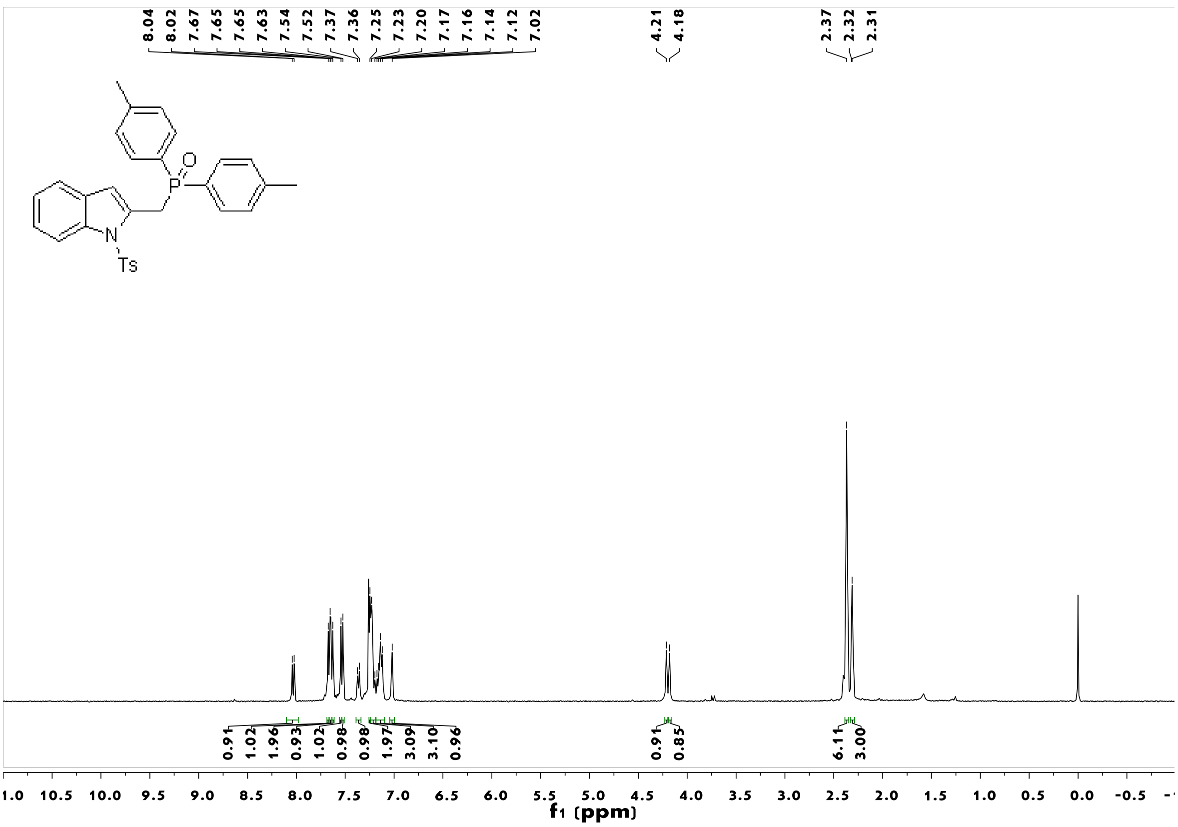
[13]C NMR Spectrum of **3e**



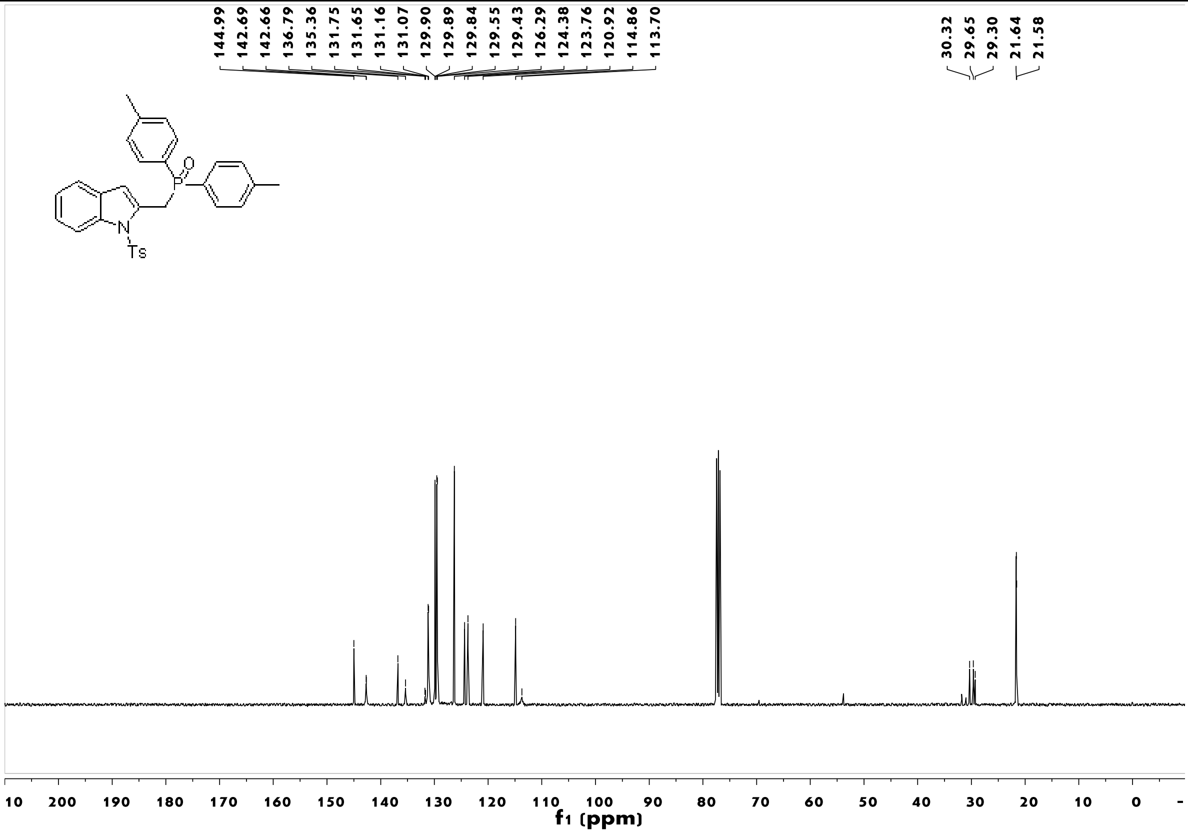
^{31}P NMR Spectrum of **3e**



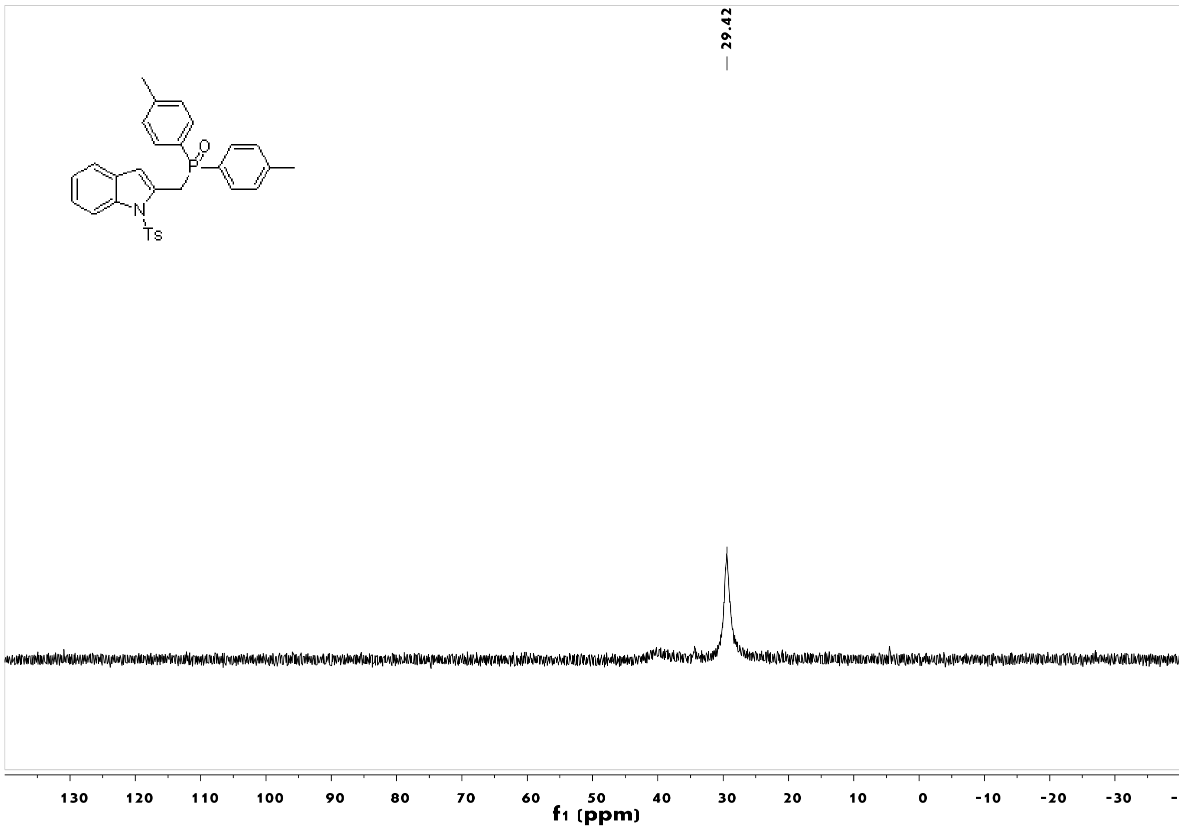
^{1}H NMR Spectrum of **3f**



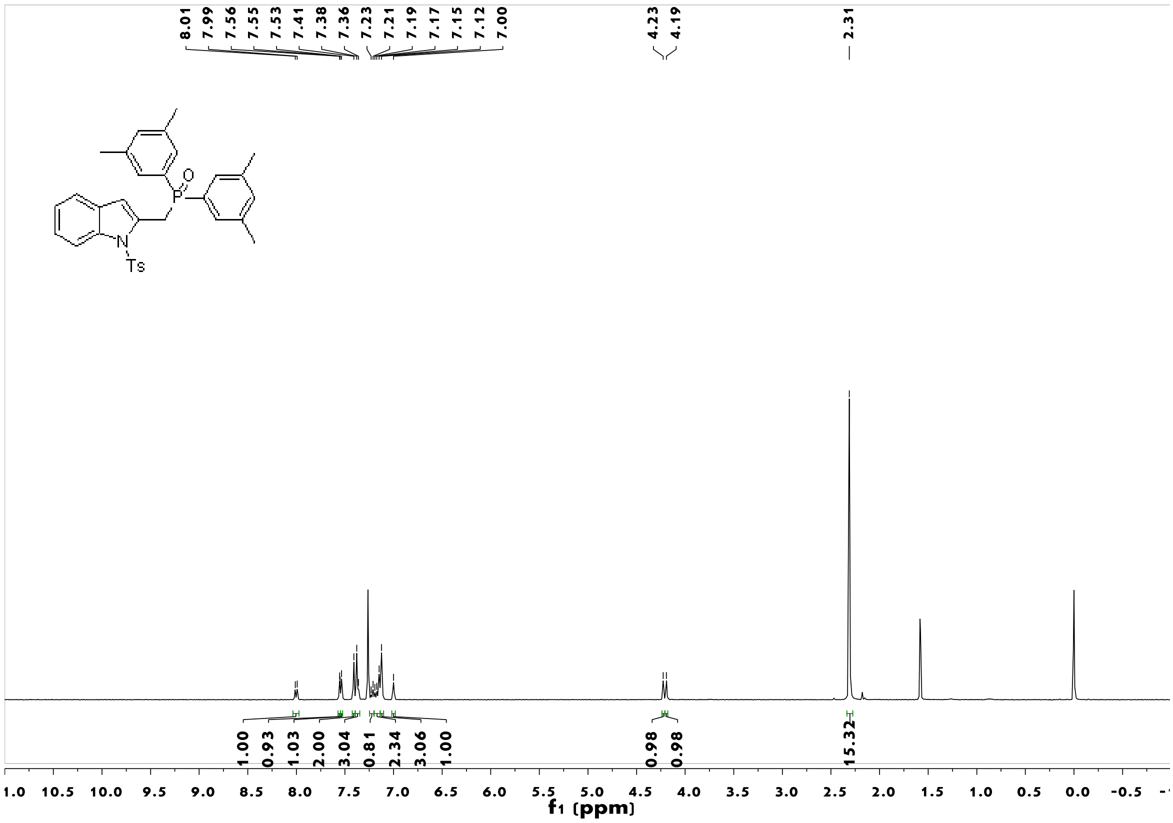
¹³C NMR Spectrum of **3f**



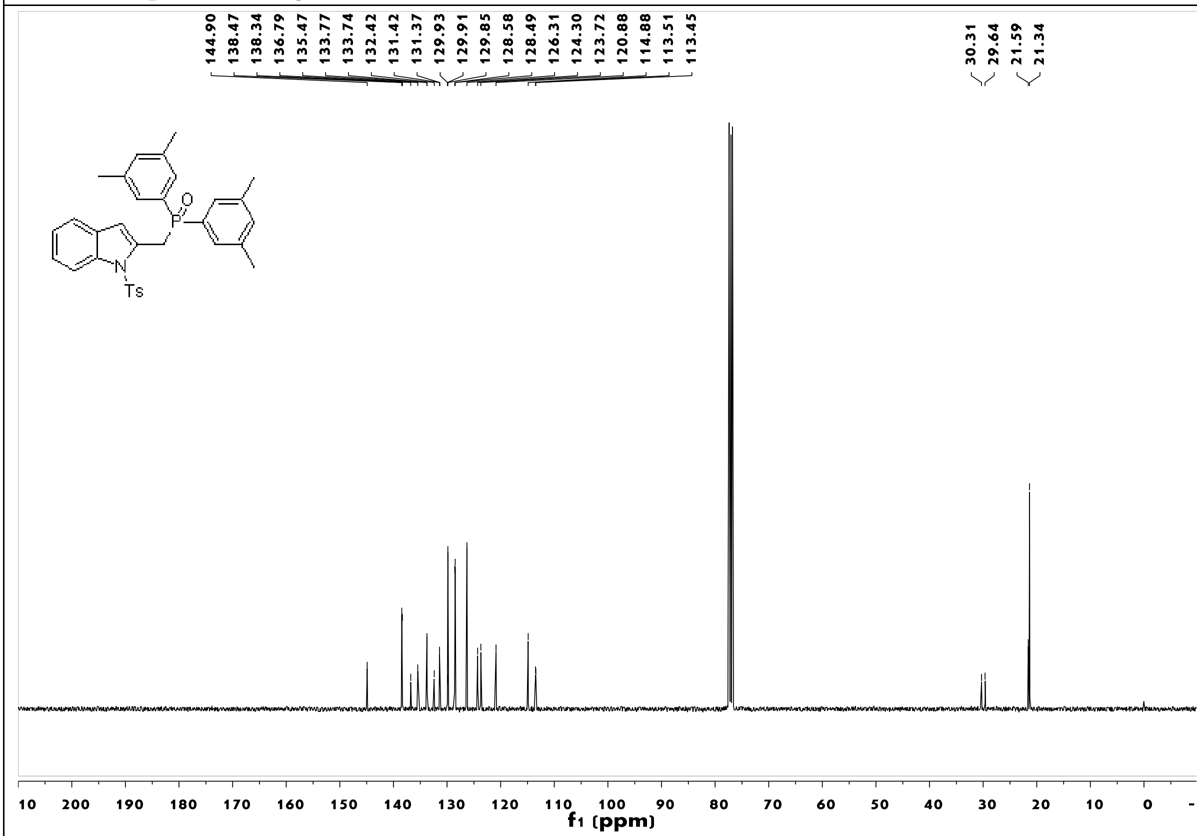
³¹P NMR Spectrum of **3f**



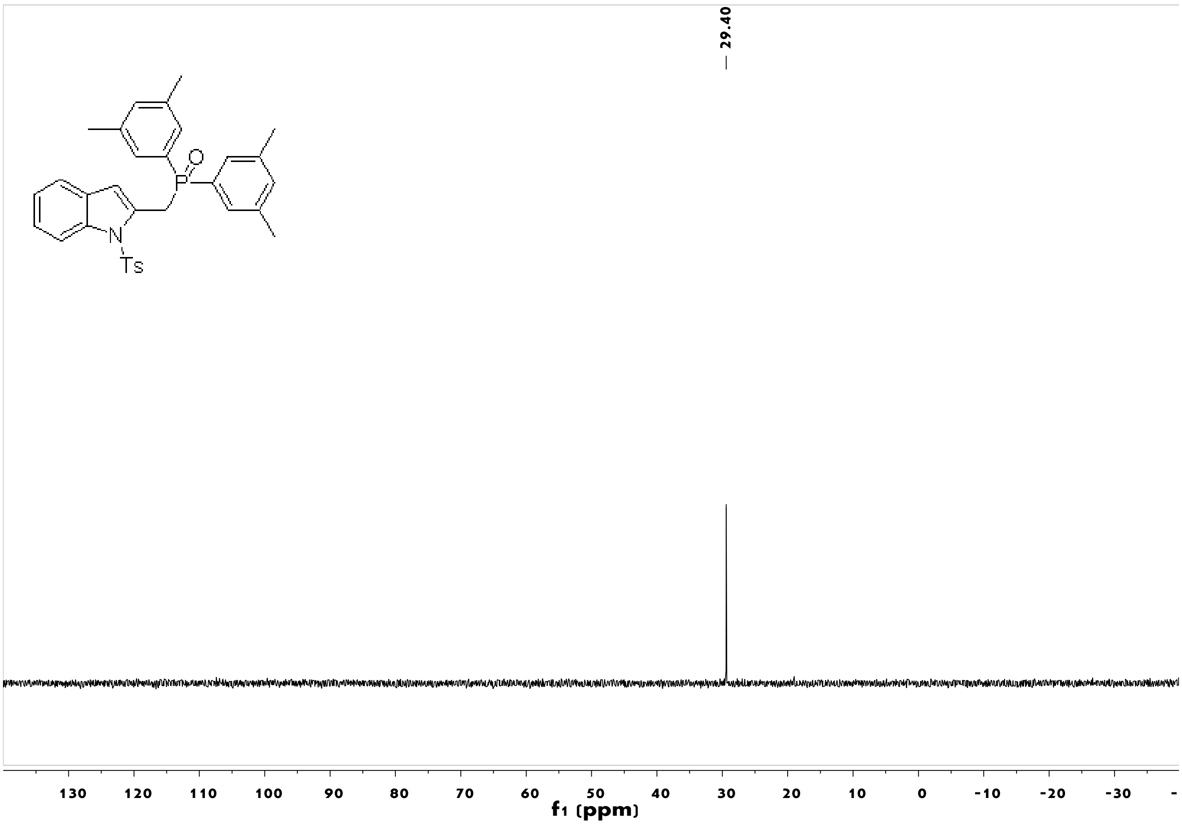
^{1}H NMR Spectrum of **3g**



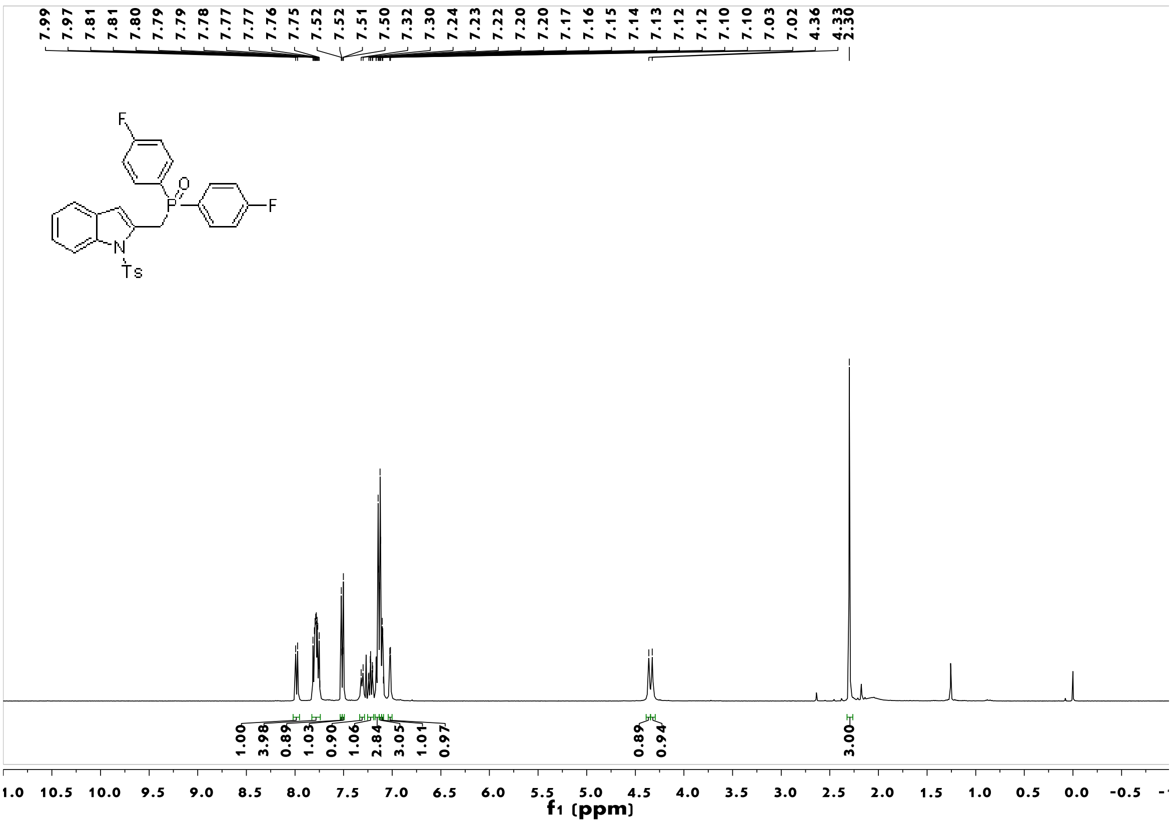
^{13}C NMR Spectrum of **3g**



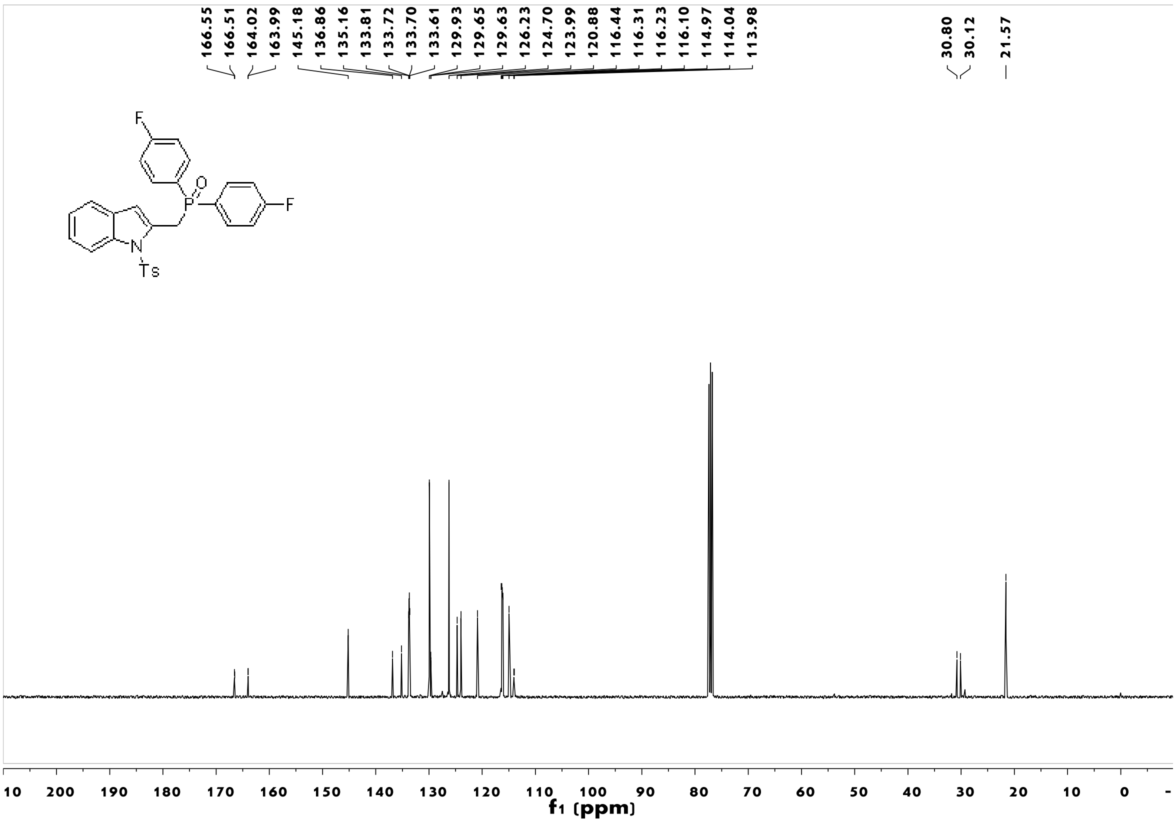
^{31}P NMR Spectrum of **3g**



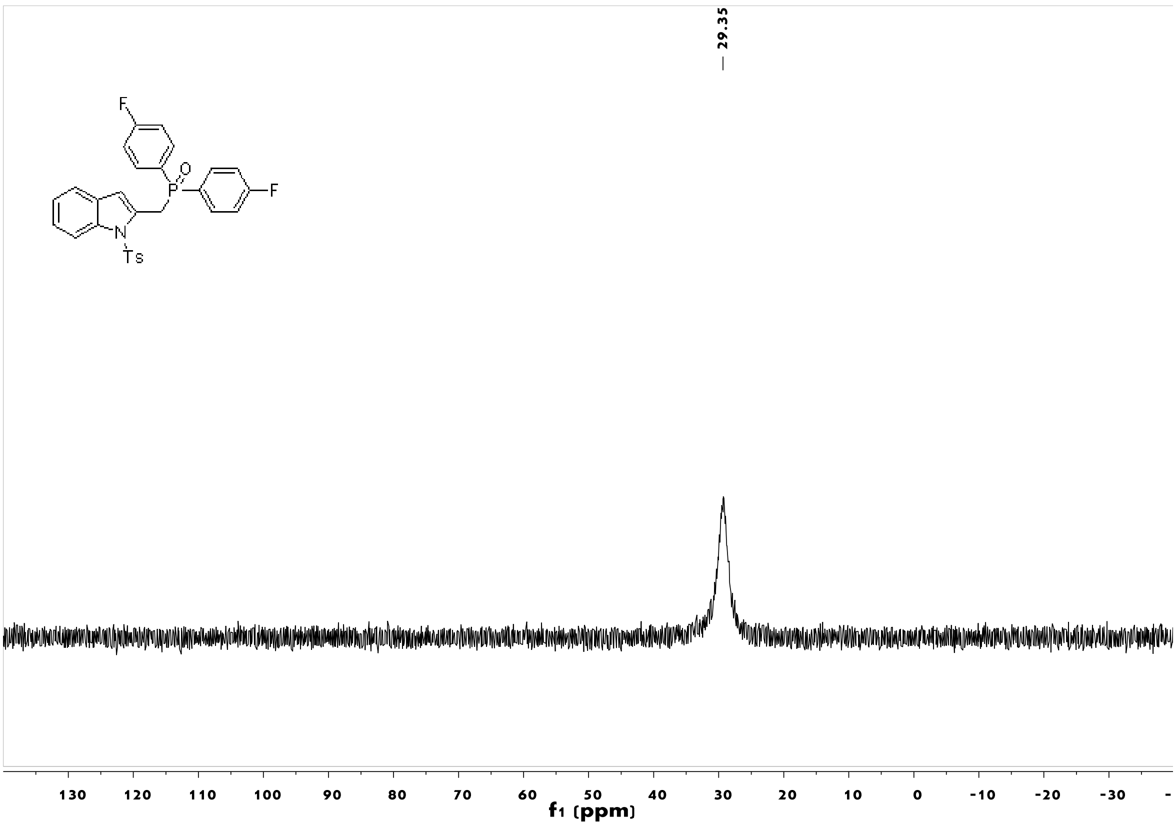
^{1}H NMR Spectrum of **3h**



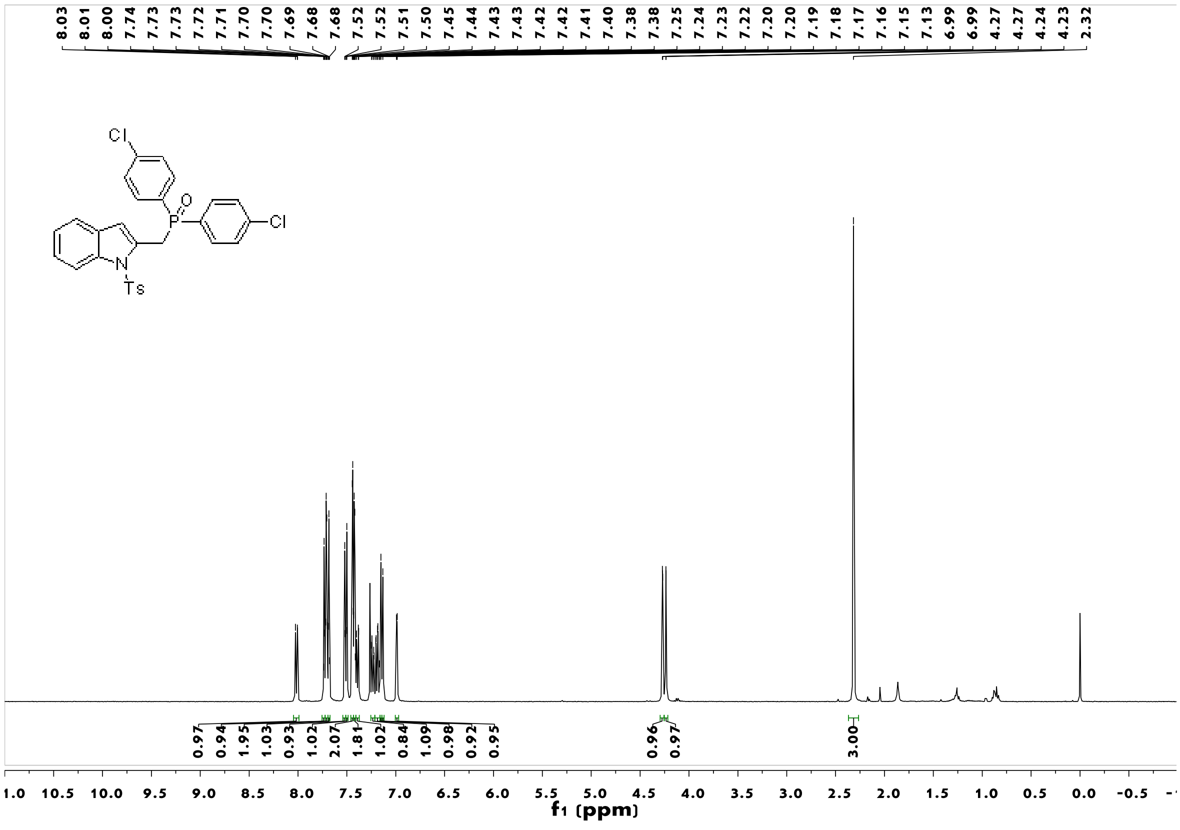
^{13}C NMR Spectrum of **3h**



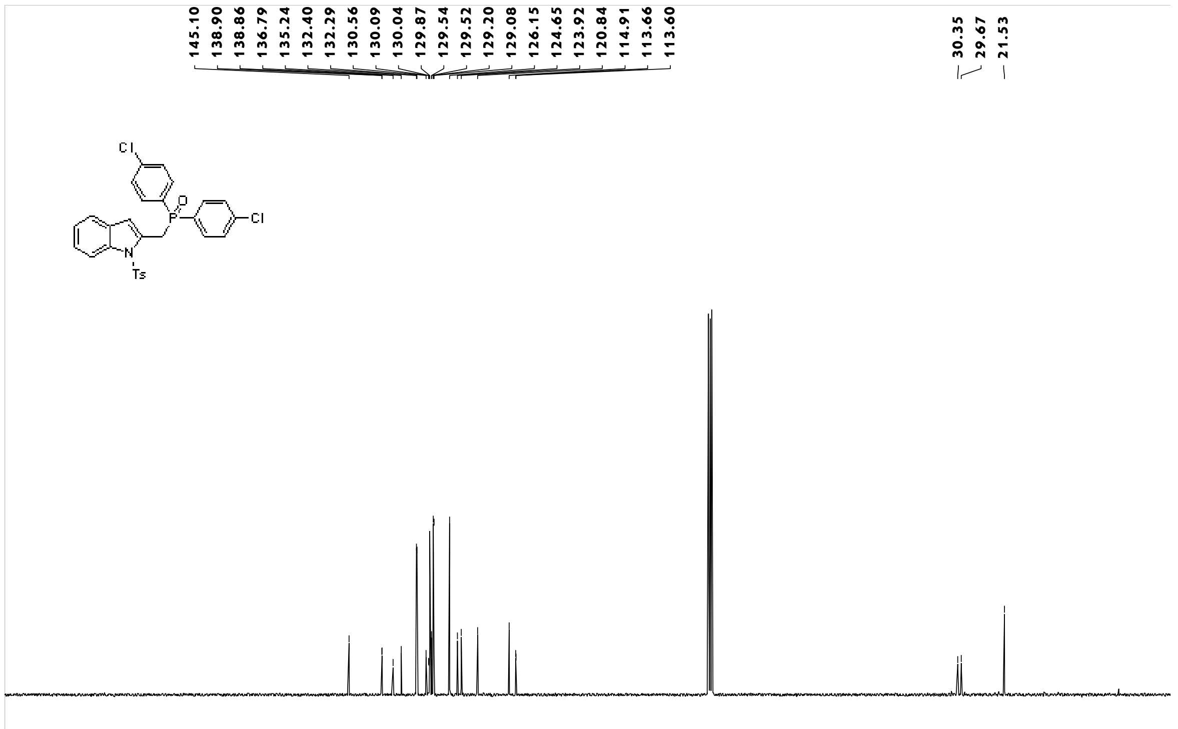
^{31}P NMR Spectrum of **3h**



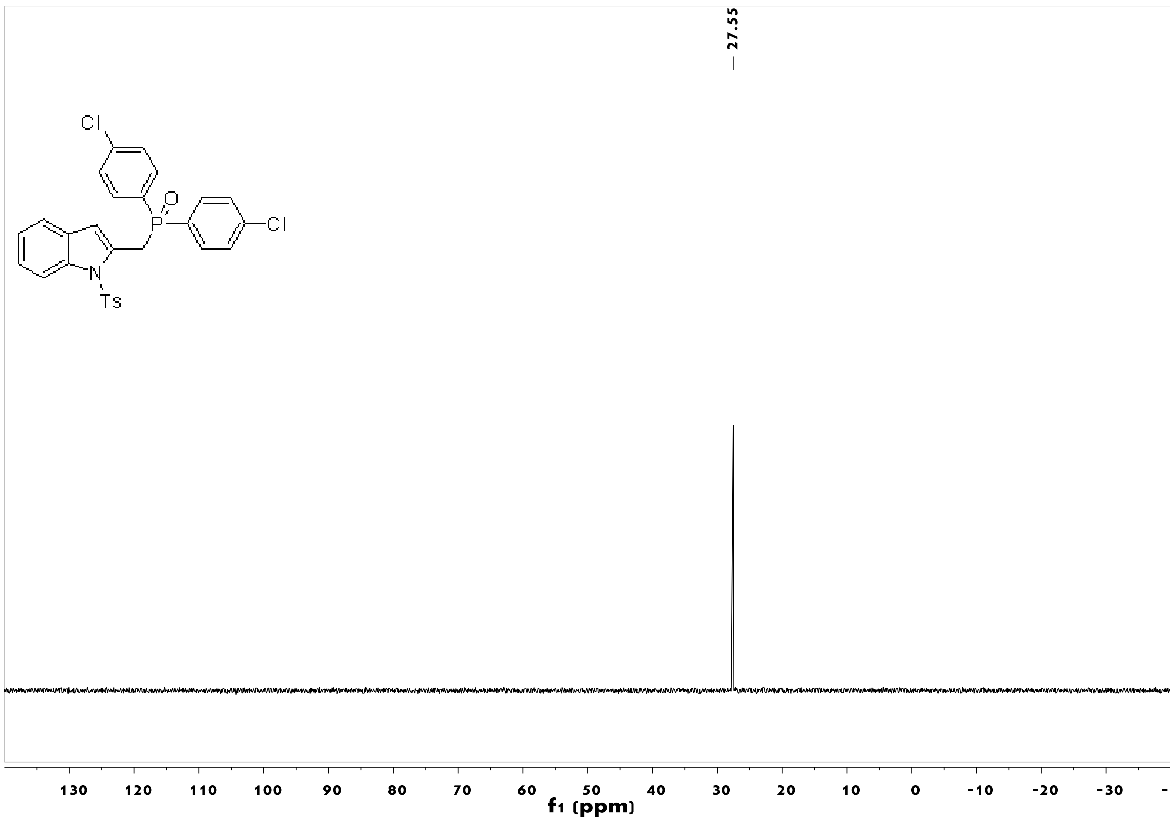
^{1}H NMR Spectrum of **3i**



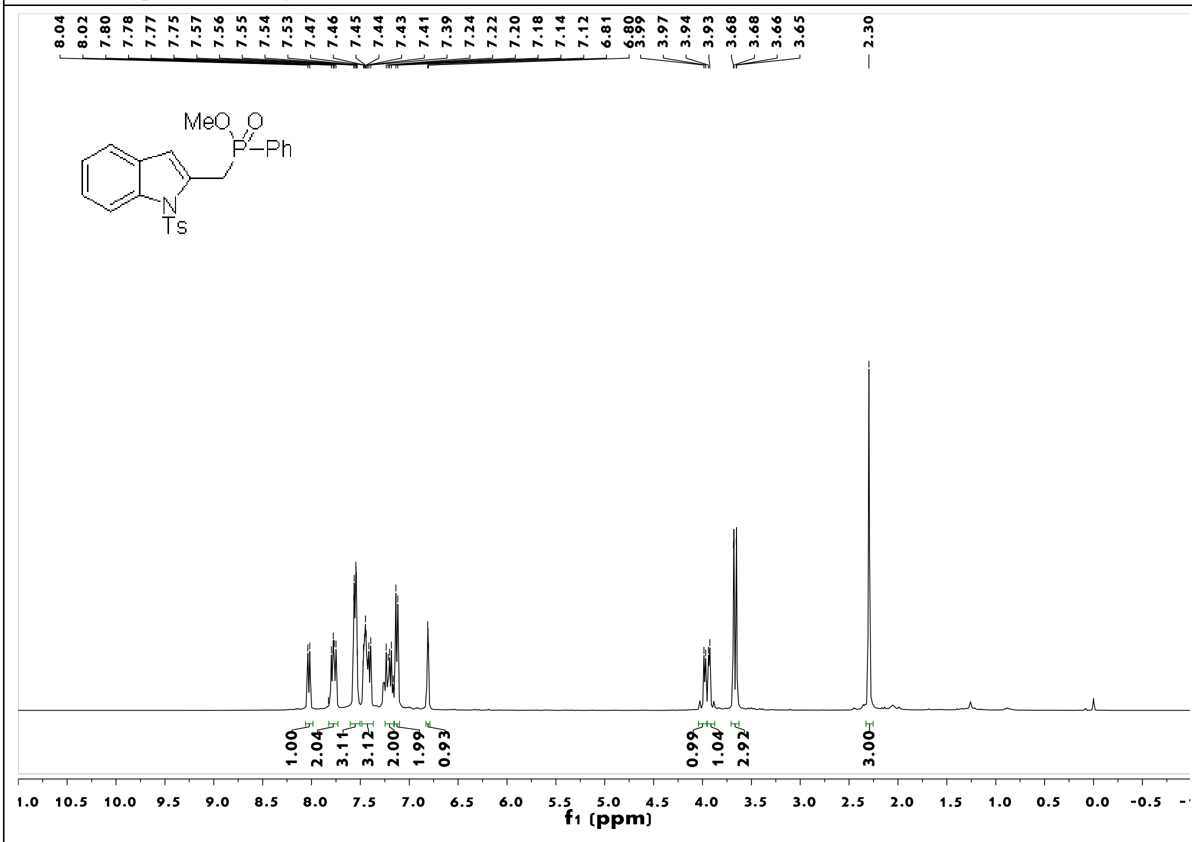
^{13}C NMR Spectrum of **3i**



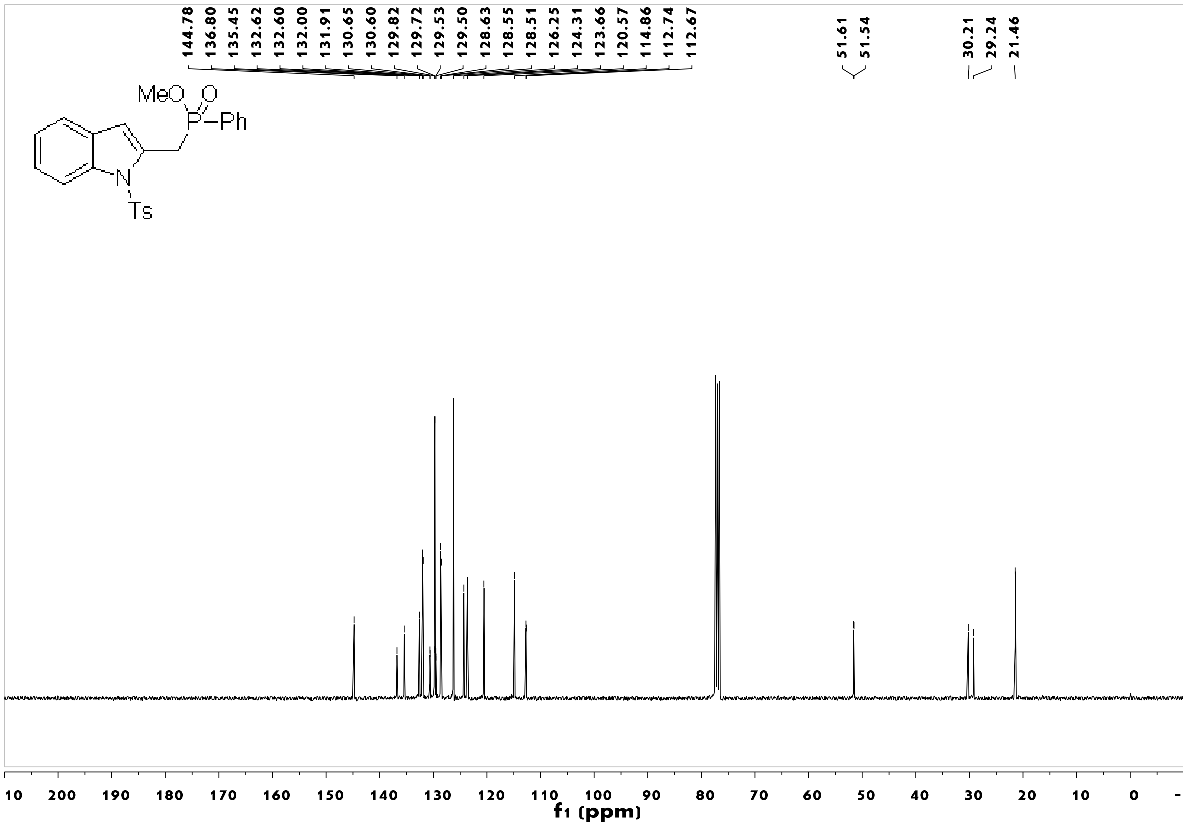
[31]P NMR Spectrum of **3i**



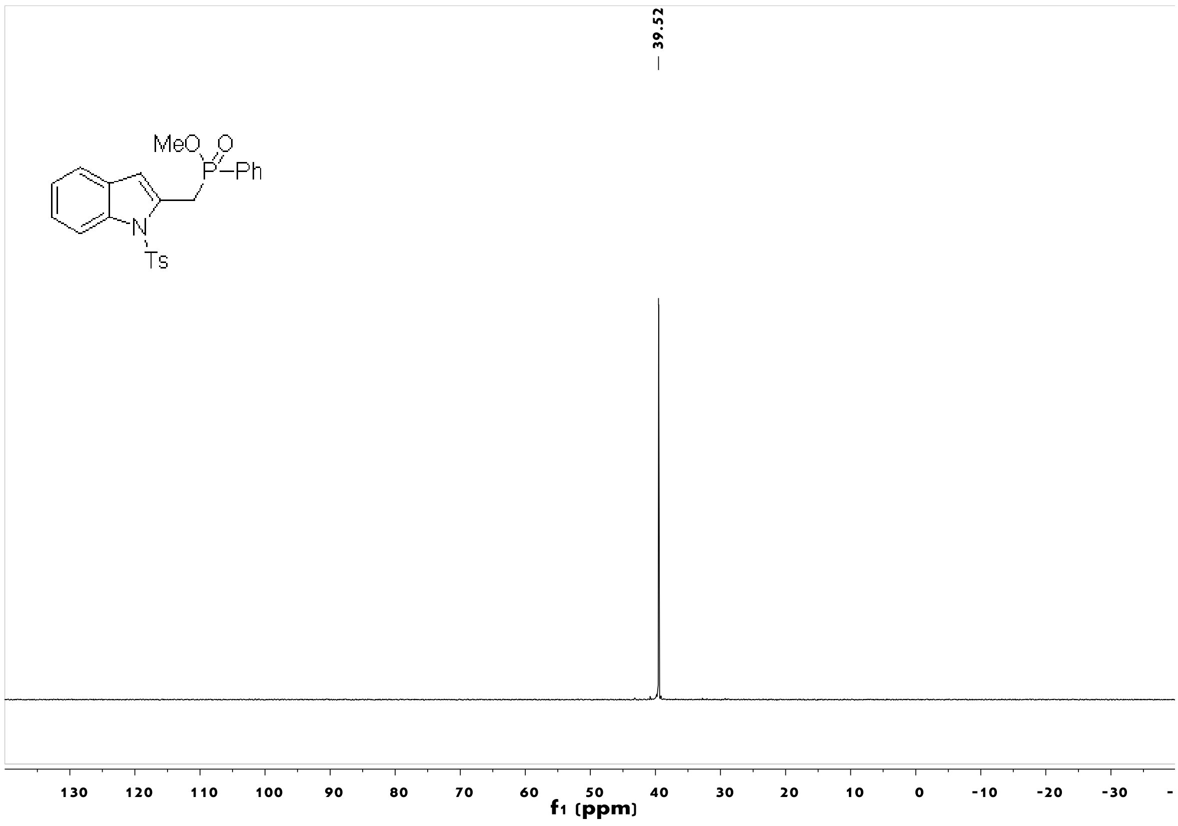
[1]H NMR Spectrum of **3j**



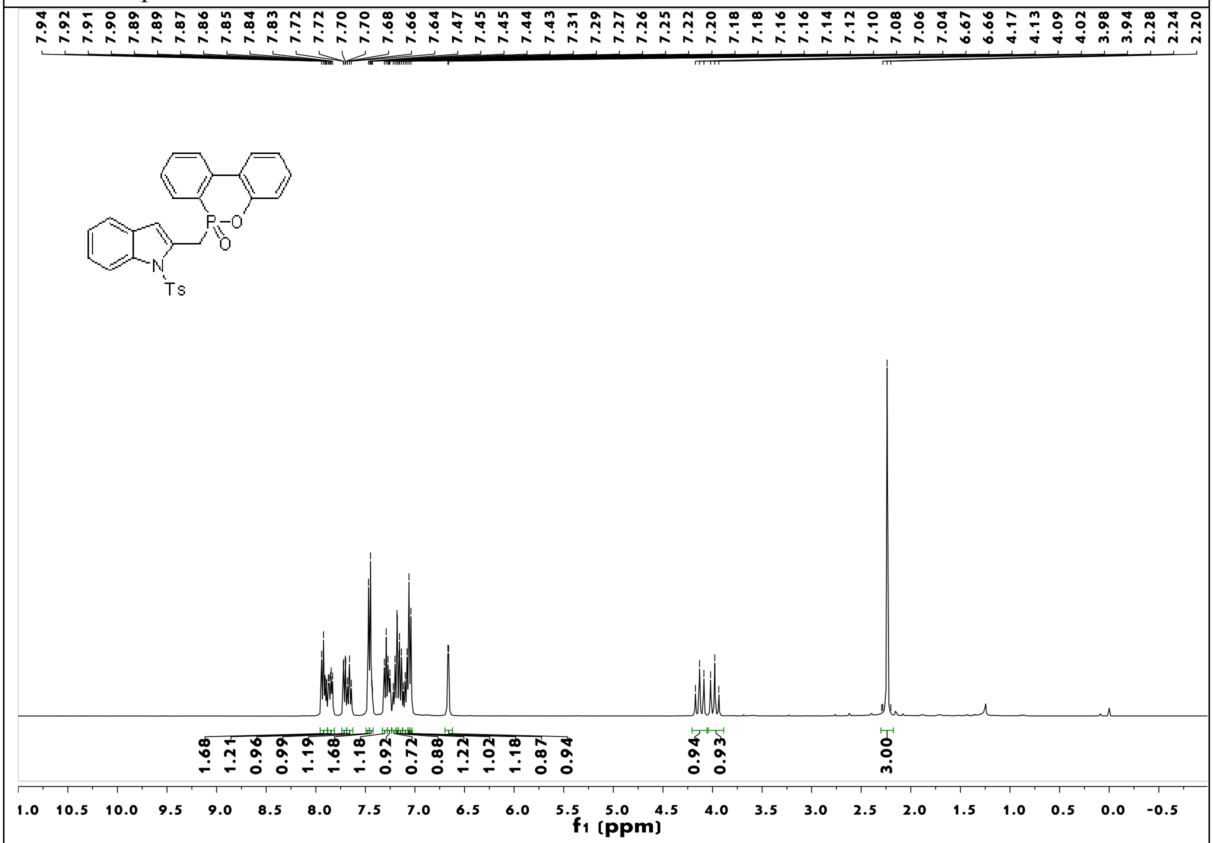
^{13}C NMR Spectrum of **3j**



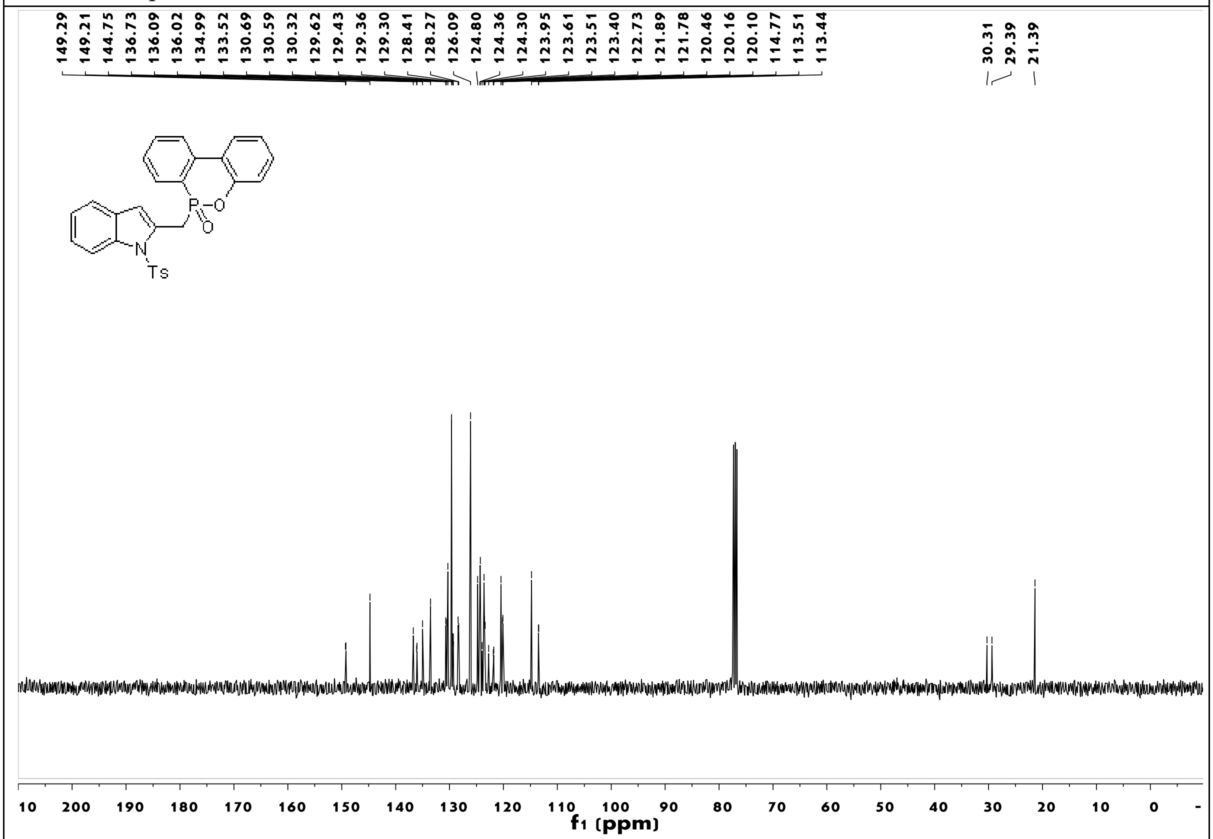
^{31}P NMR Spectrum of **3j**



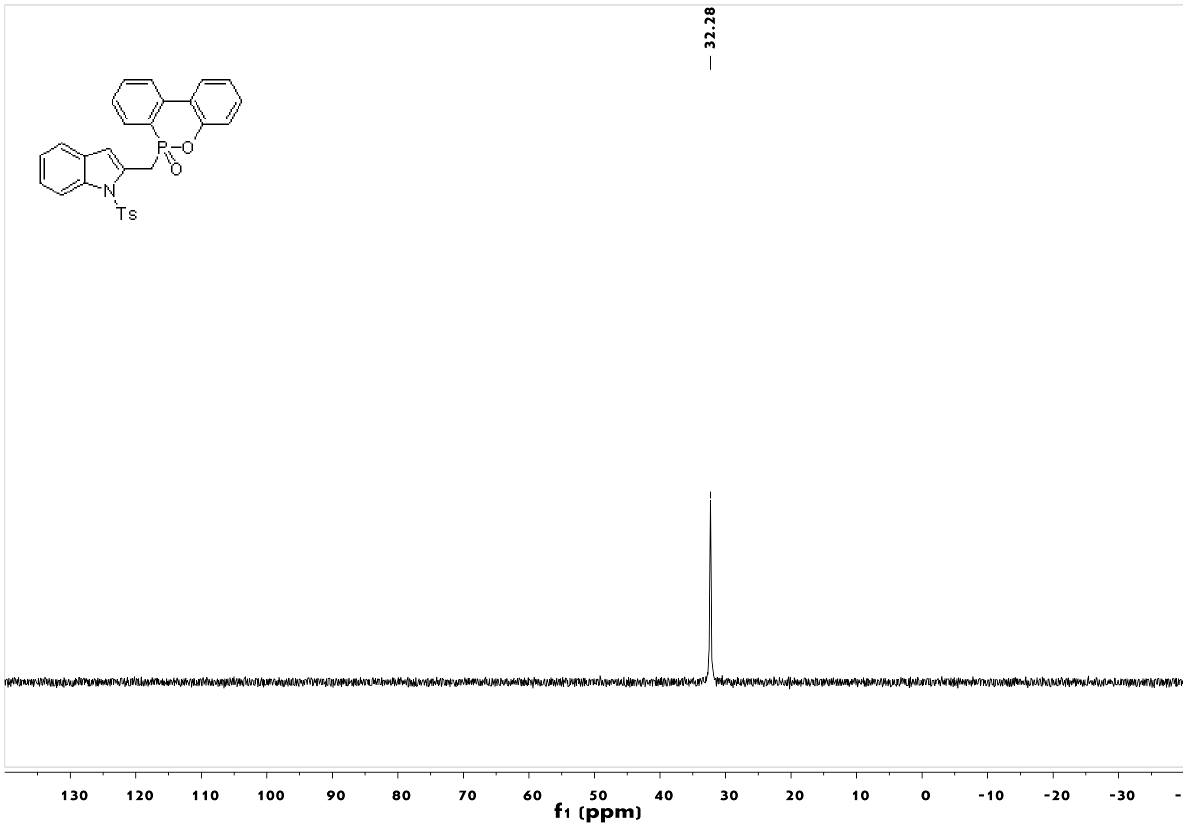
[1]H NMR Spectrum of **3k**



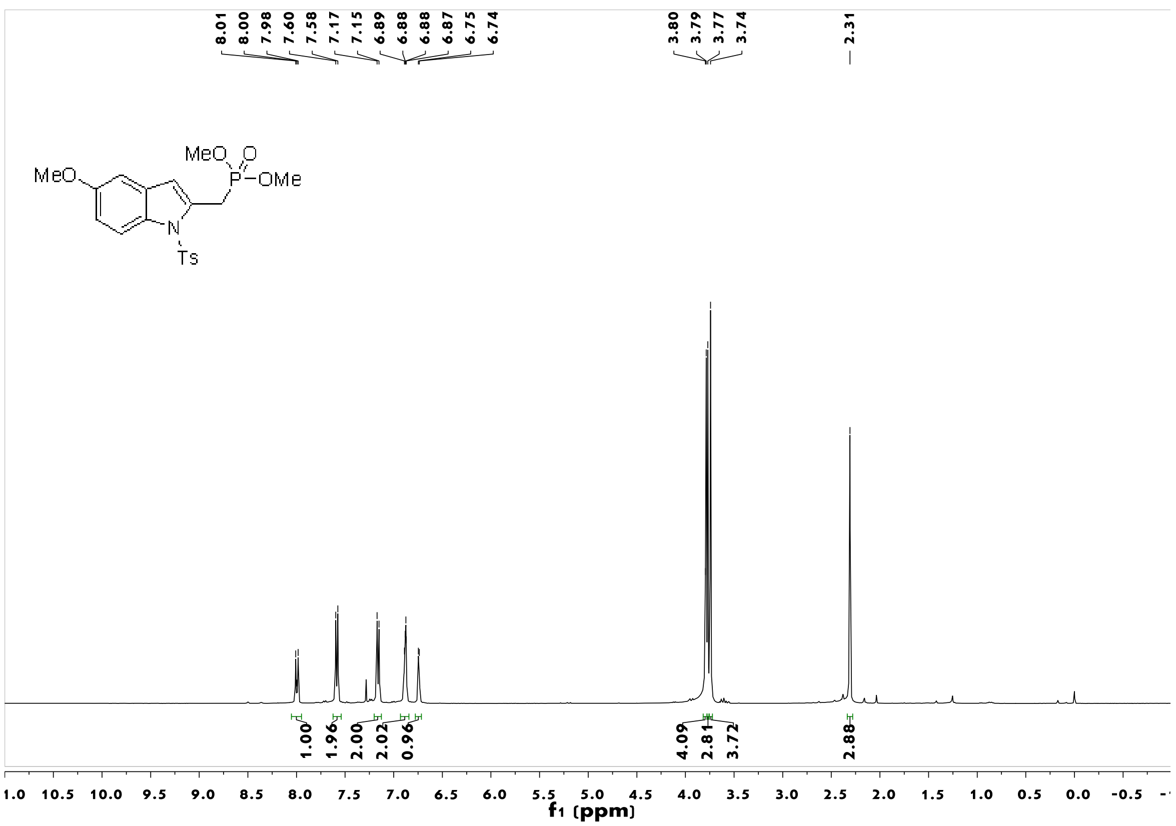
[13]C NMR Spectrum of **3k**



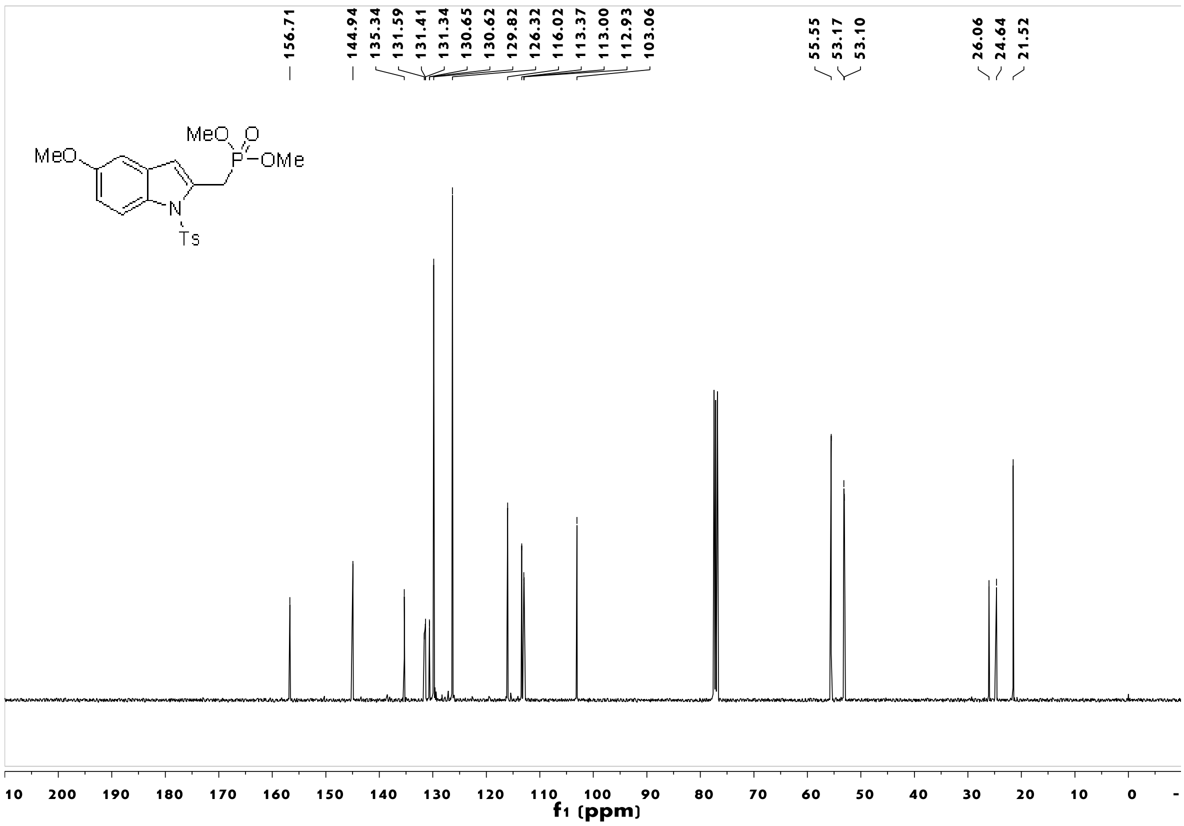
^{31}P NMR Spectrum of **3k**



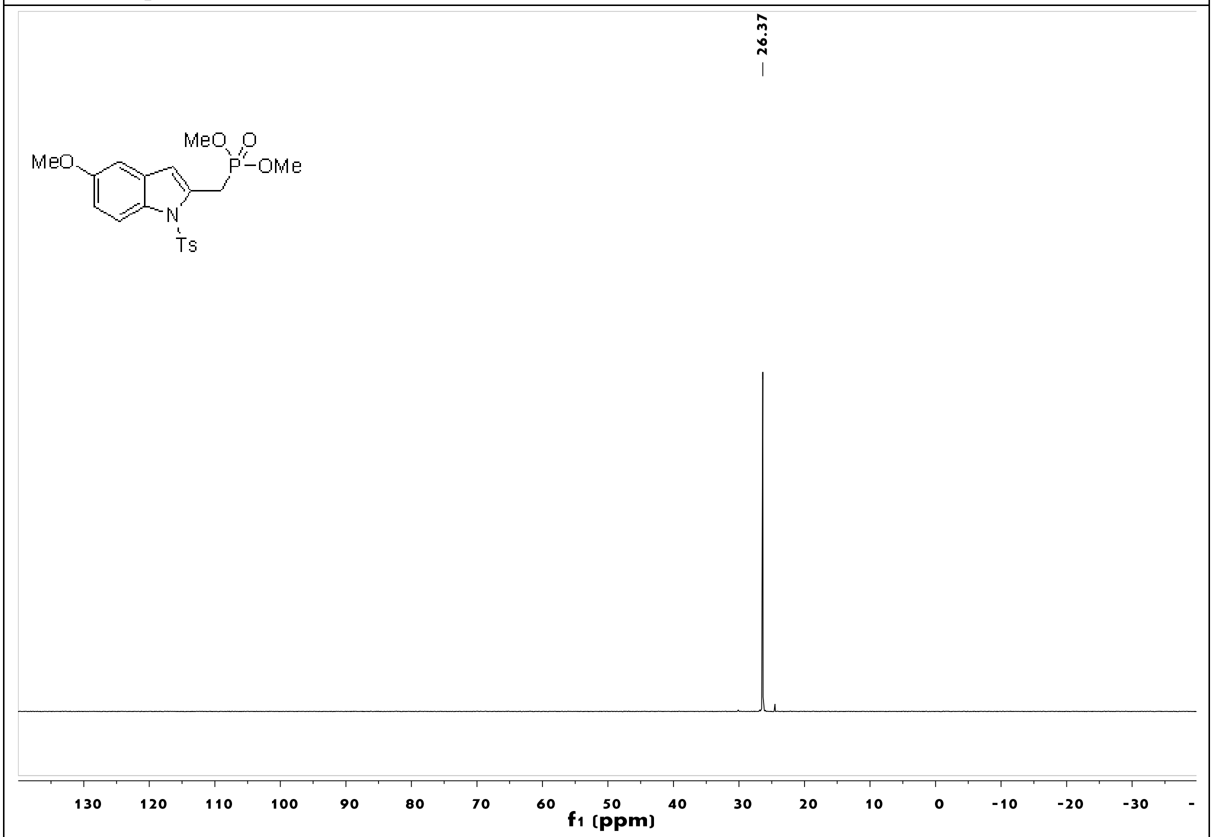
^{1}H NMR Spectrum of **3l**



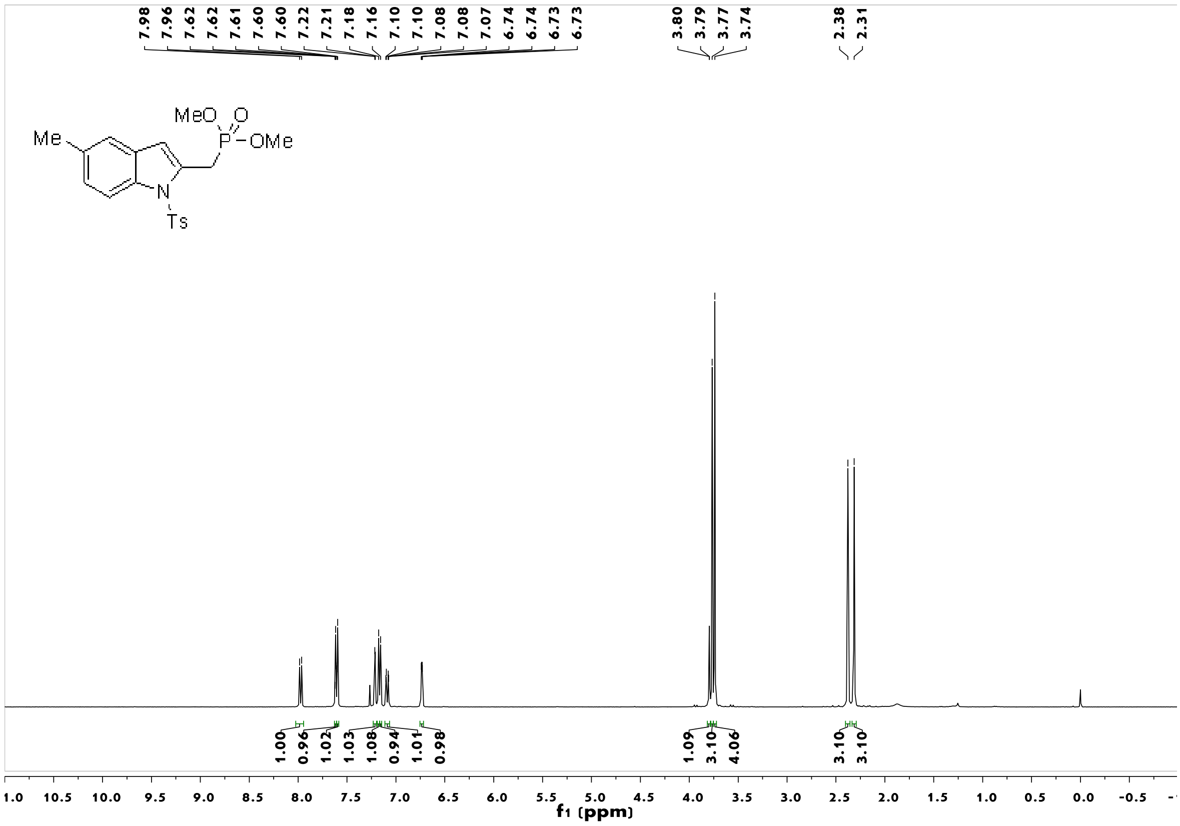
^{13}C NMR Spectrum of **3l**



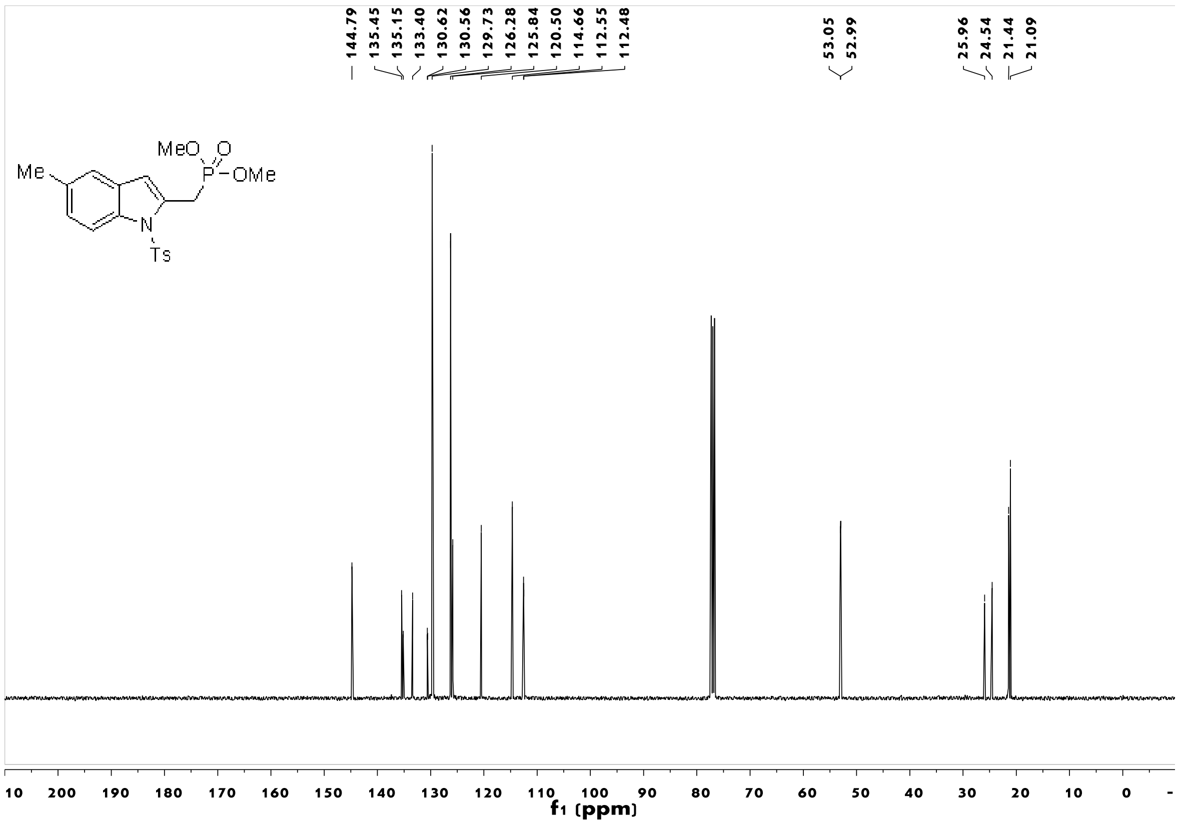
^{31}P NMR Spectrum of **3l**



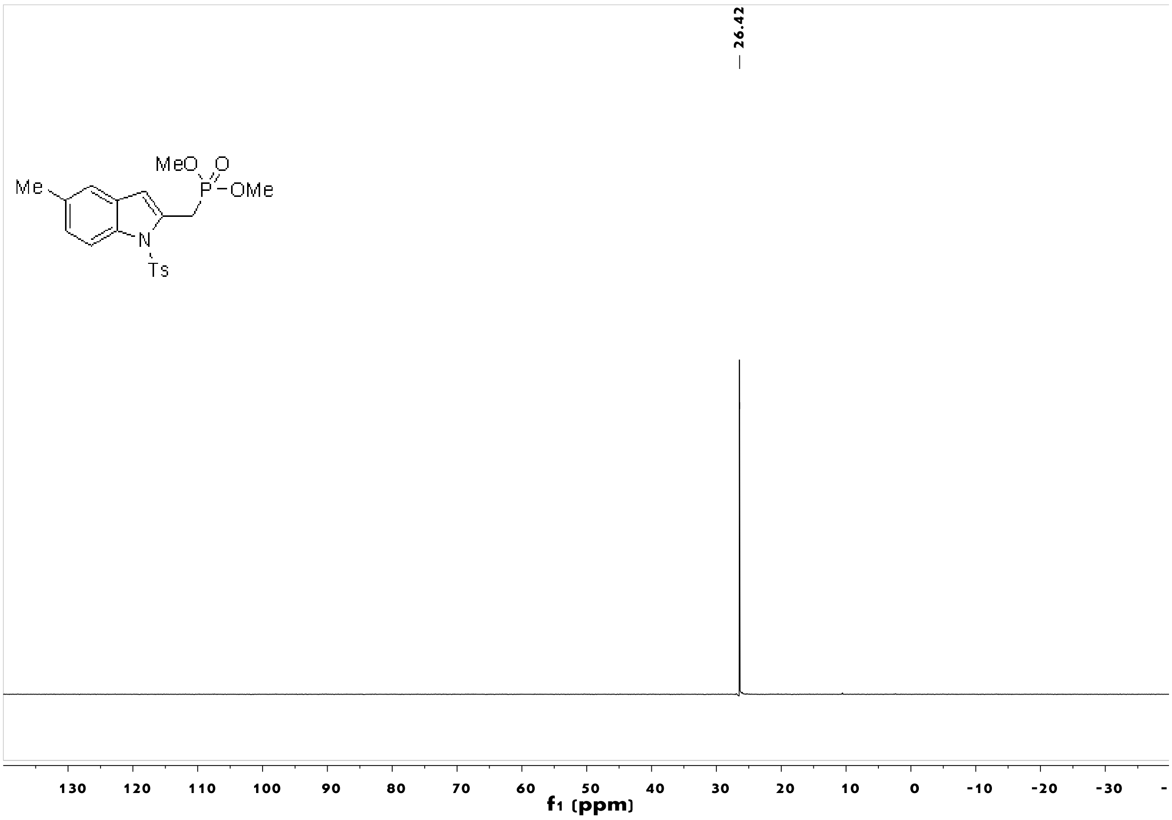
[13]H NMR Spectrum of **3m**



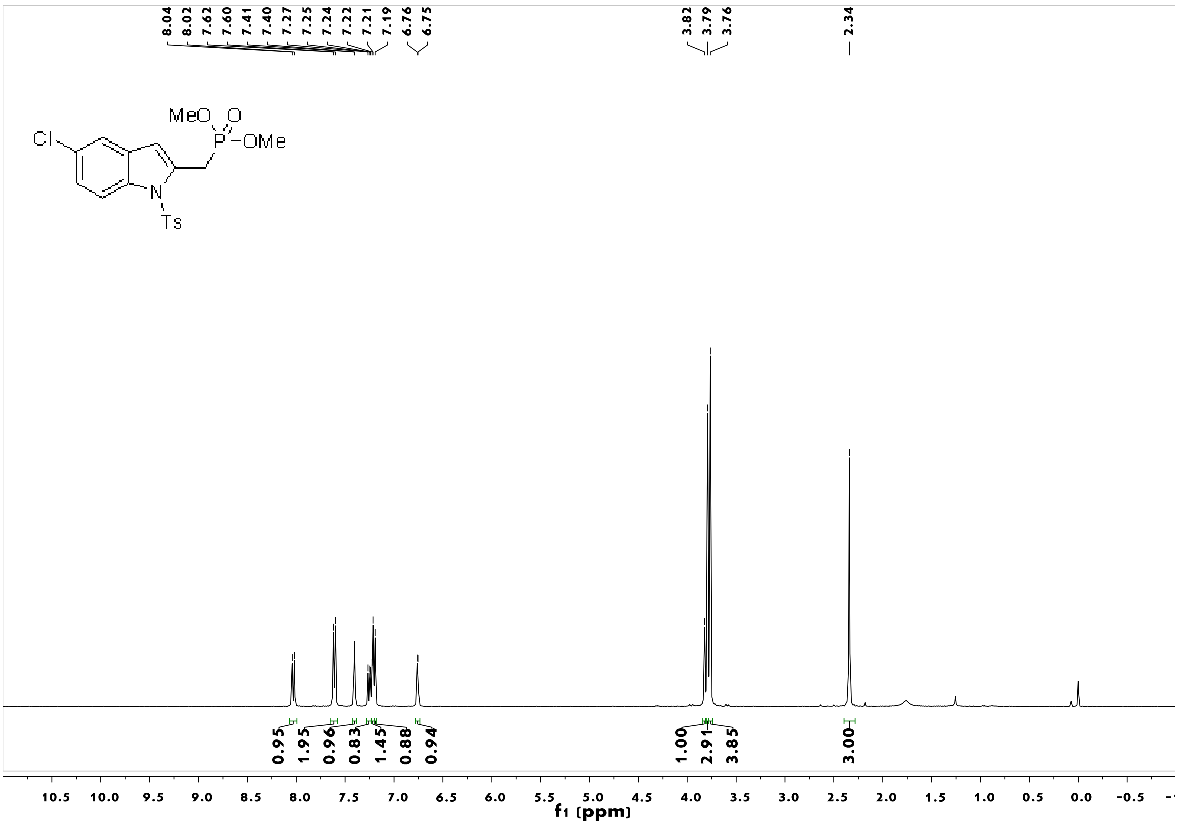
[13]C NMR Spectrum of **3m**



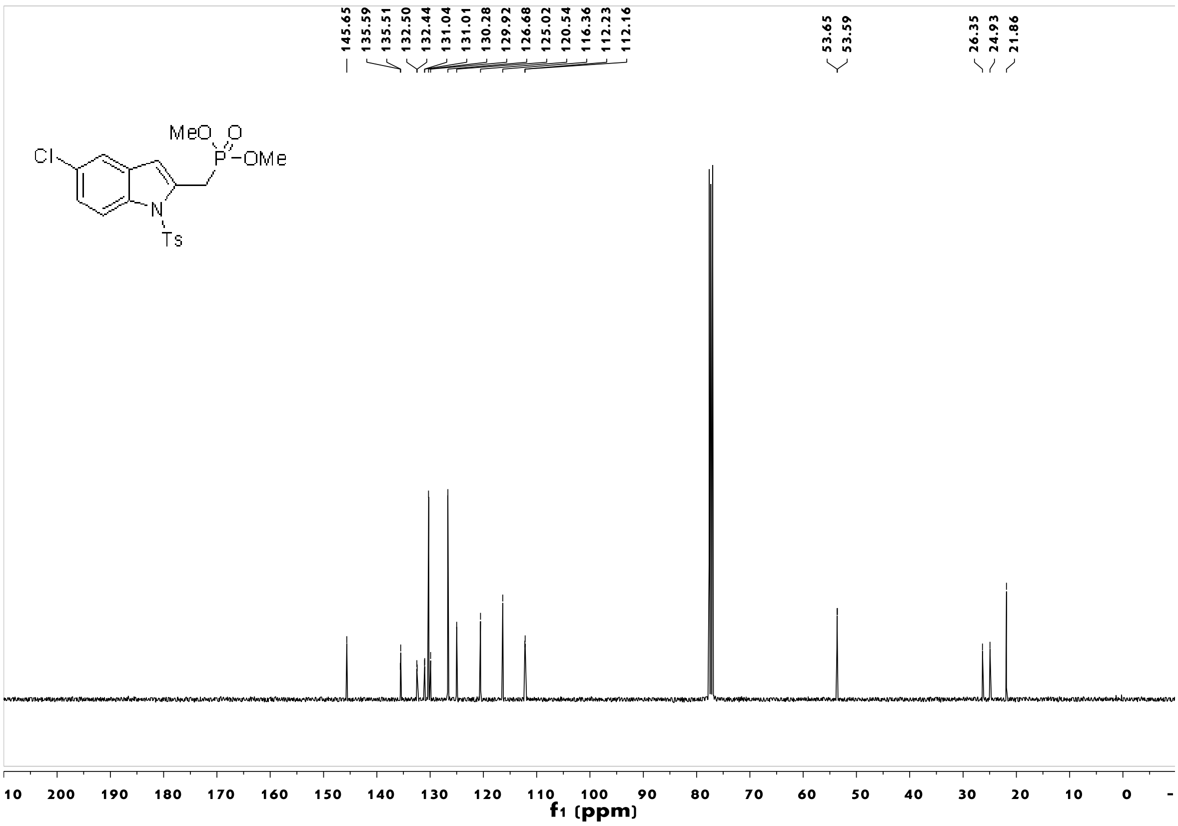
^{31}P NMR Spectrum of **3m**



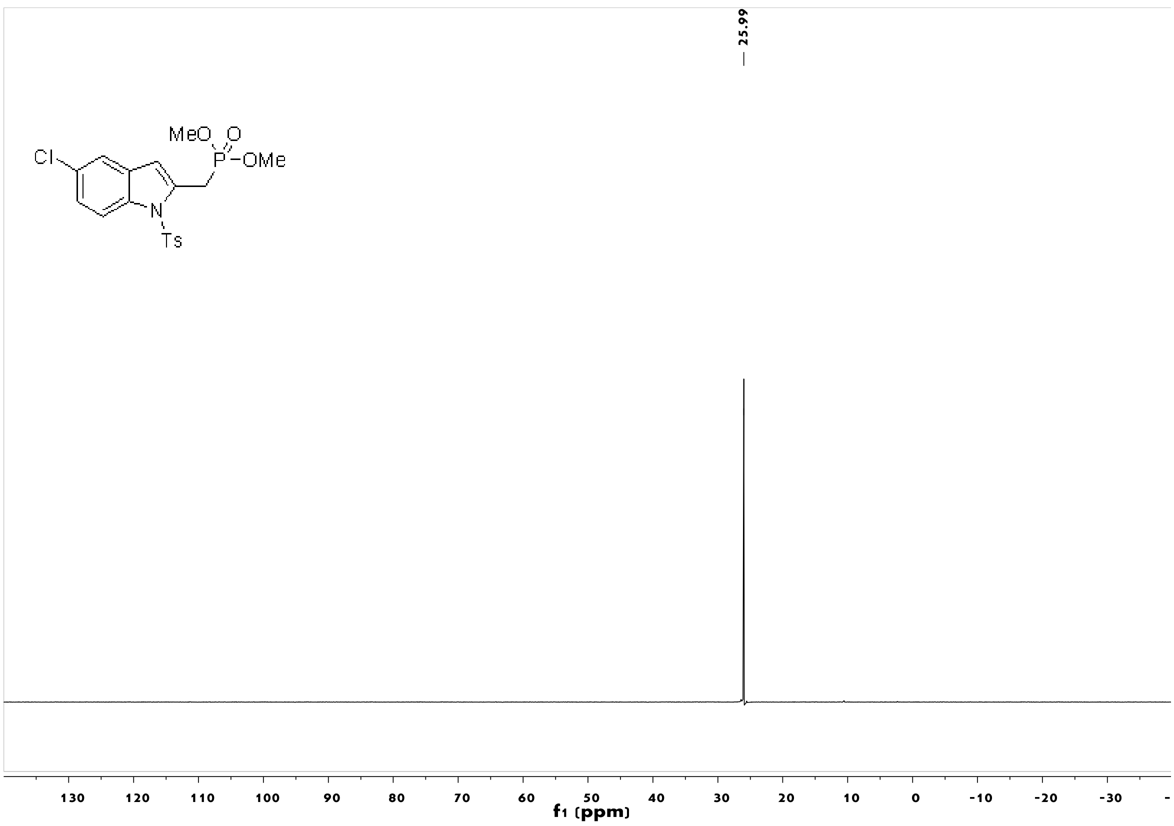
^{1}H NMR Spectrum of **3n**



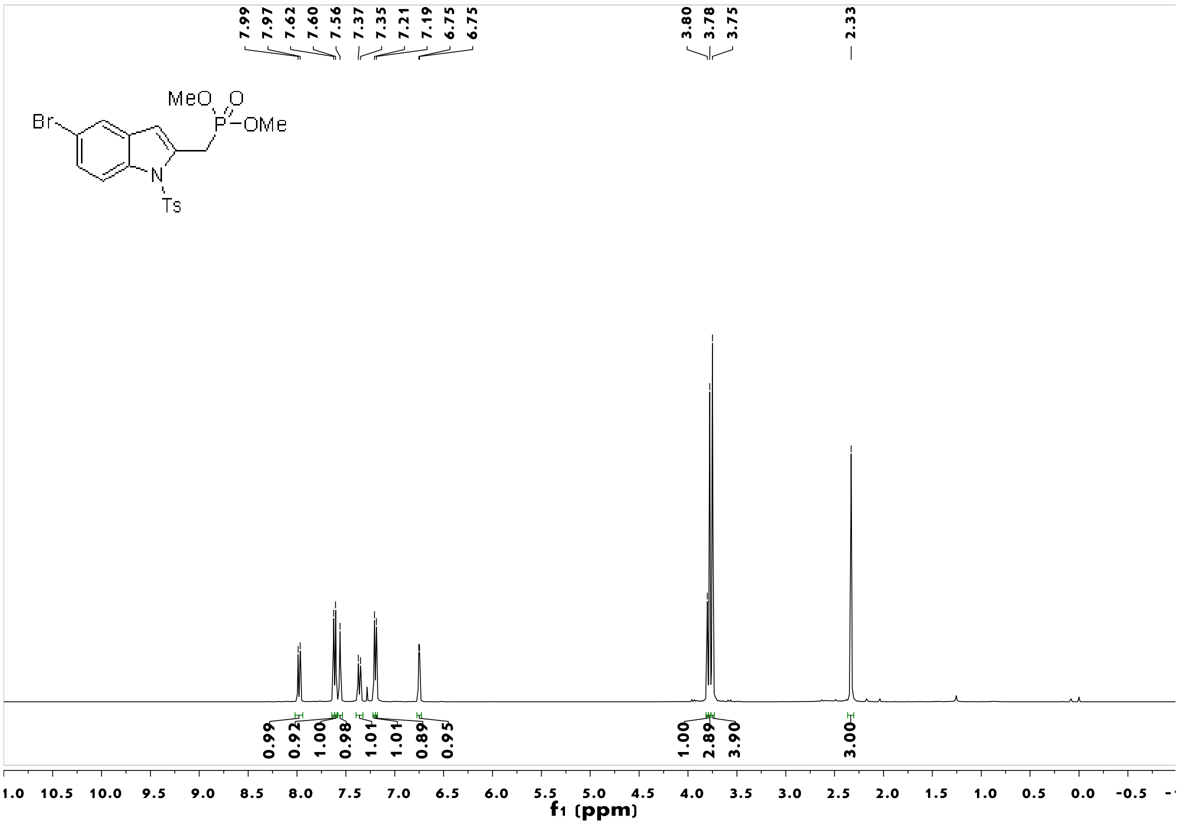
^{13}C NMR Spectrum of **3n**



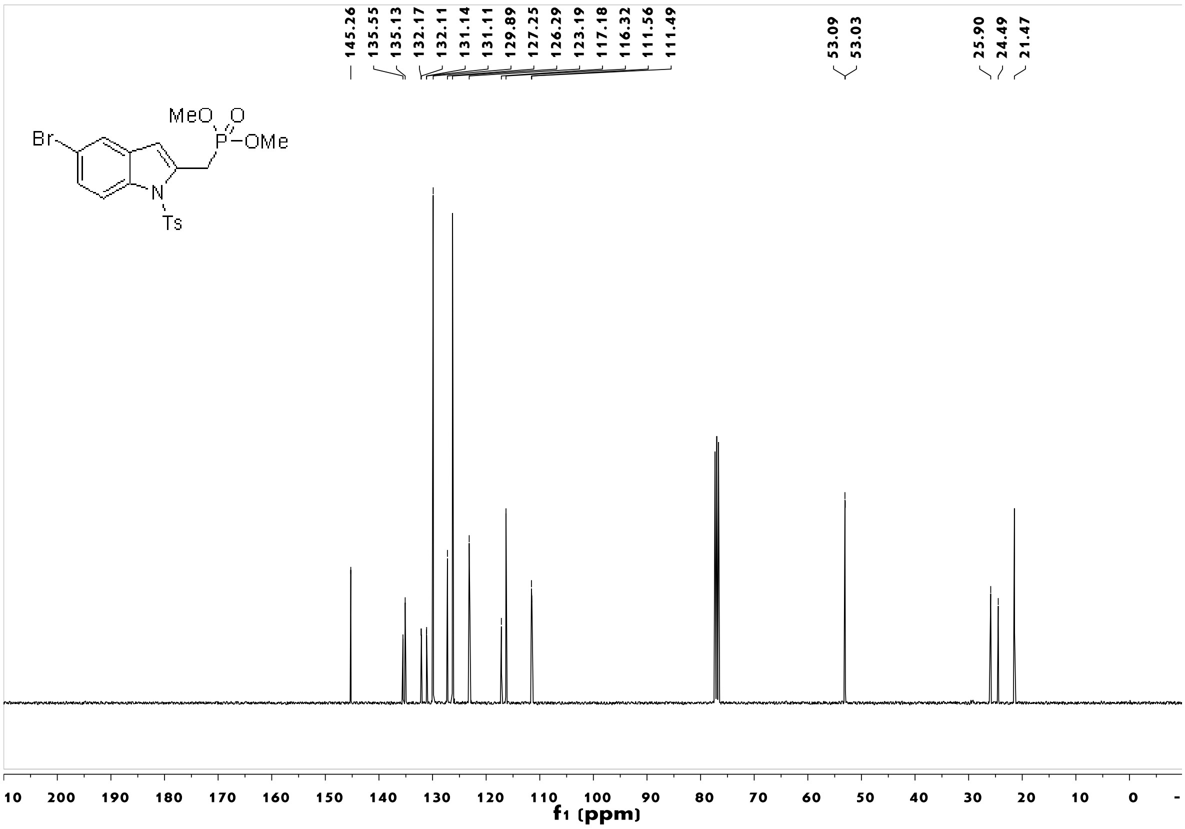
^{31}P NMR Spectrum of **3n**



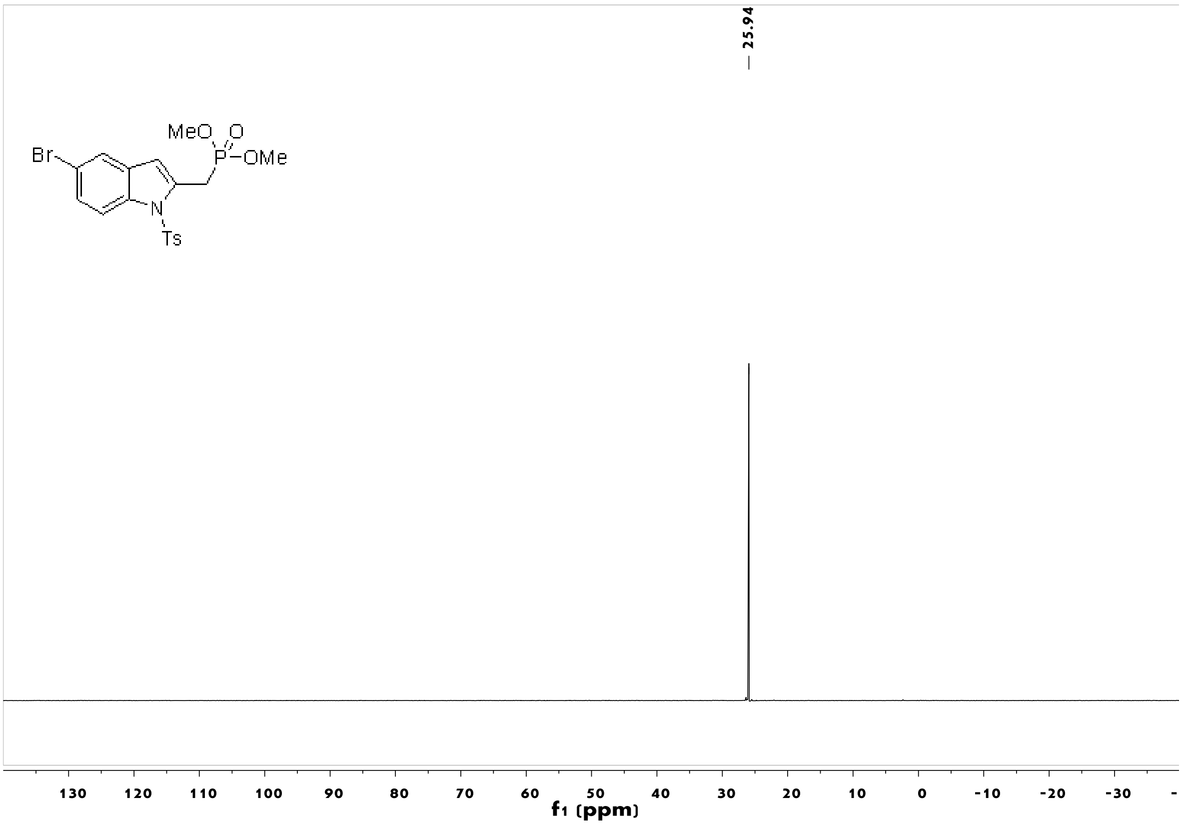
^{1}H NMR Spectrum of **3o**



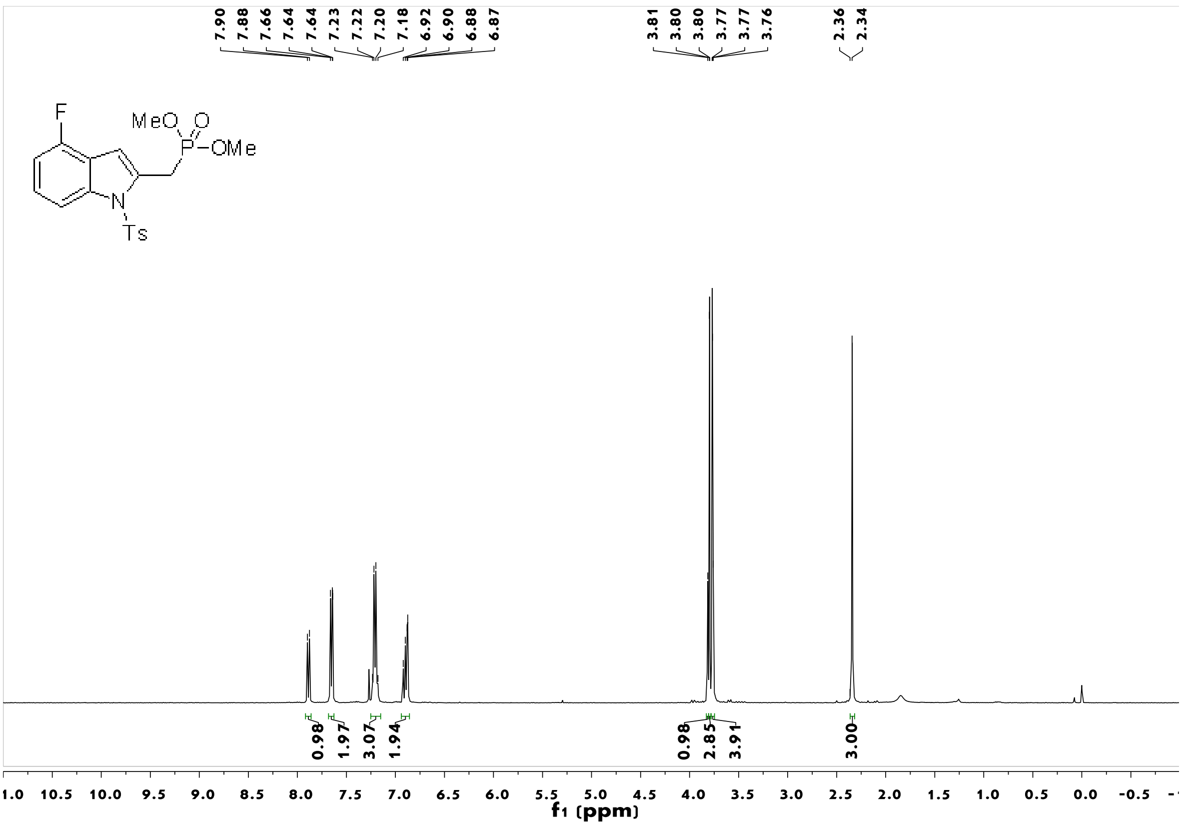
^{13}C NMR Spectrum of **3o**



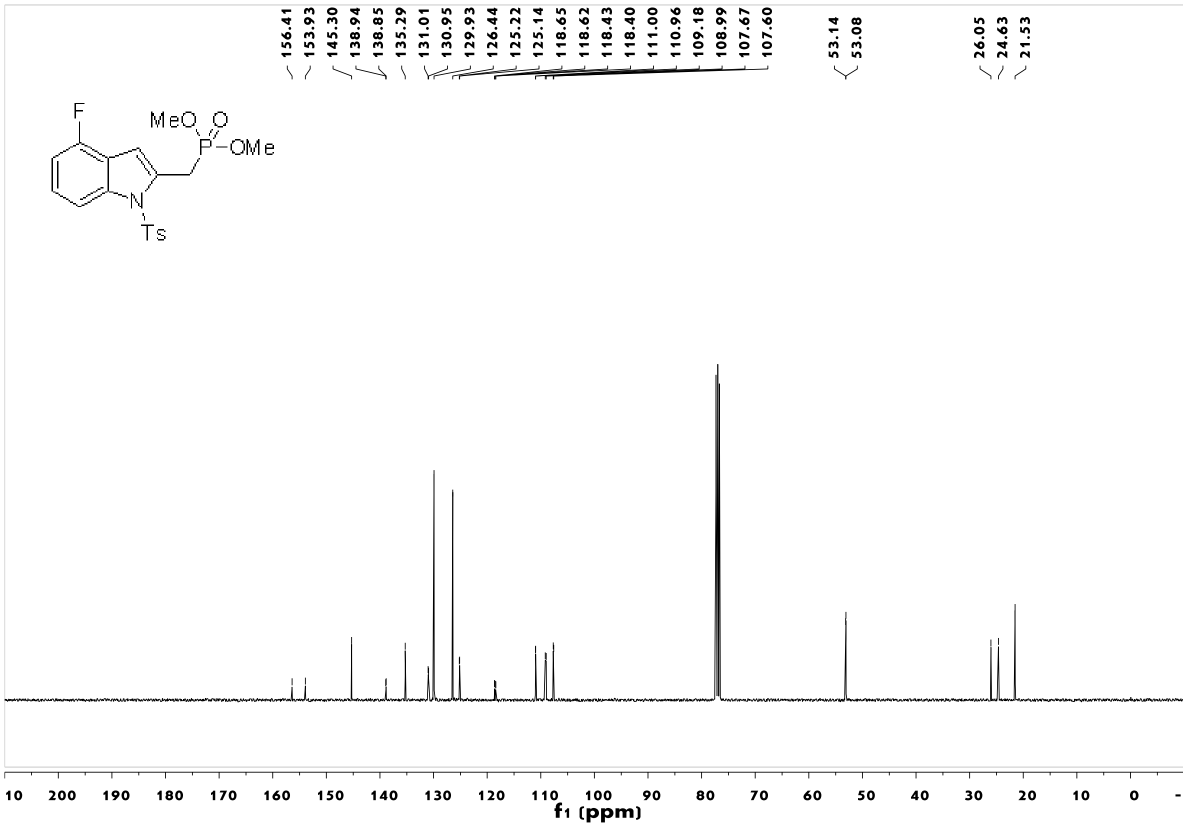
^{31}P NMR Spectrum of **3o**



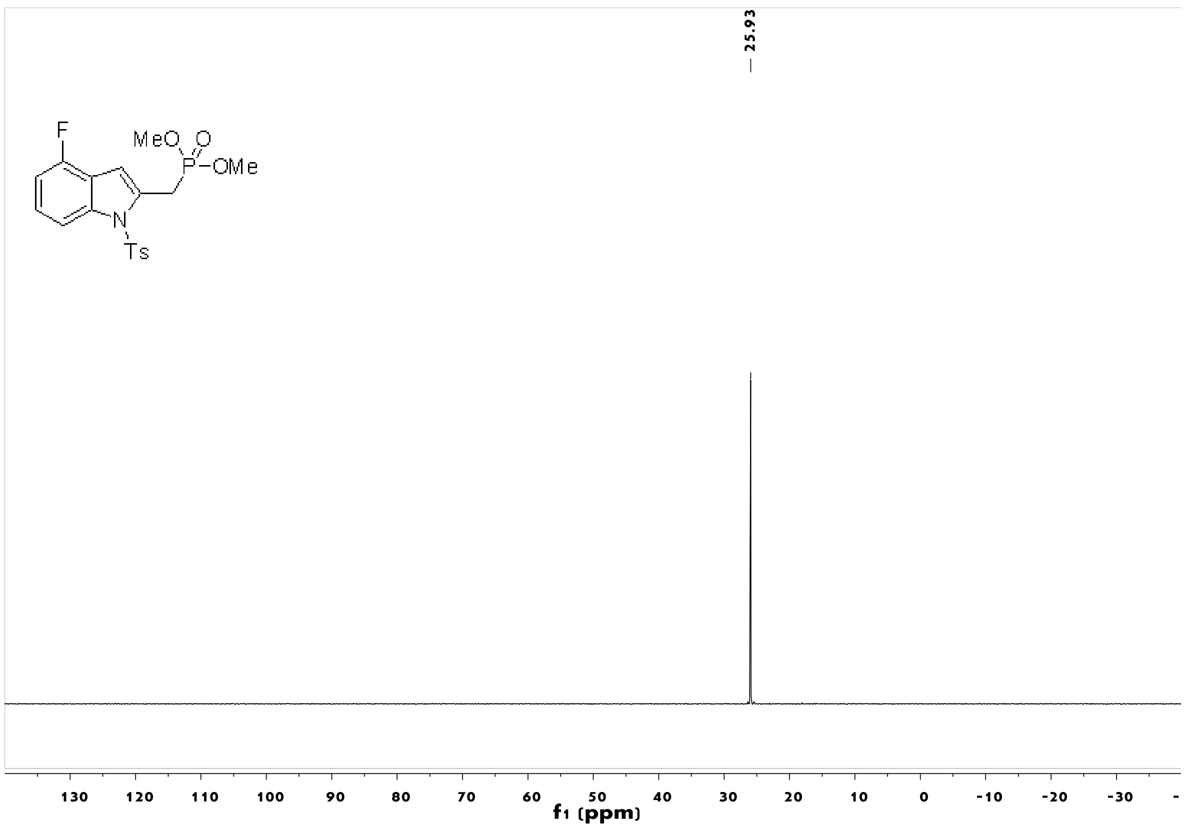
^{1}H NMR Spectrum of **3p**



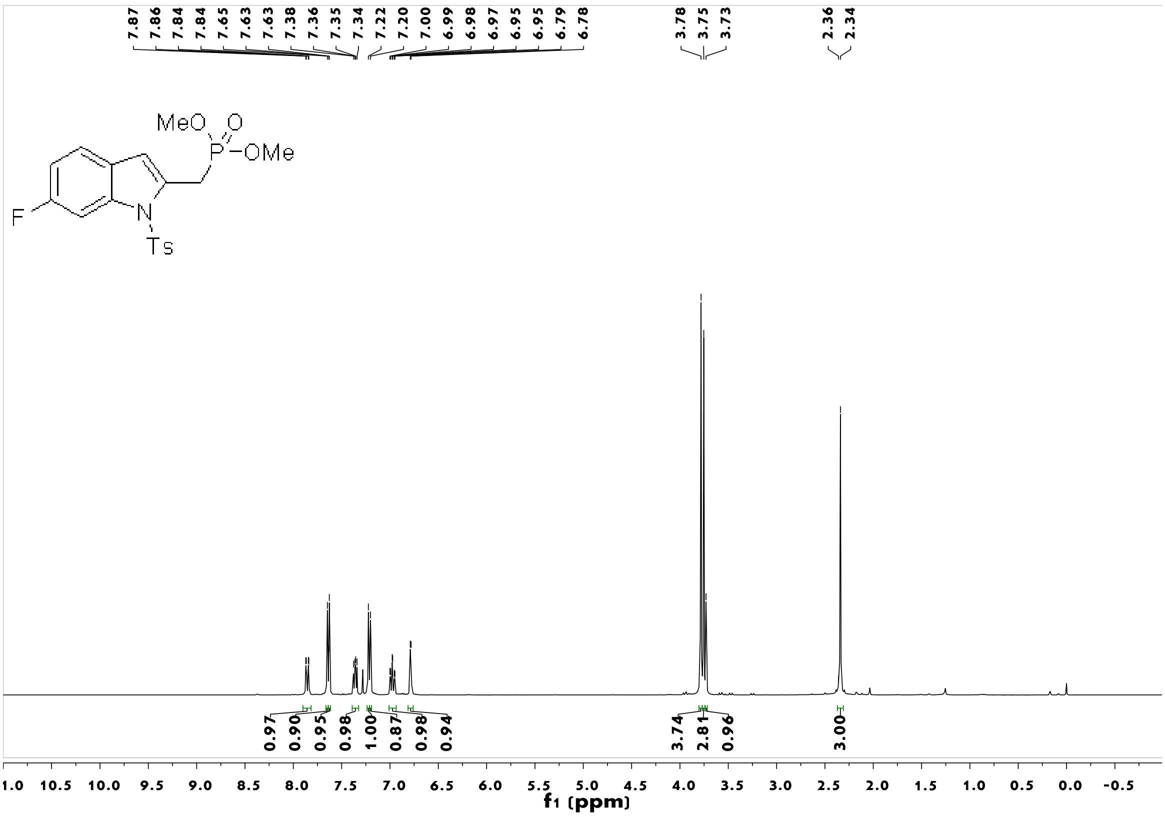
^{13}C NMR Spectrum of **3p**



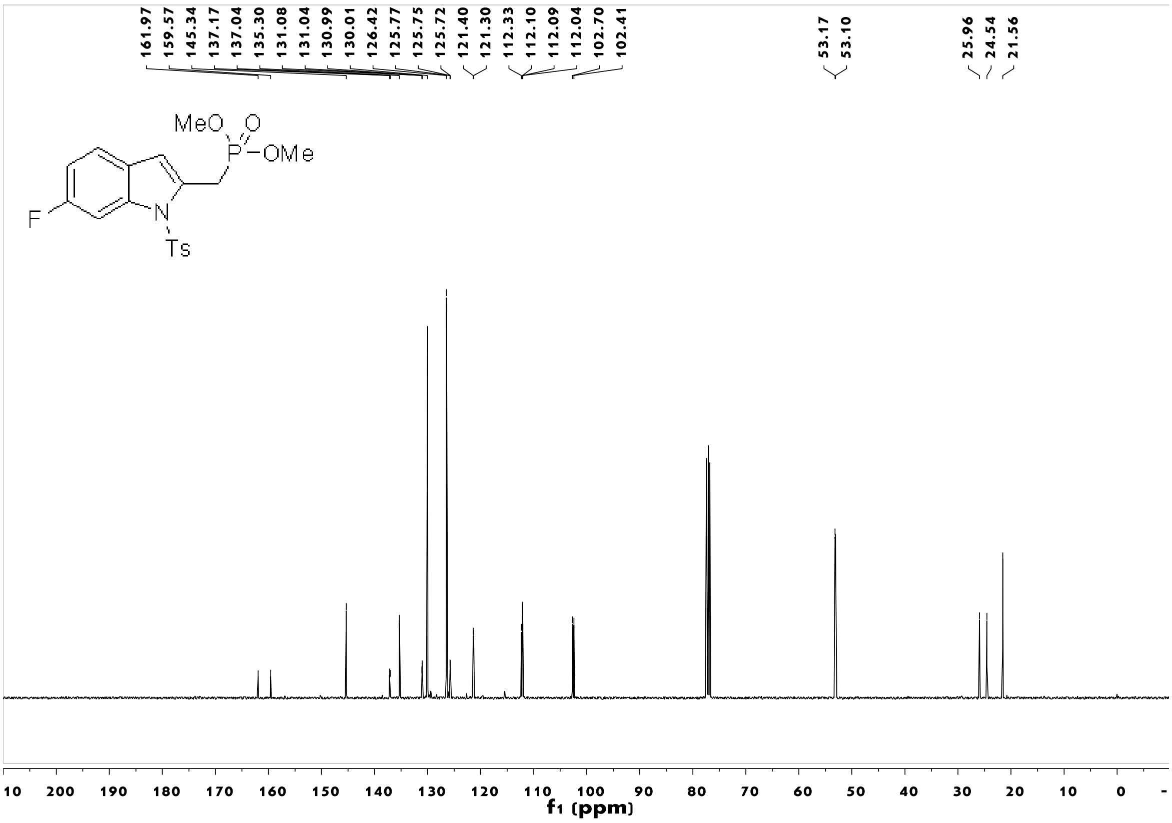
^{1}H NMR Spectrum of **3p**



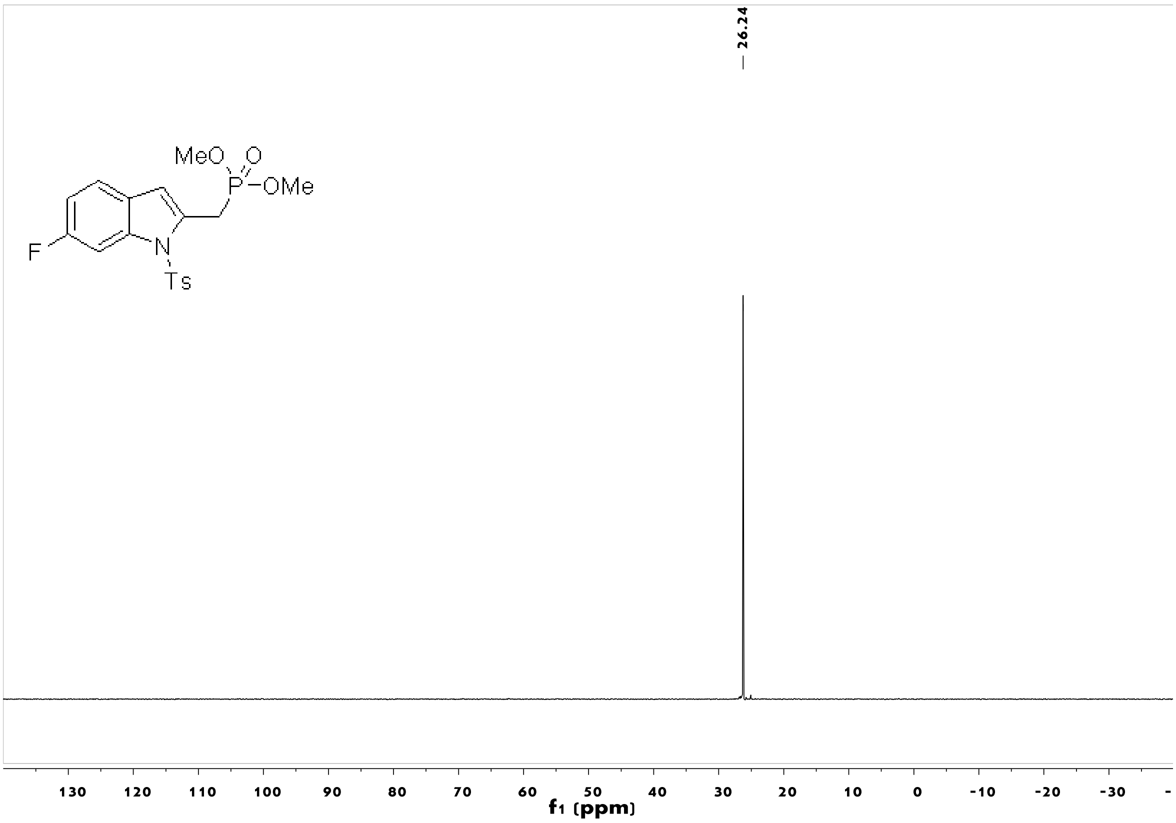
^{1}H NMR Spectrum of **3q**



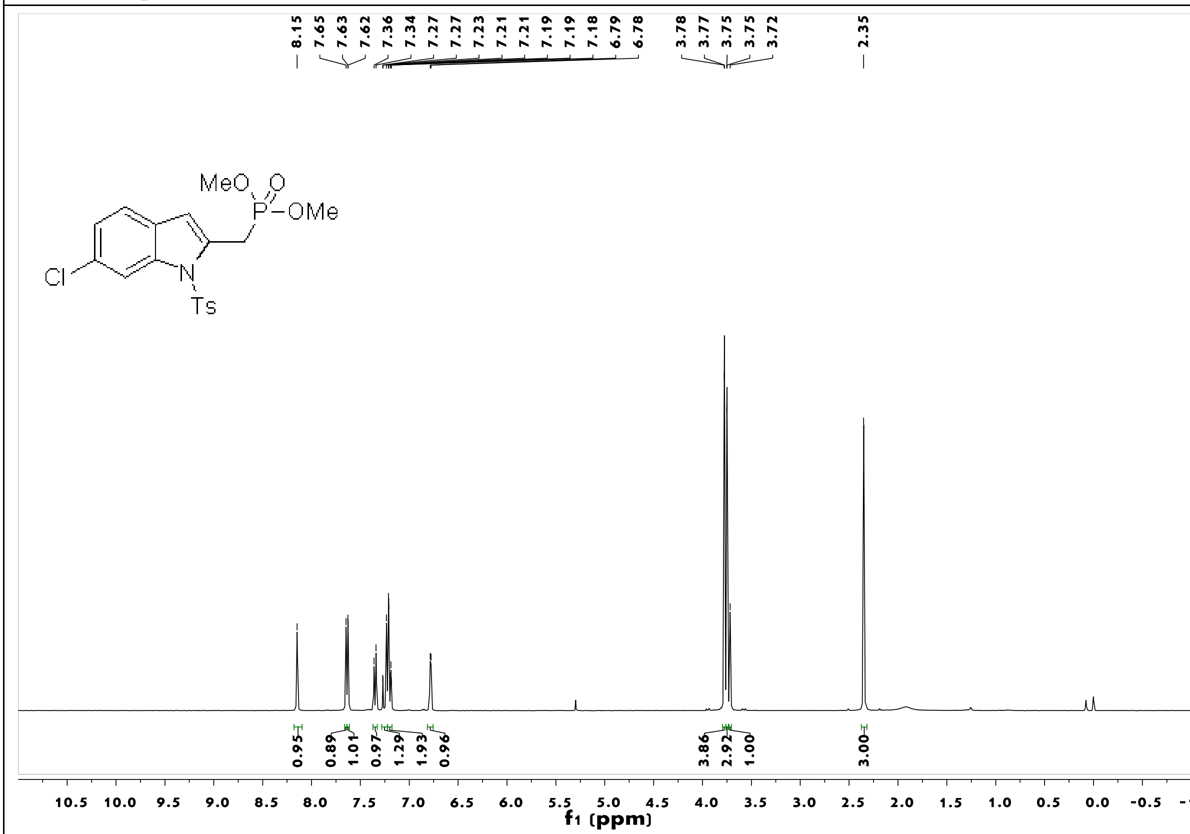
^{13}C NMR Spectrum of **3q**



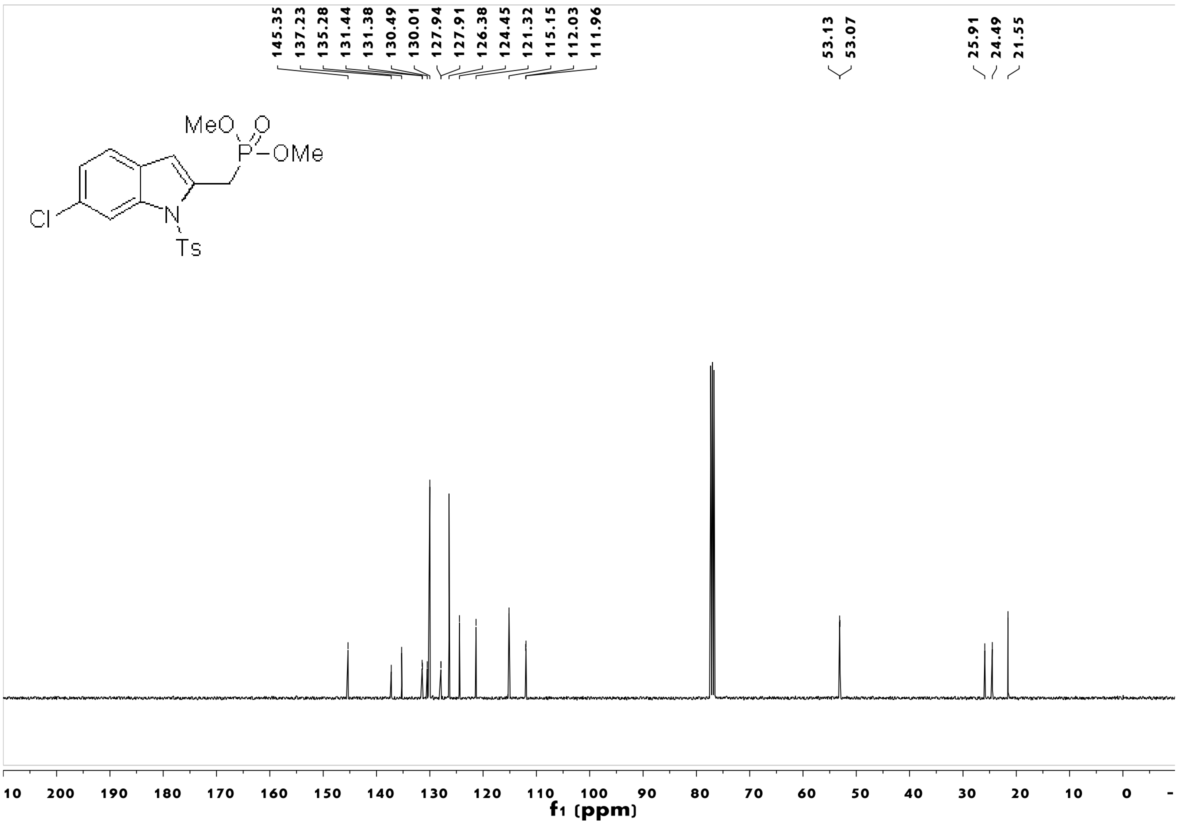
[1]H NMR Spectrum of **3q**



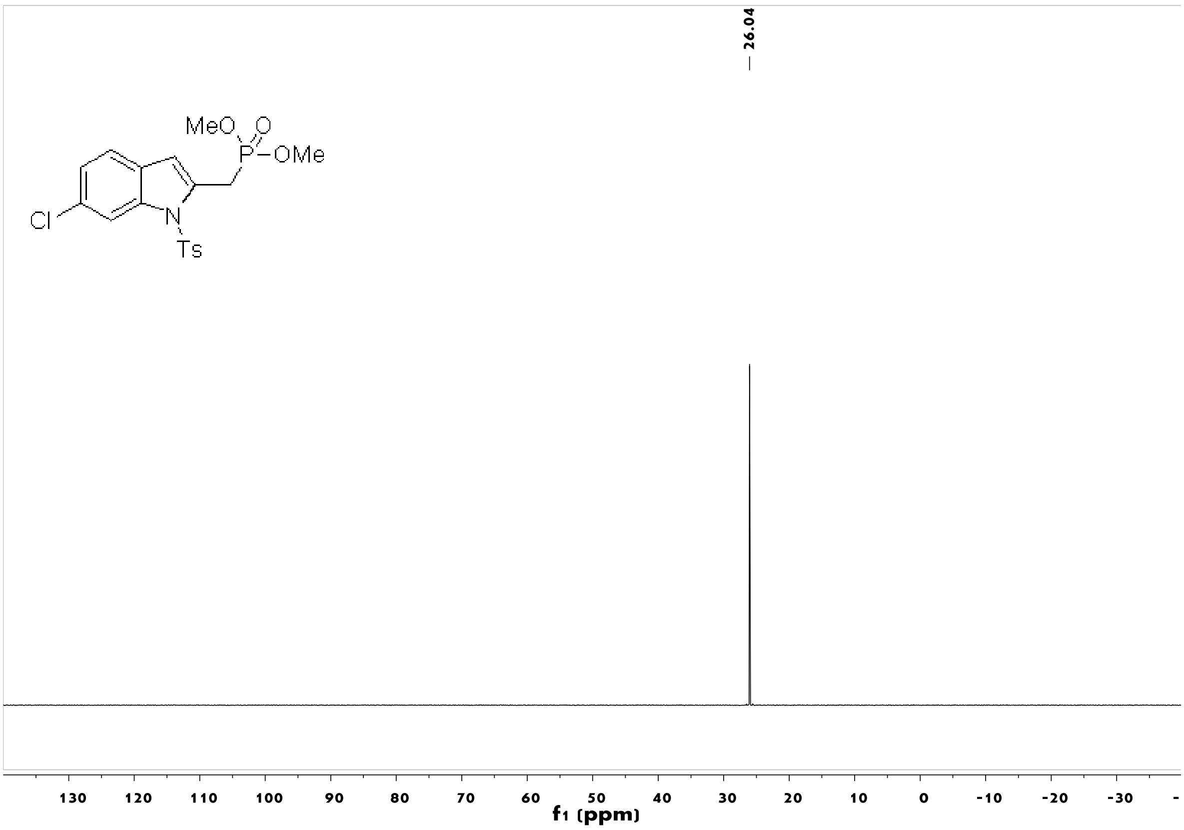
[1]H NMR Spectrum of **3r**



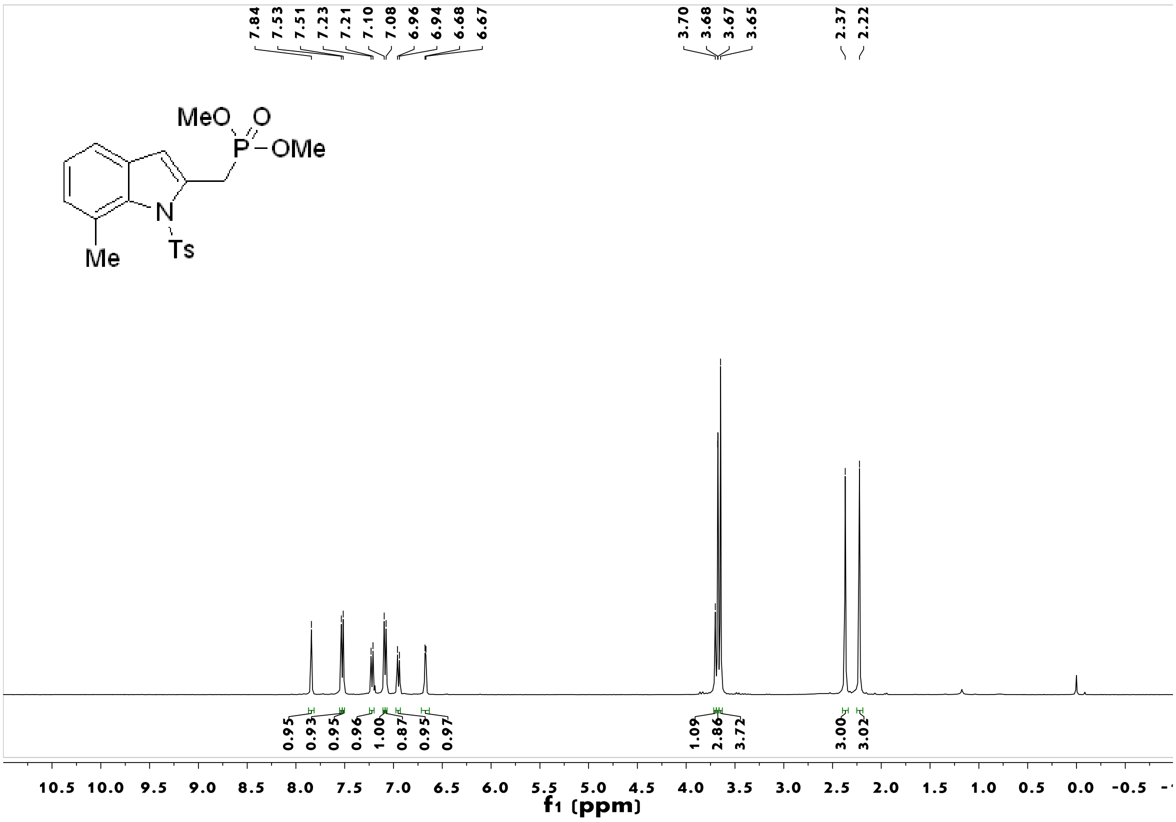
^{13}C NMR Spectrum of **3r**



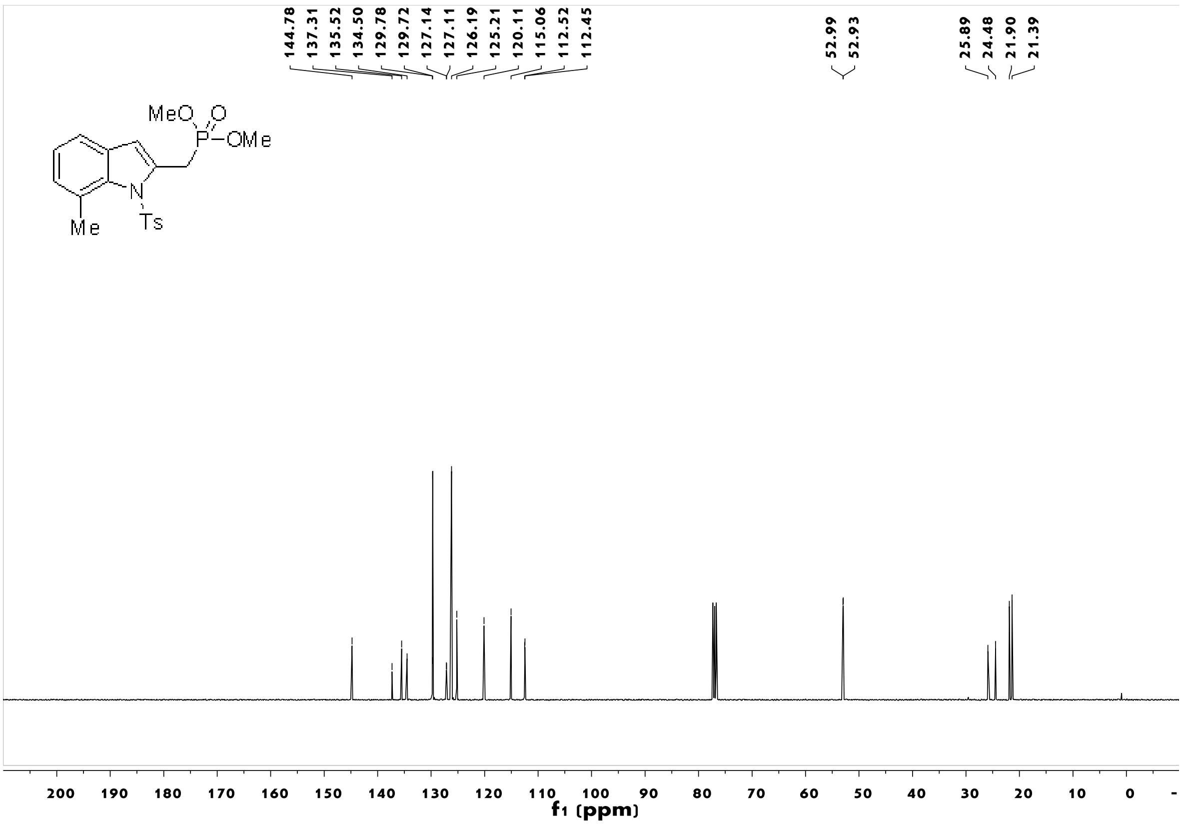
^{1}H NMR Spectrum of **3r**



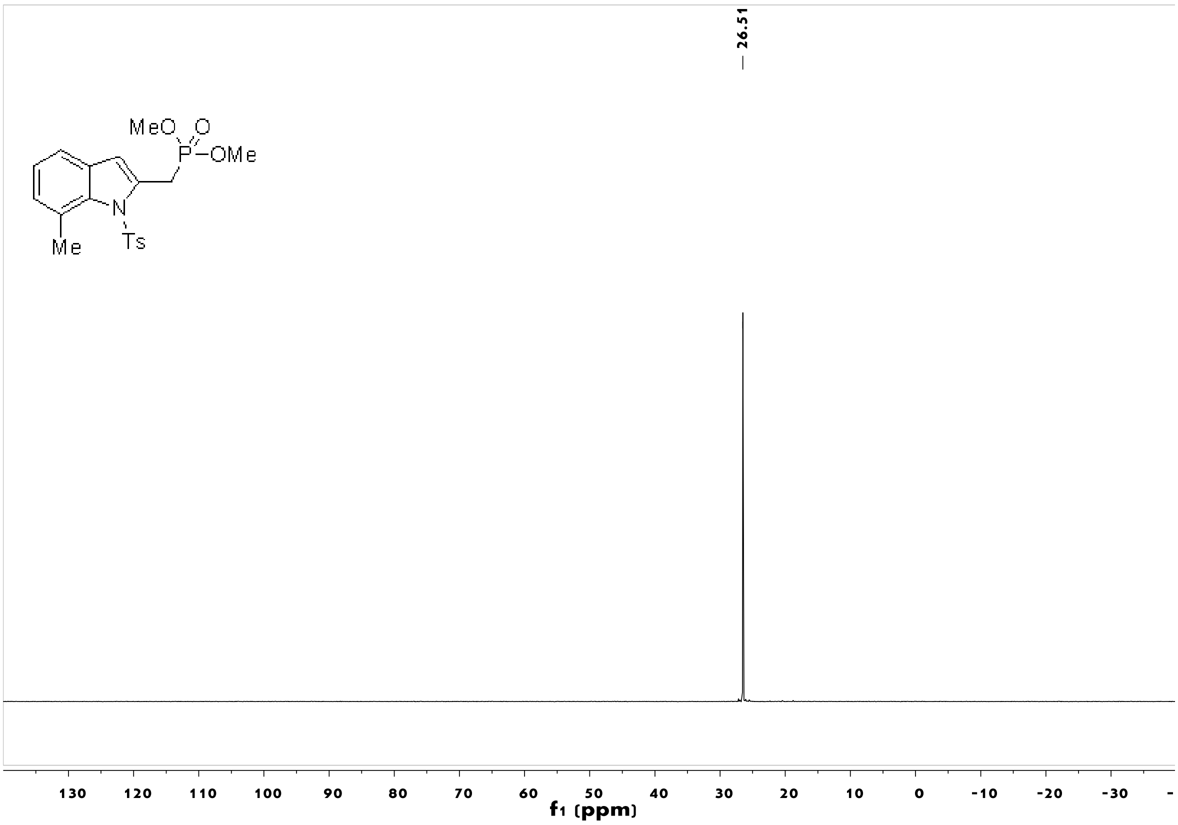
[1]H NMR Spectrum of **3s**



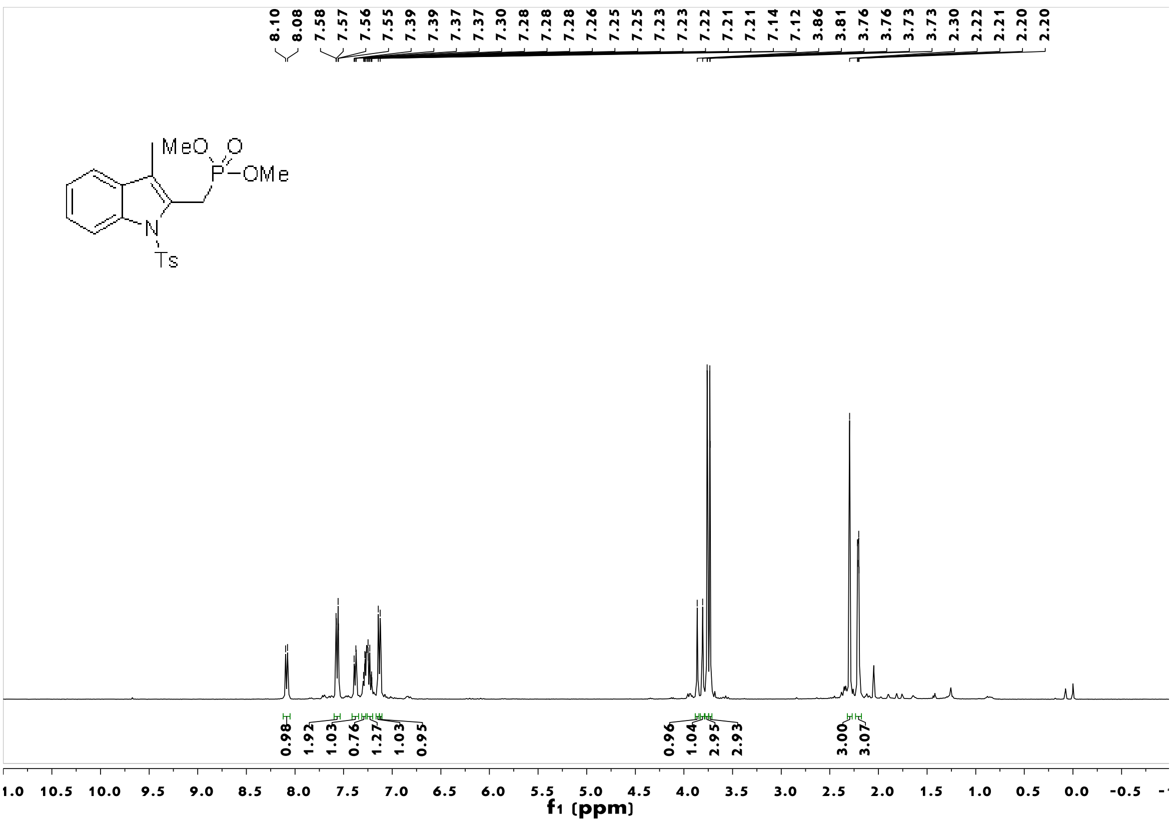
[13]C NMR Spectrum of **3s**



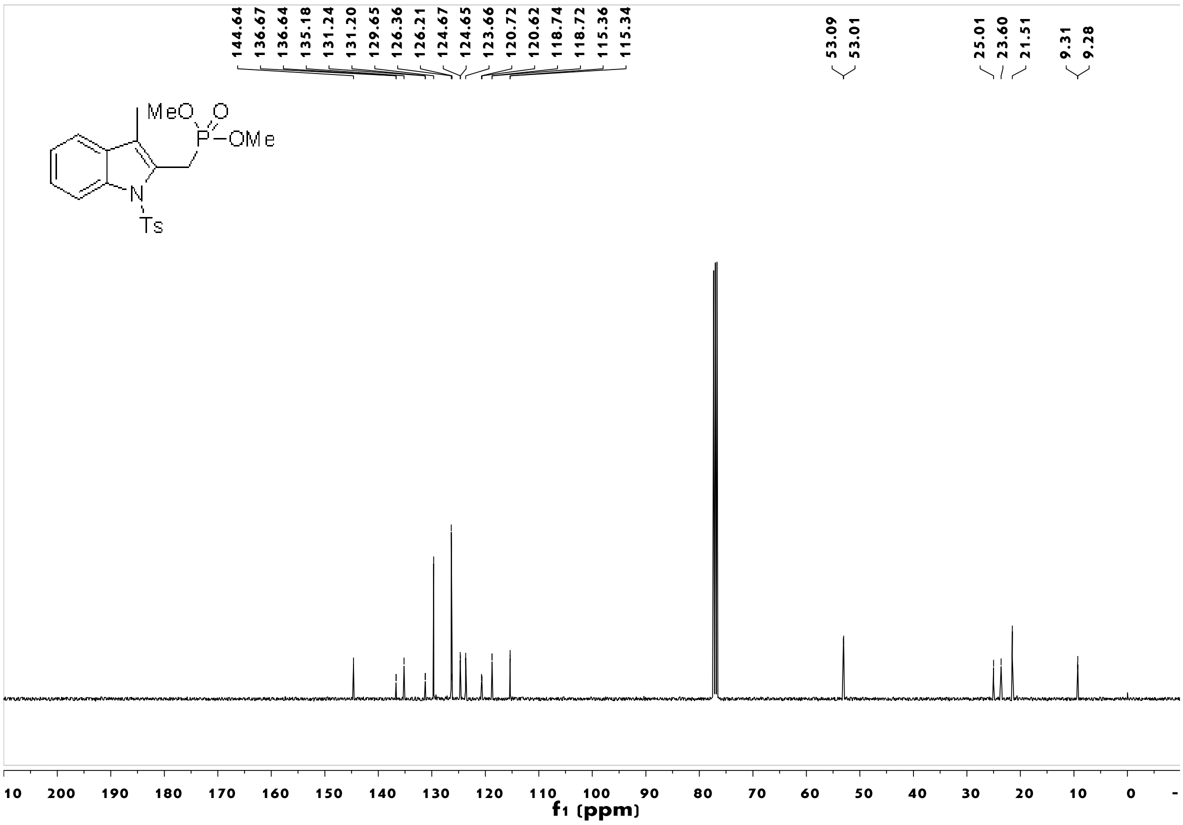
^{1}H NMR Spectrum of **3s**



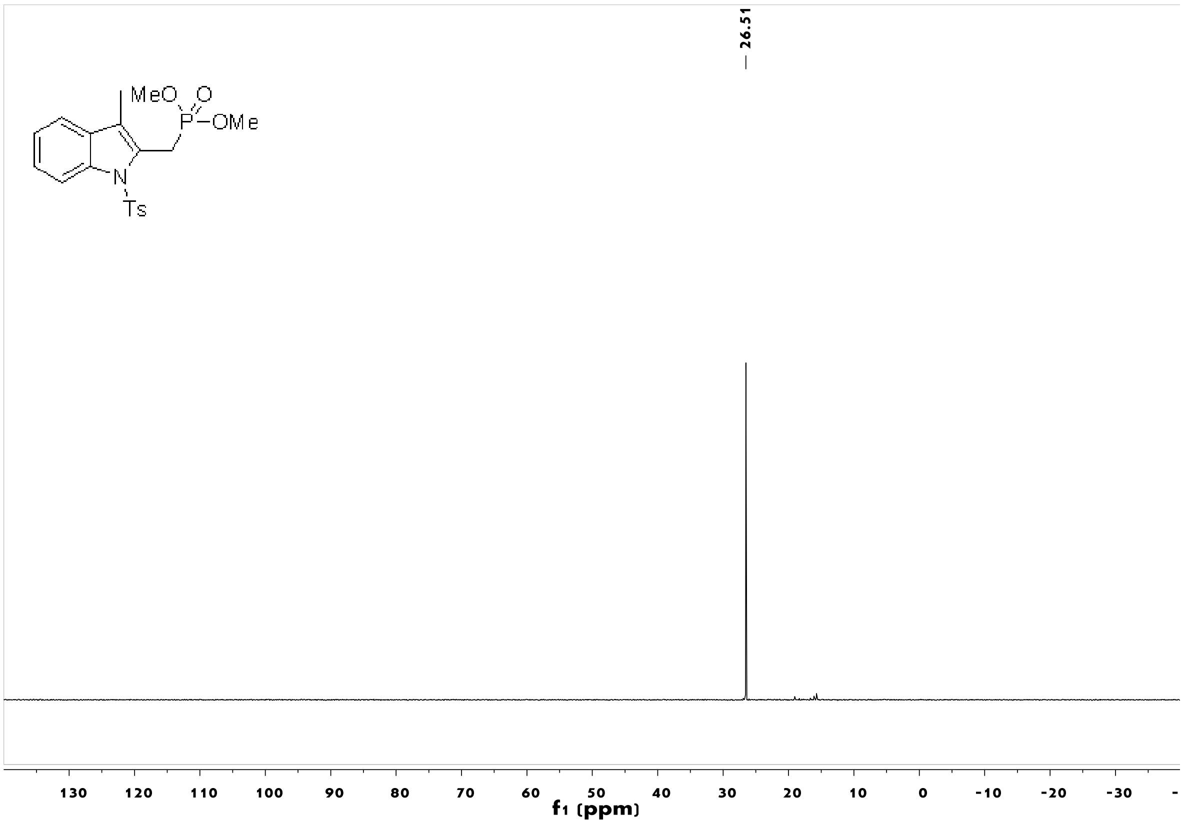
^{1}H NMR Spectrum of **3t**



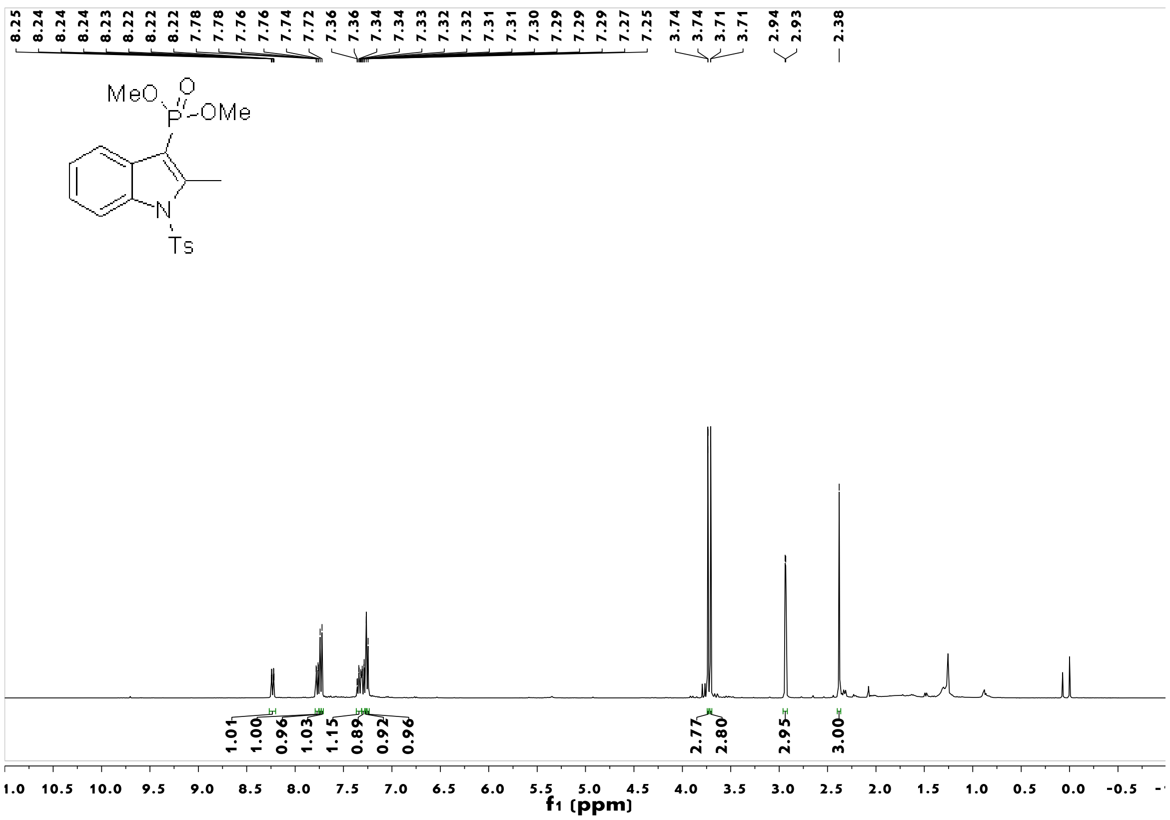
^{13}C NMR Spectrum of **3t**



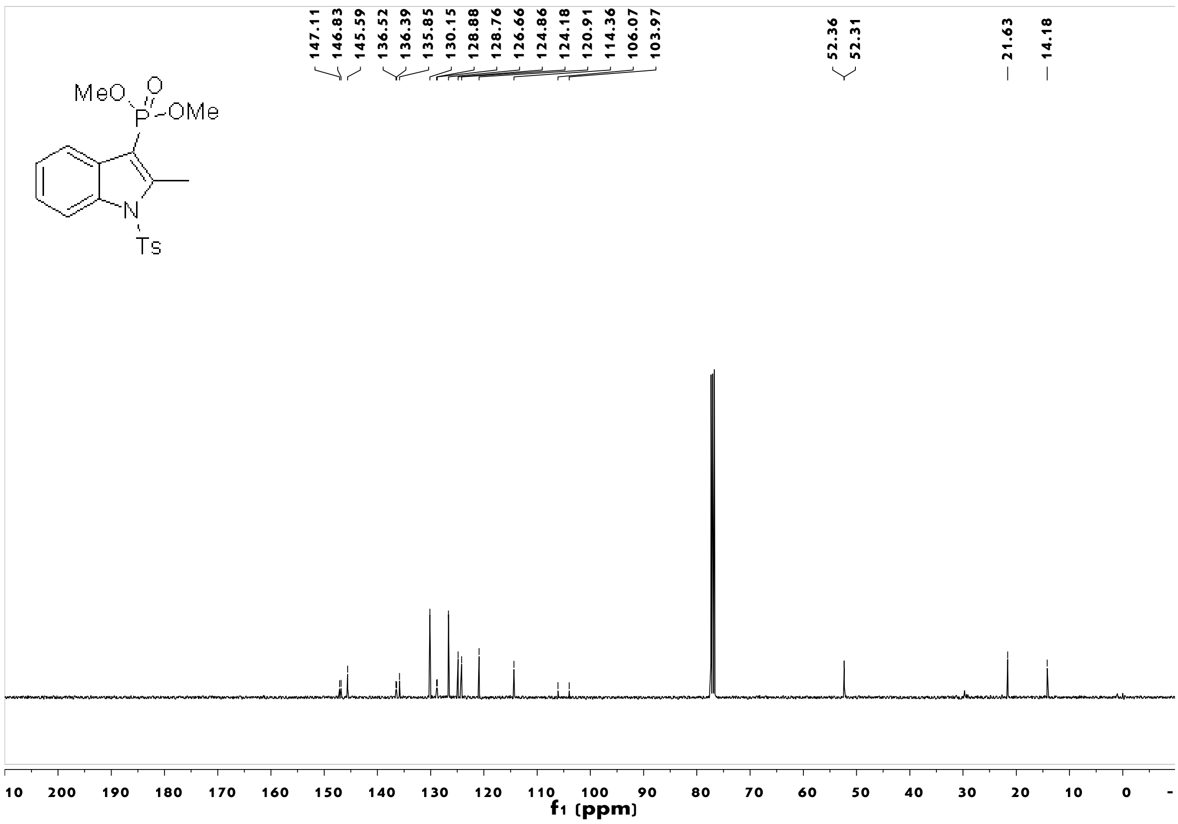
^{31}P NMR Spectrum of **3t**



[1]H NMR Spectrum of **3a’**



[13]C NMR Spectrum of **3a’**



[31]P NMR Spectrum of **3a’**