Supporting Information

Copper-Catalyzed P-H Insertions of *a*-Imino Carbenes for the Preparation of 3-Phosphinoylindoles

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General Remarks and Materials:

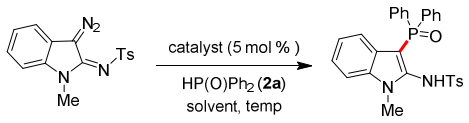
All ^{1}H NMR, and ^{13}C NMR spectra were recorded using a Brucker 600 MHz spectrometer in $CDCl_3$. Tetramethylsilane (TMS) served as an internal standard ($\delta = 0$) for ^{1}H NMR, and $CDCl_3$ was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. ^{31}P NMR spectra and ^{19}F NMR were recorded on the same instrument. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). HRMS (ESI) Mass spectra were recorded on Thermo Fisher Scientific LTQ FT Ultra. The starting materials were purchased from Aldrich, Macklin and Energy Chemicals used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-300 mesh ASTM). Substrates **1** were prepared according to the published procedures[1].

General Procedures

General Procedure for Optimization of Reaction Conditions (Table 1 and Table S1):

A solution of the **1a** (65.2 mg, 0.2 mmol) in 0.4 mL $CHCl_3$ was slowly added to a mixture solution of **2a** (40.4 mg, 0.2 mmol) and catalyst (0.01 mmol) in 0.4 mL $CHCl_3$. The reaction mixture under an argon atmosphere was stirred under the indicated temperature in table 1. Upon completion, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 3:1) to give the product **3a**.

Table S1. Optimization of the Reaction Conditions [a]



1a **3a**

entry	catalyst	solvent	temp (°C)	time (h)	yield (%)[b]
1	$Rh_2(oct)_4$	DCE	35	24	0
2	$Rh_2(OAc)_4$	DCE	35	24	0
3	$[Rh(cod)Cl]_2$	DCE	35	24	0
4	$[Ru(p\text{-cymene})Cl_2]_2$	DCE	35	24	0
5	$(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$	DCE	35	24	0
6	$Ni(cod)_2$	DCE	35	24	0
7	$Cu(OTf)_2$	DCE	35	24	20
8	$Cu(OAC)_2$	DCE	35	24	15
9	$Cu(acac)_2$	DCE	35	24	15
10	Cu_2O	DCE	35	24	23
11	$Cu(CH_3CN)_4PF_6$	DCE	35	24	42
12	$Cu(CH_3CN)_4PF_6$	DCE	35	1	42
13	$Cu(CH_3CN)_4PF_6$	DCE	50	1	56
14	$Cu(CH_3CN)_4PF_6$	DCE	15	1	trace
15	-	DCE	50	1	0

16	$Cu(CH_3CN)_4PF_6$	DCM	50	1	26
17	$Cu(CH_3CN)_4PF_6$	$CHCl_3$	50	1	82
18	$Cu(CH_3CN)_4PF_6$	1, 4-dioxane	50	1	64
19	$Cu(CH_3CN)_4PF_6$	toluene	50	1	52
20	$Cu(CH_3CN)_4PF_6$	THF	50	1	0
21	$Cu(CH_3CN)_4PF_6$	CH_3CN	50	1	0
22	$Cu(CH_3CN)_4PF_6$	DMF	50	1	5
23	$Rh_2(oct)_4$	$CHCl_3$	50	1	0 (0) [d]
24	[Ru(*p*-cymene)Cl_2]$_2$	$CHCl_3$	50	1	0
25	$(\eta^3$-$C_3H_5)_2Pd_2Cl_2$	$CHCl_3$	50	1	0
26	$Ni(cod)_2$	$CHCl_3$	50	1	0
27	$Cu(OTf)_2$	$CHCl_3$	50	1	12 (41) [d]
28	$Cu(OAC)_2$	$CHCl_3$	50	1	14 (37) [d]
29	$Cu(acac)_2$	$CHCl_3$	50	1	6
30	Cu_2O	$CHCl_3$	50	1	trace
31	-	$CHCl_3$	50	1	0
32[c]	$Cu(CH_3CN)_4PF_6$	$CHCl_3$	50	1	trace(10)[d]
33[e]	$Cu(CH_3CN)_4PF_6$	$CHCl_3$	50	1	7(13) [d]
34[f]	$Cu(CH_3CN)_4PF_6$	$CHCl_3$	50	1	18(42) [d]

[a] Reaction conduction: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (0.01 mmol), solvent (0.8 mL). [b] Isolated yield. [c] catalyst (0.001 mol). [d] The reaction was carried out for 24 h. [e] catalyst (0.002 mol). [f] catalyst (0.006 mol).

General procedure for the synthesis of compounds 3a-t (Scheme 2, Scheme 3):

A solution of the **1** (0.2 mmol) in 0.4 mL $CHCl_3$ was slowly added to a mixture solution of **2** (0.2 mmol) and $Cu(CH_3CN)_4PF_6$ (0.01 mmol) in 0.4 mL $CHCl_3$. The reaction mixture under an argon atmosphere was stirred for 1 hour at 50 °C. Upon completion, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 3:1) to give the product **3**.

A typical procedure for the preparation of optically pure H-phosphinates 4: [2]

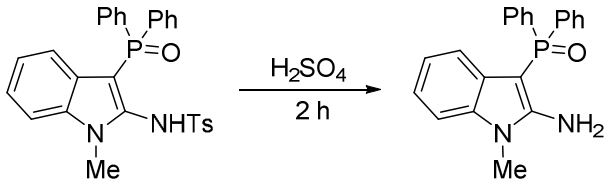
The mixture of (L)-(-)-menthol (100 g, 641 mmol) and pyridine (51.3 mL, 641 mmol) in Et_2O (200 mL) was added dropwise with stirring to a $PhPCl_2$ (87.2 mL, 641 mmol) solution in Et_2O (400 mL) at 0°C and then stirred at room temperature overnight. Water (12 mL, 667 mmol) was added, and the reaction mixture was washed with water and extracted with hexane. The hexane layer was dried over magnesium sulfate, filtered, and concentrated. Recrystallization of the mixture in hexane (twice) at -30 °C gave pure H-Phosphinates **4** a white crystal (66.4 g) in 37% yield (RP/SP>99/1).

General procedure for stereoselective synthesis of chiral 3-methoxyl-arylphosphoindoles 5a-f (Scheme 4):

A solution of the **1** (0.2 mmol) in 0.4 mL $CHCl_3$ was slowly added to a mixture solution of optically pure H-Phosphinate (56.0 mg, 0.2 mmol) and $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol) in 0.4 mL $CHCl_3$. The reaction mixture was stirred for 8 hours at 50 °C. Upon completion, the solvent

was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 6:1) to give the product **5**.

General procedure for the synthesis of 2-free amino indole 6: [3]



3a **6**, 91 % yield

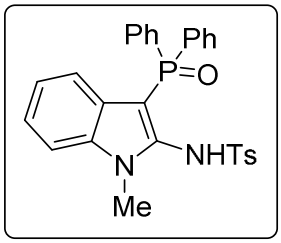
2-free amino indole

To **3a** (50 mg, 0.1 mmol) was added cold 18 M H_2SO_4 (0.5 mL) slowly at 0 °C and stirred at room temperature for 2 hours. The reaction mixture was cooled to 0 °C and quenched by cool water (50 mL) and then saturated aqueous $NaHCO_3$ (10 mL) slowly, extracted with $CHCl_3$ (20 mL × 3), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography (DCM/CH_3OH 3:1) on silica gel to give 2-free amino indole **6** (31.4 mg) in 91% yield.

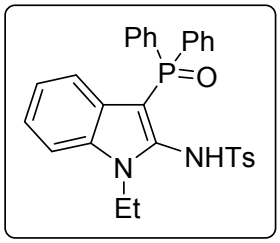
References:

1. (a) Sheng, G.; Huang, K.; Chi, Z.; Ding, H.; Xing, Y.; Lu, P.; Wang, Y. *Org. Lett.* **2014,** *16*, 5096-5099; (b) Xing, Y.; Sheng, G.; Wang, J.; Lu, P.; Wang, Y. *Org. Lett.* **2014,** *16*, 1244-1247.
2. Xu, Q.; Zhao, C. Q.; Han, L. B. *J. Am. Chem. Soc.* **2008,** *130*, 12648-12655.
3. (a) Hwang, H.; Kim, J.; Jeong, J.; Chang, S. *J. Am. Chem. Soc.* **2014,** *136*, 10770-10776; (b) Zhou, A.; Miao, L.; Wang, G.; Yang, S. *Chem. Commun.* **2014**, *50*, 8529-8532.

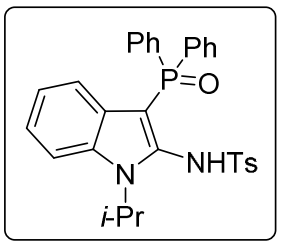
Analysis data of new compounds:



(3a): White solid; 82.0 mg; yield: 82%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.21 (s, 1H), 7.51–7.46 (m, 3H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.41–7.30 (m, 8H), 7.29–7.25 (m, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 2H), 4.03 (s, 3H), 2.08 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.65, 143.15 (d, *J* = 12.5 Hz), 136.75 (d, *J* = 11.2 Hz), 134.23, 133.29 (d, *J* = 109.5 Hz), 131.73 (d, *J* = 2.7 Hz), 131.39 (d, *J* = 11.0 Hz), 129.03, 128.26 (d, *J* = 12.7 Hz), 128.01, 126.97 (d, *J* = 9.9 Hz), 122.56, 121.73, 119.75, 110.61, 90.24 (d, *J* = 125.1 Hz), 32.40, 21.70; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 28.18; **HRMS** (ESI) Calcd. for $C_{28}H_{26}N_2O_3PS$ $(M+H)^+$ 501.1396, Found: 501.1395.

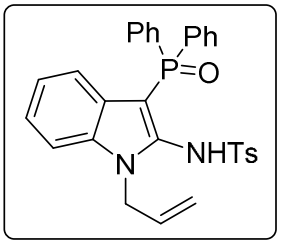


(3b): White solid; 78.1 mg; yield: 76%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.24 (s, 1H), 7.55–7.47 (m, 5H), 7.40–7.30 (m, 8H), 7.24 (t, *J* = 7.4 Hz, 1H), 6.99–6.94 (m, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 2H), 4.71–4.63 (m, 2H), 2.07 (s, 3H), 1.56 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.61 , 142.63 (d, *J* = 12.3 Hz), 135.74 (d, *J* = 11.2 Hz), 134.12 , 133.31 (d, *J* = 109.5 Hz), 131.72 (d, *J* = 2.7 Hz), 131.42 (d, *J* = 11.0 Hz), 128.99, 128.26 (d, *J* = 12.6 Hz), 128.11, 127.49 (d, *J* = 9.9 Hz), 122.45, 121.56, 119.96, 111.20, 90.69 (d, *J* = 124.5 Hz), 40.18, 21.70, 14.40; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 28.33; **HRMS** (ESI) Calcd. for $C_{29}H_{28}N_2O_3PS$ $(M+H)^+$ 515.1553, Found: 515.1553.

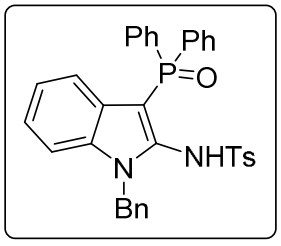


(3c): White solid; 74.9 mg; yield: 71%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.27 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.55–7.45 (m, 4H), 7.40 – 7.30 (m, 8H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 5.61–5.51 (m, 1H), 2.07 (s, 3H), 1.76 (d, *J* = 7.0 Hz, 6H); **^{13}C NMR**

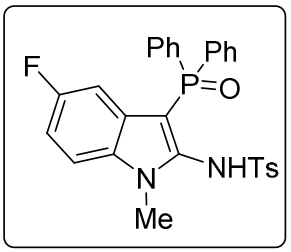
(151 MHz, Chloroform-*d*) δ 143.58, 142.44 (d, *J* = 12.3 Hz), 134.34 (d, *J* = 11.0 Hz), 134.05, 133.33 (d, *J* = 109.5 Hz), 131.67 (d, *J* = 2.6 Hz), 131.43 (d, *J* = 10.9 Hz), 128.97, 128.28, 128.20, 128.11, 121.89, 121.14, 120.26, 113.48, 90.35 (d, *J* = 124.8 Hz), 49.24, 21.71, 21.21; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 28.37; **HRMS** (ESI) Calcd. for $C_{30}H_{30}N_2O_3PS$ $(M+H)^+$ 529.1709, Found: 529.1711.



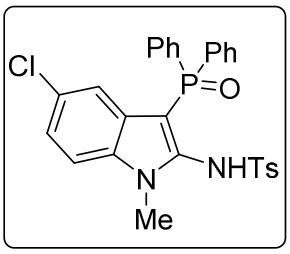
(3d): Yellow solid; 83.1 mg; yield: 79%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.26 (s, 1H), 7.56–7.46 (m, 5H), 7.41–7.31 (m, 8H), 7.21 (t, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 2H), 6.17–6.08 (m, 1H), 5.31 (d, *J* = 11.1 Hz, 1H), 5.25–5.19 (m, 3H), 2.07 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.66, 142.85 (d, *J* = 12.4 Hz), 136.43 (d, *J* = 11.1 Hz), 134.04, 133.53, 133.22 (d, *J* = 109.6 Hz), 131.76 (d, *J* = 2.7 Hz), 131.40 (d, *J* = 10.9 Hz), 129.00, 128.29 (d, *J* = 12.7 Hz), 128.14, 127.30 (d, *J* = 9.8 Hz), 122.52, 121.74, 119.84, 117.45, 111.91, 91.00 (d, *J* = 123.9 Hz), 48.15, 21.70; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 28.27; **HRMS** (ESI) Calcd. for $C_{30}H_{28}N_2O_3PS$ $(M+H)^+$ 527.1553, Found:527.1551.



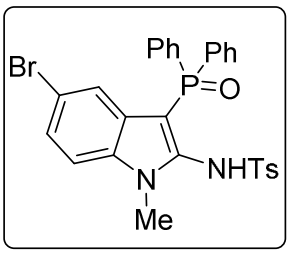
(3e): Yellow solid; 66.8 mg; yield: 58%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.31 (s, 1H), 7.58–7.49 (m, 4H), 7.45–7.34 (m, 8H), 7.34–7.30 (m, 2H), 7.29–7.24 (m, 2H), 7.17–7.09 (m, 3H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 2H), 5.88 (s, 2H), 2.09 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.72, 143.31 (d, *J* = 12.4 Hz), 136.88 , 136.14 (d, *J* = 11.0 Hz), 134.12, 133.25 (d, *J* = 109.6 Hz), 131.81 (d, *J* = 2.6 Hz), 131.42 (d, *J* = 10.9 Hz), 129.04, 128.62, 128.34 (d, *J* = 12.7 Hz), 128.21, 127.47, 127.41 , 126.74, 122.69, 121.82, 119.93, 112.07, 91.56 (d, *J* = 123.4 Hz), 48.82, 21.73; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 28.31; **HRMS** (ESI) Calcd. for $C_{34}H_{30}N_2O_3PS$ $(M+H)^+$ 577.1709, Found: 577.1708.



(3f): Yellow solid; 76.8 mg; yield: 74%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.19 (s, 1H), 7.53–7.48 (m, 4H), 7.37–7.32 (m, 9H), 7.02–6.95 (m, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.38 (dd, *J* = 9.5, 2.5 Hz, 1H), 4.01 (s, 3H), 2.09 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 158.70 (d, *J* = 237.6 Hz), 144.12 (d, *J* = 12.4 Hz), 143.77, 134.25, 133.19, 132.91 (d, *J* = 109.5 Hz), 131.91 (d, *J* = 2.7 Hz), 131.33 (d, *J* = 10.9 Hz), 129.07, 128.38 (d, *J* = 12.7 Hz), 127.95, 127.42 (t, *J* = 10.0 Hz), 111.49 (d, *J* = 9.7 Hz), 110.87 (d, *J* = 26.0 Hz), 105.07 (d, *J* = 25.0 Hz), 90.51 (d, *J* = 129.3 Hz), 32.65 , 21.70; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 27.89; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -120.59; **HRMS** (ESI) Calcd. for $C_{28}H_{25}FN_2O_3PS$ $(M+H)^+$ 519.1302, Found:519.1302.

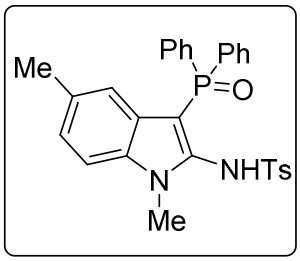


(3g): Yellow solid; 69.4 mg; yield: 65%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.23 (s, 1H), 7.56–7.47 (m, 4H), 7.39–7.31 (m, 9H), 7.20 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 1.9 Hz, 1H), 4.01 (s, 3H), 2.09 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.10 (d, *J* = 12.3 Hz), 143.80 , 135.16 (d, *J* = 10.9 Hz), 134.21, 132.86 (d, *J* = 109.8 Hz), 131.95 (d, *J* = 2.7 Hz), 131.33 (d, *J* = 11.0 Hz), 129.09, 128.41 (d, *J* = 12.7 Hz), 127.95, 127.91, 127.51, 122.98, 119.02, 111.67, 90.21 (d, *J* = 124.2 Hz), 32.63, 21.70; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 27.80; **HRMS** (ESI) Calcd. for $C_{28}H_{25}ClN_2O_3PS$ $(M+H)^+$ 535.1007, Found:535.1005.

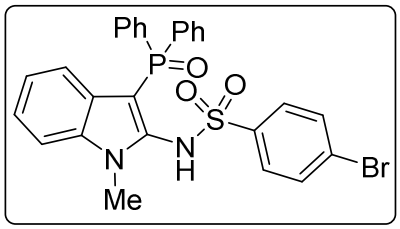


(3h): Yellow solid; 68.2 mg; yield: 59%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.25 (s, 1H), 7.56-7.47 (m, 4H), 7.40-7.29 (m, 10H), 6.83 (d, *J* = 1.8 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 4.00 (s, 3H), 2.09 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.99 (d, *J* = 12.3 Hz), 143.80, 135.46 (d, *J* = 10.9 Hz), 134.24, 132.86 (d, *J* = 109.9 Hz), 131.95 (d, *J* = 2.7 Hz), 131.33 (d, *J* = 11.0 Hz), 129.09, 128.53 (d, *J* = 9.5 Hz), 128.41 (d, *J* = 12.7 Hz), 127.94, 125.57, 122.04, 115.09, 112.07, 90.16 (d, *J* = 124.4 Hz), 32.60, 21.71;

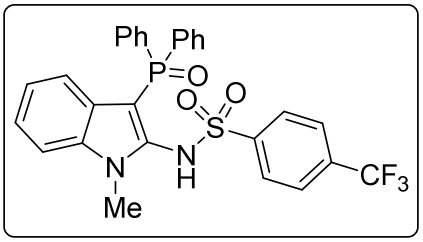
^{31}P NMR (243 MHz, $CDCl_3$) δ 27.79; **HRMS** (ESI) Calcd. for $C_{28}H_{25}BrN_2O_3PS$ $(M+H)^+$ 579.0501, Found:579.0501.



(3i): Yellow solid; 54.5 mg; yield: 53%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.19 (s, 1H), 7.54–7.45 (m, 4H), 7.41–7.29 (m, 9H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 2H), 6.54 – 6.51 (m, 1H), 4.00 (s, 3H), 2.22 (s, 3H), 2.08 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.58 , 142.99 (d, *J* = 12.7 Hz), 135.06 (d, *J* = 11.4 Hz), 134.26 , 133.36 (d, *J* = 109.4 Hz), 131.67 (d, *J* = 2.7 Hz), 131.41 (d, *J* = 10.9 Hz), 131.17, 129.01, 128.23 (d, *J* = 12.6 Hz), 128.00, 127.19 (d, *J* = 9.8 Hz), 124.07, 119.50, 110.25, 89.58 (d, *J* = 125.5 Hz), 32.40, 21.69, 21.53; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 28.39; **HRMS** (ESI) Calcd. for $C_{29}H_{28}N_2O_3PS$ $(M+H)^+$ 515.1553, Found:515.1552.

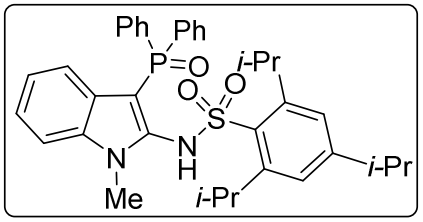


(3j): Yellow solid; 73.3 mg; yield: 65%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.31 (s, 1H), 7.55 (m, 2H), 7.49-7.43 (m, 3H), 7.40-7.35 (m, 8H), 7.30-7.27 (m, 1H), 7.06-7.03 (m, 2H), 7.02-6.99 (m, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 4.02 (s, 3H).; **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 142.44 (d, *J* = 12.5 Hz), 136.72 (d, *J* = 11.1 Hz), 136.21, 132.97 (d, *J* = 109.7 Hz), 132.22 (d, *J* = 2.7 Hz), 131.64, 131.21 (d, *J* = 11.0 Hz), 129.55, 128.55, 128.46, 126.88 (d, *J* = 9.8 Hz), 122.81, 121.93, 119.83, 110.68, 90.71 (d, *J* = 124.5 Hz), 32.36; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 28.37; **HRMS** (ESI) Calcd. for $C_{27}H_{23}BrN_2O_3PS$ $(M+H)^+$ 565.0345, Found:565.0344.

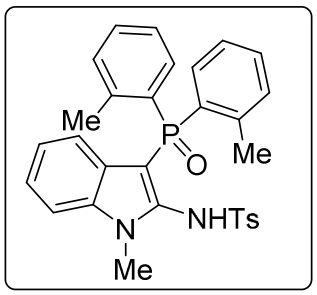


(3k): Yellow solid; 77.5 mg; yield: 70%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.44 (s, 1H), 7.80–7.78 (m, 2H), 7.52–7.48 (m, 2H), 7.47–7.44 (m, 1H), 7.39–7.32 (m, 8H), 7.31–7.27 (m, 1H), 7.22 (d, *J* = 8.3

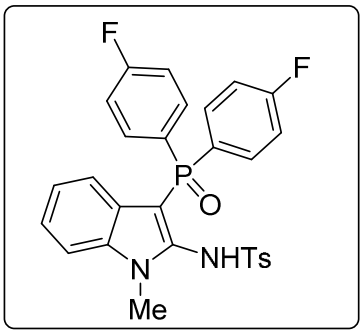
Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 4.04 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 142.16 (d, *J* = 12.2 Hz), 140.95, 136.73 (d, *J* = 11.1 Hz), 134.51, 134.29, 133.11 (d, *J* = 109.8 Hz), 132.24 (d, *J* = 2.7 Hz), 131.18 (d, *J* = 11.0 Hz), 128.75, 128.44 (d, *J* = 12.7 Hz), 126.80 (d, *J* = 9.7 Hz), 125.38 (d, *J* = 3.7 Hz), 122.91, 122.00, 119.87, 110.71, 90.73 (d, *J* = 124.1 Hz), 32.40 ; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 28.53; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.87; **HRMS** (ESI) Calcd. for $C_{28}H_{23}F_3N_2O_3PS$ $(M+H)^+$ 555.1114, Found:555.1113.



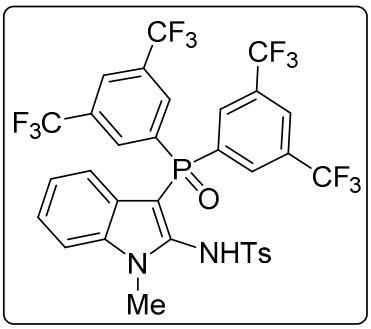
(3l): White solid; 107.7 mg; yield: 88%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.45 (s, 1H), 7.55–7.46 (m, 6H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.38–7.33 (m, 4H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.07 (s, 2H), 7.02–6.98 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 3.96 (s, 3H), 3.94–3.87 (m, 2H), 2.90–2.85 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.11 (d, *J* = 6.7 Hz, 12H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 153.04, 151.11, 143.58 (d, *J* = 12.6 Hz), 136.62 (d, *J* = 11.3 Hz), 133.62, 133.04 (d, *J* = 42.4 Hz), 131.83 (d, *J* = 2.7 Hz), 131.66 (d, *J* = 11.0 Hz), 128.28 (d, *J* = 12.6 Hz), 127.06 (d, *J* = 10.0 Hz), 123.85, 122.29, 121.59, 119.57, 110.29, 90.31 (d, *J* = 125.9 Hz), 33.96, 32.23, 30.51, 24.81, 23.48; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 28.55; **HRMS** (ESI) Calcd. for $C_{36}H_{42}N_2O_3PS$ $(M+H)^+$ 613.2648, Found:613.2646.



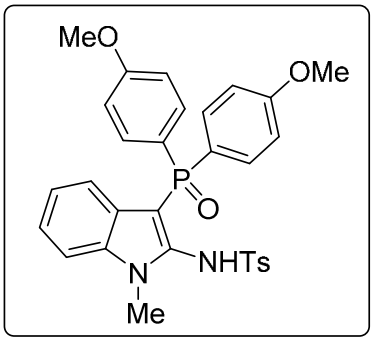
(3m): White solid; 74.9 mg; yield: 71%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.41 (s, 1H), 7.55-7.49 (m, 2H), 7.45-7.35 (m, 3H), 7.26-7.14 (m, 3H), 7.07-7.01 (m, 2H), 6.88 (m, 3H), 6.66 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 8.0 Hz, 1H), 4.04 (s, 3H), 2.36 (s, 6H), 2.05 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.39, 142.89 (d, *J* = 12.9 Hz), 136.50 (d, *J* = 10.9 Hz), 134.53, 132.20, 131.73, 131.54, 128.80, 127.84, 126.84 (d, *J* = 9.4 Hz), 125.39 (d, *J* = 13.7 Hz), 122.48, 121.62, 119.44, 110.34, 90.60 (d, *J* = 123.3 Hz), 32.04, 21.70, 21.14; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 33.51; **HRMS** (ESI) Calcd. for $C_{30}H_{30}N_2O_3PS$ $(M+H)^+$ 529.1709, Found:529.1707.



(3n): White solid; 61.1 mg; yield: 57%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.04 (s, 1H), 7.51–7.44 (m, 3H), 7.40–7.33 (m, 4H), 7.31–7.26 (m, 1H), 7.07–6.98 (m, 5H), 6.78 (d, *J* = 8.1 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.03 (s, 3H), 2.13 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 164.92 (dd, *J* = 253.8, 3.1 Hz), 143.89, 143.15 (d, *J* = 12.8 Hz), 136.76 (d, *J* = 11.3 Hz), 134.31, 133.89 (dd, *J* = 12.6, 8.8 Hz), 129.24 (d, *J* = 107.0 Hz), 128.98 , 128.05 , 126.71 (d, *J* = 10.0 Hz), 126.37, 122.42 (d, *J* = 118.5 Hz), 119.34, 115.76 (dd, *J* = 21.4, 13.9 Hz), 110.85, 89.92 (d, *J* = 127.5 Hz), 32.44, 21.50; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 26.34; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -106.27; **HRMS** (ESI) Calcd. for $C_{28}H_{24}F_2N_2O_3PS$ $(M+H)^+$ 537.1208, Found:537.1207.

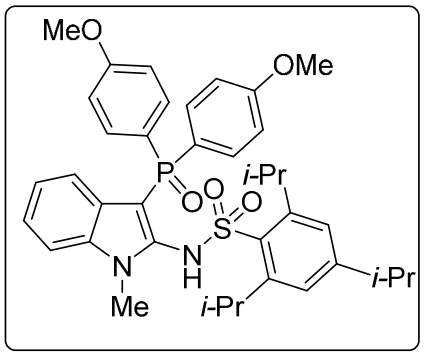


(3o): White solid; 132.8 mg; yield: 86%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 9.48 (s, 1H), 8.06 (s, 2H), 7.91–7.80 (m, 4H), 7.59–7.47 (m, 3H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.09 (s, 3H), 1.98 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.03 (d, *J* = 13.8 Hz), 143.80 , 136.90 (d, *J* = 12.2 Hz), 136.03 , 135.31 , 134.15 , 132.63 (d, *J* = 13.0 Hz), 132.40 (d, *J* = 12.8 Hz), 132.17 (d, *J* = 12.8 Hz), 131.05 (d, *J* = 11.8 Hz), 128.98, 128.21, 126.15 , 125.76 (d, *J* = 10.4 Hz), 123.79, 123.40, 123.12, 121.59, 118.15, 111.66, 86.41 (d, *J* = 132.6 Hz), 32.66, 21.13; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 23.60; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -63.15; **HRMS** (ESI) Calcd. for $C_{32}H_{22}F_{12}N_2O_3PS$ $(M+H)^+$ 773.0892, Found:773.0891.

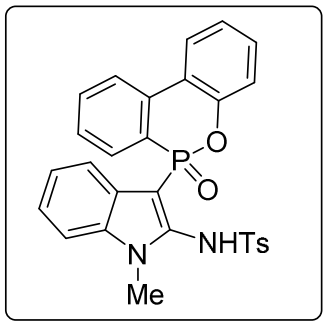


(3p): Yellow solid; 98.6 mg; yield: 88%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.38 (s, 1H), 7.53–7.50 (m, 2H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.31–7.23 (m, 5H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.84–6.81 (m, 4H), 6.79–6.76 (m, 3H), 4.01 (s, 3H),

3.83 (s, 6H), 2.10 (s, 3H) ; **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 162.18 , 143.60, 142.93 (d, *J* = 12.6 Hz), 136.72 (d, *J* = 11.1 Hz), 134.29, 133.28 (d, *J* = 12.4 Hz), 128.95, 128.06, 127.05 (d, *J* = 9.6 Hz), 125.18 (d, *J* = 116.1 Hz), 122.39, 121.58, 119.79, 113.71 (d, *J* = 13.7 Hz), 110.51, 91.13 (d, *J* = 125.3 Hz), 55.27, 32.36, 21.48; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 27.17; **HRMS** (ESI) Calcd. for $C_{30}H_{30}N_2O_5PS$ $(M+H)^+$ 561.1608, Found:561.1606.

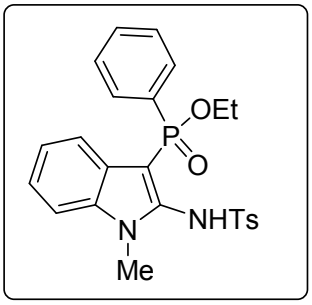


(3q): Yellow solid; 116.9 mg; yield: 87%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.60 (s, 1H), 7.45–7.37 (m, 5H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.07 (s, 2H), 7.00 (t, *J* = 7.1 Hz, 1H), 6.87–6.82 (m, 5H), 3.95 (s, 3H), 3.94–3.88 (m, 2H), 3.82 (s, 6H), 2.91-2.82 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.11 (d, *J* = 6.7 Hz, 12H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 162.22 (d, *J* = 2.7 Hz), 152.93 , 151.12 , 143.30 (d, *J* = 12.7 Hz), 136.59 (d, *J* = 11.1 Hz), 133.57 (d, *J* = 12.3 Hz), 133.25, 127.15 (d, *J* = 9.9 Hz), 125.02 (d, *J* = 115.6 Hz), 123.81, 122.14, 121.44 , 119.60, 113.76 (d, *J* = 13.7 Hz), 110.19, 91.14 (d, *J* = 126.4 Hz), 55.25, 33.95, 32.20, 30.52, 24.82, 23.47; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 27.59; **HRMS** (ESI) Calcd. for $C_{38}H_{46}N_2O_5PS$ $(M+H)^+$ 673.2860, Found:673.2856.

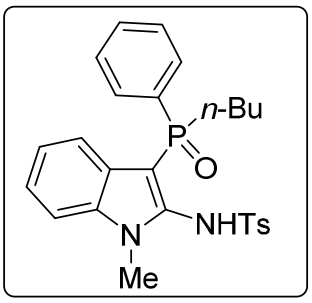


(3r): White solid; 68.9 mg; yield: 67%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 8.08–7.98 (m, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.33–7.29 (m, 3H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.18–7.13 (m, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.64 (dd, *J* = 15.1, 7.2 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 4.06 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 148.98 (d, *J* = 8.1 Hz), 144.41 , 143.77 (d, *J* = 18.3 Hz), 136.75 (d, *J* = 13.2 Hz), 135.23 (d, *J* = 6.0 Hz), 134.64 , 132.88 (d, *J* =

2.2 Hz), 130.59 (d, *J* = 13.7 Hz), 130.32, 129.64, 128.89, 127.77 (d, *J* = 15.0 Hz), 126.52 (d, *J* = 10.3 Hz), 125.44 (d, *J* = 137.1 Hz), 125.04 , 124.57, 123.61 (d, *J* = 9.8 Hz), 123.06, 122.11, 121.97 (d, *J* = 11.7 Hz), 120.55 (d, *J* = 5.9 Hz), 119.64 , 110.63, 88.76 (d, *J* = 176.5 Hz), 32.59, 21.79; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 21.39; **HRMS** (ESI) Calcd. for $C_{28}H_{24}N_2O_4PS$ $(M+H)^+$ 515.1189, Found:515.1186.

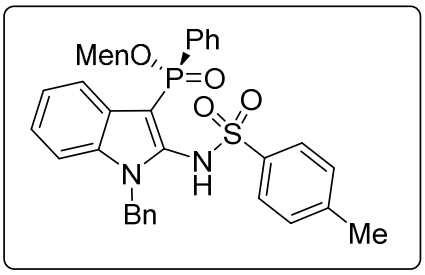


(3s): White oil; 39.3 mg; yield: 42%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 9.65 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.49–7.43 (m, 3H), 7.41–7.32 (m, 3H), 7.32–7.25 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* =8.1 Hz, 2H), 4.01 (s, 3H), 3.90–3.82 (m, 1H), 3.66–3.56 (m, 1H), 2.15 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.93 , 143.20 (d, *J* = 17.1 Hz), 136.69 (d, *J* = 12.1 Hz), 134.47 , 132.39 (d, *J* = 152.1 Hz), 131.52 (d, *J* = 2.9 Hz), 130.17 (d, *J* = 11.3 Hz), 129.26, 128.10, 128.01 (d, *J* = 14.2 Hz), 126.76 (d, *J* = 9.2 Hz), 122.93, 122.12, 119.96, 110.61, 90.29 (d, *J* = 155.8 Hz), 60.89 (d, *J* = 6.1 Hz), 32.57, 21.62, 16.36 (d, *J* = 7.0 Hz); **^{31}P NMR** (243 MHz, $CDCl_3$) δ 31.55; **HRMS** (ESI) Calcd. for $C_{24}H_{26}N_2O_4PS$ $(M+H)^+$ 469.1345, Found:469.1345.

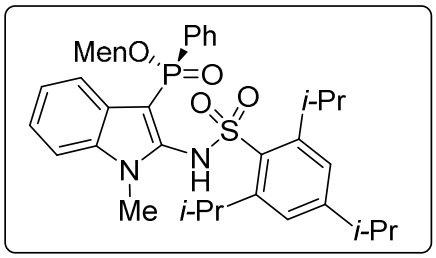


(3t): White oil; 54.7 mg; yield: 57%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.09 (s, 1H), 7.48 (t, *J* = 8.2 Hz, 4H), 7.41–7.28 (m, 5H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 2H), 4.00 (s, 3H), 2.09 (s, 3H), 2.06–1.97 (m, 1H), 1.93–1.85 (m, 1H), 1.49–1.40 (m, 1H), 1.32–1.21 (m, 3H), 0.79 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.71 , 143.07 (d, *J* = 11.3 Hz), 136.80 (d, *J* = 11.0 Hz), 134.30 , 134.11 (d, *J* = 103.5 Hz), 131.28 (d, *J* = 2.5 Hz), 129.81 (d, *J* = 10.6 Hz), 129.04 , 128.27 (d, *J* = 12.1 Hz), 128.10 , 126.36 (d, *J* = 10.1 Hz), 122.68 , 121.83 , 119.44 , 110.85 , 89.84 (d, *J* = 117.5 Hz), 32.35 (d, *J* = 75.3 Hz), 32.27 , 23.76 (d,

J = 15.5 Hz), 23.29 (d, *J* = 4.2 Hz), 21.62 , 13.49 ; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 35.36; **HRMS** (ESI) Calcd. for $C_{26}H_{30}N_2O_3PS$ $(M+H)^+$ 481.1631, Found: 481.1631.

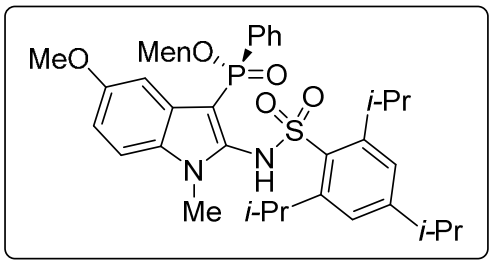


(5a): Yellow oil; 54.9 mg; yield: 42%; dr >20:1; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.48–7.44 (m, 1H), 7.30–7.22 (m, 9H), 7.17–7.12 (m, 3H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.15 (d, *J* = 16.4 Hz, 1H), 5.54 (d, *J* = 16.4 Hz, 1H), 4.06–3.97 (m, 1H), 2.30–2.24 (m, 1H), 2.17 (s, 3H), 1.72–1.65 (m, 2H), 1.63–1.59 (m, 1H), 1.56–1.51 (m, 1H), 1.42–1.24 (m, 2H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.82 (t, *J* = 10.7 Hz, 2H), 0.58 (d, *J* = 7.0 Hz, 3H), -0.06 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.04, 142.87 (d, *J* = 16.7 Hz), 136.76, 135.97 (d, *J* = 11.8 Hz), 134.26, 133.20 (d, *J* = 150.1 Hz), 131.47 (d, *J* = 2.8 Hz), 130.32 (d, *J* = 11.7 Hz), 129.31, 128.50, 128.43, 127.97 (d, *J* = 14.2 Hz), 127.44, 127.24 (d, *J* = 9.1 Hz), 126.93, 122.86, 121.58, 120.62, 111.76, 92.54 (d, *J* = 155.1 Hz), 77.73 (d, *J* = 7.2 Hz), 48.91, 48.51 (d, *J* = 6.4 Hz), 44.07, 34.02, 31.68, 24.96, 22.65, 22.02, 21.66, 20.74, 14.73; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 31.30; **HRMS** (ESI) Calcd. for $C_{38}H_{44}N_2O_4PS$ $(M+H)^+$ 655.2754, Found:655.2753.

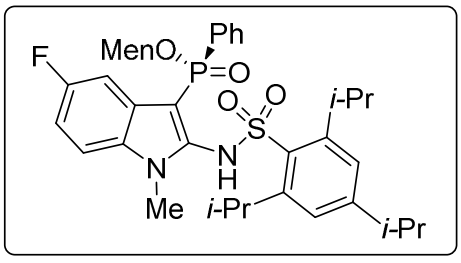


(5b): White solid; 70.4 mg; yield: 51%; dr >20:1; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.31 (s, 1H), 7.59–7.52 (m, 2H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.36–7.29 (m, 3H), 7.26–7.20 (m, 2H), 7.18 (s, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 4.30–4.20 (m, 1H), 4.09–4.02 (m, 2H), 3.85 (s, 3H), 2.99–2.90 (m, 1H), 2.38 (d, *J* = 12.6 Hz, 1H), 1.9 –1.85 (m, 1H), 1.66–1.56 (m, 2H), 1.48–1.26 (m, 15H), 1.06 (d, *J* = 6.7 Hz, 6H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.92–0.82 (m, 2H), 0.69 (d, *J* = 7.0 Hz, 3H), 0.09 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 153.36 , 151.24 , 143.16 (d, *J* = 16.5 Hz), 136.46 (d, *J* = 12.2 Hz), 133.66 (d, *J* = 150.7 Hz), 133.50, 131.54 (d, *J* = 2.7 Hz), 130.90 (d, *J* = 11.1 Hz), 128.12 (d, *J* = 13.9 Hz), 126.76

(d, *J* = 9.9 Hz), 124.05, 122.37, 121.38, 119.92 , 109.83 , 91.79 (d, *J* = 156.1 Hz), 77.40 (d, *J* = 7.1 Hz), 48.83 (d, *J* = 6.6 Hz), 44.01, 34.13, 34.10, 32.07, 31.56, 30.36, 25.10, 24.79 (d, *J* = 20.4 Hz), 23.57 (d, *J* = 15.6 Hz), 22.64, 22.09, 21.02, 14.80; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 29.32; **HRMS** (ESI) Calcd. for $C_{40}H_{56}N_2O_4PS$ $(M+H)^+$ 691.3693, Found:691.3687.

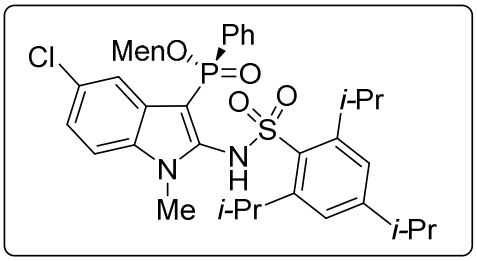


(5c): White solid; 80.6 mg; yield: 56%; dr >20:1; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.18 (s, 1H), 7.58–7.53 (m, 2H), 7.45–7.41 (m, 1H), 7.33–7.29 (m, 2H), 7.21 (dd, *J* = 8.9, 1.7 Hz, 1H), 7.17 (s, 2H), 6.86 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 4.29–4.22 (m, 1H), 4.09–4.03 (m, 2H), 3.80 (s, 3H), 3.67 (s, 3H), 2.98–2.90 (m, 1H), 2.40 (d, *J* = 12.6 Hz, 1H), 1.98–1.90 (m, 1H), 1.66–1.61 (m, 1H), 1.61–1.56 (m, 1H), 1.49–1.25 (m, 15H), 1.07 (d, *J* = 6.7 Hz, 6H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.91–0.82 (m, 2H), 0.72 (d, *J* = 7.0 Hz, 3H), 0.09 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 155.14 , 153.35 , 151.26 , 143.06 (d, *J* = 16.5 Hz), 133.63 (d, *J* = 150.3 Hz), 133.43, 131.54 (d, *J* = 2.8 Hz), 131.47 (d, *J* = 12.2 Hz), 130.92 (d, *J* = 11.0 Hz), 128.10 (d, *J* = 13.8 Hz), 127.41 (d, *J* = 9.6 Hz), 124.03, 111.82, 110.57, 102.50, 91.59 (d, *J* = 156.6 Hz), 77.30 (d, *J* = 7.1 Hz), 55.63, 48.86 (d, *J* = 6.6 Hz), 44.06, 34.14, 34.10, 32.13, 31.54, 30.32, 25.18, 24.81 (d, *J* = 14.6 Hz), 23.56 (d, *J* = 16.1 Hz), 22.65, 22.09, 21.05, 14.76; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 29.19; **HRMS** (ESI) Calcd. for $C_{41}H_{58}N_2O_5PS$ $(M+H)^+$ 721.3799, Found:721.3798.

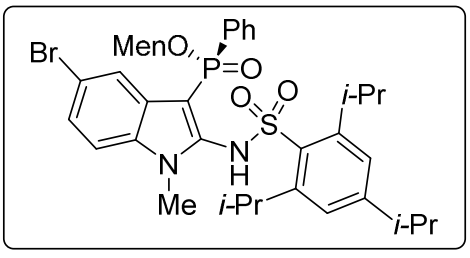


(5d): White solid; 72.2 mg; yield: 51%; dr >20:1; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.30 (s, 1H), 7.52 (dd, *J* = 13.3, 7.6 Hz, 2H), 7.47–7.43 (m, 1H), 7.34–7.30 (m, 2H), 7.26 (dd, *J* = 9.0, 4.2 Hz, 1H), 7.18 (s, 2H), 6.99–6.95 (m, 1H), 6.88 (dd, *J* = 9.5, 2.4 Hz, 1H), 4.27–4.20 (m, 1H), 4.06–4.01 (m, 2H), 3.84 (s, 3H), 3.00–2.91 (m, 1H), 2.35 (d, *J* = 12.7 Hz, 1H), 1.90–1.84 (m, 1H), 1.66–1.57 (m, 2H), 1.44–1.27 (m, 15H), 1.06 (d, *J* = 6.7 Hz, 6H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.90–0.83 (m, 2H), 0.73 (d, *J* = 7.0 Hz, 3H), 0.15 (d, *J* = 6.7 Hz, 3H); **^{13}C**

NMR (151 MHz, Chloroform-*d*) δ 158.72 (d, *J* = 237.1 Hz), 153.48, 151.23, 144.18 (d, *J* = 16.3 Hz), 133.40, 133.27 (d, *J* = 150.8 Hz), 132.93 (d, *J* = 11.9 Hz), 131.74 (d), 130.82 (d, *J* = 11.1 Hz), 128.24 (d, *J* = 13.9 Hz), 127.30 (t, *J* = 10.1 Hz), 124.10, 110.71 (d, *J* = 9.7 Hz), 110.52 (d, *J* = 26.0 Hz), 105.30 (d, *J* = 24.8 Hz), 92.16 (d, *J* = 160.3 Hz), 77.57 (d, *J* = 7.1 Hz), 48.78 (d, *J* = 6.5 Hz), 43.96, 34.10, 34.08, 32.37, 31.58, 30.39, 25.20, 24.79 (d, *J* = 18.7 Hz), 23.56 (d, *J* = 17.5 Hz), 22.62, 22.06, 21.03, 14.78; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 28.70; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -121.62; **HRMS** (ESI) Calcd. for $C_{40}H_{55}FN_2O_4PS$ $(M+H)^+$ 709.3599, Found:709.3593.

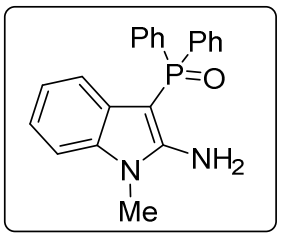


(5e): White solid; 69.5 mg; yield: 48%; dr >20:1; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.33 (s, 1H), 7.54–7.49 (m, 2H), 7.47–7.44 (m, 1H), 7.35–7.30 (m, 2H), 7.26 (dd, *J* = 9.4, 1.8 Hz, 1H), 7.21–7.16 (m, 4H), 4.23–4.16 (m, 1H), 4.05–3.99 (m, 2H), 3.84 (s, 3H), 2.97–2.91 (m, 1H), 2.37–2.33 (m, 1H), 1.92–1.85 (m, 1H), 1.66–1.57 (m, 2H), 1.44–1.26 (m, 15H), 1.05 (d, *J* = 6.8 Hz, 6H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.89–0.83 (m, 2H), 0.74 (d, *J* = 7.0 Hz, 3H), 0.14 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 153.52 , 151.22 , 144.18 (d, *J* = 16.3 Hz), 134.86 (d, *J* = 11.8 Hz), 133.33 , 133.24 (d, *J* = 151.3 Hz), 131.77, 130.76 (d, *J* = 11.1 Hz), 128.27 (d, *J* = 14.0 Hz), 127.72 (d, *J* = 9.4 Hz), 127.25, 124.11, 122.72, 119.38, 110.92, 91.70 (d, *J* = 155.4 Hz), 77.77 (d, *J* = 7.2 Hz), 48.79 (d, *J* = 6.7 Hz), 43.95, 34.10, 34.05, 32.37, 31.58, 30.39, 25.27, 24.79 (d, *J* = 14.0 Hz), 23.55 (d, *J* = 17.1 Hz), 22.62, 22.05, 21.05, 14.75; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 28.67; **HRMS** (ESI) Calcd. for $C_{40}H_{55}ClN_2O_4PS$ $(M+H)^+$ 725.3303, Found:725.3302.



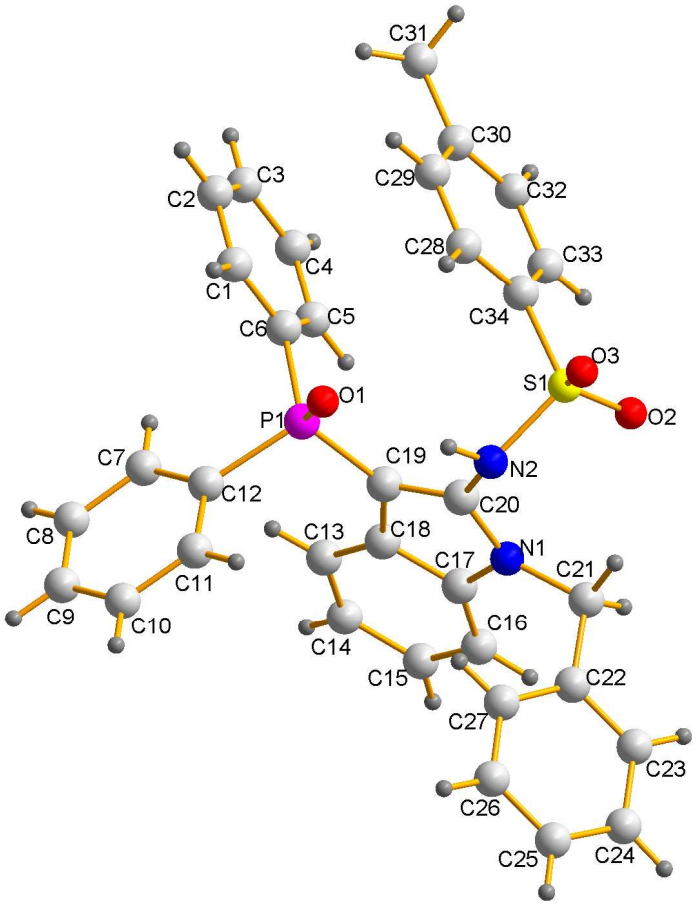
(5f): White solid; 79.9 mg; yield: 52%; dr >20:1; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 10.34 (s, 1H), 7.54–7.49 (m, 2H), 7.48–7.44 (m, 1H), 7.36 (d, *J* = 1.9 Hz, 1H), 7.35–7.31 (m, 3H), 7.21 (dd, *J*

= 8.6, 1.7 Hz, 1H), 7.18 (s, 2H), 4.22–4.16 (m, 1H), 4.05–4.00 (m, 2H), 3.84 (s, 3H), 2.97–2.92 (m, 1H), 2.38–2.33 (m, 1H), 1.93–1.86 (m, 1H), 1.66–1.57 (m, 2H), 1.45–1.25 (m, 15H), 1.05 (d, *J* = 6.8 Hz, 6H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.91–0.85 (m, 2H), 0.76 (d, *J* = 7.1 Hz, 3H), 0.13 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 153.54 , 151.22 , 144.08 (d, *J* = 16.4 Hz), 135.17 (d, *J* = 11.7 Hz), 133.32, 133.22 (d, *J* = 151.4 Hz), 131.80 (d, *J* = 2.8 Hz), 130.75 (d, *J* = 11.1 Hz), 128.28 (d, *J* = 14.0 Hz), 128.27, 125.34, 124.11, 122.41, 114.85, 111.33, 91.59 (d, *J* = 155.1 Hz), 77.81 (d, *J* = 7.2 Hz), 48.79 (d, *J* = 6.7 Hz), 43.97, 34.11, 34.06, 32.35, 31.59, 30.39, 25.29, 24.79 (d, *J* = 12.6 Hz), 23.55 (d, *J* = 17.0 Hz), 22.63, 22.05 , 21.08 , 14.76; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 28.69; **HRMS** (ESI) Calcd. for $C_{40}H_{55}BrN_2O_4PS$ $(M+H)^+$ 769.2798, Found:769.2798.



(6): Organe solid; 31.5 mg; yield: 91%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.80–7.73 (m, 4H), 7.55–7.50 (m, 2H), 7.46–7.40 (m, 4H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.06–7.01 (m, 1H), 6.92–6.86 (m, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 5.74 (s, 2H), 3.56 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 154.28 (d, *J* = 13.7 Hz), 135.17, 135.10, 134.61 (d, *J* = 107.7 Hz), 131.67 (d, *J* = 10.8 Hz), 128.83 (d, *J* = 11.4 Hz), 128.40 (d, *J* = 12.3 Hz), 120.81, 119.29, 117.66, 107.95, 76.02 (d, *J* = 136.5 Hz), 27.95; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 29.13; **HRMS** (ESI) Calcd. for $C_{21}H_{20}N_2OP$ $(M+H)^+$ 347.1308, Found:347.1306.

Single Crystal X-ray Structure Determinations of Compounds 3e (CCDC: 1486528)



Bond precision:	C-C = 0.0054 A	Wavelength=0.71073
Cell:	a=32.921(7) b=11.658(2) c=20.290(4)	
	alpha=90 beta=118.58(3) gamma=90	
Temperature:	293 K	
	Calculated	Reported
Volume	6838(3)	6838(3)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc

Moiety formula	C34 H29 N2 O3 P S, C H Cl2.57, 0.431(Cl)	C34 H29 N2 O3 P S, C H Cl3
Sum formula	C35 H30 Cl3 N2 O3 P S	C35 H30 Cl3 N2 O3 P S
Mr	695.99	695.99
Dx,g cm-3	1.352	1.352
Z	8	8
Mu (mm-1)	0.413	0.413
F000	2880.0	2880.0
F000’	2886.33	
h,k,lmax	42,15,26	42,15,26
Nref	7875	7851
Tmin,Tmax	0.921,0.956	0.667,0.746
Tmin’	0.912	

Correction method= # Reported T Limits: Tmin=0.667 Tmax=0.746

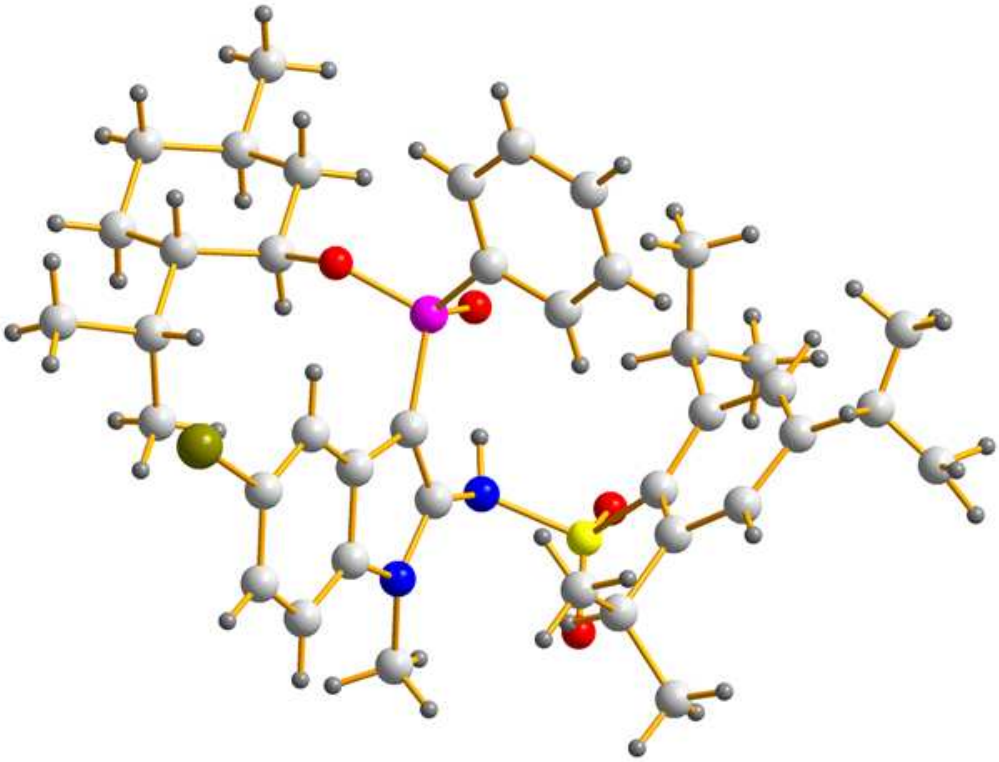
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 27.523

R(reflections)= 0.0610(4948) wR2(reflections)= 0.1836(7851)

S = 1.036 Npar= 426

Single Crystal X-ray Structure Determinations of Compounds 5f (CCDC: 1501118)



Bond precision:	C-C = 0.0059 A		Wavelength=0.71073
Cell:	a=10.7121(11)	b=9.9230(11)	c=19.323(2)
	alpha=90	beta=97.966(3)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	2034.1(4)	2034.1(4)	
Space group	P 21	P21	
Hall group	P 2yb	?	
Moiety formula	C40 H54 Br N2 O4 P S	?	
Sum formula	C40 H54 Br N2 O4 P S	C40 H54 Br N2 O4 P S	
Mr	769.78	769.79	
Dx,g cm-3	1.257	1.257	

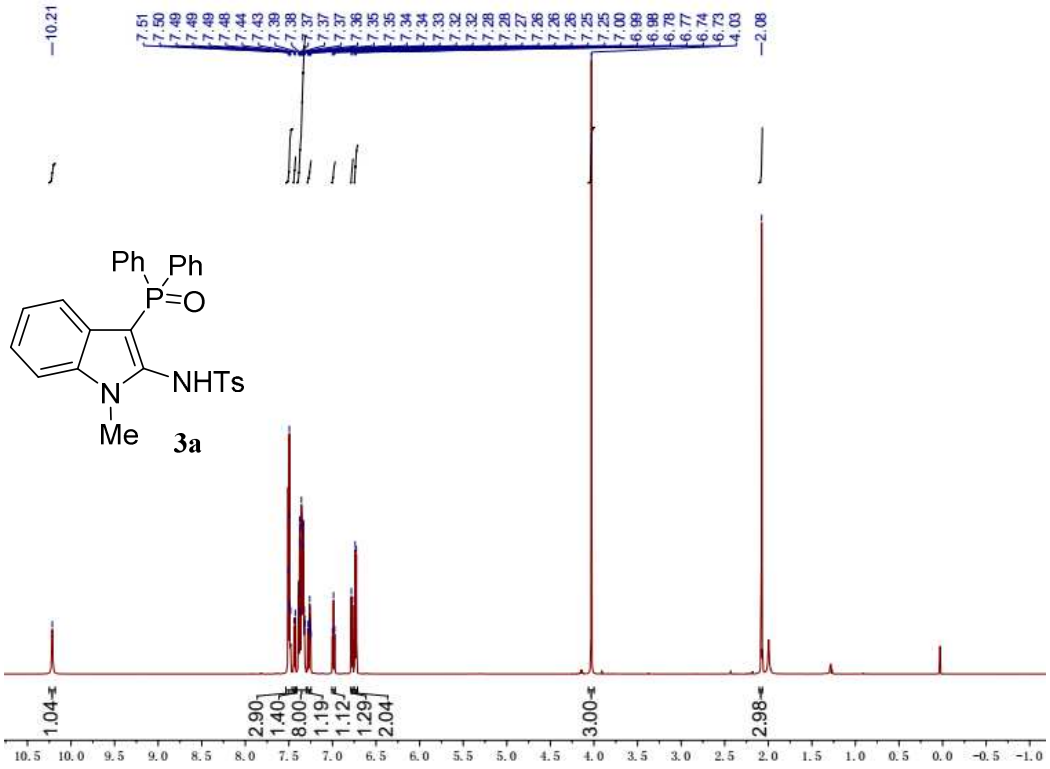
Z	2	2
Mu (mm-1)	1.141	1.141
F000	812.0	812.0
F000’	812.15	
h,k,lmax	12,11,22	12,11,22
Nref	7163[3807]	7135
Tmin,Tmax	0.575,0.662	0.603,0.683
Tmin’	0.563	

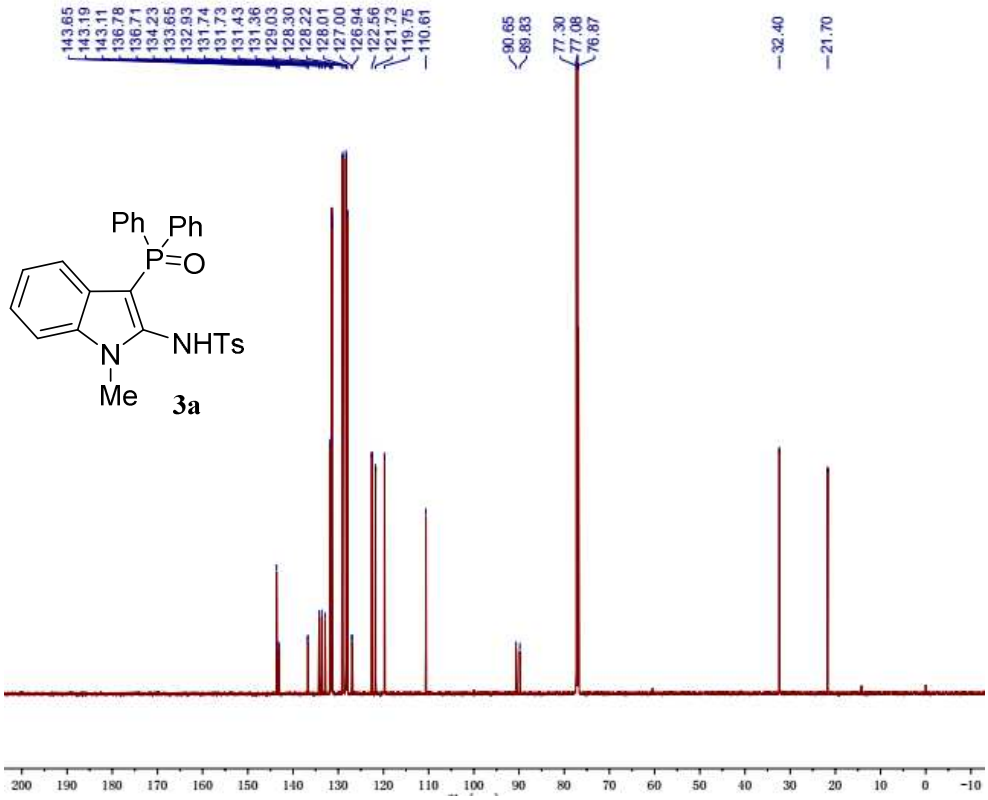
Correction method= # Reported T Limits: Tmin=0.603 Tmax=0.683

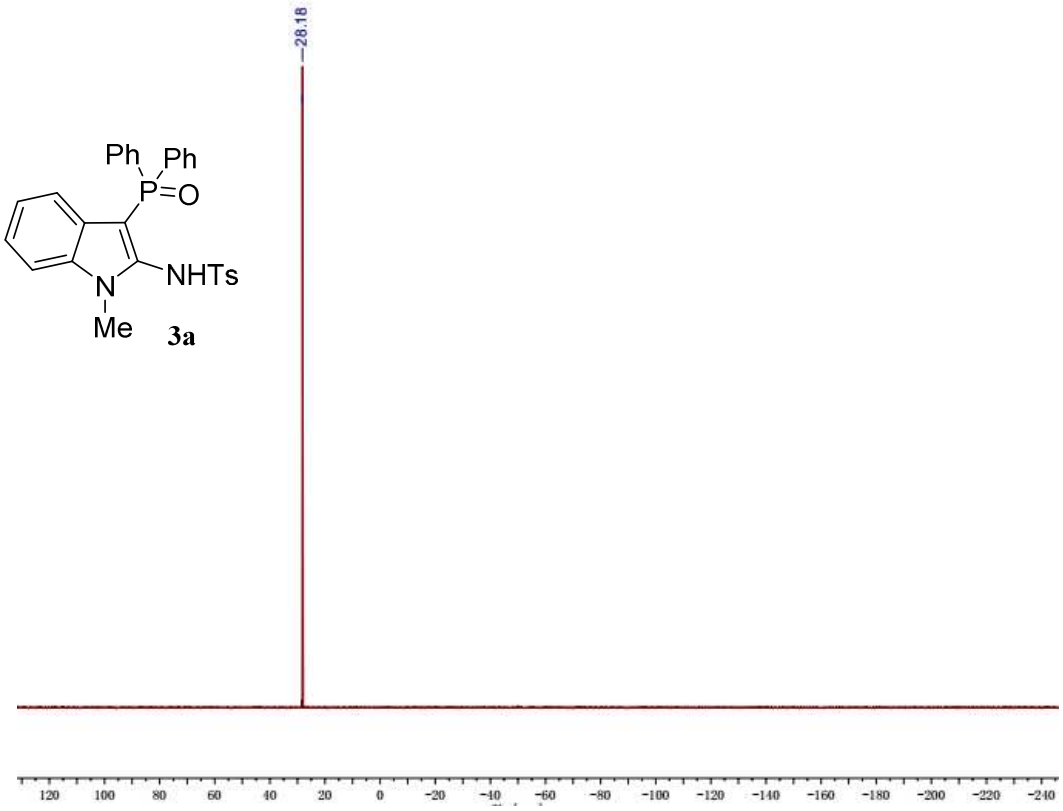
AbsCorr = MULTI-SCAN

Data completeness= 1.87/1.00	Theta(max)= 25.010
R(reflections)= 0.0500(6057)	wR2(reflections)= 0.1375(7135)
S = 1.034	Npar= 464

^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra for new compounds



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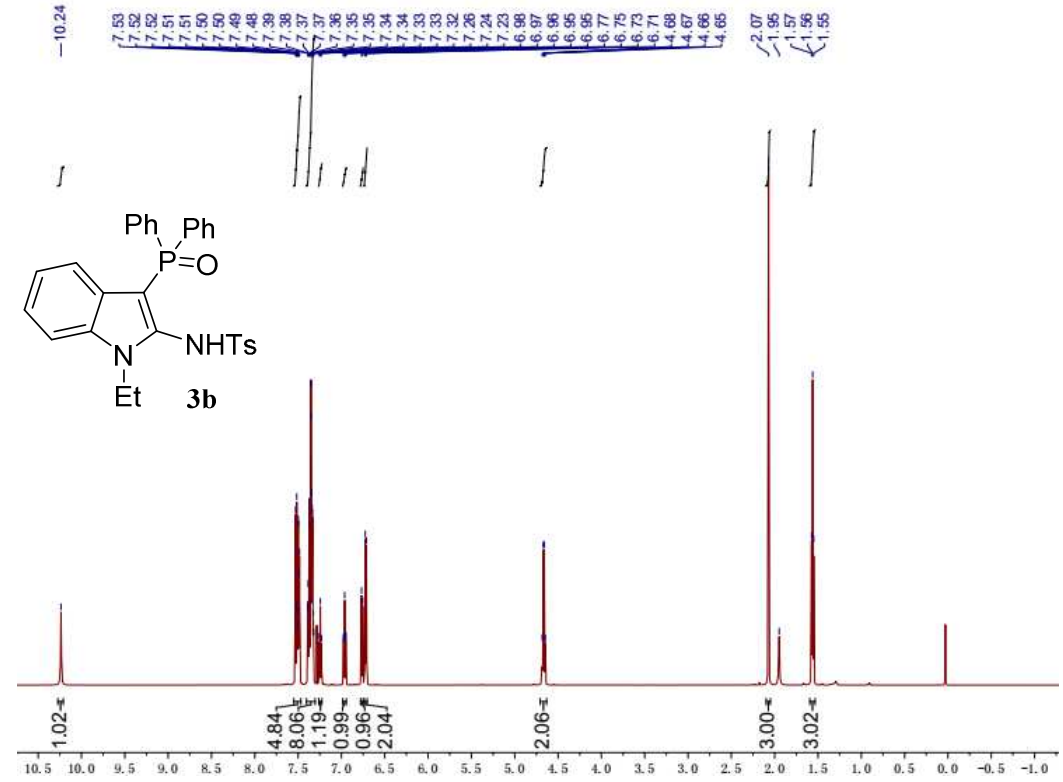
N
Me
3a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1.95
1.57
1.56
1.55
Ph
Ph
P=O
NHTs
N
Et
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0.96
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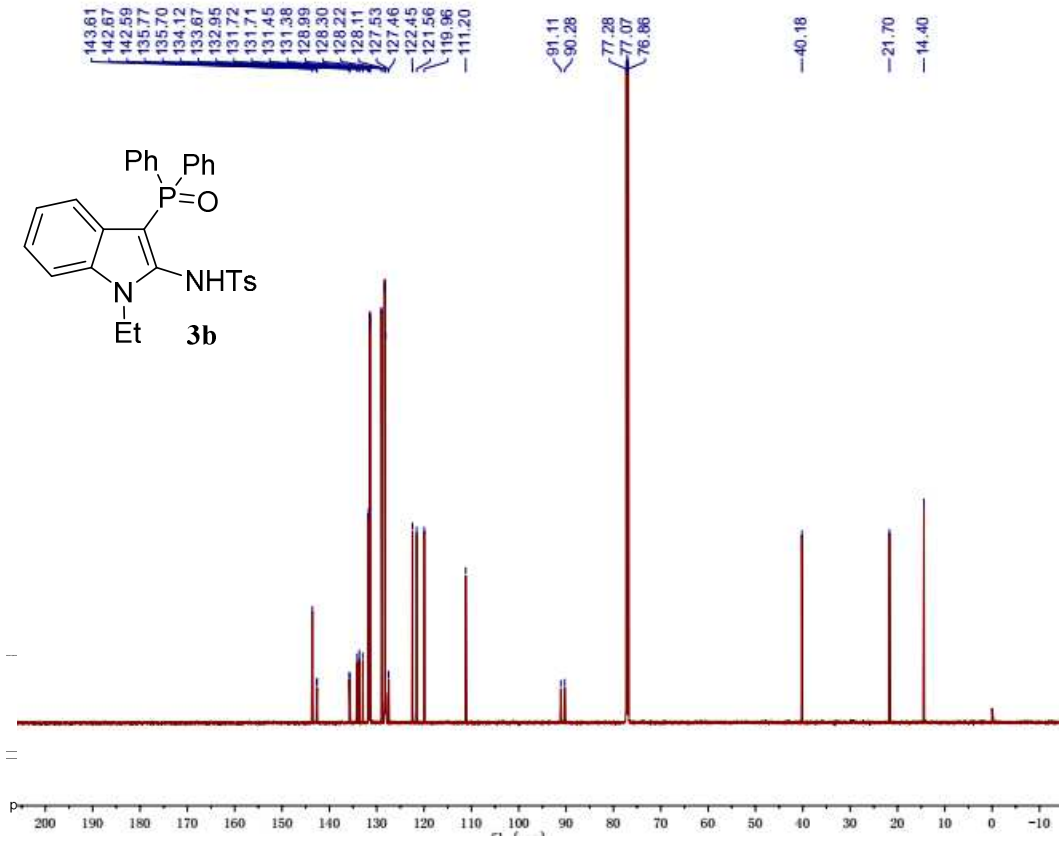
2.06
3.00
3.02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128.30
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127.46
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91.11
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Ph
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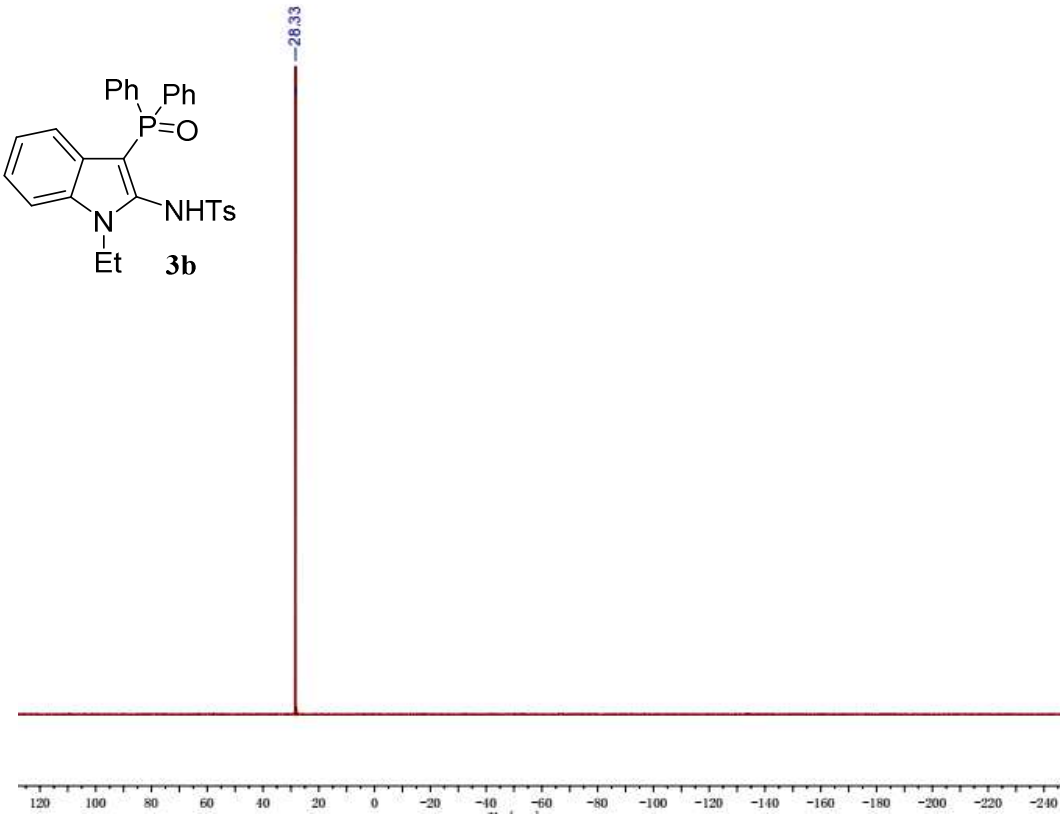
O
NHTs
N
Et
3b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Et
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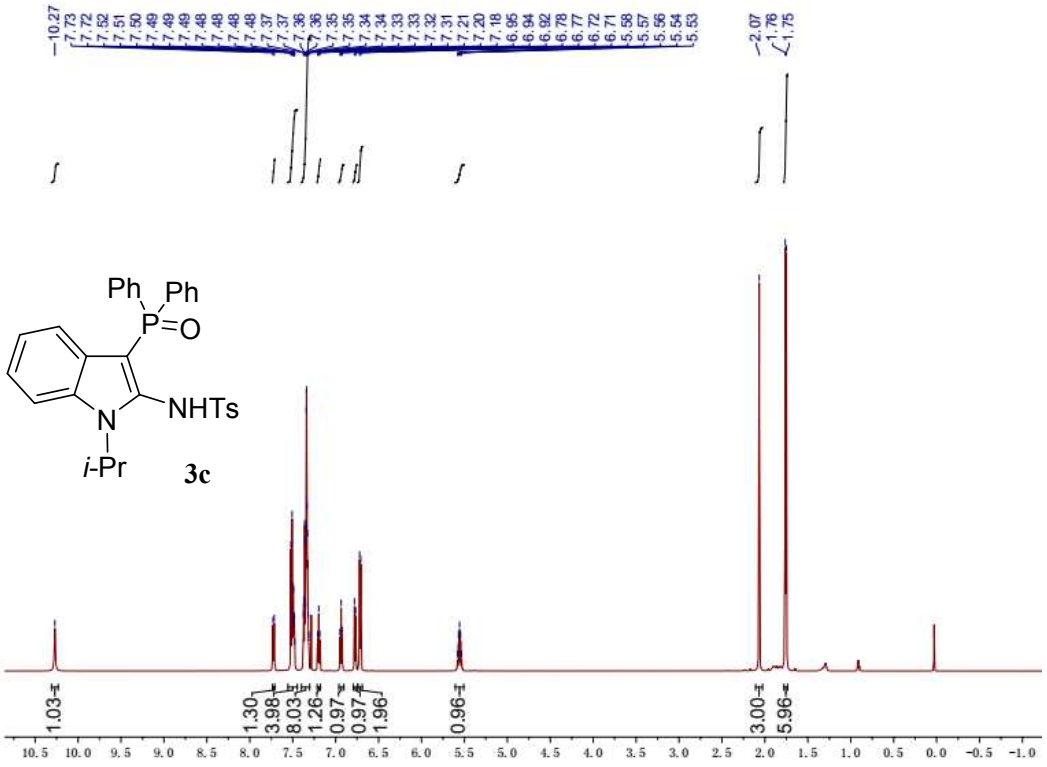
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NHTs
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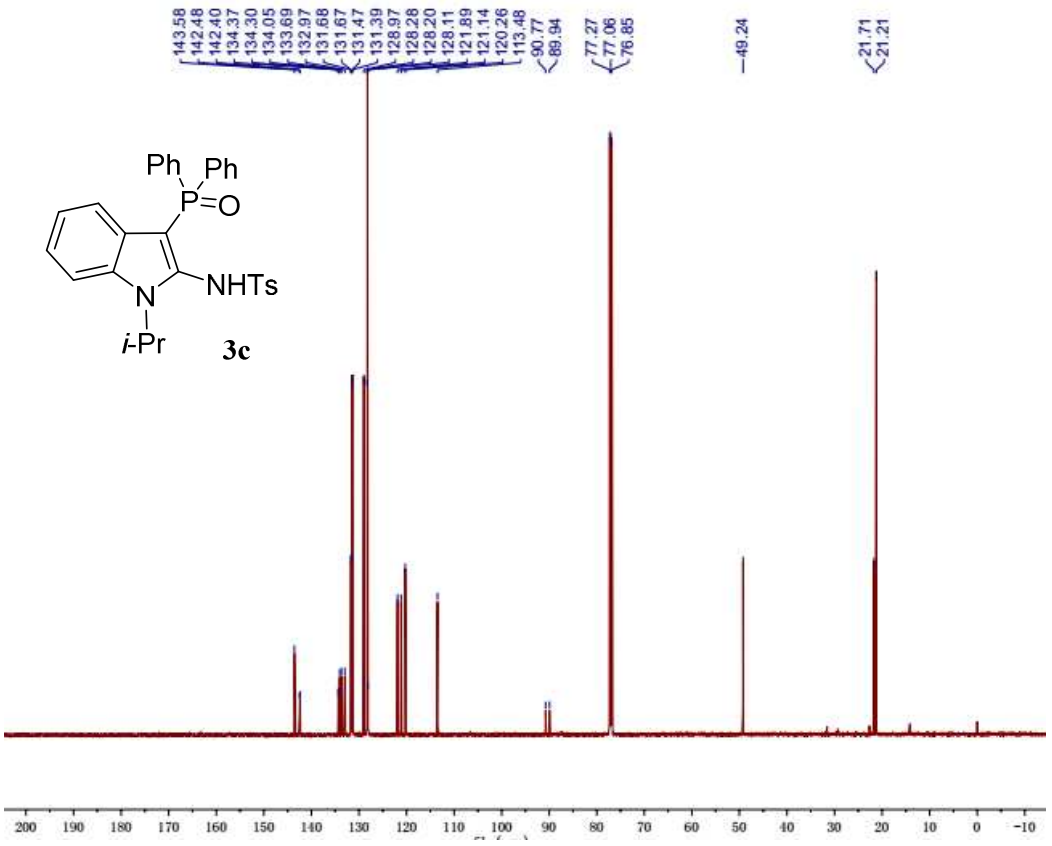
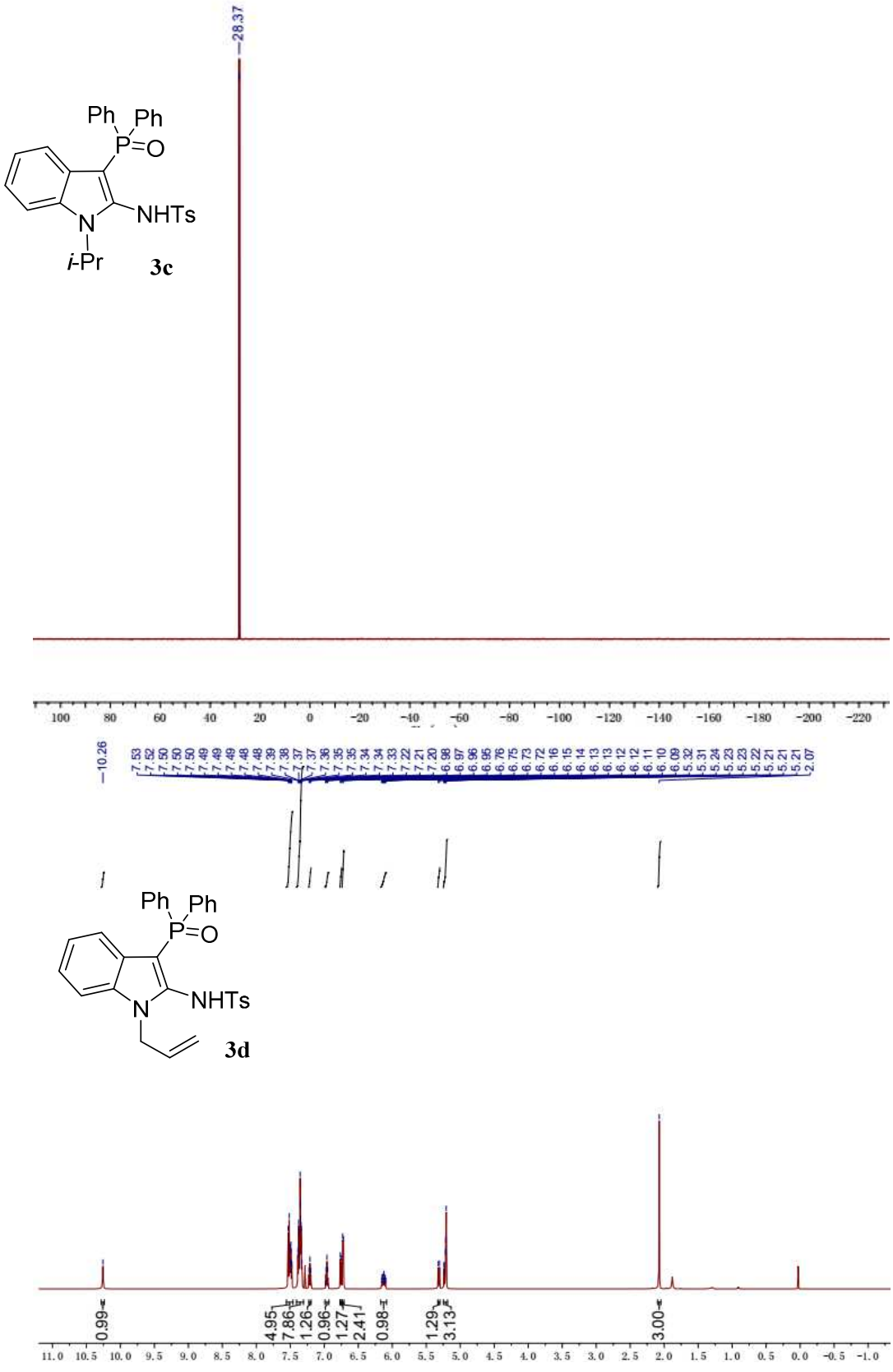
3c


Ph
Ph
P=O
NHTs
N
i-Pr
3c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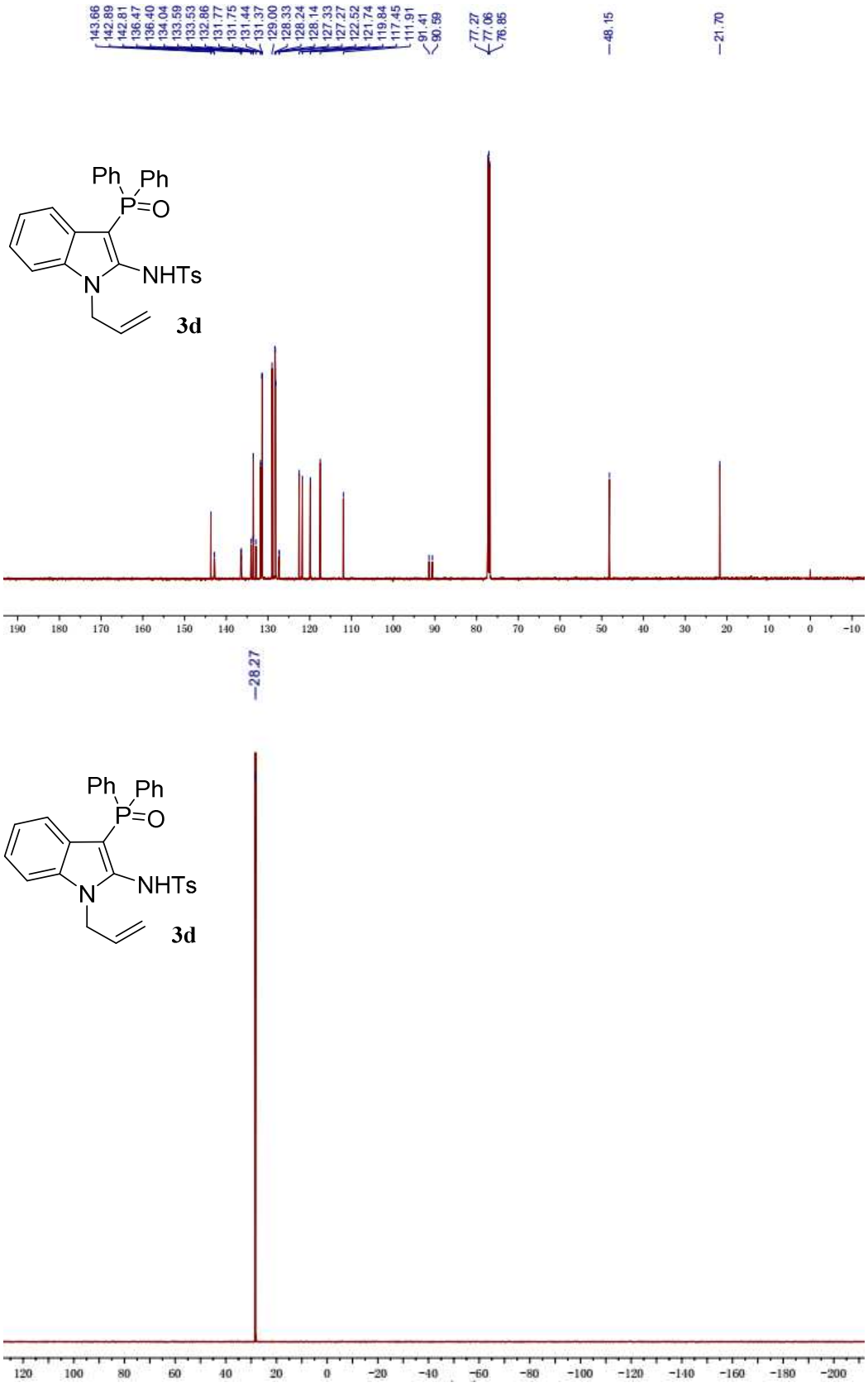
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Ph
P
O
NHTs
N
3d
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100
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10
0
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Ph
P
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NHTs
N
3d
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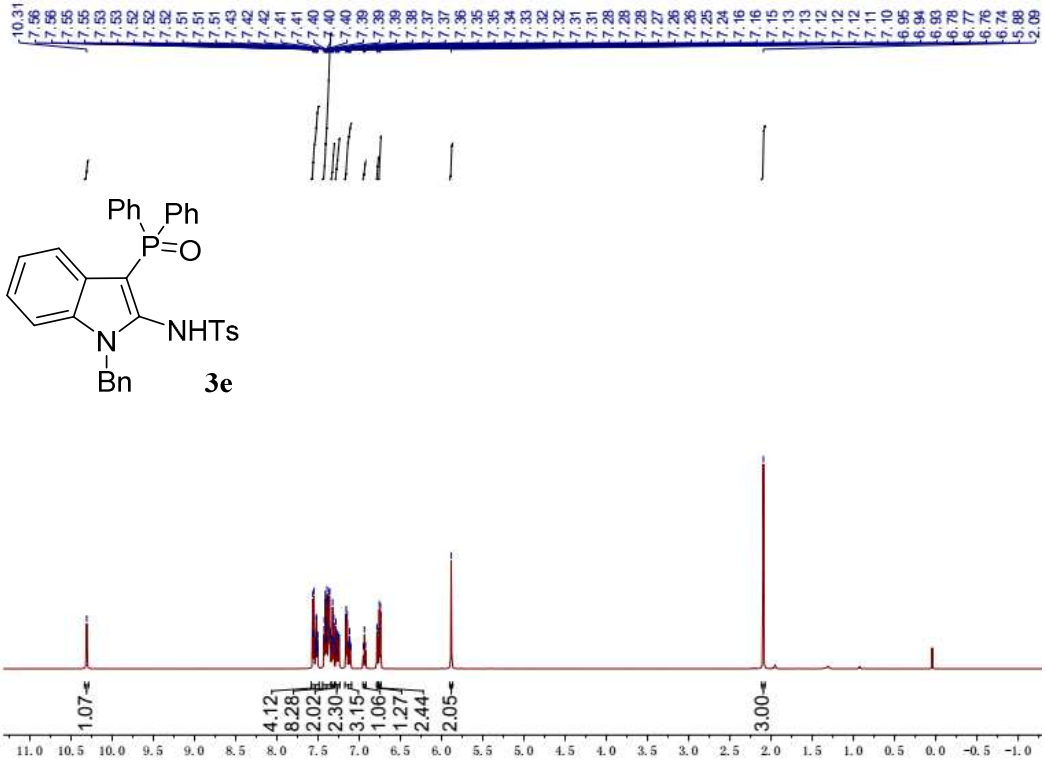
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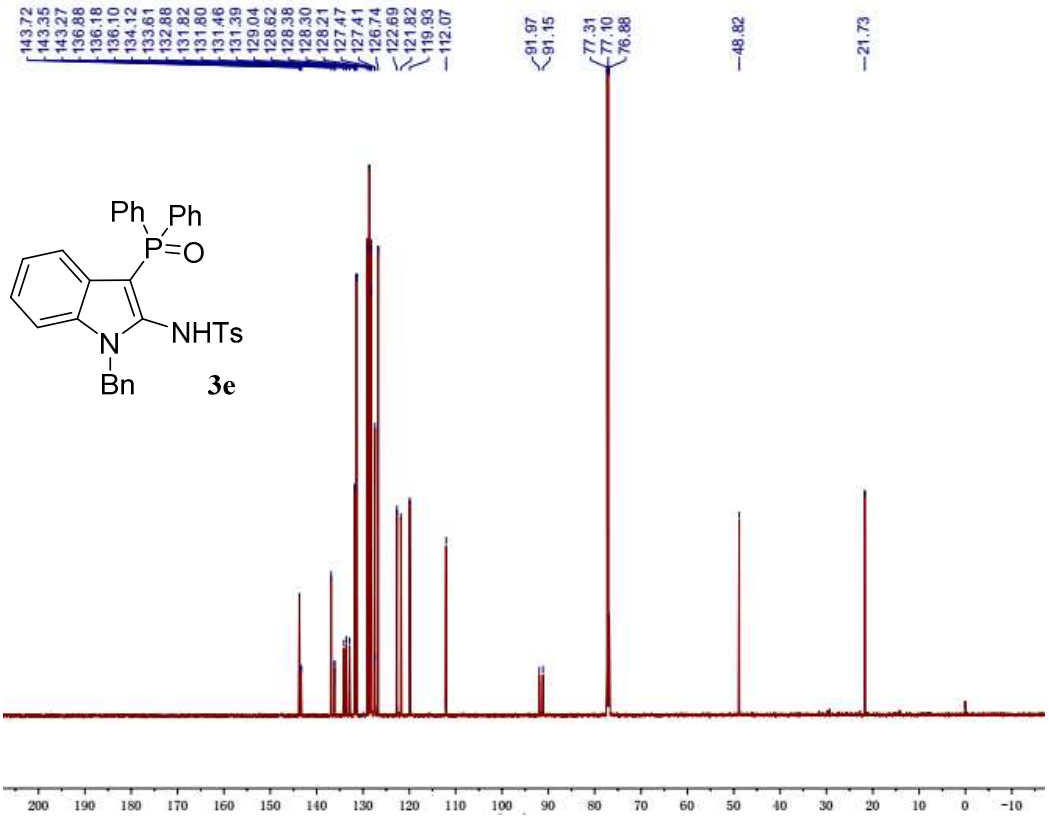
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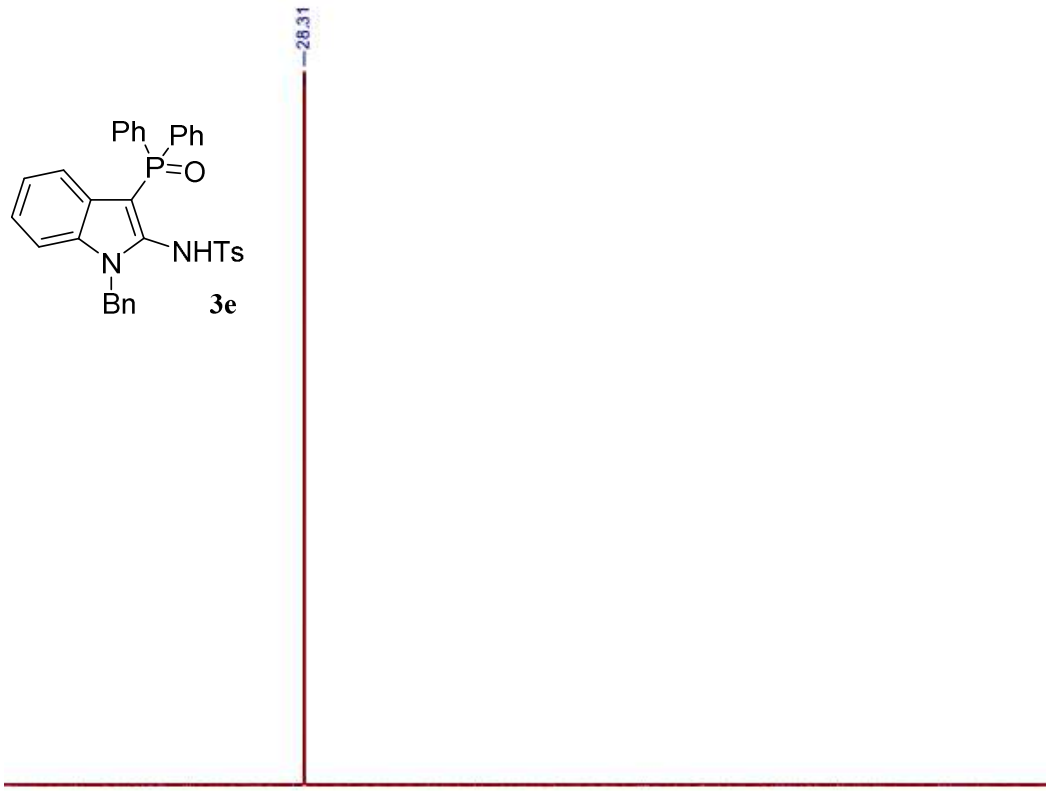
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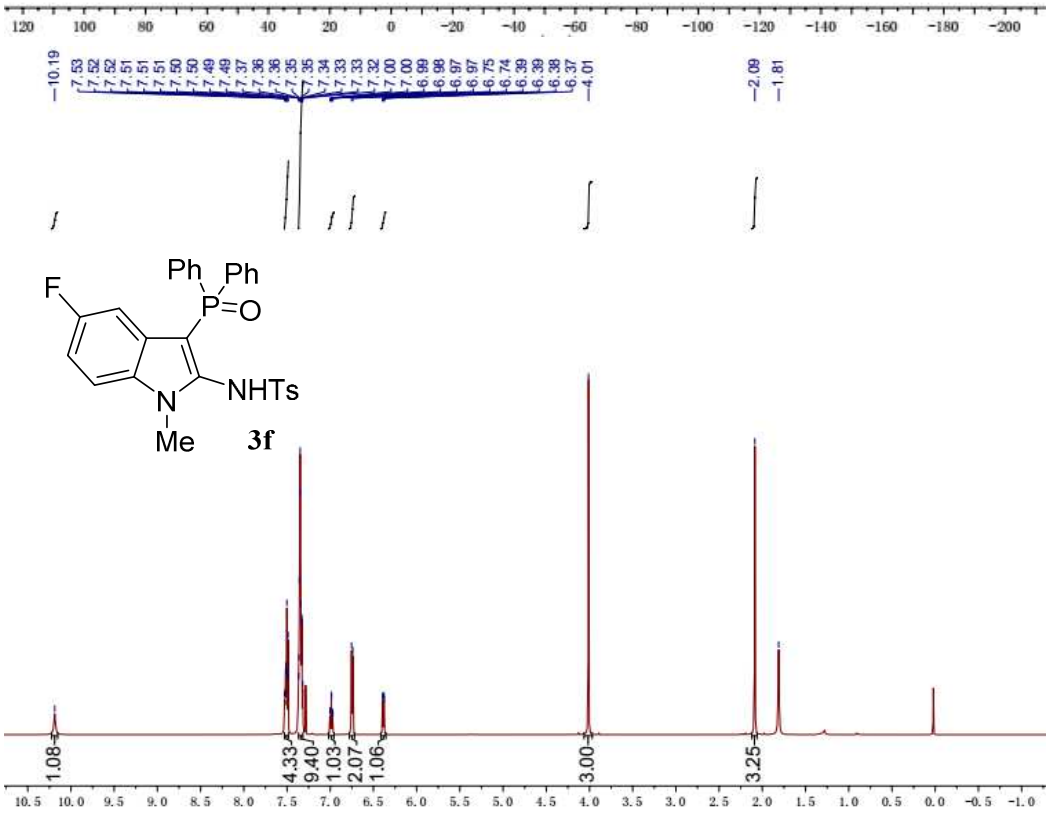
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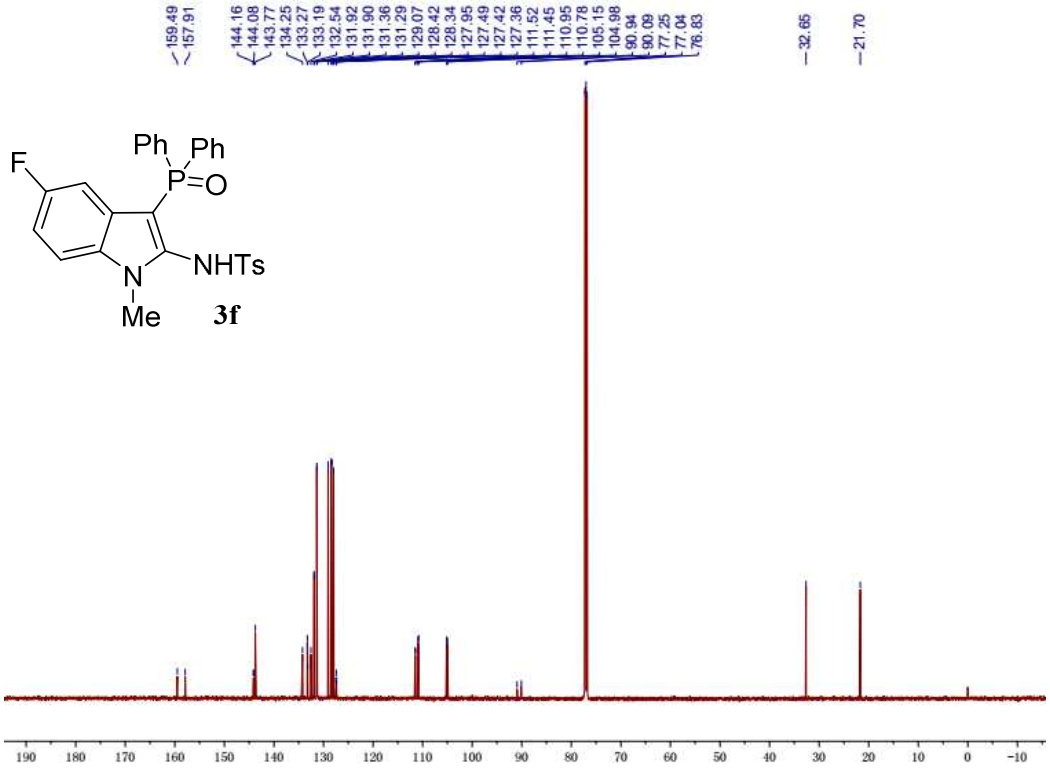
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110.78
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104.98
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90.09
77.25
77.04
76.83
32.65
21.70
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Ph
P=O
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NHTs
N
Me
3f
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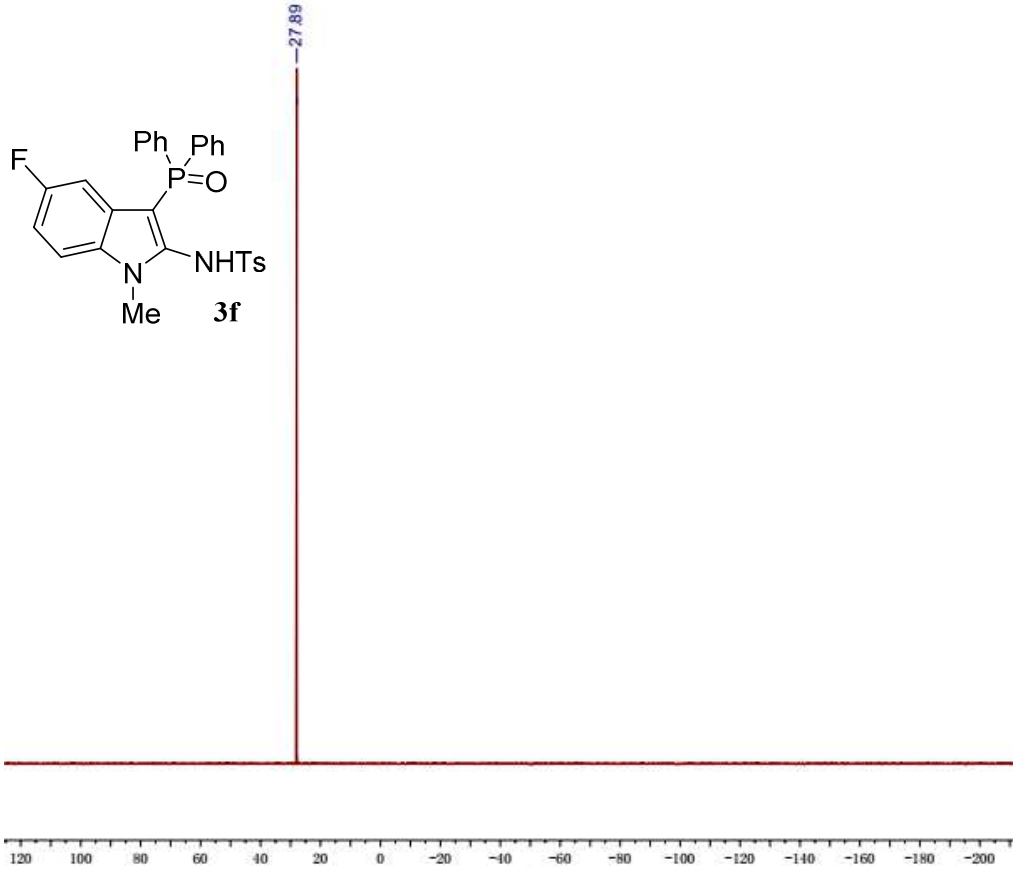
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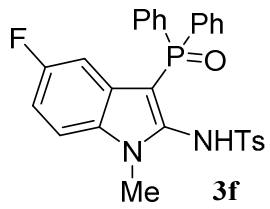
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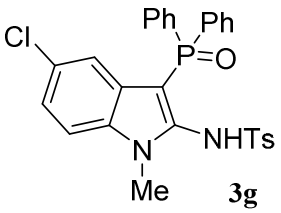
2.09
1.76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Me

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1.96
0.94
3.00
2.98
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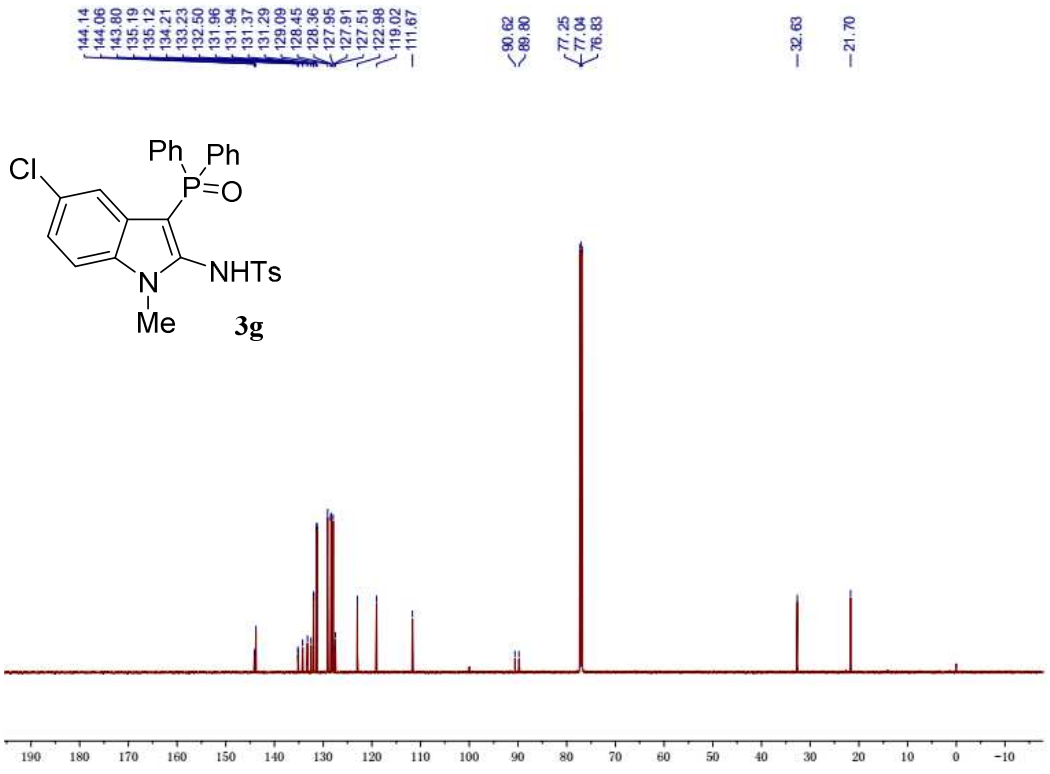
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77.04
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21.70
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Ph
P=O
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3g
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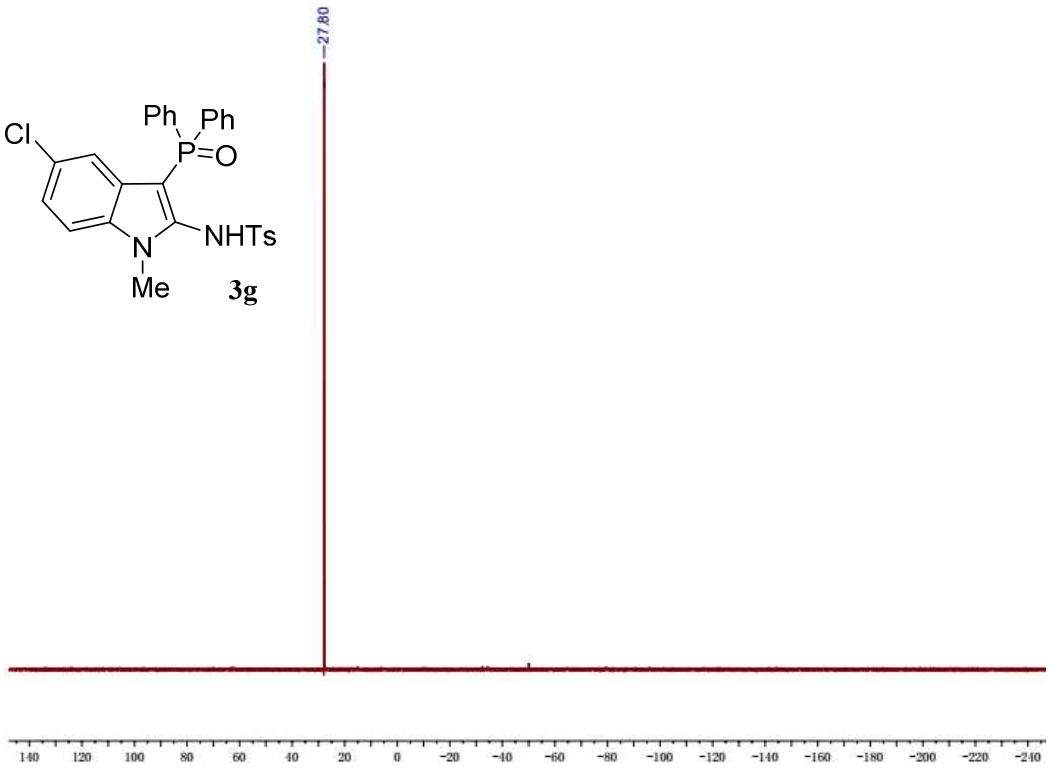
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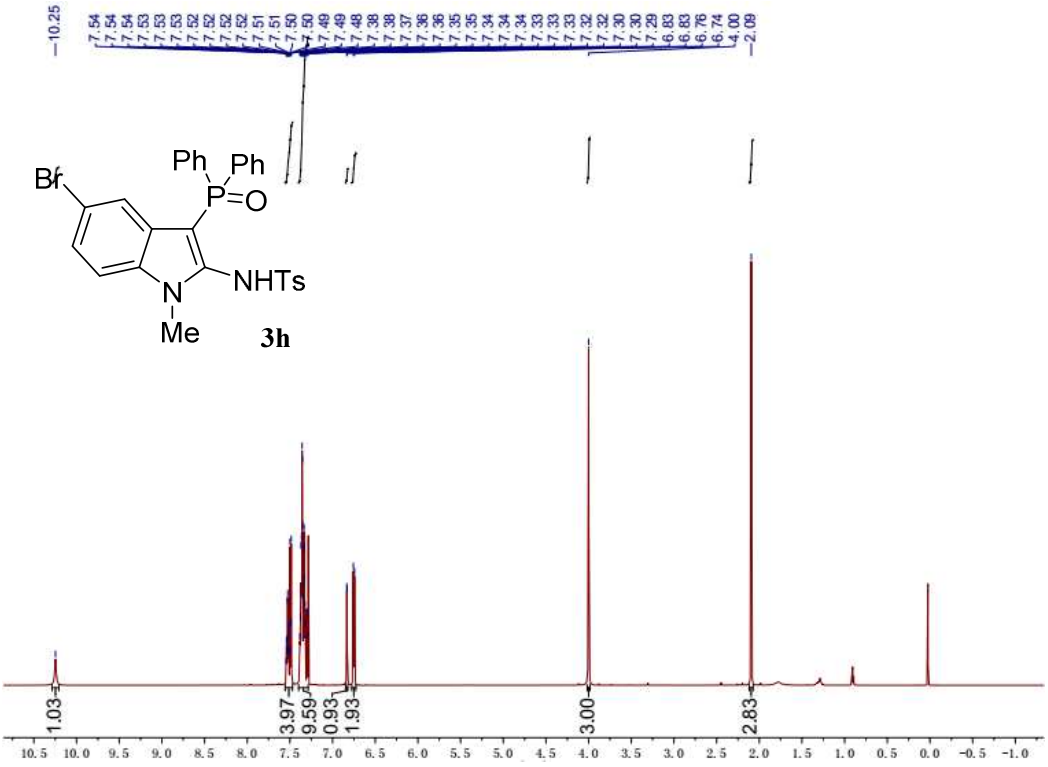
-220
-240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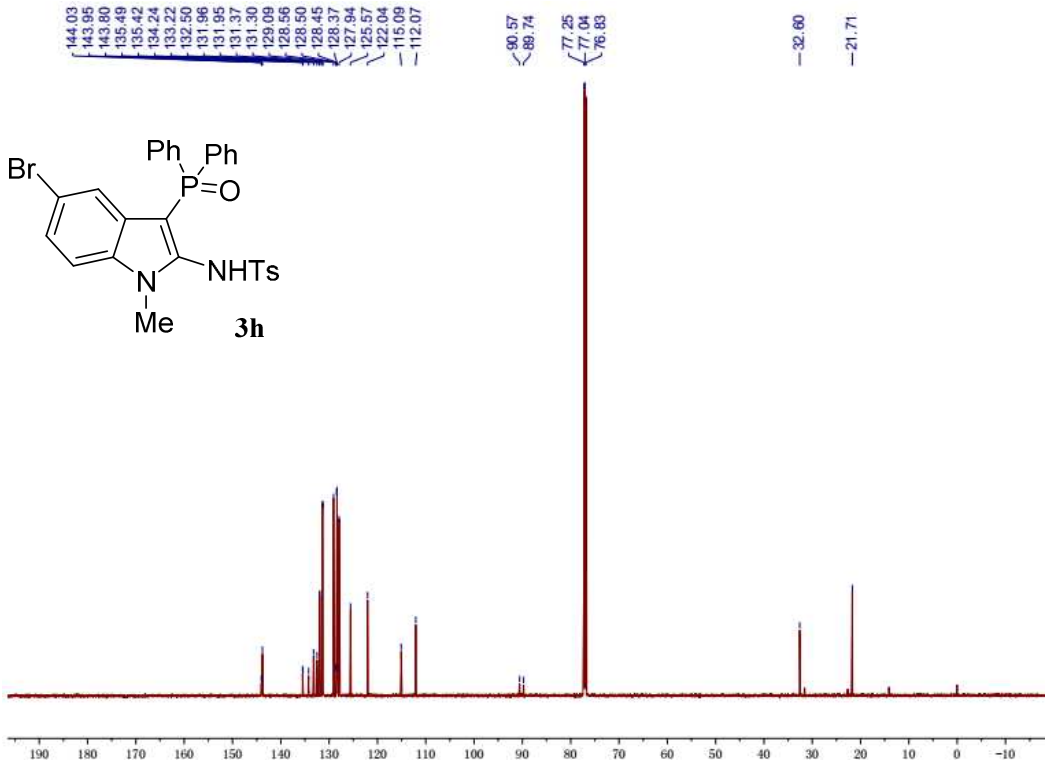
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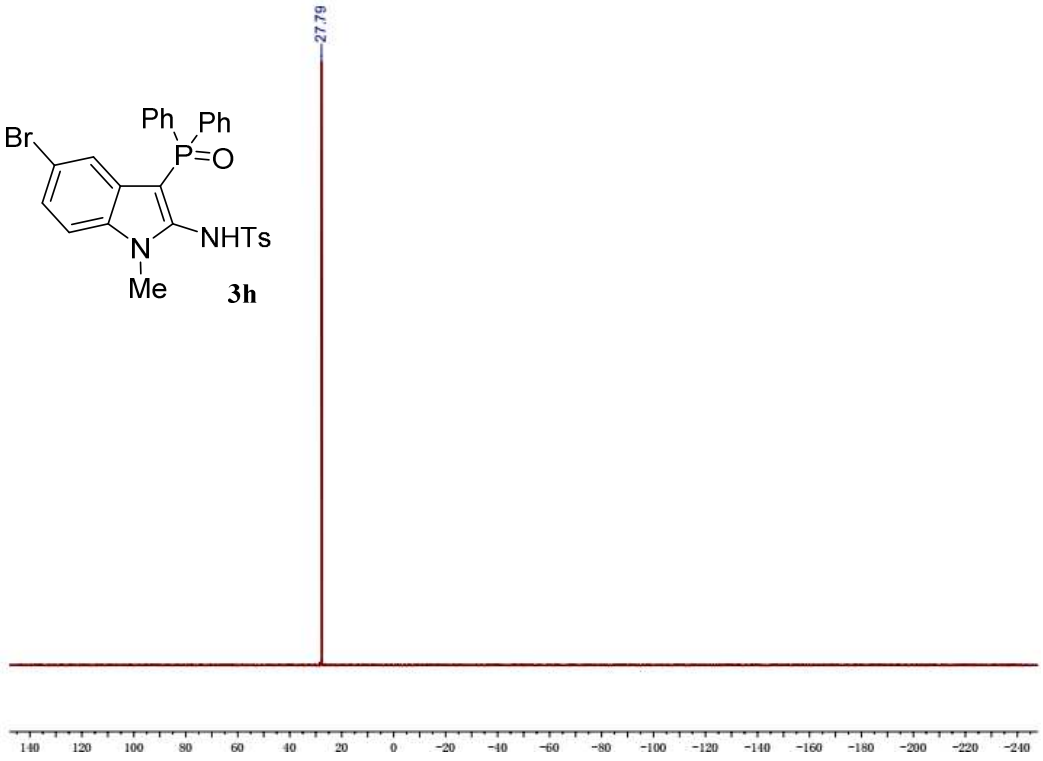
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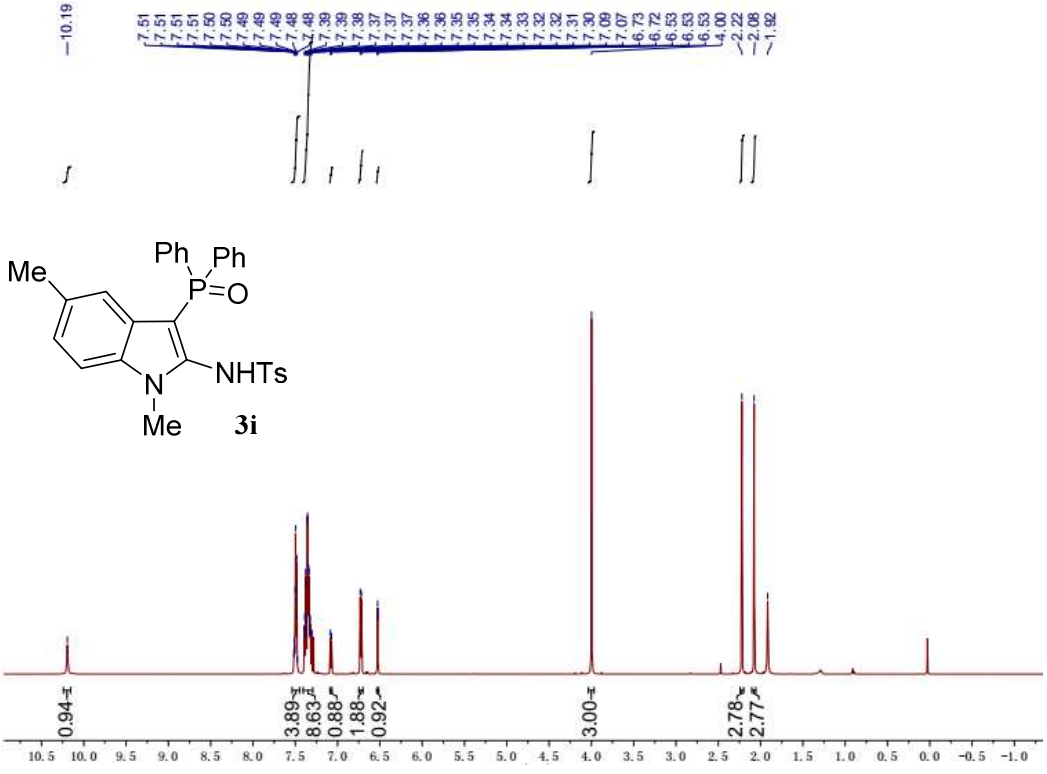
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Me
Ph
Ph
P=O
NHTs
N
Me
3i
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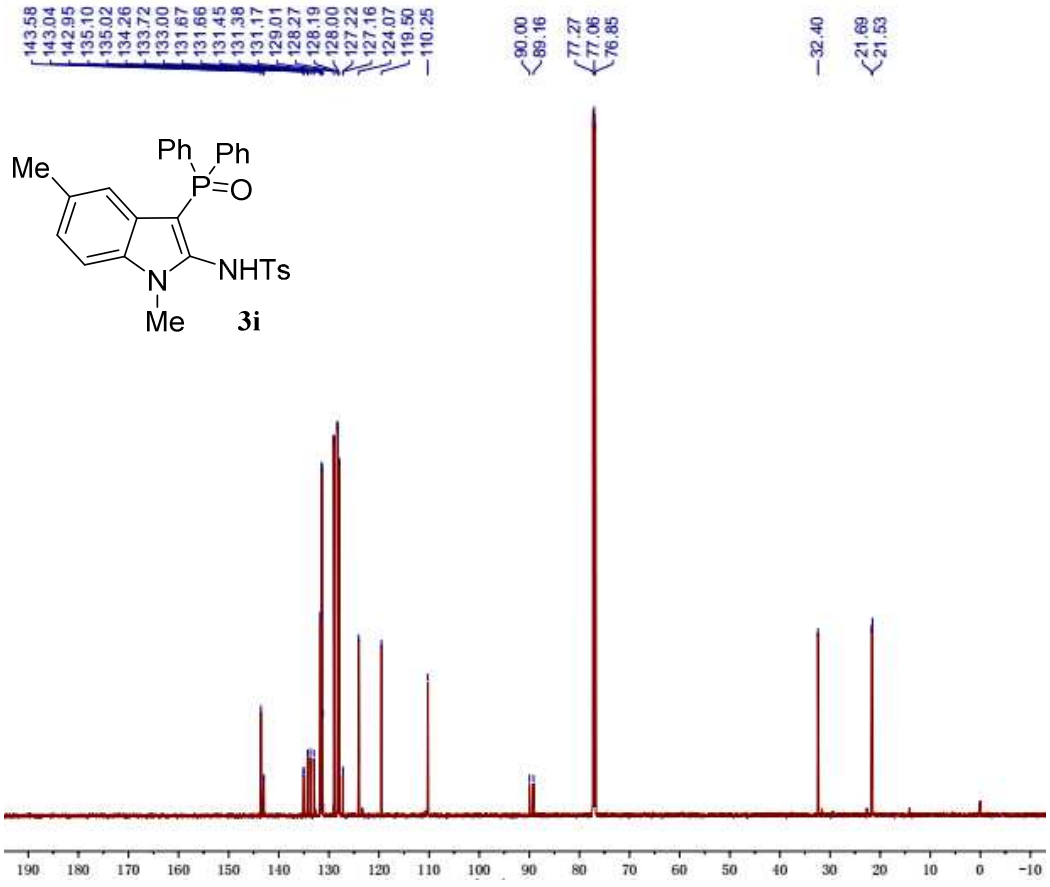
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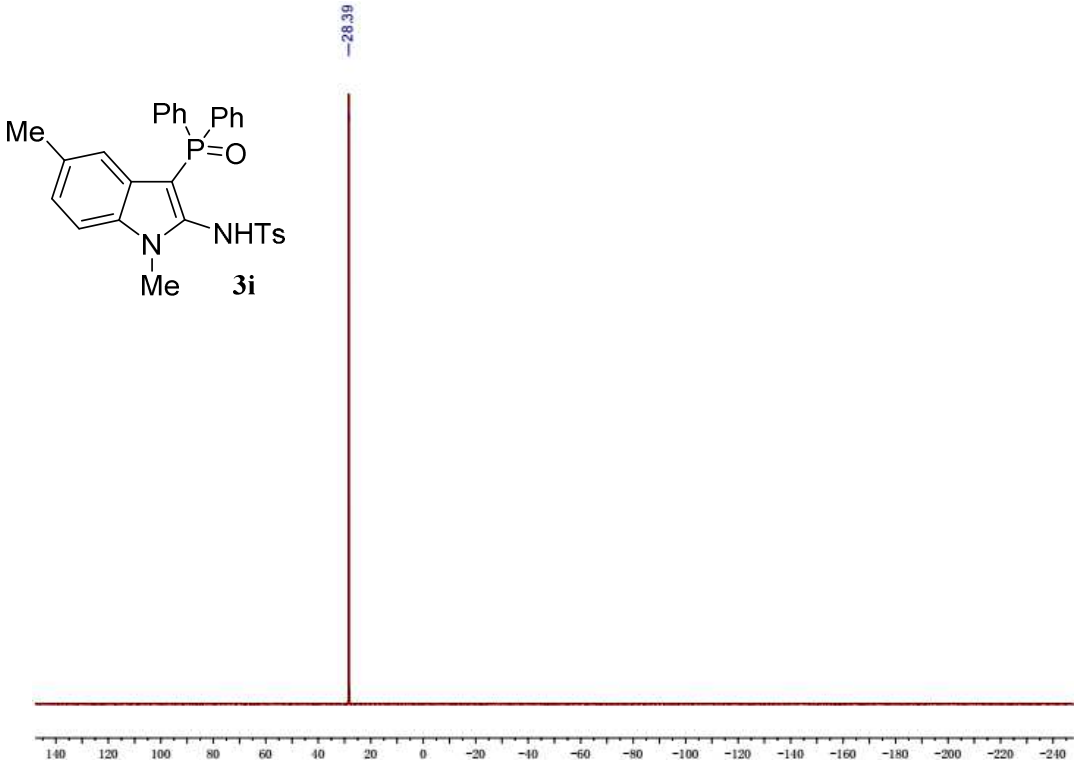
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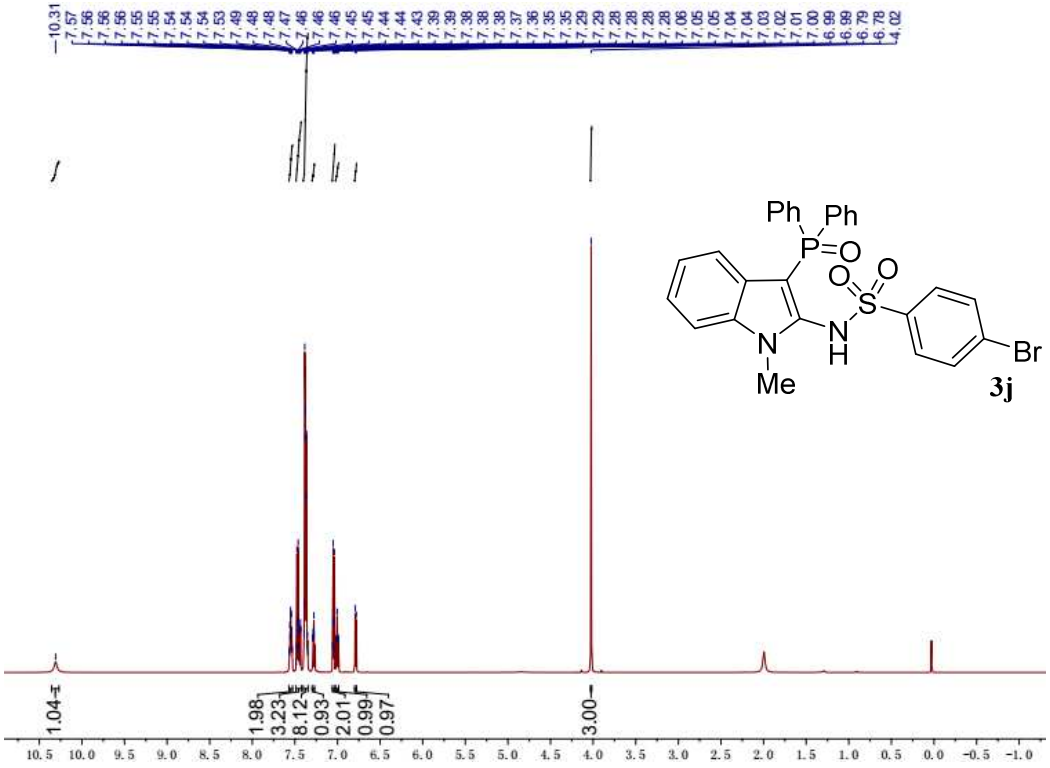
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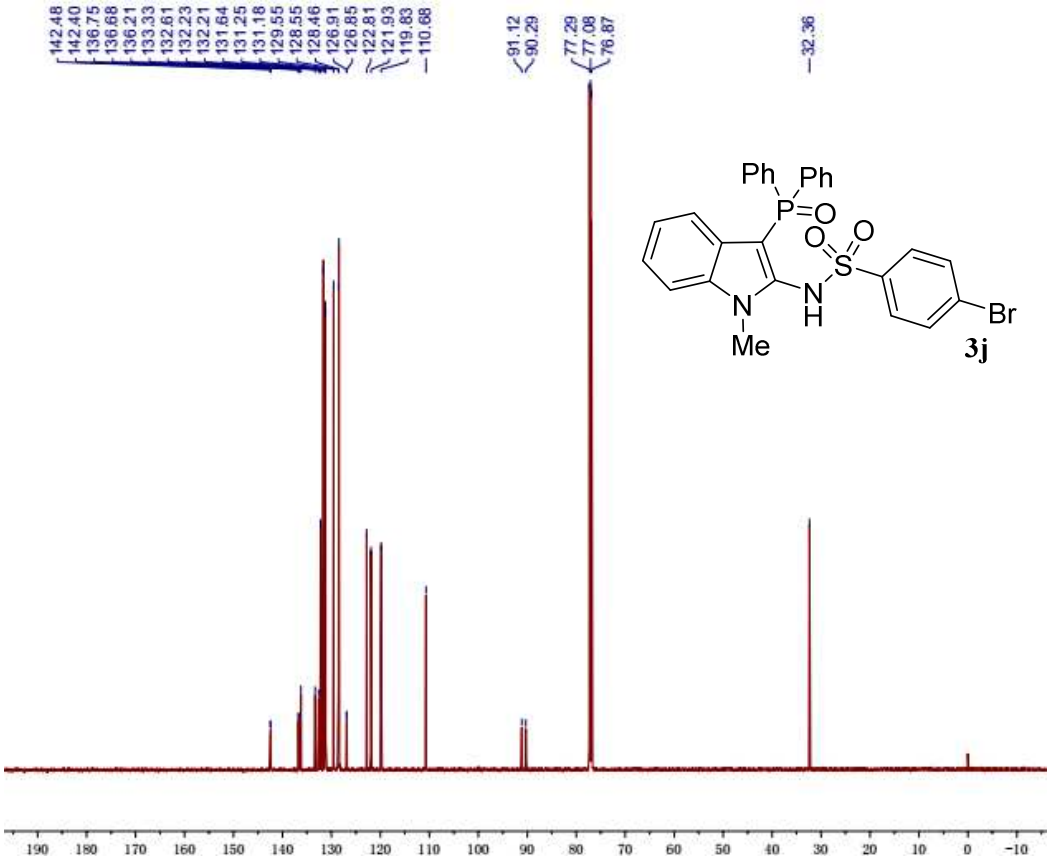
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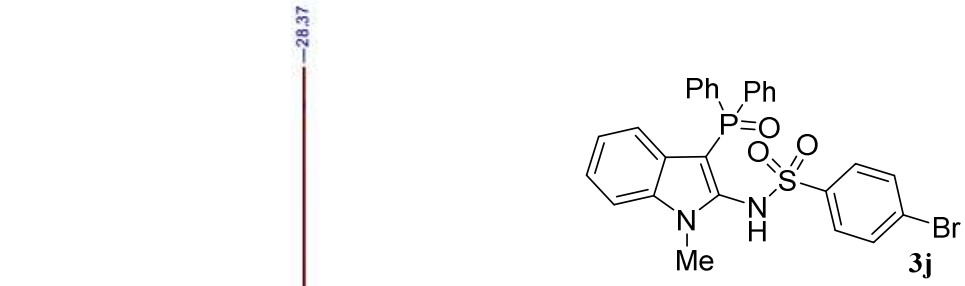
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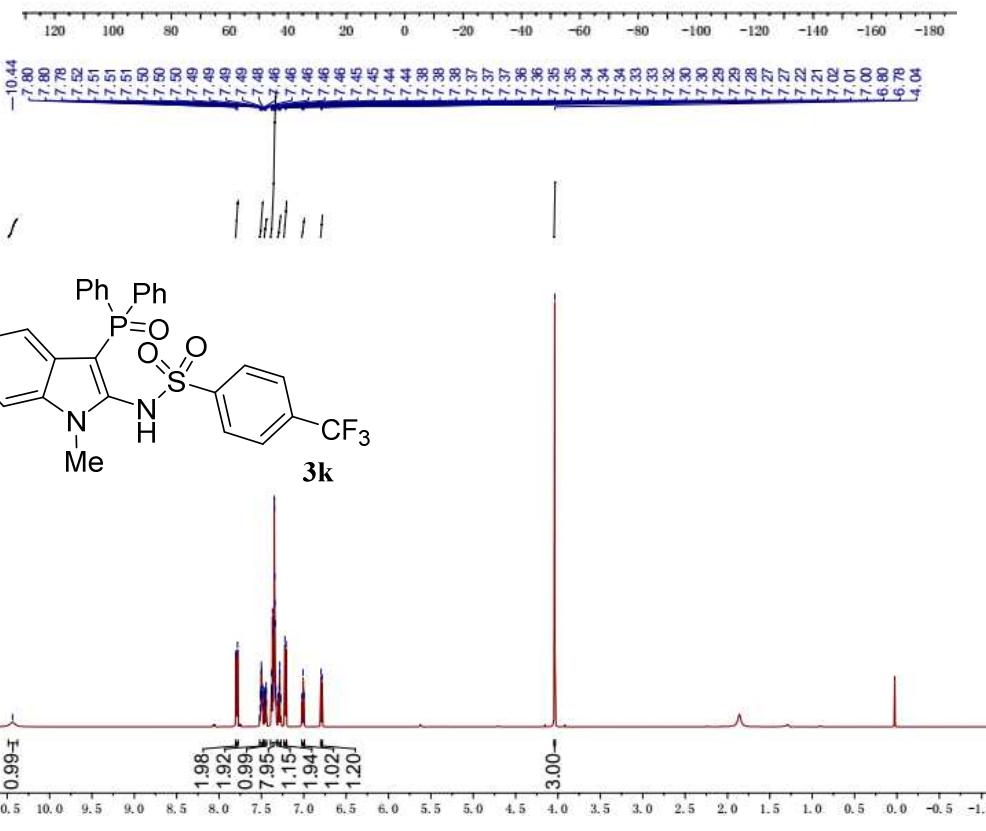
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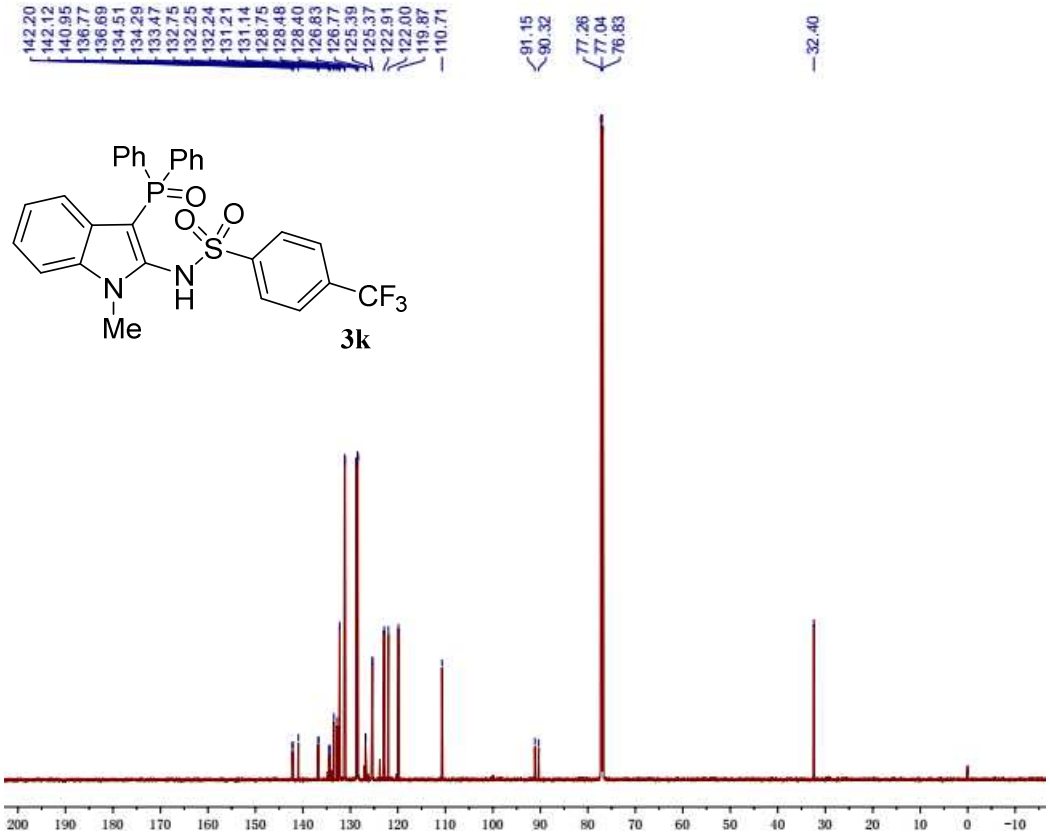
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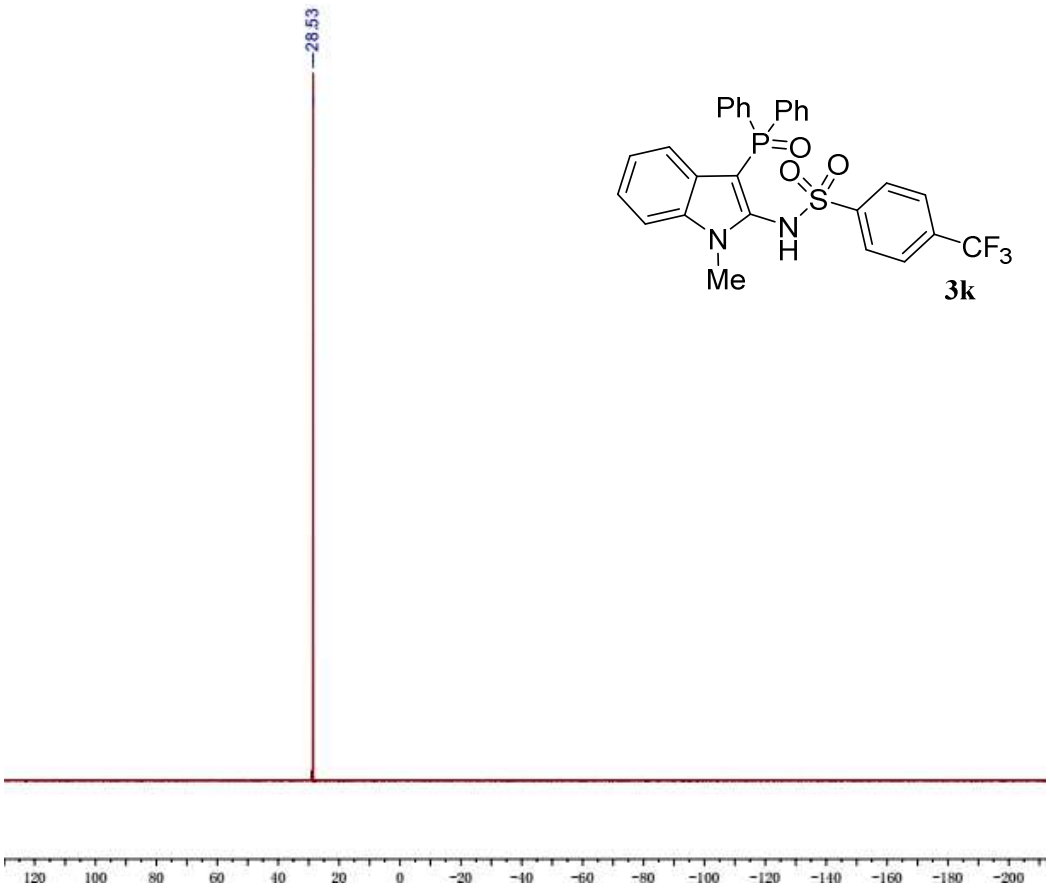
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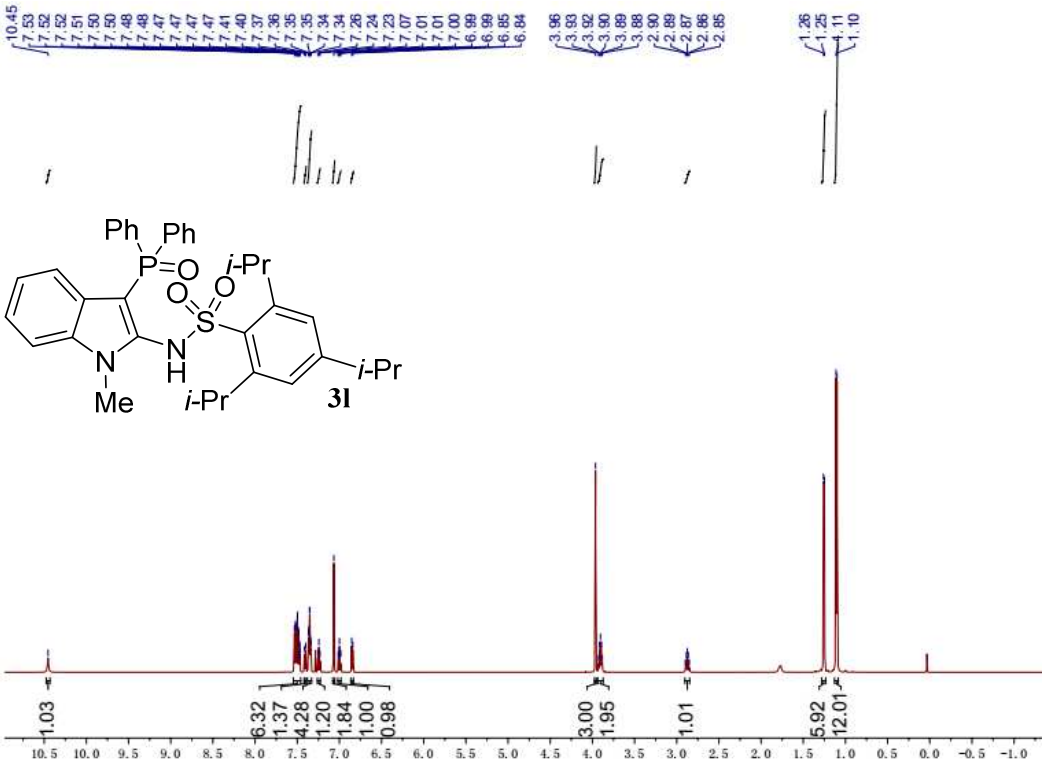
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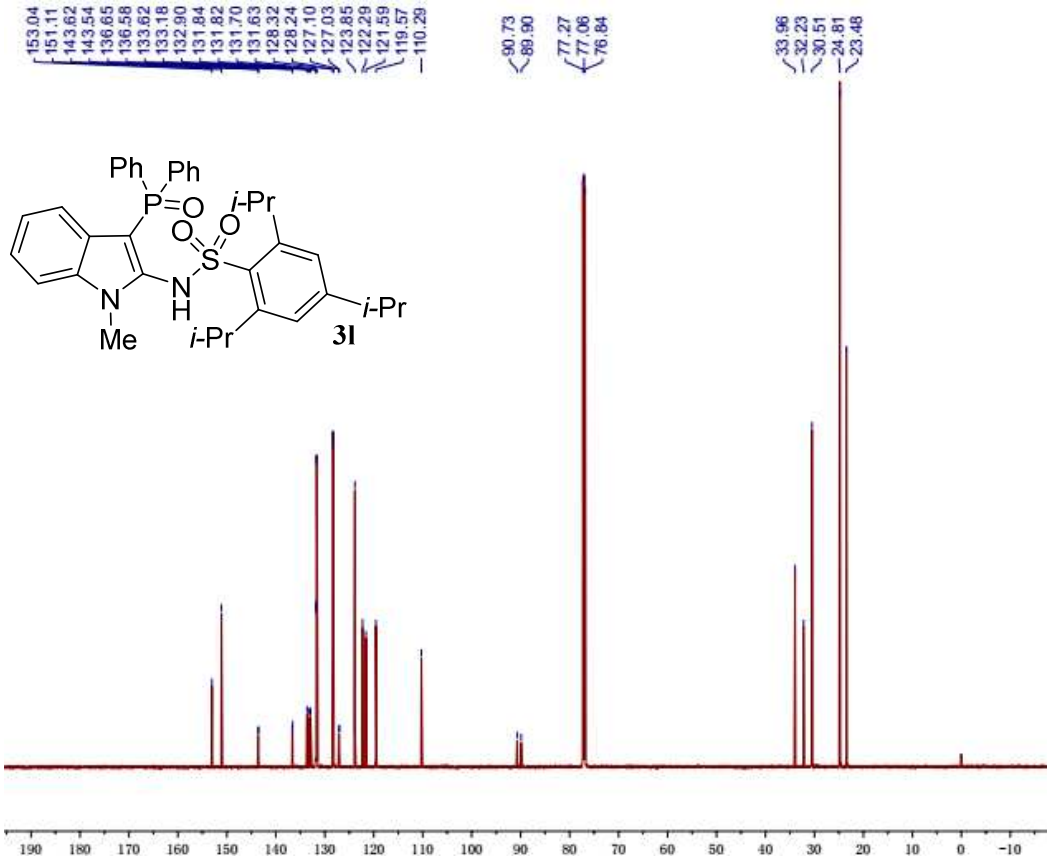
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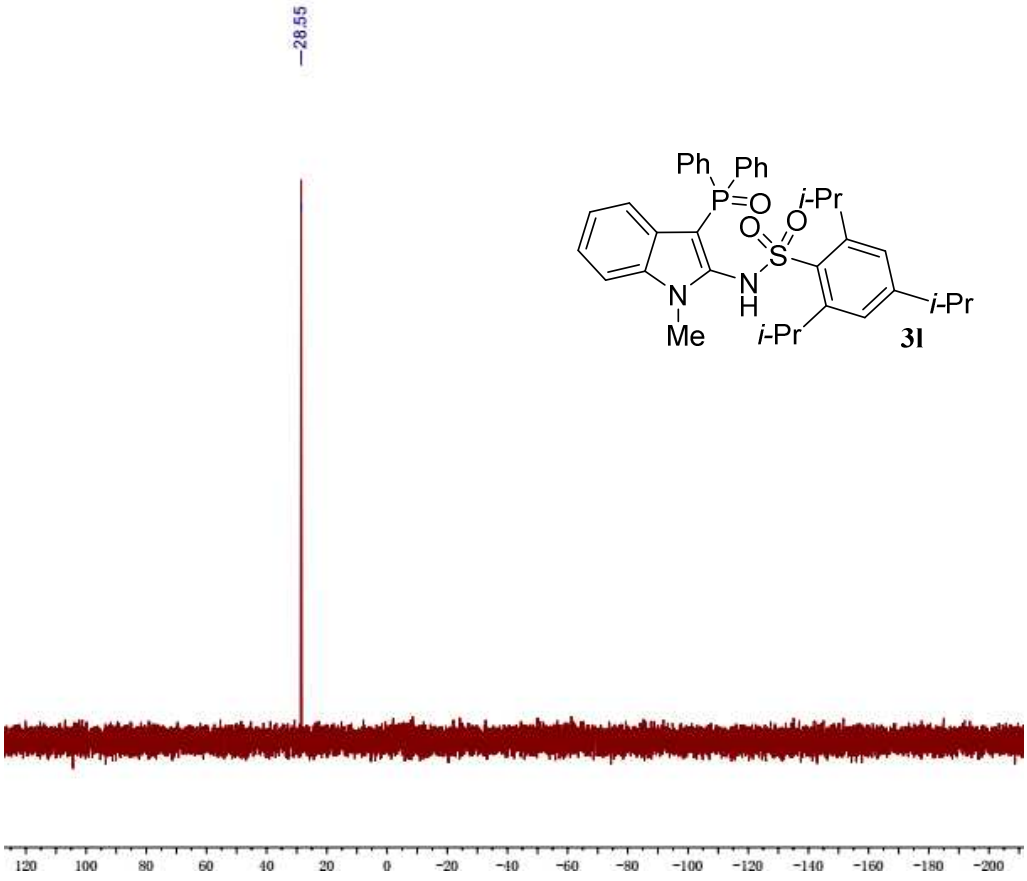
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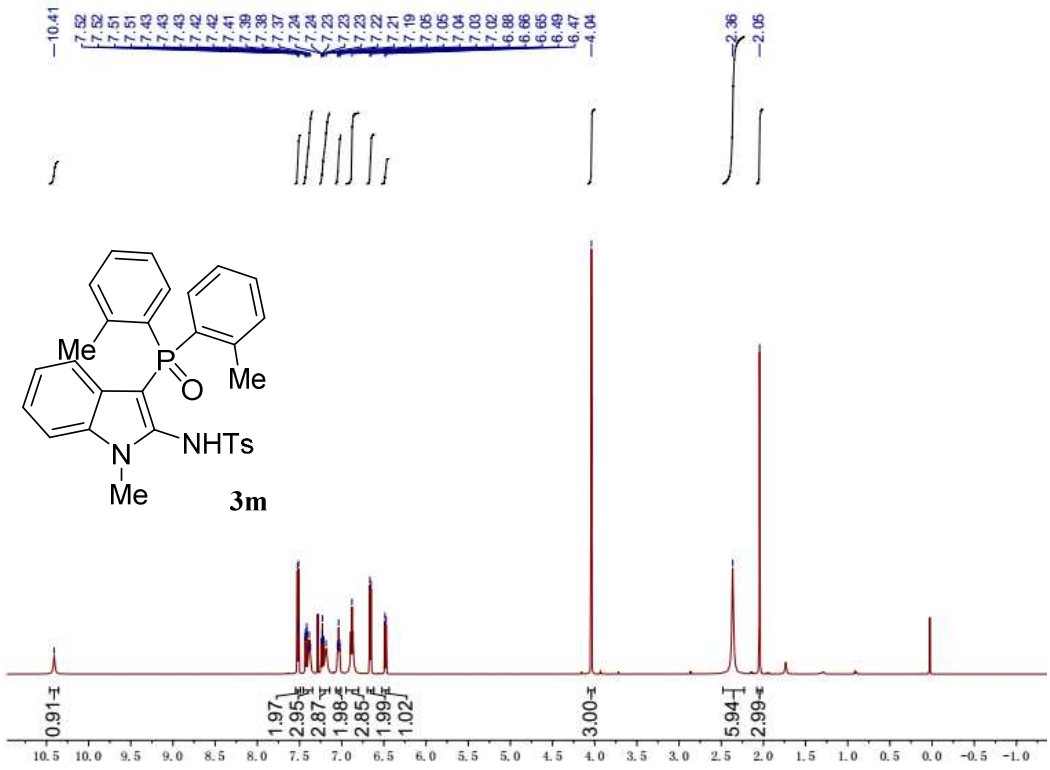
Me
i-Pr
3l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7.23
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7.19
7.05
7.05
7.04
7.03
7.02
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6.47
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2.05
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P
O
Me
NHTs
N
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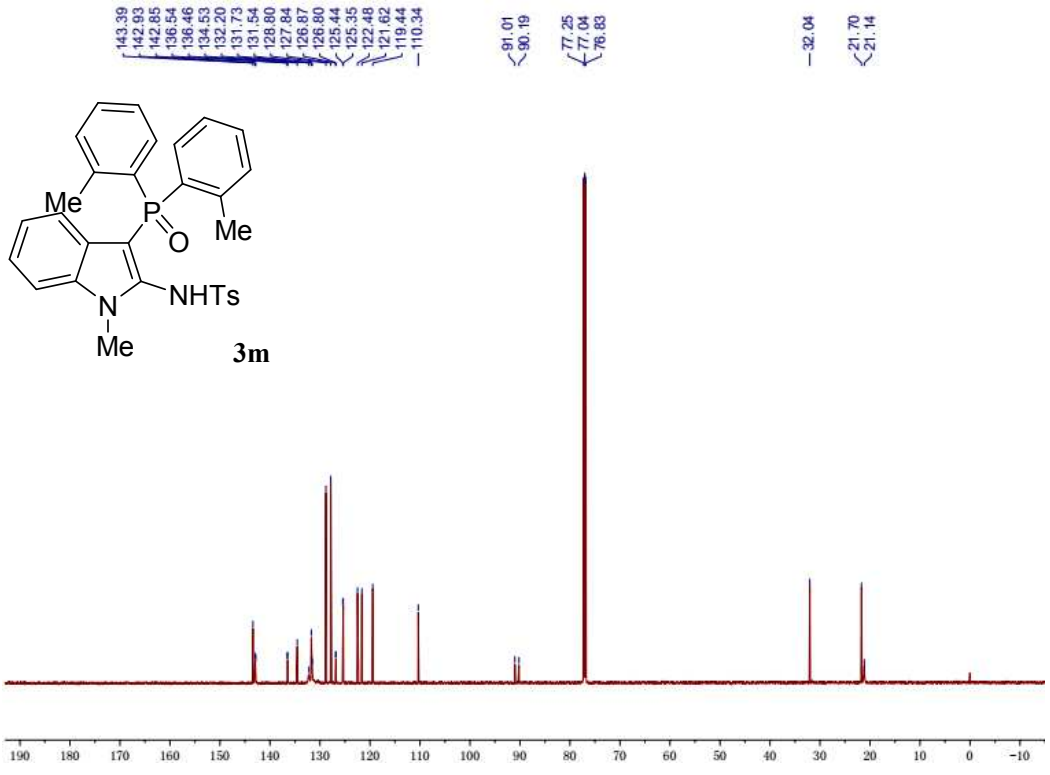
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21.14
Me
P
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Me
NHTs
N
Me
3m
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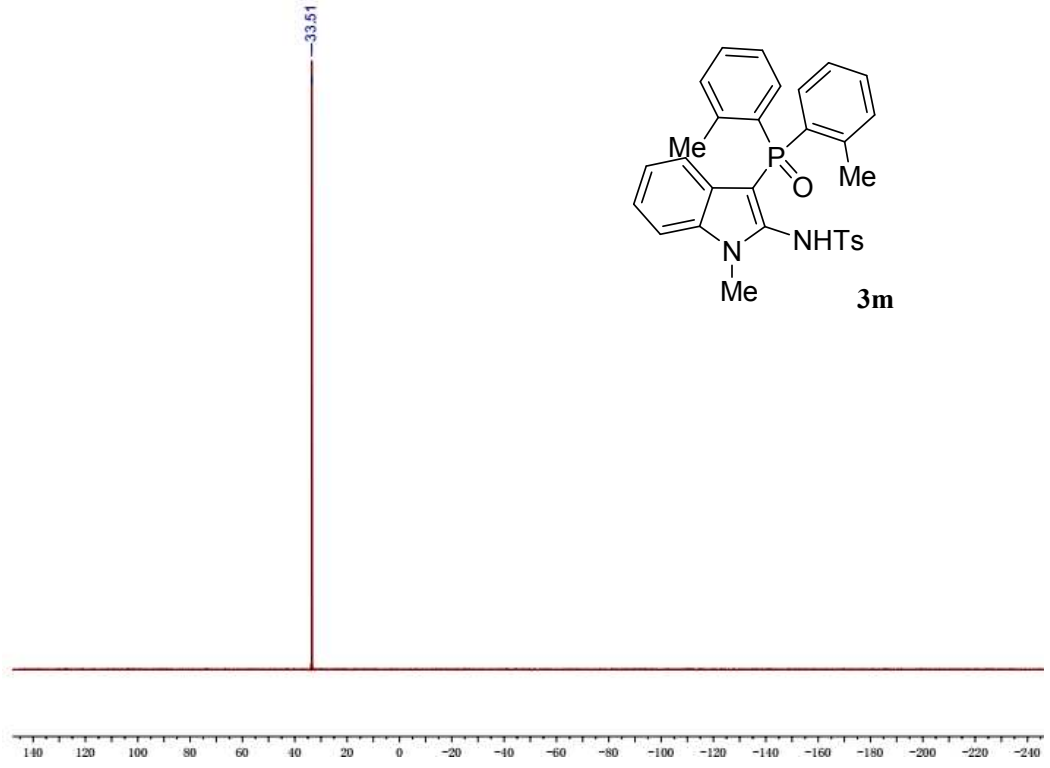
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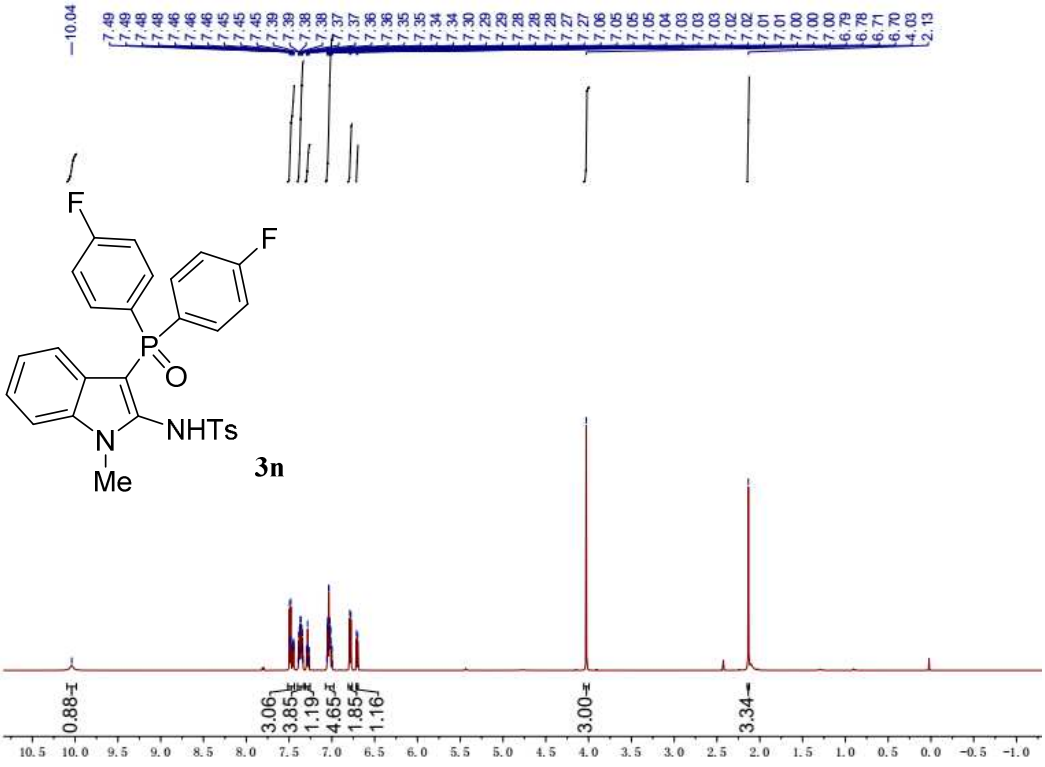
-240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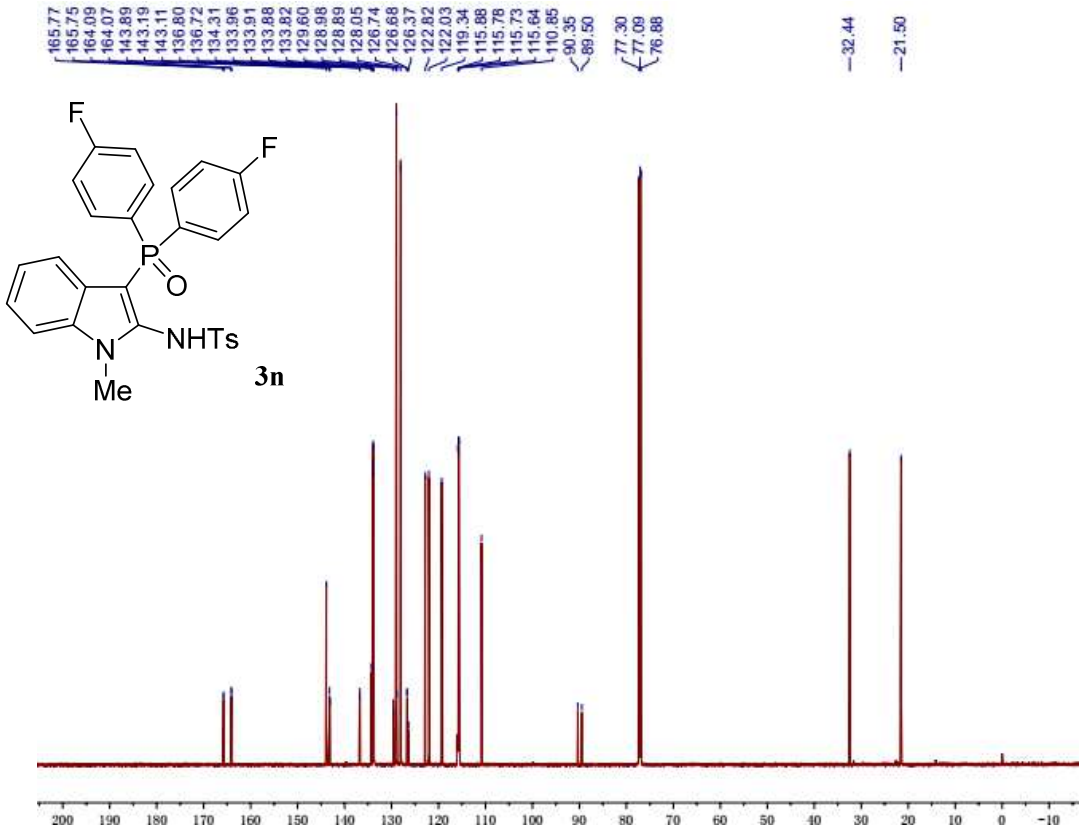
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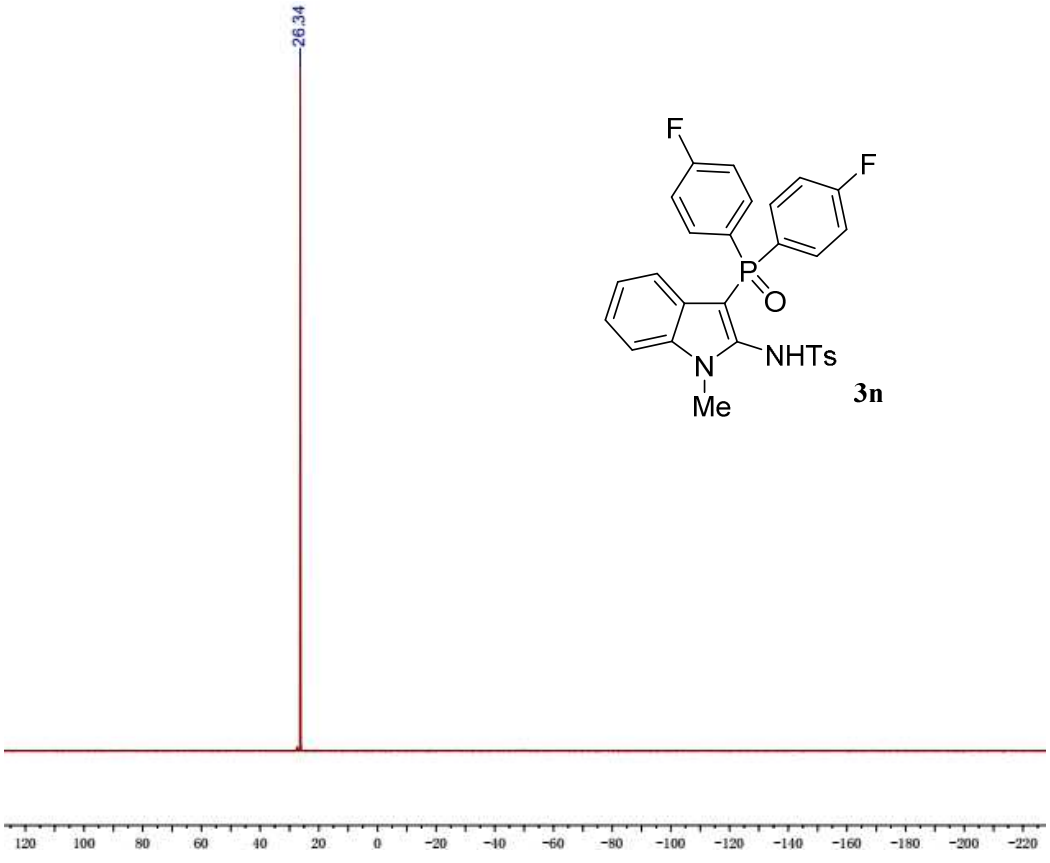
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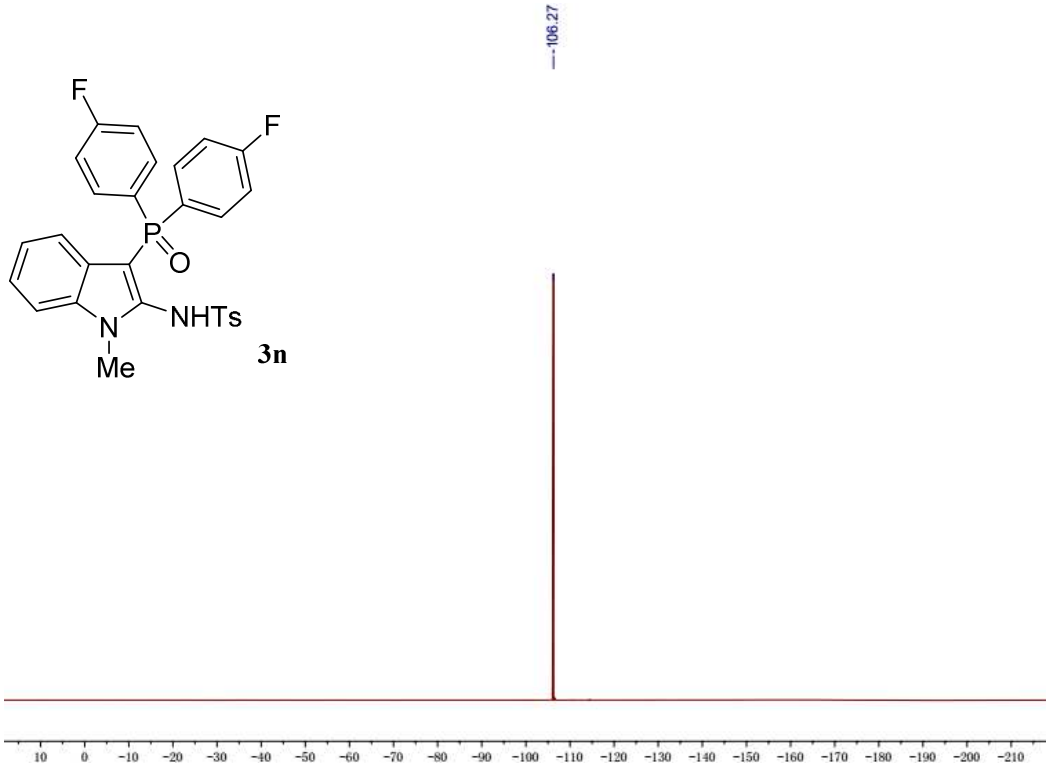
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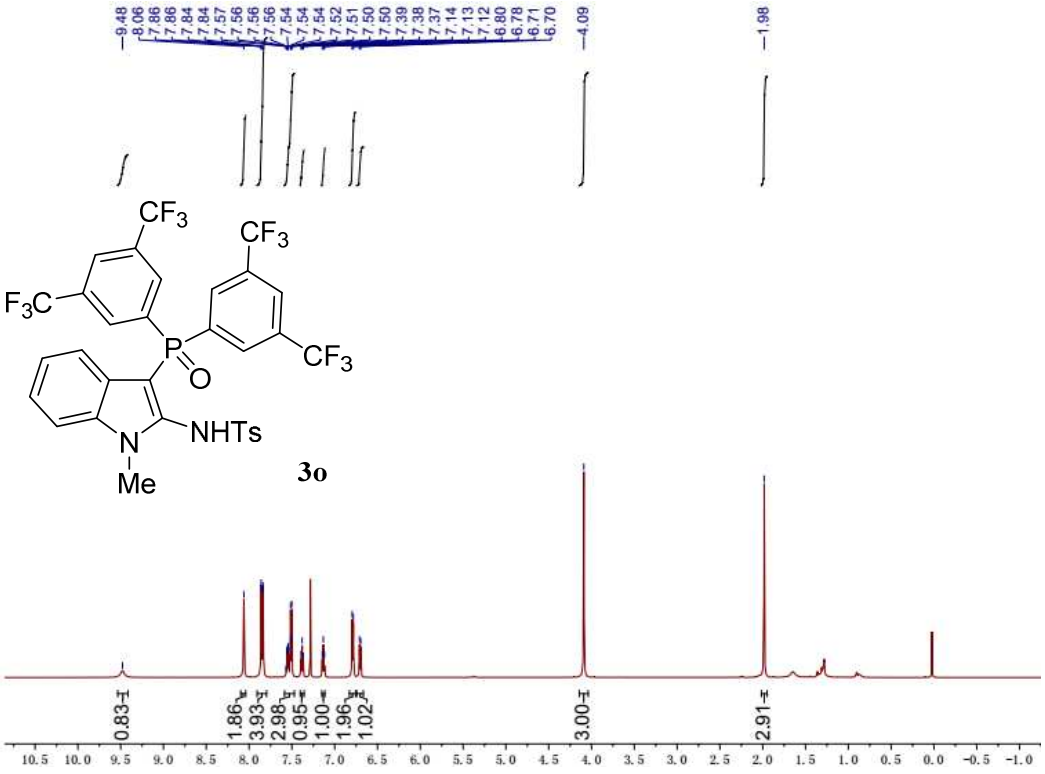
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7.51
7.50
7.50
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7.37
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7.13
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6.71
6.70
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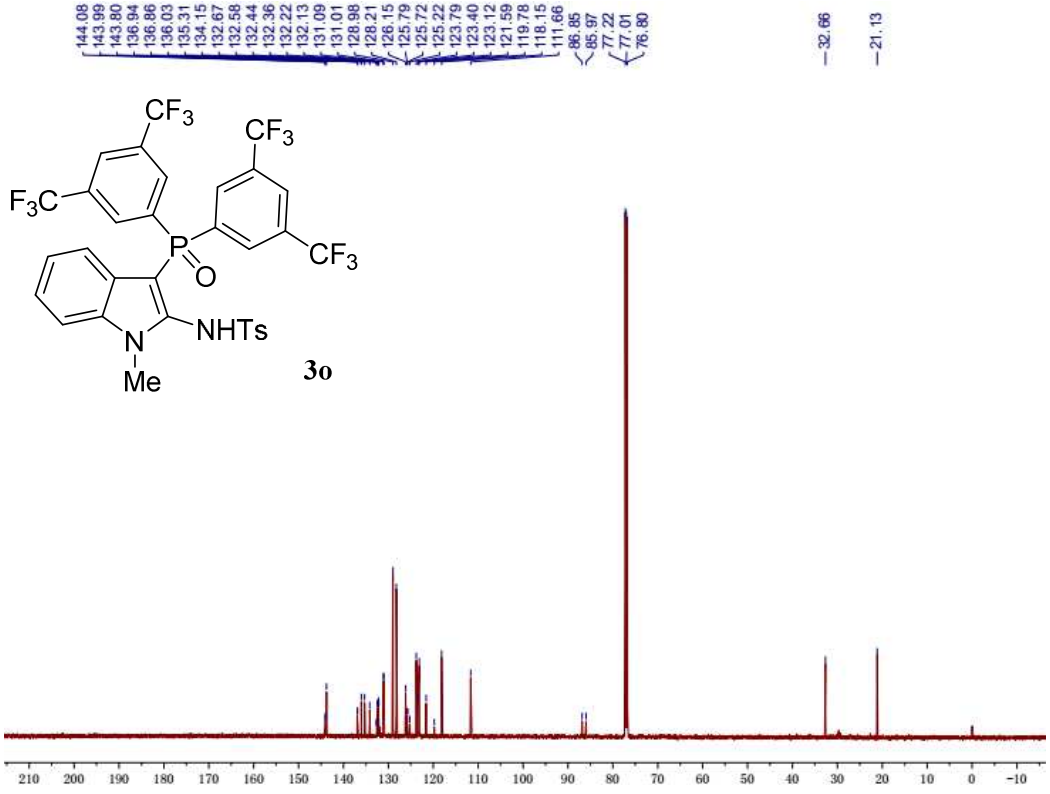
CF3
CF3
F3C
CF3
P
O
NHTs
N
Me
3o
0.83
1.86
3.93
2.98
0.95
1.00
1.96
1.02
3.00
2.91
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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86.85
85.97
77.22
77.01
76.80
32.66
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CF3
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3o
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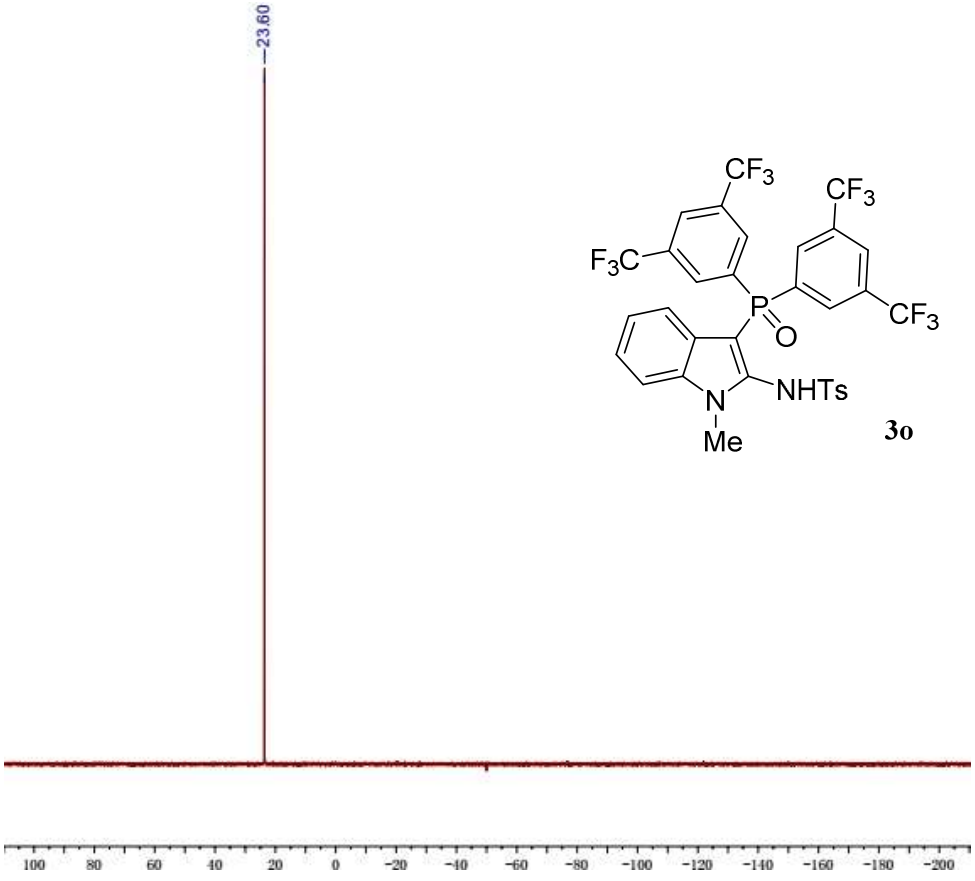
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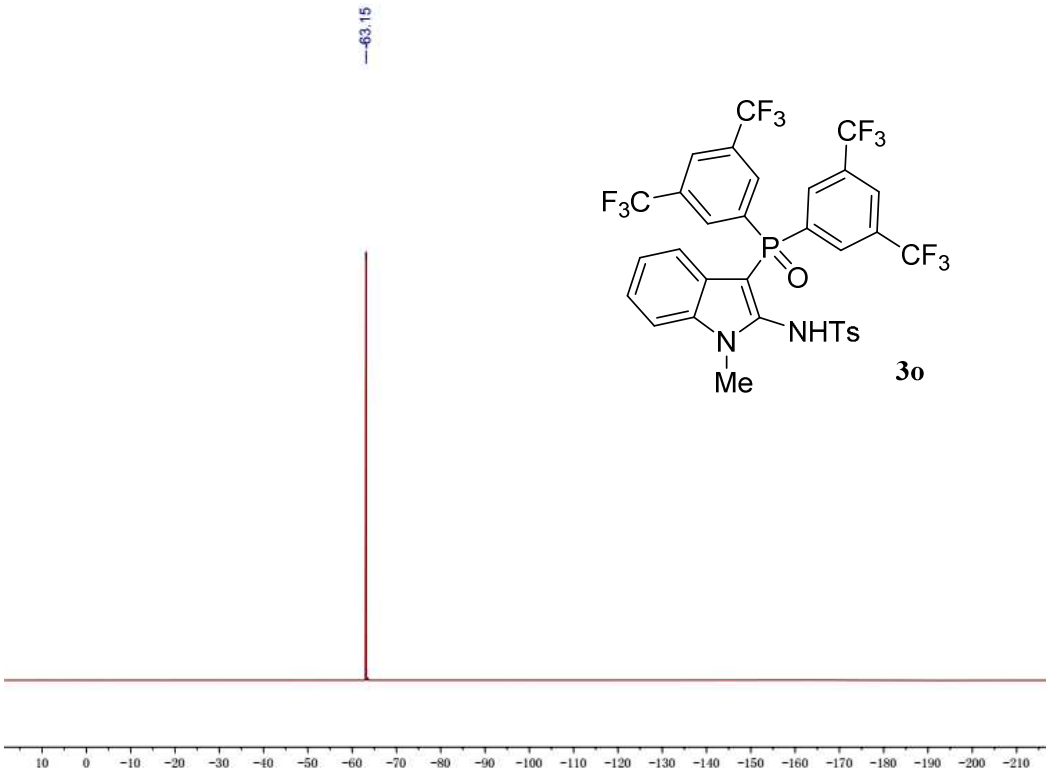
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3o
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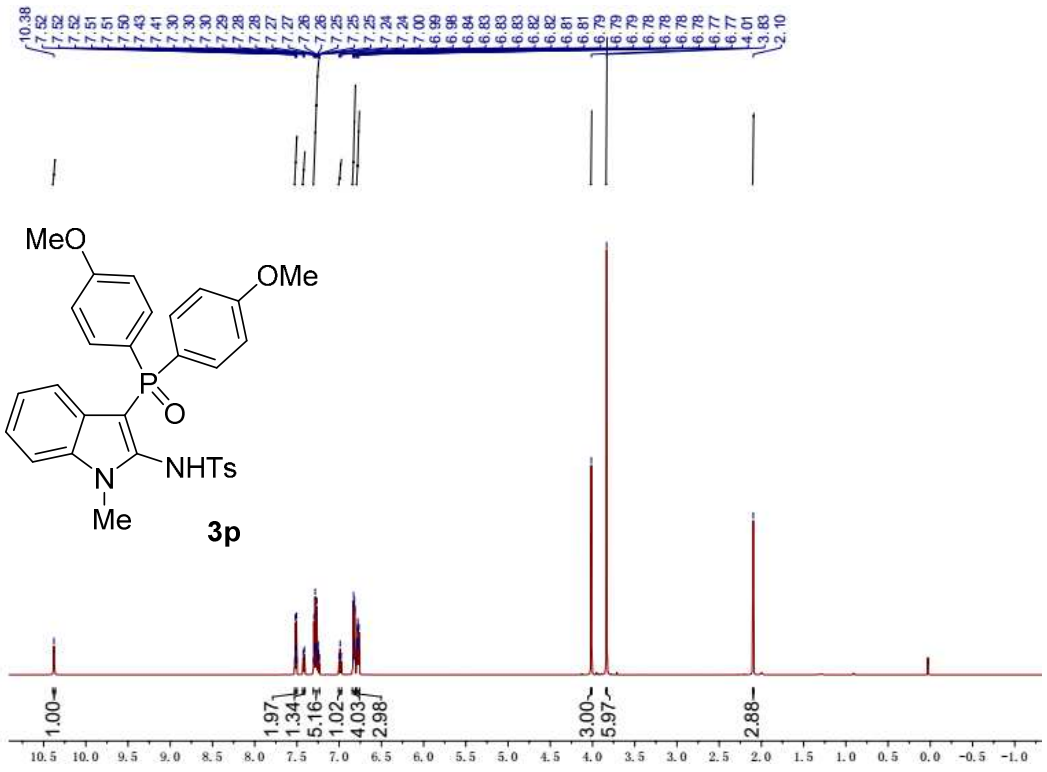
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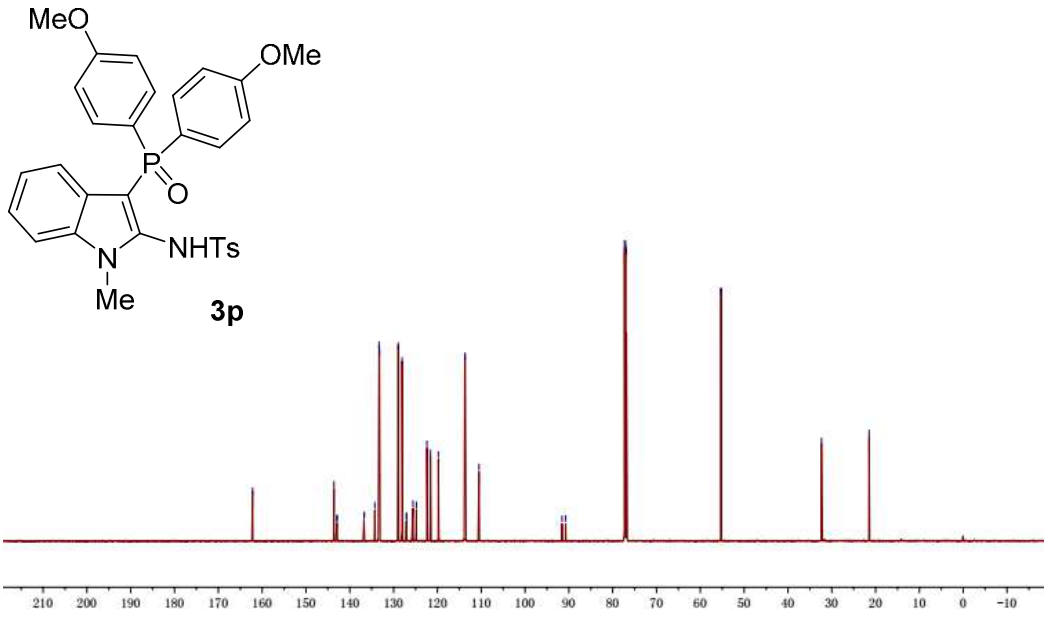
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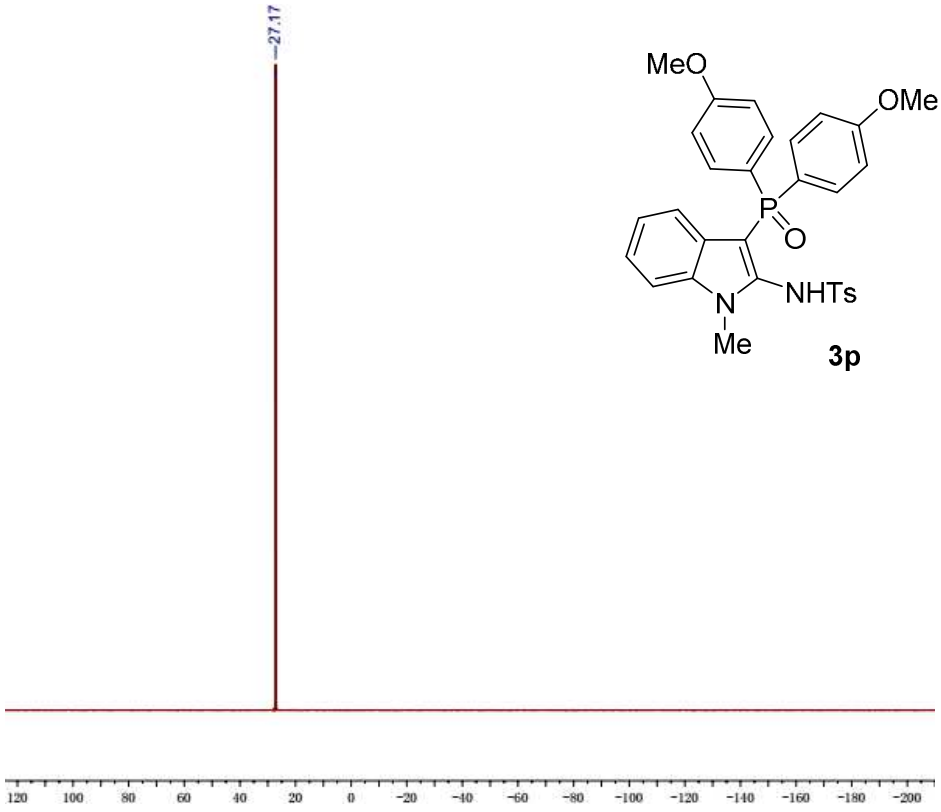
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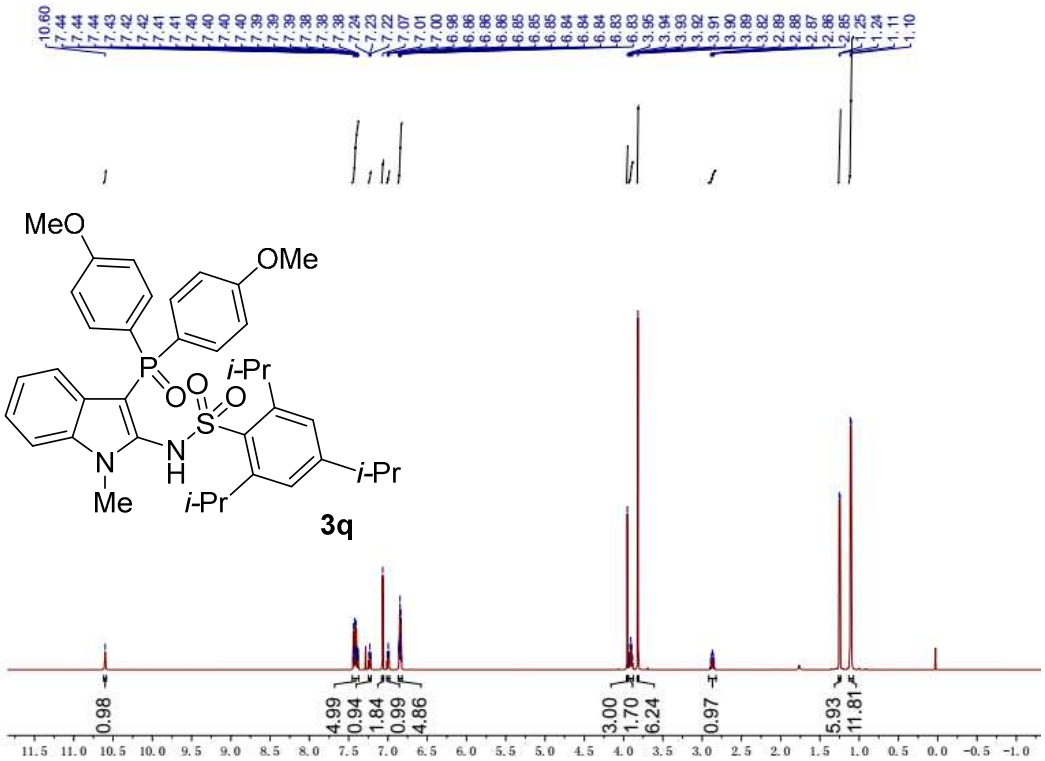
Me
3p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N
H
i-Pr
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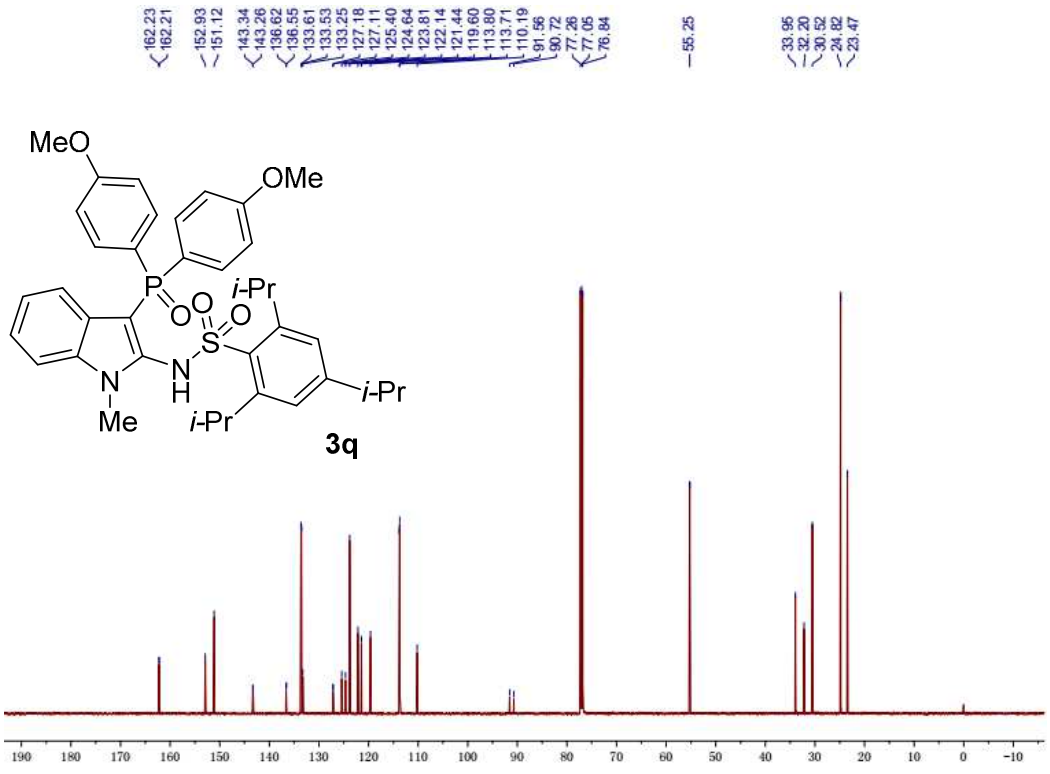
Me
i-Pr
3q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110.19
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90.72
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77.05
76.84
55.25
33.95
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24.82
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OMe
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N
H
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Me
i-Pr
i-Pr
i-Pr
3q
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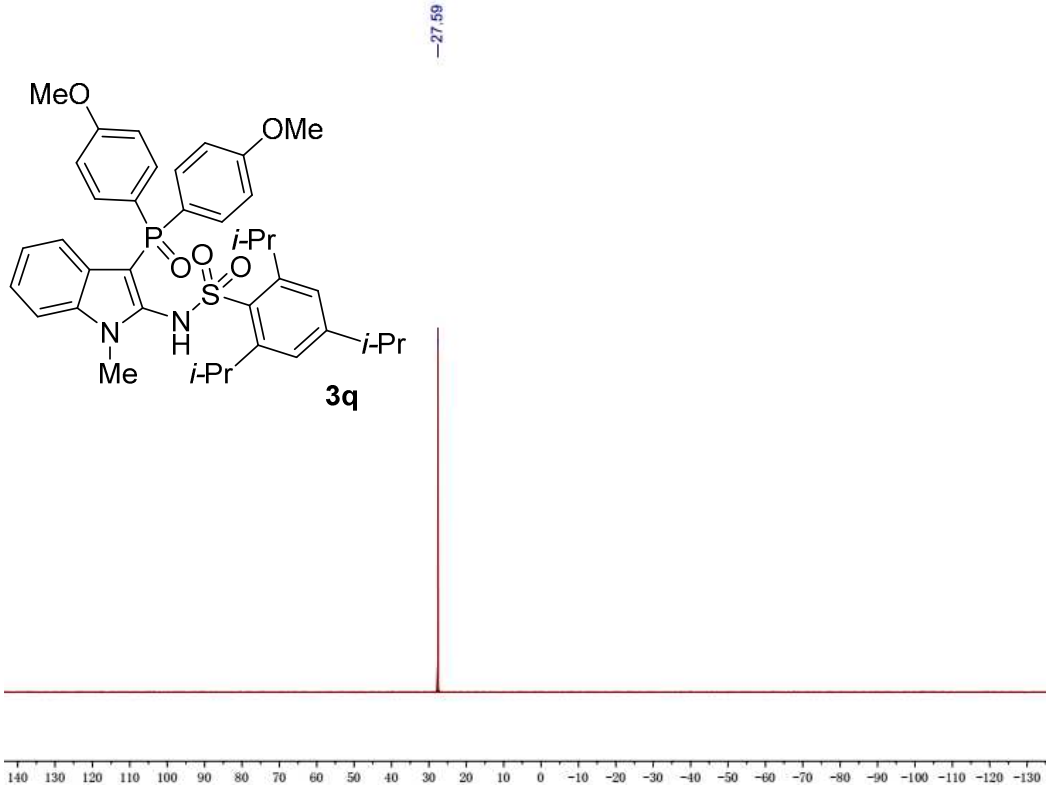
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3q
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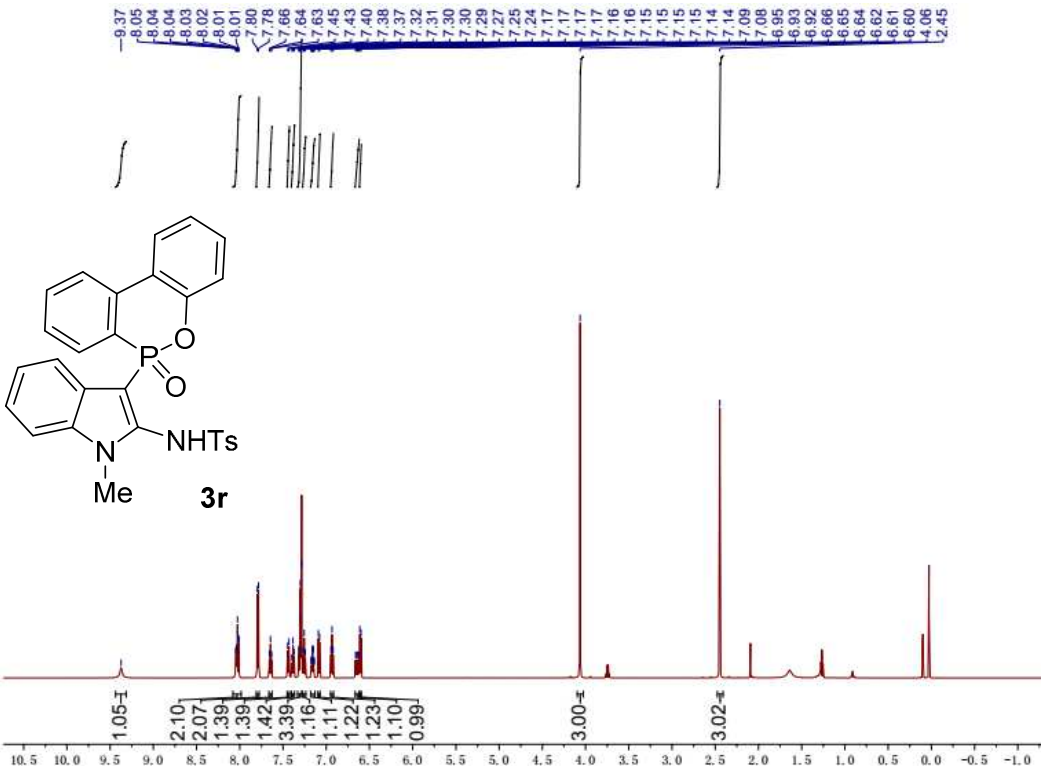
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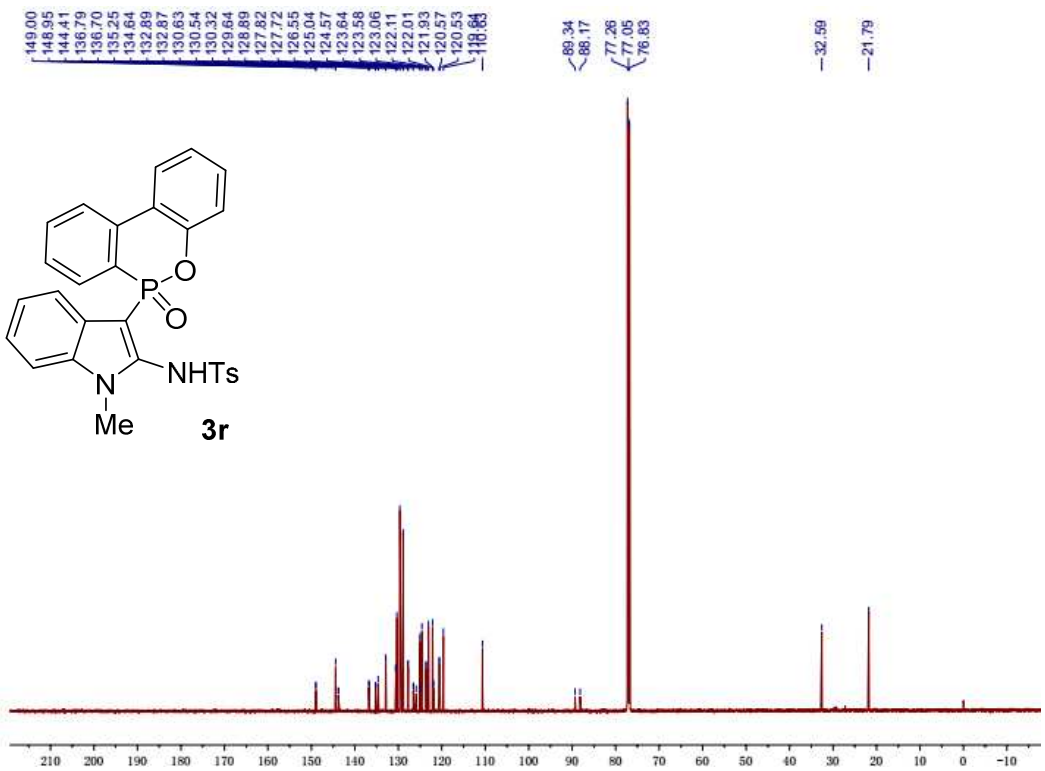
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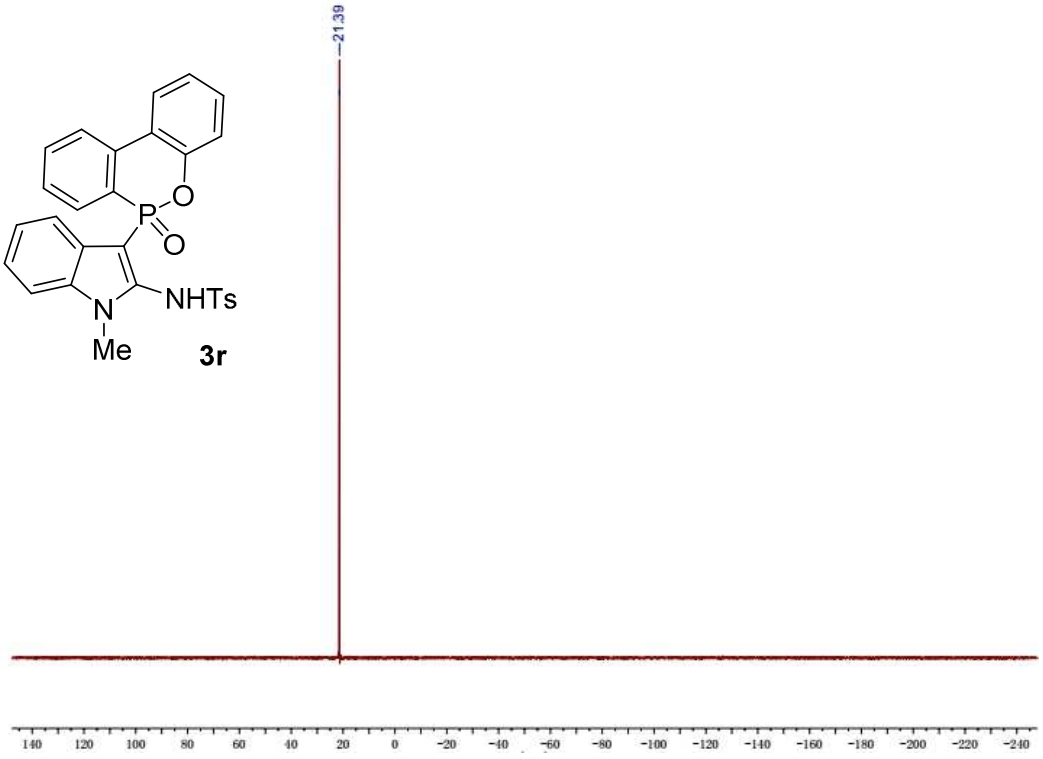
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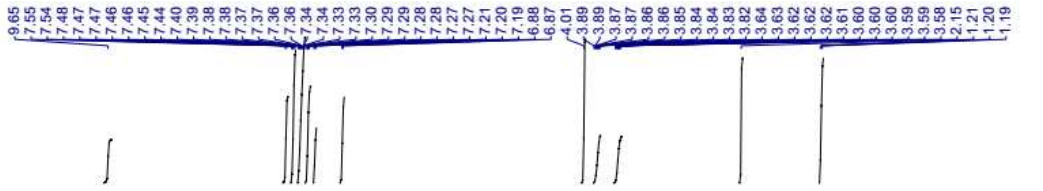
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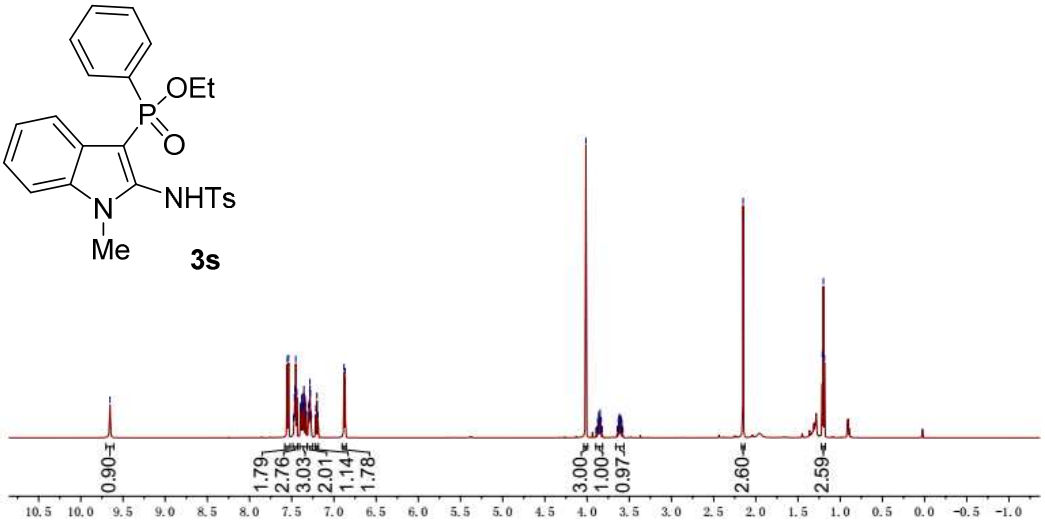
4.01 3.89 3.89 3.87 3.87 3.86 3.86 3.85 3.84 3.84 3.83 3.82 3.64 3.63 3.62 3.62 3.62 3.61 3.60 3.60 3.60 3.59 3.59 3.58 2.15 1.21 1.20 1.19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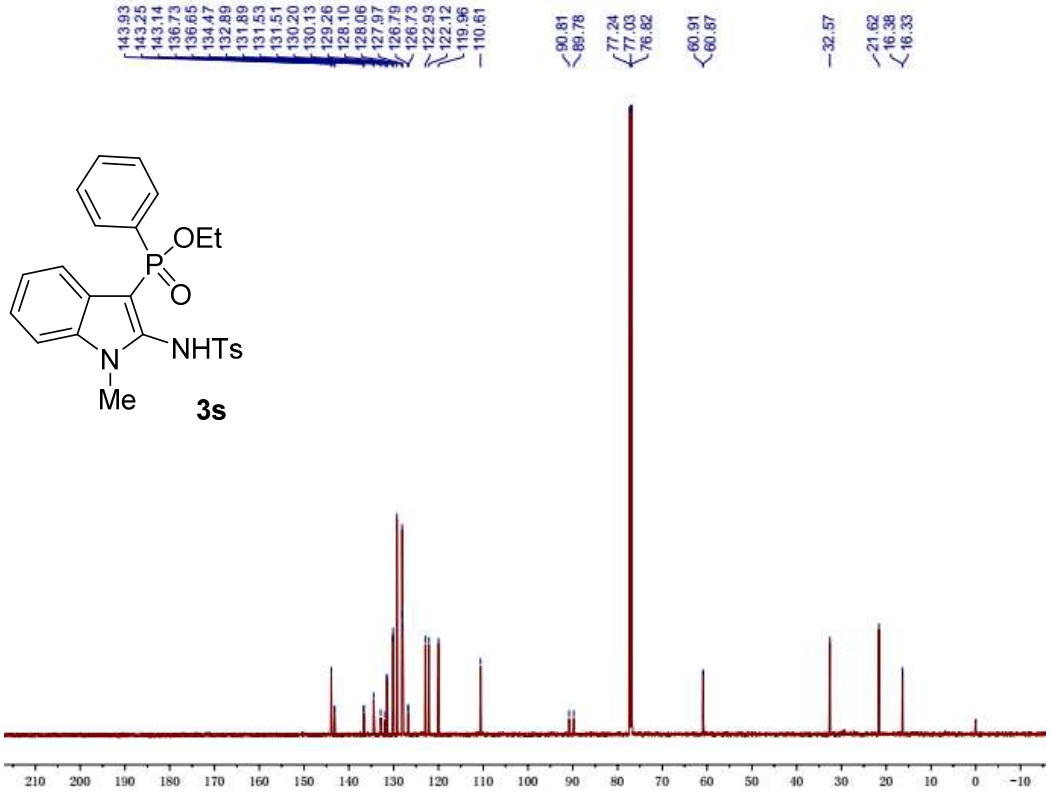
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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77.24
77.03
76.82
60.91
60.87
32.57
21.62
16.38
16.33
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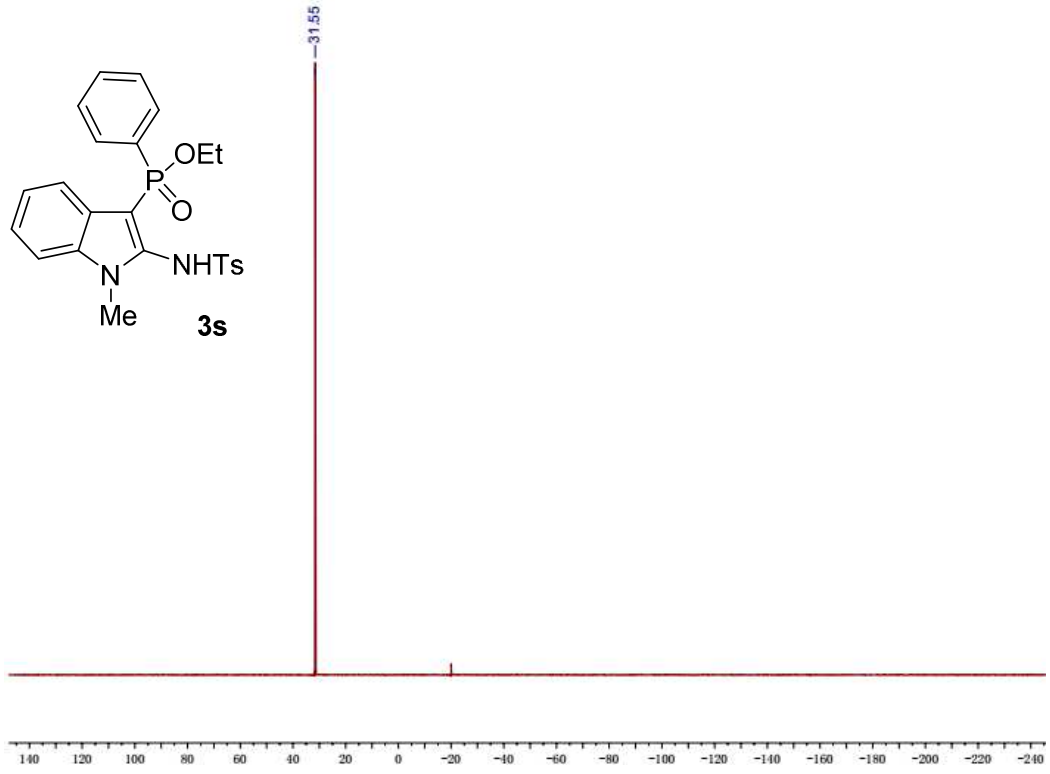
P
O
NHTs
N
Me
3s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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N
Me
3s
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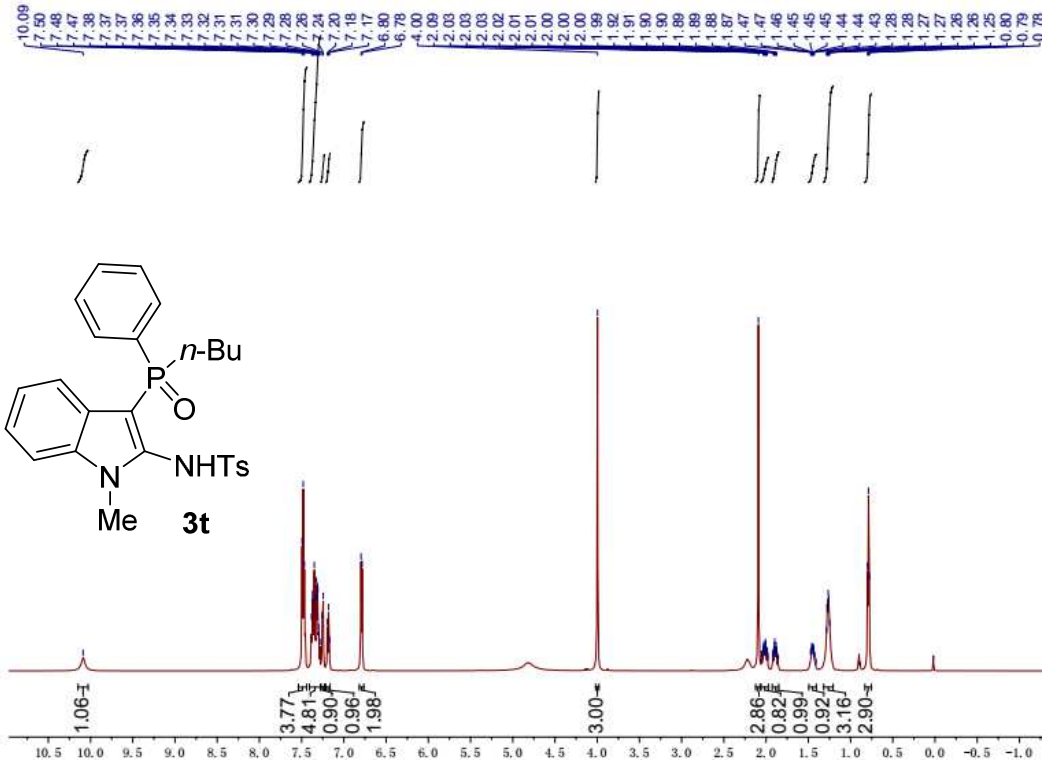
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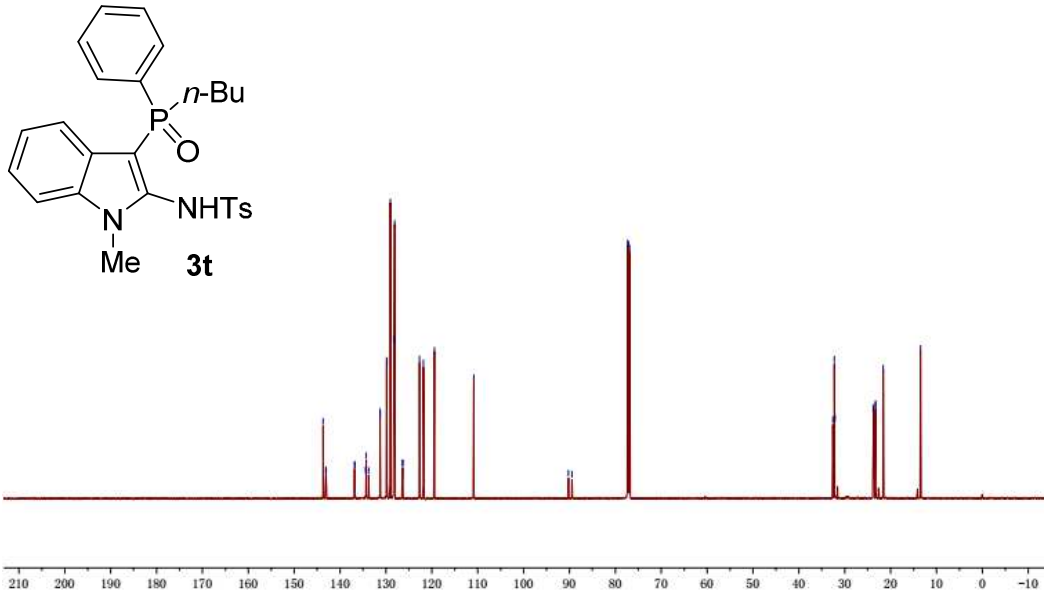
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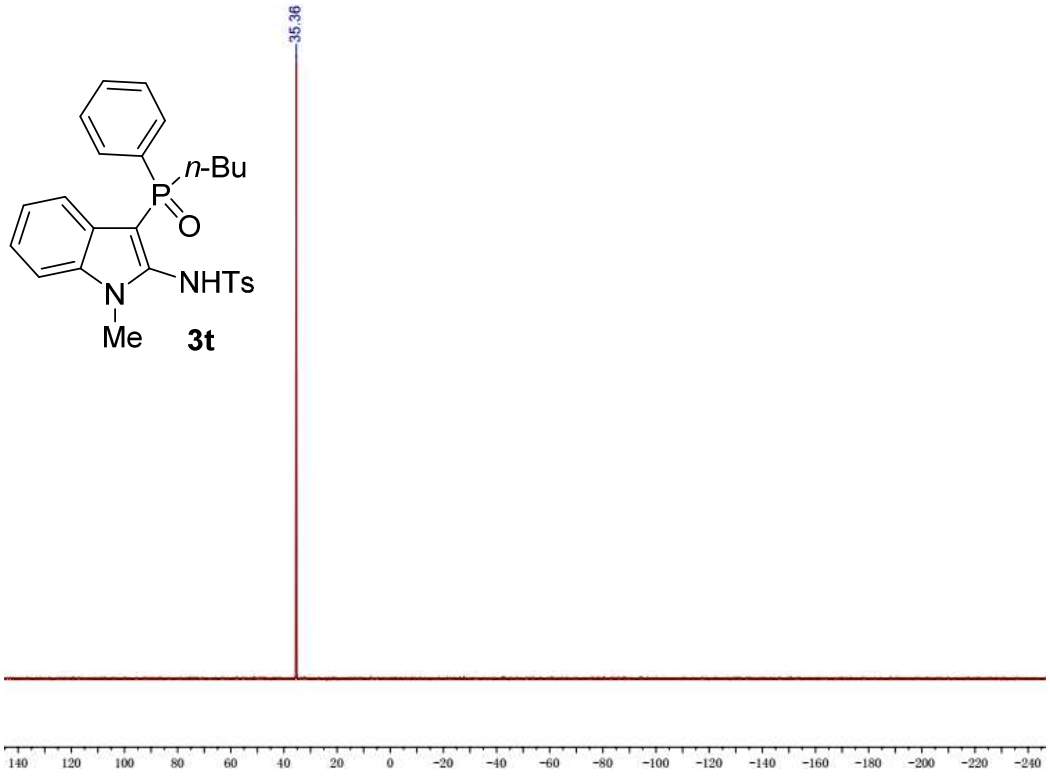
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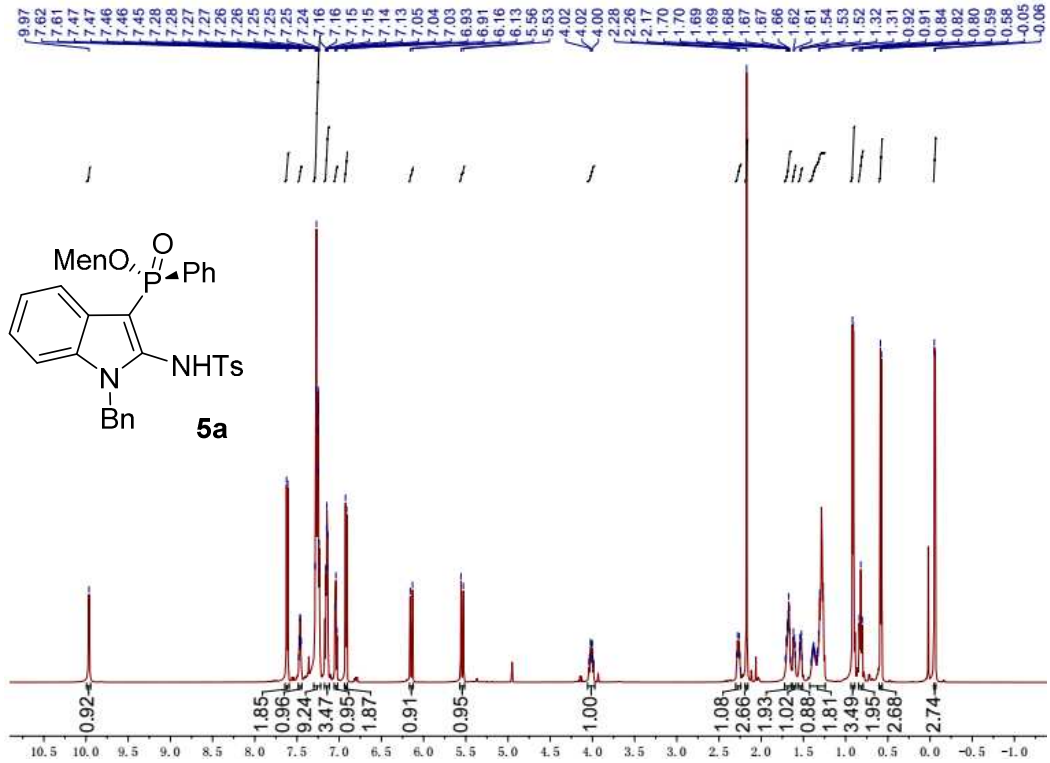
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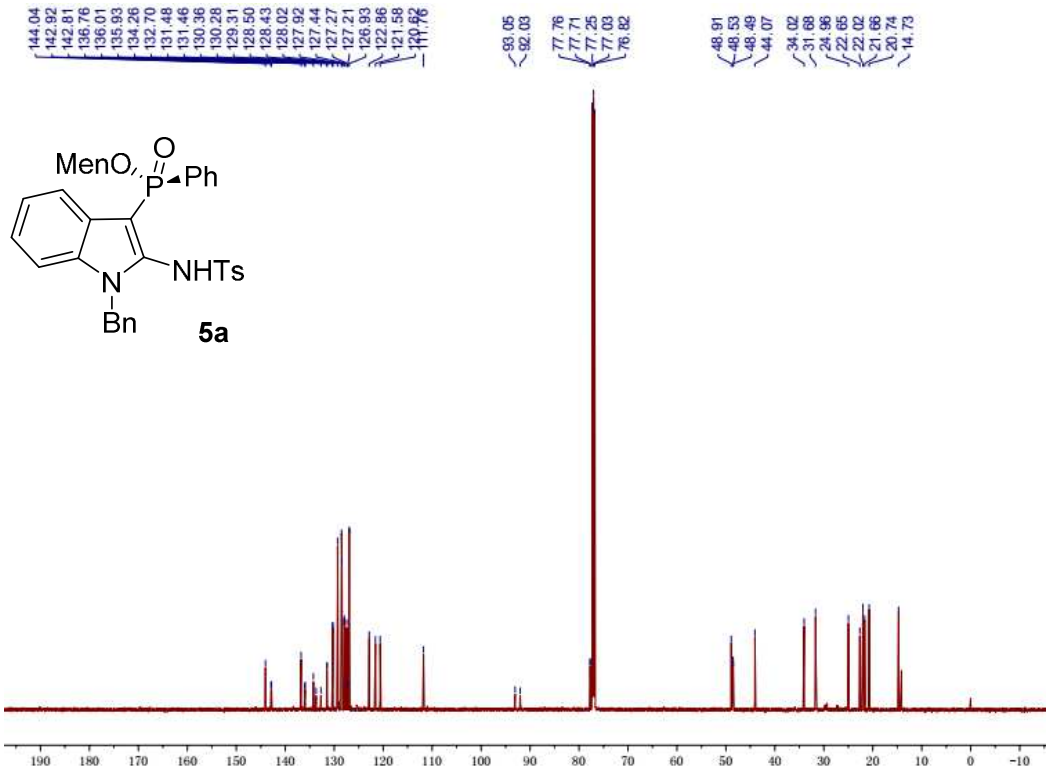
MenO
O
P
Ph
NHTs
N
Bn
5a
0.92 1.85 0.96 9.24 3.47 0.95 1.87 0.91 0.95 1.00 1.08 2.66 1.93 1.02 0.88 1.81 3.49 1.95 2.68 2.74
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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31.68
24.96
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22.02
21.66
20.74
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Bn
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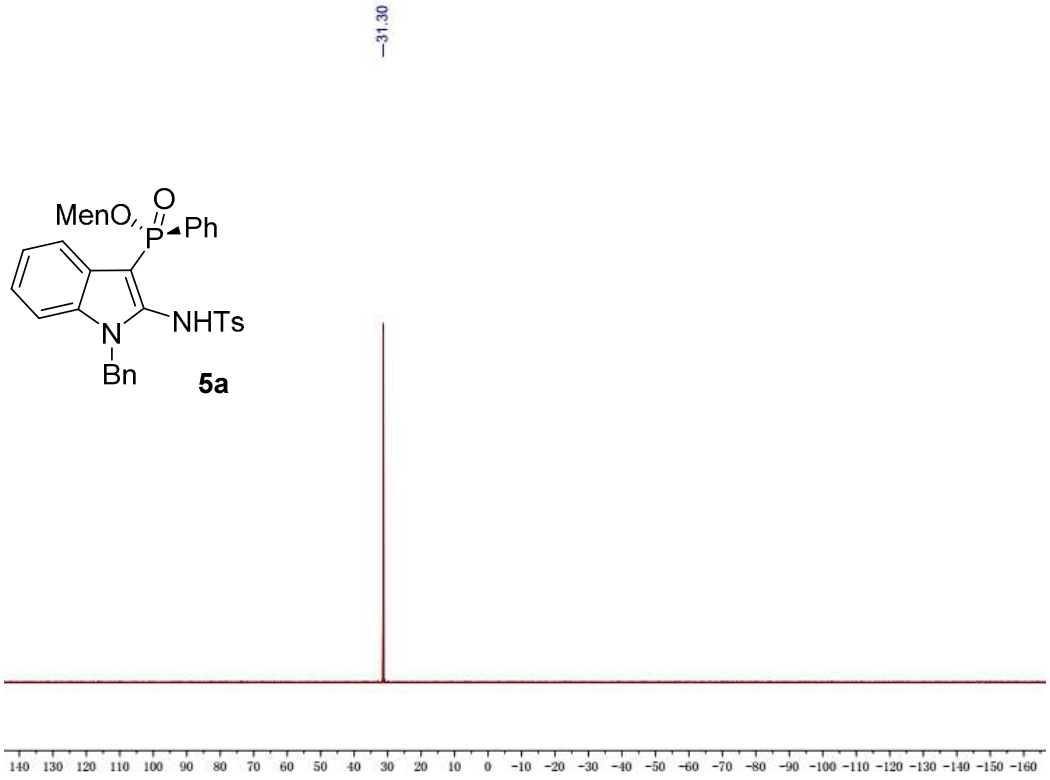
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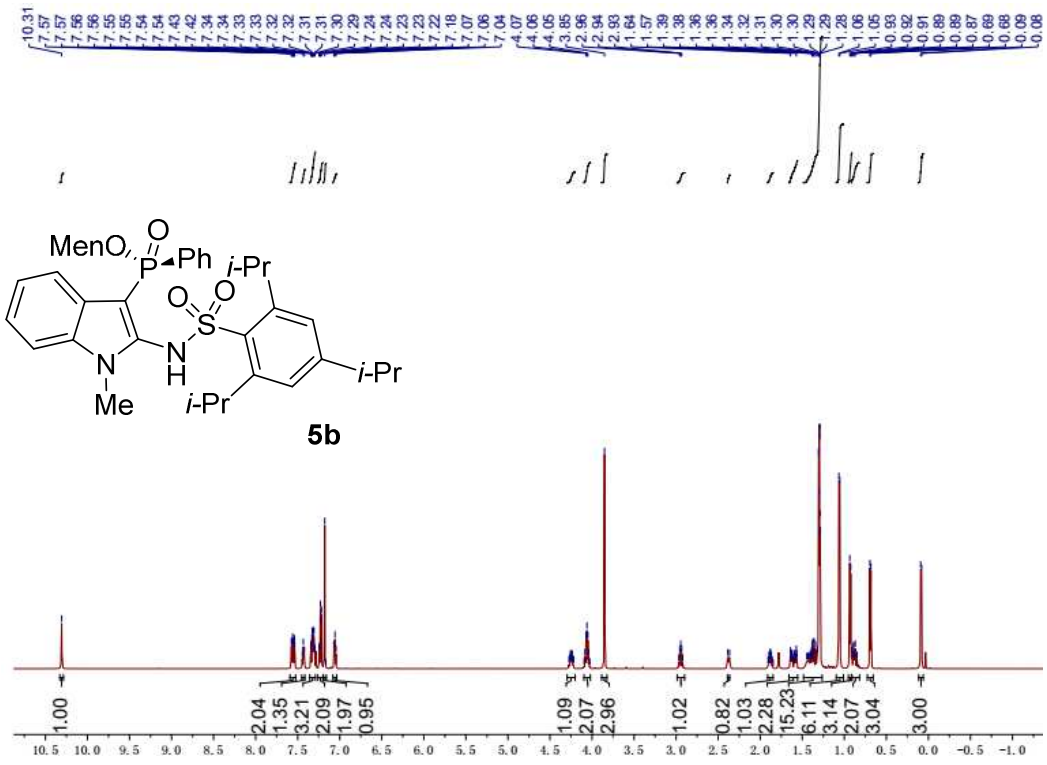
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Me
i-Pr
i-Pr

5b

MenO
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Ph
i-Pr
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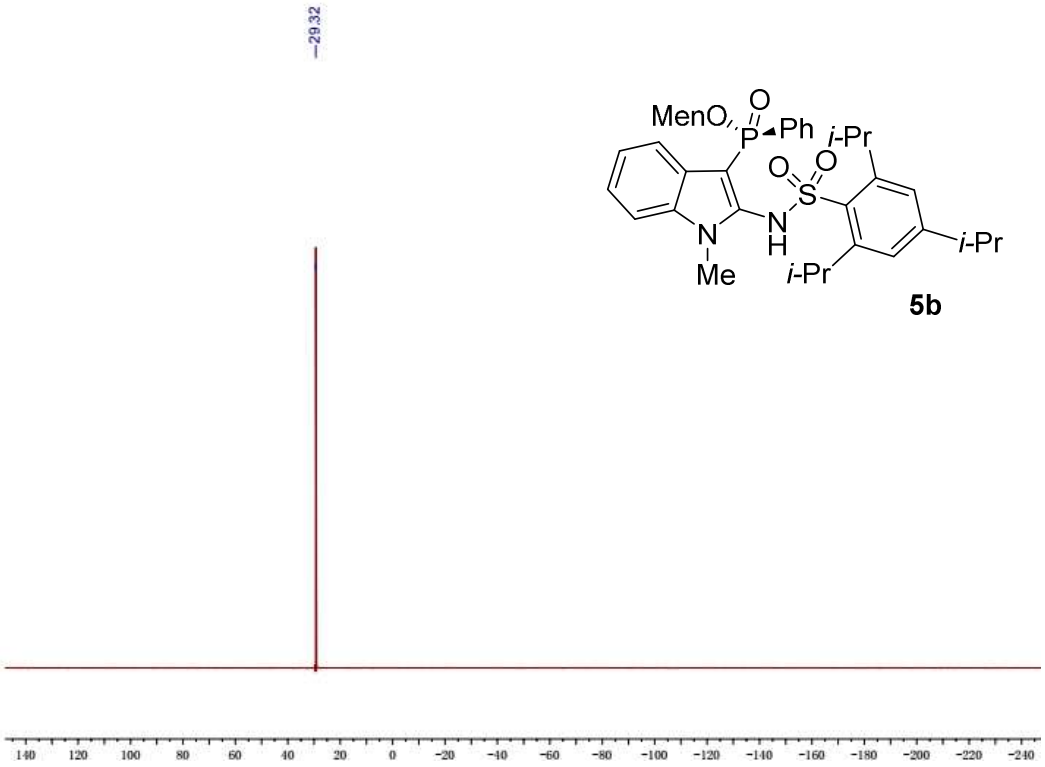
H
N
Me
i-Pr
i-Pr

5b


29.32
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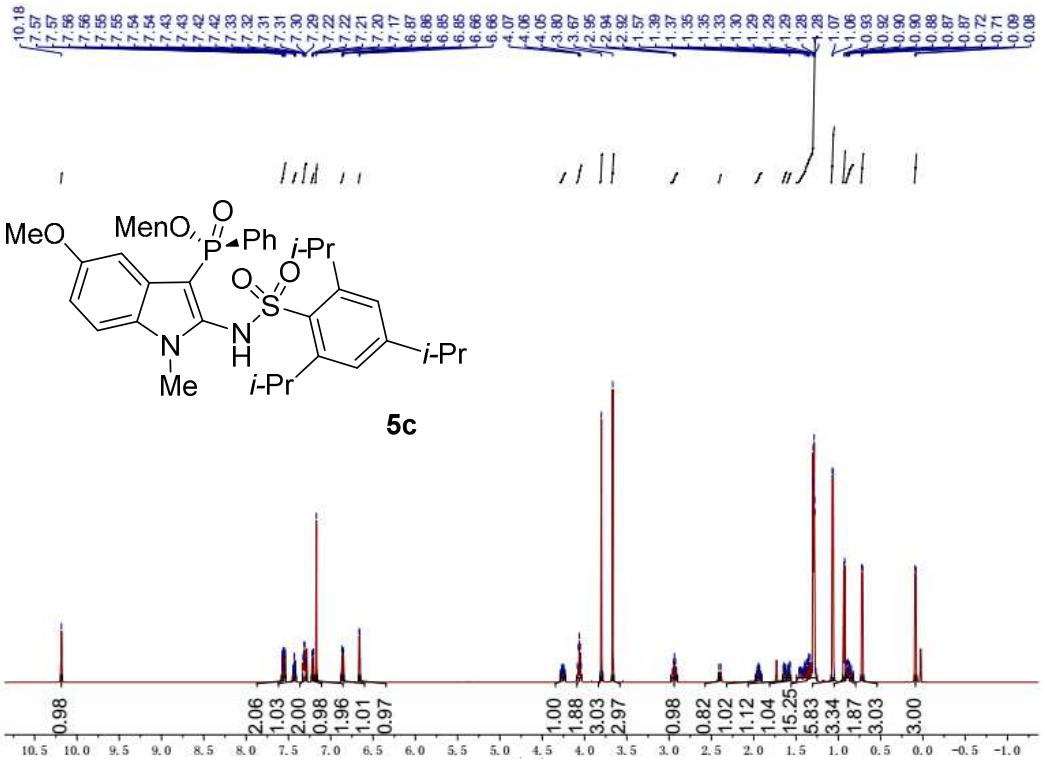
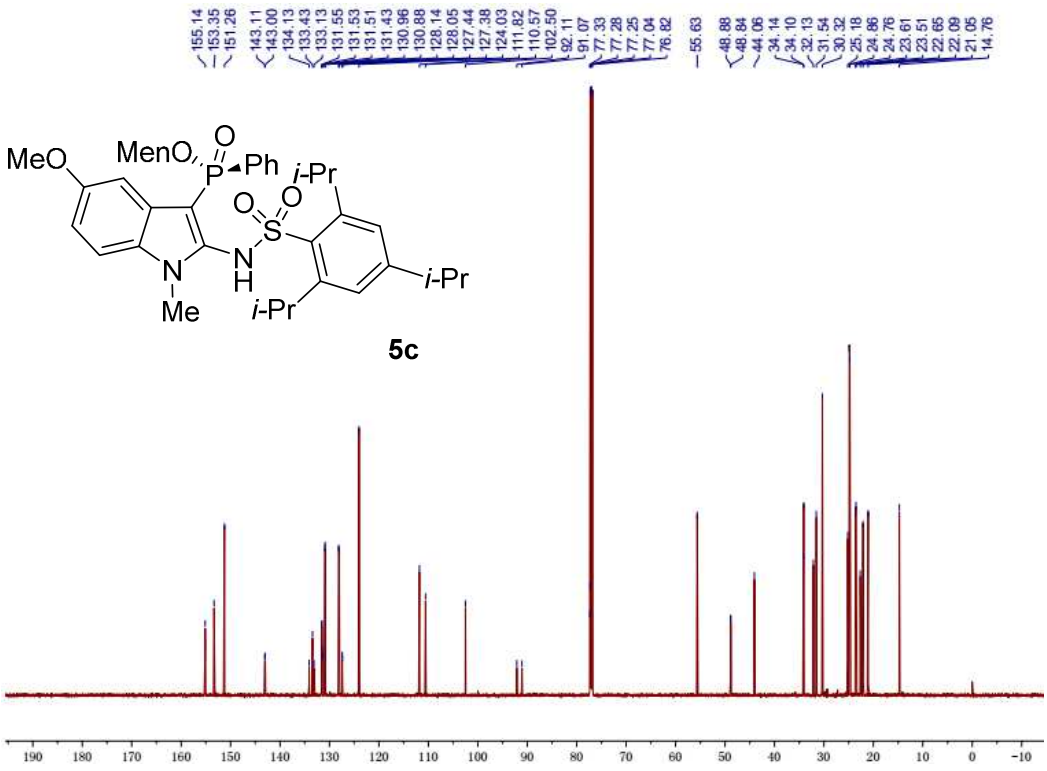
O
P
Ph
i-Pr
O
O
S
N
H
N
Me
i-Pr
i-Pr
5b


MeO
MenO
O
P
Ph
i-Pr
O
O
S
N
H
N
Me
i-Pr
i-Pr
5c


155.14
153.35
151.26
143.11
143.00
134.13
133.43
133.13
131.55
131.53
131.51
131.43
130.96
130.88
128.14
128.05
127.44
127.38
124.03
111.82
110.57
102.50
92.11
91.07
77.33
77.28
77.25
77.04
76.82
55.63
48.88
48.84
44.05
34.14
34.10
32.13
31.54
30.32
25.18
24.86
24.76
23.61
23.51
22.65
22.09
21.05
14.76
MeO
MenO
O
P
Ph
i-Pr
O
O
S
N
H
N
Me
i-Pr
i-Pr
5c
190
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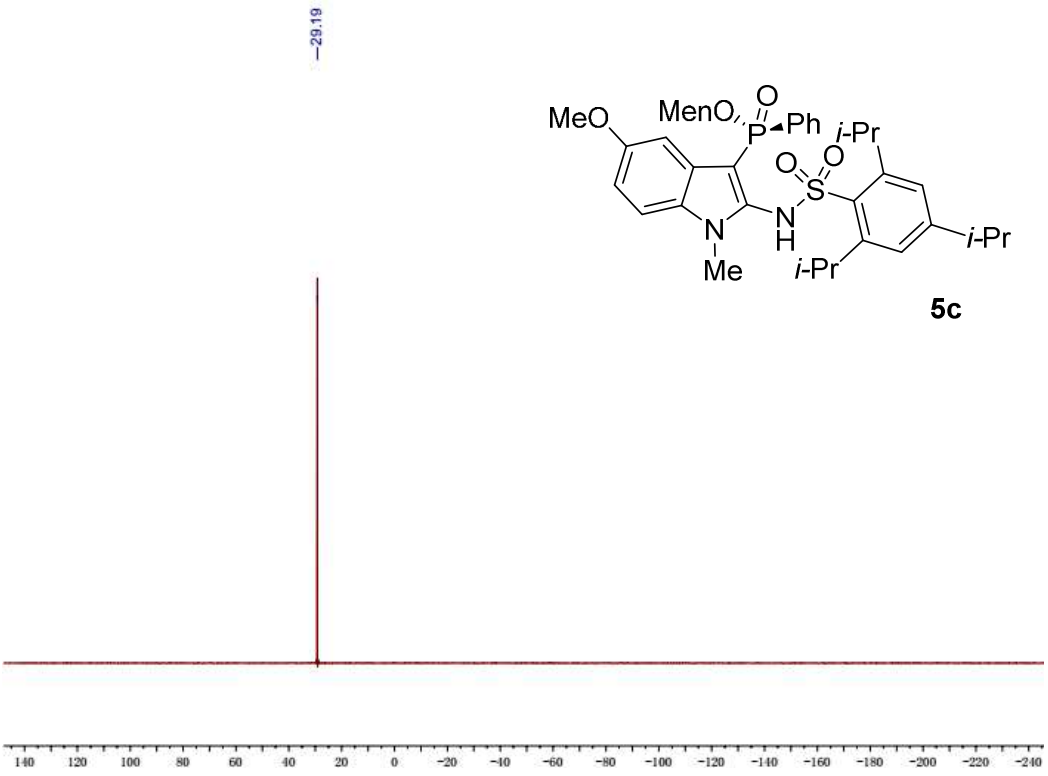
0
-10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MenO
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P
Ph
i-Pr
O
O
S
N
H
N
Me
i-Pr
i-Pr
5c
140
120
100
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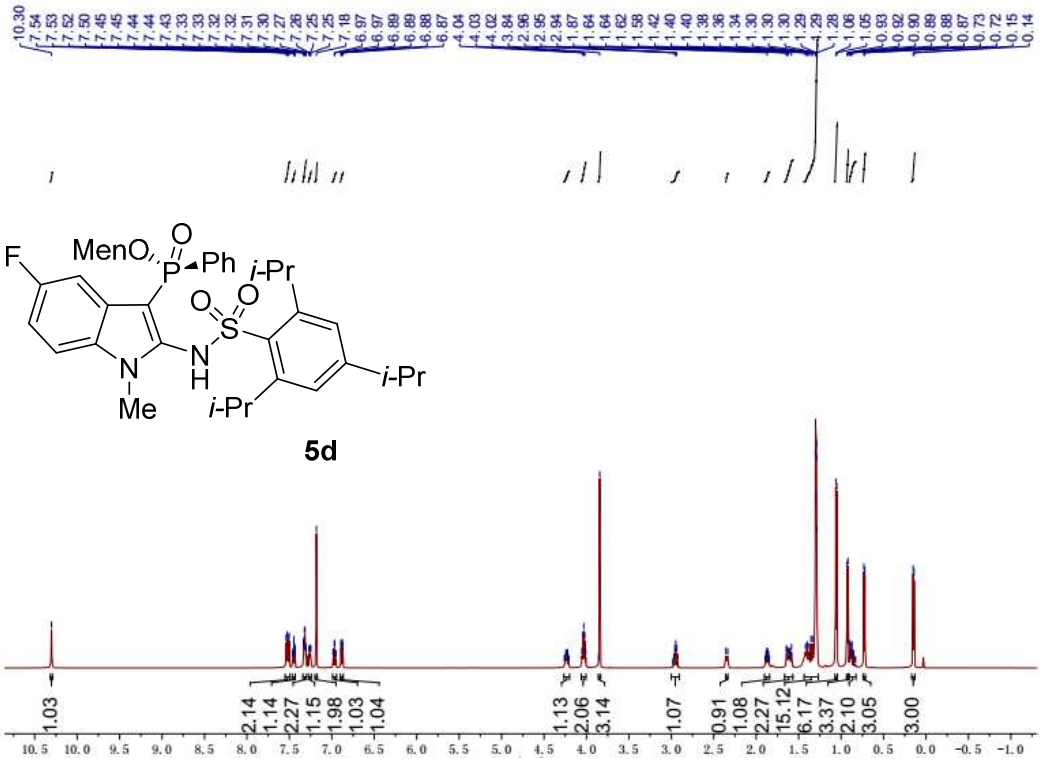
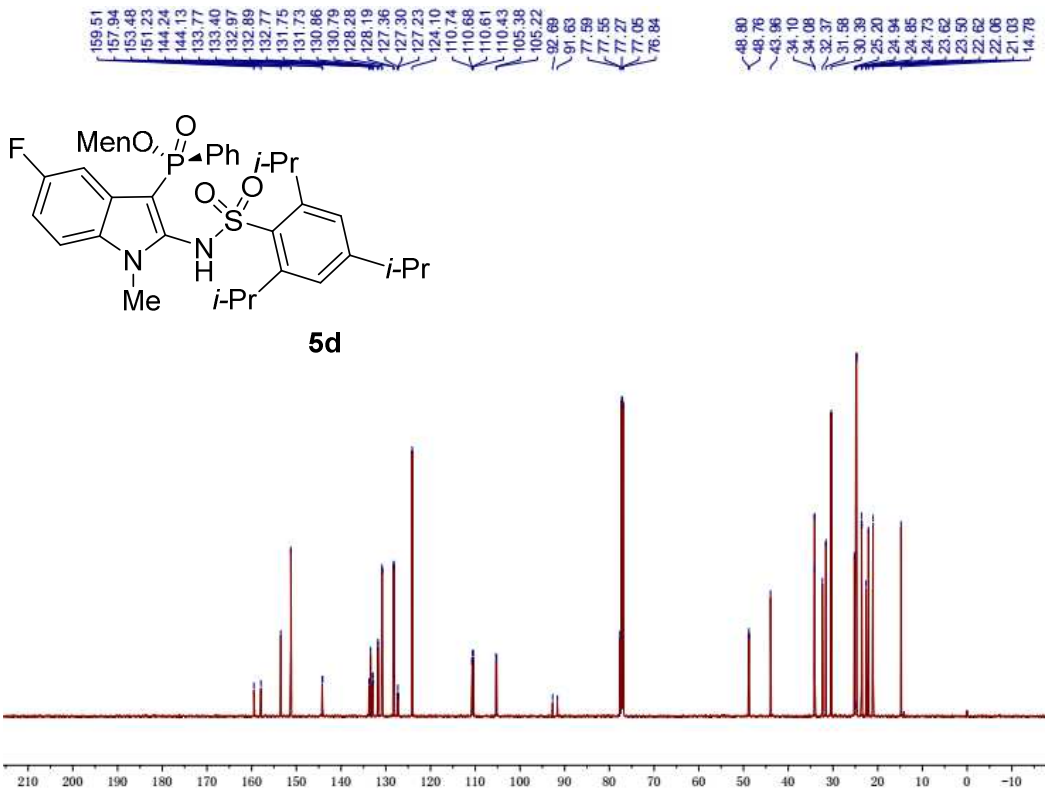
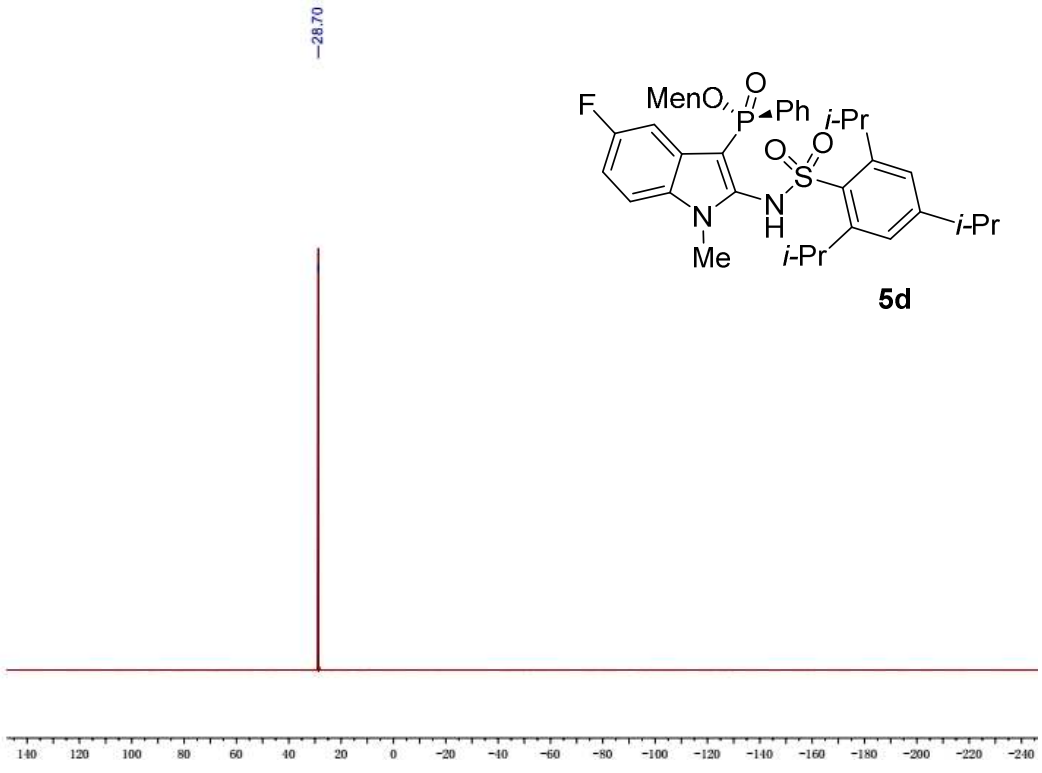
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240


MenO
O
P
Ph
i-Pr
O
O
S
F
N
H
N
Me
i-Pr
i-Pr
1.03
2.14
1.14
2.27
1.15
1.98
1.03
1.04
1.13
2.06
3.14
1.07
0.91
1.08
2.27
15.12
6.17
3.37
2.10
3.05
3.00

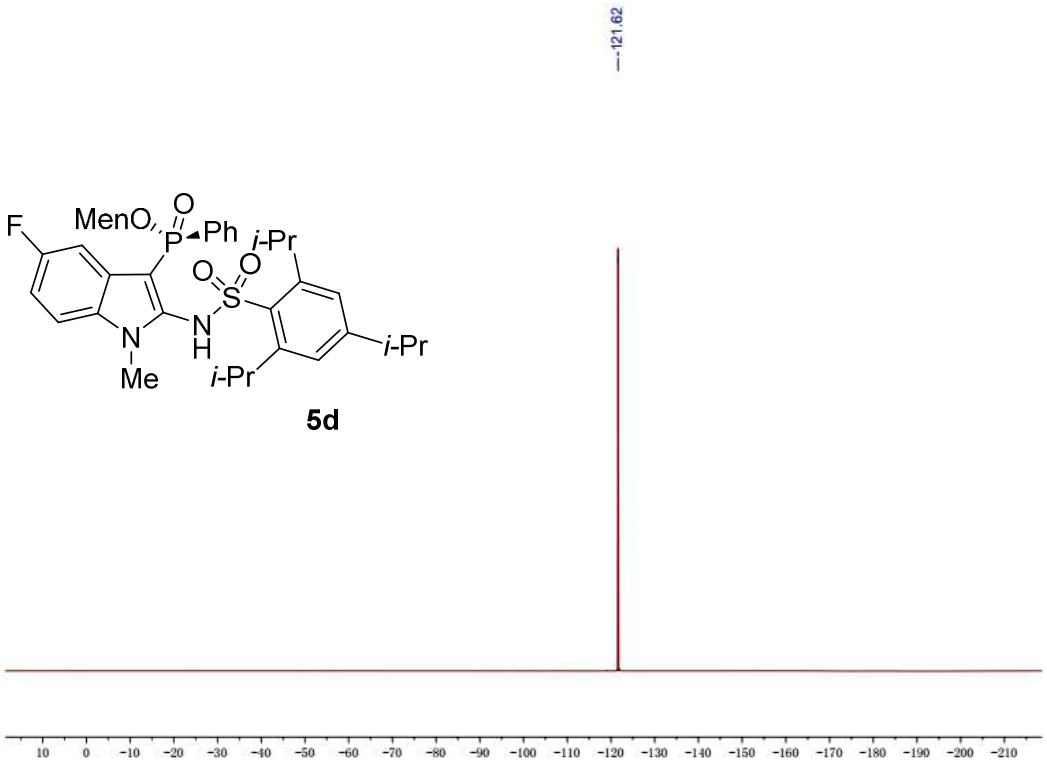
5d


MenO
O
P
Ph
i-Pr
O
O
S
F
N
H
N
Me
i-Pr
i-Pr

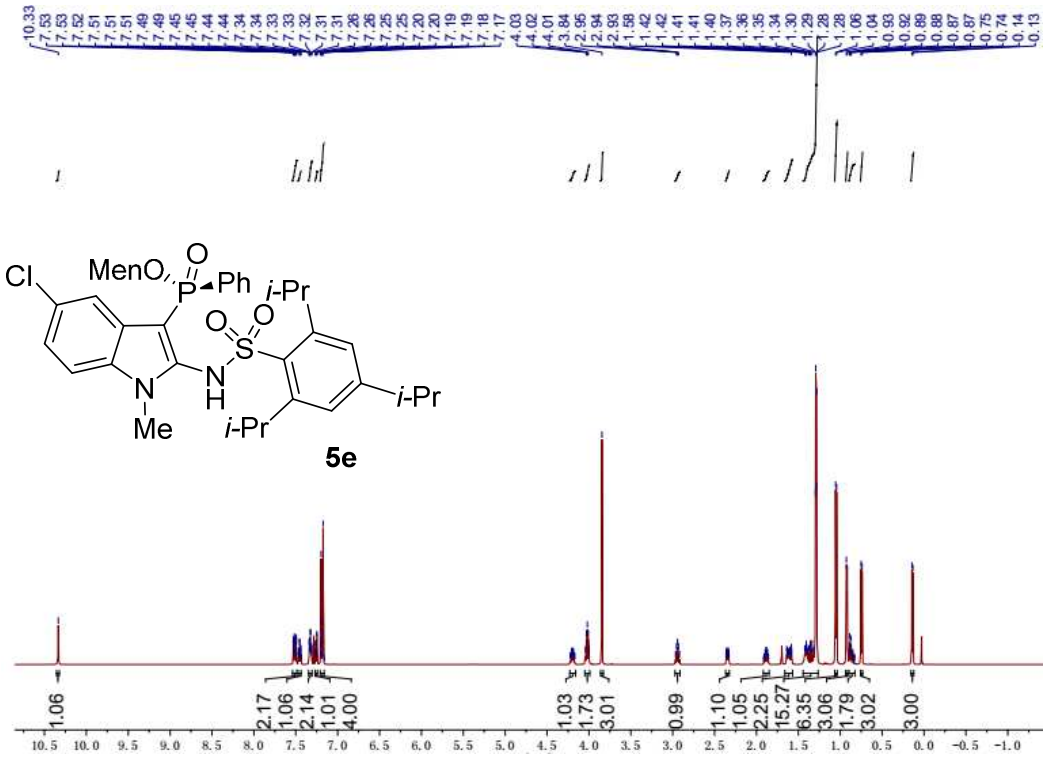
5d

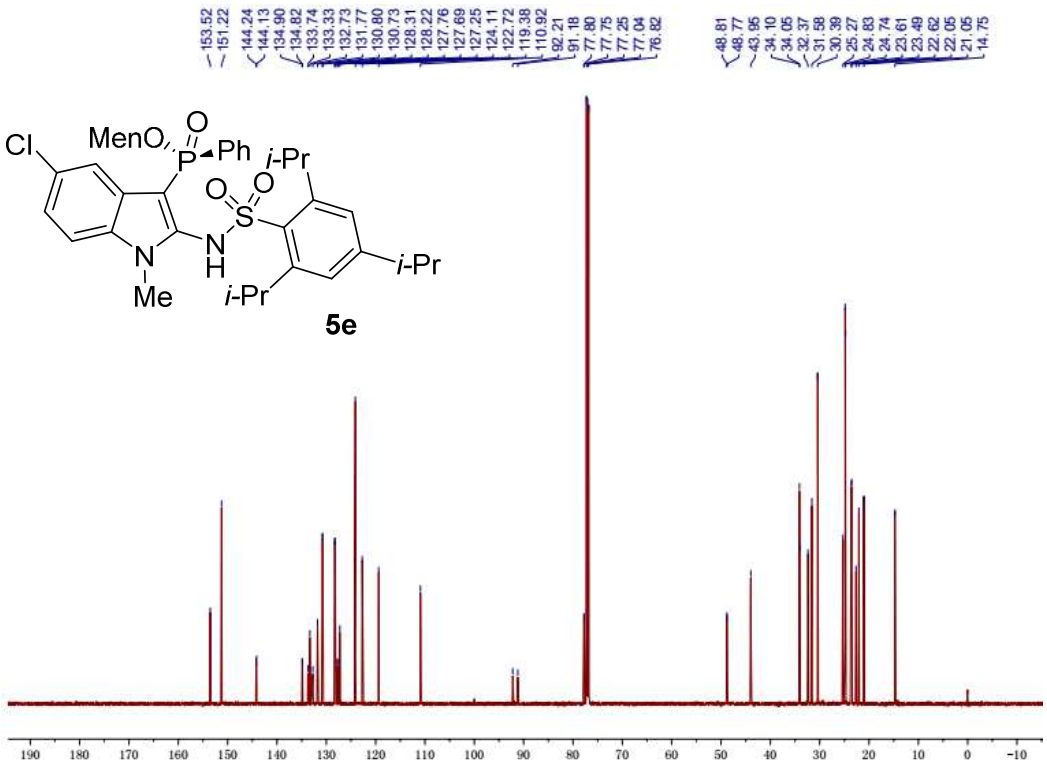

28.70
F
MenO
O
P
Ph
i-Pr
O
O
S
N
H
N
Me
i-Pr
i-Pr
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240

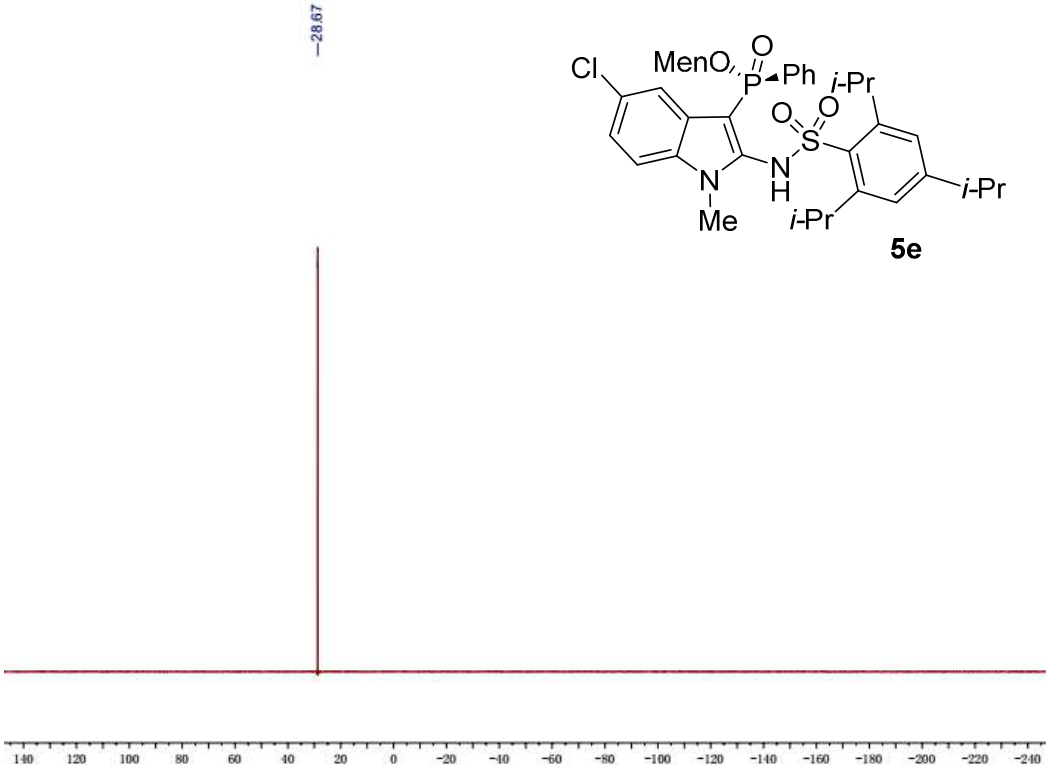
5d


121.62
F
MenO
O
P
Ph
i-Pr
O
O
S
N
H
N
Me
i-Pr
i-Pr
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

5d


Cl
MenO
P
O
Ph
i-Pr
O
S
O
N
H
N
Me
i-Pr
i-Pr
5e


Cl
MenO
P
O
Ph
i-Pr
O
S
O
N
H
N
Me
i-Pr
i-Pr
5e


28.67
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Ph
i-Pr
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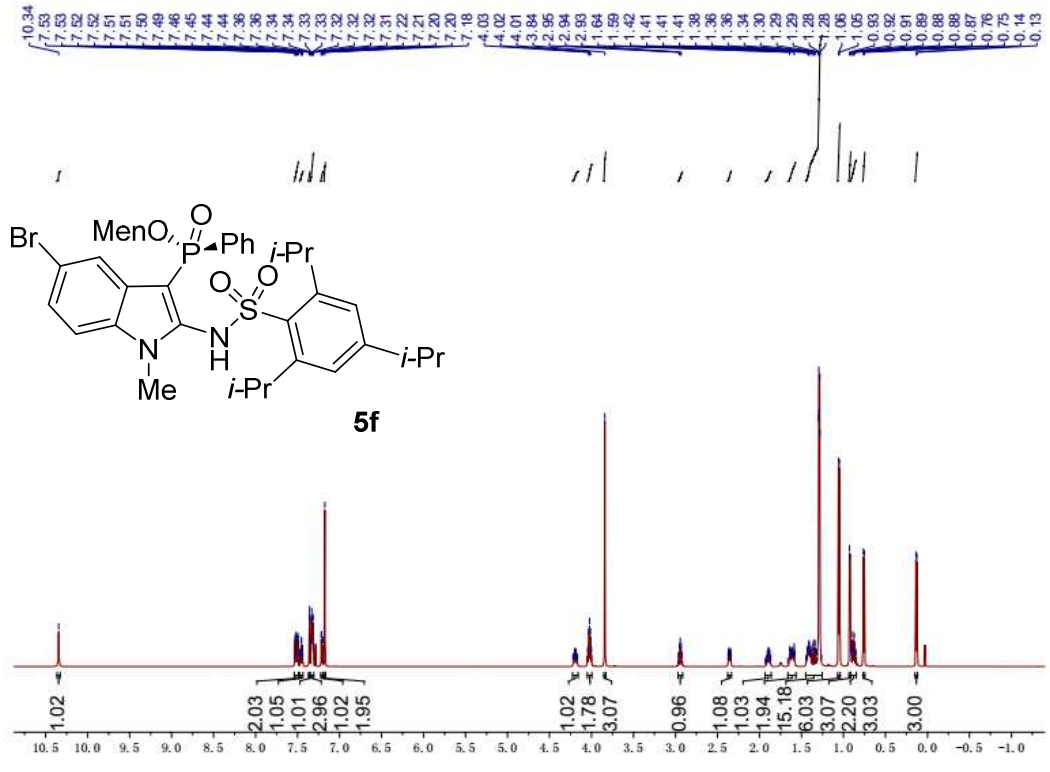
N
H
i-Pr
N
Me
i-Pr
5e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7.53
7.52
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7.51
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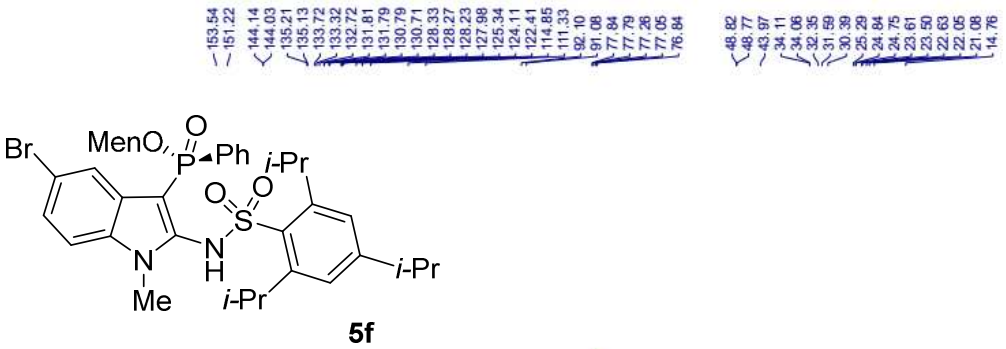
7.50
7.49
7.46
7.45
7.44
7.44
7.36
7.36
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.22
7.21
7.20
7.20
7.18
4.03
4.02
4.01
3.84
2.95
2.34
2.93
1.64
1.59
1.42
1.41
1.41
1.41
1.38
1.36
1.36
1.34
1.30
1.29
1.29
1.28
1.28
1.06
1.05
0.93
0.92
0.91
0.89
0.88
0.88
0.87
0.76
0.75
0.14
0.13
Br
MenO
O
P
Ph
i-Pr
O
S
O
N
H
i-Pr
N
Me
i-Pr
5f
1.02
2.03
1.05
1.01
2.96
1.02
1.95
1.02
1.78
3.07
0.96
1.08
1.03
1.94
15.18
6.03
3.07
2.20
3.03
3.00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144.14
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132.72
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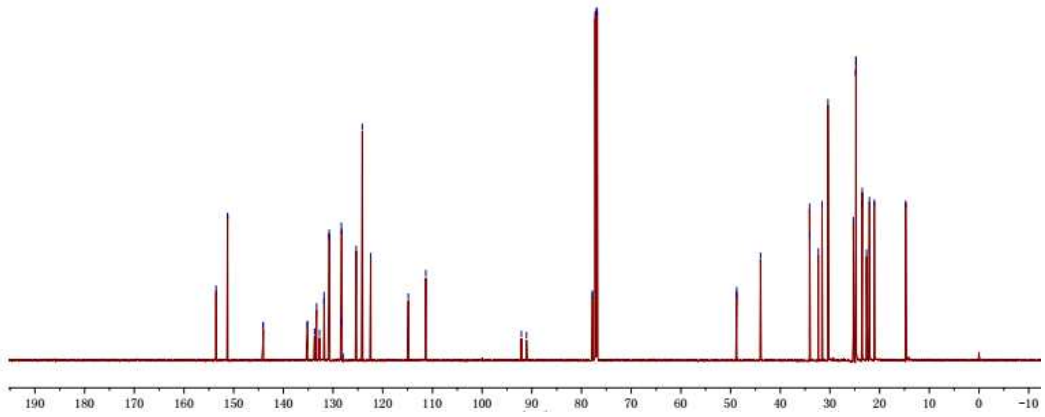
131.79
130.79
130.71
128.33
128.27
128.23
127.98
125.34
124.11
122.41
114.85
111.33
92.10
91.06
77.84
77.79
77.26
77.05
76.84
48.82
48.77
43.97
34.11
34.06
32.35
31.59
30.39
25.29
24.84
24.75
23.61
23.50
22.63
22.05
21.08
14.76

Br
MenO
O
P
Ph
i-Pr
O
O
S
N
H
N
Me
i-Pr
i-Pr

5f


190
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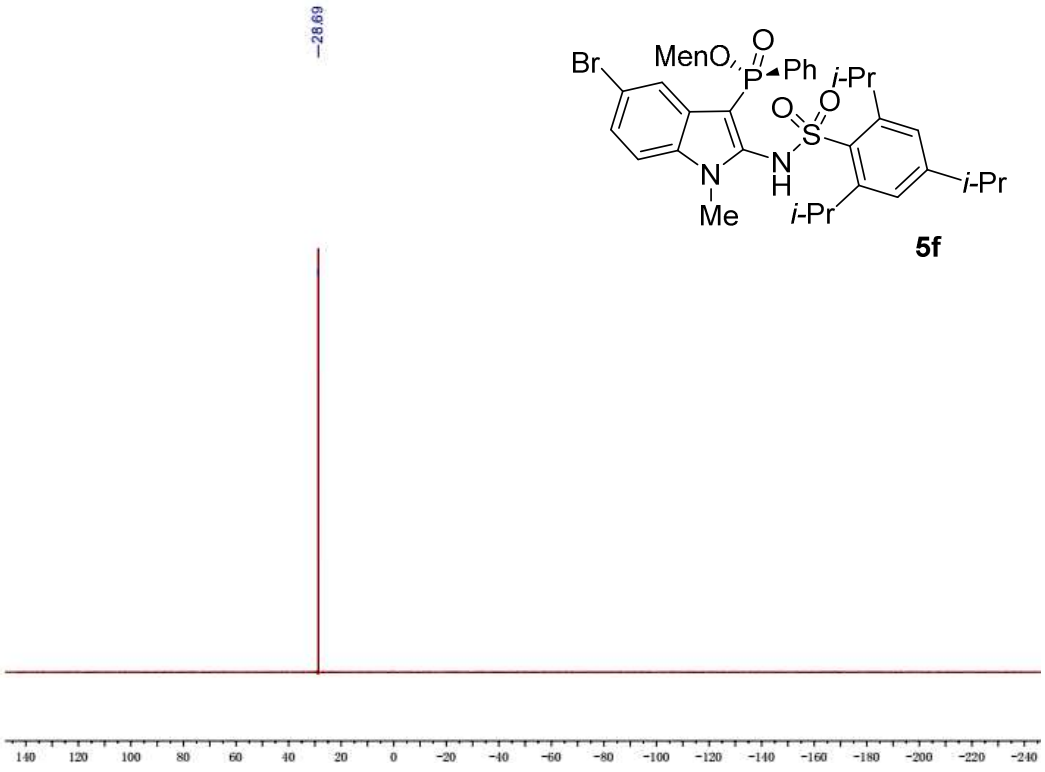
0
-10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120
100
80
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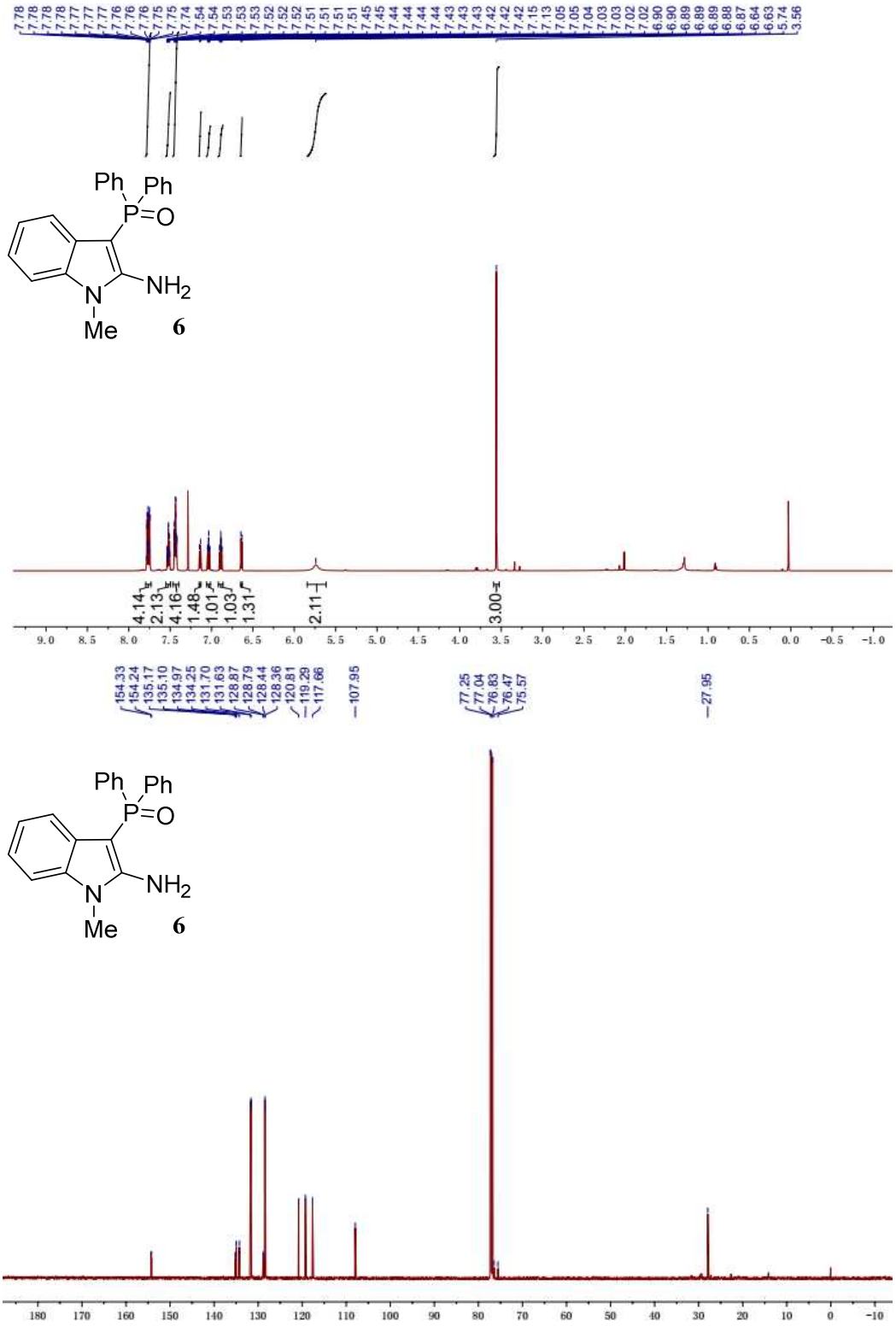
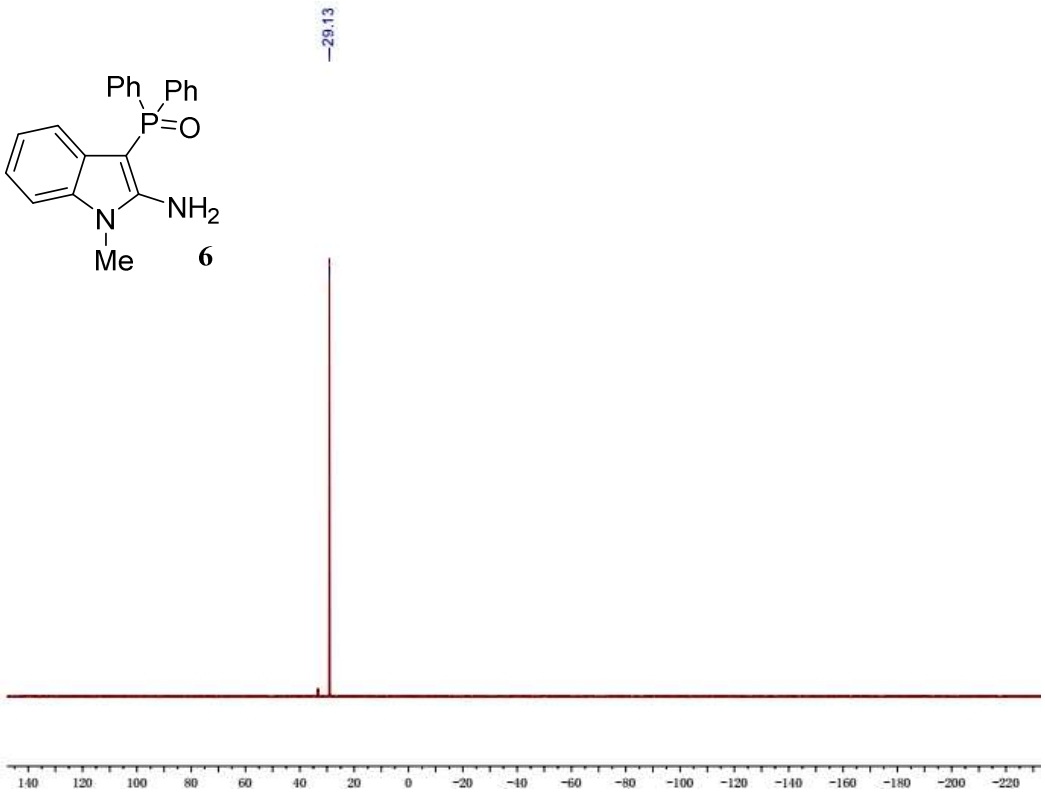
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240

Br
MenO
O
P
Ph
i-Pr
O
O
S
N
H
N
Me
i-Pr
i-Pr

5f


Ph
Ph
P=O
NH2
N
Me
6
4.14
2.13
4.16
1.48
1.01
1.03
1.31
2.11
3.00
Ph
Ph
P=O
NH2
N
Me
6


29.13
Ph
Ph
P
O
NH2
N
Me
6
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220