Visible-light-mediated tandem phosphorylation/cyclization for the synthesis of phosphorylated oxindoles

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Contents:

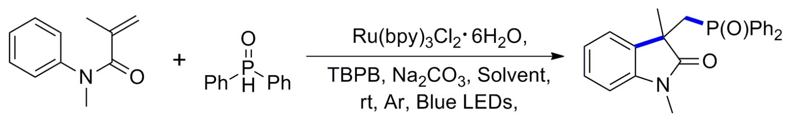
Ⅰ. General Methods and Materials

All reactions involving air- and moisture-sensitive reagents were carried out under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance III 400 spectrometer (400 MHz for ^{1}H and 101 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal standard (DMSO-d_6 δ = 2.5 for ^{1}H NMR, or δ = 40.0 for ^{13}C NMR). ^{31}P and ^{19}F NMR spectra were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, *J*, are reported in hertz. Mass data were measured with Thermo Scientific DSQ II mass spectrometer. High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionisation (ESI). The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM) Substrates were prepared according to published literature methods.[S1]

Figure S1. Devices for the photocatalytic reactions

2. Optimization of Reaction Condition

Table S1. Optimization of the Solvent[a]

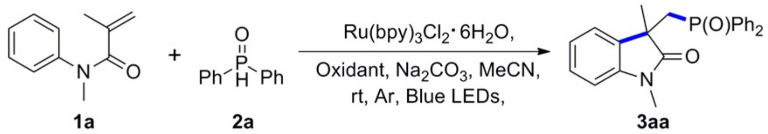


1a 2a 3aa

Entry	Photocatalyst	Oxidant	Base	Solvent	Yield (%)[b]
1	$Ru(bpy)_3Cl_2\cdot 6H_2O$	TBPB	Na_2CO_3	MeCN	84 (82)[c]
2	$Ru(bpy)_3Cl_2\cdot 6H_2O$	TBPB	Na_2CO_3	DMF	76
3	$Ru(bpy)_3Cl_2\cdot 6H_2O$	TBPB	Na_2CO_3	DCM	13
4	$Ru(bpy)_3Cl_2\cdot 6H_2O$	TBPB	Na_2CO_3	Toluene	23
5	$Ru(bpy)_3Cl_2\cdot 6H_2O$	TBPB	Na_2CO_3	Dioxane	trace
6	$Ru(bpy)_3Cl_2\cdot 6H_2O$	TBPB	Na_2CO_3	CH_3NO_2	trace

[a] The reaction was performed with **1a** (0.2 mmol), **2a** (1.3 equiv.), TBPB (2.0 equiv.), Na_2CO_3 (1.3 equiv.), $Ru(bpy)_3Cl_2\cdot 6H_2O$ (2 mol%) in solvent (2.0 mL) was irradiated by 5 W blue LEDs under Ar at rt for 24 h. [b] The yields were determined based on crude ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. [c] Isolated yields.

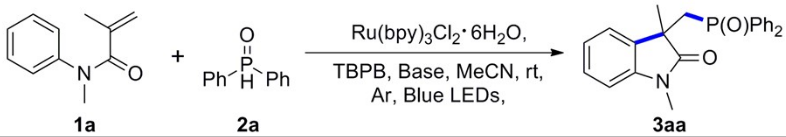
Table S2. Optimization of the Oxidant[a]



entry	photocatalyst	oxidant	base	solvent	yield (%)[b]
1	$Ru(bpy)_3Cl_2•6H_2O$	BPO	Na_2CO_3	MeCN	15
2	$Ru(bpy)_3Cl_2•6H_2O$	$K_2S_2O_8$	Na_2CO_3	MeCN	37
3	$Ru(bpy)_3Cl_2•6H_2O$	TBHP[c]	Na_2CO_3	MeCN	31
4	$Ru(bpy)_3Cl_2•6H_2O$	TBHP	Na_2CO_3	MeCN	54
5	$Ru(bpy)_3Cl_2•6H_2O$	DTBP	Na_2CO_3	MeCN	10

[a] The reaction was performed with **1a** (0.2 mmol), **2a** (1.3 equiv.), Oxidant (2.0 equiv.), Na_2CO_3 (1.3 equiv.), $Ru(bpy)_3Cl_2•6H_2O$ (2 mol%) in MeCN (2.0 mL) was irradiated by 5 W blue LEDs under Ar at rt for 24 h. [b] The yields were determined based on crude ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. [c] TBHP 70% solution in H_2O.

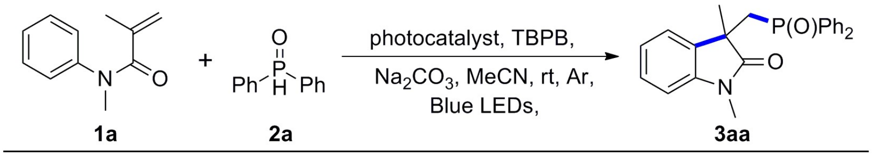
Table S3. Optimization of the Base[a]



Entry	Photocatalyst	Oxidant	Base	Solvent	Yield (%)[b]
1	$Ru(bpy)_3Cl_2•6H_2O$	TBPB	$NaHCO_3$	MeCN	60
2	$Ru(bpy)_3Cl_2•6H_2O$	TBPB	K_2CO_3	MeCN	56
3	$Ru(bpy)_3Cl_2•6H_2O$	TBPB	K_3PO_4	MeCN	78
4	$Ru(bpy)_3Cl_2•6H_2O$	TBPB	DABCO	MeCN	34
5	$Ru(bpy)_3Cl_2•6H_2O$	TBPB	Li_2CO_3	MeCN	57
6	$Ru(bpy)_3Cl_2•6H_2O$	TBPB	KH_2PO_4	MeCN	70
7	$Ru(bpy)_3Cl_2•6H_2O$	TBPB	K_2HPO_4	MeCN	62
8	$Ru(bpy)_3Cl_2•6H_2O$	TBPB	Et_3N	MeCN	31
7	$Ru(bpy)_3Cl_2•6H_2O$	TBPB	2,6-Lutidine	MeCN	68
8	$Ru(bpy)_3Cl_2•6H_2O$	TBPB	—	MeCN	21

[a] The reaction was performed with **1a** (0.2 mmol), **2a** (1.3 equiv.), TBPB (2.0 equiv.), Base (1.3 equiv.), $Ru(bpy)_3Cl_2•6H_2O$ (2 mol%) in MeCN (2.0 mL) was irradiated by 5 W blue LEDs under Ar at rt for 24 h. [b] The yields were determined based on crude ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Table S4. Optimization of the Photocatalyst and Control Experiment [a]

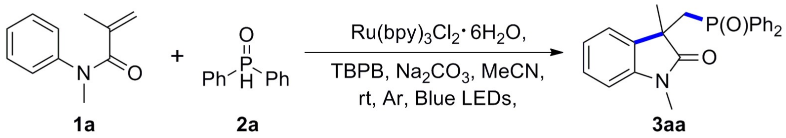


Entry	Photocatalyst	Oxidant	Base	Solvent	Yield (%)[b]
1	—	TBPB	Na_2CO_3	MeCN	trace
2	*fac*-$Ir(ppy)_3$	TBPB	Na_2CO_3	MeCN	41
3	Acid Red 94	TBPB	Na_2CO_3	MeCN	73
4	Rhodamine B	TBPB	Na_2CO_3	MeCN	trace
5[c]	$Ru(bpy)_3Cl_2•6H_2O$	TBPB	Na_2CO_3	MeCN	trace
6[d]	$Ru(bpy)_3Cl_2•6H_2O$	TBPB	Na_2CO_3	MeCN	57

[a] The reaction was performed with **1a** (0.2 mmol), **2a** (1.3 equiv.), TBPB (2.0 equiv.), Na_2CO_3 (1.3 equiv.), photocatalyst (2

mol%) in MeCN (2.0 mL) was irradiated by 5 W blue LEDs under Ar at rt for 24 h. [b] The yields were determined based on crude ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. [c] No irradiation. [d] Sunlight instead of blue LEDs.

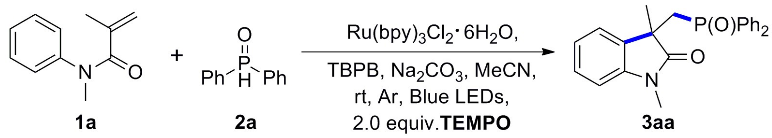
3. The General Procedures



To a Schlenk tube were added *N*-arylacrylamides **1a** (0.2 mmol, 1.0 equiv.), diphenylphosphine oxide **2a** (0.26 mmol, 1.3 equiv.), Ru(bpy)$_3$Cl$_2$· 6H$_2$O (2 mol%), Na_2CO_3 (0.26 mmol, 1.3 equiv) and charged with argon for three times. TBPB (2.0 equiv.) and MeCN (2.0 mL) was added and the mixture was then irradiated by blue LED strips at room temperature for 24 h. After substrate was consumed (monitored by TLC), the reaction was concentrated in vacuo, and the resulting residue was purified by column chromatography (PE/*i*-PrOH = 20/1) to give the desired phosphorylated oxindoles derivatives **3**.

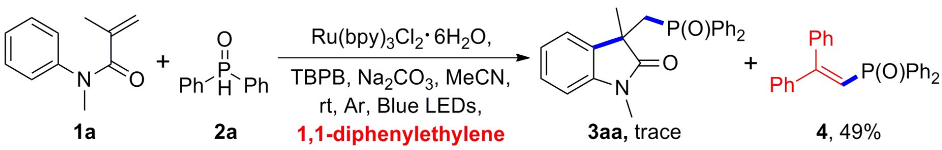
4. Preliminary mechanistic studies.

4.1 Radicals Trapping Experiments using TEMPO

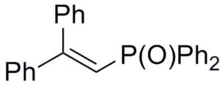


In a Schlenk tube, *N*-arylacrylamides **1** (0.2 mmol, 1.0 equiv.), diphenylphosphine oxide (0.26 mmol, 1.3 equiv.), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mol%), Na_2CO_3 (0.26 mmol, 1.3 equiv) and TEMPO (1.0 equiv) were added and charged with Ar three times. Then, TBPB (2.0 equiv.) and MeCN (2.0 mL) were added and the mixture was then irradiated by blue LED strips at room temperature for 24 h (monitored by TLC). However, no desired product **3** is generated.

4.2 Radicals Trapping Experiments using 1,1-Diphenylethylene



In a Schlenk tube, *N*-arylacrylamides **1a** (0.2 mmol, 1.0 equiv.), diphenylphosphine oxide **2a** (0.26 mmol, 1.3 equiv.), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mol%), Na_2CO_3 (0.26 mmol, 1.3 equiv) and 1,1-diphenylethylene (1.0 equiv) were added and charged with Ar three times. Then, MeCN (2.0 mL) and TBPB (2.0 equiv.) were added and the mixture was then irradiated by blue LED strips at room temperature for 24 h, After substrate was consumed (monitored by TLC), the reaction was concentrated in vacuo, and the resulting residue was purified by column chromatography to give **3aa** and **4** in trace and 49% yield, respectively. The result show that the reaction system produces the diphenylphosphine oxide radical.



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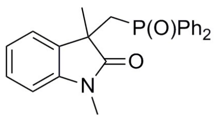
(2,2-diphenylvinyl)diphenylphosphine oxide, white solid, **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.79 – 7.61 (m, 4H), 7.38 – 7.28 (m, 10H), 7.25 – 7.21 (m, 2H), 7.10 (dt, *J* = 14.2, 6.9 Hz, 4H), 6.79 (d, *J* = 18.2 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 161.9, 141.9, 141.7, 137.9, 137.9, 134.8, 133.7, 131.0, 130.9, 130.8, 130.7, 130.2, 129.4, 128.5, 128.3, 128.2, 128.2, 128.1, 127.5, 120.9, 119.9. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 18.73. **MS (ESI**, **m/z):** calculated for $C_{26}H_{21}OP$ [M+H]$^+$: 381.1403, found: 381.4. Spectral data for this compound is consistent with that previously reported.[S1j]

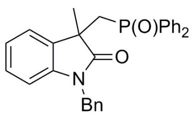
5. References

[S1] (a) Y.-M. Li, Y. Shen, K.-J. Chang and S.-D. Yang, *Tetrahedron*, **2014**, *70*, 1991; (b) Y.-M. Li, M. Sun, H.-L. Wang, Q.-P. Tian and S.-D. Yang, *Angew. Chem. Int. Ed.* **2013**, *52*, 3972. (c) C. X. Li, D. S. Tu, R. Yao, H. Yan and C. S. Lu, *Org. Lett.*, **2016**, *18*, 4928. (d) A. Pinto, Y. Jia, L. Neuville and J. Zhu, *Chem. Eur. J.* **2007**, *13*, 961. (e) H. Wei, T. Piou, J. Dufour, L. Neuville and J. Zhu, *Org. Lett.*, **2011**, *13*, 2244. (f) X. Mu, T. Wu, H. Wang, Y. Guo and G. Liu, *J. Am. Chem. Soc.* **2012**, *134*, 878. (g) S. Biros, R. Yeh and K. Raymond, *Angew. Chem., Int. Ed.* **2008**, *47*, 6062. (h) N. Campbell, A. Finch and S. Rokita, *ChemPhysChem* **2010**, *11*, 1768. (i) C. Chen, W. Sun, Y. Yan, F. Yang, Y. Wang, Y. –P. Zhu, L. Liu and B. Zhu, *Adv. Syn. Cat.*, **2020**, *362*, 2970, (j) L.-L. Mao, A.-X. Zhou, N. Liu and S.-D. Yang, *Synlett*, **2014**, *25*, 2727.

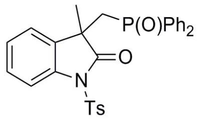
6. Characterization data of products



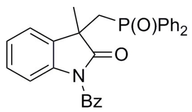
3-((diphenylphosphoryl)methyl)-1,3-dimethylindolin-2-one (3aa) White solid**; ^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.62 – 7.55 (m, 2H), 7.51 – 7.46 (m, 2H), 7.44 – 7.29 (m, 6H), 7.17 (dd, *J* = 10.7, 4.1Hz, 2H), 6.85 – 6.75 (m, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 3.09 (dd, *J* = 15.2, 10.1 Hz, 1H), 3.01 (s, 3H), 2.87 (dd, *J* = 15.2, 10.9 Hz, 1H), 1.43 (d, *J* = 1.7 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 179.4 (d, *J* = 4.3 Hz), 142.9, 133.9 (d, *J* = 76.7 Hz), 132.9 (d, *J* = 76.1 Hz), 131.4 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 2.6 Hz), 131.2 (d, *J* = 2.8 Hz), 130.6 (d, *J* = 9.4 Hz), 130.4 (d, *J* = 9.2 Hz), 128.3 (d, *J* = 11.7 Hz), 128.1 (d, *J* = 11.7 Hz), 127.9, 124.8, 122.1, 107.8, 45.4 (d, *J* = 3.8 Hz), 37.5 (d, *J* = 71.8 Hz), 26.8 (d, *J* = 12.1 Hz). 26.3. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 26.02. **MS (ESI**, **m/z):** calculated for $C_{23}H_{22}NO_2P$ [M+H]$^+$: 376.1461, found: 376.1. Spectral data for this compound is consistent with that previously reported.[S1b]



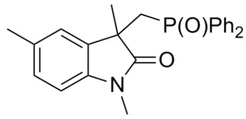
1-benzyl-3-((diphenylphosphoryl)methyl)-3-methylindolin-2-one (3ab) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.58 (m, 4H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.36 (m, 4H), 7.28 (t, *J* = 6.3 Hz, 4H), 7.24 (dd, *J* = 6.2, 2.0 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 5.04 (d, *J* = 15.8 Hz, 1H), 4.40 (d, *J* = 15.8 Hz, 1H), 3.09 (dd, *J* = 15.2, 10.9 Hz, 1H), 2.93 (dd, *J* = 15.2, 10.0 Hz, 1H), 1.49 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 179.6 (d, *J* = 5.2 Hz), 142.0, 136.1, 133.9 (d, *J* = 38.0 Hz), 132.9 (d, *J* = 37.6 Hz), 131.6 (d, *J* = 2.7 Hz), 131.4 (d, *J* = 2.8 Hz), 131.3 (d, J = 2.7 Hz), 130.7 (d, J = 9.4 Hz), 130.6 (d, J = 9.2 Hz), 128.7, 128.4 (d, J = 11.8 Hz), 128.2 (d, J = 11.8 Hz),, 127.8, 127.4, 127.1, 124.9, 122.2, 108.9, 45.6 (d, J = 3.9 Hz), 43.9, 37.3 (d, J = 71.5 Hz), 26.9 (d, J = 11.4 Hz). **^{31}P NMR (162 MHz, CDCl$_3$)** δ 26.20. **MS (ESI, m/z):** calculated for $C_{29}H_{26}NO_2P$ [M+H]$^+$: 452.1774, found: 452.2. Spectral data for this compound is consistent with that previously reported. [S1c]



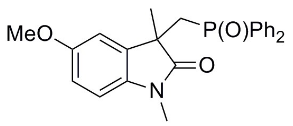
3-((diphenylphosphoryl)methyl)-3-methyl-1-tosylindolin-2-one (3ac) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.48 (s, 1H), 7.70 – 7.60 (m, 2H), 7.49 – 7.40 (m, 5H), 7.36 (m, 3H), 7.25 (dd, J = 9.5, 6.0 Hz, 4H), 7.09 (d, J = 8.2 Hz, 2H), 7.04 (t, J = 7.3 Hz, 1H), 6.81 (d, J = 8.1 Hz, 2H), 3.26 (dd, J = 15.6, 12.2 Hz, 1H), 3.09 (dd, J = 15.6, 8.5 Hz, 1H), 2.18 (s, 3H), 1.96 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 174.4 (d, J = 9.4 Hz), 138.2 (d, J = 6.0 Hz), 136.9, 134.2 (d, J = 100.3 Hz), 132.9 (d, J = 99.6 Hz), 131.3 (d, J = 2.7 Hz), 130.7 (d, J = 2.7 Hz), 130.5, 130.4, 130.3, 130.2, 128.9, 128.7, 128.4 (d, J = 11.7 Hz), 128.1 (d, J = 11.8 Hz), 127.0, 123.9, 119.7, 50.5 (d, J = 2.7 Hz), 39.3 (d, J = 71.2 Hz), 25.8 (d, J = 5.0 Hz), 20.8. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 28.69. **MS (ESI, m/z)**: calculated for $C_{29}H_{26}NO_4PS$ [M+H]$^+$: 516.1393, found: 516.0. Spectral data for this compound is consistent with that previously reported. [S1b]



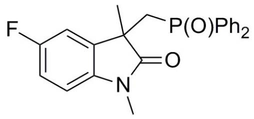
1-benzoyl-3-((diphenylphosphoryl)methyl)-3-methylindolin-2-one (3ad) White solid; M.p. = 228-230 °C, **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.18 (d, J = 7.8 Hz, 1H), 7.60 (dd, J = 11.5, 7.4 Hz, 2H), 7.49 (dd, J = 14.0, 6.7 Hz, 3H), 7.46 – 7.26 (m, 8H), 7.26 – 7.15 (m, 3H), 7.00 (d, J = 3.6 Hz, 2H), 3.79 (dd, J = 14.7, 12.5 Hz, 1H), 2.97 (dd, J = 14.9, 5.9 Hz, 1H), 1.79 (d, J = 1.6 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 175.9, 164.1, 140.7, 136.0, 133.8 (d, J = 99.7 Hz), 132.7, 132.2 (d, J = 99.0 Hz),131.4 (d, J = 75.8 Hz), 131.3 (d, J = 81.3 Hz), 130.8, 130.7, 130.6, 129.1, 128.9, 128.6, 128.5, 128.3, 128.2 (d, J = 18.2 Hz), 127.5, 126.2, 125.0, 45.4 (d, J = 3.7 Hz), 41.8 (d, J = 70.0 Hz), 32.8 (d, J = 13.8 Hz). **^{31}P NMR (162 MHz, CDCl$_3$)** δ 27.09. **HRMS (ESI, m/z)**: calculated for $C_{29}H_{24}NO_3P$ (M+Na)$^+$, 488.1386; found, 488.1384.



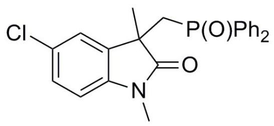
3-((diphenylphosphoryl)methyl)-1,3,5-trimethylindolin-2-one (3af) Light yellow solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.57 – 7.46 (m, 4H), 7.40 (t, J = 7.1 Hz, 2H), 7.37 – 7.28 (m, 4H), 6.93 (d, J = 7.8 Hz, 1H), 6.78 (s, 1H), 6.59 (d, J = 7.9 Hz, 1H), 3.14 – 3.02 (m, 4H), 2.82 (dd, J = 15.1, 9.5 Hz, 1H), 2.06 (s, 3H), 1.43 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 179.3 (d, J = 4.1 Hz), 140.7, 133.9 (d, J = 23.7 Hz), 132.9 (d, J = 23.2 Hz), 131.3 (d, J = 2.6 Hz), 131.2, 131.1 (d, J = 2.7 Hz), 130.9 (d, J = 2.7 Hz), 130.5 (d, J = 9.3 Hz), 130.4 (d, J = 9.2 Hz), 128.1 (d, J = 1.9 Hz), 128.1, 128.0 (d, J = 5.7 Hz), 125.4, 107.5, 45.3 (d, J = 3.9 Hz), 37.5 (d, J = 71.7 Hz), 26.6 (d, J = 12.1 Hz). 26.3, 20.8. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 25.71. **MS (ESI, m/z)**: calculated for $C_{24}H_{24}NO_2P$ [M+H]$^+$: 390.1617, found: 390.2. Spectral data for this compound is consistent with that previously reported. [S1a]



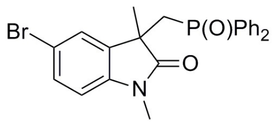
3-((diphenylphosphoryl)methyl)-5-methoxy-1,3-dimethylindolin-2-one (3ag) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.59 – 7.48 (m, 4H), 7.41 (m, 2H), 7.39 – 7.29 (m, 4H), 6.75 (d, *J* = 2.4 Hz, 1H), 6.70 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 3.64 (s, 3H), 3.15 – 3.01 (m, 4H), 2.82 (dd, *J* = 15.2, 9.9 Hz, 1H), 1.43 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ179.1 (d, *J* = 4.2 Hz), 155.4, 136.5, 133.9 (d, *J* = 50.5 Hz), 132.9 (d, *J* = 50.2 Hz), 132.5 (d, *J* = 2.6 Hz), 131.4 (d, *J* = 2.5 Hz), 131.2 (d, *J* = 2.6 Hz), 130.6 (d, *J* = 9.4 Hz), 130.5 (d, *J* = 9.3 Hz), 128.3 (d, *J* = 6.9 Hz), 128.2 (d, *J* = 6.9 Hz), 113.2, 111.5, 108.2, 55.5, 45.9 (d, *J* = 3.8 Hz), 37.4 (d, *J* = 71.6 Hz), 26.7 (d, *J* = 12.3 Hz), 26.4. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 26.02. **MS (ESI**, **m/z)**: calculated for $C_{24}H_{24}NO_3P$ $[M+H]^+$: 406.1567, found: 406.0. Spectral data for this compound is consistent with that previously reported. [S1b]



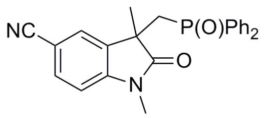
3-((diphenylphosphoryl)methyl)-5-fluoro-1,3-dimethylindolin-2-one (3ah) Light yellow solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.63 – 7.49 (m, 4H), 7.43 (m, 2H), 7.39 – 7.32 (m, 4H), 6.85 (m, 1H), 6.79 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.63 (dd, *J* = 8.5, 4.1 Hz, 1H), 3.16 – 3.00 (m, 4H), 2.83 (dd, *J* = 15.1, 9.2 Hz, 1H), 1.42 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.9 (d, *J* = 4.3 Hz), 158.6 (d, *J* = 240.2 Hz), 138.9 (d, *J* = 1.8 Hz), 133.6 (d, *J* = 16.2 Hz), 132.9 (d, *J* = 2.7 Hz), 132.8 (d, *J* = 2.6 Hz), 132.7 (d, *J* = 16.1 Hz), 131.4 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 2.7 Hz), 130.4 (d, *J* = 9.4 Hz), 130.3 (d, *J* = 9.2 Hz), 128.3 (d, *J* = 6.5 Hz), 128.2 (d, *J* = 6.5 Hz), 114.1 (d, *J* = 23.5 Hz), 112.7 (d, *J* = 25.2 Hz), 108.1 (d, *J* = 8.1 Hz), 45.7 (d, *J* = 2.2 Hz), 37.4 (d, *J* = 71.3 Hz), 26.4, 26.3. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 25.59. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -121.23. **MS (ESI): MS (ESI**, **m/z)**: calculated for $C_{23}H_{21}FNO_2P$ $[M+H]^+$: 394.1367, found: 394.4. Spectral data for this compound is consistent with that previously reported. [S1b]



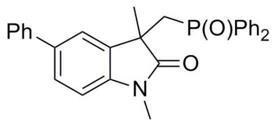
5-chloro-3-((diphenylphosphoryl)methyl)-1,3-dimethylindolin-2-one (3ai) White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 – 7.52 (m, 2H), 7.49 – 7.39 (m, 4H), 7.39 – 7.29 (m, 4H), 7.08 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.81 (d, *J* = 2.1 Hz, 1H), 6.64 (d, *J* = 8.3 Hz, 1H), 3.17 – 3.01 (m, 4H), 2.77 (dd, *J* = 15.1, 8.3 Hz, 1H), 1.40 (d, *J* = 1.8 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.9 (d, *J* = 3.7 Hz), 141.9, 133.6 (d, *J* = 41.1 Hz), 132.8 (d, *J* = 2.9 Hz), 132.6 (d, *J* = 35.6 Hz), 131.6 (d, *J* = 2.7 Hz), 131.5 (d, *J* = 2.7 Hz), 130.4 (d, *J* = 9.4 Hz), 130.3 (d, *J* = 9.3 Hz), 128.4 (d, *J* = 6.0 Hz), 128.3 (d, *J* = 6.1 Hz), 127.9, 127.2, 125.0, 108.7, 45.5 (d, *J* = 4.0 Hz), 37.6 (d, *J* = 71.3 Hz), 26.6, 26.5. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 25.52. **MS (ESI**, **m/z)**: calculated for $C_{23}H_{21}ClNO_2P$ $[M+H]^+$: 410.1071, found: 410.2. Spectral data for this compound is consistent with that previously reported. [S1b]



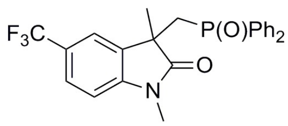
5-bromo-3-((diphenylphosphoryl)methyl)-1,3-dimethylindolin-2-one (3aj) White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.62 – 7.53 (m, 2H), 7.47 – 7.39 (m, 4H), 7.39 – 7.29 (m, 4H), 7.25 – 7.19 (m, 1H), 6.92 (d, *J* = 1.9 Hz, 1H), 6.60 (d, *J* = 8.3 Hz, 1H), 3.18 – 3.01 (m, 4H), 2.76 (dd, *J* = 15.1, 8.1 Hz, 1H), 1.40 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.8 (d, *J* = 3.5 Hz), 142.4, 133.6 (d, *J* = 56.2 Hz), 133.1 (d, *J* = 2.7 Hz), 132.6 (d, *J* = 56.3 Hz), 131.6 (d, *J* = 1.7 Hz), 130.8, 130.4 (d, *J* = 9.4 Hz), 130.2 (d, *J* = 9.3 Hz), 128.4 (d, *J* = 6.3 Hz), 128.3 (d, *J* = 6.3 Hz), 127.7, 114.6, 109.3, 45.5 (d, *J* = 4.0 Hz), 37.6 (d, *J* = 71.2 Hz), 26.5, 26.5 (d, *J* = 12.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 25.54. **MS (ESI**, **m/z)**: calculated for $C_{23}H_{21}BrNO_2P$ $[M+H]^+$: 454.0566, found: 454.5. Spectral data for this compound is consistent with that previously reported. [S1b]



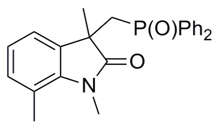
3-((diphenylphosphoryl)methyl)-1,3-dimethyl-2-oxoindoline-5-carbonitrile (3ak) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 – 7.53 (m, 2H), 7.50 – 7.29 (m, 9H), 6.88 (d, *J* = 1.2 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 3.24 – 3.03 (m, 4H), 2.80 (dd, *J* = 15.1, 7.0 Hz, 1H), 1.41 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 179.1 (d, *J* = 2.9 Hz), 147.3, 133.3 (d, *J* = 75.5 Hz), 133.1, 132.3 (d, *J* = 74.9 Hz), 131.8 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 2.8 Hz), 131.7 (d, *J* = 2.8 Hz), 130.2 (d, *J* = 10.1 Hz), 130.1, 128.4 (d, *J* = 9.1 Hz), 128.3 (d, *J* = 9.1 Hz), 127.5, 118.8, 108.3, 104.7, 44.9 (d, *J* = 4.0 Hz), 37.7 (d, *J* = 71.1 Hz), 26.7, 26.2 (d, *J* = 12.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.25. **MS (ESI**, **m/z)**: calculated for $C_{24}H_{21}N_2O_2P$ $[M+H]^+$: 401.1413, found: 401.0. Spectral data for this compound is consistent with that previously reported. [S1b]



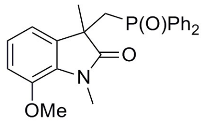
3-((diphenylphosphoryl)methyl)-1,3-dimethyl-5-phenylindolin-2-one (3al) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.46 (m, 4H), 7.45 – 7.35 (m, 6H), 7.34 – 7.25 (m, 7H), 6.75 (d, *J* = 8.1 Hz, 1H), 3.20 (dd, *J* = 15.2, 10.6 Hz, 1H), 3.09 (s, 3H), 2.93 (dd, *J* = 15.2, 10.2 Hz, 1H), 1.48 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 179.5 (d, *J* = 3.4 Hz), 142.6, 140.6, 135.3, 133.2 (d, *J* = 45.8 Hz), 132.2 (d, *J* = 45.4 Hz), 131.7 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 2.6 Hz), 131.5 (d, *J* = 2.7 Hz), 130.7 (d, *J* = 9.5 Hz), 130.4 (d, *J* = 9.4 Hz), 128.5, 128.3 (d, *J* = 7.4 Hz), 128.2 (d, *J* = 7.4 Hz), 126.8, 126.7 (d, *J* = 9.2 Hz), 123.8, 108.1, 45.5 (d, *J* = 3.8 Hz), 37.5 (d, *J* = 71.6 Hz), 27.1 (d, *J* = 12.4 Hz), 26.5. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 27.40. **MS (ESI**, **m/z)**: calculated for $C_{29}H_{26}NO_2P$ $[M+H]^+$: 452.1774, found: 452.3. Spectral data for this compound is consistent with that previously reported. [S1c]



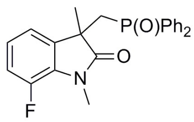
3-((diphenylphosphoryl)methyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3am) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 – 7.54 (m, 2H), 7.47 – 7.33 (m, 7H), 7.29 (td, *J* = 7.3, 2.8 Hz, 2H), 7.08 (s, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 3.30 – 3.08 (m, 4H), 2.86 (dd, *J* = 15.1, 7.8 Hz, 1H), 1.46 (d, *J* = 1.7 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 179.46 (d, *J* = 3.2 Hz), 146.40, 133.59 (d, *J* = 74.8 Hz), 132.60 (d, *J* = 74.6 Hz), 131.56 (d, *J* = 2.5 Hz), 131.47 (d, *J* = 2.7 Hz), 130.34 (d, *J* = 9.4 Hz), 130.10 (d, *J* = 9.3 Hz), 128.39 (d, *J* = 6.8 Hz), 128.27 (d, *J* = 7.0 Hz), 125.81 (dd, *J* = 11.4, *J* = 3.8 Hz), 124.71 (d, *J* = 136.6 Hz), 123.20 (d, *J* = 102.5 Hz), 121.14 (dd, *J* = 11.4, *J* = 3.8 Hz), 107.73, 45.22 (d, *J* = 4.0 Hz), 37.66 (d, *J* = 71.2 Hz), 26.65, 26.52. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 25.36. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.10. **MS (ESI**, **m/z)**: calculated for $C_{24}H_{21}F_3NO_2P$ $[M+H]^+$: 444.1335, found: 444.6. Spectral data for this compound is consistent with that previously reported. [S1c]



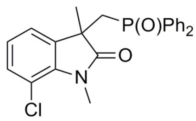
3-((diphenylphosphoryl)methyl)-1,3,7-trimethylindolin-2-one (3an) Light yellow solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.62 – 7.55 (m, 2H), 7.47 – 7.38 (m, 4H), 7.33 (tdd, *J* = 7.2, 5.3, 2.4 Hz, 4H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.69 (t, *J* = 7.6 Hz, 1H), 3.24 (s, 3H), 3.18 – 3.08 (m, 1H), 2.83 (dd, *J* = 15.2, 11.7 Hz, 1H), 2.45 (s, 3H), 1.40 (d, *J* = 1.9 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 180.0 (d, *J* = 3.4 Hz), 140.6, 133.2 (d, *J* = 197.1 Hz),133.2, 131.8 (d, *J* = 2.9 Hz), 131.6, 131.2 (d, *J* = 8.0 Hz), 131.1 (d, *J* = 2.3 Hz), 130.6 (d, *J* = 47.3 Hz), 130.6 (d, *J* = 28.7 Hz), 128.3 (d, J = 11.7 Hz), 127.9 (d, J = 11.8 Hz), 122.6, 122.0, 119.2, 44.7 (d, *J* = 3.7 Hz), 37.8 (d, *J* = 71.2 Hz),29.6, 27.4 (d, *J* = 12.5 Hz), 18.9. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 25.82. **MS (ESI**, **m/z)**: calculated for $C_{24}H_{24}NO_2P$ $[M+H]^+$: 390.1617, found: 390.2. Spectral data for this compound is consistent with that previously reported. [S1b]



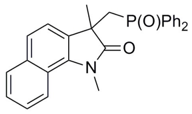
3-((diphenylphosphoryl)methyl)-7-methoxy-1,3-dimethylindolin-2-one (3ao) Light yellow solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.68 – 7.58 (m, 2H), 7.48 (dd, *J* = 11.5, 7.9 Hz, 2H), 7.44 – 7.27 (m, 6H), 6.84 (dt, *J* = 6.2, 2.3 Hz, 1H), 6.80 – 6.68 (m, 2H), 3.80 (d, *J* = 1.9 Hz, 3H), 3.26 (s, 3H), 3.08 (dd, *J* = 15.2, 10.0 Hz, 1H), 2.83 (dd, *J* = 15.2, 11.4 Hz, 1H), 1.40 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 179.4 (d, *J* = 4.2 Hz), 144.9, 133.7 (d, *J* = 99.1 Hz), 132.6 (d, *J* = 78.1 Hz), 132.6 (d, *J* = 75.3 Hz), 131.2 (d, *J* = 2.7 Hz), 131.1 (d, *J* = 2.7 Hz), 130.6 (d, *J* = 9.6 Hz), 130.4 (d, *J* = 9.1 Hz), 128.2 (d, *J* = 11.7 Hz), 127.9 (d, *J* = 11.8 Hz), 122.5, 117.5, 111.8, 55.8, 45.4 (d, *J* = 3.8 Hz), 37.6 (d, *J* = 71.2 Hz), 29.5, 26.9 (d, *J* = 12.0 Hz). **^{31}P NMR (162 MHz, CDCl$_3$)** δ 25.89. **MS (ESI**, **m/z)**: calculated for $C_{24}H_{24}NO_3P$ $[M+H]^+$: 406.1567, found: 406.3. Spectral data for this compound is consistent with that previously reported. [S1b]



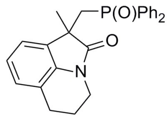
3-((diphenylphosphoryl)methyl)-7-fluoro-1,3-dimethylindolin-2-one (3ap) Light yellow solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.62 – 7.53 (m, 2H), 7.53 – 7.38 (m, 4H), 7.38 – 7.27 (m, 4H), 6.91 (d, *J* = 7.4 Hz, 1H), 6.86 (dd, *J* = 11.5, 8.4 Hz, 1H), 6.68 (m, 1H), 3.18 (d, *J* = 2.6 Hz, 3H), 3.09 (dd, *J* = 15.2, 10.1 Hz, 1H), 2.81 (dd, *J* = 15.2, 11.0 Hz, 1H), 1.40 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.9 (d, *J* = 3.7 Hz), 147.5 (d, *J* = 242.9 Hz), 134.2 (d, *J* = 5.9 Hz), 134.1 (d, *J* = 18.2 Hz), 133.1 (d, *J* = 12.0 Hz), 132.2, 131.4 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 2.7 Hz), 130.7 (d, *J* = 9.5 Hz), 130.4 (d, *J* = 9.2 Hz), 129.6 (d, *J* = 8.2 Hz), 128.3 (d, *J* = 11.7 Hz), 128.1 (d, *J* = 11.8 Hz), 122.5 (d, *J* = 6.3 Hz), 120.6 (d, *J* = 3.2 Hz), 115.7 (d, *J* = 19.1 Hz), 45.6 (dd, *J* = 3.7, 2.2 Hz), 37.7 (d, *J* = 71.0 Hz), 28.7 (d, *J* = 5.9 Hz), 27.1 (d, *J* = 12.1 Hz). **^{31}P NMR (162 MHz, CDCl$_3$)** δ 25.58. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -137.29. **MS (ESI**, **m/z)**: calculated for $C_{23}H_{21}FNO_2P$ $[M+H]^+$: 394.1367, found: 394.4. Spectral data for this compound is consistent with that previously reported. [S1b]



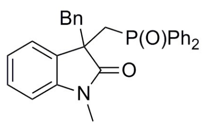
7-chloro-3-((diphenylphosphoryl)methyl)-1,3-dimethylindolin-2-one (3aq) Light yellow solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.59 (dd, *J* = 11.3, 7.4 Hz, 2H), 7.47 – 7.39 (m, 4H), 7.33 (m, 4H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.69 (m, 1H), 3.31 (s, 3H), 3.10 (dd, *J* = 15.2, 9.7 Hz, 1H), 2.80 (dd, *J* = 15.2, 11.6 Hz, 1H), 1.39 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 179.6 (d, *J* = 3.4 Hz), 138.8, 134.0 (d, *J* = 2.8 Hz), 133.5 (d, *J* = 99.5 Hz), 132.3 (d, *J* = 98.7 Hz), 131.5 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 2.7 Hz), 130.7 (d, *J* = 9.5 Hz), 130.4 (d, *J* = 9.1 Hz), 130.2, 128.4 (d, *J* = 11.7 Hz), 128.1 (d, *J* = 11.8 Hz), 123.3, 122.8, 115.1, 45.1 (d, *J* = 3.8 Hz), 37.7 (d, *J* = 70.8 Hz), 29.6, 27.3 (d, *J* = 12.1 Hz). **^{31}P NMR (162 MHz, CDCl$_3$)** δ 25.65. **MS (ESI, m/z)**: calculated for $C_{23}H_{21}ClNO_2P$ [M+H]$^+$: 410.1071, found: 410.2. Spectral data for this compound is consistent with that previously reported. [S1b]



3-((diphenylphosphoryl)methyl)-1,3-dimethyl-1H-benzo[g]indol-2(3H)-one (3ar) Gray solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.33 (m, 5H), 7.27 – 7.17 (m, 4H), 7.09 (td, *J* = 7.6, 2.7 Hz, 2H), 6.79 (d, *J* = 7.4 Hz, 1H), 3.83 (dd, *J* = 15.0, 9.9 Hz, 1H), 3.34 (s, 3H), 2.99 (dd, *J* = 15.0, 11.1 Hz, 1H), 1.74 (d, *J* = 2.2 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 172.2 (d, *J* = 2.2 Hz), 136.5, 135.3 (d, *J* = 2.4 Hz), 133.7 (d, *J* = 58.2 Hz), 133.0, 132.7 (d, *J* = 57.5 Hz), 131.0 (d, *J* = 2.6 Hz), 130.9 (d, *J* = 3.5 Hz), 130.8, 130.5 (d, *J* = 9.2 Hz), 128.0 (d, *J* = 11.8 Hz), 127.6 (d, *J* = 11.7 Hz), 126.3 (d, *J* = 4.2 Hz), 126.1, 124.1, 122.2, 119.1, 108.4, 45.2 (d, *J* = 3.5 Hz), 42.3 (d, *J* = 69.8 Hz), 34.8 (d, *J* = 13.6 Hz), 29.8. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 27.30. **MS (ESI, m/z)**: calculated for $C_{27}H_{24}NO_2P$ [M+H]$^+$: 426.1617, found: 426.4. Spectral data for this compound is consistent with that previously reported. [S1c]

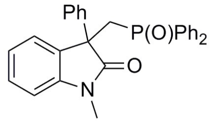


1-((diphenylphosphoryl)methyl)-1-methyl-5,6-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-2(4H)-one (3as) Light yellow oil; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.65 – 7.54 (m, 2H), 7.54 – 7.45 (m, 2H), 7.45 – 7.27 (m, 6H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.69 (t, *J* = 7.6 Hz, 1H), 3.68 – 3.52 (m, 1H), 3.34 (m, 1H), 3.07 (dd, *J* = 15.2, 10.1 Hz, 1H), 2.85 (dd, *J* = 15.2, 11.1 Hz, 1H), 2.65 (t, *J* = 7.4 Hz, 2H), 1.97 – 1.77 (m, 2H), 1.42 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.2 (d, *J* = 4.6 Hz), 138.6, 133.9 (d, *J* = 71.6 Hz), 132.9 (d, *J* = 70.9 Hz), 131.3 (d, *J* = 2.8 Hz), 131.2 (d, *J* = 2.6 Hz), 130.7 (d, *J* = 9.5 Hz), 130.5 (d, *J* = 9.1 Hz), 130.0 (d, *J* = 2.9 Hz), 128.3 (d, *J* = 11.7 Hz), 128.1 (d, *J* = 11.8 Hz), 126.6, 122.7, 121.6, 119.7, 46.6 (d, *J* = 3.8 Hz), 38.8, 37.4 (d, *J* = 71.5 Hz), 26.6 (d, *J* = 11.8 Hz), 24.4, 20.8. ^{31}P NMR (162 MHz, CDCl$_3$) δ 26.11. **MS (ESI, m/z)**: calculated for $C_{25}H_{24}NO_2P$ [M+H]$^+$: 402.1617, found: 402.4. Spectral data for this compound is consistent with that previously reported. [S1c]

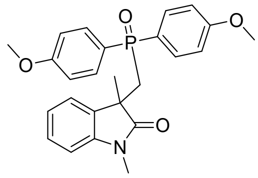


3-benzyl-3-((diphenylphosphoryl)methyl)-1-methylindolin-2-one (3at) Light yellow solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.64 – 7.57 (m, 2H), 7.49 – 7.39 (m, 3H), 7.39 – 7.32 (m, 3H), 7.27 (m, 2H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.10 – 7.04 (m, 1H), 7.04 – 6.92 (m, 3H), 6.78 (td, *J* = 7.6, 0.7 Hz, 1H), 6.76 – 6.66 (m, 2H), 6.36 (d, *J* = 7.8 Hz, 1H), 3.28 – 2.93 (m, 4H), 2.68 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 177.8 (d, *J* = 3.7 Hz), 143.4, 134.5 (d, *J* = 1.5 Hz), 133.8 (d, *J* = 99.4 Hz), 132.8 (d, *J* = 98.6 Hz), 131.2

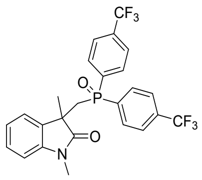
(d, J = 2.7 Hz), 130.8 (d, J = 9.5 Hz), 130.5 (d, J = 9.1 Hz), 129.9, 128.4 (d, J = 4.6 Hz), 128.1 (d, J = 25.7 Hz), 127.9 (d, J = 4.4 Hz), 127.2, 126.5, 125.8, 121.6, 107.4, 50.9 (d, J = 3.7 Hz), 46.2 (d, J = 12.2 Hz), 36.5 (d, J = 71.2 Hz), 25.8. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 25.94. **MS (ESI, m/z)**: calculated for $C_{29}H_{26}NO_2P$ $[M+H]^+$: 452.1774, found: 452.3. Spectral data for this compound is consistent with that previously reported. [S1a]



3-((diphenylphosphoryl)methyl)-1-methyl-3-phenylindolin-2-one (3au) Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 – 7.52 (m, 2H), 7.51 – 7.45 (m, 2H), 7.42 – 7.27 (m, 8H), 7.26 – 7.13 (m, 4H), 7.04 (d, J = 7.4 Hz, 1H), 6.81 – 6.65 (m, 2H), 3.71 (dd, J = 14.9, 10.9 Hz, 1H), 3.24 (dd, J = 14.9, 10.1 Hz, 1H), 3.02 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.5 (d, J = 2.2 Hz), 144.2, 140.6 (d, J = 12.3 Hz), 133.8 (d, J = 31.2 Hz), 132.9 (d, J = 30.1 Hz), 131.3 (d, J = 2.7 Hz), 131.0 (d, J = 2.7 Hz), 130.7 (d, J = 9.4 Hz), 130.4 (d, J = 9.1 Hz), 129.0 (d, J = 3.2 Hz), 128.5, 128.3 (d, J = 7.9 Hz), 128.2, 128.1 (d, J = 6.7 Hz), 127.1 (d, J = 54.9 Hz), 126.4, 121.8, 108.1, 52.6 (d, J = 3.0 Hz), 38.5 (d, J = 70.1 Hz), 26.6. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 24.91. **MS (ESI, m/z)**: calculated for $C_{28}H_{24}NO_2P$ $[M+H]^+$:438.1617, found: 438.5. Spectral data for this compound is consistent with that previously reported. [S1a]

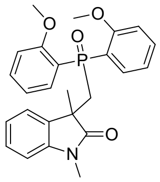


3-((bis(4-methoxyphenyl)phosphoryl)methyl)-1,3-dimethylindolin-2-one (3av) White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 – 7.44 (m, 2H), 7.41 – 7.30 (m, 2H), 7.26 – 7.15 (m, 2H), 6.84 (dd, J = 25.2, 7.3 Hz, 5H), 6.67 (d, J = 7.6 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.16 – 2.91 (m, 4H), 2.86 – 2.72 (m, 1H), 1.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 179.5, 161.8 (d, J = 2.9 Hz), 142.8, 132.6 (d, J = 10.9 Hz), 132.3 (d, J = 10.5 Hz), 131.6, 127.8, 124.8, 122.1, 113.9 (d, J = 12.7 Hz), 113.6 (d, J = 12.8 Hz), 107.7, 55.2, 45.5 (d, J = 3.7 Hz), 37.6 (d, J = 72.0 Hz), 27.0 (d, J = 12.3 Hz), 26.3. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 26.42. **MS (ESI, m/z)**: calculated for $C_{25}H_{26}NO_4P$ $[M+H]^+$:436.1672, found: 436.3. Spectral data for this compound is consistent with that previously reported.[S1i]

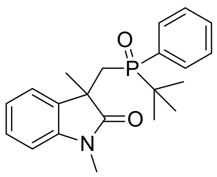


3-((bis(4-(trifluoromethyl)phenyl)phosphoryl)methyl)-1,3-dimethylindolin-2-one (3aw) White solid; M.p. = 181-183 ^{o}C, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (dd, J = 21.2, 9.8 Hz, 8H), 7.18 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 7.3 Hz, 1H), 6.74 (t, J = 7.5 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 3.21 (dd, J = 15.1, 10.4 Hz, 1H), 3.03 (s, 3H), 2.90 (dd, J = 15.1, 10.8 Hz, 1H), 1.46 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ178.9 (d, J = 3.1 Hz), 142.9, 137.2 (d, J = 96.8 Hz), 136.8, 135.9, 133.6 (d, J = 18.2 Hz), 133.5 (d, J = 18.4 Hz), 133.3 (d, J = 18.4 Hz), 133.2 (d, J = 18.3 Hz), 131.2 (d, J = 9.7 Hz), 130.8 (d, J = 9.6 Hz), 130.6 (d, J = 2.9 Hz), 128.3, 125.4 (d, J = 11.9 Hz), 125.3 (d, J = 11.9 Hz), 125.2 (d, J = 24.6 Hz), 125.1 (d, J = 11.9 Hz), 125.1 (d, J = 11.9 Hz), 124.7 (d, J = 5.4 Hz), 124.4, 122.1, 122.0 (d, J

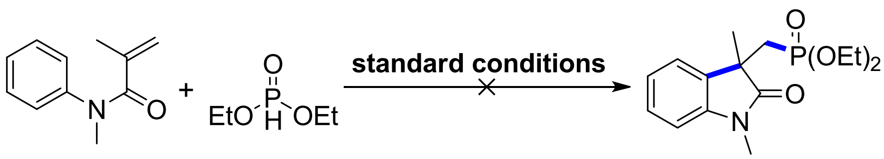
= 6.1 Hz), 108.0, 45.2 (d, J = 3.8 Hz), 37.5 (d, J = 72.2 Hz), 27.1 (d, J = 13.1 Hz), 26.3; **^{31}P NMR (162 MHz, CDCl$_3$)** δ 24.16,**^{19}F NMR (376 MHz, CDCl$_3$)** δ -63.26, -63.31. **HRMS (ESI, m/z)**: calculated for $C_{25}H_{20}F_6NO_2P$ $(M+Na)^+$, 534.1028; found, 534.1030.



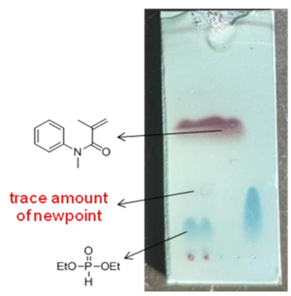
3-((bis(2-methoxyphenyl)phosphoryl)methyl)-1,3-dimethylindolin-2-one (3ax) White solid; M.p. = 151-152 °C, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.29 (m, 3H), 7.23 (dd, J = 14.1, 6.9 Hz, 2H), 7.09 (t, J = 7.6 Hz, 1H), 6.90 – 6.77 (m, 4H), 6.73 – 6.61 (m, 2H), 3.76 (s, 3H), 3.66 (s, 3H), 3.30 – 3.14 (m, 2H), 3.08 (s, 3H), 1.44 (s, 3H), **^{13}C NMR (101 MHz, CDCl$_3$)** δ179.9 (d, J = 6.3 Hz), 160.2 (d, J = 91.0 Hz), 142.9, 133.7 (d, J = 6.7 Hz), 133.5 (d, J = 7.4 Hz), 133.1 (d, J = 2.0 Hz), 132.9 (d, J = 1.9 Hz), 132.3 (d, J = 2.9 Hz), 127.4, 124.9, 122.0 (d, J = 92.6 Hz), 121.0 (d, J = 93.0 Hz), 121.7, 120.5 (d, J = 60.0 Hz), 120.4 (d, J = 60.3 Hz), 110.6 (d, J = 3.8 Hz), 110.5 (d, J = 3.9 Hz), 107.4, 55.3 (d, J = 8.0 Hz), 45.7 (d, J = 4.1 Hz), 36.0 (d, J = 75.1 Hz), 26.3, 26.2 (d, J = 11.6 Hz), **^{31}P NMR (162 MHz, CDCl$_3$)** δ 26.62. **HRMS (ESI, m/z)**: calculated for $C_{25}H_{26}NO_4P$ $(M+Na)^+$, 458.1492; found, 458.1493.



3-((tert-butyl(phenyl)phosphoryl)methyl)-1,3-dimethylindolin-2-one (3ay) Thick solid; M.p. = 184-185 °C, **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.41 (dd, J = 7.5, 0.7 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.28 – 7.22 (m, 2H), 7.06 (td, J = 7.7, 1.2 Hz, 1H), 6.82 (td, J = 7.6, 0.9 Hz, 1H), 6.46 (d, J = 7.7 Hz, 1H), 2.85 (s, 3H), 2.66 – 2.58 (m, 2H), 1.54 (d, J = 0.6 Hz, 3H), 1.08 (d, J = 14.5 Hz, 9H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ179.8 (d, J = 6.1 Hz), 142.0, 131.8, 131.7, 131.1 (d, J = 3.2 Hz), 130.8 (d, J = 2.7 Hz), 129.3 (d, J = 86.9 Hz), 127.6, 127.4, 127.3, 126.0, 121.9, 107.2, 45.3 (d, J = 4.6 Hz), 33.3 (d, J = 69.7 Hz), 30.3 (d, J = 62.3 Hz), 26.4 (d, J = 7.8 Hz), 25.9, 24.1. **^{31}P NMR (162 MHz, CDCl$_3$)** δ 43.90. **HRMS (ESI, m/z)**: calculated for $C_{21}H_{26}NO_2P$ $(M+Na)^+$, 378.1593; found, 378.1590.

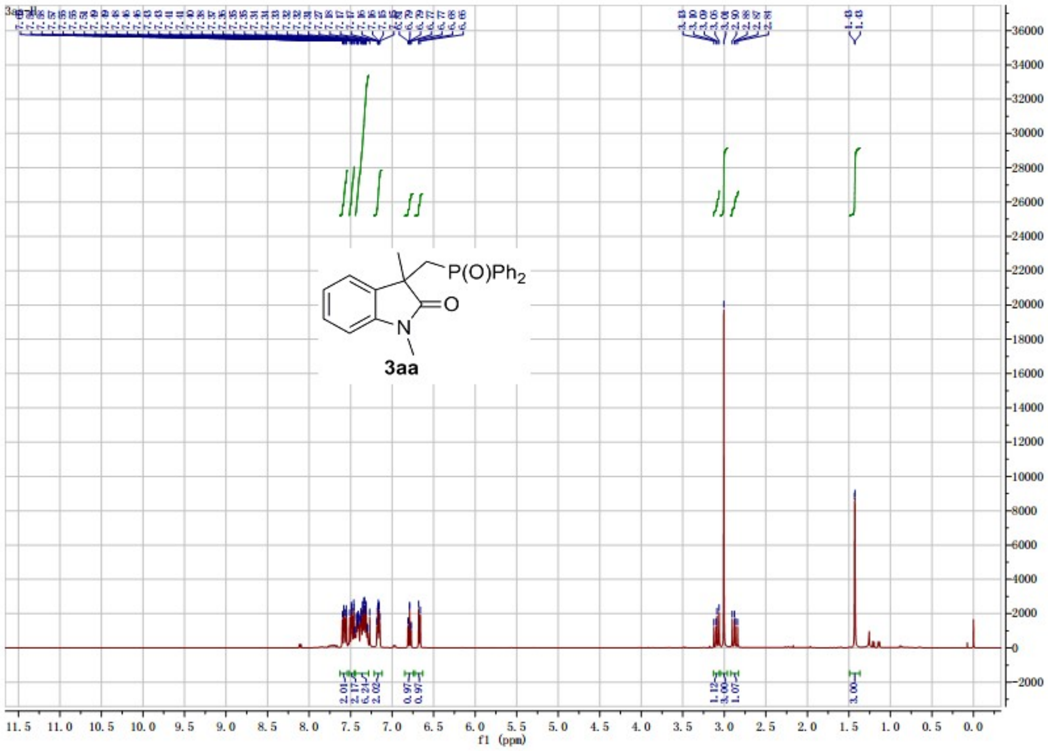


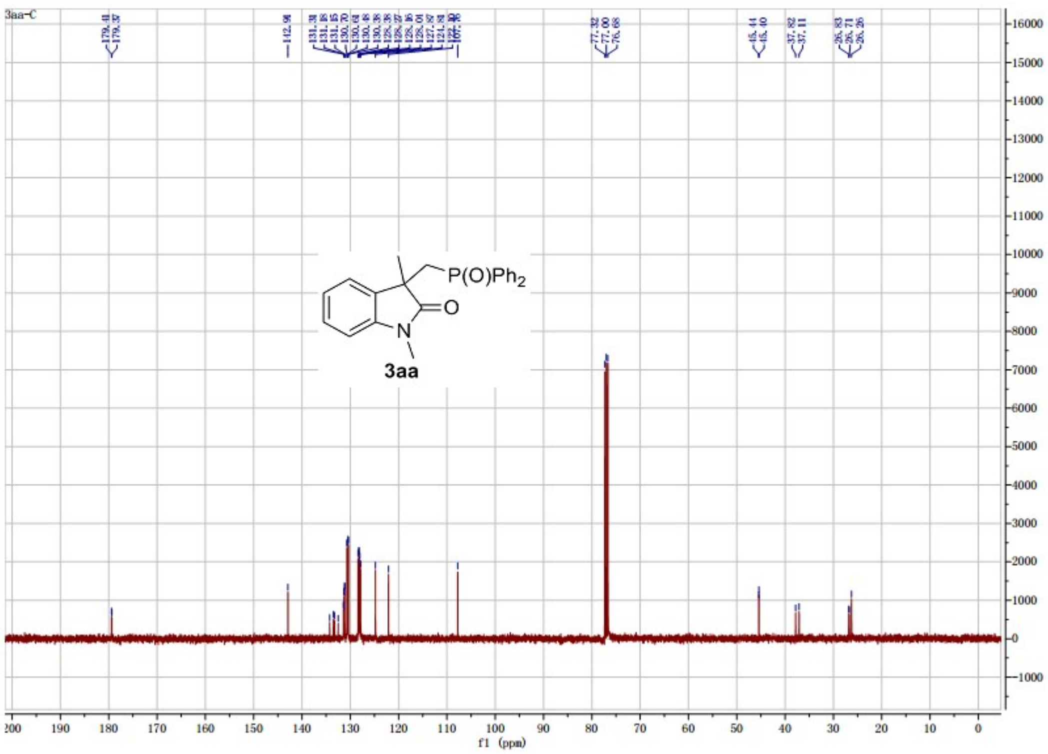
3az, 0%, not detected

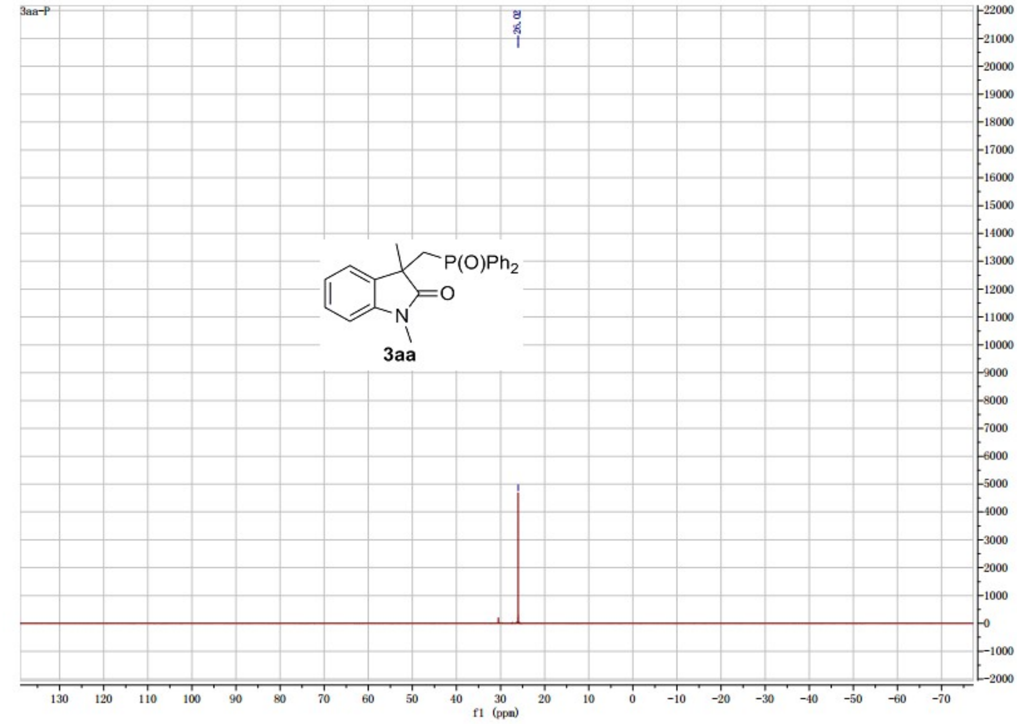


Diethyl phosphate instead of diphenylphosphine oxide under the optimal conditions, and the expected product **3az** was not detected. trace amount of newpoint can be observed which could not separated by column chromatography. It may be that diethyl phosphite has stronger nucleophilicity and is difficult to form stable intermediate phosphorus radicals through a HAT process.

7. Copies of NMR spectra



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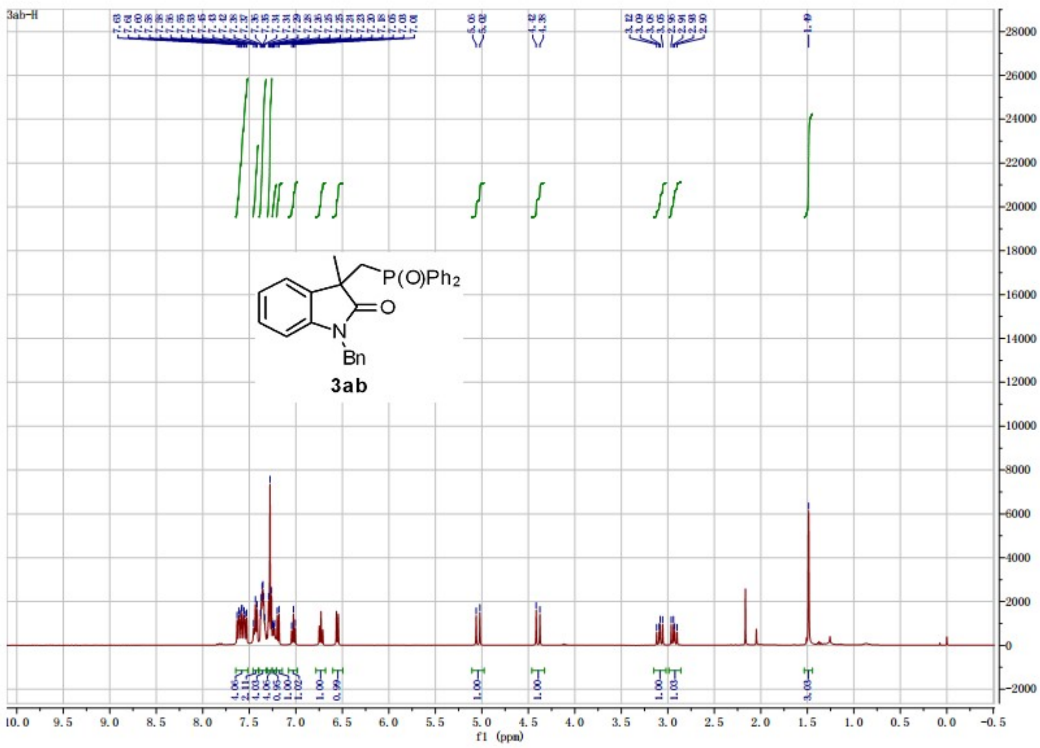
N
O
3aa
f1 (ppm)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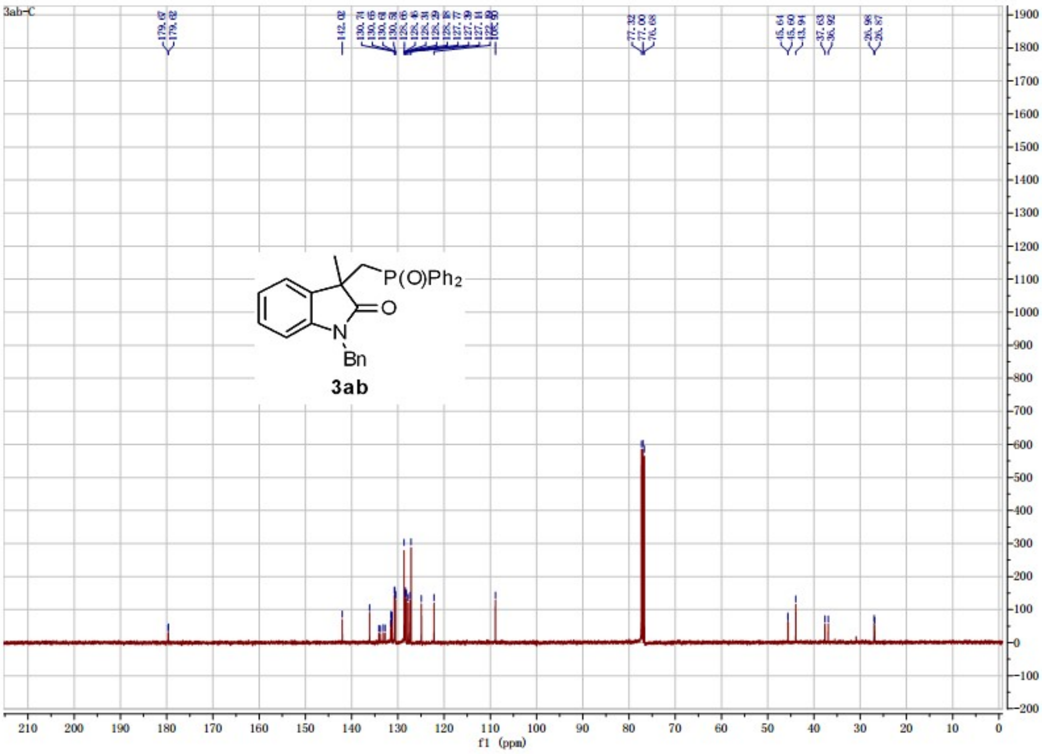
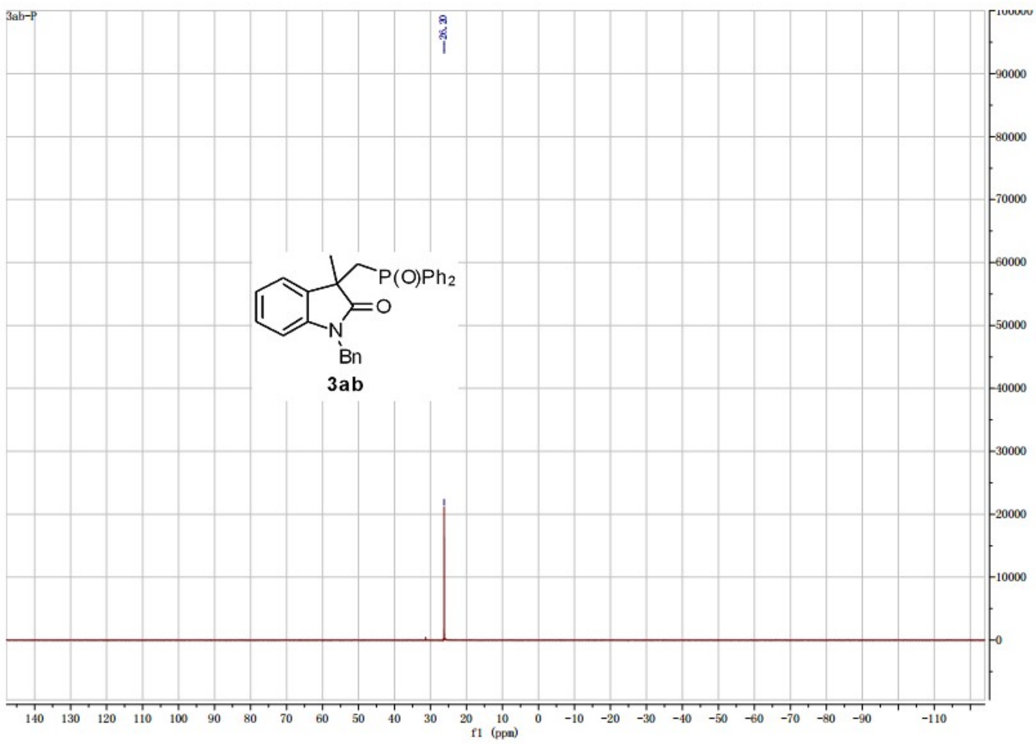
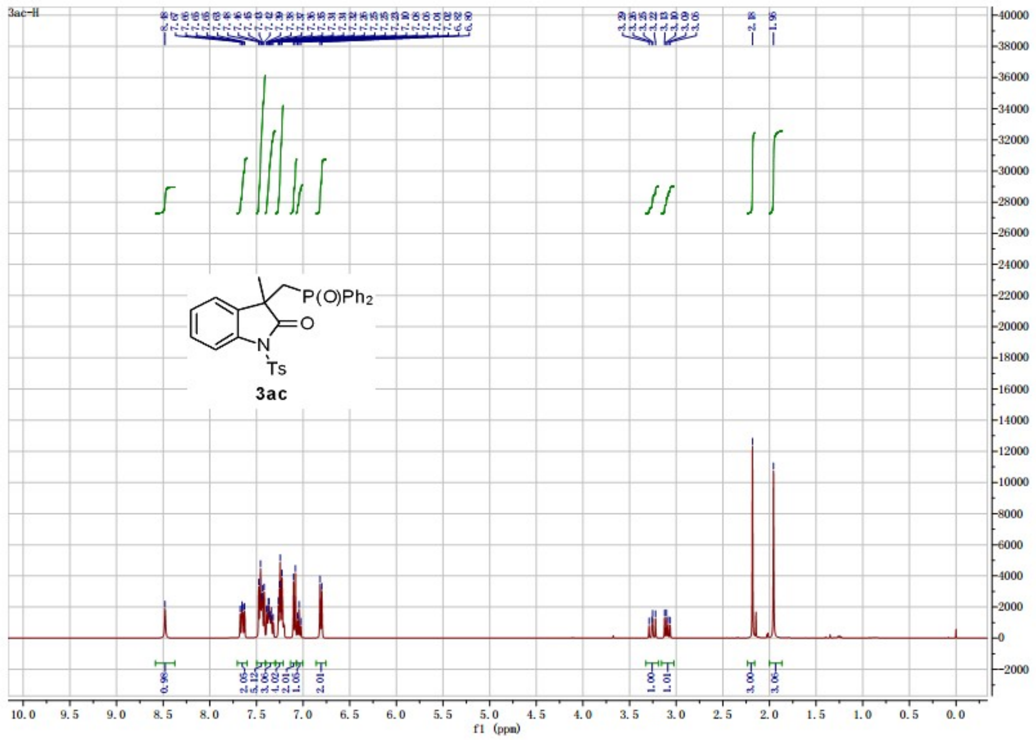
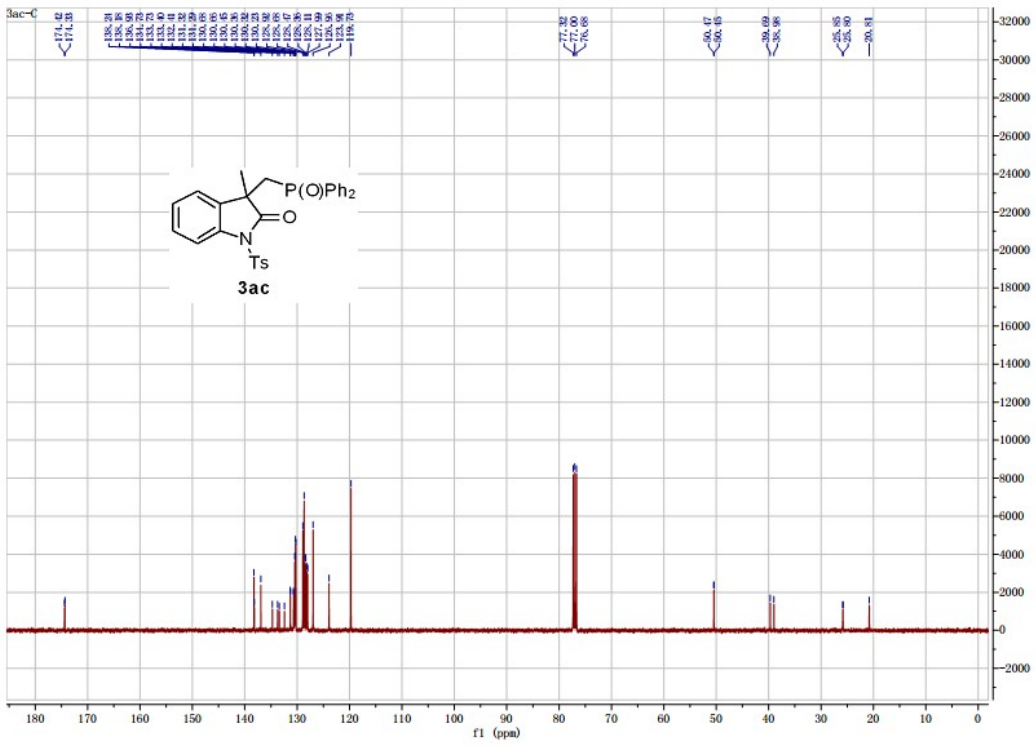
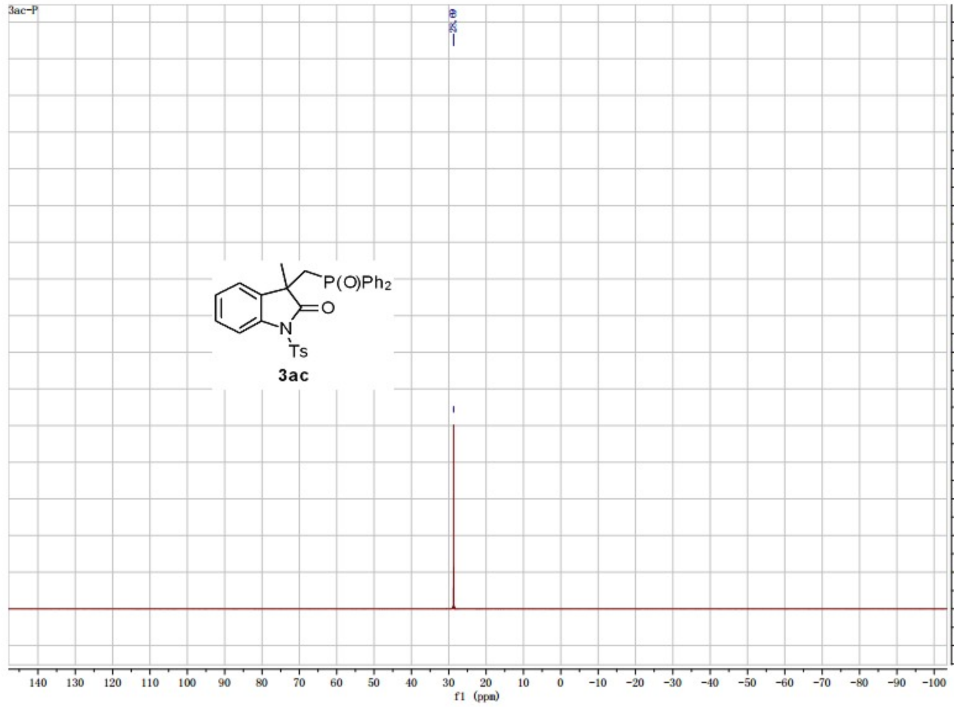
N
Bn
3ab
f1 (ppm)







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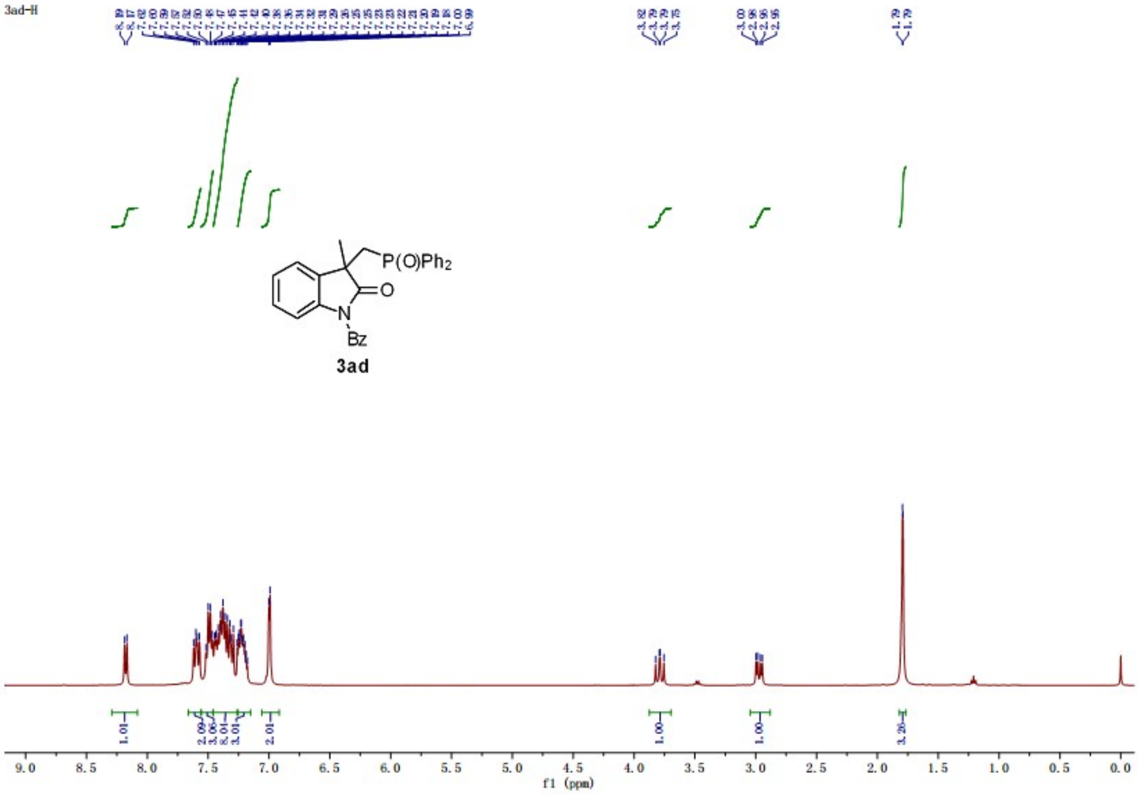
O
N
Ts
3ac
f1 (ppm)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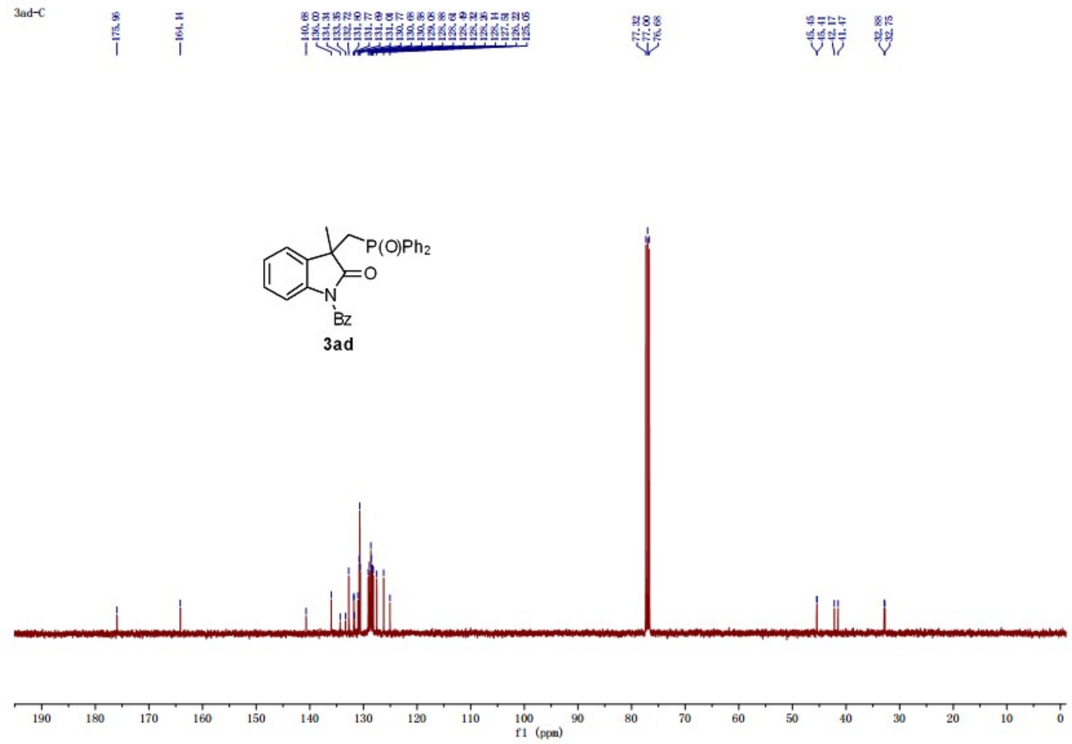
P(O)Ph2
O
N
Bz
3ad
f1 (ppm)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Bz
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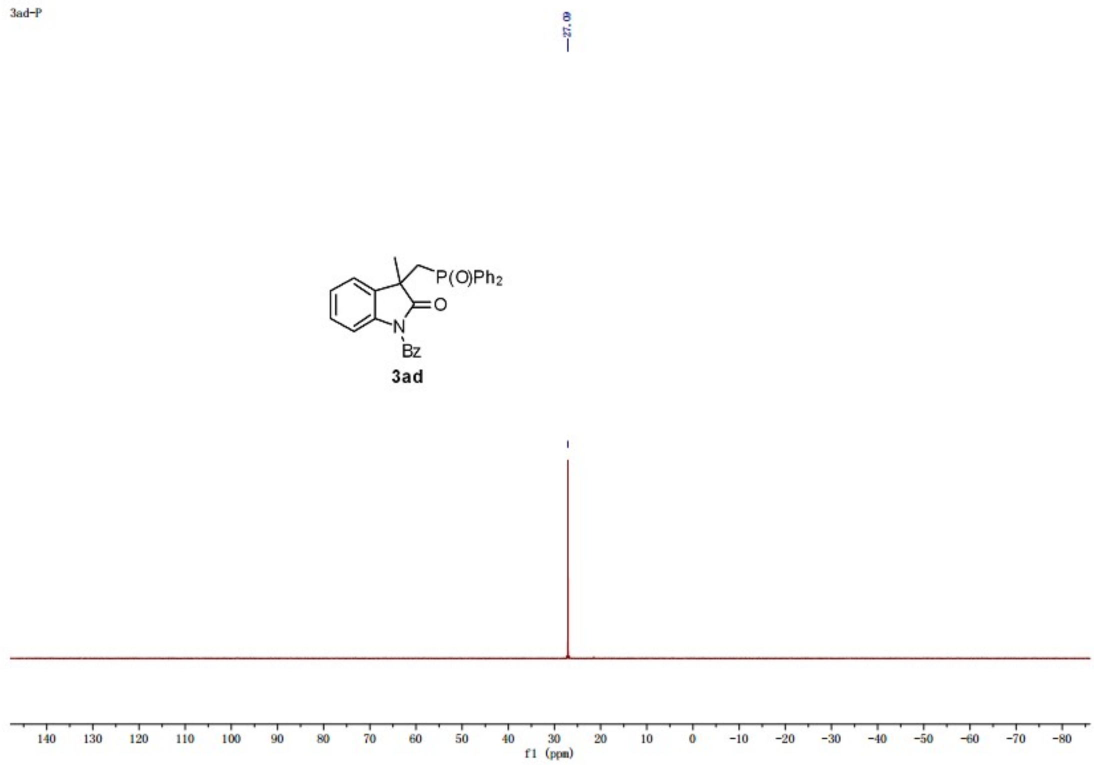
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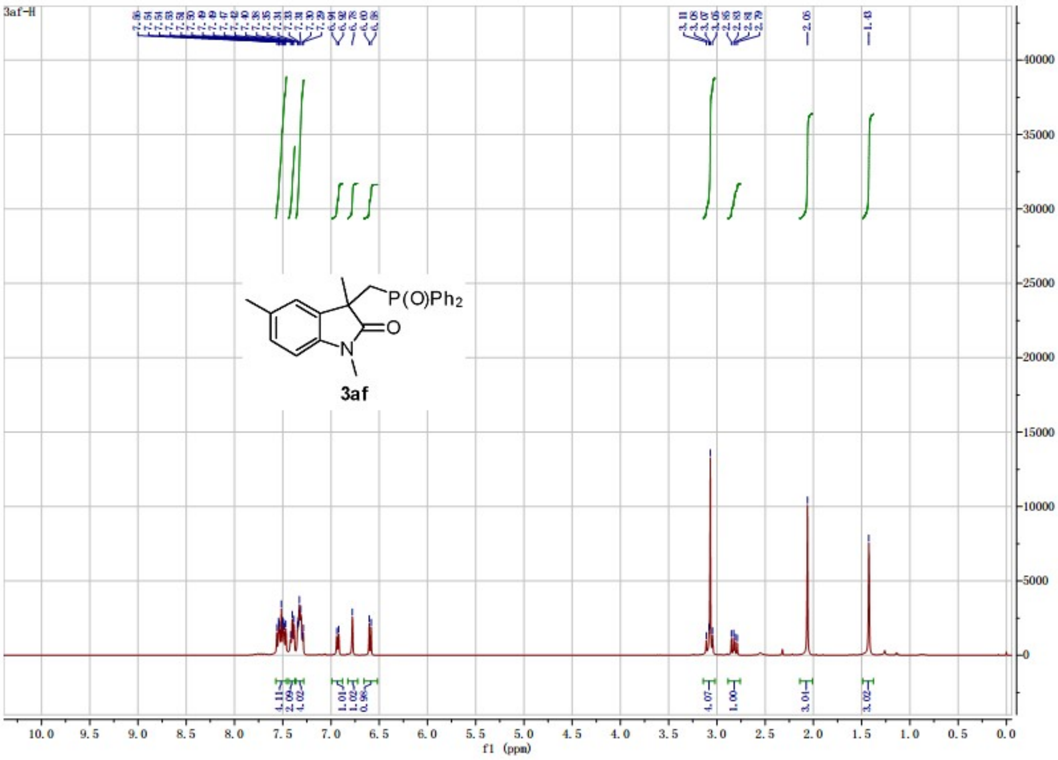

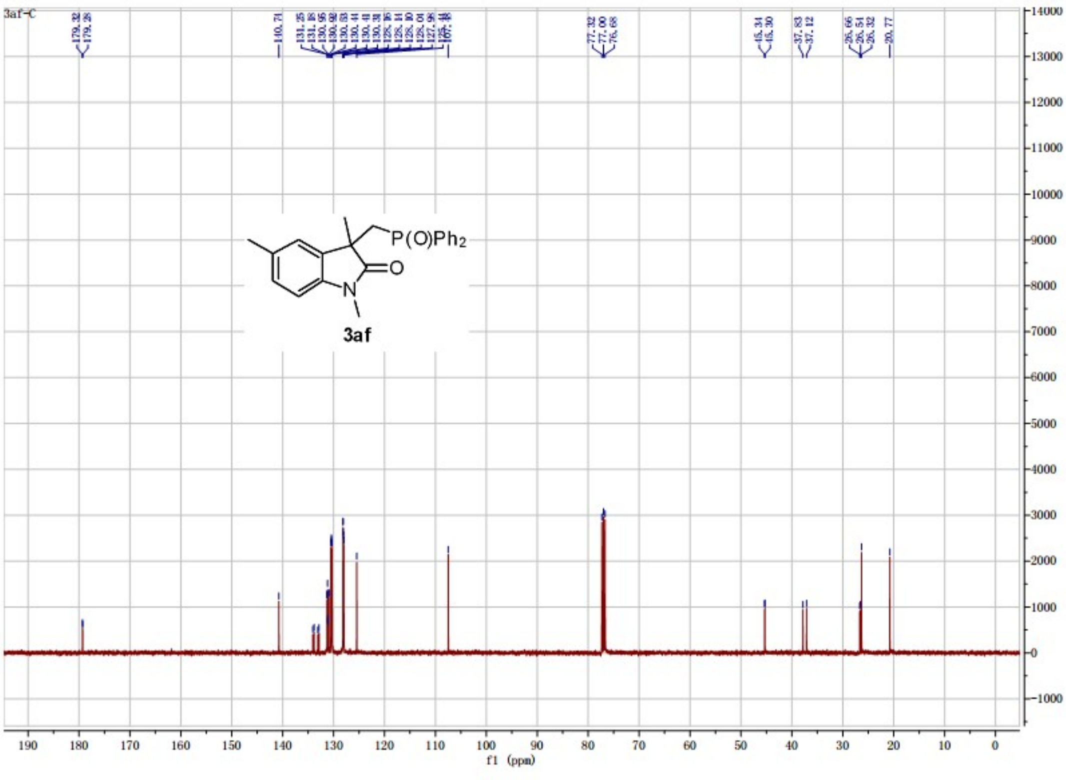

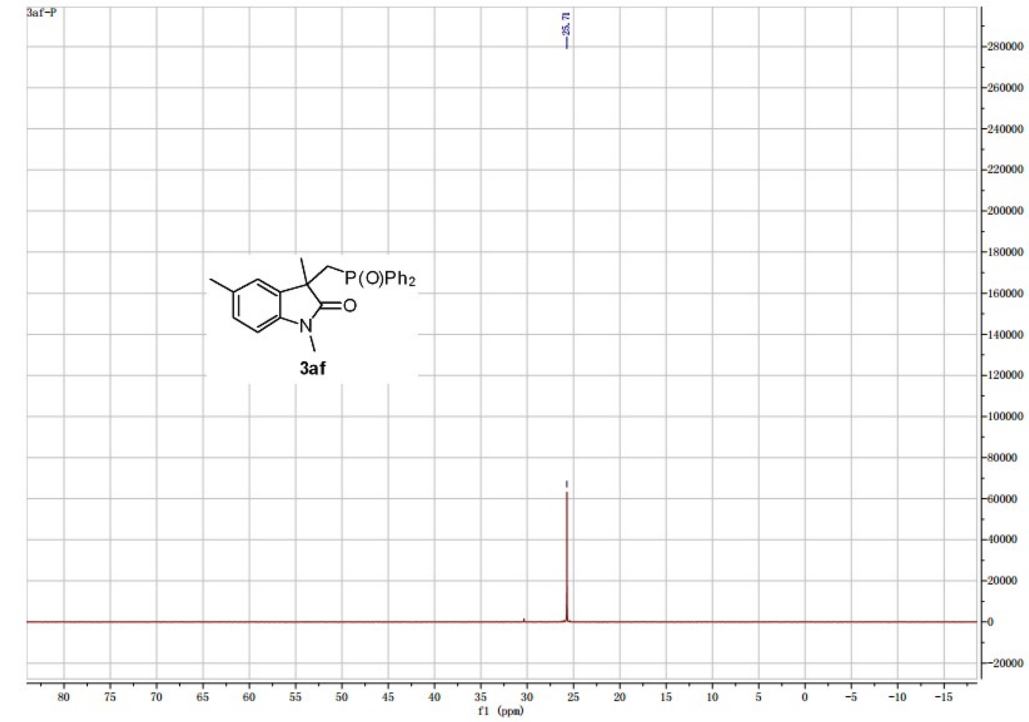
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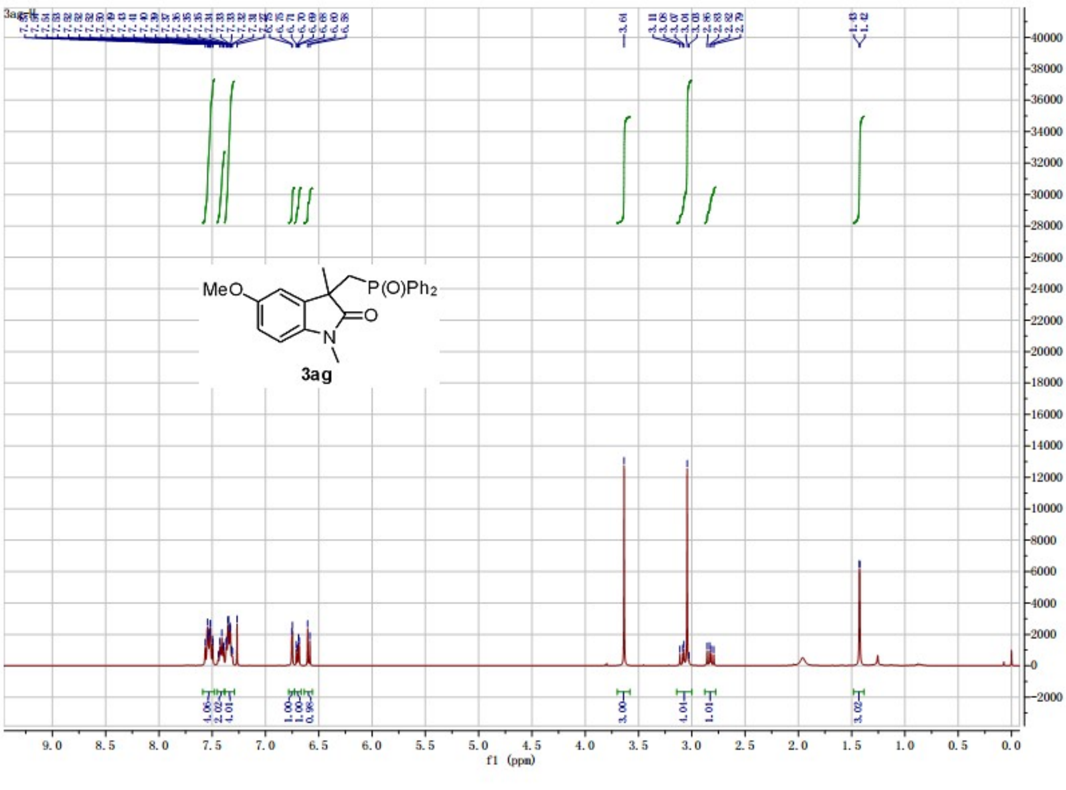
O
N
3af
f1 (ppm)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1.43
1.42
MeO
P(O)Ph2
O
N
3ag
4.06
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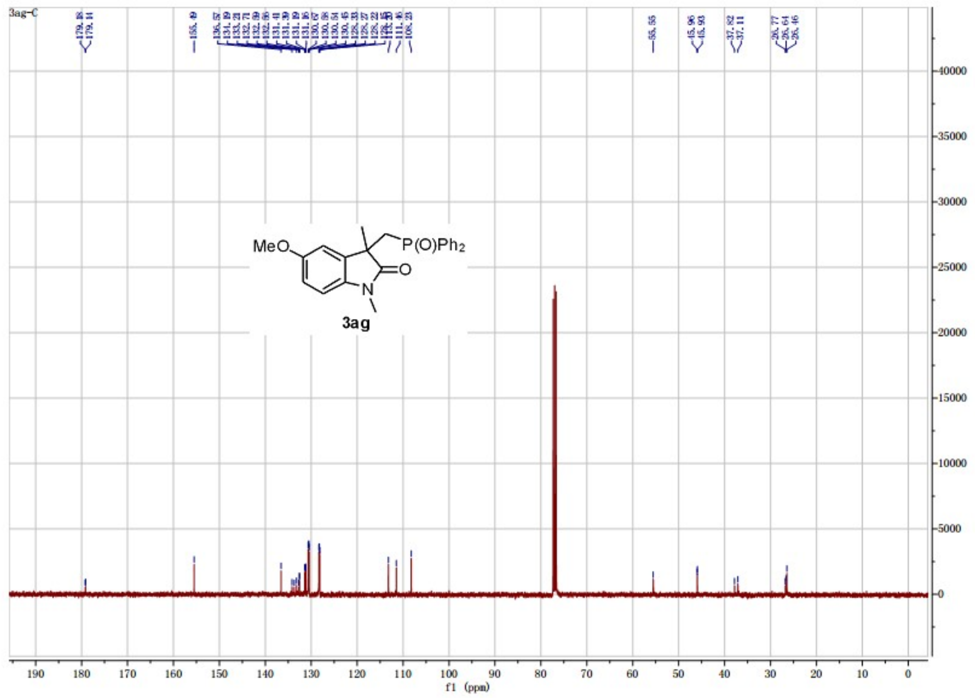
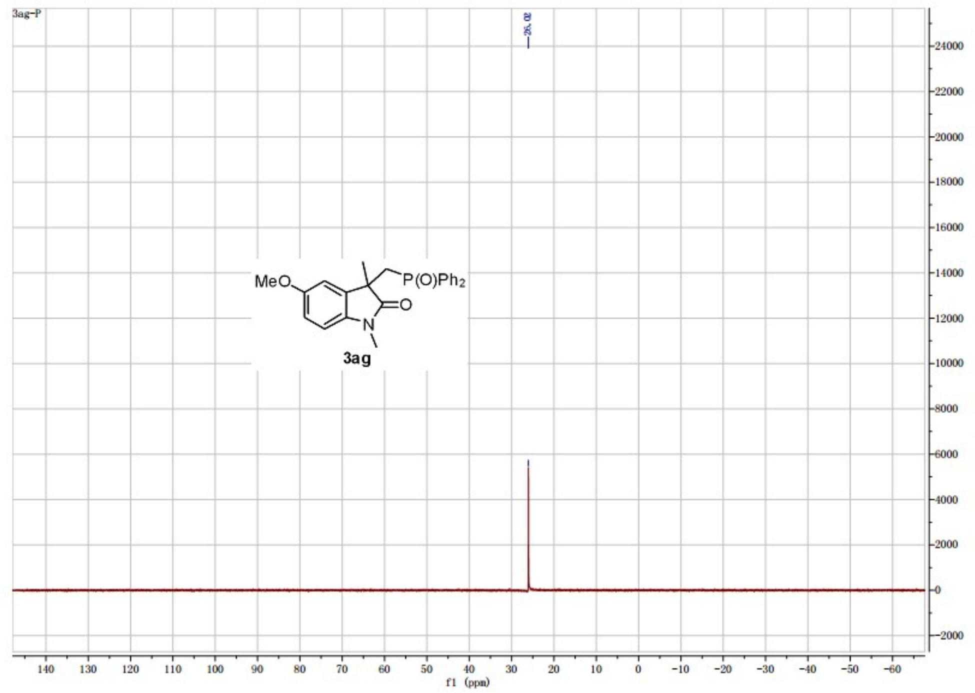
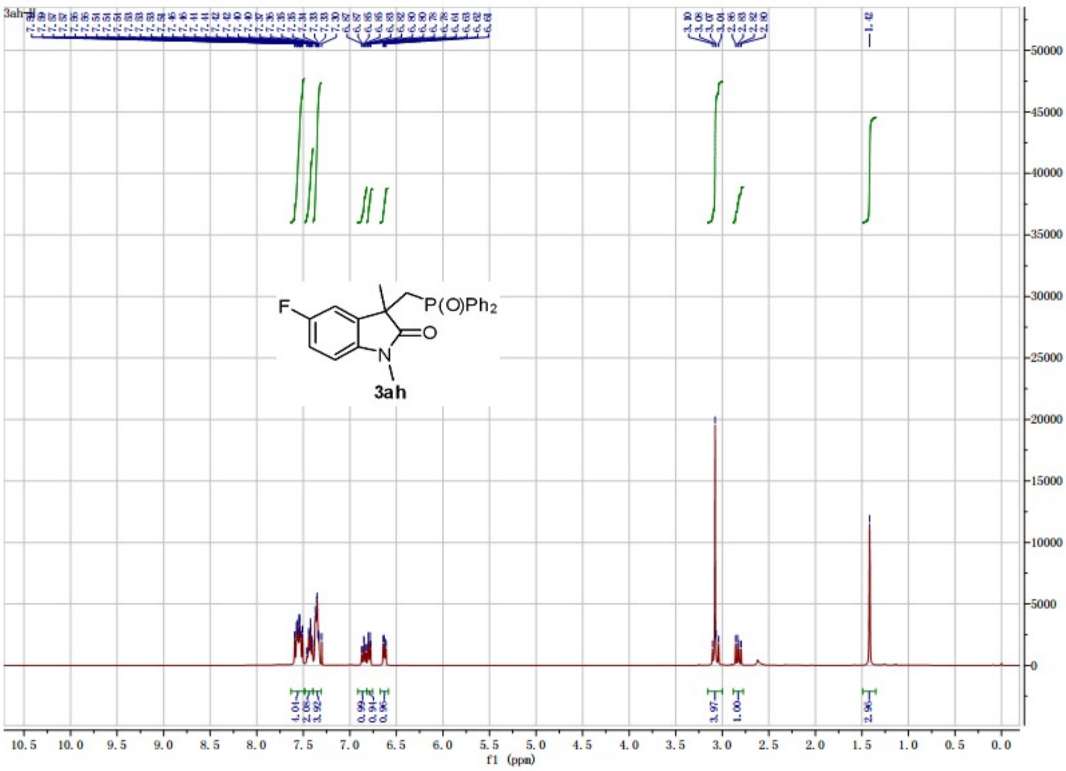
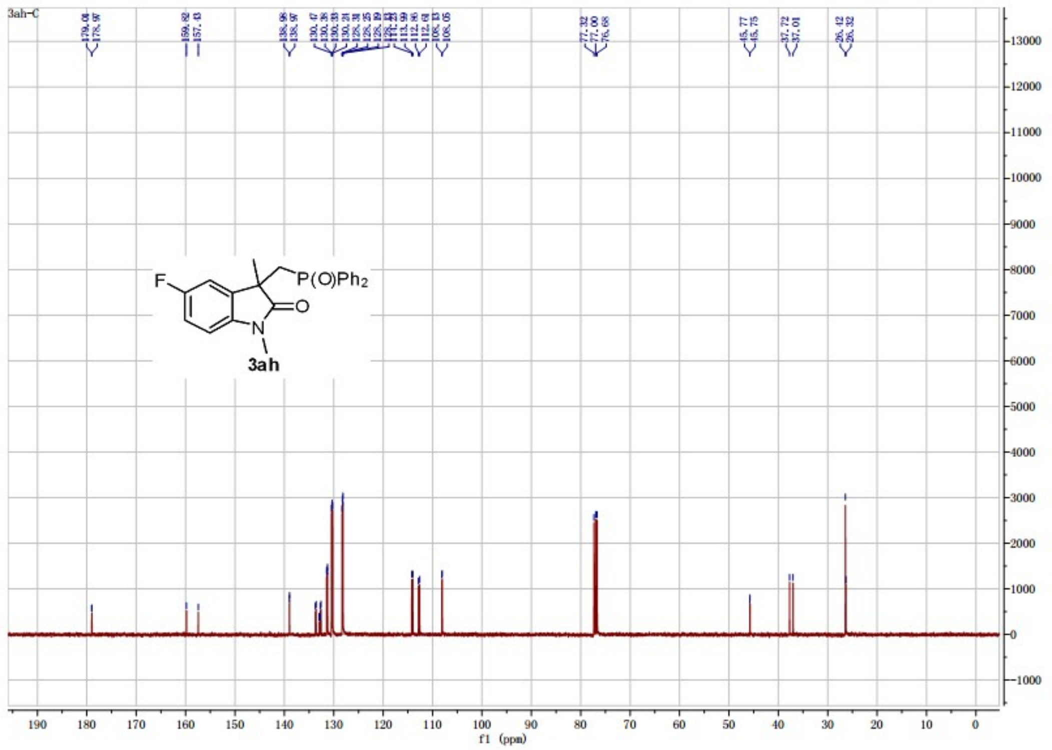
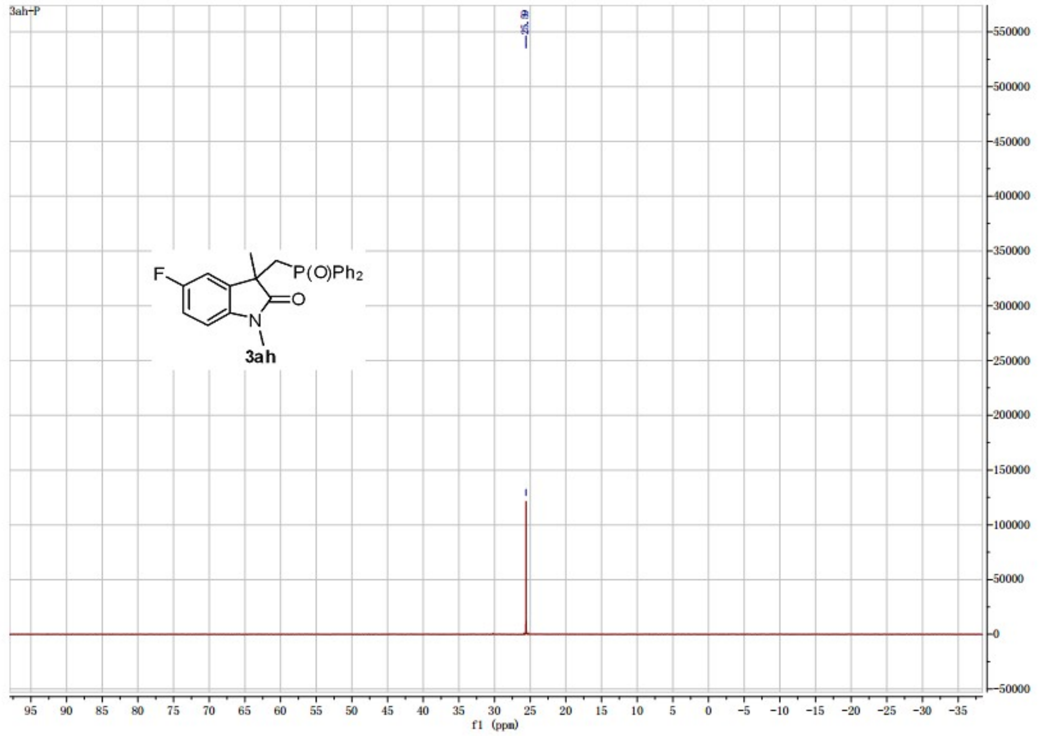
4.01
1.00
1.00
0.98
3.00
4.01
1.01
3.02
f1 (ppm)







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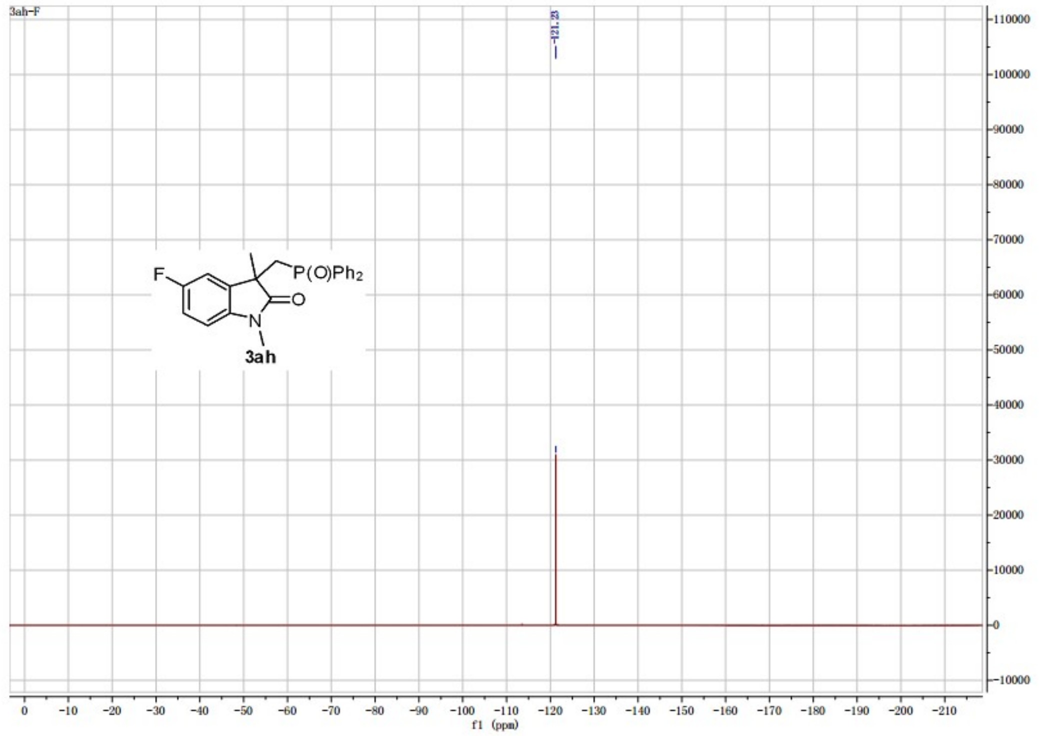
f1 (ppm)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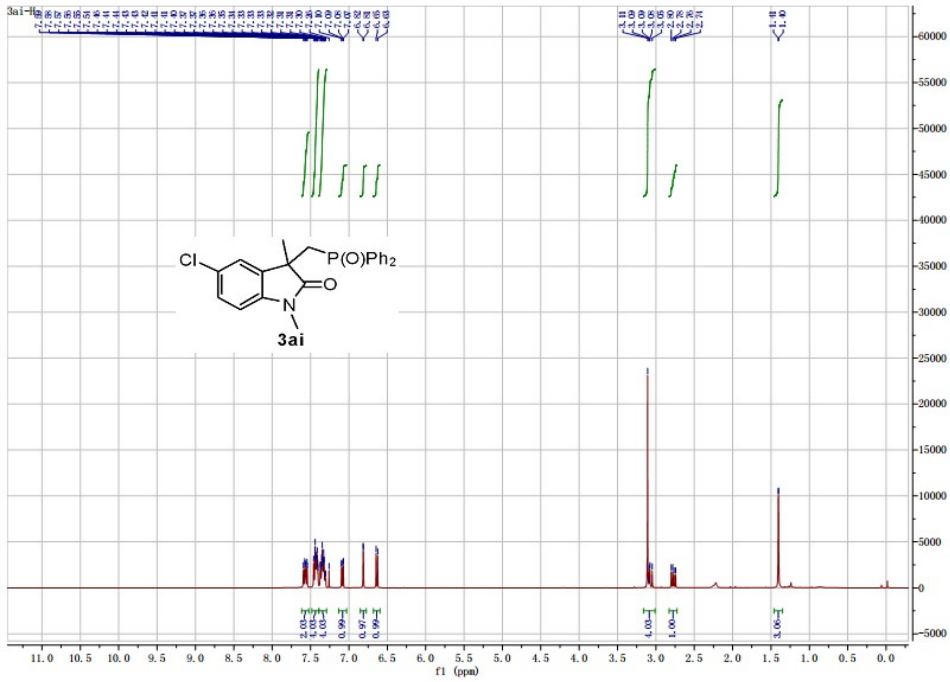
f1 (ppm)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Cl
P(O)Ph2
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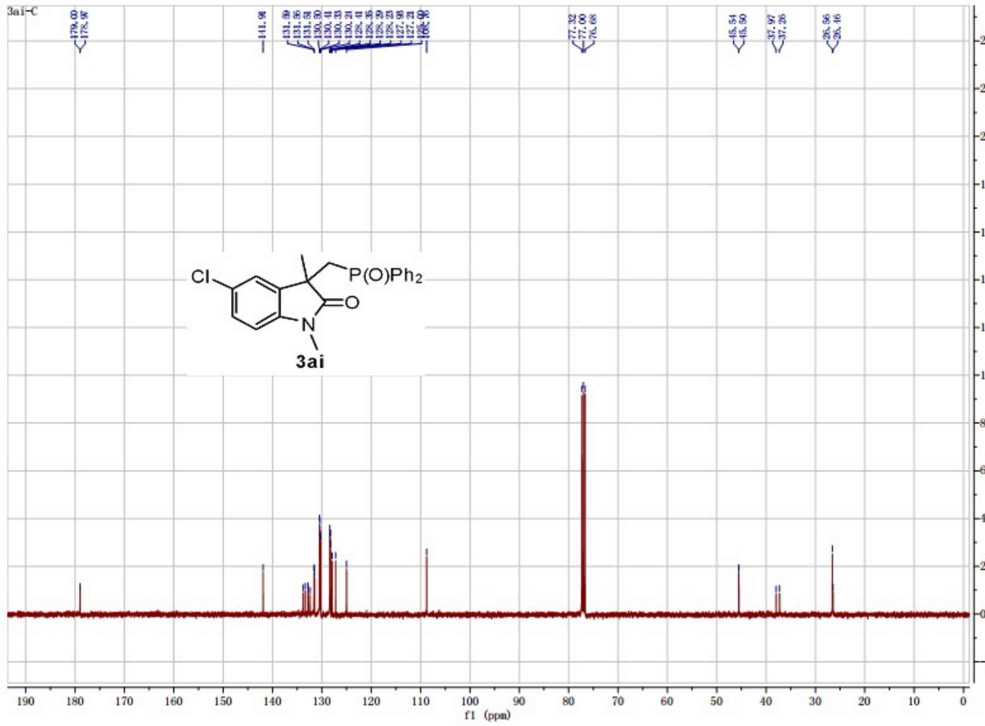
N
3ai
f1 (ppm)


3ai-C
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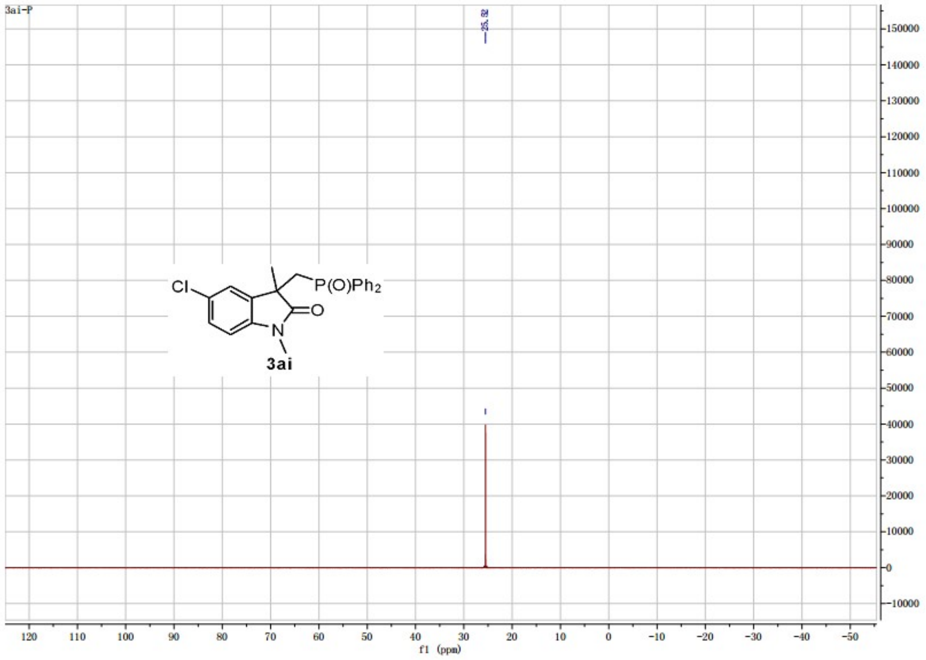
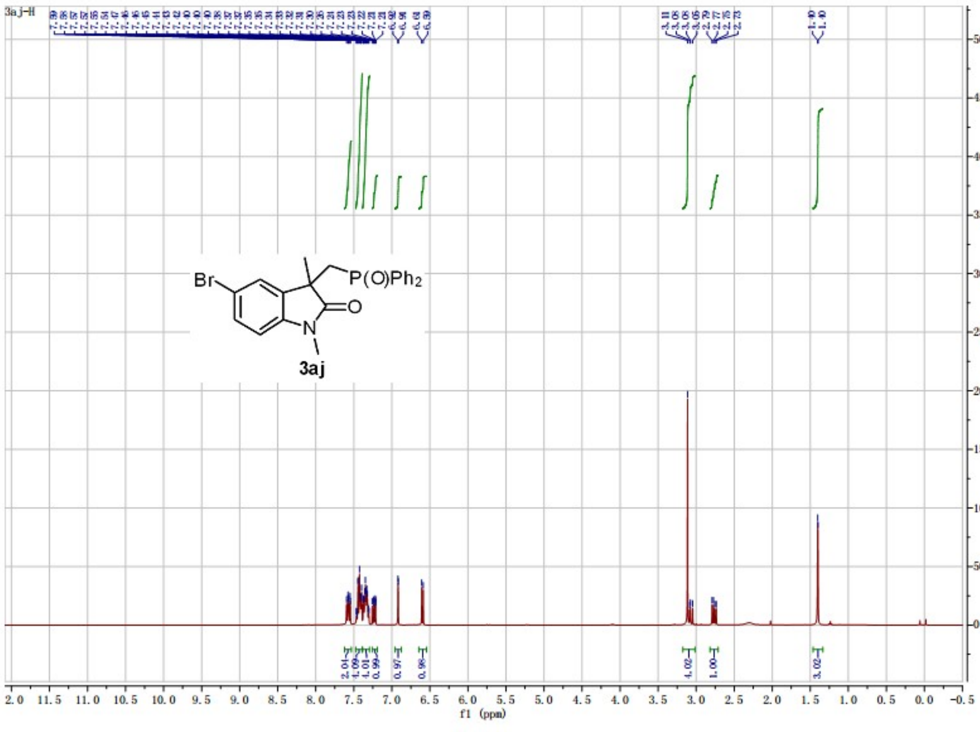
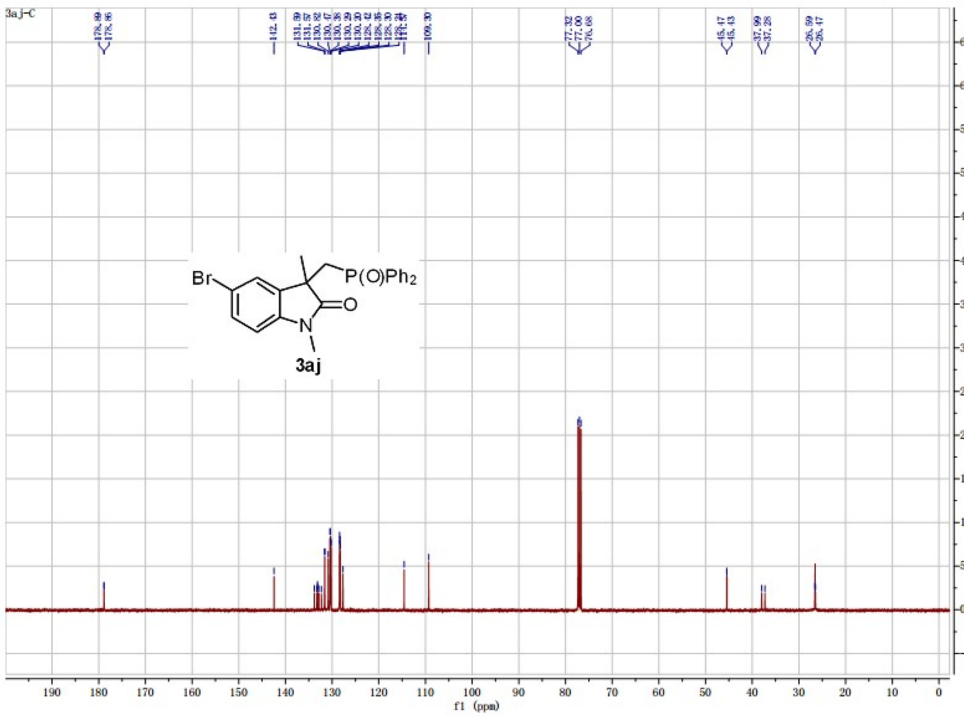
P(O)Ph2
O
N
3ai
f1 (ppm)

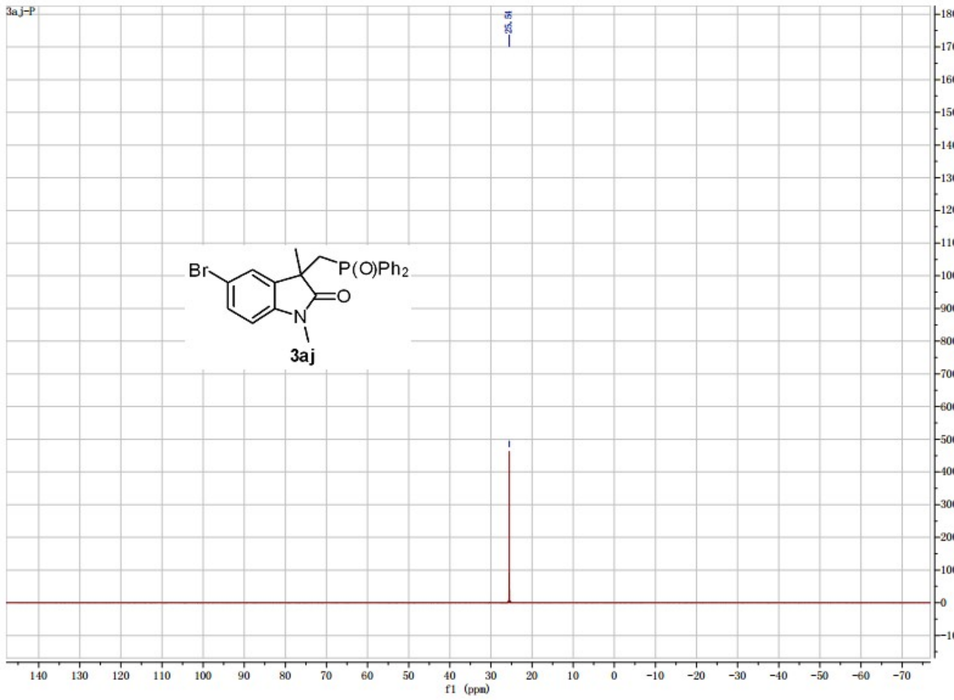


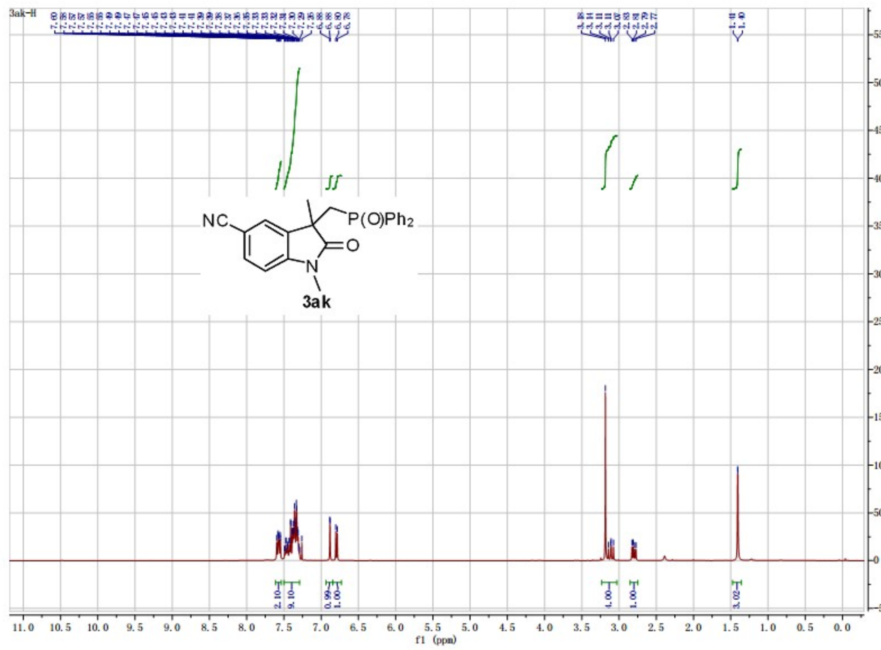
3ai-P
—25.92
Cl
P(O)Ph2
O
N
3ai
f1 (ppm)

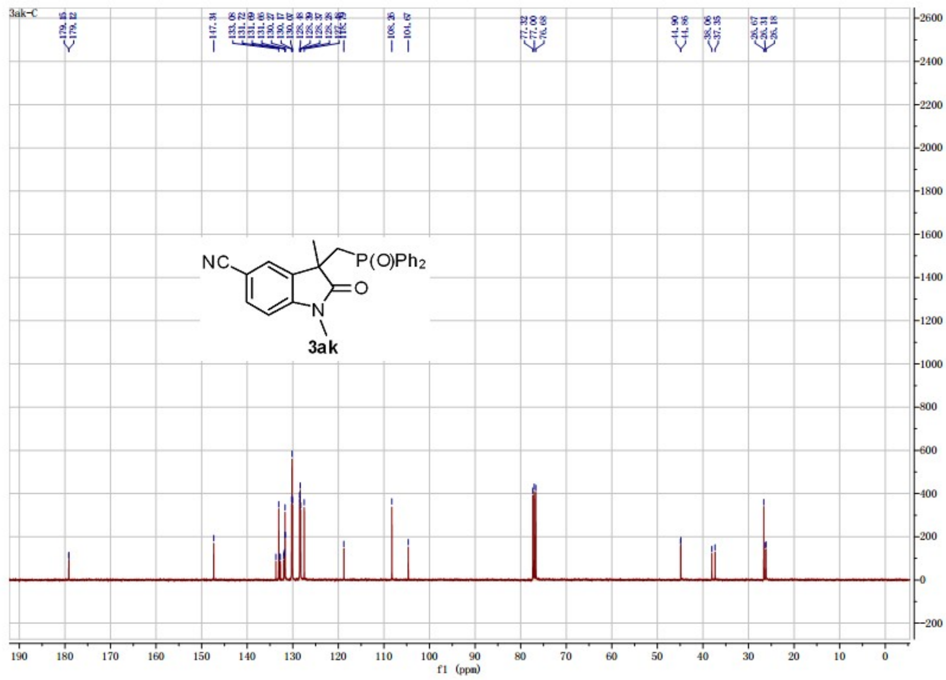


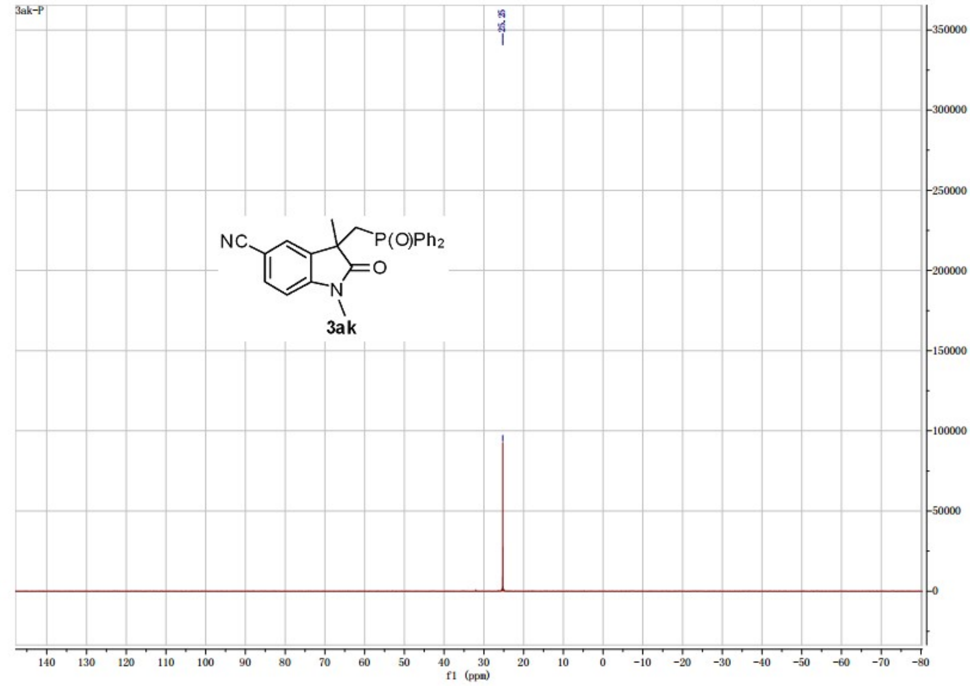
3aj-H
Br
P(O)Ph2
O
N
3aj
f1 (ppm)

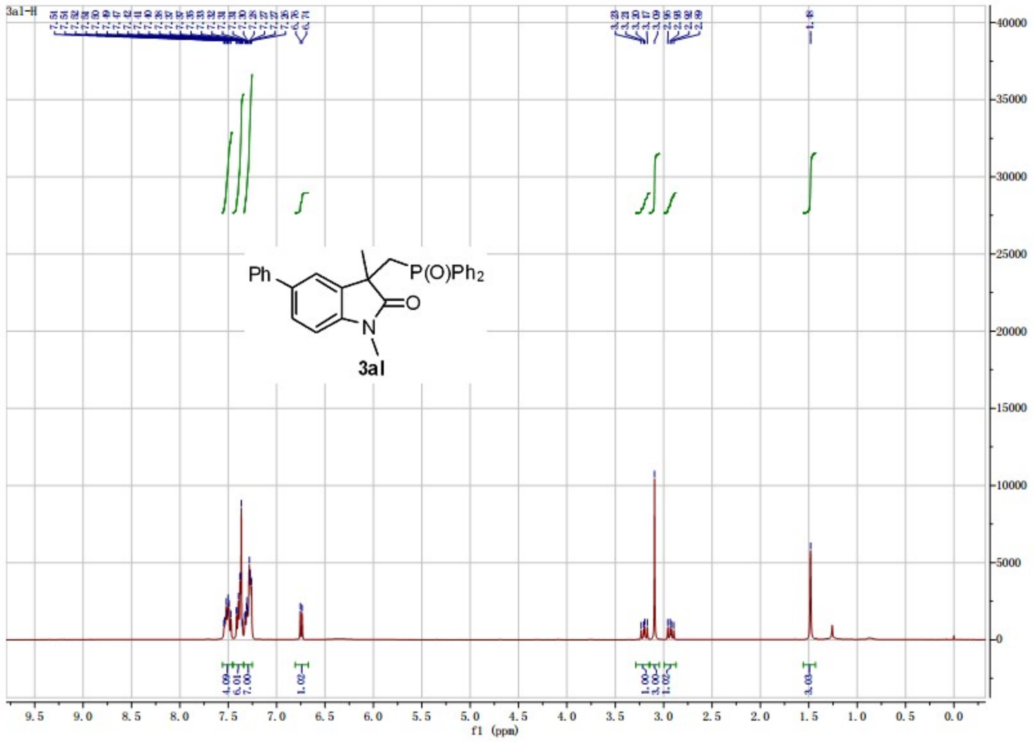


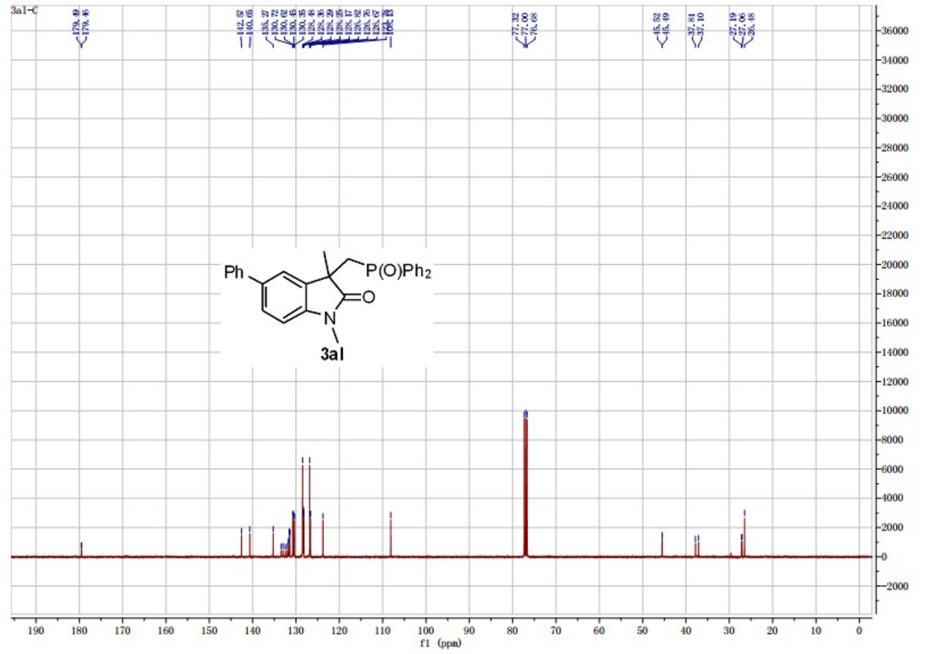


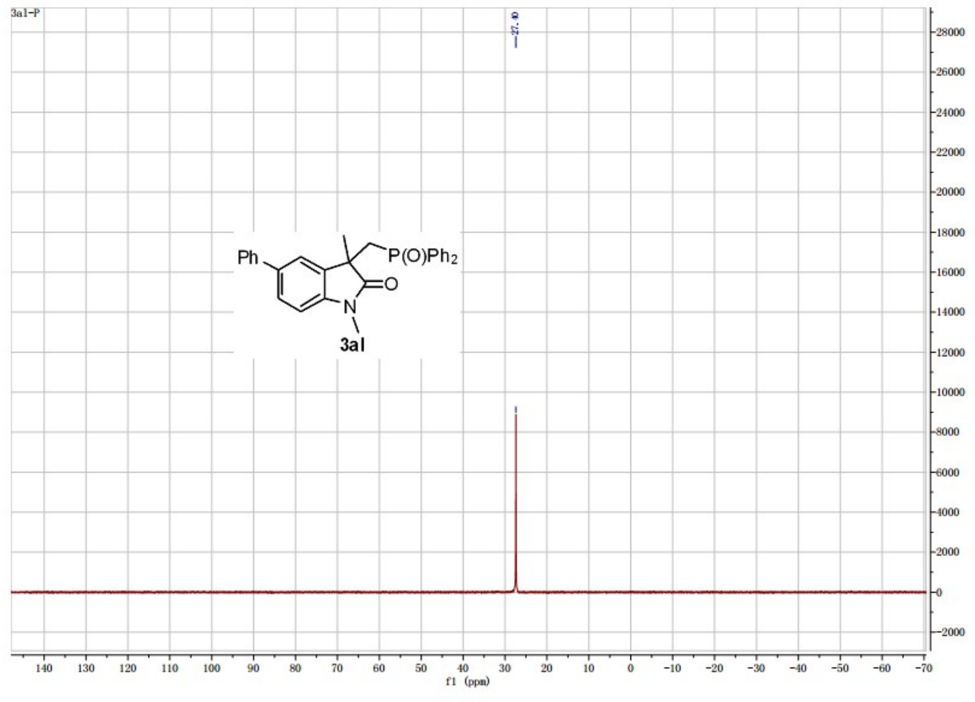


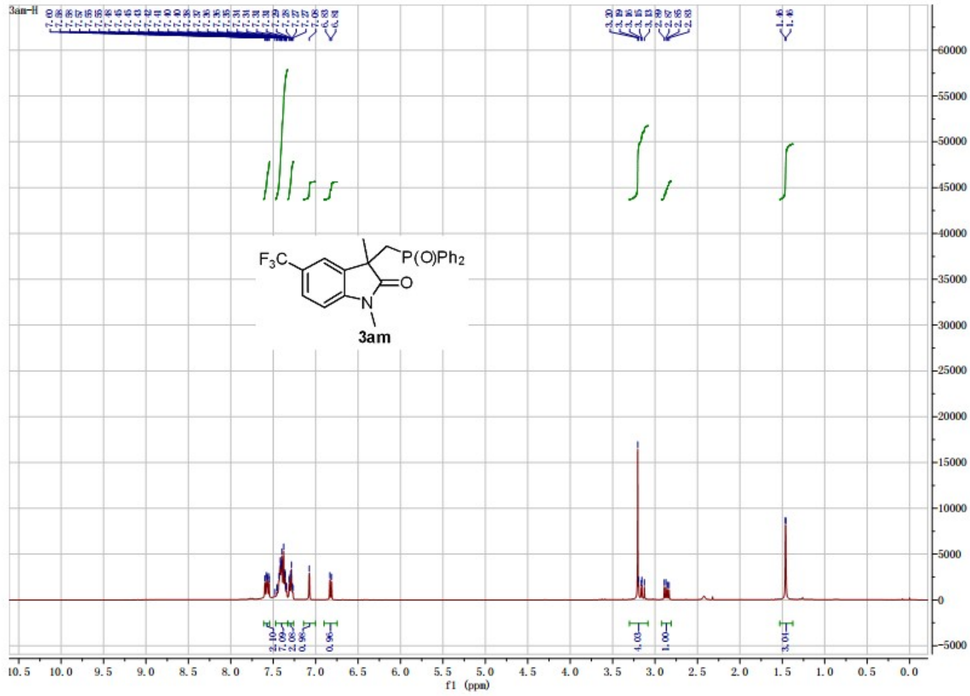


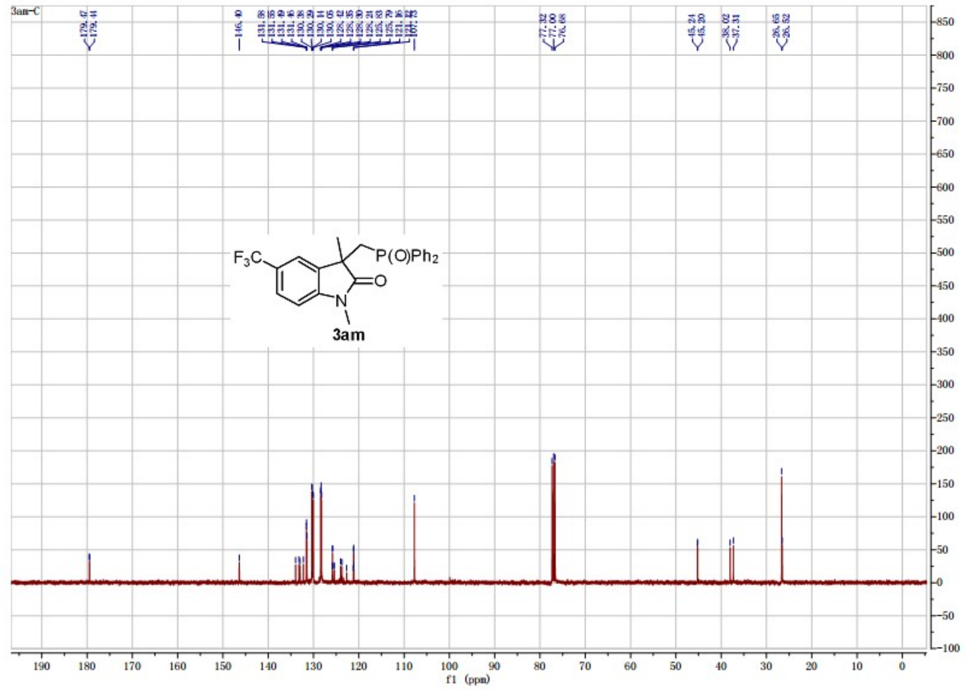

3ak-P
25.25
NC
P(O)Ph2
O
N
3ak
f1 (ppm)

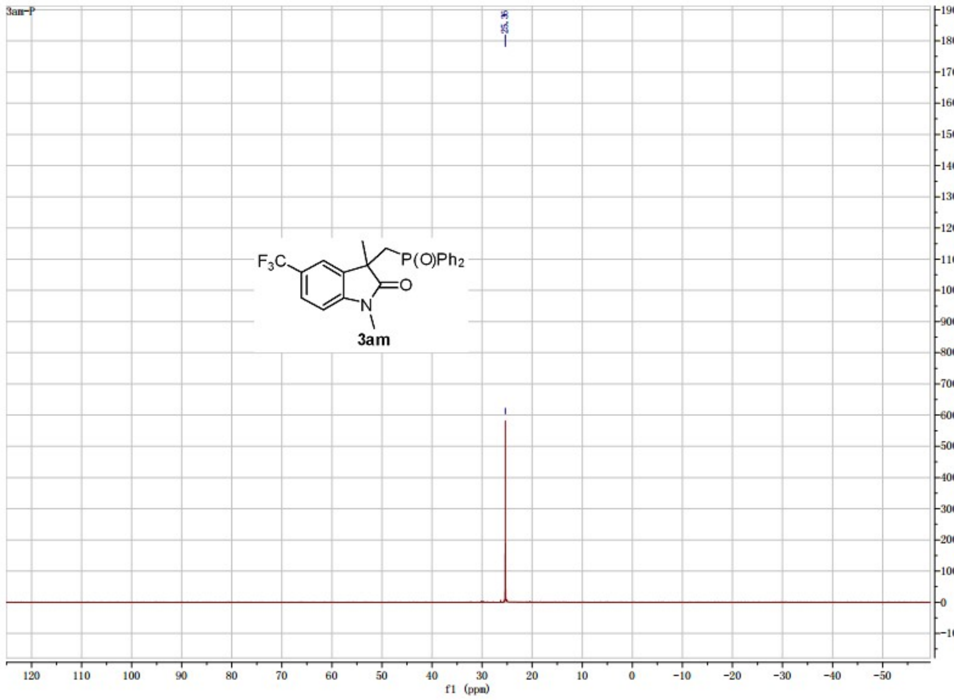

3al-H
Ph
P(O)Ph2
O
N
3al
f1 (ppm)

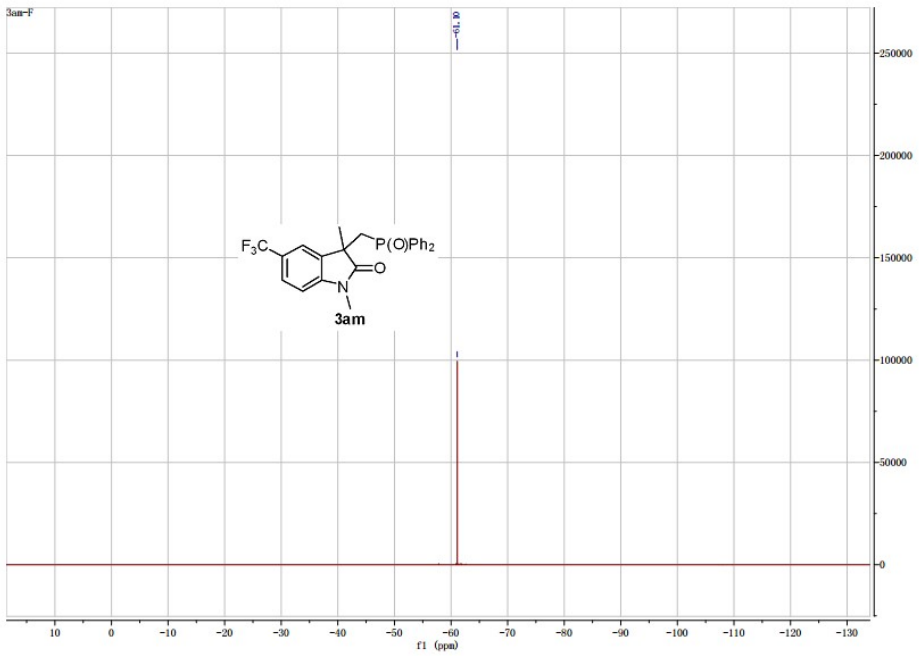


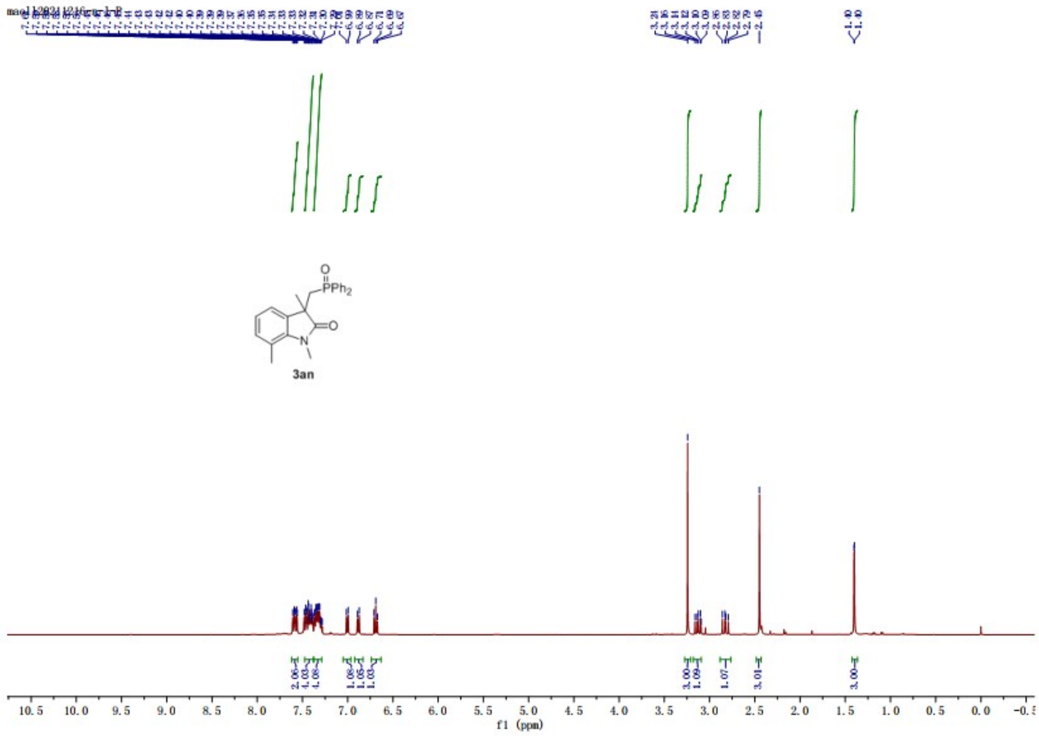


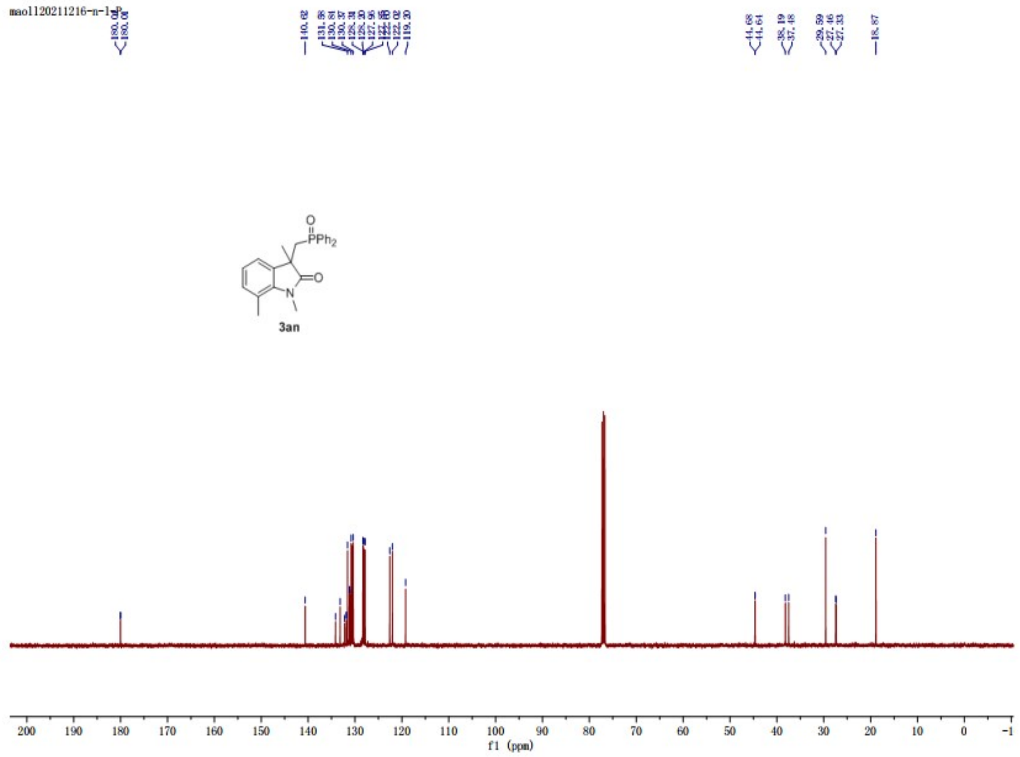


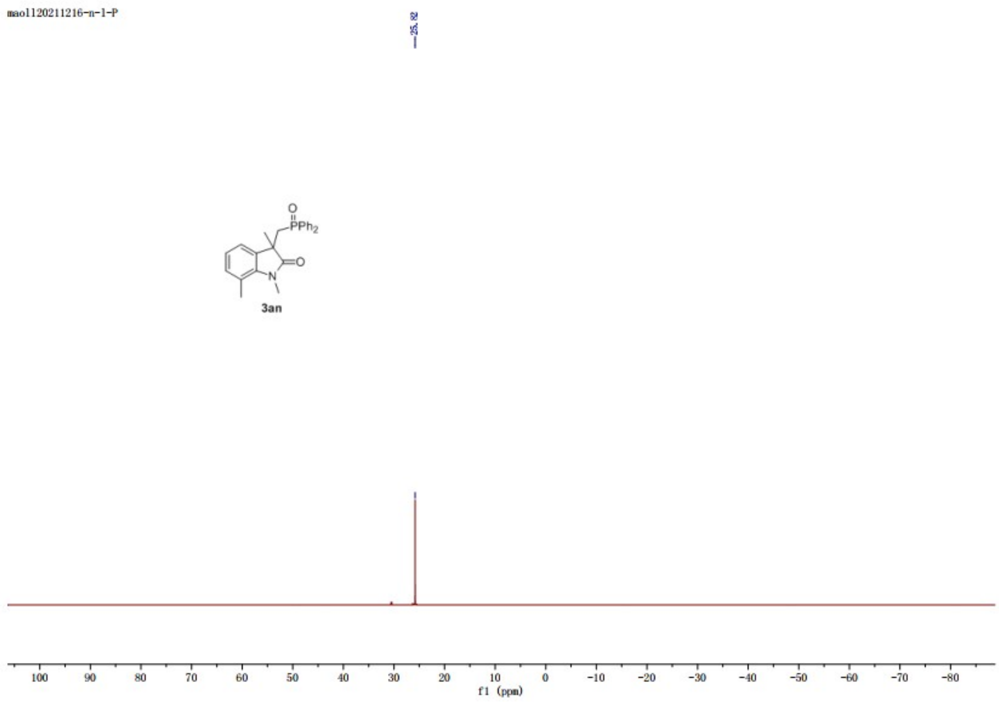


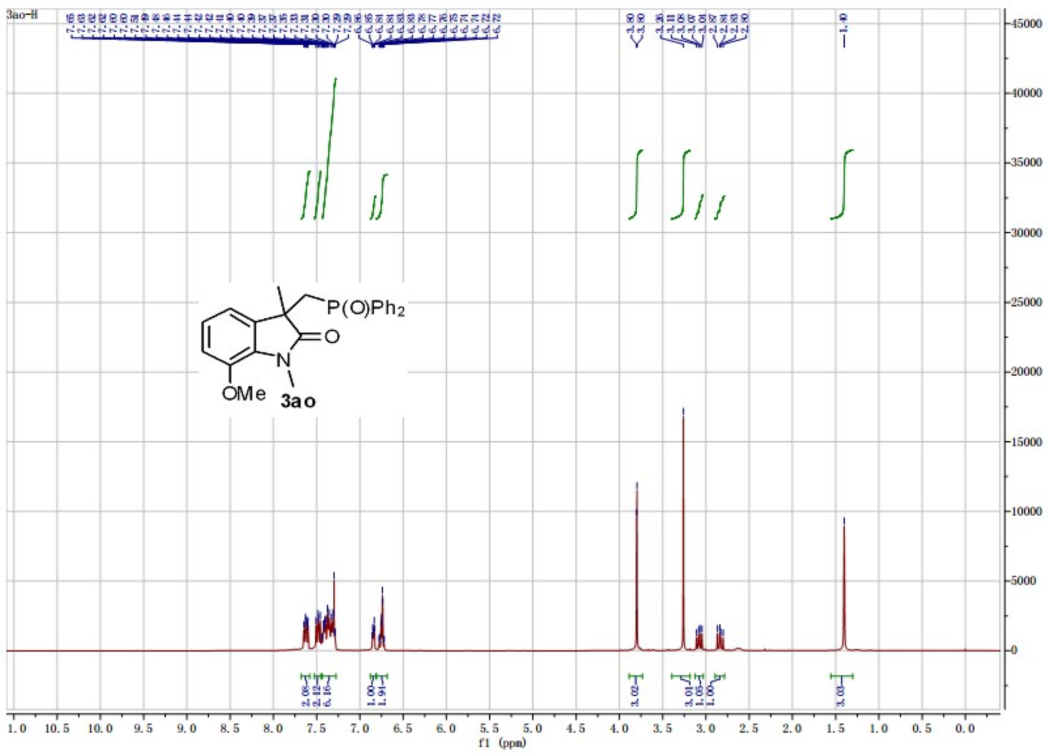

3am-P
25.36
F3C
P(O)Ph2
O
N
3am
f1 (ppm)

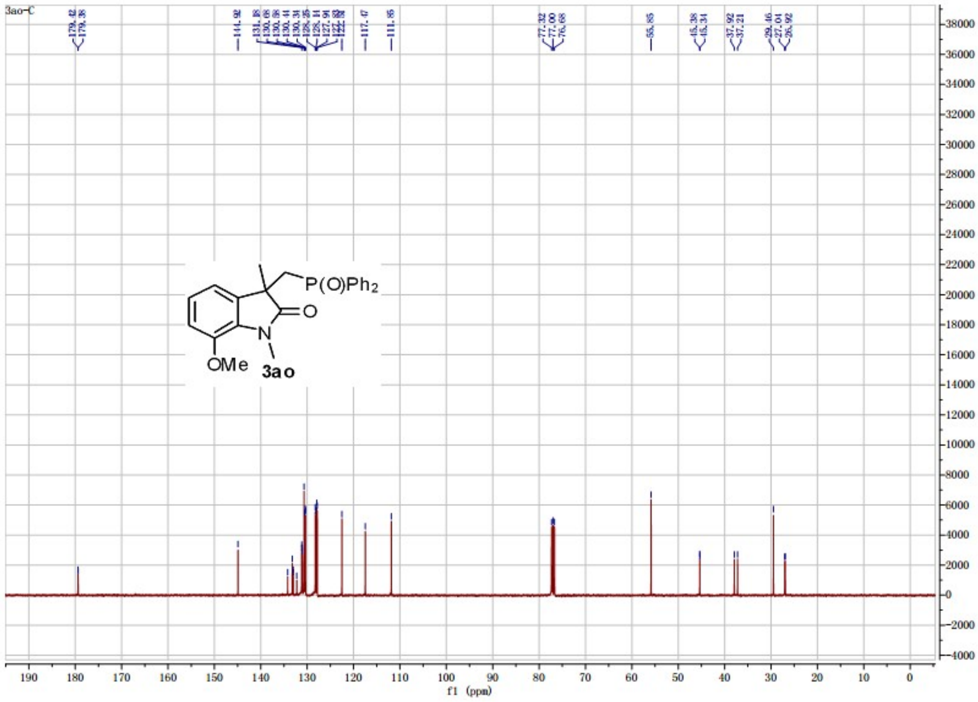

3am-F
-61.10
F3C
P(O)Ph2
O
N
3am
f1 (ppm)

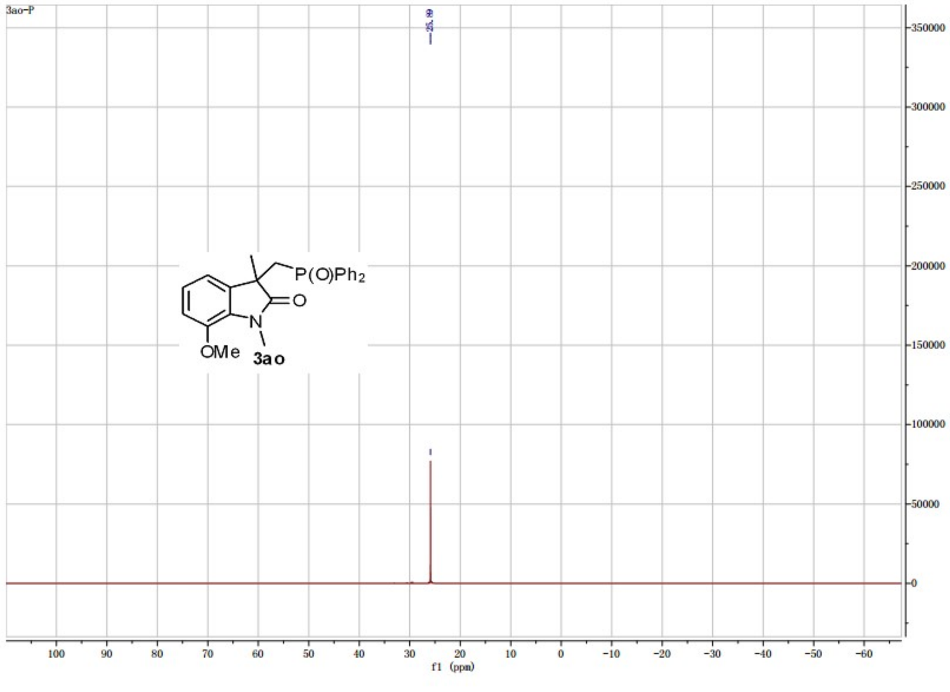


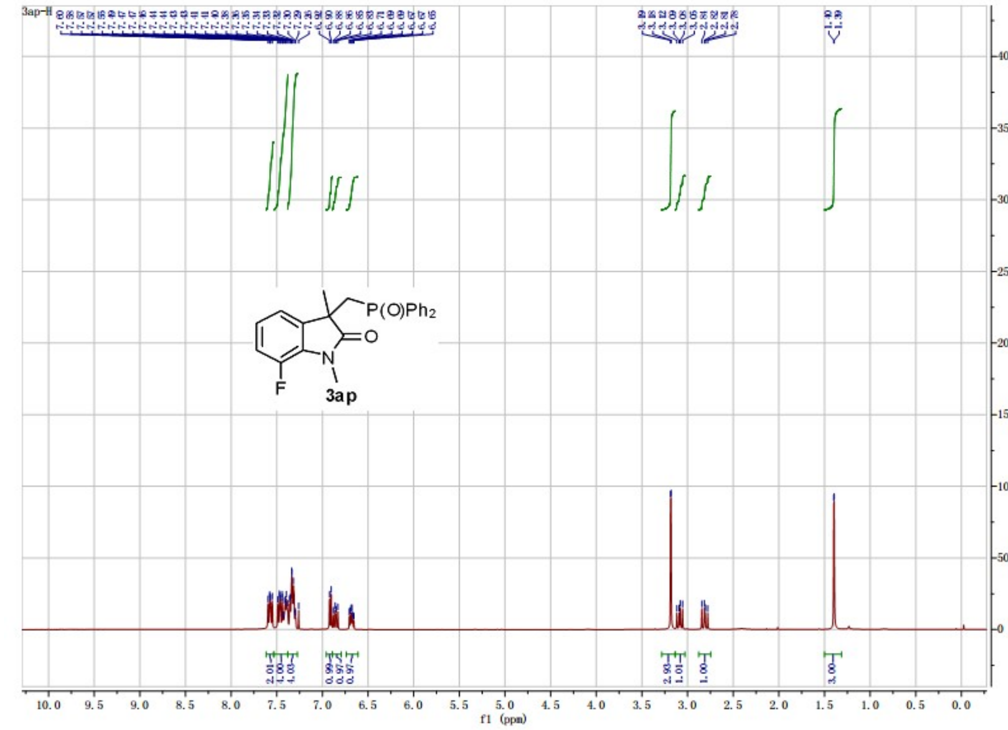


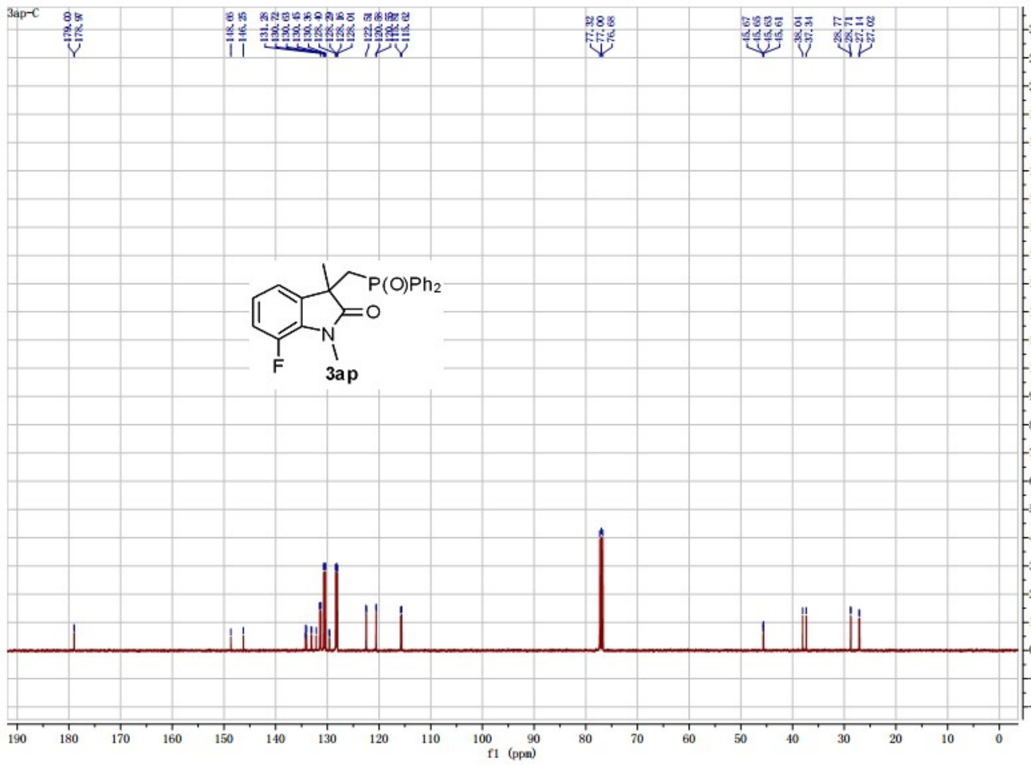

maol120211216-n-1-P
—25.92
3an
f1 (ppm)

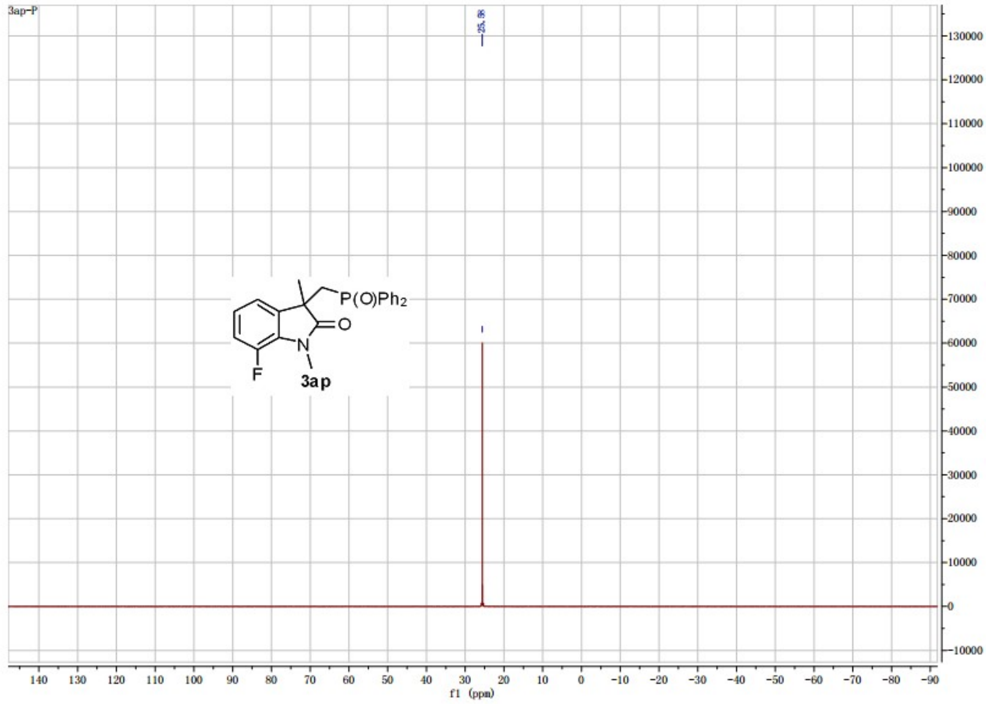

3ao-H
P(O)Ph2
OMe
3ao
f1 (ppm)

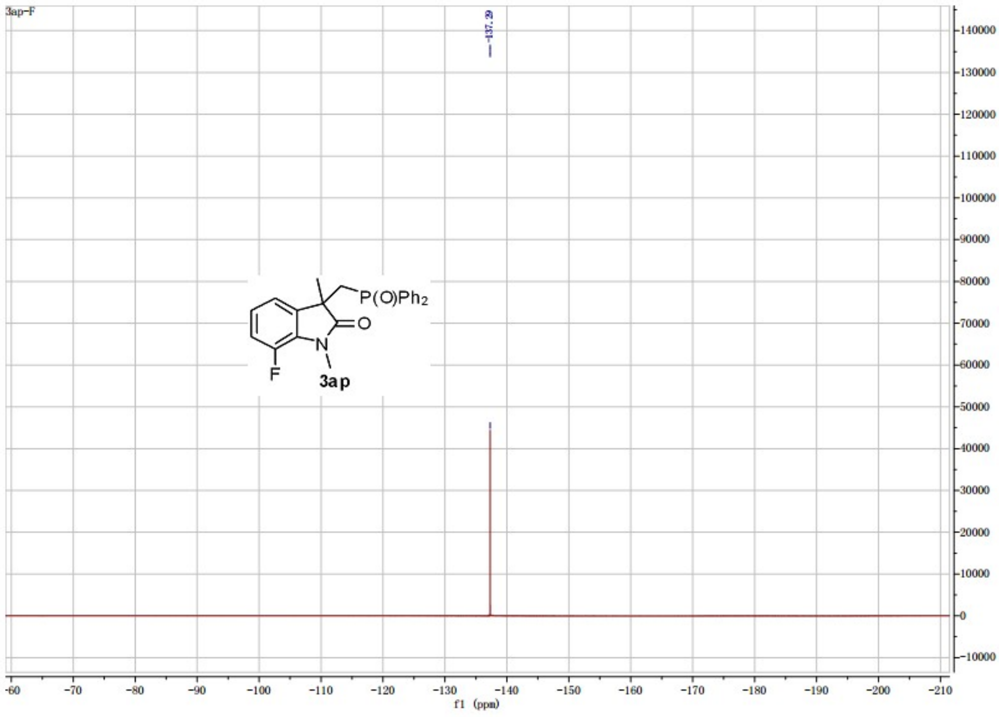

3ao-C
179.42
179.38
144.92
111.85
55.85
P(O)Ph2
O
N
OMe
3ao
f1 (ppm)

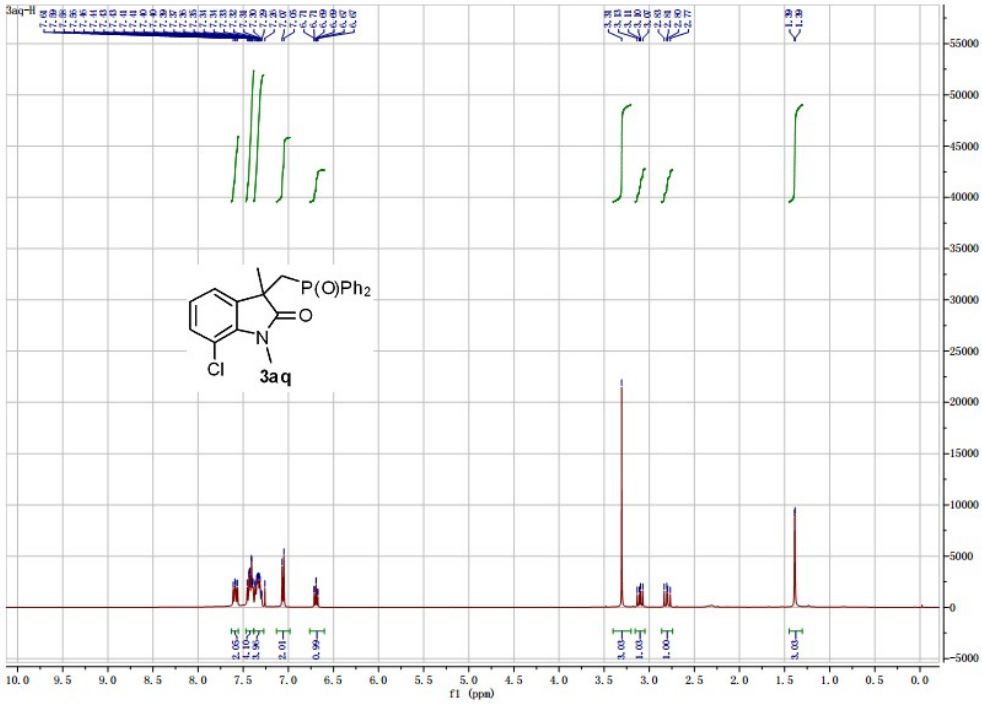

3ao-P
25.89
P(O)Ph2
O
N
OMe
3ao
f1 (ppm)

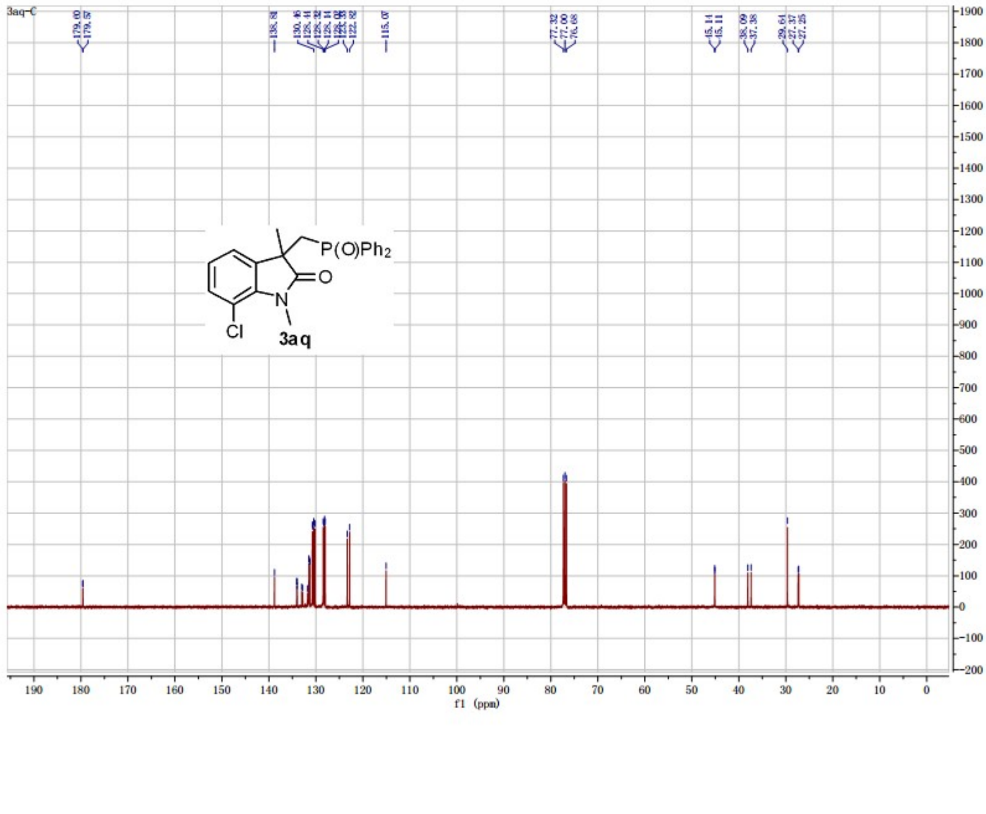

3ap-H
P(O)Ph2
O
N
F
3ap
f1 (ppm)

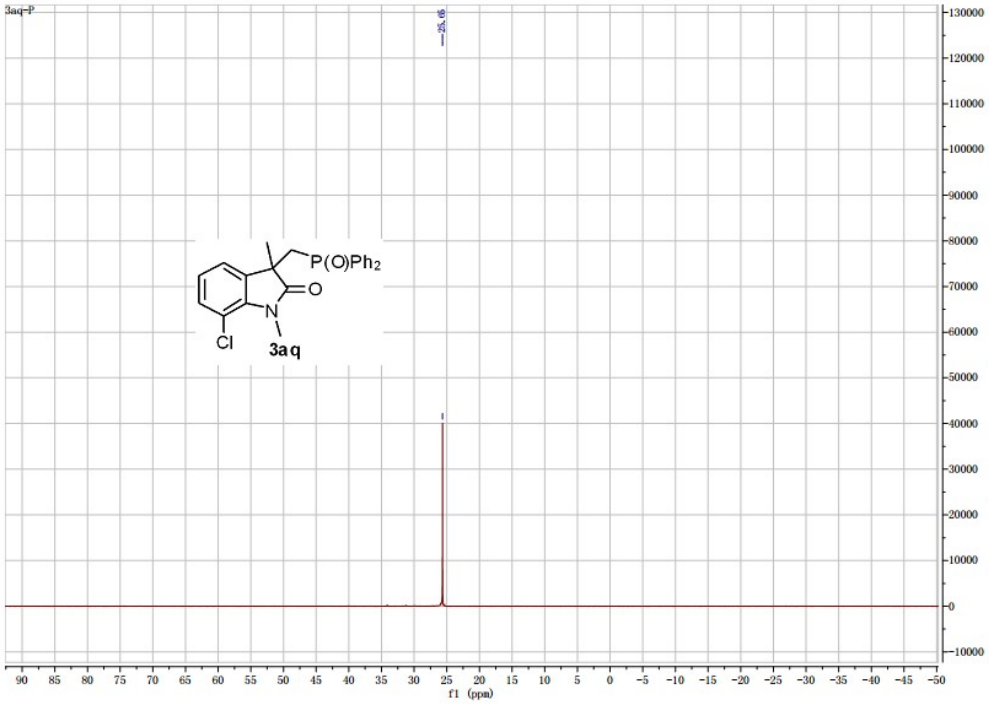

3ap-C
P(O)Ph2
O
N
F
3ap
f1 (ppm)

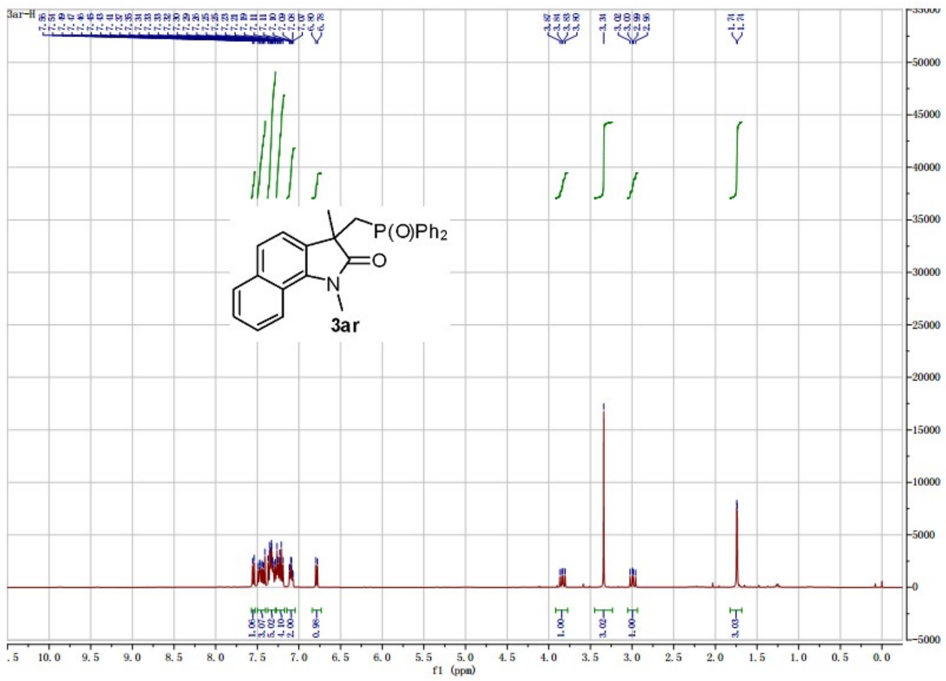

3ap-P
25.86
P(O)Ph2
O
N
F
3ap
f1 (ppm)

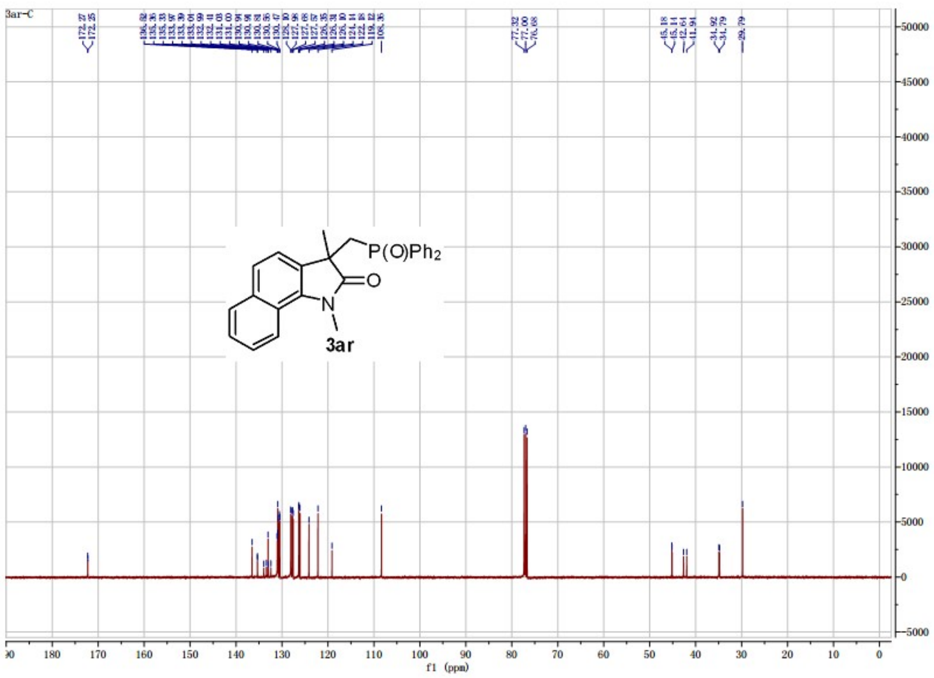

3ap-F
-137.29
P(O)Ph2
O
N
F
3ap
f1 (ppm)

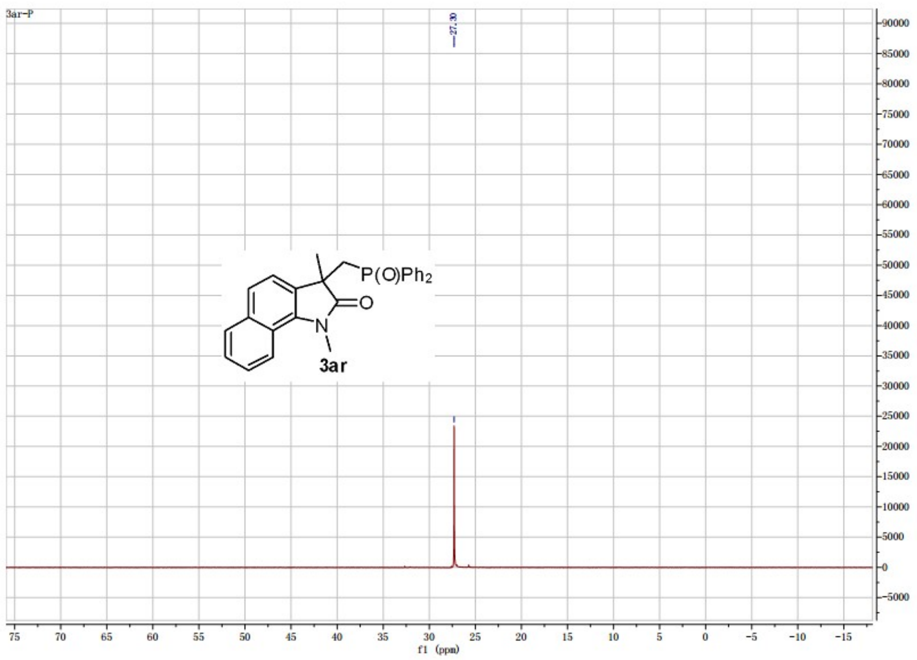

3aq-H
P(O)Ph2
O
N
Cl
3aq
f1 (ppm)

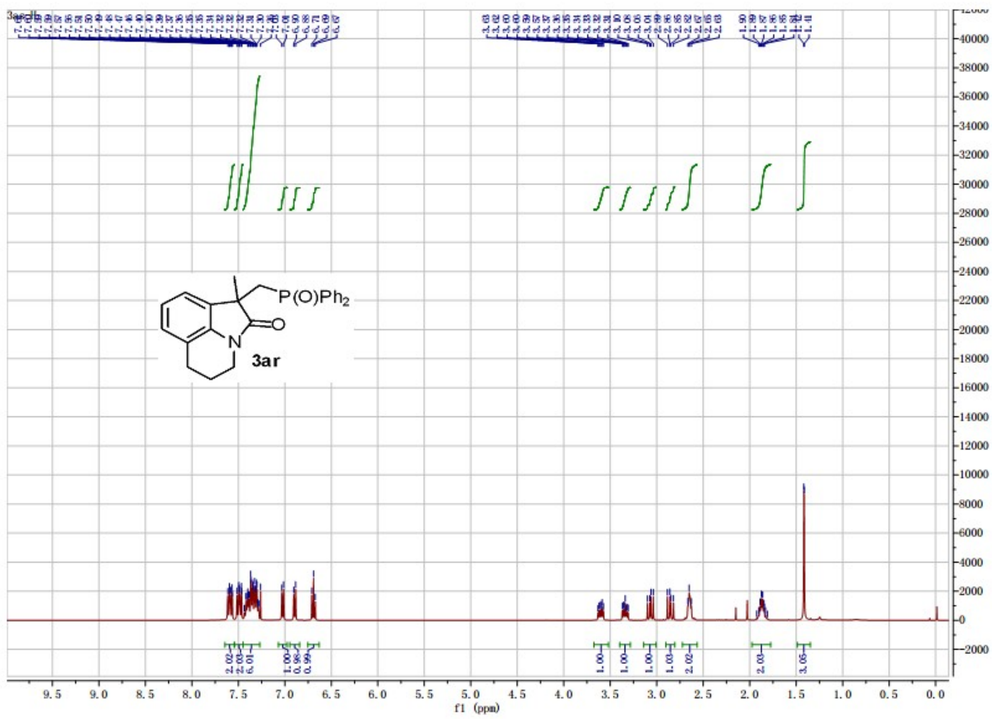

3aq-C
P(O)Ph2
O
N
Cl
3aq
f1 (ppm)

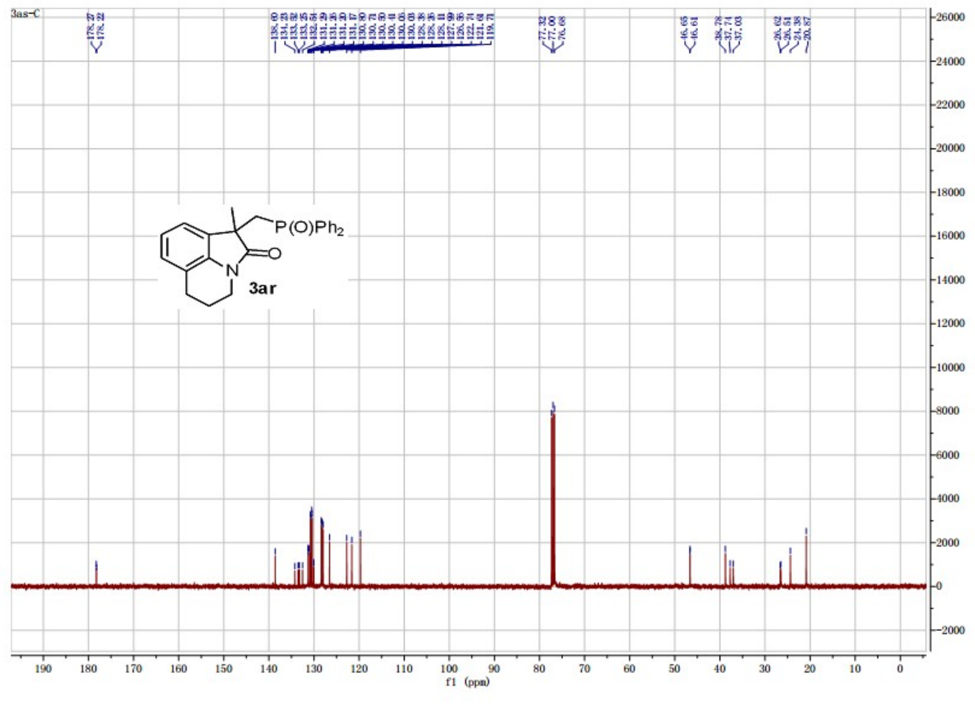

3aq-P
—25.65
P(O)Ph2
O
N
Cl
3aq
f1 (ppm)

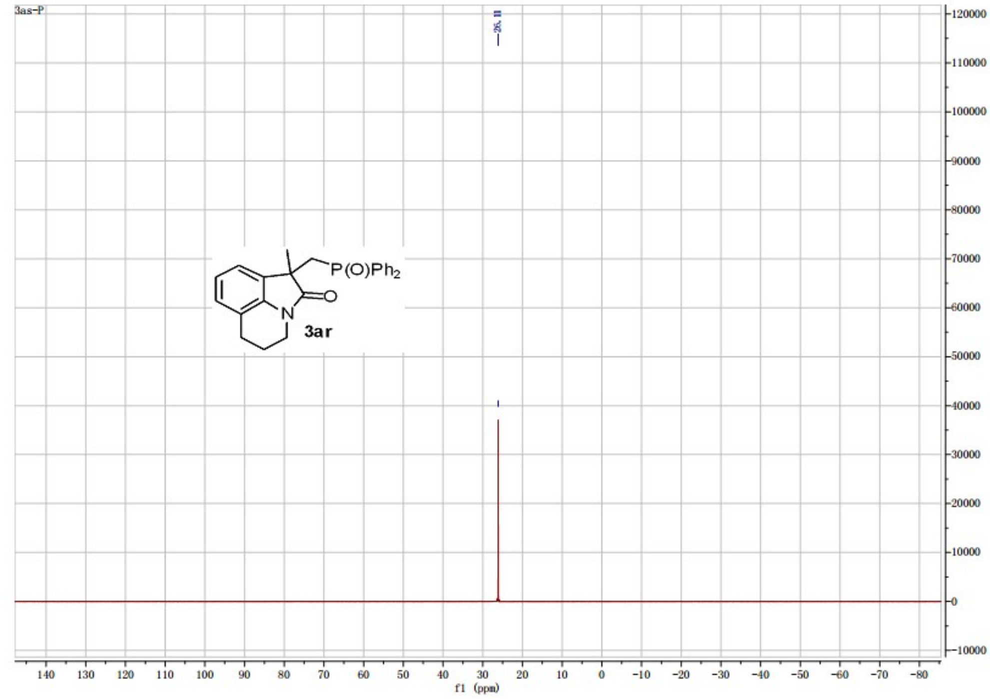

3ar-H
P(O)Ph2
O
N
3ar
f1 (ppm)

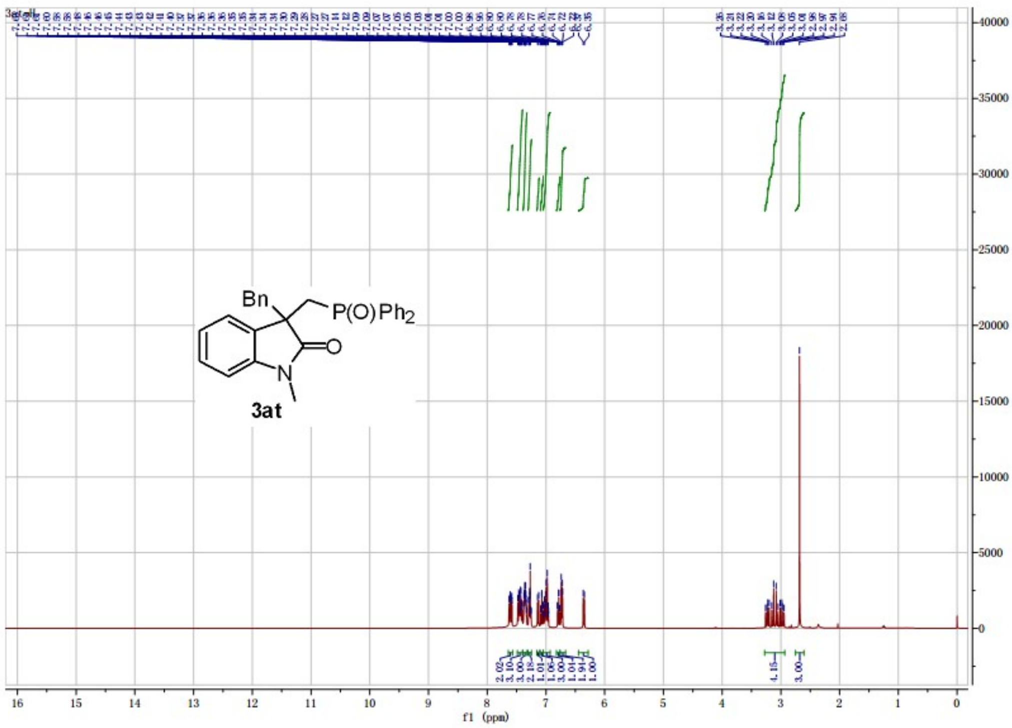


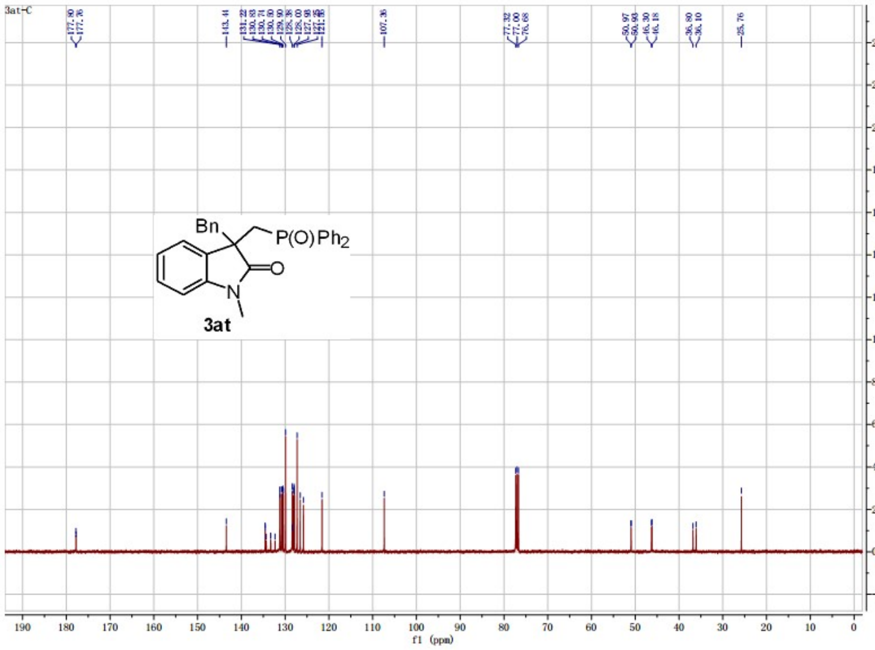


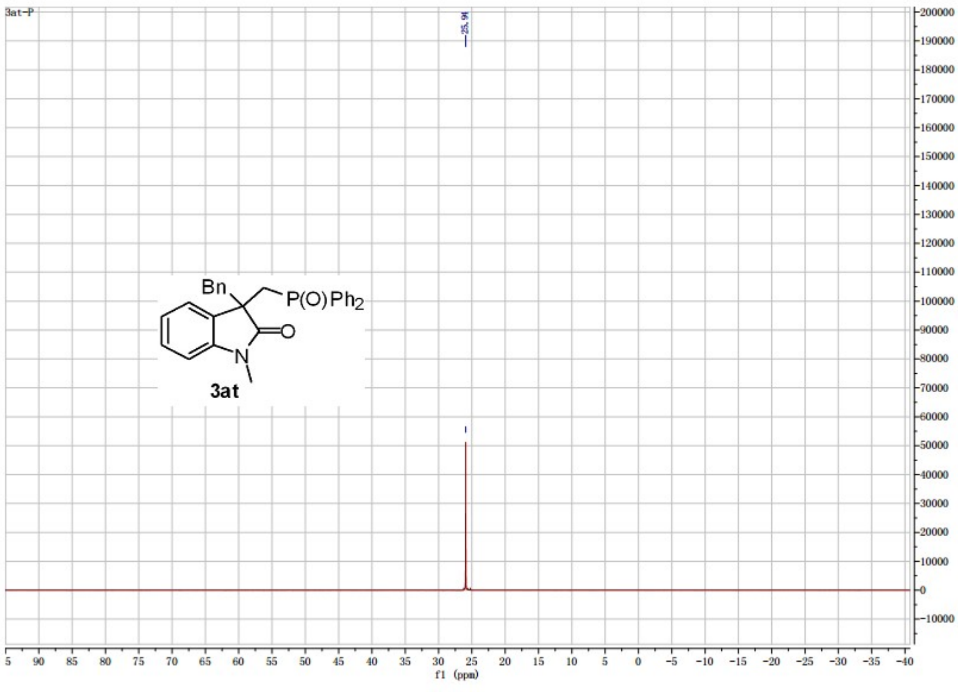


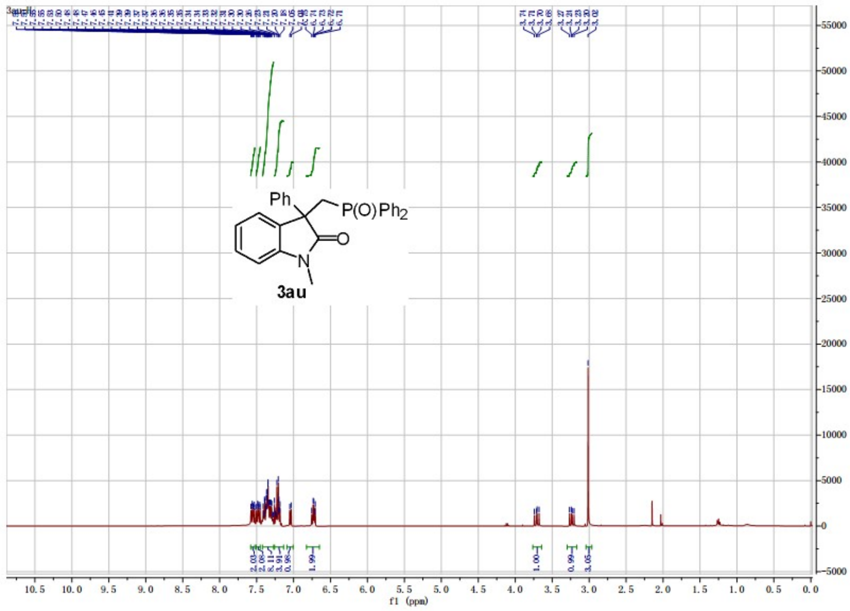


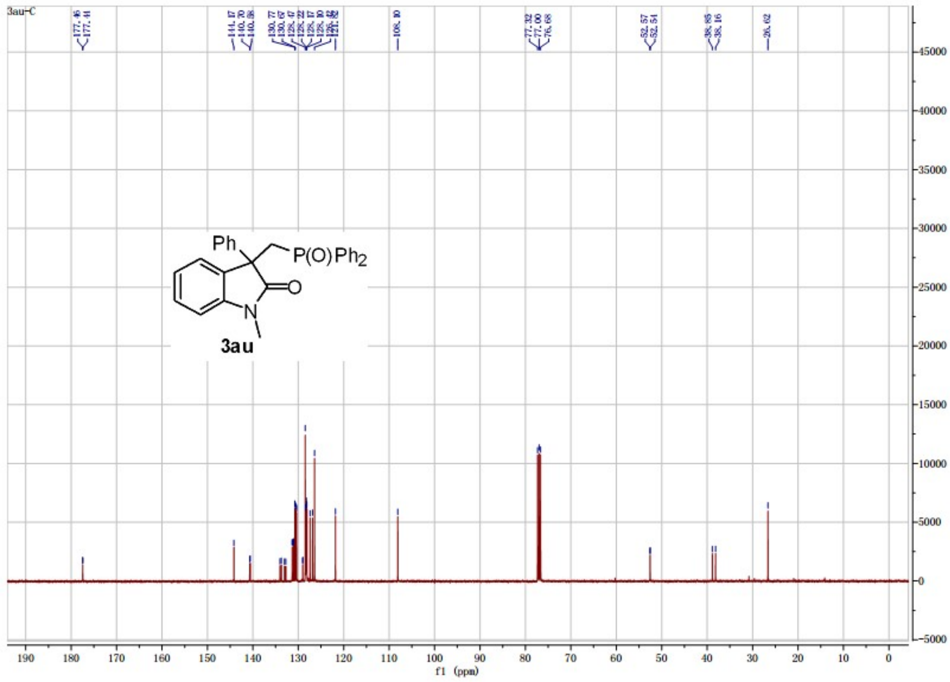

3as-P
26.11
P(O)Ph2
3ar
f1 (ppm)

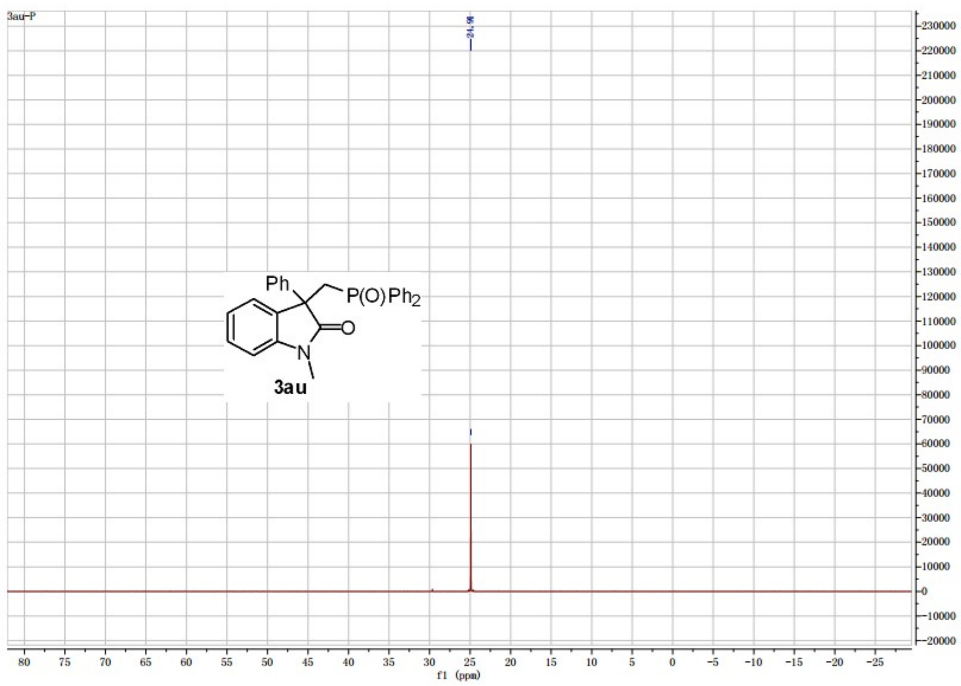

Bn
P(O)Ph2
3at
f1 (ppm)

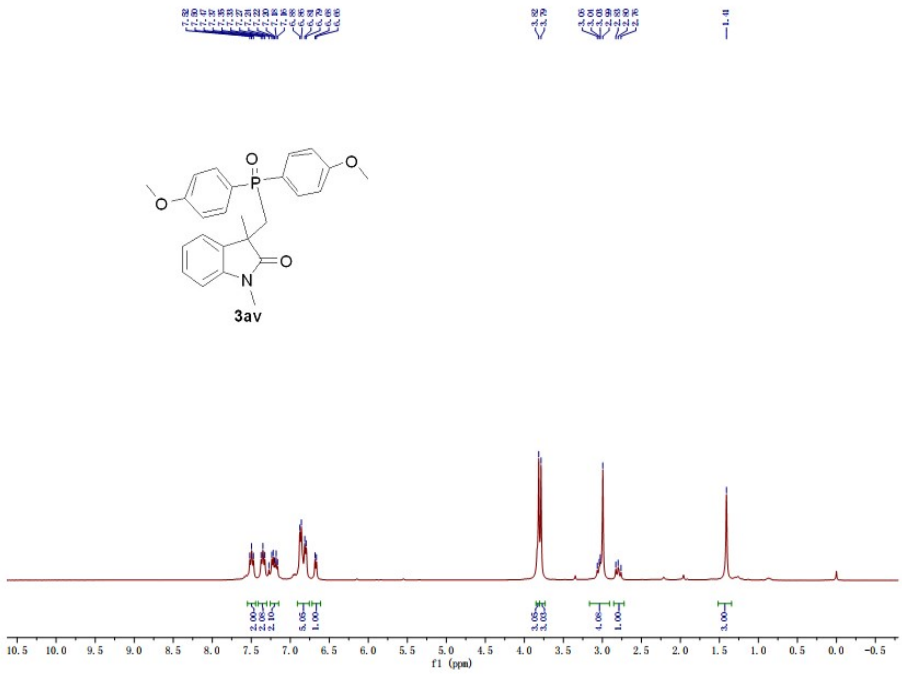

3at-C
3at
f1 (ppm)

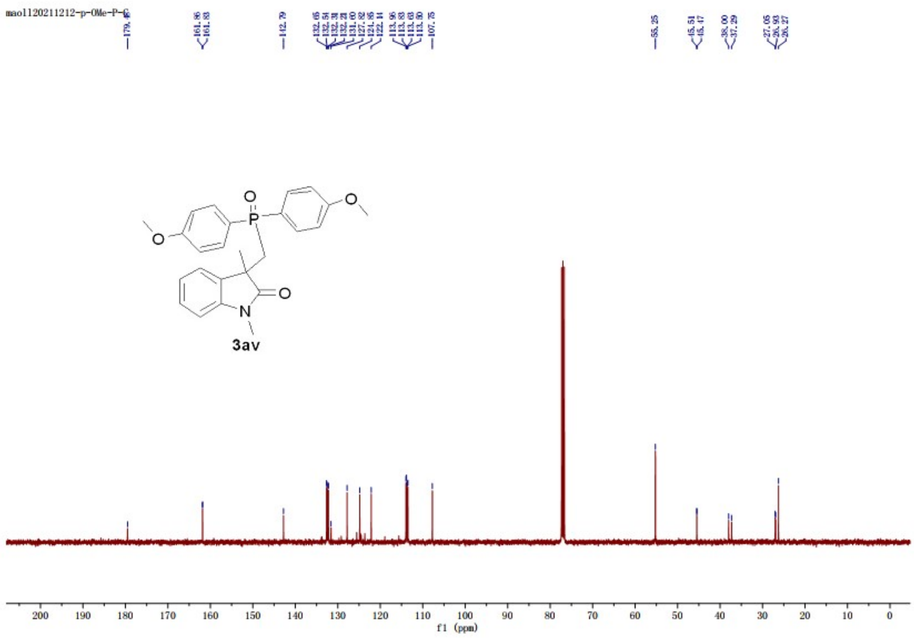

3at-P
25.99
3at
f1 (ppm)

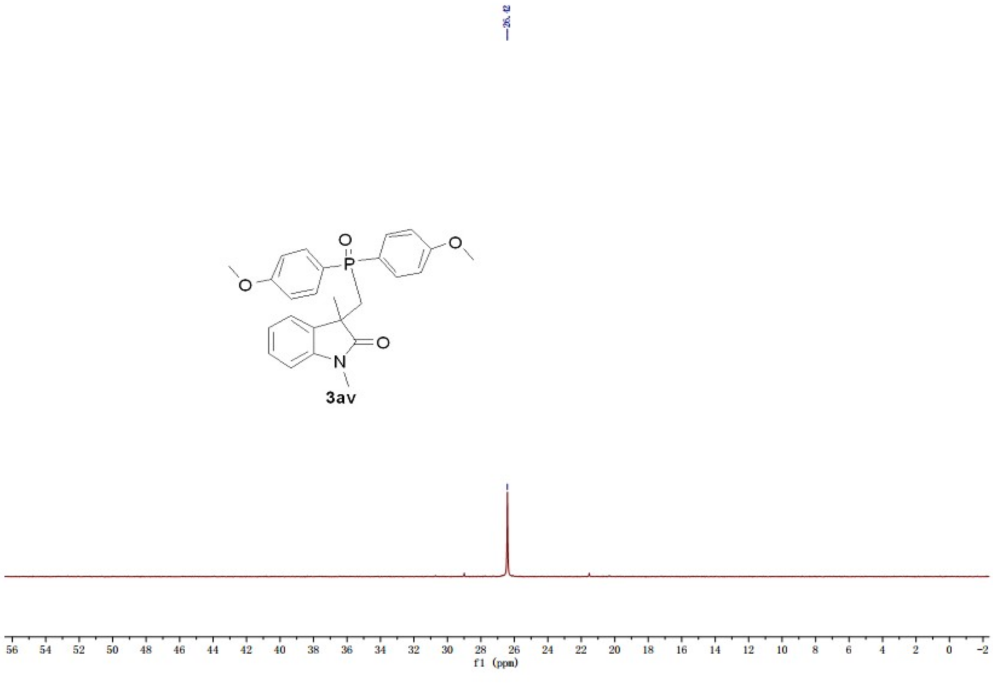


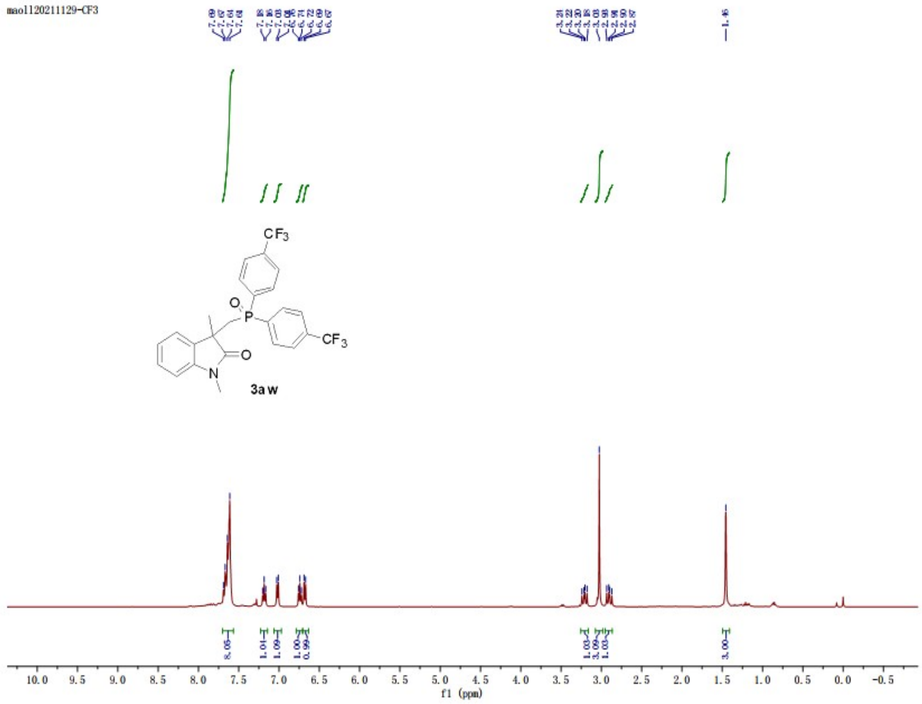


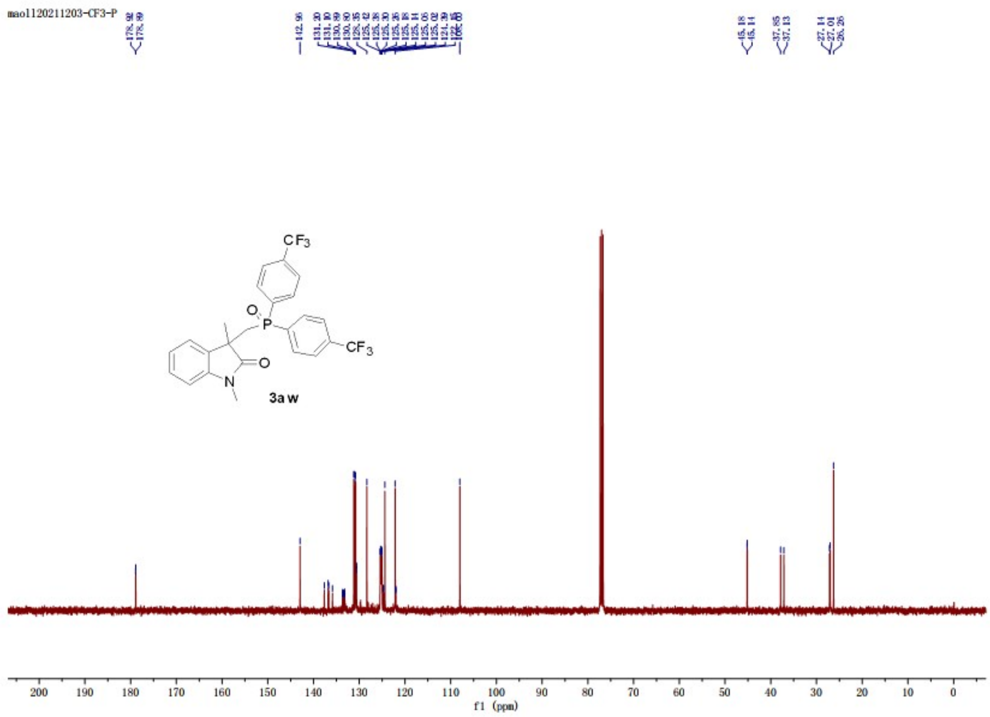

3au-P
24.98
Ph
P(O)Ph2
O
N
3au
f1 (ppm)

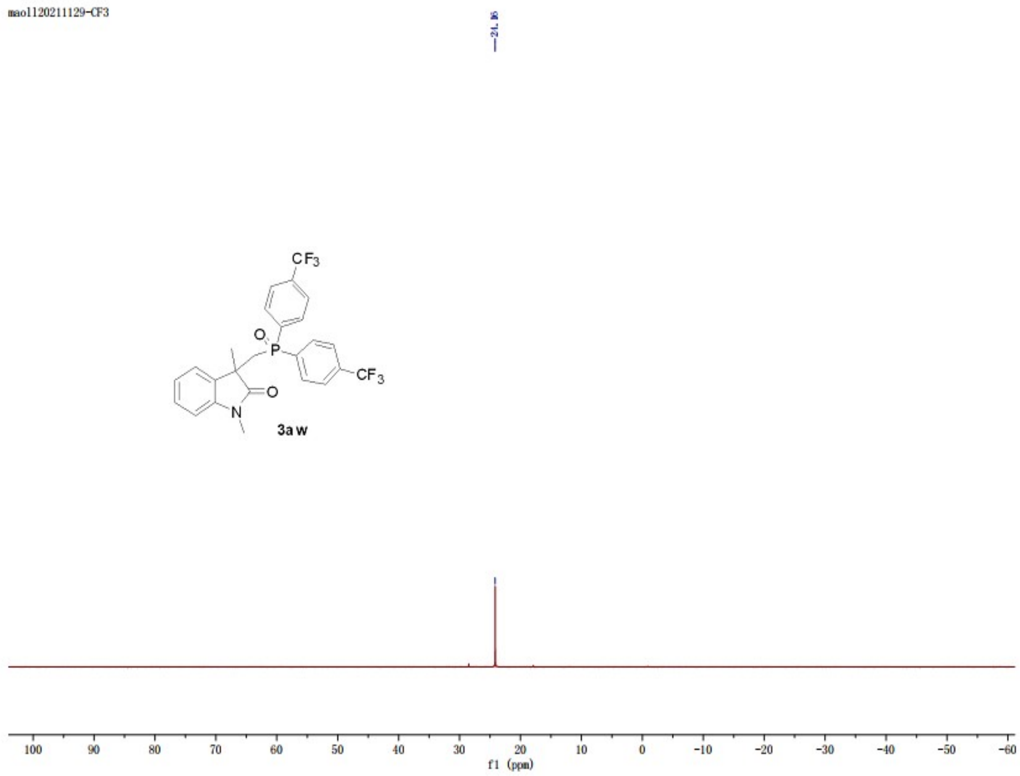

O
P
O
O
O
N
3av
f1 (ppm)

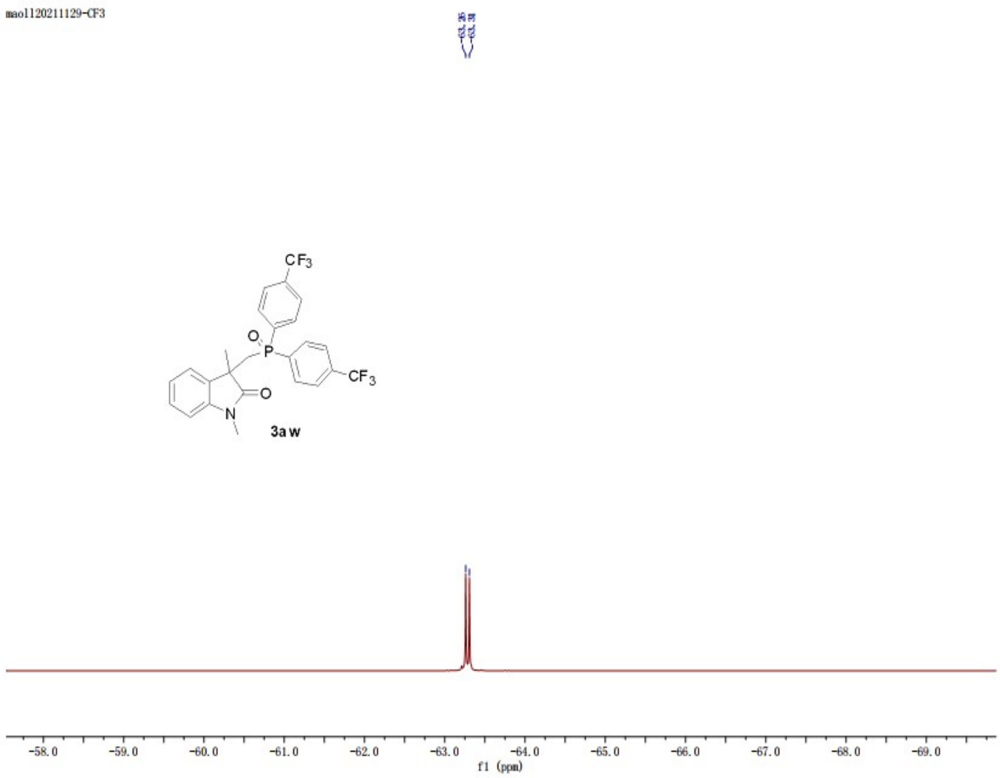


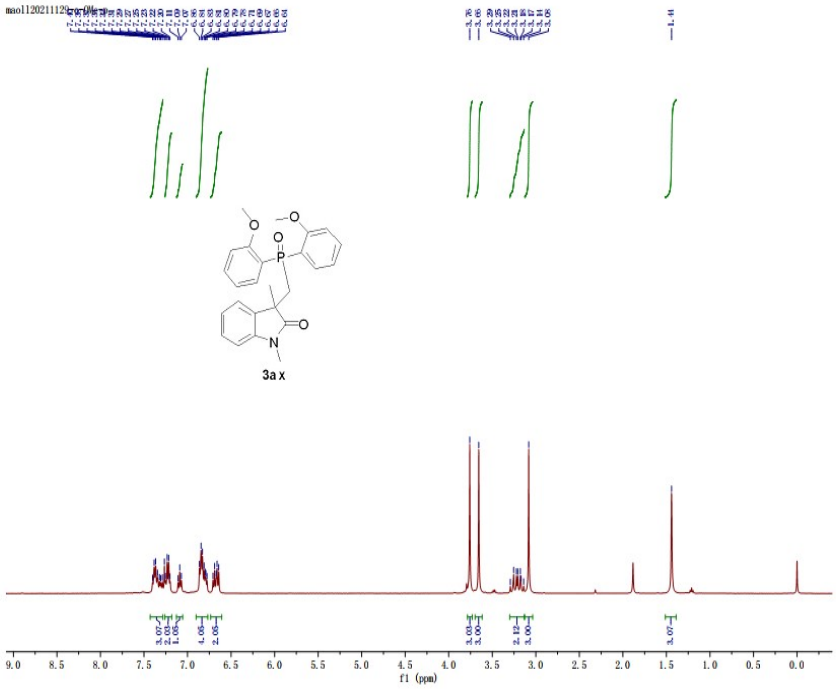


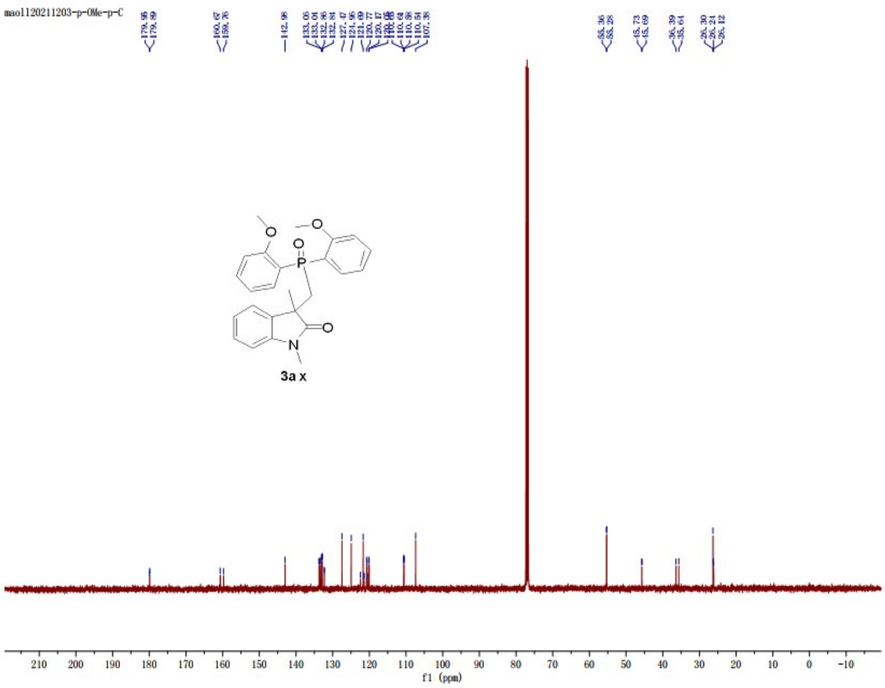

maol120211129-CF3
3aw
f1 (ppm)

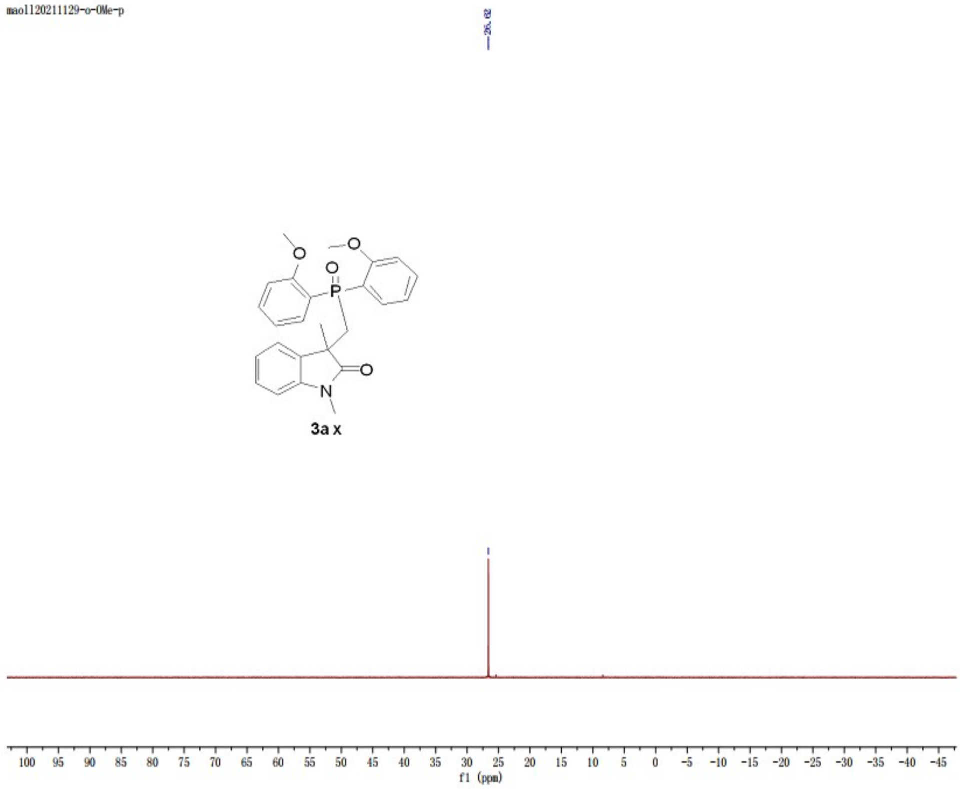

maol120211203-CF3-P
3aw
f1 (ppm)

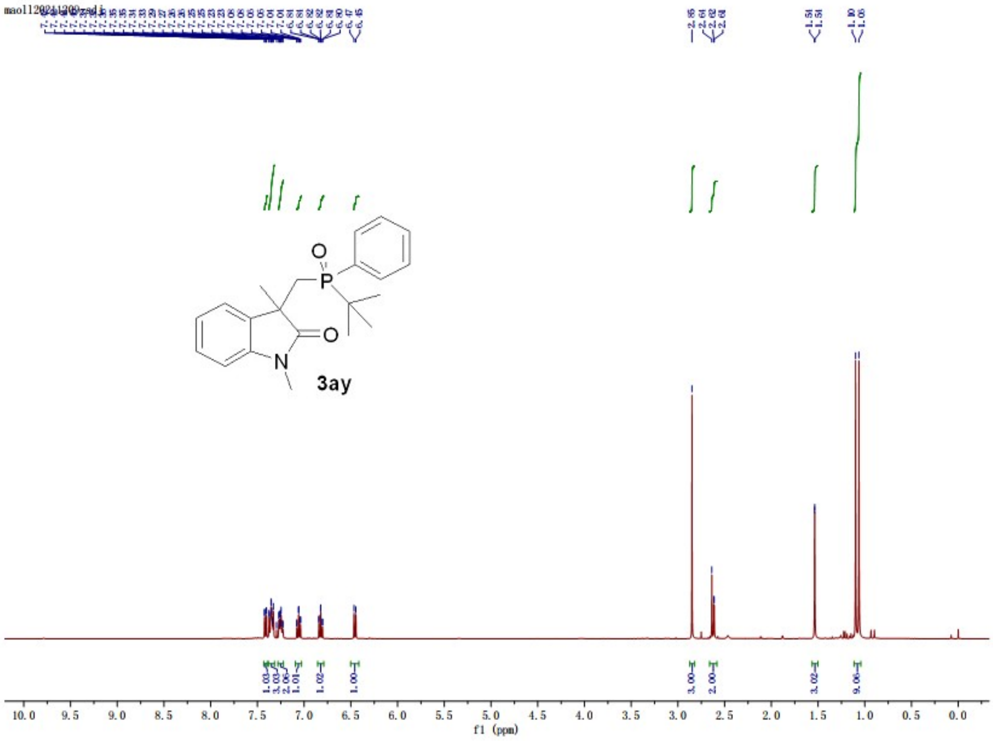

maol120211129-CF3
CF3
O
P
CF3
O
N
3aw
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
f1 (ppm)

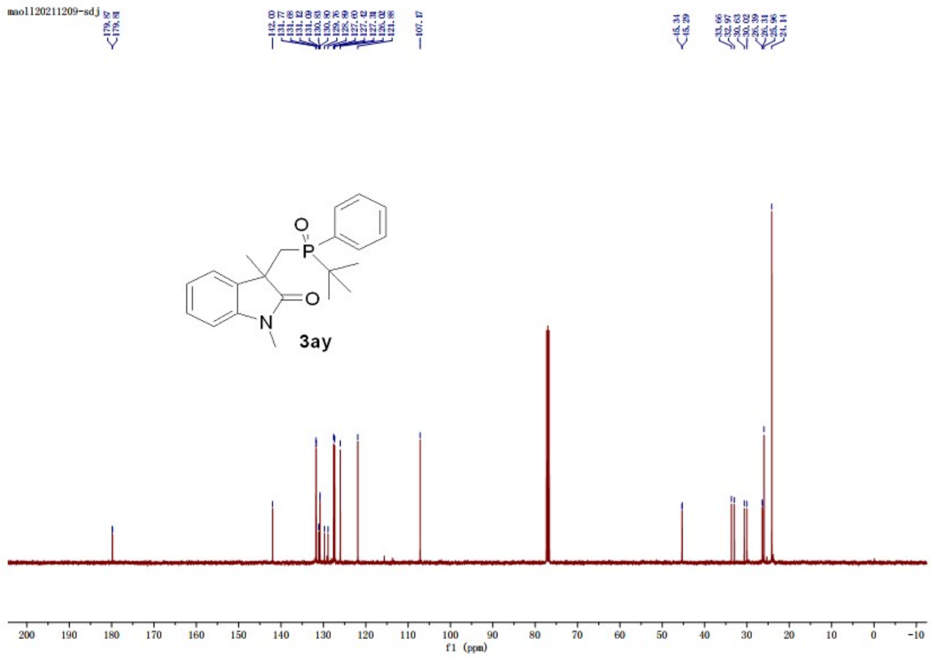

maol120211129-CF3
CF3
O
P
CF3
O
N
3aw
-58.0
-59.0
-60.0
-61.0
-62.0
-63.0
-64.0
-65.0
-66.0
-67.0
-68.0
-69.0
f1 (ppm)



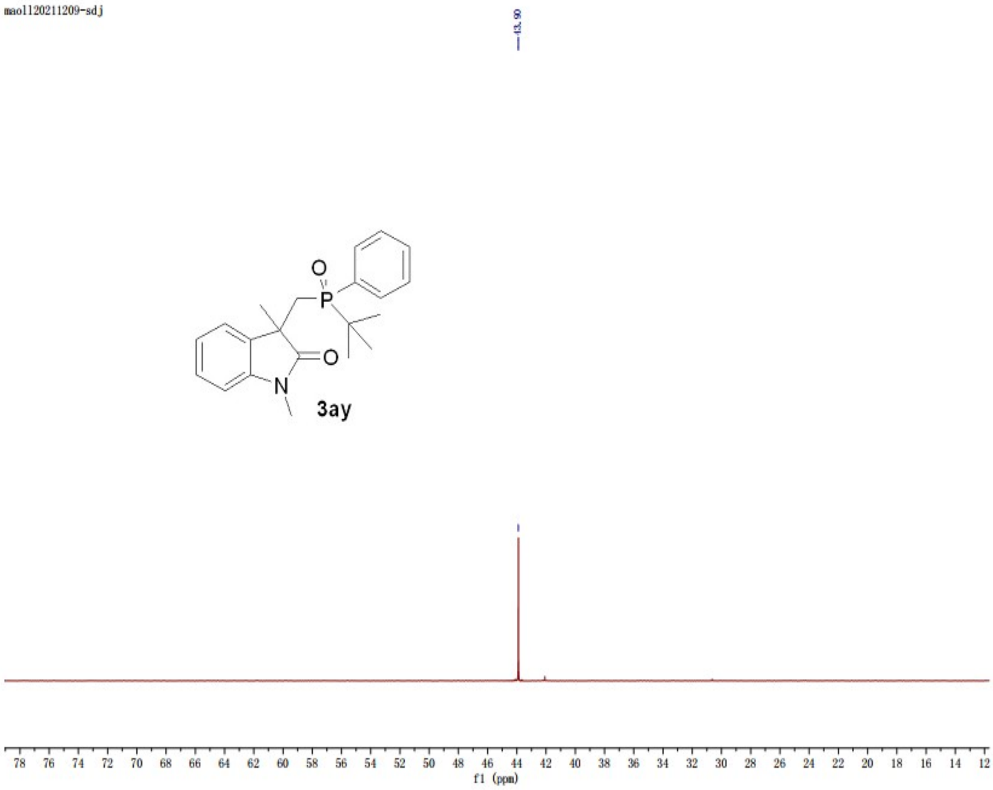



mao1120211129-o-OMe-p
26.62
3a x
f1 (ppm)

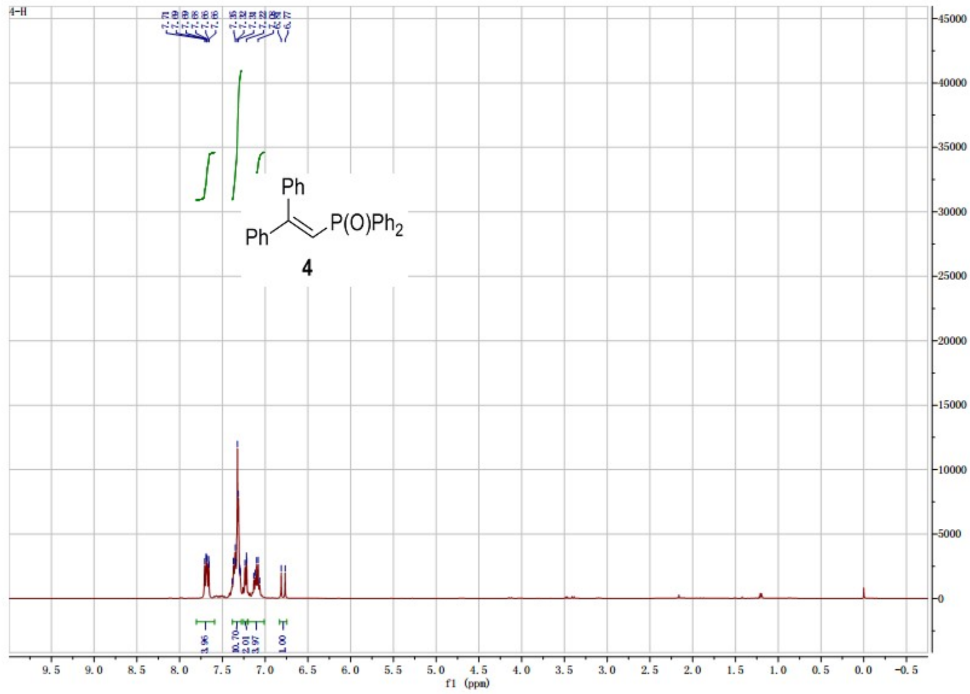

3ay
f1 (ppm)

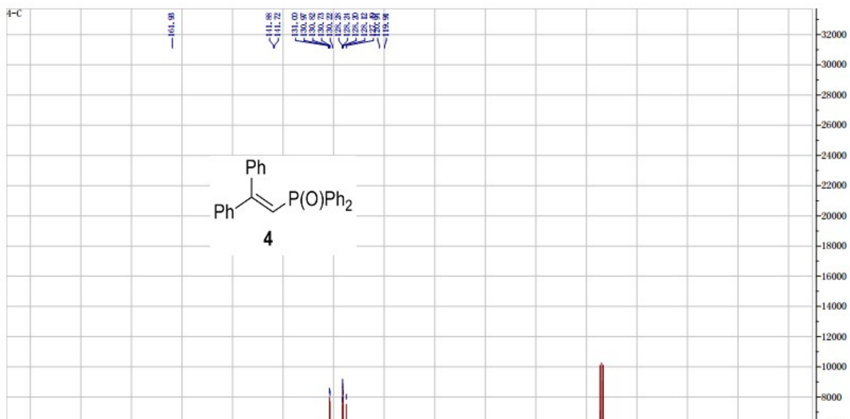


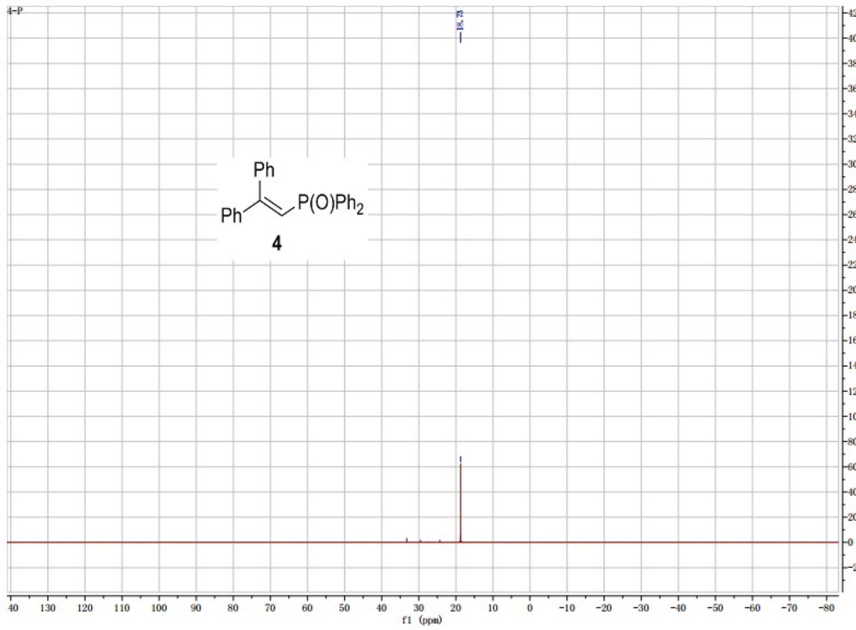
mao1120211209-sdj
3ay
f1 (ppm)



mao1120211209-sdj
43.90
3ay
f1 (ppm)


4-H
Ph
Ph
P(O)Ph2
4
f1 (ppm)


4-C
Ph
Ph
P(O)Ph2
4
f1 (ppm)


4-P
18.73
Ph
Ph
P(O)Ph2
4
f1 (ppm)