

Supporting Information

Iridium-catalyzed C–H phosphoramidation of N-aryl-7-azaindoles with phosphoryl azides

Changduo Pan,* Yun Wang, Chao Wu and Jin-Tao Yu

E-mail: panchangduo@jsut.edu.cn

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1. General experimental details

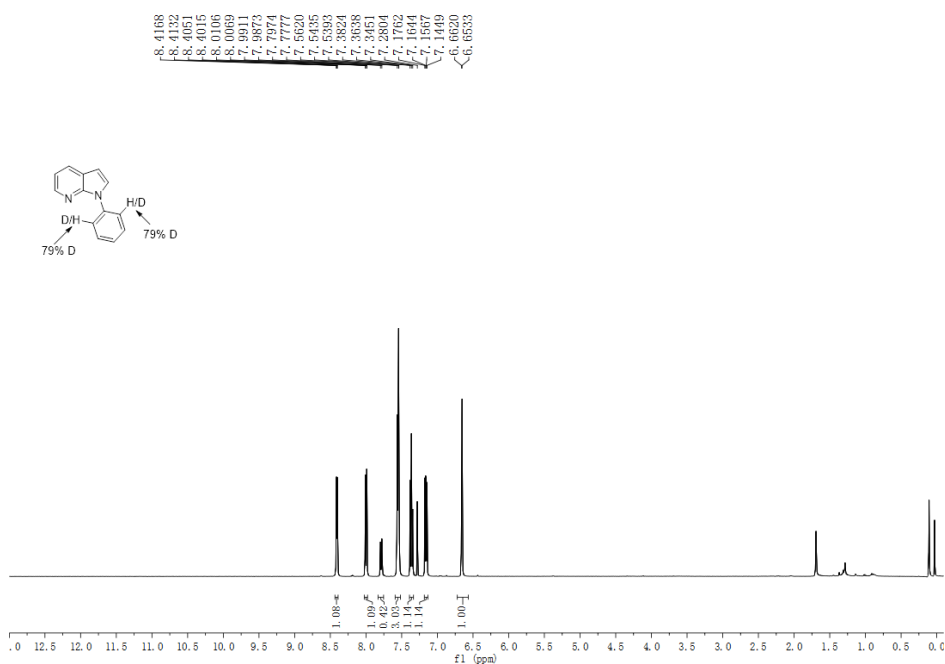
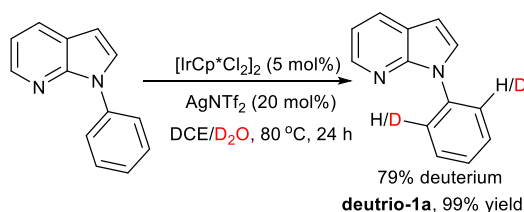
General Information: All chemicals were used as received without further purification unless stated otherwise. NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants J are given in Hz. HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode.

Experimental procedure: Under N_2 , the mixture of **1** (0.2 mmol), **2** (1.5 equiv), $[IrCp^*Cl_2]_2$ (5 mol%, 8.0 mg), $AgNTf_2$ (20 mol%, 15.5 mg) and DCE (2 mL) were added into the sealed tubed. The reaction mixture was vigorously stirred at 80 °C for 24h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the products.

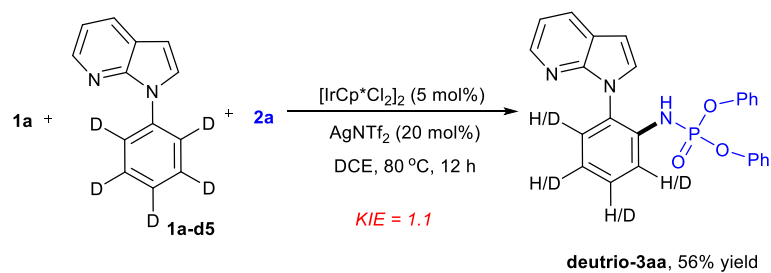
2. Mechanism Studies

The reaction of *N*-phenyl 7-azaindole **1a** with D_2O to give **deutrio-1a**:

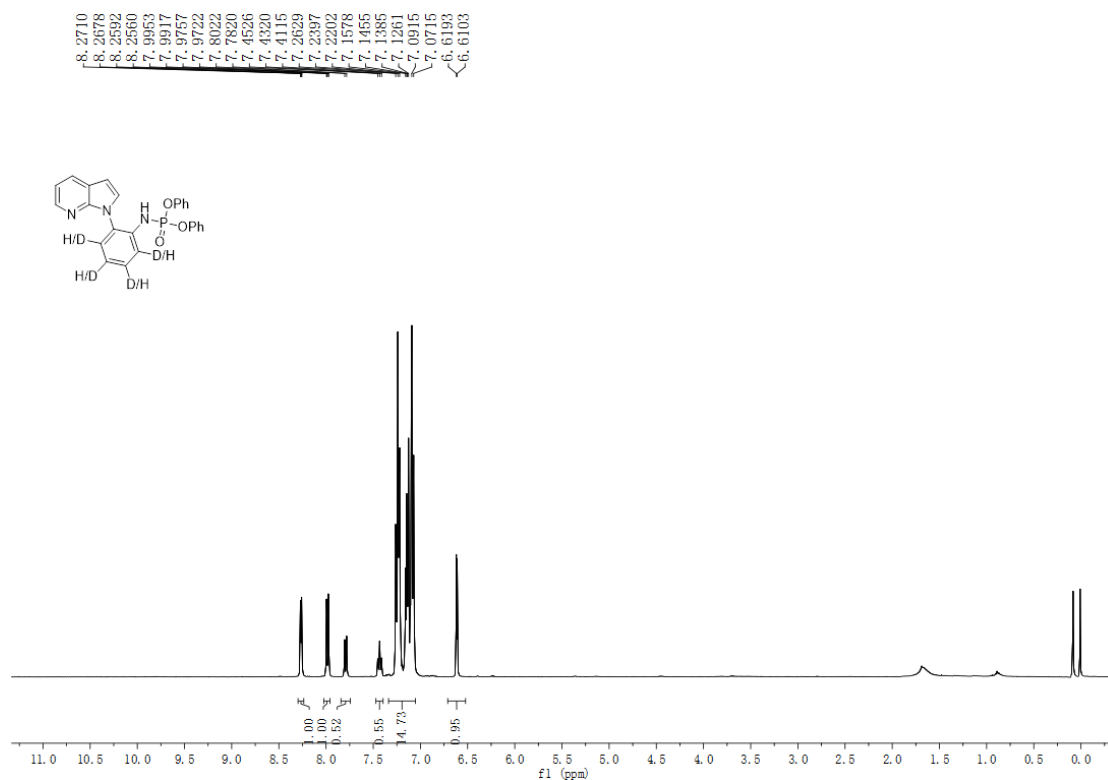
Under N_2 , the mixture of *N*-phenyl 7-azaindole **1a** (0.1 mmol, 19.4 mg), $[IrCp^*Cl_2]_2$ (5 mol%, 8.0 mg), $AgNTf_2$ (20 mol%, 15.5 mg), DCE (1 mL) and D_2O (0.1 mL) were added into the tube and sealed. The reaction mixture was vigorously stirred at 80 °C for 24 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the **deutrio-1a** in 99% yield. 1H NMR ($CDCl_3$, 400 MHz): δ 8.42-8.40 (m, 1H), 8.01-7.98 (m, 1H), 7.78 (d, $J = 7.9$ Hz, 0.42H), 7.56-7.54 (m, 3H), 7.38-7.34 (t, $J = 7.4$ Hz, 1H), 7.18-7.14 (m, 1H), 6.66 (d, $J = 3.5$ Hz, 1H).



Intermolecular competition experiment with isotopically labeled **1a-d₅**

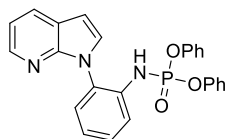


Under N₂, the mixture of **1a** (9.2 mg, 0.05 mmol), **1a-d₅** (9.9 mg, 0.05 mmol), **2a** (41.2 mg, 0.3 mmol), [IrCp*Cl₂]₂ (5 mol%, 8.0 mg), AgNTf₂ (20 mol%, 15.5 mg) and DCE (1 mL) were added into the tube and sealed. The mixture was stirred at 80 °C for 12 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the **deutrio-3aa** in 56% yield. ¹H NMR (CDCl₃, 400 MHz): δ 8.27-8.25 (m, 1H), 7.99-7.97 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 0.55H), 7.45-7.41 (m, 0.58H), 7.26-7.07 (m, 15H), 6.61 (d, *J* = 3.6 Hz, 1H).



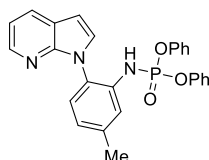
3. Characterization data of the products

diphenyl (2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (3aa)



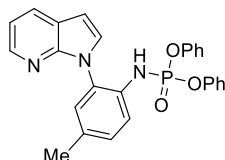
^1H NMR (CDCl_3 , 300 MHz): δ 8.26-8.24 (m, 1H), 7.98-7.95 (m, 1H), 7.78 (d, $J = 8.3$ Hz, 1H), 7.45-7.38 (m, 1H), 7.26-7.05 (m, 15H), 6.60 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.4 (d, $J = 6.7$ Hz), 147.7, 143.5, 134.2 (d, $J = 2.0$ Hz), 130.7 (d, $J = 10.3$ Hz), 130.1, 129.7, 129.3, 128.7, 127.7, 125.2, 124.5, 123.0 (d, $J = 1.0$ Hz), 121.5, 120.2 (d, $J = 4.9$ Hz), 116.8, 102.8. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta -7.32$. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{21}\text{N}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 442.1315, found 442.1317.

diphenyl (5-methyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (3ba)



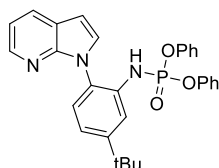
^1H NMR (CDCl_3 , 400 MHz): δ 8.27-8.25 (m, 1H), 7.99-7.97 (m, 1H), 7.59 (s, 1H), 7.28-7.24 (m, 4H), 7.16-7.02 (m, 11H), 6.61 (d, $J = 3.6$ Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.4 (d, $J = 6.8$ Hz), 147.7, 143.5, 138.9, 133.9 (d, $J = 1.9$ Hz), 129.9, 129.7, 129.4, 128.0 (d, $J = 10.3$ Hz), 127.4, 125.2, 123.4, 121.4, 120.2 (d, $J = 4.9$ Hz), 116.7, 102.5, 21.4. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta -7.26$. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{N}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 456.1472, found 456.1471.

diphenyl (4-methyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (3ca)



^1H NMR (CDCl_3 , 400 MHz): δ 8.26-8.24 (m, 1H), 7.98-7.95 (m, 1H), 7.65 (d, $J = 8.3$ Hz, 1H), 7.25-7.20 (m, 5H), 7.14-6.97 (m, 9H), 6.59 (d, $J = 3.6$ Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.4 (d, $J = 6.7$ Hz), 147.7, 143.5, 134.5, 131.4 (d, $J = 1.2$ Hz), 130.7 (d, $J = 10.2$ Hz), 129.9, 129.7, 129.3 (d, $J = 6.0$ Hz), 128.1, 125.1, 123.2, 121.5, 120.2 (d, $J = 4.8$ Hz), 116.7, 102.6, 20.7. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta -7.04$. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{N}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 456.1472, found 456.1470.

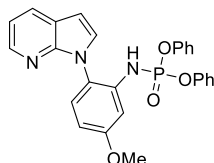
diphenyl (5-(tert-butyl)-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (3da)



^1H NMR (CDCl_3 , 400 MHz): δ 8.31-8.29 (m, 1H), 8.01-7.98 (m, 1H), 7.81-7.80 (m, 1H), 7.28-7.24 (m, 5H), 7.19-7.09 (m, 9H), 7.03-6.99 (m, 1H), 6.62 (d, $J = 3.6$ Hz, 1H), 1.40 (s, 9H).

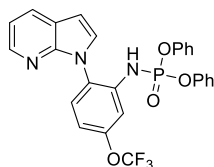
^{13}C NMR (CDCl_3 , 100 MHz): δ 151.9, 150.4 (d, $J = 6.8$ Hz), 147.7, 143.5, 133.5 (d, $J = 0.9$ Hz), 129.9, 129.7, 129.3, 127.9 (d, $J = 10.2$ Hz), 127.1, 125.2, 121.6, 121.4, 120.3 (d, $J = 1.4$ Hz), 120.2 (d, $J = 4.9$ Hz), 116.7, 102.5, 34.9, 31.4. ^{31}P NMR (CDCl_3 , 162 MHz): δ -7.19. HRMS (ESI) m/z calcd for $\text{C}_{29}\text{H}_{29}\text{N}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 498.1941, found 498.1946.

diphenyl (5-methoxy-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (3ea)



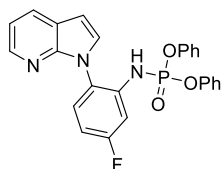
^1H NMR (CDCl_3 , 400 MHz): δ 8.28-8.26 (m, 1H), 7.99-7.97 (m, 1H), 7.34-7.26 (m, 5H), 7.18-7.12 (m, 8H), 7.05-7.04 (m, 1H), 6.83-6.74 (m, 2H), 6.60 (d, $J = 3.4$ Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 159.8, 150.2 (d, $J = 6.8$ Hz), 147.8, 143.6, 135.5, 129.9, 129.8, 129.4, 128.7, 125.3, 123.0 (d, $J = 10.6$ Hz), 121.2, 120.3 (d, $J = 4.6$ Hz), 116.7, 109.8, 107.5, 102.4, 55.7. ^{31}P NMR (CDCl_3 , 162 MHz): δ -7.63. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{23}\text{N}_3\text{O}_4\text{P}$ ($\text{M}+\text{H}$) $^+$ 472.1421, found 472.1420.

diphenyl (2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-5-(trifluoromethoxy)phenyl)phosphoramidate (3fa)



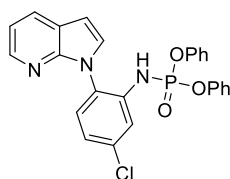
^1H NMR (CDCl_3 , 400 MHz): δ 8.28-8.27 (m, 1H), 8.01-7.99 (m, 1H), 7.70-7.69 (m, 1H), 7.30-7.25 (m, 6H), 7.19-7.06 (m, 9H), 6.65 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.2 (d, $J = 6.8$ Hz), 148.8, 147.7, 143.7, 135.8, 130.3, 129.8, 129.0, 128.7, 128.6, 127.2, 125.4, 121.5, 120.1 (d, $J = 4.7$ Hz), 117.1, 116.3, 115.1, 103.4. ^{31}P NMR (CDCl_3 , 162 MHz): δ -8.32. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{20}\text{F}_3\text{N}_3\text{O}_4\text{P}$ ($\text{M}+\text{H}$) $^+$ 526.1138, found 526.1142.

diphenyl (5-fluoro-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (3ga)



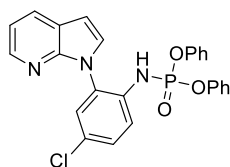
^1H NMR (CDCl_3 , 400 MHz): δ 8.27-8.26 (m, 1H), 8.00-7.98 (m, 1H), 7.56-7.53 (m, 1H), 7.31-7.26 (m, 4H), 7.23-7.04 (m, 10H), 6.94-6.89 (m, 1H), 6.63 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 162.3 (d, $J = 245.8$ Hz), 150.2 (d, $J = 7.0$ Hz), 147.8, 143.6, 136.2 (q, $J_1 = 1.7$ Hz, $J_2 = 11.3$ Hz), 130.8, 129.8 (d, $J = 0.8$ Hz), 129.2, 129.0 (d, $J = 9.9$ Hz), 126.1 (q, $J_1 = 3.1$ Hz, $J_2 = 10.7$ Hz), 125.4 (d, $J = 1.3$ Hz), 121.3, 120.2 (d, $J = 4.9$ Hz), 116.9, 109.6 (d, $J = 1.7$ Hz), 109.2 (d, $J = 1.6$ Hz), 102.9. ^{31}P NMR (CDCl_3 , 162 MHz): δ -8.17. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{FN}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 460.1221, found 460.1222.

diphenyl (5-chloro-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (3ha)



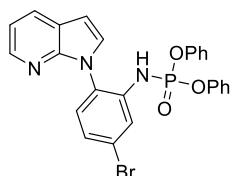
^1H NMR (CDCl_3 , 400 MHz): δ 8.26-8.25 (m, 1H), 7.99-7.97 (m, 1H), 7.80 (d, $J = 1.1$ Hz, 1H), 7.33-7.25 (m, 5H), 7.18-7.05 (m, 10H), 6.63 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.2 (d, $J = 7.0$ Hz), 147.7, 143.6, 135.4 (d, $J = 1.6$ Hz), 134.2, 130.2, 129.8, 129.1, 129.0, 128.5, 125.4, 124.4, 122.8 (d, $J = 1.0$ Hz), 121.5, 120.2 (d, $J = 4.9$ Hz), 116.9, 103.2. ^{31}P NMR (CDCl_3 , 162 MHz): δ -8.08. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{ClN}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 476.0925, found 476.0927.

diphenyl (4-chloro-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (3ia)



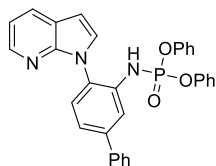
^1H NMR (CDCl_3 , 400 MHz): δ 8.26-8.27 (m, 1H), 8.02-8.00 (m, 1H), 7.73 (d, $J = 8.7$ Hz, 1H), 7.42-7.33 (m, 2H), 7.28-7.23 (m, 5H), 7.19-7.13 (m, 3H), 7.11-7.06 (m, 5H), 6.65 (d, $J = 3.5$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 150.3 (d, $J = 6.9$ Hz), 147.7, 143.5, 132.9 (d, $J = 2.2$ Hz), 131.9 (d, $J = 10.4$ Hz), 130.3, 129.7, 129.3, 129.0, 128.5, 127.4, 125.2 (d, $J = 1.3$ Hz), 124.4 (d, $J = 1.6$ Hz), 121.6, 120.1 (d, $J = 4.8$ Hz), 117.1, 103.5. ^{31}P NMR (CDCl_3 , 162 MHz): δ -7.64. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{ClN}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 476.0925, found 476.0927.

diphenyl (5-bromo-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (3ja)



^1H NMR (CDCl_3 , 400 MHz): δ 8.26-8.24 (m, 1H), 7.99-7.94 (m, 2H), 7.40-7.26 (m, 6H), 7.18-7.05 (m, 9H), 6.63 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.2 (d, $J = 7.0$ Hz), 147.7, 143.5, 135.5 (d, $J = 1.7$ Hz), 130.2, 129.8, 129.6, 128.9, 128.8, 127.4, 125.8 (d, $J = 1.2$ Hz), 125.4, 121.9, 121.5, 120.2 (d, $J = 4.9$ Hz), 117.0, 103.3. ^{31}P NMR (CDCl_3 , 162 MHz): δ -8.09. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{BrN}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 520.0420, found 520.0425.

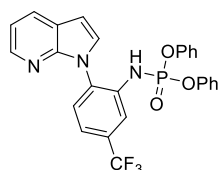
diphenyl (4-(1H-pyrrolo[2,3-b]pyridin-1-yl)-[1,1'-biphenyl]-3-yl)phosphoramidate (3ka)



^1H NMR (CDCl_3 , 400 MHz): δ 8.32-8.30 (m, 1H), 8.02-8.00 (m, 2H), 7.67-7.65 (m, 2H), 7.52-7.40 (m, 4H), 7.35-7.25 (m, 6H), 7.19-7.12 (m, 8H), 6.65 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.4 (d, $J = 6.6$ Hz), 147.8, 143.5, 141.7, 139.9, 134.4 (d, $J = 1.7$ Hz), 130.1, 129.7, 129.3, 128.9, 127.8 (d, $J = 3.1$ Hz), 127.2, 125.3, 123.2, 121.8, 121.6, 120.3 (d, $J = 4.8$ Hz), 116.8, 102.9. ^{31}P NMR (CDCl_3 , 162 MHz): δ -7.27. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{25}\text{N}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 518.1628, found 518.1631.

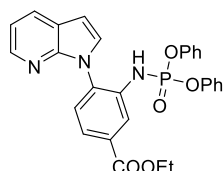
diphenyl (2-(1H-pyrrolo[2,3-b]pyridin-1-yl)-5-(trifluoromethyl)phenyl)phosphoramidate

(31a)



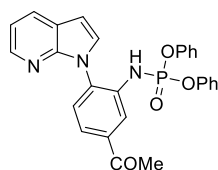
^1H NMR (CDCl_3 , 400 MHz): δ 8.29-8.28 (m, 1H), 8.05-8.01 (m, 2H), 7.63-7.59 (m, 1H), 7.47 (d, $J = 8.2$ Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 1H), 7.29-7.25 (m, 4H), 7.21-7.09 (m, 8H), 6.69 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (CDCl_3 , 150 MHz): δ 150.2 (d, $J = 6.8$ Hz), 147.7, 143.6, 134.7 (d, $J = 1.9$ Hz), 133.7 (q, $J = 1.3$ Hz), 133.6 (q, $J = 1.3$ Hz), 130.4, 129.7, 128.9, 127.9, 125.3 (d, $J = 1.1$ Hz), 123.6 (q, $J = 270.8$ Hz), 121.7, 121.1 (q, $J = 3.6$ Hz), 120.3 (q, $J = 3.7$ Hz), 120.1 (d, $J = 4.9$ Hz), 117.2, 103.9. ^{31}P NMR (CDCl_3 , 162 MHz): δ -8.16. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{20}\text{F}_3\text{N}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 510.1189, found 510.1185.

ethyl 3-((diphenoxyphosphoryl)amino)-4-(1H-pyrrolo[2,3-b]pyridin-1-yl)benzoate (3ma)



^1H NMR (CDCl_3 , 400 MHz): δ 8.51-8.50 (m, 1H), 8.29-8.27 (m, 1H), 8.00-7.98 (m, 1H), 7.92-7.89 (m, 1H), 7.71-7.67 (m, 1H), 7.32-7.24 (m, 5H), 7.19-7.12 (m, 8H), 6.65 (d, $J = 3.6$ Hz, 1H), 4.48-4.42 (q, 2H), 1.45 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 165.6, 150.4 (d, $J = 6.9$ Hz), 147.7, 143.6, 134.9 (d, $J = 10.1$ Hz), 133.9, 130.4, 130.3, 129.7, 129.0, 127.3, 125.7, 125.2, 124.7, 121.7, 120.2 (d, $J = 4.8$ Hz), 117.1, 103.7, 61.4, 14.4. ^{31}P NMR (CDCl_3 , 162 MHz): δ -7.81. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{25}\text{N}_3\text{O}_5\text{P}$ ($\text{M}+\text{H}$) $^+$ 514.1526, found 514.1530.

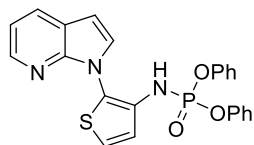
diphenyl (5-acetyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (3na)



^1H NMR (CDCl_3 , 400 MHz): δ 8.34-8.33 (m, 1H), 8.29-8.27 (m, 1H), 8.01-7.99 (m, 1H), 7.83-7.78 (m, 2H), 7.37-7.32 (m, 1H), 7.28-7.24 (m, 4H), 7.20-7.09 (m, 8H), 6.67 (d, $J = 3.6$ Hz,

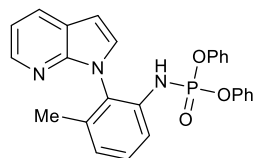
1H), 2.64 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 196.9, 150.3 (d, *J* = 6.9 Hz), 147.7, 143.5, 135.1 (d, *J* = 9.8 Hz), 134.1, 130.4, 129.7, 129.0, 127.4, 125.3, 124.3, 124.0, 121.8, 120.4 (d, *J* = 4.9 Hz), 120.2 (d, *J* = 4.9 Hz), 117.1, 103.8, 26.8. ³¹P NMR (CDCl₃, 162 MHz): δ -7.59. HRMS (ESI) *m/z* calcd for C₂₇H₂₃N₃O₄P (M+H)⁺ 484.1421, found 484.1423.

diphenyl 2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)thiophen-3-yl)phosphoramidate (3oa)



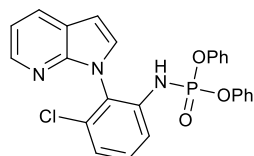
¹H NMR (CDCl₃, 400 MHz): δ 8.30-8.28 (m, 1H), 7.98-7.95 (m, 1H), 7.69-7.66 (m, 1H), 7.33-7.24 (m, 5H), 7.18-7.12 (m, 9H), 6.63 (d, *J* = 3.6 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 150.4 (d, *J* = 6.7 Hz), 147.6, 143.6, 130.2, 129.7, 129.3, 128.8 (d, *J* = 1.5 Hz), 125.2, 125.0 (d, *J* = 11.4 Hz), 123.3, 121.4, 120.8, 120.3 (d, *J* = 4.9 Hz), 117.1, 103.5. ³¹P NMR (CDCl₃, 162 MHz): δ -7.41. HRMS (ESI) *m/z* calcd for C₂₃H₁₉N₃O₃PS (M+H)⁺ 448.0879, found 448.0882.

diphenyl (3-methyl-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)phosphoramidate (3pa)



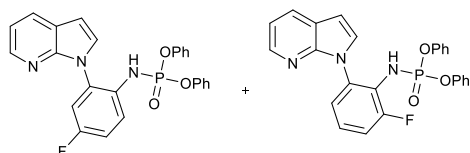
¹H NMR (CDCl₃, 600 MHz): δ 8.31-8.30 (m, 1H), 8.01-7.99 (m, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.43-7.08 (m, 12H), 7.09-7.07 (m, 1H), 6.84 (d, *J* = 3.5 Hz, 1H), 6.65 (d, *J* = 3.5 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 1.88 (s, 3H). ¹³C NMR (CDCl₃, 150 MHz): δ 150.2 (d, *J* = 6.4 Hz), 147.8, 144.3, 138.2, 136.5 (d, *J* = 2.0 Hz), 129.80, 129.79 (d, *J* = 4.9 Hz), 129.6, 129.5, 128.3, 125.4, 125.0, 120.6, 120.4 (d, *J* = 4.8 Hz), 116.9, 116.6, 102.7, 17.8. ³¹P NMR (CDCl₃, 162 MHz): δ -7.79. HRMS (ESI) *m/z* calcd for C₂₆H₂₃N₃O₃P (M+H)⁺ 456.1472, found 456.1471.

diphenyl (3-chloro-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)phosphoramidate (3qa)



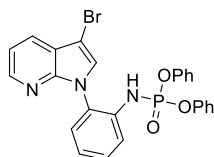
¹H NMR (CDCl₃, 600 MHz): δ 8.30 (d, *J* = 4.7 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.46-7.43 (m, 1H), 7.35-7.28 (m, 5H), 7.24-7.15 (m, 7H), 6.94-6.93 (m, 1H), 6.68-6.67 (m, 1H), 5.59 (d, *J* = 10.0 Hz, 1H). ¹³C NMR (CDCl₃, 150 MHz): δ 150.1 (d, *J* = 6.6 Hz), 147.8, 144.2, 138.2 (d, *J* = 2.6 Hz), 134.3, 130.3, 129.8, 129.6, 128.7, 125.5 (d, *J* = 4.3 Hz), 124.4, 120.7, 120.2 (d, *J* = 4.7 Hz), 118.0, 117.2, 102.9. ³¹P NMR (CDCl₃, 162 MHz): δ -7.79. HRMS (ESI) *m/z* calcd for C₂₅H₂₀ClN₃O₃P (M+H)⁺ 476.0925, found 476.0927.

diphenyl (4-fluoro-2-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)phosphoramidate (3ra) and diphenyl (2-fluoro-6-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)phosphoramidate (3ra')



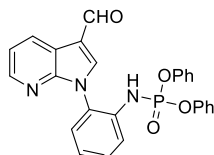
^1H NMR (CDCl_3 , 600 MHz): δ 8.29-8.26 (m, 1H), 8.02-8.00 (m, 0.8H), 7.98-7.96 (m, 0.19H), 7.75-7.73 (m, 0.81H), 7.67-7.65 (m, 0.19H), 7.41-7.36 (m, 1H), 7.26-6.94 (m, 14H), 6.65 (d, $J = 3.1$ Hz, 0.79H), 6.59 (d, $J = 3.1$ Hz, 0.18H). ^{13}C NMR (CDCl_3 , 150 MHz): δ 160.02, 160.01, 158.40, 158.39, 150.39, 150.35, 147.6, 147.4, 143.5, 142.9, 132.7, 132.6, 132.5, 130.3, 130.2, 130.04, 130.02, 130.01, 130.0, 129.9, 129.8, 129.83, 129.82, 129.7, 129.6, 129.39, 129.38, 129.35, 128.9, 125.57, 125.56, 125.52, 125.51, 125.46, 125.45, 125.14, 125.13, 124.75, 125.74, 122.02, 122.0, 121.9, 121.6, 120.1, 120.09, 120.08, 120.06, 119.9, 119.8, 117.0, 116.7, 115.26, 115.25, 115.11, 115.10, 114.4, 114.2, 103.5, 103.3. ^{31}P NMR (CDCl_3 , 162 MHz): δ -7.17, -7.36. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{FN}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 460.1221, found 460.1222.

diphenyl (2-(3-bromo-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (4aa)



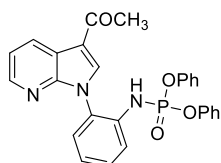
^1H NMR (CDCl_3 , 400 MHz): δ 8.30-8.28 (m, 1H), 7.94-7.92 (m, 1H), 7.79-7.77 (m, 1H), 7.48-7.43 (m, 1H), 7.28-7.15 (m, 9H), 7.11-7.06 (m, 5H), 7.01 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.3 (d, $J = 6.7$ Hz), 146.5, 144.6, 134.0, 130.1 (d, $J = 10.1$ Hz), 129.7, 129.1, 128.9, 128.1, 127.6, 125.3, 124.8, 123.6 (d, $J = 1.1$ Hz), 120.9, 120.1 (d, $J = 4.9$ Hz), 117.4, 91.7. ^{31}P NMR (CDCl_3 , 162 MHz): δ -7.50. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{BrN}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 520.0420, found 520.0424.

diphenyl (2-(3-formyl-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (4ba)



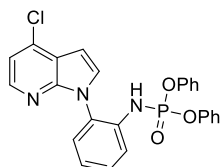
^1H NMR (CDCl_3 , 400 MHz): δ 9.93 (s, 1H), 8.63-8.60 (m, 1H), 8.35-8.33 (m, 1H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.55-7.51 (m, 2H), 7.28-7.23 (m, 7H), 7.17-7.14 (m, 2H), 7.08-7.06 (m, 4H), 6.89-6.86 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 184.8, 150.2 (d, $J = 6.7$ Hz), 148.5, 145.6, 138.9, 134.3 (d, $J = 1.8$ Hz), 131.8, 130.0, 129.8, 129.7, 127.6, 125.4, 125.1, 124.0 (d, $J = 1.2$ Hz), 120.1 (d, $J = 4.9$ Hz), 119.6, 118.4, 117.9. ^{31}P NMR (CDCl_3 , 162 MHz): δ -7.68. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_4\text{P}$ ($\text{M}+\text{H}$) $^+$ 470.1264, found 470.1261.

diphenyl (2-(3-acetyl-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (4ca)



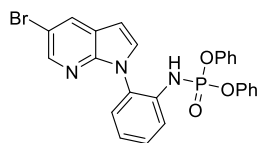
^1H NMR (CDCl_3 , 400 MHz): δ 8.72-8.69 (m, 1H), 8.32-8.31 (m, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.57 (s, 1H), 7.53-7.49 (m, 1H), 7.36-7.22 (m, 7H), 7.16-7.12 (m, 2H), 7.07-7.05 (m, 4H), 6.94-6.91 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 192.9, 150.3 (d, $J = 6.6$ Hz), 148.1, 145.1, 135.1, 134.4, 132.4, 130.1 (d, $J = 9.8$ Hz), 129.8, 129.7, 127.6, 125.3, 124.1, 120.4 (d, $J = 4.9$ Hz), 120.1 (d, $J = 6.7$ Hz), 119.3, 119.1, 117.7, 27.2. ^{31}P NMR (CDCl_3 , 162 MHz): δ -7.62. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_4\text{P}$ ($\text{M}+\text{H}$) $^+$ 484.1421, found 484.1423.

diphenyl (2-(4-chloro-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (4da)



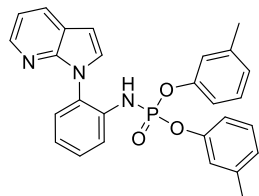
^1H NMR (CDCl_3 , 400 MHz): δ 8.14-8.13 (m, 1H), 7.79-7.77 (m, 1H), 7.49-7.44 (m, 1H), 7.28-7.23 (m, 6H), 7.17-7.09 (m, 8H), 6.96-6.93 (m, 1H), 6.71 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.3 (d, $J = 6.7$ Hz), 148.0, 143.8, 137.2, 134.1, 130.3 (d, $J = 10.3$ Hz), 129.8, 129.7, 129.3, 129.1, 127.7, 125.3, 124.7, 123.3 (d, $J = 1.1$ Hz), 120.7, 120.1 (d, $J = 4.9$ Hz), 116.9, 101.2. ^{31}P NMR (CDCl_3 , 162 MHz): δ -7.51. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{ClN}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 476.0925, found 476.0928.

diphenyl (2-(5-bromo-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (4ea)



^1H NMR (CDCl_3 , 400 MHz): δ 8.25-8.24 (m, 1H), 8.09-8.08 (m, 1H), 7.80-7.78 (m, 1H), 7.49-7.44 (m, 1H), 7.30-7.22 (m, 6H), 7.19-7.07 (m, 7H), 6.71-6.67 (m, 1H), 6.56 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.3 (d, $J = 6.8$ Hz), 146.0, 144.0, 134.3 (d, $J = 1.7$ Hz), 131.9, 130.8, 129.9, 129.8, 129.2, 127.8, 125.4, 124.5, 122.9, 122.7 (d, $J = 1.1$ Hz), 120.2 (d, $J = 4.7$ Hz), 112.7, 102.2. ^{31}P NMR (CDCl_3 , 162 MHz): δ -7.63. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{20}\text{BrN}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 520.0420, found 520.0424.

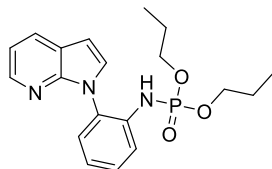
di-*m*-tolyl (2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (4ab)



^1H NMR (CDCl_3 , 400 MHz): δ 8.31-8.29 (m, 1H), 8.01-7.99 (m, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.48-7.43 (m, 1H), 7.28-7.21 (m, 2H), 7.18-7.09 (m, 5H), 6.96-6.88 (m, 6H), 6.63 (d, $J = 3.6$ Hz, 1H), 2.29 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.3 (d, $J = 6.7$ Hz), 147.7, 143.5, 139.9, 134.3, 130.6 (d, $J = 10.6$ Hz), 130.0, 129.3, 128.7, 127.6, 125.9, 124.4, 123.0, 121.5, 120.8 (d, $J =$

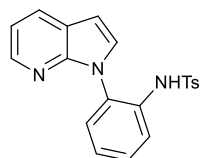
4.8 Hz), 117.1 (d, $J = 4.9$ Hz), 116.8, 102.8, 21.3. ^{31}P NMR (CDCl_3 , 162 MHz): $\delta -7.37$. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{25}\text{N}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 470.1628, found 470.1630.

dipropyl (2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)phosphoramidate (4ac)



^1H NMR (CDCl_3 , 400 MHz): δ 8.34-8.32 (m, 1H), 8.04-8.01 (m, 1H), 7.55-7.53 (m, 1H), 7.41-7.37 (m, 1H), 7.33-7.31 (m, 1H), 7.28-7.25 (m, 1H), 7.18-7.12 (m, 2H), 6.71 (d, $J = 3.6$ Hz, 1H), 6.00-5.98 (m, 1H), 4.02-3.87 (m, 4H), 1.68-1.59 (m, 4H), 0.88 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.9, 143.8, 135.8, 129.9, 129.2, 129.0, 128.7, 128.1, 123.0, 121.2, 120.6, 116.8, 102.7, 68.5, 68.4, 23.6, 23.5, 10.0. ^{31}P NMR (CDCl_3 , 162 MHz): δ 2.11. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{25}\text{N}_3\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ 374.1628, found 374.1627.

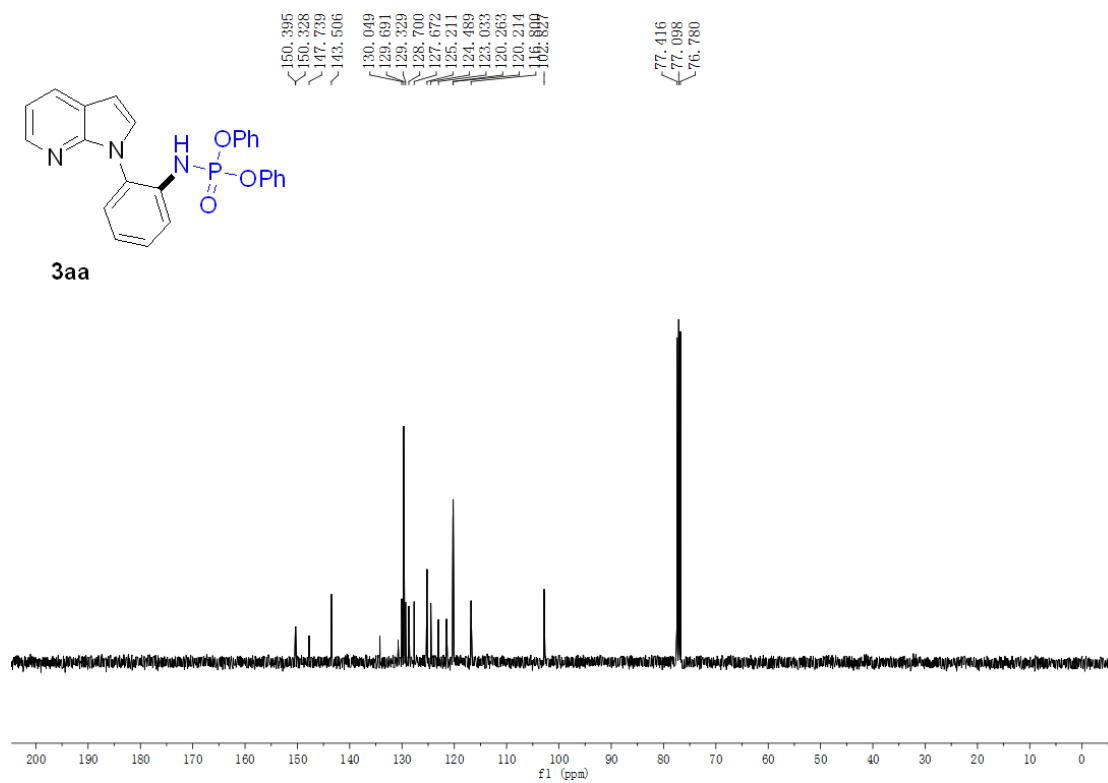
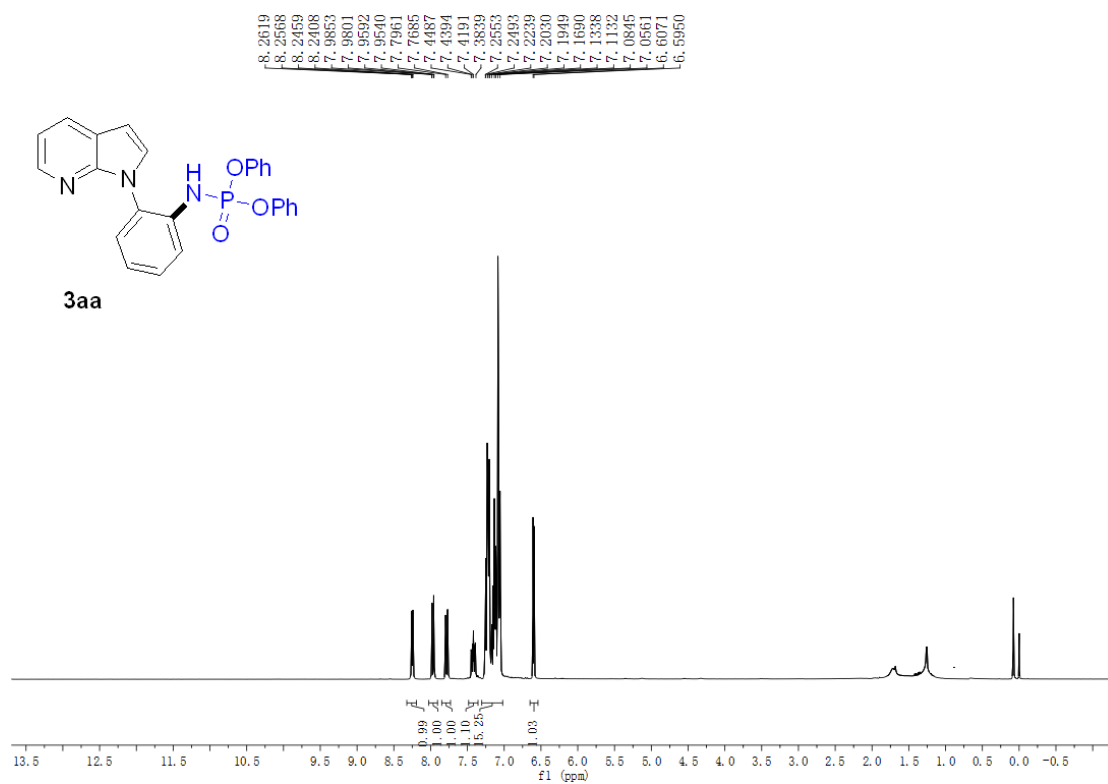
N-(2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)-4-methylbenzenesulfonamide (4ad)¹

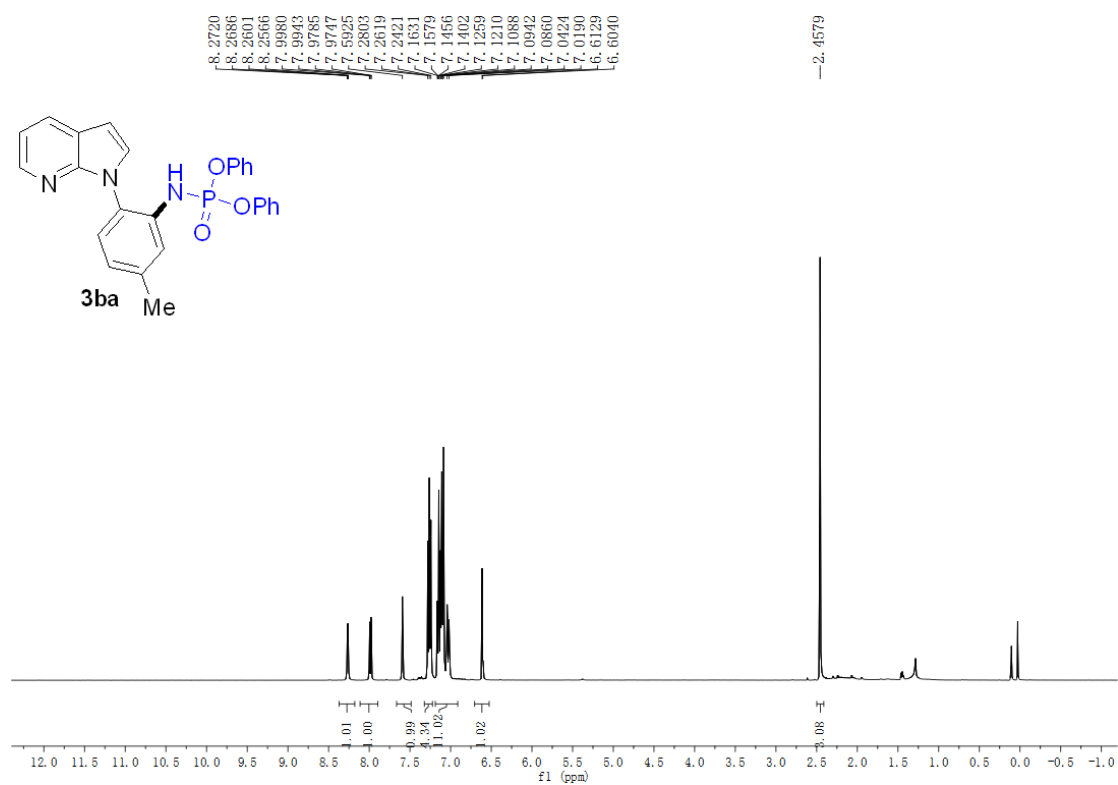
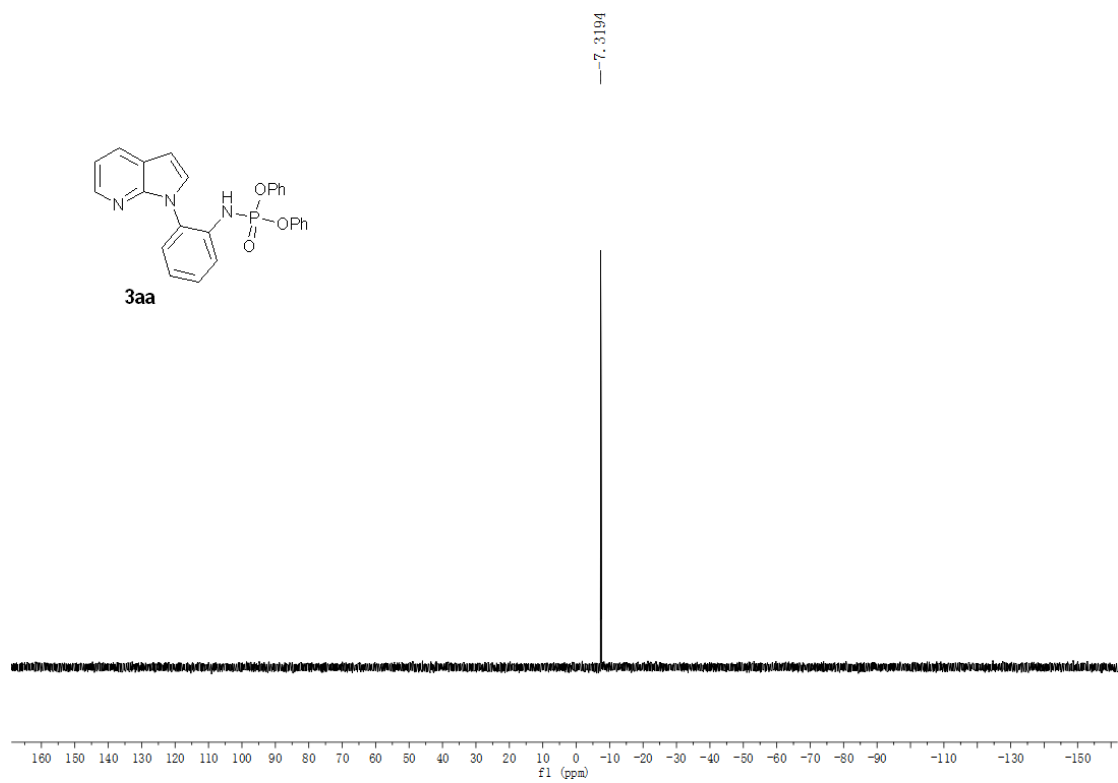


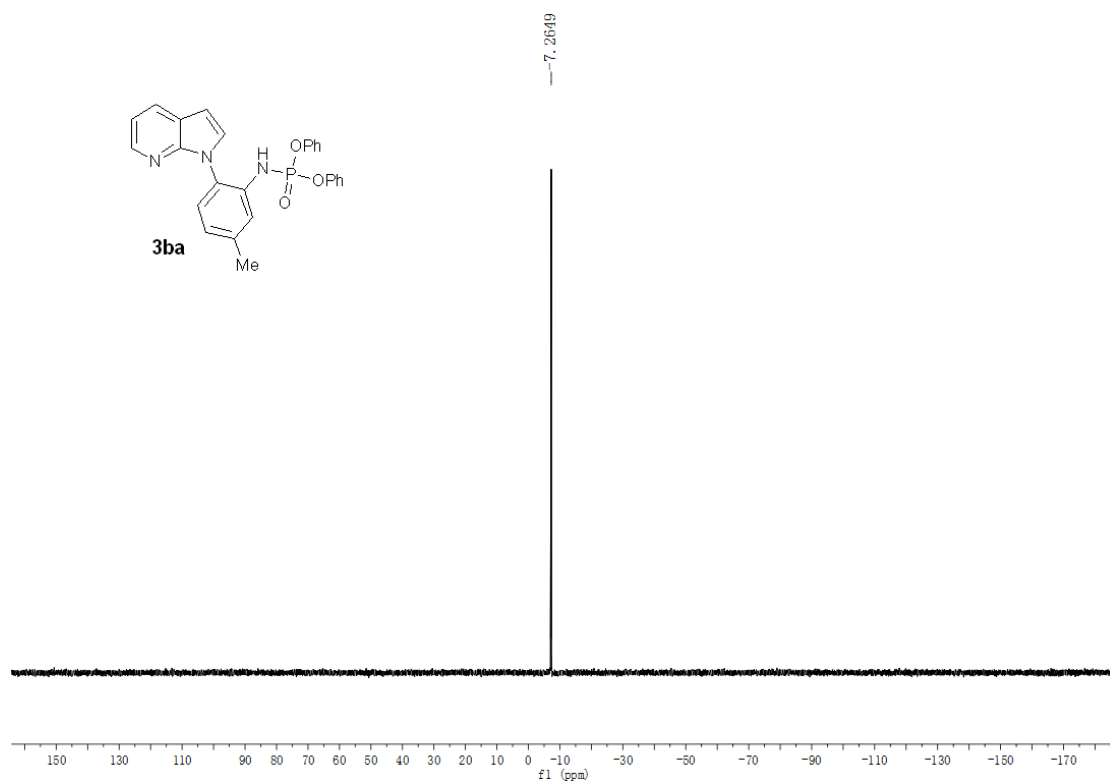
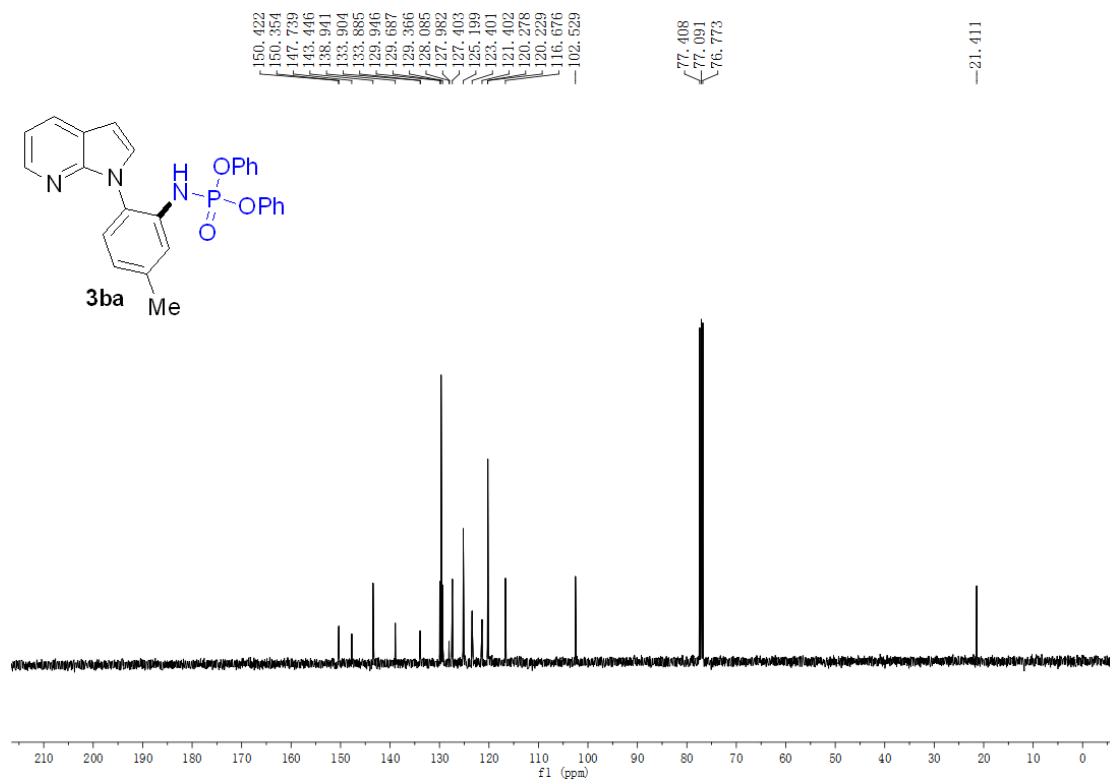
^1H NMR (CDCl_3 , 600 MHz): δ 9.37 (s, 1H), 8.40-8.39 (m, 1H), 8.01-7.99 (m, 1H), 7.82-7.80 (m, 1H), 7.46-7.43 (m, 1H), 7.36-7.33 (m, 1H), 7.23-7.21 (m, 1H), 7.13 (d, $J = 7.9$ Hz, 1H), 6.97 (d, $J = 8.2$ Hz, 2H), 6.89 (d, $J = 8.1$ Hz, 2H), 6.67 (d, $J = 3.6$ Hz, 1H), 6.47 (d, $J = 3.6$ Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (CDCl_3 , 150 MHz): δ 146.8, 143.4, 142.8, 136.8, 130.8, 130.2, 129.9, 129.1, 128.9, 128.1, 127.7, 126.4, 126.0, 121.6, 116.9, 102.7, 21.4.

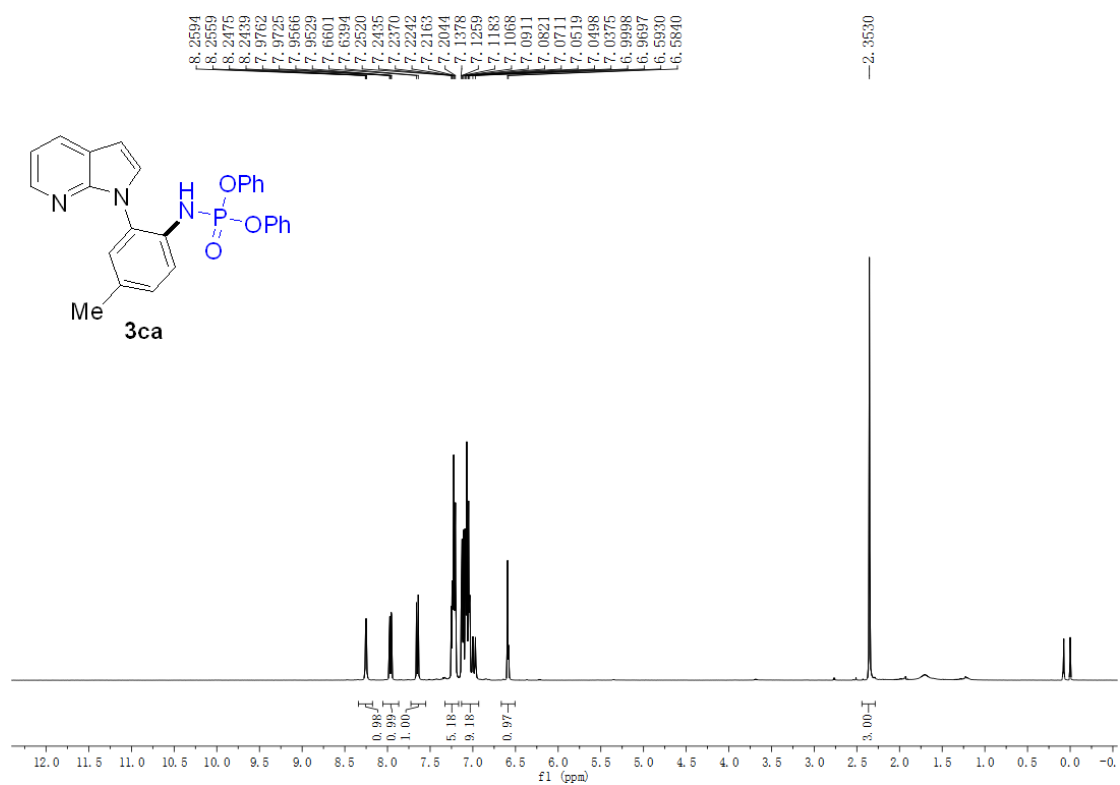
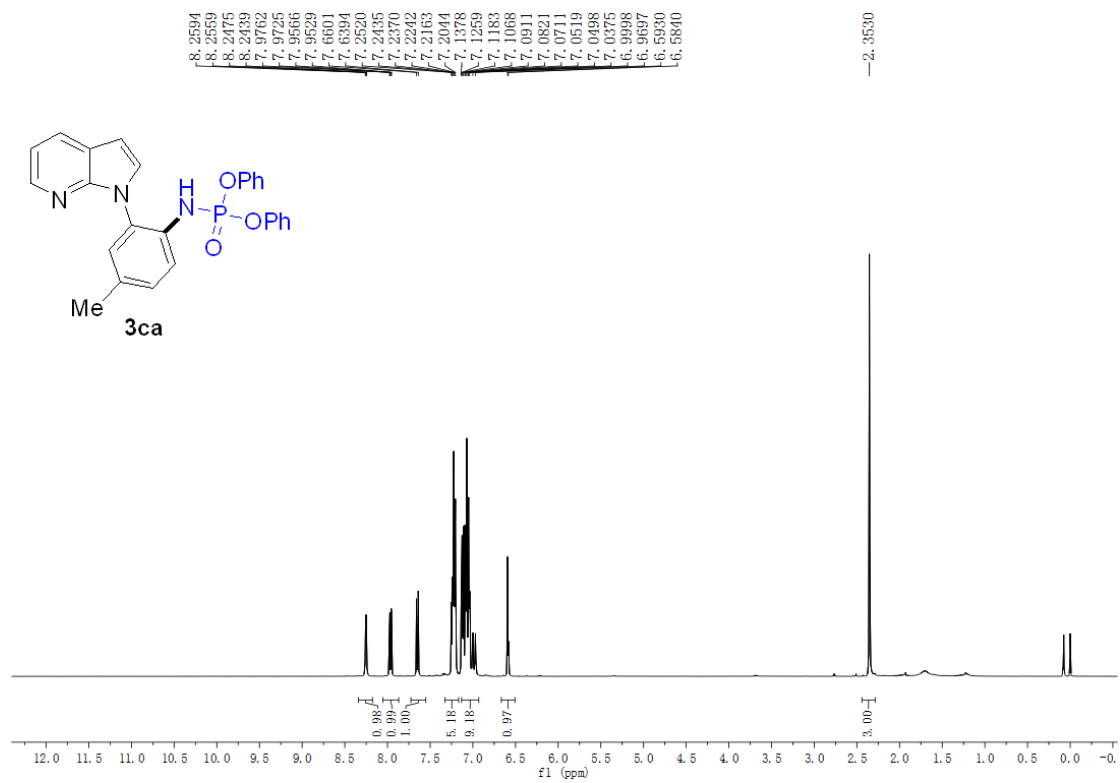
¹ M. Jeon, J. Park, P. Dey, Y. Oh, H. Oh, S. Han, S. H. Um, H. S. Kim, N. K. Mishra and I. S. Kim, *Adv. Synth. Catal.*, 2017, **359**, 3471.

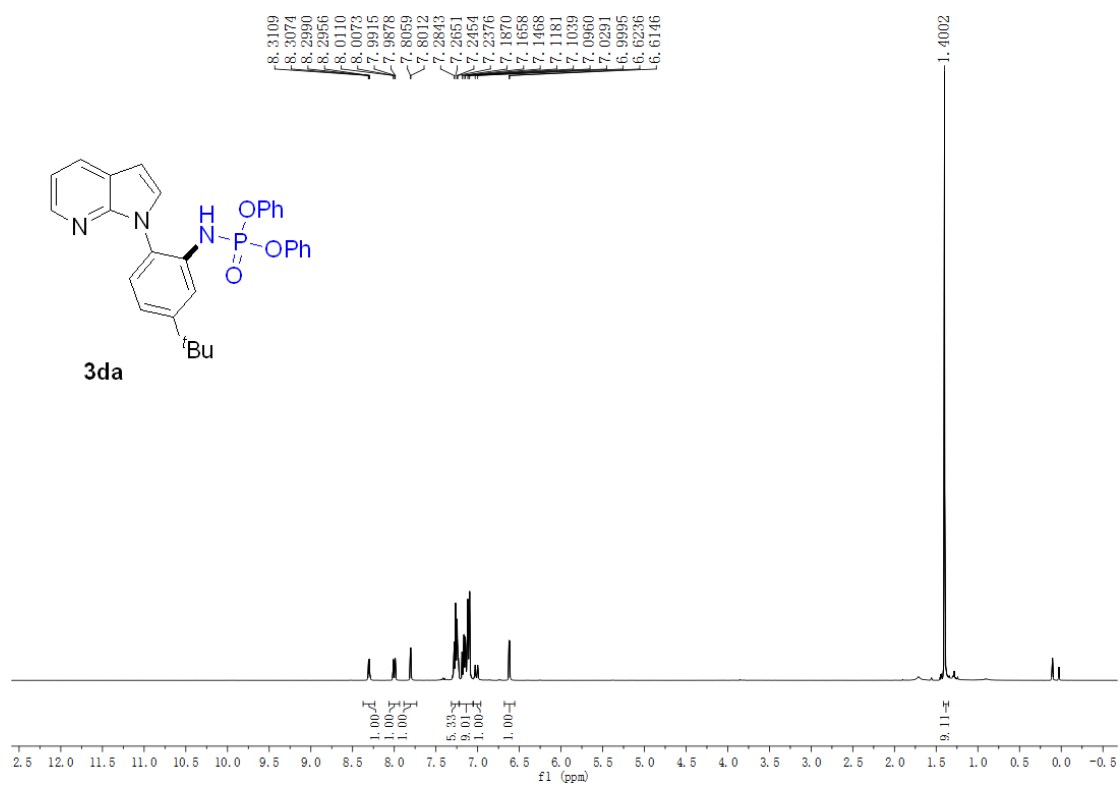
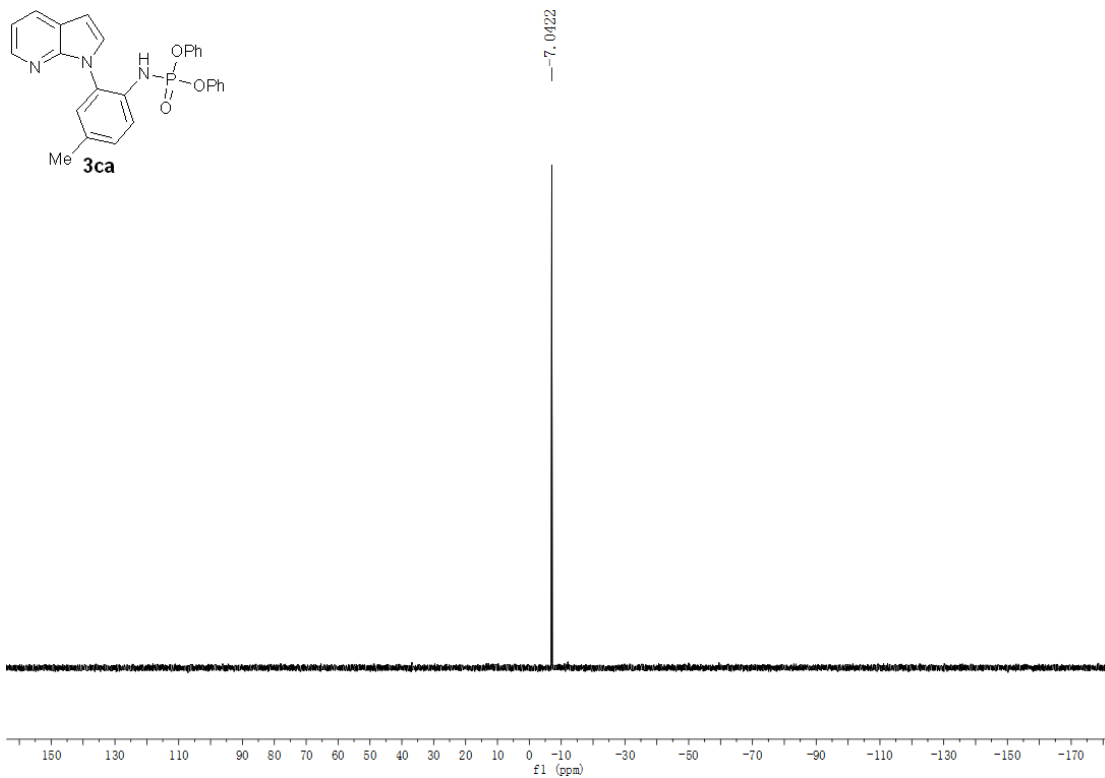
4. Copies of ^1H NMR and ^{13}C NMR spectra of the products



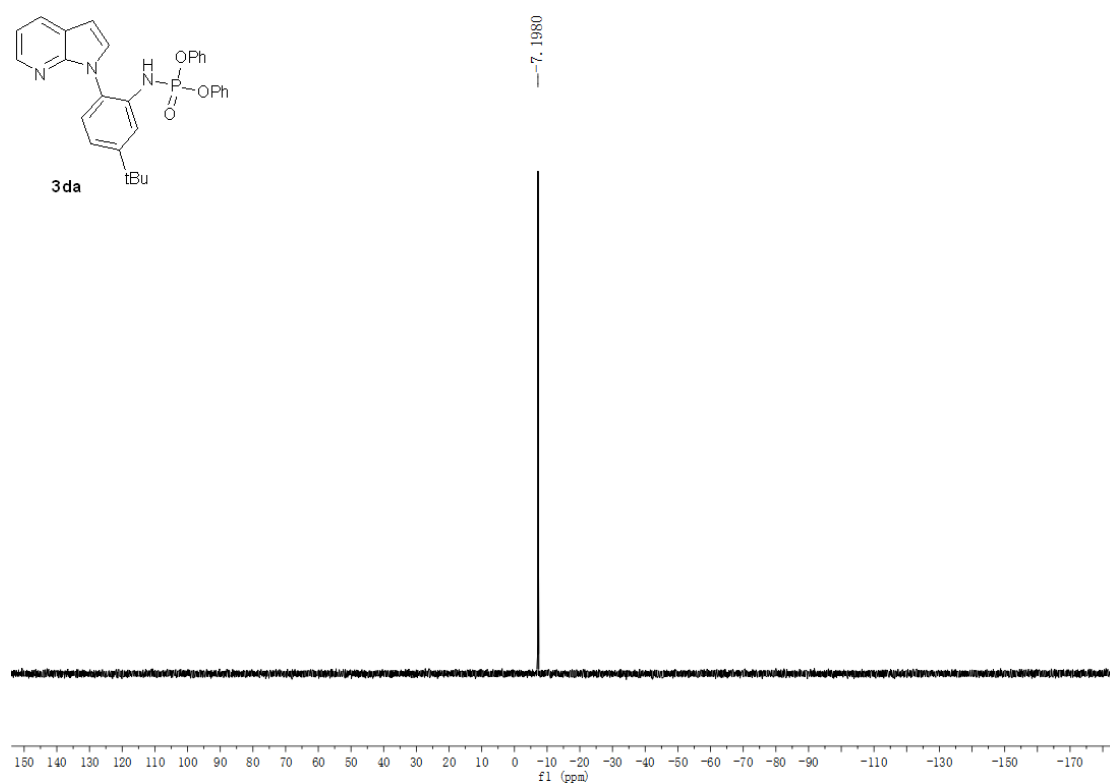
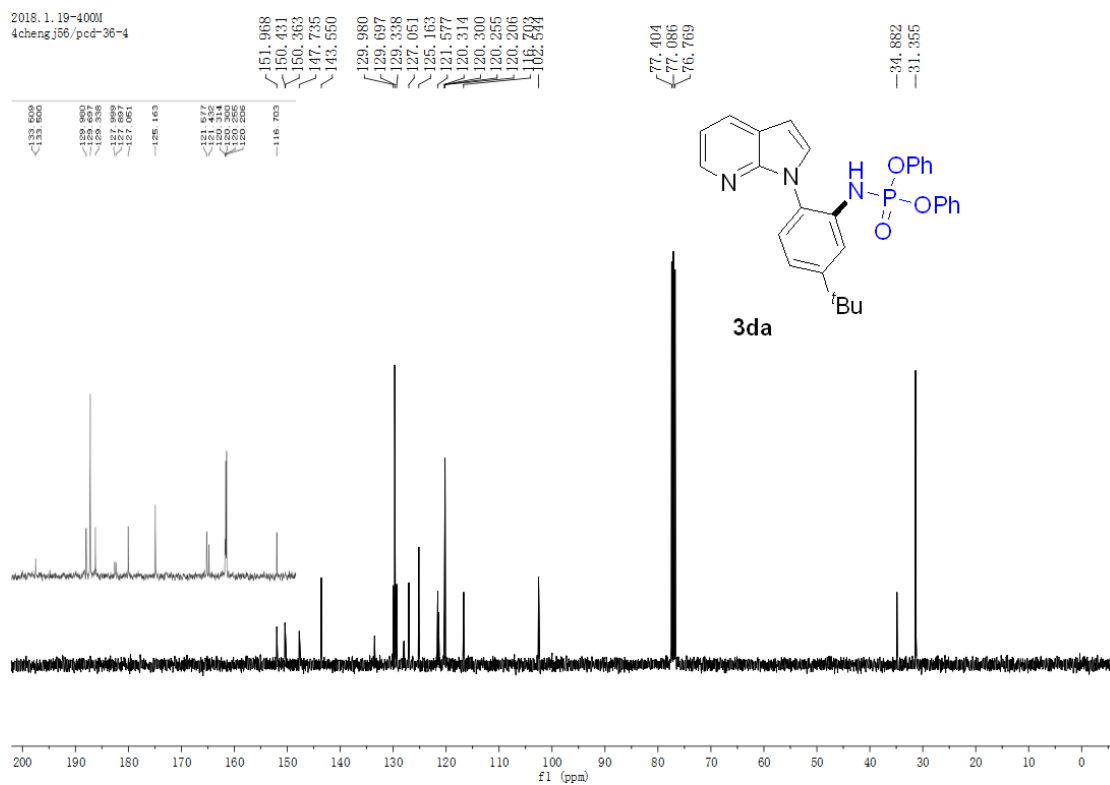


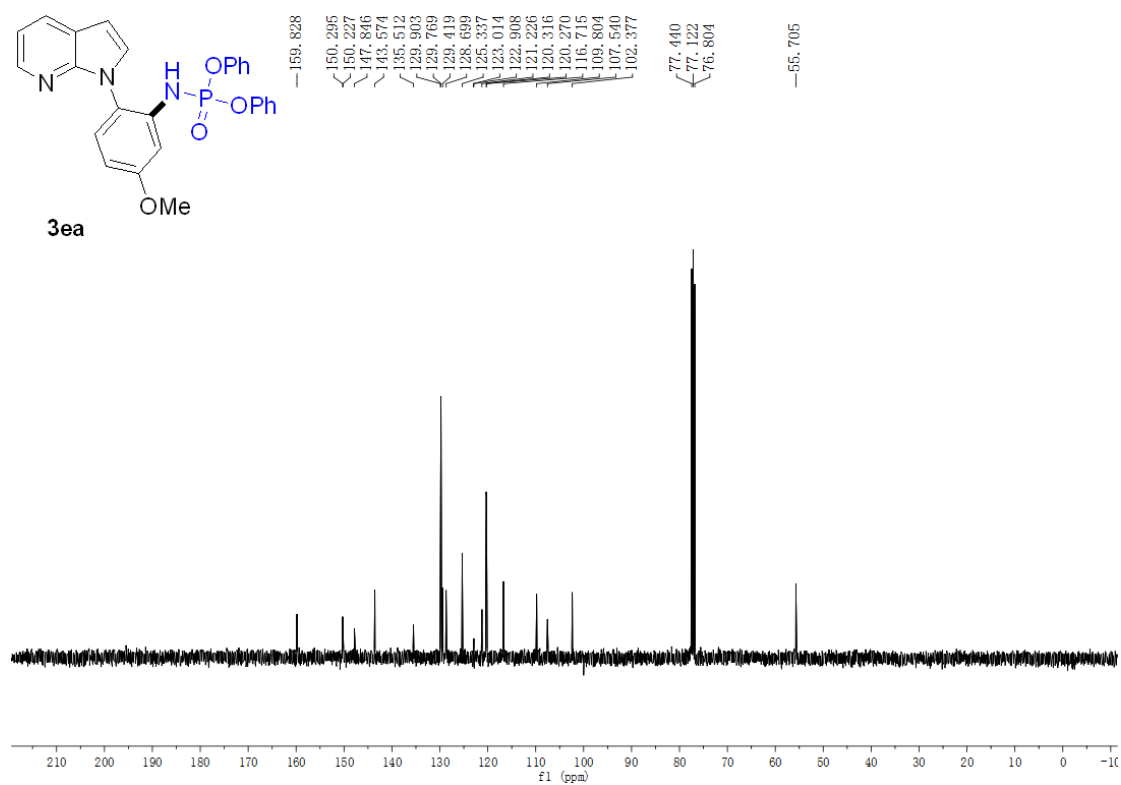
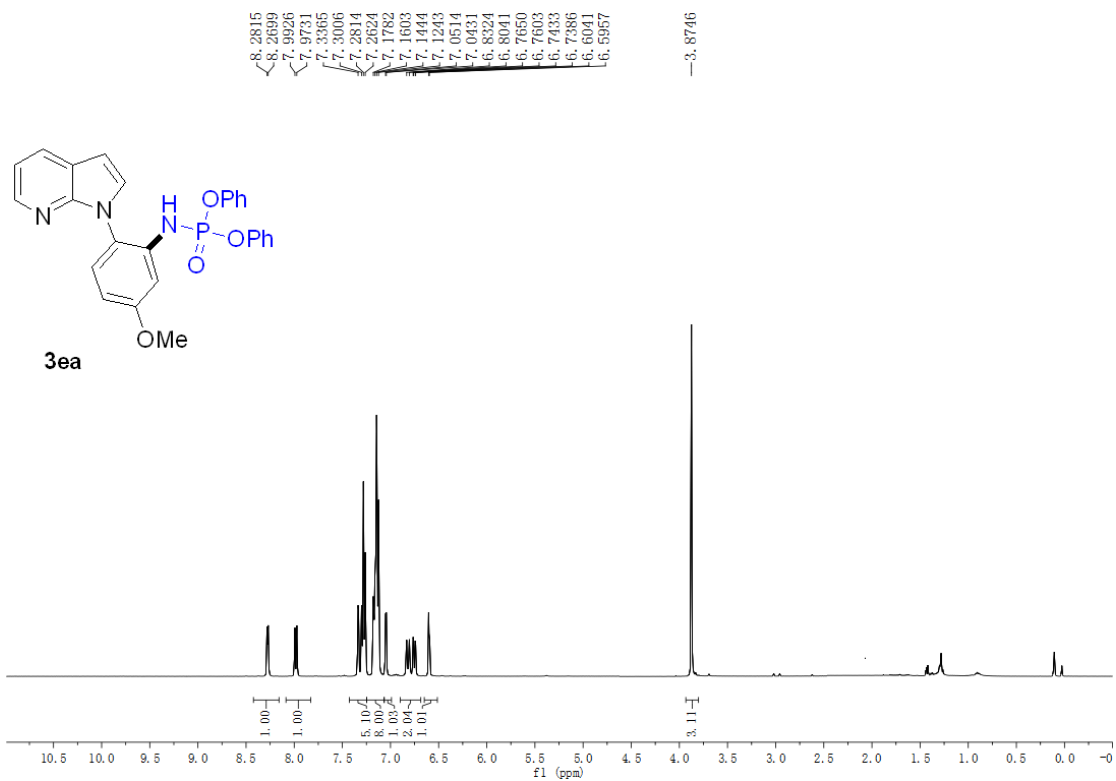


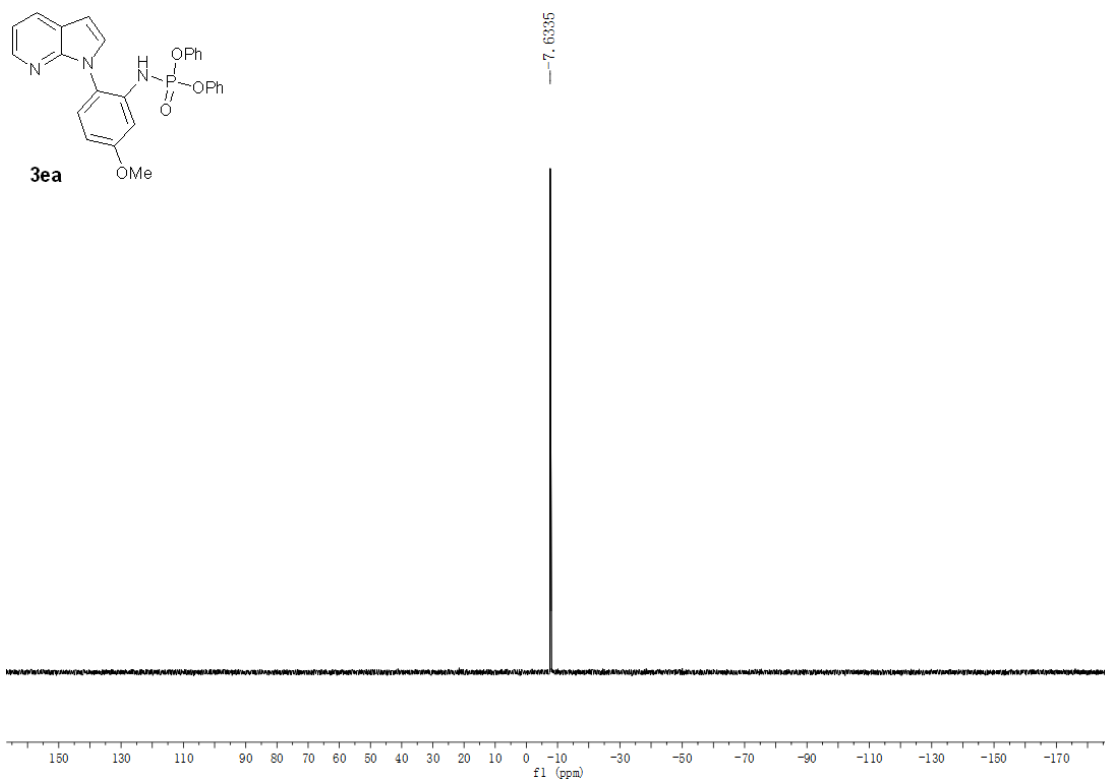




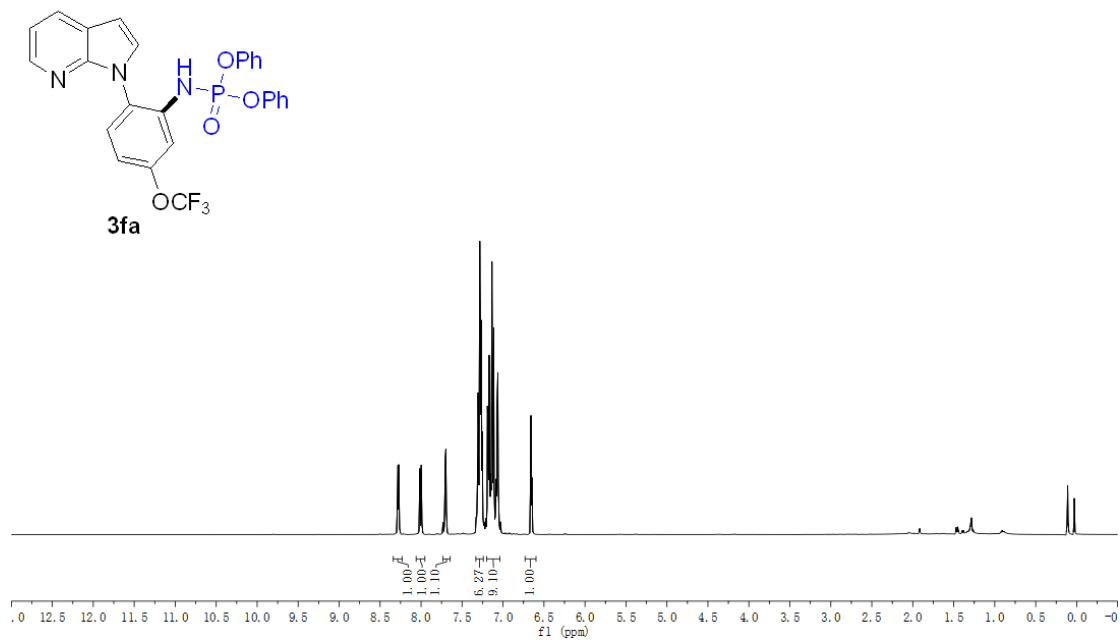
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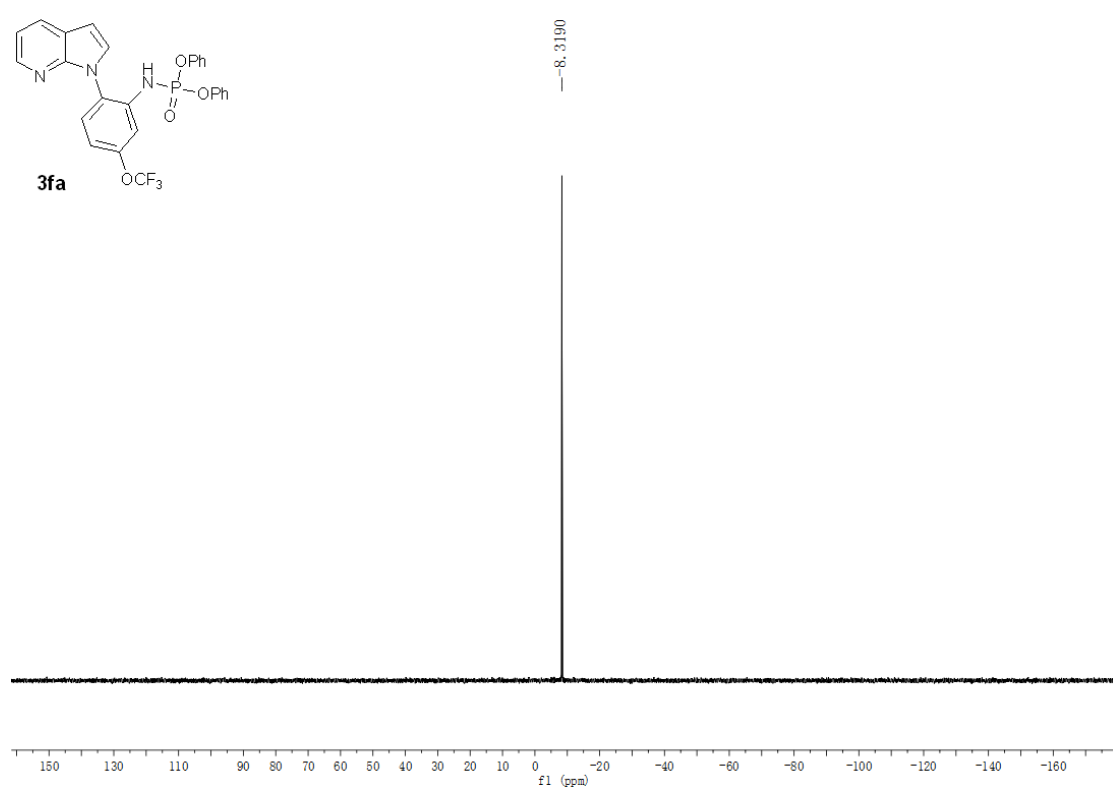
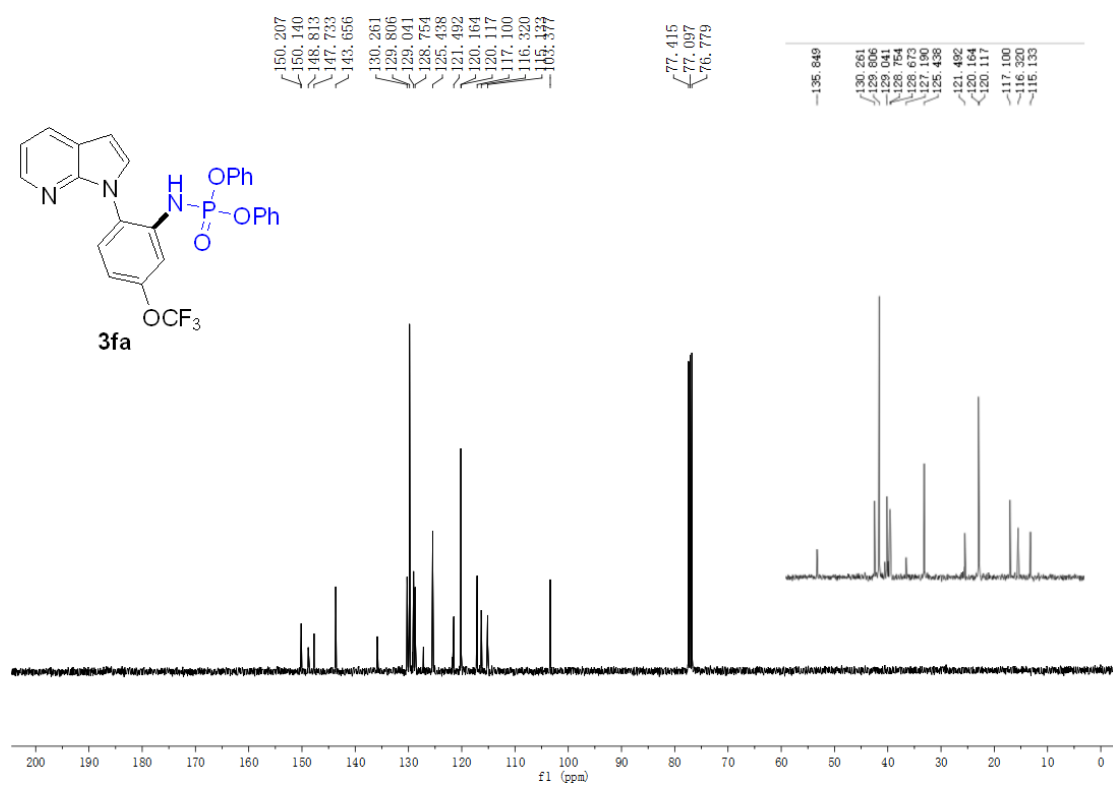


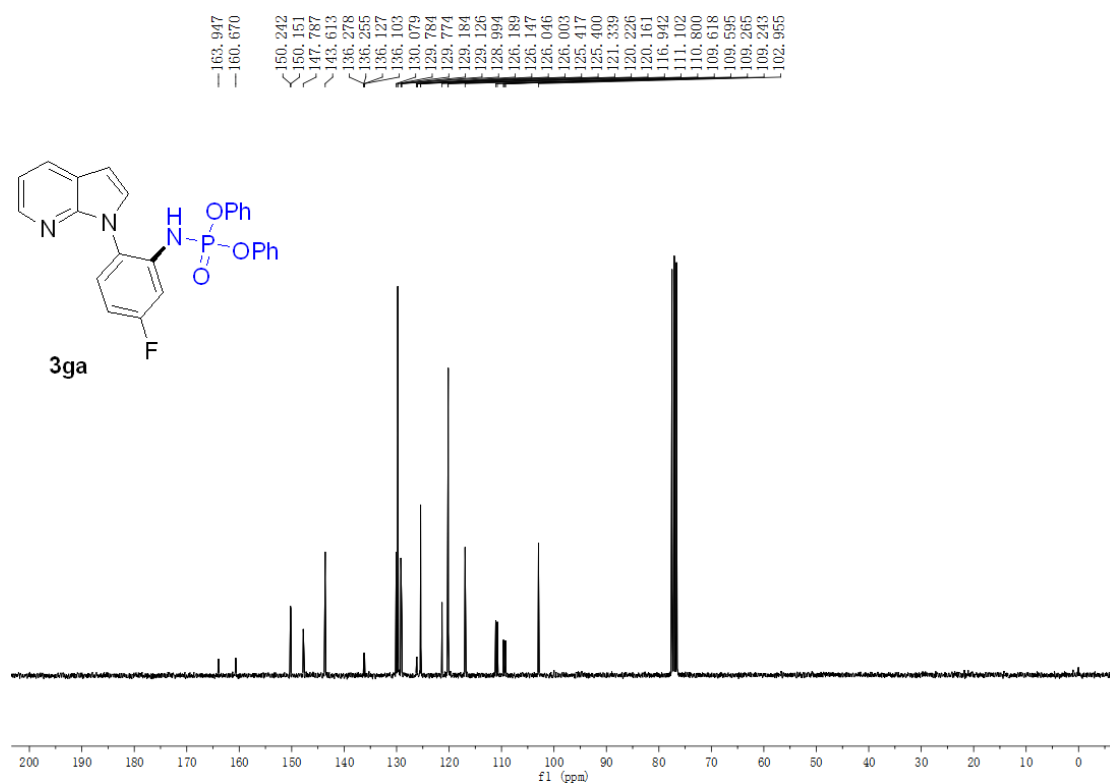
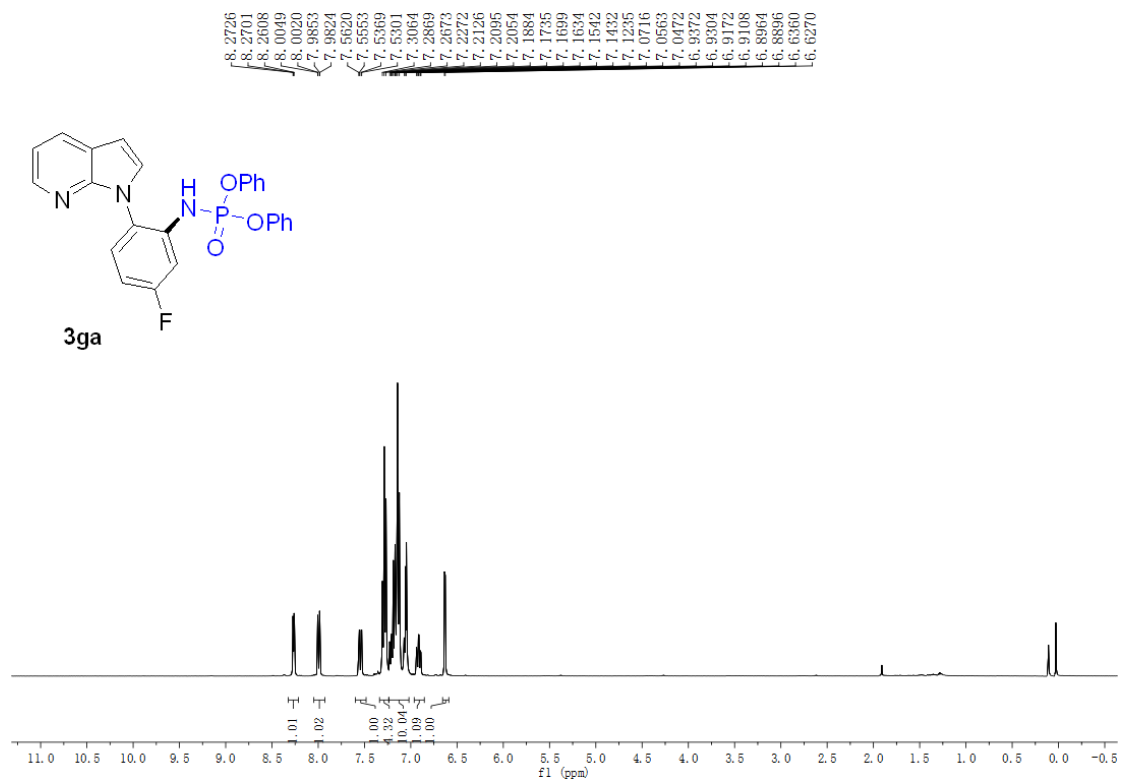


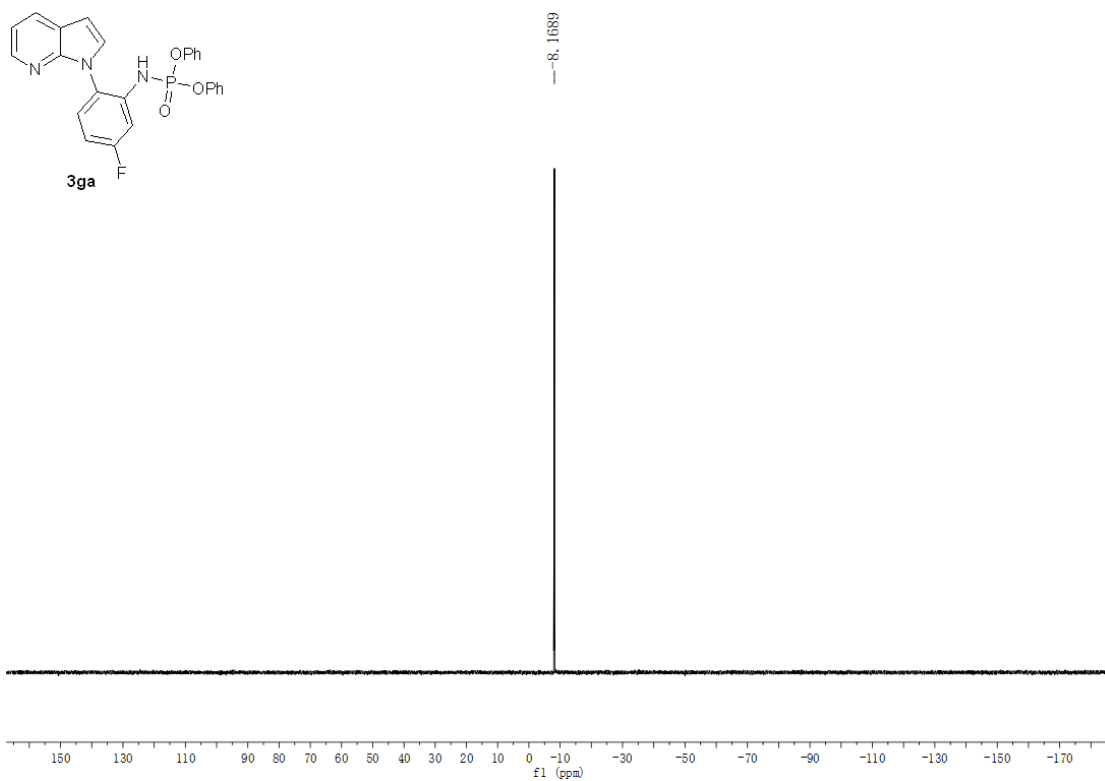


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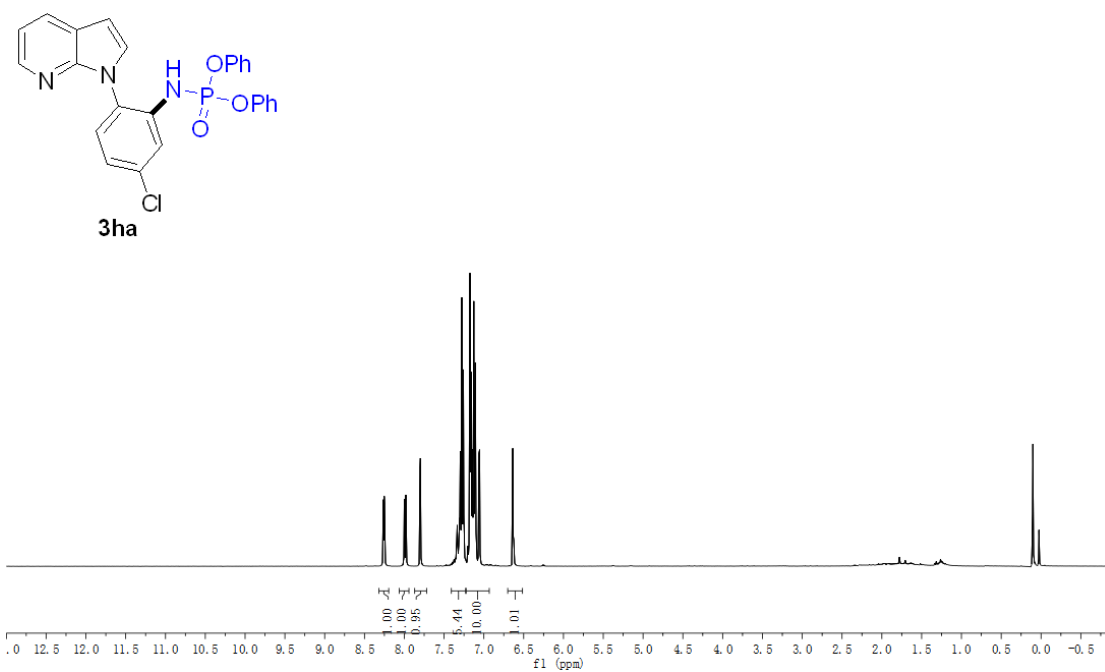


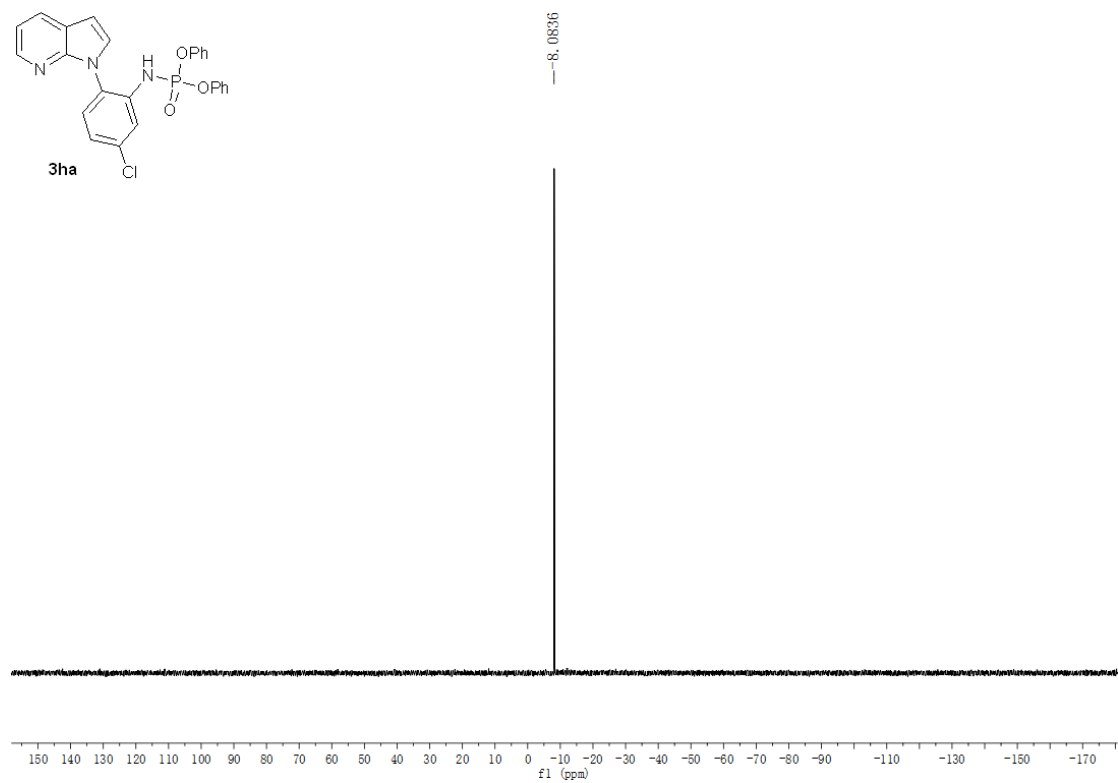
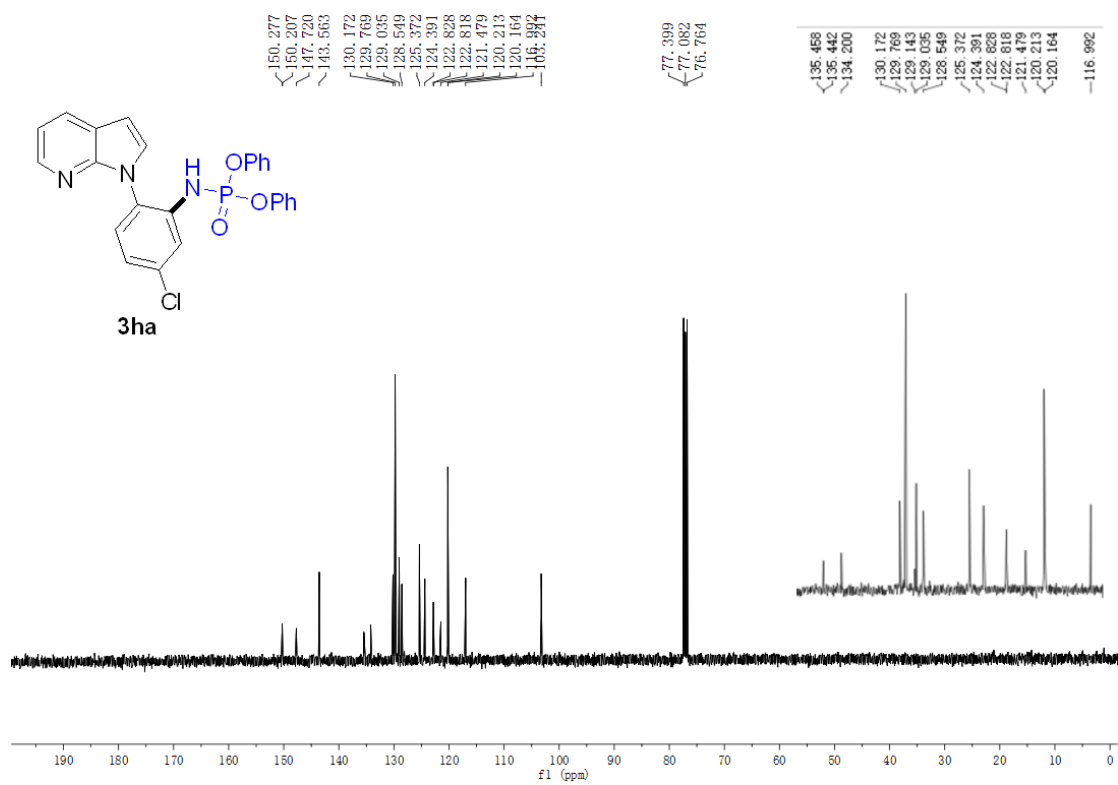


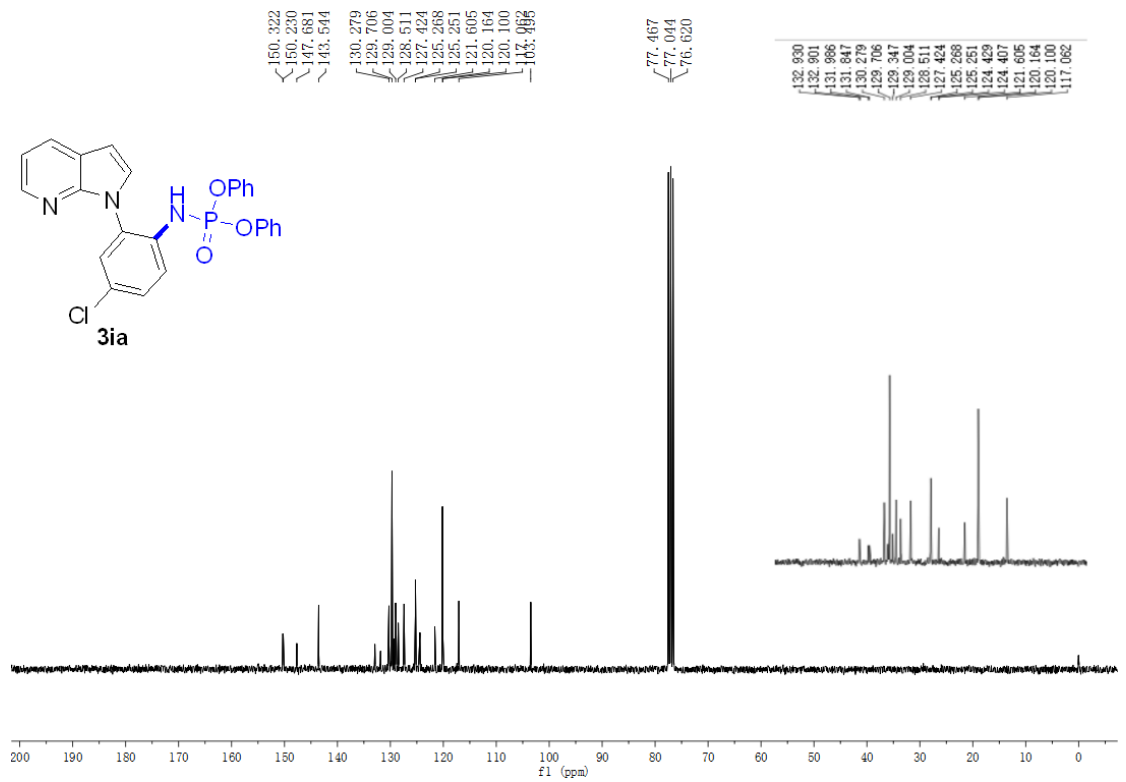
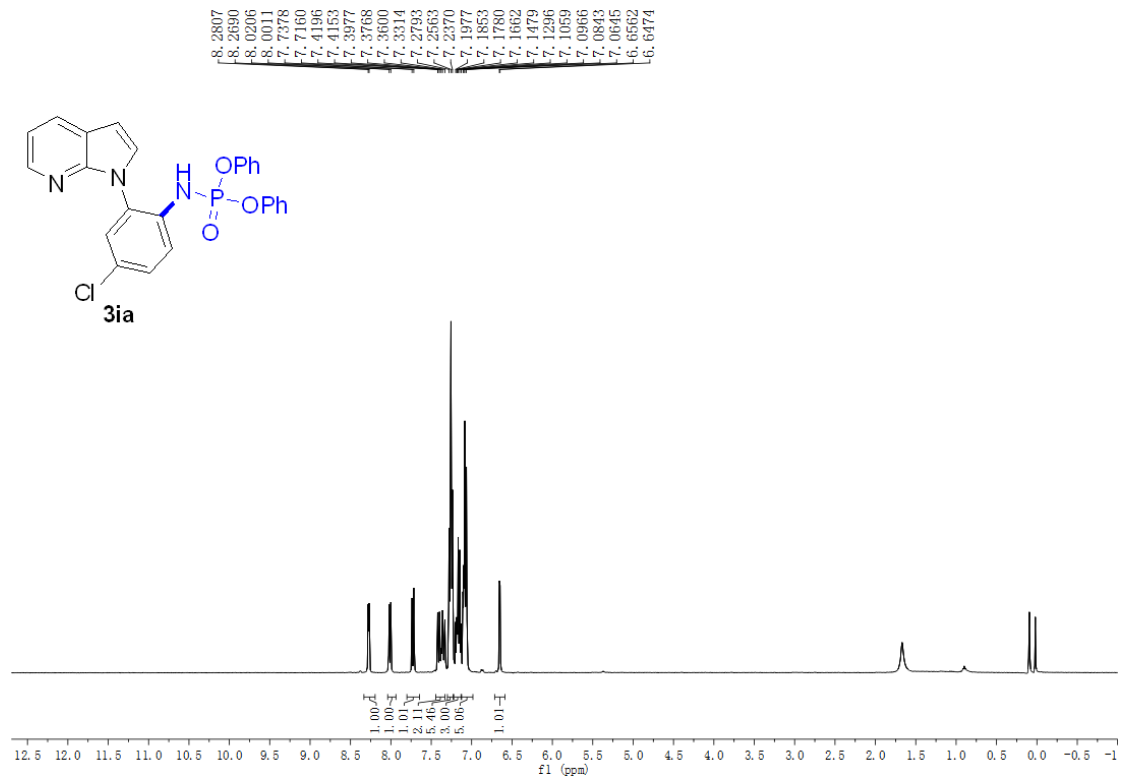


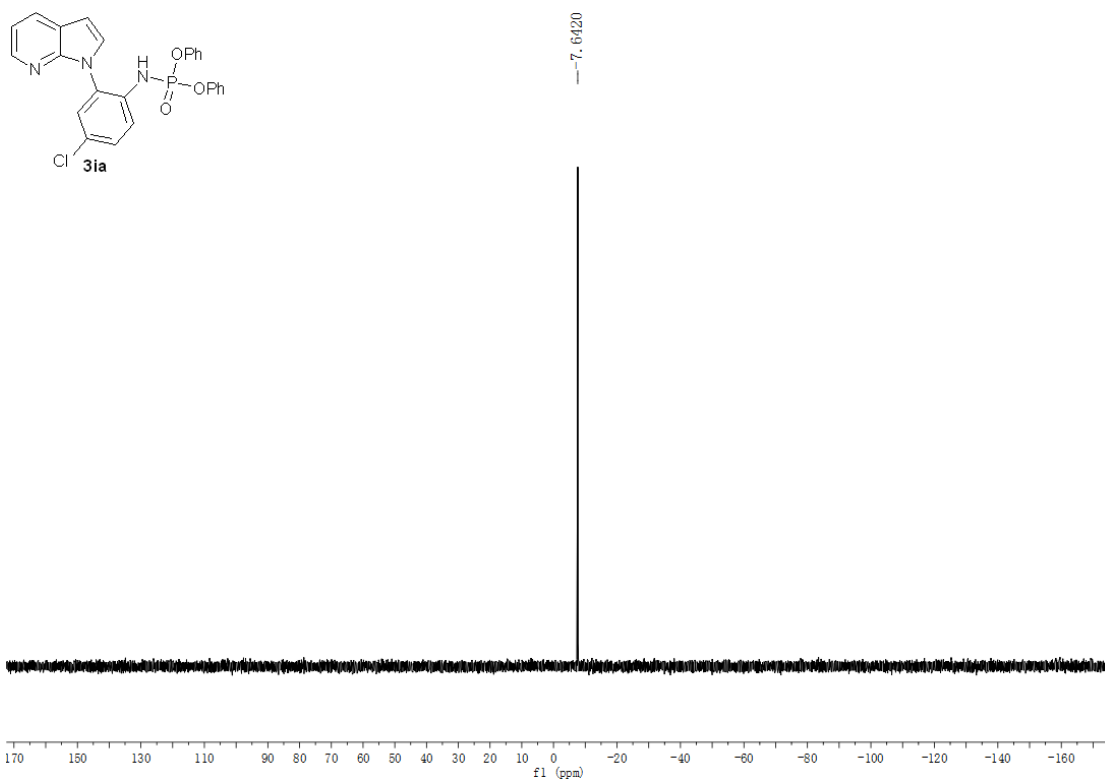


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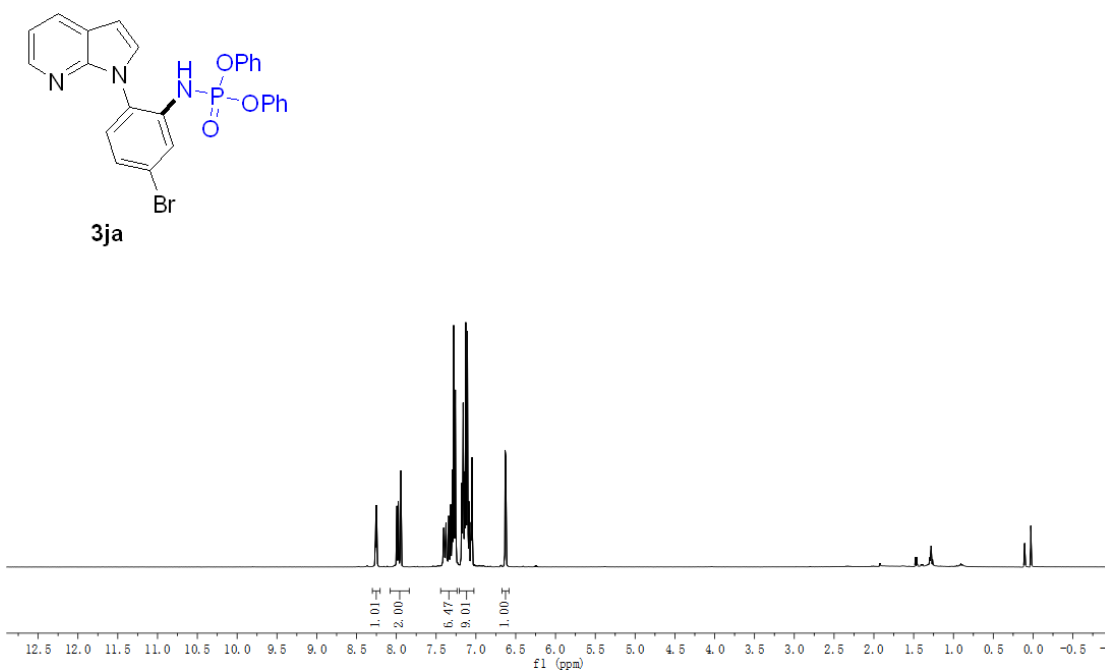


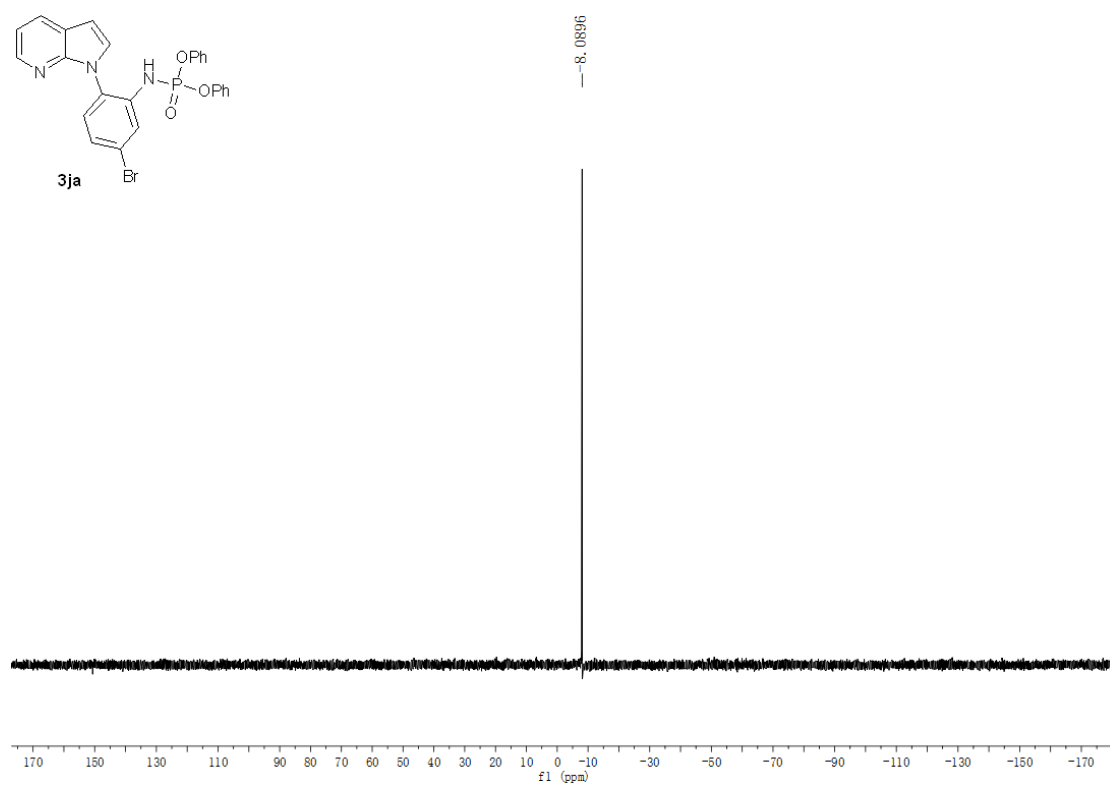
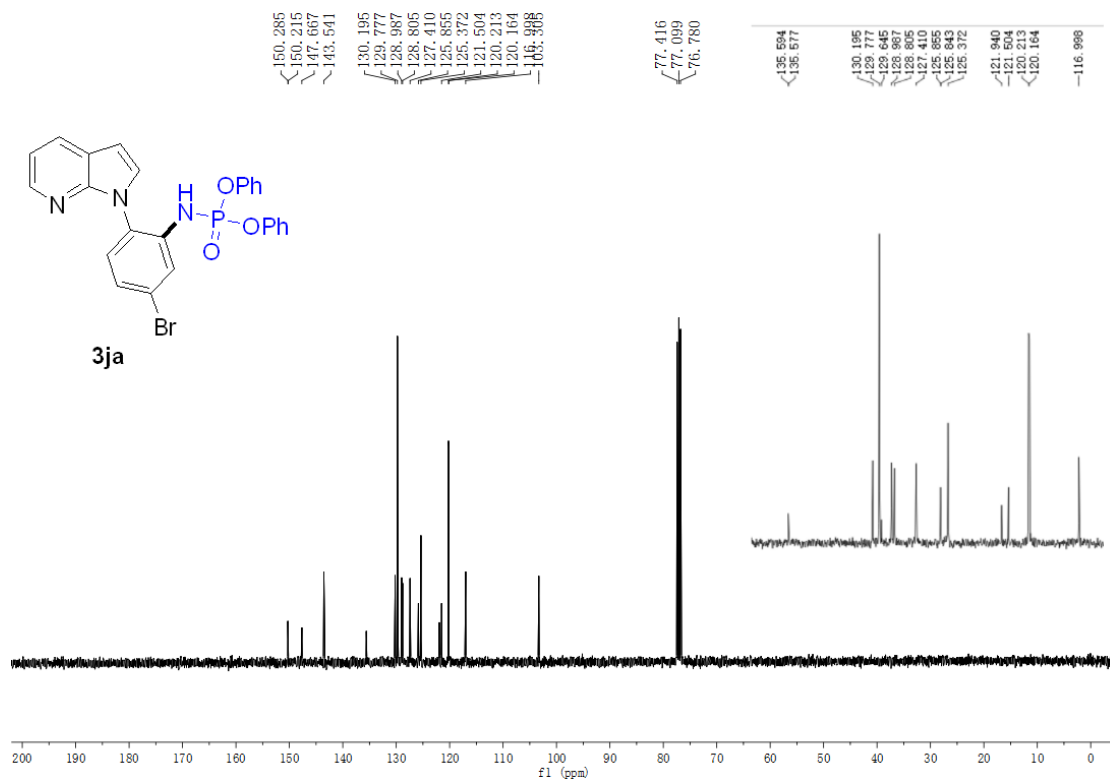


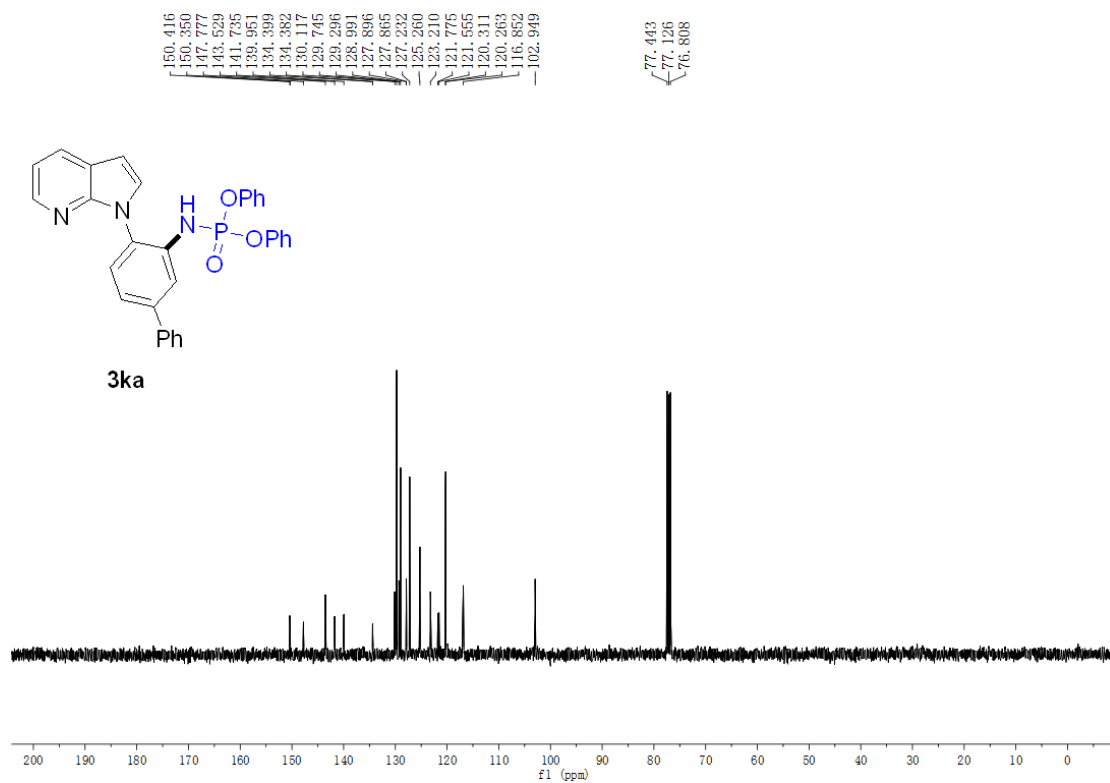
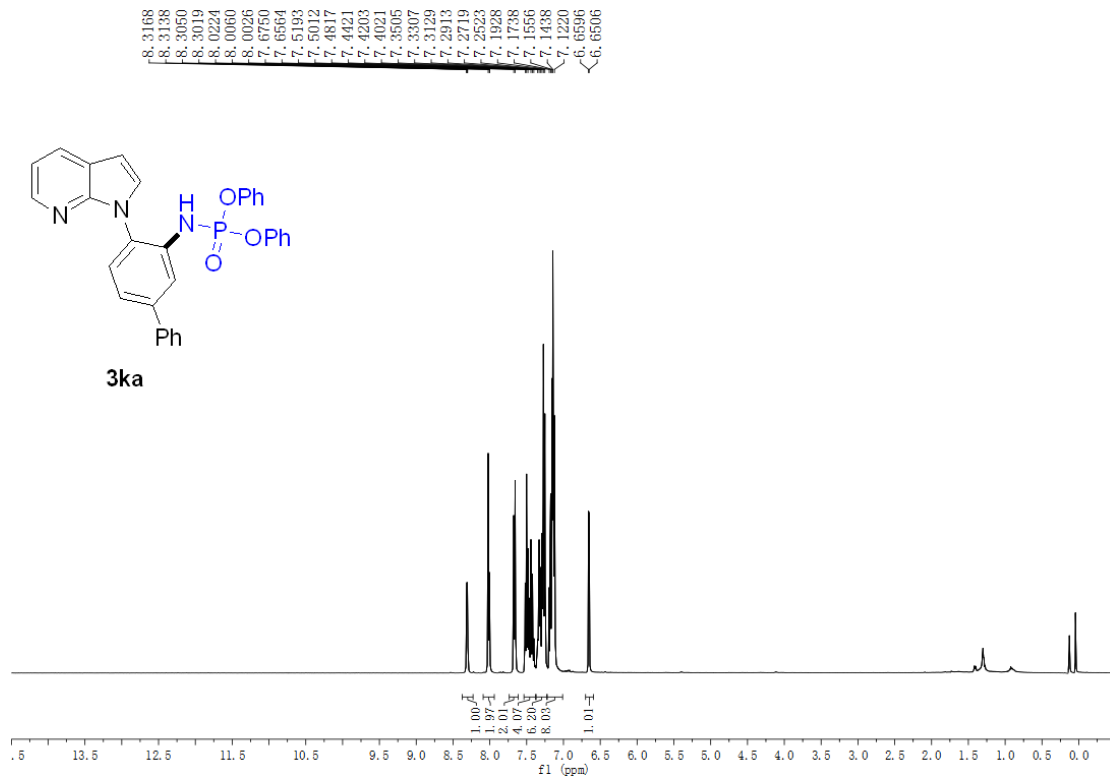


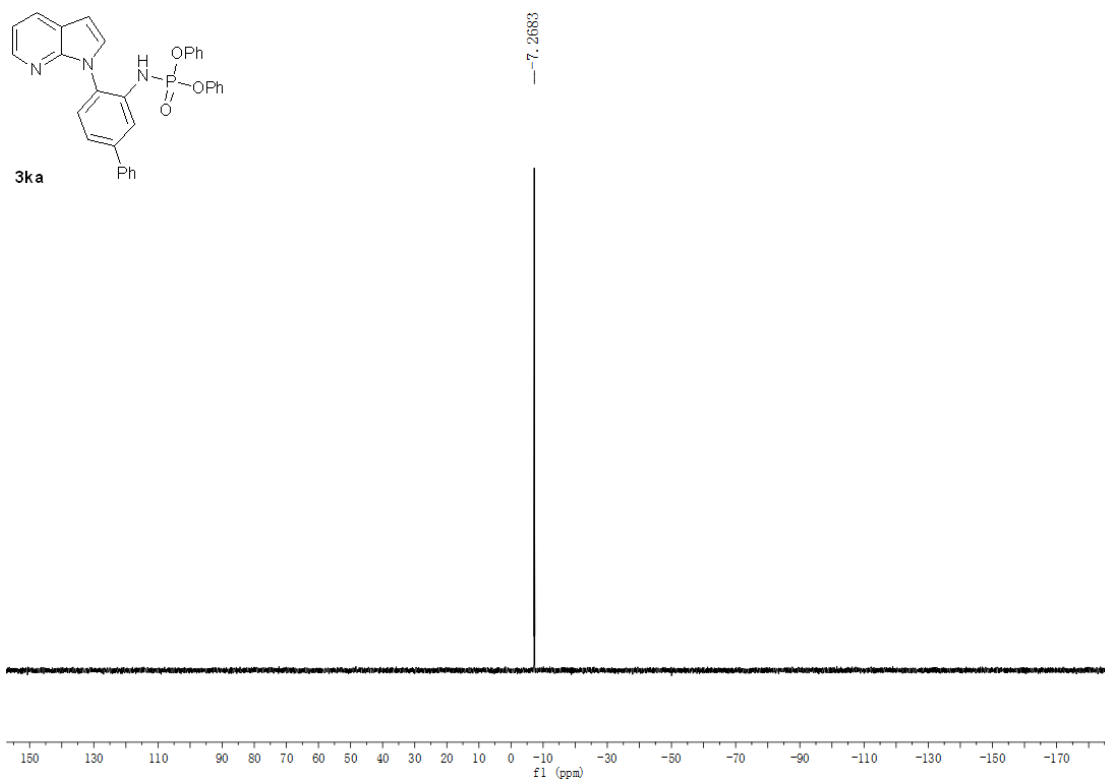


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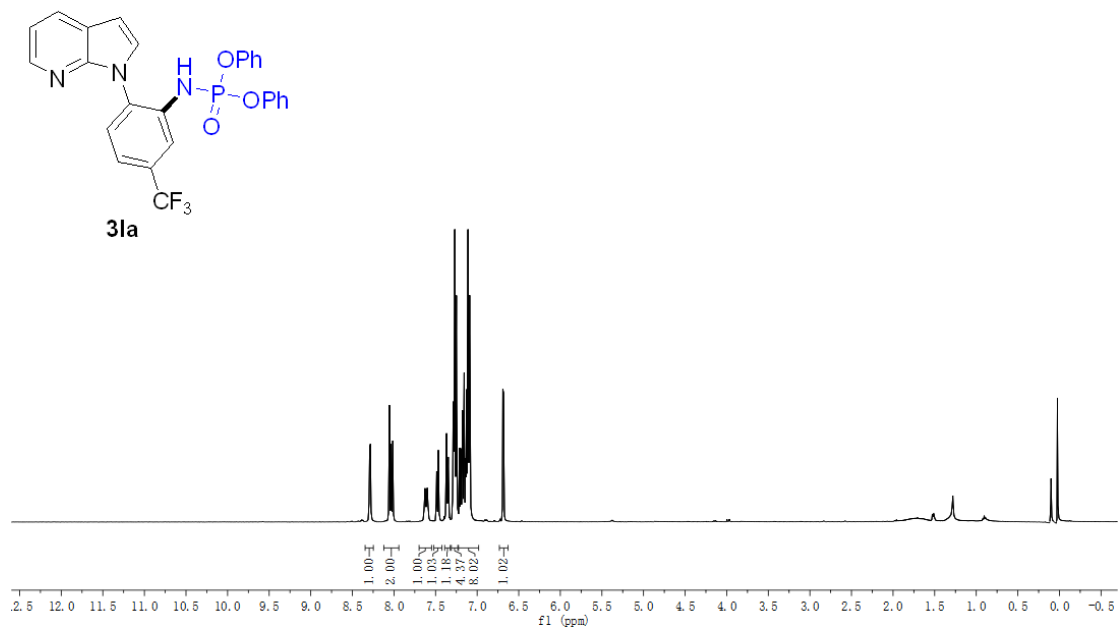


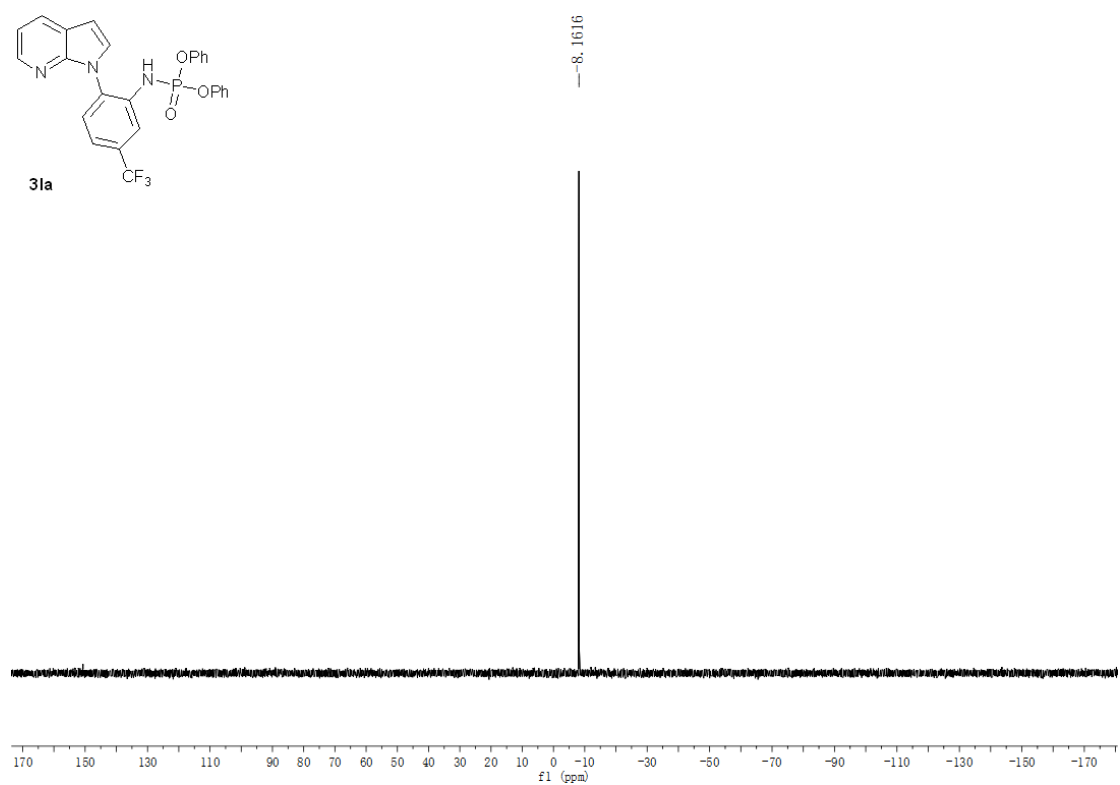
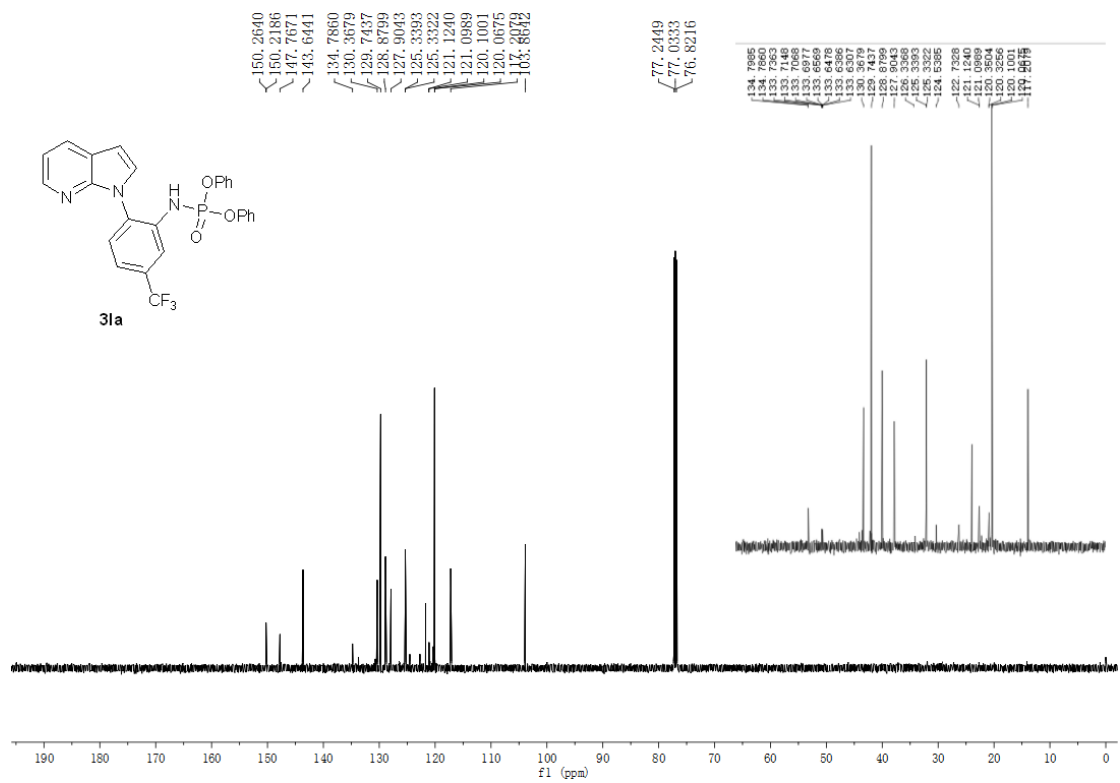


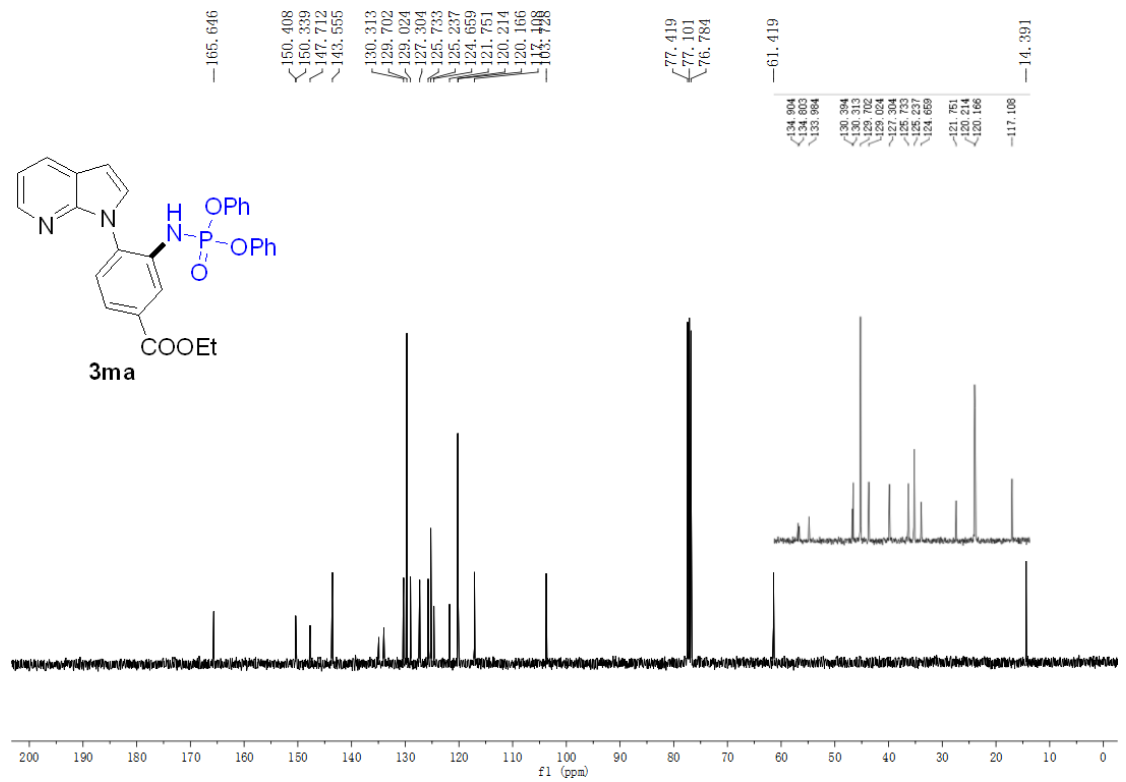
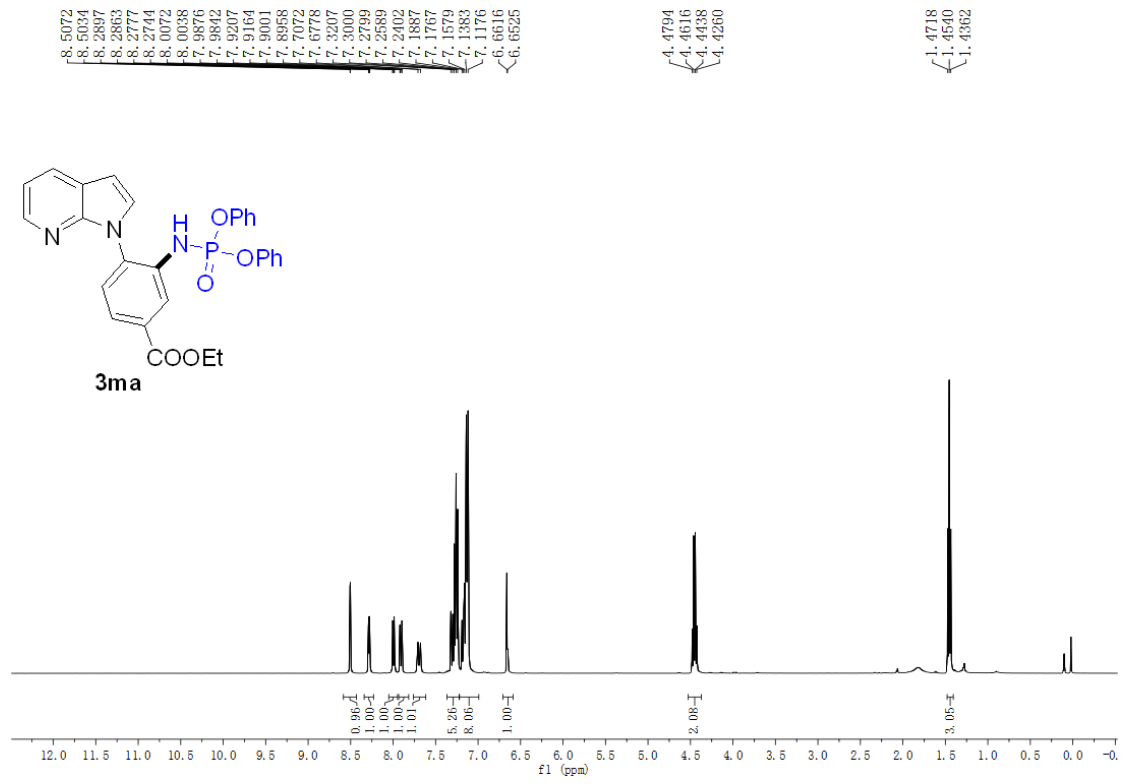


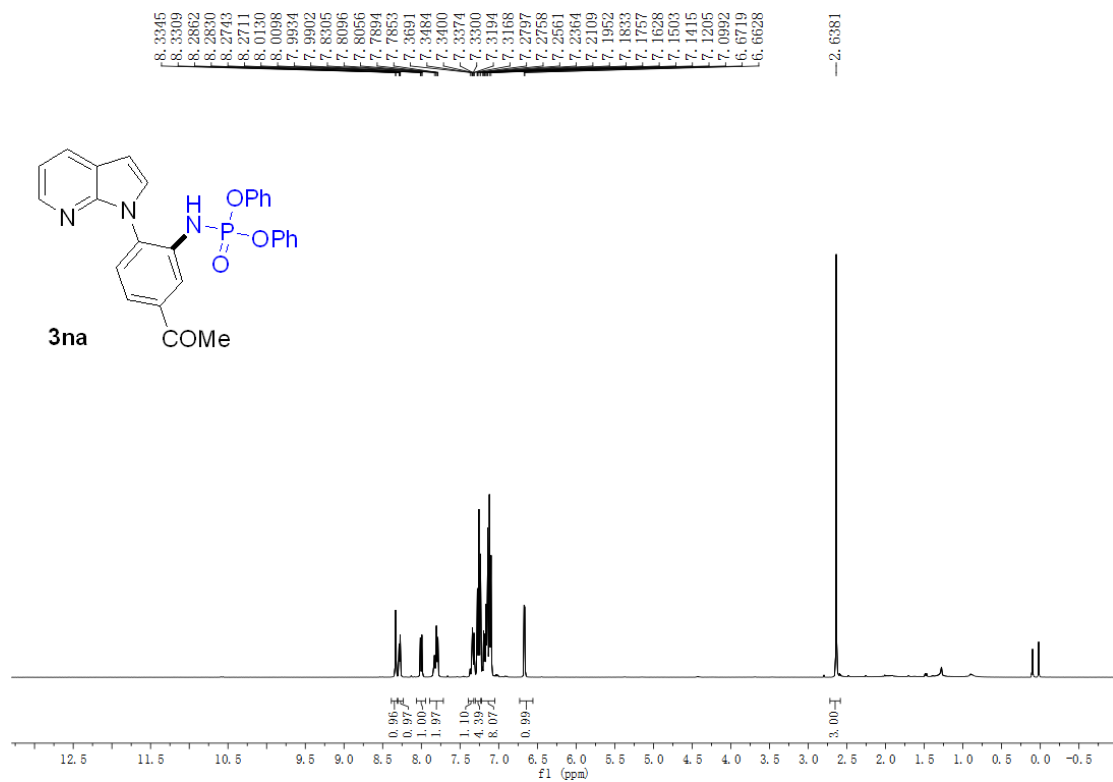
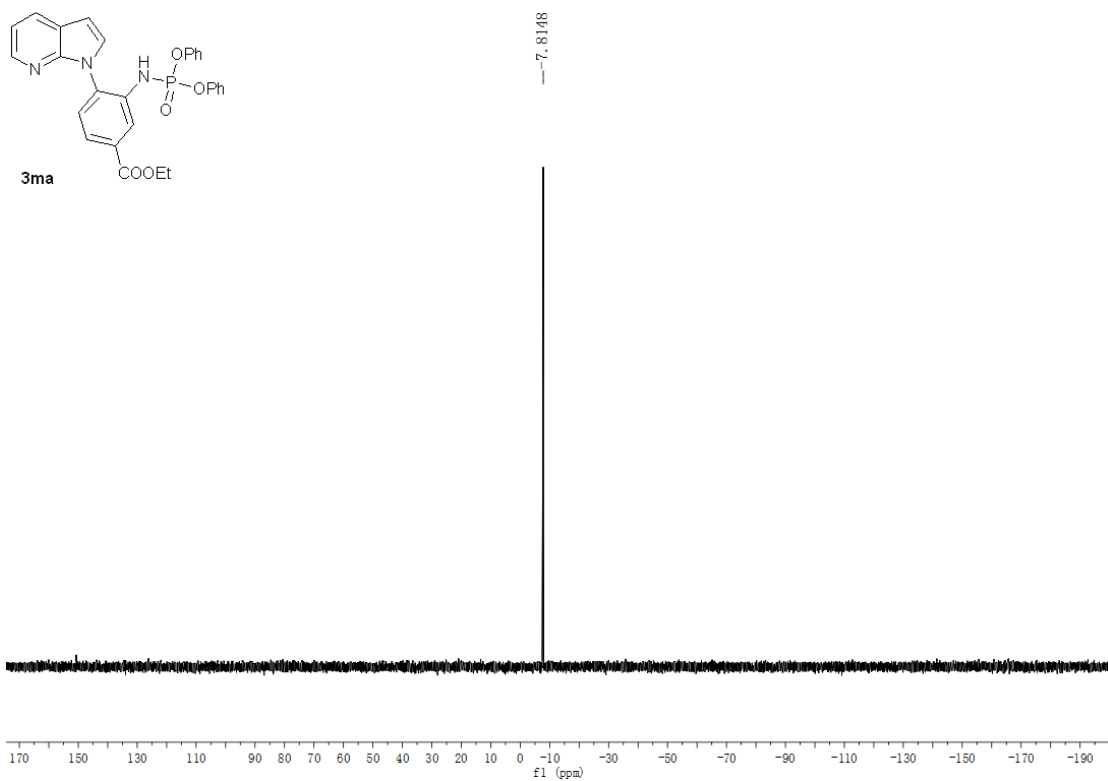


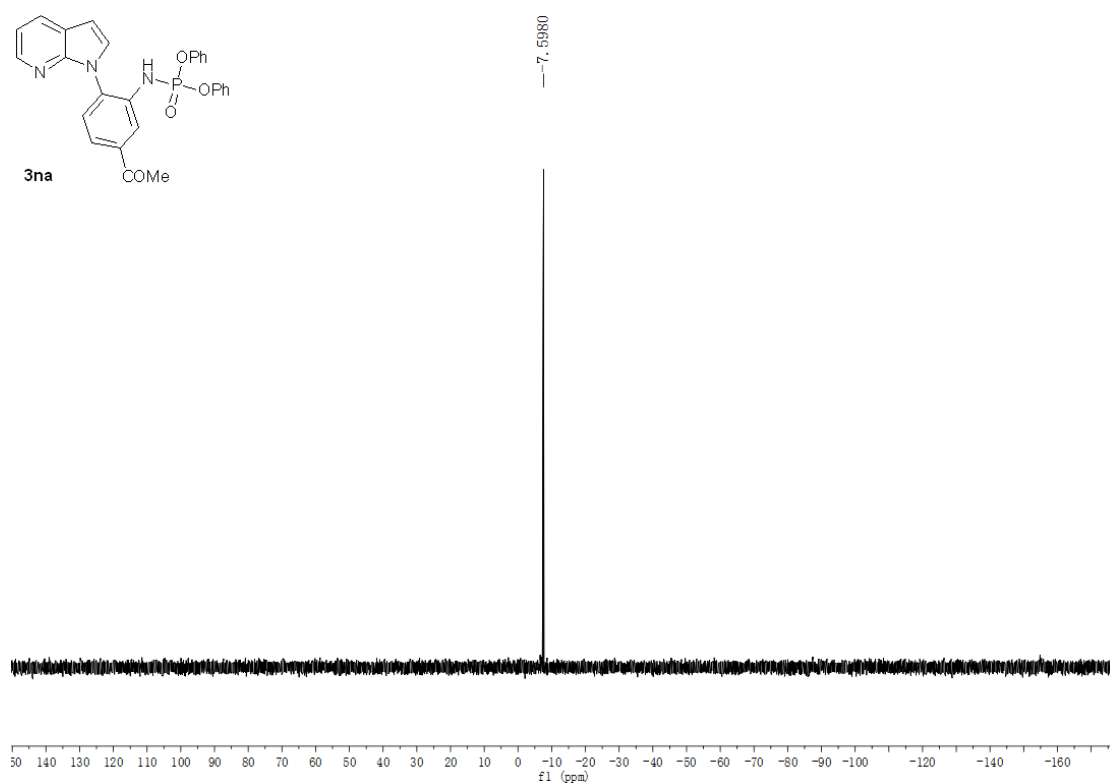
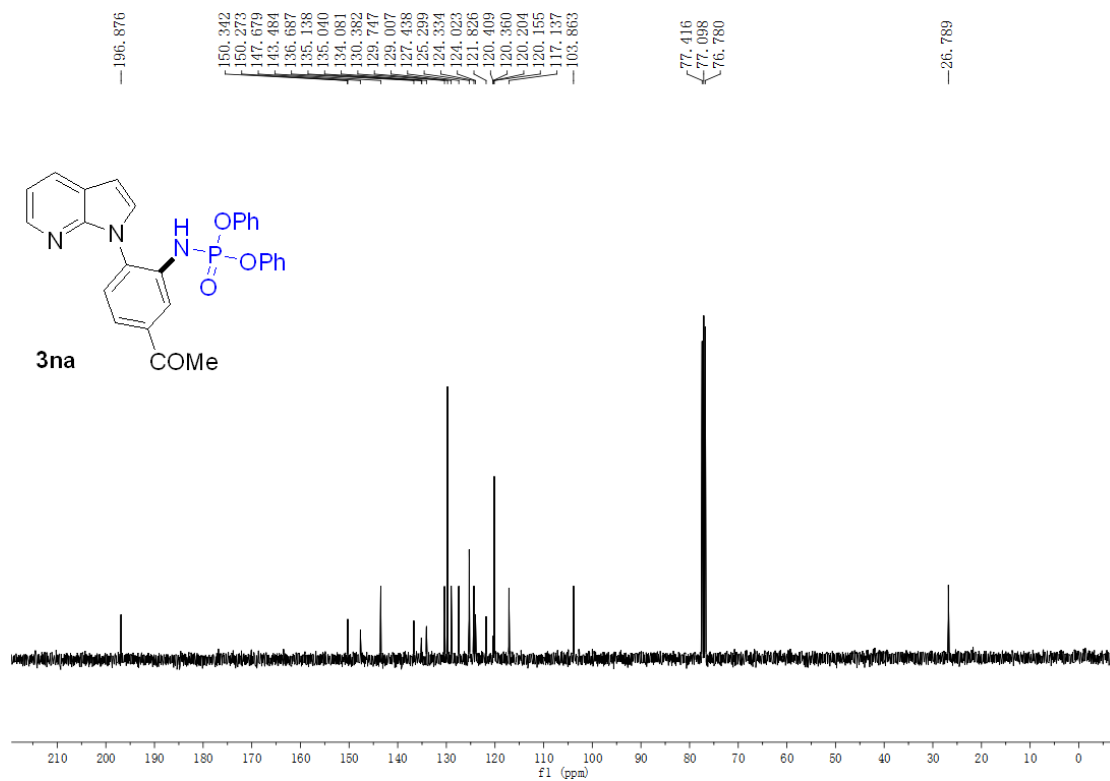
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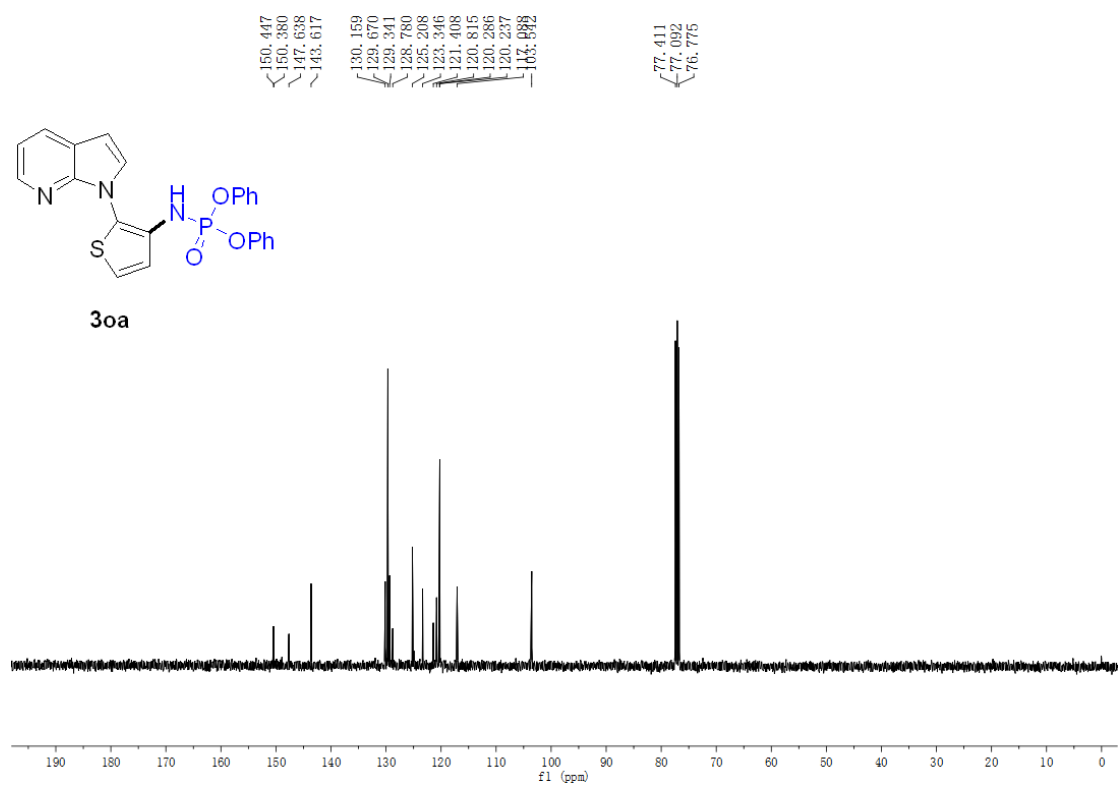
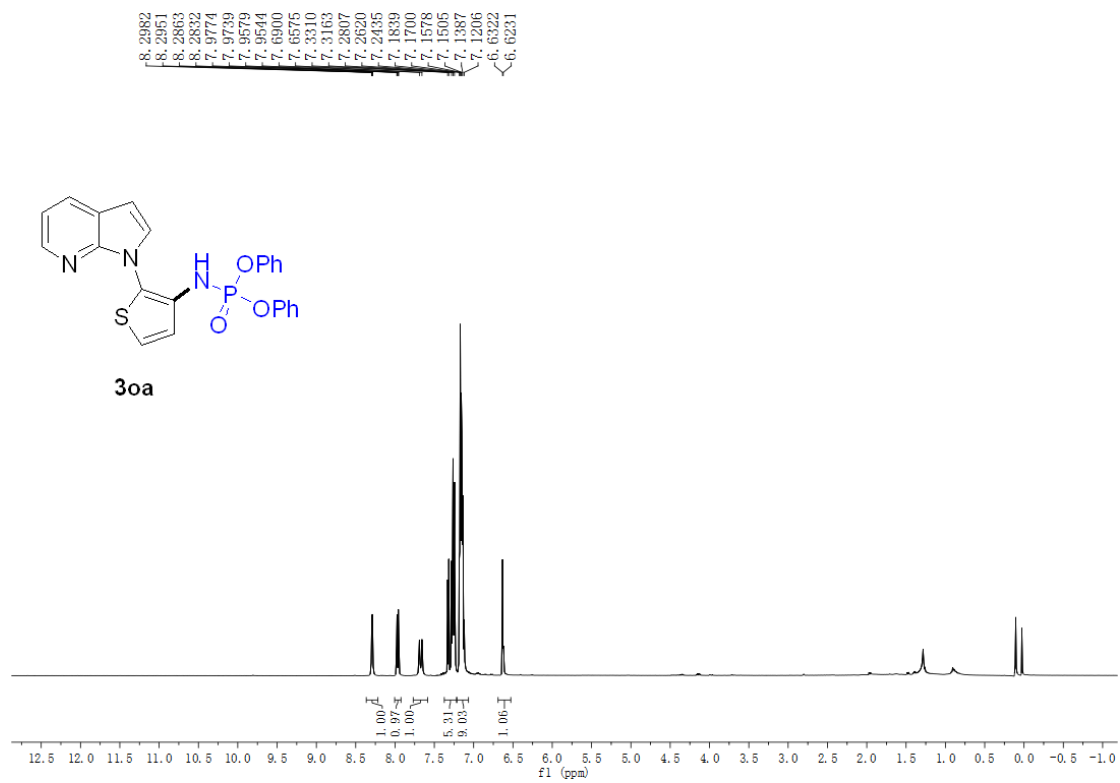


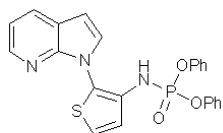




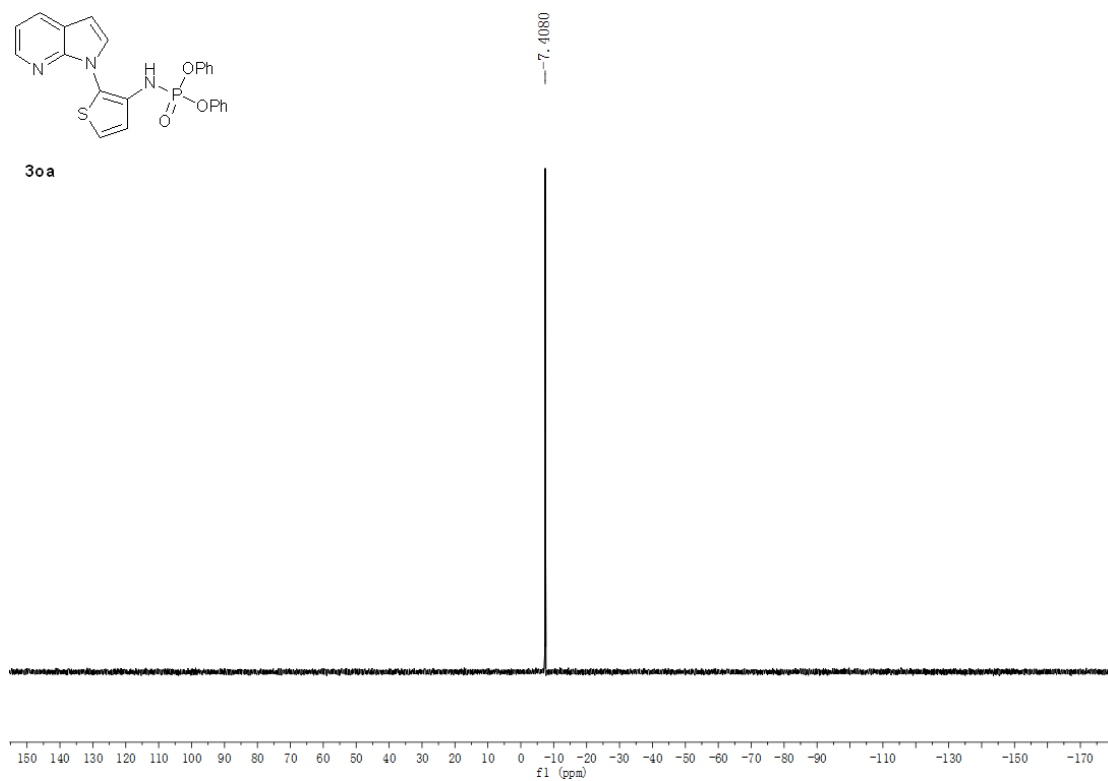






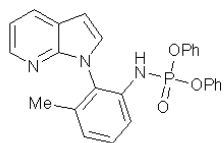


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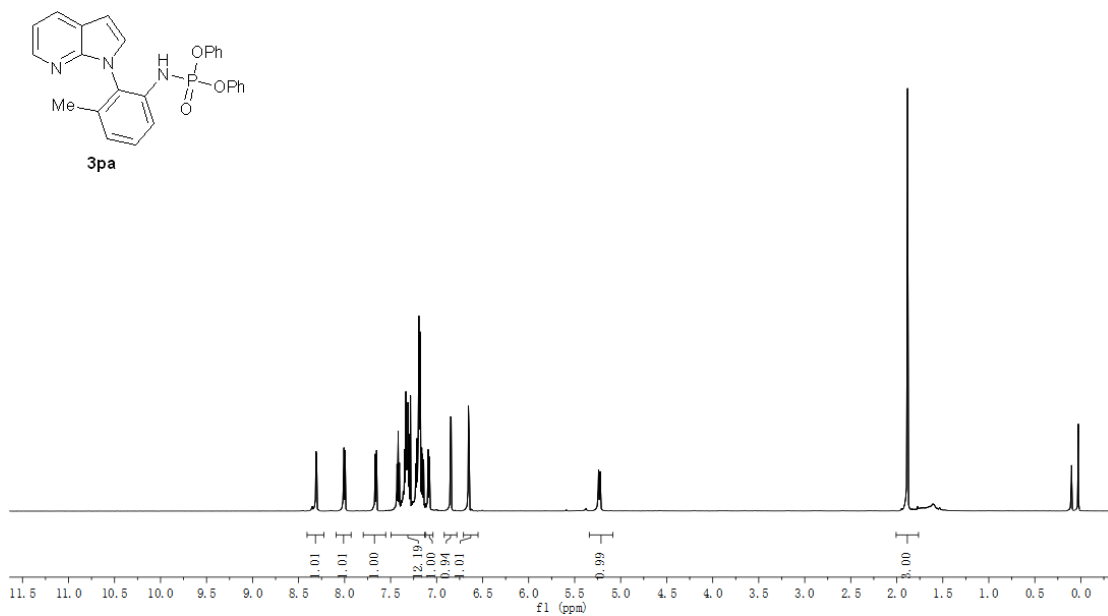


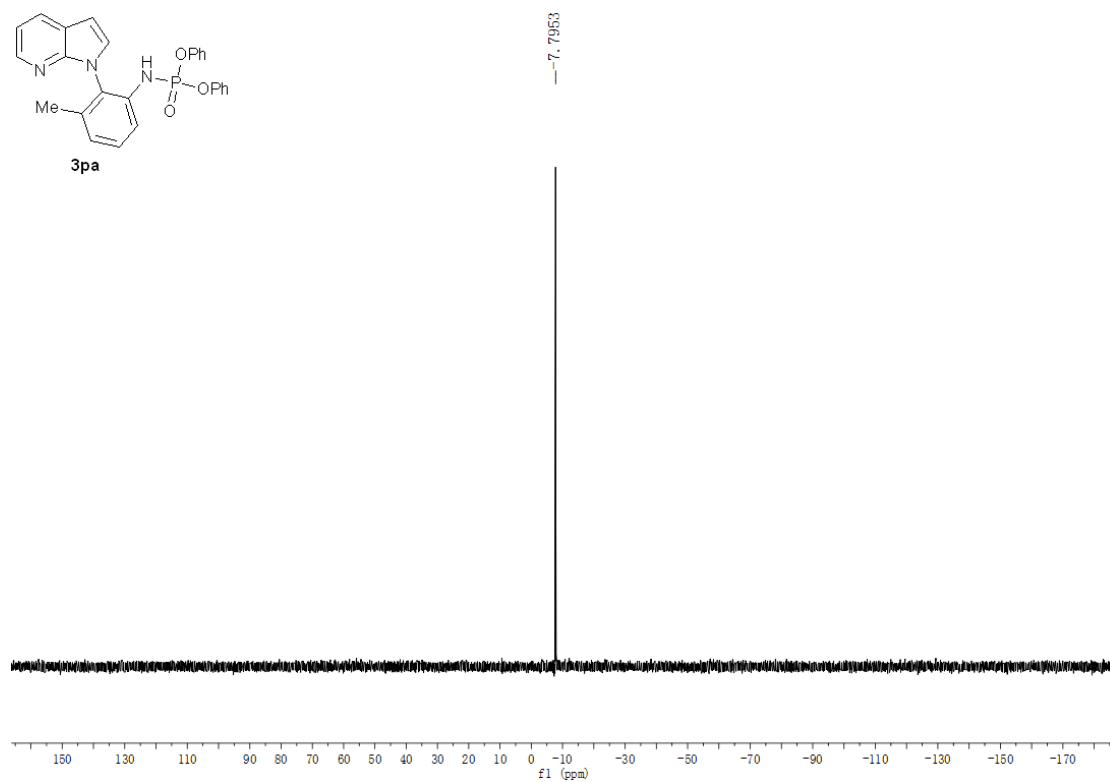
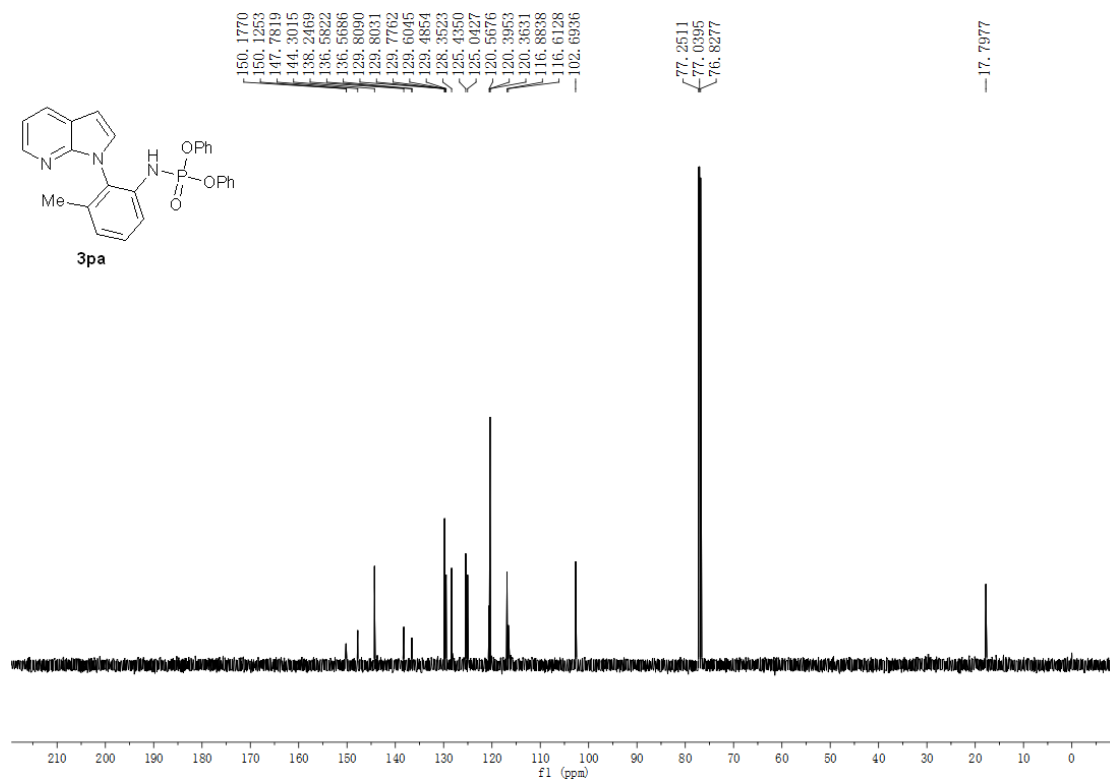
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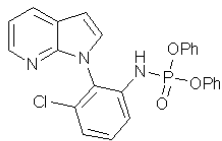


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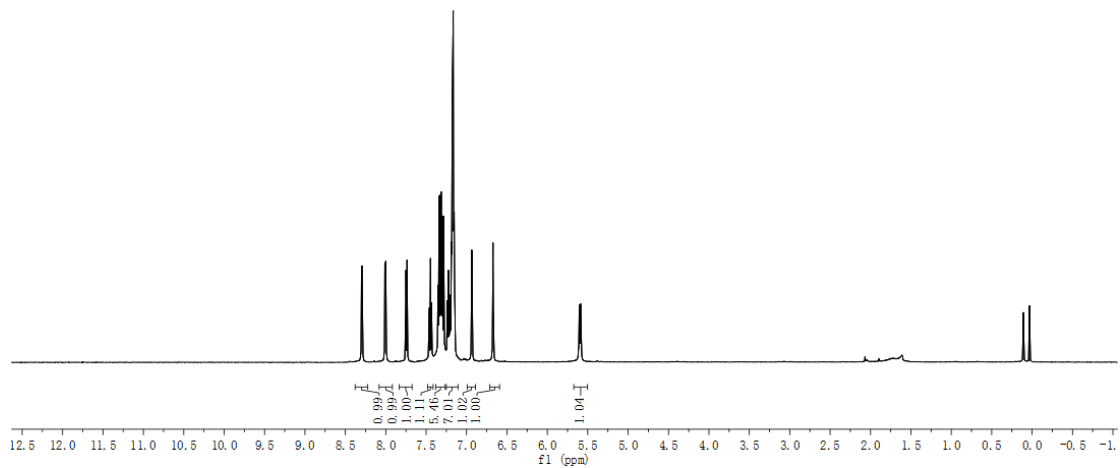




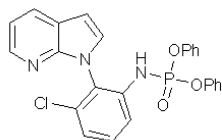
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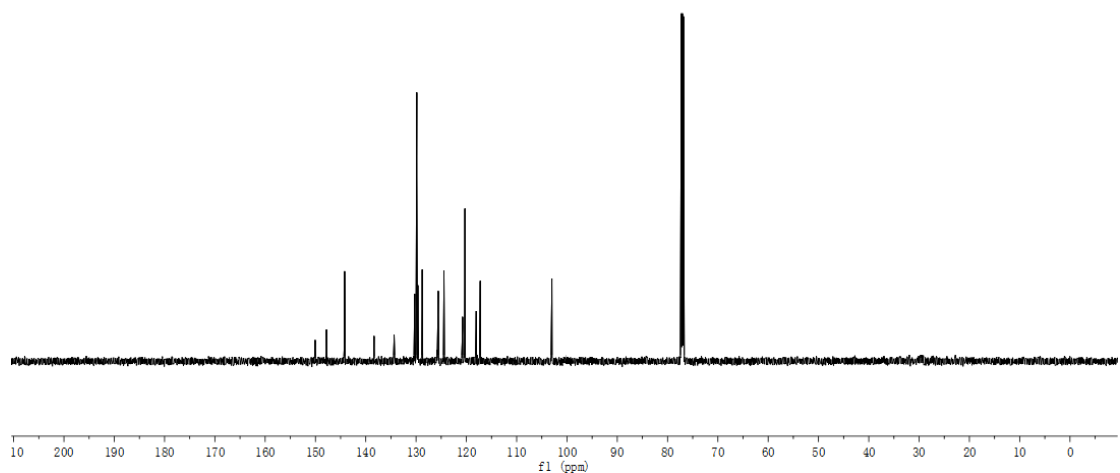
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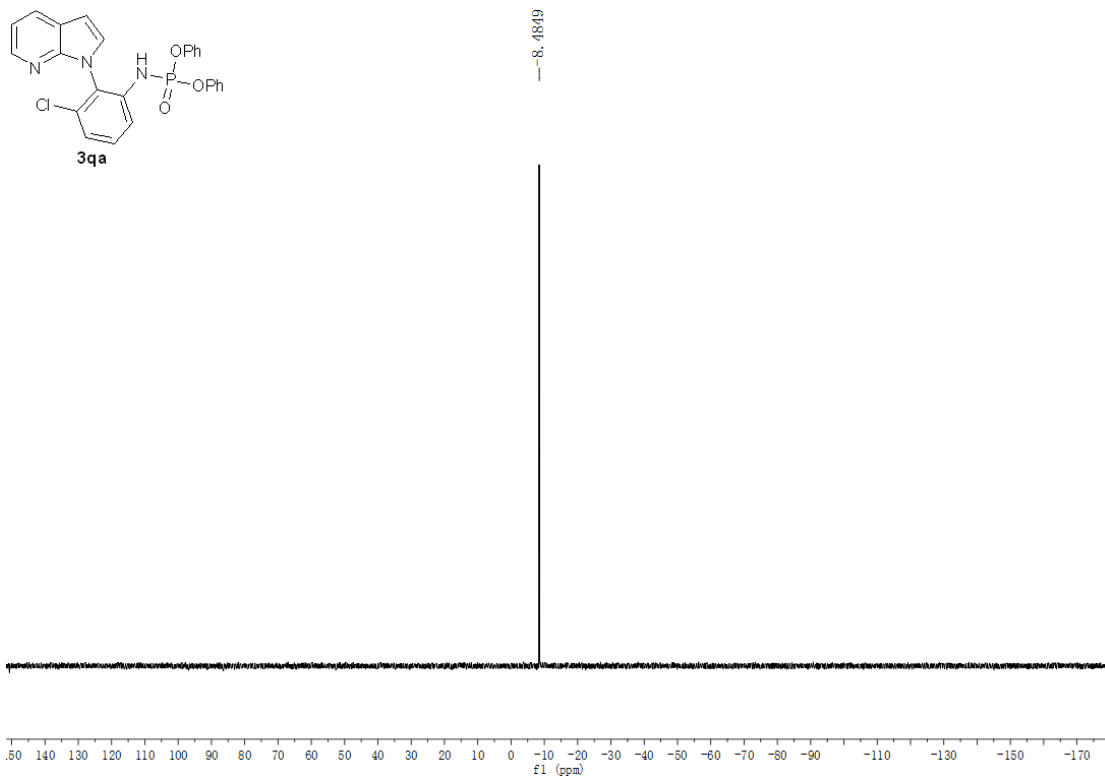


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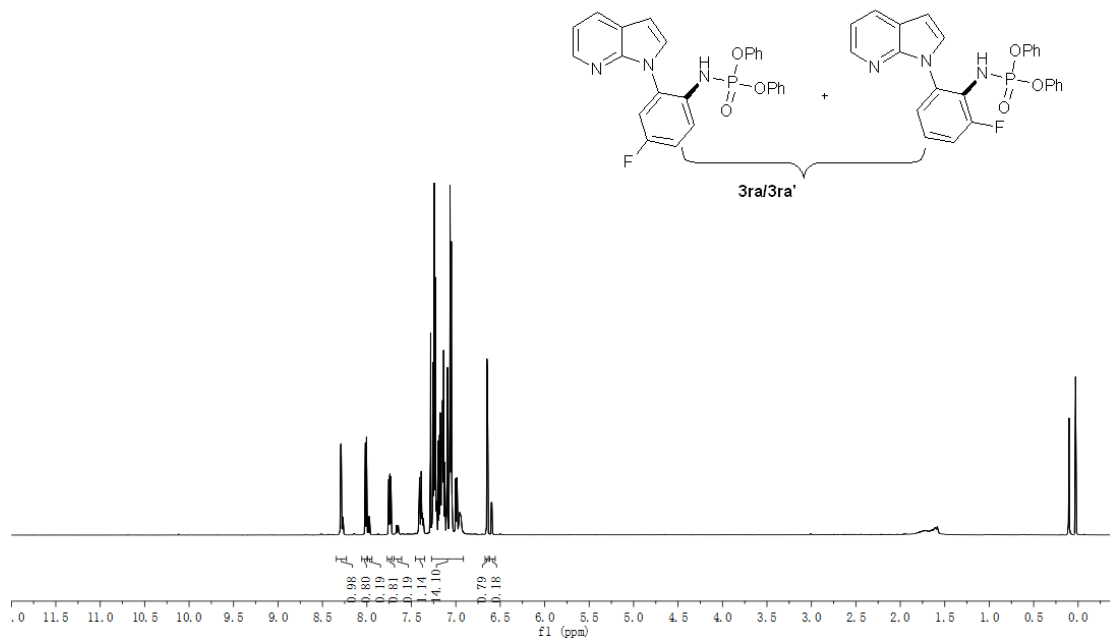


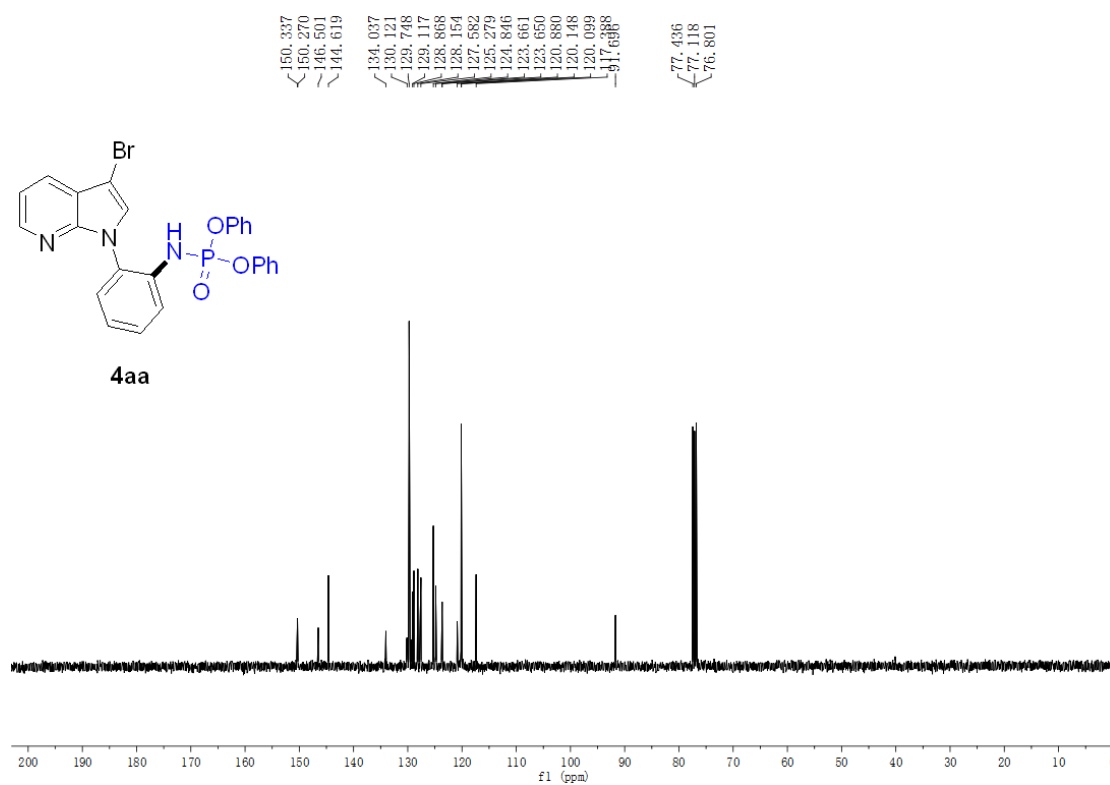
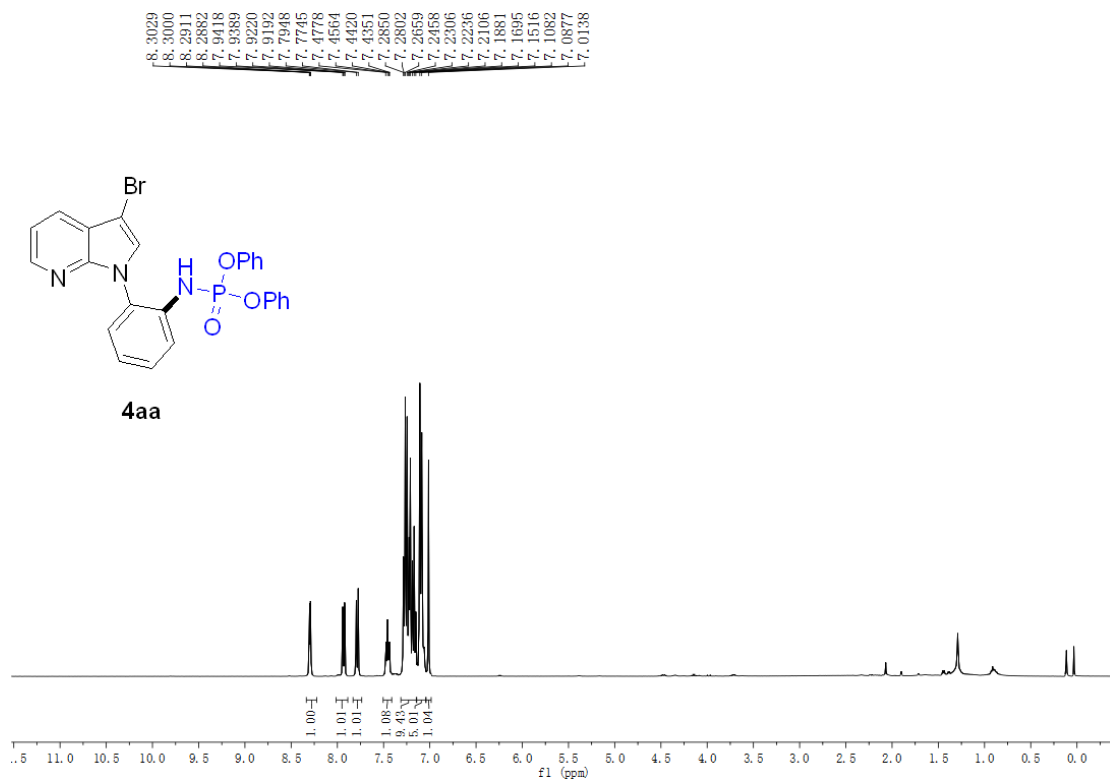
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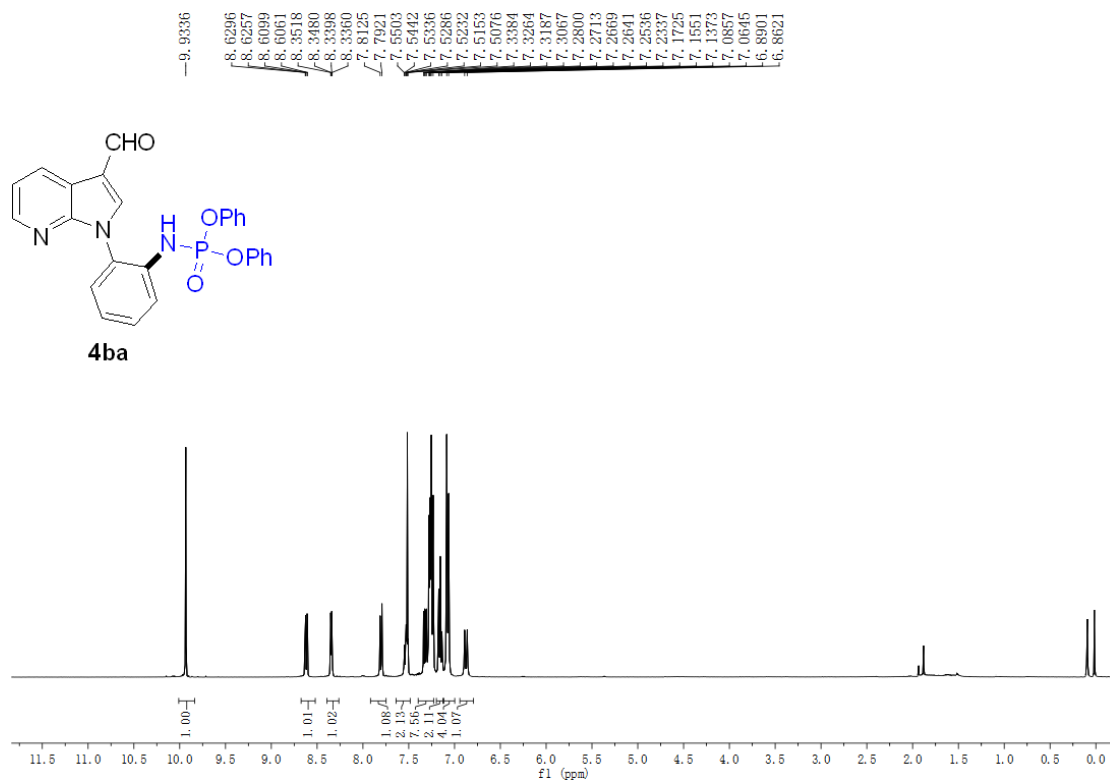
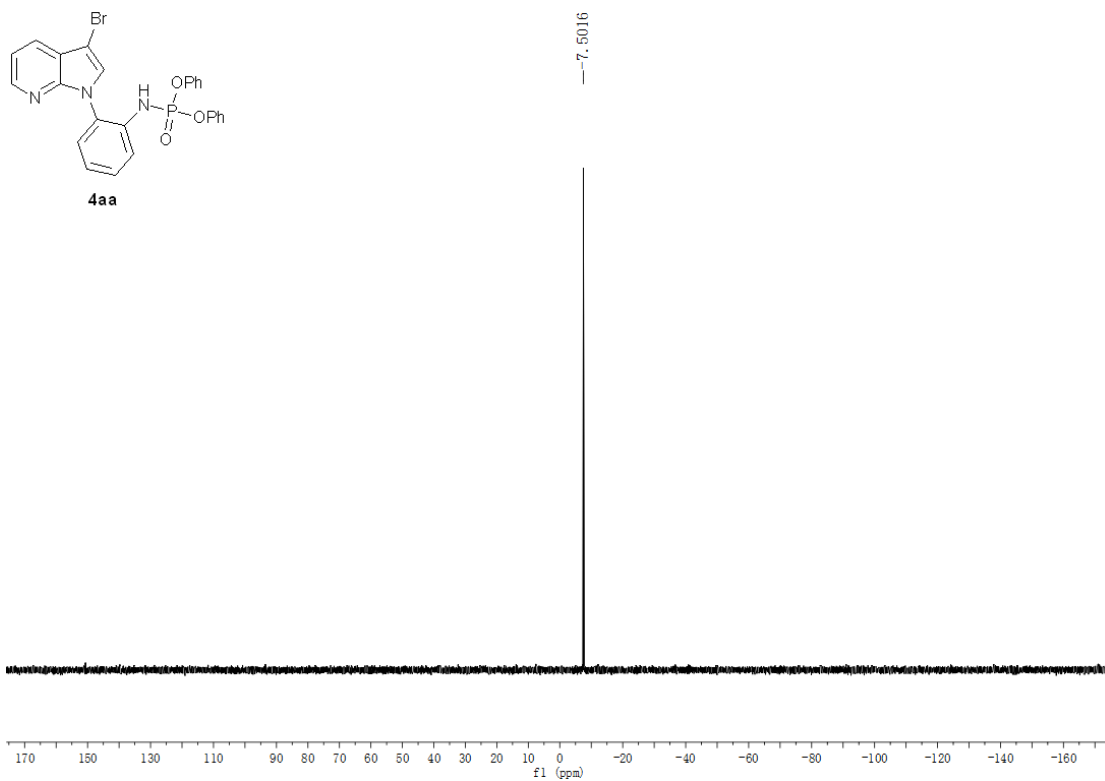


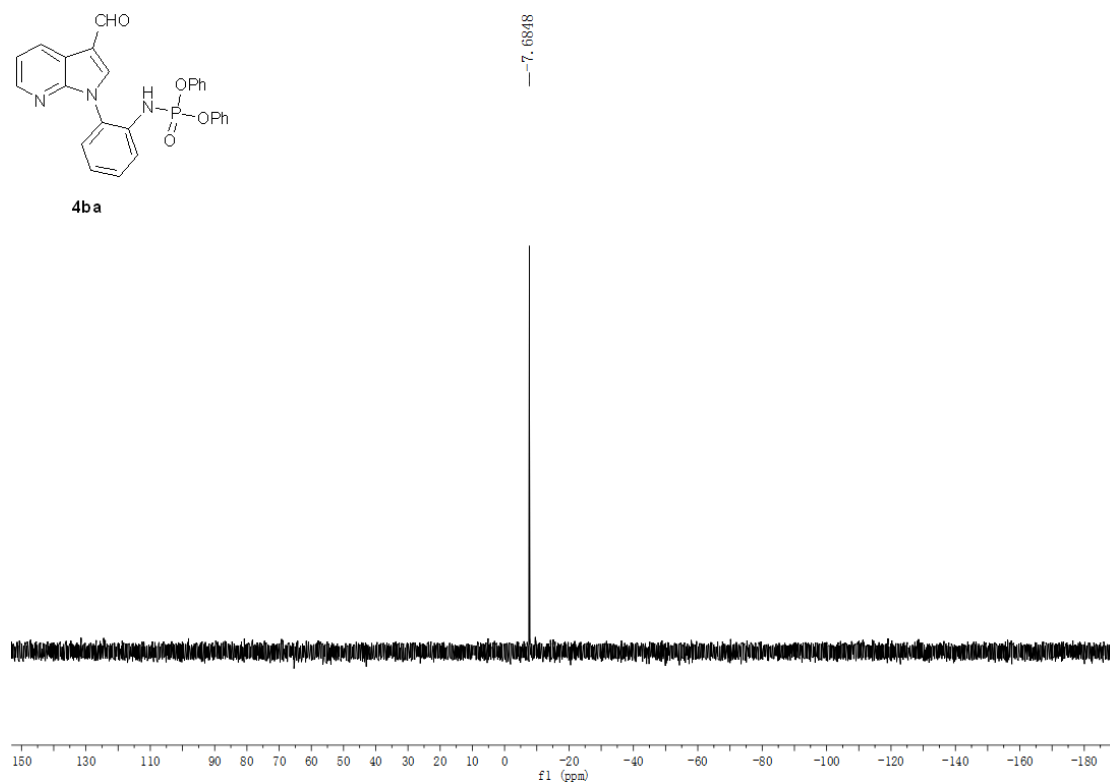
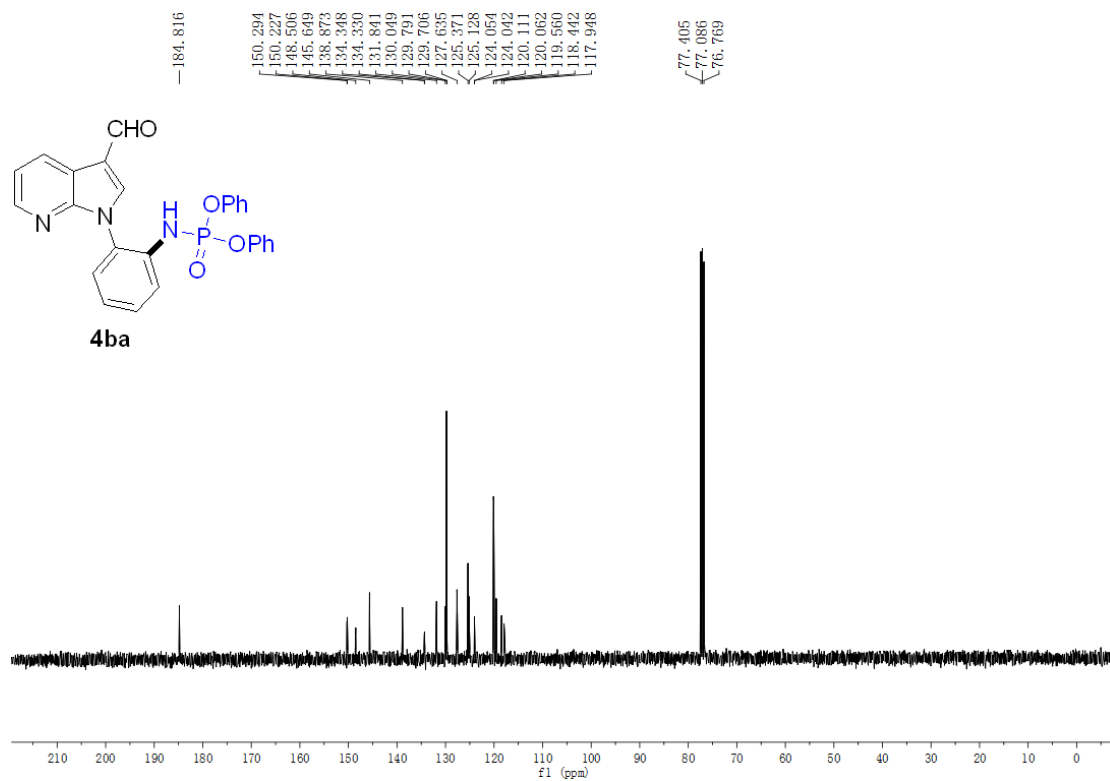


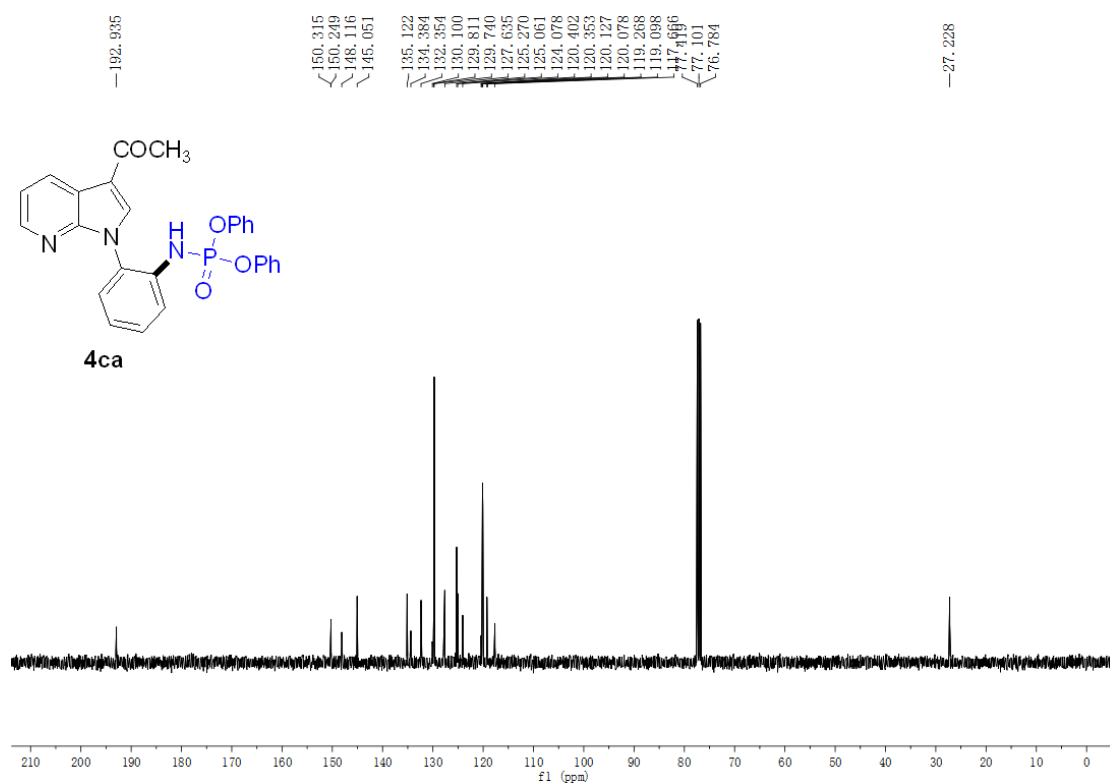
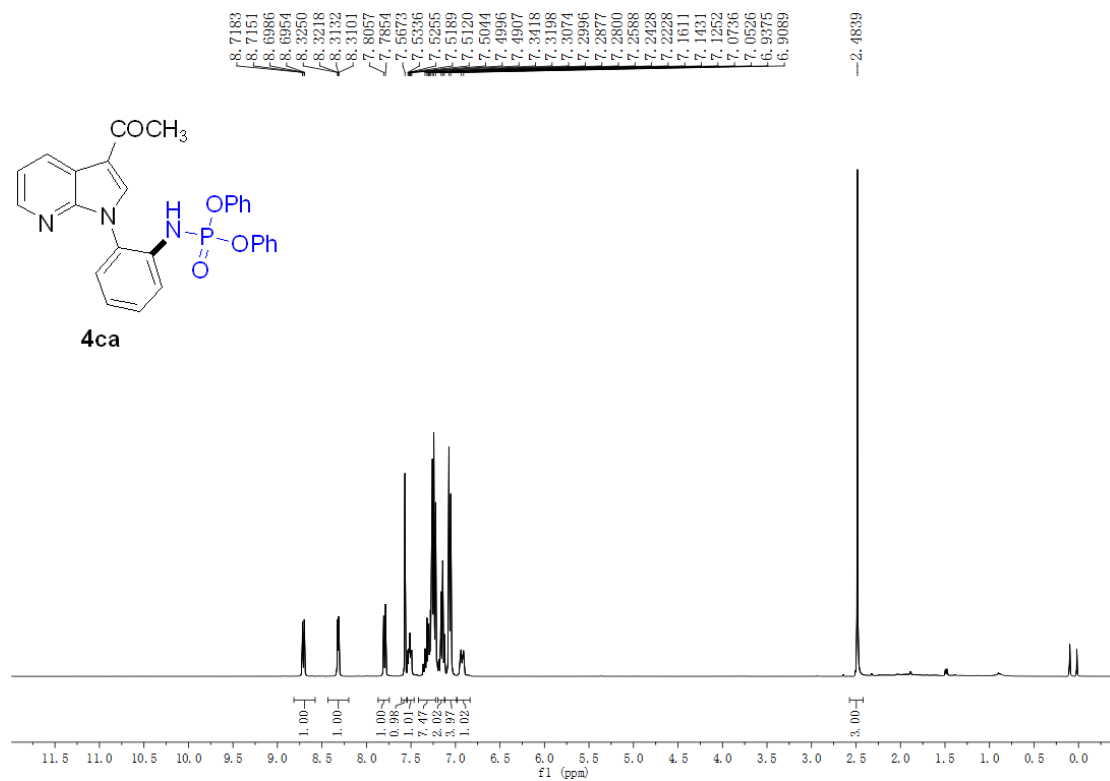
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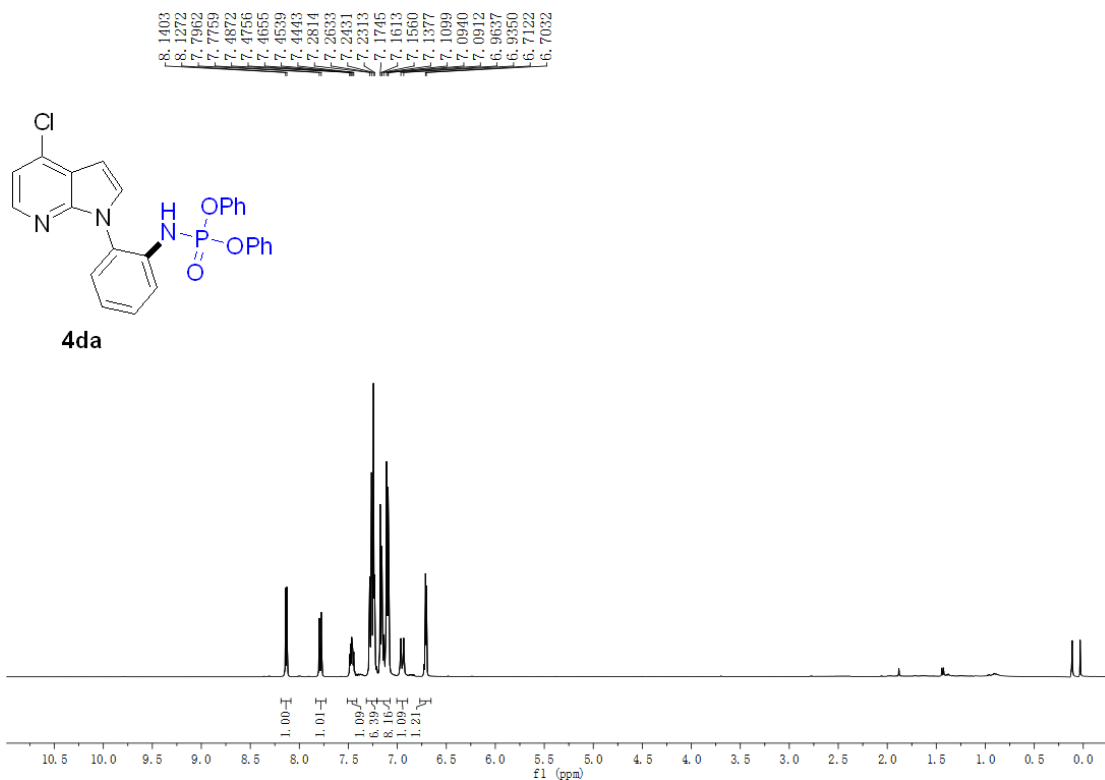
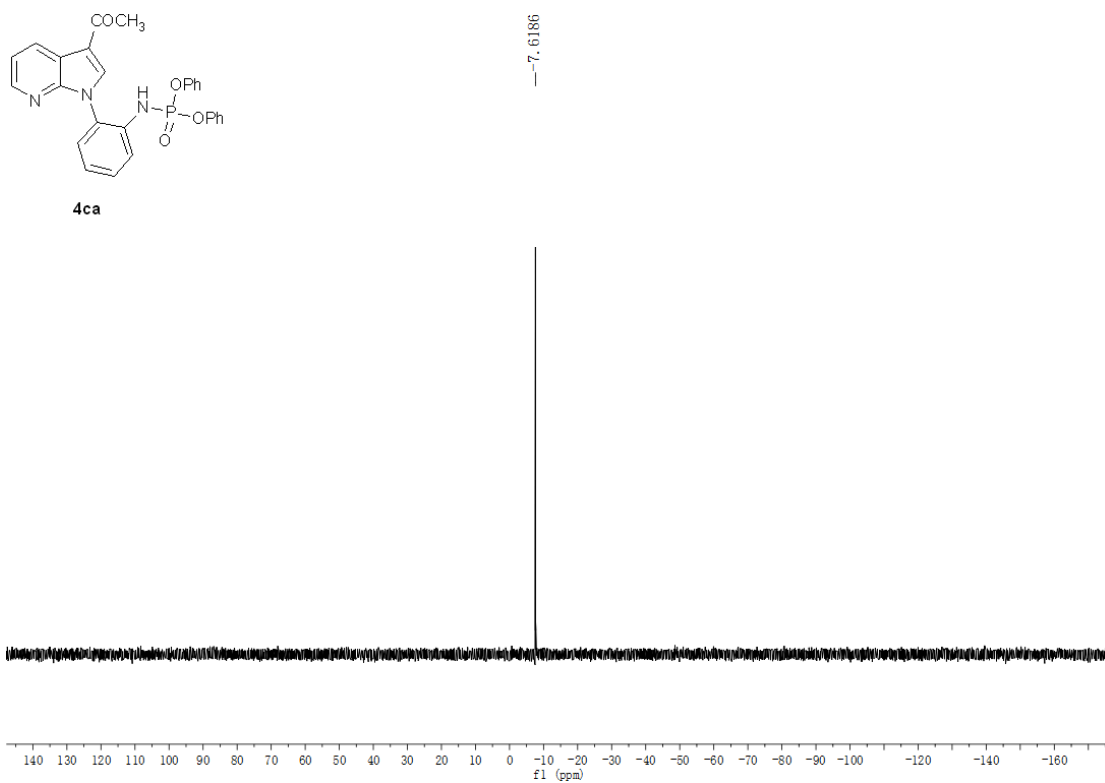


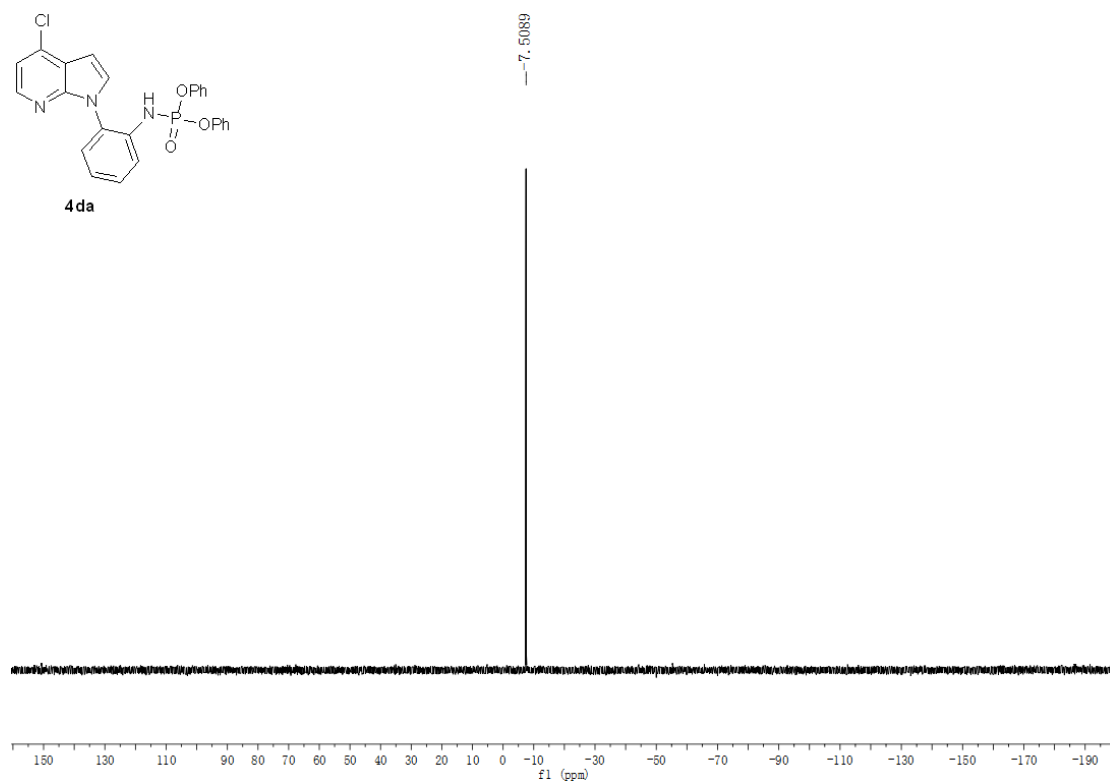
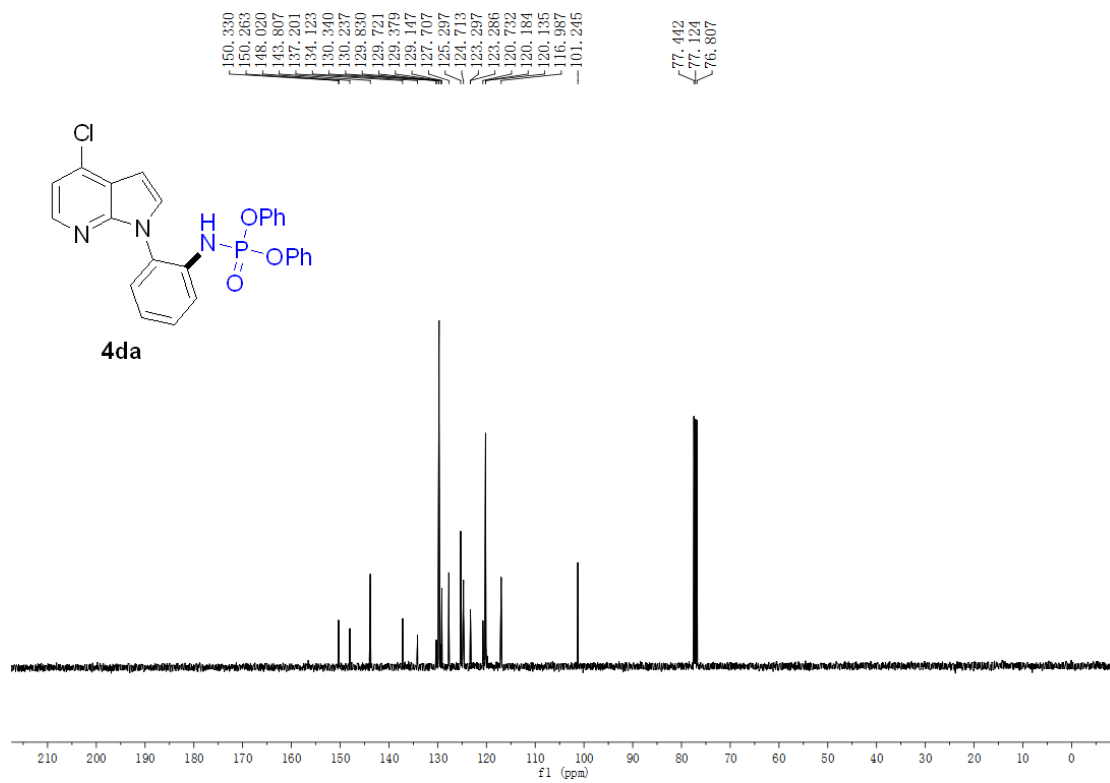


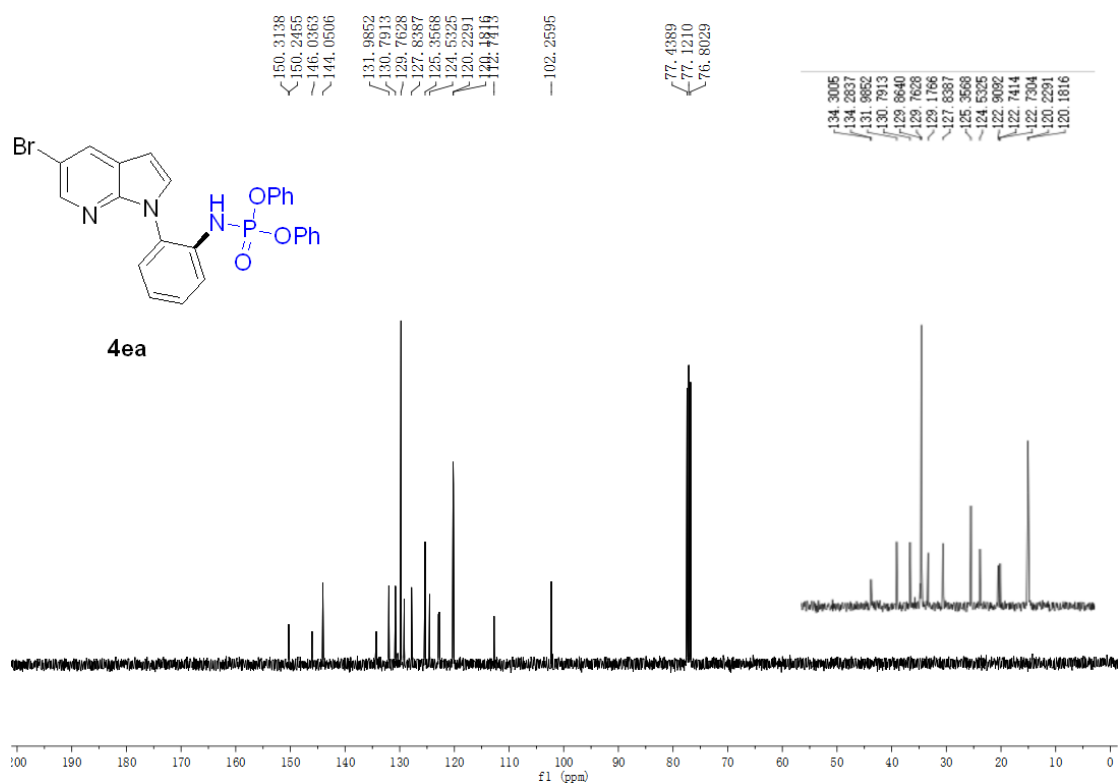
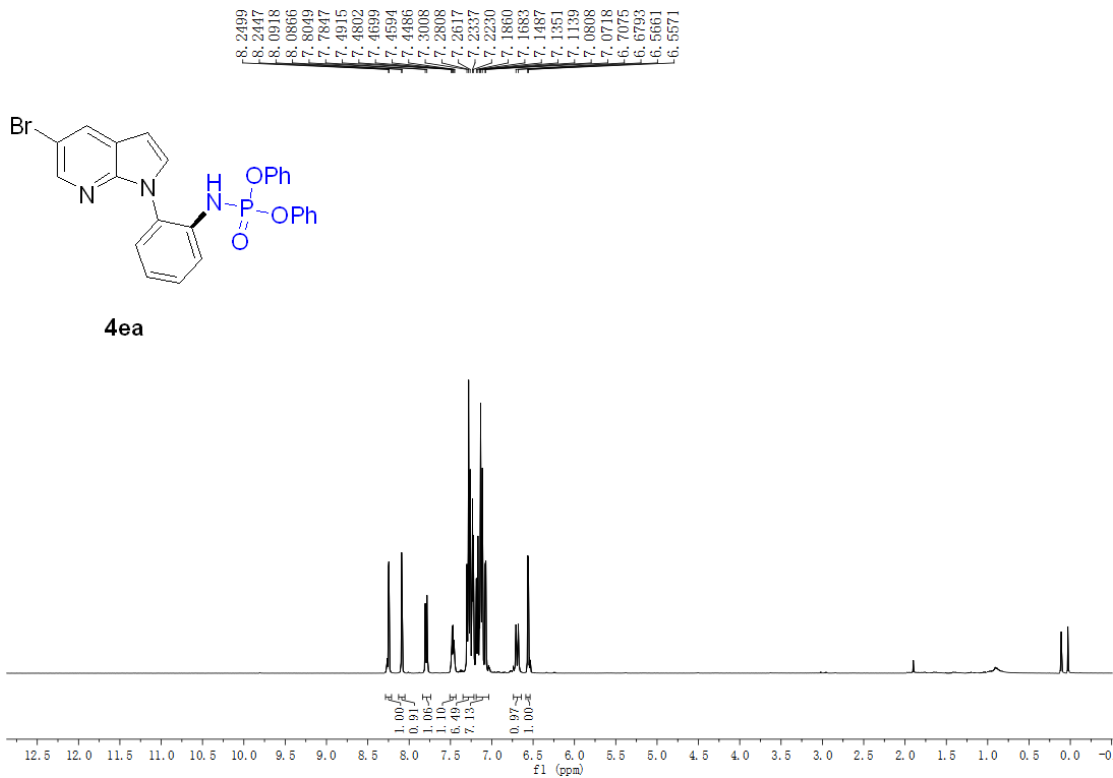


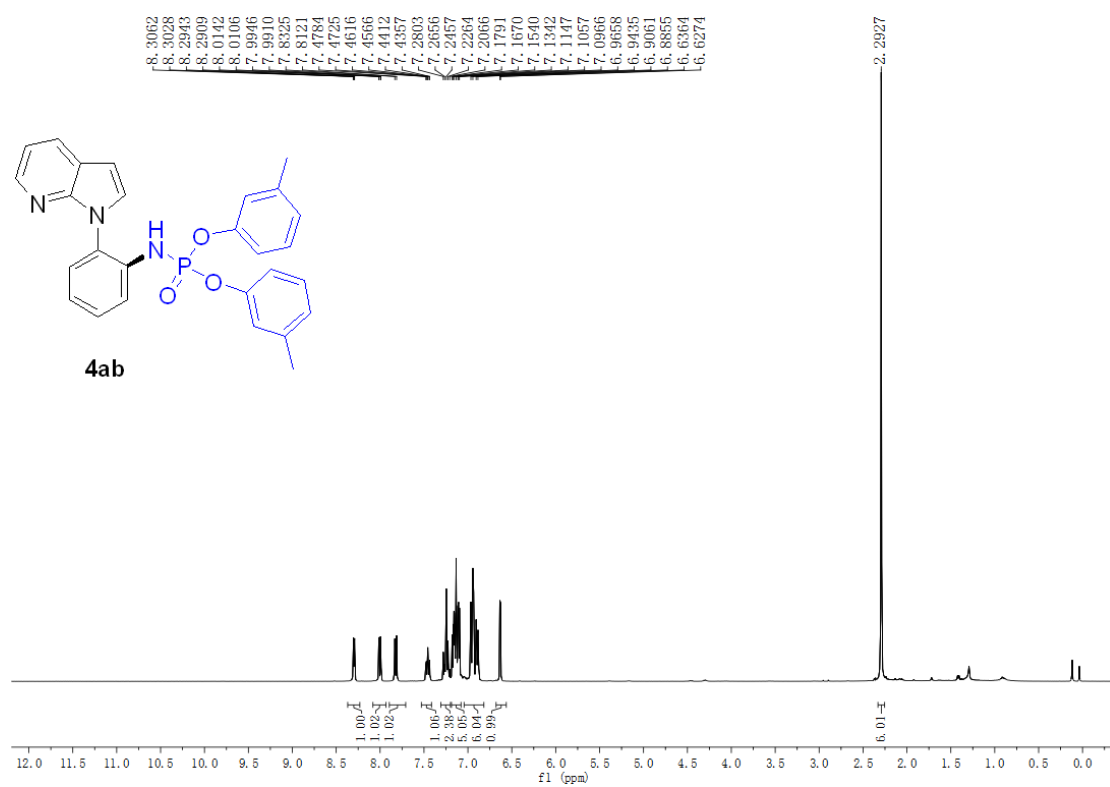
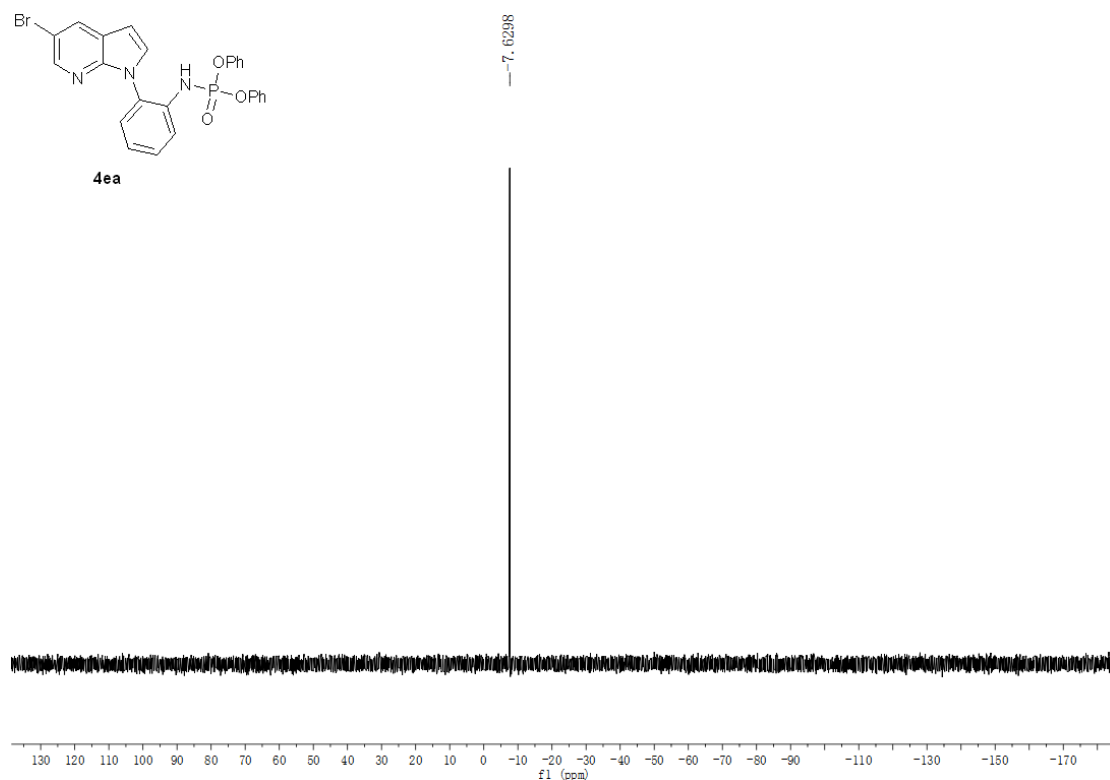


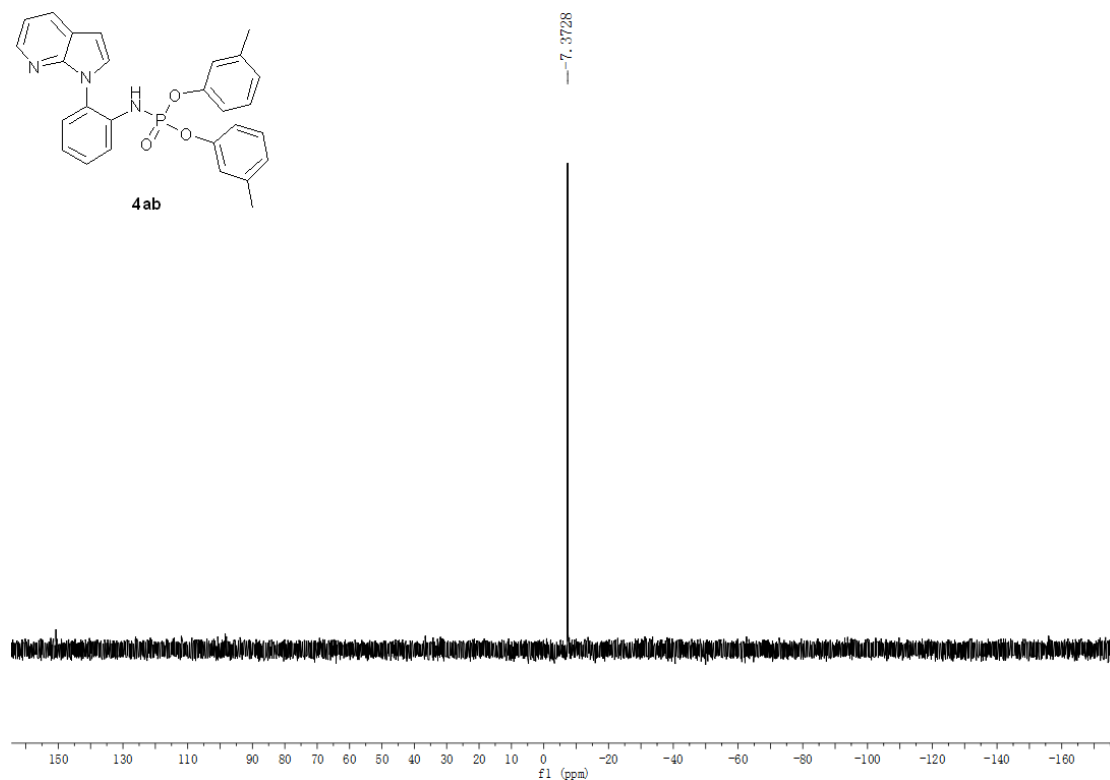
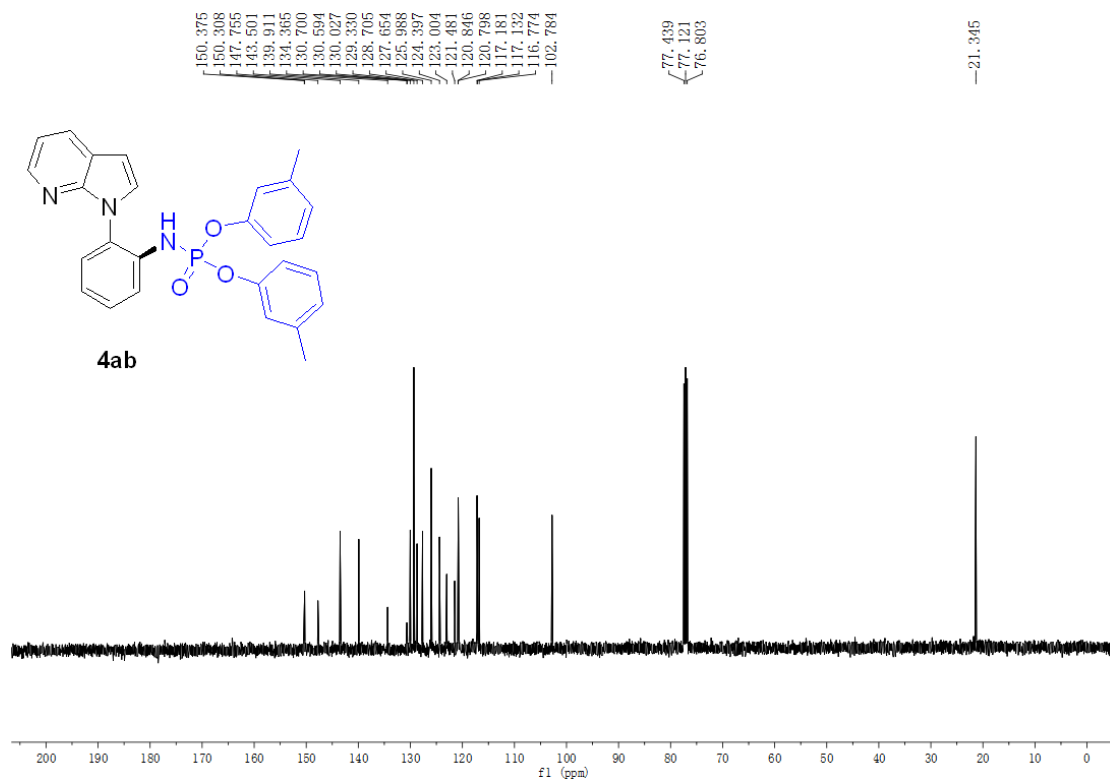


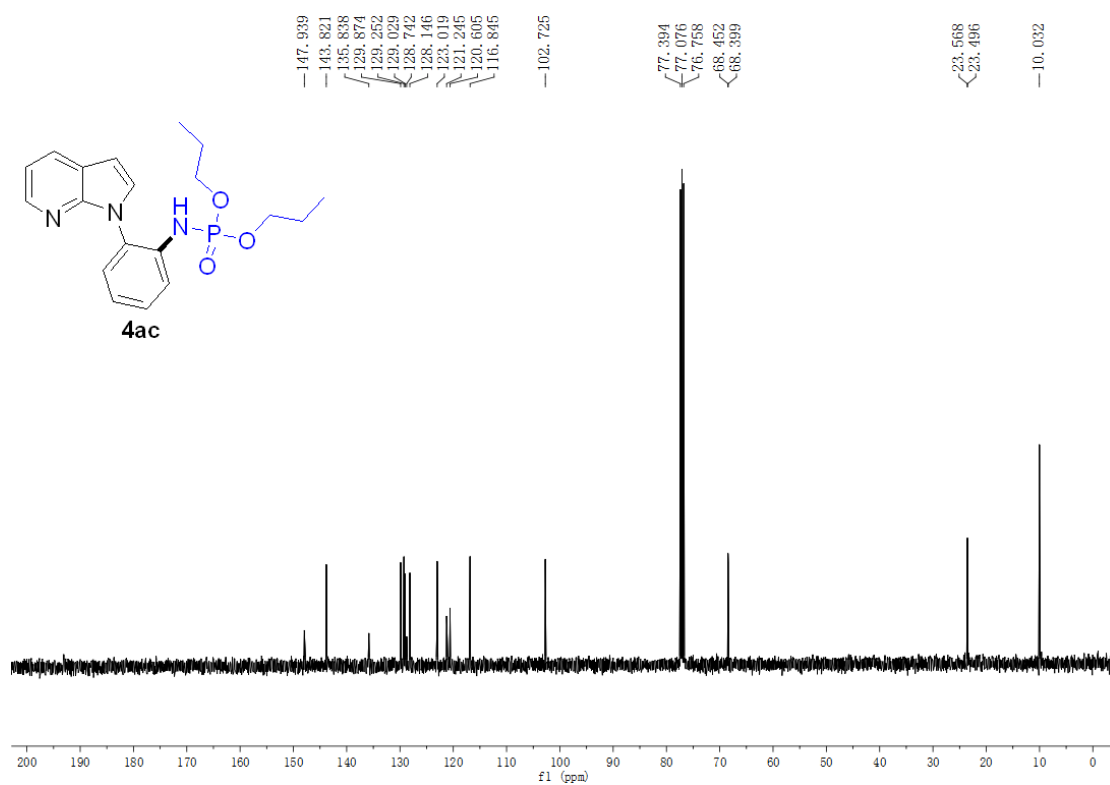
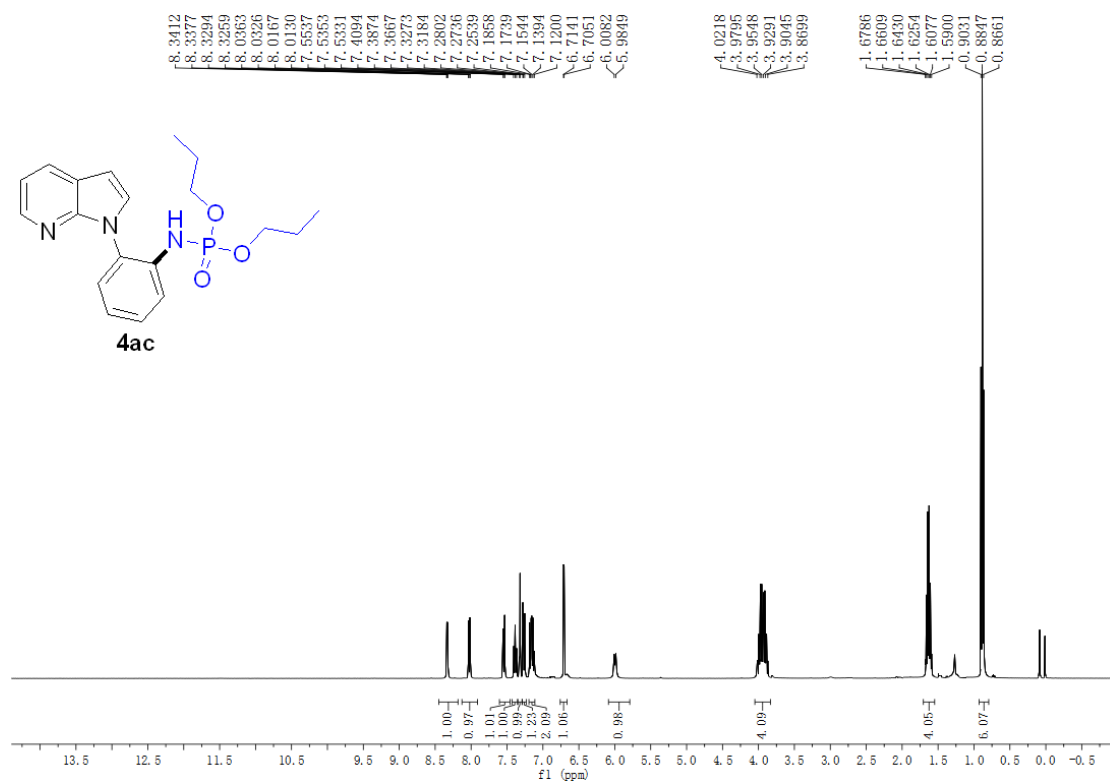


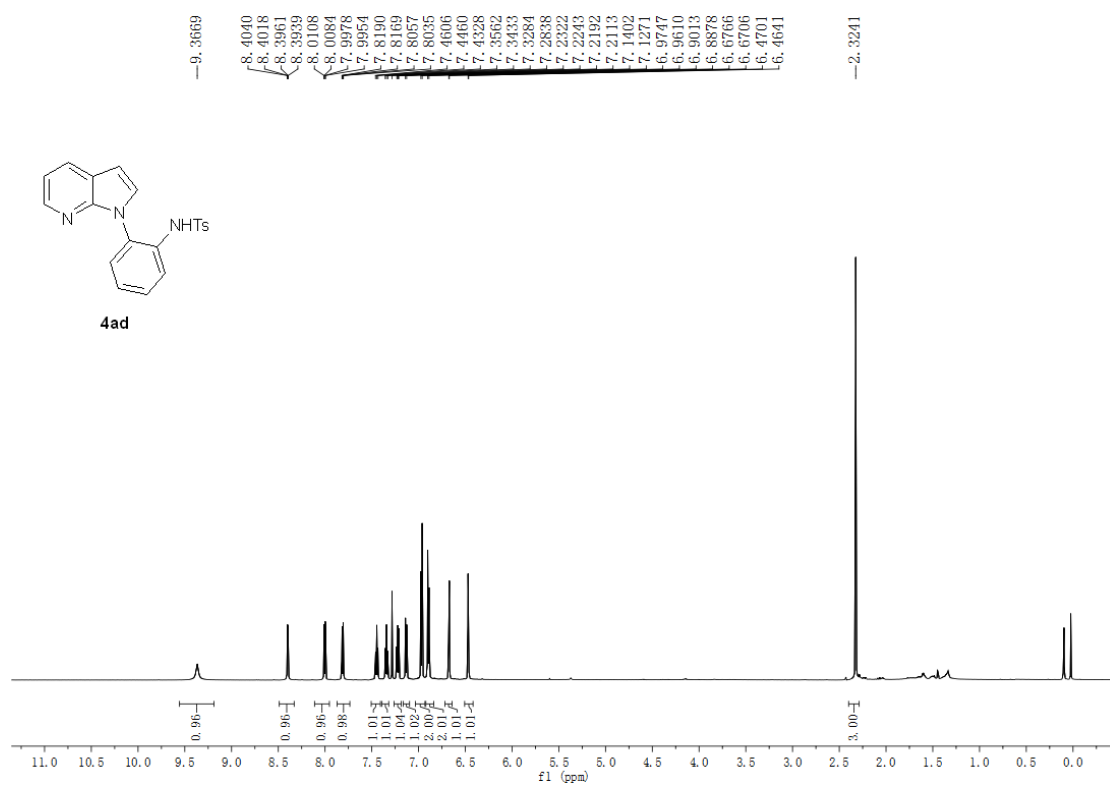
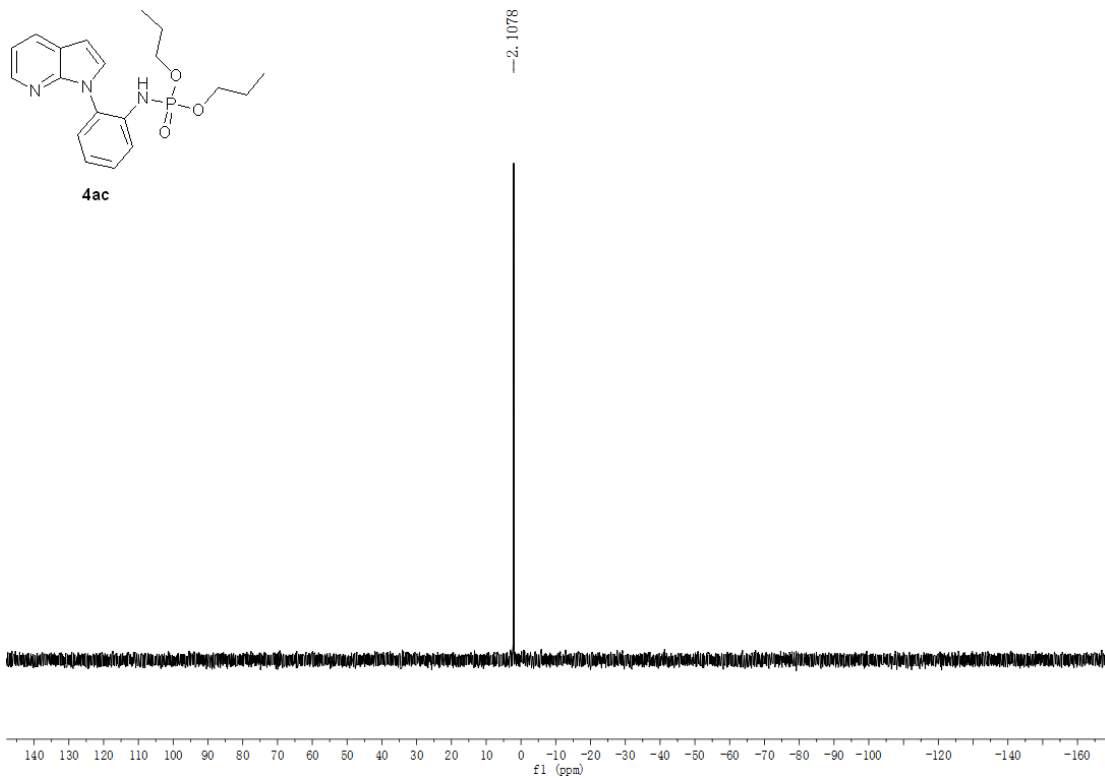


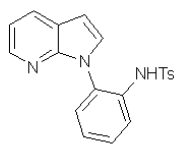












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