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Supporting Information

Manganese(III)-Promoted Tandem Phosphinoylation/Cyclization of 2-Arylindoles/2-Arylbenzimidazoles with Disubstituted Phosphine Oxides

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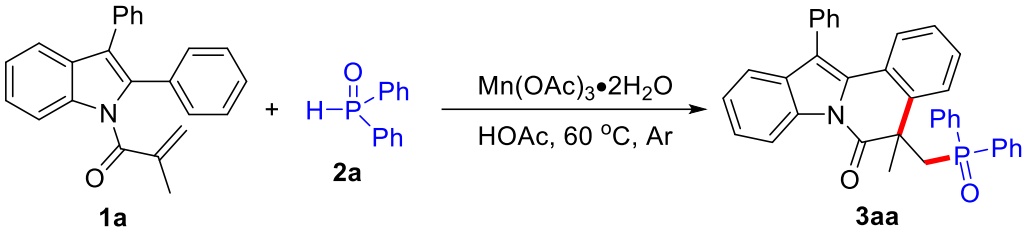
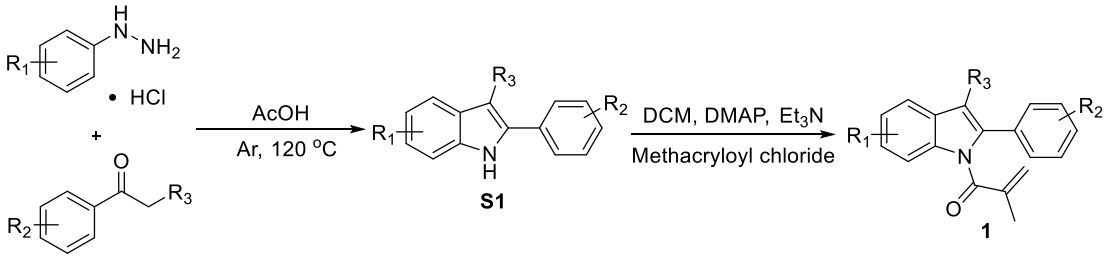
(A) Typical experimental procedure

To a Schlenk tube were added substrates **1a** (0.2 mmol), **2a** (2 equiv), $Mn(OAc)_3 \cdot 2H_2O$ (3 equiv), and HOAc (2 mL), the tube was then charged with argon. The mixture was stirred at 60 °C until complete consumption of starting material as monitored by TLC and/or GC-MS analysis (about 12 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product **3aa**.



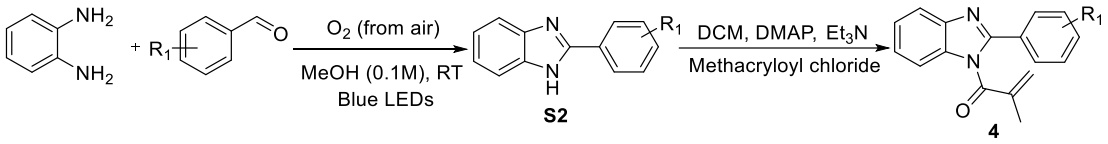
(a) General Procedures for the Synthesis of Substrates (1)



According to a modified literature procedure[1], a mixture of phenylhydrazine or substituted phenylhydrazine hydrochloride (11 mmol, 1.1 equiv.), ketone (10 mmol, 1.0 equiv.) and acetic acid (10 mL, 1.0 M) was heated to 120 °C for 12-24 h in a 100 mL round-bottomed flask under N_2 atmosphere. The reaction mixture was cooled to rt. AcOH was removed by rotory evaporation and the residue was portioned between water (50 mL) and EtOAc (20 mL). The organic and aqueous layers were separated.The aqueous layer was extracted with EtOAc (20 mL × 2), and the combined organic phase was washed with a saturated solution of sodium bicarbonate (20 mL) and brine (20 mL), dried with Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography to afford the desired product indole **S1**.

According to a modified literature procedure[1], to the solution of indole **S1** (5 mmol, 1.0 equiv) and DMAP (1.0 mmol, 0.2 equiv) in DCM (0.5 M) was added Et_3N (10 mmol, 2.0 equiv.) and methacryloyl chloride (10 mmol, 2.0 equiv) at 0 °C. The solution was warmed up to room temperature and stirred for 2-3 days. The mixture was diluted with DCM (20 mL) and saturated NH_4Cl solution (20 mL). The organic and aqueous layers were separated. The aqueous layer was extracted with DCM (20 mL × 2 times). The combined organic layer was washed with brine, dried over Na_2SO_4 , filtered and concentrated in vacuo to give a residue, which was purified by flash chromatography and then recrystallized from n-hexane/EtOAc to afford the product **1**.

(b) General Procedures for the Synthesis of Substrates (4)



According to a modified literature procedure[2], an open test tube equipped with a magnetic stir bar was charged with ophenylenediamine (5.0 mmol, 1.0 equiv.). Then MeOH (50 mL, 0.1 M) and an aldehyde (5.25 mmol, 1.1 equiv.) were added. The open test tube was placed under blue LEDs (7 W) and stirred at room temperature for 6–24 h. Reaction progress was checked by thin layer chromatography (TLC). The reaction mixture was concentrated in vacuo, and the benzimidazole (**S2**) were purified by recrystallization (with hot ethanol and water) or flash column chromatography.

According to a modified literature procedure[2], to the solution of benzimidazole **S2** (5 mmol, 1.0 equiv.) and DMAP (1.0 mmol, 0.2 equiv.) in DCM (0.5 M) was added Et_3N (10 mmol, 2.0 equiv.) and methacryloyl chloride (10 mmol, 2.0 equiv.) at 0 °C. The solution was warmed up to room temperature and stirred for 12–24 h. Reaction progress was checked by thin layer chromatography (TLC). The mixture was diluted with DCM (20 mL) and saturated $NaHCO_3$ solution (20 mL). The organic and aqueous layers were separated. The aqueous layer was extracted with DCM (20 mL × 2). The combined organic layer was washed with brine, dried over Na_2SO_4 , filtered

and concentrated in vacuo to give a residue, which was purified by flash chromatography and then recrystallized from n-hexane/EtOAc to afford the product **4**.

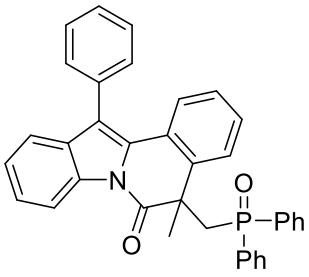
Reference

1. K. Sun, S.-J. Li, X.-L. Chen, Y. Liu, X.-Q. Huang, D.-H. Wei, L.-B. Qu, Y.-F. Zhao and B. Yu, *Chem. Commun*., 2019, **55**, 2861.

2. F.-L. Zeng, K. Sun, X.-L. Chen, X.-Y. Yuan, S.-Q. He, Y. Liu, Y.-Y. Peng, L.-B. Qu, Q.-Y. Lv, B. Yu, *Adv. Synth. Catal*., 2019, **361**, 5176.

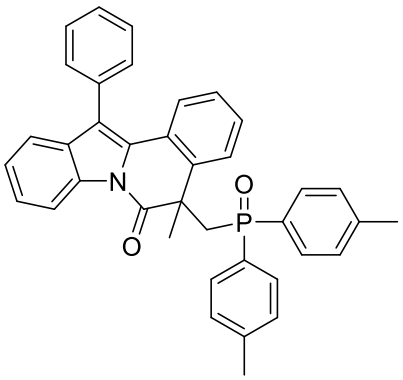
(B) Analytical data

5-((Diphenylphosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3aa):



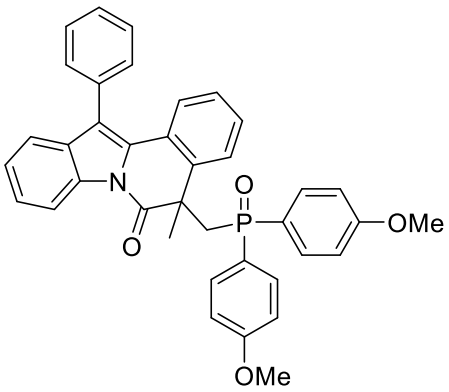
96.7 mg, 90% yield; White solid; mp 200.9-201.5 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.52 (d, *J* = 8.5 Hz, 1H), 7.65-7.61 (m, 2H), 7.57-7.47 (m, 5H), 7.43-7.38 (m, 3H), 7.35-7.29 (m, 5H), 7.23 (d, *J* = 4 Hz, 2H), 7.09-7.03 (m, 3H), 6.99-6.95 (m, 1H), 6.89-6.86 (m, 1H), 3.82-3.77 (m, 1H), 3.09-3.04 (m, 1H), 1.79 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.1 (d, *J* = 2.6 Hz), 136.1 (d, *J* = 2.4 Hz), 134.1, 134.0, 133.4 (d, *J* = 98.9 Hz), 132.0 (d, *J* = 97.9 Hz), 132.1, 131.2 (d, *J* = 2.6 Hz), 130.9 (d, *J* = 2.6 Hz), 130.7 (d, *J* = 9.5 Hz), 130.5 (d, *J* = 9.1 Hz), 130.0, 129.3, 129.1, 128.3 (d, *J* = 11.8 Hz), 127.8 (d, *J* = 14.1 Hz), 127.7, 127.4, 126.8, 125.5, 124.9, 124.7, 124.3, 120.0, 119.1, 116.6, 46.2 (d, *J* = 3.4 Hz), 40.7 (d, *J* = 68.9 Hz), 32.4 (d, *J* = 13.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.7; HRMS m/z (ESI) calcd for $C_{36}H_{29}NO_2P$ ($[M+H]^+$) 538.1930, found 538.1936.

5-((Di-*p*-tolylphosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ab):



107.4 mg, 95% yield;White solid; mp 105.7-106.3 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.44 (d, *J* = 8.0 Hz, 1H), 7.63-7.48 (m, 7H), 7.46-7.44 (m, 1H), 7.35-7.31 (m, 2H), 7.23-7.22 (m, 2H), 7.20-7.17 (m, 4H), 7.15-7.12 (m, 1H), 6.98-6.94 (m, 1H), 6.77-6.75 (m, 2H), 3.77-3.72 (m, 1H), 3.07-3.01 (m, 1H), 2.34 (s, 3H), 1.89 (s, 3H), 1.76 (d, *J* = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.9 (d, *J* = 2.3 Hz), 141.7 (d, *J* = 2.5 Hz), 136.4 (d, *J* = 2.5 Hz), 134.1, 134.0, 132.0, 130.9, 130.8, 130.6 (2C), 130.0, 129.4, 129.1 (d, *J* = 6.6 Hz), 129.0, 128.4, 128.3, 127.9 (2C), 127.8, 126.8, 125.4, 124.8, 124.6, 124.3, 119.9, 119.0, 116.7, 46.1 (d, *J* = 3.3 Hz), 40.8 (d, *J* = 68.8 Hz), 33.0 (d, *J* = 13.1 Hz), 21.2 (d, *J* = 45.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 27.5; HRMS m/z (ESI) calcd for $C_{38}H_{33}NO_2P$ ($[M+H]^+$) 566.2243, found 566.2250.

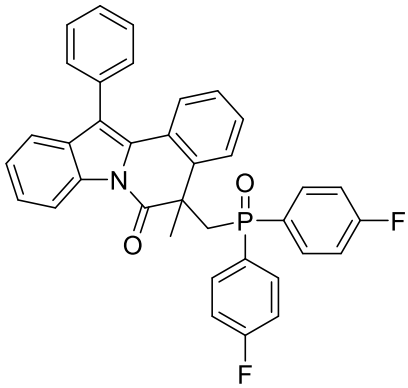
5-((Bis(4-methoxyphenyl)phosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ac):



101.5 mg, 85% yield; White solid; mp 109.3-111.6 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.41 (d, *J* = 8.0 Hz, 1H), 7.67-7.63 (m, 2H), 7.49-7.40 (m, 6H), 7.28-7.24 (m, 1H), 7.21-7.19 (m, 1H), 7.18-7.11 (m, 3H), 7.03-6.99 (m, 2H), 6.92-6.89 (m, 1H), 6.87-6.85 (m, 2H), 6.28-6.26 (m, 2H), 3.73-3.68 (m, 4H), 3.22 (s, 3H), 2.96 (t, *J* = 12.5 Hz, 1H), 1.66 (d, *J* = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.3 (d, *J* = 1.9 Hz), 162.1 (d, *J* = 2.8 Hz), 161.4 (d, *J* = 2.9 Hz), 136.4 (d, *J* = 2.4 Hz), 134.1, 133.9, 132.9 (d, *J* = 11.1 Hz), 132.5 (d, *J* = 10.3 Hz), 132.1, 130.1, 129.4, 129.2, 128.1, 128.0 (d, *J* = 7.0 Hz), 126.9, 125.4, 124.9 (d, *J* = 105.5 Hz), 124.8, 124.6, 124.3, 122.0 (d, *J* = 104.1 Hz), 119.9, 119.1, 116.7, 114.0 (d, *J* = 12.6 Hz), 113.0 (d, *J* = 12.8 Hz), 55.3, 54.7, 46.3 (d, *J* = 3.3 Hz), 41.1 (d, *J* = 69.4 Hz),

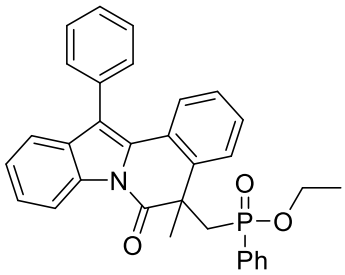
33.5 (d, J = 13.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 27.9; HRMS m/z (ESI) calcd for $C_{38}H_{33}NO_4P$ ($[M+H]^+$) 598.2142, found 598.2148.

5-((Bis(4-fluorophenyl)phosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ad):



82.5 mg, 72% yield; White solid; mp 186.1-188.1 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.50 (d, J = 8.0 Hz, 1H), 7.74-7.69 (m, 2H), 7.58-7.48 (m, 5H), 7.38-7.35 (m, 2H), 7.31-7.24 (m, 5H), 7.12-7.06 (m, 3H), 6.97-6.94 (m, 1H), 6.67-6.64 (m, 2H), 3.82-3.77 (m, 1H), 3.09-3.03 (m, 1H), 1.78 (d, J = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.1 (d, J = 2.3 Hz), 165.7 (dd, $J_{C\text{-}P}$ = 3.1 Hz, $J_{C\text{-}F}$ = 45.9 Hz), 163.5 (dd, $J_{C\text{-}P}$ = 3.3 Hz, $J_{C\text{-}F}$ = 46.1 Hz), 136.0 (d, J = 2.5 Hz), 133.9 (d, J = 5.0 Hz), 133.4 (q, J = 8.9 Hz), 133.1 (q, J = 8.5 Hz), 132.0, 130.0, 129.2 (q, J = 101.6 Hz), 129.2, 129.0, 128.0 (d, J = 13.5 Hz), 127.3 (q, J = 100.6 Hz), 127.4, 127.0, 125.7, 124.9, 124.7, 124.6, 120.4, 119.3, 116.5, 115.8 (q, J = 8.5 Hz), 115.0 (q, J = 8.4 Hz), 46.3 (d, J = 3.3 Hz), 40.9 (d, J = 69.9 Hz), 32.8 (d, J = 13.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -106.9, -107.1; HRMS m/z (ESI) calcd for $C_{36}H_{27}F_2NO_2P$ ($[M+H]^+$) 574.1742, found 574.1749.

Ethyl ((5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-a]isoquinolin-5-yl)methyl)(phenyl)phosphinate (3ae):



dr = 1:1

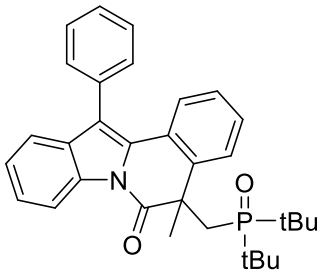
74.7 mg, 74% yield; White solid; mp 160.2-162.0 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.67 (d, J = 8.5 Hz, 1H), 7.60-7.49 (m, 7H), 7.43-7.39 (m, 3H), 7.34-7.28 (m, 5H), 7.11-7.08 (m, 1H), 6.98-6.94 (m, 1H), 3.67-3.59 (m, 1H), 3.47-3.40 (m, 2H), 2.80-2.75 (m, 1H), 1.73 (d, J = 3.0 Hz, 3H), 0.75 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.4 (d, J = 1.4 Hz), 137.0 (d, J = 2.5 Hz), 134.2 (d, J = 3.3 Hz), 132.3, 131.9 (d, J = 2.6 Hz), 131.2 (d, J = 124.6 Hz), 131.6 (d, J = 10.3 Hz), 130.2, 129.7, 129.2, 128.3 (d, J = 12.6 Hz), 128.0 (d, J =

7.1 Hz), 127.1, 126.9, 125.7, 125.1, 124.7, 124.4, 120.1, 119.3, 116.8, 60.3 (d, J = 6.3 Hz), 46.1 (d, J = 4.4 Hz), 40.5 (d, J = 98.9 Hz), 32.8 (d, J = 15.9 Hz), 15.5 (d, J = 7.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 38.2.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.48 (d, J = 8.0 Hz, 1H), 7.58-7.55 (m, 2H), 7.52-7.48 (m, 3H), 7.40 (d, J = 8.0 Hz, 1H), 7.36-7.33 (m, 2H), 7.32-7.28 (m, 2H), 7.25-7.23 (m, 2H), 7.20-7.17 (m, 1H), 7.14-7.11 (m, 1H), 7.08-7.04 (m, 2H), 6.97 (t, J = 7.5 Hz, 1H), 3.83-3.75 (m, 1H), 3.65-3.57 (m, 1H), 3.35-3.29 (m, 1H), 2.81 (t, J = 15.0 Hz, 1H), 1.74 (d, J = 3.0 Hz, 3H), 1.01 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.8 (d, J = 1.7 Hz), 136.8 (d, J = 1.9 Hz), 134.2 (d, J = 11.4 Hz), 132.2, 131.5 (d, J = 10.4Hz), 130.4 (d, J = 123.6 Hz), 129.4, 129.2, 128.0 (d, J = 3.0 Hz), 127.9 (d, J = 12.5 Hz), 127.5, 126.9, 125.6, 125.1, 124.8, 124.4, 120.1, 119.2, 116.7, 60.3 (d, J = 6.1 Hz), 45.5 (d, J = 2.1 Hz), 41.3 (d, J = 98.1 Hz), 32.3 (d, J = 15.6 Hz), 16.0 (d, J = 6.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 39.3.

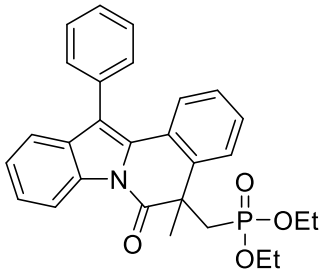
HRMS m/z (ESI) calcd for $C_{32}H_{29}NO_3P$ ($[M+H]^+$) 506.1880, found 506.1884.

5-((Di-*t*ert-butylphosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3af):



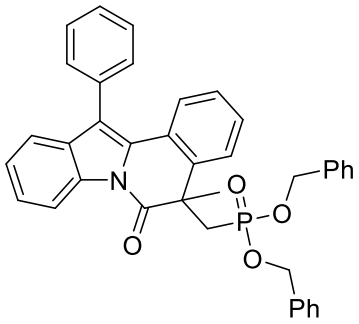
29.8 mg, 30% yield; White solid; mp 240.0-241.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.49 (d, J = 7.5 Hz, 1H), 7.76-7.74 (m, 1H), 7.48-7.44 (m, 4H), 7.42-7.39 (m, 1H), 7.34-7.31 (m, 2H), 7.25-7.16 (m, 3H), 6.93-6.90 (m, 1H), 2.37-2.33 (m, 1H), 2.25-2.20 (m, 1H), 2.04 (s, 3H), 1.04 (d, J = 13 Hz, 9H), 0.88 (d, J = 13.5Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.7 (d, J = 10.0 Hz), 137.5, 134.6, 133.9, 131.9, 130.0, 129.7, 129.6, 129.2, 128.0，127.9, 127.1, 125.9, 125.8, 125.2, 124.3, 120.2, 119.5, 116.2, 47.4 (d, J = 4.3 Hz), 36.5 (d, J = 10.6 Hz), 36.1 (d, J = 11.1 Hz), 31.8 (d, J = 49.4 Hz), 26.6, 26.3, 24.4; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 60.0; HRMS m/z (ESI) calcd for $C_{32}H_{37}NO_2P$ ($[M+H]^+$) 498.2556, found 498.2551.

Diethyl ((5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-a]isoquinolin-5-yl)methyl)phosphonate (3ag):



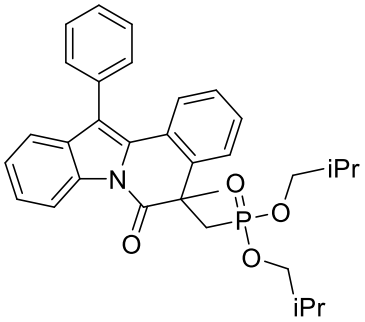
66.2 mg, 70% yield; White solid; mp 120.1-121.0 °C (uncorrected); ^{1}H NMR (500 MHZ, $CDCl_3$) δ: 8.67 (d, *J* = 8.5 Hz, 1H), 7.57-7.54 (m, 2H), 7.51-7.48 (m, 3H), 7.45-7.43 (m, 2H), 7.42-7.38 (m, 1H), 7.30-7.26 (m, 3H), 7.04-7.01 (m, 1H), 3.80-3.62 (m, 4H), 3.19-3.13 (m, 1H), 2.64-2.58 (m, 1H), 1.76 (d, *J* = 4 Hz, 3H), 0.94 (t, *J* = 7 Hz, 3H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.0 (d, *J* = 2.4 Hz), 137.2 (d, *J* = 2.4 Hz), 134.2, 134.1, 132.2, 130.1, 129.5, 129.2, 128.0 (d, *J* = 2.8 Hz), 126.9，126.8, 125.8, 125.2, 124.8, 124.4, 120.2, 119.3, 116.6, 61.6 (d, *J* = 6.4 Hz), 61.1 (d, *J* = 6.5 Hz), 45.6 (d, *J* = 4.1 Hz), 36.9 (d, *J* = 139.9 Hz), 32.2 (d, *J* = 18.8 Hz), 15.9 (d, *J* = 6.0 Hz), 15.7 (d, *J* = 6.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 25.7; HRMS m/z (ESI) calcd for $C_{28}H_{29}NO_4P$ ($[M+H]^+$) 474.1829, found 474.1836.

Dibenzyl ((5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-a]isoquinolin-5-yl)-methyl)phosphonate (3ah):



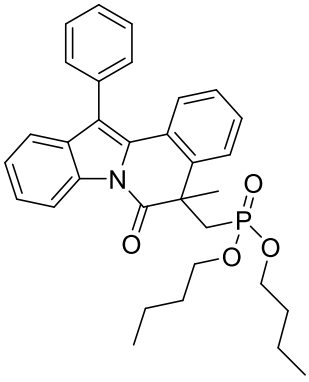
50.1 mg, 42% yield; White solid; mp 81.2-82.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.61 (d, *J* = 8.5 Hz, 1H), 7.53-7.46 (m, 3H), 7.43-7.35 (m, 5H), 7.27-7.25 (m, 2H), 7.22-7.19 (m, 1H), 7.17-7.12 (m, 4H), 7.10-7.07 (m, 2H), 7.00-6.96 (m, 3H), 6.91-6.89 (m, 2H), 4.73-4.69 (m, 1H), 4.60-4.55 (m, 2H), 4.52-4.48 (m, 1H), 3.33-3.26 (m, 1H), 2.73-2.70 (m, 1H), 1.72 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.0 (d, *J* = 2.3 Hz), 137.0 (d, *J* = 2.3 Hz), 135.9 (d, *J* = 5.8 Hz), 135.7 (d, *J* = 6.6 Hz), 134.2, 134.0, 132.2, 130.1, 129.2, 129.1, 128.2, 128.1 (2C), 128.0 (2C), 127.9, 127.8, 127.5, 126.9, 126.8, 125.8, 125.3, 124.8, 124.4, 120.3, 119.3, 116.7, 67.2 (d, *J* = 6.4 Hz), 66.7 (d, *J* = 6.5 Hz), 46.0 (d, *J* = 4.1 Hz), 36.8 (d, *J* = 139.5 Hz), 32.5 (d, *J* = 19.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 27.0; HRMS m/z (ESI) calcd for $C_{38}H_{33}NO_4P$ ($[M+H]^+$) 598.2142, found 598.2151.

Diisobutyl ((5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-a]isoquinolin-5-yl)-methyl)phosphonate (3ai):



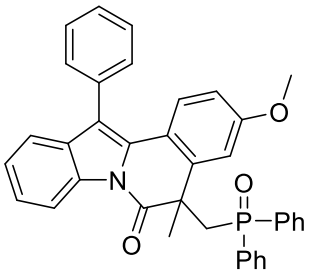
71.9 mg, 68% yield; White solid; mp 120.6-121.7 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.66 (d, *J* = 8.5 Hz, 1H), 7.56-7.53 (m, 2H), 7.50-7.48 (m, 3H), 7.45-7.42 (m, 2H), 7.41-7.38 (m, 1H), 7.29-7.26 (m, 3H), 7.03-6.99 (m, 1H), 3.54-3.43 (m, 2H), 3.39-3.33 (m, 2H), 3.22-3.15 (m, 1H), 2.67-2.60 (m, 1H), 1.75 (d, *J* = 3.5 Hz, 3H), 1.52-1.42 (m, 2H), 0.68-0.64 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.0 (d, *J* = 2.4 Hz), 137.2 (d, *J* = 2.3 Hz), 134.2, 134.1, 132.2, 130.1, 129.4, 129.2, 128.0 (d, *J* = 6.3 Hz), 126.8 (d, *J* = 7.8 Hz), 125.7, 125.2, 124.7, 124.4, 120.2, 119.3, 116.7, 71.5 (d, *J* = 6.9 Hz), 71.1 (d, *J* = 6.8 Hz), 45.6 (d, *J* = 4.0 Hz), 36.7 (d, *J* = 140.0 Hz), 32.4 (d, *J* = 18.8 Hz), 28.9 (d, *J* = 5.9 Hz), 28.8 (d, *J* = 6.8 Hz), 18.5 (d, *J* = 4.6 Hz), 18.4 (d, *J* = 10.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 25.8; HRMS m/z (ESI) calcd for $C_{32}H_{37}NO_4P$ ($[M+H]^+$) 530.2455, found 530.2459.

Dibutyl ((5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-a]isoquinolin-5-yl)methyl)phosphonate (3aj):



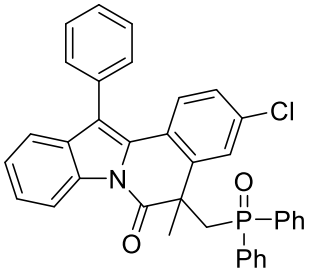
65.6 mg, 62% yield; White solid; mp 111.3-114.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.67 (d, *J* = 8.5 Hz, 1H), 7.57-7.54 (m, 2H), 7.51-7.49 (m, 3H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.41-7.38 (m, 1H), 7.29-7.26 (m, 3H), 7.04-7.00 (m, 1H), 3.76-3.53 (m, 4H), 3.21-3.14 (m, 1H), 2.64-2.58 (m, 1H), 1.75 (d, *J* = 3.5 Hz, 3H), 1.27-1.15 (m, 4H), 1.11-1.01 (m, 4H) 0.72-0.68 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.0 (d, *J* = 2.4 Hz), 137.2 (d, *J* = 2.3 Hz), 134.2, 134.1, 132.2, 130.1, 129.4, 129.2, 128.0 (d, *J* = 2.4 Hz), 126.9，126.8, 125.7, 125.1, 124.7, 124.4, 120.1, 119.3, 116.7, 65.4 (d, *J* = 6.8 Hz), 64.9 (d, *J* = 6.9 Hz), 45.6 (d, *J* = 4.1 Hz), 36.8 (d, *J* = 139.9 Hz), 32.4 (d, *J* = 18.9 Hz), 32.1 (d, *J* = 6.0 Hz), 32.0 (d, *J* = 6.5 Hz), 18.4 (d, *J* = 6.5 Hz), 13.4; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 25.7; HRMS m/z (ESI) calcd for $C_{32}H_{37}NO_4P$ ($[M+H]^+$) 530.2455, found 530.2459.

5-((Diphenylphosphoryl)methyl)-3-methoxy-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ba):



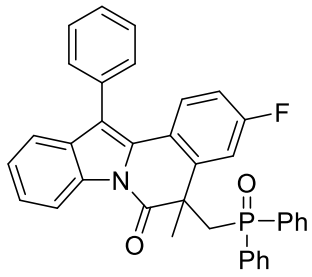
76.0 mg, 67% yield; White solid; mp 237.7-238.9 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.51 (d, *J* = 8.5 Hz, 1H), 7.66-7.62 (m, 2H), 7.57-7.46 (m, 5H), 7.45-7.40 (m, 3H), 7.37-7.30 (m, 3H), 7.23-7.20 (m, 3H), 7.16-7.13 (m, 1H), 7.12-7.08 (m, 2H), 6.82 (d, *J* = 2.5 Hz, 1H), 6.45-6.42 (m, 1H), 3.80-3.75 (m, 1H), 3.65 (s, 3H), 3.06-3.00 (m, 1H), 1.81 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.1 (d, *J* = 3.3 Hz),159.0, 138.2 (d, *J* = 2.5 Hz), 134.3, 133.7 (d, *J* = 99.0 Hz), 134.0, 131.9 (d, *J* = 98.1 Hz), 132.3, 131.2 (d, *J* = 2.8 Hz), 131.1 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 9.5 Hz), 130.5 (d, *J* = 9.3 Hz), 130.2, 129.5, 129.1, 128.3 (d, *J* = 11.8 Hz), 127.9 (d, *J* = 9.8 Hz), 127.8, 126.6, 125.1, 124.3, 118.8, 118.3, 117.8, 116.5, 113.3, 112.5, 55.1, 46.7 (d, *J* = 3.5 Hz), 40.6 (d, *J* = 69.1 Hz), 32.0 (d, *J* = 12.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.9; HRMS m/z (ESI) calcd for $C_{37}H_{31}NO_3P$ ($[M+H]^+$) 568.2036, found 568.2044.

3-Chloro-5-((diphenylphosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ca):



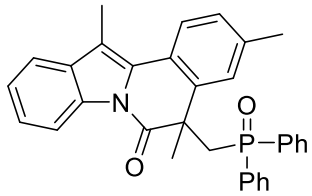
91.4 mg, 80% yield; White solid; mp 215.4-217.2 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.56 (d, *J* = 8.5 Hz, 1H), 7.56-7.49 (m, 9H), 7.40-7.30 (m, 4H), 7.27-7.19 (m, 6H), 7.11 (s, 1H), 6.79-6.76 (m, 1H), 3.79-3.74 (m, 1H), 3.01-2.96 (m, 1H), 1.80 (d, *J* = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.4 (d, *J* = 2.8 Hz), 137.9 (d, *J* = 2.4 Hz), 134.2, 133.8, 133.2 (d, *J* = 49.5 Hz), 133.3, 132.4 (d, *J* = 49.3 Hz), 132.0, 131.4 (d, *J* = 2.8 Hz), 131.3 (d, *J* = 2.8 Hz), 130.5 (d, *J* = 9.5 Hz), 130.2 (d, *J* = 9.3 Hz), 130.0, 129.2, 128.5, 128.3 (d, *J* = 11.8 Hz), 128.1 (d, *J* = 8.9 Hz), 128.0, 127.5, 127.2, 126.2, 125.8, 124.4, 123.6, 120.5, 119.2, 116.7, 46.1 (d, *J* = 3.6 Hz), 40.6 (d, *J* = 68.9 Hz), 31.8 (d, *J* = 12.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.3; HRMS m/z (ESI) calcd for $C_{36}H_{28}ClNO_2P$ ($[M+H]^+$) 572.1541, found 572.1550.

5-((Diphenylphosphoryl)methyl)-3-fluoro-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3da):



50.0 mg, 45% yield; White solid; mp 178.5-180.1 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.51 (d, *J* = 8.0 Hz, 1H), 7.59-7.49 (m, 9H), 7.43-7.40 (m, 1H), 7.36-7.32 (m, 3H), 7.29-7.24 (m, 3H), 7.18-7.13 (m, 3H), 6.92-6.89 (m, 1H), 6.58-6.54 (m, 1H), 3.77-3.72 (m, 1H), 3.00-2.95 (m, 1H), 1.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.5 (d, *J* = 2.9 Hz), 161.8 (d, $J_{C\text{-}F}$ = 248.0 Hz), 138.9 (q, *J* = 2.4 Hz), 134.1, 133.9, 133.4 (d, *J* = 98.6 Hz), 132.3 (d, *J* = 98.4 Hz), 132.1, 131.4 (d, *J* = 2.8 Hz), 131.2 (d, *J* = 2.6 Hz), 130.6 (d, *J* = 9.5 Hz), 130.4 (d, *J* = 9.1 Hz), 130.2, 129.3, 128.7, 128.4 (d, *J* = 11.8 Hz), 128.1, 128.0 (d, *J* = 9.5 Hz), 127.0 (d, *J* = 8.0 Hz), 125.6, 124.4, 121.4 (d, *J* = 3.1 Hz), 119.8 (d, *J* = 1.9 Hz), 119.2, 116.7, 114.6 (d, *J* = 21.8 Hz), 114.3 (d, *J* = 22.8 Hz), 46.3 (q, *J* = 3.3 Hz), 40.8 (d, *J* = 68.9 Hz), 31.8 (d, *J* = 12.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -111.8,; HRMS m/z (ESI) calcd for $C_{36}H_{28}FNO_2P$ ($[M+H]^+$) 556.1836, found 556.1844.

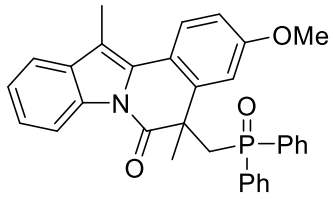
5-((Diphenylphosphoryl)methyl)-3,5,12-trimethylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ea):



44.0 mg, 45% yield; White solid; mp 228.8-230.5 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.51-8.49 (m, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.54-7.51 (m, 3H), 7.43-7.38 (m, 3H), 7.34-7.31 (m, 4H), 7.17-7.09 (m, 3H), 7.06 (s, 1H),7.02 (d, *J* = 7.5 Hz, 1H), 3.78-3.73 (m, 1H), 3.04-2.99 (m, 1H), 2.58 (s, 3H), 2.12 (s, 3H), 1.75 (d, *J* = 2.0 Hz, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.0 (d, *J* = 2.6 Hz), 137.2, 136.0 (d, *J* = 2.6 Hz), 134.2, 133.7 (d, *J* = 99.8 Hz), 132.7 (d, *J* = 98.4 Hz), 132.5, 131.2 (d, *J* = 3.0 Hz), 131.1 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 9.6 Hz), 130.6 (d, *J* = 9.1 Hz), 129.9, 128.4, 128.3 (d, *J* = 2.0 Hz), 128.2, 127.9 (d, *J* = 11.9 Hz), 125.2, 124.8, 124.0, 123.5, 118.1, 116.7, 113.4, 46.2 (d, *J* = 3.5 Hz), 40.5 (d, *J* = 69.5 Hz),

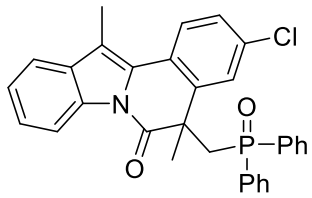
32.3 (d, *J* = 12.5 Hz), 21.3, 11.5; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.9; HRMS m/z (ESI) calcd for $C_{32}H_{29}NO_2P$ ($[M+H]^+$) 490.1930, found 490.1933.

5-((Diphenylphosphoryl)methyl)-3-methoxy-5,12-dimethylindolo[2,1-a]isoquinoli n-6(5*H*)-one (3fa):



74.7 mg, 74% yield; White solid; mp 214.8-216.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.48-8.45 (m, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.62-7.58 (m, 2H), 7.51-7.49 (m, 1H), 7.44-7.33 (m, 5H), 7.32-7.29 (m, 2H), 7.14-7.11 (m, 1H), 7.08-7.05 (m, 2H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.81-6.78 (m, 1H), 3.75-3.70 (m, 4H), 3.03-2.98 (m, 1H), 2.54 (s, 3H), 1.77 (d, *J* = 2.5 Hz, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.7 (d, *J* = 3.4 Hz), 158.6, 138.0 (d, *J* = 2.6 Hz), 133.7 (d, *J* = 98.8 Hz), 134.1, 132.3 (d, *J* = 98.1 Hz), 132.6, 131.2 (d, *J* = 2.8 Hz), 131.0 (d, *J* = 2.3 Hz), 130.7 (d, *J* = 9.5 Hz), 130.6 (d, *J* = 9.3 Hz), 129.7, 128.3 (d, *J* = 11.8 Hz), 127.8 (d, *J* = 11.9 Hz), 126.3, 124.9, 124.0, 119.2, 117.9, 116.6, 113.8, 112.9, 112.2, 55.2, 46.6 (d, *J* = 3.5 Hz), 40.6 (d, *J* = 69.0 Hz), 31.9 (d, *J* = 12.1 Hz), 11.2; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 27.2; HRMS m/z (ESI) calcd for $C_{32}H_{29}NO_3P$ ($[M+H]^+$) 506.1880, found 506.1887.

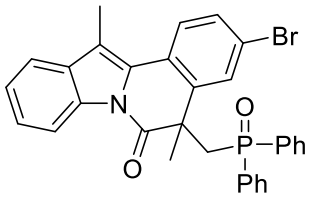
3-Chloro-5-((diphenylphosphoryl)methyl)-5,12-dimethylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ga):



56.0 mg, 55% yield; White solid; mp 225.1-226.7 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.52 (d, *J* = 7.5 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.55-7.54 (m, 1H), 7.51-7.44 (m, 4H), 7.42-7.39 (m, 1H), 7.36-7.31 (m, 4H), 7.23-7.13 (m, 5H), 3.75-3.69 (m, 1H), 2.97-2.92 (m, 1H), 2.58 (s, 3H), 1.76 (s, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1 (d, *J* = 3.1 Hz), 137.8 (d, *J* = 2.5 Hz), 134.3, 133.4 (d, *J* = 31.3 Hz), 132.8, 132.6 (d, *J* = 31.3 Hz), 132.2, 131.4 (d, *J* = 2.9 Hz), 131.2 (d, *J* = 2.9 Hz), 130.5 (d, *J* = 9.5 Hz), 130.2 (d, *J* = 9.3 Hz), 128.8, 128.3 (d, *J* = 11.8 Hz), 128.1 (d, *J* = 11.6 Hz), 127.7, 127.5, 125.9, 125.7, 124.8, 124.1, 118.3, 116.8, 114.7, 46.0 (d, *J* = 3.8 Hz), 40.6 (d, *J* = 69.3 Hz), 31.7 (d, *J* = 12.4 Hz), 11.4;

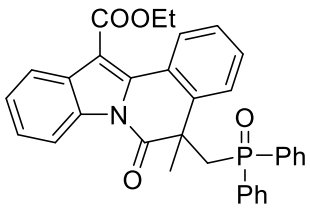
^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.1; HRMS m/z (ESI) calcd for $C_{31}H_{26}ClNO_2P$ ($[M+H]^+$) 510.1384, found 510.1392.

3-Bromo-5-((diphenylphosphoryl)methyl)-5,12-dimethylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ha):



46.5 mg, 42% yield; White solid; mp 238.4-239.5 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.57 (d, *J* = 7.0 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.56-7.54 (m, 1H), 7.52-7.40 (m, 5H), 7.37-7.27 (m, 6H), 7.25-7.18 (m, 3H), 3.75-3.70 (m, 1H), 2.97-2.92 (m, 1H), 2.58 (s, 3H), 1.76 (d, *J* = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1 (d, *J* = 3.0 Hz), 138.0 (d, *J* = 2.5 Hz), 134.3, 133.4 (d, *J* = 13.3 Hz), 132.6 (d, *J* = 13.3 Hz), 132.2, 131.5 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 2.6 Hz), 130.7, 130.6, 130.5 (d, *J* = 6.1 Hz), 130.2 (d, *J* = 9.3 Hz), 128.8, 128.3 (d, *J* = 11.8 Hz), 128.1 (d, *J* = 11.8 Hz), 126.0, 125.7, 125.2, 124.1, 121.0, 118.3, 116.8, 114.9, 46.0 (d, *J* = 3.6 Hz), 40.6 (d, *J* = 69.1 Hz), 31.7 (d, *J* = 12.3 Hz), 11.5; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.1; HRMS m/z (ESI) calcd for $C_{31}H_{26}BrNO_2P$ ($[M+H]^+$) 554.0879, found 554.0884.

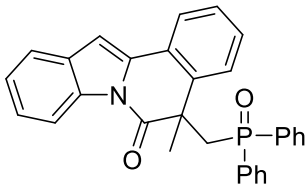
Ethyl 5-((diphenylphosphoryl)methyl)-5-methyl-6-oxo-5,6-dihydroindolo[2,1-a]-isoquinoline-12-carboxylate (3ia):



45.8 mg, 43% yield; White solid; mp 135.0-136.4 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.52-8.51 (m, 1H), 8.32-8.30 (m, 1H), 7.92-7.90 (m, 1H), 7.58-7.54 (m, 2H), 7.43-7.30 (m, 8H), 7.23-7.19 (m, 1H), 7.18-7.11 (m, 3H), 7.09-7.05 (m, 1H), 4.58-4.54 (m, 2H), 3.71-3.66 (m, 1H), 3.07-3.02 (m, 1H), 1.80 (d, *J* = 2.0 Hz, 3H), 1.52 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.6 (d, *J* = 3.1 Hz), 165.7, 137.1 (d, *J* = 2.8 Hz), 136.5, 134.1, 133.1 (d, *J* = 99.1 Hz), 132.1 (d, *J* = 98.5 Hz), 131.3 (d, *J* = 2.9 Hz), 131.2 (d, *J* = 2.6 Hz), 130.7 (d, *J* = 9.6 Hz), 130.6 (d, *J* = 9.1 Hz), 129.4, 128.9, 128.4 (d, *J* = 11.8 Hz), 128.1, 128.0, 127.6, 127.2 (d, *J* = 7.6 Hz), 126.0, 125.0, 123.3, 120.9, 116.6, 110.4, 61.2, 46.7 (d, *J* = 3.5 Hz), 40.7 (d, *J* = 68.5 Hz), 31.5 (d, *J* = 11.8 Hz), 14.4; ^{31}P NMR (202 MHz,

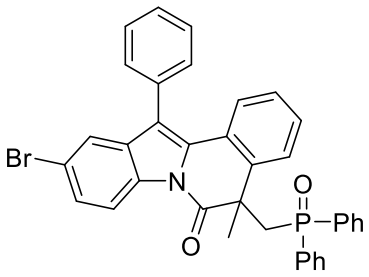
$CDCl_3$) δ: 27.0; HRMS m/z (ESI) calcd for $C_{33}H_{29}NO_4P$ ($[M+H]^+$) 534.1829, found 534.1831.

5-((diphenylphosphoryl)methyl)-5-methylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (3ja):



48.8 mg, 53% yield; White solid; mp 193.4-195.2 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.44-8.42 (m, 1H), 7.73-7.71 (m, 1H), 7.59-7.52 (m, 3H), 7.42-7.36 (m, 3H), 7.34-7.27 (m, 5H), 7.23-7.20 (m, 1H), 7.06-7.02 (m, 4H), 6.92 (s, 1H), 3.82-3.77 (m, 1H), 3.07-3.02 (m, 1H), 1.74 (d, *J* = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.9 (d, *J* = 2.1 Hz), 135.7 (d, *J* = 2.5 Hz), 135.3 (d, *J* = 6.6 Hz), 133.4 (d, *J* = 98.5 Hz), 132.2 (d, *J* = 97.9 Hz), 131.1 (d, *J* = 6.5 Hz), 131.1, 130.7 (d, *J* = 9.6 Hz), 130.6 (d, *J* = 9.3 Hz), 130.5, 128.3 (d, *J* = 11.8 Hz), 128.1, 127.9 (d, *J* = 11.8 Hz), 127.5 (d, *J* = 8.8 Hz), 124.9, 124.3, 124.2, 123.4, 120.2,116.8, 103.0, 46.2 (d, *J* = 3.5 Hz), 40.7 (d, *J* = 69.1 Hz), 32.9 (d, *J* = 13.5 Hz), ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.6; HRMS m/z (ESI) calcd for $C_{30}H_{25}NO_2P^+$ ($[M+H]^+$) 462.1617, found 462.1625.

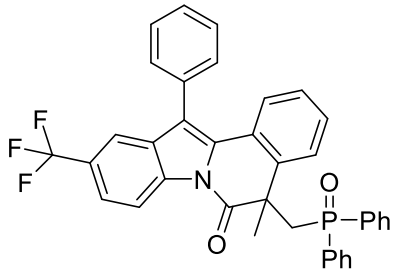
10-Bromo-5-((diphenylphosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ka):



76.3 mg, 62% yield; White solid; mp 175.1-176.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.38 (d, *J* = 8.5 Hz, 1H), 7.60-7.55 (m, 4H), 7.51-7.48 (m, 3H), 7.44-7.38 (m, 4H), 7.34-7.26 (m, 5H), 7.15-7.08 (m, 3H), 6.98-6.95 (m, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 3.80-3.75 (m, 1H), 3.09-3.03 (m, 1H), 1.79 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.1 (d, *J* = 2.3 Hz), 136.4 (d, *J* = 2.4 Hz), 134.0, 133.3 (d, *J* = 98.5 Hz), 133.5, 132.7, 132.1 (d, *J* = 97.8 Hz), 131.3 (d, *J* = 2.9 Hz), 131.2 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 9.5 Hz), 130.6, 130.5 (d, *J* = 9.1 Hz), 130.0, 129.3, 128.3 (d, *J* = 11.8 Hz), 128.2 (d, *J* = 13.3 Hz), 128.1, 127.9 (d, *J* = 11.8 Hz), 127.5, 127.0, 125.1, 124.3, 121.8, 119.0, 118.2, 117.8, 46.1 (d, *J* = 3.5 Hz), 40.9 (d, *J* = 68.8 Hz), 32.6 (d, *J* =

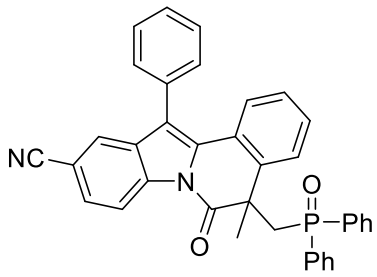
13.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.3; HRMS m/z (ESI) calcd for $C_{36}H_{28}BrNO_2P$ ($[M+H]^+$) 616.1036, found 616.1029.

5-((Diphenylphosphoryl)methyl)-5-methyl-12-phenyl-10-(trifluoromethyl)indolo[2,1-a]isoquinolin-6(5*H*)-one (3la):



96.8 mg, 80% yield; White solid; mp 210.1-211.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.65 (d, *J* = 8.5 Hz, 1H), 7.59-7.45 (m, 11H), 7.39-7.36 (m, 1H), 7.34-7.28 (m, 3H), 7.23 (d, *J* = 7 Hz, 1H), 7.14-7.11 (m, 3H), 6.95-6.92 (m, 1H), 6.90-6.86 (m, 1H), 3.82-3.77 (m, 1H), 3.11-3.06 (m, 1H), 1.81 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.4 (d, *J* = 2.3 Hz), 136.3 (d, *J* = 2.6 Hz), 135.6, 133.5, 133.3, 132.7, 132.0, 131.1, 130.6 (d, *J* = 9.5 Hz), 130.4 (d, *J* = 9.1 Hz), 130.0, 129.4, 128.3, 128.2 (d, *J* = 4.4 Hz), 128.0, 127.9, 127.3, 127.0, 126.5 (q, $J_{C\text{-}F}$ = 31.9 Hz), 125.2, 124.5 (d, $J_{C\text{-}F}$ = 270.5 Hz), 124.3, 122.1 (q, *J* = 3.5 Hz), 119.6, 117.0, 116.4 (q, *J* = 4.1 Hz), 46.1 (d, *J* = 3.5 Hz), 41.0 (d, *J* = 68.9 Hz), 32.4 (d, *J* = 13.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -61.1; HRMS m/z (ESI) calcd for $C_{37}H_{28}F_3NO_2P$ ($[M+H]^+$) 606.1804, found 606.1811.

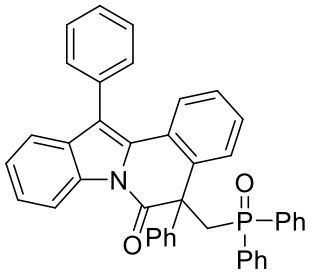
5-((Diphenylphosphoryl)methyl)-5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-a]isoquinoline-10-carbonitrile (3ma):



68.6 mg, 61% yield; White solid; mp 163.5-165.2 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.64 (d, *J* = 8.5 Hz, 1H), 7.61-7.47 (m, 11H), 7.40-7.35 (m, 2H), 7.31-7.27 (m, 2H), 7.21-7.16 (m, 4H), 6.92-6.86 (m, 2H), 3.82-3.77 (m, 1H), 3.11-3.06 (m, 1H), 1.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.6 (d, *J* = 2.0 Hz), 136.4 (d, *J* = 1.8 Hz), 136.0, 133.3 (d, *J* = 51.4 Hz), 132.9, 132.5 (d, *J* = 50.9 Hz), 131.7, 131.3 (d, *J* = 2.8 Hz), 131.2 (d, *J* = 2.6 Hz), 130.7 (d, *J* = 9.6 Hz), 130.4 (d, *J* = 9.1 Hz), 130.0, 129.5, 128.5 (d, *J* = 6.3 Hz), 128.4 (d, *J* = 6.5Hz), 128.3, 128.1 (d, *J* = 11.8 Hz), 127.4, 127.1, 125.3, 124.1, 123.9, 119.6, 119.1, 117.5, 107.6, 46.2 (d, *J* = 3.6 Hz), 41.1 (d, *J* = 68.9

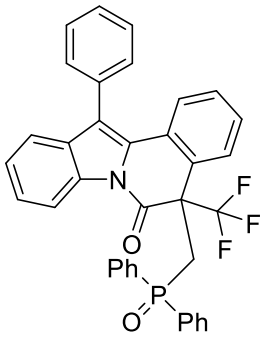
Hz), 32.5 (d, J = 13.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.3; HRMS m/z (ESI) calcd for $C_{37}H_{28}N_2O_2P^+$ ([M+H]$^+$) 563.1883, found 563.1891.

5-((Diphenylphosphoryl)methyl)-5,12-diphenylindolo[2,1-a]isoquinolin-6(5H)-one (3na):



83.9 mg, 70% yield; White solid; mp 228.4-229.5 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.44 (d, J = 8.5 Hz, 1H), 7.69-7.65 (m, 2H), 7.58-7.41 (m, 6H), 7.45-7.42 (m, 1H), 7.38-7.34 (m, 3H), 7.31-7.12 (m, 12H), 6.98 (d, J = 8.0 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.5 Hz, 1H), 4.52-4.47 (m, 1H), 3.46-3.41 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.2, 144.0 (d, J = 12.8 Hz), 135.4 (d, J = 2.5 Hz), 134.4, 134.1, 133.4 (d, J = 99.4 Hz), 132.5 (d, J = 98.0 Hz), 132.2, 131.3 (d, J = 2.4 Hz), 131.2 (d, J = 2.5 Hz), 131.0 (d, J = 9.6 Hz), 130.7 (d, J = 9.1 Hz), 130.2, 129.7, 129.5, 129.2, 128.7, 128.4 (d, J = 11.8 Hz), 128.0, 127.9, 127.6 (d, J = 5.3 Hz), 127.2, 126.8, 126.2, 125.6, 124.9, 124.4, 120.6, 119.2, 116.8, 53.8 (d, J = 2.6Hz), 39.8 (d, J = 68.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.8; HRMS m/z (ESI) calcd for $C_{41}H_{31}NO_2P$ ([M+H]$^+$) 600.2087, found 600.2081.

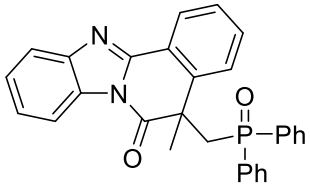
5-((Diphenylphosphoryl)methyl)-12-phenyl-5-(trifluoromethyl)indolo[2,1-a]isoquinolin-6(5*H*)-one (3oa):



66.2 mg, 56% yield; White solid; mp 237.6-239.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.57 (d, J = 8.0 Hz, 1H), 7.69-7.65 (m, 2H), 7.55-7.45 (m, 8H), 7.43-7.38 (m, 3H), 7.36-7.34 (m, 1H), 7.29-7.20 (m, 4H), 7.18-7.14 (m, 2H), 7.03-6.99 (m, 1H), 6.88-6.85 (m, 1H), 4.26-4.21 (m, 1H), 3.39-3.34 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.3, 134.4, 133.6, 132.7 (d, J = 82.3 Hz), 131.9 (d, J = 81.3 Hz), 132.0, 131.7 (d, J = 2.9 Hz), 131.6 (d, J = 2.9 Hz), 131.2 (d, J = 10.0 Hz), 130.9 (d, J = 9.1 Hz), 129.9, 129.3, 128.8, 128.6 (d, J = 7.0 Hz), 128.5, 128.2, 128.1 (d, J = 12.1 Hz), 127.4, 127.0, 126.2, 126.0 (d, $J_{C\text{-}F}$ = 1.8 Hz), 125.4, 124.9, 121.7, 119.6, 116.7, 54.9 (q, $J_{C\text{-}F}$ = 25.0 Hz),

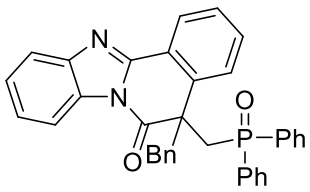
32.9 (d, J = 70.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -72.2; HRMS m/z (ESI) calcd for $C_{36}H_{26}F_3NO_2P$ ($[M+H]^+$) 592.1648, found 592.1655.

5-((Diphenylphosphoryl)methyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5*H*)-one (3pa):



71.1 mg, 77% yield; White solid; mp 231.5-232.7 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.39-8.37 (m, 1H), 8.30-8.28 (m, 1H), 7.80-7.78 (m, 1H), 7.46-7.37 (m, 7H), 7.33-7.28 (m, 3H), 7.21-7.09 (m, 5H), 3.86-3.81 (m, 1H), 3.13-3.08 (m, 1H), 1.78 (d, J = 2.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.3 (d, J = 1.6 Hz), 149.6, 143.8, 138.8, 132.7 (d, J = 30.3 Hz), 131.9 (d, J = 29.5 Hz), 131.6 (d, J = 2.6 Hz), 131.4, 131.3 (d, J = 2.8 Hz), 130.8, 130.6 (d, J = 9.6 Hz), 130.5 (d, J = 9.3 Hz), 128.4 (d, J = 11.9 Hz), 128.2 (d, J = 11.8 Hz), 127.9, 127.2, 125.6 (d, J = 2.6 Hz), 125.3, 122.6, 119.6, 115.8, 46.5 (d, J = 3.6 Hz), 41.0 (d, J = 69.0 Hz), 32.8 (d, J = 13.5 Hz), ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.6; HRMS m/z (ESI) calcd for $C_{29}H_{24}N_2O_2P$ ($[M+H]^+$) 463.1570, found 463.1567.

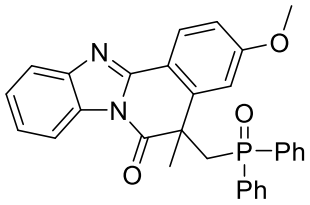
5-Benzyl-5-((diphenylphosphoryl)methyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (3qa):



64.6 mg, 60% yield; White solid; mp 160.9-162.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.27-8.25 (m, 1H), 8.16 (d, J = 7.5 Hz, 1H), 7.63-7.61 (m, 1H), 7.57-7.53 (m, 2H), 7.46-7.38 (m, 3H), 7.37-7.31 (m, 6H), 7.23-7.19 (m, 1H), 7.10-7.09 (m, 3H), 6.84 (t, J = 7.5 Hz, 1H), 6.73 (t, J = 7.5 Hz, 2H), 6.43 (d, J = 7.5 Hz, 2H), 4.06-4.01 (m, 1H), 3.56 (d, J = 13.0Hz, 1H), 3.30-3.22 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.4 (d, J = 0.8Hz), 149.1, 143.4, 136.3 (d, J = 2.5 Hz), 133.2 (d, J = 2.5 Hz), 132.7 (d, J = 77.6 Hz), 132.6 (d, J = 2.6 Hz), 132.0 (d, J = 76.9 Hz), 131.5 (d, J = 2.6 Hz), 131.4 (d, J = 2.8 Hz), 130.8, 130.7 (d, J = 12.3 Hz), 130.6, 130.4, 129.0, 128.4 (d, J = 11.9 Hz), 128.1, 128.0, 127.8, 127.6, 127.3, 125.4, 125.1 (d, J = 16.8 Hz), 124.4, 119.4, 115.4, 52.6 (d, J = 13.6 Hz), 52.4 (d, J = 3.5 Hz), 40.0

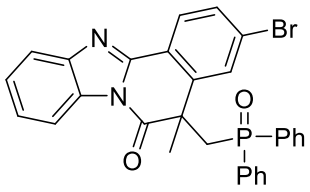
(d, J = 68.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.5; HRMS m/z (ESI) calcd for $C_{35}H_{28}N_2O_2P$ ($[M+H]^+$) 539.1883, found 539.1875.

5-((diphenylphosphoryl)methyl)-3-methoxy-5-methylbenzo[4,5]imidazo[2,1-*a*]isoquinolin-6(5*H*)-one (3ra):



79.7 mg, 81% yield; White solid; mp 239.5-240.7 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.31-8.27 (m, 2H), 7.74 (d, J = 7.0 Hz, 1H), 7.49-7.43 (m, 4H), 7.41-7.37 (m, 2H), 7.36-7.34 (m, 1H), 7.33-7.29 (m, 2H), 7.25-7.17 (m, 3H), 6.84-6.82 (m, 1H), 6.66 (d, J = 2.0 Hz, 1H), 3.84-3.79 (m, 1H), 3.67 (s, 3H), 3.06-3.02 (m, 1H), 1.77 (d, J = 2.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.4 (d, J = 1.9 Hz), 161.6, 149.8, 144.0, 140.9 (d, J = 2.4 Hz), 133.1 (d, J = 32.9 Hz), 132.3 (d, J = 30.6 Hz), 131.6 (d, J = 2.8 Hz), 131.4, 131.1 (d, J = 2.9Hz), 130.6 (d, J = 9.6 Hz), 130.5 (d, J = 9.3 Hz), 128.2 (d, J = 11.9 Hz), 127.6, 125.5, 124.8, 119.2, 115.6 (2C), 114.0, 112.6, 55.2, 46.7 (d, J = 3.6 Hz), 41.0 (d, J = 69.1 Hz), 32.7 (d, J = 13.3 Hz), ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.4; HRMS m/z (ESI) calcd for $C_{30}H_{26}N_2O_3P^+$ ($[M+H]^+$) 493.1676, found 493.1682.

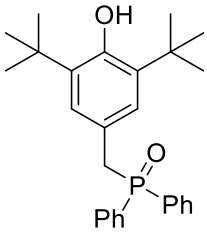
3-bromo-5-((diphenylphosphoryl)methyl)-5-methylbenzo[4,5]imidazo[2,1-*a*]isoquinolin-6(5*H*)-one (3sa):



54.0 mg, 50% yield; White solid; mp 232.1-233.9 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.35-8.33 (m, 1H), 8.24 (d, J = 8.5 Hz, 1H), 7.80-7.79 (m, 1H), 7.57-7.53 (m, 2H), 7.43-7.39 (m, 3H), 7.38-7.28 (m, 8H), 7.18 (d, J = 2.0 Hz, 1H), 3.83-3.77 (m, 1H), 3.03-2.99 (m, 1H), 1.77 (d, J = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.6 (d, J = 1.6 Hz), 148.8, 143.9, 140.6 (d, J = 2.4 Hz), 133.1 (d, J = 99.4 Hz), 132.1 (d, J = 99.0 Hz), 131.7 (d, J = 7.8 Hz), 131.7 (d, J = 2.1Hz), 131.6, 131.3, 130.4 (d, J = 8.4 Hz), 130.4, 130.2 (d, J = 9.5 Hz), 128.5 (d, J = 7.9 Hz), 128.4 (d, J = 7.9 Hz), 127.0, 125.6 (d, J = 20.0 Hz), 125.3, 122.0, 119.7, 115.8, 46.3 (d, J = 3.6 Hz), 41.1 (d, J = 69.0 Hz), 32.1 (d, J = 13.3 Hz), ^{31}P NMR (202 MHz, $CDCl_3$) δ: 26.0; HRMS m/z (ESI) calcd for $C_{29}H_{23}BrN_2O_2P^+$ ($[M+H]^+$)

541.0675, found 541.0671.

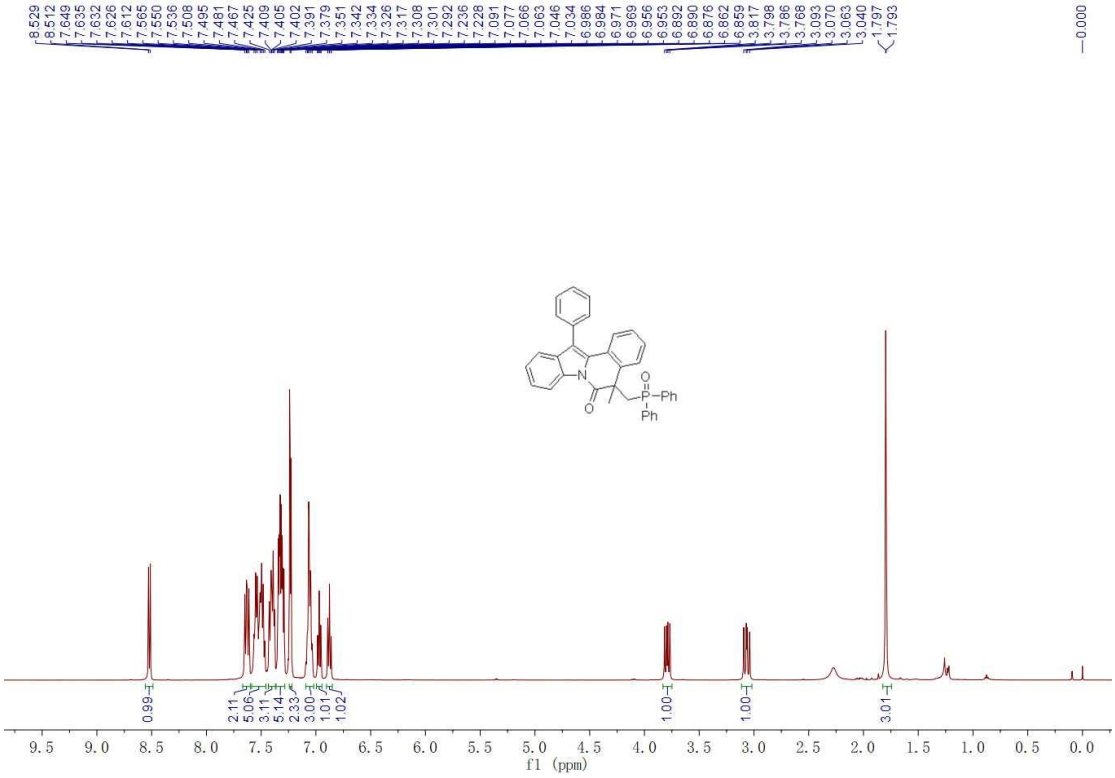
(3,5-Di-tert-butyl-4-hydroxybenzyl)diphenylphosphine oxide (4)

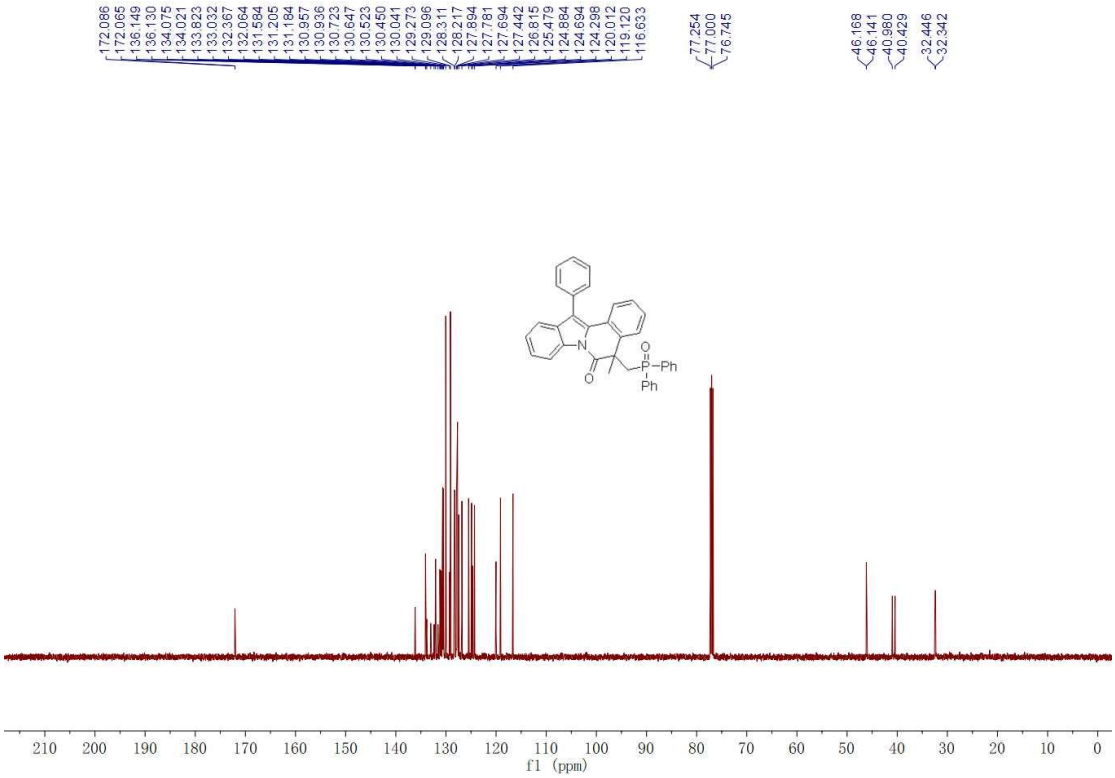


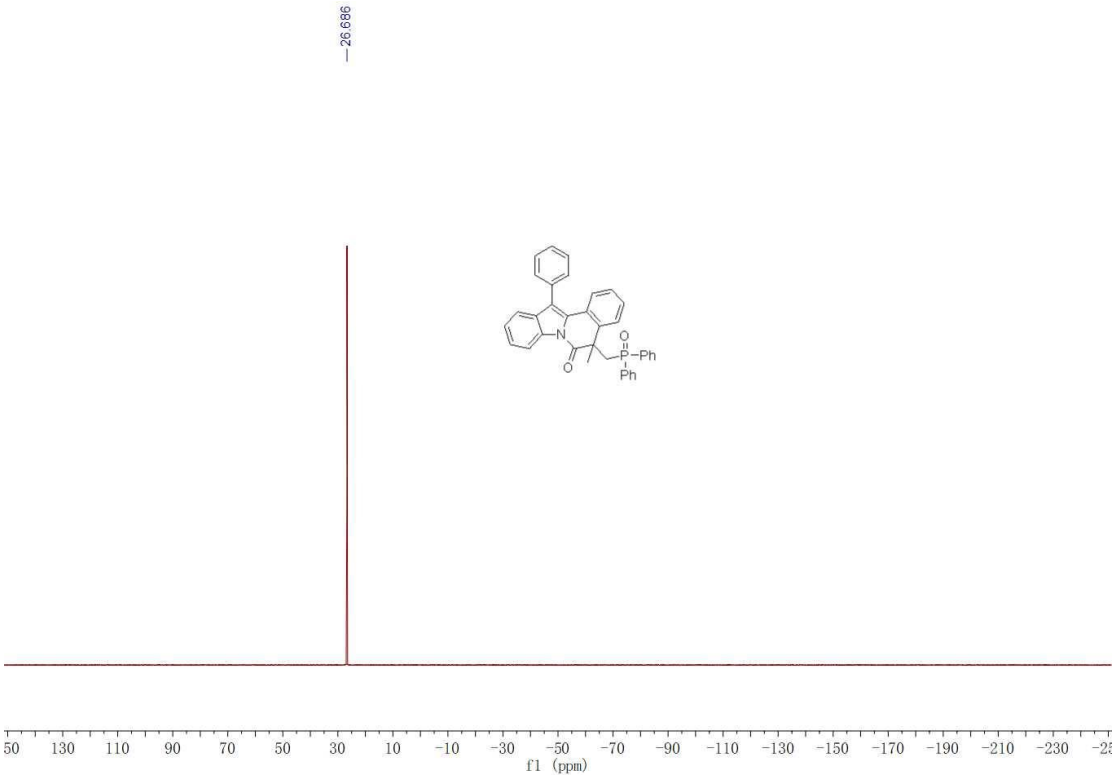
26.0 mg, 31% yield; White solid; mp 169.5-171.3 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.68-7.64 (m, 4H), 7.53-7.49 (m, 2H), 7.45-7.41 (m, 4H), 6.73 (d, *J* = 2.5 Hz, 2H), 5.09 (s, 1H), 3.59 (s, 1H), 3.56 (s, 1H), 1.28 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 152.7 (d, *J* = 3.3 Hz), 135.7 (d, *J* = 2.8 Hz), 132.7, 131.9, 131.6 (d, *J* = 2.8 Hz), 131.4 (d, *J* = 8.9 Hz), 128.3 (d, *J* = 11.4 Hz), 126.9 (d, *J* = 5.0 Hz), 121.1 (d, *J* = 8.0 Hz), 38.0 (d, *J* = 66.8 Hz), 34.1, 30.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 30.1; HRMS m/z (ESI) calcd for $C_{27}H_{34}O_2P$ ($[M+H]^+$) 421.2291, found 421.2295.

(C) Spectra

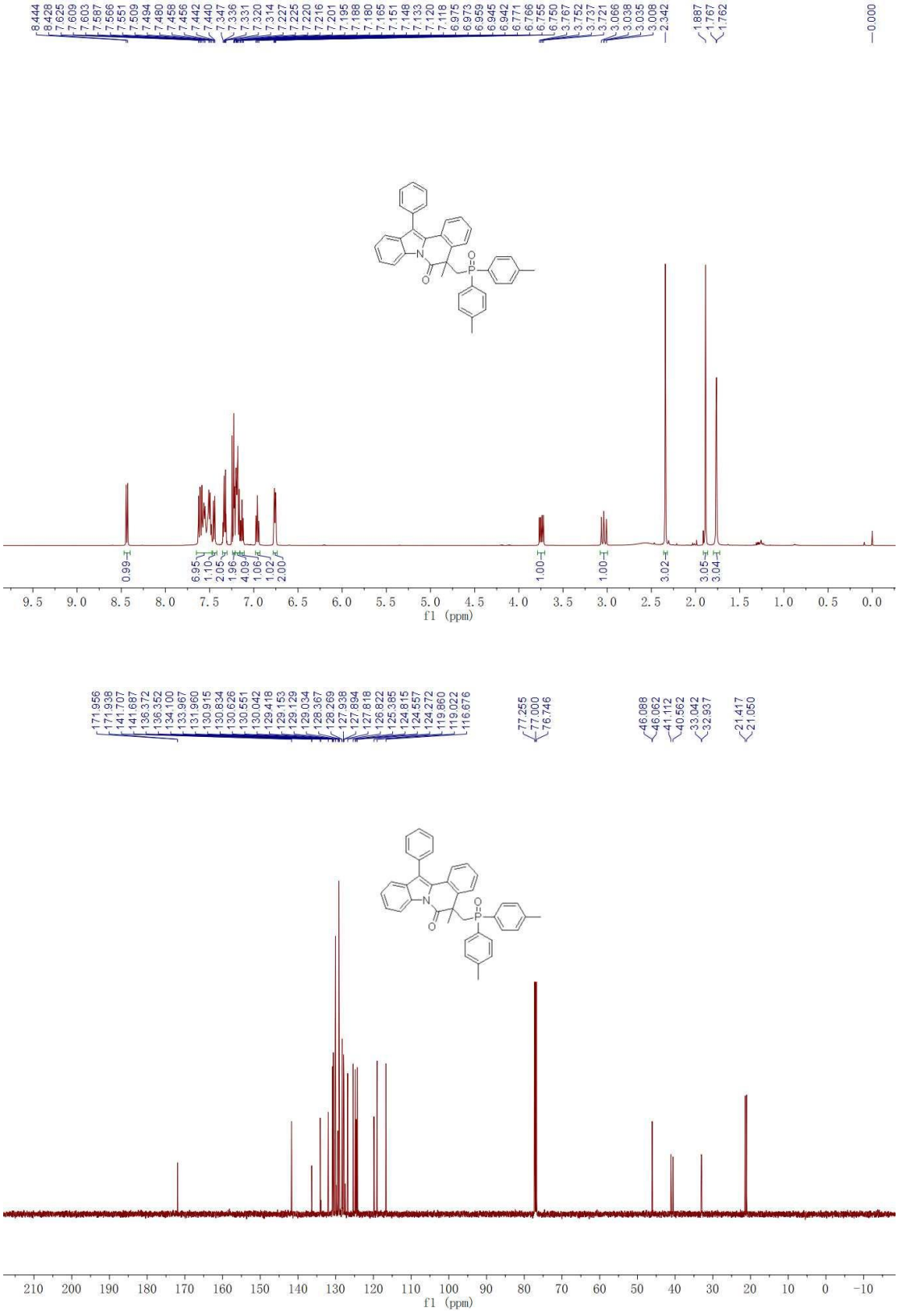
5-((Diphenylphosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3aa)

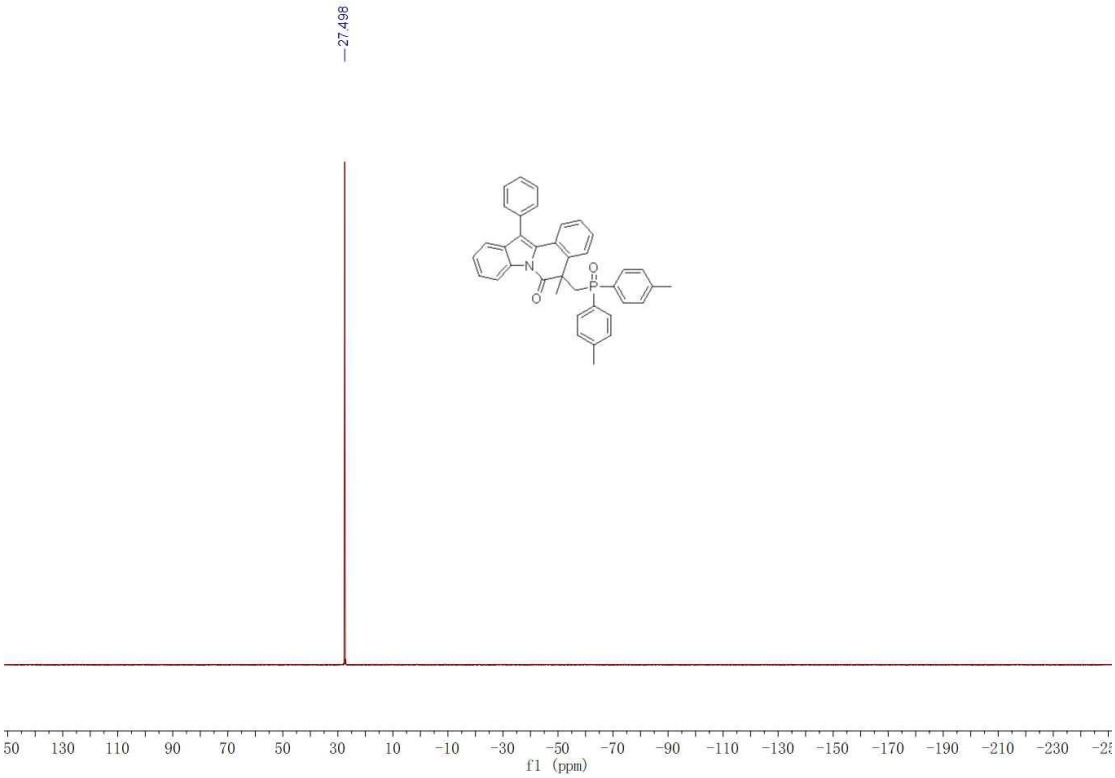




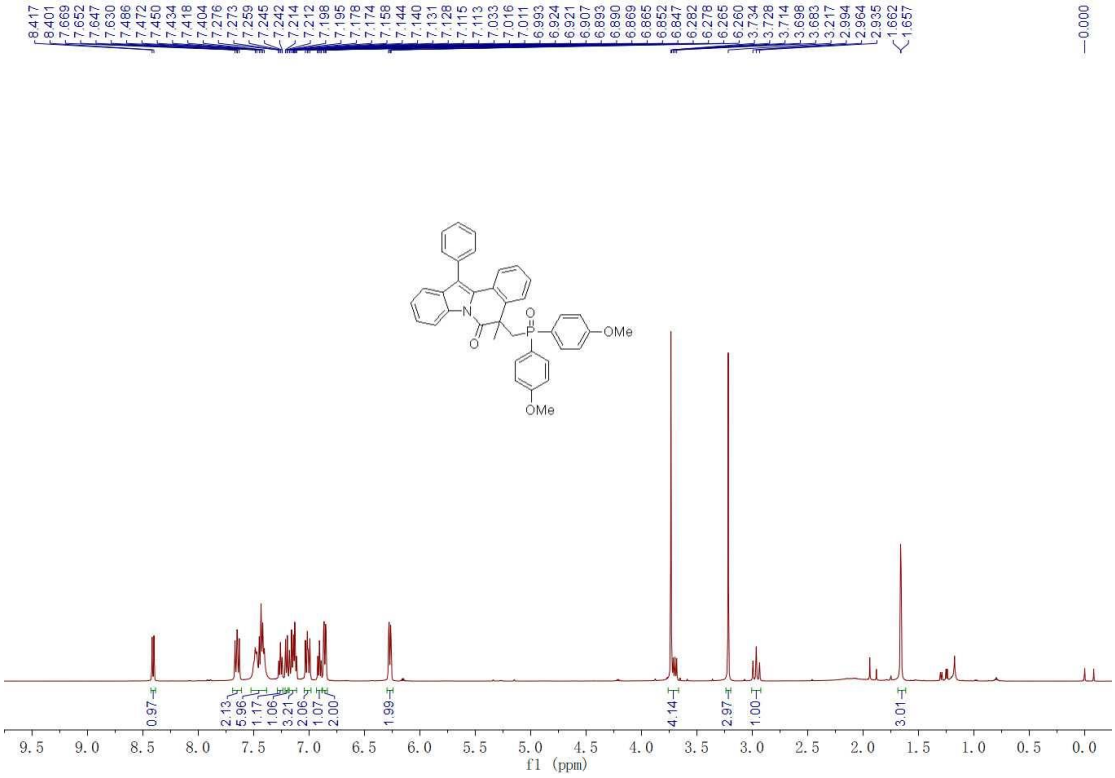

26.686
O
P–Ph
Ph
N
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

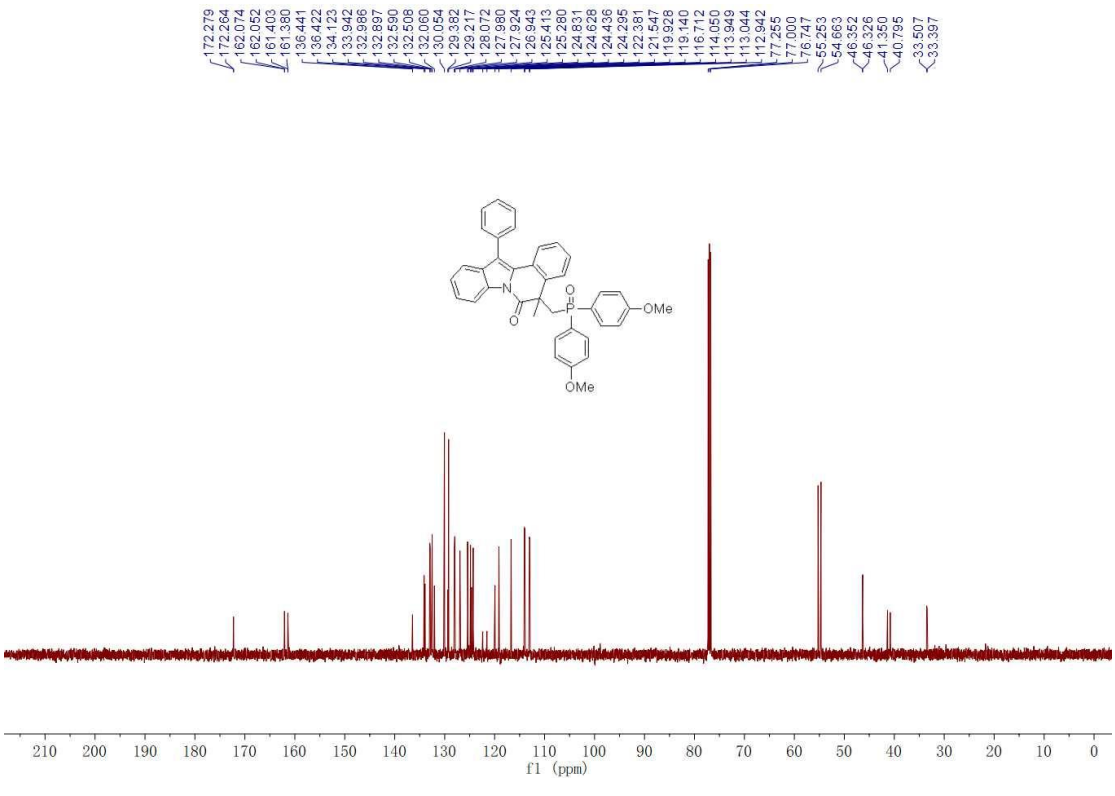
5-((Di-*p*-tolylphosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ab)

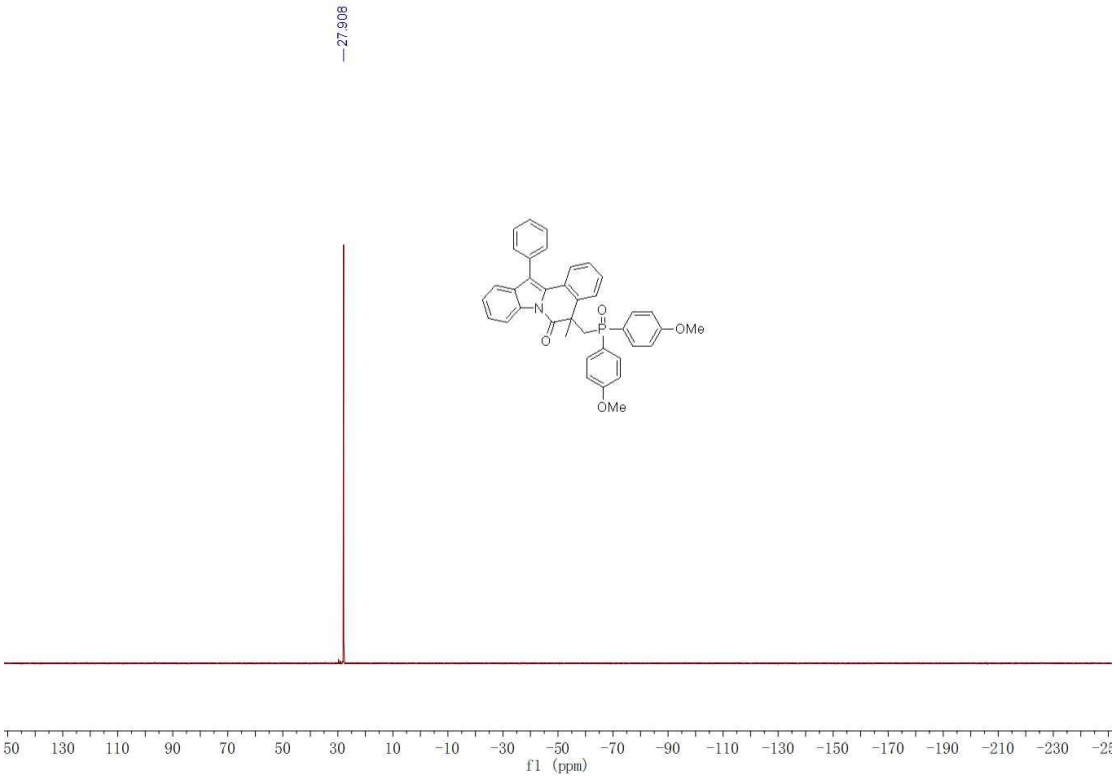



27.498
N
O
O
P
50
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
−230
f1 (ppm)

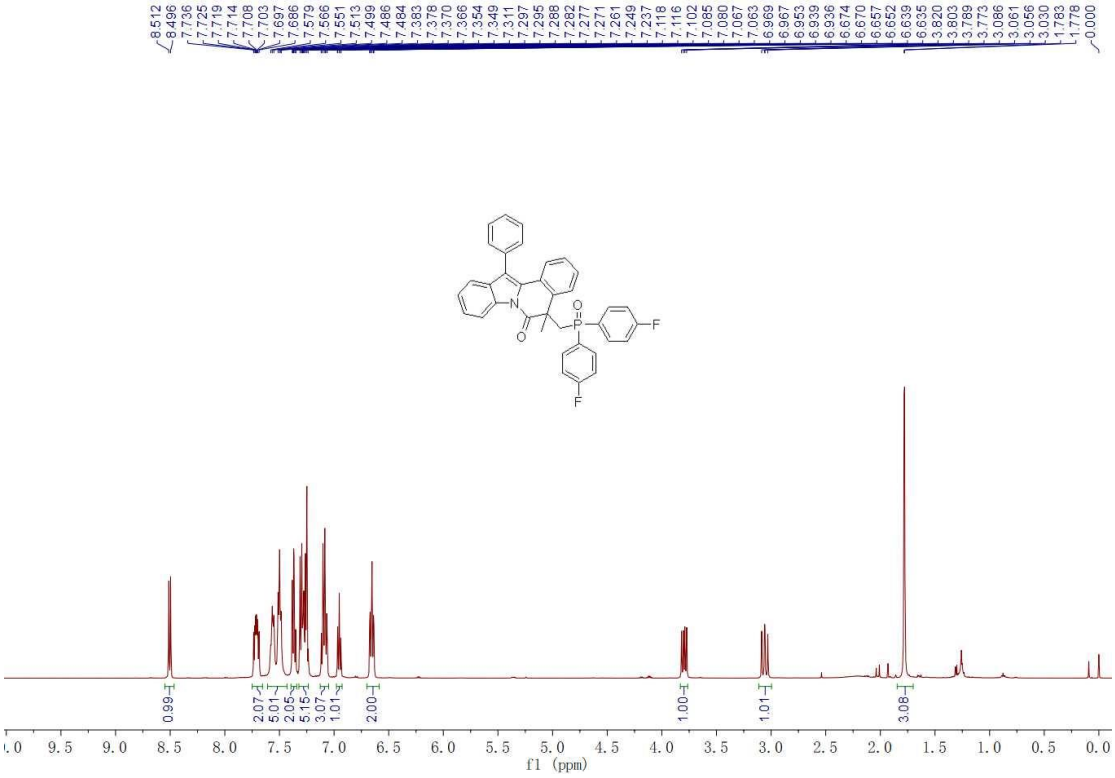
5-((Bis(4-methoxyphenyl)phosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ac)

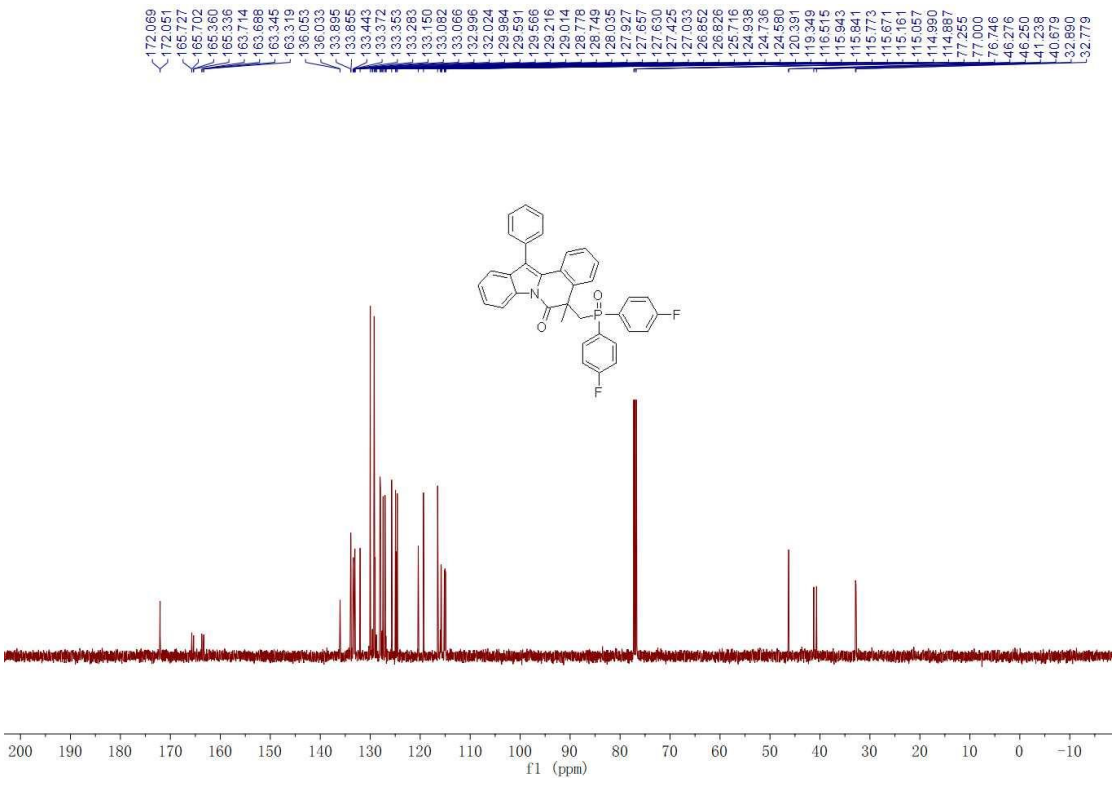


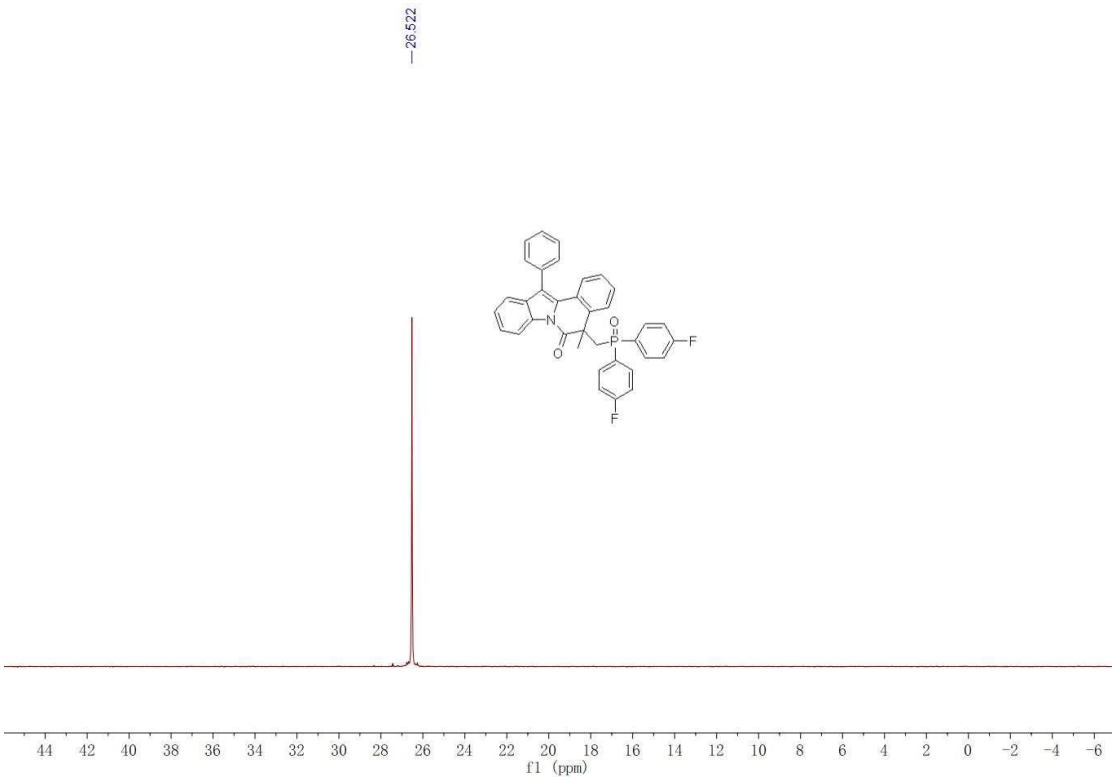


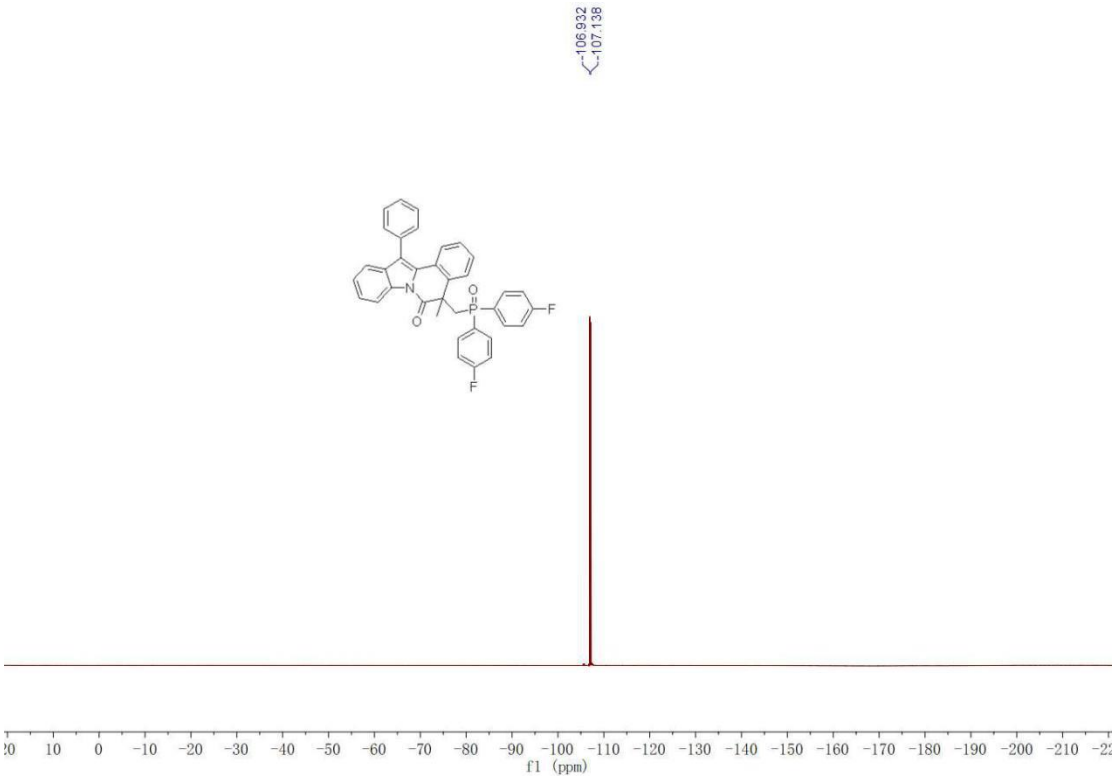

27.908
O
N
O
P
O
OMe
OMe
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

5-((Bis(4-fluorophenyl)phosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ad)

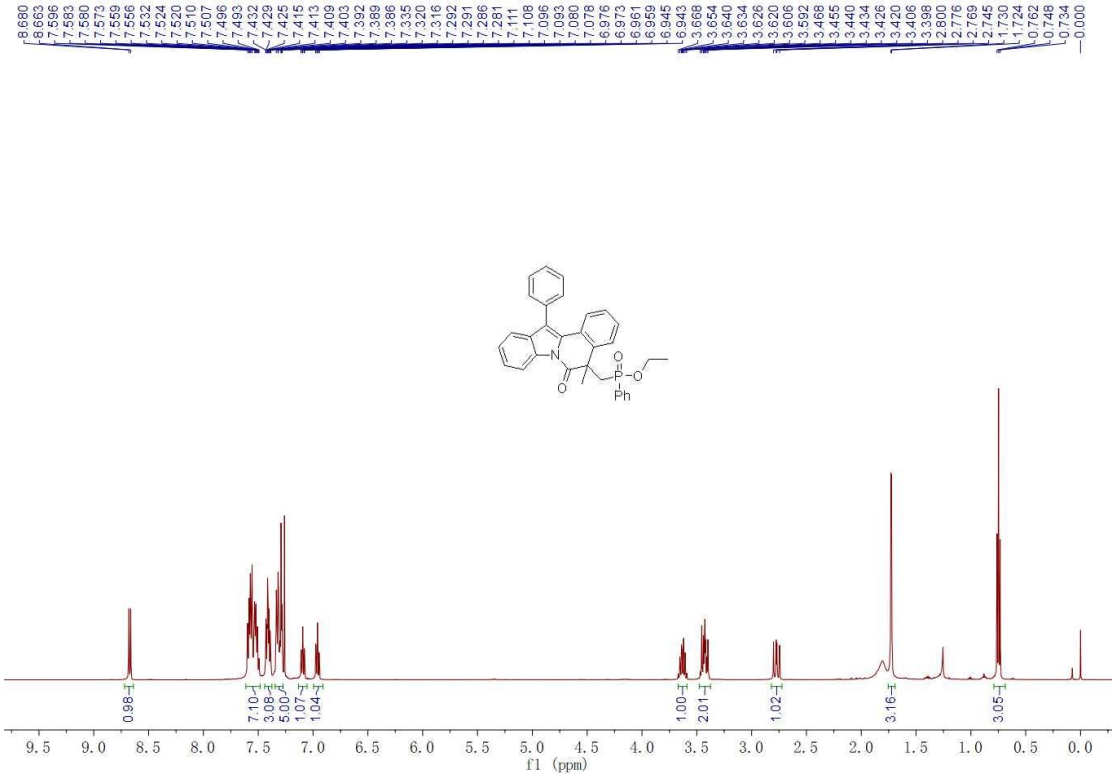


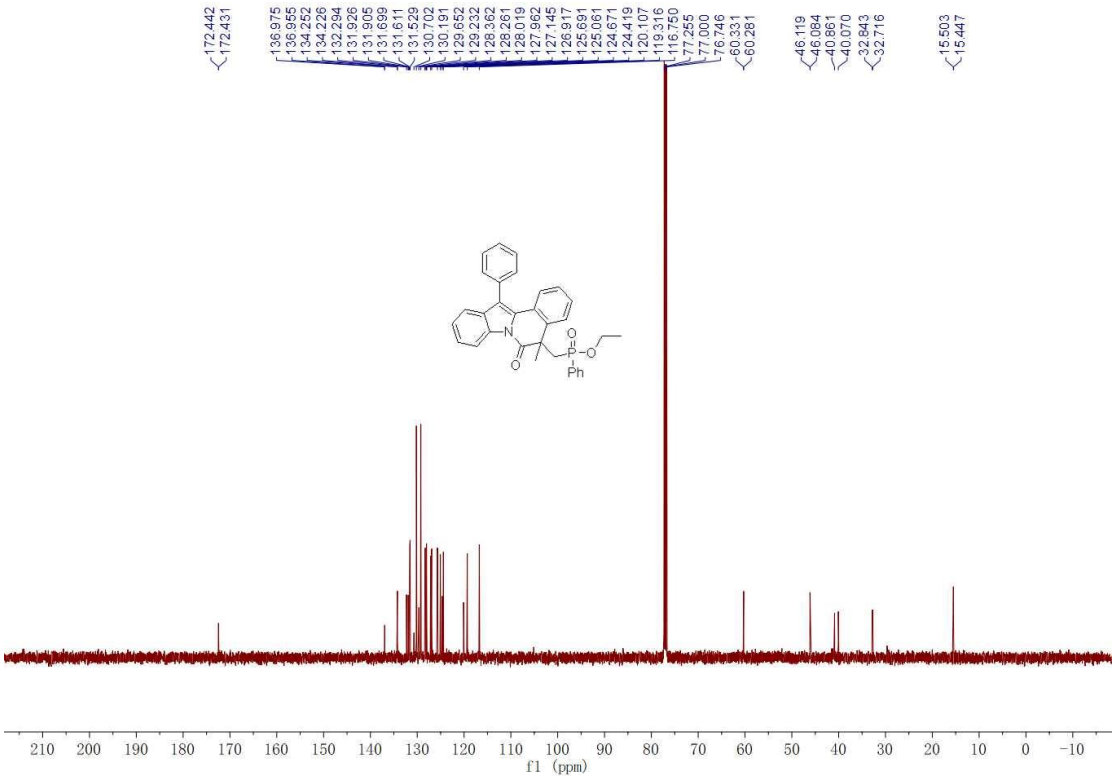


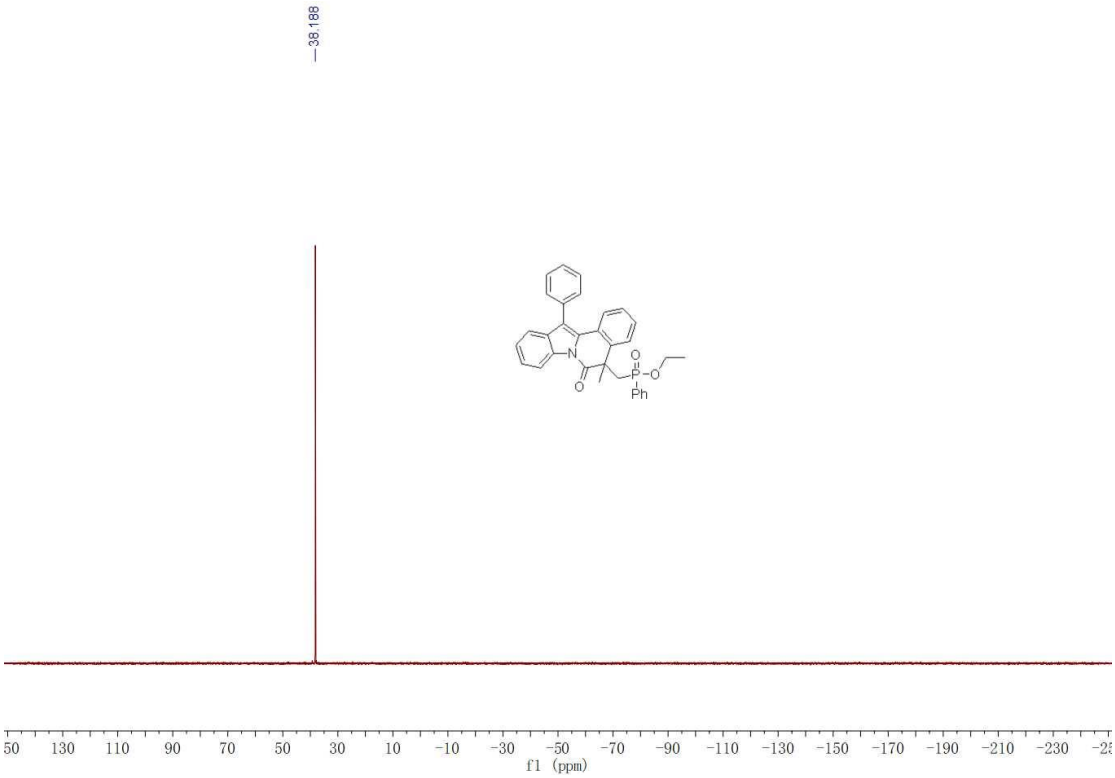

26.522
O
N
O
P
F
F
44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 −2 −4 −6
f1 (ppm)


106.932
107.138
O
N
O
P
F
F
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

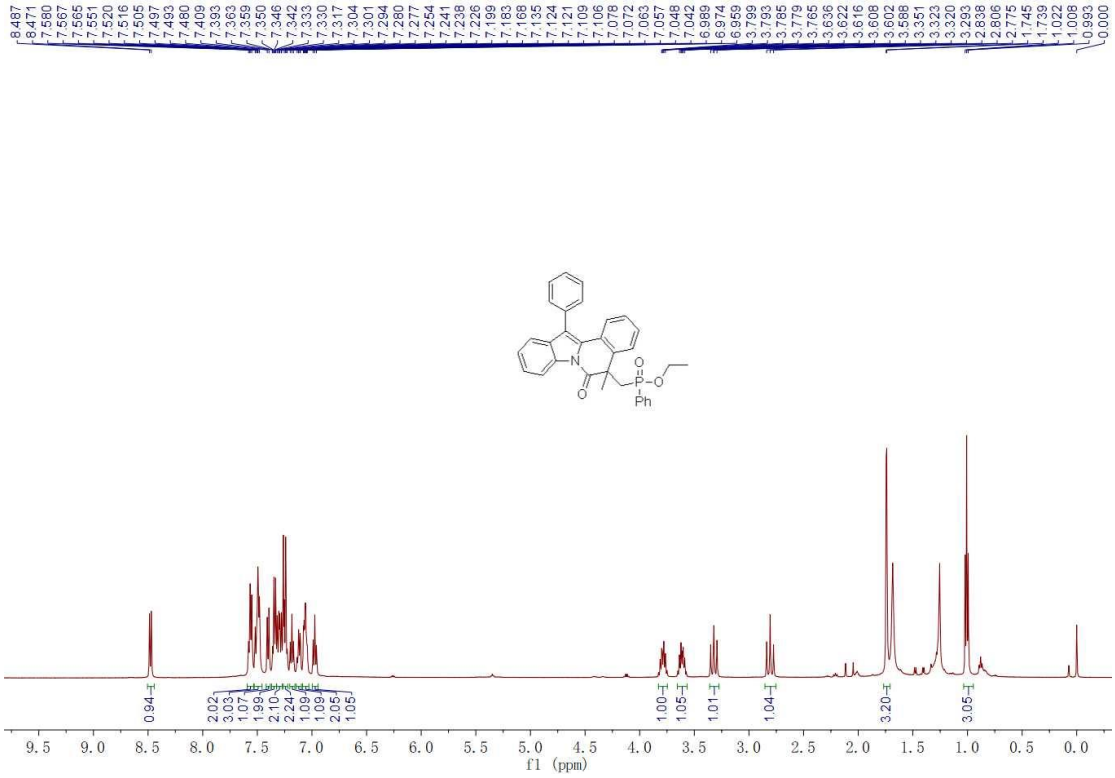
Ethyl ((5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-a]isoquinolin-5-yl)methyl)(phenyl)phosphinate (3ae)

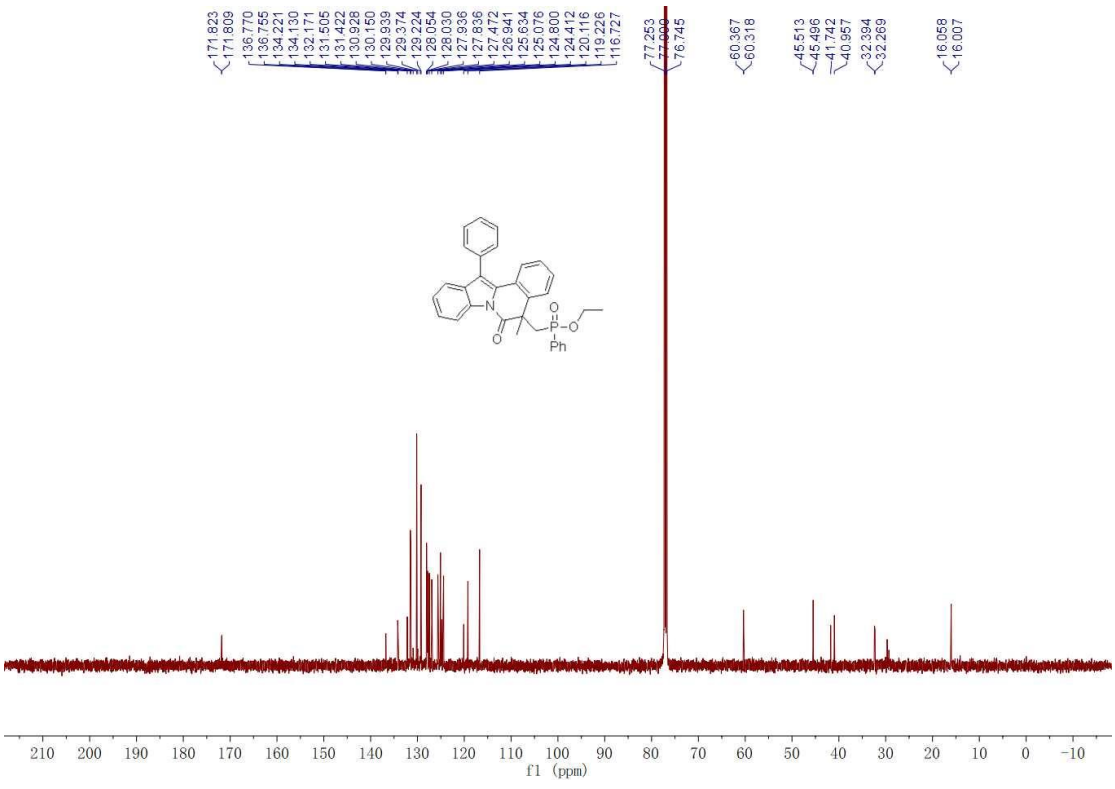


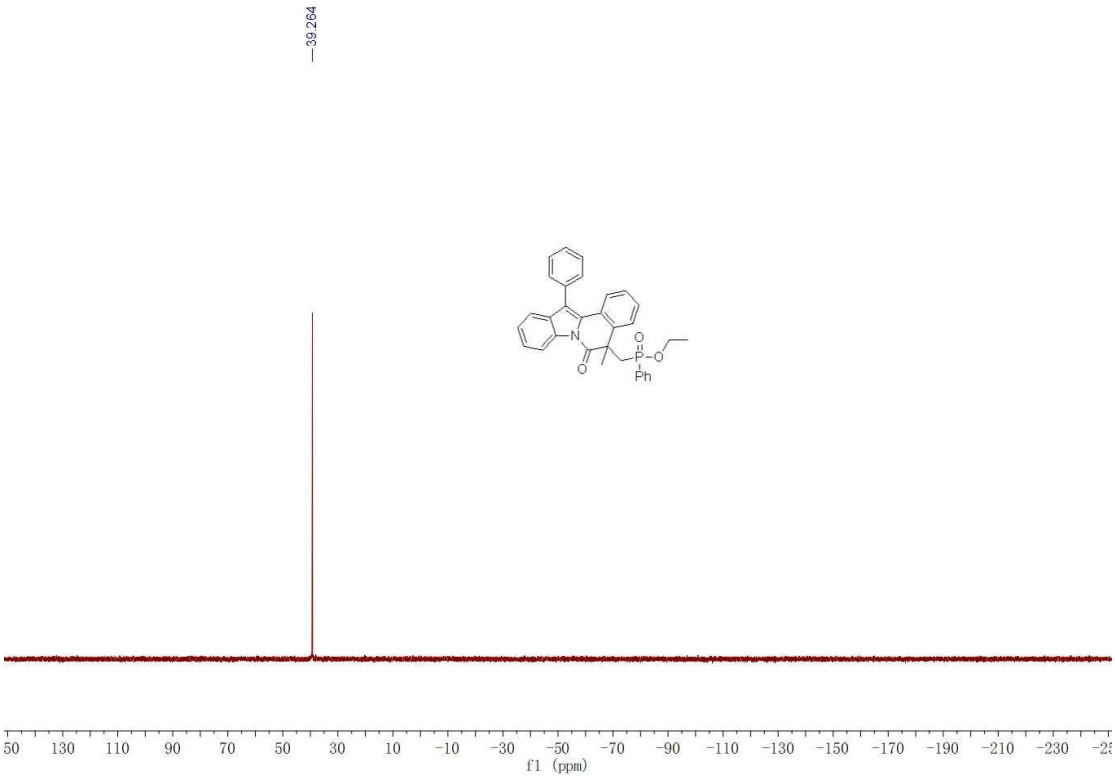



38.188
O
O
P
O
Ph
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

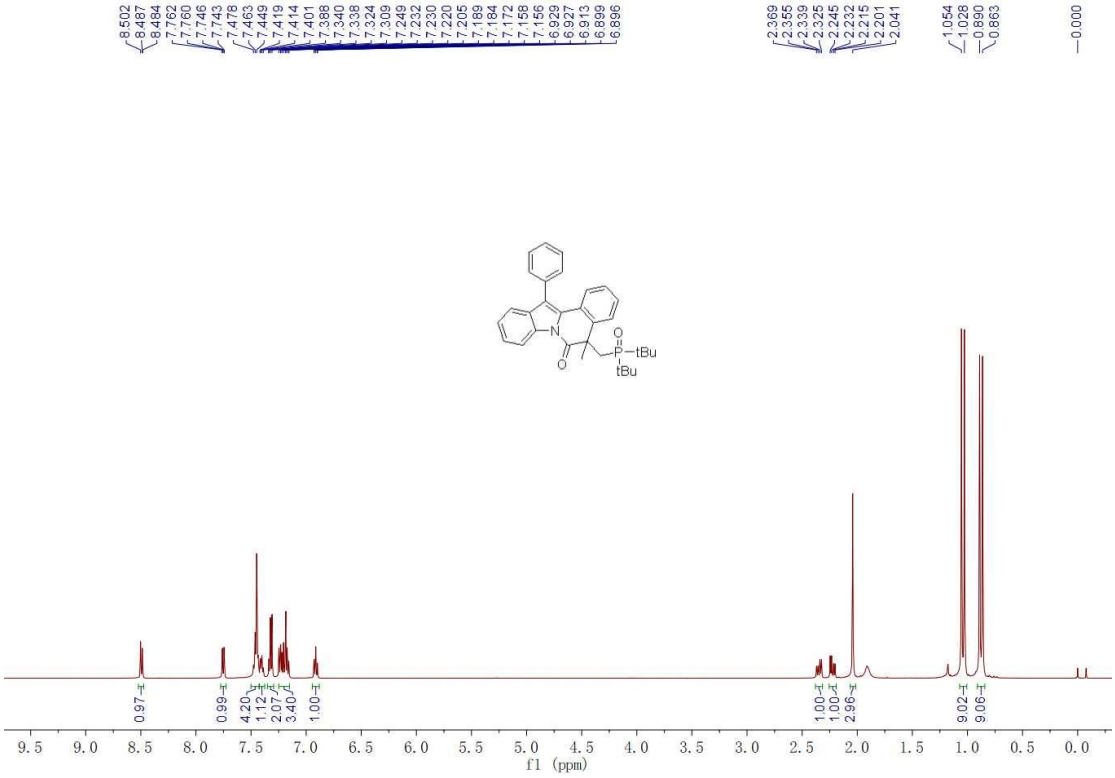
Ethyl ((5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-a]isoquinolin-5-yl)methyl)(phenyl)phosphinate (3ae)

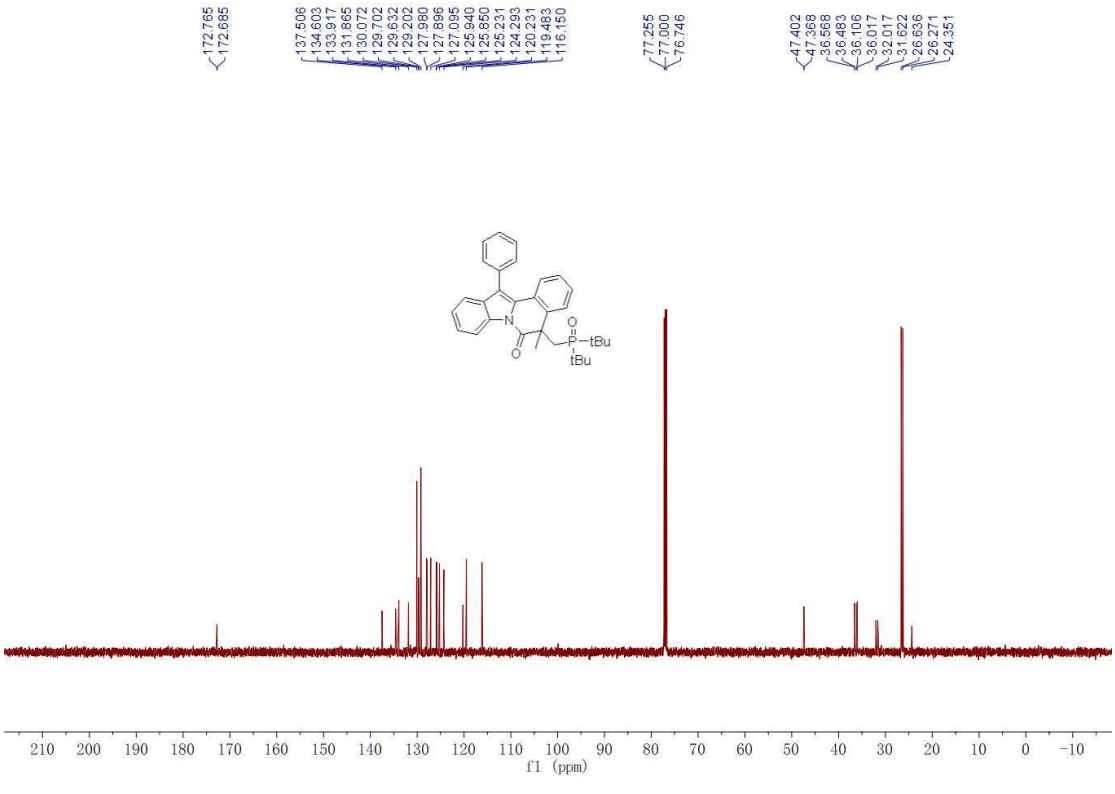


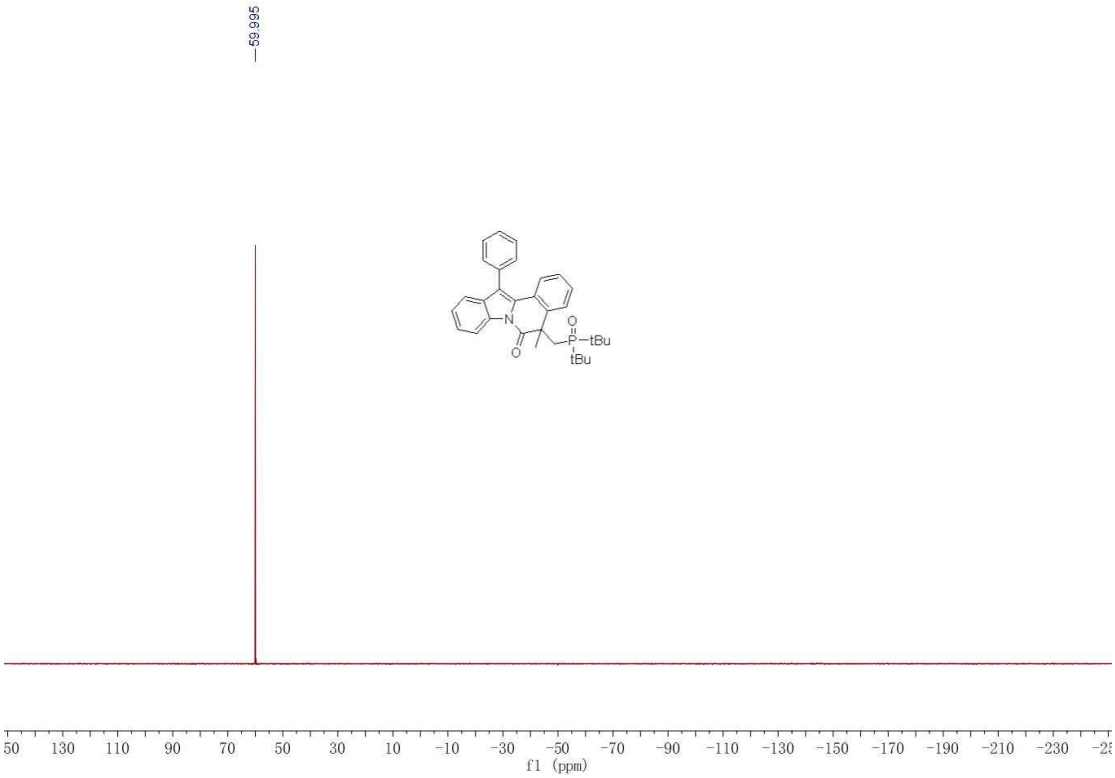



39.264
O
N
O
P
O
Ph
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

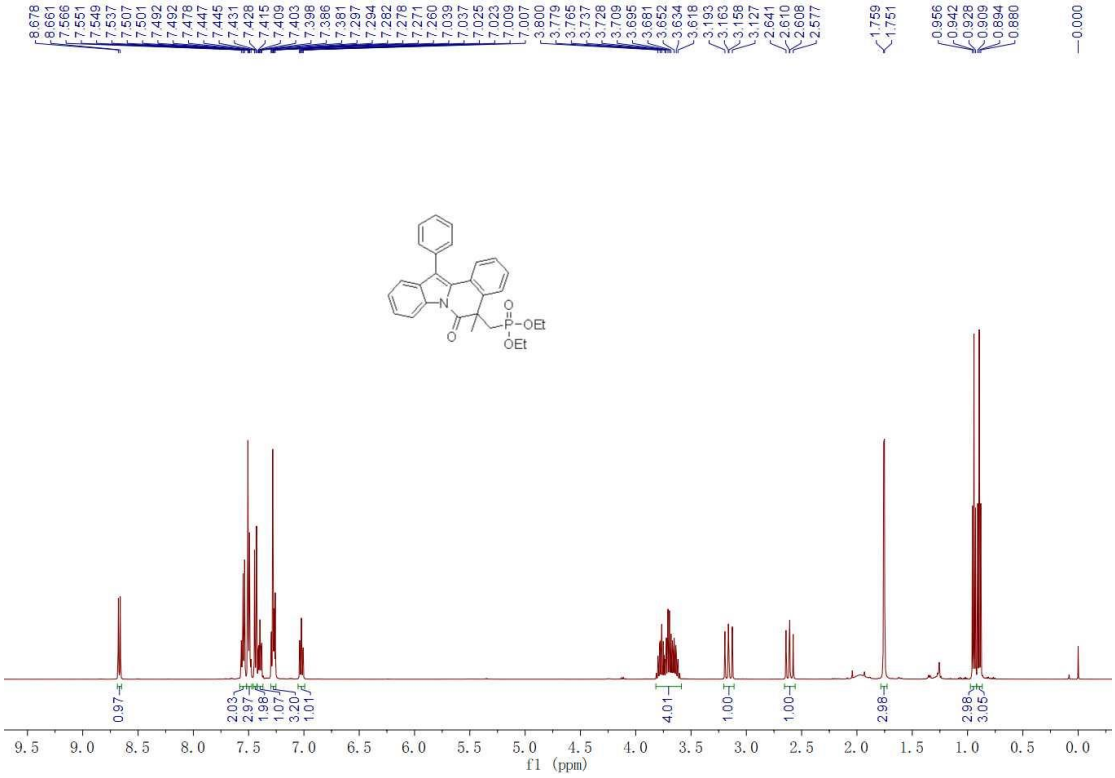
5-((Di-*tert*-butylphosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3af)

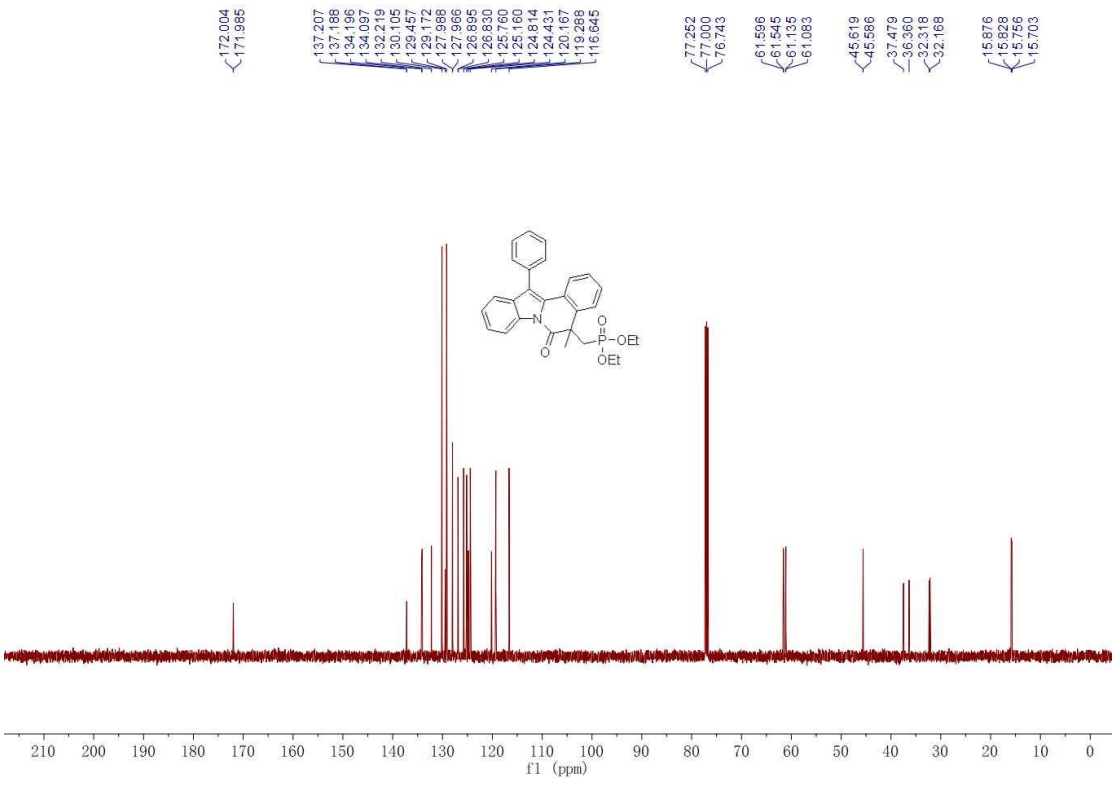


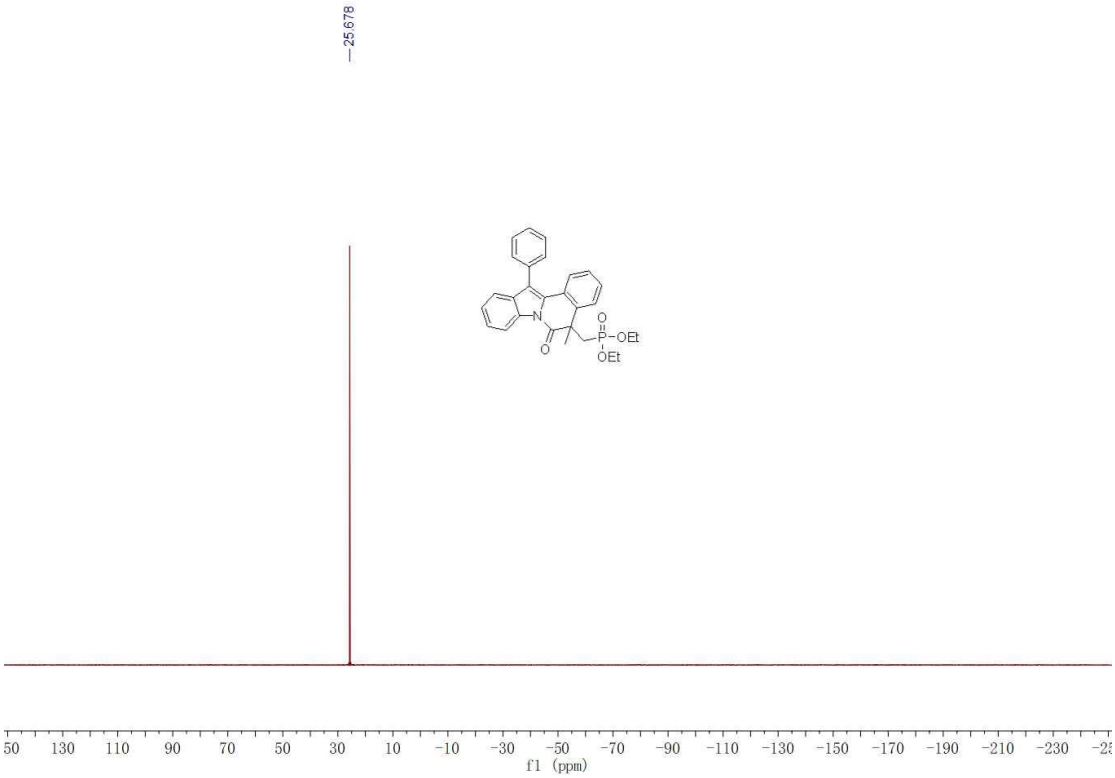



59.995
O
P—tBu
tBu
N
O
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

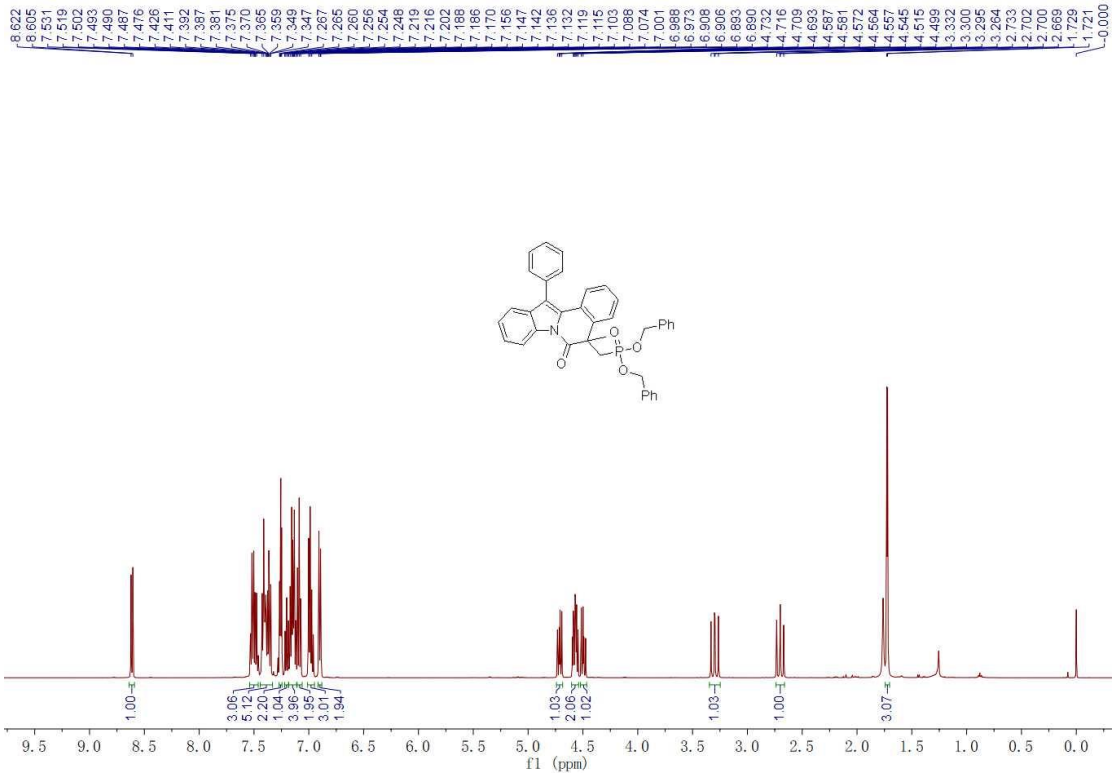
Diethyl ((5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-a]isoquinolin-5-yl)methyl)phosphonate (3ag)

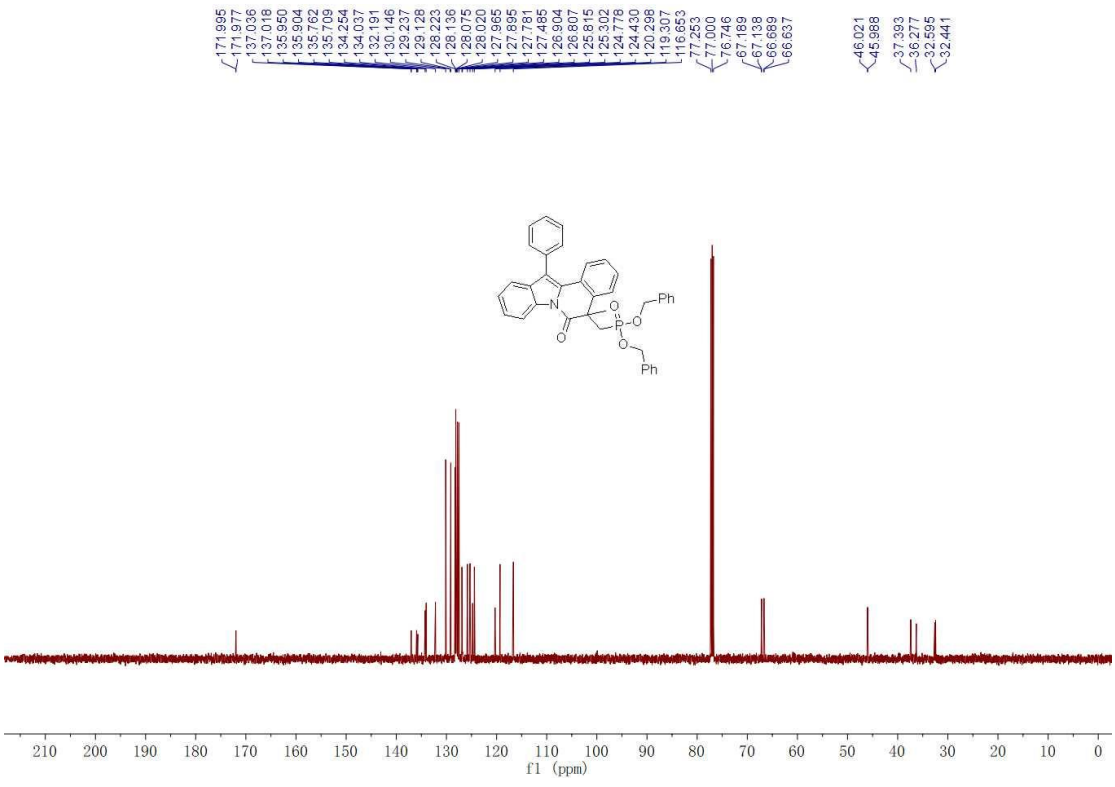


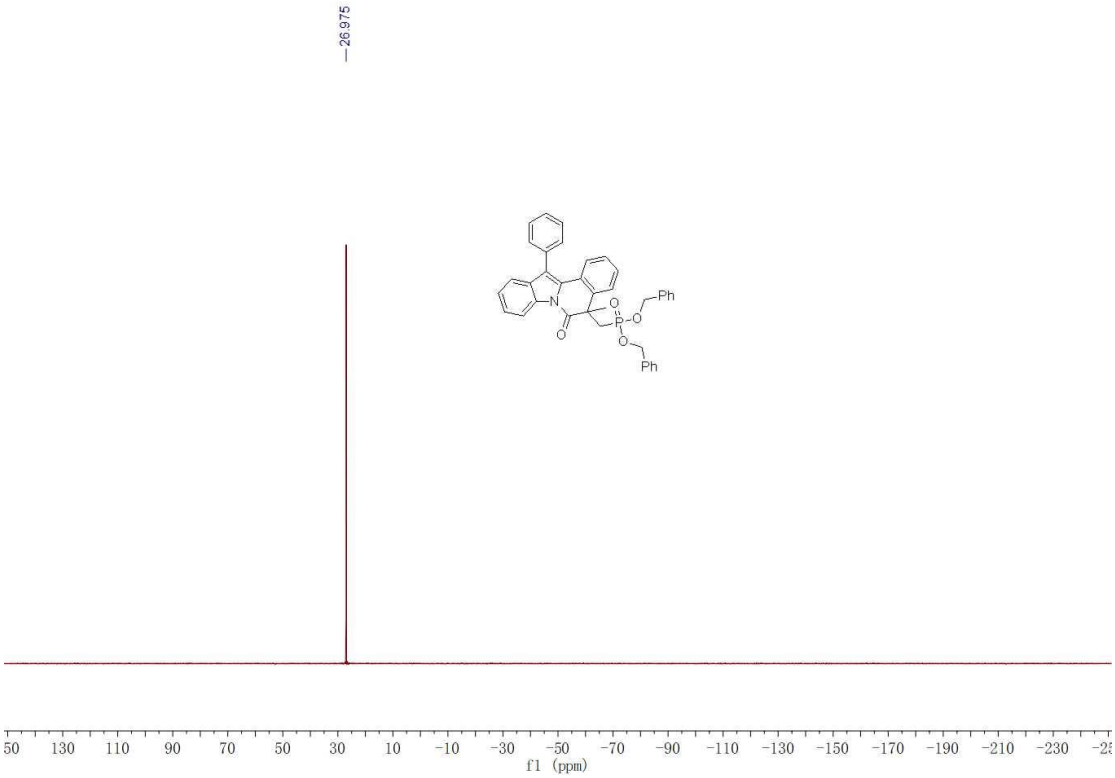



25.678
O
P
OEt
OEt
O
N
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

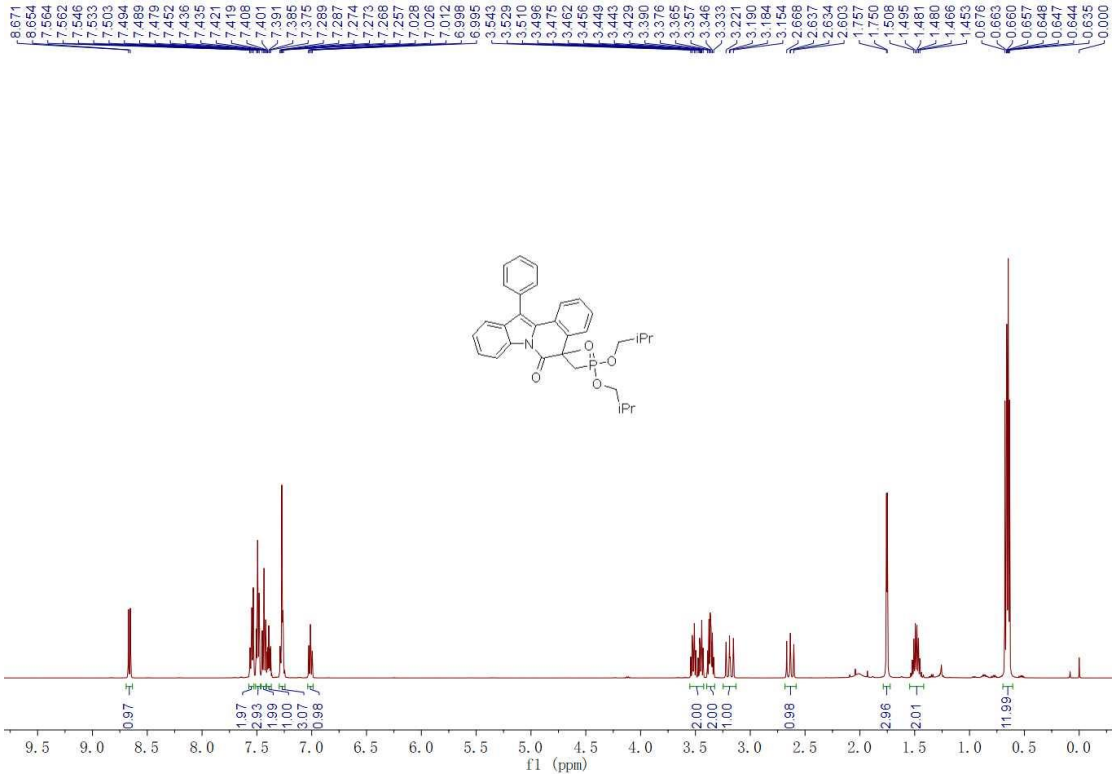
Dibenzyl ((5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-a]isoquinolin-5-yl)-methyl)phosphonate (3ah)

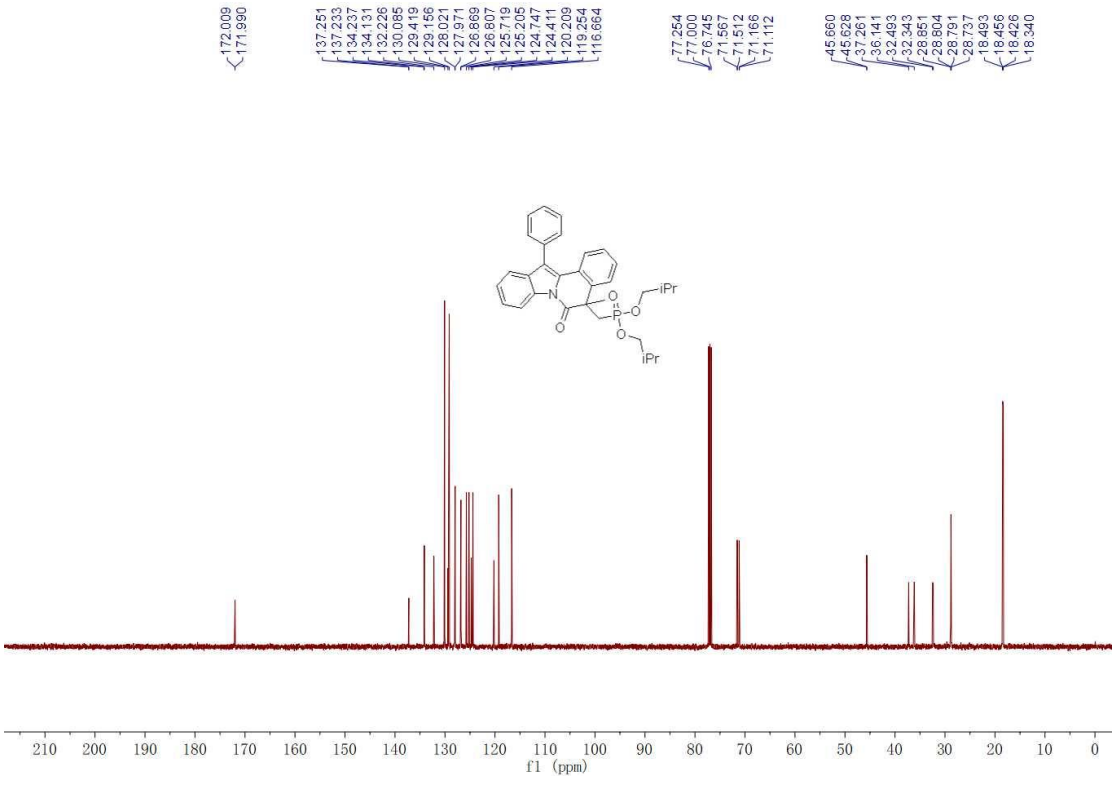


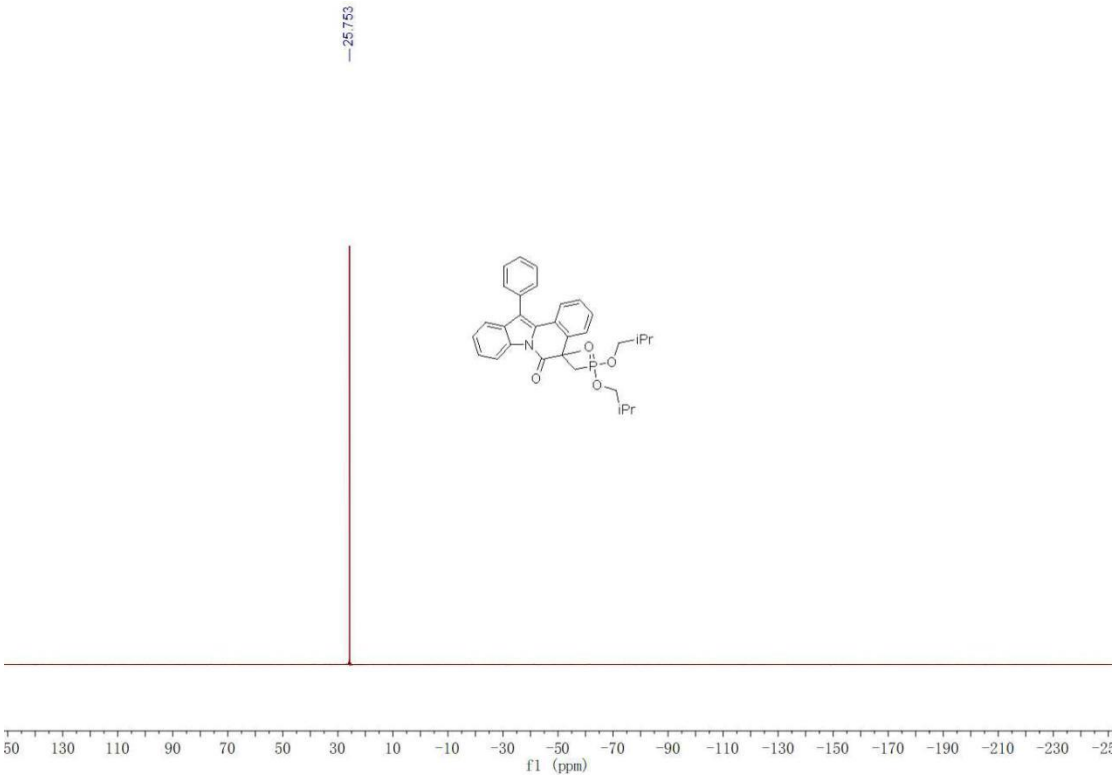



26.975
Ph
Ph
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

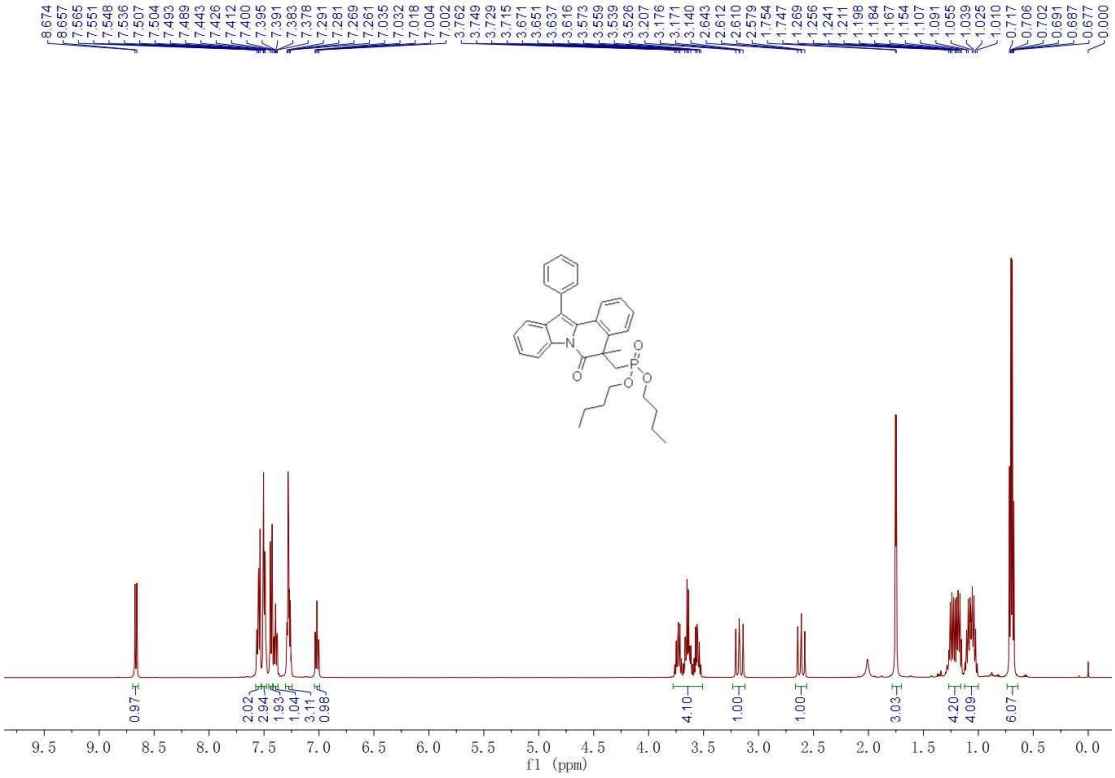
Diisobutyl ((5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-a]isoquinolin-5-yl)-methyl)phosphonate (3ai)

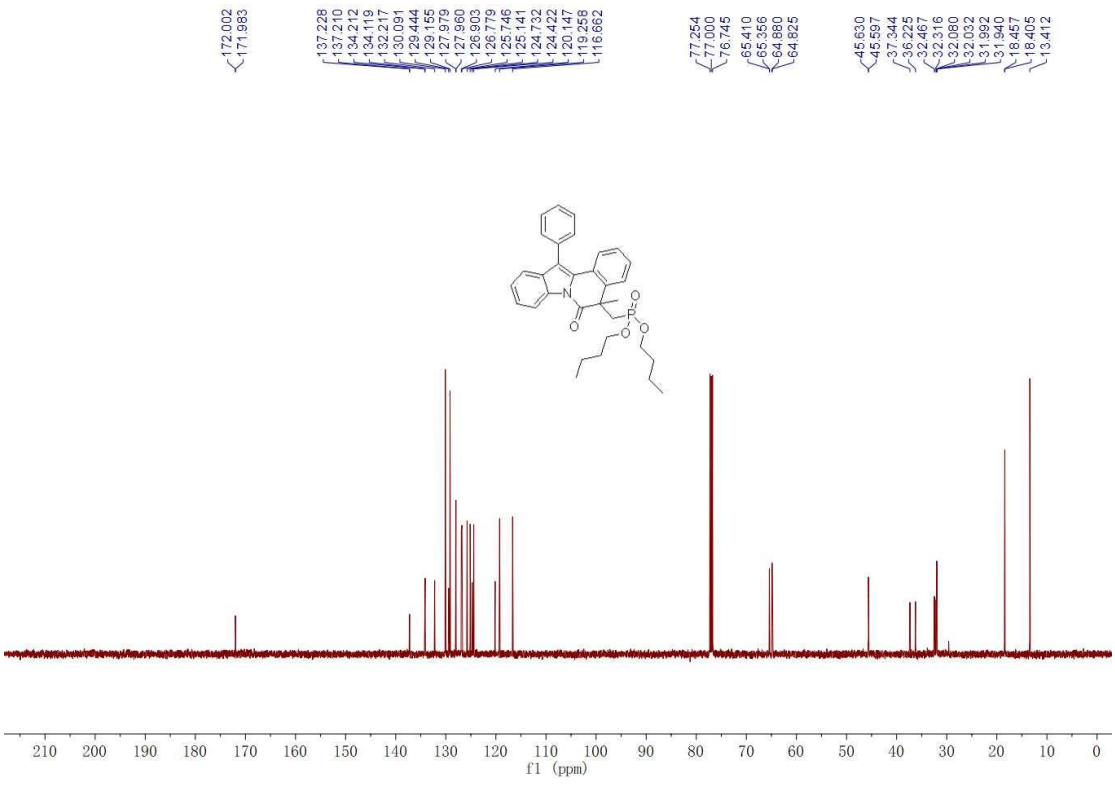


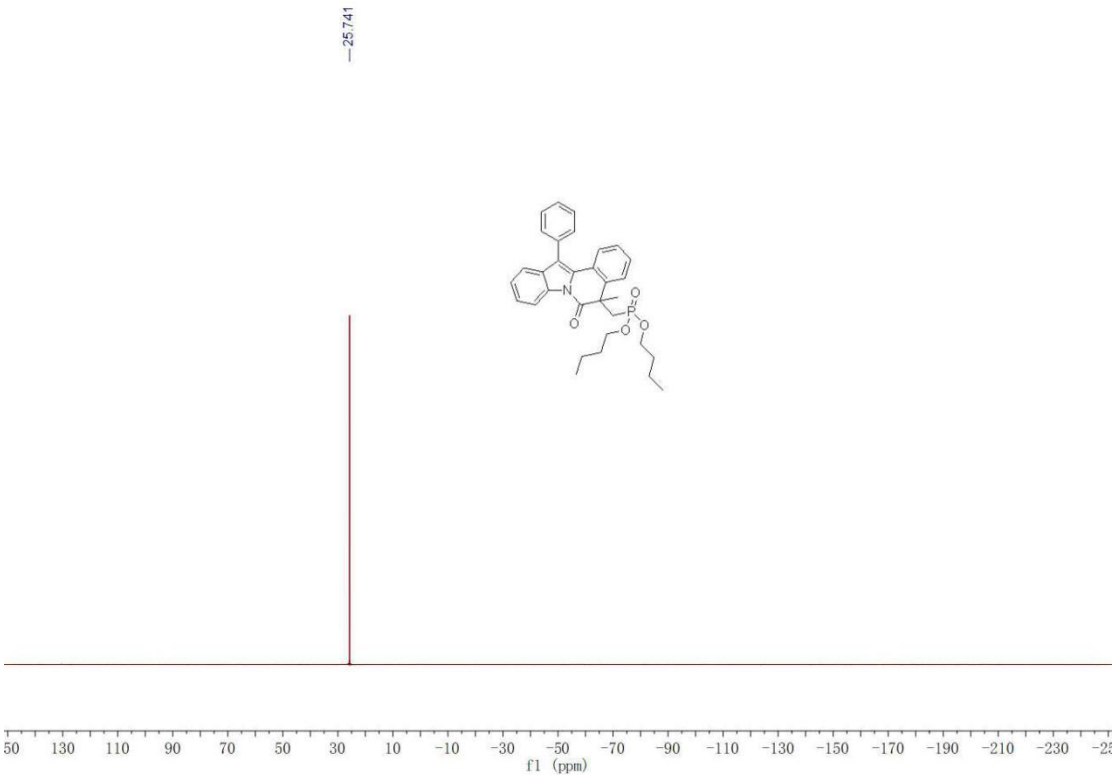



25.753
iPr
iPr
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

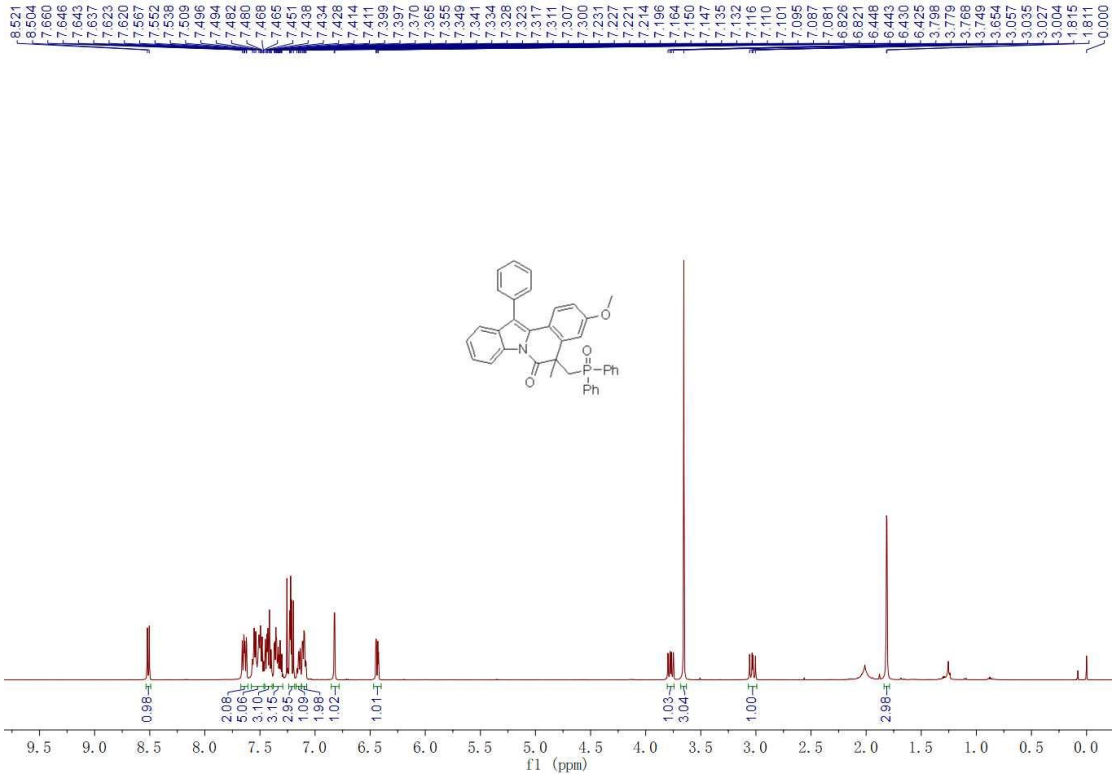
Dibutyl ((5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-a]isoquinolin-5-yl)methyl)phosphonate (3aj)

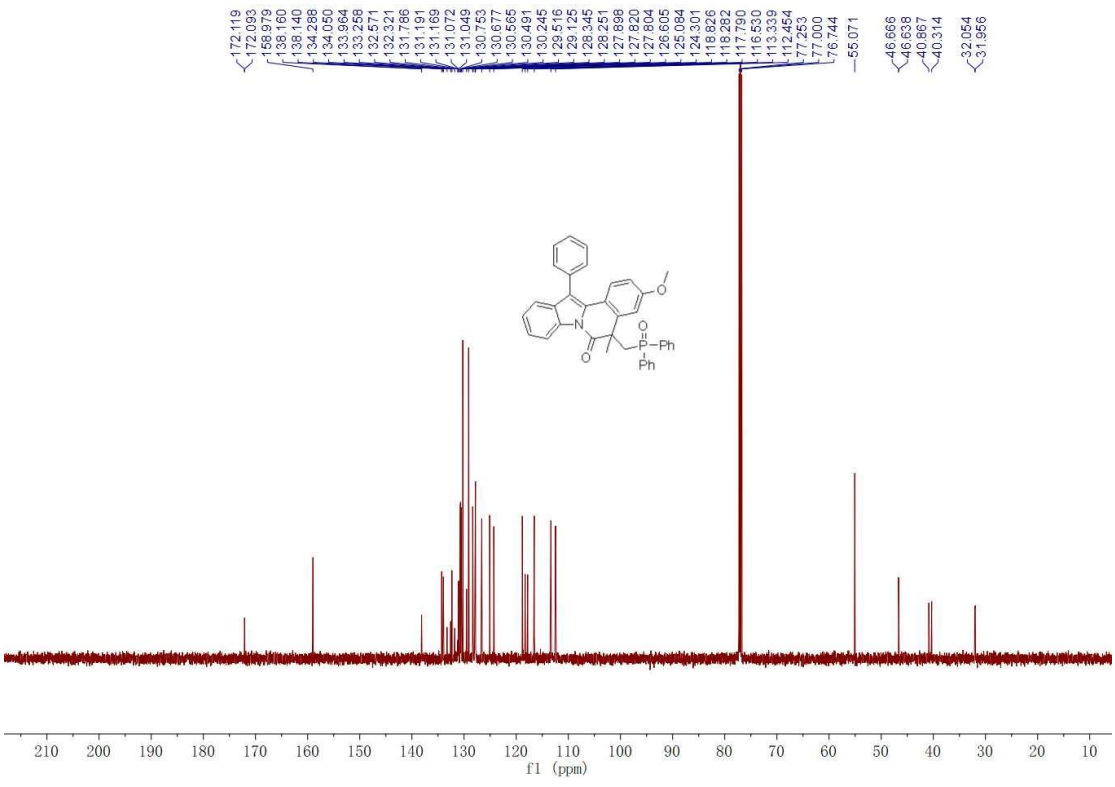


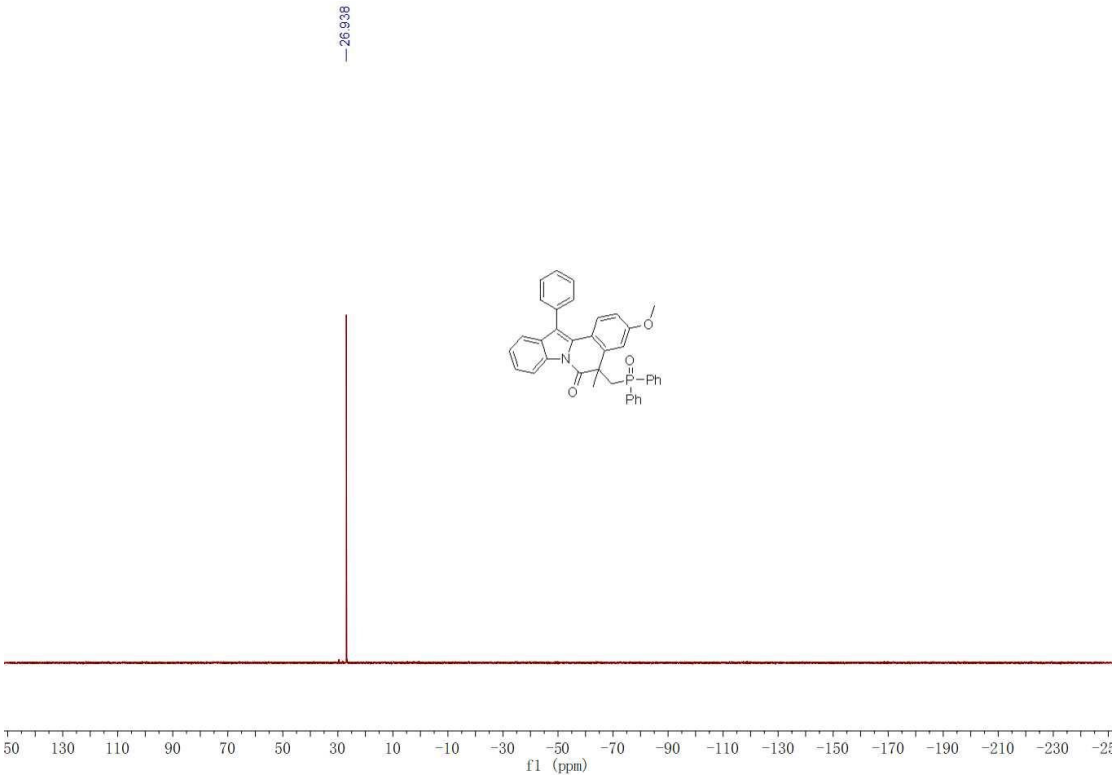



25.741
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

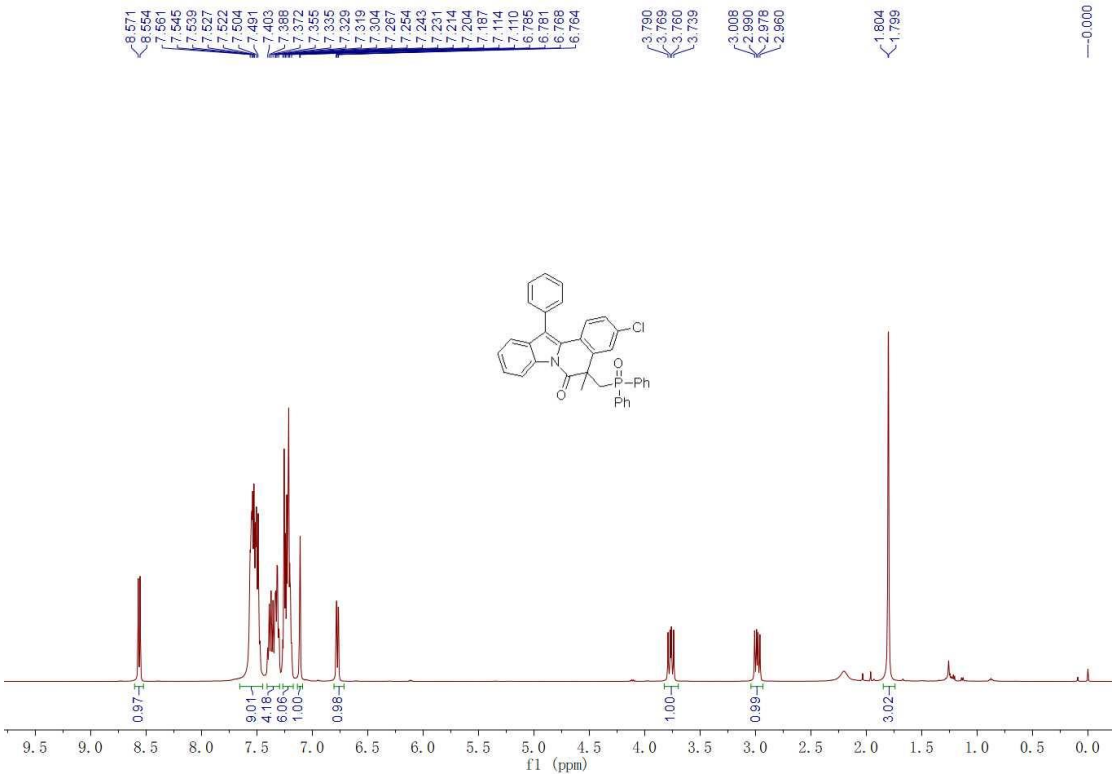
5-((Diphenylphosphoryl)methyl)-3-methoxy-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ba)

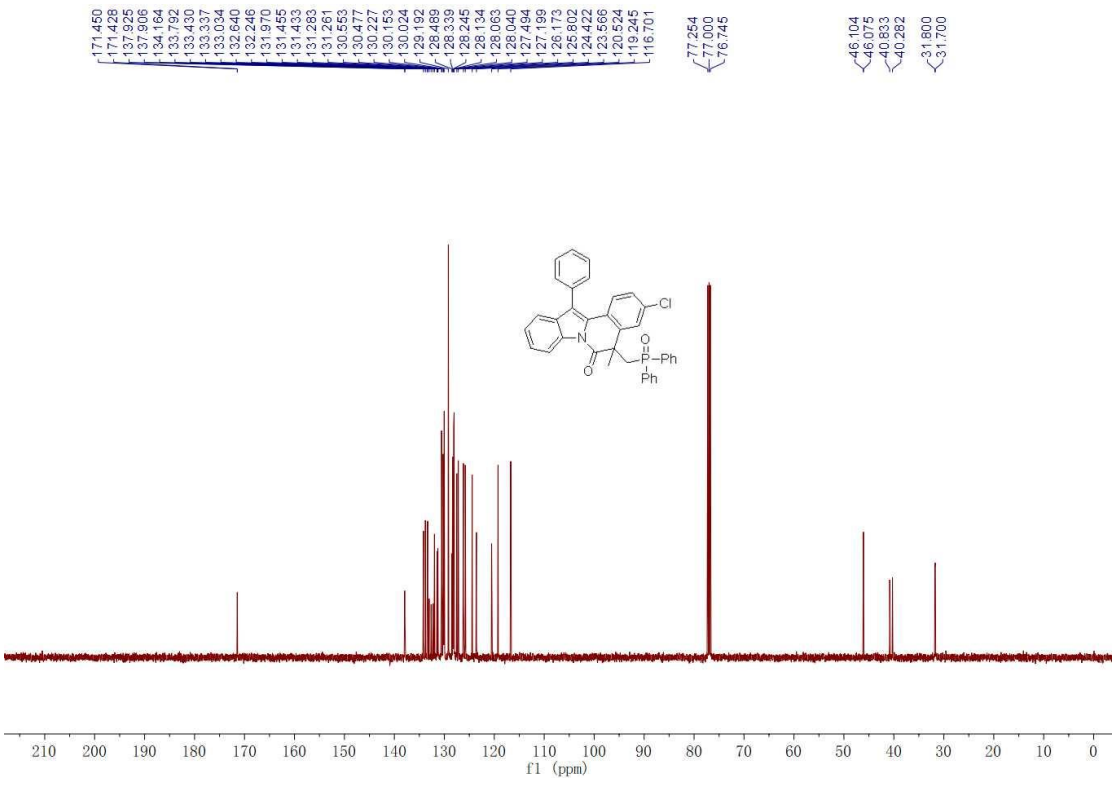


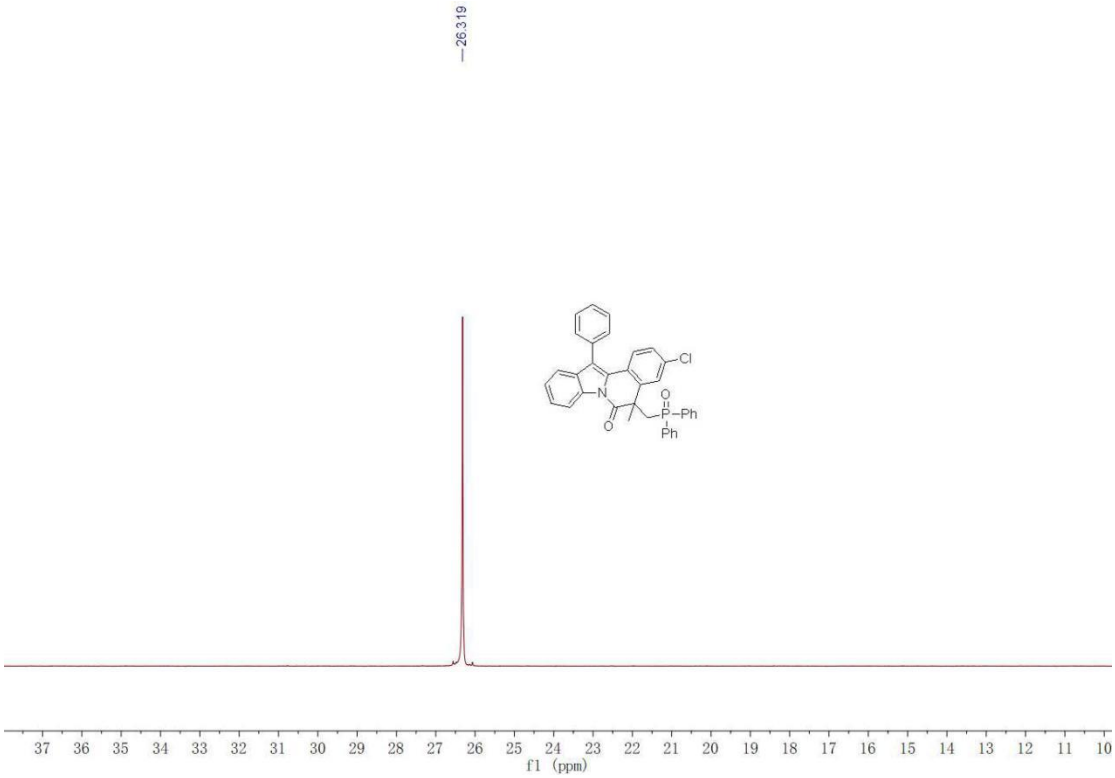



26.938
O
O
P
Ph
Ph
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

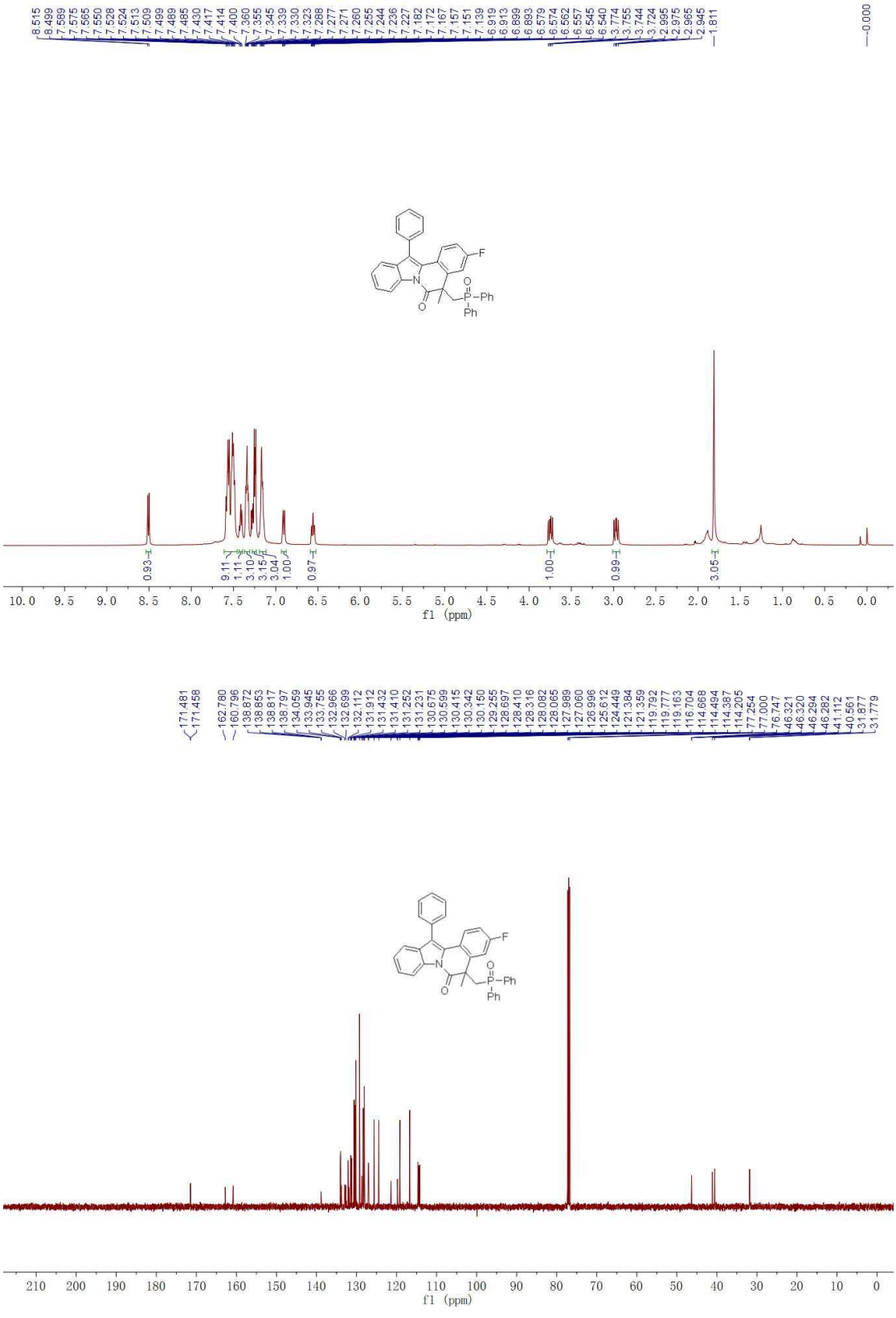
3-Chloro-5-((diphenylphosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ca)

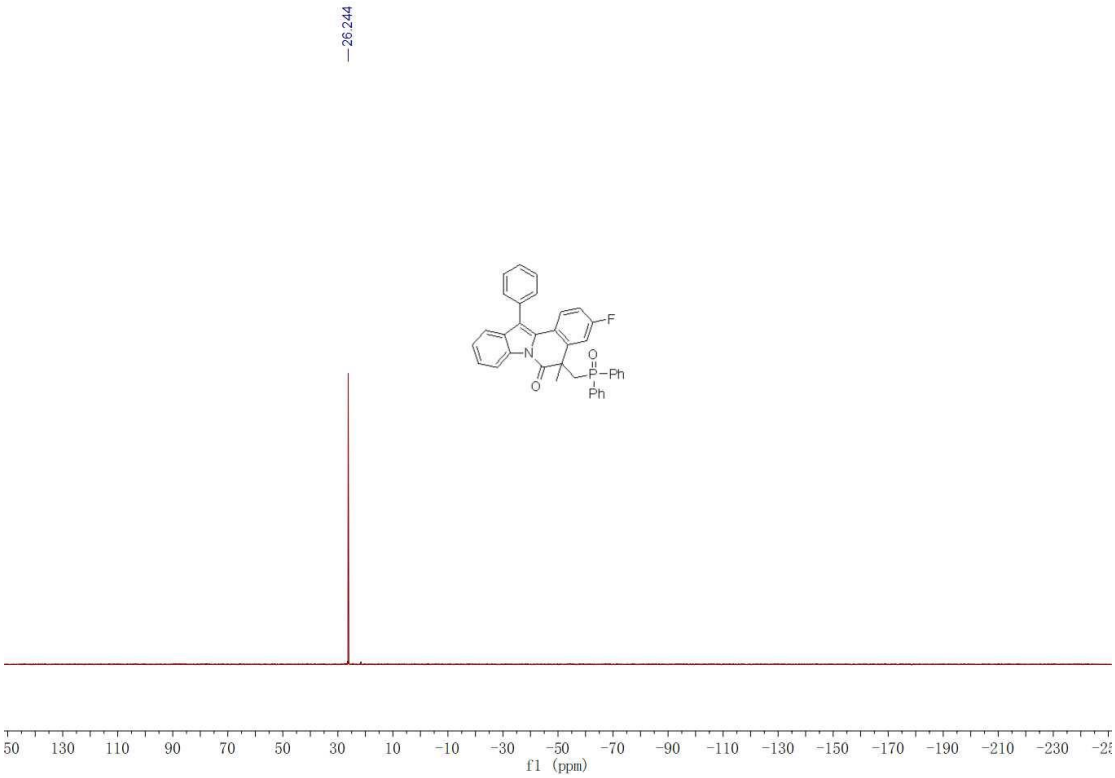


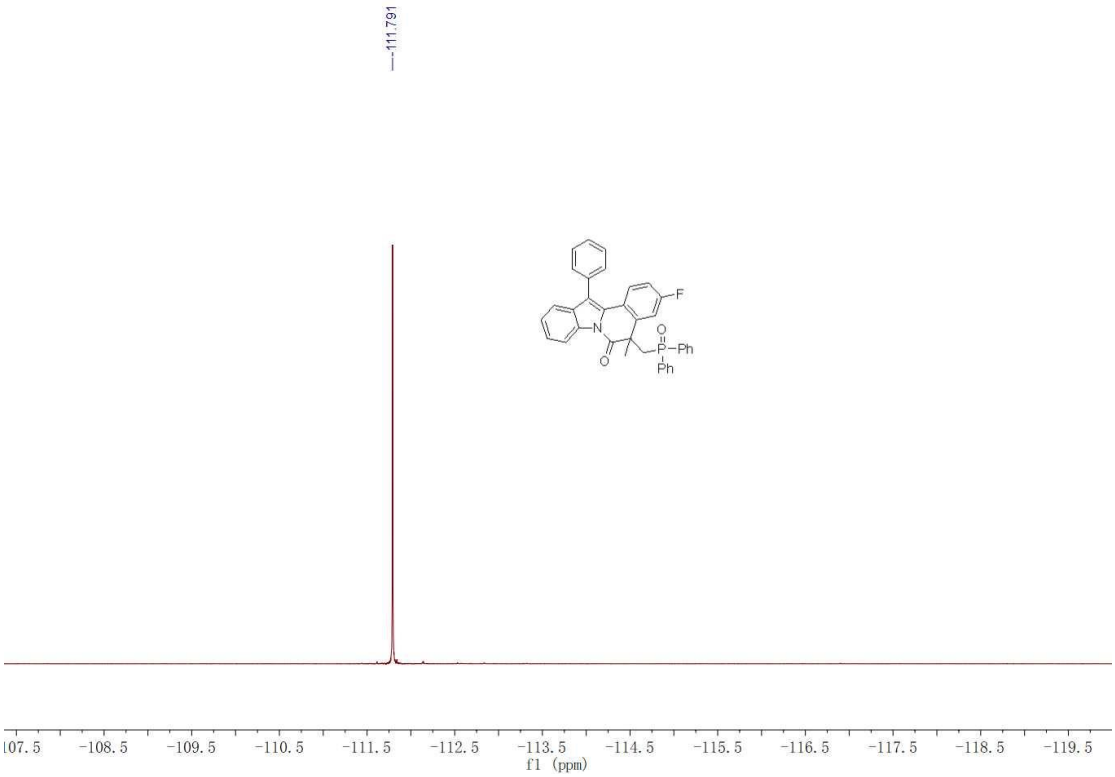



26.319
Cl
N
O
O
P
Ph
Ph
37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10
f1 (ppm)

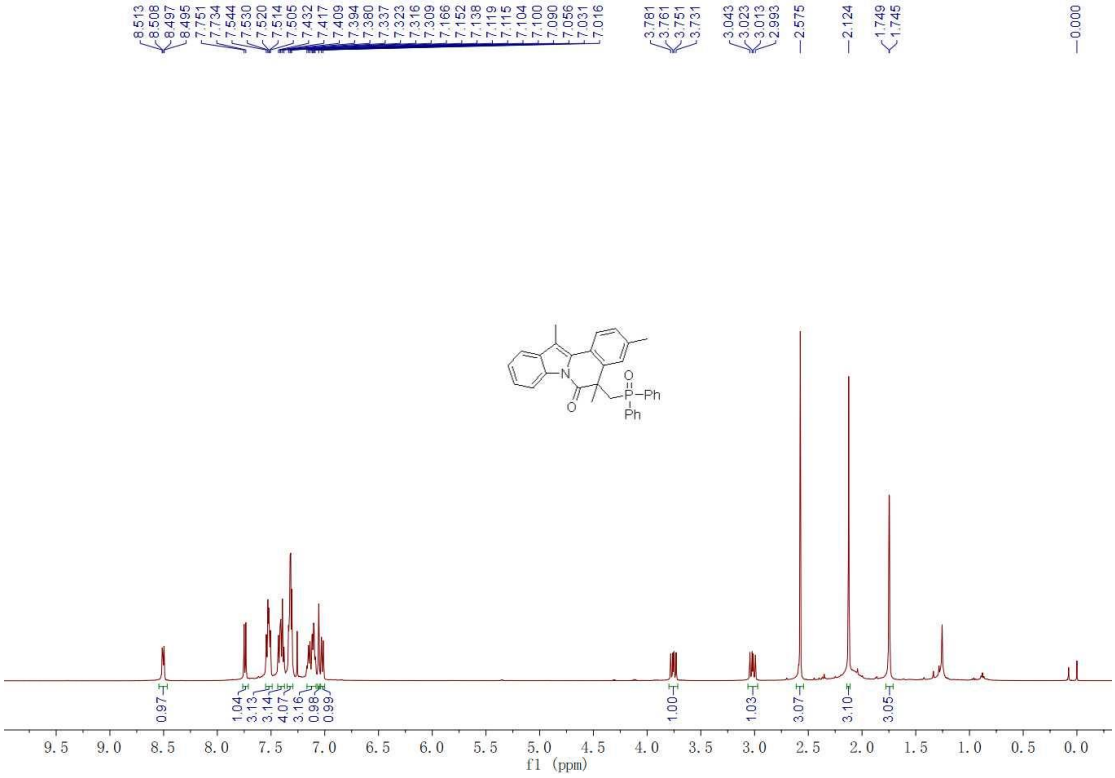
5-((Diphenylphosphoryl)methyl)-3-fluoro-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3da)

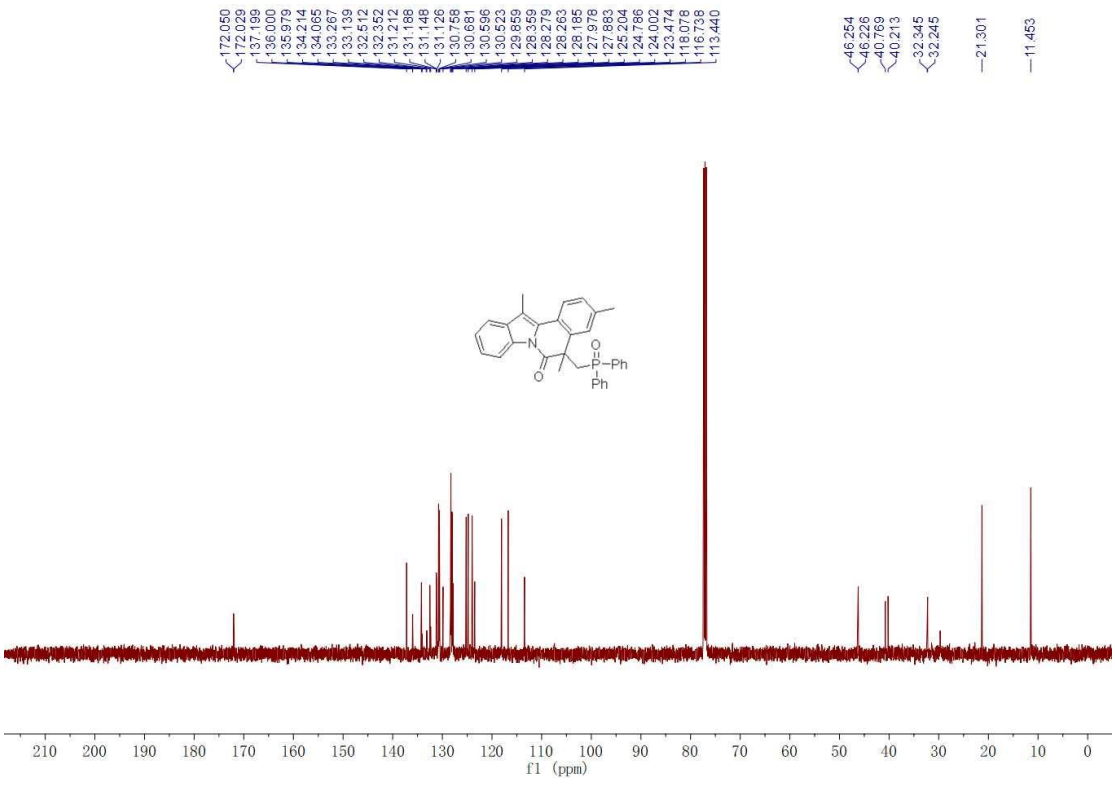


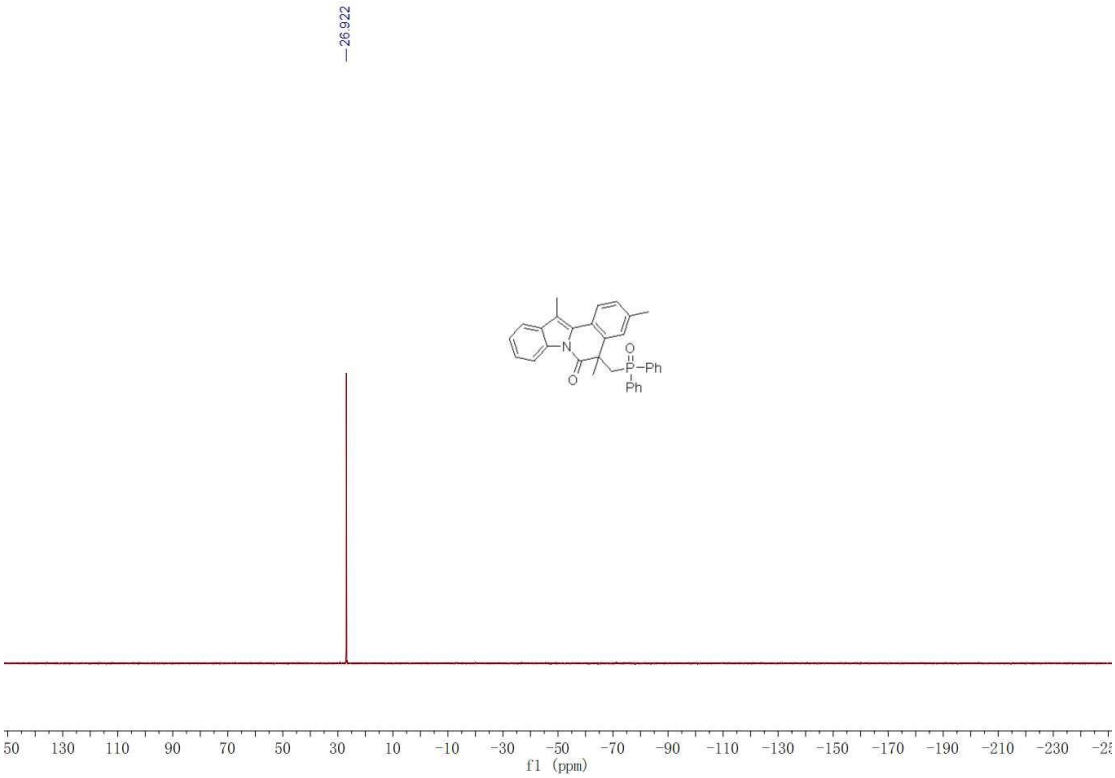

26.244
F
O
P
Ph
Ph
O
N
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


-111.791
F
O
P
Ph
Ph
O
N
107.5 -108.5 -109.5 -110.5 -111.5 -112.5 -113.5 -114.5 -115.5 -116.5 -117.5 -118.5 -119.5
f1 (ppm)

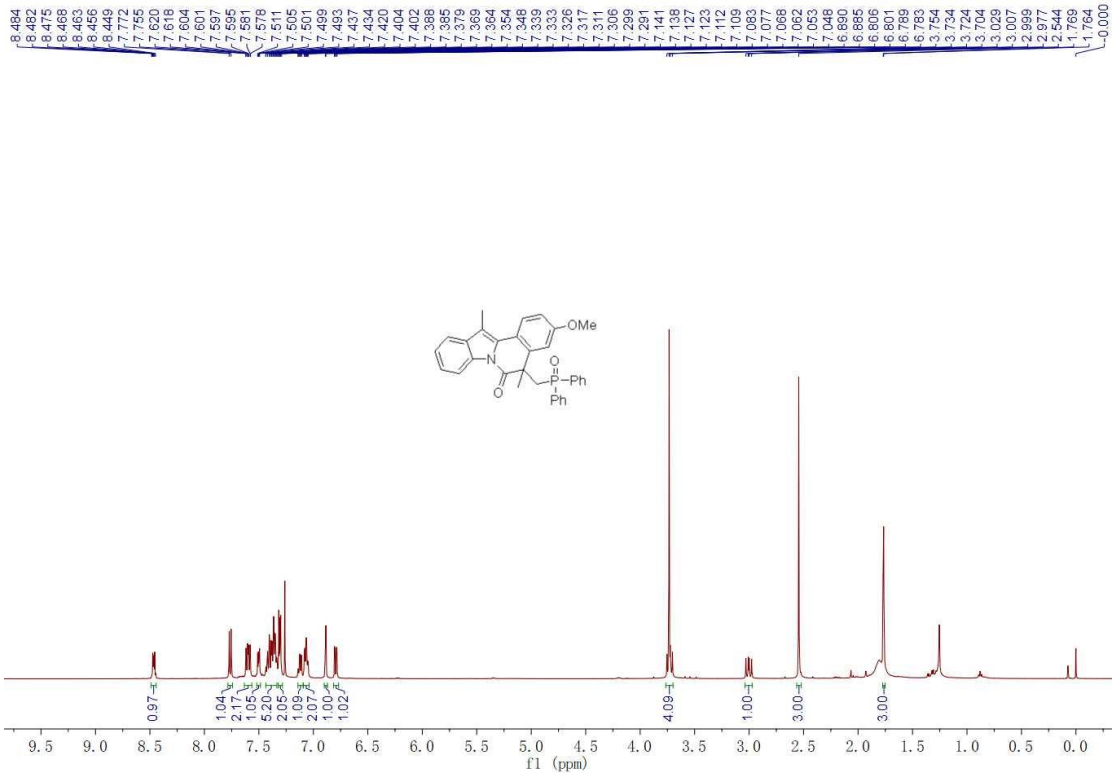
5-((Diphenylphosphoryl)methyl)-3,5,12-trimethylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ea)

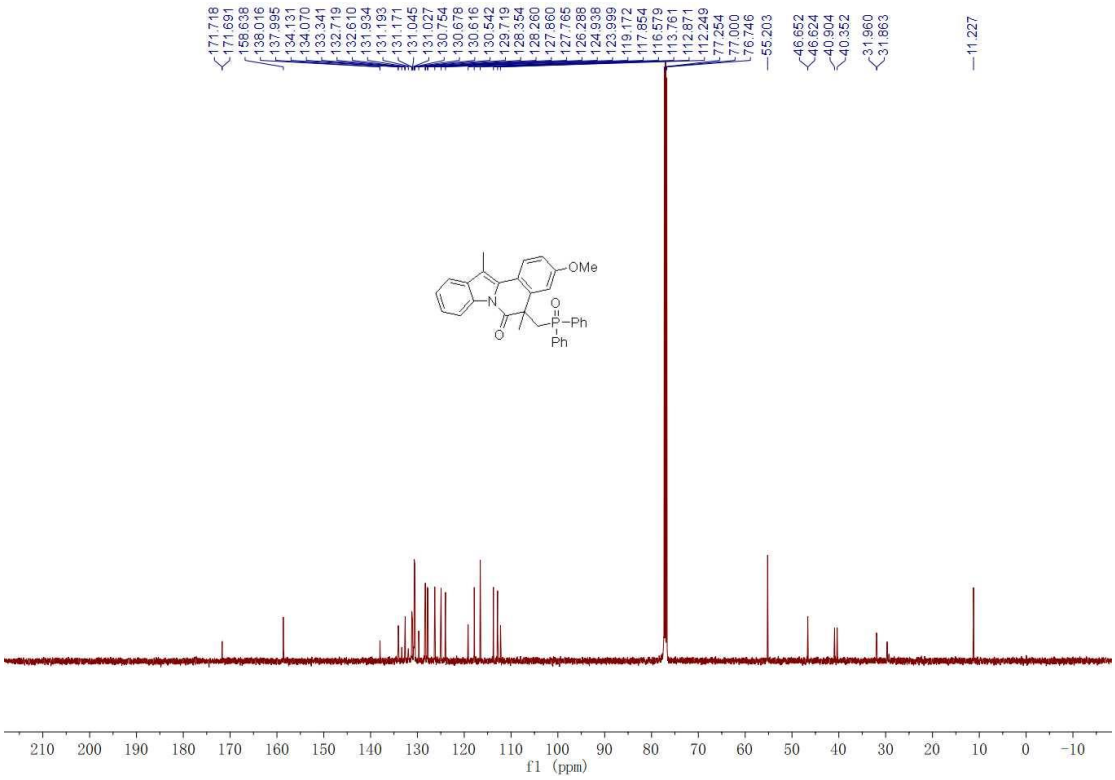


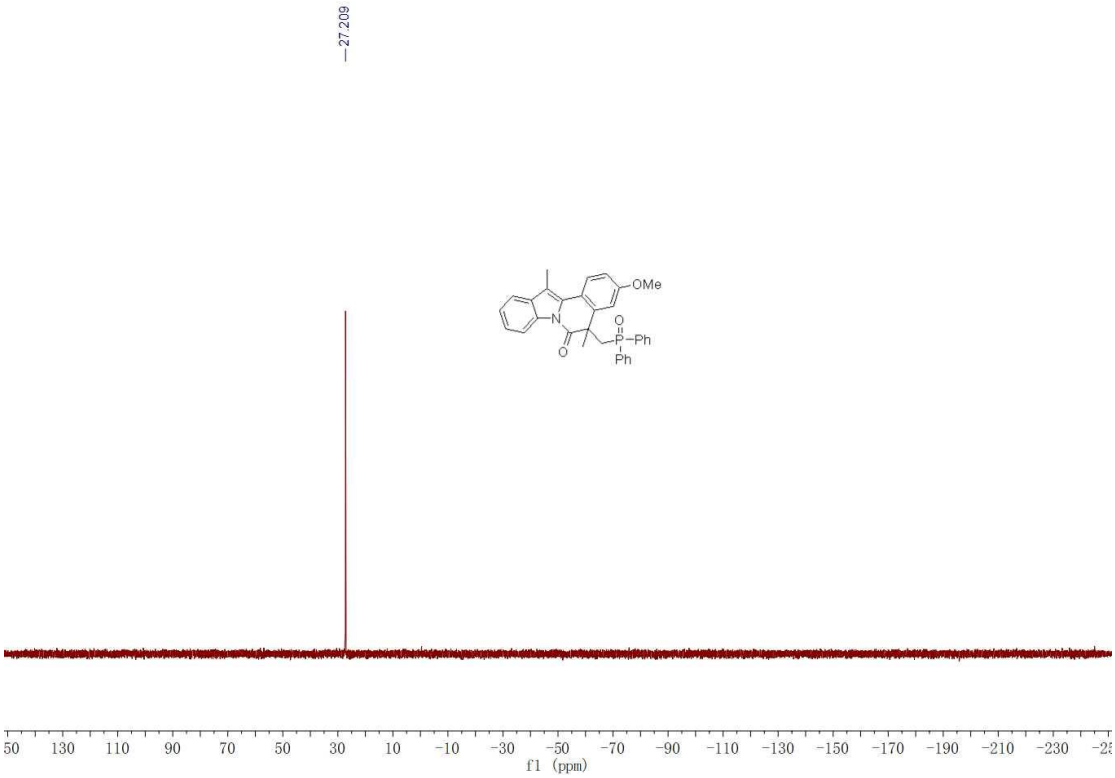



26.922
O
P–Ph
Ph
O
N
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

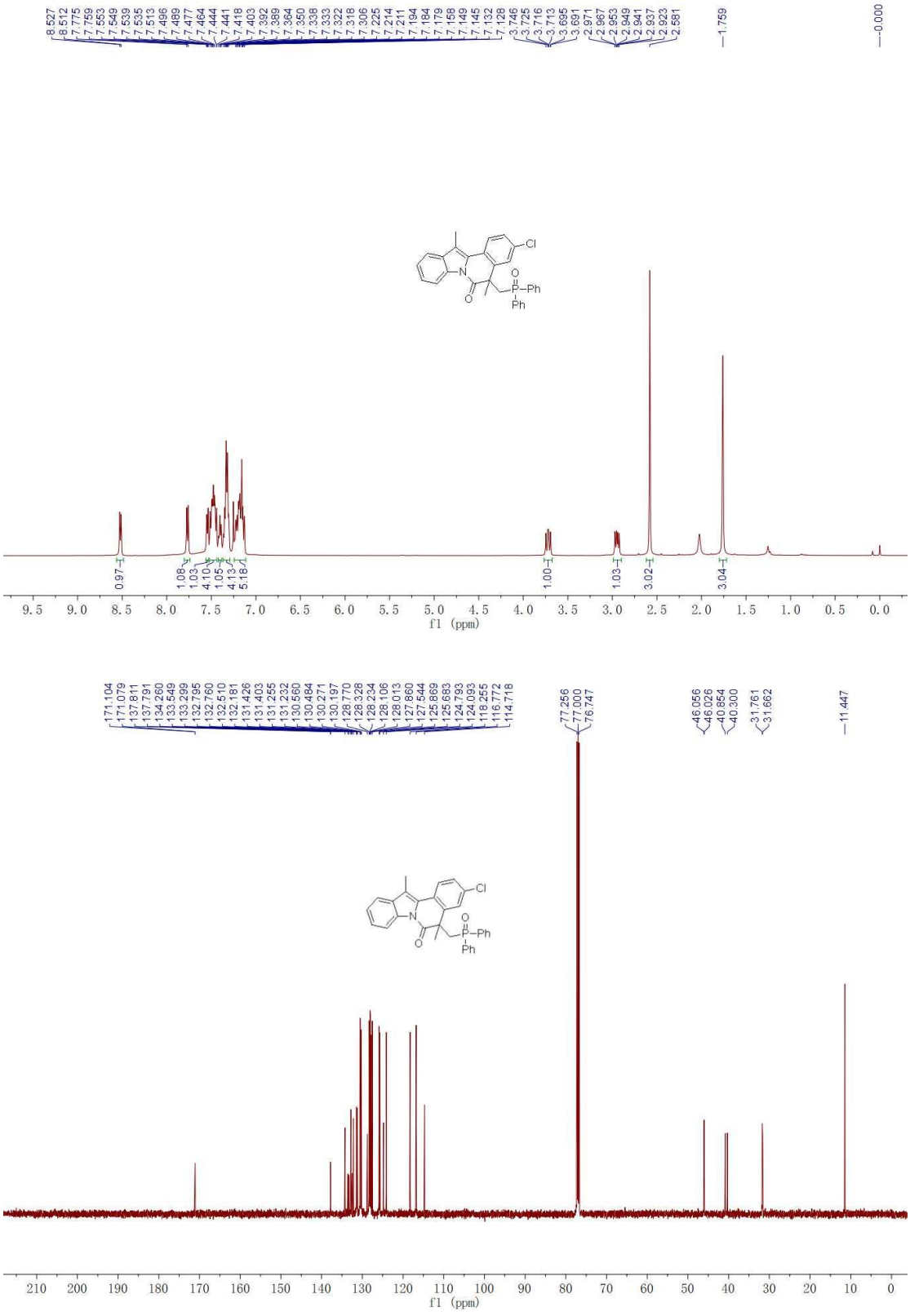
5-((Diphenylphosphoryl)methyl)-3-methoxy-5,12-dimethylindolo[2,1-a]isoquinoli n-6(5*H*)-one (3fa)

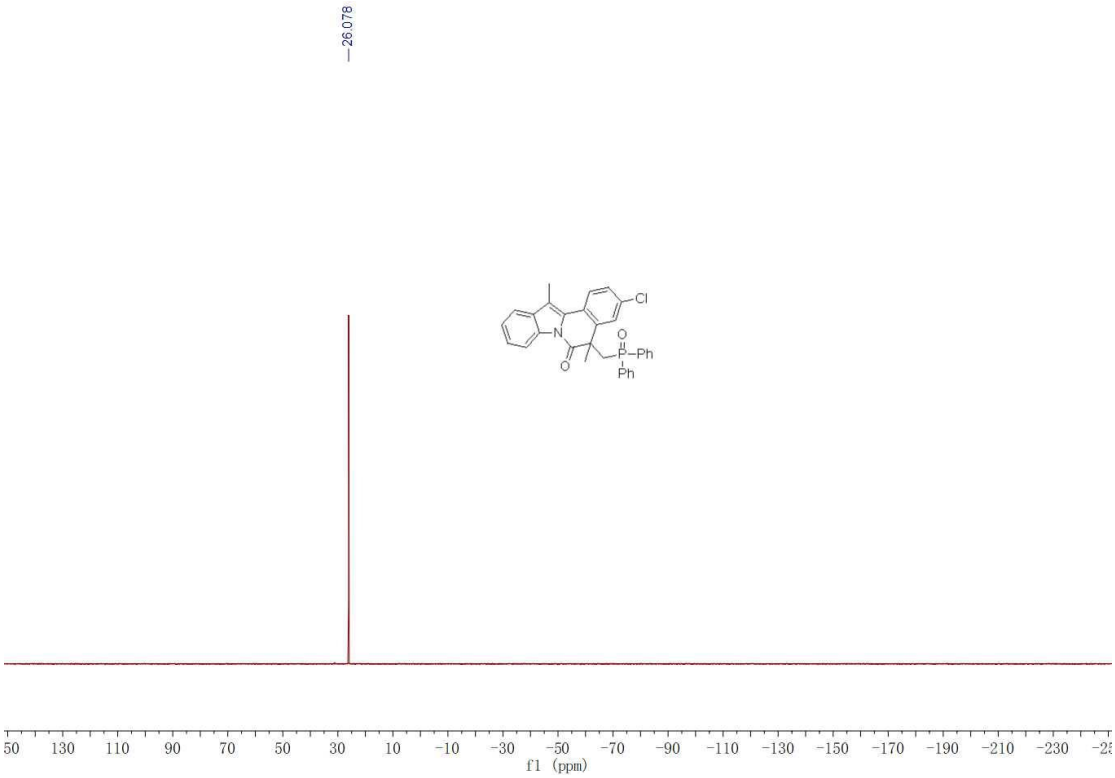




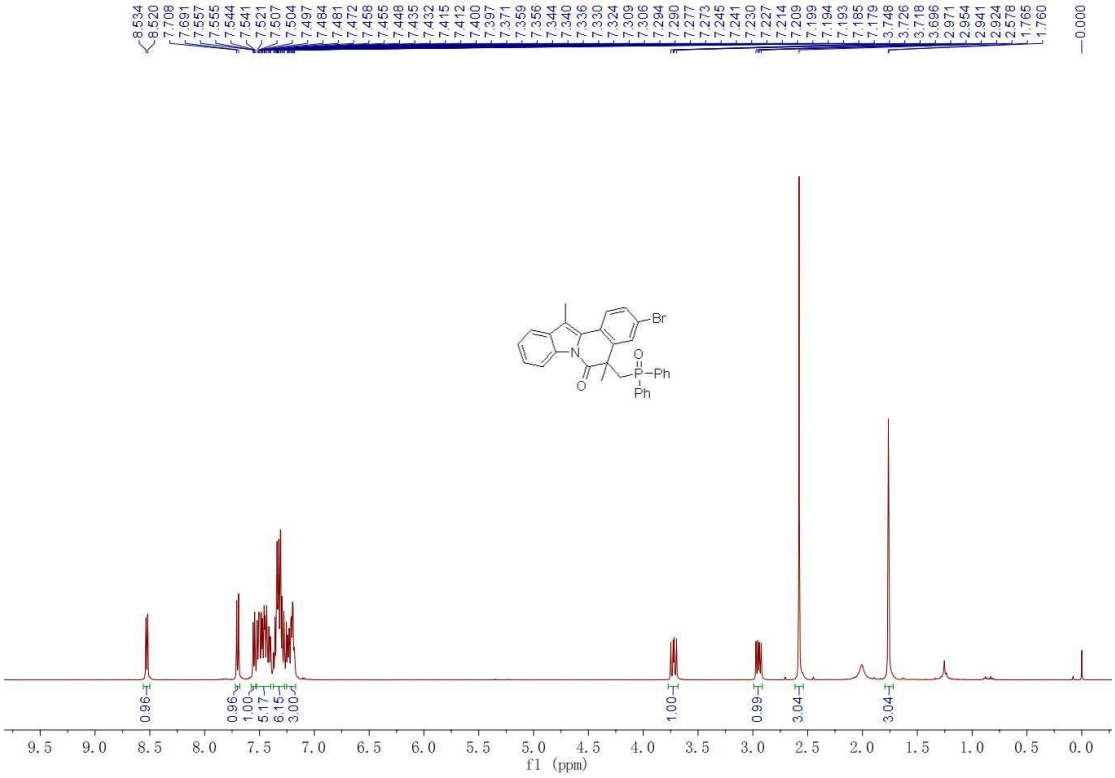

27.209
OMe
N
O
O
P
Ph
Ph
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

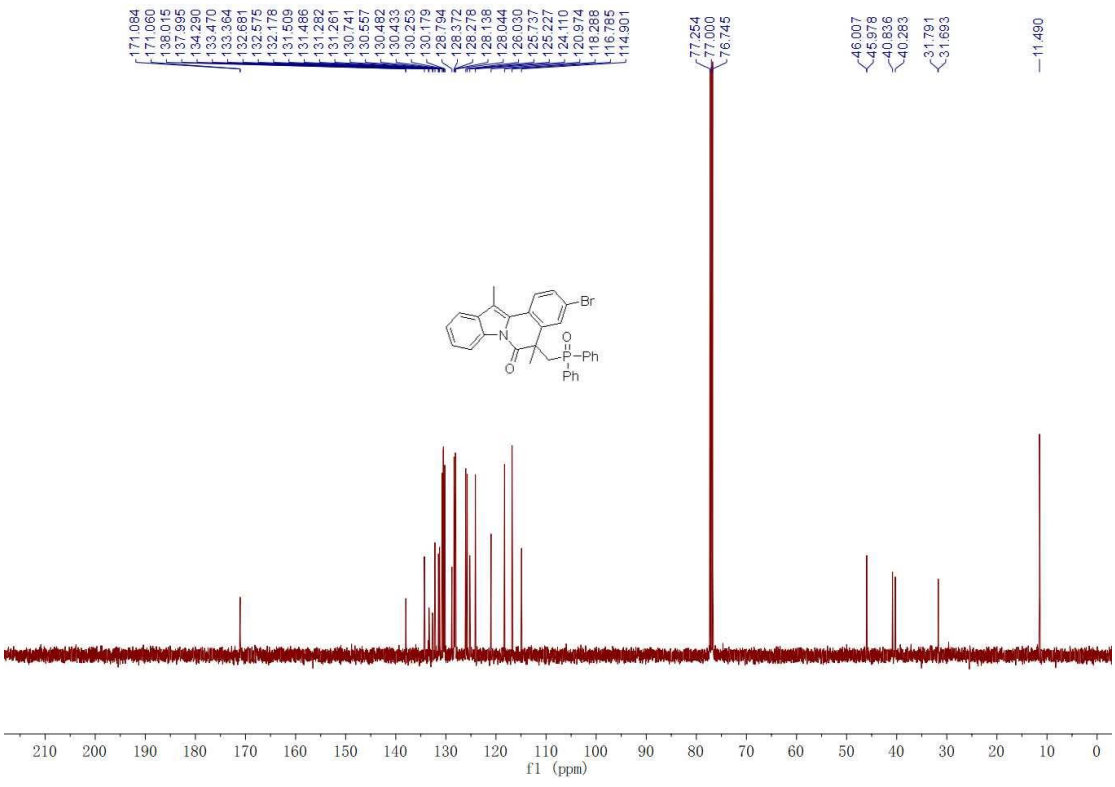
3-Chloro-5-((diphenylphosphoryl)methyl)-5,12-dimethylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ga)

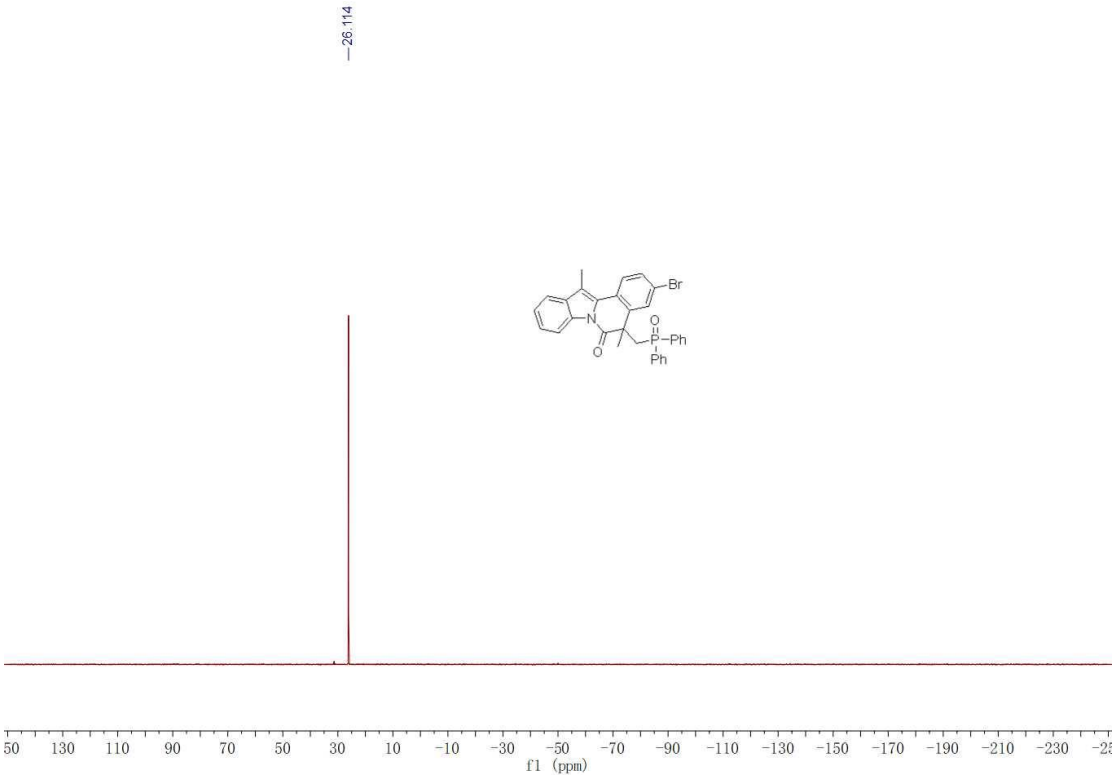



26.078
Cl
N
O
O
P–Ph
Ph
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

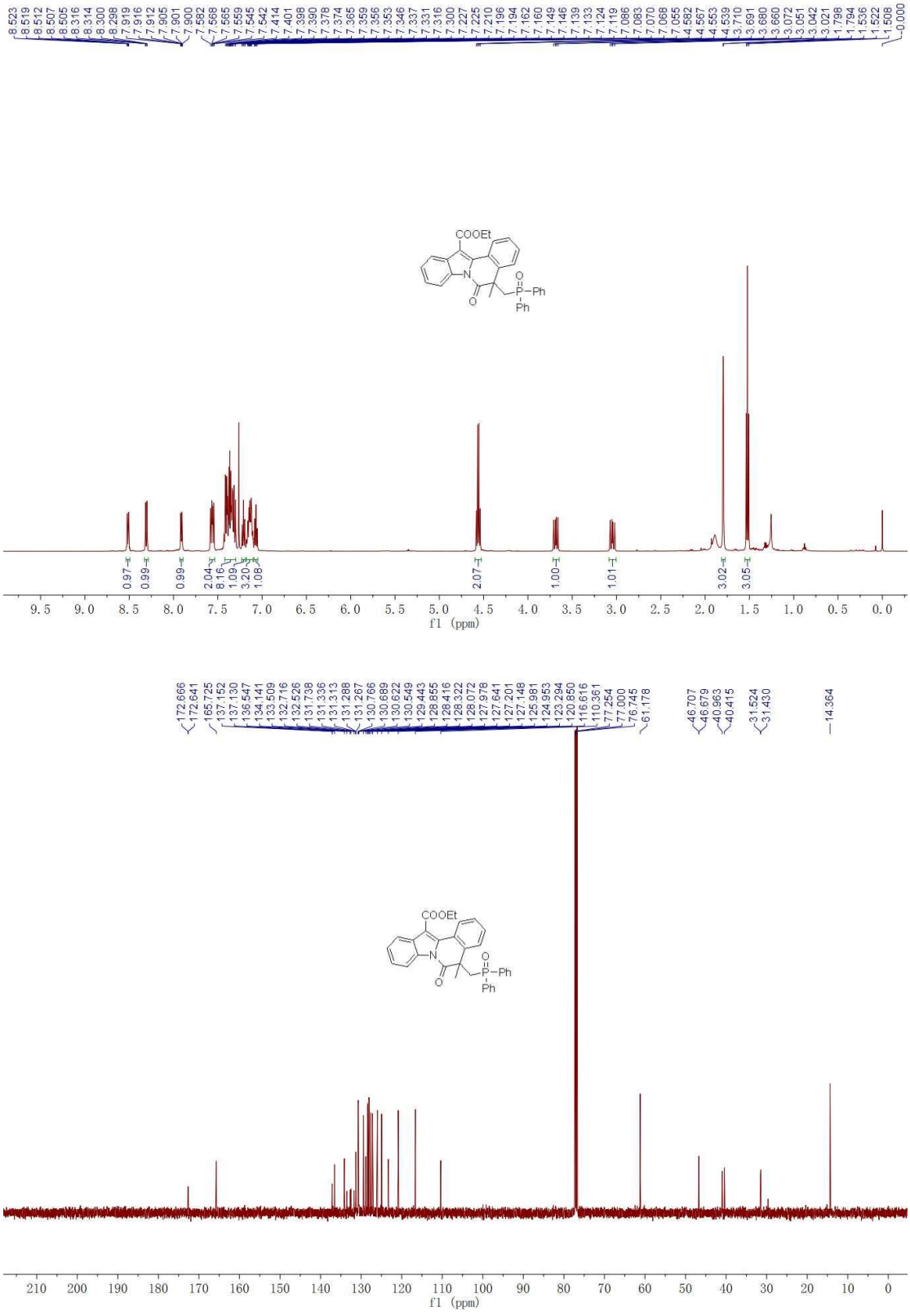
3-Bromo-5-((diphenylphosphoryl)methyl)-5,12-dimethylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ha)

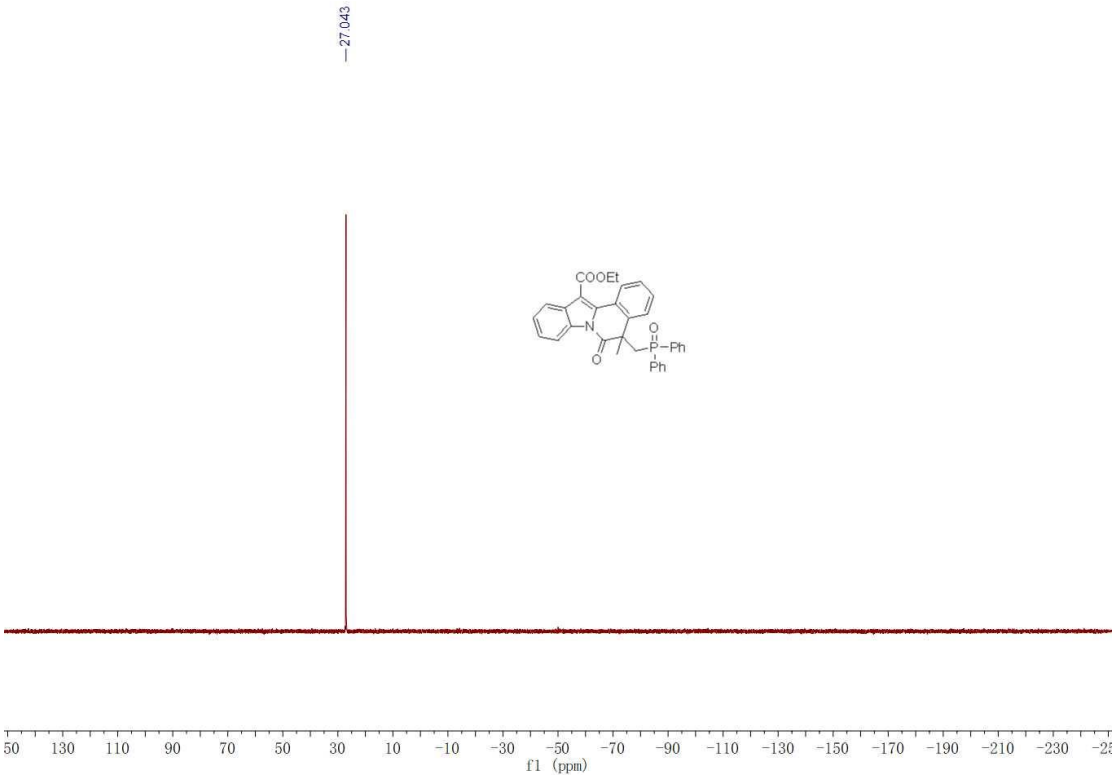




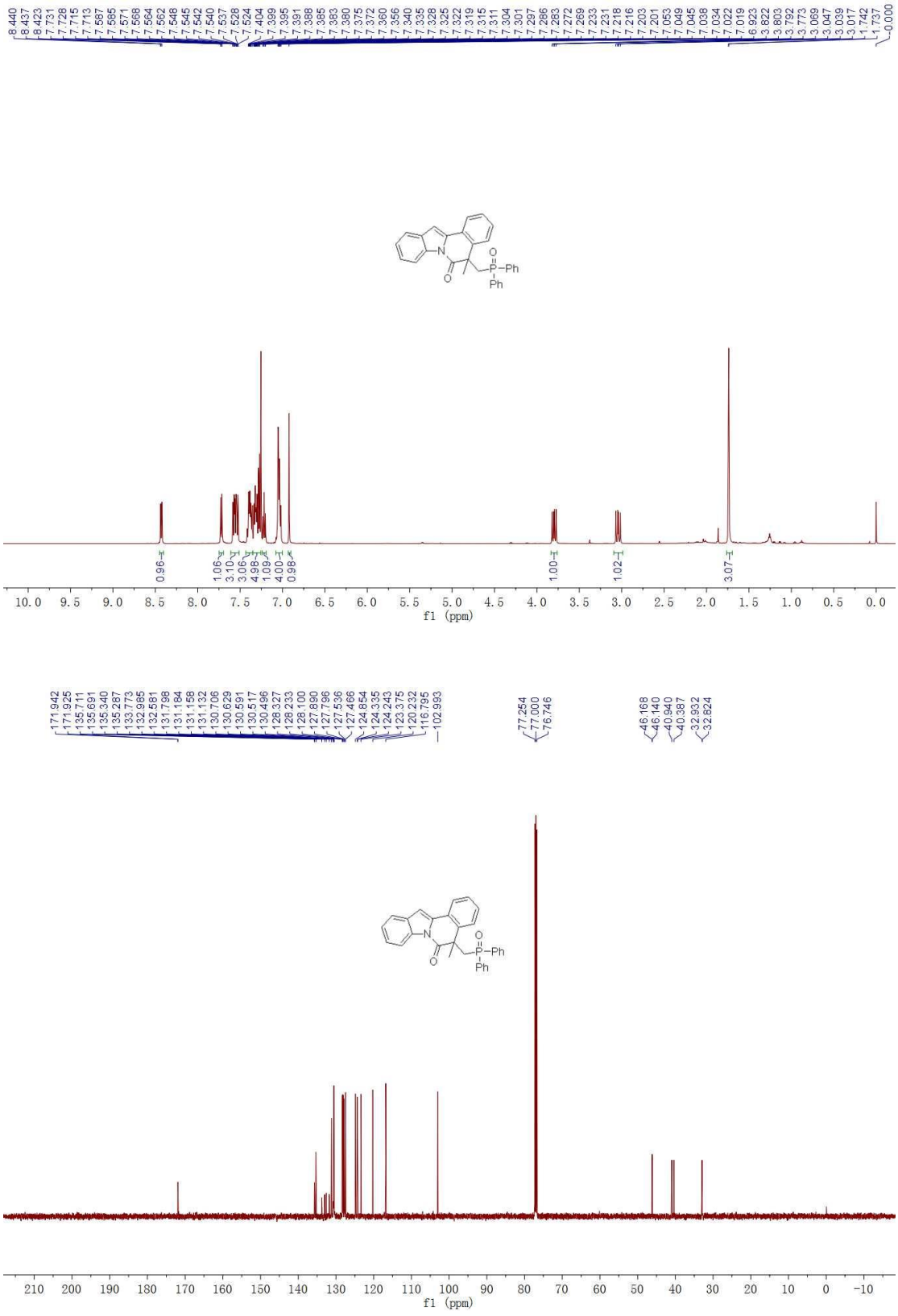

26.114
Br
O
P–Ph
Ph
O
N
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

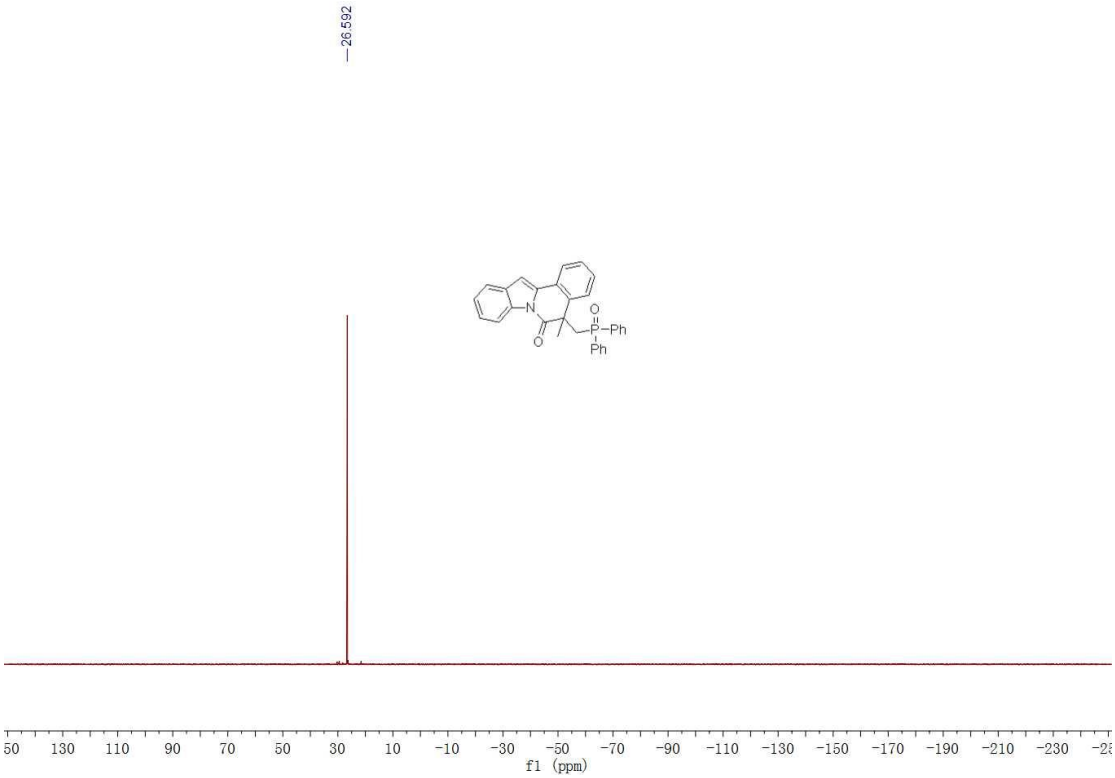
Ethyl 5-((diphenylphosphoryl)methyl)-5-methyl-6-oxo-5,6-dihydroindolo[2,1-a]-isoquinoline-12-carboxylate (3ia)



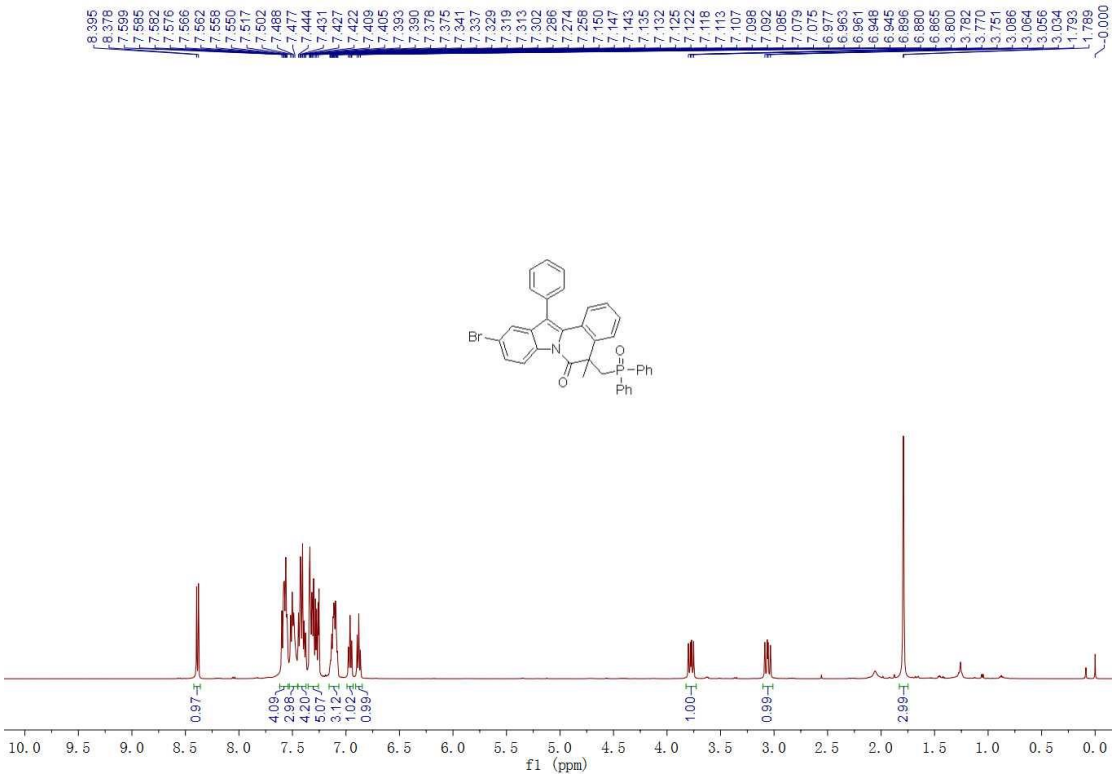

27.043
COOEt
O
P
Ph
Ph
O
N
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

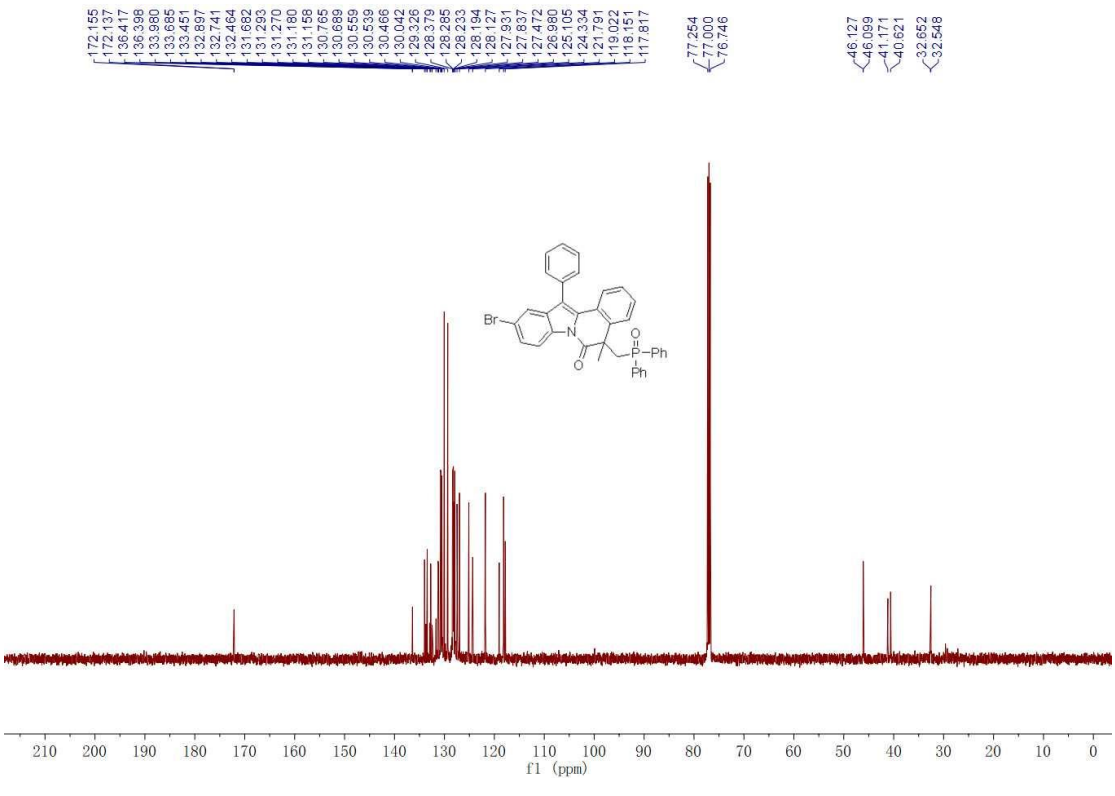
5-((diphenylphosphoryl)methyl)-5-methylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (3ja)

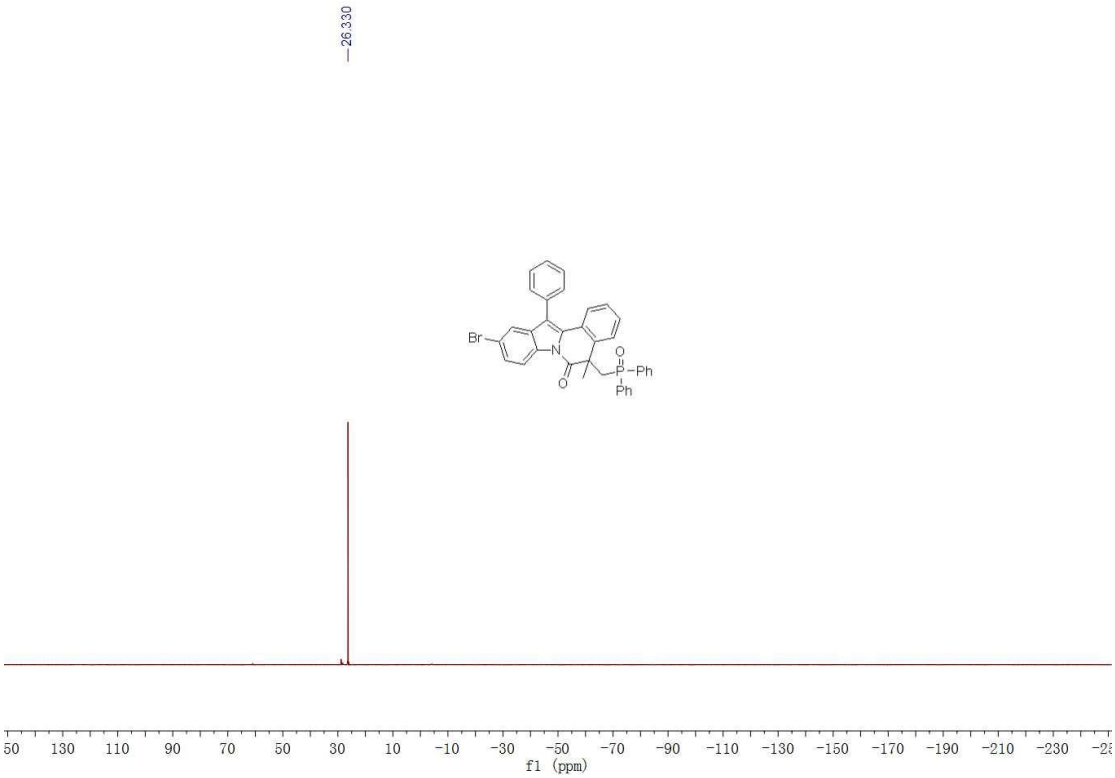



26.592
O
N
O
P
Ph
Ph
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

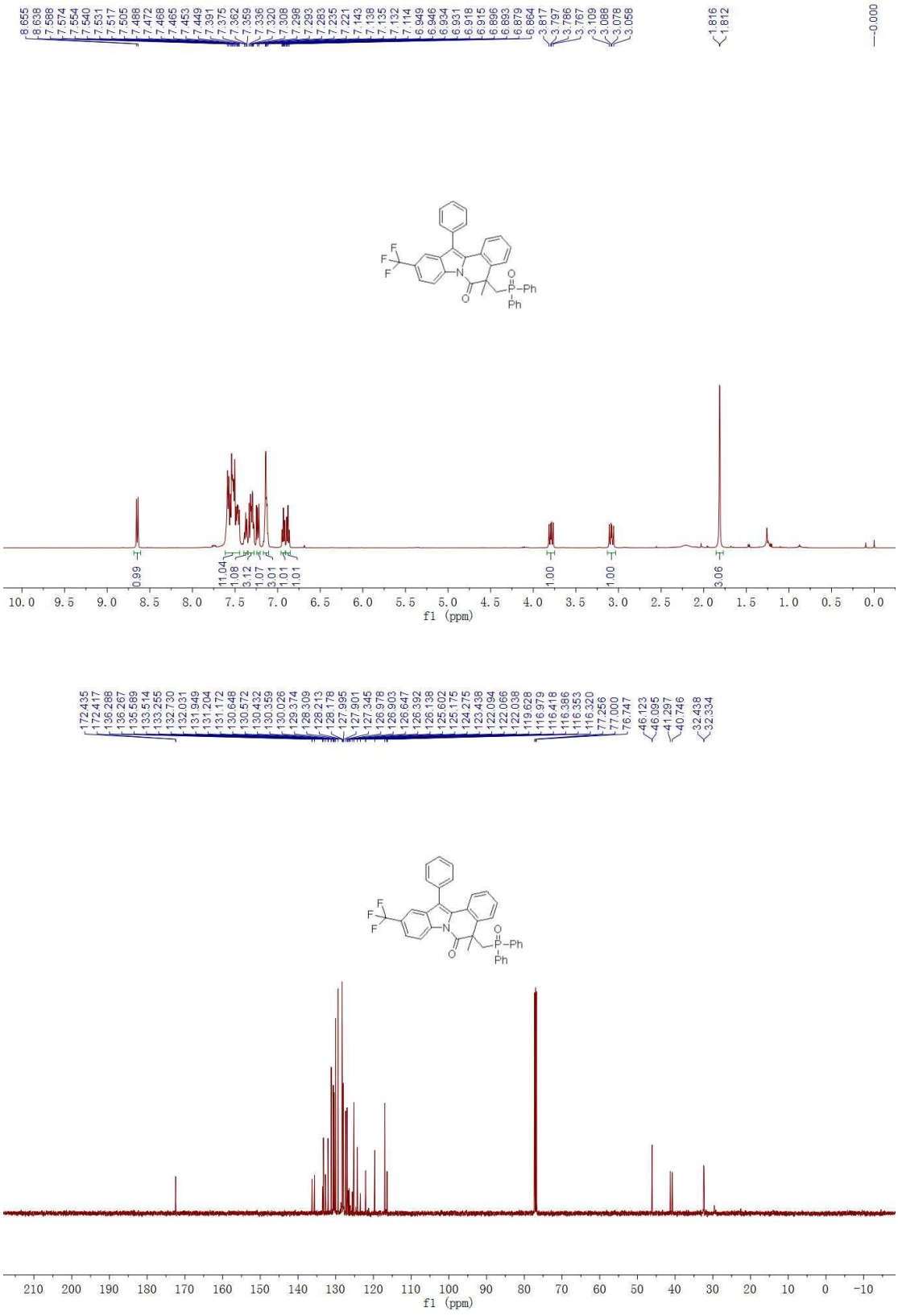
10-Bromo-5-((diphenylphosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one (3ka)

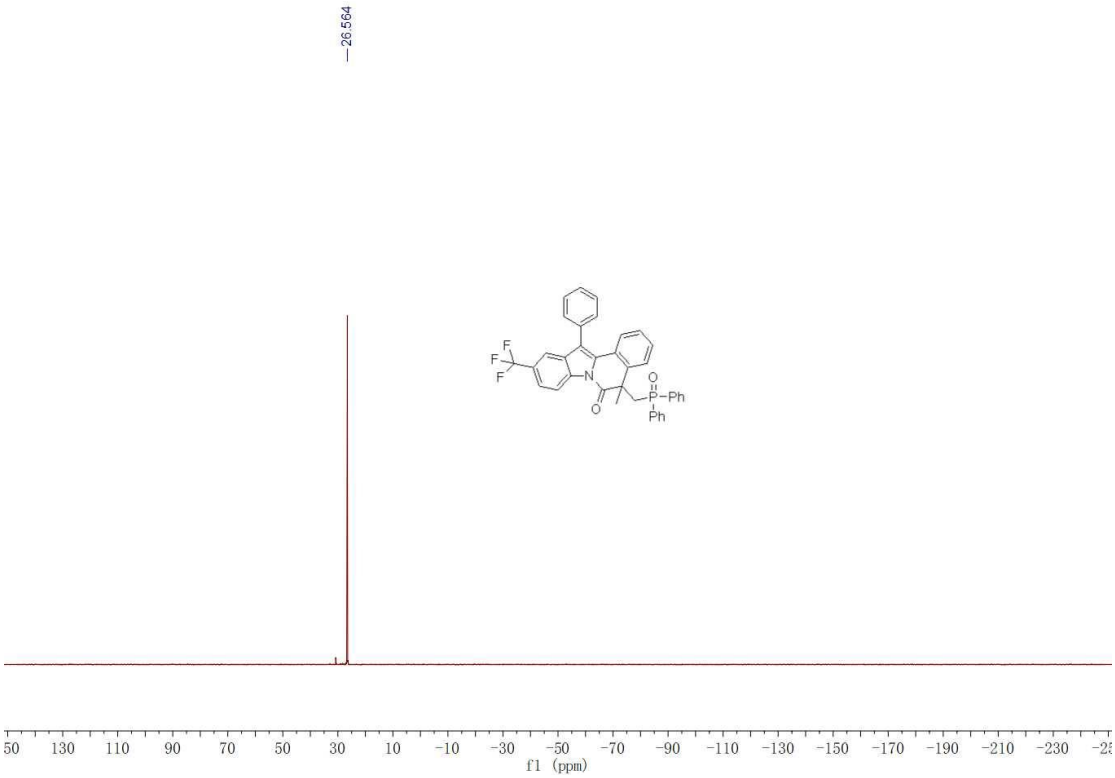


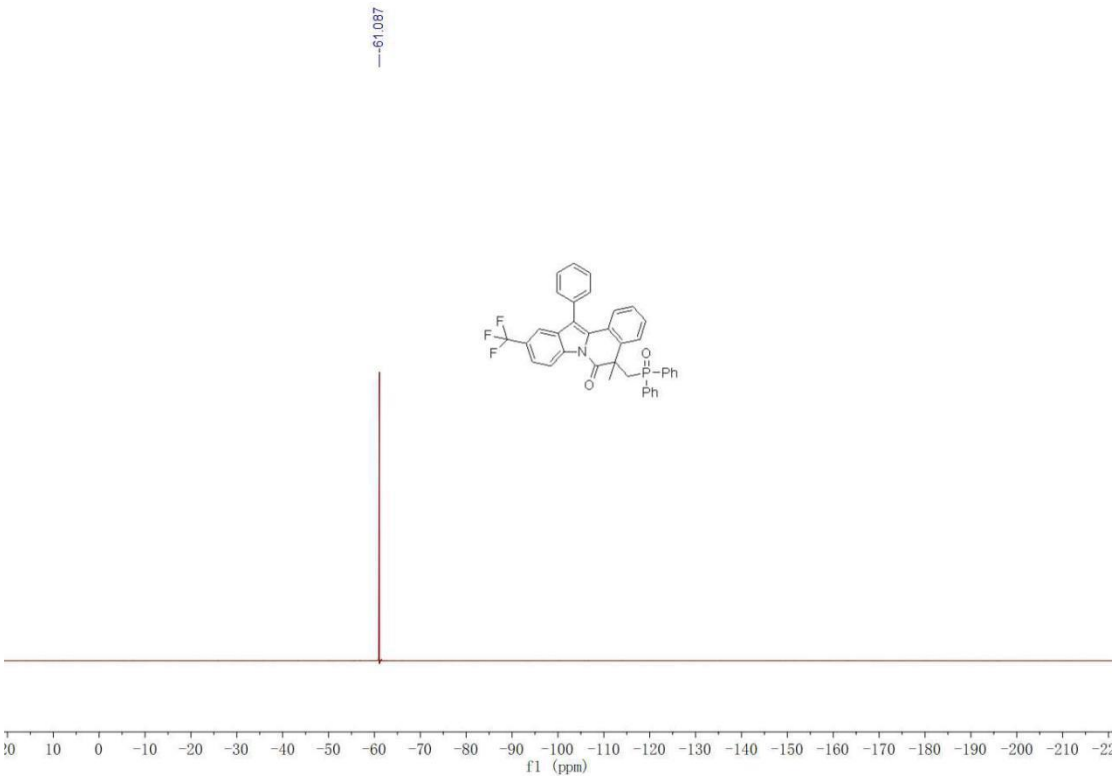



26.330
Br
N
O
O
P
Ph
Ph
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

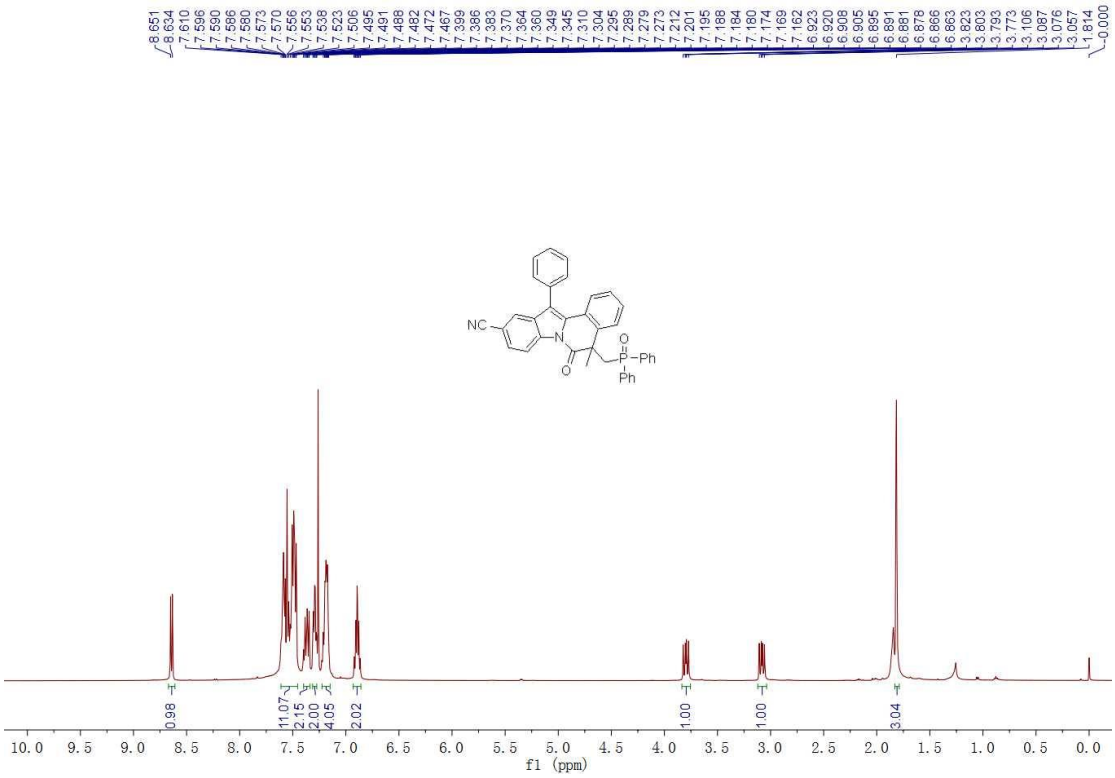
5-((Diphenylphosphoryl)methyl)-5-methyl-12-phenyl-10-(trifluoromethyl)indolo[2,1-a]isoquinolin-6(5*H*)-one (3la)

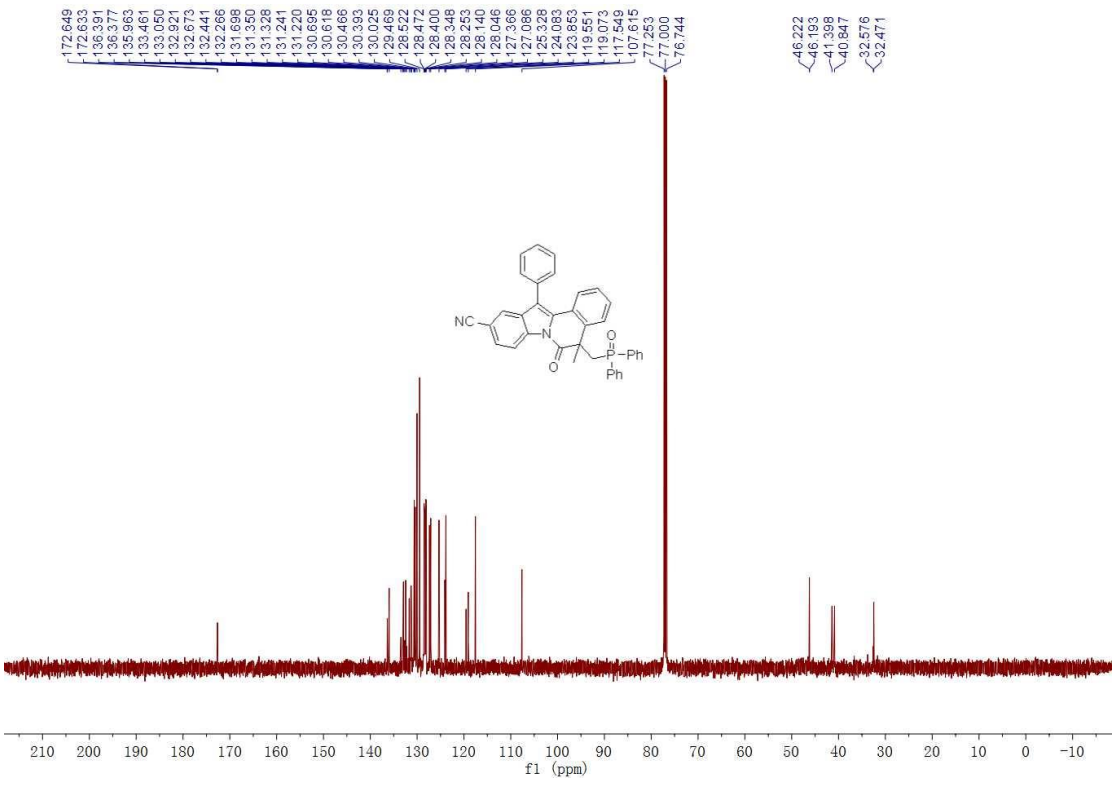


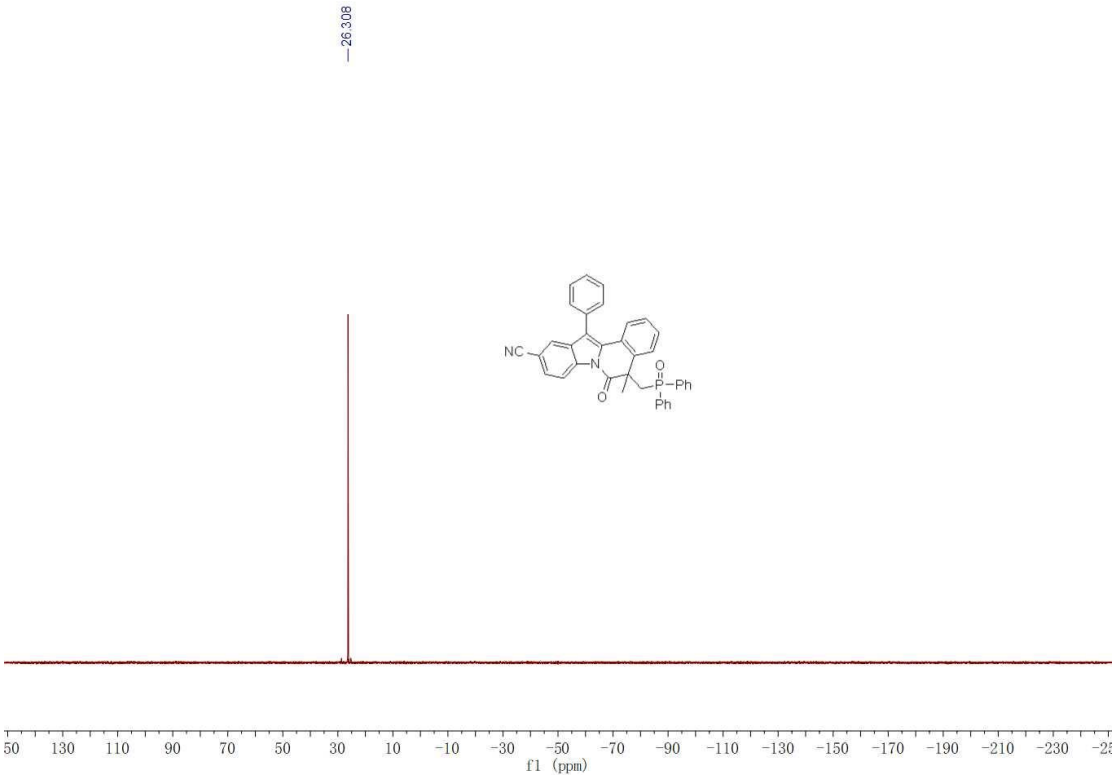

-26.564
F
F
F
N
O
O
P
Ph
Ph
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


-61.087
F
F
F
N
O
O
P
Ph
Ph
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

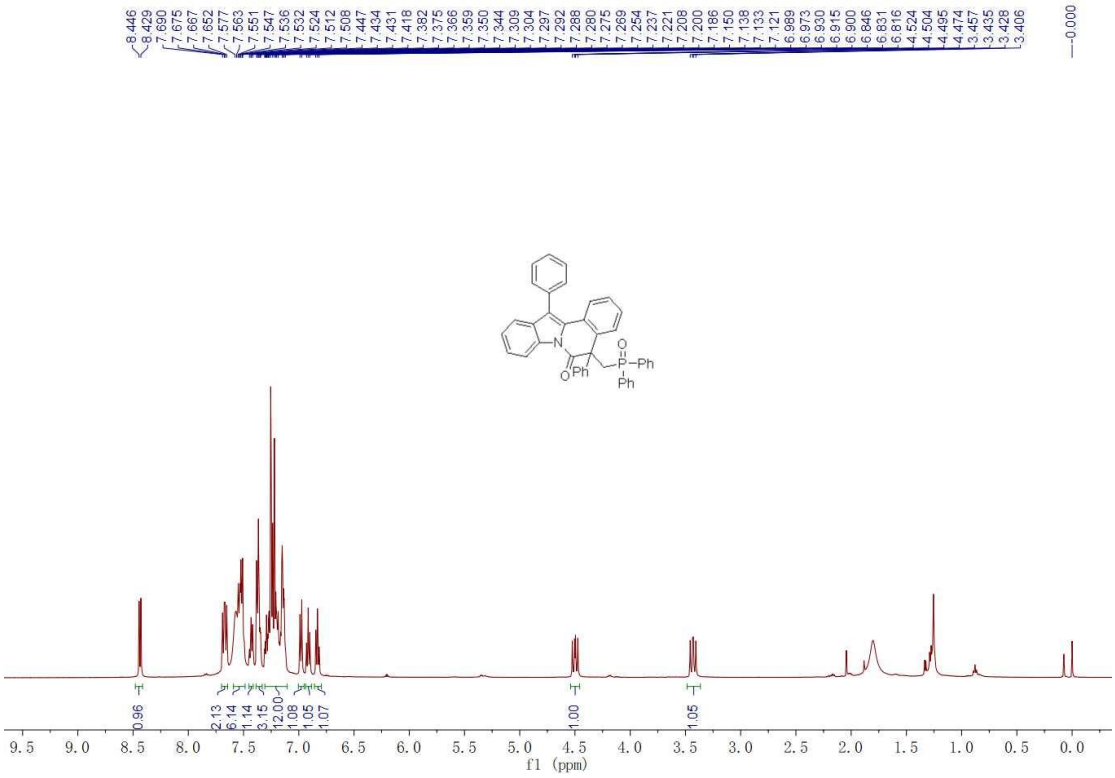
5-((Diphenylphosphoryl)methyl)-5-methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2, 1-a]isoquinoline-10-carbonitrile (3ma)

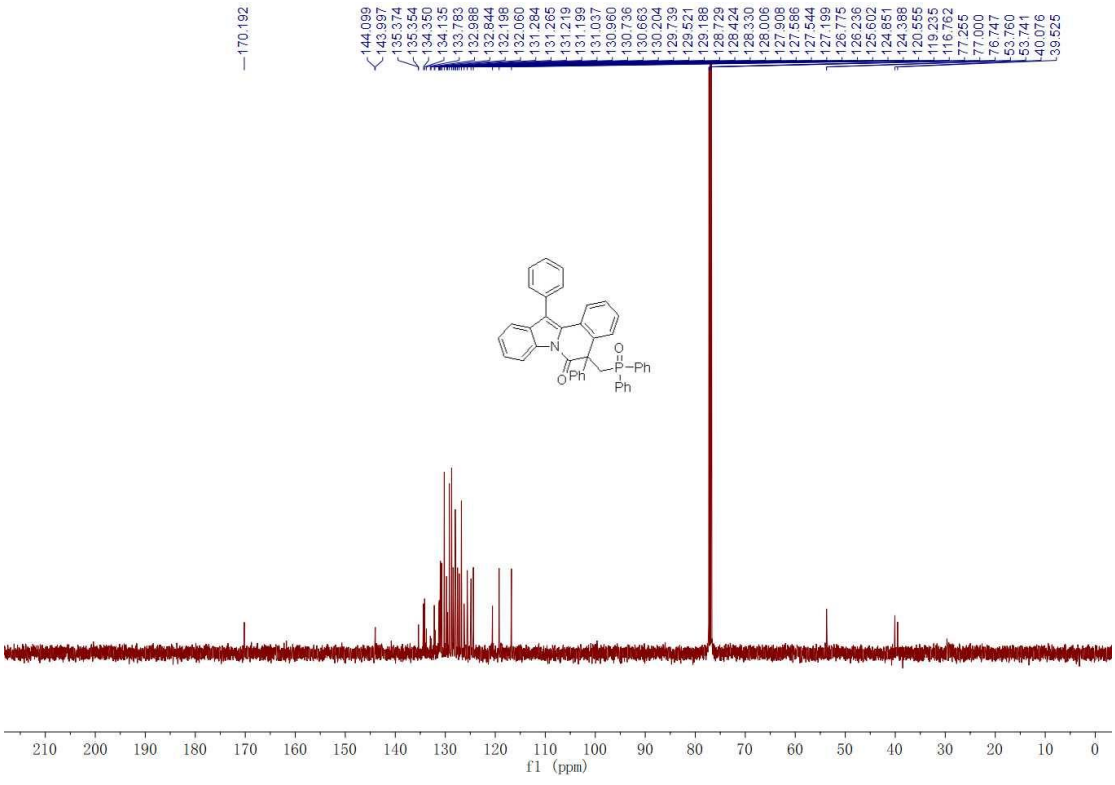


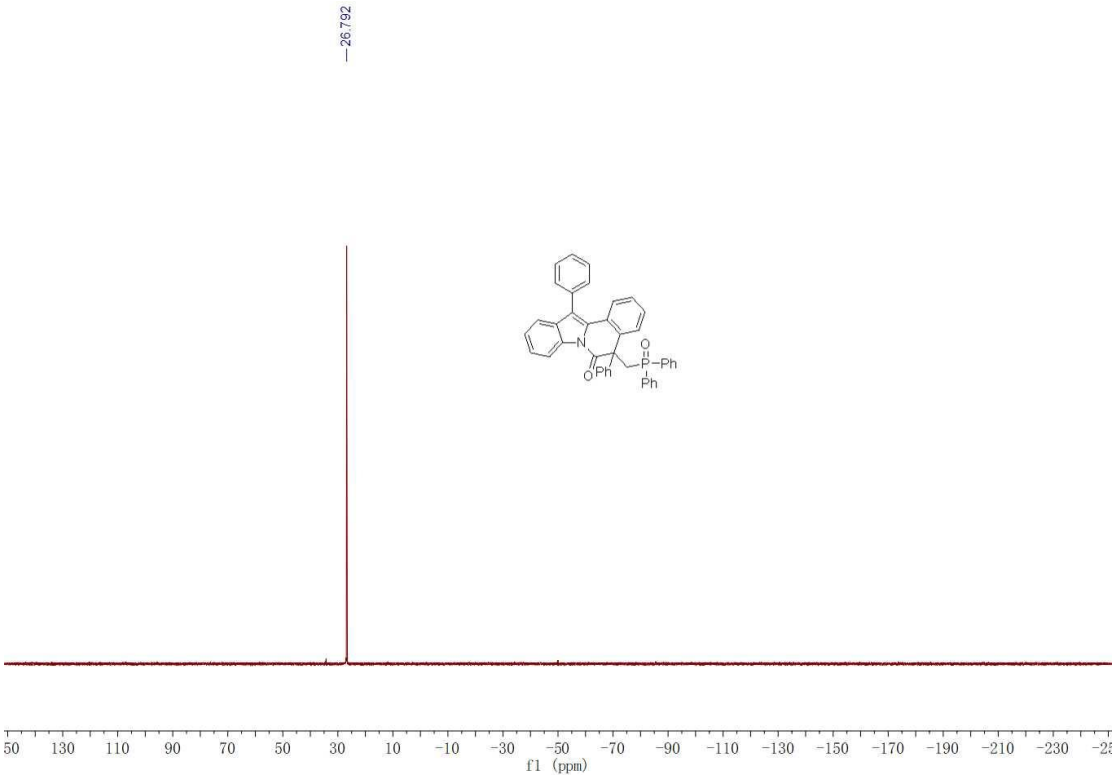



26.308
NC
O
N
O
P
Ph
Ph
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

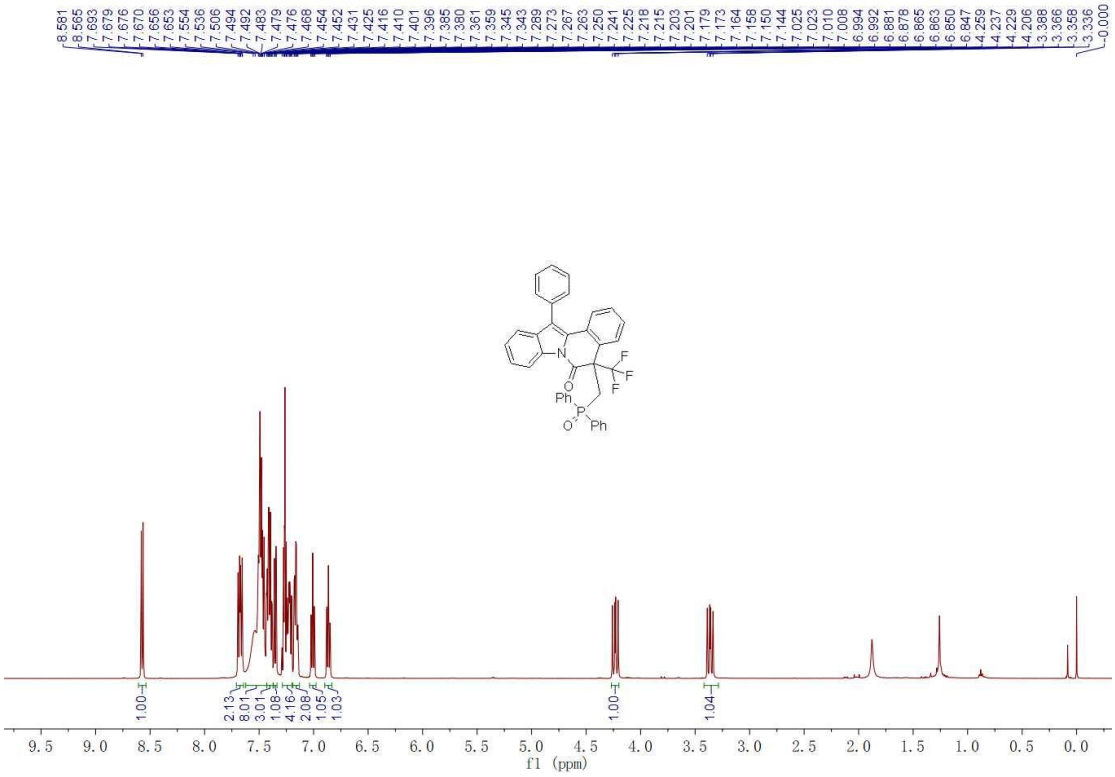
5-((Diphenylphosphoryl)methyl)-5,12-diphenylindolo[2,1-a]isoquinolin-6(5H)-one (3na)

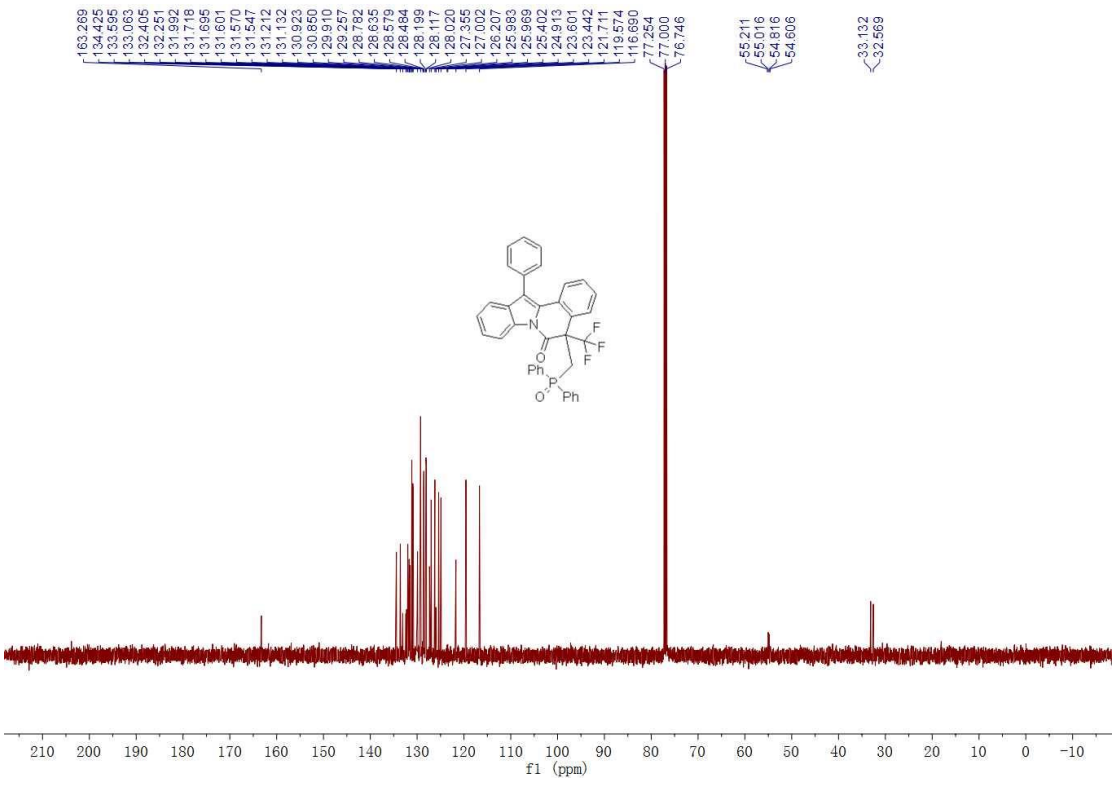


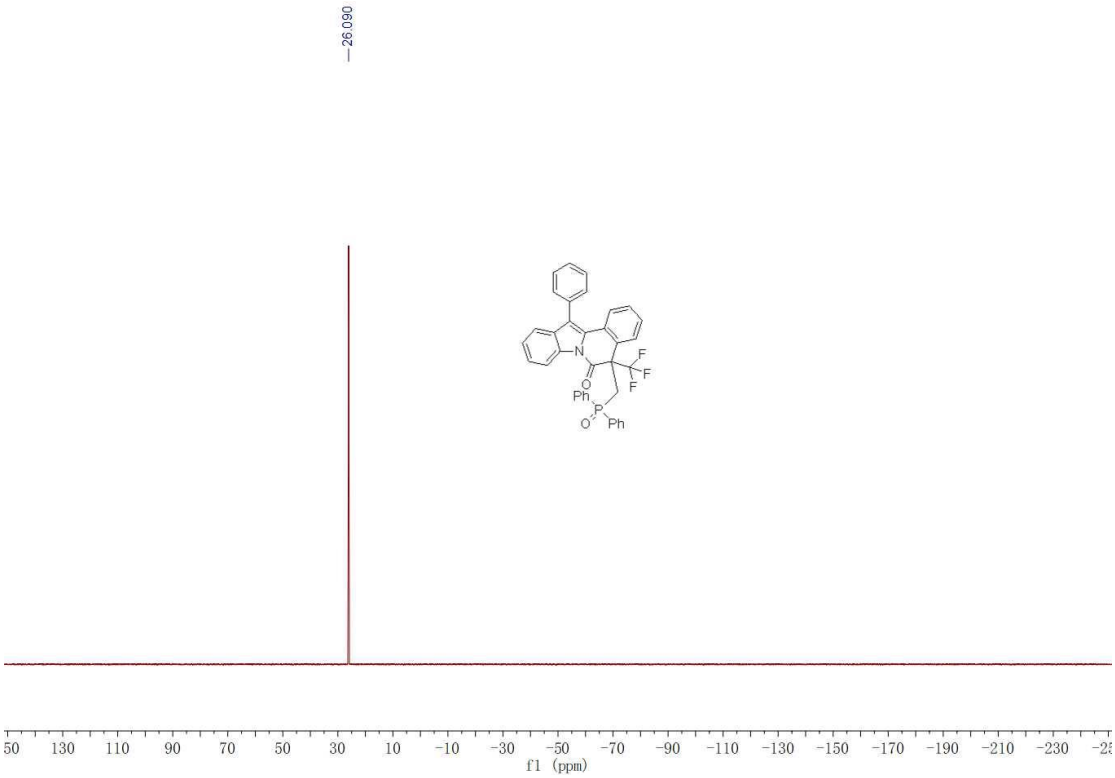


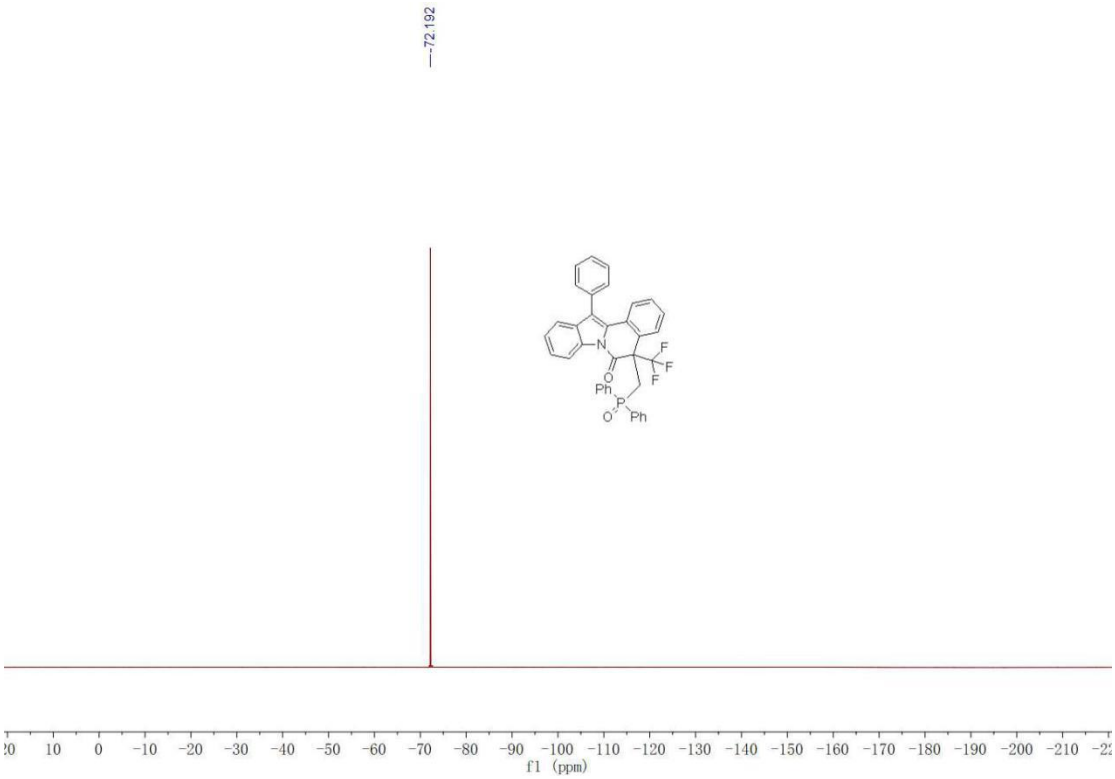

26.792
O
P–Ph
Ph
N
O
Ph
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

5-((Diphenylphosphoryl)methyl)-12-phenyl-5-(trifluoromethyl)indolo[2,1-a]isoquinolin-6(5*H*)-one (3oa)

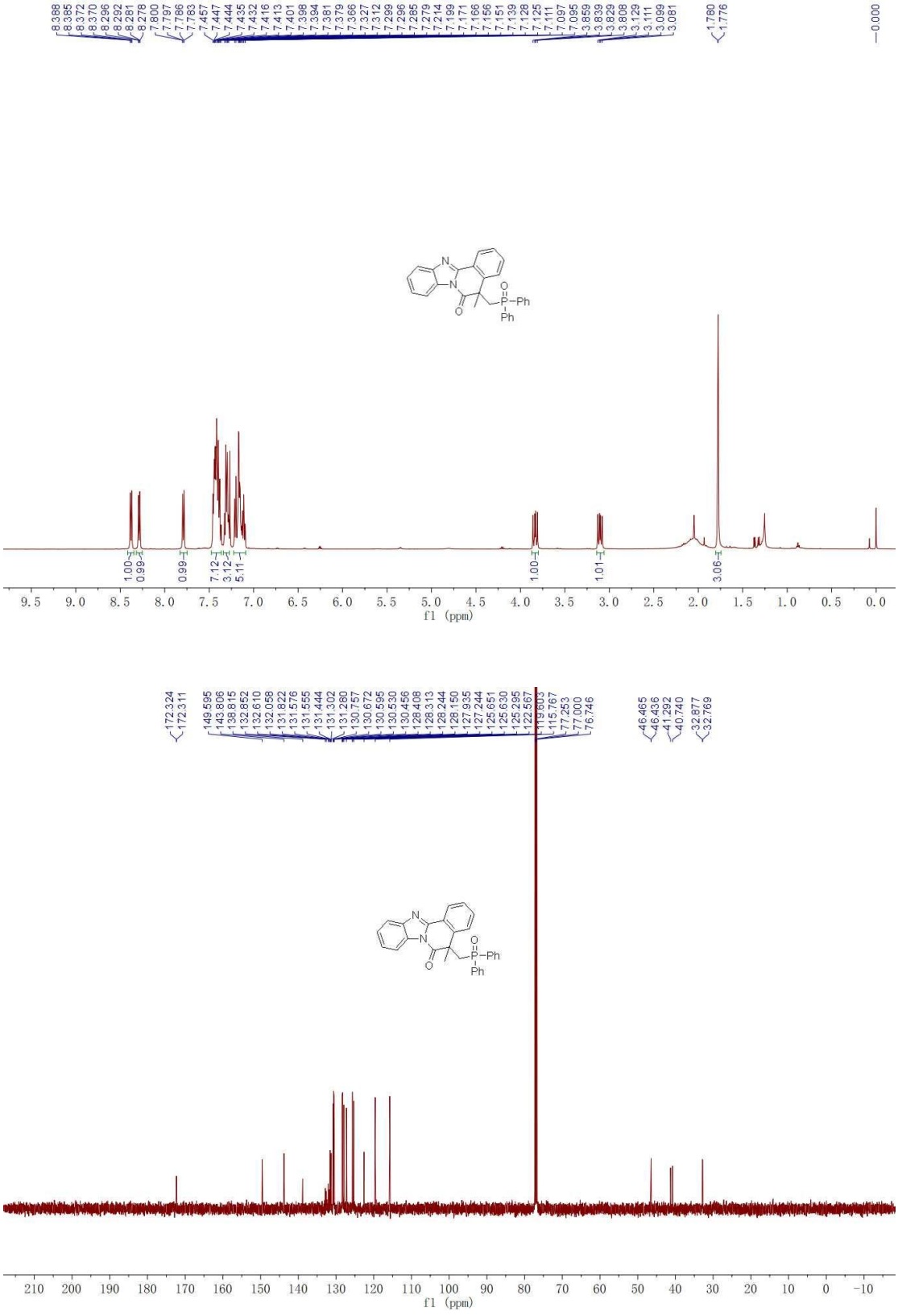


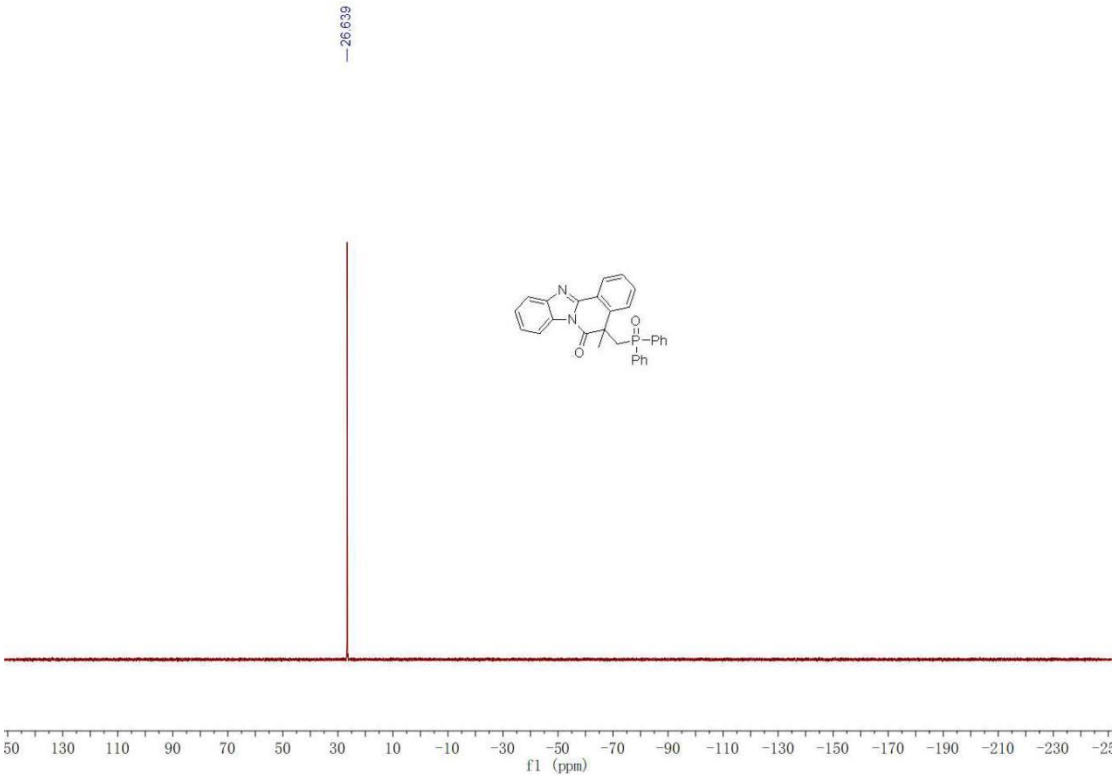



26.090
F
F
F
O
Ph
P
O
Ph
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

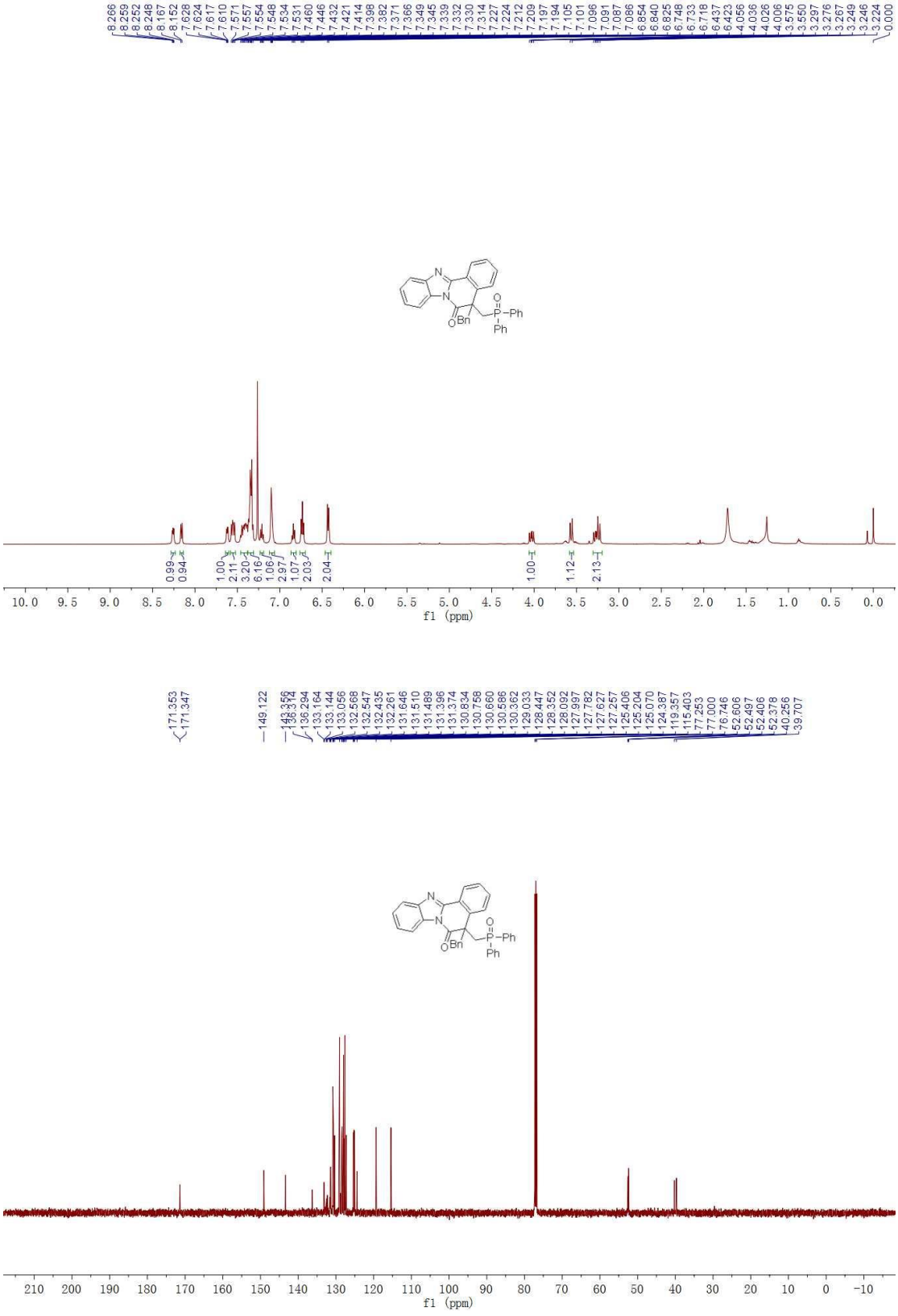

72.192
F
F
F
O
Ph
P
O
Ph
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

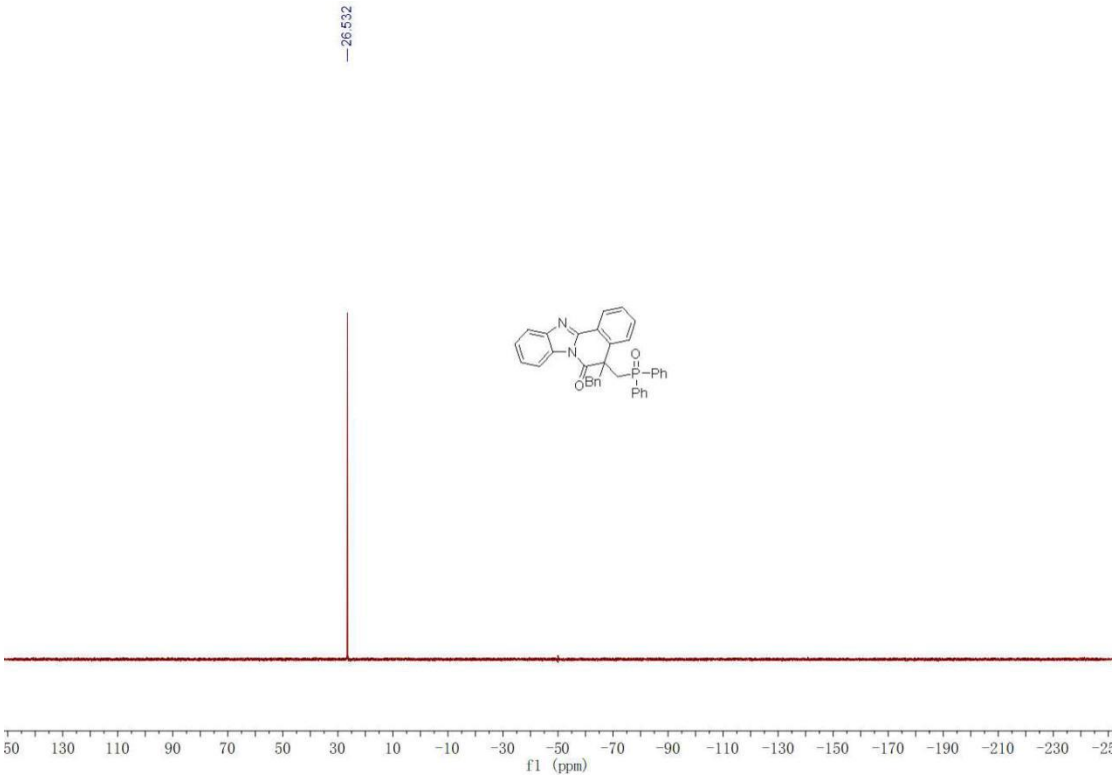
5-((Diphenylphosphoryl)methyl)-5-methylbenzo[4,5]imidazo[2,1-a]isoquinolin-6(5*H*)-one (3pa)



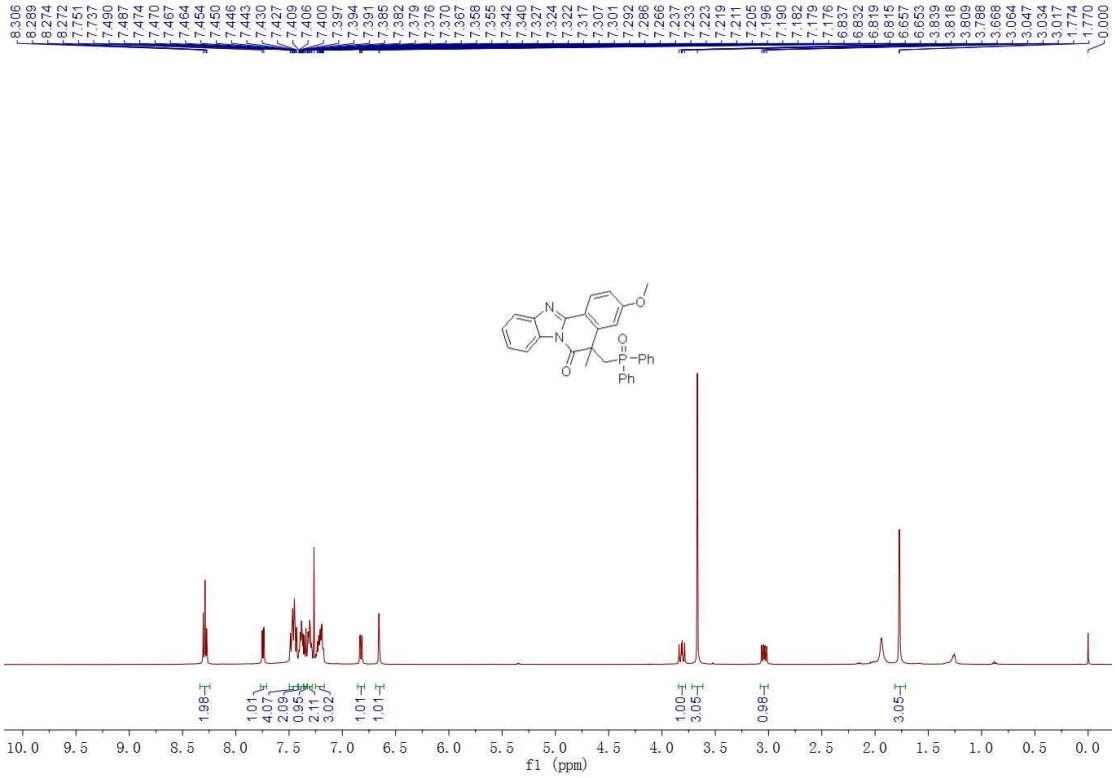

26.639
N
N
O
O
P
Ph
Ph
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

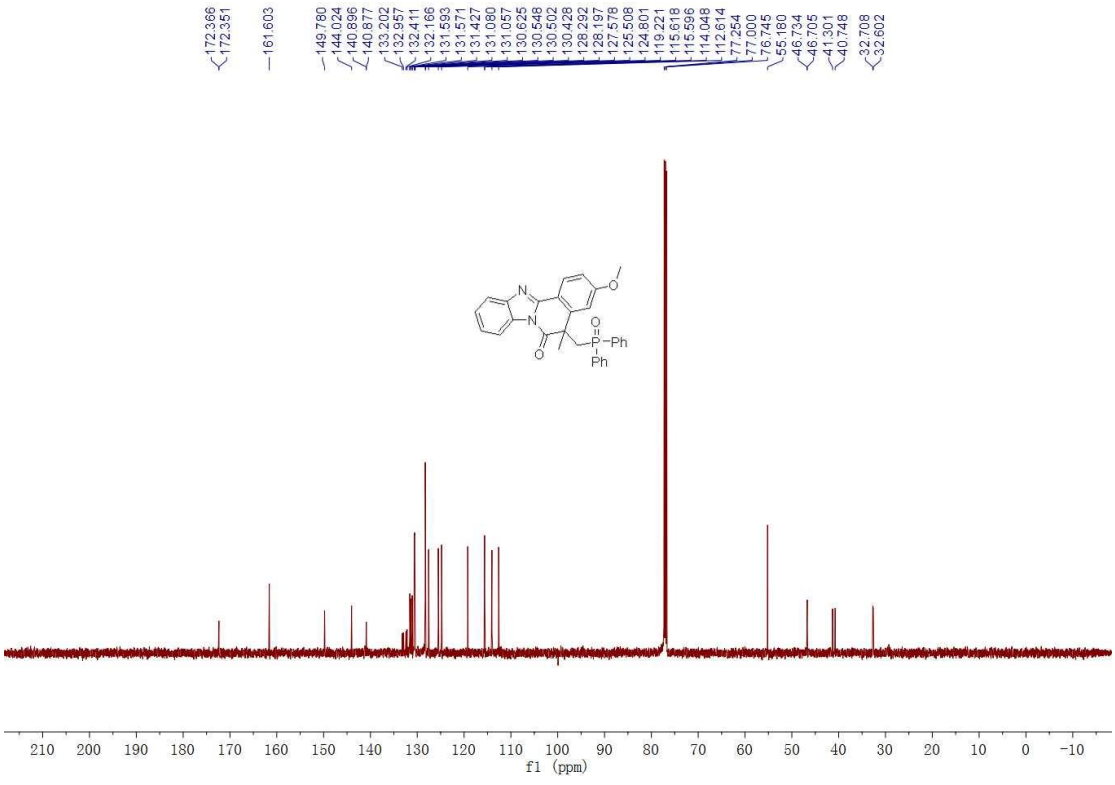
5-Benzyl-5-((diphenylphosphoryl)methyl)benzo[4,5]imidazo[2,1-a]isoquinolin-6(5H)-one (3qa)

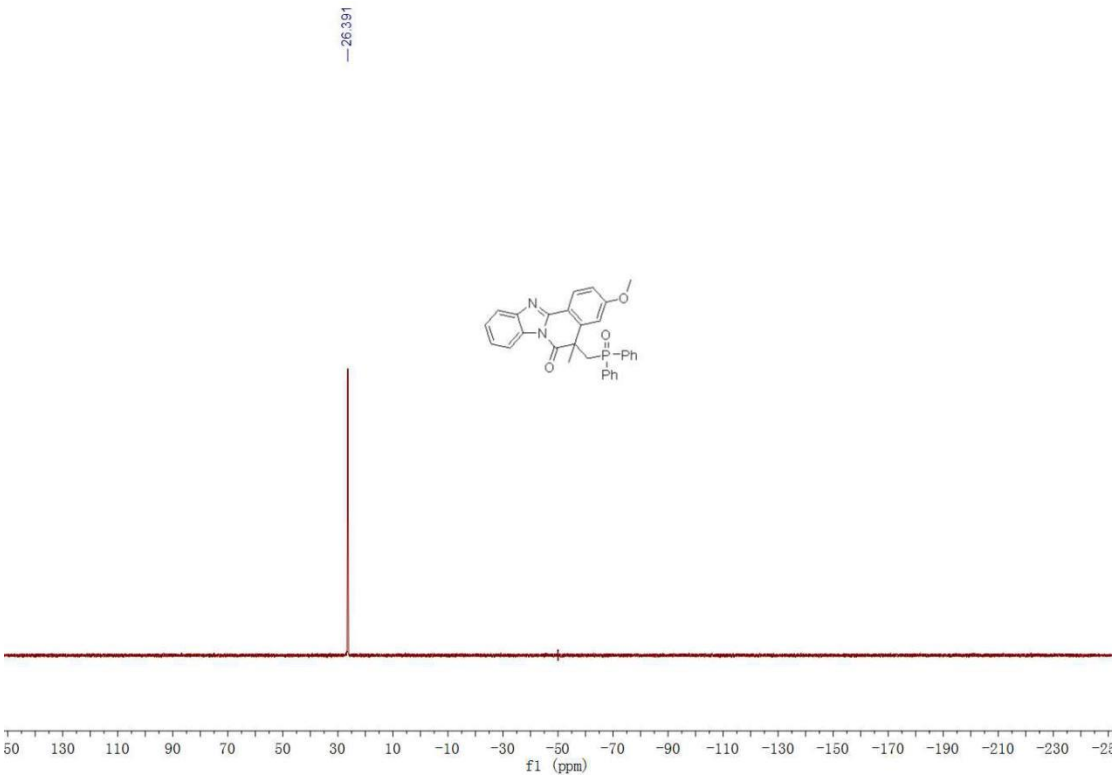



26.532
N
N
O
Bn
O
P
Ph
Ph
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

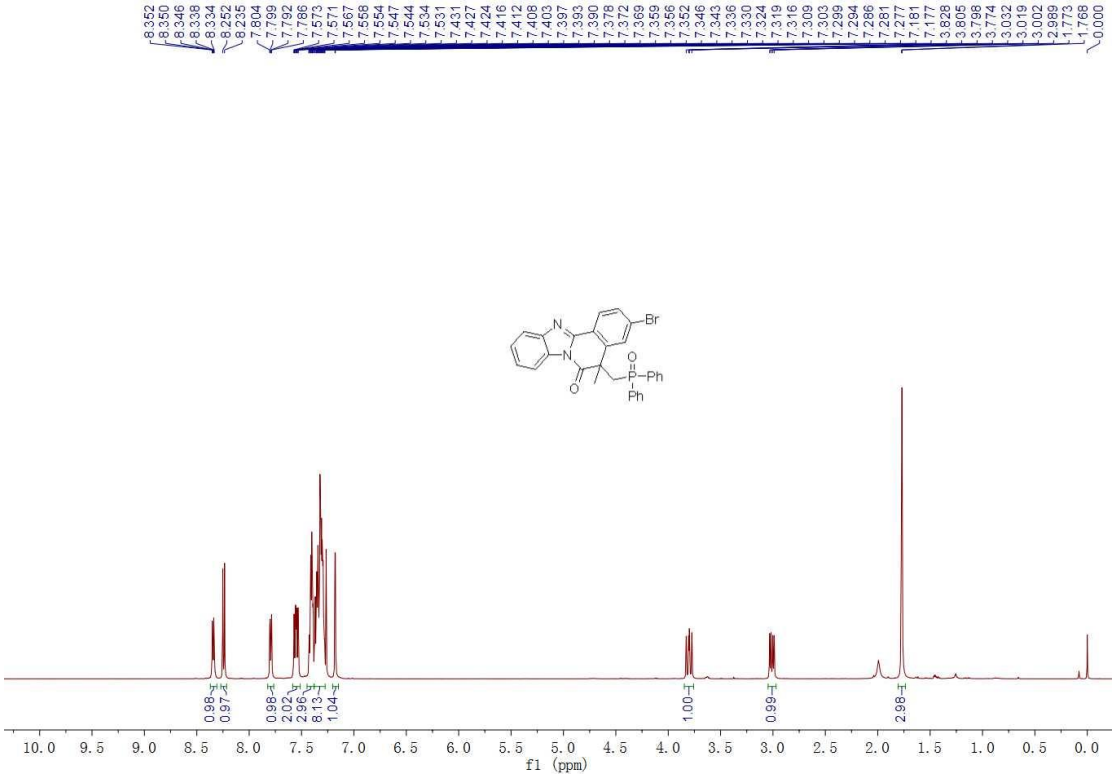
5-((diphenylphosphoryl)methyl)-3-methoxy-5-methylbenzo[4,5]imidazo[2,1-*a*]isoquinolin-6(5*H*)-one (3ra)

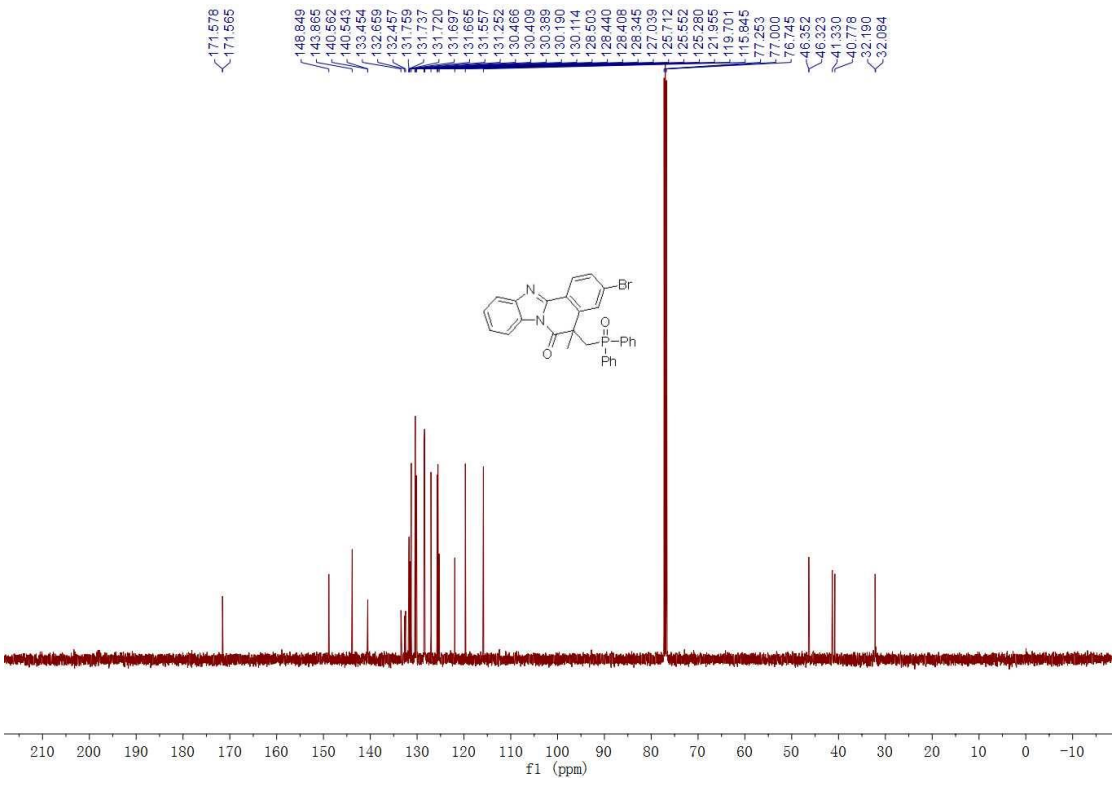


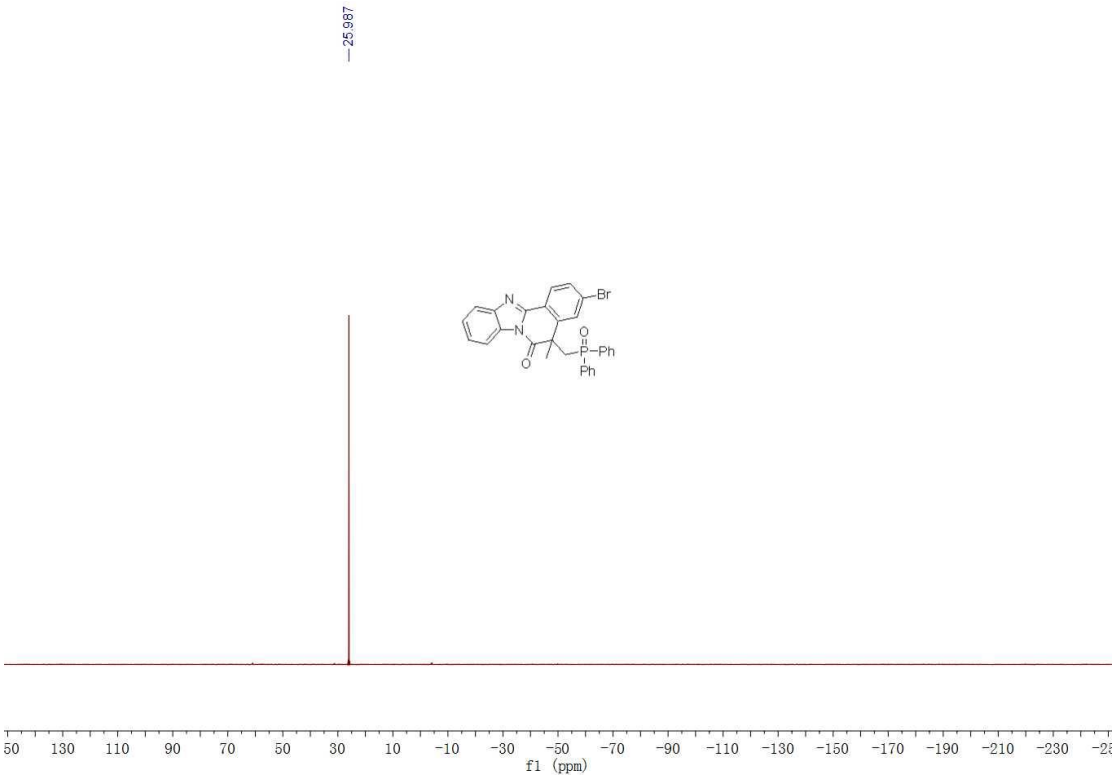



26.391
O
N
N
O
O
P
Ph
Ph
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

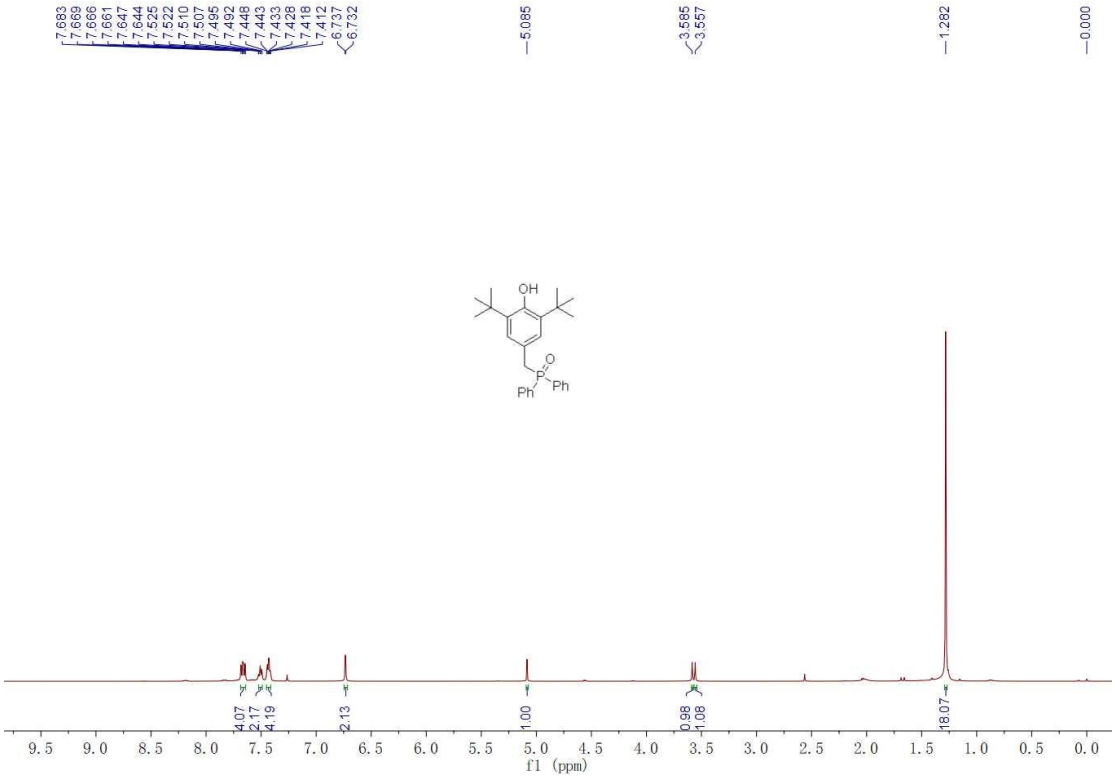
3-bromo-5-((diphenylphosphoryl)methyl)-5-methylbenzo[4,5]imidazo[2,1-*a*]isoquinolin-6(5*H*)-one (3sa)

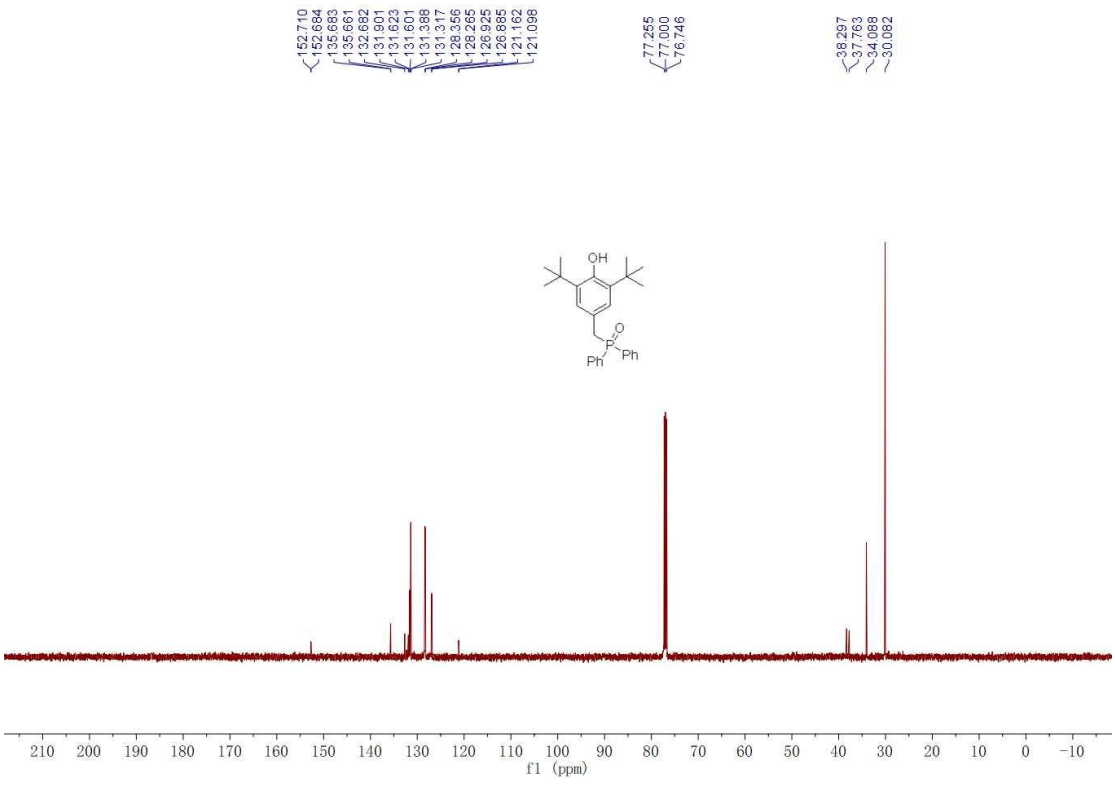


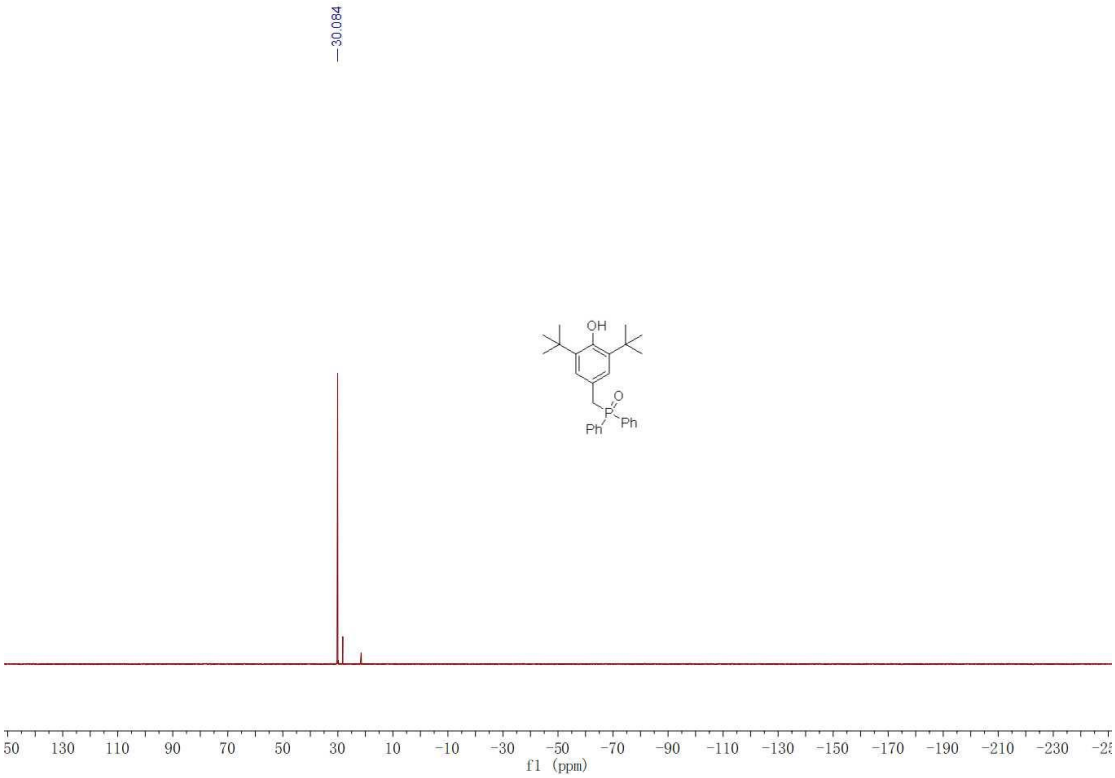



25.987
Br
N
N
O
O
P
Ph
Ph
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

(3,5-Di-tert-butyl-4-hydroxybenzyl)diphenylphosphine oxide (4)

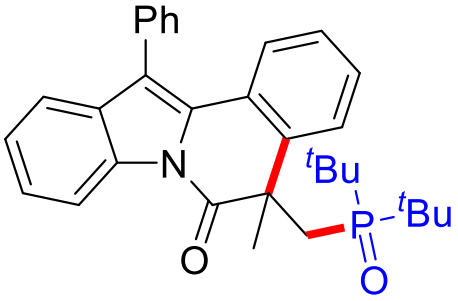





30.084
OH
O
P
Ph
Ph
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

(D) The X-ray single-crystal diffraction analysis of 3af:

5-((Di-*tert*-butylphosphoryl)methyl)-5-methyl-12-phenylindolo[2,1-a]isoquinolin-6(5*H*)-one(3af):



CCDC (1987617):