Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Electrochemical Phosphorothiolation and 1,4-S→C Phospho-Fries Rearrangement: Controlled Access to Phosphorothiolated and Mercapto-Phosphono Substituted Indolizines

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1. General considerations

Unless otherwise noted, commercial reagents were purchased from Adamas, Alfa, Aladdin, TCI, *J&K* or Macklin and used without further purification. All reactions were carried out using oven-dried glassware and all reactions proceeded without special care. Column chromatography was performed on 200-300 mesh silica gel (Huanghai, China).

^{1}H, ^{31}P and $^{13}C\{^{1}H\}$ NMR spectra were recorded on an Bruker Ascend 400 MHz spectrometer at ambient temperature. ^{1}H NMR spectra are referred to the TMS signal (δ = 0 ppm) and ^{13}C NMR spectra are referred to the residual solvent signal (δ = 77.16 ppm). Data for ^{1}H NMR are reported as follows: chemical shifts (δ ppm), multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integration.

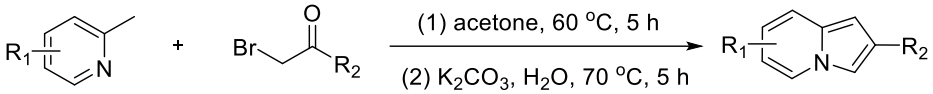
The instrument for electrolysis is ElectraSyn 2.0 Package (IKA), the anode electrode is vitreous carbon plate (52 mm×8 mm×2 mm) and cathodic electrode was platinum plate (52 mm×8 mm×2 mm); And MS-3610DS (MAISHENG), carbon plate (10 mm×10 mm×3 mm) and cathodic electrode was platinum plate (10 mm×10 mm×0.1 mm). The data of HRMS was carried out on Agilent 7250 GC/QTOF.

2. Experimental procedures and characterization data

2.1 Experimental procedures

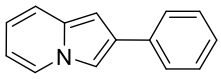
Synthesis of compounds 1 according to the following procedure[1]:

As exemplified for **1a**:



A solution of 2-picoline (0.93 g, 10 mmol, 1.0 equiv) and 2-bromoacetophenone (1.99 g, 10 mmol, 1.0 equiv) in acetone (50 mL) were added to a 100 mL round bottom flask and heated with a heating mantle for 5 hours to 60 °C. The precipitate obtained by filtration separation was redissolved in 20 mL of hot water (60 °C). Then, K_2CO_3 (2.76 g, 20 mmol, 2.0 equiv) was added and heated at 60 °C for 5 hours. After filtration and drying in vacuo, a white solid compound **1a** was obtained without further purification.

2-Phenylindolizine (1a)

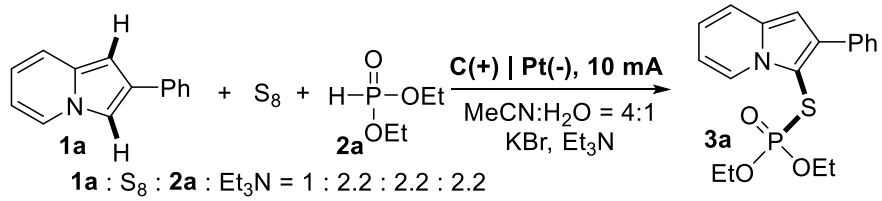


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.0 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.58 (s, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.29-7.23 (m, 1H), 6.70 (s, 1H), 6.68-6.60 (m, 1H), 6.45 (t, *J* = 6.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 133.6, 129.4, 128.7, 126.5, 126.2, 125.0, 119.0, 117.3, 110.5, 109.2, 96.6.

Indolizine derivatives **1** were known compounds and synthesized according to the known procedures, and their NMR data were in agreement with those described in the literature.[1,2]

Synthesis of products 3 according to the following procedure:

As exemplified for **3a**:

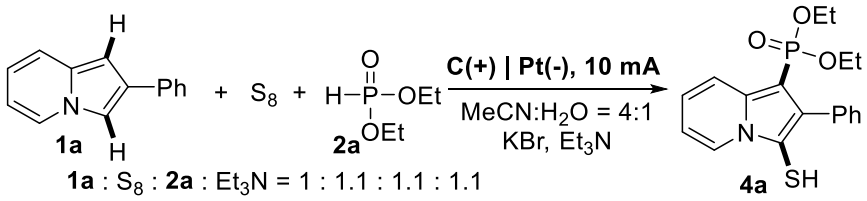


2-Phenylindolizine (0.3 mmol, 1.0 equiv), S_8 (0.66 mmol, 2.2 equiv), diethyl phosphonate (0.66 mmol, 2.2 equiv), KBr (1.2 mmol), Et_3N (0.66 mmol), CH_3CN (4 mL) and H_2O (1 mL) were placed in a 10 mL undivided electrolytic cell with a vitreous carbon plate anode (52 mm×8 mm×2 mm) and a platinum plate cathode (52 mm×8 mm×2 mm). The electrolysis was carried out at room temperature under a constant current of 10 mA for 10 hours. Then, the resulting solution was quenched with 10 mL brine and extracted

with ethyl acetate (3×10 mL). The extract was dried with Na_2SO_4. The solvent was removed with a rotary evaporator. The pure product **3a** was obtained by preparative TLC on silica gel (petroleum ether: ethyl acetate = 3: 1).

Synthesis of products 4 according to the following procedure:

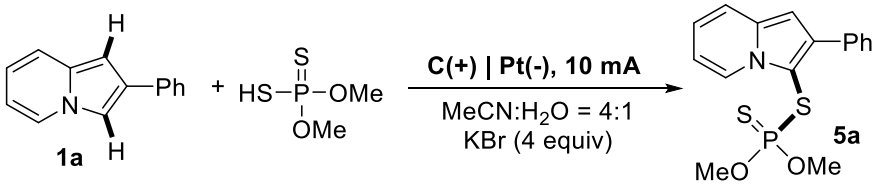
As exemplified for **4a**:



2-Phenylindolizine (0.3 mmol, 1.0 equiv), S_8 (0.33 mmol, 1.1 equiv), diethyl phosphonate (0.33 mmol, 1.1 equiv), KBr (1.2 mmol), Et_3N (0.33 mmol), CH_3CN (4 mL) and H_2O (1 mL) were placed in a 10 mL undivided electrolytic cell with a vitreous carbon plate anode (52 mm×8 mm×2 mm) and a platinum plate cathode (52 mm×8 mm×2 mm). The electrolysis was carried out at room temperature under a constant current of 10 mA for 10 hours. Then, the resulting solution was quenched with 10 mL brine and extracted with ethyl acetate (3×10 mL). The extract was dried with Na_2SO_4. The solvent was removed with a rotary evaporator. The pure product **4a** was obtained by preparative TLC on silica gel (petroleum ether: ethyl acetate = 3: 1).

Synthesis of products 5 according to the following procedure:

As exemplified for **5a**:

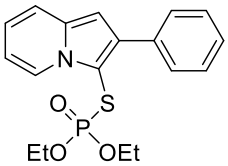


2-Phenylindolizine (0.3 mmol, 1.0 equiv), $(EtO)_2P(S)SH$ (0.33 mmol, 1.1 equiv), KBr (1.2 mmol), CH_3CN (4 mL) and H_2O (1 mL) were placed in a 10 mL undivided electrolytic cell with a vitreous carbon plate anode (52 mm×8 mm×2 mm) and a platinum plate cathode (52 mm×8 mm×2 mm). The electrolysis was carried out at room temperature under a constant current of 10 mA for 10 hours. Then, the resulting solution was quenched with 10 mL brine and extracted with ethyl acetate (3×10 mL). The extract was dried with Na_2SO_4.

The solvent was removed with a rotary evaporator. The pure product **5a** was obtained by preparative TLC on silica gel (petroleum ether: ethyl acetate = 3: 1).

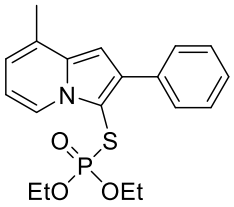
2.2 Characterization data

O,O-Diethyl S-(2-phenylindolizin-3-yl) phosphorothioate (3a)



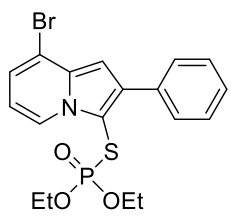
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3a**. Yellow liquid (84.5 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.1 Hz, 1H), 7.77 (d, *J* = 7.1 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.69 (t, *J* = 8.6 Hz, 2H), 3.84 (q, *J* = 8.0 Hz, 2H), 3.69 (q, *J* = 8.3 Hz, 2H), 0.99 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8 (d, *J* = 4.8 Hz), 136.2 (d, *J* = 3.0 Hz), 135.2 (d, *J* = 1.9 Hz), 129.4, 128.4, 127.2, 124.7, 119.8 (d, *J* = 2.6 Hz), 118.7 (d, *J* = 2.9 Hz), 111.0 (d, *J* = 1.5 Hz), 100.8 (d, *J* = 1.9 Hz), 97.9 (d, *J* = 8.4 Hz), 64.3 (d, *J* = 7.0 Hz), 15.9 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.85 – 19.65 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{20}NO_3PS$, 361.0902; found 361.0902.

O,O-Diethyl S-(8-methyl-2-phenylindolizin-3-yl) phosphorothioate (3b)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3b**. Green liquid (81.0 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 6.8 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 6.66 (q, *J* = 6.5 Hz, 3H), 3.84 (q, *J* = 8.0 Hz, 2H), 3.69 (q, *J* = 8.3 Hz, 2H), 2.44 (s, 3H), 1.00 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0 (d, *J* = 3.0 Hz), 136.4 (d, *J* = 4.8 Hz), 135.4 (d, *J* = 1.9 Hz), 129.4, 128.4, 127.8 (d, *J* = 2.8 Hz), 127.2, 122.6, 119.2 (d, *J* = 2.6 Hz), 111.2 (d, *J* = 1.4 Hz), 99.4 (d, *J* = 1.9 Hz), 98.4 (d, *J* = 8.2 Hz), 64.2 (d, *J* = 6.9 Hz), 17.9, 15.9 (d, *J* = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.80 – 20.0 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{19}H_{22}NO_3PS$, 375.1058; found 375.1057.

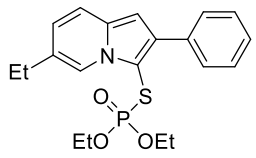
S-(8-Bromo-2-phenylindolizin-3-yl) O,O-diethyl phosphorothioate (3c)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3c**. Yellow liquid (81.7 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.0 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 1H), 6.85 (s, 1H), 6.58 (t, *J* = 7.1 Hz, 1H), 3.85 (q, *J* = 8.0 Hz, 2H), 3.70 (q, *J* = 8.6, 8.2 Hz, 2H), 1.01 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3 (d, *J* = 4.9 Hz), 135.0 (d, *J* = 3.2

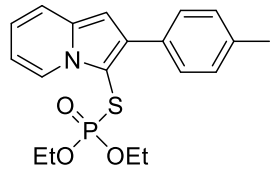
Hz), 134.7 (d, *J* = 1.9 Hz), 129.4, 128.5, 127.6, 124.1, 122.5 (d, *J* = 2.6 Hz), 112.8 (d, *J* = 3.3 Hz), 110.9, 102.7 (d, *J* = 2.2 Hz), 100.7 (d, *J* = 8.5 Hz), 64.5 (d, *J* = 7.2 Hz), 16.0 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.5 (t, *J* = 4.0 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}BrNO_3PS$, 439.0007; found 439.0008.

O,O-Diethyl S-(6-ethyl-2-phenylindolizin-3-yl) phosphorothioate (3d)



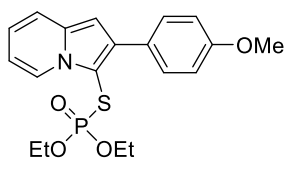
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3d**. Yellow liquid (85.2 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.75 (d, *J* = 7.1 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.28 (m, 2H), 6.77 (d, *J* = 9.1 Hz, 1H), 6.63 (s, 1H), 3.81 (q, *J* = 8.0 Hz, 2H), 3.65 (s, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H), 0.97 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5 (d, *J* = 4.7 Hz), 135.5 (d, *J* = 1.9 Hz), 135.2 (d, *J* = 2.9 Hz), 129.4, 128.4, 127.1, 126.8 (d, *J* = 1.6 Hz), 122.1 (d, *J* = 2.7 Hz), 121.6, 118.4 (d, *J* = 2.9 Hz), 100.4 (d, *J* = 1.9 Hz), 97.6 (d, *J* = 8.4 Hz), 64.2 (d, *J* = 6.9 Hz), 26.3, 15.9 (d, *J* = 7.3 Hz), 15.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.93 – 20.12 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{20}H_{24}NO_3PS$, 389.1215; found 389.1222.

O,O-Diethyl S-(2-(p-tolyl)indolizin-3-yl) phosphorothioate (3e)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3e**. Black liquid (67.5 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.1 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.85 (t, *J* = 7.7 Hz, 1H), 6.72 – 6.63 (m, 2H), 3.88 – 3.82 (m, 2H), 3.71 (q, *J* = 8.1 Hz, 2H), 2.40 (s, 3H), 1.00 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 136.9 (d, *J* = 4.8 Hz), 136.2 (d, *J* = 3.1 Hz), 132.3 (d, *J* = 1.8 Hz), 129.3, 129.1, 124.7, 119.8 (d, *J* = 2.8 Hz), 118.7 (d, *J* = 2.9 Hz), 111.0 (d, *J* = 1.5 Hz), 100.7 (d, *J* = 1.9 Hz), 97.7 (d, *J* = 8.2 Hz), 64.3 (d, *J* = 7.0 Hz), 21.3, 15.9 (d, *J* = 7.2 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{19}H_{22}NO_3PS$, 375.1058; found 375.1054.

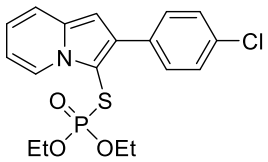
O,O-Diethyl S-(2-(4-methoxyphenyl)indolizin-3-yl) phosphorothioate (3f)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3f**. Yellow liquid (75.5 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.1 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.9 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.85 (t, *J* = 7.8 Hz, 1H), 6.70 – 6.65 (m, 1H), 6.63 (s, 1H), 3.87 -3.85 (m, 5H), 3.79 – 3.67 (m, 2H), 1.02 (t, *J* = 7.1

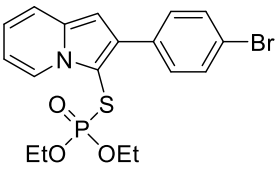
Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 136.6 (d, *J* = 4.8 Hz), 136.2 (d, *J* = 3.3 Hz), 130.5, 127.8 (d, *J* = 1.8 Hz), 124.7, 119.8 (d, *J* = 2.8 Hz), 118.7 (d, *J* = 3.0 Hz), 113.9, 110.9 (d, *J* = 1.6 Hz), 100.5 (d, *J* = 2.0 Hz), 64.4 (d, *J* = 7.0 Hz), 55.5, 16.0 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.02 - 19.82 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}N_2O_5PS$, 406.0752; found 406.0757.

S-(2-(4-Chlorophenyl)indolizin-3-yl) O,O-diethyl phosphorothioate (3g)



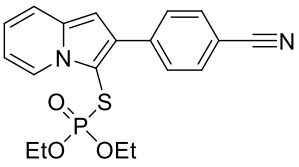
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3g**. Black liquid (87.7 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.1 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.40 (t, *J* = 9.0 Hz, 3H), 6.87 (t, *J* = 7.8 Hz, 1H), 6.70 (td, *J* = 6.9, 1.3 Hz, 1H), 6.64 (s, 1H), 3.92 – 3.86 (m, 2H), 3.79 – 3.72 (m, 2H), 1.03 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2 (d, *J* = 3.1 Hz), 135.5 (d, *J* = 4.8 Hz), 133.7 (d, *J* = 1.9 Hz), 133.2, 130.6, 128.5, 124.7, 120.1 (d, *J* = 2.6 Hz), 118.8 (d, *J* = 2.8 Hz), 111.3 (d, *J* = 1.4 Hz), 100.7 (d, *J* = 1.9 Hz), 97.9 (d, *J* = 8.3 Hz), 64.4 (d, *J* = 7.1 Hz), 15.9 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.85 – 19.64 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}ClNO_3PS$, 395.0512; found 395.0510.

S-(2-(4-Bromophenyl)indolizin-3-yl) O,O-diethyl phosphorothioate (3h)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3h**. Green liquid (86.9 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.1 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 1H), 6.88 (t, *J* = 7.7 Hz, 1H), 6.75 – 6.66 (m, 1H), 6.65 (s, 1H), 3.88 (t, *J* = 8.0 Hz, 2H), 3.80 – 3.74 (m, 2H), 1.04 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3 (d, *J* = 3.1 Hz), 135.6 (d, *J* = 4.7 Hz), 134.3 (d, *J* = 1.8 Hz), 131.6, 131.0, 124.8, 121.4, 120.2 (d, *J* = 2.9 Hz), 118.9 (d, *J* = 2.8 Hz), 111.4, 100.7 (d, *J* = 1.8 Hz), 98.0 (d, *J* = 8.0 Hz), 64.5 (d, *J* = 7.2 Hz), 16.0 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.82 – 19.62 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}BrNO_3PS$, 439.0007; found 439.0011.

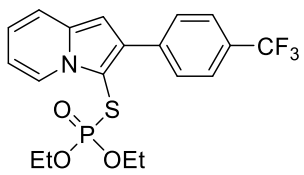
S-(2-(4-Cyanophenyl)indolizin-3-yl) O,O-diethyl phosphorothioate (3i)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3i**. Green liquid (84.5 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.1 Hz, 1H),

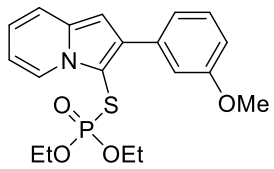
7.92 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 3H), 7.42 (d, *J* = 8.9 Hz, 1H), 6.90 (t, *J* = 7.8 Hz, 1H), 6.73 (t, *J* = 6.9 Hz, 1H), 6.69 (s, 1H), 3.92 (q, *J* = 8.1, 7.7 Hz, 2H), 3.80 (q, *J* = 8.2 Hz, 2H), 1.05 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1 (d, *J* = 1.9 Hz), 136.4 (d, *J* = 2.9 Hz), 134.6 (d, *J* = 4.7 Hz), 132.2, 129.8, 124.7, 120.5 (d, *J* = 2.6 Hz), 119.1, 119.1 (d, *J* = 2.7 Hz), 111.8 (d, *J* = 1.4 Hz), 110.6, 101.0 (d, *J* = 1.6 Hz), 98.5 (d, *J* = 8.2 Hz), 64.6 (d, *J* = 7.3 Hz), 16.0 (d, *J* = 6.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.70 – 19.50 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{19}H_{19}N_2O_3PS$, 386.0854; found 386.0848.

O,O-Diethyl S-(2-(4-(trifluoromethyl)phenyl)indolizin-3-yl) phosphorothioate (3j)



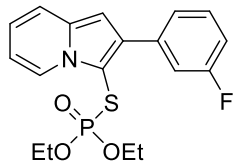
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3j**. Yellow liquid (87.5 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.1 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 6.77 – 6.68 (m, 2H), 3.88 (q, *J* = 8.0 Hz, 2H), 3.75 (q, *J* = 8.1 Hz, 2H), 1.01 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 136.4 (d, *J* = 3.0 Hz), 135.2 (d, *J* = 4.7 Hz), 129.6, 129.2 (d, *J* = 32.5 Hz), 125.3 (q, *J* = 3.8 Hz), 124.8, 124.4 (d, *J* = 272.0 Hz), 120.3 (d, *J* = 2.6 Hz), 119.0 (d, *J* = 2.7 Hz), 111.6 (d, *J* = 1.4 Hz), 100.9 (d, *J* = 1.7 Hz), 98.4 (d, *J* = 8.3 Hz), 64.5 (d, *J* = 7.3 Hz), 15.9 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.69 – 19.49 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{19}H_{19}F_3NO_3PS$, 429.0775; found 429.0773.

O,O-Diethyl S-(2-(3-methoxyphenyl)indolizin-3-yl) phosphorothioate (3k)



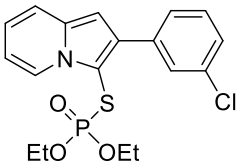
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3k**. Green liquid (89.1 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.1 Hz, 1H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.35 (d, *J* = 5.9 Hz, 3H), 6.92 – 6.81 (m, 2H), 6.71 – 6.66 (m, 2H), 3.87 – 3.77 (m, 5H), 3.79 – 3.67 (m, 2H), 1.01 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 136.7 (d, *J* = 4.8 Hz), 136.6 (d, *J* = 1.9 Hz), 136.1 (d, *J* = 3.1 Hz), 129.4, 124.7, 121.9, 119.9 (d, *J* = 2.8 Hz), 118.8 (d, *J* = 2.9 Hz), 114.8, 113.0, 111.1 (d, *J* = 1.4 Hz), 100.9 (d, *J* = 1.9 Hz), 98.0 (d, *J* = 8.3 Hz), 64.3 (d, *J* = 7.1 Hz), 55.4, 15.9 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.91 – 19.71 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{19}H_{22}NO_4PS$, 391.1007; found 391.1006.

O,O-Diethyl S-(2-(3-fluorophenyl)indolizin-3-yl) phosphorothioate (3l)



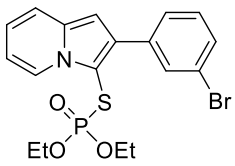
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3l**. Black liquid (84.1 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.2 Hz, 1H), 7.54 (dd, *J* = 12.2, 9.4 Hz, 2H), 7.44 – 7.34 (m, 2H), 7.03 (t, *J* = 8.5 Hz, 1H), 6.87 (t, *J* = 7.8 Hz, 1H), 6.70 (t, *J* = 6.8 Hz, 1H), 6.66 (s, 1H), 3.92 – 3.86 (m, 2H), 3.84 – 3.70 (m, 2H), 1.03 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, *J* = 244.9 Hz), 137.7 – 137.2 (m), 136.2 (d, *J* = 3.0 Hz), 135.7 – 135.1 (m), 129.8 (d, *J* = 8.4 Hz), 125.0 (d, *J* = 2.9 Hz), 124.7, 120.1 (d, *J* = 2.6 Hz), 118.9 (d, *J* = 2.9 Hz), 116.1 (d, *J* = 22.1 Hz), 113.9 (d, *J* = 21.0 Hz), 111.4 (d, *J* = 1.4 Hz), 100.8 (d, *J* = 1.8 Hz), 98.1 (d, *J* = 8.3 Hz), 64.4 (d, *J* = 7.1 Hz), 15.9 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.76 – 19.55 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}FNO_3PS$, 379.0807; found 379.0811.

S-(2-(3-Chlorophenyl)indolizin-3-yl) O,O-diethyl phosphorothioate (3m)



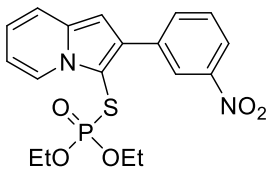
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3m**. Yellow liquid (91.0 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.1 Hz, 1H), 7.79 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.27 (m, 3H), 6.87 (t, *J* = 7.8 Hz, 1H), 6.70 (t, *J* = 6.9 Hz, 1H), 6.66 (s, 1H), 3.89 (q, *J* = 8.3 Hz, 2H), 3.77 (q, *J* = 8.1 Hz, 2H), 1.04 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1 (d, *J* = 1.8 Hz), 136.2 (d, *J* = 2.9 Hz), 135.2 (d, *J* = 4.8 Hz), 134.2, 129.6, 129.2, 127.5, 127.2, 124.7, 120.1 (d, *J* = 2.6 Hz), 118.9 (d, *J* = 2.9 Hz), 111.4, 100.8 (d, *J* = 1.7 Hz), 98.2 (d, *J* = 8.3 Hz), 64.4 (d, *J* = 7.2 Hz), 15.9 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.76 – 19.56 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}ClNO_3PS$, 394.0512; found 394.0522.

S-(2-(3-Bromophenyl)indolizin-3-yl) O,O-diethyl phosphorothioate (3n)



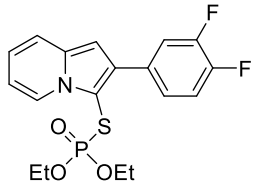
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3n**. Green liquid (93.5 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.1 Hz, 1H), 7.95 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.9 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 6.87 (t, *J* = 7.8 Hz, 1H), 6.70 (t, *J* = 6.8 Hz, 1H), 6.66 (s, 1H), 3.90 (q, *J* = 8.1 Hz, 2H), 3.77 (q, *J* = 8.4 Hz, 2H), 1.04 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5 (d, *J* = 1.9 Hz), 136.2 (d, *J* = 3.0 Hz), 135.1 (d, *J* = 4.8 Hz), 132.1, 130.1, 129.9, 128.0, 124.7, 122.4, 120.1 (d, *J* = 2.6 Hz), 118.9 (d, *J* = 2.8 Hz), 111.4 (d, *J* = 1.5 Hz), 100.8 (d, *J* = 1.9 Hz), 98.2 (d, *J* = 8.2 Hz), 64.5 (d, *J* = 7.1 Hz), 16.0 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.77 – 19.56 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}BrNO_3PS$, 439.0007; found 439.0005.

O,O-Diethyl S-(2-(3-nitrophenyl)indolizin-3-yl) phosphorothioate (3o)



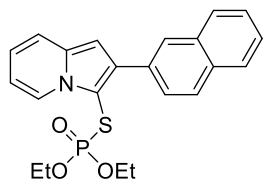
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3o**. Yellow liquid (63.3 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.54 (d, *J* = 7.1 Hz, 1H), 8.23 – 8.13 (m, 2H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 6.92 (t, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 6.6 Hz, 2H), 3.96 (q, *J* = 8.3 Hz, 2H), 3.86 (q, *J* = 8.3 Hz, 2H), 1.08 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 137.2, 136.5, 135.3, 134.2, 129.4, 124.8, 124.0, 122.0, 120.6 (d, *J* = 2.6 Hz), 119.1 (d, *J* = 2.8 Hz), 111.8, 100.9, 98.4, 64.7 (d, *J* = 7.3 Hz), 16.1 (d, *J* = 6.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.81 – 19.60 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}N_2O_5PS$, 406.0752; found 406.0757.

T-(2-(3,4-Difluorophenyl)indolizin-3-yl) O,O-diethyl phosphorothioate (3p)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3p**. Yellow liquid (66.7 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.1 Hz, 1H), 7.66 (t, 1H), 7.50 (t, 1H), 7.40 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 10.2 Hz, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 6.71 (t, *J* = 6.8 Hz, 1H), 6.63 (s, 1H), 3.94 – 3.91 (m, 2H), 3.86 – 3.80 (m, 2H), 1.08 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8 – 150.7 (m), 149.2 – 148.3 (m), 136.3 (d, *J* = 2.9 Hz), 134.7 (d, *J* = 3.8 Hz), 132.4, 125.4 (t), 124.7, 120.3 (d, *J* = 2.7 Hz), 118.9 (d, *J* = 2.9 Hz), 118.2 (d, *J* = 18.0 Hz), 117.2 (d, *J* = 17.2 Hz), 111.5 (d, *J* = 1.4 Hz), 100.8 (d, *J* = 1.6 Hz), 98.0 (d, *J* = 8.2 Hz), 64.5 (d, *J* = 7.2 Hz), 16.0 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.89 – 19.69 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{18}F_2NO_3PS$, 397.0713; found 397.0710.

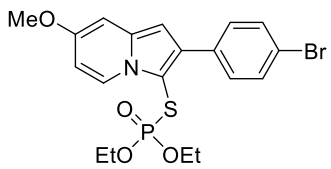
O,O-Diethyl S-(2-(naphthalen-2-yl)indolizin-3-yl) phosphorothioate (3q)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3q**. Yellow liquid (78.9 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.1 Hz, 1H), 8.27 (s, 1H), 7.94 – 7.85 (m, 4H), 7.86 (d, *J* = 5.9 Hz, 1H), 7.56 – 7.44 (m, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 6.80 (s, 1H), 6.72 (t, *J* = 6.9 Hz, 1H), 3.90 – 3.75 (m, 2H), 3.70 – 3.64 (m, 2H), 0.91 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8 (d, *J* = 4.8 Hz), 136.4 (d, *J* = 3.1 Hz), 133.5, 132.7 (d, *J* = 1.9 Hz), 132.6, 128.2, 128.1, 127.9, 127.7, 127.7, 126.3, 126.1, 124.8, 120.0 (d, *J* = 2.7 Hz), 118.9 (d, *J* = 2.9 Hz), 111.2 (d, *J* = 1.4 Hz), 101.1 (d, *J* = 1.9 Hz),

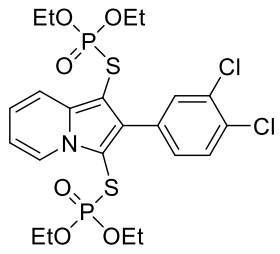
98.3 (d, *J* = 8.1 Hz), 64.4 (d, *J* = 7.0 Hz), 15.9 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.91 – 19.71 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{22}NO_3PS$, 411.1058; found 411.1049.

S-(2-(4-Bromophenyl)-7-methoxyindolizin-3-yl) O,O-diethyl phosphorothioate (3r)



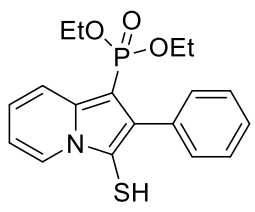
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3r**. Yellow liquid (77.4 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 6.65 (d, *J* = 2.4 Hz, 1H), 6.45 (t, 2H), 3.91 – 3.89 (m, 2H), 3.83 (s, 3H), 3.83 – 3.72 (m, 2H), 1.05 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4 (d, *J* = 1.9 Hz), 137.2 (d, *J* = 2.8 Hz), 136.2 (2 C), 134.5 (d, *J* = 1.7 Hz), 131.5, 130.8, 126.0, 121.3, 106.5, 98.8, 95.5 (d, *J* = 2.4 Hz), 64.5 (d, *J* = 7.2 Hz), 55.5, 16.1 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.93 – 19.73 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{19}H_{21}BrNO_4PS$, 469.0112; found 469.0107.

S,S'-(2-(3,4-Dichlorophenyl)indolizine-1,3-diyl) O,O,O',O'-tetraethyl bis(phosphorothioate) (3s)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **3s**. Yellow liquid (94.9 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.0 Hz, 1H), 7.91 (s, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.57 (s, 2H), 7.12 (t, *J* = 7.9 Hz, 1H), 6.86 (t, *J* = 6.8 Hz, 1H), 4.01 – 3.90 (m, 4H), 3.87 – 3.80 (m, 4H), 1.18 – 1.09 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 138.4, 133.4, 133.1, 132.1, 132.0, 130.9, 130.0, 125.4, 122.6, 118.3, 113.0, 101.9, 91.4, 64.7 (d, *J* = 7.2 Hz), 64.1 (d, *J* = 6.7 Hz), 16.1 (2 C). ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.65, 19.25. HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{27}Cl_2NO_6P_2S_2$, 597.0132; found 597.0123.

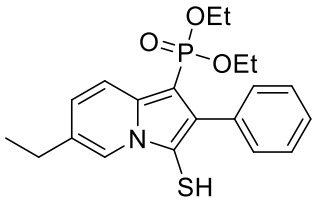
Diethyl (3-mercapto-2-phenylindolizin-1-yl)phosphonate (4a)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4a**. Black liquid (87.7 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.1 Hz, 1H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.51 – 7.45 (m, 3H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.03 – 6.93 (m, 1H), 6.76 (t, *J* = 6.8 Hz, 1H), 3.87 – 3.75 (m, 2H), 3.71 – 3.58 (m, 2H), 1.04 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4 (d, *J* = 4.7 Hz), 134.2 (d, *J* = 3.2 Hz), 133.0 (d, *J* = 1.7 Hz), 131.0, 128.1, 127.9, 124.9, 121.0 (d, *J* = 2.6 Hz), 117.7 (d, *J* = 2.9 Hz), 112.0 (d, *J* = 1.4 Hz), 99.8 (d, *J* = 8.4

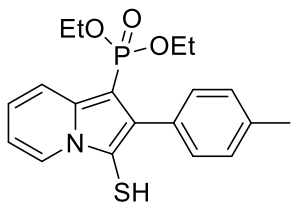
Hz), 87.8 (d, *J* = 2.2 Hz), 64.4 (d2, *J* = 7.1 Hz), 16.0 (d, *J* = 7.1 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{20}NO_3PS$, 361.0902; found 361.0901.

Diethyl (6-ethyl-3-mercapto-2-phenylindolizin-1-yl)phosphonate (4b)



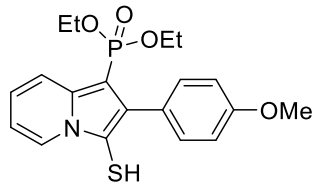
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4b**. Yellow liquid (72.4 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.45 -7.36 (m, 2H), 6.88 (d, *J* = 9.1 Hz, 1H), 3.80 (q, *J* = 8.0 Hz, 2H), 3.60 (s, 2H), 2.66 (q, *J* = 7.5 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9 (d, *J* = 4.7 Hz), 133.3 (d, *J* = 3.3 Hz), 133.1 (d, *J* = 1.7 Hz), 130.9, 128.1, 127.8 (d, *J* = 1.4 Hz), 127.7, 123.1 (d, *J* = 2.6 Hz), 121.7, 117.3 (d, *J* = 2.8 Hz), 99.3 (d, *J* = 8.2 Hz), 87.3 (d, *J* = 1.9 Hz), 64.2 (d, *J* = 6.9 Hz), 26.2, 16.0 (d, *J* = 7.2 Hz), 15.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.84 - 19.64 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{20}H_{24}NO_3PS$, 389.1215; found 389.1214.

Diethyl (3-mercapto-2-(p-tolyl)indolizin-1-yl)phosphonate (4c)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4c**. Black liquid (73.1 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.1 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.74 (t, *J* = 6.8 Hz, 1H), 3.83 (q, *J* = 8.0 Hz, 2H), 3.73 – 3.62 (m, 2H), 2.42 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 135.4 (d, *J* = 4.6 Hz), 134.2 (d, *J* = 3.2 Hz), 130.8, 129.9, 128.8, 124.8, 120.9 (d, *J* = 2.6 Hz), 117.6 (d, *J* = 2.9 Hz), 111.8, 99.6 (d, *J* = 8.4 Hz), 87.8, 64.3 (d, *J* = 7.3 Hz), 21.4, 16.0 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.61 – 19.41 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{19}H_{22}NO_3PS$, 375.1058; found 375.1063.

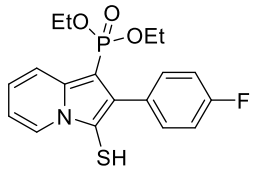
Diethyl (3-mercapto-2-(4-methoxyphenyl)indolizin-1-yl)phosphonate (4d)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4d**. Black liquid (65.7 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.1 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 3H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.74 (t, *J* = 6.8 Hz, 1H), 3.87 – 3.80 (m, 5H), 3.74 – 3.66 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 135.2 (d, *J* = 4.8 Hz), 134.2 (d,

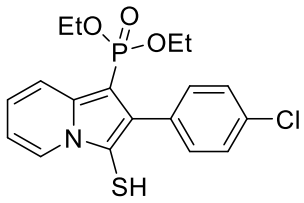
J = 3.2 Hz), 132.1, 125.3 (d, *J* = 1.7 Hz), 124.9, 120.9 (d, *J* = 2.6 Hz), 117.6 (d, *J* = 2.9 Hz), 113.6, 111.8, 99.5 (d, *J* = 8.2 Hz), 87.9 (d, *J* = 2.1 Hz), 64.4 (d, *J* = 7.2 Hz), 55.5, 16.1 (d, *J* = 7.2 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{19}H_{22}NO_4PS$, 391.1007; found 391.1007.

Diethyl (2-(4-fluorophenyl)-3-mercaptoindolizin-1-yl)phosphonate (4e)



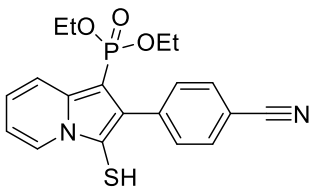
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4e**. Green liquid (81.9 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.1 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.47 (d, *J* = 9.0 Hz, 1H), 7.18 (t, *J* = 8.7 Hz, 2H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.76 (t, *J* = 6.8 Hz, 1H), 3.87 (q, *J* = 8.0 Hz, 2H), 3.73 (q, *J* = 8.5 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 247.6 Hz), 134.5 (d, *J* = 5.0 Hz), 134.2 (d, *J* = 3.2 Hz), 132.7 (d, *J* = 8.1 Hz), 129.0, 124.9, 121.1 (d, *J* = 2.7 Hz), 117.7 (d, *J* = 2.8 Hz), 115.2 (d, *J* = 21.4 Hz), 112.1, 99.7 (d, *J* = 8.0 Hz), 87.8 (d, *J* = 2.2 Hz), 64.5 (d, *J* = 7.1 Hz), 16.1 (d, *J* = 7.1 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}FNO_3PS$, 379.0807; found 379.0801.

Diethyl (2-(4-chlorophenyl)-3-mercaptoindolizin-1-yl)phosphonate (4f)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4f**. Green liquid (83.0 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.1 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.9 Hz, 3H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.77 (t, *J* = 6.8 Hz, 1H), 3.93 – 3.82 (m, 2H), 3.80 – 3.69 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3 (2 C), 134.0, 132.3, 131.5 (d, *J* = 1.6 Hz), 128.4, 124.9, 121.2 (d, *J* = 2.6 Hz), 117.8 (d, *J* = 2.8 Hz), 112.2, 99.7, 87.7, 64.5 (d, *J* = 7.3 Hz), 16.1 (d, *J* = 7.0 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}ClNO_3PS$, 395.0512; found 395.0507.

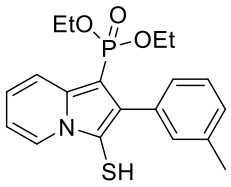
Diethyl (2-(4-cyanophenyl)-3-mercaptoindolizin-1-yl)phosphonate (4g)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4g**. Green liquid (67.2 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.1 Hz, 1H), 7.79 (d, *J* = 2.5 Hz, 4H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.07 – 6.97 (m, 1H), 6.85 – 6.76 (m, 1H), 3.91 (q, *J* = 8.1 Hz, 2H), 3.78 (q, *J* = 9.0 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0 (d, *J* = 1.7 Hz), 134.5 (d, *J* = 2.9 Hz), 133.5 (d, *J* = 4.8 Hz), 131.9, 131.7, 124.9, 121.5 (d, *J* = 2.5 Hz), 119.0, 117.9 (d, *J* = 2.6 Hz), 112.6, 111.4, 100.0 (d, *J* = 8.1 Hz),

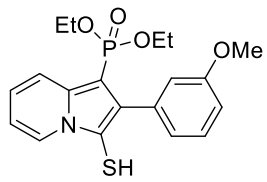
87.6, 64.6 (d, *J* = 7.3 Hz), 16.1 (d, *J* = 6.9 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{19}H_{19}N_2O_3PS$, 386.0854; found 386.0864.

Diethyl (3-mercapto-2-(m-tolyl)indolizin-1-yl)phosphonate (4h)



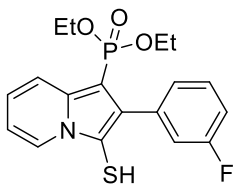
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4h**. Yellow liquid (72.0 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.0 Hz, 1H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.42 (d, *J* = 10.1 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.9 Hz, 1H), 6.75 (t, *J* = 6.8 Hz, 1H), 3.82 (q, *J* = 7.8 Hz, 2H), 3.71 – 3.59 (m, 2H), 2.44 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 135.6 (d, *J* = 4.7 Hz), 134.2 (d, *J* = 3.2 Hz), 132.8 (d, *J* = 1.7 Hz), 131.6, 128.6, 128.3, 128.0, 124.9, 120.9 (d, *J* = 2.7 Hz), 117.7 (d, *J* = 2.8 Hz), 111.9 (d, *J* = 1.4 Hz), 99.7 (d, *J* = 8.3 Hz), 87.8 (d, *J* = 2.1 Hz), 64.3 (d, *J* = 7.0 Hz), 21.6, 16.0 (d, *J* = 7.3 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{19}H_{22}NO_3PS$, 375.1058; found 375.1059.

Diethyl (3-mercapto-2-(3-methoxyphenyl)indolizin-1-yl)phosphonate (4i)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4i**. Black liquid (78.6 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.1 Hz, 1H), 7.48 (d, *J* = 9.0 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 9.1 Hz, 2H), 7.01 – 6.92 (m, 2H), 6.76 (t, *J* = 6.9 Hz, 1H), 3.87 (s, 3H), 3.87 - 3.84 (m, 2H), 3.73 – 3.65 (m, 2H), 1.07 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 135.3 (d, *J* = 4.8 Hz), 134.2 (2 C), 129.1, 124.9, 123.4, 121.0 (d, *J* = 2.7 Hz), 117.7 (d, *J* = 2.8 Hz), 116.4, 113.7, 112.0, 99.8 (d, *J* = 8.2 Hz), 87.8 (d, *J* = 2.1 Hz), 64.4 (d, *J* = 7.1 Hz), 55.5, 16.0 (d, *J* = 7.1 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{19}H_{22}NO_4PS$, 391.1007; found 391.1017.

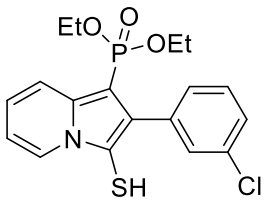
Diethyl (2-(3-fluorophenyl)-3-mercaptoindolizin-1-yl)phosphonate (4j)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4j**. Black liquid (76.2 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.1 Hz, 1H), 7.49 – 7.43 (m, 4H), 7.15 – 7.05 (m, 1H), 6.99 (t, *J* = 7.9 Hz, 1H), 6.77 (t, *J* = 6.9 Hz, 1H), 3.88 (q, *J* = 8.1 Hz, 2H), 3.74 (q, *J* = 8.5 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 245.5 Hz), 135.2 – 135.1 (m), 134.3 (d, *J* = 3.1 Hz), 134.2 – 134.1 (m), 129.6 (d, *J* = 8.4 Hz), 126.8 (d, *J* = 3.1 Hz), 124.9, 121.2 (d, *J* = 2.6 Hz), 118.0, 117.8 (d, *J* = 2.9 Hz), 114.7 (d, *J* =

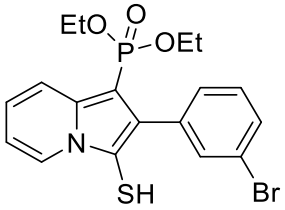
21.0 Hz), 112.2 (d, *J* = 1.3 Hz), 99.9 (d, *J* = 8.2 Hz), 87.7 (d, *J* = 1.9 Hz), 64.5 (d, *J* = 7.1 Hz), 16.0 (d, *J* = 7.0 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}FNO_3PS$, 379.0807; found 379.0798.

Diethyl (2-(3-chlorophenyl)-3-mercaptoindolizin-1-yl)phosphonate (4k)



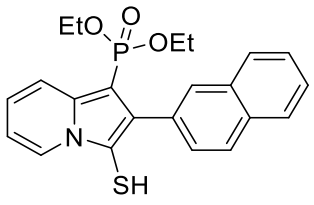
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4k**. Black liquid (87.7 mg, 74%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.49 (d, *J* = 7.1 Hz, 1H), 7.66 (s, 1H), 7.54 – 7.33 (m, 4H), 7.01 – 6.93 (m, 1H), 6.75 (t, *J* = 6.9 Hz, 1H), 3.94 – 3.83 (m, 2H), 3.81 – 3.69 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.8 (d, *J* = 1.7 Hz), 134.1 (d, *J* = 3.1 Hz), 133.9 (2 C), 130.8, 129.3, 129.1, 127.8, 124.8, 121.1 (d, *J* = 2.6 Hz), 117.7 (d, *J* = 2.9 Hz), 112.2 (d, *J* = 1.2 Hz), 99.9 (d, *J* = 8.1 Hz), 87.6 (d, *J* = 1.9 Hz), 64.4 (d, *J* = 7.2 Hz), 16.0 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.48 – 19.27 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}ClNO_3PS$, 395.0512; found 395.0506.

Diethyl (2-(3-bromophenyl)-3-mercaptoindolizin-1-yl)phosphonate (4l)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4l**. Green liquid (84.3 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.1 Hz, 1H), 7.82 (d, *J* = 2.1 Hz, 1H), 7.55 (t, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 9.0 Hz, 1H), 7.36 (td, *J* = 7.9, 1.9 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.78 (t, *J* = 6.9 Hz, 1H), 3.90 (q, *J* = 8.1 Hz, 2H), 3.76 (q, *J* = 8.2 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 134.3 (d, *J* = 3.0 Hz), 134.0, 133.9, 133.7, 130.8, 129.7, 124.9, 122.1, 121.2 (d, *J* = 2.5 Hz), 117.8 (d, *J* = 2.7 Hz), 112.3, 100.1, 87.7, 64.6 (d, *J* = 7.2 Hz), 16.1 (d, *J* = 7.1 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{19}BrNO_3PS$, 439.0007; found 439.0010.

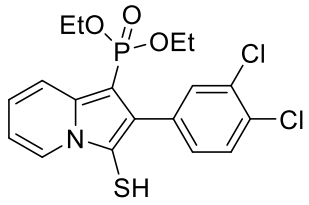
Diethyl (3-mercapto-2-(naphthalen-2-yl)indolizin-1-yl)phosphonate (4m)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4m**. Black liquid (80.1 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.1 Hz, 1H), 8.12 (s, 1H), 7.98 – 7.86 (m, 3H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.78 (t, *J* = 6.8 Hz, 1H), 3.78 (t, *J* = 8.0 Hz, 2H), 3.61 (t, *J* = 8.4 Hz, 2H), 0.97 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4 (d, *J* = 4.8 Hz), 134.3 (d, *J* = 3.2 Hz), 133.2, 132.8, 130.5 (d, *J* = 1.8 Hz), 130.2, 128.7, 128.3, 127.8, 127.6, 126.4, 126.3, 124.9,

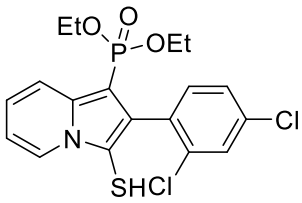
121.0 (d, J = 2.6 Hz), 117.7 (d, J = 2.8 Hz), 112.0, 100.0 (d, J = 8.3 Hz), 88.0 (d, J = 2.1 Hz), 64.4 (d, J = 7.1 Hz), 15.9 (d, J = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.47 (p, J = 8.5 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{22}NO_3PS$, 411.1058; found 411.1049.

Diethyl (2-(3,4-dichlorophenyl)-3-mercaptoindolizin-1-yl)phosphonate (4n)



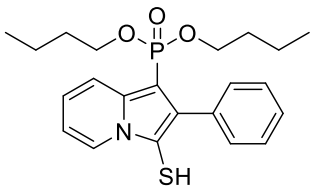
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4n**. Black liquid (73.4 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 7.1 Hz, 1H), 7.79 (s, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.04 – 6.95 (m, 1H), 6.78 (t, J = 6.9 Hz, 1H), 3.95 (q, J = 8.0 Hz, 2H), 3.84 (q, J = 8.8 Hz, 2H), 1.14 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3 (d, J = 3.1 Hz), 133.1 (d, J = 1.5 Hz), 133.0, 132.6, 132.2, 132.0, 130.3, 130.1, 124.9, 121.3 (d, J = 2.6 Hz), 117.8 (d, J = 2.8 Hz), 112.4 (d, J = 1.3 Hz), 99.9 (d, J = 8.0 Hz), 87.6 (d, J = 1.9 Hz), 64.6 (d, J = 7.2 Hz), 16.1 (d, J = 7.0 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{18}Cl_2NO_3PS$, 429.0122; found 429.0116.

Diethyl (2-(2,4-dichlorophenyl)-3-mercaptoindolizin-1-yl)phosphonate (4o)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4o**. Green liquid (90.1 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 7.1 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.48 (d, J = 9.0 Hz, 1H), 7.38 (q, J = 8.3 Hz, 2H), 6.99 (t, J = 8.0 Hz, 1H), 6.83 – 6.74 (m, 1H), 3.99 – 3.71 (m, 4H), 1.20 – 1.08 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 134.9, 134.1 (d, J = 1.8 Hz), 134.0 (d, J = 3.0 Hz), 132.7 (d, J = 4.7 Hz), 131.0 (d, J = 1.6 Hz), 129.5, 126.8, 124.8, 121.0 (d, J = 2.5 Hz), 117.8 (d, J = 2.7 Hz), 112.3, 100.9 (d, J = 8.0 Hz), 88.7, 64.6 (dd, J = 18.2, 7.4 Hz), 16.1 (dd, J = 10.5, 6.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.38 – 19.16 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{18}H_{18}Cl_2NO_3PS$, 429.0122; found 429.0115.

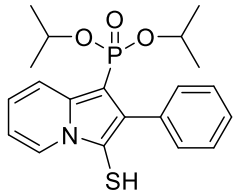
Dibutyl (3-mercapto-2-phenylindolizin-1-yl)phosphonate (4p)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4p**. Black liquid (83.8 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 7.0 Hz, 1H), 7.62 (d, J = 7.2 Hz, 2H), 7.52 – 7.44 (m, 3H), 7.39 (t, J = 7.3 Hz, 1H), 6.98 (t, J = 7.8 Hz, 1H), 6.75 (t, J = 6.4 Hz, 1H), 3.73 (t, J = 8.3 Hz, 2H), 3.57 (d, J = 8.2 Hz, 2H), 1.35 (q, J = 7.1 Hz, 4H), 1.15 (q, J = 7.5 Hz, 4H), 0.81 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz,

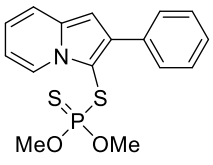
$CDCl_3$) δ 135.4 (d, *J* = 4.6 Hz), 134.2 (d, *J* = 3.1 Hz), 133.0 (d, *J* = 1.5 Hz), 131.5, 131.0, 128.1, 127.8, 124.9, 121.0, 117.7 (d, *J* = 2.9 Hz), 112.0, 99.8 (d, *J* = 7.9 Hz), 87.8, 68.0 (d, *J* = 7.3 Hz), 32.1 (d, *J* = 7.0 Hz), 18.6 (d, *J* = 6.4 Hz), 13.7 (d, *J* = 5.2 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{22}H_{28}NO_3PS$, 417.1528; found 417.1525.

Diisopropyl (3-mercapto-2-phenylindolizin-1-yl)phosphonate (4q)



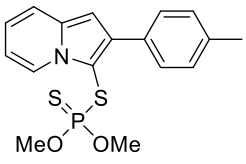
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **4q**. Green liquid (84.0 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.1 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.1 Hz, 3H), 7.39 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.75 (t, *J* = 6.9 Hz, 1H), 4.56 – 4.46 (m, 2H), 1.13 (d, *J* = 6.2 Hz, 6H), 1.05 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4 (d, *J* = 5.1 Hz), 134.1 (d, *J* = 3.3 Hz), 133.1 (d, *J* = 1.8 Hz), 131.1, 128.1, 127.8, 125.3, 120.9 (d, *J* = 2.6 Hz), 117.6 (d, *J* = 2.9 Hz), 111.7, 100.5 (d, *J* = 8.2 Hz), 87.8, 74.1 (d, *J* = 7.8 Hz), 23.8 (d, *J* = 4.3 Hz), 23.5 (d, *J* = 5.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.94 (t, *J* = 8.2 Hz). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{20}H_{24}NO_3PS$, 389.1215; found 389.1205.

O,O-Dimethyl S-(2-phenylindolizin-3-yl) phosphorodithioate (5a)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **5a**. Green liquid (69.1 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.1 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 3H), 7.52 – 7.46 (m, 3H), 7.40 (t, *J* = 7.3 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.78 (t, *J* = 6.8 Hz, 1H), 3.34 (s, 3H), 3.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 133.0, 131.5, 131.0, 128.2, 128.0, 124.6, 123.8 (d, *J* = 256.0 Hz), 121.1, 117.8 (d, *J* = 2.8 Hz), 112.2, 87.9, 54.2 (d, *J* = 6.5 Hz), 53.8 (d, *J* = 5.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.84 – 22.53 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{16}H_{16}NO_2PS_2$, 349.0360; found 349.0363.

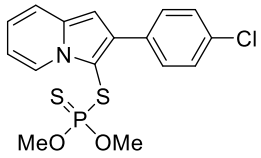
O,O-Dimethyl S-(2-(p-tolyl)indolizin-3-yl) phosphorodithioate (5b)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **5b**. Green liquid (74.1 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 7.1 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 3H), 7.30 (d, *J* = 7.8 Hz, 3H), 6.99 (t, 1H), 6.77 (t, *J* = 6.9 Hz, 1H), 3.37 (s,

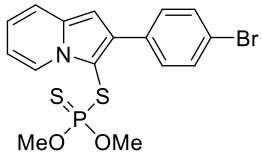
3H), 3.34 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 135.8 (d, *J* = 4.7 Hz), 134.3 (d, *J* = 2.9 Hz), 130.9, 130.0, 129.1, 129.0, 124.6, 121.0, 117.8, 112.1, 88.0, 54.2, 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.84 – 22.53 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{17}H_{18}NO_2PS_2$, 363.0517; found 363.0511.

S-(2-(4-Chlorophenyl)indolizin-3-yl) O,O-dimethyl phosphorodithioate (5c)



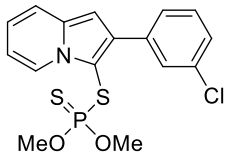
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **5c**. Green liquid (71.1 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 6.4 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.48 (t, *J* = 7.1 Hz, 3H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.79 (t, *J* = 6.8 Hz, 2H), 3.43 (s, 3H), 3.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4 (d, *J* = 3.1 Hz), 134.1, 132.3, 131.5 (d, *J* = 1.4 Hz), 128.5, 128.3 (d, *J* = 14.3 Hz), 124.6, 121.3 (d, *J* = 2.6 Hz), 117.9 (d, *J* = 2.8 Hz), 112.4, 99.0 (d, *J* = 5.4 Hz), 87.9 (d, *J* = 1.8 Hz), 54.3 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.62 -22.32 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{16}H_{15}ClNO_2PS_2$, 382.9970; found 382.9972.

S-(2-(4-Bromophenyl)indolizin-3-yl) O,O-dimethyl phosphorodithioate (5d)



Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **5d**. Green liquid (80.5 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.0 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 4H), 7.00 (t, *J* = 8.2 Hz, 1H), 6.79 (t, *J* = 6.9 Hz, 1H), 3.43 (s, 3H), 3.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5 (d, *J* = 4.8 Hz), 134.4 (d, *J* = 3.1 Hz), 132.6, 132.0 (d, *J* = 1.4 Hz), 131.5, 124.6, 122.3, 121.3 (d, *J* = 2.7 Hz), 117.9 (d, *J* = 2.8 Hz), 112.5, 99.0 (d, *J* = 8.3 Hz), 87.8 (d, *J* = 1.8 Hz), 54.3 (d, *J* = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.62 – 22.31 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{16}H_{15}BrNO_2PS_2$, 426.9465; found 426.9463.

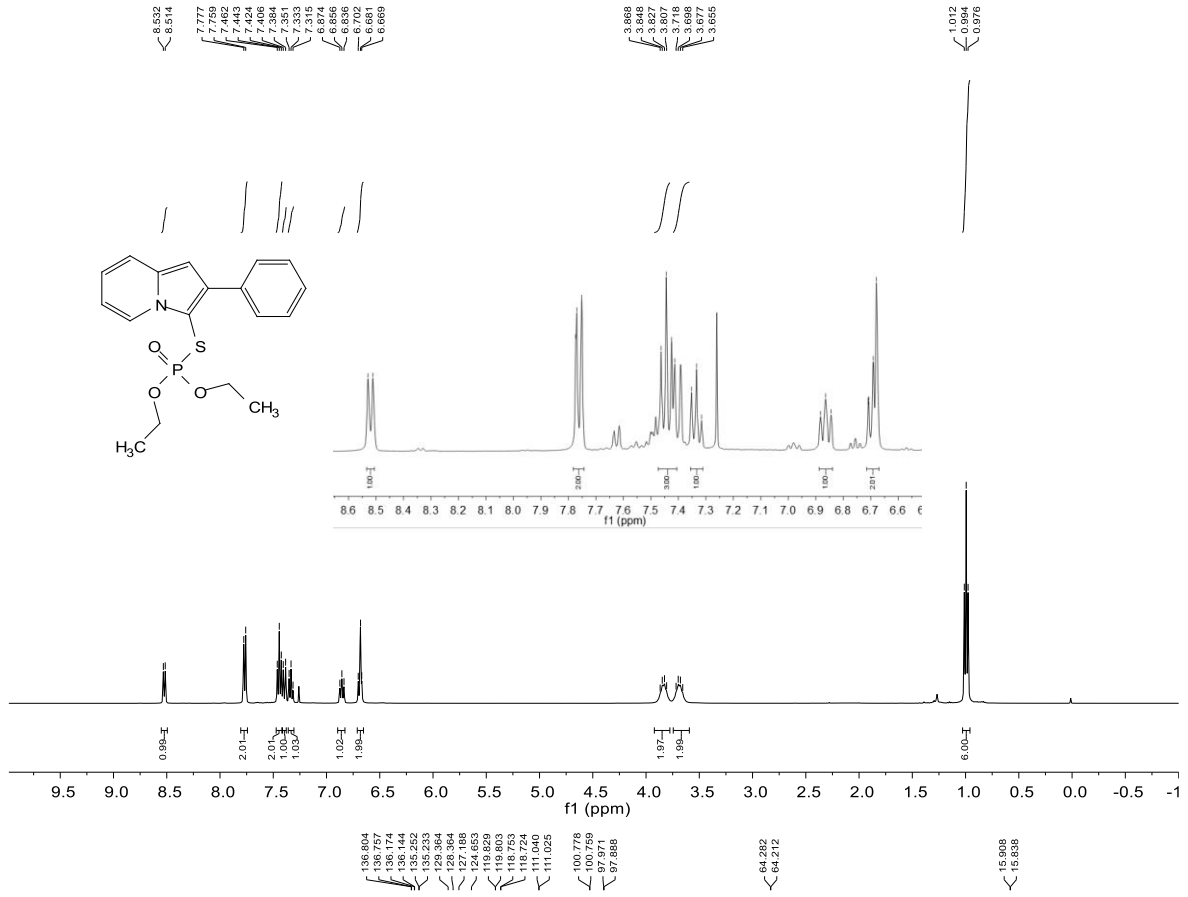
S-(2-(3-Chlorophenyl)indolizin-3-yl) O,O-dimethyl phosphorodithioate (5e)

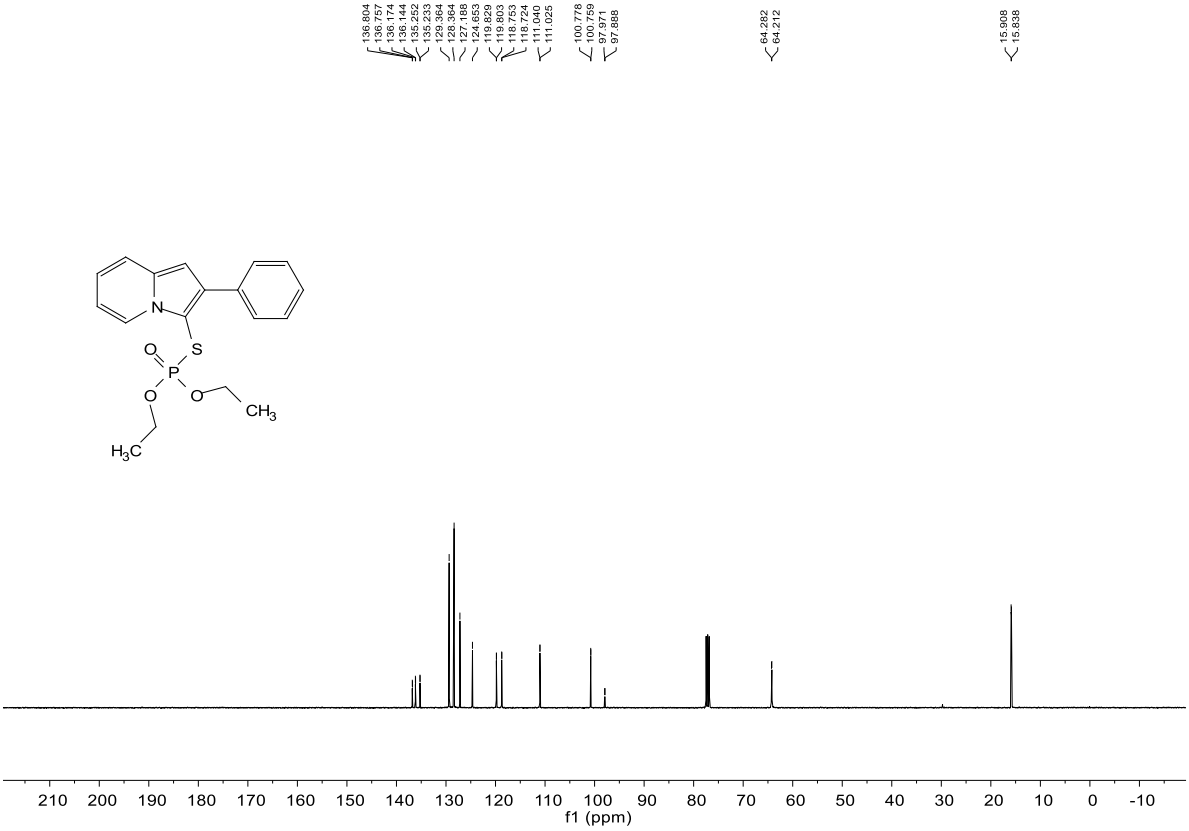


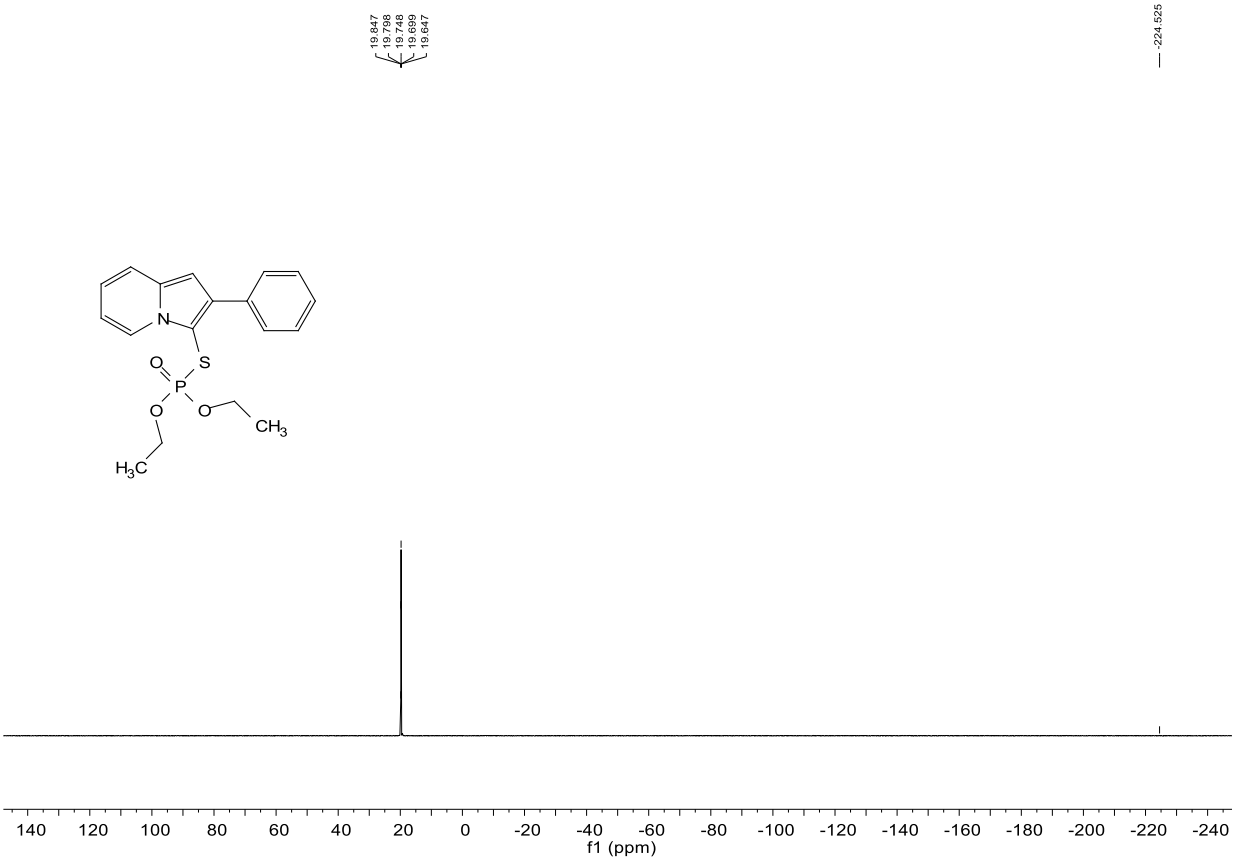
Preparative TLC on silica gel (eluent: PE/EA = 3/1, v/v) to afford **5e**. Green liquid (68.8 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.1 Hz, 1H), 7.62 (s, 1H), 7.49 (d, *J* = 9.2 Hz, 3H), 7.47 – 7.35 (m, 2H), 7.01 (t, *J* = 7.9 Hz, 1H), 6.79 (t, *J* = 6.8 Hz, 1H), 3.45 (s, 3H), 3.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.8 (d, *J* = 1.4 Hz), 134.2 (d, *J* = 3.3 Hz), 134.2, 133.9, 130.8, 129.4, 129.1, 127.9, 124.5, 121.2 (d, *J* = 2.5 Hz), 117.8 (d, *J* = 2.8 Hz), 112.4, 99.2 (d, *J* = 7.8 Hz), 87.7 (d, *J* = 1.7 Hz), 54.2 (d, *J* = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.64 – 22.34 (m). HRMS (GC/QTOF) m/z: $[M]^+$ calcd for $C_{16}H_{15}ClNO_2PS_2$, 382.9970; found 382.9978.

3. NMR spectra for new compounds

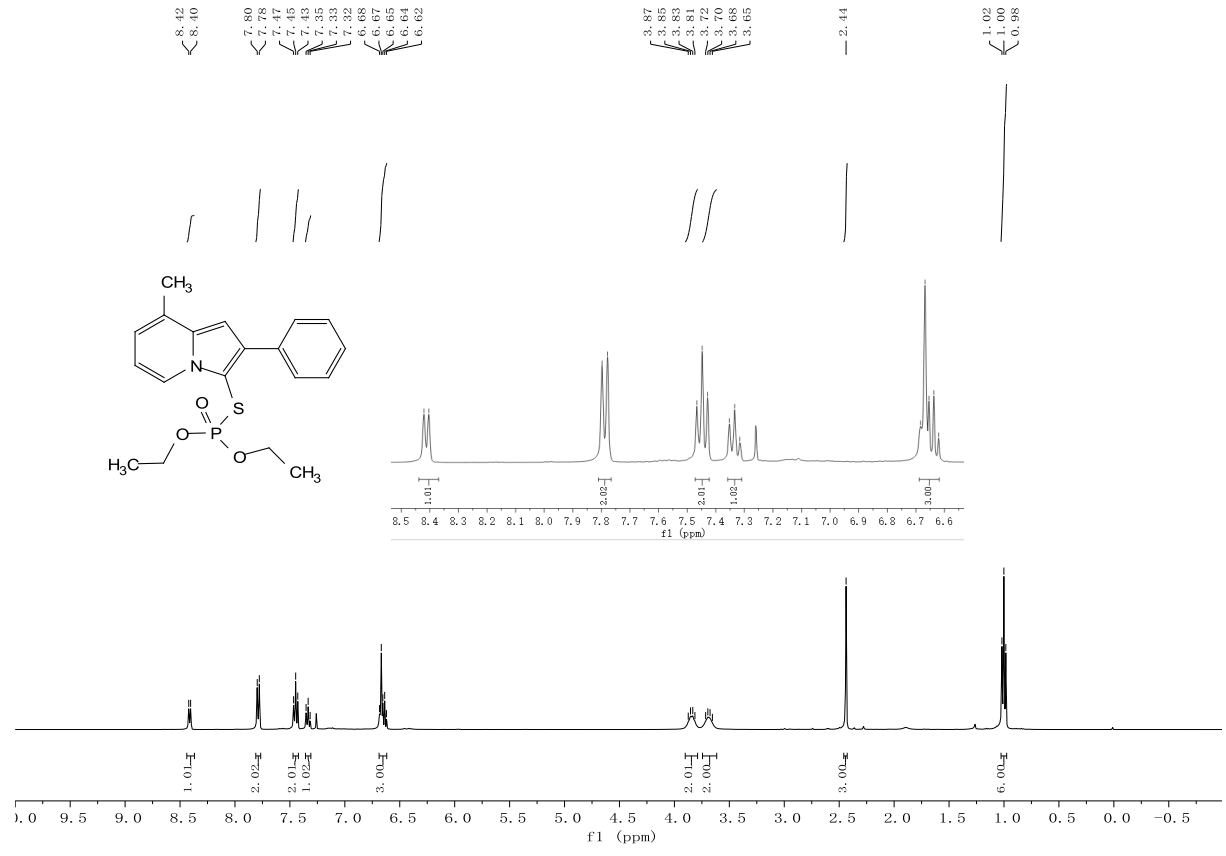
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3a**

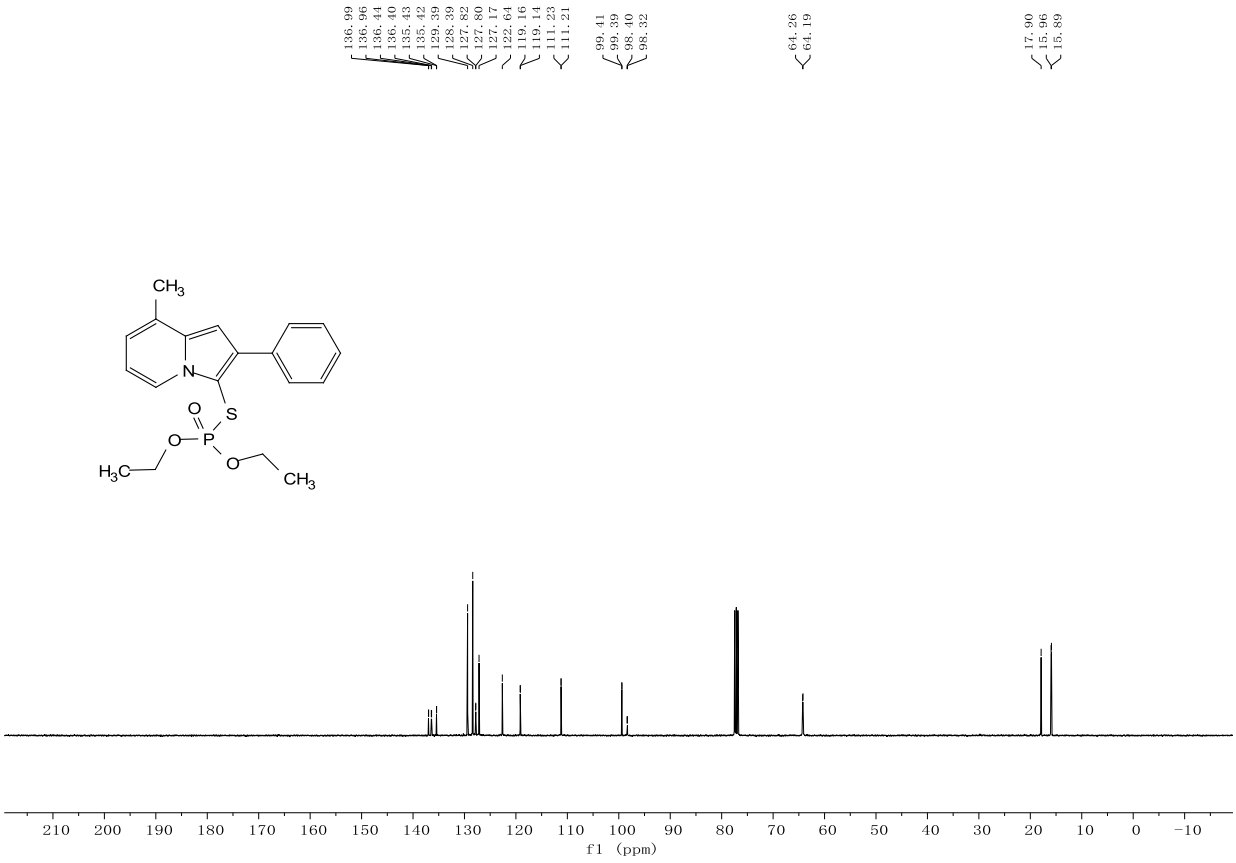


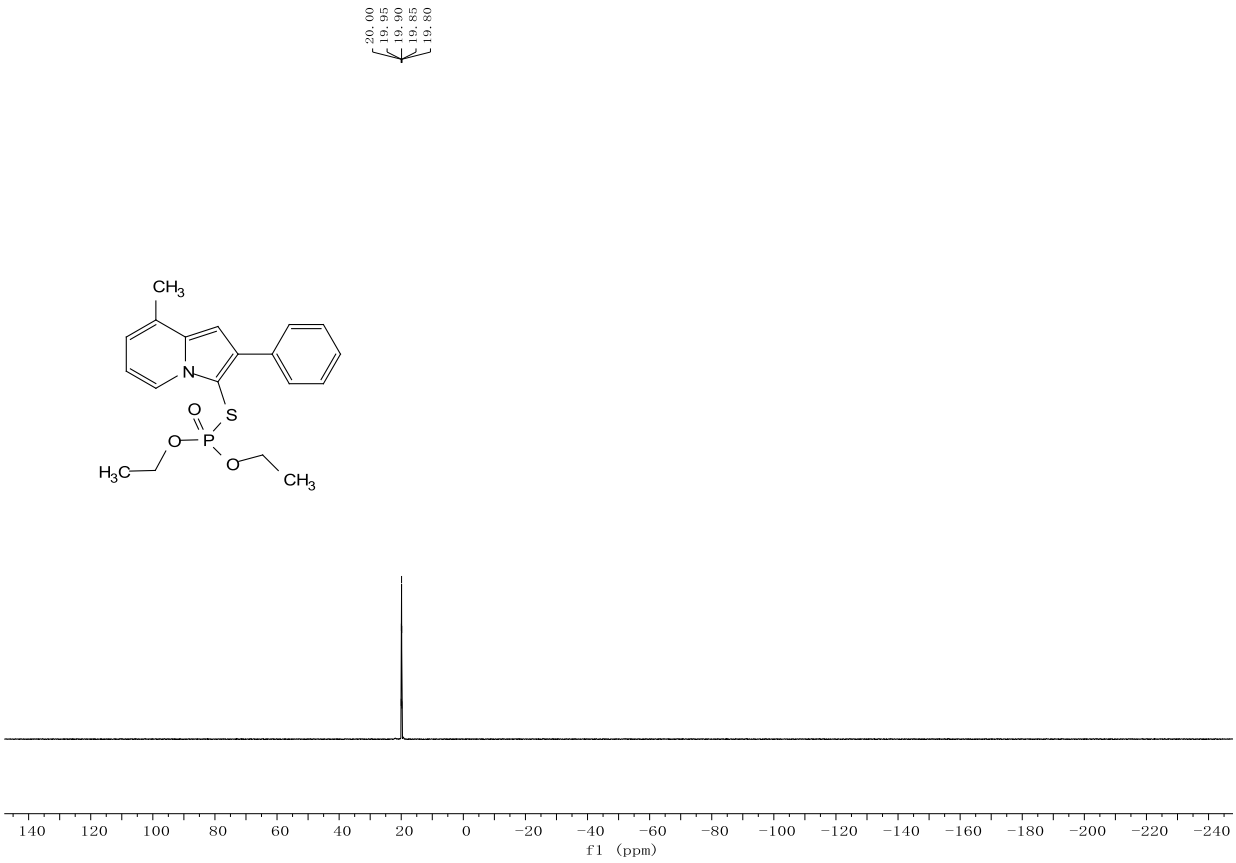




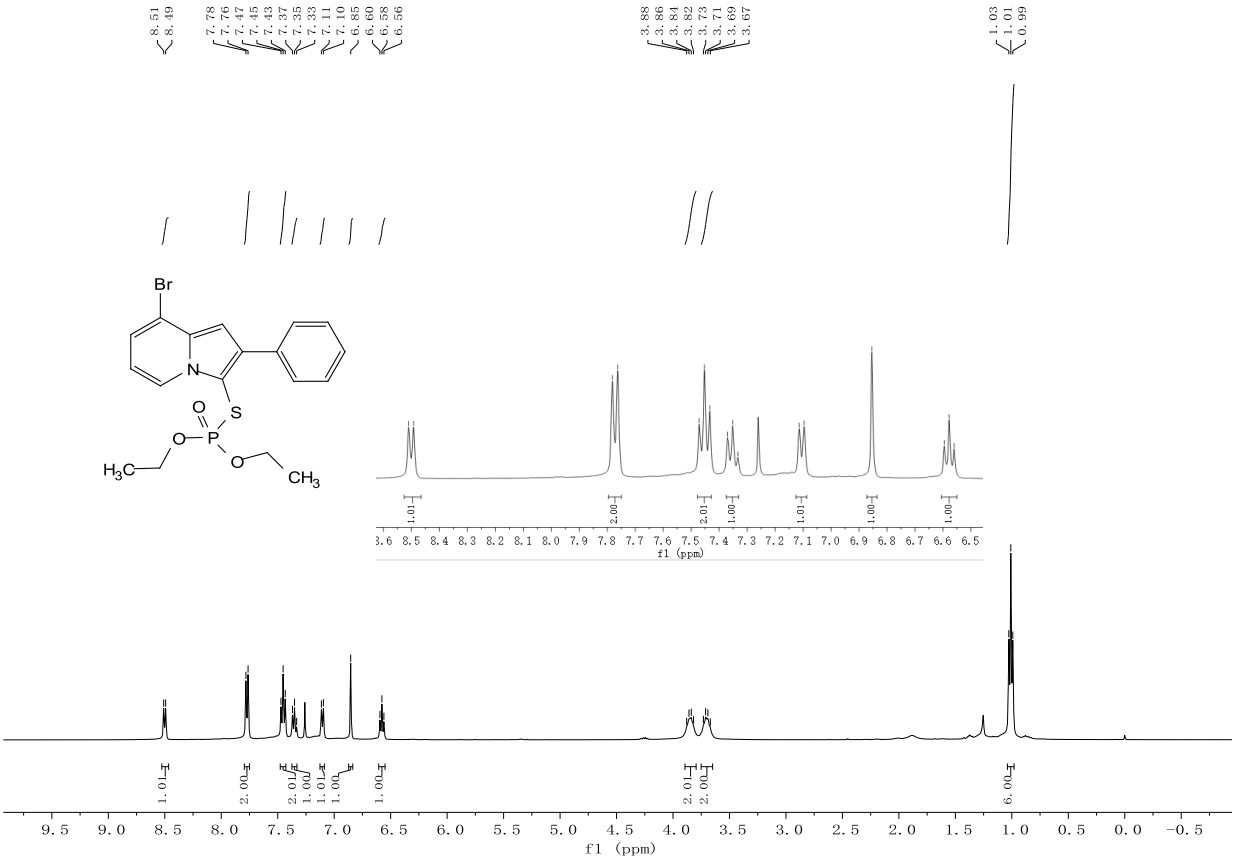
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3b**

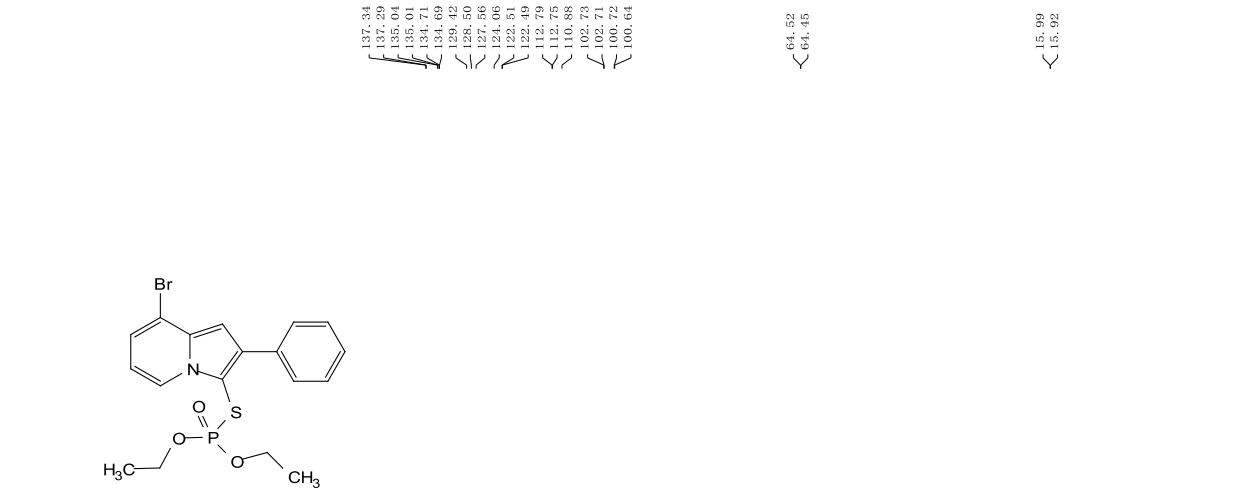


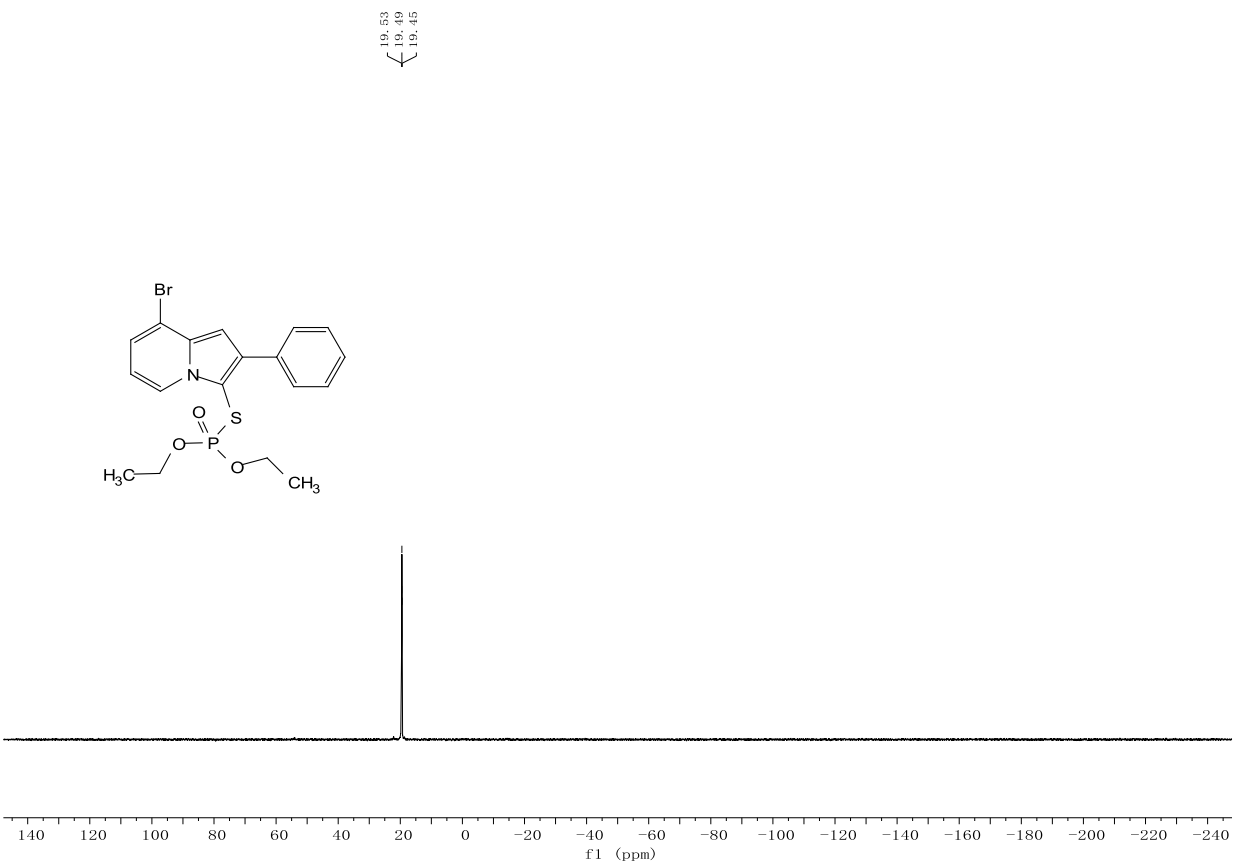

136.99
136.96
136.44
136.40
135.43
135.42
129.39
128.39
127.82
127.80
127.17
122.64
119.16
119.14
111.23
111.21
99.41
99.39
98.40
98.32
64.26
64.19
17.90
15.96
15.89
CH3
N
O
S
O
P
O
H3C
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


20.00
19.95
19.90
19.85
19.80
CH3
N
O
S
O
P
O
H3C
CH3
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

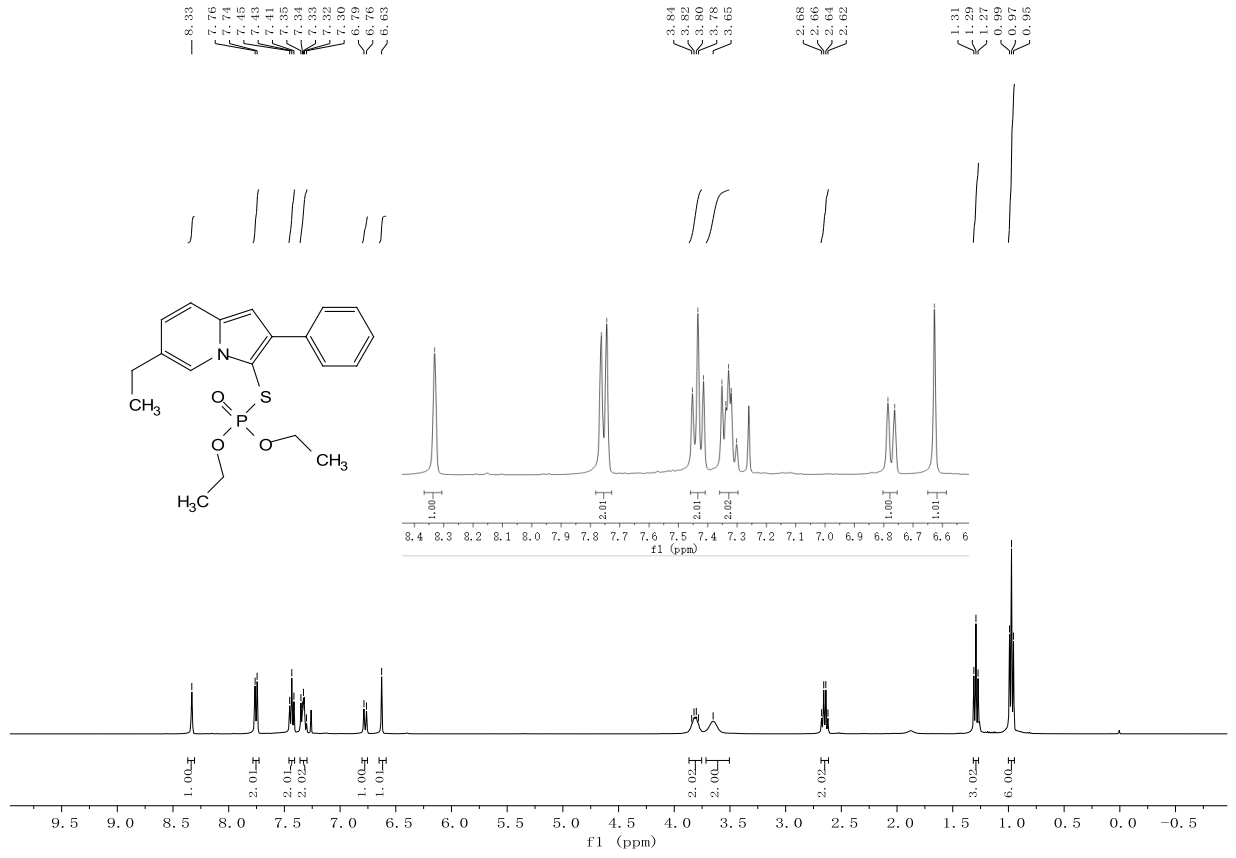
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3c**

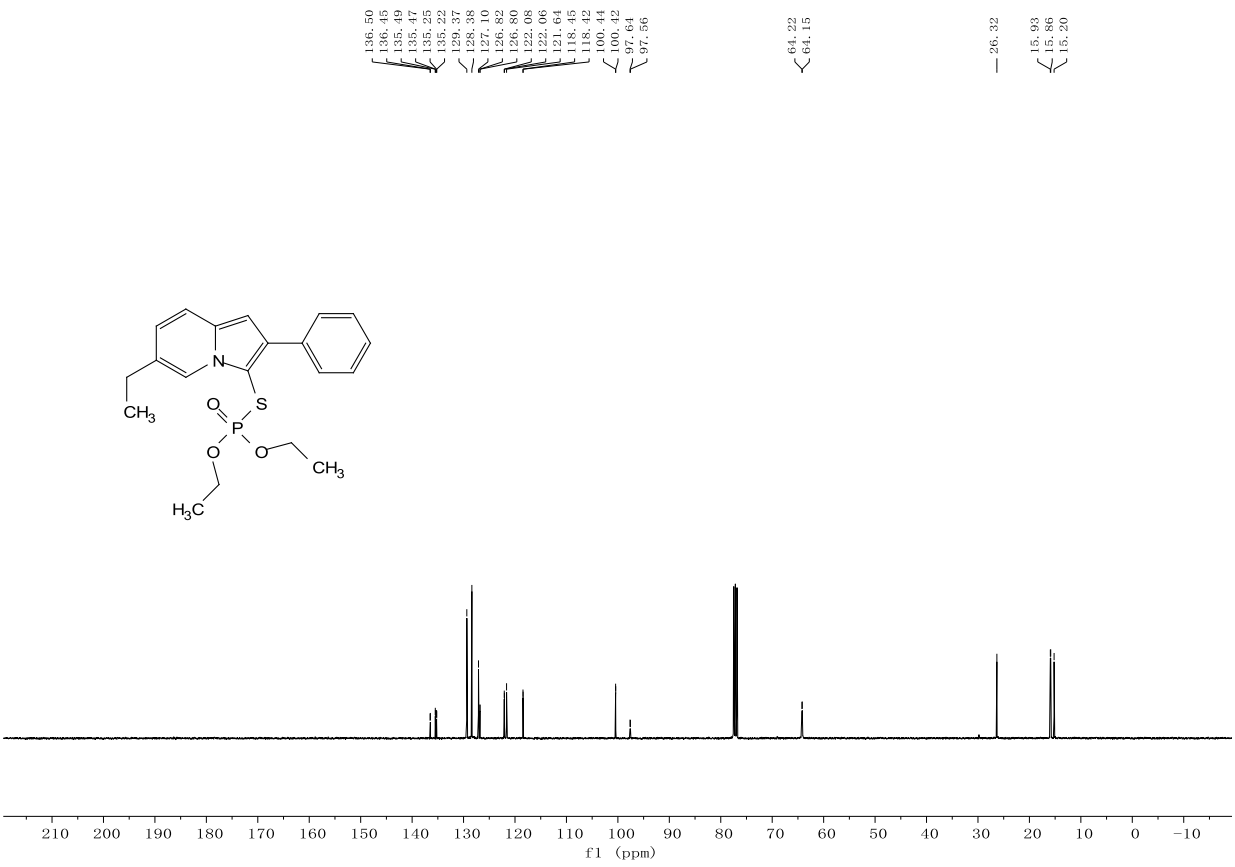


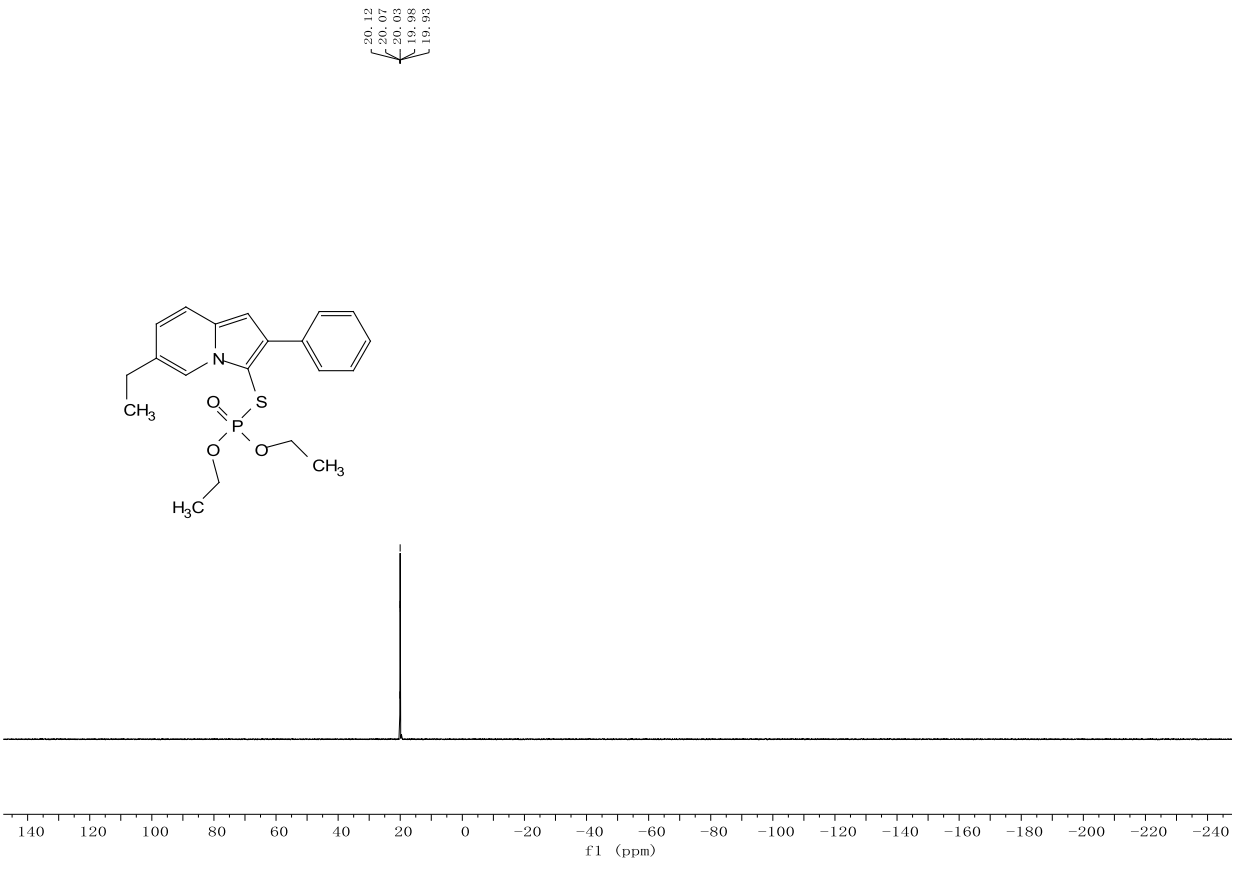




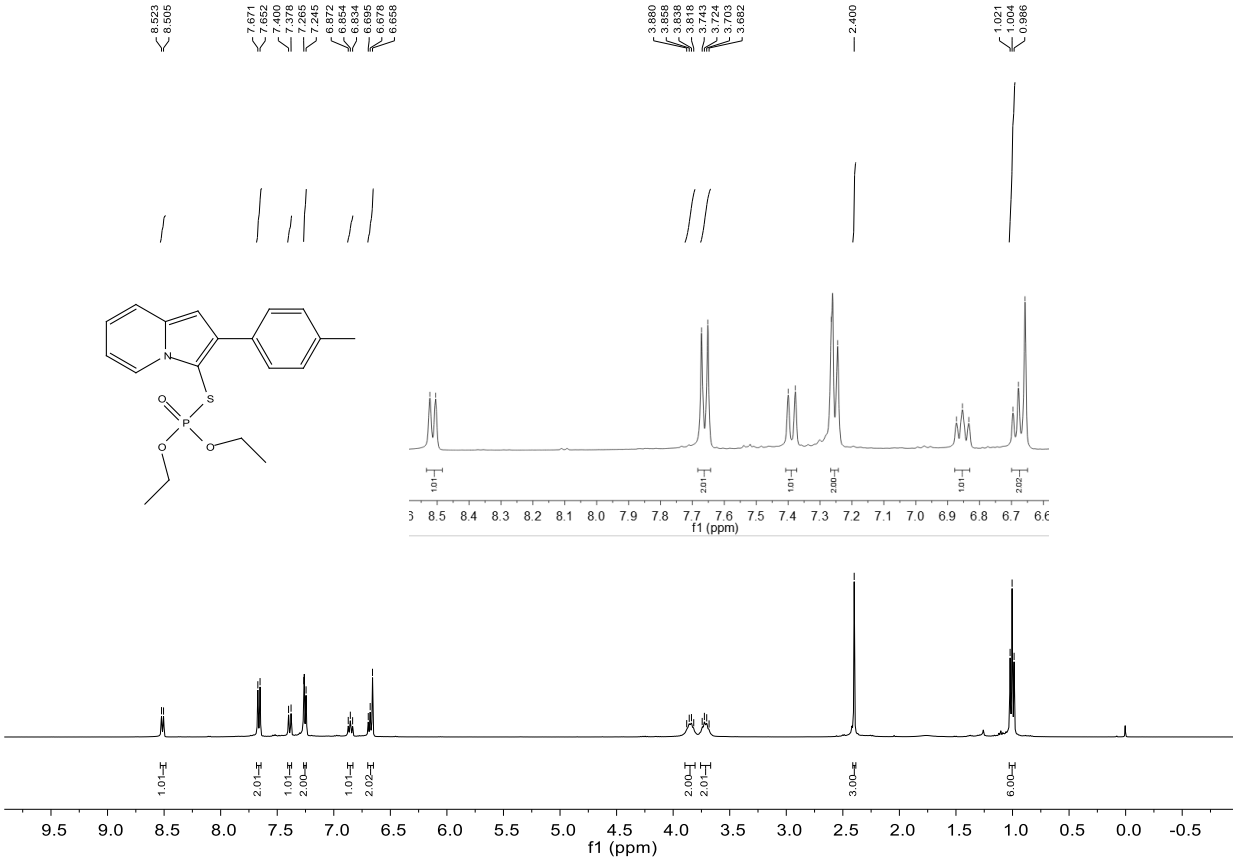
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3d**

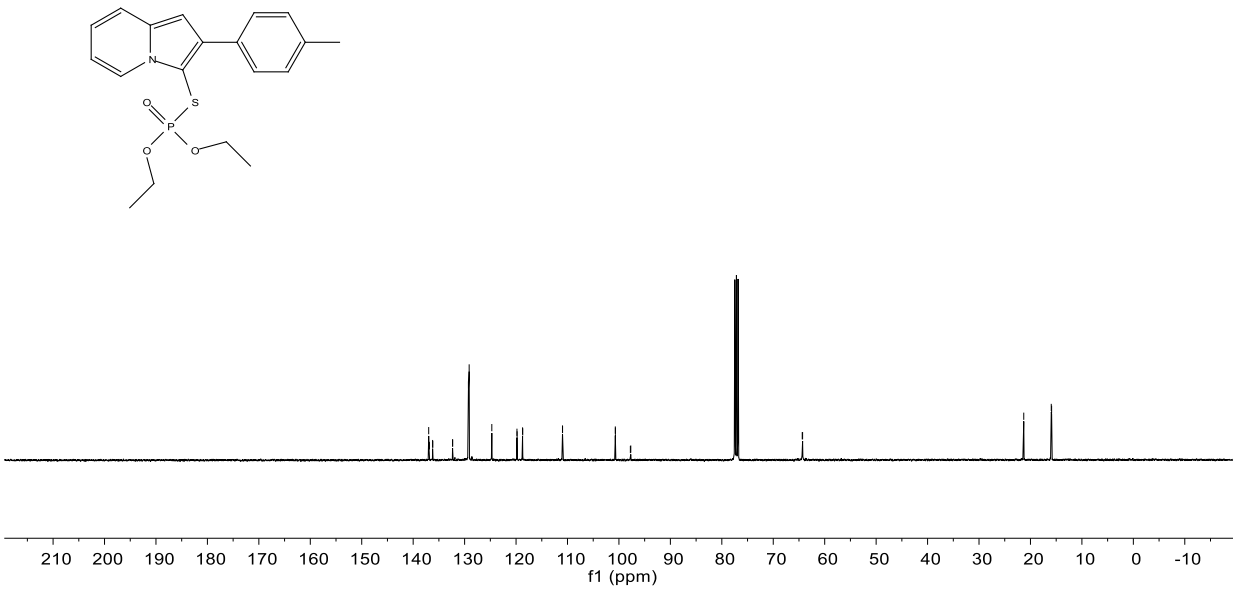



136.50
136.45
135.49
135.47
135.25
135.22
129.37
128.38
127.10
126.82
126.80
122.08
122.06
121.64
118.45
118.42
100.44
100.42
97.64
97.56
64.22
64.15
26.32
15.93
15.86
15.20
CH3
O
S
P
O
O
CH3
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

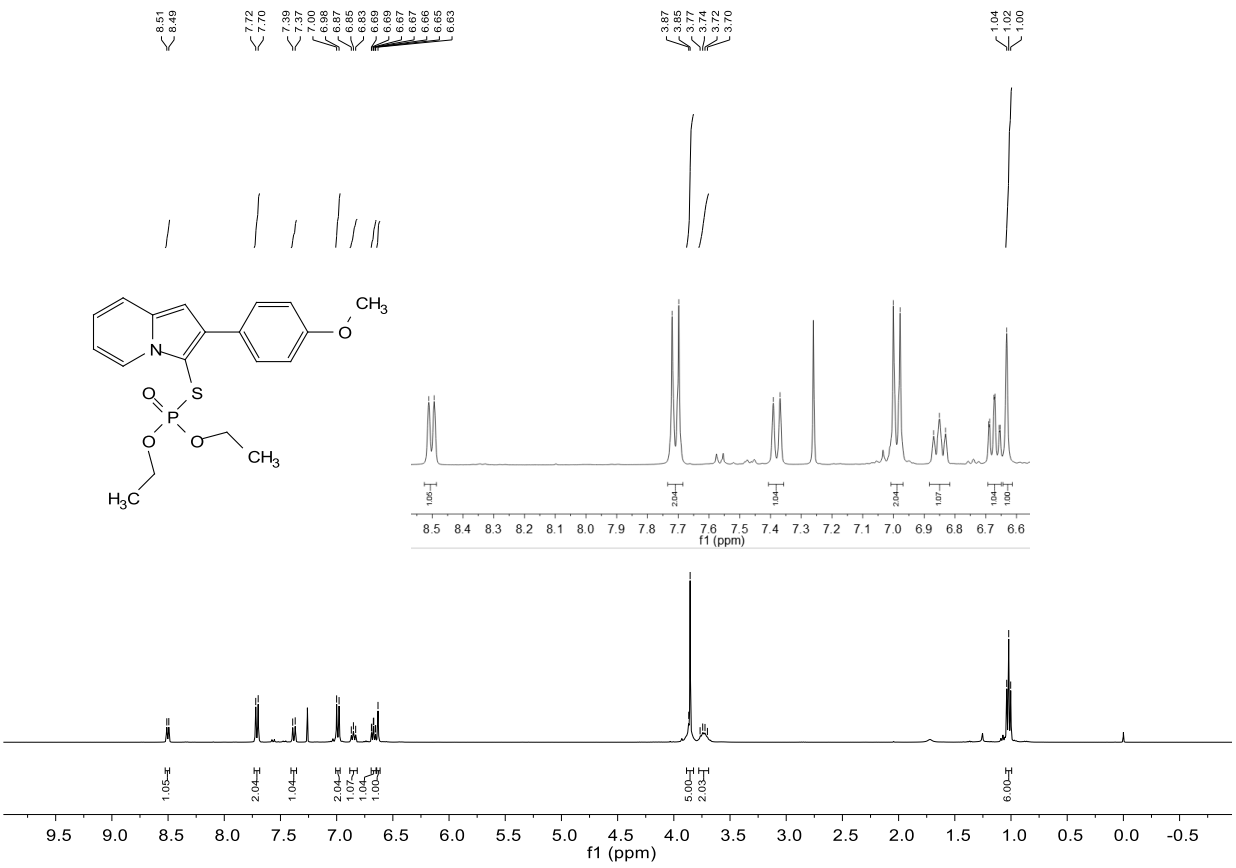

20.12
20.07
20.03
19.98
19.93
CH3
O
S
P
O
O
CH3
H3C
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

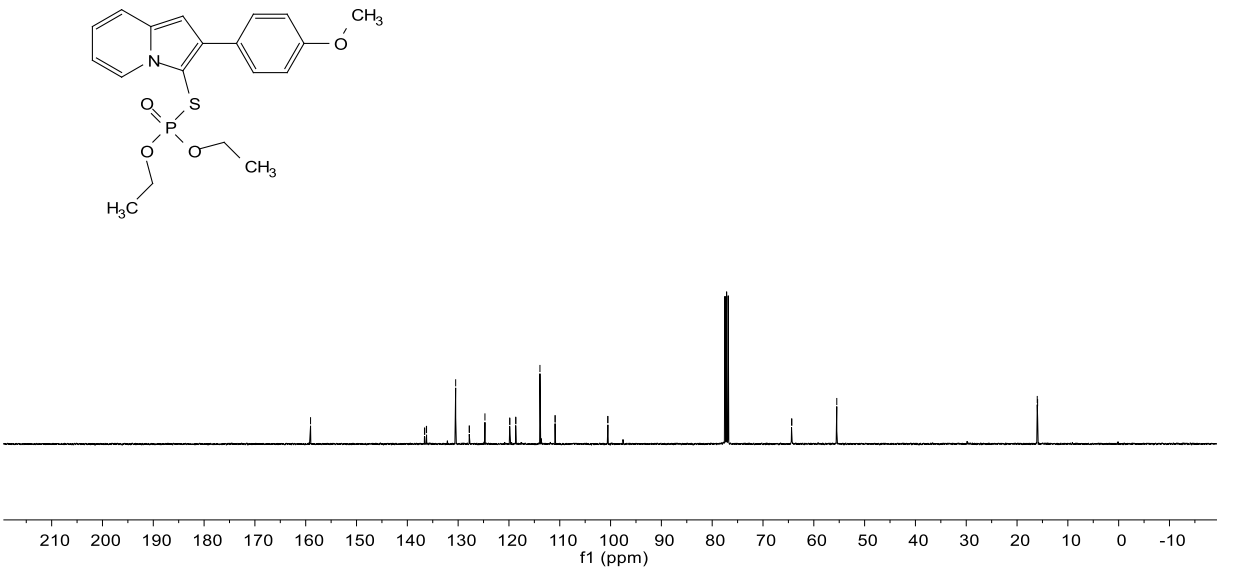
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3e**

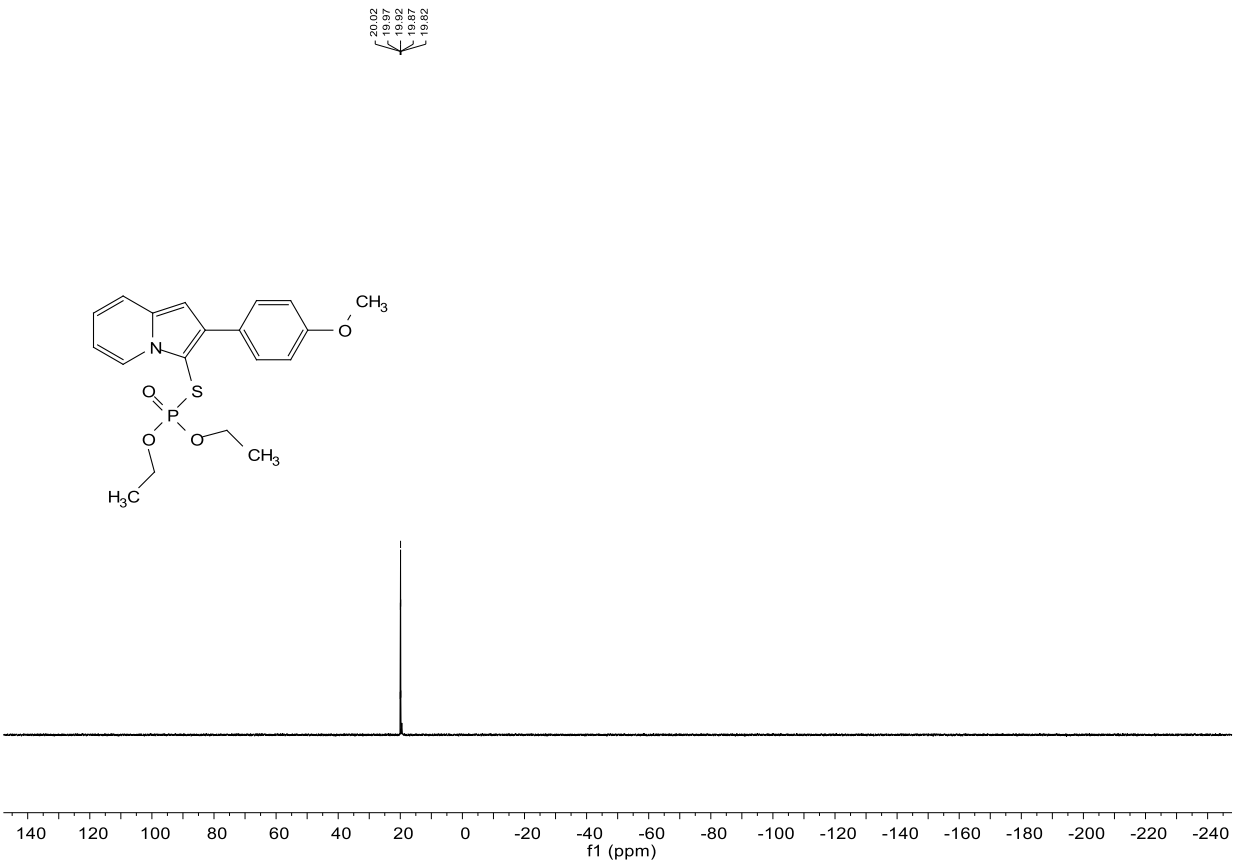




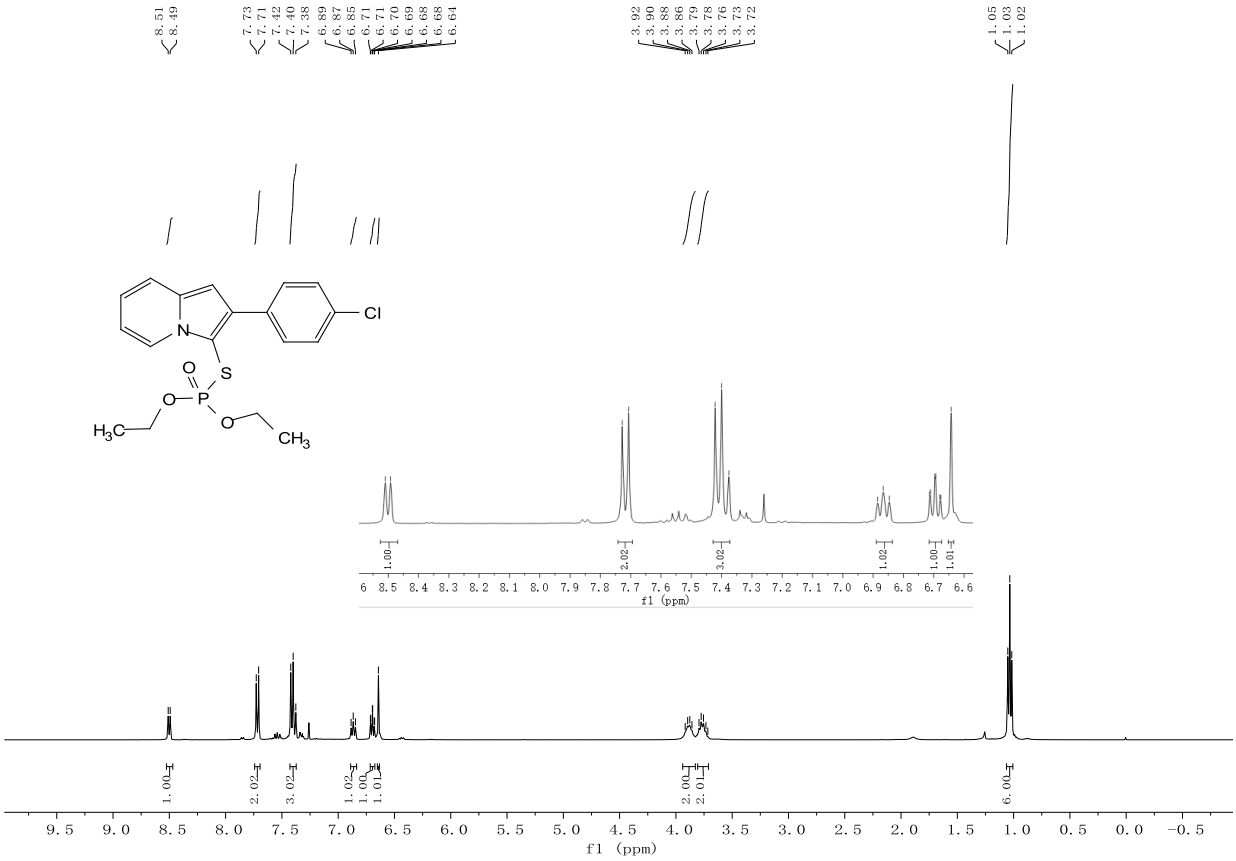
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3f**

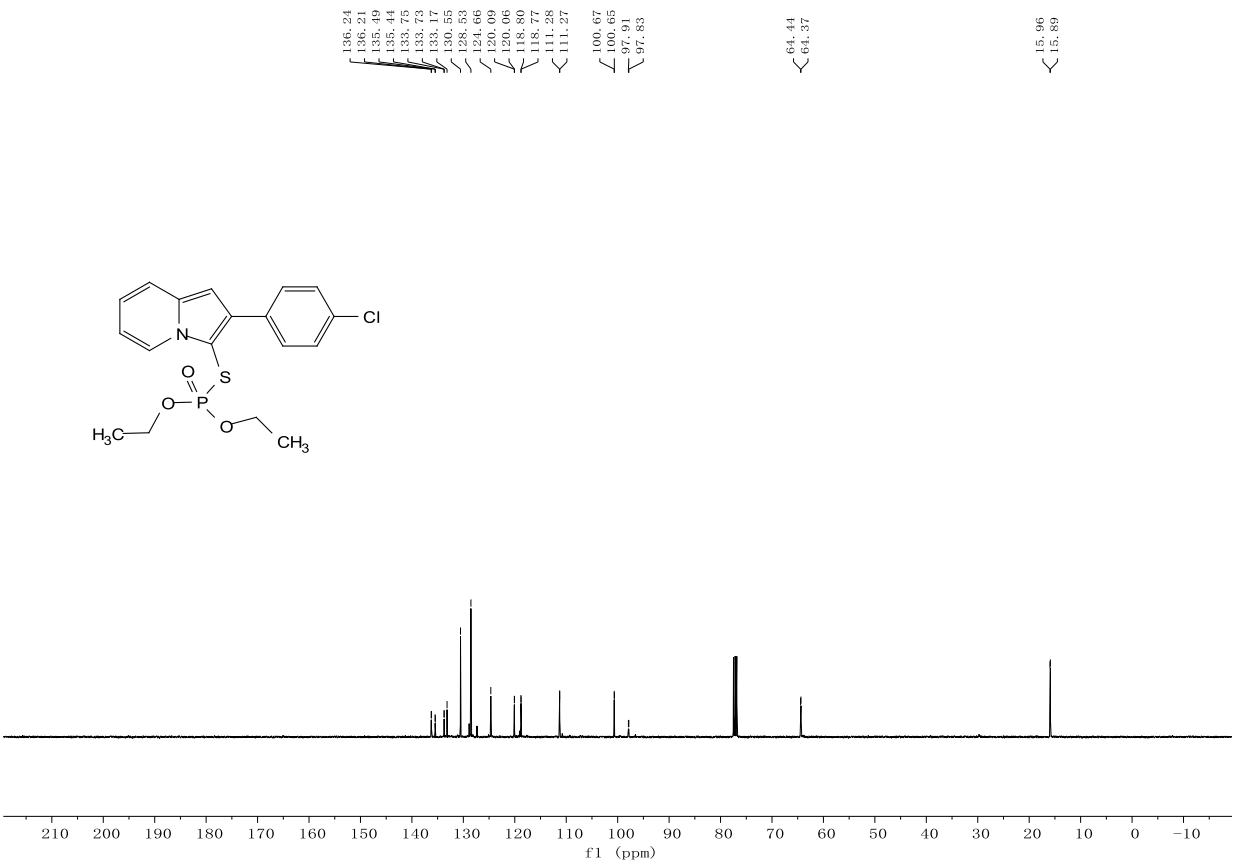


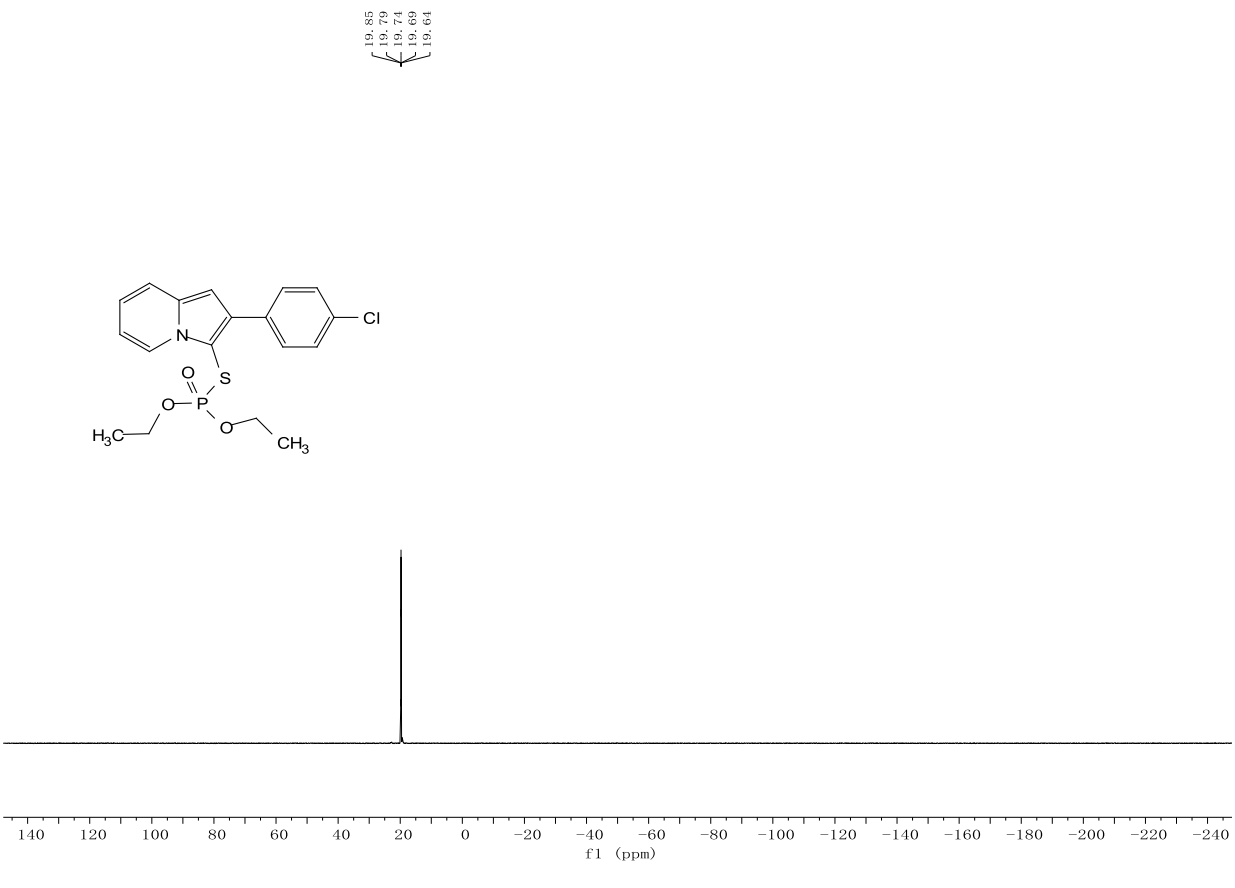




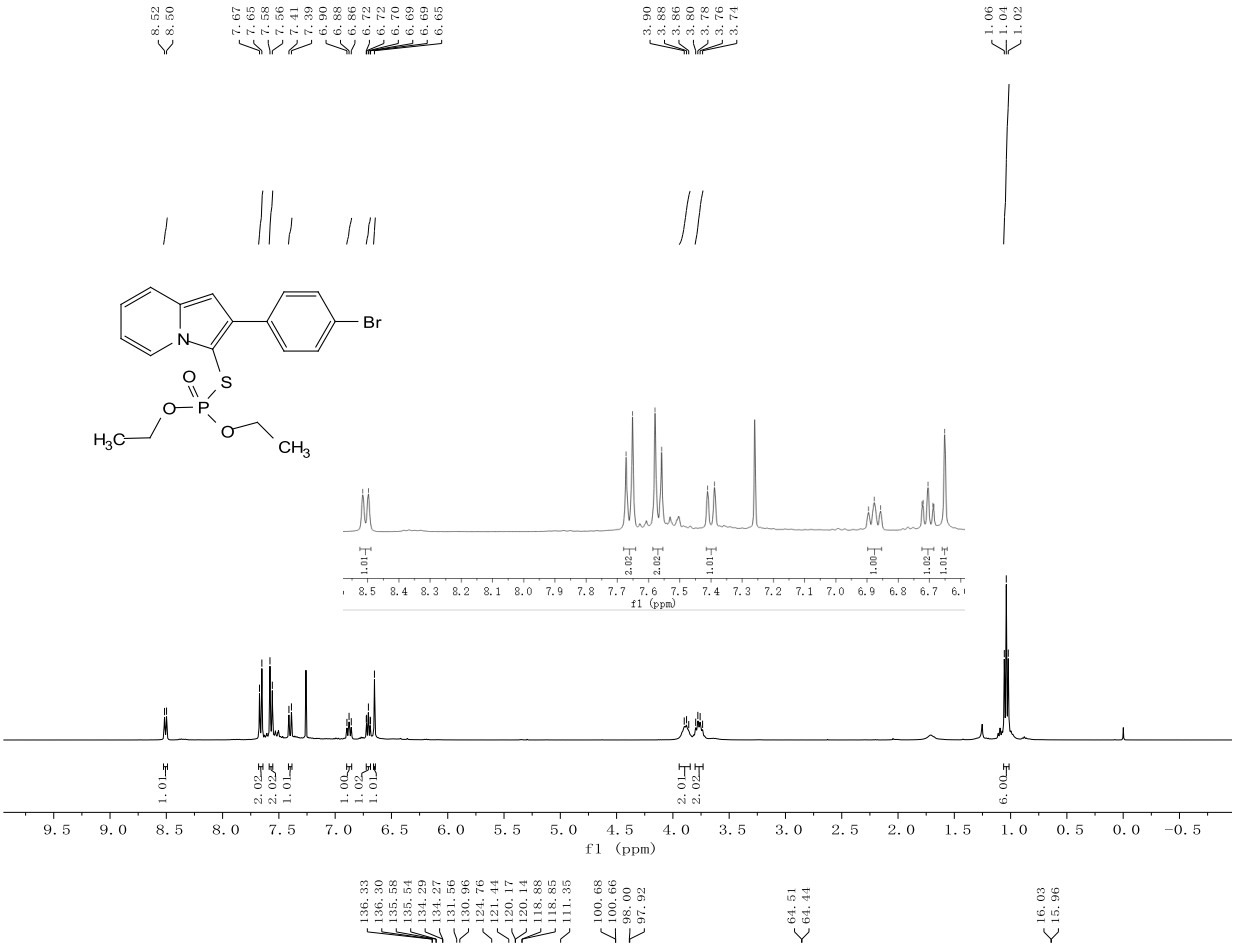
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3g**

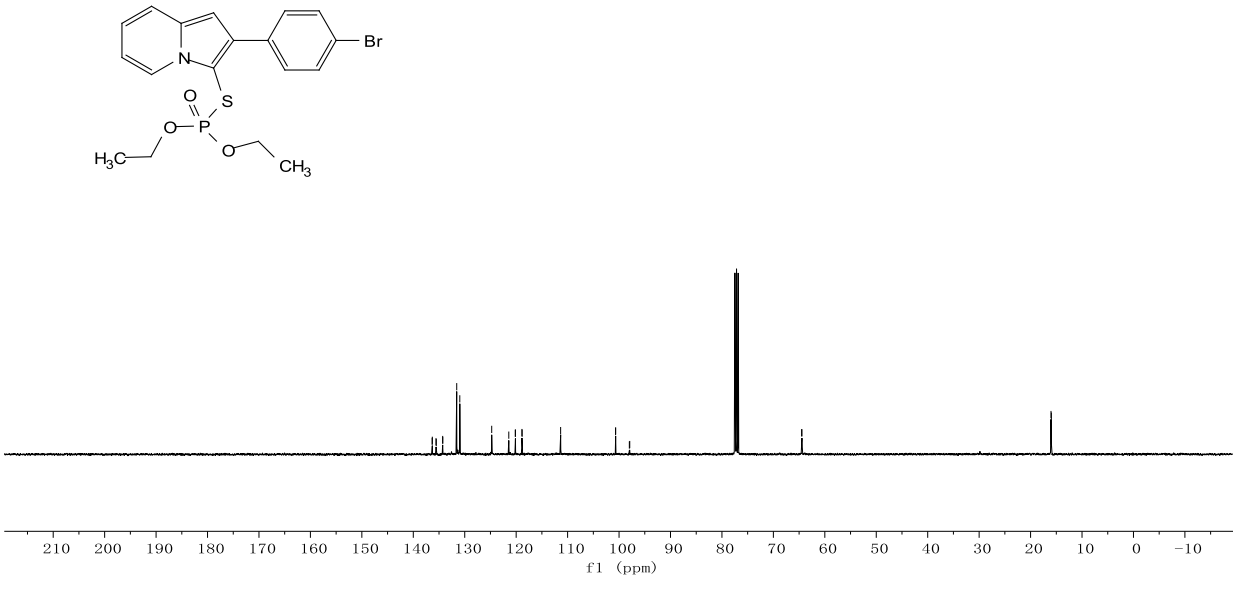



136.24
136.21
135.49
135.44
133.75
133.73
133.17
130.55
128.53
124.66
120.09
120.06
118.80
118.77
111.28
111.27
100.67
100.65
97.91
97.83
64.44
64.37
15.96
15.89
Cl
N
O
S
O
P
O
H3C
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

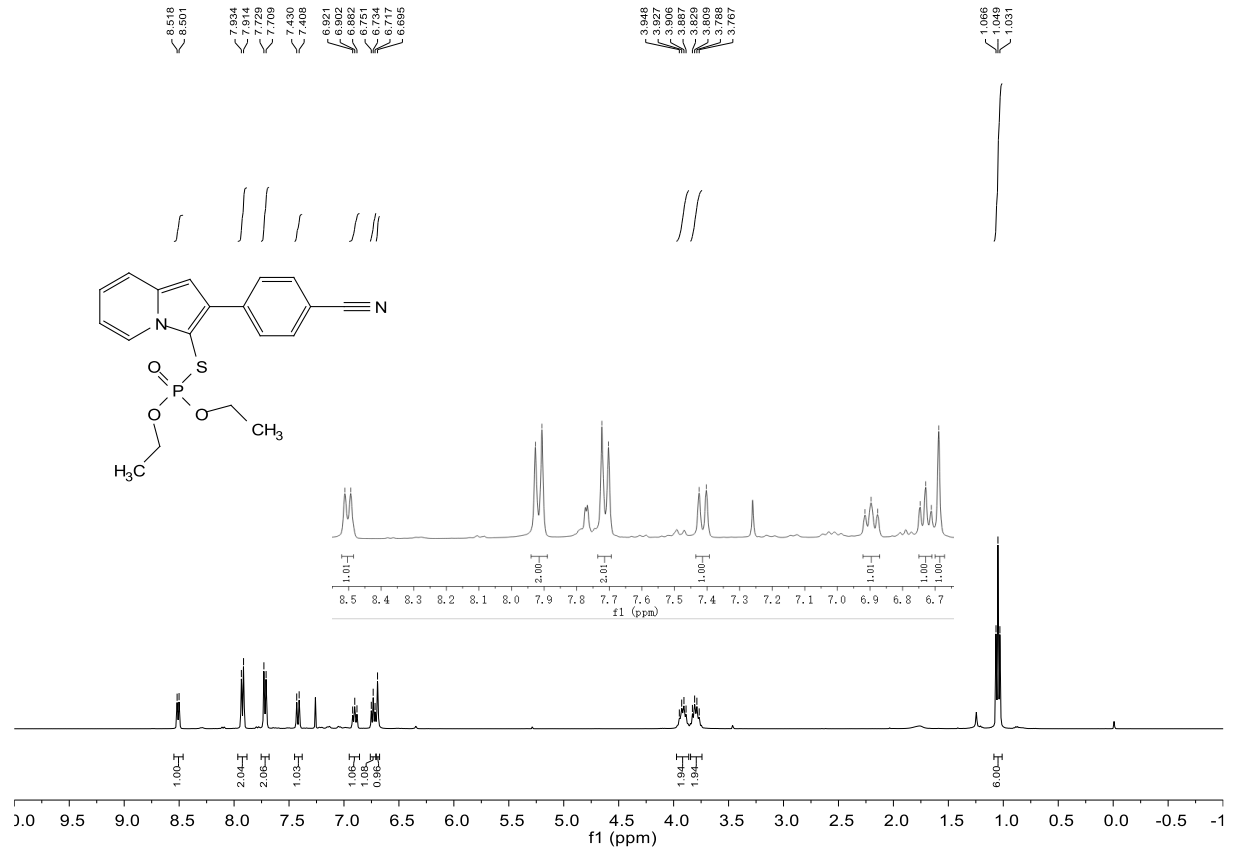

19.85
19.79
19.74
19.69
19.64
Cl
N
O
S
O
P
O
H3C
CH3
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
f1 (ppm)

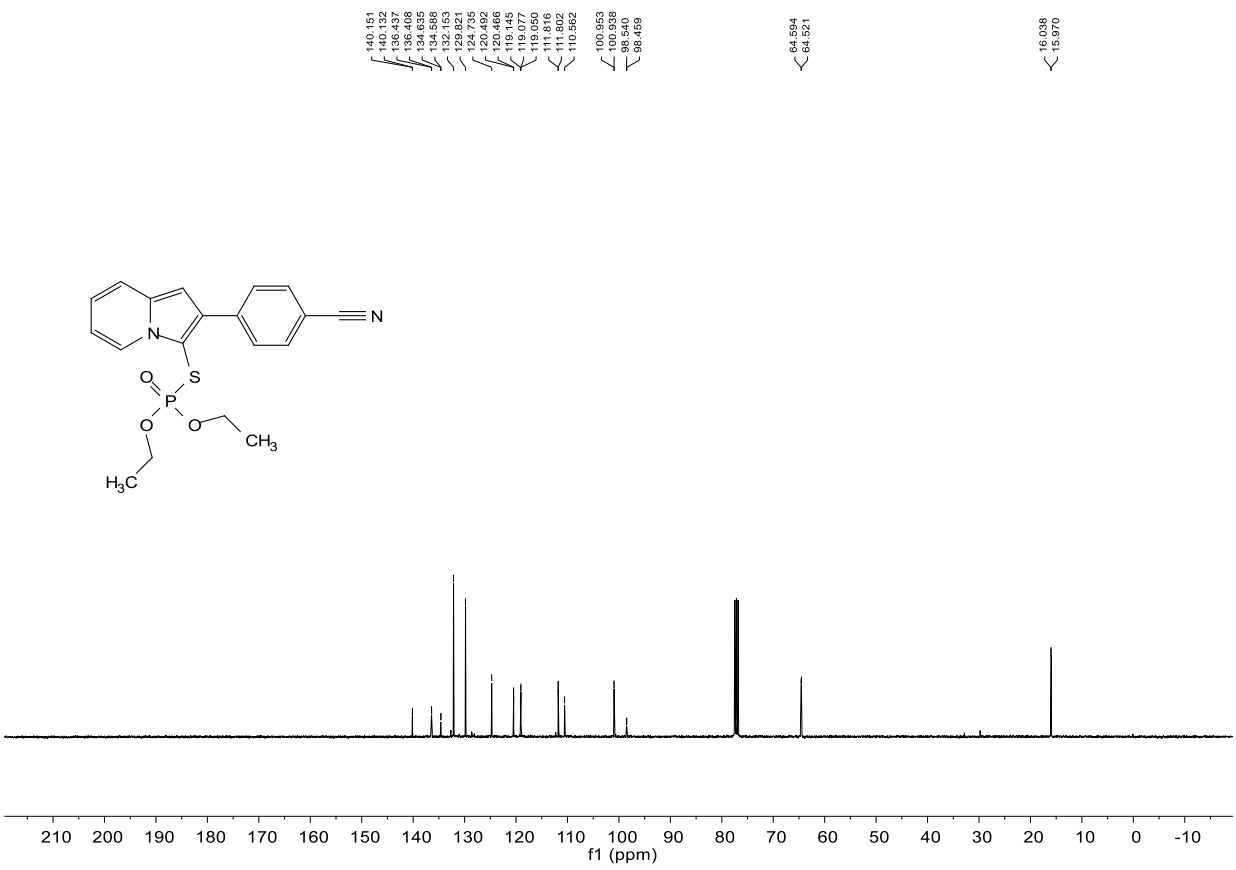
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3h**

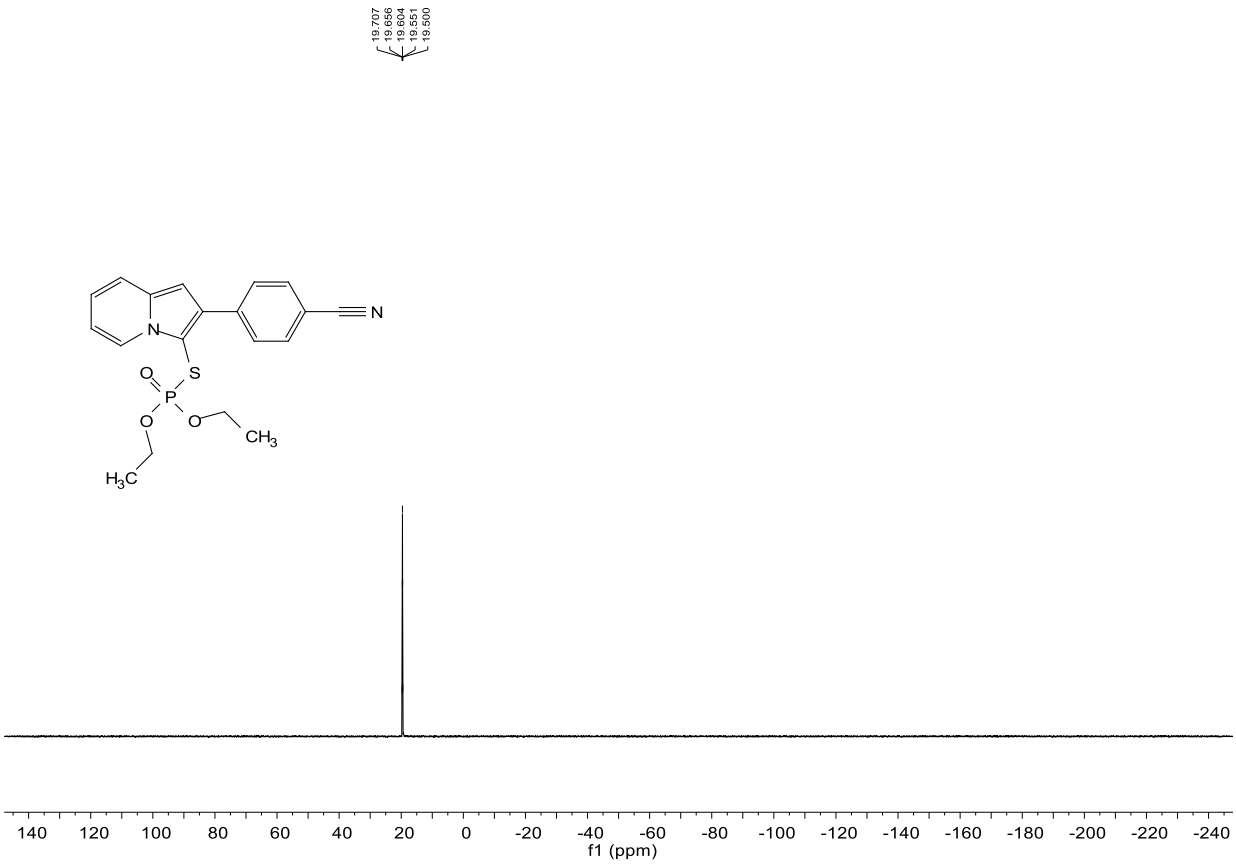




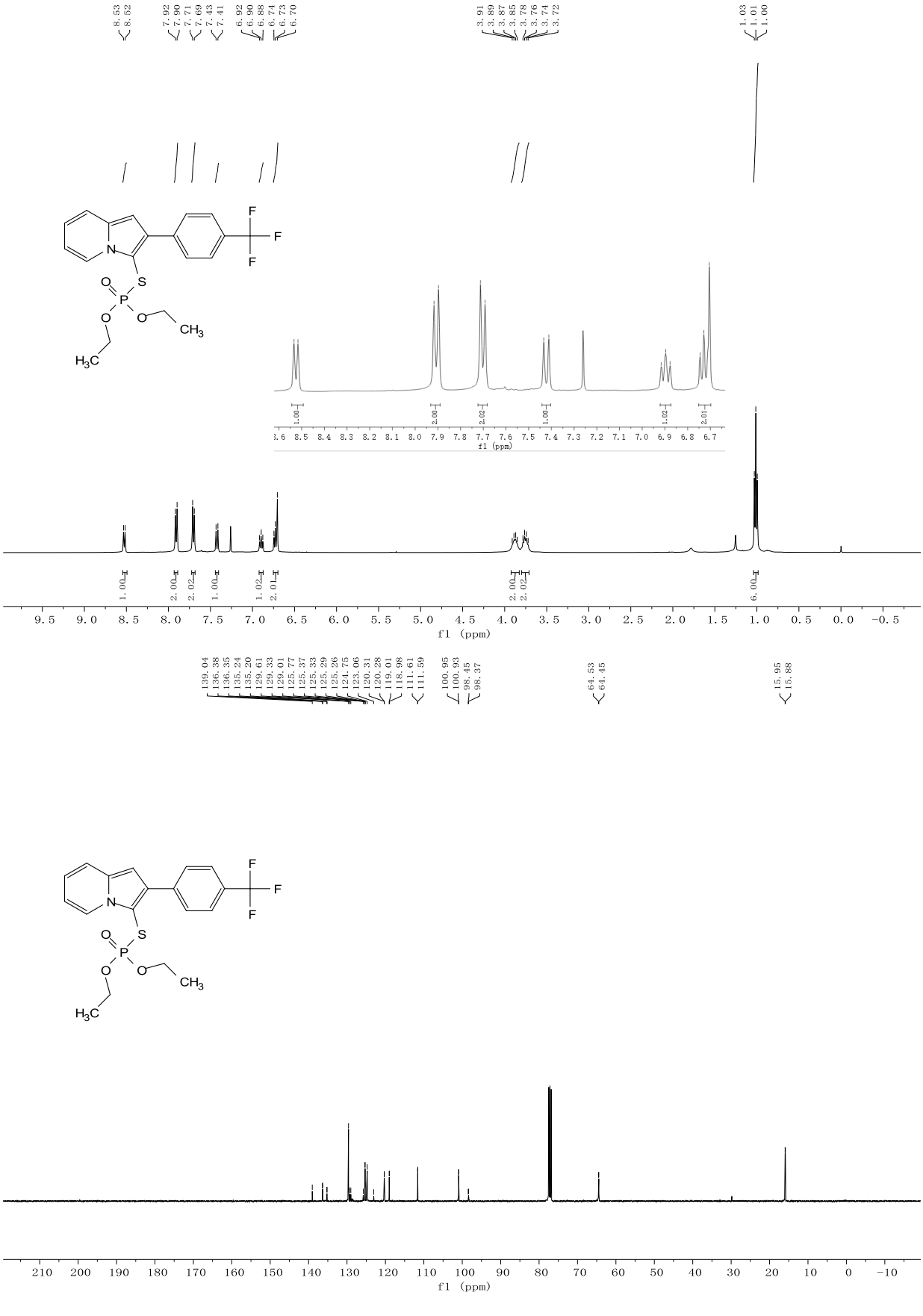
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3i**

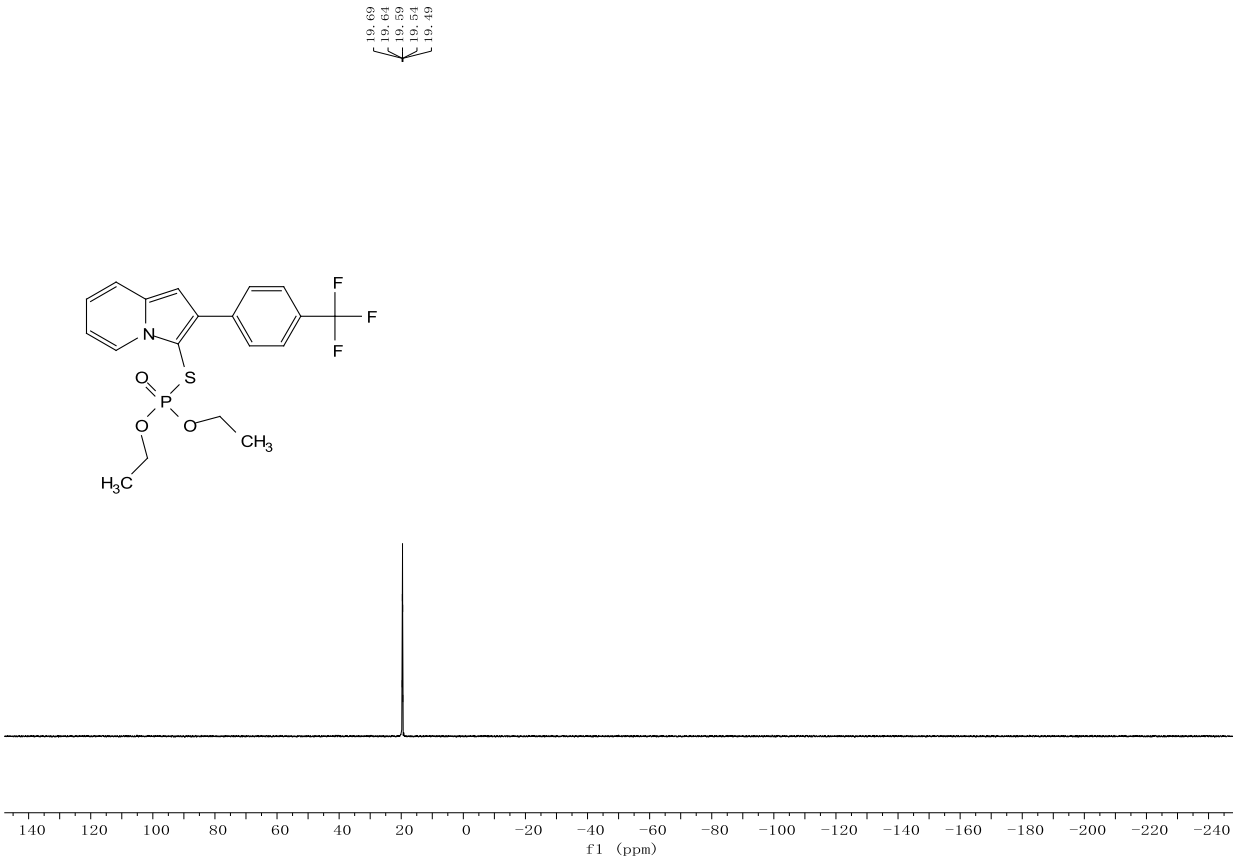



140.151
140.132
136.437
136.408
134.635
134.588
132.153
129.821
124.735
120.492
120.466
119.145
119.077
119.050
111.816
111.802
110.562
100.953
100.938
98.540
98.459
64.594
64.521
16.038
15.970
N
S
O
P
O
O
CH3
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

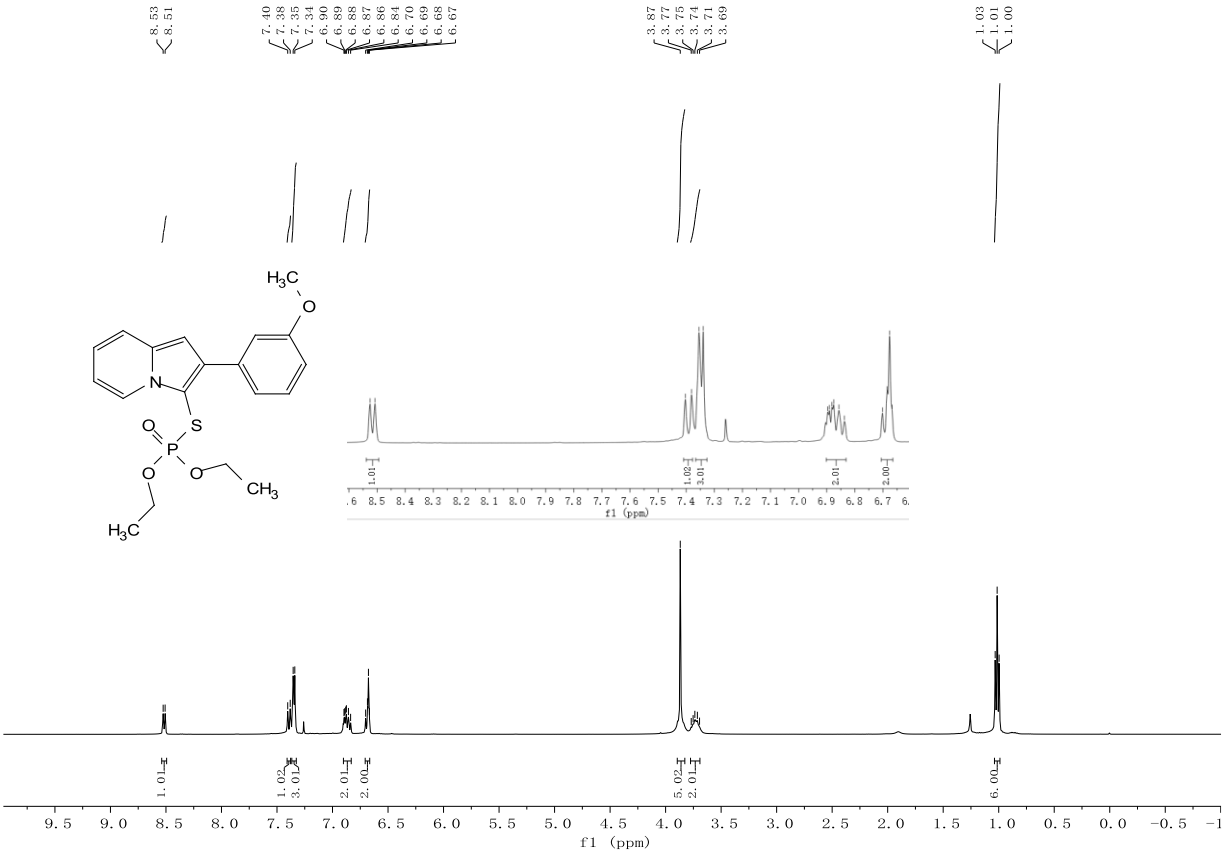

19.707
19.656
19.604
19.551
19.500
N
S
O
P
O
O
CH3
H3C
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

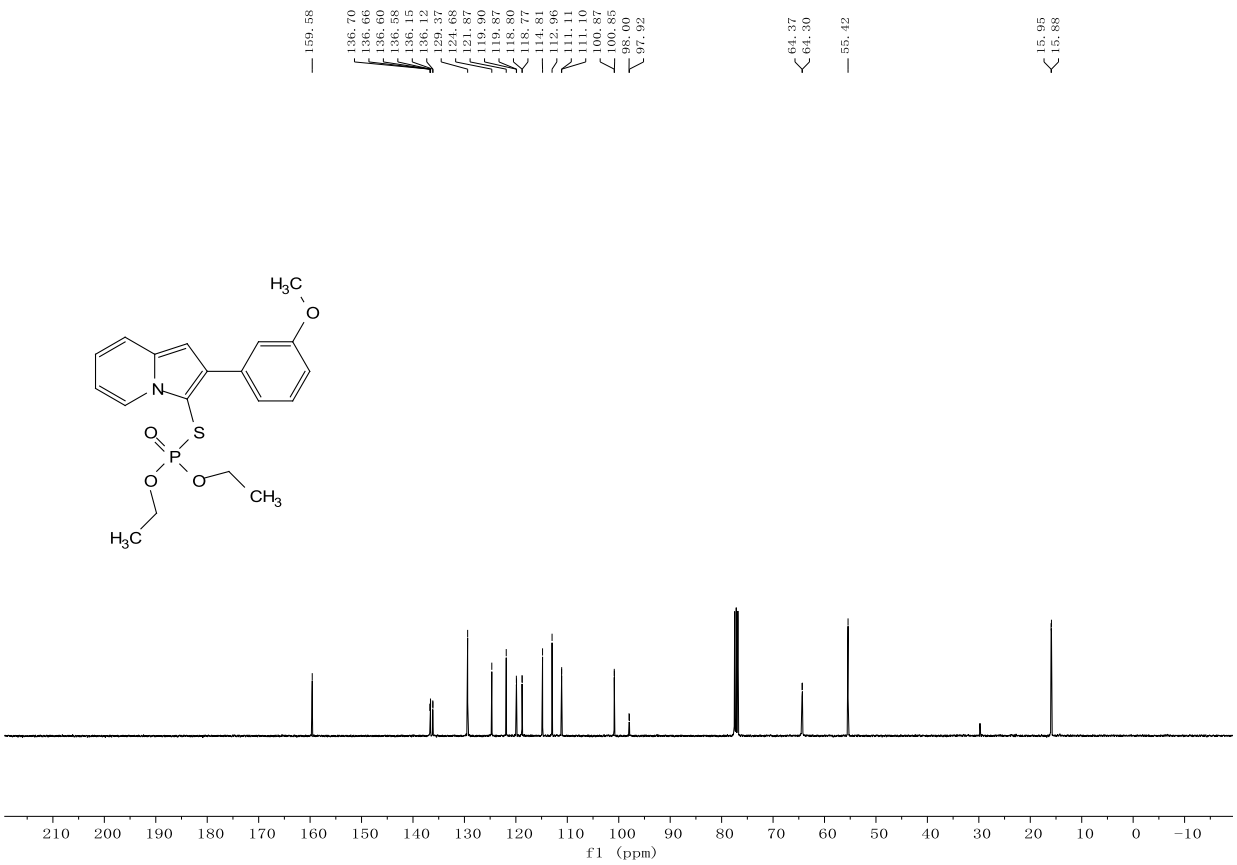
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3j**

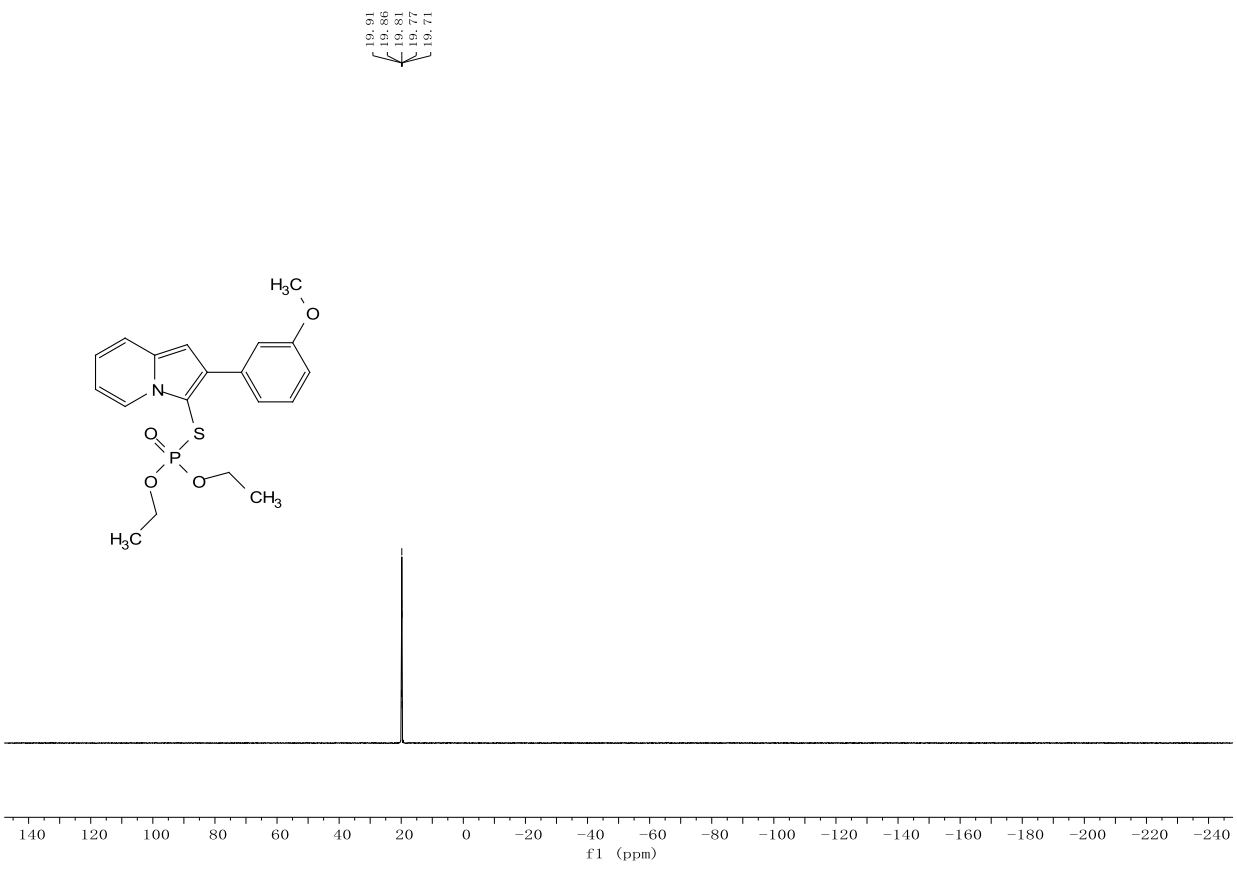




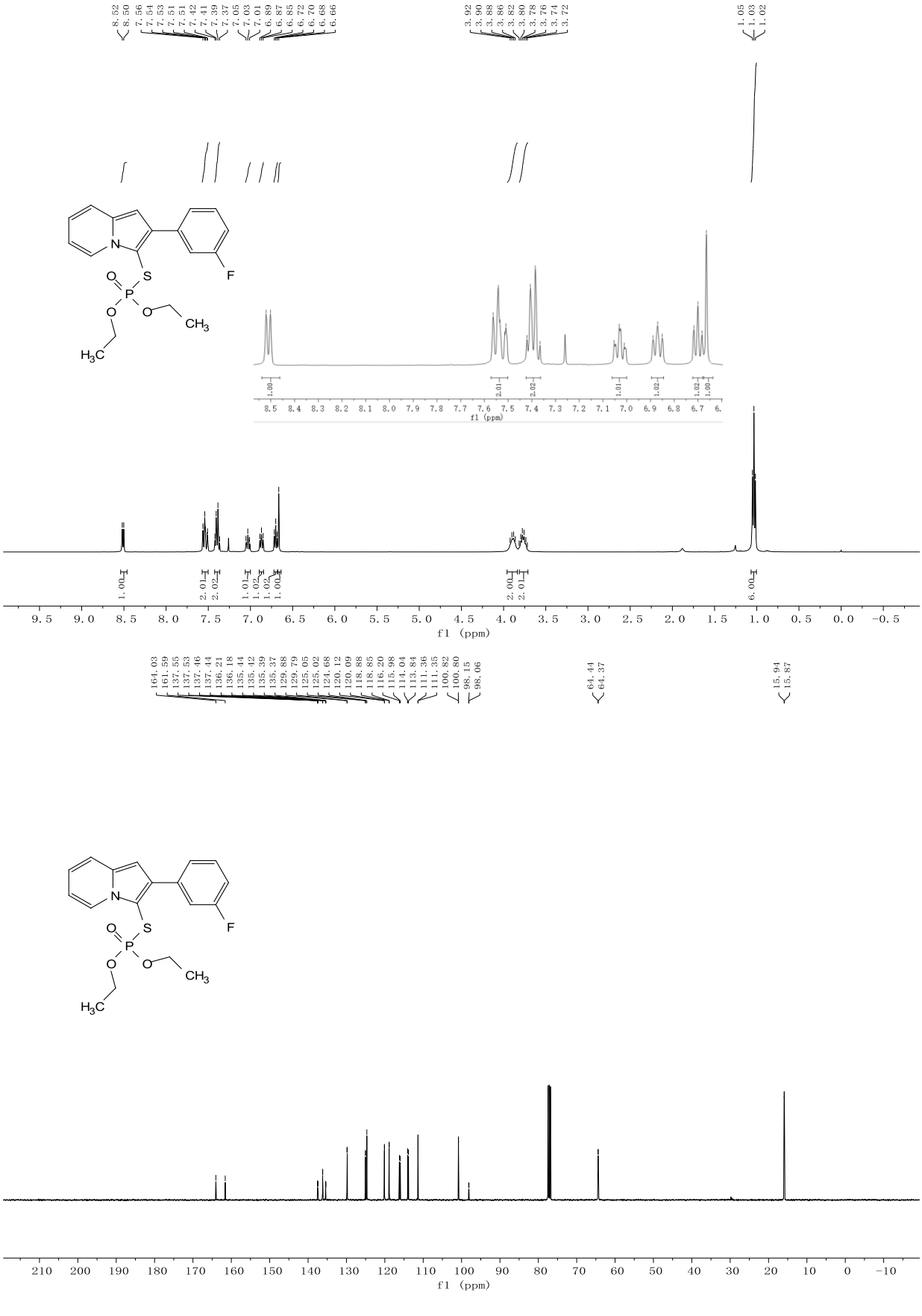
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3k**

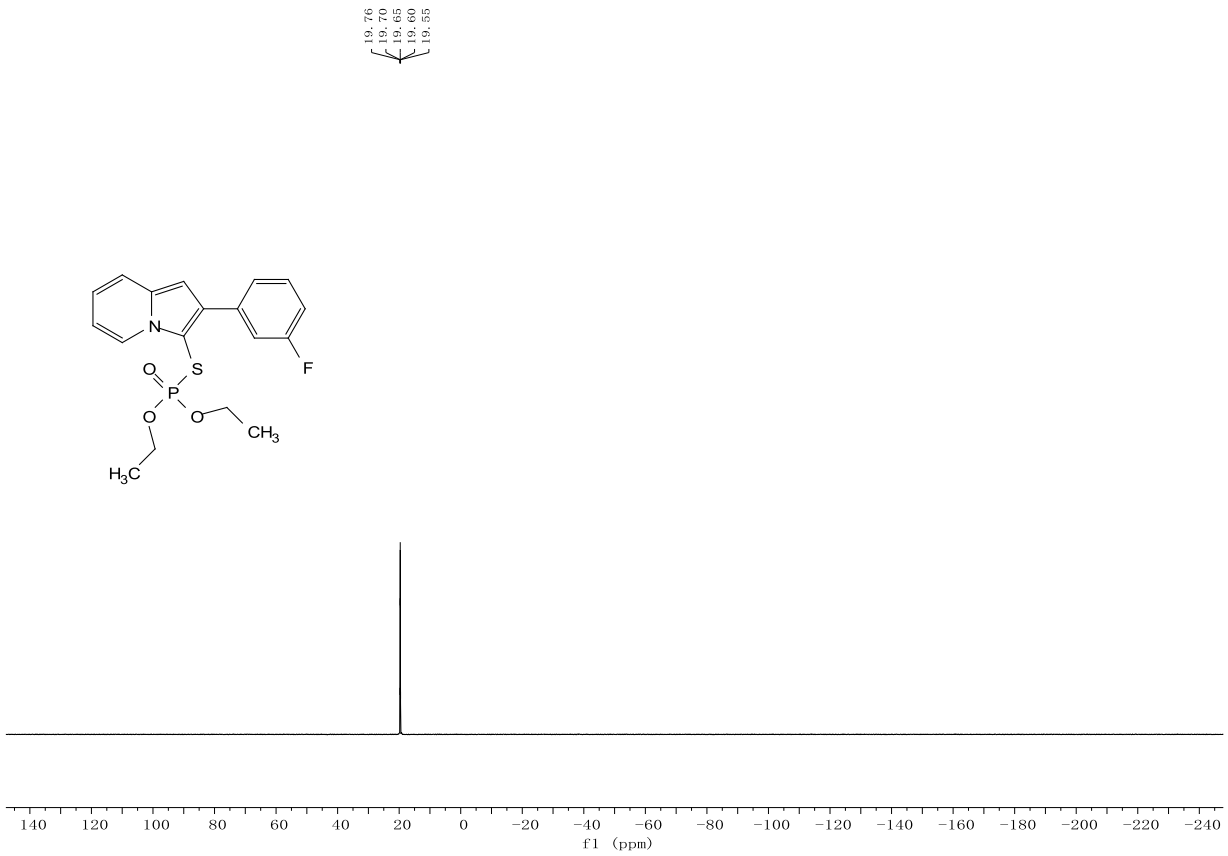



159.58
136.70
136.66
136.60
136.58
136.15
136.12
129.37
124.68
121.87
119.90
119.87
118.80
118.77
114.81
112.96
111.11
111.10
100.87
100.85
98.00
97.92
64.37
64.30
55.42
15.95
15.88
H3C
O
N
S
O
P
O
O
CH3
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

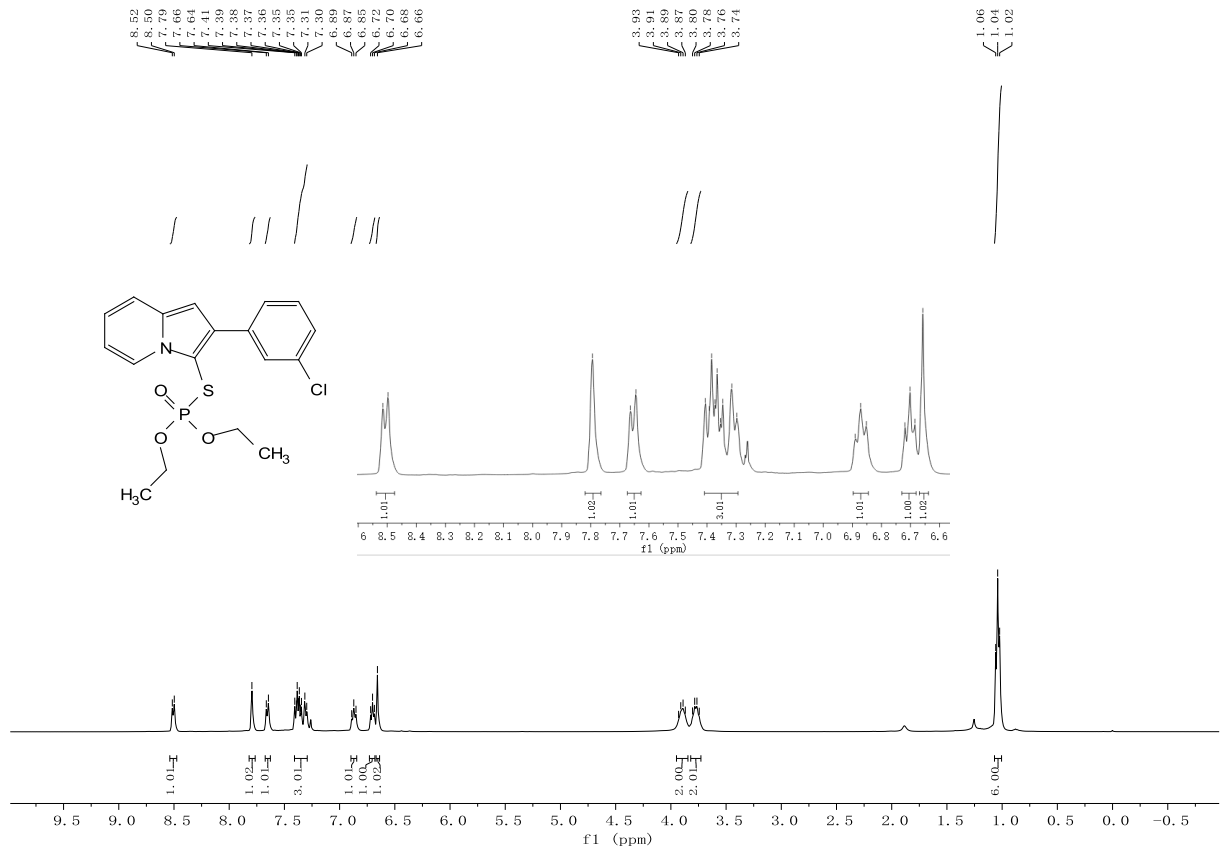

19.91
19.86
19.81
19.77
19.71
H3C
O
N
S
O
P
O
O
CH3
H3C
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

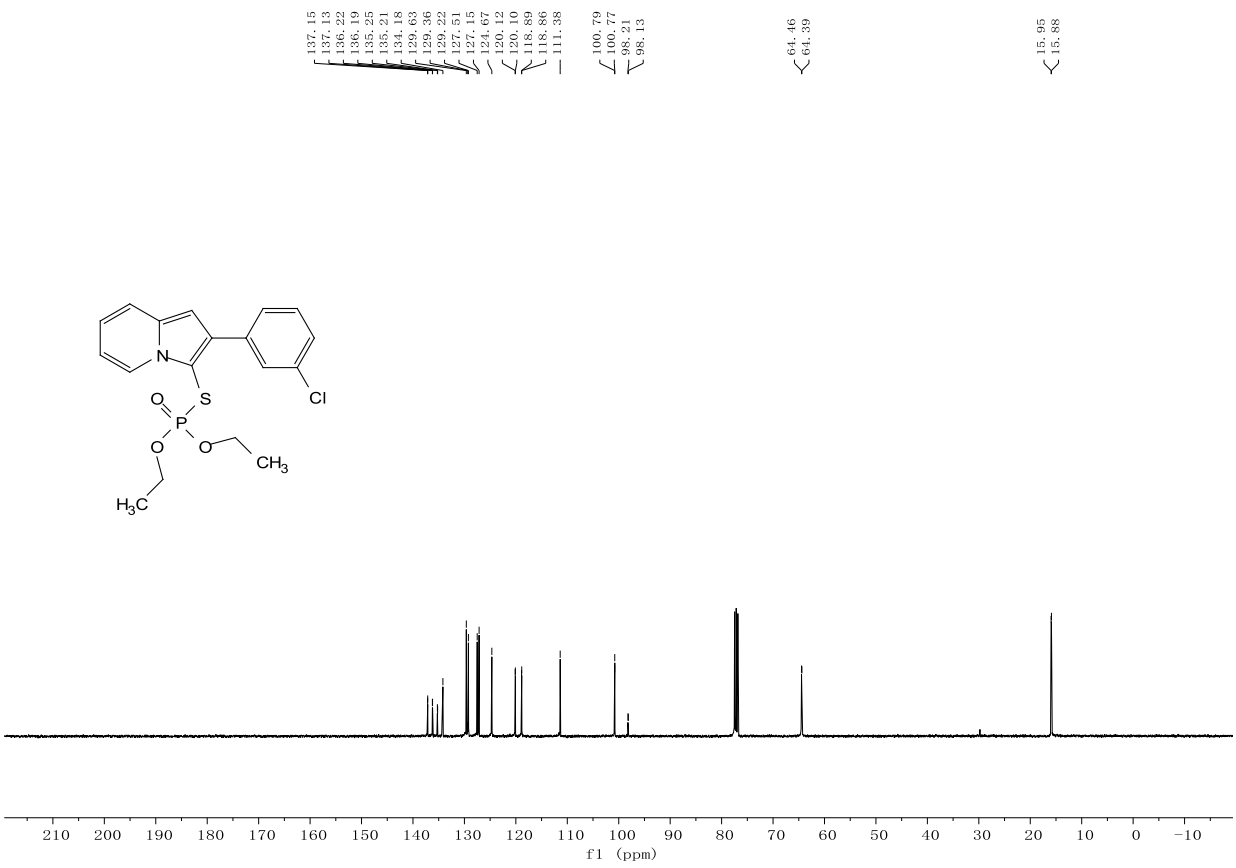
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3l**

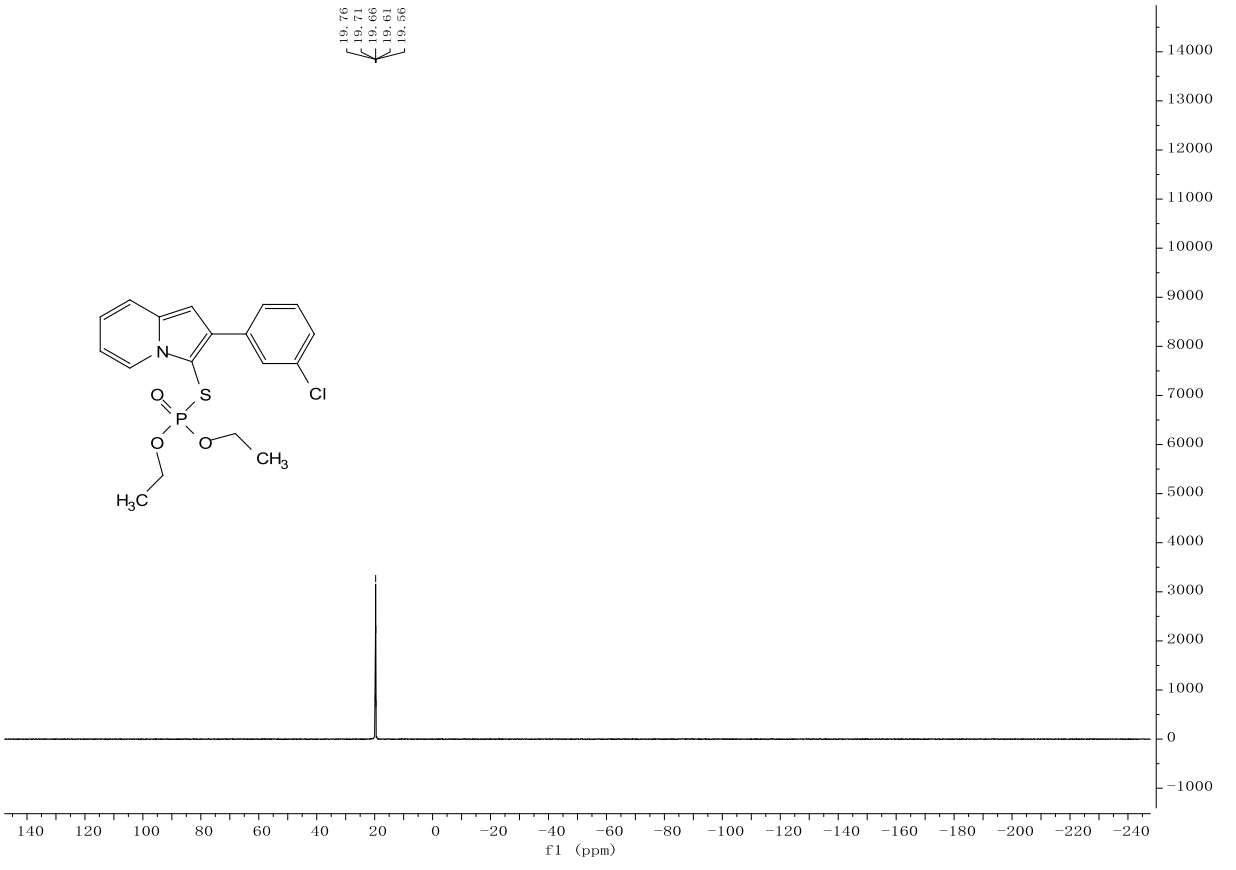




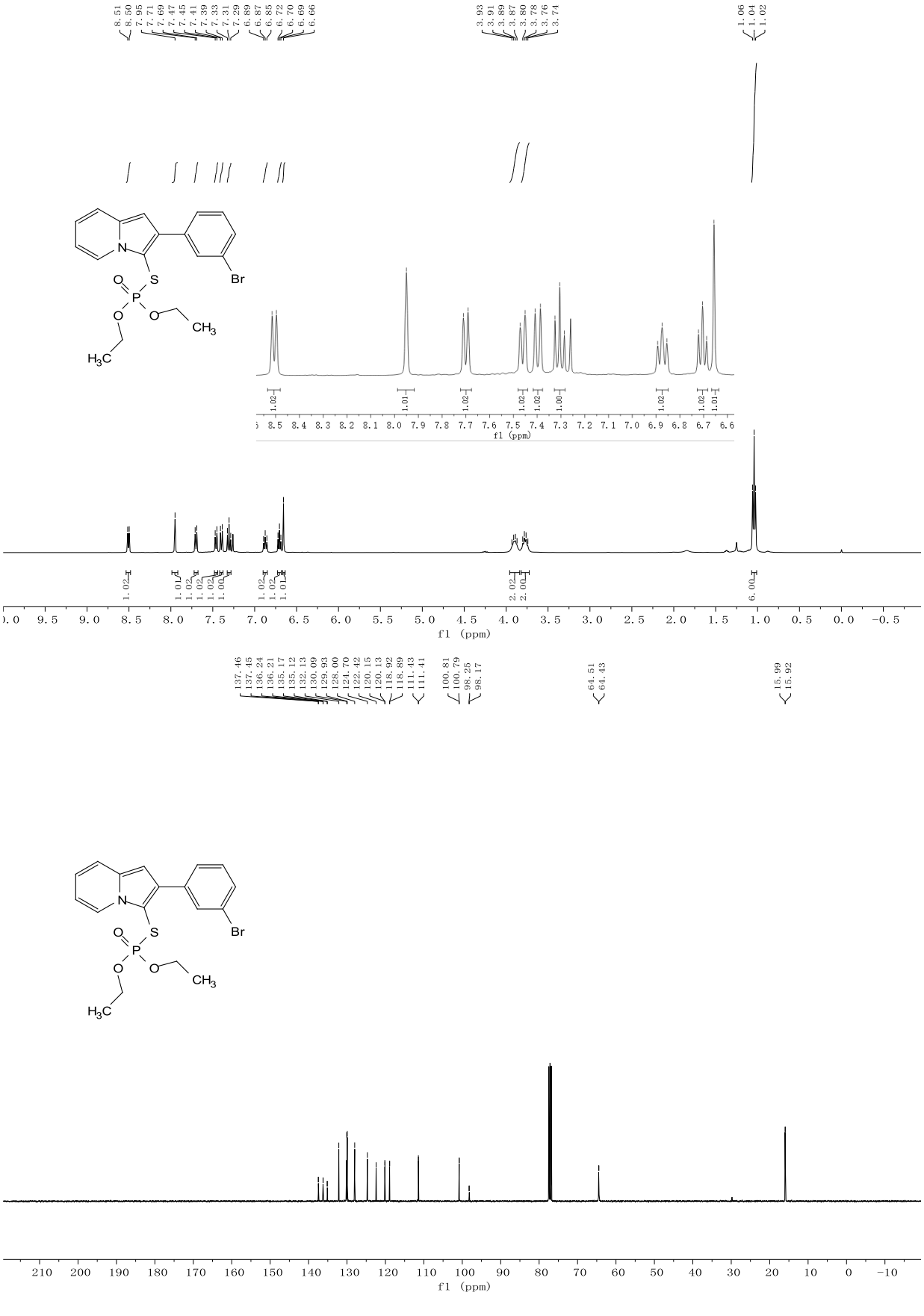
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3m**

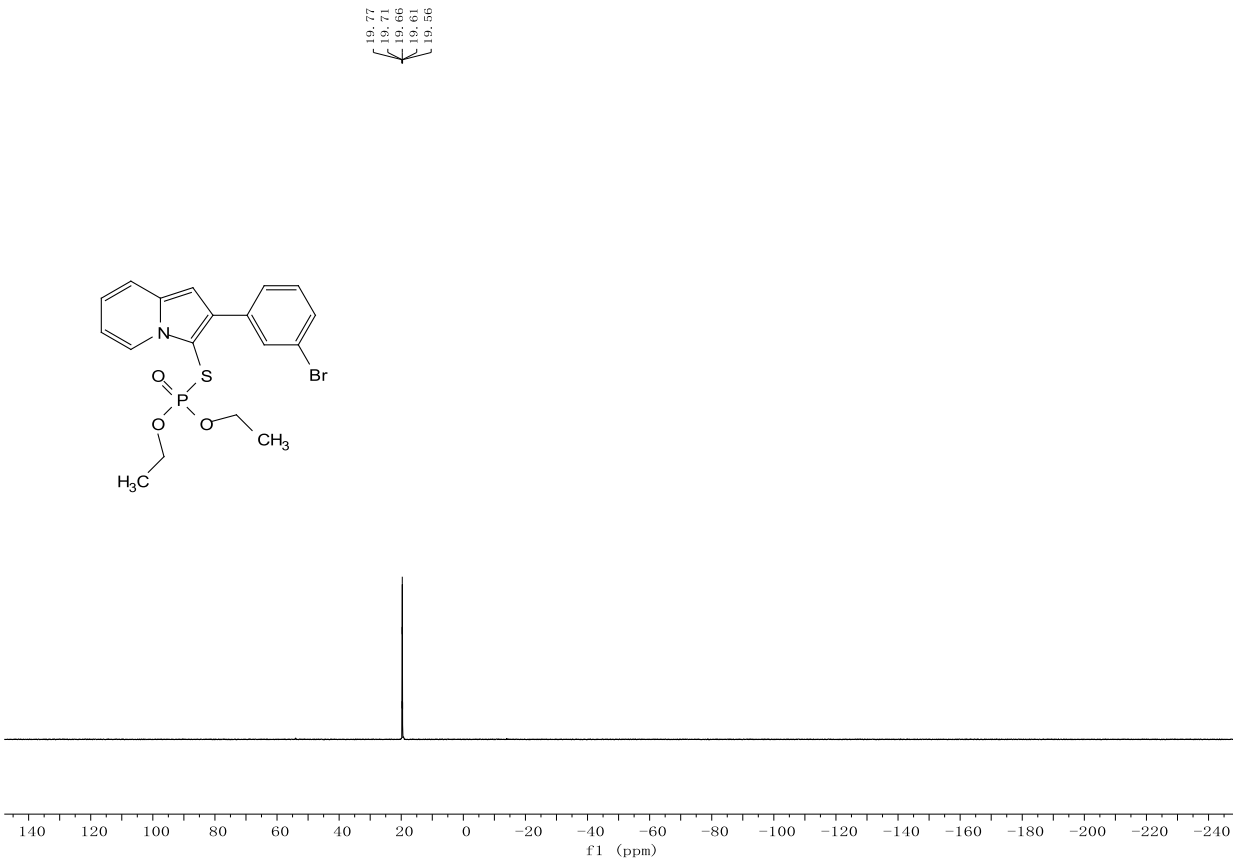



137.15
137.13
136.22
136.19
135.25
135.21
134.18
129.63
129.36
129.22
127.51
127.15
124.67
120.12
120.10
118.89
118.86
111.38
100.79
100.77
98.21
98.13
64.46
64.39
15.95
15.88
Cl
O
S
P
O
O
CH3
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

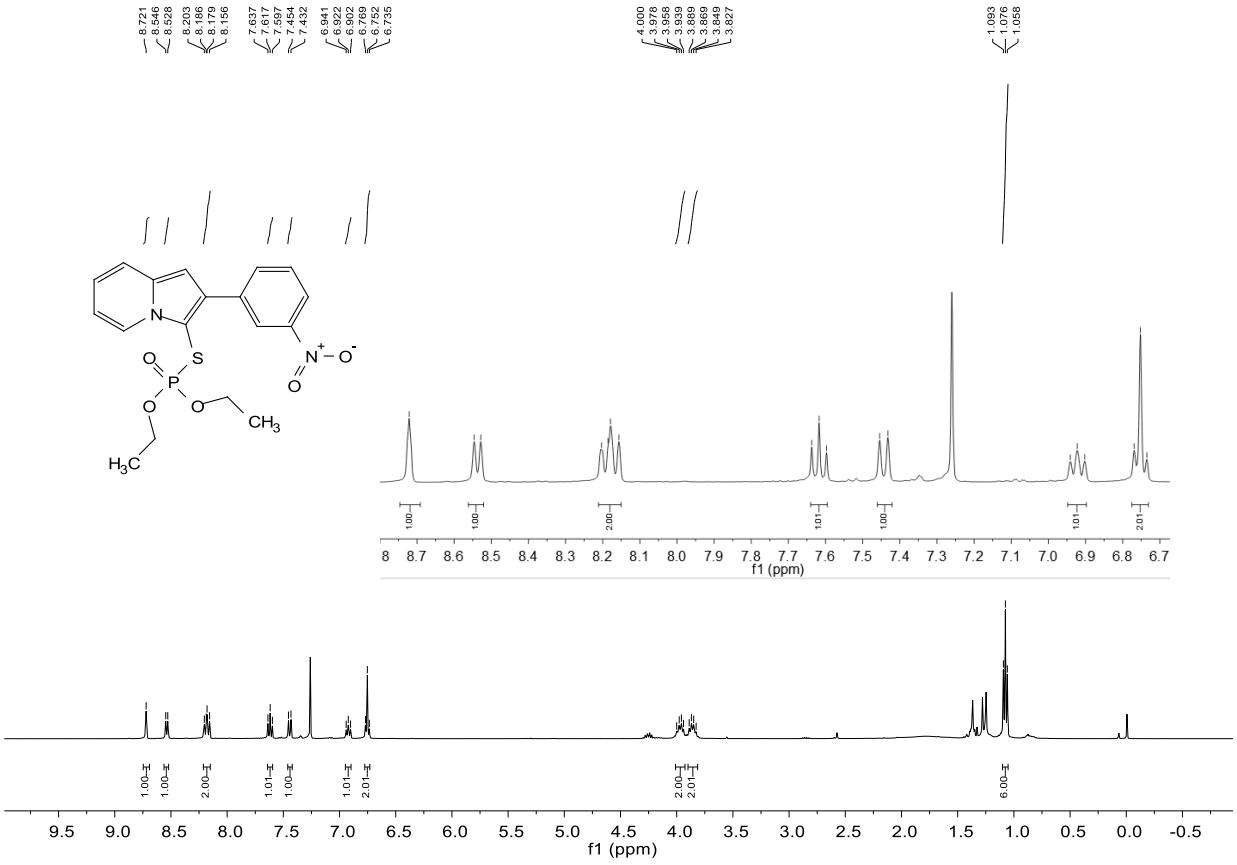

19.76
19.71
19.66
19.61
19.56
Cl
O
S
P
O
O
CH3
H3C
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

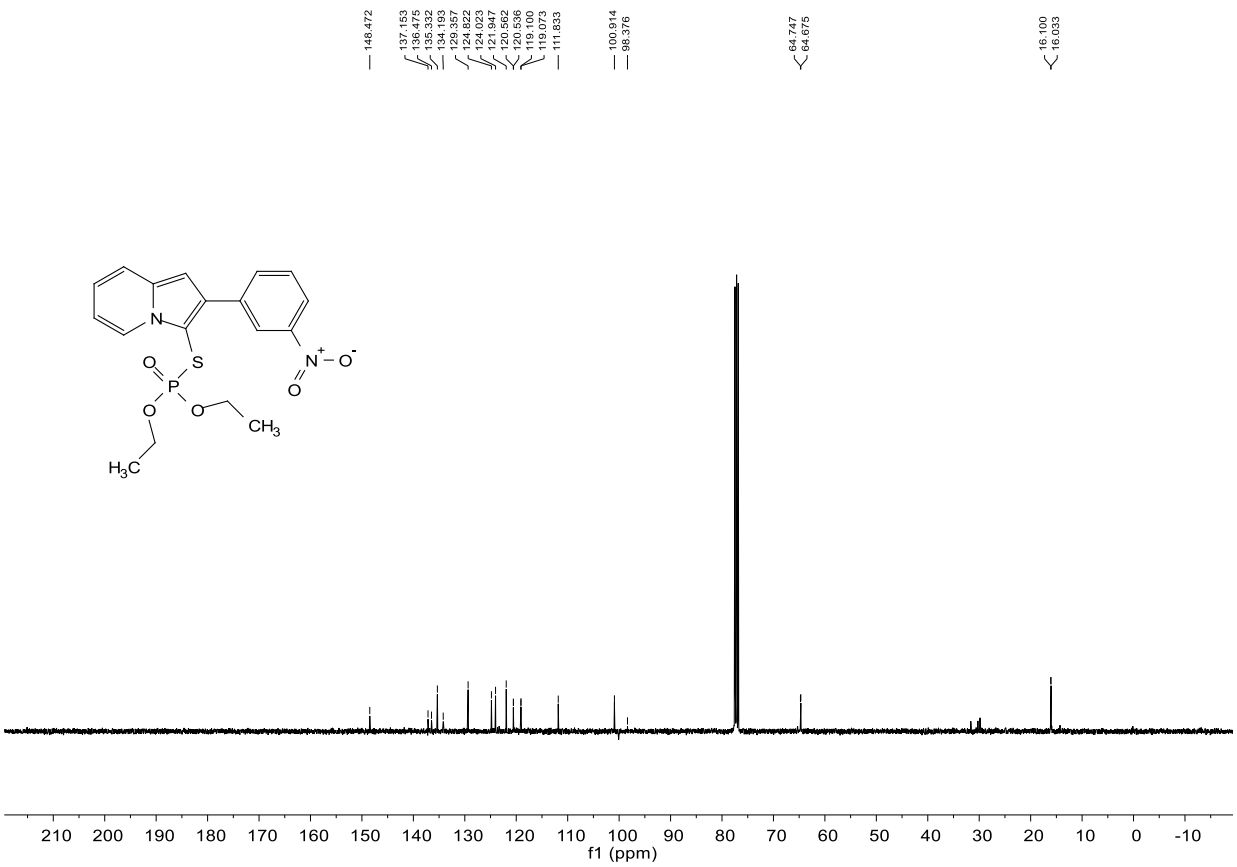
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3n**

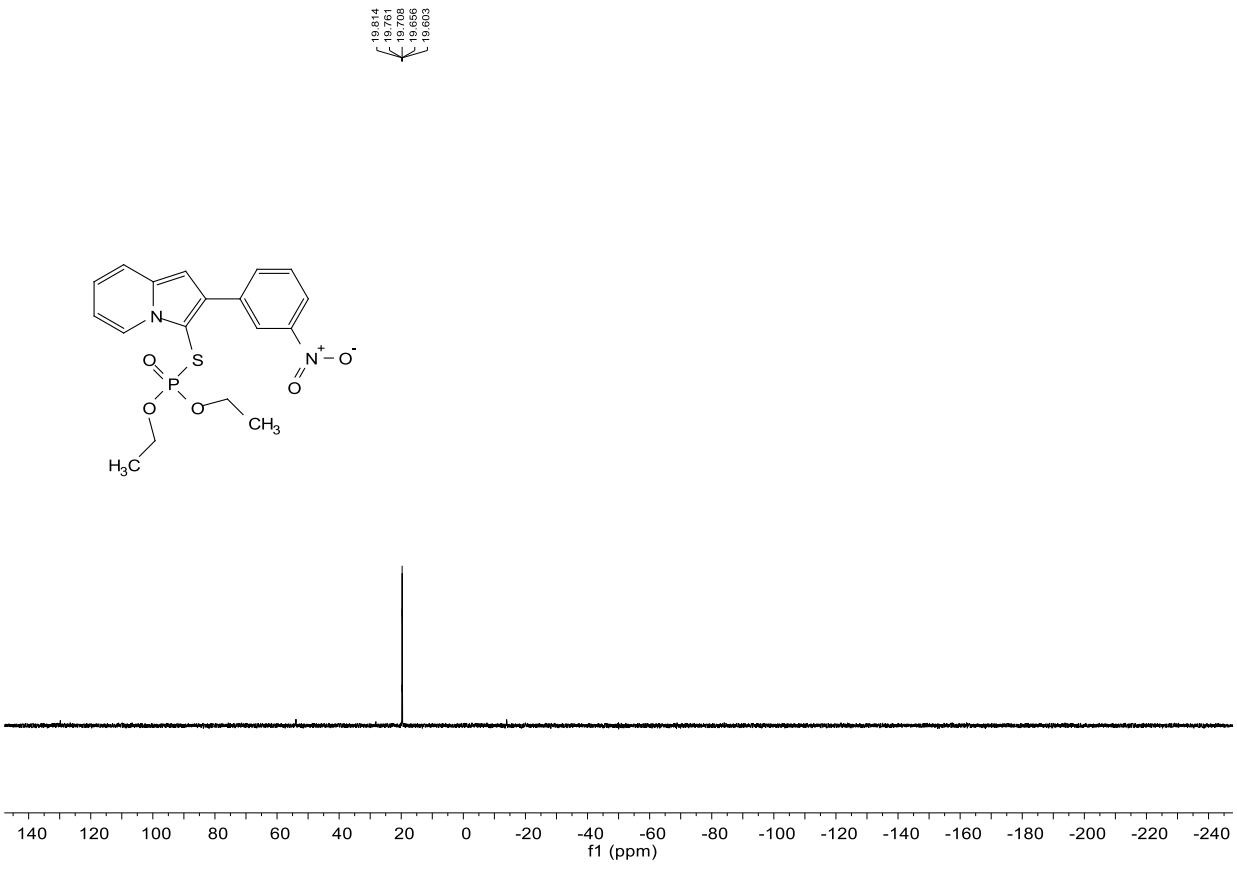




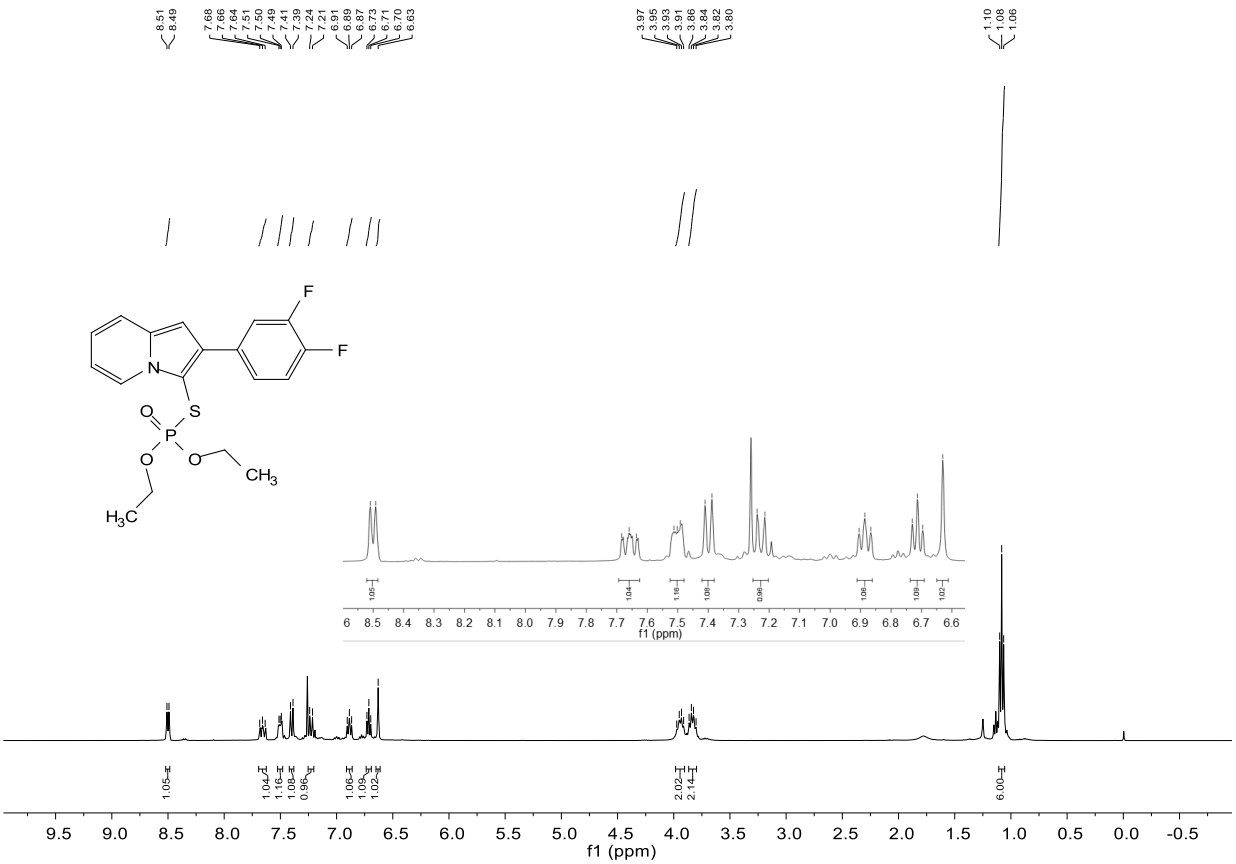
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3o**

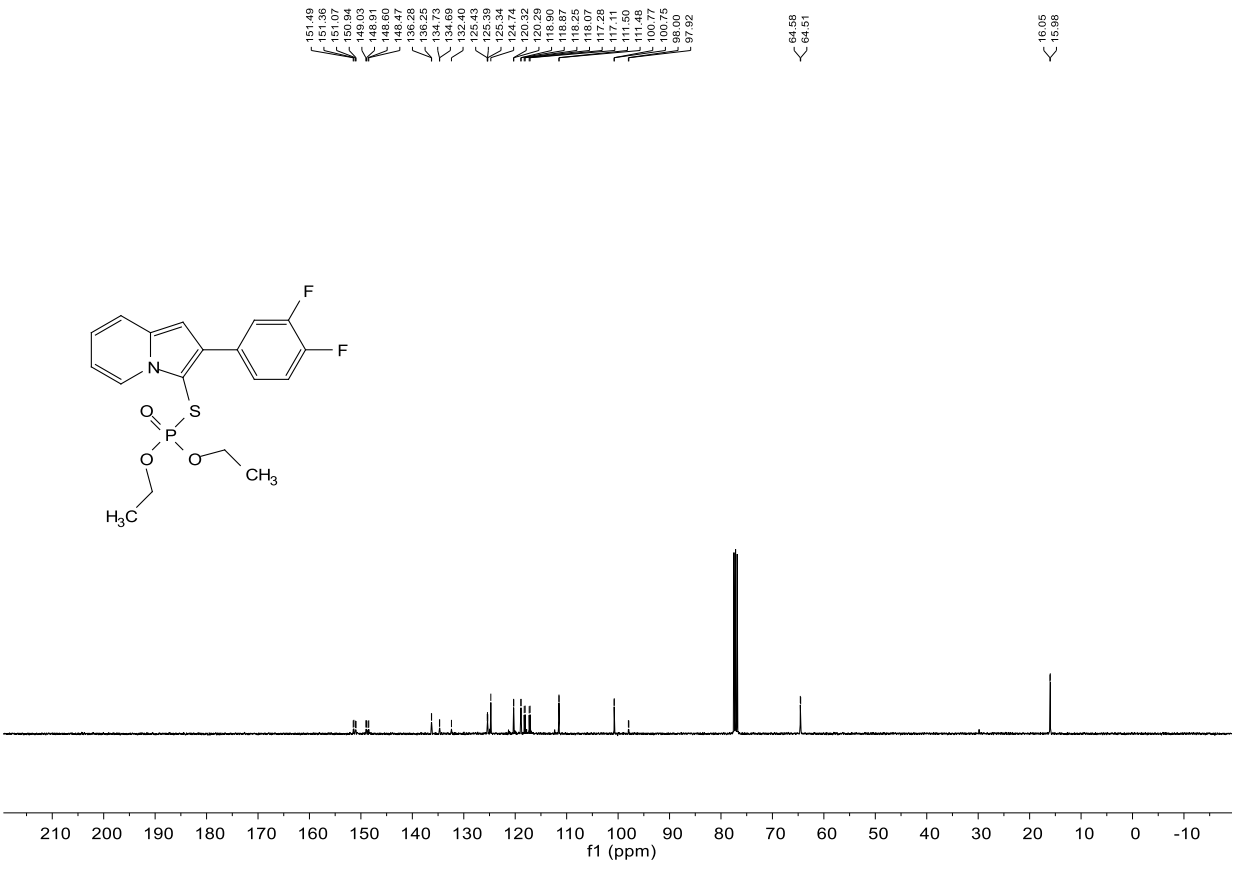


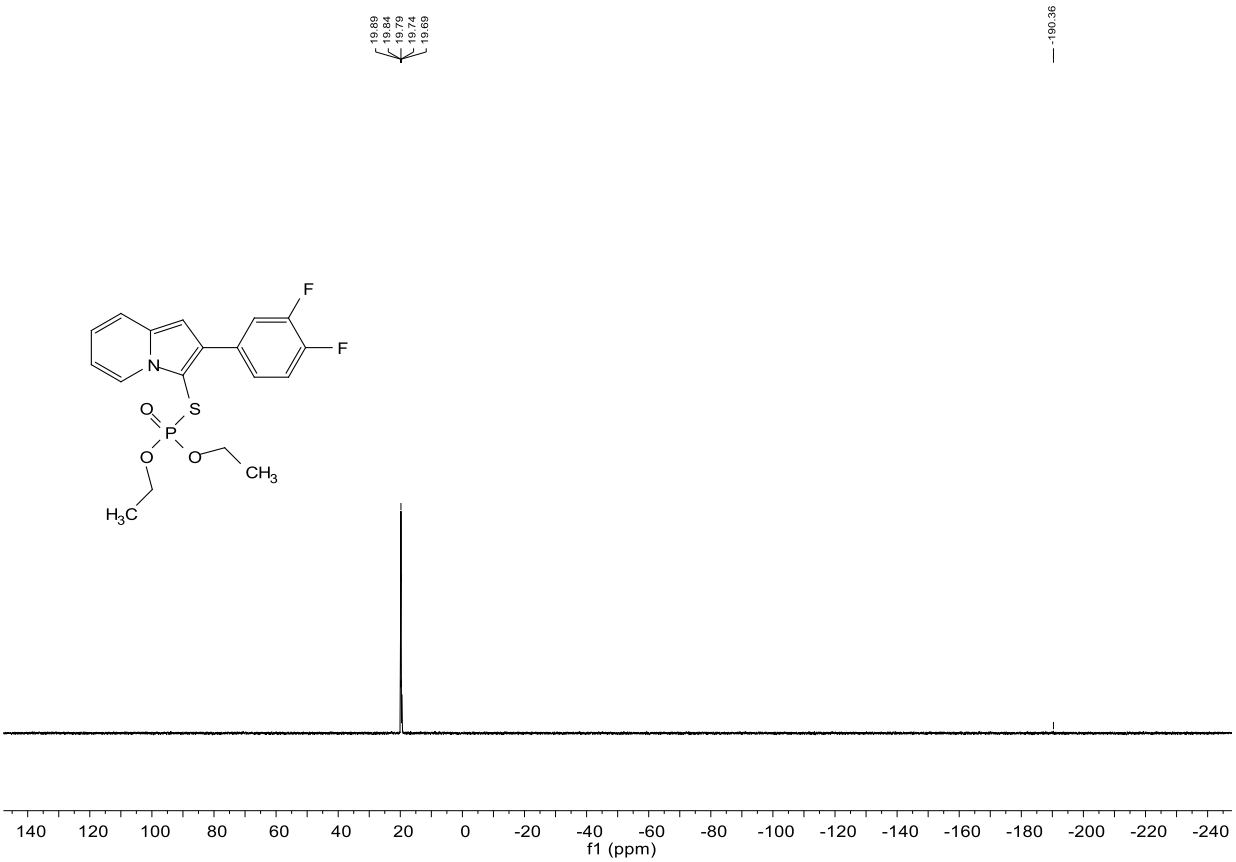

148.472
137.153
136.475
135.332
134.193
129.357
124.822
124.073
121.947
120.562
120.536
119.100
119.073
111.833
100.914
98.376
64.747
64.675
16.100
16.033
N
S
O
P
O
O
O
CH3
H3C
N+ O-
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


19.814
19.761
19.708
19.656
19.603
N
S
O
P
O
O
O
CH3
H3C
N+ O-
O
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

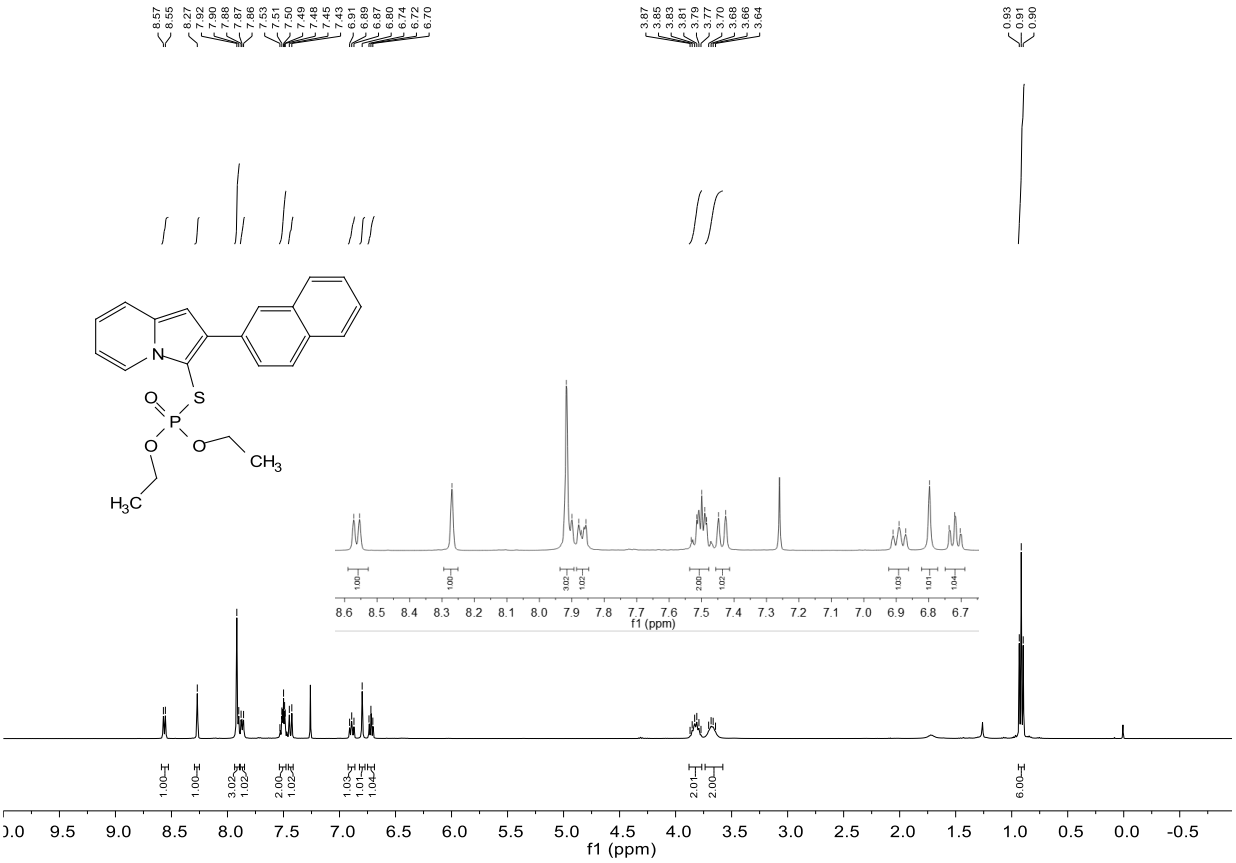
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3p**

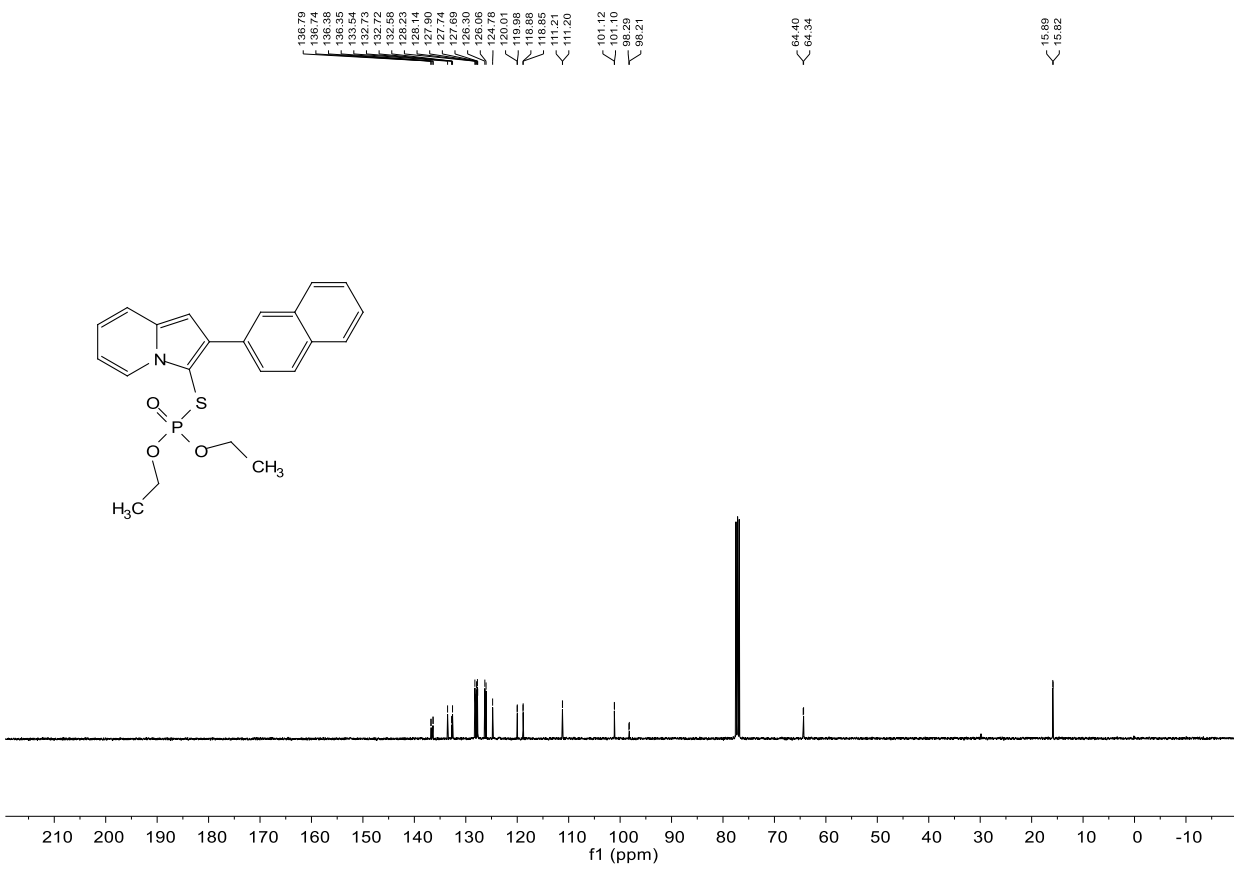






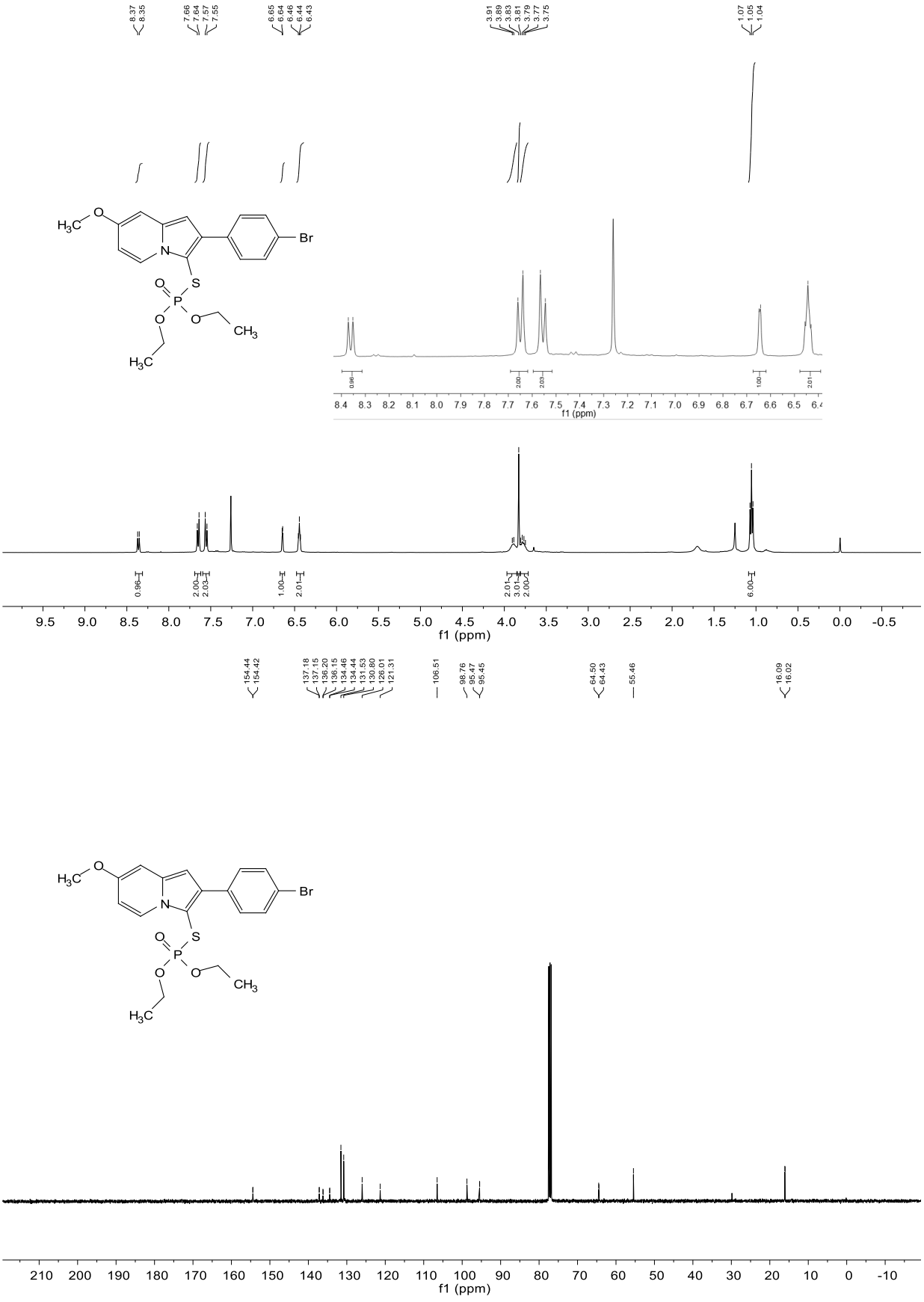
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3q**

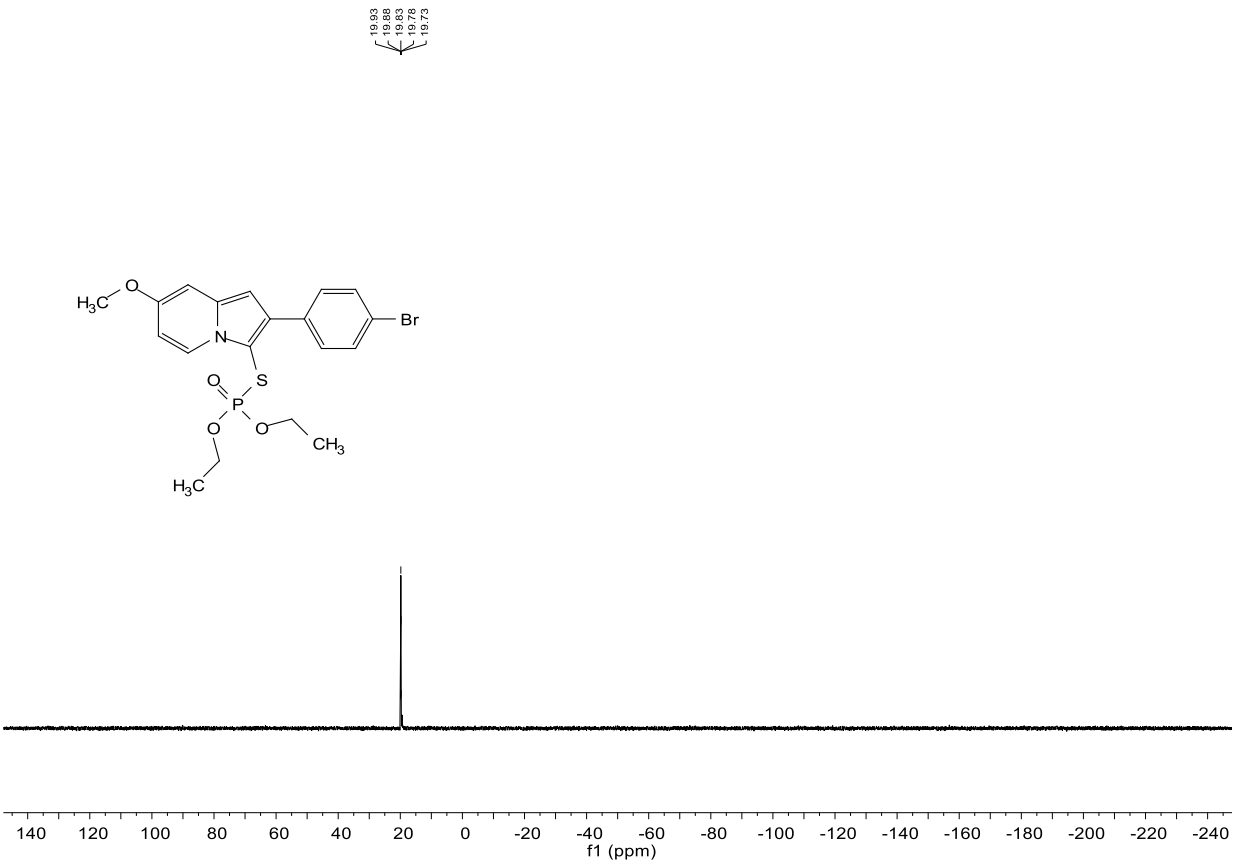



136.79
136.74
136.68
136.35
133.54
132.73
132.72
132.58
128.23
128.14
127.90
127.74
127.69
126.30
126.06
124.78
120.01
119.98
118.88
118.85
111.21
111.20
101.12
101.10
98.29
98.21
64.40
64.34
15.89
15.82
O
S
P
O
O
CH3
H3C
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

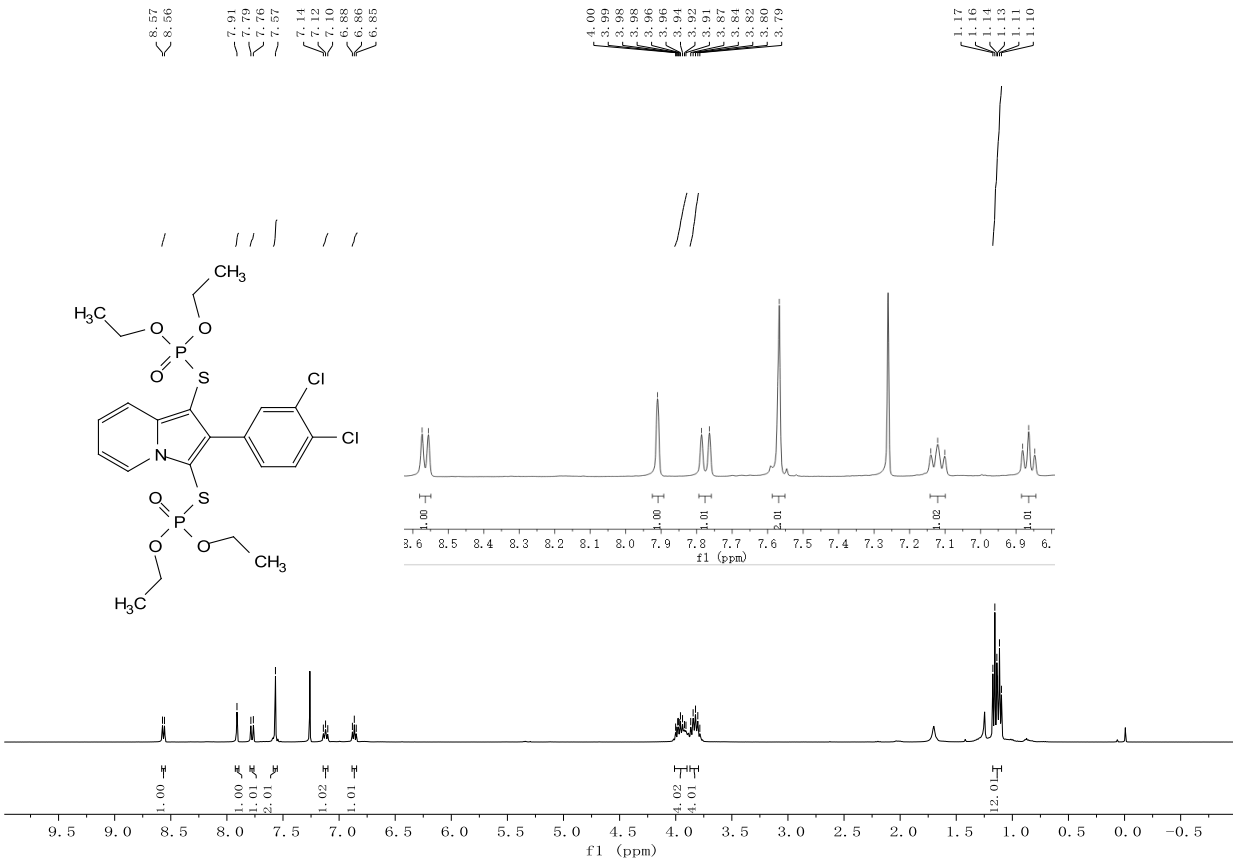

19.91
19.86
19.81
19.76
19.71
O
S
P
O
O
CH3
H3C
N
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

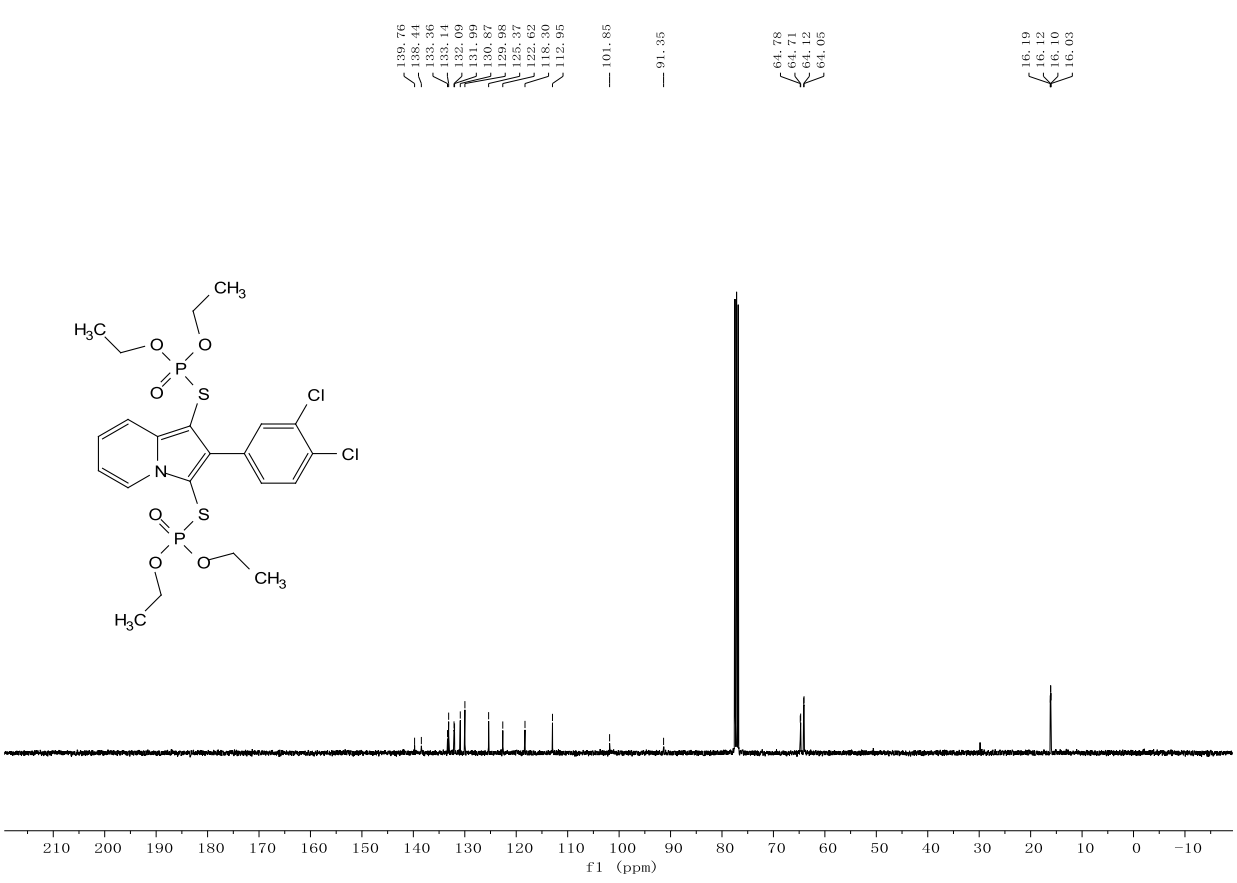
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3r**

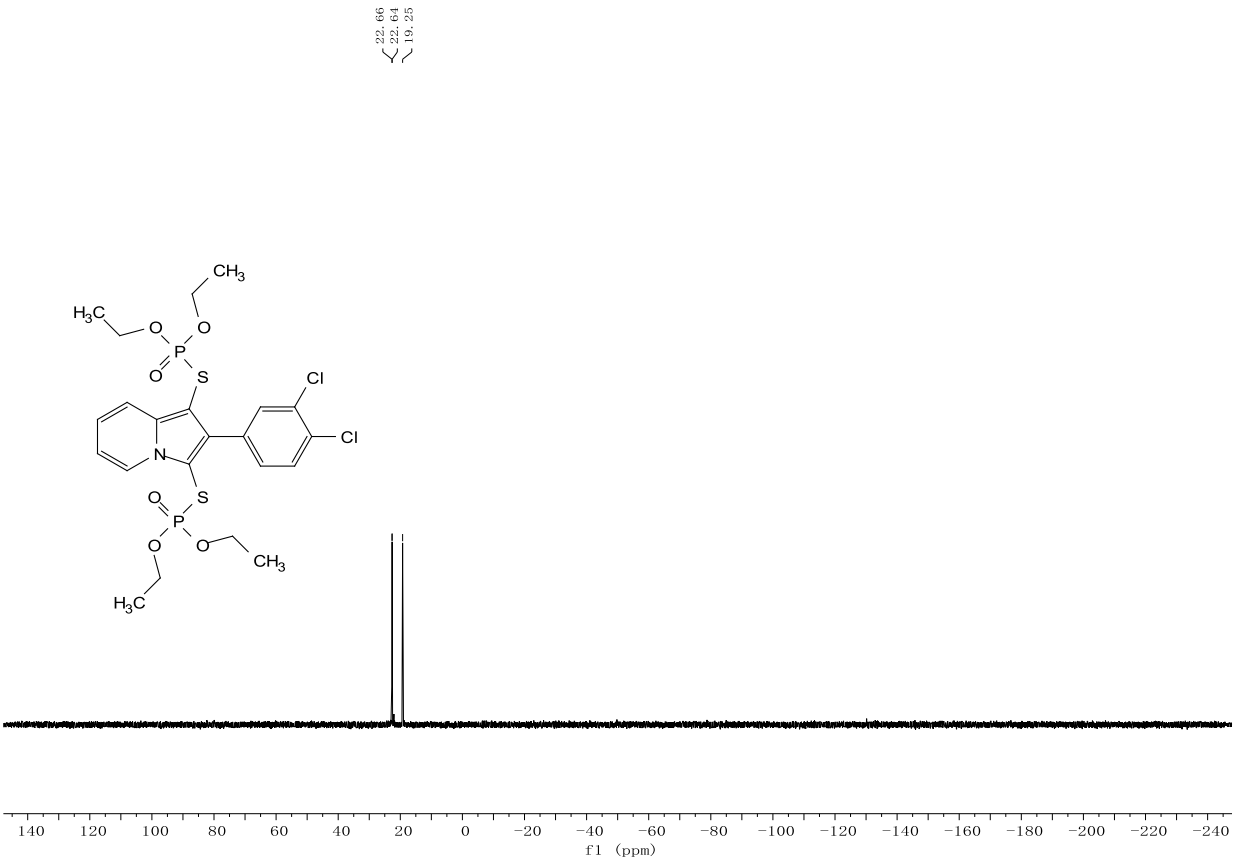




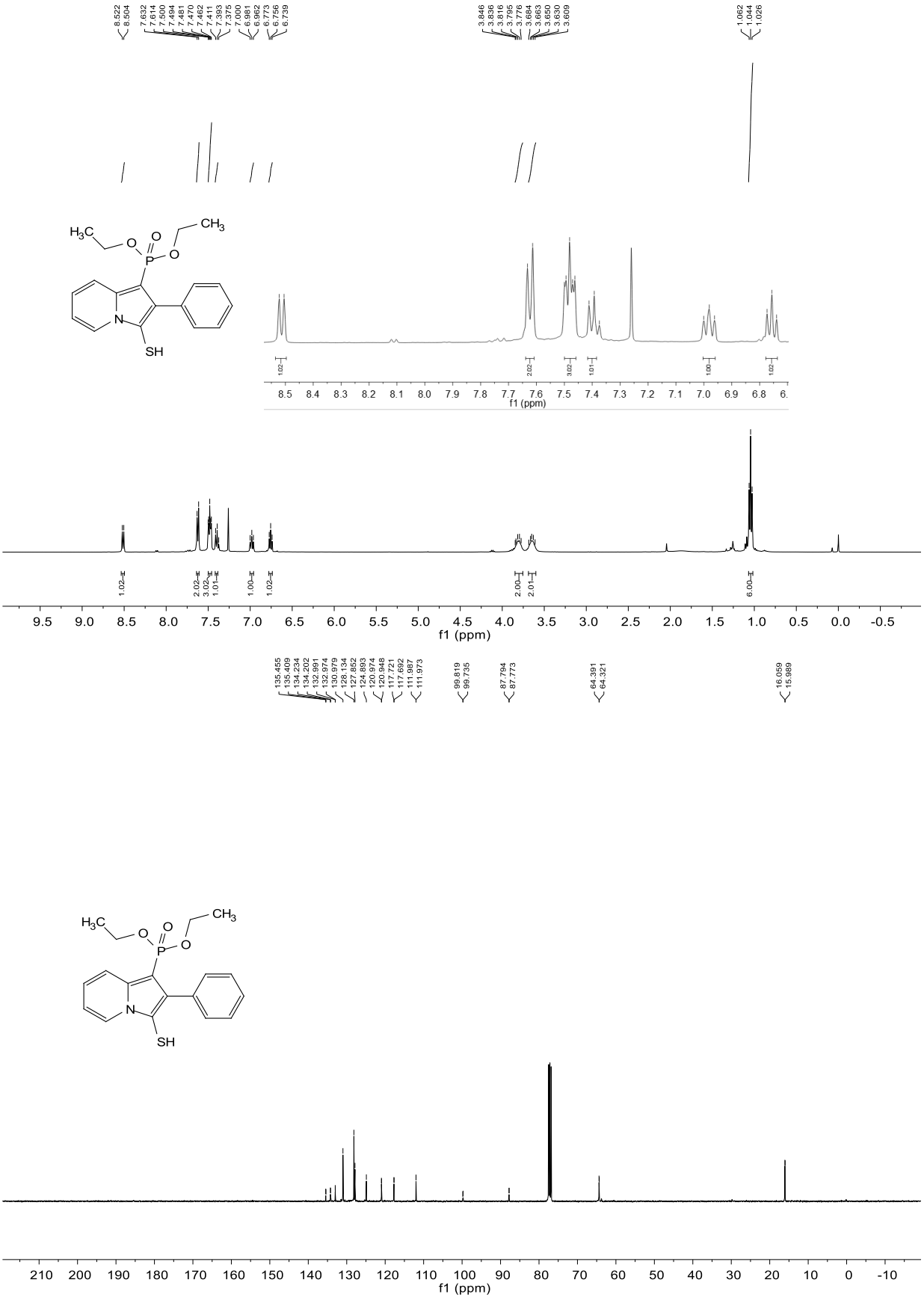
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **3s**



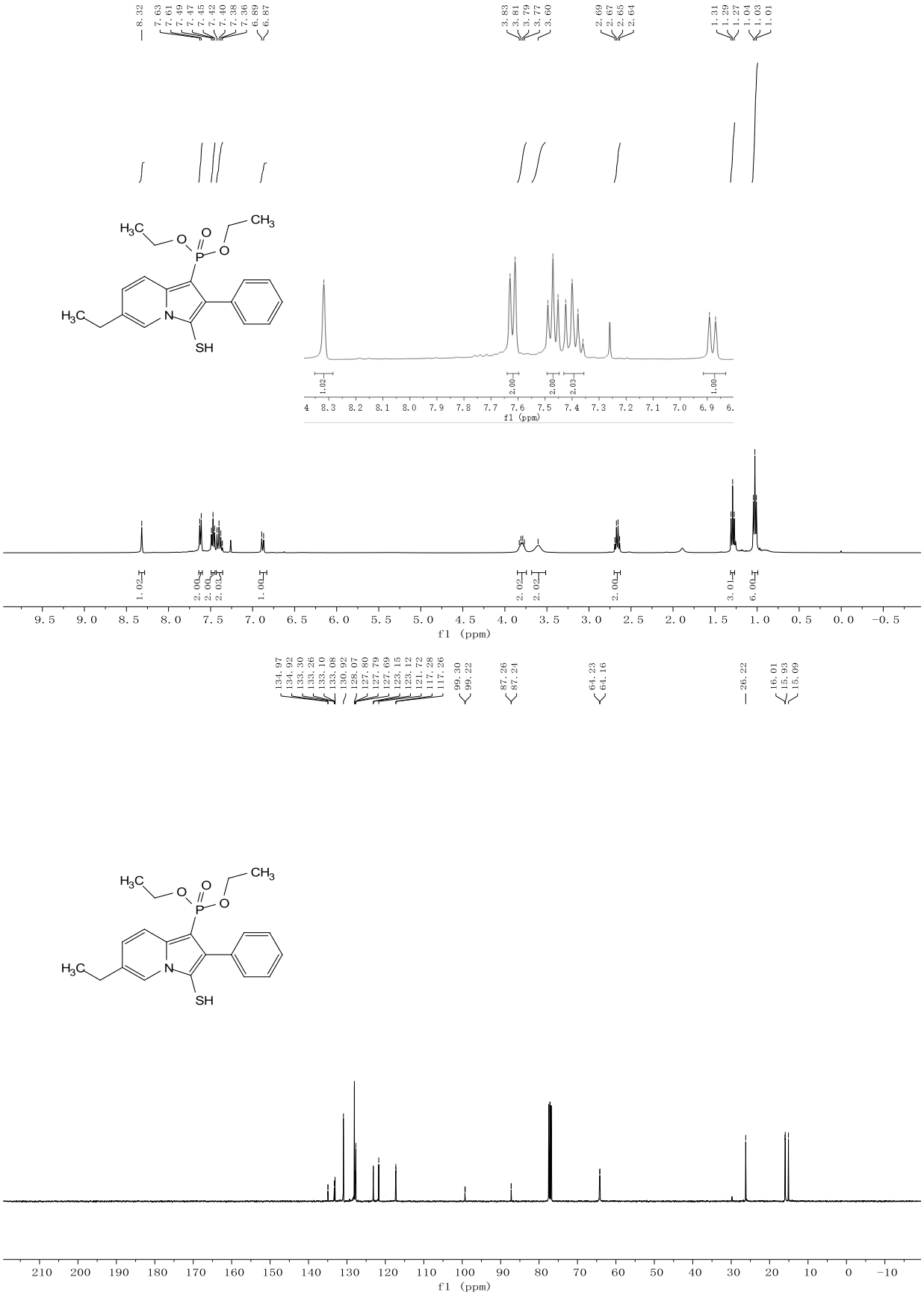

139.76
138.44
133.36
133.14
132.09
131.99
130.87
129.98
125.37
122.62
118.30
112.95
101.85
91.35
64.78
64.71
64.12
64.05
16.19
16.12
16.10
16.03
CH3
H3C
O
O
P
O
S
Cl
Cl
N
S
O
P
O
O
CH3
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

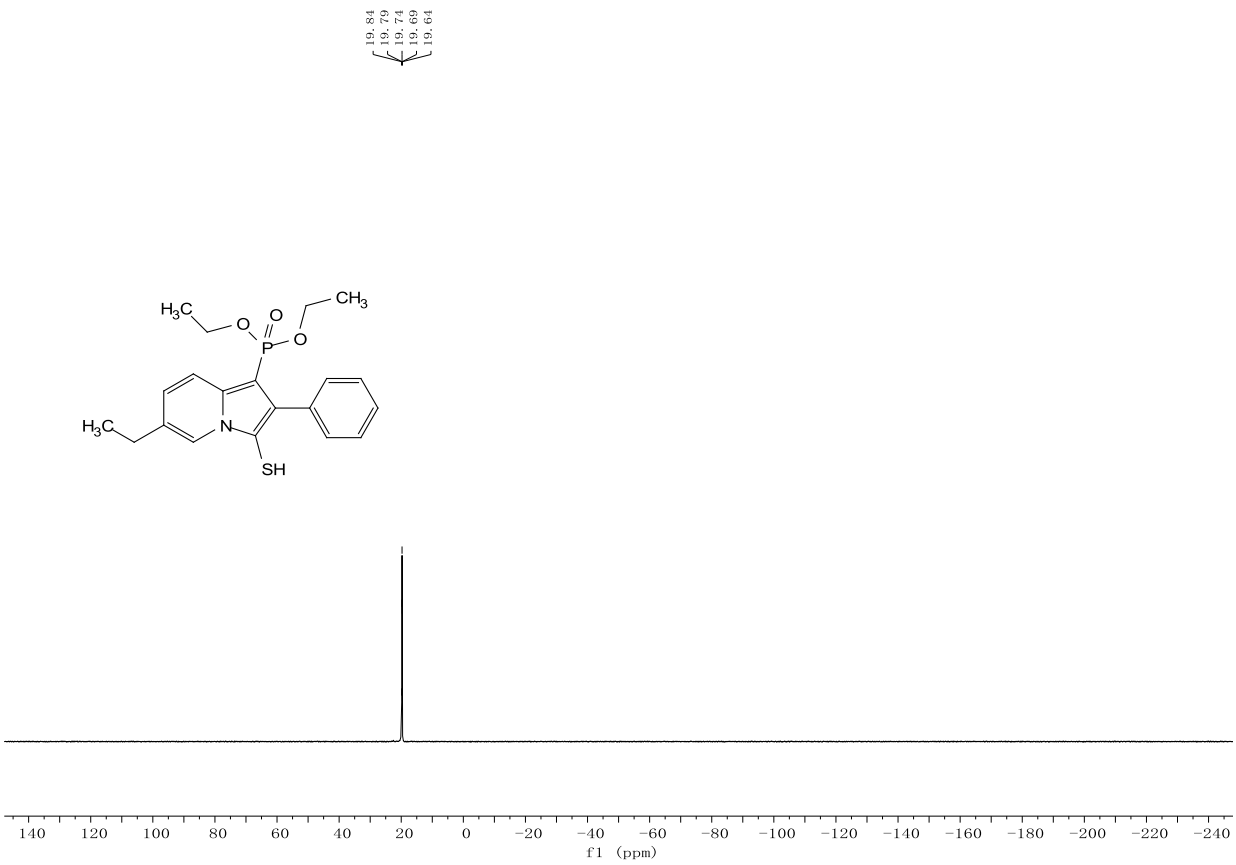

22.66
22.64
19.25
CH3
H3C
O
O
P
O
S
Cl
Cl
N
S
O
P
O
O
CH3
H3C
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4a**

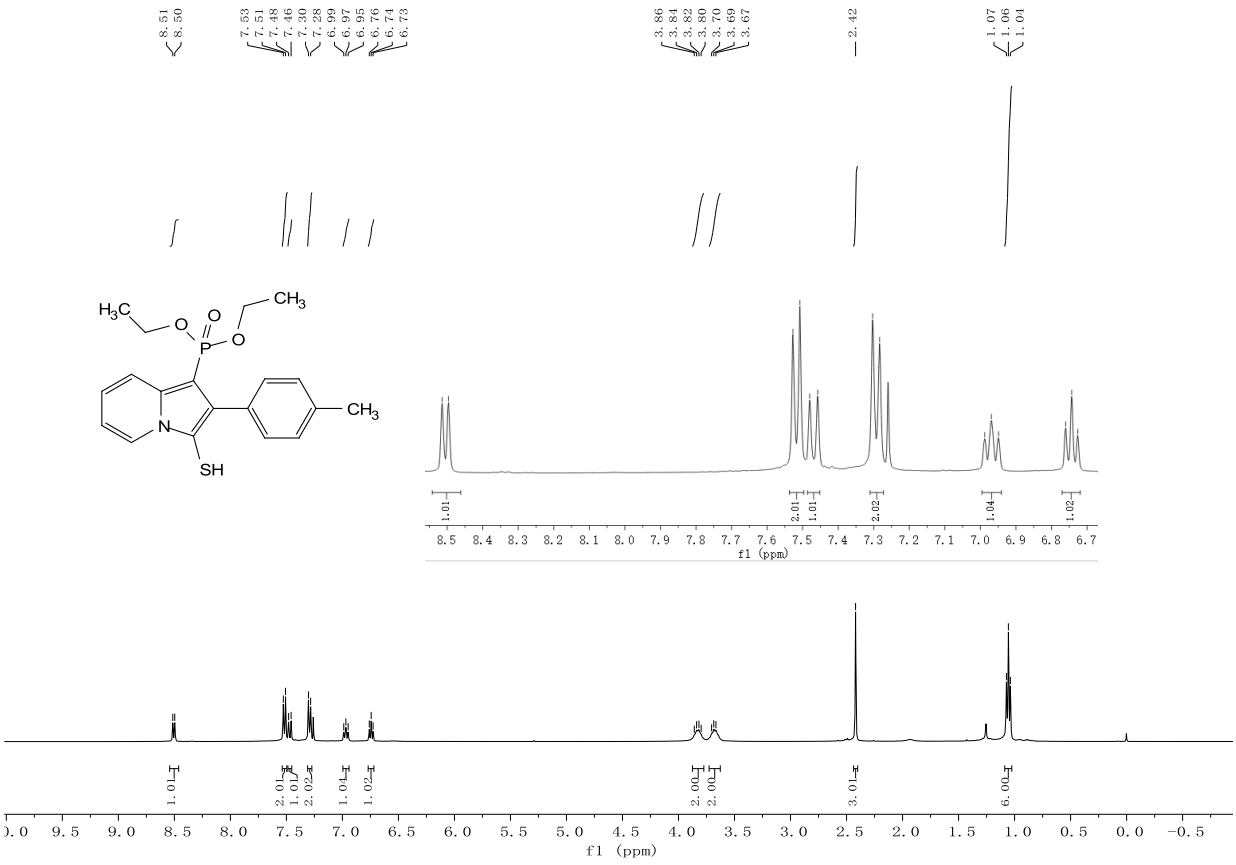


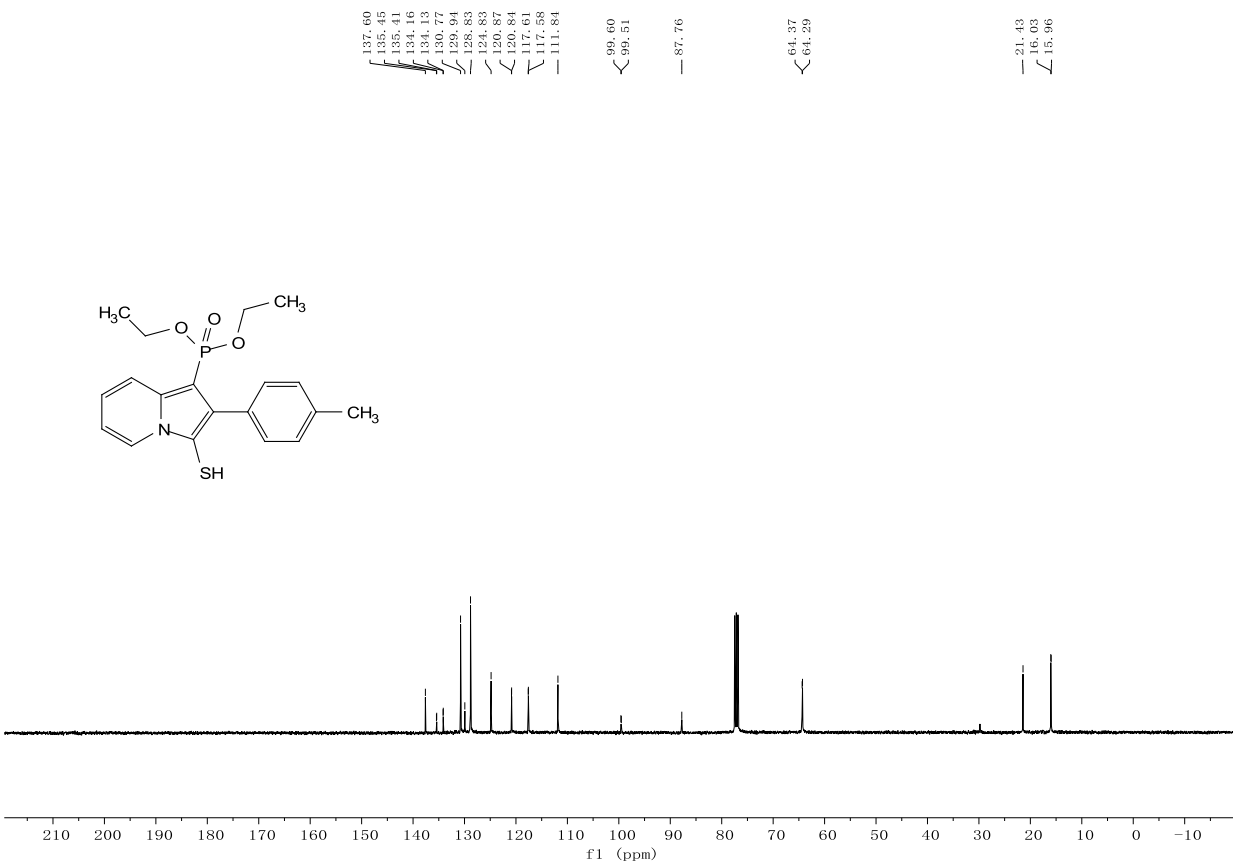
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **4b**

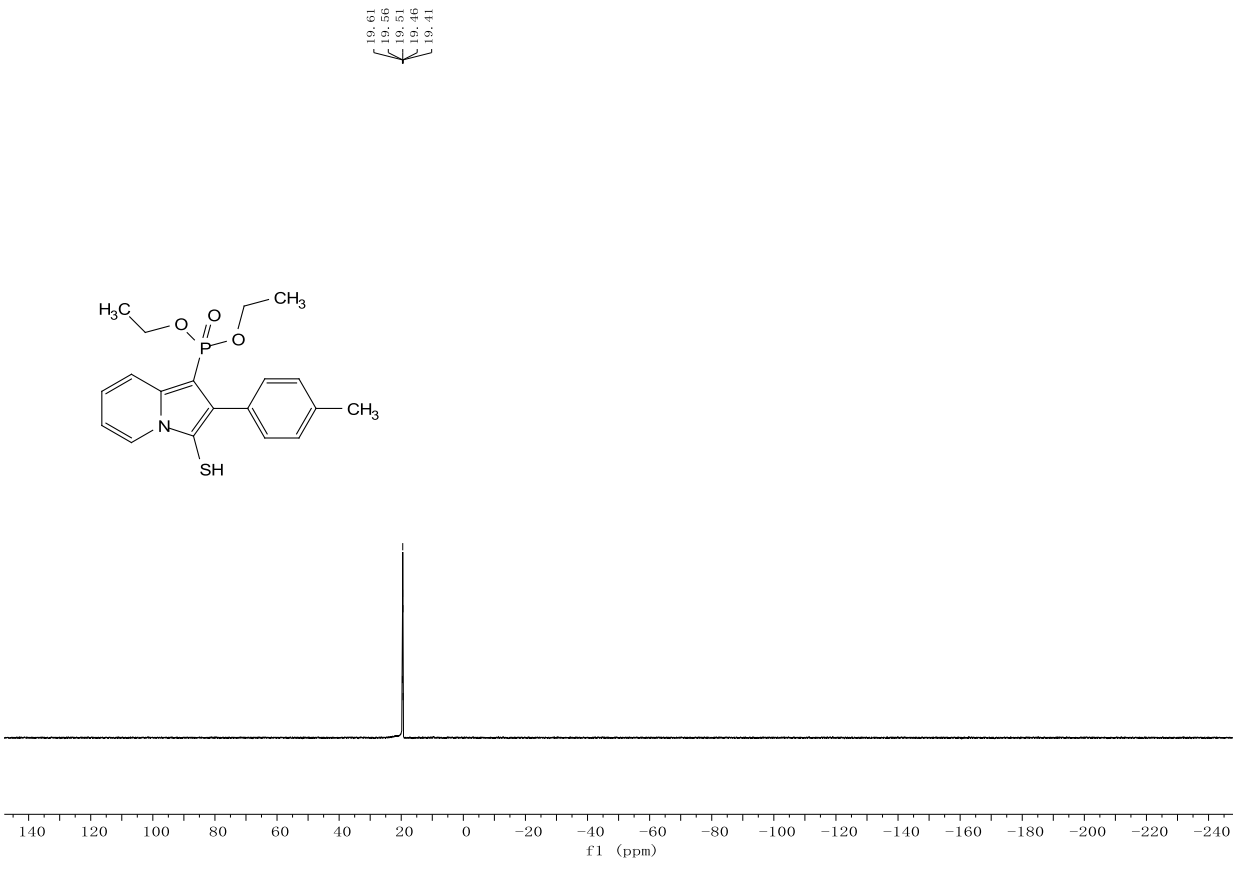




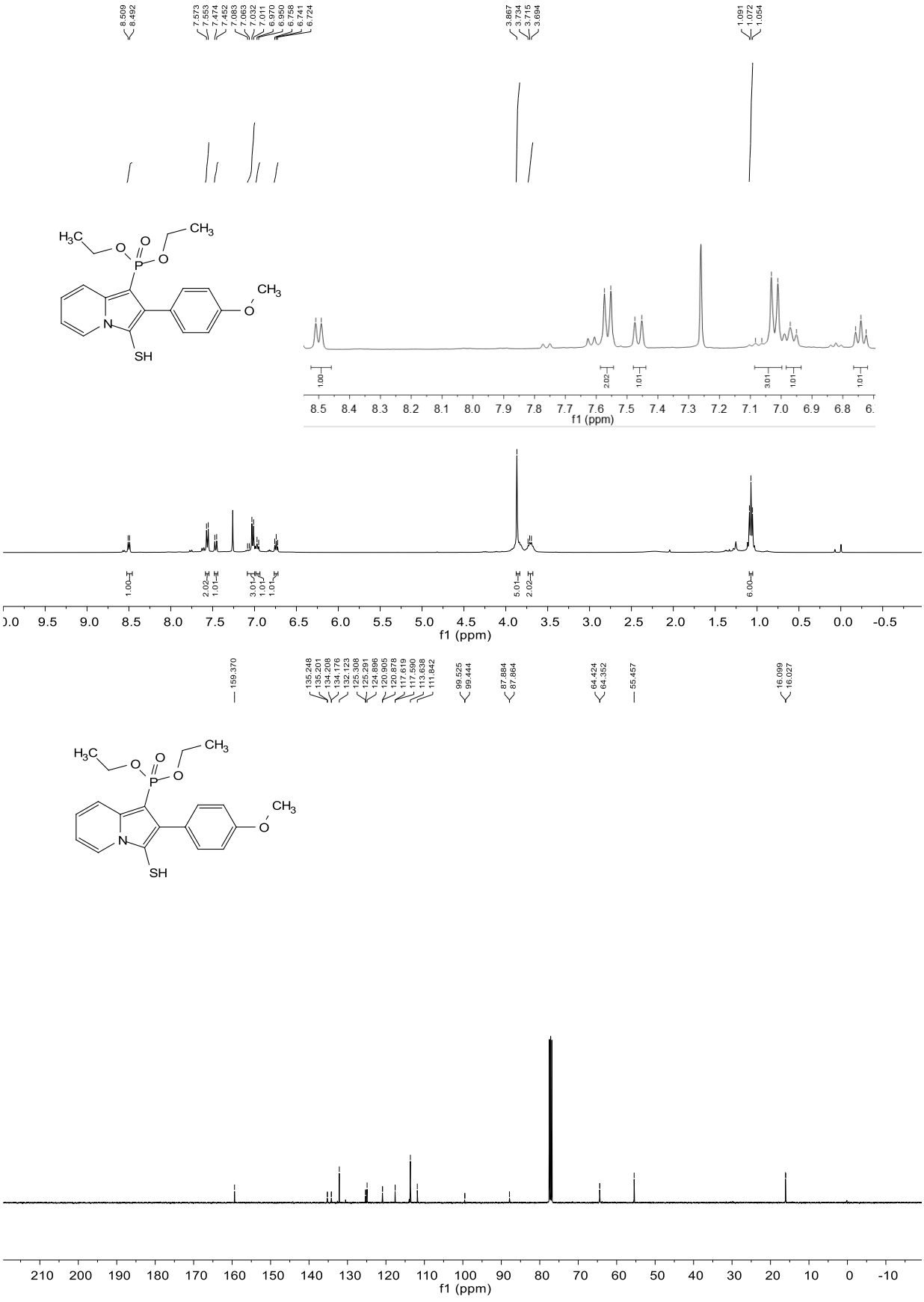
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **4c**



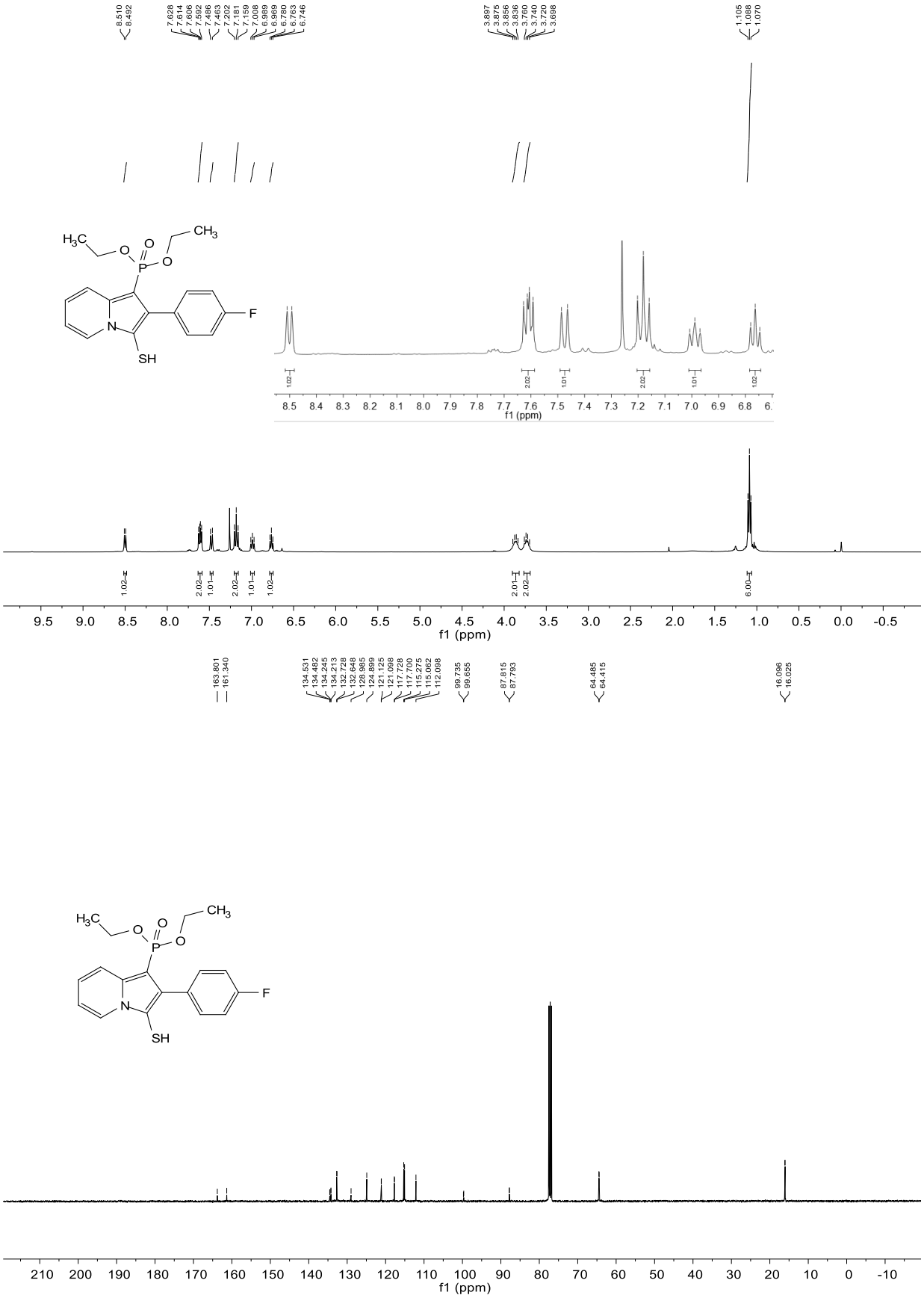

137.60
135.45
135.41
134.16
134.13
130.77
129.94
128.83
124.83
120.87
120.84
117.61
117.58
111.84
99.60
99.51
87.76
64.37
64.29
21.43
16.03
15.96
H3C
O
O
P
O
CH3
N
SH
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


19.61
19.56
19.51
19.46
19.41
H3C
O
O
P
O
CH3
N
SH
CH3
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

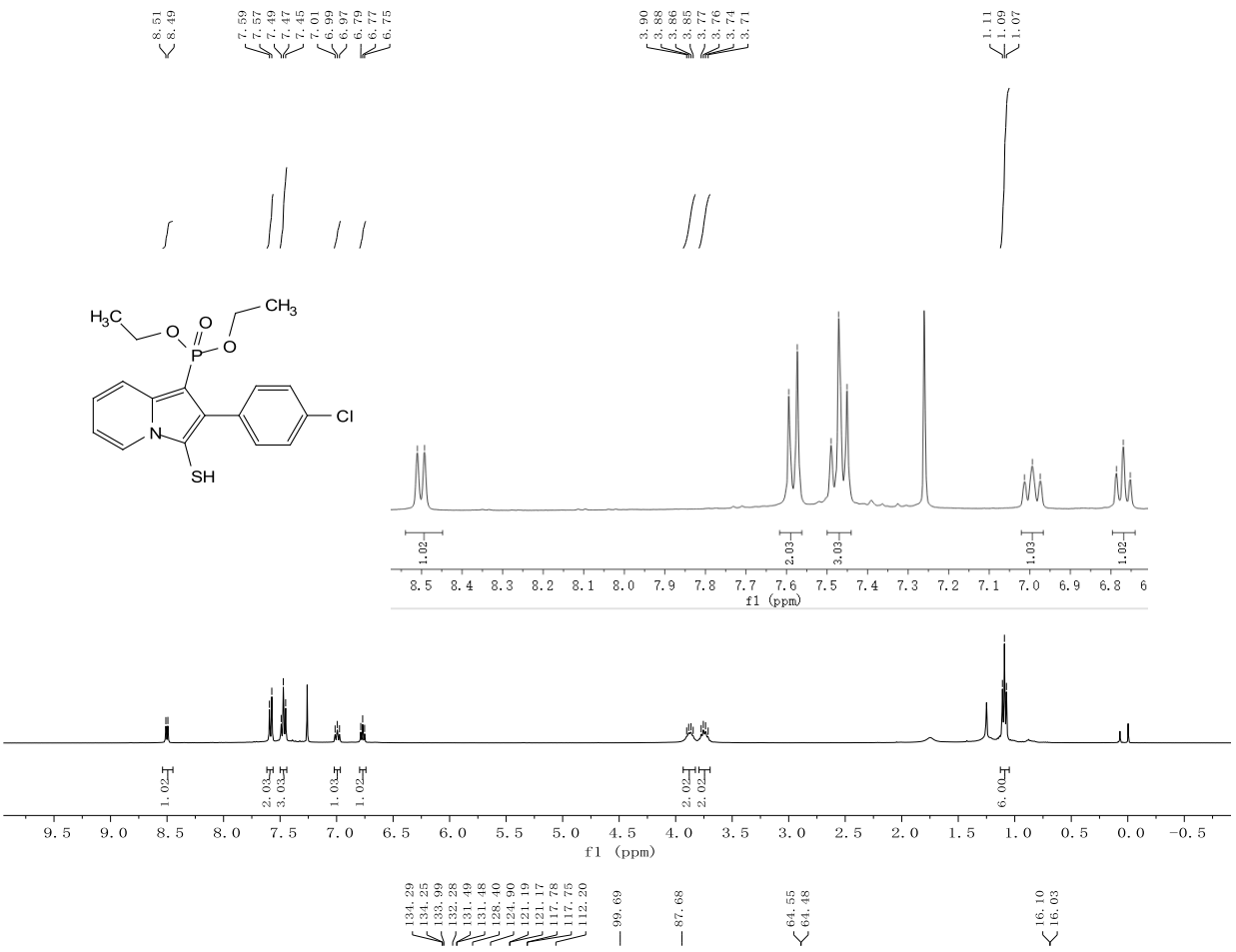
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4d**

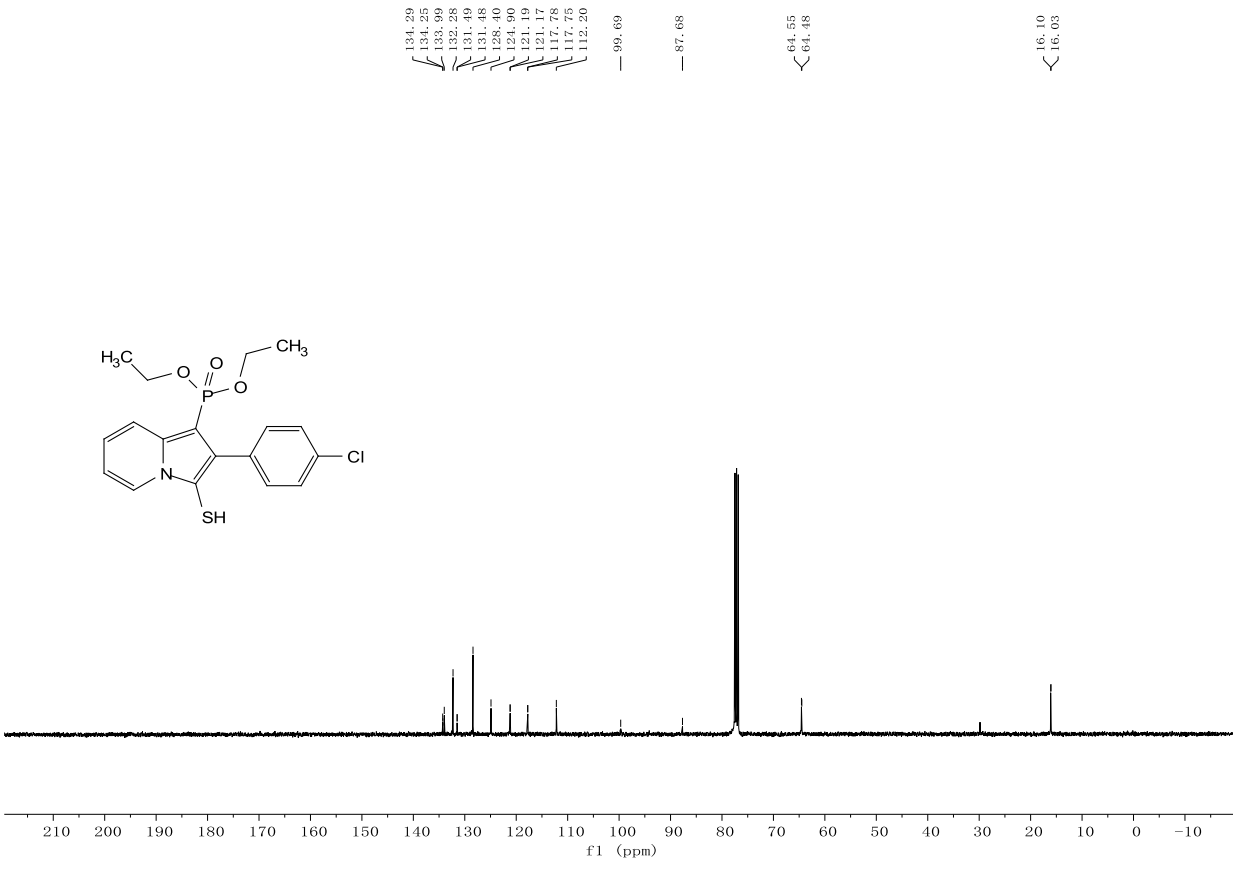


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4e**



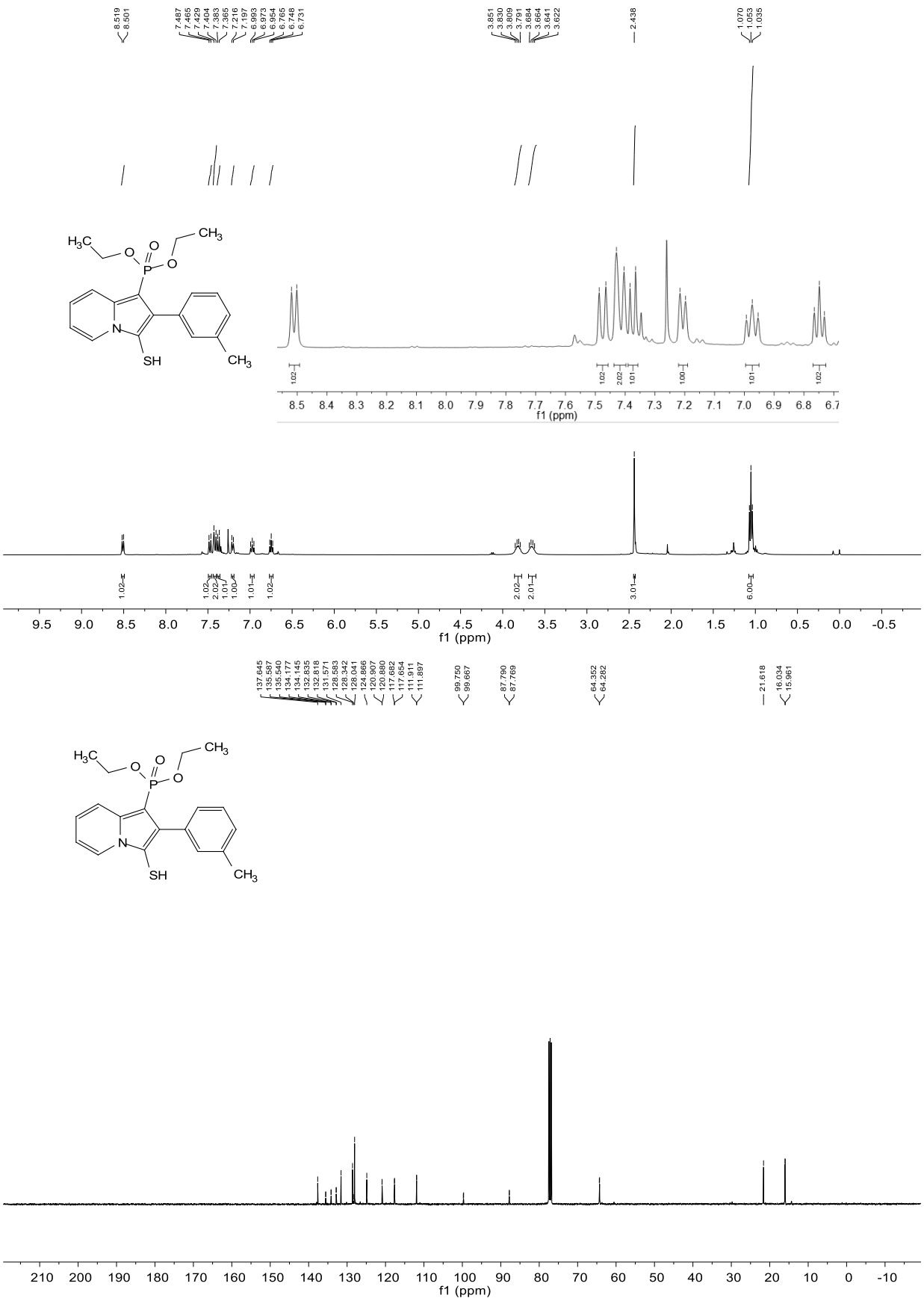
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4f**



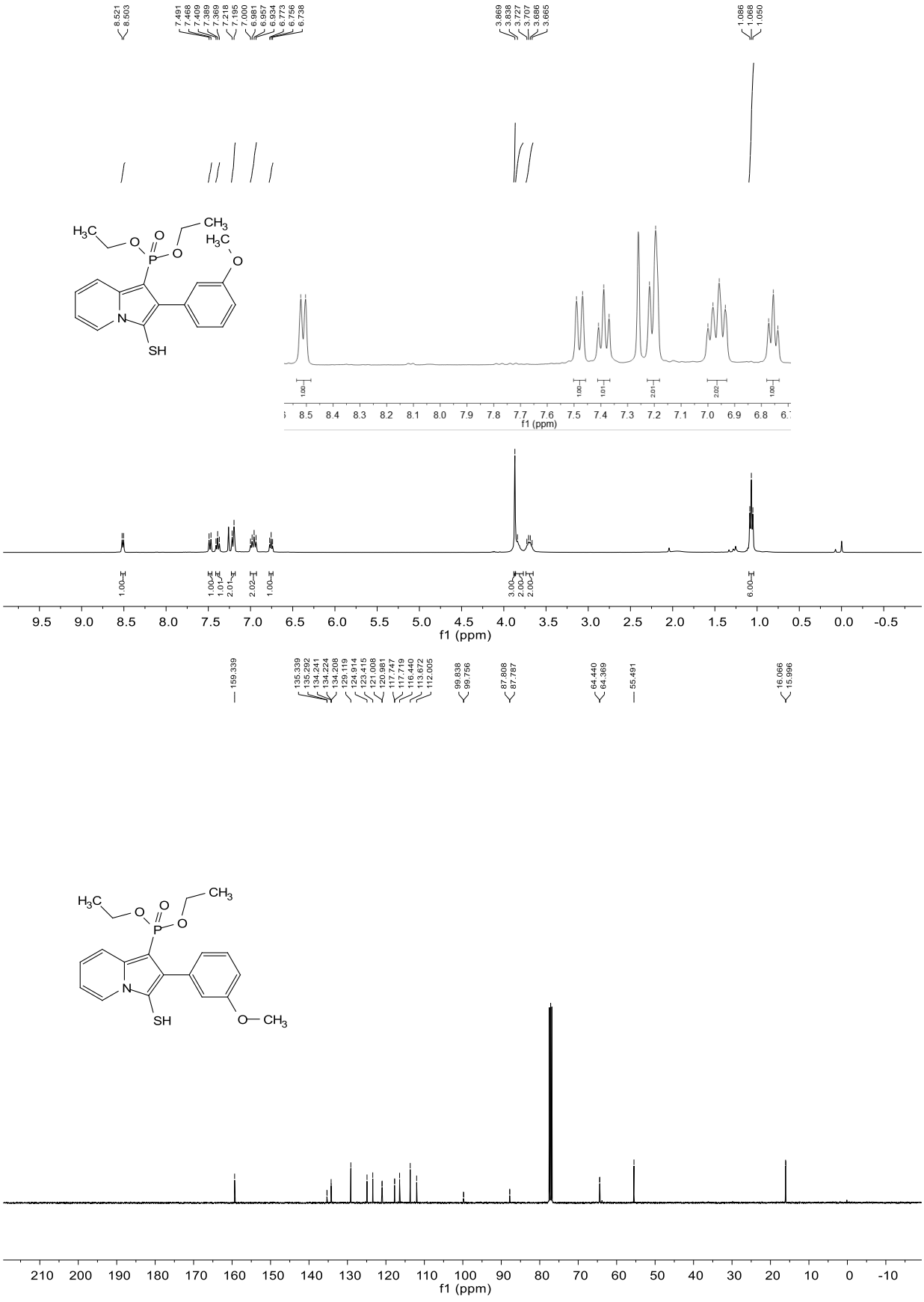


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4g**

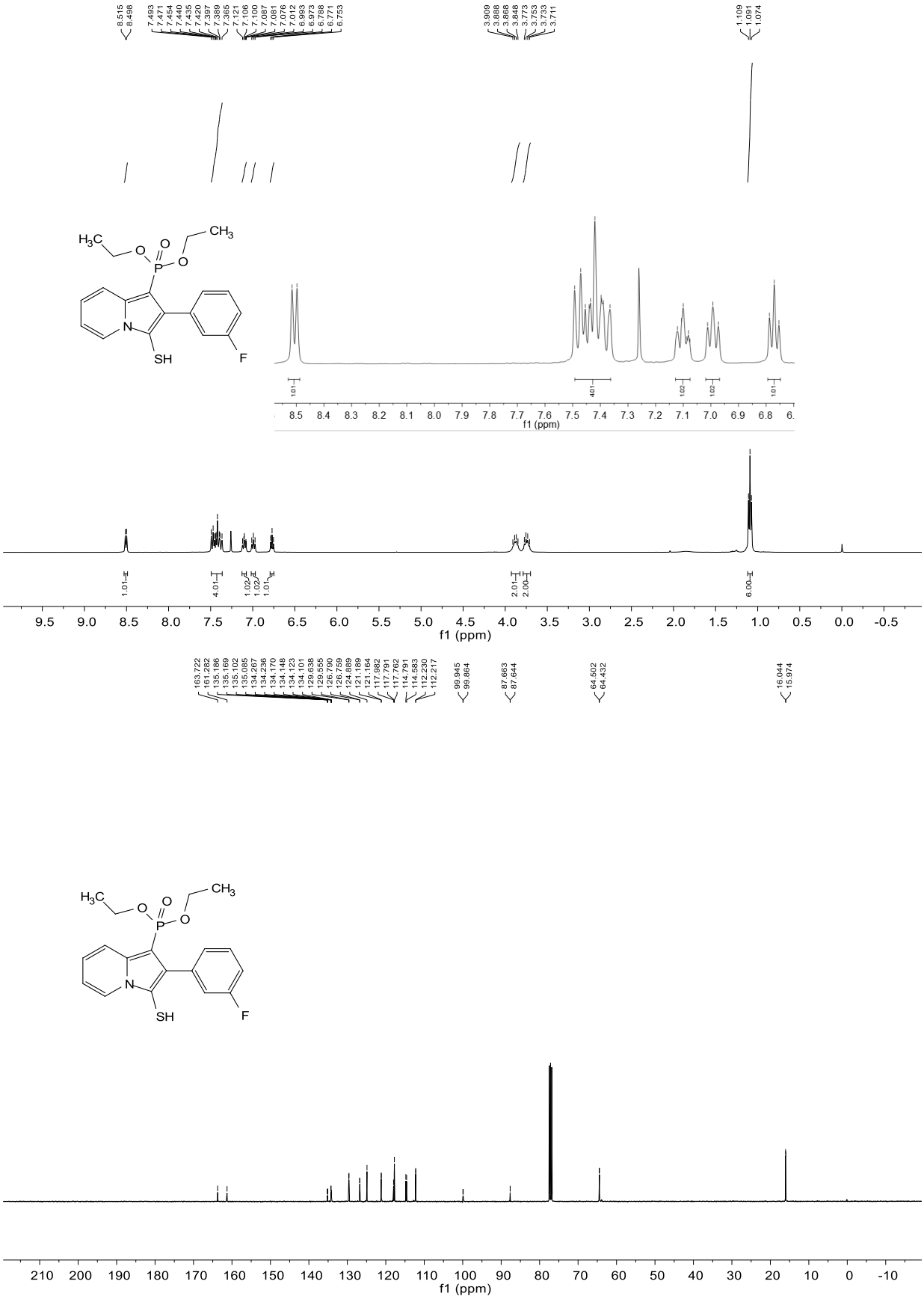
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4h**



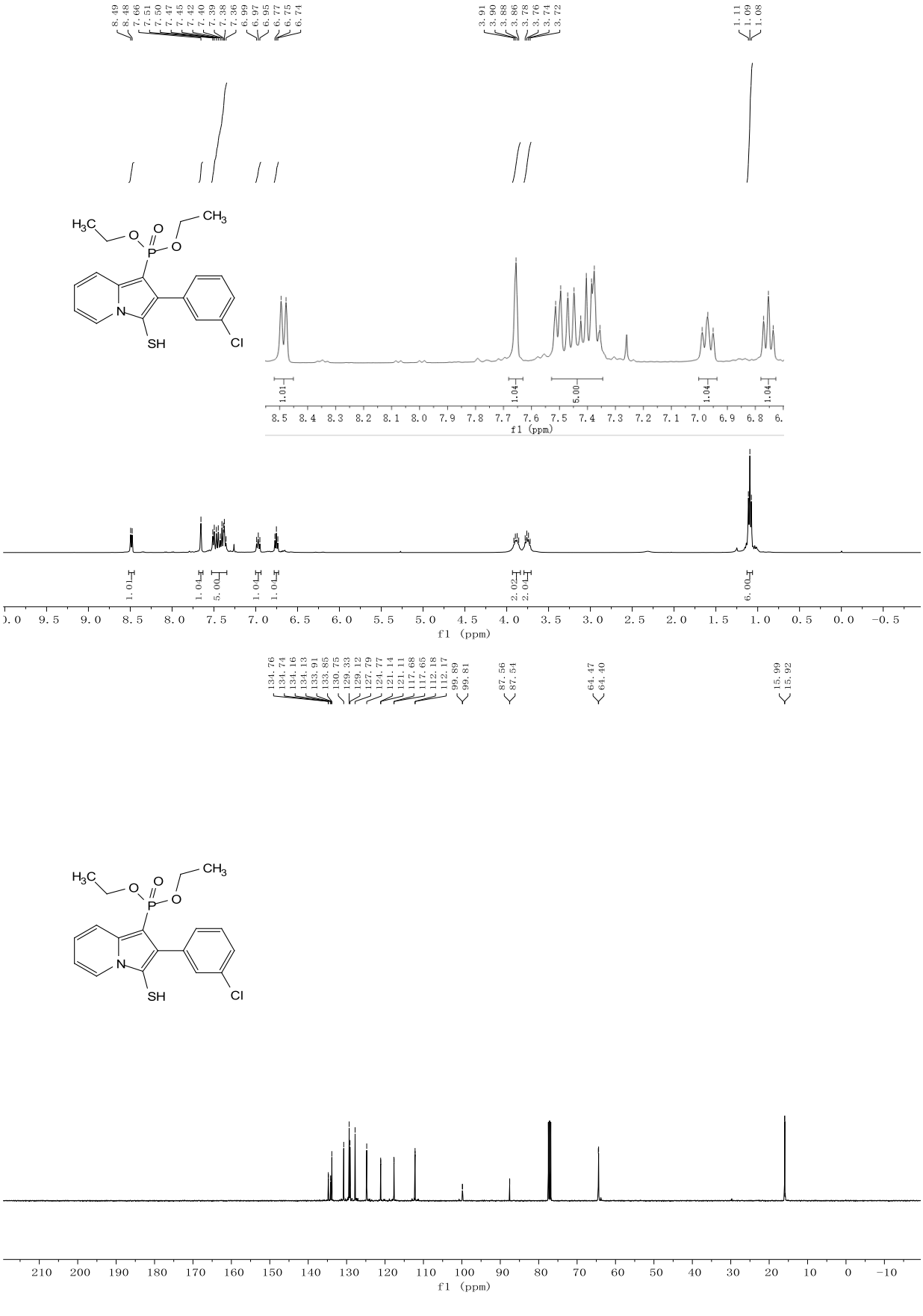
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4i**

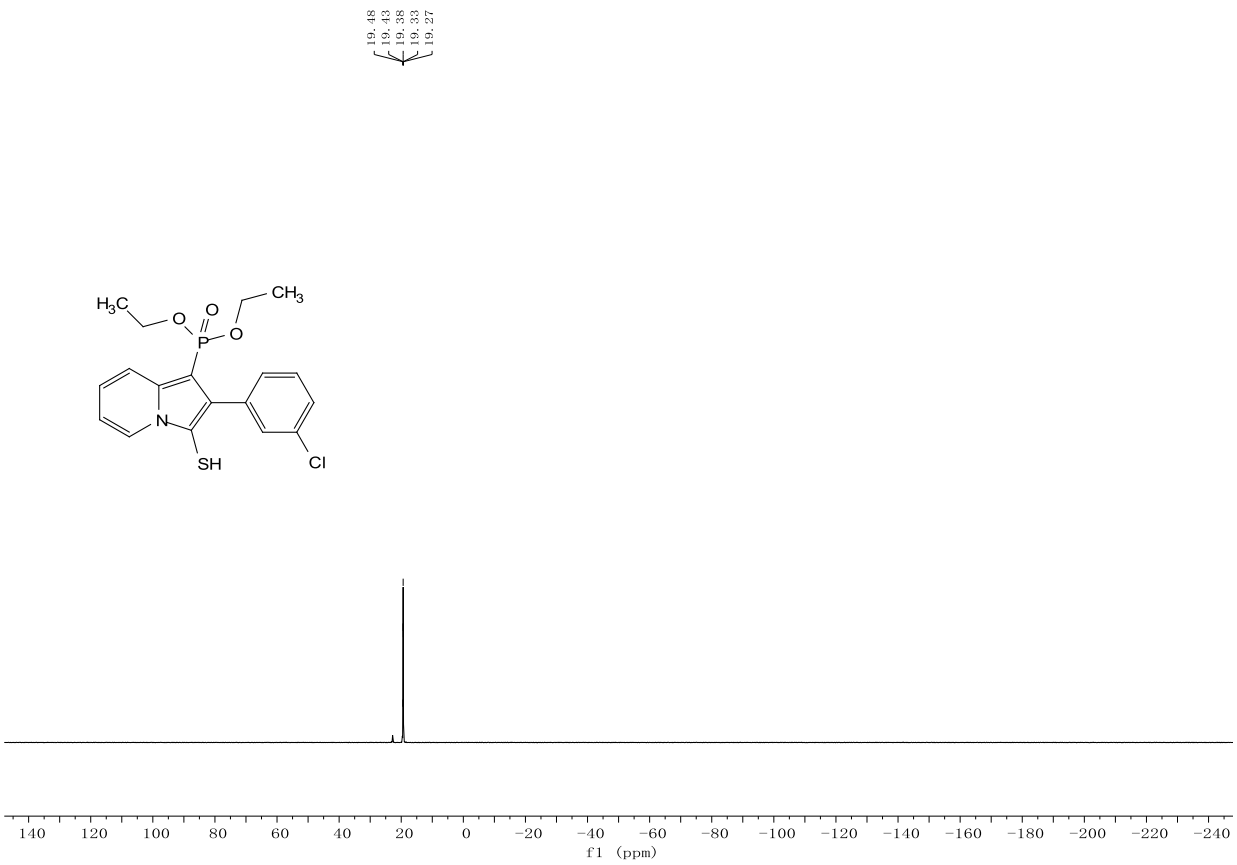


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4j**

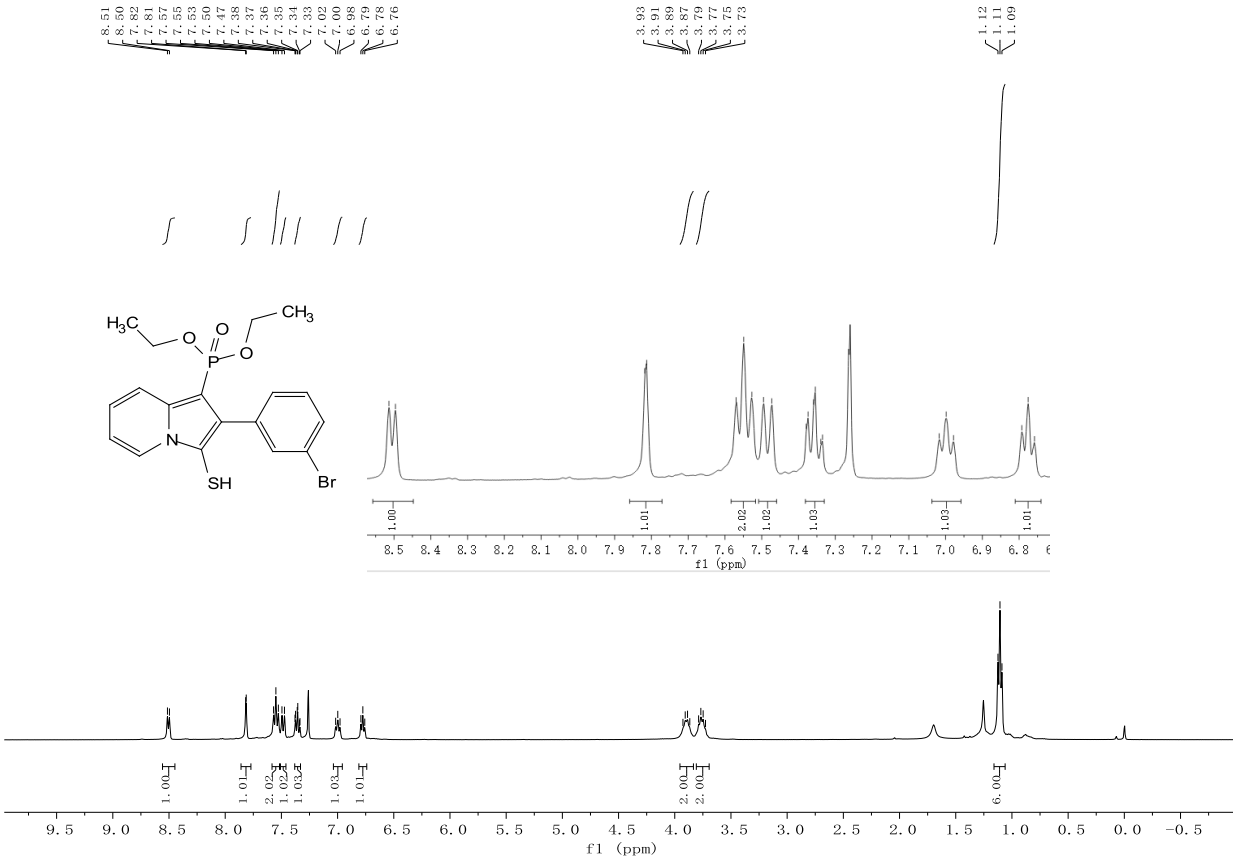


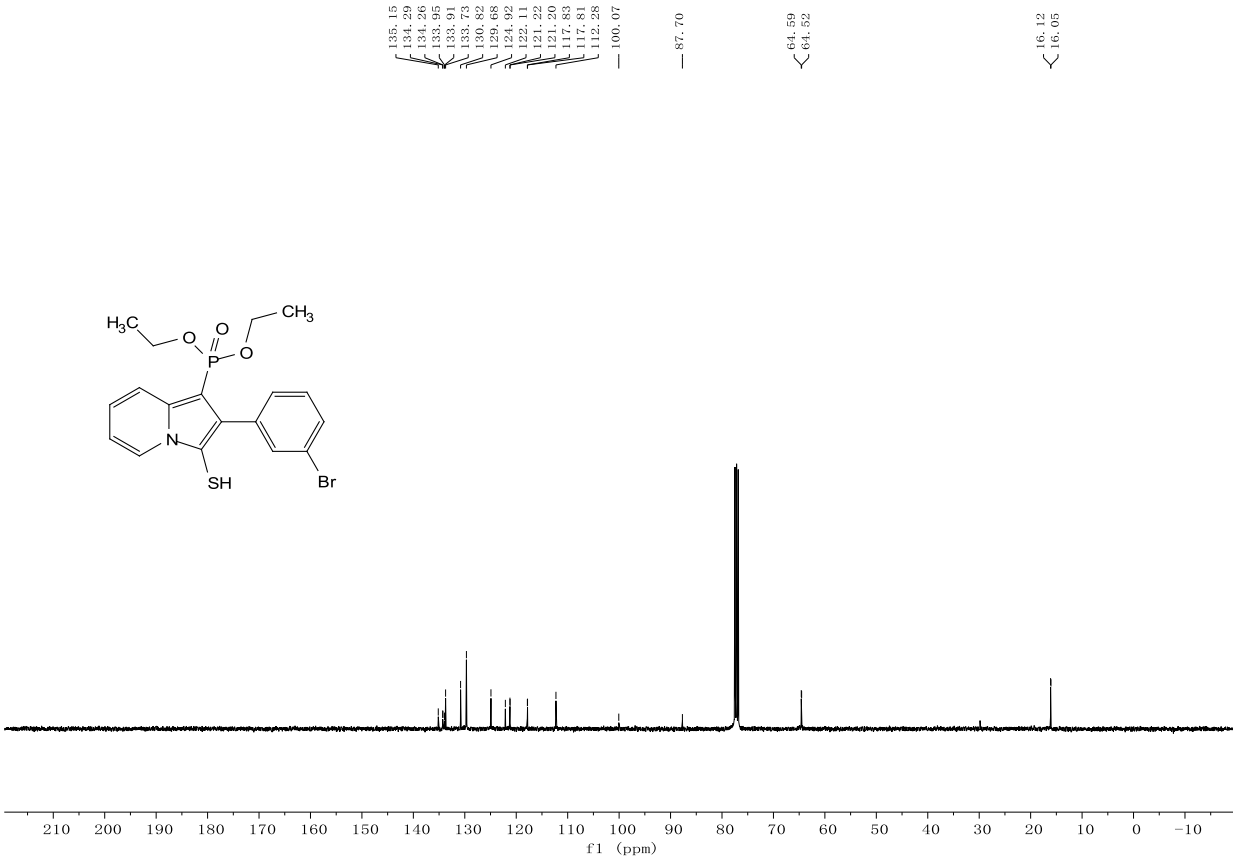
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **4k**



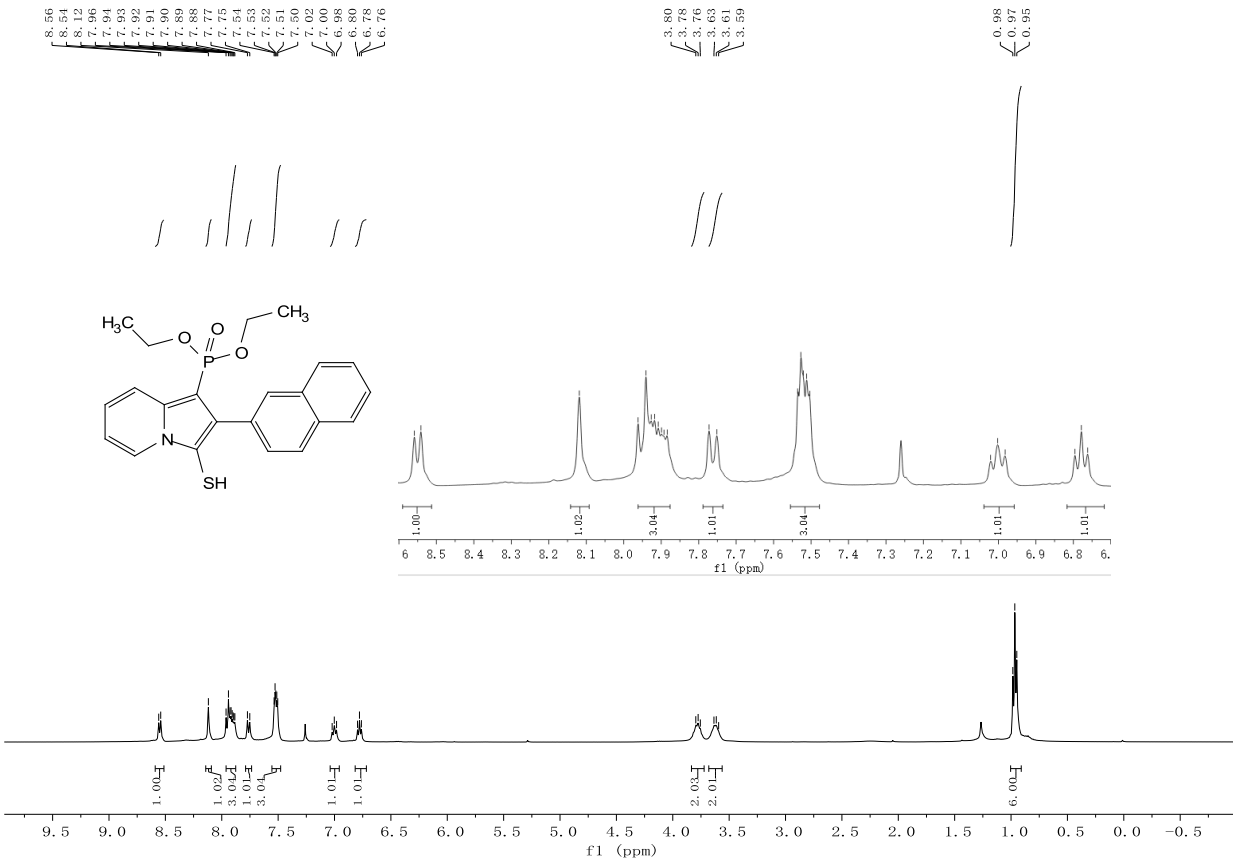


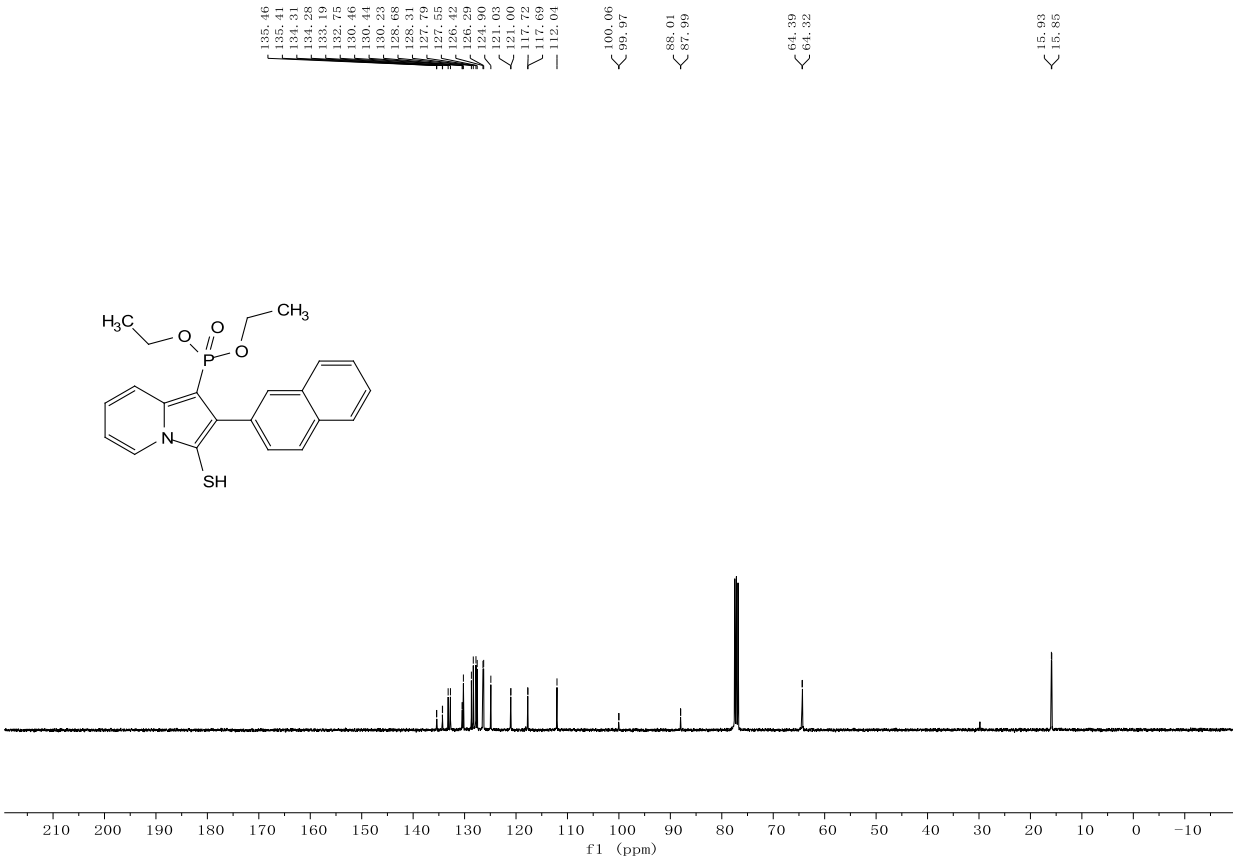
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4l**

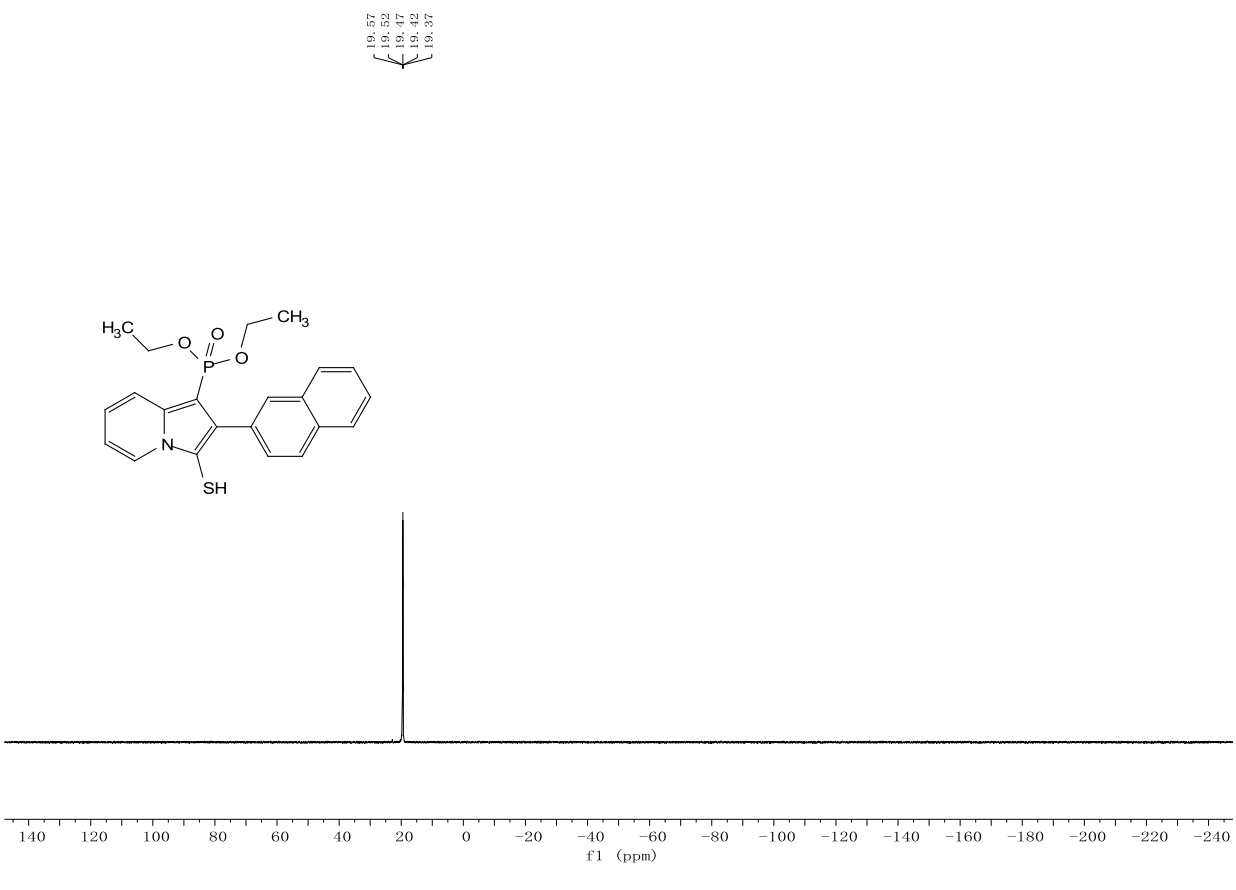




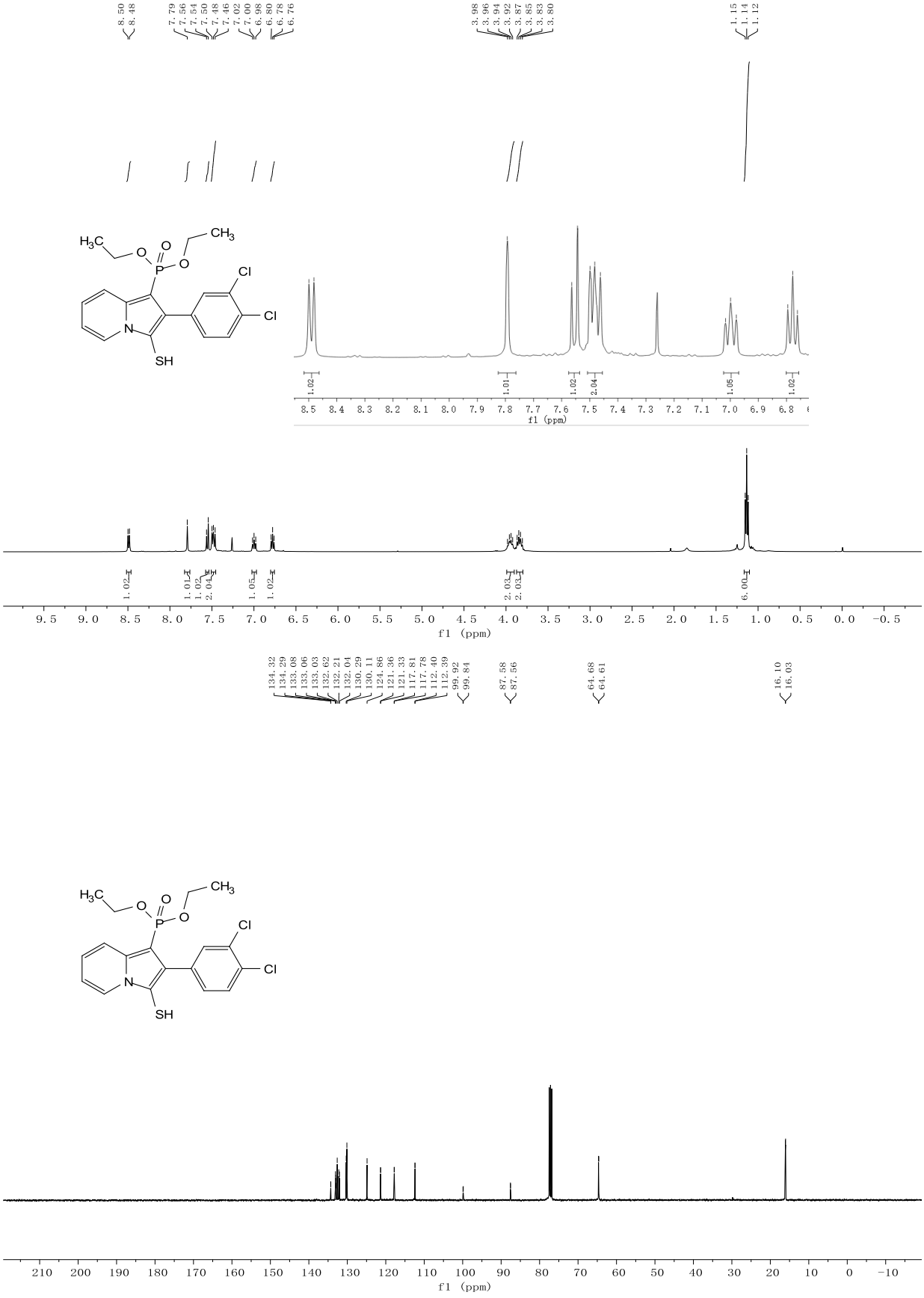
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **4m**



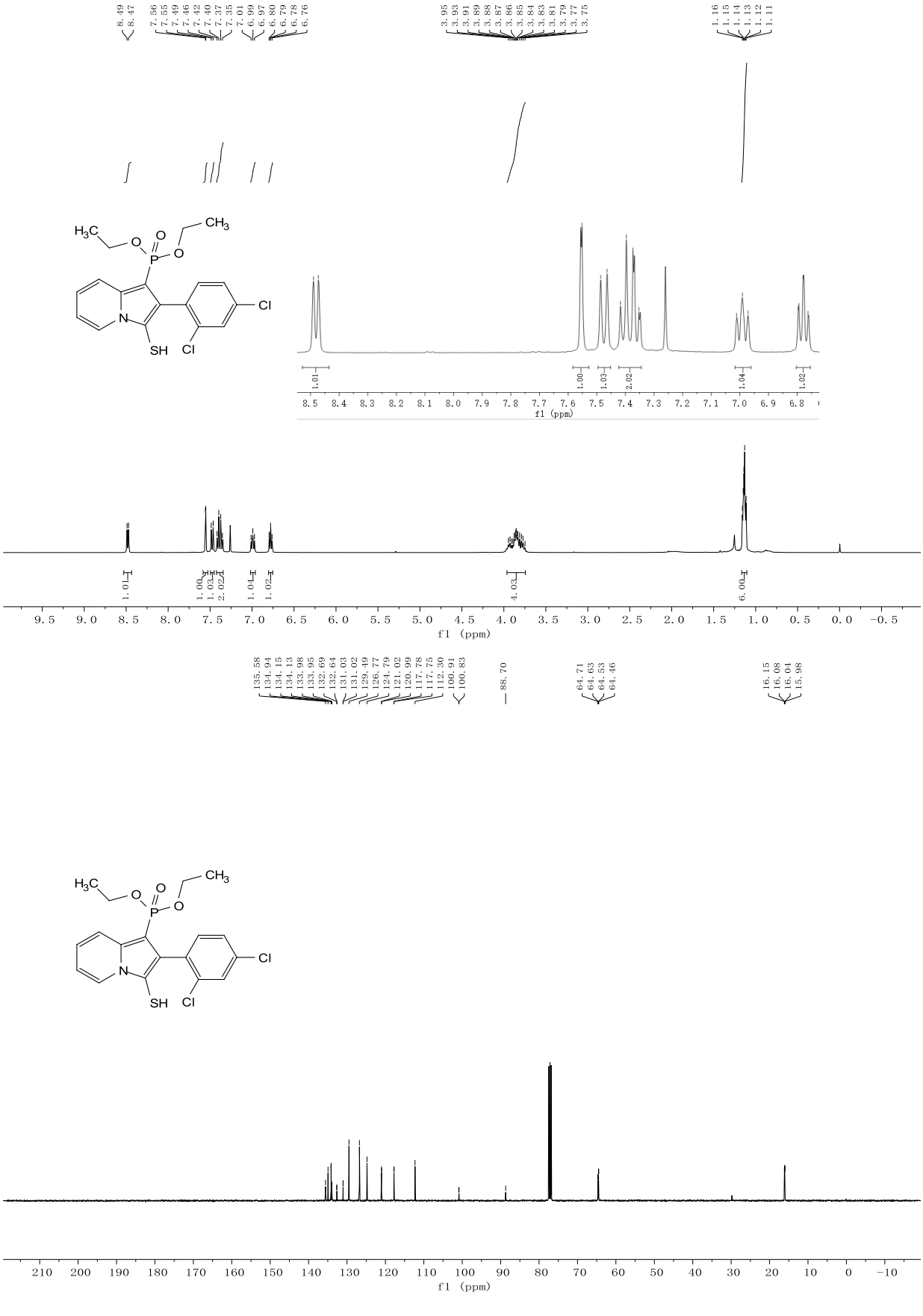

135.46
135.41
134.31
134.28
133.19
132.75
130.46
130.44
130.23
128.68
128.31
127.79
127.55
126.42
126.29
124.90
121.03
121.00
117.72
117.69
112.04
100.06
99.97
88.01
87.99
64.39
64.32
15.93
15.85
H3C
O
O
P
O
CH3
N
SH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

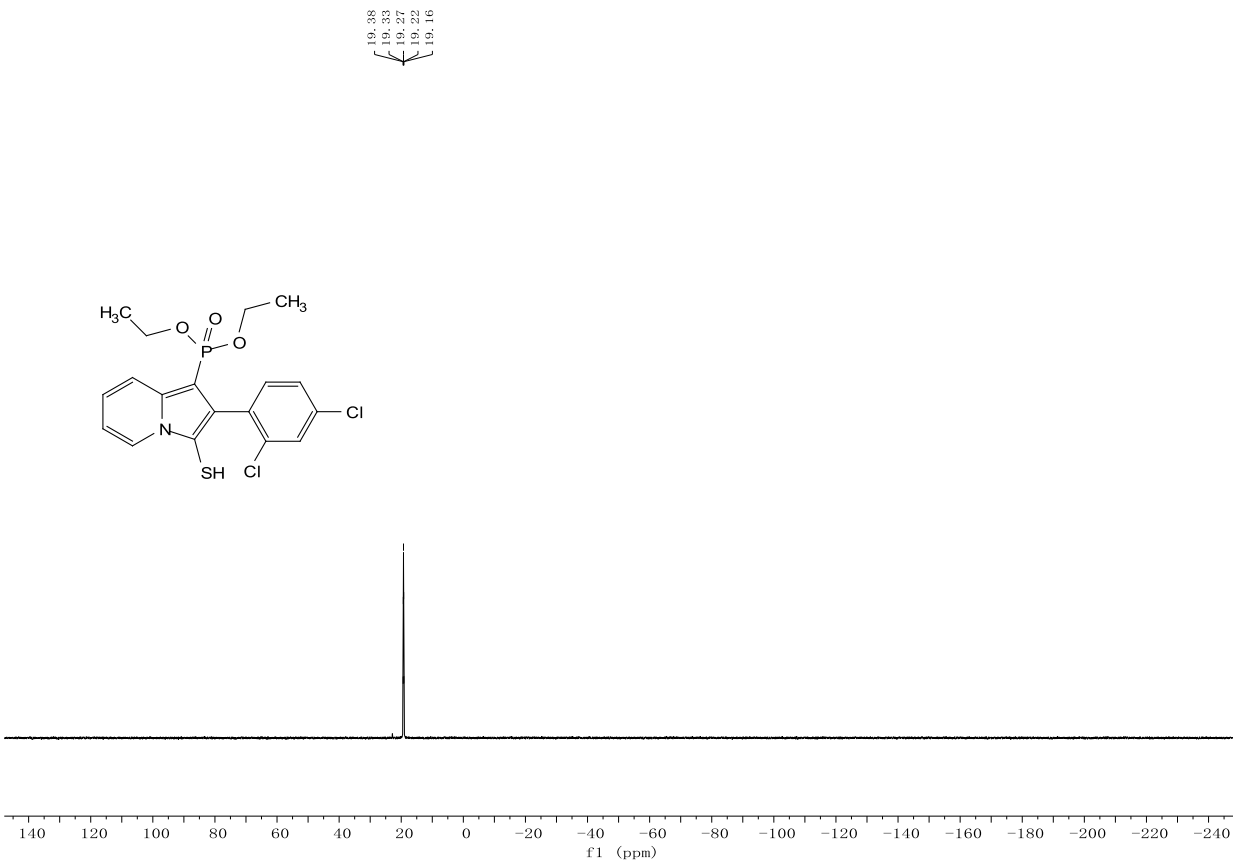

19.57
19.52
19.47
19.42
19.37
H3C
O
O
P
O
CH3
N
SH
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4n**

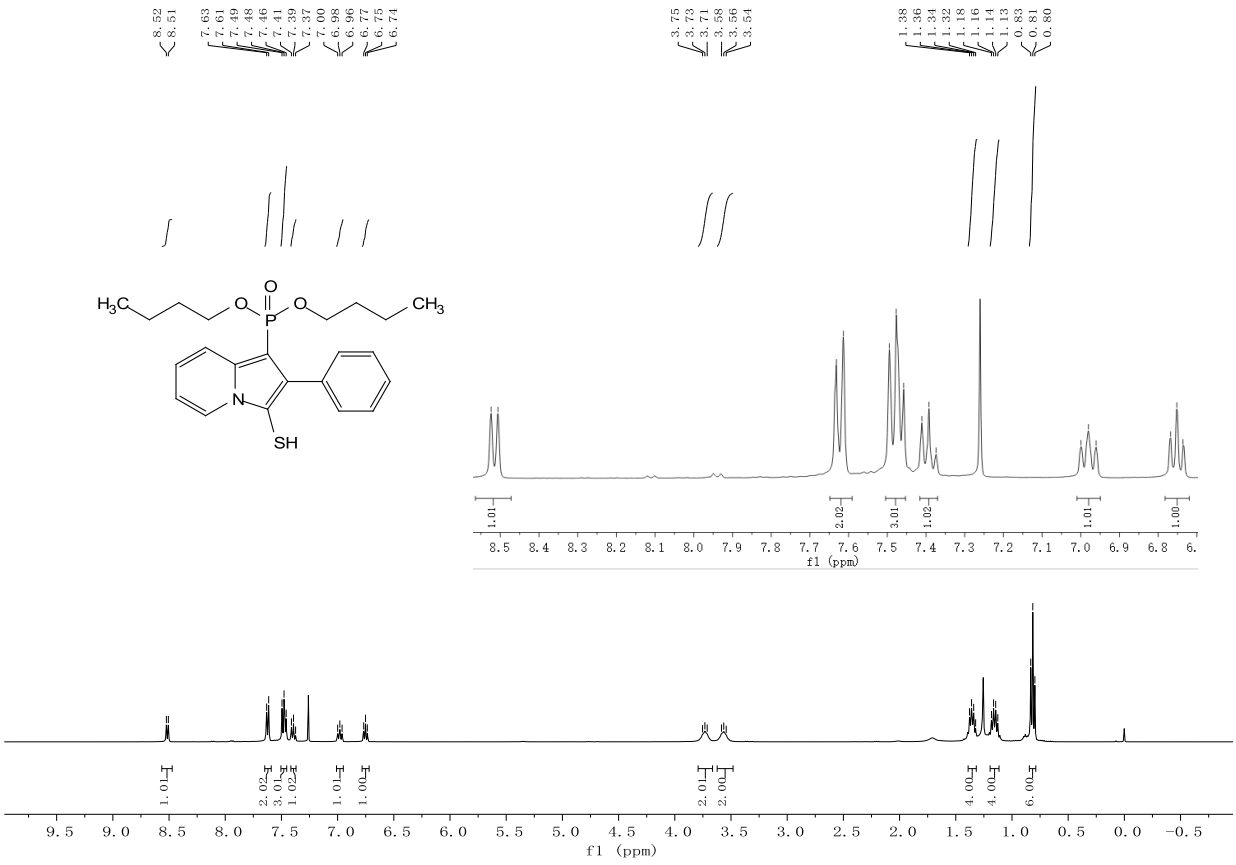


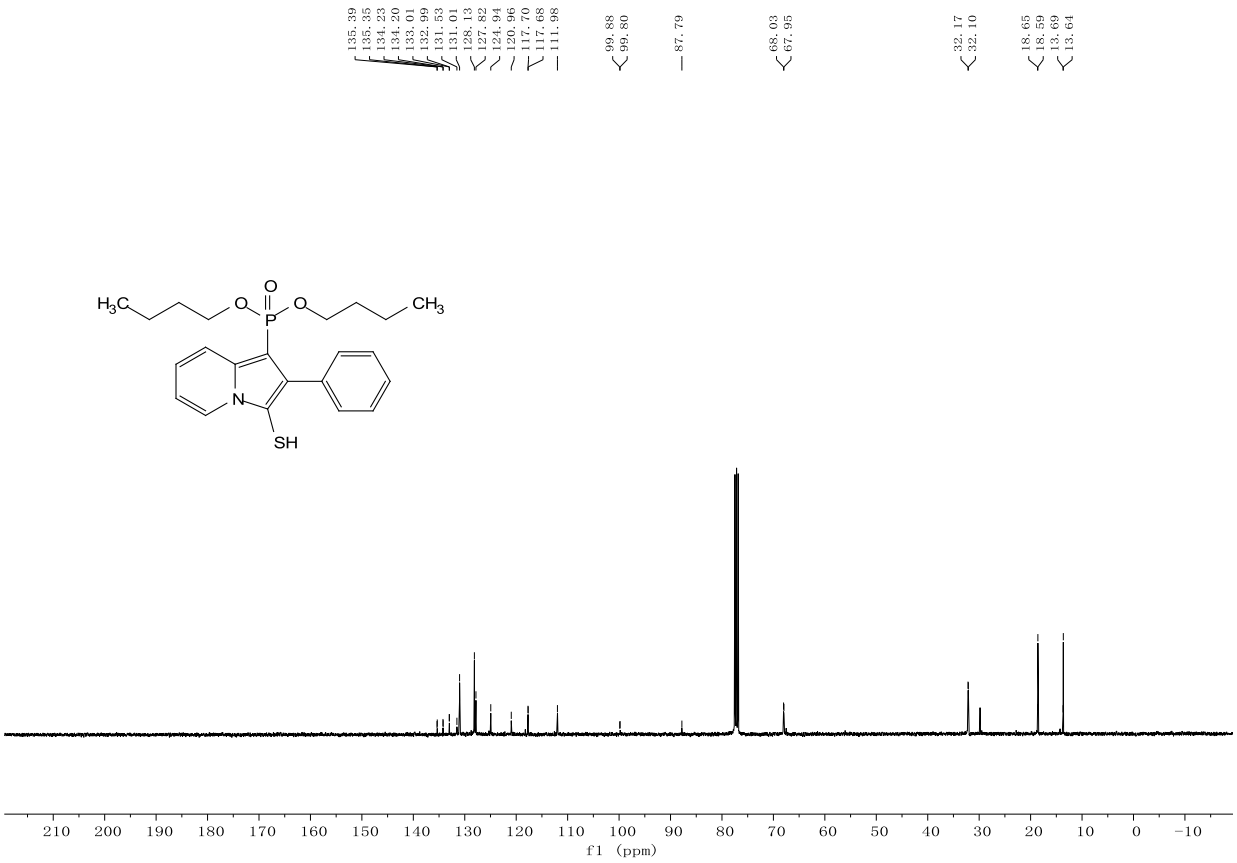
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **4o**



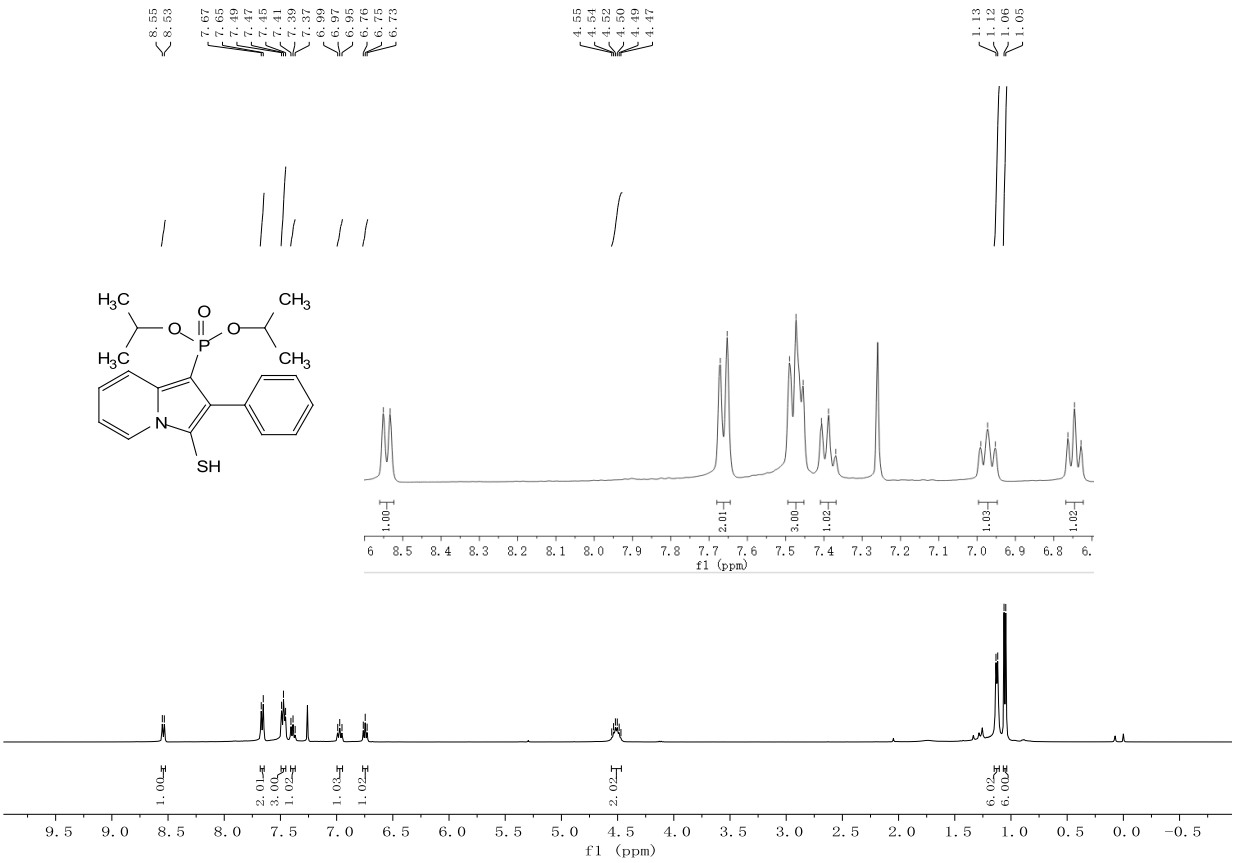


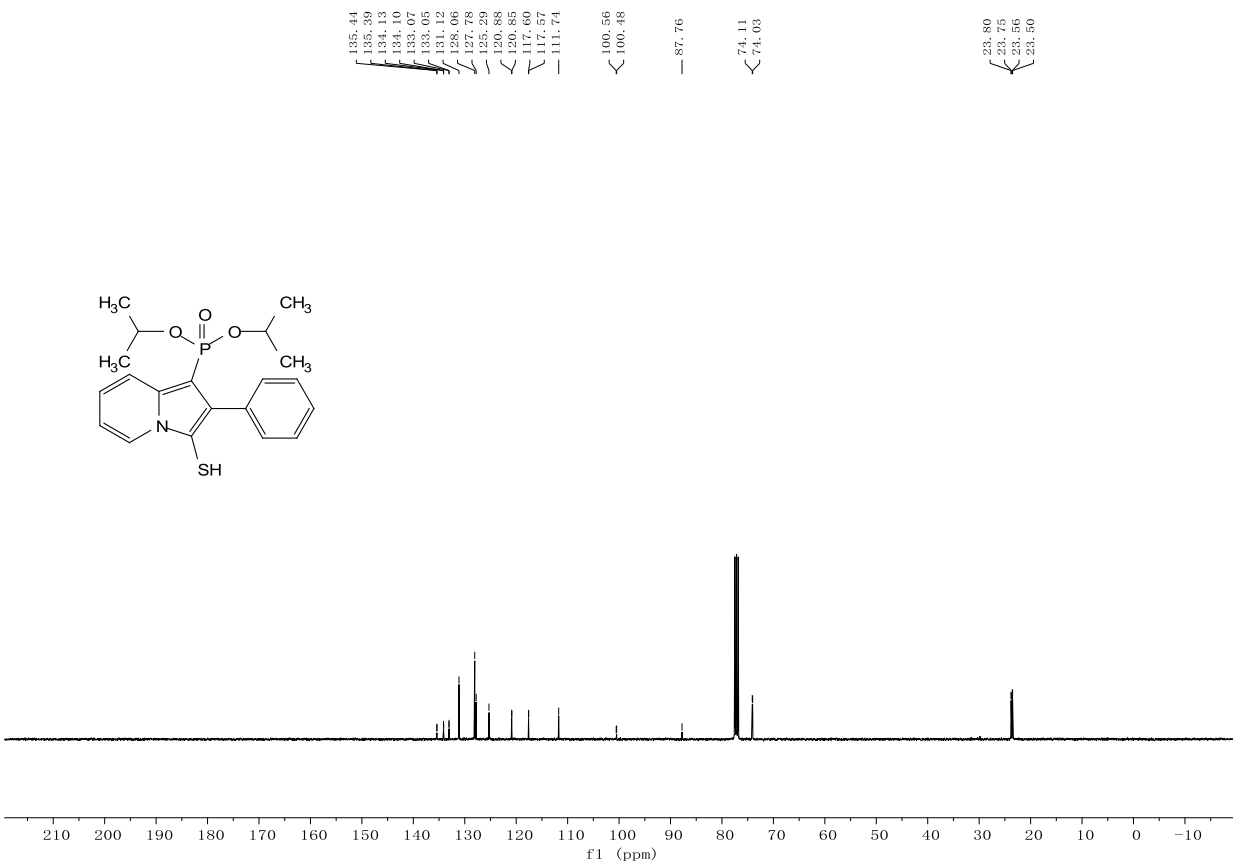
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4p**

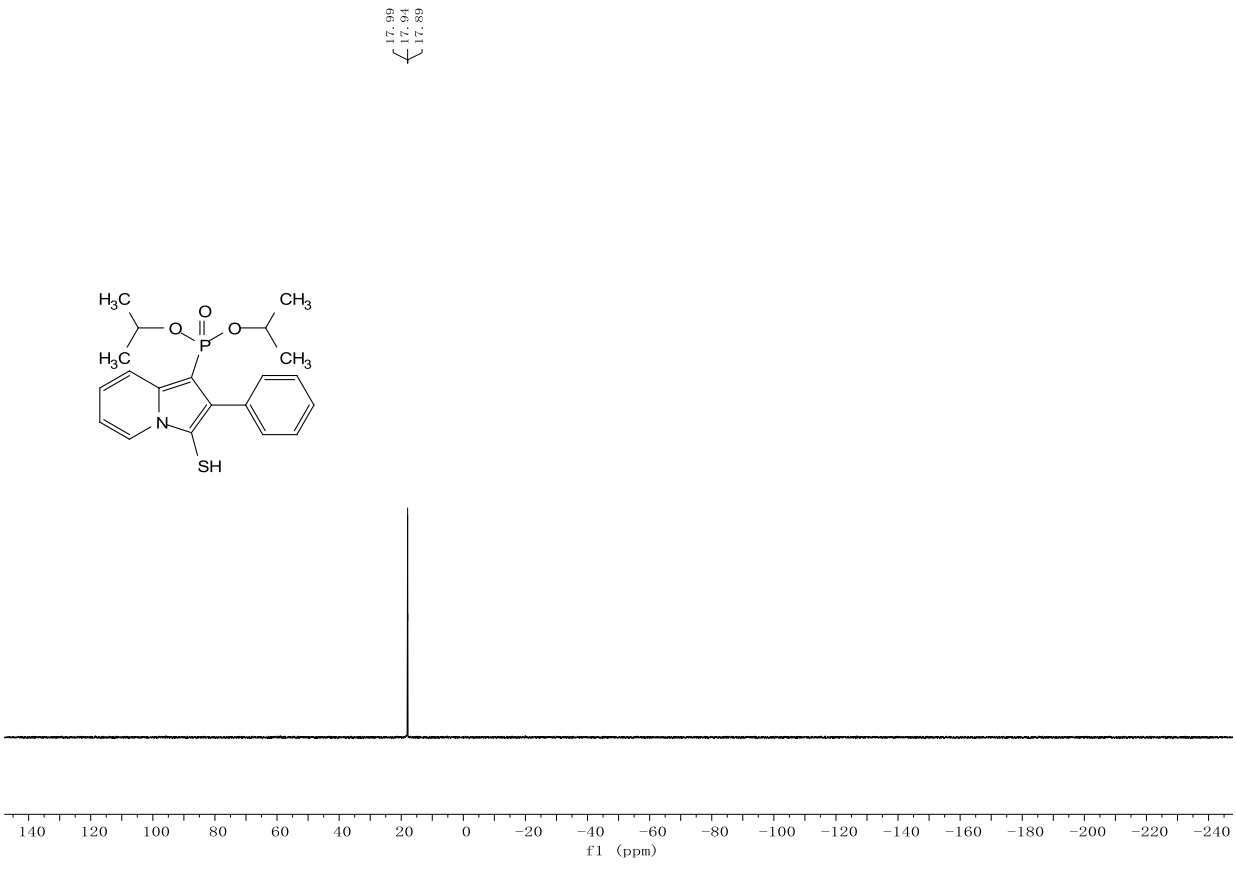




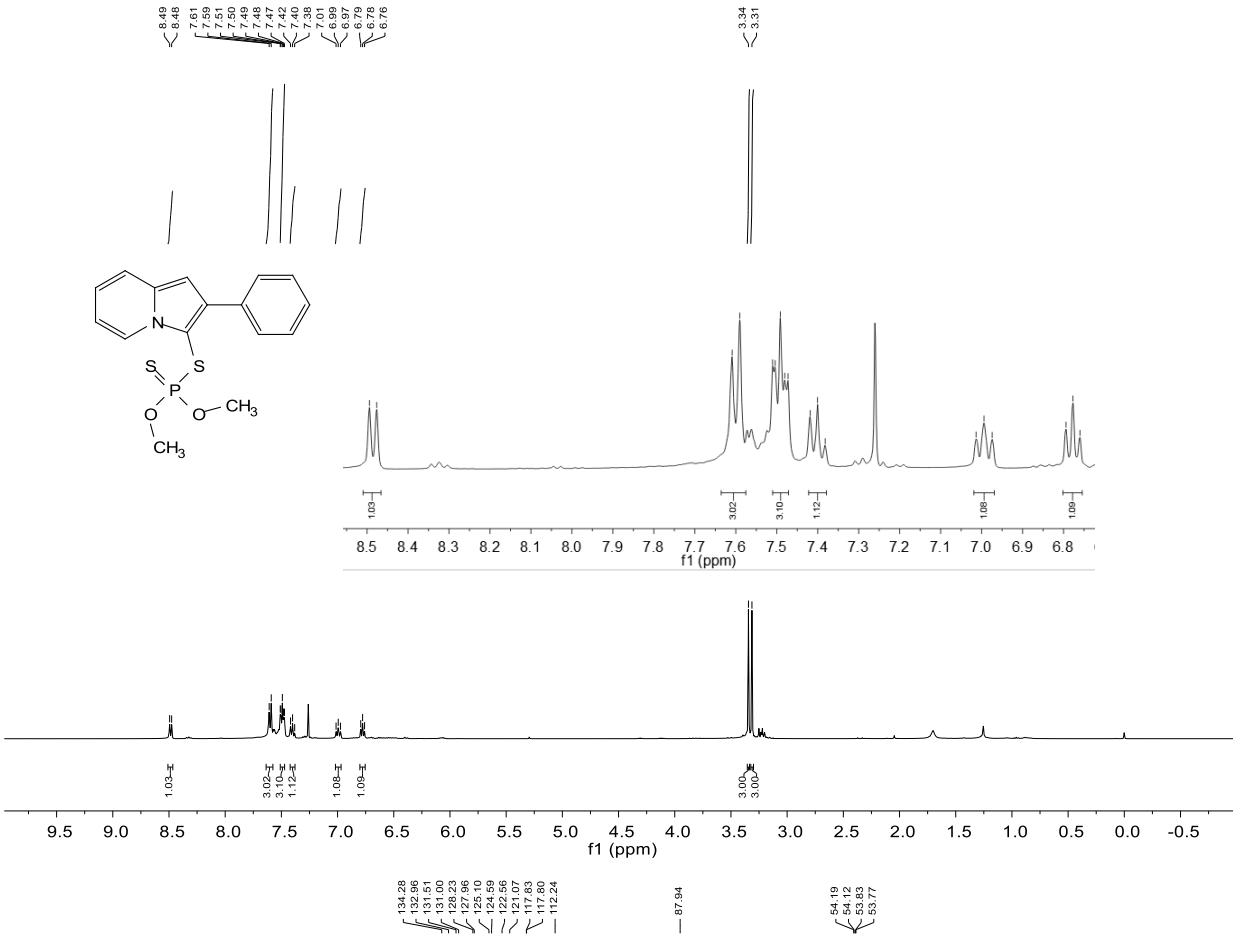
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **4q**

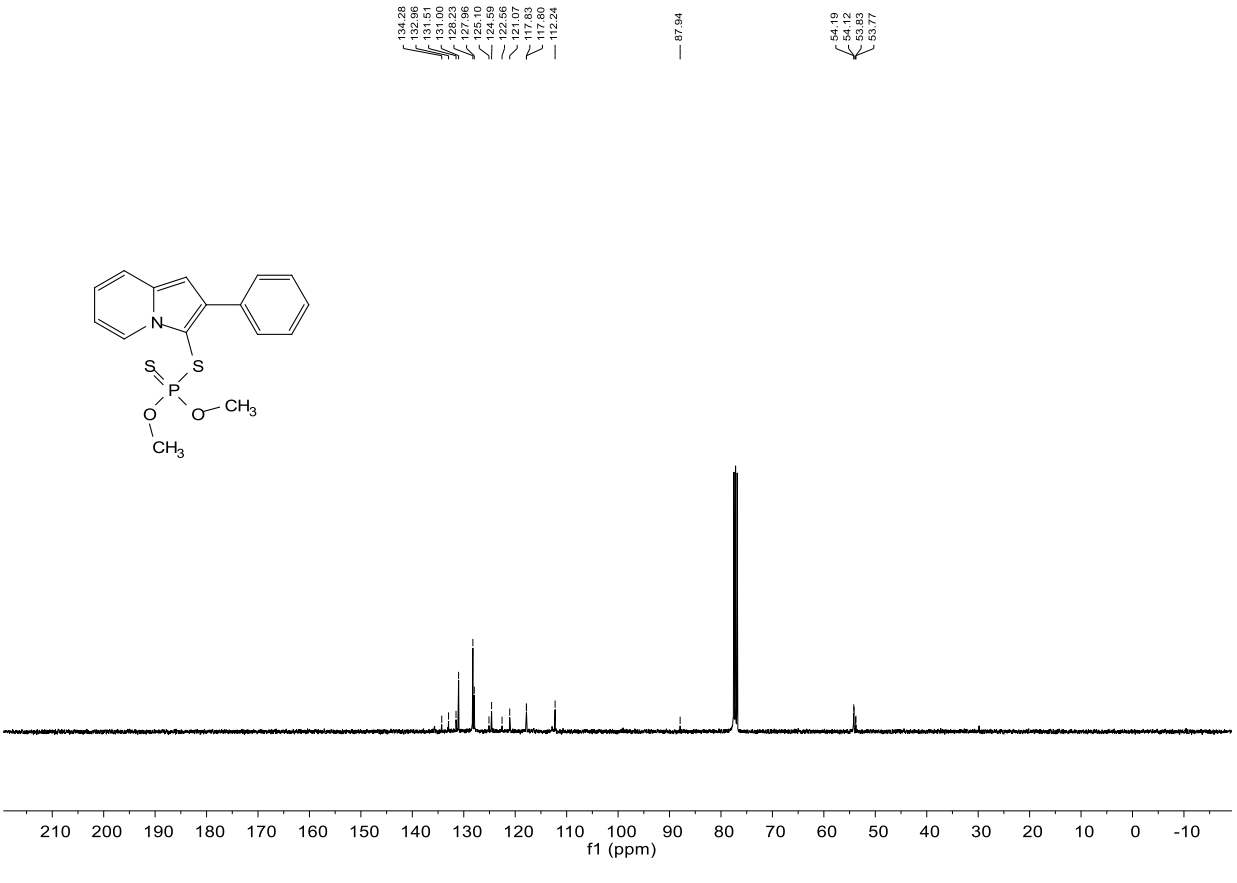


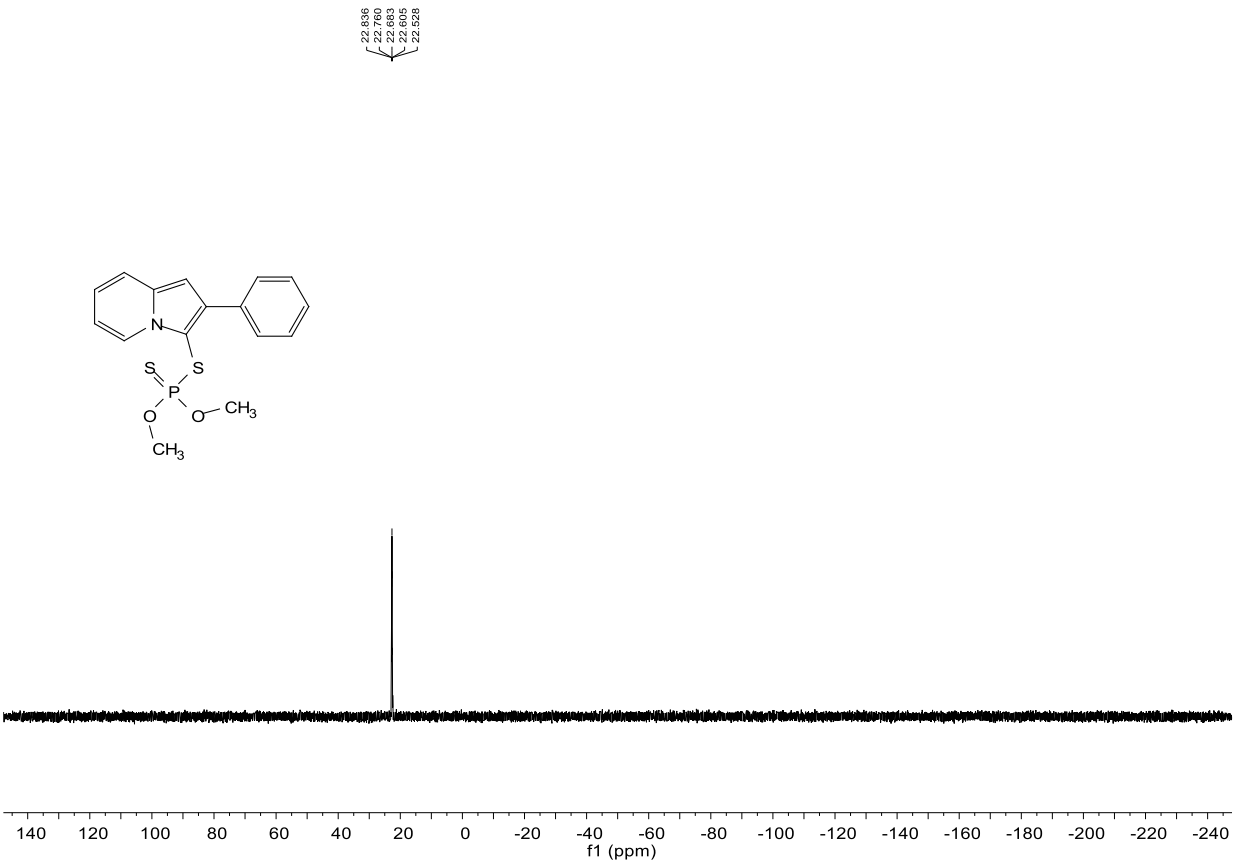

135.44
135.39
134.13
134.10
133.07
133.05
131.12
128.06
127.78
125.29
120.88
120.85
117.60
117.57
111.74
100.56
100.48
87.76
74.11
74.03
23.80
23.75
23.56
23.50
H3C
CH3
O
O
P
O
H3C
CH3
N
SH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


17.99
17.94
17.89
H3C
CH3
O
O
P
O
H3C
CH3
N
SH
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240
f1 (ppm)

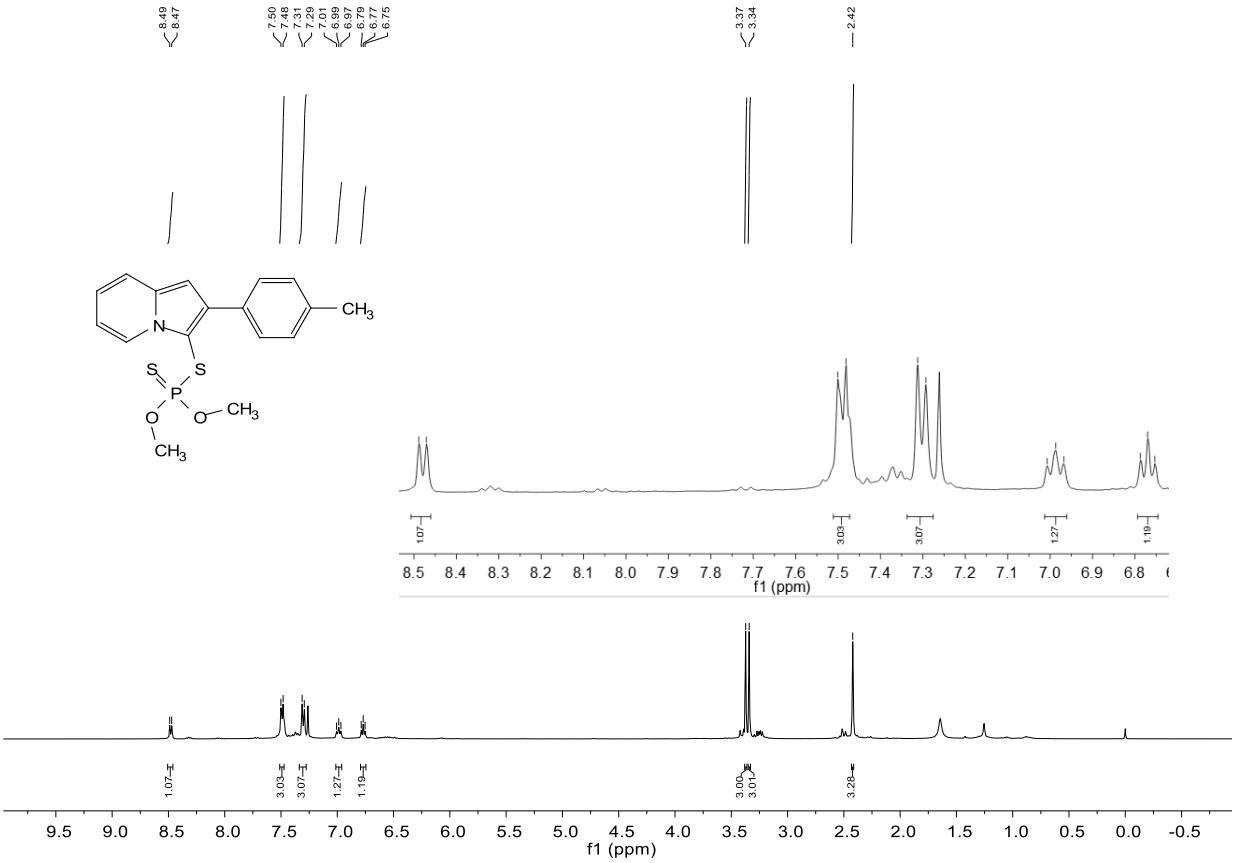
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **5a**

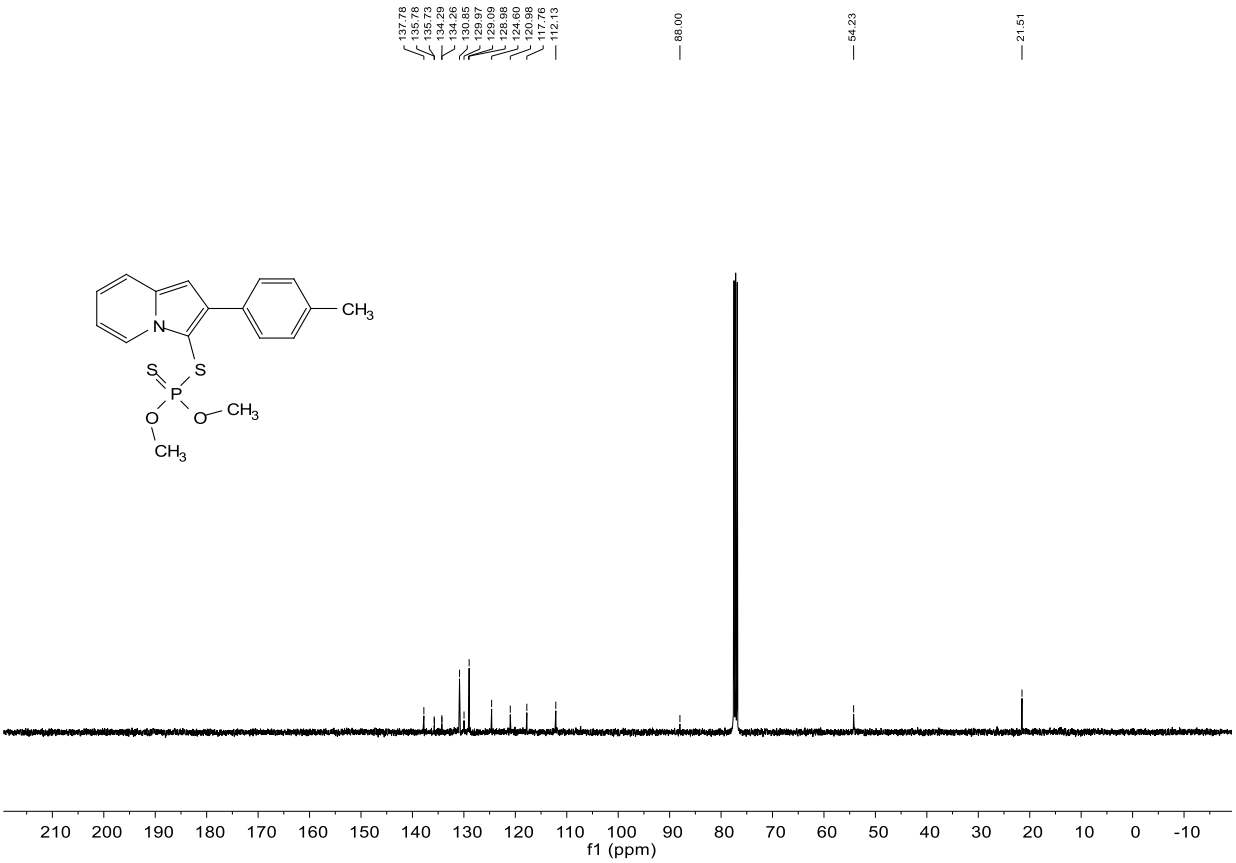


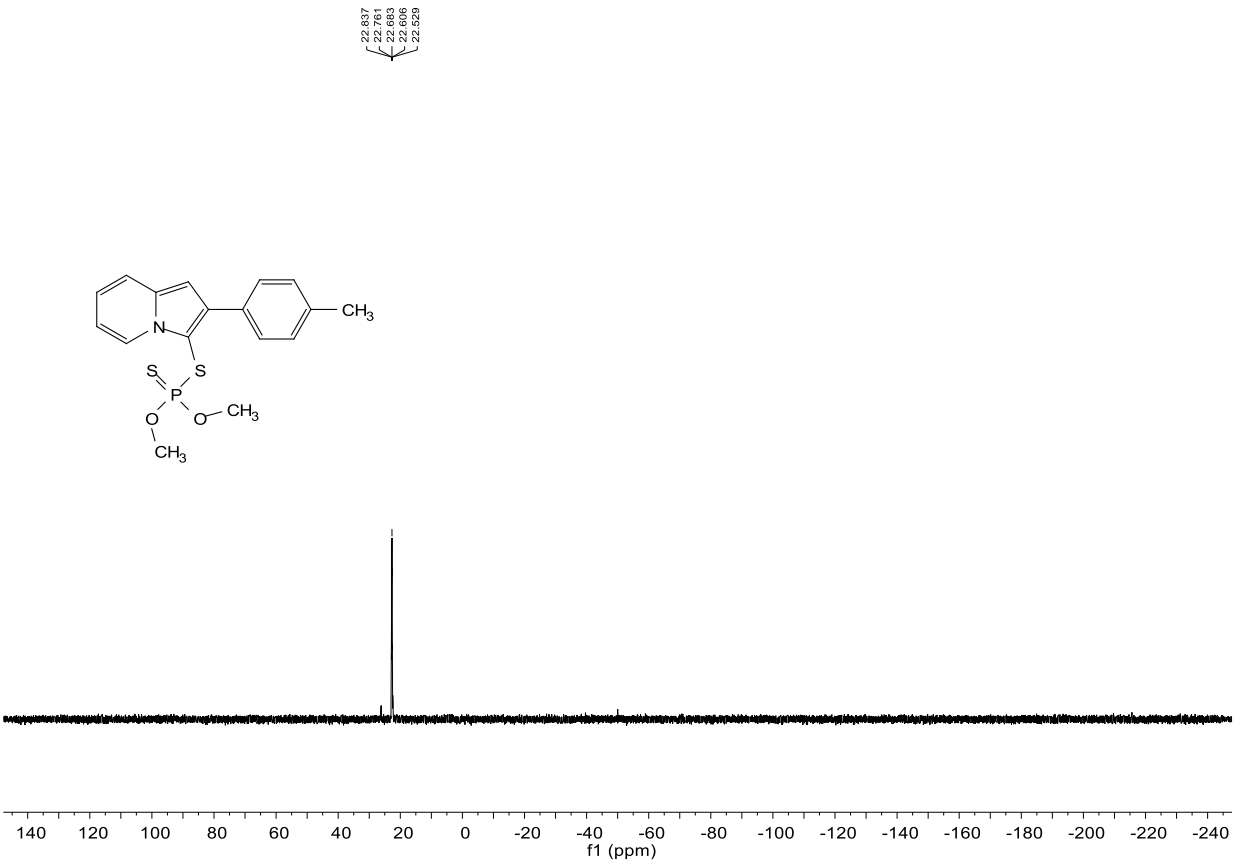




^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **5b**

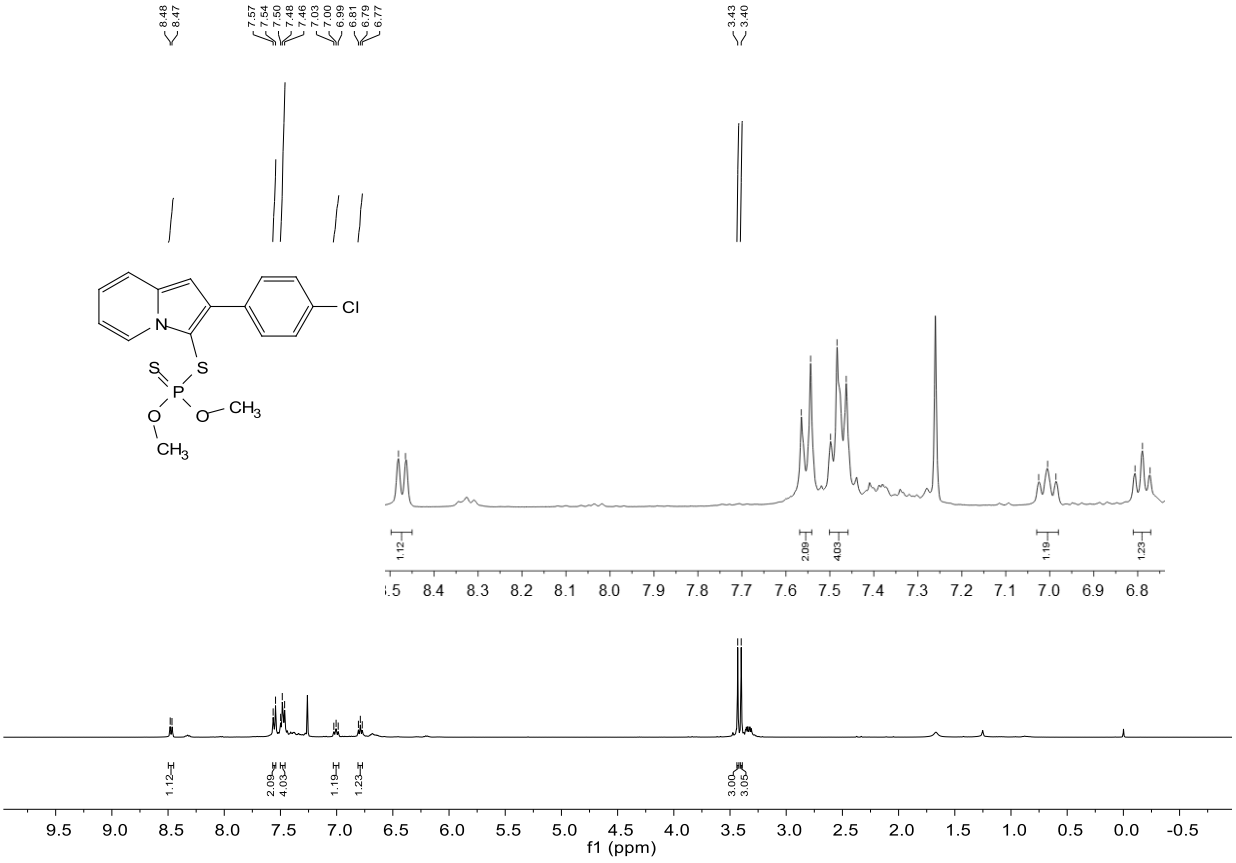


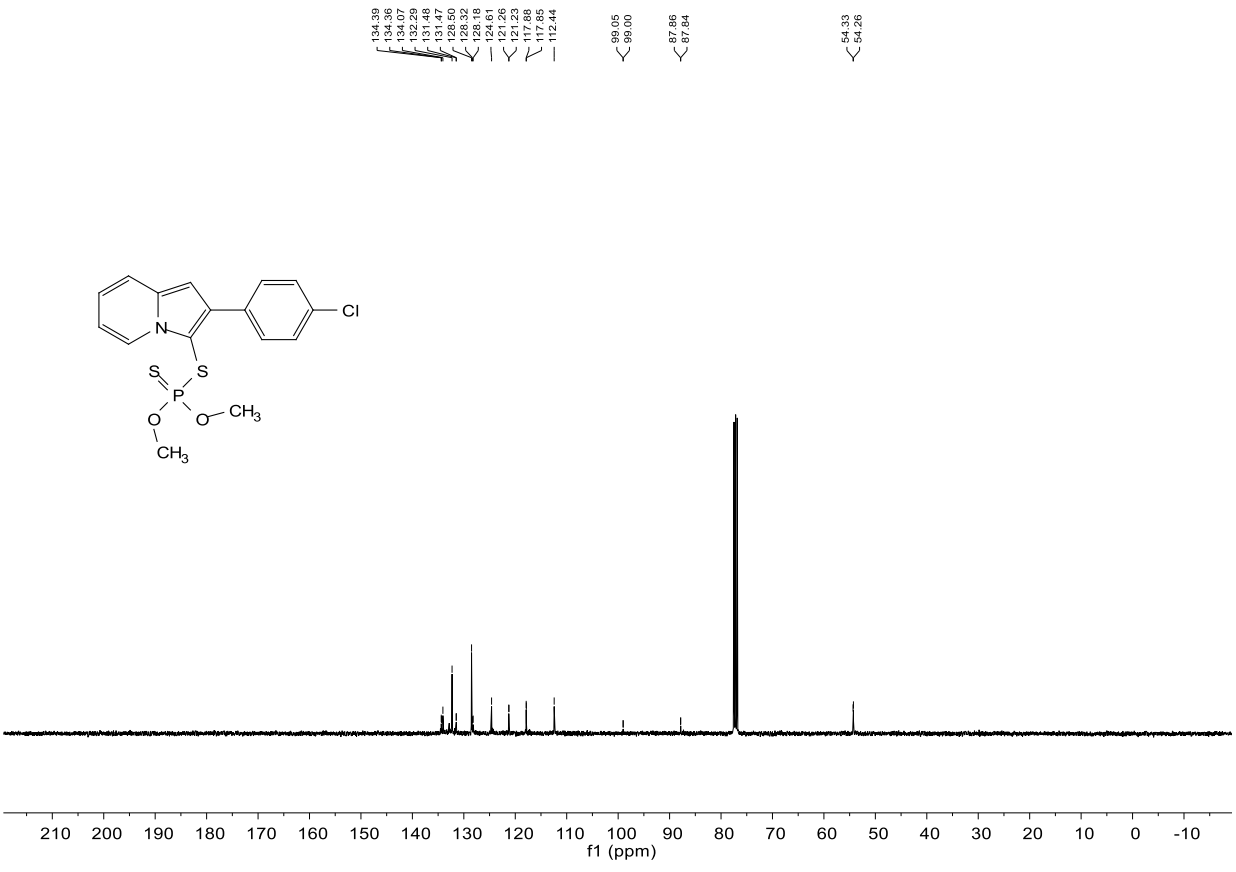


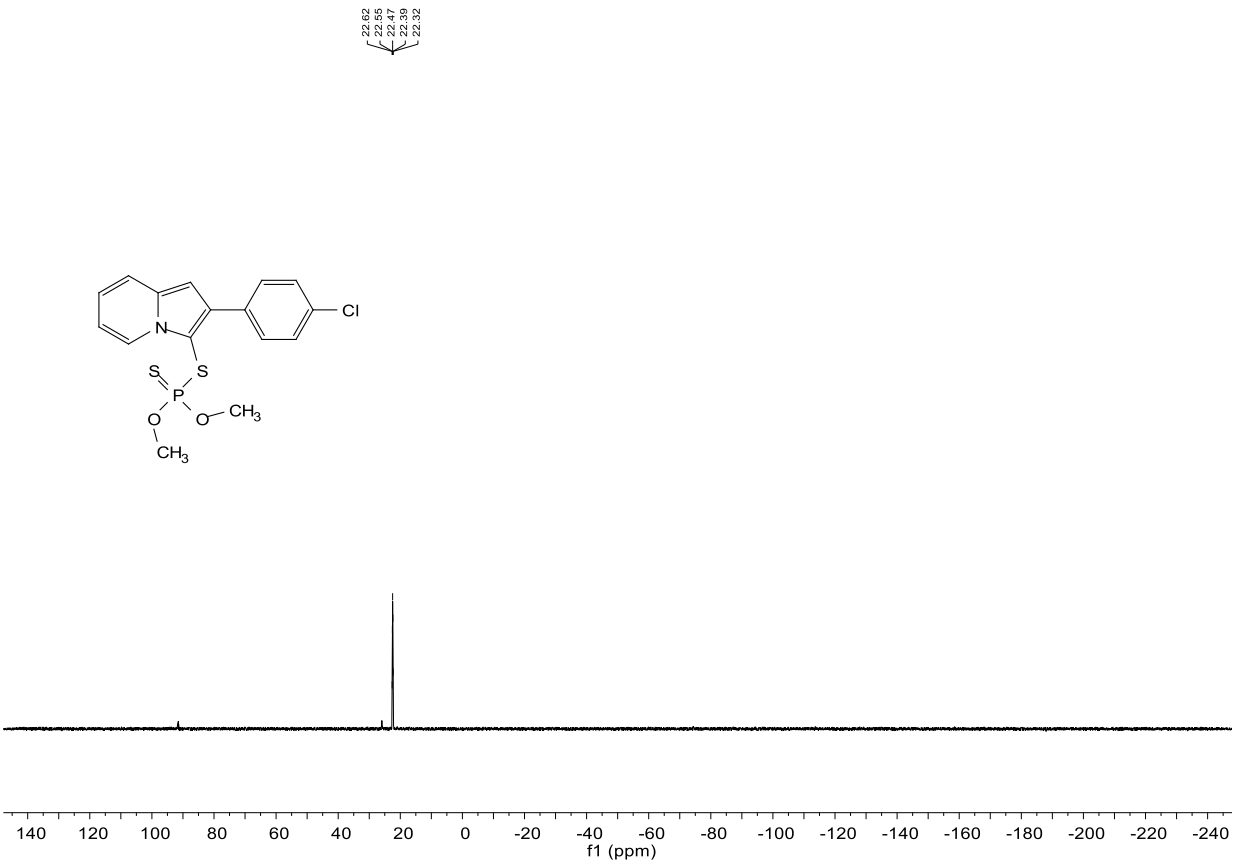


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$)

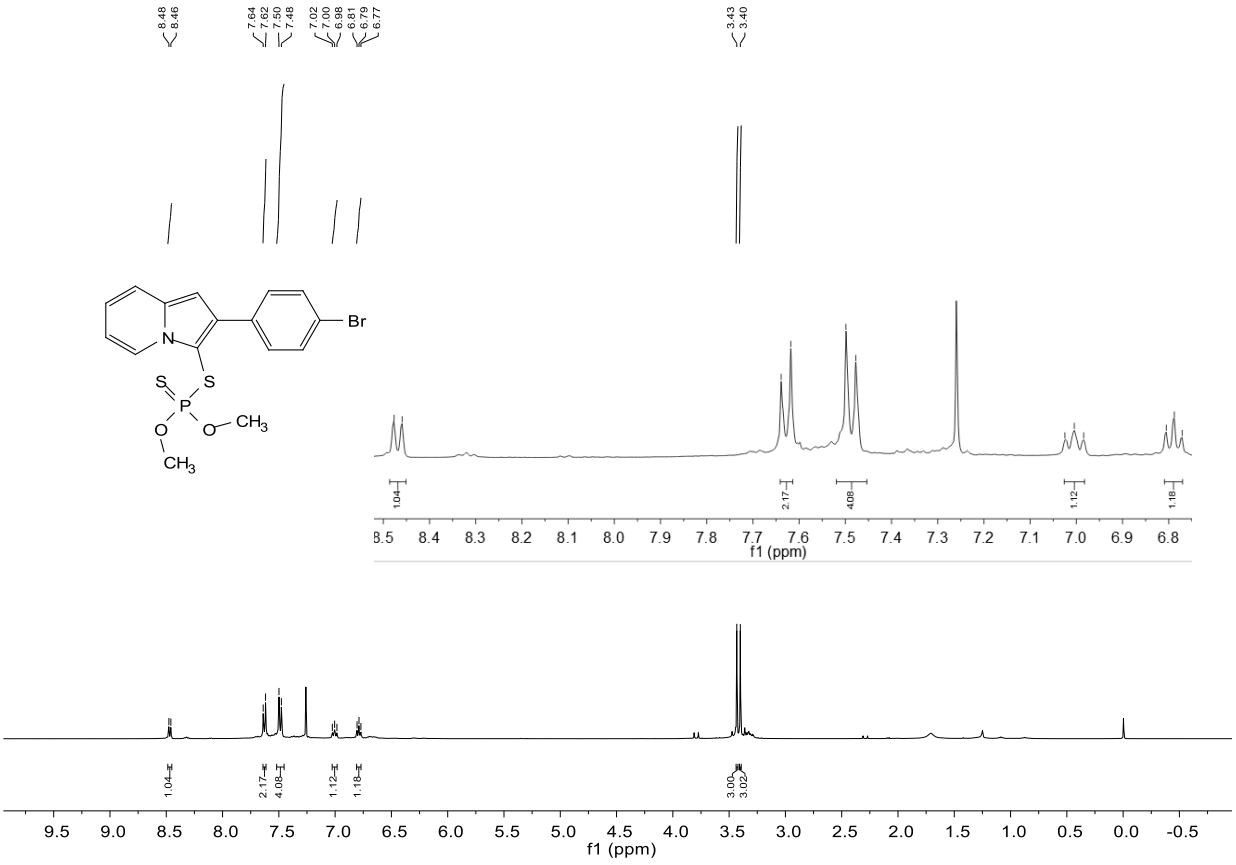
spectrum of compound **5c**

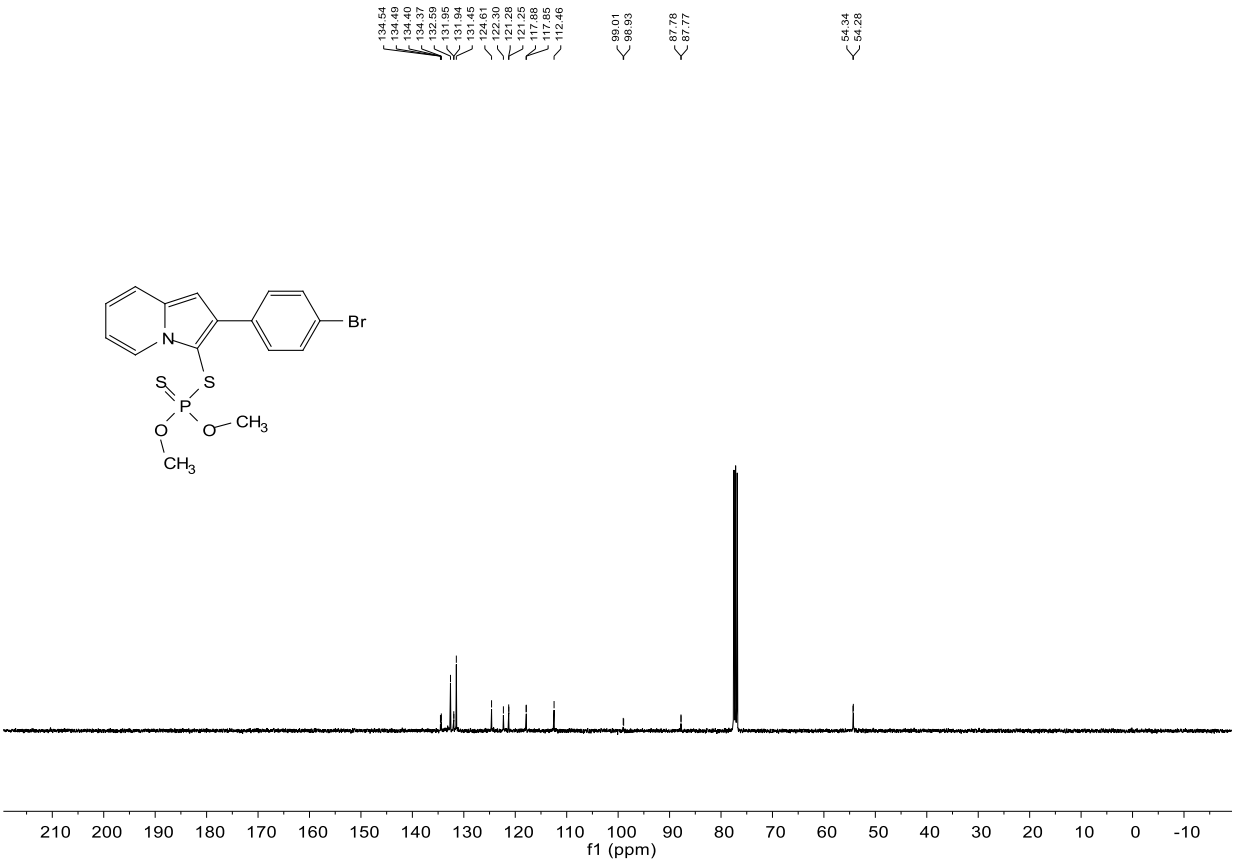


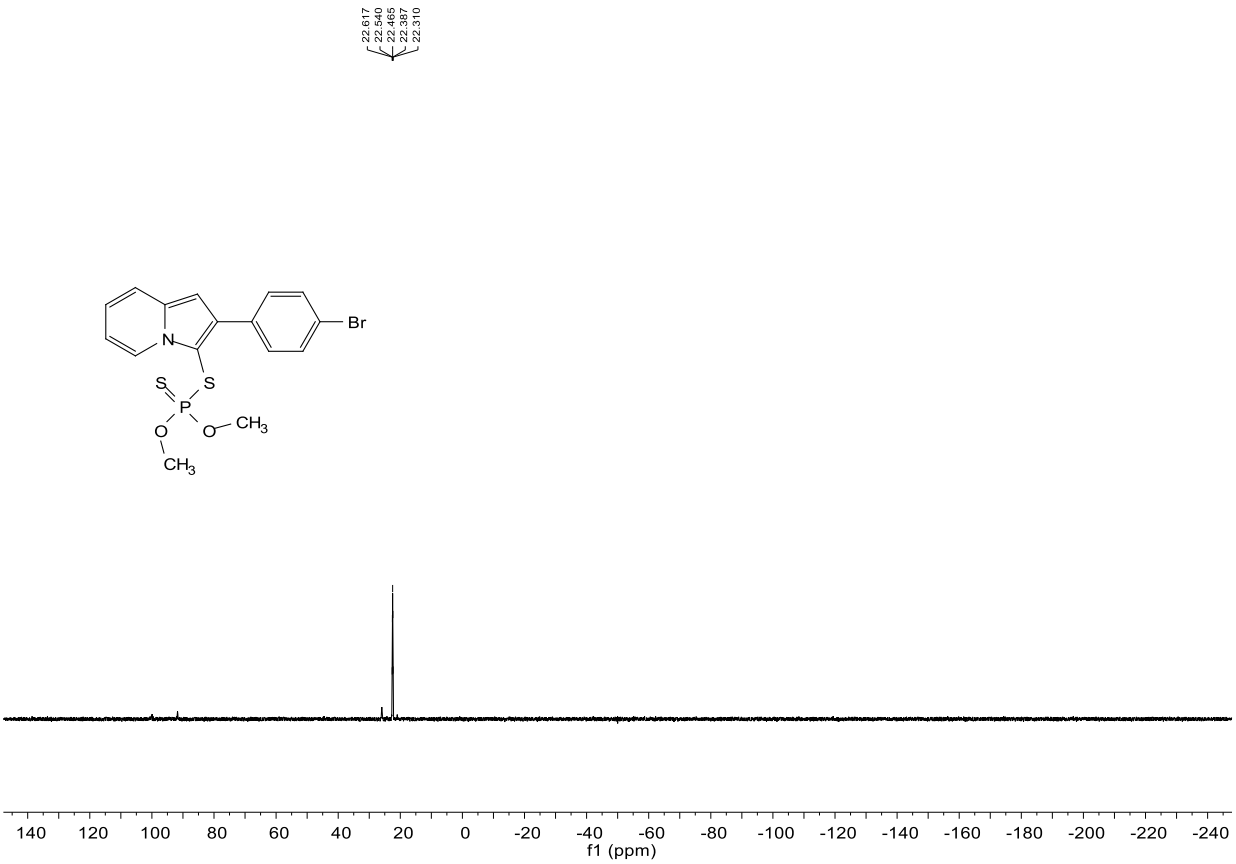




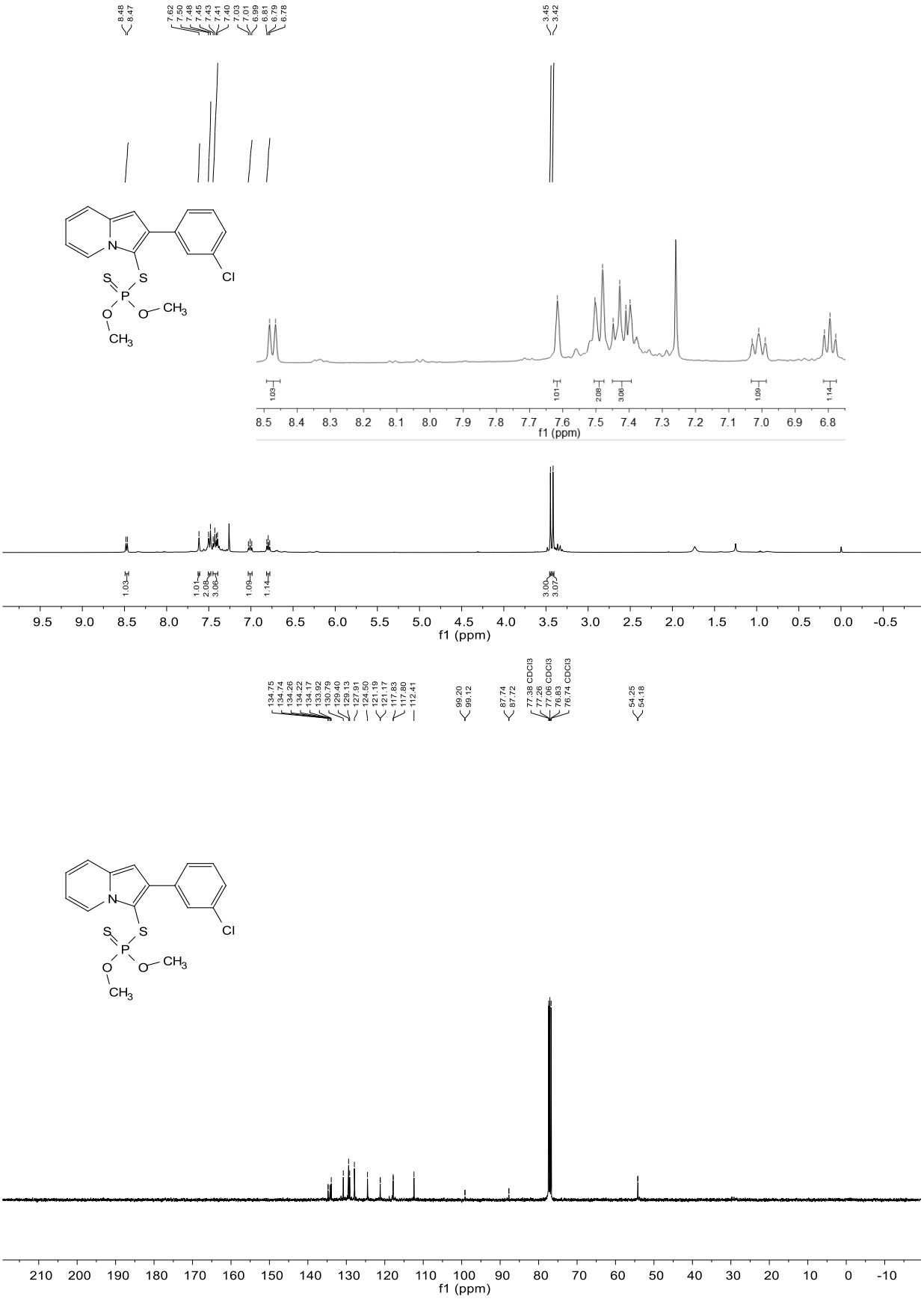
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **5d**

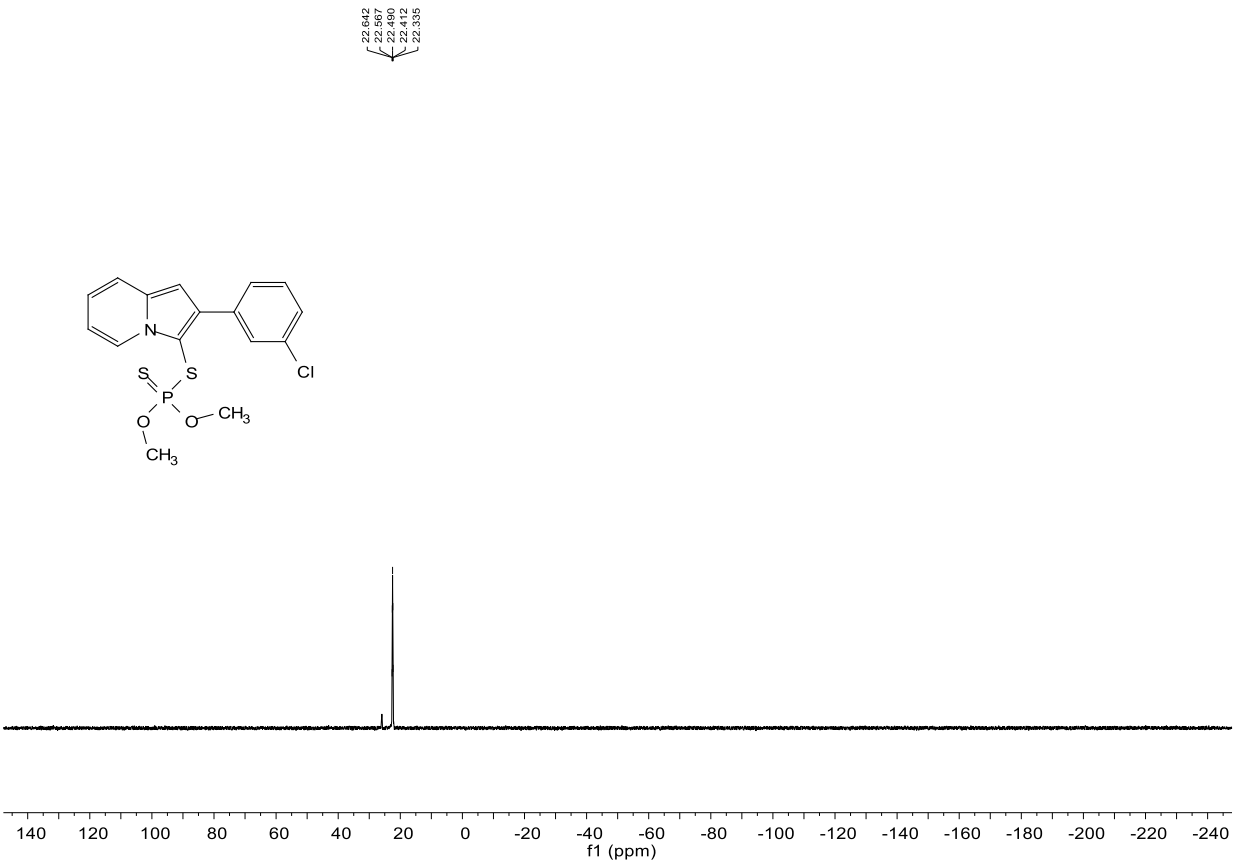



134.54
134.46
134.40
134.37
132.59
131.95
131.94
131.45
124.61
122.30
121.28
121.25
117.88
117.85
112.46
99.01
98.93
87.78
87.77
54.34
54.28
Br
N
S
S
P
O
O
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


22.617
22.540
22.465
22.387
22.310
Br
N
S
S
P
O
O
CH3
CH3
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound **5e**





4. References

1. (a) L. Teng, X. Liu, P. Guo, Y. Yu and H. Cao, *Org. Lett.*, 2020, **22**, 3841-3845; (b) J. Zhou, X. Shi, H. Zheng, G. Chen, C. Zhang, X. Liu and H. Cao, *Org. Lett.*, 2022, **24**, 3238-3243.

2. W. Kim, H. Y. Kim and K. Oh, *J. Org. Chem.*, 2021, **86**, 15973-15991.