Supporting Information

Efficient late-stage synthesis of quaternary phosphonium salts from organothianthrenium salts by photocatalysis

Jun Liu,[†,a] Zhaoyu Feng,[†,a] Hanxiang Li,[c] Zhengze Yu,[*,c] Hongyu Wang,[*,a] and Bo Tang[b]

[a] Key laboratory of marine drugs, ministry of education; Molecular synthesis center, and School of medicine and pharmacy, Ocean university of china, Qingdao 266003; Laboratory for marine drugs and bioproducts, Qingdao marine science and technology center, Qingdao, 266237, (P. R. China).

[b] Laoshan laboratory, Qingdao 266237 (P. R. China).

[c] College of chemistry and chemical engineering, Qingdao university, Qingdao 266071 (P.R. China).

Table of Contents

General information

The commercial materials and photocatalyst were purchased from Adamas-beta®, Shanghai Bidepharm®, and Tianjin Heowns®. Solvents were treated by the standard methods. Flash column chromatography was carried out on silica gel (300–400 mesh) using a forced flow of eluent. For TLC, silica gel plates were used and visualized by fluorescence quenching under UV light. All the NMR spectra were recorded on Bruker NMR spectrometers or JEOL NMR spectrometers. Chemical shifts (δ) for ^{1}H NMR (400 Hz), ^{13}C NMR (101 Hz or 125 Hz), ^{31}P NMR (162 Hz), and ^{19}F NMR (376 Hz) were given in ppm. ^{1}H NMR chemical shifts were recorded relative to $SiMe_4$ (δ 0.00). ^{13}C NMR chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.16, DMSO-d_6: δ 39.98). Data were reported as follows: chemical shift, integration, multiplicity (s = single, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). High performance liquid chromatography (HPLC) was performed on Shimadzu 20A instruments using Daicel Chiralpak AD-H (4.6 mm × 250 mm) columns. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics maXis UHR-TOF MS or Thermo Fisher LTQ Orbitrap XL. UV−vis spectroscopic was measured by Beijing PERSEE TU-1901. The confocal fluorescence image was taken by a Nikon AIR HD25. The purple light source (390 nm) was provided by Shanghai 3S Technology 022-AM1-0086 LED (Figure S1). The blue light source (456 nm) was provided by Shanghai 3S Technology 022-AM1-0004 LED.

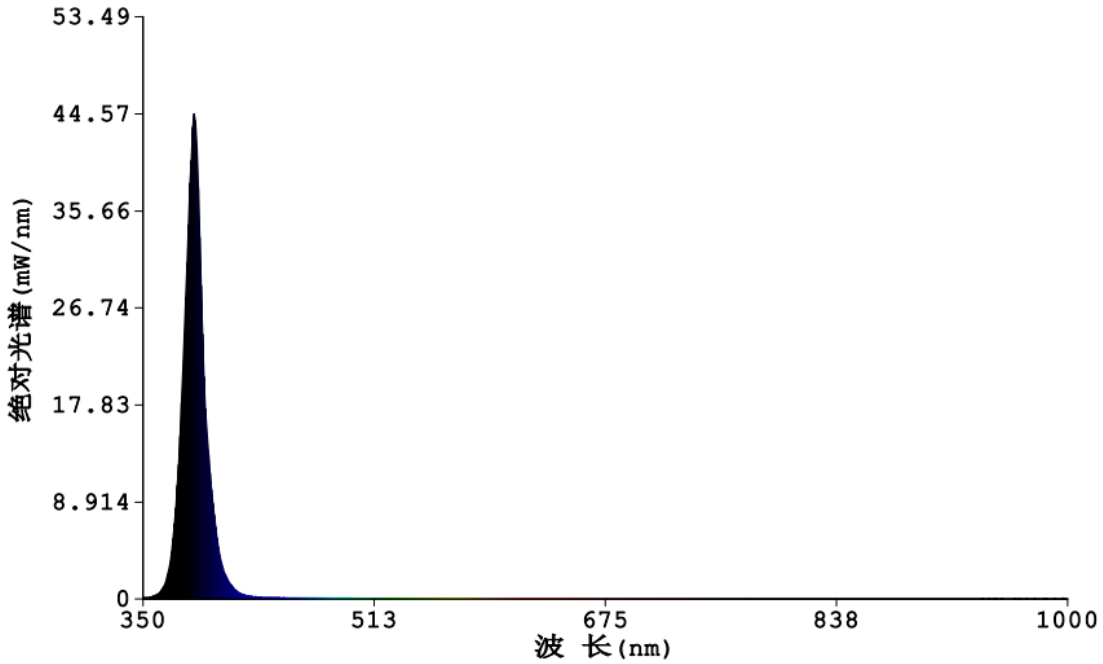
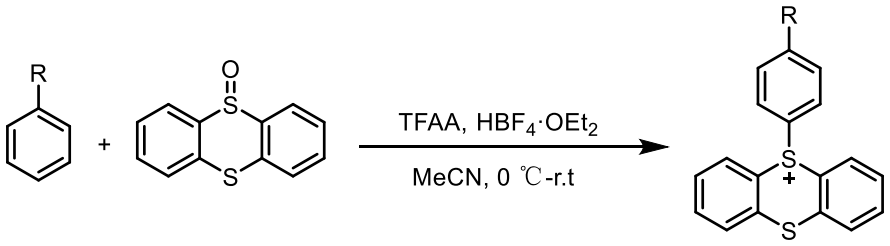


Figure S1. 022-AM1-0086 LED spectral test report

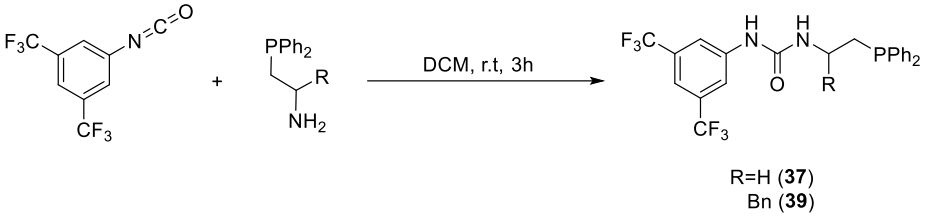
General procedure for the synthesis of substrates

The procedure for synthesizing thianthrenium salts (Procedure 1)



Thianthrenium salts are synthesized via a modified procedure according to the previous literature.[1] A 20 ml glass vial was charged with arenes (1 equiv., 2 mmol) and dry MeCN (8 mL, c = 0.25M) under air. Then $HBF_4{\cdot}OEt_2$ (1.0 equiv., 2 mmol) was added to the vial while stirring the reaction mixture. After cooling to 0 ℃, thianthrene-5-oxide (1 equiv., 2 mmol), trifluoroacetic anhydride (0.83 ml, 6 mmol, 3.0 equiv.) and $HBF_4{\cdot}OEt_2$ (2.0 equiv., 4 mmol) was added in one portion, resulting in a color change to deep purple. The mixture was stirred at 0 °C for 1 h, subsequently, the reaction mixture was warmed to 25 °C and stirred until the intensity of the purple color decreased. The solution was diluted with 5 mL DCM and poured into a mixture of 20 ml DCM, 20 ml saturated aqueous Na_2CO_3 solution, and 10 ml water respectively. After stirring for 5 min at 25 °C, the mixture was poured into a separatory funnel, and the organic layers were separated. The organic layer was washed with $NaBF_4$ (0.25 M) solution, then dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with DCM/MeOH (v/v 100:1-20:1) to give corresponding products.

The procedure of synthesizing substrates 37 and 39 (Procedure 2)

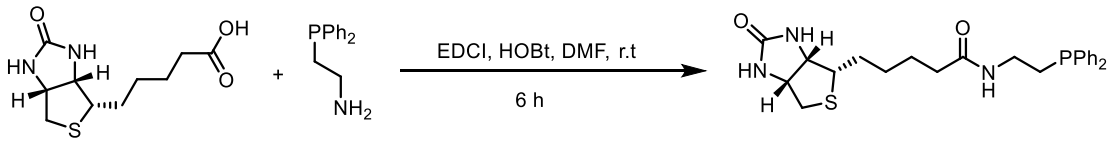


Based on a modified literature procedure.[2] A solution of amine (1.0 equiv, 0.5 mmol) in DCM (8 mL) was equipped with a stirring bar, after stirring for 5 min, 1-isocyanato-3,5-bis(trifluoromethyl)benzene (1.0 equiv, 0.5 mmol) was added into the mixture. After further stirring for 3 h at 25 °C, diluted with water (20 mL) and extracted with ethyl acetate. The organic layer was washed with water and dried over Na_2SO_4. The solvent was then evaporated under reduced pressure. The residue was purified via flash column chromatography on silica gel using ethyl acetate/petroleum (v/v, 1:10) as eluent to generate the corresponding compounds (193 mg, 80% yield; 218 mg, 76% yield).

The procedure of synthesizing substrate 38 (Procedure 3)

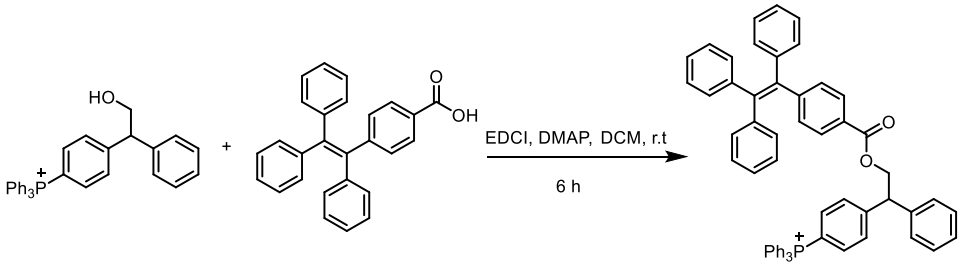
Based on a modified literature procedure.[3] A 20 ml glass vial was charged with (*S*)-(2'-methoxy-[1,1'-binaphthalen]-2-yl) diphenylphosphine (1.0 equiv, 0.5 mmol) and DCM (8 mL) under air. After cooling to 0°C, tribromoborane (5 equiv, 2.5 mmol) was added dropwise. Heat reaction to room temperature and continue to react for 2 hours. The mixture was quenched with water, washed with saturated sodium bicarbonate, and extracted with ethyl acetate. The organic phases were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure to give the product (117 mg, 95% yield).

The procedure of synthesizing substrate 40 (Procedure 4)

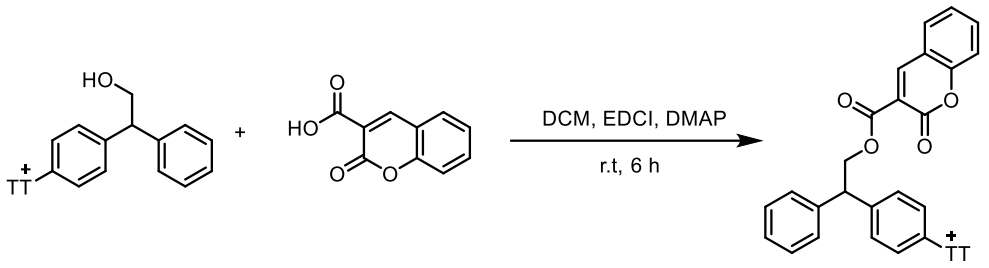


Based on a modified literature procedure.[4] To a DMF solution of Biotin (1.5 equiv, 1.5 mmol), EDCI (2.0 equiv, 2 mmol) was added HOBt (2.0 equiv, 2 mmol). The mixture was stirred under room temperature for 10 min, and then the amine (1equiv, 1 mmol) was added. After stirring for 6 h at room temperature. The mixture was quenched with water, washed with saturated saline, and extracted with ethyl acetate. The organic phases were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified via flash column chromatography on silica gel using ethyl DCM/MeOH (v/v 15:1-3:1) as eluent to obtain the corresponding compound (530 mg, 77% yield).

The procedure of synthesizing substrate 9 and 42 (Procedure 5)



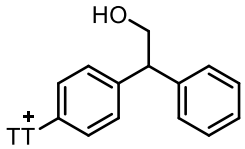
Based on a modified literature procedure.[5] To a CH_2Cl_2 solution of carboxylic acid (2.0 equiv., 0.3 mmol), EDCI (2.0 equiv., 0.3 mmol) was added DMAP (2.0 equiv., 0.3 mmol). The mixture was stirred under room temperature for 10 min, and then the quaternary phosphonium salt (1.0 equiv., 0.15 mmol) was added. After stirring for 6 h at room temperature. The mixture was quenched with water, washed with saturated saline, and extracted with DCM. The organic phases were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified via flash column chromatography on silica gel using ethyl DCM/MeOH (v/v 100:1-20:1) as eluent to obtain the corresponding compound (108mg, 88% yield).



To a CH_2Cl_2 solution of carboxylic acid (2.0 equiv., 1 mmol), EDCI (2.0 equiv., 1 mmol) was added DMAP (2.0 equiv., 1mmol). The mixture was stirred under room temperature for 10 min, and then the thianthrenium salt (1.0 equiv., 0.5 mmol) was added. After stirring for 6 h at room temperature. The mixture was quenched with water, washed with saturated saline, and extracted with DCM. The organic phases were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified via flash column chromatography on silica gel using ethyl DCM/MeOH (v/v 100:1-20:1) as eluent to obtain the corresponding compound (215 mg, 64% yield).

Characterization data for the substrates

5-(4-(2-hydroxy-1-phenylethyl)phenyl)-5H-thianthren-5-ium (Substrate 8)



The compound was prepared according to the **Procedure 1**. White solid; 30% yield (300 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45-8.43 (d, *J* = 8.0 Hz, 2H), 7.79-7.73 (m, 4H), 7.71-7.76 (m, 2H), 7.33-7.31 (d, *J* = 8.2 Hz, 2H), 7.24-7.21 (m, 2H), 7.18-7.14 (m, 1H), 7.10-7.06 (dd, *J* = 12.8, 8.0 Hz, 4H), 4.17-4.13 (t, *J* = 8.0 Hz, 1H), 4.02-4.01 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.5, 140.1, 136.5, 135.2, 134.9, 131.0, 130.3, 128.9, 128.4, 128.2, 127.2, 121.4, 118.8, 65.4, 53.1.

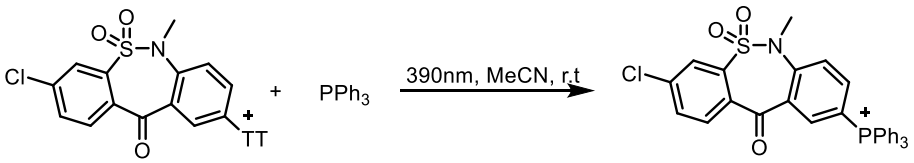
HRMS (ESI) *m/z* calcd for $C_{26}H_{21}OS_2^+$: 413.1028; found: 413.1036.

General procedure for the generation of QPS by visible-light

(PC 1)

To a 4 mL vial containing thianthrenium salts (0.1 mmol) and $PR_1R_2R_3$ (0.15 mmol) was added acetonitrile (1 mL) by syringe. Then the mixture was stirred at room temperature utilizing purple LED until completion of the reaction determined by TLC analysis. The crude product was directly purified by flash chromatography on silica gel (eluent: DCM/MeOH v/v 100:1-20:1) to afford the compounds.

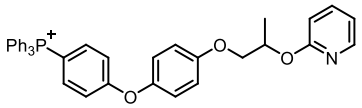
The gram scale synthesis



To a 100 mL flask was added thianthrenium salts (1.6 mmol, 920mg) and PPh_3 (2.4 mmol), then injected acetonitrile (16 mL) by syringe. After that, the mixture was stirred at room temperature utilizing purple LED until completion of the reaction determined by TLC analysis. The crude product was directly purified by flash chromatography on silica gel (eluent: DCM/MeOH v/v 100:1-20:1) to afford 81% yield (802 mg).

Characterization data of the products

Triphenyl(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)phosphonium (2)



The compound was prepared according to the **PC 1**. Pale yellow solid; 95% yield (60.4 mg).

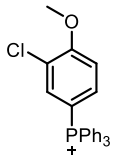
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15-8.13 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.89-7.85 (m, 3H), 7.78-7.73 (td, *J* = 8.0, 4.0 Hz, 6H), 7.65-7.60 (dd, *J* = 12.8, 8.0 Hz, 6H), 7.57-7.55 (m, 1H), 7.51-7.46 (dd, *J* = 12.0, 8.6 Hz, 2H), 7.19-7.16 (dd, *J* = 8.8, 2.6 Hz, 2H), 7.06-7.04 (d, *J* = 8.8 Hz, 2H), 7.00-6.98 (d, *J* = 8.8 Hz, 2H), 6.88-6.85 (m, 1H), 6.75-6.73 (d, *J* = 8.4 Hz, 1H), 5.61-5.54 (m, 1H), 4.22-4.18 (m, 1H), 4.10-4.07 (m, 1H), 1.48-1.47 (d, *J* = 6.4 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.5.

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.1, 163.2, 156.8, 147.3, 146.8, 138.8, 136.7 (d, *J* = 11.8 Hz), 135.7 (d, *J* = 2.7 Hz), 134.4 (d, *J* = 10.2 Hz), 130.8 (d, *J* = 13.0 Hz), 122.1, 118.4 (d, *J* = 14.1 Hz), 118.1 (d, *J* = 90.2 Hz), 116.9, 116.4, 111.7, 108.6 (d, *J* = 95.7 Hz), 71.1, 69.2, 17.0.

HRMS (ESI) *m/z* calcd for $C_{38}H_{33}NO_3P^+$: 582.2193; found: 582.2209.

(3-chloro-4-methoxyphenyl)triphenylphosphonium (3)



The compound was prepared according to the **PC 1**. Pale yellow solid; 86% yield (47.3 mg).

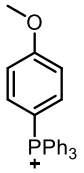
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.84 (m, 3H), 7.76-7.72 (td, *J* = 8.0, 3.6 Hz, 6H), 7.64-7.63 (m, 1H), 7.59-7.55 (m, 6H), 7.50-7.47 (dd, *J* = 8.8, 3.2 Hz, 1H), 7.39-7.36 (dd, *J* = 12.4, 2.2 Hz, 1H), 4.04 (s, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.9.

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.0 (d, *J* = 2.6 Hz), 136.0 (d, *J* = 10.9 Hz), 135.9 (d, *J* = 2.8 Hz), 134.7 (d, *J* = 12.8 Hz), 134.4 (d, *J* = 10.4 Hz), 130.9 (d, *J* = 12.9 Hz), 125.3 (d, *J* = 17.7 Hz), 117.8 (d, *J* = 90.2 Hz), 115.0 (d, *J* = 15.0 Hz), 108.1 (d, *J* = 96.4 Hz), 57.3.

HRMS (ESI) *m/z* calcd for $C_{25}H_{21}ClOP^+$: 403.1013; found: 403.1041.

(4-methoxyphenyl)triphenylphosphonium (4)



The compound was prepared according to the **PC 1**. Pale yellow solid; 96% yield (43.8 mg).

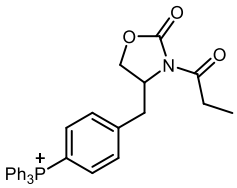
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.82 (dd, *J* = 8.6, 6.4 Hz, 3H), 7.74-7.70 (td, *J* = 7.8, 3.6 Hz, 6H), 7.65-7.64 (m, 1H), 7.62-7.55 (dd, *J* = 12.8, 7.8 Hz, 6H), 7.51-7.50 (m, 1H), 7.46-7.43 (d, *J* = 7.6, 2.6 Hz, 1H), 7.24-7.22 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.93 (s, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.4.

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.4, 136.5 (d, *J* = 11.9 Hz), 135.5 (d, *J* = 3.0 Hz), 134.3 (d, *J* = 10.3 Hz), 132.1 (d, *J* = 9.9 Hz), 130.6 (d, *J* = 12.8Hz), 128.5 (d, *J* = 12.1 Hz), 118.3 (d, *J* = 90.0 Hz), 116.6 (d, *J* = 14.1 Hz), 106.5 (d, *J* = 97.4 Hz), 56.2.

HRMS (ESI) *m/z* calcd for $C_{25}H_{22}OP^+$: 369.1403; found: 369.1415.

(4-((2-oxo-3-propionyloxazolidin-4-yl)methyl)phenyl)triphenylphosphonium (5)



The compound was prepared according to the **PC 1**. Pale yellow solid; 67% yield (39 mg).

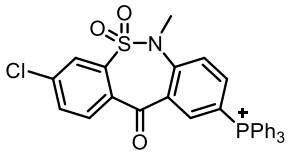
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.85 (m, 3H), 7.78-7.73 (td, *J* = 7.8, 3.6 Hz, 6H), 7.66-7.60 (m, 8H), 7.58-7.53 (dd, *J* = 12.8, 8.0 Hz, 2H), 4.85-4.79 (m, 1H), 4.44-4.40 (dd, *J* = 9.8, 7.8 Hz, 1H), 4.31-4.28 (dd, *J* = 9.8, 2.4 Hz, 1H), 3.42-3.37 (dd, *J* = 13.4, 3.6 Hz, 1H), 3.09-3.04 (dd, *J* = 13.4, 8.4 Hz, 1H), 2.97-2.84 (m, 2H), 1.17-1.13 (t, *J* = 7.2 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.9.

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.0, 153.7, 144.8, 135.7 (d, *J* = 3.0 Hz), 134.8 (d, *J* = 10.7 Hz), 134.5 (d, *J* = 10.3 Hz), 131.9 (d, *J* = 13.5 Hz), 130.7 (d, *J* = 13.0 Hz), 117.7 (d, *J* = 89.4 Hz), 115.8 (d, *J* = 91.2 Hz), 67.0, 54.8, 38.0, 29.1, 8.3.

HRMS (ESI) *m/z* calcd for $C_{31}H_{29}NO_3P^+$: 494.1880; found: 494.1881.

(3-chloro-6-methyl-5,5-dioxido-11-oxo-6,11-dihydrodibenzo[c,f][1,2]thiazepin-9-yl)triphenylphosphonium (6)



The compound was prepared according to the **PC 1**. Pale yellow solid; 72% yield (44.6 mg).

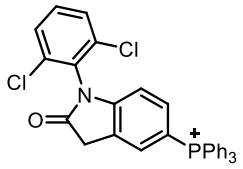
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43-8.39 (d, *J* = 14.0 Hz, 1H), 7.88-7.83 (m, 5H), 7.80-7.73 (m, 8H), 7.68-7.63 (dd, *J* = 13.0, 8.0 Hz, 7H), 3.57 (s, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.7.

^{13}C NMR (101 MHz, $CDCl_3$): δ 189.0, 147.2, 139.5 (d, *J* = 11.4 Hz), 139.1, 138.4 (d, *J* = 13.1 Hz), 138.0, 135.9 (d, *J* = 2.6 Hz), 134.6 (d, *J* = 10.5 Hz), 134.1, 134.0, 133.4, 130.9 (d, *J* = 13.0 Hz), 130.7, 126.0 (d, *J* = 13.0 Hz), 124.6, 117.4 (d, *J* = 89.9 Hz), 113.3 (d, *J* = 94.9 Hz), 38.3.

HRMS (ESI) *m/z* calcd for $C_{32}H_{24}ClNO_3PS^+$: 568.0898; found: 568.0906.

(1-(2,6-dichlorophenyl)-2-oxoindolin-5-yl)triphenylphosphonium (7)



The compound was prepared according to the **PC 1**. Pale yellow solid; 52% yield (32.7 mg).

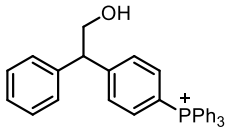
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.83 (t, *J* = 7.6 Hz, 3H), 7.77-7.72 (m, 7H), 7.66-7.60 (dd, *J* = 13.0, 7.8 Hz, 6H), 7.51-7.49 (d, *J* = 8.0 Hz, 2H), 7.43-7.38 (m, 2H), 6.66-6.64 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 2H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 23.9.

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.8, 149.7, 135.8, 135.7, 135.6, 135.2, 134.5 (d, *J* = 10.3 Hz), 131.7, 130.8 (d, *J* = 12.9 Hz), 129.3, 129.2, 127.6 (d, *J*=15.0 Hz), 118.0 (d, *J* = 89.9 Hz), 110.7 (d, *J* = 3.1 Hz), 110.2 (d, *J* = 84.2 Hz), 35.3.

HRMS (ESI) *m/z* calcd for $C_{32}H_{23}Cl_2NOP^+$: 538.0889; found: 538.0890.

(4-(2-hydroxy-1-phenylethyl)phenyl)triphenylphosphonium (8)



The compound was prepared according to the **PC 1**. Pale yellow solid; 53% yield (29.1 mg).

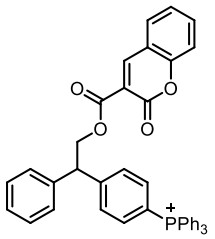
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (m, 3H), 7.73-7.67 (m, 9H), 7.61-7.55 (m, 7H), 7.50-7.45 (dd, *J* = 12.8, 8.0 Hz, 2H), 7.29-7.25 (m, 3H), 7.22-7.20 (m, 1H), 4.38-4.35 (m, 1H), 4.26-4.22 (m, 1H), 4.16-4.12 (m, 1H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 23.4.

^{13}C NMR (101 MHz, $CDCl_3$): δ 151.6, 140.5, 135.6 (d, *J* = 3.2 Hz), 134.4 (d, *J* = 10.3 Hz), 134.4 (d, *J* = 10.7 Hz), 131.1 (d, *J* = 13.2 Hz), 130.6 (d, *J* = 12.9 Hz), 128.7 (d, *J* = 36.3 Hz), 128.5 (d, *J* = 38.5 Hz), 127.1, 117.8 (d, *J* = 89.6 Hz), 114.3 (d, *J* = 91.6 Hz), 65.3, 53.7.

HRMS (ESI) *m/z* calcd for $C_{32}H_{28}OP^+$: 459.1872; found: 459.1888.

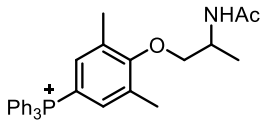
(4-(2-((2-oxo-2H-chromene-3-carbonyl)oxy)-1-phenylethyl)phenyl)triphenylphosphonium (9)



The compound was prepared according to the **PC 1**. Pale yellow solid; 67% yield (48.1 mg).

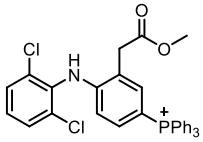
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 7.86-7.82 (m, 3H), 7.81-7.78 (m, 1H), 7.74-7.69 (m, 7H), 7.63-7.53 (m, 11H), 7.34-7.31 (m, 5H), 4.98-4.92 (m, 1H), 4.88-4.84 (m, 1H), 4.78-4.74 (dd, *J* = 8.6, 5.6 Hz, 1H).
^{31}P NMR (162 MHz, $CDCl_3$): δ 22.3.
^{13}C NMR (101 MHz, $CDCl_3$): δ 162.8, 156.9, 155.2, 150.1, 149.9, 139.1, 135.8 (d, *J* = 2.6 Hz), 134.8, 134.7, 134.5 (d, *J* = 10.3 Hz), 131.1 (d, *J* = 13.2 Hz), 130.8 (d, *J* = 12.9 Hz), 130.5, 129.2, 128.5, 127.7, 125.2, 118.0, 117.7 (d, *J* = 89.7 Hz), 117.3, 116.5, 115.4 (d, *J* = 91.1 Hz), 67.3, 49.9.
HRMS (ESI) *m/z* calcd for $C_{42}H_{32}O_4P^+$: 631.2033; found: 631.2035.

(4-(2-acetamidopropoxy)-3,5-dimethylphenyl)triphenylphosphonium (10)



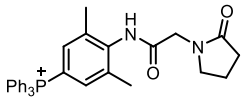
The compound was prepared according to the **PC 1**. Pale yellow solid; 72% yield (41.2 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.86 (m, 3H), 7.78-7.73 (td, *J* = 8.0, 3.6 Hz, 6H), 7.65-7.59 (m, 6H), 7.14-7.10 (d, *J* = 16.0 Hz, 2H), 6.64-6.62 (d, *J* = 8.6 Hz, 1H), 4.46-4.39 (dq, *J* = 8.4, 6.0 Hz, 1H), 4.02-3.92 (m, 2H), 2.33 (s, 6H), 1.98 (s, 3H), 1.31-1.33 (d, *J* = 6.8 Hz, 3H).
^{31}P NMR (162 MHz, $CDCl_3$): δ 22.5.
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 162.6, 135.6 (d, *J* = 2.7 Hz), 135.0 (d, *J* = 11.0 Hz), 134.6 (d, *J* = 14.5 Hz), 134.4 (d, *J* = 10.3 Hz), 130.7 (d, *J* = 12.8 Hz), 118.3 (d, *J* = 89.5 Hz), 110.2 (d, *J* = 92.8 Hz), 75.1, 45.5, 23.3, 17.4, 17.1.
HRMS (ESI) *m/z* calcd for $C_{31}H_{33}NO_2P^+$: 482.2243; found: 482.2248.

(4-((2,6-dichlorophenyl)amino)-3-(2-methoxy-2-oxoethyl)phenyl)triphenylphosphonium (11)



The compound was prepared according to the **PC 1**. Pale yellow solid; 50% yield (32.9 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.86 (m, 3H), 7.78-7.73 (td, *J* = 7.8, 3.6 Hz, 6H), 7.64-7.58 (m, 6H), 7.52 (s, 1H), 7.44-7.42 (d, *J* = 8.0 Hz, 2H), 7.41-7.37 (m, 1H), 7.26-7.23 (m, 1H), 7.21-7.17 (m, 1H), 6.62-6.59 (dd, *J* = 8.6, 3.2 Hz, 1H), 3.84 (s, 2H), 3.78 (s, 3H).
^{31}P NMR (162 MHz, $CDCl_3$): δ 22.2.
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.7, 149.8, 137.1 (d, *J* = 11.9 Hz), 135.6 (d, *J* = 2.6 Hz), 134.9 (d, *J* = 11.1 Hz), 134.5 (d, *J* = 5.6 Hz), 134.4 (d, *J* = 10.3 Hz), 132.2, 130.7 (d, *J* = 12.8 Hz), 129.2, 127.5, 123.8 (d, *J* = 14.0 Hz), 118.4 (d, *J* = 90.1 Hz), 116.7 (d, *J* = 14.2 Hz), 105.5 (d, *J* = 97.9 Hz), 53.1, 38.6.
HRMS (ESI) *m/z* calcd for $C_{33}H_{27}Cl_2NO_2P^+$: 570.1151; found: 570.1154.

(3,5-dimethyl-4-(2-(2-oxopyrrolidin-1-yl)acetamido)phenyl)triphenylphosphonium (12)



The compound was prepared according to the **PC 1**. Pale yellow solid; 57% yield (33.5 mg).

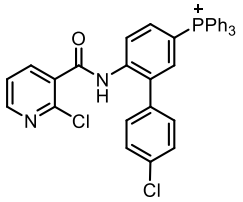
^{1}H NMR (400 MHz, Methanol-d_4): δ 7.94-7.89 (m, 3H), 7.79-7.70 (m, 12H), 7.44-7.40 (d, J = 16.0 Hz, 2H), 4.23 (s, 2H), 3.61-3.57 (m, 1H), 2.45-2.41 (m, 1H), 2.27 (s, 6H), 2.13-2.09 (m, 2H).

^{31}P NMR (162 MHz, Methanol-d_4): δ 23.2.

^{13}C NMR (101 MHz, DMSO-d_6): δ 175.2, 167.0, 142.2 (d, J = 3.6 Hz), 138.3 (d, J = 14.0 Hz), 135.8 (d, J = 2.8 Hz), 135.0 (d, J = 10.5 Hz), 134.0 (d, J = 10.9 Hz), 130.9 (d, J = 12.8 Hz), 118.3 (d, J = 89.2 Hz), 115.5 (d, J = 89.7 Hz), 63.3, 47.9, 30.4, 18.9, 18.0.

HRMS (ESI) *m/z* calcd for $C_{32}H_{32}N_2O_2P^+$: 507.2196; found: 507.2204.

(4'-chloro-6-(2-chloronicotinamido)-[1,1'-biphenyl]-3-yl)triphenylphosphonium (13)



The compound was prepared according to the **PC 1**. Pale yellow solid; 63% yield (43.8 mg).

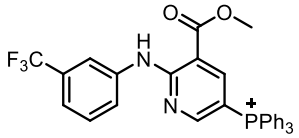
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.73-8.70 (dd, J = 8.6, 3.2 Hz, 1H), 8.39-8.37 (dd, J = 4.8, 2.0 Hz, 1H), 8.12-8.09 (dd, J = 8.0, 2.0 Hz, 1H), 7.91-7.86 (m, 3H), 7.80-7.75 (td, J = 8.0, 3.8 Hz, 7H), 7.71-7.65 (m, 6H), 7.63-7.57 (ddd, J = 12.4, 8.6, 2.2 Hz, 1H), 7.40 (d, J = 2.8 Hz, 4H), 7.38-7.36 (m, 1H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.7.

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.5, 151.6, 146.8, 141.6 (d, J = 3.1 Hz), 140.0, 135.9 (d, J = 2.7 Hz), 135.5, 134.9 (d, J = 10.5 Hz), 134.5 (d, J = 10.4 Hz), 134.0, 132.1 (d, J = 10.0 Hz), 130.9 (d, J = 12.9 Hz), 130.8, 130.5, 129.8, 128.6 (d, J = 12.1 Hz), 124.0 (d, J = 13.3 Hz), 123.2, 117.6 (d, J = 89.8 Hz), 112.8 (d, J = 92.8 Hz).

HRMS (ESI) m/z calcd for $C_{36}H_{26}Cl_2N_2OP^+$: 603.1154; found: 603.1175.

(5-(methoxycarbonyl)-6-((3-(trifluoromethyl)phenyl)amino)pyridin-3-yl)triphenylphosphonium (14)



The compound was prepared according to the **PC 1**. Pale yellow solid; 86% yield (59.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.95 (s, 1H), 8.44-8.40 (dd, J = 12.0, 2.4 Hz, 1H), 8.36-8.34 (dd, J = 6.0, 2.4 Hz, 1H), 8.01 (s, 1H), 7.93-7.89 (m, 3H), 7.82-7.78 (td, J =

8.0, 3.8 Hz, 6H), 7.70-7.65 (m, 7H), 7.50-7.48 (d, *J* = 8.0 Hz, 1H), 7.43-7.41 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 3H).

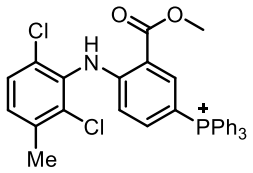
^{19}F NMR (376 MHz, $CDCl_3$): δ -62.6, -78.2, -153.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ 20.0.

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 158.2, 157.6 (d, *J* = 13.8 Hz), 145.2 (d, *J* = 11.0 Hz), 138.1, 136.0 (d, *J* = 2.8 Hz), 134.4 (d, *J* = 10.6 Hz), 131.4 (d, *J* = 32.6 Hz), 131.0 (d, *J* = 13.1 Hz), 130.6 (dd, *J* = 13.0, 9.2 Hz), 129.7, 125.8, 120.5 (dd, *J* = 257.6, 3.9 Hz), 117.3 (d, *J* = 90.7 Hz), 108.9 (d, *J* = 10.2 Hz), 101.3 (d, *J* = 99.6 Hz), 53.5.

HRMS (ESI) *m/z* calcd for $C_{32}H_{25}F_3N_2O_2P^+$: 557.1600; found: 557.1605.

(4-((2,6-dichloro-3-methylphenyl)amino)-3-(methoxycarbonyl)phenyl)triphenylphosphonium (15)



The compound was prepared according to the **PC 1**. Pale yellow solid; 89% yield (59 mg).

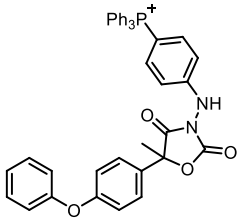
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 8.19-8.15 (dd, *J* = 13.4, 2.2 Hz, 1H), 7.93-7.88 (m, 3H), 7.80-7.75 (td, *J* = 8.0, 3.6 Hz, 6H), 7.65-7.59 (m, 6H), 7.38-7.32 (m, 2H), 7.28-7.23 (t, *J* = 9.6 Hz, 1H), 6.57-6.54 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.90 (s, 3H), 2.42 (s, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.2.

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.1, 151.5, 137.8 (d, *J* = 12.6 Hz), 137.1 (d, *J* = 11.6 Hz), 136.1, 134.7 (d, *J* = 3.0 Hz), 133.3, 133.2 (d, *J* = 10.4 Hz), 131.5, 130.2, 129.7 (d, *J* = 12.9 Hz), 129.5, 127.1, 117.0 (d, *J* = 90.4 Hz), 114.8 (d, *J* = 13.0 Hz), 111.5 (d, *J* = 13.7 Hz), 101.0 (d, *J* = 101.0 Hz), 51.8, 19.5.

HRMS (ESI) *m/z* calcd for $C_{33}H_{27}Cl_2NO_2P^+$: 570.1151; found: 570.1159.

(4-((5-methyl-2,4-dioxo-5-(4-phenoxyphenyl)oxazolidin-3-yl)amino)phenyl)triphenylphosphonium (16)



The compound was prepared according to the **PC 1**. Pale yellow solid; 70% yield (50.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.87-7.82 (m, 3H), 7.72-7.68 (td, *J* = 8.0, 3.6 Hz, 6H), 7.58-7.54 (m, 5H), 7.52-7.49 (m, 3H), 7.35-7.29 (m, 4H), 7.15-7.11 (m, 1H), 7.01-6.96 (m, 6H), 1.98 (s, 3H).

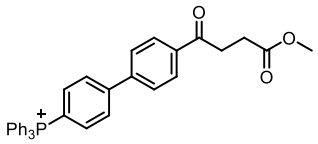
^{31}P NMR (162 MHz, $CDCl_3$): δ 22.3.

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.5, 158.4, 156.3, 152.1, 151.7, 136.0 (d, *J* = 11.9 Hz), 135.6, 134.3 (d, *J* = 10.3 Hz), 132.2, 130.6 (d, *J* = 12.8 Hz), 130.0, 126.3, 124.1,

119.5, 118.7, 118.5 (d, J = 90.1 Hz), 114.0 (d, J = 13.9 Hz), 105.3 (d, J = 98.9 Hz), 85.3, 25.4 .

HRMS (ESI) *m/z* calcd for $C_{40}H_{32}N_2O_4P^+$: 635.2094; found: 635.2109.

(4'-(4-methoxy-4-oxobutanoyl)-[1,1'-biphenyl]-4-yl)triphenylphosphonium (17)



The compound was prepared according to the **PC 1**. Pale yellow solid; 64% yield (39.8 mg).

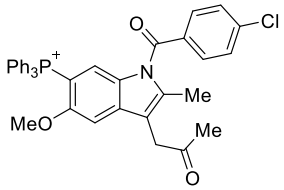
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.09 (m, 2H), 8.02-7.99 (dd, J = 8.4, 3.2 Hz, 2H), 7.91-7.87 (m, 3H), 7.81-7.76 (td, J = 8.0, 3.4 Hz, 10H), 7.71-7.65 (m, 6H), 3.71 (s, 3H), 3.37-3.34 (t, J = 6.4 Hz, 2H), 2.81-2.78 (t, J = 6.4 Hz, 2H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.9.

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.8, 173.3, 146.9, 142.8, 136.7, 135.9 (d, J = 2.7 Hz), 135.2 (d, J = 10.7 Hz), 134.5 (d, J = 10.3 Hz), 130.9 (d, J = 12.9 Hz), 129.4 (d, J = 13.3 Hz), 129.0, 127.9, 117.6 (d, J = 89.7 Hz), 116.8 (d, J = 90.7 Hz), 51.9, 33.6, 28.1.

HRMS (ESI) *m/z* calcd for $C_{35}H_{30}O_3P^+$: 529.1927; found: 529.1933.

(1-(4-chlorobenzoyl)-5-methoxy-3-(2-methoxy-2-oxoethyl)-2-methyl-1H-indol-6-yl)triphenylphosphonium (18)



The compound was prepared according to the **PC 1**. Pale yellow solid; 78% yield (56.2 mg).

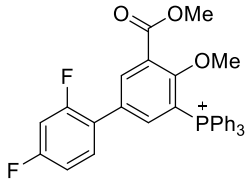
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.75 (m, 3H), 7.66-7.61 (td, J = 8.0, 3.6 Hz, 7H), 7.57-7.55 (m, 2H), 7.52-7.46 (m, 6H), 7.37-7.34 (m, 3H), 3.82 (s, 2H), 3.76 (s, 3H), 3.56 (s, 3H), 2.43 (s, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 23.1.

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.1, 167.4, 157.3, 142.3, 140.4, 137.9, 134.9, 133.8 (d, J = 10.3 Hz), 132.2, 132.1, 131.5, 130.2 (d, J = 13.0 Hz), 129.6, 121.2 (d, J = 12.9 Hz), 119.0 (d, J = 92.1 Hz), 113.2, 102.9 (d, J = 7.3 Hz), 99.9 (d, J = 99.0 Hz), 56.6, 52.5, 29.8, 13.4.

HRMS (ESI) *m/z* calcd for $C_{38}H_{32}ClNO_4P^+$: 632.1752; found: 632.1763.

(2',4'-difluoro-4-methoxy-5-(methoxycarbonyl)-[1,1'-biphenyl]-3-yl)triphenylphosphonium (19)



The compound was prepared according to the **PC 1**. Pale yellow solid; 87% yield (59.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37-8.36 (m, 1H), 7.98-7.85 (m, 3H), 7.79-7.75 (td, *J* = 8.0, 3.8 Hz, 6H), 7.71-7.66 (m, 6H), 7.50-7.44 (td, *J* = 8.8, 6.2 Hz, 1H), 7.40-7.36(ddd, *J* = 14.8, 2.4, 1.2 Hz, 1H), 7.01-6.97 (td, *J* = 8.0, 1.6 Hz, 1H), 6.87-6.82 (ddd, *J* = 12.0, 8.8, 2.4 Hz, 1H), 3.99 (s, 3H), 3.11 (s, 3H).

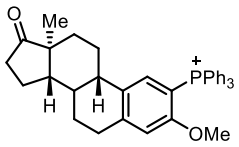
^{19}F NMR (376 MHz, $CDCl_3$): δ -108.3, -114.7, -153.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.9.

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.8 (d, *J* = 2.6 Hz), 163.1 (dd, *J*=251.8, 12.0), 161.7 (d, *J* = 2.2 Hz), 159.5 (dd, *J* = 250.4, 11.7 Hz), 140.4, 139.4 (dd, *J* = 10.2, 4.0 Hz), 135.5 (d, *J* = 2.7 Hz), 134.1 (d, *J* = 10.6 Hz), 131.8 (dd, *J* = 9.9, 3.9 Hz), 131.7 (d, *J* = 14.0 Hz), 130.8 (d, *J* = 13.2 Hz), 124.6 (d, *J* = 7.2 Hz), 121.5 (dd, *J* = 12.6, 3.8 Hz), 118.0 (d, *J* = 91.8 Hz), 113.8 (d, *J* = 94.2 Hz), 112.8 (dd, *J* = 21.6, 3.5 Hz), 104.6 (t, *J* = 25.9 Hz), 62.1, 53.3.

HRMS (ESI) *m/z* calcd for $C_{33}H_{26}F_2O_3P^+$: 539.1582; found: 539.1597.

((9S,13S,14S)-3-methoxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)triphenylphosphonium (20)



The compound was prepared according to the **PC 1**. Pale yellow solid; 48% yield (30.1 mg).

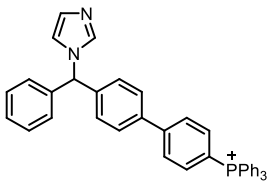
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.82 (m, 3H), 7.74-7.70 (m, 6H), 7.61-7.56 (m, 6H), 7.10-7.08 (d, *J* = 6.2 Hz, 1H), 6.87-6.83 (d, *J* = 16.0 Hz, 1H), 3.58 (s, 3H), 3.13-3.10 (m, 2H), 2.53-2.46 (dd, *J* = 18.6, 8.8 Hz, 1H), 2.17-2.03 (m, 4H), 1.81-1.78 (m, 1H), 1.69-1.56 (m, 5H), 1.49-1.43 (m, 2H), 0.87 (s, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.5.

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.8, 149.7, 135.0 (d, *J* = 3.0 Hz), 134.8 (d, *J* = 12.4 Hz), 133.8 (d, *J* = 10.5 Hz), 132.7 (d, *J* = 9.7 Hz), 132.1 (d, *J* = 10.1 Hz), 130.3 (d, *J* = 13.1 Hz), 118.9 (d, *J* = 91.7 Hz), 114.2 (d, *J* = 7.0 Hz), 101.7 (d, *J* = 95.7 Hz), 56.4, 50.2, 47.7, 43.5, 37.6, 35.8, 31.3, 30.2, 25.9, 25.2, 21.5, 13.8.

HRMS (ESI) *m/z* calcd for $C_{37}H_{38}O_2P^+$: 546.2688; found: 546.2693.

(4'-((1H-imidazol-1-yl)(phenyl)methyl)-[1,1'-biphenyl]-4-yl)triphenylphosphonium (21)



The compound was prepared according to the **PC 1**. Pale yellow solid; 60% yield (39.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.91 (m, 2H), 7.87-7.83 (t, *J* = 7.6 Hz, 3H), 7.76-7.71 (m, 7H), 7.65-7.60 (m, 9H), 7.43 (s, 1H), 7.35-7.33 (d, *J* = 6.6 Hz, 3H), 7.22-

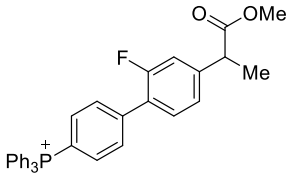
7.20(d, *J* = 8.0 Hz, 2H), 7.13-7.11 (d, *J* = 6.8 Hz, 2H), 7.06 (s, 1H), 6.87 (s, 1H), 6.59 (s, 1H)

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.9.

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.6, 147.5 (d, *J* = 3.0 Hz), 140.4, 138.7, 138.4, 137.4, 135.8 (d, *J* = 2.5 Hz), 135.1 (d, *J* = 10.7 Hz), 134.5 (d, *J* = 10.3 Hz), 130.8 (d, *J* = 12.9 Hz), 129.4, 129.3, 129.1, 129.0 (d, *J* = 10.3 Hz), 128.7, 128.2 (d, *J* = 15.5 Hz), 119.5, 117.7 (d, *J* = 89.6 Hz), 116.0 (d, *J* = 91.3 Hz), 64.7.

HRMS (ESI) *m/z* calcd for $C_{40}H_{32}N_2P^+$: 571.2298; found: 571.2300.

(2'-fluoro-4'-(1-methoxy-1-oxopropan-2-yl)-[1,1'-biphenyl]-4-yl)triphenylphosphonium (22)



The compound was prepared according to the **PC 1**. Pale yellow solid; 92% yield (55.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 7.92-7.88 (m, 5H), 7.81-7.76 (td, *J* = 8.0, 3.8 Hz, 6H), 7.71-7.64 (m, 8H), 7.55-7.51 (t, *J* = 8.0 Hz, 1H), 7.24-7.22 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.19-7.15 (dd, *J* = 12.0, 1.8 Hz, 1H), 3.82-3.76 (m, 1H), 3.70 (s, 3H), 1.55-1.53 (d, *J* = 8.0 Hz, 3H).

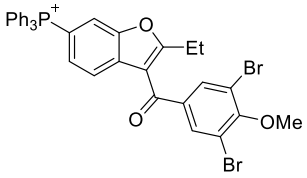
^{19}F NMR (376 MHz, $CDCl_3$, 25 °C, δ): -117.0, -153.8.

^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, δ): 22.9.

^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, δ): 174.2 , 161.0 , 158.5 , 144.2 (d, *J* = 7.9 Hz), 143.0 , 135.9 (d, *J* = 2.6 Hz), 134.7 (d, *J* = 10.7 Hz), 134.5 (d, *J* = 10.3 Hz), 131.1 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 12.9 Hz), 125.1 (d, *J* = 12.8 Hz), 124.5 (d, *J* = 2.9 Hz), 117.6 (d, *J* = 89.6 Hz), 116.4 (d, *J* = 90.7 Hz), 115.6 (d, *J* = 23.2 Hz), 52.4 , 45.0 , 18.4 .

HRMS (ESI) *m/z* calcd for $C_{34}H_{29}FO_2P^+$: 519.1884; found: 519.1888.

(3-(3,5-dibromo-4-methoxybenzoyl)-2-ethylbenzofuran-6-yl)triphenylphosphonium (23)



The compound was prepared according to the **PC 1**. Pale yellow solid; 86% yield (67.3 mg).

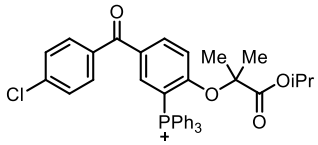
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 7.98 (s, 2H), 7.93-7.90 (m, 3H), 7.88-7.86 (dd, *J* = 8.2, 3.2 Hz, 1H), 7.82-7.77 (td, *J* = 8.0, 3.6 Hz, 6H), 7.75-7.71 (dd, *J* = 13.8, 1.6 Hz, 1H), 7.70-7.65 (m, 6H), 7.50-7.44 (ddd, *J* = 12.4, 8.2, 1.6 Hz, 1H), 3.98 (s, 3H), 2.94-2.88 (q, *J* = 7.5 Hz, 2H), 1.39-1.36 (t, *J* = 7.4 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, δ): 24.3.

^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, δ): 187.0, 170.7, 158.4, 153.4 (d, *J* = 19.6 Hz), 136.3, 135.9 (d, *J* = 3.2 Hz), 134.5 (d, *J* = 10.3 Hz), 133.5, 133.4 (d, *J* = 2.7 Hz, 130.8

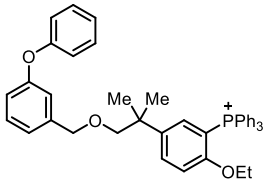
(d, *J* = 13.0 Hz), 129.1 (d, *J* = 10.9 Hz), 123.4 (d, *J* = 14.9 Hz), 118.9 , 117.9 (d, *J* = 12.5 Hz), 117.6 (d, *J* = 89.9 Hz), 115.7, 113.0 (d, *J* = 93.1 Hz), 61.0, 22.5, 11.9.
HRMS (ESI) *m/z* calcd for $C_{36}H_{28}Br_2O_3P^+$: 697.0137; found: 697.0141.

(5-(4-chlorobenzoyl)-2-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)triphenylphosphonium (24)



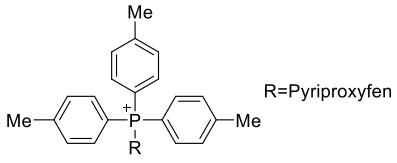
The compound was prepared according to the **PC 1**. Pale yellow solid; 57% yield (40.2 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22-8.19 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.86-7.83 (m, 3H), 7.78-7.75 (m, 5H), 7.74-7.67 (m, 10H), 7.44-7.42 (d, *J* = 8.0 Hz, 2H), 6.94-6.89 (dd, *J* = 8.8, 5.4 Hz, 1H), 5.14-5.04 (m, 1H), 1.28-1.26 (d, *J* = 6.2 Hz, 6H), 1.10 (s, 6H).
^{31}P NMR (162 MHz, $CDCl_3$): δ 23.1.
^{13}C NMR (101 MHz, $CDCl_3$): δ 192.5, 171.1, 161.0, 139.6, 139.5, 139.2, 139.1, 135.4 (d, *J* = 3.1 Hz), 134.7, 134.2, 131.4, 130.5 (d, *J* = 13.3 Hz), 129.0, 117.7 (d, *J* = 91.6 Hz), 115.6 (d, *J* = 6.0 Hz), 107.7 (d, *J* = 93.5 Hz), 82.1, 70.6, 24.4, 21.7.
HRMS (ESI) *m/z* calcd for $C_{38}H_{35}ClO_4P^+$: 621.1956; found: 621.1958.

(3-(3-((2-(4-ethoxyphenyl)-2-methylpropoxy)methyl)phenoxy)phenyl)triphenylphosphonium (25)



The compound was prepared according to the **PC 1**. Pale yellow solid; 81% yield (59.2 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.77 (m, 4H), 7.67-7.64 (m, 6H), 7.57-7.52 (dd, *J* = 13.4, 8.0 Hz, 6H), 7.32-7.27 (m, 2H), 7.19-7.15 (dd, *J* = 8.8, 6.6 Hz, 2H), 7.10-7.06 (t, *J* = 7.4 Hz,1H), 7.03-6.98 (dd, *J* = 16.0, 2.4 Hz, 1H), 6.92-6.90 (d, *J* = 8.0 Hz, 2H), 6.85-6.81 (t, *J* = 8.2 Hz, 2H), 6.75 (s, 1H), 4.27 (s, 2H), 3.89 (m, 2H), 3.27 (s, 2H), 1.13 (s, 6H), 0.64-0.61 (t, *J* = 6.0 Hz, 3H).
^{31}P NMR (162 MHz, $CDCl_3$): δ 22.5.
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 157.3, 157.1, 141.9 (d, *J* = 11.8 Hz), 140.7, 136.9 (d, *J* = 2.0 Hz), 135.1 (d, *J* = 2.8 Hz), 133.9 (d, *J* = 10.6 Hz), 133.8, 130.3 (d, *J* = 13.1 Hz), 129.9, 129.7, 123.5, 121.9, 118.9, 118.7 (d, *J* = 91.7 Hz), 117.6, 117.4, 113.7 (d, *J* = 6.3 Hz), 104.1 (d, *J* = 93.3 Hz), 79.4, 72.5, 65.3, 38.9, 26.0, 13.6.
HRMS (ESI) *m/z* calcd for $C_{43}H_{42}O_3P^+$: 637.2866; found: 637.2896.

(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)tri-p-tolylphosphonium (26)



The compound was prepared according to the **PC 1**. Pale yellow solid; 65% yield (46.3 mg).

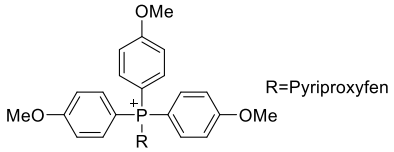
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14-8.12 (dd, *J* = 5.4, 2.0 Hz, 1H), 7.58-7.53 (m, 1H), 7.52-7.49 (m, 6H), 7.48-7.41 (m, 8H), 7.14-7.11 (dd, *J* = 8.8, 2.8 Hz, 2H), 7.04-7.02 (d, *J* = 8.8 H, 2H), 6.98-6.96 (d, *J* = 8.8 Hz, 2H), 6.86-6.83 (m, 1H), 6.74-6.71 (d, *J* = 8.4 Hz, 1H), 5.59-5.54 (m, 1H), 4.21-4.17 (m, 1H), 4.09-4.05 (m, 1H), 2.49 (s, 9H), 1.47-1.45 (d, *J* = 8.0 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 21.0.

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.7 , 163.1 , 156.7 , 147.3 , 147.0 (d, *J* = 2.9 Hz), 146.7 , 138.8 , 136.4 (d, *J* = 11.9 Hz), 134.2 (d, *J* = 10.7 Hz), 131.3 (d, *J* = 13.3 Hz), 122.0 , 118.1 (d, *J* = 13.9 Hz), 116.9 , 116.3 , 114.9 (d, *J* = 92.8 Hz), 111.7 , 109.6 (d, *J* = 96.2 Hz), 71.0 , 69.2 , 21.9 , 17.0 .

HRMS (ESI) *m/z* calcd for $C_{41}H_{39}NO_3P^+$: 624.2662; found: 624.2681.

Tris(4-methoxyphenyl)(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)phosphonium (27)



The compound was prepared according to the **PC 1**. Pale yellow solid; 63% yield (47.6 mg).

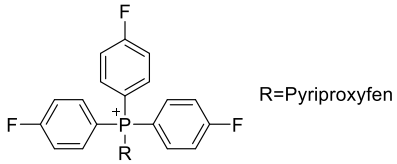
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-8.11 (m, 1H), 7.56-7.53 (t, *J* = 7.6 Hz, 1H), 7.49-7.38 (m, 8H), 7.20-7.16 (m, 6H), 7.12-7.08 (m, 2H), 7.03-7.01 (d, *J* = 8.4 Hz, 2H), 6.97-6.95 (d, *J* = 8.6 Hz, 2H), 6.85-6.82 (t, *J* = 6.2 Hz, 1H), 6.72-6.70 (d, *J* = 8.2 Hz, 1H), 5.58-5.54 (m, 1H), 4.20-4.16 (m, 1H), 4.08-4.04 (m, 1H), 3.91 (s, 9H), 1.46-1.44 (d, *J* = 8.0 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.3.

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.1 (d, *J* = 2.6 Hz), 164.6 (d, *J* = 2.8 Hz), 163.2 , 156.7 , 147.5 , 146.8 , 138.8 , 136.2 (d, *J* = 11.9 Hz), 122.0 , 118.1 (d, *J* = 13.9 Hz), 116.9 , 116.4 (d, *J* = 13.9 Hz), 116.3, 111.7 , 111.1 (d, *J* = 97.1 Hz), 108.9 (d, *J* = 98.5 Hz), 71.1 , 69.2 , 56.1 , 17.0 .

HRMS (ESI) *m/z* calcd for $C_{41}H_{39}NO_6P^+$: 672.2510; found: 672.2504.

Tris(4-fluorophenyl)(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)phosphonium (28)



The compound was prepared according to the **PC 1**. Pale yellow solid; 60% yield (50.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15-8.13 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.73-7.66 (m, 6H), 7.59-7.55 (ddd, *J* = 8.8, 7.2, 2.0 Hz, 1H), 7.49-7.42 (m, 8H), 7.19-7.16 (m, 2H), 7.06-7.04 (d, *J* = 8.8 Hz, 2H), 6.99-6.97 (d, *J* = 8.8 Hz, 2H), 6.88-6.85 (dd, *J* = 7.2, 5.0 Hz,

1H), 6.75-6.73 (d, *J* = 8.2 Hz, 1H), 5.60-5.56 (m, 1H), 4.22-4.18 (m, 1H), 4.10-4.07 (m, 1H), 1.48-1.47 (d, *J* = 6.4 Hz, 3H).

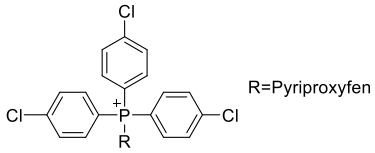
^{19}F NMR (376 MHz, $CDCl_3$): δ -98.7, -153.0.

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.5.

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.1 (dd, *J* = 261.5, 3.2 Hz), 165.2 (d, *J* = 2.9 Hz), 163.2, 156.8, 147.3, 146.8, 138.8, 137.4 (dd, *J* = 12.0, 10.0 Hz), 136.6 (d, *J* = 12.3 Hz), 134.6 (dd, *J* = 11.1, 9.4 Hz), 122.0, 118.7 (dd, *J* = 22.3, 14.4 Hz), 118.6 (d, *J* = 14.2 Hz), 116.9, 116.4, 116.2 (d, *J* = 21.2 Hz), 113.8 (dd, *J* = 95.1, 3.0 Hz), 111.7, 108.3 (d, *J* = 97.7 Hz), 71.1, 69.2, 17.0.

HRMS (ESI) *m/z* calcd for $C_{37}H_{28}F_3NO_3P^+$: 636.1910; found: 636.1924.

Tris(4-chlorophenyl)(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)phosphonium (29)



The compound was prepared according to the **PC 1**. Pale yellow solid; 54% yield (41.6 mg).

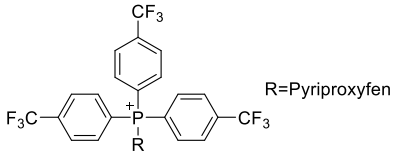
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15-8.13 (dd, *J* = 5.4, 2.0 Hz, 1H), 7.73-7.70 (dd, *J* = 8.6, 2.8 Hz, 6H), 7.63-7.58 (m, 6H), 7.57-7.55 (m, 1H), 7.49-7.44 (dd, *J* = 12.4, 8.8 Hz 2H), 7.19-7.16 (dd, *J* = 8.8, 2.8 Hz, 2H), 7.05-7.03 (d, *J* = 12.0 Hz, 2H), 6.99-6.96 (d, *J* = 12.0 Hz, 2H), 6.88-6.84 (ddd, *J* = 7.0, 5.0, 1.0 Hz, 1H), 6.75-6.73 (d, *J* = 8.4 Hz, 1H), 5.57 (m, 1H), 4.21-4.15 (m, 1H), 4.10-4.06 (m, 1H), 1.48-1.46 (d, *J* = 8.0 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.7.

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.4 , 163.2 , 156.8 , 147.2 , 146.8 , 143.2 (d, *J* = 3.5 Hz), 138.9 , 136.6 (d, *J* = 12.1 Hz), 135.8 (d, *J* = 11.6 Hz), 131.4 (d, *J* = 13.8 Hz), 122.0 , 118.7 (d, *J* = 14.2 Hz), 116.9 , 116.5, 116.0 (d, *J* = 93.1 Hz), 111.7 , 107.4 (d, *J* = 97.6 Hz), 71.1 , 69.3 , 17.0 .

HRMS (ESI) *m/z* calcd for $C_{38}H_{30}Cl_3NO_3P^+$: 684.1023; found: 684.1025.

(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)tris(4-(trifluoromethyl)phenyl)phosphonium (30)



The compound was prepared according to the **PC 1**. Pale yellow solid; 61% yield (53.2 mg).

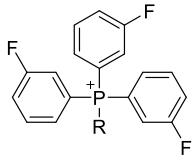
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-8.10 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.99-7.96 (m, 6H), 7.90-7.85 (dd, *J* = 12.8, 8.0 Hz, 6H), 7.56-7.47 (m, 3H), 7.21-7.18 (dd, *J* = 8.8, 3.0 Hz, 2H), 7.03-7.01 (d, *J* = 8.8 Hz, 2H), 6.96-6.94 (d, *J* = 8.8 Hz, 1H), 6.85-6.82 (dd, *J* = 7.2, 5.2 Hz, 1H), 6.72-6.70 (d, *J* = 8.4 Hz, 1H), 5.57-5.52 (m, 1H), 4.18-4.15 (m, 1H), 4.07-4.03 (m, 1H), 1.43-1.45 (d, *J* = 8.0 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.6, -152.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.3.

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.8, 163.1, 156.9, 147.1, 146.8, 138.9, 137.3 (dd, *J* = 33.7, 3.1 Hz), 136.9 (d, *J* = 12.4 Hz), 135.5 (d, *J* = 11.1 Hz), 127.8 (dd, *J* = 13.4, 3.3 Hz), 124.2(q, *J* = 273.2 Hz), 122.0, 121.5 (d, *J* = 89.5 Hz), 118.9 (d, *J* = 14.6 Hz), 116.9, 116.4, 111.7, 105.6 (d, *J* = 96.8 Hz), 71.1, 69.3, 17.0.
HRMS (ESI) *m/z* calcd for $C_{41}H_{30}F_9NO_3P^+$: 786.1814; found: 786.1819.

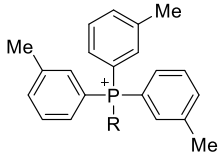
Tris(3-fluorophenyl)(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)phosphonium (31)



R=Pyriproxyfen

The compound was prepared according to the **PC 1**. Pale yellow solid; 52% yield (37.1 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.12 (m, 1H), 7.90-7.83 (m, 3H), 7.60-7.49 (m, 9H), 7.25-7.18 (m, 6H), 7.06-7.03 (m, 2H), 6.99-6.96 (m, 2H), 6.86-6.83 (t, *J* = 6.4 Hz, 1H), 6.73-6.71 (d, *J* = 8.2 Hz, 1H), 5.59-5.54 (m, 1H), 4.21-4.17 (m, 1H), 4.09-4.05 (m, 1H), 1.47-1.45 (d, *J* = 8.0 Hz, 1H).
^{19}F NMR (376 MHz, $CDCl_3$): δ -105.8, -153.2.
^{31}P NMR (162 MHz, $CDCl_3$): δ 22.8.
^{13}C NMR (101 MHz, $CDCl_3$): δ 165.7 (d, *J* = 3.0 Hz), 163.2, 163.1 (dd, *J* = 255.3, 18.5 Hz), 156.9, 147.1, 146.9, 138.8, 136.8 (d, *J* = 12.2 Hz), 133.8 (dd, *J* = 15.3, 7.8 Hz), 131.1 (dd, *J* = 9.9, 3.1 Hz), 123.6 (d, *J* = 22.6 Hz), 122.1, 120.8 (dd, *J* = 24.3, 12.0 Hz), 119.5 (dd, *J* = 91.3, 6.5 Hz), 118.8 (d, *J* = 14.6 Hz), 116.9, 116.4, 111.7, 106.3 (d, *J* = 97.1 Hz), 71.1, 69.2, 17.0.
HRMS (ESI) *m/z* calcd for $C_{38}H_{30}F_3NO_3P^+$: 636.1910; found: 636.1919.

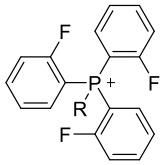
(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)tri-m-tolylphosphonium (32)



R=Pyriproxyfen

The compound was prepared according to the **PC 1**. Pale yellow solid; 30% yield (21.4 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.12 (m, 1H), 7.64-7.60 (m, 6H), 7.58-7.53 (m, 1H), 7.49-7.43 (ddd, *J* = 12.0, 8.8, 2.0 Hz, 2H), 7.40-7.30 (m, 6H), 7.17-7.15 (m, 2H), 7.06-7.03 (m, 2H), 6.99-6.96 (m, 2H), 6.86-6.83 (m, 1H), 6.73-6.71 (d, *J* = 8.4 Hz, 1H), 5.59-5.54 (m, 1H), 4.20-4.17 (m, 1H), 4.09-4.05 (m, 1H), 2.44 (s, 9H), 1.46-1.45 (d, *J* = 6.4 Hz, 3H).
^{31}P NMR (162 MHz, $CDCl_3$): δ 23.0.
^{13}C NMR (101 MHz, $CDCl_3$): δ 165.0, 163.2, 156.8, 147.3, 146.8, 141.1 (d, *J* = 12.7 Hz), 138.8, 136.6 (d, *J* = 11.9 Hz), 136.5 (d, *J* = 2.7 Hz), 134.3 (d, *J* = 10.3 Hz), 131.7 (d, *J* = 10.2 Hz), 130.6 (d, *J* = 13.6 Hz), 122.1, 118.3 (d, *J* = 14.0 Hz), 118.1 (d, *J* = 89.2 Hz), 116.9 , 116.4 , 109.0 (d, *J* = 95.5 Hz), 71.1, 69.2, 21.7, 17.0.
HRMS (ESI) *m/z* calcd for $C_{41}H_{39}NO_3P^+$: 624.2662; found: 624.2669.

Tris(2-fluorophenyl)(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)phosphonium (33)



R=Pyriproxyfen

The compound was prepared according to the **PC 1**. Pale yellow solid; 57% yield (41.3mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.11 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.89-7.92 (m, 3H), 7.60-7.47 (m, 9H), 7.43-7.37 (td, *J* = 9.2, 5.8 Hz, 3H), 7.18-7.15 (dd, *J* = 8.8, 3.2 Hz, 2H), 7.04-7.01 (m, 2H), 6.98-6.96 (m, 2H), 6.86-6.83 (m, 1H), 6.73-6.71 (d, *J* = 8.4 Hz, 1H), 5.60-5.53 (m, 1H), 4.20-4.16 (m, 1H), 4.09-4.05 (m, 1H), 1.44-1.46 (d, *J* = 8.0 Hz, 3H).

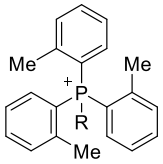
^{19}F NMR (376 MHz, $CDCl_3$): δ -95.2, -153.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ 14.8.

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.2 (d, *J* = 3.2 Hz), 163.7 (d, *J* = 254.3 Hz), 163.2, 156.9, 147.2, 146.8, 139.6 (d, *J* = 9.2 Hz), 138.9, 135.8 (d, *J* = 14.0 Hz), 135.4 (d, *J* = 7.9 Hz), 127.2 (d, *J* = 13.1 Hz), 122.1, 118.5 (d, *J* = 15.5 Hz), 118.0 (dd, *J* = 21.0, 5.9 Hz), 116.9, 116.4, 111.7, 105.9 (d, *J* = 102.9 Hz),105.3 (dd, *J* = 97.4, 15.5 Hz), 71.1, 69.3, 17.0.

HRMS (ESI) *m/z* calcd for $C_{38}H_{30}F_3NO_3P^+$: 636.1910; found: 636.1934.

(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)tri-o-tolylphosphonium (34)



R=Pyriproxyfen

The compound was prepared according to the **PC 1**. Pale yellow solid; 30% yield (21 mg).

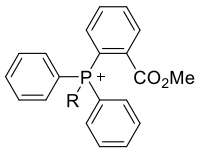
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.12 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.79-7.73 (m, 3H), 7.75-7.51 (m, 10H), 7.46-7.41 (m, 2H), 7.17-7.14 (dd, *J* = 9.2, 2.8 Hz, 2H), 7.05-7.03 (m, 2H), 6.99-6.97 (m, 2H), 6.86-6.83 (ddd, *J* = 7.2, 5.0, 1.0 Hz, 1H), 6.73-6.71 (d, *J* = 8.0 Hz, 1H), 5.58-5.54 (m, 1H), 4.21-4.17 (m, 1H), 4.09-4.05 (m, 1H), 1.94 (s, 9H), 1.46-1.45 (d, *J* = 6.4 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 25.1.

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.43, 162.05, 155.74, 146.09, 145.72, 142.60 (d, *J* = 8.0 Hz), 137.79, 135.62 (d, *J* = 11.2 Hz), 134.76 (d, *J* = 2.1 Hz), 134.15 (d, *J* = 12.4 Hz), 133.31 (d, *J* = 11.0 Hz), 127.36 (d, *J* = 12.8 Hz), 121.02, 117.44 (d, *J* = 14.1 Hz), 115.84, 115.36 (d, *J* = 86.0 Hz), 115.32, 110.64, 107.76 (d, *J* = 94.1 Hz), 70.07, 68.16, 22.04 (d, *J* = 4.5 Hz), 15.96.

HRMS (ESI) *m/z* calcd for $C_{40}H_{35}NO_5P^+$: 624.2662; found: 624.2669.

(2-(methoxycarbonyl)phenyl)diphenyl(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)phosphonium (35)



The compound was prepared according to the **PC 1**. Pale yellow solid; 57% yield (41.4 mg).

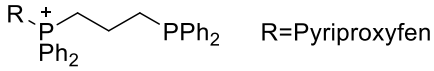
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44-8.41 (m, 1H), 8.14-8.13 (d, *J* = 5.2 Hz, 1H), 8.07-8.03 (t, *J* = 7.8 Hz, 1H), 7.96-7.92 (m, 1H), 7.81-7.77 (t, *J* = 7.6 Hz, 2H), 7.70-7.65 (m, 4H), 7.59-7.54 (m, 5H), 7.48-7.37 (m, 3H), 7.11-7.08 (dd, *J* = 8.8, 2.8 Hz, 2H), 7.06-7.04 (d, *J* = 8.8 Hz, 1H), 6.99-6.97 (d, *J* = 8.8 Hz, 2H), 6.88-6.85 (t, *J* = 6.0 Hz, 1H), 6.75-6.73 (d, *J* = 8.4 Hz, 1H), 5.61-5.54 (m, 1H), 4.21-4.18 (m, 1H), 4.10-4.06 (m, 1H), 3.48 (s, 3H), 1.48-1.46 (d, *J* = 8.0 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 28.6.

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.5, 164.2, 163.1, 156.6, 147.3 , 146.7, 138.8, 138.5 (d, *J* = 11.2 Hz), 136.4 (d, *J* = 11.7 Hz), 136.2, 134.7 (d, *J* = 13.1 Hz), 134.6 (d, *J* = 2.8 Hz), 134.1 (d, *J* = 4.9 Hz), 133.4 (d, *J* = 10.1 Hz), 133.3, 130.1 (d, *J* = 13.3 Hz), 122.0, 120.5 (d, *J* = 94.4 Hz), 119.0 (d, *J* = 89.4 Hz), 117.7 (d, *J* = 14.3 Hz), 116.9, 116.2, 111.7, 110.7, 71.0, 69.2, 53.3, 17.0 .

HRMS (ESI) *m/z* calcd for $C_{40}H_{35}NO_5P^+$: 640.2247; found: 640.2255.

(2-(diphenylphosphaneyl)propyl)diphenyl(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)phosphonium (36)



The compound was prepared according to the **PC 1**. Pale yellow solid; 62% yield (50.2 mg).

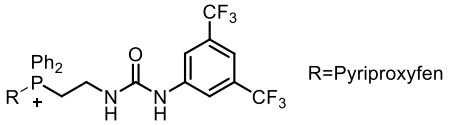
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.12 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.73-7.70 (m, 3H), 7.61-7.58 (m, 8H), 7.55-7.53 (m, 2H), 7.50-7.45 (dd, *J* = 12.0, 8.8 Hz, 3H), 7.36-7.31 (m, 5H), 7.26-7.25 (m, 3H), 7.06-7.03 (dd, *J* = 8.8, 2.6 Hz, 2H), 6.98 (s, 4H), 6.86-6.82 (ddd, *J* = 7.0, 5.0, 1.0 Hz, 1H), 6.73-6.71 (d, *J* = 8.4 Hz, 1H), 5.61-5.54 (m, 1H), 4.21-4.18 (m, 2H), 4.10-4.06 (m, 1H), 3.45-3.38 (m, 2H), 2.38-2.35 (t, *J* = 7.6 Hz, 2H), 1.76-7.63 (m, 2H), 1.48-1.46 (d, *J* = 8.0 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 23.2, -17.6.

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.6, 163.2, 156.8, 147.4, 146.9, 138.8, 137.3 (d, *J* = 11.5 Hz), 135.6 (d, *J* = 11.5 Hz), 135.1, 133.3 (d, *J* = 10.0 Hz), 132.8 (d, *J* = 18.6 Hz), 130.5 (d, *J* = 12.5 Hz), 128.9, 128.7 (d, *J* = 6.8 Hz), 122.0, 118.5 (d, *J* = 86.3 Hz), 118.3 (d, *J* = 13.7 Hz), 116.9, 116.3, 111.7, 109.0 (d, *J* = 92.4 Hz), 71.1, 69.2, 53.5, 29.8, 17.1, 14.2 .

HRMS (ESI) *m/z* calcd for $C_{47}H_{44}NO_3P_2^+$: 732.2791; found:732.2799 .

(2-(3-(3,5-bis(trifluoromethyl)phenyl)ureido)ethyl)diphenyl(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)benzyl)phosphonium (37)



The compound was prepared according to the **PC 1**. Pale yellow solid; 42% yield (37.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14-8.13 (m, 1H), 7.85 (s, 1H), 7.81 (s, 2H), 7.75-7.70 (m, 4H), 7.67-7.62 (m, 7H), 7.60-7.54 (m, 3H), 7.40 (s, 1H), 7.14-7.12 (d, *J* = 8.0 Hz, 2H), 6.95 (s, 3H), 6.86-6.83 (t, *J* = 6.0 Hz, 1H), 6.58 (s, 1H), 6.58 (s, 1H), 5.58 (m, 1H), 4.21-4.17 (m, 1H), 4.09-4.05 (m, 1H), 3.71-3.66 (m, 1H), 3.40-3.37 (m, 1H), 1.48-1.46 (d, *J* = 8.0 Hz, 3H).

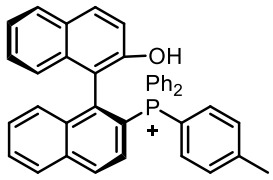
^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7, -149.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ 22.7.

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.9 (d, *J* = 3.0 Hz), 163.1, 156.7, 155.4, 147.2, 146.8, 141.2, 138.8, 135.6 (d, *J* = 11.8 Hz), 135.2 (d, *J* = 2.8 Hz), 133.3 (d, *J* = 10.3 Hz), 131.7 (q, *J* = 32.9 Hz), 130.5 (d, *J* = 12.7 Hz), 123.37 (q, *J* = 272.9 Hz), 121.9, 118.3 (d, *J* = 13.8 Hz), 118.2 (d, *J* = 86.8 Hz), 118.1 (d, *J* = 4.3 Hz), 116.9, 116.3, 114.9, 111.7, 108.3 (d, *J* = 92.7 Hz), 71.0, 69.1, 33.8, 24.1 (d, *J* = 51.1 Hz), 17.0.

HRMS (ESI) *m/z* calcd for $C_{43}H_{37}F_6N_3O_4P^+$: 804.2403; found: 804.2413.

(S)-(2'-hydroxy-[1,1'-binaphthalen]-2-yl)diphenyl(p-tolyl)phosphonium (38)



The compound was prepared according to the **PC 1**. Pale yellow solid; 66% yield (41.7 mg).

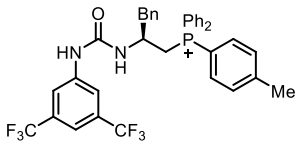
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.05-7.97 (dd, *J* = 25.4, 8.4 Hz, 2H), 7.66-7.62 (t, *J* = 7.6 Hz, 1H), 7.56-7.51 (q, *J* = 6.8, 5.0 Hz, 3H), 7.40-7.33 (m, 10H), 7.32-7.28 (m, 1H), 7.25-7.13 (m, 6H), 7.11-7.07 (t, *J* = 7.8 Hz, 1H), 6.97-6.95 (d, *J* = 8.8 Hz, 1H), 6.78-6.76 (d, *J* = 8.0 Hz, 1H), 2.34 (s, 3H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 26.7.

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.5, 146.8 (d, *J* = 9.1 Hz), 145.8 (d, *J* = 3.1 Hz), 135.7 (d, *J* = 2.5 Hz), 134.4 (d, *J* = 4.0 Hz), 134.3 (d, *J* = 3.3 Hz), 134.1 (d, *J* = 1.6 Hz), 134.1 (d, *J* = 3.9 Hz), 134.0 (d, *J* = 4.2 Hz), 133.9 (d, *J* = 2.0 Hz), 131.3, 130.4, 130.3, 130.2, 129.5 (d, *J* = 12.8 Hz), 129.1 (d, *J* = 13.0 Hz), 128.7 (d, *J* = 13.7 Hz), 128.4 (d, *J* = 6.4 Hz), 128.0, 127.6, 126.8, 123.5, 122.9, 119.9 (dd, *J* = 89.0, 16.9 Hz), 118.7, 115.6 (d, *J* = 91.3 Hz), 114.8 (d, *J* = 92.4 Hz), 113.4 (d, *J* = 5.4 Hz), 21.7.

HRMS (ESI) *m/z* calcd for $C_{39}H_{30}OP^+$: 545.2029; found: 545.2038.

(S)-(2-(3-(3,5-bis(trifluoromethyl)phenyl)ureido)-3-phenylpropyl)diphenyl(p-tolyl)phosphonium (39)



The compound was prepared according to the **PC 1**. Pale yellow solid; 43% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 2H), 7.67-7.61 (m, 2H), 7.56-7.52 (m, 6H), 7.51-7.47 (t, *J* = 7.2 Hz, 3H), 7.42-7.37 (m, 3H), 7.34-7.28 (m, 5H), 7.22-7.20 (m, 2H),

6.55-6.52 (d, *J* = 9.2 Hz, 1H), 4.58-4.46 (m, 1H), 3.55-3.46 (dt, *J* = 15.8, 11.2 Hz, 1H), 3.24-3.18 (dt, *J* = 13.6, 4.8 Hz, 1H), 3.00-2.93 (m, 1H), 2.85-2.80 (dd, *J* = 13.6, 10.0 Hz, 1H), 2.25 (s, 3H).

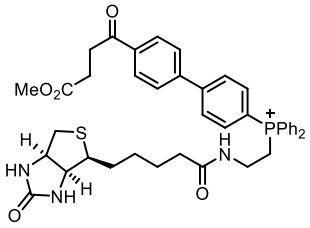
^{31}F NMR (376 MHz, $CDCl_3$): δ -62.7, -148.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 20.8.

^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, δ): 154.7, 141.4, 137.7, 132.8 (d, *J* = 100.8 Hz), 132.3 (dd, *J* = 32.9, 2.3 Hz), 131.4 (q, *J* = 33.0 Hz), 130.5 (d, *J* = 9.5 Hz), 130.4 (d, *J* = 100.5 Hz), 130.1 (d, *J* = 9.6 Hz), 129.3, 129.0 (dd, *J* = 22.6, 11.8 Hz), 128.6, 126.7, 123.3 (q, *J* = 272.6 Hz), 117.2, 114.2, 47.8 (d, *J* = 5.3 Hz), 42.8 (d, *J* = 10.5 Hz), 32.6 (d, *J* = 72.3 Hz), 29.7.

HRMS (ESI) *m/z* calcd for $C_{37}H_{32}F_6N_2OP^+$:665.2151; found: 665.2159.

(4'-(4-methoxy-4-oxobutanoyl)-[1,1'-biphenyl]-4-yl)(2-(5-((3aS,4S,6aR)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl)pentanamido)ethyl)diphenylphosphonium (40)



The compound was prepared according to the **PC 1**. Pale yellow solid; 31% yield (25.4 mg).

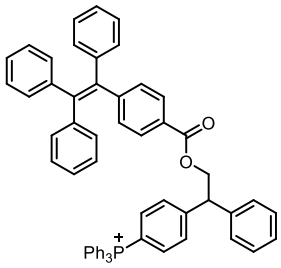
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.08 (d, *J* = 8.4 Hz, 2H), 7.94-7.92 (dd, *J* = 8.4, 3.2 Hz, 2H), 7.88-7.85 (m, 1H), 7.83-7.67 (m, 13H), 6.64 (s, 1H), 5.80-5.76 (m, 1H), 4.45-4.42 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.26-4.23 (dd, *J* = 8.0, 4.4 Hz, 1H), 3.69 (s, 3H), 3.65-3.55 (m, 4H), 3.36-3.33 (t, *J* = 6.4 Hz, 2H), 3.10-3.05 (m, 1H), 2.85-2.81 (dd, *J* = 12.8, 4.8 Hz, 1H), 2.79-2.75 (t, *J* = 6.4 Hz, 2H), 2.69-2.65 (d, *J* = 12.8 Hz, 1H), 2.15-2.06 (m, 2H), 1.69-1.60 (m, 1H), 1.58-1.52 (m, 2H), 1.38-1.33 (m, 2H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 21.9.

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.7 , 174.8 , 174.1 , 173.4 , 146.4 , 142.8 , 136.6 , 135.4 , 134.2 (d, *J* = 10.7 Hz), 133.5 (dd, *J* = 10.1, 5.3 Hz), 132.1 , 130.6 (d, *J* = 12.8 Hz), 129.0 (d, *J* = 5.3 Hz), 128.9 (d, *J* = 12.2 Hz), 127.7 , 117.8 (d, *J* = 78.4 Hz), 61.7 , 60.3 , 55.7 , 51.9 , 40.6 , 35.5 , 33.6 , 28.0, 29.7 , 27.9 (d, *J* = 17.4 Hz), 25.2 , 22.1 (d, *J* = 50.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{41}H_{45}N_3O_5PS^+$: 722.2812; found: 722.2820.

Triphenyl(4-(1-phenyl-2-((4-(1,2,2-triphenylvinyl)benzoyl)oxy)ethyl)phenyl)phosphonium (42)



The compound was prepared according to the **Procedure 5**. Pale yellow solid; 88% yield (108 mg).

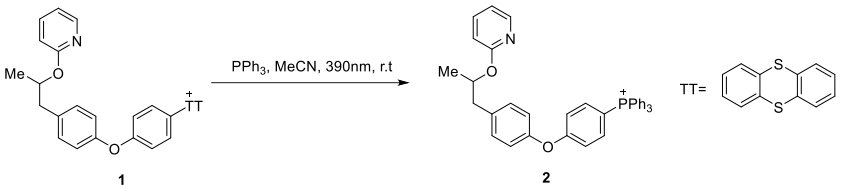
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.83 (m, 3H), 7.74-7.69 (td, *J* = 7.8, 3.6 Hz, 6H), 7.67-7.63 (m, 3H), 7.62-7.59 (m, 5H), 7.58-7.52 (m, 6H), 7.36-7.32 (m, 2H), 7.29-7.26 (m, 3H), 7.10–7.06 (m, 9H), 7.00-6.95 (m, 7H), 4.87-4.82 (m, 2H), 4.64-4.60 (t, *J* = 7.4 Hz, 1H).

^{31}P NMR (162 MHz, $CDCl_3$): δ 23.3.

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.2, 150.2, 150.2, 149.2, 143.2, 143.1, 143.1, 142.8, 139.8, 139.3, 135.9 (d, *J* = 2.5 Hz), 134.8 (d, *J* = 10.6 Hz), 134.4 (d, *J* = 10.3 Hz), 131.4, 131.3, 131.3, 130.9, 130.8, 130.7, 129.2, 129.1, 128.4, 128.0, 128.0, 127.8, 127.7, 127.5, 127.0, 126.9, 117.5 (d, *J* = 89.7 Hz), 116.3, 66.5, 50.1.

HRMS (ESI) *m/z* calcd for $C_{59}H_{46}O_2P^+$: 817.3230; found: 817.3243.

Table S1. Optimization of reaction conditions.[1]



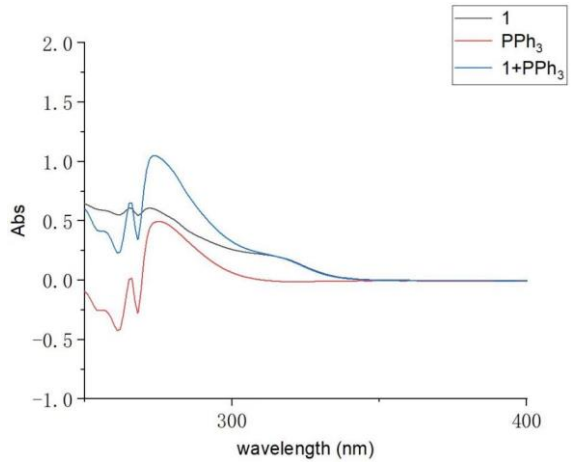
1 2

Entry	Variations from standard conditions	Yield (**2a**)
1	None	95%
2	No light	n.d.
3	456 nm	47%
4	DMA, instead of MeCN	76%
5	toluene, instead of MeCN	49%
6	THF, instead of MeCN	50%
7	DMF, instead of MeCN	30%
8	$PhCF_3$, instead of MeCN	72%
9	DMSO, instead of MeCN	53%
10	ethyl acetate, instead of MeCN	24%
11	1, 4-dixoane, instead of MeCN	56%

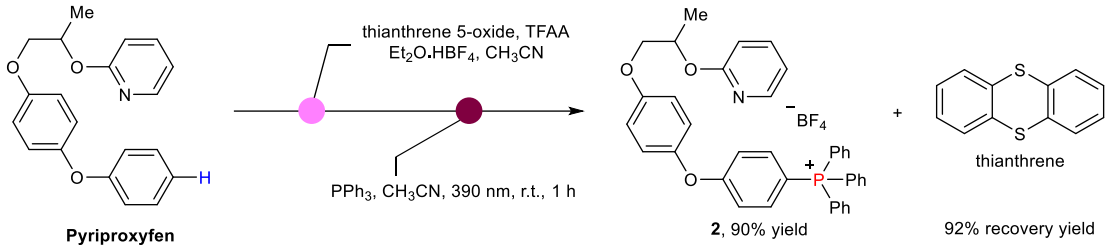
[1]The reactions were carried out with **1** (0.1 mmol) and PPh_3 in MeCN (1 mL). Yields of **2** are isolated yields. n.d: no reaction.

UV−vis spectroscopic measurements

The UV/vis absorption spectra of **1** (0.005 M), PPh_3 (0.005 M) and their mixture in MeCN were recorded in 1 cm path quartz cuvettes respectively (Figure S2).[6]

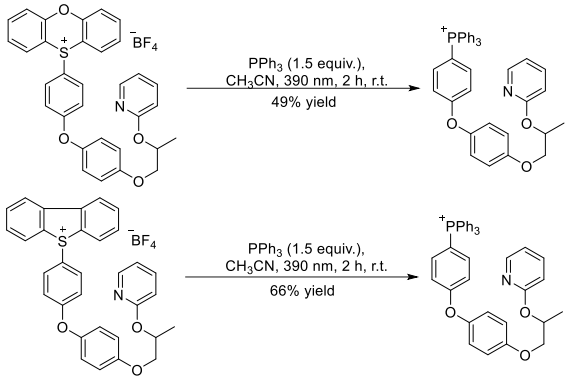


In-situ generation of QPS via C-H functionalization



0.2 mmol of Pyriproxyfen was prepared by procedure 1 to obtain thiamine salt crude product without further purification. The crude product was washed with saturated sodium bicarbonate and then treated directly by PC1. Finally, we got 90% yield of **2** and recovered 92% yield of thianthrene.

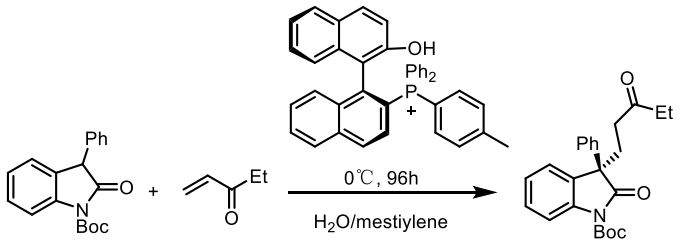
Reactivity of other triarylsulfonium salts.



Dibenzothiophene and phenoxathiine derived triarylsulfonium salts were also examined via the procedure of PC 1, which gave the quaternary phosphonium salts with 49% yield and 66% yield respectively.

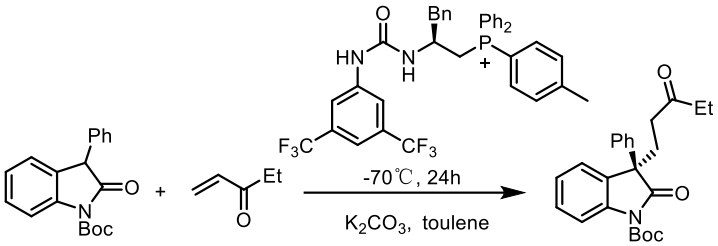
Investigations on the asymmetric catalysis using the new chiral quaternary phosphonium salts

Asymmetric Michael addition reaction catalyzed by 38:



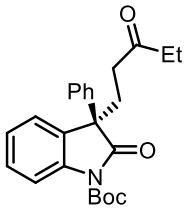
Based on a modified literature procedure.[7] To a 4 mL vial equipped with a stir bar was added the quaternary phosphonium salt **38** (10% mol), *tert*-butyl 2-oxo-3-phenylindoline-1-carboxylate (0.05 mmol) and mesitylene (1.0 mL), then the mixture was cooled to 0 ℃. After that, water (1.0 mL) and pent-1-en-3-one (0.15 mmol) were added into the mixture, and stirred for 96 h at 0 ℃. When the reaction finished determined by TLC analysis, the reaction mixture was diluted with Et_2O, and organic phase was separated. After the aqueous phase was extracted with Et_2O, the combined extracts were then dried over Na_2SO_4 and concentrated. The residue was directly purified by column chromatography on silica gel to obtain the Michael addition product (93% yield, 18.2 mg).

Asymmetric Michael addition reaction catalyzed by **39**:



Based on a modified literature procedure.[8] To a 4 mL vial equipped with a stir bar was added the quaternary phosphonium salt **39** (10% mol), *tert*-butyl 2-oxo-3-phenylindoline-1-carboxylate (0.1 mmol), potassium carbonate (0.5 mmol) and toluene (1.0 mL) under N_2, then the mixture was cooled to -70 ℃. After 15 min, pent-1-en-3-one (0.12 mmol) was added into the mixture, and stirred for 24 h at -70 ℃. When the reaction finished determined by TLC analysis, the residue was directly purified by column chromatography on silica gel to obtain the pure product (99% yield, 38.9 mg).

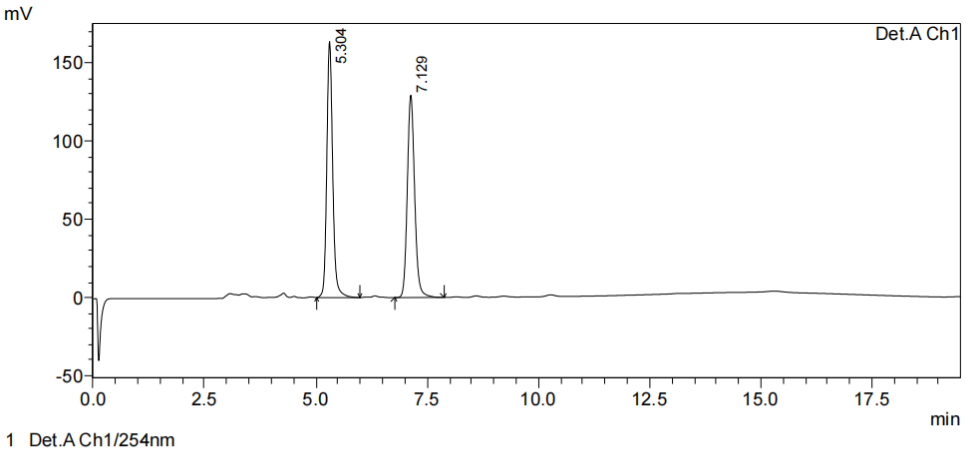
Tert-butyl (R)-2-oxo-3-(3-oxopentyl)-3-phenylindoline-1-carboxylate



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.93 (d, *J* = 12.0 Hz, 1H), 7.40-7.35 (m, 1H), 7.32-7.7.27 (m, 5H), 7.25-7.18 (m, 2H), 2.79-2.72 (m, 1H), 2.55-2.48 (m, 1H), 2.38-2.18 (m, 3H), 2.08–2.00 (m, 1H), 1.63 (s, 9H), 0.97-0.93 (m, *J* = 8.0 Hz, 3H).

Using 38, HPLC analysis (26% ee): Daicel Chiralpak AD-3, hexane/2-propanol = 9:1, flow rate = 1 mL/min, 254 nm; retention time: 5.3 min (major) and 7.1 min (minor).

Using 39, HPLC analysis (-13% ee): Daicel Chiralpak AD-3, hexane/2-propanol = 9:1, flow rate = 1 mL/min, 254 nm; retention time: 5.3 min (minor) and 6.9 min (major).

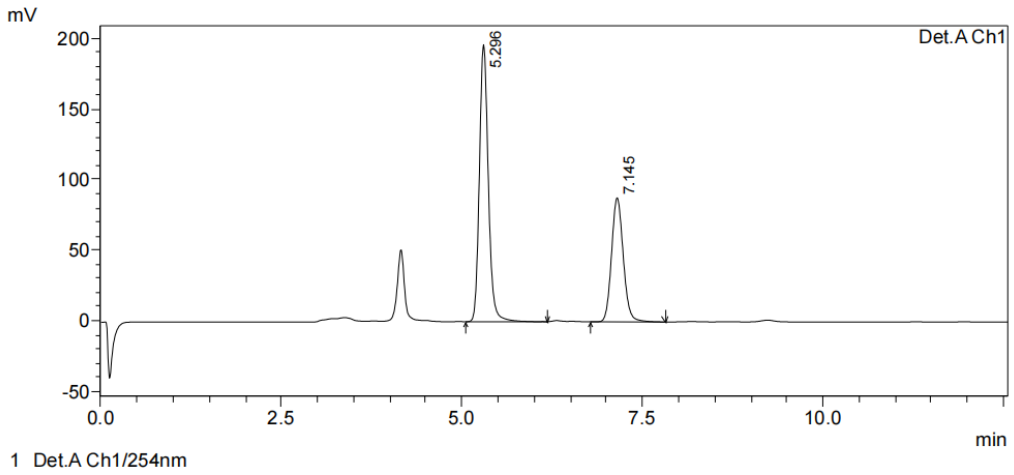


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.304	1513092	163473	50.337	55.855
2	7.129	1492826	129203	49.663	44.145
Total		3005917	292677	100.000	100.000

Using 38:

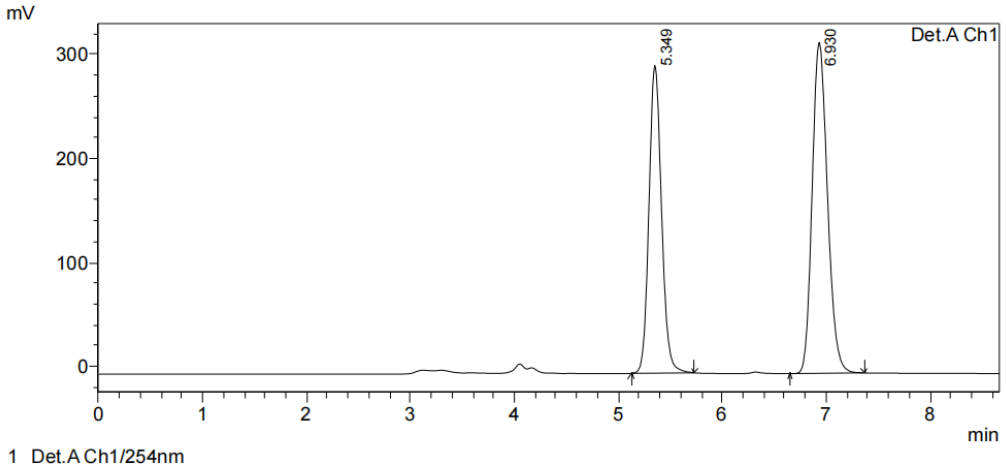


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.296	1687032	196090	63.010	69.083
2	7.145	990385	87755	36.990	30.917
Total		2677416	283845	100.000	100.000

Using 39:



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.349	2481878	295525	43.253	48.183
2	6.930	3256128	317813	56.747	51.817
Total		5738006	613337	100.000	100.000

Investigation on the mitochondria-targeting ability of 42

1. Preparation of NPs

Compound **42** (1.5 mg) and DSPE-PEG_{2000} (4 mg) were dissolved into a CH_2Cl_2 (400 μL) solution. After 10 min of sonication, the above solution was quickly poured into 1.5 mL H_2O and stirred overnight at room temperature. Then CH_2Cl_2 was removed by injection N_2 into the mixed solutions to obtain NPs aqueous solution (1 mg/mL).

2. Colocalization experiments of NPs with Mito Tracker.

4T1 cells/MBA-MD-231cell were seeded in 24-well plates with a density of 10^5 cells per well. After incubating for 12 h, the incubate was replaced with 1000 μL medium containing NPs（50 $\mu g mL^{-1}$）,then cells were incubated for another 6 h. the old culture medium was discarded and washed with PBS for 3 times. Then, the cells were incubated with medium containing Mito Tracker Green FM (200nM) for 20 min. Finally, the fluorescence images of cells were obtained by an inverted fluorescence microscope. The blue fluorescence of NPs overlapped with the green fluorescence of Mito Tracker Green FM, indicating the localization of NPs in the mitochondria.

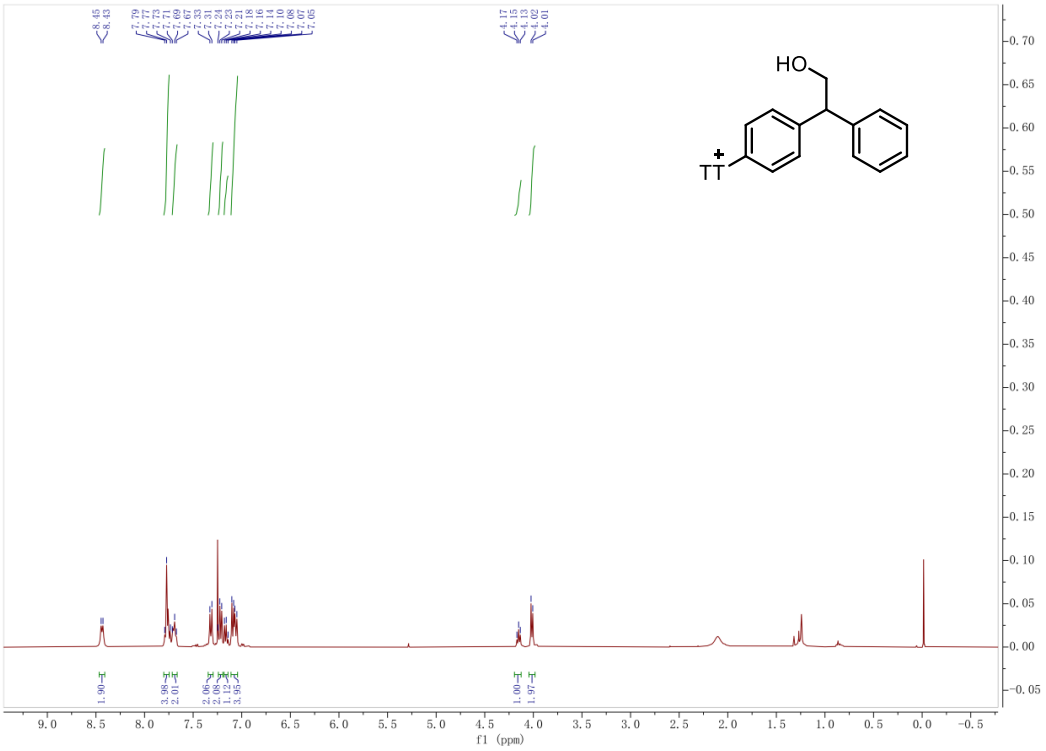
Reference

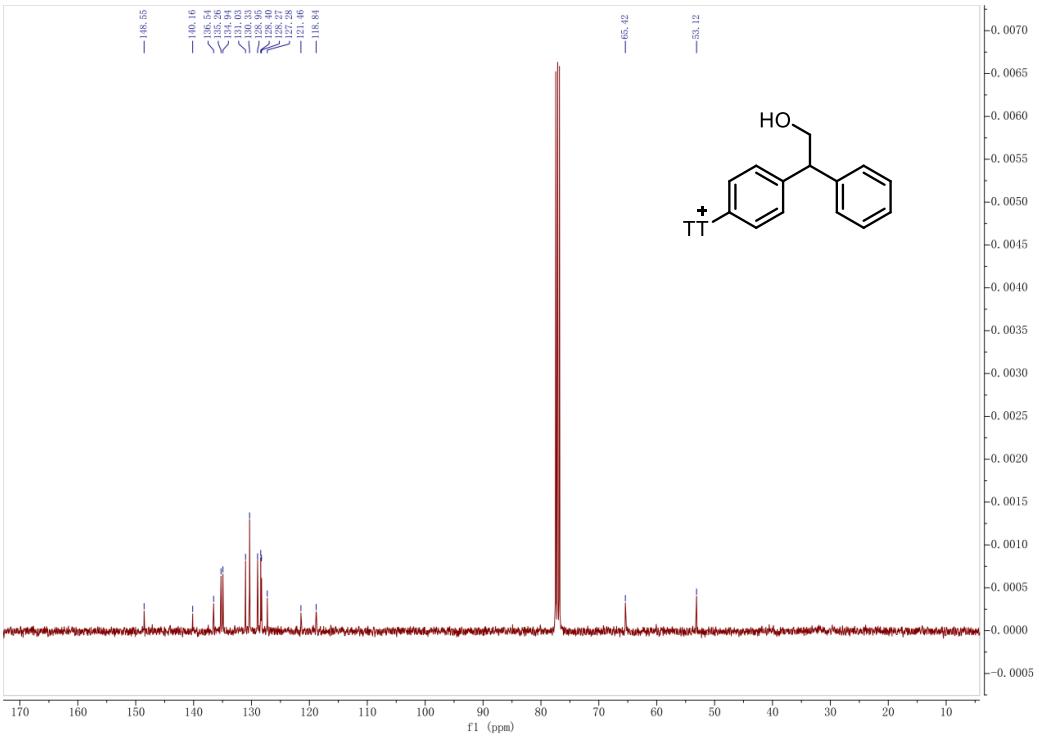
[1] (a) F. Berger, M. B. Plutschack, J. Riegger, W. Yu, S. Speicher, M. Ho, N. Frank, T. Ritter, *Nature* 2019, **567**, 223–228; (b) Y. Cai, S. Chatterjee, T. Ritter. *J. Am. Chem. Soc.* 2023, **145**, 13542-13548; (c) W. Zhang, T. Liu, H. T. Ang, P. Luo, Z. Lei, X. Luo, M. J. Koh, J. Wu, *Angew. Chem. Int. Ed.* 2023, **62**, e202310978; (d) D. Zhao, R. Petzold, J. Yan, D. Muri, T. Ritter, *Nature* 2021, **600**, 444–449.

[2] Y. Lou, C.-W. Zheng, R.-M. Pan, Q.-W. Jin, G. Zhao, Z. Li. *Org. Lett*. 2015, **17**, 688-691.
[3] E. Brenner, R. M. Baldwin, G. Tamagnan, *Tetrahedron. Lett.* 2004, **45**, 3607-3610.
[4] S. S. Gunatilleke, A. M. Barrios, *J. Inorg. Biochem.* 2008, **102**, 555-563.
[5] J. Sheehan, P. Cruickshank, G. Boshart. *J. Org. Chem.* 1961, **26**, 2525–2528.
[6] A. Dewanji, L. v. Dalsen, J. A. Rossi-Ashton, E. Gasson, G. E. M. Crisenza, D. J. Procter, *Nat. Chem.* 2023, **15**, 43–52.
[7] S. Shirakawa, A. Kasai, T. Tokuda, K. Maruoka, *Chem. Sci.* 2013, **4**, 2248-2252.
[8] X. Wu, Q. Liu, Y. Liu, Q. Wang, Y. Zhang, J. Chen, W. Cao, G. Zhao, *Adv. Synth. Catal*. 2013, **355**, 2701-2706.

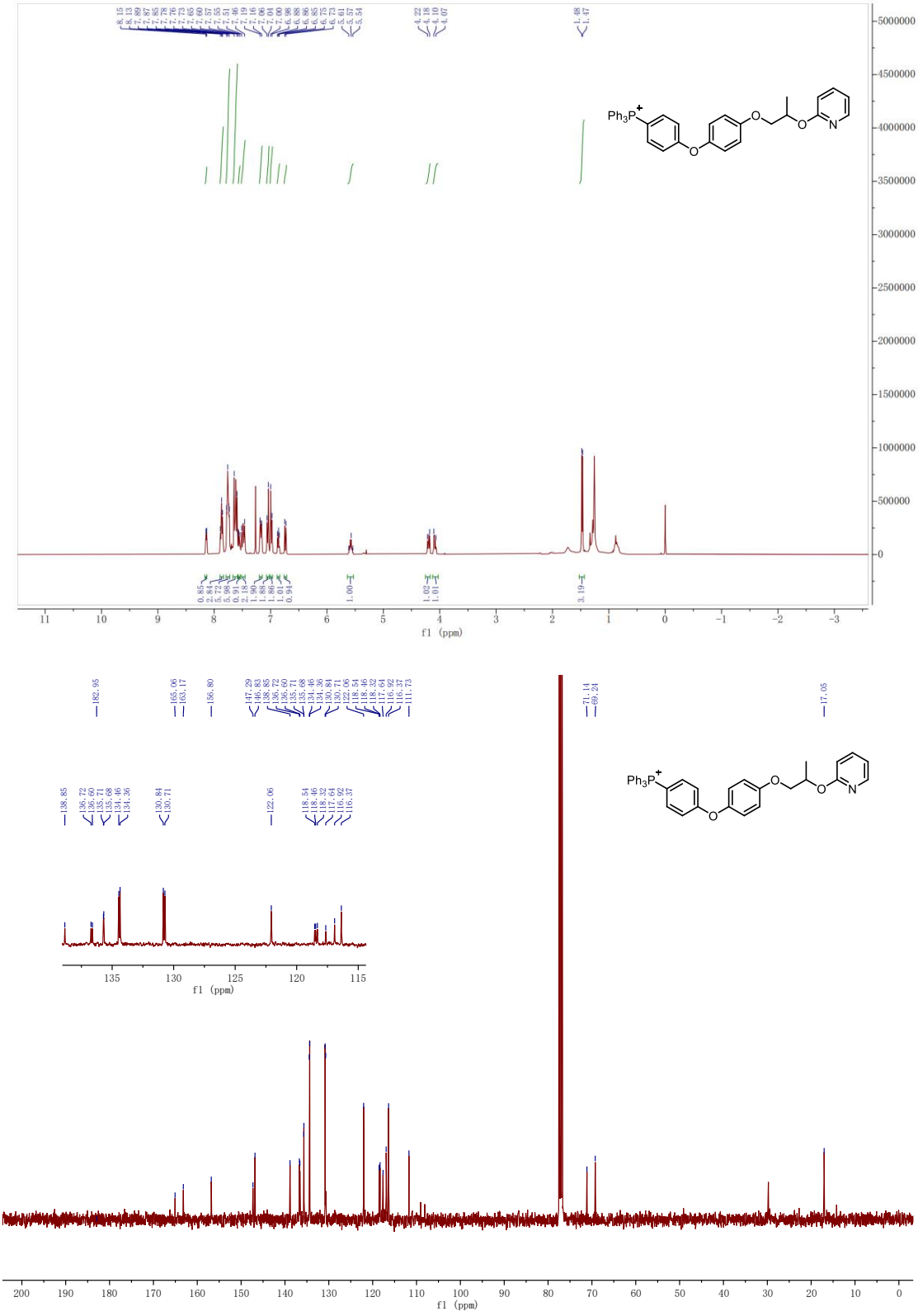
^{1}H, ^{13}C, ^{19}F-NMR Spectra

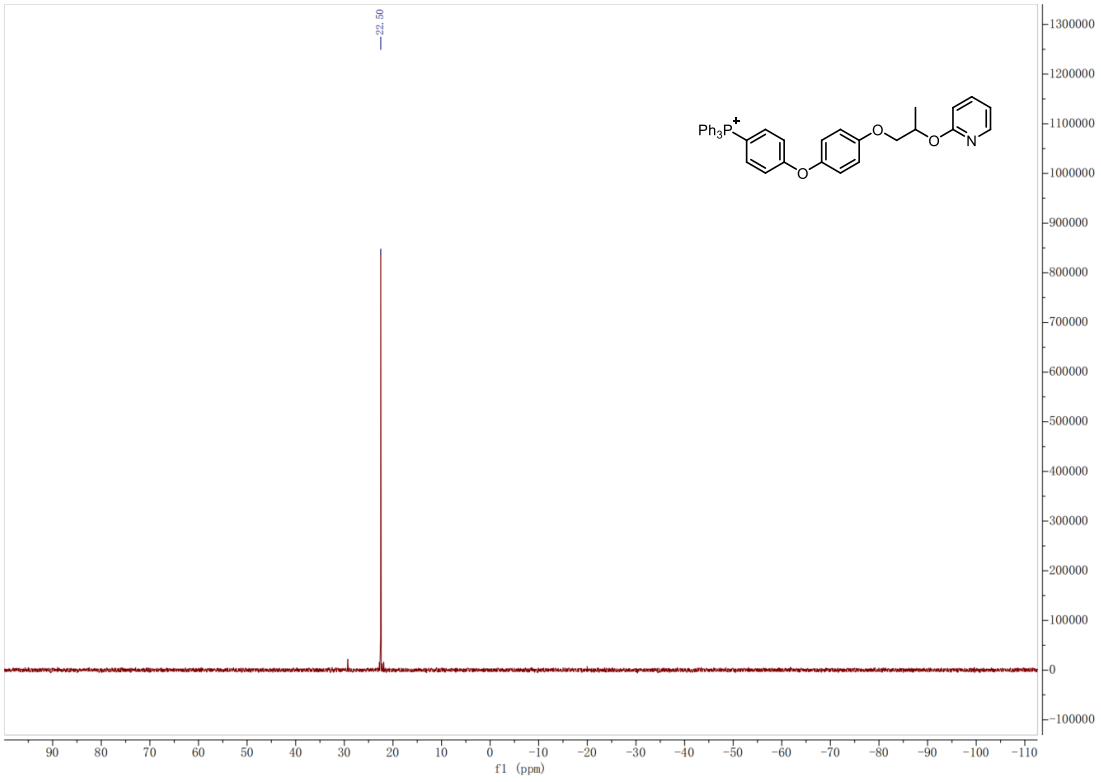
NMR Spectra of substrate **8**



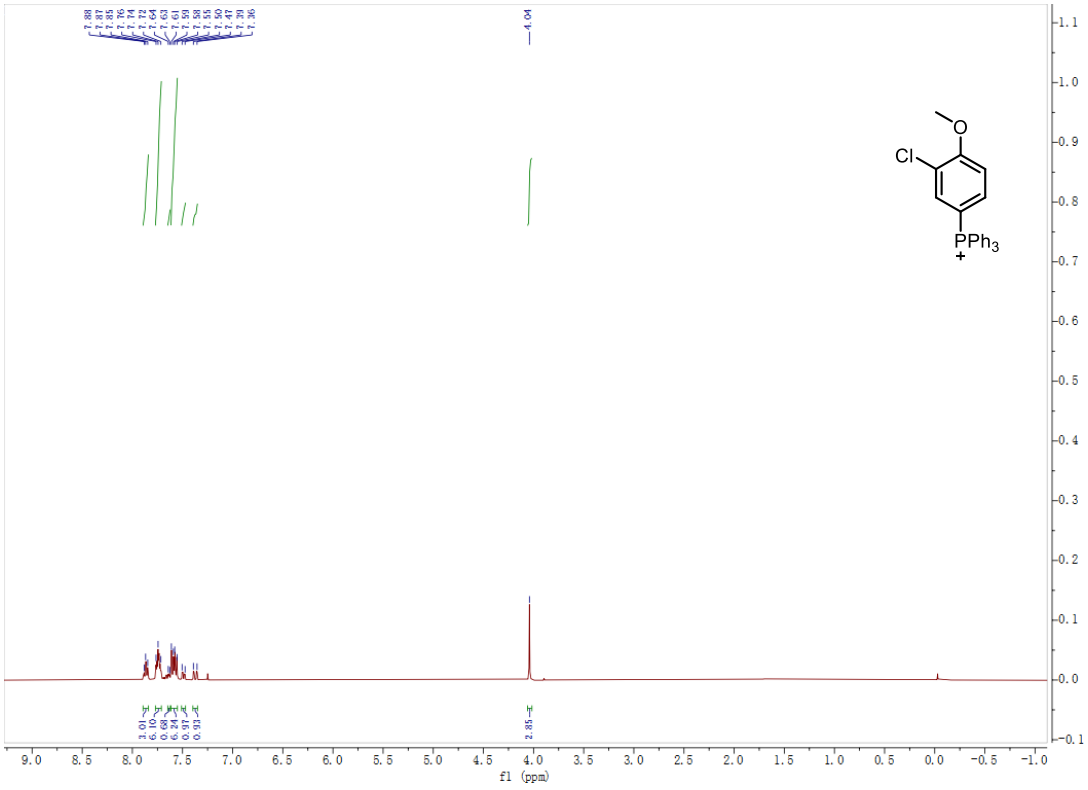


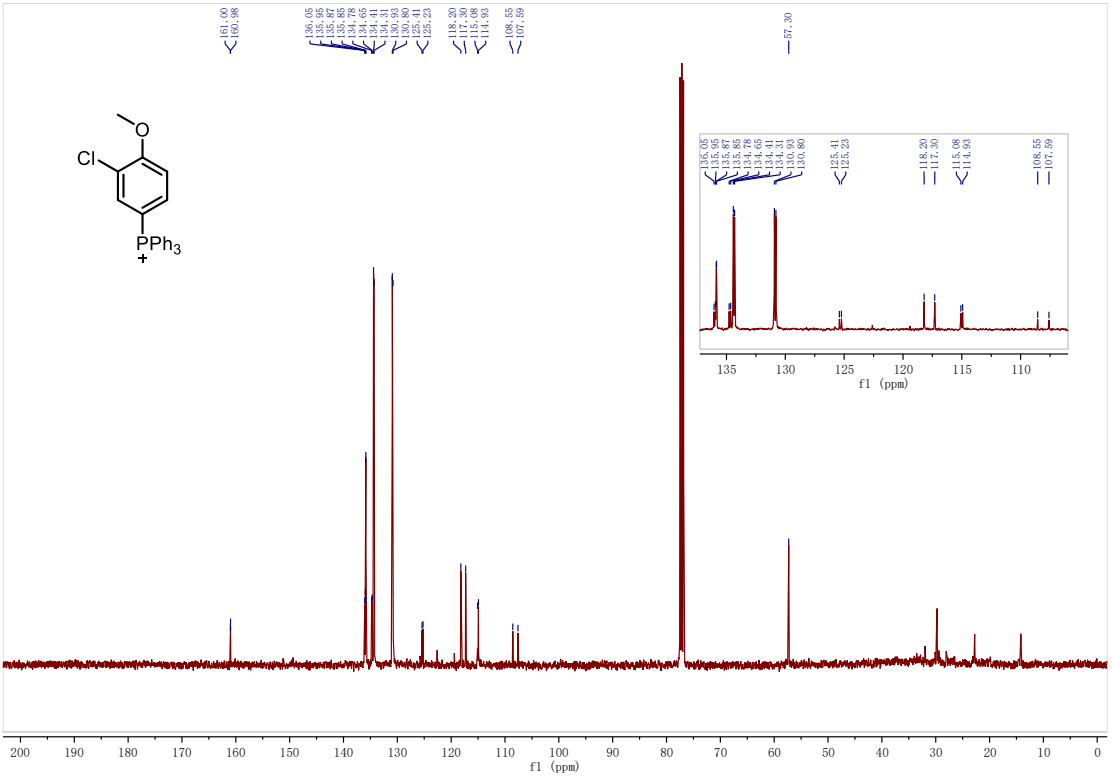
NMR Spectra of **2**

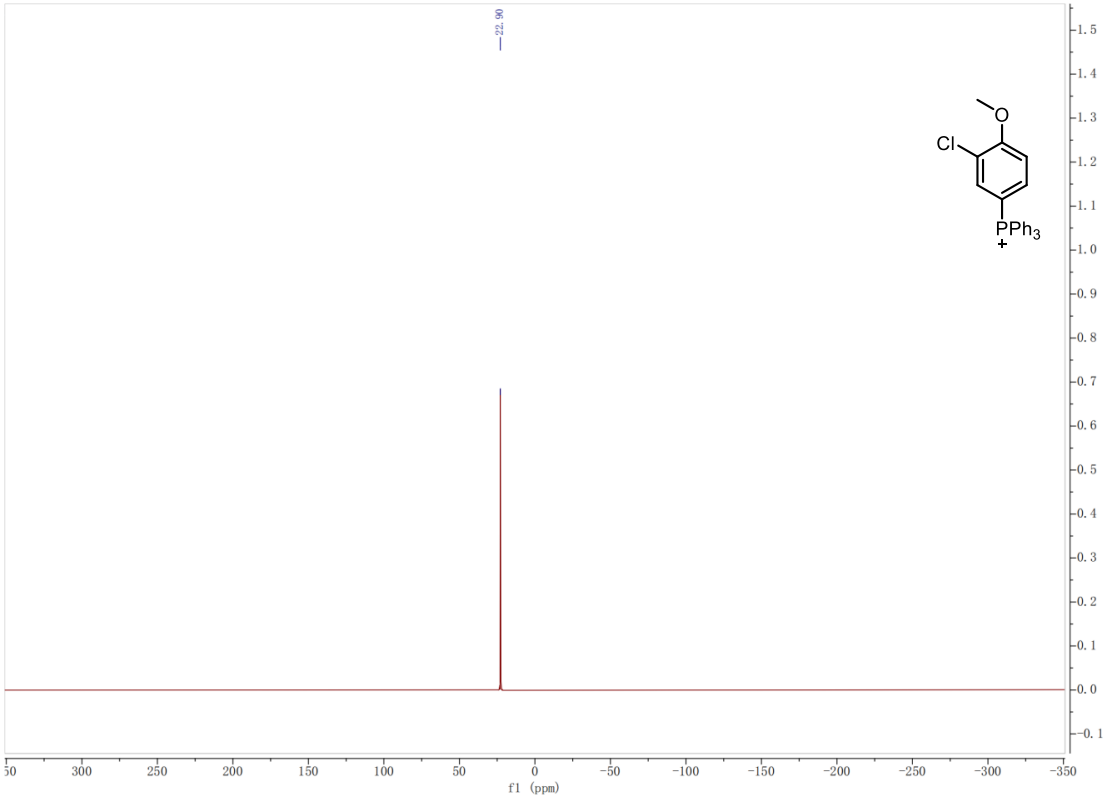




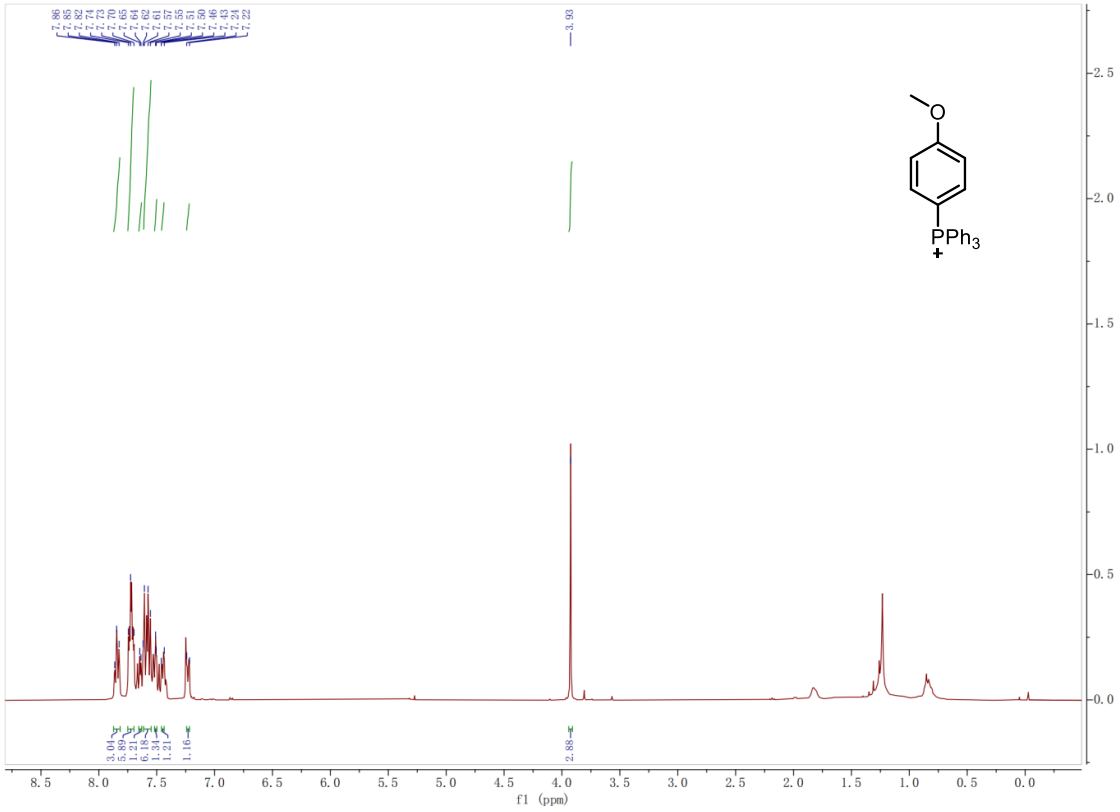
NMR Spectra of **3**

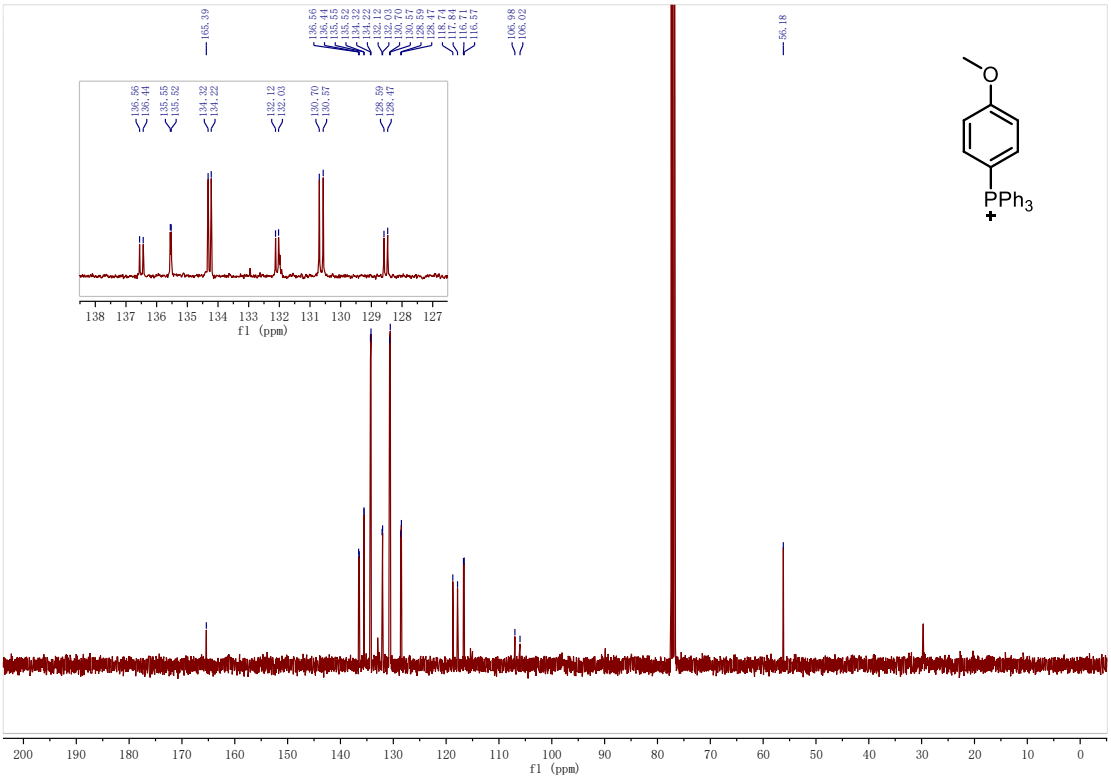


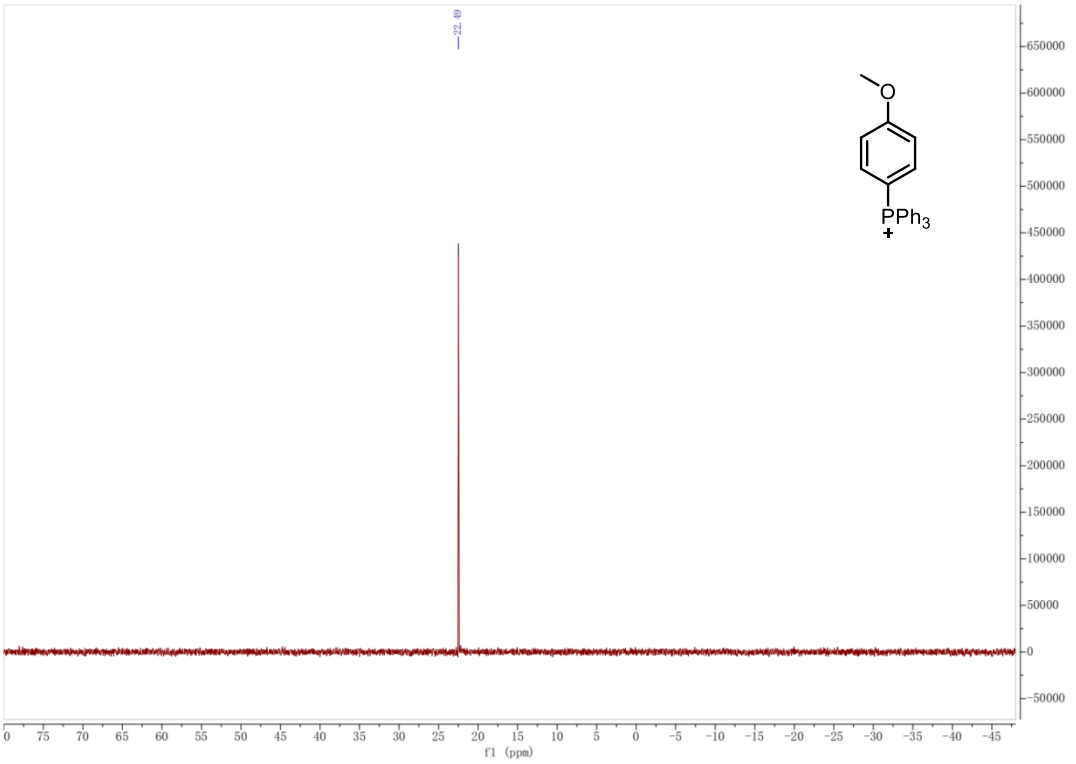

161.00
160.98
136.05
135.95
135.87
135.85
134.78
134.65
134.41
134.31
130.93
130.80
125.41
125.23
118.20
117.30
115.08
114.93
108.55
107.59
57.30
O
Cl
PPh3
+
f1 (ppm)


22.90
O
Cl
PPh3
+
f1 (ppm)

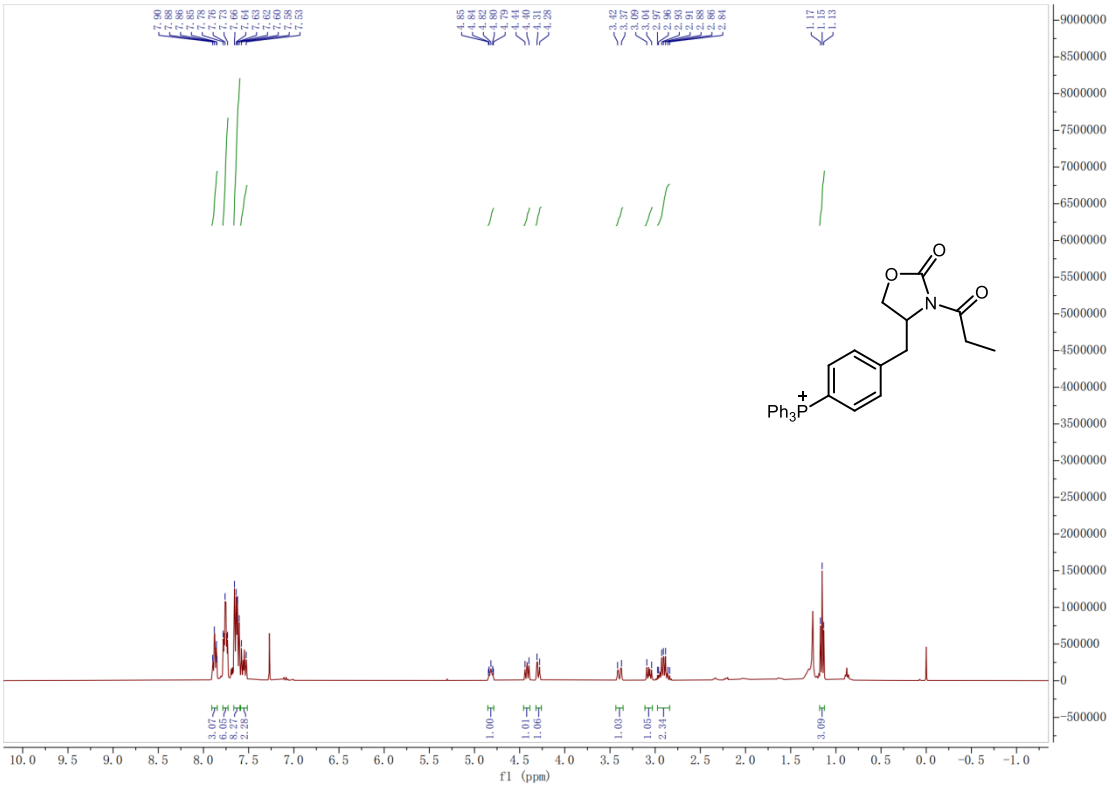
NMR Spectra of **4**

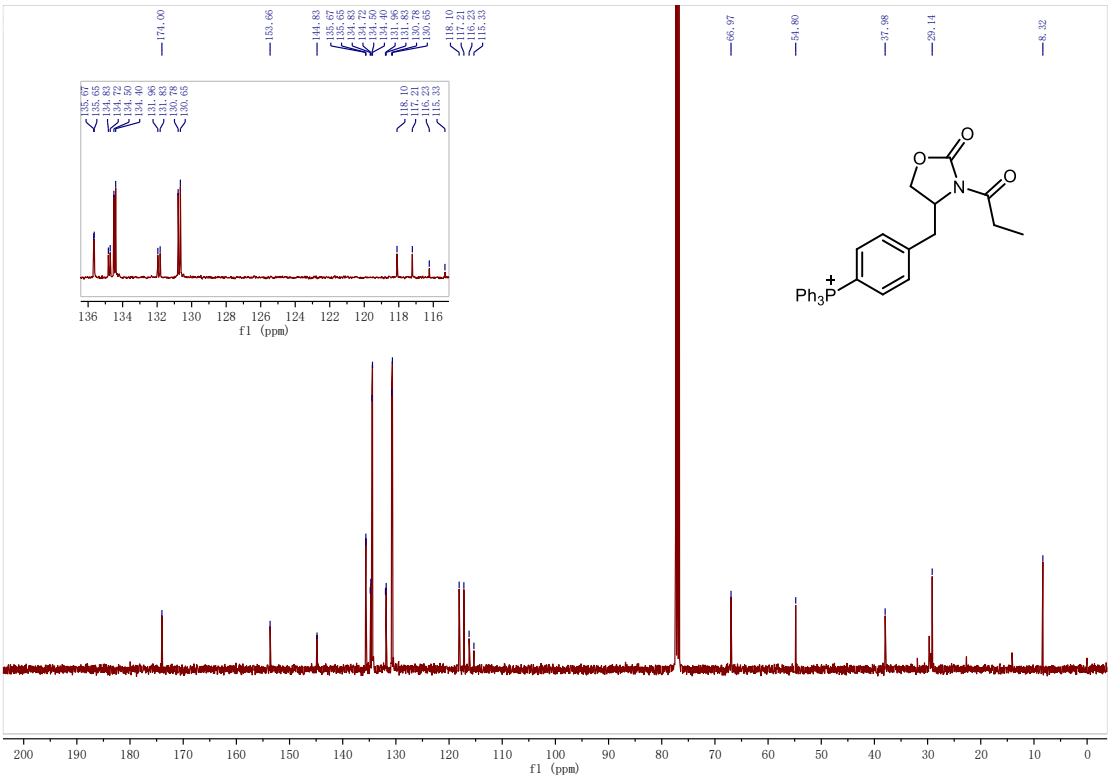


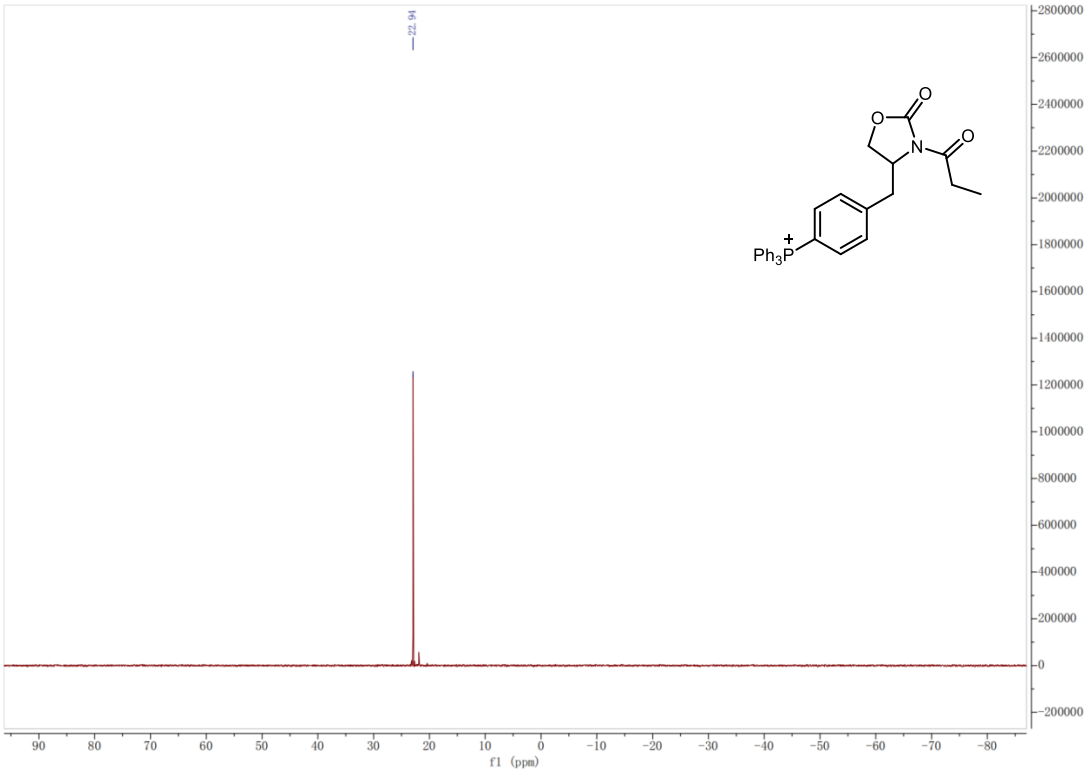




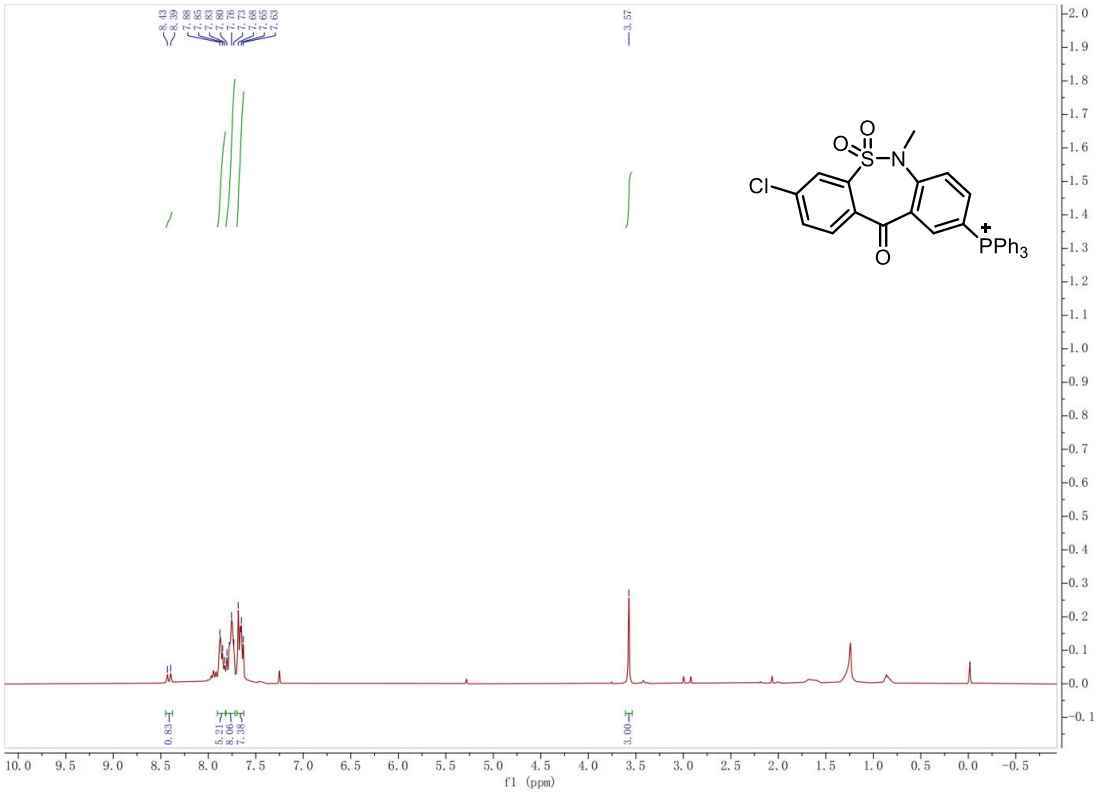
NMR Spectra of **5**

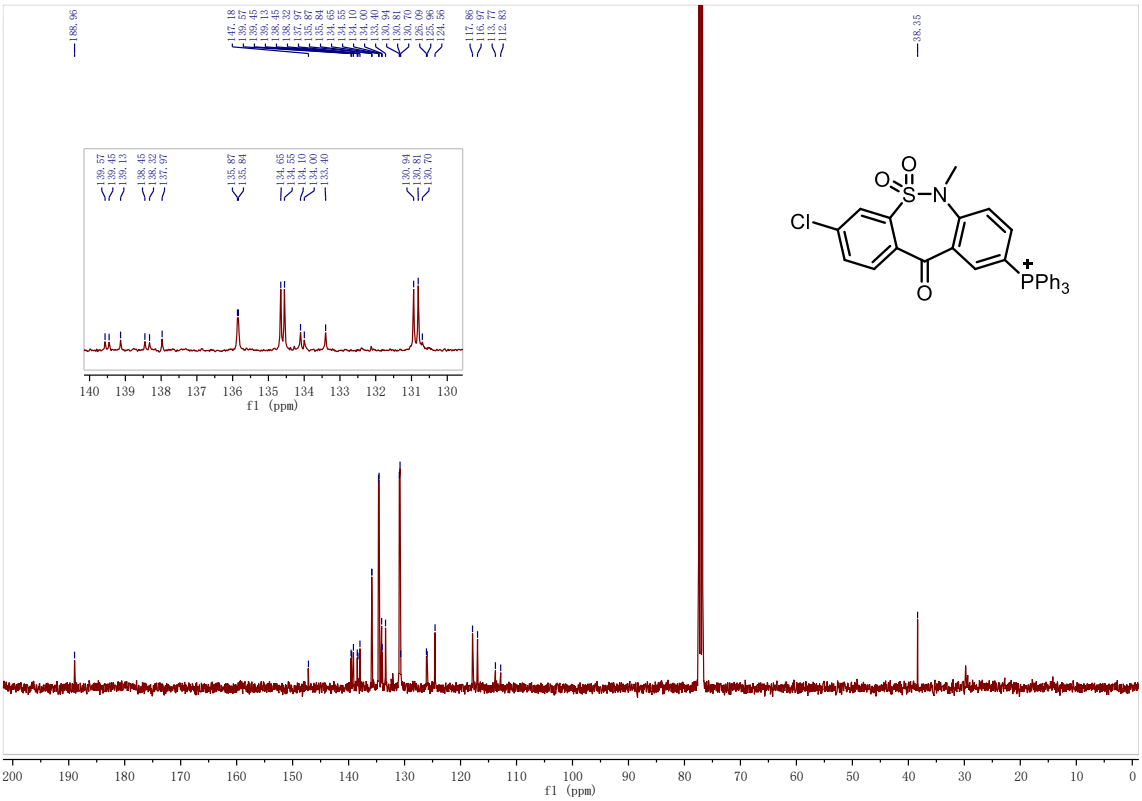


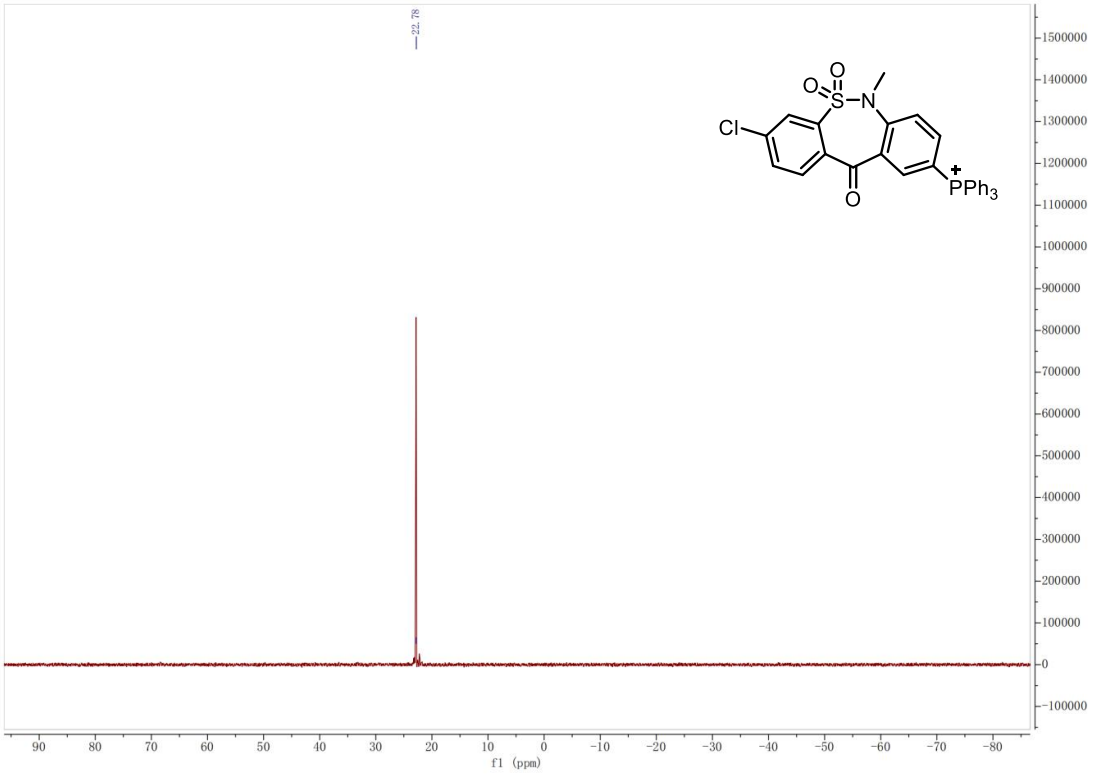

174.00
153.66
144.83
135.67
135.65
134.83
134.72
134.50
134.40
131.96
131.83
130.78
130.65
118.10
117.21
116.23
115.33
66.97
54.80
37.98
29.14
8.32
O
O
N
O
Ph3P
f1 (ppm)


22.94
O
O
N
O
Ph3P
f1 (ppm)

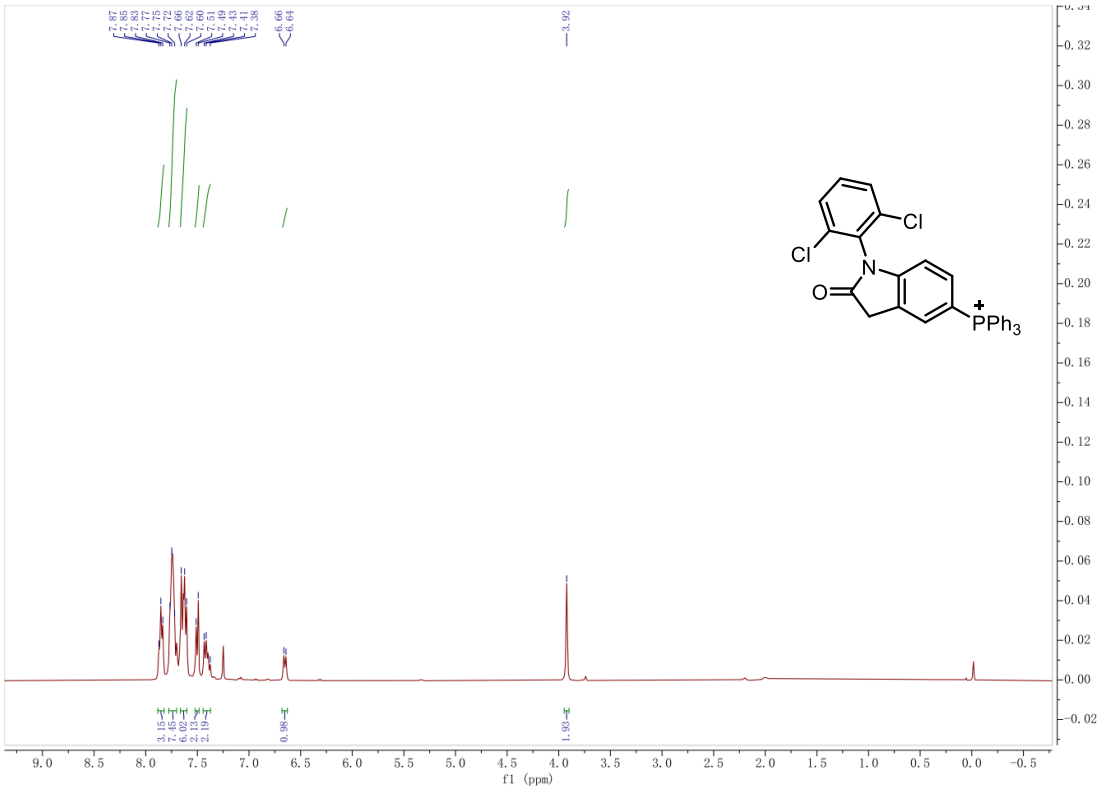
NMR Spectra of **6**

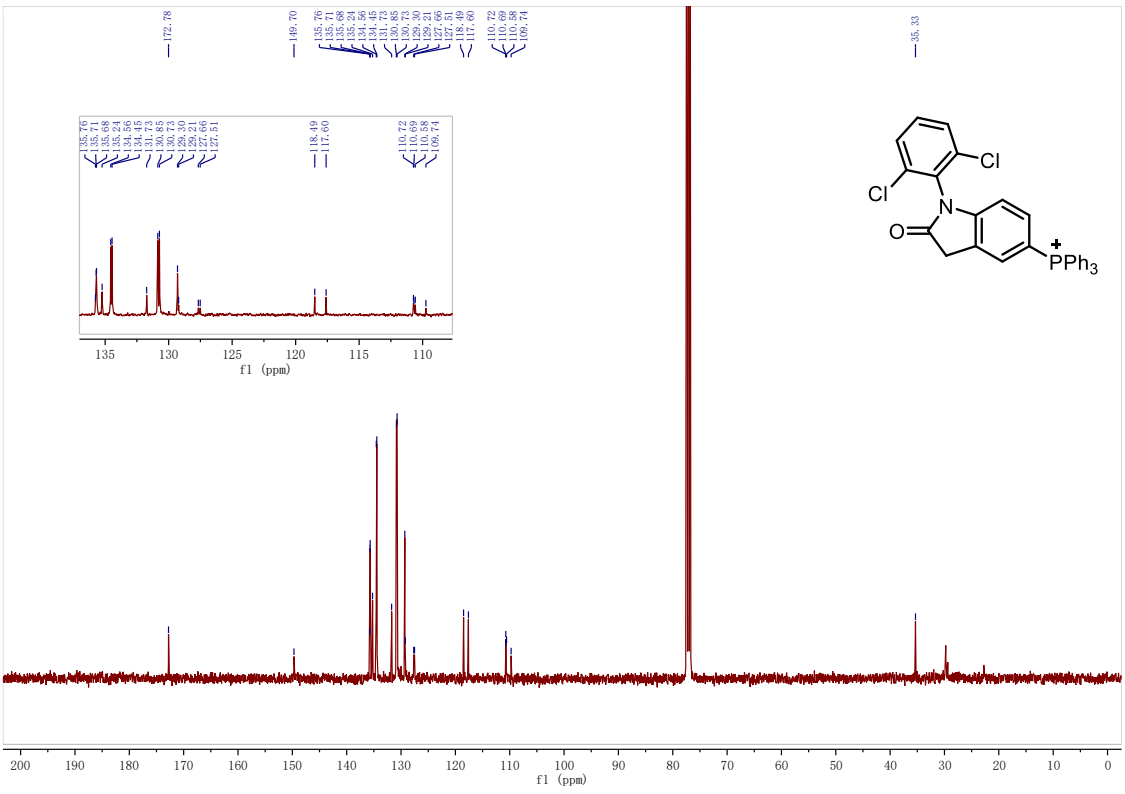


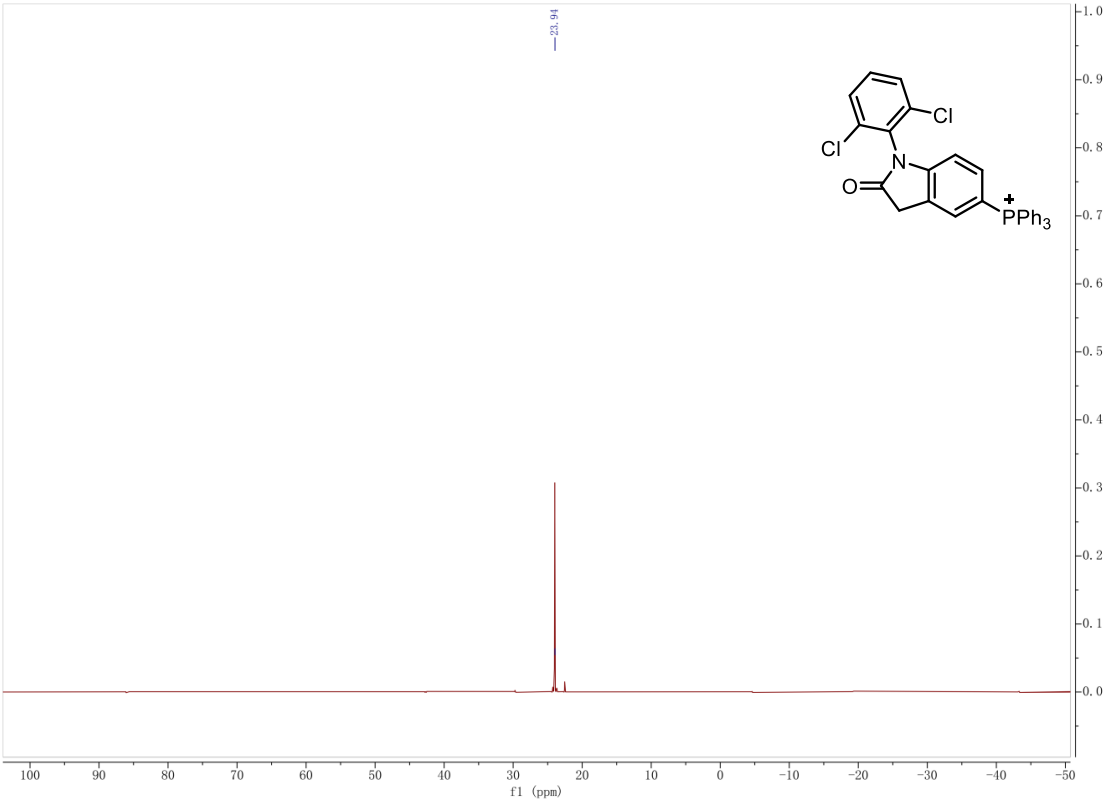




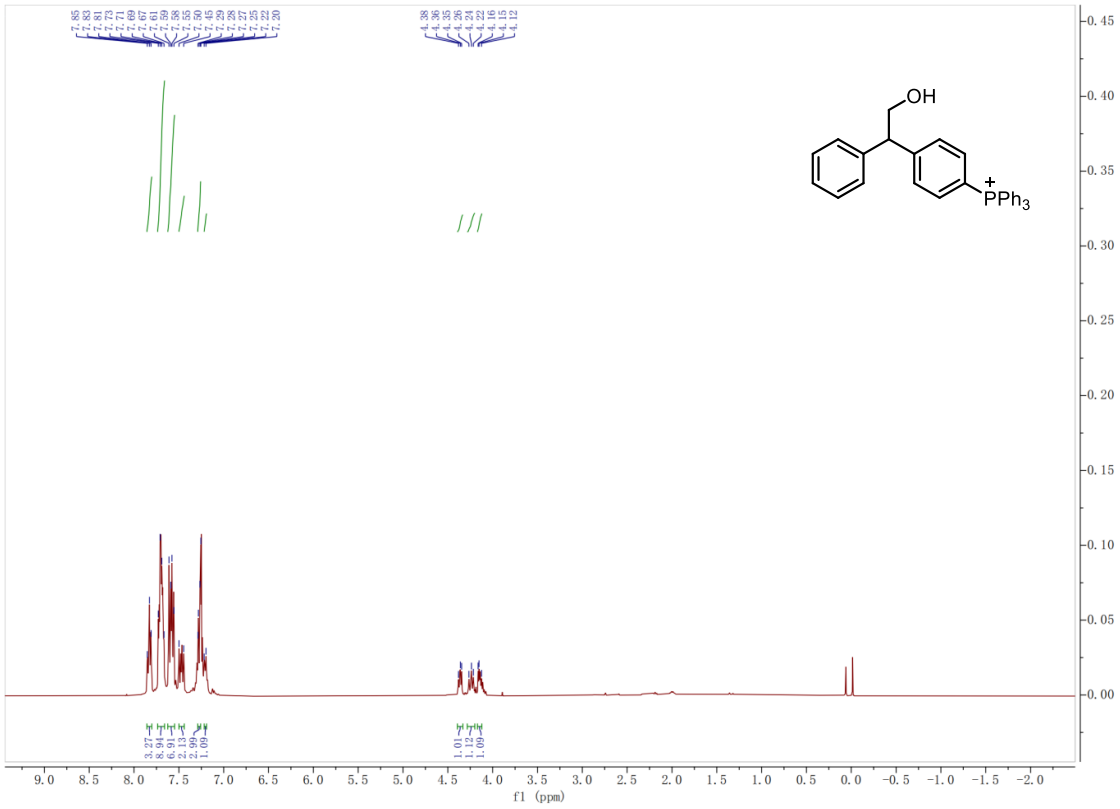
NMR Spectra of **7**

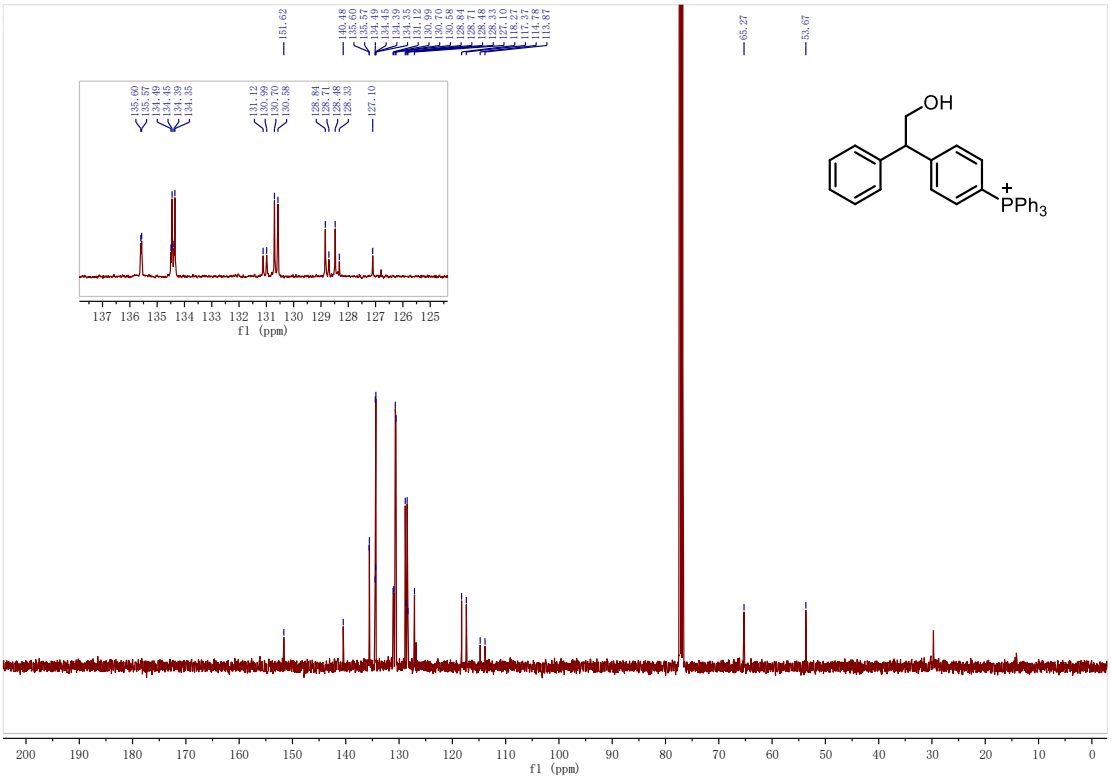


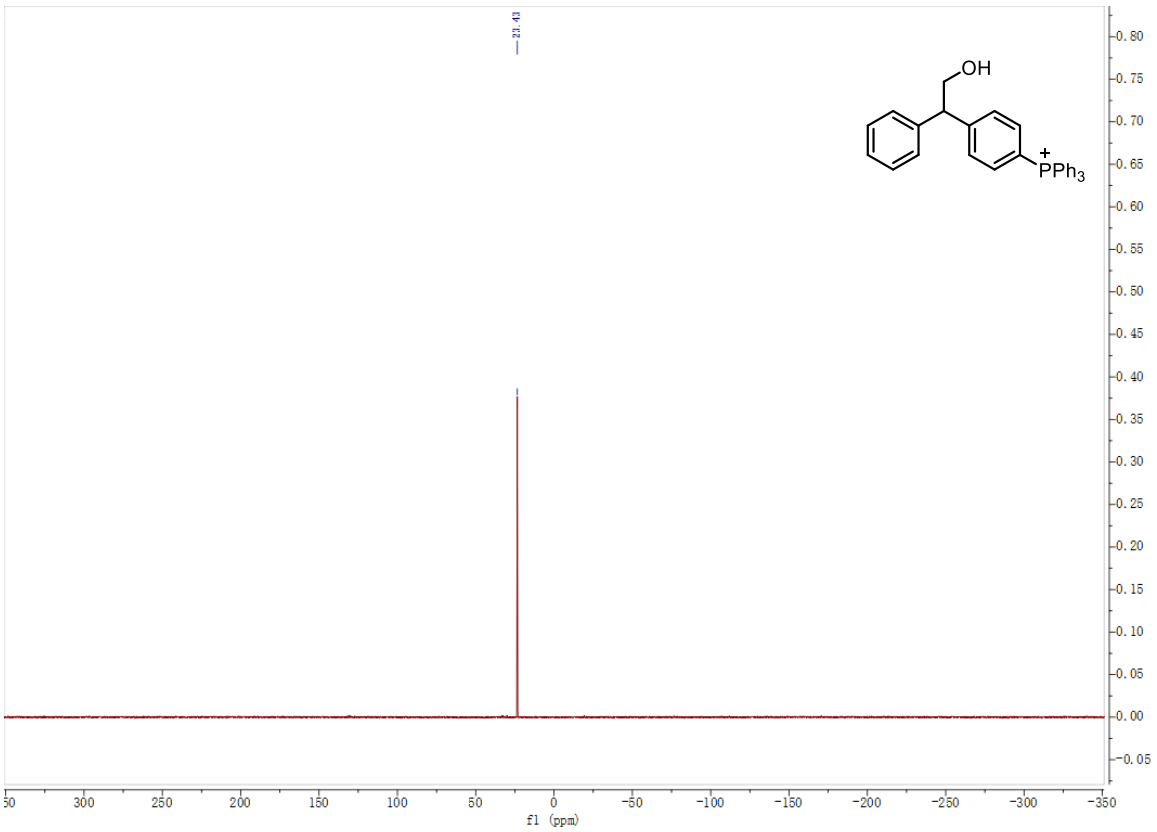

172.78
149.70
135.76
135.71
135.68
135.24
134.66
134.45
131.73
130.85
130.73
129.30
129.21
127.66
127.51
118.49
117.60
110.72
110.69
110.58
109.74
35.33
Cl
Cl
N
O
PPh3
f1 (ppm)


23.94
Cl
Cl
N
O
PPh3
f1 (ppm)

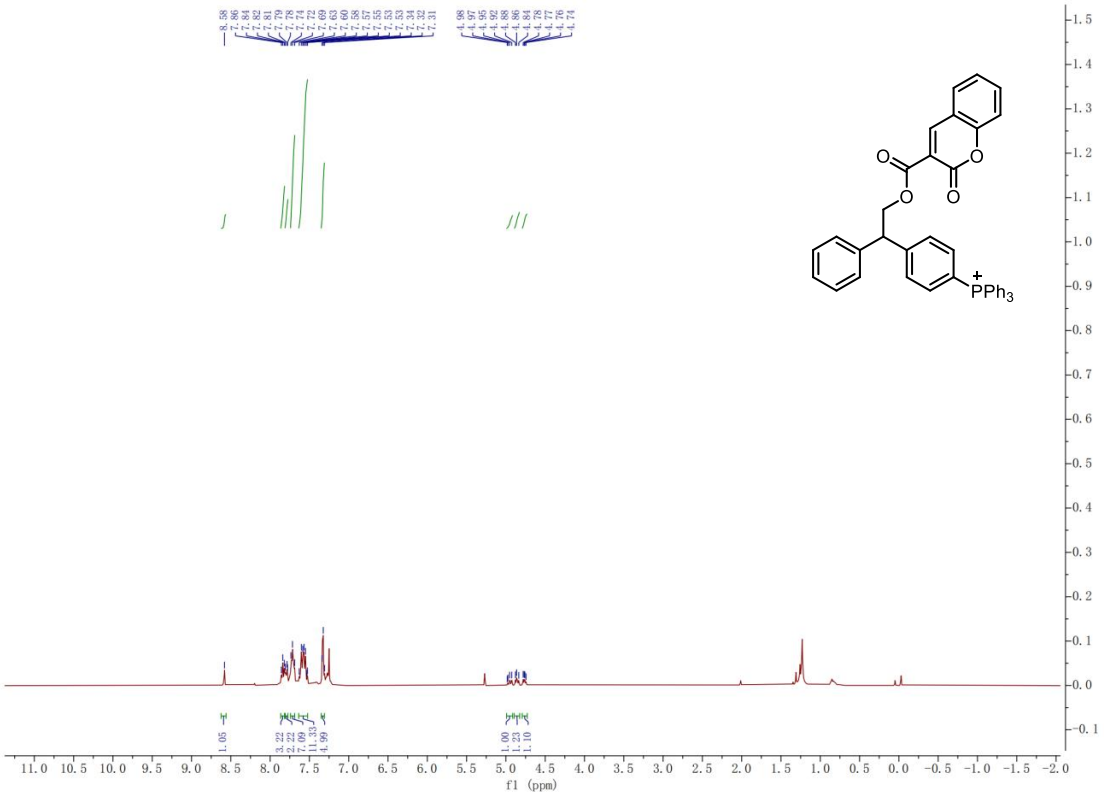
NMR Spectra of **8**

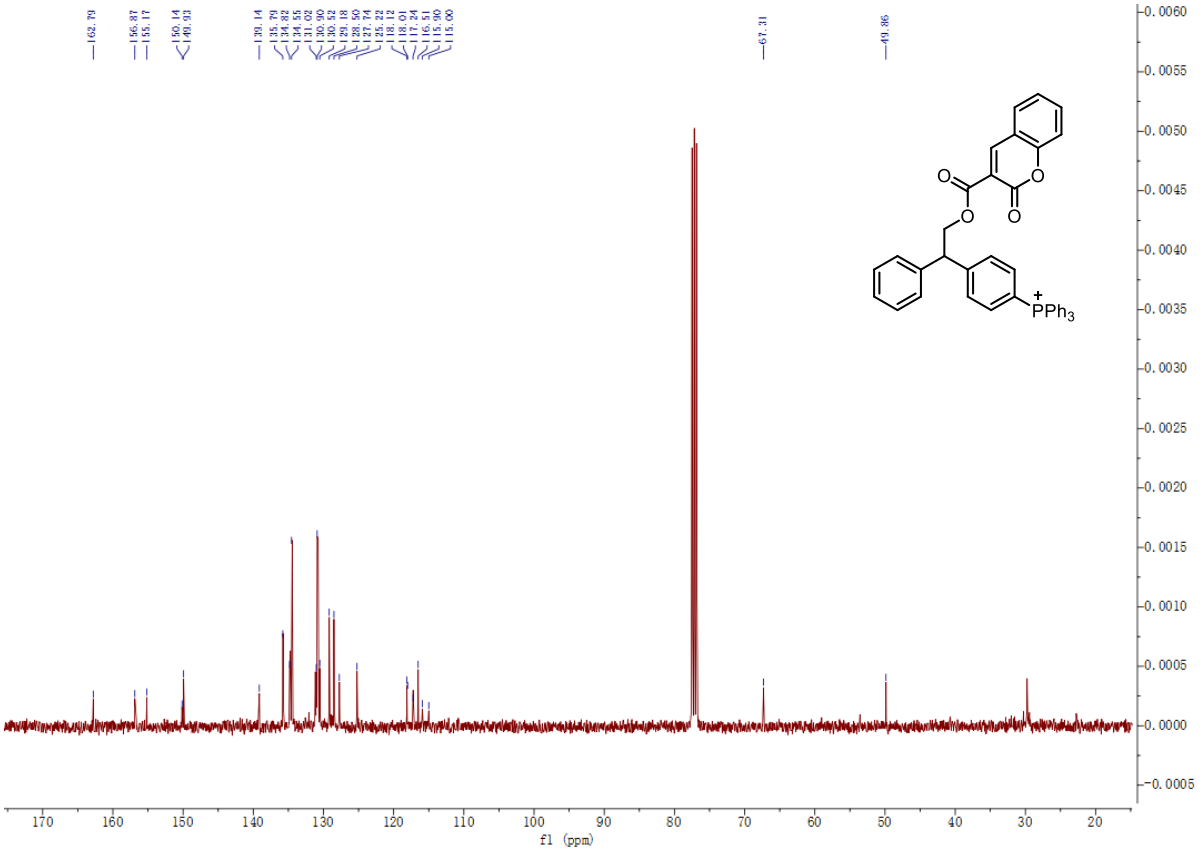


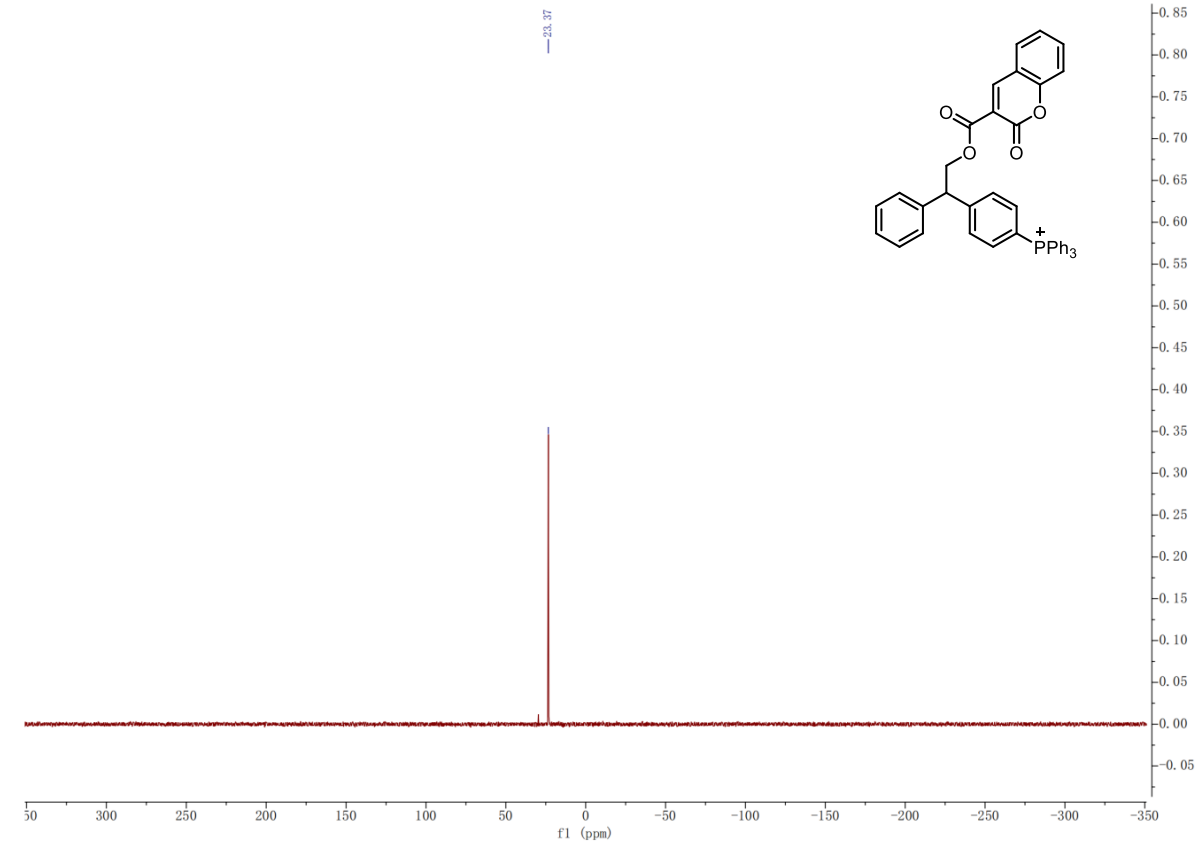




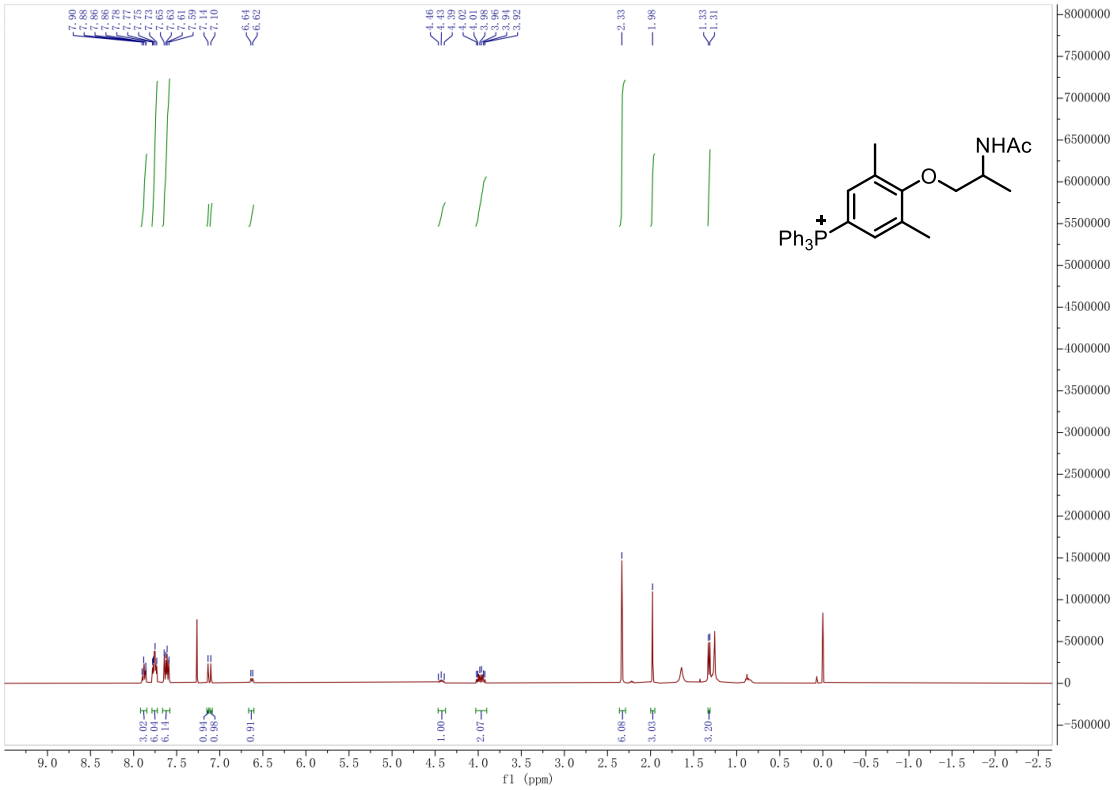
NMR Spectra of **9**

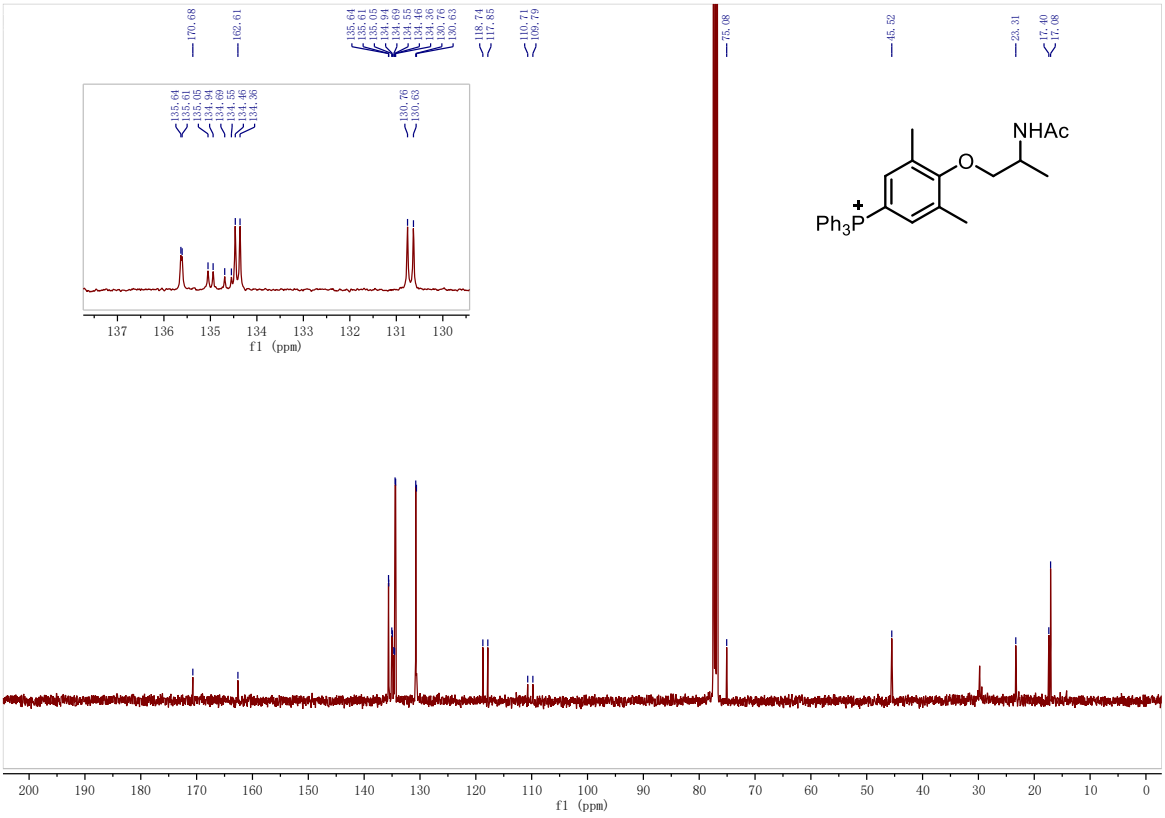


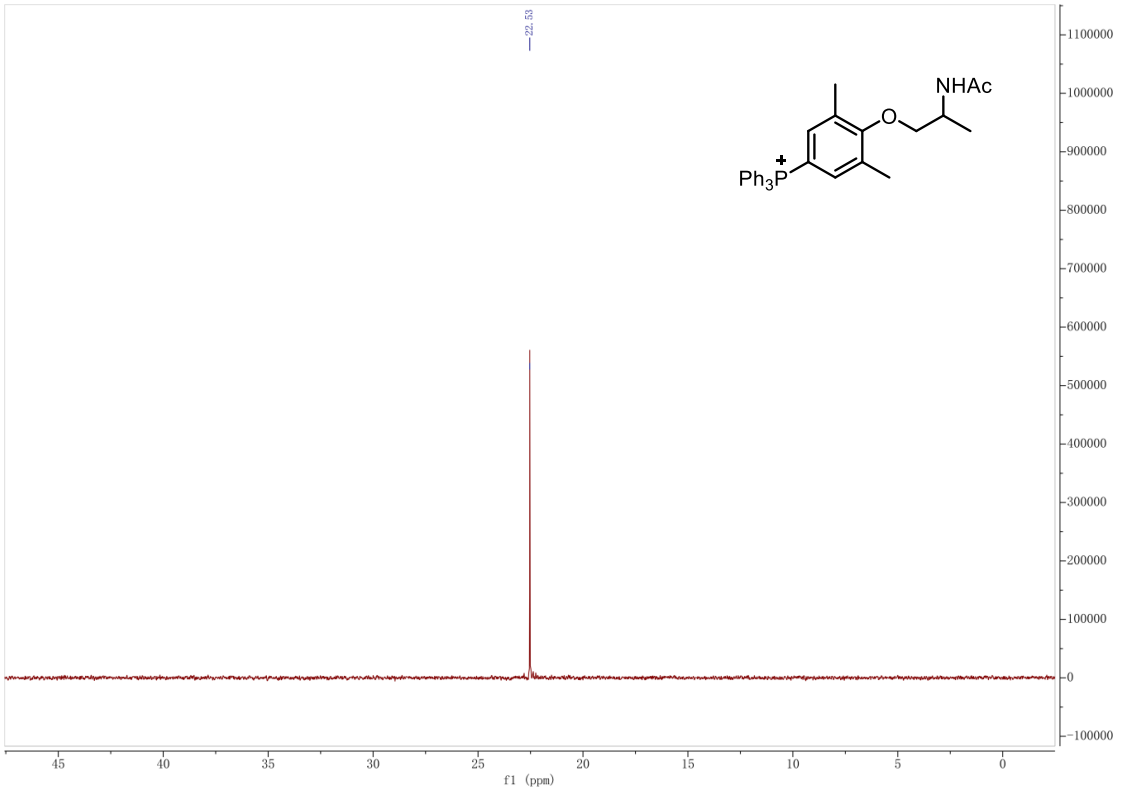

162.79
156.87
155.17
150.14
149.93
139.14
135.79
134.82
134.55
131.02
130.90
130.52
129.18
128.90
127.74
125.22
118.12
118.01
117.24
116.51
115.90
115.60
67.31
49.86
f1 (ppm)


23.37
f1 (ppm)

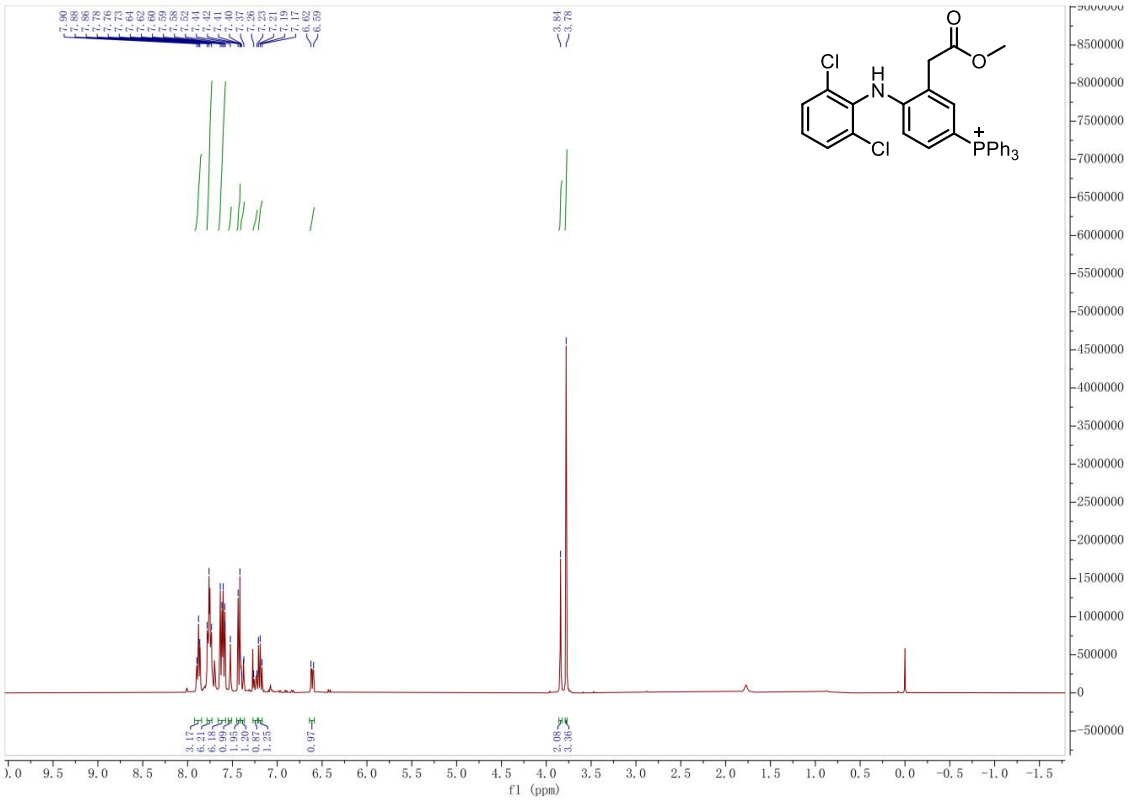
NMR Spectra of **10**

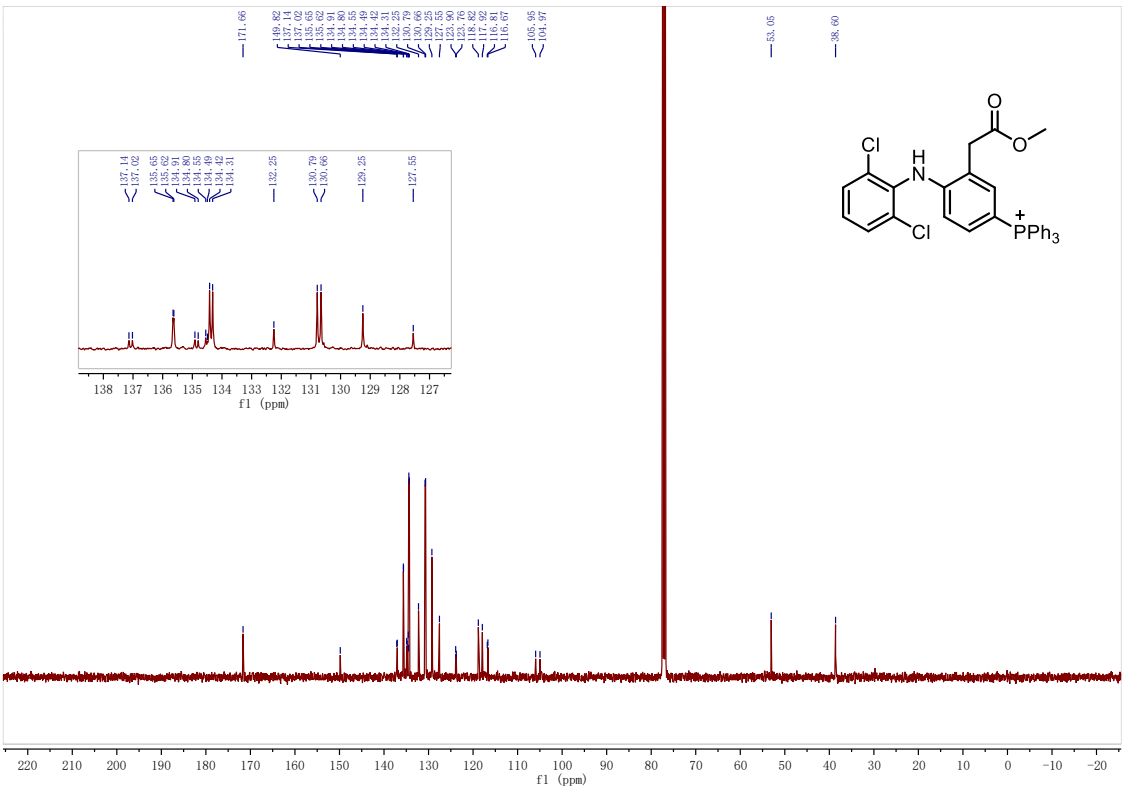


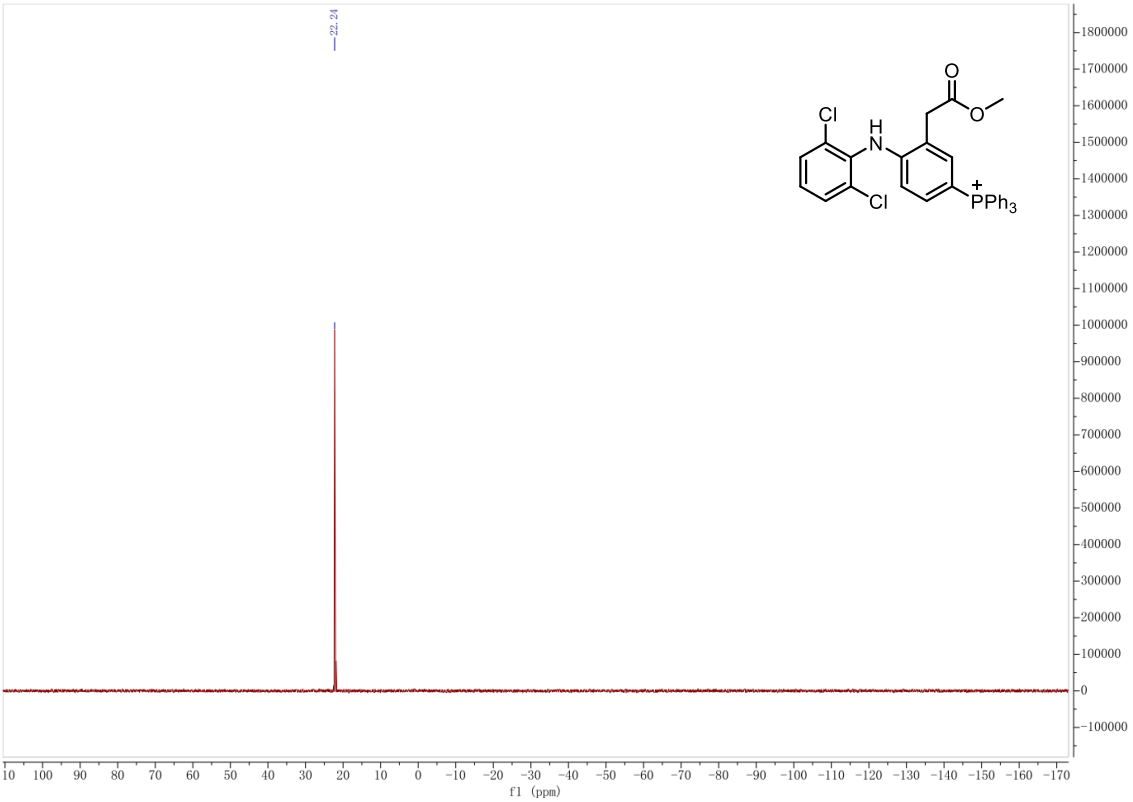




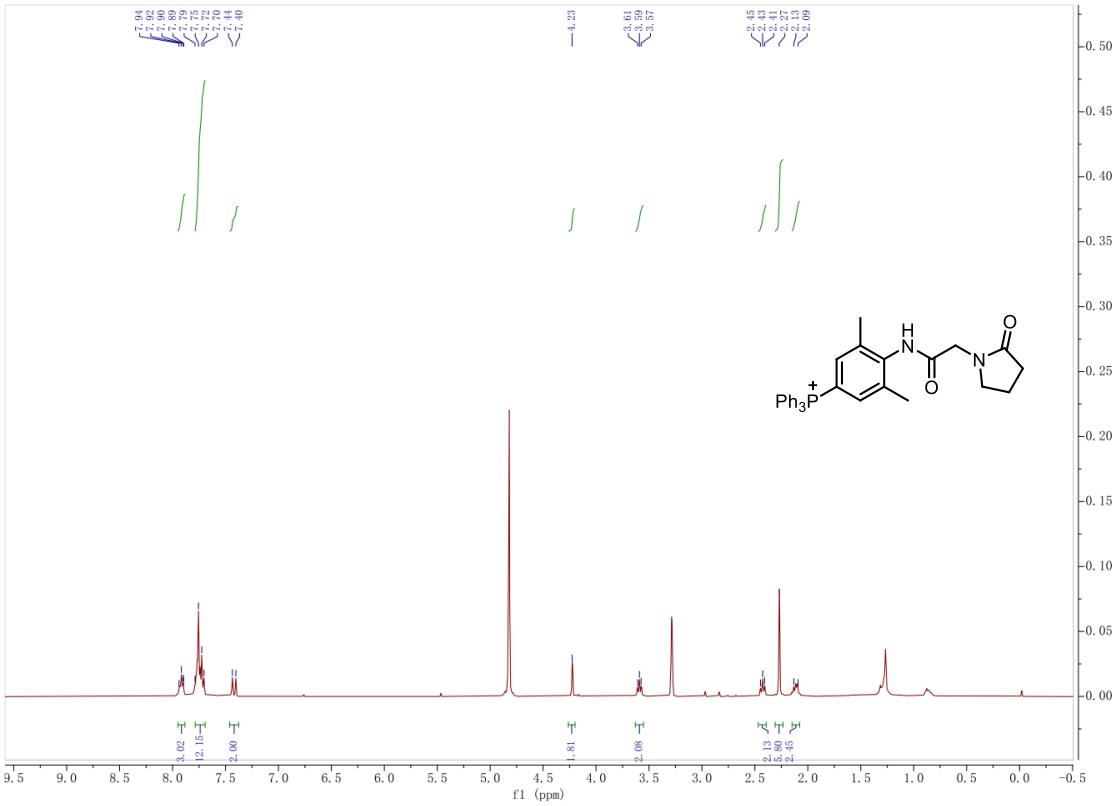
NMR Spectra of **11**

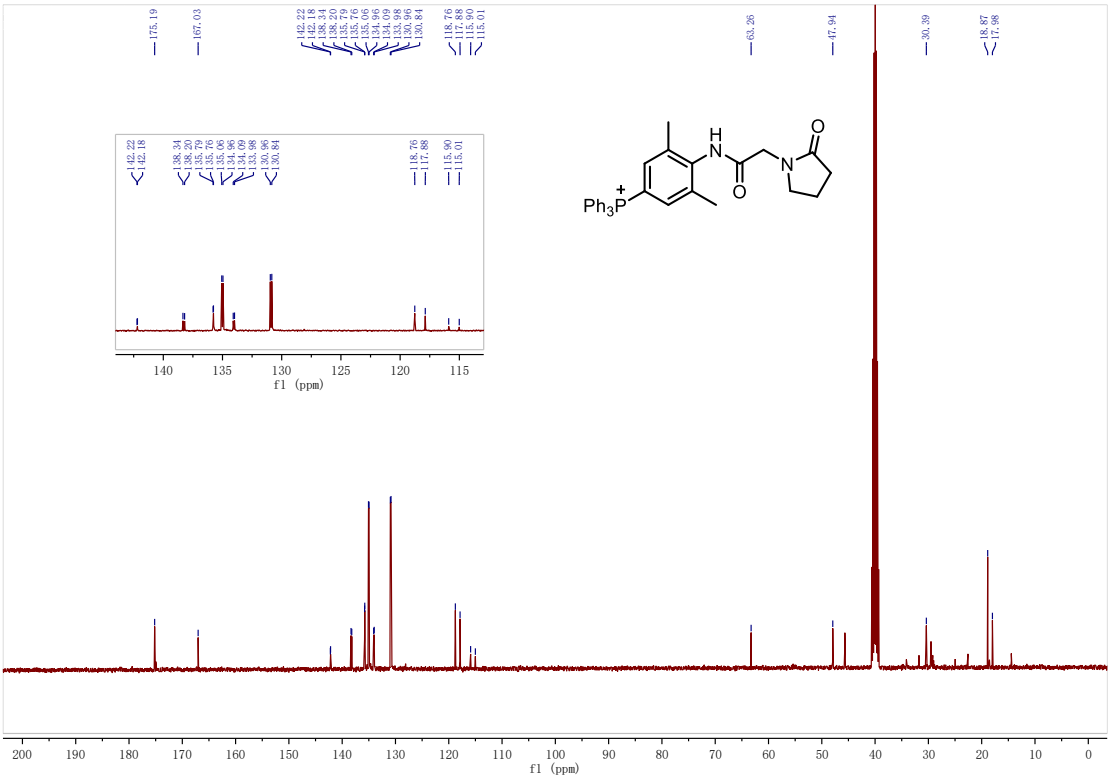


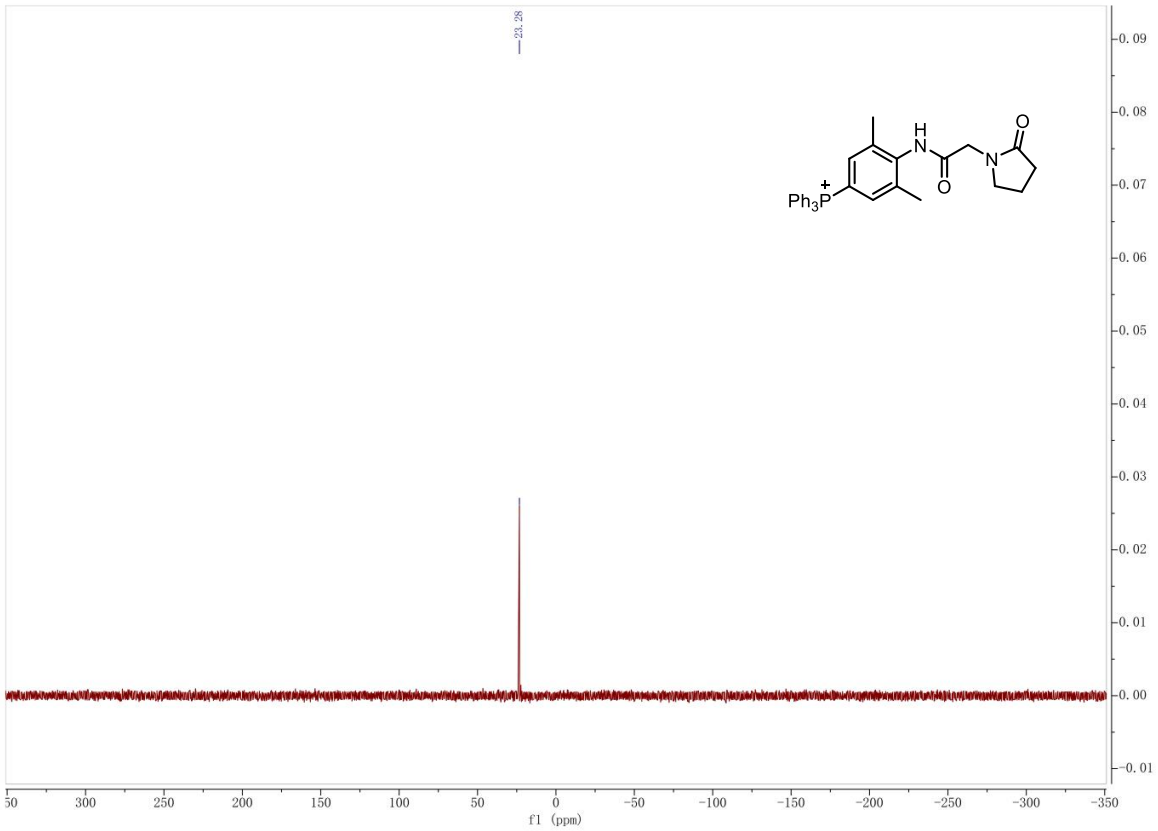

171.66
149.82
137.14
137.02
135.65
135.62
134.91
134.80
134.55
134.49
134.42
134.31
132.25
130.79
130.66
129.25
127.55
123.90
123.76
118.82
117.92
116.81
116.67
105.96
104.97
53.05
38.60
Cl
H
N
Cl
O
O
+
PPh3
f1 (ppm)


22.24
Cl
H
N
Cl
O
O
+
PPh3
f1 (ppm)

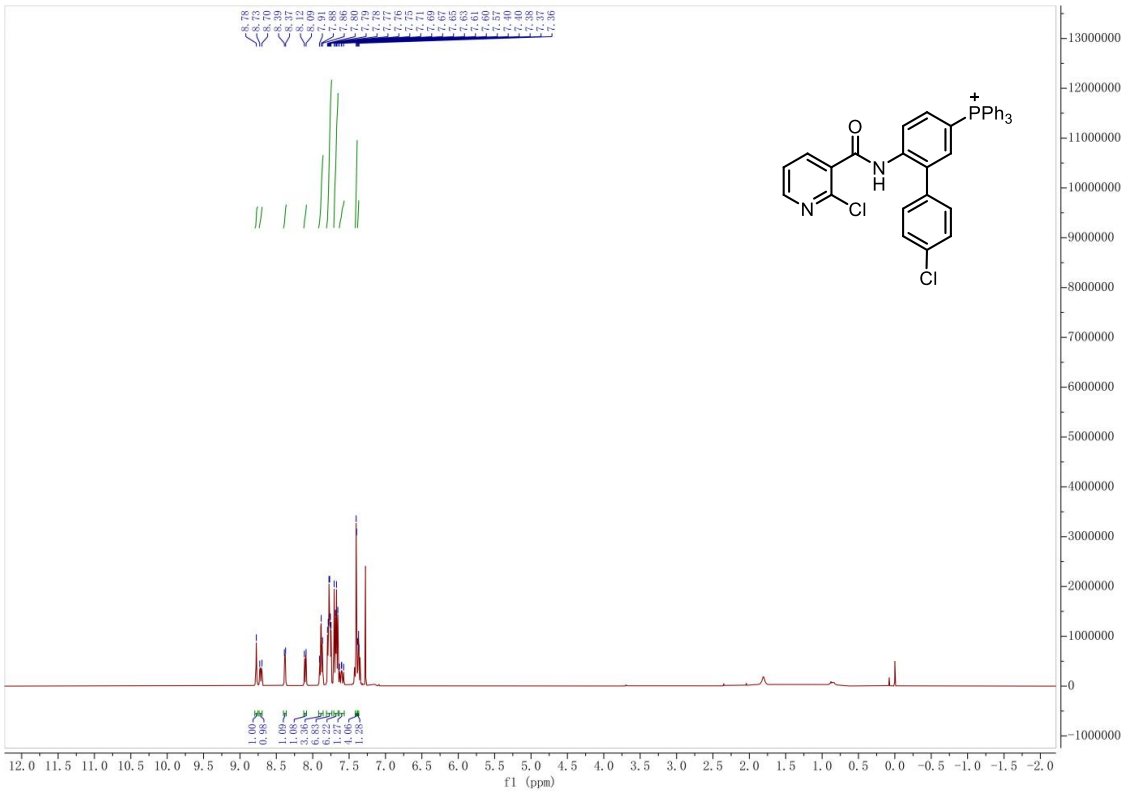
NMR Spectra of **12**

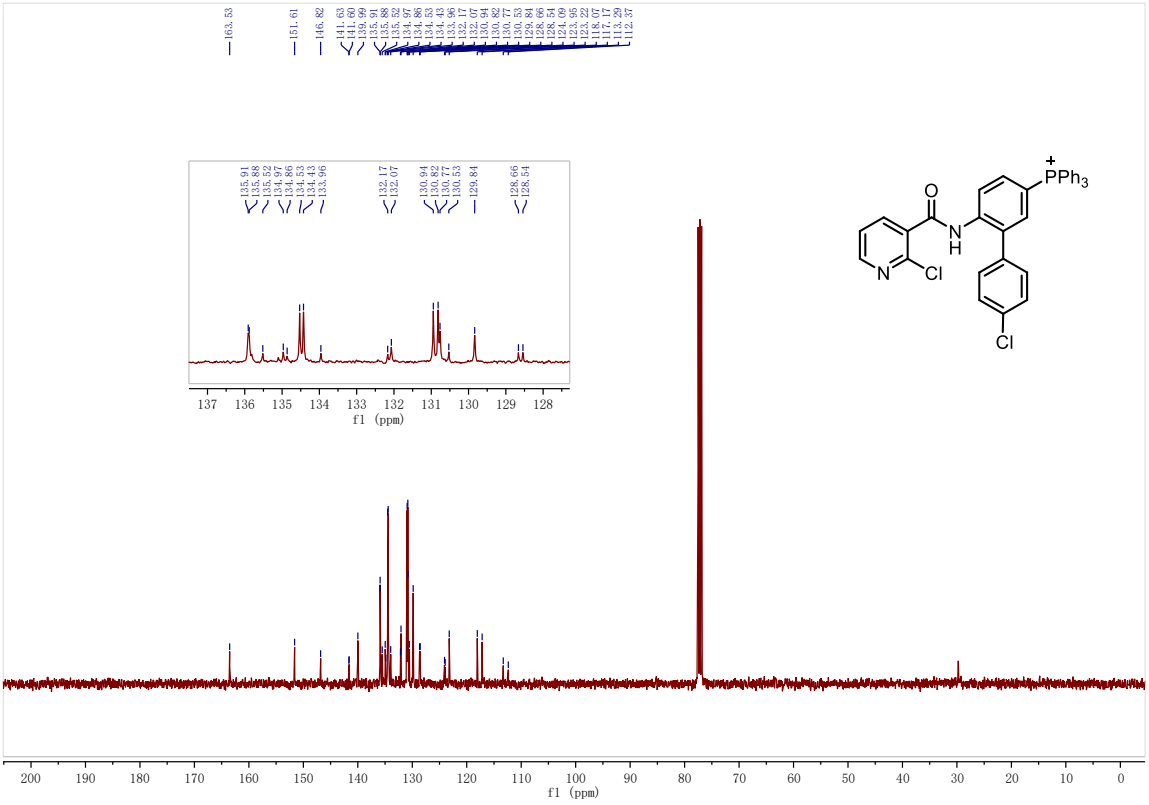


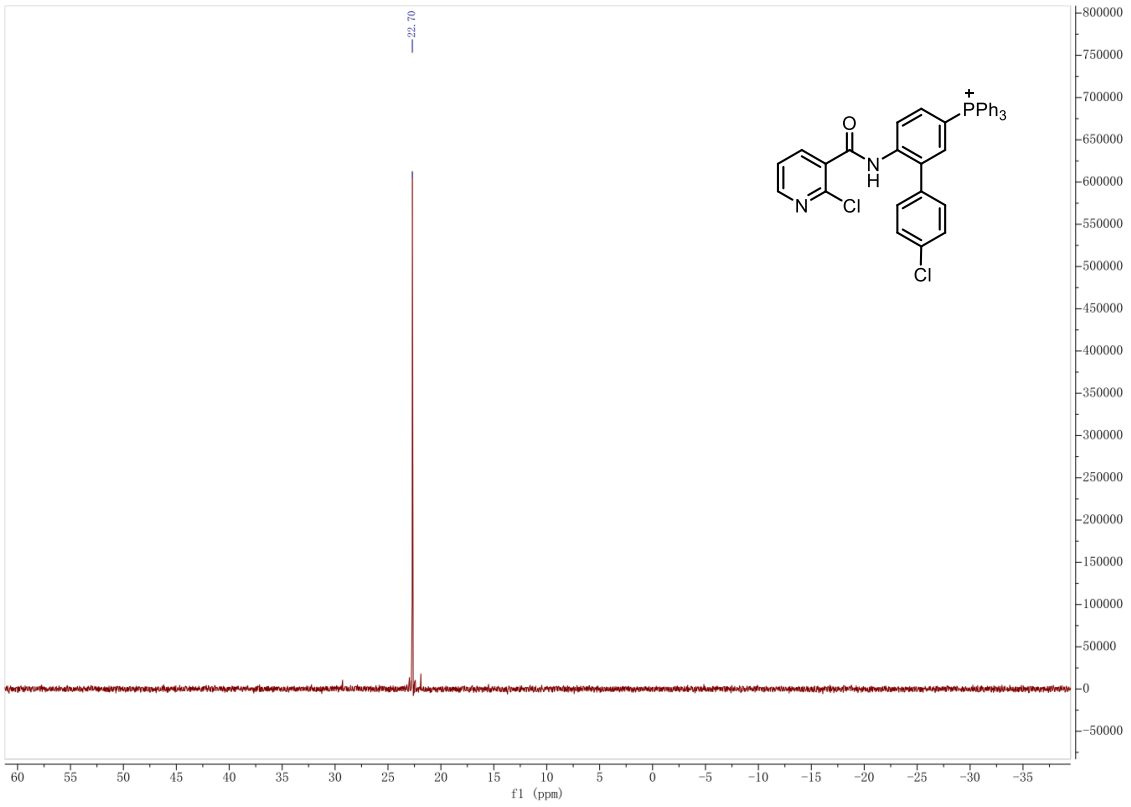




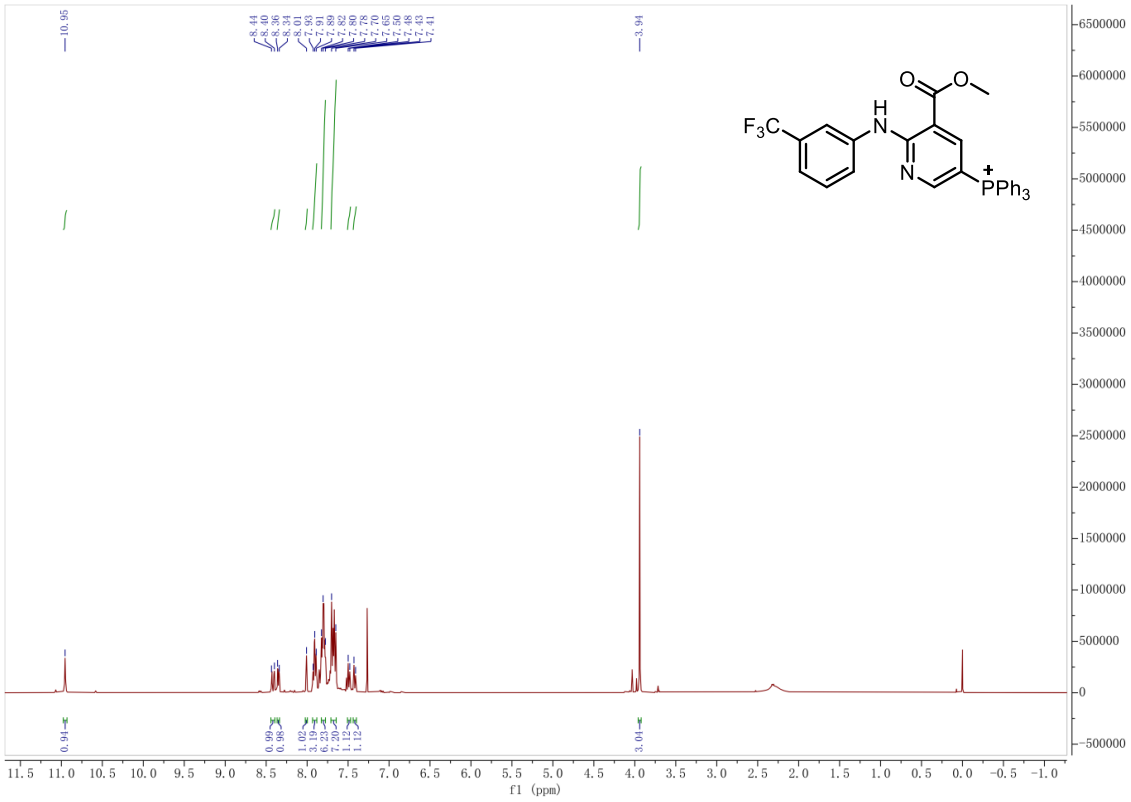
NMR Spectra of **13**

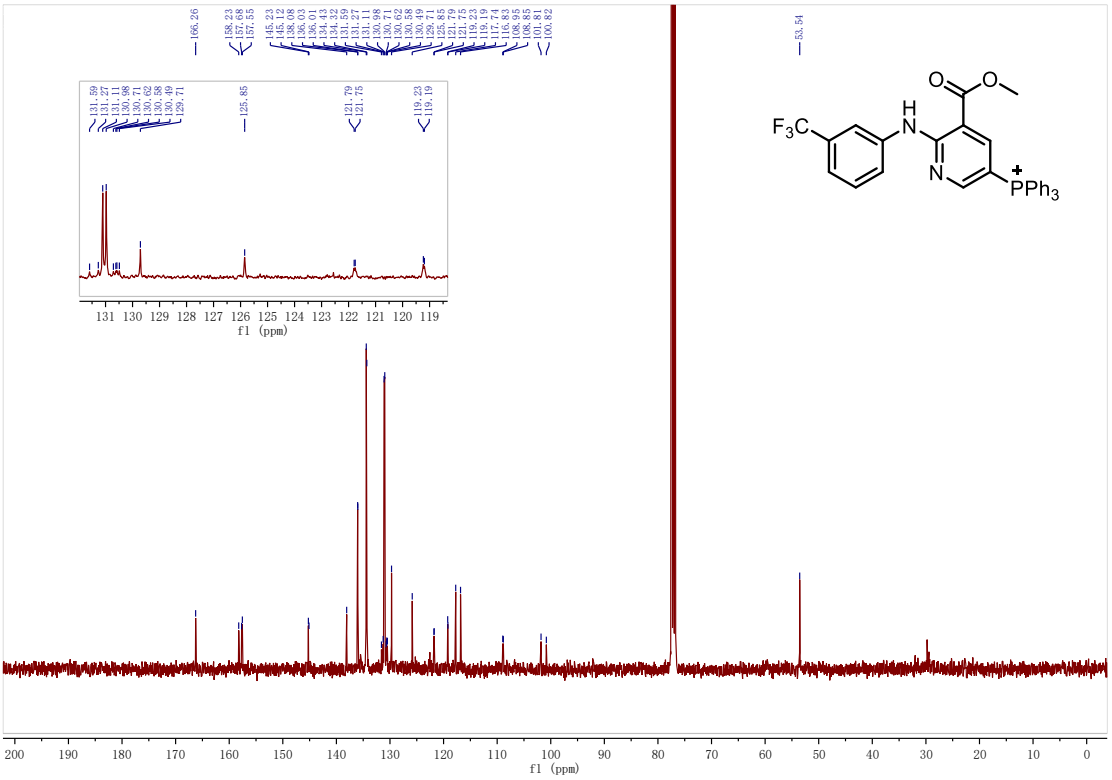


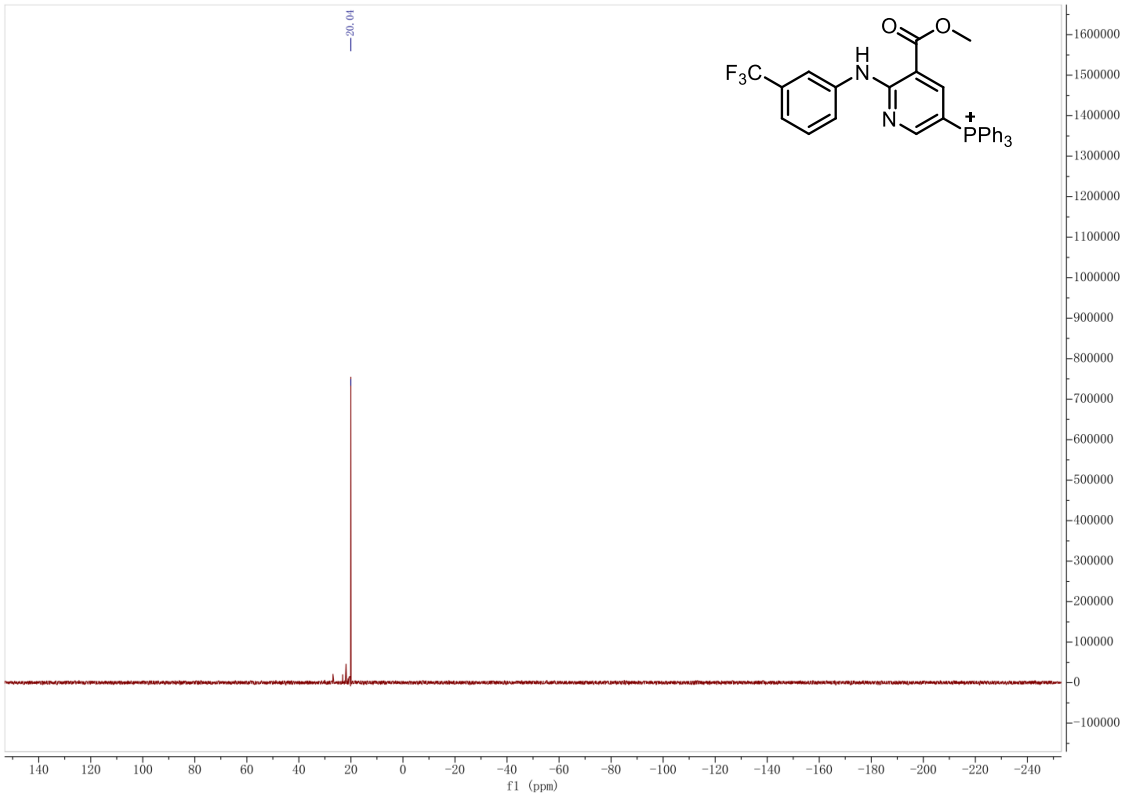

163.53
151.61
146.82
141.63
141.60
138.99
135.91
135.88
135.52
134.97
134.86
134.53
134.43
133.96
132.17
132.07
130.94
130.89
130.77
130.53
129.84
128.66
128.54
PPh3
O
N
H
N
Cl
Cl
137 136 135 134 133 132 131 130 129 128
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

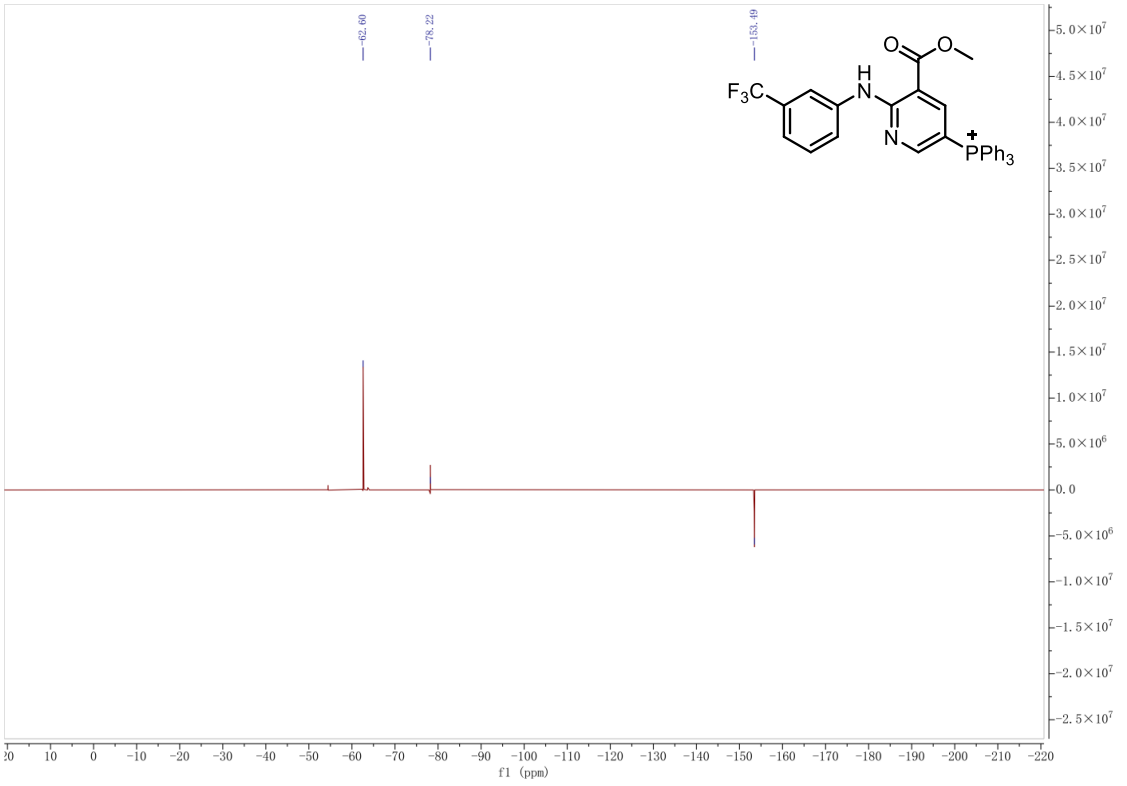

22.70
PPh3
O
N
H
N
Cl
Cl
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
f1 (ppm)

NMR Spectra of **14**

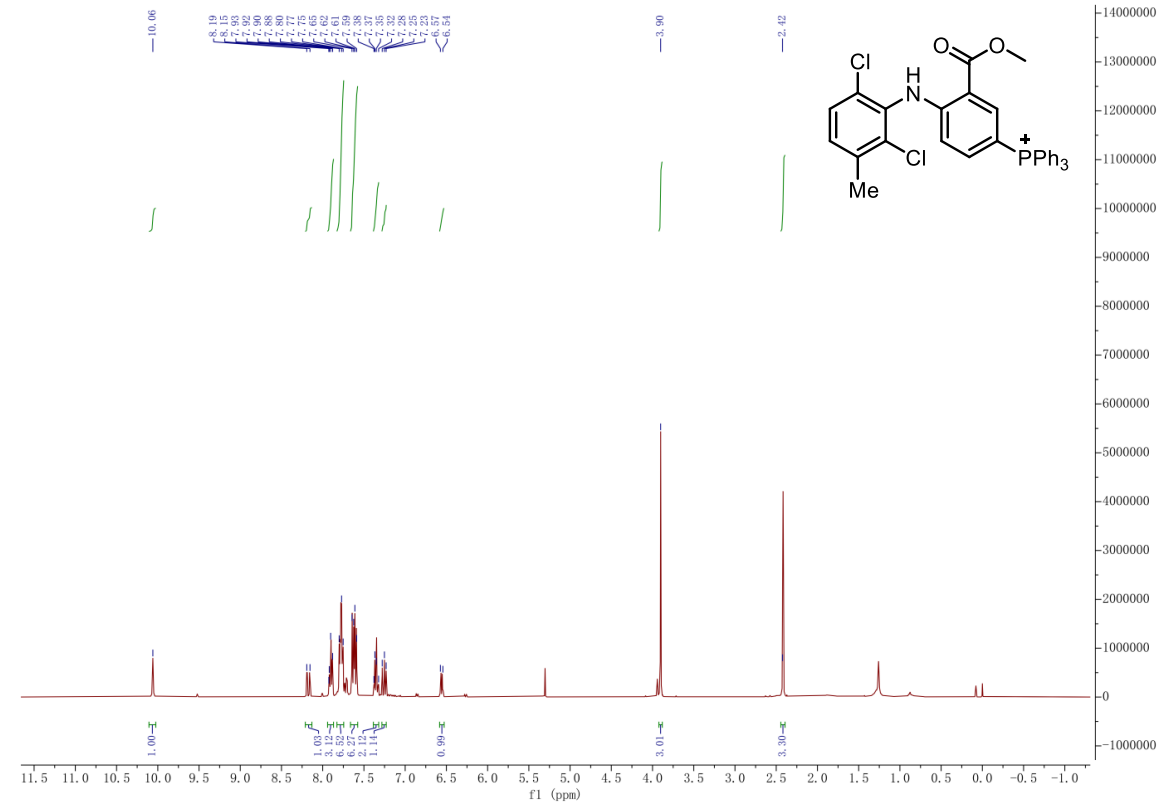


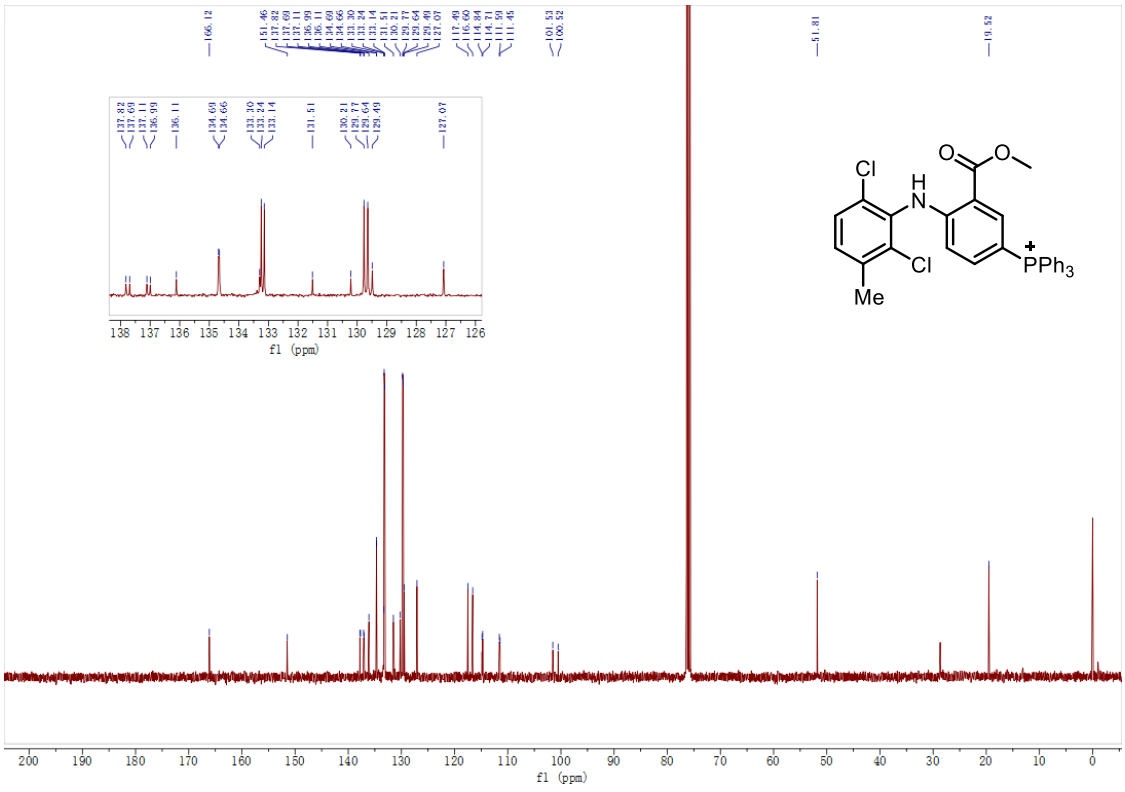


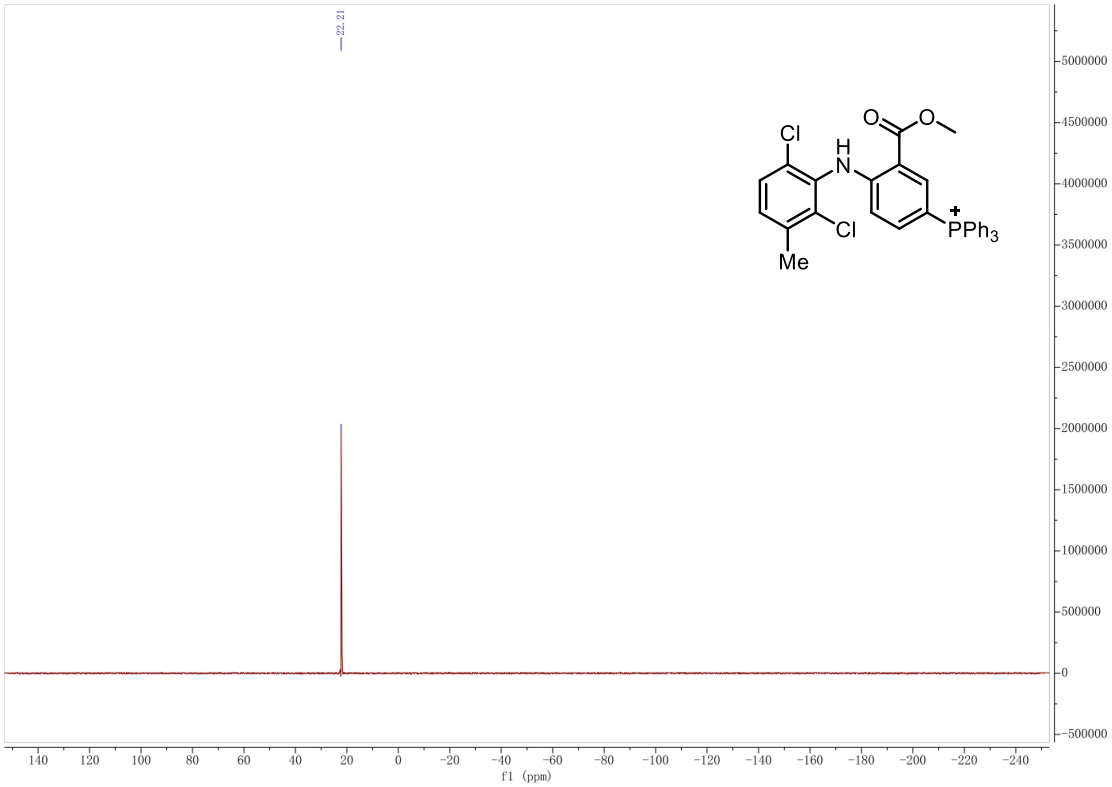

20.04
O
O
H
N
F3C
N
PPh3
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240
f1 (ppm)


62.60
78.22
153.49
O
O
H
N
F3C
N
PPh3
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
−5.0×10^6
−1.0×10^7
−1.5×10^7
−2.0×10^7
−2.5×10^7
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

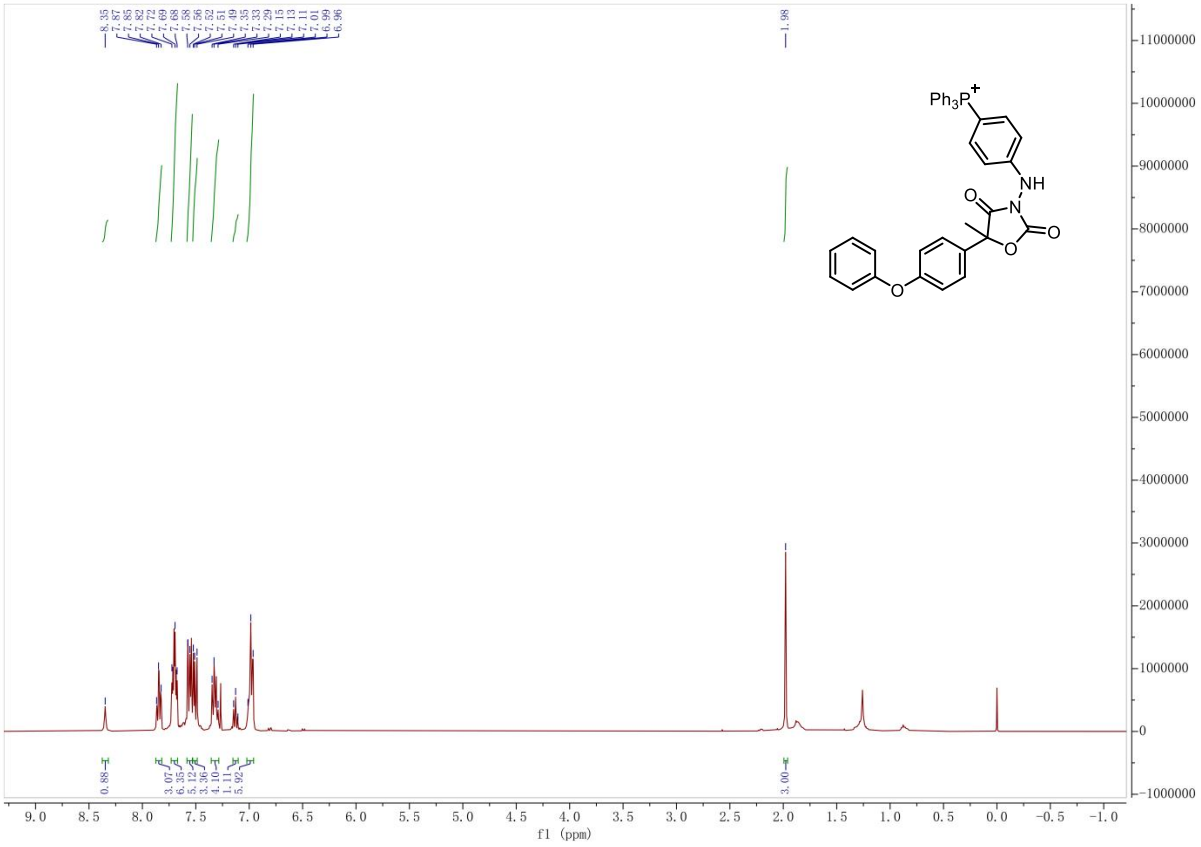
NMR Spectra of **15**

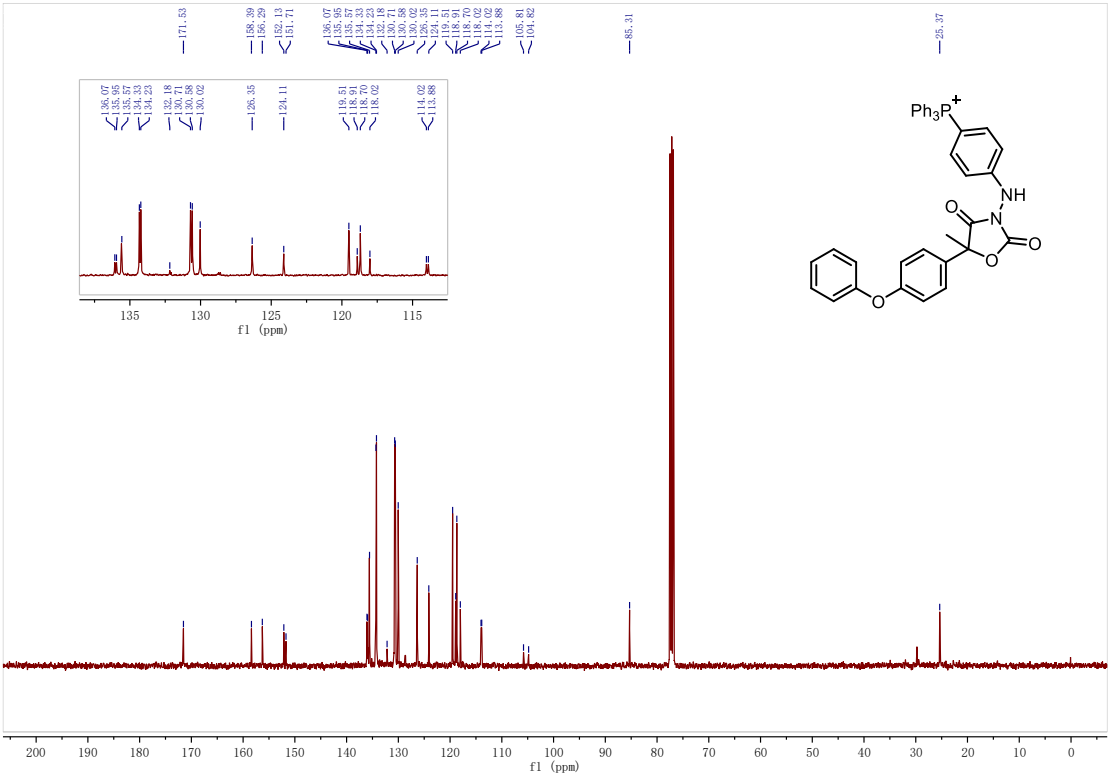


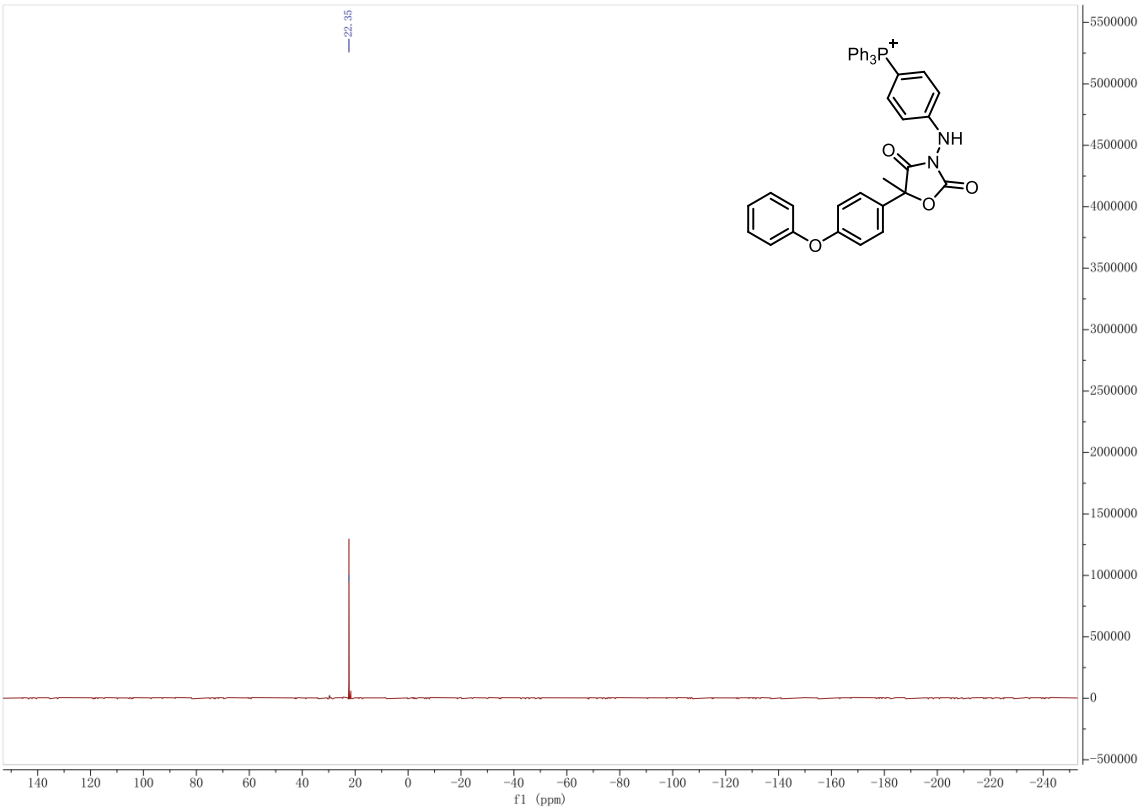




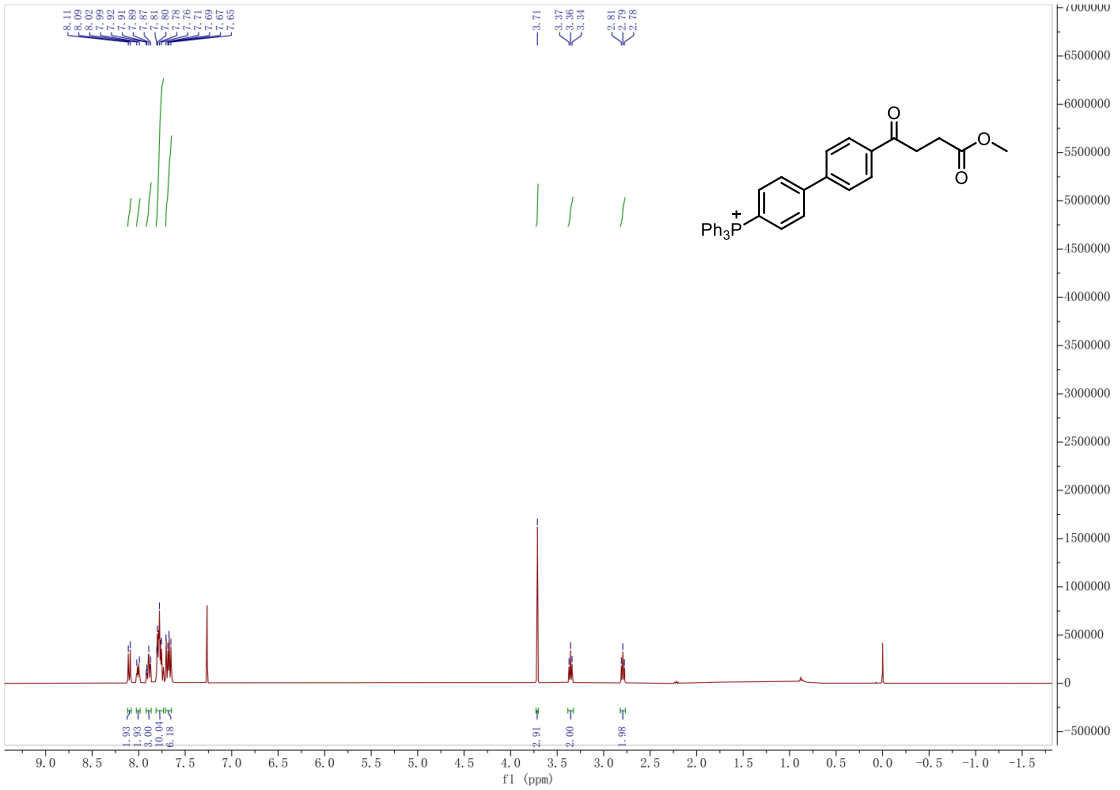
NMR Spectra of **16**

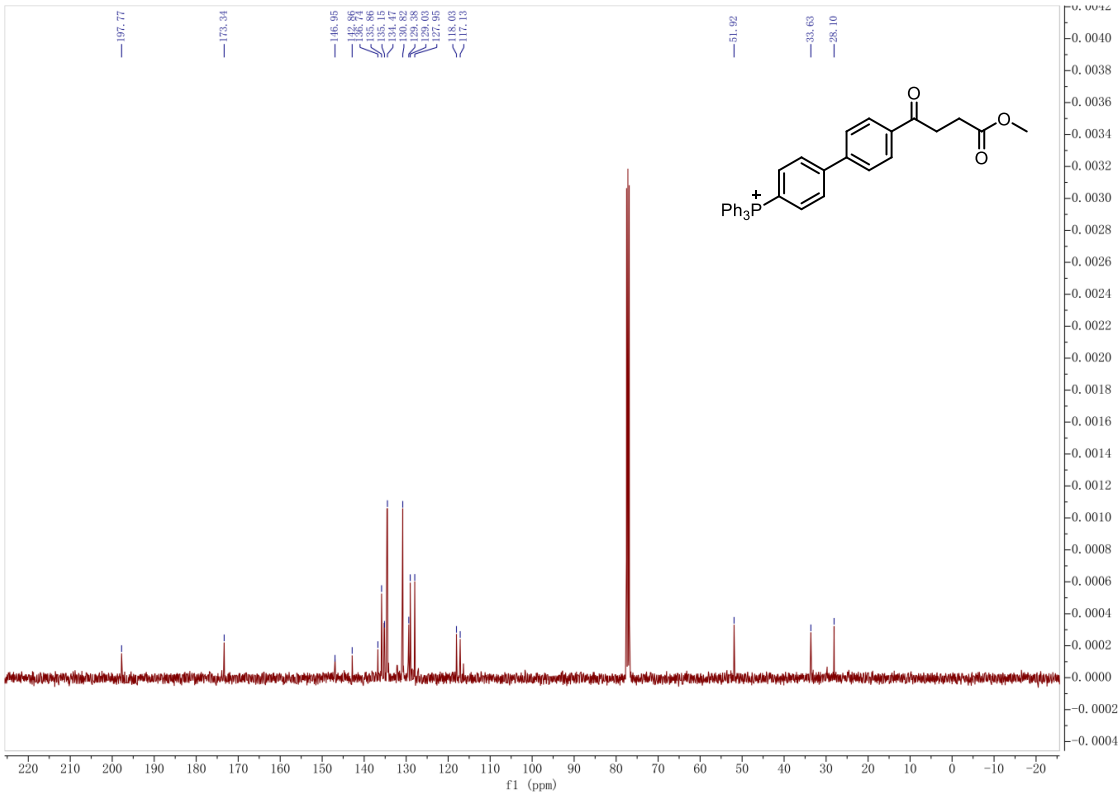


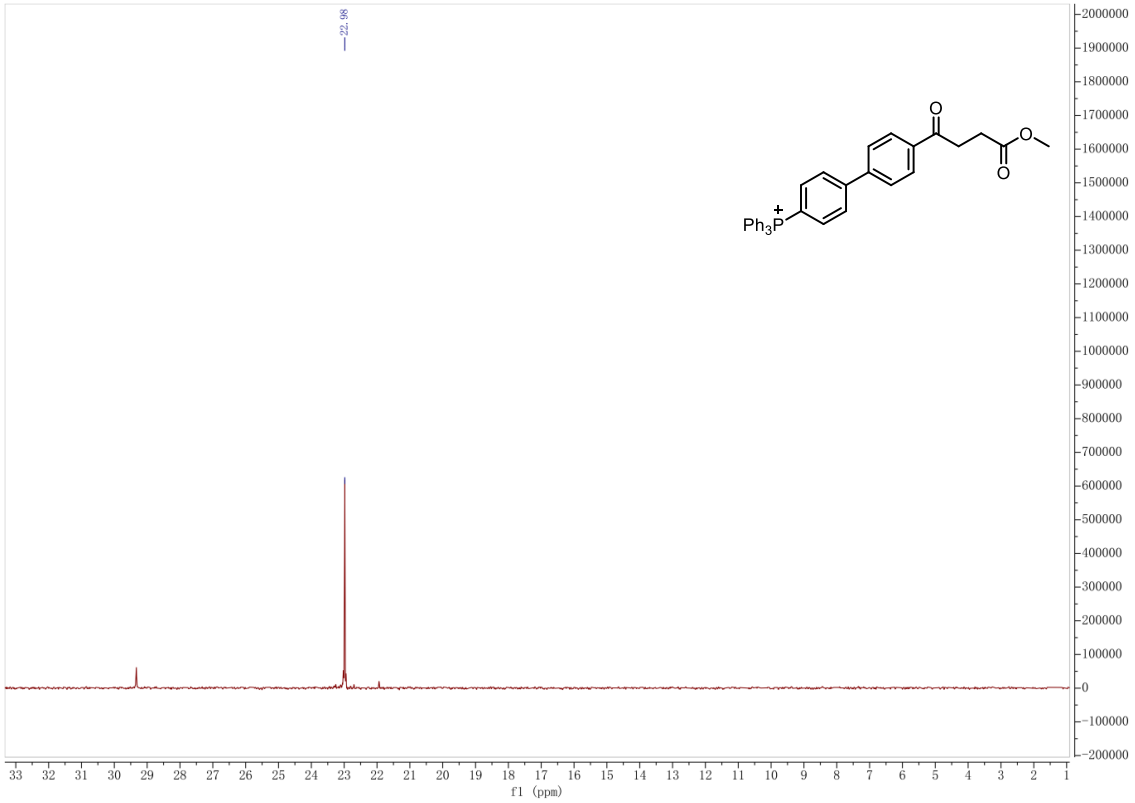

171.53
168.39
166.29
152.13
151.71
136.07
135.95
135.57
134.33
134.23
132.18
130.71
130.58
130.02
126.35
124.11
119.51
118.91
118.70
118.02
114.02
113.88
105.81
101.82
85.31
25.37
Ph3P+
NH
O
N
O
O
O
f1 (ppm)


22.35
Ph3P+
NH
O
N
O
O
O
f1 (ppm)

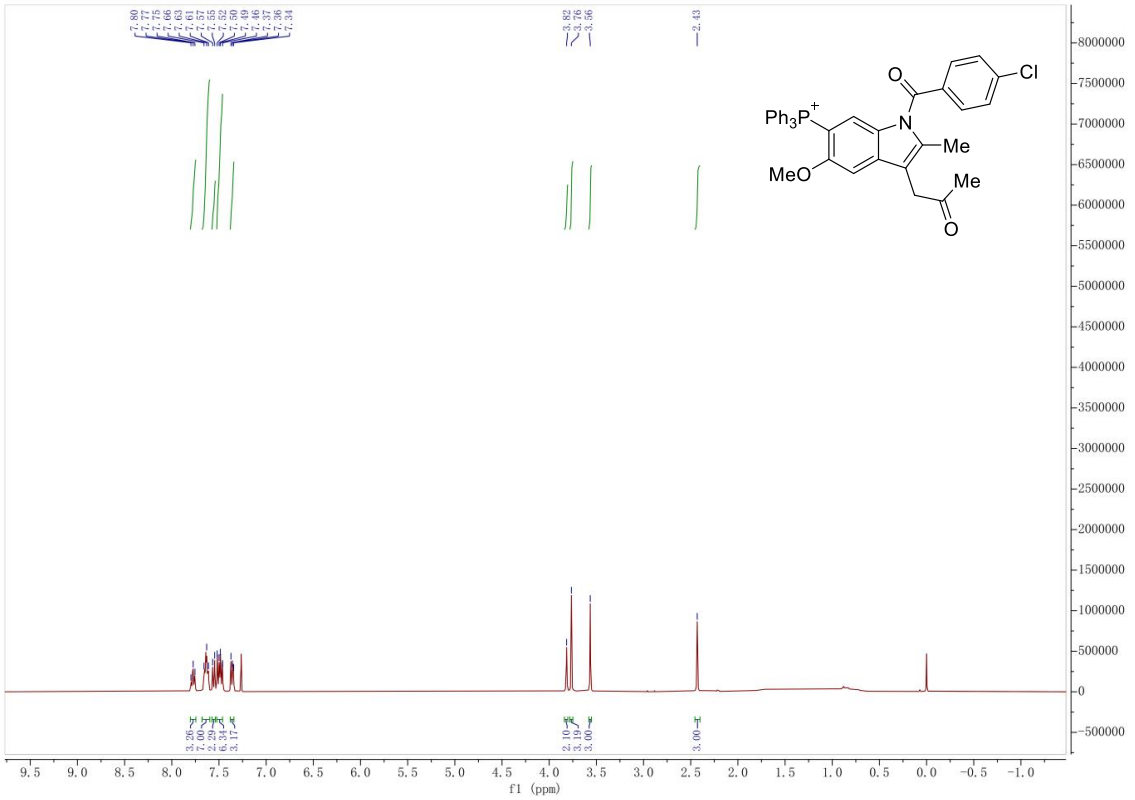
NMR Spectra of **17**

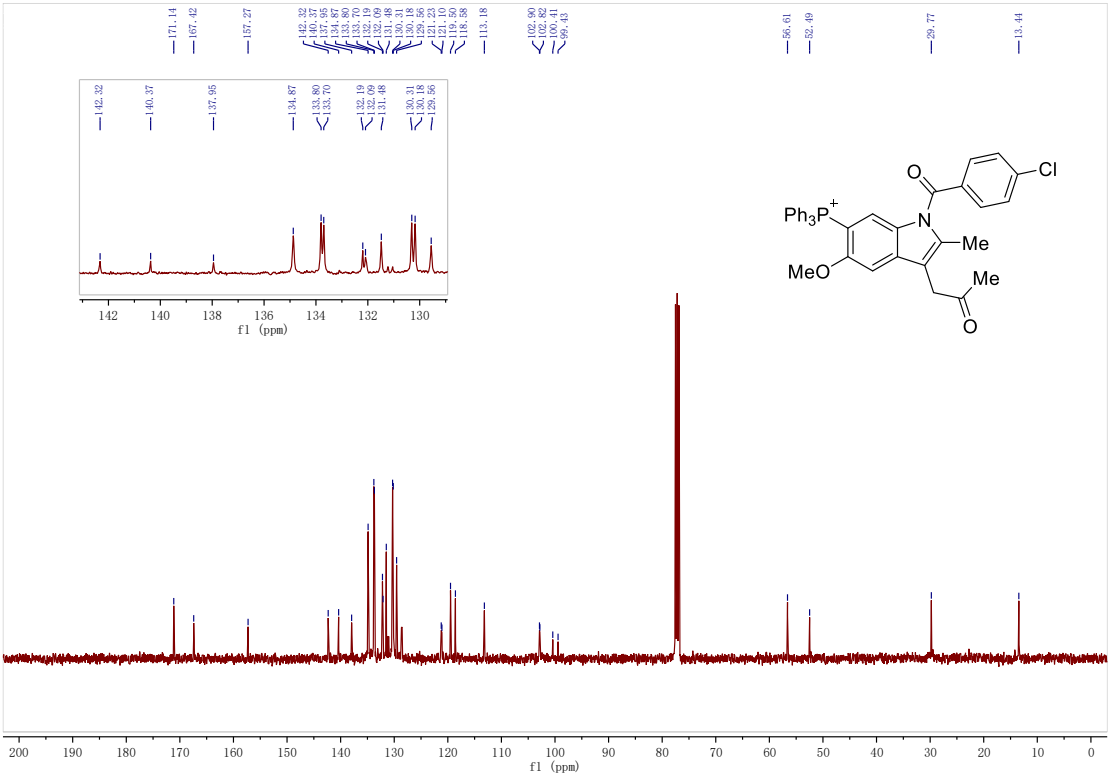


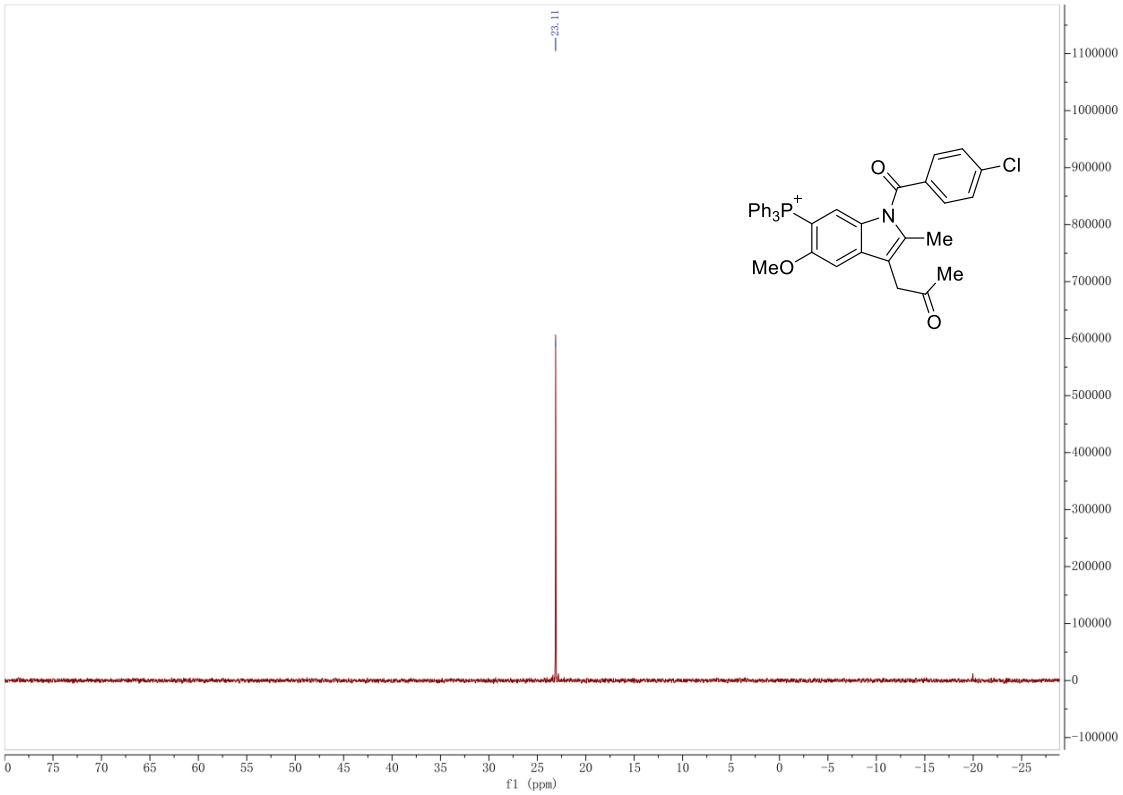




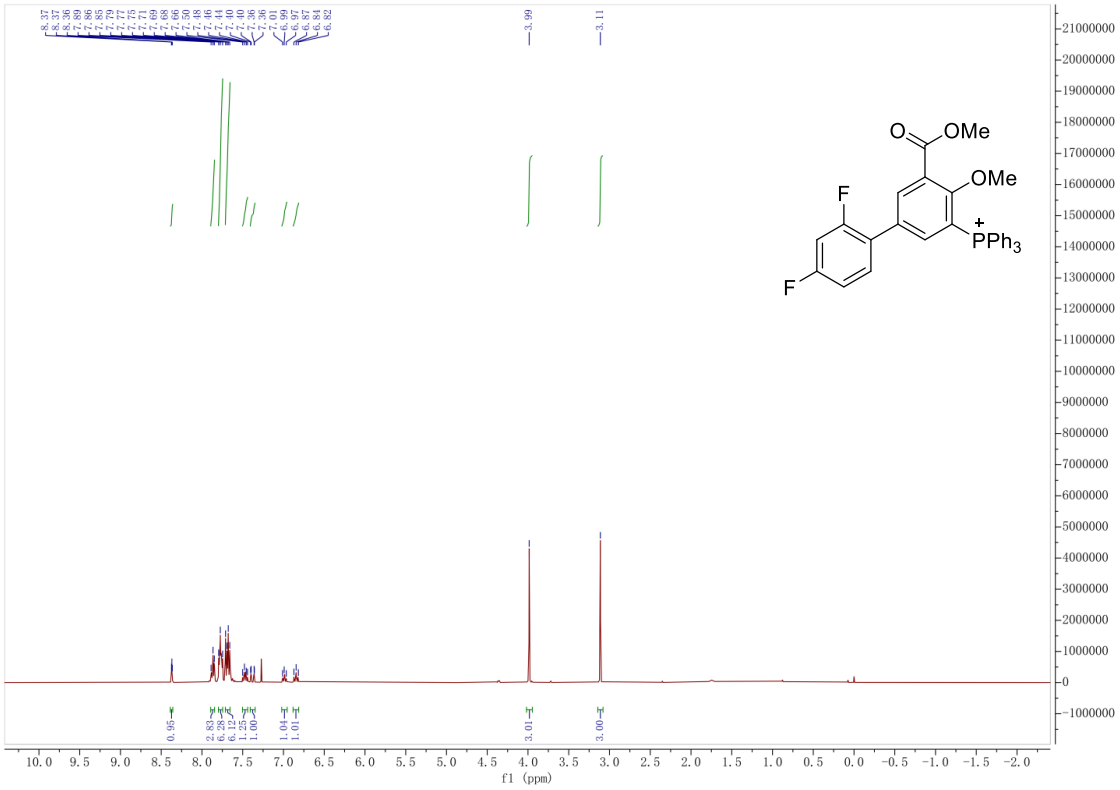
NMR Spectra of **18**

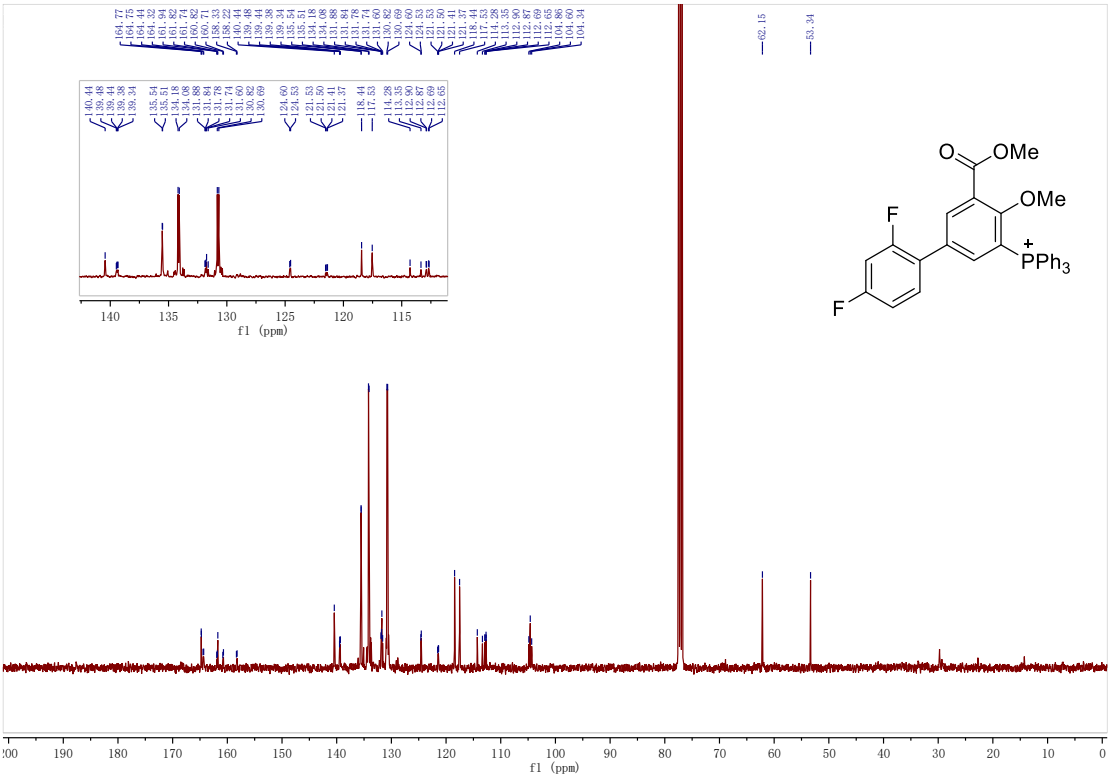


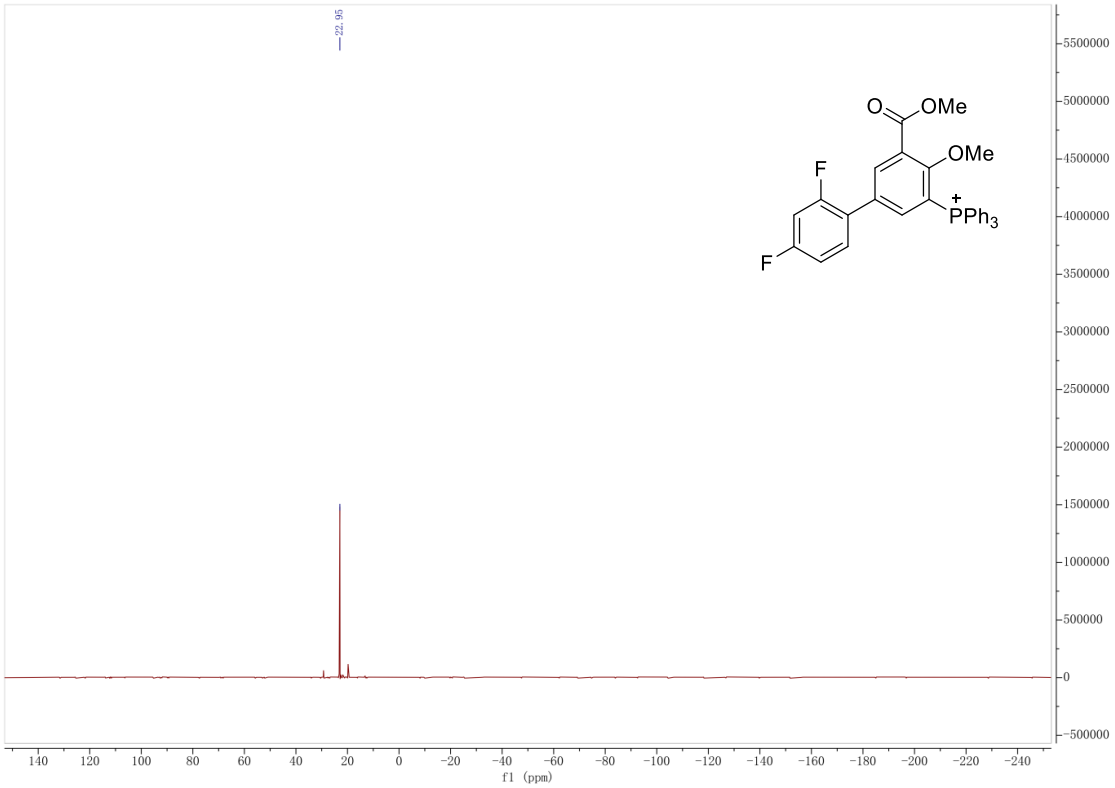

171.14
167.42
157.27
142.32
140.37
137.95
134.87
133.80
133.70
132.19
132.09
131.48
130.31
130.18
129.95
129.95
121.10
119.50
118.38
113.18
102.90
102.82
100.41
99.43
56.61
52.49
29.77
13.44
f1 (ppm)
Cl
O
N
Me
MeO
Me
O
Ph3P+

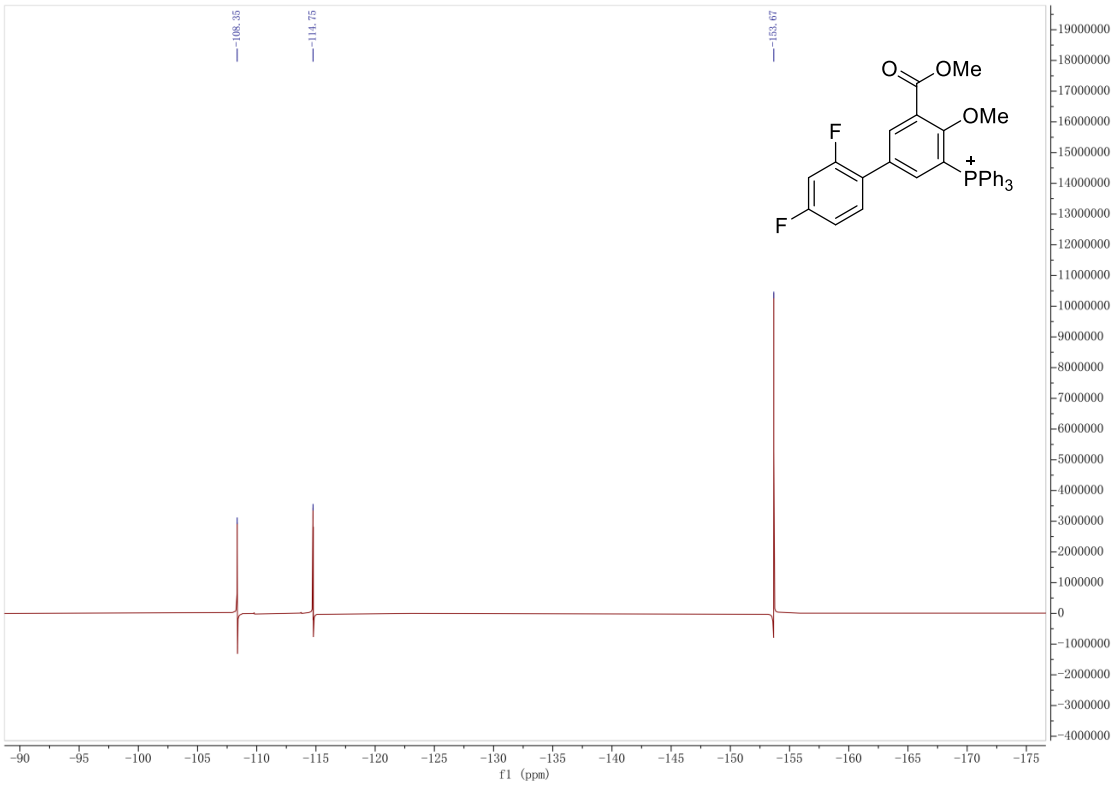

23.11
f1 (ppm)
Cl
O
N
Me
MeO
Me
O
Ph3P+

NMR Spectra of **19**

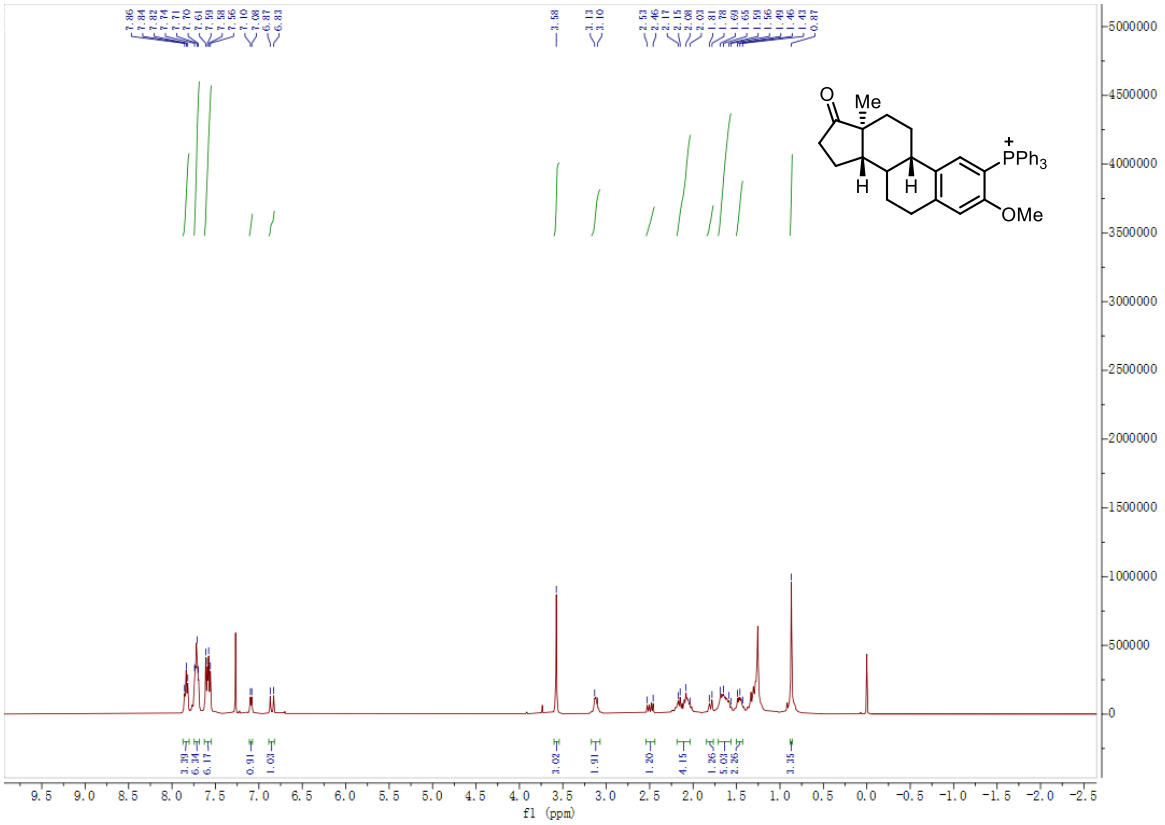


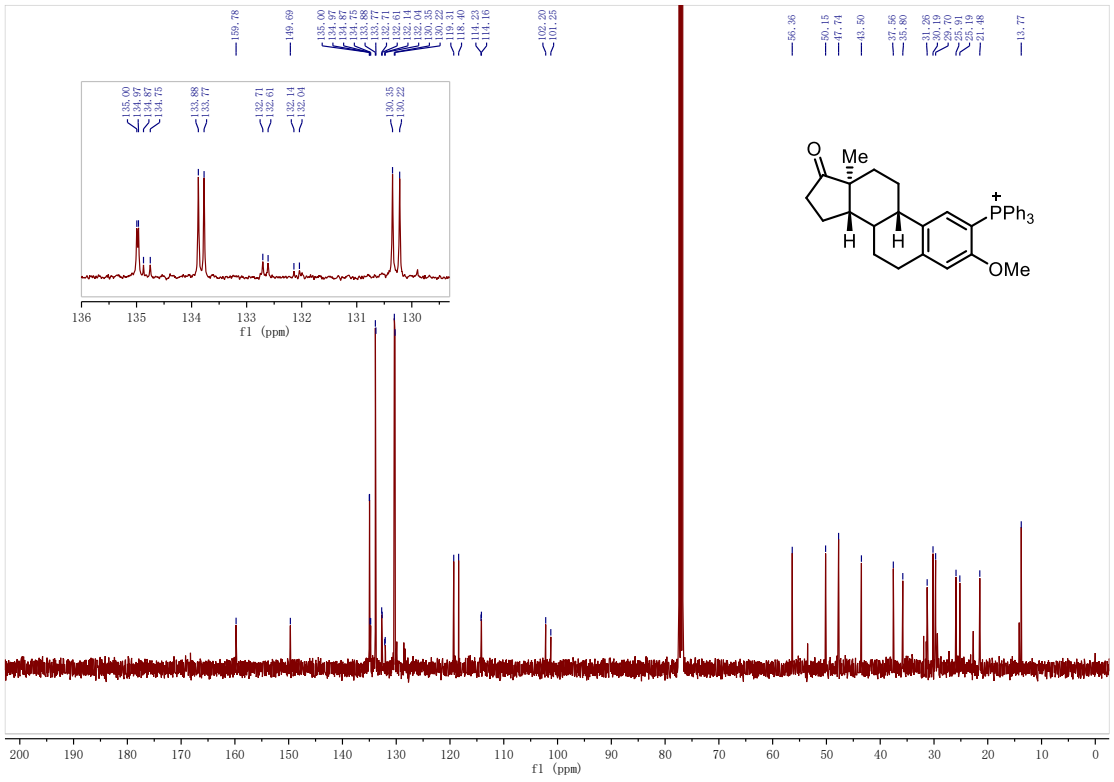


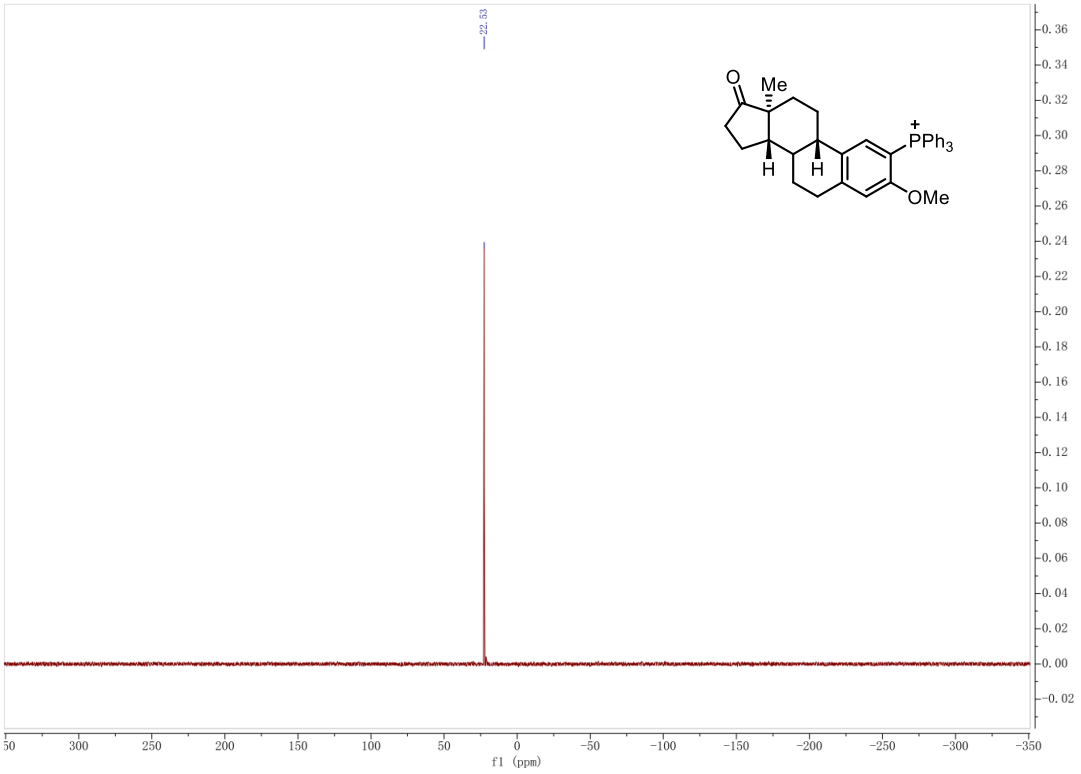

22.95
O
OMe
OMe
F
PPh3
F
f1 (ppm)


-108.35
-114.75
-153.67
O
OMe
OMe
F
PPh3
F
f1 (ppm)

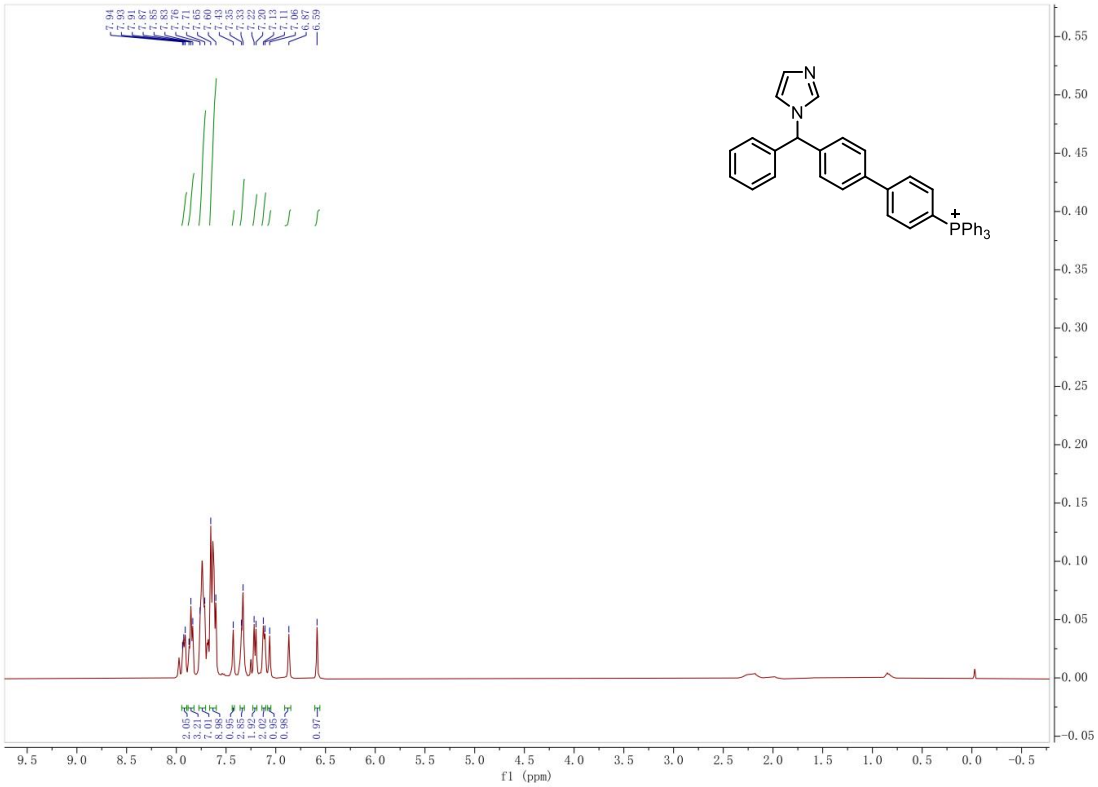
NMR Spectra of **20**

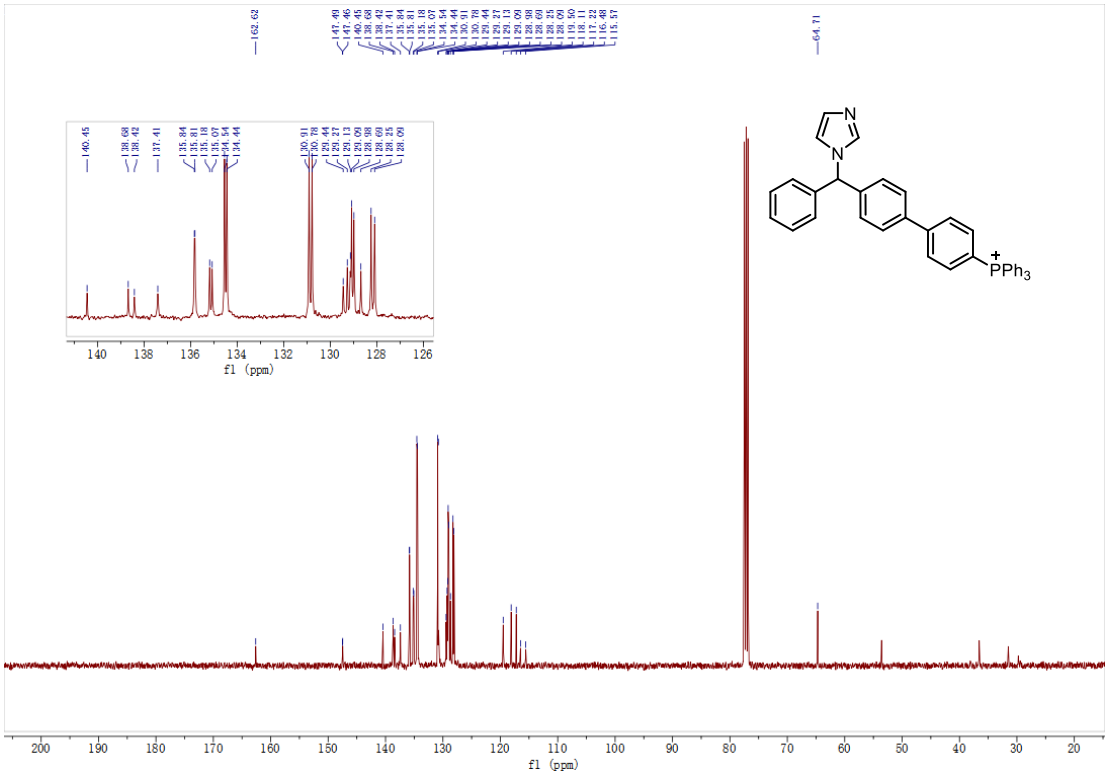


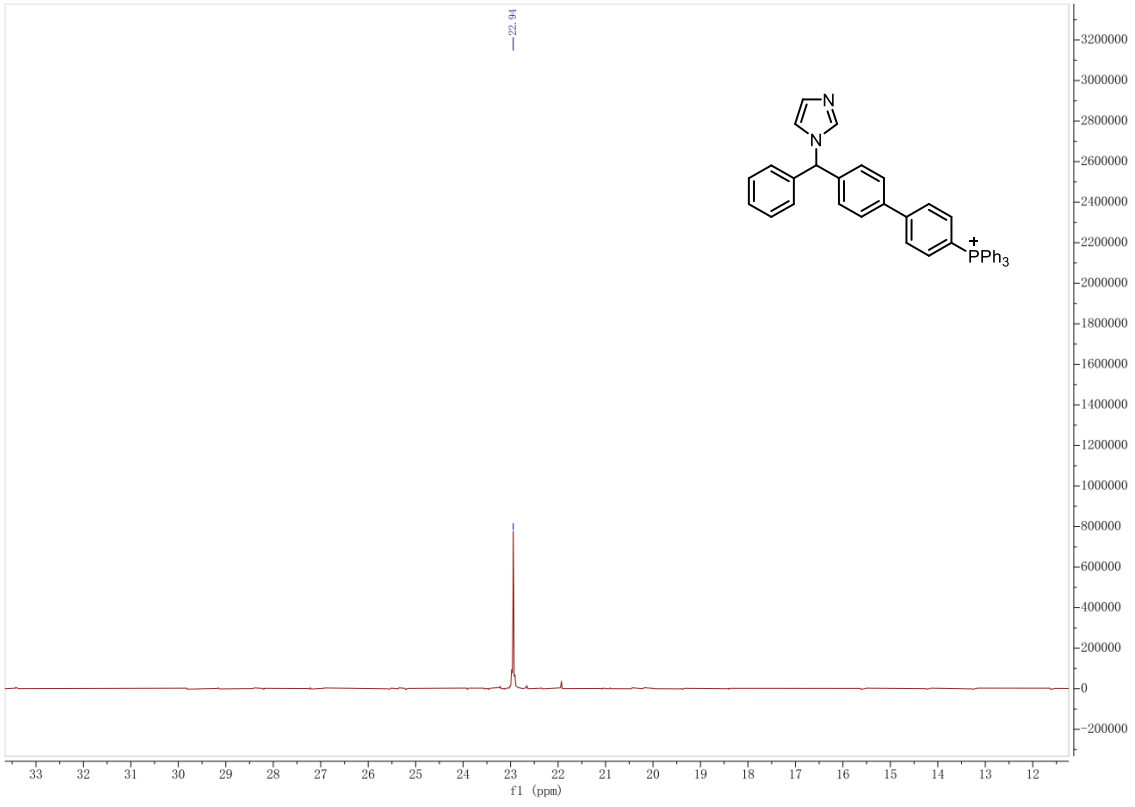




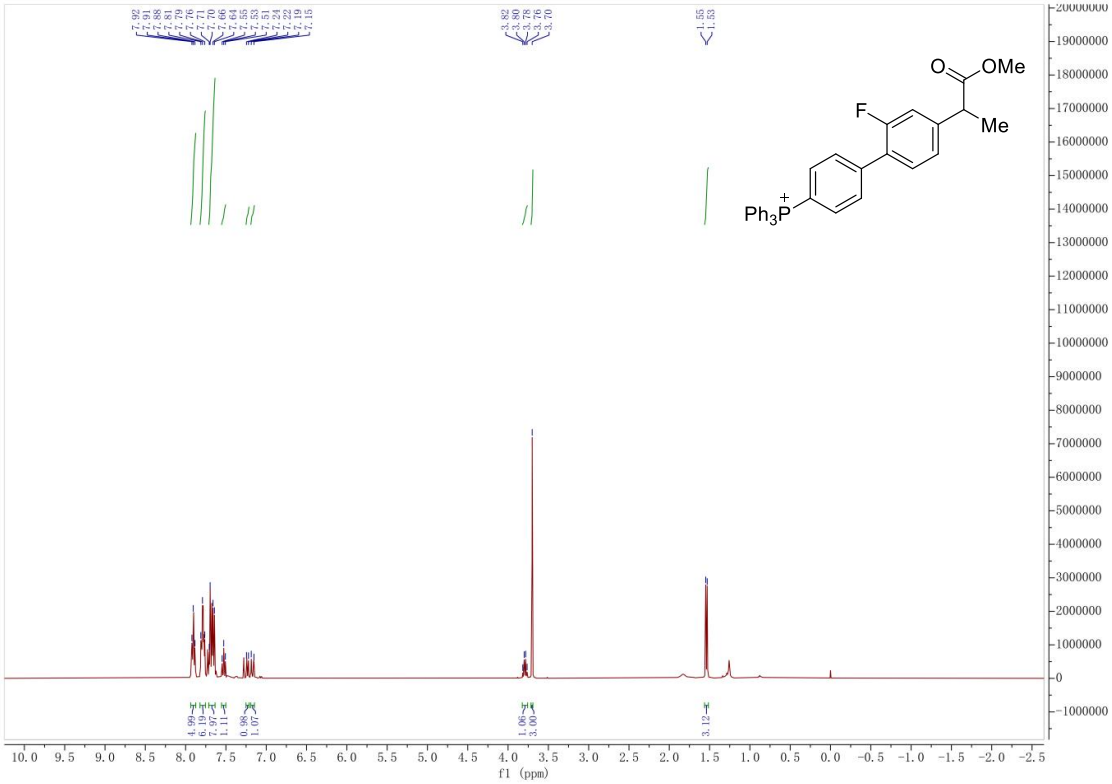
NMR Spectra of **21**

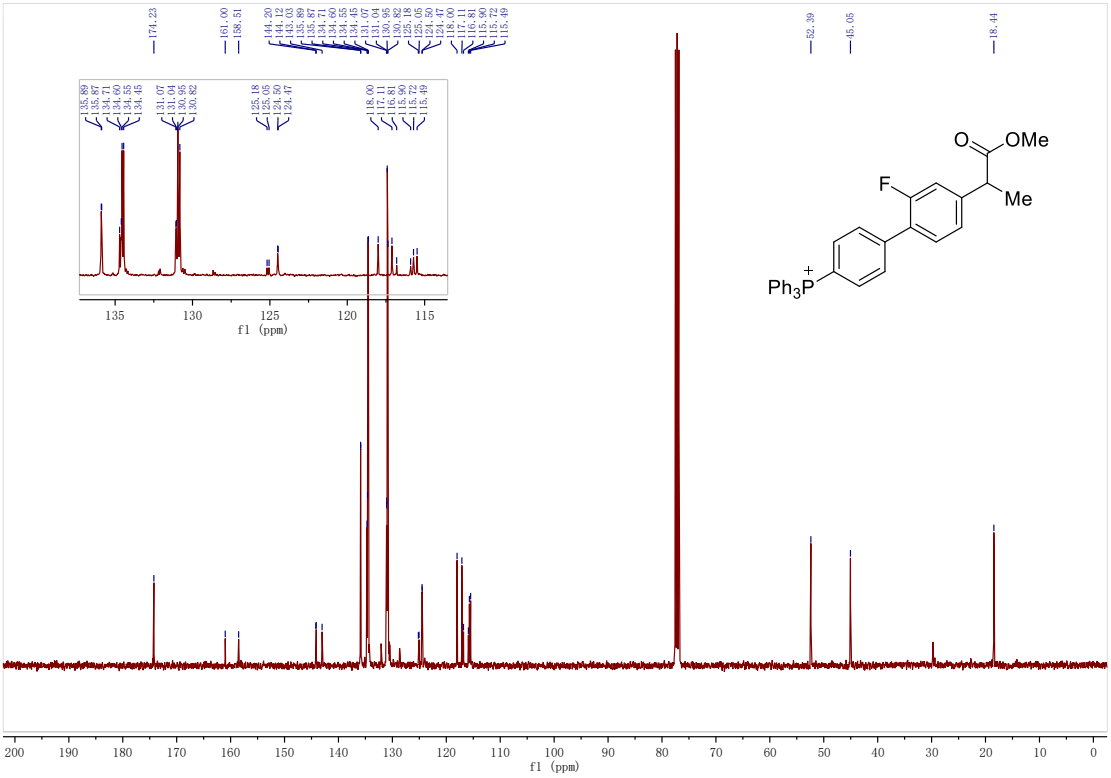


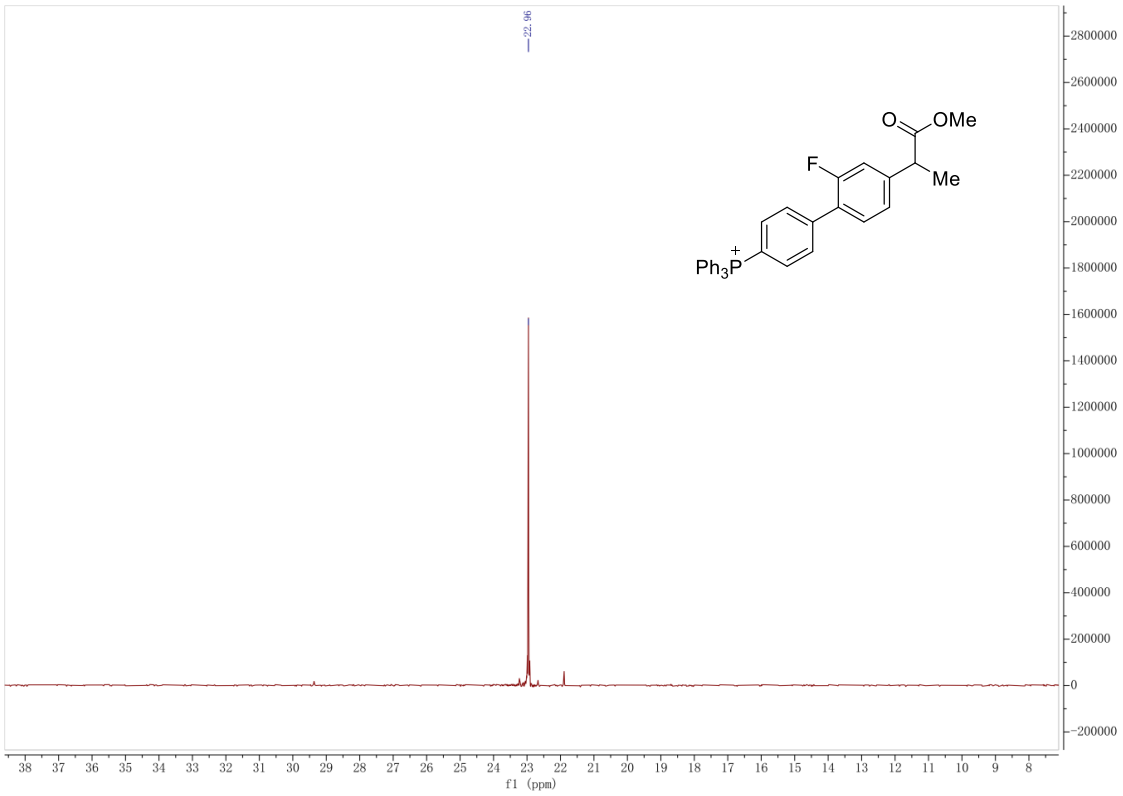

162.62
147.49
147.46
140.45
138.68
138.42
137.41
135.84
135.81
135.18
135.07
134.54
134.44
130.91
130.78
129.44
129.27
129.13
129.09
128.98
128.69
128.25
128.09
118.11
117.22
116.48
115.57
64.71
N
N
PPh3
f1 (ppm)

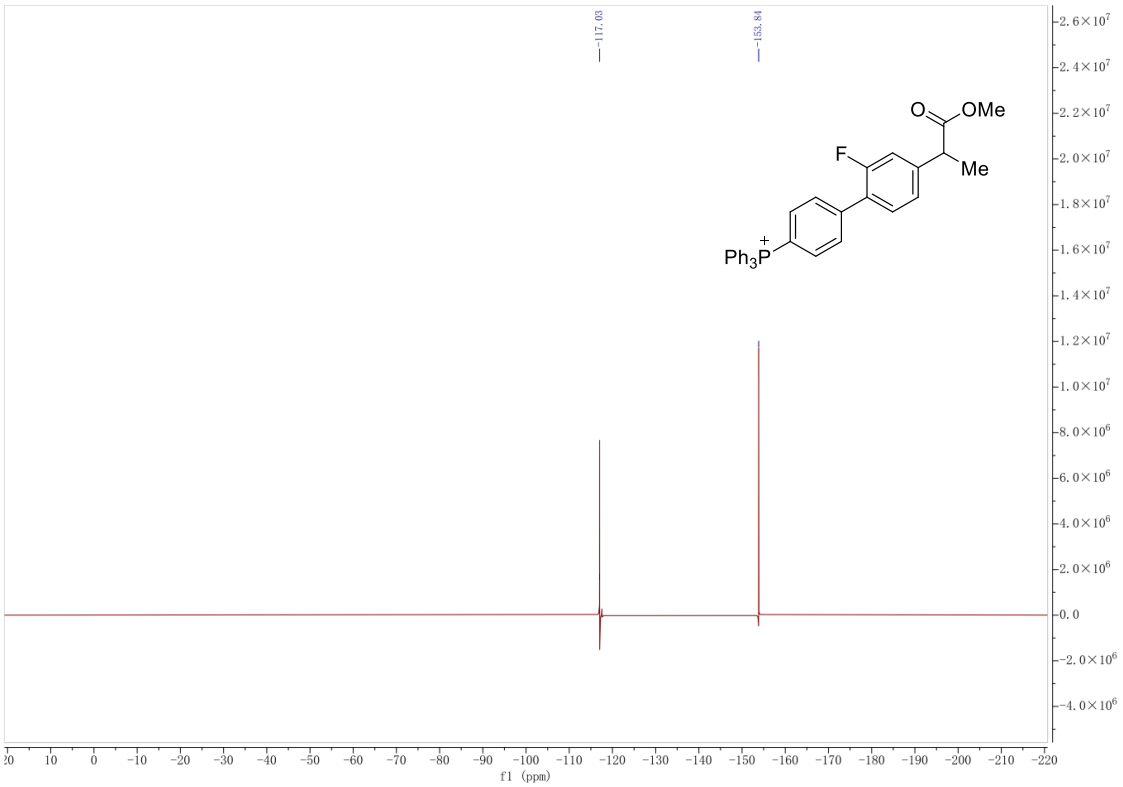

22.94
N
N
PPh3
f1 (ppm)

NMR Spectra of **22**

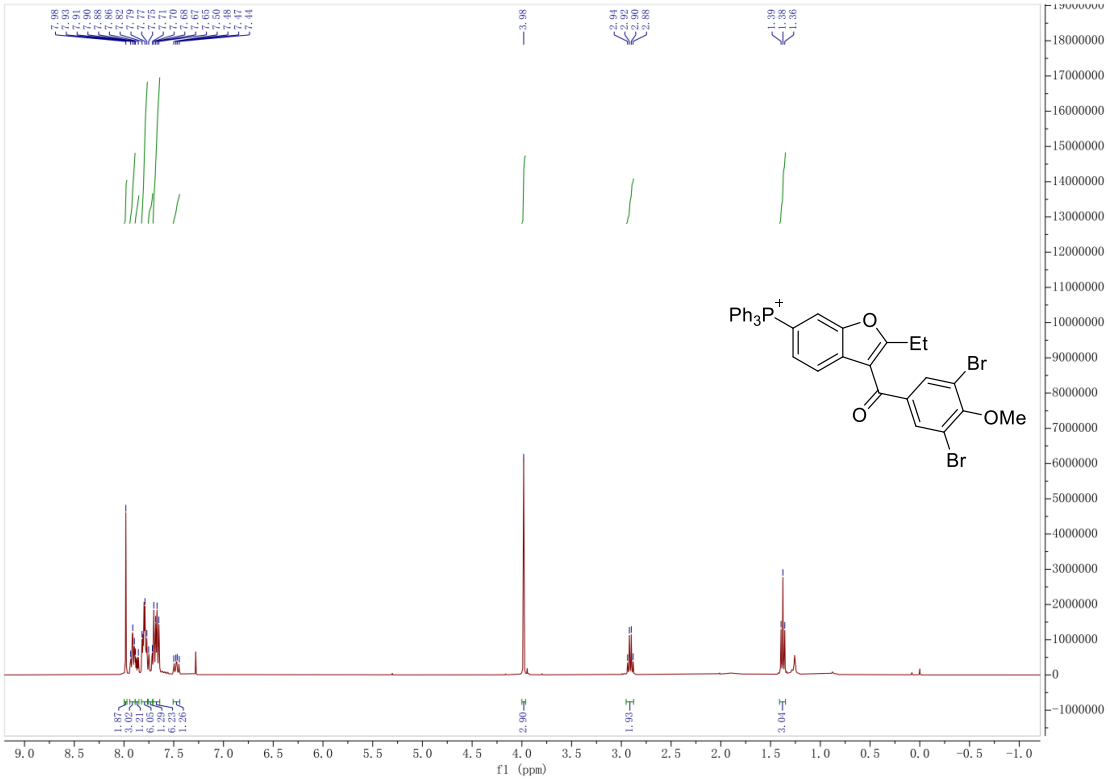


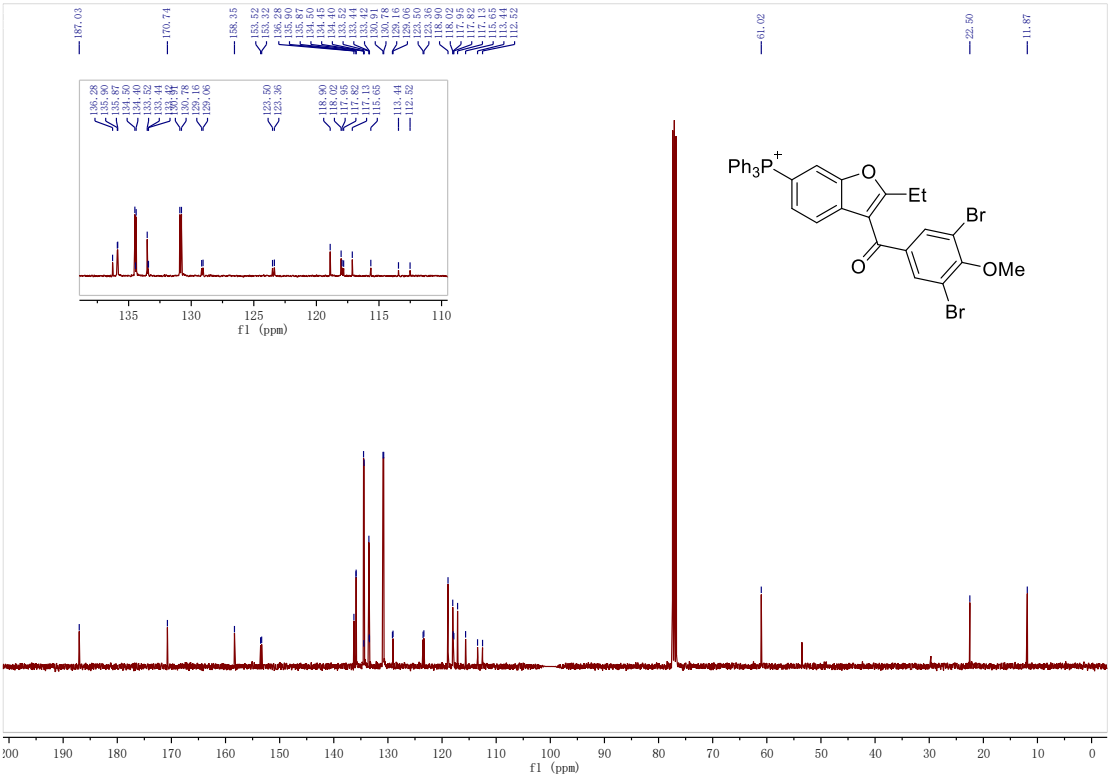


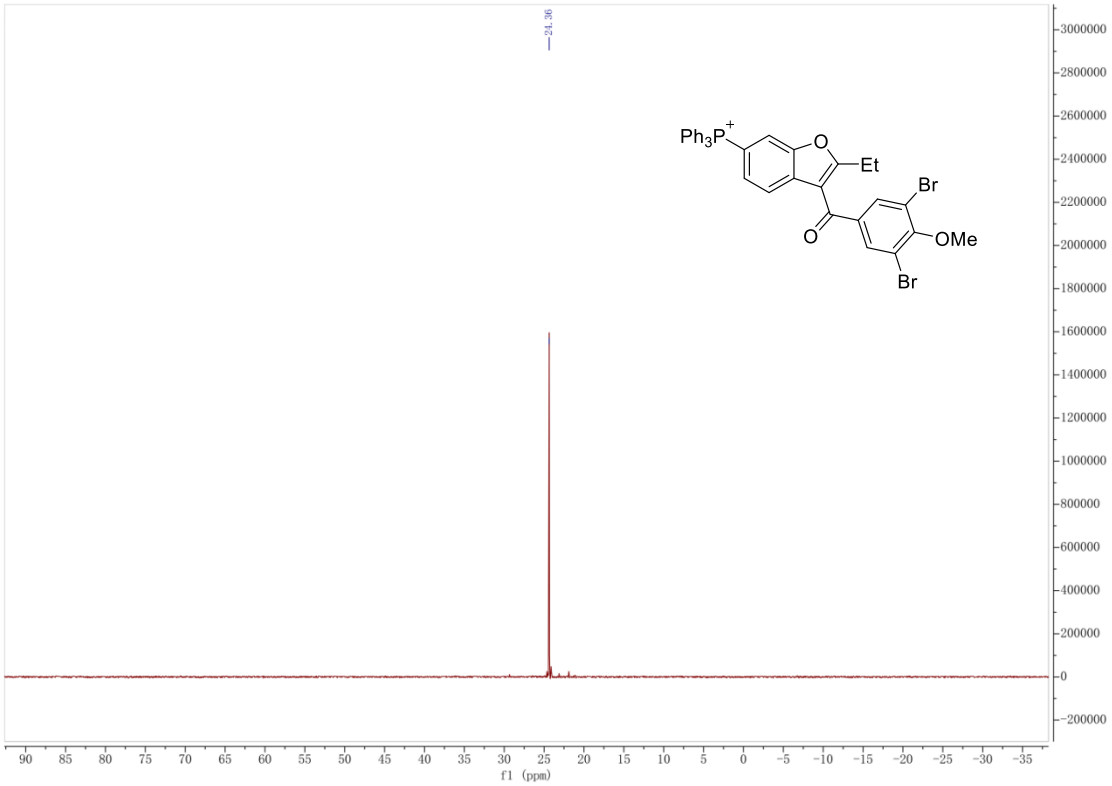

22.96
O
OMe
F
Me
Ph3P
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8
f1 (ppm)


-117.03
-153.84
O
OMe
F
Me
Ph3P
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
-4.0×10^6
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

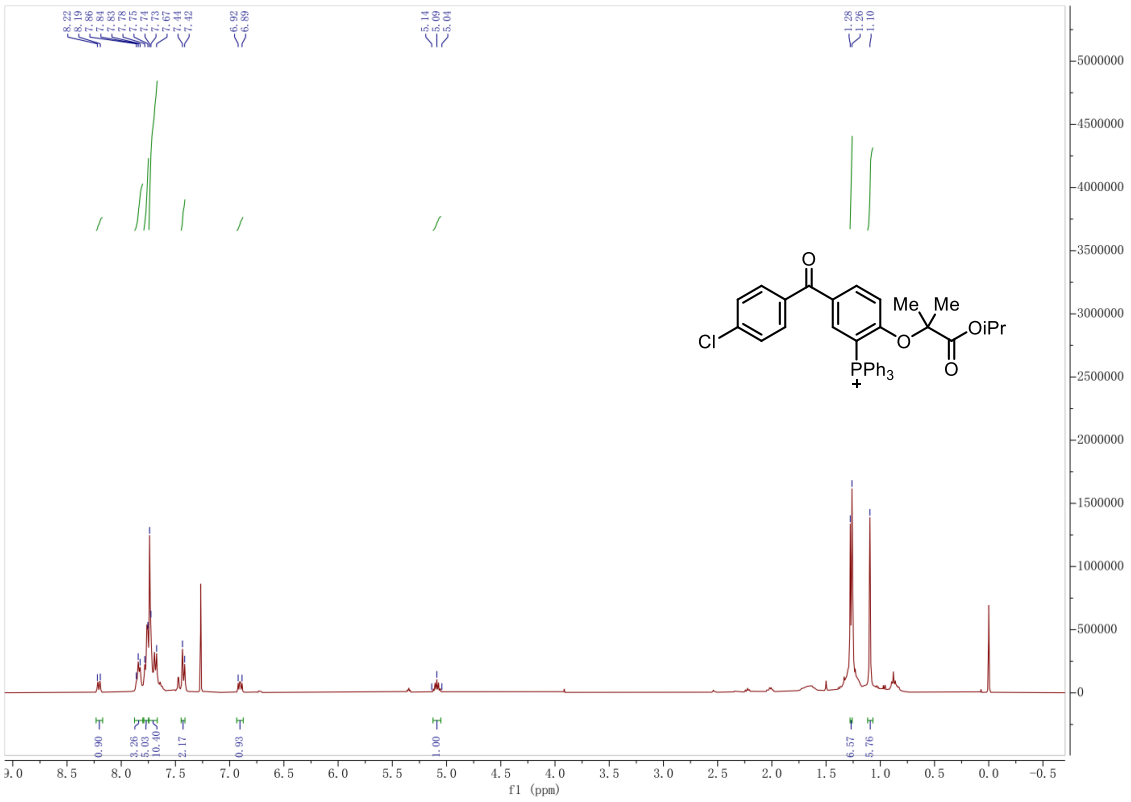
NMR Spectra of **23**

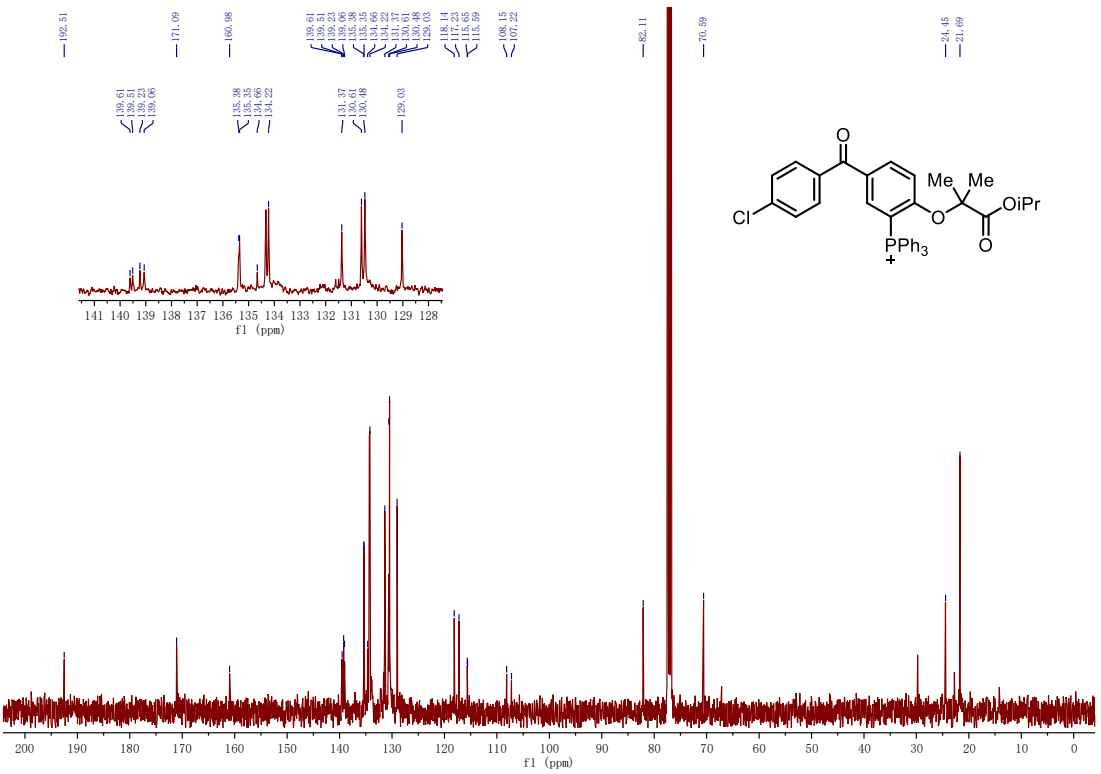


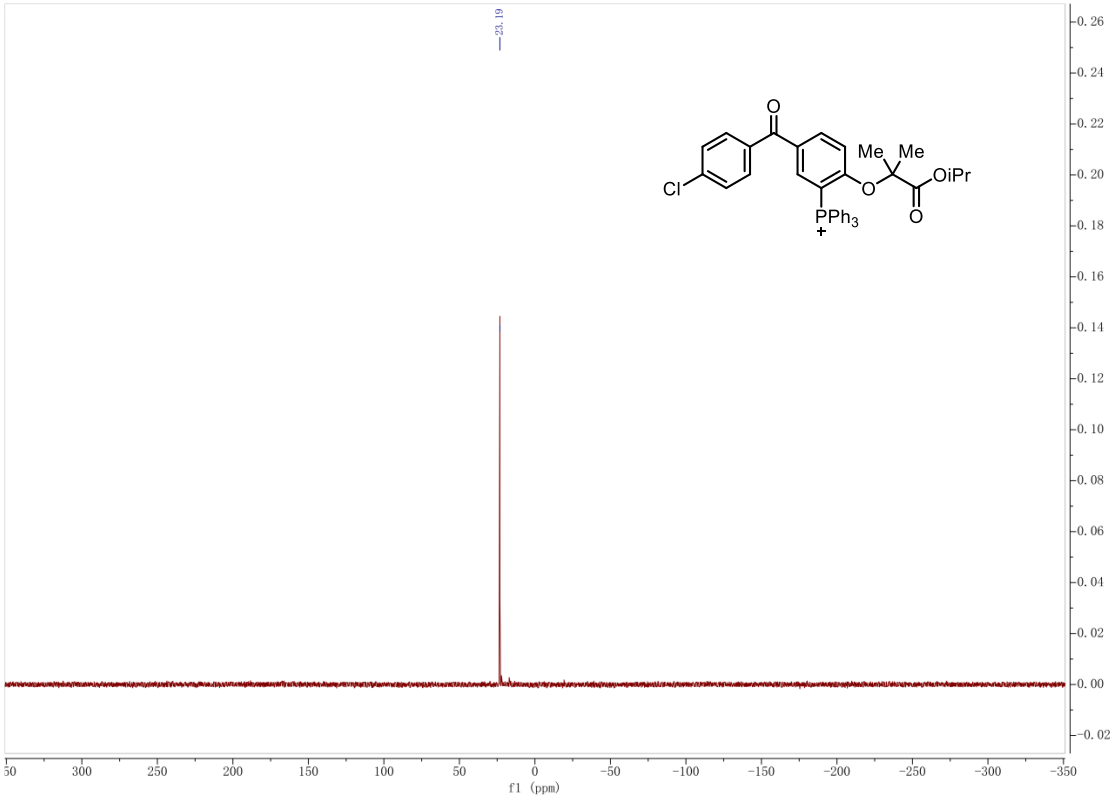




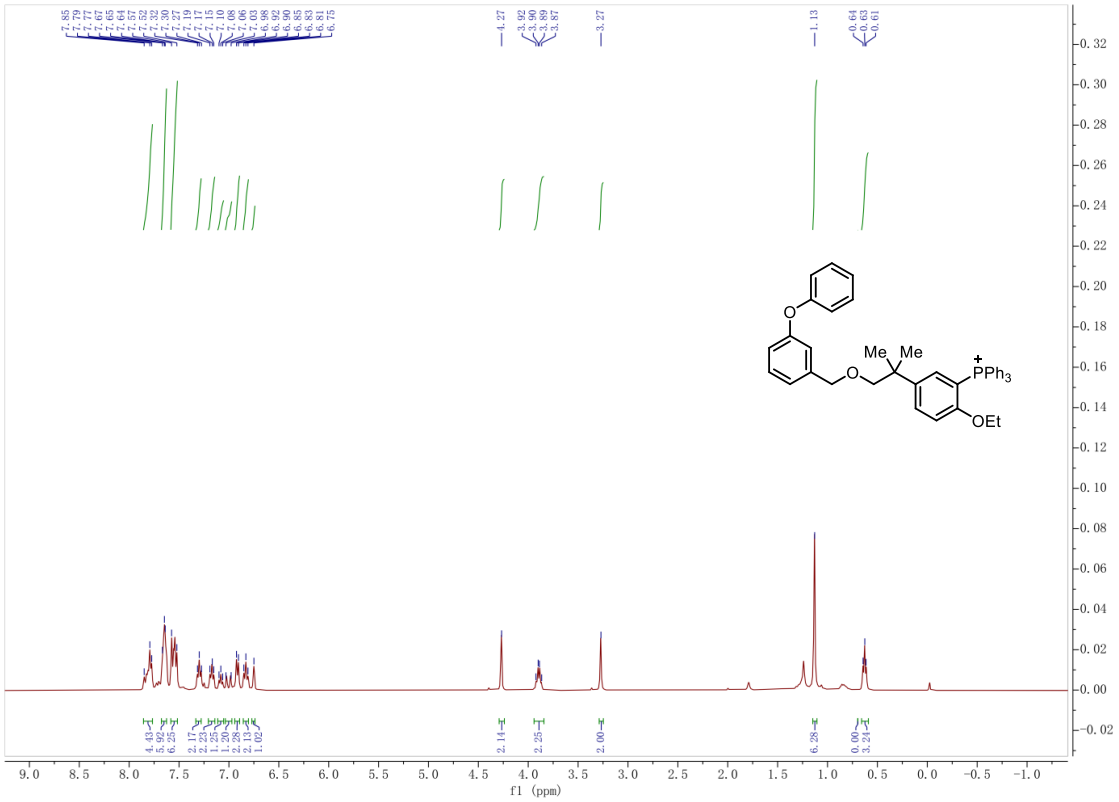
NMR Spectra of **24**

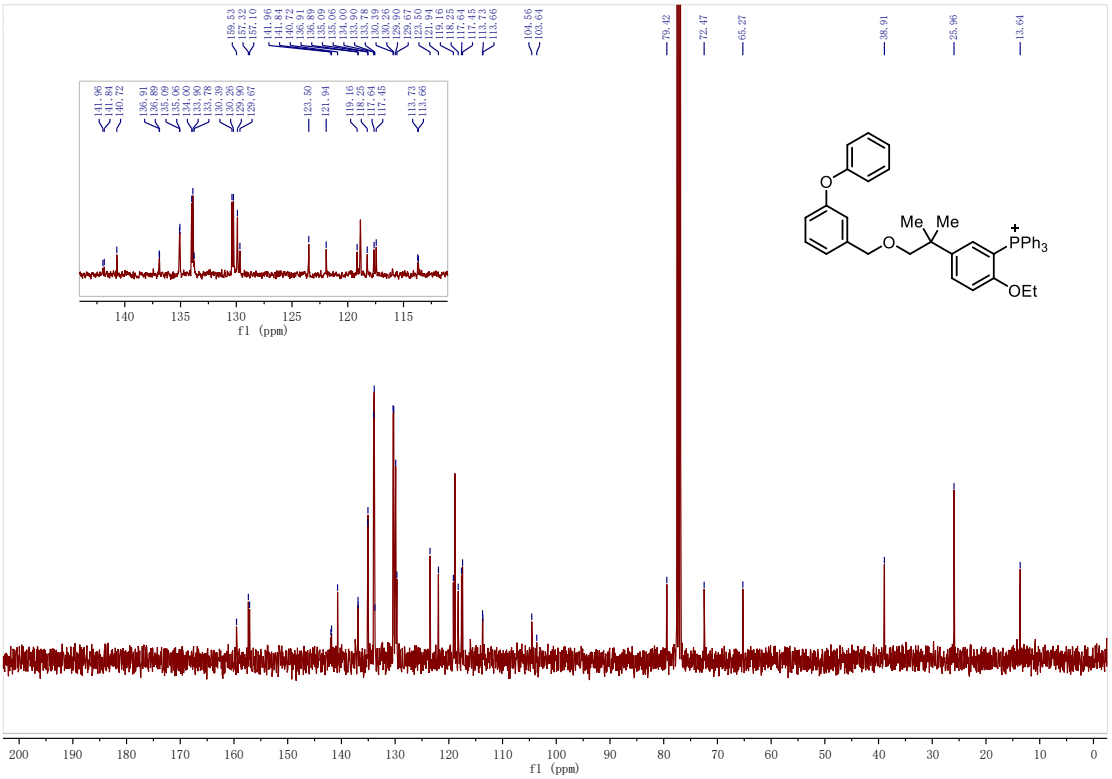


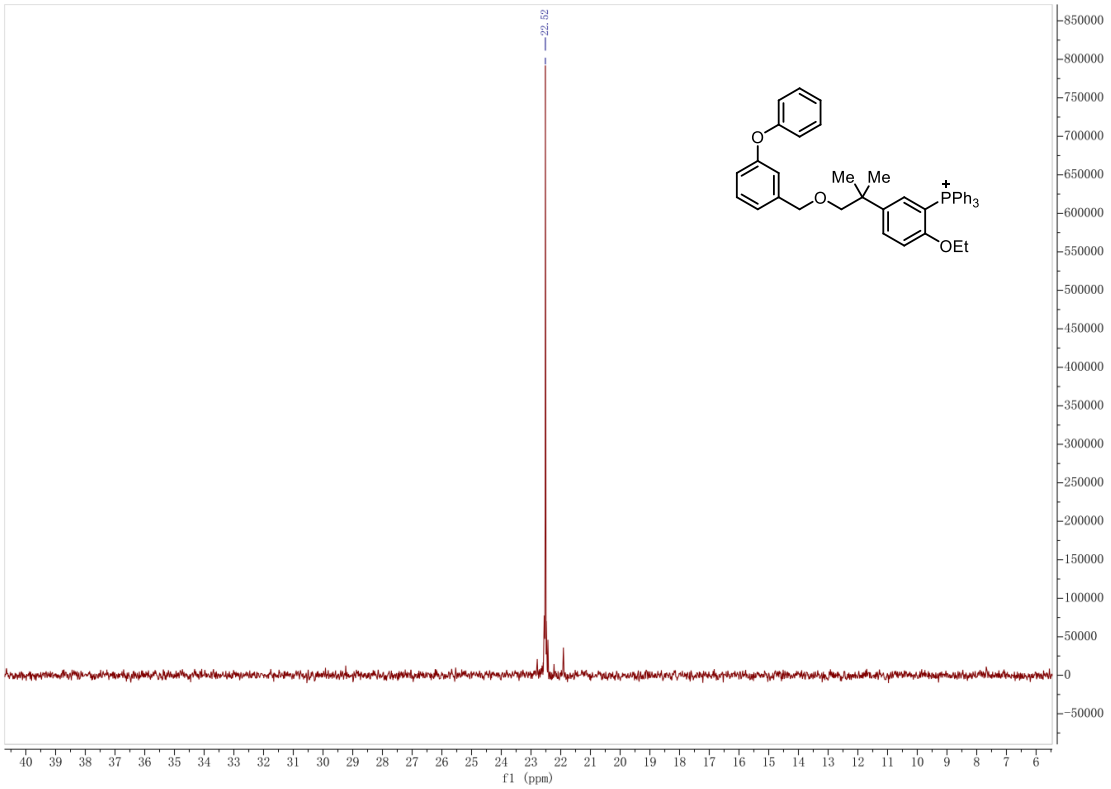

192.51
171.09
160.98
139.61
139.51
139.23
139.06
135.38
135.35
134.66
134.22
131.37
130.61
130.48
129.03
118.14
117.23
115.65
115.59
108.15
107.22
82.11
70.89
24.45
21.69
Cl
Me
Me
OiPr
O
PPh3
f1 (ppm)


23.19
Cl
Me
Me
OiPr
O
PPh3
f1 (ppm)

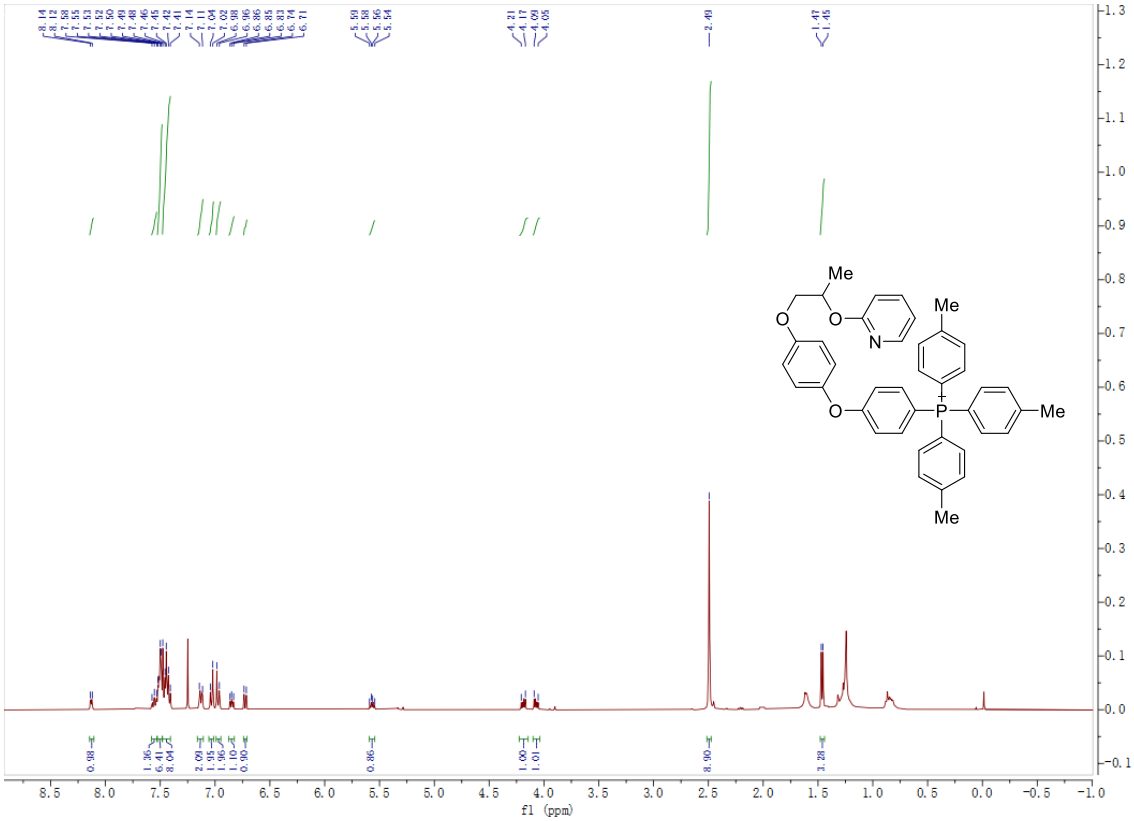
NMR Spectra of **25**

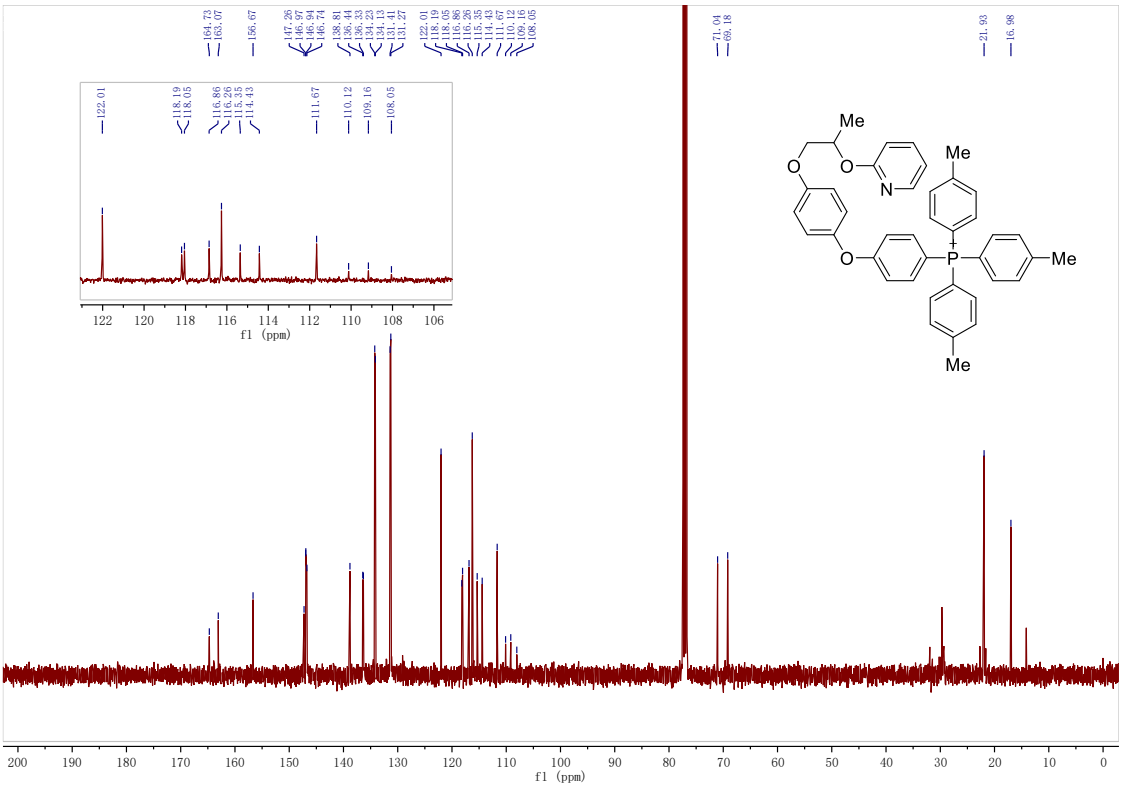


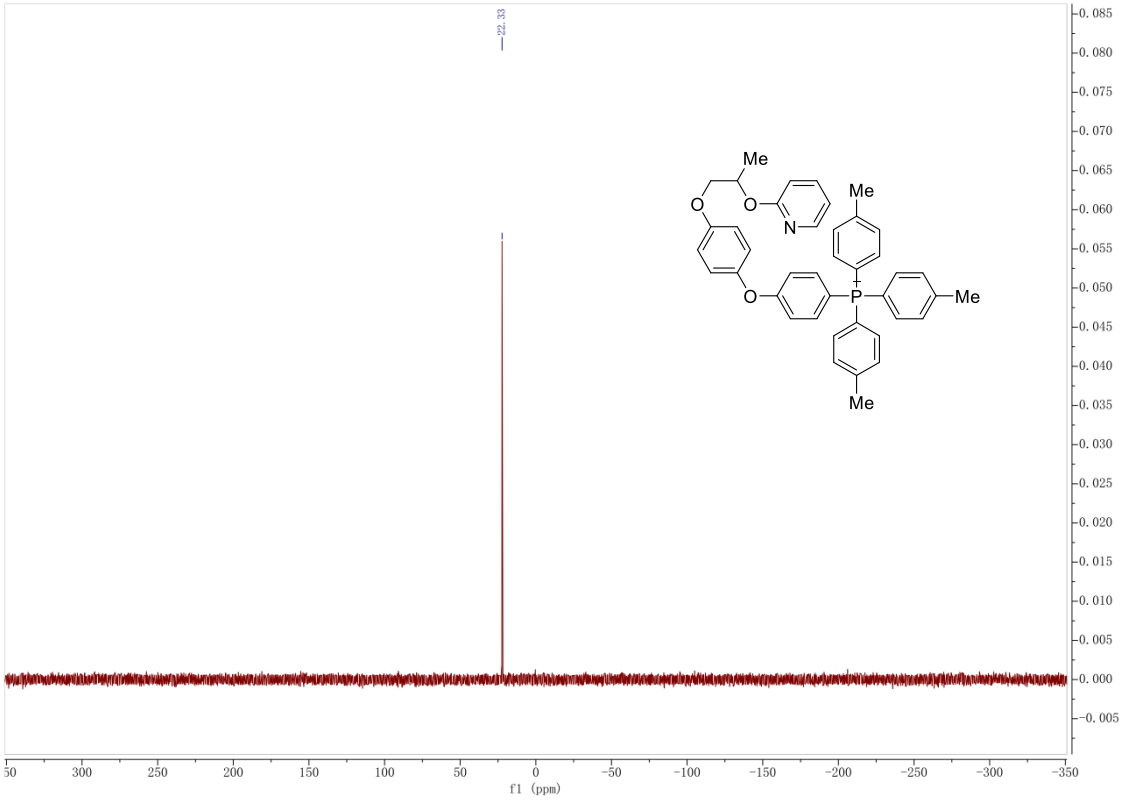




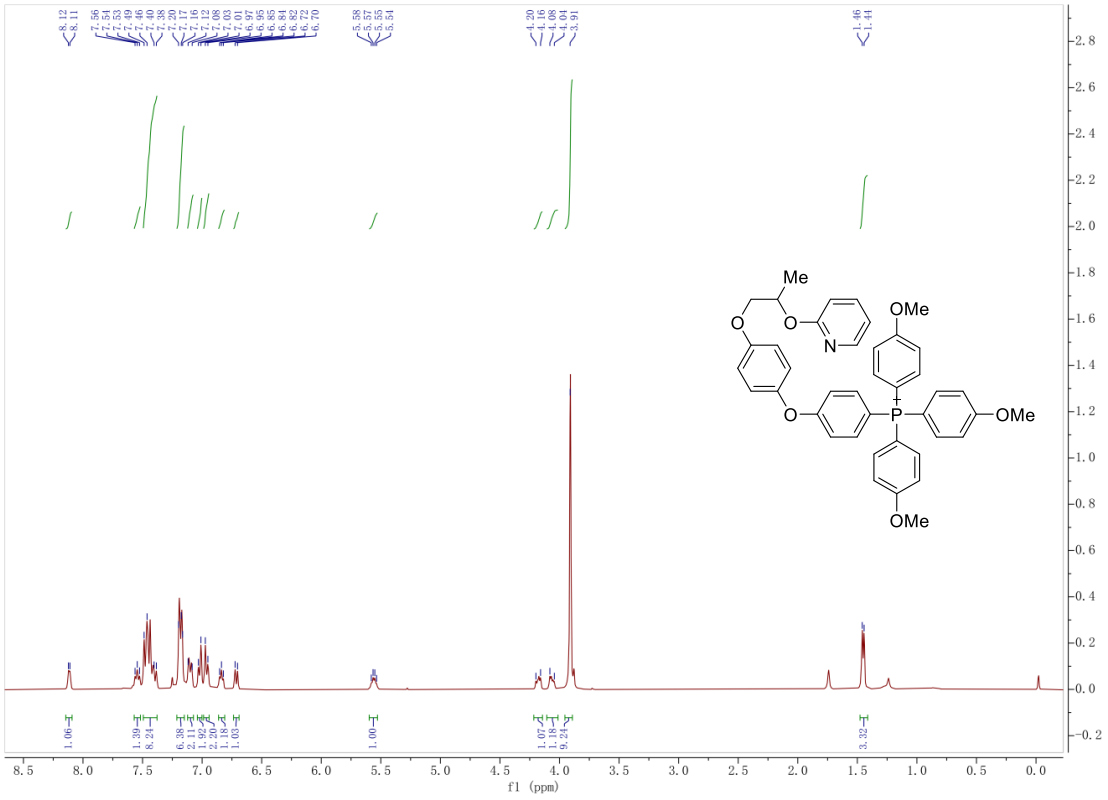
NMR Spectra of **26**

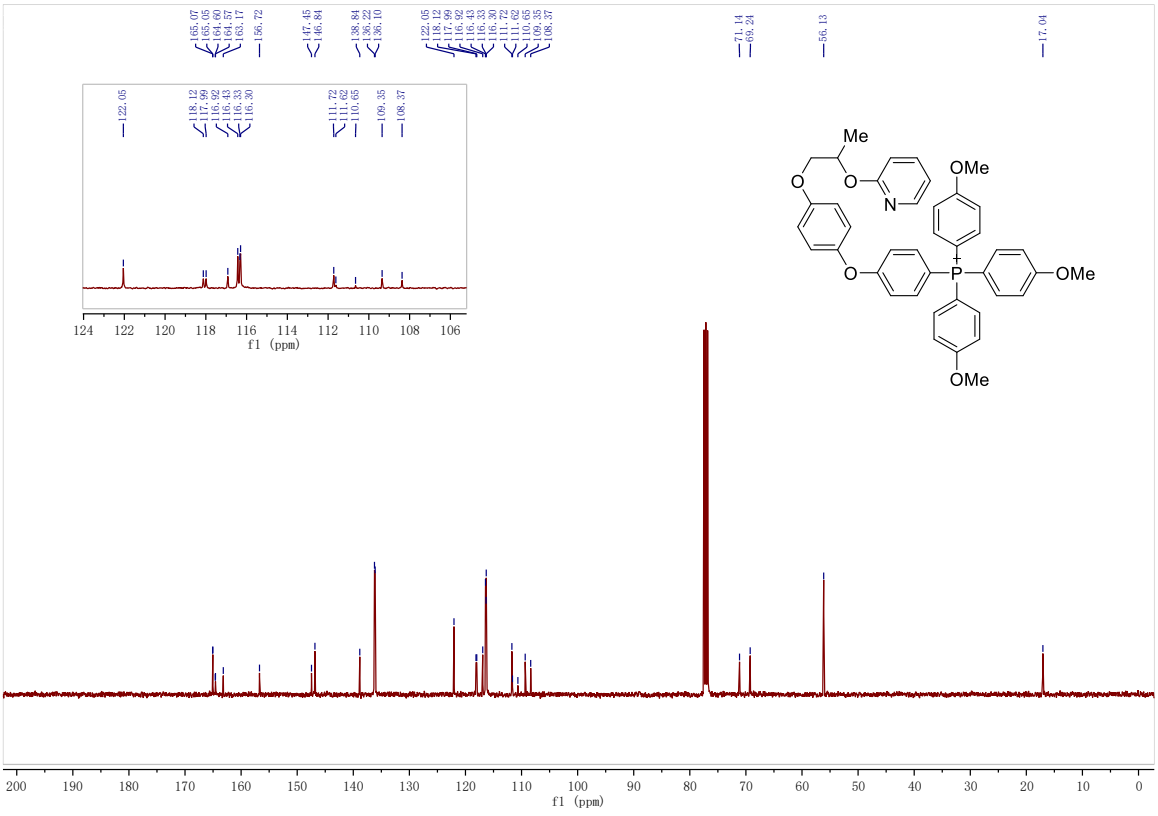


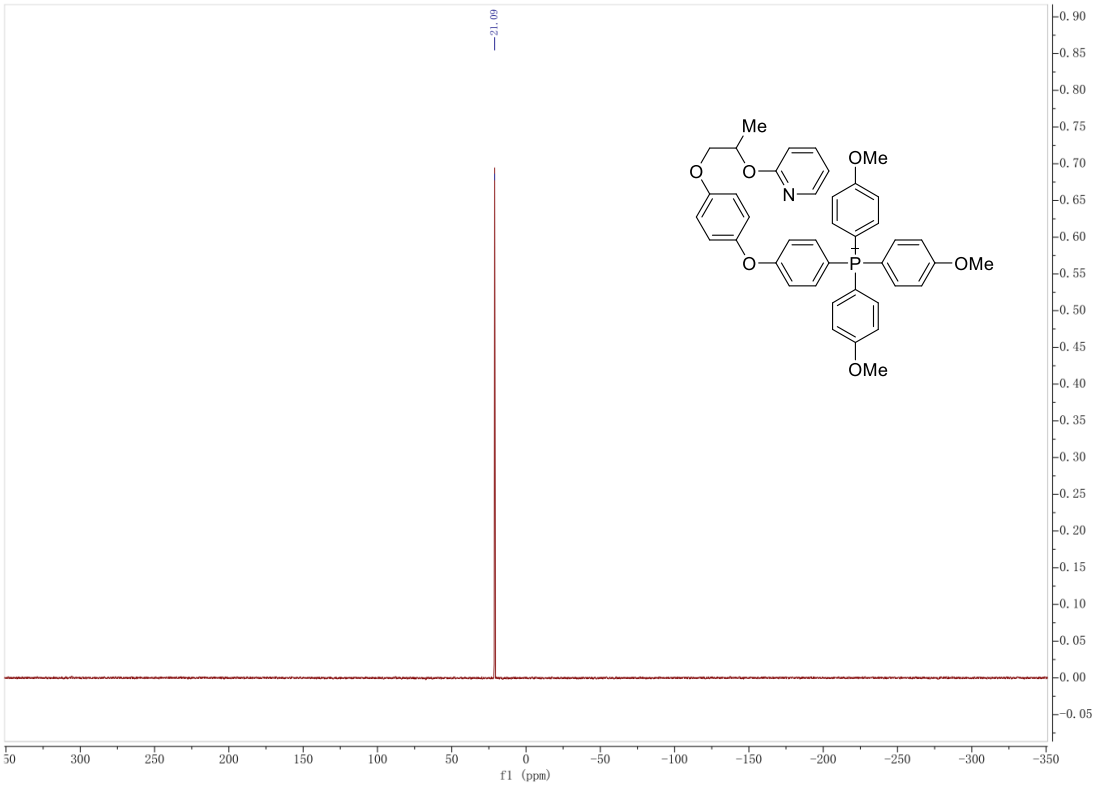

164.73
163.07
156.67
147.26
146.97
146.94
146.74
138.81
138.44
136.33
134.23
134.13
131.41
131.27
122.01
118.19
118.05
116.86
116.26
115.35
115.43
111.67
110.12
109.16
108.05
71.04
69.18
21.93
16.98
Me
O
O
N
Me
O
P
Me
Me
f1 (ppm)


22.33
Me
O
O
N
Me
O
P
Me
Me
f1 (ppm)

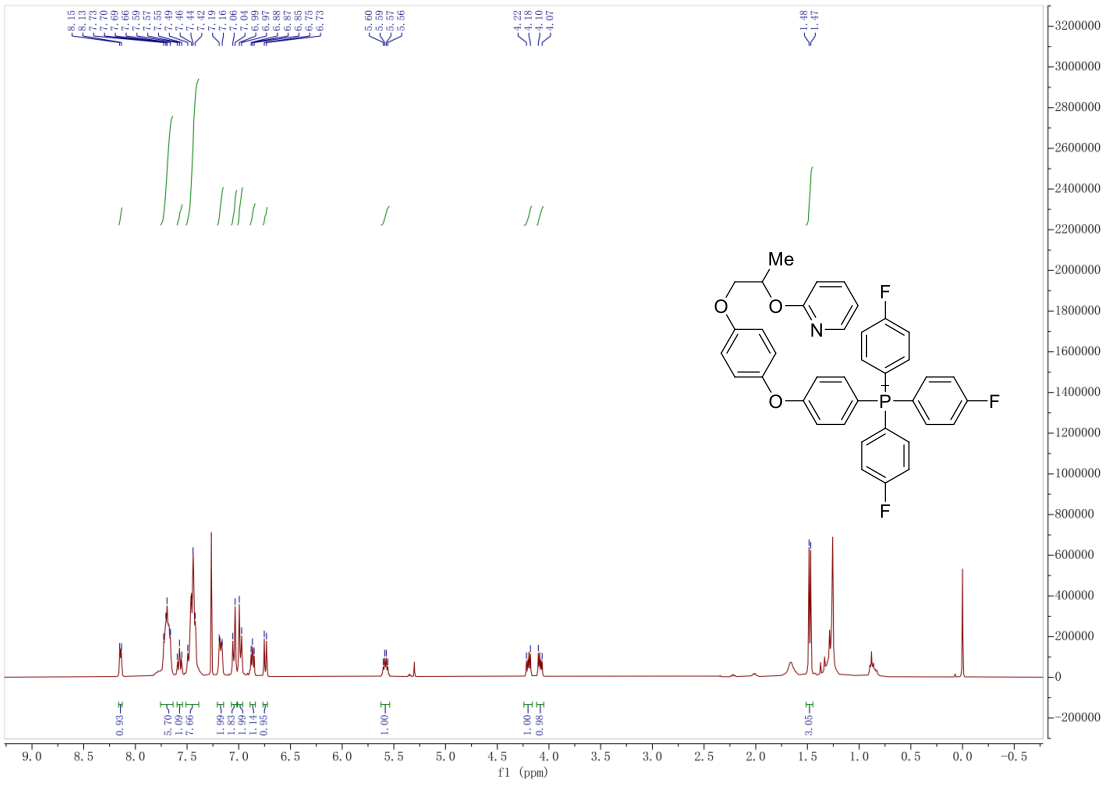
NMR Spectra of **27**

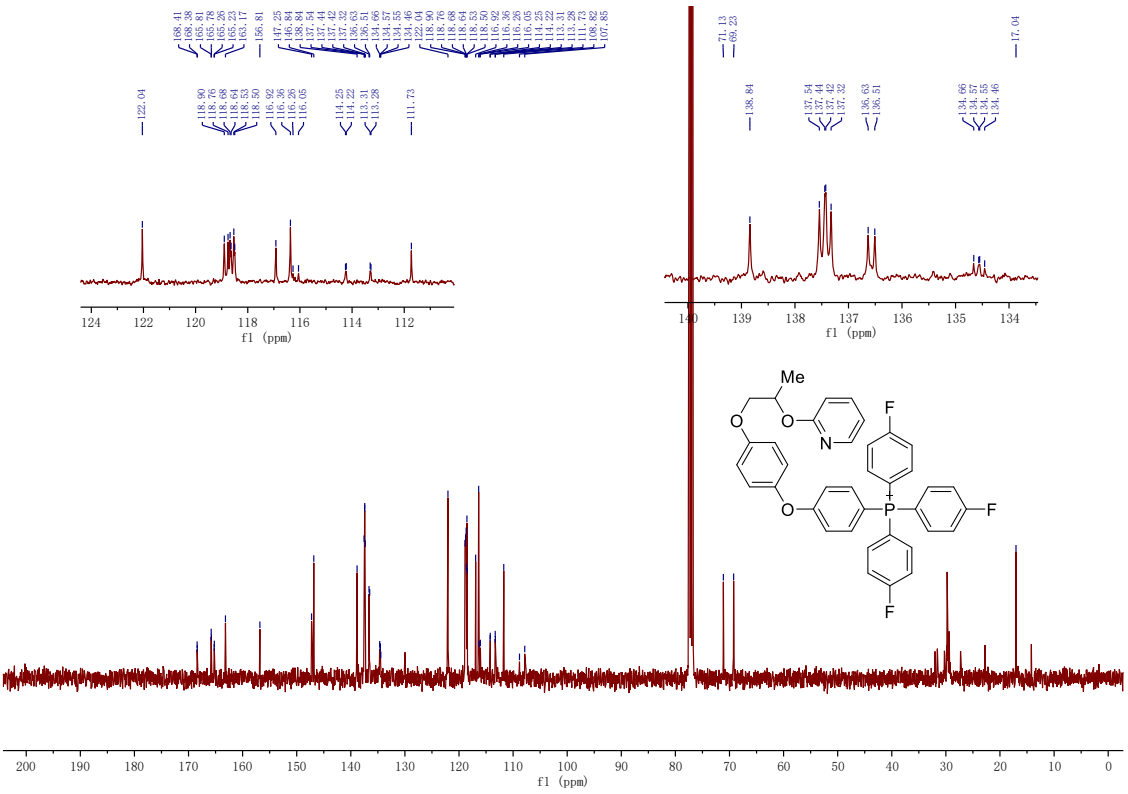


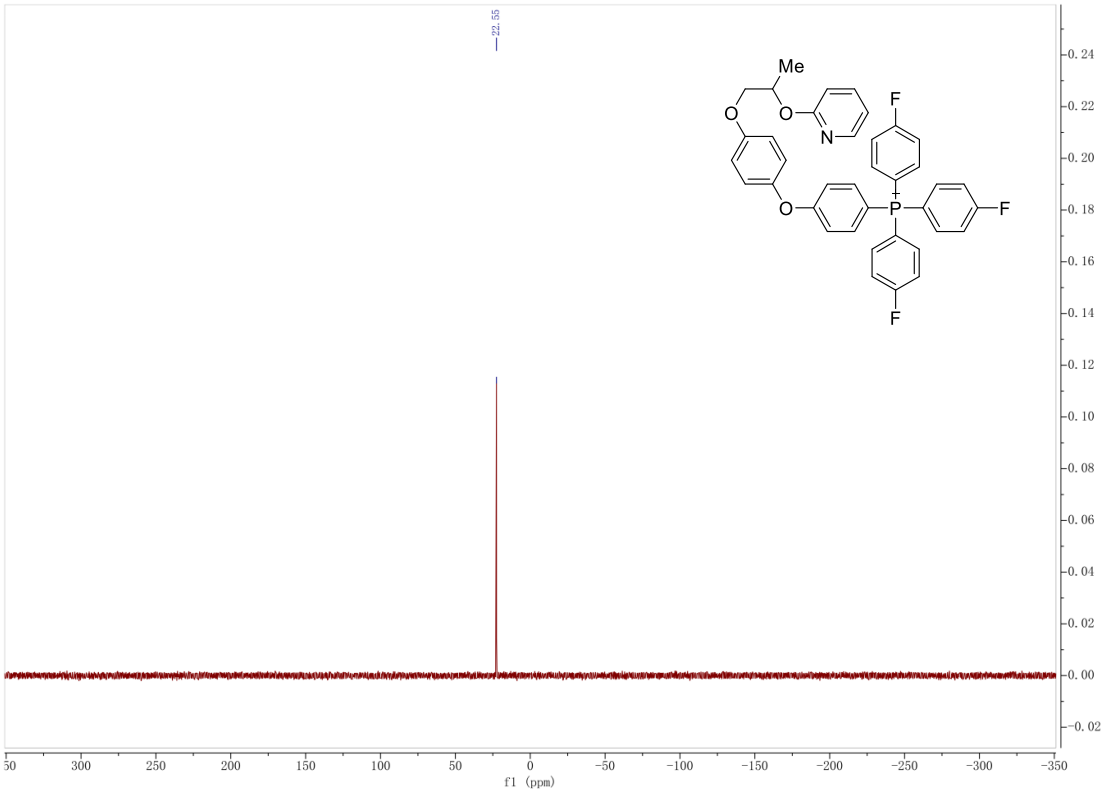


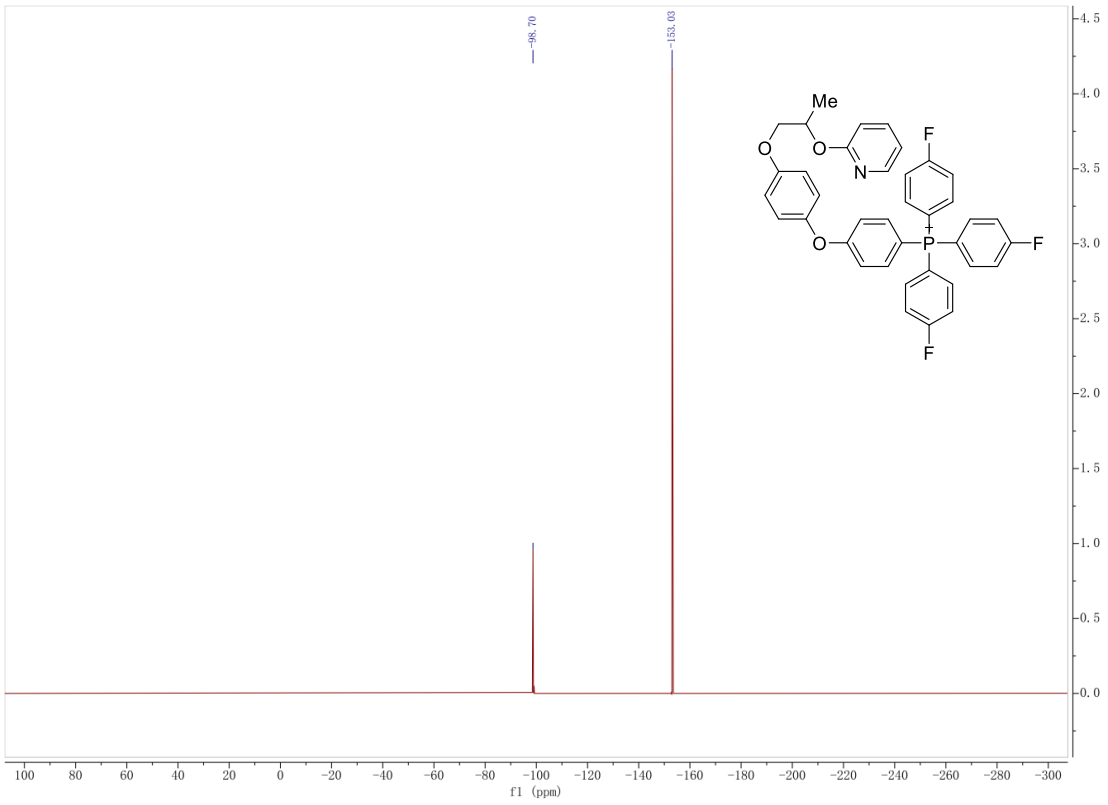


NMR Spectra of **28**

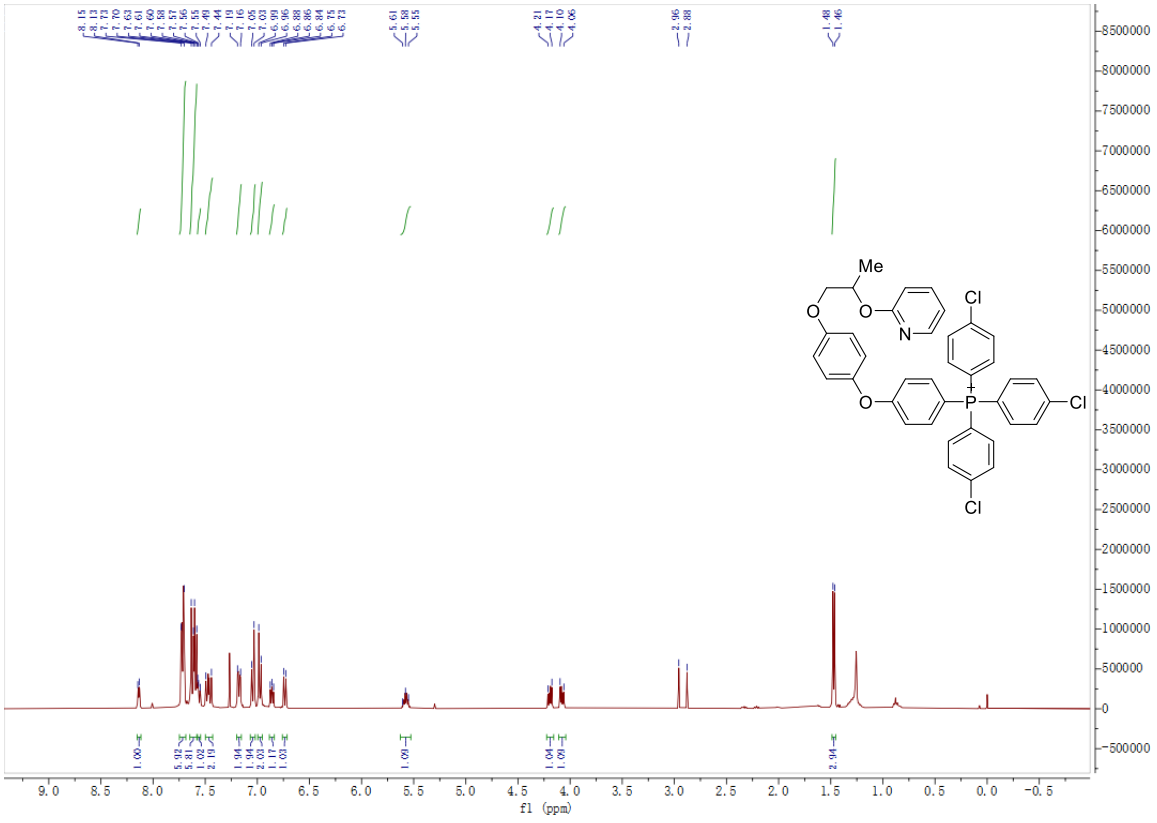


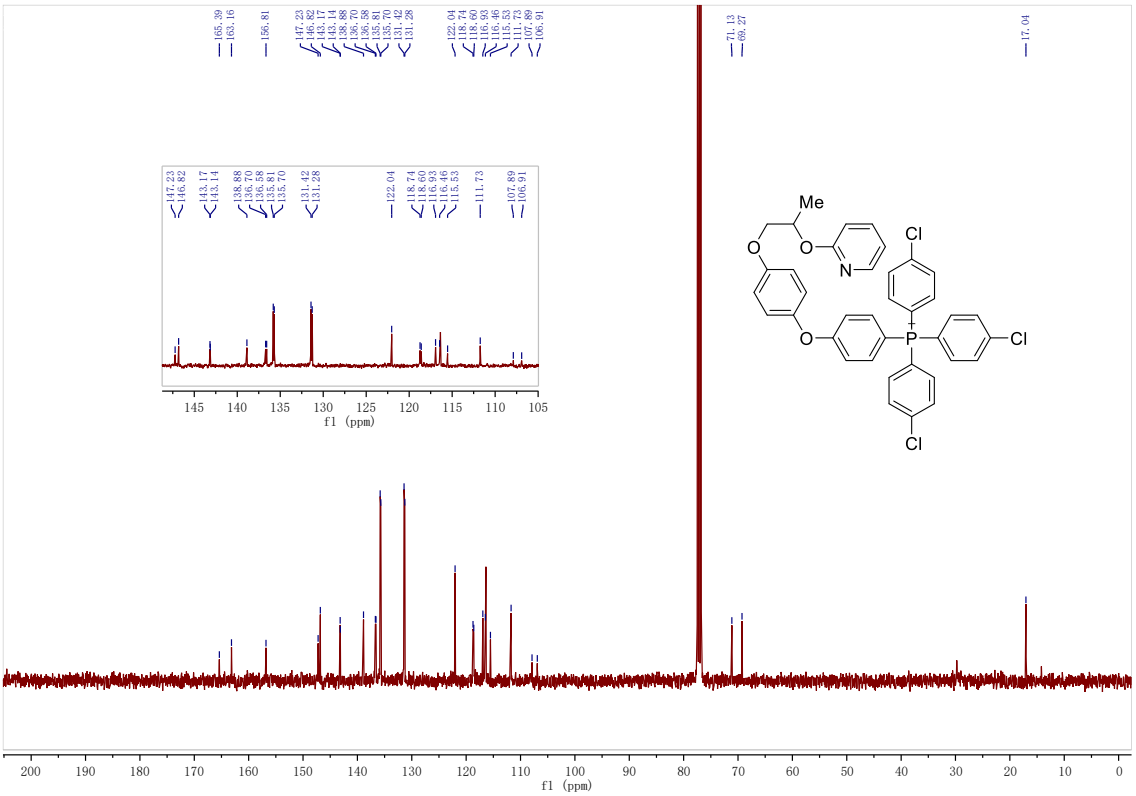

Me
O
O
N
F
O
P
F
F
f1 (ppm)

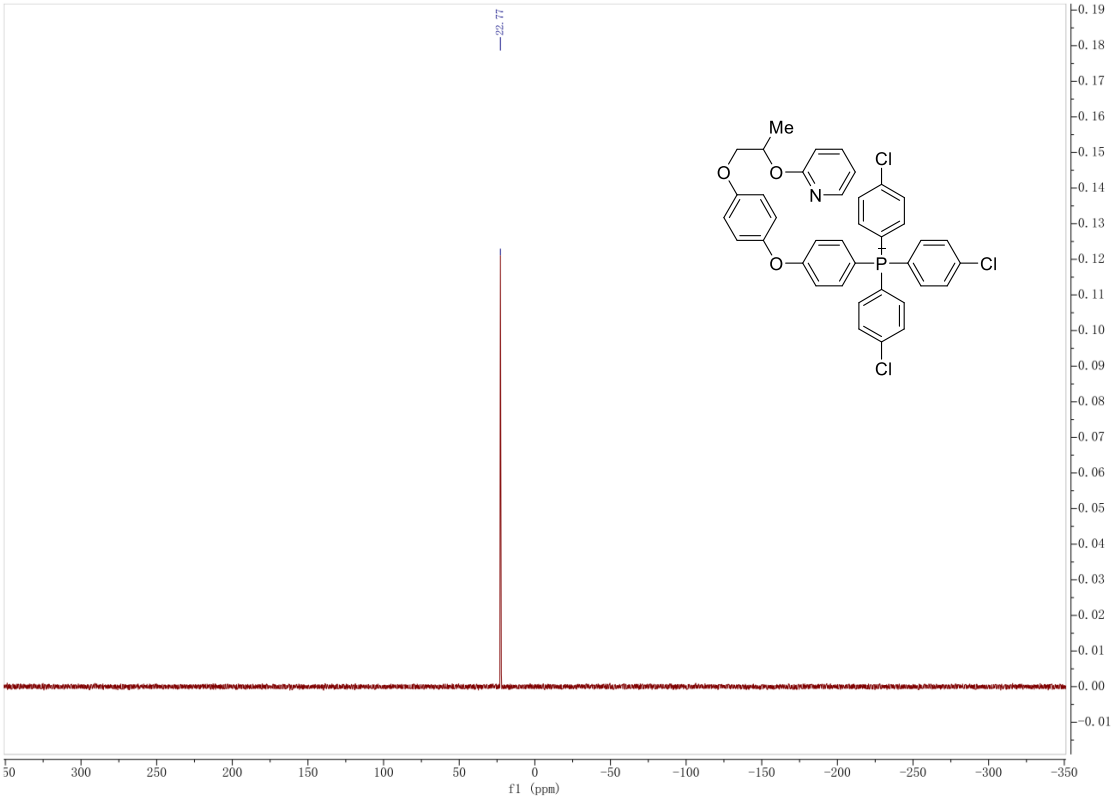

22.55
Me
O
O
N
F
O
P
F
F
f1 (ppm)



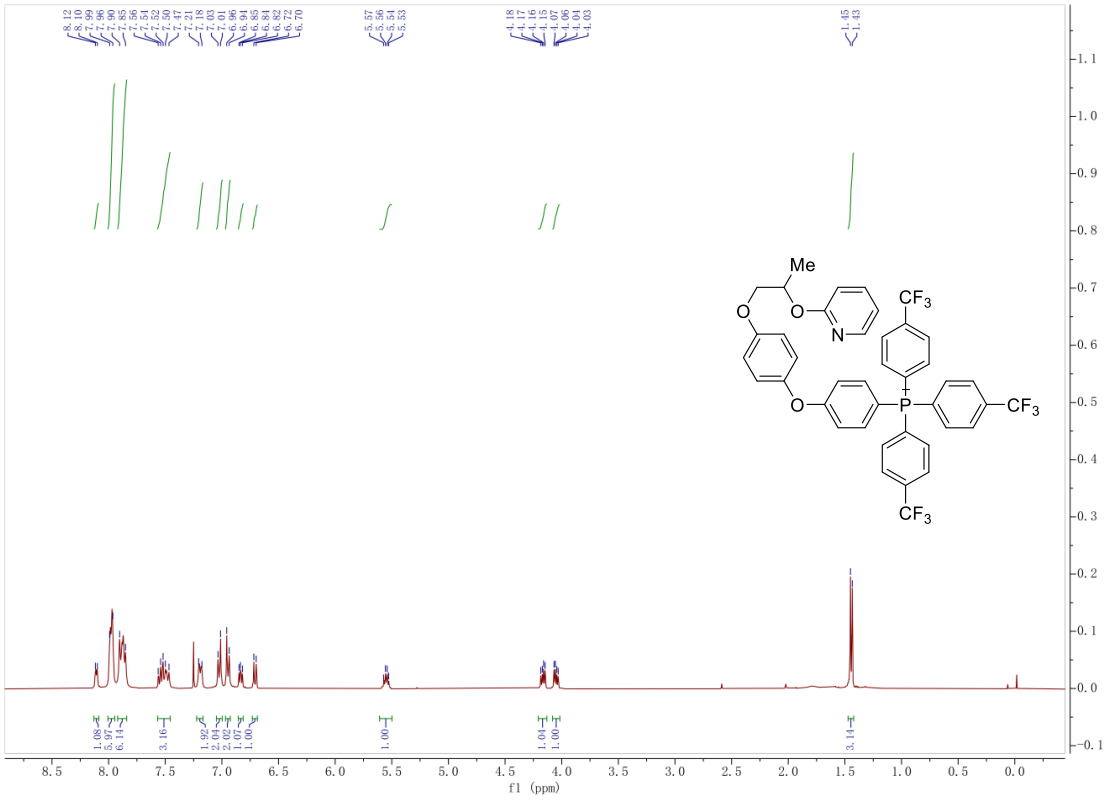
NMR Spectra of **29**

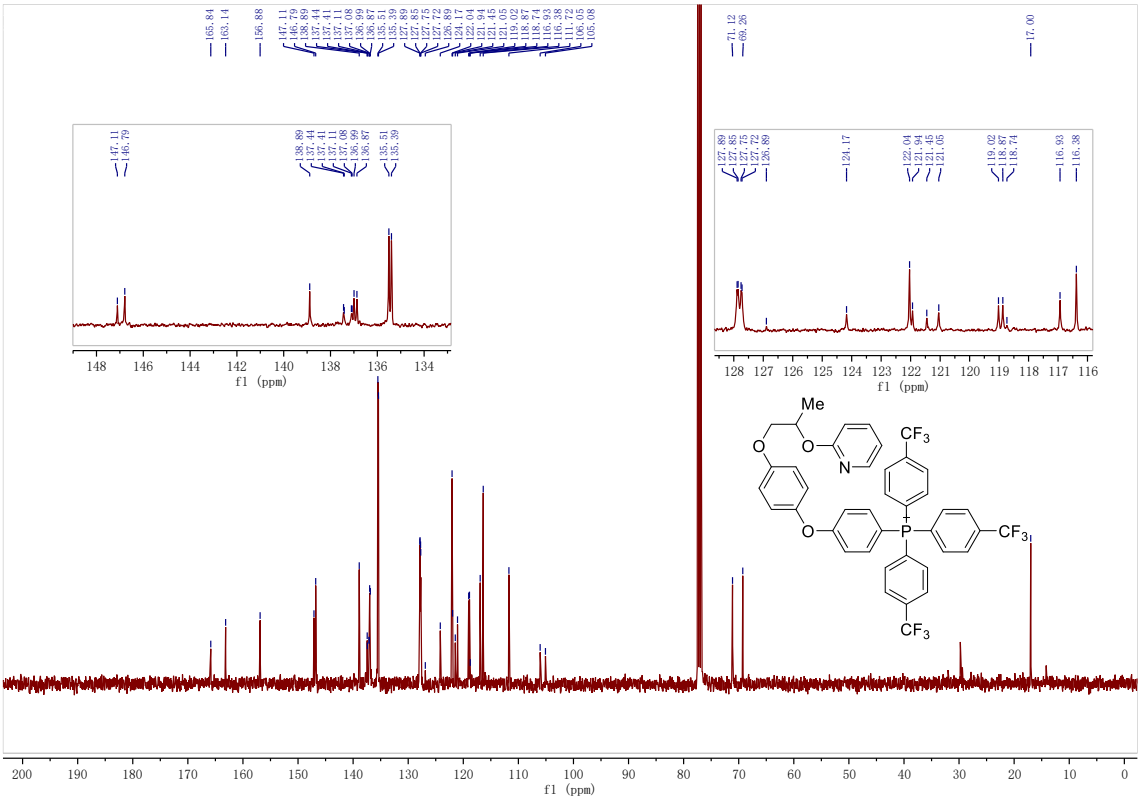


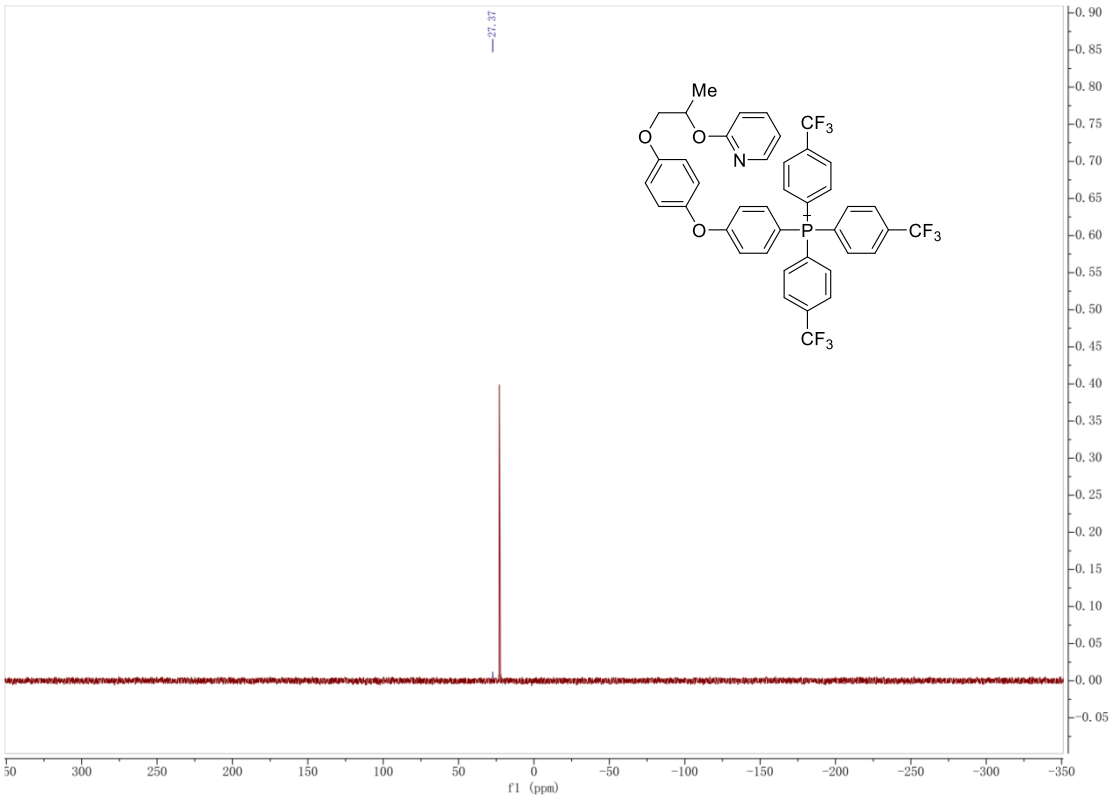

165.39
163.16
156.81
147.23
146.82
144.17
143.14
138.88
136.70
135.81
135.70
131.42
131.28
122.04
118.74
118.60
116.93
116.46
115.53
111.73
107.89
106.91
71.13
69.27
17.04
Me
O
O
N
Cl
O
P
Cl
Cl
f1 (ppm)

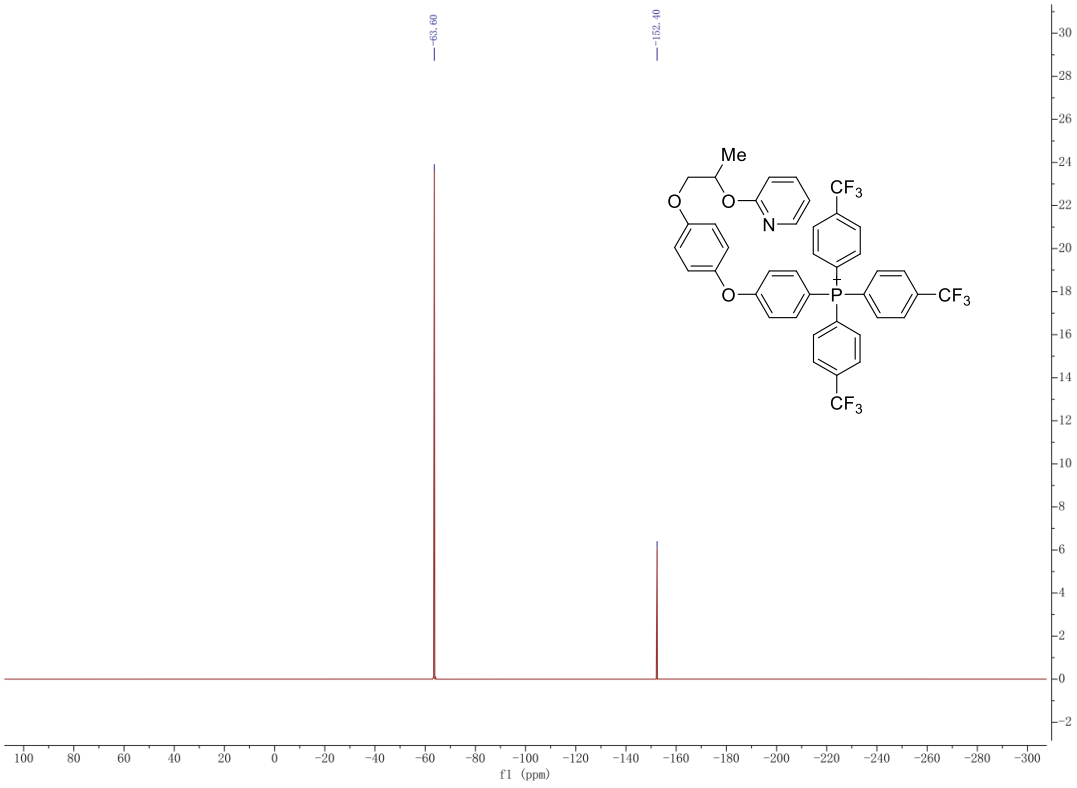

22.77
Me
O
O
N
Cl
O
P
Cl
Cl
f1 (ppm)

NMR Spectra of **30**

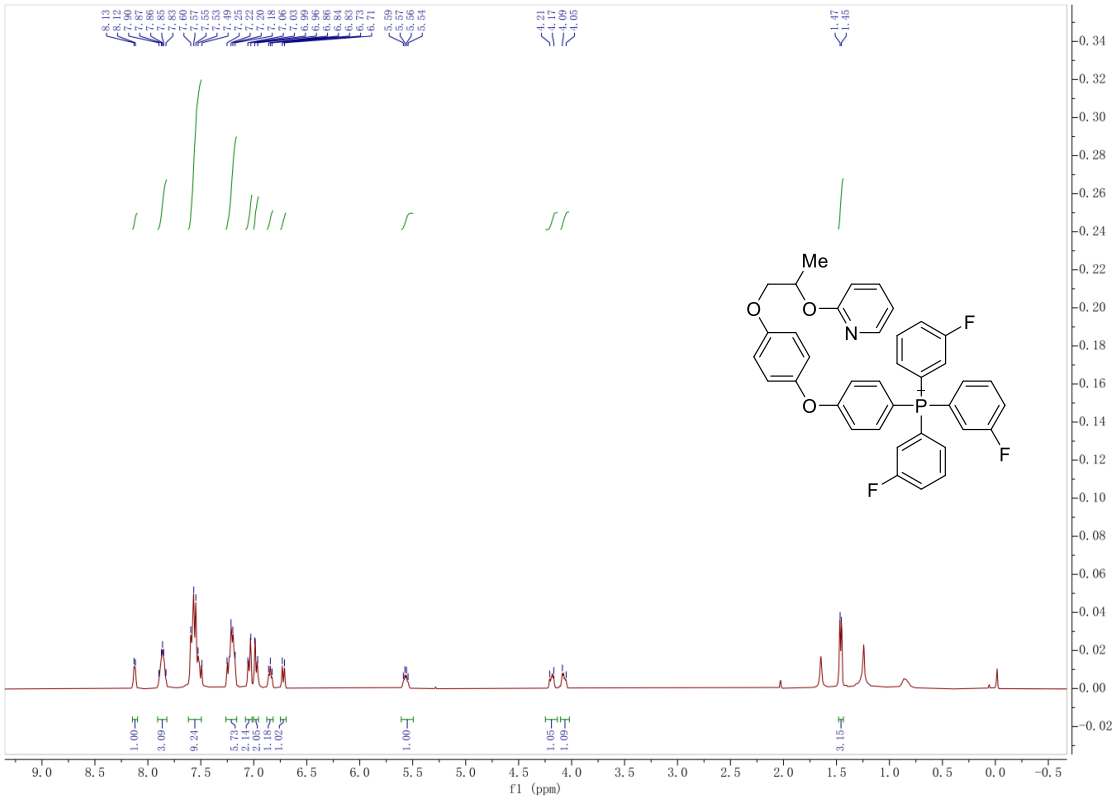


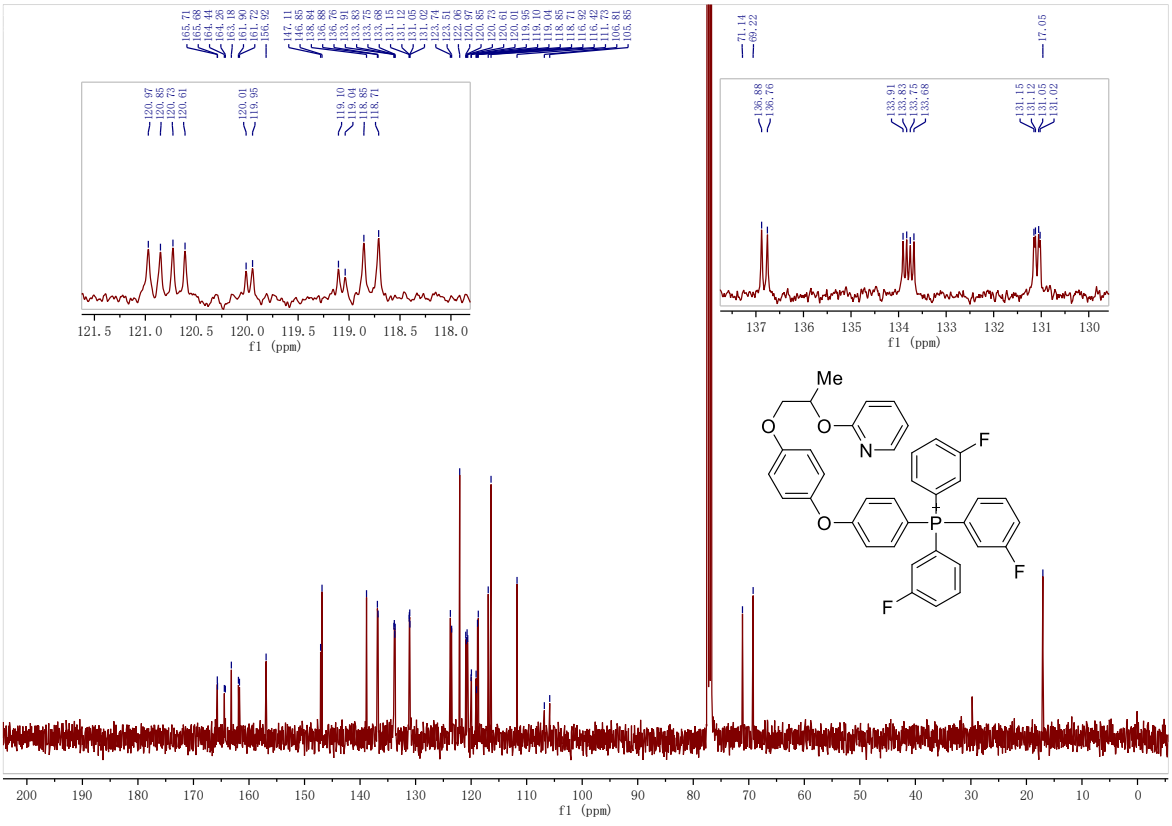


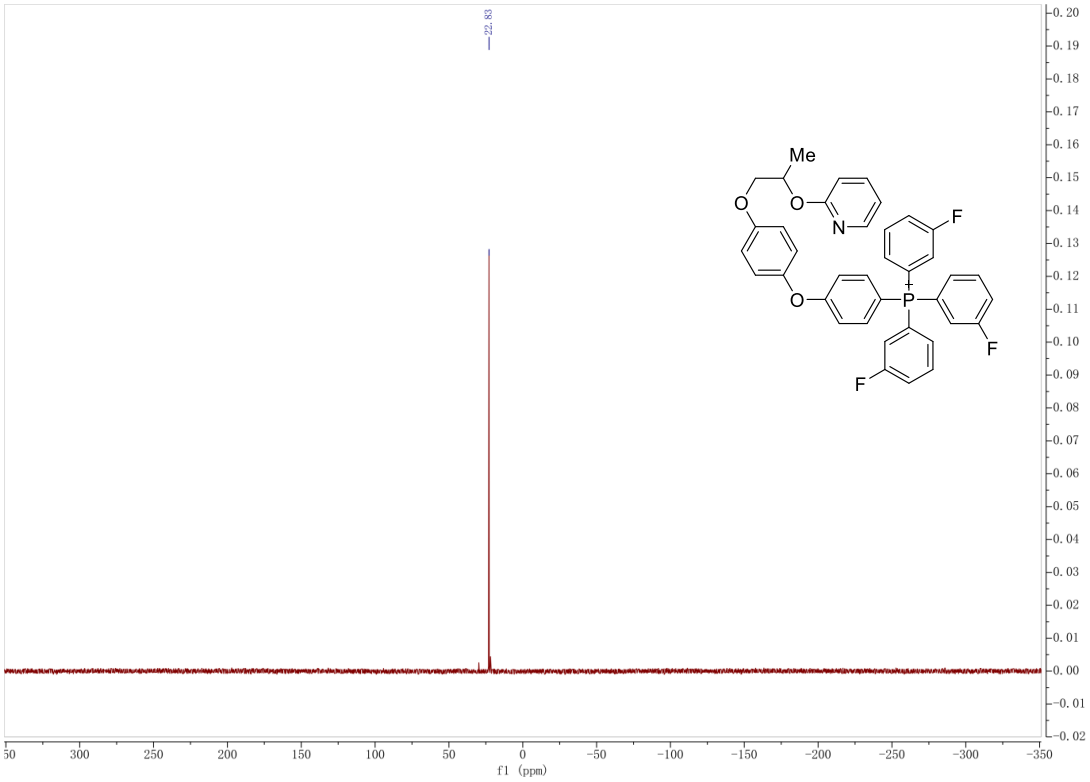

27.37
Me
O
O
N
CF3
O
P
CF3
CF3
f1 (ppm)

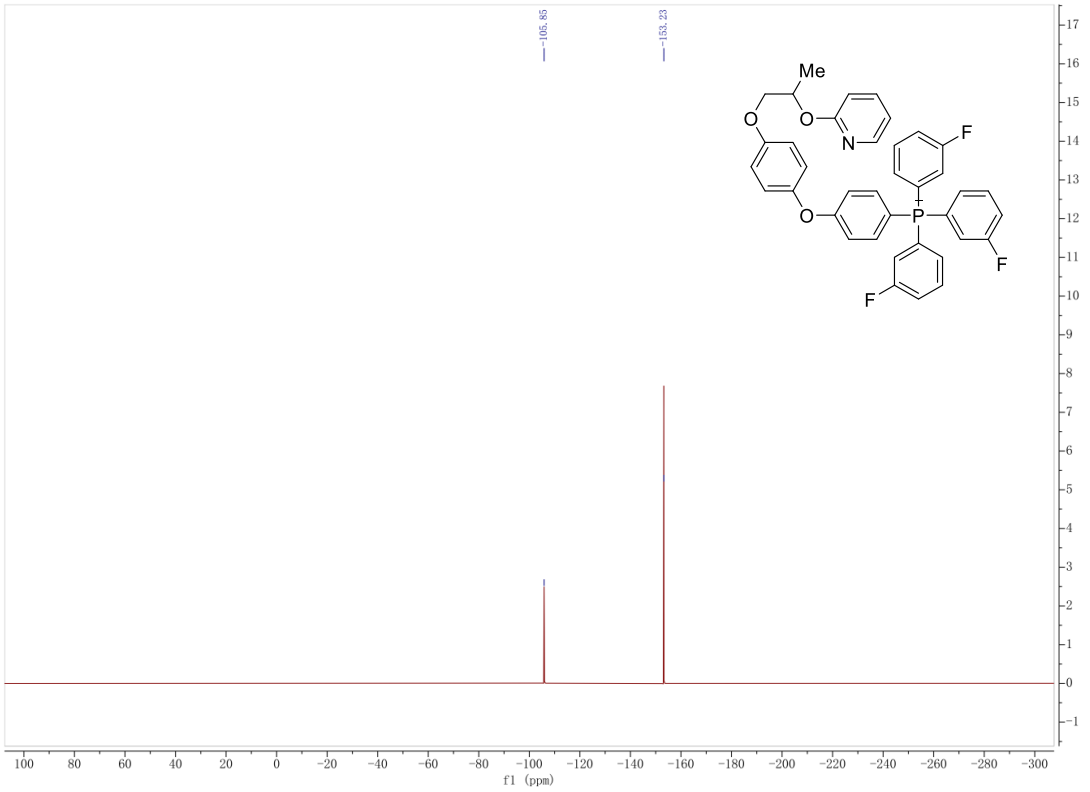

-63.60
-152.40
Me
O
O
N
CF3
O
P
CF3
CF3
f1 (ppm)

NMR Spectra of **31**

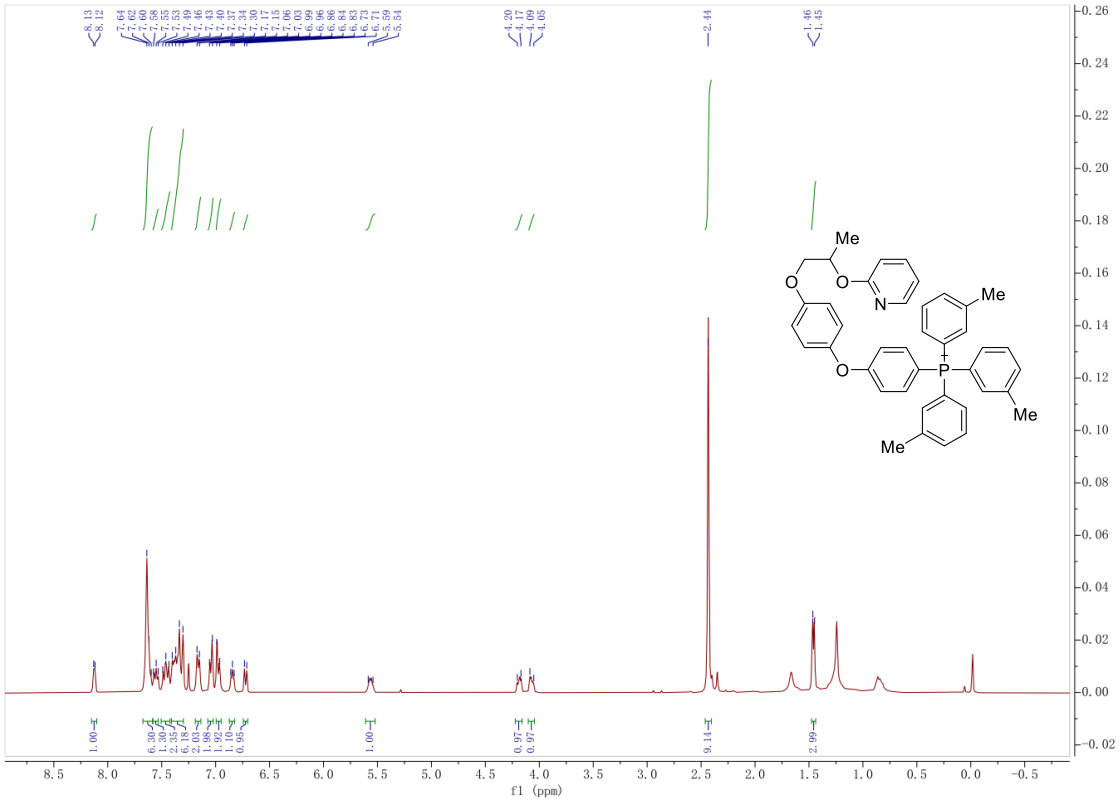


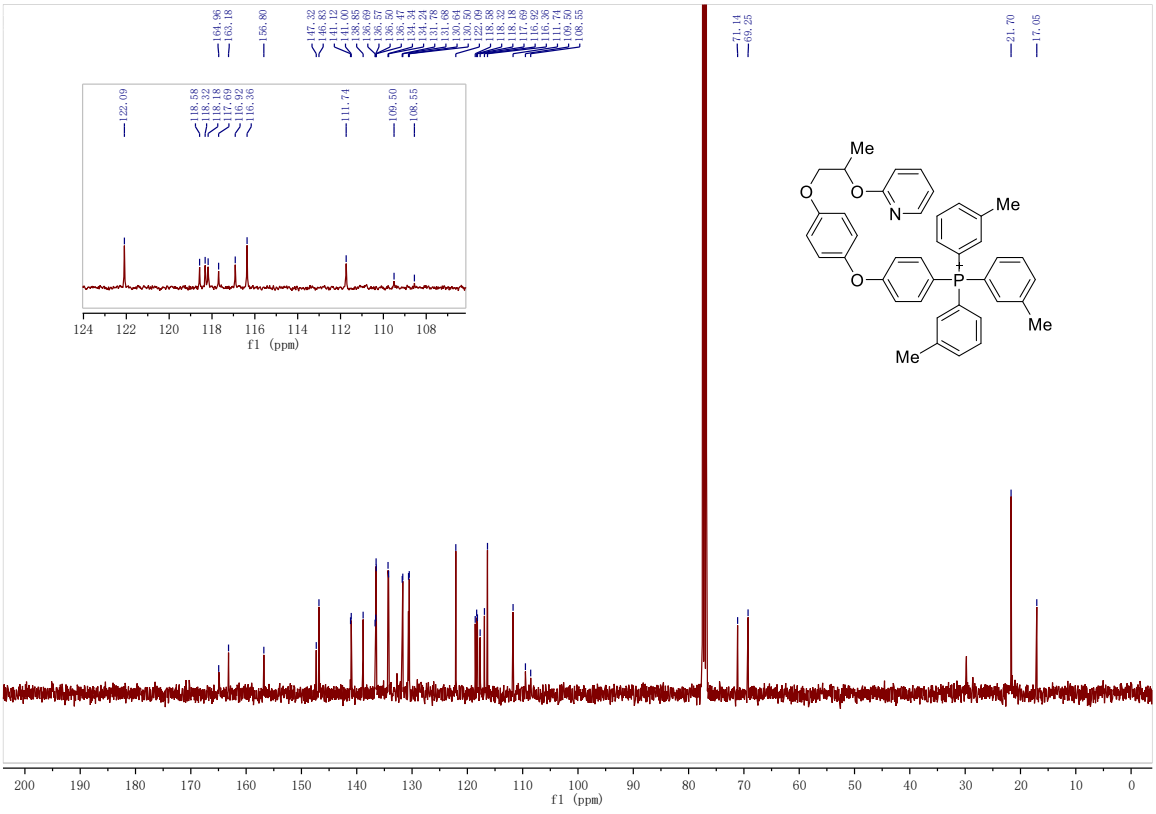


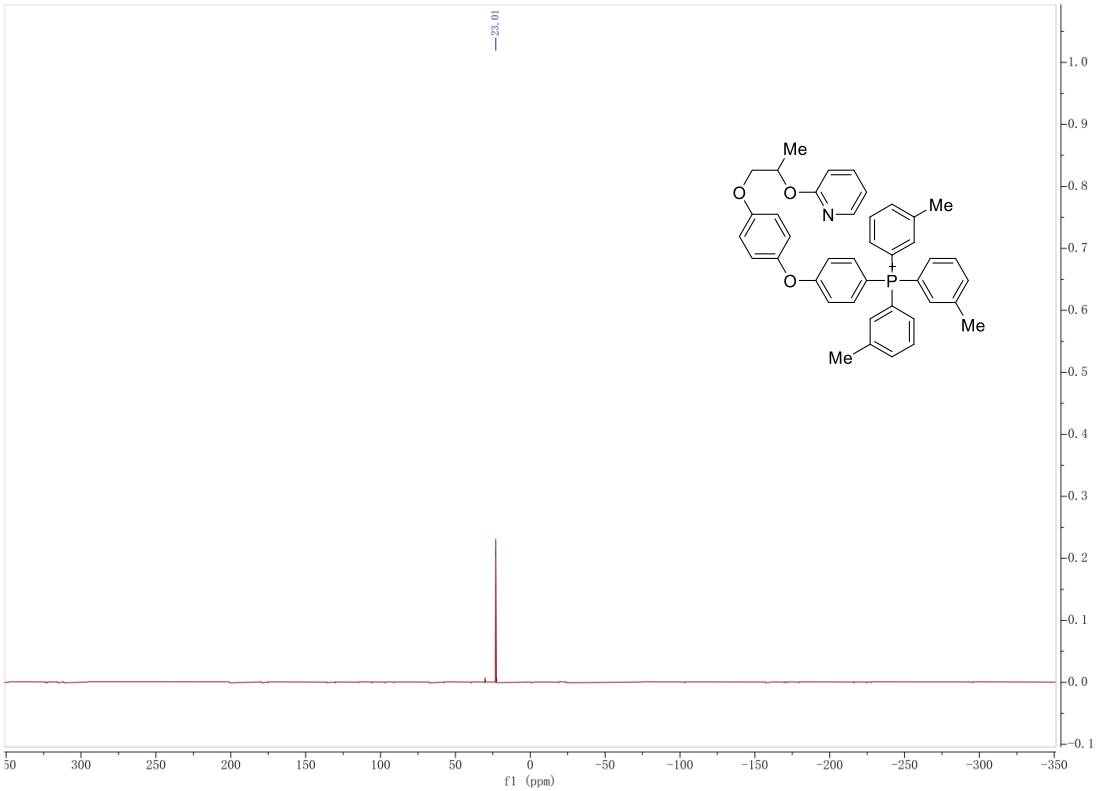

22.83
Me
O
O
N
O
P
F
F
F
F
f1 (ppm)


-105.85
-153.23
Me
O
O
N
O
P
F
F
F
F
f1 (ppm)

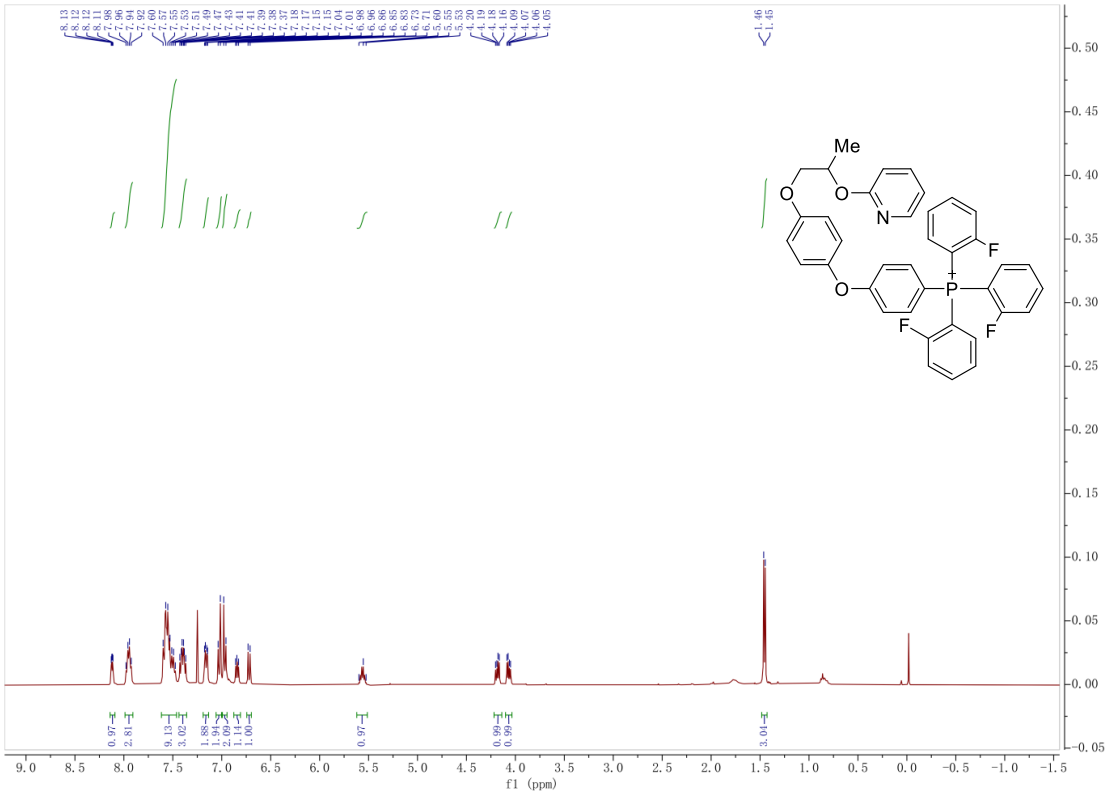
NMR Spectra of **32**

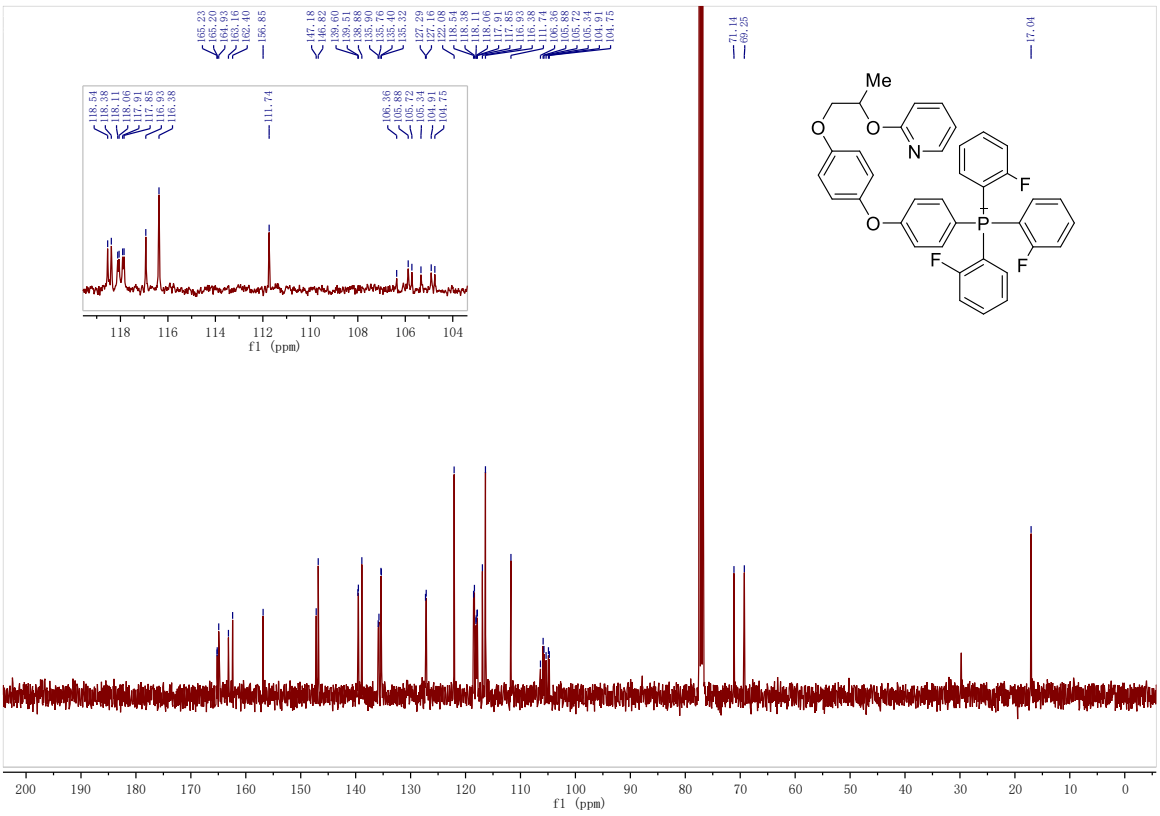


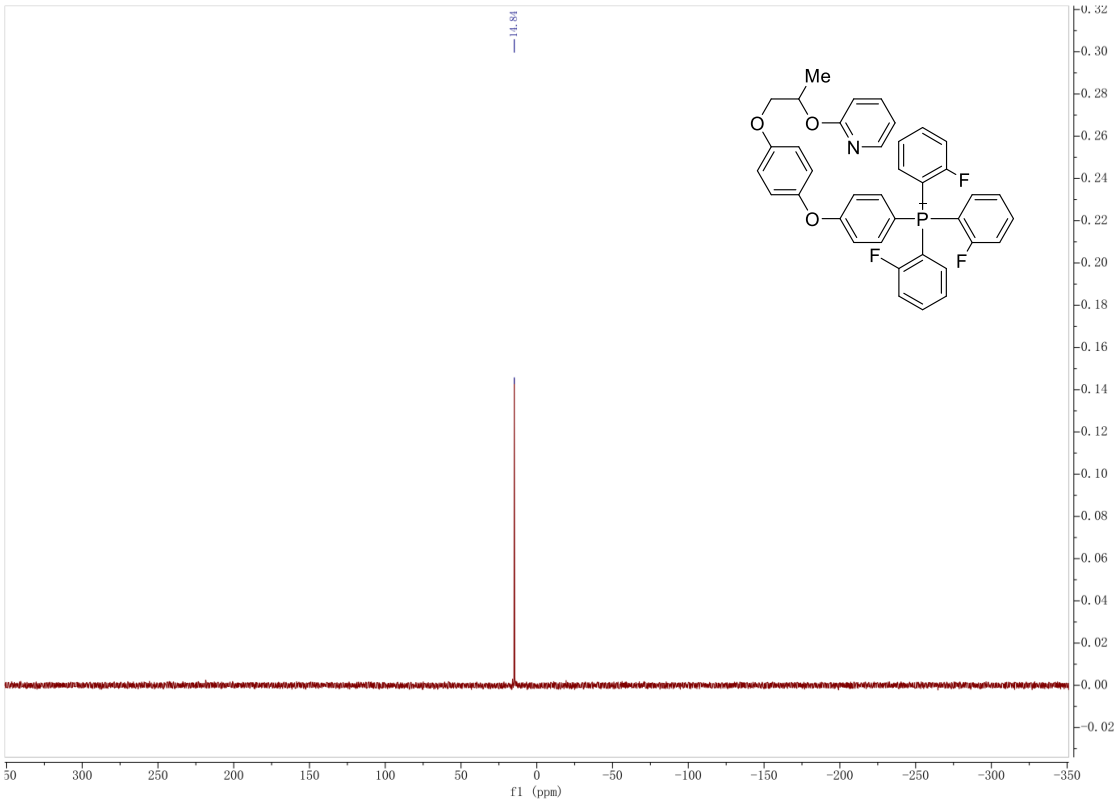


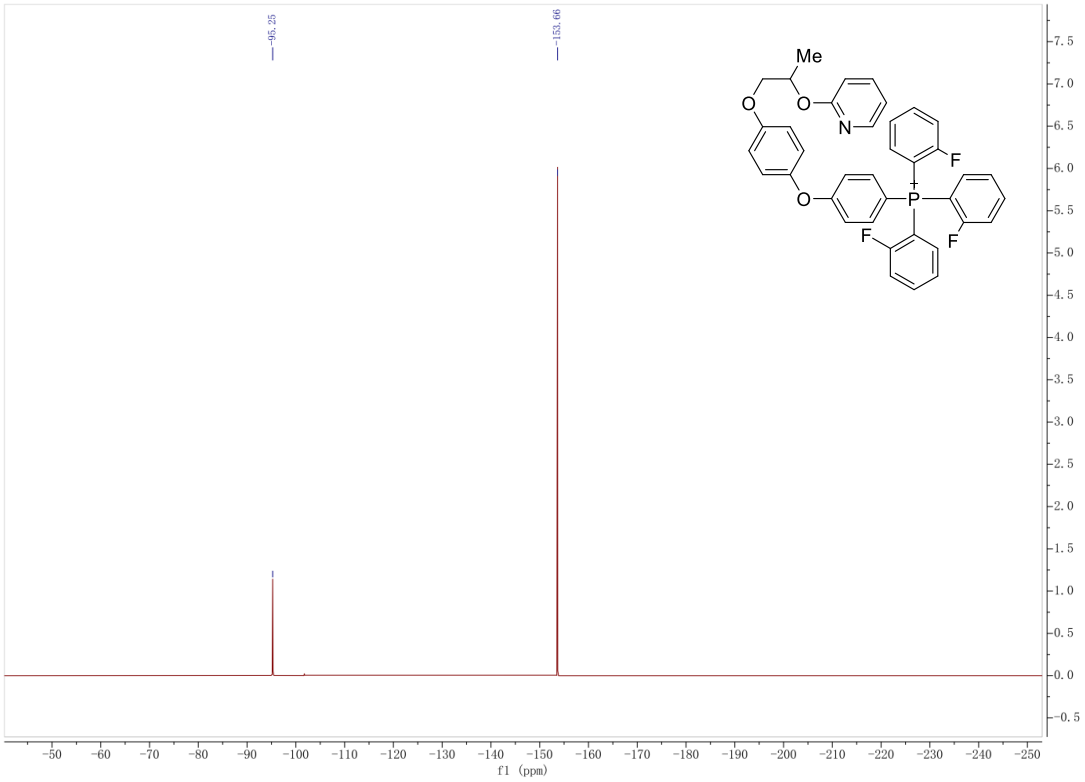


NMR Spectra of **33**

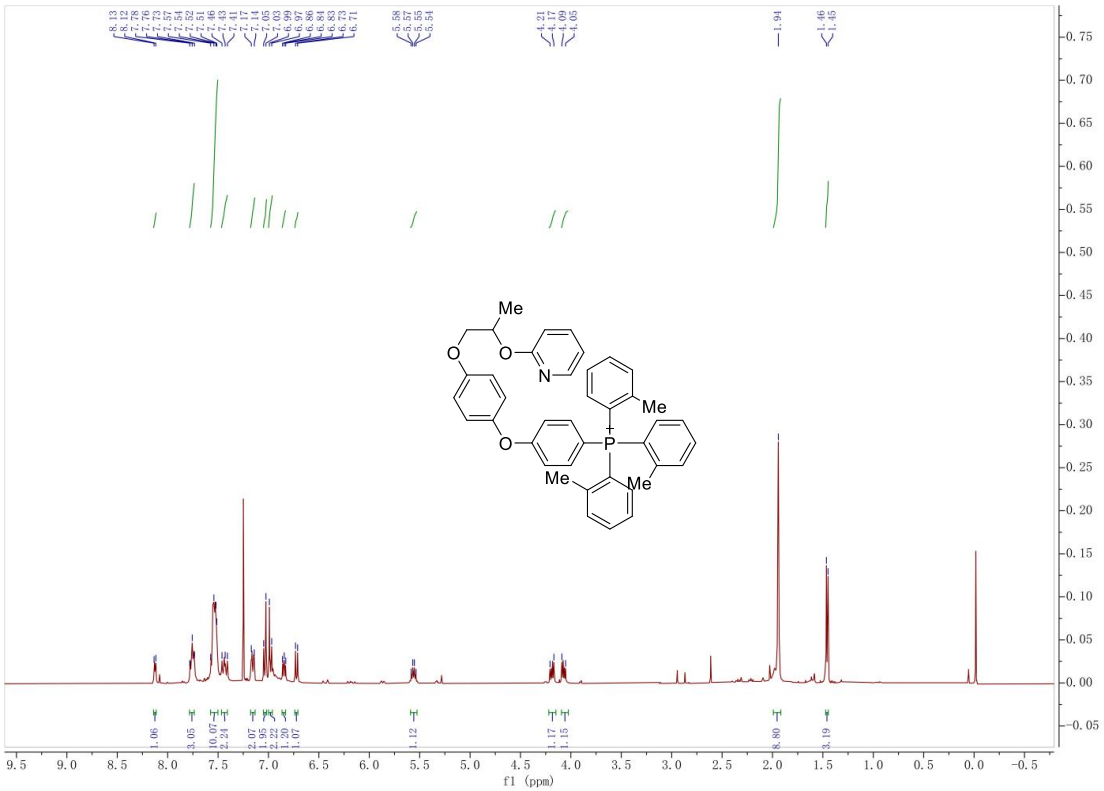


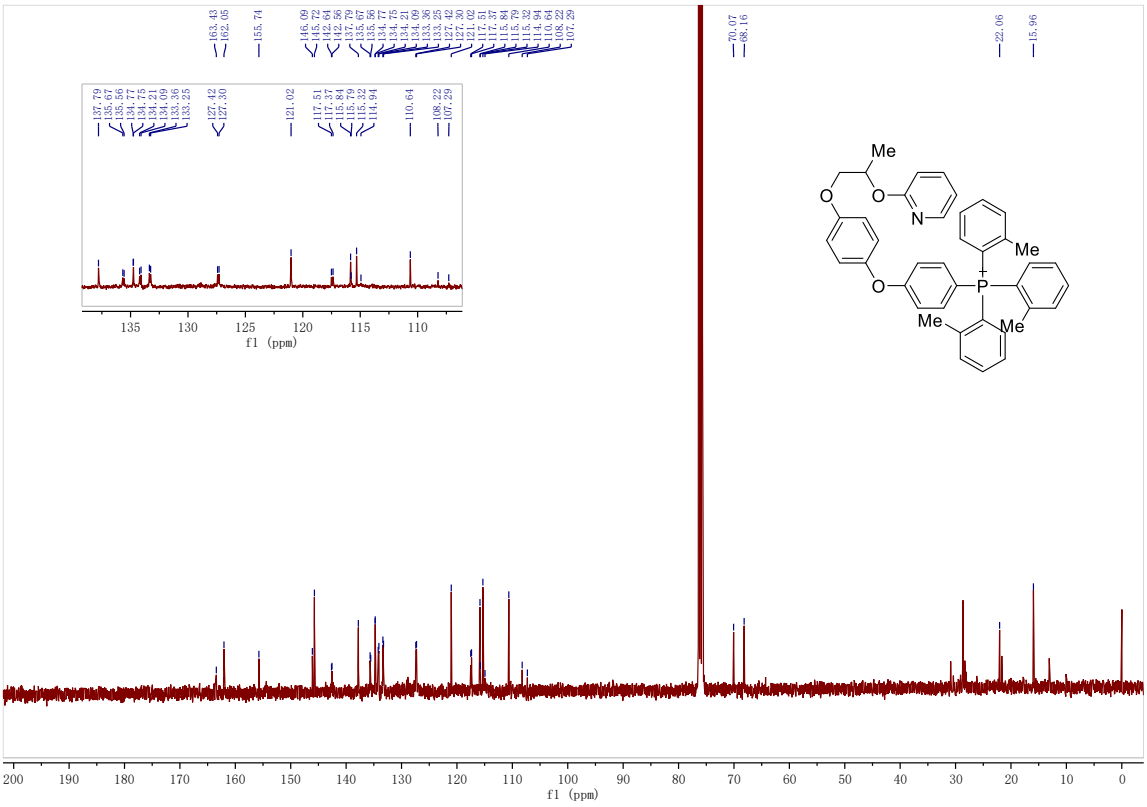

Me
O
O
N
F
O
P
F
F
f1 (ppm)

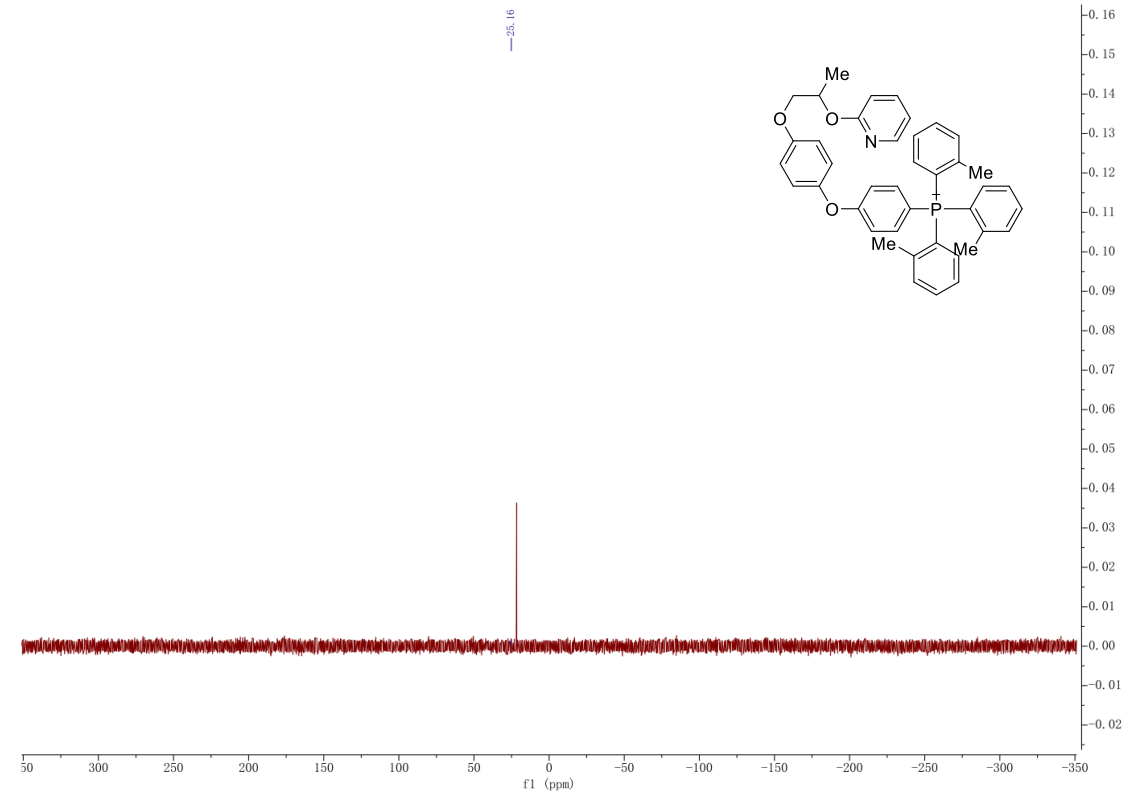

Me
O
O
N
F
O
P
F
F
f1 (ppm)



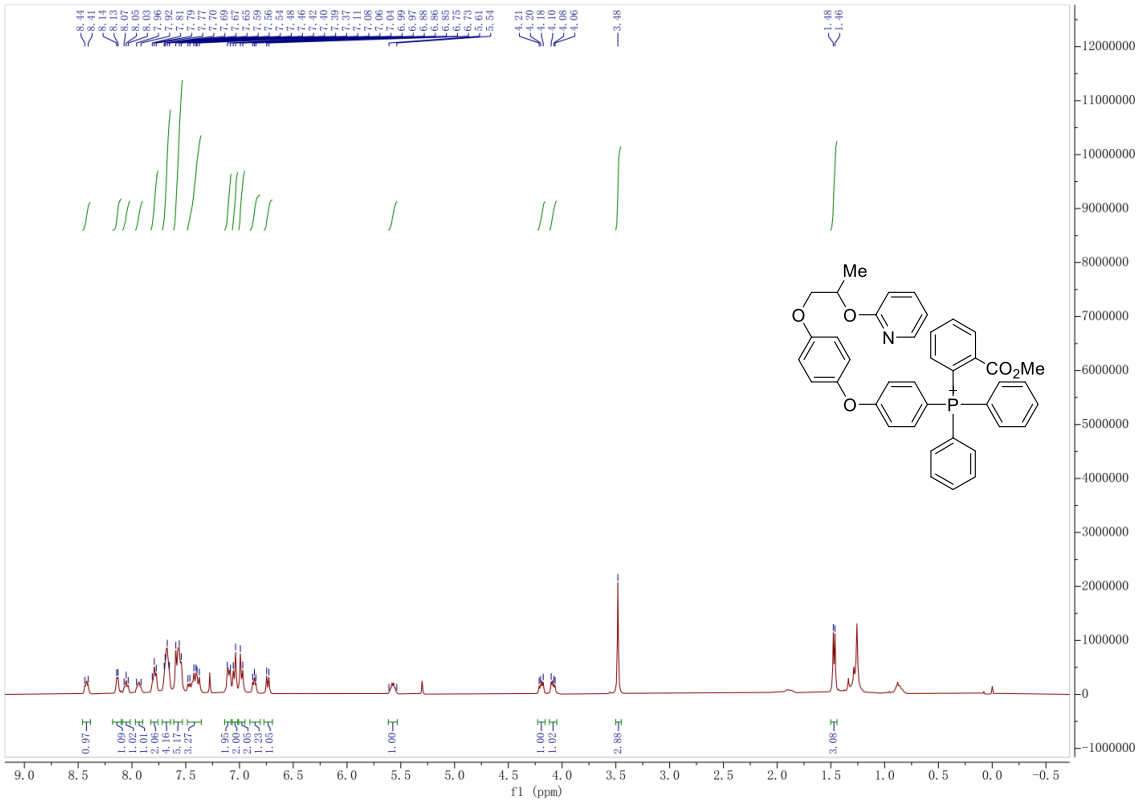
NMR Spectra of **34**

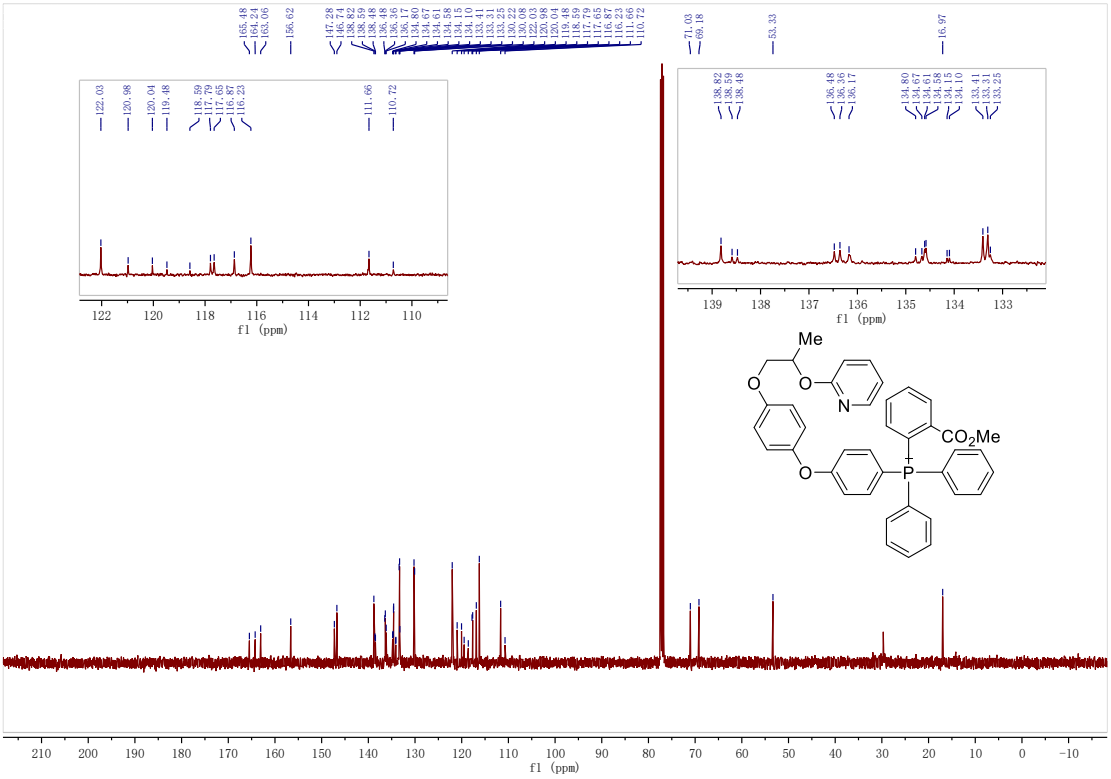


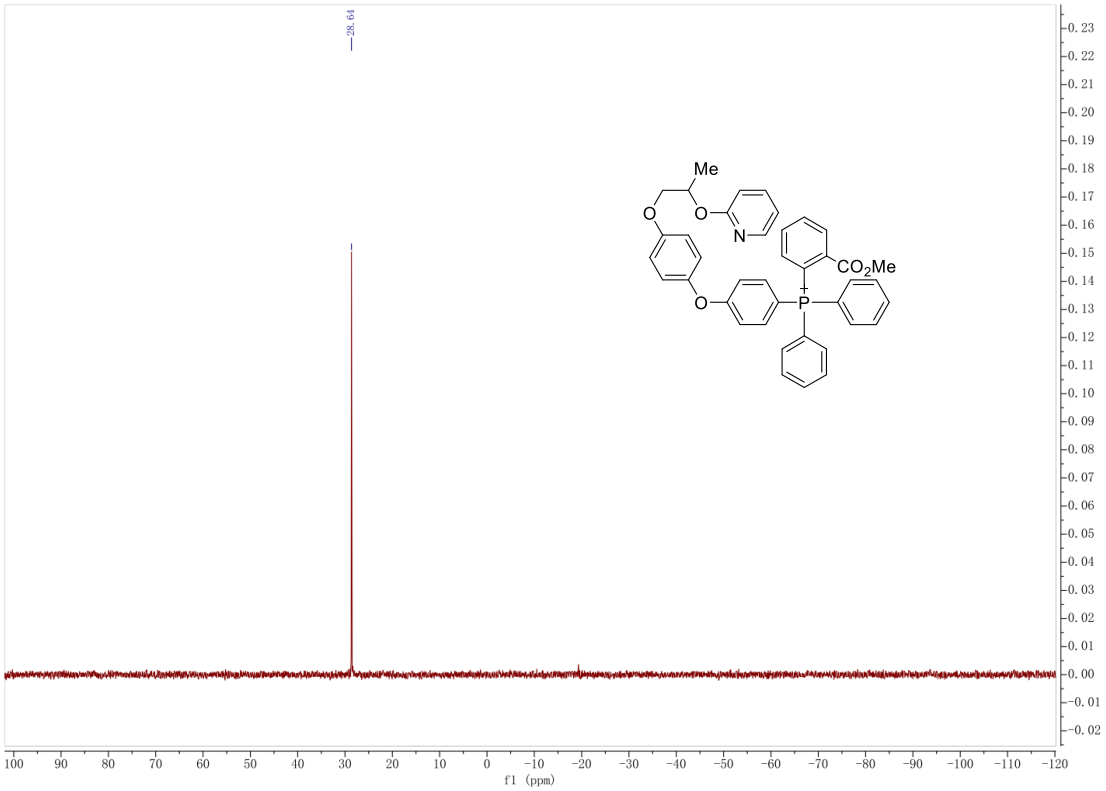

163.43
162.05
155.74
146.09
145.72
142.64
142.36
137.79
135.67
135.56
134.77
134.75
134.21
134.09
133.36
133.25
127.42
127.30
121.02
117.51
117.37
115.84
115.79
115.32
114.94
110.64
108.22
107.29
70.07
68.16
22.06
15.96
Me
O
O
N
Me
O
P
Me
Me
Me
f1 (ppm)


25.16
Me
O
O
N
Me
O
P
Me
Me
f1 (ppm)

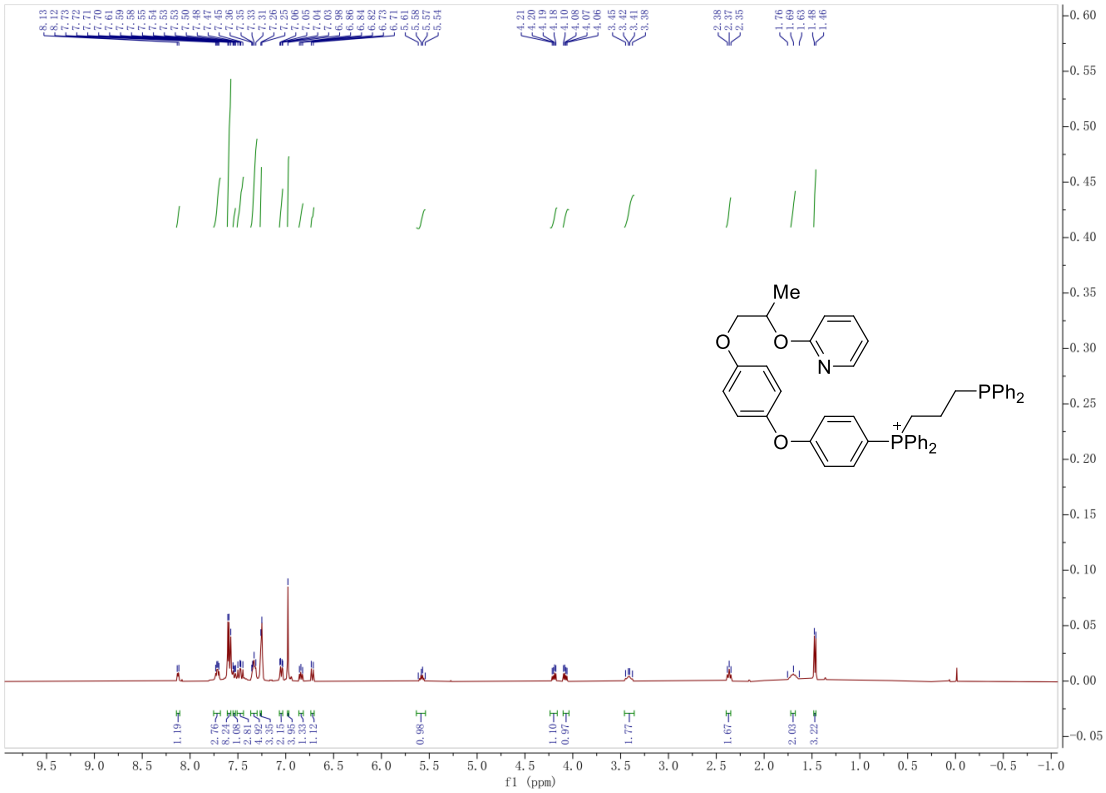
NMR Spectra of **35**

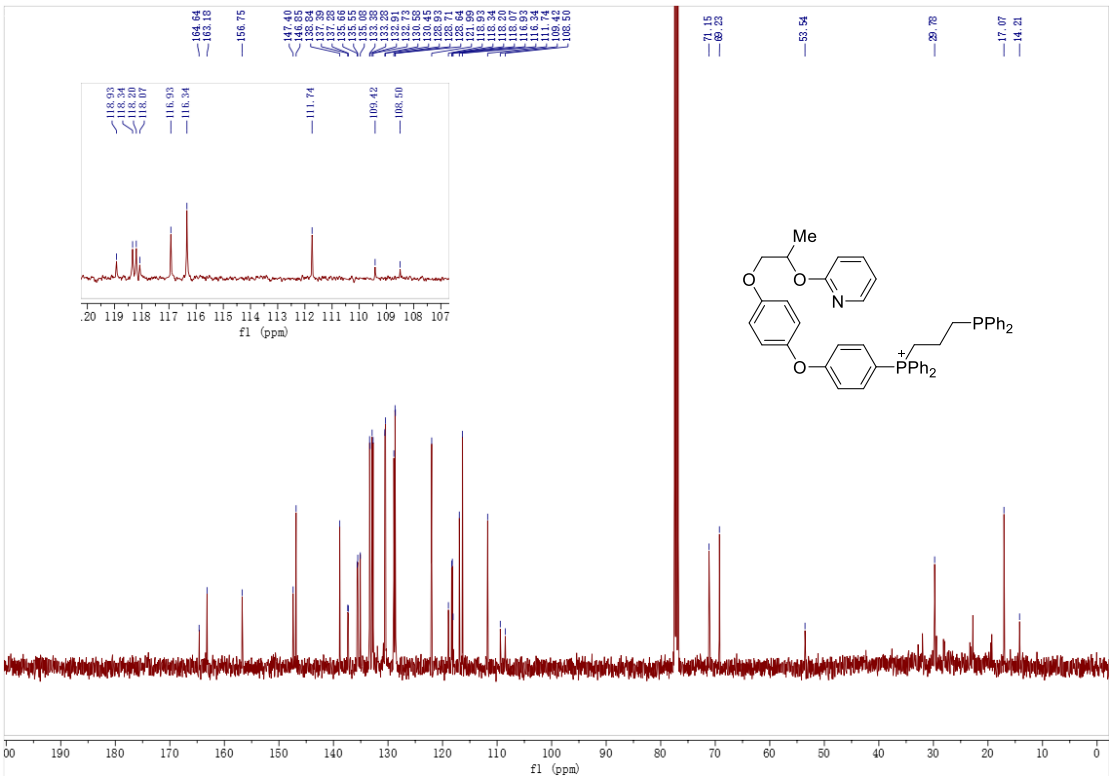


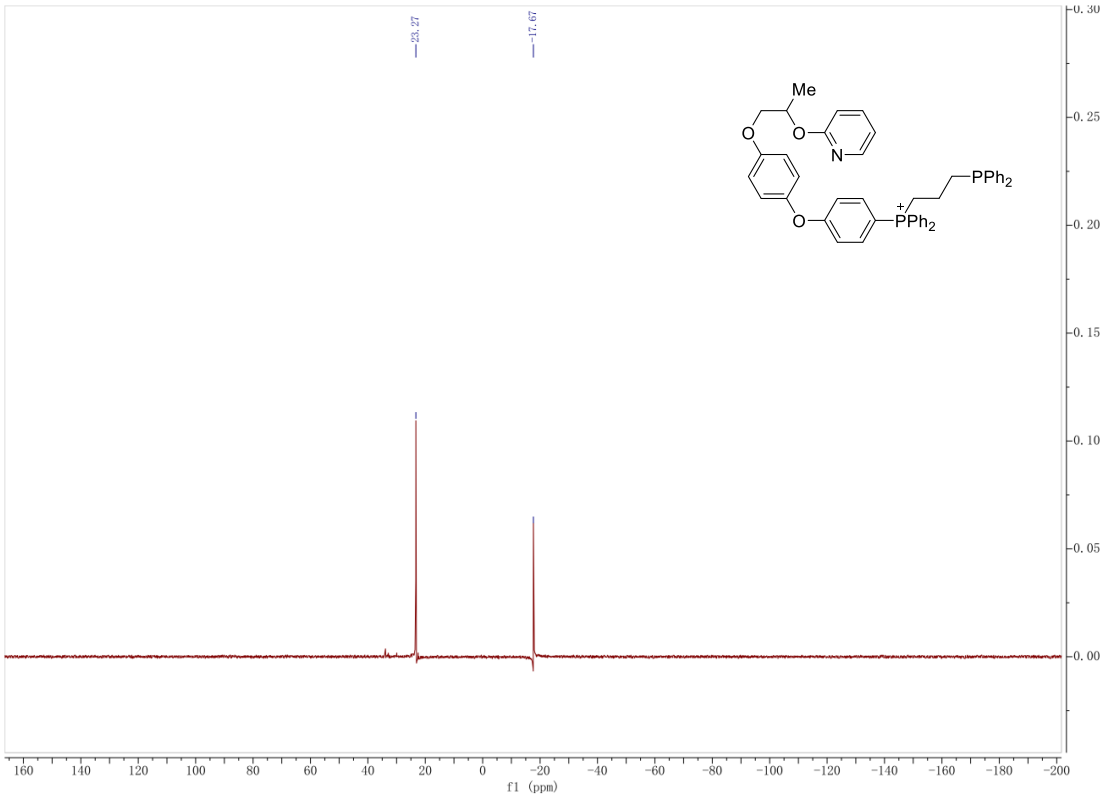




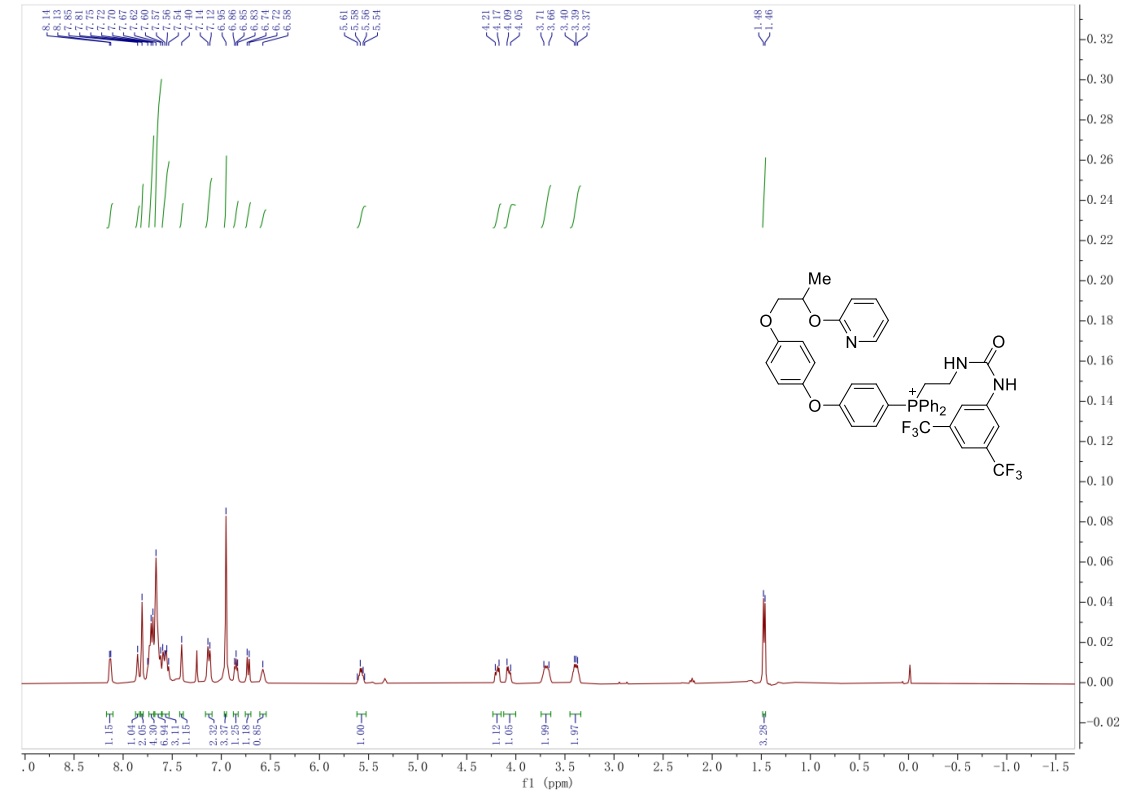
NMR Spectra of **36**

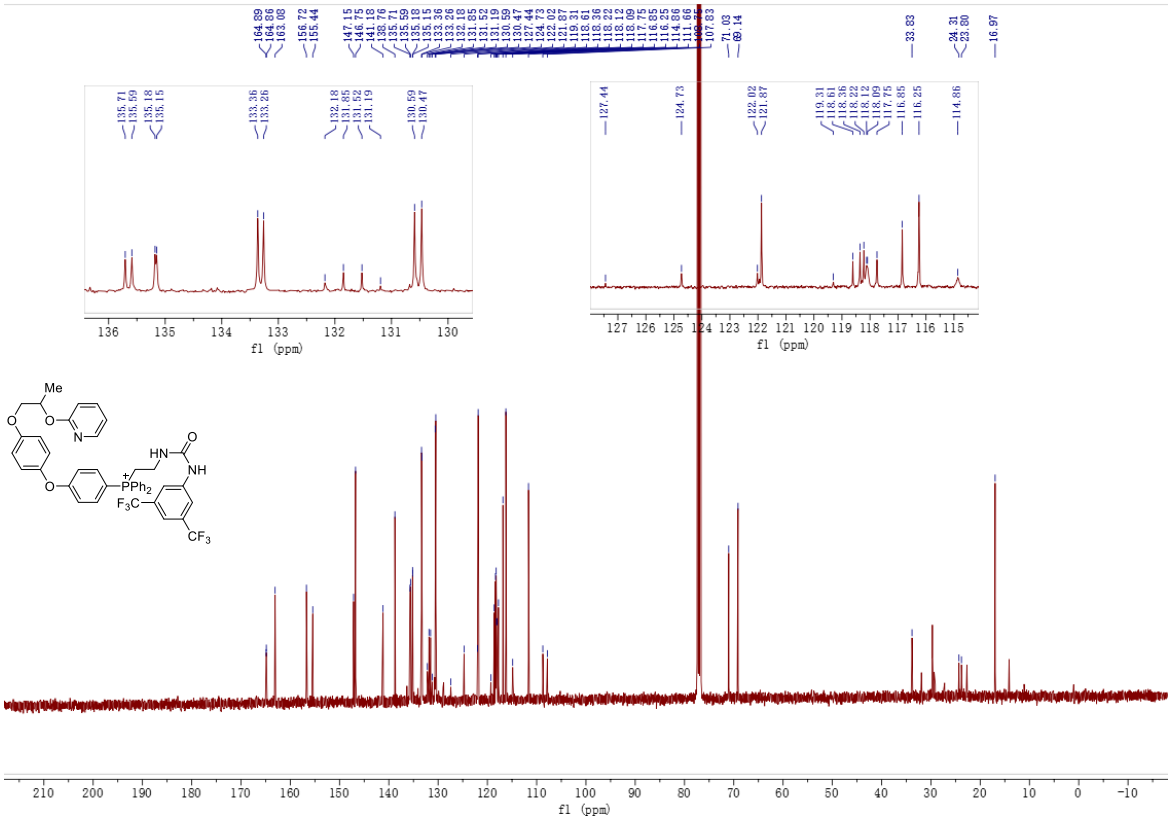


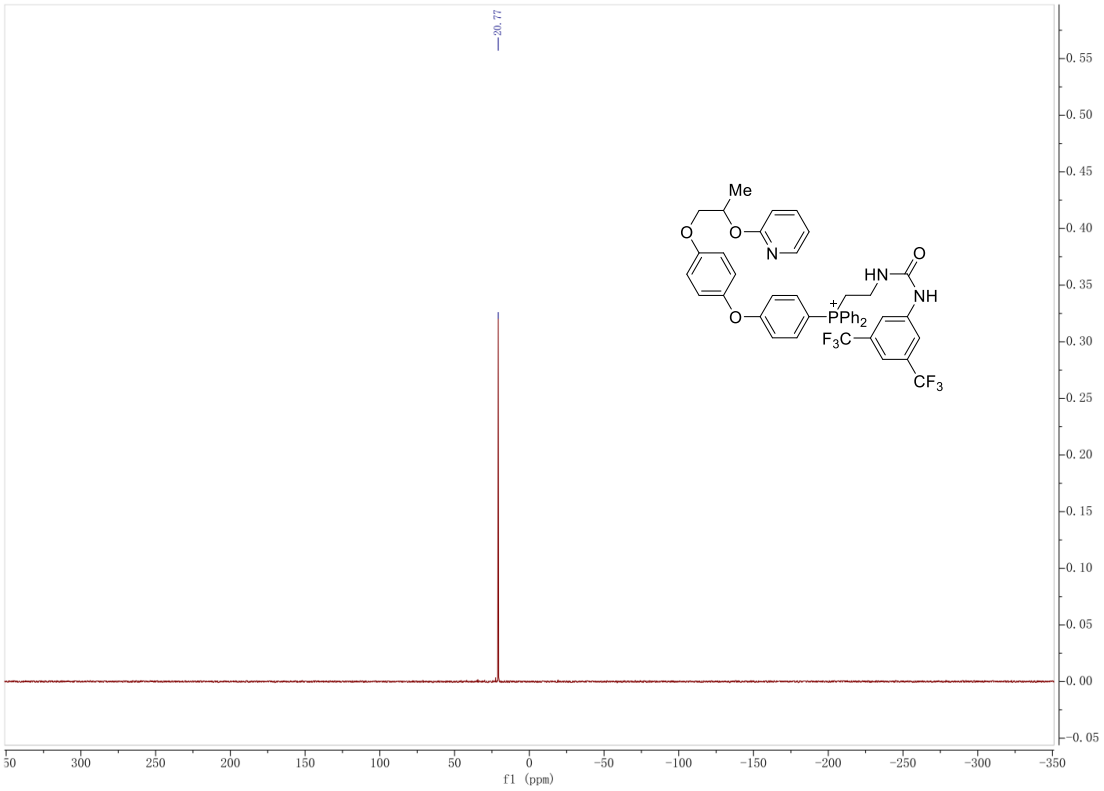

Me
O
O
N
O
PPh2
+
PPh2
f1 (ppm)

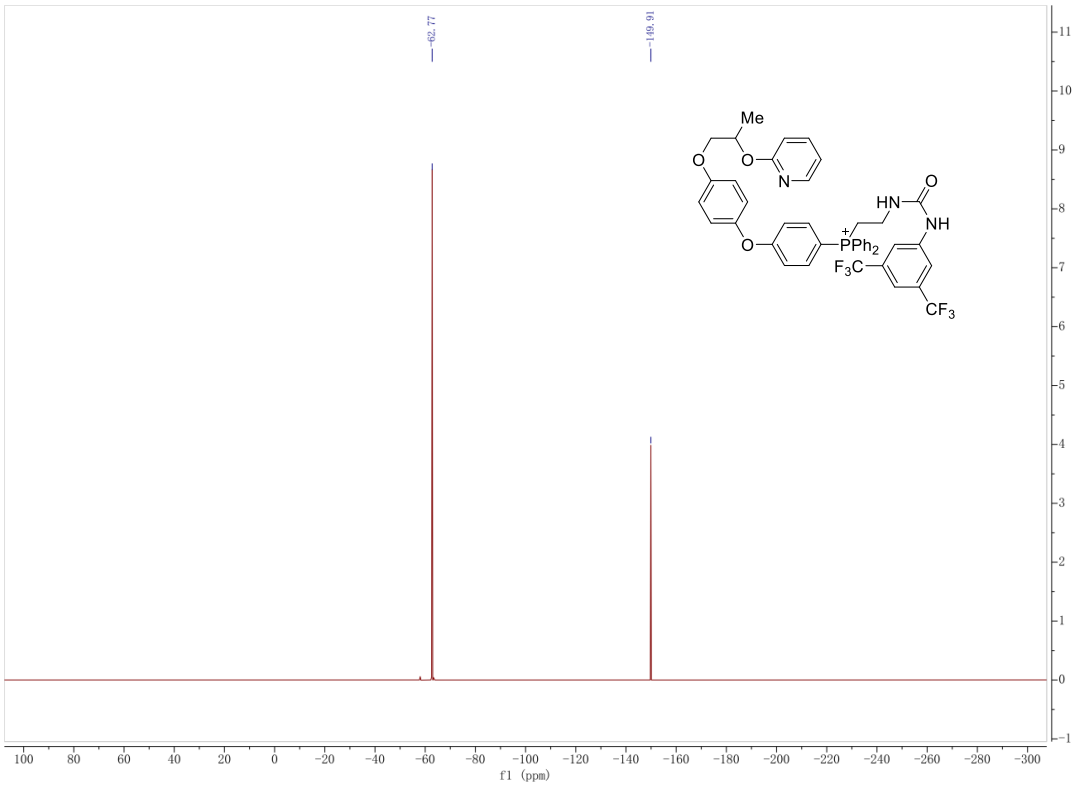

Me
O
O
N
O
PPh2
+
PPh2
f1 (ppm)

NMR Spectra of **37**

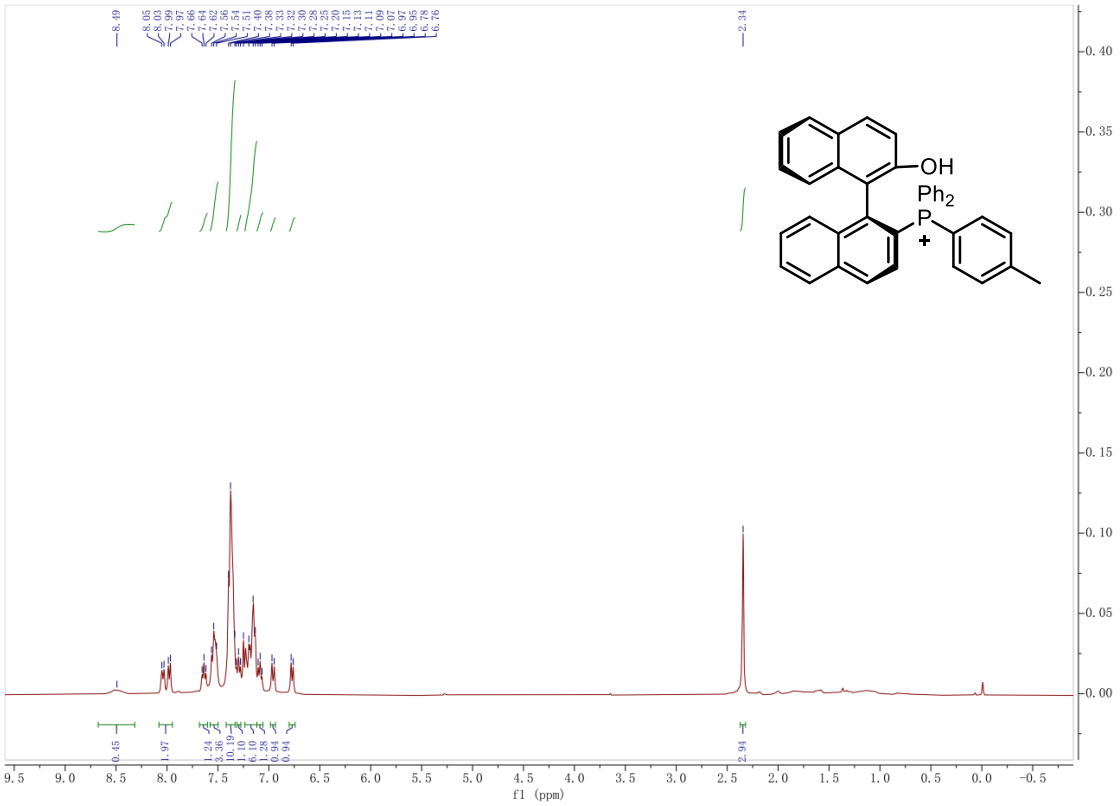


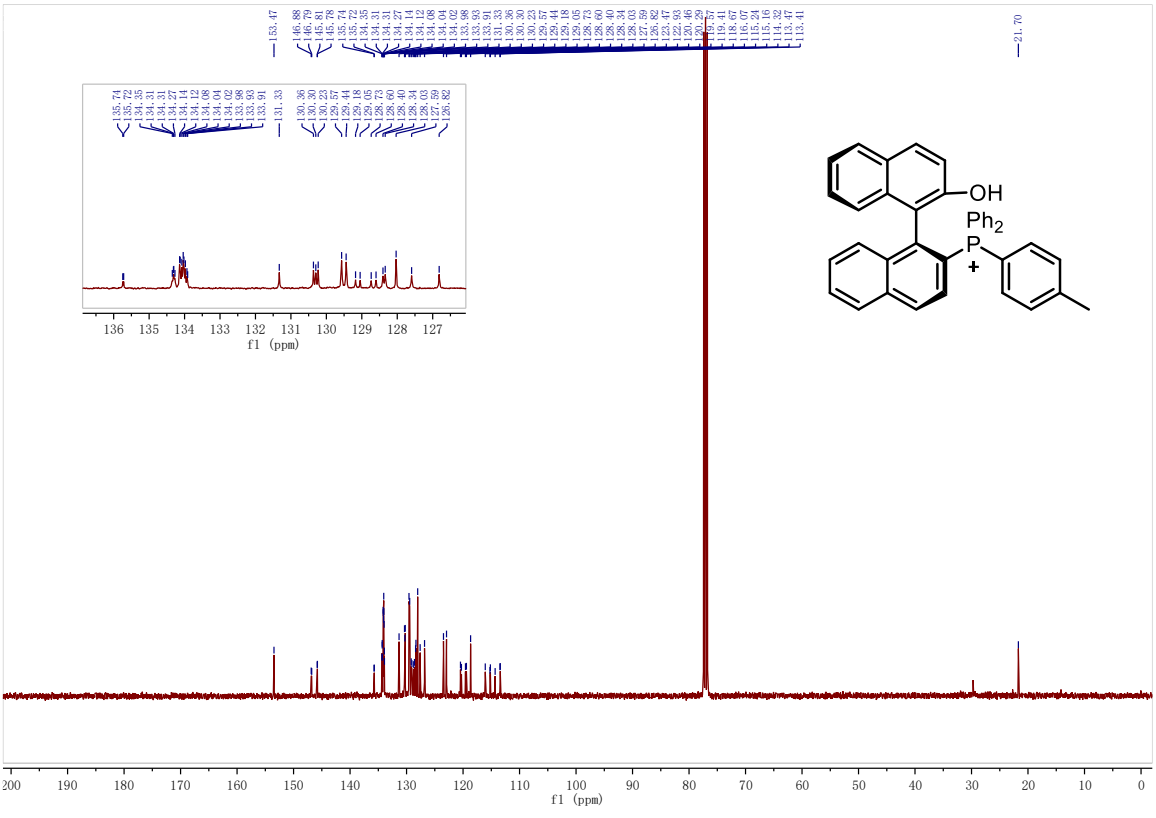


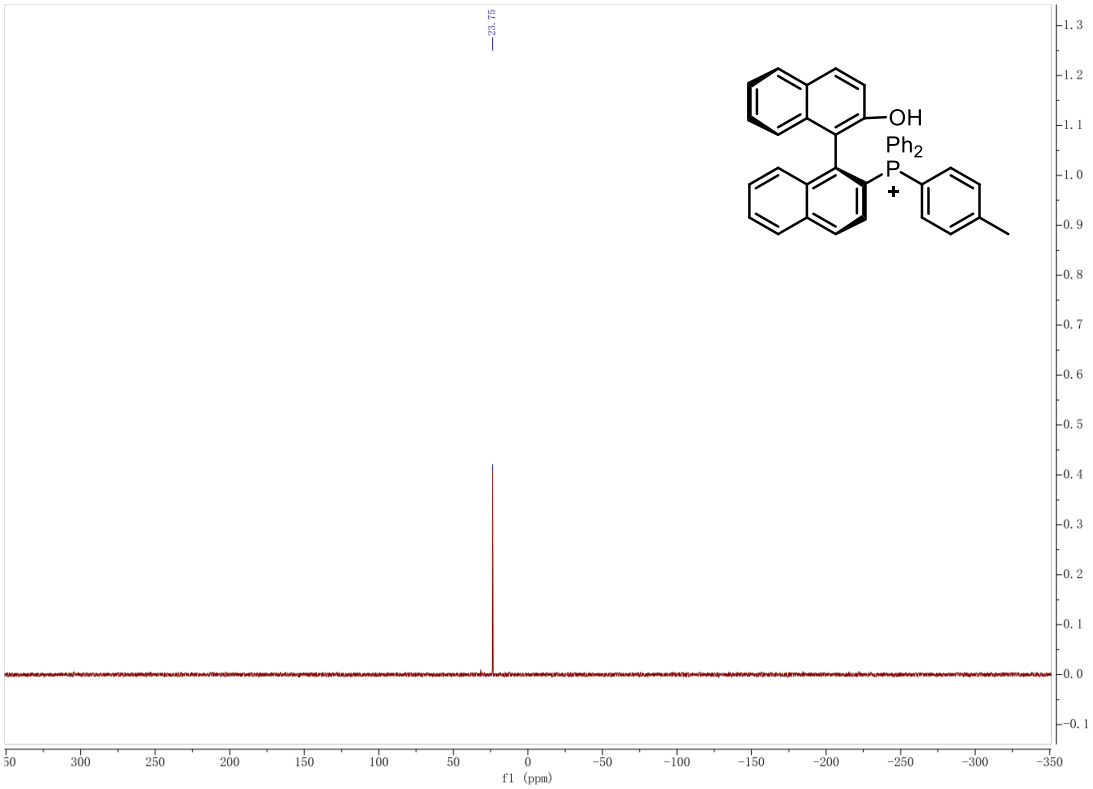

20.77
Me
O
O
N
HN
O
NH
O
PPh2
F3C
CF3
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
f1 (ppm)


-62.77
-149.91
Me
O
O
N
HN
O
NH
O
PPh2
F3C
CF3
11
10
9
8
7
6
5
4
3
2
1
0
-1
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)

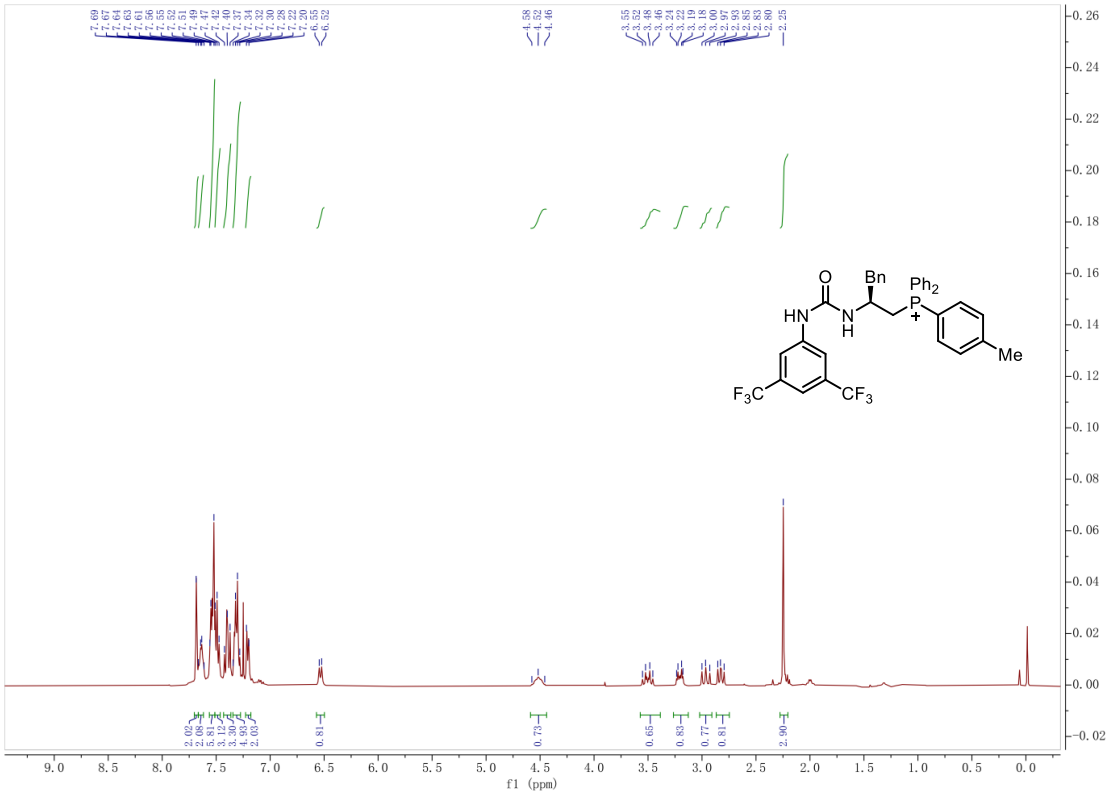
NMR Spectra of **38**

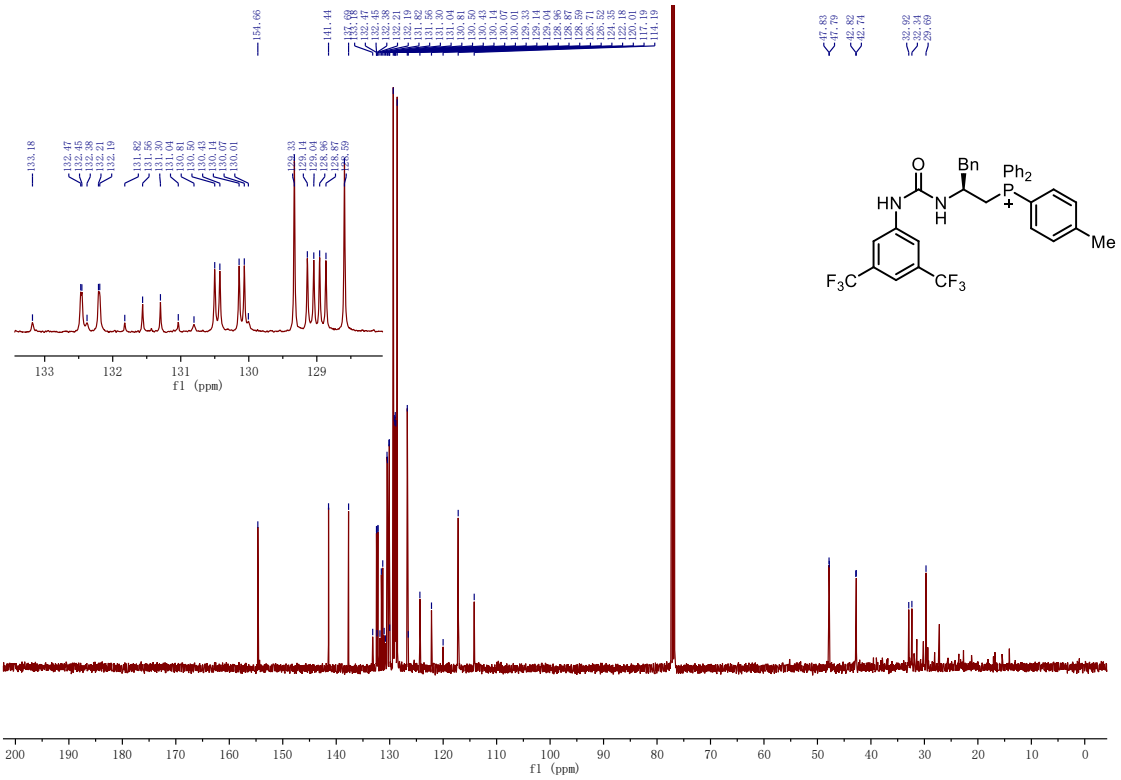


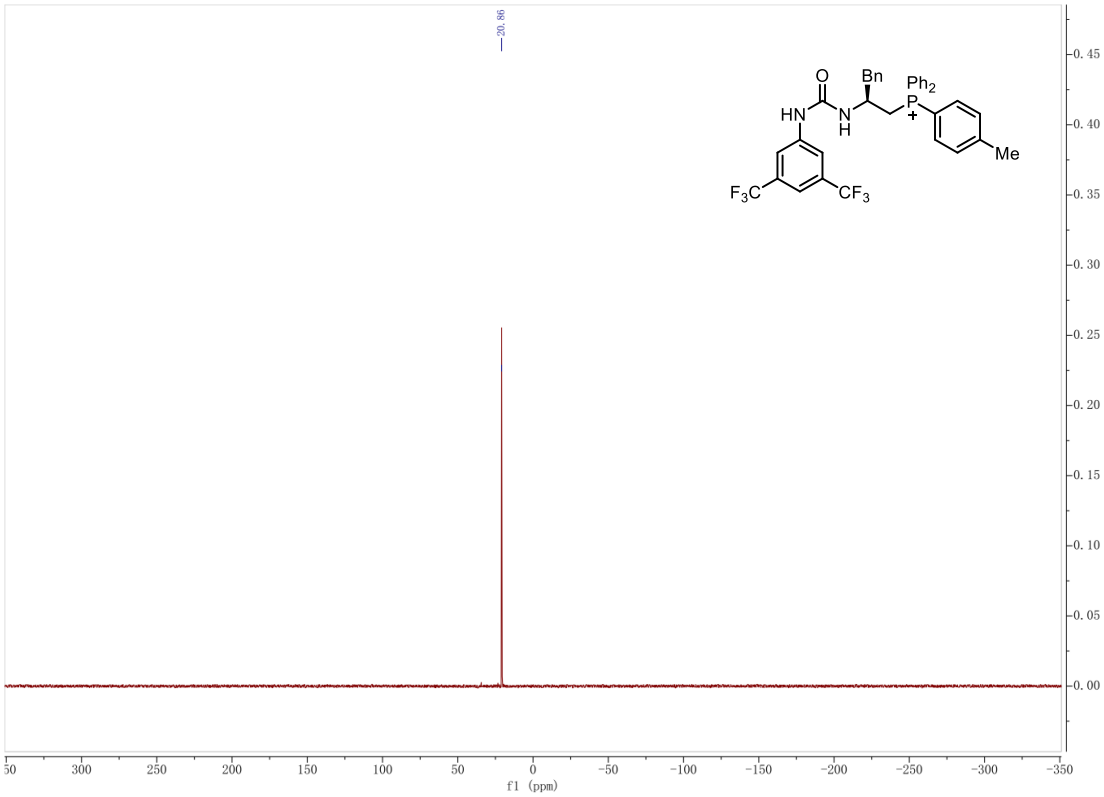


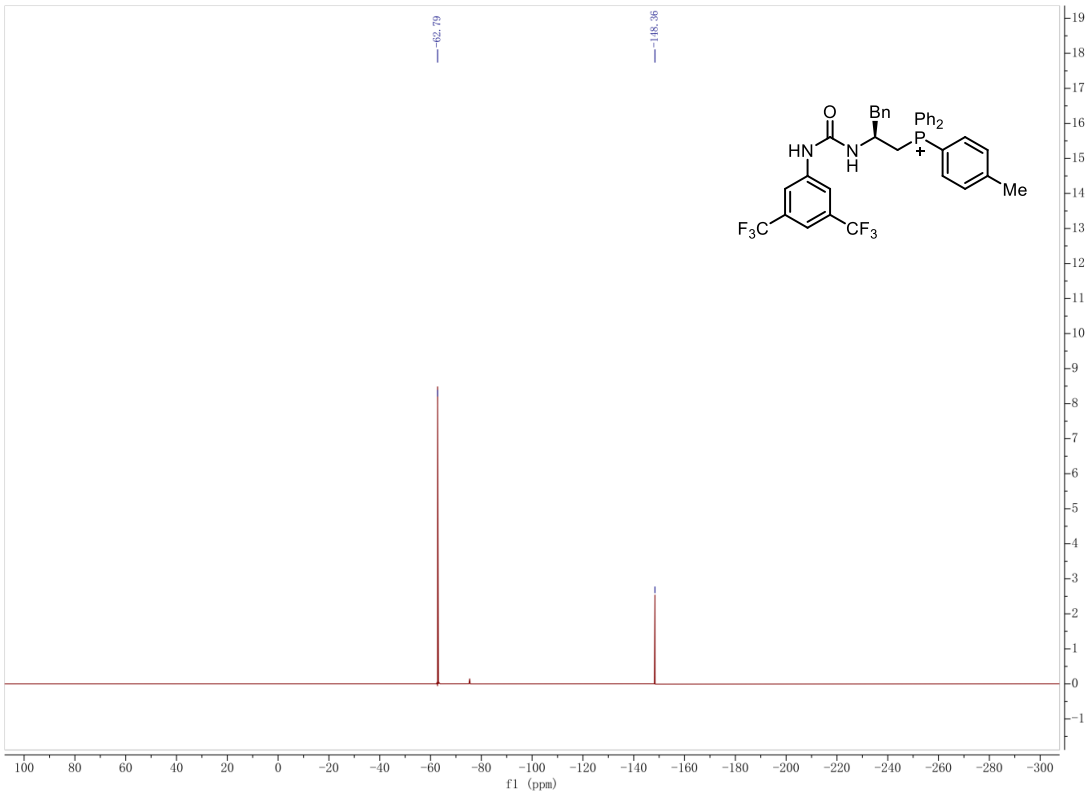


NMR Spectra of **39**

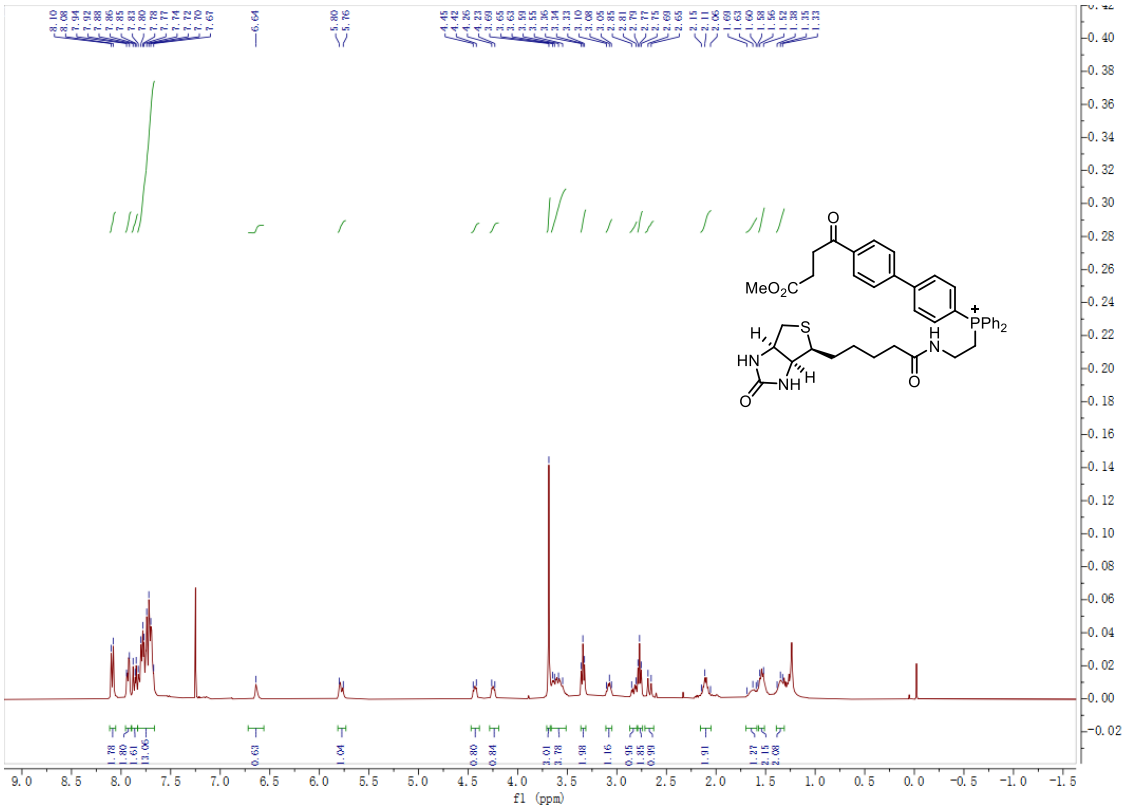


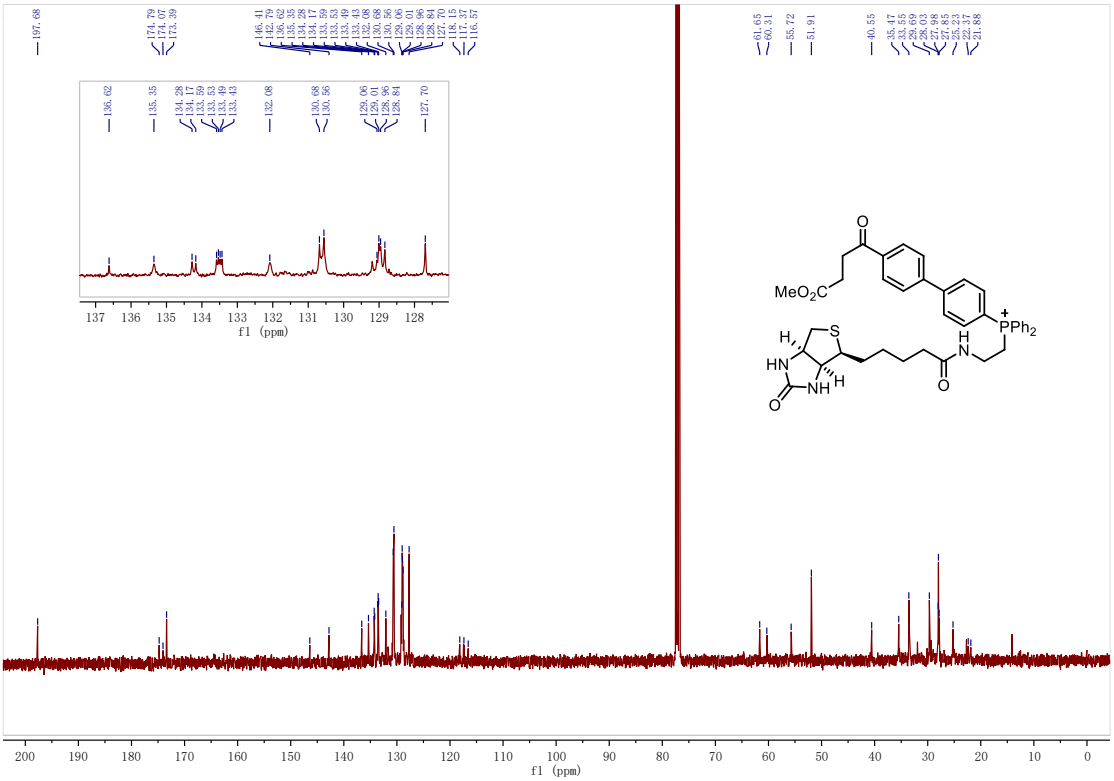

154.66
141.44
137.69
133.18
132.47
132.45
132.38
132.21
132.19
131.82
131.56
131.30
131.04
130.81
130.50
130.43
130.14
130.07
130.01
129.33
129.14
129.04
128.96
128.87
128.59
126.71
126.52
124.35
122.18
120.01
117.59
114.19
47.83
47.79
42.82
42.74
32.92
32.34
29.69
O
Bn
Ph2
HN
N
H
P
Me
F3C
CF3
f1 (ppm)

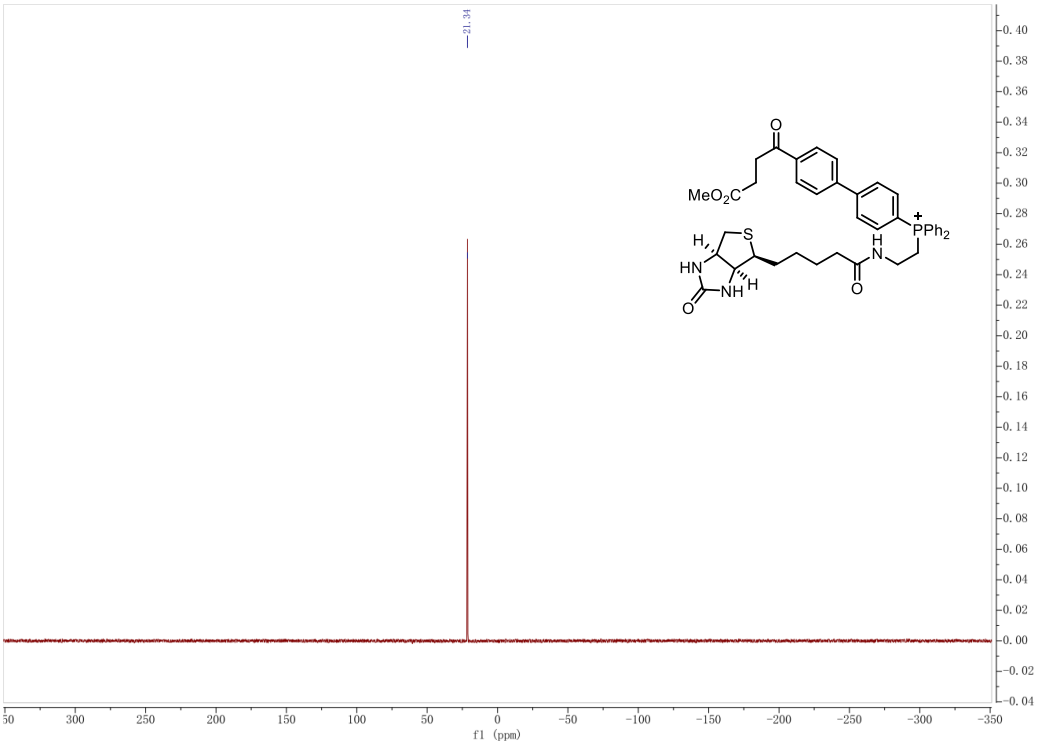

20.86
O
Bn
Ph2
HN
N
H
P
Me
F3C
CF3
f1 (ppm)



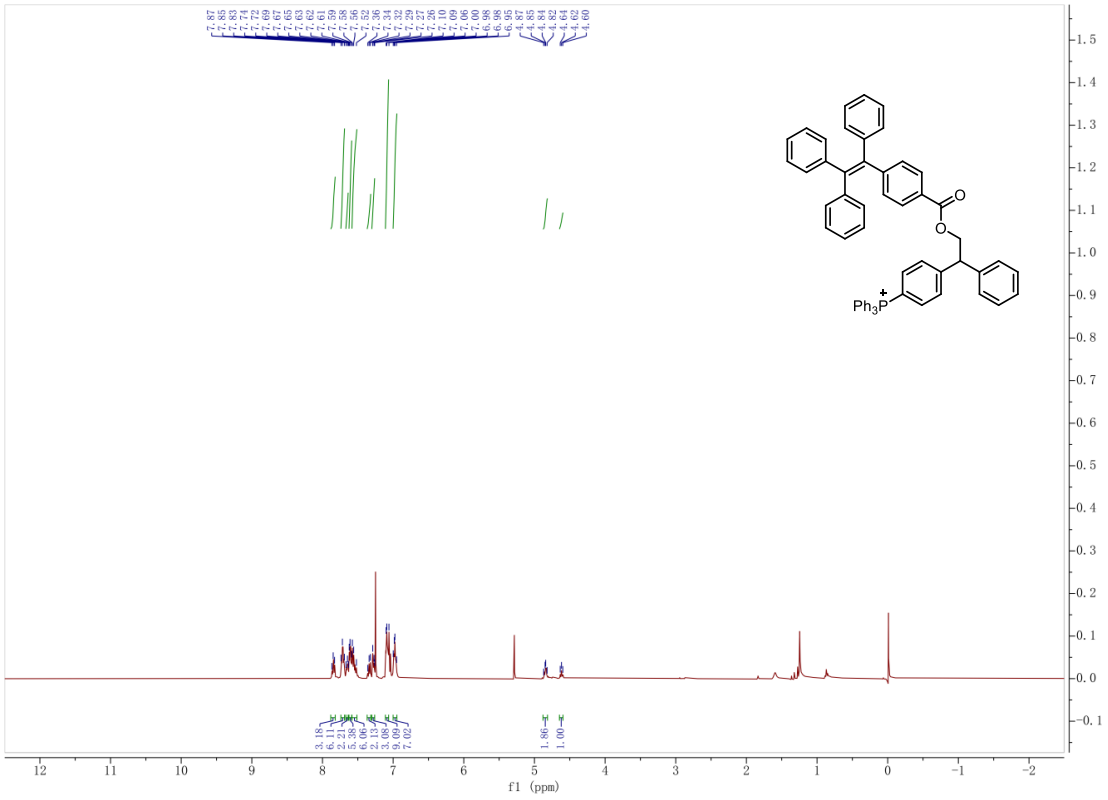
NMR Spectra of **40**

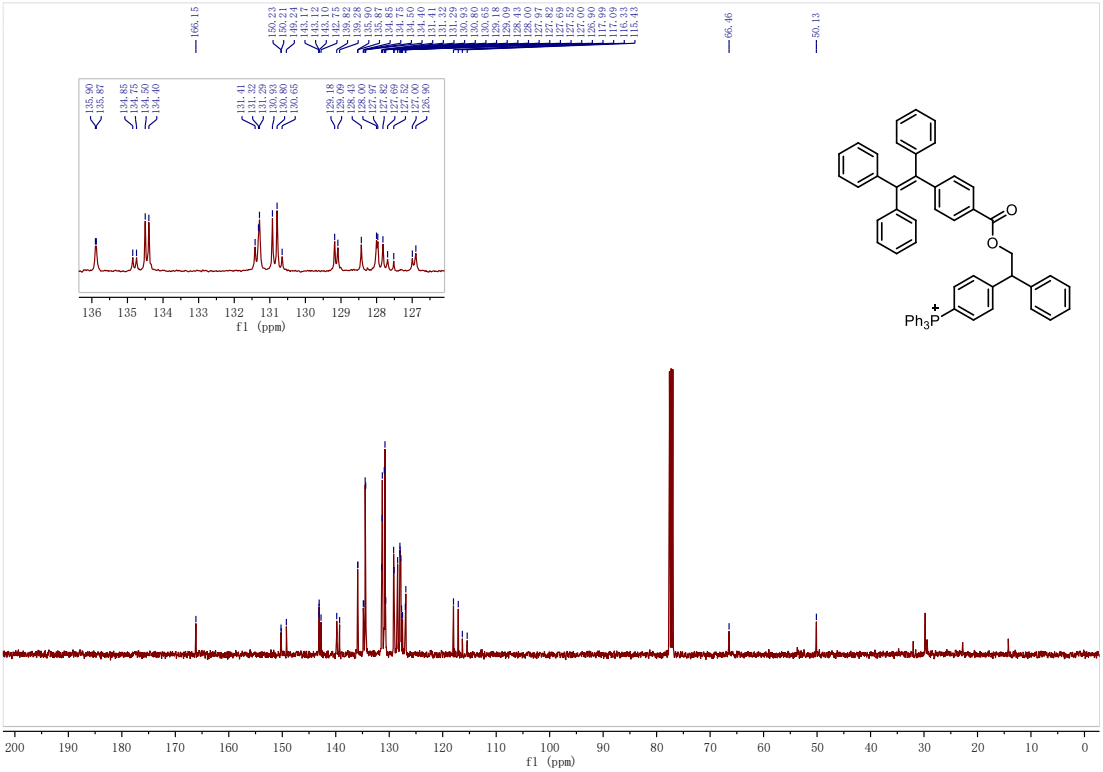


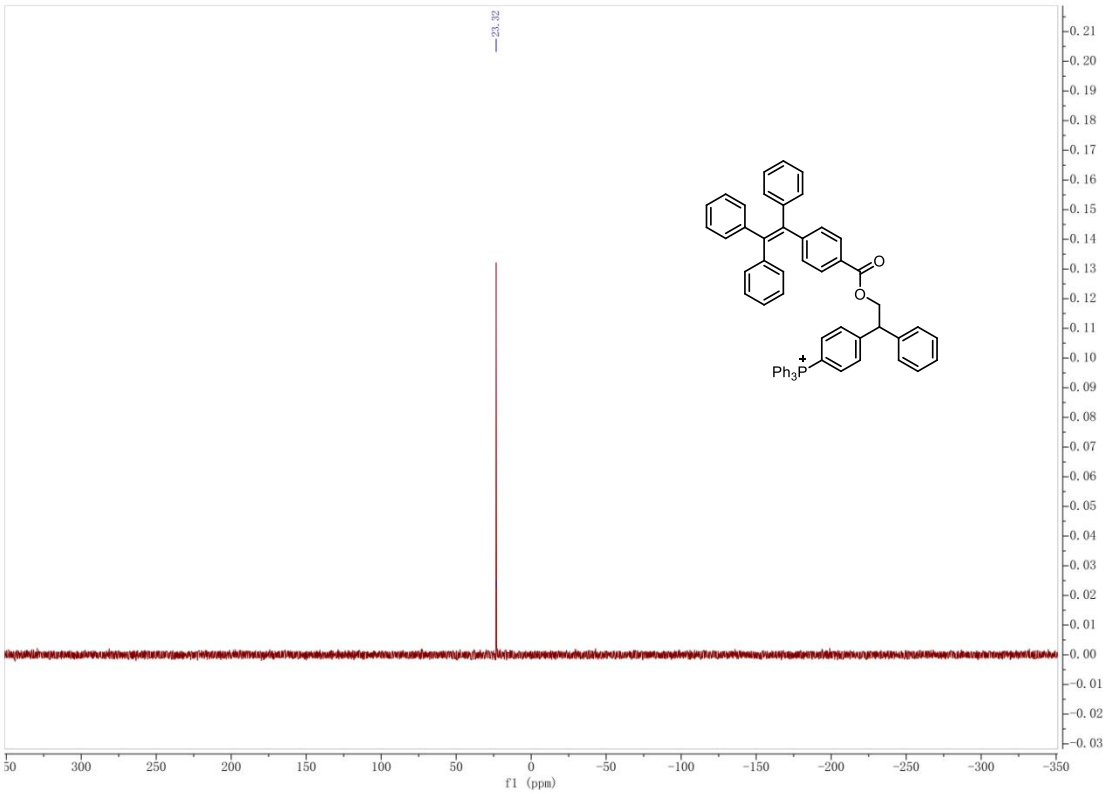

197.68
174.79
174.07
173.39
146.41
142.79
136.62
135.35
134.28
134.17
133.59
133.53
133.49
133.43
132.08
130.68
130.56
129.06
129.01
128.96
128.84
127.70
118.15
117.57
116.87
61.65
60.31
55.72
51.91
40.55
35.47
33.55
29.69
28.03
27.98
27.85
25.23
22.17
21.88
MeO2C
PPh2
HN
NH
S
H
N
O
f1 (ppm)


21.34
MeO2C
PPh2
HN
NH
S
H
N
O
f1 (ppm)

NMR Spectra of **42**







NMR Spectra of Tert-butyl (R)-2-oxo-3-(3-oxopentyl)-3-phenylindoline-1-carboxylate