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Supporting Information

Highly Chemo- and Regioselective C-P Cross-coupling reaction of Quinone Imine Ketals with $Ar_2P(O)H$ to Construct *Ortho*-amino Triarylphosphine Derivatives

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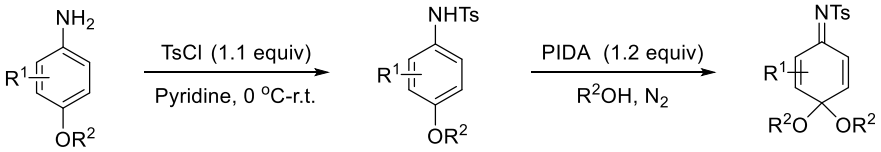
General Information

All compounds were fully characterised by spectroscopic data. The NMR spectra were recorded on a Bruker DRX400. Chemical shifts (δ) are expressed in ppm, J values are given in Hz, and deuterated $CDCl_3$ was used as solvent. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. The melting points were determined on a XT-4A melting point apparatus and are uncorrected. HRMs were performed on an Agilent LC/Msd TOF instrument.

General Procedure for the Preparation raw material 1 and 2

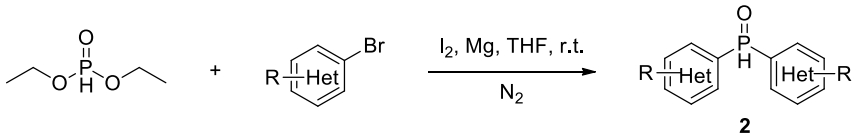


Scheme 1. Synthesis of raw material **1**

To a stirred solution of the corresponding aniline (10 mmol, 1.0 equiv) in pyridine (20 mL) at 0 °C, the corresponding sulfonyl chloride (11 mmol, 1.1 equiv) was added slowly. The reaction mixture was allowed to warm to ambient temperature and was stirred for overnight, monitored by TLC analysis. When the corresponding aniline was completely consumed, then the pyridine was evaporated under reduced pressure. The residue was quenched with EtOAc (10 mL) and 1N HCl (10 mL), then the mixture was extracted with EtOAc (3 x 20 mL) and saturated $NaHCO_3$ (3 x 10 mL). The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding *N*-protected aniline (petroleum ether/EtOAc, 10:1-4:1).

To a solution of the corresponding *N*-protected aniline (2 mmol, 1.0 equiv) in distilled MeOH (20 mL) was added phenyliodoso diacetate (PIDA) (2.4 mmol, 1.2 equiv) under nitrogen atmosphere, and the mixture was stirred at room temperature and monitored by TLC analysis. When the corresponding *N*-protected aniline was completely consumed, The reaction was quenched with saturated $NaHCO_3$ (20 mL) and then extracted with EtOAc (3 × 20 mL). The combined organic layers were

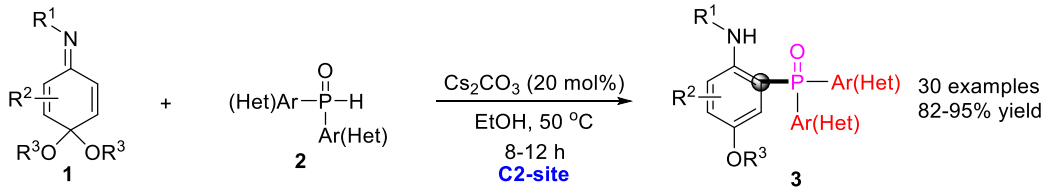
washed with brine (20 mL) and dried with anhydrous Na_2SO_4, then the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding quinine imine ketals **1** (petroleum ether/EtOAc, 15:1-6:1).



Scheme 2. Synthesis of raw material **2**

The mixture of magnesium turnings (3.3 mmol, 3.3 equiv), a piece of iodine and small amount of 1-bromo-4-butylbenzene in THF (20 ml) was vigorously stirred under N_2. The flask was heated until the reaction was initiated (the solution become colorless). A solution of Aryl bromide (30.0 mmol, 3.0 equiv) in THF (30 ml) was added dropwise and stirred for 1 h. The flask was cooled to 0 °C by an ice-bath and diethyl phosphite (1.30 ml, 10.0 mmol, 1.0 equiv) in THF (10 ml) was added over 30 min. After stirring for additional 2 h at room temperature, the reaction was quenched by the addition of 2 M HCl (20 ml) at 0 °C, and stirred for 15 min. The mixture was filtrated through a celite pad, and the filtrate was extracted with EtOAc three times. The combined organic layer was washed with brine and dried over Na_2SO_4. After evaporation, the residue was purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to afford desired product **2**.

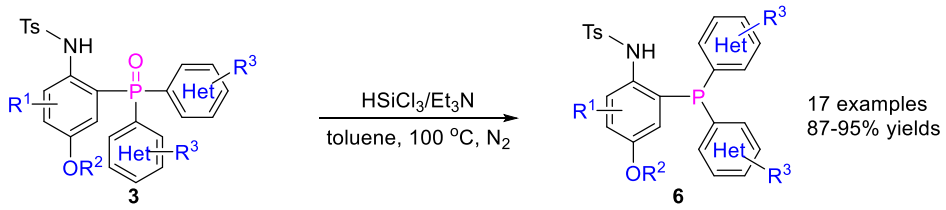
General Procedure for the Preparation of Compound 3 and 6



Scheme 3. Synthesis of compound **3**

A 10 mL round-bottom flask was charged with quinone imine ketals (QIKs) **1** (0.1 mmol), $Ar_2P(O)H$ **2** (0.11 mmol) and C_2CO_3 in EtOH (2 mL), and the solution was stirred for 8–12 h under 40 °C until quinone imine ketals (QIKs) **1** were completely consumed as indicated by TLC. Then, the crude products were condensed under the

reduced pressure. Then, the crude products was purified by flash column chromatography (petroleum ether/EtOAc = 10:1–2:1), afforded the pure products **3** in 82–95% yields.

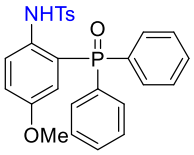


Scheme 4. Synthesis of compound **6**

A 10 mL round-bottom flask was charged with compound **3** (0.05 mmol), $HSiCl_3$ (0.5 mmol) and Et_3N (1.0 mmol) in toluene 2.0 mL under nitrogen atmosphere, and the solution was stirred for 2–6 h under 100 °C until compound **3** were completely consumed as indicated by TLC. Then, NaOH (1.0 mol/L) was added to solution, the solution was extracted with EtOAc (3 x 10 mL). The organic phases were washed with brine, dried by anhydrous Na_2SO_4 and condensed under the reduced pressure to give a residue, which was further purified by flash column chromatography (petroleum ether/EtOAc = 6:1–1:2), afforded the pure products **6** in 87–95% yields.

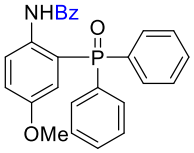
Spectroscopic Data of 3, 6 and 7-10

_N_-(2-(diphenylphosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3aa)



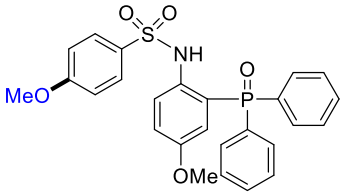
White solid; Mp: 160-162 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.76 (br, 1H, NH), 7.84-7.88 (m, 1H, ArH), 7.51-7.57 (m, 5H, ArH), 7.37-7.44 (m, 7H, ArH), 7.00-7.03 (m, 1H, ArH), 6.87-6.89 (m, 2H, ArH), 6.37-6.41 (m, 1H, ArH), 3.64 (s, 3H, $ArOCH_3$), 2.25 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 154.8, 142.9, 137.0, 136.5, 132.3, 132.0, 131.9, 131.8, 130.9, 129.2, 128.7, 128.6, 127.2, 123.9, 123.8, 118.8, 118.7, 118.0, 55.5, 21.6. HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{24}NO_4PSNa$ [M + Na]$^{+}$, 500.1056, found, 500.1056.

_N_-(2-(diphenylphosphoryl)-4-methoxyphenyl)benzamide (3ab)



White solid; Mp: 160-162 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.65 (br, 1H, NH), 8.71-8.75 (m, 1H, ArH), 8.05-8.07 (m, 2H, ArH), 7.64-7.69 (m, 4H, ArH), 7.43-7.59 (m, 9H, ArH), 7.11-7.14 (m, 1H, ArH), 6.54-6.59 (m, 1H, ArH), 3.71 (s, 3H, $ArOCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2, 154.7, 154.5, 137.8, 134.4, 132.6, 132.5, 132.1, 132.0, 131.7, 131.6, 130.6, 128.9, 128.7, 128.6, 127.4, 124.0, 123.9, 119.8, 118.9, 118.7, 117.6, 55.5. HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{22}NO_3PNa$ [M + Na]$^{+}$, 450.1230, found, 450.1228.

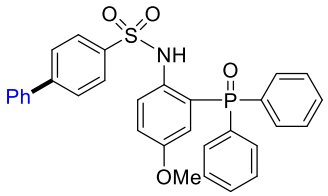
_N_-(2-(diphenylphosphoryl)-4-methoxyphenyl)-4-methoxybenzenesulfonamide (3ac)



White solid; Mp: 158-160 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.72 (br, 1H, NH),

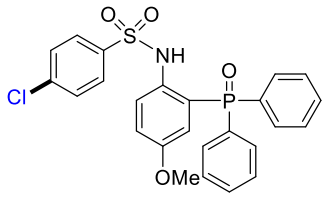
7.85-7.88 (m, 1H, ArH), 7.53-7.57 (m, 4H, ArH), 7.38-7.41 (m, 8H, ArH), 7.00-7.03 (m, 1H, ArH), 6.54-6.56 (m, 2H, ArH), 6.38-6.42 (m, 1H, ArH), 3.74 (s, 3H, $ArOCH_3$), 3.64 (s, 3H, $ArOCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5, 155.0, 154.9, 137.1, 137.0, 131.9, 131.8, 128.7, 128.5, 124.1, 124.0, 118.7, 118.6, 118.0, 113.7, 55.4, 55.3. HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{24}NO_5PSNa$ $[M + Na]^+$, 516.1005, found, 516.1004.

_N_-(2-(diphenylphosphoryl)-4-methoxyphenyl)-[1,1'-biphenyl]-4-sulfonamide (3ad)



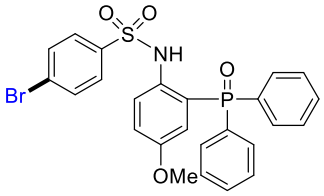
White solid; Mp: 201-203 ºC, ^1H NMR (400 MHz, $CDCl_3$): δ = 10.85 (br, 1H, NH), 7.91-7.94 (m, 1H, ArH), 7.69-7.72 (m, 2H, ArH), 7.31-7.51 (m, 17H, ArH), 7.03-7.06 (m, 1H, ArH), 6.38-6.43 (m, 1H, ArH), 3.65 (s, 3H, $ArOCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.1, 155.0, 144.9, 139.0, 138.0, 136.8, 136.7, 132.5, 132.4, 131.9, 131.8, 131.7, 130.8, 129.0, 128.8, 128.6, 128.4, 127.7, 127.2, 127.0, 124.0, 123.9, 118.9, 118.7, 118.1, 118.0, 55.5. HRMS (ESI-TOF): *m*/*z* calcd for $C_{31}H_{27}NO_4PS$ $[M + H]^+$, 540.1393, found, 540.1393.

4-chloro-_N_-(2-(diphenylphosphoryl)-4-methoxyphenyl)benzenesulfonamide (3ae)



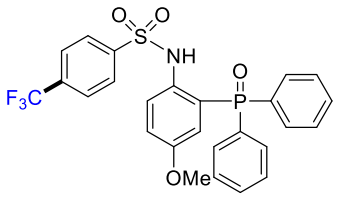
White solid; Mp: 209-211 ºC, ^1H NMR (400 MHz, $CDCl_3$): δ = 10.83 (br, 1H, NH), 7.88-7.91 (m, 1H, ArH), 7.56-7.60 (m, 2H, ArH), 7.51-7.54 (m, 2H, ArH), 7.33-7.43 (m, 8H, ArH), 7.03-7.06 (m, 1H, ArH), 6.97-7.00 (m, 2H, ArH), 6.37-6.42 (m, 1H, ArH), 3.66 (s, 3H, $ArOCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 155.2, 138.8, 137.8, 136.3, 132.6, 132.5, 131.8, 131.7, 130.7, 129.4, 128.8, 128.7, 128.5, 128.0, 124.7, 124.6, 119.9, 119.0, 118.9, 118.1, 118.0, 55.5. HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{22}ClNO_4PS$ $[M + H]^+$, 498.0690, found, 498.0690.

4-bromo-*N*-(2-(diphenylphosphoryl)-4-methoxyphenyl)benzenesulfonamide (3af)



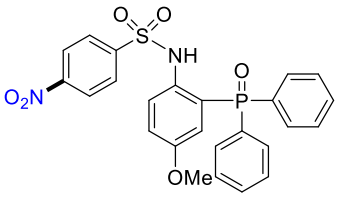
White solid; Mp: 212-214 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.86 (br, 1H, NH), 7.88-7.91 (m, 1H, ArH), 7.57-7.61 (m, 2H, ArH), 7.33-7.46 (m, 10H, ArH), 7.13-7.16 (m, 2H, ArH), 7.03-7.06 (m, 1H, ArH), 6.37-6.42 (m, 1H, ArH), 3.66 (s, 3H, $ArOCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 155.3, 138.3, 136.3, 136.2, 132.6, 132.5, 131.8, 131.7, 131.6, 130.7, 128.9, 128.7, 128.6, 127.5, 124.6, 124.5, 119.9, 119.0, 118.9, 118.8, 118.1, 118.0, 55.5. HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{22}BrNO_4PS$ [M + H]$^{+}$, 542.0185, found, 542.0185.

***N*-(2-(diphenylphosphoryl)-4-methoxyphenyl)-4-(trifluoromethyl)benzenesulfonamide (3ag)**



White solid; Mp: 156-158 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.98 (br, 1H, NH), 7.90-7.94 (m, 1H, ArH), 7.73-7.75 (m, 2H, ArH), 7.53-7.57 (m, 2H, ArH), 7.30-7.42 (m, 10H, ArH), 7.04-7.07 (m, 1H, ArH), 6.38-6.42 (m, 1H, ArH), 3.66 (s, 3H, $ArOCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5, 155.3, 142.9, 136.0, 134.0, 133.7, 132.8, 132.7, 131.7, 131.6, 130.6, 128.8, 128.7, 127.6, 125.6 (q, *J* = 8.0 Hz), 124.5, 124.3, 124.2, 121.8, 119.9, 119.0, 118.9, 118.1, 55.5. HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{21}F_3NO_4PS$ [M + Na]$^{+}$, 554.0773, found, 554.0772.

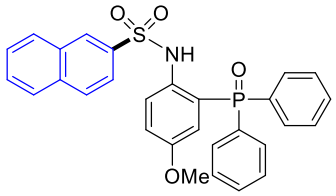
***N*-(2-(diphenylphosphoryl)-4-methoxyphenyl)-4-nitrobenzenesulfonamide (3ah)**



White solid; Mp: 177-179 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.00 (br, 1H, NH), 7.90-7.94 (m, 1H, ArH), 7.69-7.78 (m, 4H, ArH), 7.47-7.52 (m, 2H, ArH), 7.27-7.37

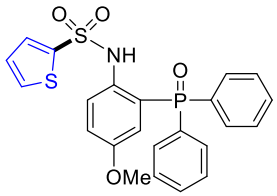
(m, 8H, ArH), 7.06-7.09 (m, 1H, ArH), 6.36-6.40 (m, 1H, ArH), 3.66 (s, 3H, $ArOCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.8, 155.7, 149.6, 144.9, 135.6, 132.7, 132.6, 131.8, 131.6, 131.5, 130.7, 128.8, 128.7, 128.1, 125.7, 125.6, 123.7, 120.3, 119.2, 119.1, 118.2, 118.1, 55.5. HRMS (ESI-TOF): *m/z* calcd for $C_{25}H_{21}N_2O_6PSNa$ $[M + Na]^+$, 531.0750, found, 531.0749.

***N*-(2-(diphenylphosphoryl)-4-methoxyphenyl)naphthalene-2-sulfonamide (3ai)**



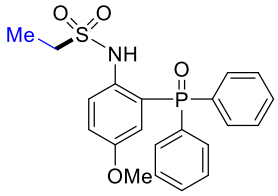
White solid; Mp: 206-208 ºC, ^1H NMR (400 MHz, $CDCl_3$): δ = 10.90 (br, 1H, NH), 8.24 (s, 1H, ArH), 7.94-7.98 (m, 1H, ArH), 7.70-7.85 (m, 4H, ArH), 7.43-7.59 (m, 6H, ArH), 7.16-7.38 (m, 6H, ArH), 7.02-7.06 (m, 1H, ArH), 6.32-6.36 (m, 1H, ArH), 3.62 (s, 3H, $ArOCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 155.0, 136.7, 136.6, 136.5, 134.7, 132.3, 132.2, 131.9, 131.7, 131.6, 131.5, 130.6, 129.4, 128.9, 128.7, 128.5, 128.4, 128.3, 127.9, 127.1, 124.3, 124.2, 122.6, 119.6, 118.8, 118.7, 118.6, 118.1, 118.0, 55.5. HRMS (ESI-TOF): *m/z* calcd for $C_{29}H_{24}NO_4PSNa$ $[M + Na]^+$, 536.1056, found, 536.1055.

***N*-(2-(diphenylphosphoryl)-4-methoxyphenyl)thiophene-2-sulfonamide (3aj)**



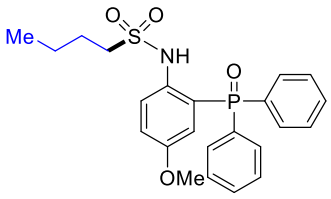
White solid; Mp: 177-179 ºC, ^1H NMR (400 MHz, $CDCl_3$): δ = 10.95 (br, 1H, NH), 7.88-7.91 (m, 1H, ArH), 7.79-7.85 (m, 2H, ArH), 7.53-7.58 (m, 2H, ArH), 7.44-7.48 (m, 3H, ArH), 7.43-7.44 (m, 3H, ArH), 7.30-7.32 (m, 1H, ArH), 7.19-7.20 (m, 1H, ArH), 7.04-7.07 (m, 1H, ArH), 6.64-6.66 (m, 1H, ArH), 6.43-6.47 (m, 1H, ArH), 3.67 (s, 3H, $ArOCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 155.2, 139.8, 136.5, 136.4, 132.5, 132.4, 132.2, 132.1, 132.0, 131.9, 131.8, 131.7, 132.6, 130.8, 128.8, 128.7, 128.6, 128.5, 127.1, 124.0, 123.9, 120.0, 119.0, 118.9, 117.9, 55.5. HRMS (ESI-TOF): *m/z* calcd for $C_{23}H_{21}NO_4PS_2$ $[M + H]^+$, 470.0644, found, 470.0644.

***N*-(2-(diphenylphosphoryl)-4-methoxyphenyl)ethanesulfonamide (3ak)**



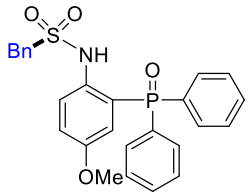
White solid; Mp: 154-156 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.99 (br, 1H, NH), 7.76-7.84 (m, 2H, ArH), 7.60-7.68 (m, 5H, ArH), 7.46-7.54 (m, 4H, ArH), 7.04-7.07 (m, 1H, ArH), 6.51-6.55 (m, 1H, ArH), 3.68 (s, 3H, $ArOCH_3$), 2.77 (q, J = 8.0 Hz, 2H, CH_2), 1.10 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.1, 154.9, 136.7, 136.6, 132.9, 132.8, 132.5, 132.4, 132.2, 132.1, 131.7, 131.6, 131.3, 130.2, 129.0, 128.9, 128.8, 128.7, 128.6, 122.8, 122.7, 119.3, 119.2, 118.2, 118.1, 55.5, 46.6, 7.9. HRMS (ESI-TOF): *m*/*z* calcd for $C_{21}H_{22}NO_4PSNa$ $[M + Na]^+$, 438.0899, found, 438.0899.

***N*-(2-(diphenylphosphoryl)-4-methoxyphenyl)butane-1-sulfonamide (3al)**



White solid; Mp: 132-134 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.10 (br, 1H, NH), 7.76-7.79 (m, 1H, ArH), 7.59-7.68 (m, 6H, ArH), 7.49-7.53 (m, 4H, ArH), 7.04-7.07 (m, 1H, ArH), 6.51-6.56 (m, 1H, ArH), 3.69 (s, 3H, $ArOCH_3$), 1.53-1.61 (m, 2H, ArH), 1.04-1.14 (m, 2H, ArH), 0.72 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.1, 154.9, 136.7, 132.8, 132.1, 132.0, 128.9, 128.8, 123.2, 123.1, 119.2, 119.1, 118.1, 55.6, 51.9, 25.0, 21.4, 13.5. HRMS (ESI-TOF): *m*/*z* calcd for $C_{23}H_{26}NO_4PSNa$ $[M + Na]^+$, 466.1212, found, 466.1212.

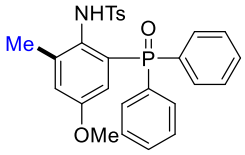
***N*-(2-(diphenylphosphoryl)-4-methoxyphenyl)-1-phenylmethanesulfonamide (3am)**



White solid; Mp: 153-155 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (br, 1H, NH),

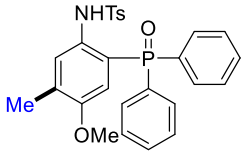
7.79-7.85 (m, 2H, ArH), 7.58-7.69 (m, 5H, ArH), 7.45-7.55 (m, 6H, ArH), 7.20-7.25 (m, 3H, ArH), 6.95-6.98 (m, 1H, ArH), 6.50-6.54 (m, 1H, ArH), 3.99 (s, 2H, $ArCH_2$), 3.68 (s, 3H, $ArOCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 154.8, 136.6, 136.5, 133.0, 132.9, 132.5, 132.4, 132.2, 132.1, 131.7, 131.6, 131.1, 130.8, 130.7, 130.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 122.8, 122.7, 120.0, 119.2, 119.1, 118.1, 118.0, 58.6, 55.6. HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{24}NO_4PSNa$ $[M + Na]^+$, 500.1056, found, 500.1056.

***N*-(2-(diphenylphosphoryl)-4-methoxy-6-methylphenyl)-4-methylbenzenesulfonamide (3an)**



White solid; Mp: 166-168 ºC, ^1H NMR (400 MHz, $CDCl_3$): δ = 10.01 (br, 1H, NH), 7.50-7.54 (m, 4H, ArH), 7.37-7.44 (m, 8H, ArH), 6.95-6.96 (m, 1H, ArH), 6.89-6.91 (m, 2H, ArH), 6.31-6.35 (m, 1H, ArH), 3.67 (s, 3H, $ArOCH_3$), 2.51 (s, 3H, $ArCH_3$), 2.21 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1, 155.9, 142.8, 140.5, 140.4, 137.1, 134.4, 132.5, 132.1, 132.0, 131.9, 131.8, 131.5, 129.0, 128.5, 128.4, 127.5, 124.7, 123.8, 119.8, 117.7, 117.6, 55.4, 21.6, 20.8. HRMS (ESI-TOF): *m*/*z* calcd for $C_{27}H_{26}NO_4PSNa$ $[M + Na]^+$, 514.1212, found, 514.1212.

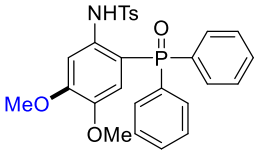
***N*-(2-(diphenylphosphoryl)-4-methoxy-5-methylphenyl)-4-methylbenzenesulfonamide (3o)**



White solid; Mp: 128-130 ºC, ^1H NMR (400 MHz, $CDCl_3$): δ = 10.76 (br, 1H, NH), 7.72-7.74 (m, 1H, ArH), 7.52-7.57 (m, 4H, ArH), 7.36-7.45 (m, 8H, ArH), 6.87 (d, *J* = 8.0 Hz, 2H, ArH), 6.20 (d, *J* = 16.0 Hz, 1H, ArH), 3.47 (s, 3H, $ArOCH_3$), 2.23-2.24 (m, 6H, $ArCH_3$, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 153.4, 142.8, 137.2, 137.1, 136.5, 133.4, 133.3, 132.5, 132.2, 132.1, 131.9, 131.8, 131.6, 131.5, 131.4, 129.2, 129.1, 128.7, 128.6, 128.5, 127.5, 127.2, 125.1, 125.0, 115.4, 114.4, 113.2,

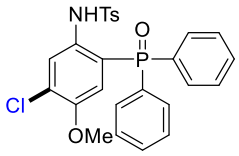
113.0, 55.3, 21.6, 16.7. HRMS (ESI-TOF): *m*/*z* calcd for $C_{27}H_{26}NO_4PSNa$ $[M + Na]^+$, 514.1212, found, 514.1212.

_N_-(2-(diphenylphosphoryl)-4,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (3ap)



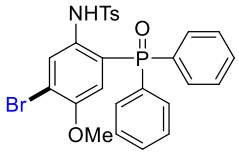
White solid; Mp: 163-165 ^oC, ^1H NMR (400 MHz, $CDCl_3$): δ = 10.93 (br, 1H, NH), 7.80-7.85 (m, 1H, ArH), 7.51-7.58 (m, 5H,ArH), 7.36-7.41 (m, 7H, ArH), 6.88 (d, *J* = 8.0 Hz, 2H, ArH), 6.22-6.26 (m, 1H, ArH), 3.96 (s, 3H, $ArOCH_3$), 3.54 (s, 3H, $ArOCH_3$), 2.26 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.9, 144.9, 144.7, 143.1, 139.2, 139.1, 136.3, 132.5, 132.2, 131.8, 131.7, 131.6, 131.5, 129.2, 128.7, 128.6, 127.2, 114.5, 114.4, 107.9, 106.9, 105.9, 105.8, 56.3, 56.0, 21.6. HRMS (ESI-TOF): *m*/*z* calcd for $C_{27}H_{26}NO_5PSNa$ $[M + Na]^+$, 530.1162, found, 530.1162.

_N_-(5-chloro-2-(diphenylphosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3aq)



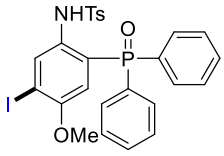
White solid; Mp: 152-154 ^oC, ^1H NMR (400 MHz, $CDCl_3$): δ = 10.84 (br, 1H, NH), 8.00 (d, *J* = 8.0 Hz, 1H, ArH), 7.53-7.61 (m, 4H, ArH), 7.37-7.45 (m, 8H,ArH), 6.90-6.92 (m, 2H, ArH), 6.31 (d, *J* = 16.0 Hz, 1H, ArH), 3.54 (s, 3H, $ArOCH_3$), 2.27 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8, 150.7, 143.3, 137.8, 137.7, 137.5, 136.2, 132.6, 132.5, 131.8, 131.7, 130.7, 129.3, 128.9, 128.7, 128.4, 127.2, 124.2, 124.1, 117.1, 116.1, 115.4, 115.2, 56.2, 21.6. HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{23}ClNO_4PSNa$ $[M + Na]^+$, 534.0666, found, 534.0665.

_N_-(5-bromo-2-(diphenylphosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3ar)



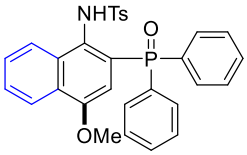
White solid; Mp: 174-176 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.31 (br, 1H, NH), 8.04-8.08 (m, 1H, ArH), 7.46-7.59 (m, 8H, ArH), 7.36-7.40 (m, 4H, ArH), 7.12 (d, *J* = 8.0 Hz, 1H, ArH), 6.93 (d, *J* = 8.0 Hz, 2H, ArH), 3.85 (s, 3H, $ArOCH_3$), 2.30 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 152.6, 143.1, 140.3, 143.2, 136.3, 132.3, 132.2, 132.1, 132.0, 131.6, 130.4, 129.8, 129.3, 128.4, 128.3, 127.5, 126.5, 124.1, 124.0, 119.1, 118.1, 116.1, 116.0, 115.8, 115.7, 56.6, 21.7. HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{23}BrNO_4PSNa$ $[M + Na]^+$, 578.0161, found, 578.0160.

_N_-(2-(diphenylphosphoryl)-5-iodo-4-methoxyphenyl)-4-methylbenzenesulfonamide (3as)



White solid; Mp: 151-153 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.75 (br, 1H, NH), 8.38 (d, *J* = 8.0 Hz, 1H, ArH), 7.53-7.59 (m, 4H, ArH), 7.37-7.44 (m, 8H, ArH), 6.90 (d, *J* = 8.0 Hz, 2H, ArH), 6.16 (d, *J* = 16.0 Hz, 1H, ArH), 3.51 (s, 3H, $ArOCH_3$), 2.26 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.0, 153.8, 143.2, 138.0, 137.9, 136.2, 133.5, 133.4, 132.6, 132.5, 131.9, 131.8, 130.6, 129.3, 128.8, 128.7, 127.2, 118.9, 117.9, 113.4, 113.3, 93.1, 93.0, 56.4, 21.6. HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{23}INO_4PSNa$ $[M + Na]^+$, 626.0022, found, 626.0022.

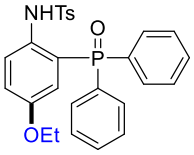
_N_-(2-(diphenylphosphoryl)-4-methoxynaphthalen-1-yl)-4-methylbenzenesulfonamide (3at)



White solid; Mp: 151-153 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.68 (br, 1H, NH), 8.70-8.73 (m, 1H, ArH), 8.18-8.21 (m, 1H, ArH), 7.61-7.66 (m, 2H, ArH), 7.35-7.54 (m, 12H, ArH), 6.80-6.82 (m, 2H, ArH), 6.18-6.22 (m, 1H, ArH), 3.68 (s, 3H, $ArOCH_3$), 2.16 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 152.6, 143.0,

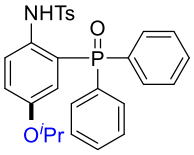
132.1, 132.0, 131.9, 131.8, 130.0, 128.5, 128.4, 128.1, 127.7, 126.9, 121.3, 118.1, 117.1, 104.9, 104.8, 55.5, 21.7. HRMS (ESI-TOF): *m*/*z* calcd for $C_{30}H_{26}NO_4PSNa$ [M + Na]$^+$, 550.1212, found, 550.1212.

***N*-(2-(diphenylphosphoryl)-4-ethoxyphenyl)-4-methylbenzenesulfonamide (3au)**



White solid; Mp: 150-152 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.77 (br, 1H, NH), 7.83-7.87 (m, 1H, ArH), 7.51-7.57 (m, 4H, ArH), 7.37-7.43 (m, 8H, ArH), 6.99-7.02 (m, 1H, ArH), 6.86-6.88 (m, 2H, ArH), 6.36-6.41 (m, 1H, ArH), 3.84 (q, *J* = 8.0 Hz, 2H, CH_2), 2.24 (s, 3H, $ArCH_3$), 1.30 (t, *J* = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 154.3, 142.9, 136.8, 136.7, 136.4, 132.3, 132.2, 132.0, 131.9, 131.8, 131.0, 129.2, 128.7, 128.6, 127.2, 124.0, 123.9, 119.3, 119.1, 119.0, 118.7, 118.6, 118.3, 63.8, 21.6, 14.6. HRMS (ESI-TOF): *m*/*z* calcd for $C_{27}H_{26}NO_4PSNa$ [M + Na]$^+$, 514.1212, found, 514.1211.

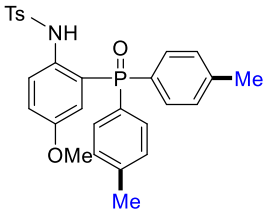
***N*-(2-(diphenylphosphoryl)-4-isopropoxyphenyl)-4-methylbenzenesulfonamide (3av)**



3av

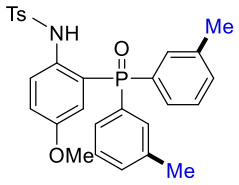
White solid; Mp: 177-179 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.74 (br, 1H, NH), 7.81-7.87 (m, 4H, ArH), 7.51-7.57 (m, 4H, ArH), 7.38-7.44 (m, 8H, ArH), 6.98-7.02 (m, 1H, ArH), 6.86-6.89 (m, 2H, ArH), 6.33-6.37 (m, 1H, ArH), 4.24-4.30 (m, 1H, CH), 2.25 (s, 3H, $ArCH_3$), 1.19 (s, 3H, CH_3), 1.17 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3, 153.1, 142.9, 136.7, 136.5, 132.3, 132.2, 132.0, 131.9, 131.8, 131.0, 129.2, 128.7, 128.6, 127.2, 123.9, 123.8, 120.4, 120.3, 120.2, 70.5, 21.8, 21.6. HRMS (ESI-TOF): *m*/*z* calcd for $C_{28}H_{28}NO_4PSNa$ [M + Na]$^+$, 528.1369, found, 528.1367.

***N*-(2-(di-p-tolylphosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3ba)**



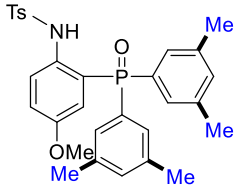
White solid; Mp: 194-196 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.84 (br, 1H, NH), 7.82-7.86 (m, 1H, ArH), 7.53-7.55 (m, 2H, ArH), 7.25-7.32 (m, 5H, ArH), 7.18-7.20 (m, 3H, ArH), 6.97-7.00 (m, 1H, ArH), 6.88-6.90 (m, 2H, ArH), 6.37-6.41 (m, 1H, ArH), 3.64 (s, 3H, $ArOCH_3$), 2.41 (s, 3H, $2ArCH_3$), 2.26 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 154.8, 142.9, 142.8, 136.8, 136.5, 131.9, 131.8, 129.4, 129.3, 129.1, 127.3, 123.7, 118.9, 117.7, 55.5, 21.7, 21.6. HRMS (ESI-TOF): *m*/*z* calcd for $C_{28}H_{28}NO_4PSNa$ $[M + Na]^+$, 528.1369, found, 528.1368.

***N*-(2-(di-m-tolylphosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3bb)**



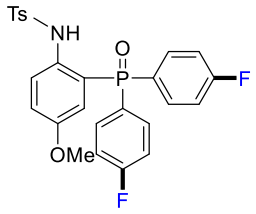
White solid; Mp: 173-175 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.81 (br, 1H, NH), 7.82-7.87 (m, 1H, ArH), 7.52-7.54 (m, 2H, ArH), 7.23-7.35 (m, 6H, ArH), 7.08-7.13 (m, 2H, ArH), 6.99-7.02 (m, 1H, ArH), 6.87-6.89 (m, 2H, ArH), 6.38-6.43 (m, 1H, ArH), 3.65 (s, 3H, $ArOCH_3$), 2.33 (s, 3H, $2ArCH_3$), 2.24 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 154.8, 142.8, 138.6, 138.5, 136.9, 136.8, 136.6, 133.1, 132.3, 132.2, 131.9, 130.9, 129.7, 129.1, 129.0, 128.9, 128.5, 128.3, 127.2, 126.5, 123.6, 123.5, 119.7, 119.0, 118.9, 118.7, 117.8, 55.5, 21.5, 21.4. HRMS (ESI-TOF): *m*/*z* calcd for $C_{28}H_{28}NO_4PSNa$ $[M + Na]^+$, 528.1369, found, 528.1368.

***N*-(2-(bis(3,5-dimethylphenyl)phosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3bc)**



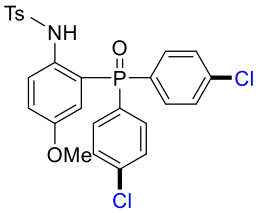
White solid; Mp: 154-156 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.85 (br, 1H, NH), 7.82-7.86 (m, 1H, ArH), 7.58-7.59 (m, 1H, ArH), 7.52-7.54 (m, 2H, ArH), 7.15 (s, 2H, ArH), 6.99-7.02 (m, 5H, ArH), 6.88-6.90 (m, 2H, ArH), 6.40-6.44 (m, 1H, ArH), 3.66 (s, 3H, $ArOCH_3$), 2.28 (s, 12H, $4ArCH_3$), 2.24 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 154.6, 142.6, 138.3, 138.2, 138.1, 136.7, 136.6, 133.5, 134.1, 134.0, 131.8, 130.7, 129.7, 129.5, 129.4, 129.3, 129.2, 128.9, 127.3, 127.2, 126.5, 123.3, 123.2, 119.9, 119.2, 119.1, 118.9, 117.5, 117.4, 115.8, 111.3, 109.2, 55.5, 21.5, 21.3. HRMS (ESI-TOF): *m*/*z* calcd for $C_{30}H_{32}NO_4PSNa$ $[M + Na]^+$, 556.1682, found, 556.1680.

***N*-(2-(bis(4-fluorophenyl)phosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3bd)**



White solid; Mp: 132-134 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.54 (br, 1H, NH), 7.88-7.91 (m, 1H, ArH), 7.49-7.51 (m, 2H, ArH), 7.35-7.42 (m, 4H, ArH), 7.03-7.12 (m, 5H, ArH), 6.90-6.92 (m, 2H, ArH), 6.31-6.35 (m, 1H, ArH), 3.67 (s, 3H, $ArOCH_3$), 2.28 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6 (d, J = 3.0 Hz), 166.5 (d, J = 4.0 Hz), 164.1, 164.0, 155.2, 155.0, 143.2, 136.8, 136.7, 136.5, 134.5, 134.4, 134.3, 134.2, 129.1, 127.1, 119.3, 118.7, 118.6, 118.3, 118.2, 118.1, 116.4, 116.2, 116.1, 116.0, 55.5, 21.4. HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{22}F_2NO_4PSNa$ $[M + Na]^+$, 536.0867, found, 536.0867.

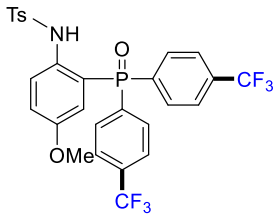
***N*-(2-(bis(4-chlorophenyl)phosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3be)**



White solid; Mp: 185-187 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.46 (br, 1H, NH),

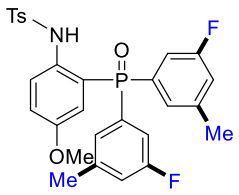
7.90-7.93 (m, 1H, ArH), 7.46-7.48 (m, 2H, ArH), 7.36-7.39 (m, 4H, ArH), 7.27-7.32 (m, 4H, ArH), 7.04-7.07 (m, 1H, ArH), 6.88-6.90 (m, 2H, ArH), 6.30-6.34 (m, 1H, ArH), 3.67 (s, 3H, $ArOCH_3$), 2.30 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 155.1, 143.4, 139.4, 139.3, 136.8, 136.7, 136.5, 133.2, 133.0, 130.2, 129.2, 129.1, 129.0, 127.1, 124.6, 124.5, 118.9, 118.7, 118.6, 118.2, 117.9, 55.5, 21.6. HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{22}Cl_2NO_4PSNa$ $[M + Na]^+$, 568.0276, found, 568.0276.

***N*-(2-(bis(4-(trifluoromethyl)phenyl)phosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3bf)**



White solid; Mp: 185-187 °C, ^1H NMR (400 MHz, DMSO-d_6): δ = 10.09 (br, 1H, NH), 7.90-7.92 (m, 4H, ArH), 7.70-7.75 (m, 4H, ArH), 7.49-7.51 (m, 2H, ArH), 7.38-7.41 (m, 1H, ArH), 7.31-7.35 (m, 3H, ArH), 7.08-7.12 (m, 1H, ArH), 3.50 (s, 3H, $ArOCH_3$), 2.31 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 157.7, 157.6, 143.7, 138.0, 137.0, 136.6, 132.7, 132.6, 131.6, 131.5, 130.1, 129.2, 127.7, 127.6, 127.2, 126.0, 125.9 (q, J = 8.0 Hz), 125.8, 125.6, 122.9, 119.5, 118.5, 113.8, 113.7, 56.1, 21.4. HRMS (ESI-TOF): *m*/*z* calcd for $C_{28}H_{22}F_6NO_4PSNa$ $[M + Na]^+$, 636.0804, found, 636.0804.

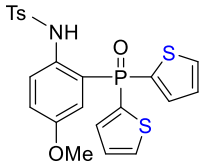
***N*-(2-(bis(3-fluoro-5-methylphenyl)phosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3bg)**



White solid; Mp: 185-187 °C, ^1H NMR (400 MHz, $CDCl_3$): δ = 9.32 (br, 1H, NH), 7.69-7.76 (m, 2H, ArH), 7.47-7.49 (m, 2H, ArH), 7.35-7.39 (m, 2H, ArH), 6.98-7.09 (m, 6H, ArH), 6.82-6.85 (m, 1H, ArH), 3.54 (s, 3H, $ArOCH_3$), 2.36 (s, 3H, $2ArCH_3$),

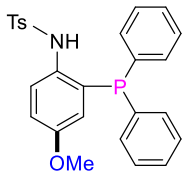
2.32 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5 (d, J = 19.0 Hz), 163.3, 161.0 (d, J = 19.0 Hz), 160.8, 157.0, 143.3, 141.2, 141.1, 141.0, 140.9, 136.5, 134.7, 134.6, 133.7, 133.6, 132.0, 131.9, 129.4, 128.5, 128.4, 128.3, 128.1, 128.0, 127.2, 127.1, 119.8, 119.6, 119.5, 118.5, 115.8, 115.7, 115.6, 115.5, 112.2, 112.2, 55.4, 21.5, 21.4. HRMS (ESI-TOF): m/z calcd for $C_{28}H_{26}F_2NO_4PSNa$ $[M + Na]^+$, 564.1180, found, 564.1180.

***N*-(2-(di(thiophen-2-yl)phosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3bh)**



White solid; Mp: 185-187 ^oC, ^1H NMR (400 MHz, $CDCl_3$): δ = 10.60 (br, 1H, NH), 7.84-7.88 (m, 1H, ArH), 7.72-7.75 (m, 2H, ArH), 7.58-7.60 (m, 2H, ArH), 7.27-7.29 (m, 2H, ArH), 7.03-7.14 (m, 3H, ArH), 6.95-6.97 (m, 2H, ArH), 6.58-6.63 (m, 1H, ArH), 3.67 (s, 3H, $ArOCH_3$), 2.27 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 155.1, 143.1, 137.5, 137.3, 136.4, 136.3, 136.2, 134.8, 134.7, 133.9, 132.7, 129.2, 128.5, 128.3, 127.3, 124.1, 124.0, 120.3, 119.2, 118.9, 117.9, 117.7, 55.5, 21.6. HRMS (ESI-TOF): m/z calcd for $C_{22}H_{20}NO_4PS_3Na$ $[M + Na]^+$, 512.0184, found, 512.0184.

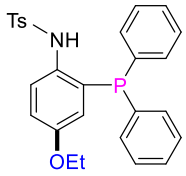
***N*-(2-(diphenylphosphanyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6a)**



White solid; Mp: 101-103 ^oC， ^1H NMR (400 MHz, $CDCl_3$): δ = 7.67-7.70 (m, 1H, ArH), 7.48-7.50 (m, 2H,ArH), 7.23-7.41 (m, 7H,ArH), 6.97-7.01 (m, 6H, ArH), 6.88-6.91 (m, 1H,ArH), 6.35 (br,1H, NH), 3.59 (s, 3H, $ArOCH_3$), 2.30 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 143.4, 135.8, 134.7, 134.6, 133.9, 133.6, 133.4, 133.2, 130.3, 130.2, 129.3, 129.0, 128.7, 128.6, 127.4, 124.4, 120.0, 115.7, 55.3, 21.6; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -24.2; HRMS (ESI-TOF): m/z calcd for

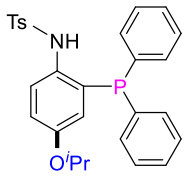
$C_{26}H_{24}NO_3PSNa$ $[M + Na]^+$, 484.1107, found, 484.1108.

***N*-(2-(diphenylphosphanyl)-4-ethoxyphenyl)-4-methylbenzenesulfonamide (6b)**



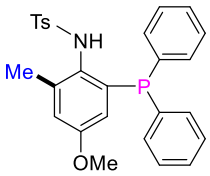
White solid; Mp: 134-136 ^oC, ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.69 (m, 1H, ArH), 7.47-7.55 (m, 2H, ArH), 7.38-7.42 (m, 1H, ArH), 7.29-7.34 (m, 2H, ArH), 7.23-7.27 (m, 5H, ArH), 6.96-7.02 (m, 5H, ArH), 6.86-6.90 (m, 1H, ArH), 6.34-6.36 (m, 1H, ArH), 3.75-3.81 (m, 2H, ArH), 2.30 (s, 3H, $ArCH_3$), 1.27 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4, 143.4, 135.8, 134.7, 134.6, 133.4, 133.2, 129.3, 129.0, 128.7, 128.6, 127.4, 124.4, 120.3, 116.5, 63.5, 21.6, 14.6; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -24.3; HRMS (ESI-TOF): *m/z* calcd for $C_{27}H_{26}NO_3PSNa$ $[M + Na]^+$, 498.1263, found, 498.1260.

***N*-(2-(diphenylphosphanyl)-4-isopropoxyphenyl)-4-methylbenzenesulfonamide (6c)**



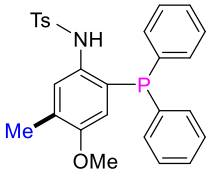
White solid; Mp: 134-136 ^oC, ^1H NMR (400 MHz, $CDCl_3$): δ = 7.64-7.69 (m, 1H, ArH), 7.48-7.52 (m, 2H, ArH), 7.38-7.43 (m, 1H, ArH), 7.30-7.34 (m, 2H, ArH), 7.23-7.27 (m, 5H, ArH), 6.96-7.01 (m, 6H, ArH), 6.86-6.90 (m, 1H, ArH), 6.30-6.36 (m, 1H, ArH), 4.17-4.23 (m, 1H, ArH), 2.30 (s, 3H, $ArCH_3$), 1.15 (s, 3H, CH_3), 1.13 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 143.4, 135.8, 134.8, 134.7, 133.7, 133.5, 133.4, 133.3, 133.2, 133.1, 129.9, 129.8, 129.3, 129.0, 128.9, 128.7, 128.6, 127.4, 124.5, 124.4, 121.4, 120.4, 118.4, 116.5, 70.1, 21.7, 21.6; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -24.4; HRMS (ESI-TOF): *m/z* calcd for $C_{28}H_{28}NO_3PSNa$ $[M + Na]^+$, 512.1420, found, 512.1421.

***N*-(2-(diphenylphosphanyl)-4-methoxy-6-methylphenyl)-4-methylbenzenesulfonamide (6d)**



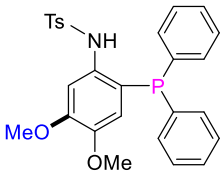
White solid; Mp: 134-136 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.61 (m, 2H, ArH), 7.24-7.33 (m, 7H, ArH), 7.18-7.20 (m, 2H, ArH), 6.94-6.98 (m, 4H, ArH), 6.78-6.79 (m, 1H, ArH), 6.11-6.13 (m, 2H, ArH), 3.60 (s, 3H, $ArOCH_3$), 2.46 (s, 3H, $ArCH_3$), 2.40 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 143.4, 140.8, 140.7, 138.9, 138.8, 137.3, 137.2, 135.8, 135.7, 133.8, 133.6, 130.2, 130.0, 129.2, 129.0, 128.7, 128.6, 128.0, 127.9, 117.7, 116.9, 55.1, 21.7, 21.3; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -15.7; HRMS (ESI-TOF): *m/z* calcd for $C_{27}H_{26}NO_3PSNa$ $[M + Na]^+$, 498.1263, found, 498.1263.

***N*-(2-(diphenylphosphanyl)-4-methoxy-5-methylphenyl)-4-methylbenzenesulfonamide (6e)**



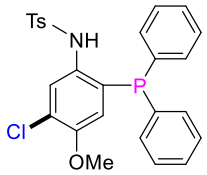
White solid; Mp: 175-177 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.57 (m, 1H, ArH), 7.47-7.50 (m, 2H, ArH), 7.28-7.32 (m, 2H, ArH), 7.22-7.26 (m, 5H, ArH), 6.96-7.04 (m, 6H, ArH), 6.22-6.23 (m, 1H, ArH), 3.43 (s, 3H, $ArOCH_3$), 2.28 (s, 3H, $ArCH_3$), 2.22 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 143.4, 135.8, 135.4, 135.3, 134.1, 133.8, 133.2, 133.0, 130.2, 129.4, 129.3, 128.8, 128.6, 128.5, 127.4, 125.9, 125.8, 125.5, 125.4, 115.3, 55.2, 21.6, 16.4; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -25.1; HRMS (ESI-TOF): *m/z* calcd for $C_{27}H_{26}NO_3PSNa$ $[M + Na]^+$, 498.1263, found, 498.1263.

***N*-(2-(diphenylphosphanyl)-4,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (6f)**



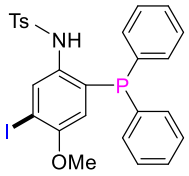
White solid; Mp: 142-144 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.0 Hz, 1H, ArH), 7.48-7.50 (m, 2H, ArH), 7.38-7.39 (m, 1H, ArH), 7.28-7.32 (m, 2H, ArH), 7.21-7.26 (m, 4H, ArH), 6.94-6.98 (m, 6H, ArH), 6.31 (d, J = 4.0 Hz, 1H, ArH), 3.95 (s, 3H, $ArOCH_3$), 3.50 (s, 3H, $ArOCH_3$), 2.27 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.0, 146.7, 143.6, 135.8, 135.5, 135.4, 133.0, 132.8, 132.2, 131.8, 131.7, 129.4, 129.2, 128.7, 128.6, 128.5, 127.3, 127.2, 117.9, 117.8, 116.5, 106.1, 56.2, 55.7, 21.6. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -27.2; HRMS (ESI-TOF): m/z calcd for $C_{27}H_{26}NO_4PSNa$ $[M + Na]^+$, 514.1212, found, 514.1215.

_N_-(5-chloro-2-(diphenylphosphanyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6g)



White solid; Mp: 132-134 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.0 Hz, 1H, ArH), 7.50-7.52 (m, 2H, ArH), 7.32-7.36 (m, 2H, ArH), 7.25-7.30 (m, 5H, ArH), 6.97-7.02 (m, 6H, ArH), 6.30-6.31 (m, 1H, ArH), 3.49 (s, 3H, $ArOCH_3$), 2.31 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 143.7, 135.5, 134.4, 134.3, 134.2, 133.2, 132.1, 129.4, 129.2, 128.8, 128.7, 127.9, 127.8, 127.4, 125.1, 124.5, 124.4, 117.2, 55.9, 21.6. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -24.7; HRMS (ESI-TOF): m/z calcd for $C_{26}H_{23}ClNO_3PSNa$ $[M + Na]^+$, 518.0717, found, 518.0716.

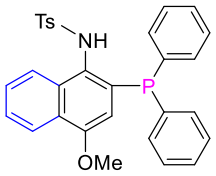
_N_-(2-(diphenylphosphanyl)-5-iodo-4-methoxyphenyl)-4-methylbenzenesulfonamide (6h)



White solid; Mp: 145-147 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67-7.71 (m, 1H, ArH), 7.48-7.50 (m, 2H, ArH), 7.37-7.42 (m, 2H, ArH), 7.30-7.32 (m, 2H, ArH), 7.23-7.26 (m, 2H, ArH), 6.97-7.01 (m, 6H, ArH), 6.88-6.91 (m, 1H, ArH), 6.33-6.35 (m, 1H, ArH), 3.60 (s, 3H, $ArOCH_3$), 2.31 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz,

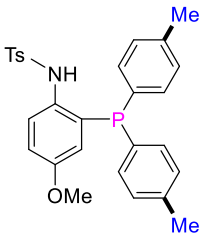
$CDCl_3$): δ = 157.0, 143.4, 135.8, 134.7, 134.6, 133.6, 133.4, 133.2, 131.9, 131.8, 129.3, 129.0, 128.7, 127.6, 128.5, 127.4, 127.2, 124.4, 120.0, 115.7, 55.3, 21.6. ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -24.2; HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{23}INO_3PSNa$ $[M + Na]^+$, 610.0073, found, 610.0073.

***N*-(2-(diphenylphosphanyl)-4-methoxynaphthalen-1-yl)-4-methylbenzenesulfonamide (6i)**



White solid; Mp: 120-122 °C, ^1H NMR (400 MHz, $CDCl_3$): δ = 8.39-8.41 (m, 1H, ArH), 8.17-8.20 (m, 1H, ArH), 7.51-7.57 (m, 5H, ArH), 7.37-7.41 (m, 1H, ArH), 7.28-7.33 (m, 4H, ArH), 7.09-7.11 (m, 2H, ArH), 7.00-7.04 (m, 4H, ArH), 6.80-6.82 (m, 1H, ArH), 6.21-6.22 (m, 1H, ArH), 3.61 (s, 3H, $ArOCH_3$), 2.33 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 143.5, 136.1, 136.0, 133.5, 133.3, 129.2, 128.8, 128.6, 128.5, 128.2, 127.1, 126.8, 125.9, 121.6, 107.3, 55.3, 21.6; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -16.8; HRMS (ESI-TOF): *m*/*z* calcd for $C_{30}H_{26}NO_3PSNa$ $[M + Na]^+$, 534.1263, found, 534.1263.

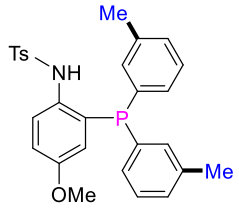
***N*-(2-(di-p-tolylphosphanyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6j)**



White solid; Mp: 125-127 °C, ^1H NMR (400 MHz, $CDCl_3$): δ = 7.64-7.68 (m, 1H, ArH), 7.48-7.50 (m, 2H, ArH), 7.33-7.35 (m, 1H, ArH), 7.06-7.07 (m, 4H, ArH), 6.99-7.01 (m, 2H, ArH), 6.86-6.90 (m, 5H, ArH), 6.35-6.36 (m, 1H, ArH), 3.61 (s, 3H, $ArOCH_3$), 2.33 (s, 6H, $2ArCH_3$), 2.31 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 143.4, 139.1, 135.8, 133.6, 133.5, 133.4, 133.3, 131.2, 131.1, 131.0, 130.9, 129.5, 129.4, 129.2, 127.4, 124.3, 124.2, 120.0, 115.2, 55.3, 21.6, 21.4; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -25.6; HRMS (ESI-TOF): *m*/*z* calcd for $C_{28}H_{28}NO_3PSNa$ [M

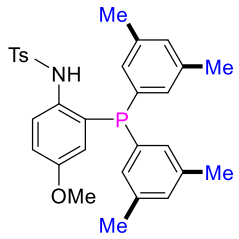
+ Na]$^+$, 512.1420, found, 512.1420.

***N*-(2-(di-m-tolylphosphanyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6k)**



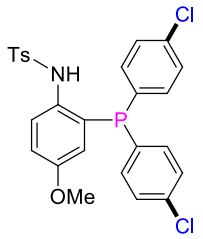
White solid; Mp: 145-147 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.69 (m, 1H, ArH), 7.49-7.51 (m, 2H, ArH), 7.35-7.37 (m, 1H, ArH), 7.11-7.16 (m, 4H, ArH), 7.00-7.03 (m, 2H, ArH), 6.87-6.90 (m, 1H, ArH), 6.83-6.86 (m, 2H, ArH), 6.73-6.78 (m, 2H, ArH), 6.34-6.36 (m, 1H, ArH), 3.61 (s, 3H, $ArOCH_3$), 2.31 (s, 3H, $ArCH_3$), 2.26 (s, 6H, $2ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 143.0, 138.3, 138.2, 135.9, 134.4, 134.3, 134.2, 134.0, 133.7, 133.4, 130.6, 130.5, 130.3, 129.9, 129.3, 128.6, 128.5, 127.5, 124.3, 124.2, 120.1, 115.4, 55.3, 21.6, 21.5; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -24.0; HRMS (ESI-TOF): *m*/*z* calcd for $C_{28}H_{28}NO_3PSNa$ [M + Na]$^+$, 512.1420, found, 512.1420.

***N*-(2-(bis(3,5-dimethylphenyl)phosphanyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6l)**



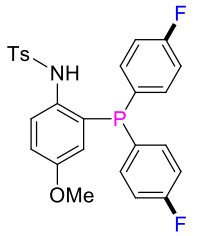
White solid; Mp: 166-168 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63-7.67 (m, 1H, ArH), 7.49-7.51 (m, 3H, ArH), 7.01-7.04 (m, 3H, ArH), 6.94 (m, 3H, ArH), 6.85-6.89 (m, 1H, ArH), 6.61-6.63 (m, 2H, ArH), 6.35-6.38 (m, 2H, ArH), 3.63 (s, 3H, $ArOCH_3$), 2.21 (s, 3H, $5ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 156.2, 143.2, 143.1, 138.1, 138.0, 137.9, 135.9, 134.1, 134.0, 133.5, 133.3, 131.2, 131.0, 130.9, 130.8, 129.1, 127.5, 127.4, 124.1, 120.4, 120.1, 116.0, 115.1, 55.3, 21.5, 21.3; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -23.5; HRMS (ESI-TOF): *m*/*z* calcd for $C_{30}H_{32}NO_3PSNa$ [M + Na]$^+$, 540.1733, found, 540.1733.

***N*-(2-(bis(4-chlorophenyl)phosphino)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6m)**



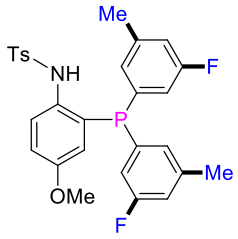
White solid; Mp: 160-162 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71-7.74 (m, 1H, ArH), 7.43-7.45 (m, 2H, ArH), 7.32-7.34 (m, 1H, ArH), 7.21-7.24 (m, 4H, ArH), 6.86-6.98 (m, 7H, ArH), 6.30 (t, J = 4.0 Hz, 1H, ArH), 3.64 (s, 3H, $ArOCH_3$), 2.32 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 143.8, 135.8, 135.7, 134.6, 134.4, 133.9, 133.7, 132.9, 132.8, 129.3, 129.1, 129.0, 127.2, 124.8, 124.7, 120.1, 115.9, 55.4, 21.6; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -26.3; HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{22}Cl_2NO_3PSNa$ $[M + Na]^+$, 552.0327, found, 552.0326.

***N*-(2-(bis(4-fluorophenyl)phosphino)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6n)**



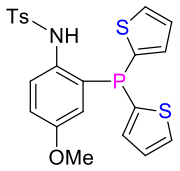
White solid; Mp: 146-148 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69-7.72 (m, 1H, ArH), 7.45-7.47 (m, 2H, ArH), 7.26-7.30 (m, 2H, ArH), 6.91-7.01 (m, 10H, ArH), 6.29 (m, 1H, ArH), 3.63 (s, 3H, $ArOCH_3$), 2.32 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8 (d, J = 249.0 Hz), 162.3, 157.1, 143.6, 135.9, 135.4, 134.3, 135.2, 135.1, 133.7, 133.4, 129.9, 129.3, 127.3, 124.7, 123.2, 119.9, 116.2, 116.1, 116.0, 115.9, 115.7, 55.3, 21.5; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -26.4; HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{22}F_2NO_3PSNa$ $[M + Na]^+$, 520.0918, found, 520.0918.

***N*-(2-(bis(3-fluoro-5-methylphenyl)phosphino)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6o)**



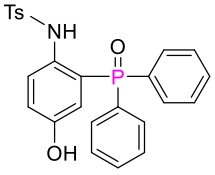
White solid; Mp: 177-179 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.43 (m, 2H, ArH), 7.25-7.27 (m, 1H, ArH), 7.19-7.21 (m, 2H, ArH), 6.81-6.87 (m, 5H, ArH), ArH), 6.31-6.35 (m, 2H, ArH), 6.25 (m, 1H, ArH), 5.99 (t, J = 8.0 H, 1H, ArH), 3.71 (s, 3H, $ArOCH_3$), 2.35 (s, 3H, $ArCH_3$), 2.31 (s, 3H, $2ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0 (d, J = 7.0 Hz), 163.9, 161.5 (d, J = 6.0 Hz), 161.4, 159.4, 159.2, 143.9, 140.7, 140.6, 140.6, 140.5, 138.0, 137.9, 137.8, 135.3, 130.7, 130.6, 130.4, 130.3, 129.6, 129.4, 128.8, 127.3, 127.1, 125.9, 125.7, 125.5, 117.0, 116.8, 116.7, 116.6, 116.5, 111.0, 56.1, 21.4, 21.3; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -16.6; HRMS (ESI-TOF): m/z calcd for $C_{28}H_{26}F_2NO_3PSNa$ $[M + Na]^+$, 548.1231, found, 548.1231.

***N*-(2-(di(thiophen-2-yl)phosphino)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6p)**



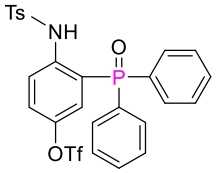
White solid; Mp: 165-167 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.58 (m, 3H, ArH), 7.50-7.52 (m, 2H, ArH), 7.04-7.10 (m, 6H, ArH), 6.86-6.90 (m, 2H, ArH), 6.63-6.65 (m, 1H, ArH), 3.67 (s, 3H, $ArOCH_3$), 2.35 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 143.6, 136.2, 136.0, 135.9, 135.8, 135.6, 132.9, 132.8, 132.6, 132.1, 131.9, 129.4, 128.4, 128.3, 127.4, 127.3, 126.0, 118.4, 115.8, 55.3, 21.6; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -47.9; HRMS (ESI-TOF): m/z calcd for $C_{22}H_{20}NO_3PS_3Na$ $[M + Na]^+$, 496.0235, found, 496.0235.

***N*-(2-(diphenylphosphoryl)-4-hydroxyphenyl)-4-methylbenzenesulfonamide (7)**



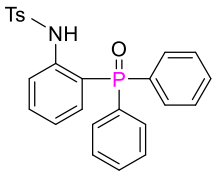
White solid; Mp: 179-181 ^{o}C, ^{1}H NMR (400 MHz, CDOD): δ = 7.73-7.76 (m, 1H, ArH), 7.61-7.66 (m, 2H, ArH), 7.44-7.51 (m, 4H, ArH), 7.32-7.39 (m, 6H, ArH), 6.97-7.01 (m, 1H, ArH), 6.88-6.90 (m, 2H, ArH), 6.32-6.36 (m, 1H, ArH), 2.24 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, CDOD): δ = 153.7, 153.6, 143.6, 135.8, 135.0, 134.9, 132.6, 132.5, 131.5, 131.4, 131.3, 130.3, 129.1, 128.8, 128.6, 126.7, 124.1, 124.0, 120.6, 119.1, 119.0, 118.7, 117.7, 20.2; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 39.1; HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{22}NO_4PSNa$ $[M + Na]^+$, 486.0899, found, 486.0899.

3-(diphenylphosphoryl)-4-((4-methylphenyl)sulfonamido)phenyltrifluoromethanesulfonate (8)



White solid; Mp: 163-165 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.19 (br, 1H, NH), 7.91-7.95 (m, 1H, ArH), 7.58-7.63 (m, 4H, ArH), 7.43-7.48 (m, 8H, ArH), 7.31-7.34 (m, 1H, ArH), 6.99-7.01 (m, 2H, ArH), 6.74-6.79 (m, 1H, ArH), 2.31 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 143.9, 143.8, 143.7, 136.2, 133.0, 132.9, 131.9, 131.8, 130.7, 129.6, 129.5, 129.1, 128.9, 127.1, 126.1, 125.9, 125.8, 123.3, 122.4, 122.3, 120.1, 120.0, 119.0, 117.0 (q, *J* = 319.0 Hz), 113.8, 21.6; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 35.9; F^{19} NMR (376 MHz, $CDCl_3$): δ = -72.5; HRMS (ESI-TOF): *m*/*z* calcd for $C_{26}H_{21}F_3NO_6PS_2Na$ $[M + Na]^+$, 618.0392, found, 618.0392.

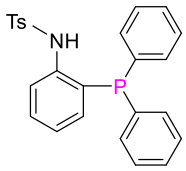
***N*-(2-(diphenylphosphoryl)phenyl)-4-methylbenzenesulfonamide (9)**



White solid; Mp > 400 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.13 (br, 1H, NH), 7.85-7.89 (m, 1H, ArH), 7.54-7.60 (m, 4H, ArH), 7.39-7.47 (m, 9H, ArH), 6.87-7.00 (m, 4H, ArH), 2.27 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 143.1, 136.6, 133.4, 133.3, 133.2, 133.1, 132.4, 132.3, 132.1, 132.0, 131.9, 131.0, 129.3,

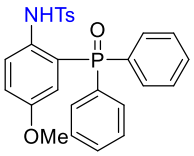
128.7, 128.6, 127.2, 122.9, 122.8, 121.1, 121.0, 117.6, 116.6, 21.6; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 37.1; HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{22}NO_3PSNa$ [M + Na]$^+$, 470.0950, found, 470.0950.

***N*-(2-(diphenylphosphanyl)phenyl)-4-methylbenzenesulfonamide (10)**



White solid; Mp: 140-141 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83-7.85 (m, 1H, ArH), 7.55-7.60 (m, 1H, ArH), 7.47-7.51 (m, 2H, ArH), 7.41-7.46 (m, 1H, ArH), 7.31-7.36 (m, 3H, ArH), 7.28-7.29 (m, 1H, ArH), 7.24-7.25 (m, 1H, ArH), 6.93-7.05 (m, 7H, ArH), 6.85-6.89 (m, 1H, ArH), 2.29 (s, 3H, $ArCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 143.5, 135.8, 135.1, 134.5, 133.4, 133.2, 132.0, 131.9, 130.8, 129.4, 129.3, 128.9, 128.7, 128.6, 127.2, 127.1, 125.1, 121.0, 21.6; ^{31}P NMR ($CDCl_3$, 160 MHz): δ = -26.6; HRMS (ESI-TOF): *m*/*z* calcd for $C_{25}H_{22}NO_2PSNa$ [M + Na]$^+$, 454.1001, found, 454.1001.

Copies of ^{1}H and ^{13}C spectra of 3, 6 and 7-10



3aa

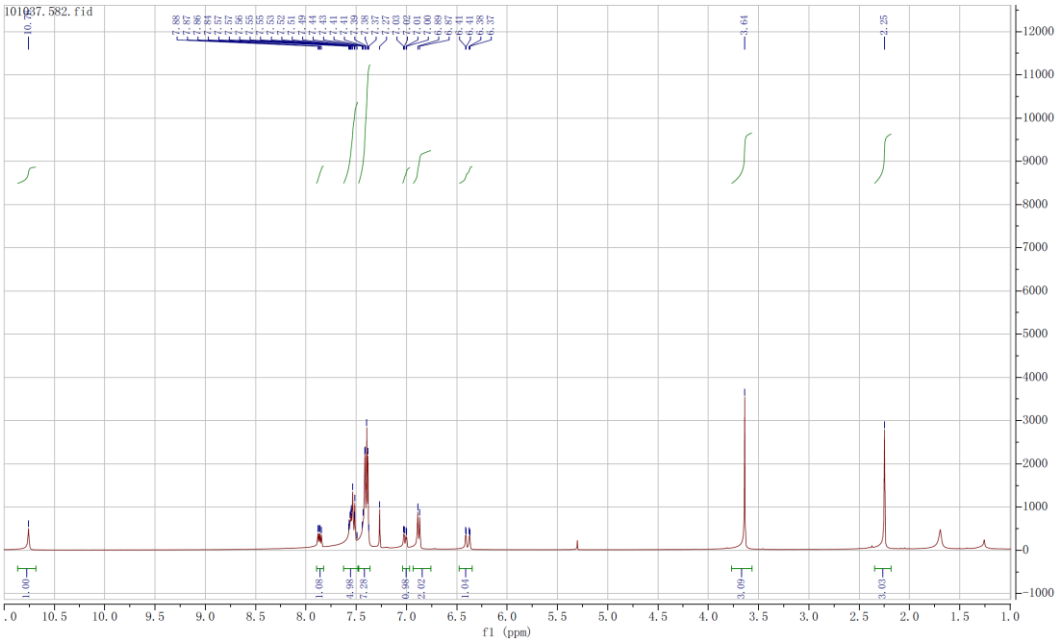


Figure S1. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3aa**

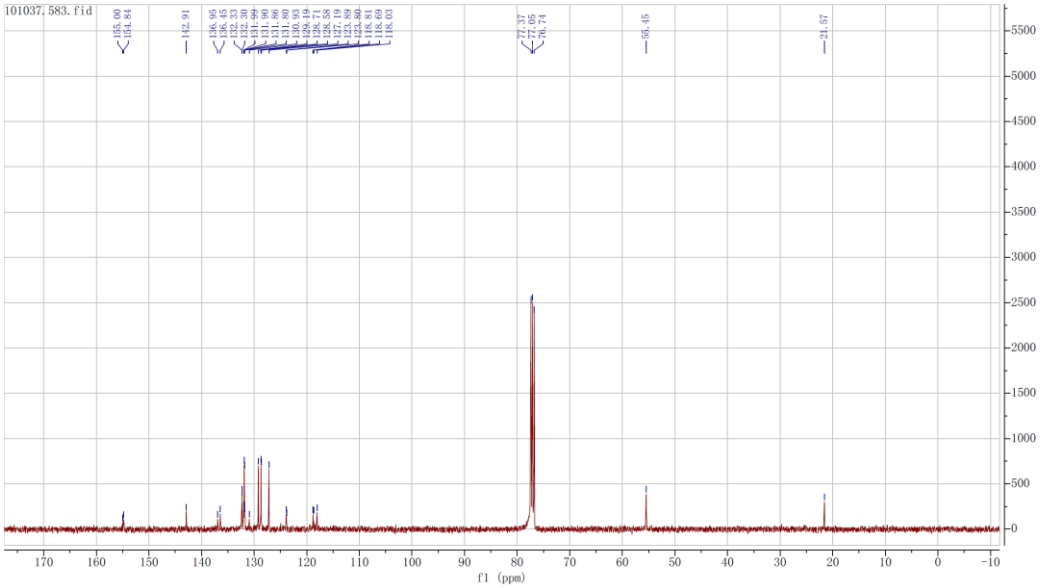


Figure S2. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3aa**

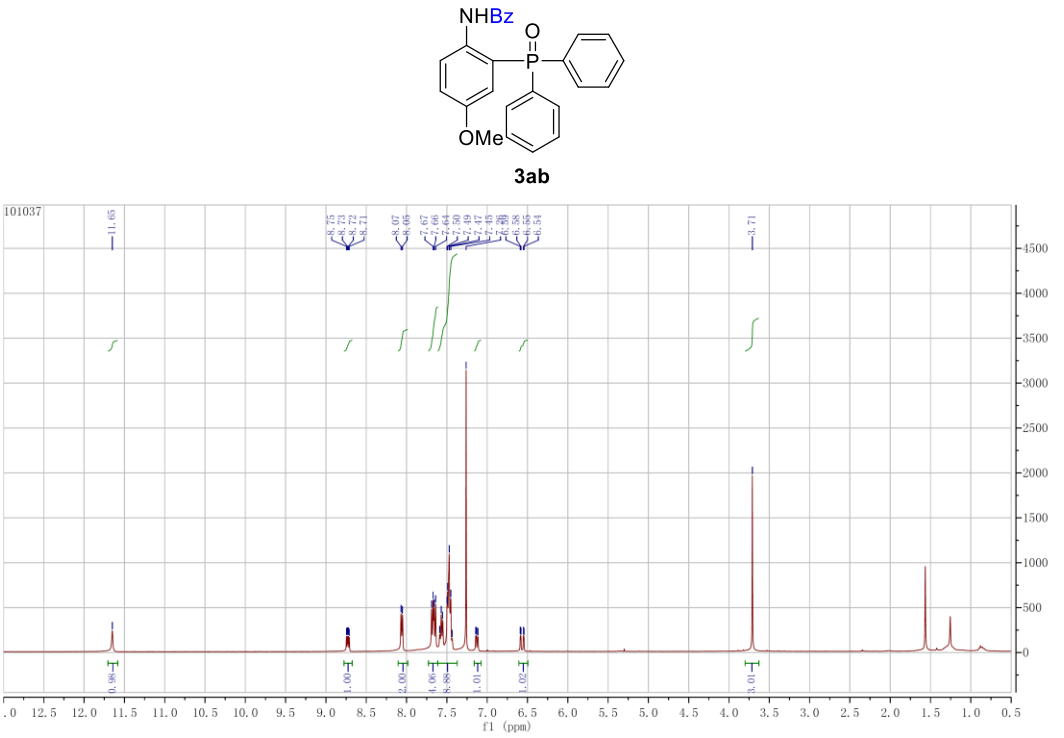


Figure S3. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3ab**

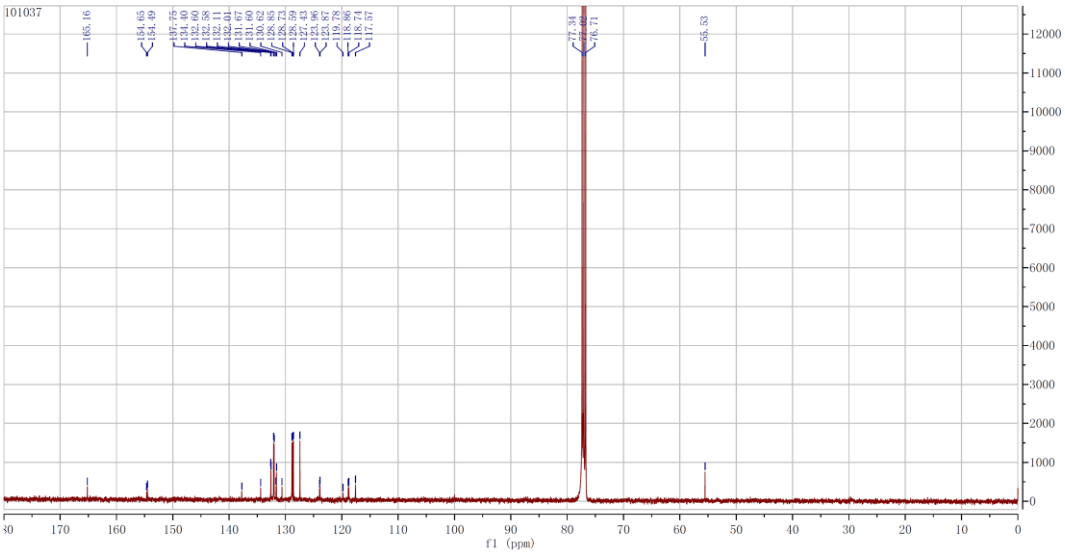
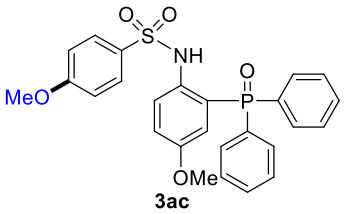


Figure S4. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3ab**



3ac

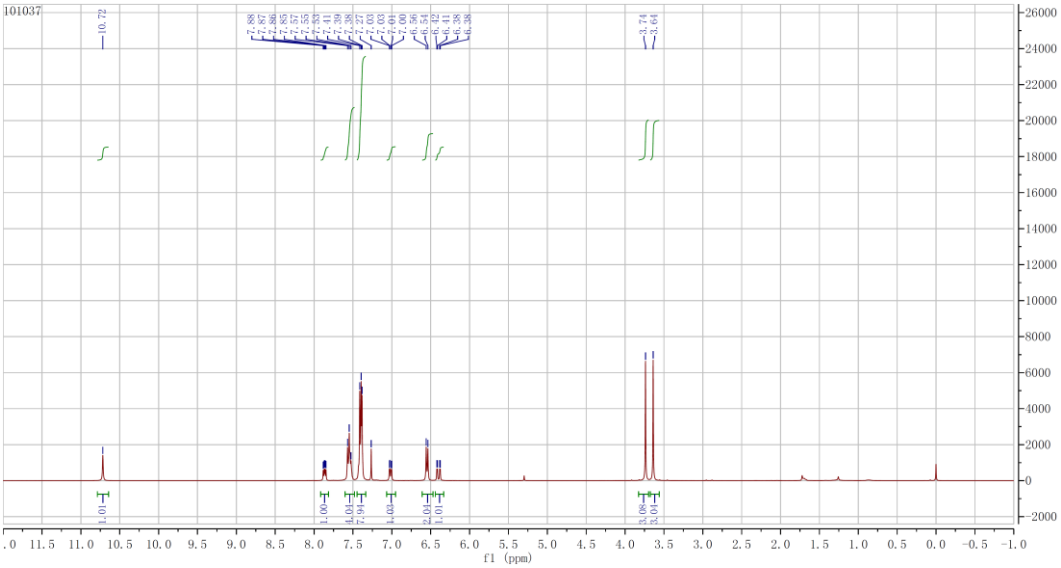


Figure S5. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3ac**

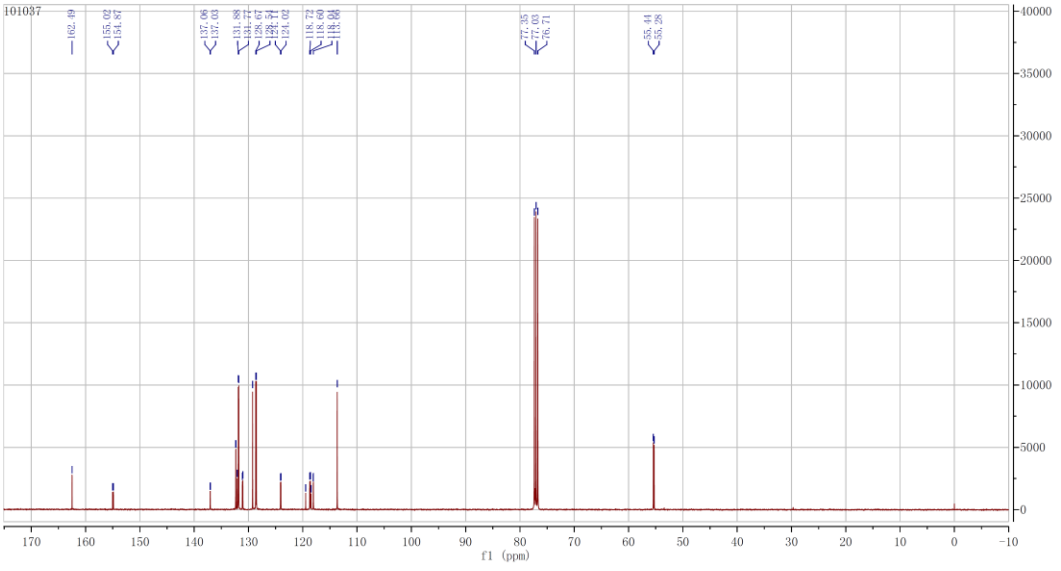
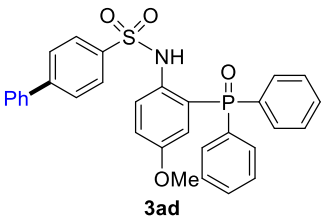


Figure S6. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3ac**



3ad

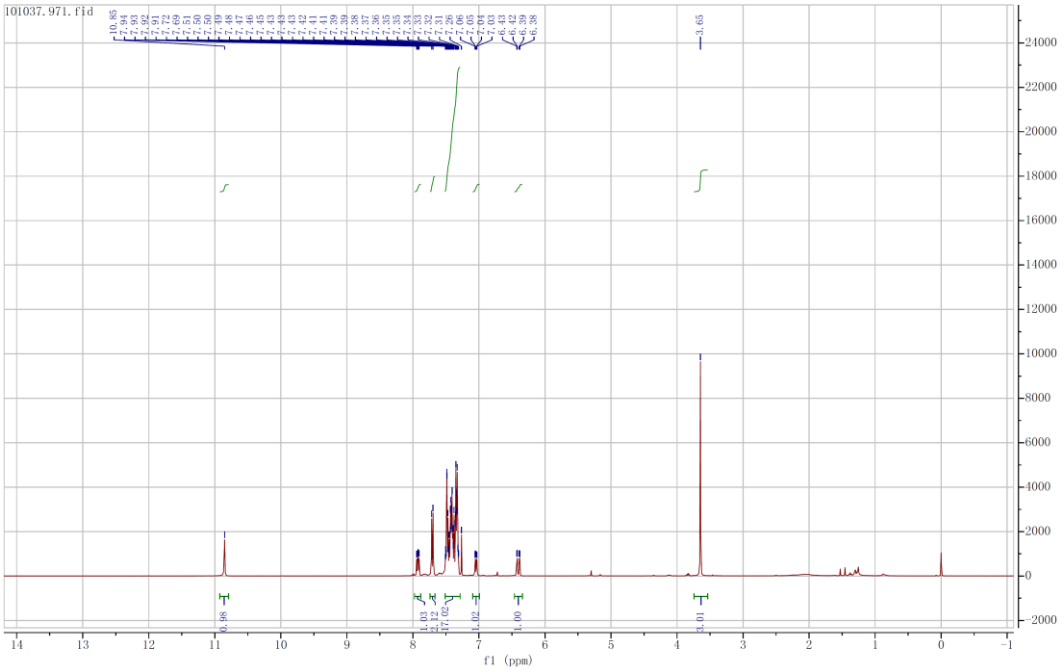


Figure S7. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3ad**

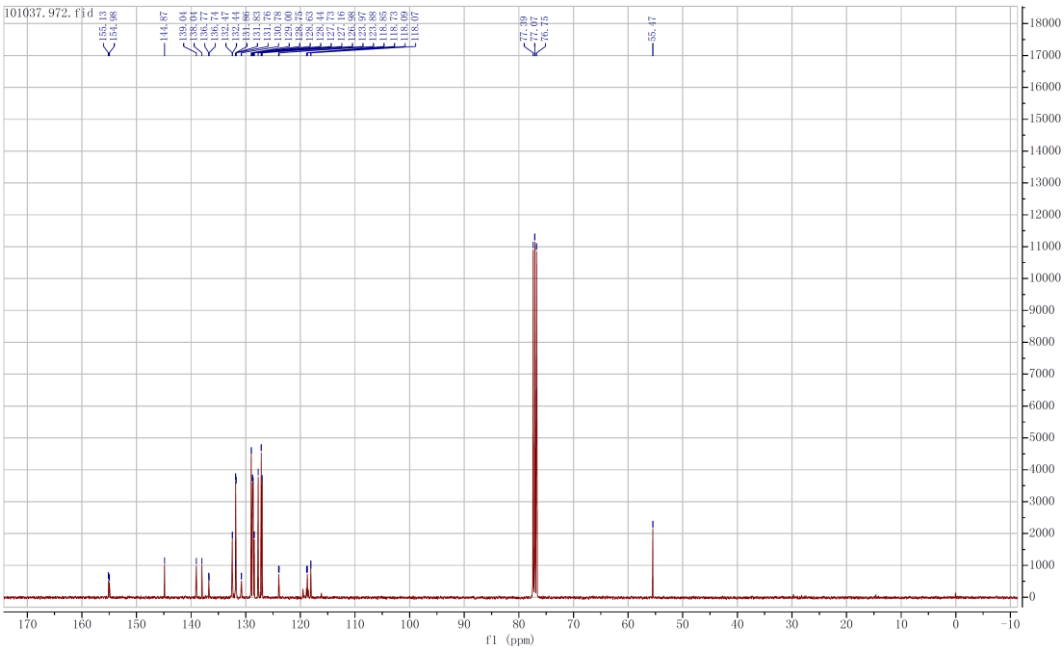
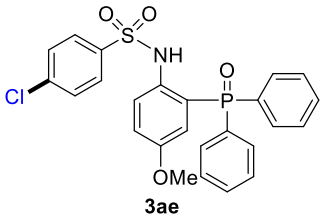


Figure S8. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3ad**



3ae

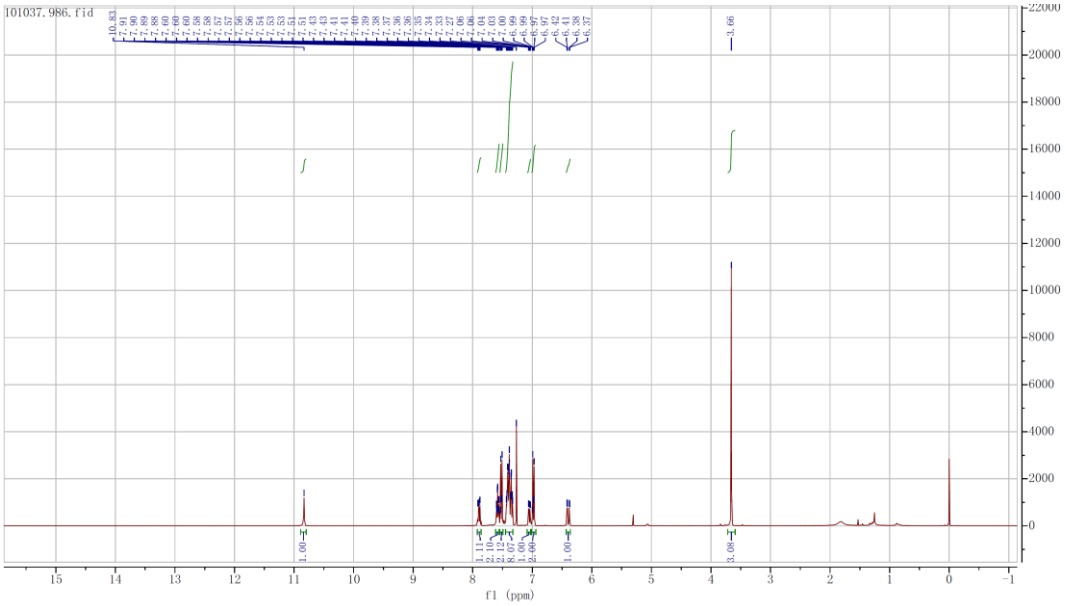


Figure S9. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3ae**

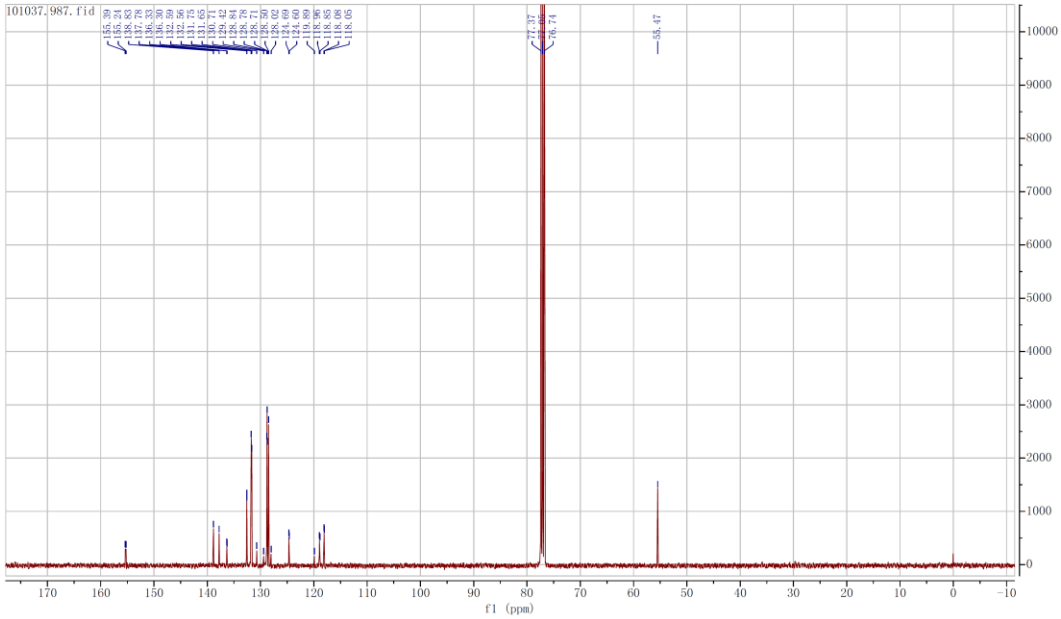
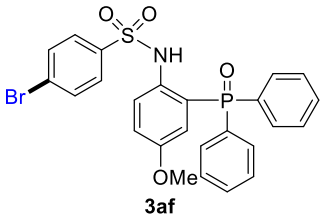


Figure S10. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3ae**



3af

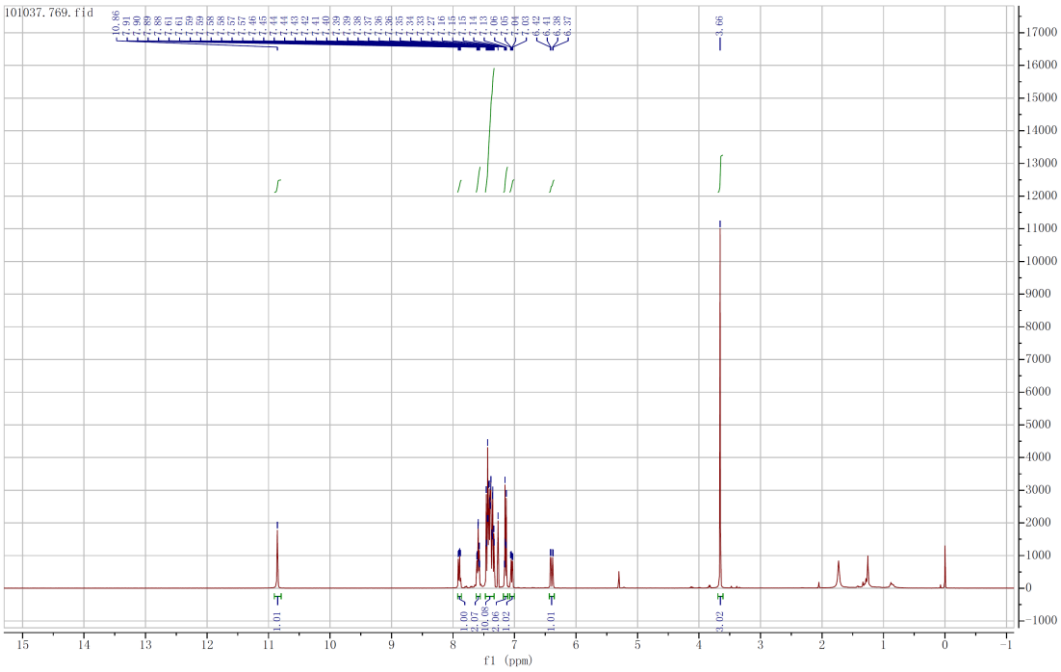


Figure S11. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3af**

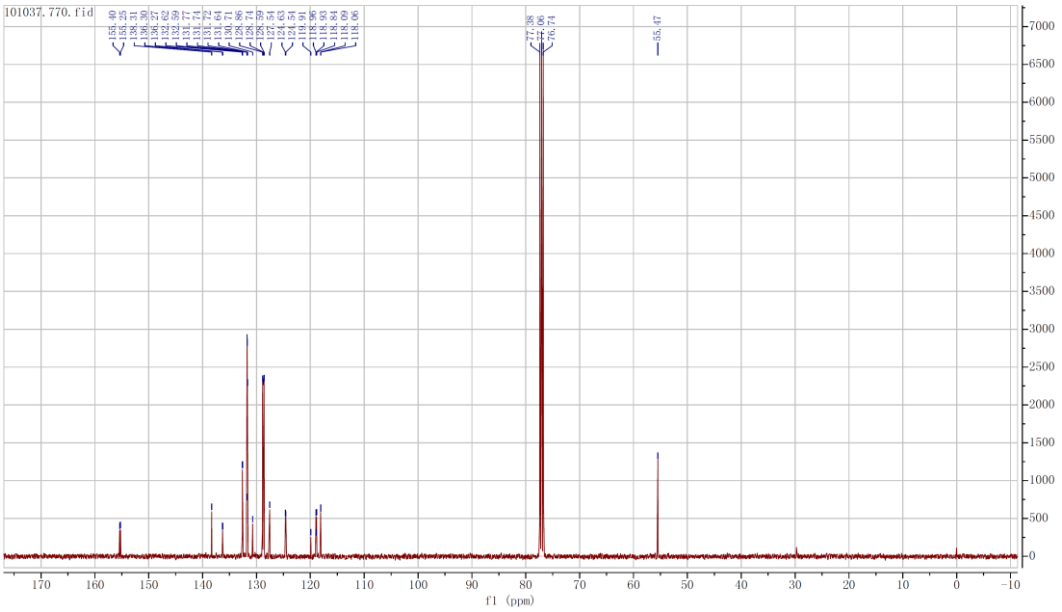
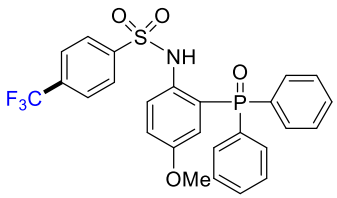


Figure S12. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3af**



3ag

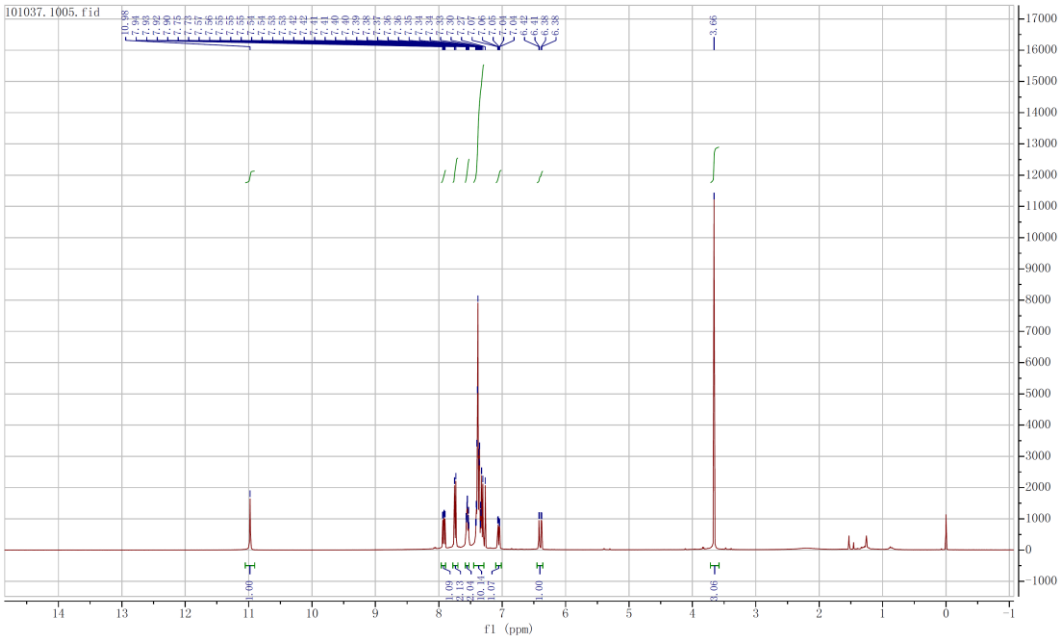


Figure S13. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3ag**

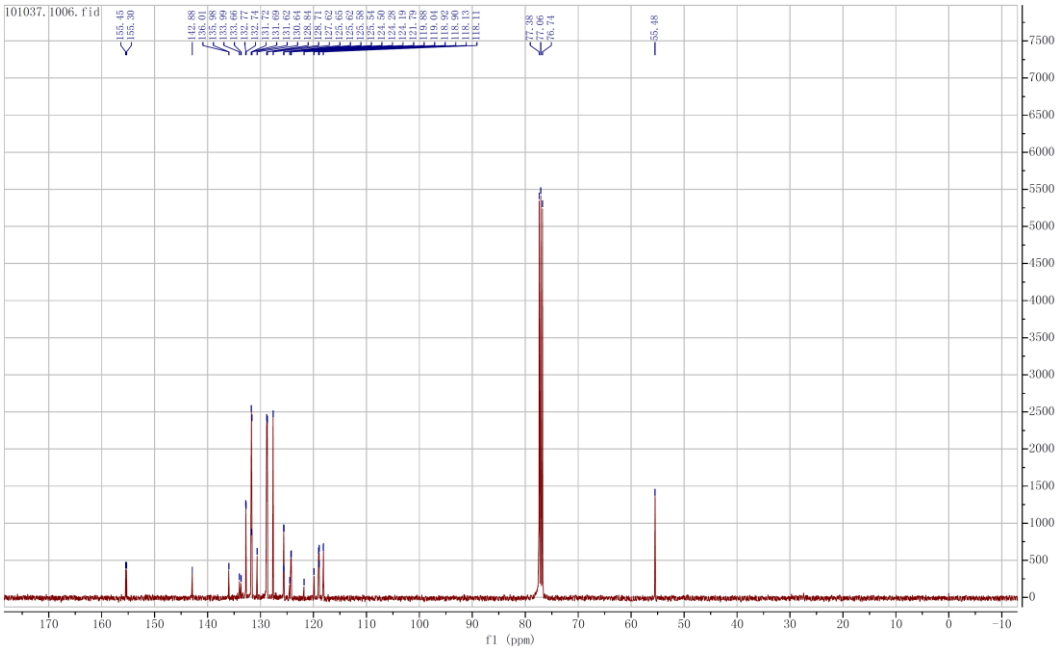
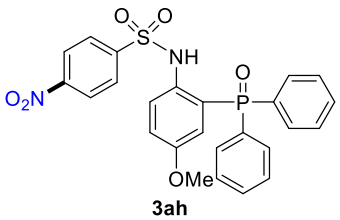


Figure S14. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3ag**



3ah

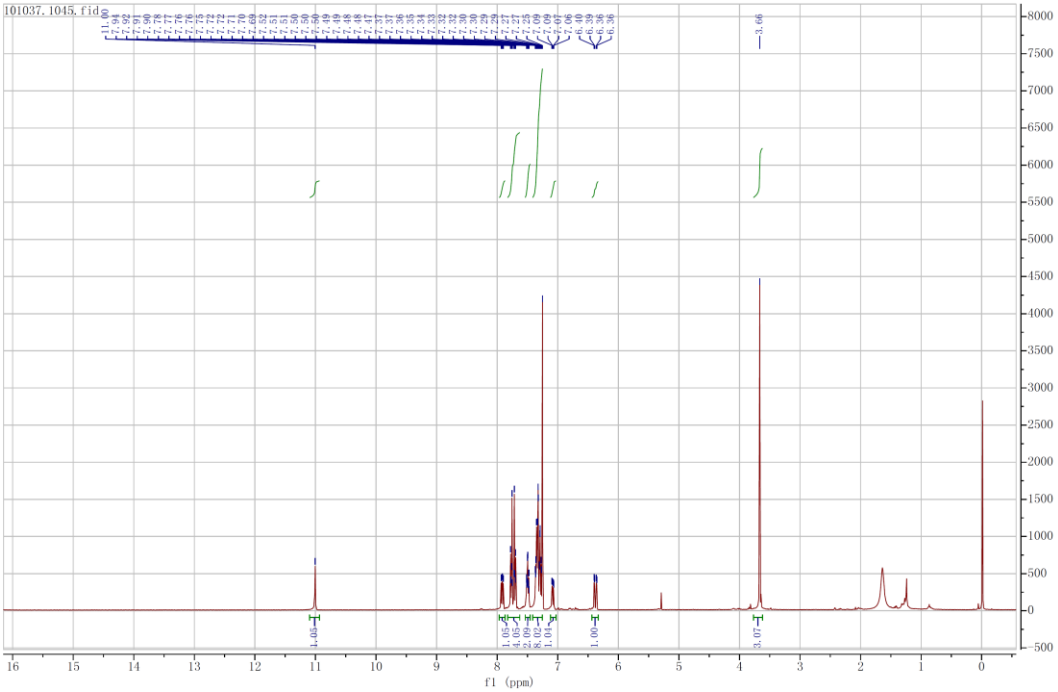


Figure S15. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3ah**

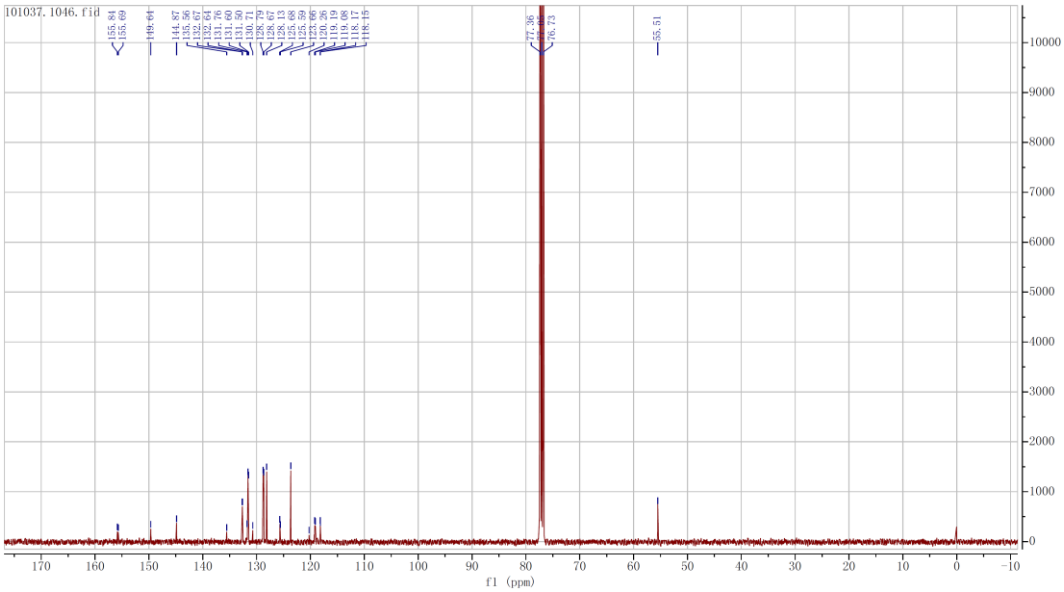
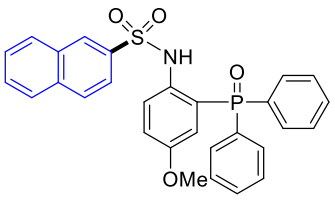


Figure S16. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3ah**



3ai

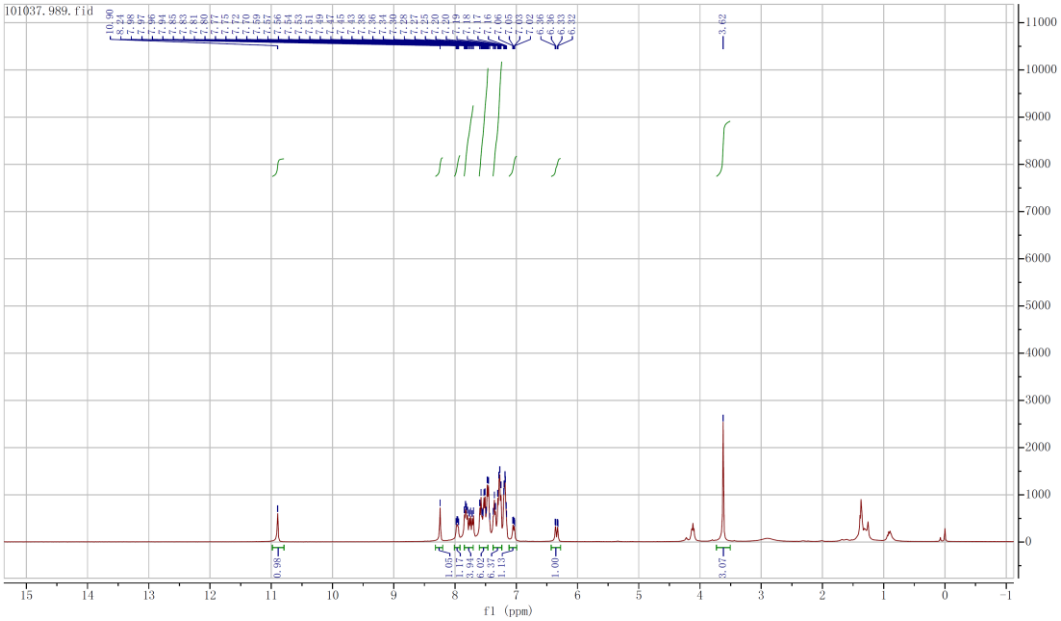


Figure S17. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3ai**

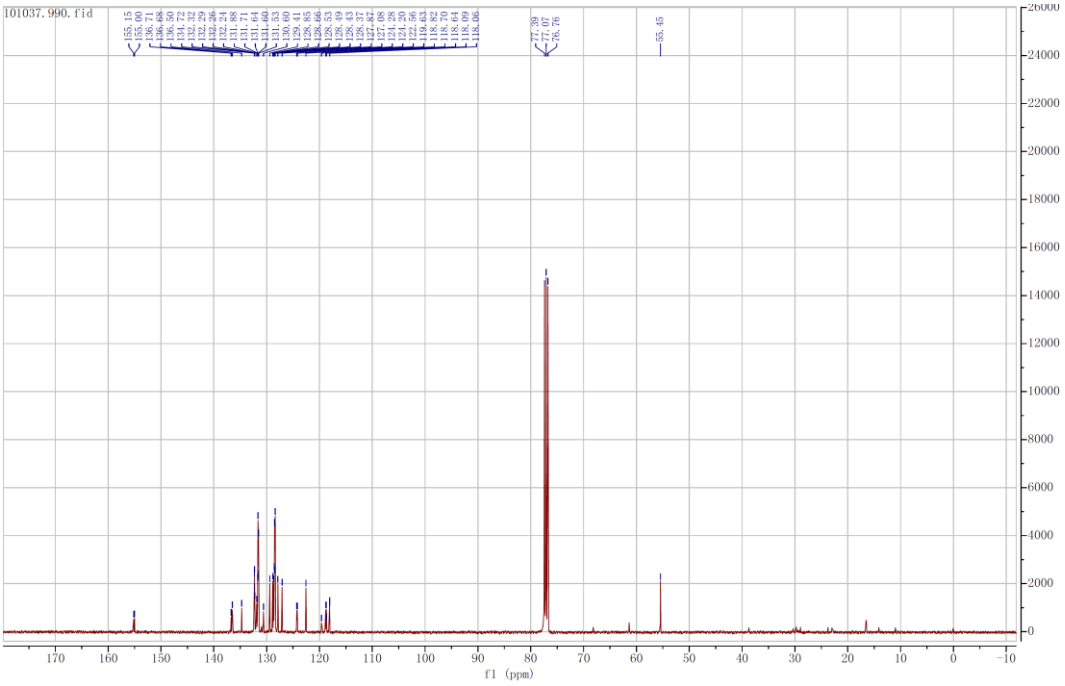
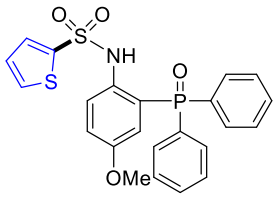


Figure S18. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3ai**



3aj

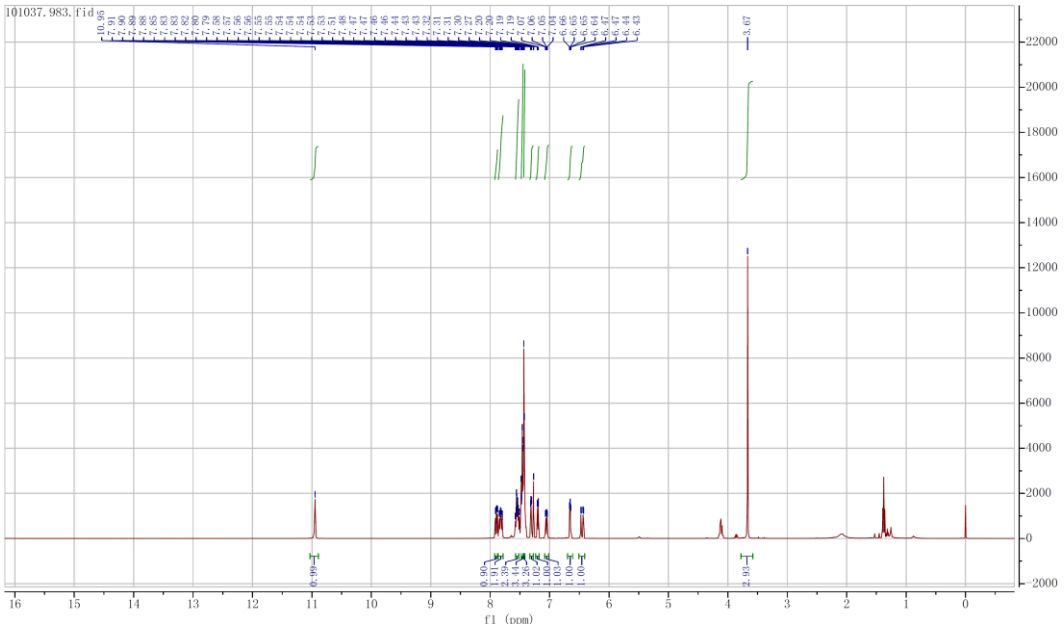


Figure S19. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3aj**

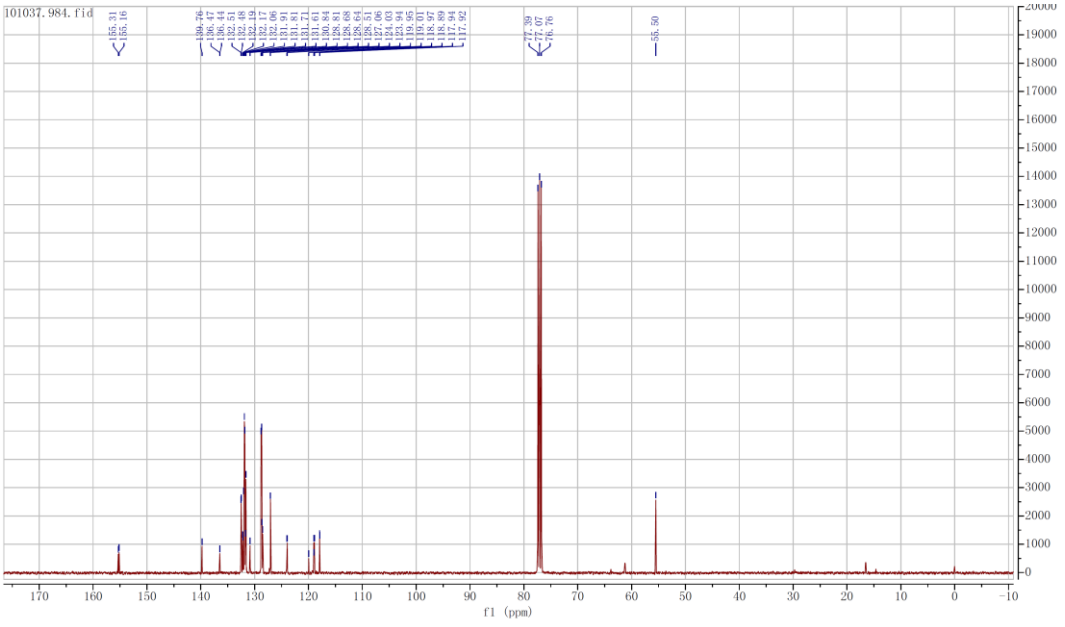
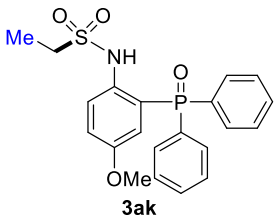


Figure S20. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3aj**



3ak

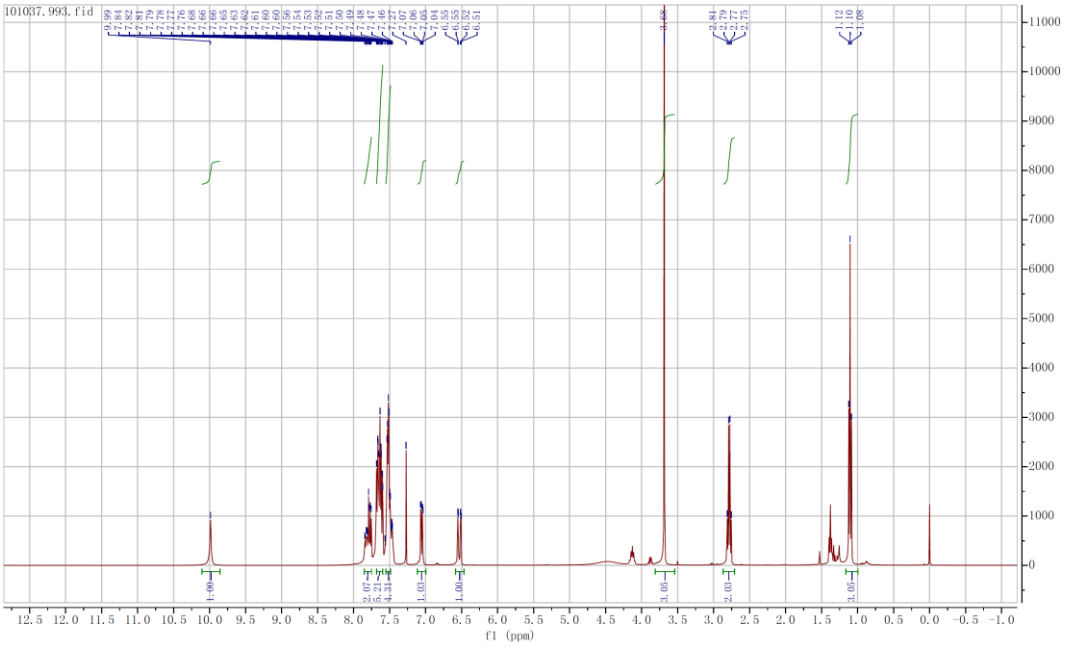


Figure S21. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3ak**

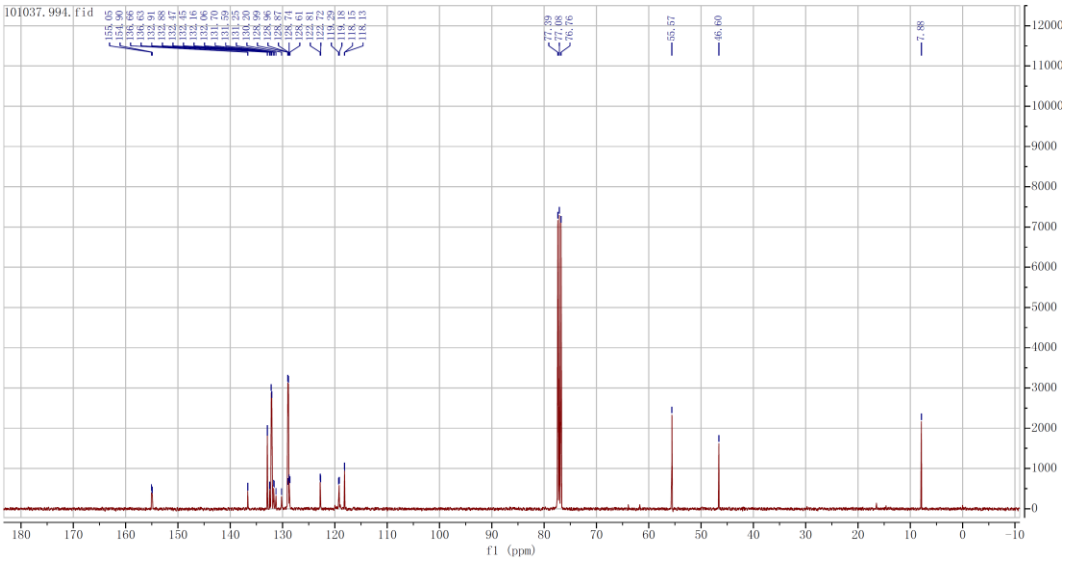
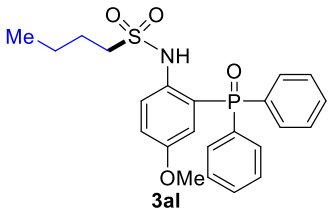


Figure S22. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3ak**



3al

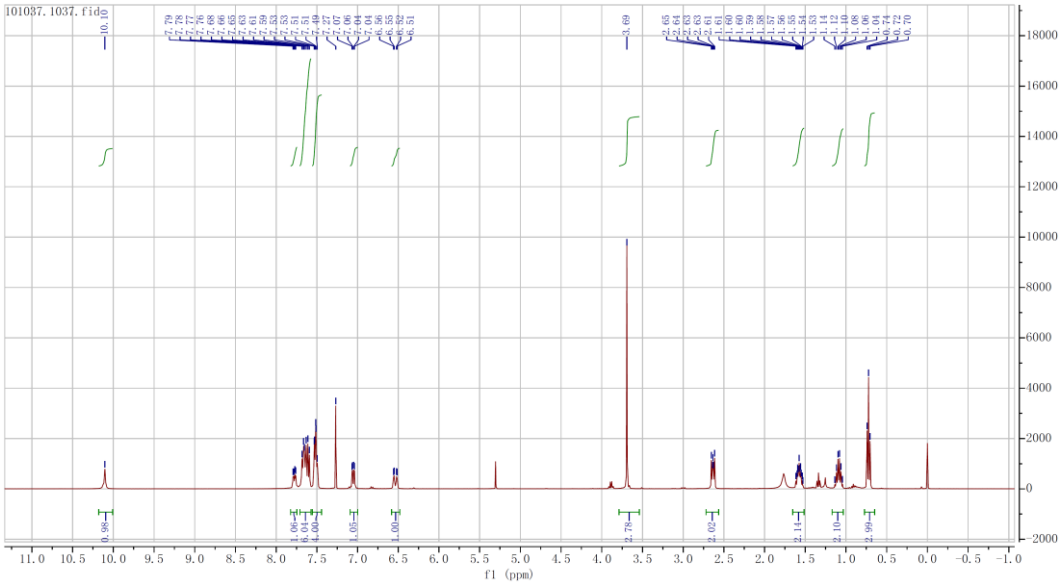


Figure S23. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3al**

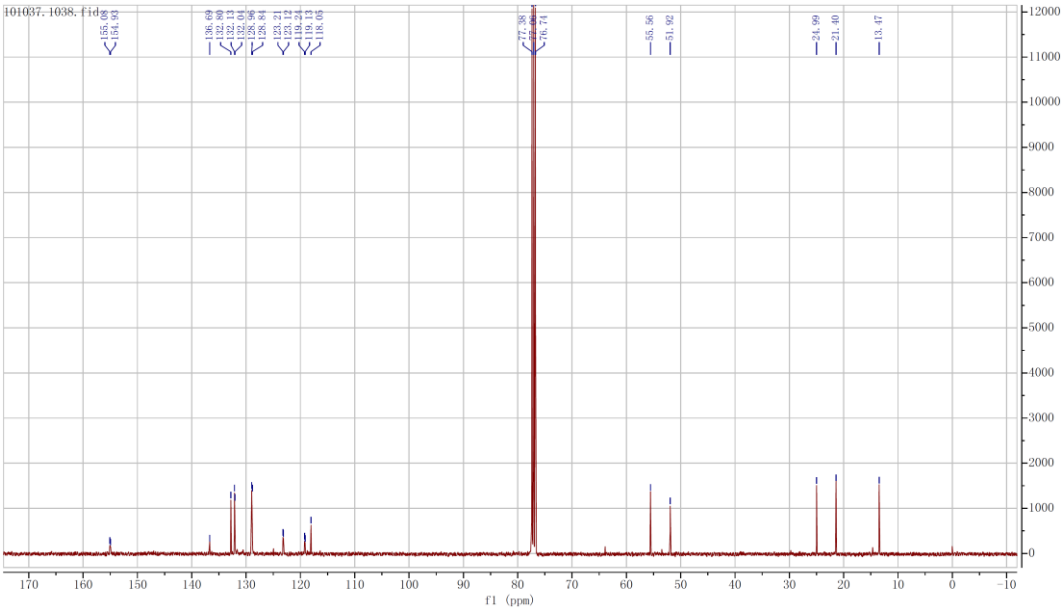


Figure S24. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3al**

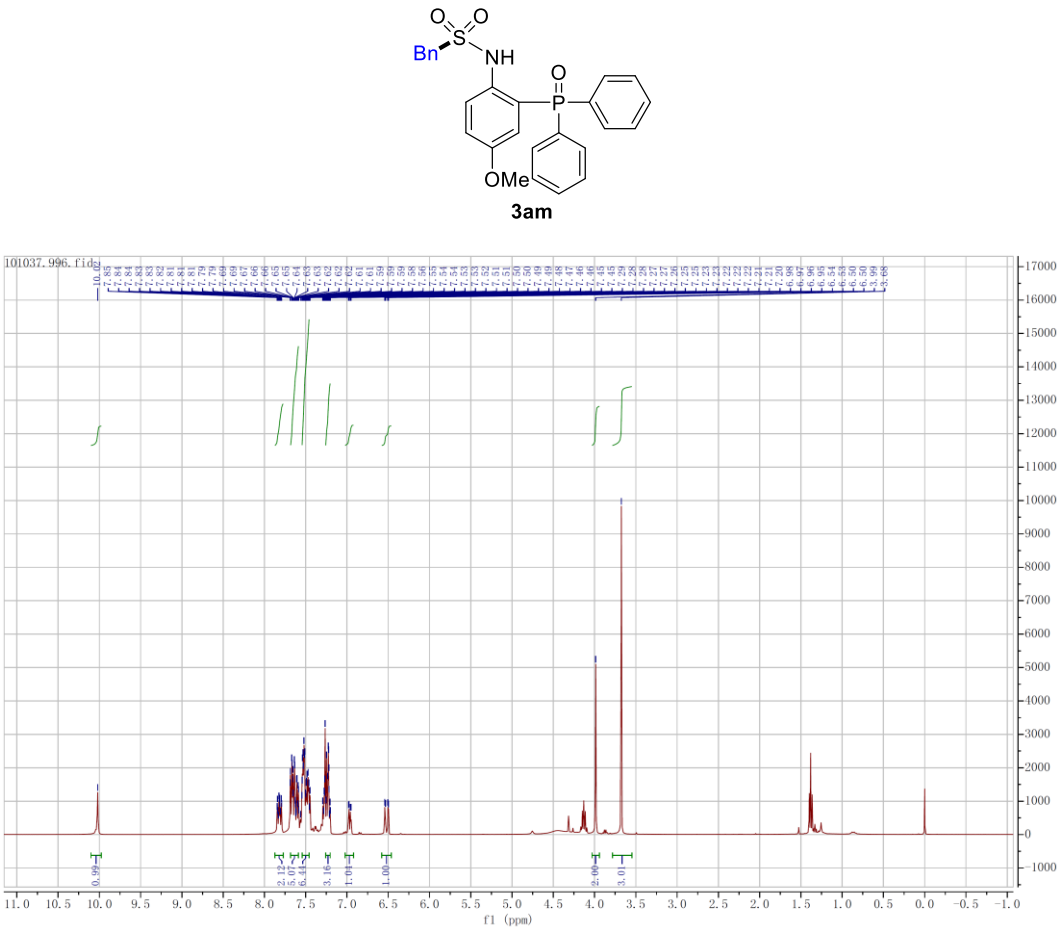


Figure S25. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3am**

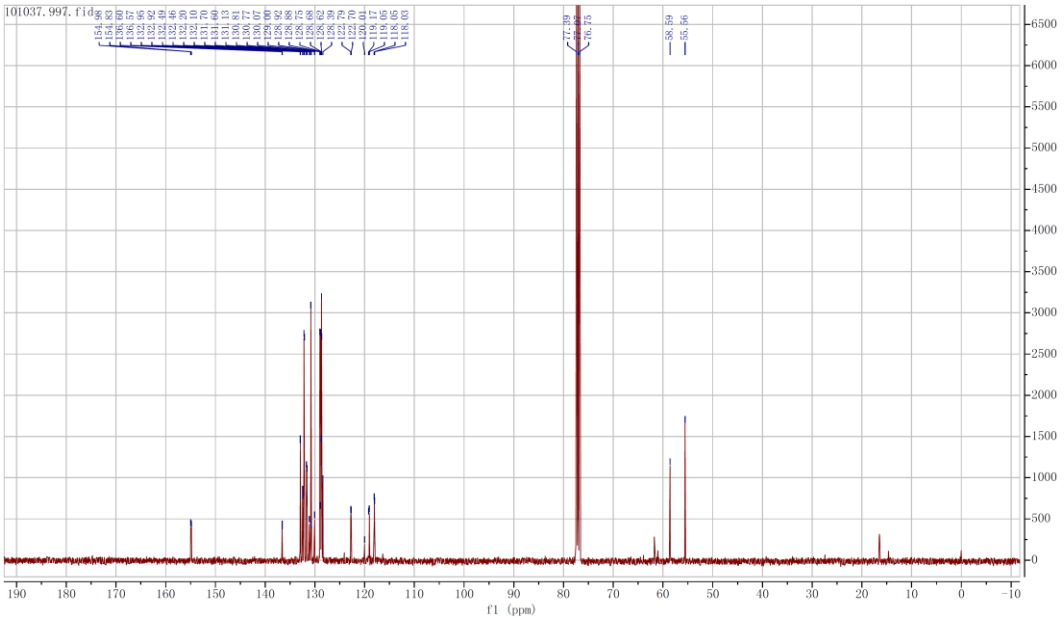
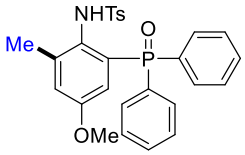


Figure S26. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3am**



3an

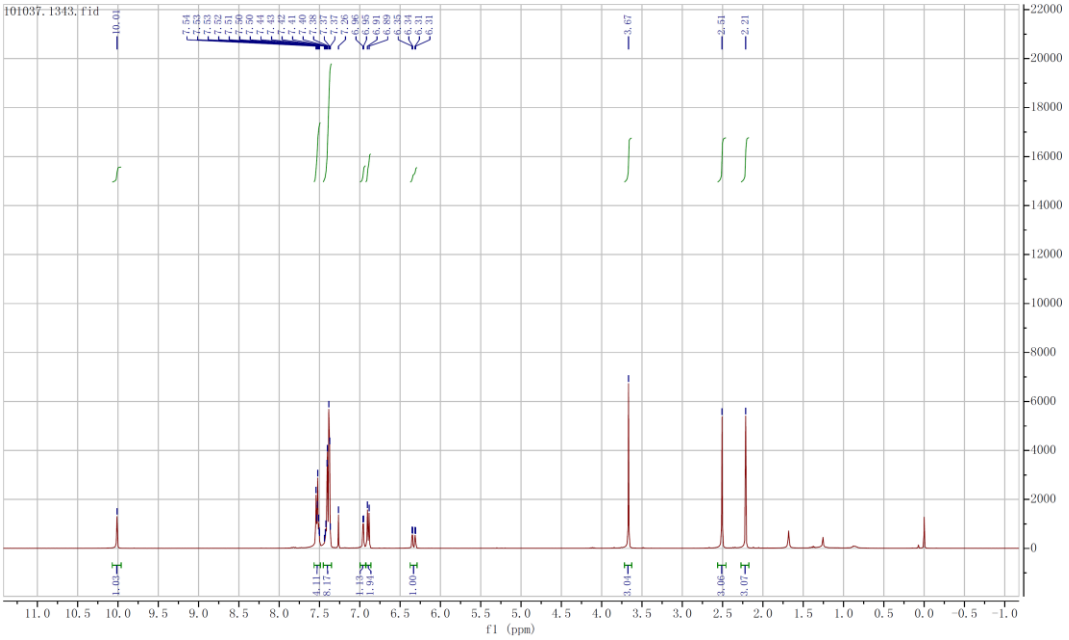


Figure S27 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3an**

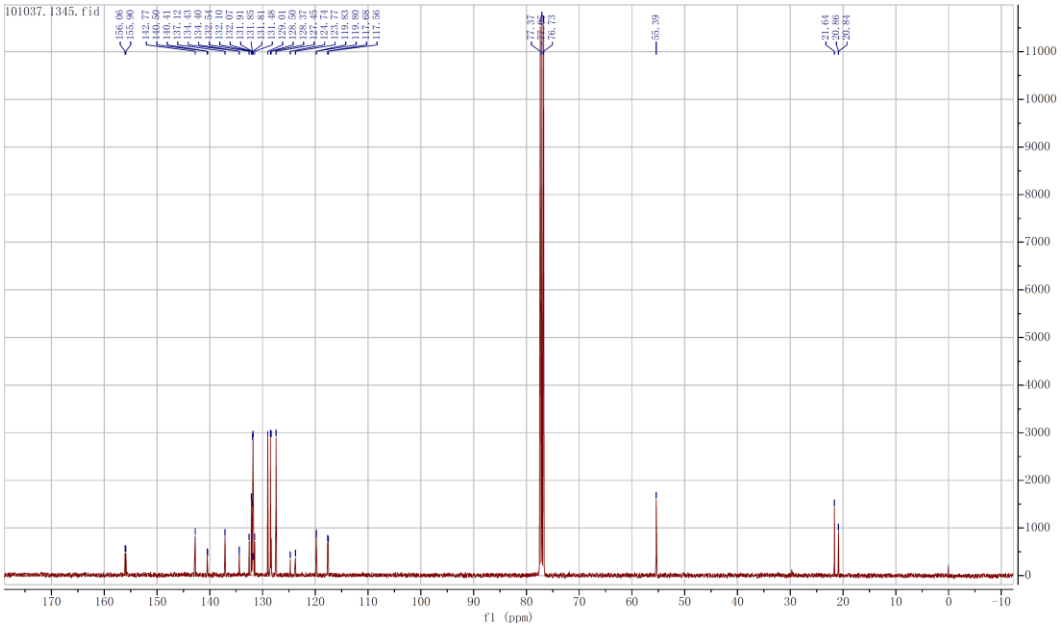
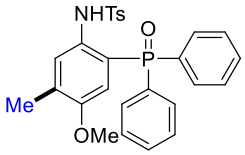


Figure S28. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3an**



3ao

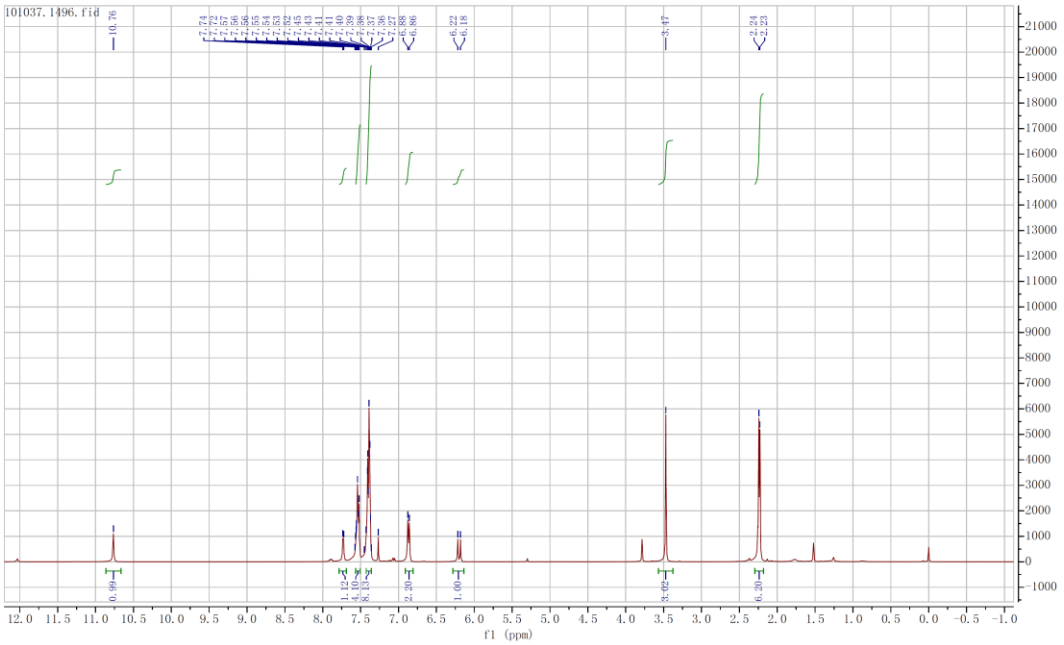


Figure S29 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3ao**

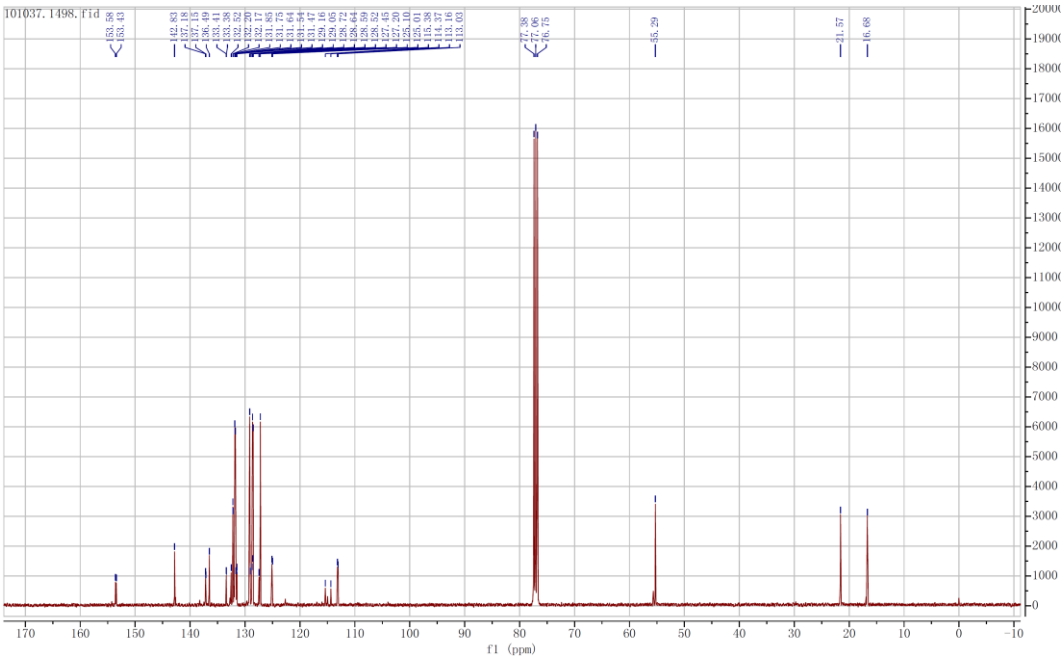
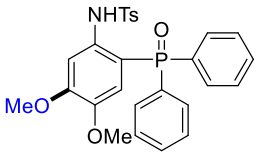


Figure S30. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3ao**



3ap

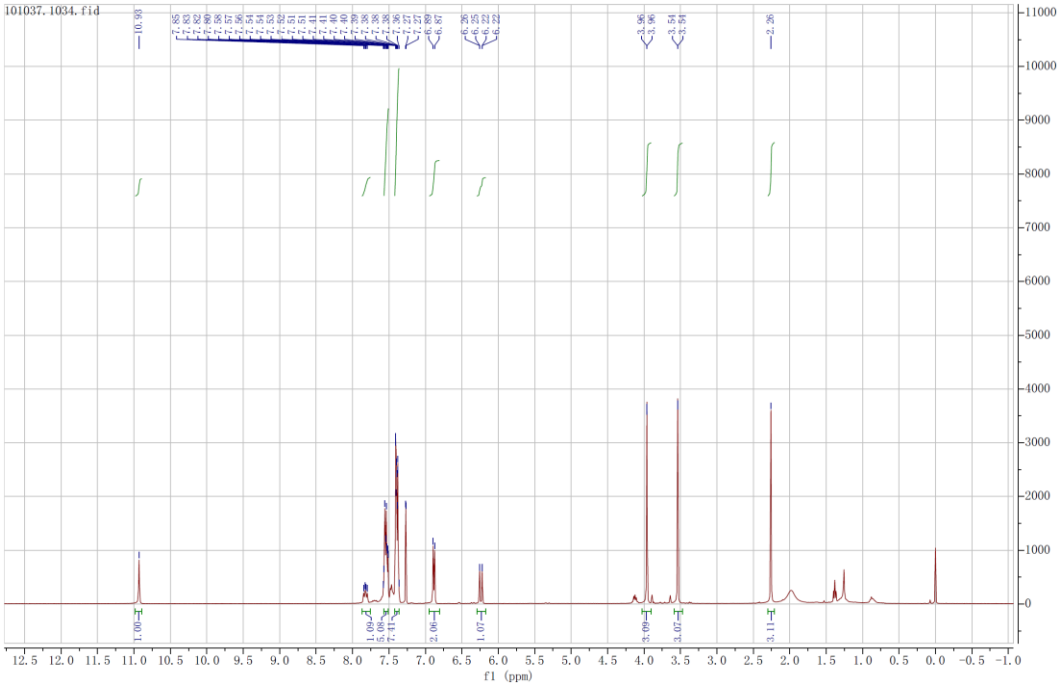


Figure 31. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3ap**

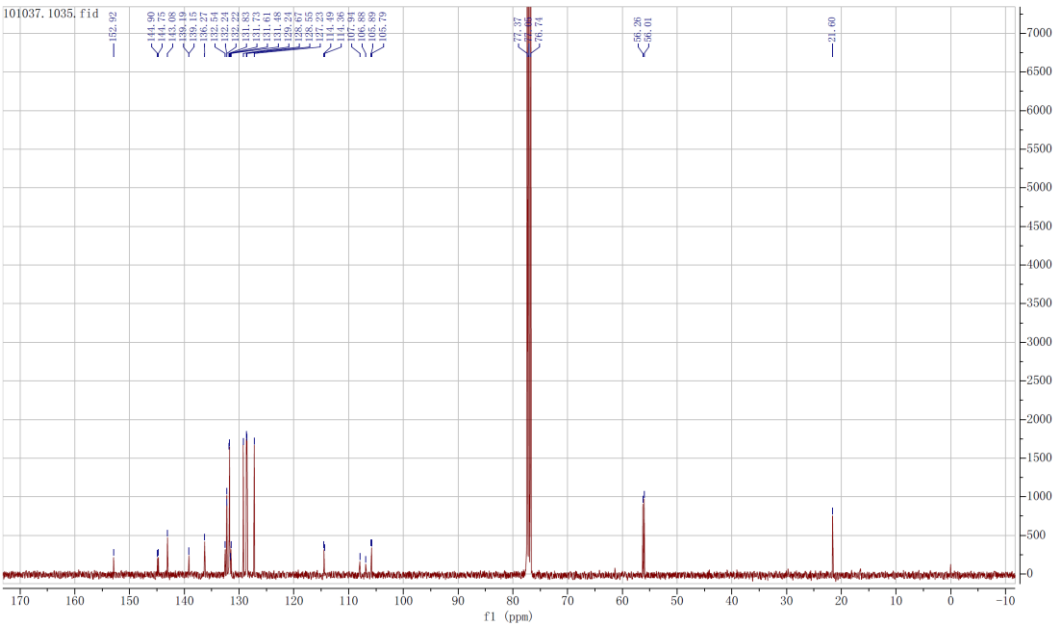
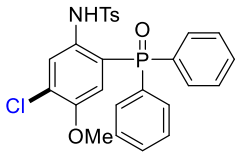


Figure 32. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3ap**



3aq

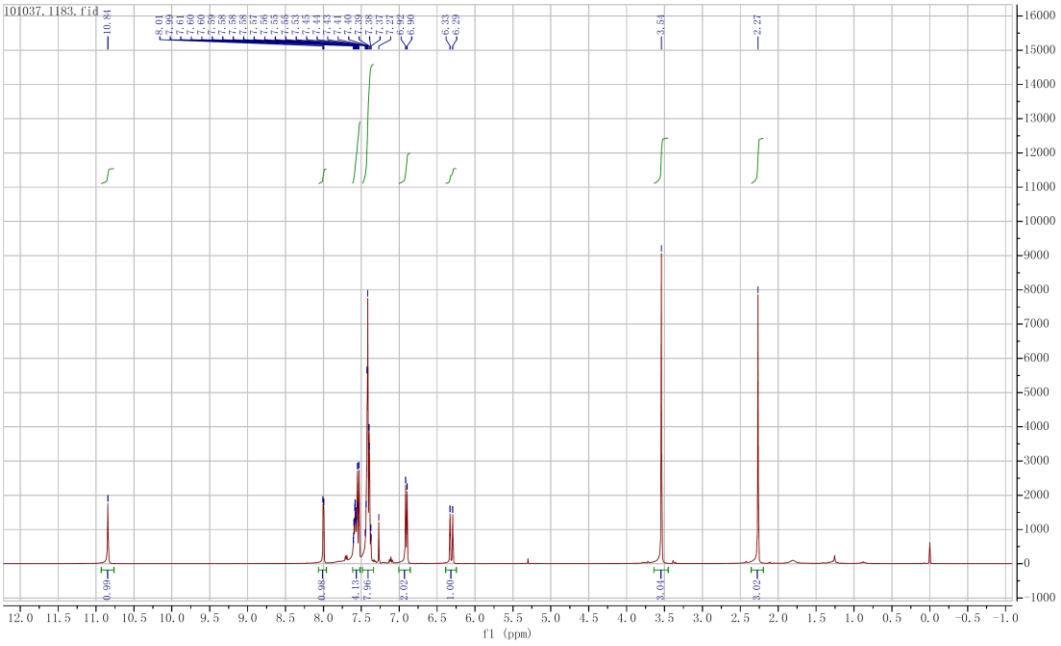


Figure 33. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3aq**

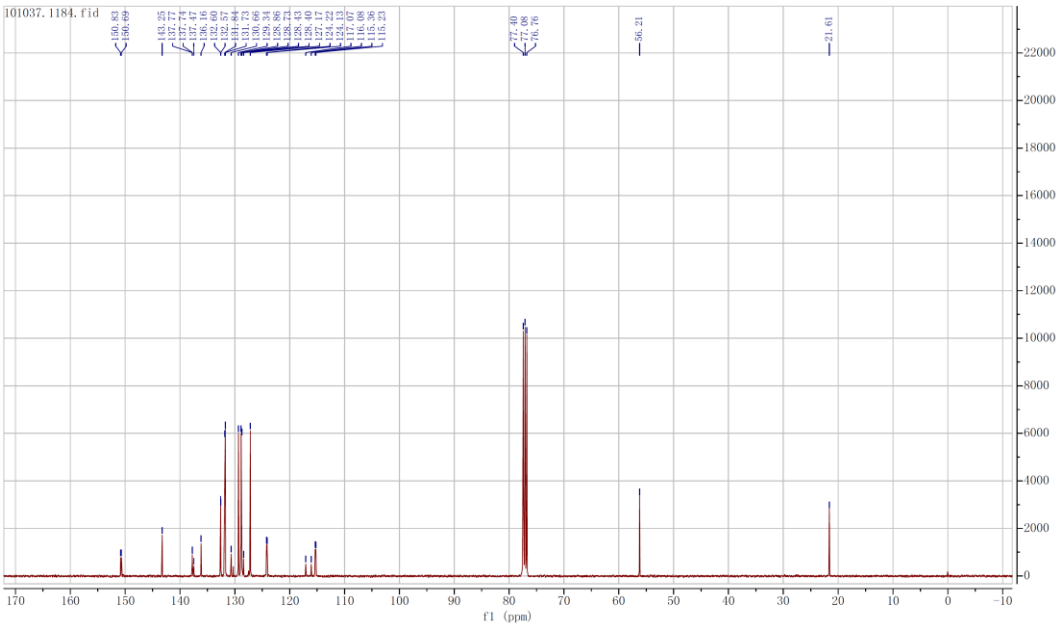
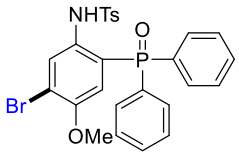


Figure 34. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3aq**



3ar

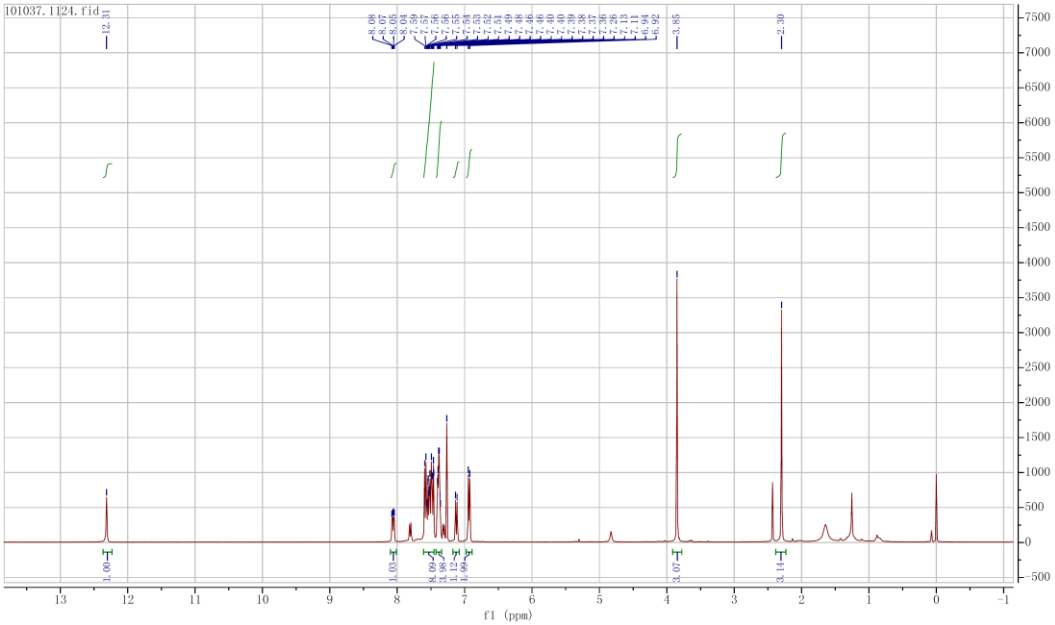


Figure 35. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3ar**

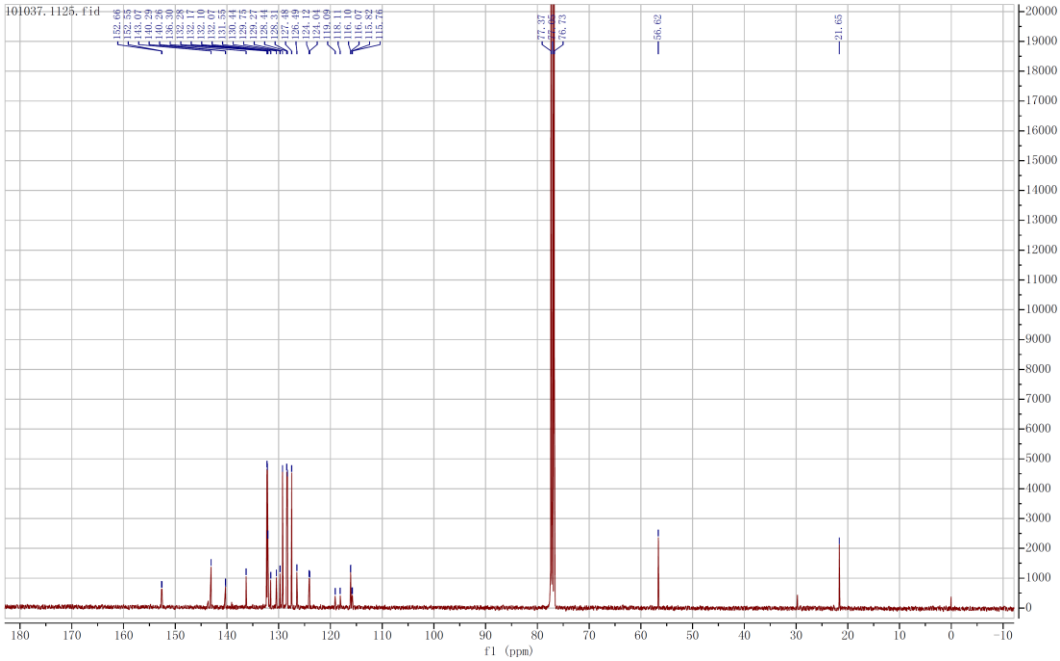
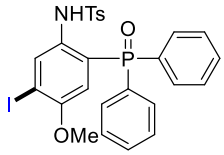


Figure 36. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3ar**



3as

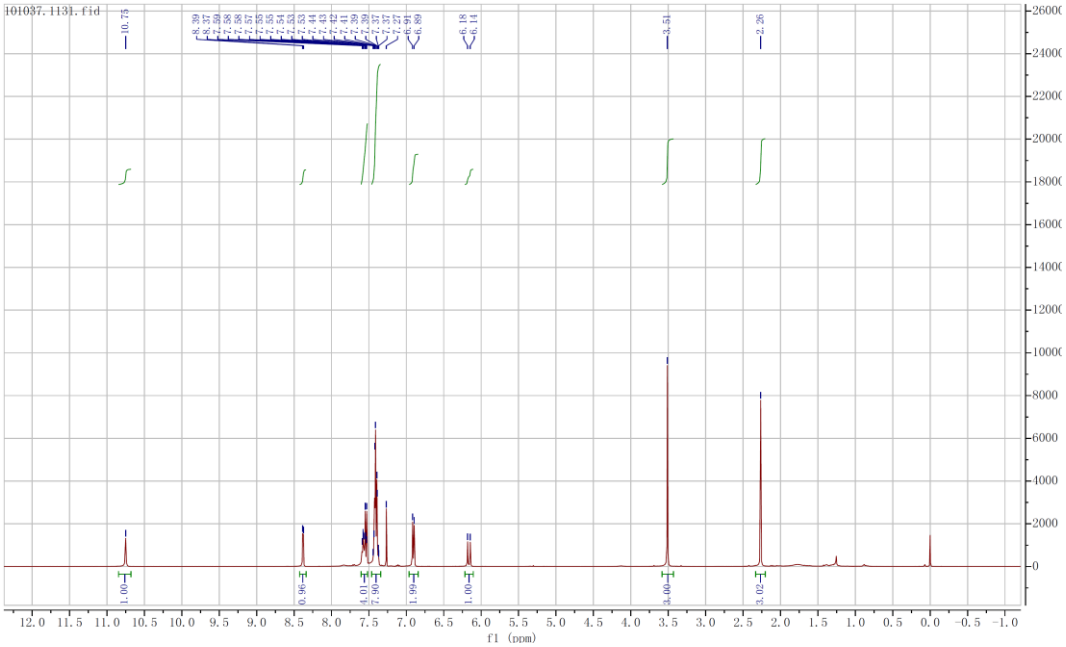


Figure 37. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3as**

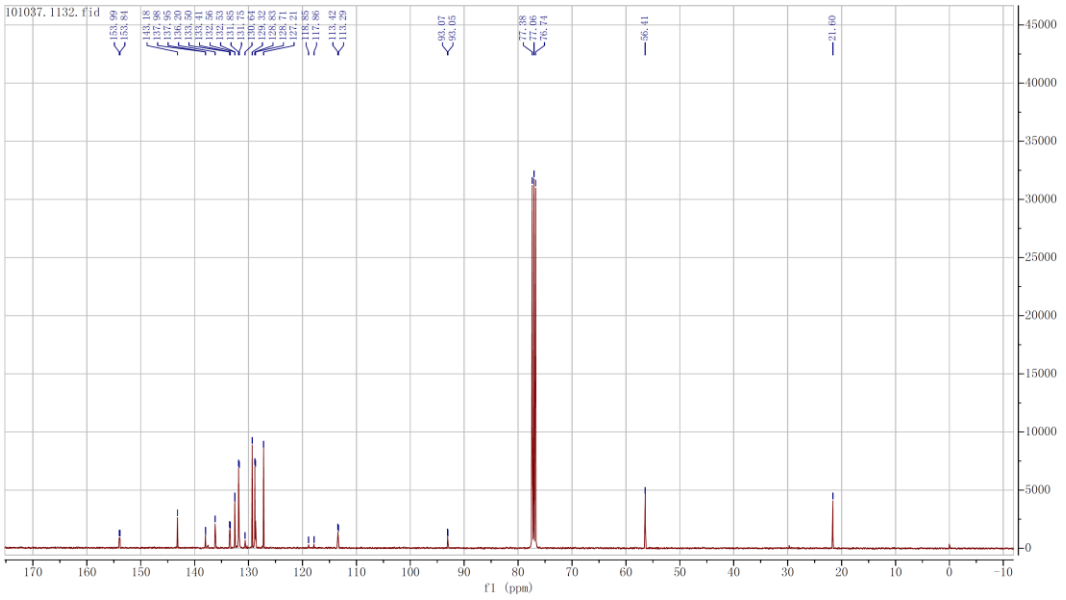
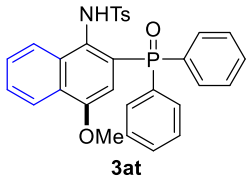


Figure 38 ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3as**



3at

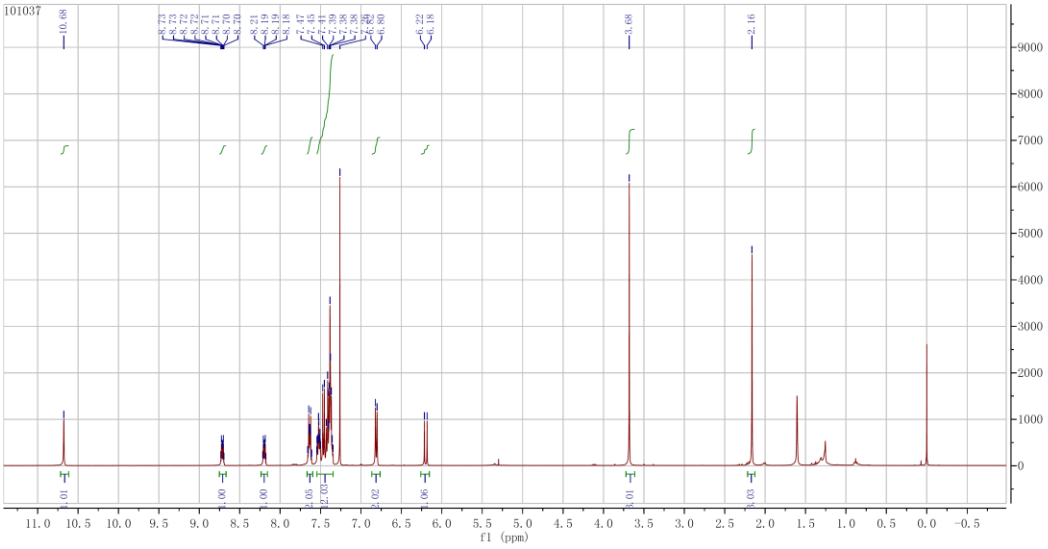


Figure 39 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3at**

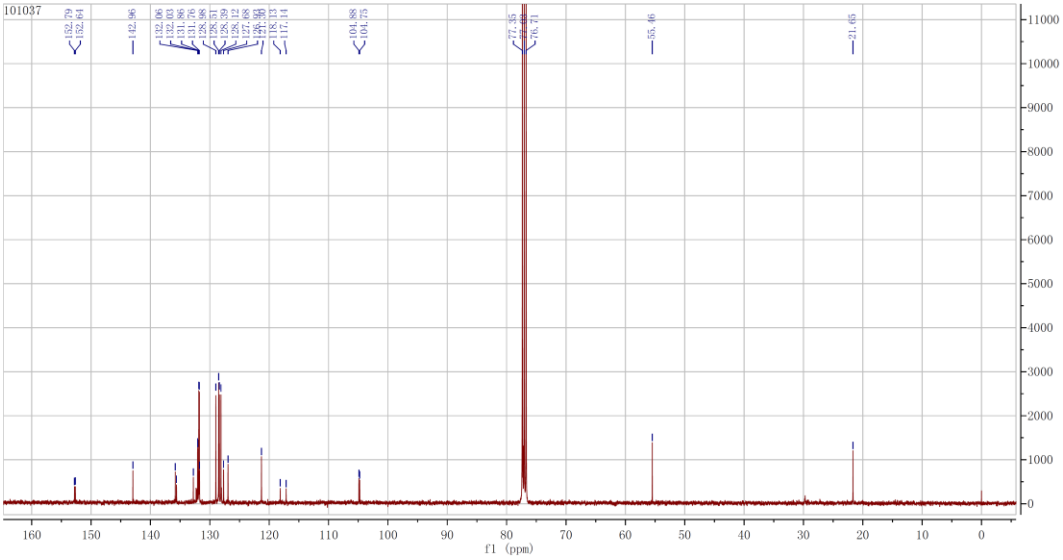
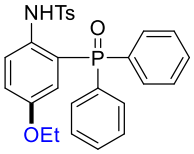


Figure 40 ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3at**



3au

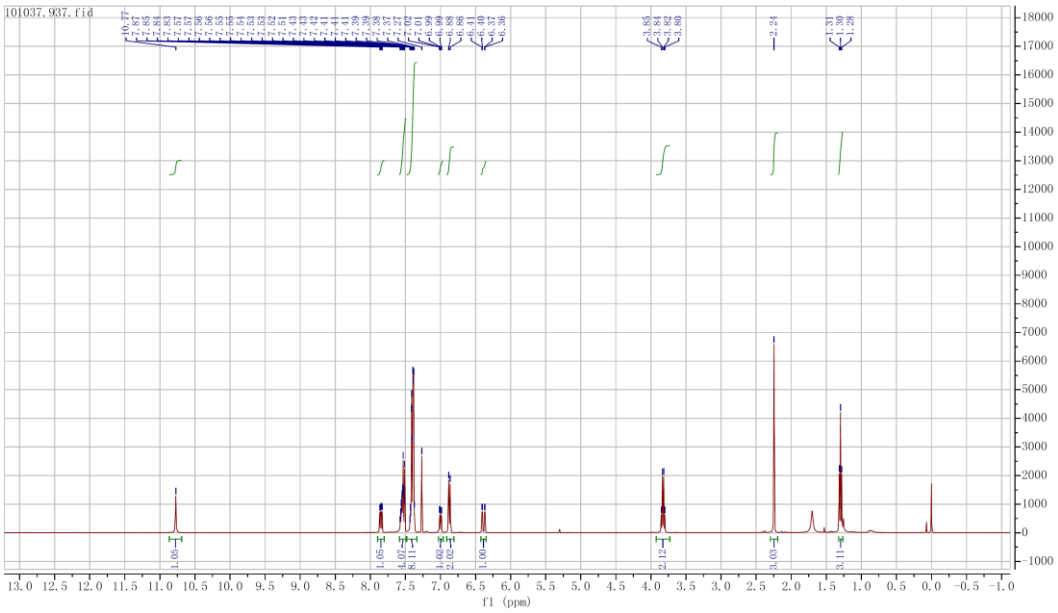


Figure 41 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3au**

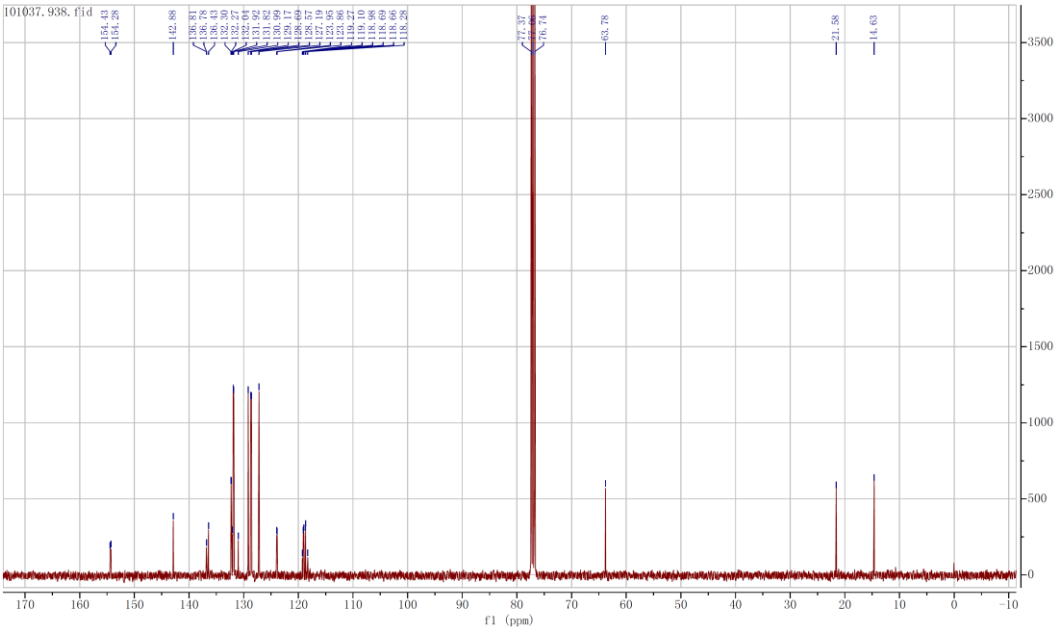
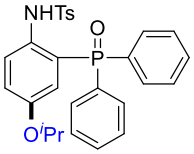


Figure 42 ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3au**



3av

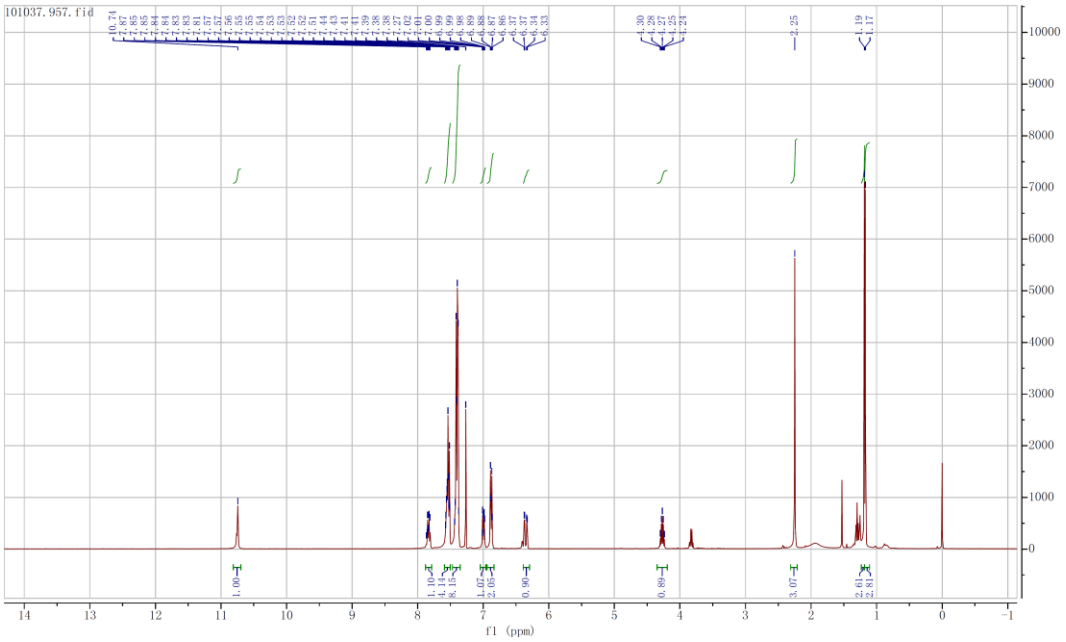


Figure 43 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3av**

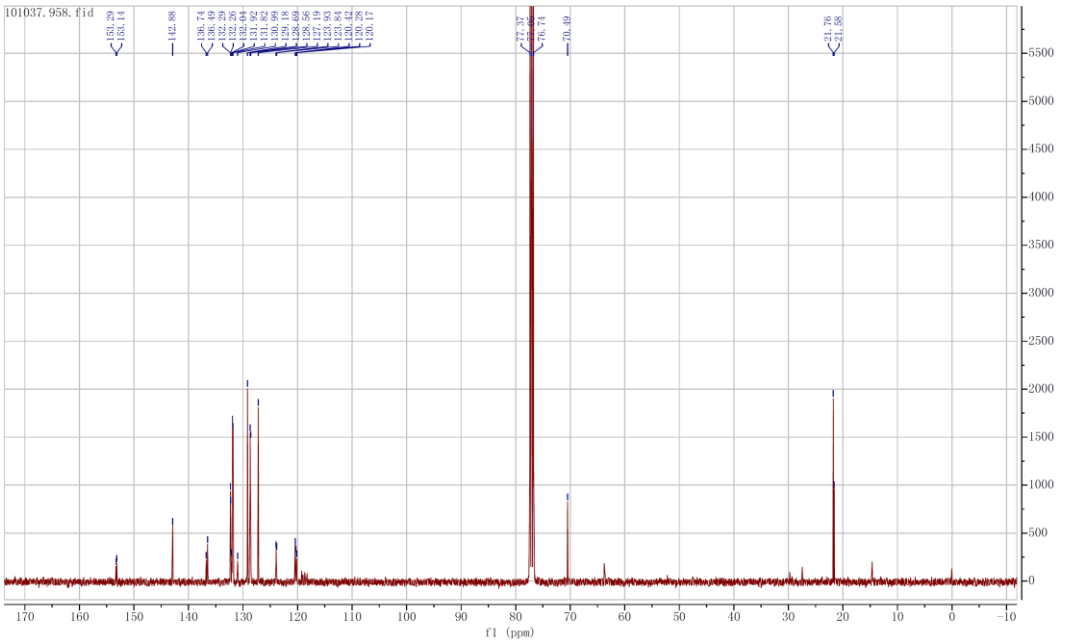
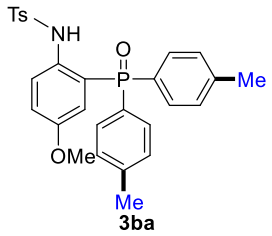


Figure 44 ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3av**



3ba

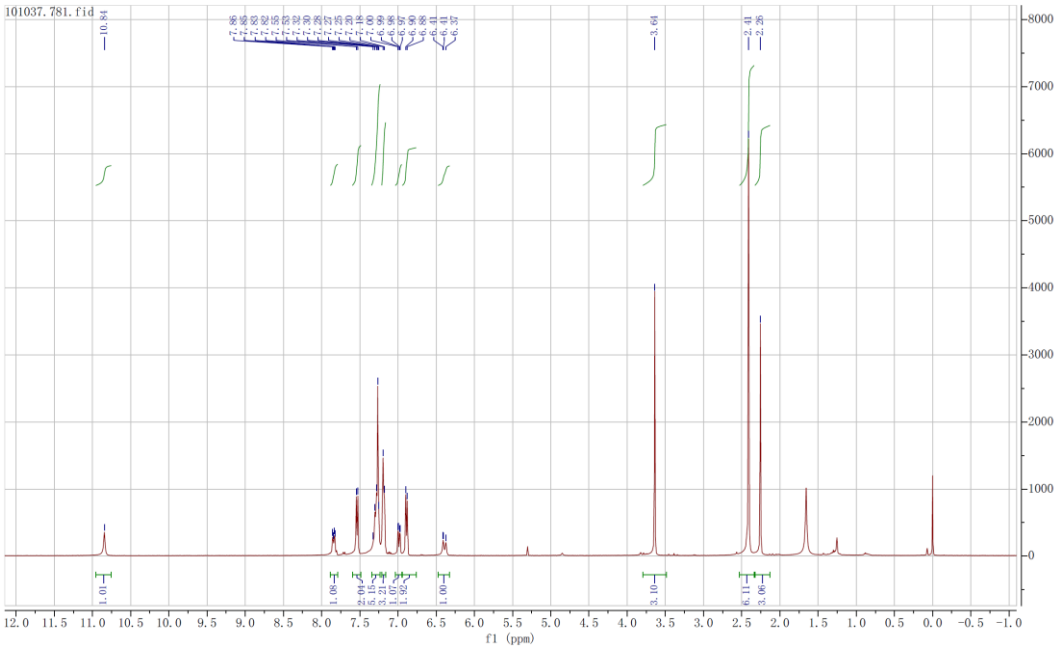


Figure 45 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3ba**

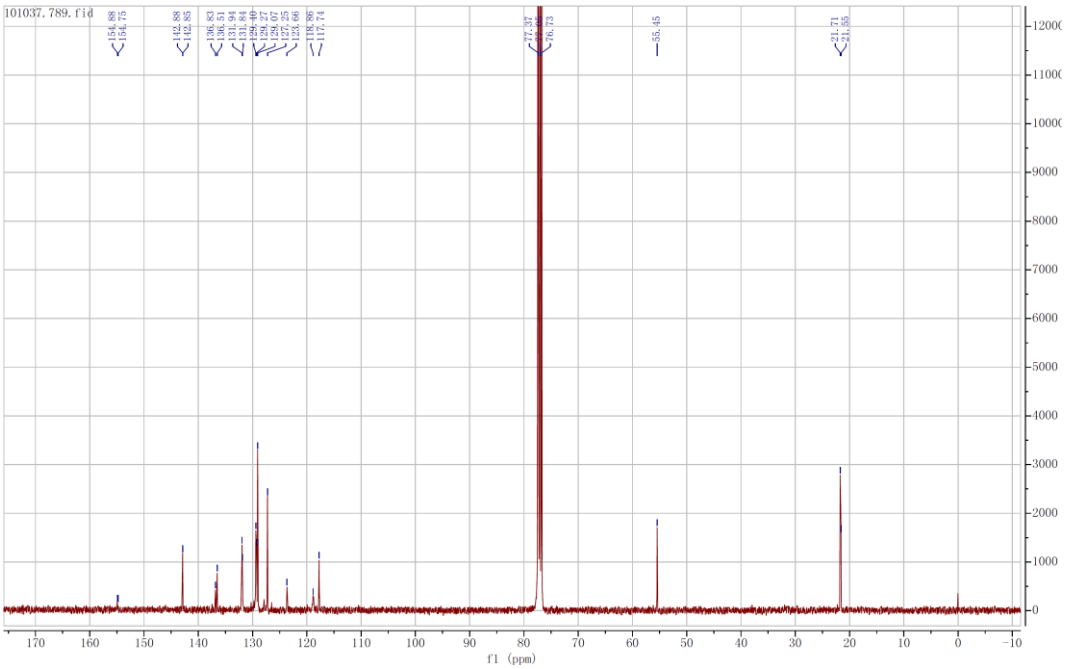
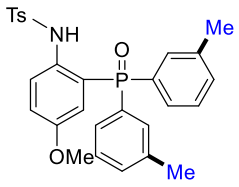


Figure 46 ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3ba**



3bb

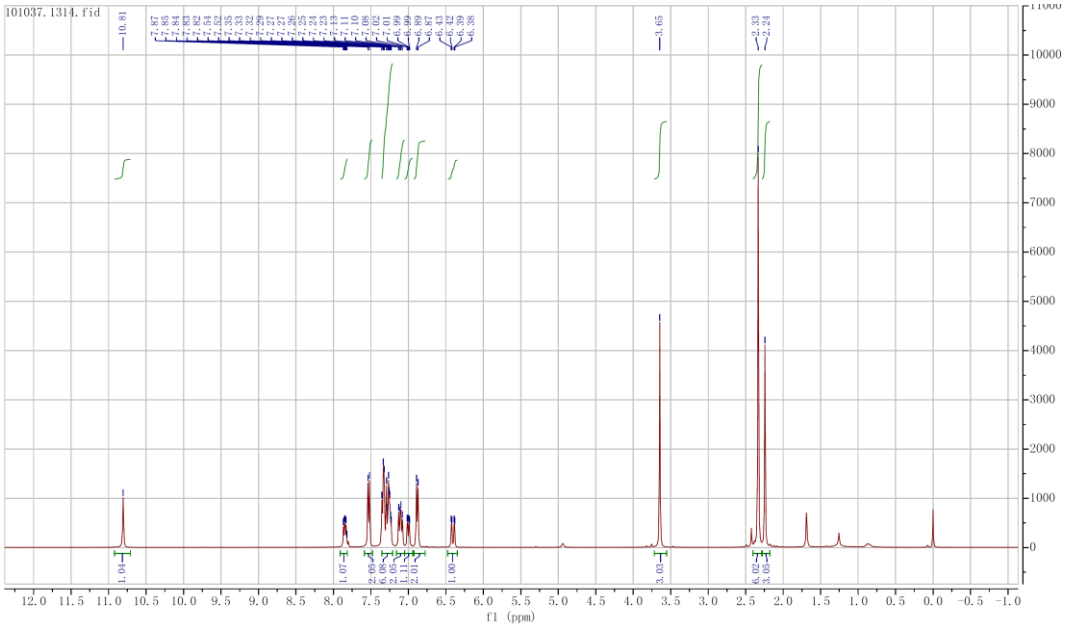


Figure 47 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3bb**

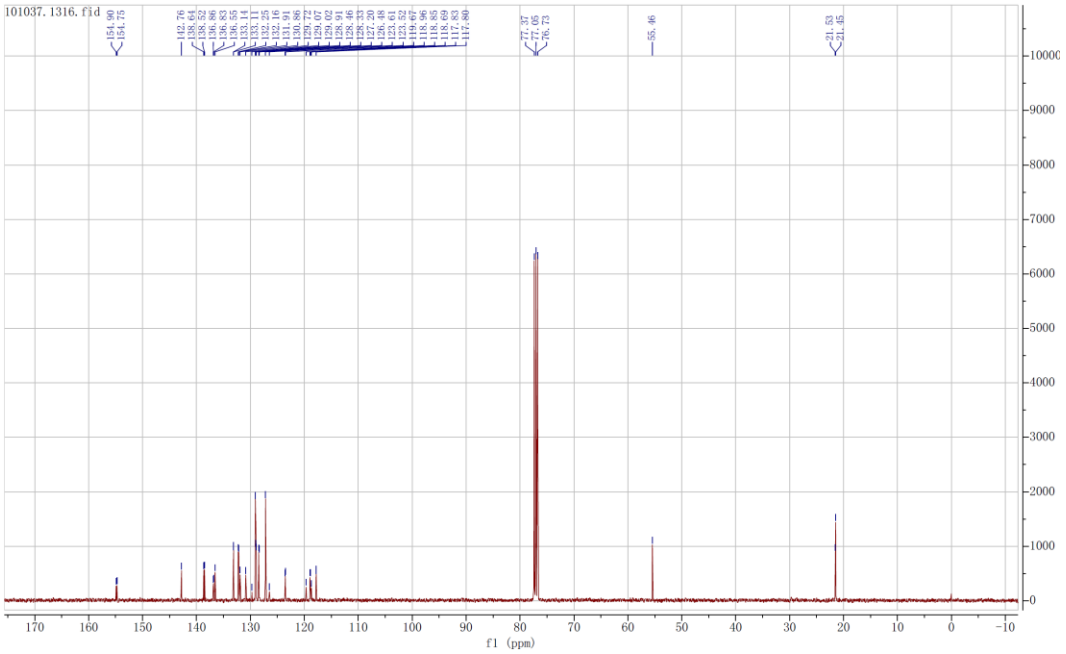
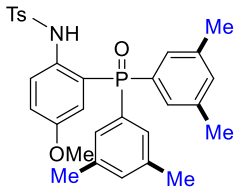


Figure 48 ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3bb**



3bc

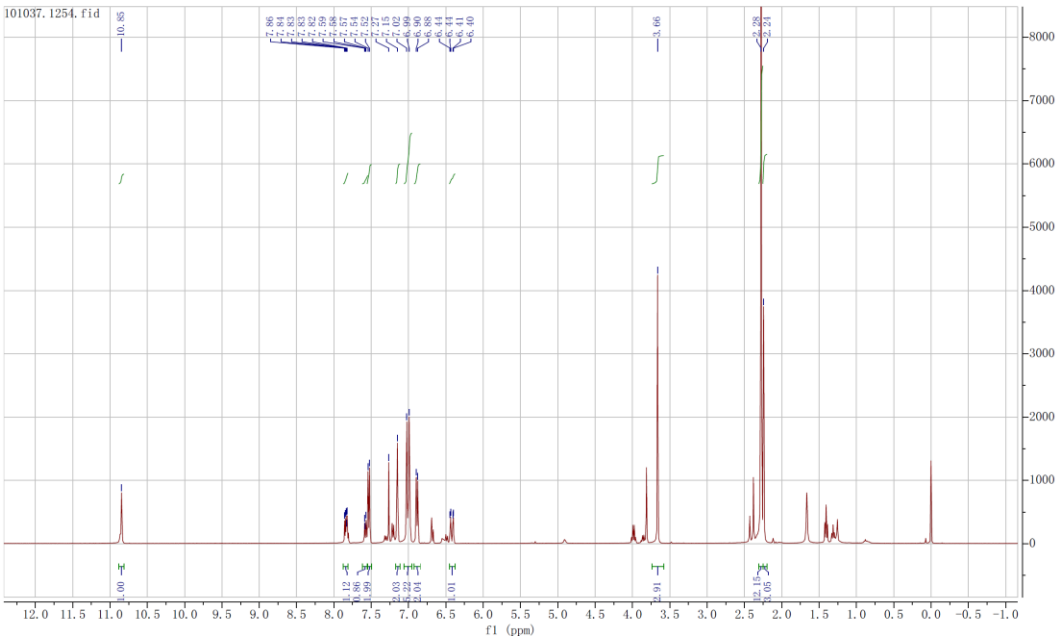


Figure 49 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3bc**

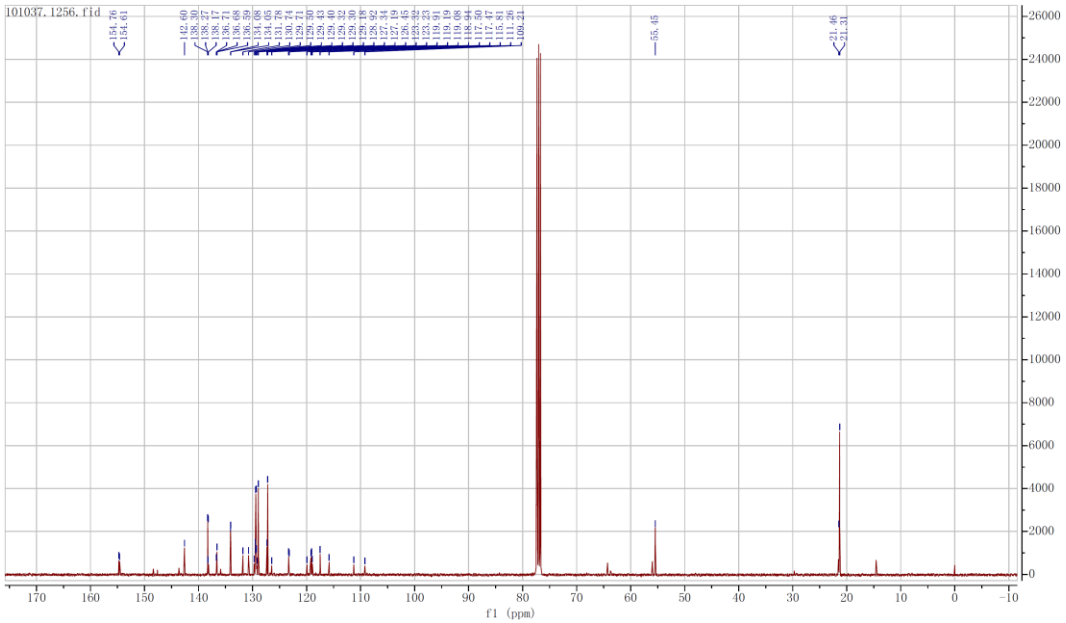
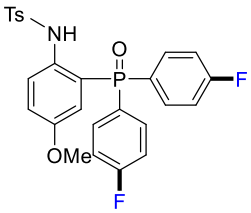


Figure 50 ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3bc**



3bd

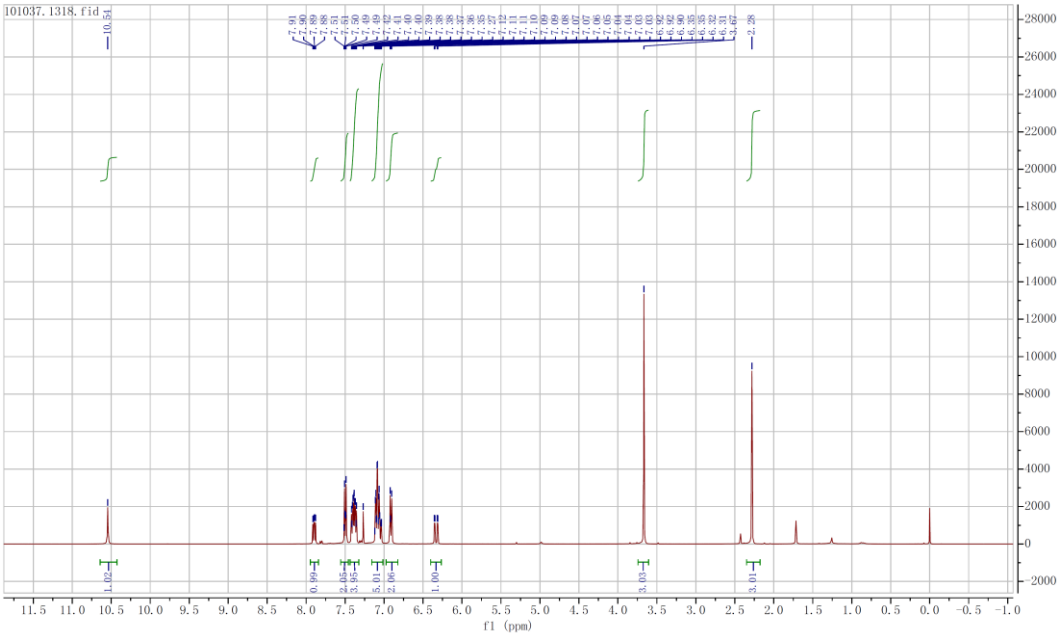


Figure 51 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3bd**

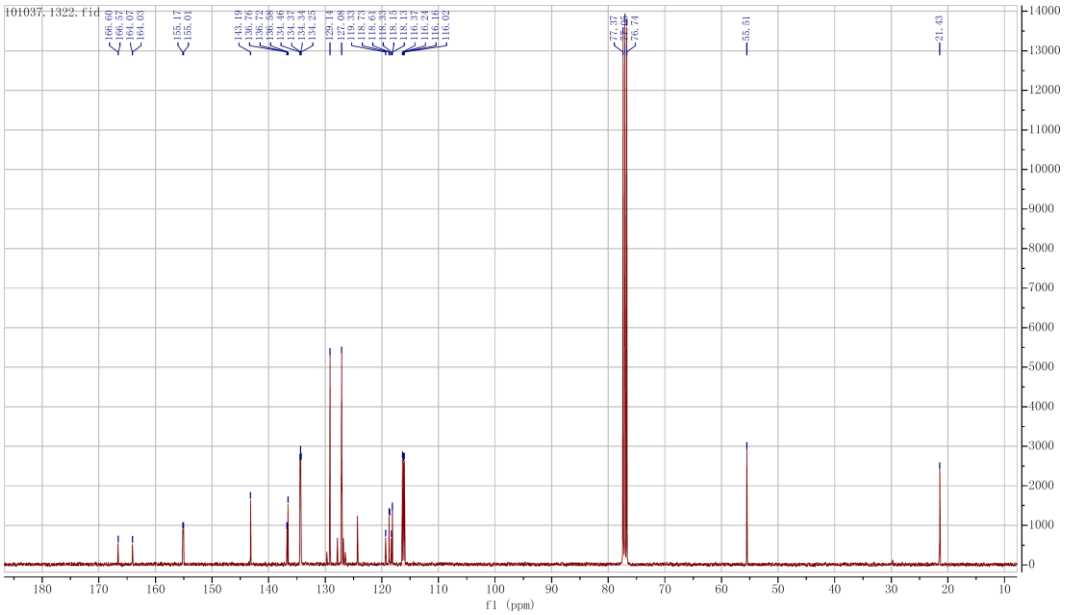
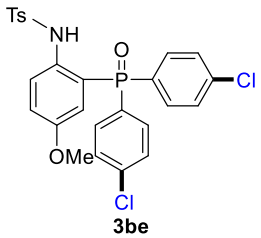


Figure 52 ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3bd**



3be

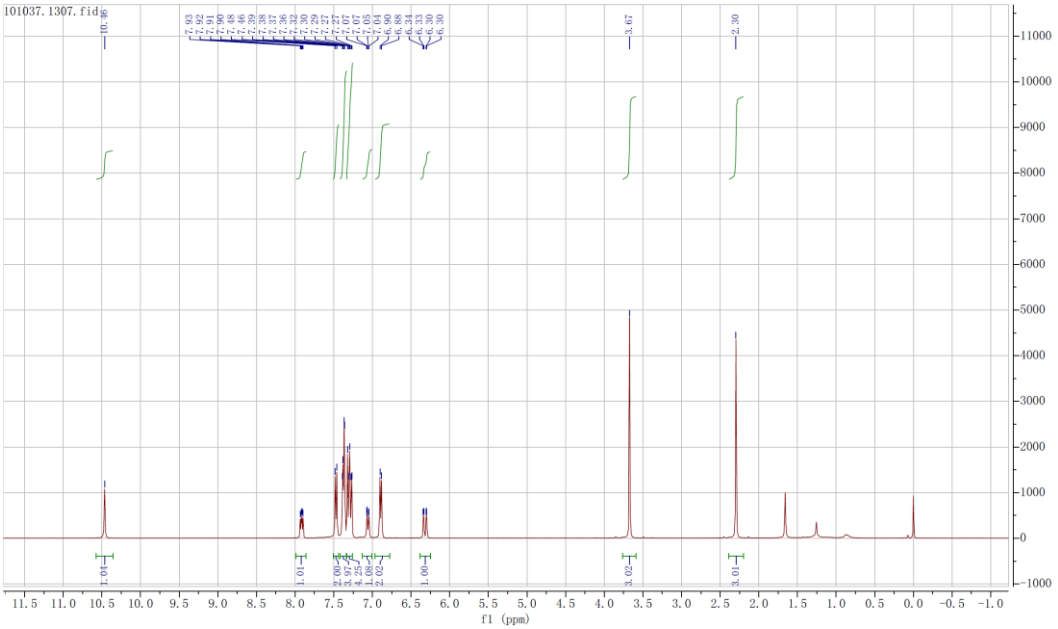


Figure 53 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3be**

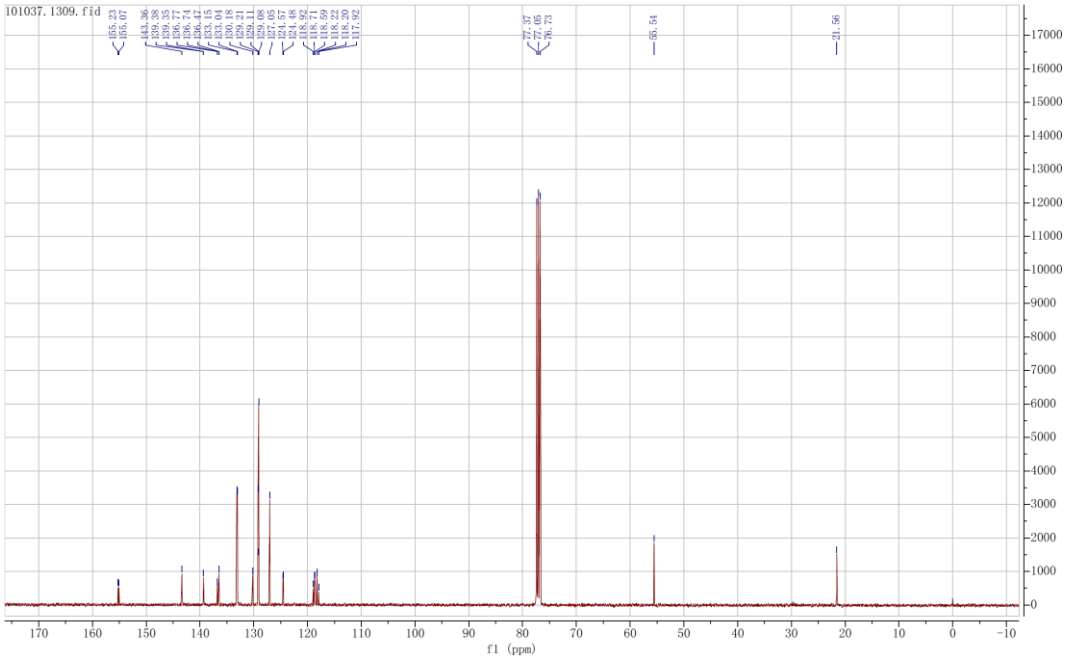
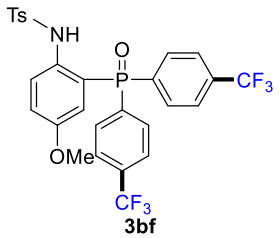


Figure 54 ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3be**



3bf

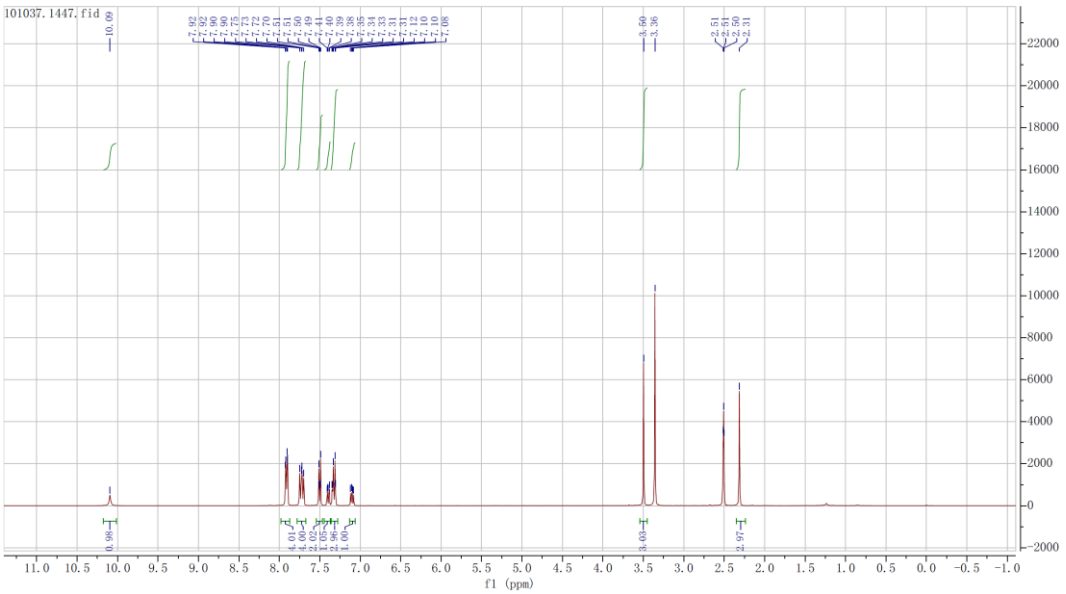


Figure 55 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3bf**

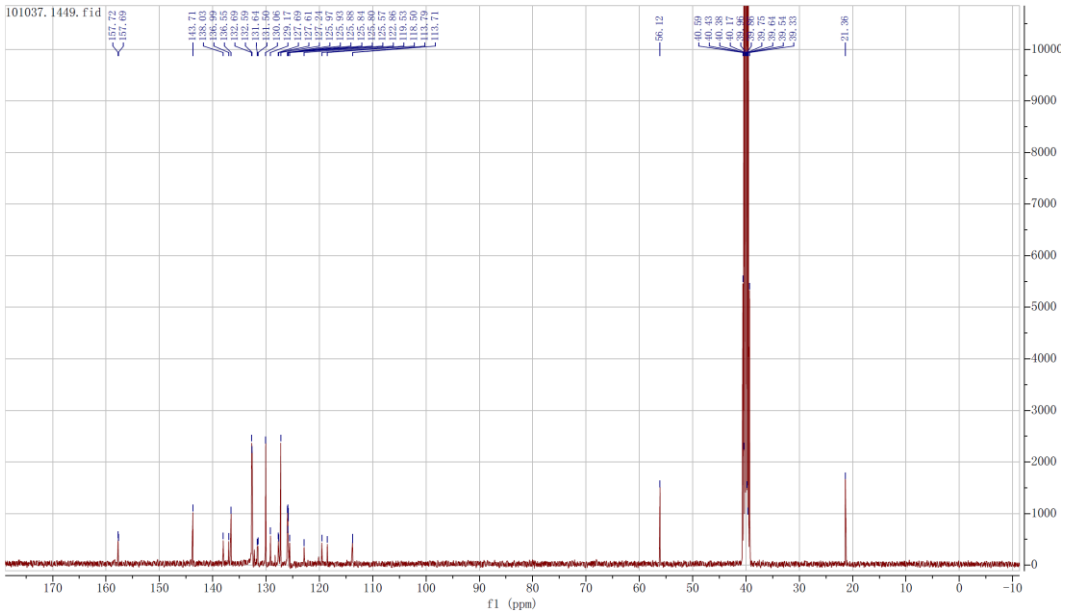
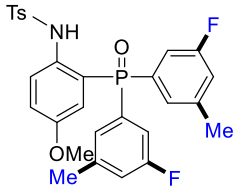


Figure 56 ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3bf**



3bg

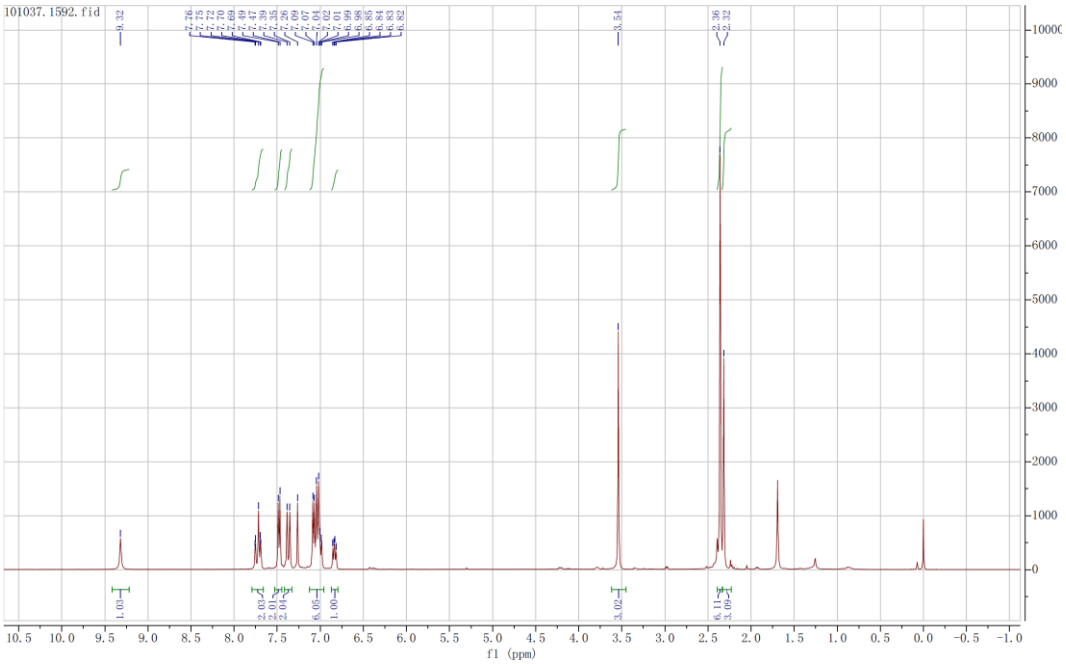


Figure 57 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3bg**

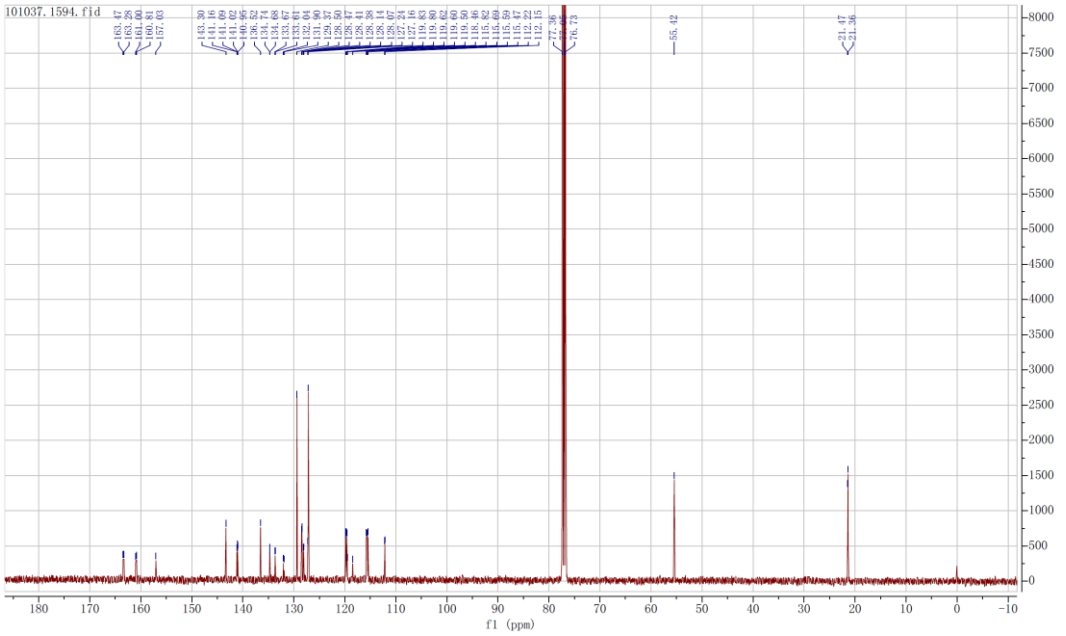
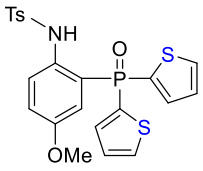


Figure 58 ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3bg**



3bh

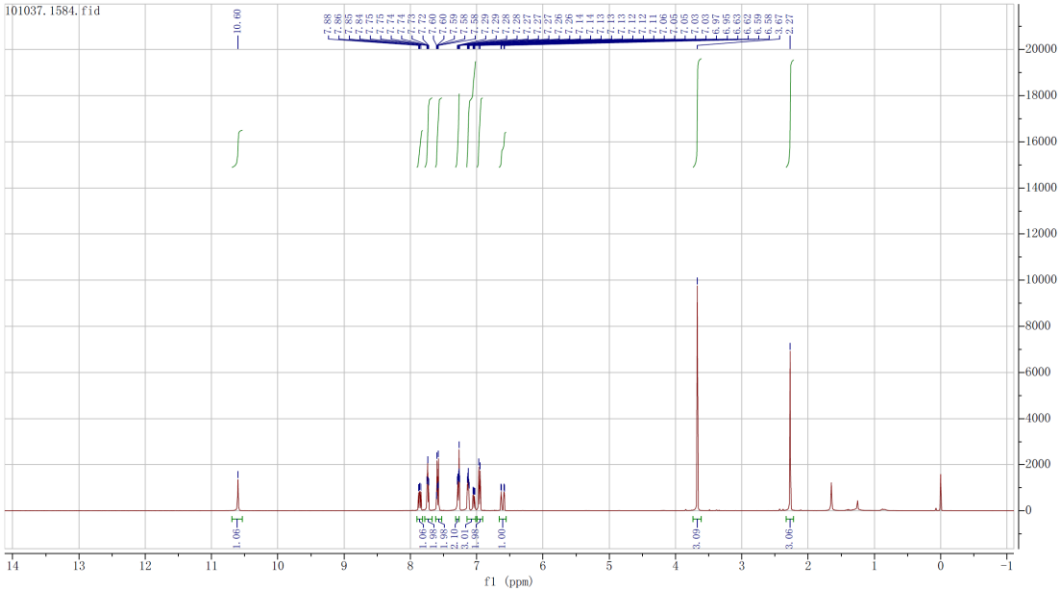


Figure 59 ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3bh**

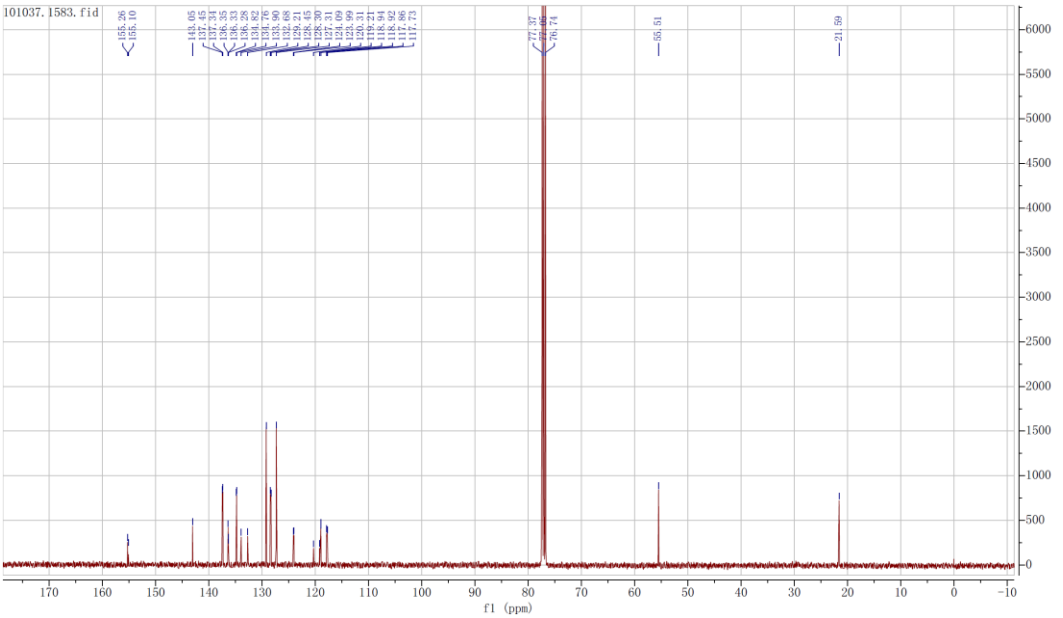
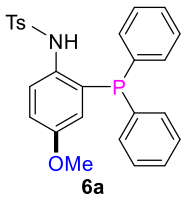


Figure 60 ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3bh**



6a

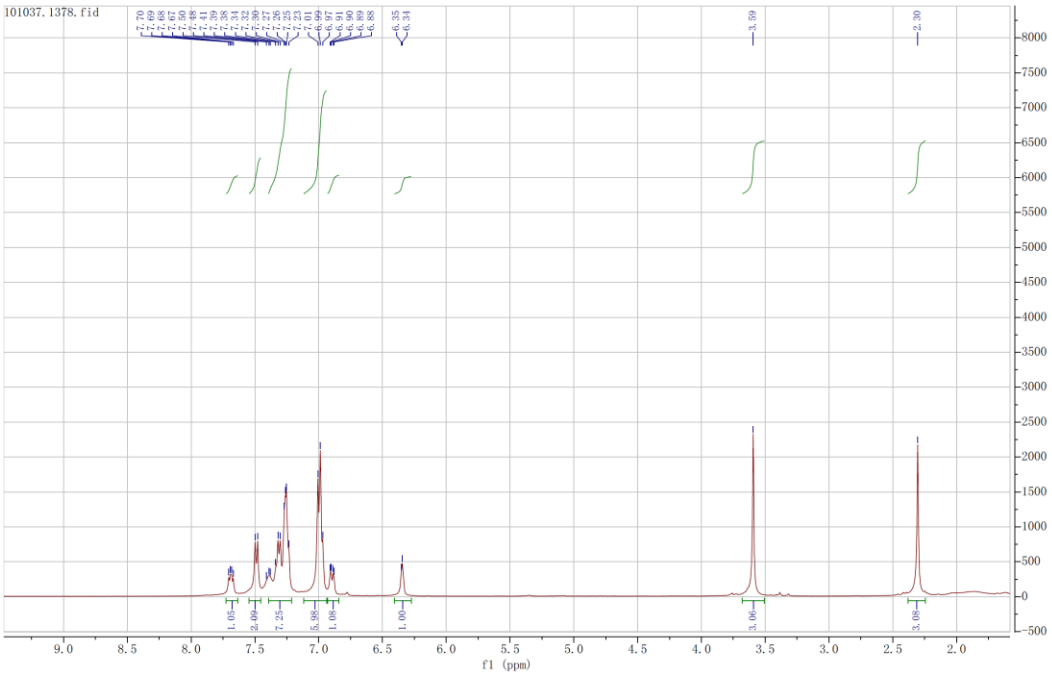


Figure 61. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6a**

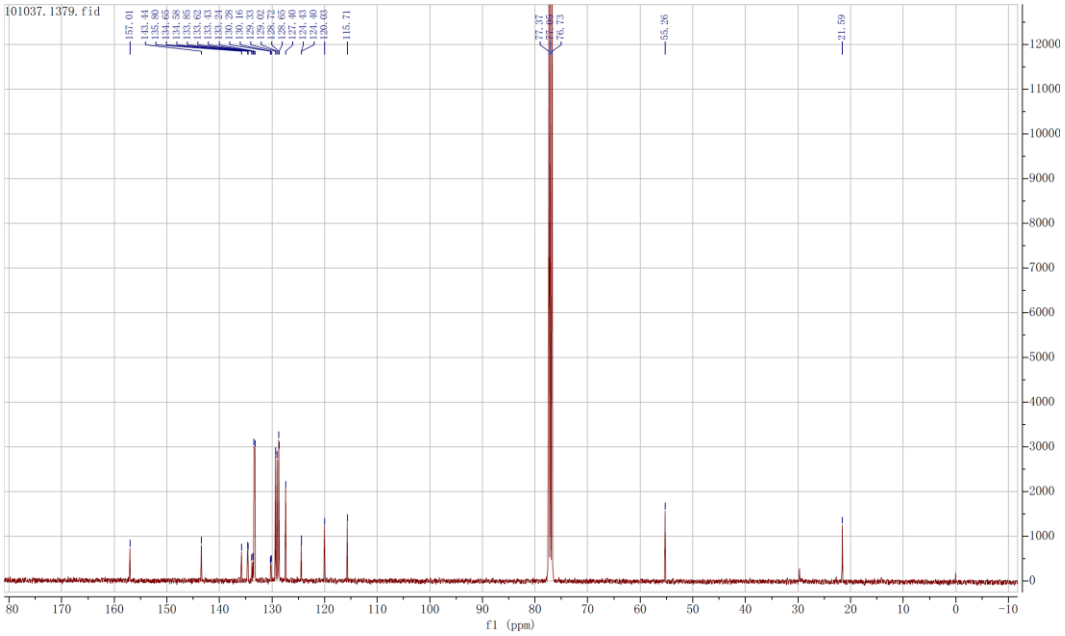


Figure 62. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6a**

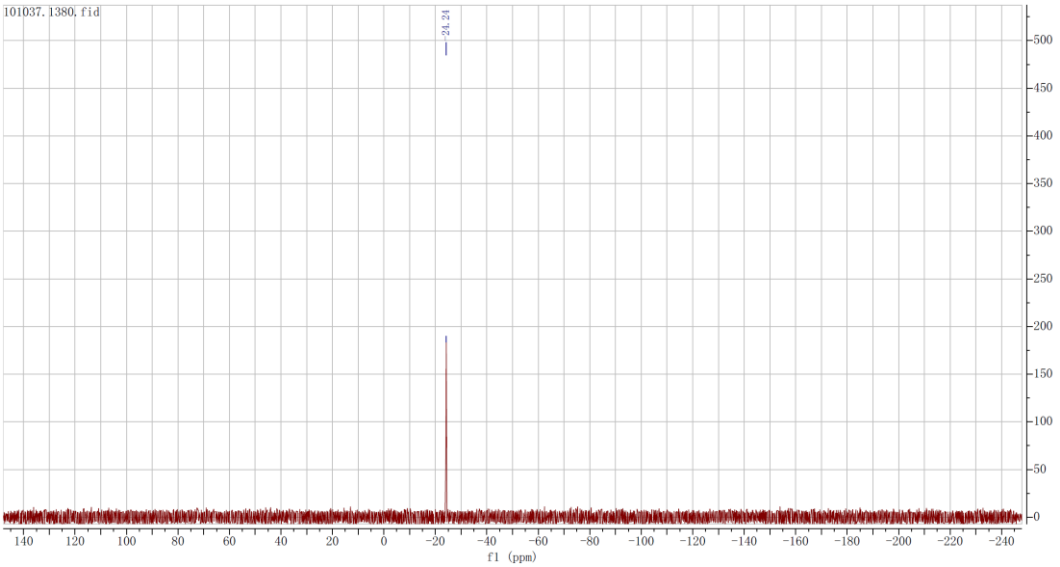
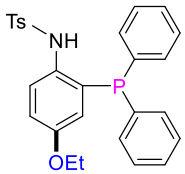


Figure 63. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6a**



6b

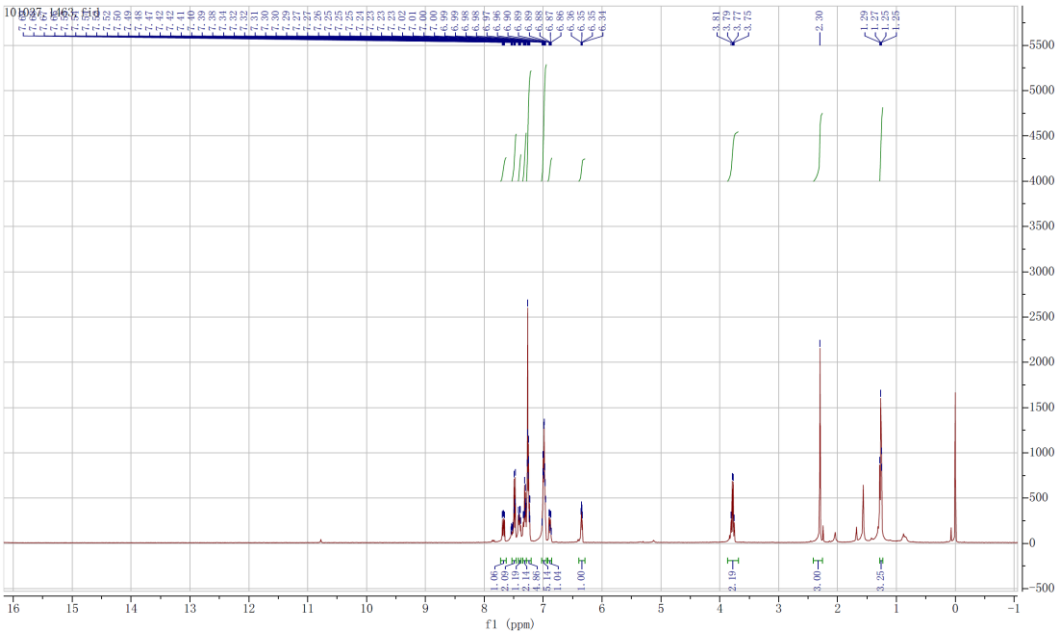


Figure 64. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6b**

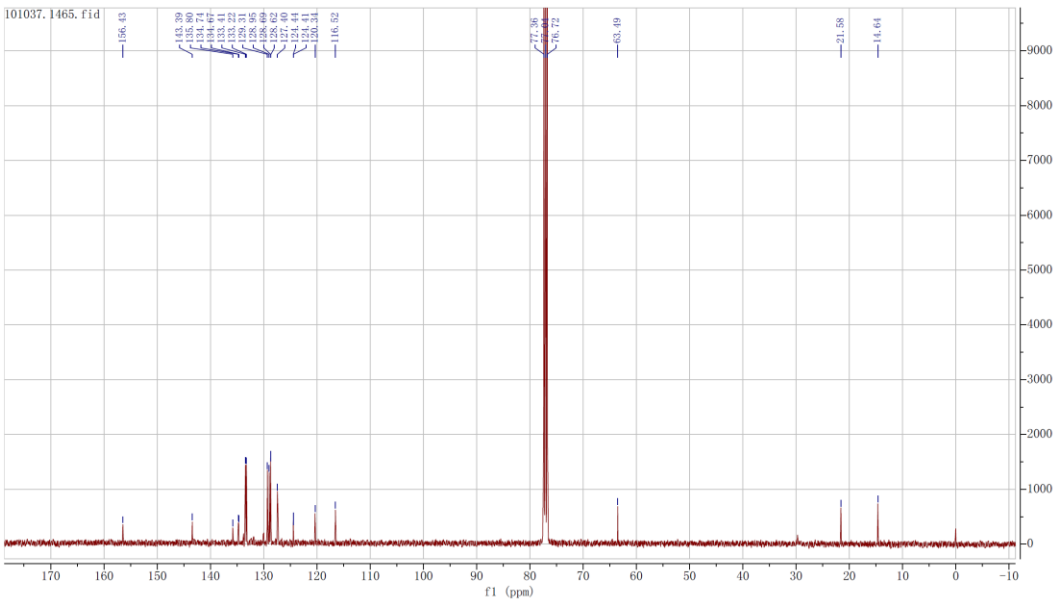


Figure 65. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6b**

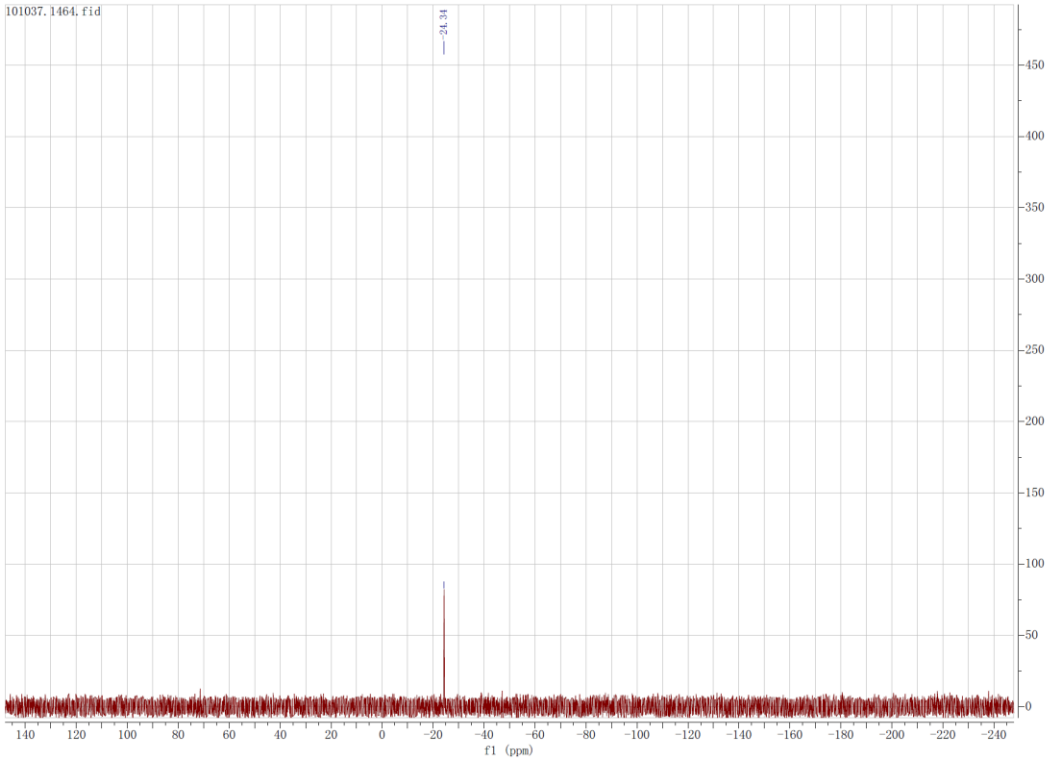
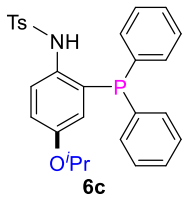


Figure 66. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6b**



6c

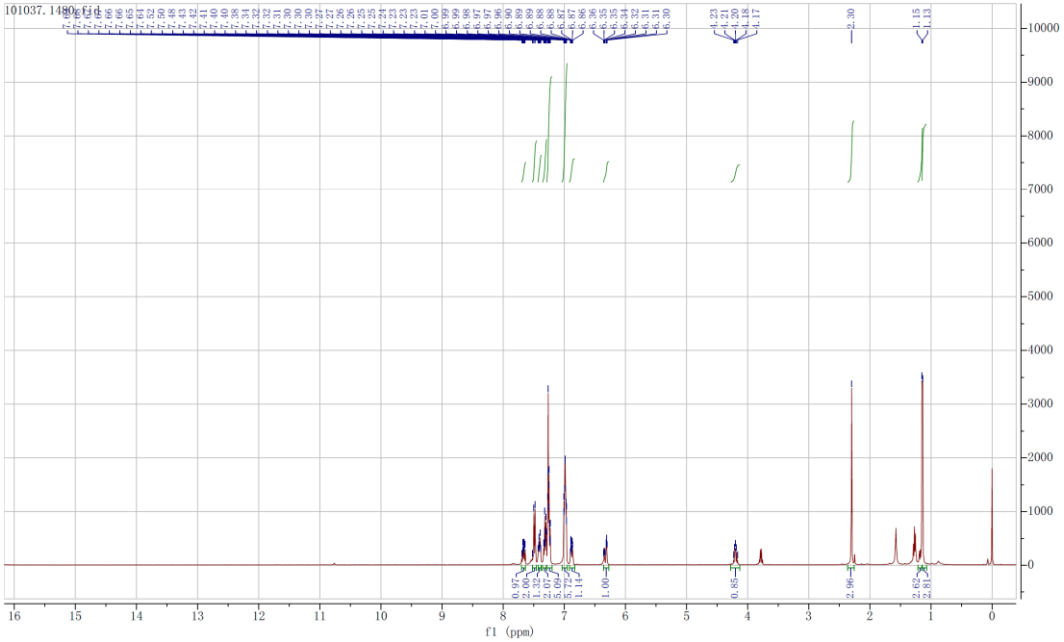


Figure 67. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6c**

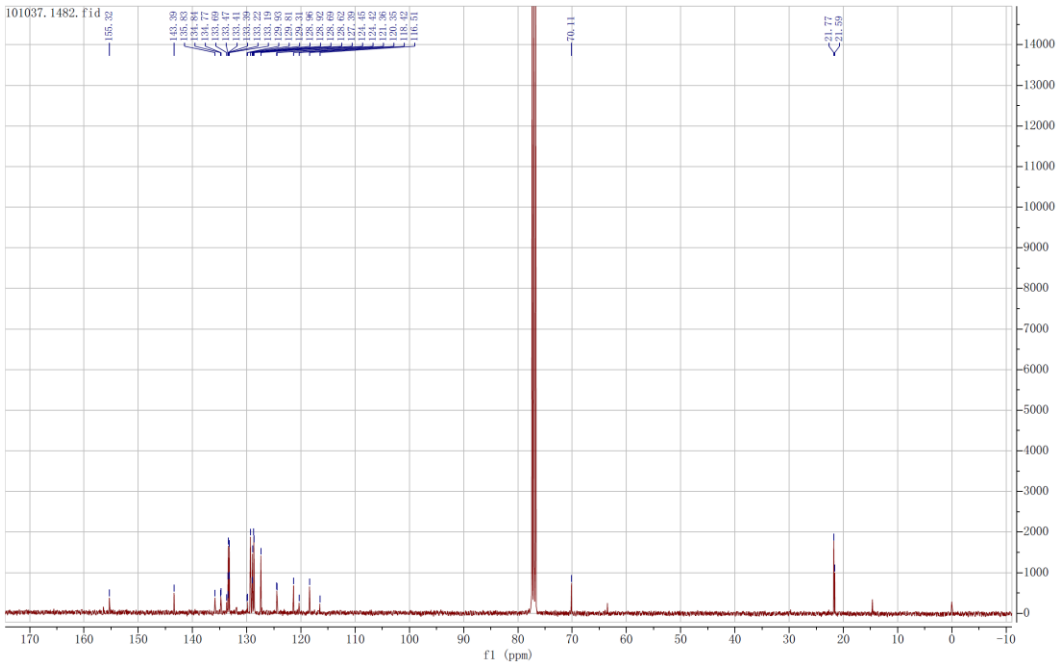


Figure 68. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6c**

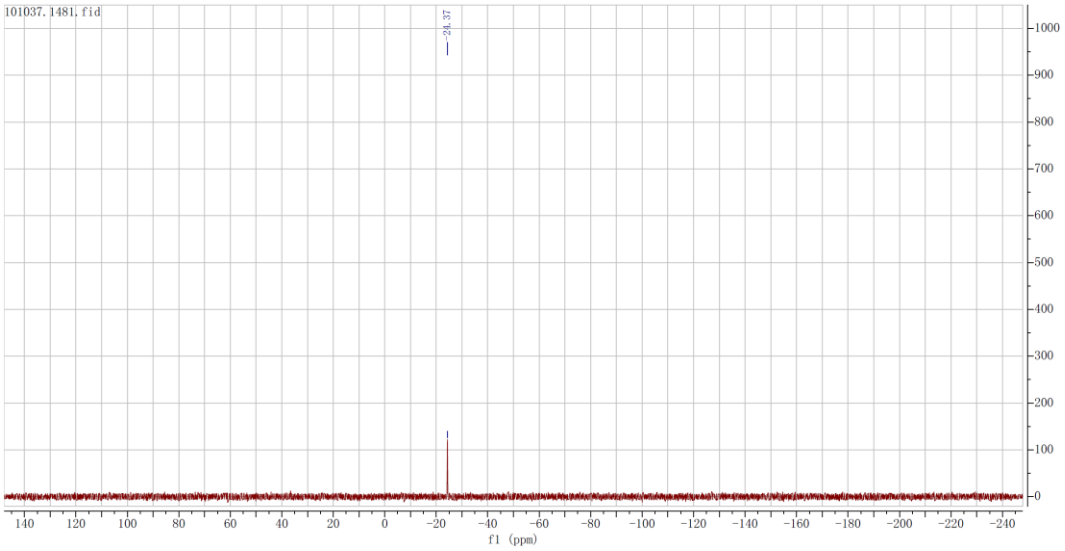
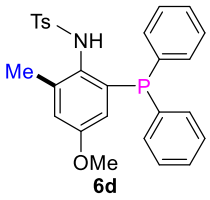


Figure 69. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6c**



6d

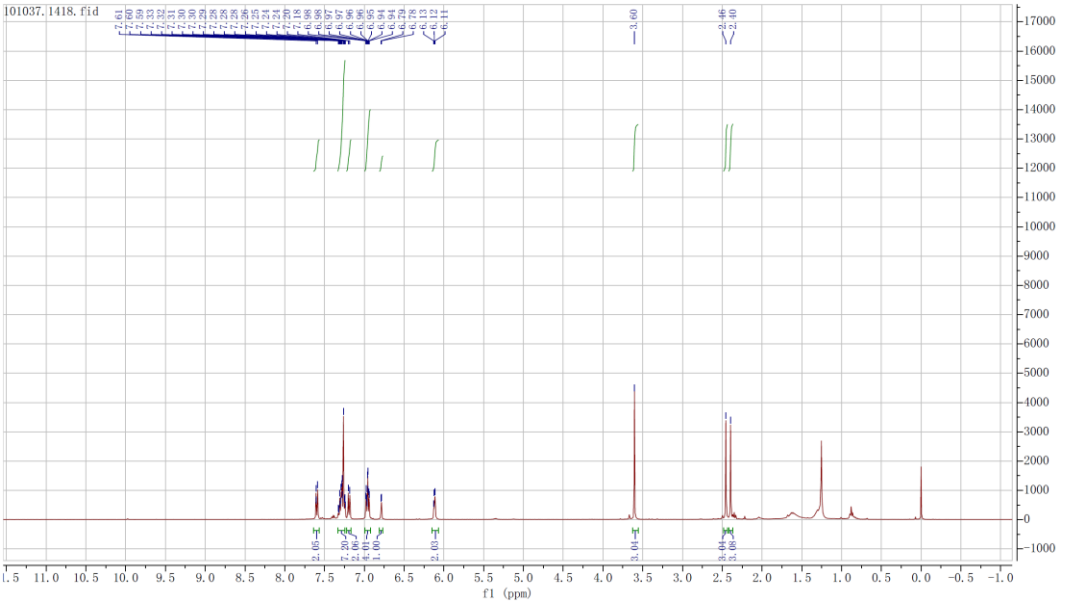


Figure 70. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6d**

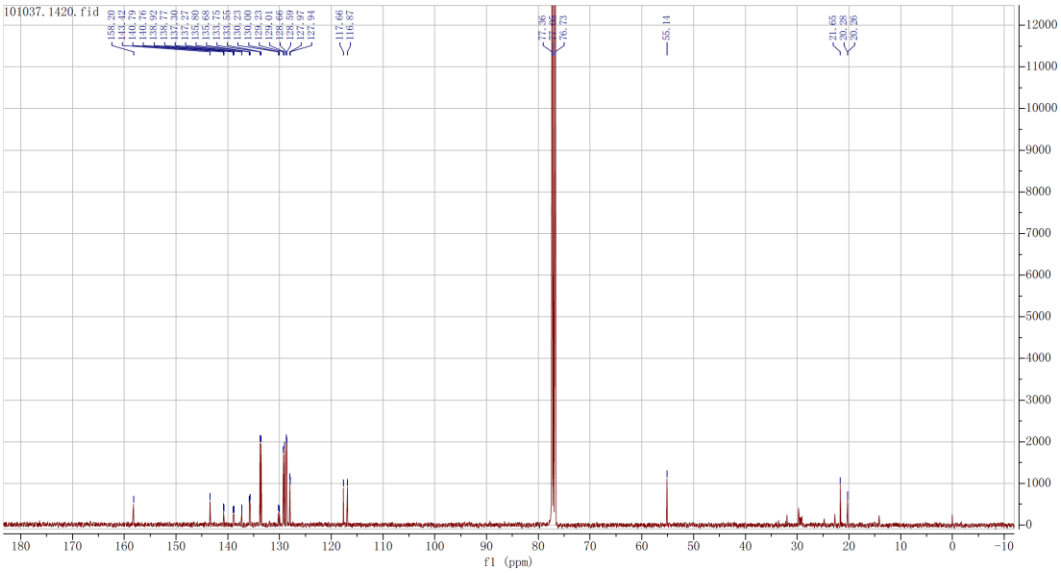


Figure 71. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6d**

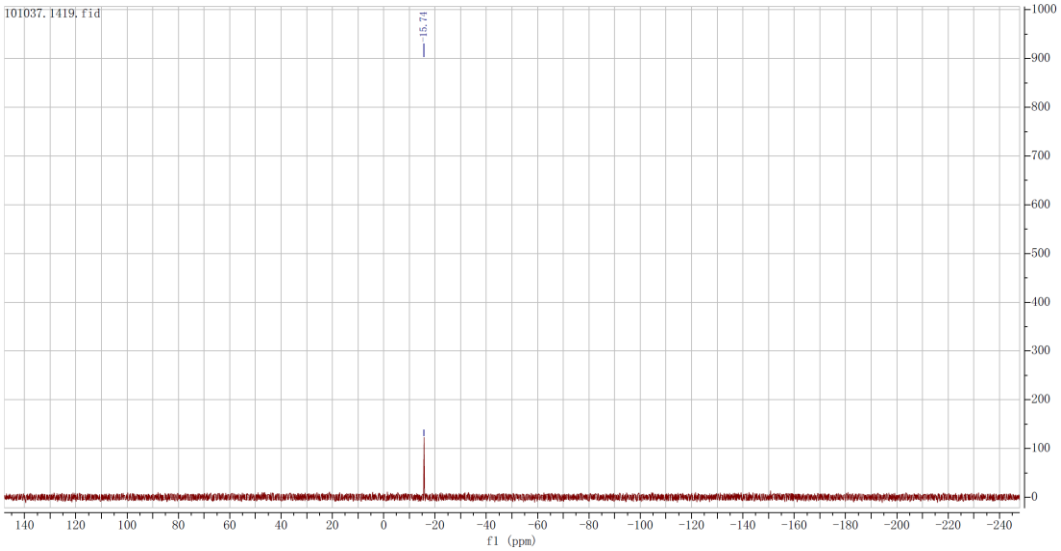
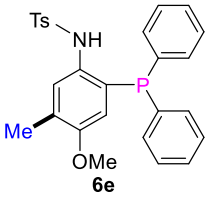


Figure 72. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6d**



6e

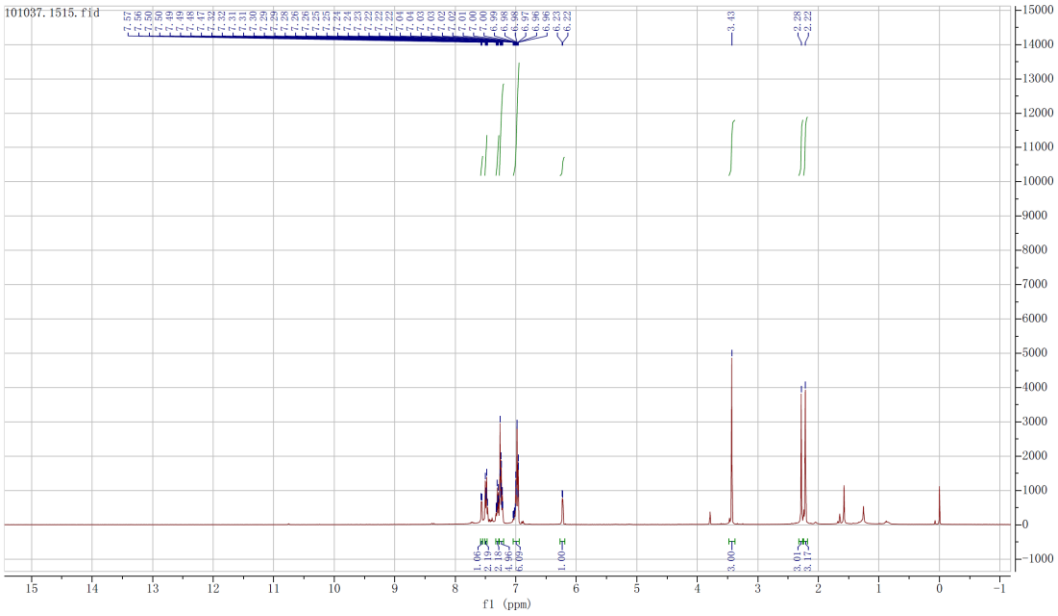


Figure 73. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6e**

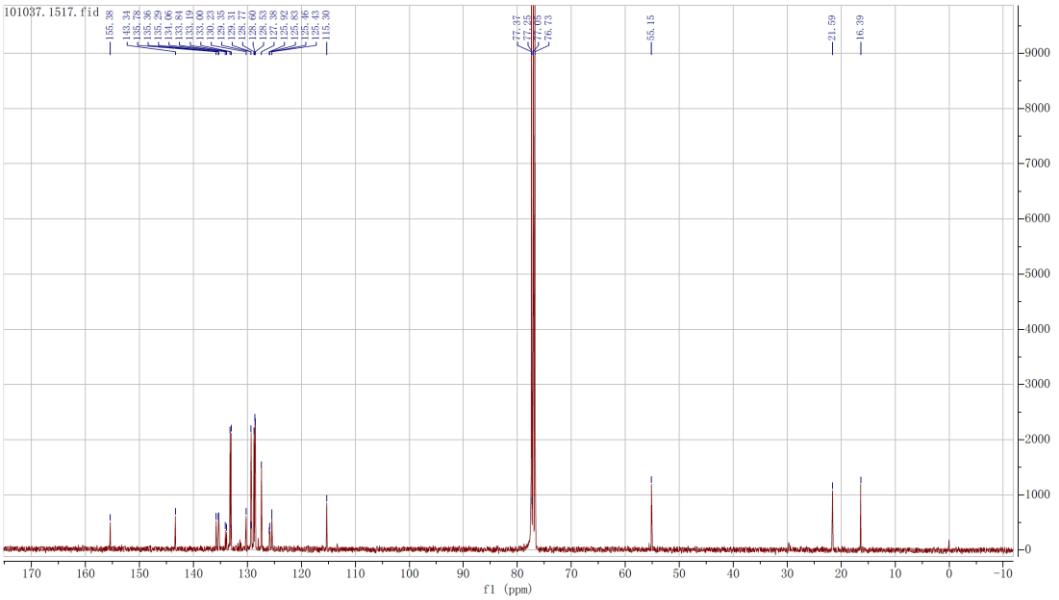


Figure 74. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6e**

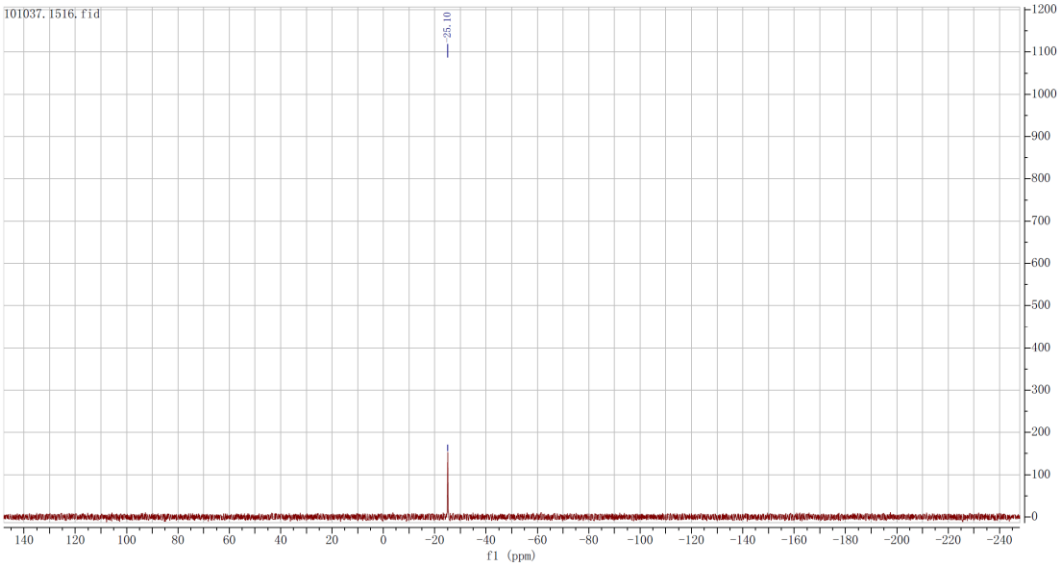
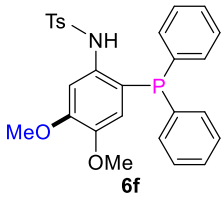


Figure 75. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6e**



6f

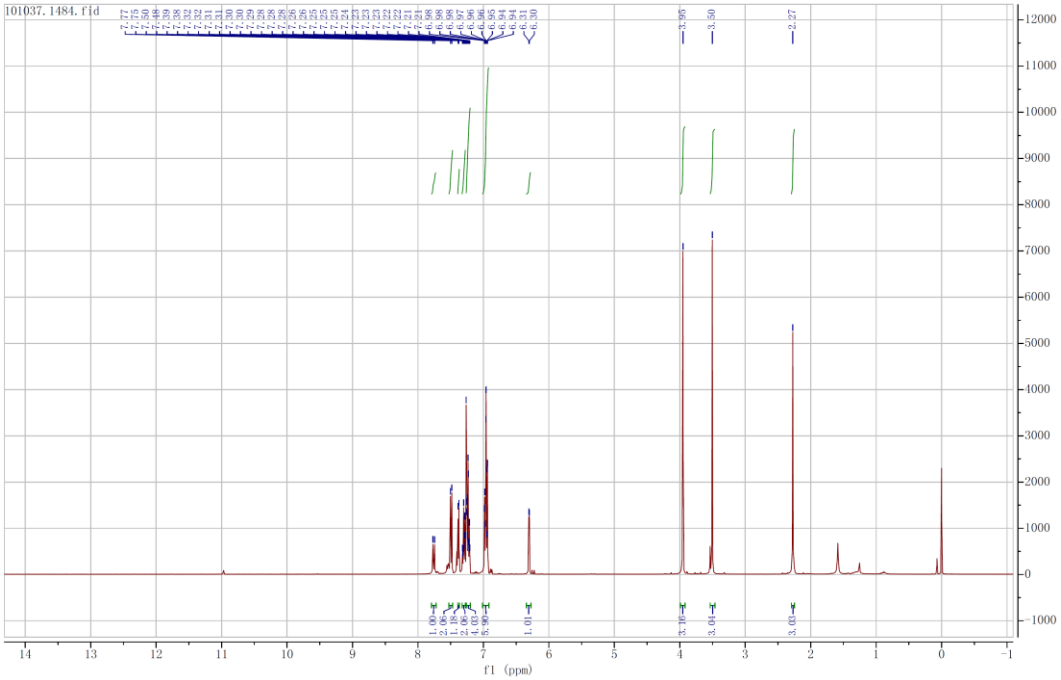


Figure 76. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6f**

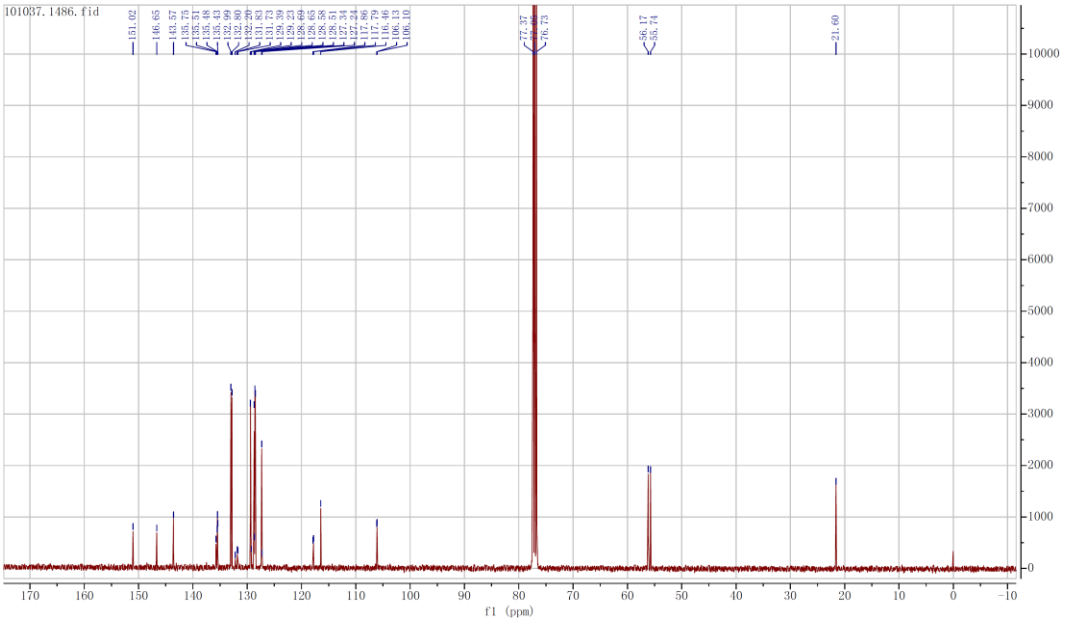


Figure 77. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6f**

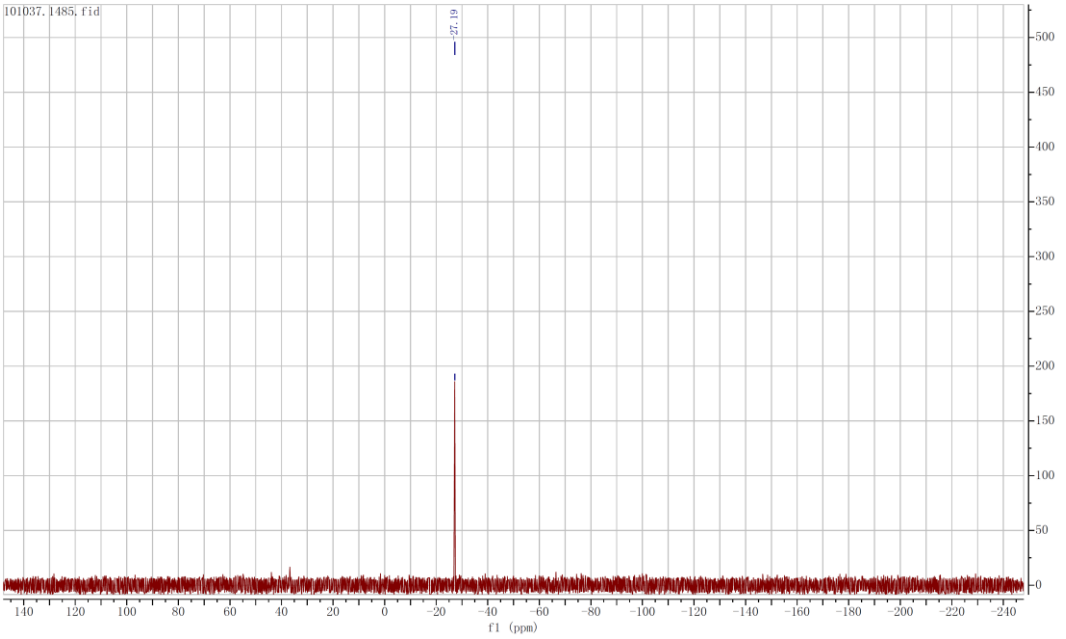
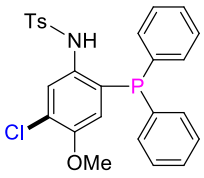


Figure 78. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6f**



6g

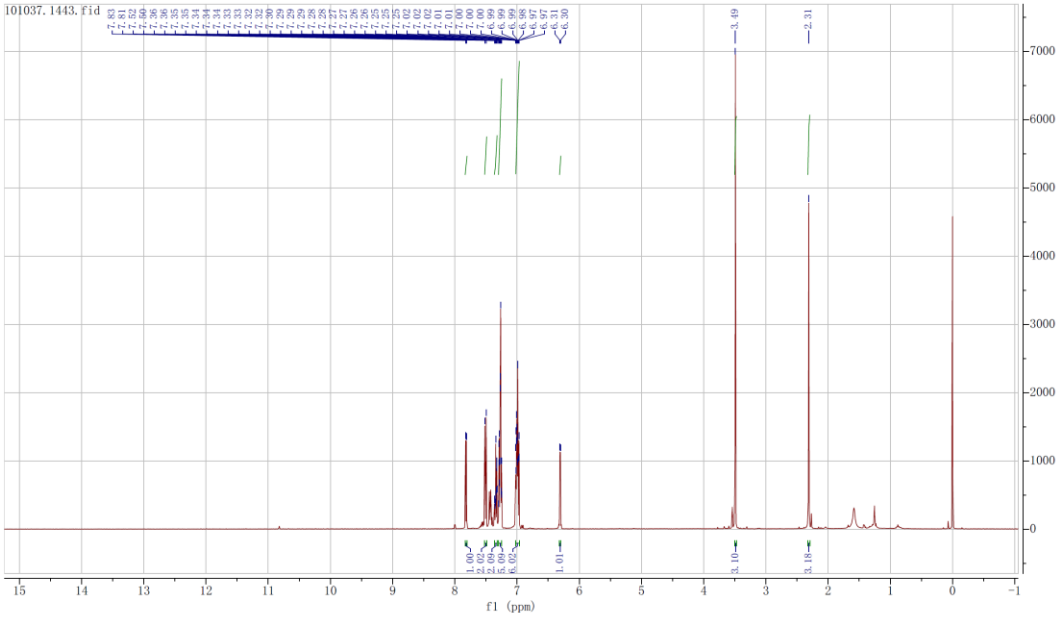


Figure 79. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6g**

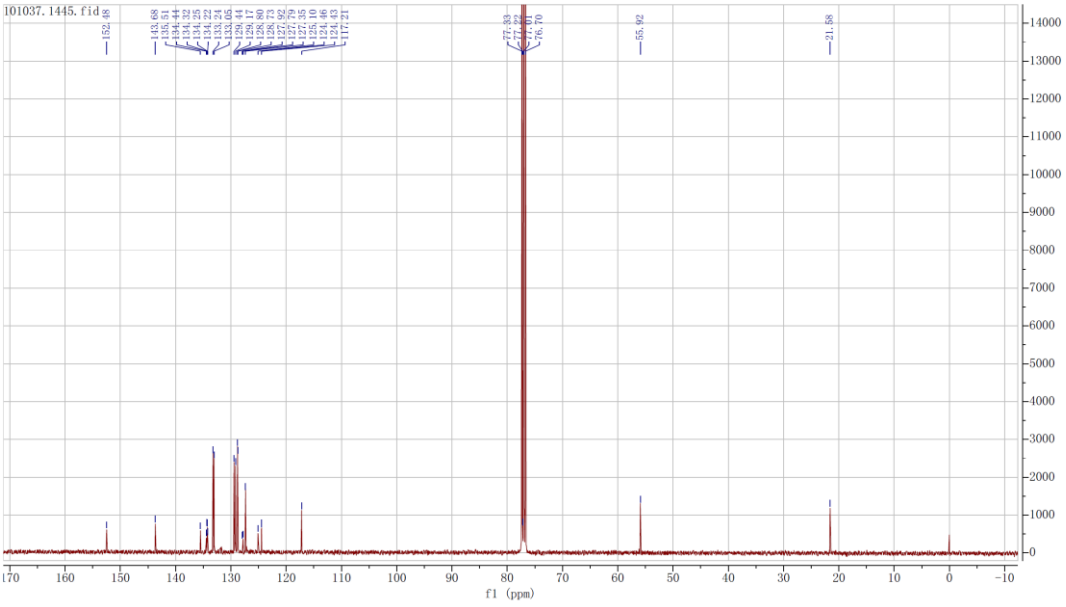


Figure 80. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6g**

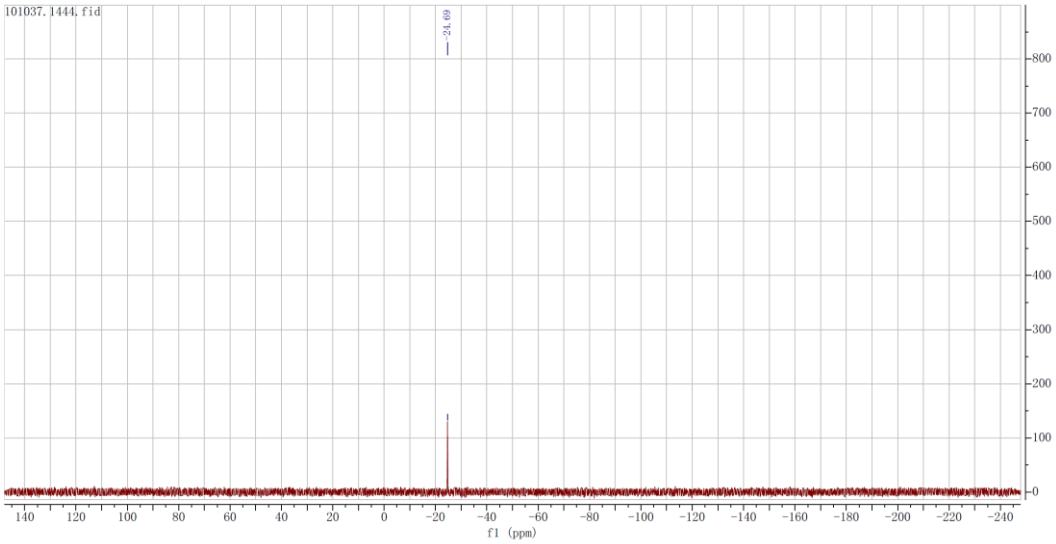
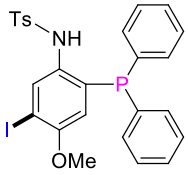


Figure 81. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6g**



6h

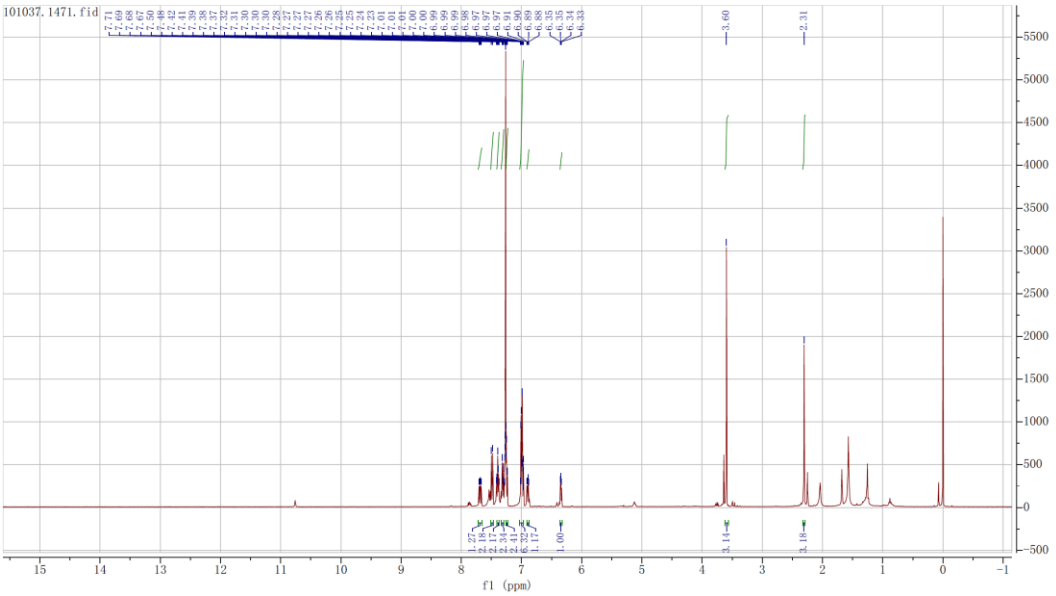


Figure 82. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6h**

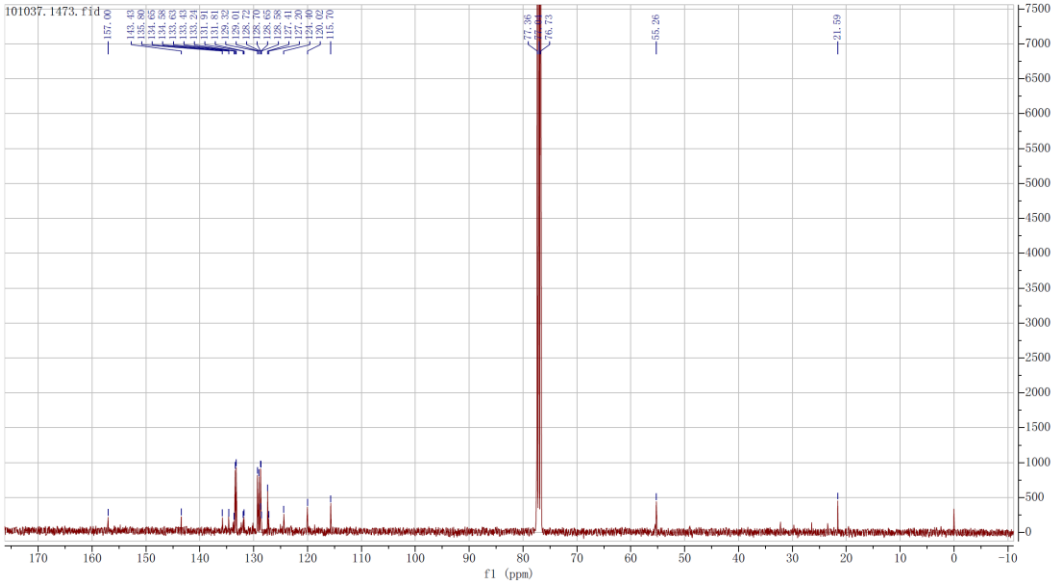


Figure 83. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6h**

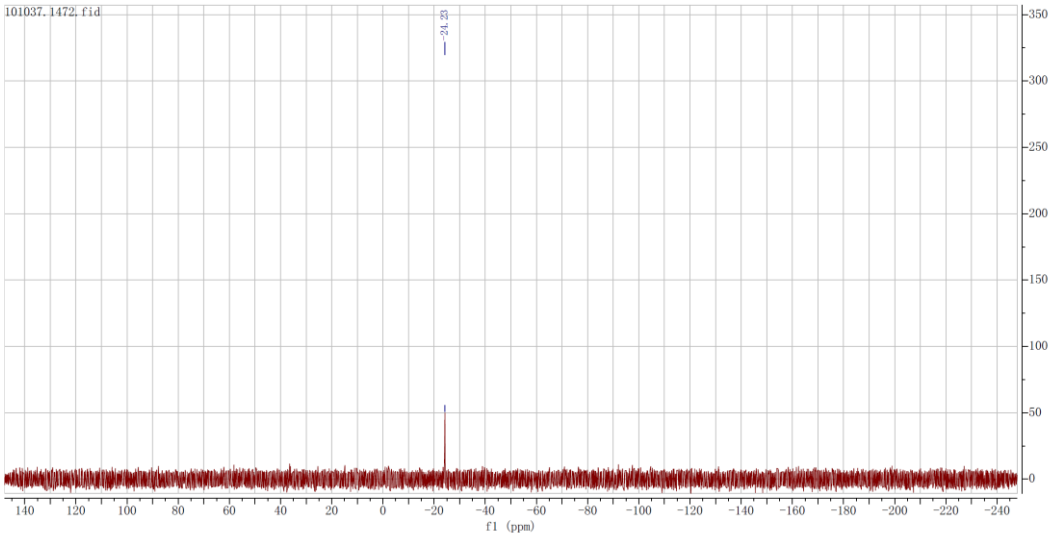
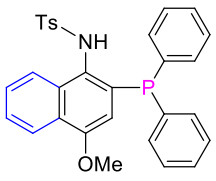


Figure 84. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6h**



6i

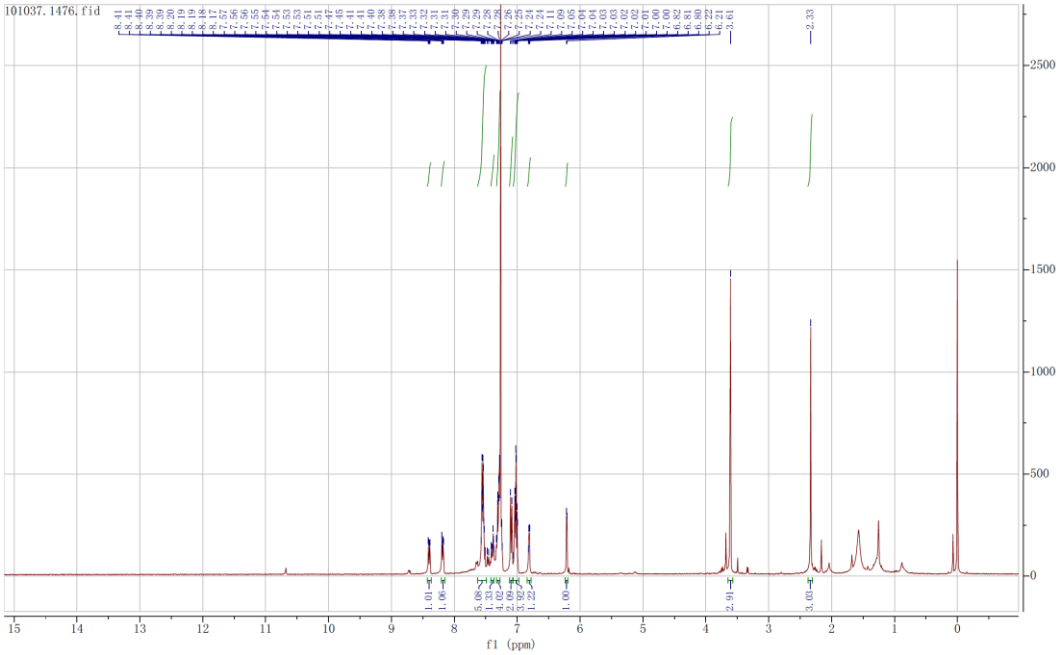


Figure 85. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6i**

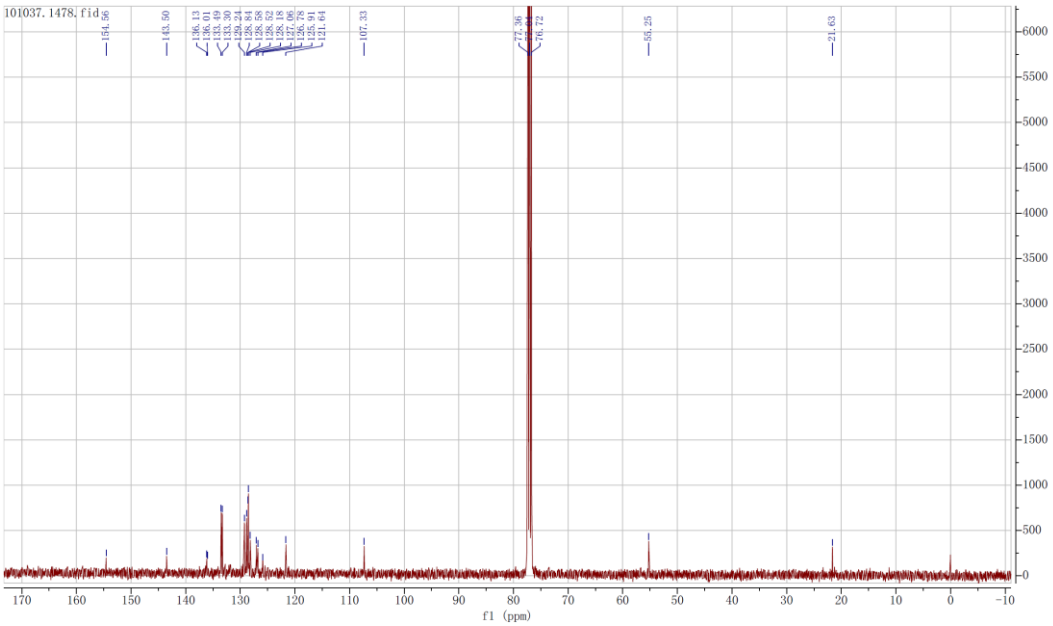


Figure 86. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6i**

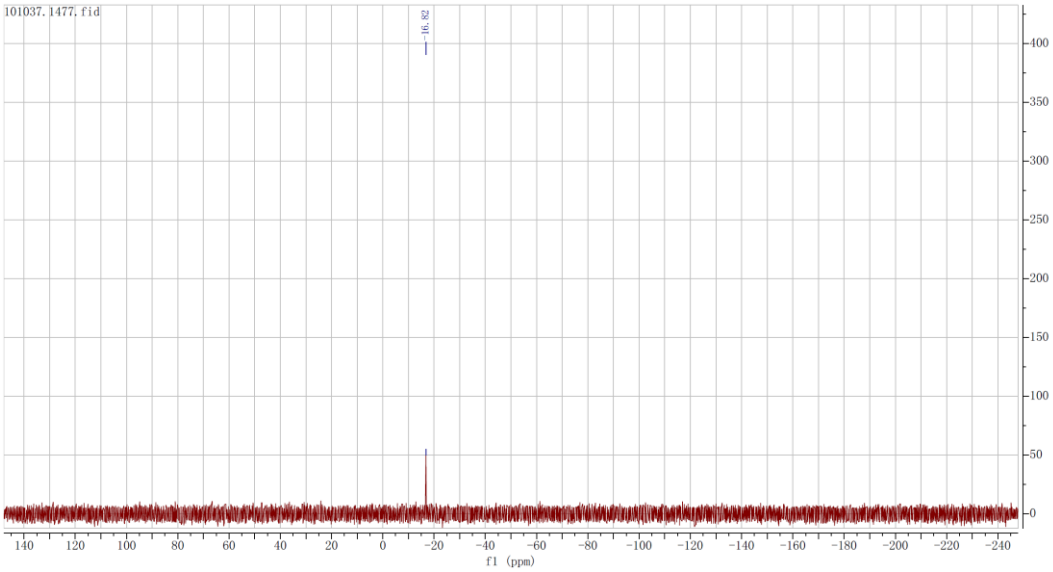
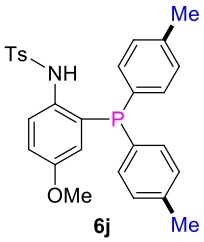


Figure 87. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6i**



6j

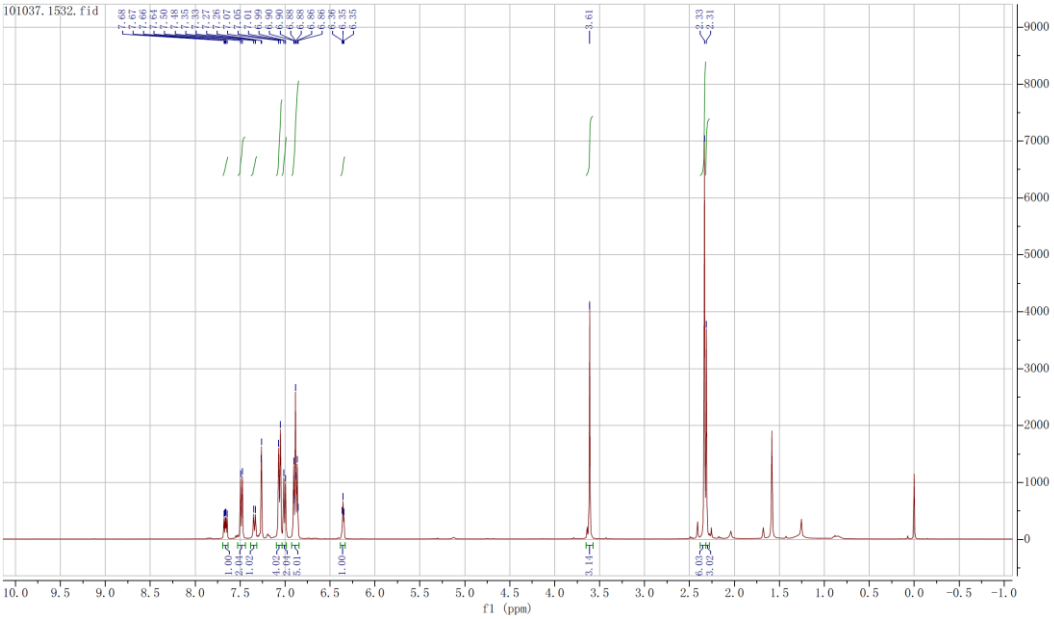


Figure 88. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6j**

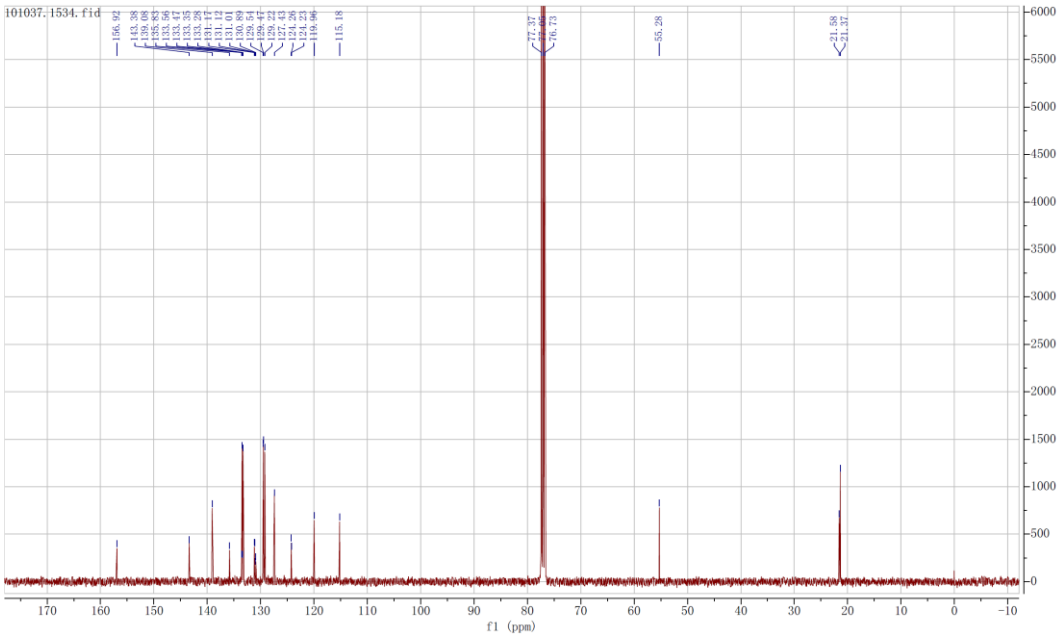


Figure 89. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6j**

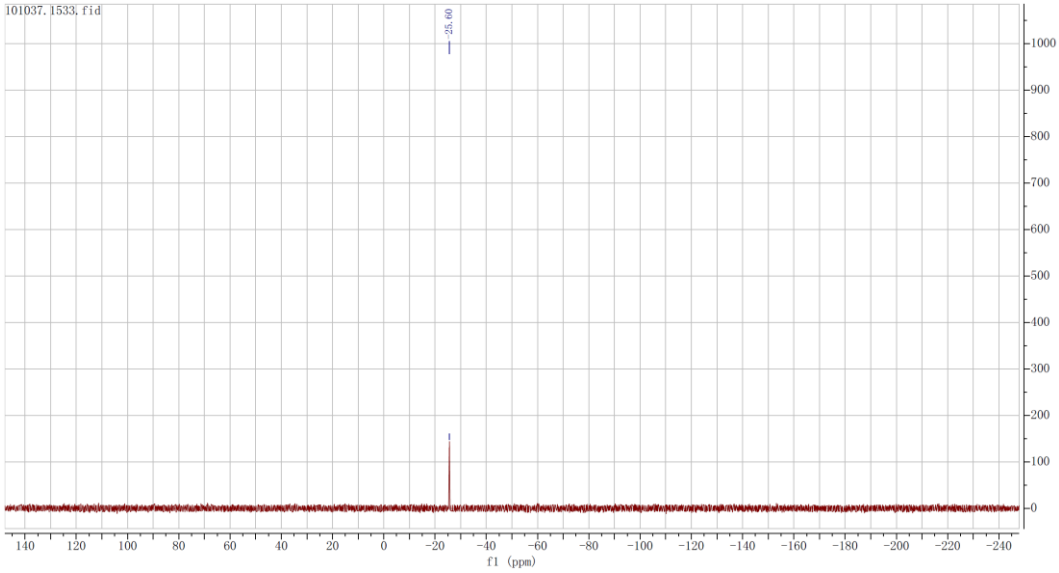


Figure 90. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6j**

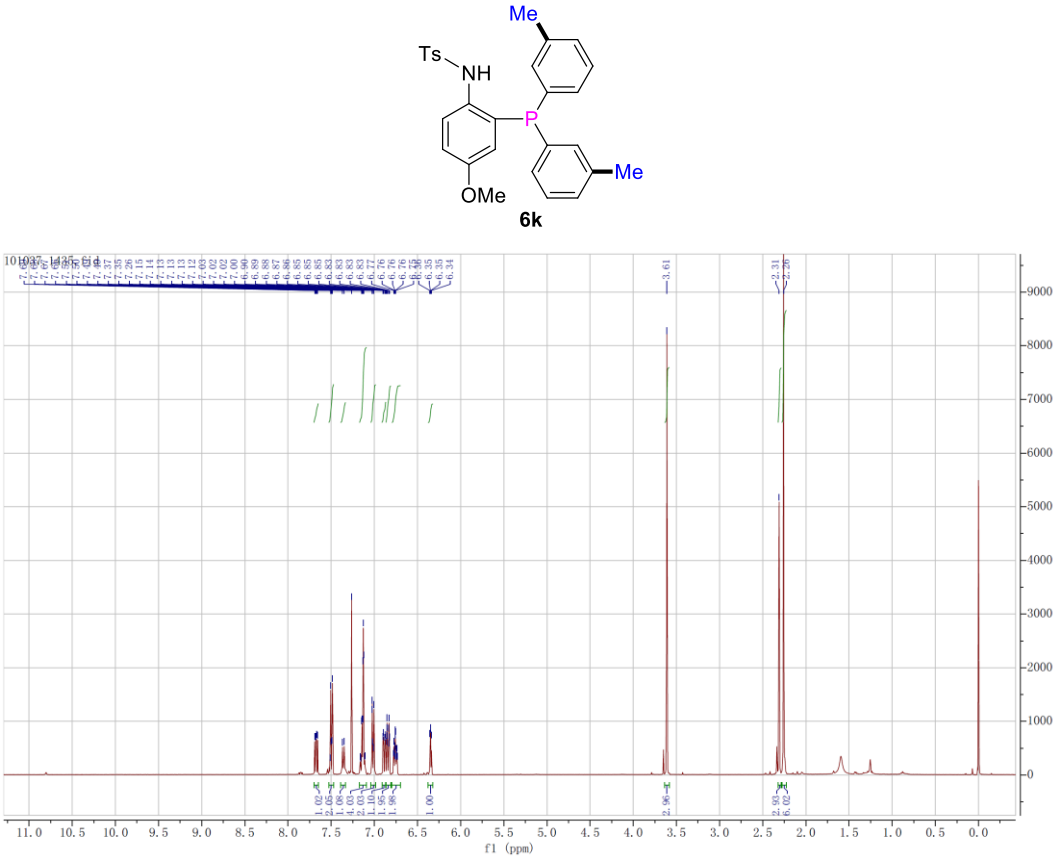


Figure 91. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6k**

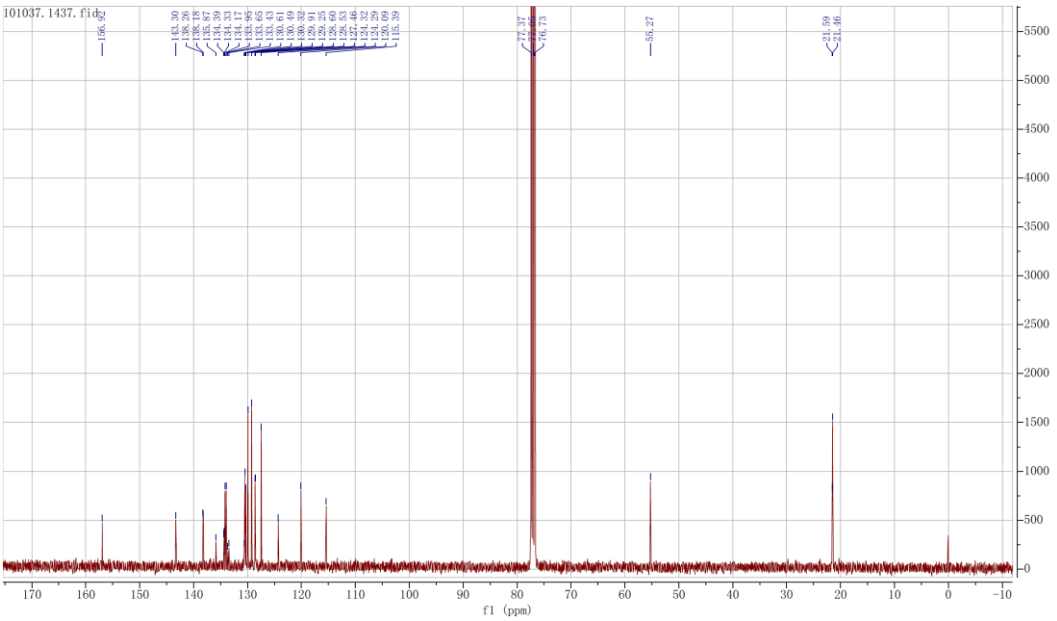


Figure 92. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6k**

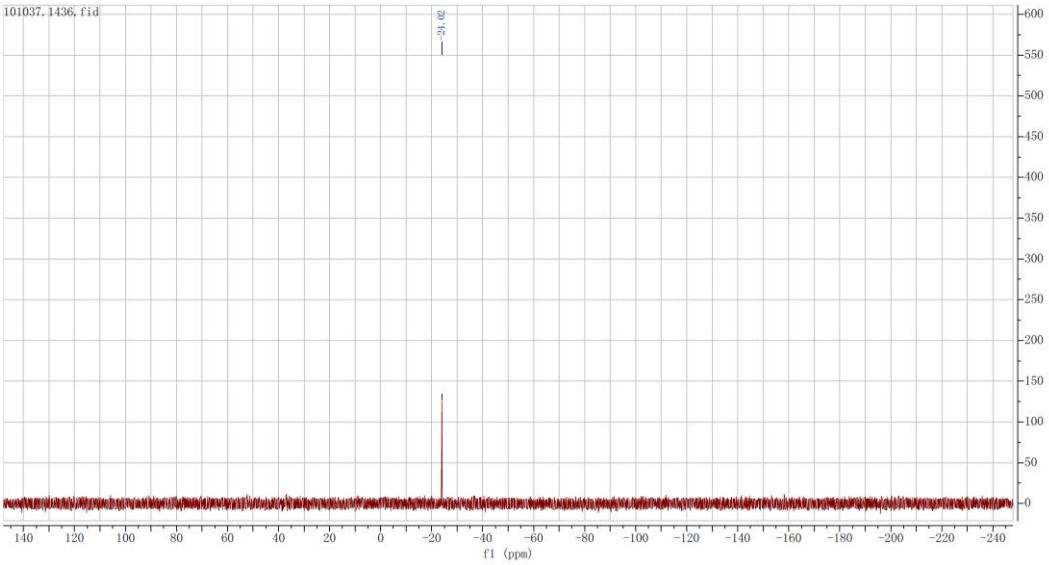
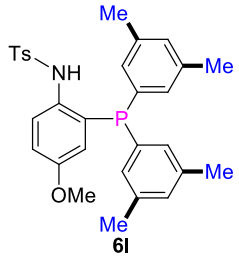


Figure 93. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6k**



6l

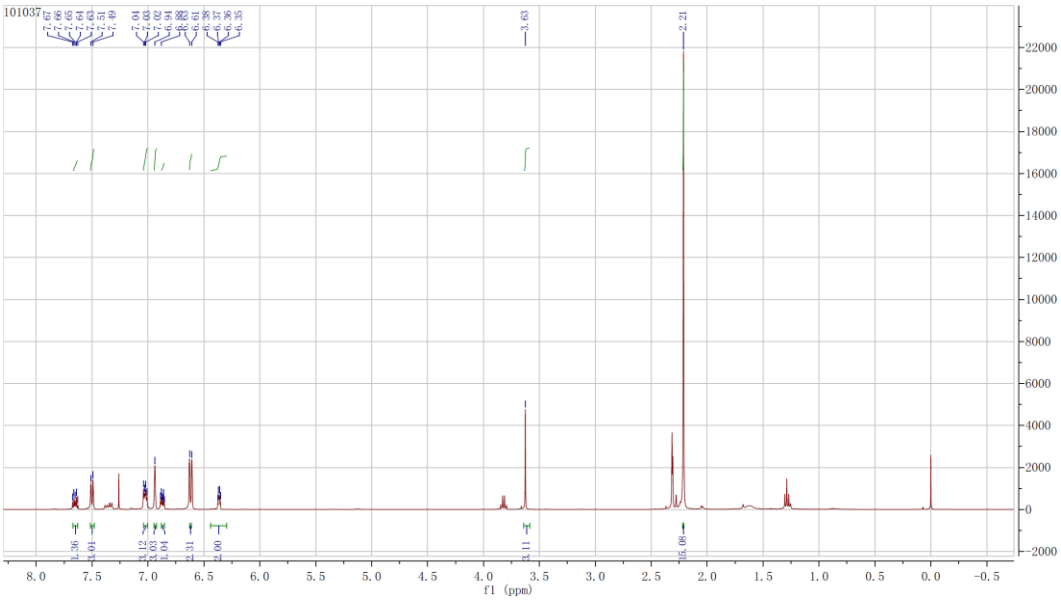


Figure 94. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6l**

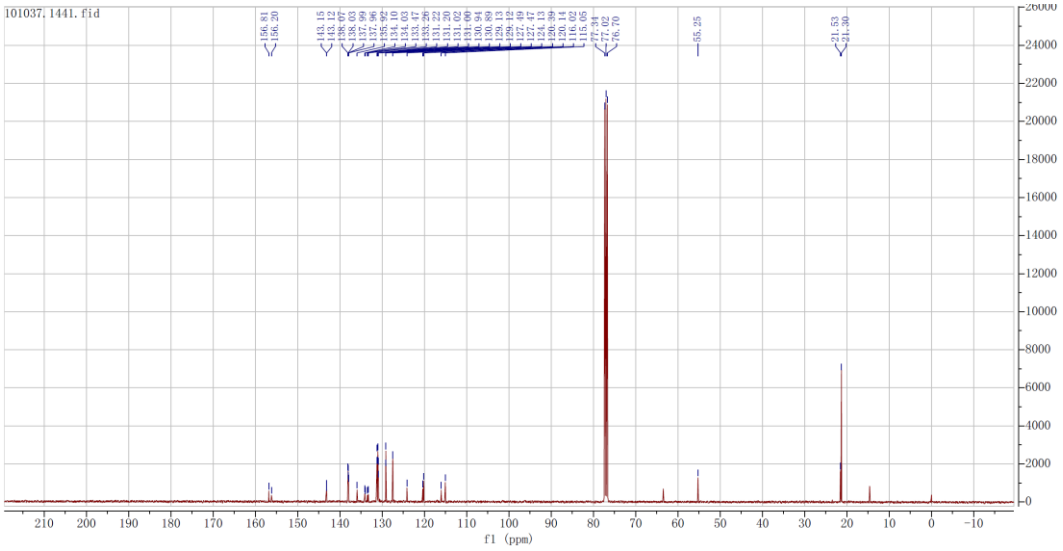


Figure 95. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6l**

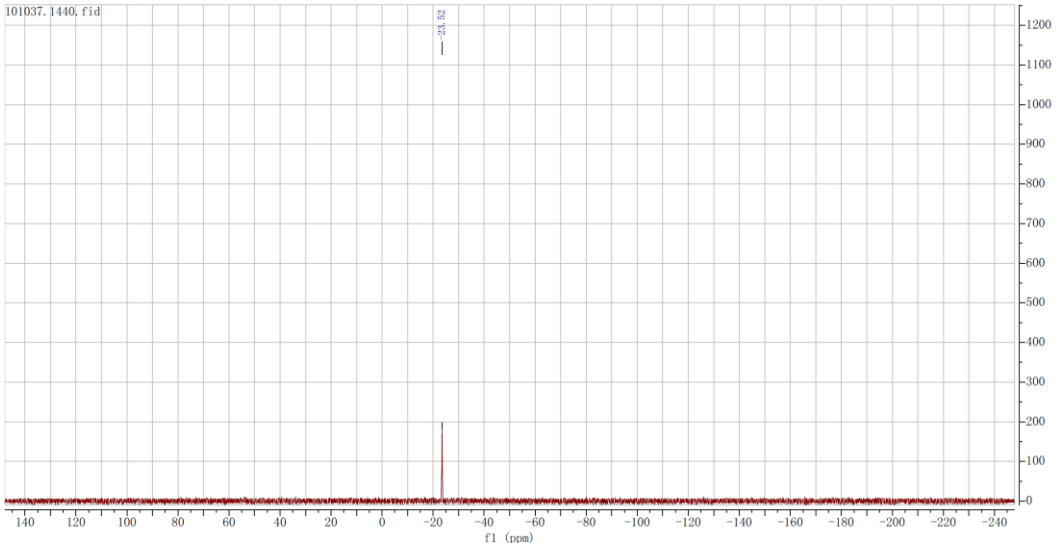


Figure 96. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6l**

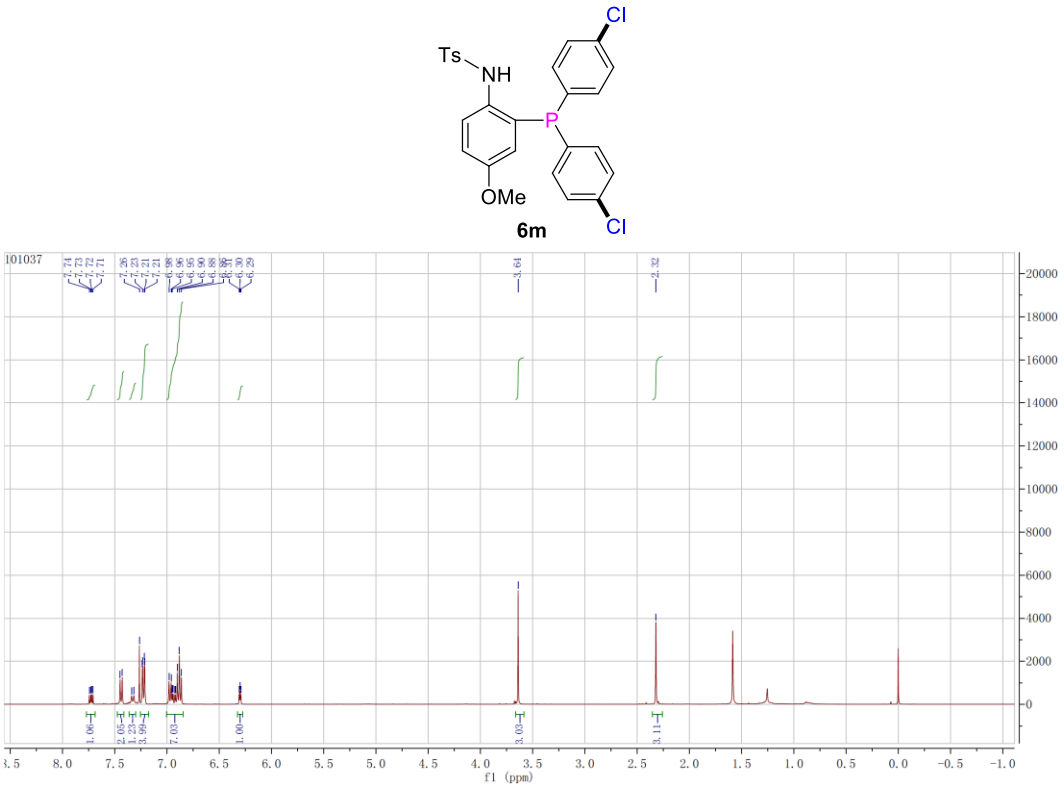


Figure 97. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6m**

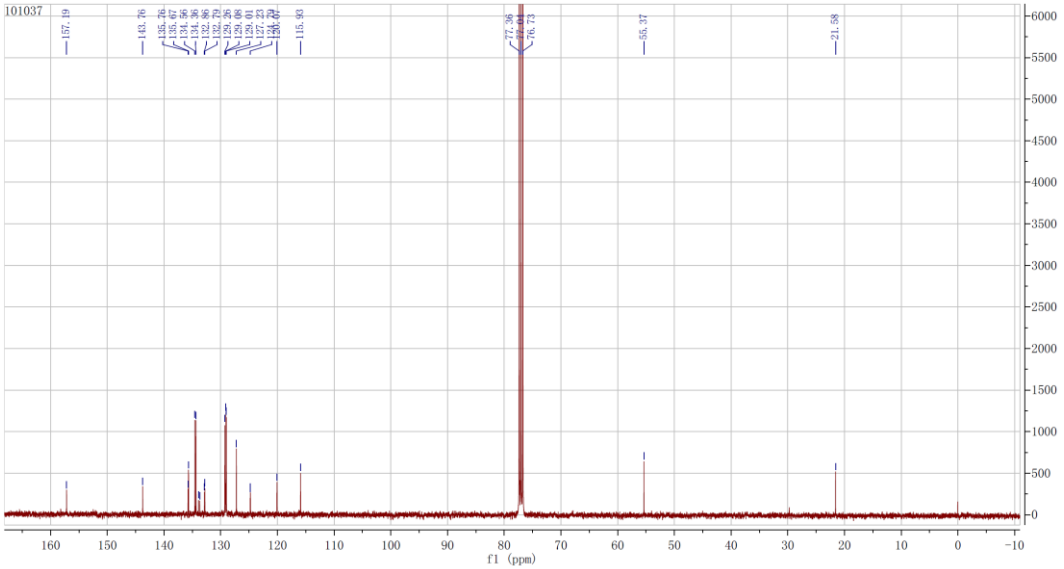


Figure 98. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6m**

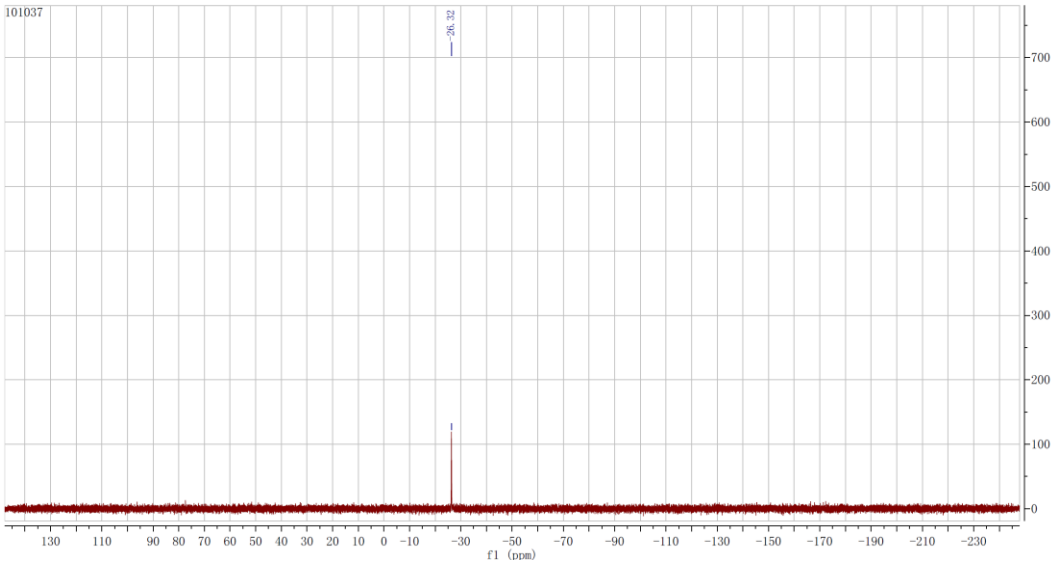
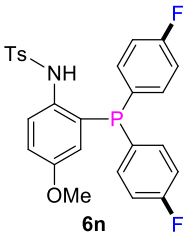


Figure 99. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6m**



6n

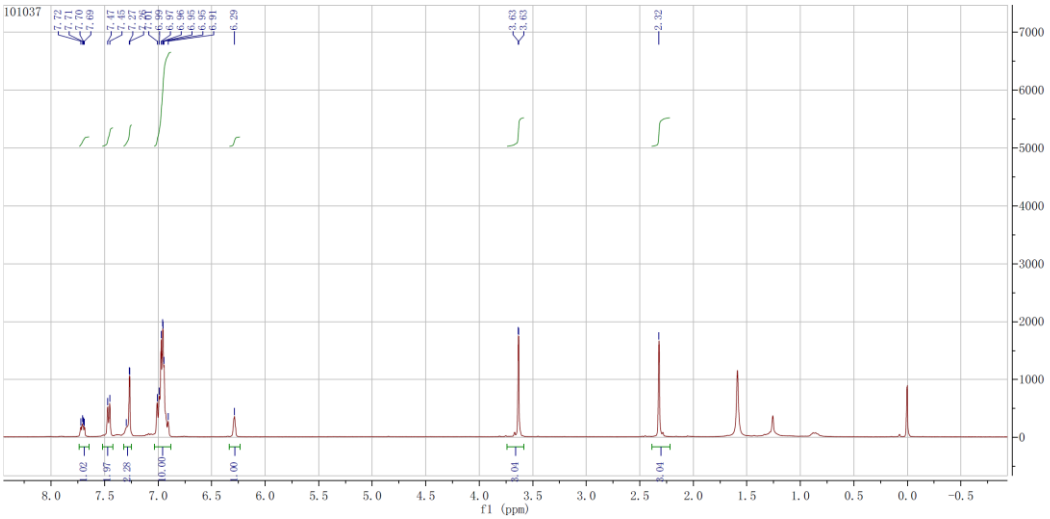


Figure 100. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6n**

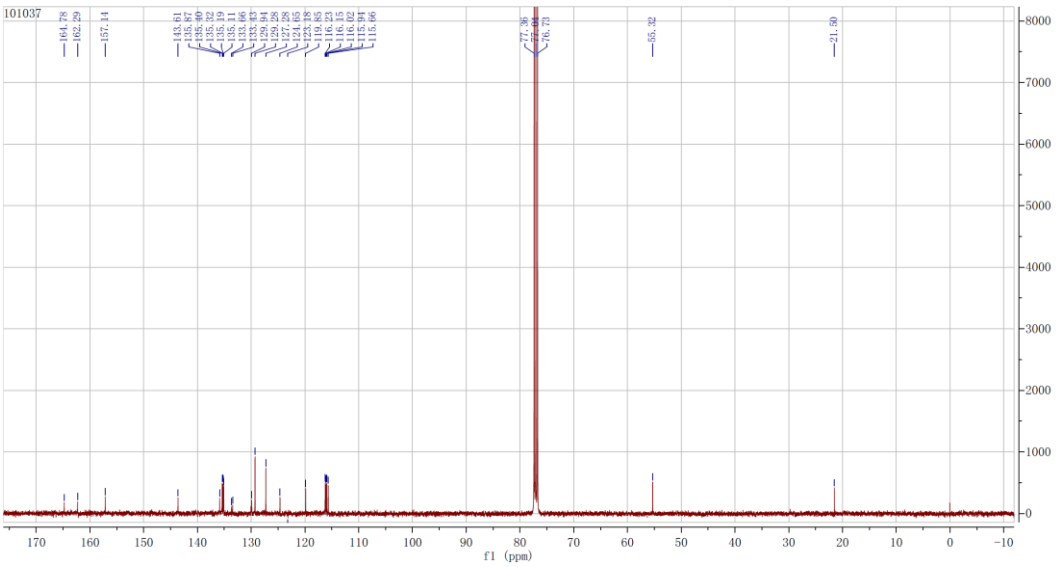


Figure 101. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6n**

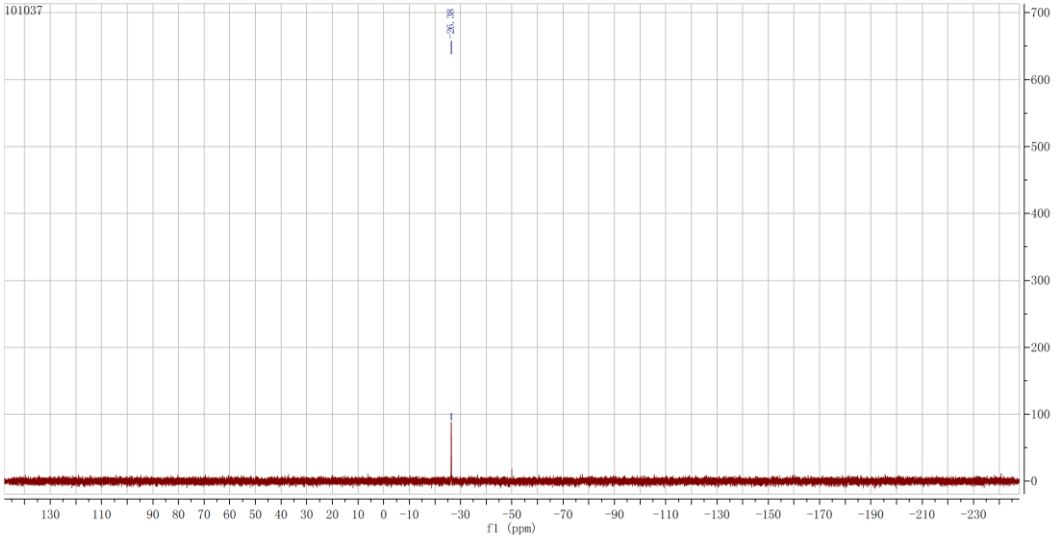
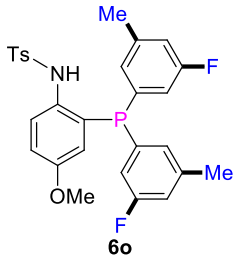


Figure 102. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6n**



6o

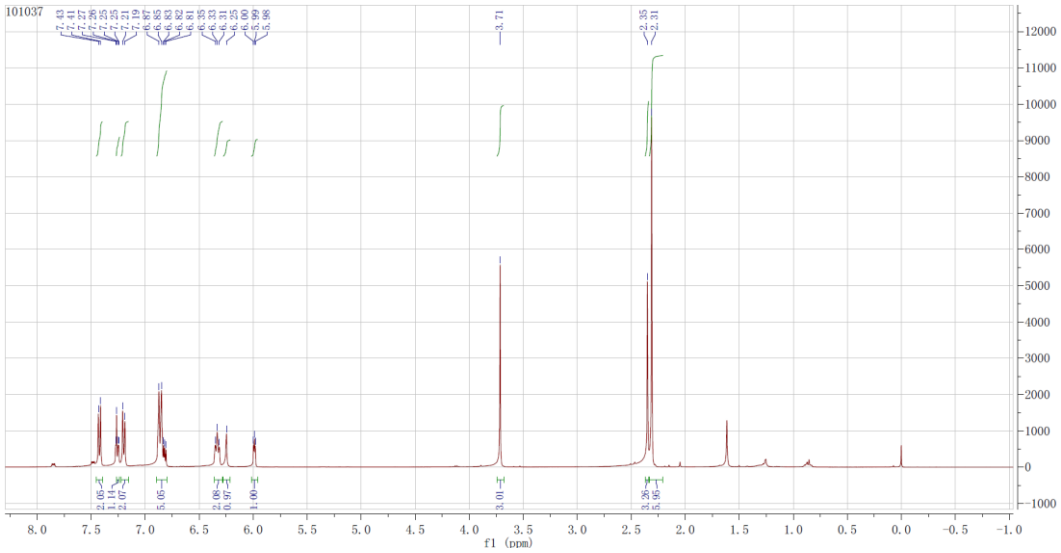


Figure 103. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6o**

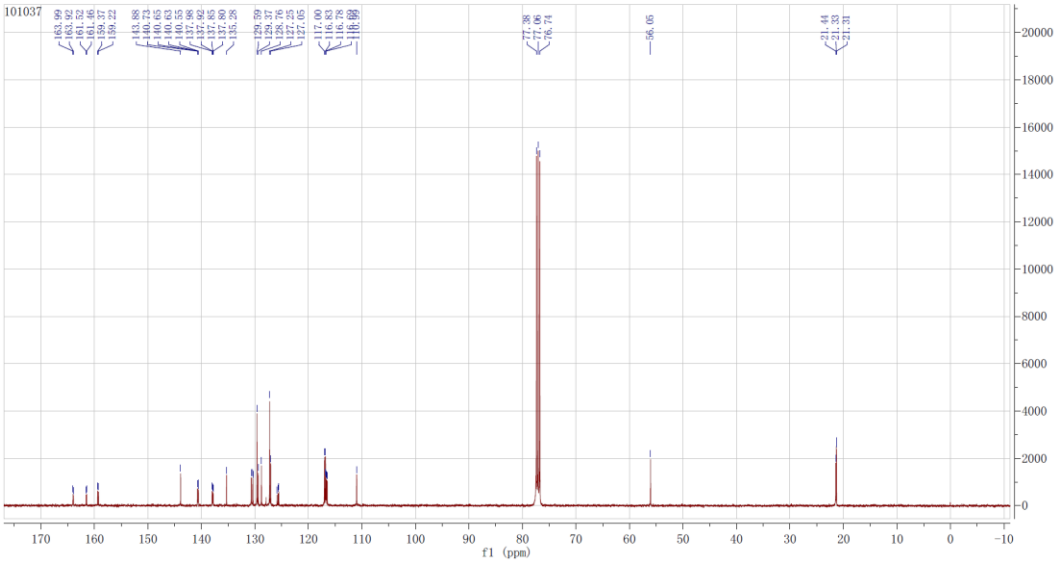


Figure 104. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6o**

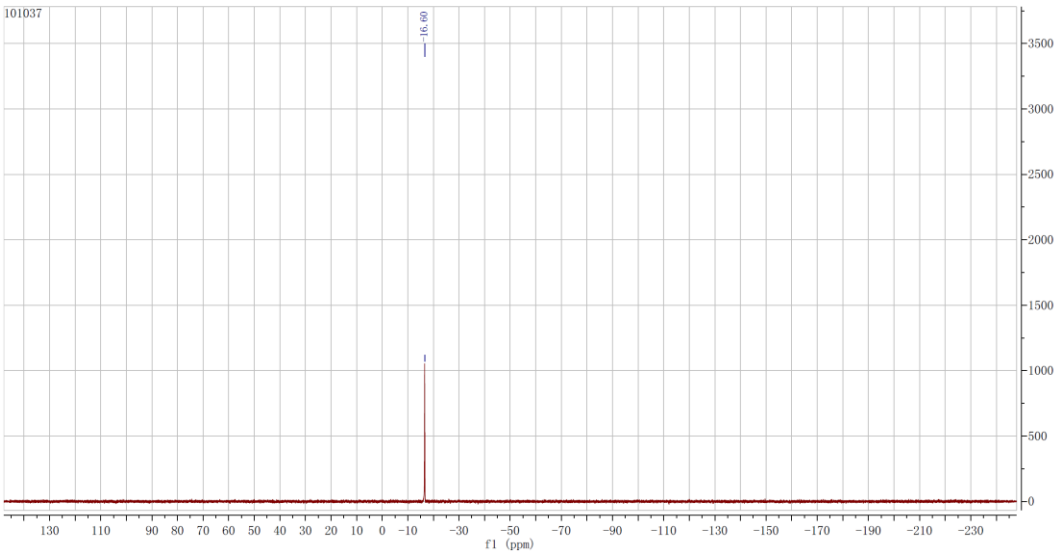
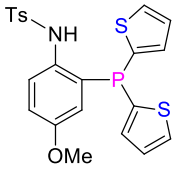


Figure 105. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6o**



6p

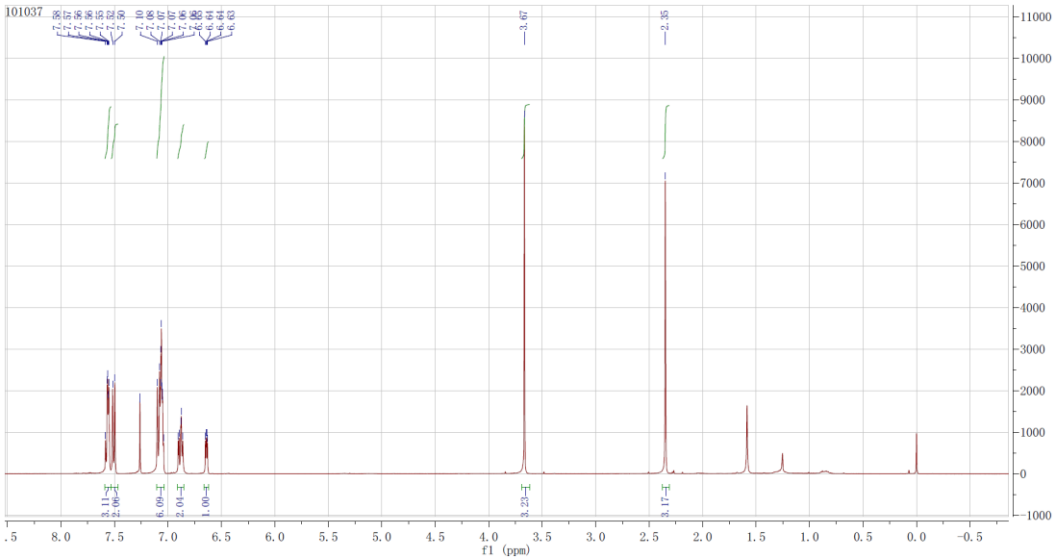


Figure 106. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6p**

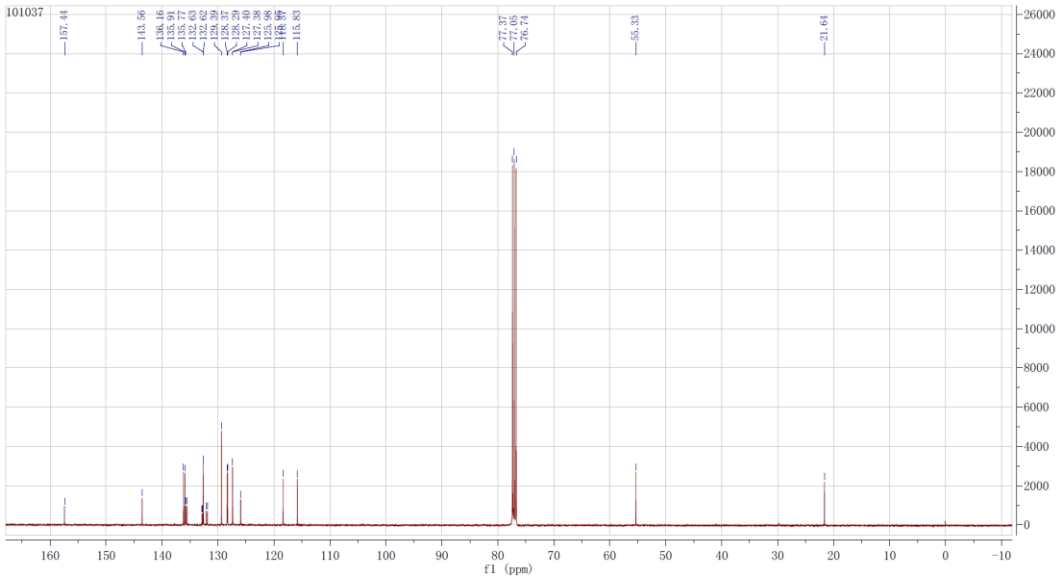


Figure 107. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6p**

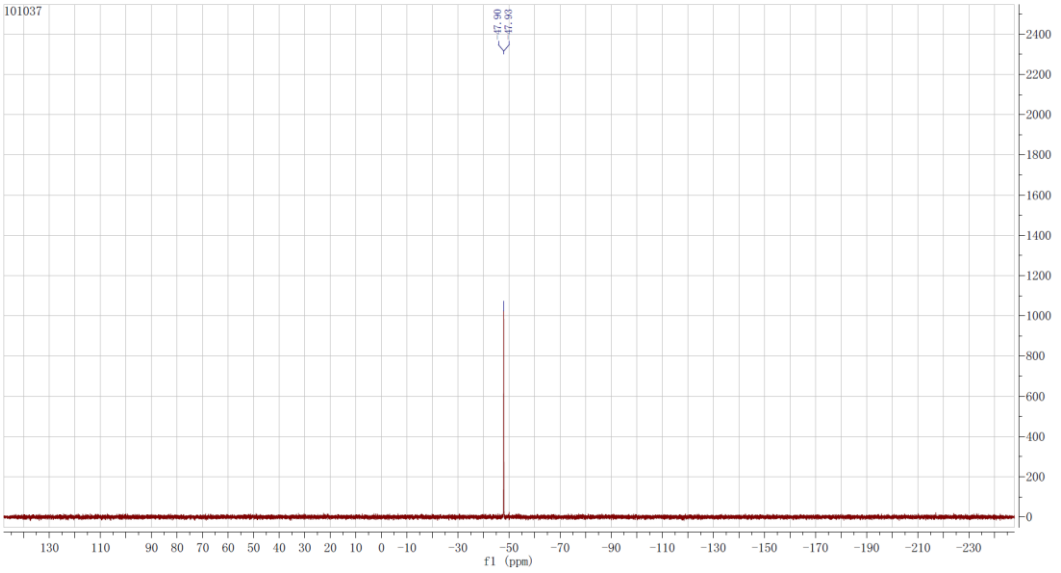
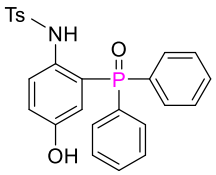


Figure 108. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **6o**



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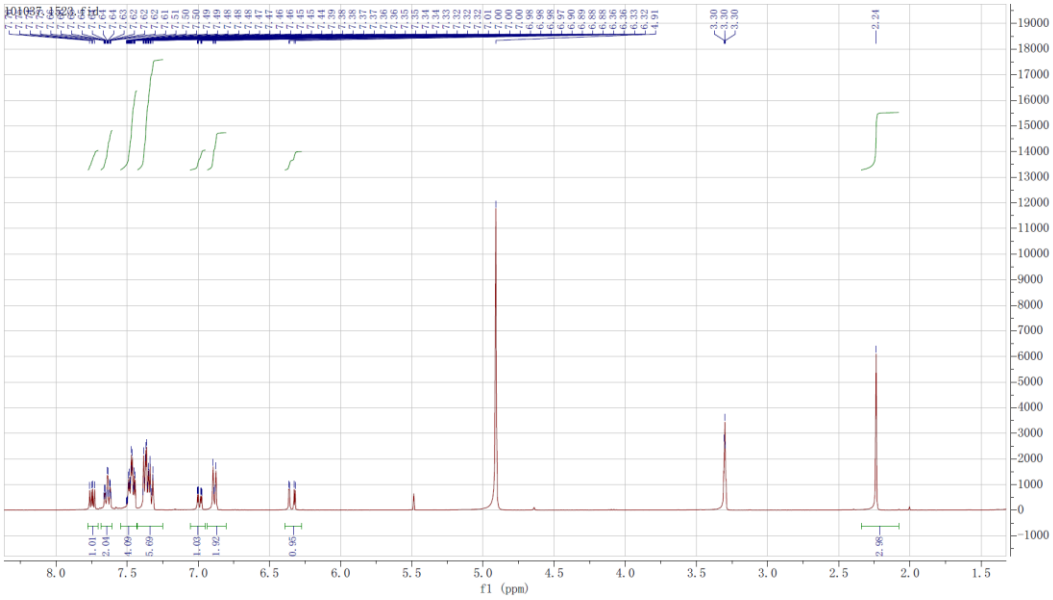


Figure 109. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **7**

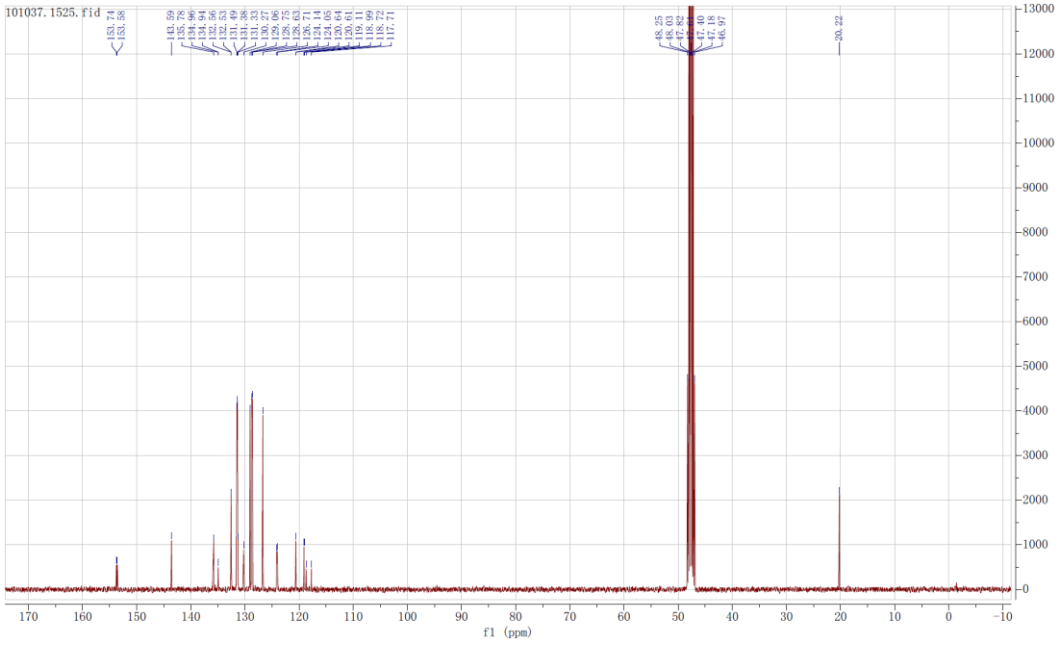


Figure 110. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **7**

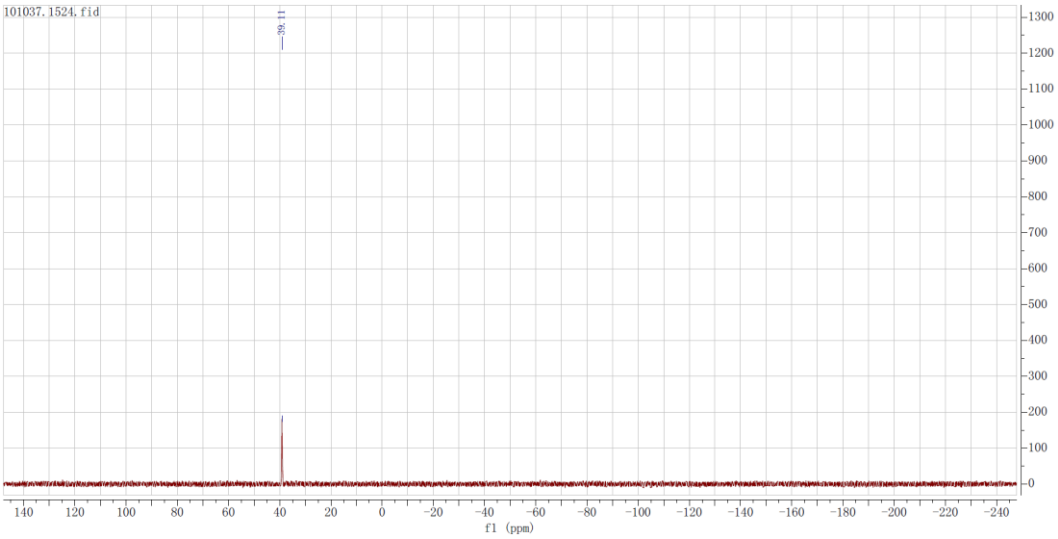
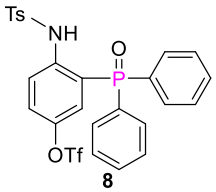


Figure 111. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **7**



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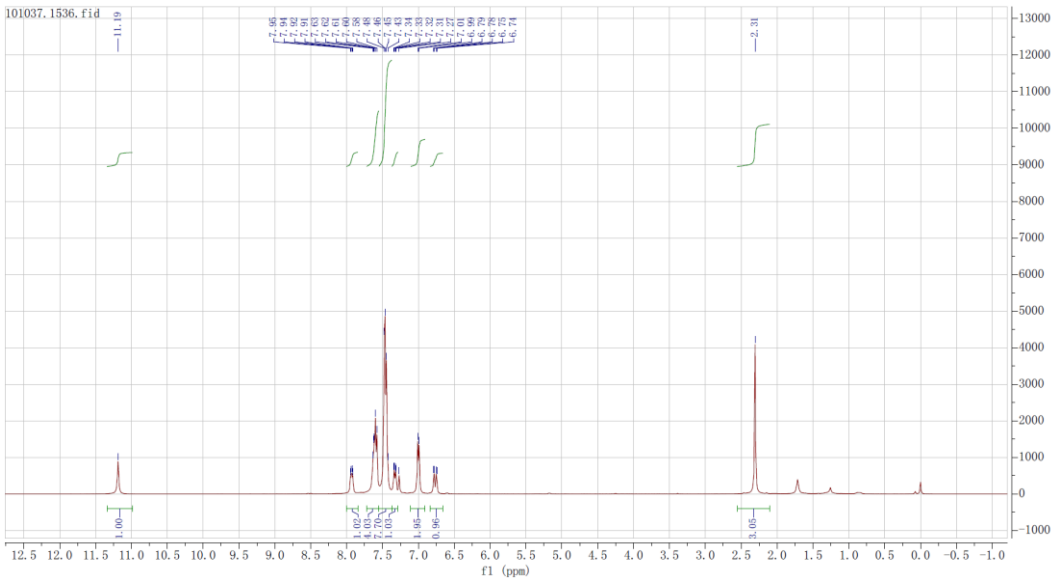


Figure 112. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **8**

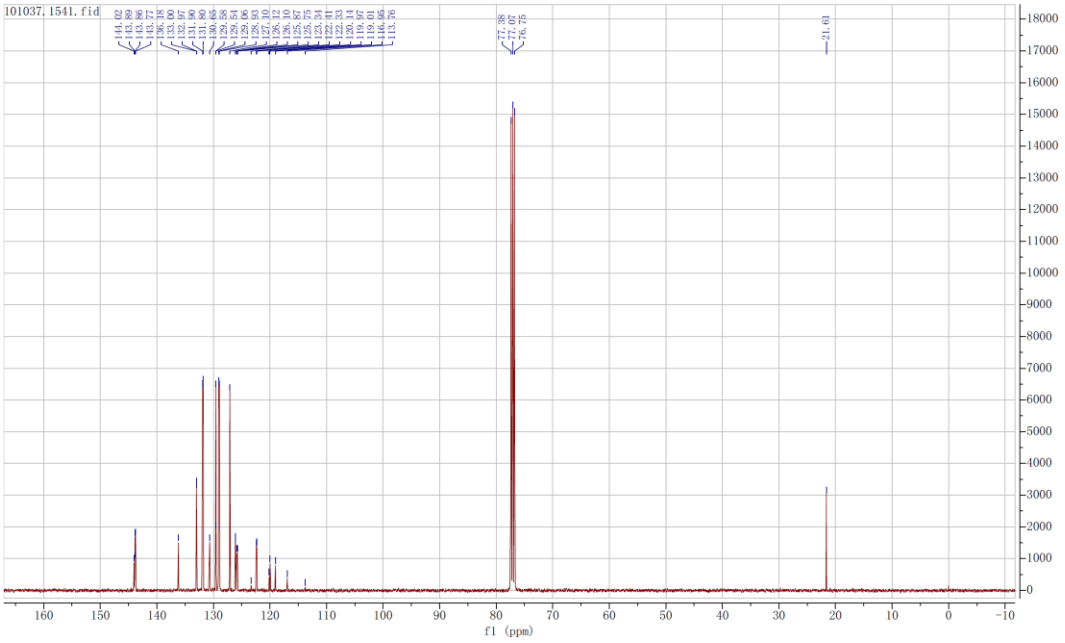


Figure 113. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **8**

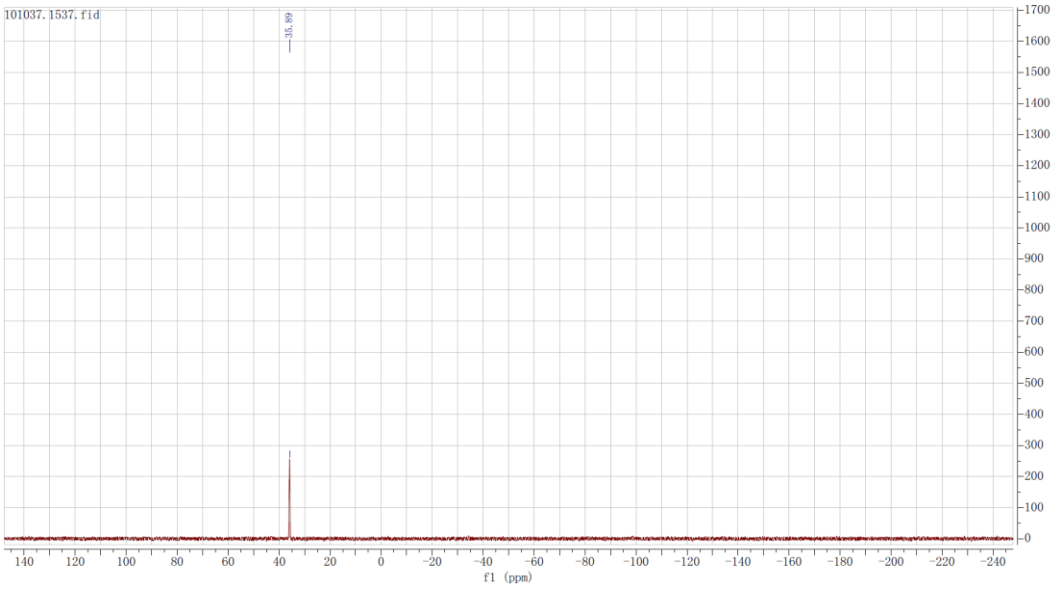


Figure 114. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **8**

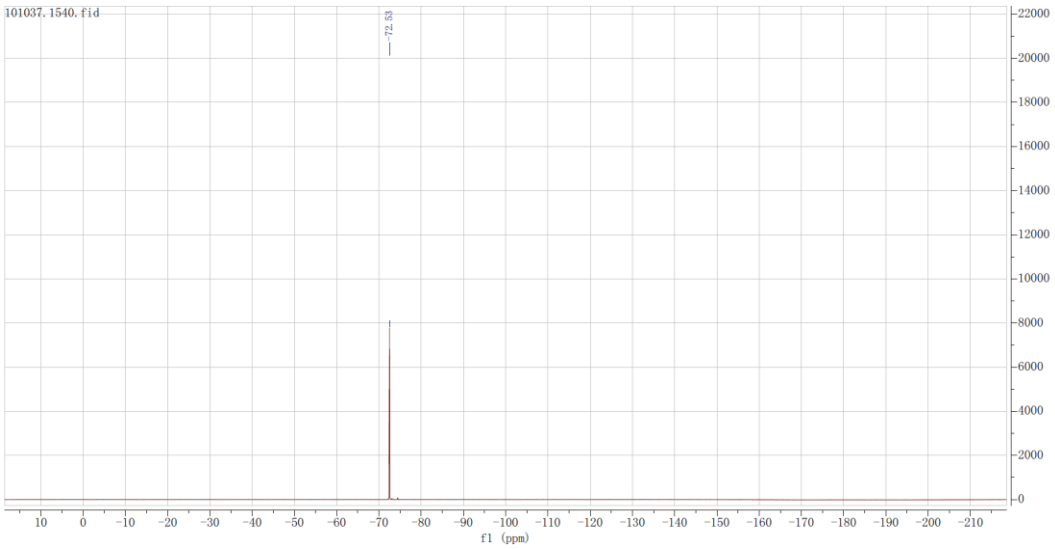
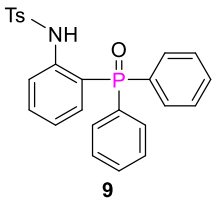


Figure 115. ^{19}FNMR ($CDCl_3$, 160 MHz) spectra of compound **8**



9

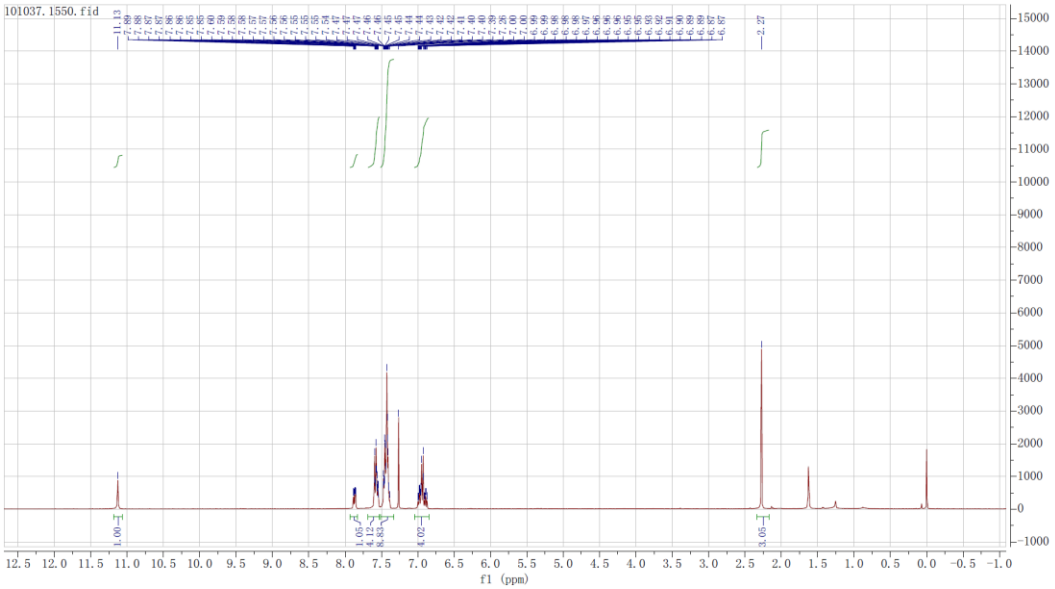


Figure 116. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **9**

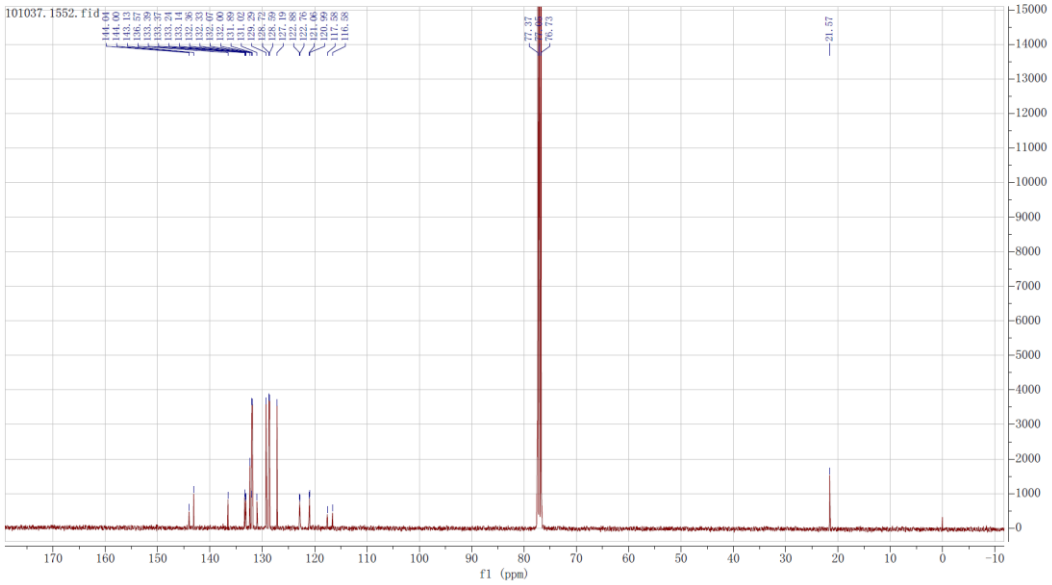


Figure 117. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **9**

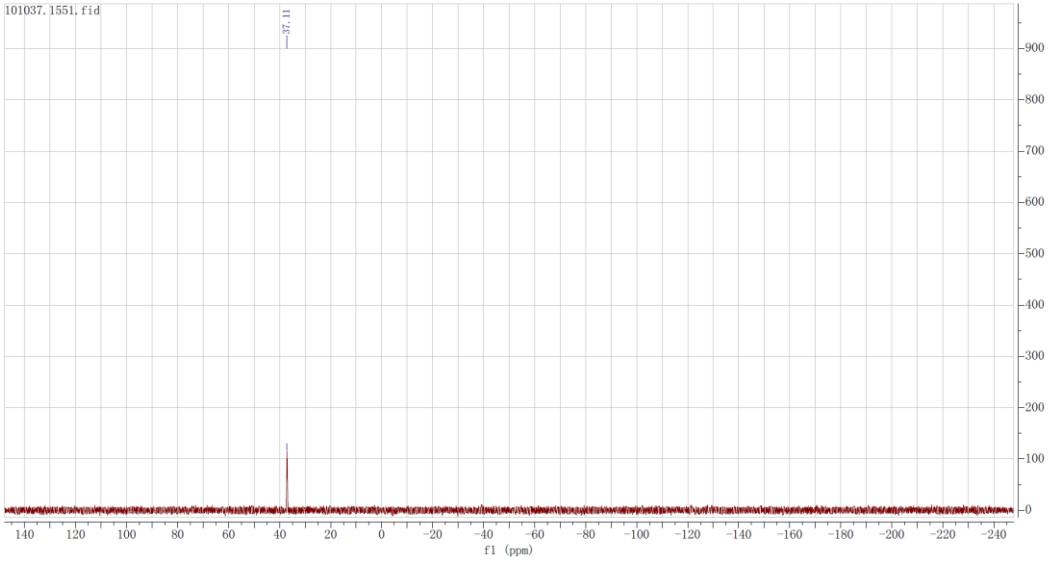
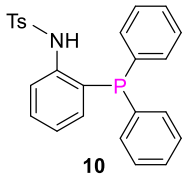


Figure 118. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **9**



10

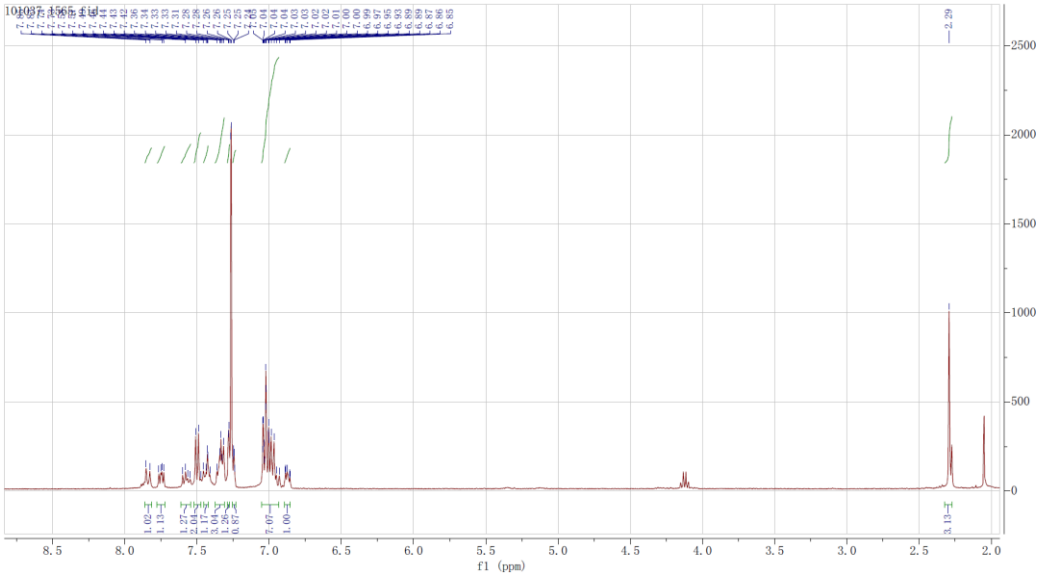


Figure 119. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **10**

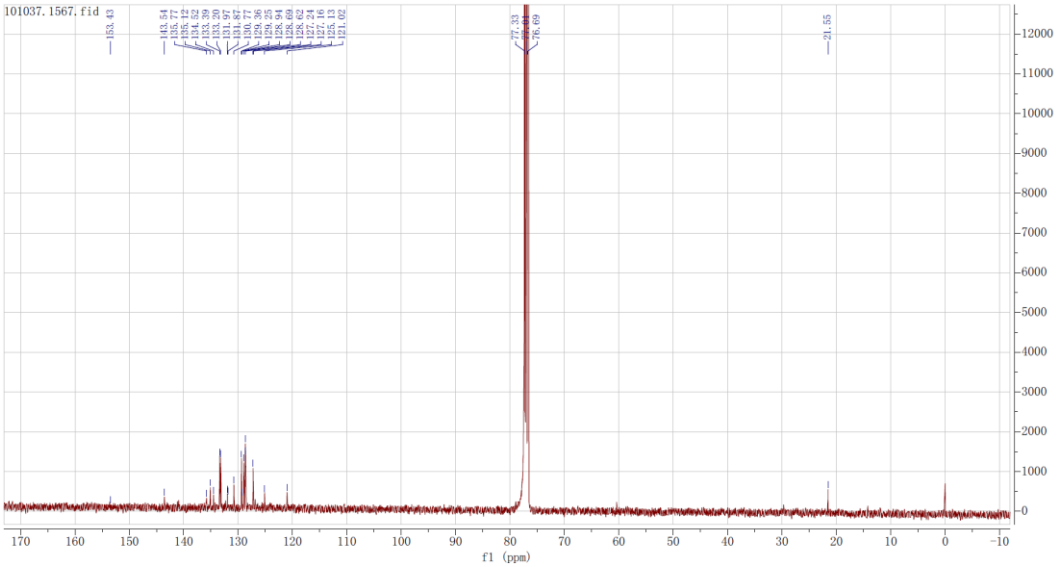


Figure 120. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **10**

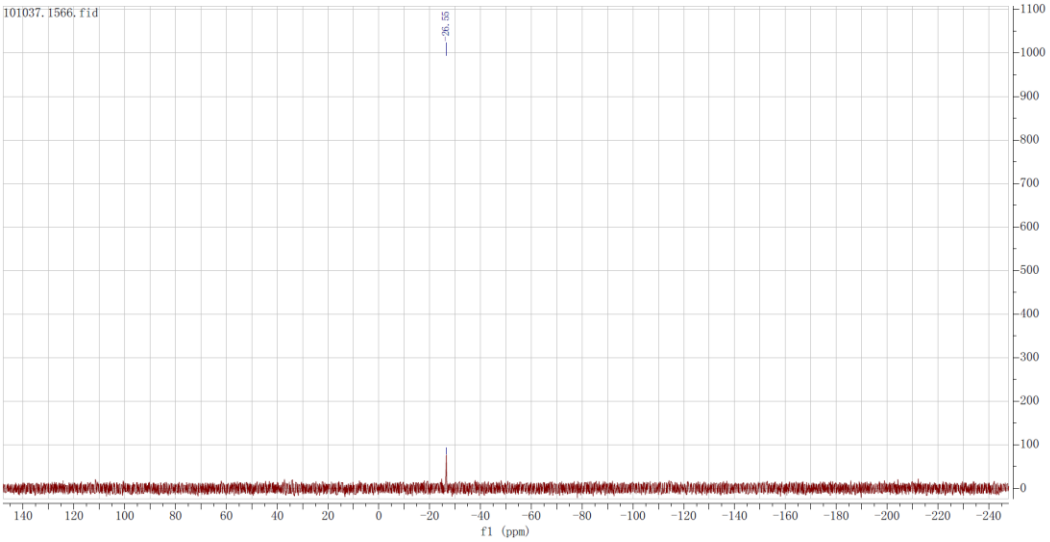
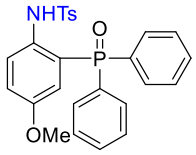


Figure 121. ^{31}P NMR ($CDCl_3$, 160 MHz) spectra of compound **10**



3aa

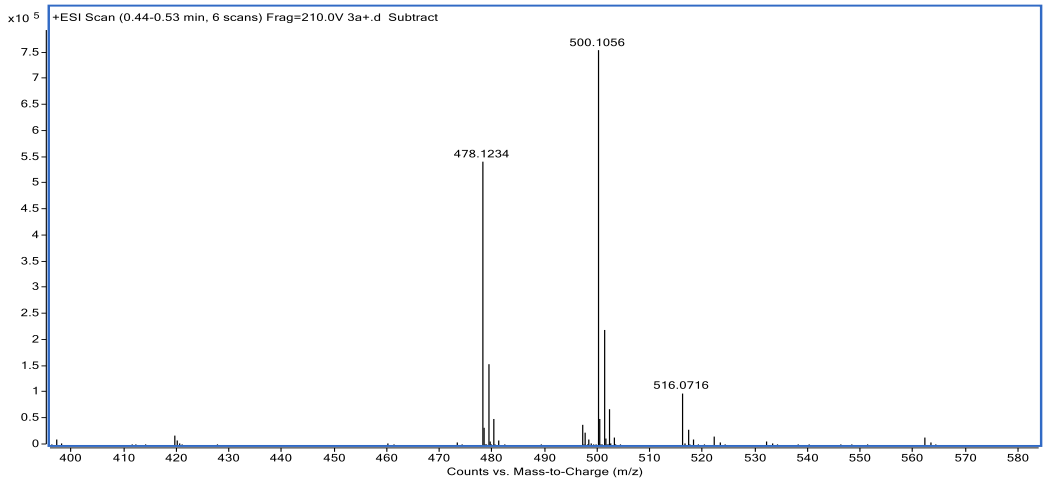


Figure 122. HRMS (ESI-TOF): spectra of compound **3aa**