

Nickel-catalyzed reductive coupling of nitroarenes and phosphine oxides to access phosphinic amides

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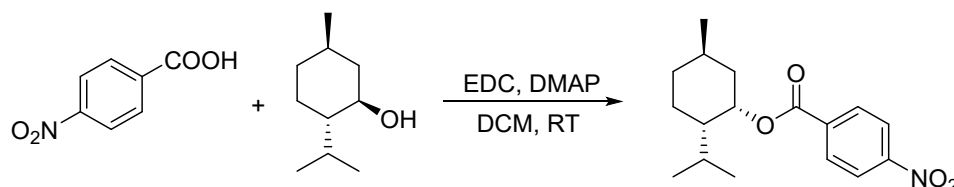
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1. General information

All commercially available reagent grade chemicals were purchased from Adamas, Aldrich, Accela, Alfa Aesar, TCI and used as received without further purification unless otherwise stated. All solvents were dried according to standard procedures. ^1H NMR, ^{13}C NMR and ^{31}P NMR were recorded in CDCl_3 or DMSO-d_6 on a Bruker Avance III 400 spectrometer with TMS as internal standard (400 MHz ^1H , 101 MHz ^{13}C , 162/202 MHz ^{31}P NMR) at room temperature, the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Column chromatography was performed on silica gel (200-300 mesh).

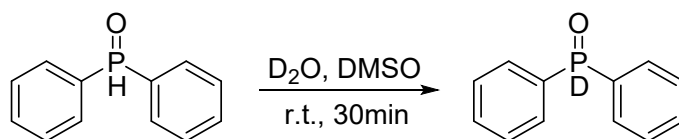
2. Synthesis of reactants

Synthesis of (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-((diphenylphosphoryl)amino)benzoate^[1]



4-Nitrobenzoic acid (0.50 g, 3.0 mmol) was added to a mixture of D-Menthol (0.47 g, 3.0 mmol), EDC (1.73 g, 9.0 mmol) and DMAP (0.65 g, 5.7 mmol) in dichloromethane (25 mL). The resulting solution was stirred at room temperature for 12h, and quenched by water. The organic layer was washed with deionized water (10 mL \times 3) and brine (10 mL \times 3), dried over anhydrous Na_2SO_4 and concentrated to dryness. The isolated residue was further purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate =4/1, v/v) to give it as a white waxy solid (1.3 g, 91% yield).

Synthesis of deuterated diphenylphosphine oxide-*d* (*d*-2a)^[2]



A sample of diphenylphosphine oxide (0.02 g, 0.1 mmol) dissolved in 1 mL of dimethyl sulfoxide (DMSO) was added with 0.01 mL of D_2O and then stirred at room temperature for 30 min. Upon completion of the reaction, the solvent was removed under reduced pressure to obtain the deuterated diphenylphosphine oxide-*d*.

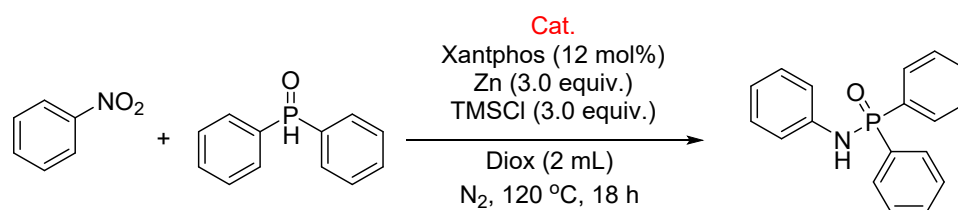
3. General procedure for Synthesis of 3 and 4

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with nitroarenes **1** (0.3 mmol, 1.0 equiv.), phosphine oxides **2** (0.6 mmol, 2.0 equiv.), NiCl_2

(3.9 mg, 0.03 mmol, 10 mol%), Xantphos (18 mg, 0.036 mmol, 12 mol%), Zn (59 mg, 0.9 mmol, 3.0 equiv.), and TMSCl (98 mg, 0.9 mmol, 3.0 equiv.). Then, dioxane (2.0 mL) was added into the mixture under nitrogen. Later, the reaction system kept stirring at room temperature for 18 h. After that, the mixture was filtered by silica gel and extracted with EtOAc (5 × 30 mL). The organic layers were combined and dried using anhydrous Na₂SO₄. After filtered, the volatiles were removed under reduced pressure. The residue was purified using flash chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to afford the corresponding product **3** and **4**.

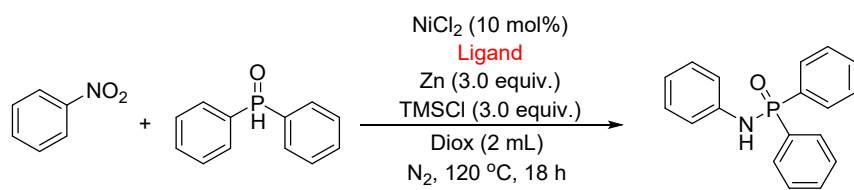
4. Optimization of the Reaction Conditions

Table 1

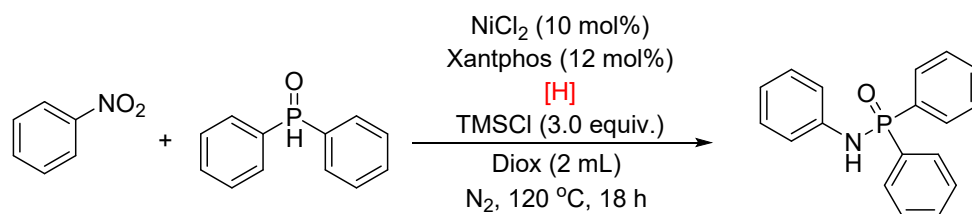


Entry	Cat.	X mol%	Yield
1	NiCl ₂	10%	90%
2	NiF ₂	10%	22%
3	Ni(acac) ₂	10%	trace
4	NiCl ₂ (dppp)	10%	50%
5	NiCl ₂ (dppf)	10%	37%
6	NiCl ₂ (PPh ₃) ₂	10%	40%
7	NiCl ₂ (PCy ₃) ₂	10%	27%
8	Ni(OAc) ₂	10%	18%
9	NiBr ₂	10%	23%
10	NiBr ₂ (dme)	10%	35%
11	NiCp ₂	10%	trace
12	Ni(OTf) ₂	10%	52%
13	CuBr	10%	30%
14	Pd(OAc) ₂	10%	trace
15	CoCl ₂ (PPh ₃) ₂	10%	trace
16	Cp ₂ TiCl ₂	10%	trace
17	Fe(acac) ₃	10%	33%
18	Zn(OAc) ₂	10%	25%
19	Sc(OTf) ₃	10%	trace
20	NiCl ₂	20%	92%
21	NiCl ₂	5%	50%
22	NiCl ₂	0	N.D.

Table 2

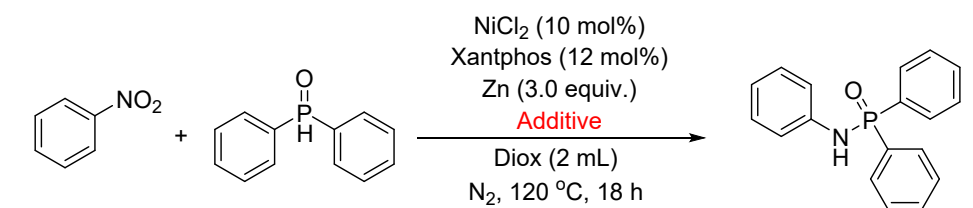


Entry	Ligand	X mol%	Yield
1		12%	66%
2		12%	42%
3		12%	28%
4		12%	trace
5		12%	trace
6		12%	58%
7		12%	60%
8		12%	44%
9		12%	42%
10		12%	90%
11		24%	trace
12		12%	30%
13	none	0	N.D.

Table 3

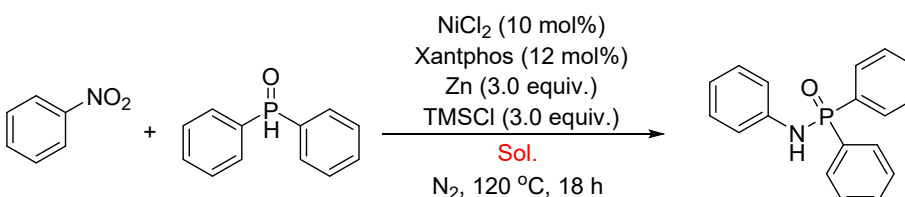
Entry	[H] (3.0 equiv.)	Yield
1	Zn	90%
2	Mn	56%
3	Et_3SiH	trace
4	Ph_2SiH_2	32%
5	$i\text{Pr}_3\text{SiH}$	trace
6	Ph_3SiH	trace
7	$t\text{BuMe}_2\text{SiH}$	trace
8	PhMe_2SiH	trace
9	$t\text{Bu}_2\text{SiH}_2$	trace
10	none	N.D.
11 ^a	Zn	N.D.
12 ^b	Zn	N.D.
13 ^c	Zn	66%

^a Under O_2 atmosphere. ^b Under air instead of N_2 . ^c Zn (2.0 equiv.)

Table 4

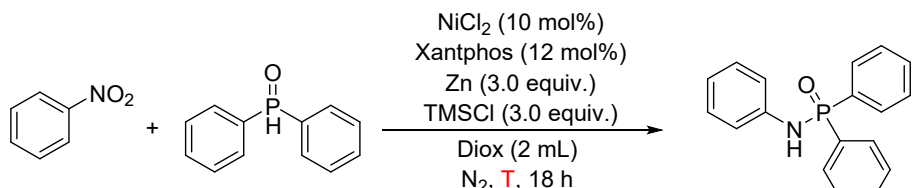
Entry	Additive	X equiv.	Yield
1	TMSCl	3.0 equiv.	90%
2	TMSCl	1.5 equiv.	75%
3	TMSCl	4.0 equiv.	60%
4	Et_3SiCl	3.0 equiv.	50%
5	$t\text{BuMe}_2\text{SiCl}$	3.0 equiv.	56%
6	TMSCl	0	27%

Table 5



Entry	Sol. (2 mL)	Yield
1	Dioxane	90%
2	DCM	33%
3	DCE	trace
4	CH ₃ OH	36%
5	CH ₃ CN	trace
6	DMF	trace
7	DMAc	trace
8	THF	trace
9	DMSO	trace
10	Toluene	43%

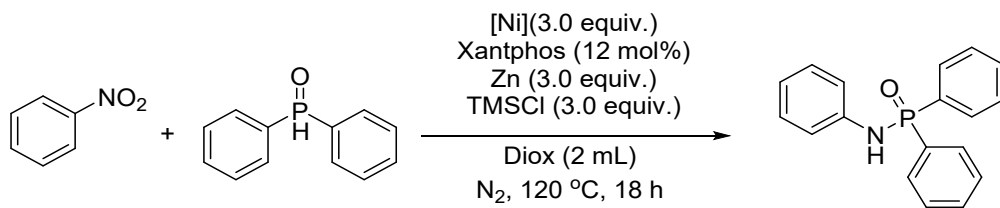
Table 6



Entry	T/°C	Yield
1	100°C	69%
2	120°C	90%
3	150°C	78%
4 ^a	120°C	55%
5 ^b	120°C	91%

^a 12 h. ^b 24 h.

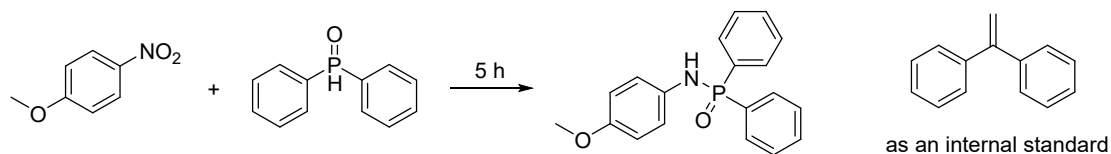
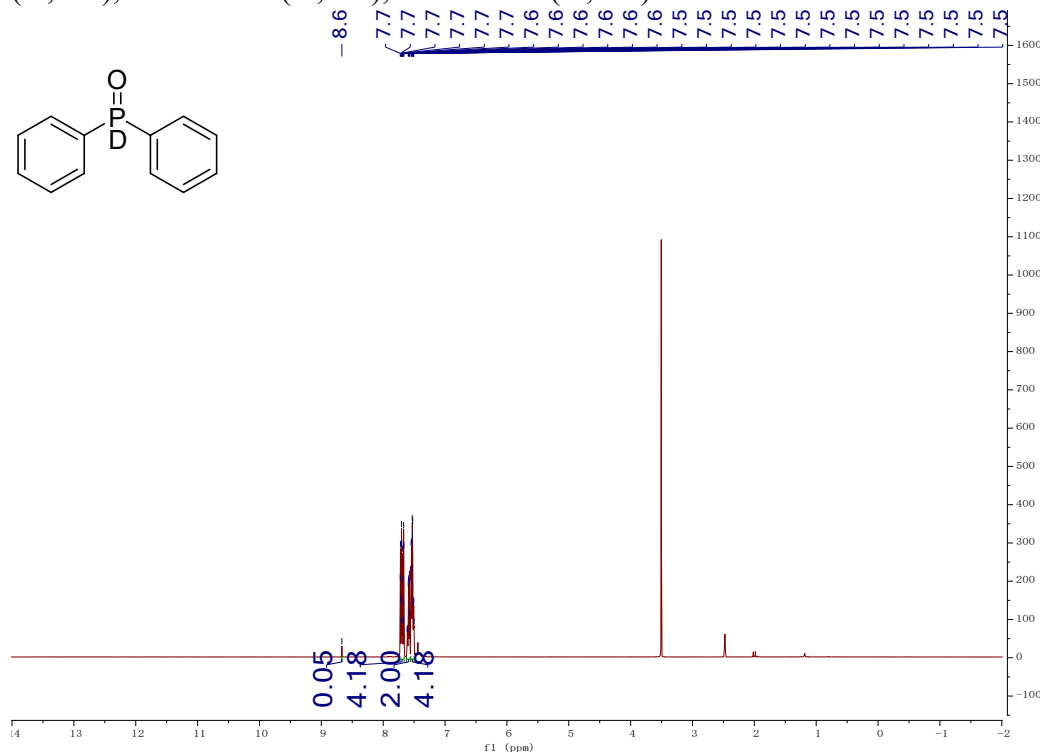
Table 7

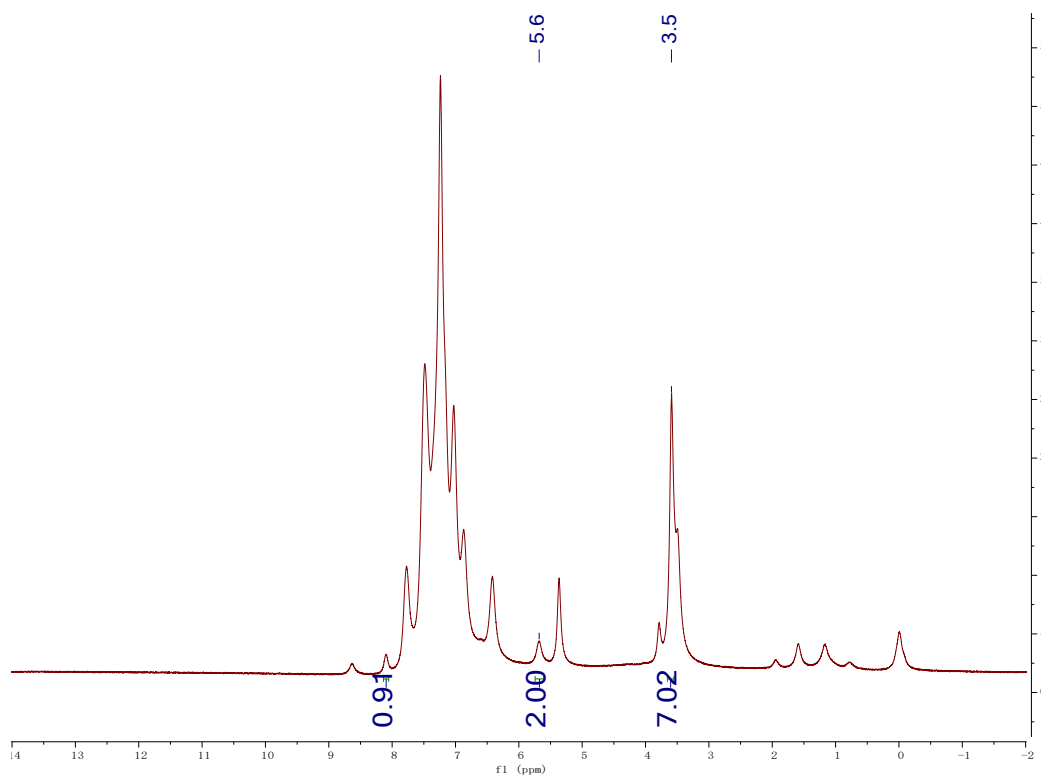
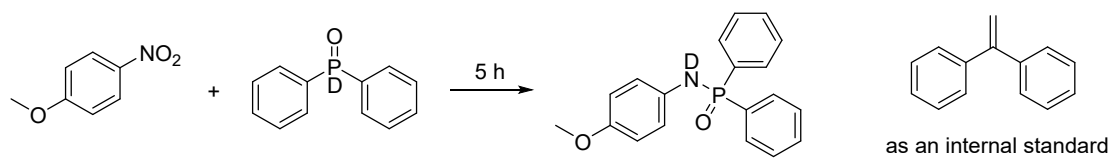
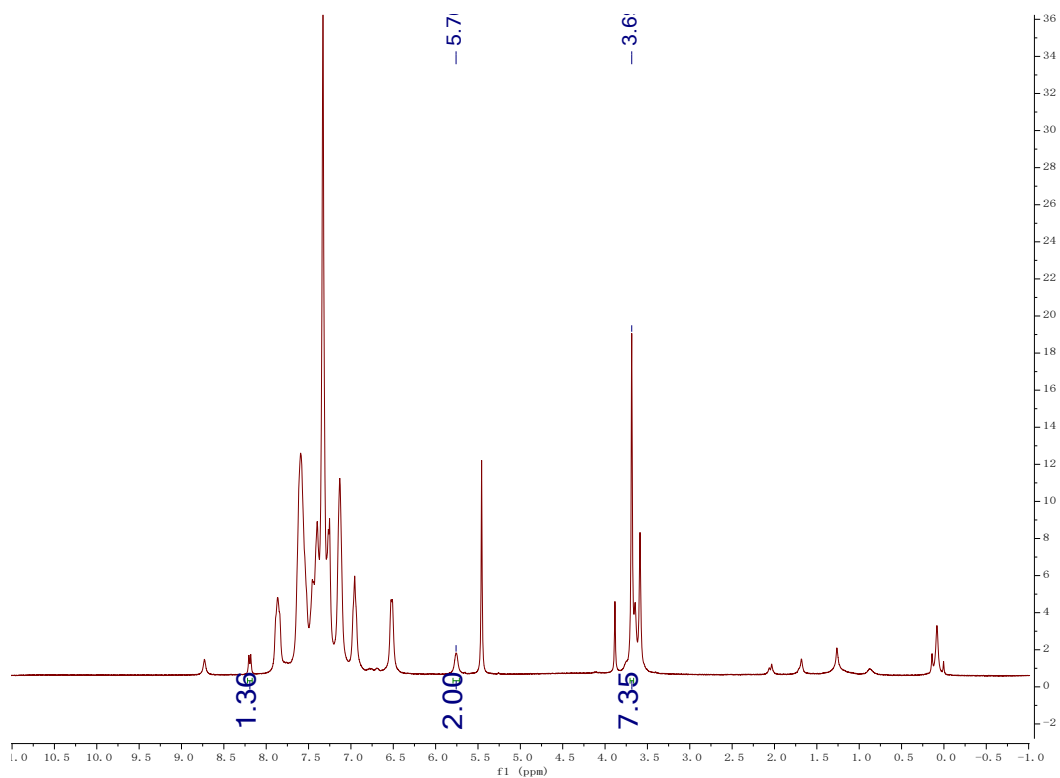


Entry	NiCl ₂ or Zn	X mol%	PhNO ₂	Yield
1	Ni(COD) ₂ & w/o Zn	300%	10%	46%
2	Zn & w/o [Ni]	300%	trace	trace

5. Kinetic isotope effect (KIE) experiment

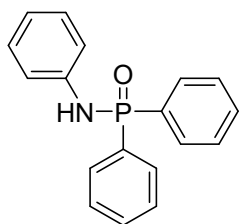
diphenylphosphine oxide-d 95% yield.¹H NMR (400 MHz, DMSO-d₆) δ 7.73 – 7.66 (m, 4H), 7.62 – 7.56 (m, 2H), 7.55 – 7.50 (m, 4H).



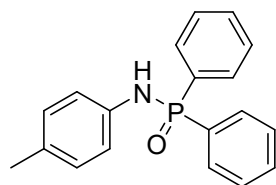


6. Experimental characterization data for products

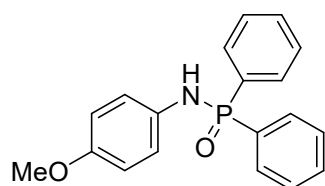
N,P,P-triphenylphosphinic amide (3a): White solid, 90% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.88 (m, $J = 12.5, 8.0, 1.6$ Hz, 4H), 7.55 – 7.50 (m, 2H), 7.45 (m, $J = 7.5, 3.2$ Hz, 4H), 7.13 (t, $J = 7.7$ Hz, 2H), 6.97 (d, $J = 8.0$ Hz, 2H), 6.91 – 6.86 (m, 1H), 5.35 (d, $J = 9.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.3 (d, $J = 1.0$ Hz), 131.9 (d, $J = 129.0$ Hz), 132.2 (d, $J = 3.0$ Hz), 132.0 (d, $J = 10.0$ Hz), 129.3, 128.8 (d, $J = 13.0$ Hz), 121.8, 118.5 (d, $J = 6.0$ Hz). ^{31}P NMR (202 MHz, CDCl_3) δ 18.47. HRMS: calcd for $\text{C}_{18}\text{H}_{16}\text{NOP}$ $[\text{M}-\text{H}]^-$: 292.0894, found: 292.0901.



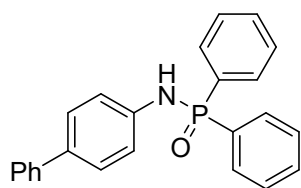
P,P-diphenyl-N-(p-tolyl)phosphinic amide (3b): White solid, 84% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.90 – 7.82 (m, 4H), 7.53 – 7.47 (m, 2H), 7.43 (td, $J = 7.6, 3.4$ Hz, 4H), 6.90 (q, $J = 8.5$ Hz, 4H), 5.37 (d, $J = 9.4$ Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.6 (d, $J = 2.0$ Hz), 132.6, 132.1 (d, $J = 3.0$ Hz), 132.0 (d, $J = 10.0$ Hz), 131.3 (d, $J = 8.0$ Hz), 129.7, 128.7 (d, $J = 13.0$ Hz), 118.7 (d, $J = 6.0$ Hz), 20.56. ^{31}P NMR (202 MHz, CDCl_3) δ 18.50. HRMS: calcd for $\text{C}_{19}\text{H}_{18}\text{NOP}$ $[\text{M}-\text{H}]^-$: 306.1052, found: 306.1058.



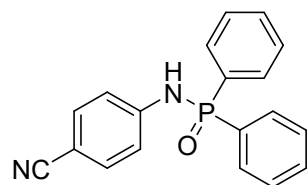
N-(4-methoxyphenyl)-P,P-diphenylphosphinic amide (3c): White solid, 76% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.89 – 7.81 (m, 4H), 7.50 – 7.45 (m, 2H), 7.43 – 7.37 (m, 4H), 6.98 – 6.93 (m, 2H), 6.69 – 6.63 (m, 2H), 5.41 (d, $J = 8.9$ Hz, 1H), 3.67 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.0, 133.3 (d, $J = 2.0$ Hz), 132.0 (d, $J = 129.0$ Hz), 132.1 (d, $J = 1.0$ Hz), 132.0 (d, $J = 6.0$ Hz), 128.7 (d, $J = 12.0$ Hz), 120.7 (d, $J = 6.0$ Hz), 114.5, 55.4. ^{31}P NMR (162 MHz, CDCl_3) δ 18.72. HRMS: calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_2\text{P}$ $[\text{M}-\text{H}]^-$: 322.1002, found: 322.1009.



N-([1,1'-biphenyl]-4-yl)-P,P-diphenylphosphinic amide (3d): White solid, 42% yield. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.35 (d, $J = 11.7$ Hz, 1H), 7.86 – 7.72 (m, 2H), 7.62 (s, 2H), 7.59 (d, $J = 4.2$ Hz, 3H), 7.57 (s, 2H), 7.52 (dd, $J = 7.4, 4.2$ Hz, 7H), 7.42 (d, $J = 8.4$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.13 (d, $J = 8.5$ Hz, 1H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 142.1, 140.2, 134.0, 133.7, 132.5 (d, $J = 2.0$ Hz), 132.1 (d, $J = 10.0$ Hz), 131.9 (d, $J = 10.0$ Hz), 129.2 (d, $J = 12.0$ Hz), 127.5, 127.0, 126.4, 119.0 (d, $J = 7.0$ Hz). ^{31}P NMR (162 MHz, $\text{DMSO}-d_6$) δ 25.57. HRMS: calcd for $\text{C}_{24}\text{H}_{20}\text{NOP}$ $[\text{M}-\text{H}]^-$: 368.1210, found: 368.1222.

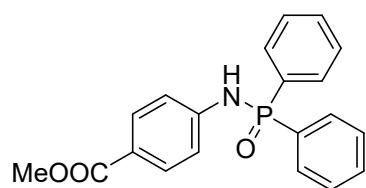


N-(4-cyanophenyl)-P,P-diphenylphosphinic amide (3e): White solid, 83% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.78 (dd, $J = 12.6, 7.5$ Hz, 4H), 7.51 (t, $J = 7.5$ Hz, 2H), 7.41 (td, $J = 7.5, 2.9$ Hz, 4H), 7.31 (d, $J = 8.3$ Hz, 2H), 7.05 (d, $J = 8.3$ Hz, 2H), 6.71 (d, $J = 10.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.5, 133.4, 132.6 (d, $J = 1.0$ Hz), 132.60, 131.8 (d, $J = 10.0$ Hz), 130.3, 128.9



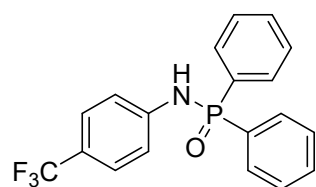
(d, $J = 13.0$ Hz), 119.2, 118.3 (d, $J = 6.0$ Hz), 104.2. ^{31}P NMR (202 MHz, CDCl_3) δ 19.40. HRMS: calcd for $\text{C}_{19}\text{H}_{15}\text{N}_2\text{OP}$ $[\text{M}-\text{H}]^-$: 317.0849, found: 317.0859.

Methyl 4-((diphenylphosphoryl)amino)benzoate (3f): White solid, 73% yield. ^1H



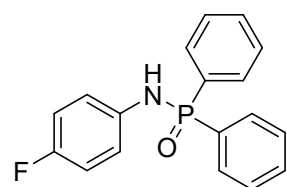
NMR (400 MHz, CDCl_3) δ 7.82 (dd, $J = 13.0, 7.7$ Hz, 4H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.44 (t, $J = 7.4$ Hz, 2H), 7.30 (d, $J = 3.5$ Hz, 2H), 7.09 (dt, $J = 8.1, 4.0$ Hz, 2H), 6.94 (d, $J = 8.5$ Hz, 2H), 6.84 (d, $J = 8.5$ Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.6, 143.7, 132.2 (d, $J = 11.0$ Hz), 131.2 (d, $J = 10.0$ Hz), 130.9, 129.1 (d, $J = 14.0$ Hz), 127.9 (d, $J = 13.0$ Hz), 123.8, 118.8 (d, $J = 8.0$ Hz), 51.8. ^{31}P NMR (162 MHz, CDCl_3) δ 25.22. HRMS: calcd for $\text{C}_{20}\text{H}_{18}\text{NO}_3\text{P}$ $[\text{M}-\text{H}]^-$: 350.0952, found: 350.0960.

P,P-diphenyl-N-(4-(trifluoromethyl)phenyl)phosphinic amide (3g): White solid,



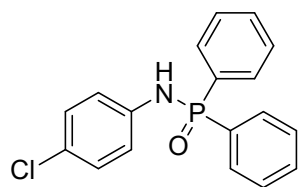
73% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.81 (dd, $J = 12.6, 7.6$ Hz, 4H), 7.48 (t, $J = 7.4$ Hz, 2H), 7.38 (td, $J = 7.6, 3.3$ Hz, 4H), 7.28 – 7.23 (m, 2H), 7.05 (d, $J = 8.4$ Hz, 2H), 6.54 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.1, 132.5 (d, $J = 2.0$ Hz), 131.9 (d, $J = 10.0$ Hz), 130.6, 128.9 (d, $J = 13.0$ Hz), 126.4 (d, $J = 3.0$ Hz), 125.7, 123.4 (d, $J = 33.0$ Hz), 118.0 (d, $J = 7.0$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 19.16. HRMS: calcd for $\text{C}_{29}\text{H}_{15}\text{F}_3\text{NOP}$ $[\text{M}+\text{H}]^+$: 362.0916, found: 362.0918.

N-(4-fluorophenyl)-P,P-diphenylphosphinic amide (3h): White solid, 67% yield. ^1H



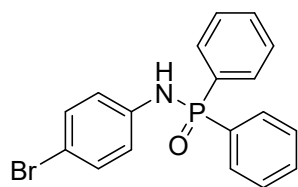
NMR (400 MHz, CDCl_3) δ 7.87 – 7.78 (m, 4H), 7.53 – 7.46 (m, 2H), 7.41 (td, $J = 7.4, 3.4$ Hz, 4H), 6.97 – 6.93 (m, 2H), 6.79 (t, $J = 8.7$ Hz, 2H), 5.72 (d, $J = 9.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.7 (d, $J = 241.0$ Hz), 136.4 (dd, $J_1 = 1.01$ Hz, $J_2 = 2.02$ Hz), 132.3 (d, $J = 3.03$ Hz), 132.0 (d, $J = 10.1$ Hz), 130.9, 128.8 (d, $J = 13.1$ Hz), 120.1 (t, $J = 7.06$ Hz), 115.8 (d, $J = 23.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 18.90. HRMS: calcd for $\text{C}_{18}\text{H}_{15}\text{FNOP}$ $[\text{M}-\text{H}]^-$: 310.0803, found: 310.0812.

N-(4-chlorophenyl)-P,P-diphenylphosphinic amide (3i): White solid, 55% yield. ^1H



NMR (400 MHz, CDCl_3) δ 7.88 – 7.77 (m, 4H), 7.56 – 7.48 (m, 2H), 7.43 (td, $J = 7.4, 3.4$ Hz, 4H), 7.11 – 7.01 (m, 2H), 6.95 – 6.89 (m, 2H), 5.60 (d, $J = 9.4$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.0 (d, $J = 1.0$ Hz), 132.4 (d, $J = 3.0$ Hz), 131.9 (d, $J = 10.0$ Hz), 130.7, 129.2, 128.8 (d, $J = 13.0$ Hz), 127.0, 119.8 (d, $J = 6.0$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 19.02. HRMS: calcd for $\text{C}_{18}\text{H}_{15}\text{ClNOP}$ $[\text{M}-\text{H}]^-$: 326.0507, found: 326.0511.

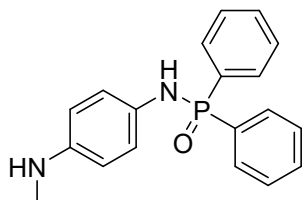
N-(4-bromophenyl)-P,P-diphenylphosphinic amide (3j): White solid, 37% yield. ^1H



NMR (400 MHz, CDCl_3) δ 7.92 – 7.75 (m, 4H), 7.56 – 7.48

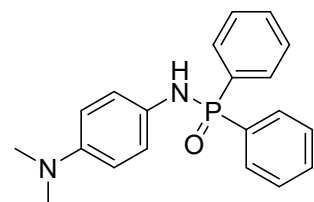
(m, 2H), 7.44 (td, $J = 7.5, 3.5$ Hz, 4H), 7.23 – 7.10 (m, 1H), 7.08 – 7.05 (m, 1H), 6.96 – 6.85 (m, 2H), 5.57 (t, $J = 8.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.4 (d, $J = 53.0$ Hz), 132.5 (d, $J = 2.0$ Hz), 132.2, 132.0 (d, $J = 10.0$ Hz), 129.3, 128.9 (d, $J = 13.0$ Hz), 120.1 (d, $J = 7.0$ Hz), 119.7 (d, $J = 7.0$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 18.87. HRMS: calcd for $\text{C}_{18}\text{H}_{15}\text{BrNOP}$ $[\text{M}-\text{H}]^-$: 370.0002, found: 370.0010.

N-(4-(methylamino)phenyl)-P,P-diphenylphosphinic amide (3l): White solid, 61%



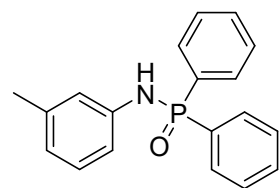
yield. ^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.83 (m, 5H), 7.48 (dt, $J = 7.4, 2.0$ Hz, 2H), 7.44 – 7.40 (m, 4H), 6.92 – 6.89 (m, 2H), 6.44 – 6.38 (m, 2H), 5.12 (d, $J = 8.7$ Hz, 1H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.1, 132.7, 132.1 (d, $J = 10.0$ Hz), 132.0 (d, $J = 3.0$ Hz), 130.2 (d, $J = 2.0$ Hz), 128.6 (d, $J = 13.0$ Hz), 121.6 (d, $J = 6.0$ Hz), 113.3, 31.1. ^{31}P NMR (202 MHz, CDCl_3) δ 18.67. HRMS: calcd for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{OP}$ $[\text{M}-\text{H}]^-$: 321.1161, found: 321.1171.

N-(4-(dimethylamino)phenyl)-P,P-diphenylphosphinic amide (3m): White solid,



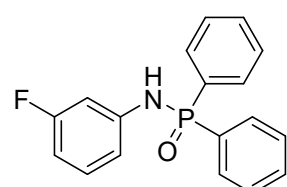
56% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.84 (m, 4H), 7.51 – 7.46 (m, 2H), 7.45 – 7.40 (m, 4H), 6.94 (d, $J = 8.4$ Hz, 2H), 6.56 (d, $J = 8.3$ Hz, 2H), 5.15 (d, $J = 8.1$ Hz, 1H), 2.81 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.7, 132.7, 132.1, 132.0 (d, $J = 3.0$ Hz), 130.8 (d, $J = 134.0$ Hz), 128.7 (d, $J = 13.0$ Hz), 121.1 (d, $J = 6.0$ Hz), 114.0, 41.2. ^{31}P NMR (202 MHz, CDCl_3) δ 18.63. HRMS: calcd for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{OP}$ $[\text{M}-\text{H}]^-$: 335.1319, found: 335.1330.

P,P-diphenyl-N-(m-tolyl)phosphinic amide (3n): White solid, 80% yield. ^1H NMR



(400 MHz, CDCl_3) δ 7.90 – 7.82 (m, 4H), 7.52 – 7.47 (m, 2H), 7.45 – 7.39 (m, 4H), 6.98 (td, $J = 7.8, 2.0$ Hz, 1H), 6.81 – 6.75 (m, 2H), 6.69 (d, $J = 7.6$ Hz, 1H), 5.45 (d, $J = 9.1$ Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.1, 139.1, 132.2 (d, $J = 2.0$ Hz), 132.0 (d, $J = 10.0$ Hz), 129.0, 128.7 (d, $J = 13.0$ Hz), 128.5 (d, $J = 12.0$ Hz), 122.8, 119.3 (d, $J = 7.0$ Hz), 115.7 (d, $J = 7.0$ Hz), 21.4. ^{31}P NMR (162 MHz, CDCl_3) δ 18.87. HRMS: calcd for $\text{C}_{19}\text{H}_{18}\text{NOP}$ $[\text{M}-\text{H}]^-$: 306.1052, found: 306.1063.

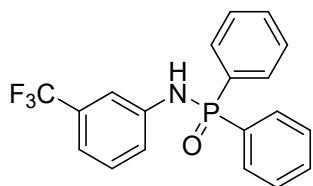
N-(3-fluorophenyl)-P,P-diphenylphosphinic amide (3o): White solid, 61% yield. ^1H



NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.48 (d, $J = 11.7$ Hz, 1H), 7.77 (dd, $J = 12.1, 7.4$ Hz, 4H), 7.59 – 7.54 (m, 2H), 7.50 (td, $J = 7.3, 3.1$ Hz, 4H), 7.11 (q, $J = 7.8$ Hz, 1H), 6.85 (t, $J = 10.5$ Hz, 2H), 6.59 (td, $J = 8.6, 2.5$ Hz, 1H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 163.8 (d, $J = 39.3$ Hz), 144.6 (d, $J = 11.11$ Hz), 132.9 (d, $J = 126.25$ Hz), 132.5 (d, $J = 2.02$ Hz), 132.0 (d, $J = 10.1$ Hz), 130.9 (d, $J = 10.1$ Hz), 129.2 (d, $J = 13.1$ Hz), 114.6 (dd, $J_1 = 2.0$ Hz, $J = 7.07$ Hz), 107.4 (d, $J = 21.21$ Hz),

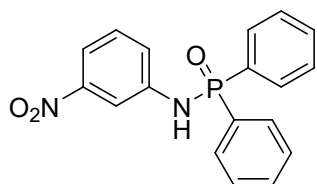
105.26 (dd, $J_1 = 7.07$ Hz, $J_2 = 25.25$ Hz). ^{31}P NMR (162 MHz, $\text{DMSO-}d_6$) δ 17.08. HRMS: calcd for $\text{C}_{18}\text{H}_{15}\text{FNOP}$ $[\text{M-H}]^-$: 310.0803, found: 310.0809.

P,P-diphenyl-N-(3-(trifluoromethyl)phenyl)phosphinic amide (3p): White solid,



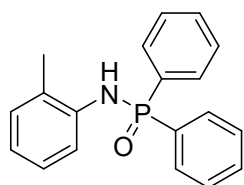
64% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.76 (m, 4H), 7.53 – 7.46 (m, 2H), 7.45 – 7.37 (m, 4H), 7.22 (s, 1H), 7.19 – 7.13 (m, 2H), 7.10 (d, $J = 6.4$ Hz, 1H), 6.18 (d, $J = 9.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.2, 132.4 (d, $J = 2.0$ Hz), 131.9 (d, $J = 10.0$ Hz), 131.4 (d, $J = 33.0$ Hz), 130.6, 129.7, 128.8 (d, $J = 13.0$ Hz), 125.1, 121.3 (d, $J = 6.0$ Hz), 118.2 (q, $J = 4.0$ Hz), 115.1 (q, $J = 4.0$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 18.94. HRMS: calcd for $\text{C}_{19}\text{H}_{15}\text{F}_3\text{NOP}$ $[\text{M+H}]^+$: 362.0916, found: 362.0918.

N-(3-nitrophenyl)-P,P-diphenylphosphinic amide (3q): White solid, 53% yield. ^1H



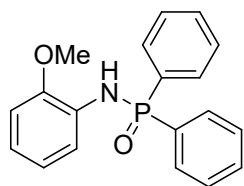
NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.81 (d, $J = 11.6$ Hz, 1H), 7.95 (t, $J = 2.0$ Hz, 1H), 7.80 (dd, $J = 12.3, 7.2$ Hz, 4H), 7.66 – 7.62 (m, 1H), 7.57 (d, $J = 7.1$ Hz, 2H), 7.53 (dd, $J = 7.4, 2.7$ Hz, 4H), 7.45 (d, $J = 8.5$ Hz, 1H), 7.40 (d, $J = 8.1$ Hz, 1H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 148.6, 144.1, 133.1, 132.7 (d, $J = 3.0$ Hz), 132.0 (d, $J = 10.0$ Hz), 130.7, 129.3 (d, $J = 13.0$ Hz), 124.6 (d, $J = 6.0$ Hz), 115.6, 112.6 (d, $J = 7.0$ Hz). ^{31}P NMR (162 MHz, $\text{DMSO-}d_6$) δ 17.65. HRMS: calcd for $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}_3\text{P}$ $[\text{M+H}]^+$: 339.0893, found: 339.0885.

P,P-diphenyl-N-(o-tolyl)phosphinic amide (3r): White solid, 82% yield. ^1H NMR



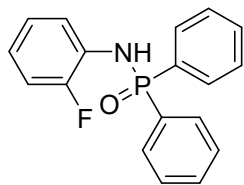
(400 MHz, CDCl_3) δ 7.92 – 7.81 (m, 4H), 7.52 – 7.47 (m, 2H), 7.46 – 7.40 (m, 4H), 7.17 (d, $J = 8.0$ Hz, 1H), 7.09 (d, $J = 7.4$ Hz, 1H), 6.91 (t, $J = 7.7$ Hz, 1H), 6.81 (t, $J = 7.3$ Hz, 1H), 5.12 (d, $J = 8.8$ Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.6 (d, $J = 1.0$ Hz), 132.2 (d, $J = 3.0$ Hz), 131.9 (d, $J = 10.0$ Hz), 131.9 (d, $J = 129.0$ Hz), 130.5, 128.8 (d, $J = 13.0$ Hz), 127.0, 125.6 (d, $J = 8.0$ Hz), 122.1, 118.9 (d, $J = 4.0$ Hz), 17.8. ^{31}P NMR (202 MHz, CDCl_3) δ 18.59. HRMS: calcd for $\text{C}_{19}\text{H}_{18}\text{NOP}$ $[\text{M-H}]^-$: 306.1052, found: 306.1059.

N-(2-methoxyphenyl)-P,P-diphenylphosphinic amide (3s): White solid, 71% yield.



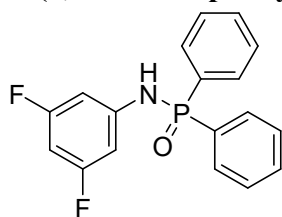
^1H NMR (400 MHz, CDCl_3) δ 7.92 – 7.83 (m, 4H), 7.53 – 7.48 (m, 2H), 7.47 – 7.42 (m, 4H), 7.09 (d, $J = 8.0$ Hz, 1H), 6.84 – 6.77 (m, 2H), 6.69 – 6.64 (m, 1H), 5.87 (d, $J = 11.2$ Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.8 (d, $J = 8.0$ Hz), 132.6, 132.2 (d, $J = 3.0$ Hz), 131.9 (d, $J = 10.0$ Hz), 131.4, 129.9, 128.8 (d, $J = 13.0$ Hz), 121.2 (d, $J = 52.0$ Hz), 117.5 (d, $J = 4.0$ Hz), 110.1, 55.6. ^{31}P NMR (202 MHz, CDCl_3) δ 18.78. HRMS: calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_2\text{P}$ $[\text{M-H}]^-$: 322.1002, found: 322.1009.

N-(2-fluorophenyl)-P,P-diphenylphosphinic amide (3t): White solid, 64% yield. ¹H



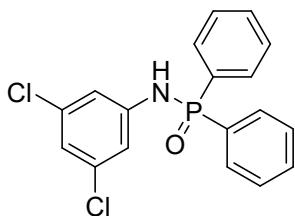
NMR (400 MHz, DMSO-*d*₆) δ 8.03 (d, *J* = 10.0 Hz, 1H), 7.80 (dd, *J* = 12.1, 6.9 Hz, 4H), 7.56 – 7.44 (m, 6H), 7.28 – 7.21 (m, 1H), 7.16 – 7.09 (m, 1H), 6.87 (dd, *J* = 6.5, 3.2 Hz, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) 154.0 (dd, *J* = 242.0, 8.0 Hz), 133.2 (d, *J* = 27.27 Hz), 132.4 (d, *J* = 2.02 Hz), 132.1 (d, *J* = 10.1 Hz), 129.7 (d, *J* = 13.13 Hz), 129.1 (d, *J* = 13.13 Hz), 124.8 (d, *J* = 3.03 Hz), 123.1 (d, *J* = 7.07 Hz), 122.5 (dd, *J*₁ = 2.02 Hz, *J*₂ = 4.04 Hz), 116.0 (d, *J* = 20.2 Hz). ³¹P NMR (162 MHz, DMSO-*d*₆) δ 17.59. HRMS: calcd for C₁₈H₁₅FNOP [M+H]⁺: 312.0948, found: 322.0944.

N-(3,5-difluorophenyl)-P,P-diphenylphosphinic amide (3u): White solid, 60%



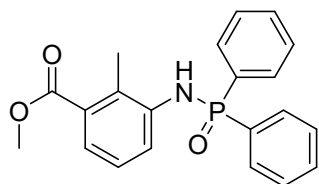
yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.74 (d, *J* = 11.5 Hz, 1H), 7.83 – 7.73 (m, 4H), 7.62 – 7.56 (m, 2H), 7.56 – 7.48 (m, 4H), 6.75 – 6.67 (m, 2H), 6.60 (tt, *J* = 9.4, 2.3 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 161.9 (dd, *J*₁ = 15.15 Hz, *J*₂ = 243.41 Hz), 145.67 (t, *J* = 14.14 Hz), 132.8 (d, *J* = 3.03 Hz), 132.0 (d, *J* = 10.1 Hz), 129.4 (d, *J* = 13.13 Hz), 101.35-101.75 (m), 96.30 (t, *J* = 26.26 Hz). ³¹P NMR (162 MHz, DMSO-*d*₆) δ 17.84. HRMS: calcd for C₁₈H₁₄F₂NOP [M-H]⁻: 328.0708, found: 328.0722.

N-(3,5-dichlorophenyl)-P,P-diphenylphosphinic amide (3v): White solid, 42%



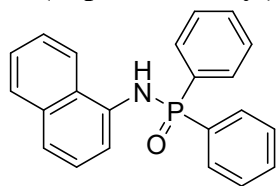
yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.69 (d, *J* = 11.7 Hz, 1H), 7.81 – 7.72 (m, 4H), 7.62 – 7.56 (m, 2H), 7.56 – 7.48 (m, 4H), 7.06 (d, *J* = 1.8 Hz, 2H), 6.98 (t, *J* = 1.8 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 145.3, 134.6, 132.9 (d, *J* = 2.0 Hz), 132.2 (d, *J* = 132.0 Hz), 132.0 (d, *J* = 10.0 Hz), 129.4 (d, *J* = 13.0 Hz), 120.4, 116.8 (d, *J* = 7.0 Hz). ³¹P NMR (162 MHz, DMSO-*d*₆) δ 18.09. HRMS: calcd for C₁₈H₁₄Cl₂NOP [M-H]⁻: 360.0117, found: 360.0129.

Methyl 3-((diphenylphosphoryl)amino)-2-methylbenzoate (3w): White solid, 54%



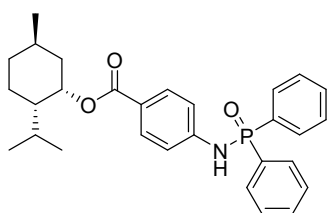
yield. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (dd, *J* = 12.5, 7.5 Hz, 4H), 7.63 (dd, *J* = 12.1, 7.6 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.41 (q, *J* = 4.0 Hz, 4H), 7.36 (d, *J* = 7.8 Hz, 1H), 6.88 (t, *J* = 8.0 Hz, 1H), 5.38 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 2.48 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.5, 139.3, 132.5 (d, *J* = 2.0 Hz), 132.2 (d, *J* = 10.0 Hz), 132.0 (d, *J* = 10.0 Hz), 131.5, 128.9 (d, *J* = 13.0 Hz), 128.6 (d, *J* = 12.0 Hz), 127.7 (d, *J* = 13.0 Hz), 126.2, 124.5, 52.1, 14.5. ³¹P NMR (162 MHz, CDCl₃) δ 20.76. HRMS: calcd for C₂₁H₂₀NO₃P [M-H]⁻: 364.1108, found: 364.1115.

N-(naphthalen-1-yl)-P,P-diphenylphosphinic amide (3x): White solid, 57% yield.



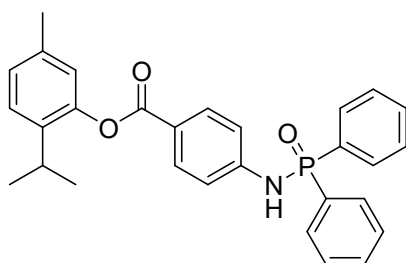
^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.89 (m, 5H), 7.82 (d, J = 8.0 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.49 – 7.46 (m, 3H), 7.45 – 7.38 (m, 5H), 7.17 (t, J = 7.8 Hz, 1H), 5.87 (d, J = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 135.33 (d, J = 1.0 Hz), 134.2, 132.3 (d, J = 2.0 Hz), 132.1, 132.0 (d, J = 10.0 Hz), 131.0, 128.9 (d, J = 2.0 Hz), 128.8, 128.5 (d, J = 12.0 Hz), 126.2 (d, J = 8.0 Hz), 126.0, 123.1, 120.2, 116.9 (d, J = 4.0 Hz). ^{31}P NMR (202 MHz, CDCl_3) δ 19.32. HRMS: calcd for $\text{C}_{22}\text{H}_{18}\text{NOP}$ $[\text{M}-\text{H}]^-$: 342.1055, found: 342.1062.

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-((diphenylphosphoryl)amino)benzoate (3y)



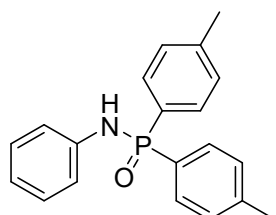
benzoate (3y): White solid, 67% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.74 (m, 6H), 7.50 (t, J = 7.3 Hz, 2H), 7.41 (td, J = 7.6, 3.1 Hz, 4H), 7.01 (d, J = 8.6 Hz, 2H), 6.21 (d, J = 10.1 Hz, 1H), 4.83 (td, J = 10.8, 4.3 Hz, 1H), 2.08 – 2.01 (m, 1H), 1.89 (pd, J = 7.0, 2.6 Hz, 1H), 1.68 (d, J = 11.2 Hz, 2H), 1.48 (qt, J = 10.9, 3.1 Hz, 2H), 1.12 – 0.99 (m, 2H), 0.87 (t, J = 6.7 Hz, 7H), 0.74 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.8, 145.1, 132.4 (d, J = 2.0 Hz), 131.9 (dd, J = 10.0, 4.0 Hz), 131.0, 128.8 (d, J = 13.0 Hz), 123.8, 117.5 (d, J = 6.0 Hz), 74.4, 47.2, 40.0, 34.3, 31.4, 26.4, 23.6, 22.0, 20.7, 16.5. ^{31}P NMR (162 MHz, CDCl_3) δ 18.79. HRMS: calcd for $\text{C}_{29}\text{H}_{34}\text{NO}_3\text{P}$ $[\text{M}-\text{H}]^-$: 474.2204, found: 474.2218.

2-isopropyl-5-methylphenyl 4-((diphenylphosphoryl)amino)benzoate (3z): White



solid, 36% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 8.6 Hz, 2H), 7.88 (dd, J = 12.5, 7.2 Hz, 4H), 7.64 (dd, J = 11.5, 7.6 Hz, 1H), 7.55 (dd, J = 7.4, 1.5 Hz, 2H), 7.49 (d, J = 3.1 Hz, 1H), 7.47 (d, J = 3.1 Hz, 2H), 7.46 – 7.45 (m, 1H), 7.20 (d, J = 7.9 Hz, 1H), 7.07 (d, J = 8.6 Hz, 2H), 6.87 (s, 1H), 6.02 (d, J = 10.0 Hz, 1H), 2.99 (dt, J = 13.9, 6.8 Hz, 1H), 2.30 (s, 3H), 1.16 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.0, 148.1, 145.7, 136.8 (d, J = 68.0 Hz), 132.6 (d, J = 3.0 Hz), 132.1, 132.0 (d, J = 9.0 Hz), 131.8 (d, J = 6.0 Hz), 130.6, 129.8, 128.9 (d, J = 13.0 Hz), 128.5 (d, J = 12.0 Hz), 126.7 (d, J = 61.0 Hz), 122.7 (d, J = 32.0 Hz), 117.7 (d, J = 6.0 Hz), 27.2, 23.0, 20.8. ^{31}P NMR (162 MHz, CDCl_3) δ 19.18. HRMS: calcd for $\text{C}_{29}\text{H}_{28}\text{NO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 470.1880, found: 470.1882.

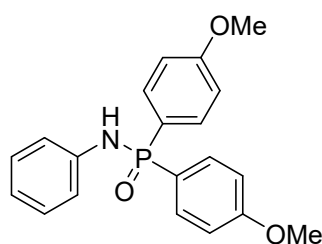
N-phenyl-P,P-di-p-tolylphosphinic amide (4a): White solid, 73% yield. ^1H NMR



(400 MHz, CDCl_3) δ 7.73 (dd, J = 12.4, 8.0 Hz, 4H), 7.16 (dd, J = 8.1, 3.1 Hz, 3H), 7.03 (t, J = 7.7 Hz, 2H), 6.96 (d, J = 7.9 Hz, 2H), 6.83 (t, J = 7.2 Hz, 2H), 5.83 (s, 1H), 2.31 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.9 (d, J = 3.0 Hz), 140.1, 132.1 (d, J = 11.0 Hz), 129.5 (d, J = 14.0 Hz), 129.1, 128.3 (d, J =

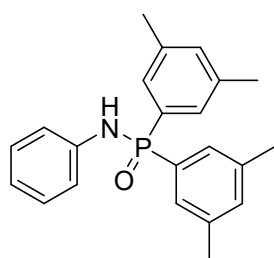
13.0 Hz), 121.9, 119.2, 21.6. ^{31}P NMR (162 MHz, CDCl_3) δ 18.87. HRMS: calcd for $\text{C}_{20}\text{H}_{20}\text{NOP}$ $[\text{M}-\text{H}]^-$: 320.1210, found: 320.1217.

P,P-bis(4-methoxyphenyl)-N-phenylphosphinic amide (4b): White solid, 70% yield.



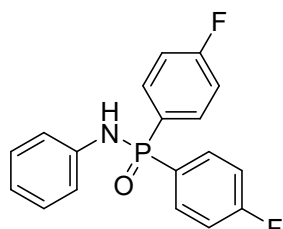
^1H NMR (400 MHz, CDCl_3) δ 7.79 – 7.73 (m, 4H), 7.10 (t, $J = 7.9$ Hz, 2H), 6.96 (s, 1H), 6.94 (s, 1H), 6.92 (t, $J = 2.2$ Hz, 2H), 6.91 (t, $J = 2.2$ Hz, 2H), 6.85 (t, $J = 7.4$ Hz, 1H), 5.43 (d, $J = 9.3$ Hz, 1H), 3.80 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.6 (d, $J = 3.0$ Hz), 140.7 (d, $J = 1.0$ Hz), 133.8 (d, $J = 11.0$ Hz), 129.1, 123.5 (d, $J = 136.0$ Hz), 121.5, 118.4 (d, $J = 6.0$ Hz), 114.3 (d, $J = 14.0$ Hz), 55.3. ^{31}P NMR (162 MHz, CDCl_3) δ 18.81. HRMS: calcd for $\text{C}_{20}\text{H}_{20}\text{NO}_3\text{P}$ $[\text{M}-\text{H}]^-$: 352.1108, found: 352.1114.

P,P-bis(3,5-dimethylphenyl)-N-phenylphosphinic amide (4c): White solid, 68% yield.



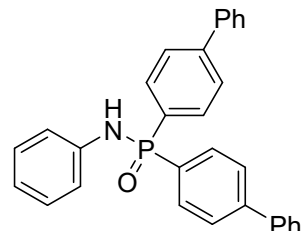
^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 12.7$ Hz, 4H), 7.15 – 7.05 (m, 4H), 6.97 (d, $J = 8.4$ Hz, 2H), 6.85 (t, $J = 7.1$ Hz, 1H), 5.45 (d, $J = 8.1$ Hz, 1H), 2.29 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.7, 138.4 (d, $J = 14.0$ Hz), 133.9 (d, $J = 3.0$ Hz), 132.4 (d, $J = 28.0$ Hz), 129.4 (d, $J = 10.0$ Hz), 129.1, 121.5, 118.4 (d, $J = 7.0$ Hz), 21.3. ^{31}P NMR (162 MHz, CDCl_3) δ 19.30. HRMS: calcd for $\text{C}_{22}\text{H}_{24}\text{NOP}$ $[\text{M}-\text{H}]^-$: 348.1523, found: 348.1526.

P,P-bis(4-fluorophenyl)-N-phenylphosphinic amide (4d): White solid, 60% yield.



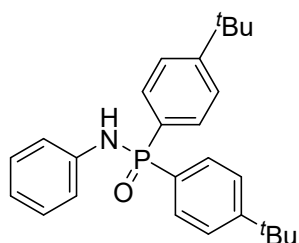
^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.76 (m, 4H), 7.08 (dd, $J = 10.6, 4.1$ Hz, 6H), 6.97 (d, $J = 7.9$ Hz, 2H), 6.88 (t, $J = 7.5$ Hz, 1H), 5.94 (d, $J = 9.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.5 (dd, $J_1 = 3.03$ Hz, $J_2 = 255.53$ Hz), 140.1, 134.5 (dd, $J_1 = 9.09$, $J_2 = 12.12$ Hz), 129.2, 127.01 (dd $J_1 = 4.04$, $J_2 = 134.33$ Hz), 122.0, 118.7 (d, $J = 8.08$ Hz), 116.2 (dd, $J_1 = 23.23$, $J_2 = 21.21$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 16.71. HRMS: calcd for $\text{C}_{18}\text{H}_{14}\text{F}_2\text{NOP}$ $[\text{M}-\text{H}]^-$: 328.0708, found: 328.0717.

P,P-di([1,1'-biphenyl]-4-yl)-N-phenylphosphinic amide (4e): White solid, 48% yield.



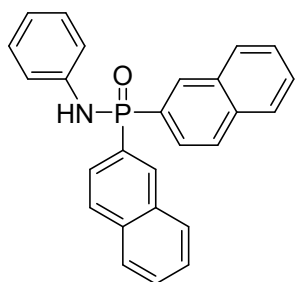
^1H NMR (400 MHz, CDCl_3) δ 8.04 – 7.94 (m, 2H), 7.85 – 7.78 (m, 2H), 7.74 – 7.66 (m, 4H), 7.60 (dd, $J = 16.1, 7.6$ Hz, 5H), 7.51 – 7.30 (m, 7H), 7.20 – 7.13 (m, 1H), 7.05 (d, $J = 7.7$ Hz, 1H), 6.91 (t, $J = 7.4$ Hz, 1H), 5.58 (d, $J = 9.3$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.9 (dd, $J = 23.0, 3.0$ Hz), 139.8 (dd, $J = 8.0, 1.0$ Hz), 132.5 (dd, $J = 11.0, 2.0$ Hz), 131.4 (d, $J = 48.0$ Hz), 130.2 (d, $J = 73.0$ Hz), 129.3, 128.9 (d, $J = 2.0$ Hz), 128.2, 127.5 (d, $J = 14.0$ Hz), 127.2 (dd, $J = 8.0, 4.0$ Hz), 121.8, 118.5 (d, $J = 7.0$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 18.94. HRMS: calcd for $\text{C}_{30}\text{H}_{24}\text{NOP}$ $[\text{M}-\text{H}]^-$: 444.1523, found: 444.1538.

P,P-bis(4-(tert-butyl)phenyl)-N-phenylphosphinic amide (4f): White solid, 53%



yield. ^1H NMR (400 MHz, CDCl_3) δ 7.79 (dd, $J = 12.1, 8.3$ Hz, 2H), 7.58 (dd, $J = 11.6, 8.2$ Hz, 4H), 7.45 (t, $J = 2.4$ Hz, 2H), 7.43 (d, $J = 2.7$ Hz, 2H), 7.10 (t, $J = 7.8$ Hz, 1H), 6.98 (d, $J = 8.0$ Hz, 1H), 6.85 (t, $J = 7.3$ Hz, 1H), 5.59 (t, $J = 7.8$ Hz, 1H), 1.30 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.1 (d, $J = 3.0$ Hz), 131.9 (t, $J = 10.0$ Hz), 130.2, 129.1, 125.7 (d, $J = 13.0$ Hz), 125.4 (d, $J = 12.0$ Hz), 121.4, 118.3 (d, $J = 7.0$ Hz), 35.0, 31.1. ^{31}P NMR (162 MHz, CDCl_3) δ 18.47. HRMS: calcd for $\text{C}_{26}\text{H}_{32}\text{NOP}$ $[\text{M}-\text{H}]^-$: 404.2149, found: 404.2156.

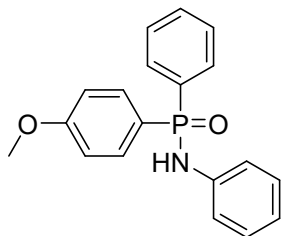
P,P-di(naphthalen-2-yl)-N-phenylphosphinic amide (4g): White solid, 64% yield.



^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.53 (d, $J = 13.9$ Hz, 2H), 8.45 (d, $J = 11.4$ Hz, 1H), 8.05 (d, $J = 7.7$ Hz, 2H), 8.00 (dd, $J = 8.5, 3.1$ Hz, 2H), 7.93 (d, $J = 7.9$ Hz, 2H), 7.86 (t, $J = 9.3$ Hz, 2H), 7.58 (dt, $J = 15.2, 6.8$ Hz, 4H), 7.16 – 7.02 (m, 4H), 6.76 (t, $J = 6.9$ Hz, 1H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 142.5, 134.6 (d, $J = 3.0$ Hz), 133.8 (d, $J = 10.0$ Hz), 132.6 (d, $J = 14.0$ Hz), 131.4, 130.2, 129.3, 128.8, 128.7, 128.1, 127.4, 127.2 (d, $J = 10.0$ Hz), 121.1, 118.7 (d, $J = 7.0$ Hz). ^{31}P NMR

(162 MHz, $\text{DMSO}-d_6$) δ 16.04. HRMS: calcd for $\text{C}_{26}\text{H}_{20}\text{NOP}$ $[\text{M}+\text{H}]^+$: 394.1355, found: 394.1349.

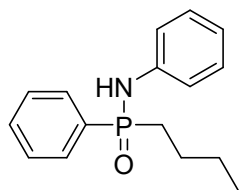
P-(4-methoxyphenyl)-N,P-diphenylphosphinic amide (4h): ^1H NMR (400 MHz,



CDCl_3) δ 7.83 (ddd, $J = 23.3, 12.2, 8.3$ Hz, 4H), 7.52 – 7.41 (m, 3H), 7.12 (t, $J = 7.8$ Hz, 2H), 6.96 (t, $J = 8.8$ Hz, 4H), 6.88 (t, $J = 7.3$ Hz, 1H), 5.43 (d, $J = 9.3$ Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.69, 140.48, 133.98, 133.87, 132.03, 132.01, 131.82, 131.72, 129.17, 128.76, 128.63, 121.63, 118.43, 118.37, 114.39, 114.25, 55.30. ^{31}P NMR (162

MHz, CDCl_3) δ 18.76. HRMS: calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_2\text{P}$ $[\text{M}+\text{H}]^+$: 324.1148, found: 324.1153.

P-butyl-N,P-diphenylphosphinic amide (4i): ^1H NMR (400 MHz, CDCl_3) δ 7.87 –



7.79 (m, 2H), 7.52 – 7.43 (m, 3H), 7.10 (t, $J = 8.0$ Hz, 2H), 6.97 (d, $J = 7.4$ Hz, 2H), 6.85 (t, $J = 7.4$ Hz, 1H), 5.82 (d, $J = 10.3$ Hz, 1H), 2.13 – 1.99 (m, 2H), 1.34 – 1.22 (m, 4H), 0.81 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.57, 131.92, 131.82, 129.12, 128.71, 128.59, 121.46, 118.45, 118.39, 113.51, 113.29,

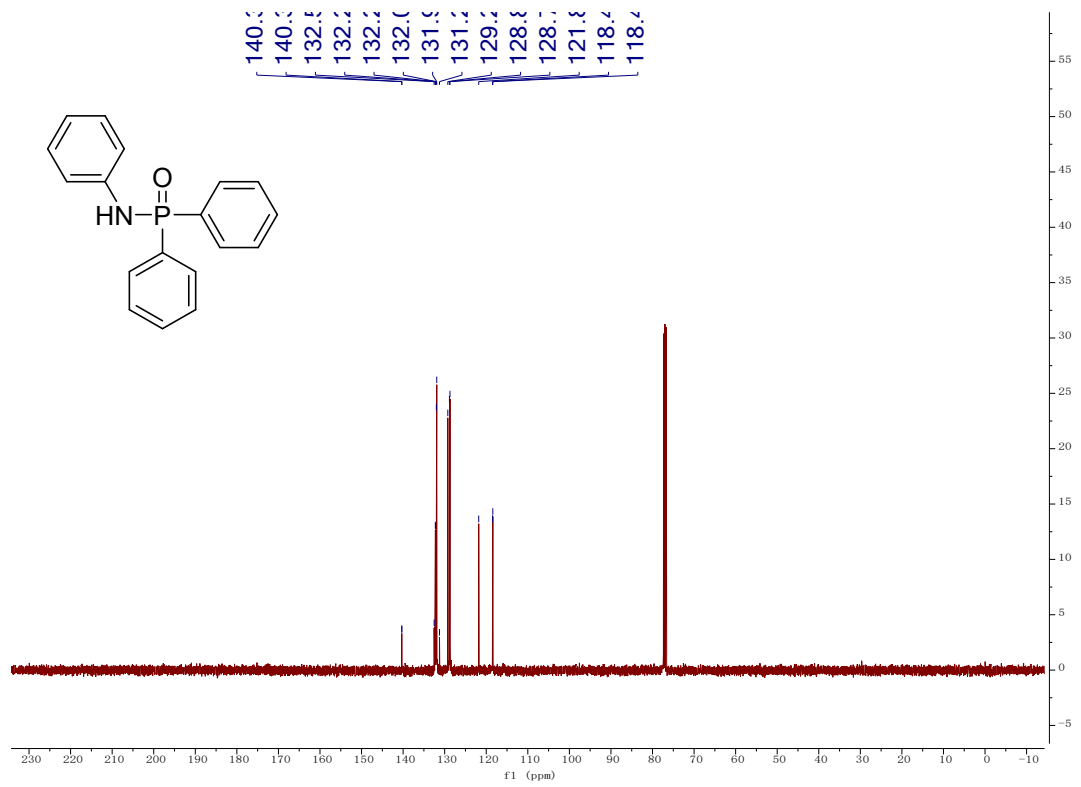
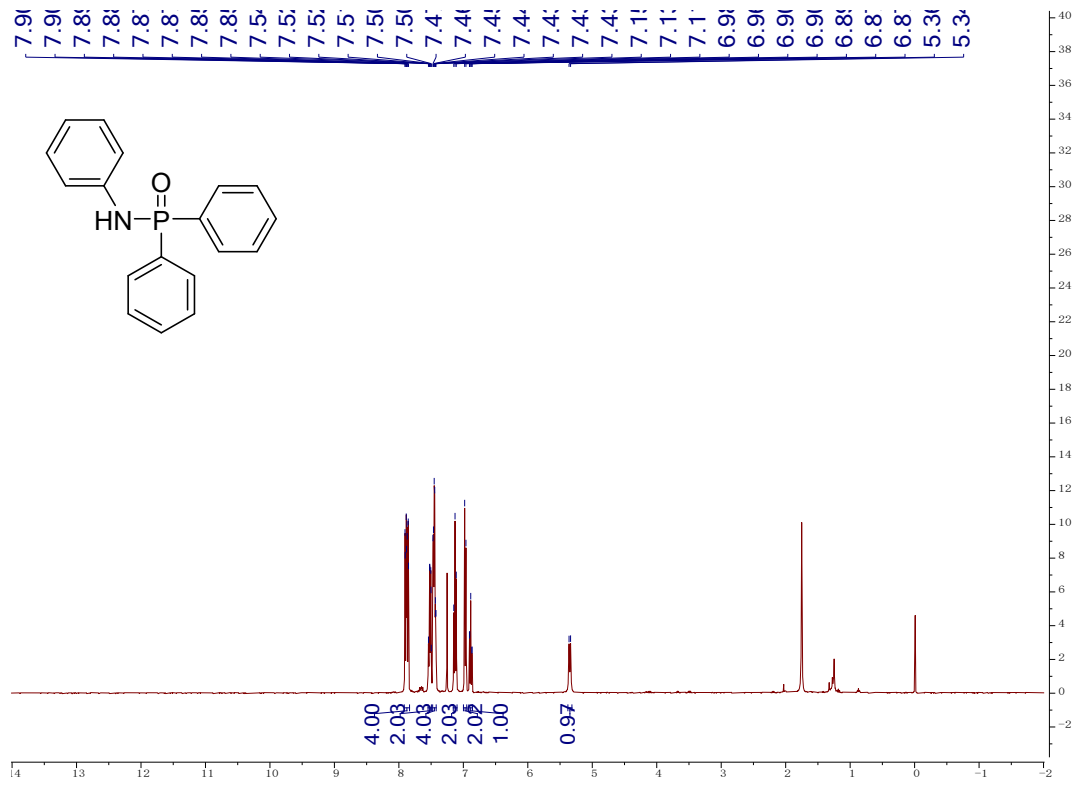
30.48, 29.58, 23.96, 13.49. ^{31}P NMR (162 MHz, CDCl_3) δ 29.17. HRMS: calcd for $\text{C}_{16}\text{H}_{20}\text{NOP}$ $[\text{M}+\text{H}]^+$: 274.1355, found: 274.1359.

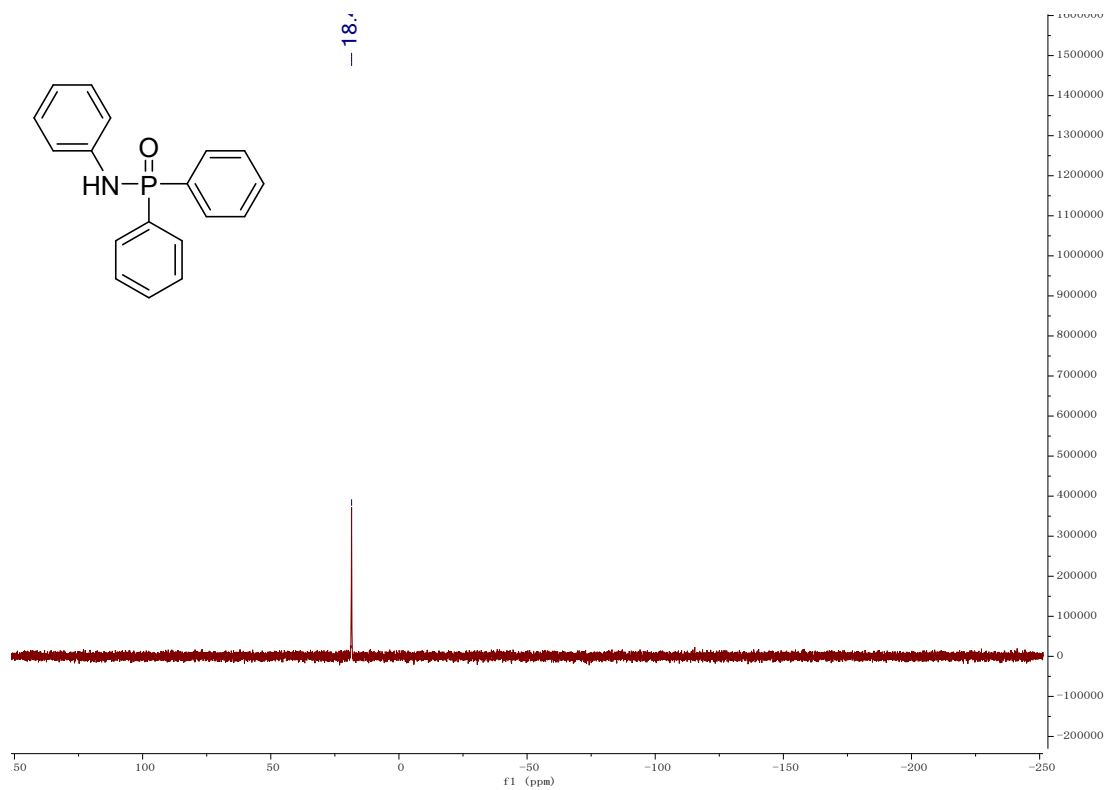
7. References

- [1]. H. Qian, X.-F. Shen, H.-L. Huang, Y. Zhang, M.-T. Zhang, H.-Q. Wang, Z.-K. Wang, *Carbohydr. Polym.*, 2020, **231**, 115731.
- [2]. G. Brahmachari, *Adv. Synth. Catal.*, 2020, **362**, 5411.

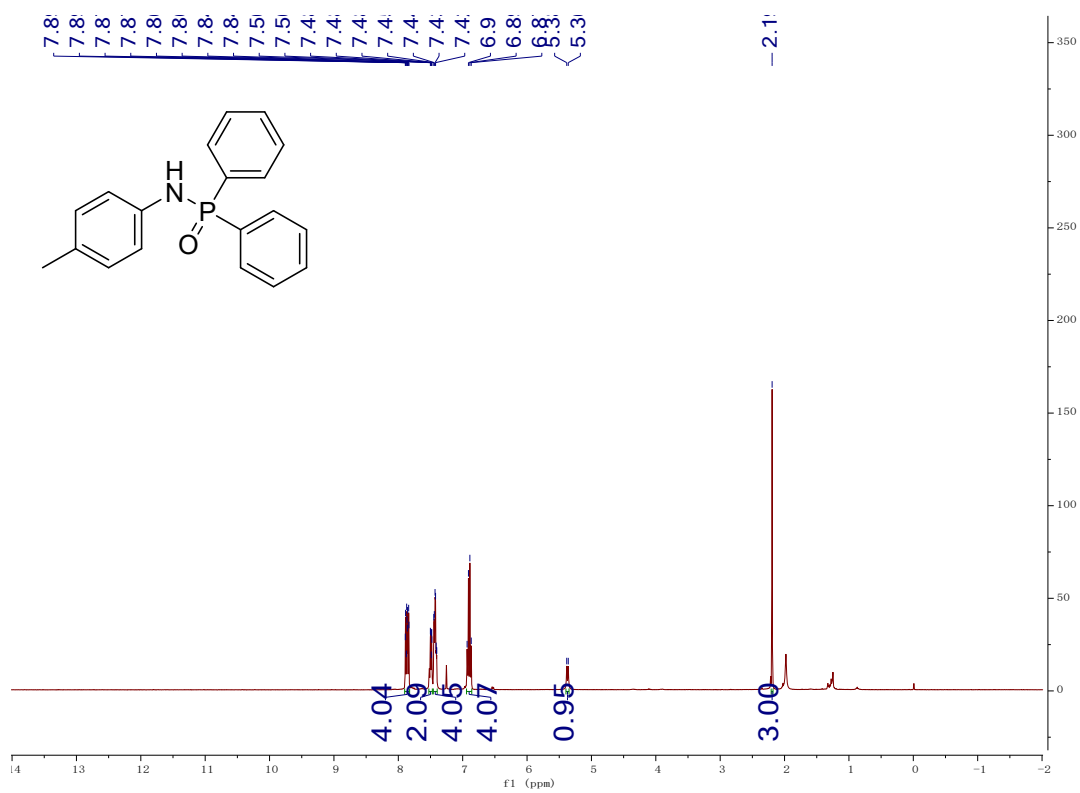
8. Copies of product ^1H NMR, ^{13}C NMR and ^{31}P NMR

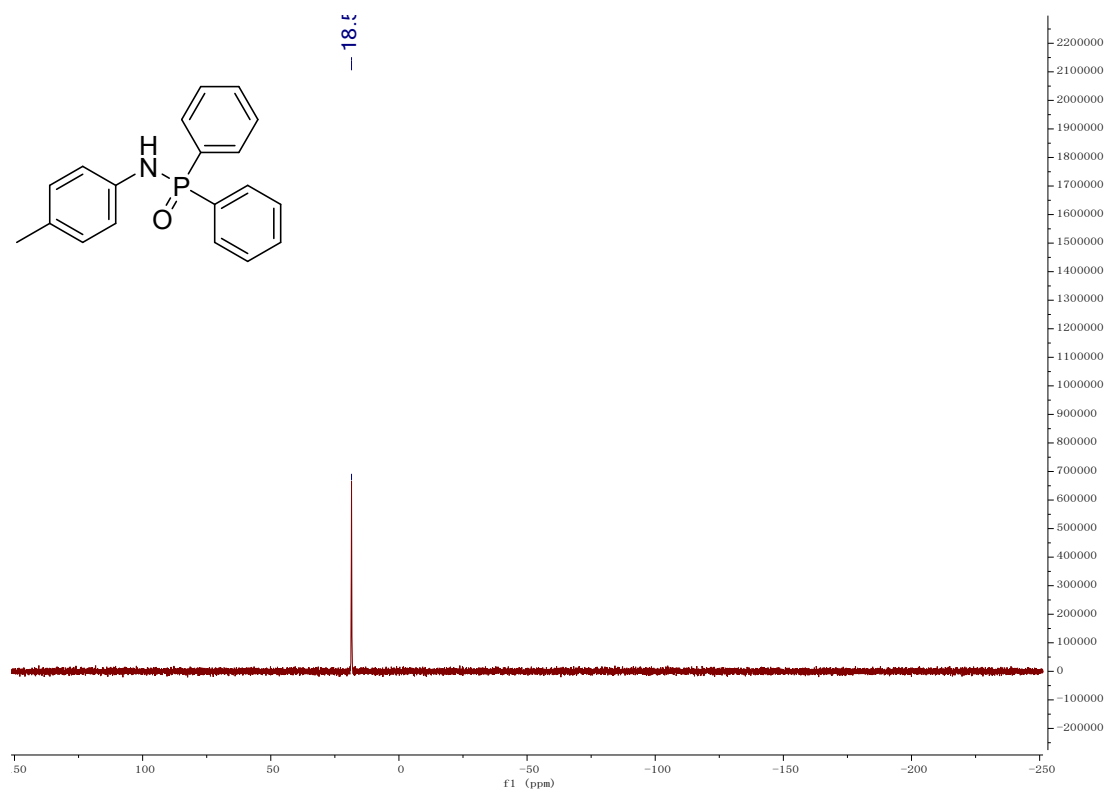
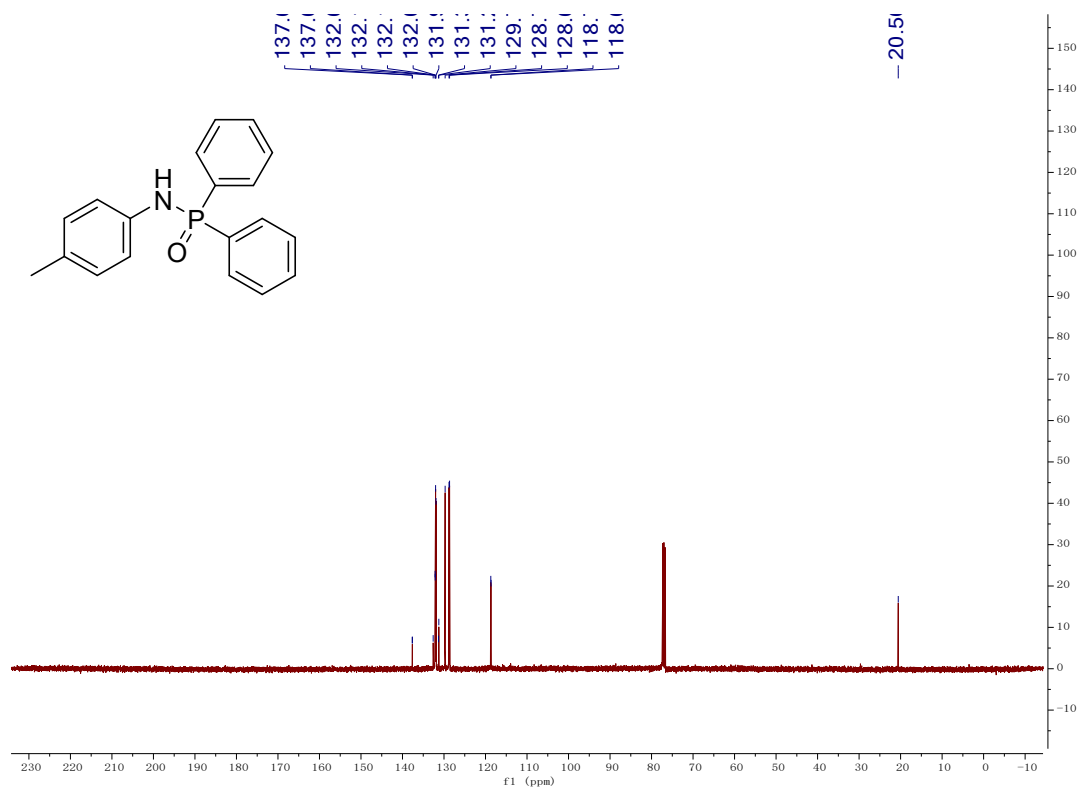
N,P,P-triphenylphosphinic amide (3a):



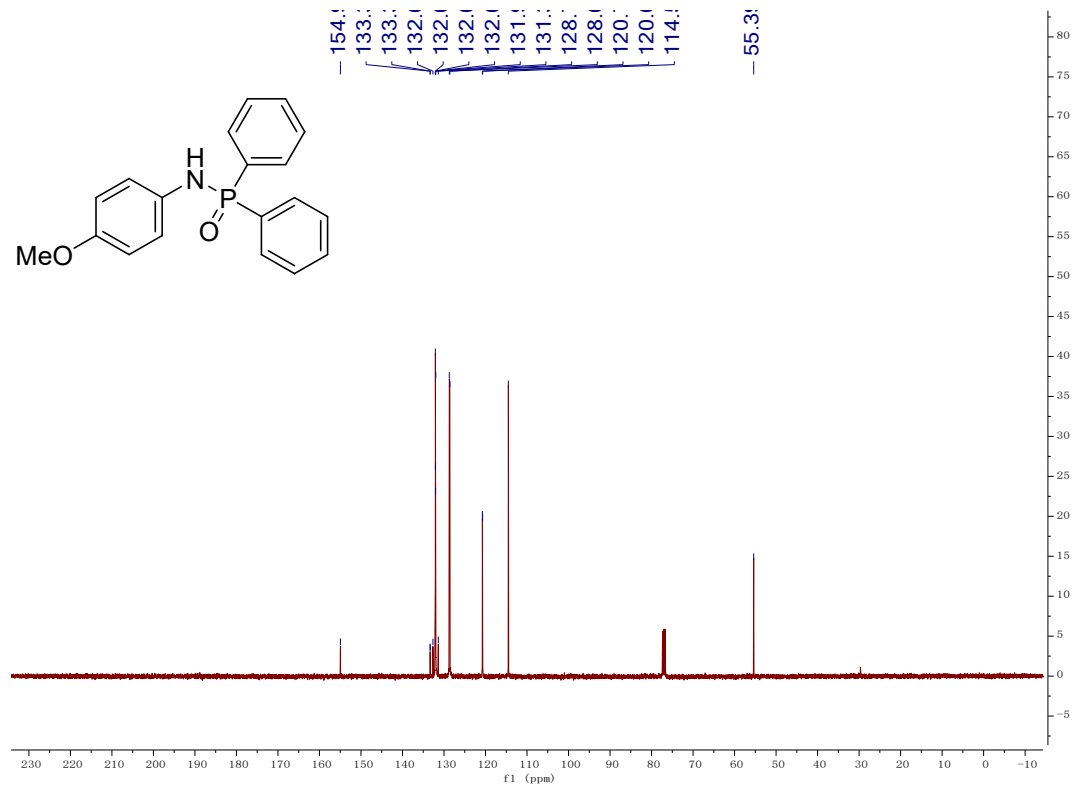
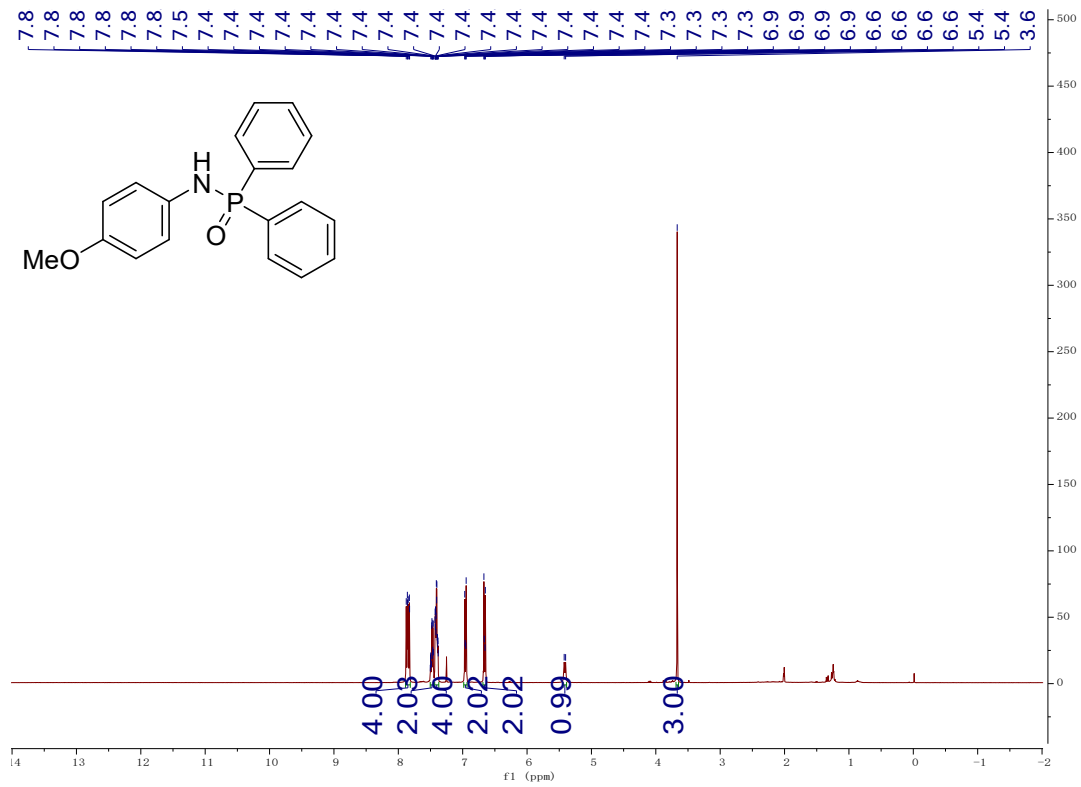


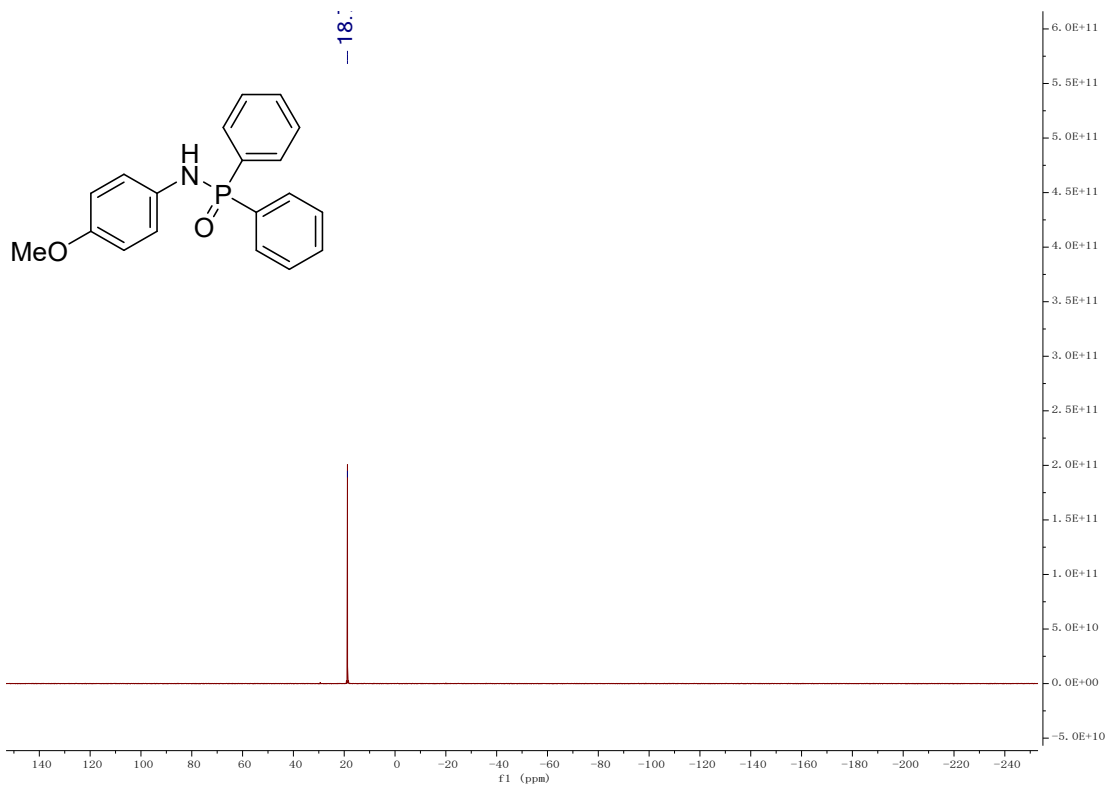
P,P-diphenyl-N-(p-tolyl)phosphinic amide (3b)



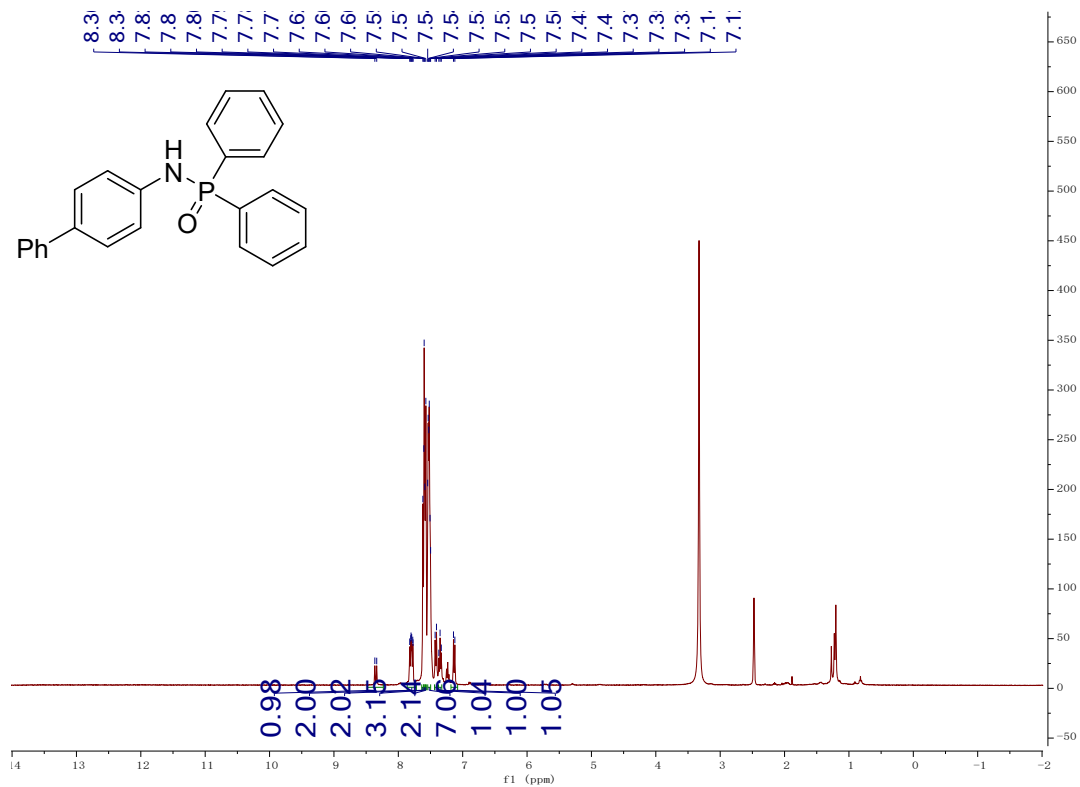


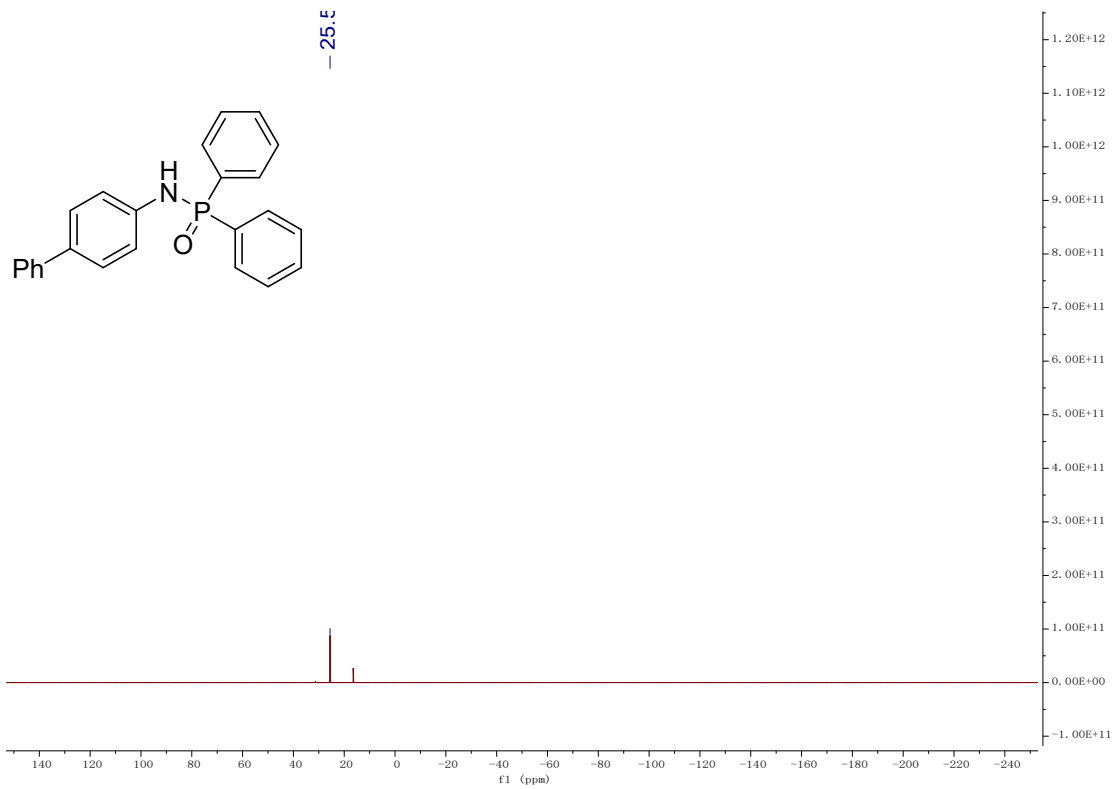
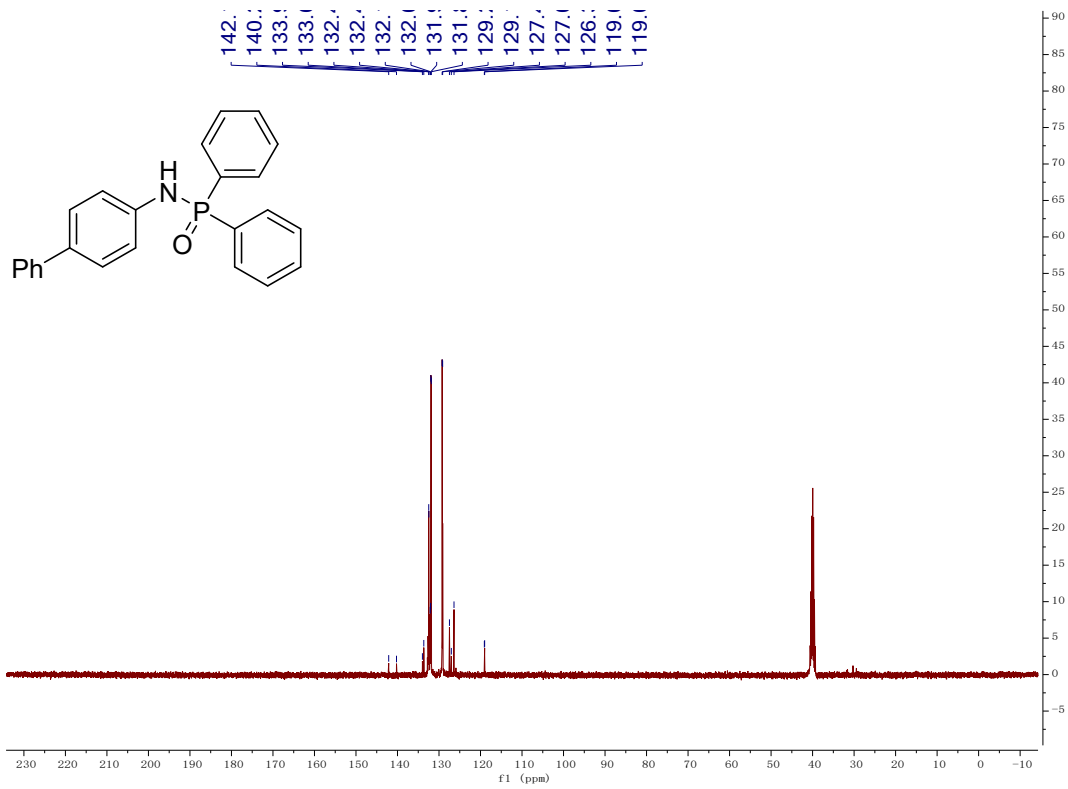
N-(4-methoxyphenyl)-P,P-diphenylphosphinic amide (3c)



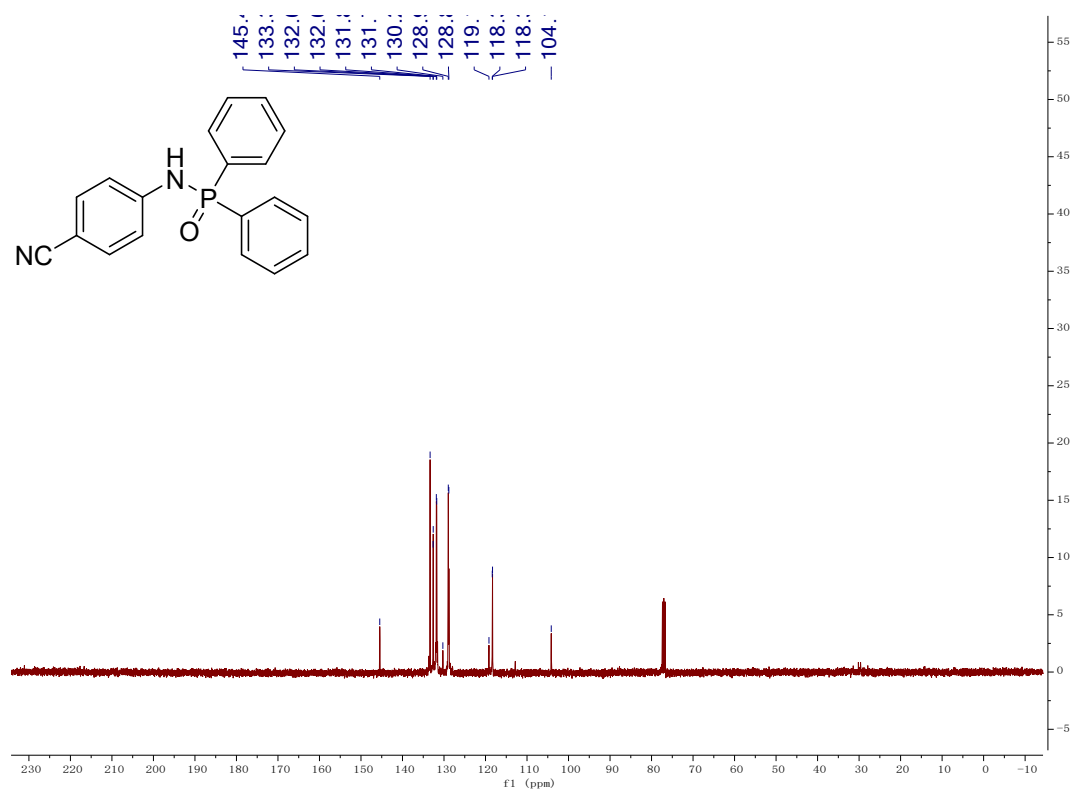
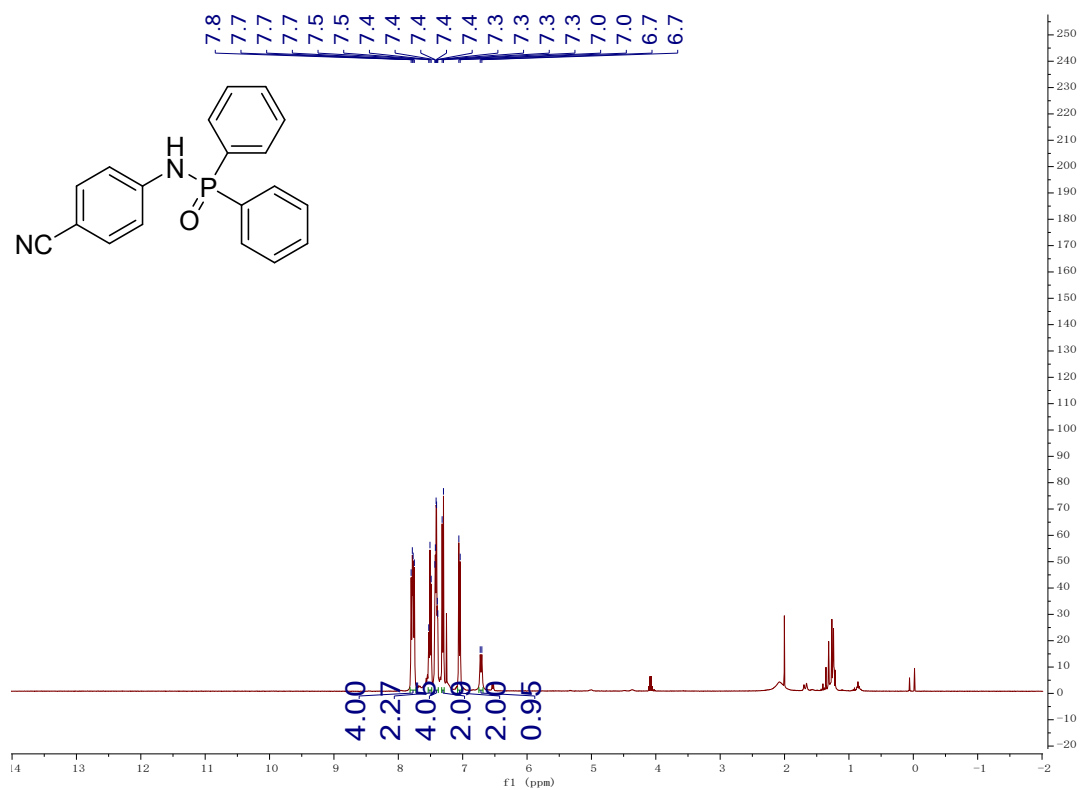


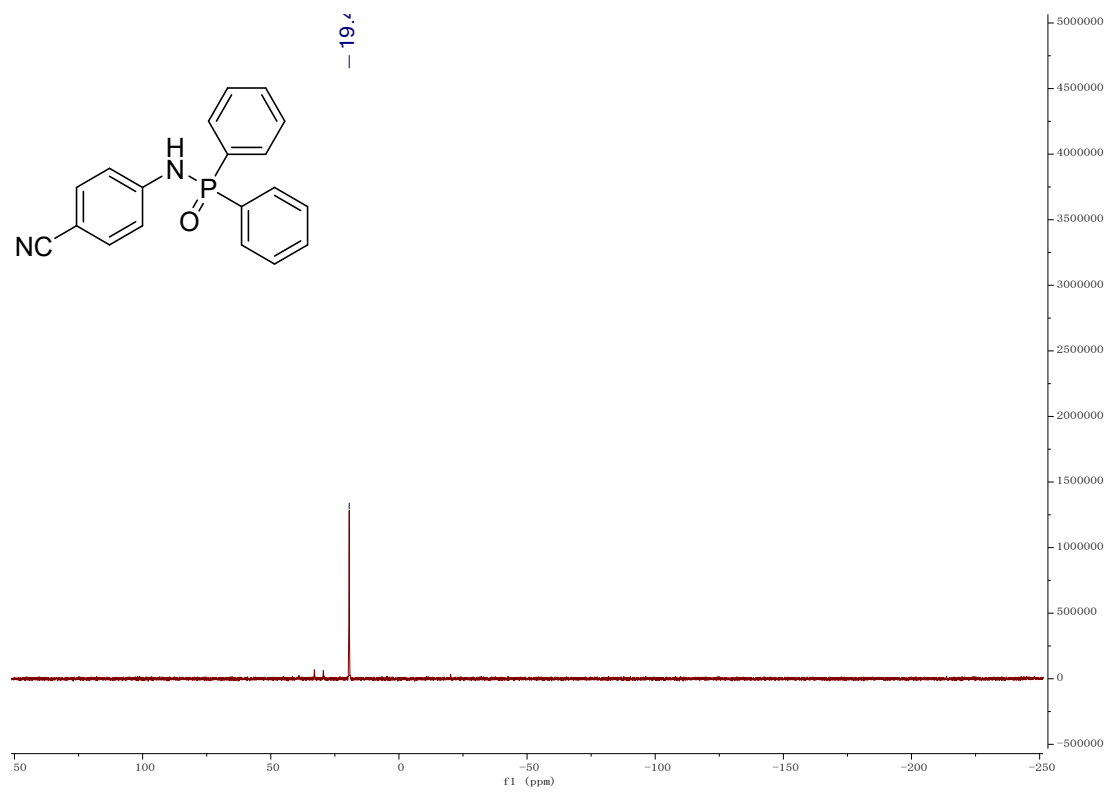
N-([1,1'-biphenyl]-4-yl)-P,P-diphenylphosphinic amide (3d)



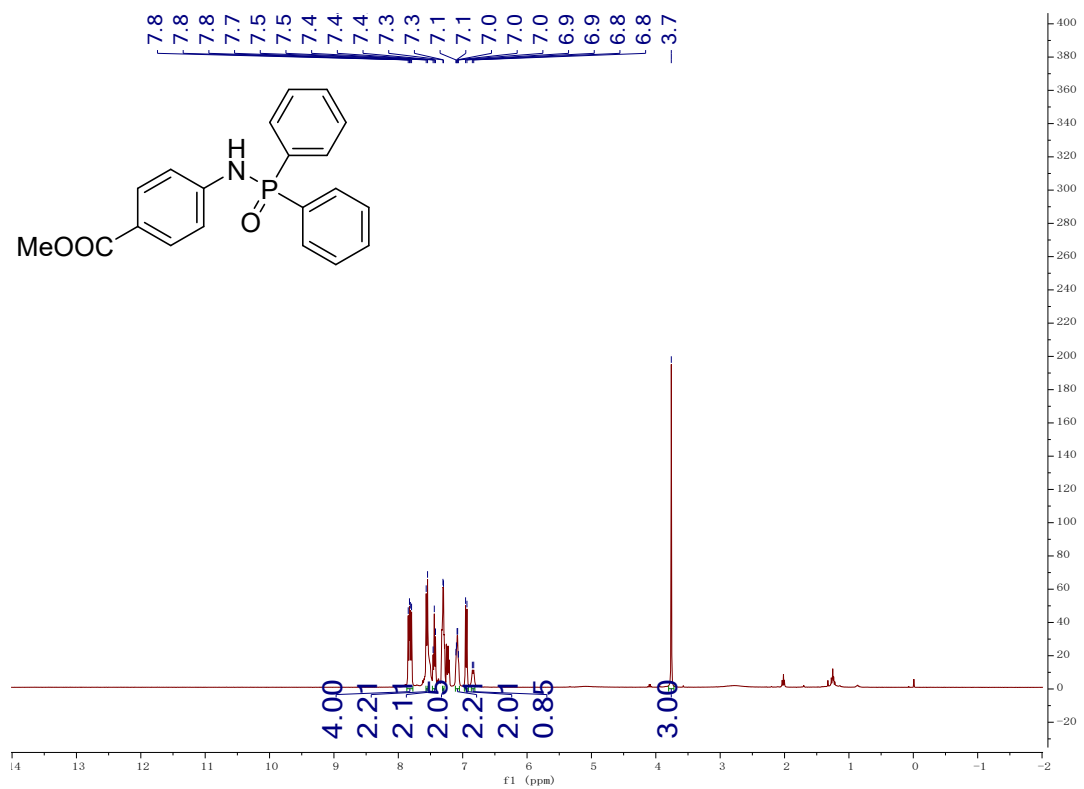


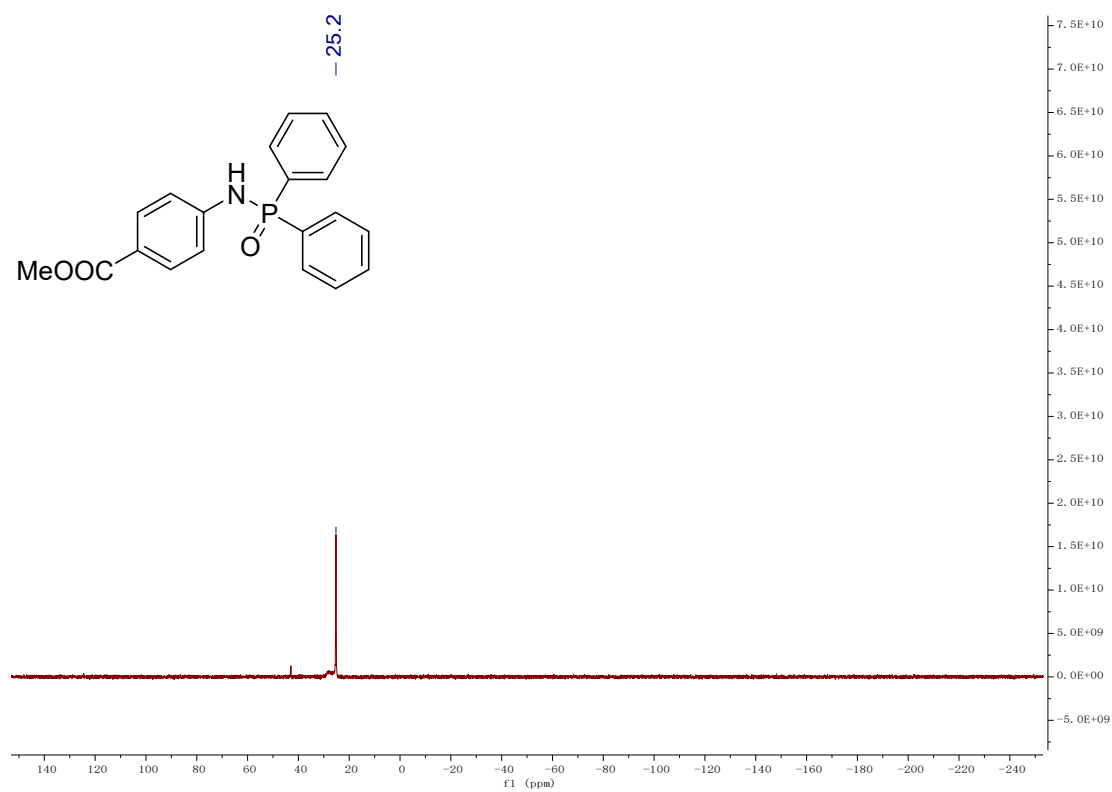
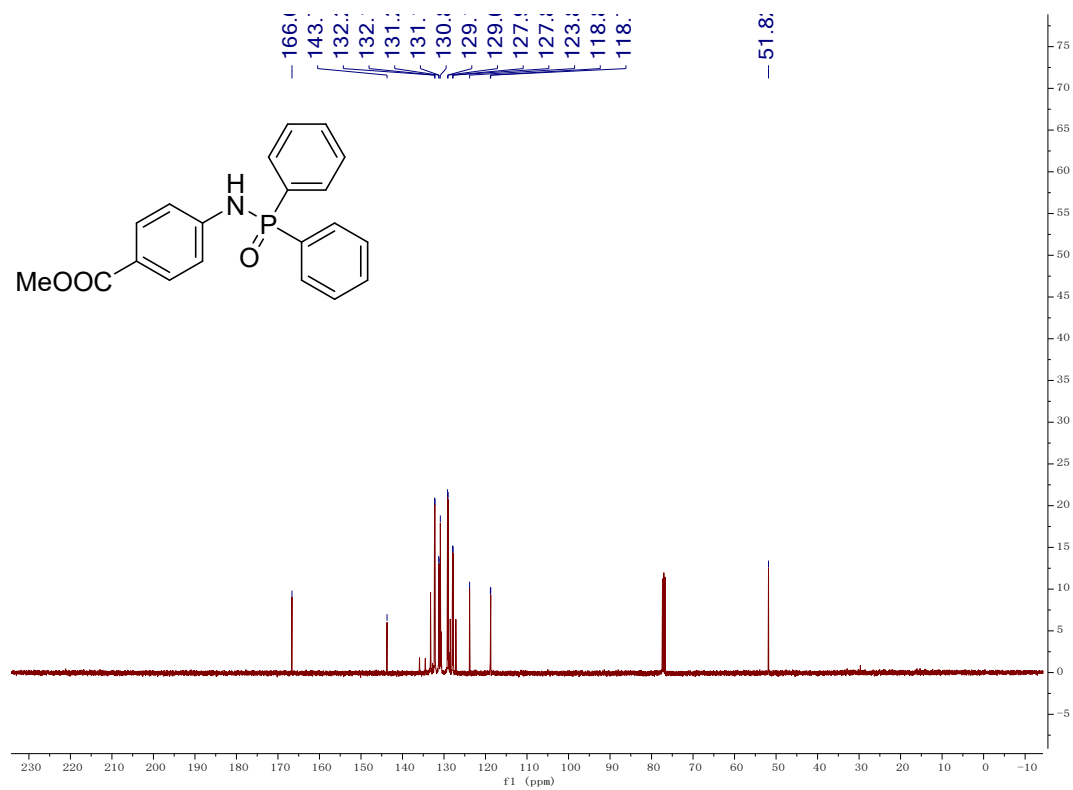
N-(4-cyanophenyl)-P,P-diphenylphosphinic amide (3e)



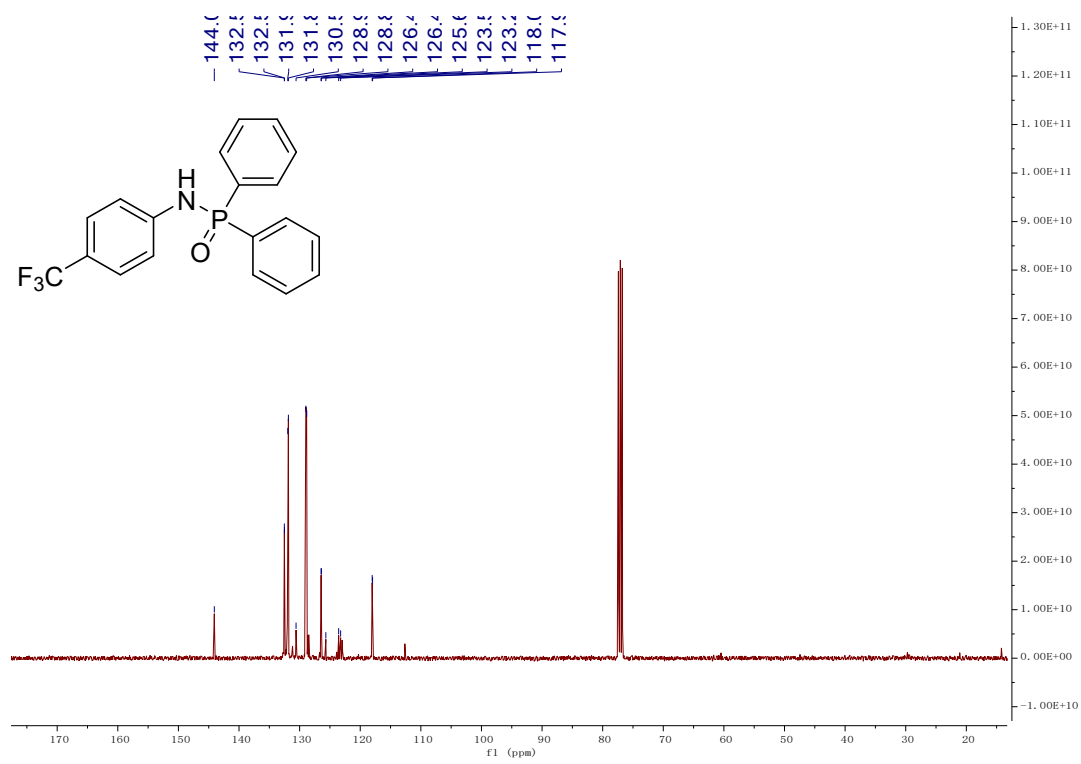
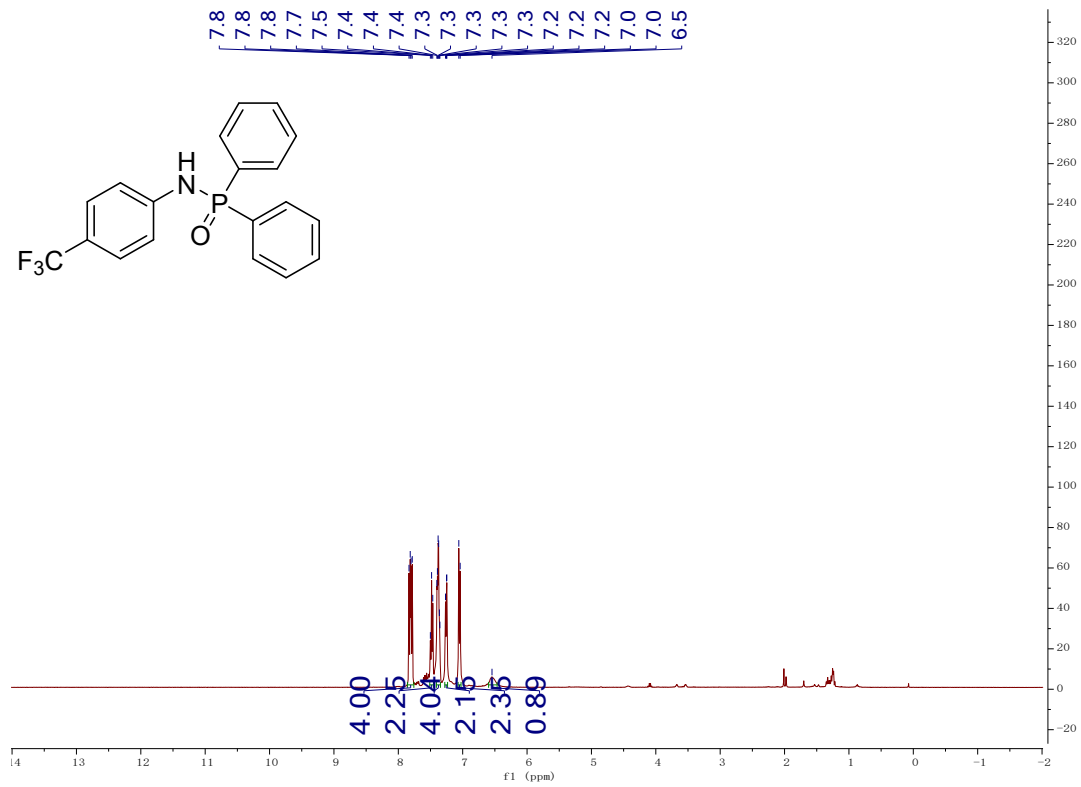


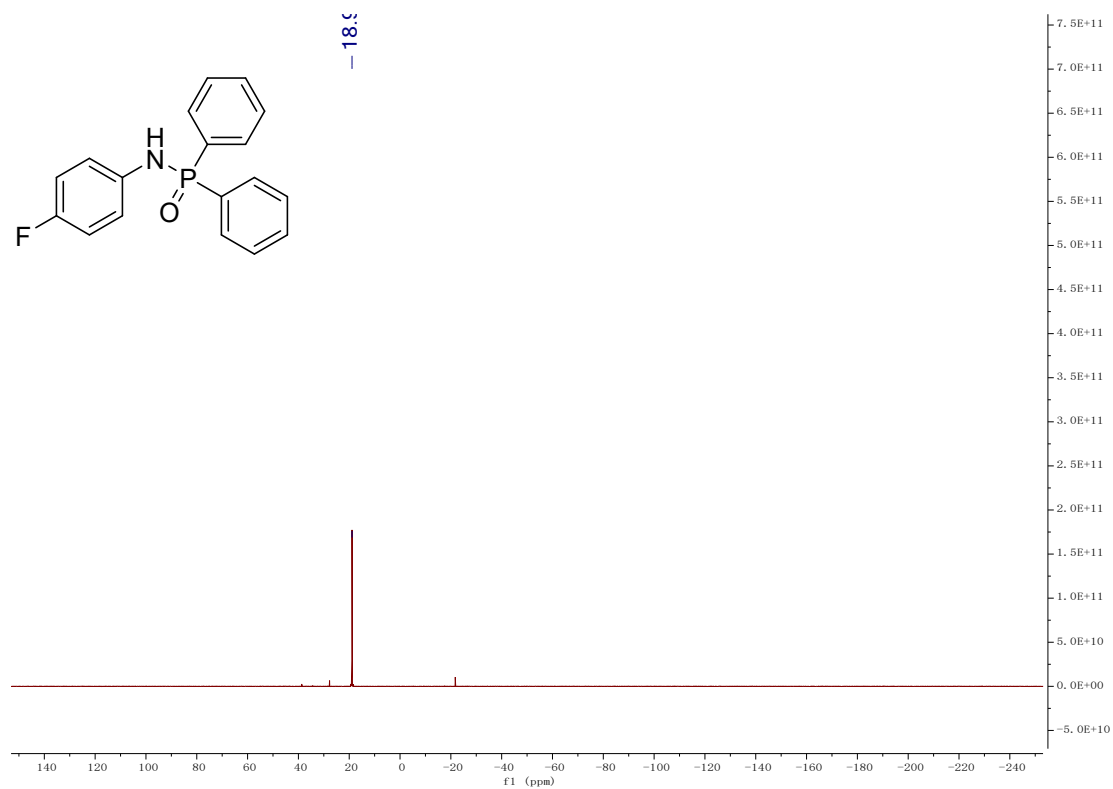
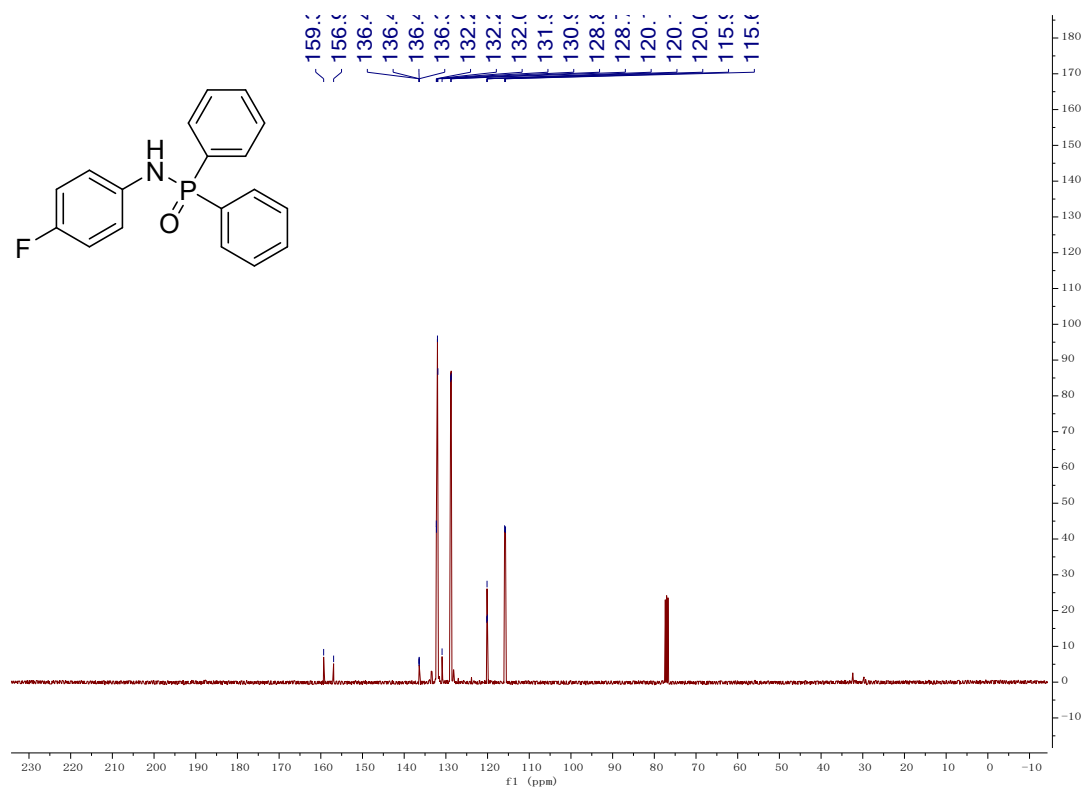
Methyl 4-((diphenylphosphoryl)amino)benzoate (3f):



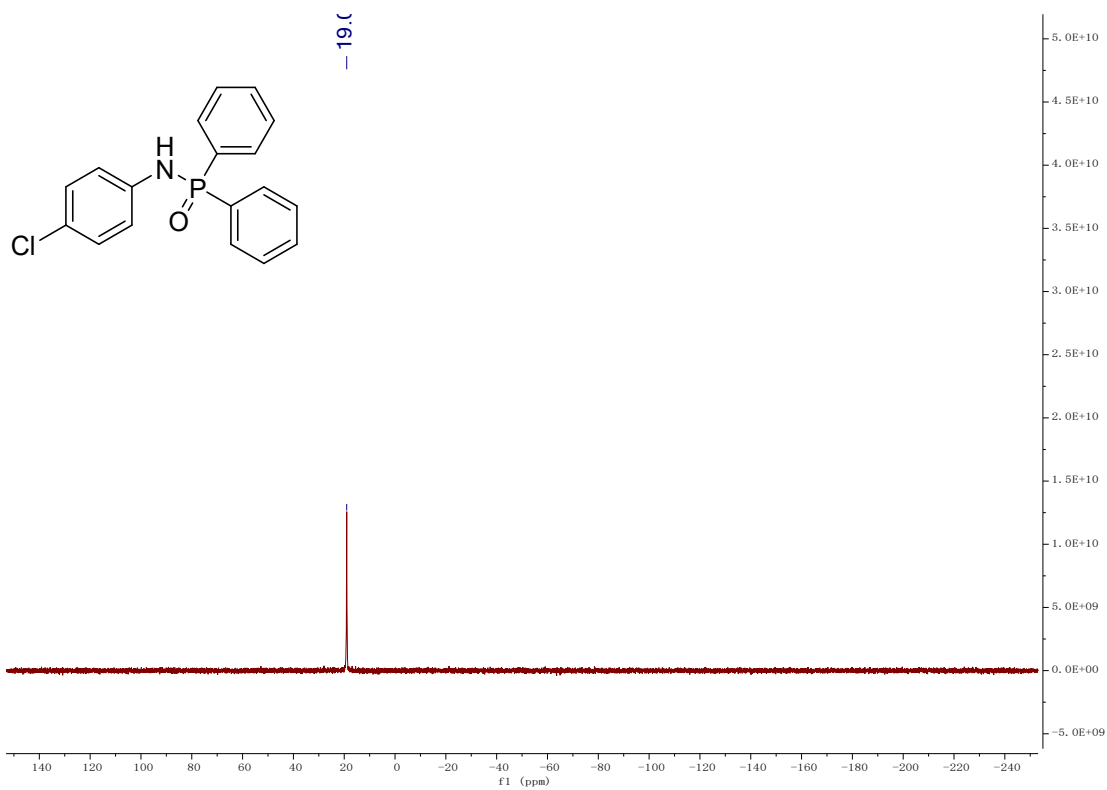


P,P-diphenyl-N-(4-(trifluoromethyl)phenyl)phosphinic amide (3g)

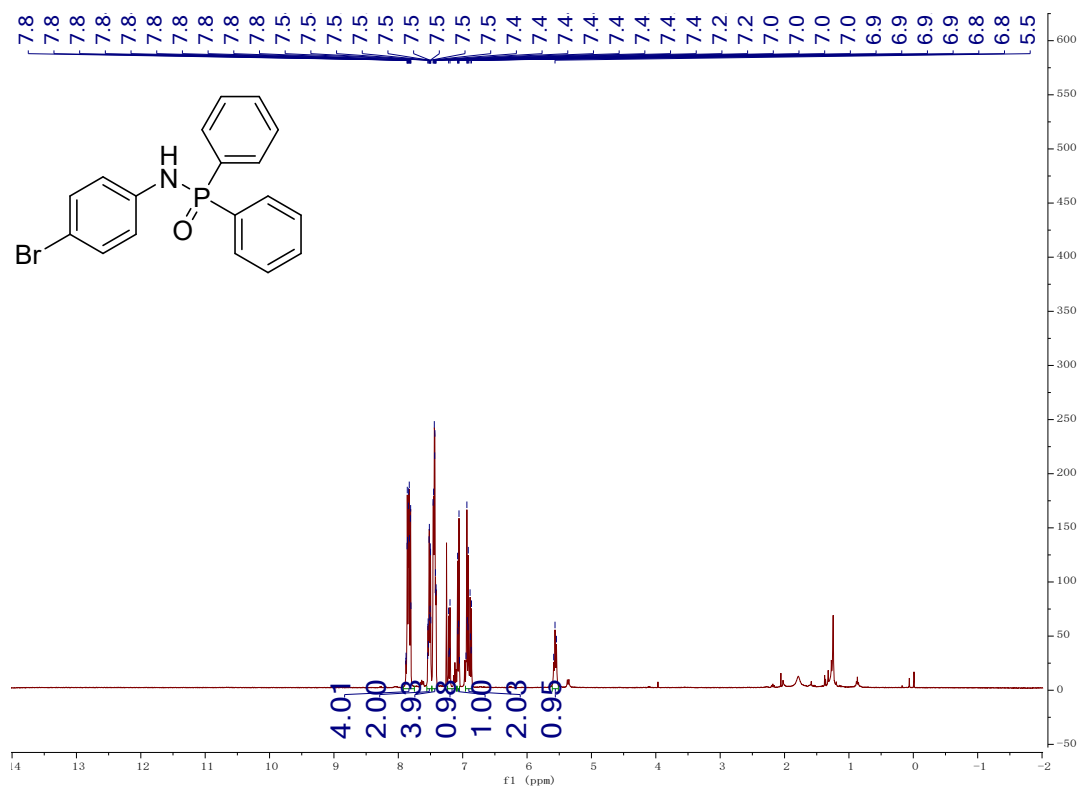


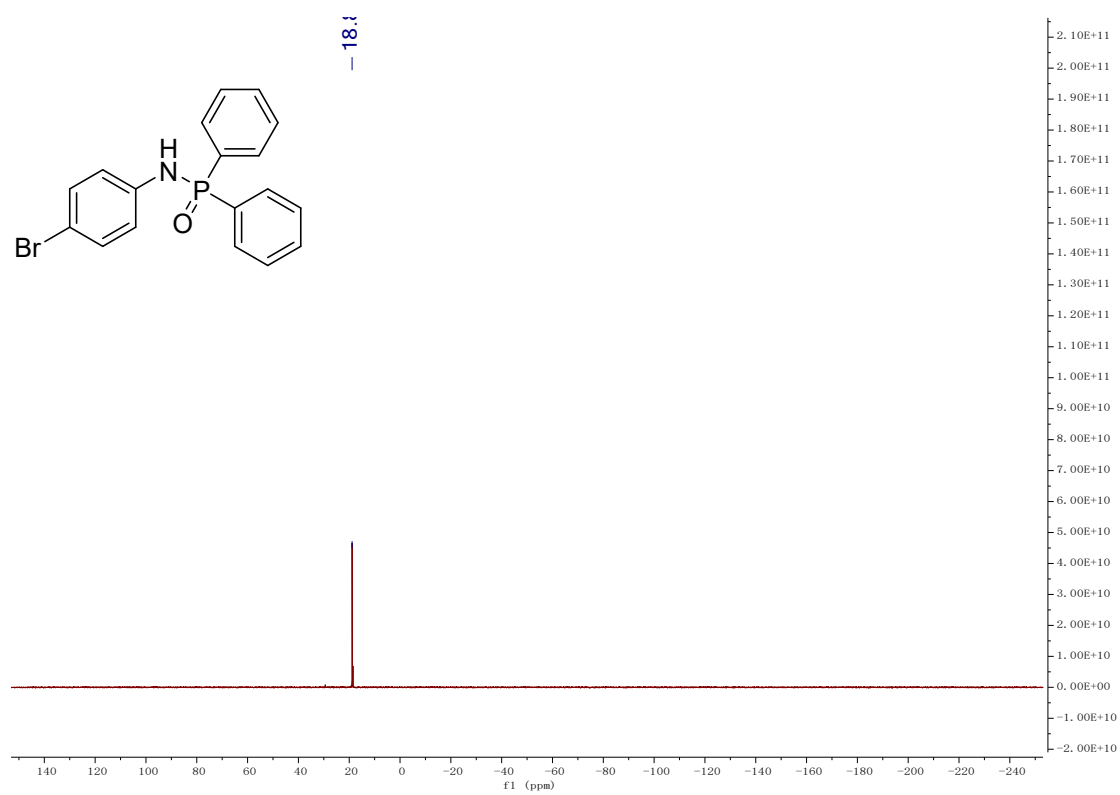
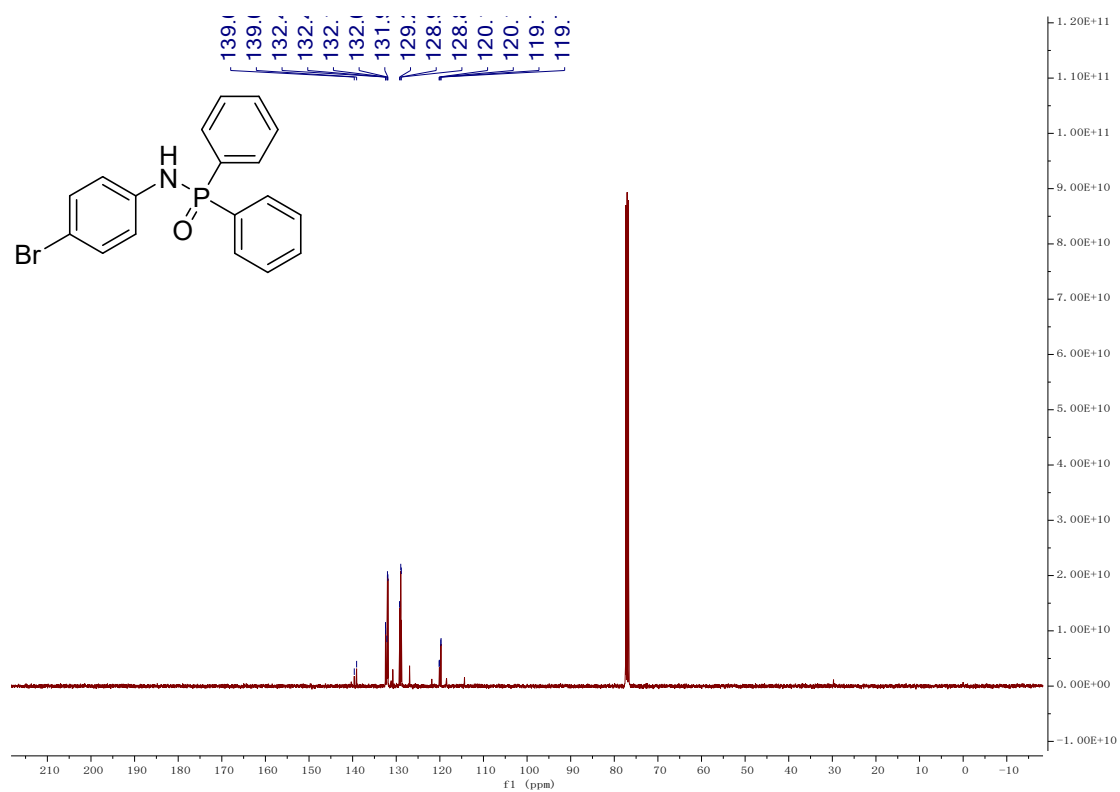


N-(4-chlorophenyl)-P,P-diphenylphosphinic amide (3i)

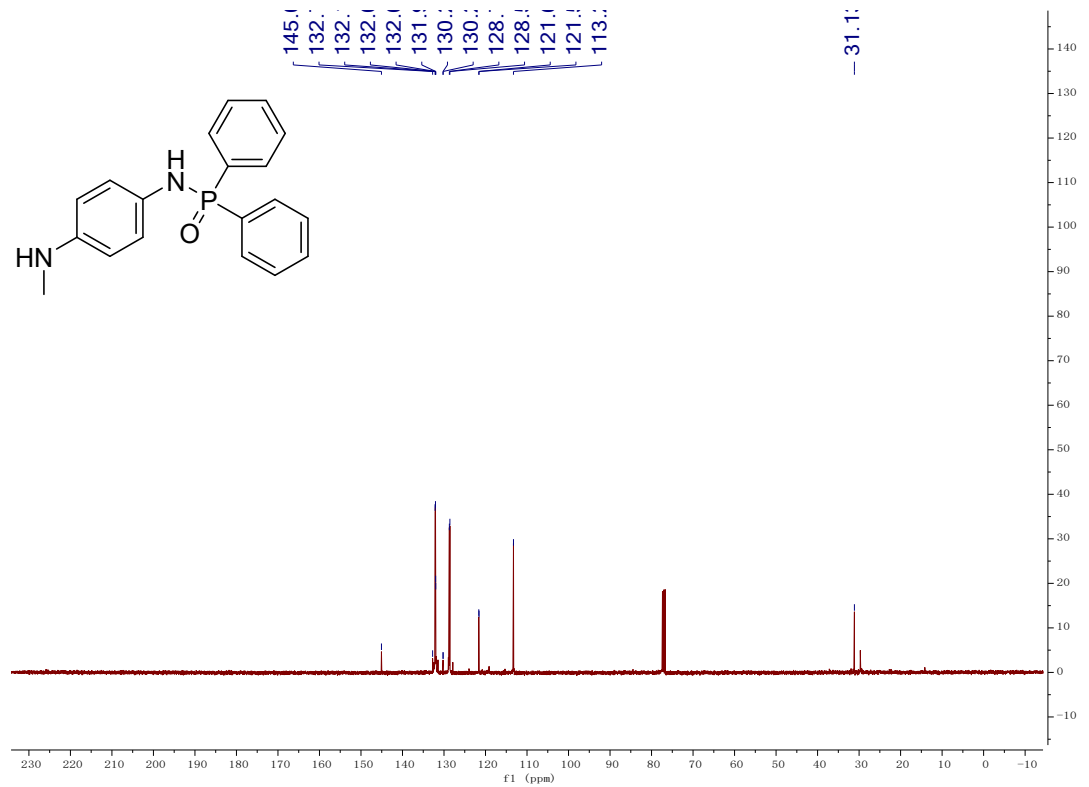
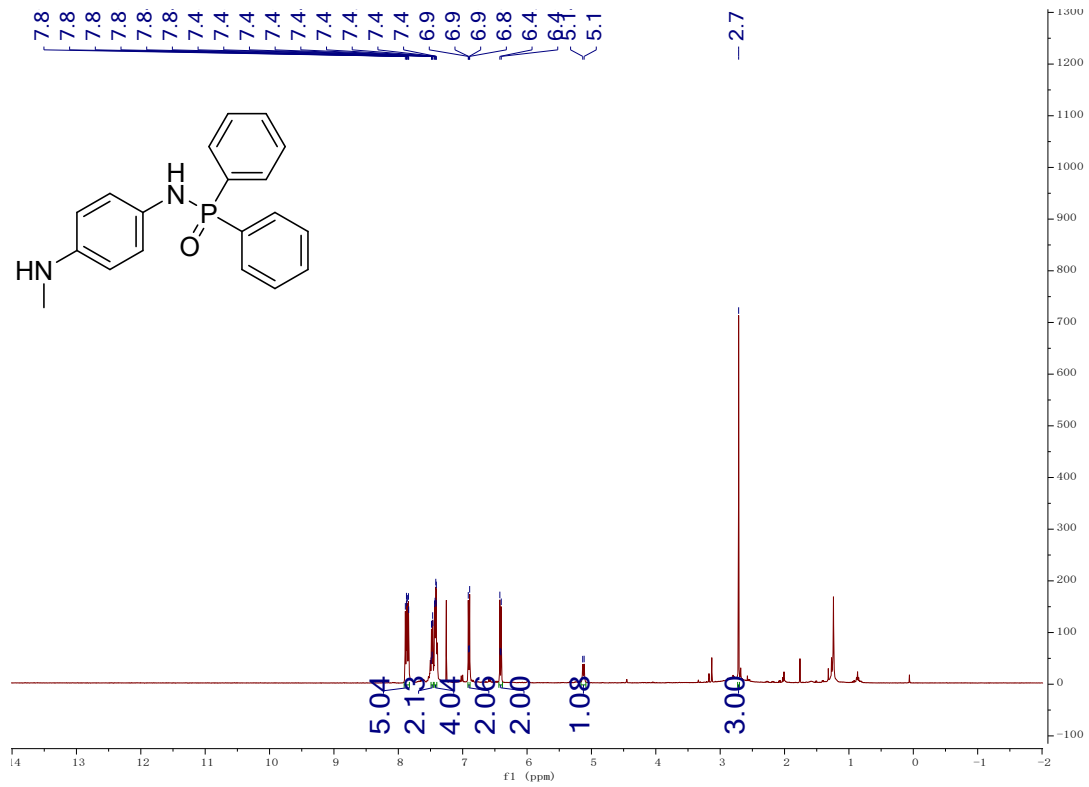


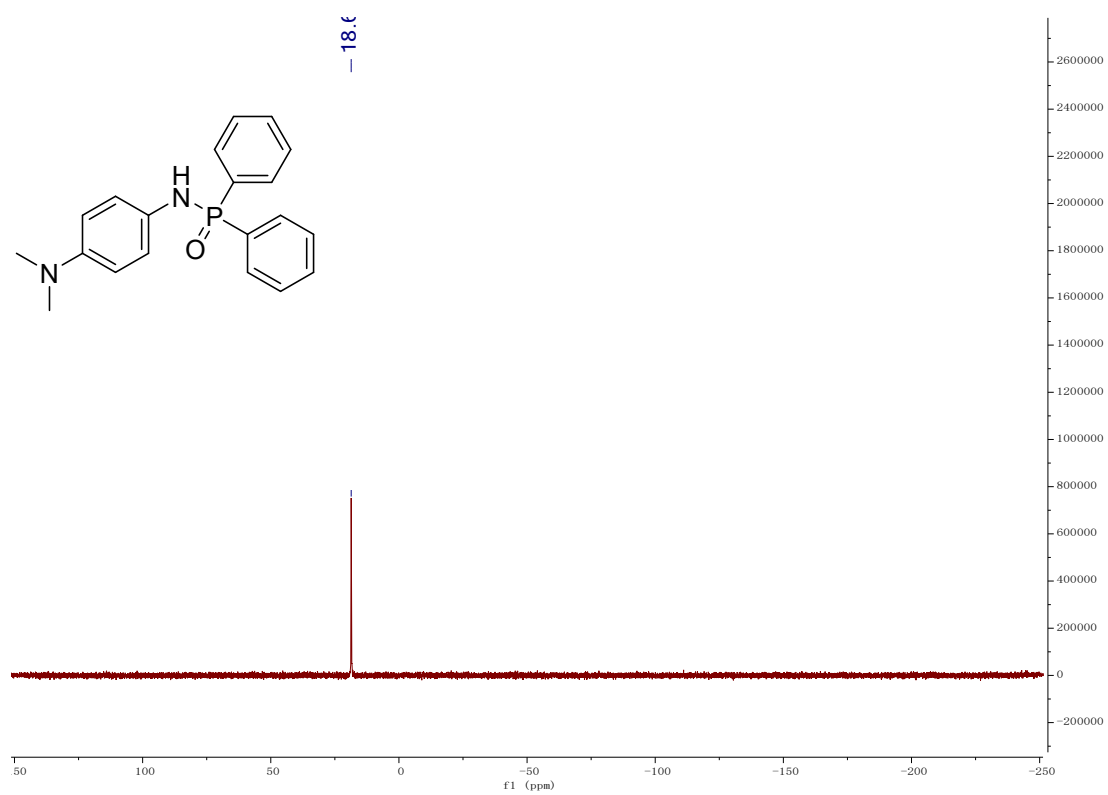
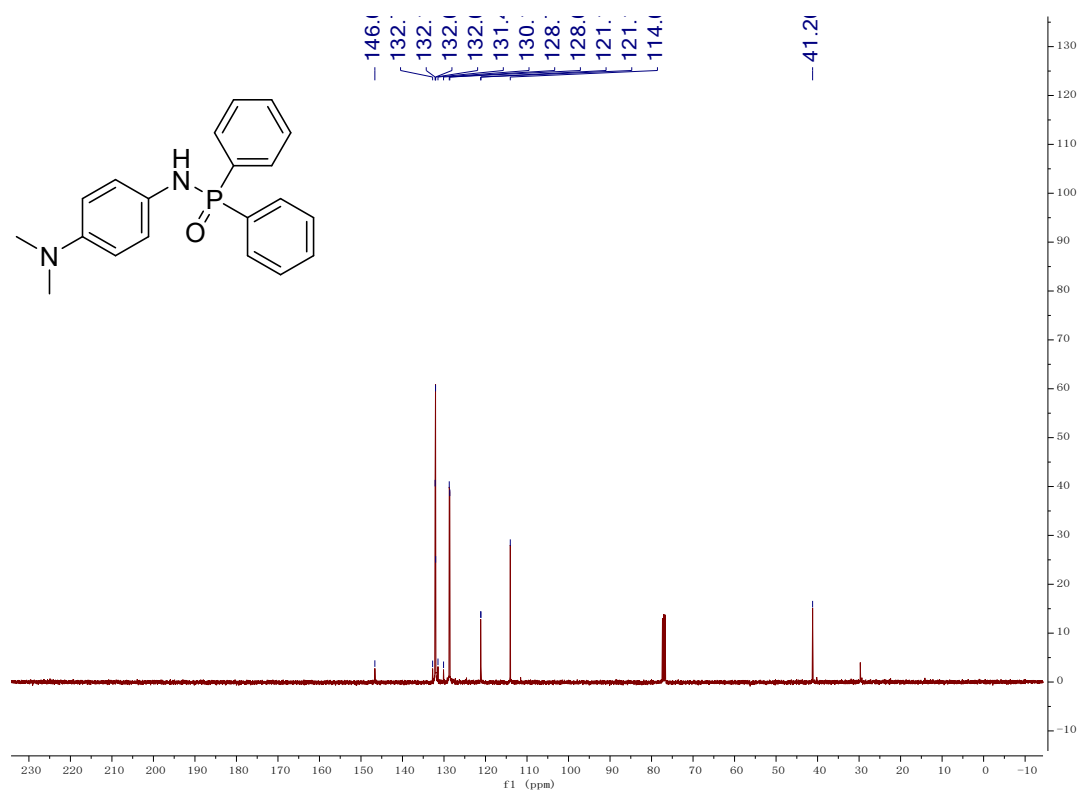
N-(4-bromophenyl)-P,P-diphenylphosphinic amide (3j)



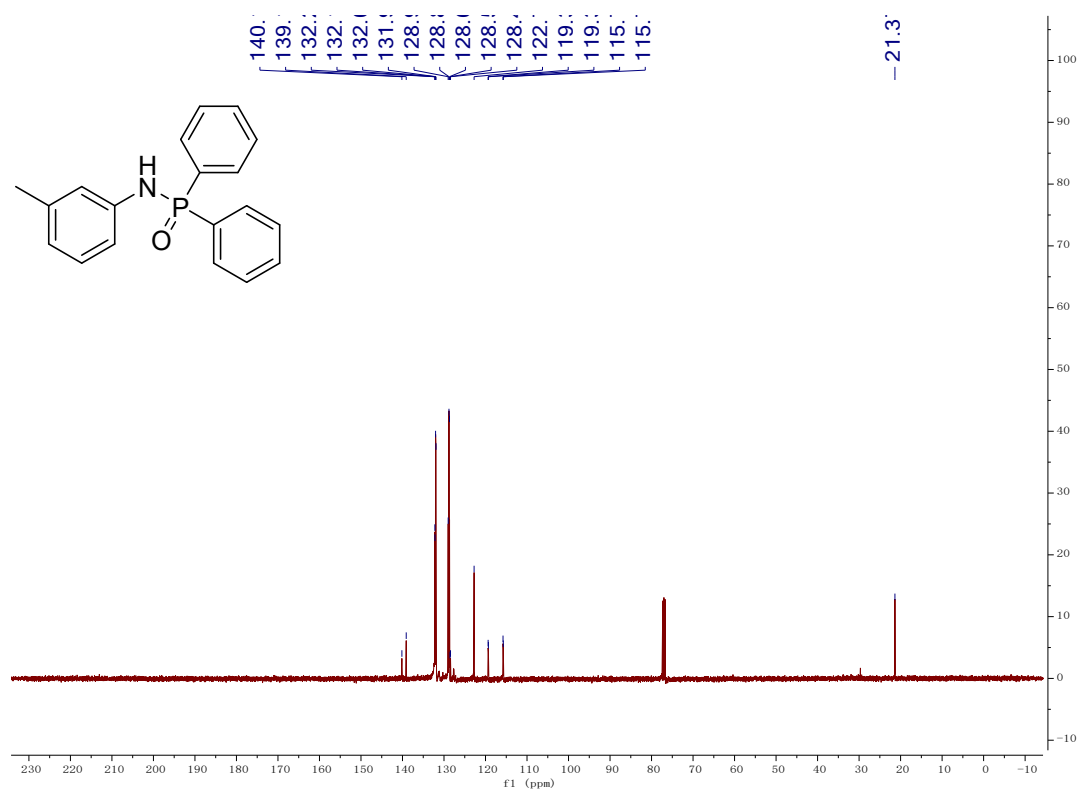
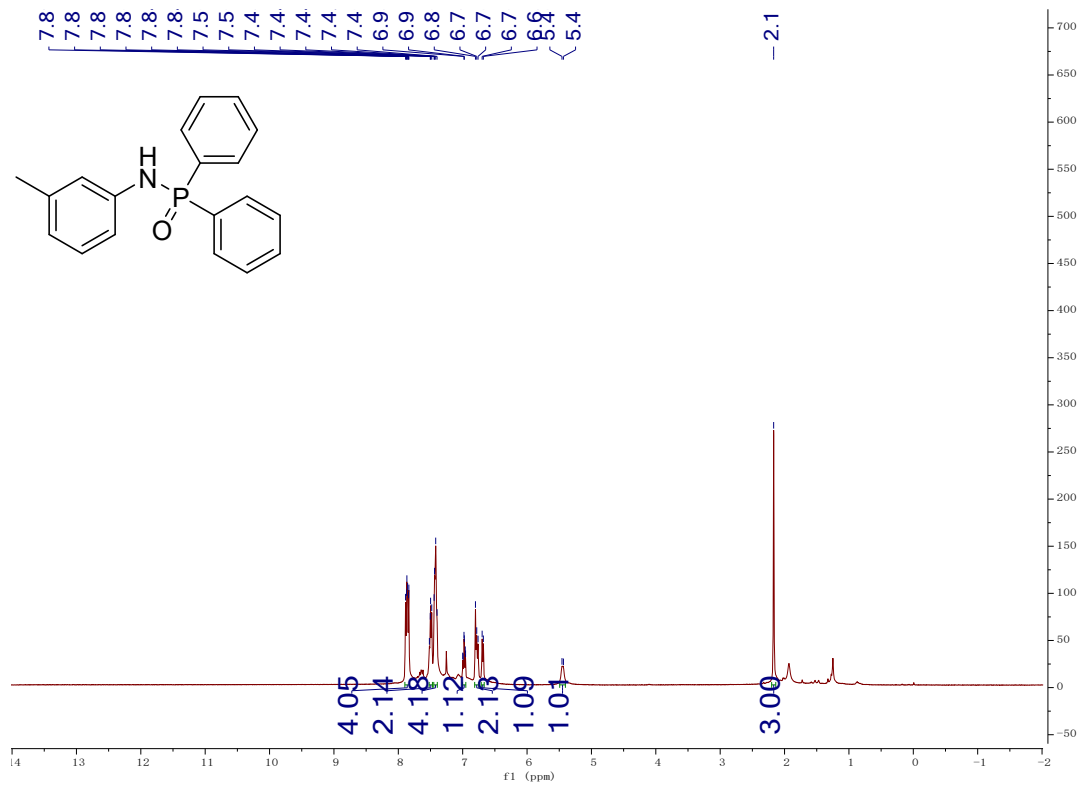


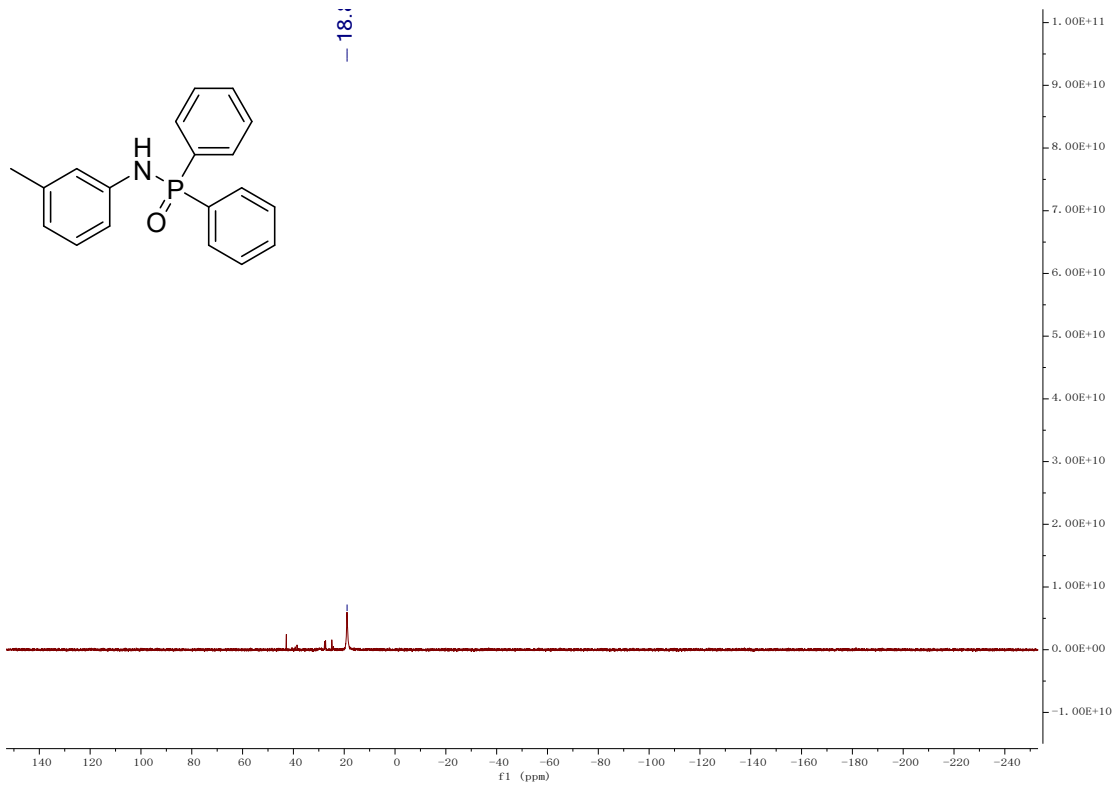
N-(4-(methylamino)phenyl)-P,P-diphenylphosphinic amide (31)



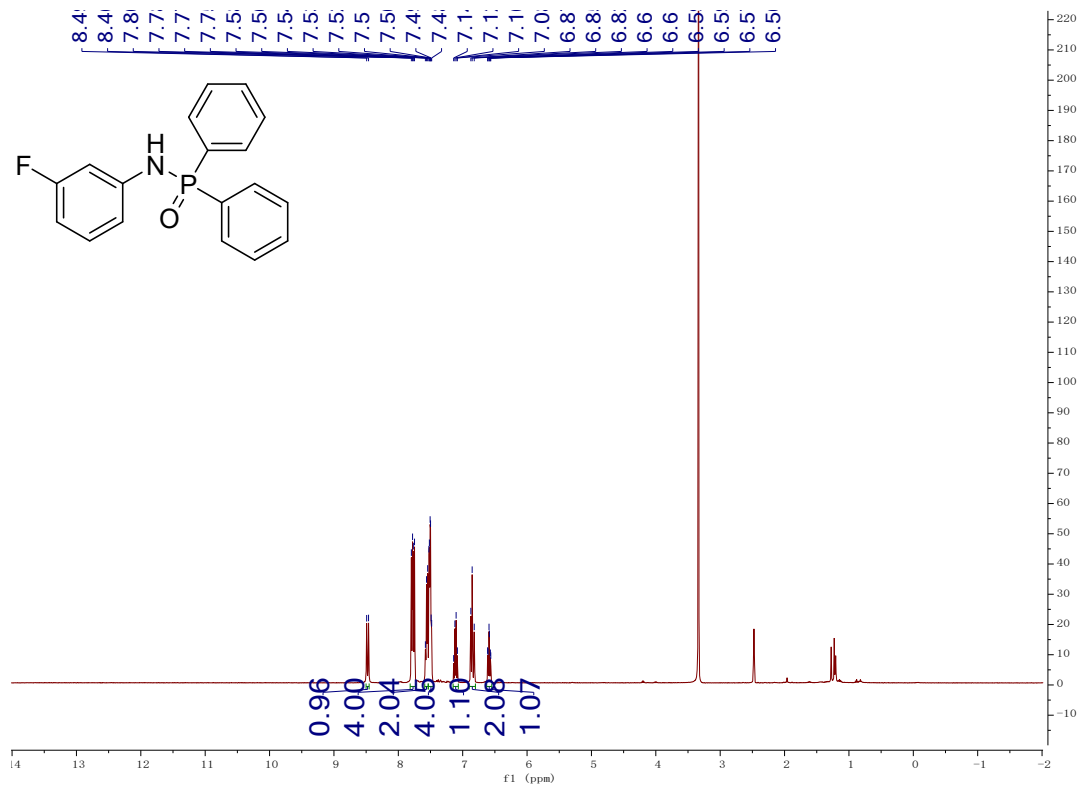


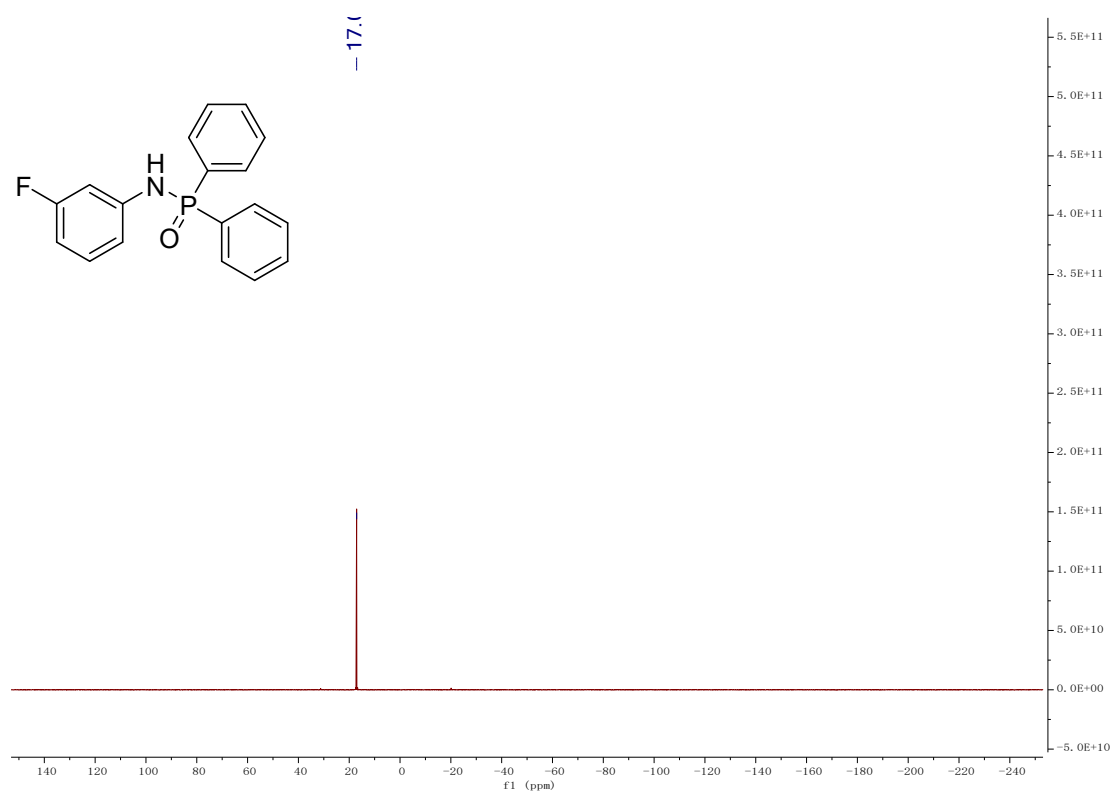
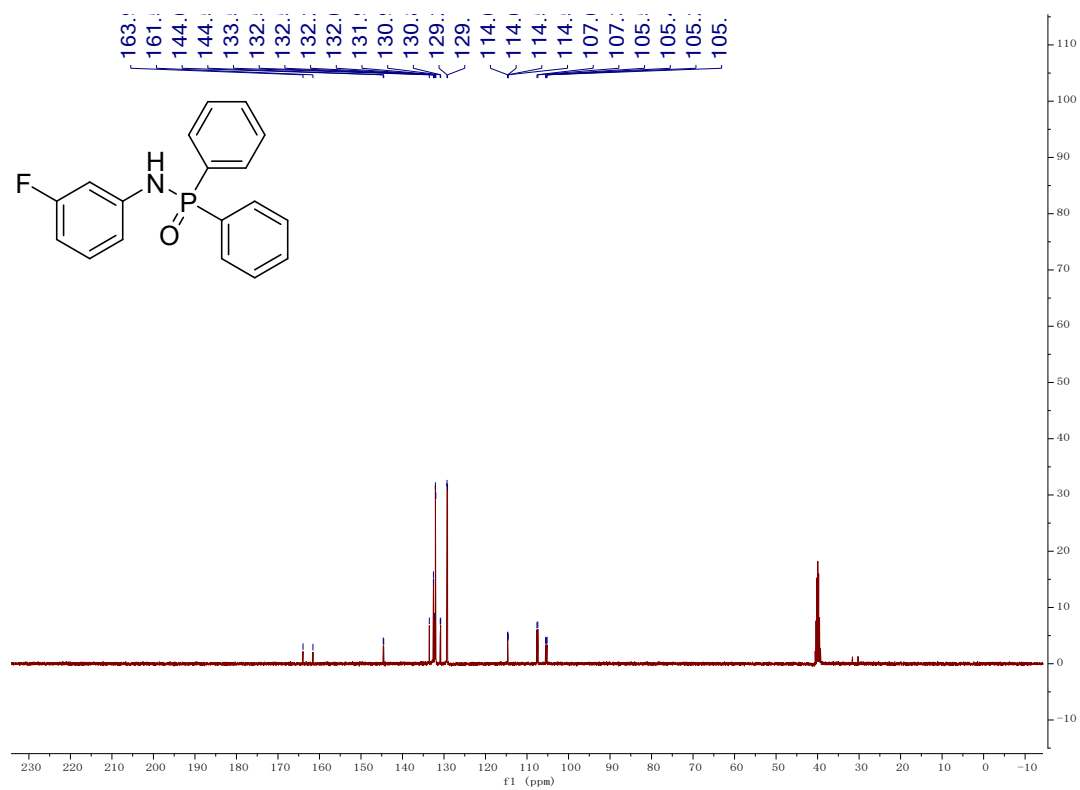
P,P-diphenyl-N-(m-tolyl)phosphinic amide (3n)



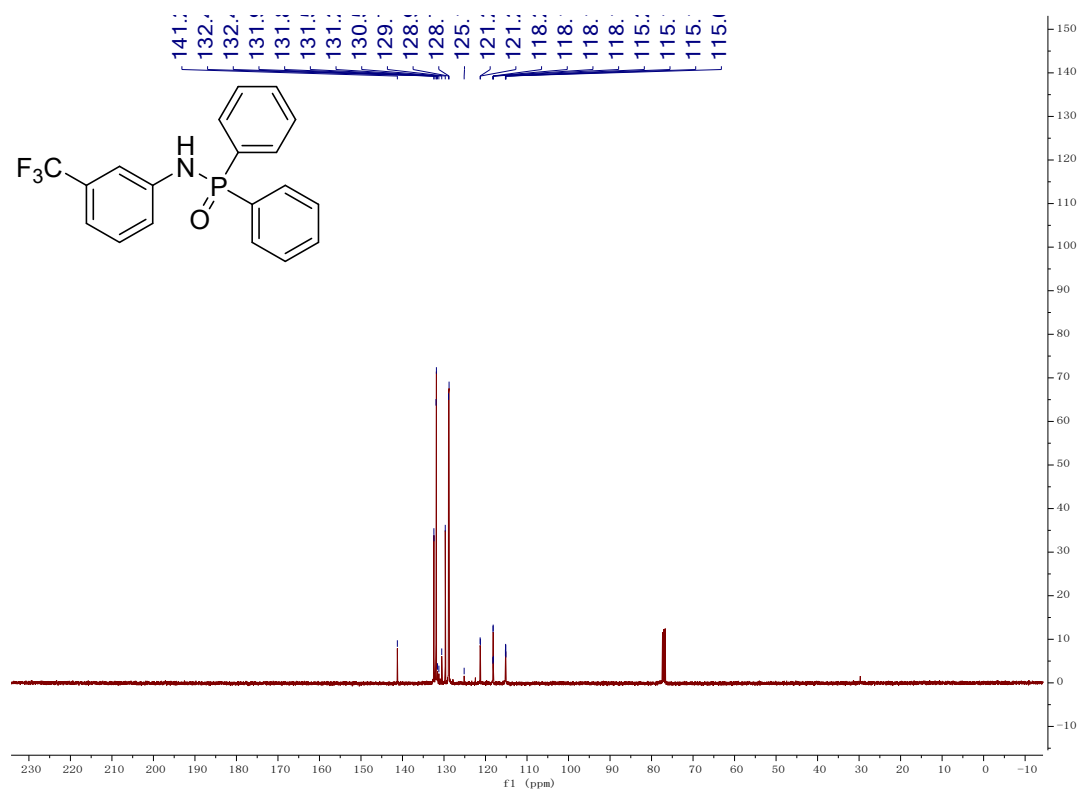
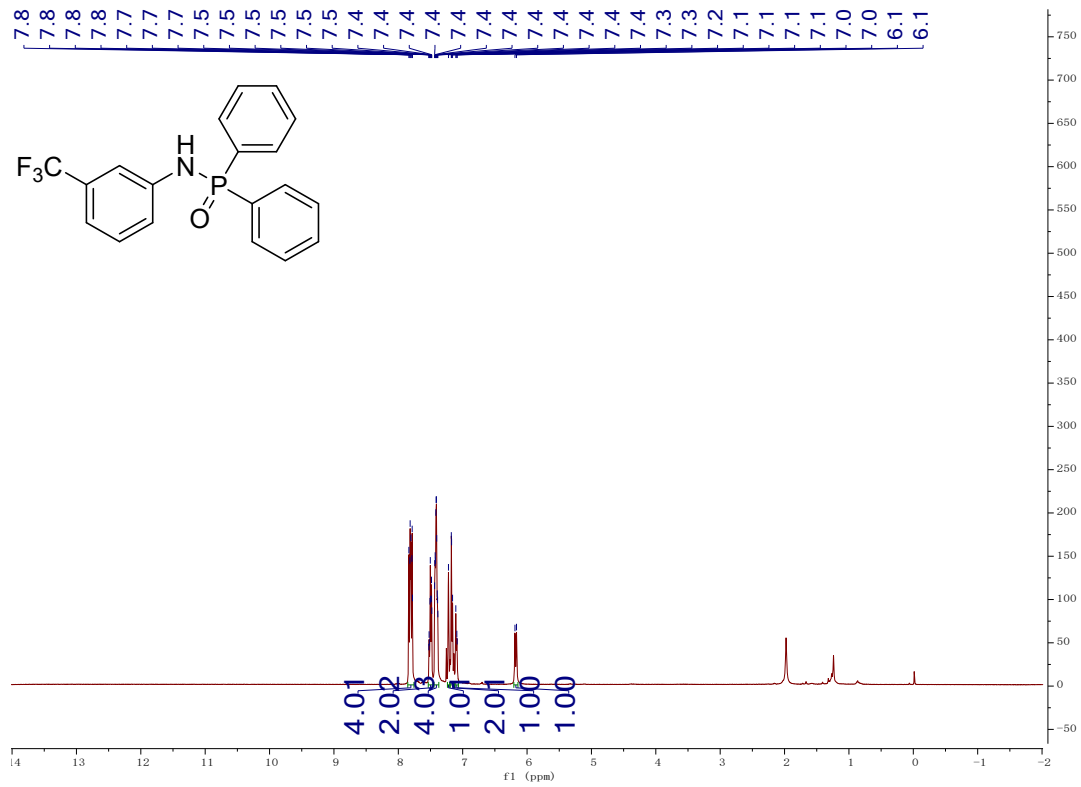


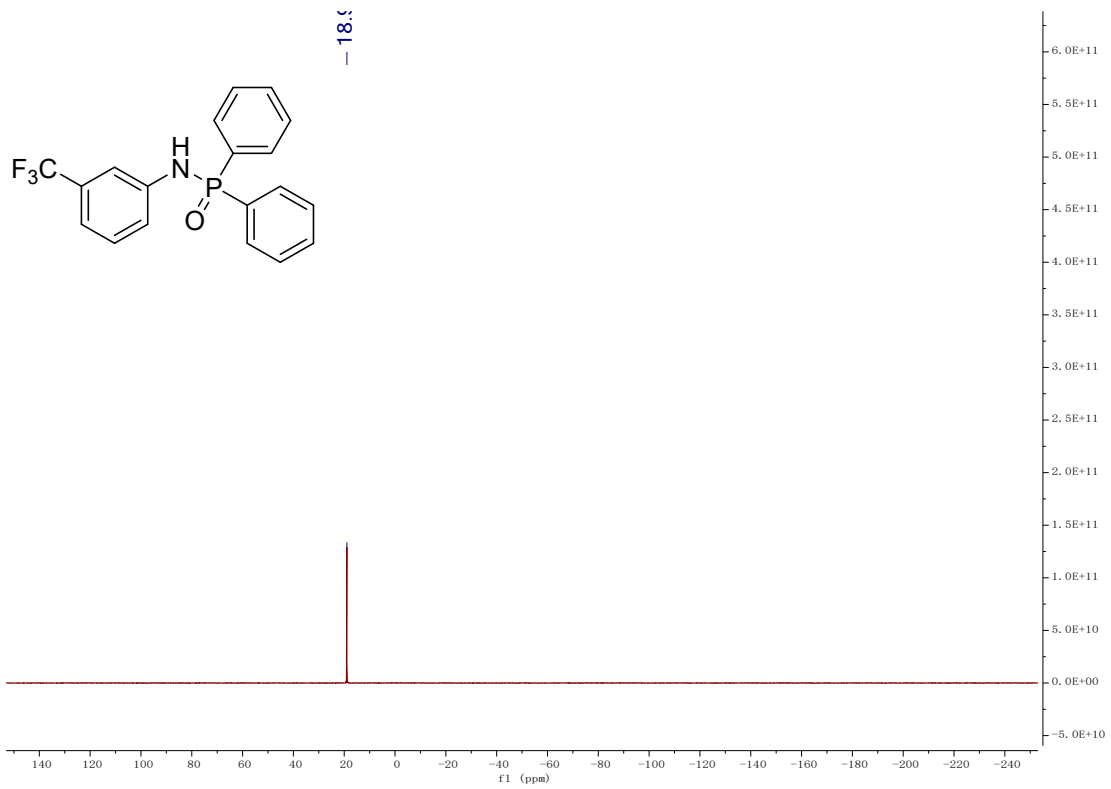
N-(3-fluorophenyl)-P,P-diphenylphosphinic amide (3o)



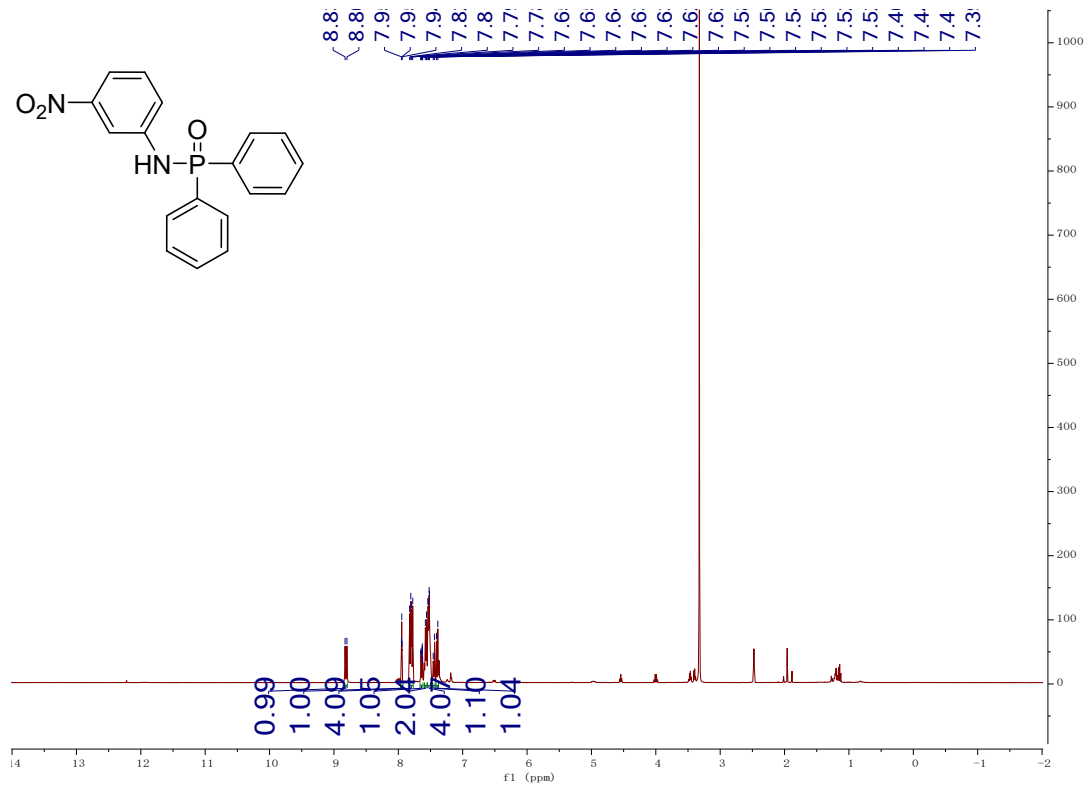


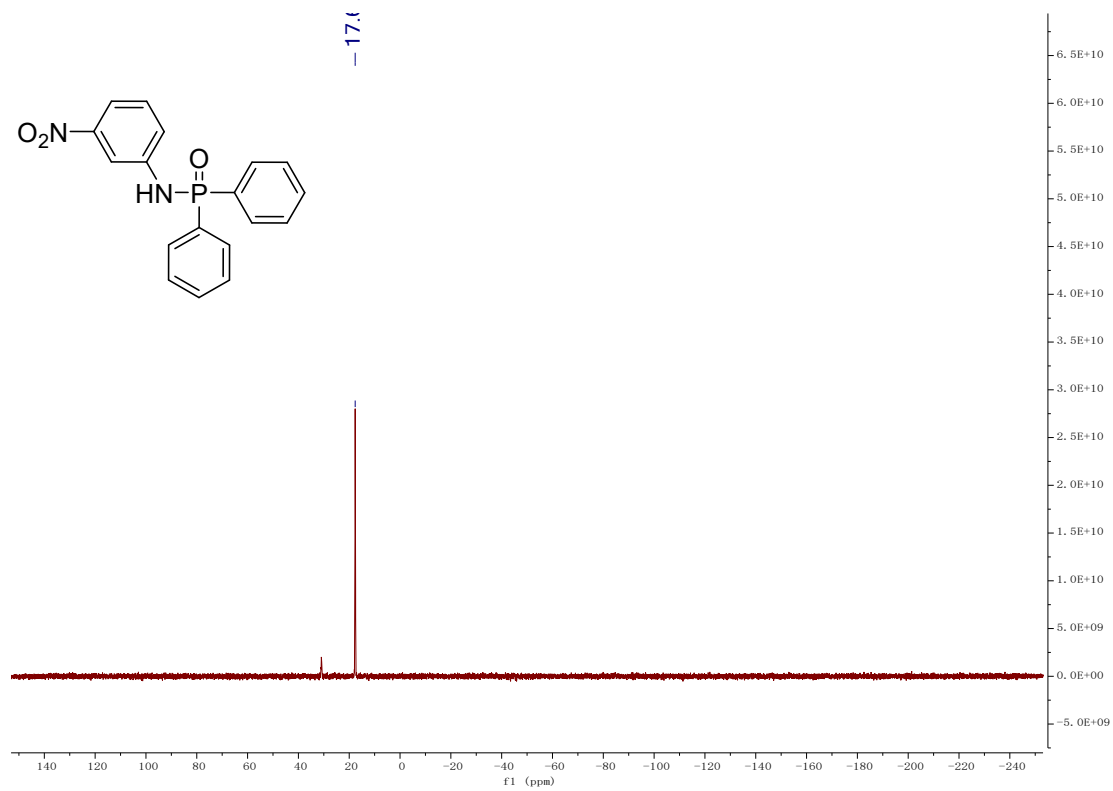
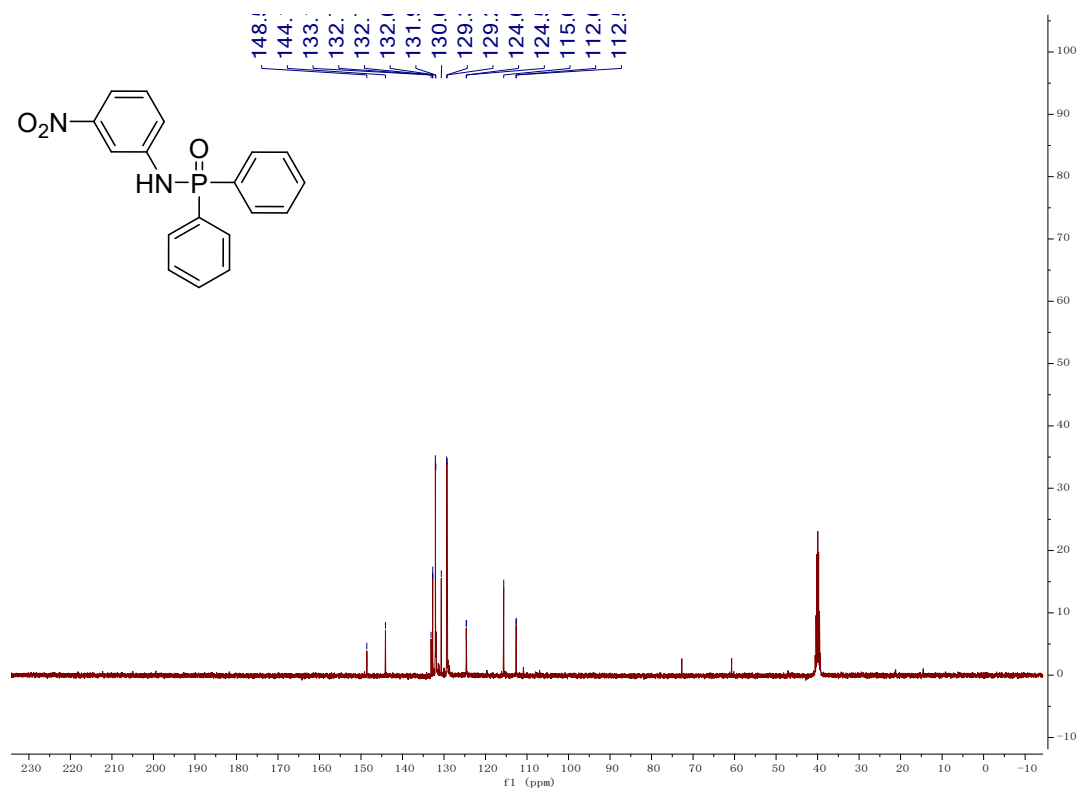
P,P-diphenyl-N-(3-(trifluoromethyl)phenyl)phosphinic amide (3p)



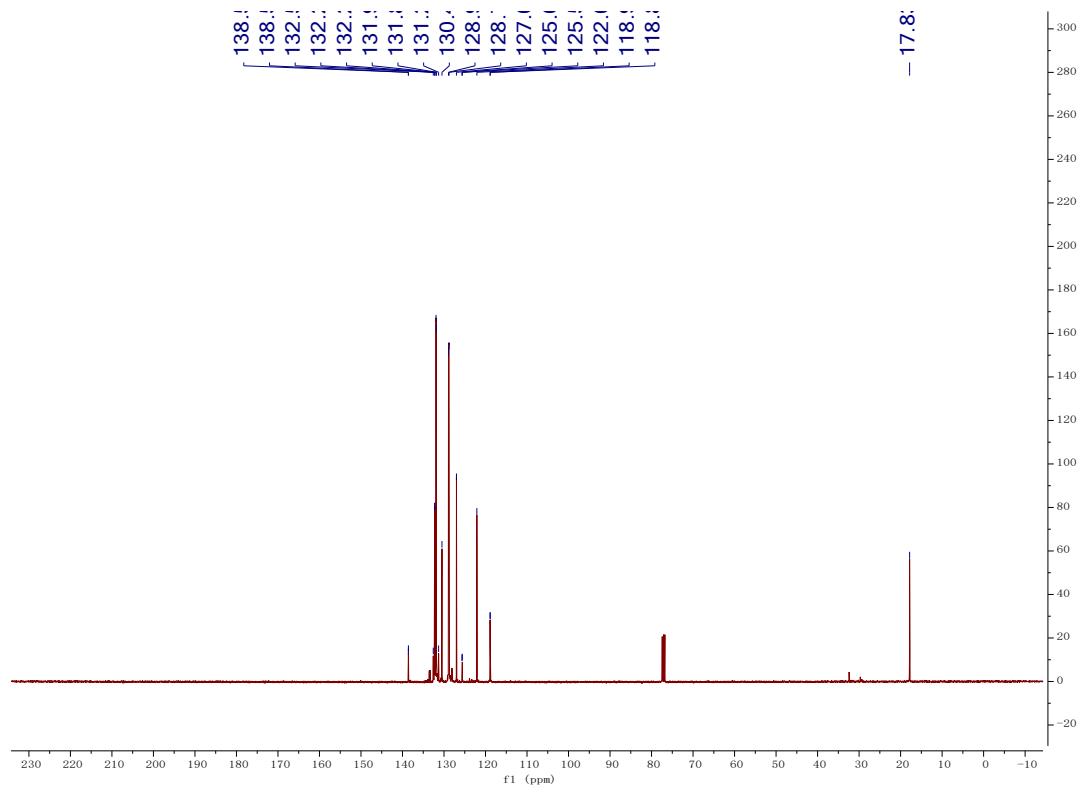
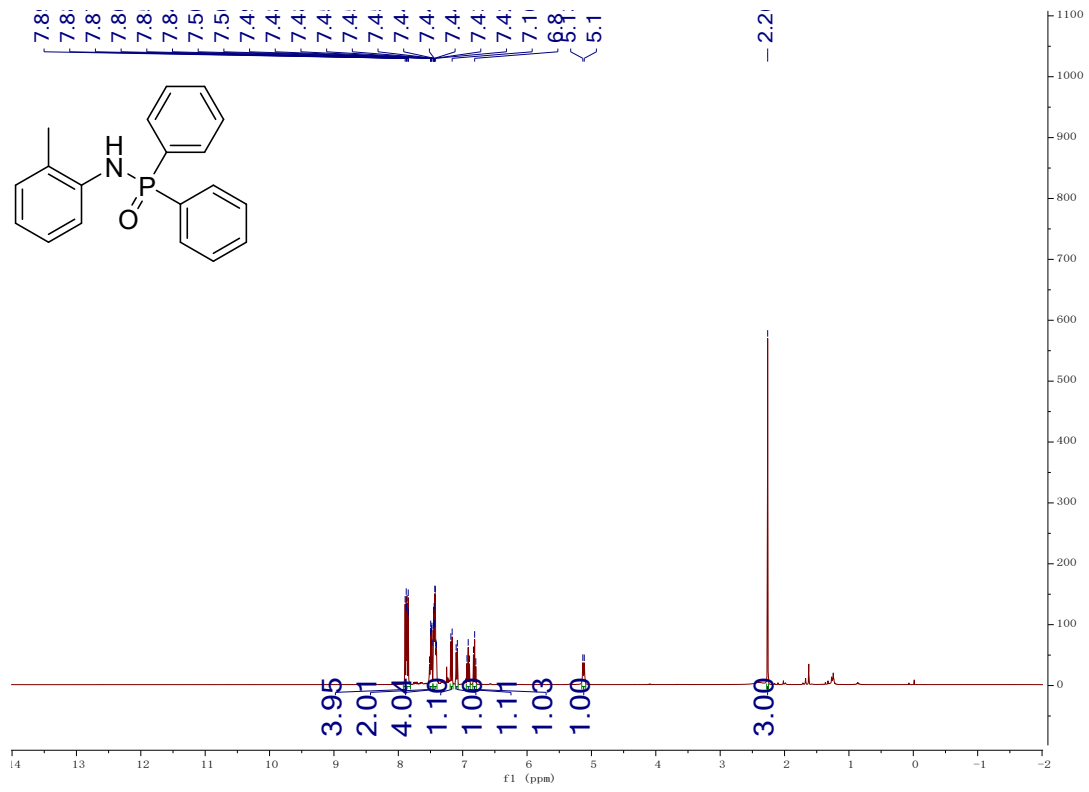


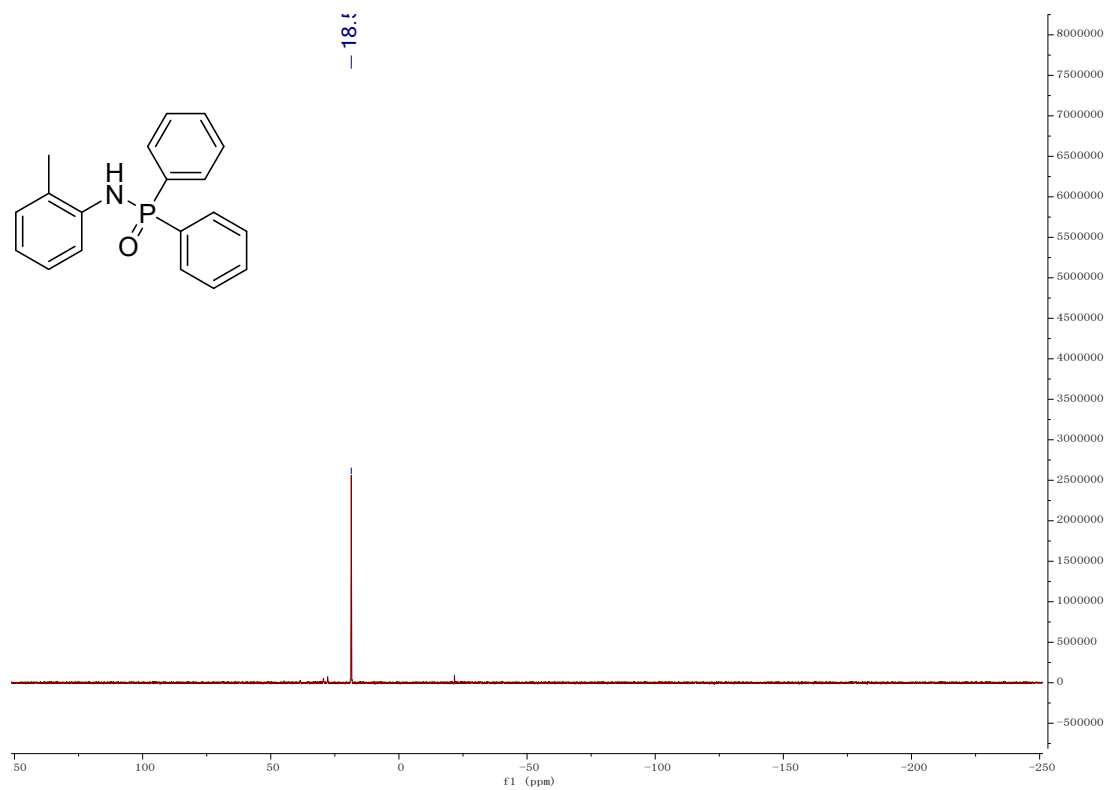
N-(3-nitrophenyl)-P,P-diphenylphosphinic amide (3q)



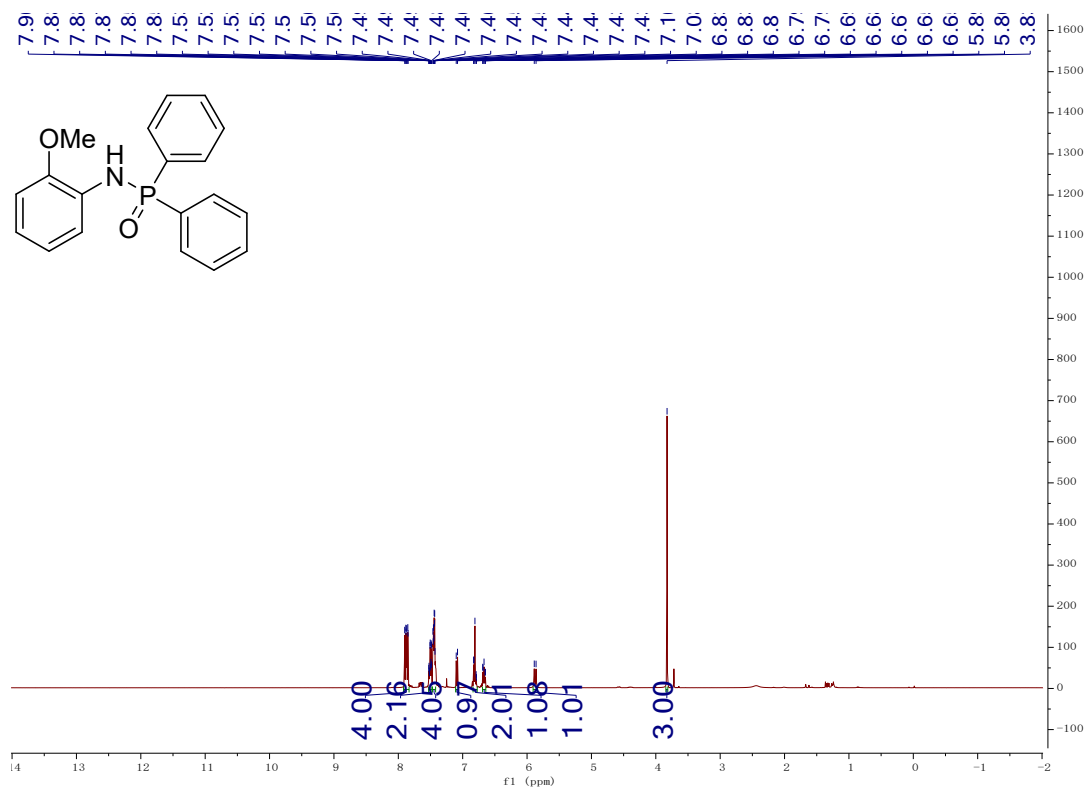


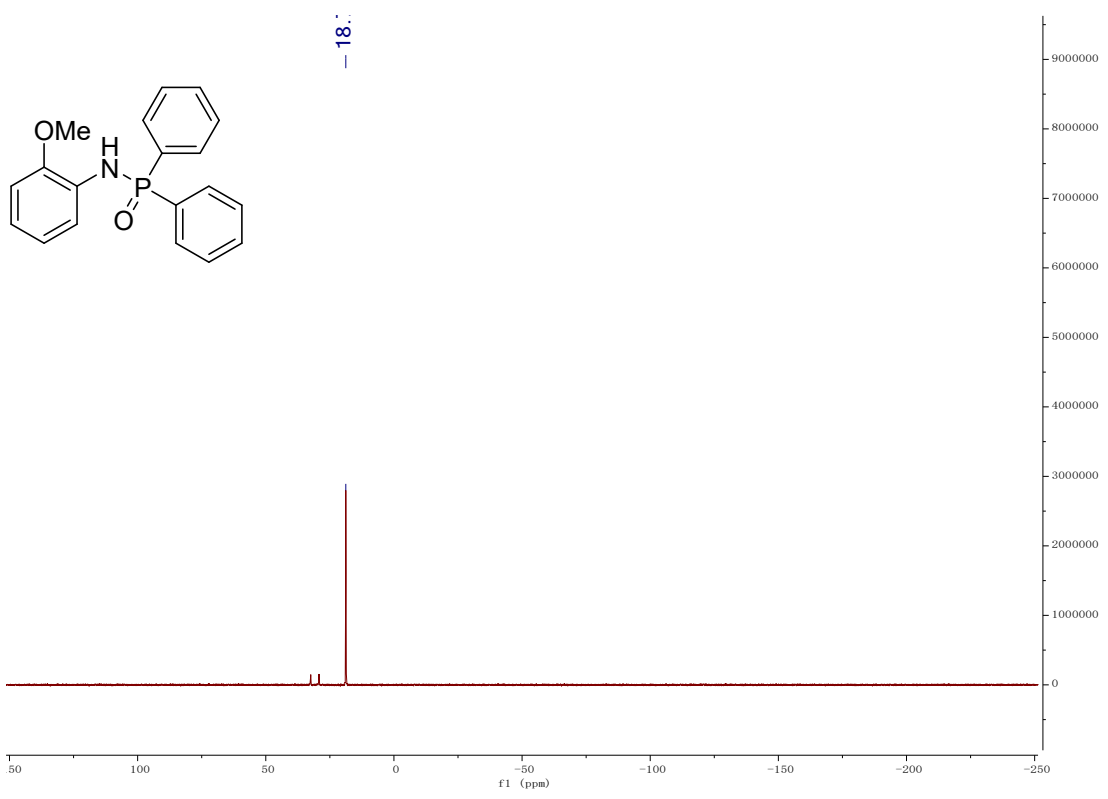
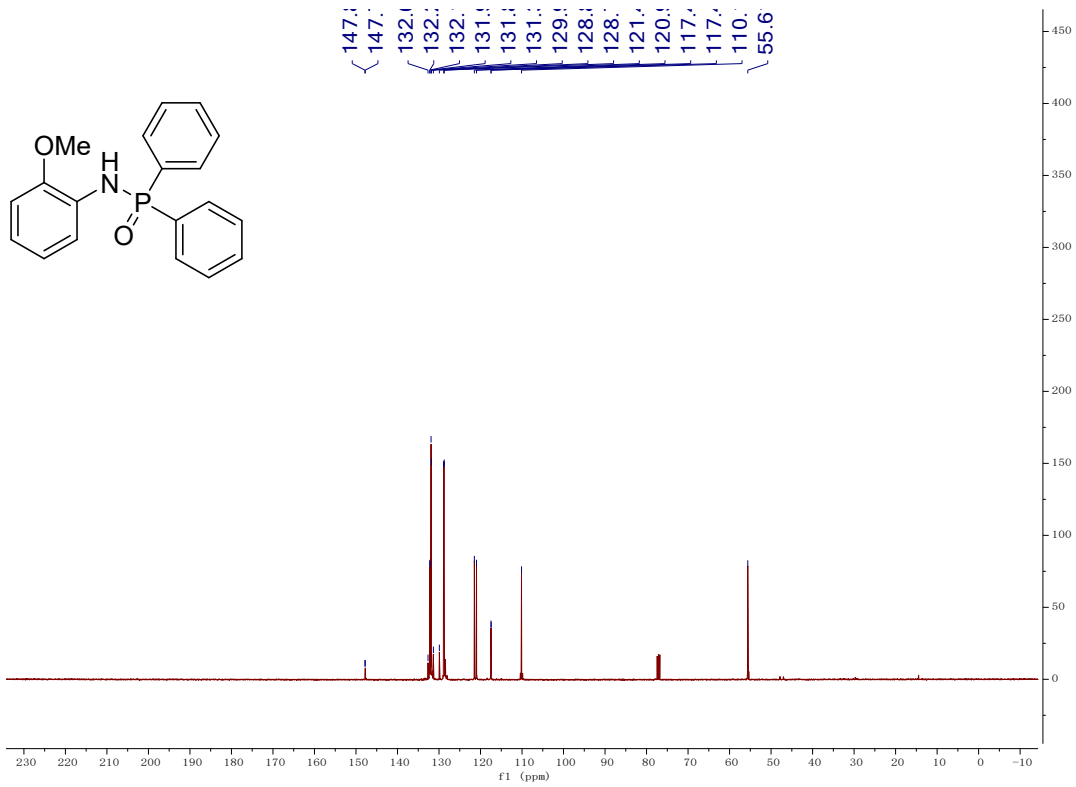
P,P-diphenyl-N-(o-tolyl)phosphinic amide (3r)



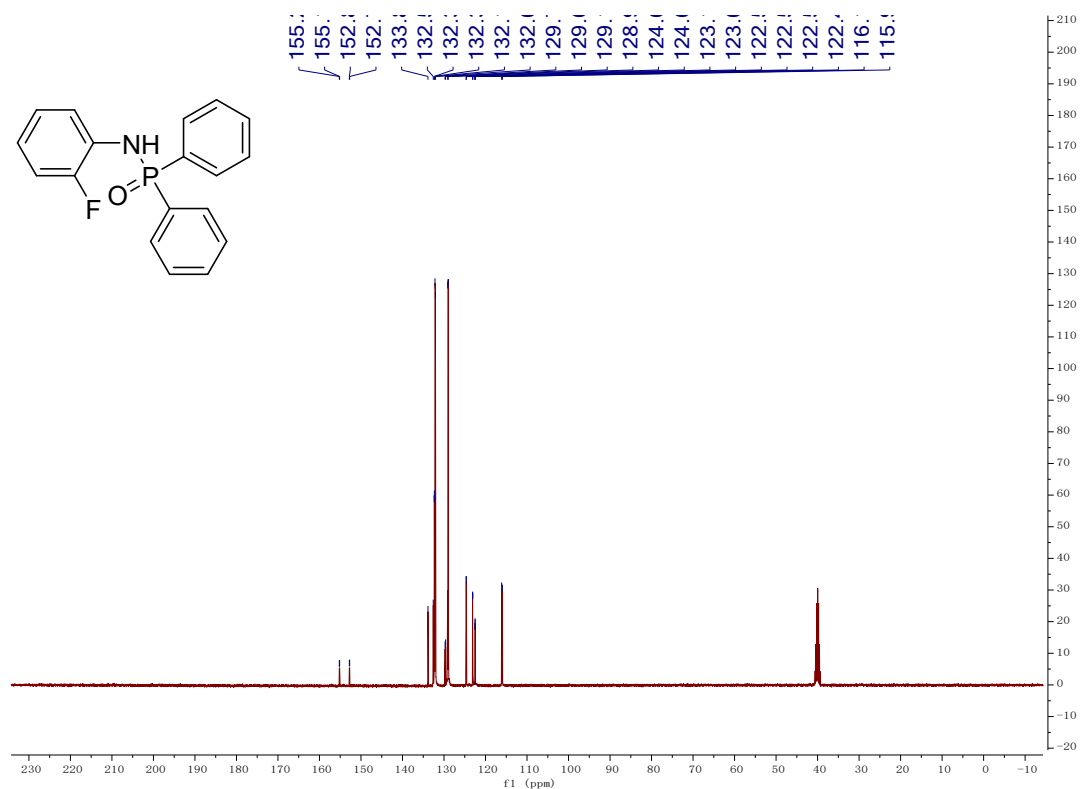
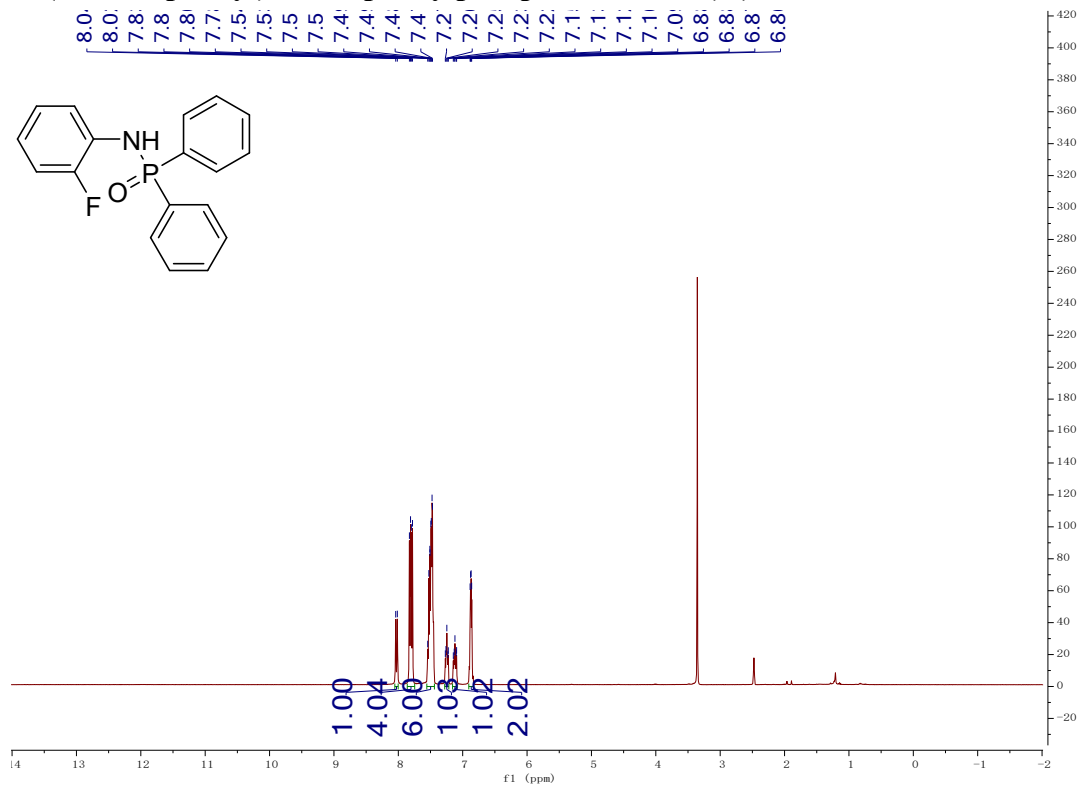


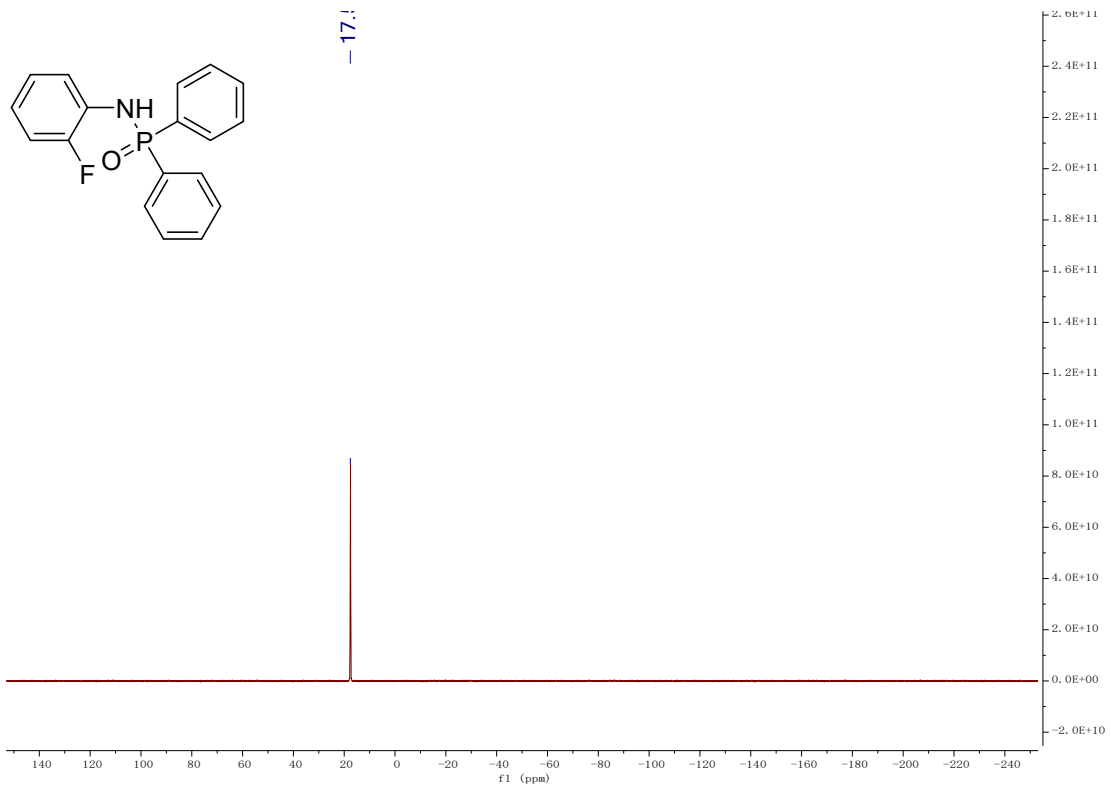
N-(2-methoxyphenyl)-P,P-diphenylphosphinic amide (3s)



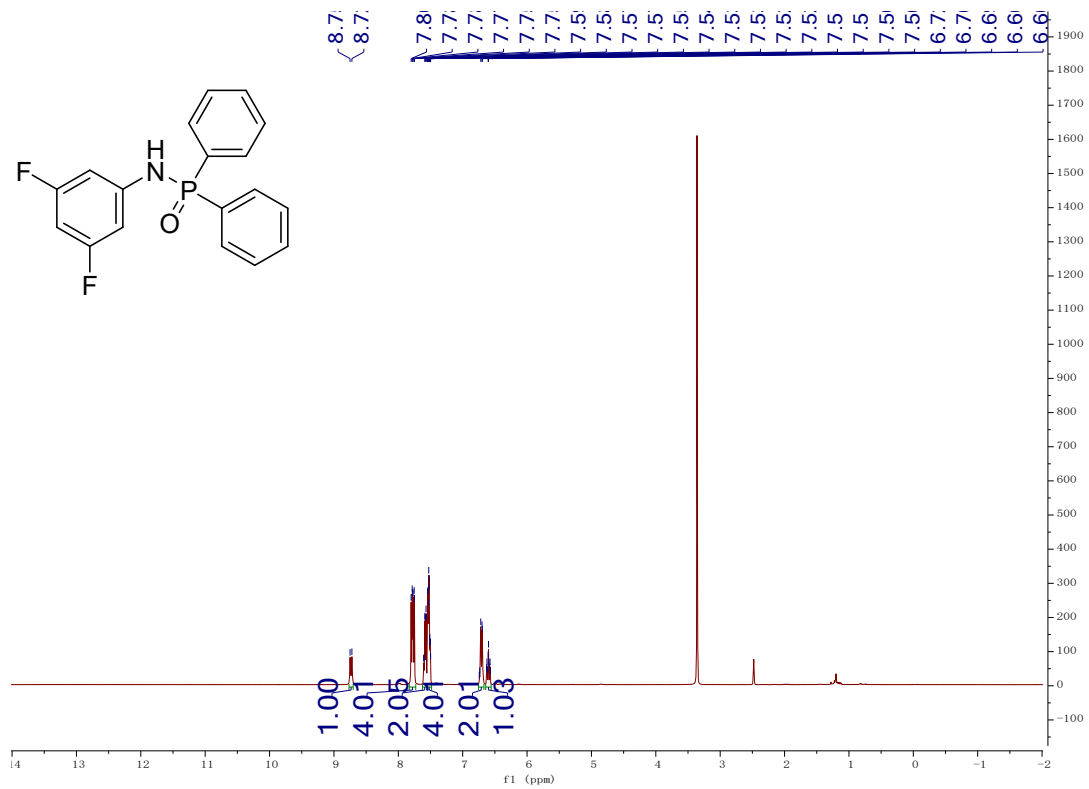


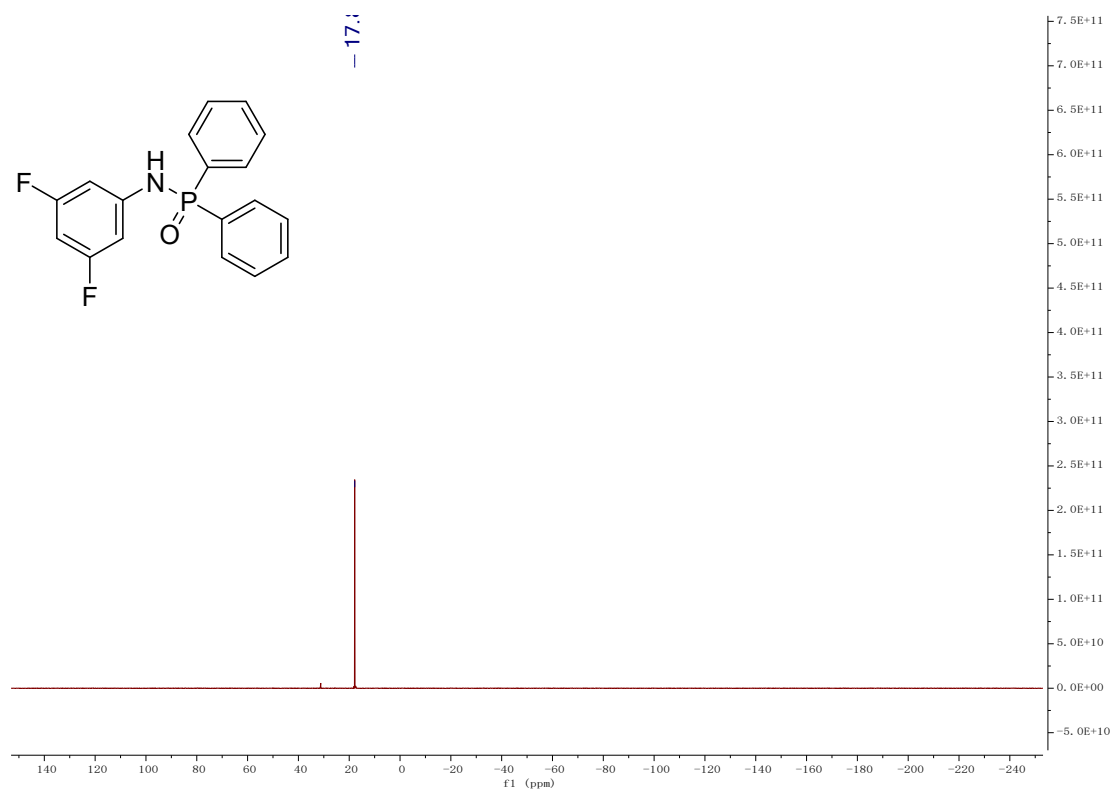
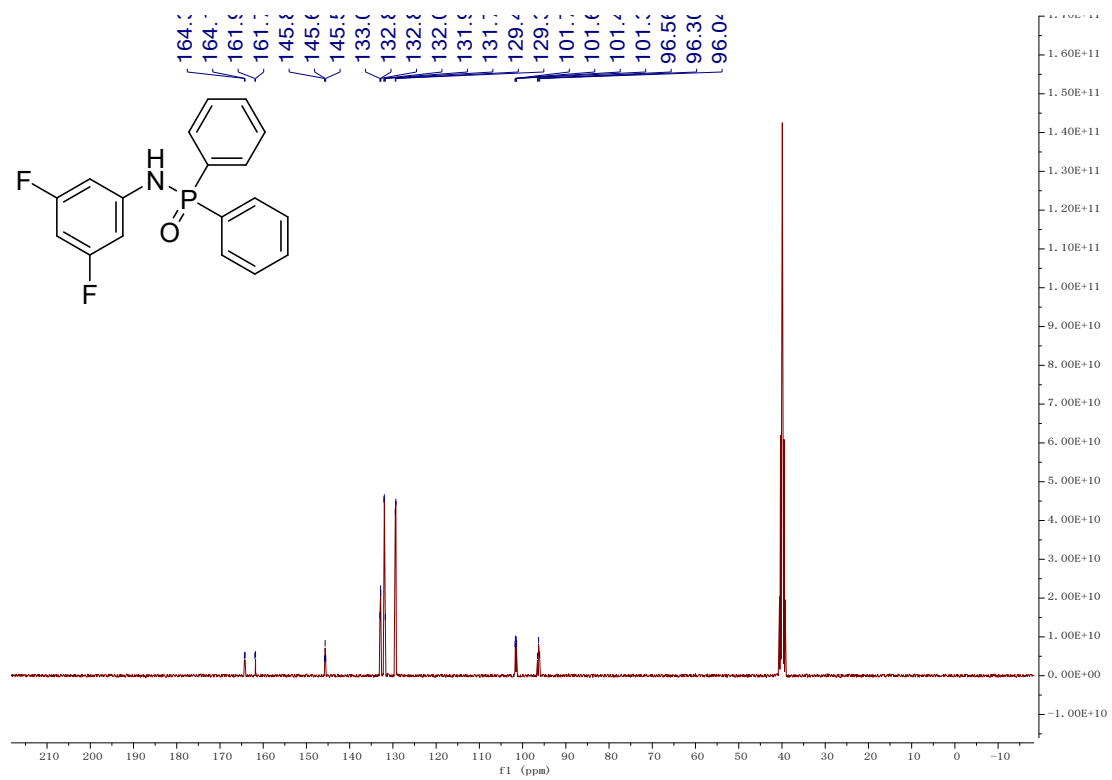
N-(2-fluorophenyl)-P,P-diphenylphosphinic amide (3t)



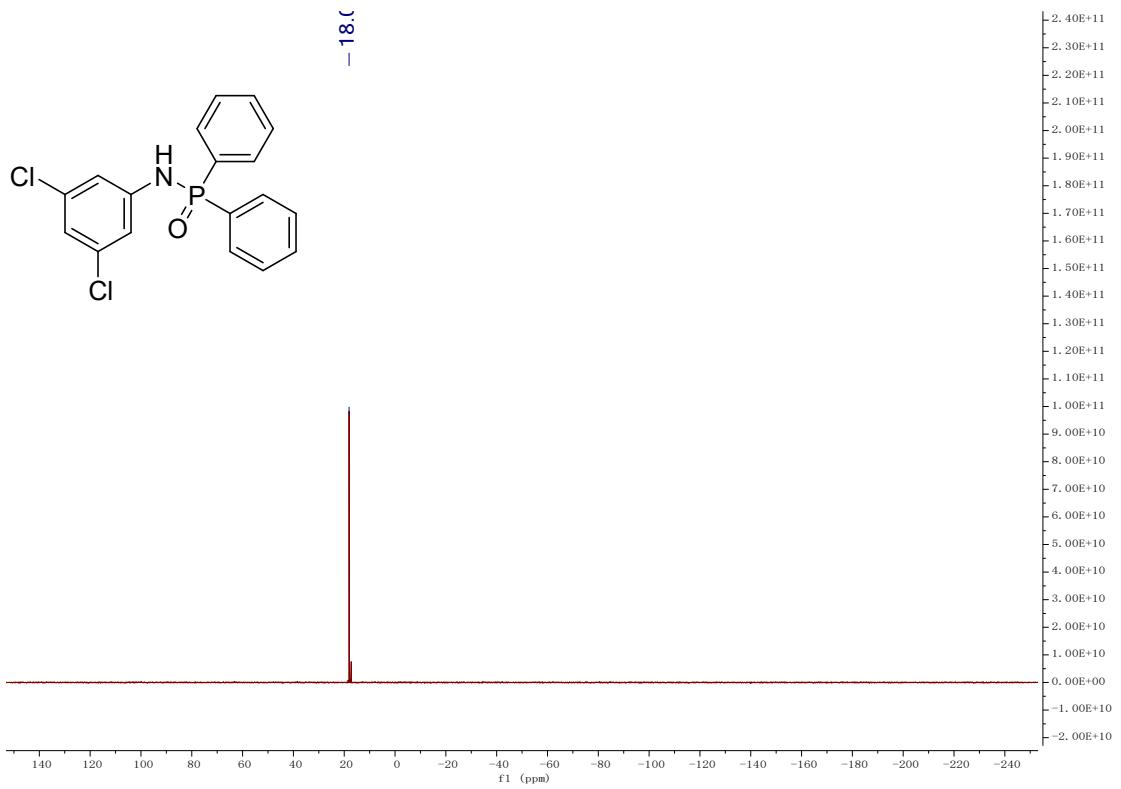


N-(3,5-difluorophenyl)-P,P-diphenylphosphinic amide (3u)

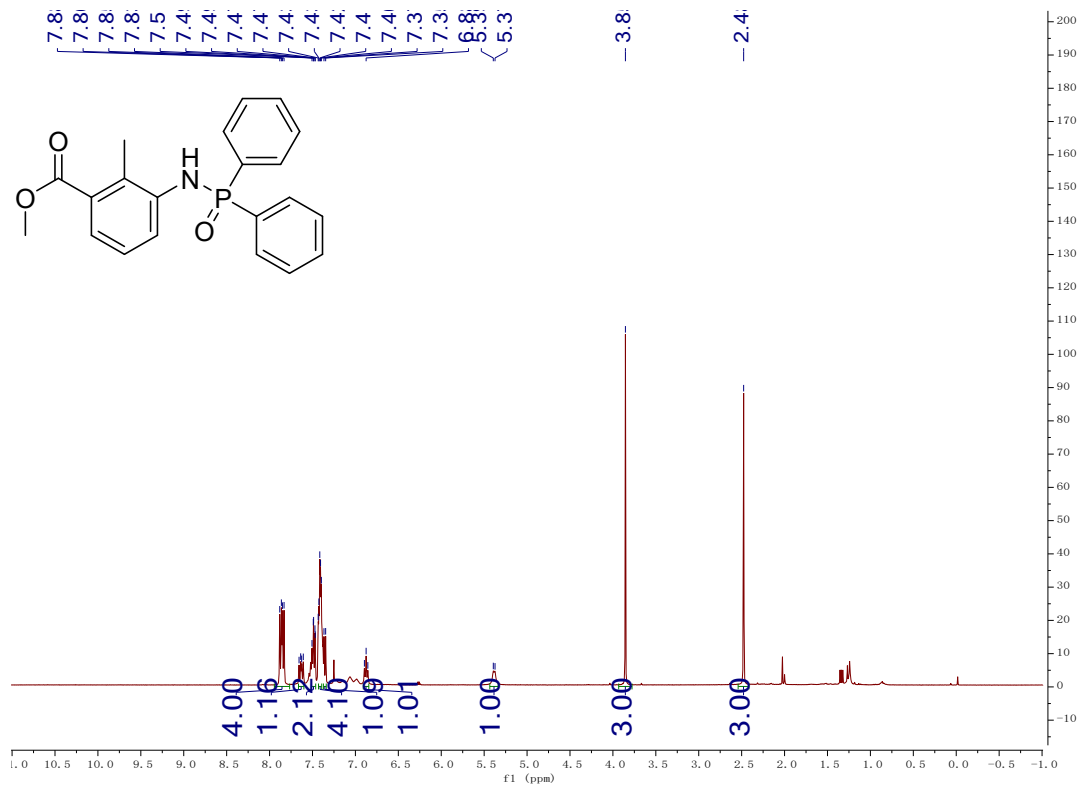


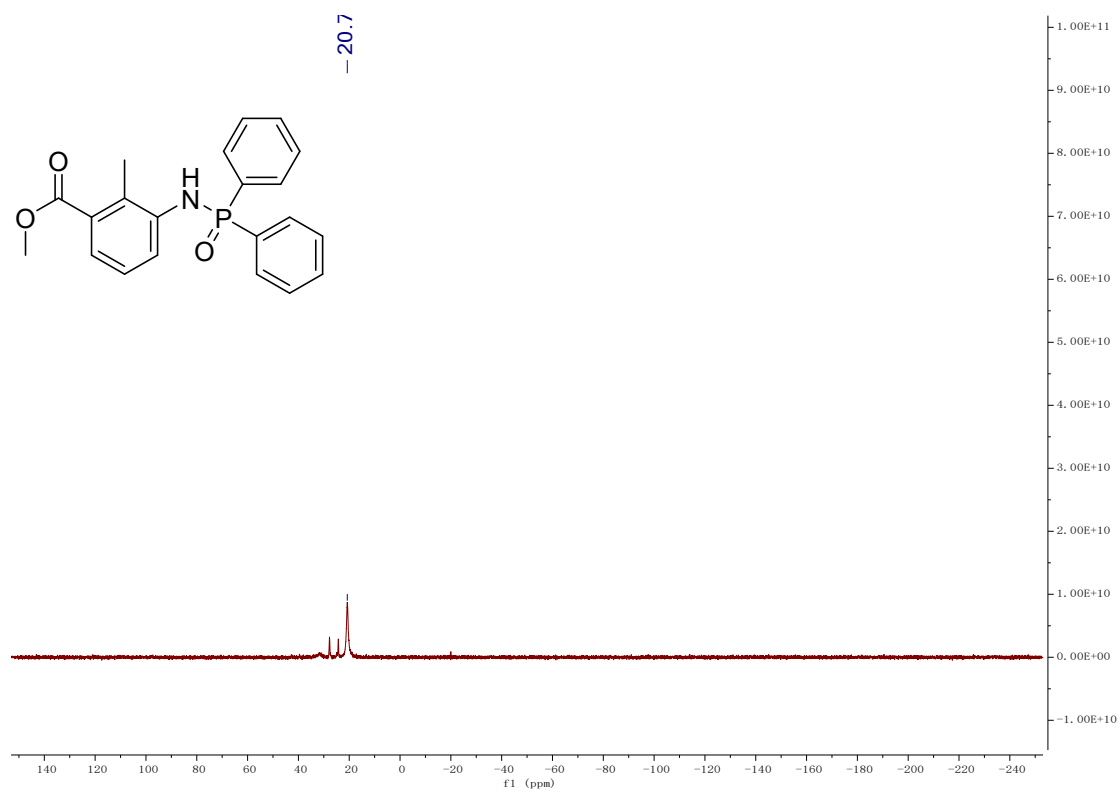
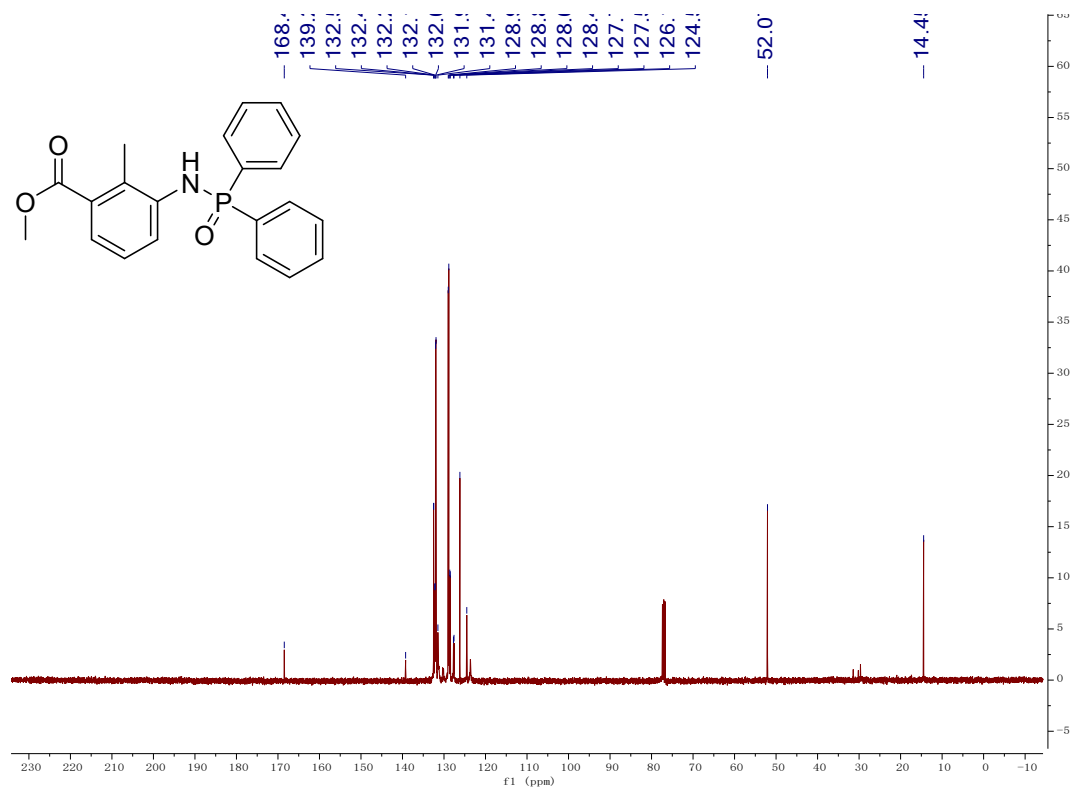


N-(3,5-dichlorophenyl)-P,P-diphenylphosphinic amide (3v)

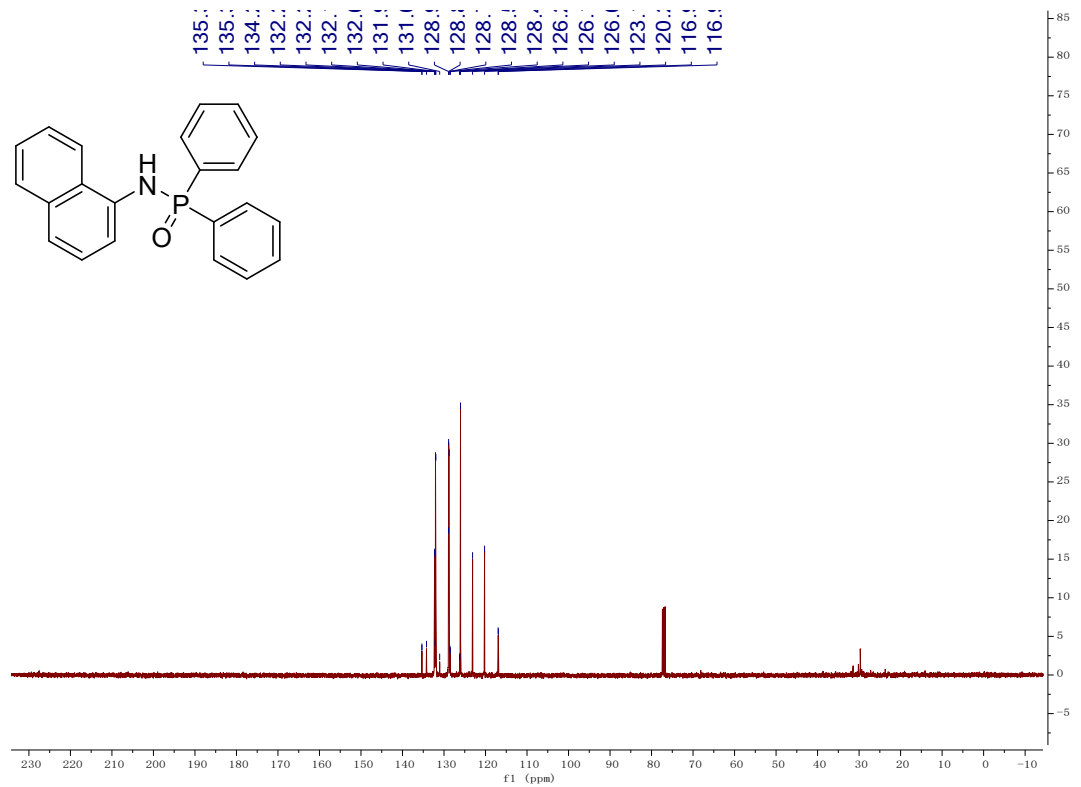
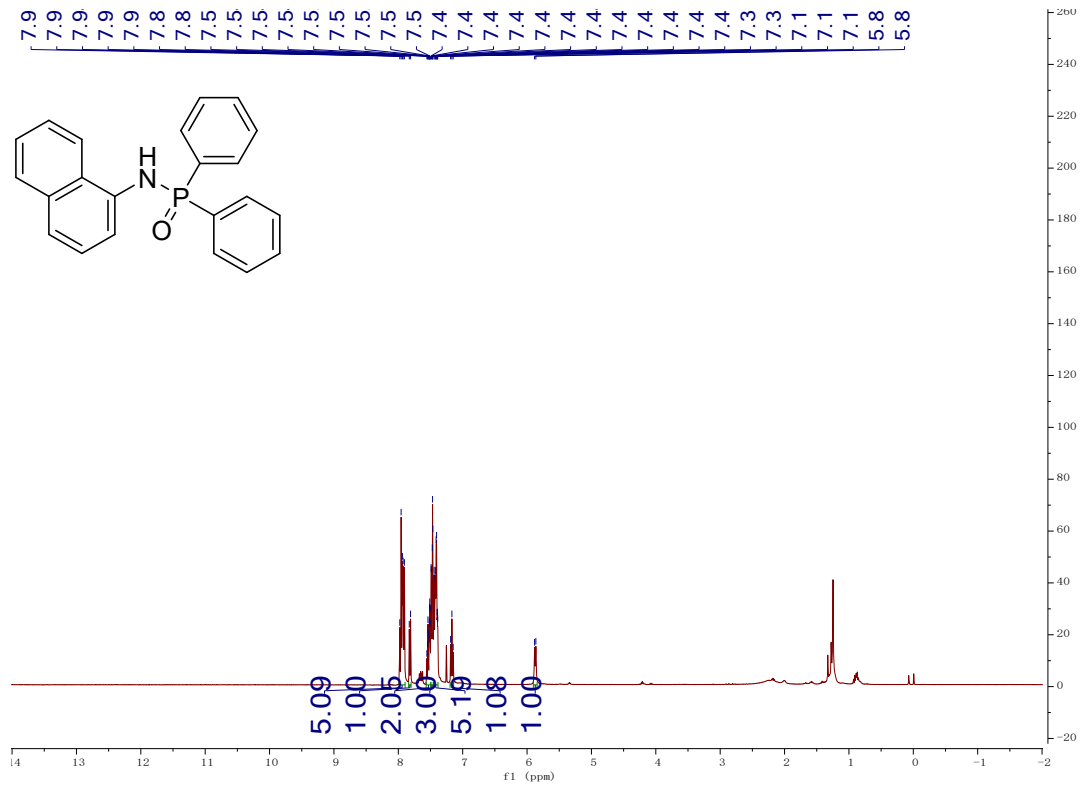


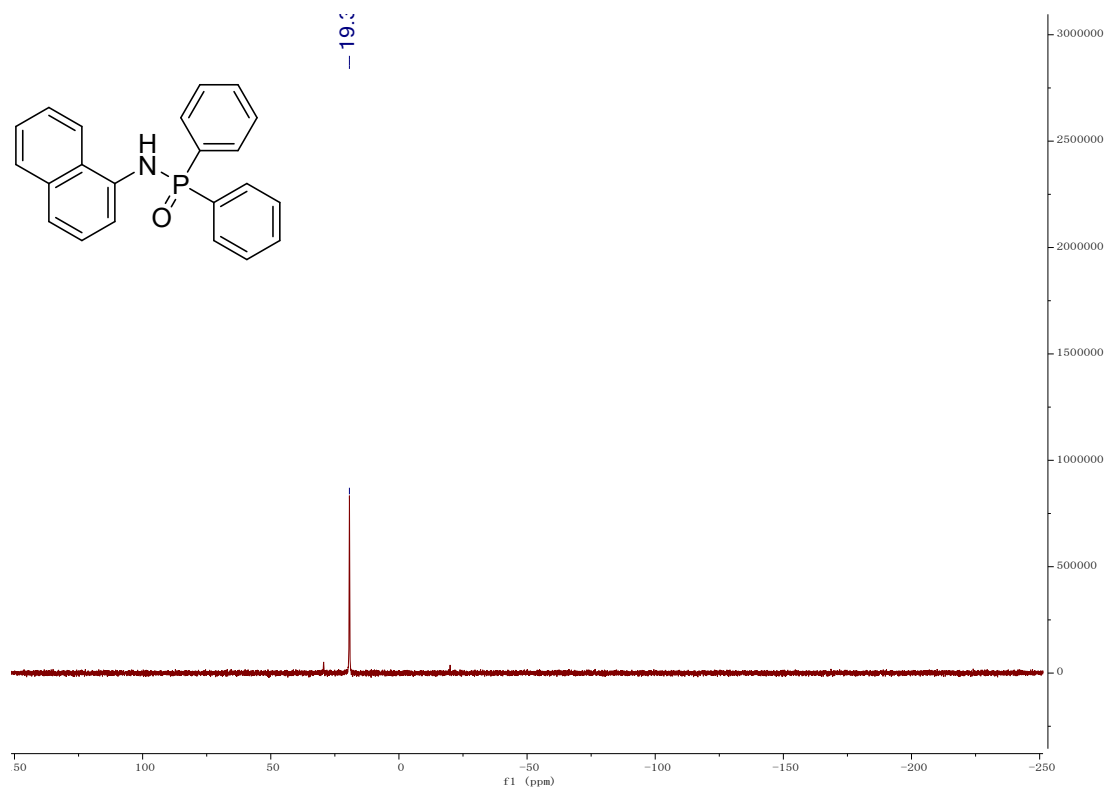
Methyl 3-((diphenylphosphoryl)amino)-2-methylbenzoate (3w)



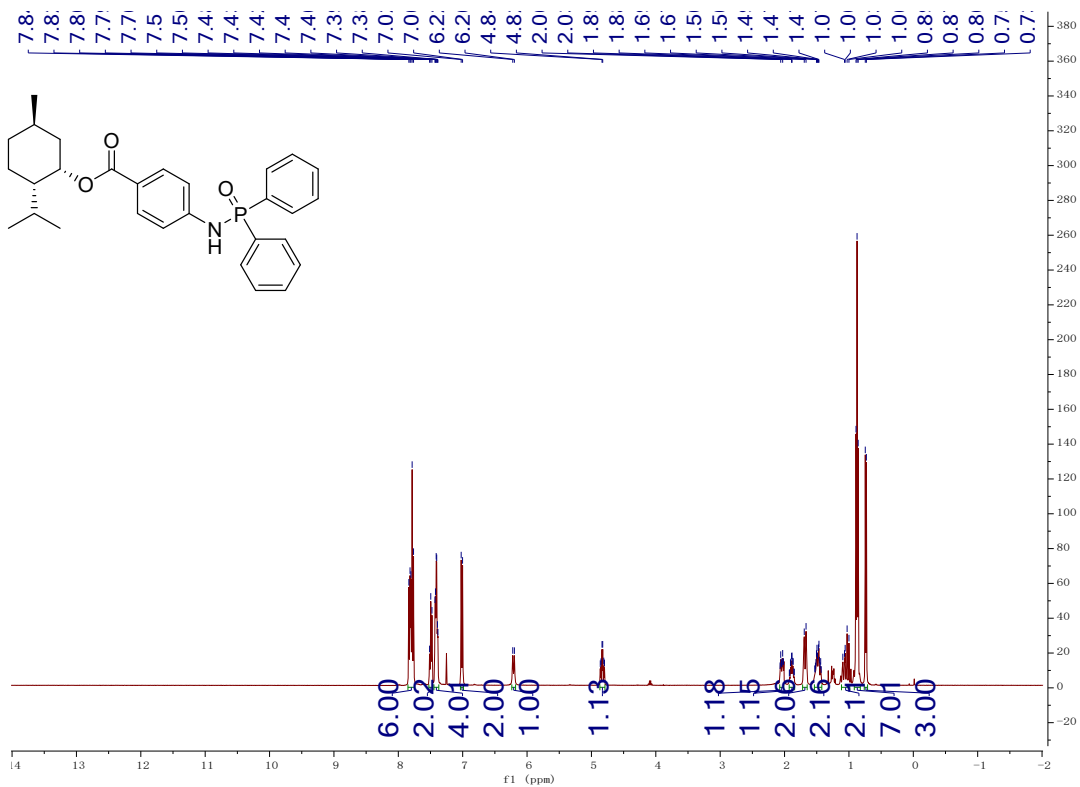


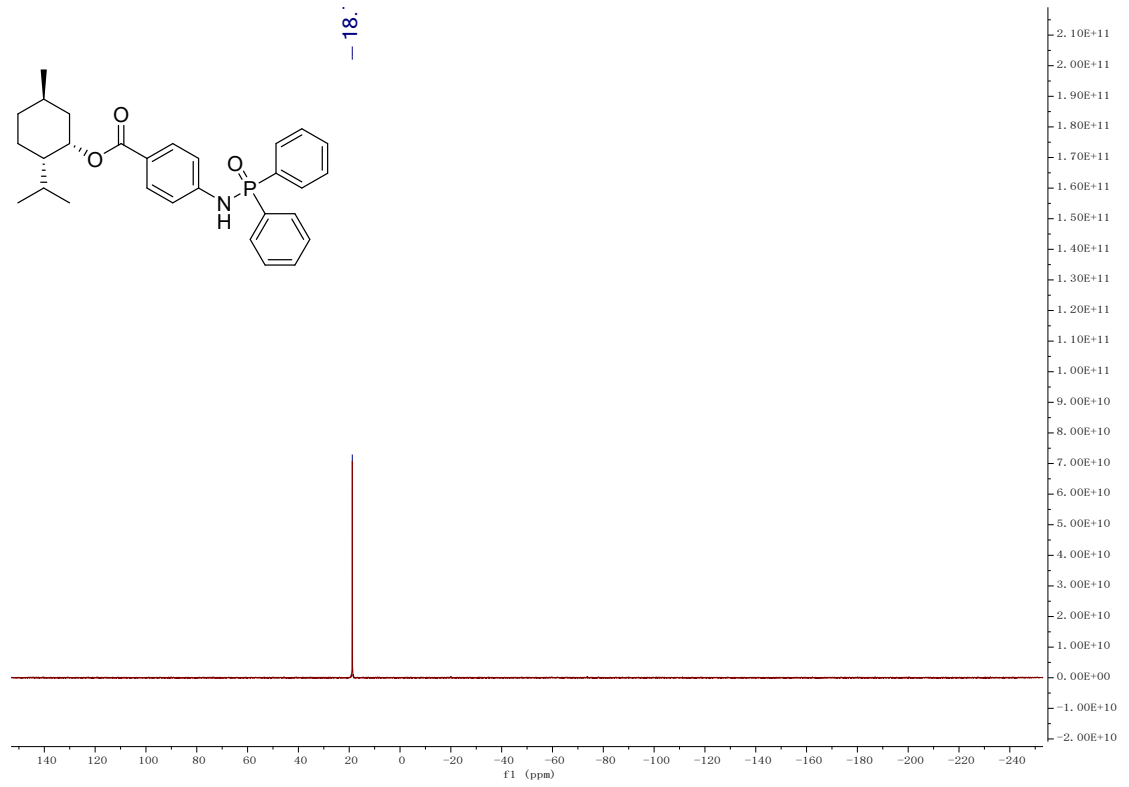
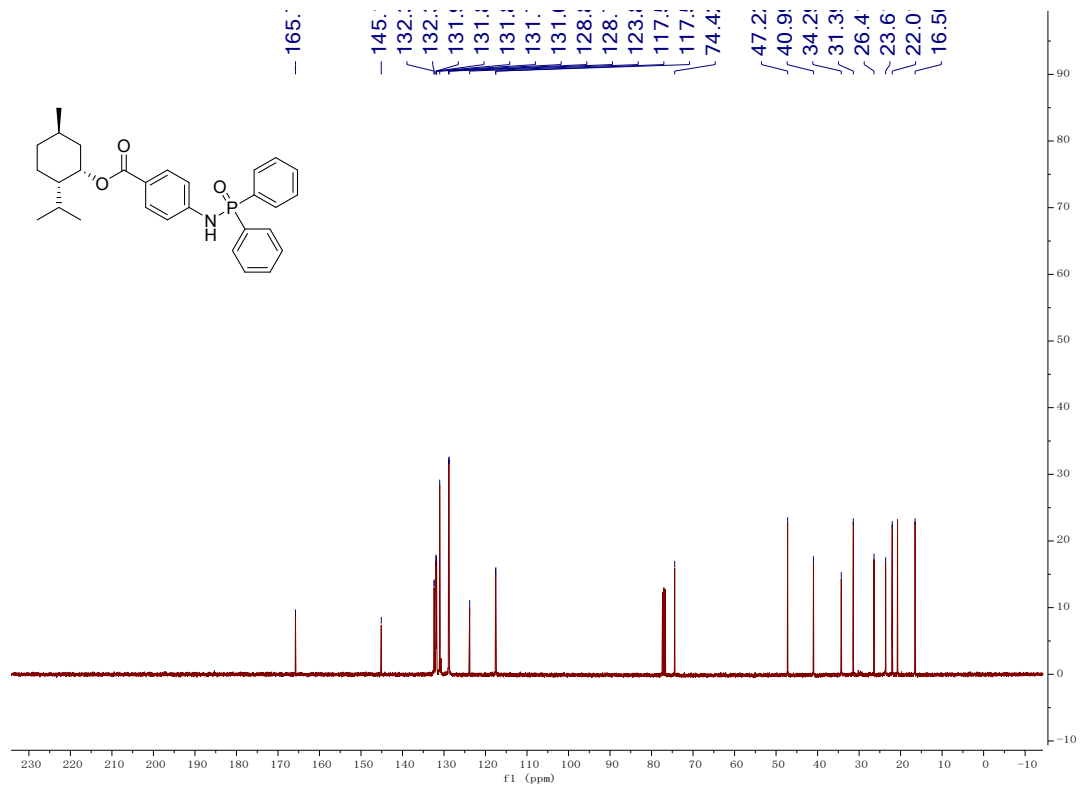
N-(naphthalen-1-yl)-P,P-diphenylphosphinic amide (3x)



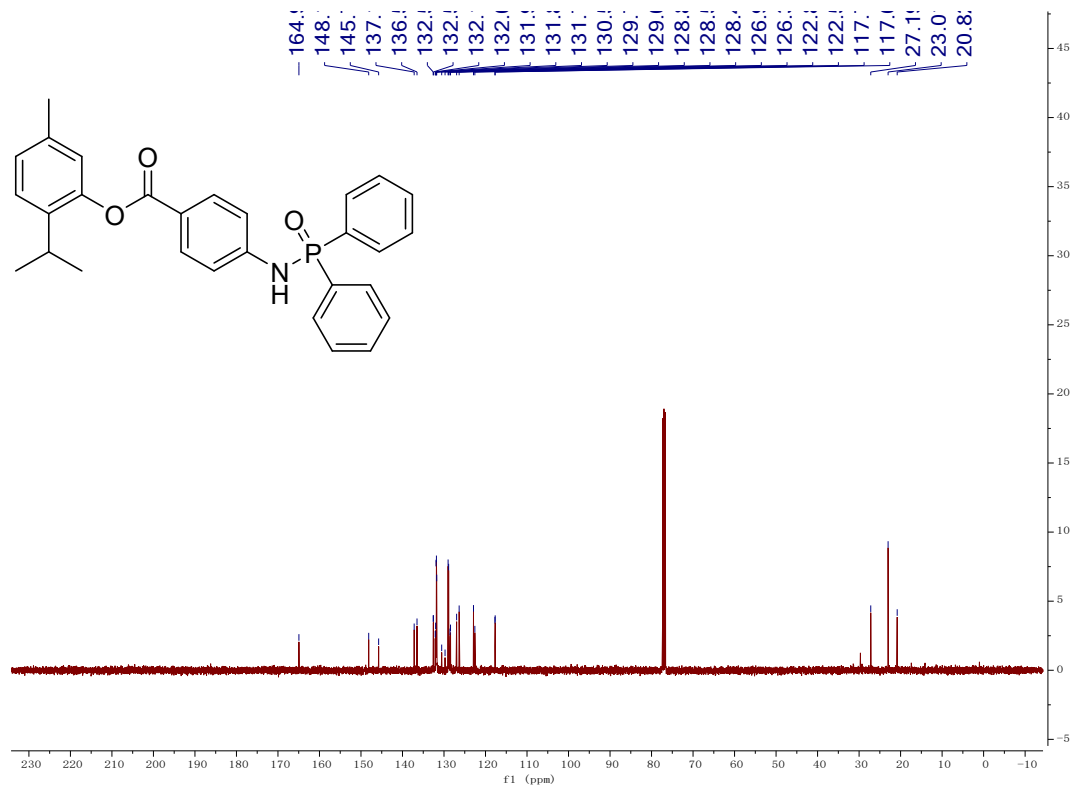
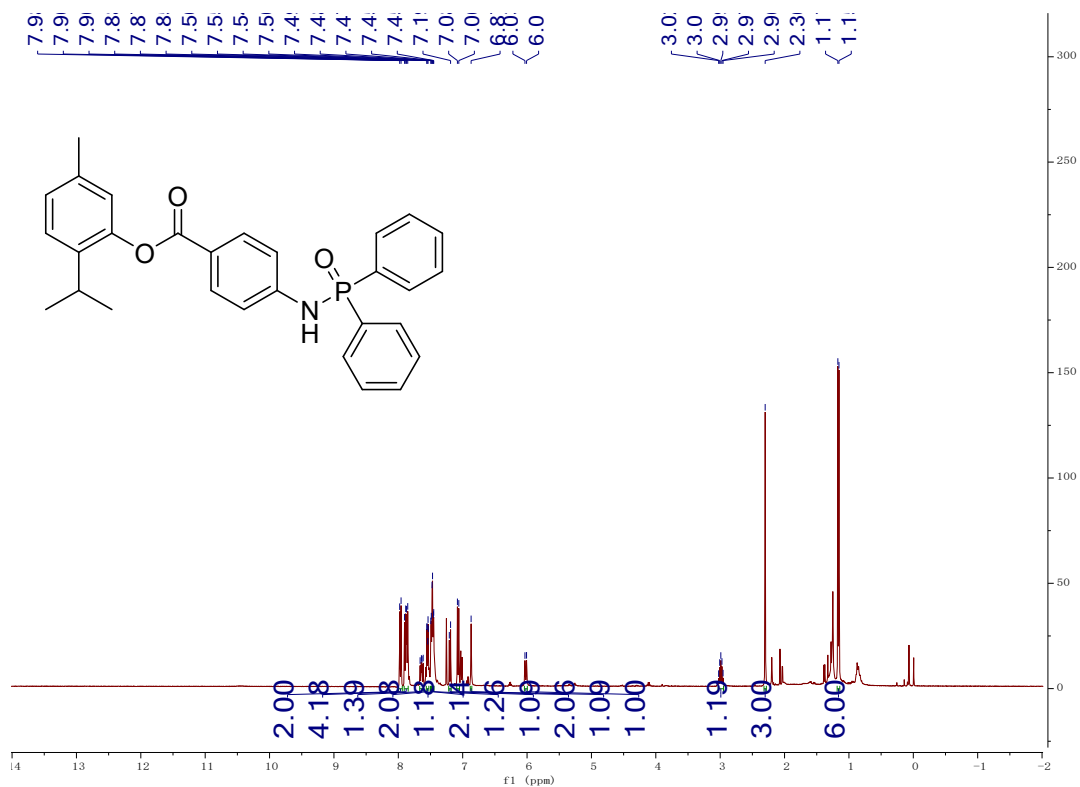


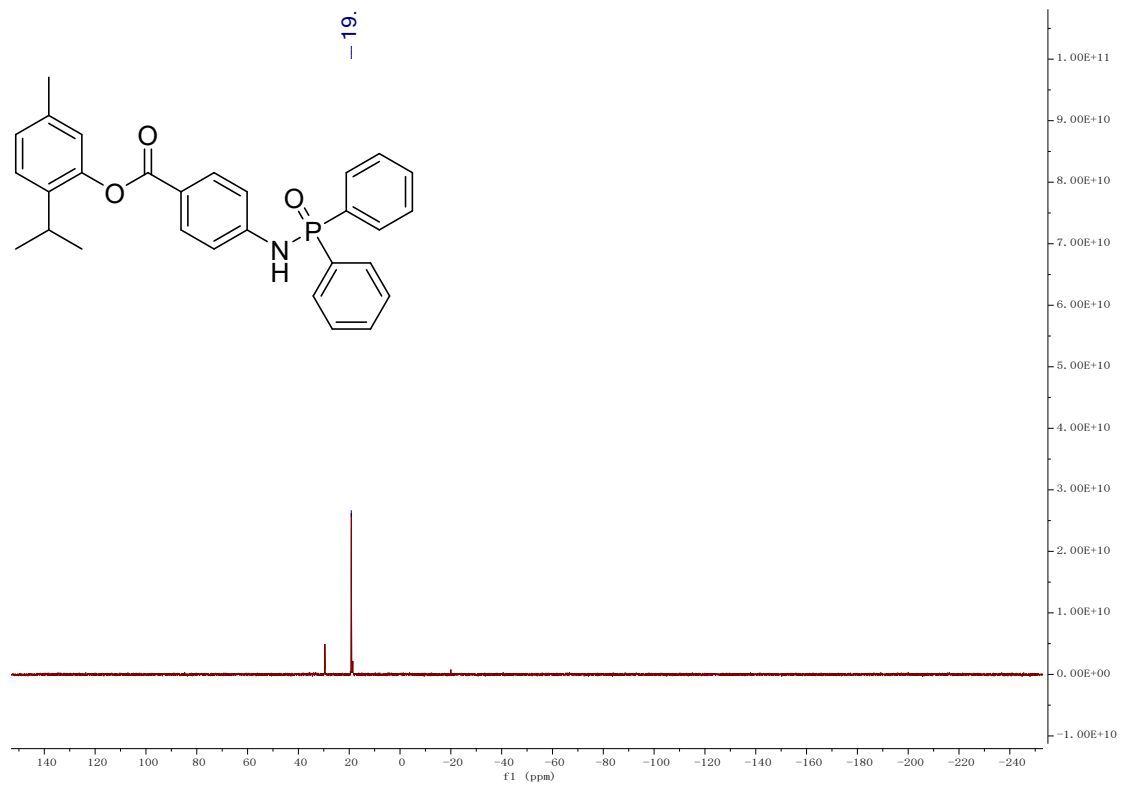
(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-((diphenylphosphoryl)amino) benzoate (3y)



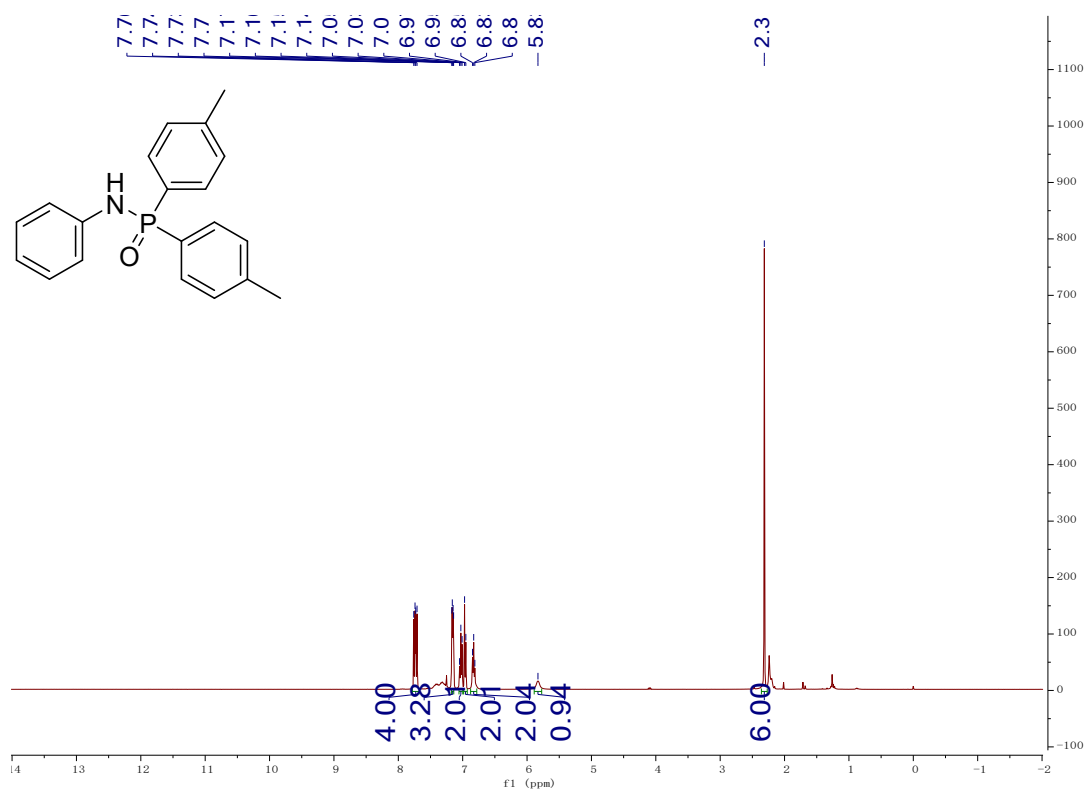


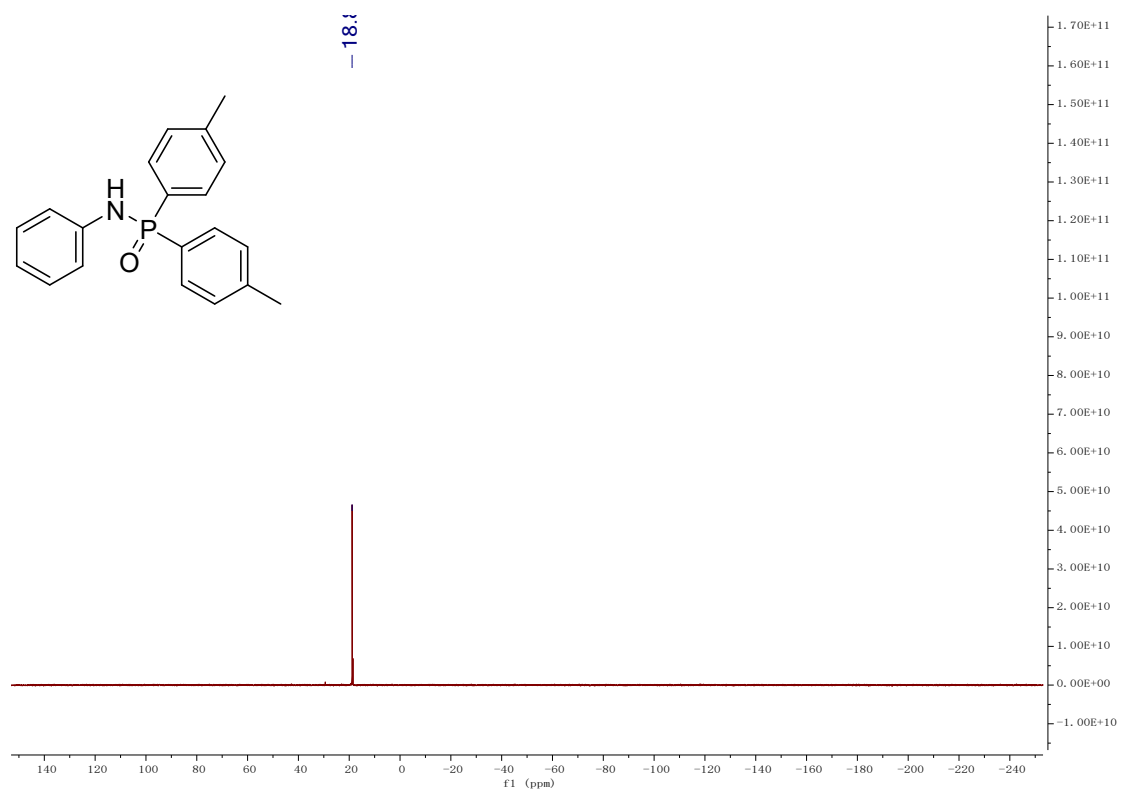
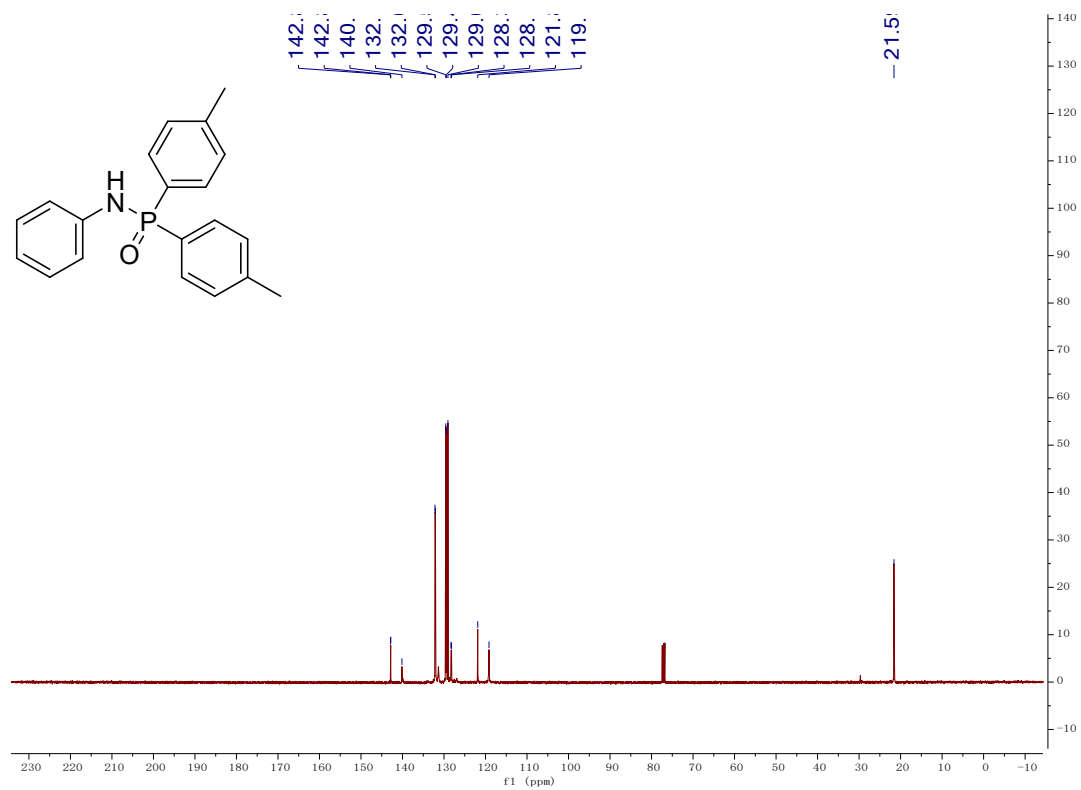
2-isopropyl-5-methylphenyl 4-((diphenylphosphoryl)amino)benzoate (3z)



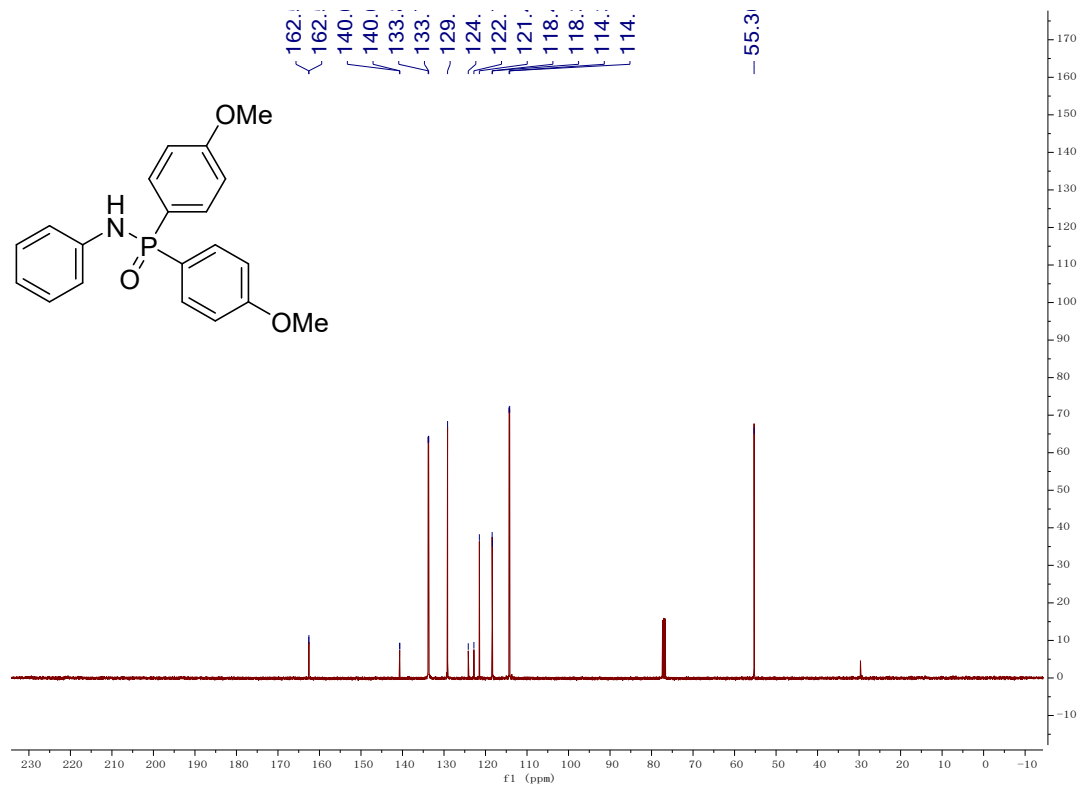
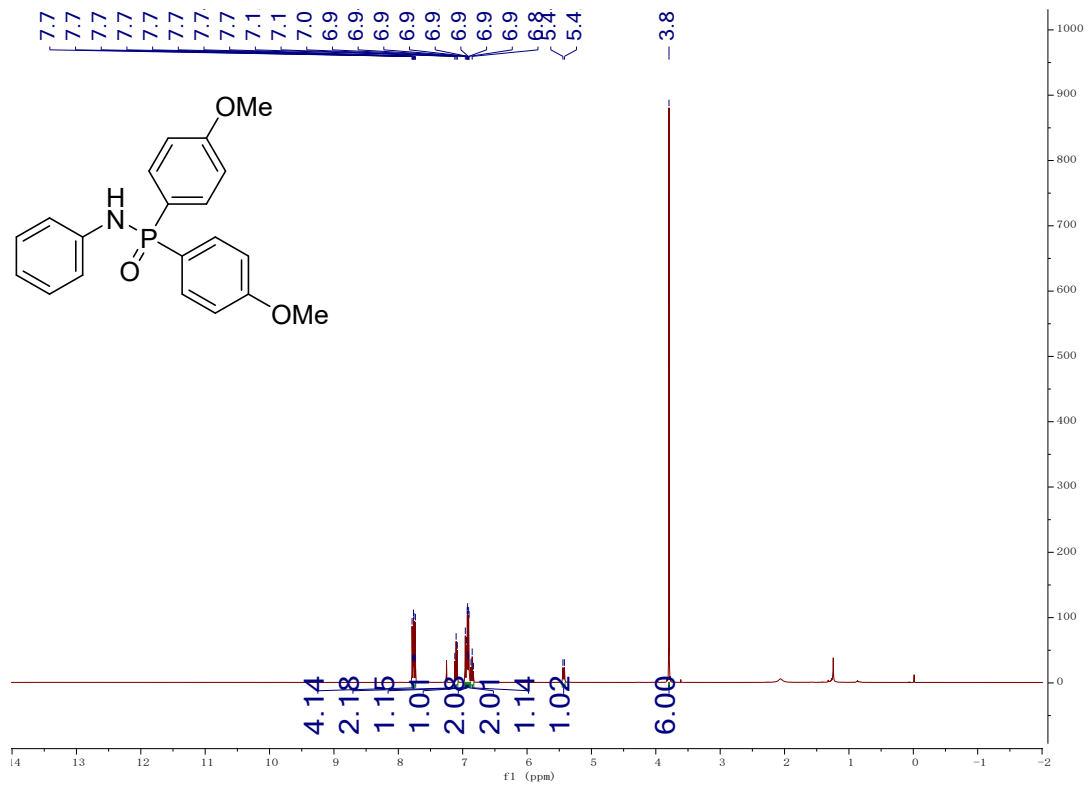


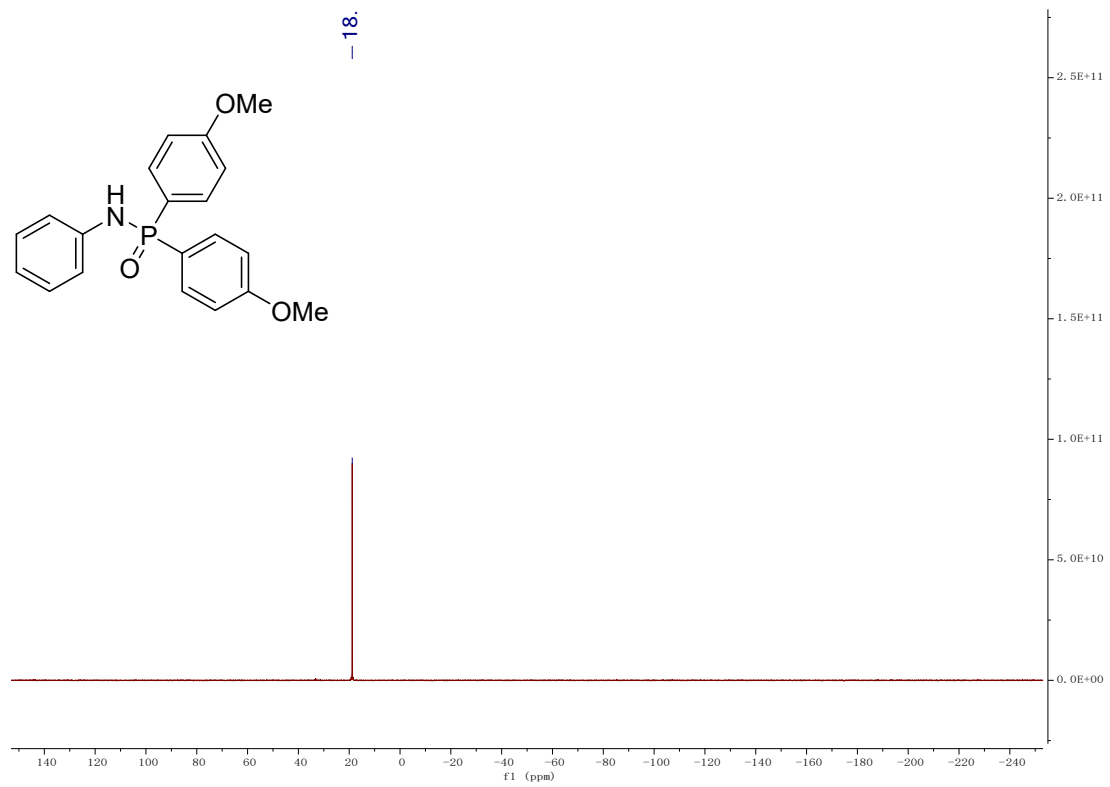
N-phenyl-P,P-di-p-tolylphosphinic amide (4a)



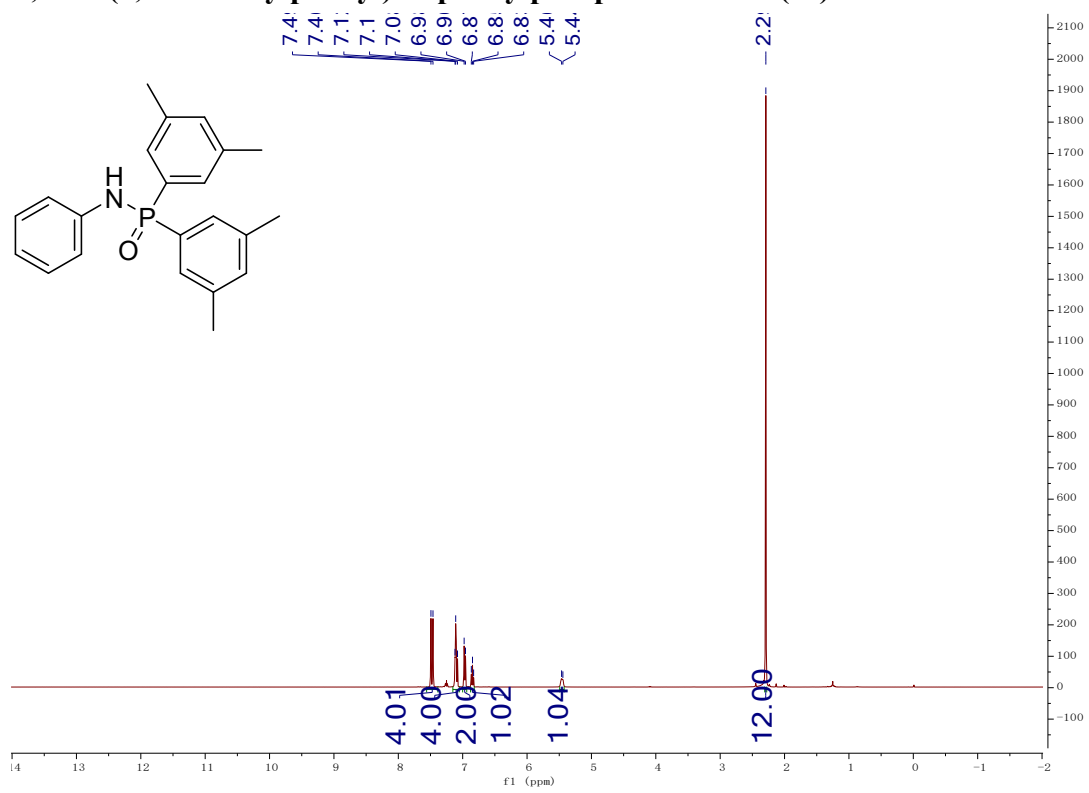


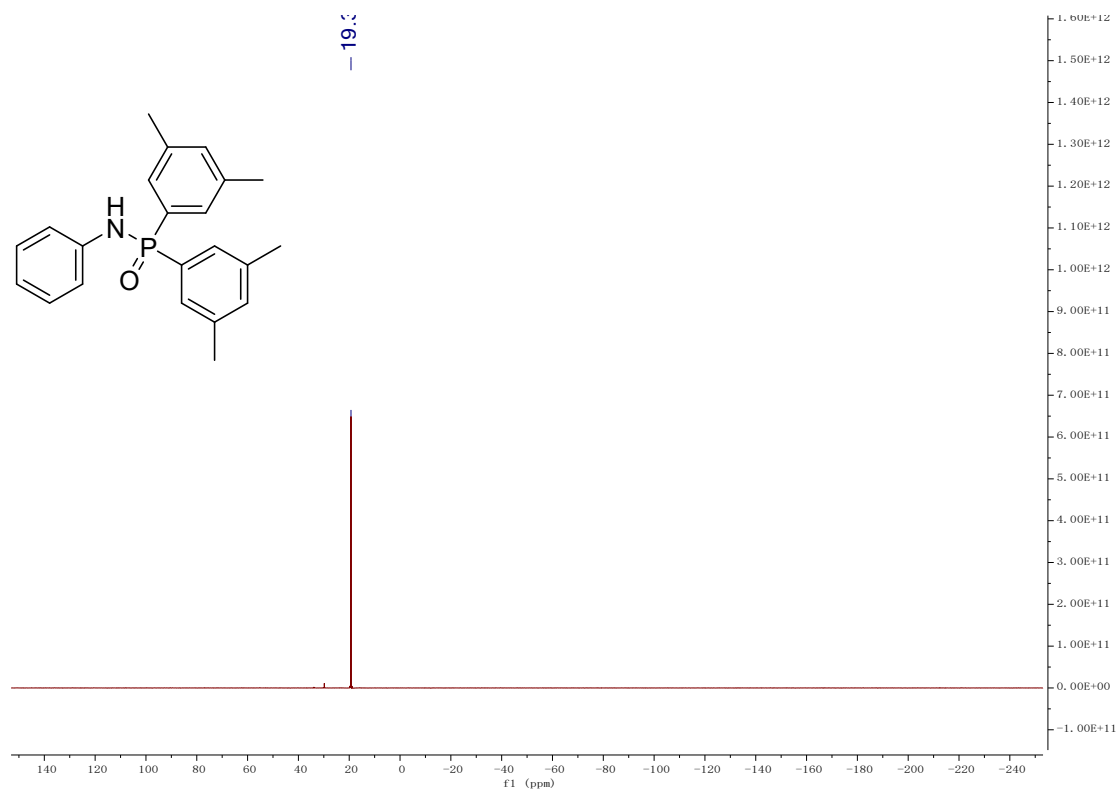
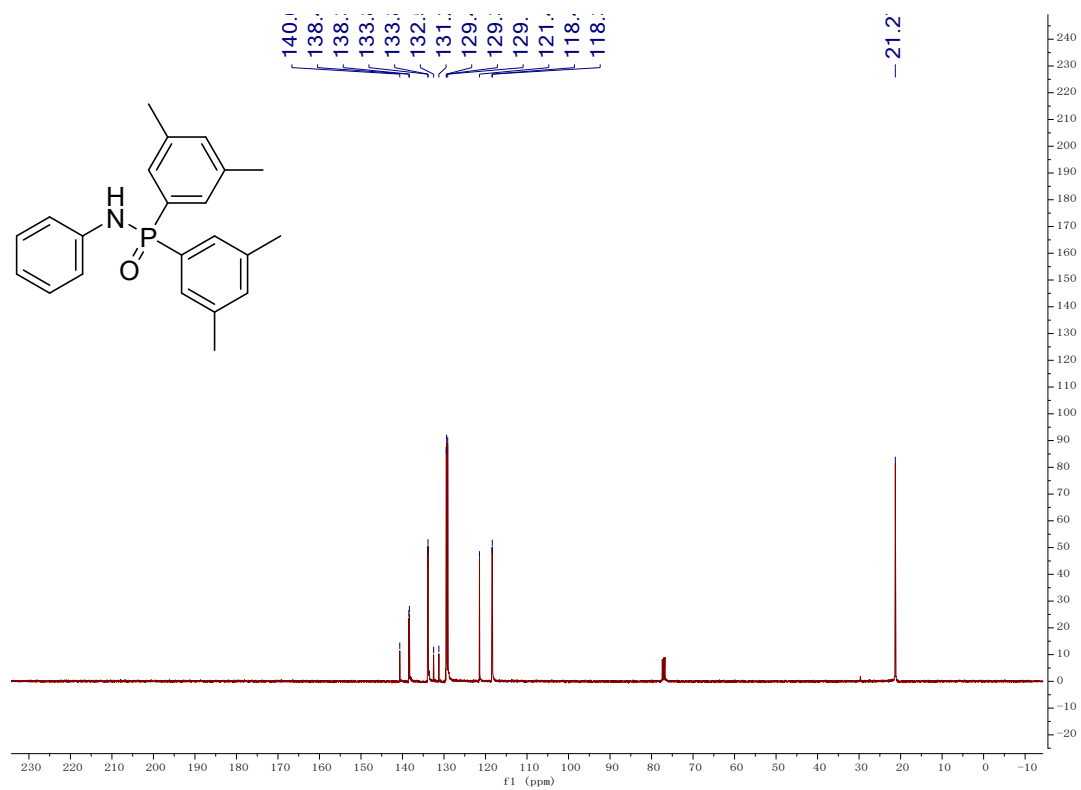
P,P-bis(4-methoxyphenyl)-N-phenylphosphinic amide (4b)



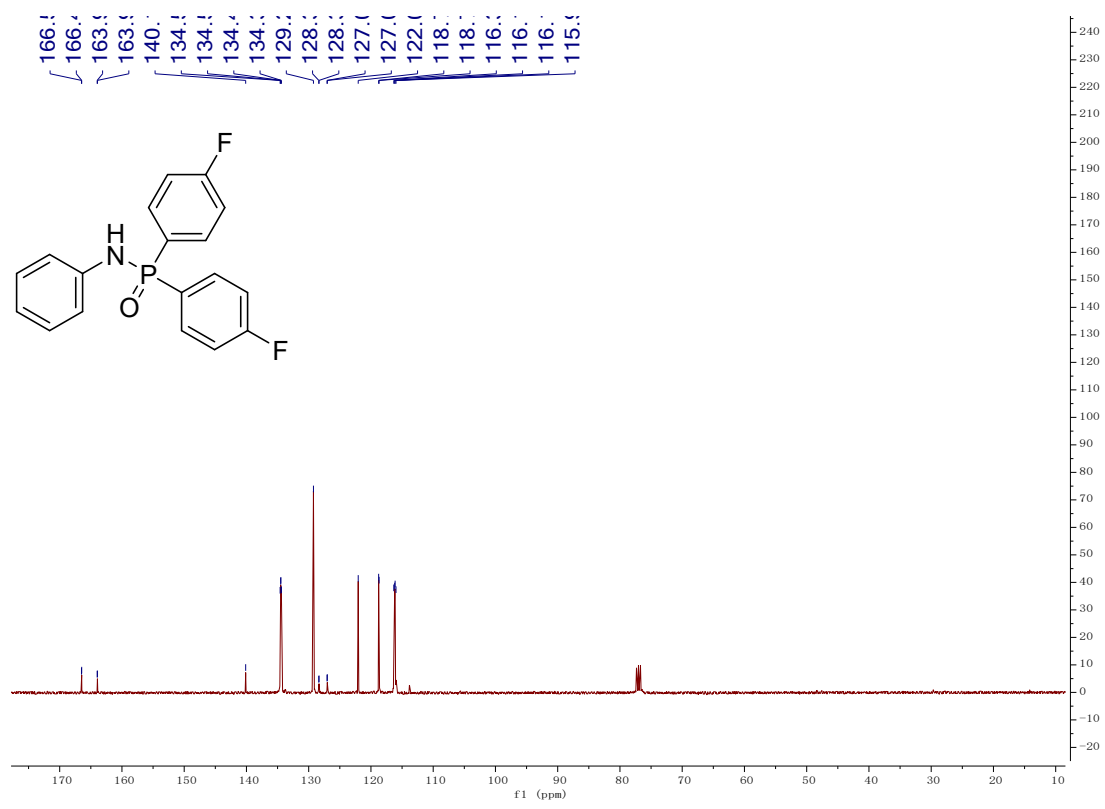
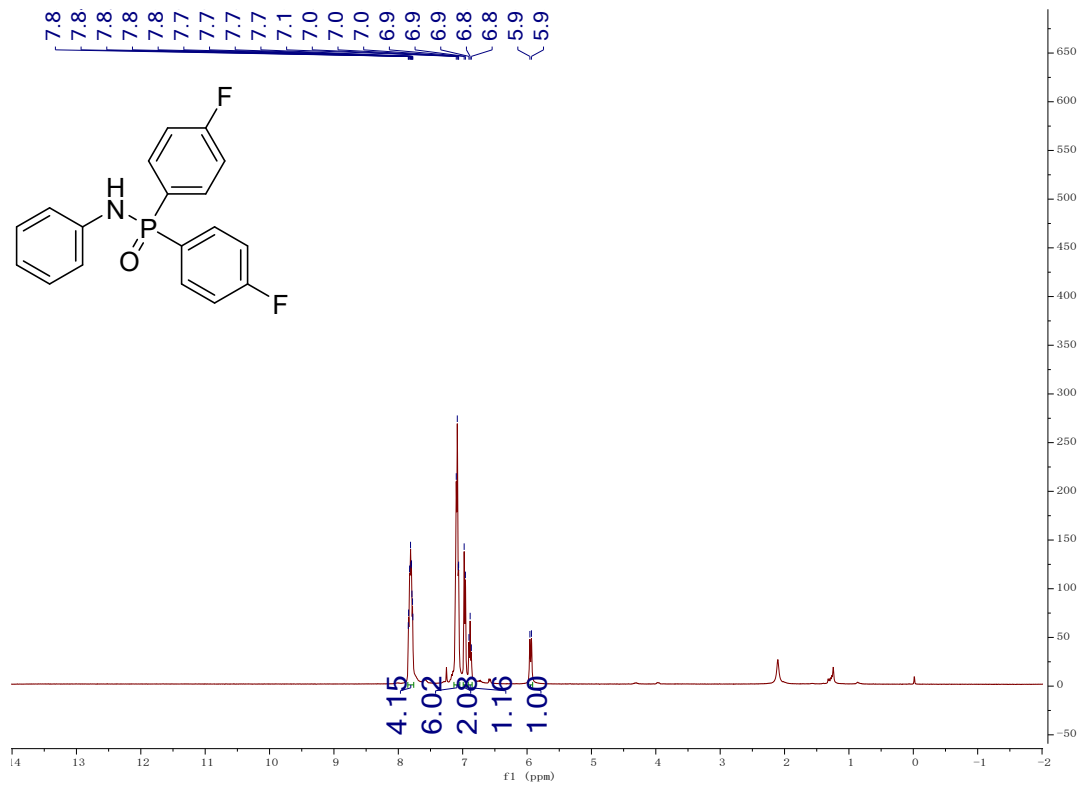


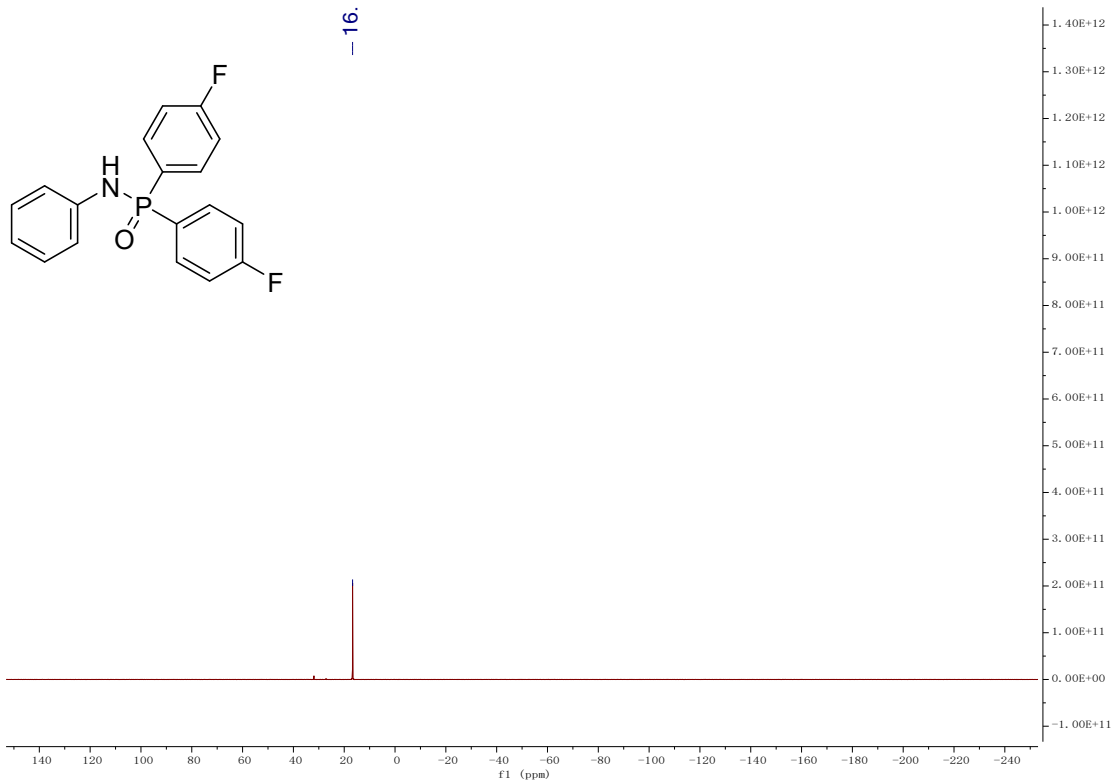
P,P-bis(3,5-dimethylphenyl)-N-phenylphosphinic amide (4c)



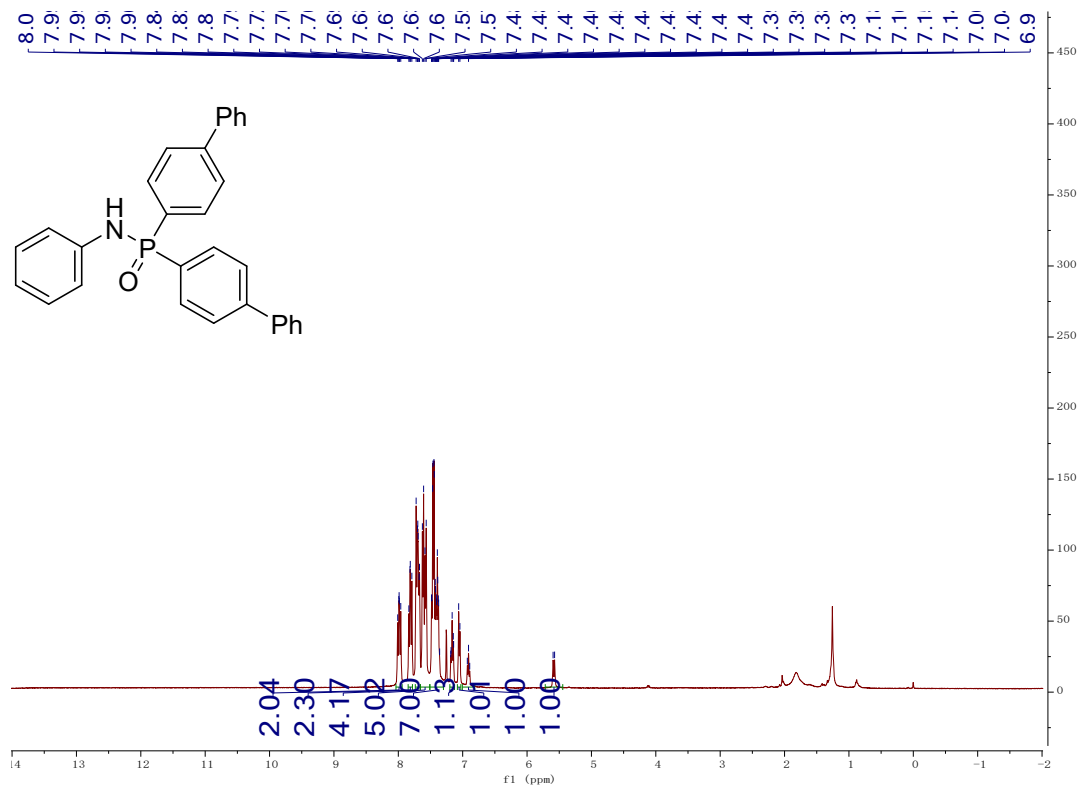


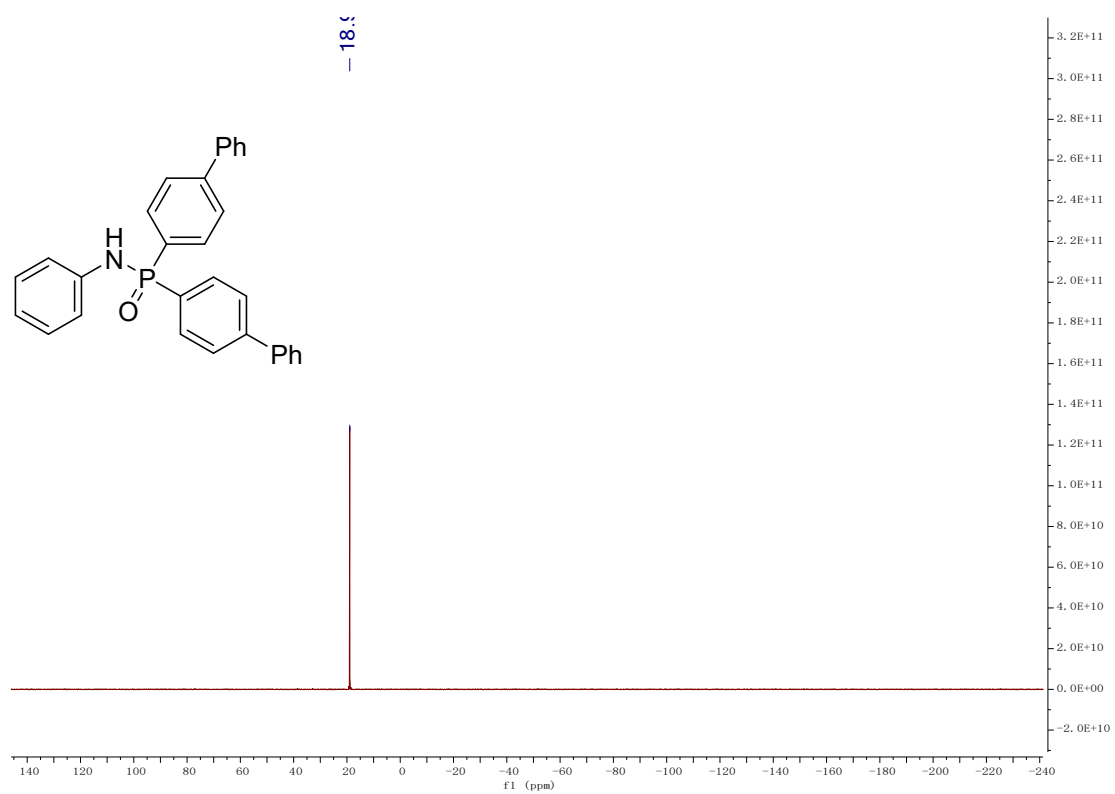
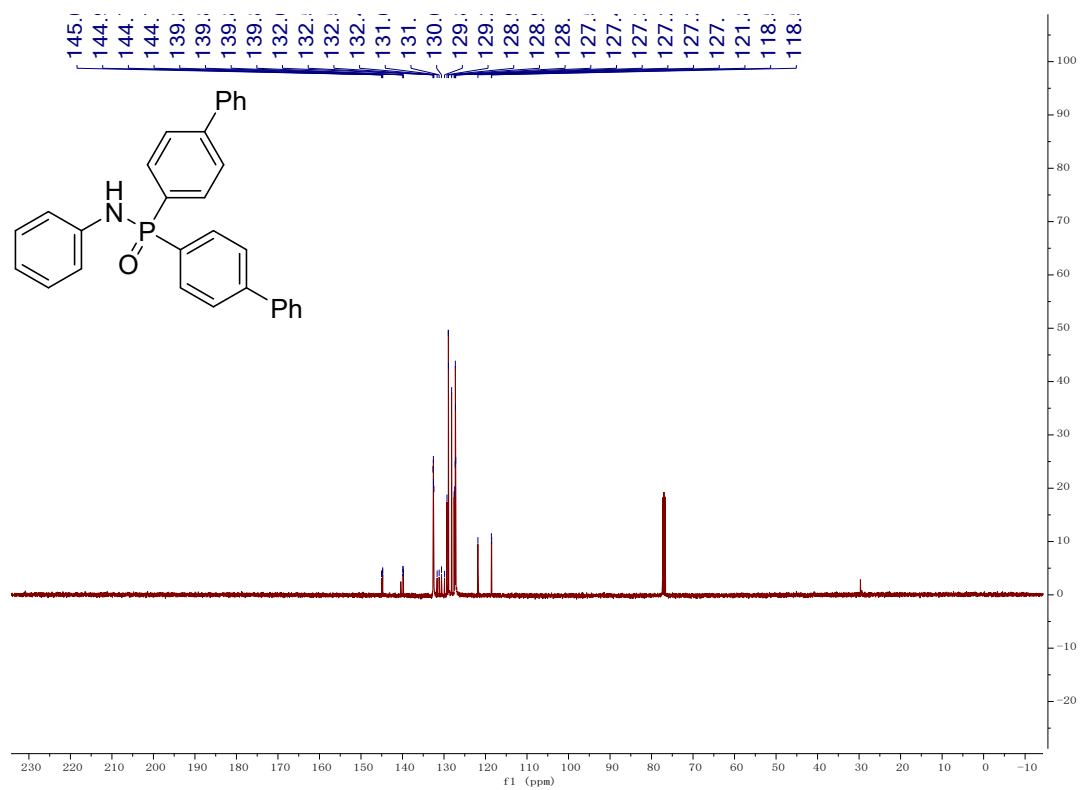
P,P-bis(4-fluorophenyl)-N-phenylphosphinic amide (4d)



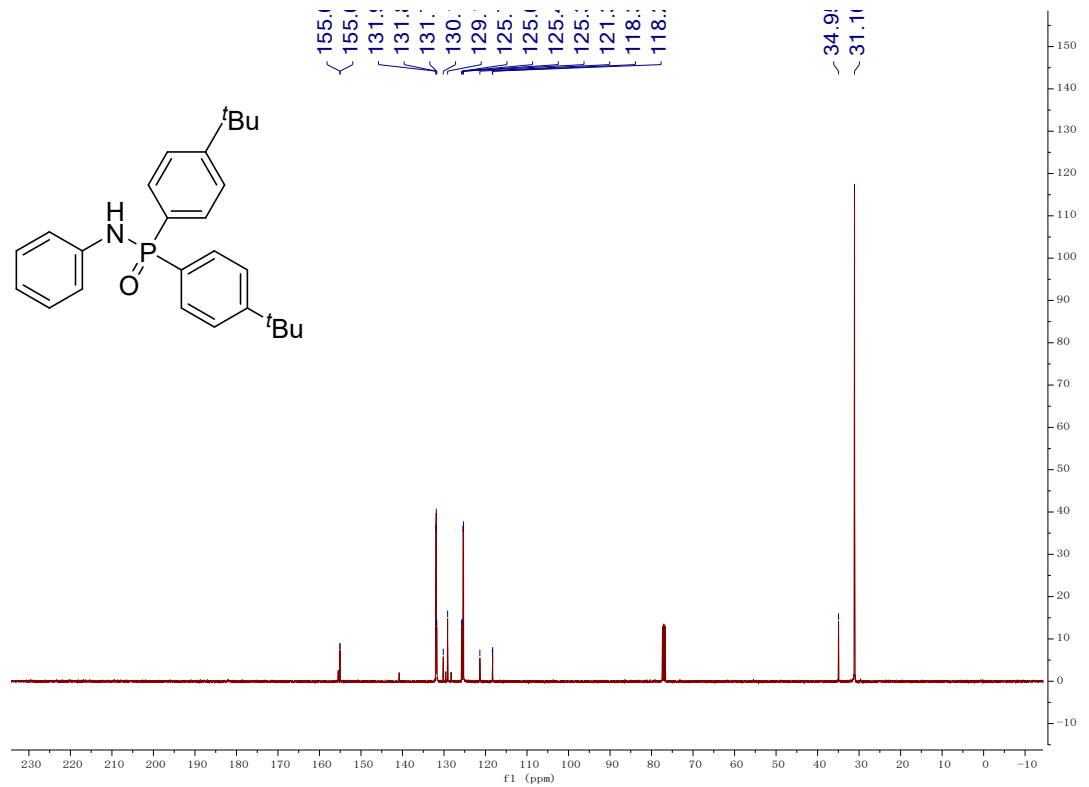
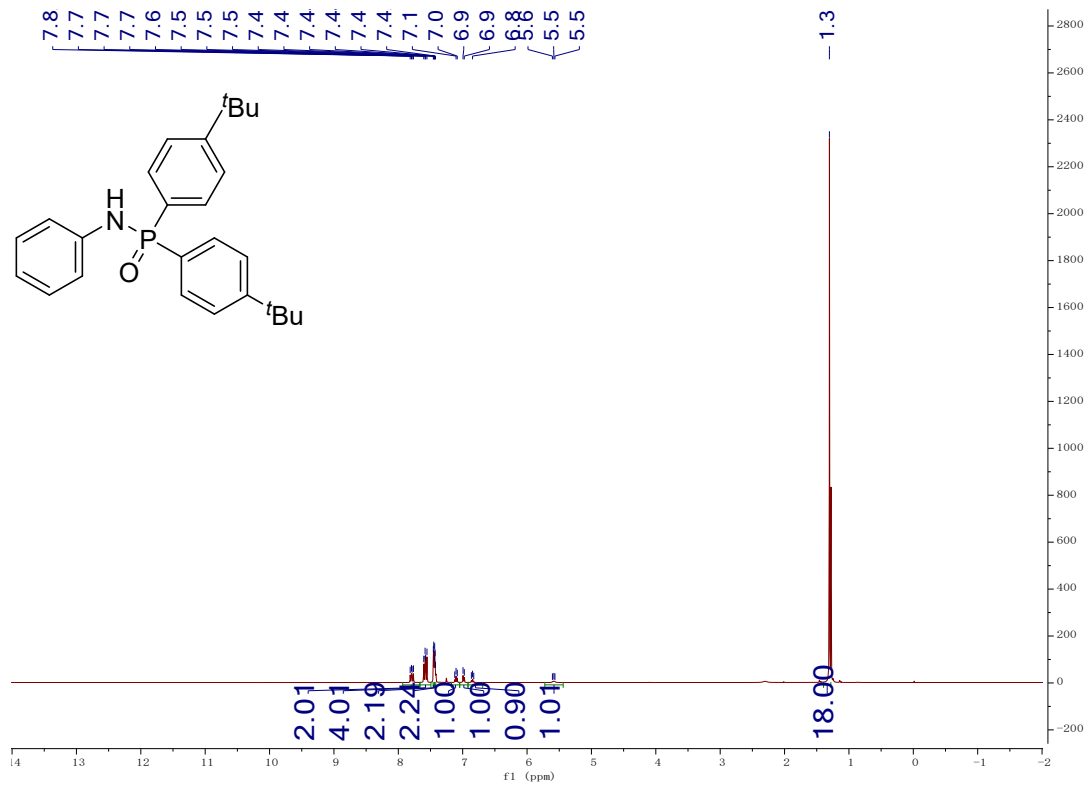


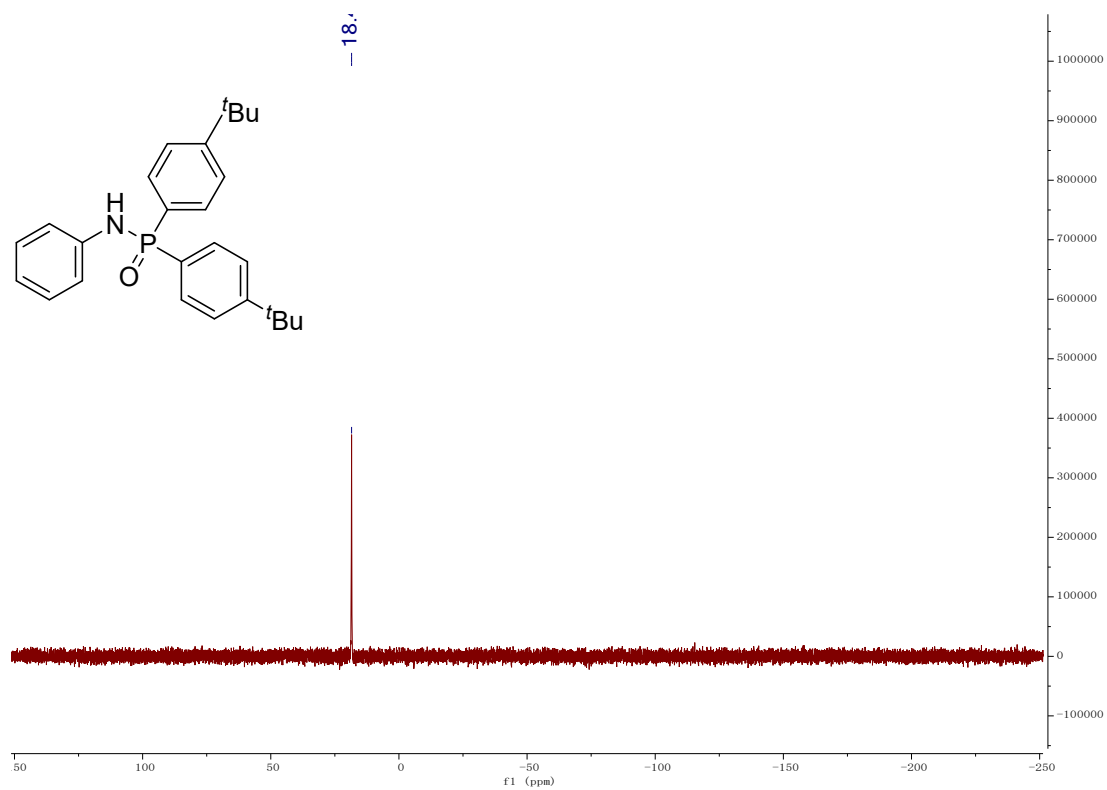
P,P-di([1,1'-biphenyl]-4-yl)-N-phenylphosphinic amide (4e)



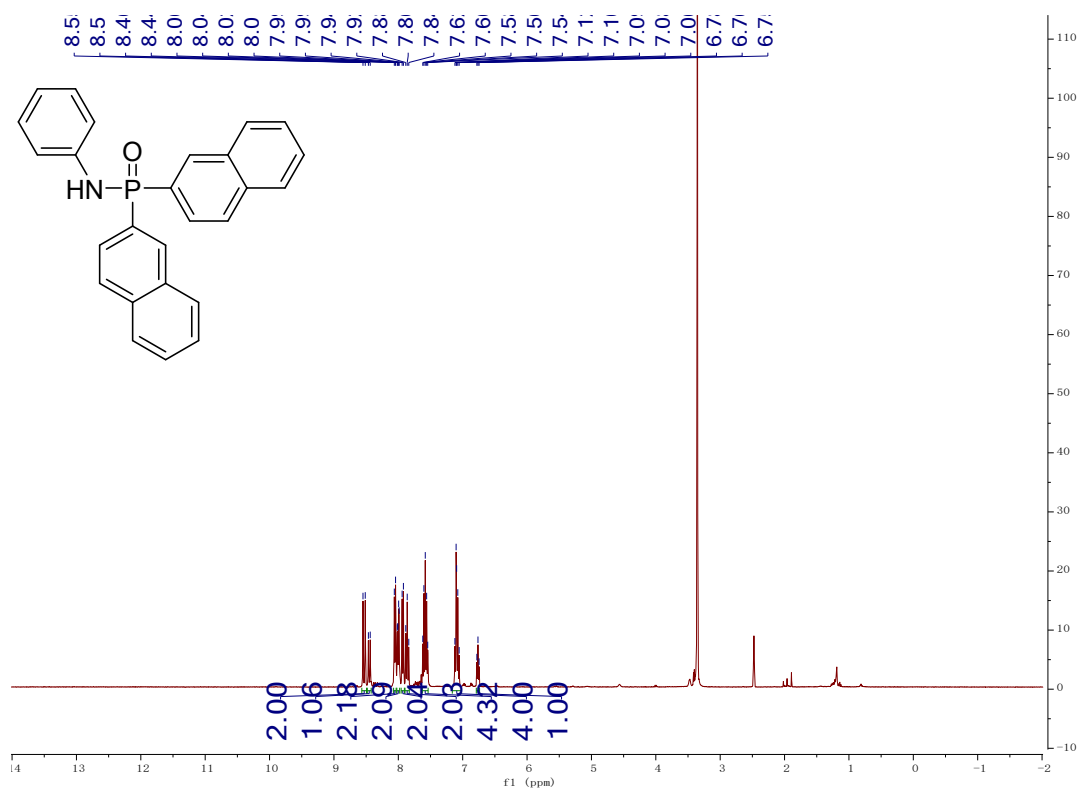


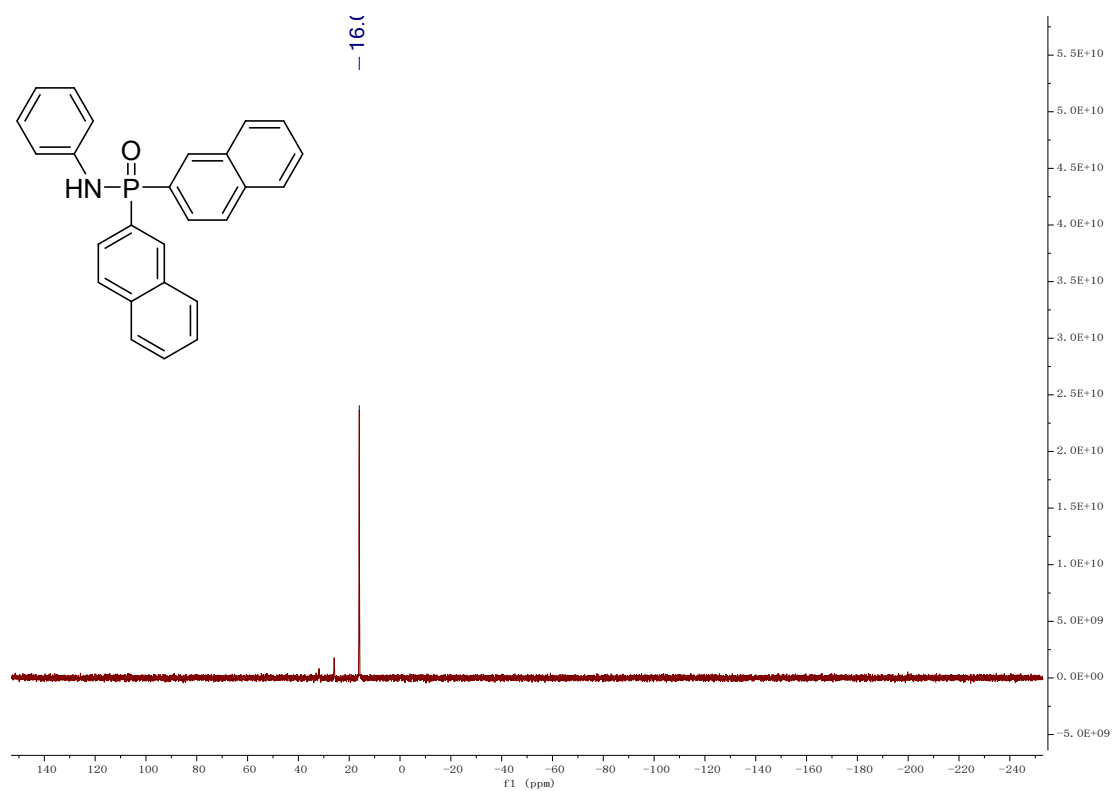
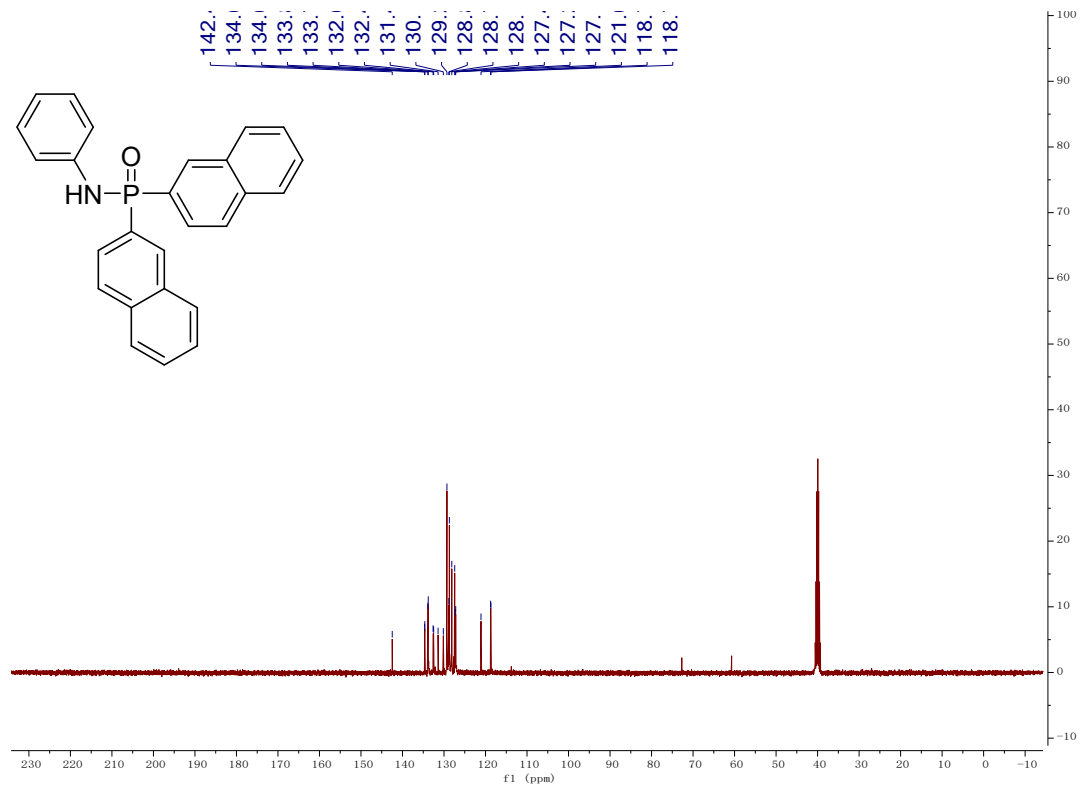
P,P-bis(4-(tert-butyl)phenyl)-N-phenylphosphinic amide (4f)



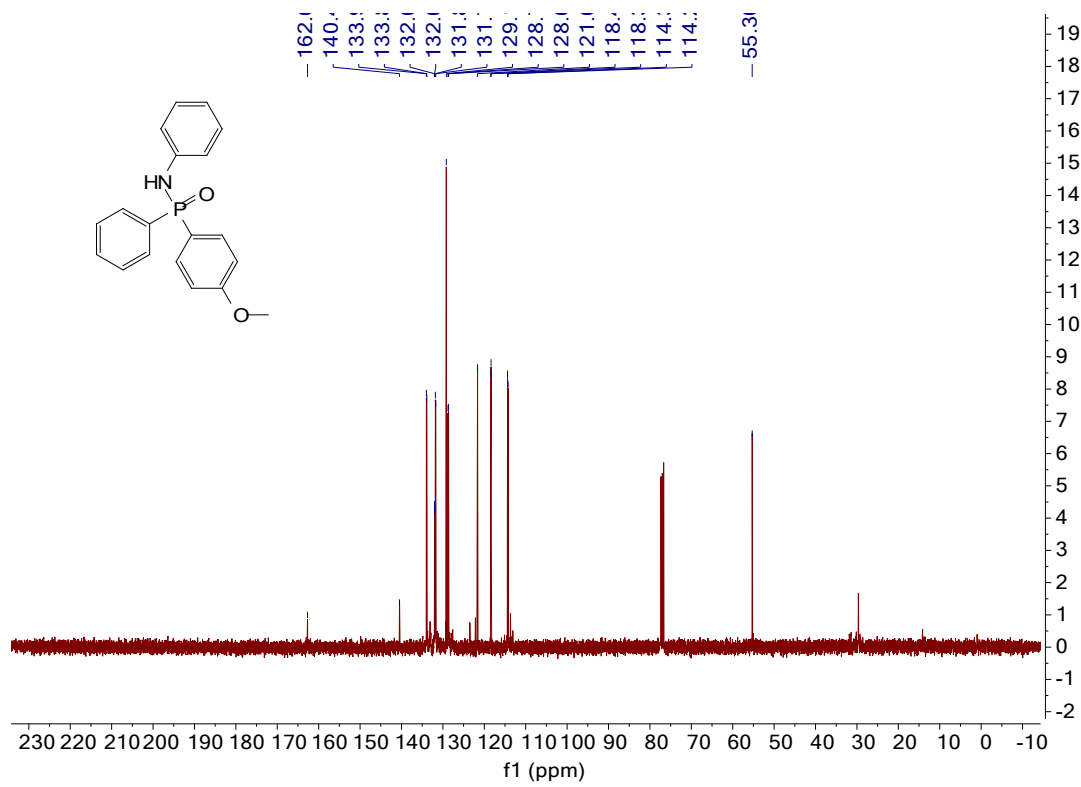
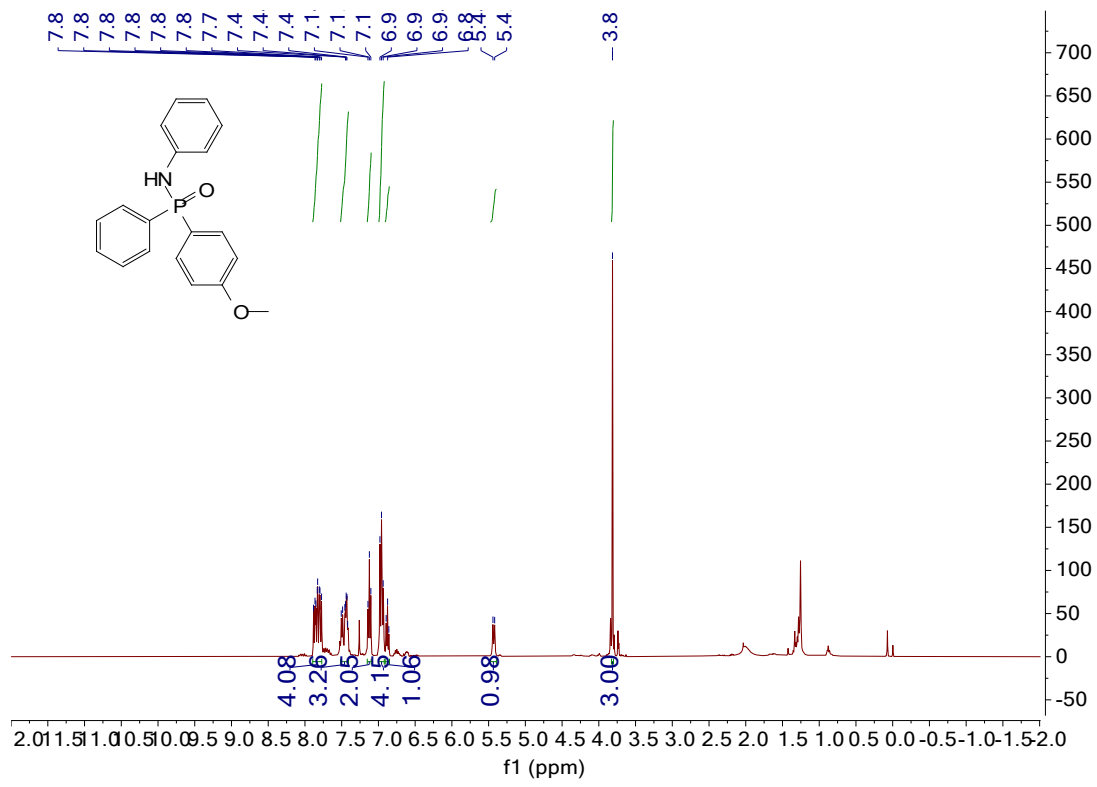


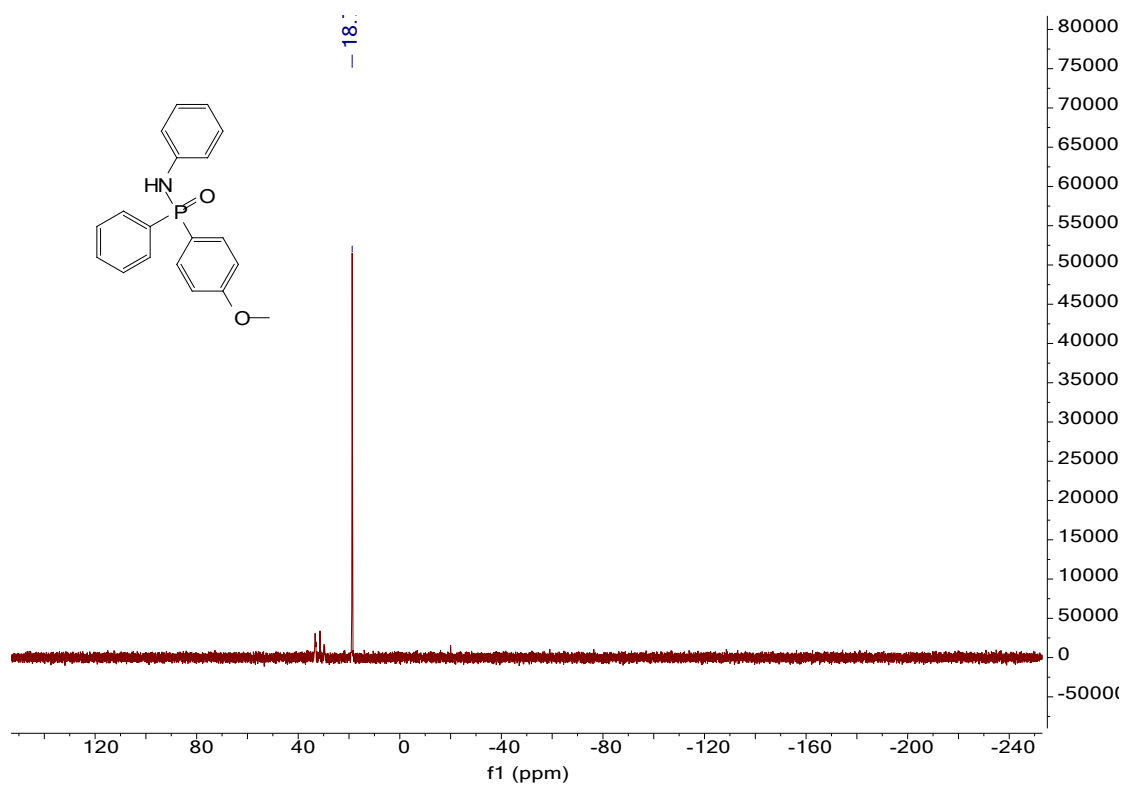
P,P-di(naphthalen-2-yl)-N-phenylphosphinic amide (4g)





P-(4-methoxyphenyl)-N,P-diphenylphosphinic amide (4g):





P-butyl-N,P-diphenylphosphinic amide(4h):

