Lewis Acid-Controlled Regioselective Phosphorylation of 2-Indolylmethanols with Diarylphosphine Oxides: Synthesis of Highly Substituted Indoles

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SUPPORTING INFORMATION

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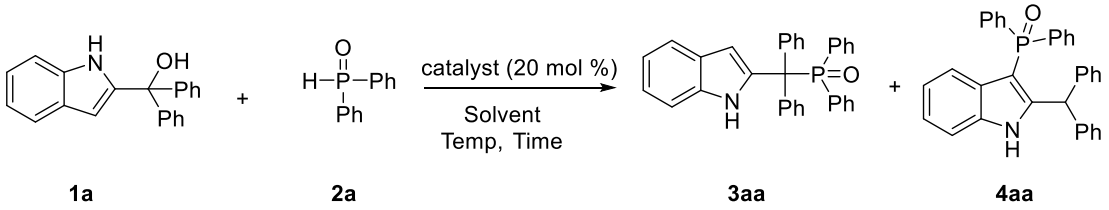
EXPERIMENTAL SECTION

1.1 Optimization of the Reaction Conditions[a]

Table S1. Optimization of the Reaction Conditions.

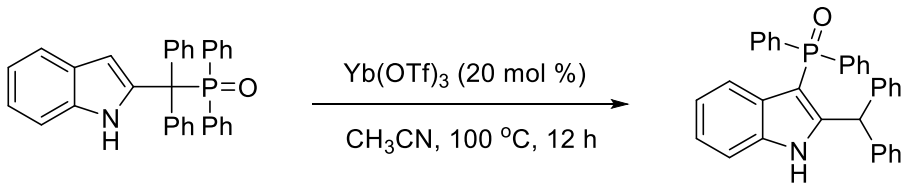


1a **2a** **3aa** **4aa**

Entry	Catalyst (20 mol %)	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	$Y(Pfb)_3$	DCE	100	12	72/0
2	$Y(Pfb)_3$	DCM	100	12	69/trace
3	$Y(Pfb)_3$	$CHCl_3$	100	12	84/0
4	$Y(Pfb)_3$	DMSO	100	12	53/0
5	$Y(Pfb)_3$	DMF	100	12	69/trace
6	$Y(Pfb)_3$	CH_3CN	120	12	79/trace
7	$Y(Pfb)_3$	CH_3CN	80	12	62/trace
8	$Y(Pfb)_3$	CH_3CN	100	16	80/trace
9	$Y(Pfb)_3$	CH_3CN	100	8	83/trace
10	$Y(Pfb)_3$ (10)	CH_3CN	100	12	76/trace
11	$Y(Pfb)_3$ (30)	CH_3CN	100	12	88/trace
12	$Yb(OTf)_3$	DCE	100	12	0/63
13	$Yb(OTf)_3$	DCM	100	12	0/32
14	$Yb(OTf)_3$	$CHCl_3$	100	12	0/40
15	$Yb(OTf)_3$	DMSO	100	12	Trace/43
16	$Yb(OTf)_3$	DMF	100	12	Trace/47
17	$Yb(OTf)_3$	CH_3CN	120	12	0/73
18	$Yb(OTf)_3$	CH_3CN	80	12	0/69
19	$Yb(OTf)_3$	CH_3CN	100	16	0/76
20	$Yb(OTf)_3$	CH_3CN	100	8	Trace/70
21	$Yb(OTf)_3$ (10)	CH_3CN	100	12	Trace/55
22	$Yb(OTf)_3$ (30)	CH_3CN	100	12	0/74

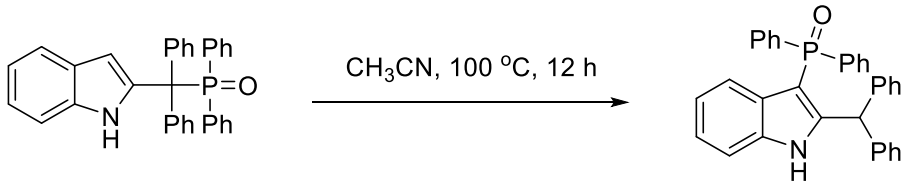
[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.375 mmol), catalyst (20 mol %), CH_3CN (2 mL) at indicated temperature for indicated time, under air.

1.2 Mechanistic Probes



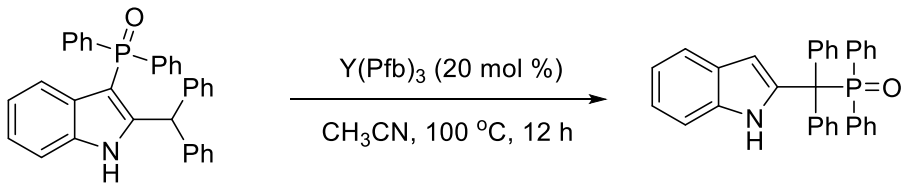
3aa **4aa**, 73%

((1H-indol-2-yl)diphenylmethyl)diphenylphosphine oxide **3aa** (120.89 mg, 0.25 mmol, 1 equiv.), $Yb(OTf)_3$ (31.01 mg, 0.05 mmol, 0.2 equiv), dry CH_3CN (2 mL) and a stir bar were added to a sealed tube. After being stirred at 100 °C for 12 h, the mixture was evaporated under vacuum. The corresponding product **4aa** was isolated by silica gel column chromatography with a dichloromethane/ethyl acetate (10/1) mixture as eluent to afford **4aa** (352.99 mg) in 73% yield.



3aa **4aa**, 0%

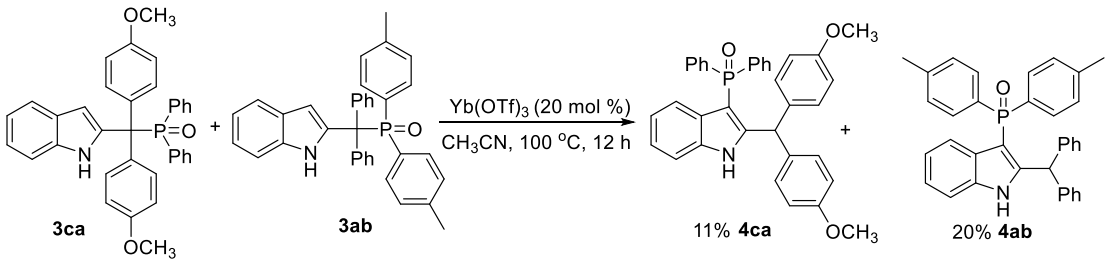
The same procedure was followed using **3aa** without adding $Yb(OTf)_3$ (31.01 mg, 0.05 mmol, 0.2 equiv.), no desired product **4aa** was detected.



4aa **3aa**, 0%

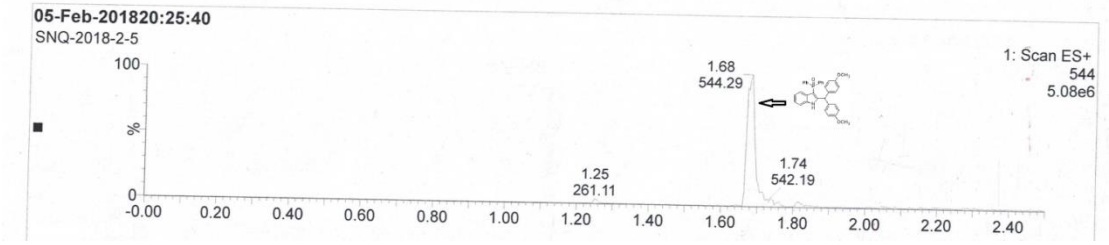
The same procedure was followed using **4aa** with adding $Y(Pfb)_3$ (36.10 mg, 0.05 mmol, 0.2 equiv.), no desired product **3aa** was detected.

1.3 Crossover Experiment and LCMS Spectra

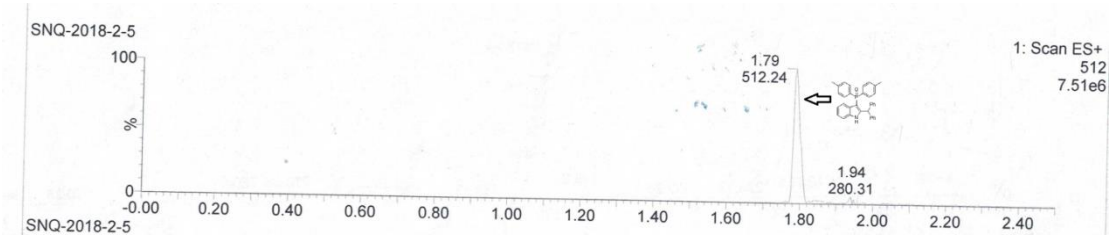


3ca (543.60 mg, 0.1 mmol, 1 equiv.), **3ab** (511.60 mg, 0.1 mmol, 1 equiv.), dry CH_3CN (2 mL), $Yb(OTf)_3$ (31.01 mg, 0.05 mmol, 20 mol %) and a stir bar were added to a sealed tube. After being stirred at 100 °C for 12 h, the mixture was evaporated under vacuum. The rearranged products **4ca** (59.80 mg, 11% yield) and **4ab** (102.3 mg, 20% yield) were isolated by silica gel column chromatography with a dichloromethane/ethyl acetate (100/1 to 10/1) mixture as eluent. No crossover products were observed by LCMS. (See below)

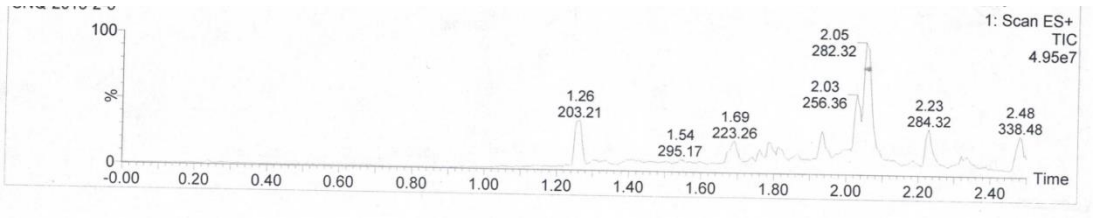
(a)



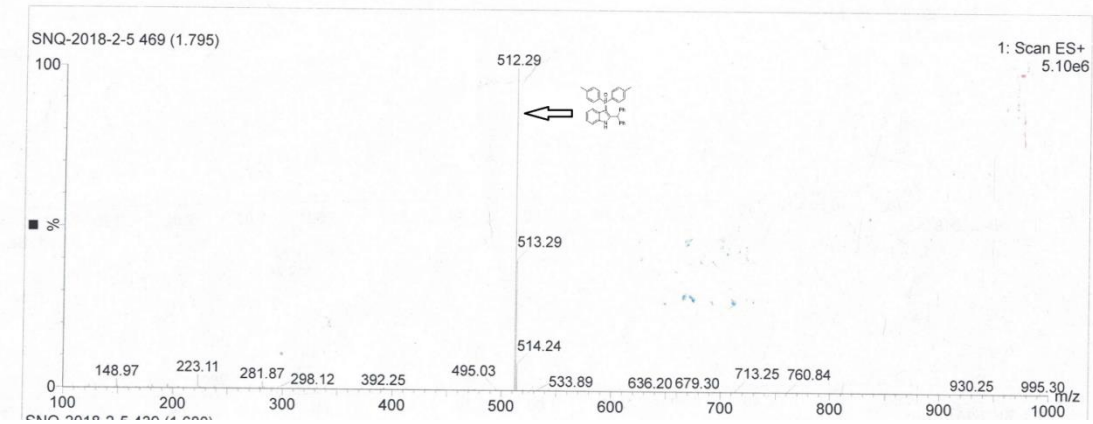
(b)



(c)



(d)



(e)

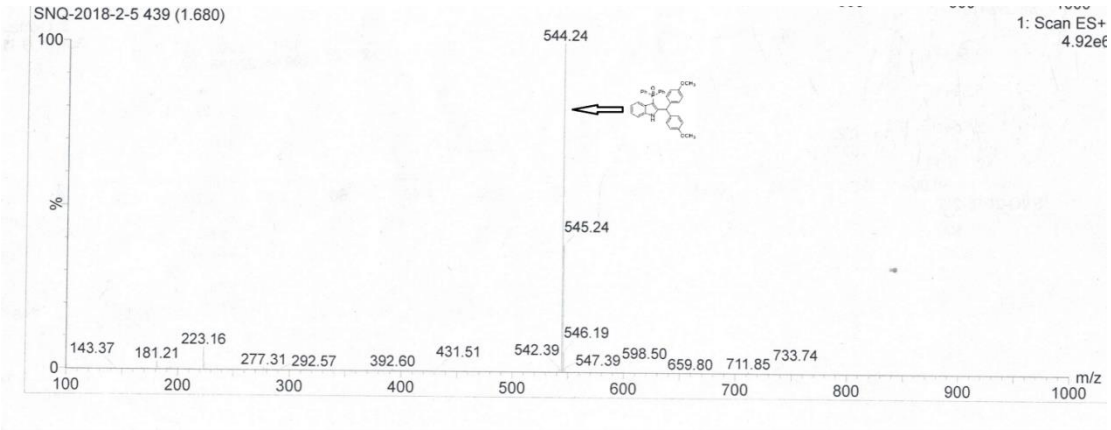
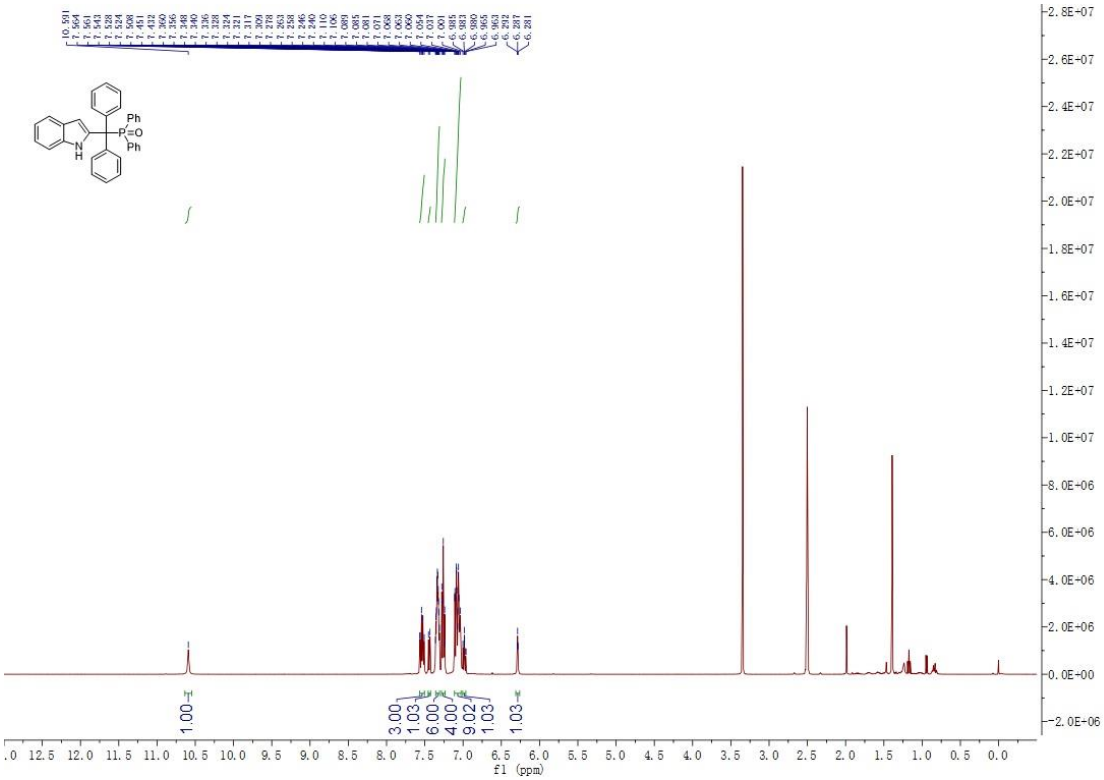
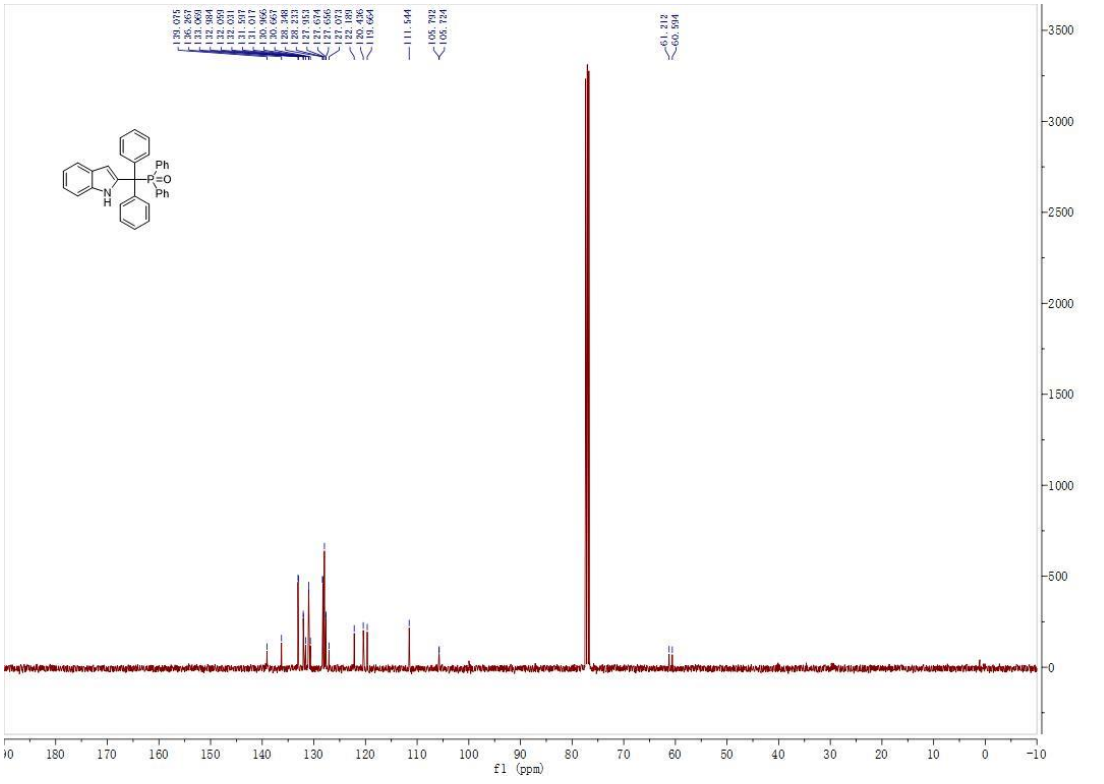


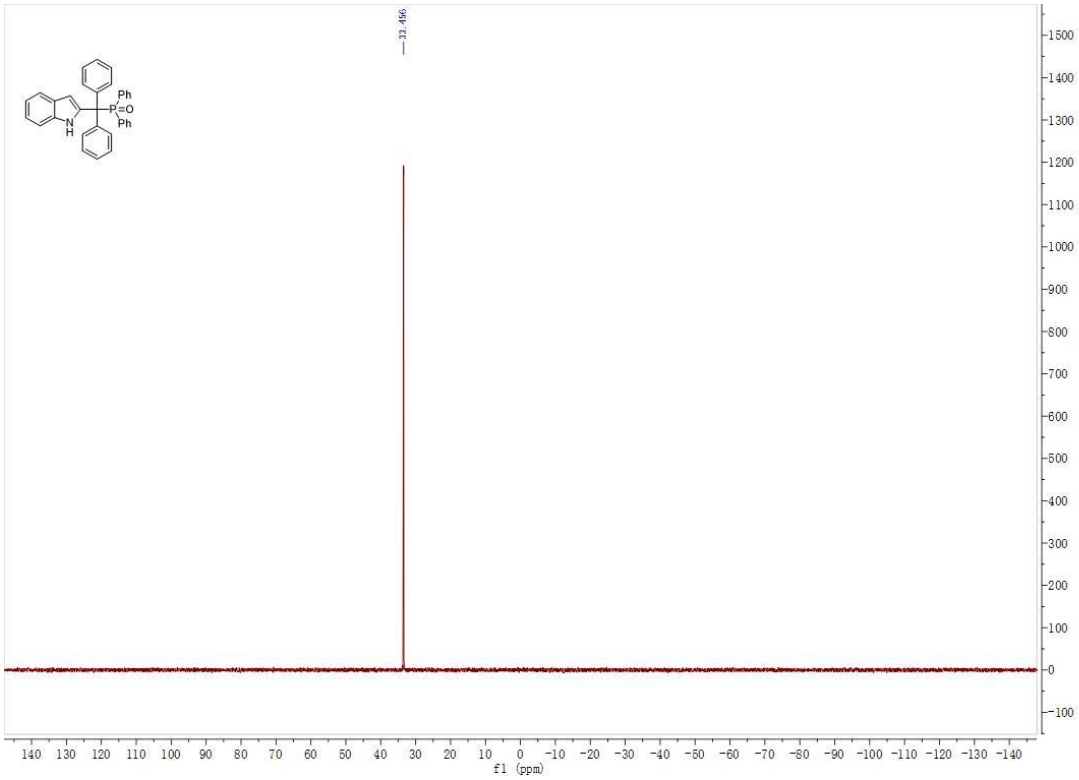
Figure S1. (a) Retention time of **4ca**. (b) Retention time of **4ab**. (c) Reaction LCMS (d) MS of **4ab**. (e) MS of **4ca.**

Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR

3aa



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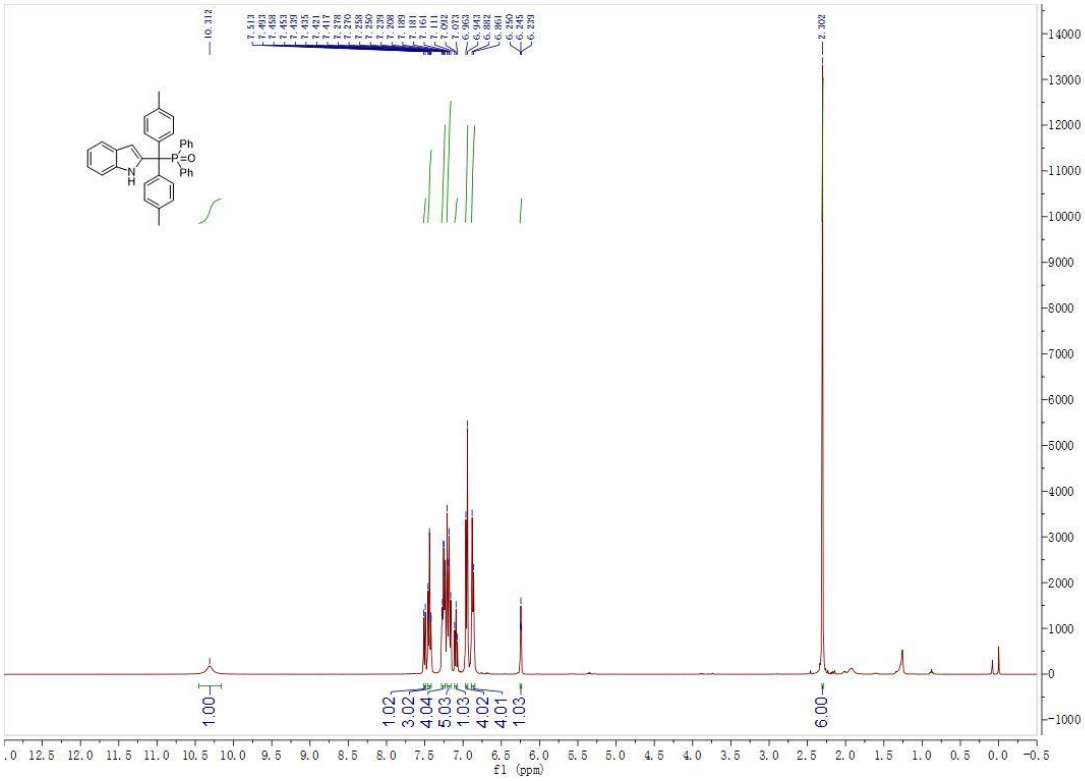
P=O
Ph
N
H
fl (ppm)

3ba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2.302
Ph
P=O
Ph
N
H
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1.02
3.02
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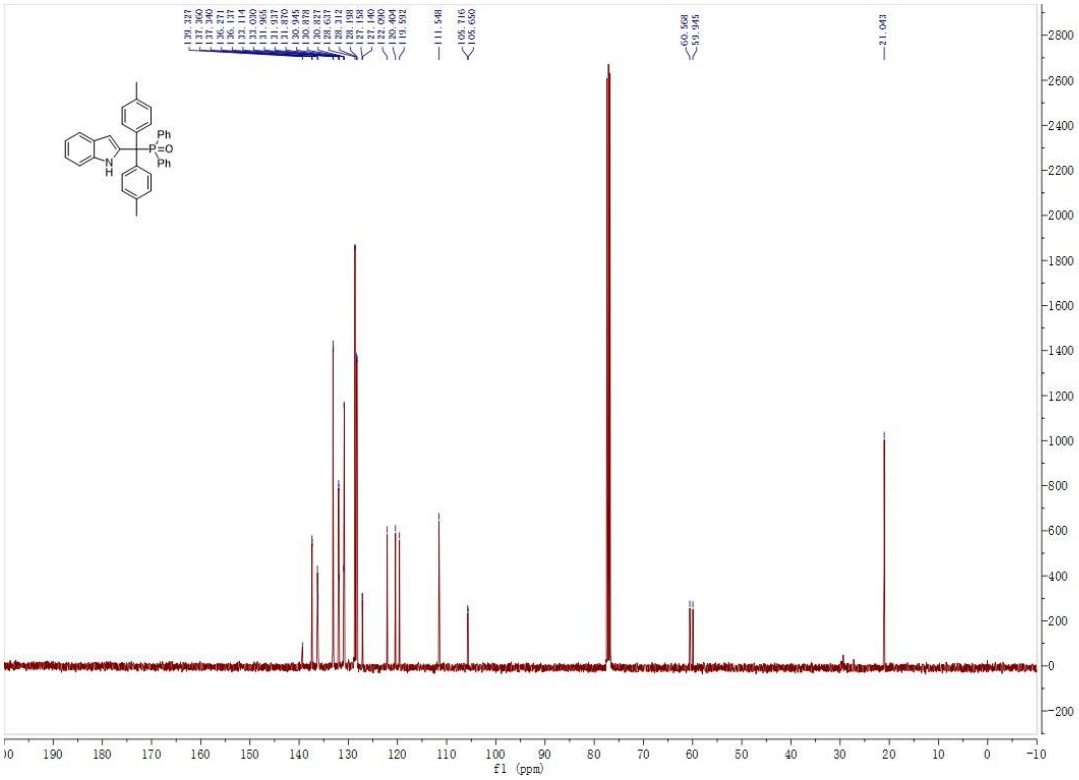
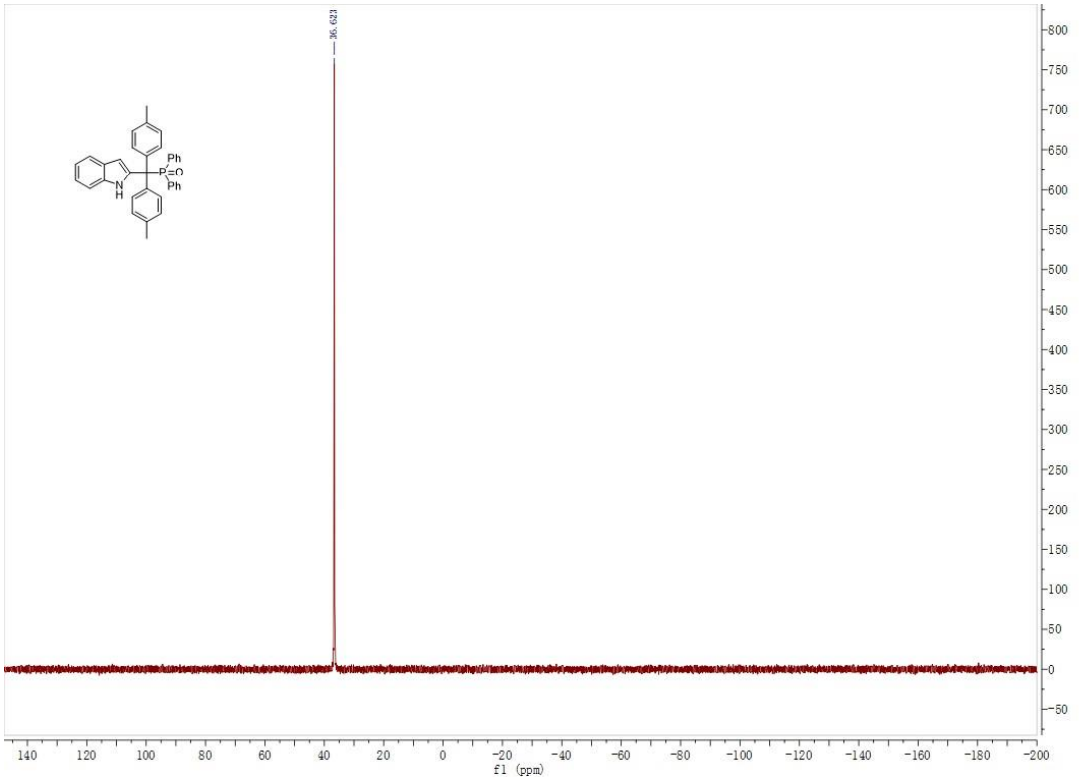
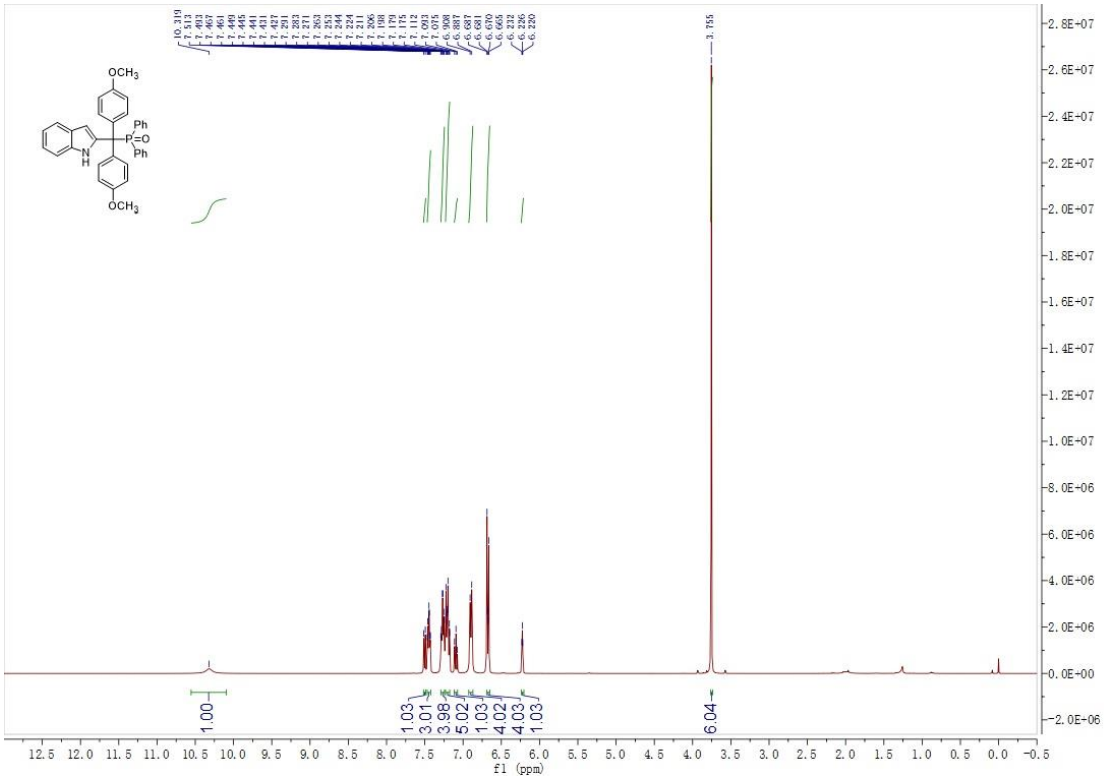
5.03
1.03
4.02
4.01
1.03
6.00
fl (ppm)





3ca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Ph
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Ph
OCH3
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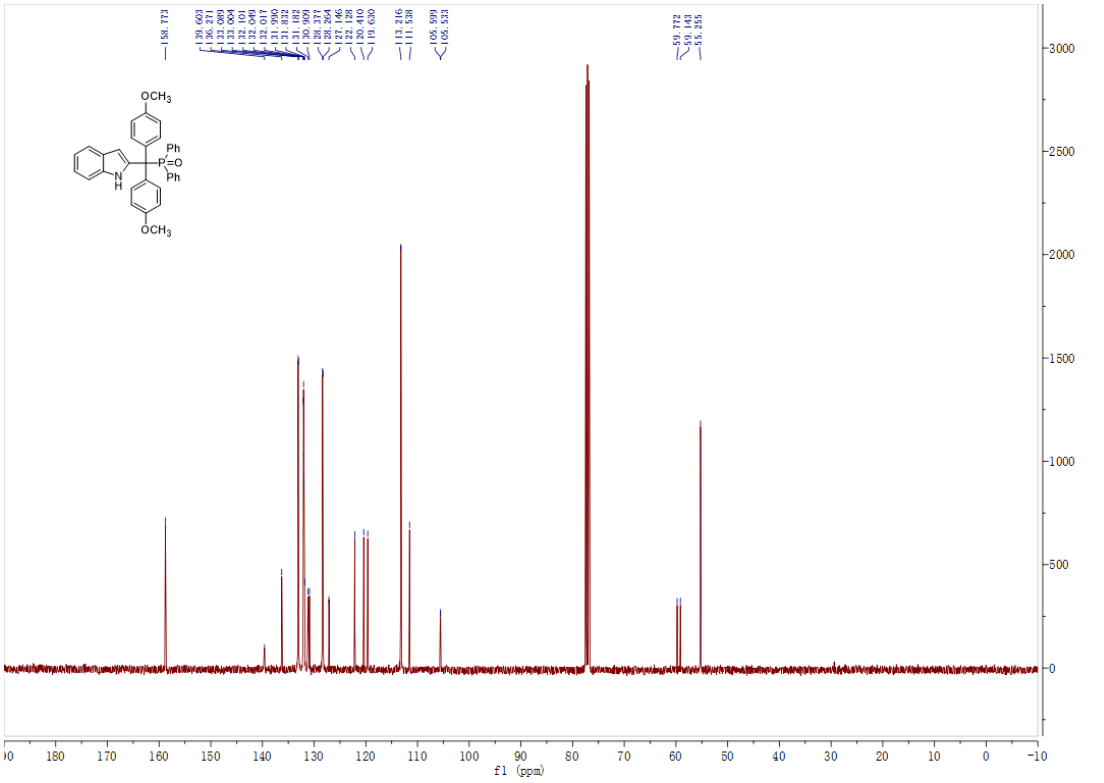
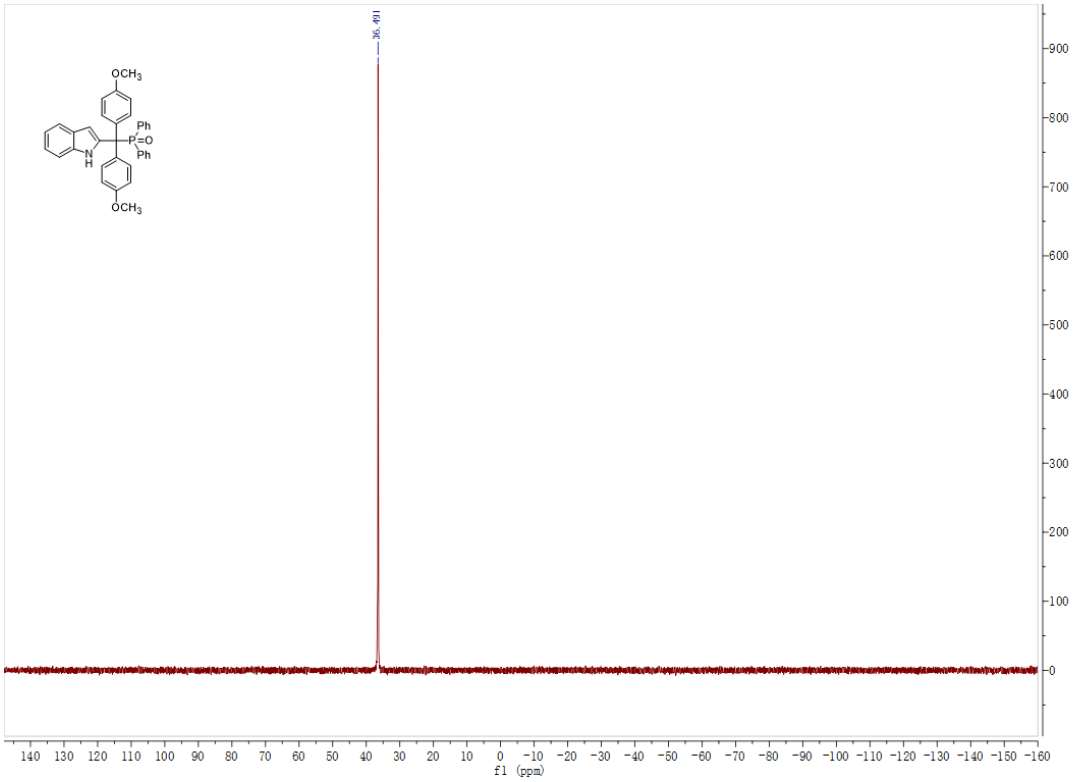
5.02
1.03
4.02
4.03
1.03
6.04
f1 (ppm)


OCH3
Ph
P=O
Ph
OCH3
f1 (ppm)


OCH3
Ph
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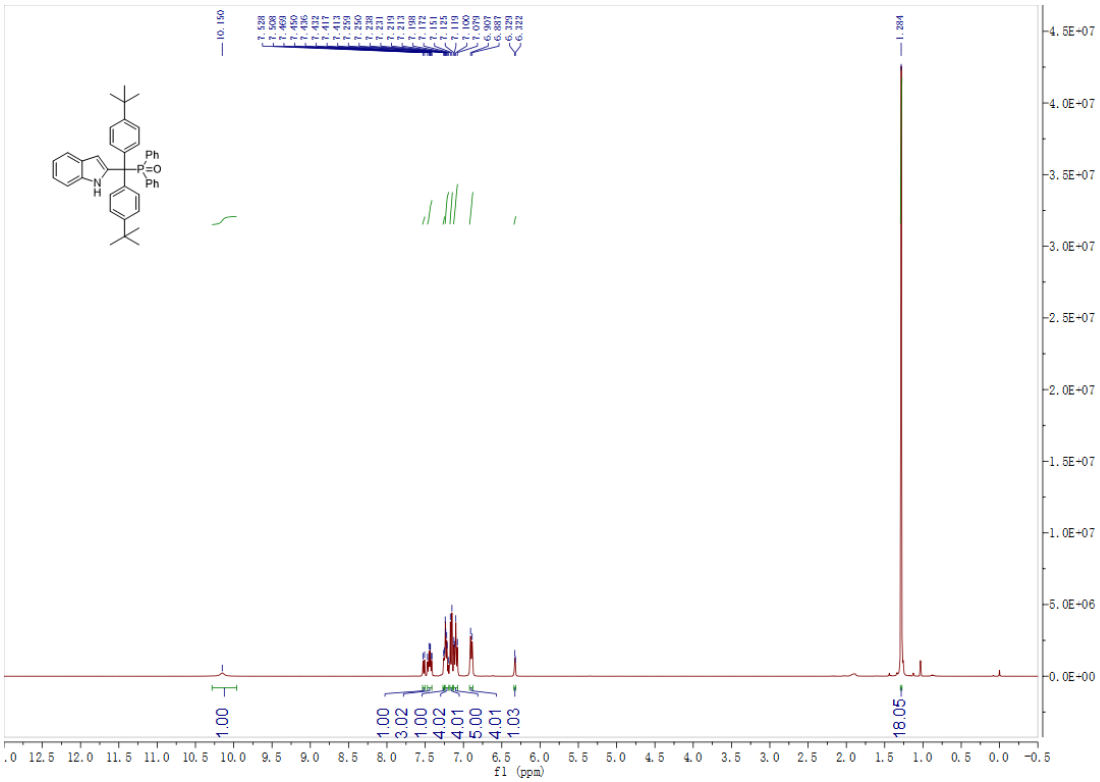
Ph
N
H
OCH3
36.491
f1 (ppm)

3da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P=O
Ph
N
H
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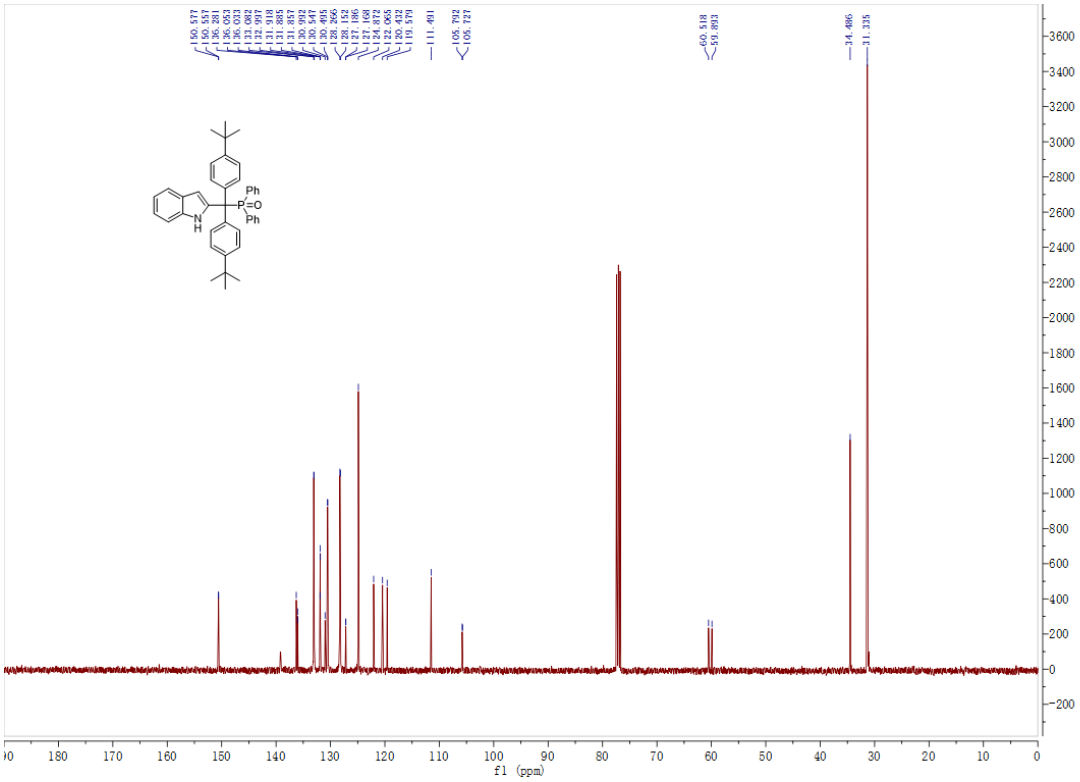
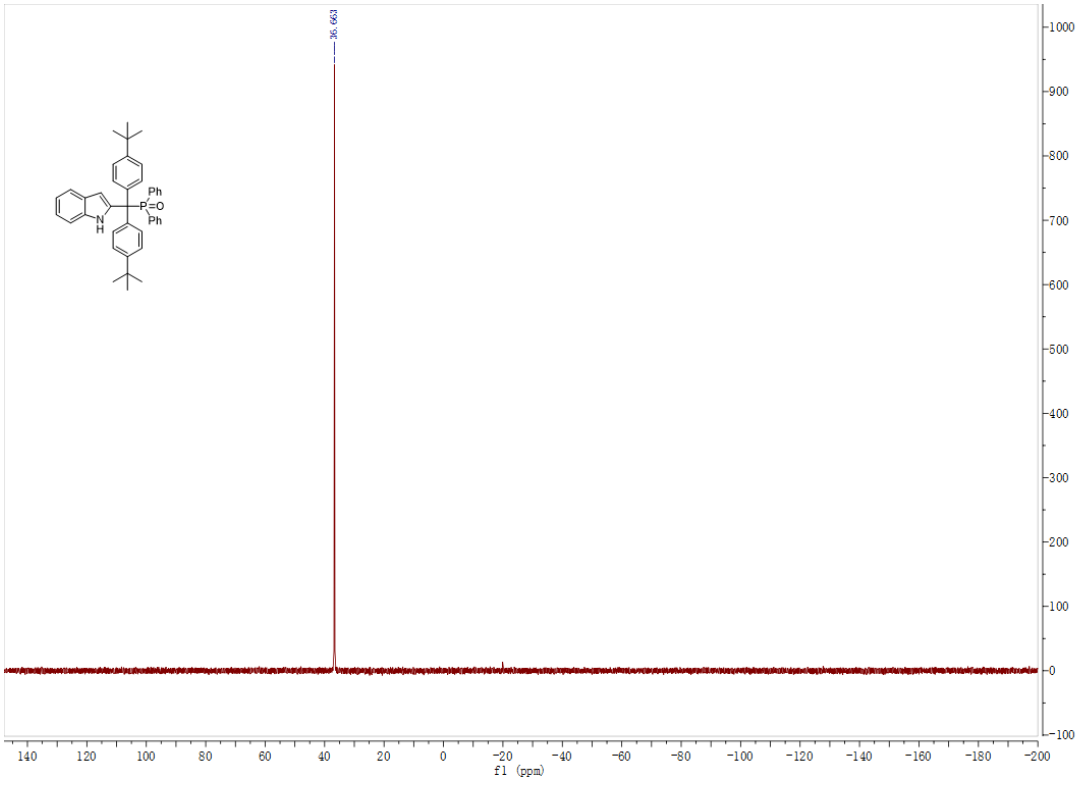
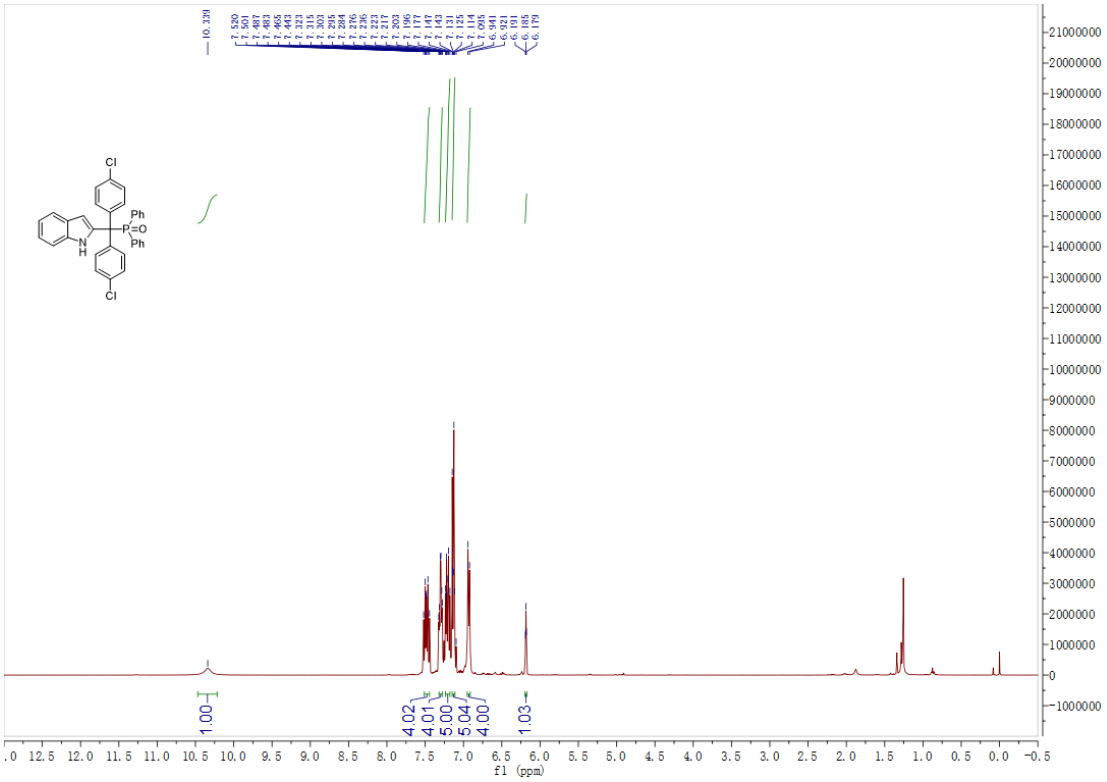
1.00
3.02
1.00
4.02
4.01
5.00
4.01
1.03
18.05
f1 (ppm)





3ea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Ph
P=O
Ph
N
H
Cl
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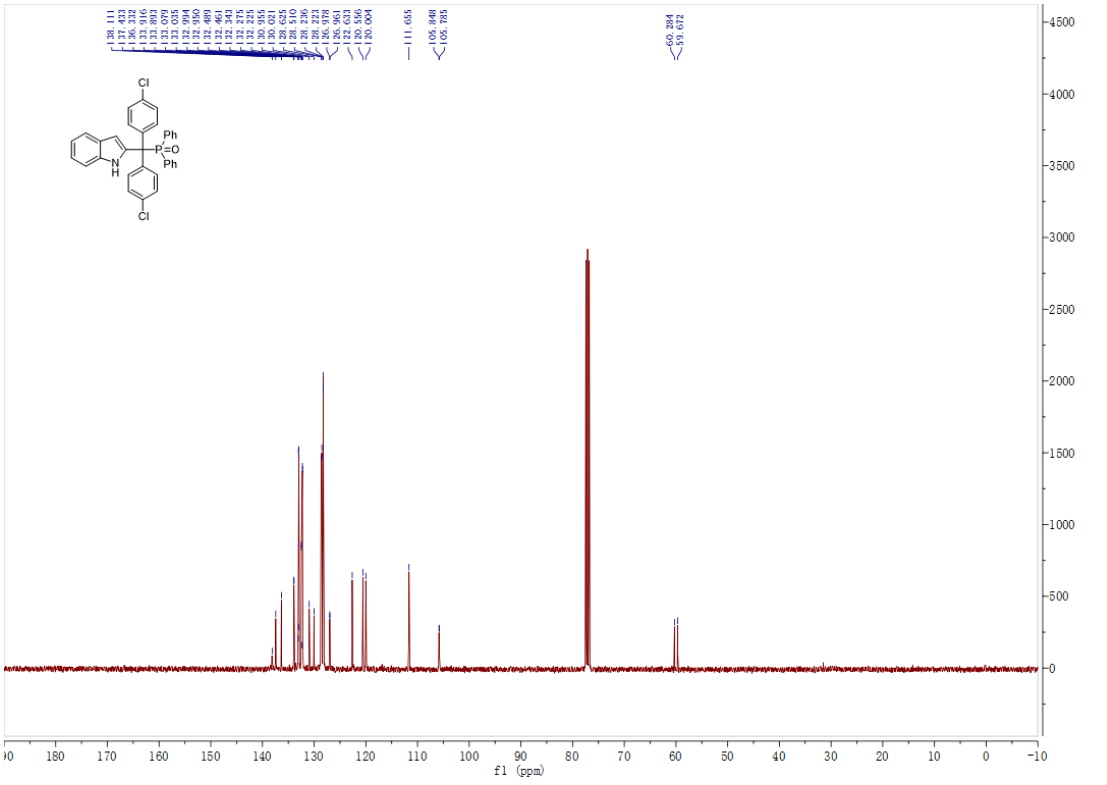
4.01
5.00
5.04
4.00
1.03
f1 (ppm)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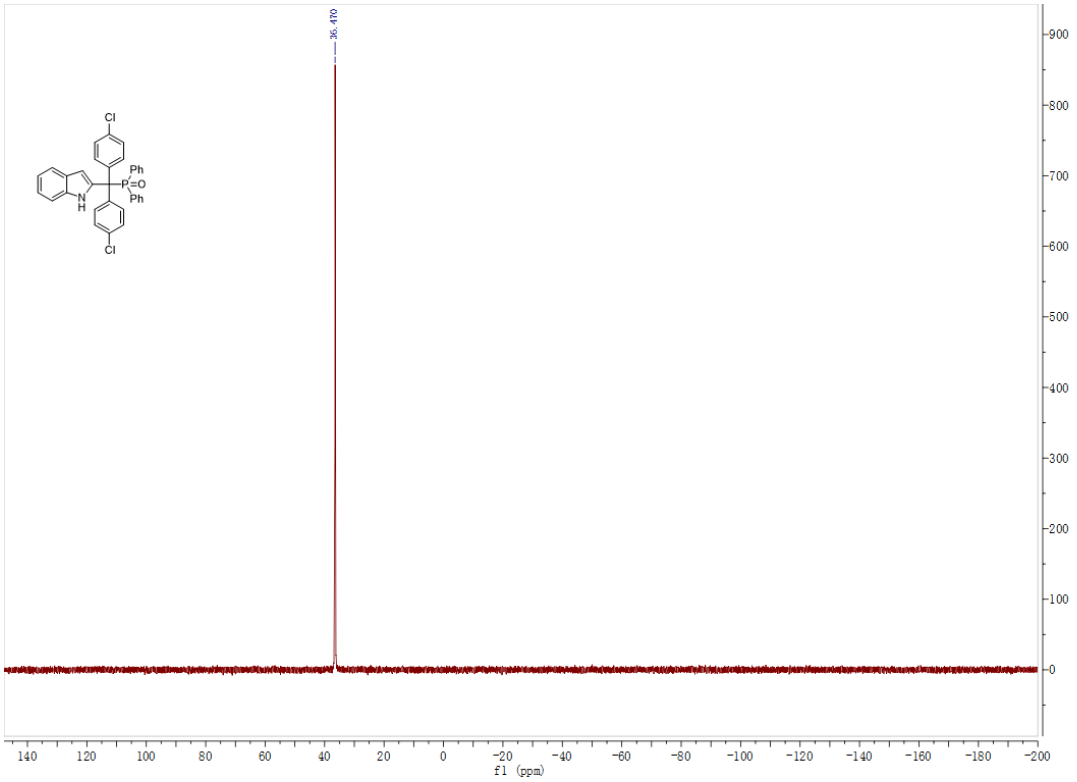
Ph
P=O
Ph
N
H
Cl
f1 (ppm)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Ph
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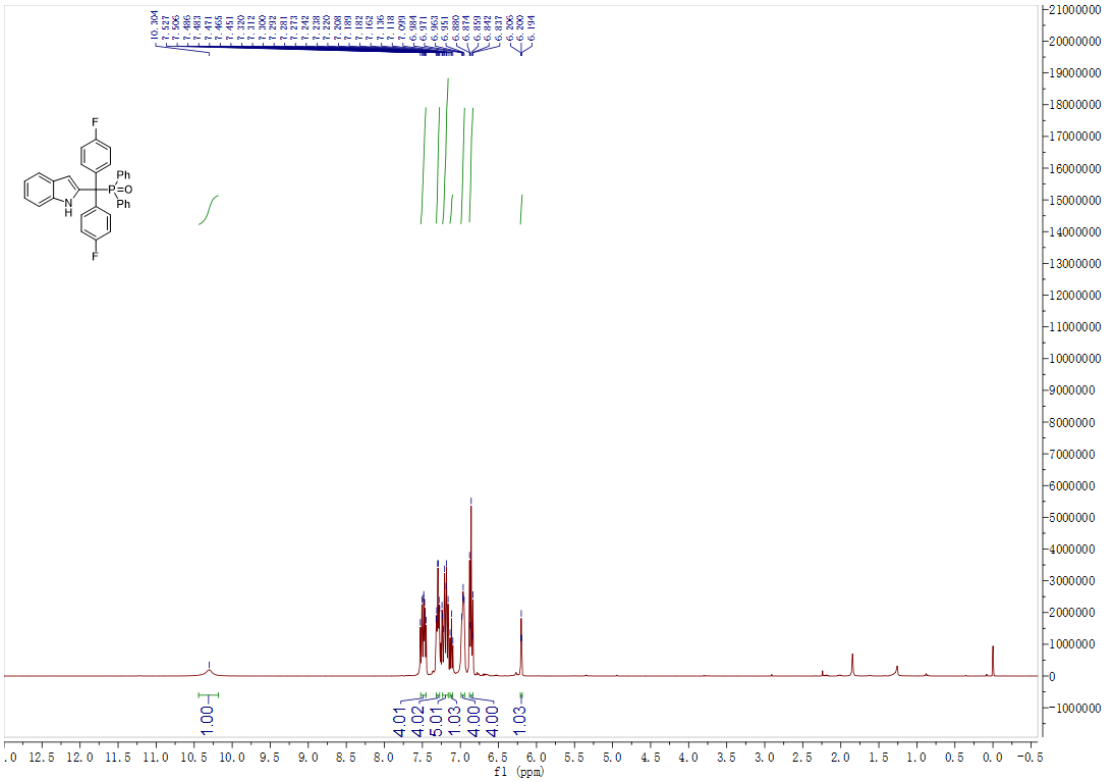
Ph
N
H
Cl
f1 (ppm)

3fa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P=O
Ph
N
H
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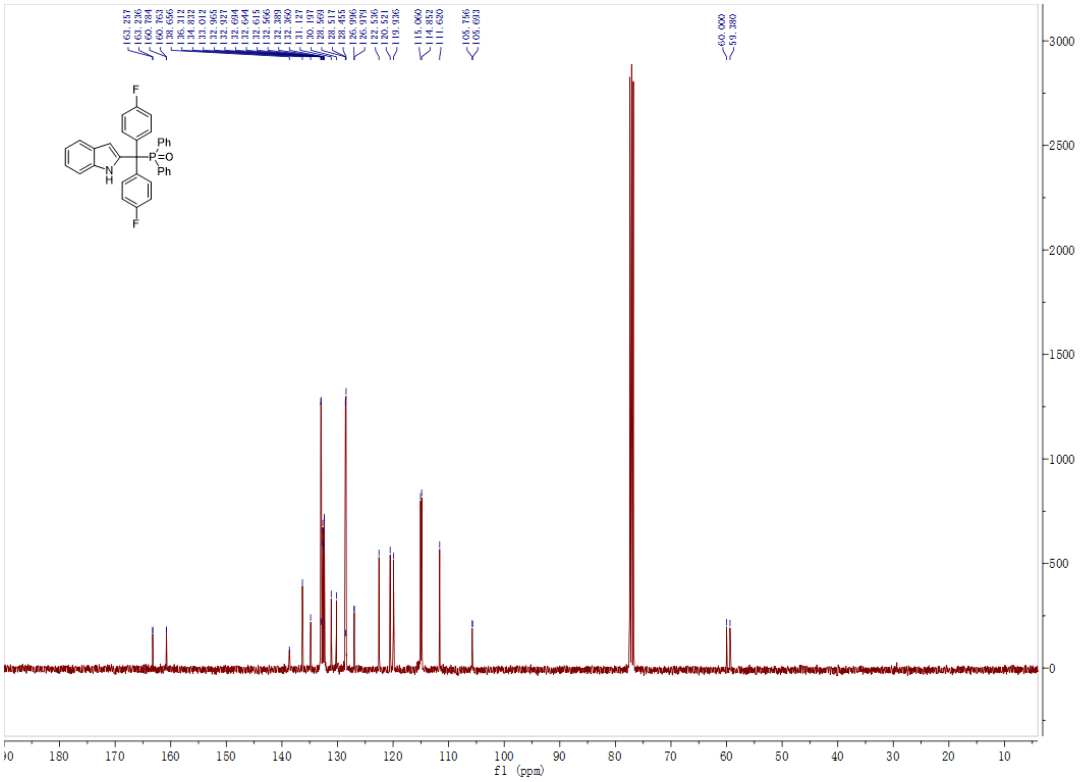
4.02
5.01
1.03
4.00
4.00
1.03
f1 (ppm)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Ph
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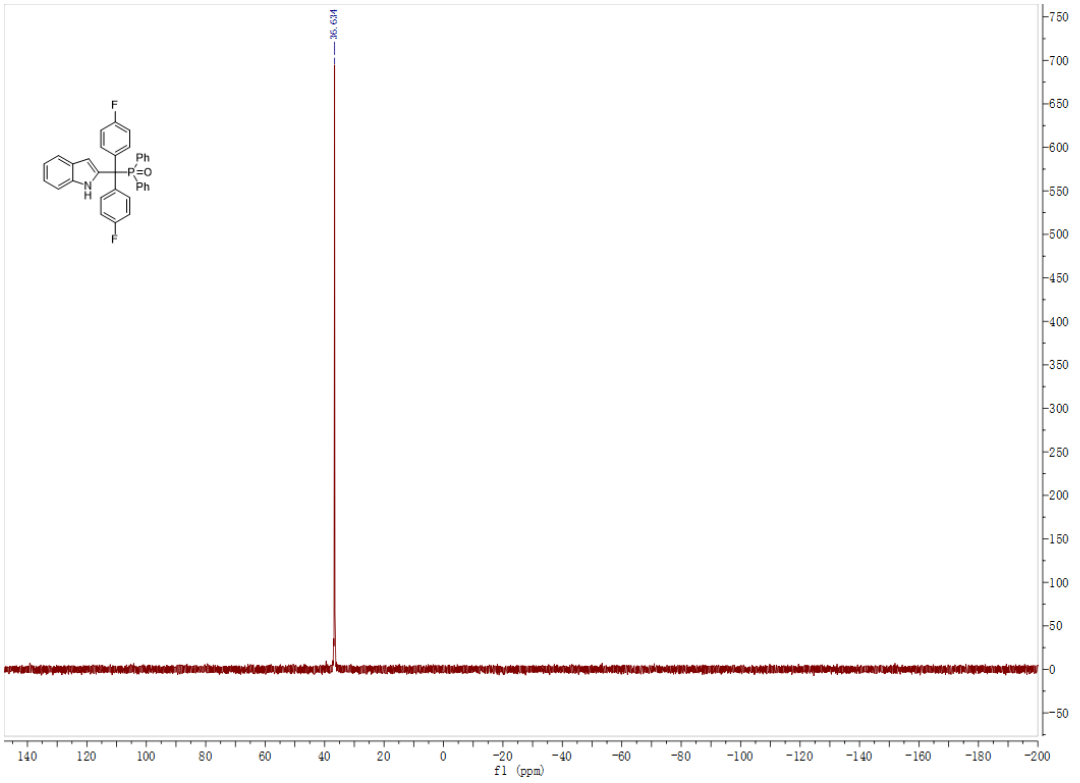
Ph
N
H
F
f1 (ppm)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Ph
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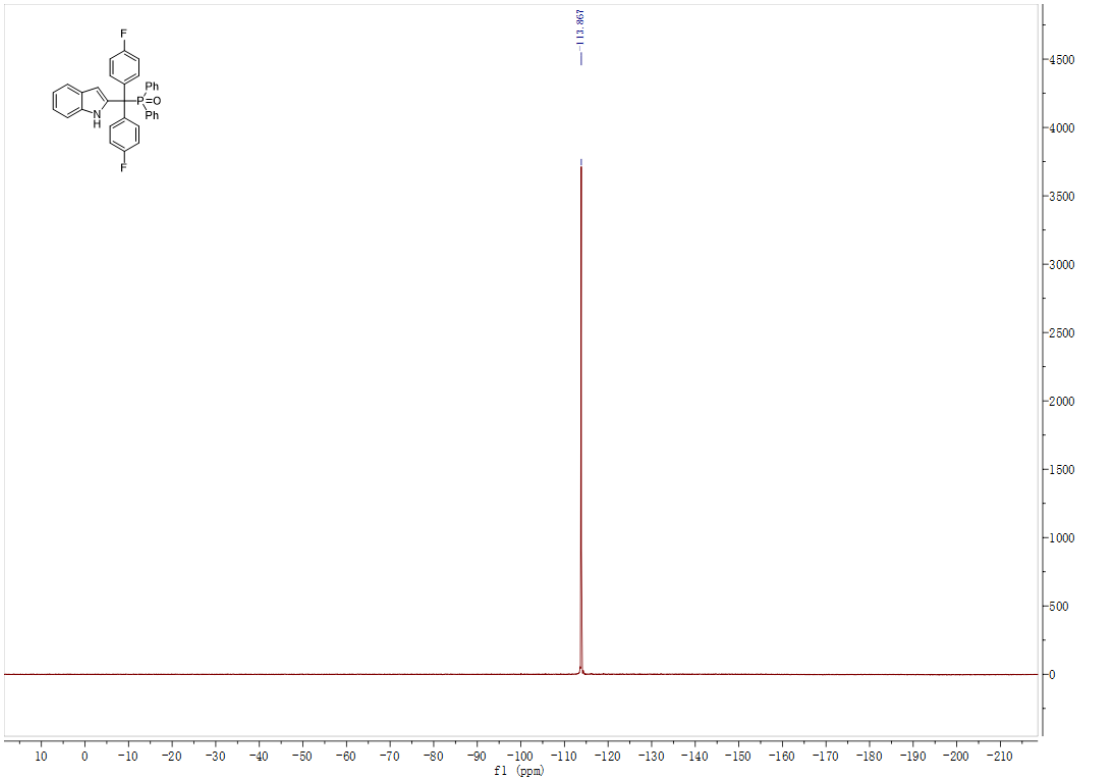
Ph
N
H
F
f1 (ppm)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H
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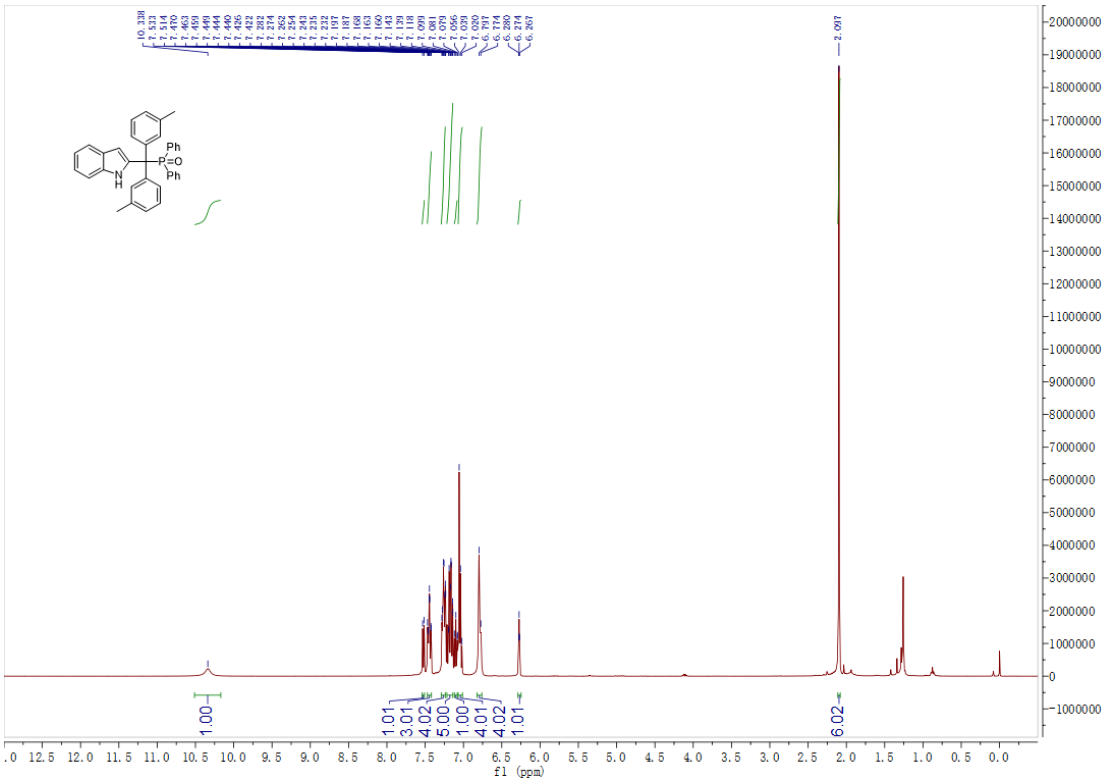
f1 (ppm)

3ha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7.422
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7.274
7.263
7.254
7.243
7.235
7.232
7.197
7.187
7.168
7.163
7.160
7.143
7.139
7.118
7.099
7.081
7.079
7.066
7.059
7.030
6.797
6.774
6.269
6.267
2.097
Ph
P=O
Ph
N
H
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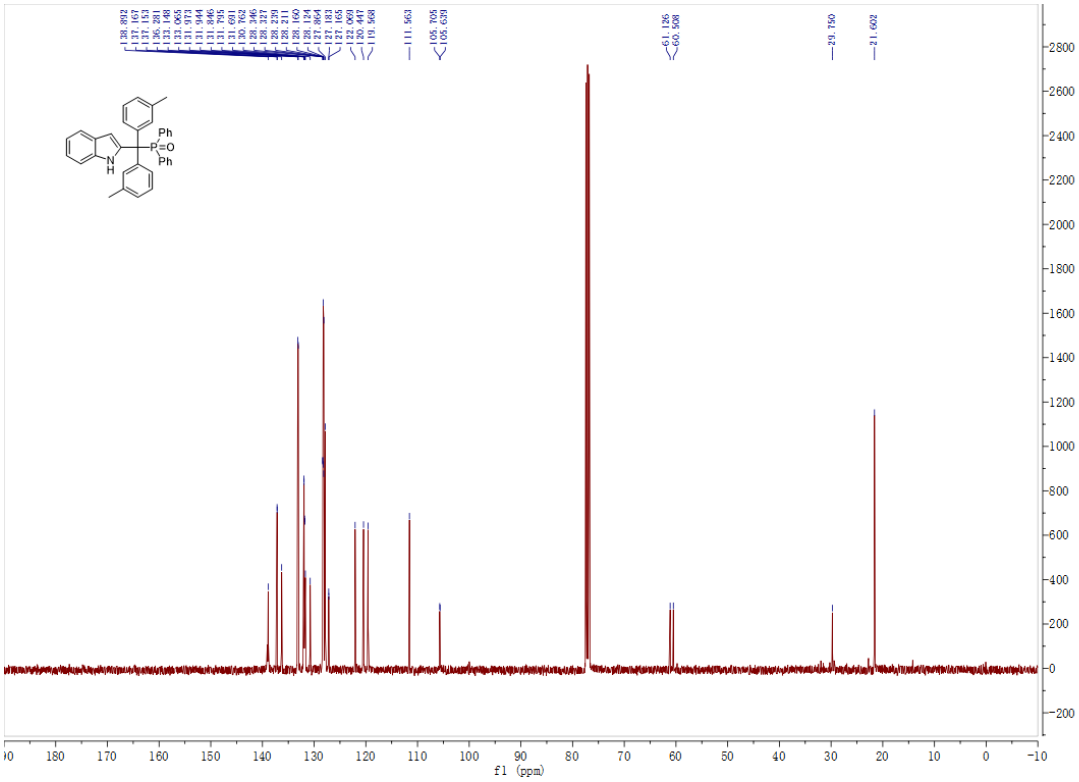
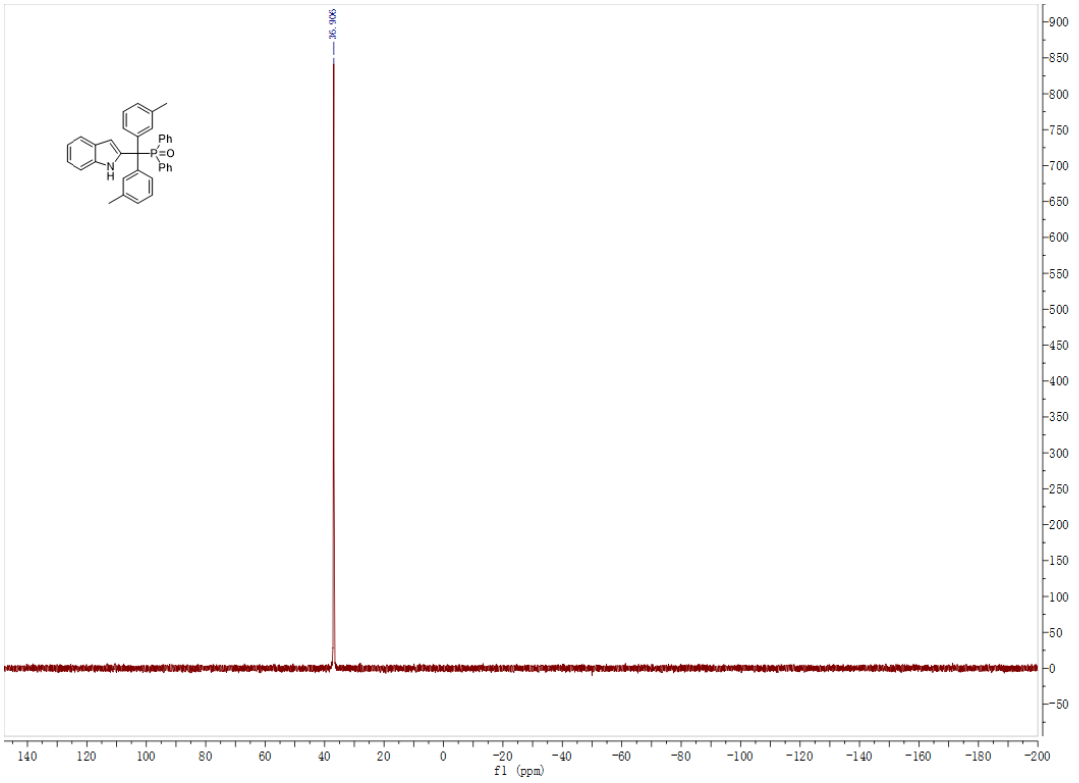
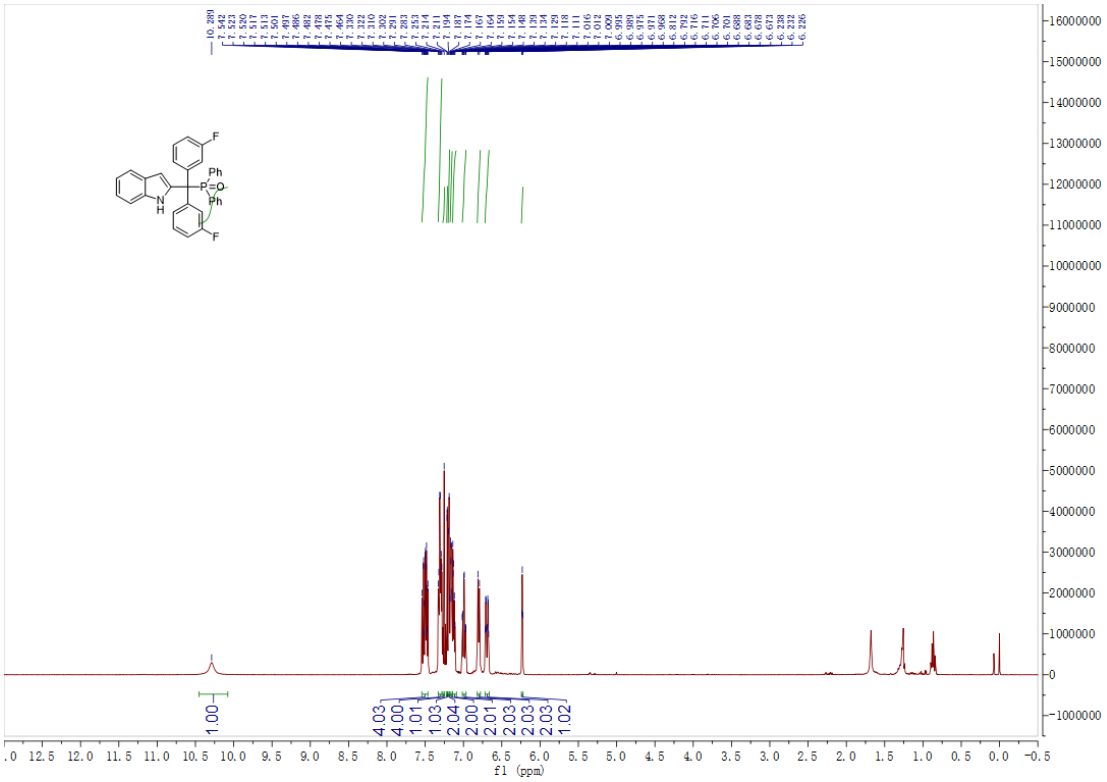
3.01
4.02
5.00
1.00
4.01
4.02
1.01
6.02
f1 (ppm)





3ia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Ph
P=O
Ph
N
H
F
1.00
4.03
4.00
1.01
1.03
2.04
2.00
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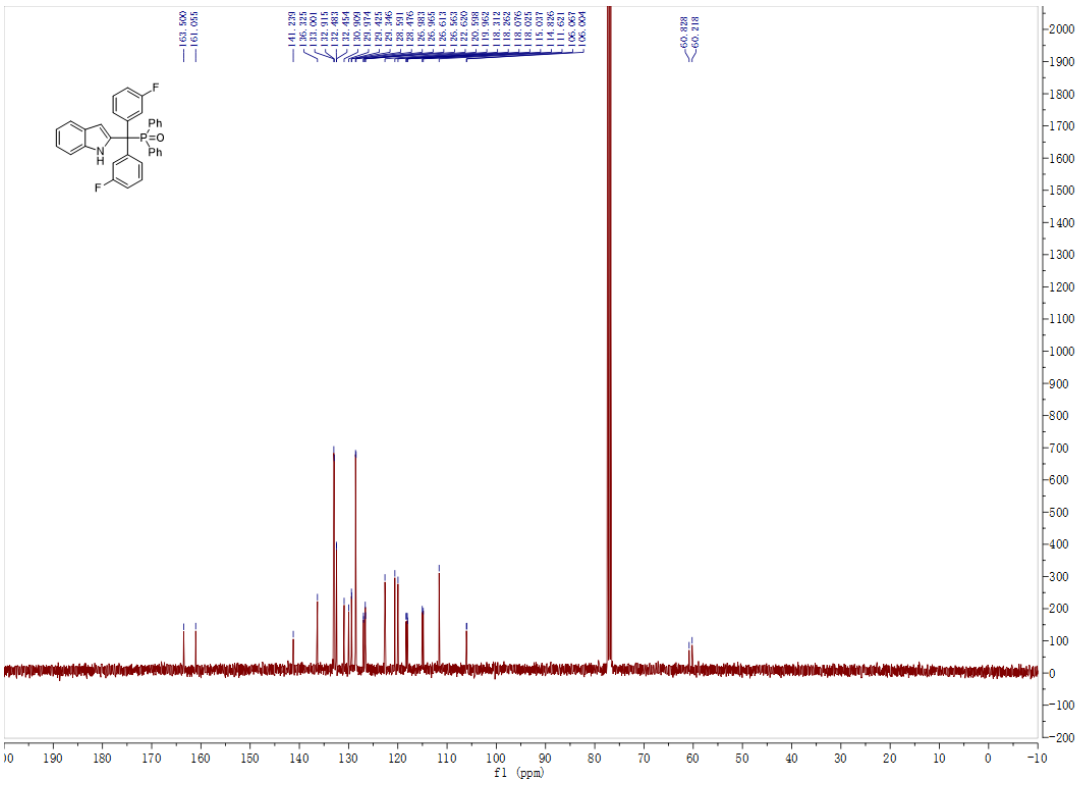
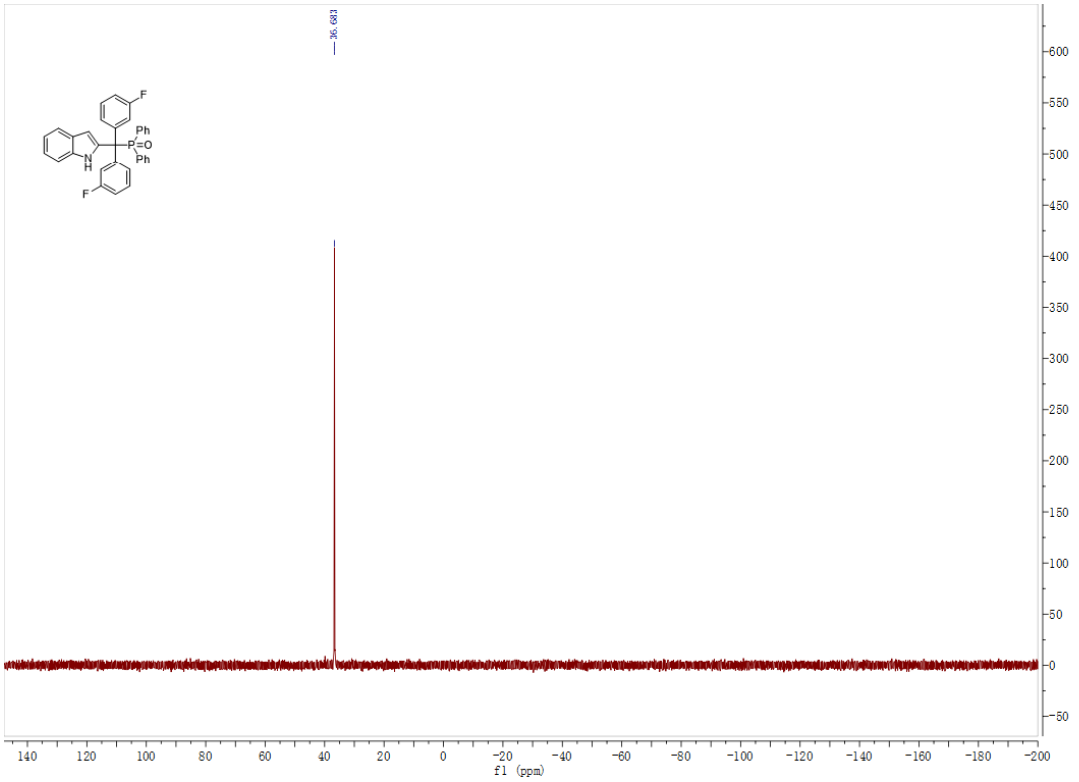
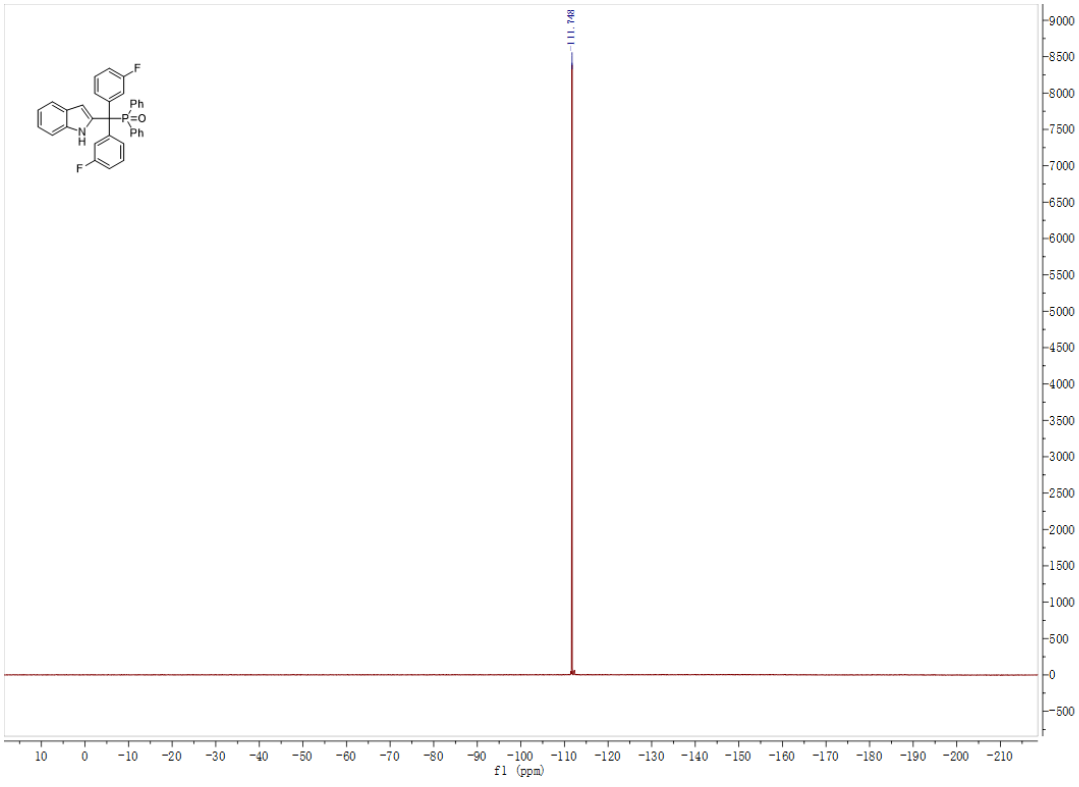
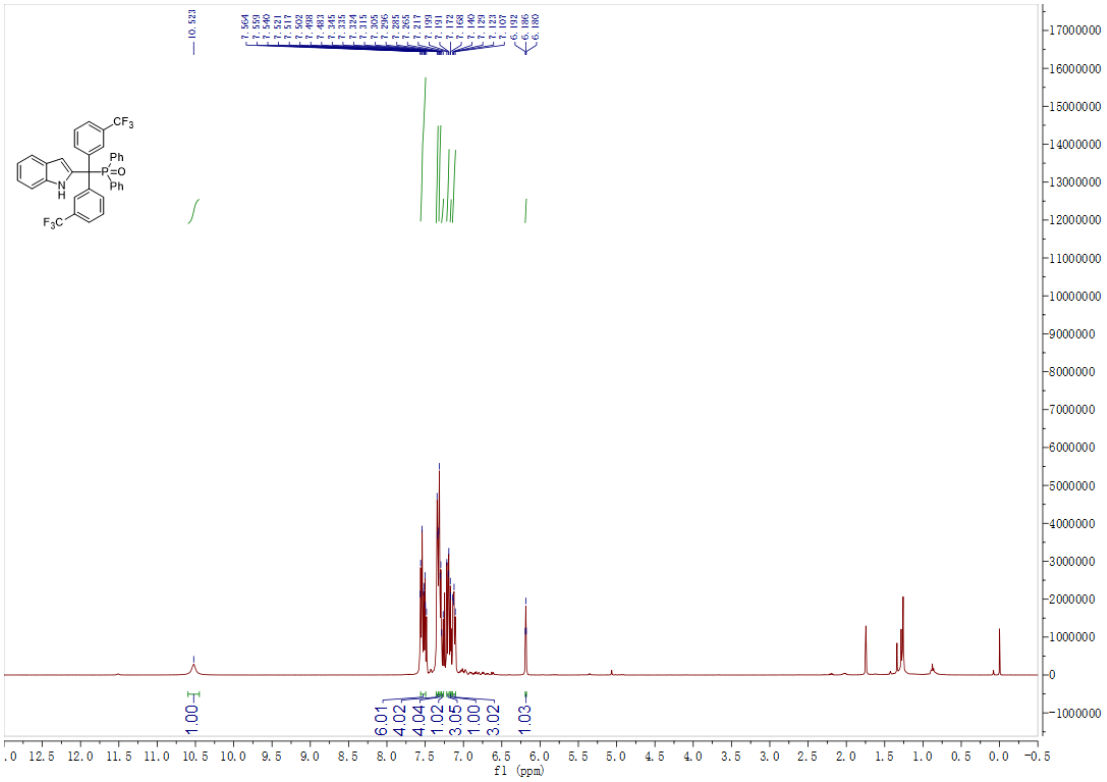
1.02
f1 (ppm)


F
Ph
P=O
Ph
N
H
F
f1 (ppm)


36.683
F
Ph
P=O
Ph
N
H
F
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)


111.748
F
Ph
P=O
Ph
N
H
F
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3ja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7.550
7.546
7.521
7.517
7.502
7.488
7.483
7.345
7.335
7.314
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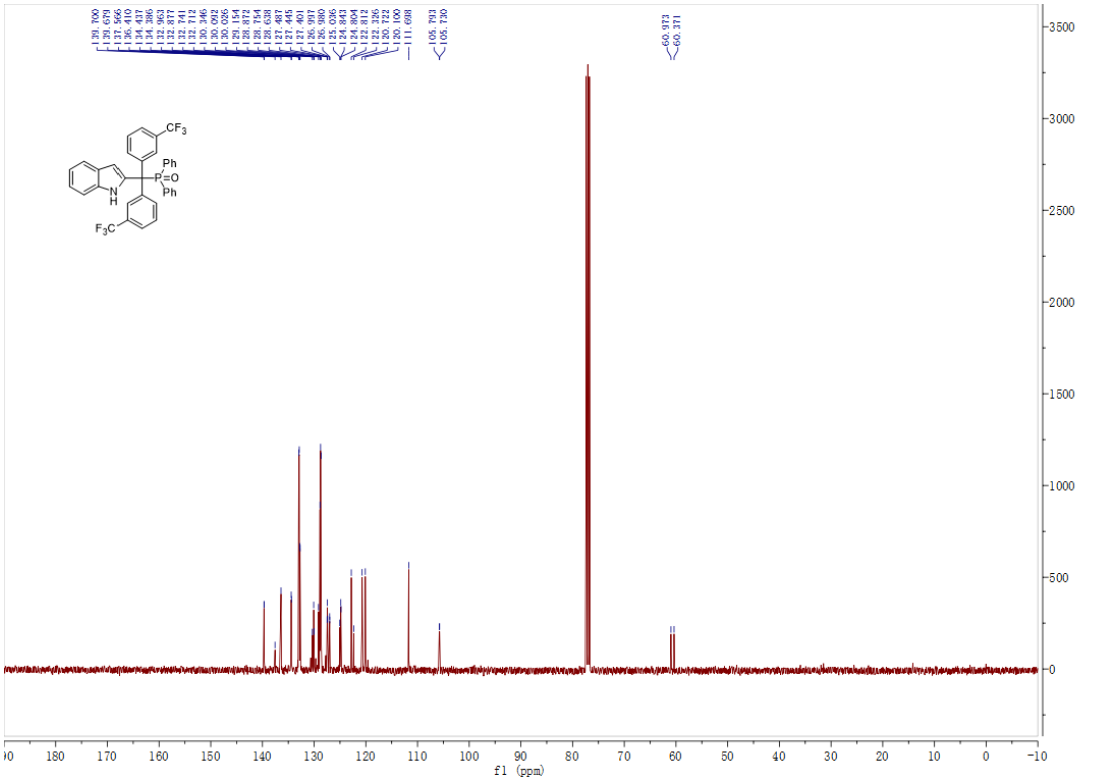
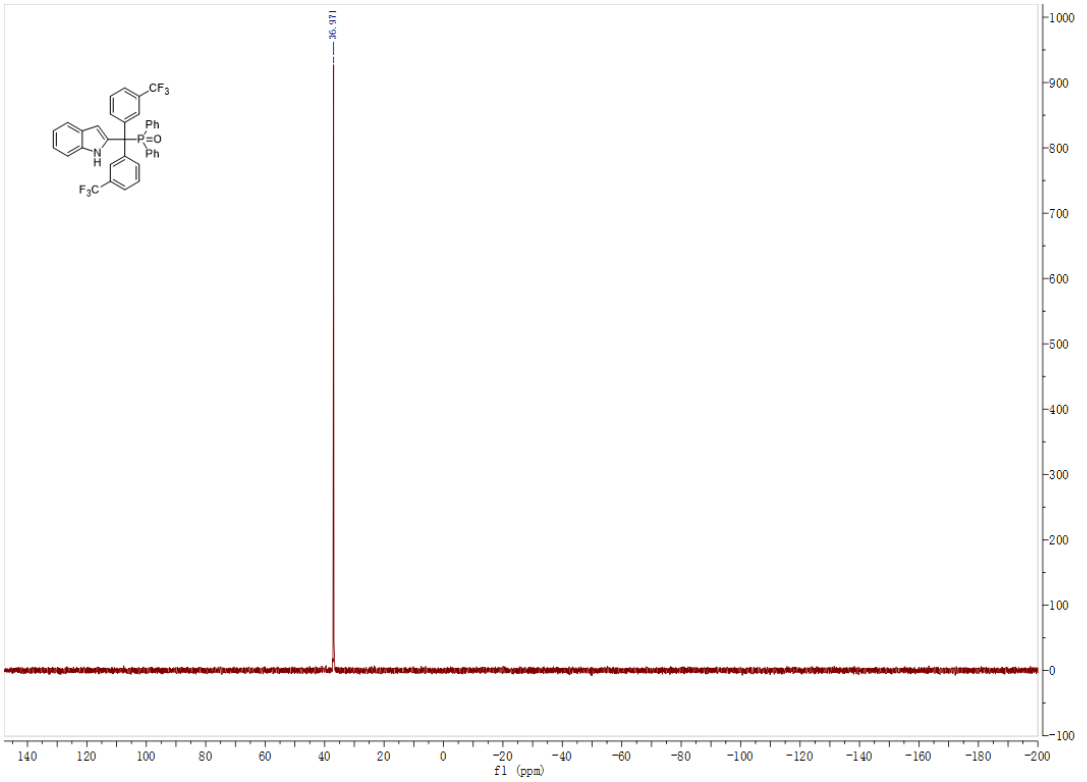
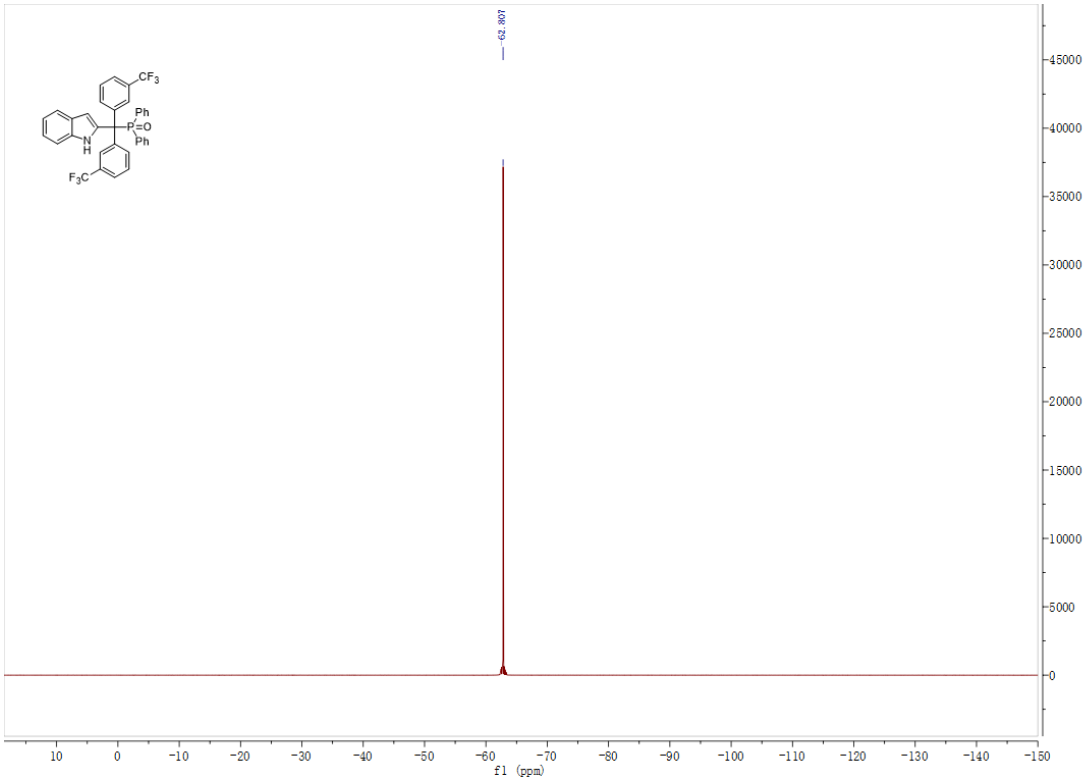
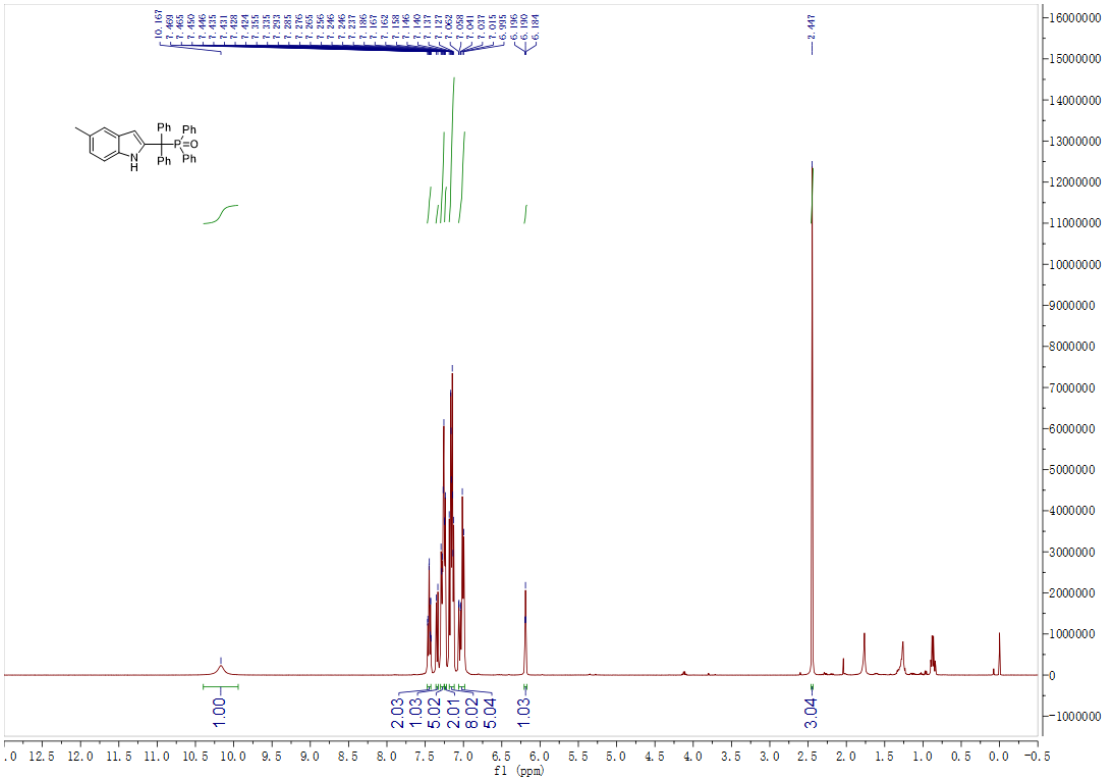
7.305
7.296
7.285
7.268
7.217
7.199
7.191
7.173
7.168
7.140
7.129
7.123
7.107
6.192
6.186
6.180
CF3
Ph
P=O
Ph
N
H
F3C
1.00
6.01
4.02
4.04
1.02
3.05
1.00
3.02
1.03
f1 (ppm)

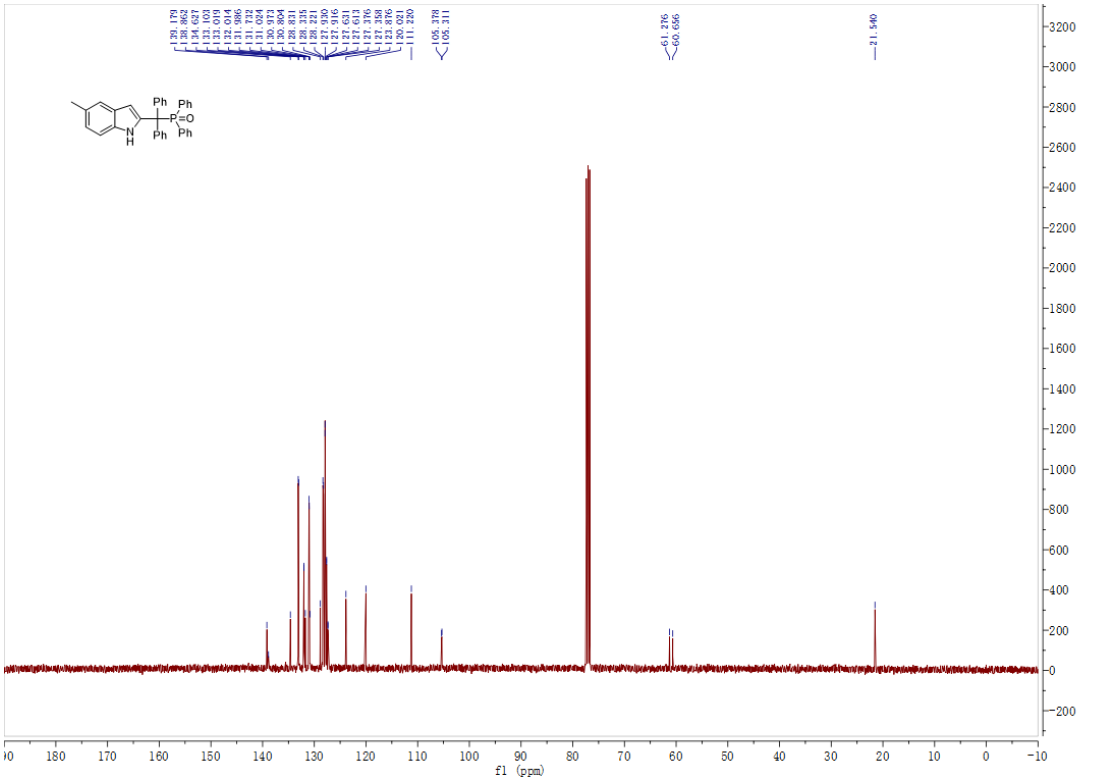

139.700
139.679
137.666
136.410
136.417
134.386
132.953
132.671
132.641
132.712
130.346
130.092
130.036
129.154
128.872
128.754
128.698
127.487
127.445
127.401
125.980
125.690
125.036
124.843
124.804
122.312
122.326
120.722
120.100
111.688
105.793
105.730
60.973
60.371
CF3
Ph
P=O
Ph
N
H
F3C
f1 (ppm)

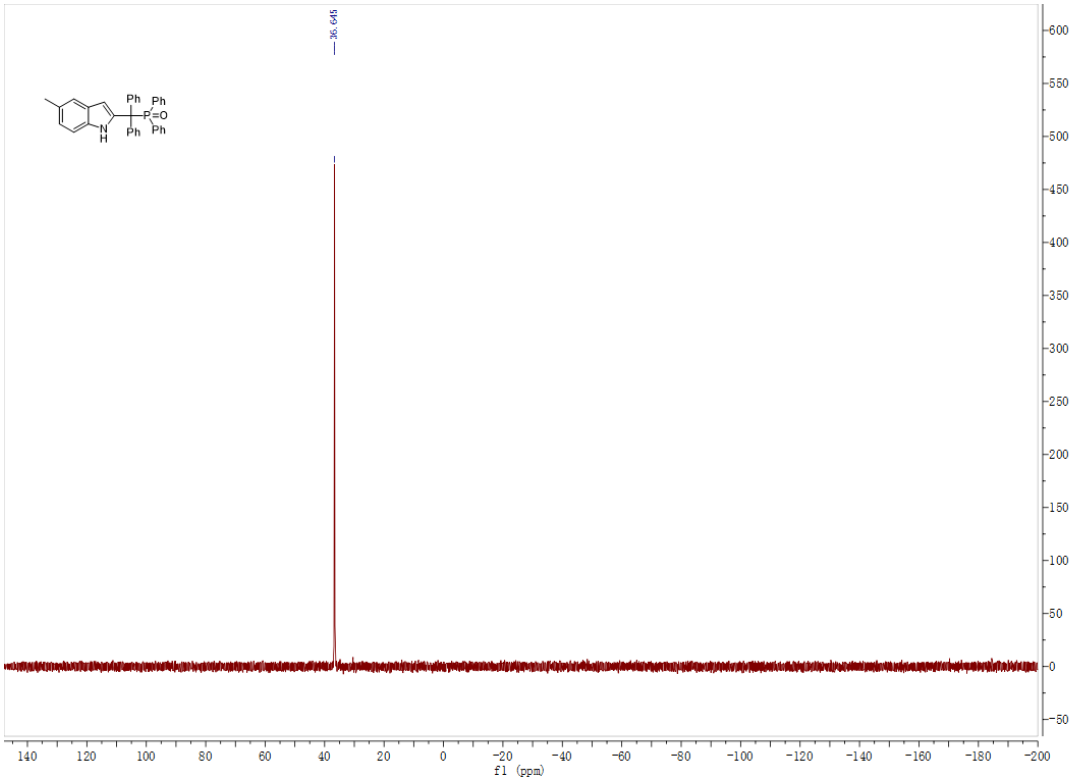




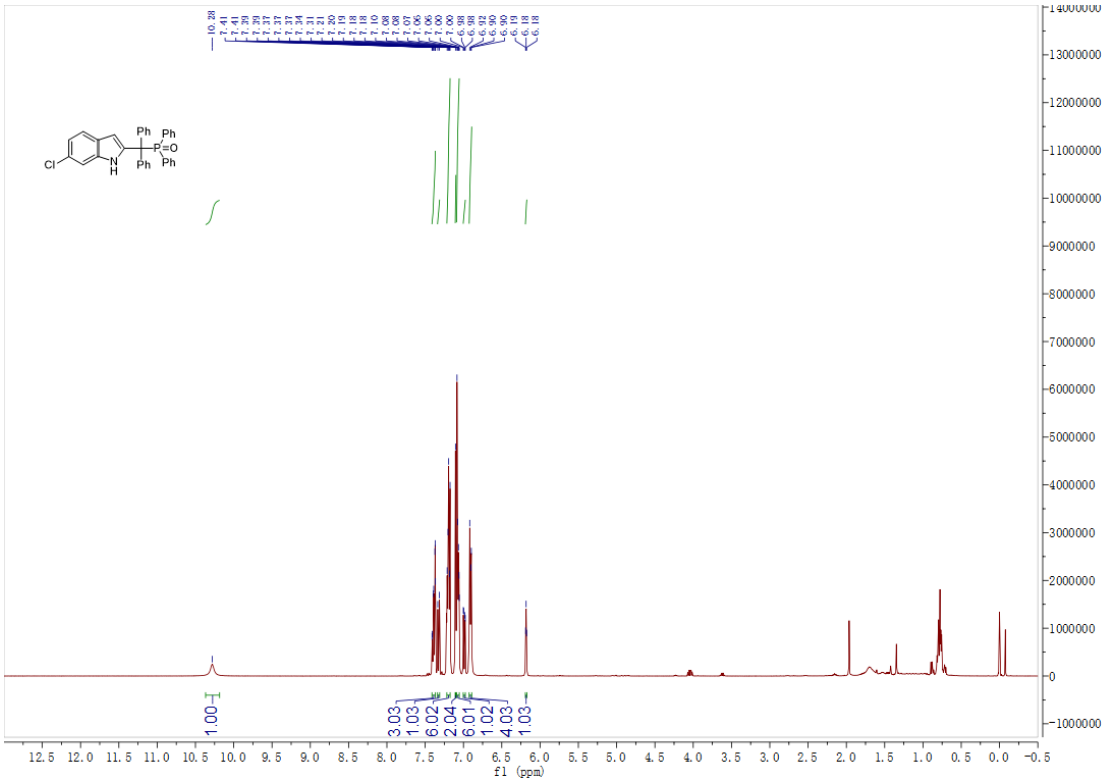
3ka

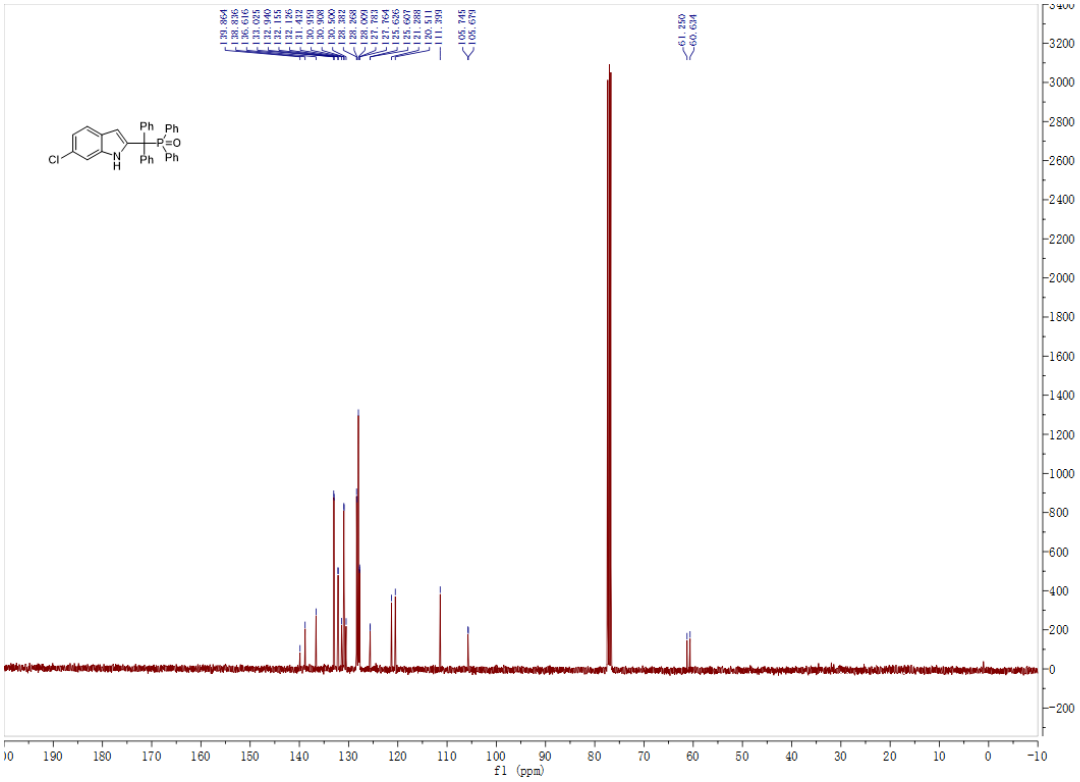

Ph
Ph
P=O
Ph
Ph
N
H
10.167
7.466
7.465
7.450
7.446
7.433
7.431
7.428
7.424
7.335
7.333
7.293
7.285
7.276
7.265
7.256
7.246
7.237
7.196
7.167
7.162
7.138
7.146
7.140
7.137
7.127
7.058
7.041
7.037
7.015
6.995
6.196
6.190
6.184
2.447
1.00
2.03
1.03
5.02
2.01
8.02
5.04
1.03
3.04
f1 (ppm)

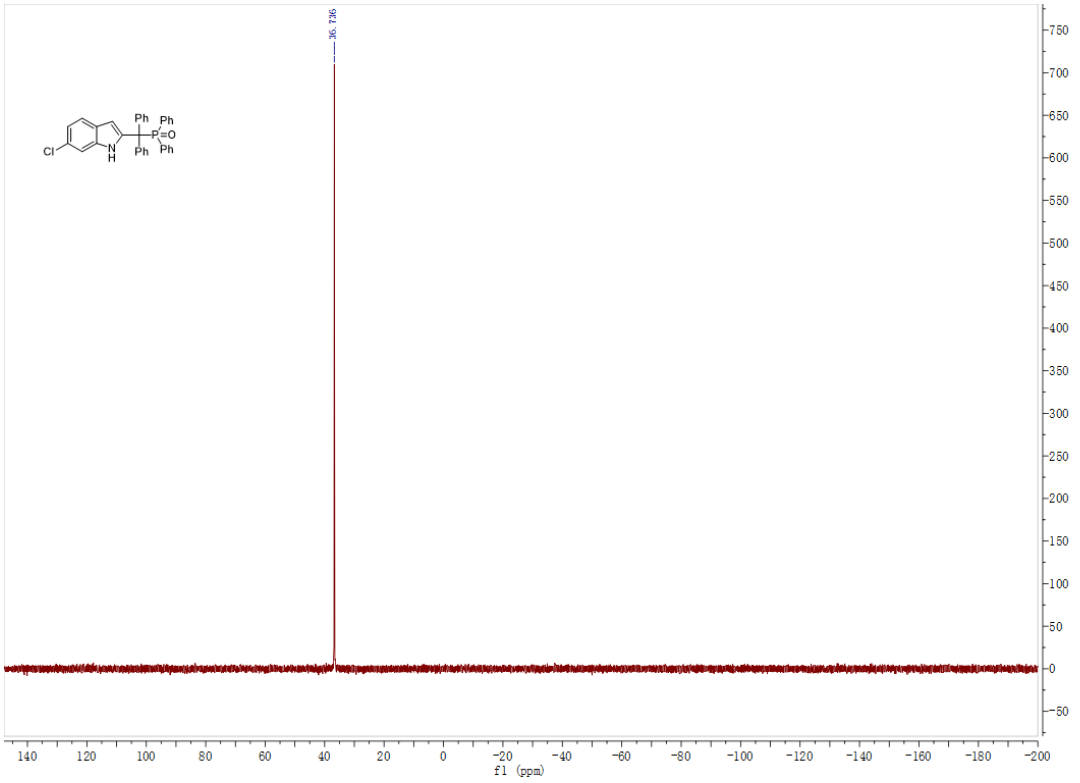

Ph
Ph
P=O
Ph
Ph
N
H
139.179
138.962
138.457
133.103
133.019
132.014
131.996
131.732
131.024
130.973
130.964
128.831
128.335
128.321
128.170
127.940
127.631
127.613
127.376
127.358
123.876
120.021
111.220
105.378
105.311
61.276
60.666
21.540
f1 (ppm)



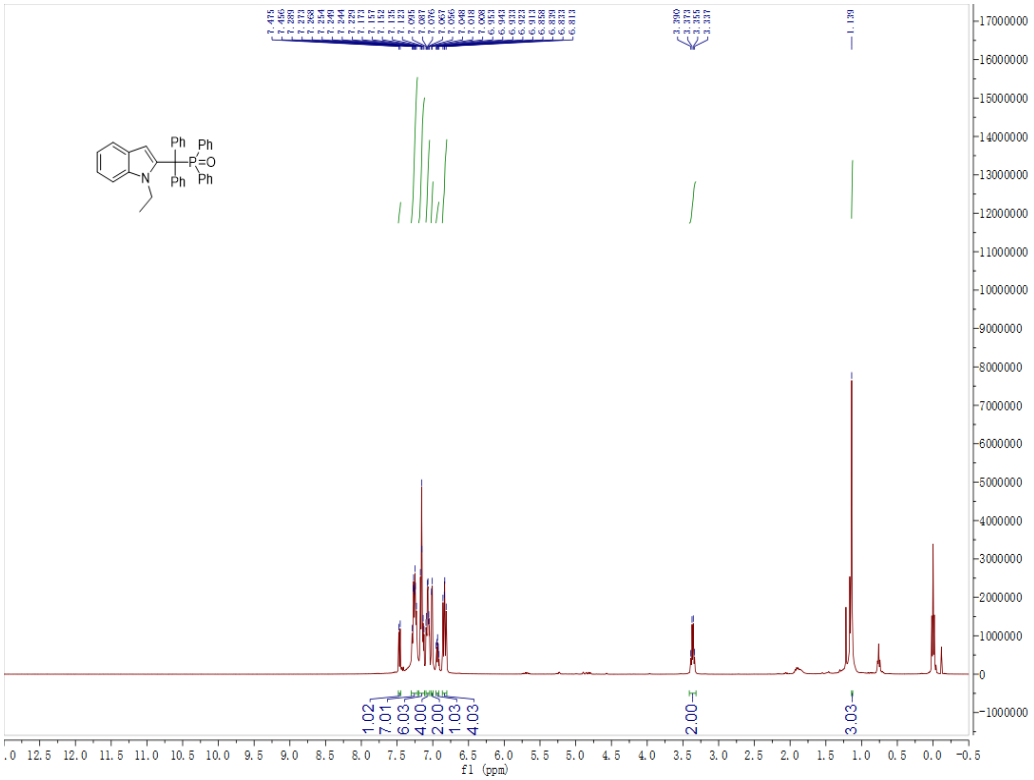
3la

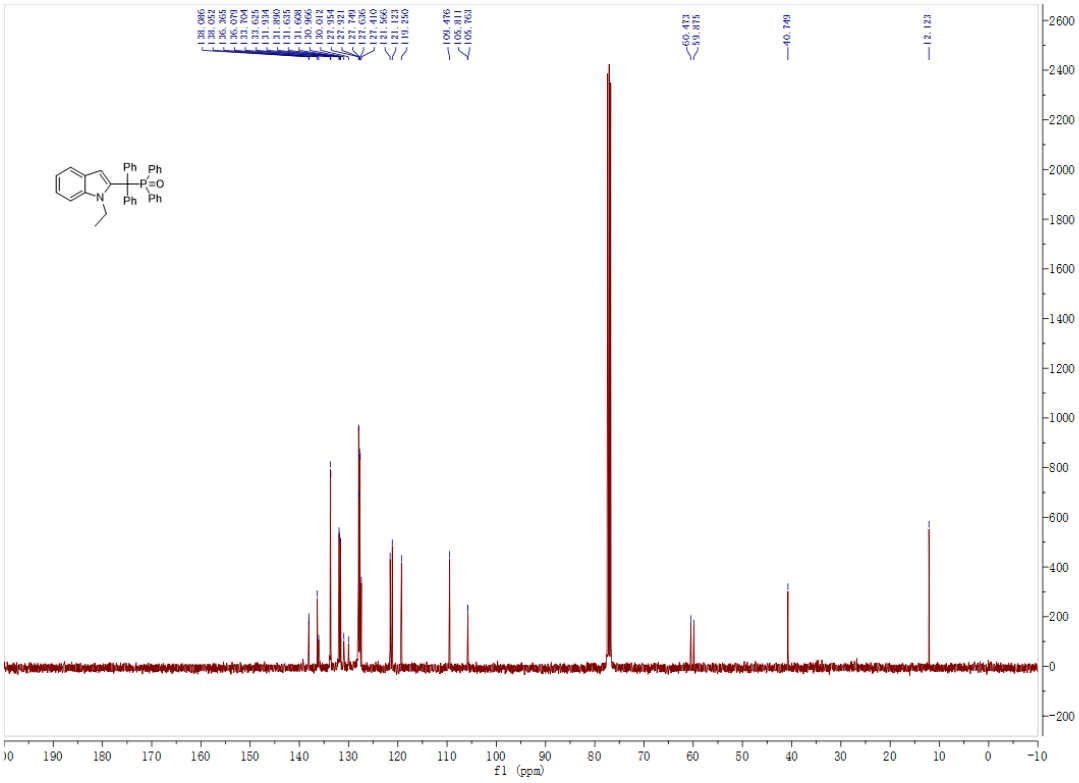


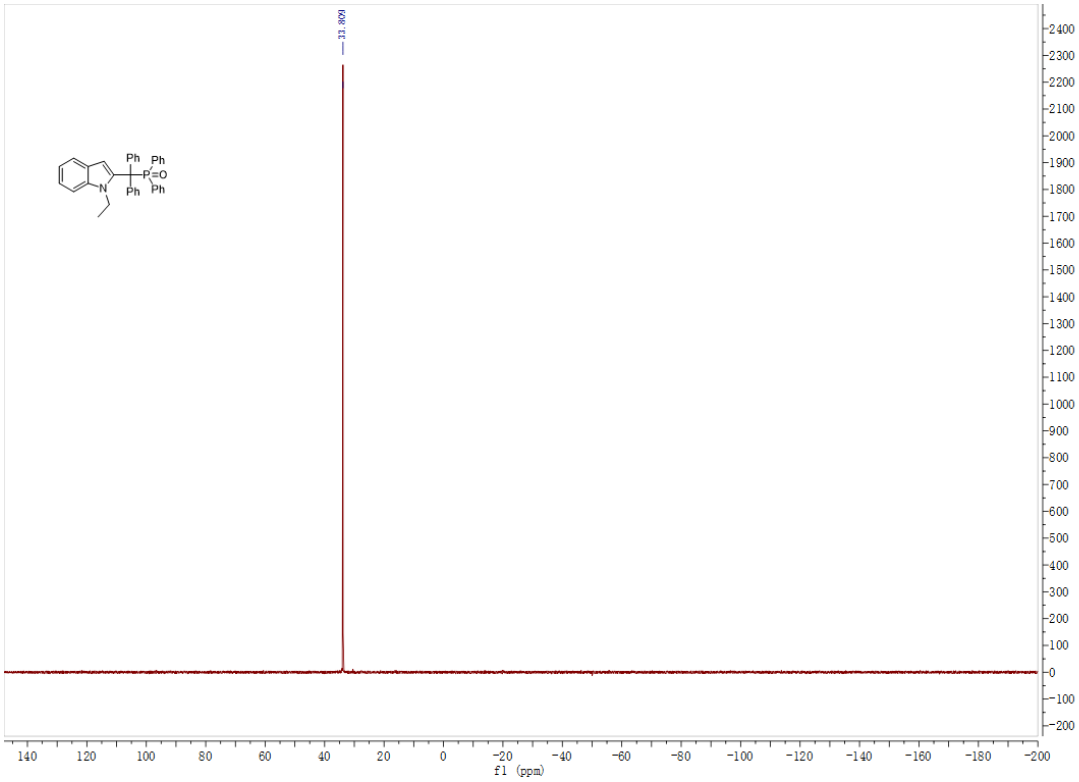




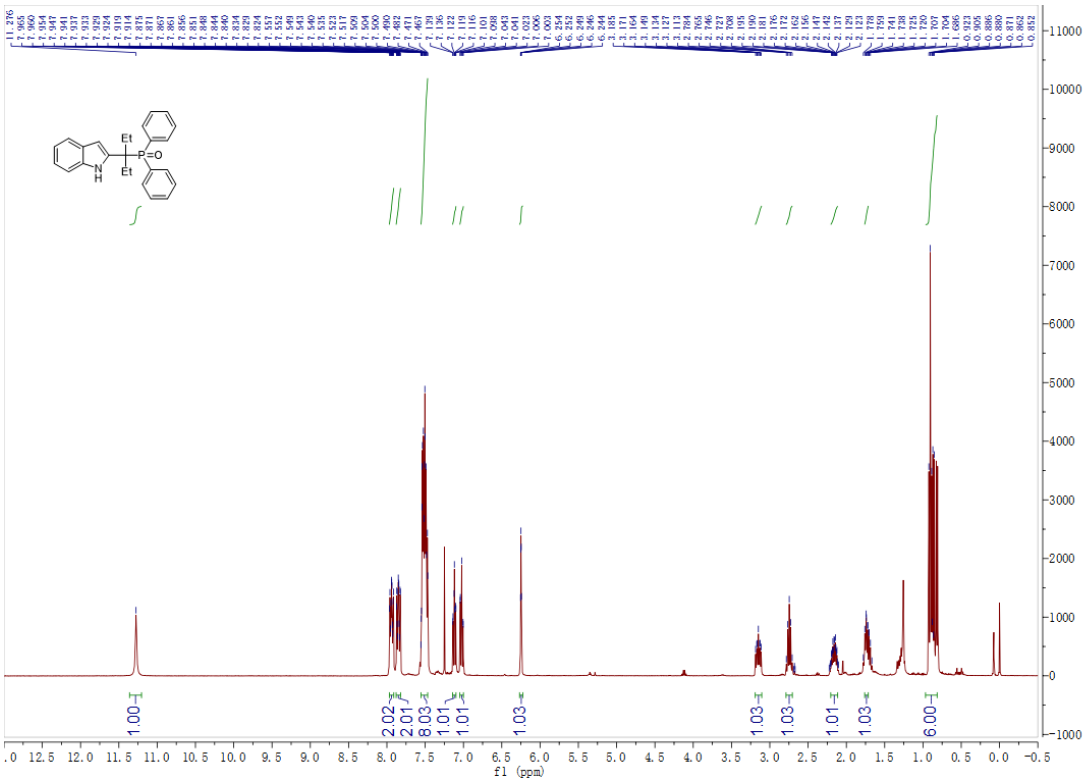
3ma

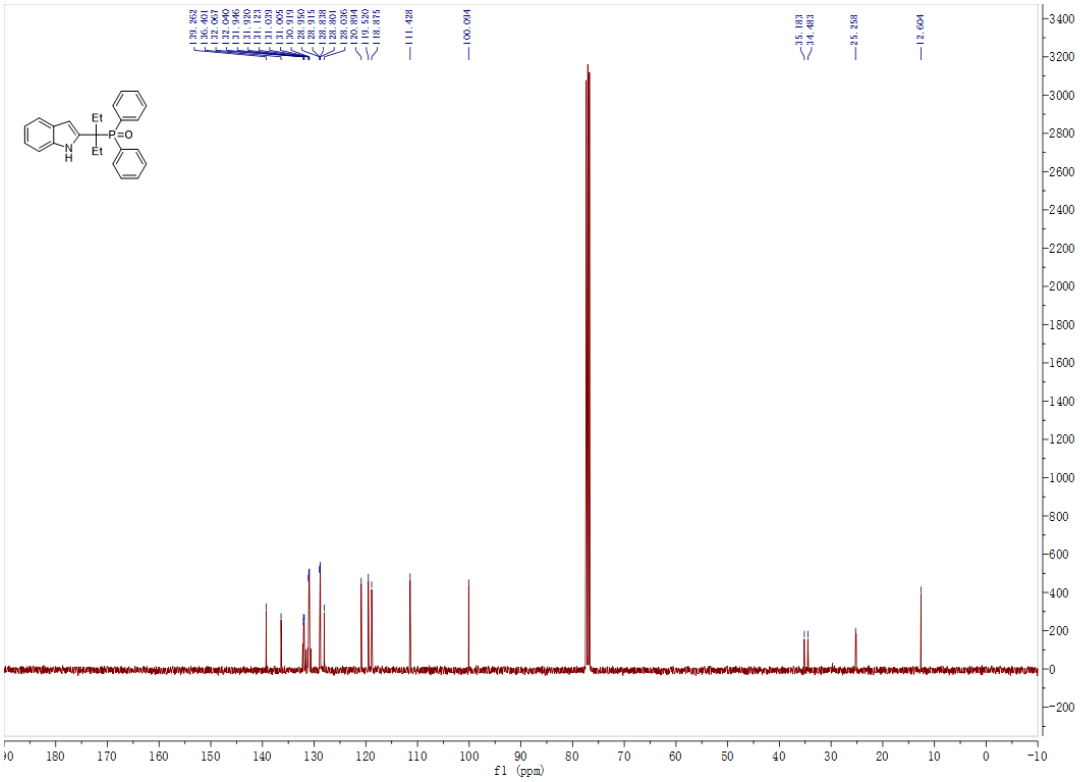

Ph
Ph
P=O
Ph
Ph
N
1.02
7.01
6.03
4.00
2.00
1.03
4.03
2.00
3.03
f1 (ppm)

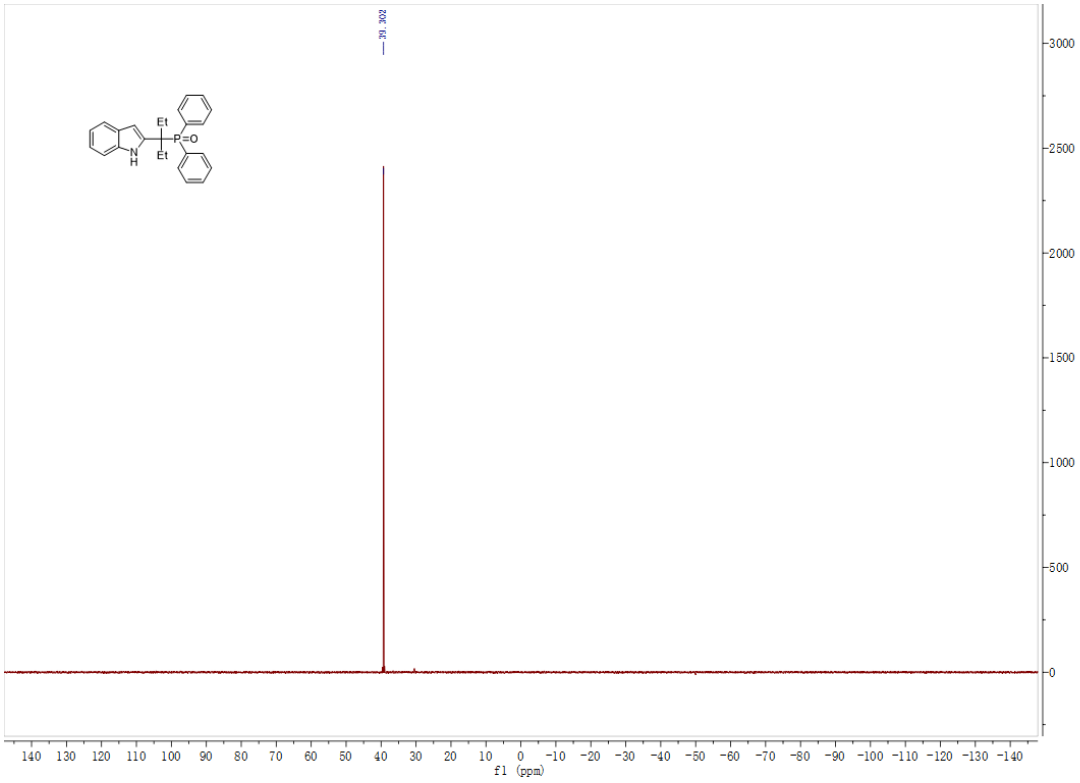

Ph
Ph
P=O
Ph
Ph
N
f1 (ppm)


33.809
Ph
Ph
P=O
Ph
Ph
N
f1 (ppm)

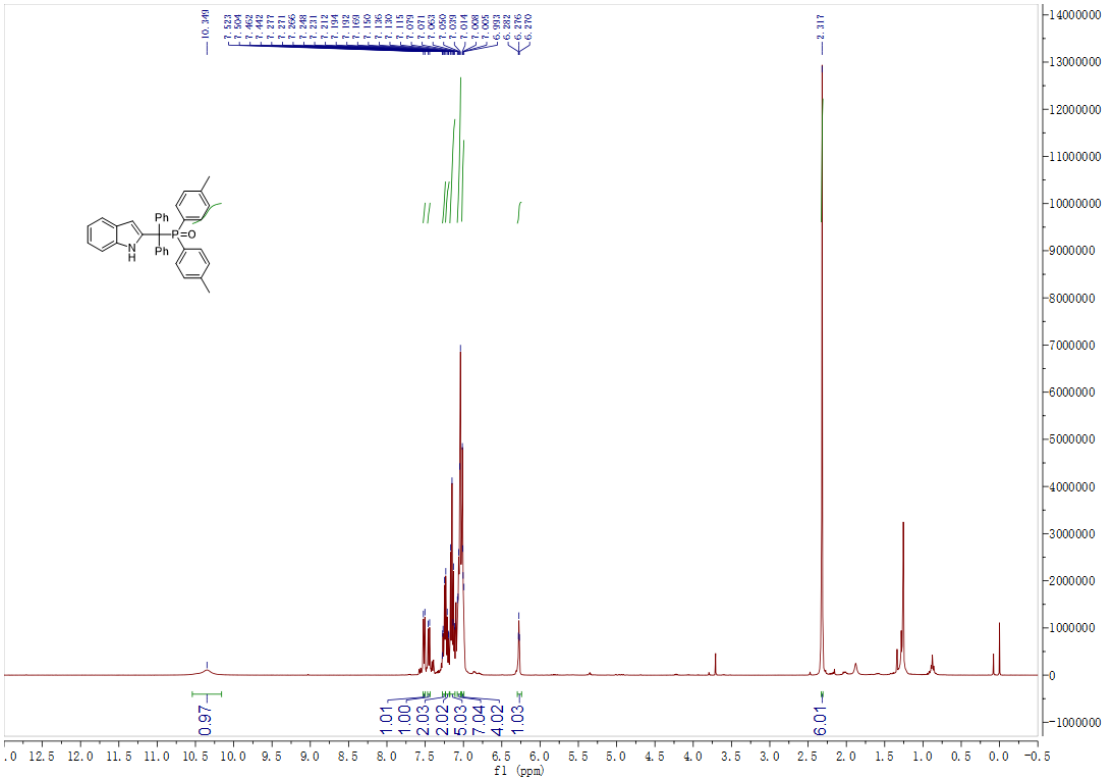
3na

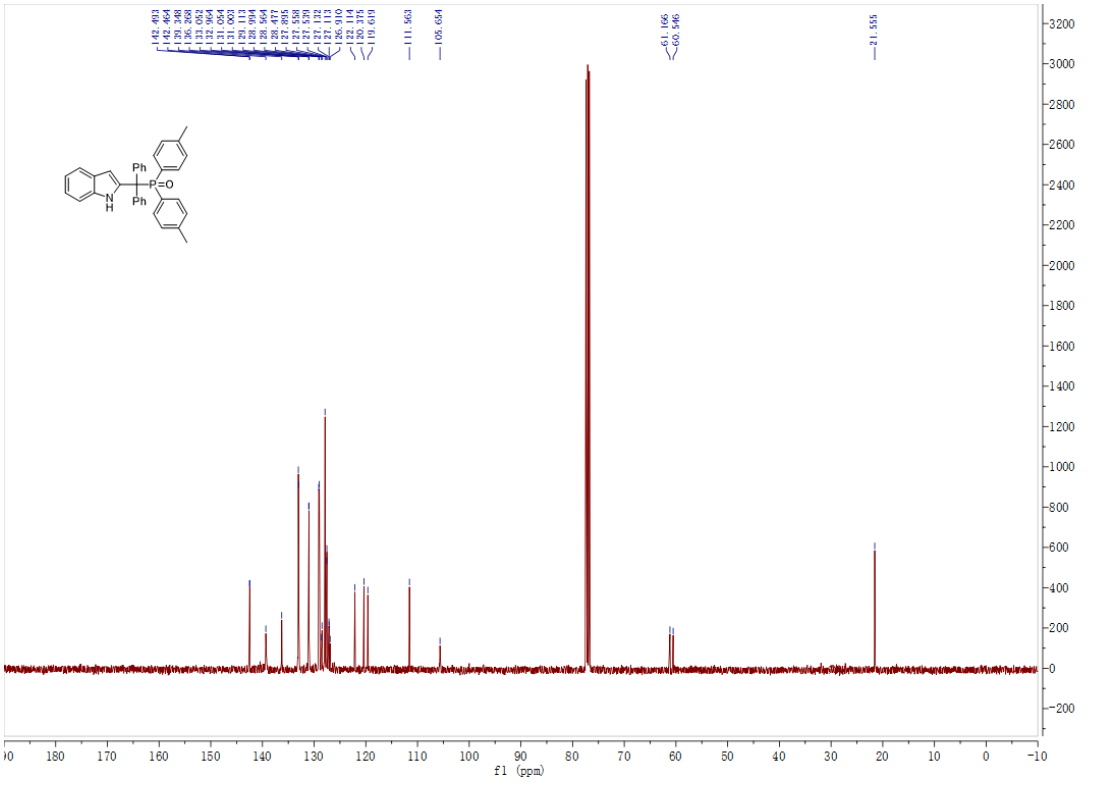

Et
Et
P=O
N
H
1.00
2.02
2.01
8.03
1.01
1.01
1.03
1.03
1.03
1.01
1.03
6.00
f1 (ppm)

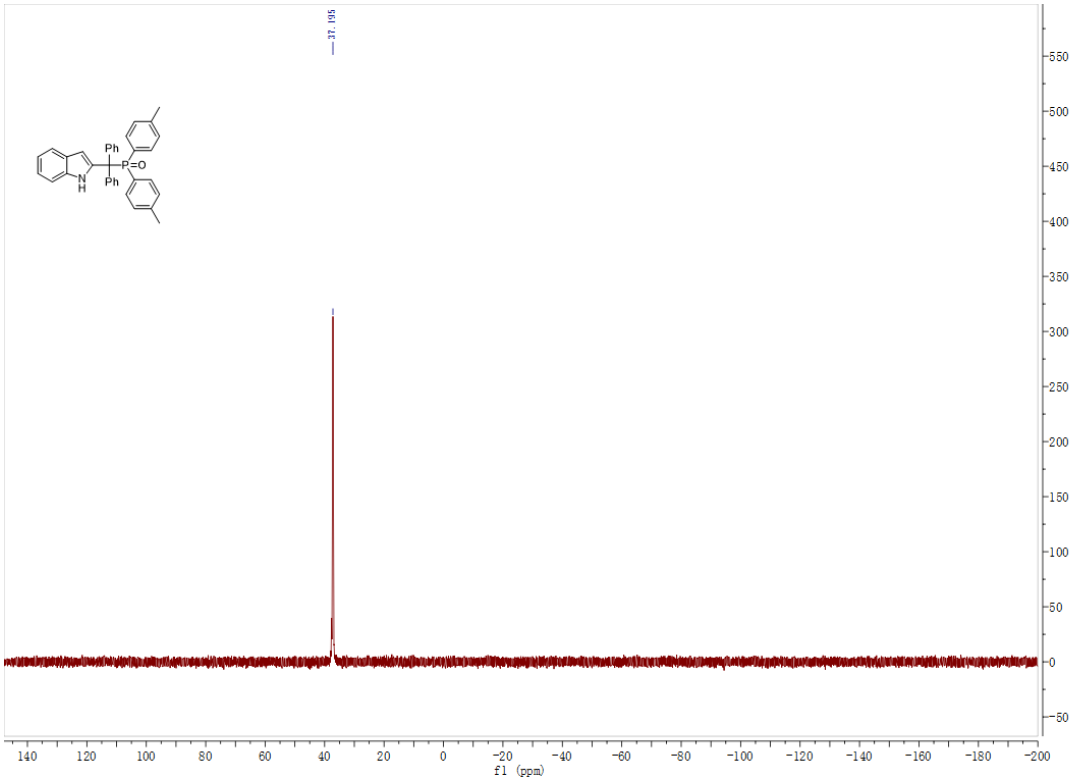




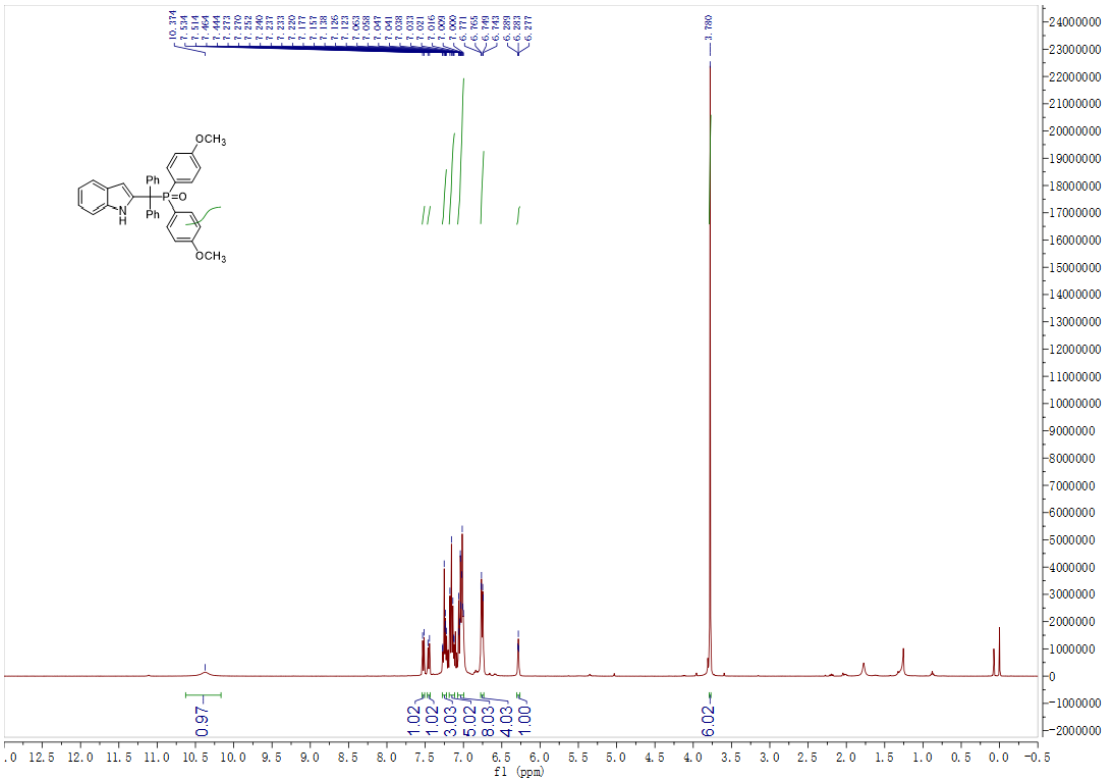
3ab

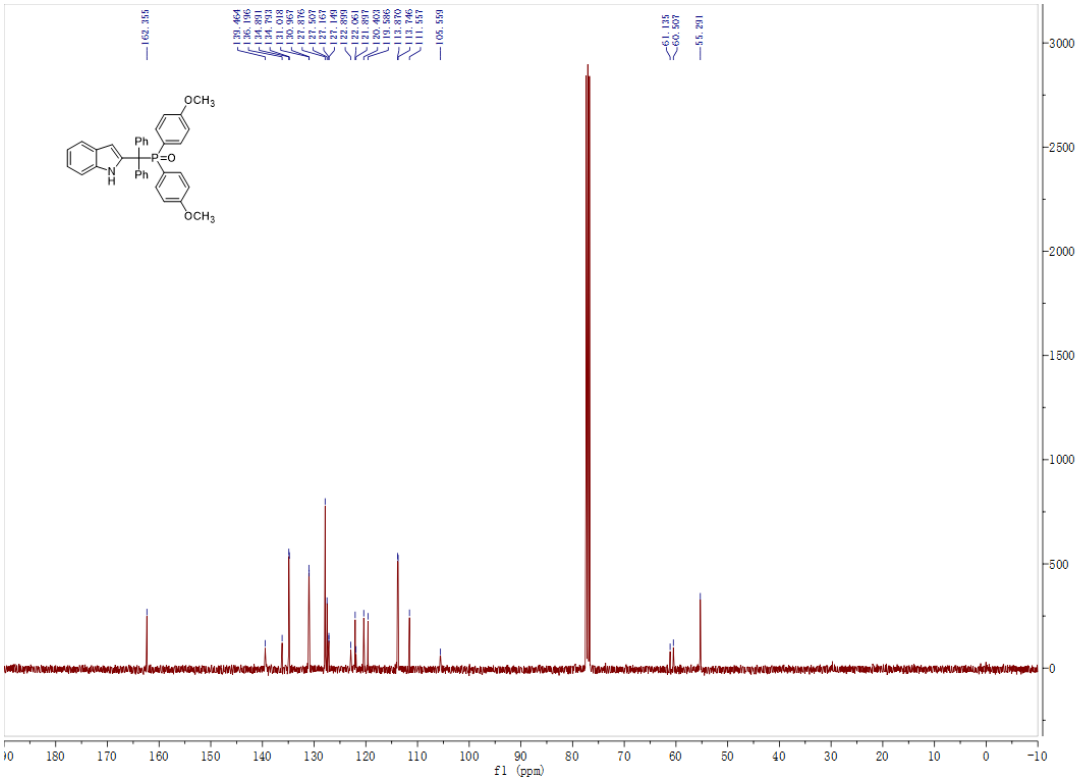

10.340
7.523
7.504
7.462
7.442
7.277
7.273
7.266
7.248
7.231
7.213
7.194
7.192
7.169
7.150
7.136
7.115
7.079
7.071
7.063
7.050
7.033
7.014
7.008
7.006
6.993
6.292
6.276
6.270
2.317
Ph
P=O
Ph
N
H
0.97
1.01
1.00
2.03
2.02
5.03
7.04
4.02
1.03
6.01
f1 (ppm)

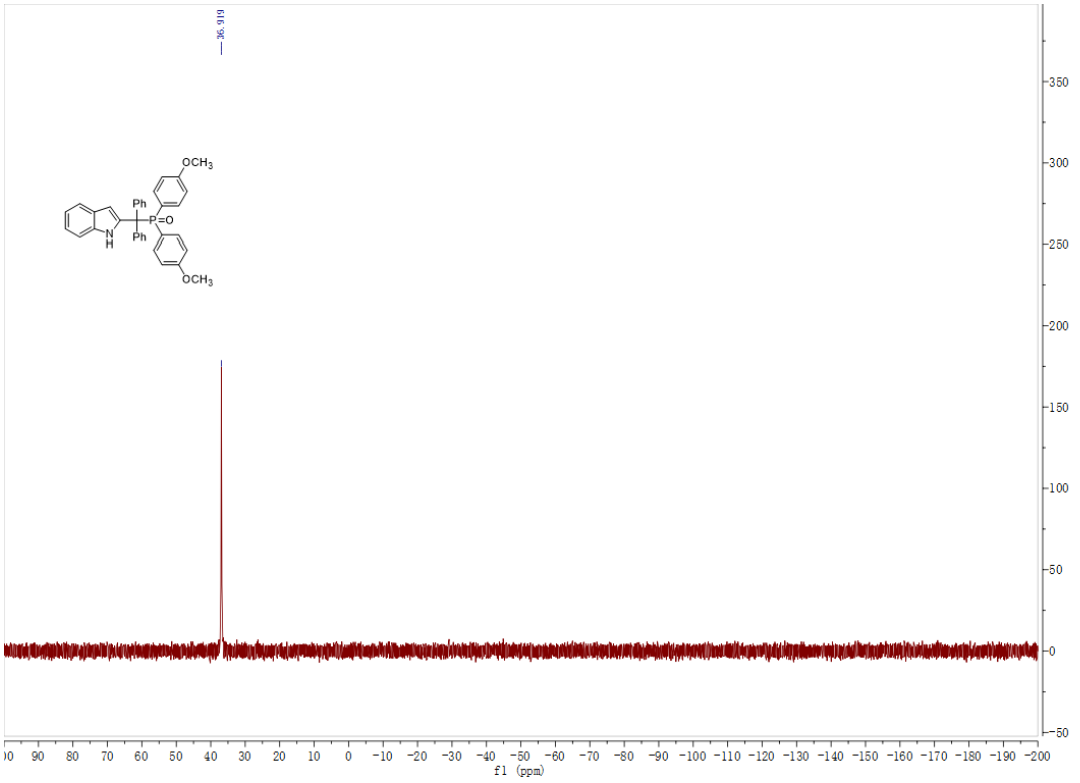

142.493
142.464
139.348
136.898
132.052
131.964
131.054
131.003
129.113
128.984
128.564
128.477
127.895
127.858
127.539
127.132
127.113
125.910
122.141
120.375
119.619
111.563
105.654
61.166
60.946
21.555
Ph
P=O
Ph
N
H
f1 (ppm)


37.195
Ph
P=O
Ph
N
H
f1 (ppm)

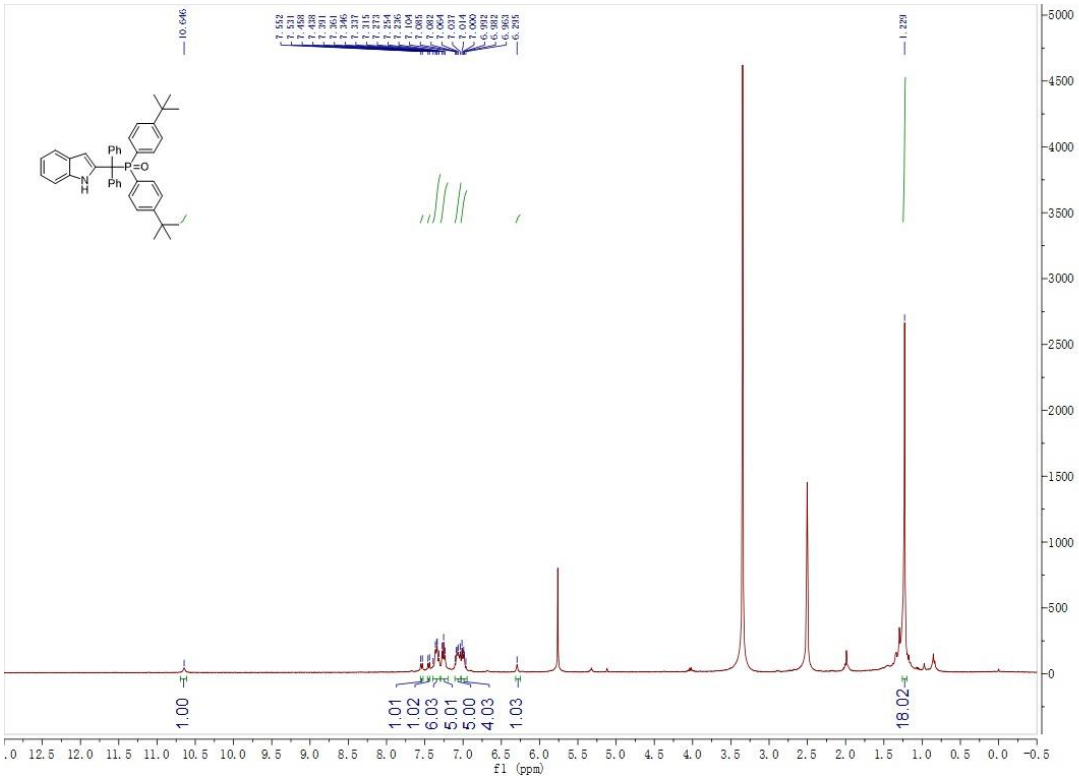
3ac

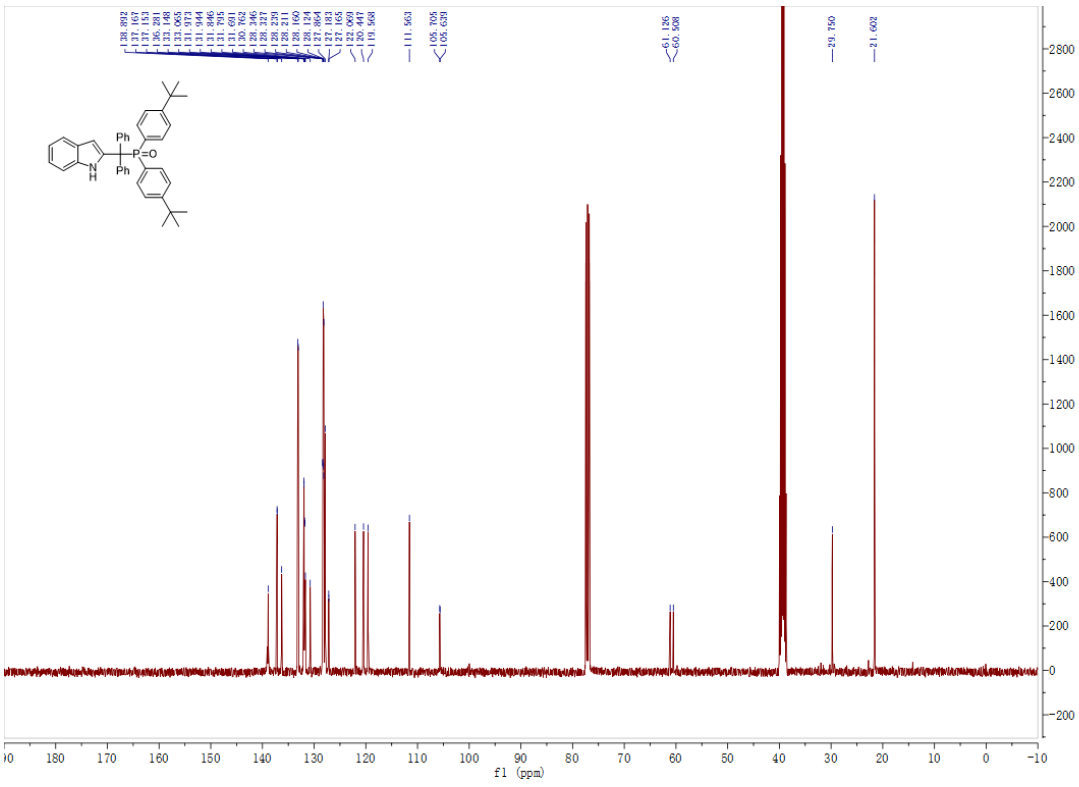

OCH3
Ph
P=O
Ph
N
H
OCH3
3.780
0.97
1.02
1.02
3.03
5.02
8.03
4.03
1.00
6.02
f1 (ppm)

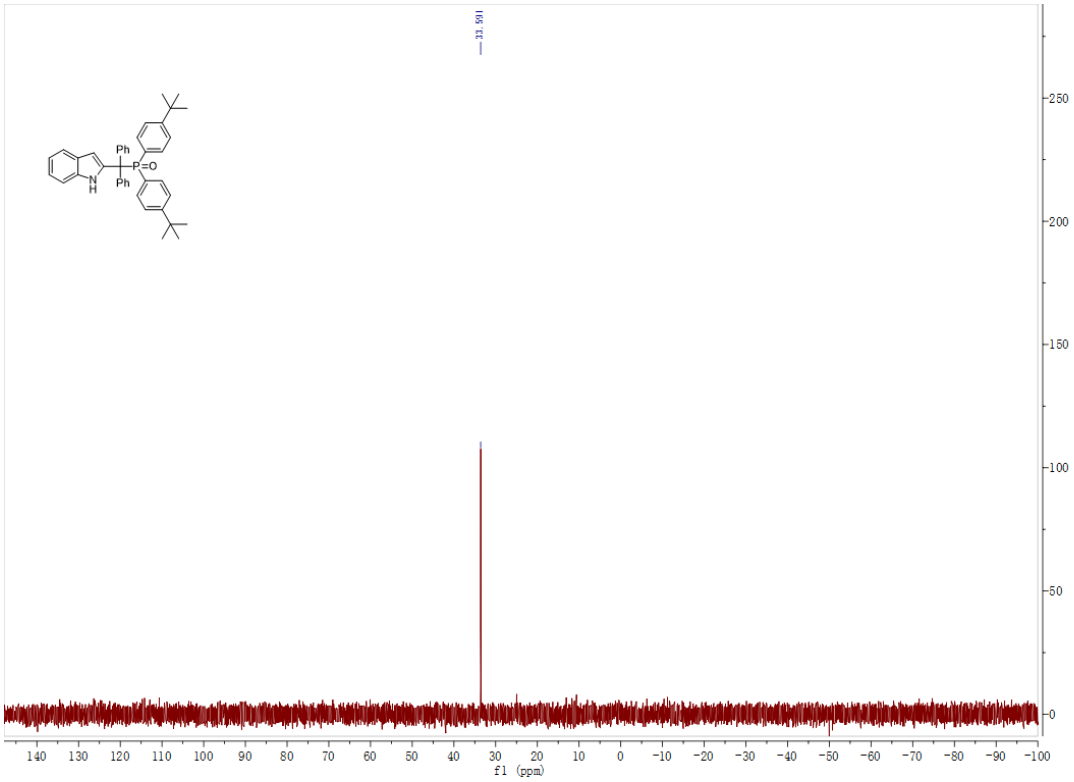




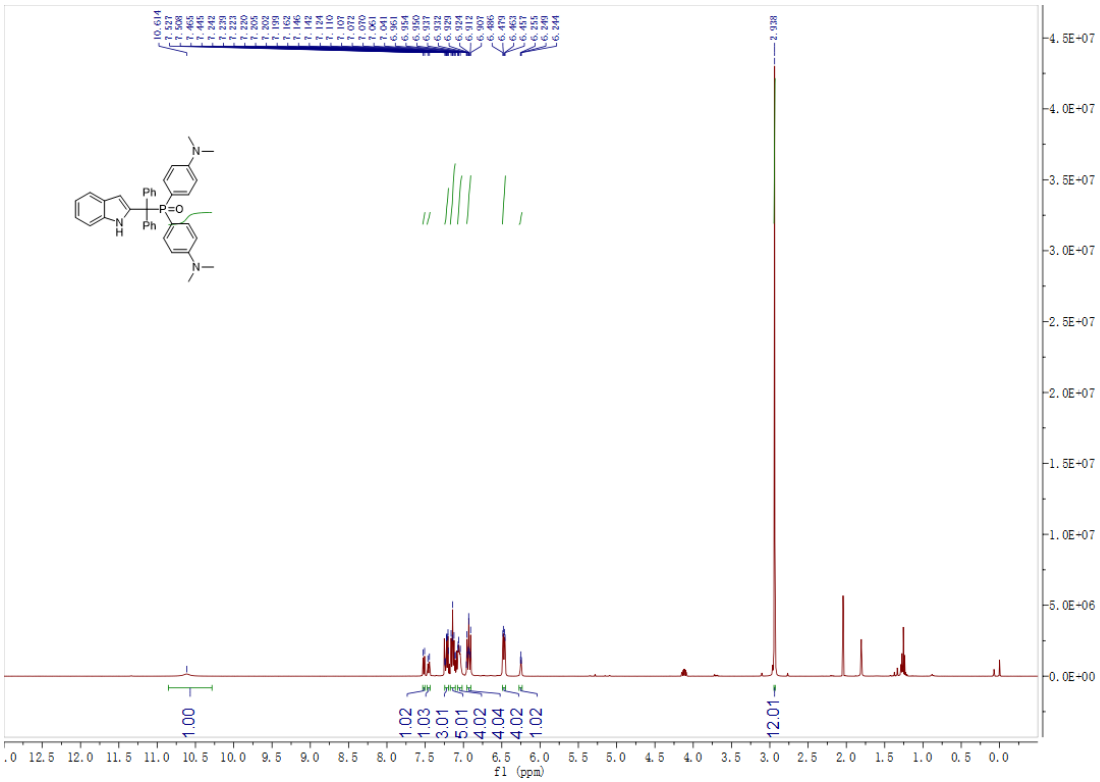
3ad

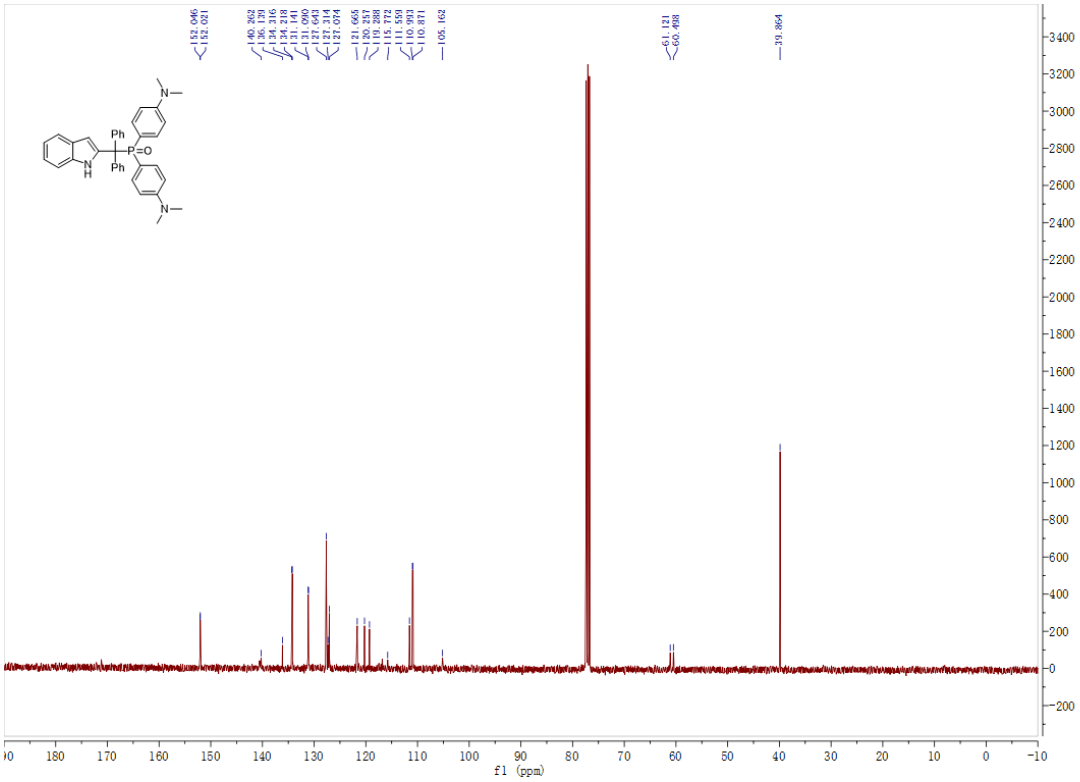

10.646
7.552
7.531
7.458
7.438
7.431
7.361
7.346
7.337
7.315
7.273
7.254
7.236
7.164
7.085
7.082
7.064
7.037
7.014
7.000
6.992
6.982
6.955
6.295
1.229
Ph
P=O
Ph
N
H
1.00
1.01
1.02
6.03
5.01
5.00
4.03
1.03
18.02
f1 (ppm)

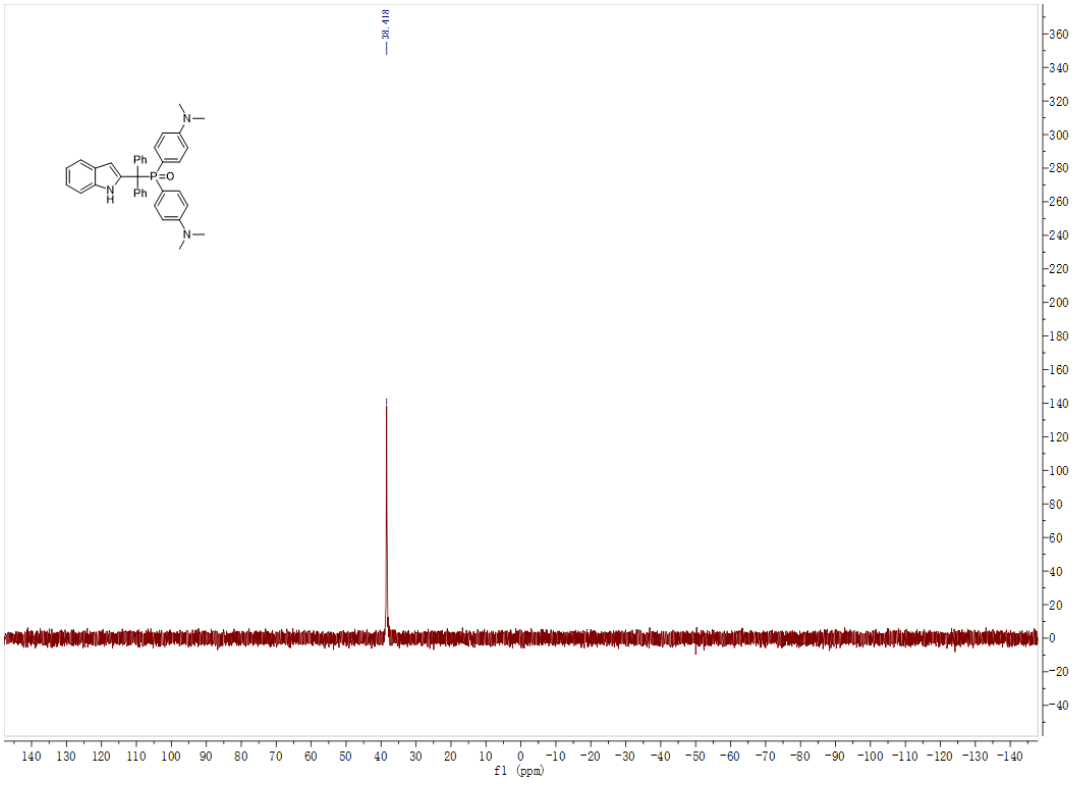

138.892
137.167
137.153
135.391
135.148
133.055
131.973
131.944
131.946
131.795
131.691
130.762
130.446
128.327
128.239
128.211
128.169
128.134
127.864
127.183
127.166
123.466
120.447
119.568
111.563
105.705
105.639
61.126
60.958
29.750
21.602
Ph
P=O
Ph
N
H
f1 (ppm)


33.591
Ph
P=O
Ph
N
H
250
200
150
100
50
0
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

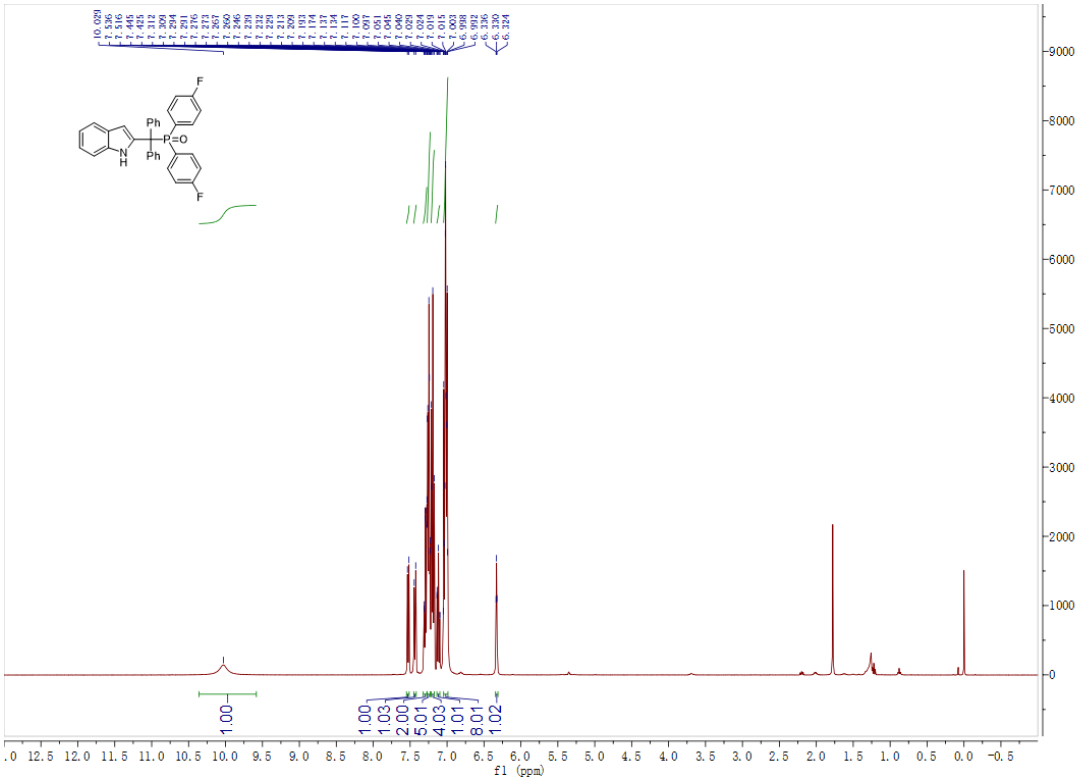
3ae

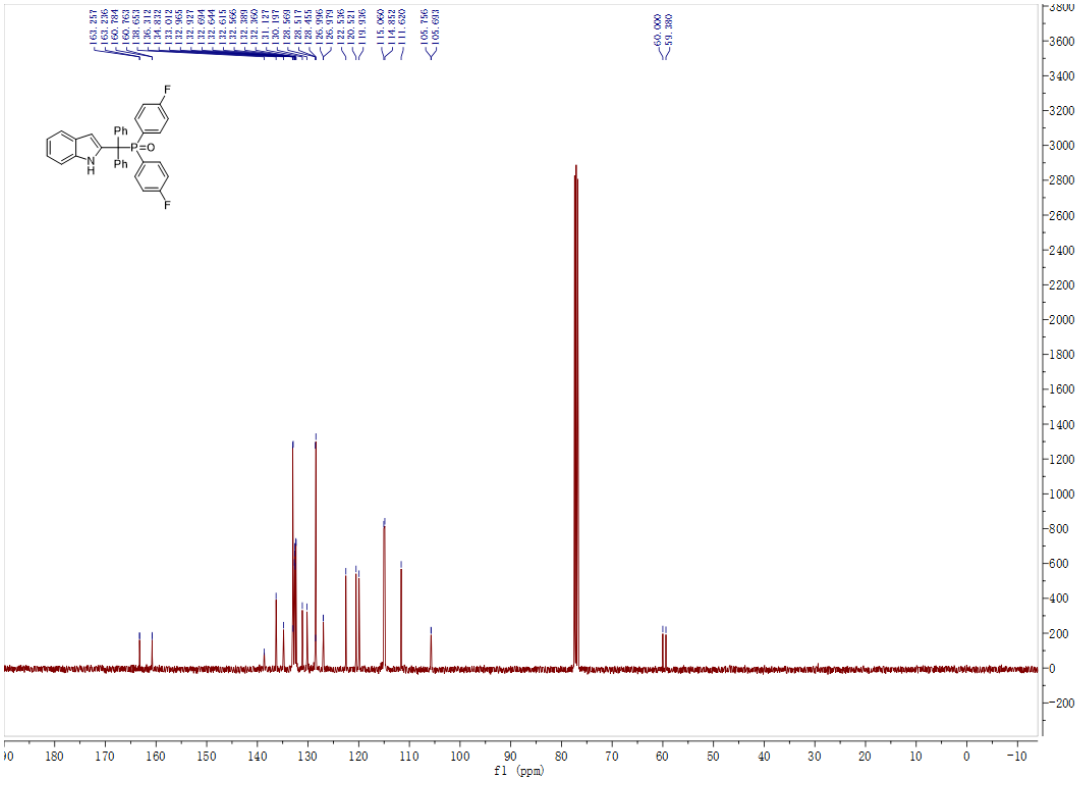

10.614
7.573
7.568
7.465
7.445
7.243
7.239
7.223
7.220
7.205
7.202
7.199
7.162
7.146
7.143
7.124
7.110
7.107
7.072
7.070
7.061
7.041
6.961
6.954
6.950
6.937
6.932
6.924
6.912
6.497
6.496
6.479
6.463
6.457
6.455
6.249
6.244
2.938
N
Ph
P=O
Ph
N
H
N
4.5E-07
4.0E-07
3.5E-07
3.0E-07
2.5E-07
2.0E-07
1.5E-07
1.0E-07
5.0E-06
0.0E+00
1.00
1.02
1.03
3.01
5.01
4.02
4.04
4.02
1.02
12.01
f1 (ppm)

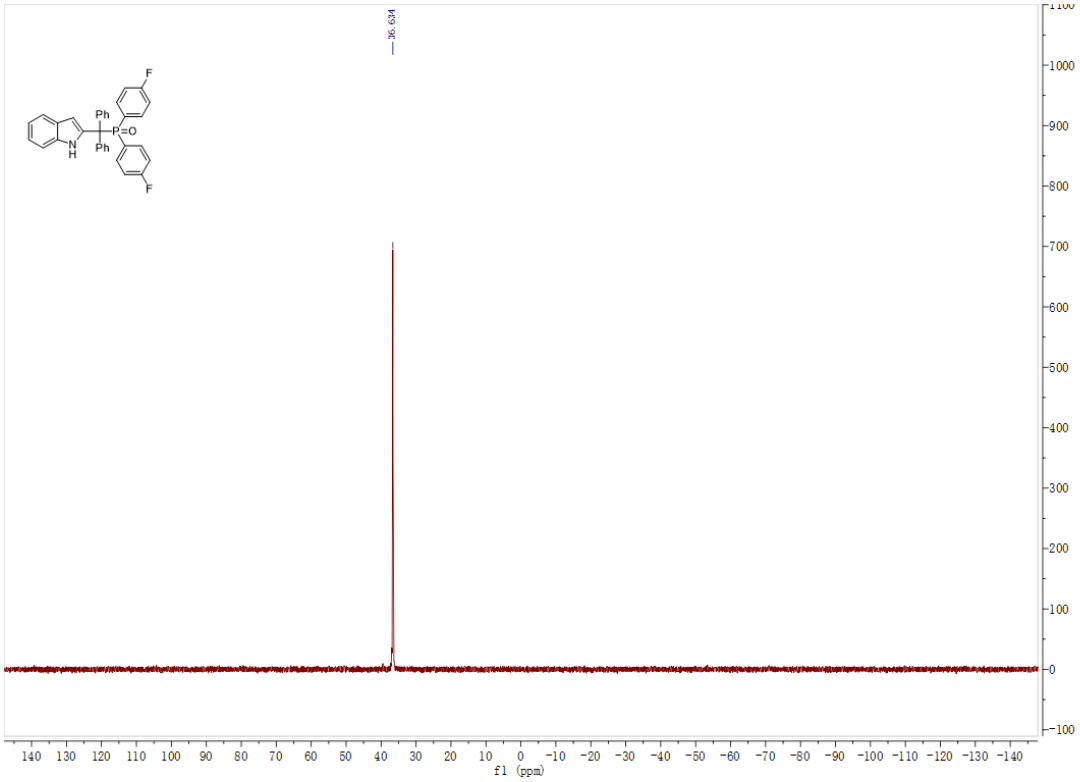

152.046
152.021
140.262
136.139
134.316
134.218
131.141
131.090
127.643
127.314
127.074
121.665
119.317
119.288
115.772
111.559
110.993
110.871
105.162
61.121
60.498
39.864
N
Ph
P=O
Ph
N
H
N
f1 (ppm)

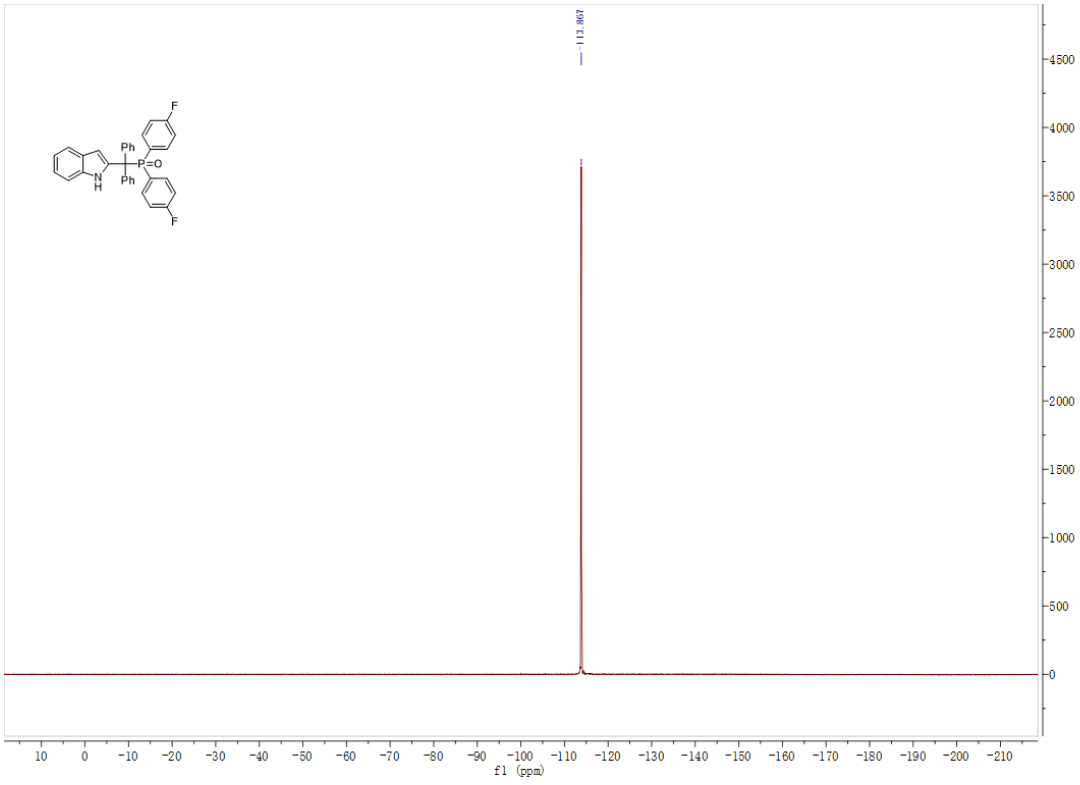

28.418
N
Ph
P=O
Ph
N
H
N
f1 (ppm)

3af

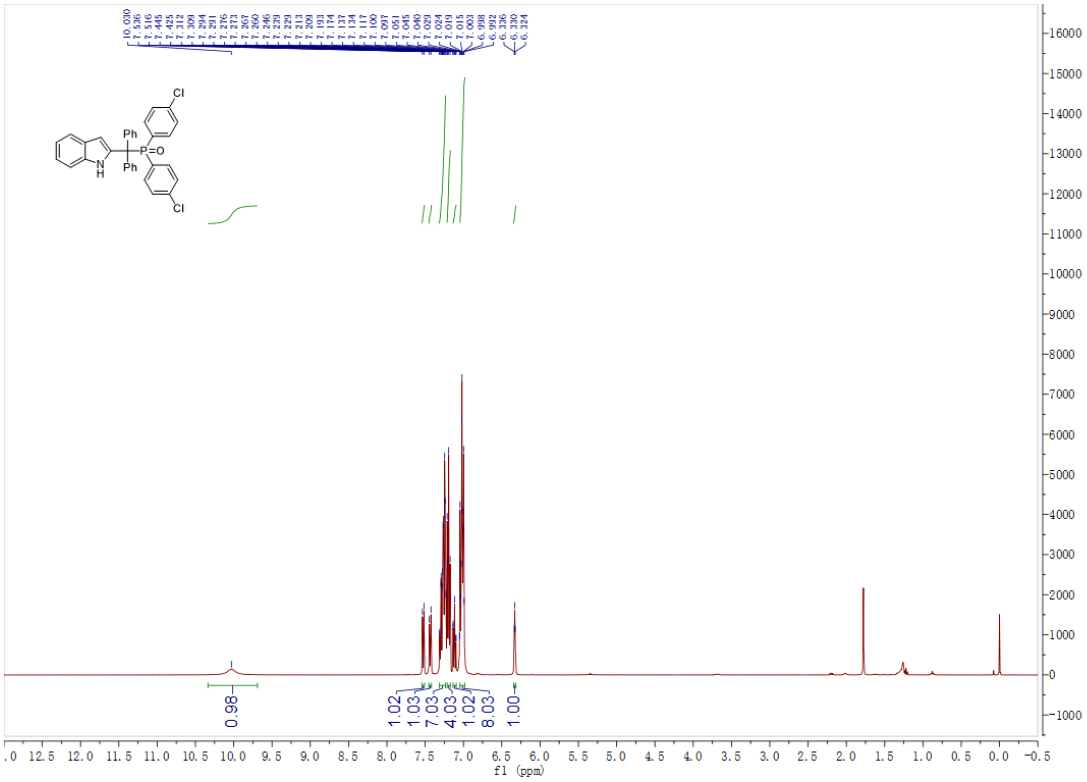

F
Ph
P=O
Ph
N
H
F
f1 (ppm)

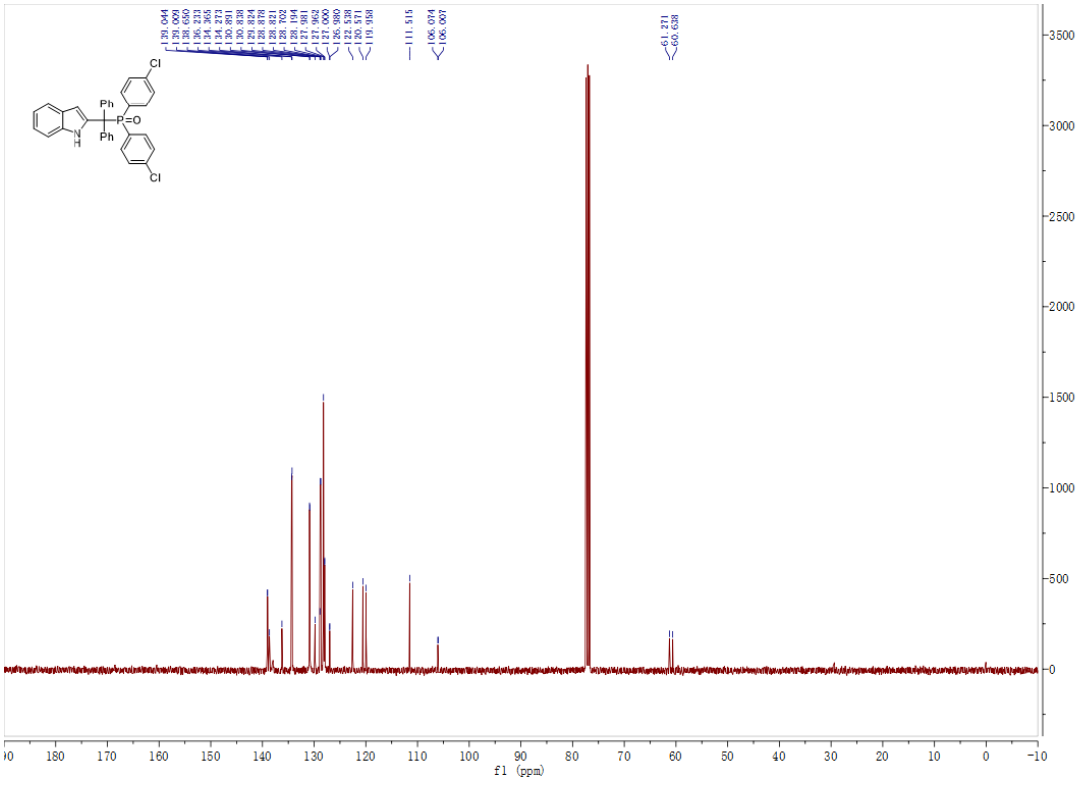

F
Ph
P=O
Ph
N
H
F
f1 (ppm)

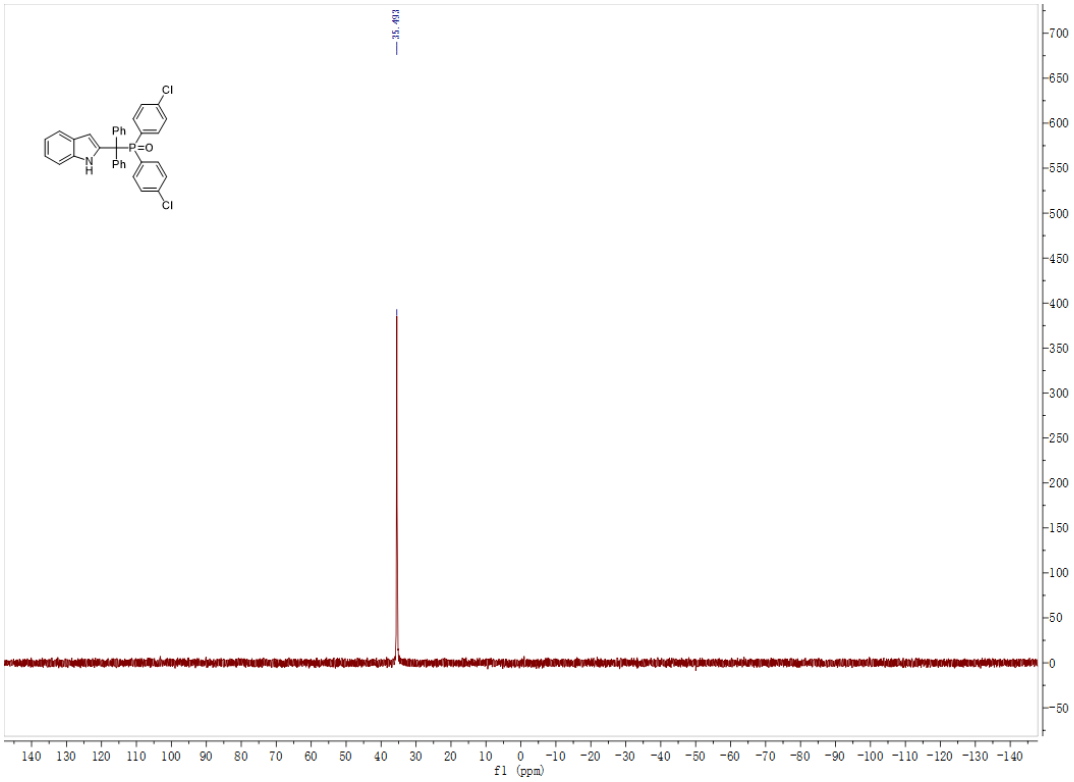

36.634
F
Ph
P=O
Ph
N
H
F
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)


-113.867
F
Ph
P=O
Ph
N
H
F
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

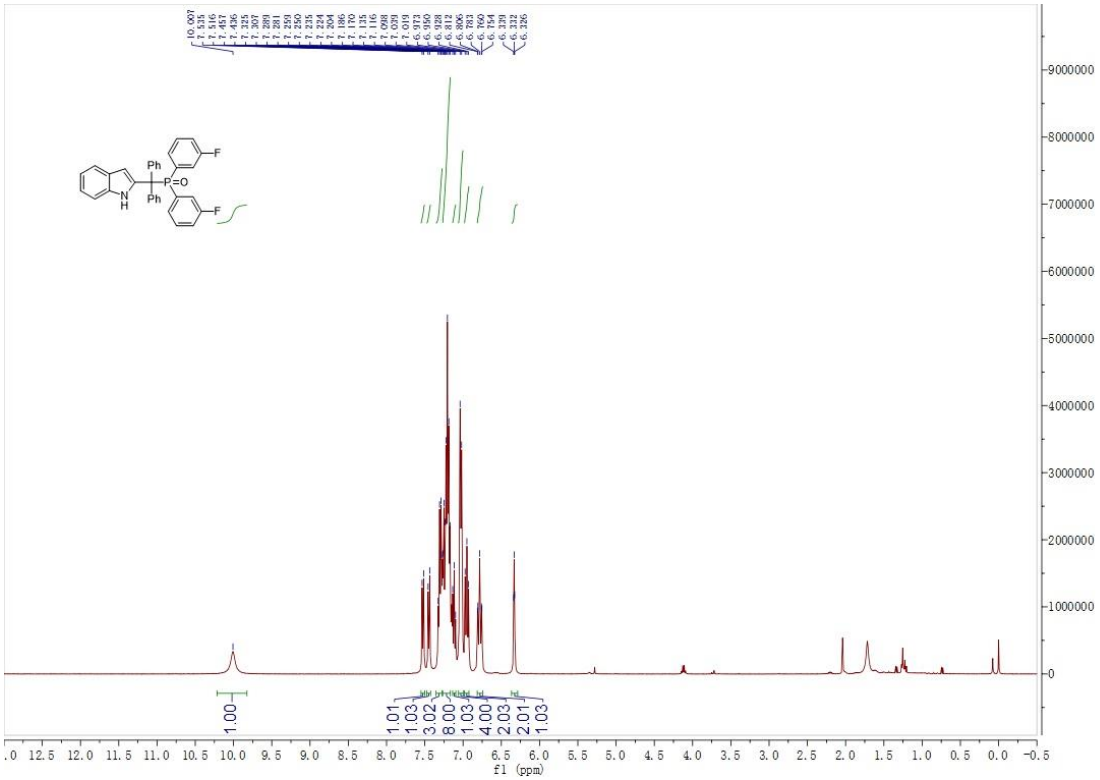
3ag

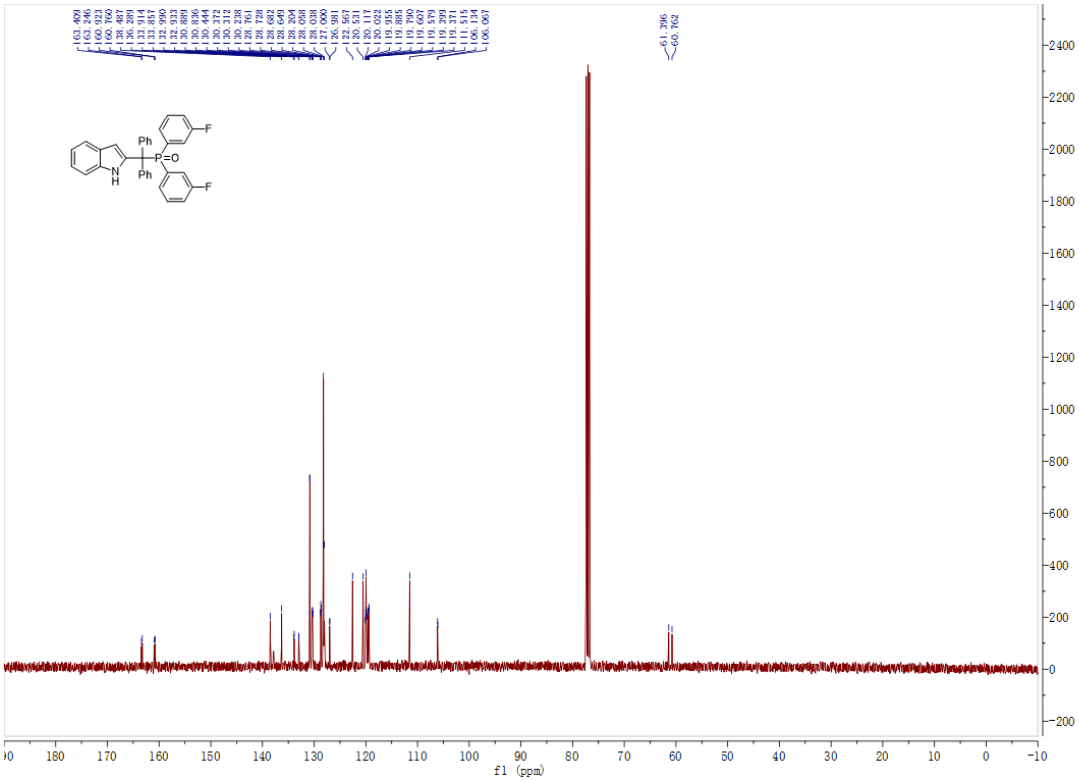

Cl
Ph
P=O
Ph
N
H
Cl
0.98
1.02
1.03
7.03
4.03
1.02
8.03
1.00
f1 (ppm)

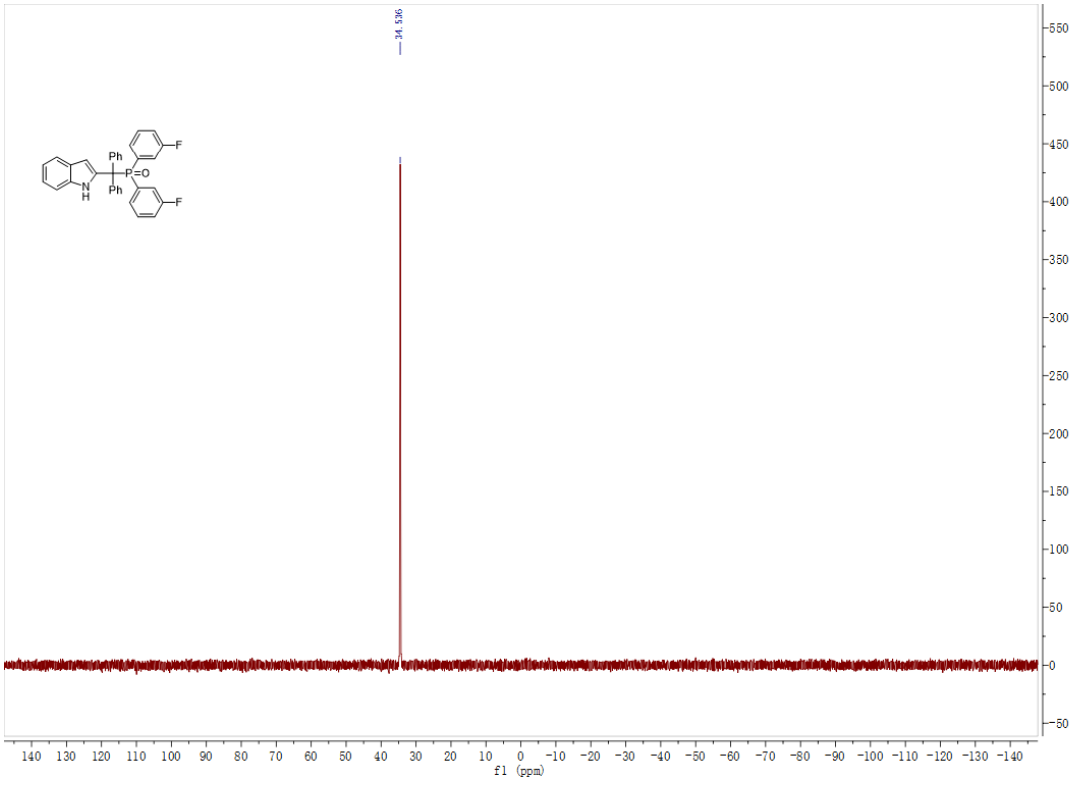

Cl
Ph
P=O
Ph
N
H
Cl
f1 (ppm)

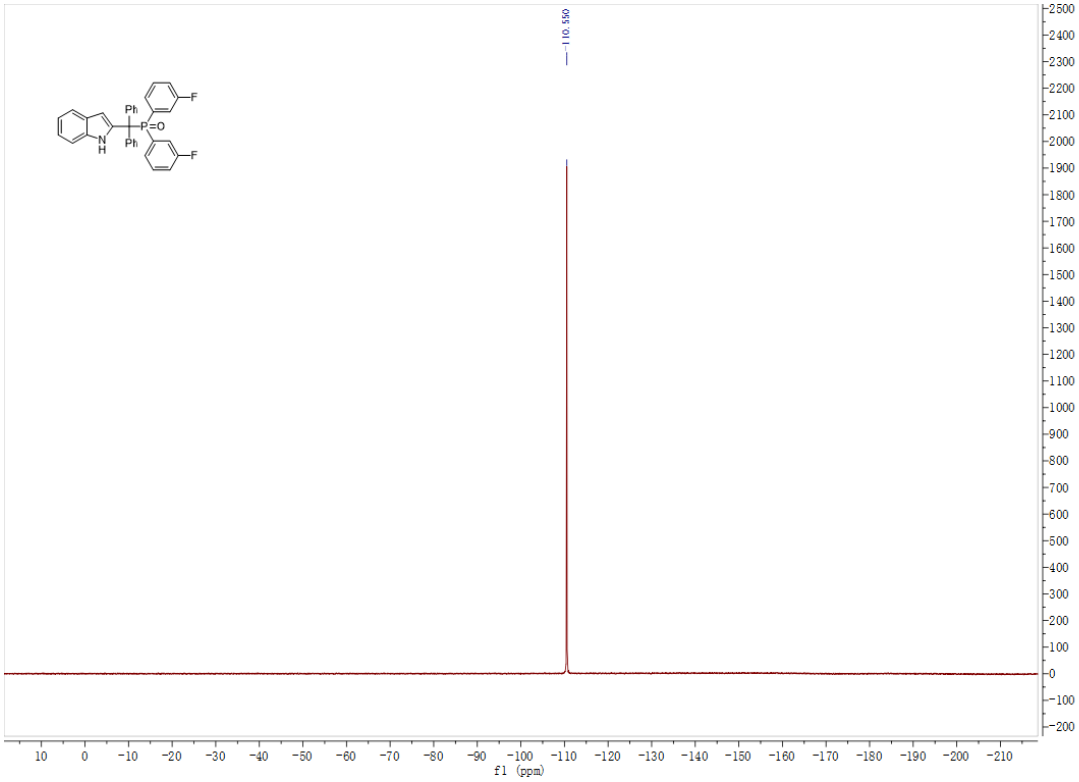

35.493
Cl
Ph
P=O
Ph
N
H
Cl
f1 (ppm)

3ah

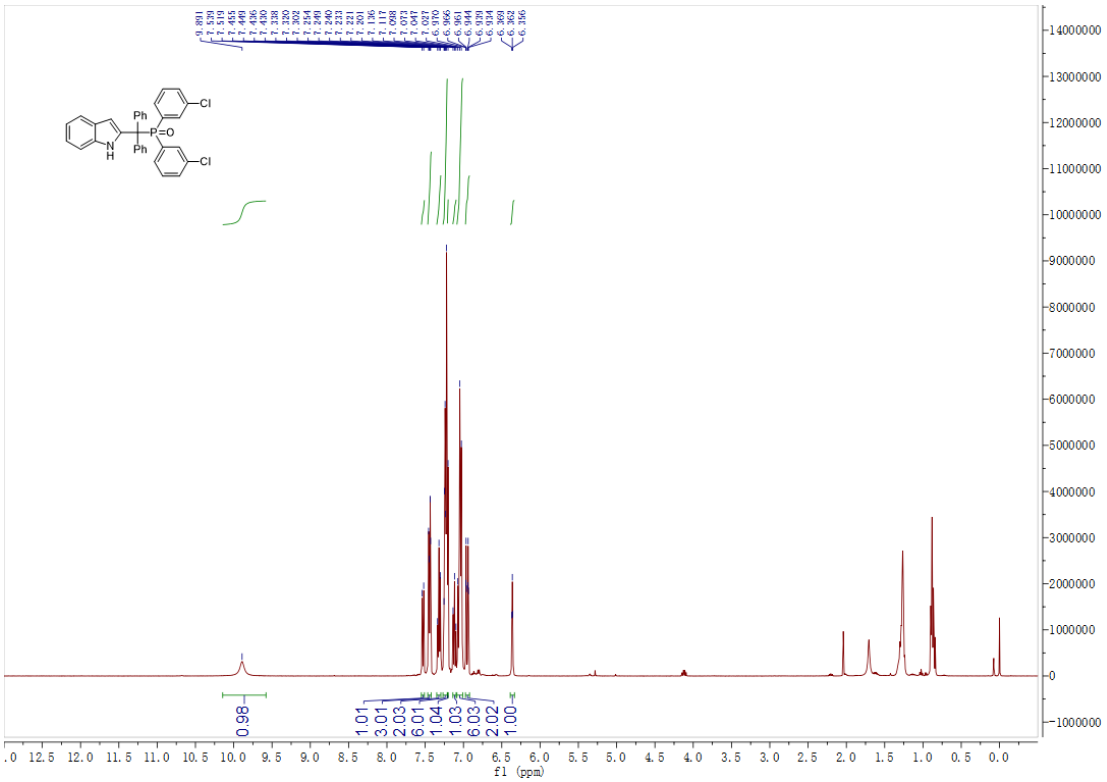

F
Ph
P=O
Ph
N
H
F
1.00
1.01
1.03
3.02
8.00
1.03
4.00
2.03
2.01
1.03
f1 (ppm)

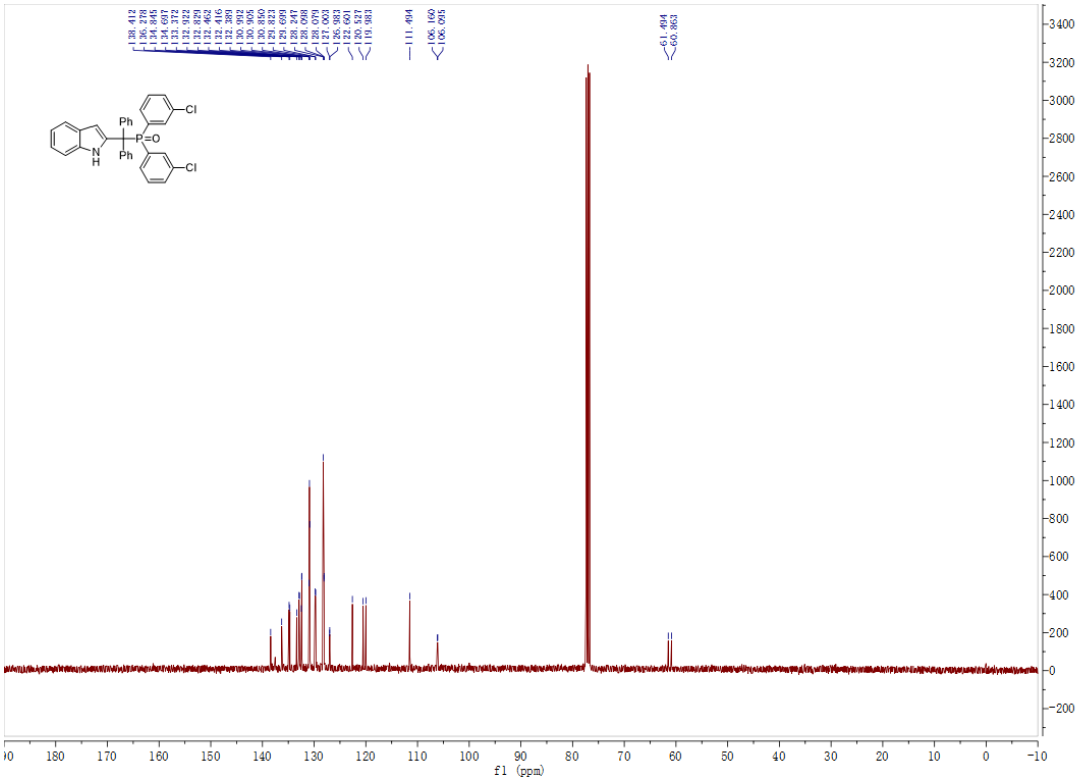

Ph
P=O
Ph
F
F
N
H
61.396
60.762
f1 (ppm)

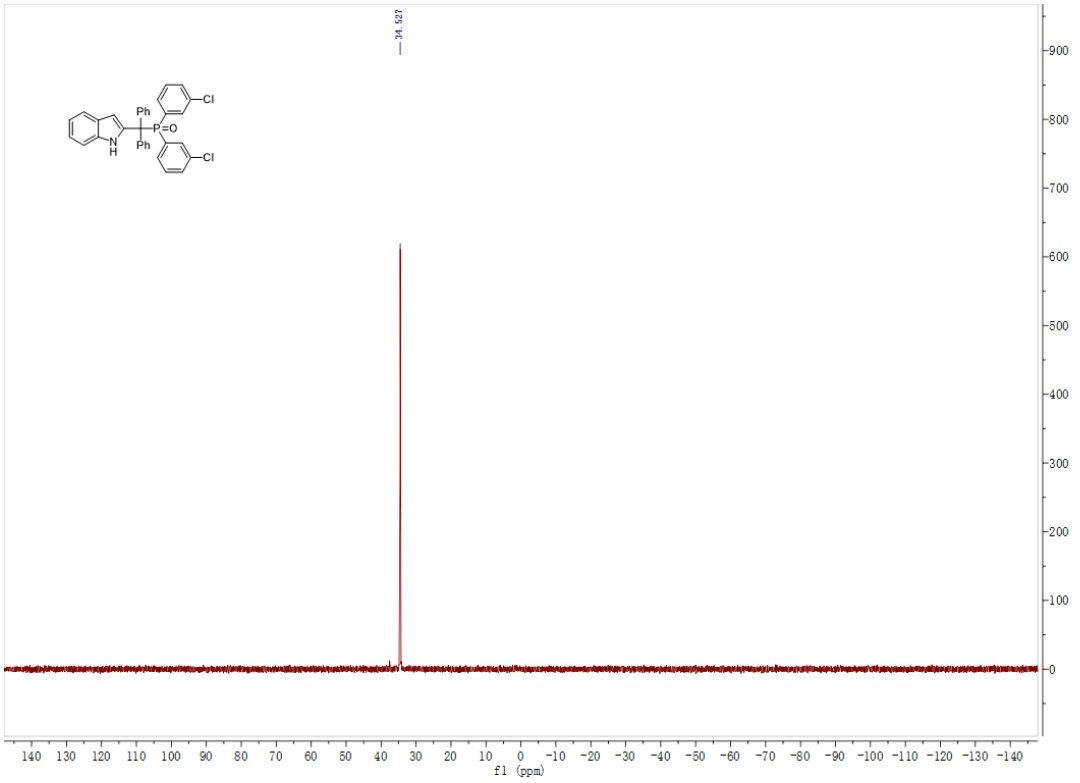

Ph
P=O
Ph
F
F
N
H
34.536
f1 (ppm)



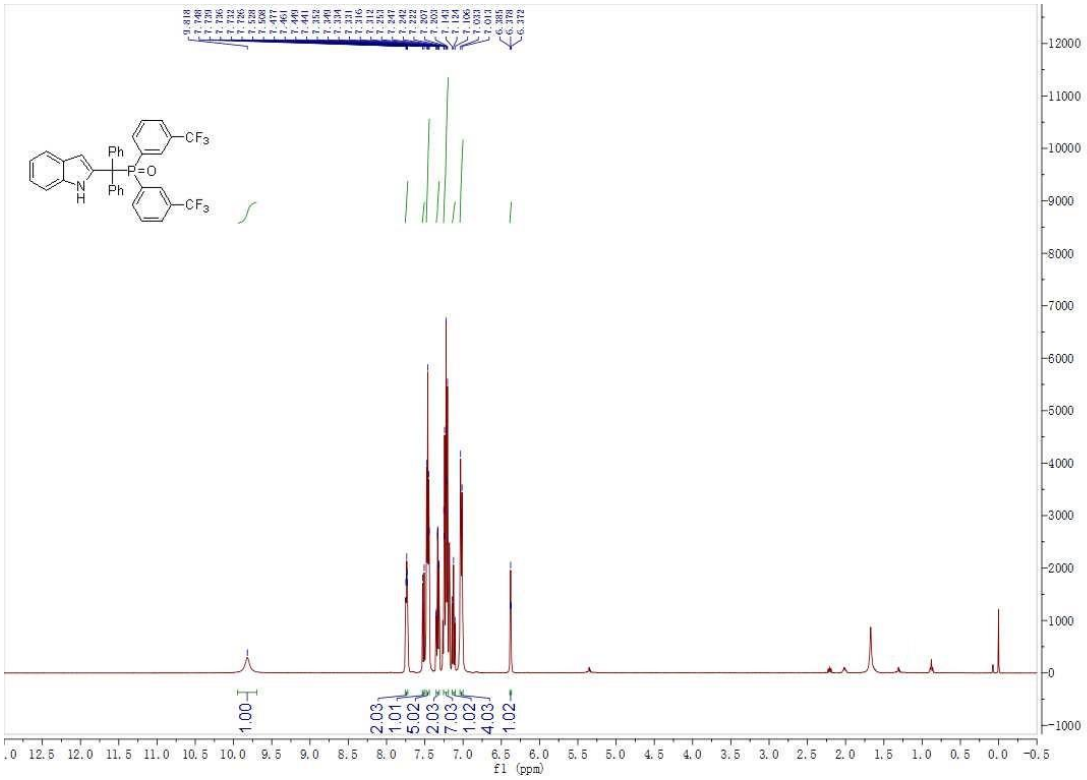
3ai

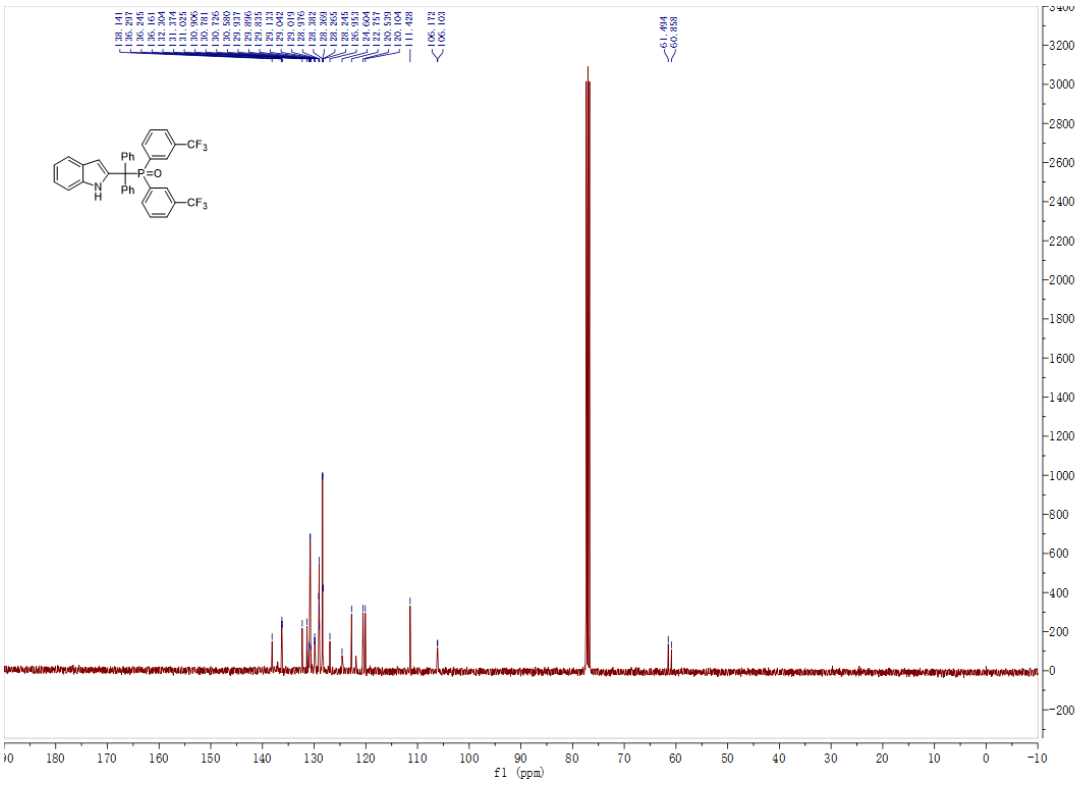


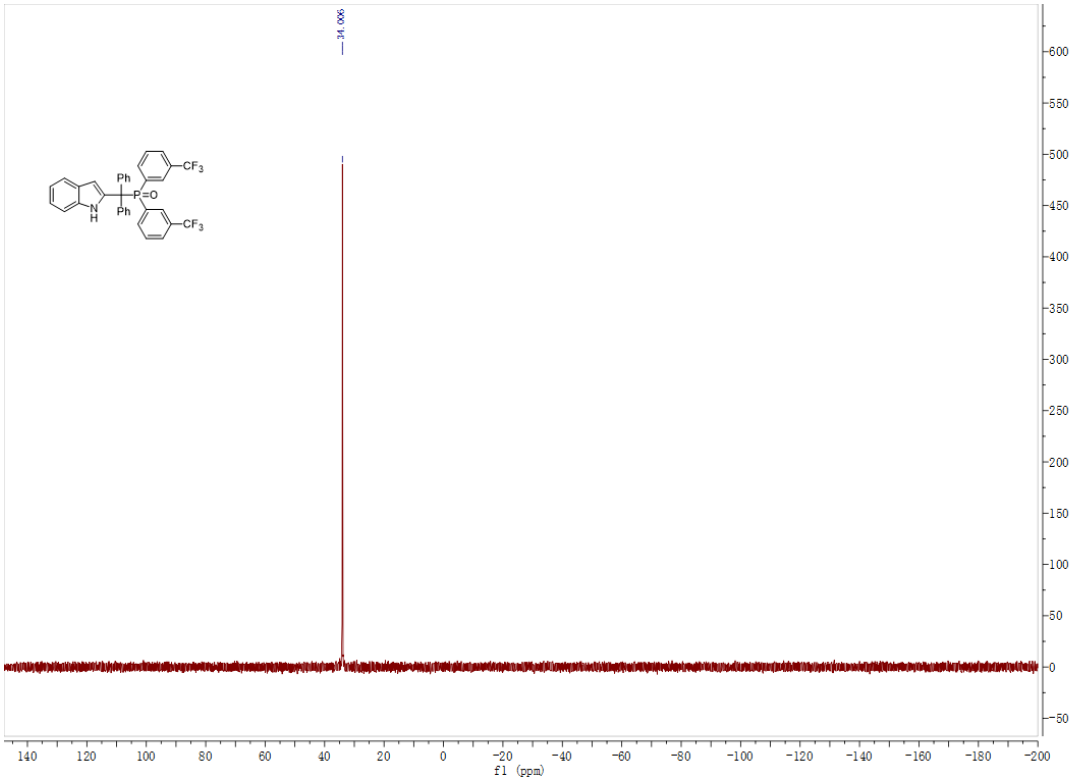


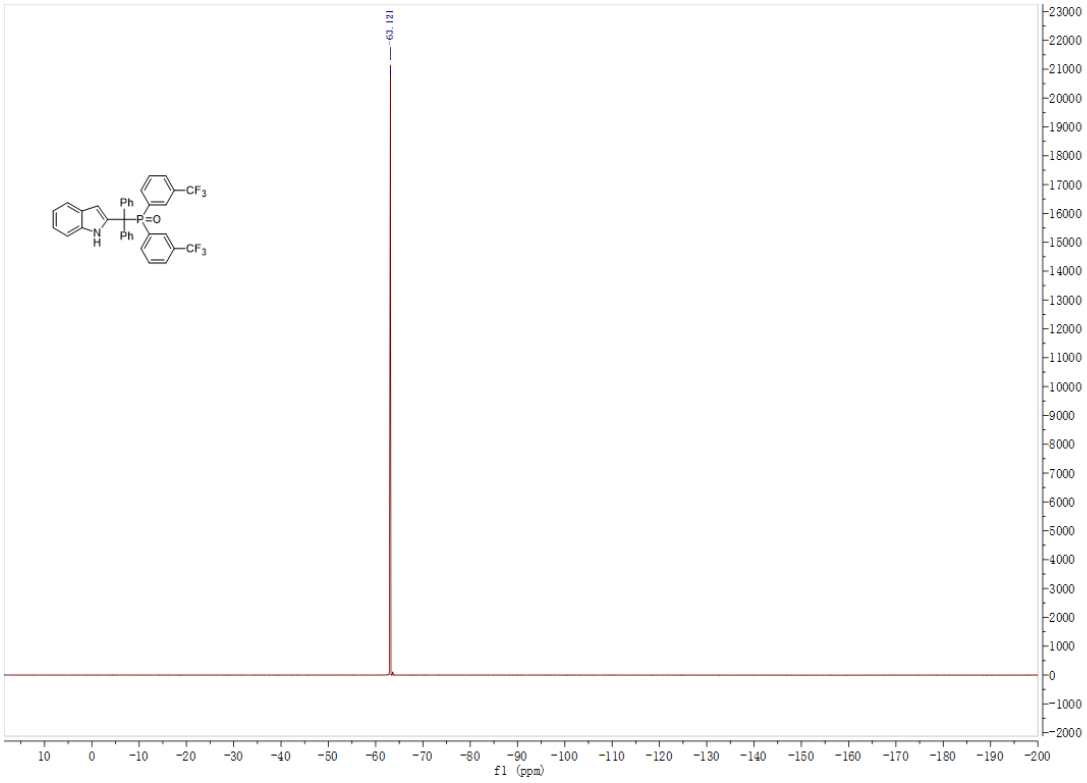


3aj

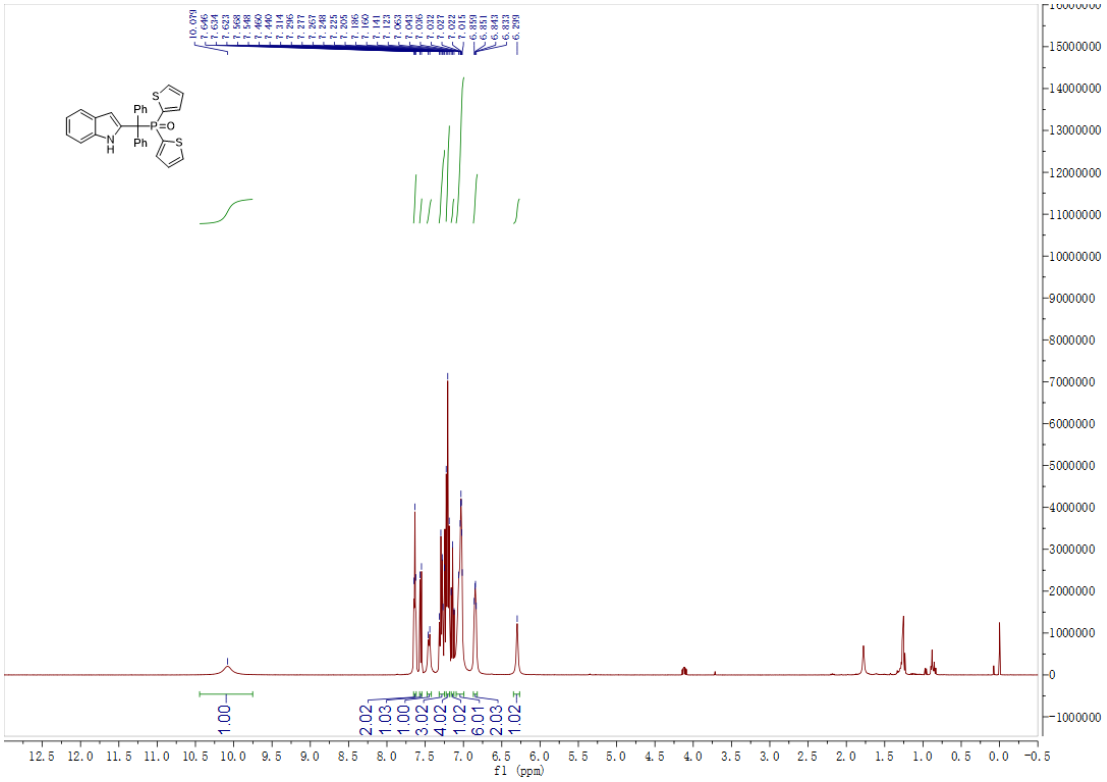

Ph
P=O
Ph
CF3
CF3
N
H
1.00
2.03
1.01
5.02
2.03
7.03
1.02
4.03
1.02
f1 (ppm)

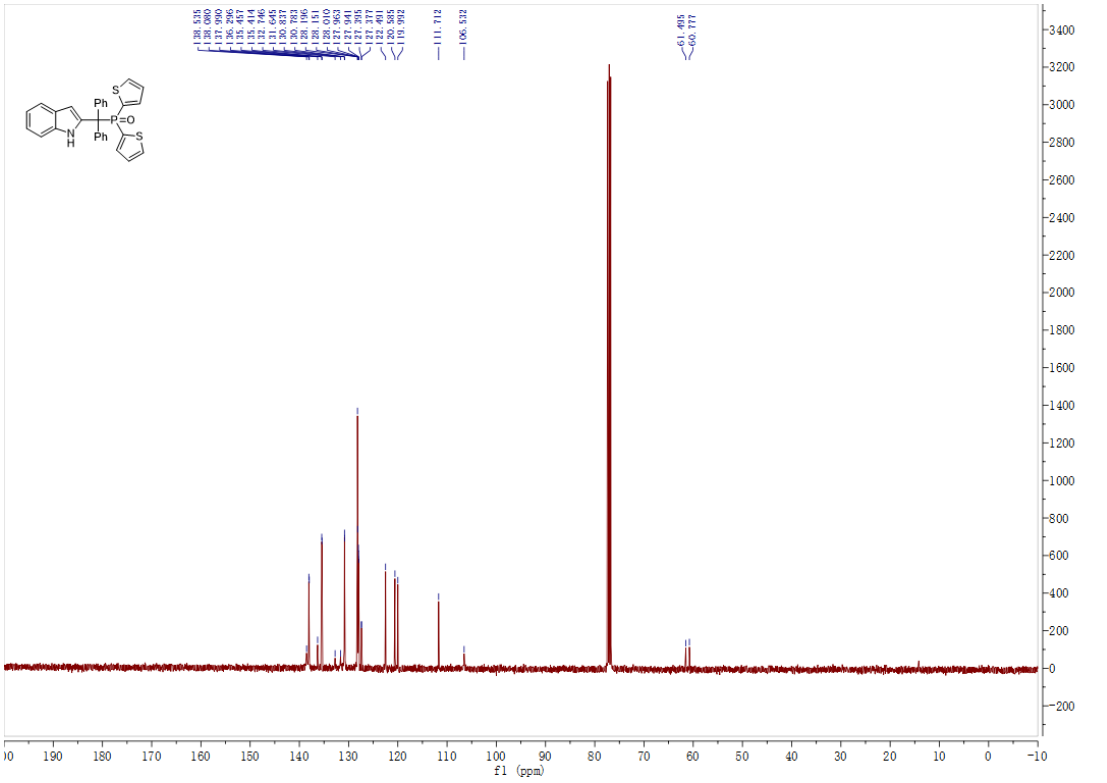

Ph
P=O
Ph
CF3
CF3
N
H
f1 (ppm)

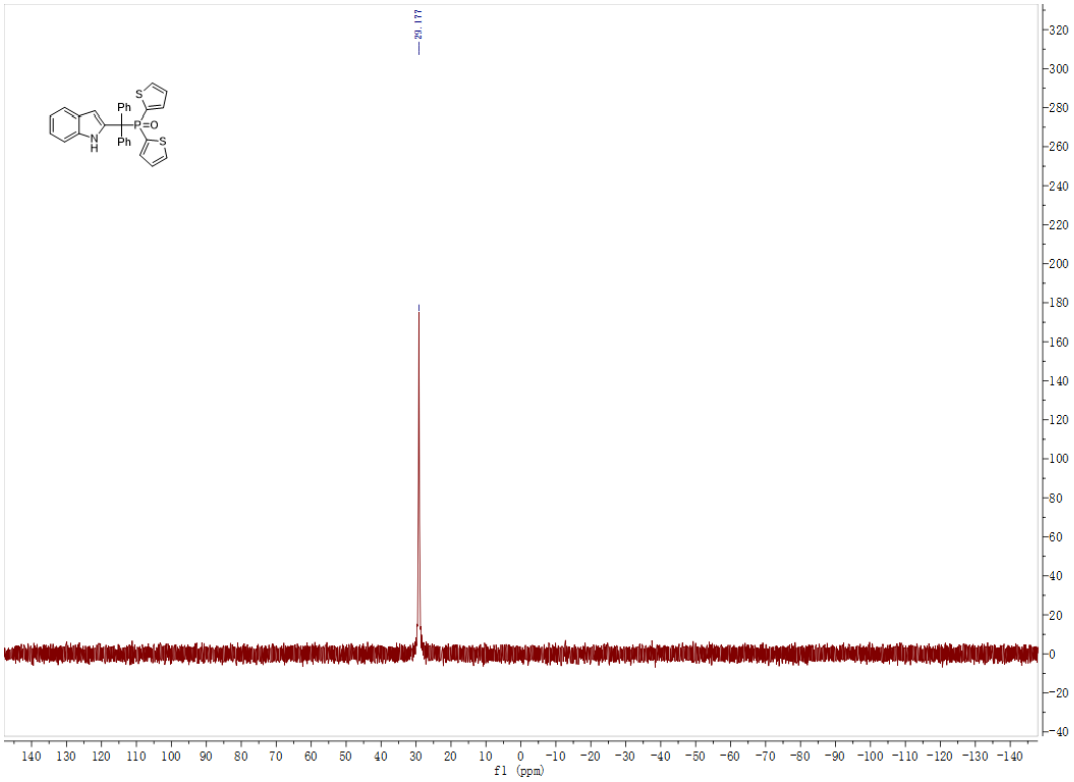




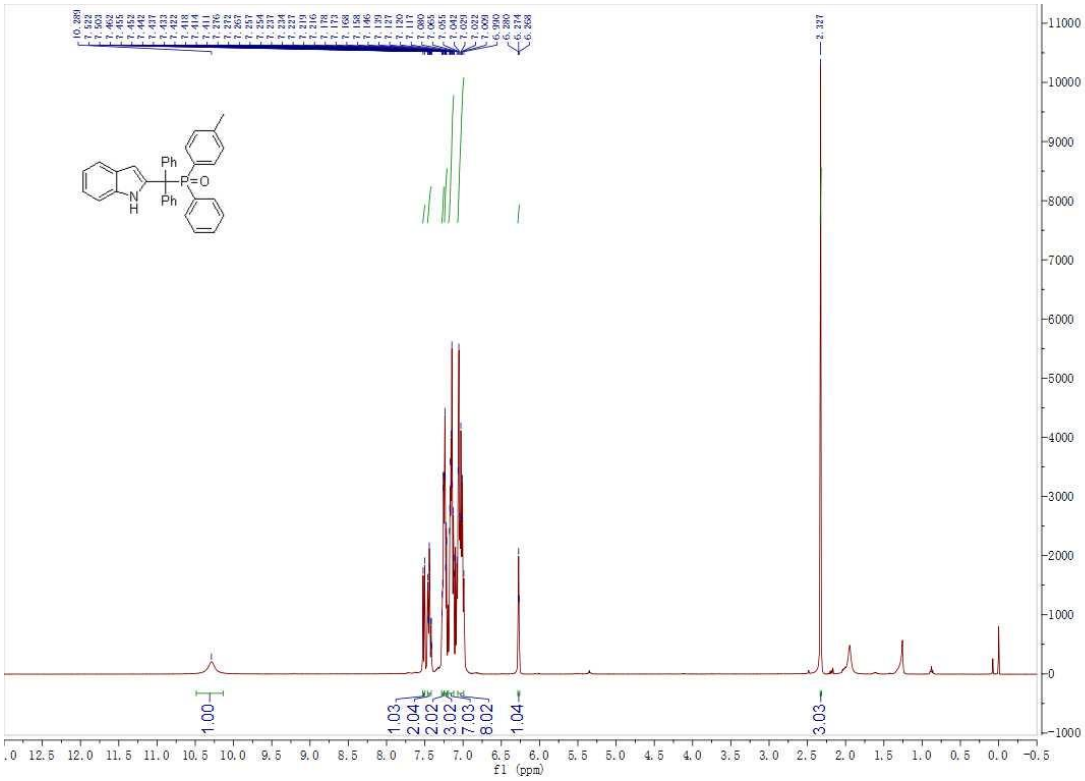
3am

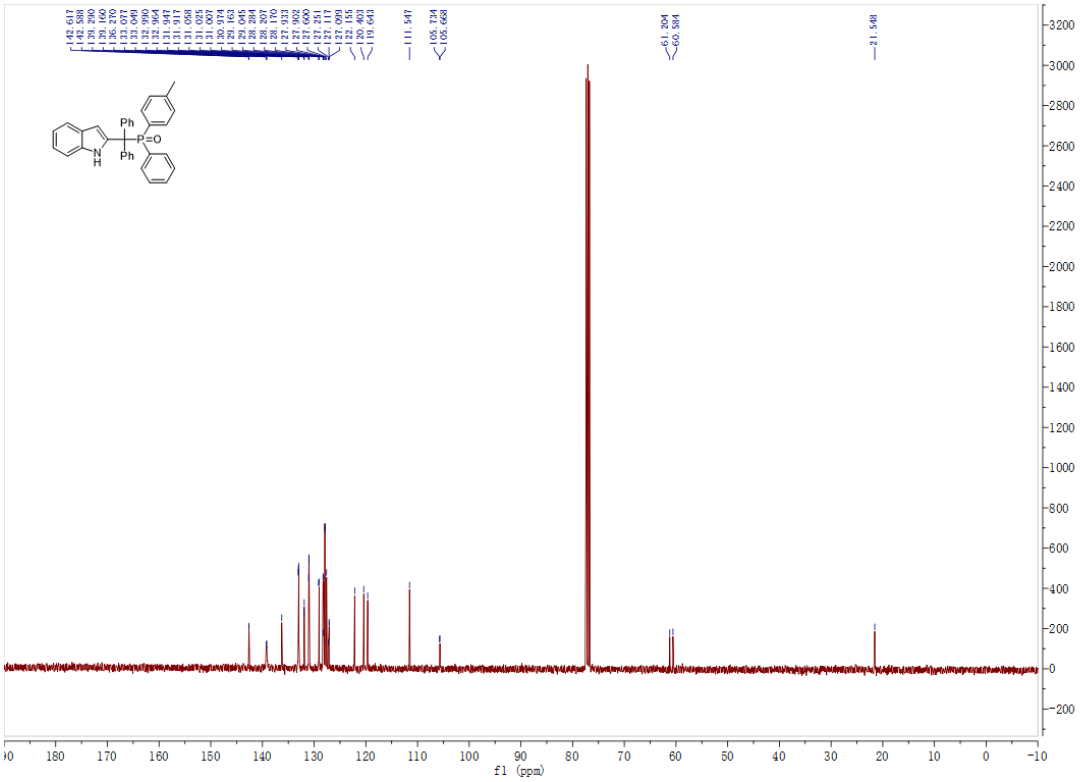

Ph
S
P=O
Ph
N
H
S
1.00
2.02
1.03
1.00
3.02
4.02
1.02
6.01
2.03
1.02
f1 (ppm)

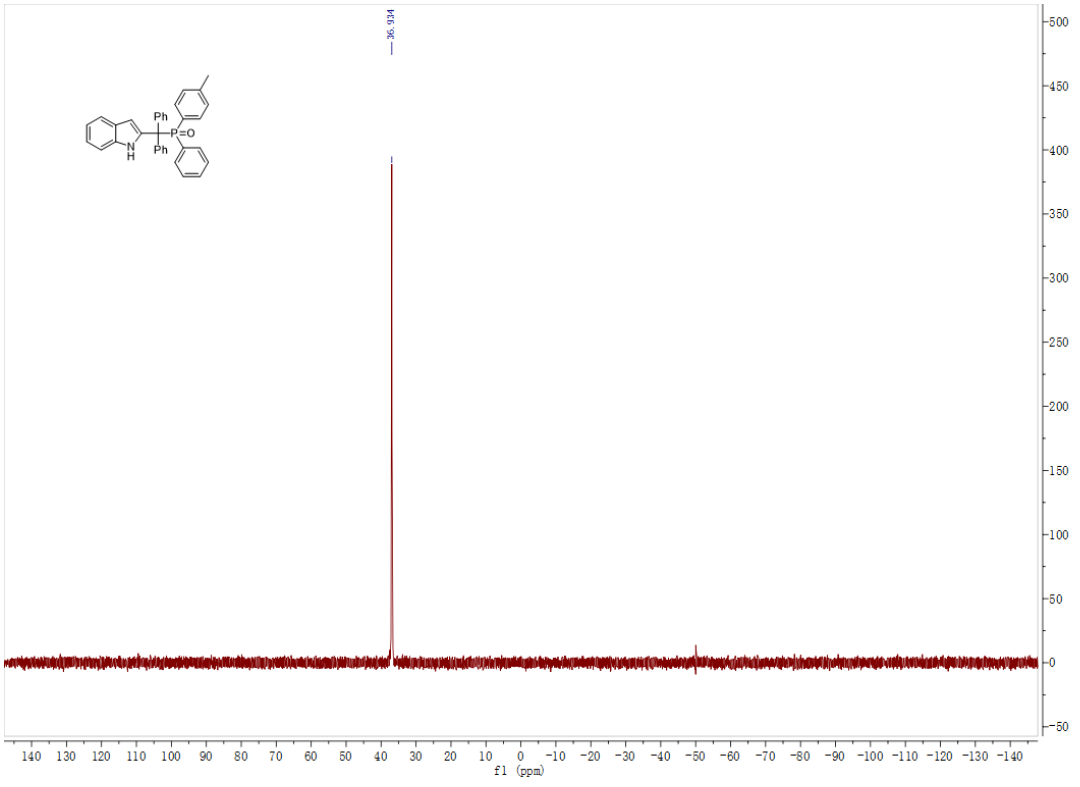

Ph
S
P=O
Ph
N
H
S
f1 (ppm)


29.177
Ph
S
P=O
Ph
S
N
H
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

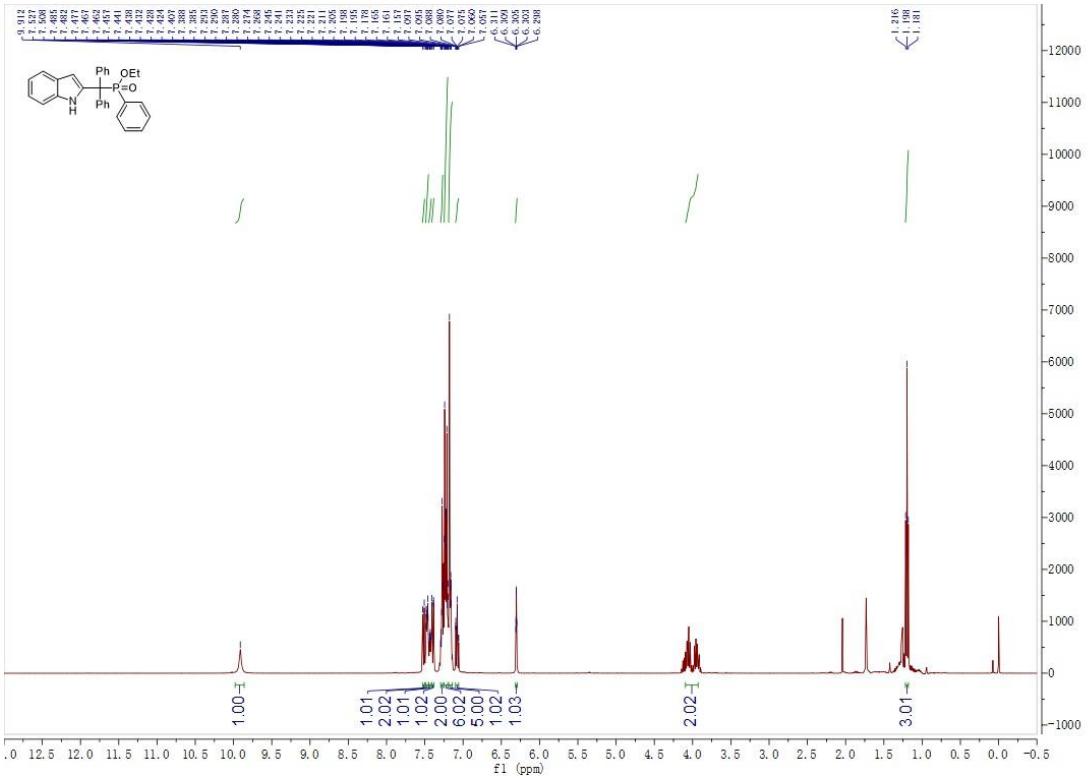
3an

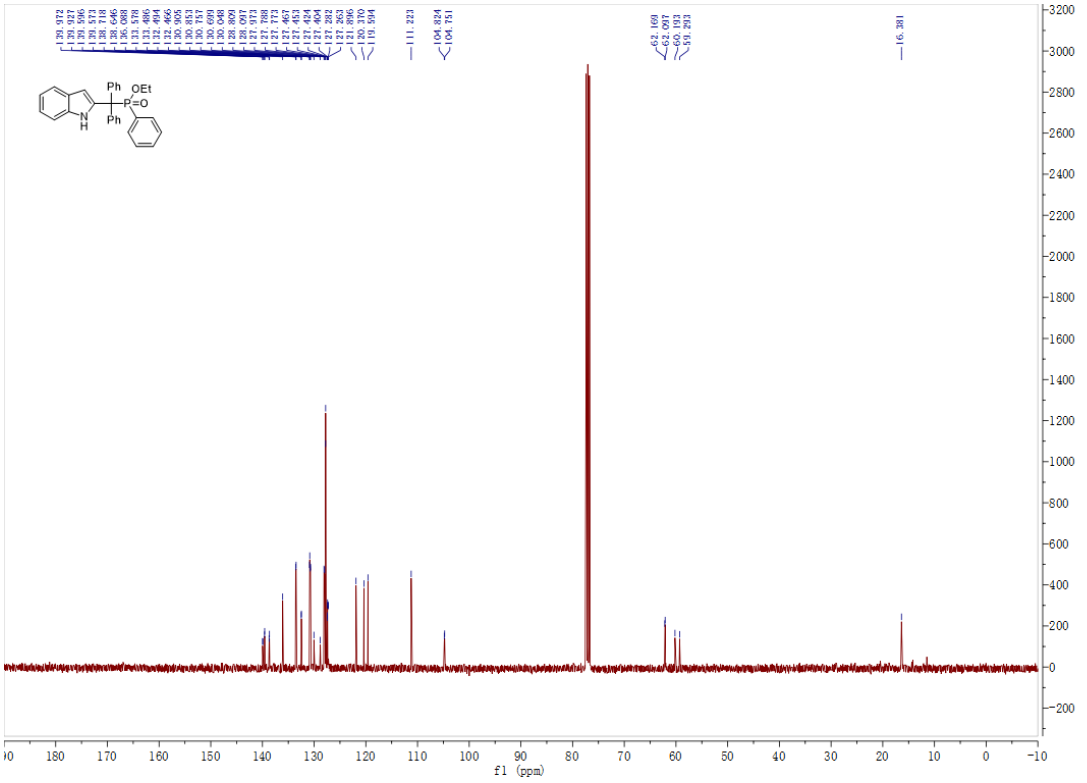

2.327
Ph
P=O
Ph
N
H
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
1.03
2.04
2.02
3.02
7.03
8.02
1.04
3.03
f1 (ppm)

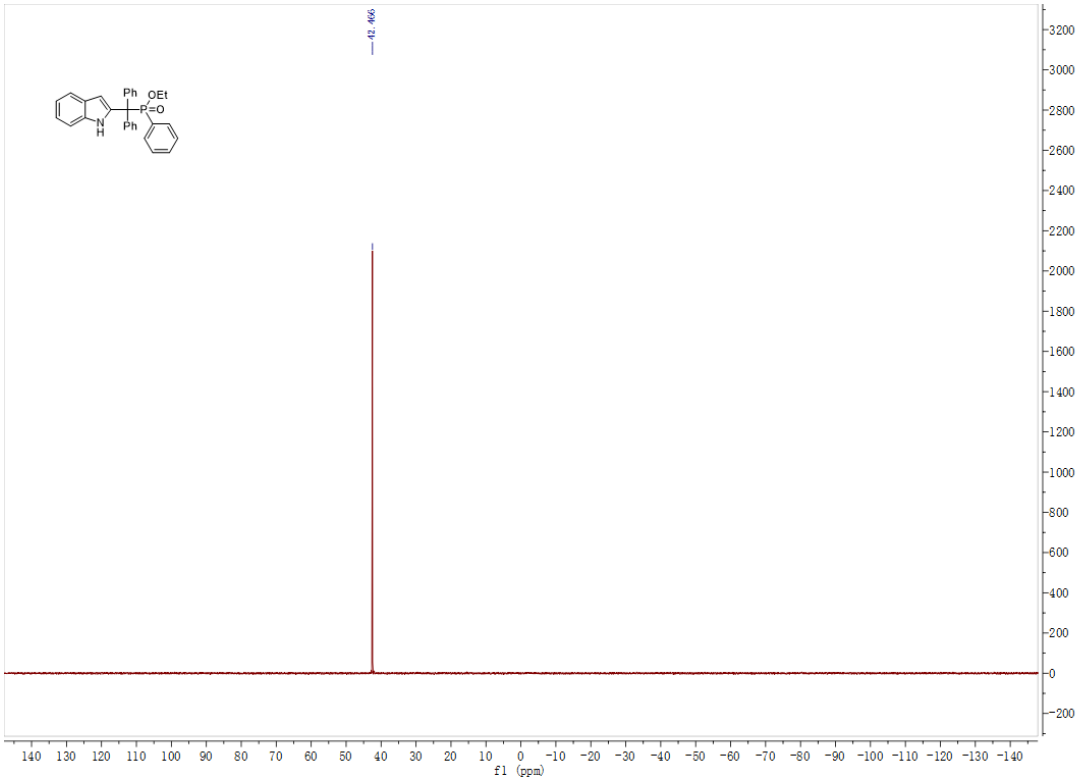




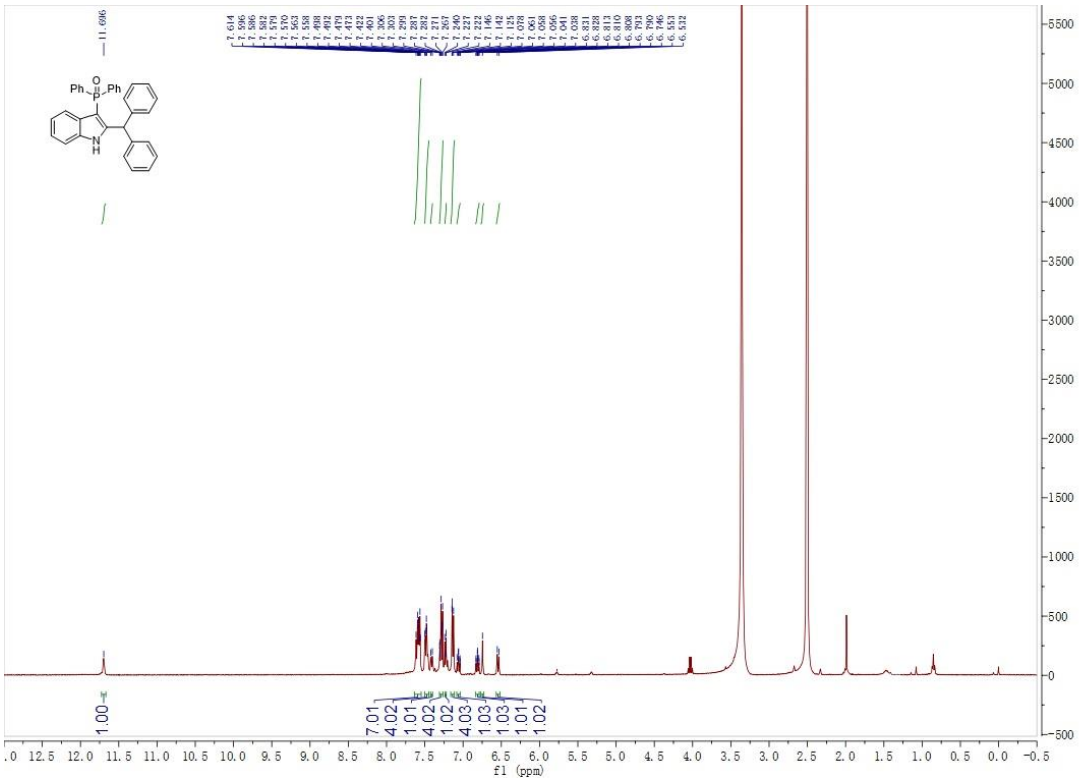
3ao

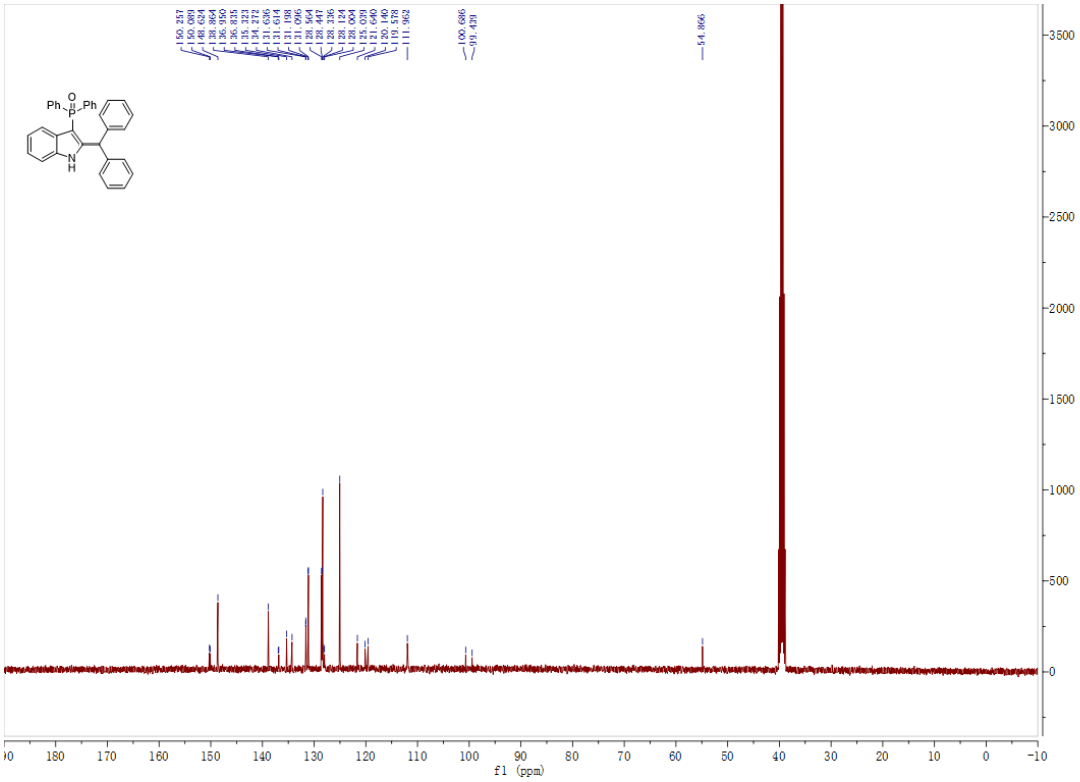

Ph
OEt
P=O
Ph
N
H
1.00
1.01
2.02
1.01
1.02
2.00
6.02
5.00
1.02
1.03
2.02
3.01
f1 (ppm)

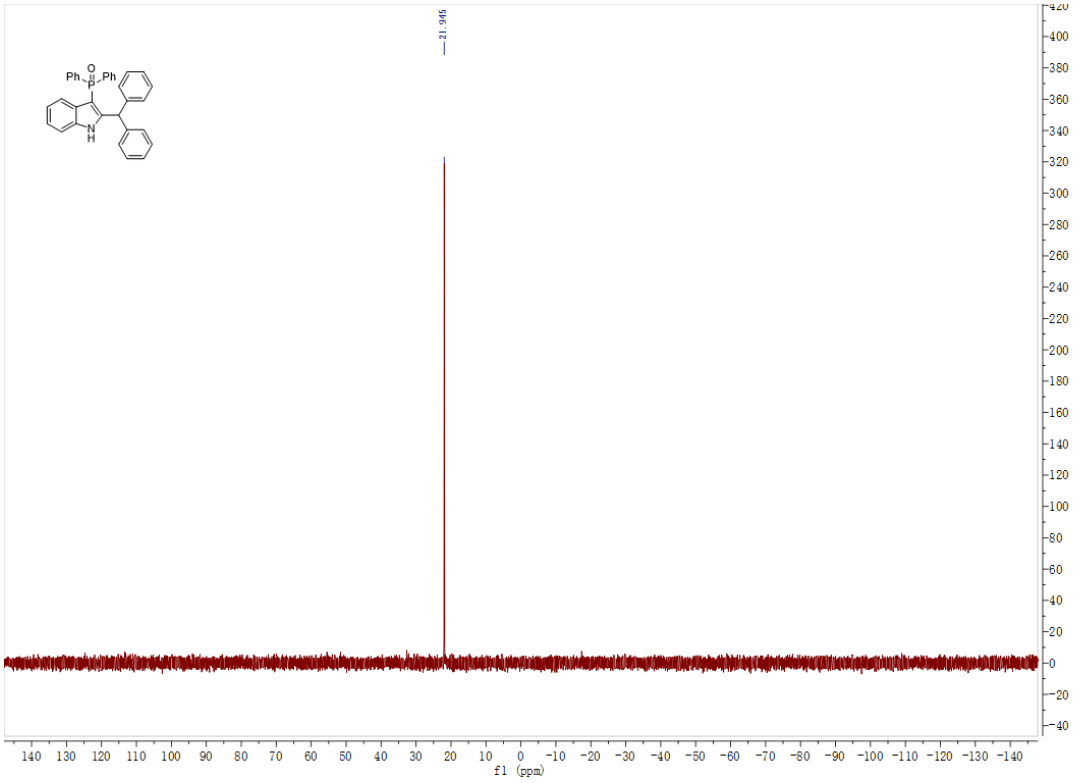

Ph
OEt
P=O
Ph
N
H
f1 (ppm)


42.466
Ph
OEt
P=O
Ph
N
H
f1 (ppm)

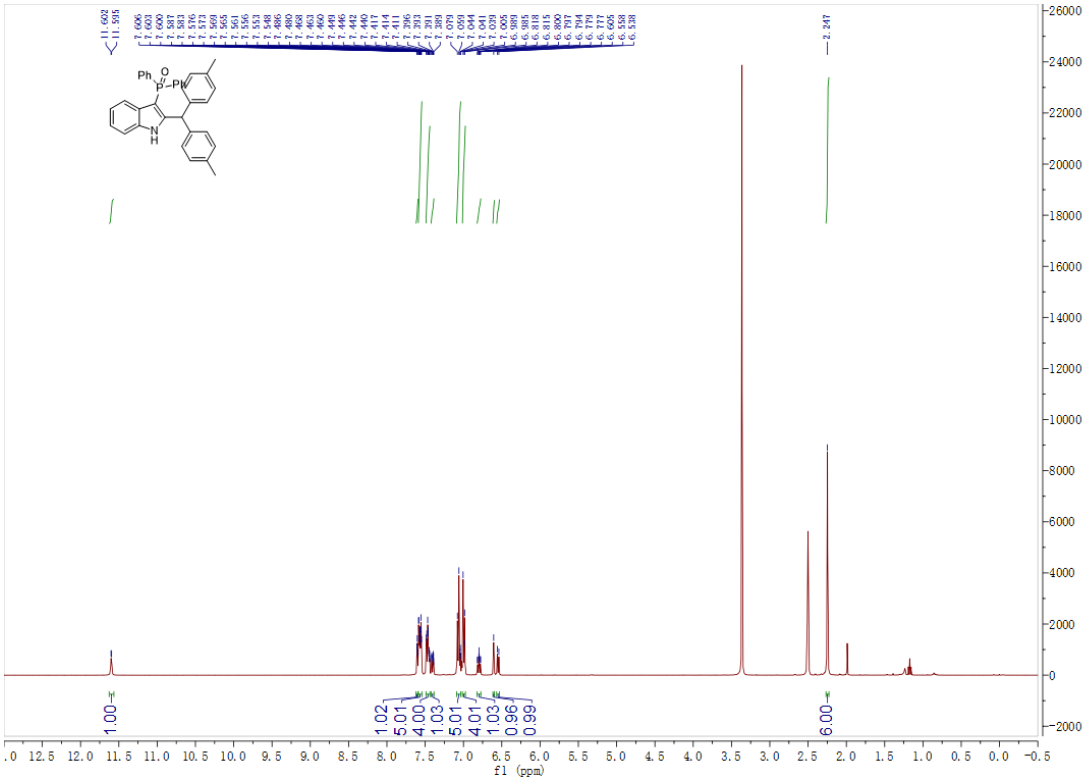
4aa


11.696
Ph
Ph
N
H
1.00
7.01
4.02
1.01
4.02
1.02
4.03
1.03
1.03
1.01
1.02
f1 (ppm)





4ba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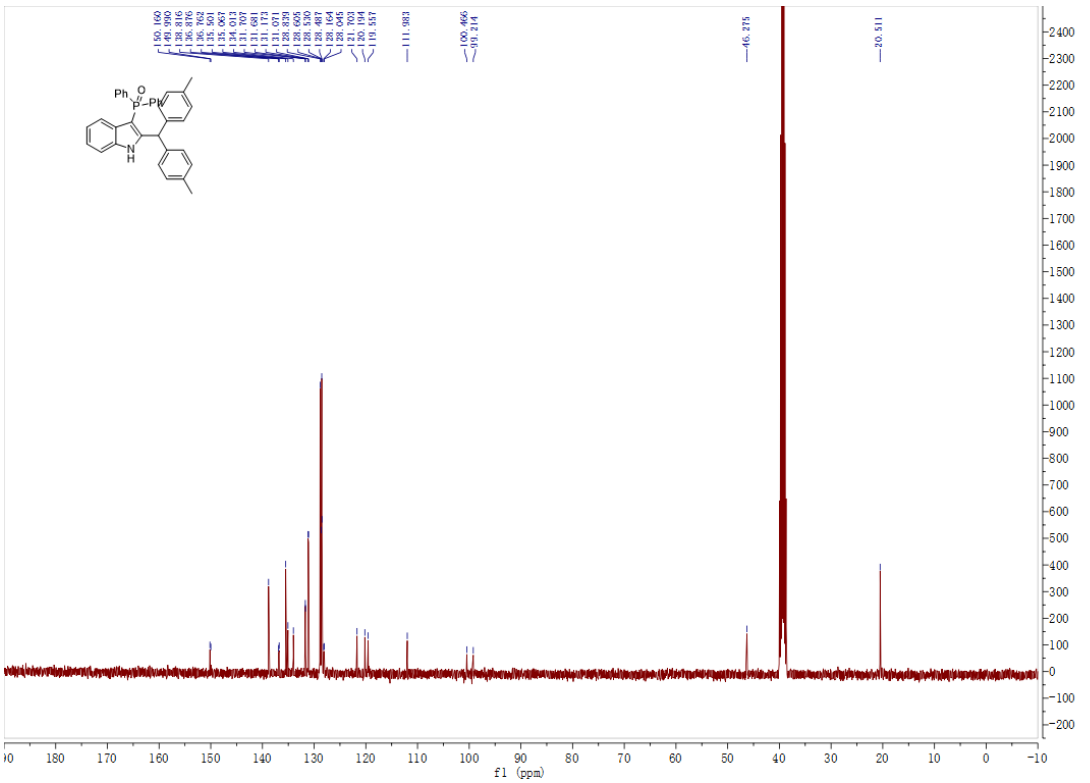
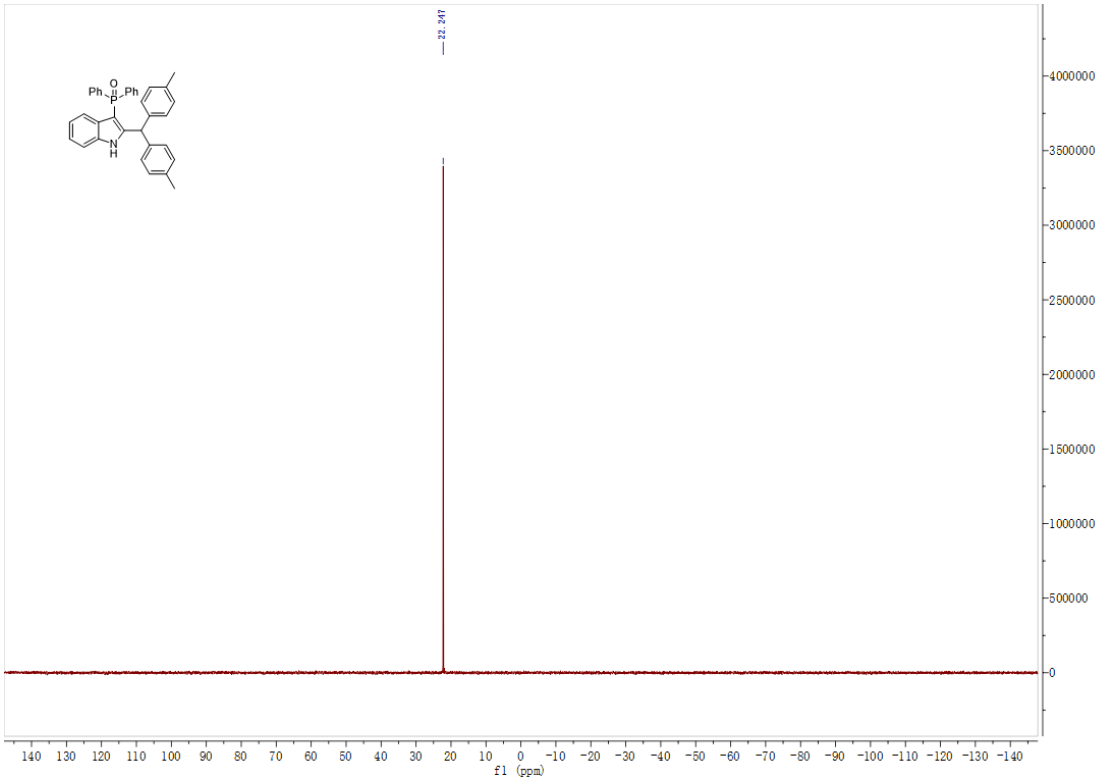
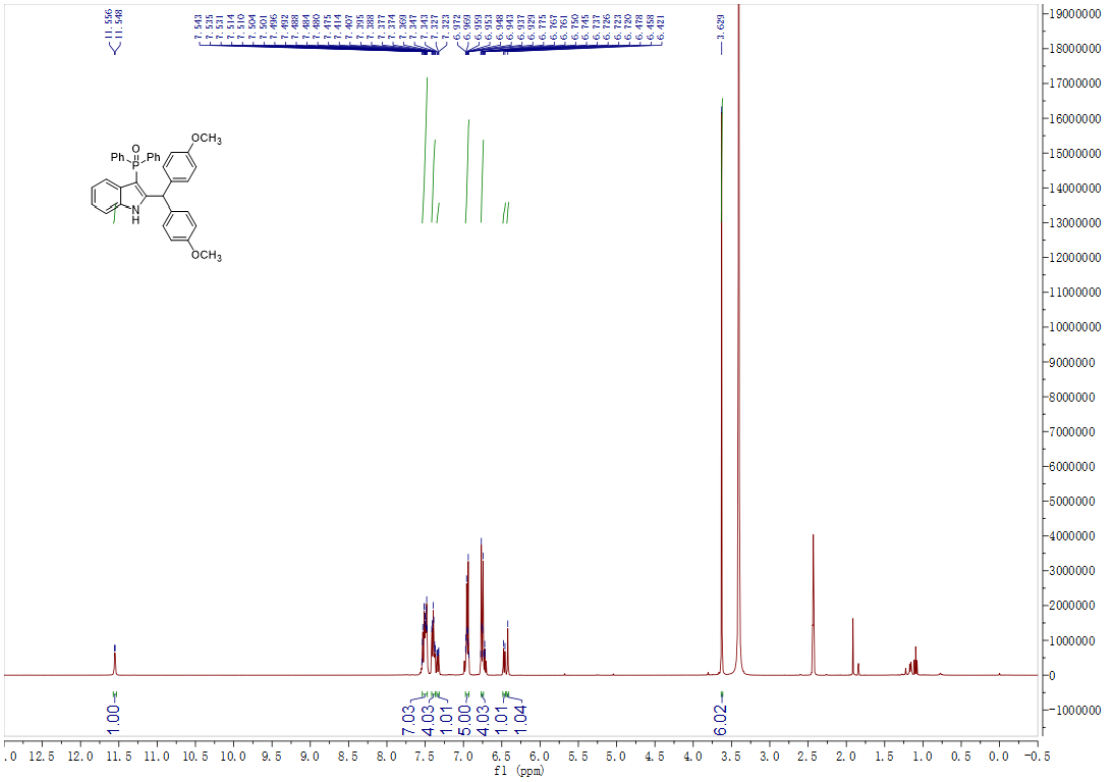
11.595
7.606
7.603
7.600
7.587
7.583
7.576
7.573
7.560
7.558
7.556
7.553
7.548
7.486
7.480
7.468
7.465
7.462
7.449
7.446
7.442
7.440
7.417
7.414
7.411
7.395
7.393
7.391
7.389
7.389
7.059
7.044
7.041
7.039
7.038
6.985
6.818
6.815
6.805
6.797
6.794
6.779
6.177
6.605
6.538
6.538
2.247
Ph
P
O
Ph
N
H
1.00
1.02
5.01
4.00
1.03
5.01
4.01
1.03
0.96
0.99
6.00
f1 (ppm)


150.169
149.990
138.816
136.876
136.762
135.561
135.067
134.013
131.707
131.661
131.171
131.071
128.859
128.656
128.565
128.487
128.164
128.045
121.703
120.194
119.557
111.983
100.466
93.214
46.275
20.511
Ph
P
O
Ph
N
H
f1 (ppm)


22.247
Ph
O
P
Ph
N
H
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

4ca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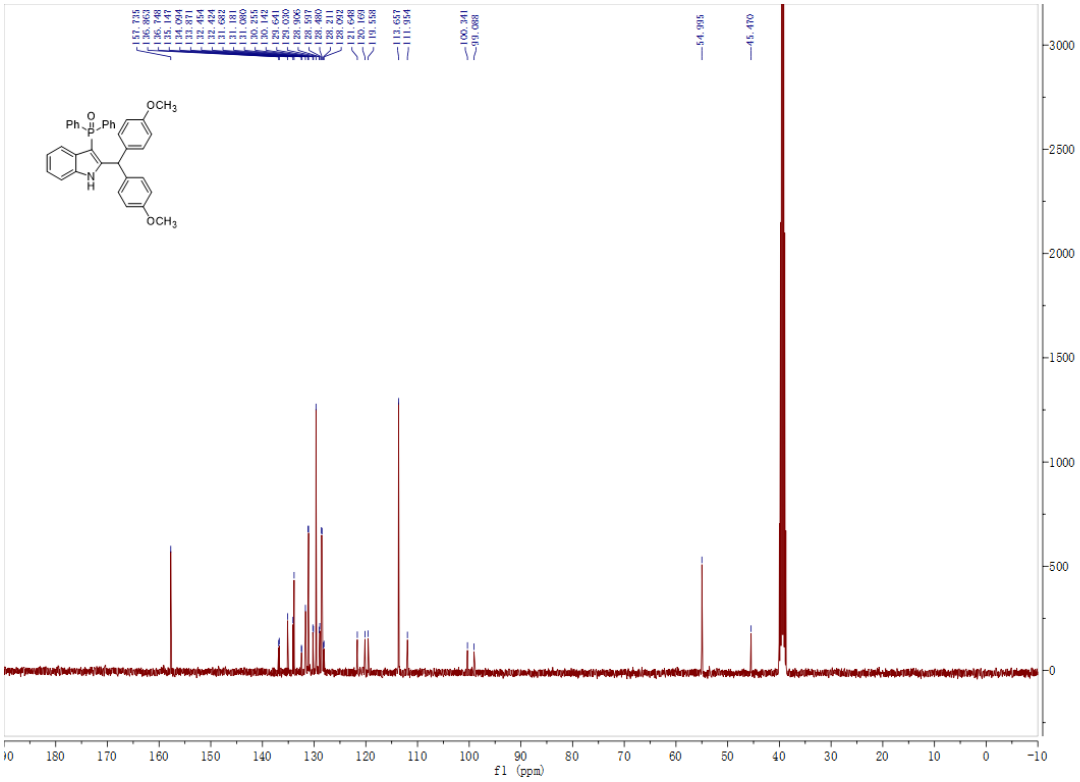
11.548
7.543
7.535
7.531
7.514
7.510
7.504
7.501
7.496
7.492
7.488
7.484
7.480
7.475
7.414
7.407
7.395
7.388
7.377
7.374
7.369
7.347
7.343
7.327
7.323
6.972
6.969
6.951
6.948
6.943
6.937
6.775
6.767
6.751
6.599
6.596
6.145
6.737
6.726
6.723
6.720
6.478
6.458
6.421
3.629
OCH3
Ph
O
P
Ph
N
H
OCH3
19000000
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
1.00
7.03
4.03
1.01
5.00
4.03
1.01
1.04
6.02
.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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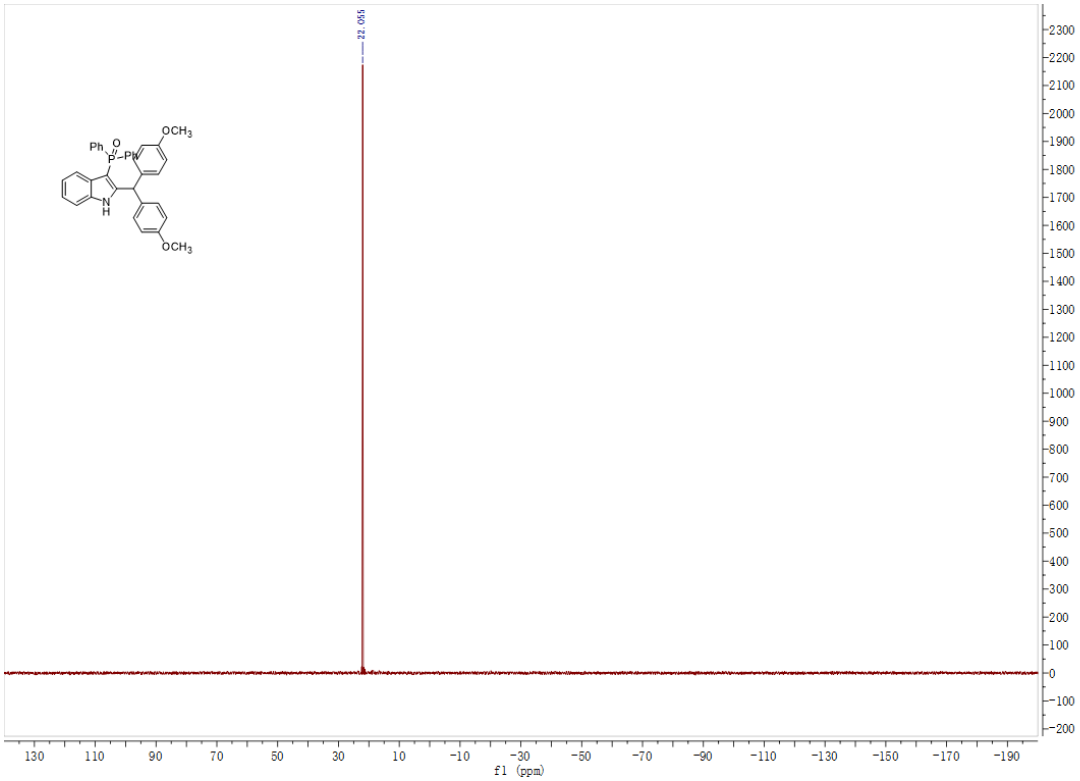
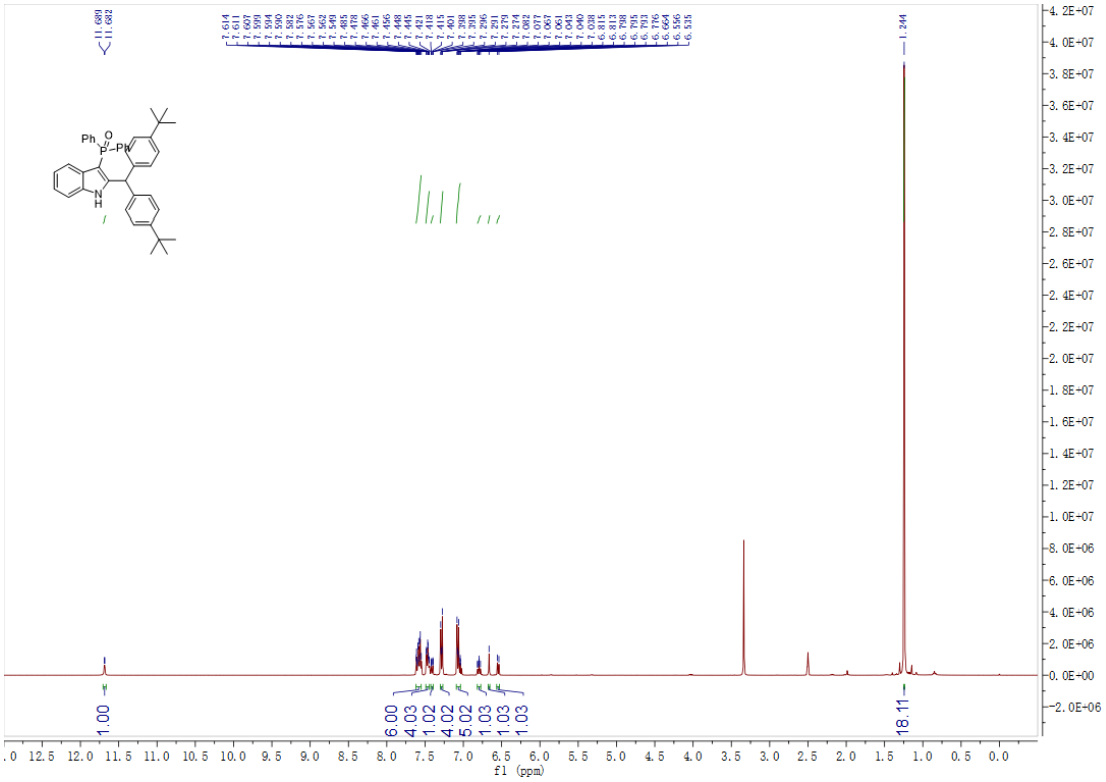
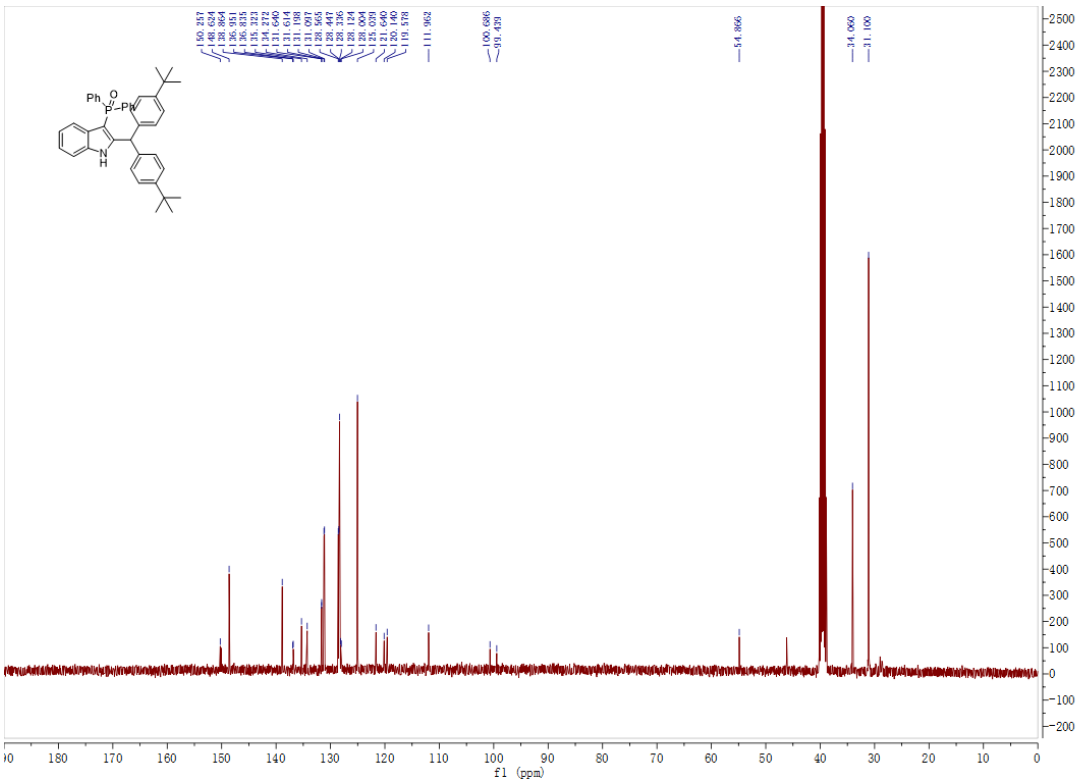
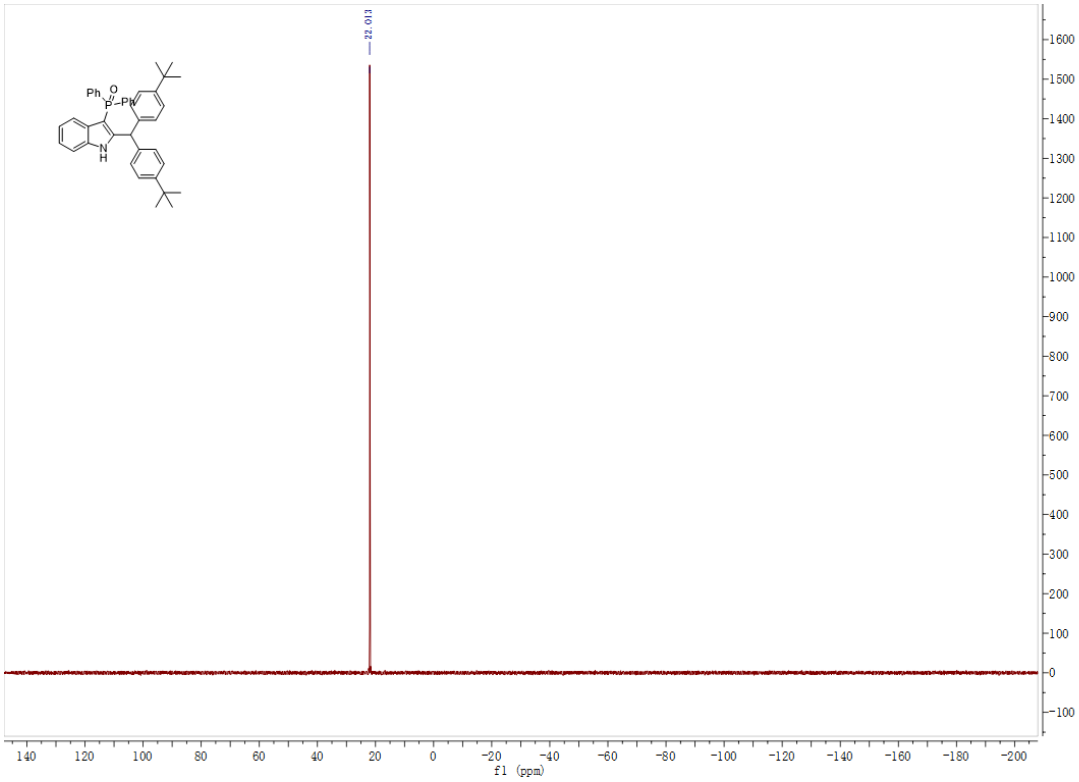
135.148
134.145
134.094
133.871
132.454
132.454
131.682
131.181
131.080
130.315
130.142
129.641
129.030
128.906
128.357
128.480
128.211
128.092
121.668
120.169
119.558
113.653
111.594
100.341
99.088
64.995
45.470
OCH3
Ph
O
P
Ph
N
H
OCH3
f1 (ppm)


32.055
OCH3
Ph
O
P
Ph
N
H
OCH3
f1 (ppm)

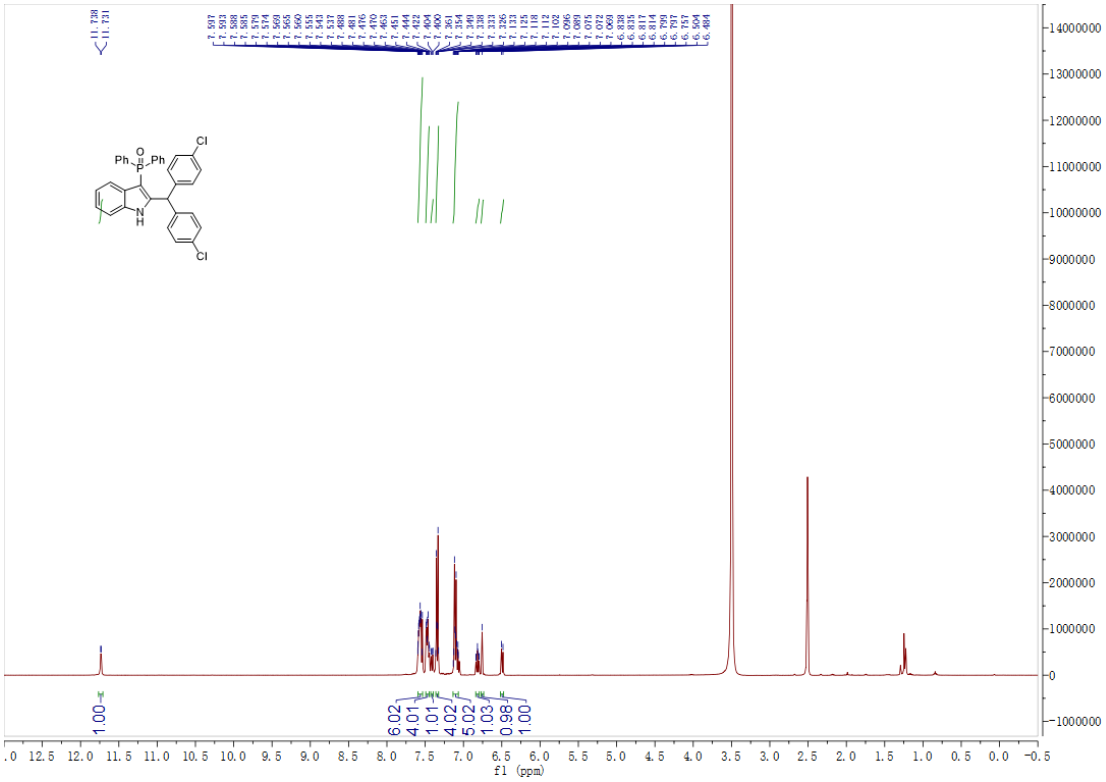
4da

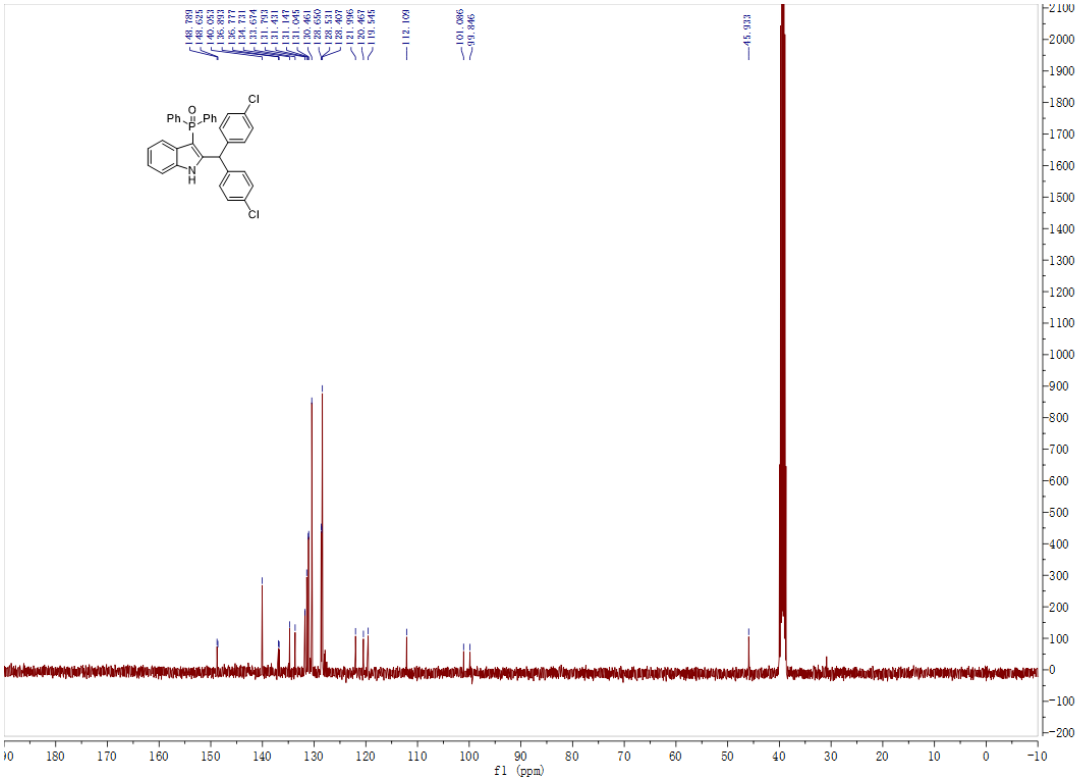

f1 (ppm)

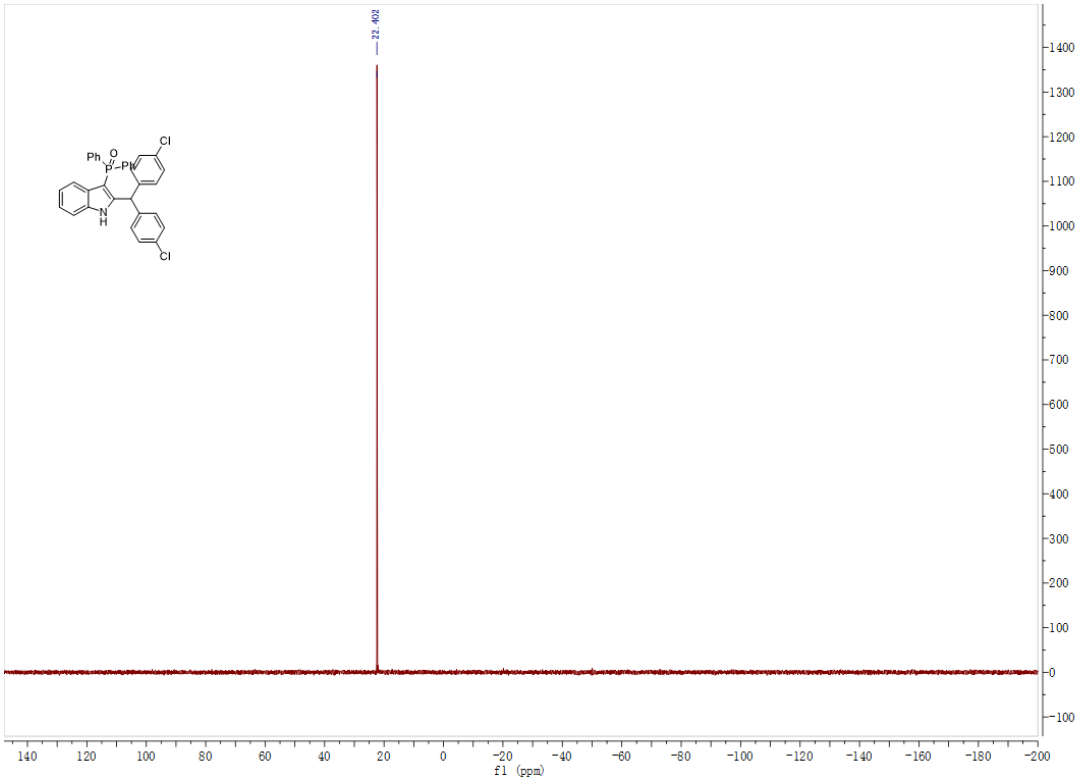

f1 (ppm)


22.013
f1 (ppm)

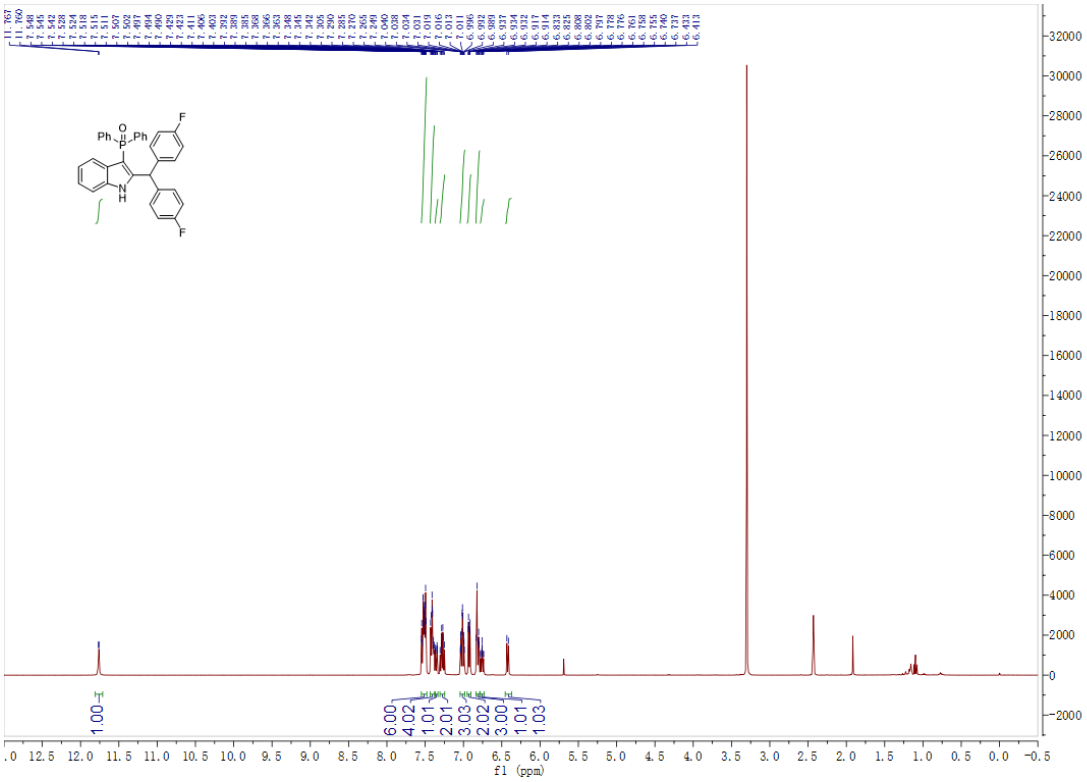
4ea


11.738
11.731
1.00
6.02
4.01
1.01
4.02
5.02
1.03
0.98
1.00
f1 (ppm)





4fa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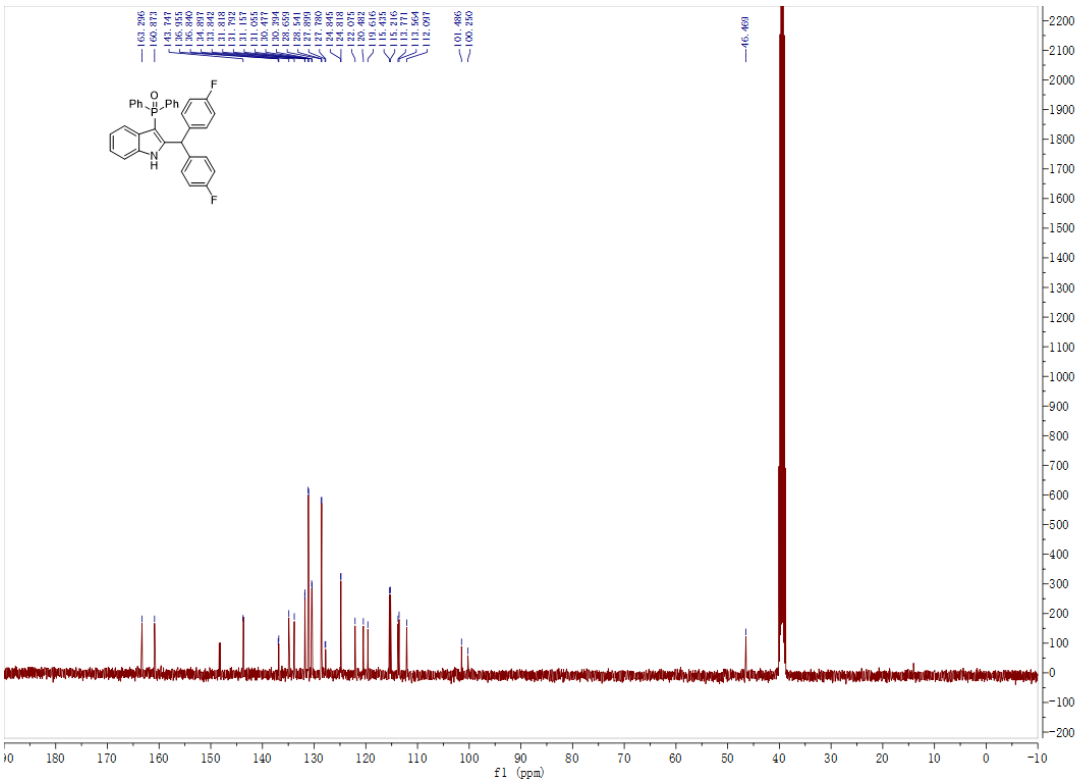
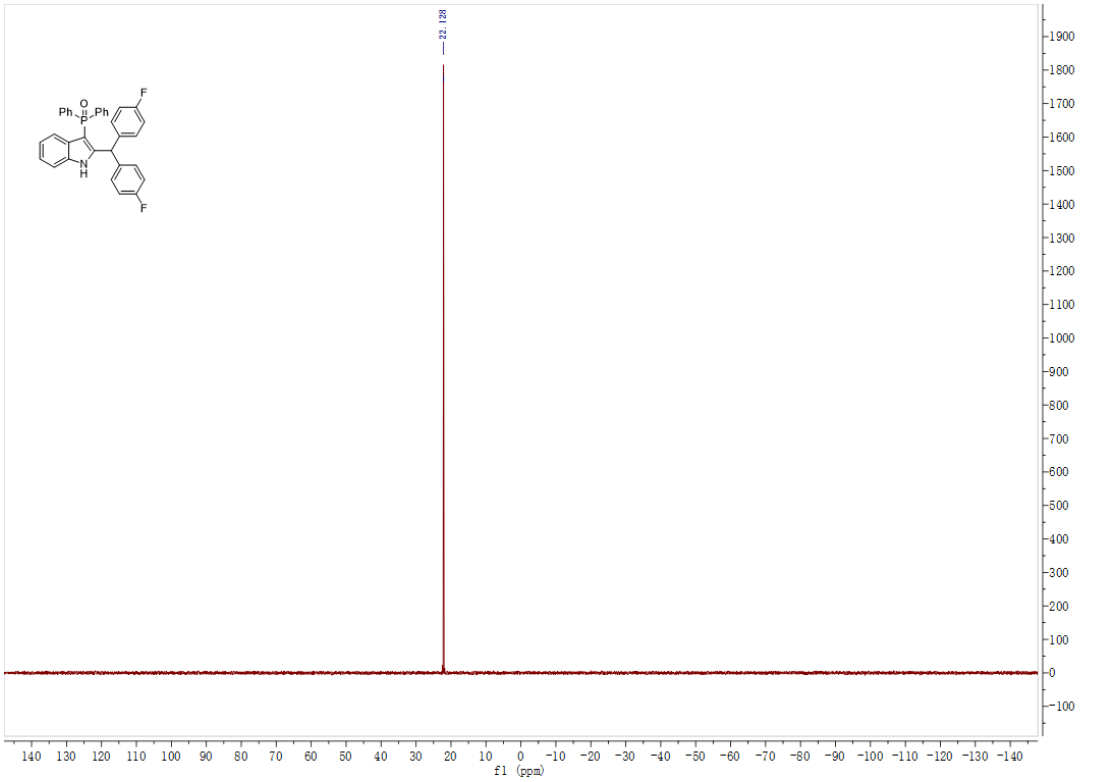
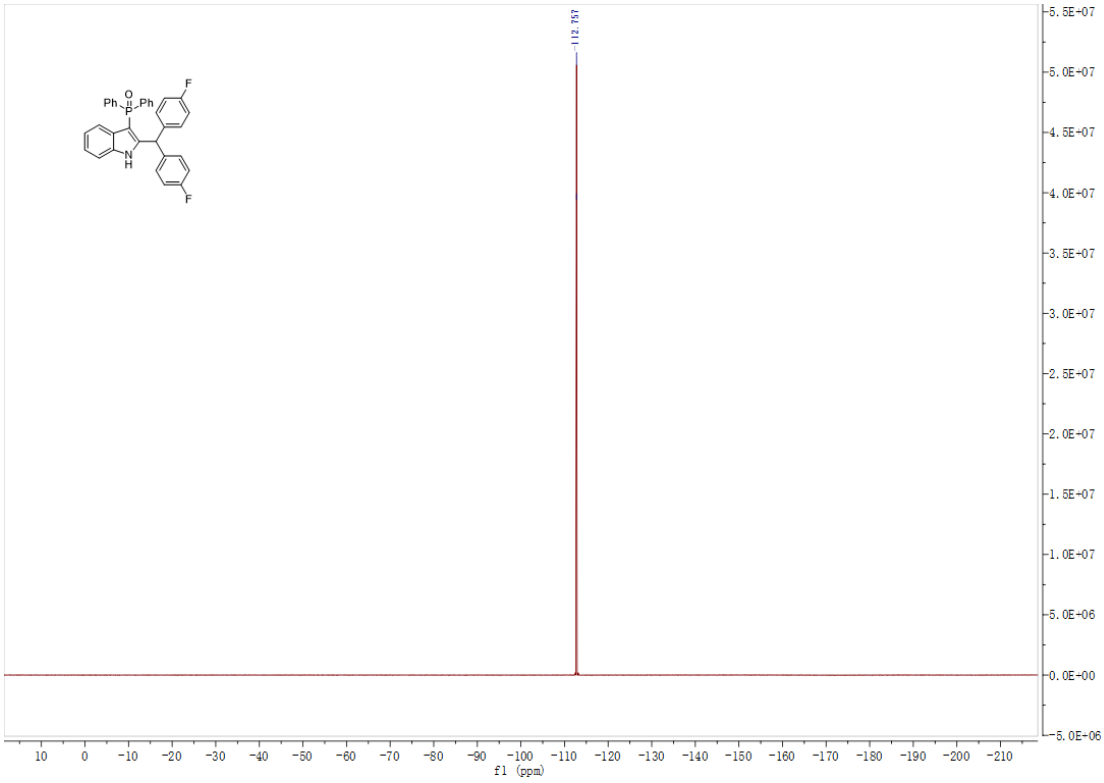
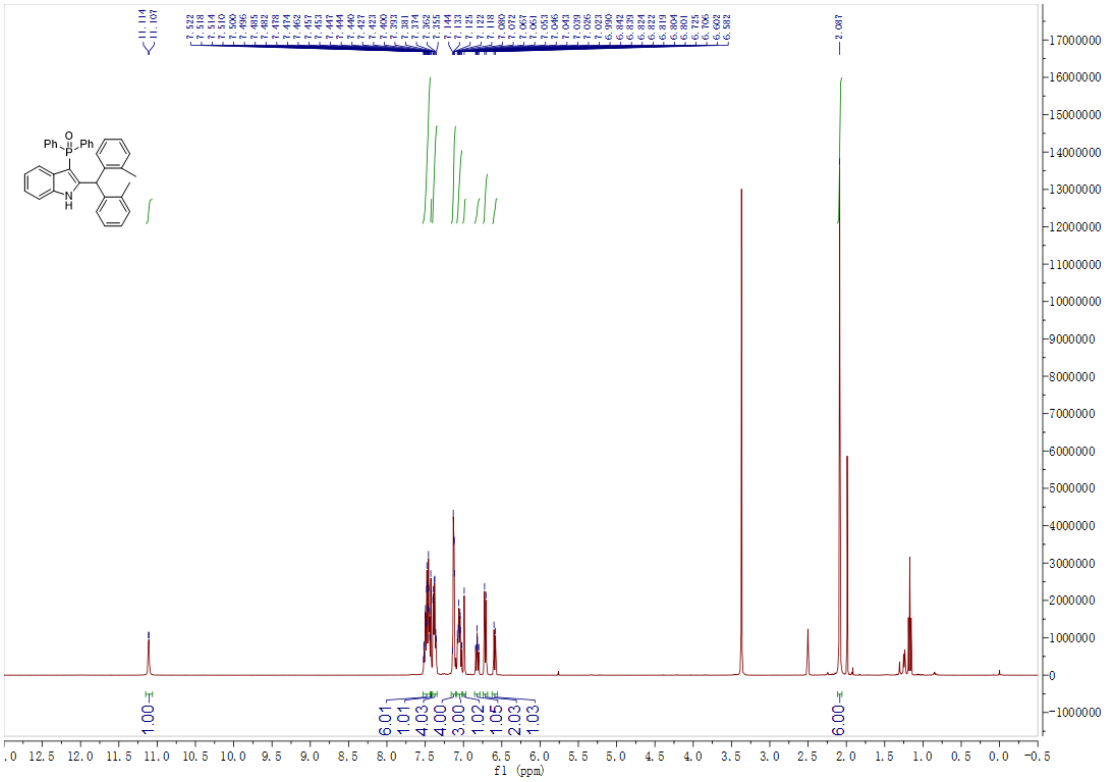
11.760
7.546
7.545
7.542
7.528
7.524
7.518
7.515
7.511
7.507
7.502
7.497
7.494
7.490
7.485
7.423
7.411
7.406
7.403
7.392
7.389
7.385
7.366
7.363
7.348
7.345
7.341
7.305
7.290
7.283
7.270
7.265
7.249
7.046
7.038
7.031
7.019
7.016
7.011
7.011
6.996
6.992
6.988
6.937
6.934
6.932
6.911
6.908
6.833
6.825
6.808
6.802
6.797
6.778
6.776
6.761
6.758
6.755
6.746
6.737
6.433
6.413
Ph
O
P
Ph
N
H
F
F
1.00
6.00
4.02
1.01
2.01
3.03
2.02
3.00
1.01
1.03
f1 (ppm)

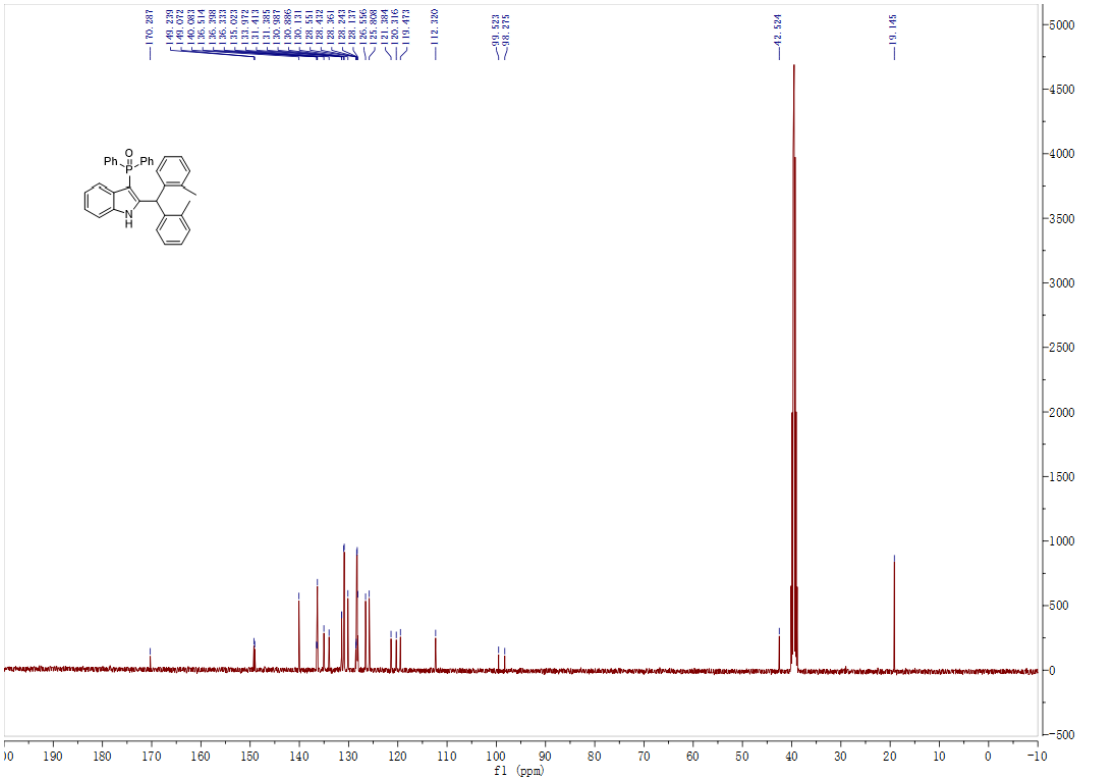

163.296
160.873
143.747
136.946
136.955
134.897
134.868
131.818
131.792
131.157
131.146
130.477
130.394
128.650
128.641
127.891
127.780
124.845
124.818
123.970
120.482
119.616
115.435
115.176
113.771
113.564
112.097
101.486
100.250
46.469
Ph
O
P
Ph
N
H
F
F
f1 (ppm)





4ga


11.114
11.107
7.522
7.518
7.514
7.510
7.500
7.496
7.481
7.478
7.474
7.462
7.455
7.453
7.447
7.444
7.440
7.427
7.423
7.400
7.393
7.381
7.374
7.362
7.355
7.144
7.133
7.125
7.122
7.118
7.080
7.072
7.067
7.061
7.051
7.046
7.043
7.039
7.036
7.023
6.990
6.842
6.839
6.824
6.822
6.819
6.804
6.801
6.725
6.706
6.702
6.582
2.087
Ph
O
P
Ph
N
H
1.00
6.01
1.01
4.03
4.00
3.00
1.02
1.05
2.03
1.03
6.00
f1 (ppm)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149.072
140.083
136.514
136.398
135.330
135.023
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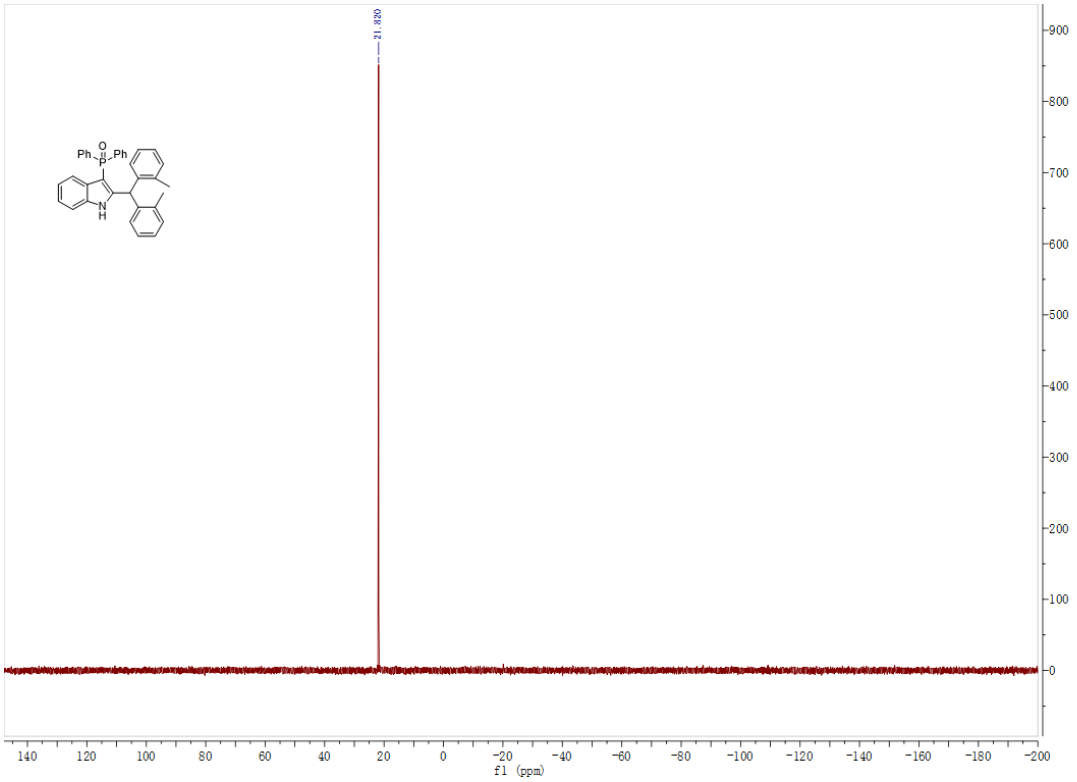
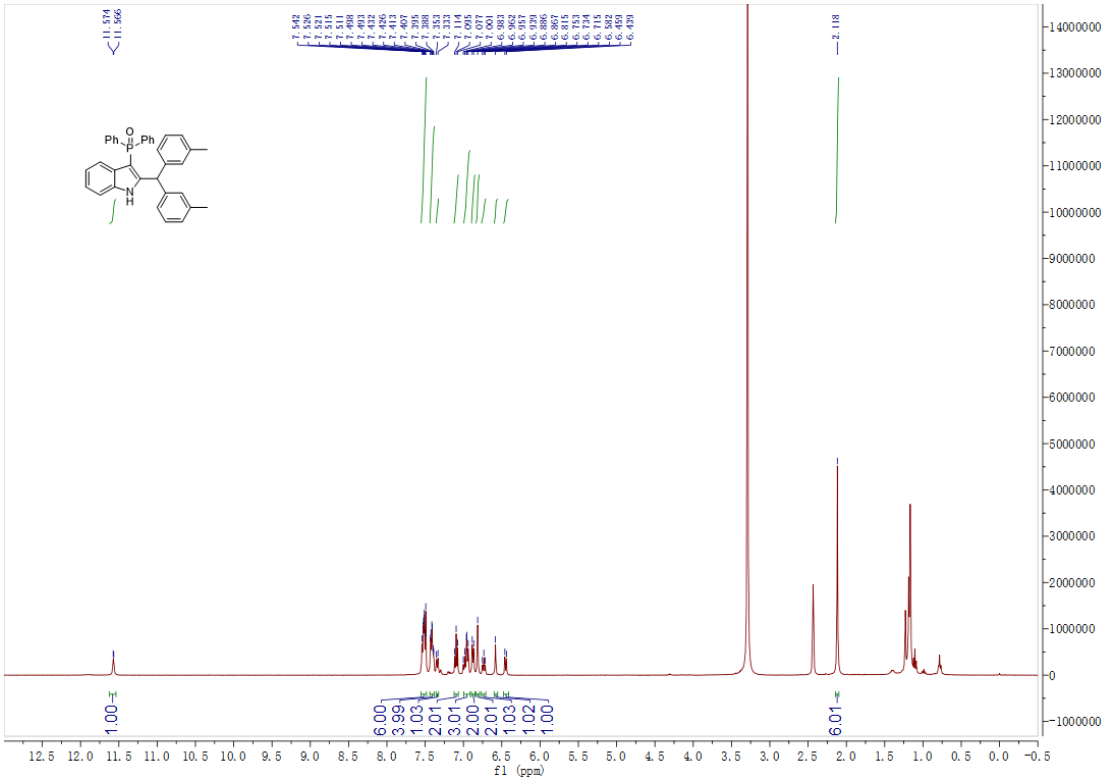
131.401
131.365
130.987
130.886
130.131
128.551
128.432
128.361
128.243
128.137
125.156
125.008
121.394
120.316
119.472
112.320
93.523
93.275
42.524
19.145
Ph
O
P
Ph
N
H
f1 (ppm)


21.820
Ph
O
P
Ph
N
H
f1 (ppm)

4ha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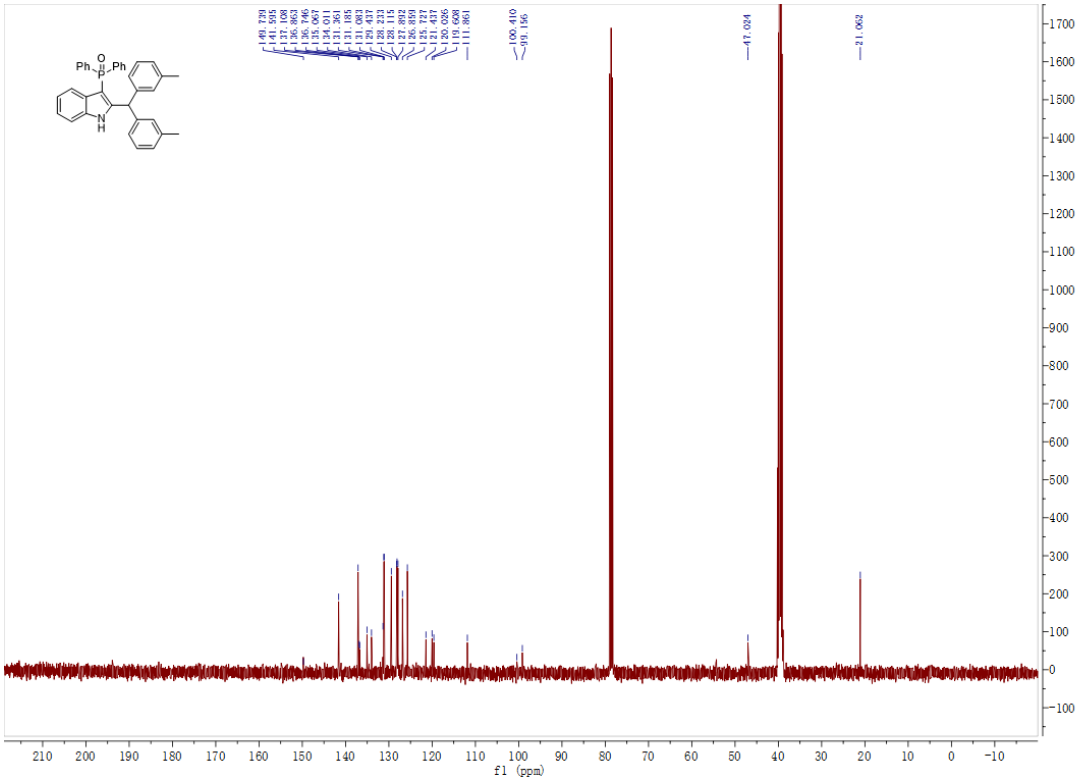
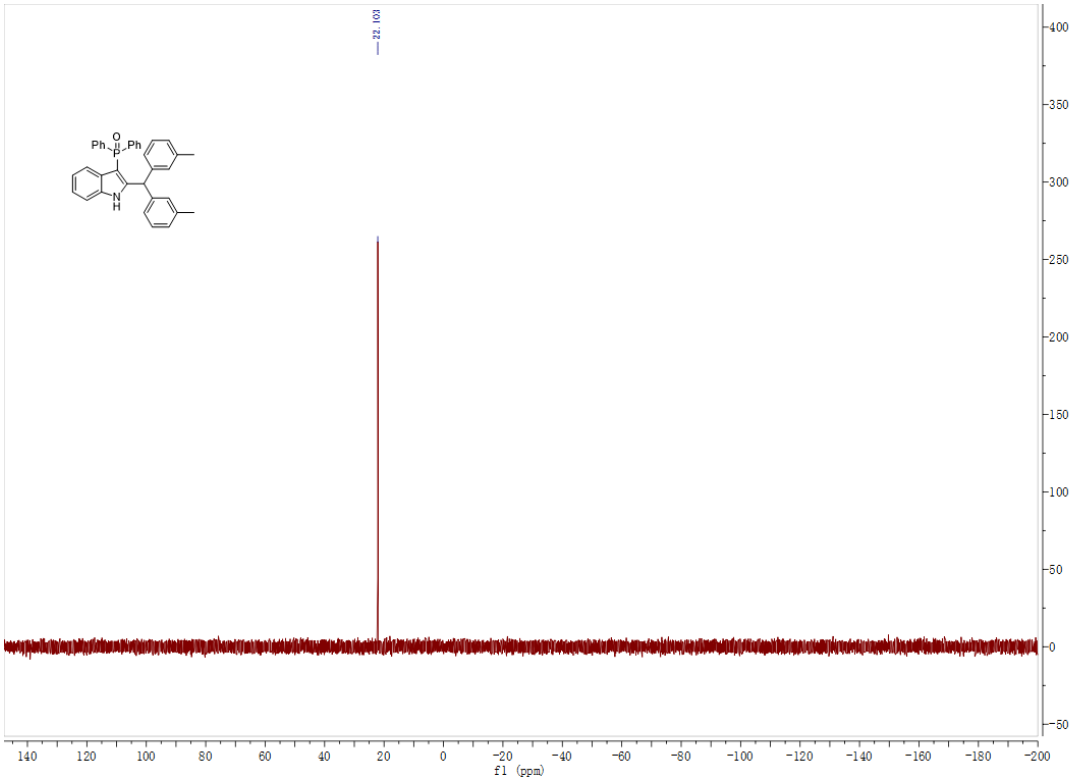
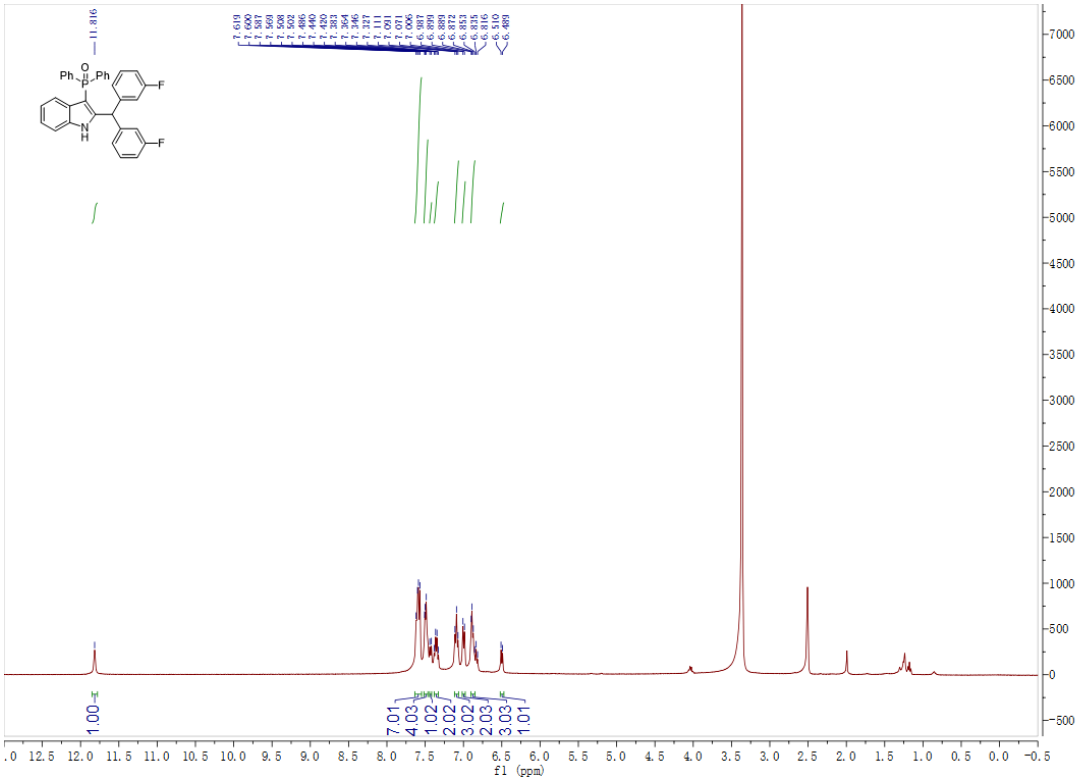
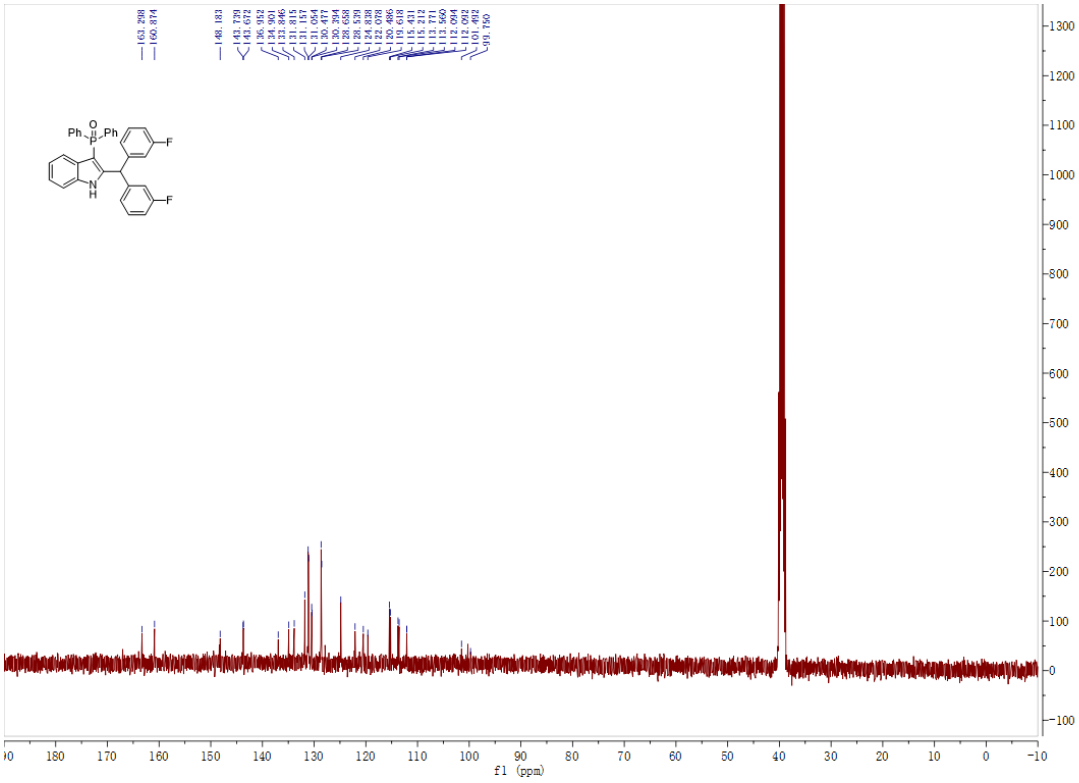
11.566
7.542
7.536
7.521
7.515
7.511
7.498
7.493
7.432
7.426
7.413
7.407
7.395
7.388
7.351
7.332
7.114
7.095
7.077
7.030
6.983
6.962
6.957
6.939
6.886
6.867
6.815
6.753
6.734
6.715
6.582
6.459
6.439
2.118
Ph
O
P
Ph
N
H
1.00
6.00
3.99
1.03
2.01
3.01
2.00
2.01
1.03
1.02
1.00
6.01
f1 (ppm)

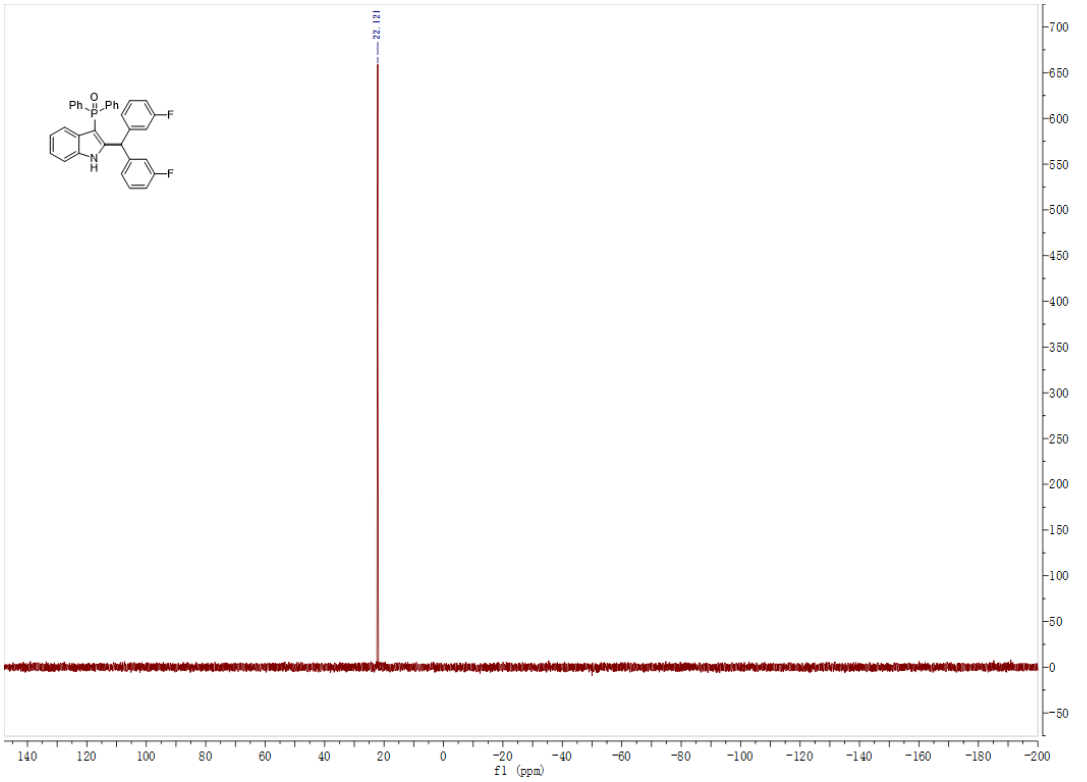


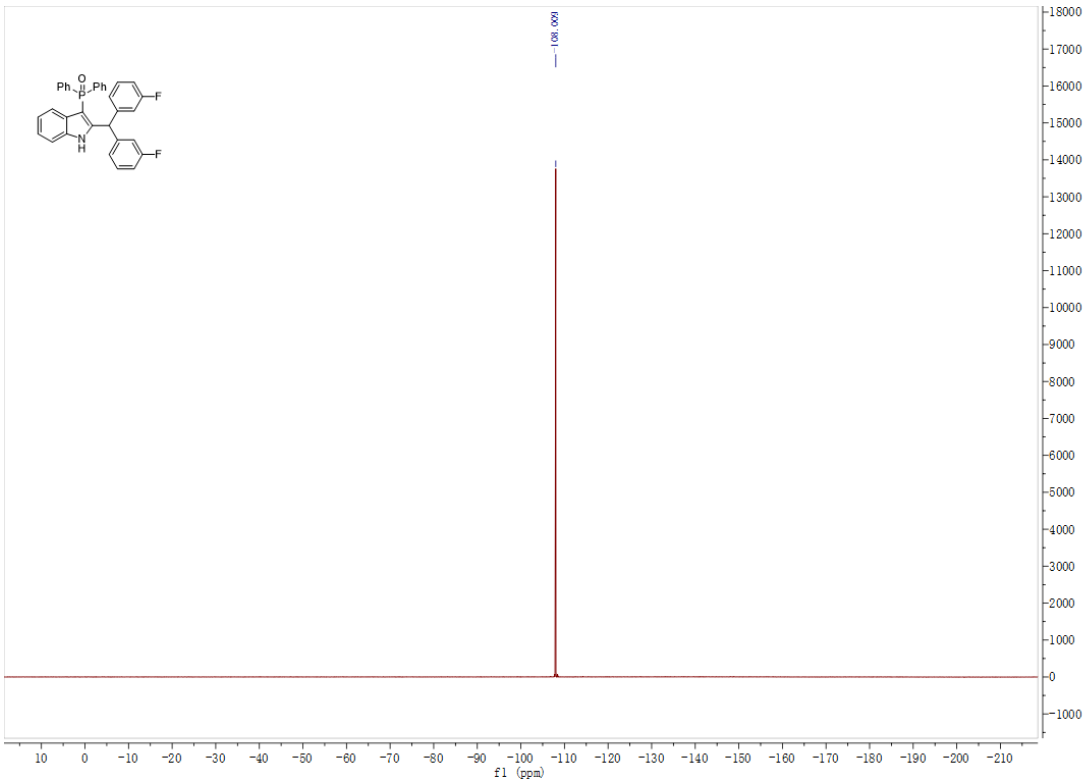


4ia

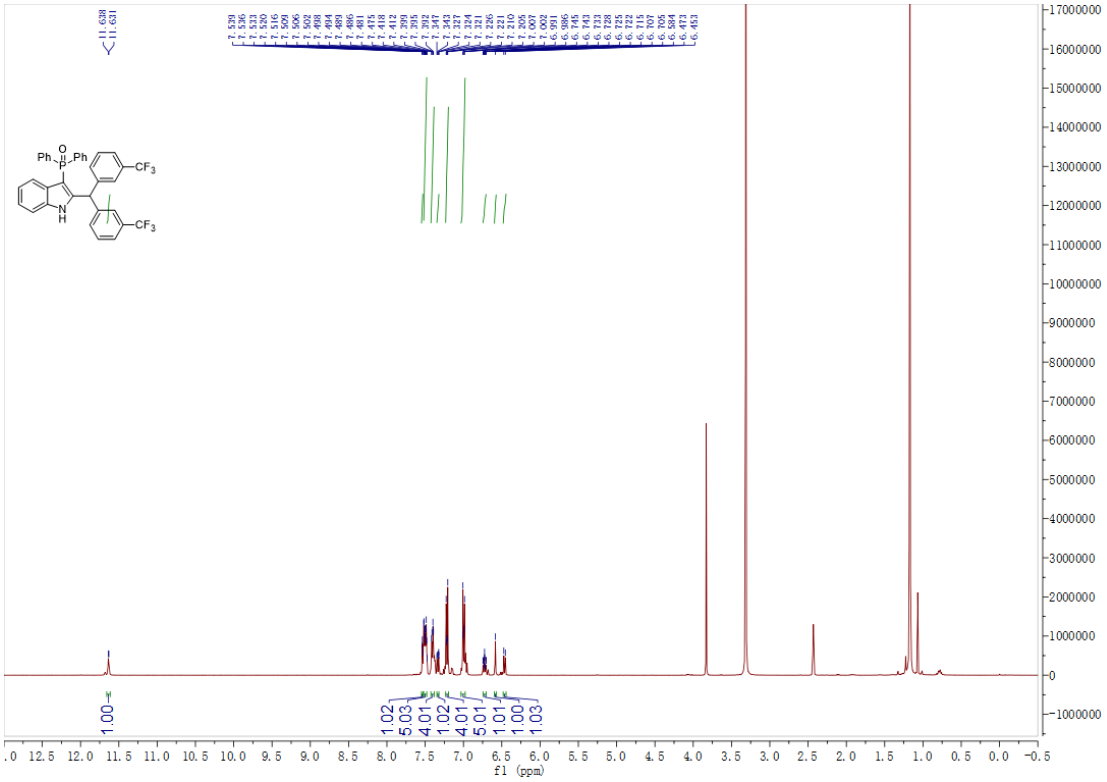

11.816
7.619
7.600
7.587
7.569
7.508
7.502
7.486
7.460
7.445
7.383
7.364
7.346
7.137
7.111
7.091
7.071
7.066
6.895
6.889
6.872
6.853
6.835
6.816
6.510
6.493
1.00
7.01
4.03
1.02
2.02
3.02
2.03
3.03
1.01
f1 (ppm)

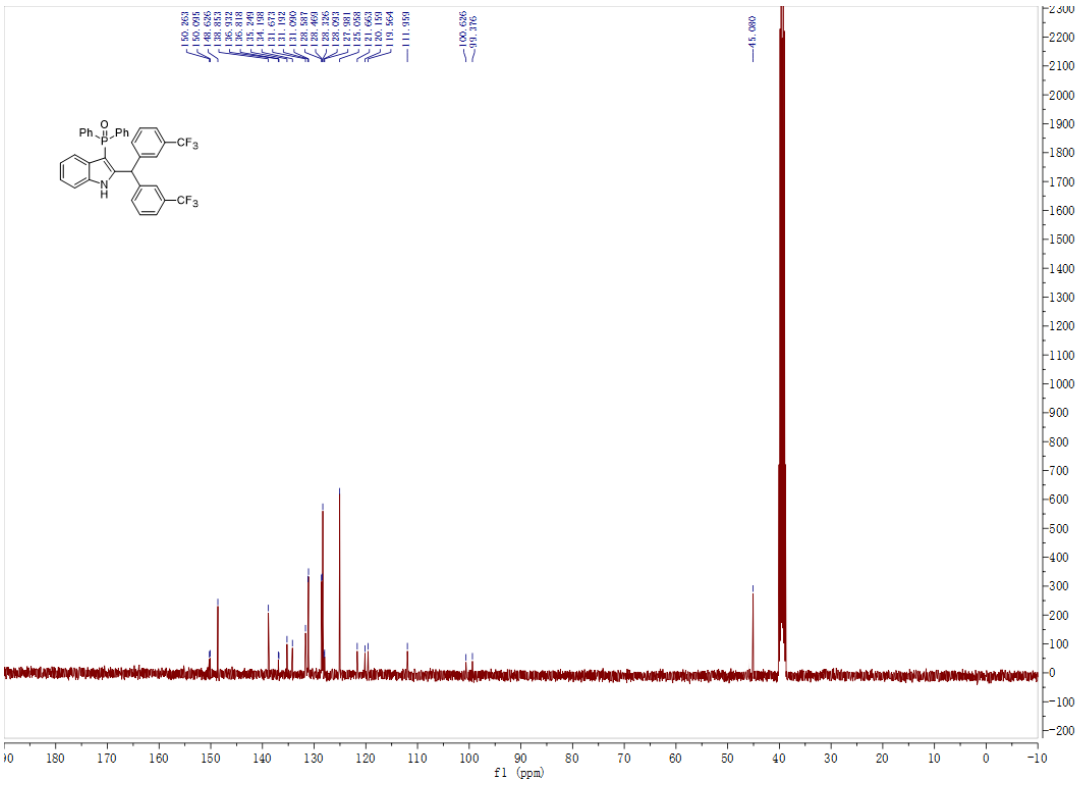

163.398
160.874
148.183
143.739
143.672
136.952
134.901
133.946
131.815
131.157
131.054
130.947
130.394
128.658
128.539
124.838
123.709
120.486
119.618
115.431
115.171
113.171
113.560
112.094
112.002
103.492
93.750
f1 (ppm)

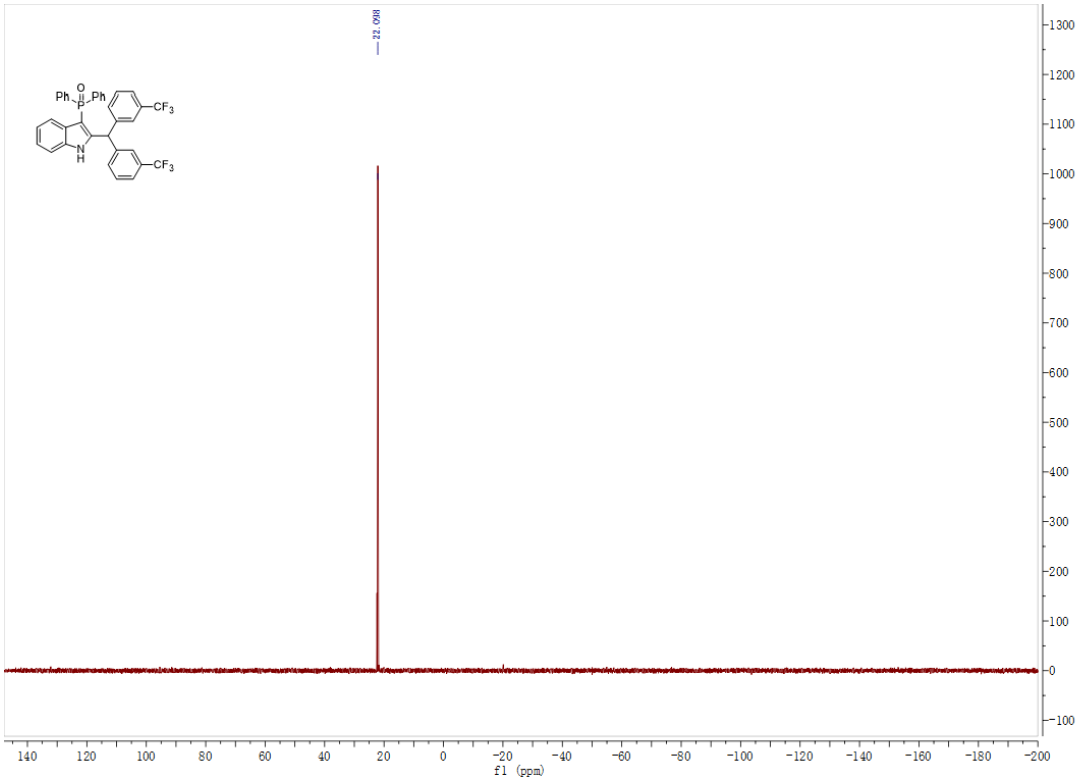

22.121
Ph
O
P
Ph
F
F
N
H
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

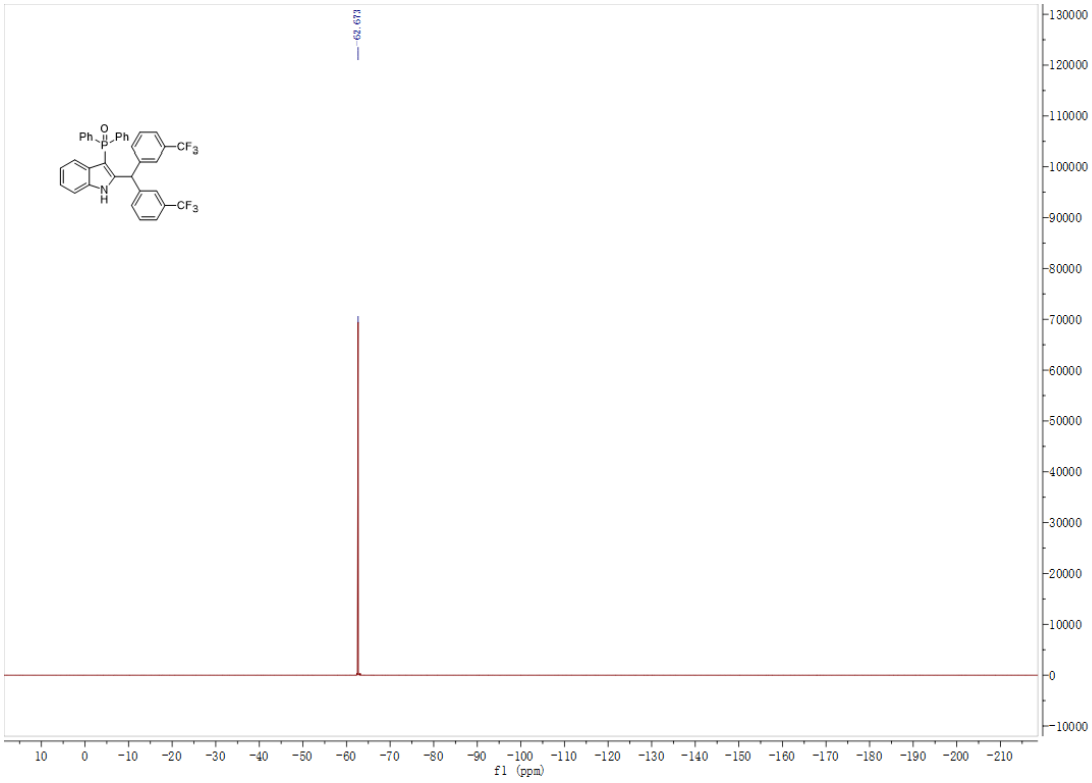

108.009
Ph
O
P
Ph
F
F
N
H
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

4ja

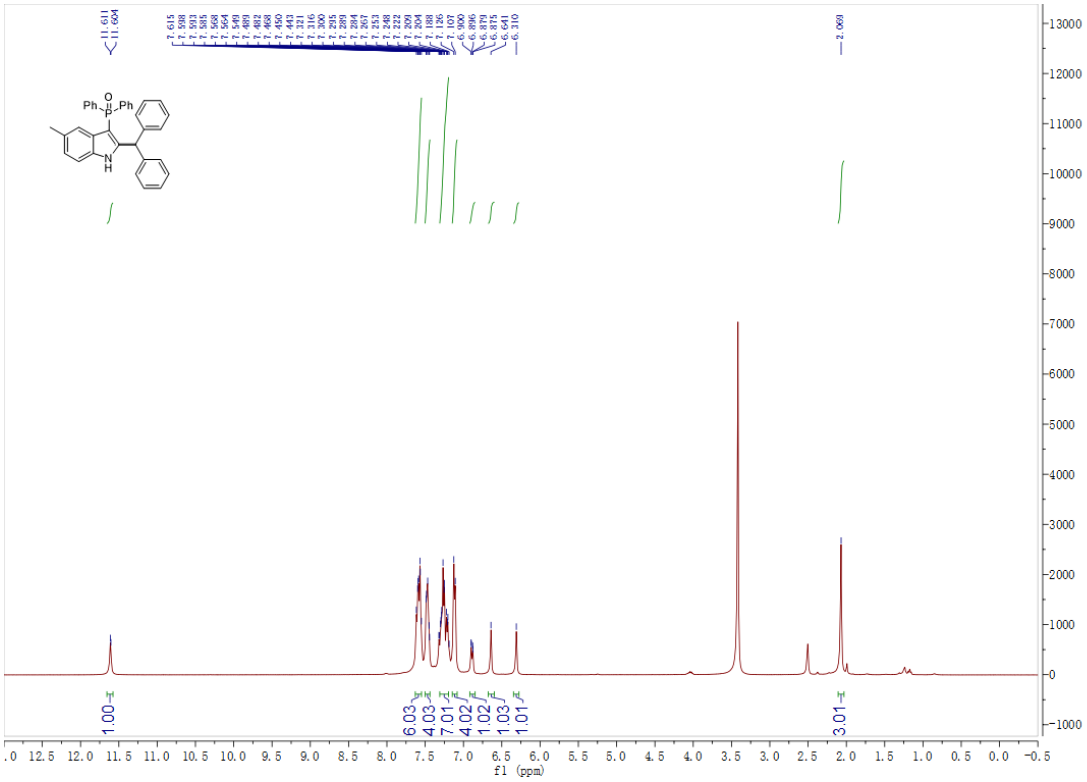

11.638
11.631
7.539
7.536
7.533
7.520
7.516
7.509
7.506
7.502
7.498
7.494
7.493
7.486
7.481
7.475
7.418
7.414
7.412
7.399
7.395
7.392
7.345
7.343
7.337
7.334
7.331
7.326
7.221
7.216
7.205
7.009
7.002
6.991
6.986
6.646
6.643
6.141
6.133
6.128
6.123
6.122
6.715
6.707
6.636
6.634
6.484
6.473
6.453
Ph
P
O
Ph
CF3
N
H
CF3
1.00
1.02
5.03
4.01
1.02
4.01
5.01
1.01
1.00
1.03
f1 (ppm)

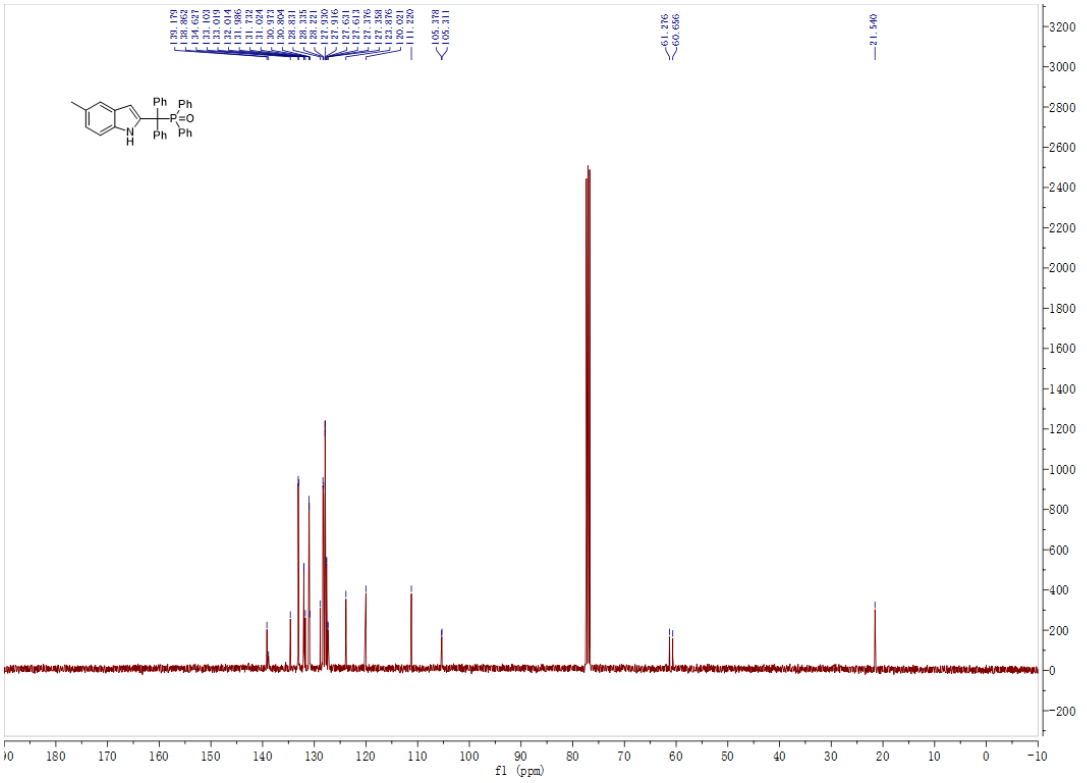

150.363
140.070
138.626
138.053
136.932
136.618
135.249
134.198
131.673
131.193
131.026
128.587
128.469
128.285
127.981
125.058
121.663
120.316
119.564
111.950
100.626
91.376
45.080
Ph
P
O
Ph
CF3
N
H
CF3
f1 (ppm)

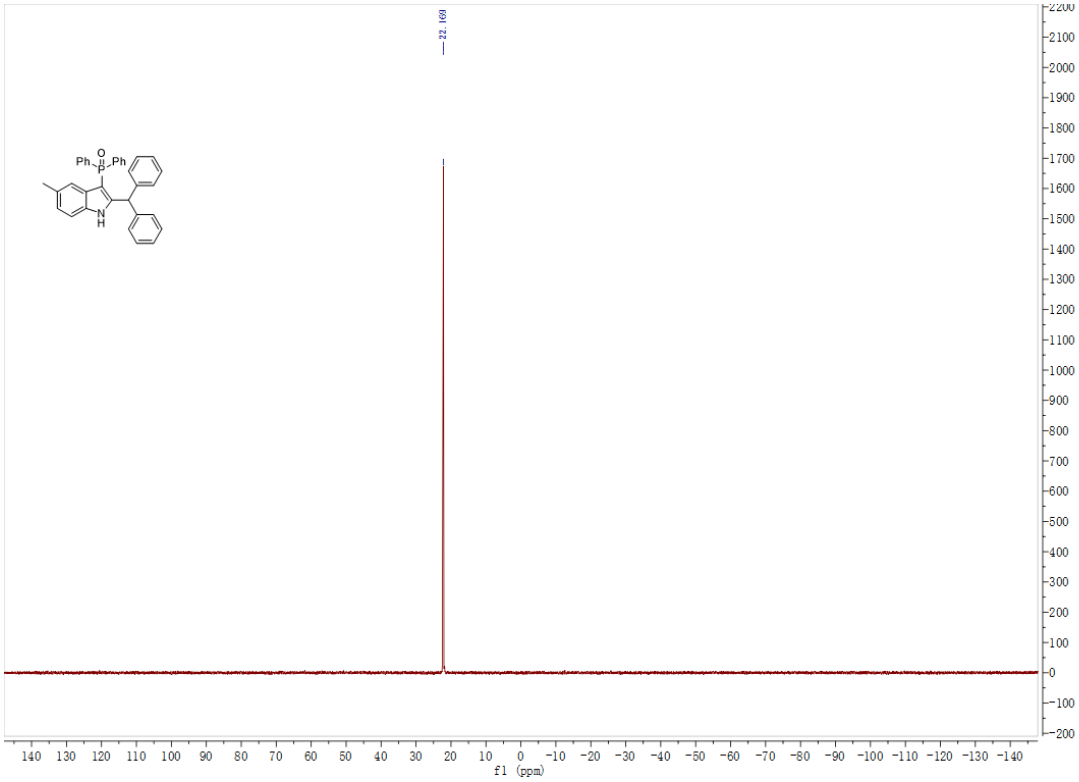




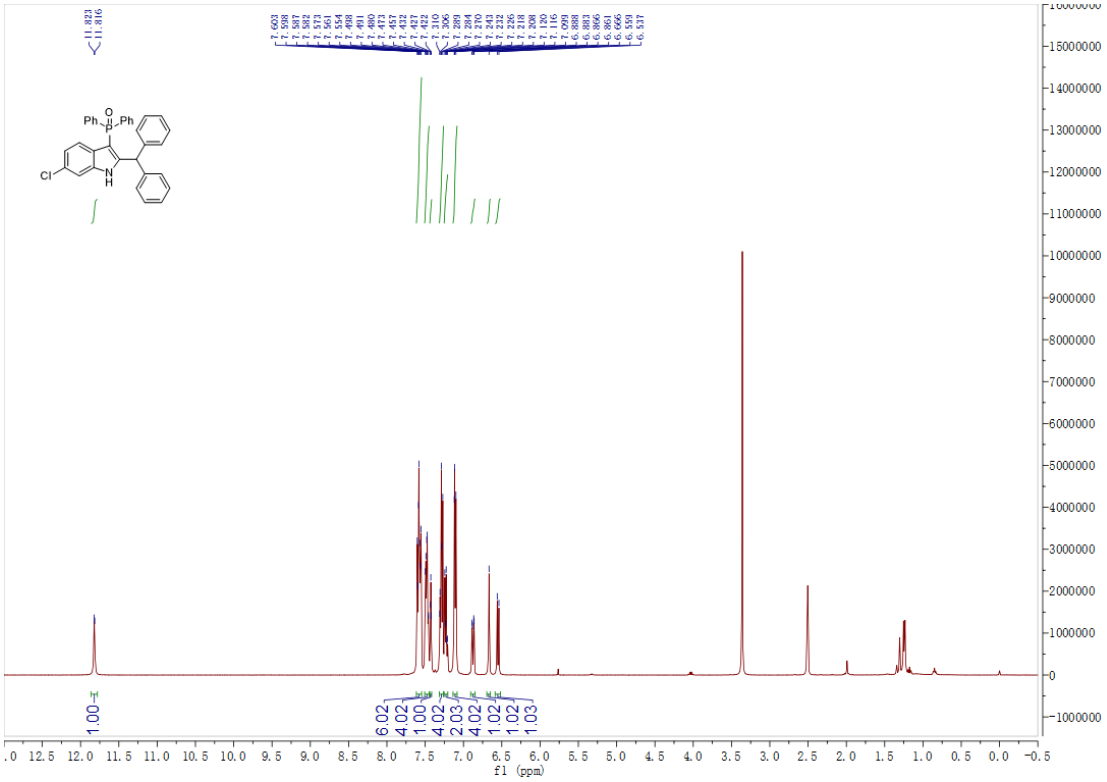
4ka

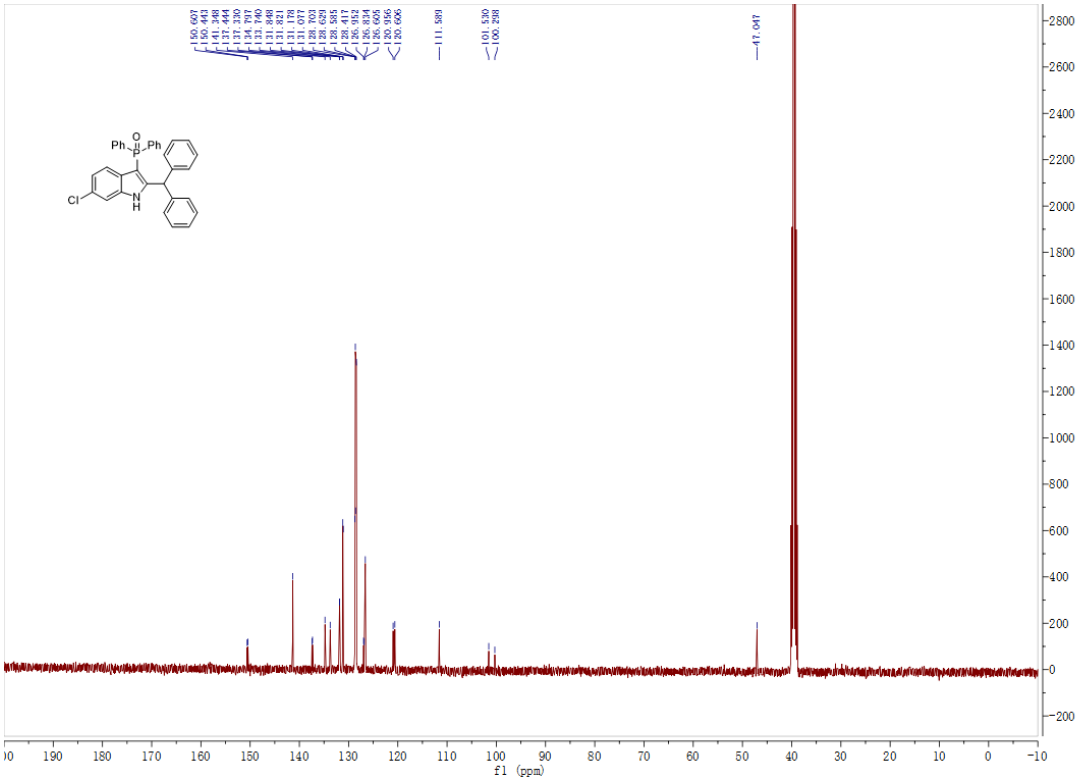

11.611
11.604
7.615
7.598
7.593
7.585
7.568
7.564
7.540
7.489
7.482
7.466
7.455
7.443
7.321
7.316
7.300
7.295
7.289
7.284
7.267
7.253
7.248
7.222
7.203
7.204
7.188
7.126
7.105
6.909
6.896
6.879
6.875
6.644
6.310
2.069
1.00
6.03
4.03
7.01
4.02
1.02
1.03
1.01
3.01
f1 (ppm)

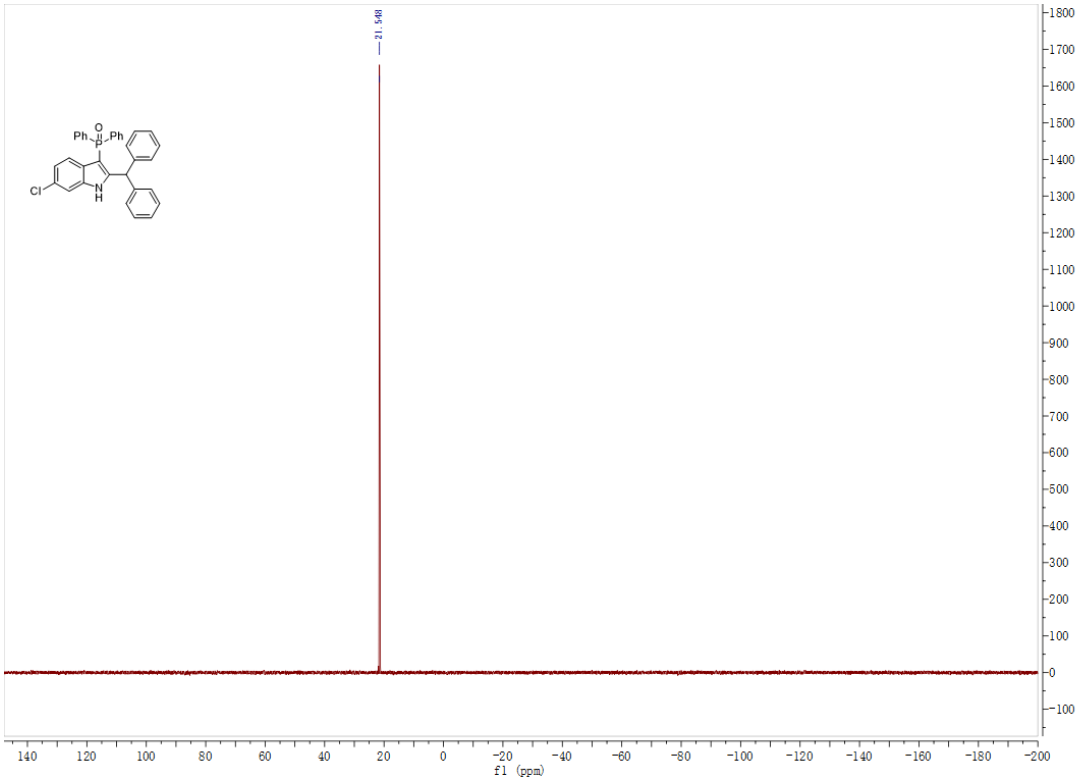

139.179
138.982
134.637
133.103
133.019
132.044
131.986
131.732
131.024
130.973
130.904
128.831
128.336
128.221
128.010
127.316
127.631
127.613
127.376
127.356
123.876
120.021
111.220
105.378
105.311
61.276
60.656
21.540
f1 (ppm)


22.169
Ph
O
P
Ph
N
H
f1 (ppm)

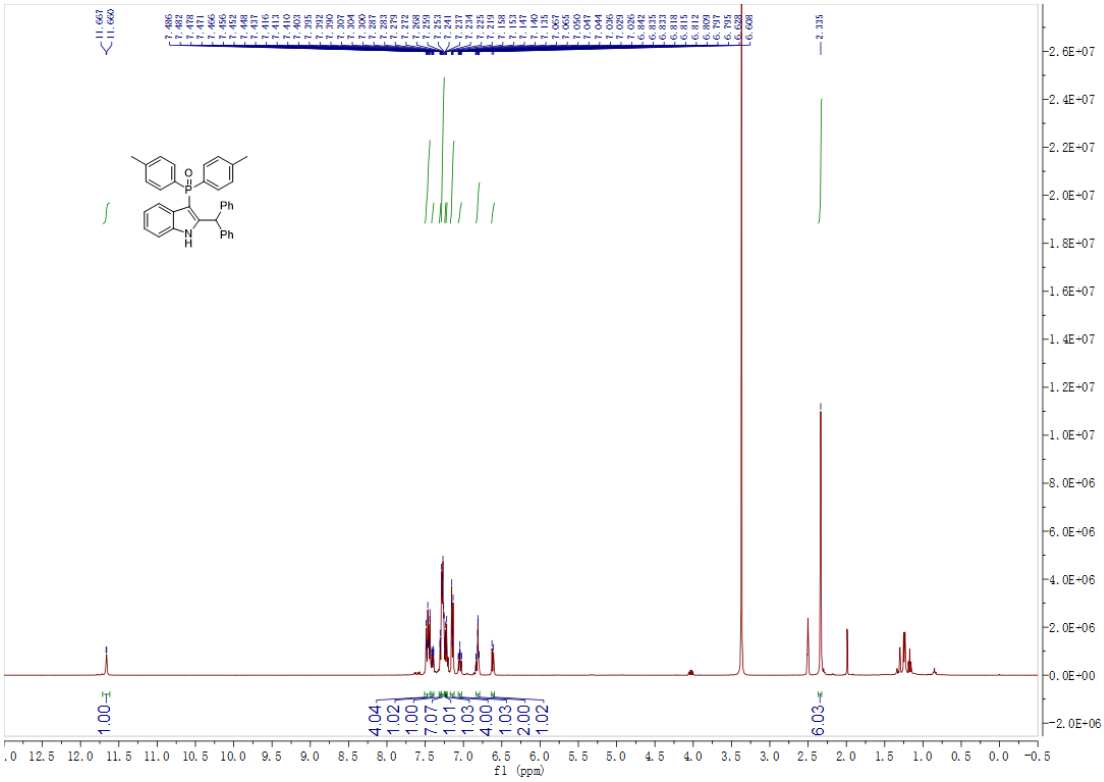
4la


11.823
11.816
Ph
O
P
Ph
Cl
N
H
1.00
6.02
4.02
1.00
4.02
2.03
4.02
1.02
1.02
1.03
f1 (ppm)


150.607
150.443
141.348
137.464
137.330
134.797
133.740
131.868
131.821
131.178
131.077
128.703
128.650
128.585
128.417
126.932
126.814
126.604
120.956
120.666
111.589
101.530
100.298
47.047
f1 (ppm)


21.540
f1 (ppm)

4ab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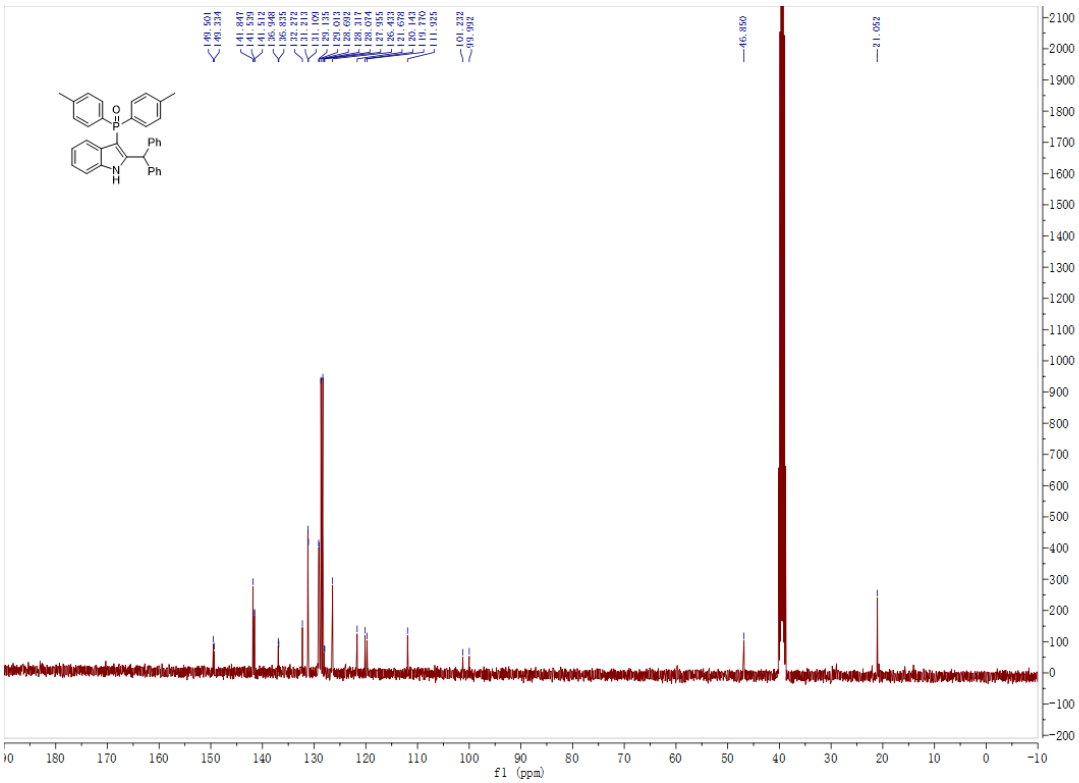
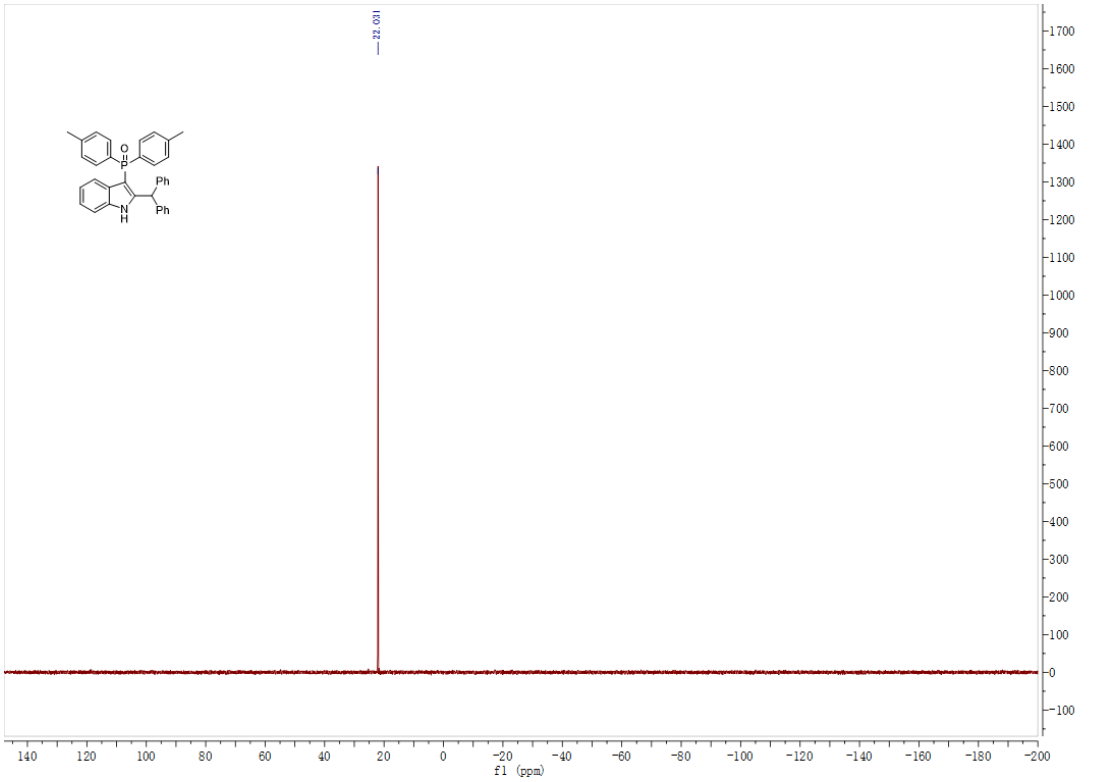
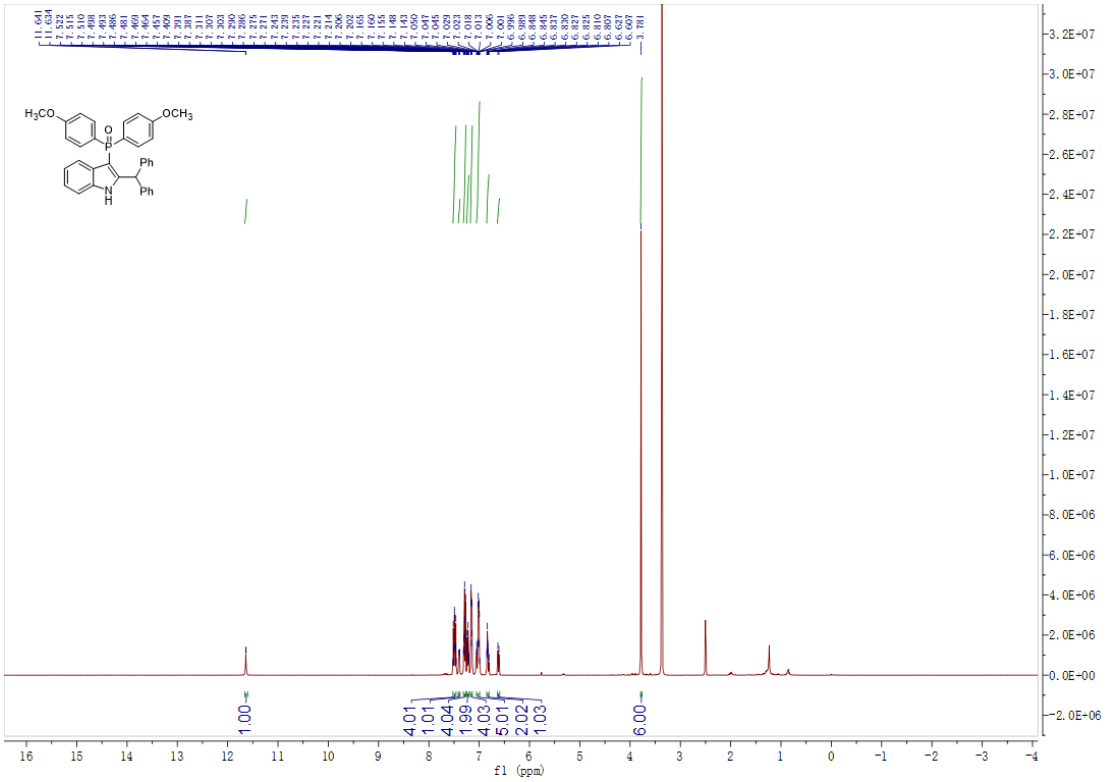
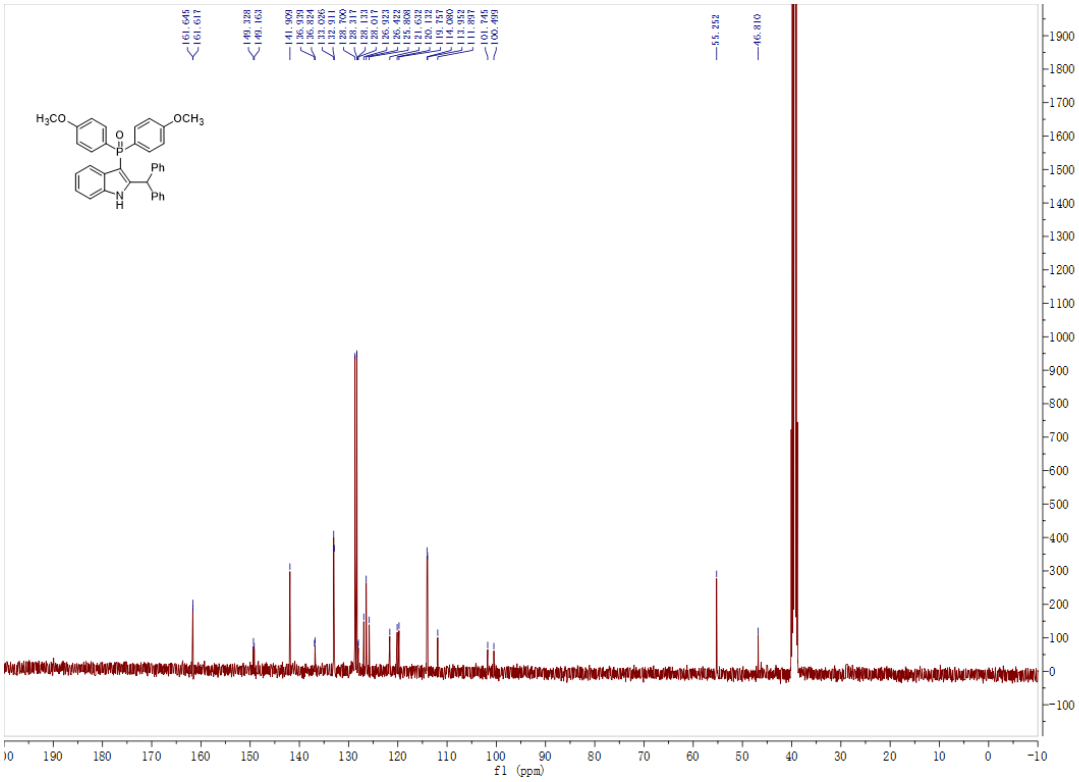
7.482
7.478
7.471
7.466
7.456
7.452
7.448
7.437
7.416
7.413
7.410
7.403
7.392
7.390
7.307
7.304
7.300
7.287
7.283
7.273
7.272
7.268
7.259
7.253
7.244
7.237
7.234
7.225
7.213
7.158
7.153
7.147
7.140
7.135
7.067
7.065
7.050
7.047
7.044
7.036
7.029
7.026
6.842
6.835
6.833
6.818
6.815
6.812
6.809
6.797
6.795
6.628
6.606
2.335
O
P
Ph
Ph
N
H
1.00
4.04
1.02
1.00
7.07
1.01
1.03
4.00
1.03
2.00
1.02
6.03
f1 (ppm)

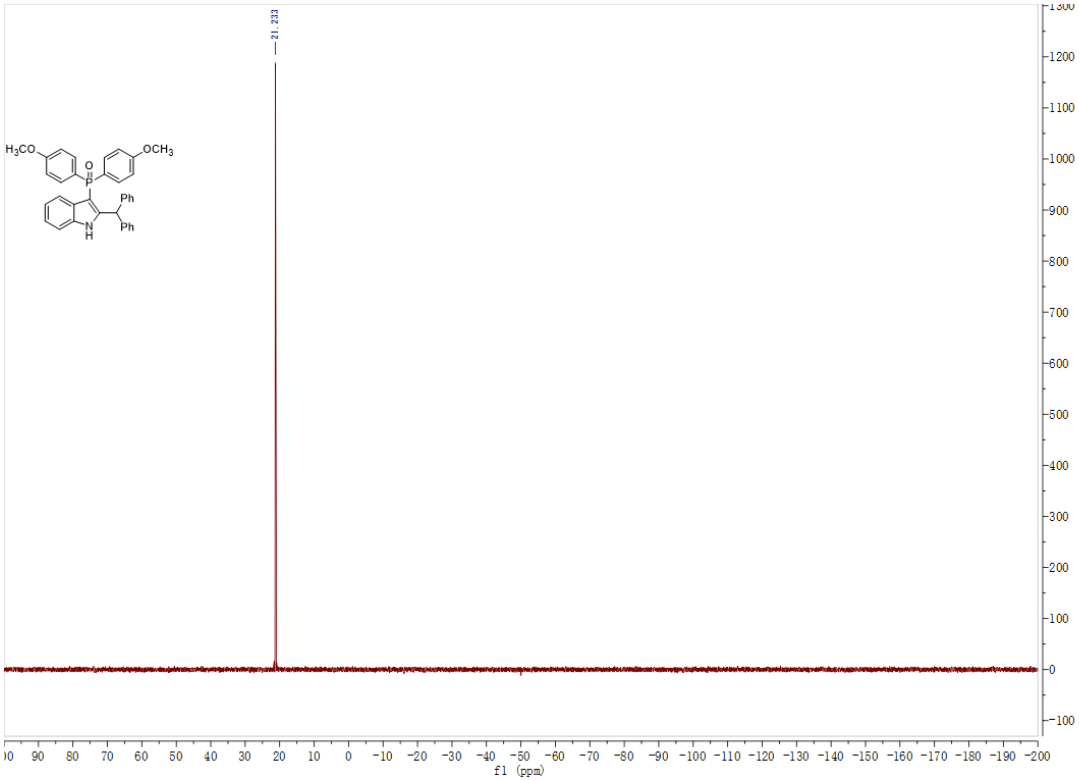

149.501
149.334
141.847
141.539
141.512
136.948
135.935
132.232
131.213
131.109
129.135
128.933
128.692
128.317
128.074
127.955
125.433
121.678
120.143
119.870
111.925
101.232
99.992
46.850
21.052
O
P
Ph
Ph
N
H
f1 (ppm)


22.031
O
P
N
H
Ph
Ph
f1 (ppm)

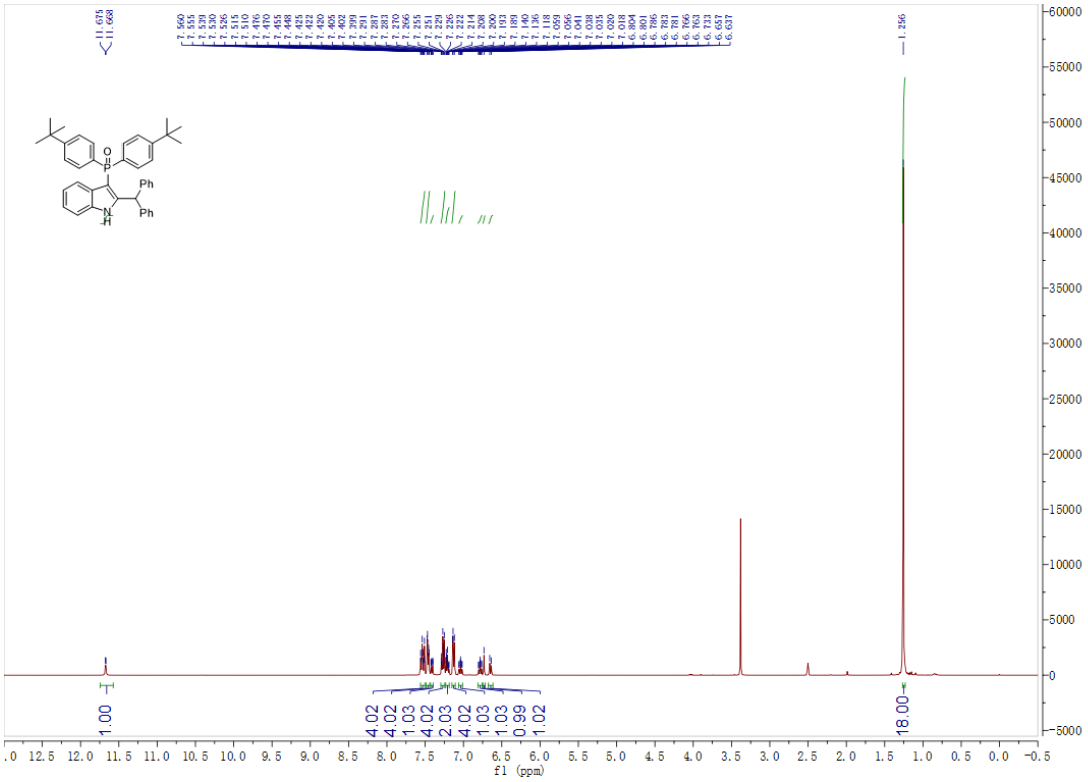
4ac


H3CO
OCH3
O
P
N
H
Ph
Ph
1.00
4.01
1.01
4.04
1.99
4.03
5.01
2.02
1.03
6.00
f1 (ppm)


161.645
161.617
149.328
149.163
141.909
136.930
136.324
135.096
132.911
128.700
128.317
128.111
128.017
126.923
126.422
125.866
121.632
120.132
119.757
114.090
113.952
111.897
101.745
100.499
55.252
46.810
H3CO
OCH3
O
P
N
H
Ph
Ph
f1 (ppm)


21.233
H3CO
OCH3
O
P
N
H
Ph
Ph
f1 (ppm)

4ad


11.675
11.668
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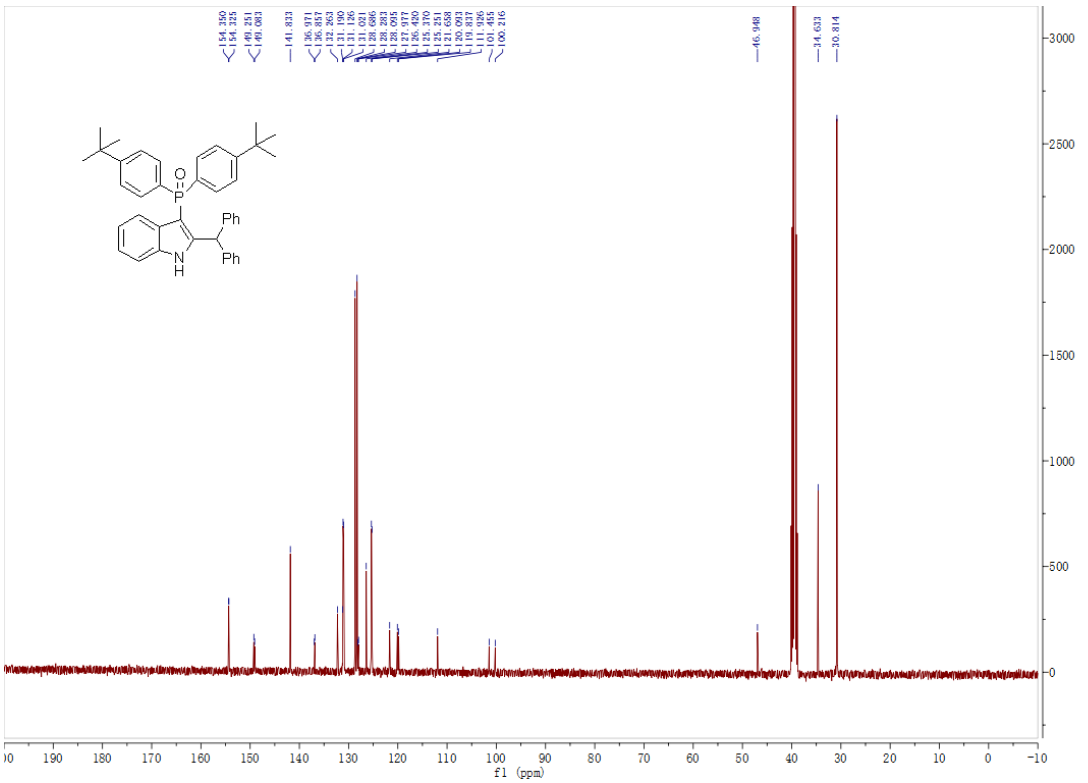
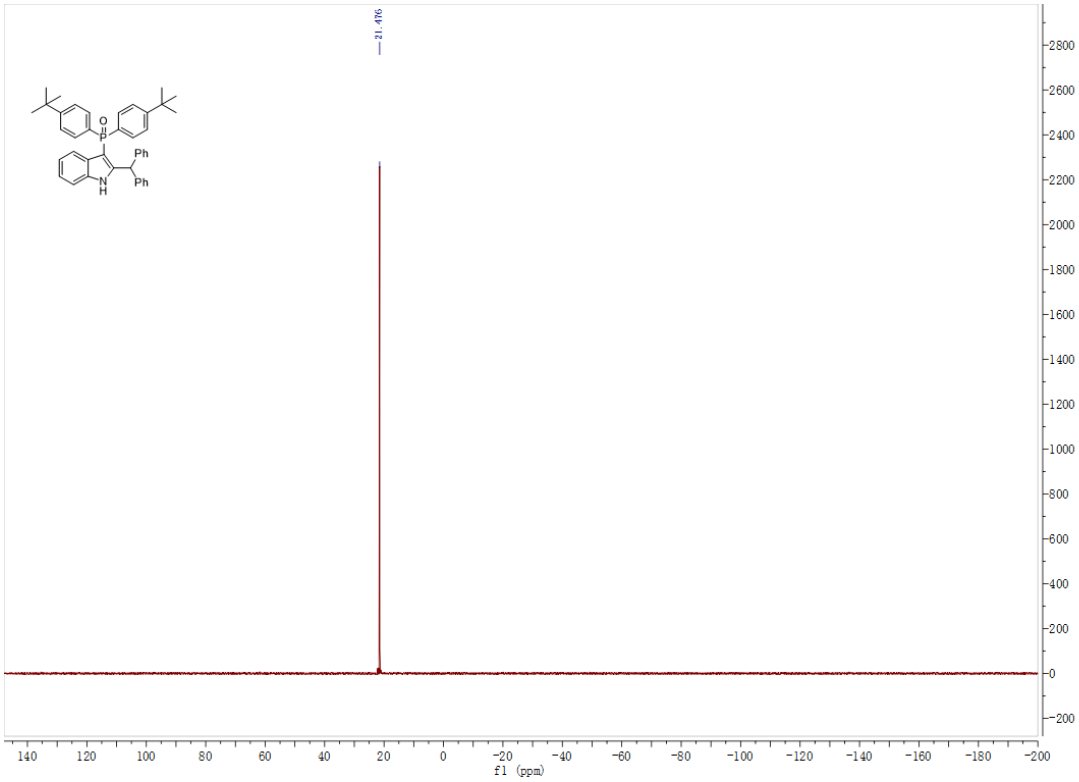
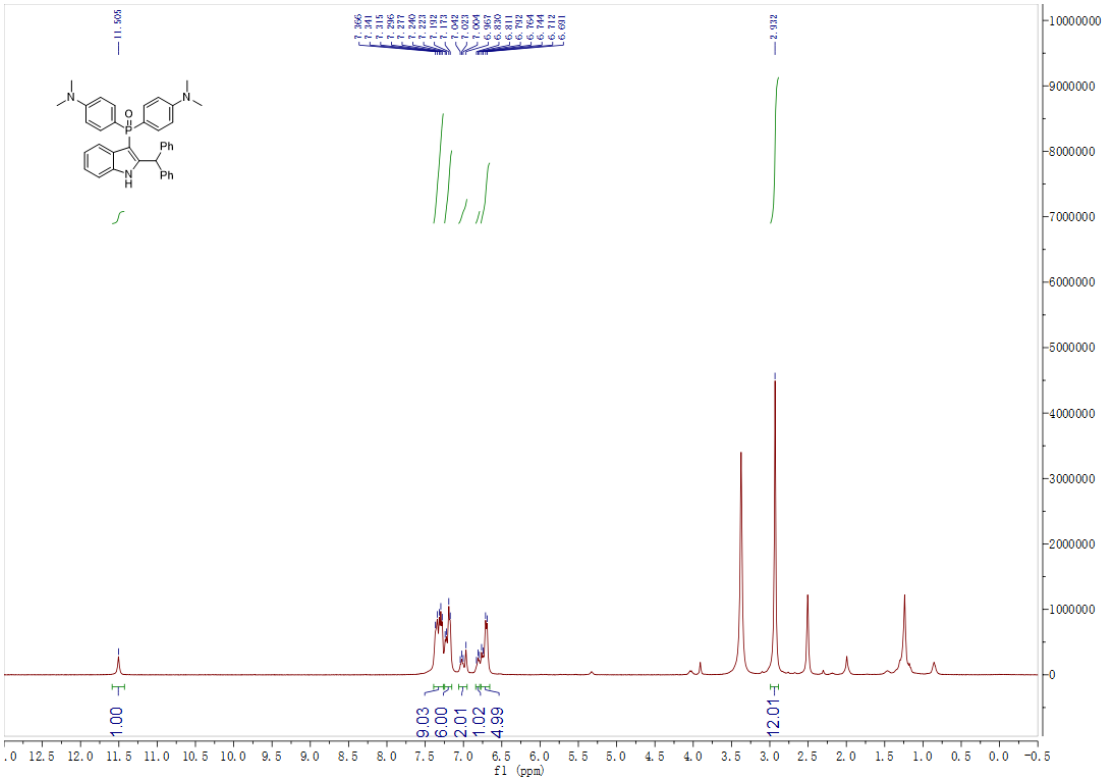
7.555
7.539
7.535
7.526
7.515
7.510
7.476
7.469
7.455
7.448
7.425
7.422
7.420
7.405
7.402
7.399
7.371
7.287
7.283
7.270
7.266
7.255
7.251
7.229
7.225
7.222
7.214
7.208
7.200
7.193
7.189
7.140
7.136
7.118
7.113
7.059
7.056
7.041
7.038
7.035
7.020
7.018
6.994
6.984
6.980
6.786
6.783
6.781
6.766
6.763
6.733
6.637
6.637
1.256
Ph
Ph
1.00
4.02
4.02
1.03
4.02
2.03
4.02
1.03
1.03
0.99
1.02
18.00
f1 (ppm)


154.350
154.325
149.251
149.083
141.833
136.971
136.857
132.353
131.190
131.136
131.021
128.686
128.393
128.295
127.977
126.420
125.370
125.251
123.588
120.923
119.837
111.326
104.466
100.216
46.948
34.633
30.814
Ph
Ph
f1 (ppm)


21.476
f1 (ppm)

4ae


11.505
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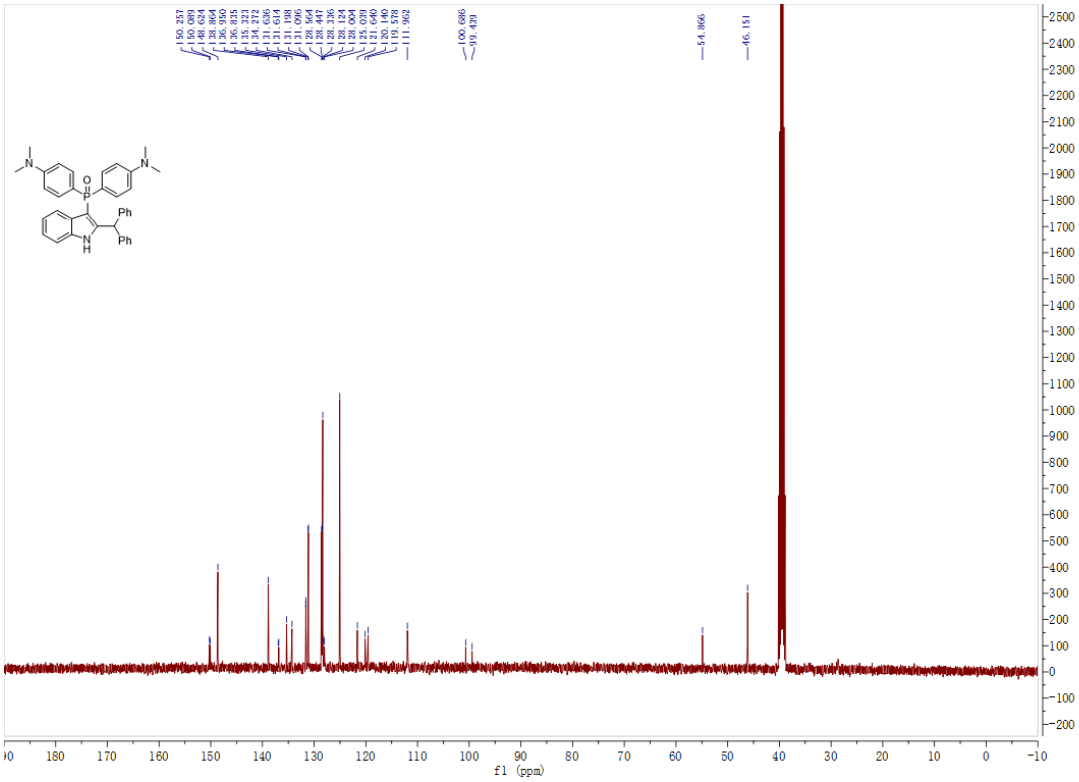
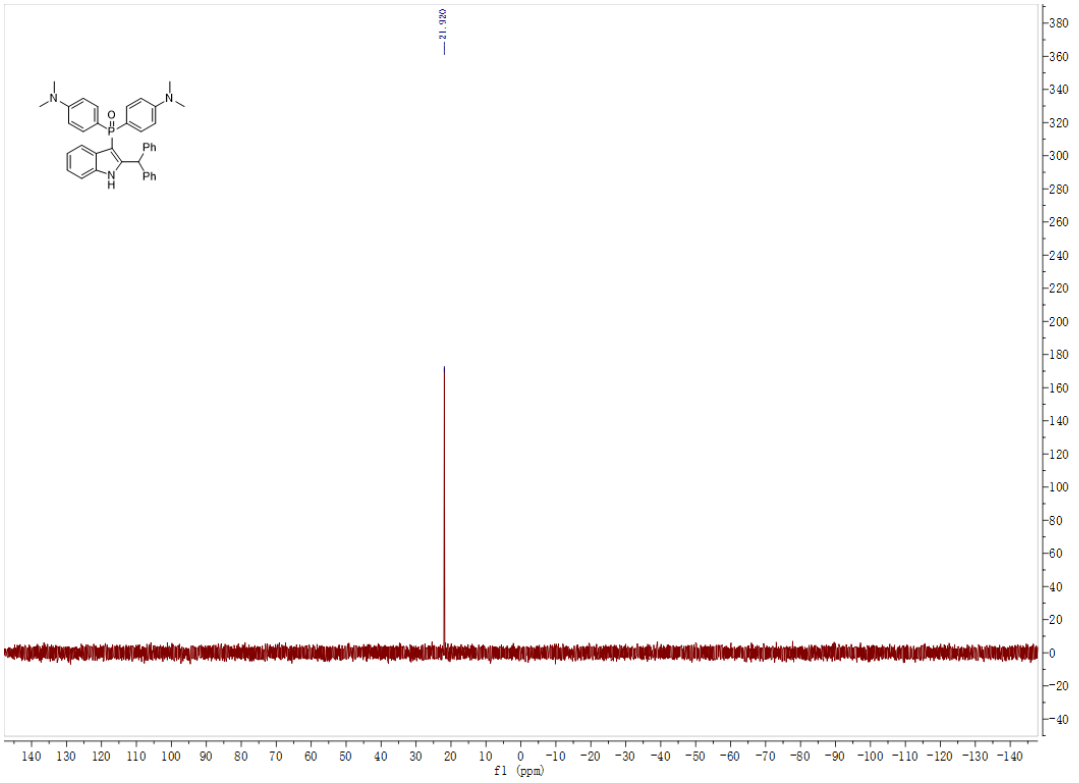
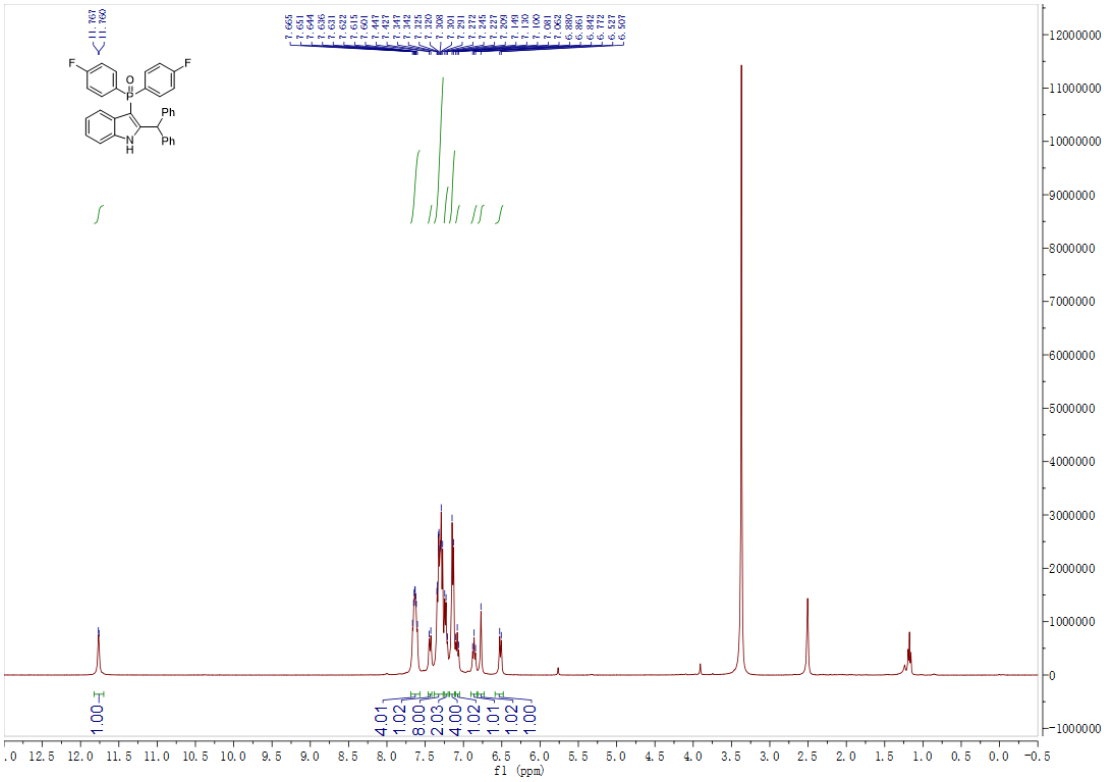
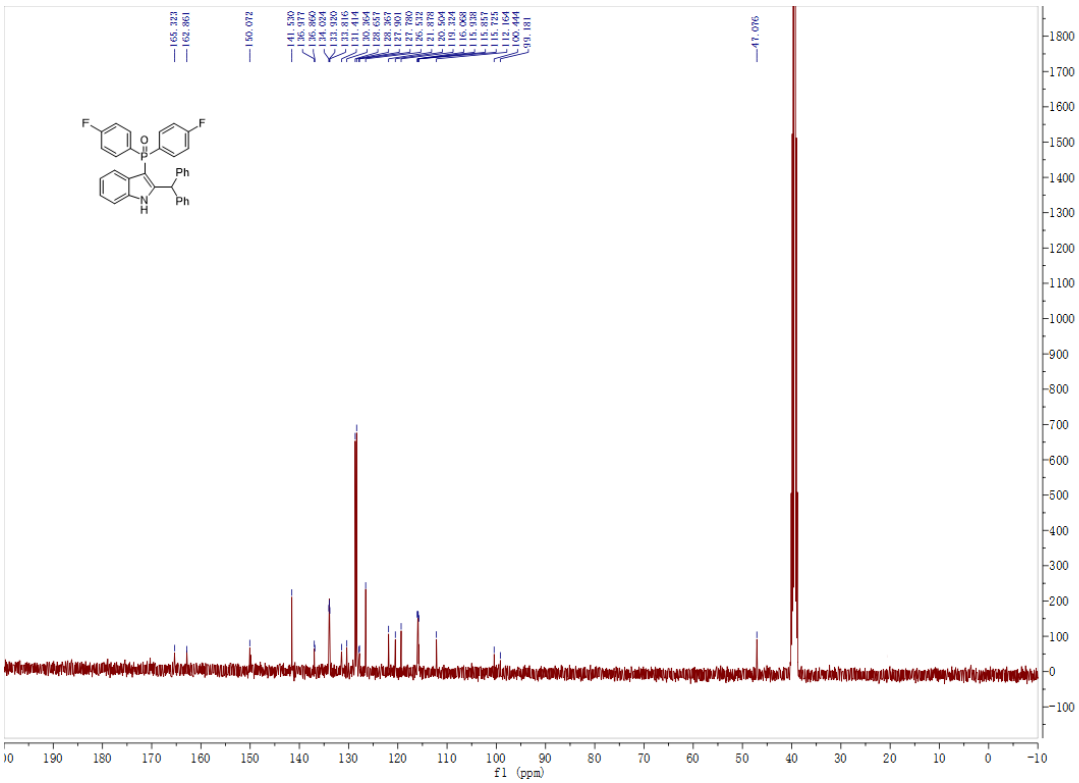
7.341
7.315
7.296
7.277
7.240
7.233
7.192
7.173
7.042
7.033
7.004
6.967
6.830
6.811
6.792
6.764
6.744
6.712
6.691
2.932
1.00
9.03
6.00
2.01
1.02
4.99
12.01
f1 (ppm)

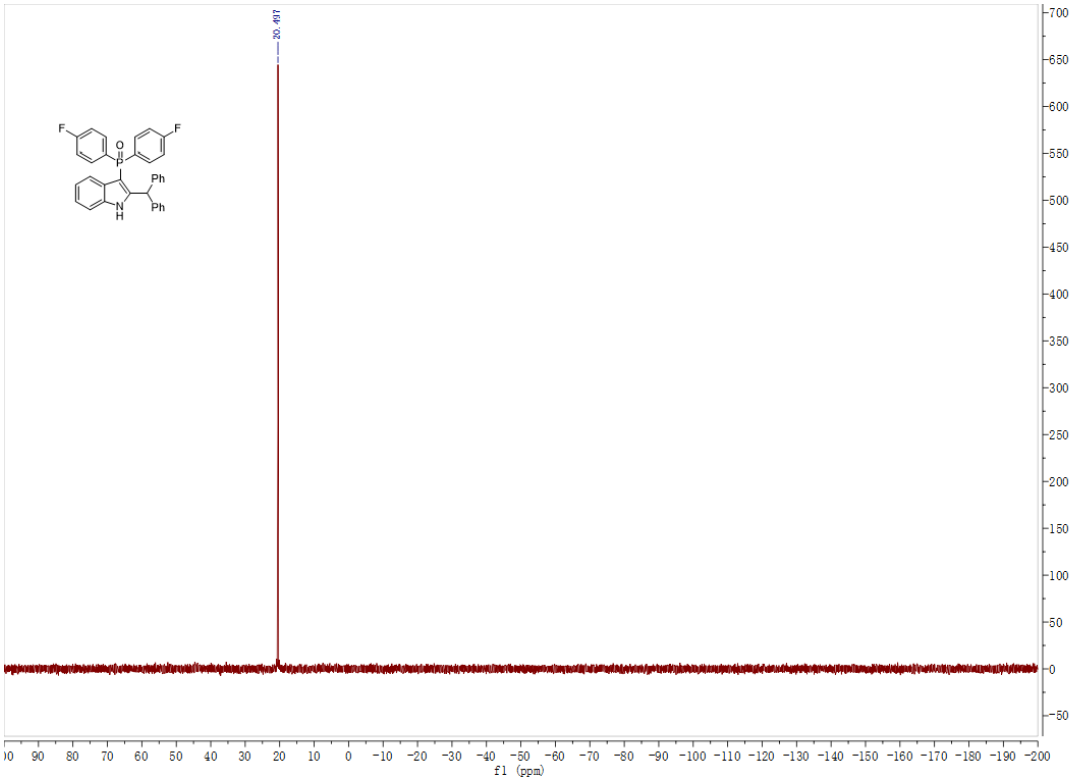

150.257
150.080
148.624
138.964
136.955
136.835
135.323
134.272
131.656
131.614
131.198
131.096
128.964
128.447
128.336
128.124
128.054
125.020
121.640
120.140
119.578
119.302
111.962
100.686
99.439
54.866
46.151
Ph
Ph
f1 (ppm)

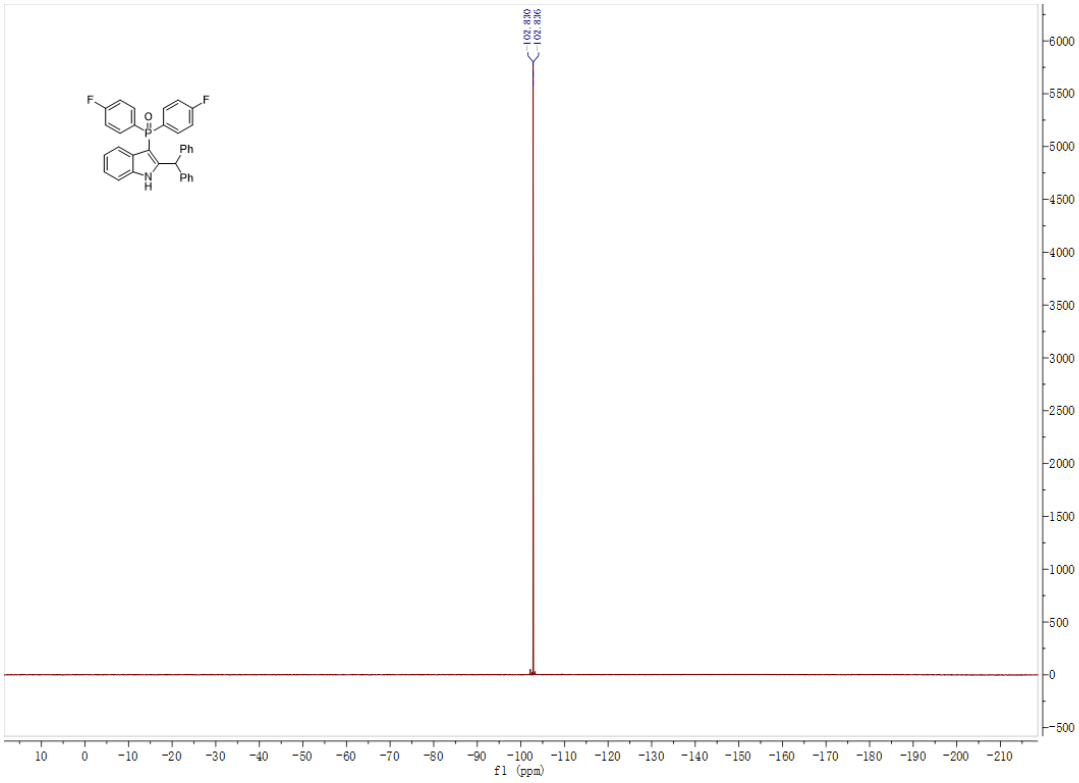

21.920
Ph
Ph
f1 (ppm)

4af

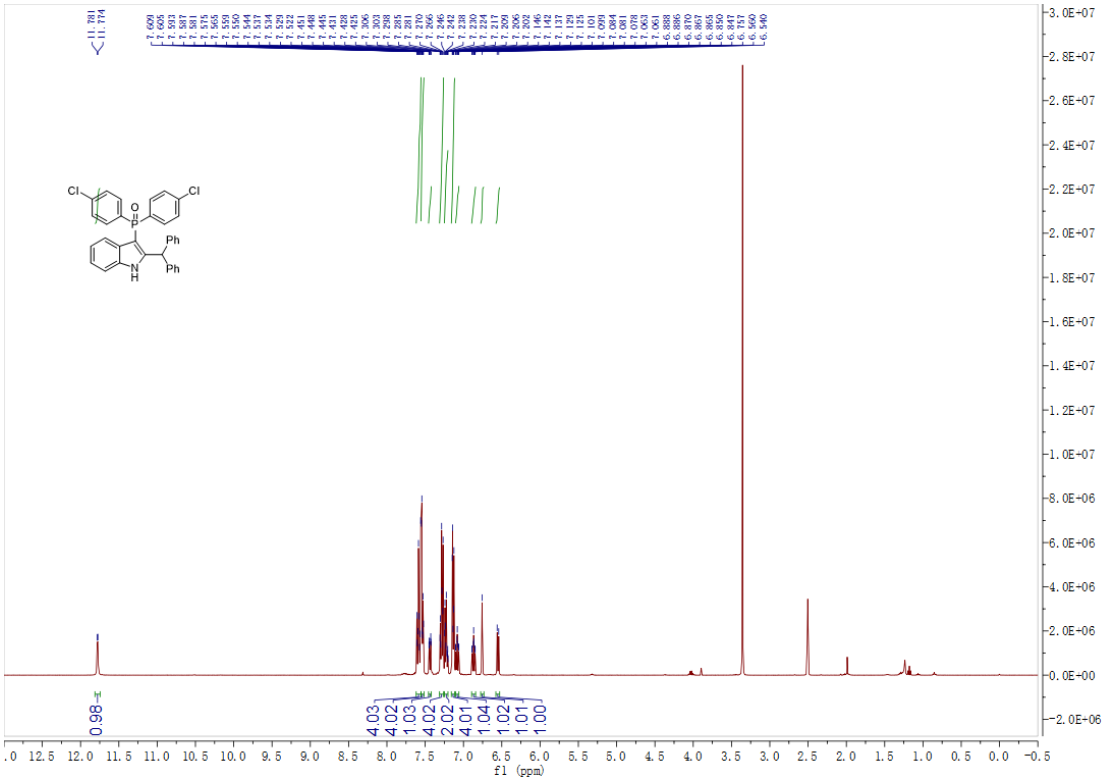

F
F
O
P
Ph
Ph
N
H
f1 (ppm)


F
F
O
P
Ph
Ph
N
H
f1 (ppm)





4ag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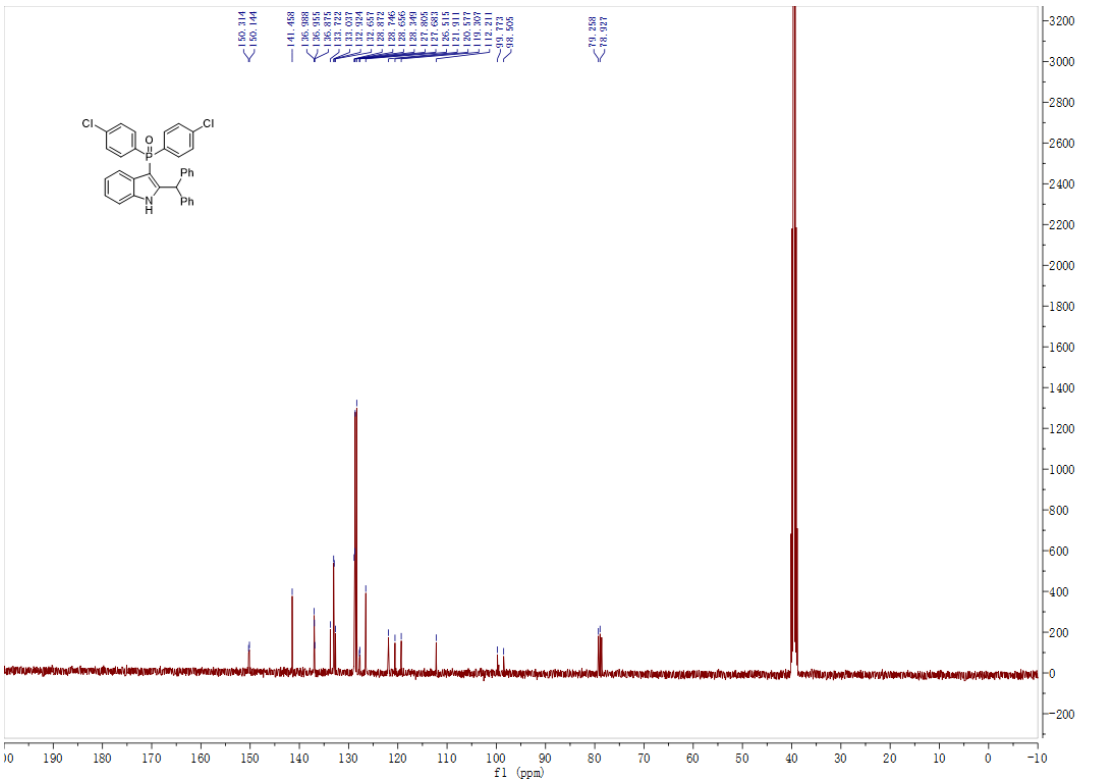
7.605
7.593
7.587
7.581
7.575
7.565
7.555
7.550
7.544
7.537
7.534
7.529
7.522
7.451
7.446
7.440
7.431
7.428
7.425
7.306
7.303
7.298
7.285
7.281
7.270
7.266
7.246
7.242
7.238
7.230
7.224
7.217
7.213
7.205
7.202
7.146
7.145
7.137
7.129
7.125
7.091
7.090
7.084
7.081
7.078
7.064
7.061
6.888
6.886
6.870
6.867
6.865
6.850
6.847
6.841
6.837
6.560
6.540
Cl
Cl
O
P
N
H
Ph
Ph
0.98
4.03
4.02
1.03
4.02
2.02
4.01
1.04
1.02
1.01
1.00
f1 (ppm)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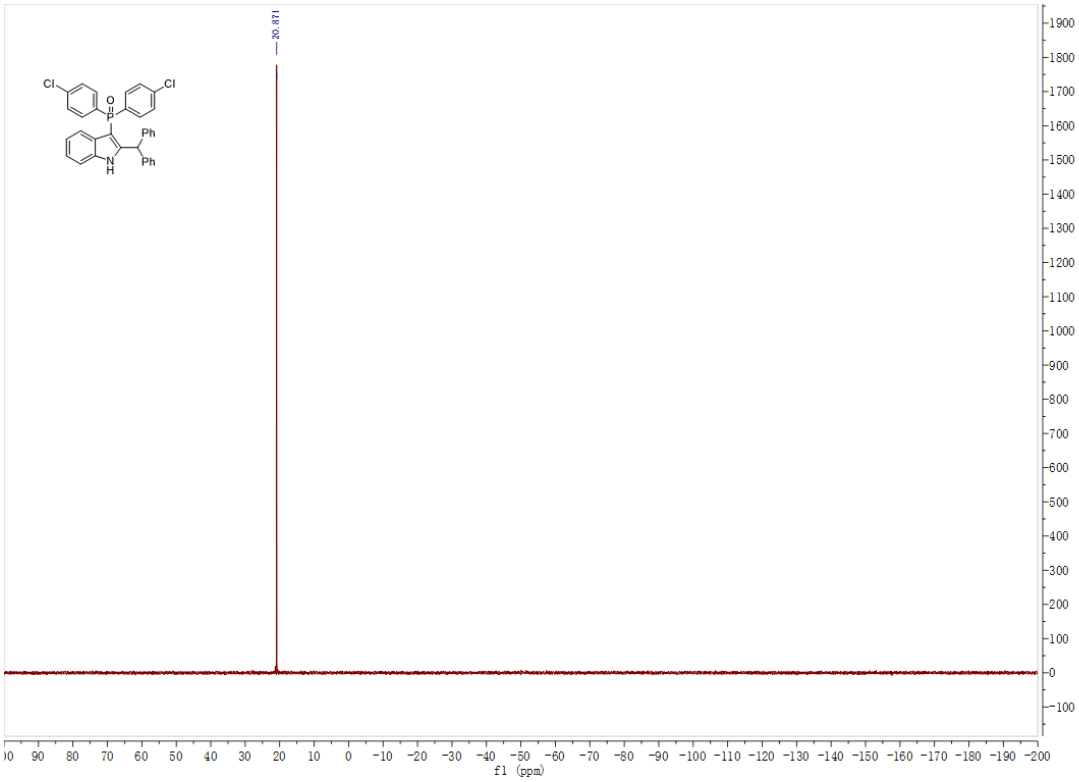
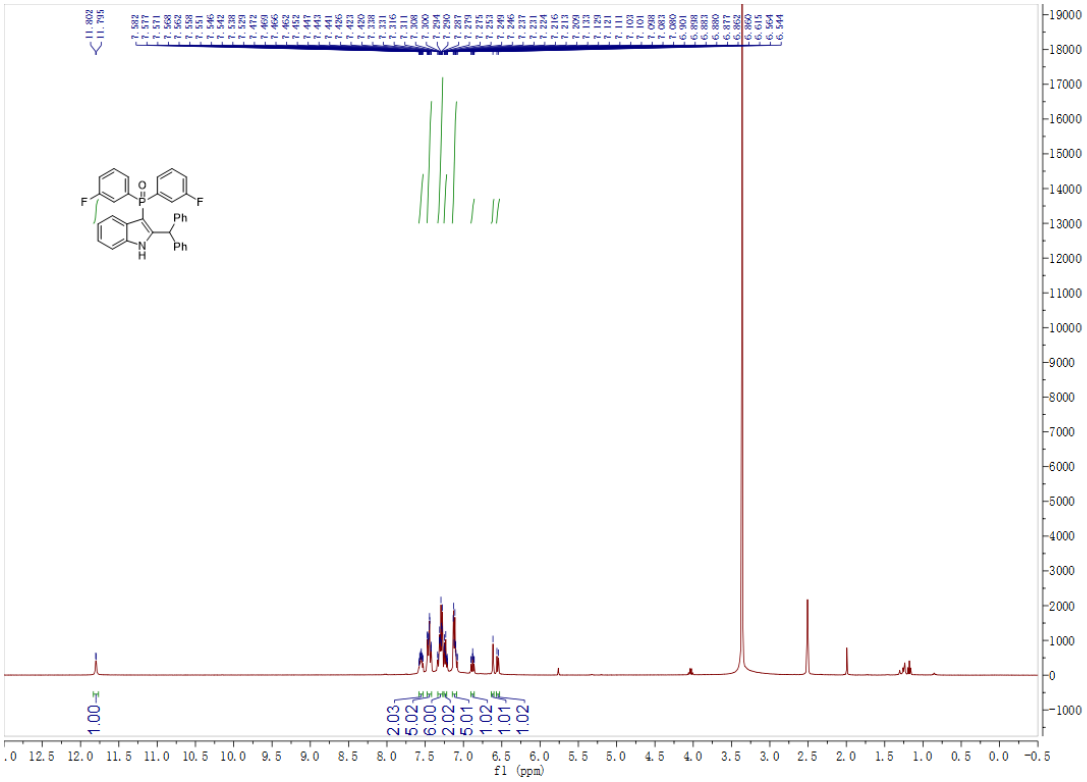
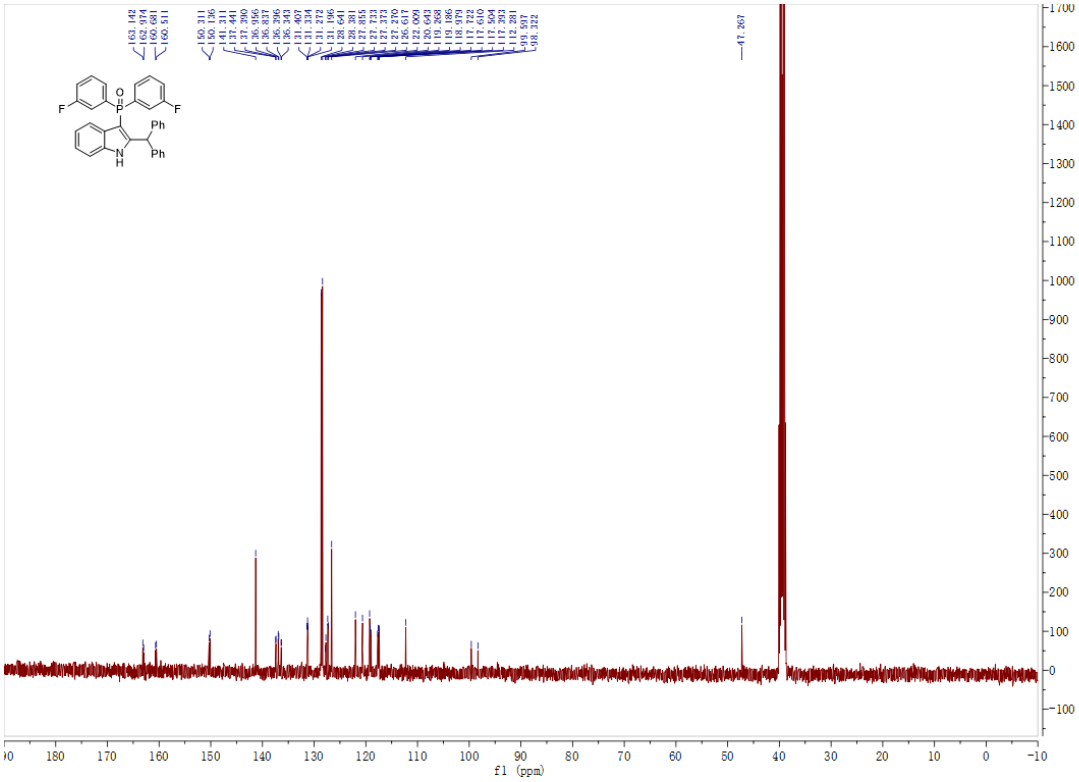
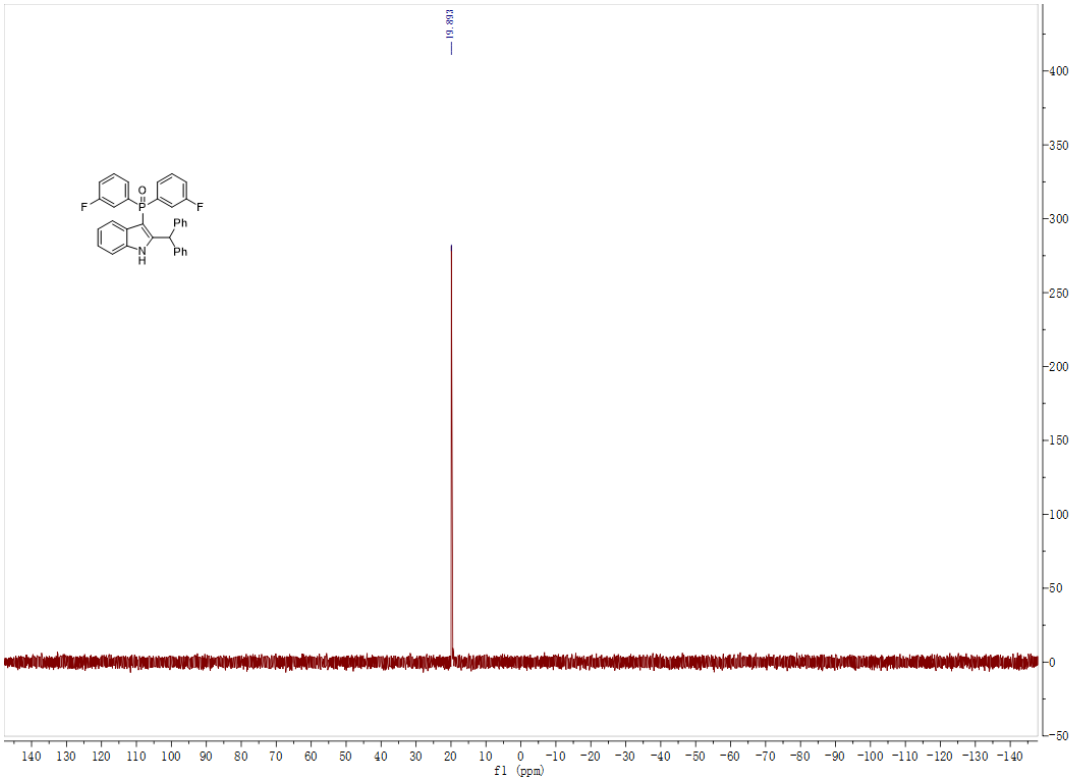
150.144
141.458
136.988
136.956
136.875
133.732
133.037
132.924
132.657
132.372
128.746
128.656
128.349
127.895
127.668
125.515
121.911
120.577
119.307
112.211
93.773
93.505
79.258
78.927
Cl
Cl
O
P
N
H
Ph
Ph
f1 (ppm)

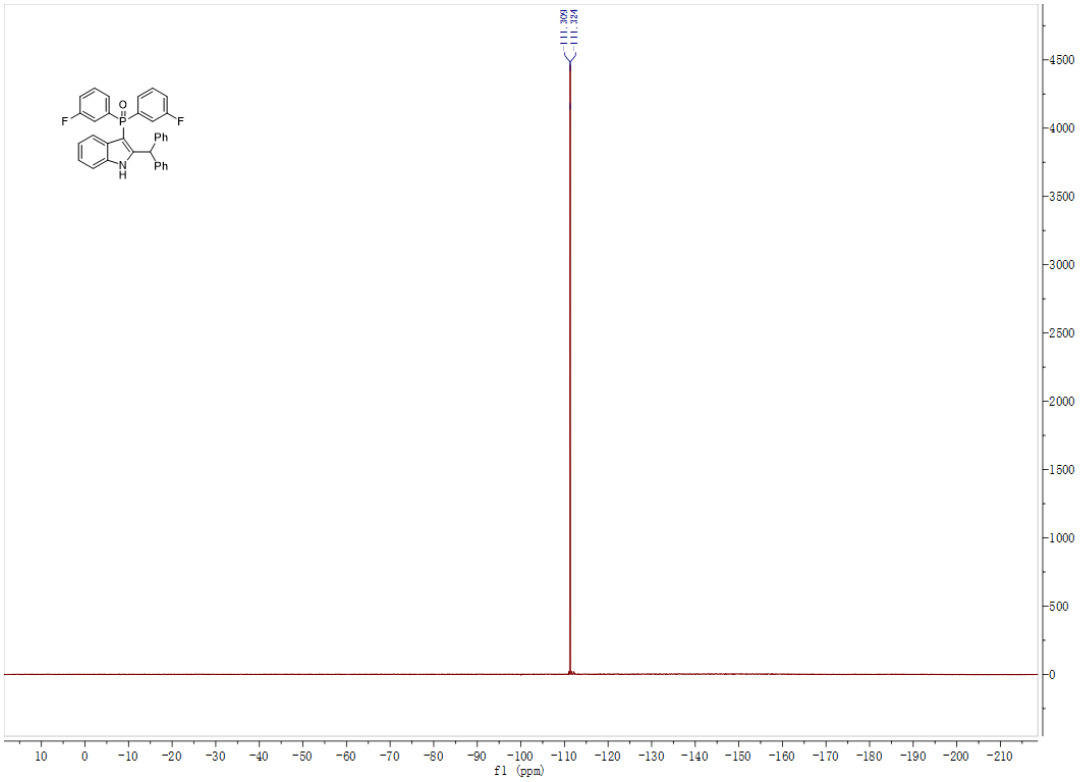

20.871
Cl
Cl
O
P
Ph
Ph
N
H
f1 (ppm)

4ah

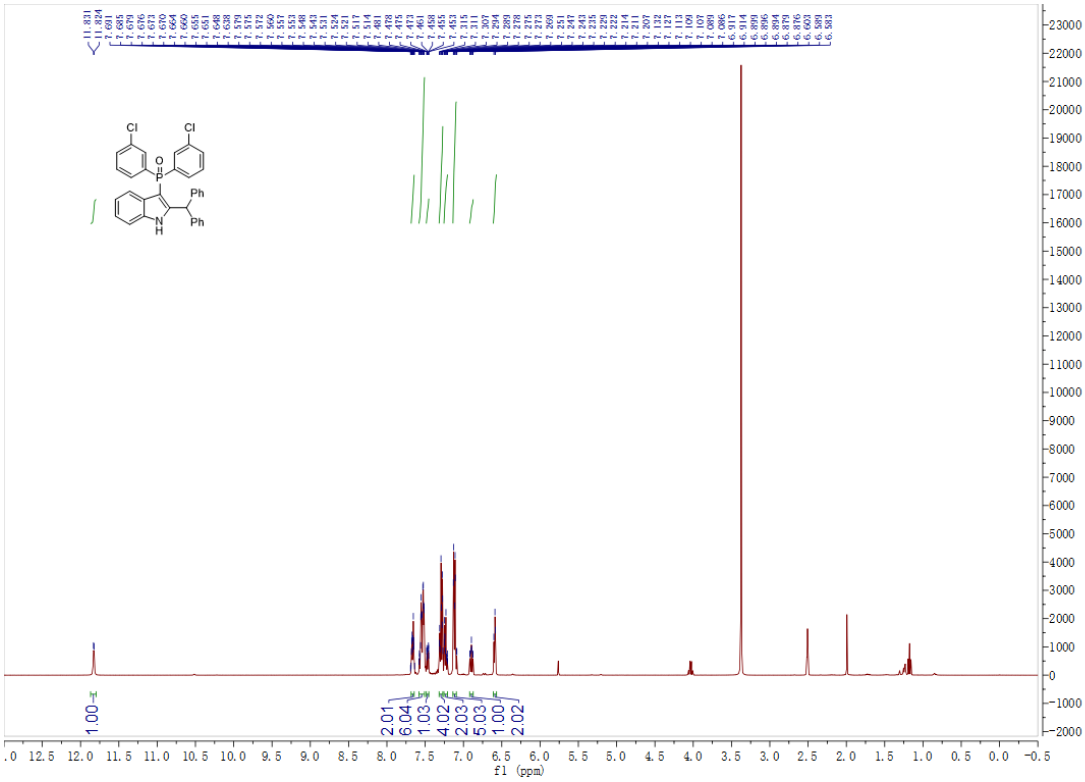

11.802
11.795
F
F
O
P
Ph
Ph
N
H
1.00
2.03
5.02
6.00
2.02
5.01
1.02
1.01
1.02
f1 (ppm)

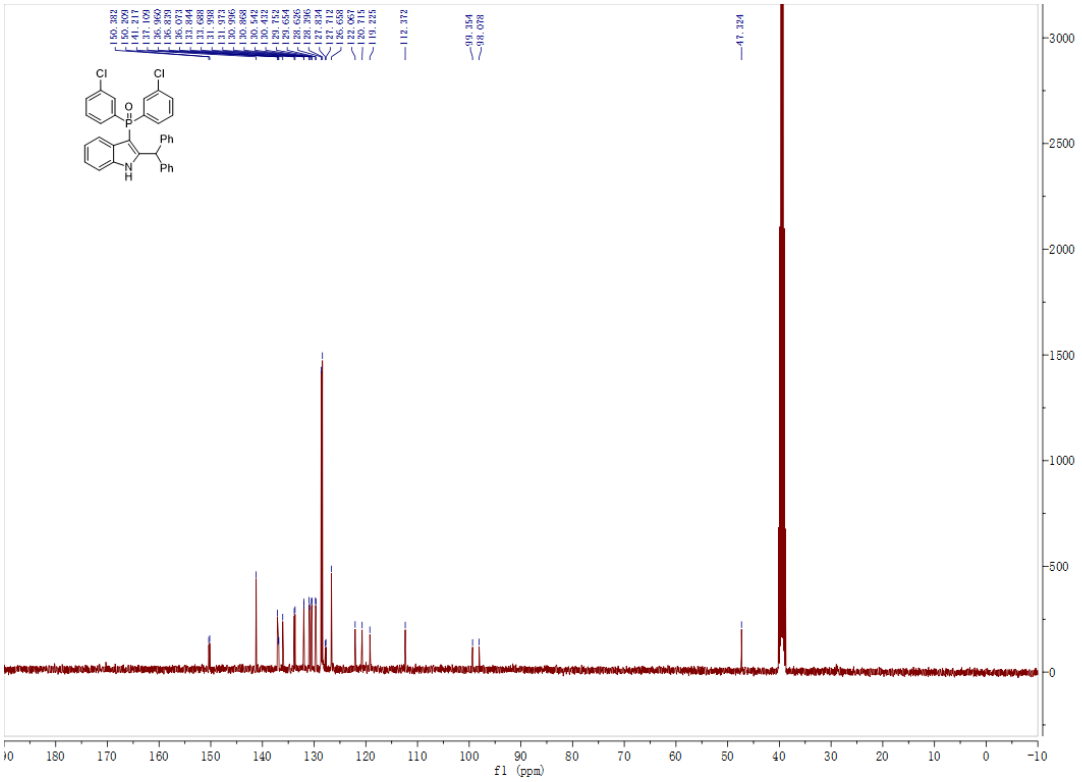

F
O
P
H
F
Ph
Ph
N
H
47.367
f1 (ppm)

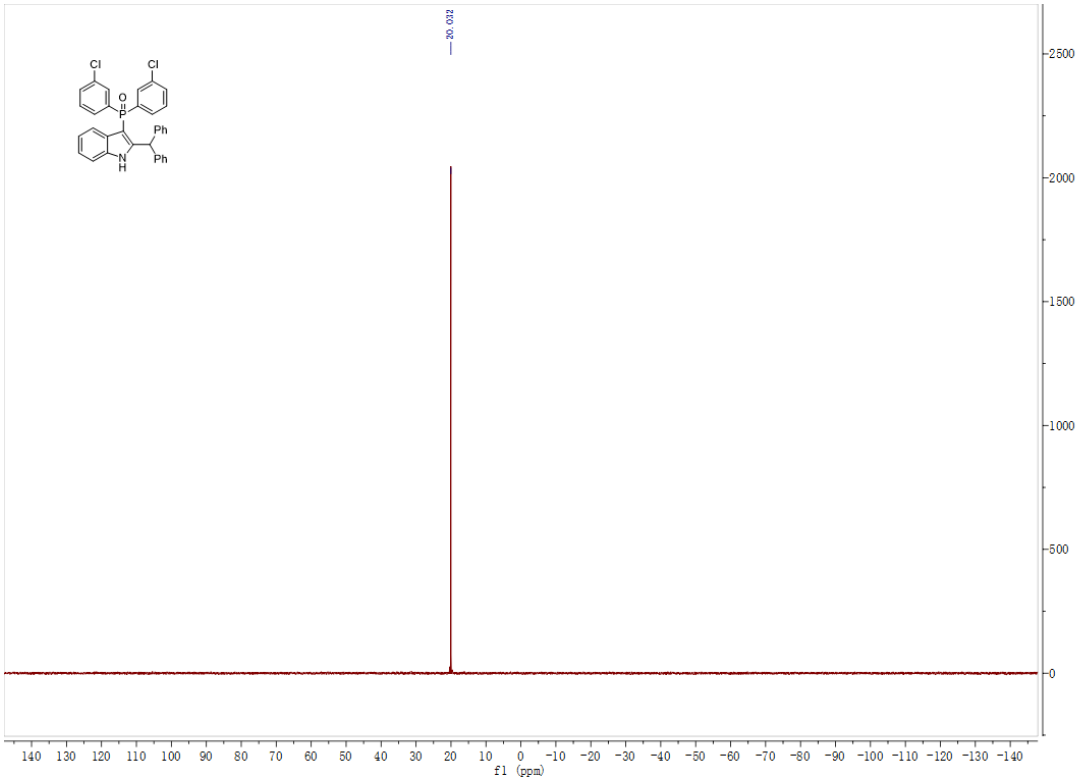

19.893
F
O
P
F
Ph
Ph
N
H
f1 (ppm)


F
O
P
F
Ph
Ph
N
H
111.309
111.324
f1 (ppm)

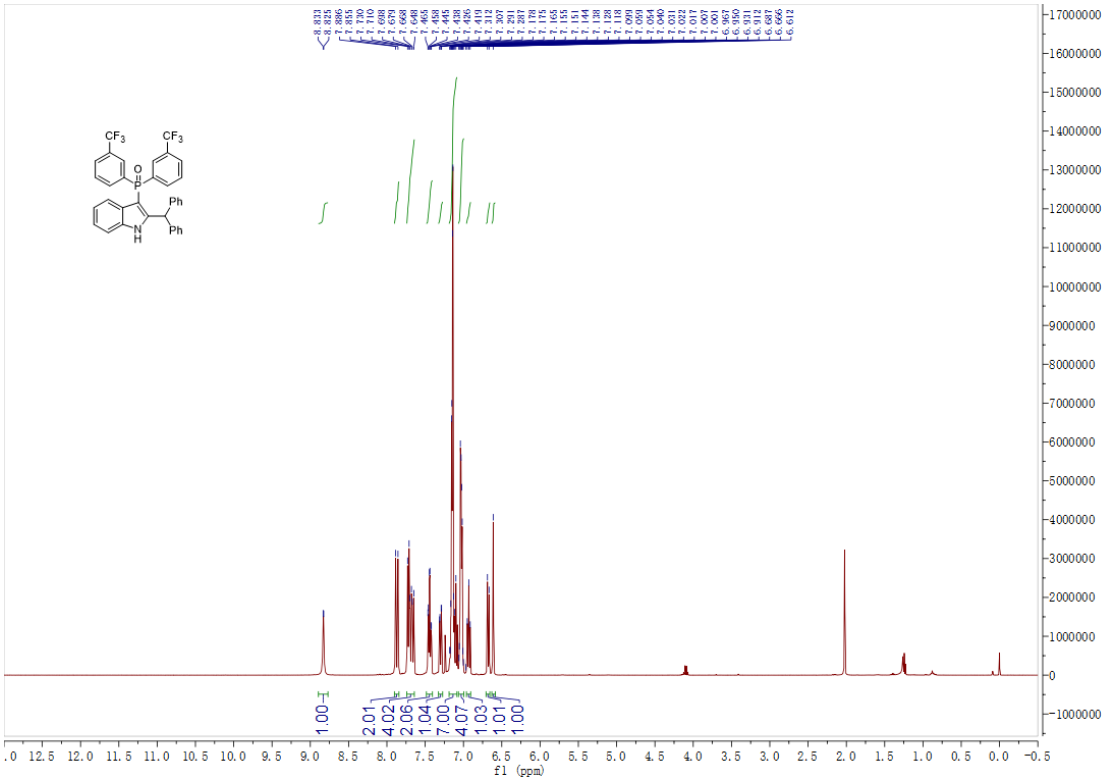
4ai

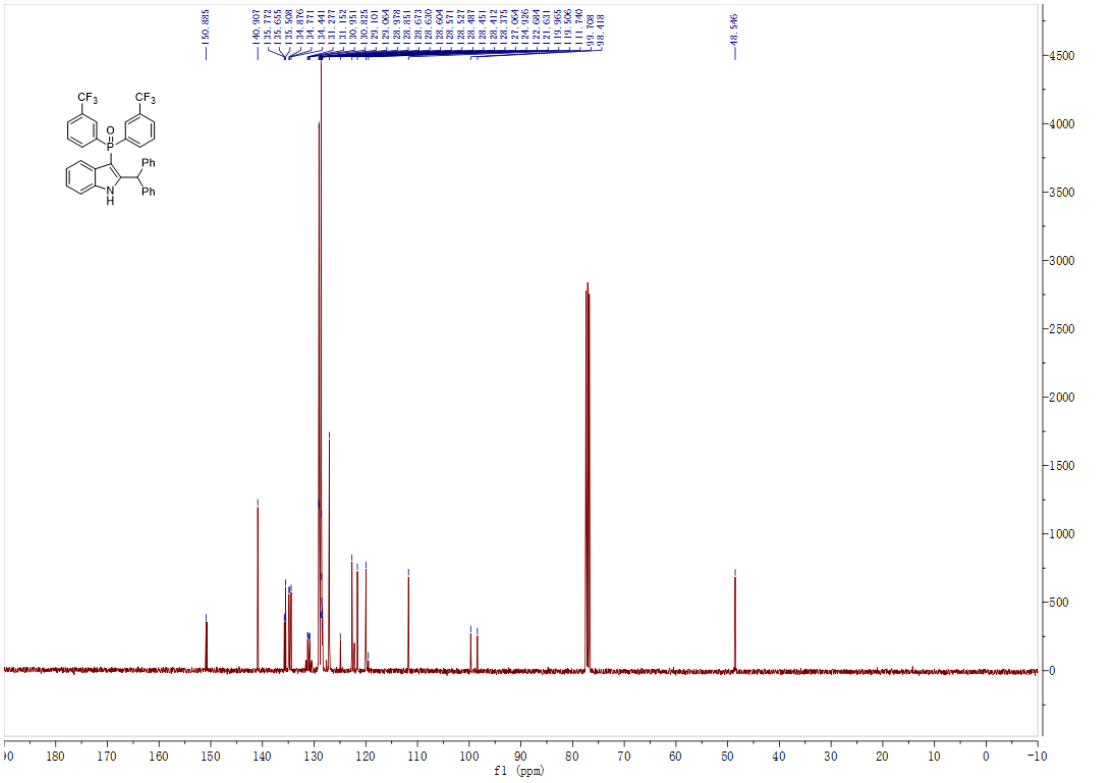

Cl
Cl
O
P
Ph
Ph
N
H
1.00
2.01
6.04
1.03
4.02
2.03
5.03
1.00
2.02
f1 (ppm)

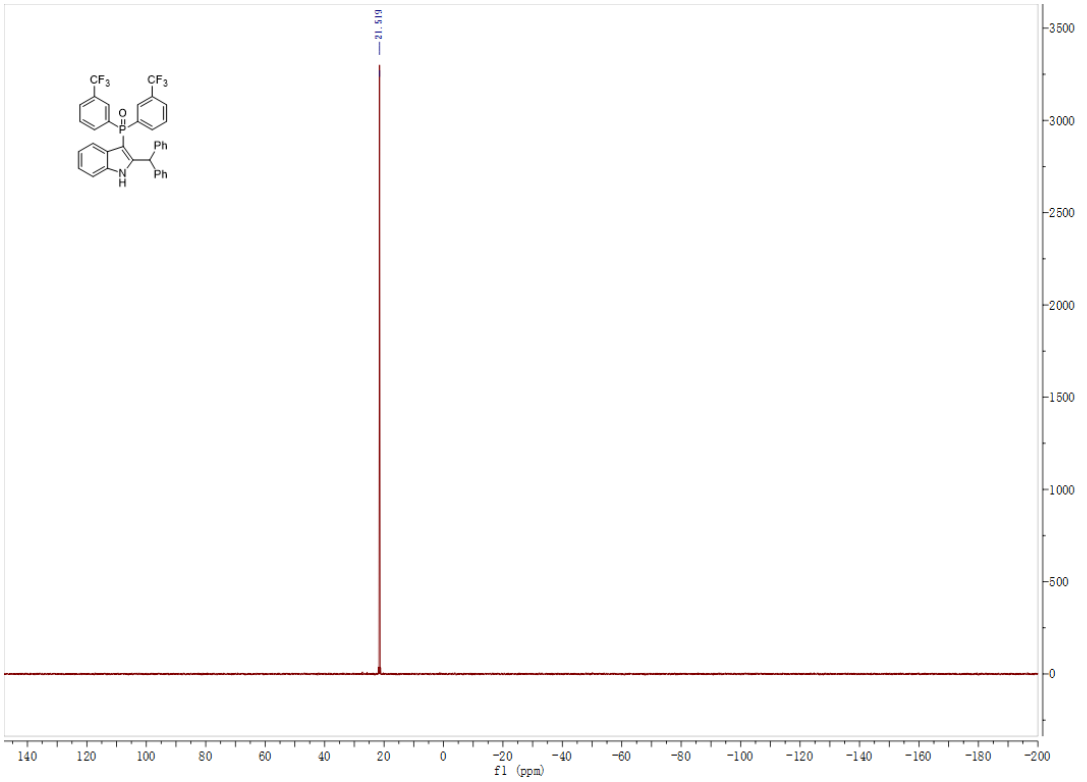

150.382
150.209
141.217
137.109
135.950
135.353
135.073
133.844
131.668
131.598
131.373
130.996
130.868
130.541
130.432
129.752
129.654
128.595
128.396
127.834
127.712
126.668
123.667
120.715
119.225
112.372
99.354
98.078
47.324
Cl
Cl
O
P
Ph
Ph
N
H
f1 (ppm)

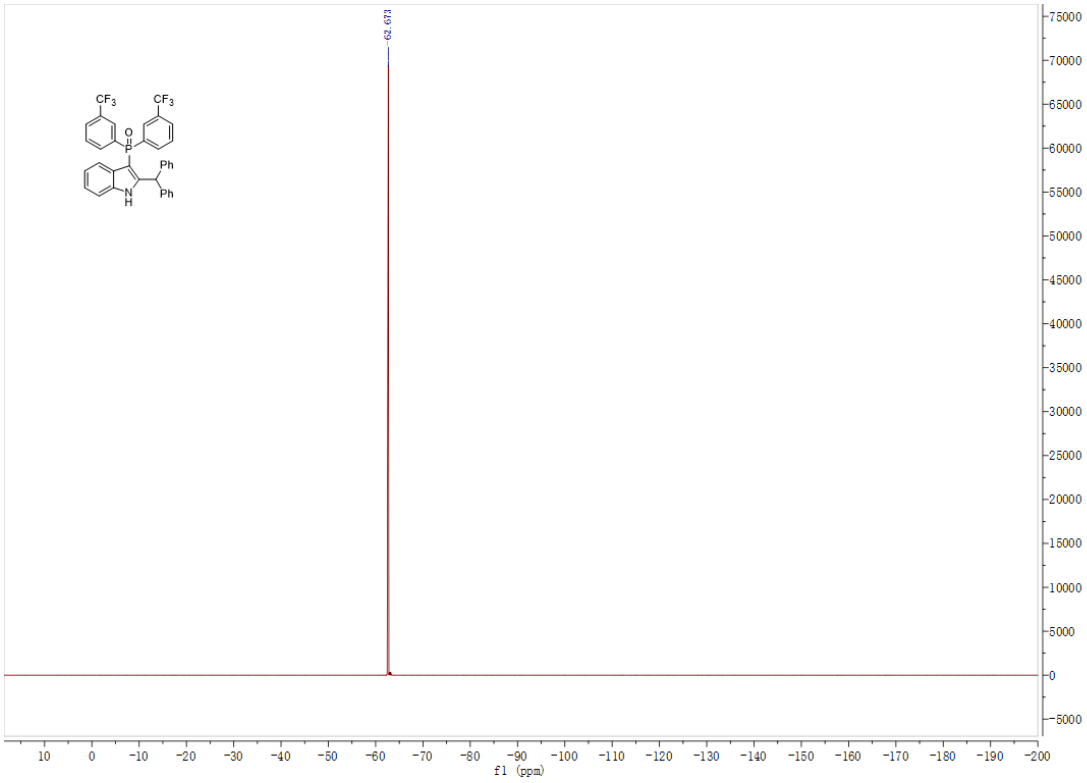

30.032
Cl
Cl
O
P
Ph
Ph
N
H
f1 (ppm)

4aj

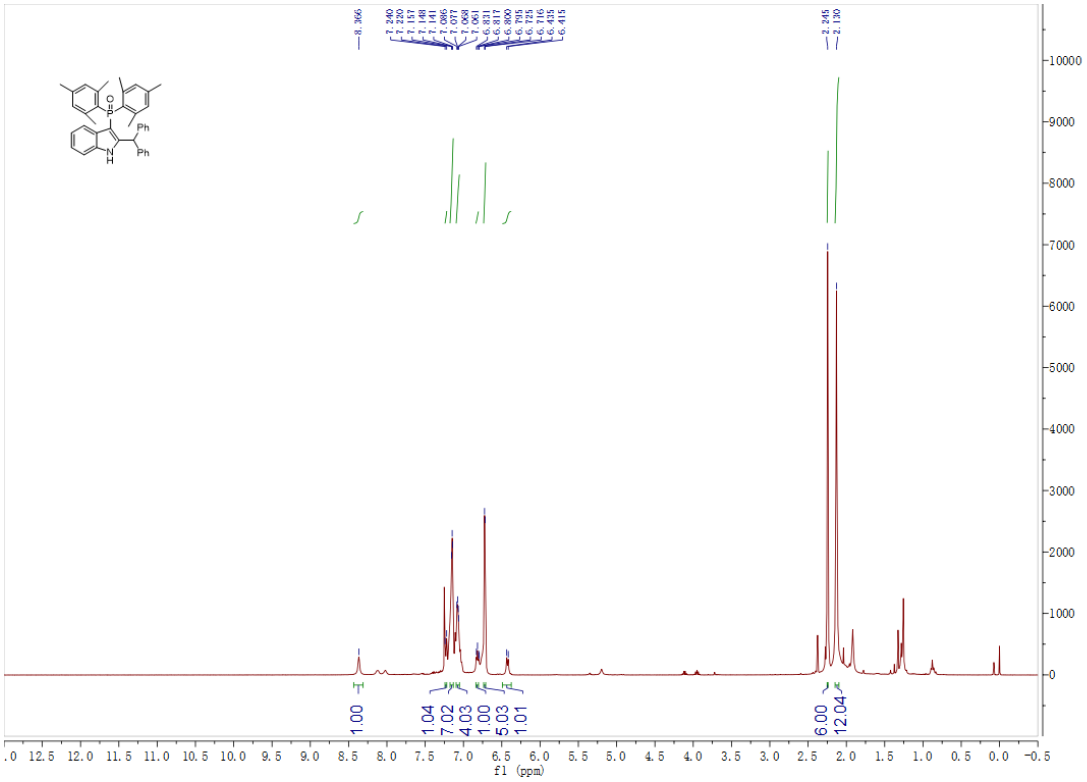

CF3
CF3
O
P
Ph
Ph
N
H
1.00
2.01
4.02
2.06
1.04
7.00
4.07
1.03
1.01
1.00
f1 (ppm)


CF3
CF3
O
P
Ph
Ph
N
H
f1 (ppm)


21.519
CF3
CF3
O
P
N
H
Ph
Ph
3500
3000
2500
2000
1500
1000
500
0
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)


62.673
CF3
CF3
O
P
N
H
Ph
Ph
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

4ak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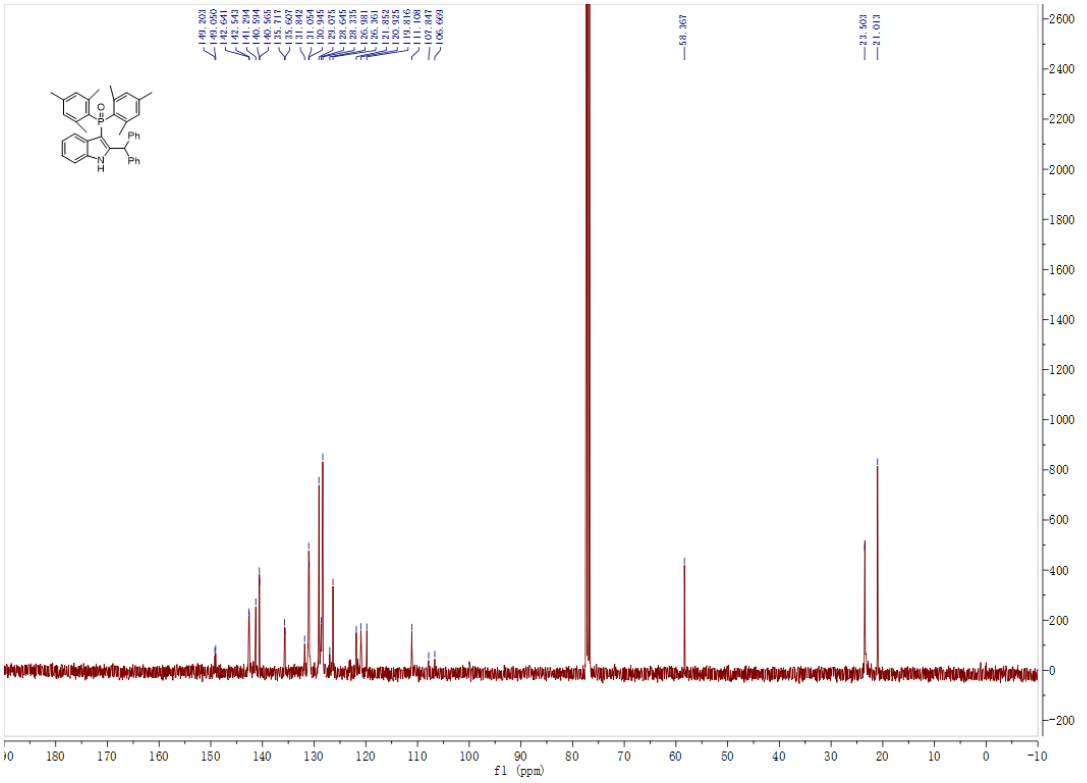
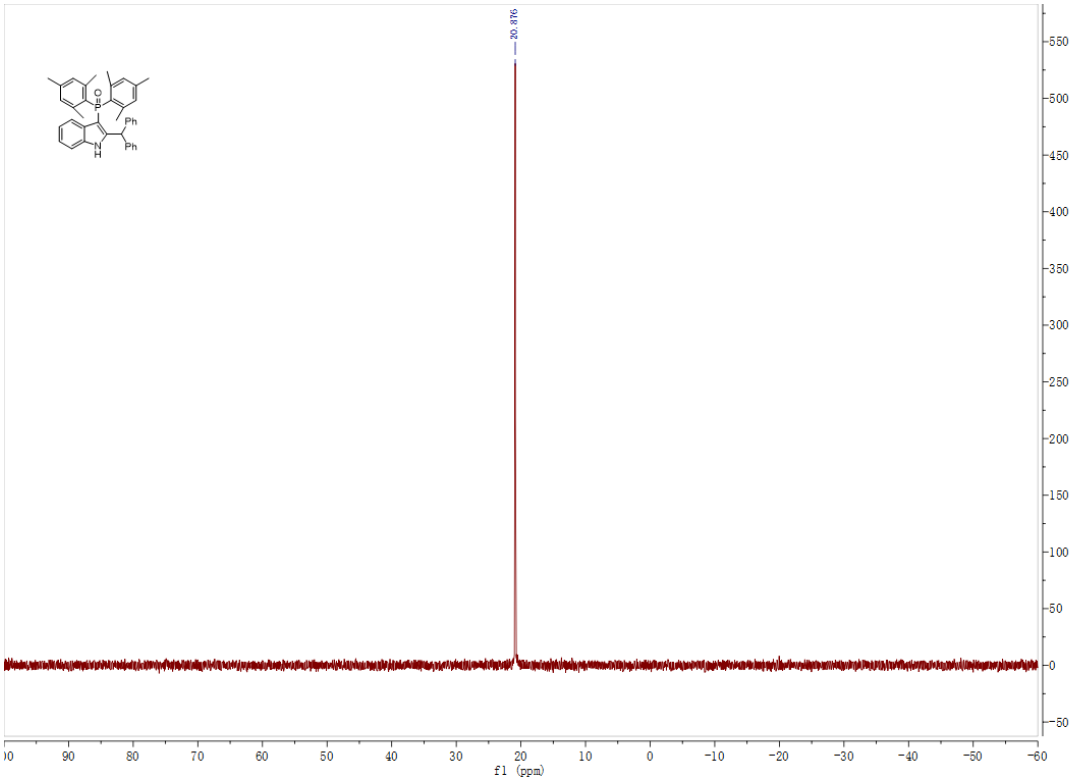
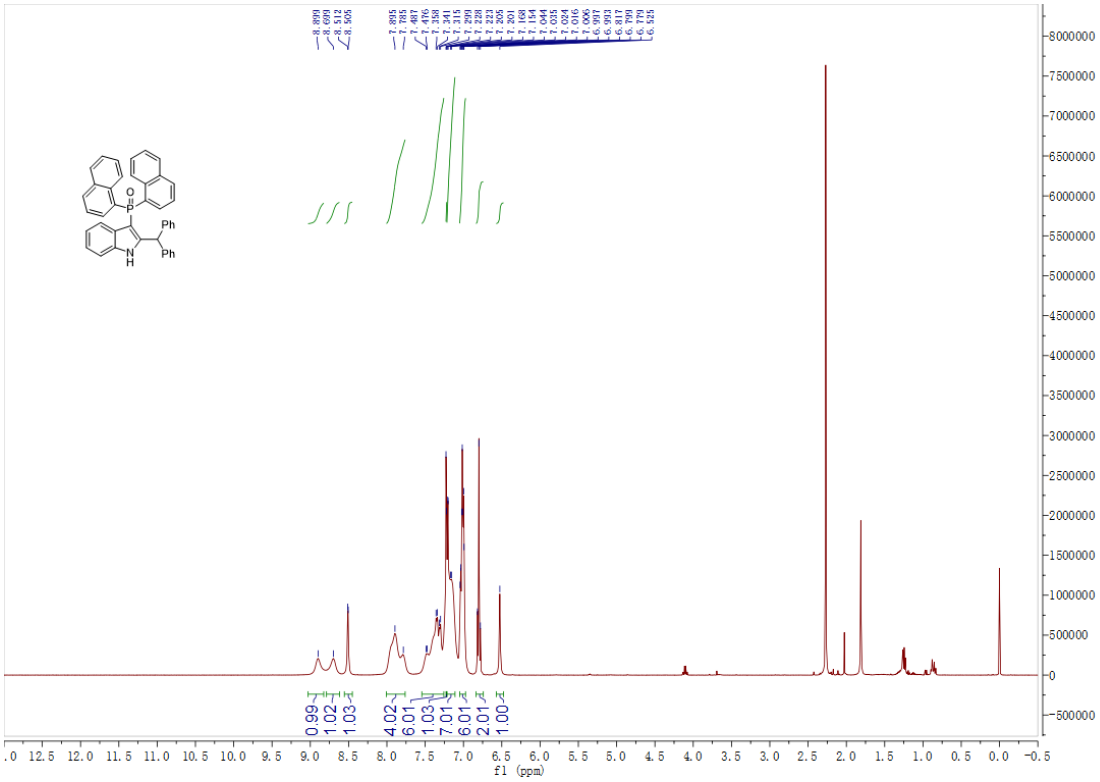
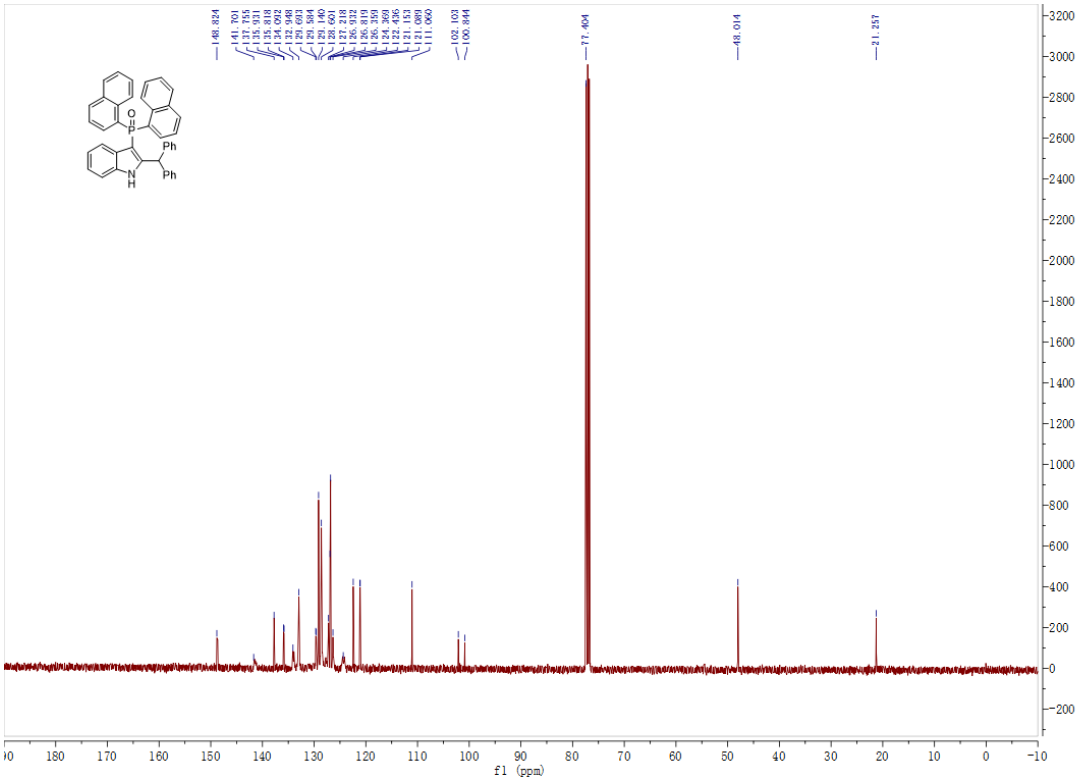
7.240
7.220
7.157
7.148
7.141
7.086
7.077
7.068
7.061
6.831
6.817
6.800
6.795
6.725
6.716
6.435
6.415
2.245
2.130
1.00
1.04
7.02
4.03
1.00
5.03
1.01
6.00
12.04
f1 (ppm)

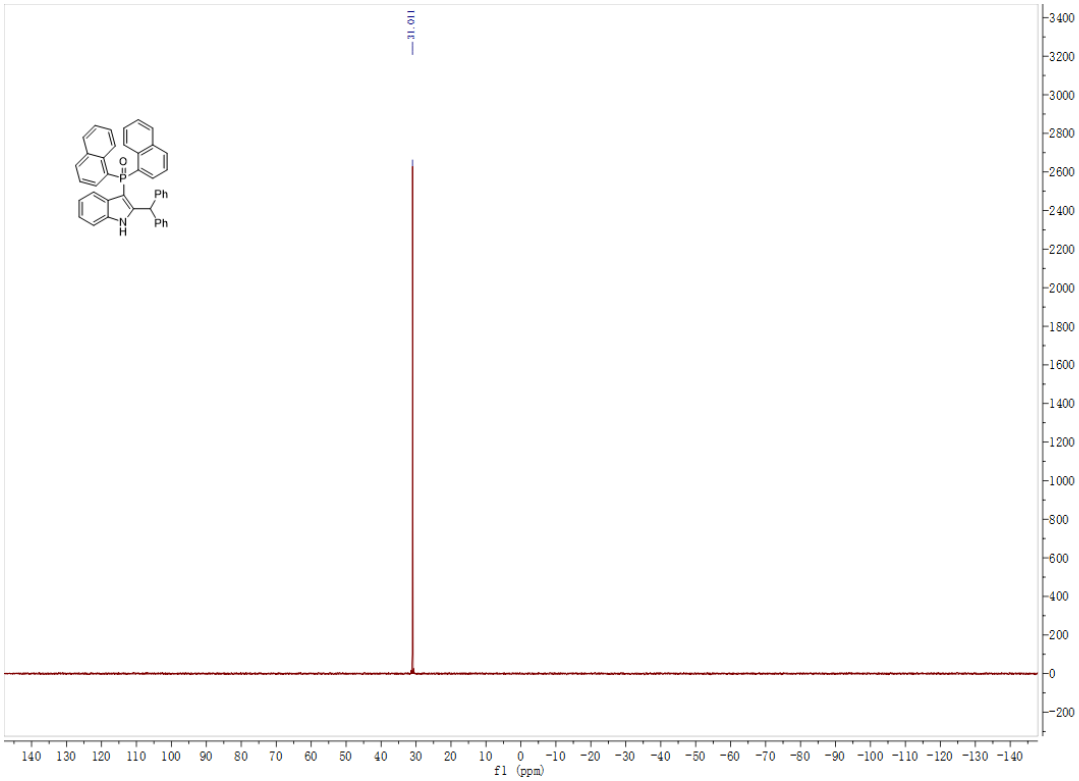

149.203
149.050
142.543
141.294
140.594
140.456
135.717
135.607
131.882
131.664
130.945
129.075
128.645
128.335
126.361
121.852
120.325
119.916
111.108
107.847
106.660
58.367
23.503
21.013
f1 (ppm)


20.876
f1 (ppm)

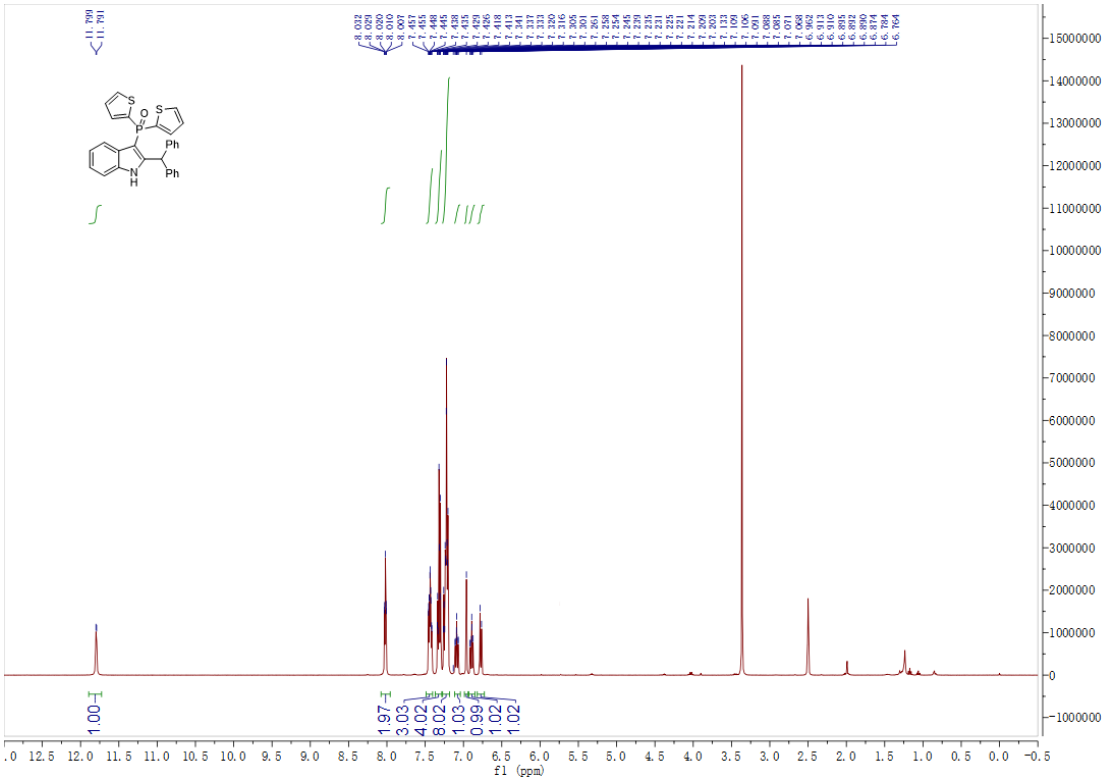
4al


8.899
8.699
8.513
8.508
7.895
7.785
7.487
7.476
7.358
7.344
7.315
7.299
7.233
7.223
7.205
7.201
7.158
7.144
7.044
7.035
7.024
7.016
7.006
6.997
6.993
6.917
6.797
6.779
6.525
0.99
1.02
1.03
4.02
6.01
1.03
7.01
6.01
2.01
1.00
f1 (ppm)





4am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11.791
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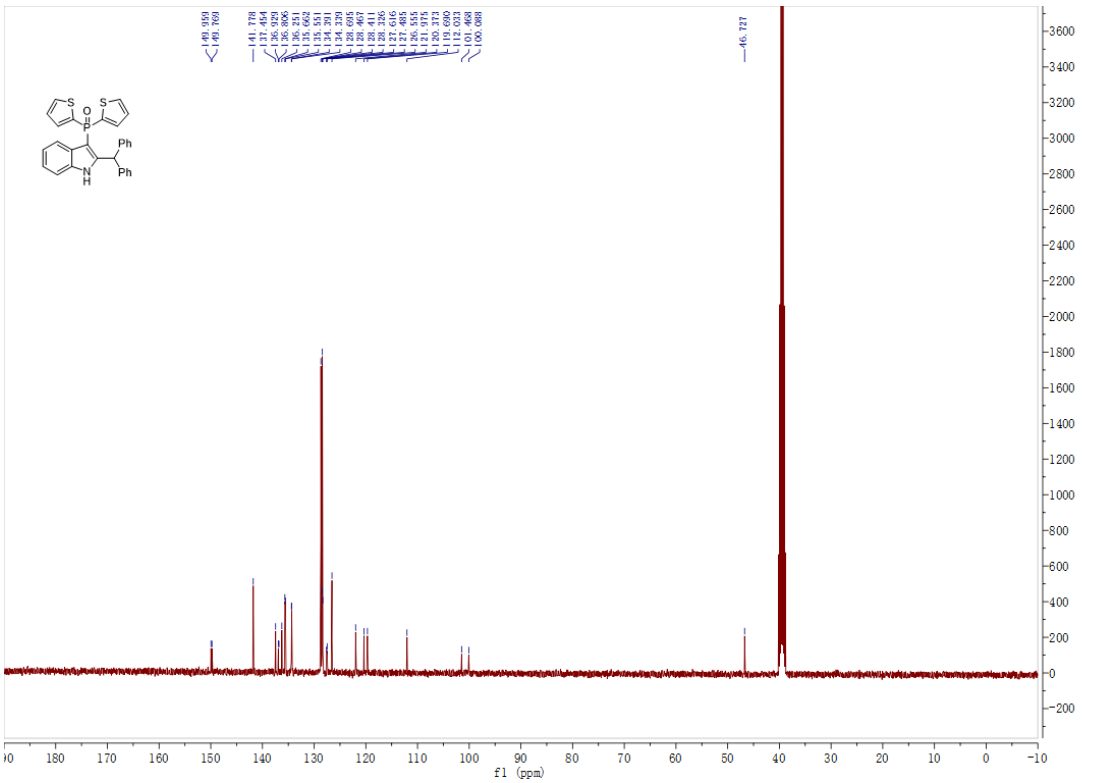
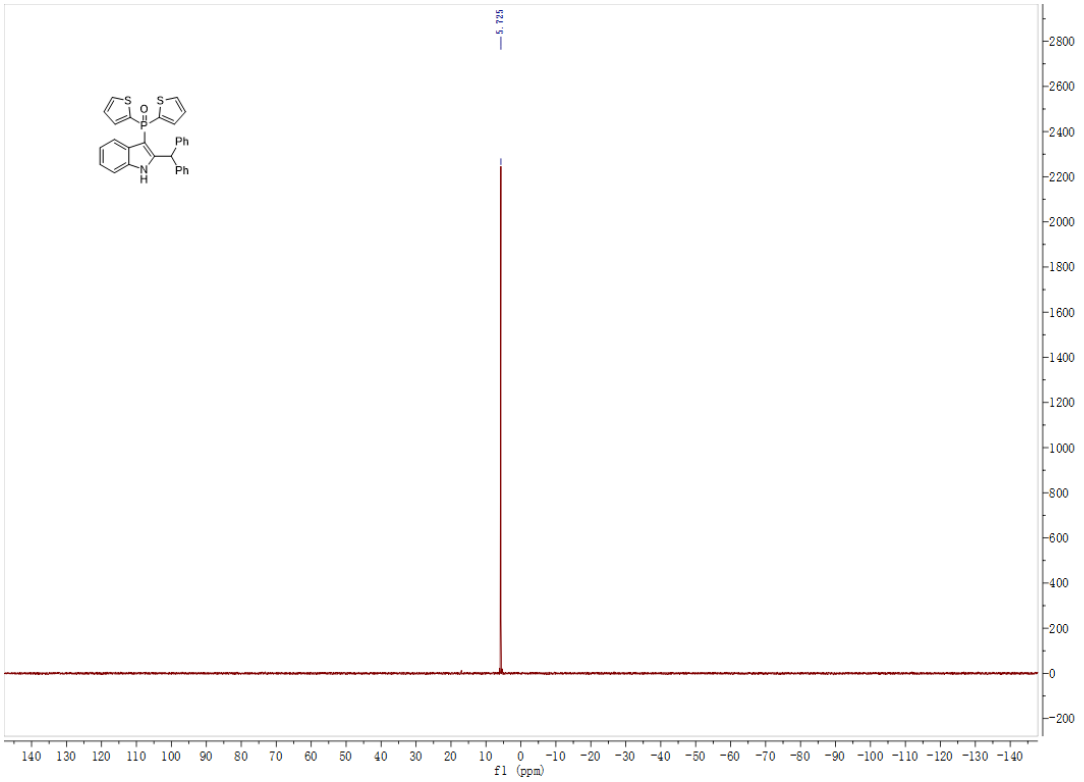
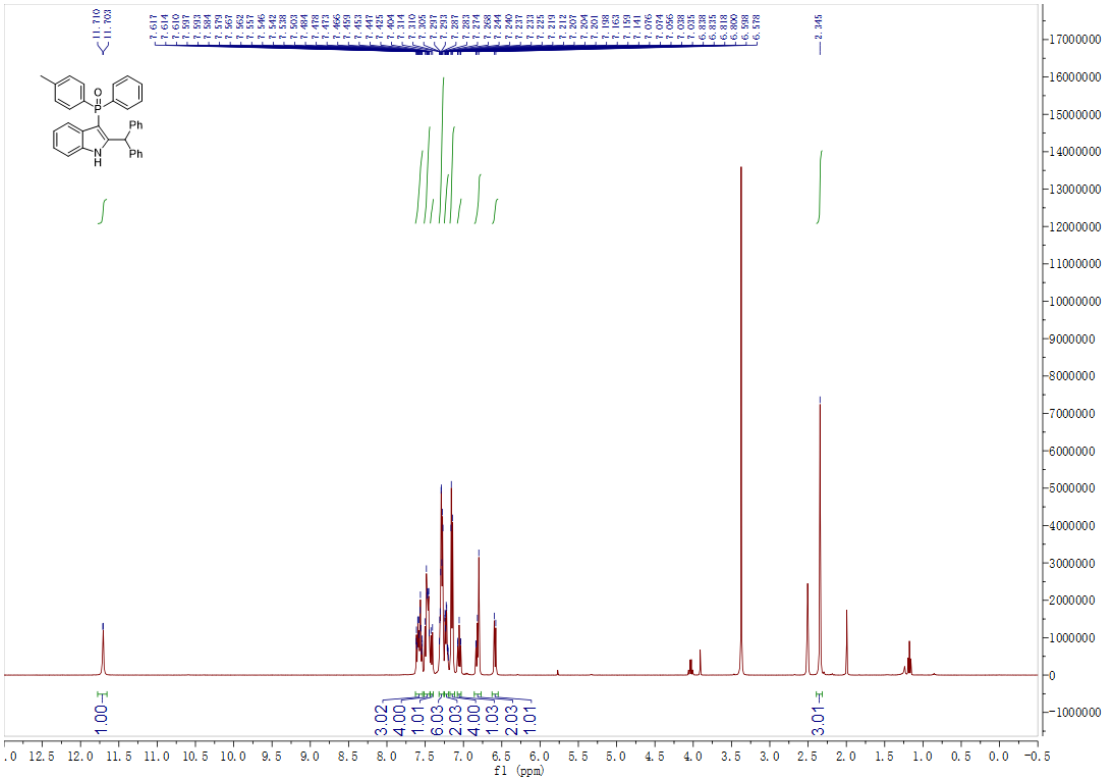
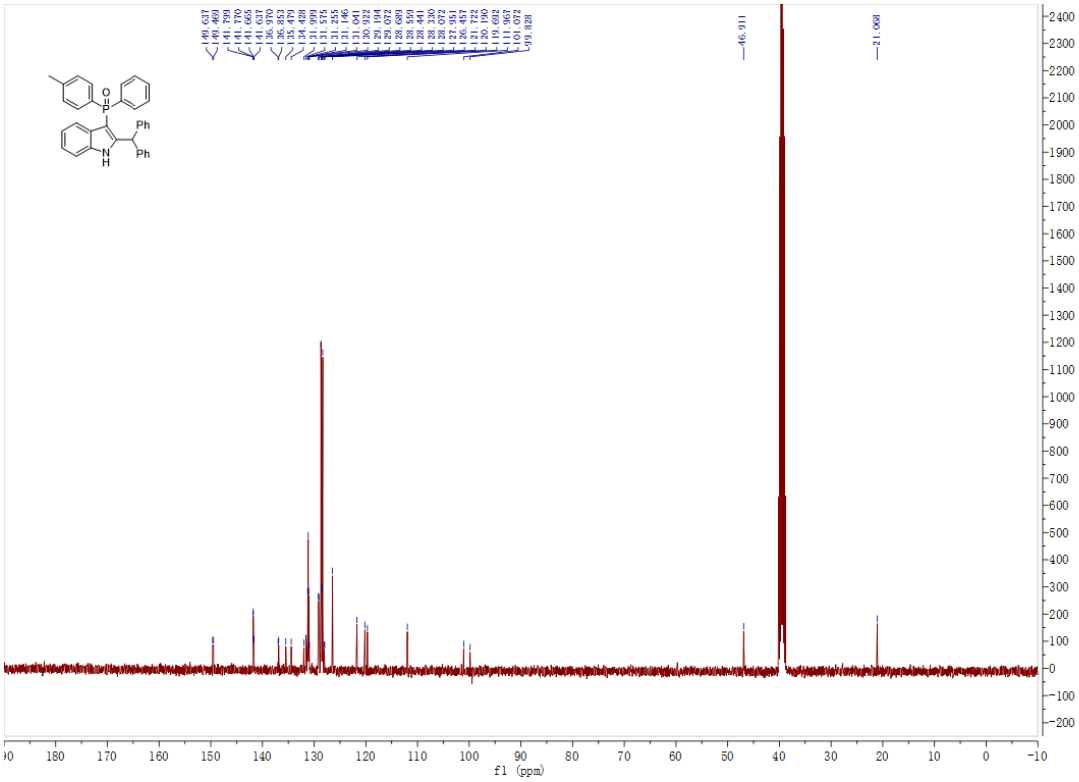
8.009
8.010
8.007
7.457
7.448
7.446
7.445
7.438
7.435
7.430
7.426
7.418
7.413
7.411
7.341
7.337
7.333
7.320
7.316
7.305
7.301
7.261
7.258
7.254
7.245
7.239
7.235
7.231
7.225
7.221
7.214
7.209
7.203
7.133
7.109
7.106
7.101
7.088
7.085
7.071
7.068
6.962
6.913
6.910
6.895
6.892
6.890
6.874
6.871
6.784
6.784
S
O
P
S
Ph
Ph
N
H
1.00
1.97
3.03
4.02
8.02
1.03
0.99
1.02
1.02
f1 (ppm)

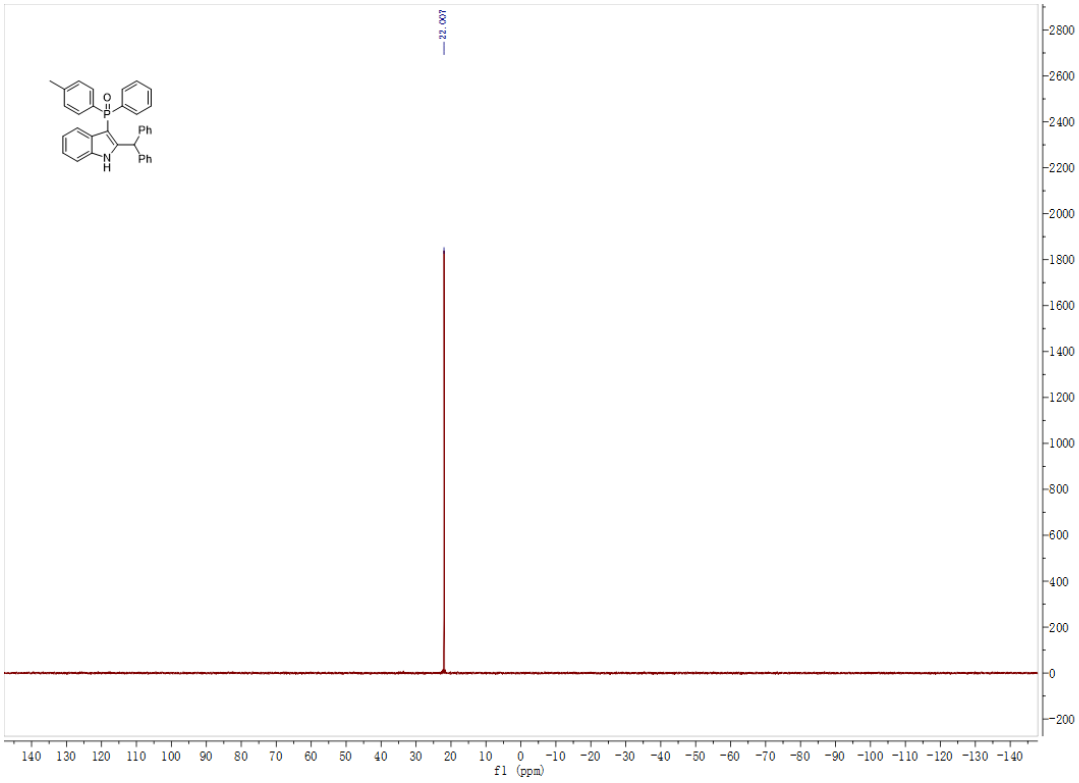

149.959
149.769
141.778
137.454
136.929
136.806
135.511
135.482
135.551
134.391
134.233
128.650
128.467
128.336
127.956
127.485
126.555
121.975
121.372
119.690
112.033
101.468
100.088
46.727
S
O
P
S
Ph
Ph
N
H
f1 (ppm)


5.725
Ph
Ph
f1 (ppm)

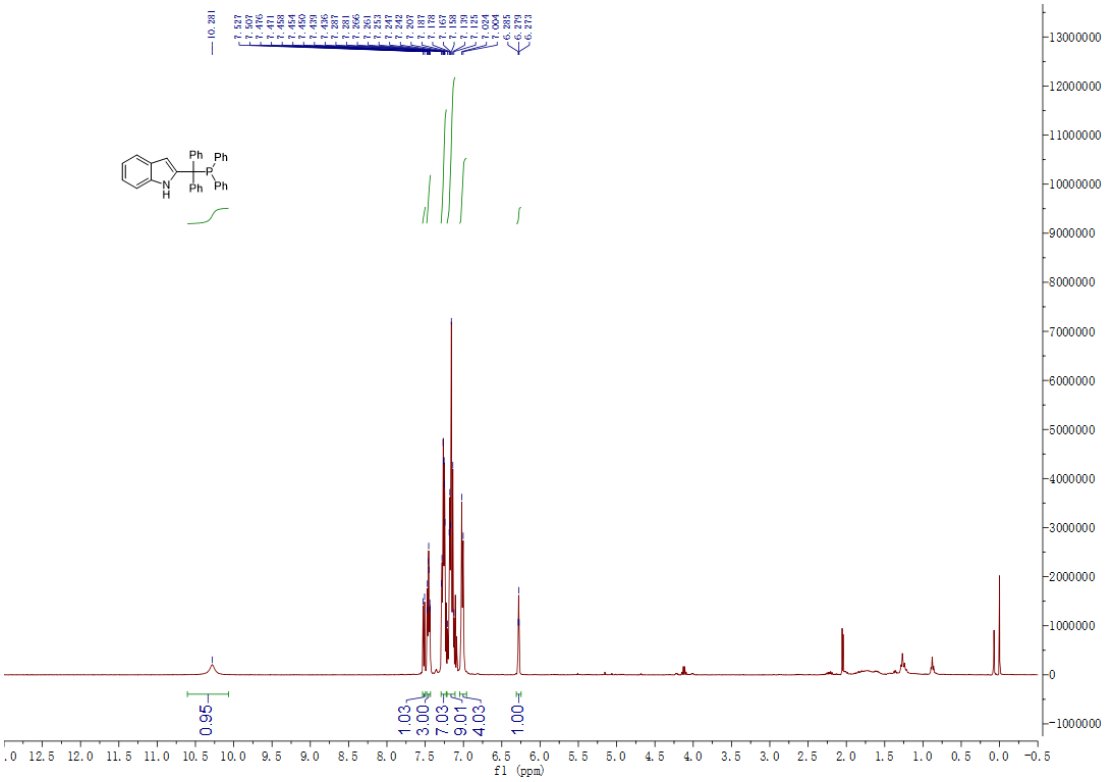
4an


11.710
11.703
2.345
Ph
Ph
1.00
3.02
4.00
1.01
6.03
2.03
4.00
1.03
2.03
1.01
3.01
f1 (ppm)





5


10.281
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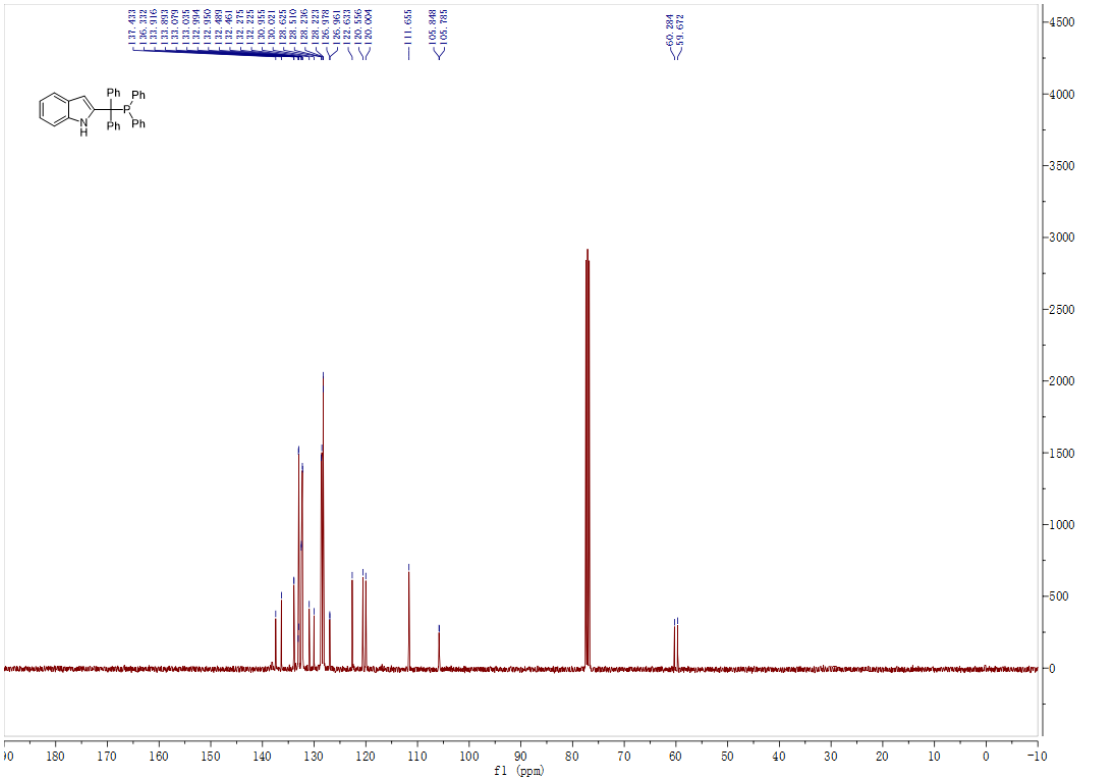
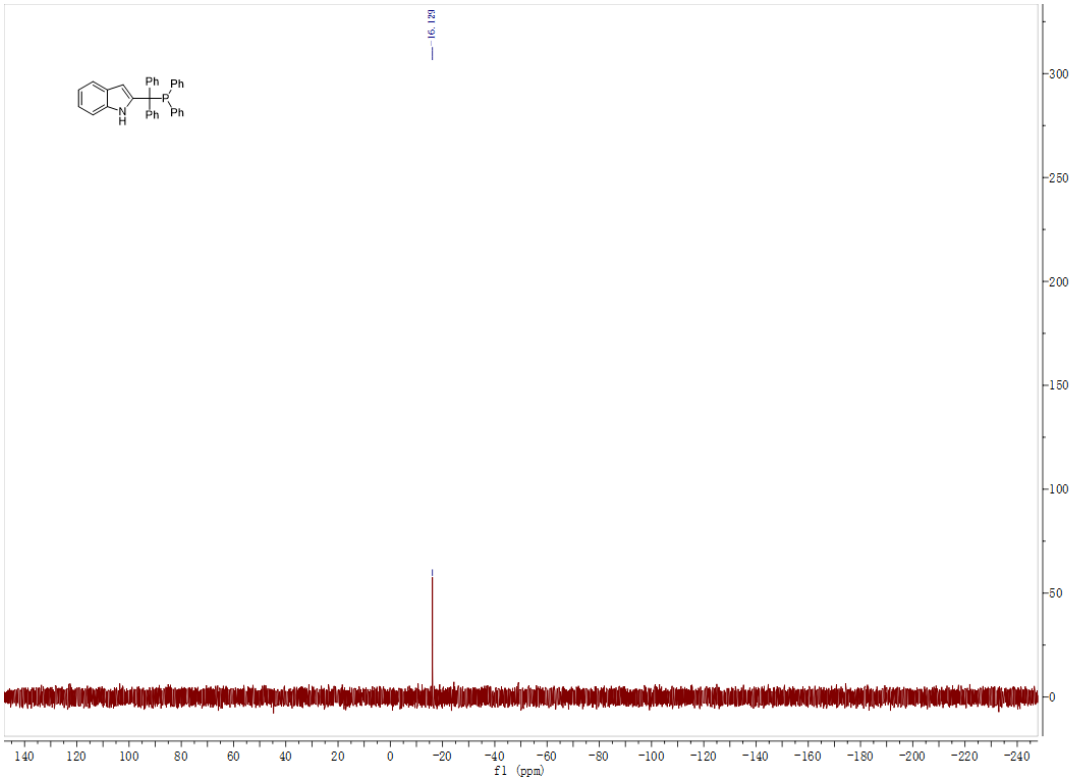
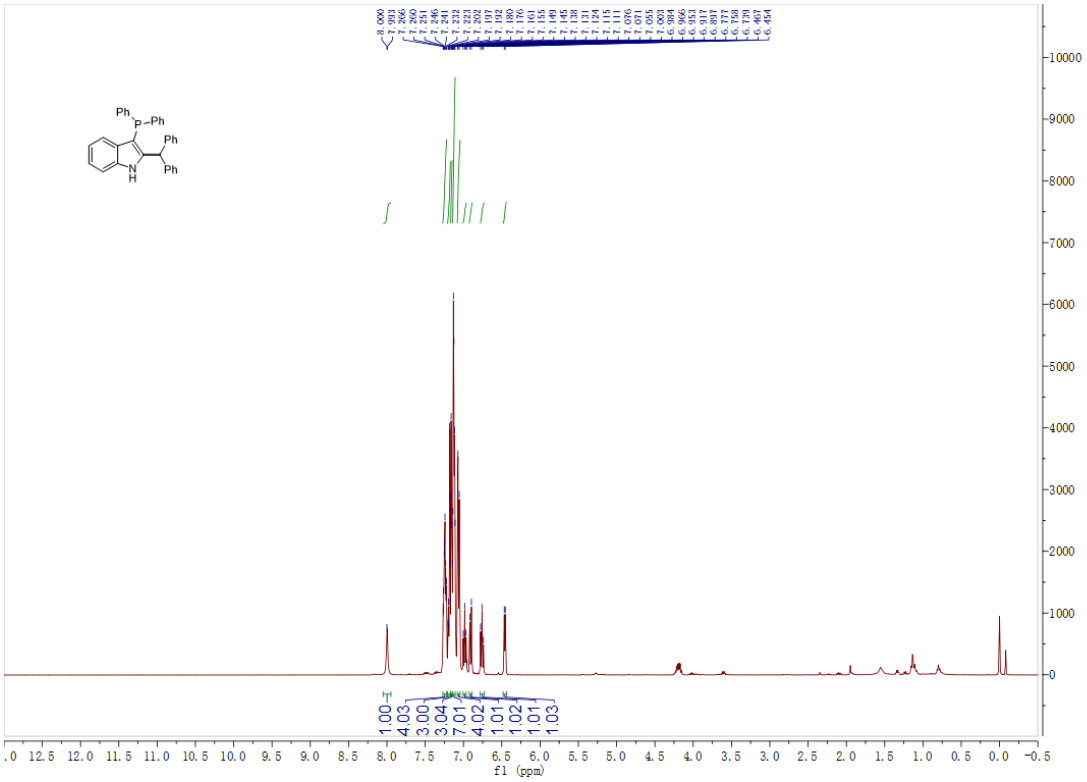
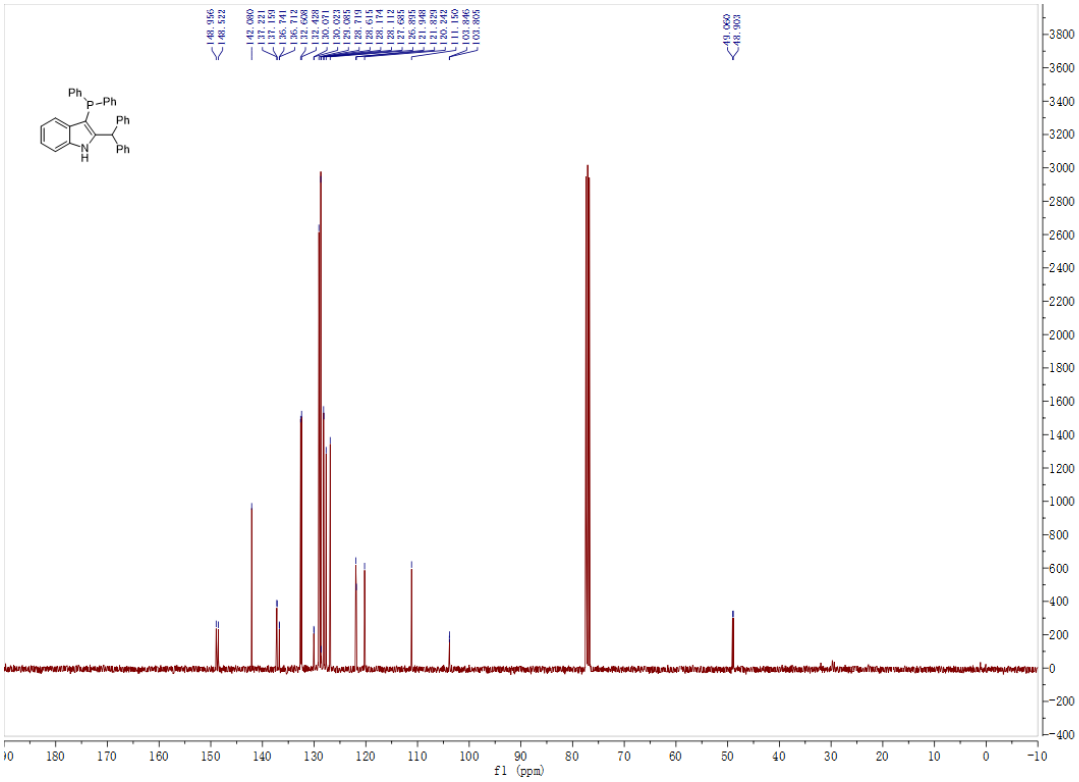
7.507
7.476
7.471
7.468
7.454
7.450
7.439
7.436
7.285
7.281
7.266
7.251
7.233
7.247
7.242
7.207
7.197
7.178
7.167
7.158
7.139
7.125
7.024
7.004
6.295
6.279
6.273
Ph
Ph
P
Ph
Ph
N
H
0.95
1.03
3.00
7.03
9.01
4.03
1.00
f1 (ppm)

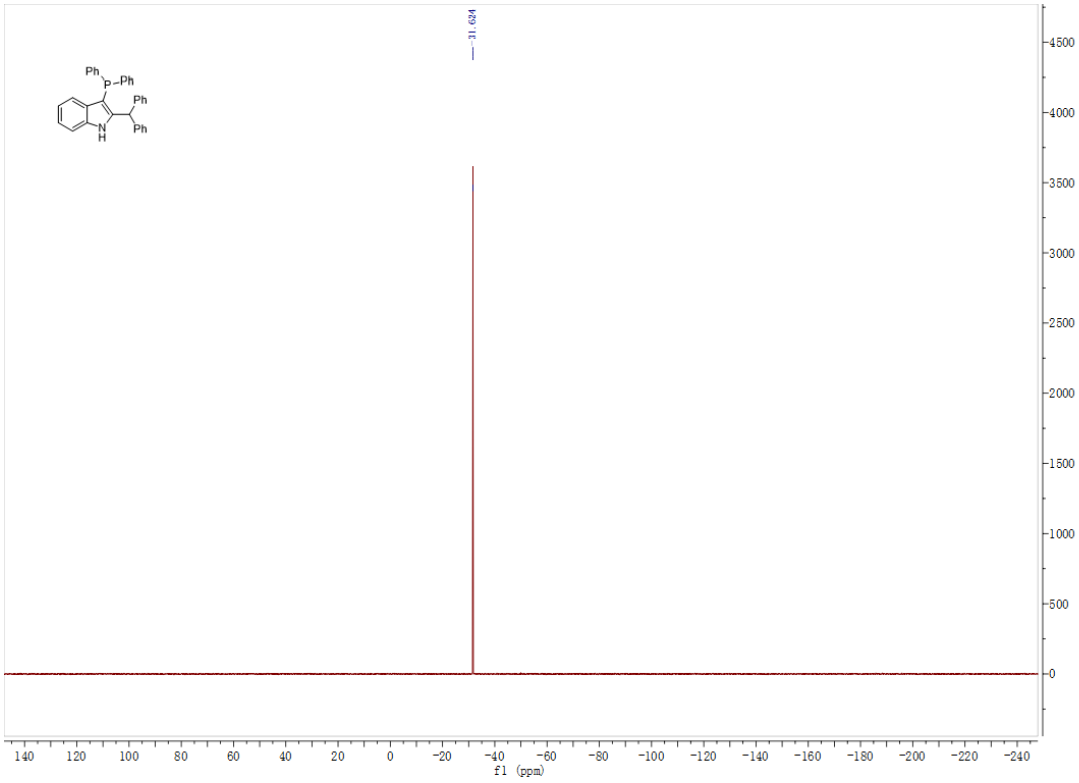

137.433
135.332
134.316
133.893
133.079
132.956
132.950
132.489
132.461
132.375
132.225
130.956
130.021
128.455
128.150
128.236
128.223
126.978
126.961
122.631
120.566
120.004
111.655
105.849
105.785
60.284
53.672
Ph
Ph
P
Ph
Ph
N
H
f1 (ppm)


16.129
Ph
Ph
P
Ph
Ph
N
H
f1 (ppm)

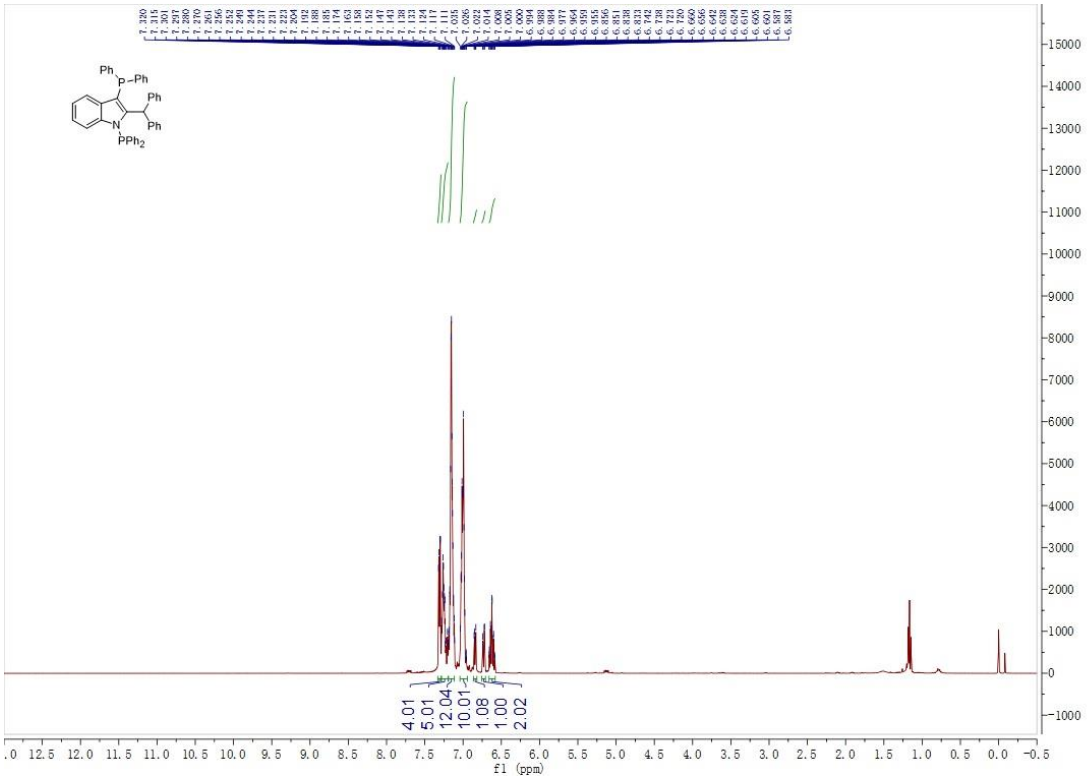
6

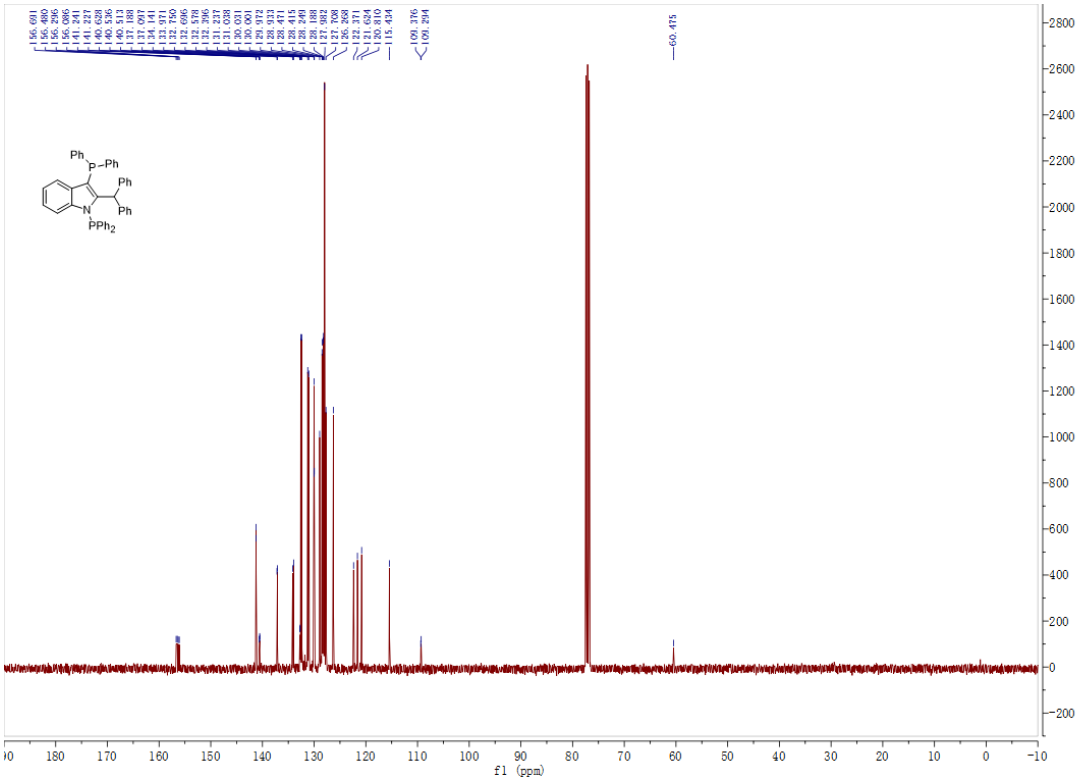

Ph
P
Ph
Ph
Ph
N
H
1.00
4.03
3.00
3.04
7.01
4.02
1.01
1.02
1.01
1.03
f1 (ppm)

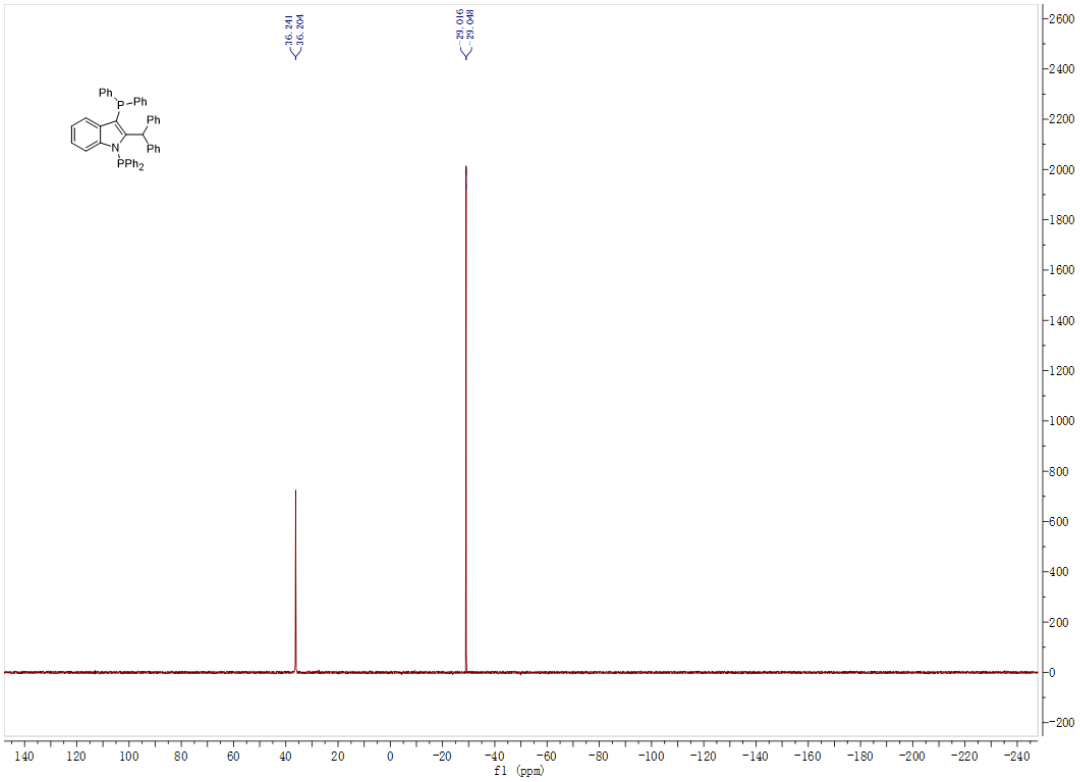




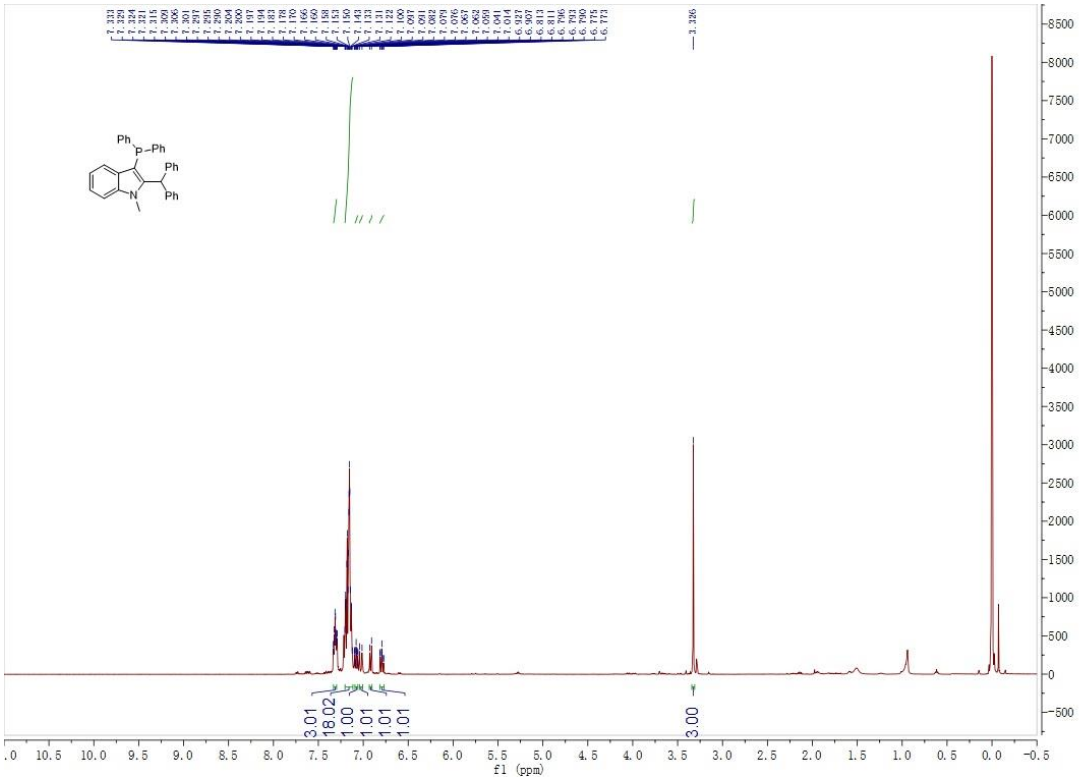
7

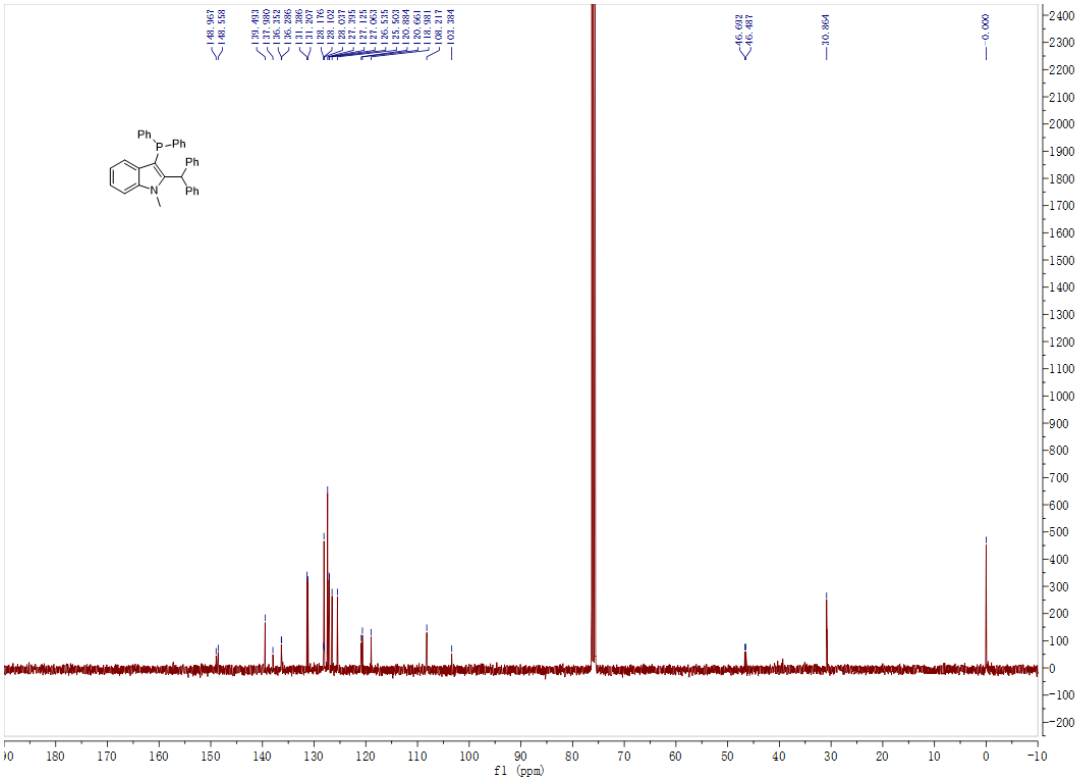

4.01
5.01
12.04
10.01
1.08
1.00
2.02
f1 (ppm)

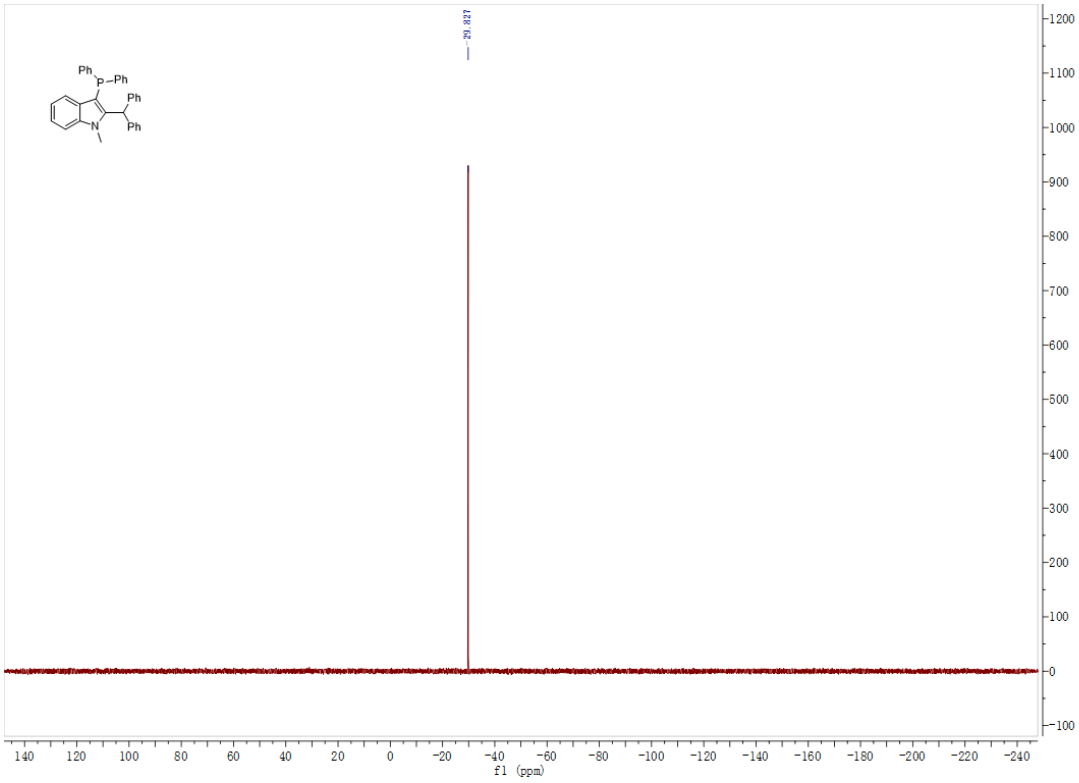

f1 (ppm)


16.241
16.204
29.016
29.048
f1 (ppm)

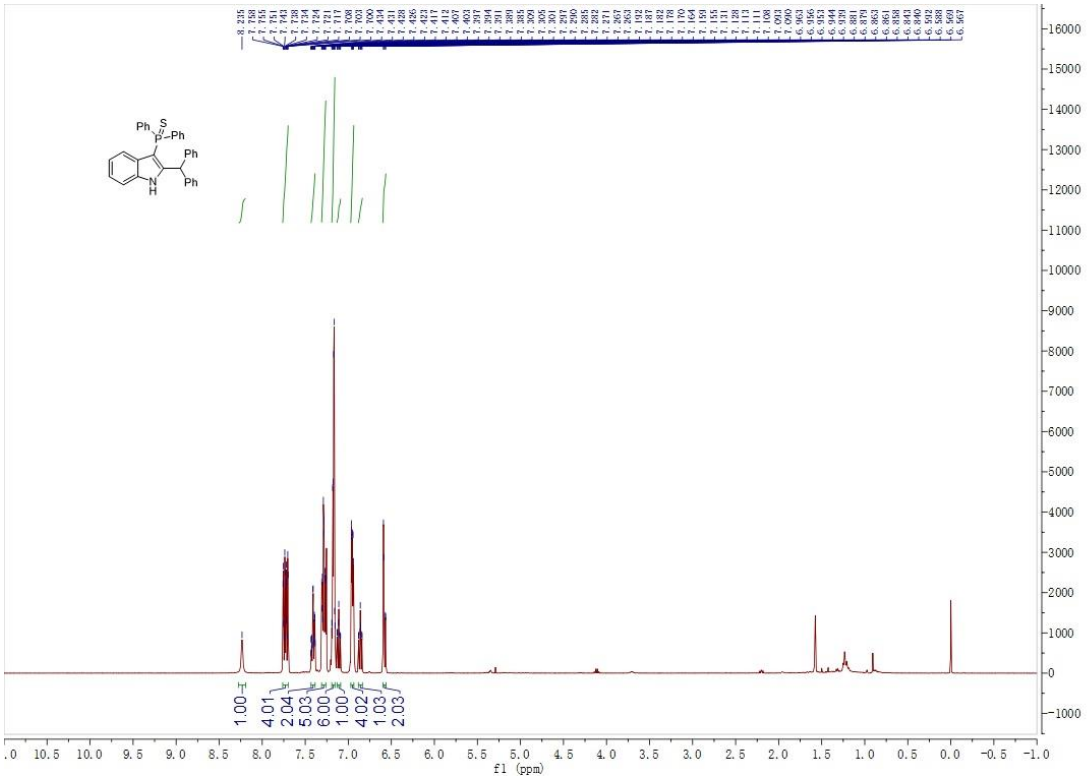
8

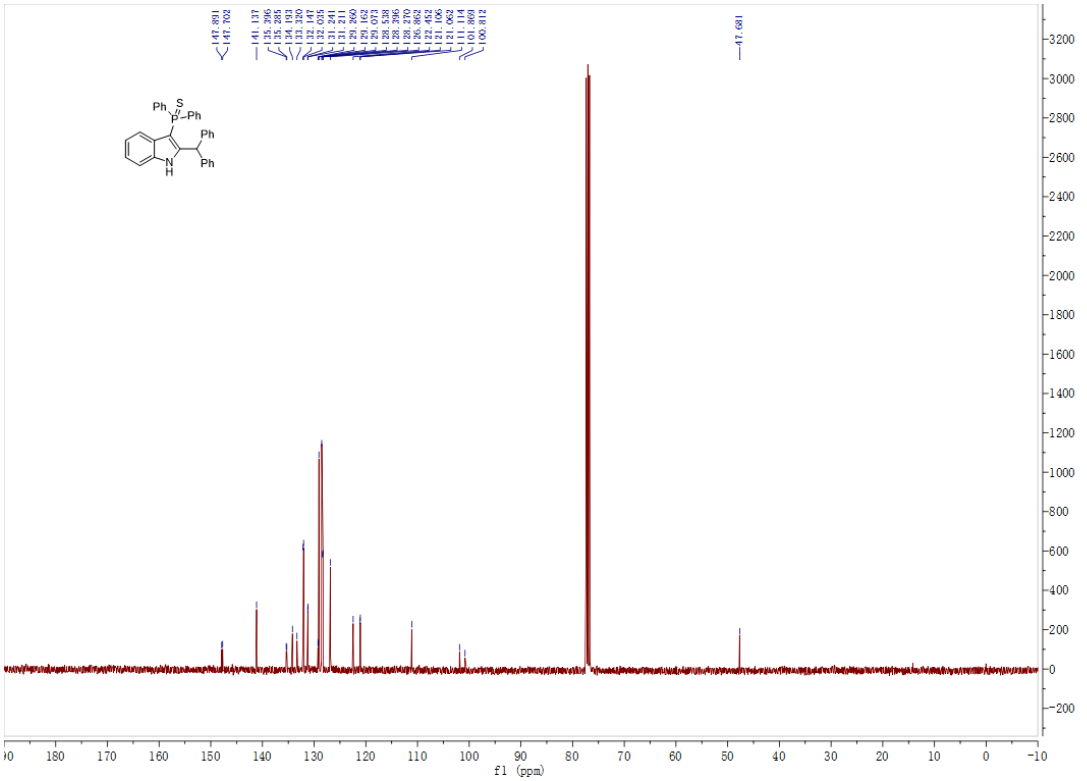

3.01
18.02
1.00
1.01
1.01
1.01
3.00
f1 (ppm)

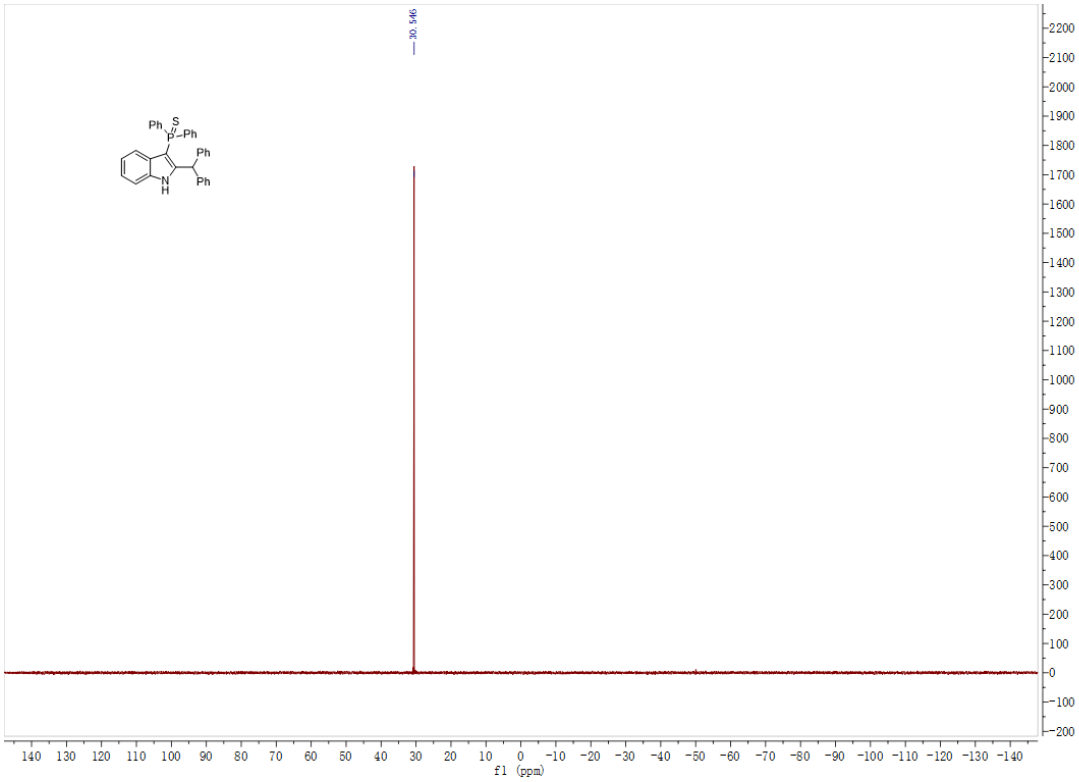




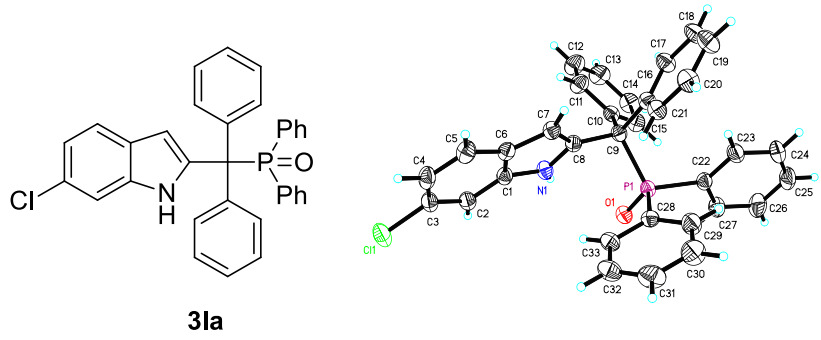
9


f1 (ppm)


f1 (ppm)


30.546
Ph
S
P
Ph
Ph
Ph
N
H
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

Crystallographic Data for Compounds **3la** and **4ag**



3la

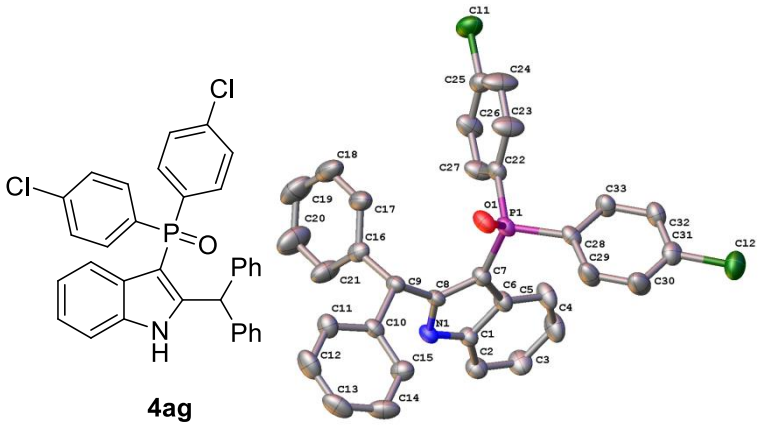
The thermal ellipsoid was drawn at the 30% probability level.

The crystal structure of **3la** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 1824762.

Table 1. Crystal data and structure refinement for **3la**.

Identification code	mo_d8v17423_0m	
Empirical formula	C34 H28 Cl4 N O2 P	
Formula weight	655.34	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.0969(3) Å	a= 90°
	b = 24.9962(7) Å	b= 110.0340(10)°
	c = 13.2961(4) Å	γ = 90°
Volume	3152.67(16) $Å^3$	
Z	4	
Density (calculated)	1.381 Mg/m^3	
Absorption coefficient	0.459 mm^{-1}	
F(000)	1352	

Crystal size	0.180 x 0.160 x 0.120 mm^3
Theta range for data collection	1.822 to 25.499°
Index ranges	-12<=h<=12, -30<=k<=30, -16<=l<=16
Reflections collected	55408
Independent reflections	5850 [R(int) = 0.0486]
Completeness to theta = 25.242?	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6724
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5850 / 24 / 423
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0643, wR2 = 0.1730
R indices (all data)	R1 = 0.0798, wR2 = 0.1898
Largest diff. peak and hole	0.834 and -0.843 e.$Å^{-3}$



The thermal ellipsoid was drawn at the 30% probability level.

The crystal structure of **4ag** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 1824763.

Table 2. Crystal data and structure refinement for **4ag**.

Identification code	4ag	
Empirical formula	C37 H32 Cl2 N O3 P	
Formula weight	640.50	
Temperature	173.01 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 13.4763(8) Å	a= 90°
	b = 18.3817(10) Å	b= 90°
	c = 25.4001(13) Å	g = 90°
Volume	6292.0(6) $Å^3$	
Z	8	

Density (calculated)	1.352 Mg/m^3
Absorption coefficient	0.296 mm^{-1}
F(000)	2672
Crystal size	0.22 x 0.2 x 0.15 mm^3
Theta range for data collection	2.357 to 26.998°
Index ranges	-14<=h<=17, -22<=k<=23, -32<=l<=31
Reflections collected	32407
Independent reflections	6813 [R(int) = 0.1004]
Completeness to theta = 25.242?	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6053
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6813 / 82 / 420
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0785, wR2 = 0.1926
R indices (all data)	R1 = 0.1197, wR2 = 0.2189
Extinction coefficient	0.0050(6)
Largest diff. peak and hole	1.187 and -0.425 $e.Å^{-3}$