Supplementary Information

The C-OH/P-H Dehydrative Cross-Coupling for the Construction of P-C Bond under Metal-free Conditions

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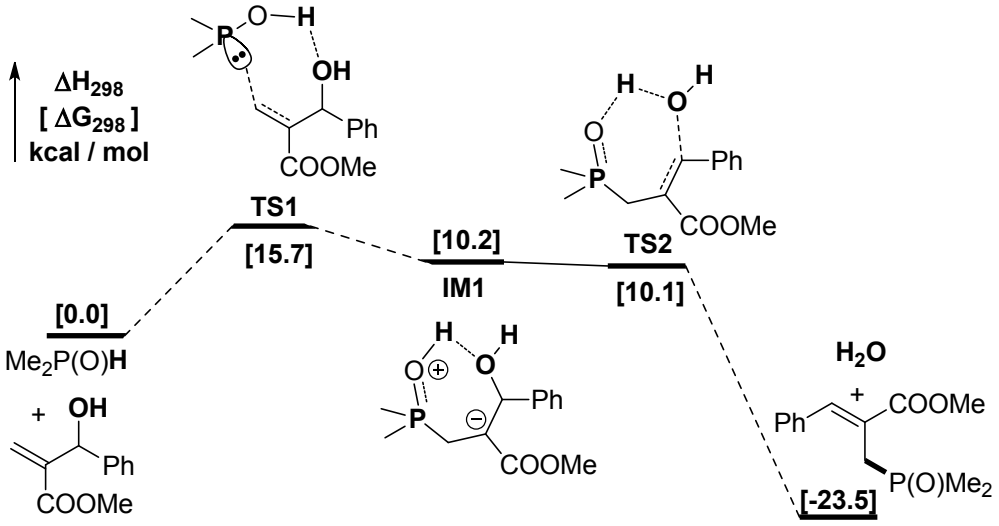
Contents

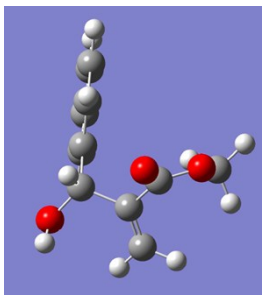
1. General Information

Unless otherwise noted, all commercially available compounds were used as received. All solvents were purified according to standard procedures. The ^{1}H NMR and spectra was recorded at 400MHz, ^{13}C NMR was recorded at 101MHz. ^{31}P NMR was recorded at 162 MHz. ^{1}H and ^{13}C NMR Chemical shifts were calibrated to tetramethylsilane as an external reference. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet); coupling constants (*J*) are in Hertz (Hz). HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. The starting materials **2a** purchased from *J&K Chemical Ltd* (Shanghai). Other phosphine oxides **2**[1], (R_P)-menthylphosphine oxide [2] and allylic alcohols [3] were readily prepared according to the related literatures.

Computational methods: All of the DFT calculations were performed with the Gaussian 09 series of programs.[4] The geometry optimization of all the minima and transition states involved were performed at the B3LYP levels of theory with the 6-31+G(d) basis set used.[5] The vibrational frequencies were computed at the same level of theory to check whether each optimized structure is an energy minimum or a transition state and to evaluate its zero-point vibrational energy (ZPVE). The computed structures are illustrated as was shown, P: yellow, C: gray, O: red, H: white.

2 Coordinates of All Stationary Points





1

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4	6	0	-1.007310	0.539758	-0.336432
5	6	0	-1.404486	-0.485223	-1.204321
6	6	0	-2.552617	-1.237034	-0.934637
7	6	0	-3.318253	-0.963415	0.201069
8	6	0	-2.930173	0.065902	1.065660
9	6	0	-1.778555	0.810327	0.802336
10	6	0	1.993225	-0.562103	-0.534834
11	8	0	2.282714	-0.569759	-1.713605
12	8	0	2.177345	-1.685780	0.194353
13	6	0	1.595630	-1.863429	1.500138
14	1	0	2.928997	0.788903	1.646280
15	1	0	1.732184	2.202042	1.559666
16	1	0	-0.817770	-0.695472	-2.095793
17	1	0	-2.850727	-2.028122	-1.617993
18	1	0	-4.215155	-1.541798	0.407909
19	1	0	-3.527588	0.291389	1.945709
20	1	0	-1.483921	1.616206	1.467815
21	1	0	1.515454	-2.944070	1.629673
22	1	0	2.249125	-1.449705	2.273049
23	1	0	0.605263	-1.407200	1.563261
24	8	0	0.062553	2.674044	-0.221020
25	1	0	0.815936	3.200897	-0.531948
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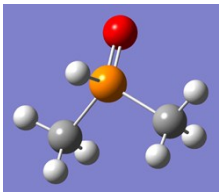

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Standard orientation:

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5	8	0	0.000000	1.592804	-0.294935
6	1	0	2.366463	-0.292276	0.145408
7	1	0	1.490287	-0.963134	-1.245276
8	1	0	1.421006	-1.795201	0.335320
9	1	0	-2.366463	-0.292276	0.145409
10	1	0	-1.490288	-0.963133	-1.245277
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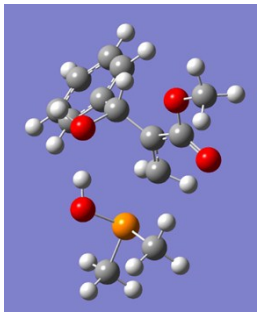

TS1

Standard orientation:

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3	6	0	-2.085215	0.383082	0.273324
4	6	0	-2.498940	-0.914537	0.603654
5	6	0	-3.751265	-1.390310	0.197225
6	6	0	-4.606394	-0.575464	-0.546868
7	6	0	-4.202019	0.721974	-0.881565
8	6	0	-2.954407	1.194318	-0.472883
9	6	0	1.758319	-3.721082	-0.503373
10	6	0	3.469573	-1.396458	-0.226454
11	6	0	1.404814	1.800259	-0.431329
12	8	0	2.429550	1.702494	-1.113263
13	8	0	1.173138	2.921305	0.329007
14	6	0	2.185573	3.931284	0.270235
15	1	0	1.088328	-0.197511	-2.077317
16	1	0	-1.842938	-1.556348	1.185644
17	1	0	-4.056135	-2.399089	0.465735
18	1	0	-5.580429	-0.943317	-0.859320
19	1	0	-4.862063	1.367593	-1.455797

20	1	0	-2.643958	2.203094	-0.737484
21	1	0	2.374179	-4.212445	0.259905
22	1	0	2.177280	-3.926387	-1.494339
23	1	0	0.744525	-4.130221	-0.455989
24	1	0	3.903345	-1.606861	-1.210979
25	1	0	3.535991	-0.318497	-0.056198
26	1	0	4.029604	-1.938485	0.544474
27	1	0	1.838719	4.728842	0.930371
28	1	0	2.304993	4.305760	-0.751018
29	1	0	3.146784	3.540309	0.617921
30	6	0	-0.728305	0.941668	0.682295
31	1	0	-0.846876	2.001179	0.922915
32	1	0	-0.433870	-0.907651	-1.372327
33	15	0	1.705680	-1.900904	-0.208314
34	8	0	1.260615	-1.869590	1.361868
35	1	0	0.725916	-1.064201	1.615537
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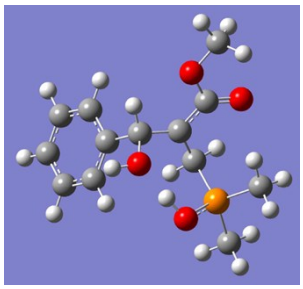

IM1

Standard orientation:

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1	6	0	0.449380	0.666352	-0.184314
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3	6	0	-2.018548	0.346763	0.329331
4	6	0	-2.517062	-0.953819	0.497170
5	6	0	-3.778880	-1.308786	0.003388
6	6	0	-4.563126	-0.368478	-0.665910
7	6	0	-4.076245	0.933076	-0.837978
8	6	0	-2.819357	1.283356	-0.345621
9	6	0	1.757217	-3.420262	-0.932658
10	6	0	3.367530	-1.162441	0.039044
11	6	0	1.404307	1.688600	-0.399122
12	8	0	2.385880	1.615226	-1.165423

13	8	0	1.176612	2.854549	0.319619
14	6	0	2.124501	3.901043	0.113025
15	1	0	1.109384	-0.336319	-1.977402
16	1	0	-1.924888	-1.696273	1.025952
17	1	0	-4.146627	-2.322148	0.147903
18	1	0	-5.544454	-0.641775	-1.045353
19	1	0	-4.679962	1.676762	-1.352632
20	1	0	-2.442580	2.293688	-0.489859
21	1	0	2.344213	-4.107558	-0.314827
22	1	0	2.221864	-3.337682	-1.920714
23	1	0	0.745625	-3.822269	-1.043824
24	1	0	3.856445	-1.112239	-0.938733
25	1	0	3.335519	-0.149510	0.446561
26	1	0	3.924510	-1.827114	0.707455
27	1	0	1.789313	4.726579	0.745896
28	1	0	2.147782	4.213905	-0.935944
29	1	0	3.132495	3.588139	0.406130
30	6	0	-0.640017	0.785928	0.806755
31	1	0	-0.691598	1.825608	1.132819
32	1	0	-0.334492	-1.080448	-1.234057
33	15	0	1.673997	-1.780116	-0.144063
34	8	0	1.050576	-2.079948	1.297354
35	1	0	0.536106	-1.282233	1.690489
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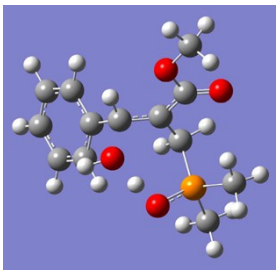

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Standard orientation:

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3	6	0	-1.972687	0.475461	0.248672
4	6	0	-2.436366	-0.848020	0.330797
5	6	0	-3.733605	-1.179471	-0.075724

6	6	0	-4.590583	-0.195628	-0.572737
7	6	0	-4.141941	1.126915	-0.654748
8	6	0	-2.849639	1.456511	-0.244688
9	6	0	1.349355	-3.530884	-0.816923
10	6	0	3.260038	-1.488869	0.063399
11	6	0	1.577818	1.615304	-0.449872
12	8	0	2.593975	1.440628	-1.143134
13	8	0	1.407215	2.798898	0.244396
14	6	0	2.461304	3.753179	0.108298
15	1	0	1.229989	-0.441011	-1.995978
16	1	0	-1.791522	-1.624951	0.732211
17	1	0	-4.073166	-2.209734	0.001629
18	1	0	-5.599017	-0.453329	-0.886043
19	1	0	-4.801761	1.904241	-1.032245
20	1	0	-2.506753	2.486397	-0.314747
21	1	0	1.843800	-4.270715	-0.179155
22	1	0	1.810910	-3.545613	-1.809995
23	1	0	0.292220	-3.798289	-0.909275
24	1	0	3.745897	-1.582555	-0.913065
25	1	0	3.379352	-0.455785	0.398219
26	1	0	3.722983	-2.175274	0.779937
27	1	0	2.159599	4.608045	0.717994
28	1	0	2.586057	4.057018	-0.935909
29	1	0	3.411121	3.347091	0.471567
30	6	0	-0.573276	0.906162	0.627155
31	1	0	-0.568777	1.935040	0.977021
32	1	0	-0.333671	-1.021480	-1.369914
33	15	0	1.490507	-1.872483	-0.073175
34	8	0	0.828419	-1.959419	1.350819
35	1	0	0.339554	-0.995484	1.735093
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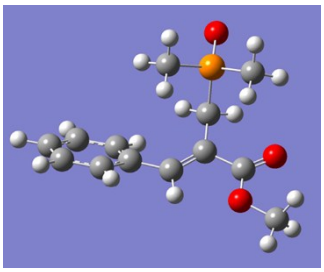

3

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4	8	0	1.168578	3.462434	-0.659261
5	6	0	-1.861573	-0.879498	-0.079806
6	6	0	-2.461351	-0.211504	-1.164295
7	6	0	-3.817355	0.116567	-1.139867
8	6	0	-4.604903	-0.210889	-0.031980
9	6	0	-4.030439	-0.894443	1.043651
10	6	0	-2.678926	-1.237455	1.011048
11	15	0	1.095126	2.166109	0.104883
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13	1	0	-0.184684	1.045614	-1.542798
14	1	0	-1.878812	0.017585	-2.050479
15	1	0	-4.260886	0.623568	-1.992865
16	1	0	-5.659459	0.051127	-0.014132
17	1	0	-4.636314	-1.168964	1.903312
18	1	0	-2.241464	-1.782853	1.844591
19	1	0	-0.280959	-2.260260	0.418989
20	6	0	-0.235516	2.138621	1.367156
21	1	0	-1.195766	2.345309	0.884957
22	1	0	-0.296350	1.179016	1.890058
23	1	0	-0.036107	2.933730	2.093687
24	6	0	2.624414	1.763940	1.027950
25	1	0	2.524151	0.849023	1.621225
26	1	0	3.453245	1.642118	0.325589
27	1	0	2.844678	2.603207	1.696594
28	6	0	1.987163	-1.343547	-0.385647
29	8	0	3.021650	-0.887518	-0.843221
30	8	0	1.940150	-2.543599	0.238896
31	6	0	3.183919	-3.264881	0.304274
32	1	0	3.931158	-2.688990	0.856679
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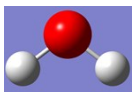

H_2O

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
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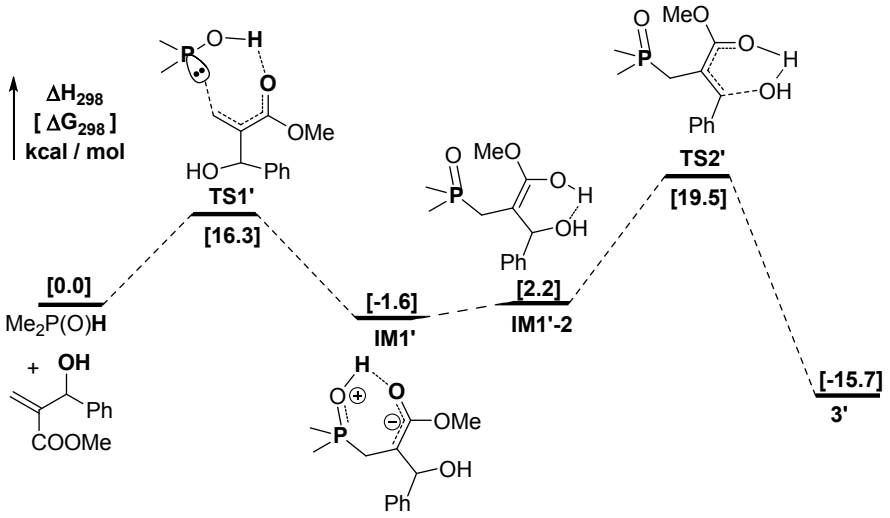

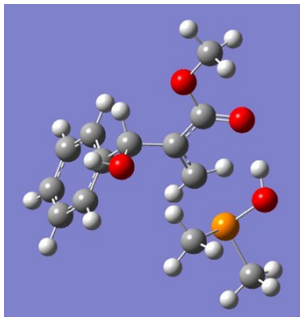

TS1’

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.236695	0.786142	-0.297918
2	6	0	0.369370	-0.372984	-1.090249
3	6	0	-2.209316	0.320707	0.249755
4	6	0	-2.618954	-0.905373	0.788537
5	6	0	-3.818829	-1.500024	0.380859
6	6	0	-4.626394	-0.874588	-0.571357
7	6	0	-4.226720	0.352655	-1.112867
8	6	0	-3.029963	0.942765	-0.703615
9	6	0	1.754412	-1.915463	1.628831
10	6	0	2.451365	-3.513095	-0.680530

11	6	0	1.297630	1.754656	-0.357573
12	8	0	2.425132	1.561251	-0.860837
13	8	0	0.997497	2.968407	0.177471
14	6	0	2.049723	3.943227	0.174089
15	1	0	0.961321	-0.289404	-1.999711
16	1	0	-1.995780	-1.388215	1.536008
17	1	0	-4.122069	-2.451468	0.811879
18	1	0	-5.560491	-1.333488	-0.885518
19	1	0	-4.850969	0.852151	-1.849940
20	1	0	-2.723604	1.896440	-1.129364
21	1	0	2.743312	-2.097923	2.064918
22	1	0	1.076591	-2.730223	1.909861
23	1	0	1.343331	-0.977328	2.015113
24	1	0	1.696637	-4.255602	-0.400063
25	1	0	2.603415	-3.552838	-1.763393
26	1	0	3.400038	-3.751065	-0.183367
27	1	0	1.633261	4.816433	0.679215
28	1	0	2.340855	4.196227	-0.849318
29	1	0	2.924922	3.569128	0.712859
30	6	0	-0.904013	0.991656	0.668079
31	1	0	-1.086382	2.070542	0.731263
32	1	0	-0.502858	-1.011283	-1.197035
33	15	0	1.889568	-1.821963	-0.198069
34	8	0	3.245299	-0.961567	-0.504337
35	1	0	3.035997	0.000861	-0.693526
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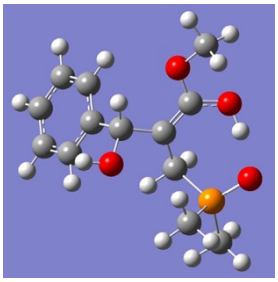
37	1	0	-1.129025	0.846346	2.637391



IM1’

Standard orientation:

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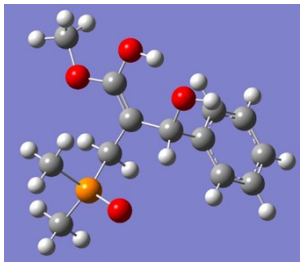
3	8	0	-0.002031	2.814270	0.179762

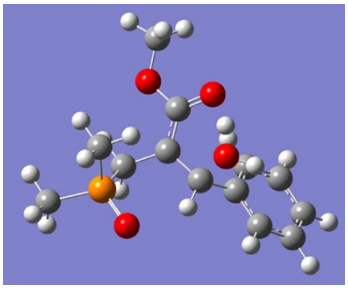
4	15	0	2.552442	-1.119017	-0.236930
5	6	0	2.705885	-1.527593	1.532856
6	6	0	2.977802	-2.650906	-1.145149
7	1	0	2.328992	-0.691979	2.127842
8	1	0	3.763074	-1.694100	1.764872
9	1	0	2.125313	-2.420202	1.786511
10	1	0	4.027390	-2.900979	-0.958179
11	1	0	2.347818	-3.491933	-0.835404
12	1	0	2.851022	-2.481717	-2.219329
13	6	0	0.241060	0.473177	0.076055
14	6	0	0.736019	4.040311	0.308880
15	1	0	0.036009	4.745726	0.760624
16	1	0	1.605070	3.904862	0.962198
17	1	0	1.065435	4.405976	-0.666354
18	6	0	-0.888331	0.290521	1.061791
19	8	0	-0.430690	-0.633896	2.076004
20	1	0	-1.146927	-0.752733	2.721306
21	8	0	3.427262	0.059774	-0.657275
22	1	0	2.431010	1.318524	-0.992769
23	6	0	0.787049	-0.763807	-0.609293
24	1	0	0.186865	-1.637104	-0.332498
25	1	0	0.737627	-0.675669	-1.705911
26	6	0	-2.182915	-0.195910	0.405545
27	6	0	-2.571464	-1.542101	0.417615
28	6	0	-3.006393	0.735001	-0.248249
29	6	0	-3.753084	-1.950710	-0.212482
30	1	0	-1.951736	-2.274588	0.928030
31	6	0	-4.184361	0.329995	-0.876395
32	1	0	-2.713523	1.782491	-0.266166
33	6	0	-4.562852	-1.017634	-0.862075
34	1	0	-4.038623	-2.999969	-0.192169
35	1	0	-4.810547	1.066272	-1.374629
36	1	0	-5.482148	-1.333629	-1.348737
37	1	0	-1.089446	1.261051	1.526329



IM1’-2

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.959463	1.826190	0.054259
2	8	0	-2.004933	2.089588	-0.775918
3	8	0	-0.597307	2.895843	0.799544
4	15	0	-1.925240	-1.800651	0.014582
5	6	0	-3.418096	-0.950938	0.650844
6	6	0	-2.530509	-2.876648	-1.345693
7	1	0	-3.118265	-0.229041	1.416487
8	1	0	-4.079715	-1.692862	1.110135
9	1	0	-3.954610	-0.421103	-0.143237
10	1	0	-3.172277	-3.657433	-0.923951
11	1	0	-3.096347	-2.312237	-2.095317
12	1	0	-1.676180	-3.361459	-1.829716
13	6	0	-0.413021	0.587279	0.090640
14	6	0	0.707799	0.171592	1.029688
15	8	0	0.875988	1.188256	2.061458
16	1	0	1.742484	1.064531	2.479398
17	8	0	-1.161528	-2.556783	1.078237
18	6	0	-0.916354	-0.497650	-0.831990
19	1	0	-1.512750	-0.066128	-1.642172
20	1	0	-0.074829	-1.035117	-1.294014
21	6	0	2.034934	-0.083193	0.322803
22	6	0	2.661081	0.921455	-0.432048
23	6	0	2.659154	-1.331463	0.443697
24	6	0	3.893949	0.685180	-1.040884
25	1	0	2.174969	1.887845	-0.544246
26	6	0	3.890966	-1.573984	-0.175276
27	1	0	2.170346	-2.118272	1.014387
28	6	0	4.511807	-0.565412	-0.914629
29	1	0	4.371638	1.471888	-1.619866
30	1	0	4.361578	-2.549224	-0.078416
31	1	0	5.469773	-0.750441	-1.394268
32	1	0	0.406834	-0.757569	1.527965
33	6	0	-2.286929	3.461020	-1.087396
34	1	0	-2.572668	4.019633	-0.192488
35	1	0	-1.422533	3.942141	-1.558576
36	1	0	-3.120748	3.425228	-1.790741
37	1	0	0.072210	2.573592	1.449258



TS2’

Standard orientation:

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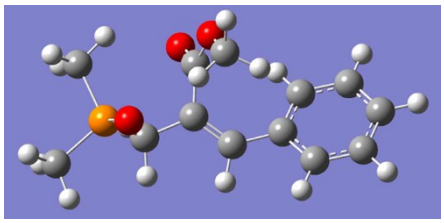
1	6	0	-0.282359	1.750889	0.020391
2	8	0	-1.108232	2.604355	-0.643689
3	8	0	0.464178	2.221771	0.955836
4	15	0	-2.623096	-1.294792	-0.130387
5	6	0	-3.444903	-0.221197	1.106769
6	6	0	-3.948894	-1.767884	-1.309995
7	1	0	-2.691171	0.166944	1.798640
8	1	0	-4.163191	-0.820950	1.675525
9	1	0	-3.965980	0.618201	0.633220
10	1	0	-4.679797	-2.398054	-0.792233
11	1	0	-4.459573	-0.892841	-1.727405
12	1	0	-3.511847	-2.352370	-2.126438
13	6	0	-0.351525	0.393116	-0.294523
14	6	0	0.597489	-0.501853	0.344241
15	8	0	0.635312	0.046039	2.045139
16	1	0	1.512018	-0.170430	2.411064
17	8	0	-1.918657	-2.486746	0.479406
18	6	0	-1.492891	-0.193765	-1.098465
19	1	0	-2.084248	0.619374	-1.532180
20	1	0	-1.135851	-0.806180	-1.940493
21	6	0	2.059370	-0.539131	0.016336
22	6	0	2.698916	0.464552	-0.728487
23	6	0	2.809399	-1.656566	0.428162
24	6	0	4.057778	0.366143	-1.026771
25	1	0	2.124122	1.314917	-1.079287
26	6	0	4.169224	-1.756748	0.127826
27	1	0	2.315753	-2.458891	0.974030
28	6	0	4.798189	-0.741240	-0.597952
29	1	0	4.539914	1.151986	-1.602638
30	1	0	4.731624	-2.630017	0.448117
31	1	0	5.855037	-0.817857	-0.840488

32	1	0	0.189250	-1.502345	0.492907
33	6	0	-1.156647	3.957081	-0.168023
34	1	0	-1.471859	3.992934	0.879092
35	1	0	-0.179900	4.439228	-0.263668
36	1	0	-1.889760	4.456747	-0.803844
37	1	0	0.652200	1.107753	1.741296

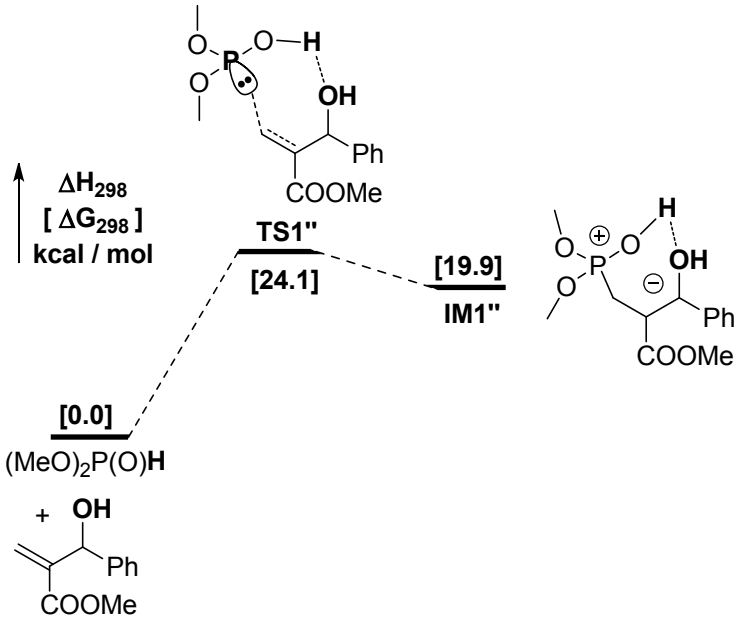


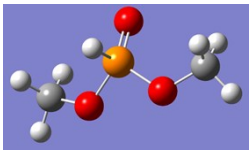
3’

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.150496	0.816189	-0.373343
2	6	0	4.925369	-0.215680	0.164875
3	6	0	4.341589	-1.463615	0.404824
4	6	0	2.993151	-1.670601	0.115779
5	6	0	2.192730	-0.632552	-0.400948
6	6	0	2.800017	0.611377	-0.659227
7	6	0	0.774945	-0.913501	-0.684446
8	6	0	-0.282091	-0.076521	-0.686842
9	6	0	-1.646508	-0.539365	-1.148943
10	15	0	-2.969024	-0.514768	0.163572
11	8	0	-2.478821	-0.993053	1.508623
12	6	0	-4.304145	-1.543233	-0.557946
13	6	0	-3.653483	1.184952	0.189463
14	6	0	-0.206531	1.397972	-0.378713
15	8	0	-0.474701	2.222548	-1.233398
16	8	0	0.093589	1.816596	0.864105
17	6	0	0.287645	0.901418	1.972898
18	1	0	4.600457	1.783025	-0.583599
19	1	0	5.977460	-0.052696	0.383656
20	1	0	4.937149	-2.276302	0.812862
21	1	0	2.544417	-2.643843	0.303033
22	1	0	2.226765	1.414944	-1.111101
23	1	0	0.566984	-1.953445	-0.938435
24	1	0	-1.579656	-1.574827	-1.502280
25	1	0	-1.982889	0.079738	-1.991638

26	1	0	-5.180215	-1.505292	0.097877
27	1	0	-4.589979	-1.196644	-1.557437
28	1	0	-3.965742	-2.582637	-0.619197
29	1	0	-4.487404	1.209739	0.899204
30	1	0	-4.009768	1.493296	-0.799241
31	1	0	-2.893172	1.895840	0.525581
32	1	0	0.233605	1.535582	2.858972
33	1	0	-0.498679	0.143285	2.000910
34	1	0	1.276393	0.441996	1.908035



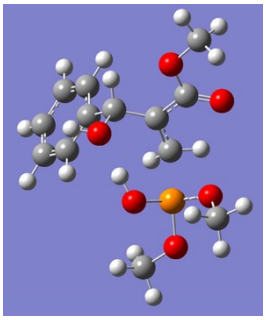


2’

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.000288	0.202933	0.331638
2	1	0	-0.003219	0.194461	1.740242
3	8	0	0.001342	1.575060	-0.238054
4	8	0	1.217070	-0.771980	-0.066379
5	8	0	-1.216849	-0.771207	-0.071016
6	6	0	2.548554	-0.232698	-0.195134
7	1	0	2.949734	0.039200	0.787945
8	1	0	3.152660	-1.031461	-0.627577
9	1	0	2.548140	0.640346	-0.852926

10	6	0	-2.549026	-0.232363	-0.193872
11	1	0	-3.154229	-1.030408	-0.626100
12	1	0	-2.947140	0.037075	0.791164
13	1	0	-2.551299	0.642186	-0.849692

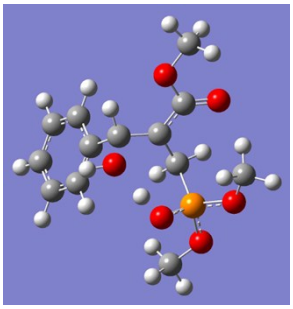


TS1''

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.112711	1.100414	-0.340989
2	6	0	0.256194	0.009191	-1.191618
3	6	0	-2.362301	0.117887	0.327854
4	6	0	-2.495975	-1.232202	0.678481
5	6	0	-3.617350	-1.969483	0.277580
6	6	0	-4.621645	-1.366066	-0.480518
7	6	0	-4.498391	-0.017251	-0.834760
8	6	0	-3.380988	0.714346	-0.432762
9	6	0	0.638782	2.323000	-0.486546
10	8	0	1.554601	2.519667	-1.286495
11	8	0	0.215313	3.330199	0.358798
12	6	0	0.895607	4.579447	0.212918
13	1	0	0.810606	0.290977	-2.086891
14	1	0	-1.724761	-1.713987	1.273778
15	1	0	-3.703329	-3.015419	0.563010
16	1	0	-5.494086	-1.936237	-0.789278
17	1	0	-5.276781	0.465497	-1.420611
18	1	0	-3.287576	1.760620	-0.715951
19	1	0	0.441859	5.246179	0.949577
20	1	0	0.765032	4.982122	-0.796580
21	1	0	1.966229	4.466500	0.410069
22	6	0	-1.156278	0.963749	0.718476
23	1	0	-1.502002	1.963809	0.989015
24	1	0	-0.507013	-0.743651	-1.393159
25	15	0	1.723702	-1.168699	-0.261487

26	8	0	1.343637	-1.312159	1.294094
27	1	0	0.652923	-0.646048	1.615507
28	8	0	-0.518433	0.416950	1.947415
29	1	0	-1.180522	0.308931	2.652342
30	8	0	2.255763	-2.683431	-0.601857
31	6	0	1.436924	-3.838436	-0.342097
32	1	0	2.020688	-4.700501	-0.669466
33	1	0	1.216445	-3.917416	0.726247
34	1	0	0.503809	-3.794299	-0.915720
35	8	0	3.079271	-0.331137	-0.393319
36	6	0	4.249082	-0.575789	0.419983
37	1	0	4.954122	0.215699	0.163924
38	1	0	3.989103	-0.520960	1.480601
39	1	0	4.672797	-1.554887	0.180798



IM1''

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.326510	0.936661	-0.187604
2	6	0	0.460784	-0.323252	-0.996754
3	6	0	-2.133552	0.622015	0.366199
4	6	0	-2.656057	-0.644509	0.665014
5	6	0	-3.921231	-1.028878	0.201347
6	6	0	-4.683962	-0.151871	-0.570054
7	6	0	-4.172192	1.115381	-0.875182
8	6	0	-2.912793	1.494680	-0.412113
9	6	0	1.257180	1.965300	-0.461764
10	8	0	2.218477	1.890492	-1.253881
11	8	0	1.029800	3.147003	0.230871
12	6	0	1.945691	4.207911	-0.040028
13	1	0	1.018177	-0.137447	-1.922933
14	1	0	-2.082126	-1.339540	1.272670
15	1	0	-4.308521	-2.014263	0.450449

16	1	0	-5.667387	-0.446907	-0.926772
17	1	0	-4.758412	1.810259	-1.471538
18	1	0	-2.516632	2.477068	-0.659580
19	1	0	1.609578	5.046158	0.575236
20	1	0	1.929935	4.484960	-1.098994
21	1	0	2.969051	3.928837	0.232833
22	6	0	-0.752969	1.094643	0.805259
23	1	0	-0.809120	2.144281	1.095009
24	1	0	-0.510336	-0.768872	-1.263170
25	15	0	1.376051	-1.637280	-0.111266
26	8	0	0.900441	-1.714410	1.388184
27	1	0	0.383490	-0.878015	1.742308
28	8	0	-0.360821	0.369128	2.088247
29	1	0	-1.109582	0.343060	2.711359
30	8	0	2.950118	-1.531355	-0.211652
31	8	0	1.193881	-3.094358	-0.750044
32	6	0	-0.018020	-3.859352	-0.572030
33	1	0	-0.192910	-4.047089	0.490408
34	1	0	-0.874829	-3.340303	-1.013132
35	1	0	0.151808	-4.799602	-1.097559
36	6	0	3.737846	-0.415340	0.303652
37	1	0	3.524501	-0.280166	1.367481
38	1	0	4.774358	-0.723029	0.164358
39	1	0	3.509607	0.487465	-0.268899

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3. Tables of the Computed Energies

Structure	E_0	H_{298}	G_{298}	TCGFE
1	-651.845364	-651.830743	-651.887403	0.167012
2	-496.944623	-496.937780	-496.973283	0.060445
TS1	-1148.785950	-1148.765096	-1148.835653	0.251408
IM1	-1148.795224	-1148.774323	-1148.844402	0.252105
TS2	-1148.796378	-1148.775988	-1148.844550	0.249904
3	-1072.429745	-1072.410284	-1072.478413	0.227850
H_2O	-76.401475	-76.397696	-76.419790	0.002782
TS1'	-1148.785287	-1148.764567	-1148.834638	0.251982
IM1'	-1148.813911	-1148.793136	-1148.863287	0.253909
IM1'-2	-1148.806372	-1148.785218	-1148.857183	0.252820
TS2'	-1148.780554	-1148.760030	-1148.829593	0.250229
3'	-1072.418187	-1072.398759	-1072.465945	0.228274
2'	-647.401924	-647.392569	-647.437614	0.064661

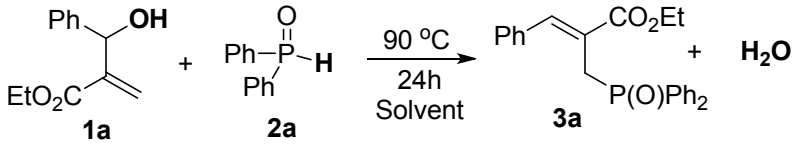
TS1''	-1299.232440	-1299.209333	-1299.286559	0.257468
IM1''	-1299.240526	-1299.217511	-1299.293345	0.259253

E_0：Sum of electronic and zero-point Energies
H_{298}：Sum of electronic and thermal Enthalpies
G_{298}：Sum of electronic and thermal Free Energies
TCGFE：Thermal Correction to Gibbs Free Energy

4. General Procedure for the C_{SP3}-OH/P-H Dehydrative Cross-Coupling

Phosphine oxide **2** (0.45 mmol) was added to allylic alcohol **1** (0.3 mmol). The reaction was stirred at 90 °C or 60 °C for 12-24 h. After complete conversion, the residue was purified *via* PTLC (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 3:1) or column chromatography (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 5:1) to afford the corresponding products **3a-3aa**.

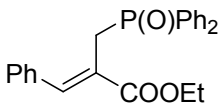
5. Screen reaction conditions



Entry[a]	Solvent	Cat. [mol%]	Temp. [°C] [b]	Yield [%] [c]
1	**Toluene**	--	**90**	**56**
2	**THF**	--	**reflux**	**66**
3	**$PhCF_3$**	--	**90**	**67**
4	***i*-PrOH**	--	**reflux**	**43**
5	**DCE**	--	**90**	**50**
6	**CH_3CN**	--	**reflux**	**39**

6. Analytical Data for All New Compounds

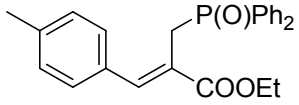
(Z)-ethyl 2-((diphenylphosphoryl)methyl)-3-phenylacrylate (3a)



Following the general procedure, **3a** was isolated as white solid. Mp: 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.73 (m, 5H), 7.67 (d, J = 7.2 Hz, 2H), 7.53 – 7.47 (m, 2H), 7.47 – 7.39 (m, 4H), 7.38 – 7.29 (m, 3H), 3.89 (q, J = 7.1 Hz, 2H), 3.75 (d, $J_{H\text{-}P}$ = 14.4 Hz, 2H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.52, 142.39 (d, $J_{C\text{-}P}$ = 8.8 Hz), 134.80 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.24, 132.26,

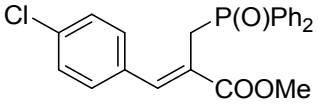
131.76 (d, J_{C-P} = 2.7 Hz), 131.41, 131.32, 129.46, 128.93, 128.60, 128.44, 128.32, 124.04 (d, J_{C-P} = 9.6 Hz), 61.09, 30.92 (d, J_{C-P} = 67.5 Hz), 14.05. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.58.HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{24}H_{24}O_3P$ 391.1458, found 391.1463.

(Z)-ethyl 2-((diphenylphosphoryl)methyl)-3-(p-tolyl)acrylate (3b)



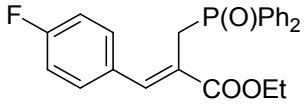
Following the general procedure, the reaction was conducted at 90 °C for 24h. **3b** was isolated as colorless sticky oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.72 (m, 5H), 7.59 – 7.47 (m, 4H), 7.47 – 7.39 (m, 4H), 7.16 (d, *J* = 7.9 Hz, 2H), 3.88 (q, *J* = 7.1 Hz, 2H), 3.76 (d, *J* = 14.4 Hz, 2H), 2.35 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.67, 142.61 (d, J_{C-P} = 8.8 Hz), 139.20, 133.00, 132.01, 131.89, 131.80 (d, J_{C-P} = 2.6 Hz), 131.42, 131.32, 129.53, 129.34, 128.45, 128.33, 122.91 (d, J_{C-P} = 9.7 Hz), 61.06, 30.90 (d, J_{C-P} = 67.8 Hz), 21.37, 14.04. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.27. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{25}H_{26}O_3P$ 405.1614, found 405.1620.

(Z)-methyl 3-(4-chlorophenyl)-2-((diphenylphosphoryl)methyl)acrylate (3c)



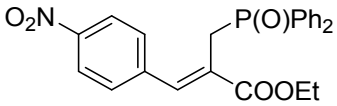
Following the general procedure, the reaction was conducted at 90 °C for 24h. **3c** was isolated as white solid. Mp: 112-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 5H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.49 – 7.42 (m, 4H), 7.31 (d, *J* = 8.5 Hz, 2H), 3.70 (d, J_{H-P} = 14.2 Hz, 2H), 3.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.69, 141.54 (d, J_{C-P} = 8.8 Hz), 135.04, 133.12 (d, J_{C-P} = 2.9 Hz), 132.84, 131.94 (d, J_{C-P} = 2.7 Hz), 131.85, 131.32, 131.23, 130.77, 128.83, 128.54, 128.42, 124.14 (d, J_{C-P} = 9.8 Hz), 52.08, 30.79 (d, J_{C-P} = 67.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.51. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{23}H_{21}ClO_3P$ 411.0911, found 411.0917.

(Z)-ethyl 2-((diphenylphosphoryl)methyl)-3-(4-fluorophenyl)acrylate (3d)



Following the general procedure, the reaction was conducted at 60 °C for 24h. **3d** was isolated as white solid. Mp: 118-120 °C., ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.66 (m, 7H), 7.59 – 7.40 (m, 6H), 7.05 (t, *J* = 8.6 Hz, 2H), 3.87 (q, *J* = 7.0 Hz, 2H), 3.72 (d, J_{H-P} = 14.3 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.41, 164.33, 161.84, 141.42 (d, J_{C-P} = 8.8 Hz), 132.86, 131.90 (d, J_{C-P} = 2.7 Hz), 131.61, 131.53, 131.40, 131.31, 130.83, 128.50, 128.38, 123.65 (d, J_{C-P} = 9.5 Hz), 115.76, 115.55, 61.16, 30.81 (d, J_{C-P} = 67.5 Hz), 14.01. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.94. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{24}H_{23}FO_3P$ 409.1363, found 409.1367.

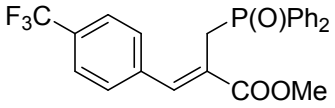
(Z)-ethyl 2-((diphenylphosphoryl)methyl)-3-(4-nitrophenyl)acrylate (3e)



Following the general procedure, the reaction was conducted at 60 °C for 24h. **3e** was isolated as white solid, Mp: 125-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.85 – 7.72 (m, 5H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.51 – 7.42 (m, 4H), 3.90 (q, *J* = 7.1 Hz, 2H), 3.69 (d, J_{H-P} = 14.3 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.75, 147.70, 141.25,

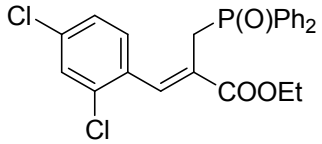
139.75 (d, J_{C-P} = 8.8 Hz), 132.68, 132.07 (d, J_{C-P} = 2.6 Hz), 131.68, 131.32, 131.22, 130.21, 128.61, 128.49, 127.33 (d, J_{C-P} = 9.7 Hz), 123.72, 61.54, 30.94 (d, J_{C-P} = 66.2 Hz), 13.98. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.92. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{24}H_{23}NO_5P$ 436.1308, found 436.1314.

(Z)-methyl 2-((diphenylphosphoryl)methyl)-3-(4-(trifluoromethyl)phenyl)acrylate (3f)



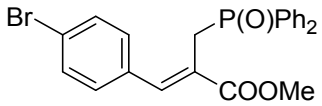
Following the general procedure, the reaction was conducted at 60 °C for 24h. **3f** was isolated as colorless sticky oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 4.6 Hz, 1H), 7.79 – 7.70 (m, 6H), 7.58 (d, J = 8.1 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.49 – 7.40 (m, 4H), 3.69 (d, J_{H-P} = 14.2 Hz, 2H), 3.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.45, 141.00 (d, J_{C-P} = 8.9 Hz), 138.25, 132.77, 131.99 (d, J = 2.7 Hz), 131.78, 131.29, 131.19, 129.48, 128.57, 128.45, 125.77 (d, J_{C-P} = 9.7 Hz), 125.48 (d, J_{C-P} = 3.7 Hz), 52.21, 30.72 (d, J_{C-P} = 66.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.07. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{24}H_{21}F_3O_3P$ 445.1175, found 445.1194.

(Z)-ethyl 3-(2,4-dichlorophenyl)-2-((diphenylphosphoryl)methyl)acrylate (3g)



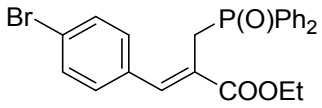
Following the general procedure, the reaction was conducted at 90 °C for 24h. **3g** was isolated as colorless sticky oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 4.7 Hz, 1H), 7.74 (dd, J = 11.4, 7.7 Hz, 4H), 7.51 (d, J = 7.3 Hz, 2H), 7.49 – 7.40 (m, 4H), 7.35 (s, 1H), 7.23 (d, J = 8.3 Hz, 1H), 3.90 (q, J = 7.1 Hz, 2H), 3.61 (d, J_{H-P} = 14.3 Hz, 2H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.76, 138.10 (d, J_{C-P} = 9.1 Hz), 135.27, 134.69 (d, J_{C-P} = 2.1 Hz), 132.71, 131.95 (d, J_{C-P} = 2.7 Hz), 131.79, 131.74, 131.72, 131.28, 131.19, 129.32, 128.56, 128.44, 127.33, 126.45 (d, J_{C-P} = 9.7 Hz), 61.40, 30.83 (d, J_{C-P} = 66.9 Hz), 13.96. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.13. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{24}H_{22}Cl_2O_3P$ 459.0678, found 459.0688.

(Z)-methyl 3-(4-bromophenyl)-2-((diphenylphosphoryl)methyl)acrylate (3h)



Following the general procedure, the reaction was conducted at 90 °C for 24h. **3h** was isolated as white solid. Mp: 120-123 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.70 (m, 5H), 7.57 – 7.50 (m, 4H), 7.49 – 7.41 (m, 6H), 3.69 (d, J_{H-P} = 14.2 Hz, 2H), 3.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.66, 141.58 (d, J_{C-P} = 8.9 Hz), 133.56 (d, J_{C-P} = 2.9 Hz), 132.77, 131.95 (d, J_{C-P} = 2.6 Hz), 131.80, 131.31, 131.22, 130.95, 128.55, 128.43, 124.29, 124.20, 123.39, 52.10, 30.78 (d, J_{C-P} = 67.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.52. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{23}H_{21}BrO_3P$ 455.0406, found 455.0417.

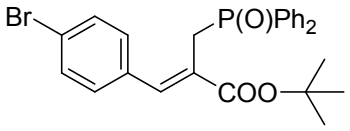
(Z)-ethyl 3-(4-bromophenyl)-2-((diphenylphosphoryl)methyl)acrylate (3i)



Following the general procedure, the reaction was conducted at 90 °C for 24h. **3i** was isolated as white solid. Mp: 126-128 °C., ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.69 (m, 5H), 7.64 – 7.38 (m, 10H), 3.88 (q, J = 7.1 Hz, 2H), 3.70 (d, J_{H-P} = 14.3 Hz, 2H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)

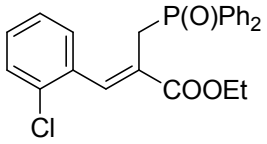
δ 167.25, 141.18 (d, J_{C-P} = 8.8 Hz), 133.65 (d, J = 2.9 Hz), 132.87, 131.91 (d, J_{C-P} = 2.8 Hz), 131.77, 131.36, 131.26, 131.01, 128.52, 128.40, 124.62 (d, J_{C-P} = 9.6 Hz), 123.34, 61.24, 30.82 (d, J_{C-P} = 67.1 Hz), 14.01. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.48. HRMS (ESI/$[M+H]^+$) Calcd. for: $C_{24}H_{23}BrO_3P$ 469.0563, found 469.0575.

(Z)-tert-butyl 3-(4-bromophenyl)-2-((diphenylphosphoryl)methyl)acrylate (3j)



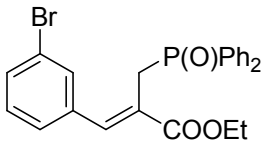
Following the general procedure, the reaction was conducted at 90 °C for 24h (For the gram scale reaction, the ratio between phosphine oxide 2 and MBH alcohol is 1.2/1). **3j** was isolated as white solid, Mp: 158-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 4H), 7.67 (d, J = 4.7 Hz, 1H), 7.60 (d, J = 8.3 Hz, 2H), 7.54 – 7.40 (m, 8H), 3.68 (d, J_{H-P} = 14.5 Hz, 2H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.28, 140.52 (d, J_{C-P} = 8.9 Hz), 133.90, 133.15, 132.16, 131.79 (d, J_{C-P} = 2.5 Hz), 131.71, 131.42, 131.33, 131.06, 128.51, 128.40, 125.91 (d, J_{C-P} = 9.6 Hz), 123.15, 81.30, 30.66 (d, J_{C-P} = 67.4 Hz), 27.82. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.26. HRMS (ESI/$[M+H]^+$) Calcd. for: $C_{26}H_{27}BrO_3P$ 497.0876, found 497.0878.

(Z)-ethyl 3-(2-chlorophenyl)-2-((diphenylphosphoryl)methyl)acrylate (3k)



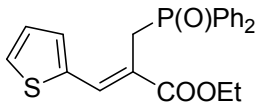
Following the general procedure, the reaction was conducted at 90 °C for 24h. **3k** was isolated as colorless sticky oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 5.4, 3.8 Hz, 1H), 7.89 (d, J = 4.7 Hz, 1H), 7.82 – 7.67 (m, 4H), 7.54 – 7.47 (m, 2H), 7.46 – 7.39 (m, 4H), 7.37 – 7.31 (m, 1H), 7.29 – 7.22 (m, 2H), 3.92 (q, J = 7.1 Hz, 2H), 3.65 (d, J_{H-P} = 14.4 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.99, 139.17 (d, J_{C-P} = 9.0 Hz), 134.00, 133.98, 133.24 (d, J_{C-P} = 2.7 Hz), 132.99, 132.00, 131.82 (d, J_{C-P} = 2.6 Hz), 131.31, 131.22, 130.92, 129.97, 129.43, 128.49, 128.38, 126.97, 125.98 (d, J_{C-P} = 9.5 Hz), 61.28, 30.83 (d, J_{C-P} = 67.2 Hz), 13.99. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.01. HRMS (ESI/$[M+H]^+$) Calcd. for: $C_{24}H_{23}ClO_3P$ 425.1068, found 425.1081.

(Z)-ethyl 3-(3-bromophenyl)-2-((diphenylphosphoryl)methyl)acrylate (3l)



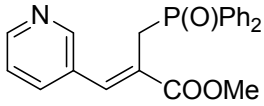
Following the general procedure, the reaction was conducted at 90 °C for 24h. **3l** was isolated as colorless sticky oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 5H), 7.66 (d, J = 8.9 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.48 – 7.39 (m, 5H), 7.22 (t, J = 7.8 Hz, 1H), 3.93 (q, J = 7.1 Hz, 2H), 3.70 (d, J_{H-P} = 14.3 Hz, 2H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.11, 140.61 (d, J_{C-P} = 8.9 Hz), 136.90, 136.87, 132.84, 132.06 (d, J_{C-P} = 1.3 Hz), 131.91 (d, J_{C-P} = 2.6 Hz), 131.85, 131.74, 131.32, 131.22, 130.16, 128.51, 128.40, 127.70, 125.47 (d, J_{C-P} = 9.7 Hz), 122.58, 61.31, 30.76 (d, J_{C-P} = 66.8 Hz), 14.01. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.19. HRMS (ESI/$[M+H]^+$) Calcd. for: $C_{24}H_{23}BrO_3P$ 469.0563, found 469.0573.

(Z)-ethyl 2-((diphenylphosphoryl)methyl)-3-(thiophen-2-yl)acrylate (3m)



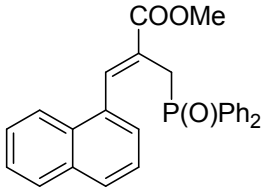
Following the general procedure, the reaction was conducted at 90 °C for 24h. **3m** was isolated as colorless sticky oil,, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 4.6 Hz, 1H), 7.88 – 7.77 (m, 4H), 7.68 (d, J = 3.3 Hz, 1H), 7.57 – 7.40 (m, 7H), 7.07 (dd, J = 4.9, 3.8 Hz, 1H), 3.97 – 3.79 (m, 4H), 1.08 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.30, 137.89 (d, $J_{C\text{-}P}$ = 3.7 Hz), 134.66 (d, $J_{C\text{-}P}$ = 8.6 Hz), 133.05, 132.49, 132.06, 131.85 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.41, 131.31, 129.36, 128.44, 128.32, 127.81, 120.13 (d, $J_{C\text{-}P}$ = 10.0 Hz), 61.10, 31.86 (d, $J_{C\text{-}P}$ = 67.3 Hz), 14.06. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.40. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{22}H_{22}O_3PS$ 397.1022, found 397.1036.

(Z)-methyl 2-((diphenylphosphoryl)methyl)-3-(pyridin-3-yl)acrylate (3n)



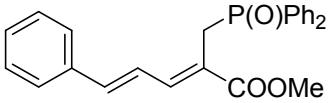
Following the general procedure, the reaction was conducted at 60 °C for 12h. **3n** was isolated as colorless sticky oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.54 (d, J = 4.3 Hz, 1H), 8.32 (d, J = 7.9 Hz, 1H), 7.84 – 7.68 (m, 5H), 7.60 – 7.50 (m, 2H), 7.49 – 7.40 (m, 4H), 7.35 – 7.23 (m, 1H), 3.71 (d, $J_{H\text{-}P}$ = 14.2 Hz, 2H), 3.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.30, 150.14, 149.48, 138.92 (d, $J_{C\text{-}P}$ = 8.8 Hz), 136.50, 132.44, 132.07 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.45, 131.29, 131.20, 130.77, 128.59, 128.48, 125.97 (d, $J_{C\text{-}P}$ = 9.8 Hz), 123.65, 52.23, 30.74 (d, $J_{C\text{-}P}$ = 66.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.58. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{22}H_{21}NO_3P$ 378.1259, found 378.1274.

(Z)-methyl 2-((diphenylphosphoryl)methyl)-3-(naphthalen-1-yl)acrylate (3o)



Following the general procedure, the reaction was conducted at 90 °C for 24h. **3o** was isolated as colorless sticky oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 4.5 Hz, 1H), 7.84 – 7.76 (m, 2H), 7.75 – 7.65 (m, 3H), 7.63 – 7.55 (m, 3H), 7.52 – 7.42 (m, 3H), 7.40 – 7.33 (m, 3H), 7.31 – 7.23 (m, 3H), 3.70 (d, J = 14.0 Hz, 2H), 3.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.62, 140.80 (d, $J_{C\text{-}P}$ = 9.1 Hz), 133.36, 132.97, 132.66 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.61 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.05, 130.96, 130.79, 130.68, 129.11, 129.01, 128.40, 128.24, 126.74, 126.46, 126.11, 125.43, 124.52, 52.23, 30.67 (d, J = 67.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.16. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{27}H_{24}O_3P$ 427.1458, found 427.1455.

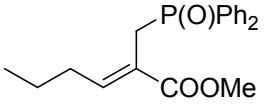
(2Z,4E)-methyl 2-((diphenylphosphoryl)methyl)-5-phenylpenta-2,4-dienoate (3p)



Following the general procedure, the reaction was conducted at 90 °C for 24h. **3p** was isolated as white solid, Mp: 119-121 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 4H), 7.56 – 7.41 (m, 9H), 7.36 – 7.25 (m, 3H), 7.14 (dd, J = 15.3, 11.5 Hz, 1H), 6.84 (d, J = 15.4 Hz, 1H), 3.72 (d, $J_{H\text{-}P}$ = 14.7 Hz, 2H), 3.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.64, 142.53 (d, $J_{C\text{-}P}$ = 8.2 Hz), 141.33 (d, $J_{C\text{-}P}$ = 3.4 Hz), 136.32, 132.86, 131.90 (d, J = 2.8 Hz), 131.36, 131.26, 128.98, 128.67, 128.50, 128.38, 127.60,

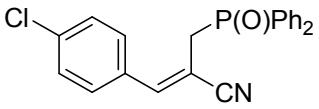
124.45 (d, J_{C-P} = 4.6 Hz), 121.02 (d, J_{C-P} = 10.1 Hz), 51.99, 30.31 (d, J_{C-P} = 67.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.60. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{25}H_{24}O_3P$ 403.1463, found 430.1481.

(Z)-methyl 2-((diphenylphosphoryl)methyl)hex-2-enoate (3q)



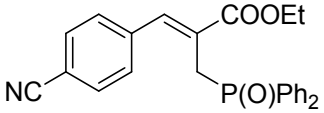
Following the general procedure, the reaction was conducted at 90 ^{o}C for 24h. **3q** was isolated as colorless sticky oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 4H), 7.58 – 7.41 (m, 6H), 7.01 – 6.93 (m, 1H), 3.52 (d, J_{H-P} = 14.1 Hz, 2H), 3.42 (s, 3H), 2.24 (qd, J = 7.4, 3.9 Hz, 2H), 1.49 – 1.36 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.31, 147.91, 147.82, 133.01, 132.03, 131.79 (d, J_{C-P} = 2.7 Hz), 131.28, 131.19, 128.45, 128.33, 122.33 (d, J_{C-P} = 9.3 Hz), 51.75, 31.60, 29.73 (d, J_{C-P} = 68.1 Hz), 21.82, 13.87. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.33. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{20}H_{24}O_3P$ 343.1463, found 343.1480.

3-(4-chlorophenyl)-2-((diphenylphosphoryl)methyl)acrylonitrile (3r)



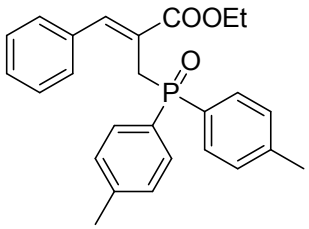
Following the general procedure, the reaction was conducted at 90 ^{o}C for 24h. The two isomers were isolated as white solid. (Major isomer was proposed as Z-configuration) Mp: 152-154 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.76 (m, 4H), 7.65 – 7.57 (m, 4H), 7.56 – 7.48 (m, 4H), 7.39 (dd, J = 9.4, 6.4 Hz, 3H), 3.45 (d, J_{H-P} = 13.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.14 (d, J_{C-P} = 8.7 Hz), 136.12, 132.70 (d, J_{C-P} = 2.6 Hz), 131.57, 131.53, 131.19, 131.10, 130.57, 130.48, 129.13, 129.00, 128.88, 118.97, 105.64 (d, J_{C-P} = 10.3 Hz), 32.63 (d, J_{C-P} = 65.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.56. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{22}H_{18}NOPCl$ 378.0815, found 378.0816; (Minor isomer) white solid, Mp: 168-170 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 4H), 7.62 – 7.48 (m, 8H), 7.34 – 7.30 (m, 2H), 7.21 (d, J = 4.1 Hz, 1H), 3.39 (d, J_{H-P} = 13.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.37 (d, J_{C-P} = 7.9 Hz), 136.44, 132.62 (d, J_{C-P} = 2.7 Hz), 131.75 (d, J_{C-P} = 3.1 Hz), 131.42, 131.17, 131.07, 130.80, 130.41, 130.14, 129.05, 129.02, 128.90, 118.14 (d, J_{C-P} = 4.9 Hz), 100.55 (d, J_{C-P} = 9.9 Hz), 36.74 (d, J_{C-P} = 65.1 Hz). HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{22}H_{18}NOPCl$ 378.0815, found 378.0844.

(Z)-ethyl 3-(4-cyanophenyl)-2-((diphenylphosphoryl)methyl)acrylate (3s)



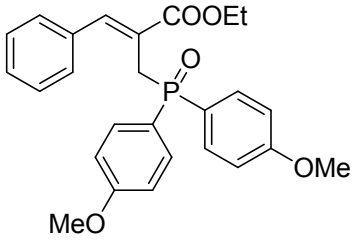
Following the general procedure, the reaction was conducted at 60 ^{o}C for 12h. **3s** was isolated as white solid, Mp: 140-142 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (d, J = 8.2 Hz, 2H), 7.81 – 7.72 (m, 5H), 7.63 (d, J = 8.2 Hz, 2H), 7.57 – 7.51 (m, 2H), 7.50 – 7.43 (m, 4H), 3.88 (q, J = 7.1 Hz, 2H), 3.68 (d, J_{P-H} = 14.3 Hz, 2H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.83, 140.15 (d, J = 8.8 Hz), 139.30 (d, J = 2.9 Hz), 132.76, 132.27, 132.04, 131.77, 131.33, 131.23, 129.95 (d, J = 1.2 Hz), 128.58, 128.46, 126.86 (d, J = 9.8 Hz), 118.62, 112.29, 61.46, 30.91 (d, J = 66.2 Hz), 13.97. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.96. HRMS (ESI/[M+H]$^+$) Calcd. for: $C_{25}H_{23}NO_3P$ 416.1416, found 416.1431.

(Z)-ethyl 2-((di-p-tolylphosphoryl)methyl)-3-phenylacrylate (3t)



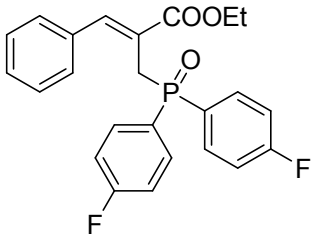
Following the general procedure, the reaction was conducted at 90 °C for 24h. **3t** was isolated as white solid, Mp: 142-144 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 4.6 Hz, 1H), 7.70 – 7.54 (m, 6H), 7.39 – 7.30 (m, 3H), 7.24 – 7.16 (m, 4H), 3.91 (q, J = 7.1 Hz, 2H), 3.71 (d, $J_{H\text{-}P}$ = 14.4 Hz, 2H), 2.37 (s, 6H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.62, 142.17, 142.11, 134.83 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.40, 131.31, 129.92, 129.45, 129.15, 129.03, 128.91, 128.84, 128.54, 124.21 (d, $J_{C\text{-}P}$ = 9.5 Hz), 61.08, 30.96 (d, $J_{C\text{-}P}$ = 67.6 Hz), 21.55, 13.99. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.16. HRMS (ESI/$[M+H]^+$) Calcd. for: $C_{26}H_{28}O_3P$ 419.1776, found 419.1767.

(Z)-ethyl 2-((bis(4-methoxyphenyl)phosphoryl)methyl)-3-phenylacrylate (3u)



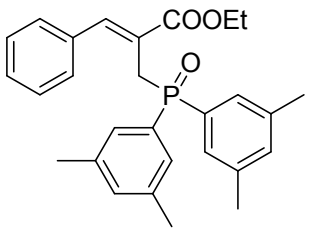
Following the general procedure, the reaction was conducted at 90 °C for 24h. 3u was isolated as white solid, Mp: 122-124 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 4.7 Hz, 1H), 7.72 – 7.60 (m, 6H), 7.40 – 7.29 (m, 3H), 6.93 (dd, J = 8.8, 2.2 Hz, 4H), 3.94 (q, J = 7.1 Hz, 2H), 3.83 (s, 6H), 3.70 (d, $J_{H\text{-}P}$ = 14.5 Hz, 2H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.70, 162.34, 142.03 (d, $J_{C\text{-}P}$ = 8.9 Hz), 134.85, 133.25, 133.14, 129.45, 128.87, 128.57, 124.44, 124.32 (d, $J_{C\text{-}P}$ = 9.5 Hz), 123.39, 113.91 (d, $J_{C\text{-}P}$ = 12.8 Hz), 61.13, 55.33, 31.15 (d, $J_{C\text{-}P}$ = 68.4 Hz), 14.06. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.06. HRMS (ESI/$[M+H]^+$) Calcd. for: $C_{26}H_{28}O_5P$ 451.1674, found 451.1686.

(Z)-ethyl 2-((bis(4-fluorophenyl)phosphoryl)methyl)-3-phenylacrylate (3v)



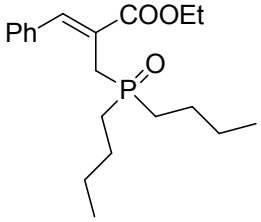
Following the general procedure, the reaction was conducted at 90 °C for 24h. **3v** was isolated as colorless sticky oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 4.7 Hz, 1H), 7.79 – 7.70 (m, 4H), 7.62 (d, J = 7.2 Hz, 2H), 7.40 – 7.30 (m, 3H), 7.17 – 7.08 (m, 4H), 3.98 (q, J = 7.1 Hz, 2H), 3.74 (d, $J_{H\text{-}P}$ = 14.5 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.46, 166.33, 163.80, 142.62 (d, $J_{C\text{-}P}$ = 9.0 Hz), 134.62 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.91, 133.81, 133.72, 129.31, 129.09, 128.67, 127.71, 123.54 (d, $J_{C\text{-}P}$ = 9.9 Hz), 116.00, 115.87, 115.79, 115.66, 61.30, 30.94 (d, $J_{C\text{-}P}$ = 68.7 Hz), 14.06. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.92. HRMS (ESI/$[M+H]^+$) Calcd. for: $C_{24}H_{22}F_2O_3P$ 427.1275, found 427.1290.

(Z)-ethyl 2-((bis(3,5-dimethylphenyl)phosphoryl)methyl)-3-phenylacrylate (3w)



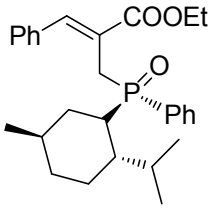
Following the general procedure, the reaction was conducted at 90 °C in DMSO solvent 2.0 mL for 24h. **3w** was isolated as white solid, Mp: 148-151 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 4.6 Hz, 1H), 7.60 (d, J = 6.8 Hz, 2H), 7.40 – 7.24 (m, 7H), 7.11 (s, 2H), 3.91 (q, J = 7.1 Hz, 2H), 3.71 (d, $J_{H\text{-}P}$ = 14.3 Hz, 2H), 2.31 (s, 12H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.62, 141.99 (d, $J_{C\text{-}P}$ = 8.8 Hz), 138.09, 137.96, 134.92 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.45 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.99, 132.01, 129.39, 128.90, 128.81, 128.73, 128.49, 124.35 (d, $J_{C\text{-}P}$ = 9.6 Hz), 61.03, 30.64 (d, $J_{C\text{-}P}$ = 67.1 Hz), 21.30, 13.97. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.15. HRMS (ESI/$[M+H]^+$) Calcd. for: $C_{28}H_{32}O_3P$ 447.2089, found 447.2095.

(Z)-ethyl 2-((dibutylphosphoryl)methyl)-3-phenylacrylate (3x)



Following the general procedure, the reaction was conducted at 90 °C for 24h. **3x** was isolated as colorless sticky oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 4.3 Hz, 1H), 7.65 (d, J = 7.4 Hz, 2H), 7.42 (t, J = 7.3 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.18 (d, $J_{H\text{-}P}$ = 14.6 Hz, 2H), 1.76 – 1.62 (m, 4H), 1.55 – 1.45 (m, 4H), 1.39 – 1.33 (m, 7H), 0.88 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.83, 142.51 (d, $J_{C\text{-}P}$ = 8.1 Hz), 134.89, 129.35, 129.05, 128.70, 124.17 (d, $J_{C\text{-}P}$ = 9.0 Hz), 61.46, 28.46 (d, $J_{C\text{-}P}$ = 65.1 Hz), 28.18 (d, $J_{C\text{-}P}$ = 60.1 Hz), 24.21 (d, $J_{C\text{-}P}$ = 14.7 Hz), 23.58 (d, $J_{C\text{-}P}$ = 4.0 Hz), 14.27, 13.55. ^{31}P NMR (162 MHz, $CDCl_3$) δ 49.36. HRMS (ESI/$[M+H]^+$) Calcd. for: $C_{20}H_{32}O_3P$ 351.2089, found 351.2096.

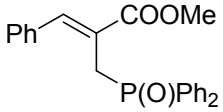
(Z)-ethyl-2-(((R)-((1S,2S,5R)-2-isopropyl-5-methylcyclohexyl)(phenyl)phosphoryl)methyl)-3-phenylacrylate (3z)



Following the general procedure, the reaction was conducted at 90 °C for 24h, **3z** (only one isomer was detected) was isolated as colorless sticky oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H), 7.60 – 7.53 (m, 3H), 7.46 – 7.38 (m, 1H), 7.38 – 7.27 (m, 5H), 3.91 (q, J = 7.1 Hz, 2H), 3.49 (dd, $J_{H\text{-}P}$ = 16.6, J = 14.0 Hz, 1H), 3.32 (dd, J = 14.0, $J_{H\text{-}P}$ = 9.2 Hz, 1H), 2.19 – 2.06 (m, 1H), 2.06 – 1.96 (m, 1H), 1.89 – 1.79 (m, 1H), 1.77 – 1.66 (m, 3H), 1.45 – 1.29 (m, 2H), 1.15 (t, J = 7.1 Hz, 3H), 1.05 – 0.94 (m, 2H), 0.92 (d, J = 5.7 Hz, 3H), 0.77 (d, J = 6.7 Hz, 3H), 0.30 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.06, 141.23 (d, $J_{C\text{-}P}$ = 8.2 Hz), 134.93 (d, $J_{C\text{-}P}$ = 2.8 Hz), 134.04, 133.16, 131.09, 131.00, 130.95, 129.28, 128.62, 128.46, 127.88, 127.77, 124.83 (d, $J_{C\text{-}P}$ = 9.0 Hz), 60.98, 43.13 (d, $J_{C\text{-}P}$ = 3.5

Hz), 40.68 (d, $J_{C\text{-}P}$ = 66.1 Hz), 34.75, 34.13, 33.26 (d, $J_{C\text{-}P}$ = 12.8 Hz), 28.83 (d, $J_{C\text{-}P}$ = 61.4 Hz), 28.06, 24.57 (d, $J_{C\text{-}P}$ = 12.1 Hz), 22.60, 21.41, 15.31, 14.05. ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.44. HRMS (ESI/$[M+H]^+$) Calcd. for: $C_{28}H_{38}O_3P$ 453.2559, found 453.2544.

(Z)-methyl-2-((diphenylphosphoryl)methyl)-3-phenylacrylate (3aa)



Phosphine oxide **2** (48.0 mmol) was added to allylic alcohol **2** (40.0 mmol). The reaction was stirred at 60 °C for 24 h. After complete conversion, the residue was purified *via* column chromatography (Petroleum ether (bp: 60-90 °C)/ethyl acetate = 4:1) to afford the corresponding product **3aa** as white solid (10.8g, 72% yield). Mp: 84-86 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 4.6 Hz, 1H), 7.80 – 7.72 (m, 4H), 7.67 – 7.61 (m, 2H), 7.54 – 7.47 (m, 2H), 7.47 – 7.40 (m, 4H), 7.39 – 7.29 (m, 3H), 3.74 (d, *J* = 14.3 Hz, 2H), 3.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.94, 142.77 (d, *J* = 8.8 Hz), 134.73 (d, *J* = 2.9 Hz), 133.18, 132.19, 131.77 (d, *J* = 2.7 Hz), 131.37, 131.28, 129.43, 128.96, 128.61, 128.45, 128.33, 123.67 (d, *J* = 9.6 Hz), 51.98, 30.88 (d, *J* = 67.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.30. HRMS (ESI/$[M+H]^+$) Calcd. for: $C_{23}H_{22}O_3P$ 377.1307, found 177.1318.

7. References

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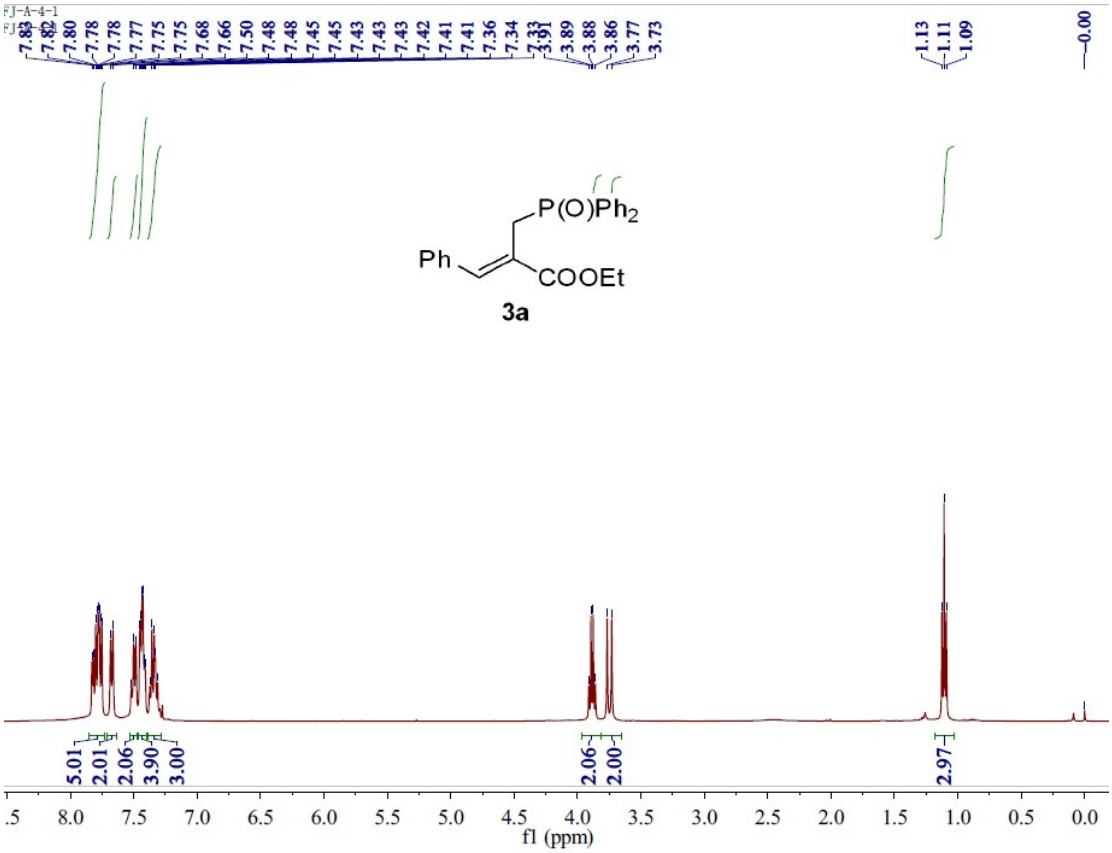
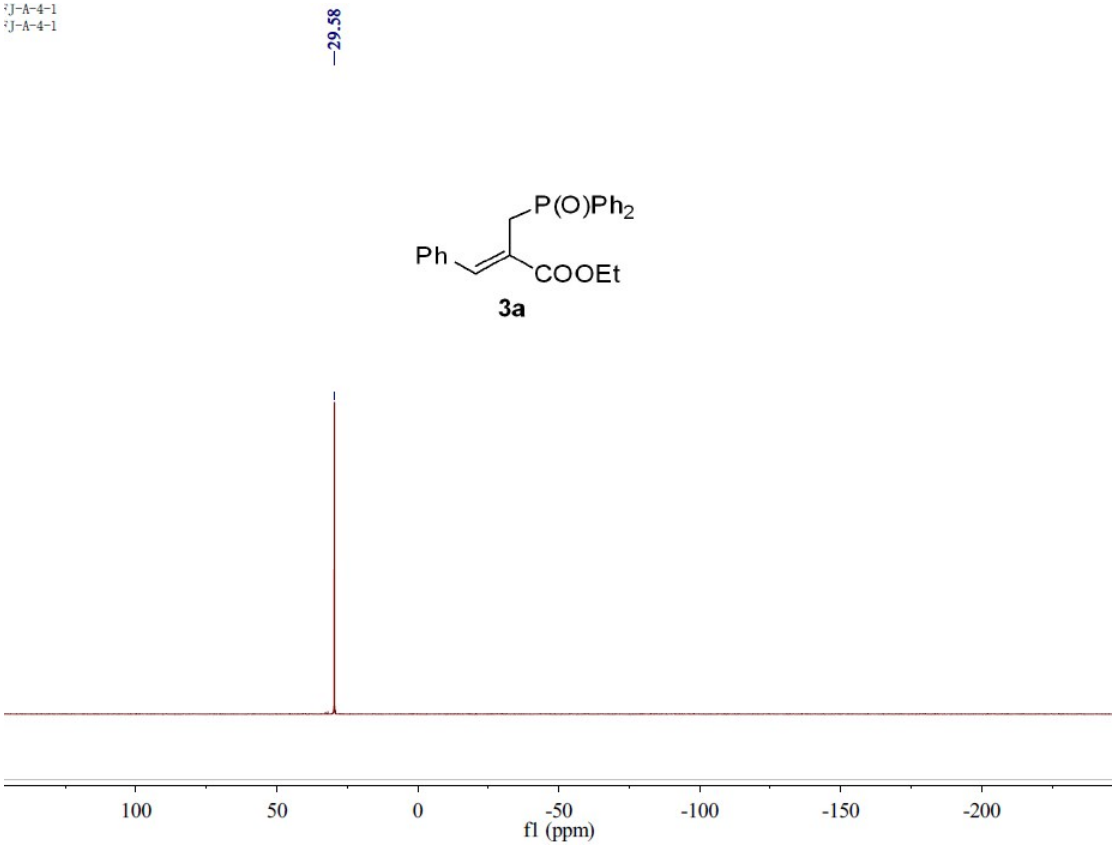
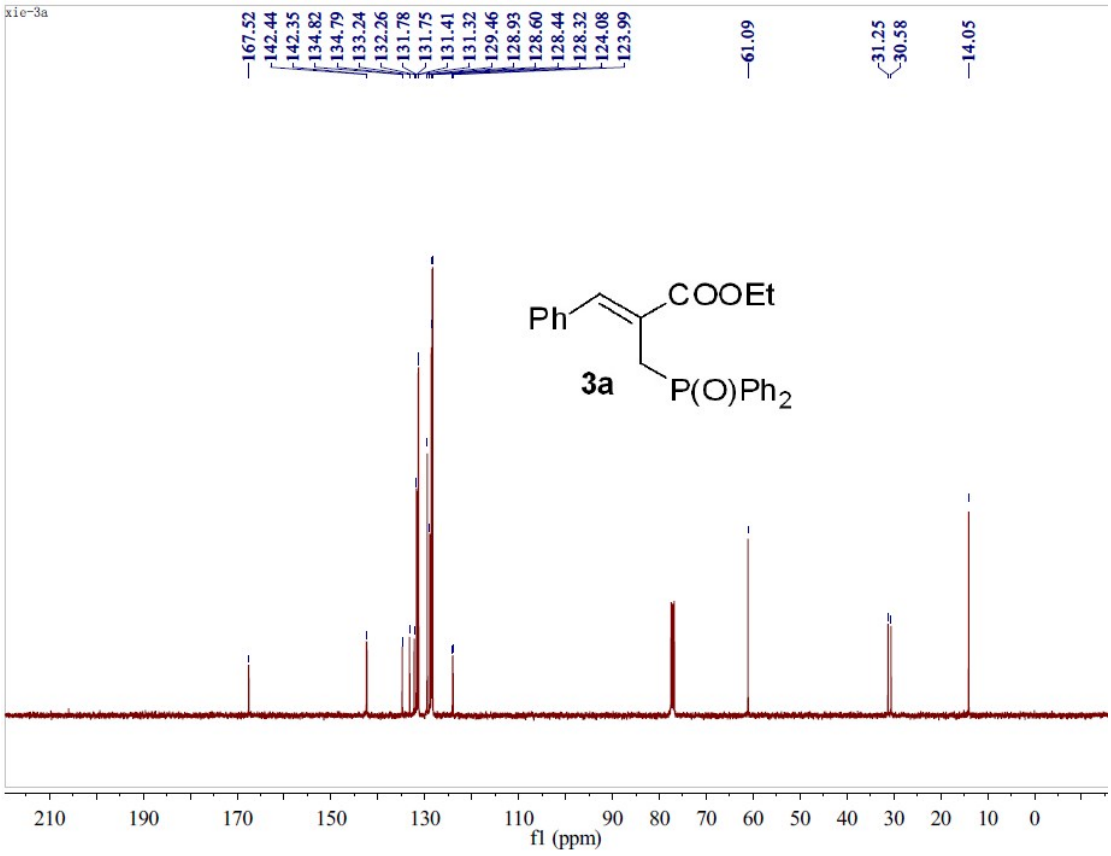
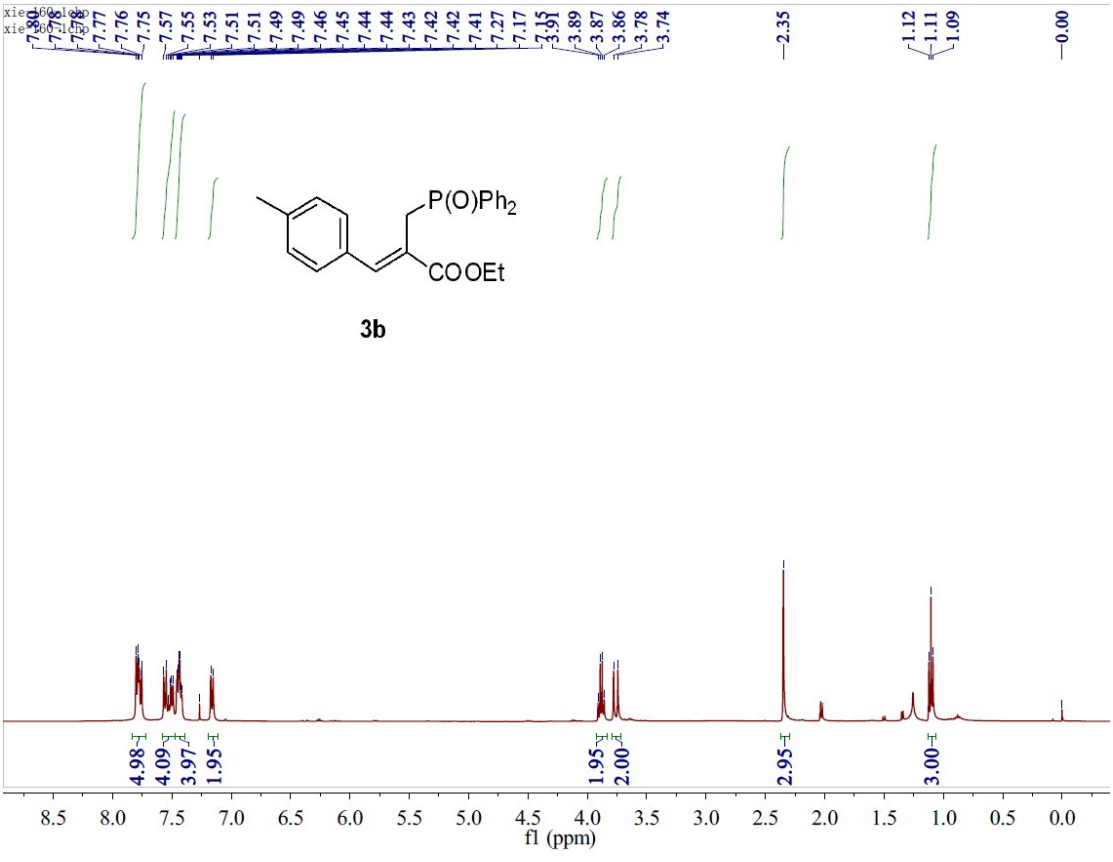
[5] a) A. D. Becke, J. Chem. Phys. **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B **1988**, *37*, 785; c) A. D. Becke, Phys. Rev. A **1988**, *38*, 3098.

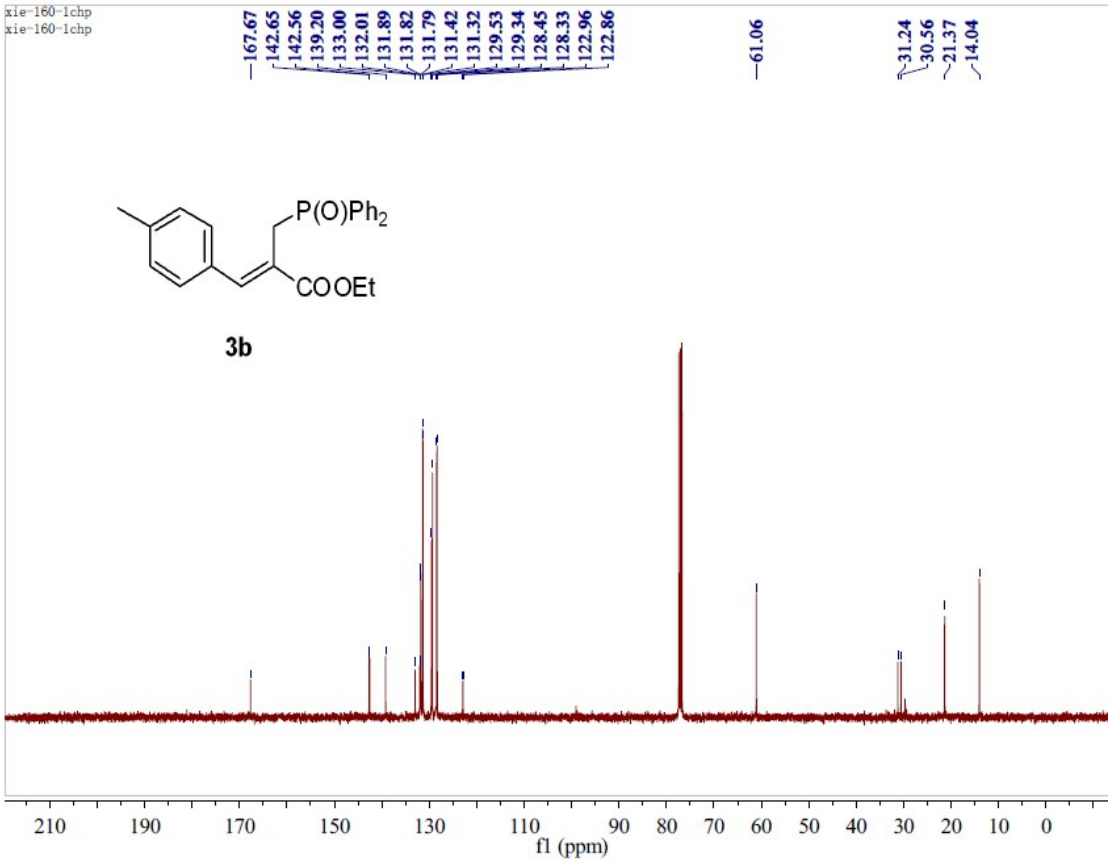
8. NMR Spectra for New Compounds

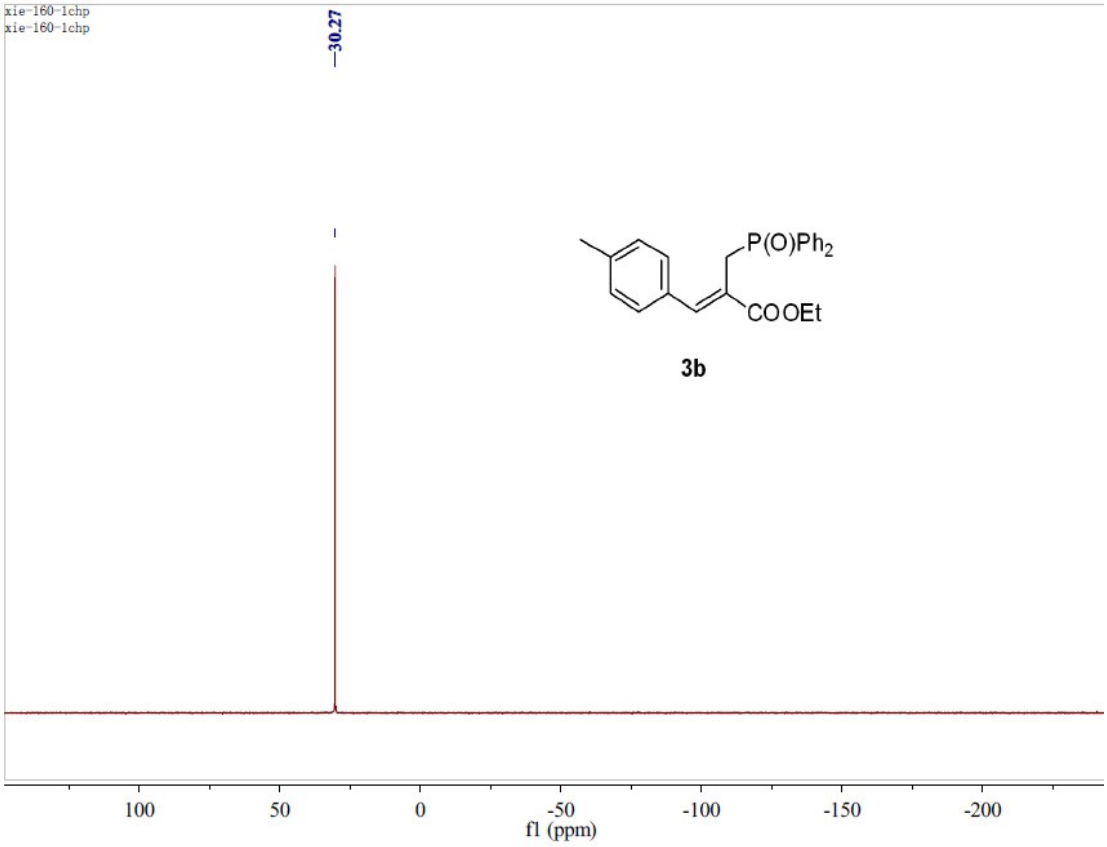


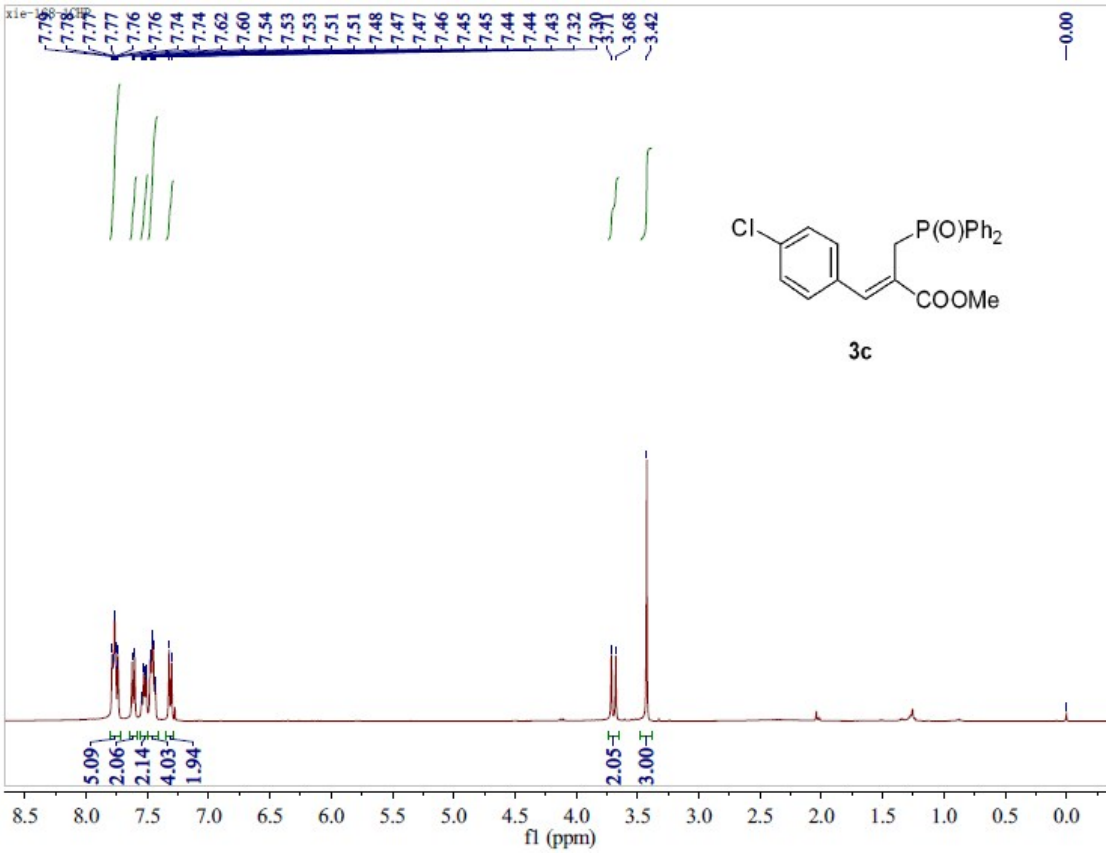


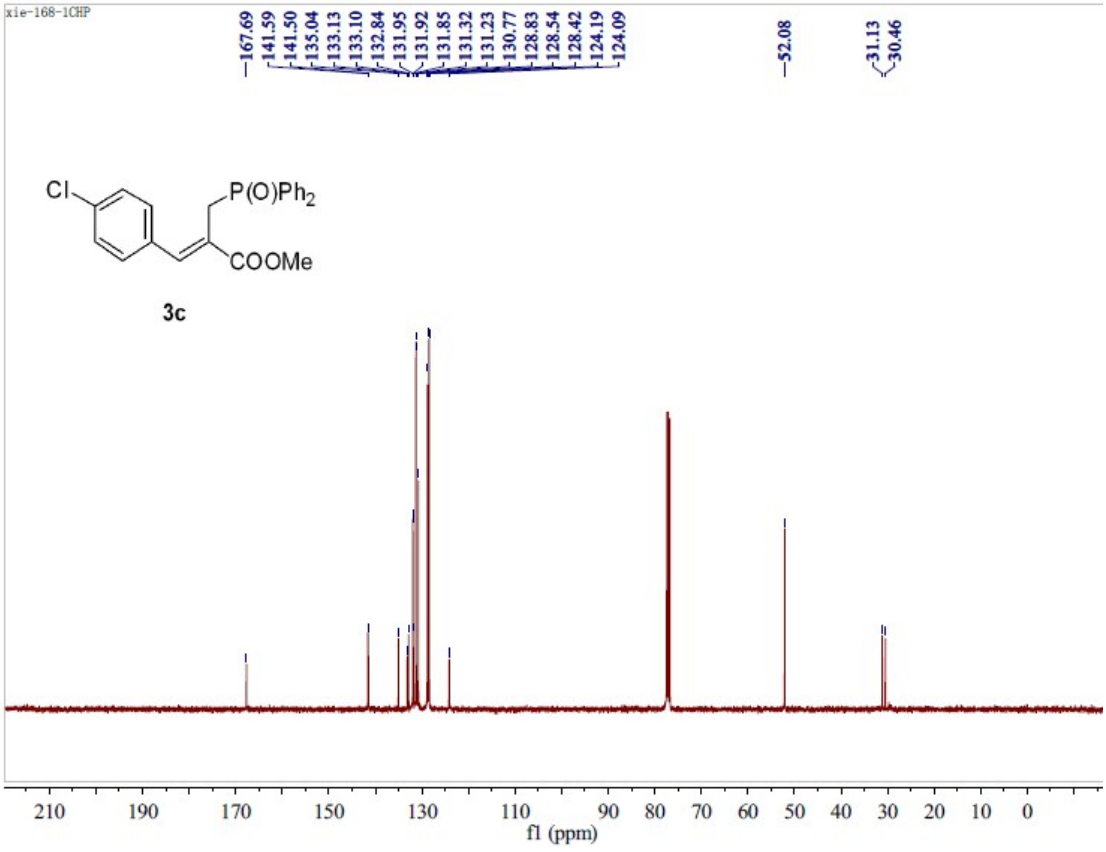

xie-3a
167.52
142.44
142.35
134.82
134.79
133.24
132.26
131.78
131.75
131.41
131.32
129.46
128.93
128.60
128.44
128.32
124.08
123.99
61.09
31.25
30.58
14.05
Ph
COOEt
P(O)Ph2
3a
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

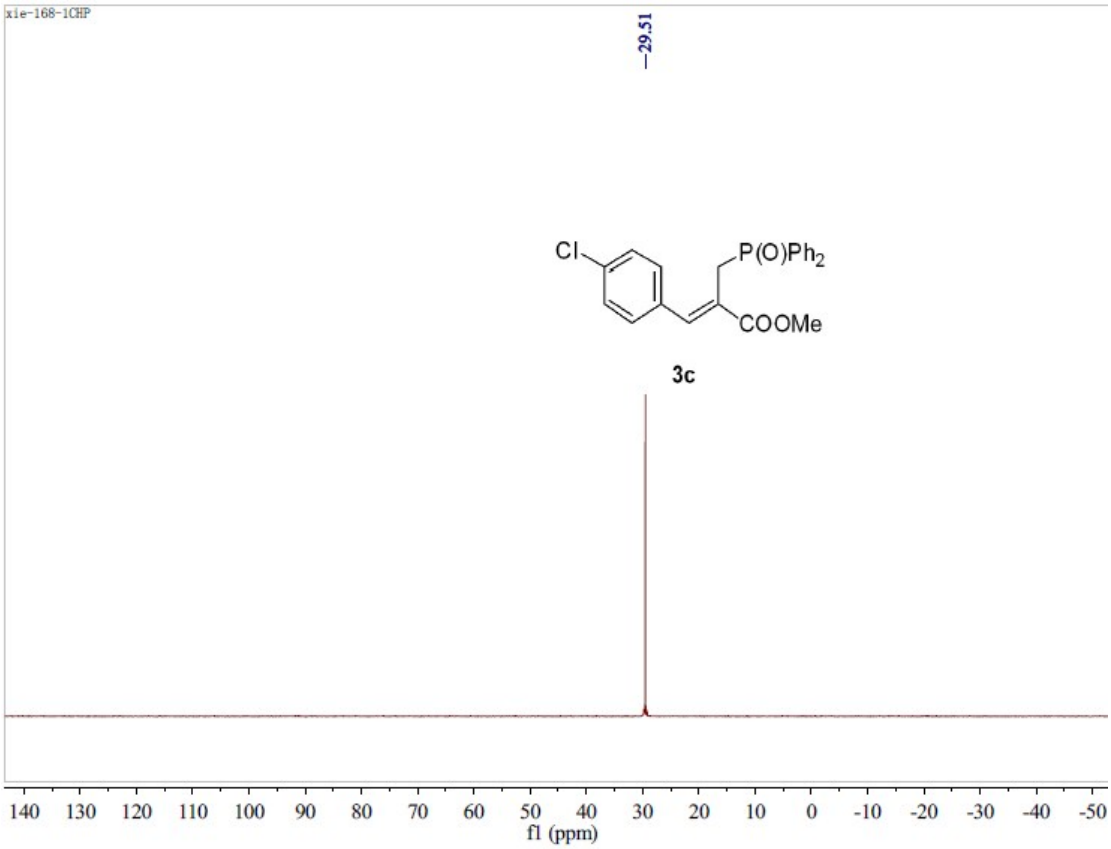

7.80
7.78
7.77
7.76
7.75
7.57
7.55
7.53
7.51
7.51
7.49
7.49
7.46
7.45
7.44
7.44
7.43
7.42
7.42
7.41
7.27
7.17
7.15
3.91
3.89
3.87
3.86
3.78
3.74
2.35
1.12
1.11
1.09
0.00
P(O)Ph2
COOEt
3b
4.98
4.09
3.97
1.95
1.95
2.00
2.95
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

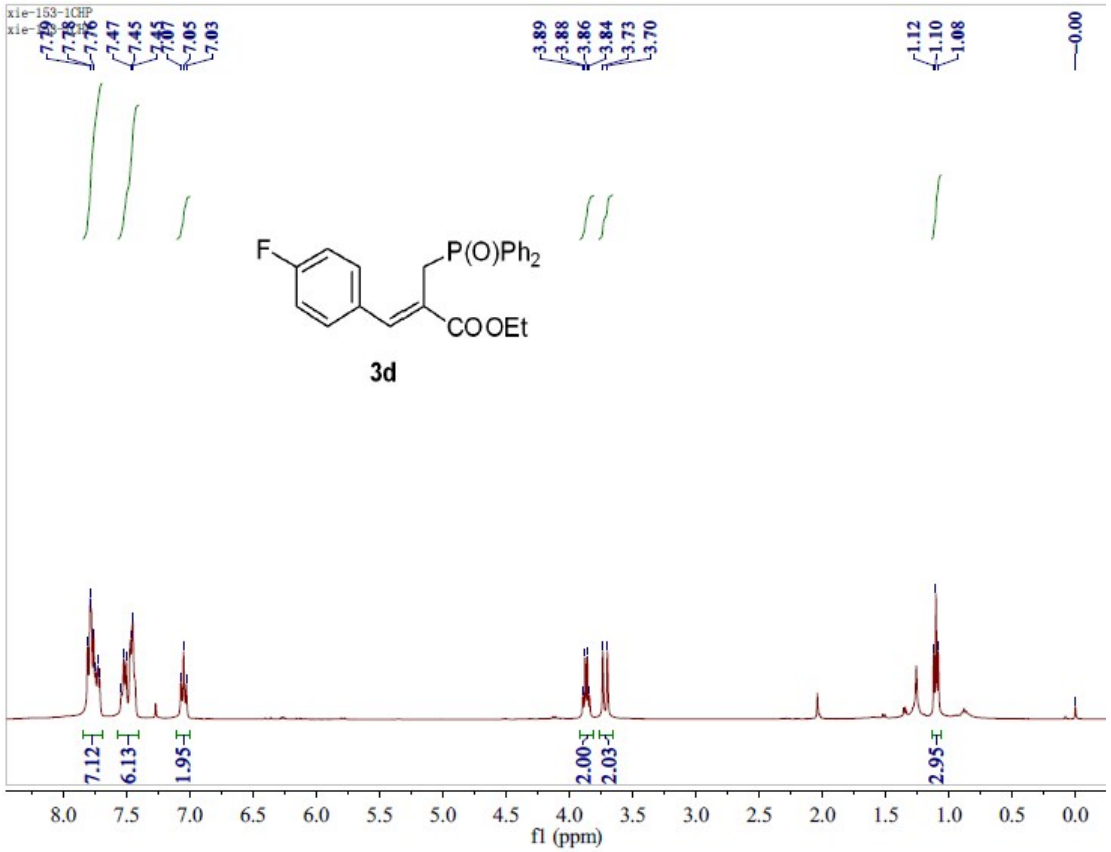

xie-160-1chp
xie-160-1chp
167.67
142.65
142.56
139.20
133.00
132.01
131.89
131.82
131.79
131.42
131.32
129.53
129.34
128.45
128.33
122.96
122.86
61.06
31.24
30.56
21.37
14.04
P(O)Ph2
COOEt
3b
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

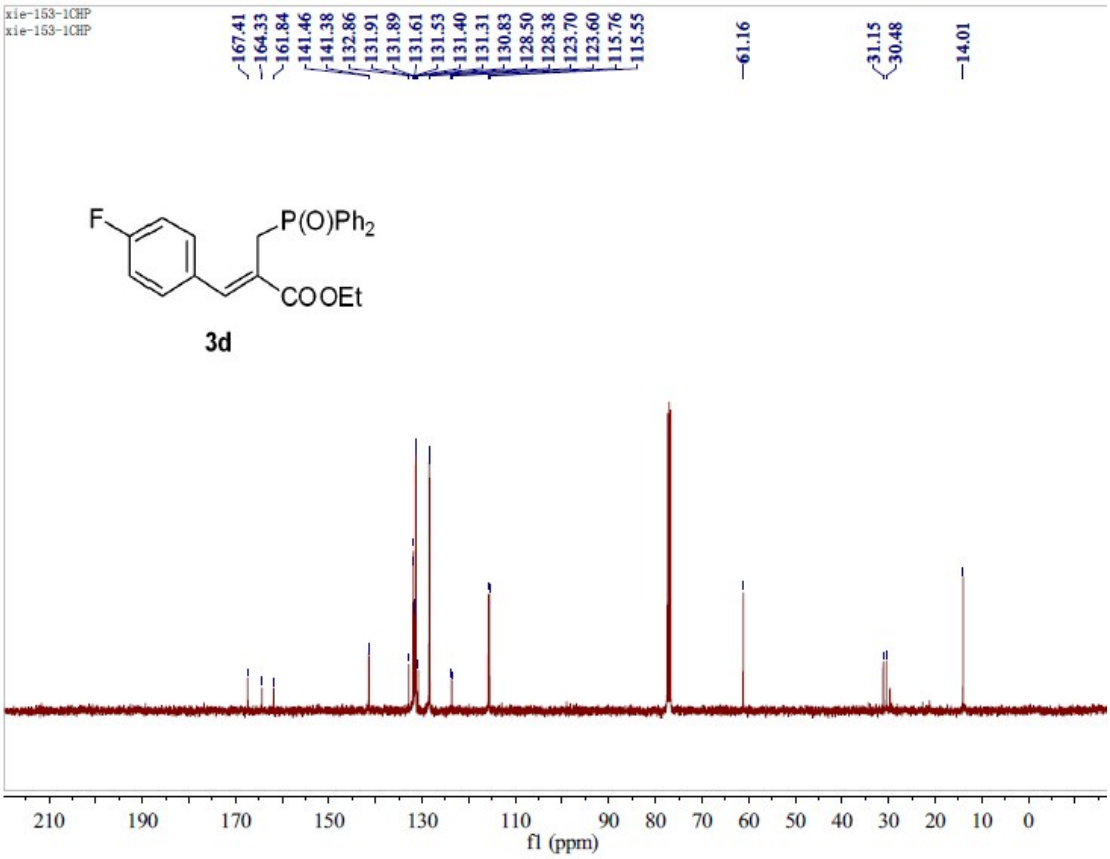

xie-160-1chp
xie-160-1chp
30.27
P(O)Ph2
COOEt
3b
100
50
0
-50
-100
-150
-200
f1 (ppm)

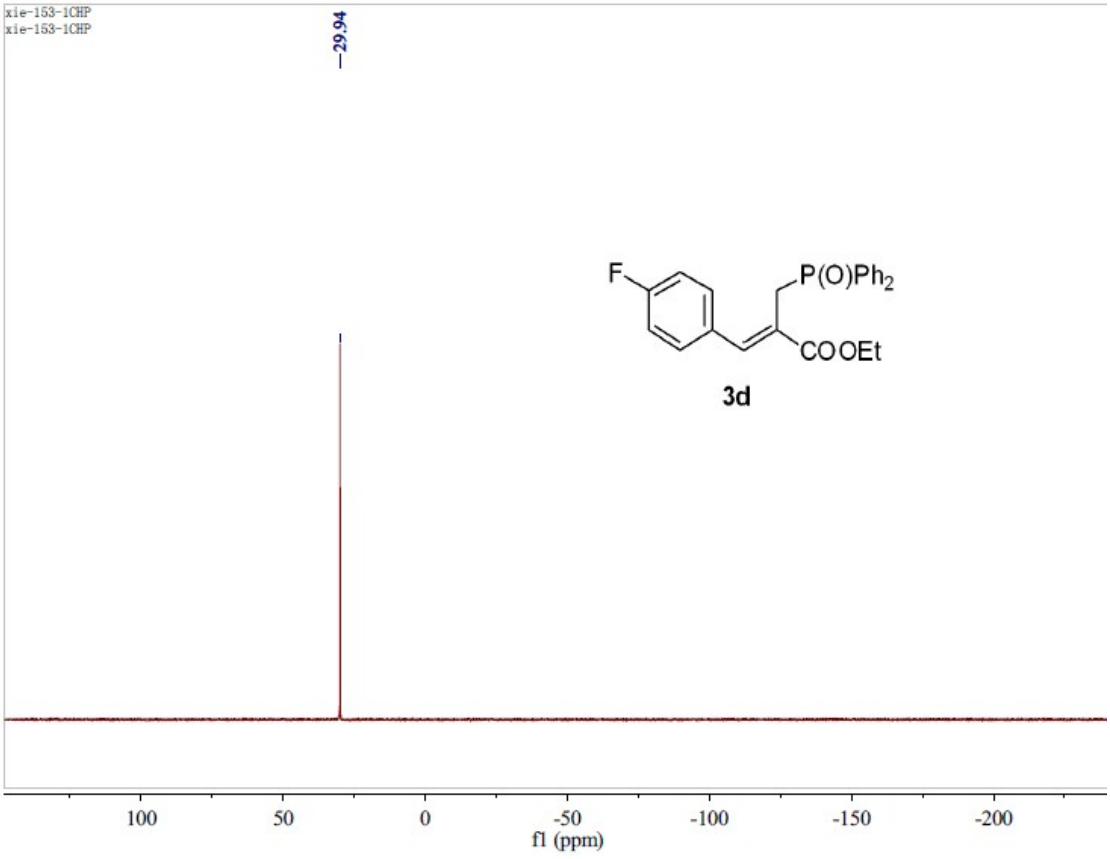

7.79
7.78
7.77
7.77
7.76
7.76
7.74
7.74
7.62
7.60
7.54
7.53
7.53
7.51
7.51
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.32
7.30
3.71
3.68
3.42
0.00
Cl
P(O)Ph2
COOMe
3c
5.09
2.06
2.14
4.03
1.94
2.05
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

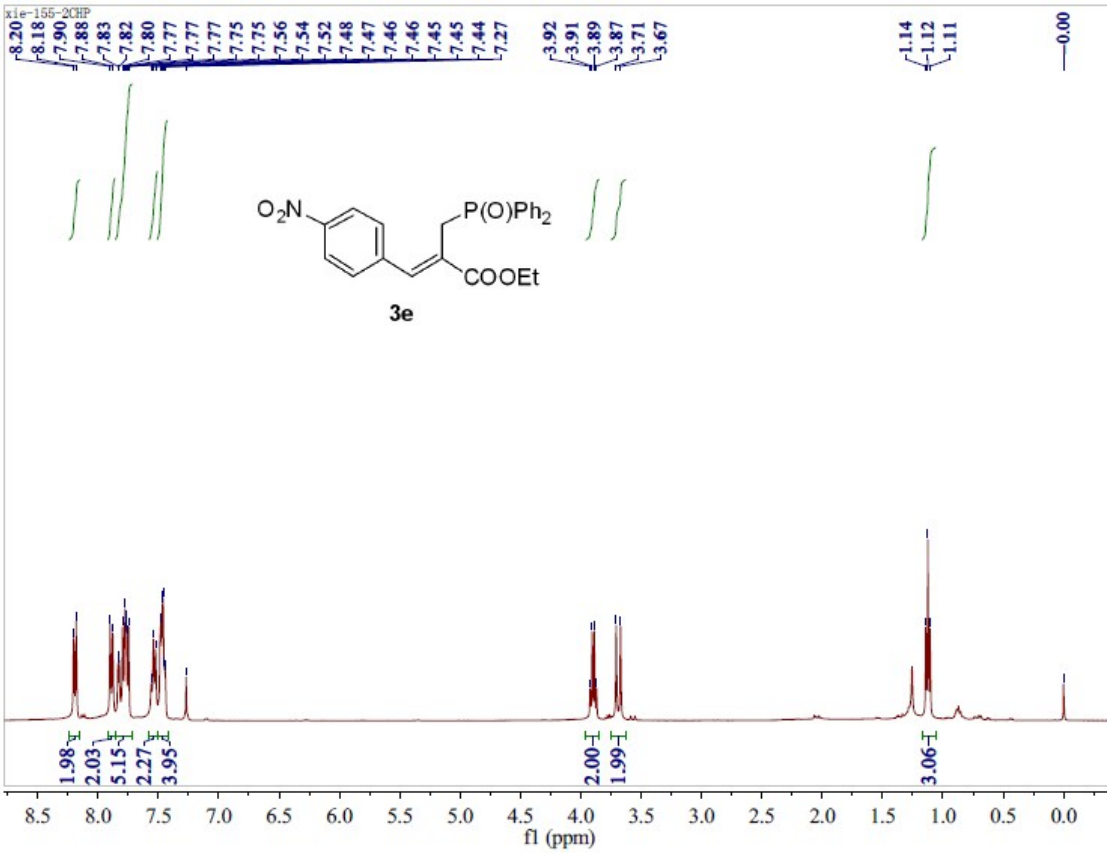

xie-168-1CHP
167.69
141.59
141.50
135.04
133.13
133.10
132.84
131.95
131.92
131.85
131.32
131.23
130.77
128.83
128.54
128.42
124.19
124.09
52.08
31.13
30.46
Cl
P(O)Ph2
COOMe
3c
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

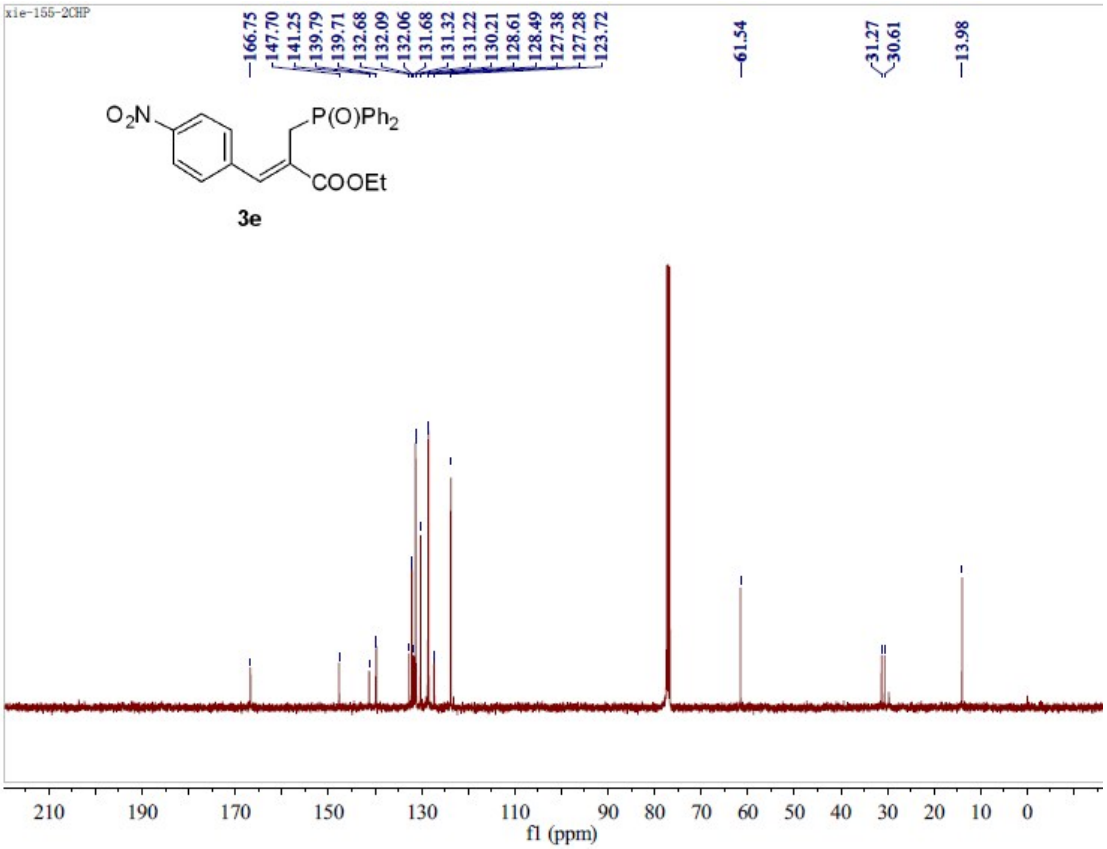

xie-168-1CHP
29.51
Cl
P(O)Ph2
COOMe
3c
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

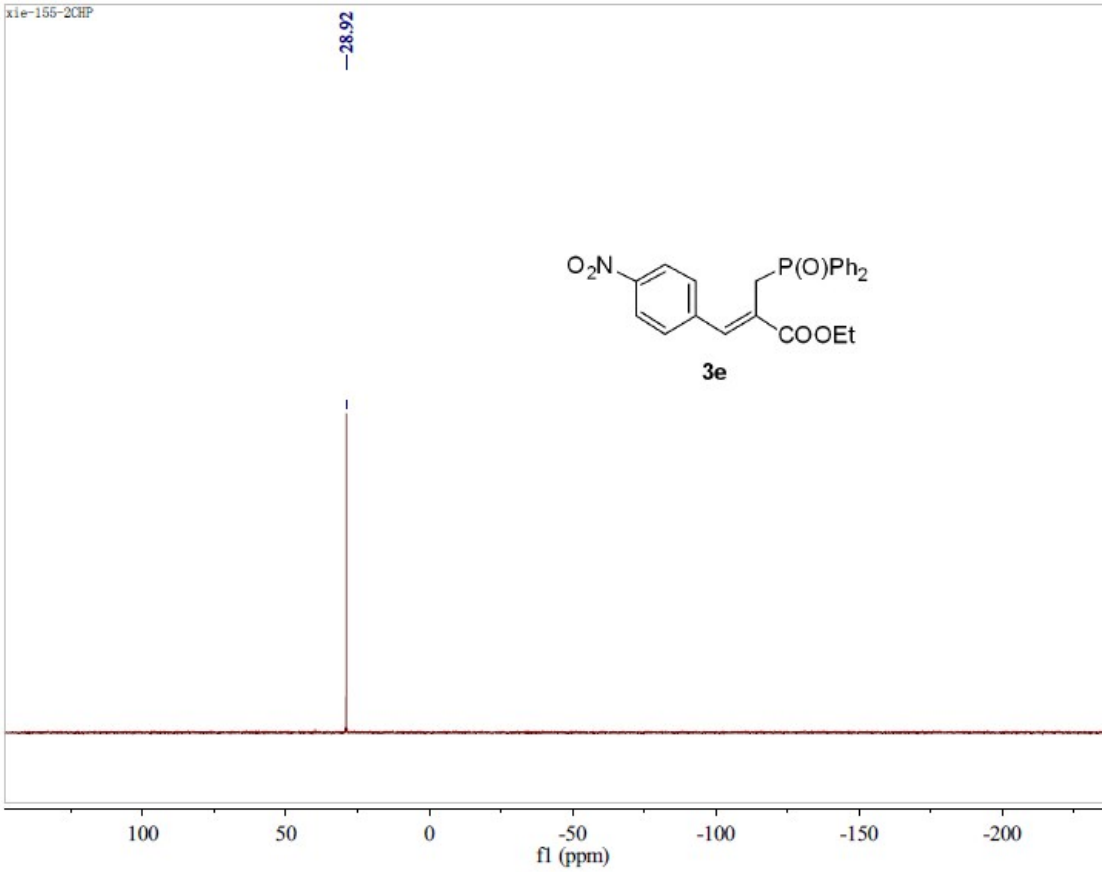

xie-153-1CHP
7.79 7.78 7.76 7.47 7.45 7.07 7.05 7.03
3.89 3.88 3.86 3.84 3.73 3.70
1.12 1.10 1.08
0.00
F
P(O)Ph2
COOEt
3d
7.12 6.13 1.95 2.00 2.03 2.95
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

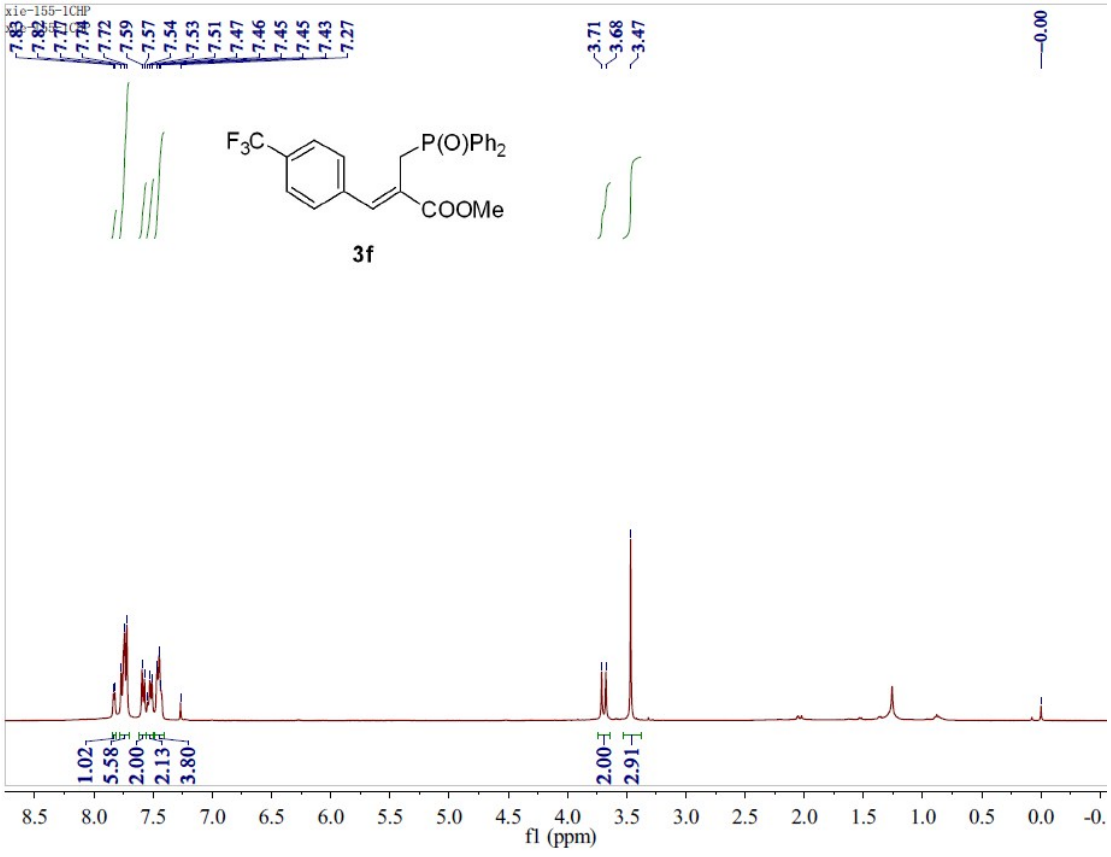

xie-153-1CHP
xie-153-1CHP
167.41
164.33
161.84
141.46
141.38
132.86
131.91
131.89
131.61
131.53
131.40
131.31
130.83
128.50
128.38
123.70
123.60
115.76
115.55
61.16
31.15
30.48
14.01
F
P(O)Ph2
COOEt
3d
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

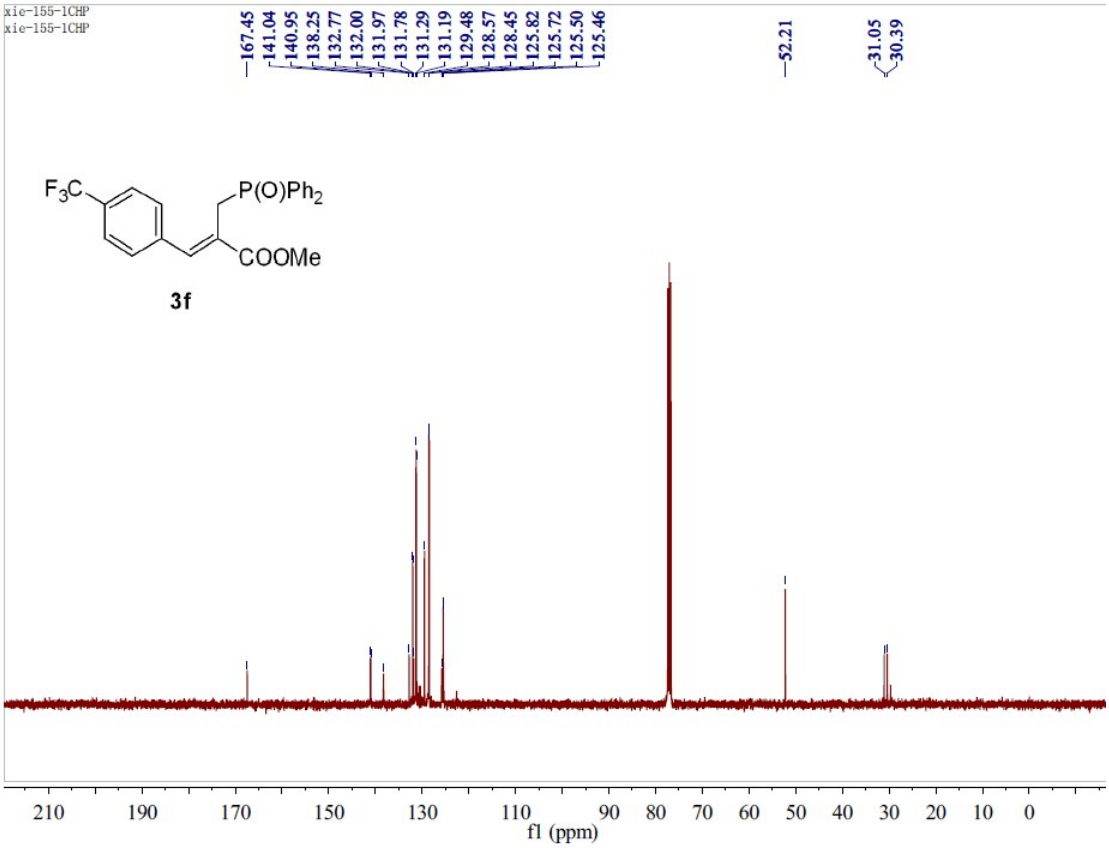

xie-153-1CHP
xie-153-1CHP
29.94
F
P(O)Ph2
COOEt
3d
100
50
0
-50
-100
-150
-200
f1 (ppm)

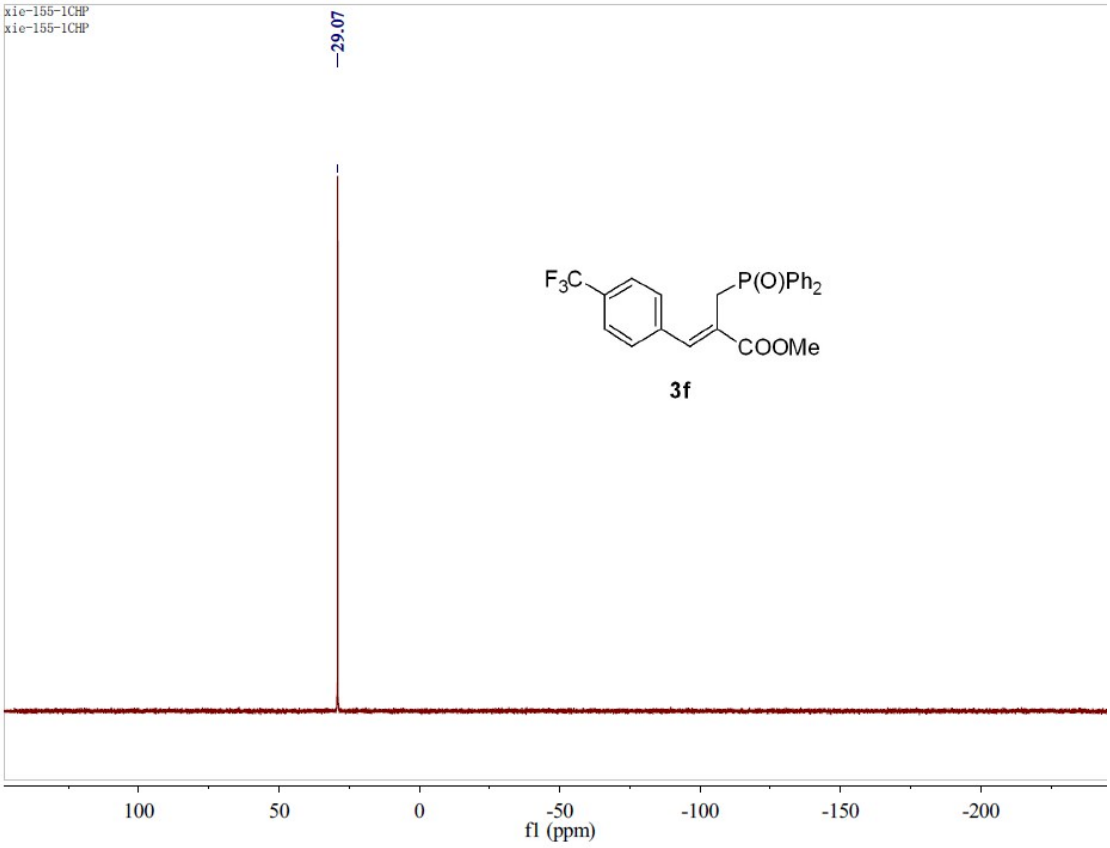

xie-155-2CHP
8.20
8.18
7.90
7.88
7.83
7.82
7.80
7.77
7.77
7.77
7.75
7.75
7.56
7.54
7.52
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.27
3.92
3.91
3.89
3.87
3.71
3.67
1.14
1.12
1.11
0.00
O2N
P(O)Ph2
COOEt
3e
1.98
2.03
5.15
2.27
3.95
2.00
1.99
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

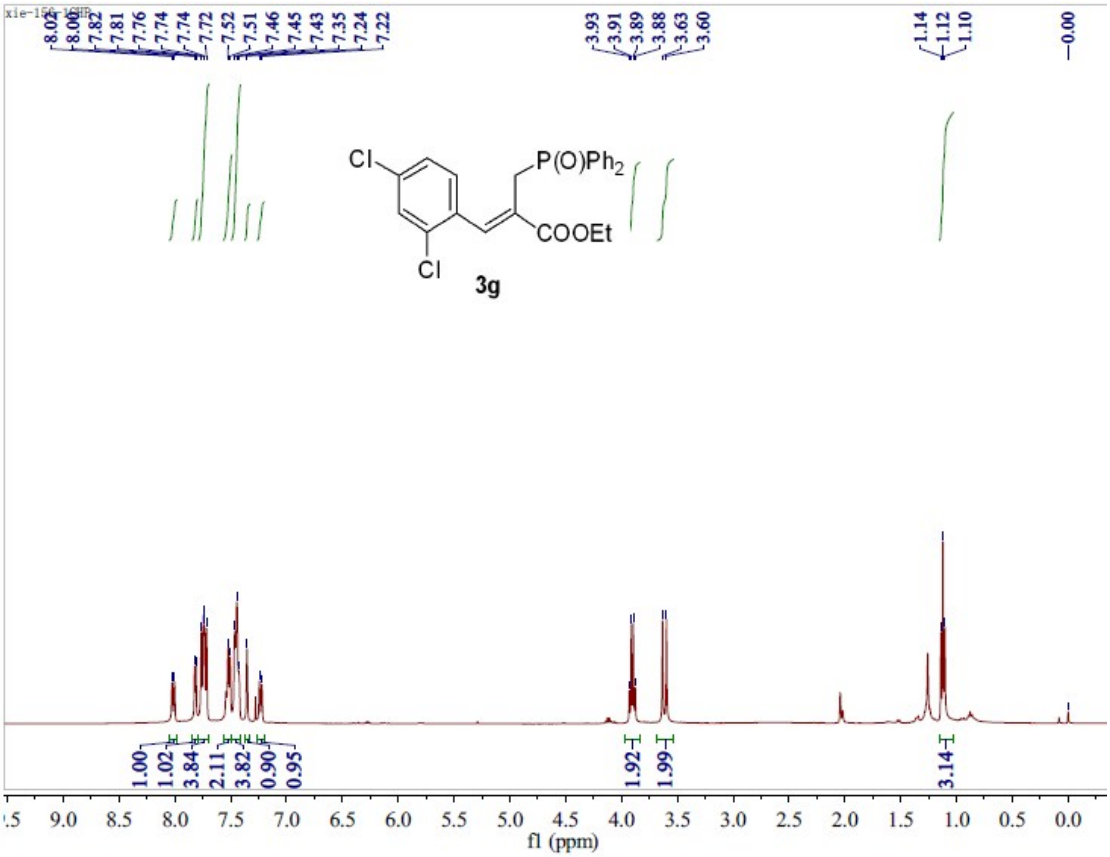

xie-155-2CHP
166.75
147.70
141.25
139.79
139.71
132.68
132.09
132.06
131.68
131.32
131.22
130.21
128.61
128.49
127.38
127.28
123.72
61.54
31.27
30.61
13.98
O2N
P(O)Ph2
COOEt
3e
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

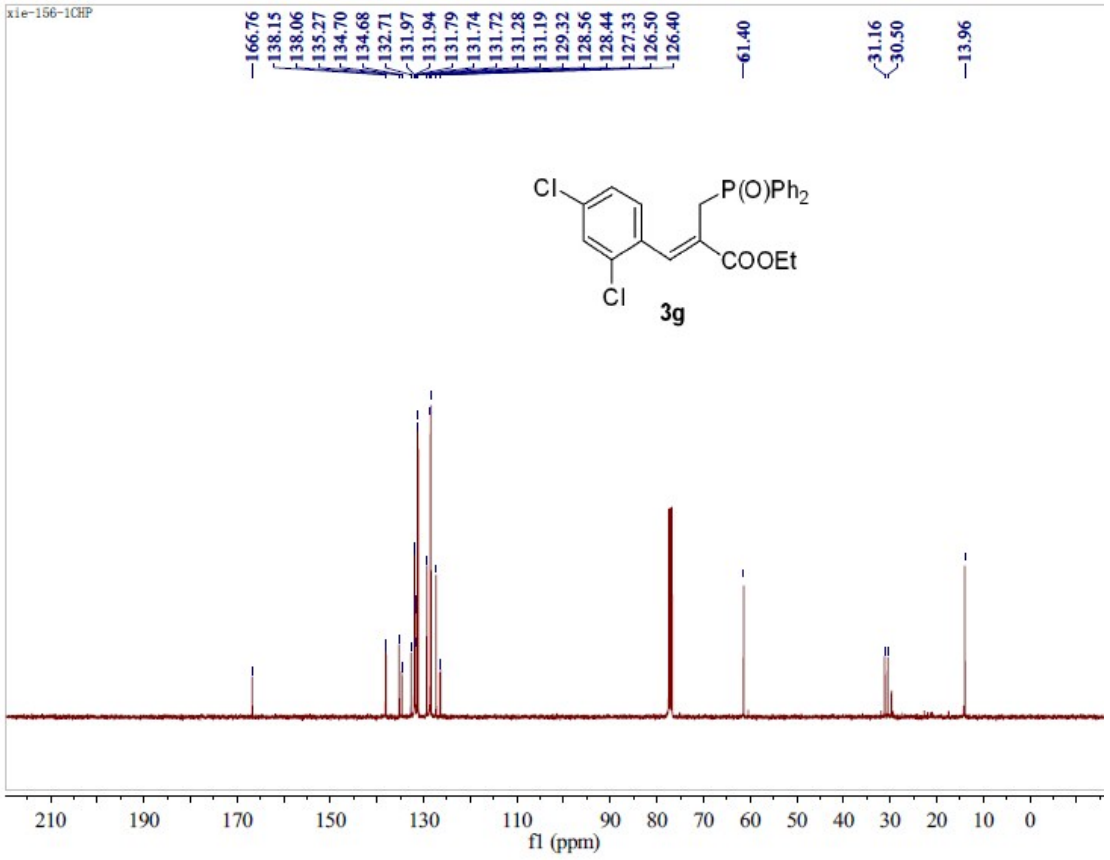

xie-155-2CHP
28.92
O2N
P(O)Ph2
COOEt
3e
100
50
0
-50
-100
-150
-200
f1 (ppm)

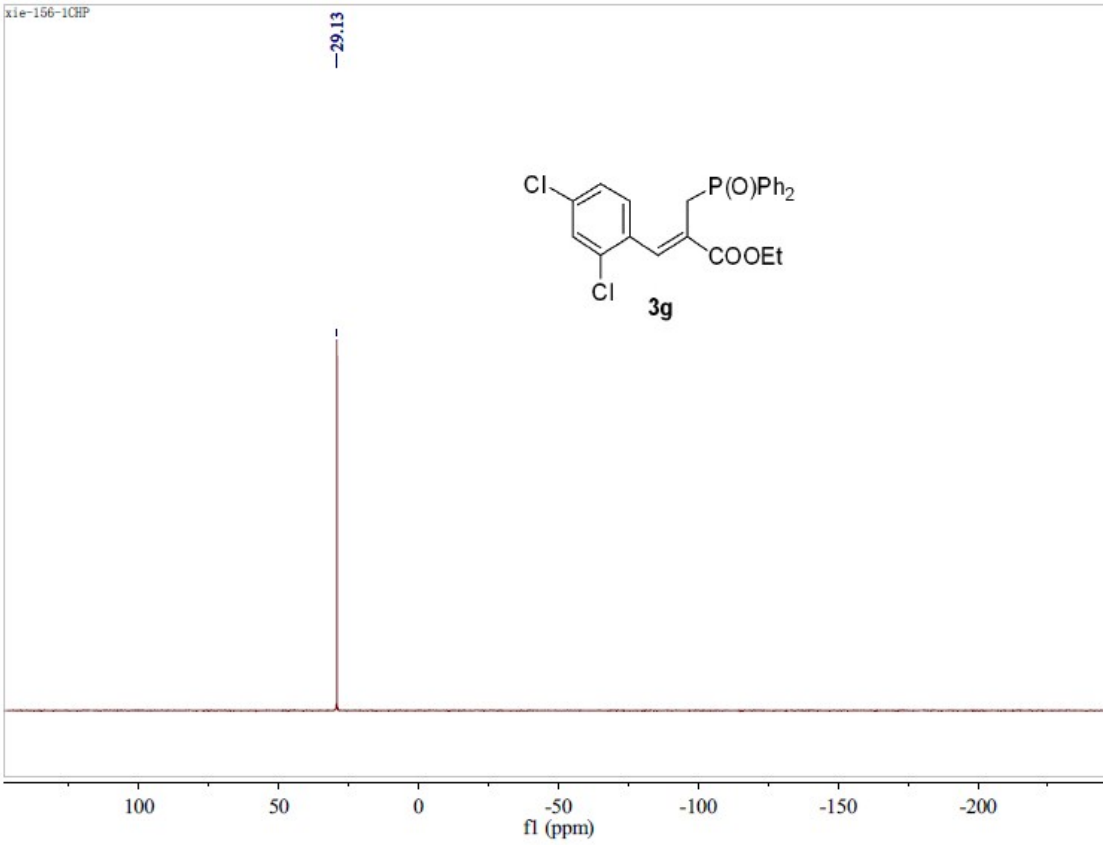

xie-155-1CHP
7.83
7.82
7.72
7.59
7.57
7.54
7.53
7.51
7.47
7.46
7.45
7.45
7.43
7.27
3.71
3.68
3.47
0.00
F3C
P(O)Ph2
COOMe
3f
1.02
5.58
2.00
2.13
3.80
2.00
2.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

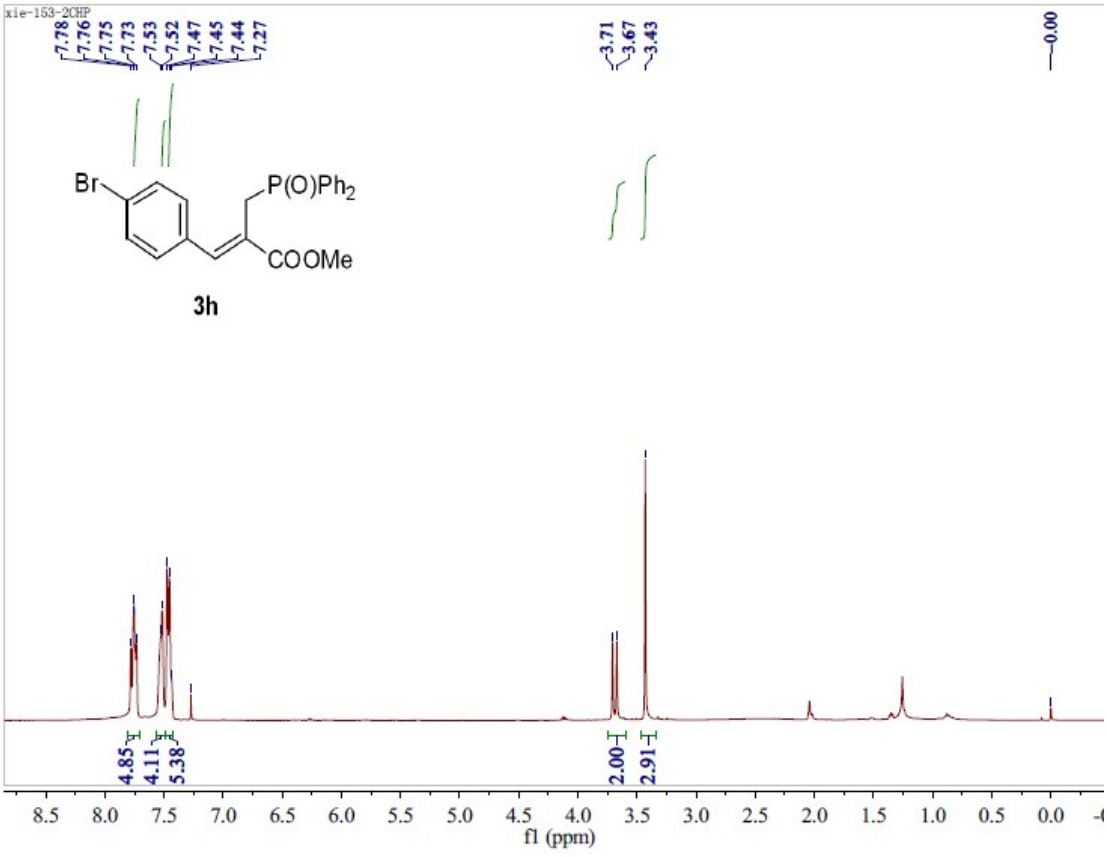

xie-155-1CHP
xie-155-1CHP
167.45
141.04
140.95
138.25
132.77
132.00
131.97
131.78
131.29
131.19
129.48
128.57
128.45
125.82
125.72
125.50
125.46
52.21
31.05
30.39
F3C
P(O)Ph2
COOMe
3f
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

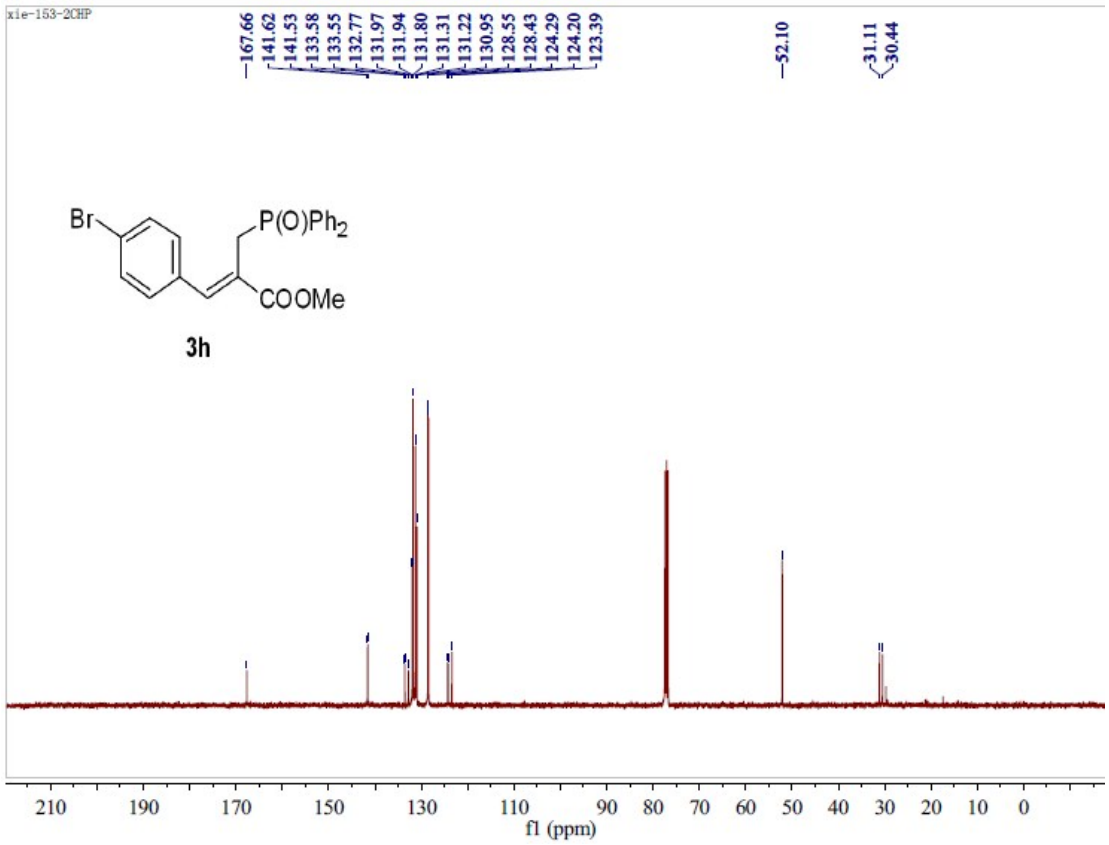

xie-155-1CHP
xie-155-1CHP
29.07
F3C
P(O)Ph2
COOMe
3f
100
50
0
-50
-100
-150
-200
f1 (ppm)

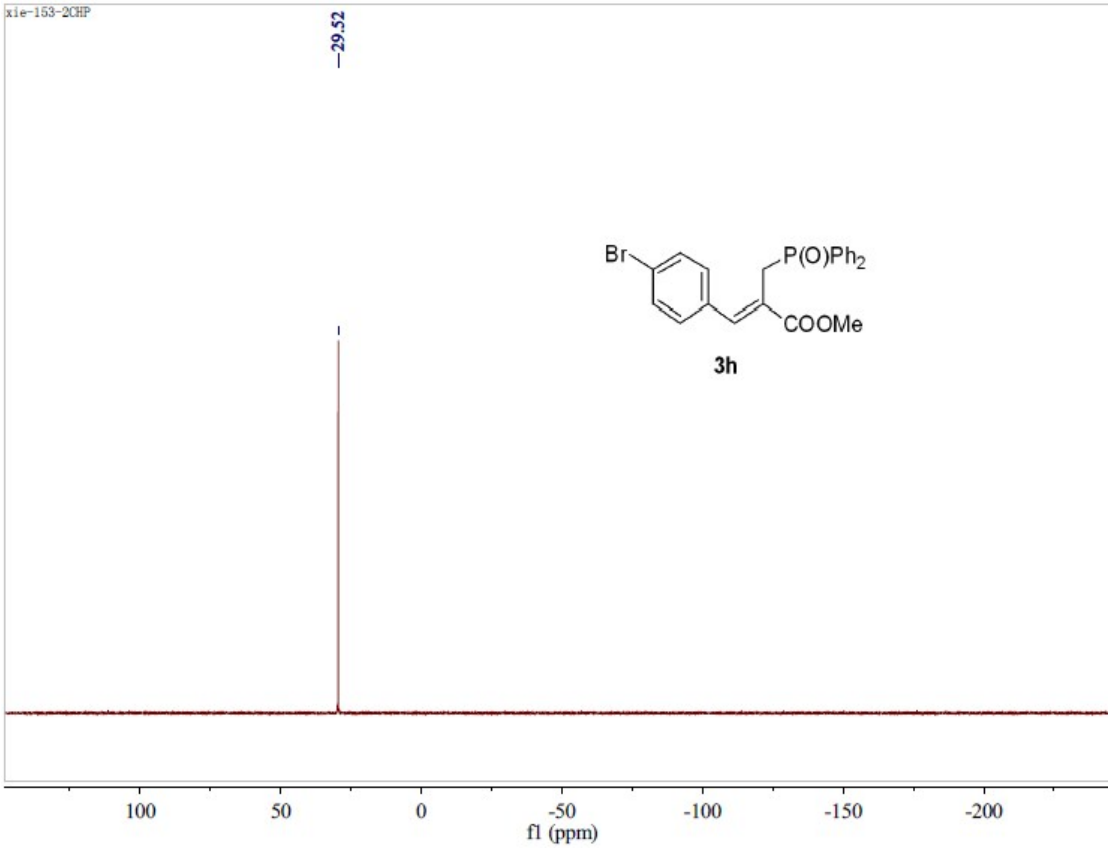

xie-156-1CHP
8.02
8.00
7.82
7.81
7.76
7.74
7.74
7.72
7.52
7.51
7.46
7.45
7.43
7.35
7.24
7.22
3.93
3.91
3.89
3.88
3.63
3.60
1.14
1.12
1.10
0.00
Cl
P(O)Ph2
COOEt
Cl
3g
1.00
1.02
3.84
2.11
3.82
0.90
0.95
1.92
1.99
3.14
f1 (ppm)

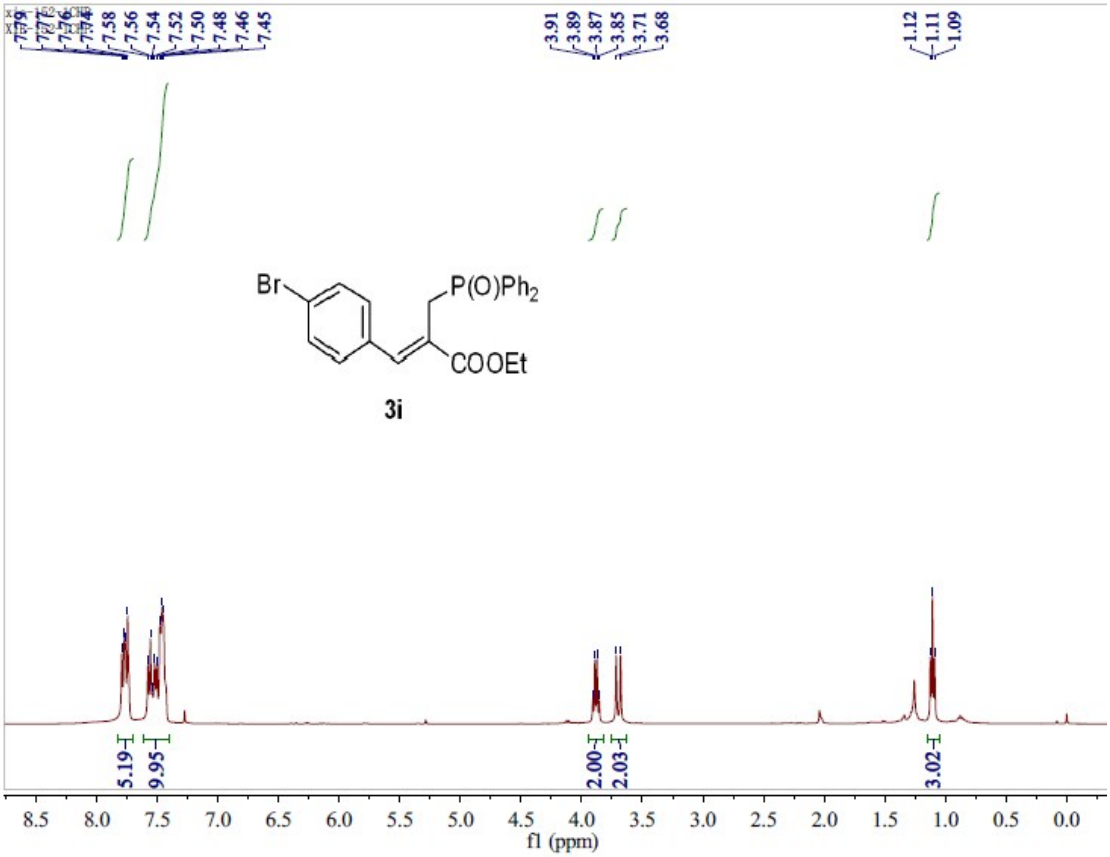

xie-156-1CHP
166.76
138.15
138.06
135.27
134.70
134.68
132.71
131.97
131.94
131.79
131.74
131.72
131.28
131.19
129.32
128.56
128.44
127.33
126.50
126.40
61.40
31.16
30.50
13.96
Cl
P(O)Ph2
COOEt
Cl
3g
f1 (ppm)

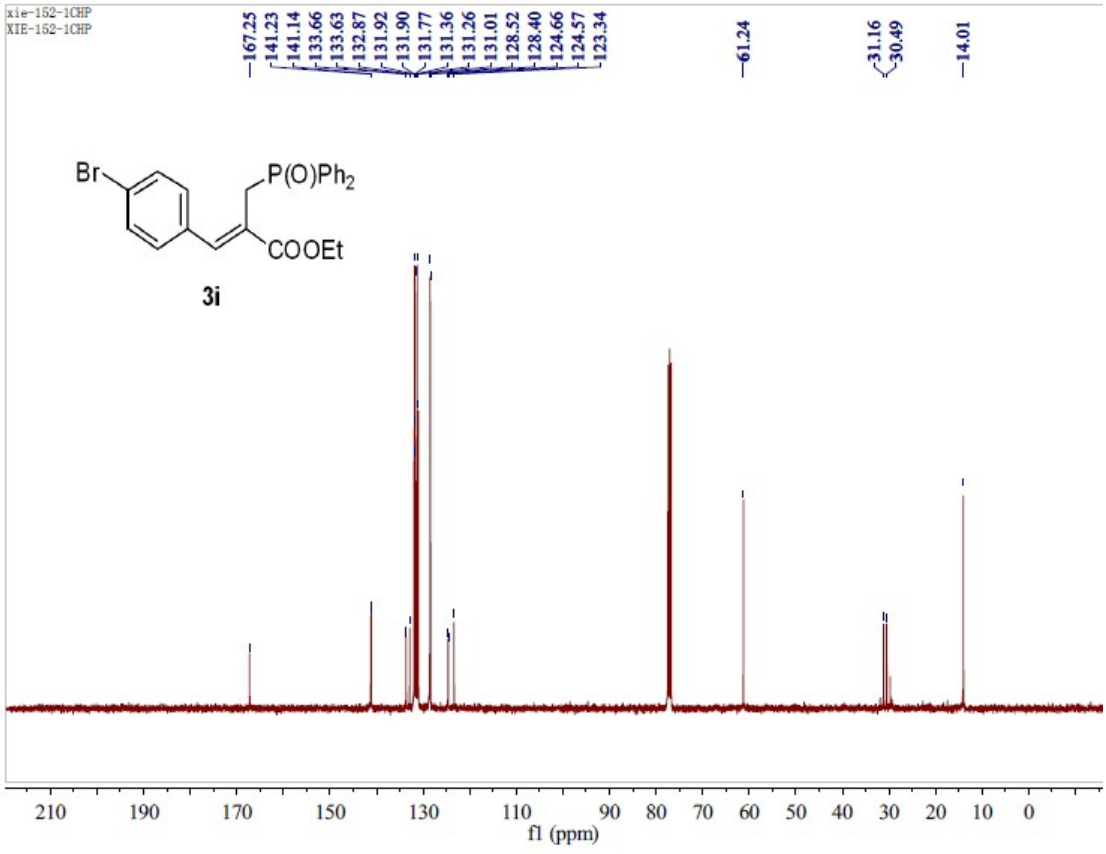

xie-156-1CHP
29.13
Cl
P(O)Ph2
COOEt
Cl
3g
100
50
0
-50
-100
-150
-200
f1 (ppm)

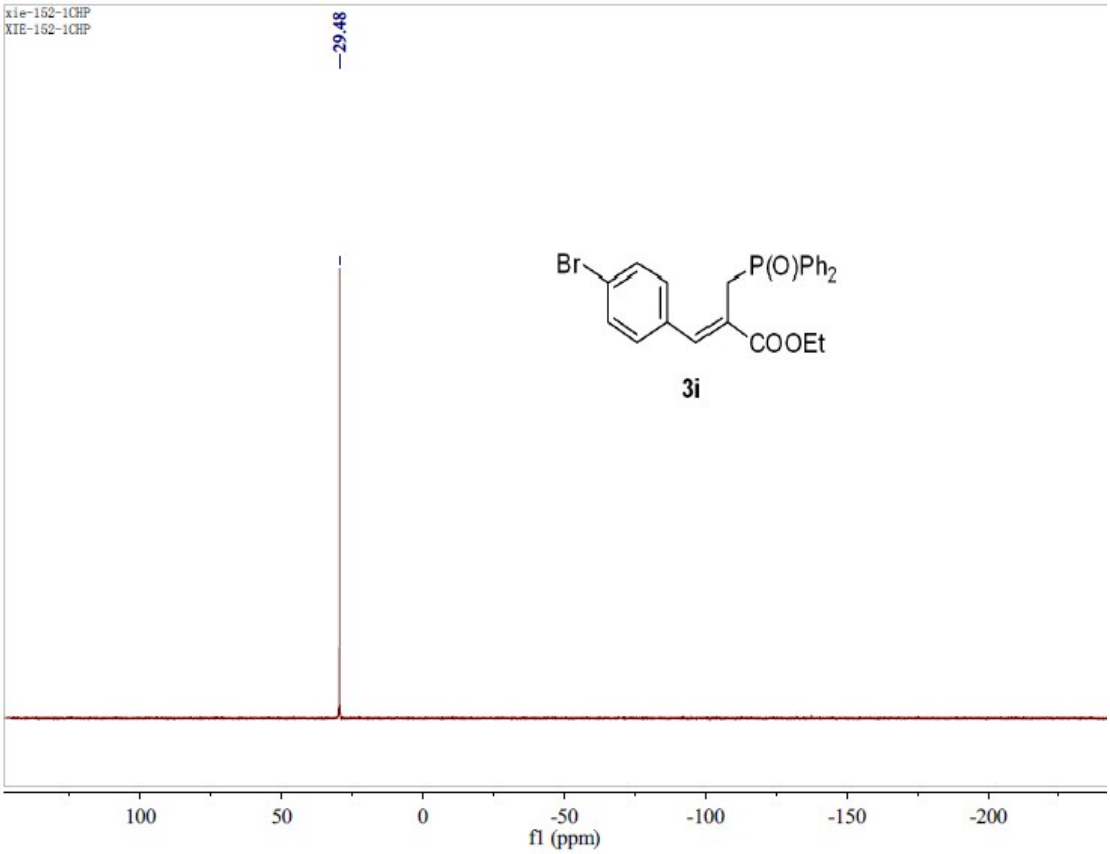

xie-153-2CHP
7.78
7.76
7.75
7.73
7.53
7.52
7.47
7.45
7.44
7.27
3.71
3.67
3.43
0.00
Br
P(O)Ph2
COOMe
3h
4.85
4.11
5.38
2.00
2.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

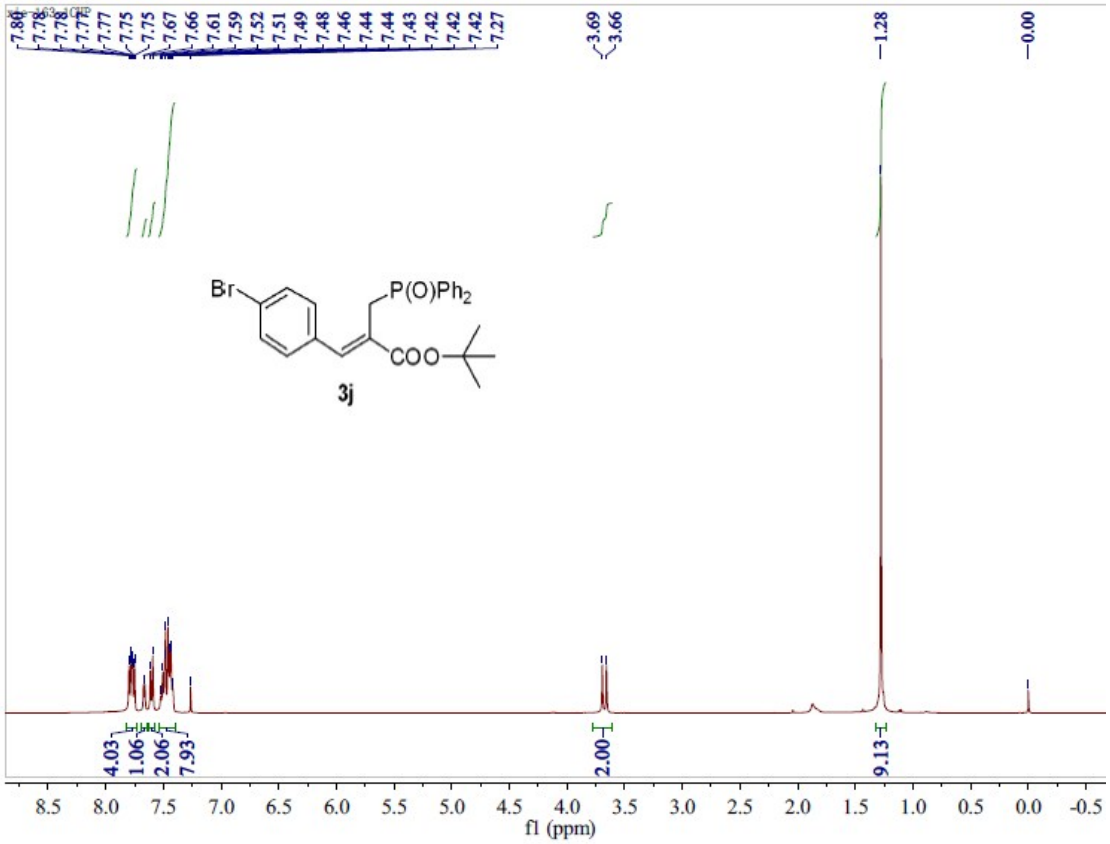

xie-153-2CHP
167.66
141.62
141.53
133.58
133.55
132.77
131.97
131.94
131.80
131.31
131.22
130.95
128.55
128.43
124.29
124.20
123.39
52.10
31.11
30.44
Br
P(O)Ph2
COOMe
3h
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

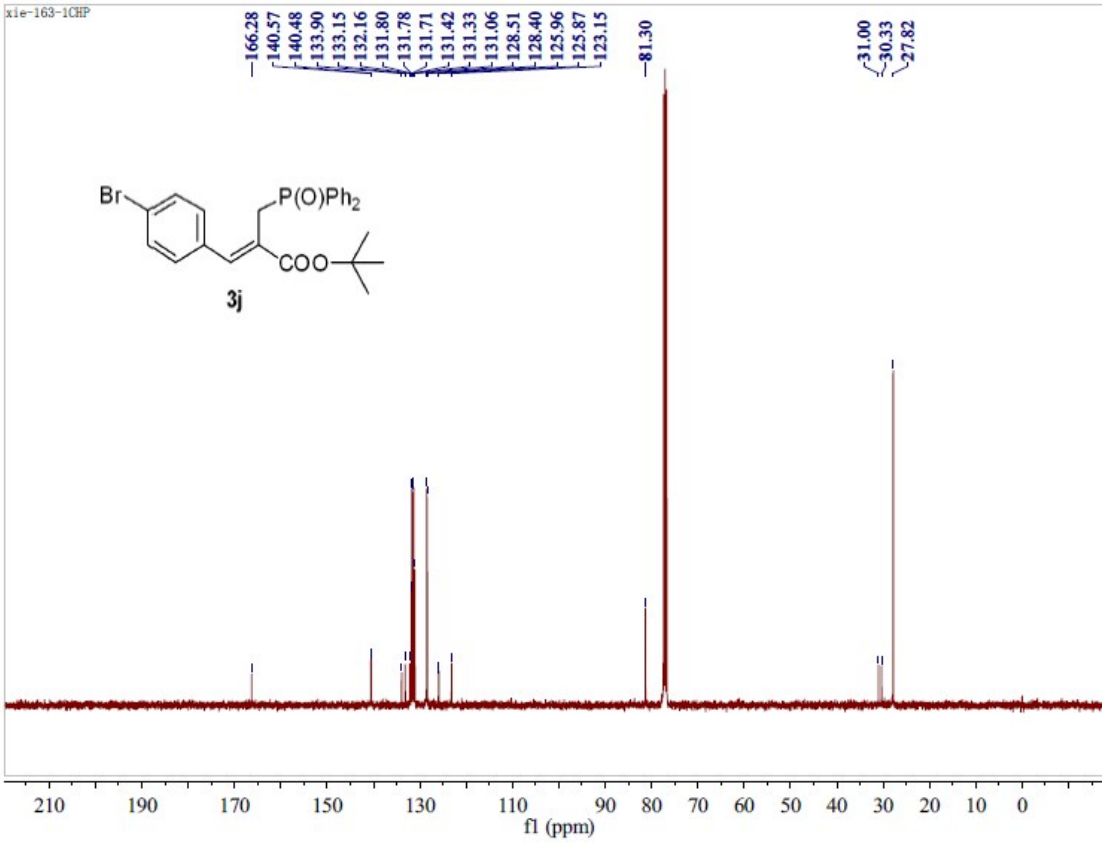

xie-153-2CHP
29.52
Br
P(O)Ph2
COOMe
3h
100
50
0
-50
-100
-150
-200
f1 (ppm)

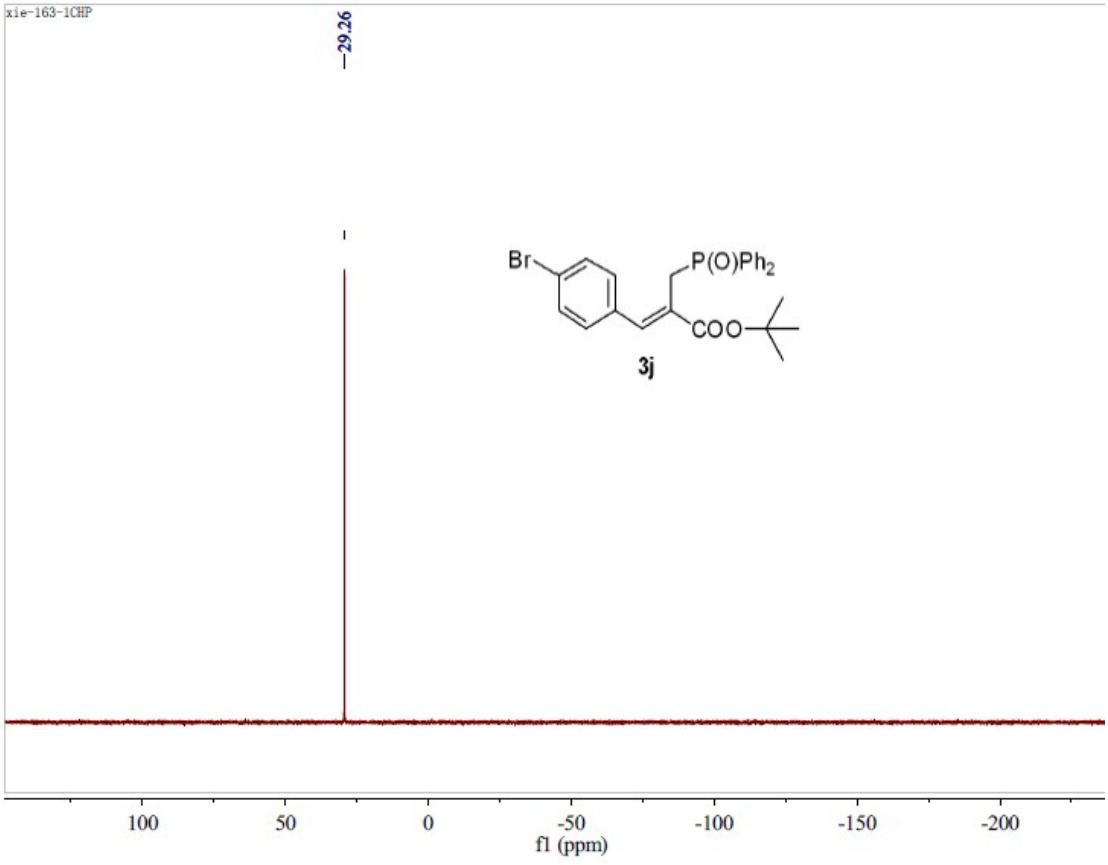

7.79
7.77
7.76
7.74
7.58
7.56
7.54
7.52
7.50
7.48
7.46
7.45
3.91
3.89
3.87
3.85
3.71
3.68
1.12
1.11
1.09
Br
P(O)Ph2
COOEt
3i
5.19
9.95
2.00
2.03
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

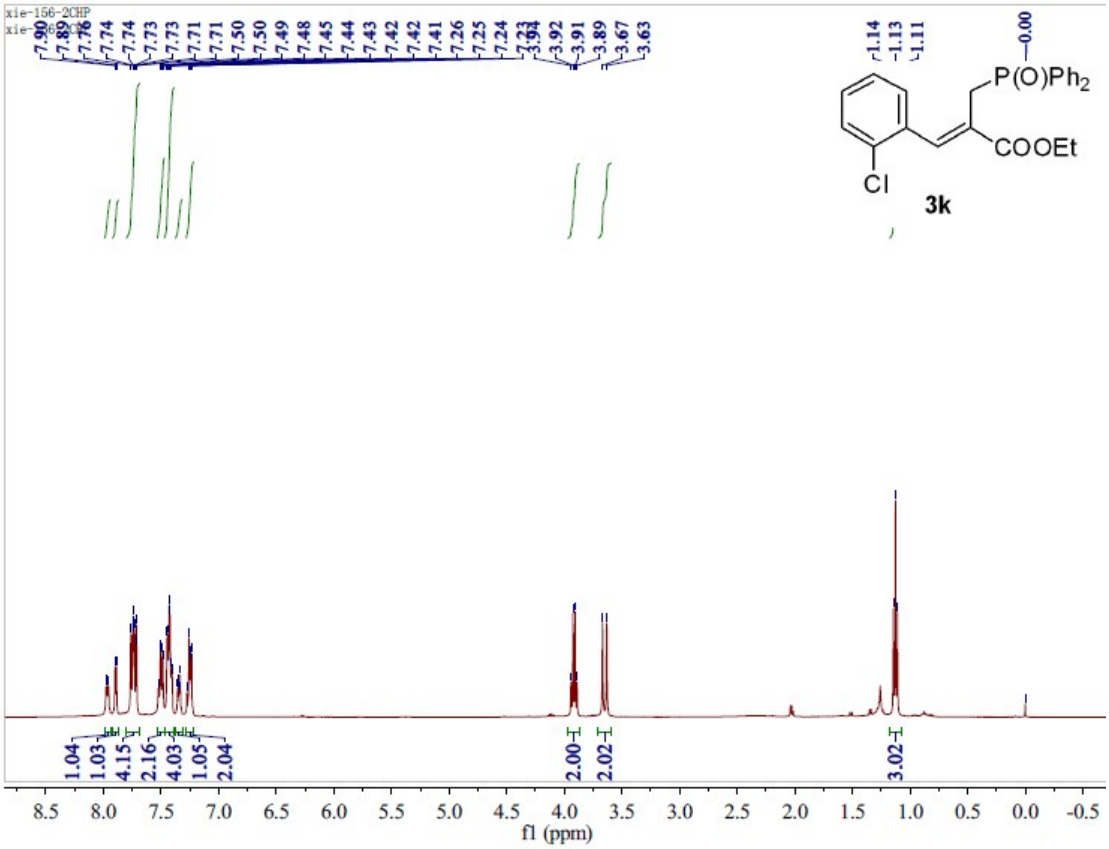

xie-152-1CHP
XIE-152-1CHP
167.25
141.23
141.14
133.66
133.63
132.87
131.92
131.90
131.77
131.36
131.26
131.01
128.52
128.40
124.66
124.57
123.34
61.24
31.16
30.49
14.01
Br
P(O)Ph2
COOEt
3i
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

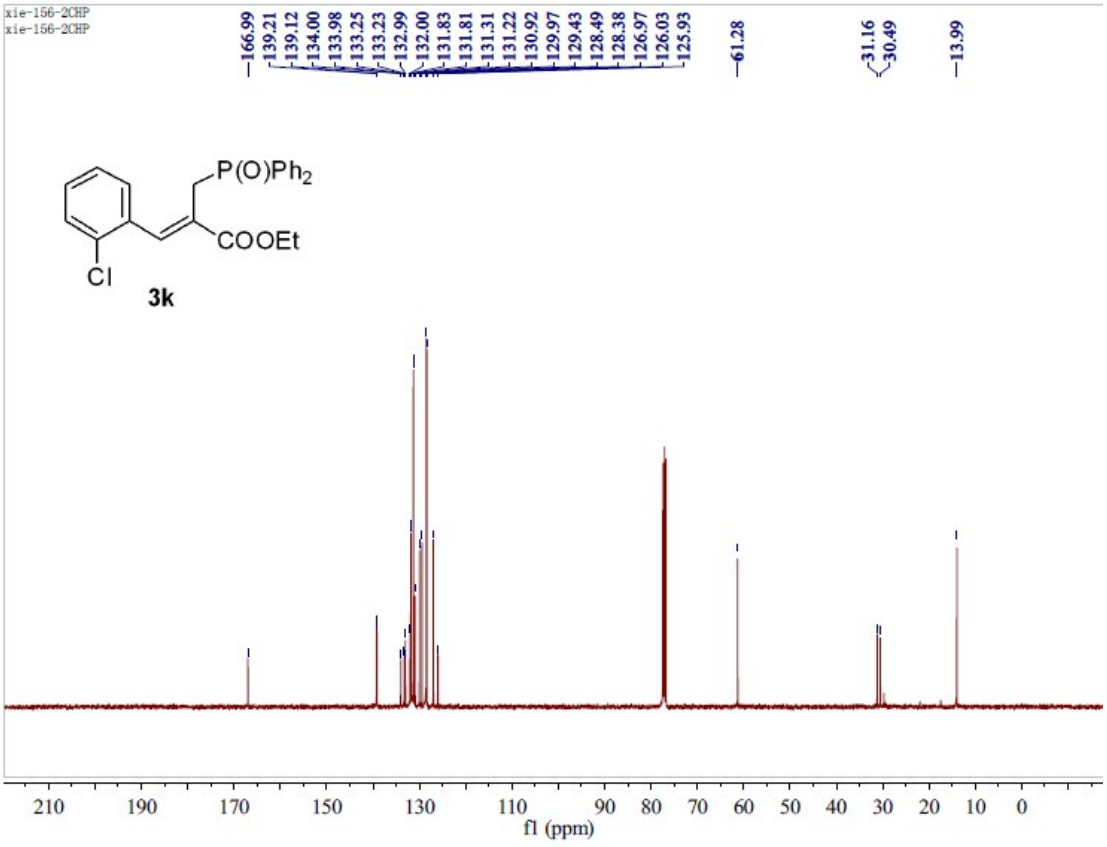

xie-152-1CHP
XIE-152-1CHP
29.48
Br
P(O)Ph2
COOEt
3i
100
50
0
-50
-100
-150
-200
f1 (ppm)

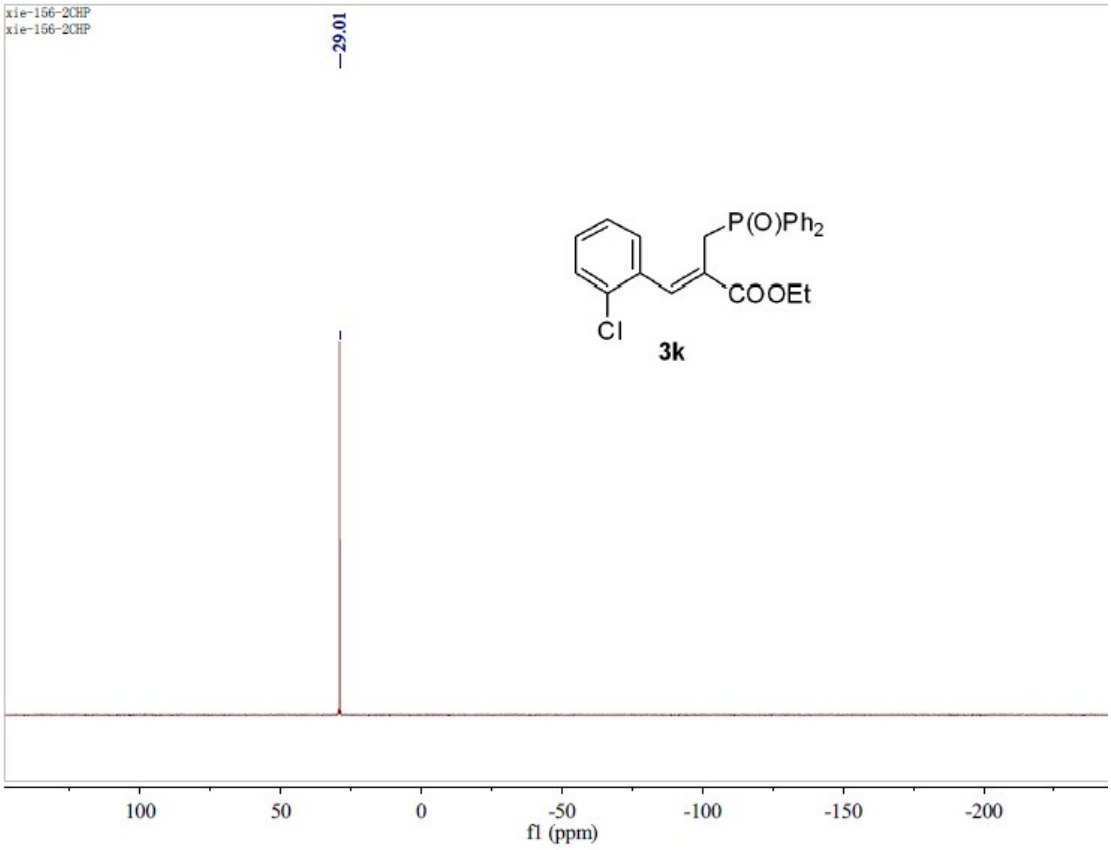

7.80
7.78
7.78
7.77
7.77
7.75
7.75
7.67
7.66
7.61
7.59
7.52
7.51
7.49
7.48
7.46
7.44
7.44
7.43
7.42
7.42
7.42
7.27
3.69
3.66
1.28
0.00
Br
P(O)Ph2
COO
3j
4.03
1.06
2.06
7.93
2.00
9.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

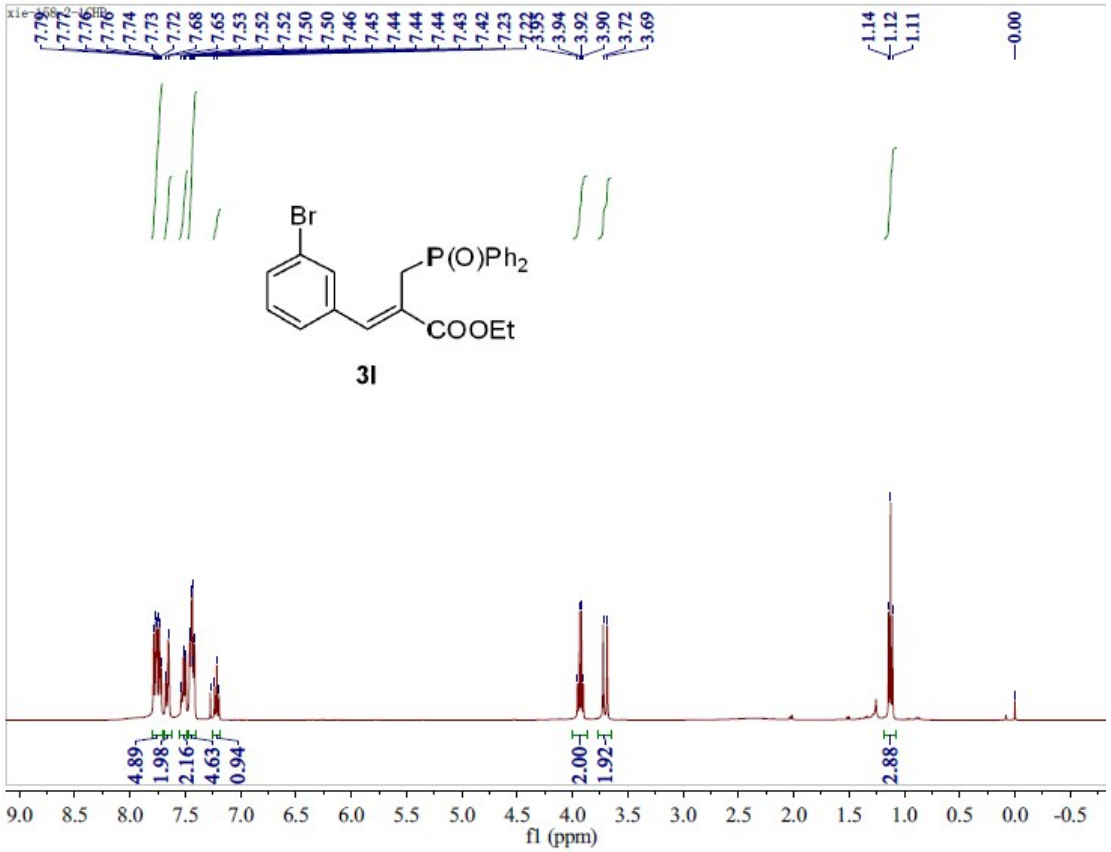

xie-163-1CHP
166.28
140.57
140.48
133.90
133.15
132.16
131.80
131.78
131.71
131.42
131.33
131.06
128.51
128.40
125.96
125.87
123.15
81.30
31.00
30.33
27.82
Br
P(O)Ph2
COO
3j
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

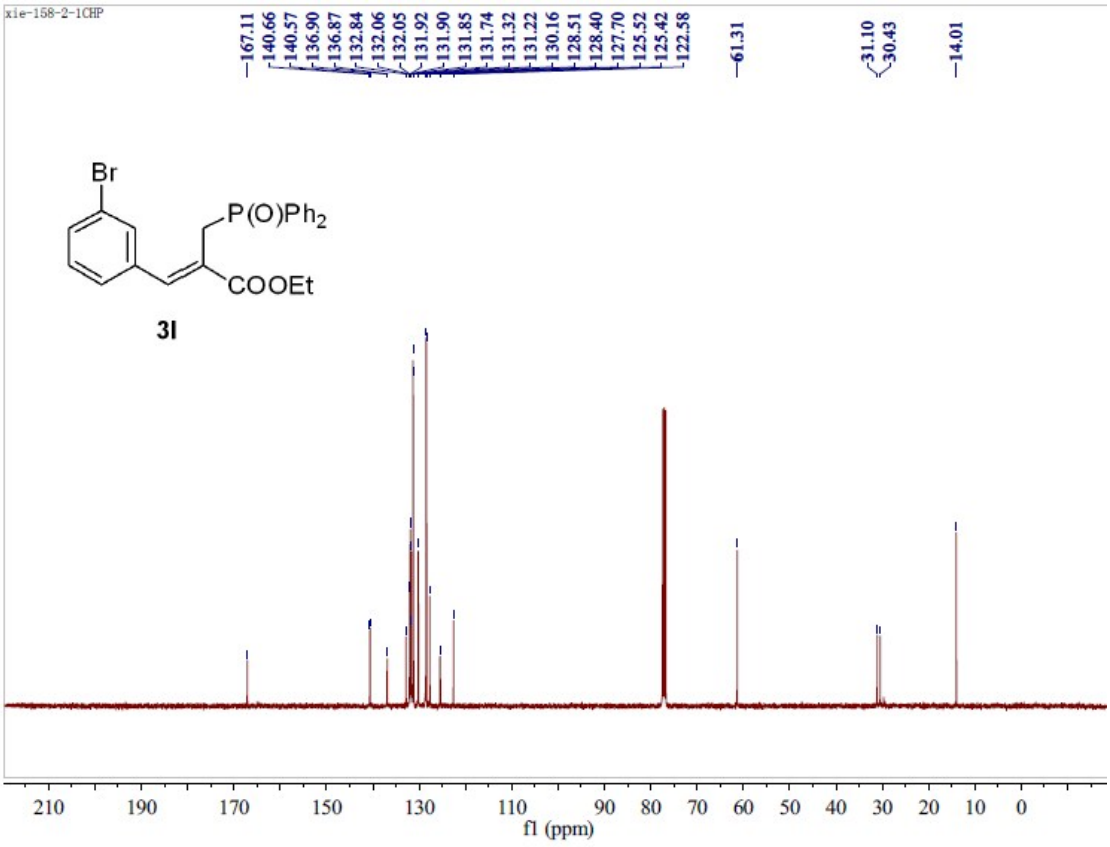

xie-163-1CHP
29.26
Br
P(O)Ph2
COO
3j
100
50
0
-50
-100
-150
-200
f1 (ppm)

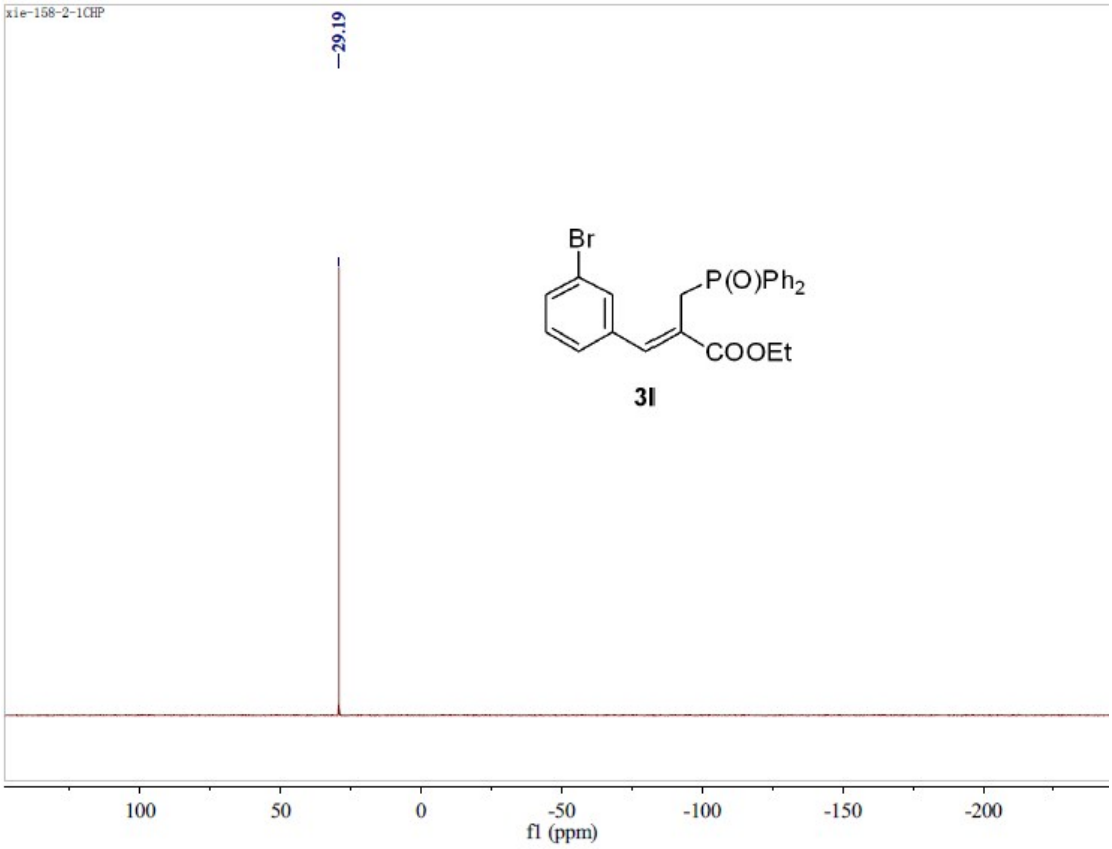

xie-156-2CHP
P(O)Ph2
COOEt
Cl
3k
fl (ppm)

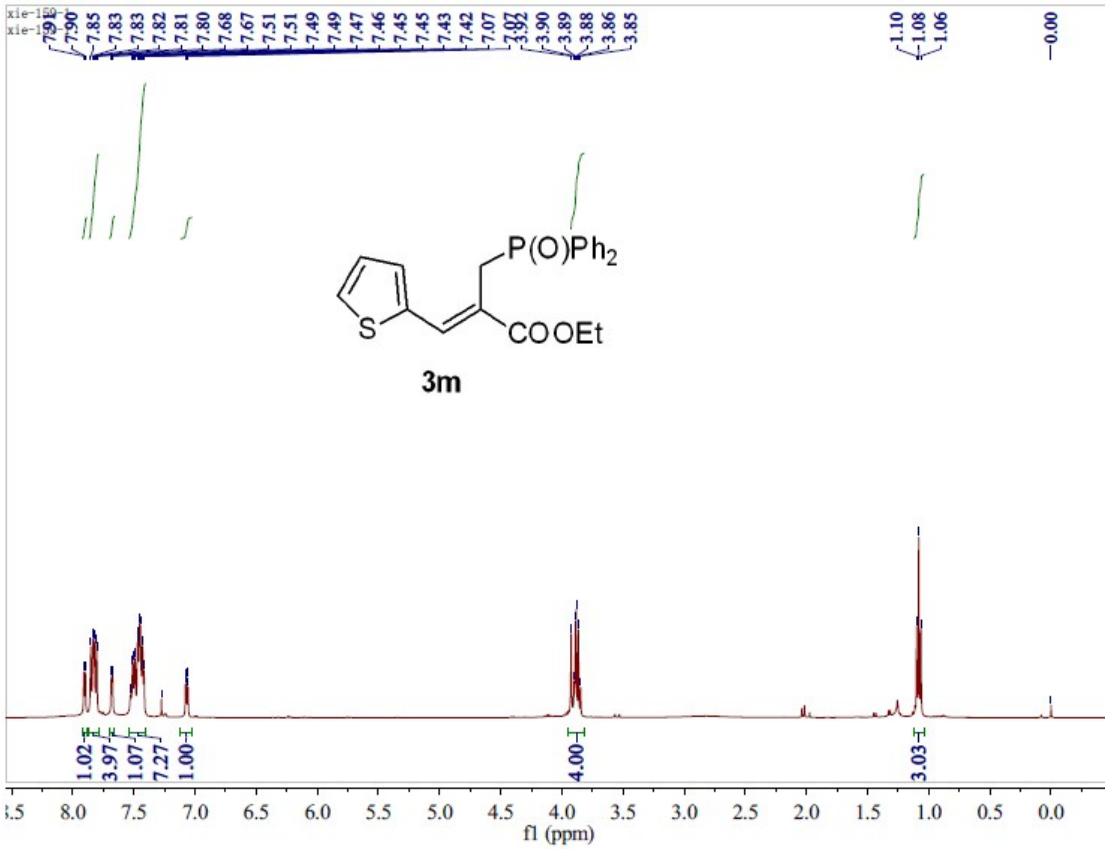

xie-156-2CHP
P(O)Ph2
COOEt
Cl
3k
fl (ppm)

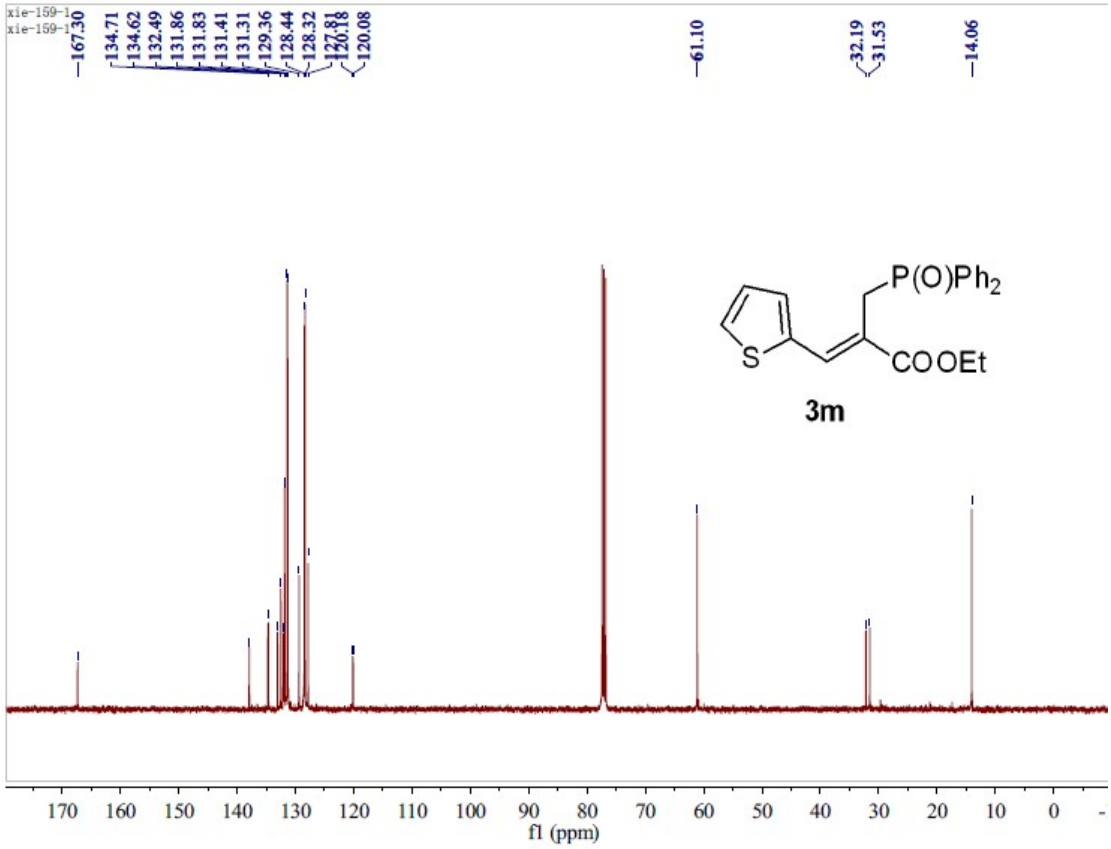

xie-156-2CHP
xie-156-2CHP
29.01
P(O)Ph2
COOEt
Cl
3k
100
50
0
-50
-100
-150
-200
f1 (ppm)

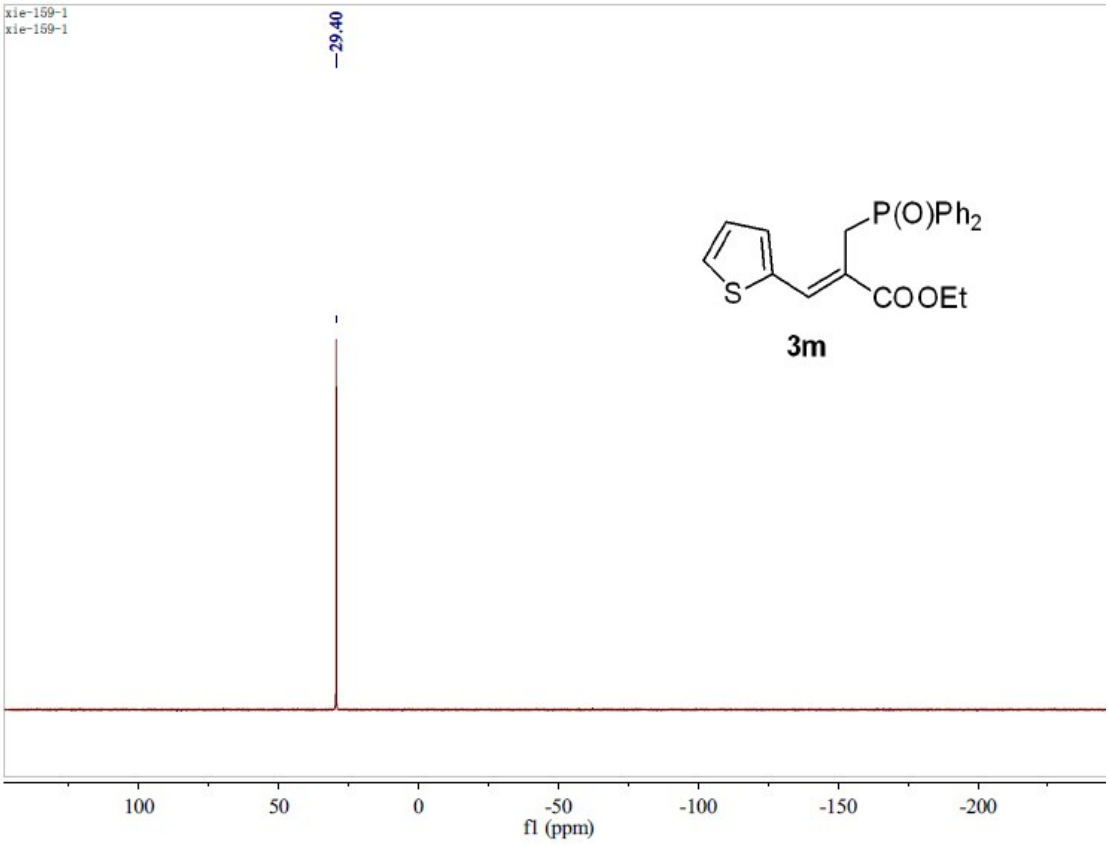

7.79
7.77
7.76
7.76
7.74
7.73
7.72
7.68
7.65
7.53
7.52
7.52
7.50
7.50
7.46
7.45
7.44
7.44
7.44
7.43
7.42
7.23
3.94
3.92
3.90
3.72
3.69
1.14
1.12
1.11
0.00
Br
P(O)Ph2
COOEt
3l
4.89
1.98
2.16
4.63
0.94
2.00
1.92
2.88
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

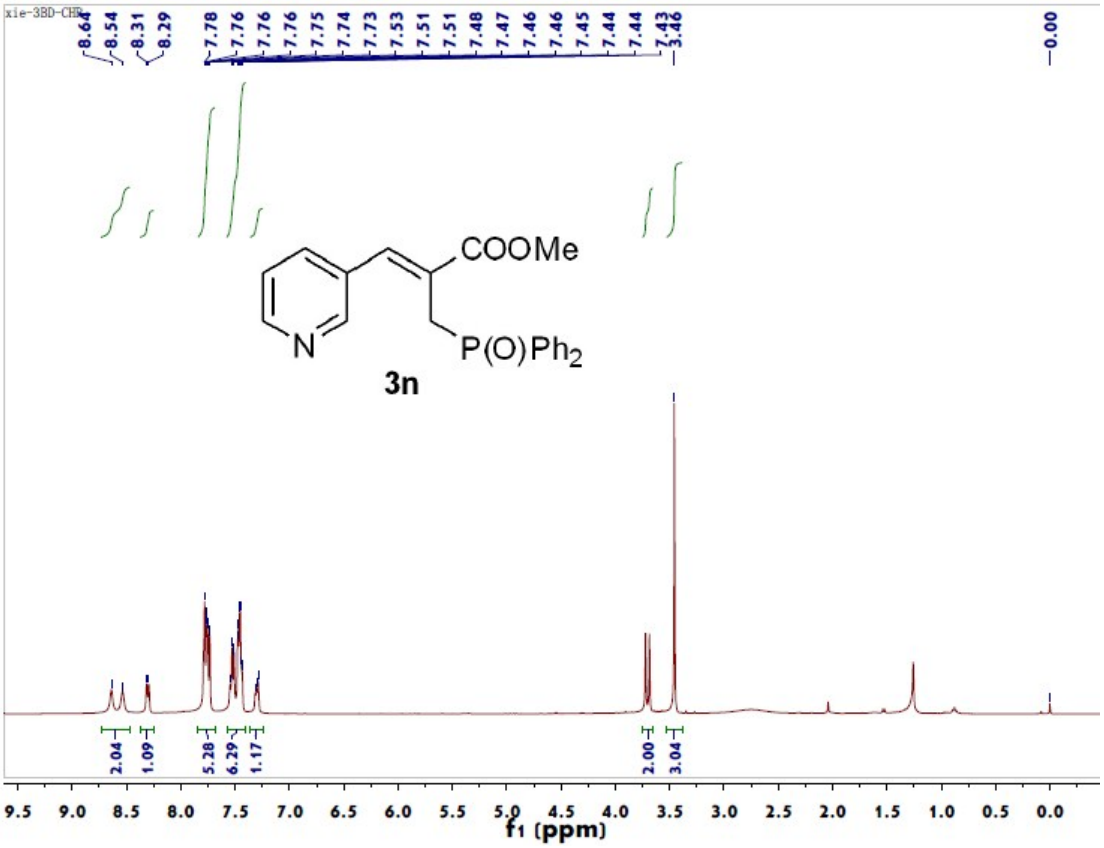

xie-158-2-1CHP
167.11
140.66
140.57
136.90
136.87
132.84
132.06
132.05
131.92
131.90
131.85
131.74
131.32
131.22
130.16
128.51
128.40
127.70
125.52
125.42
122.58
61.31
31.10
30.43
14.01
Br
P(O)Ph2
COOEt
3l
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

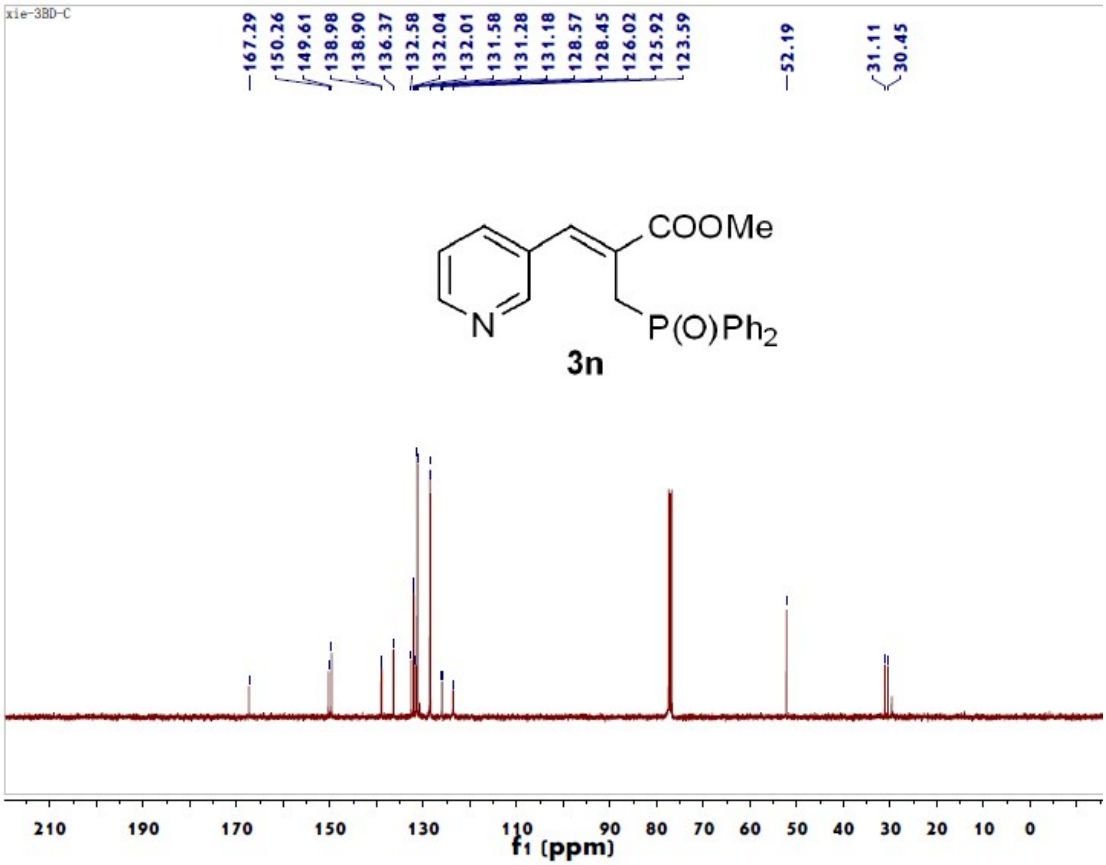

xie-158-2-1CHP
29.19
Br
P(O)Ph2
COOEt
3l
100
50
0
-50
-100
-150
-200
f1 (ppm)

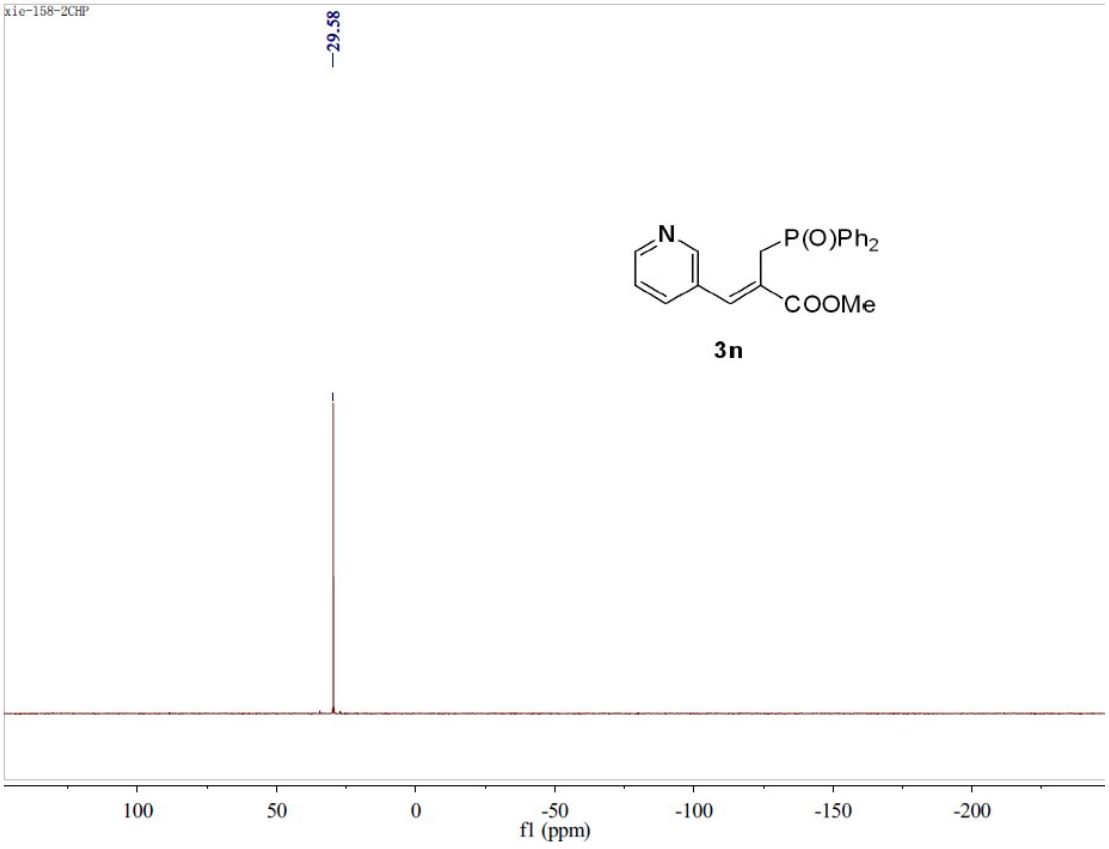

P(O)Ph2
S
COOEt
3m
fl (ppm)

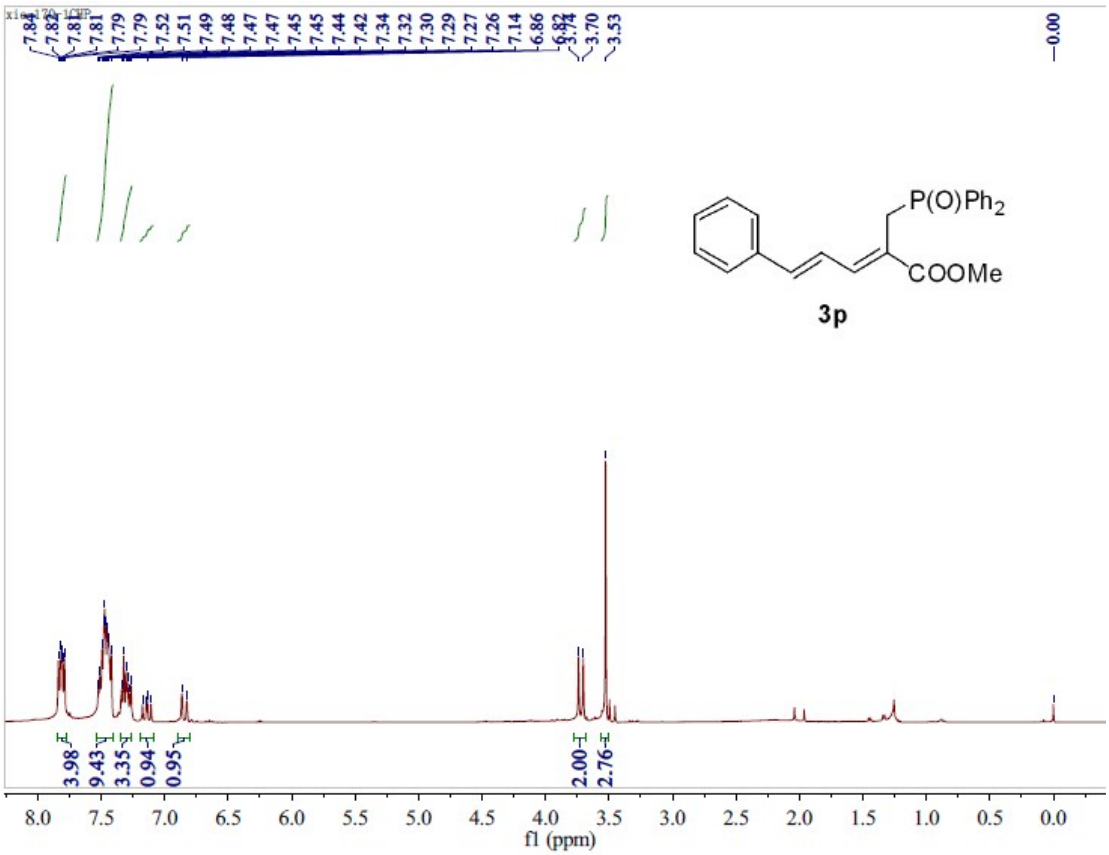

P(O)Ph2
S
COOEt
3m
fl (ppm)

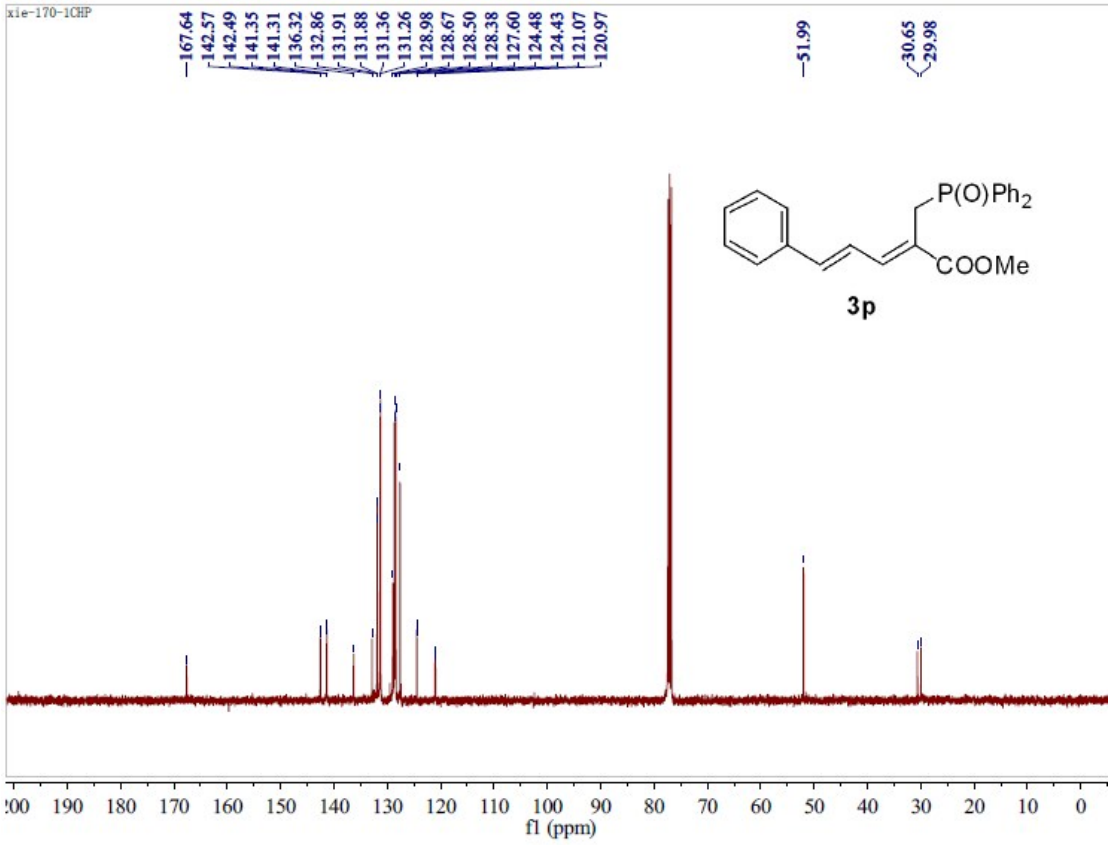

xie-159-1
xie-159-1
29.40
P(O)Ph2
S
COOEt
3m
100
50
0
-50
-100
-150
-200
f1 (ppm)

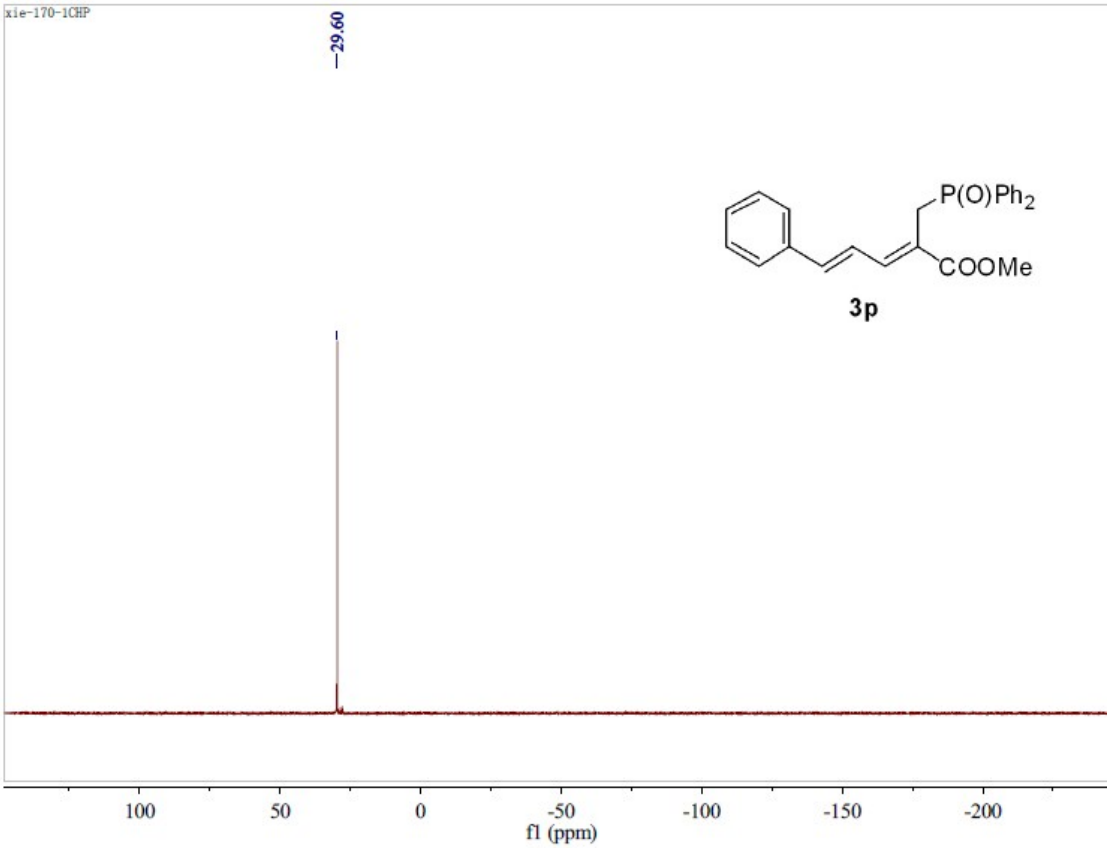

xie-3BD-CHP
8.64
8.54
8.31
8.29
7.78
7.76
7.76
7.76
7.75
7.74
7.73
7.53
7.51
7.51
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.40
0.00
COOMe
N
P(O)Ph2
3n
2.04
1.09
5.28
6.29
1.17
2.00
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

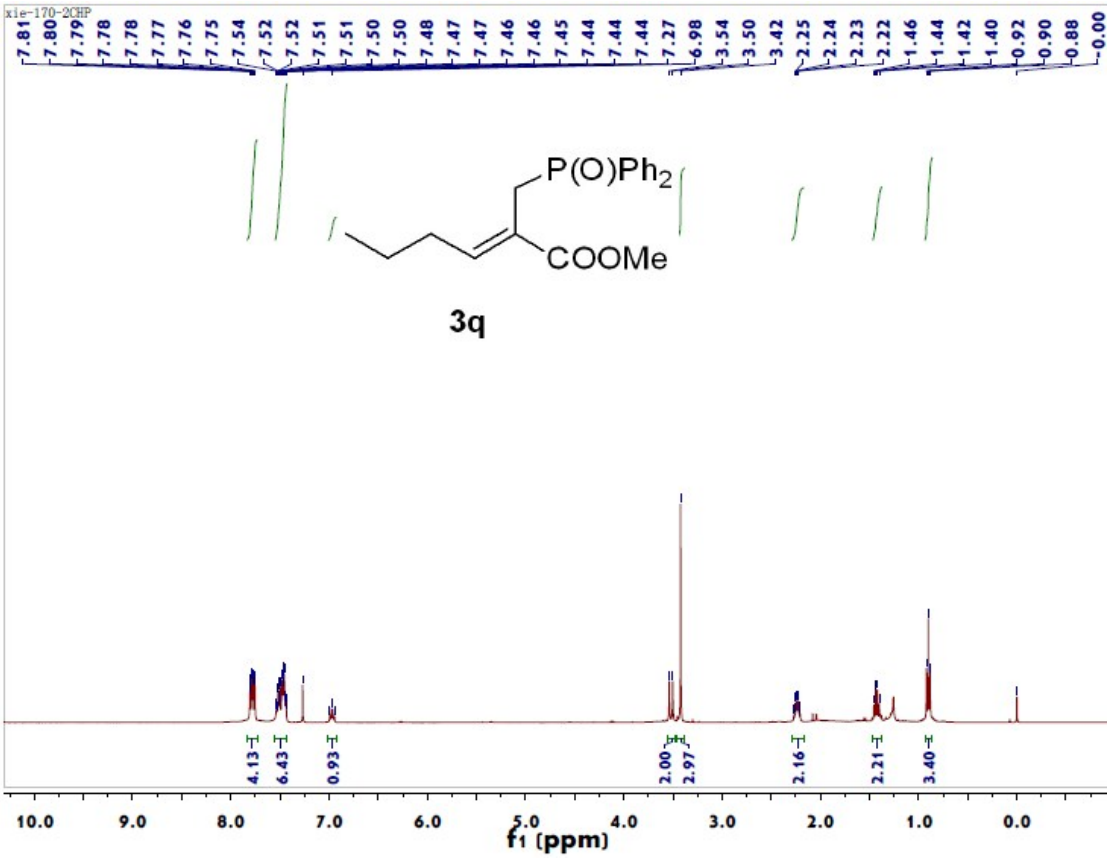

xie-3BD-C
167.29
150.26
149.61
138.98
138.90
136.37
132.58
132.04
132.01
131.58
131.28
131.18
128.57
128.45
126.02
125.92
123.59
52.19
31.11
30.45
COOMe
N
P(O)Ph2
3n
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

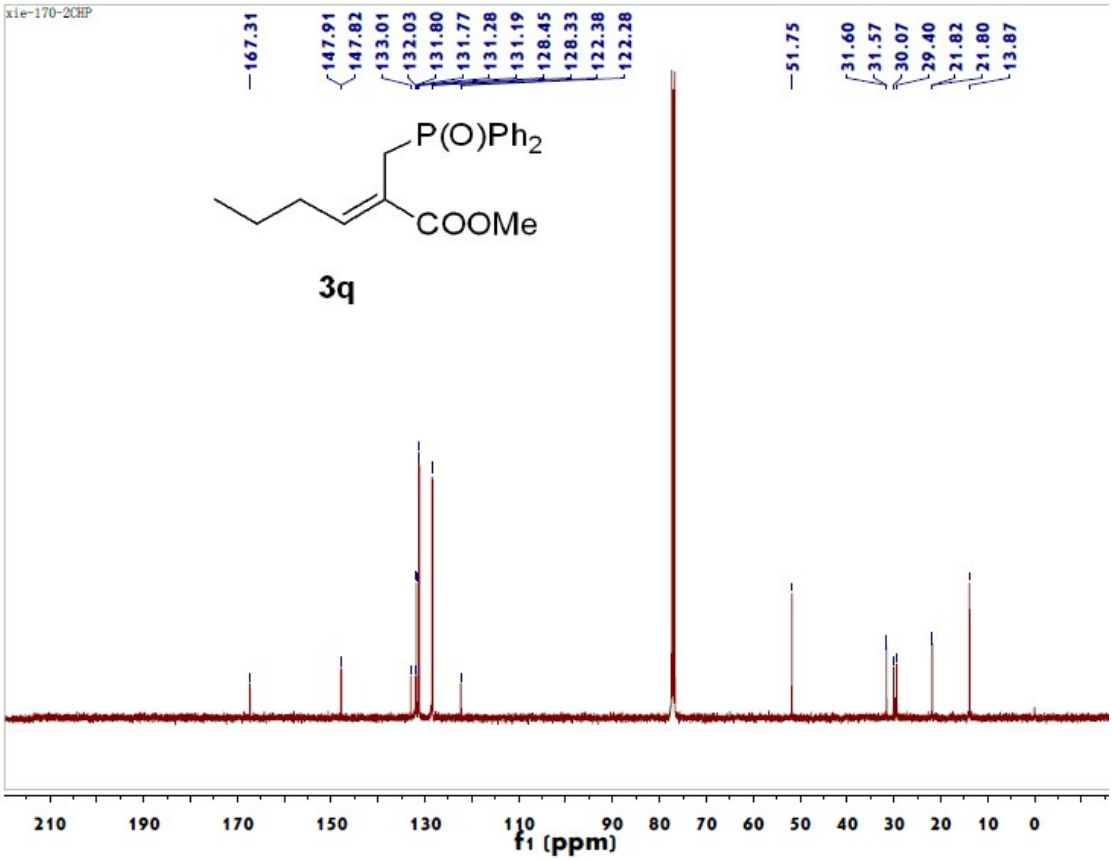

xie-158-2CHP
29.58
N
P(O)Ph2
COOMe
3n
100
50
0
-50
-100
-150
-200
f1 (ppm)

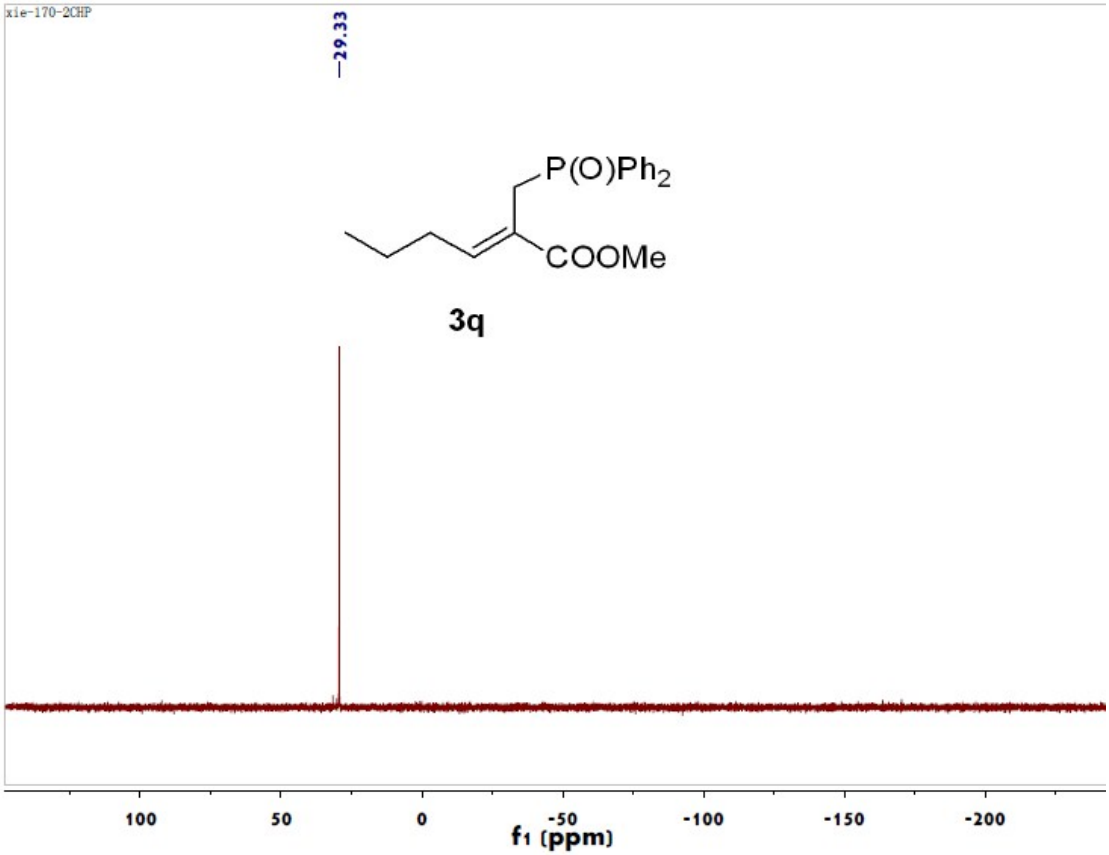

7.84
7.82
7.81
7.81
7.79
7.79
7.52
7.51
7.49
7.48
7.47
7.47
7.45
7.45
7.44
7.42
7.34
7.32
7.30
7.29
7.27
7.26
7.14
6.86
3.74
3.70
3.53
0.00
P(O)Ph2
COOMe
3p
3.98
9.43
3.35
0.94
0.95
2.00
2.76
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

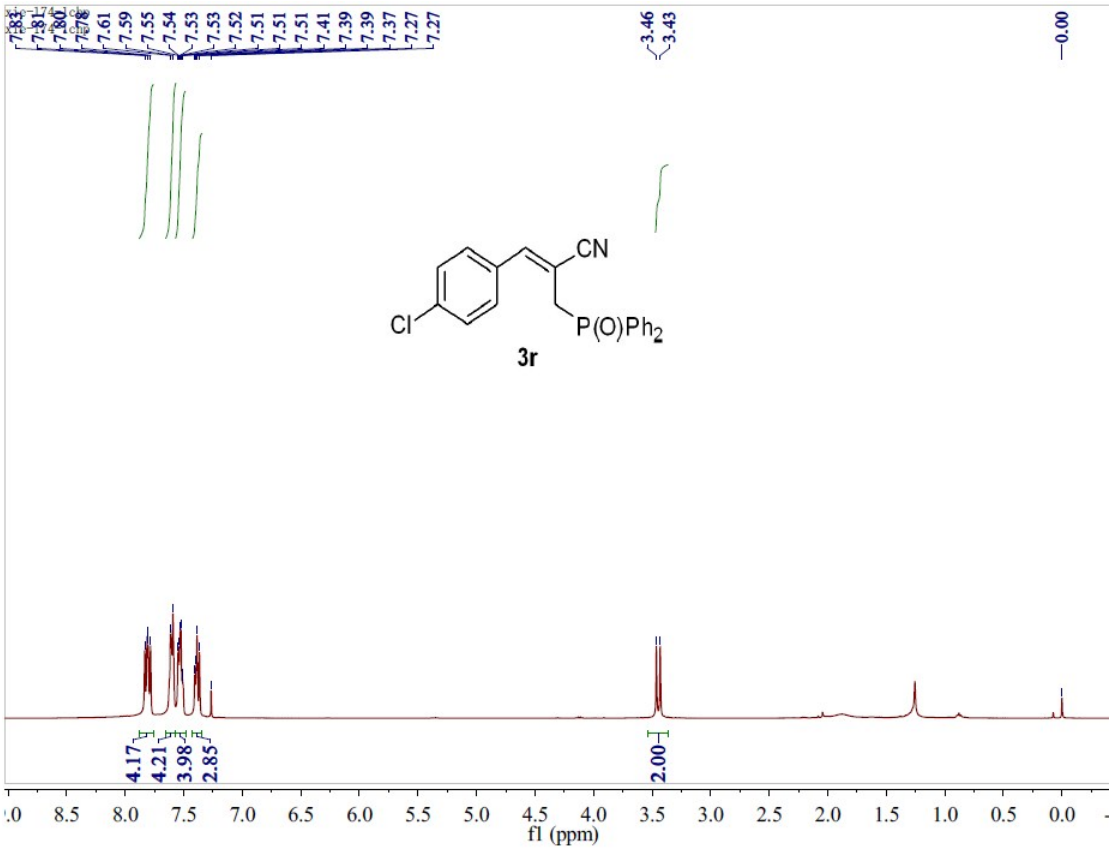

xie-170-1CHP
167.64
142.57
142.49
141.35
141.31
136.32
132.86
131.91
131.88
131.36
131.26
128.98
128.67
128.50
128.38
127.60
124.48
124.43
121.07
120.97
51.99
30.65
29.98
P(O)Ph2
COOMe
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

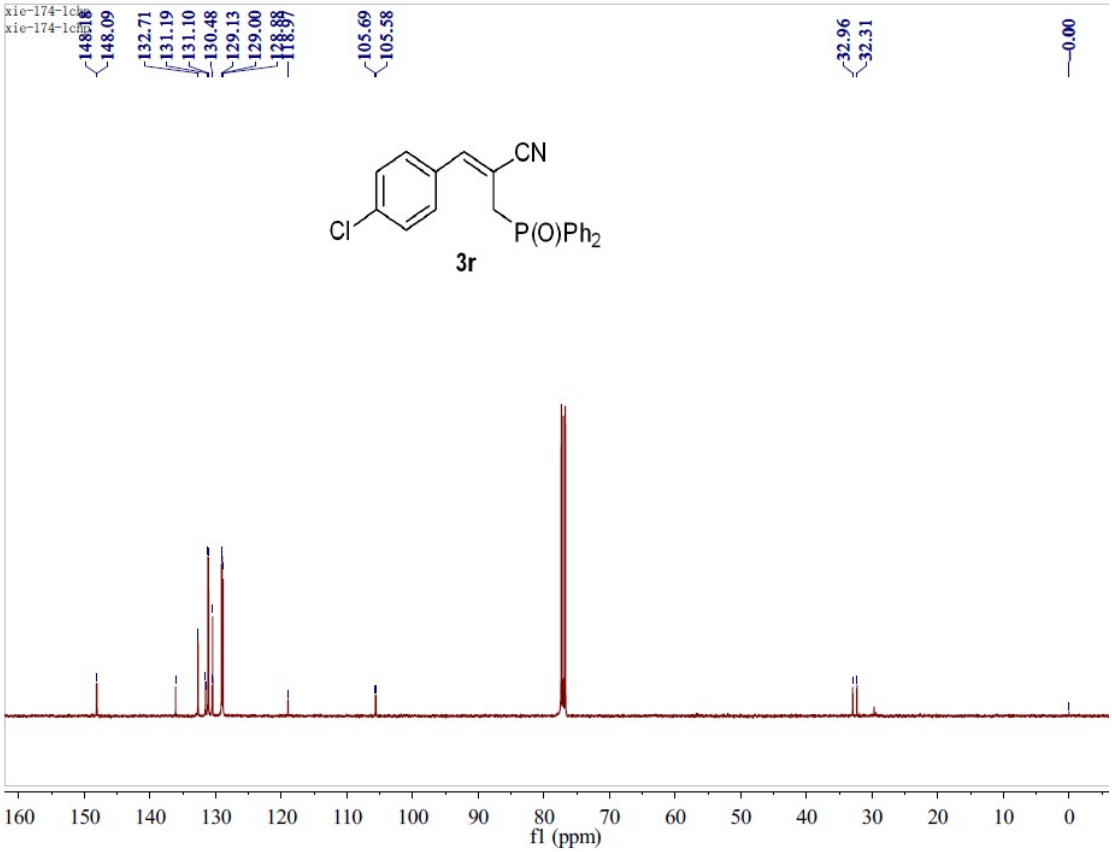

xie-170-1CHP
29.60
P(O)Ph2
COOMe
3p
100
50
0
-50
-100
-150
-200
f1 (ppm)

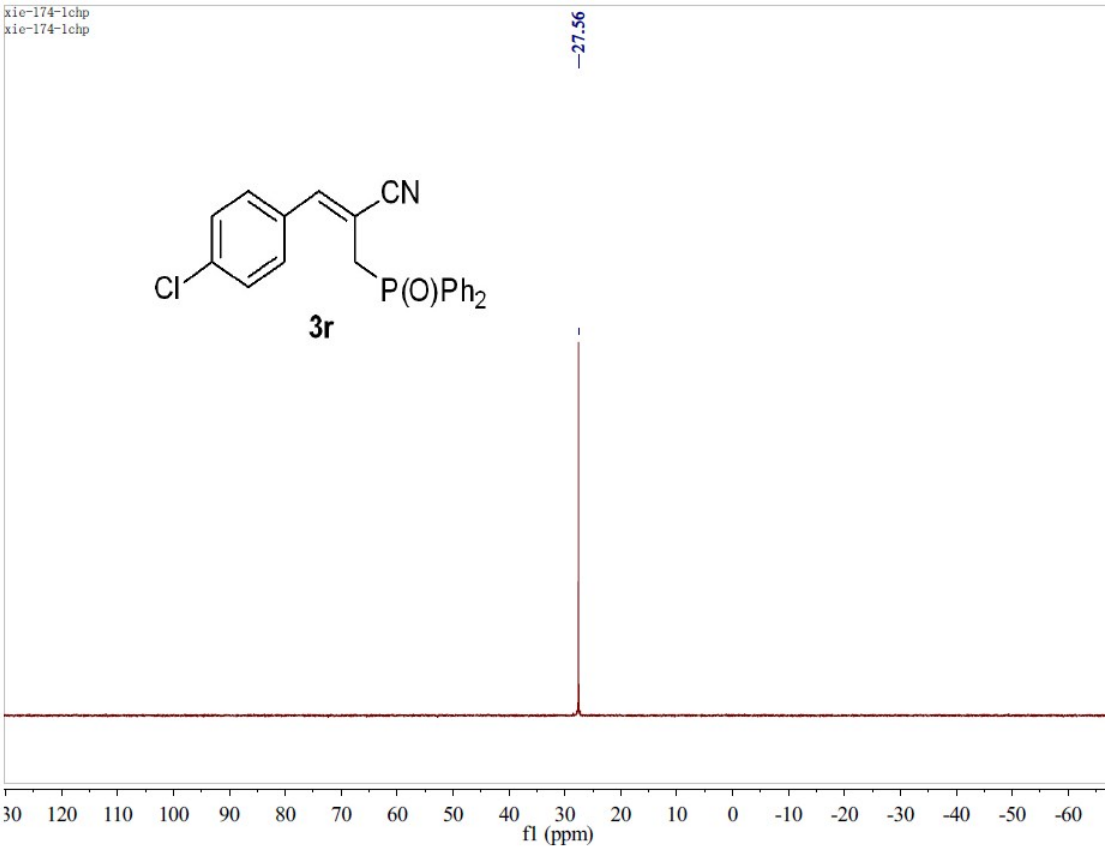

xie-170-2CHP
P(O)Ph2
COOMe
3q
4.13
6.43
0.93
2.00
2.97
2.16
2.21
3.40
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

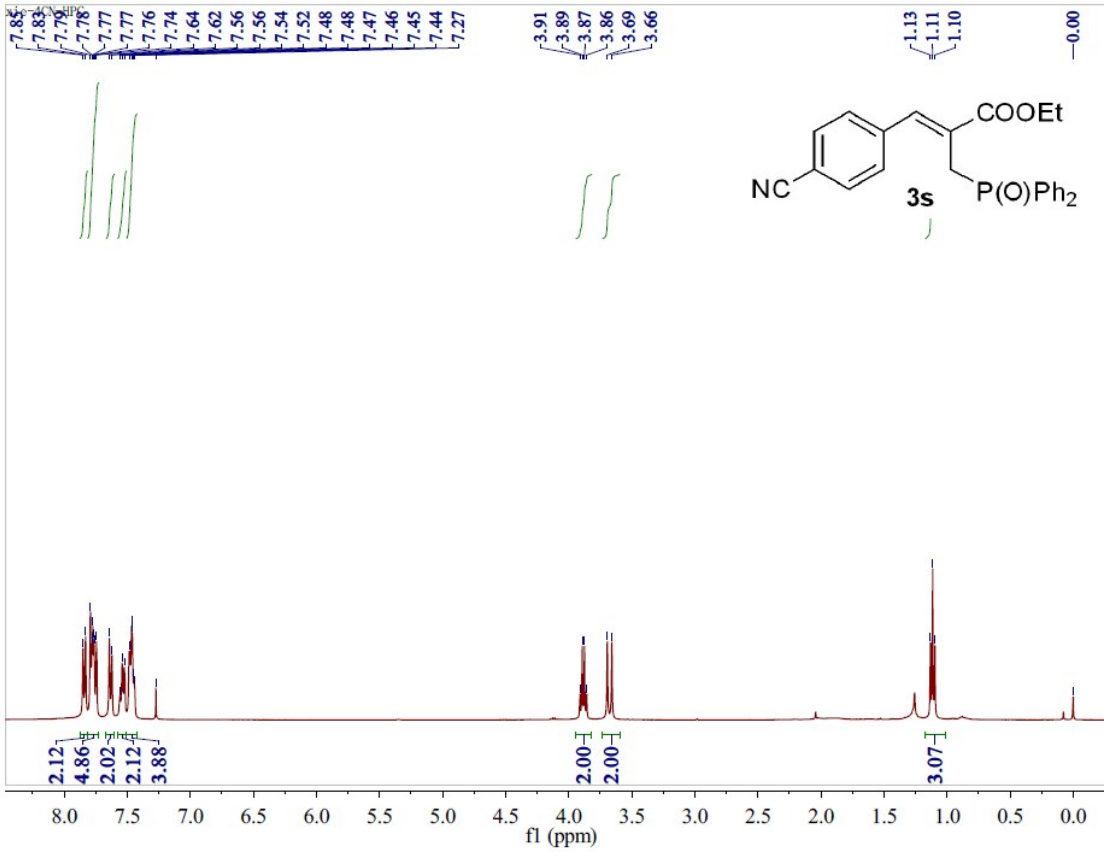

xie-170-2CHP
167.31
147.91
147.82
133.01
132.03
131.80
131.77
131.28
131.19
128.45
128.33
122.38
122.28
51.75
31.60
31.57
30.07
29.40
21.82
21.80
13.87
P(O)Ph2
COOMe
3q
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

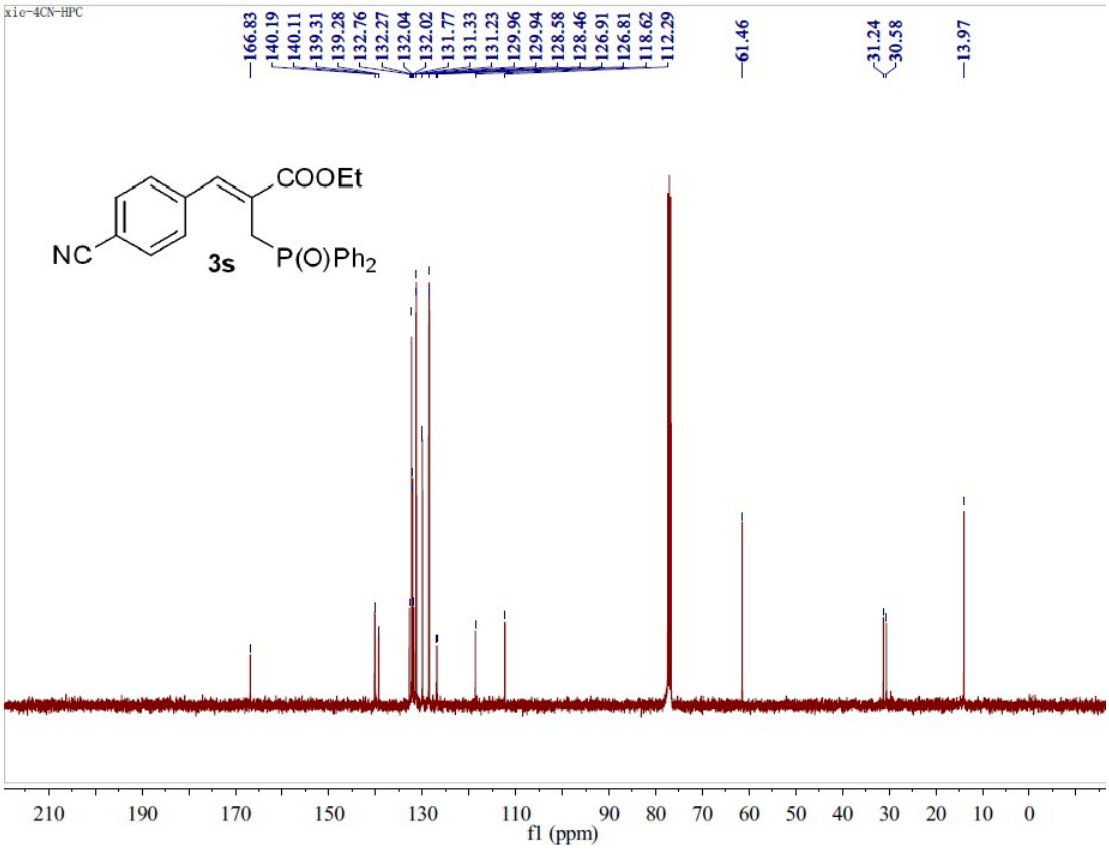

xie-170-2CHP
29.33
P(O)Ph2
COOMe
3q
100
50
0
-50
-100
-150
-200
f1 (ppm)

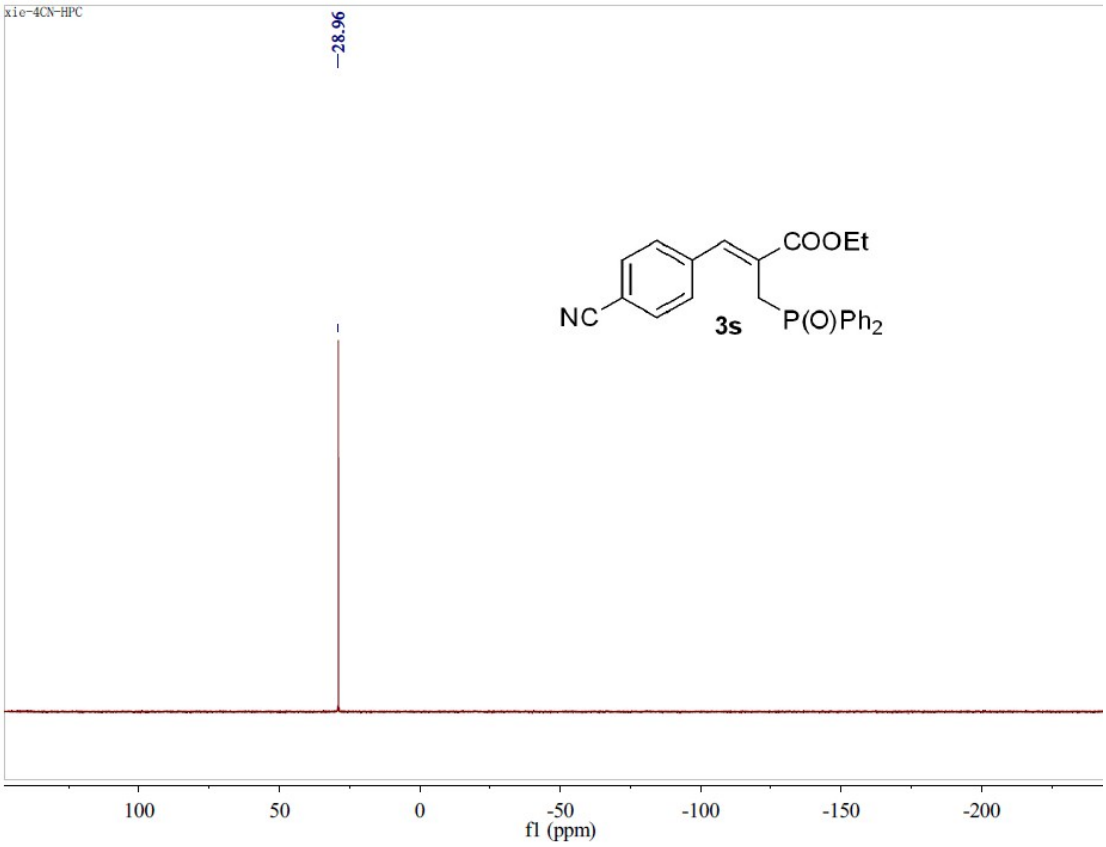

7.83
7.81
7.80
7.78
7.61
7.59
7.55
7.54
7.53
7.53
7.52
7.51
7.51
7.51
7.41
7.39
7.39
7.37
7.27
7.27
3.46
3.43
0.00
CN
Cl
P(O)Ph2
3r
4.17
4.21
3.98
2.85
2.00
f1 (ppm)

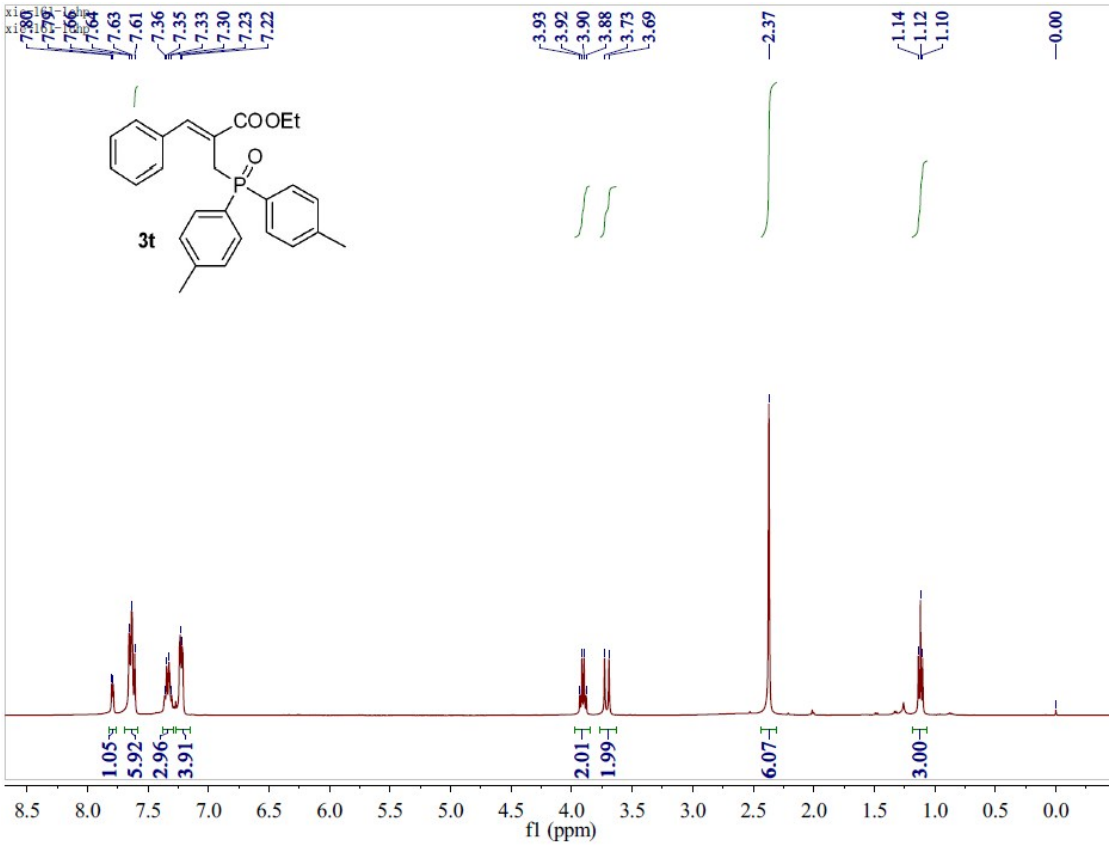

148.18
148.09
132.71
131.19
131.10
130.48
129.13
129.00
105.69
105.58
32.96
32.31
0.00
CN
Cl
P(O)Ph2
3r
f1 (ppm)

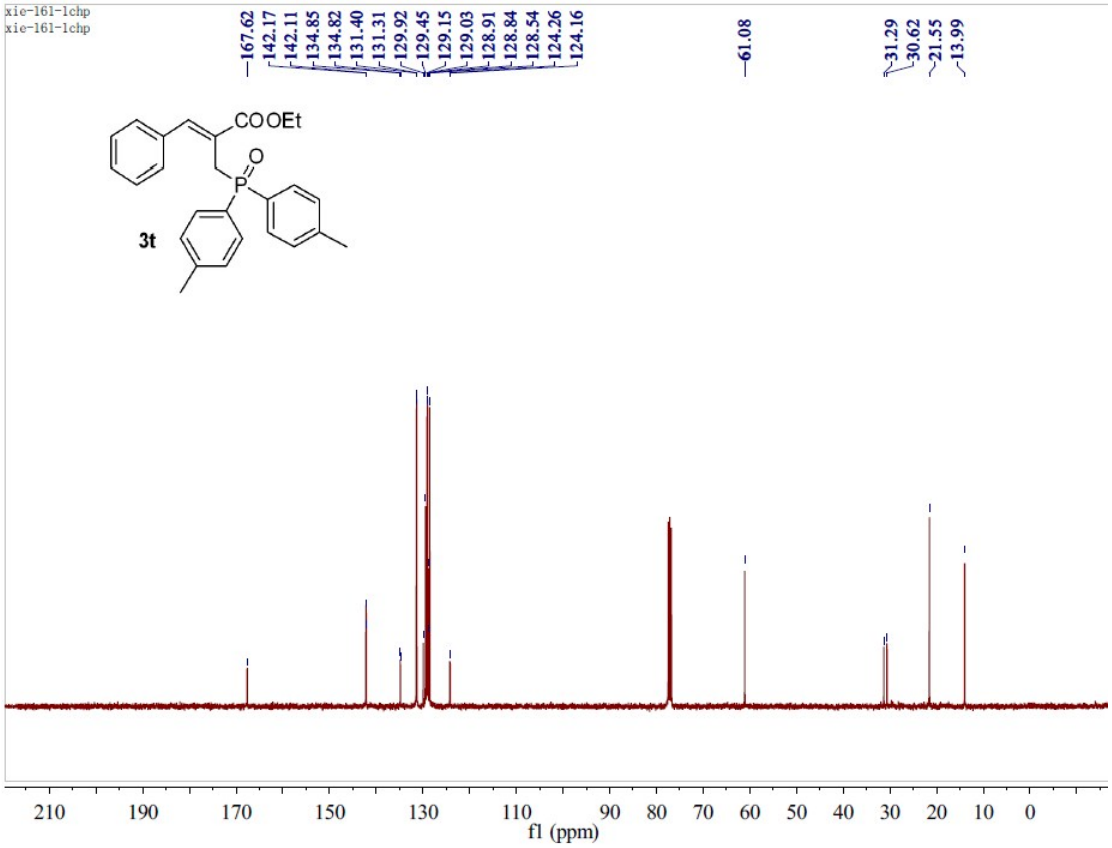

xie-174-1chp
xie-174-1chp
27.56
CN
Cl
P(O)Ph2
3r
fl (ppm)

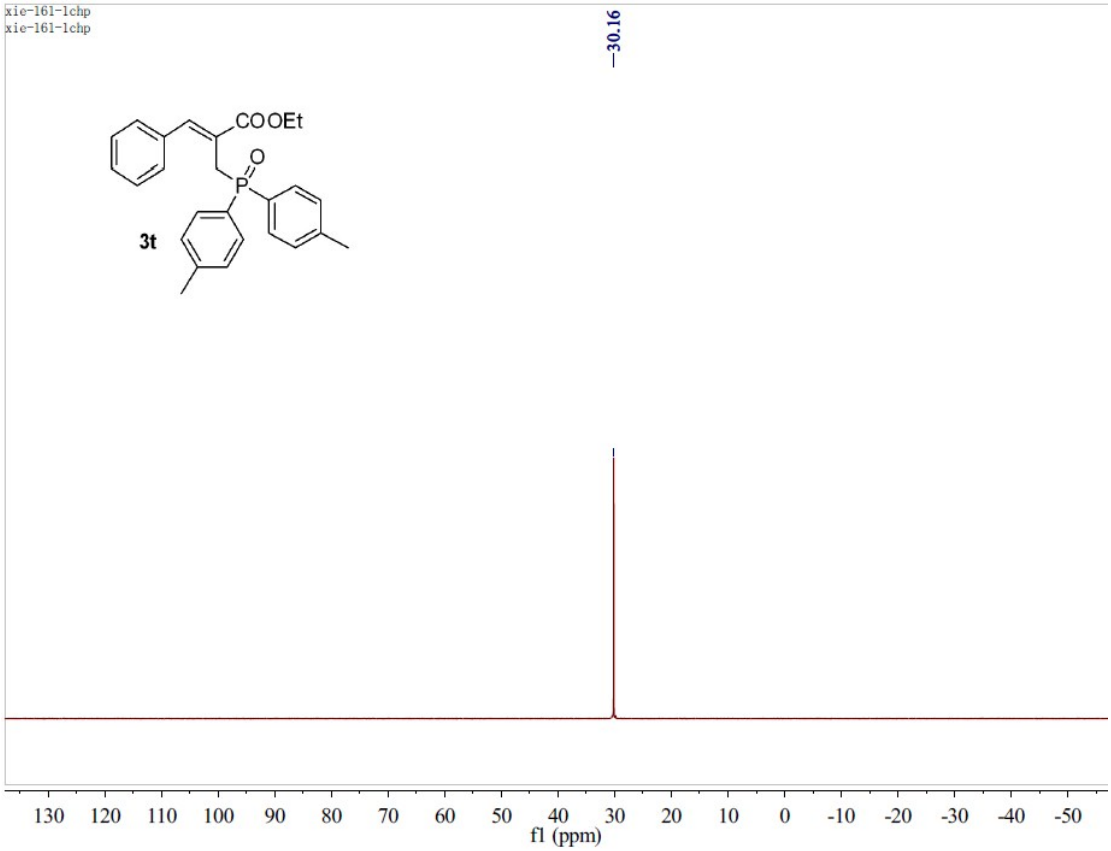

7.83
7.79
7.78
7.77
7.76
7.74
7.64
7.62
7.56
7.54
7.52
7.48
7.47
7.46
7.45
7.44
7.27
3.91
3.89
3.87
3.86
3.69
3.66
1.13
1.11
1.10
0.00
COOEt
NC
P(O)Ph2
3s
2.12
4.86
2.02
2.12
3.88
2.00
2.00
3.07
fl (ppm)

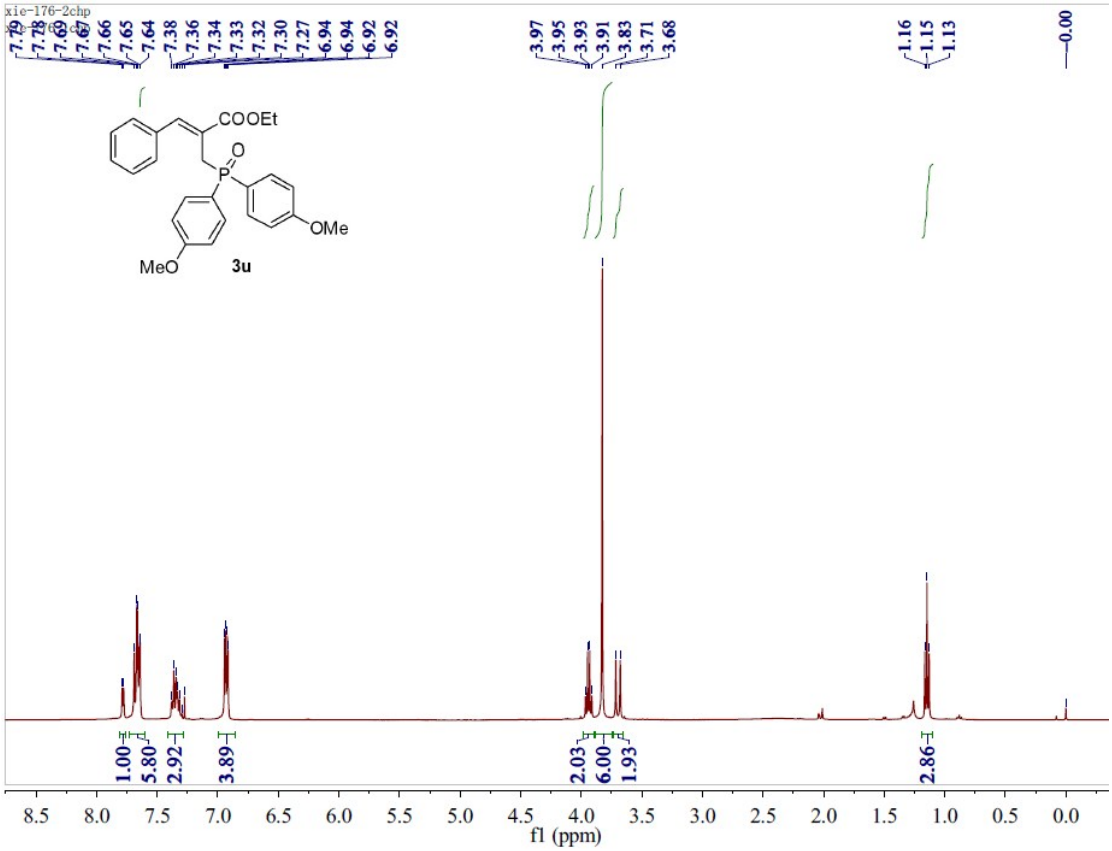

xie-4CN-HPC
166.83
140.19
140.11
139.31
139.28
132.76
132.27
132.04
132.02
131.77
131.33
131.23
129.96
129.94
128.58
128.46
126.91
126.81
118.62
112.29
61.46
31.24
30.58
13.97
COOEt
NC
3s
P(O)Ph2
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

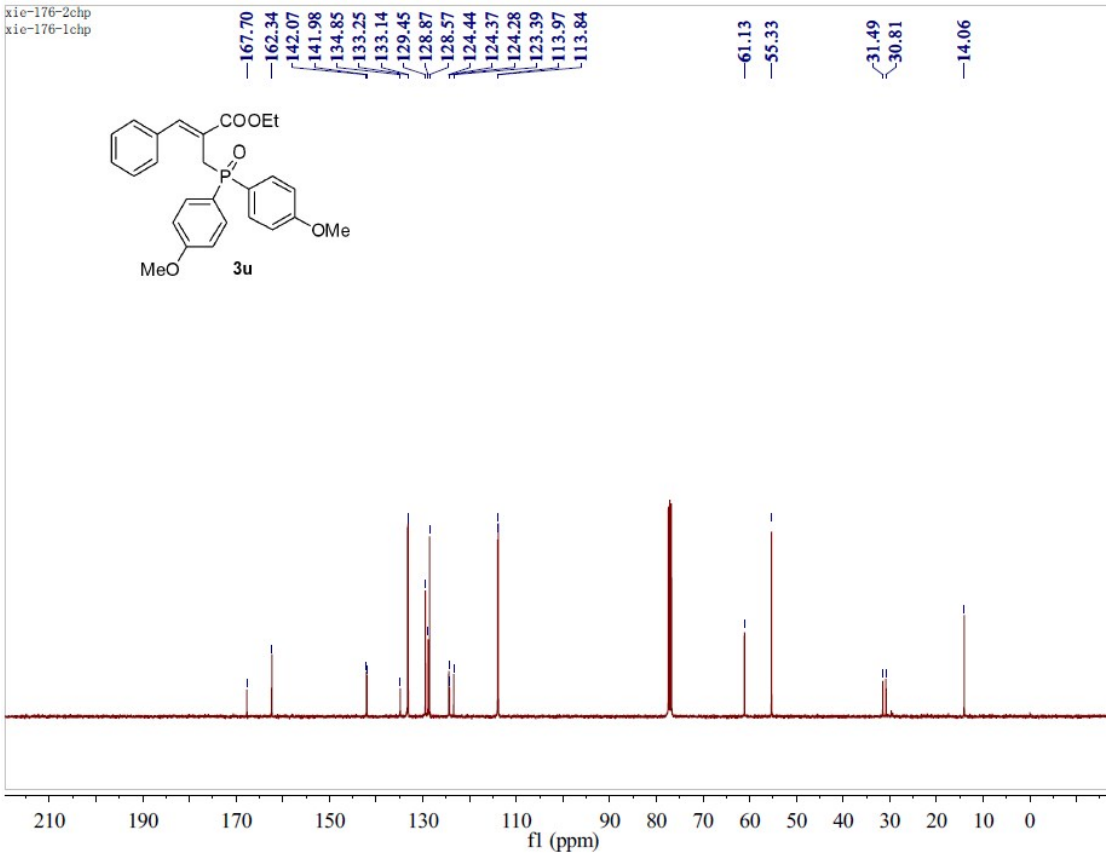

xie-4CN-HPC
28.96
COOEt
NC
3s
P(O)Ph2
100
50
0
-50
-100
-150
-200
f1 (ppm)

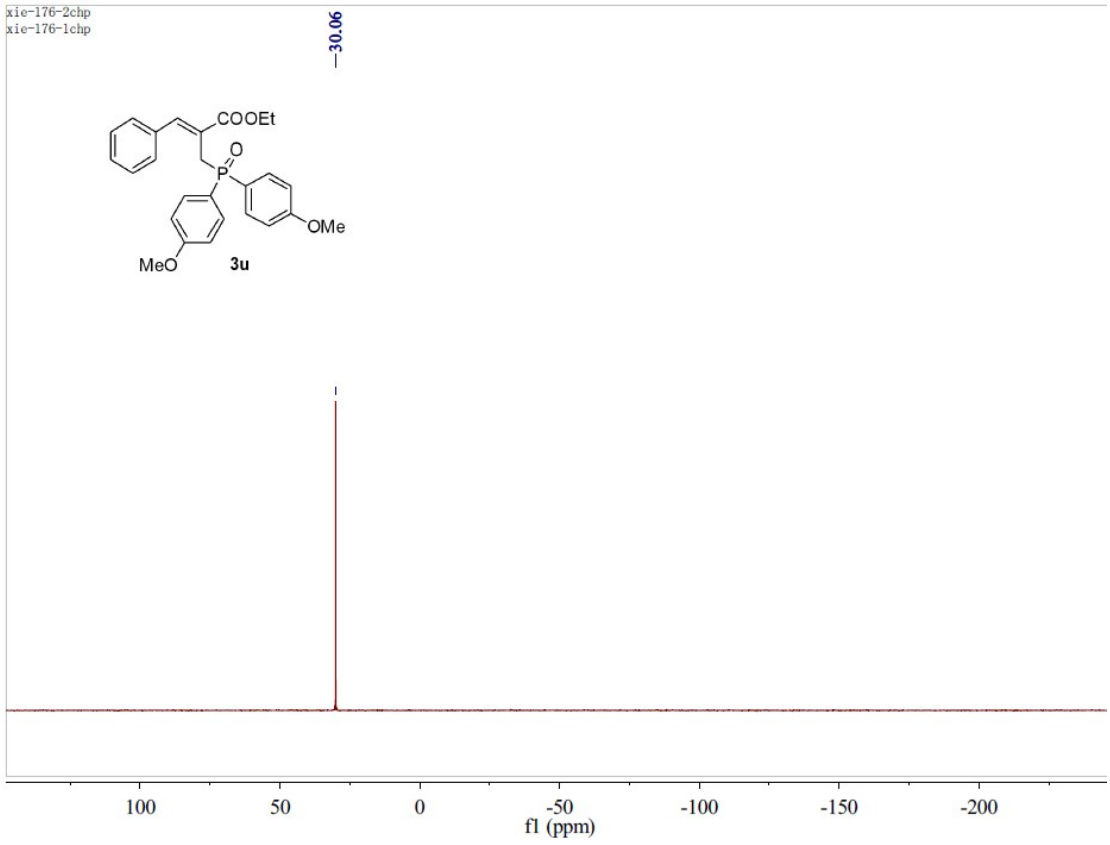

7.80
7.79
7.66
7.64
7.63
7.61
7.36
7.35
7.33
7.30
7.23
7.22
3.93
3.92
3.90
3.88
3.73
3.69
2.37
1.14
1.12
1.10
0.00
COOEt
O
P
3t
1.05
5.92
2.96
3.91
2.01
1.99
6.07
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

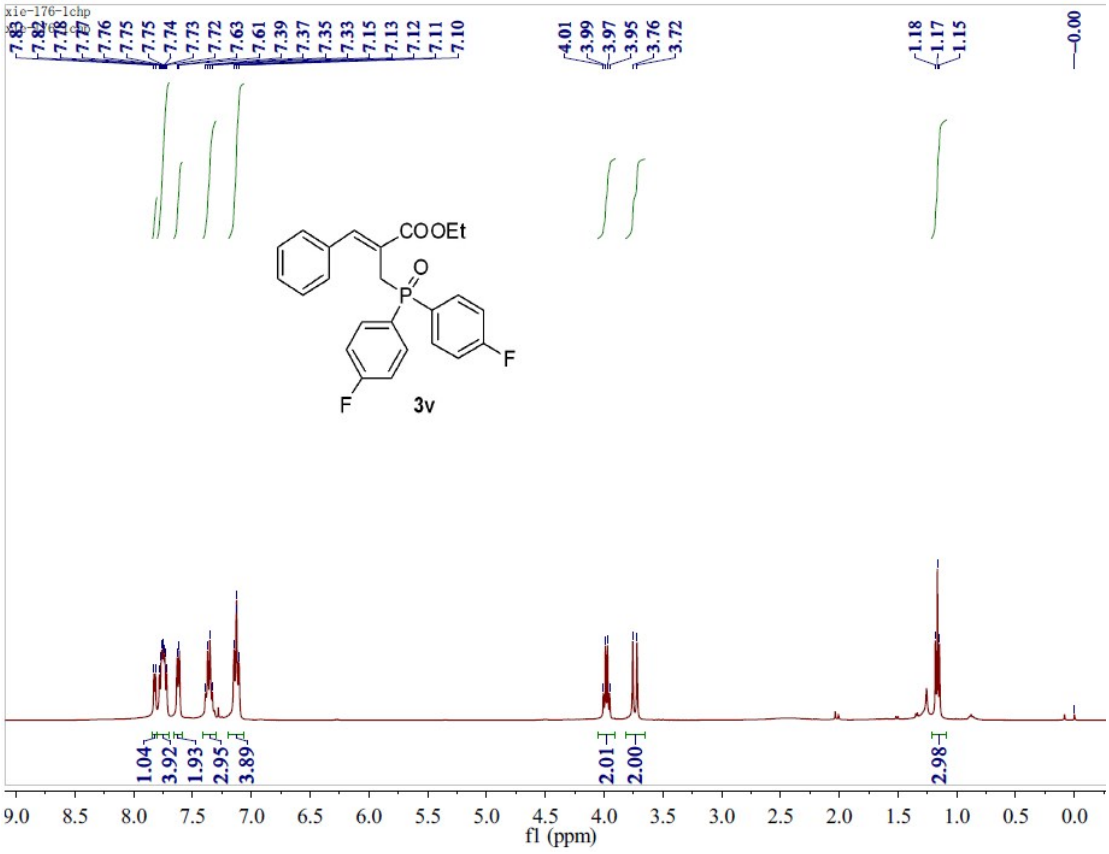

xie-161-1chp
xie-161-1chp
167.62
142.17
142.11
134.85
134.82
131.40
131.31
129.92
129.45
129.15
129.03
128.91
128.84
128.54
124.26
124.16
61.08
31.29
30.62
21.55
13.99
COOEt
O
P
3t
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

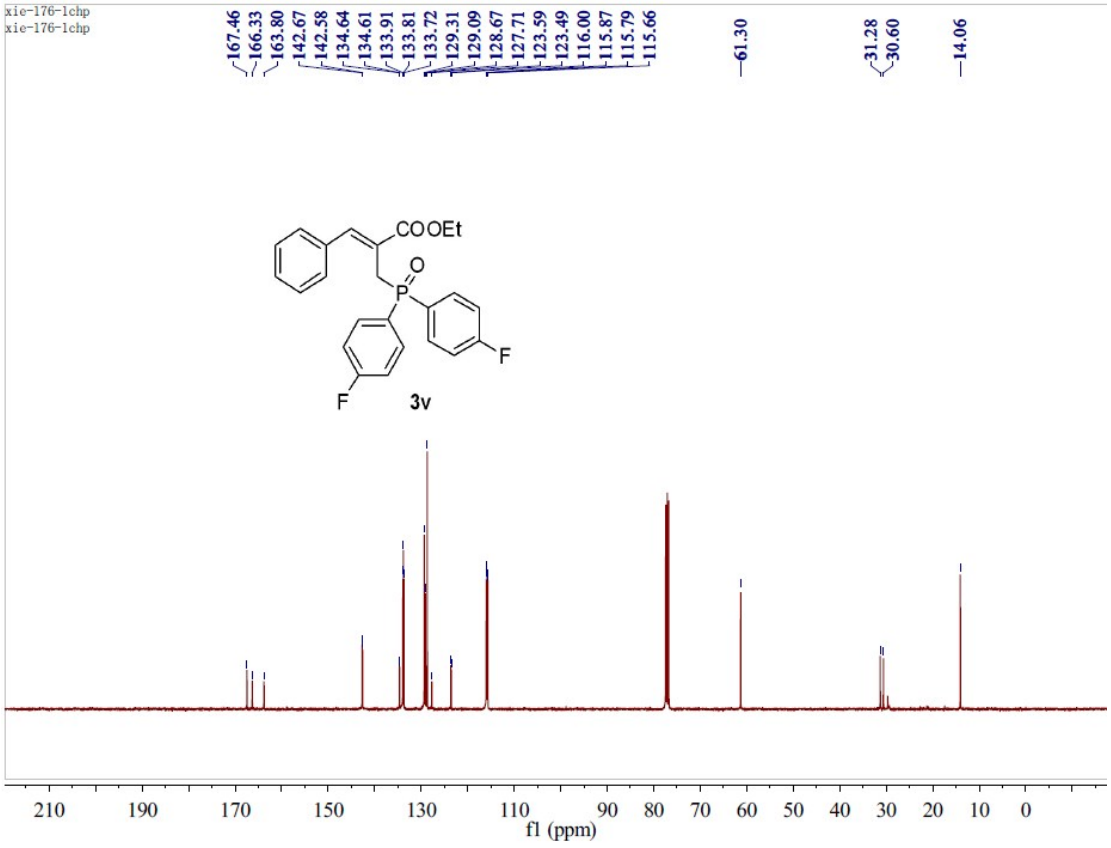

xie-161-1chp
xie-161-1chp
30.16
COOEt
O
P
3t
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

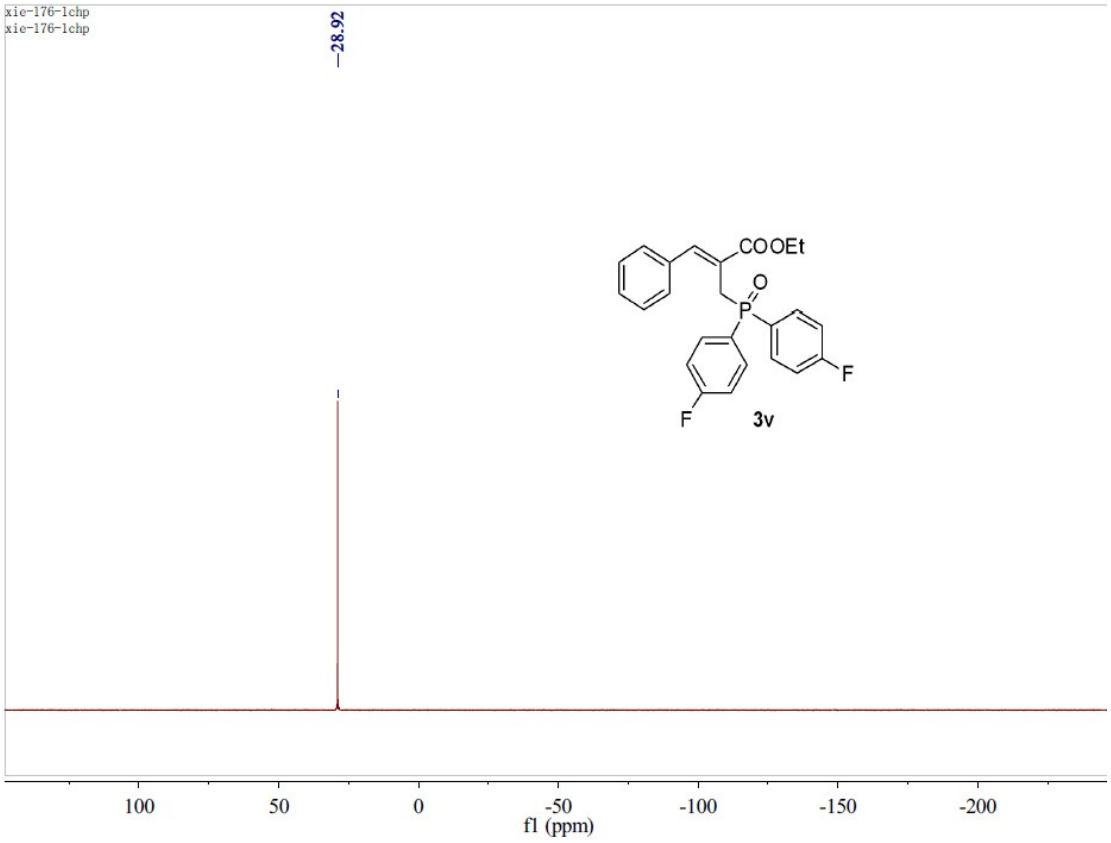

xie-176-2chp
7.79 7.78 7.69 7.67 7.66 7.65 7.64 7.38 7.36 7.34 7.33 7.32 7.30 7.27 6.94 6.94 6.92 6.92
3.97 3.95 3.93 3.91 3.83 3.71 3.68
1.16 1.15 1.13
0.00
COOEt
O
P
OMe
MeO
3u
1.00 5.80 2.92 3.89 2.03 6.00 1.93 2.86
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

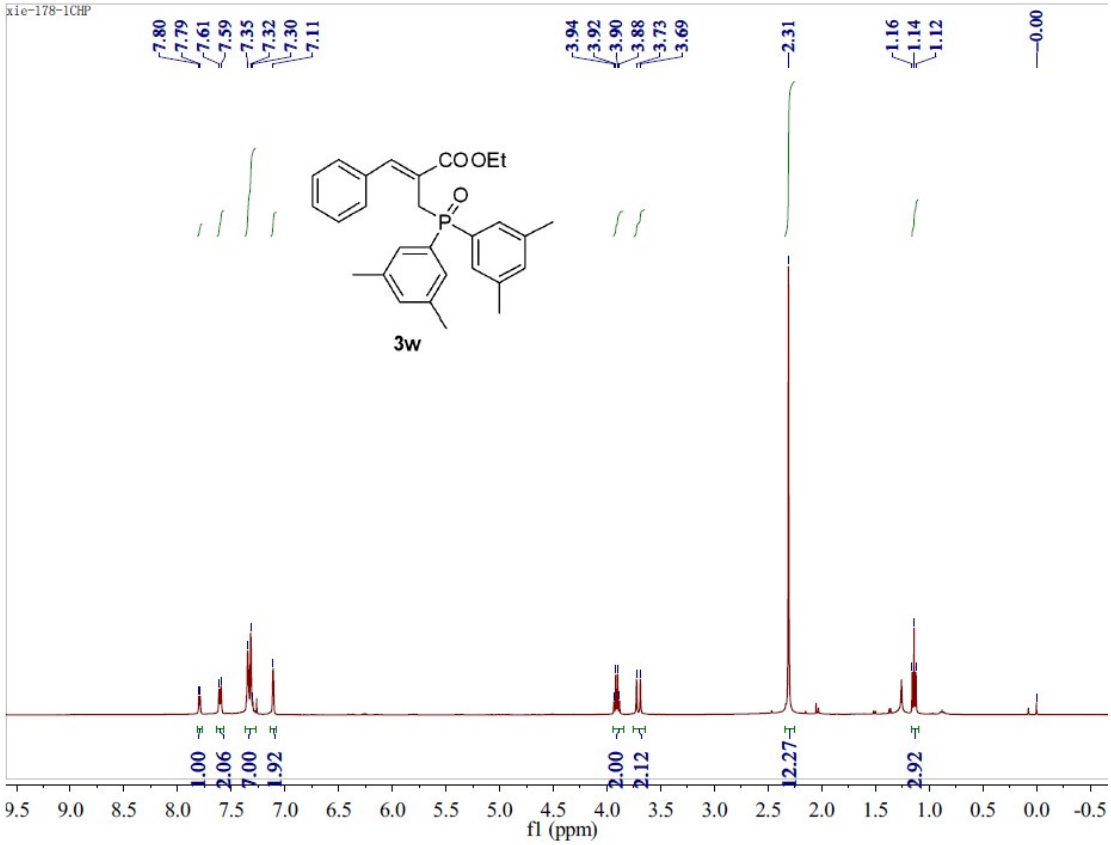

xie-176-2chp
xie-176-1chp
167.70
162.34
142.07
141.98
134.85
133.25
133.14
129.45
128.87
128.57
124.44
124.37
124.28
123.39
113.97
113.84
61.13
55.33
31.49
30.81
14.06
COOEt
O
P
OMe
MeO
3u
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

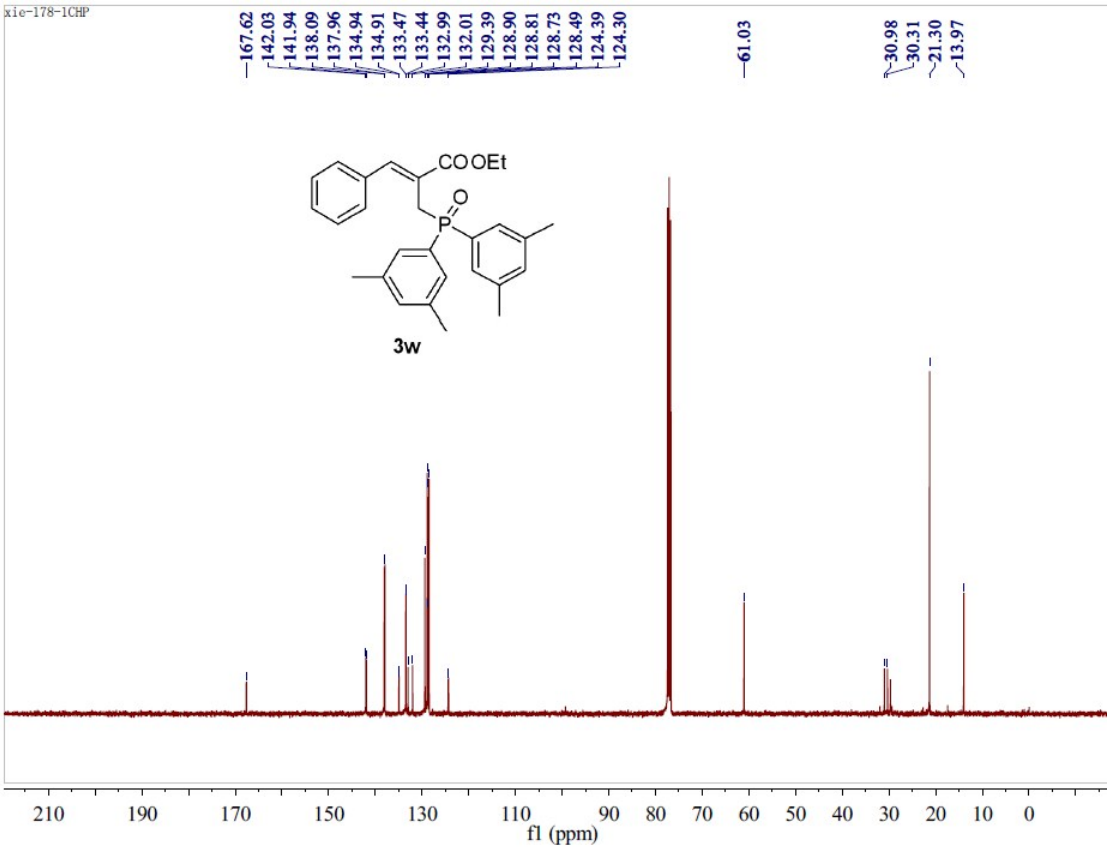

xie-176-2chp
xie-176-1chp
30.06
COOEt
O
P
OMe
MeO
3u
100
50
0
-50
-100
-150
-200
f1 (ppm)

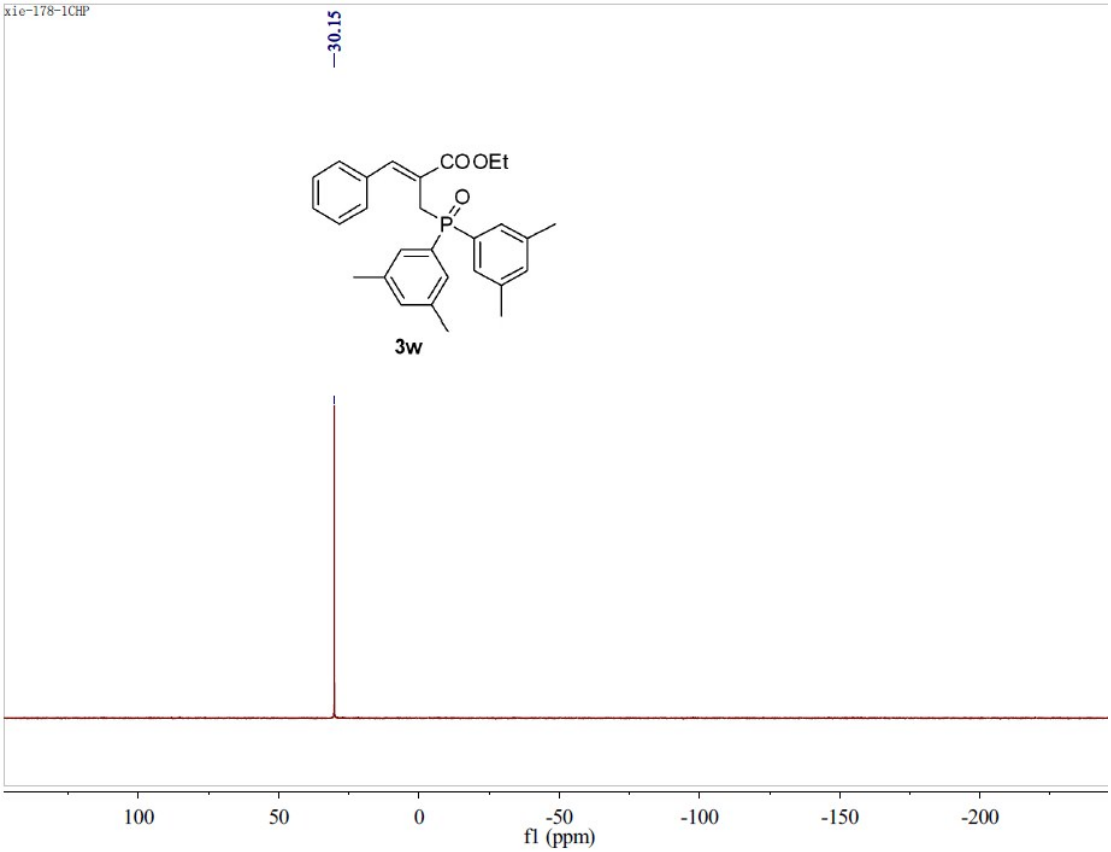

xie-176-1chp
7.83
7.82
7.78
7.77
7.76
7.75
7.75
7.74
7.73
7.72
7.63
7.61
7.39
7.37
7.35
7.33
7.15
7.13
7.12
7.11
7.10
4.01
3.99
3.97
3.95
3.76
3.72
1.18
1.17
1.15
0.00
COOEt
O
P
F
F
3v
1.04
3.92
1.93
2.95
3.89
2.01
2.00
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

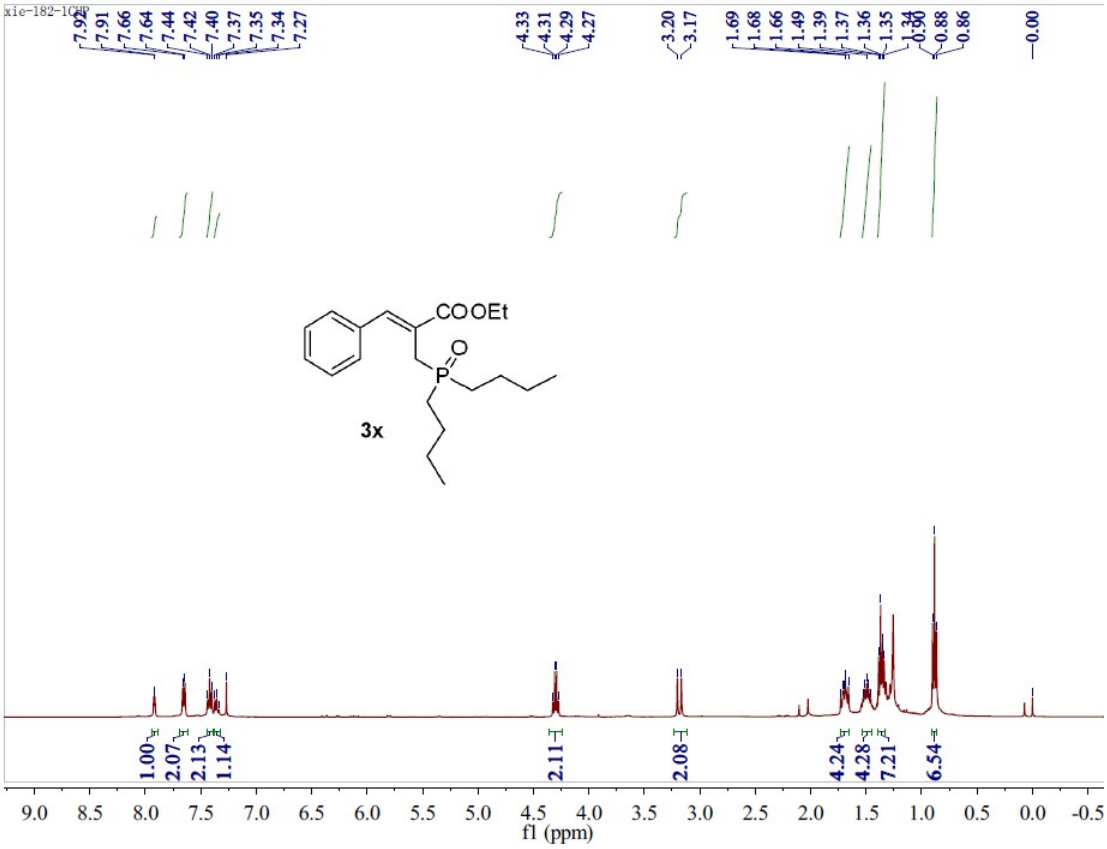

xie-176-1chp
xie-176-1chp
167.46
166.33
163.80
142.67
142.58
134.64
134.61
133.91
133.81
133.72
129.31
129.09
128.67
127.71
123.59
123.49
116.00
115.87
115.79
115.66
61.30
31.28
30.60
14.06
COOEt
O
P
F
F
3v
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

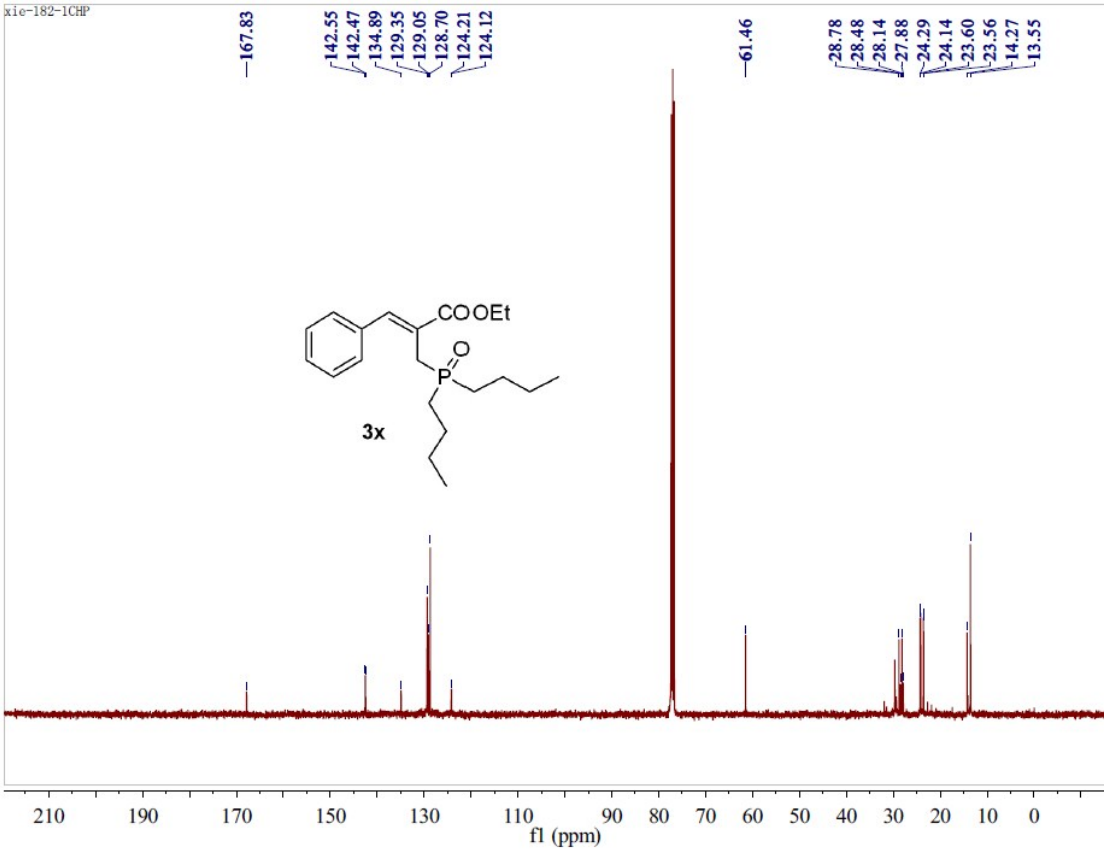

xie-176-1chp
xie-176-1chp
-28.92
COOEt
O
P
F
F
3v
100
50
0
-50
-100
-150
-200
f1 (ppm)

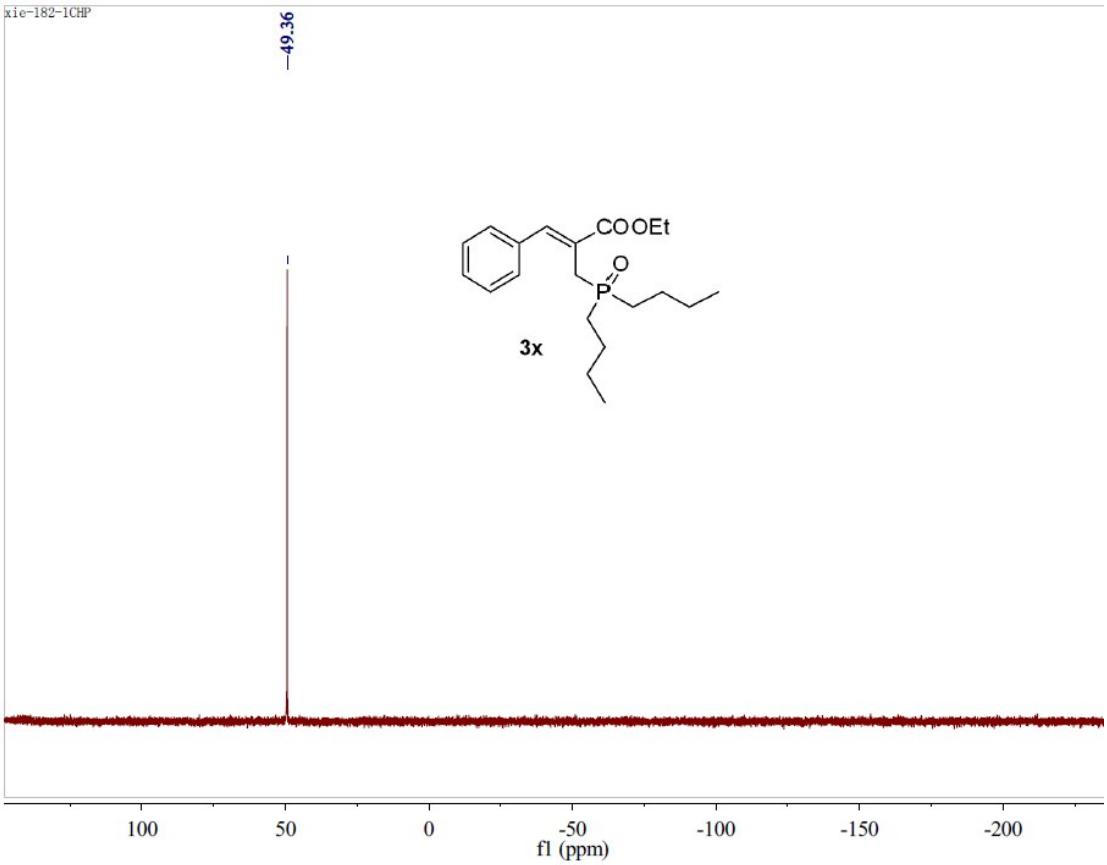

xie-178-1CHP
7.80
7.79
7.61
7.59
7.35
7.32
7.30
7.11
3.94
3.92
3.90
3.88
3.73
3.69
2.31
1.16
1.14
1.12
0.00
COOEt
O
P
3w
1.00
2.06
7.00
1.92
2.00
2.12
12.27
2.92
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

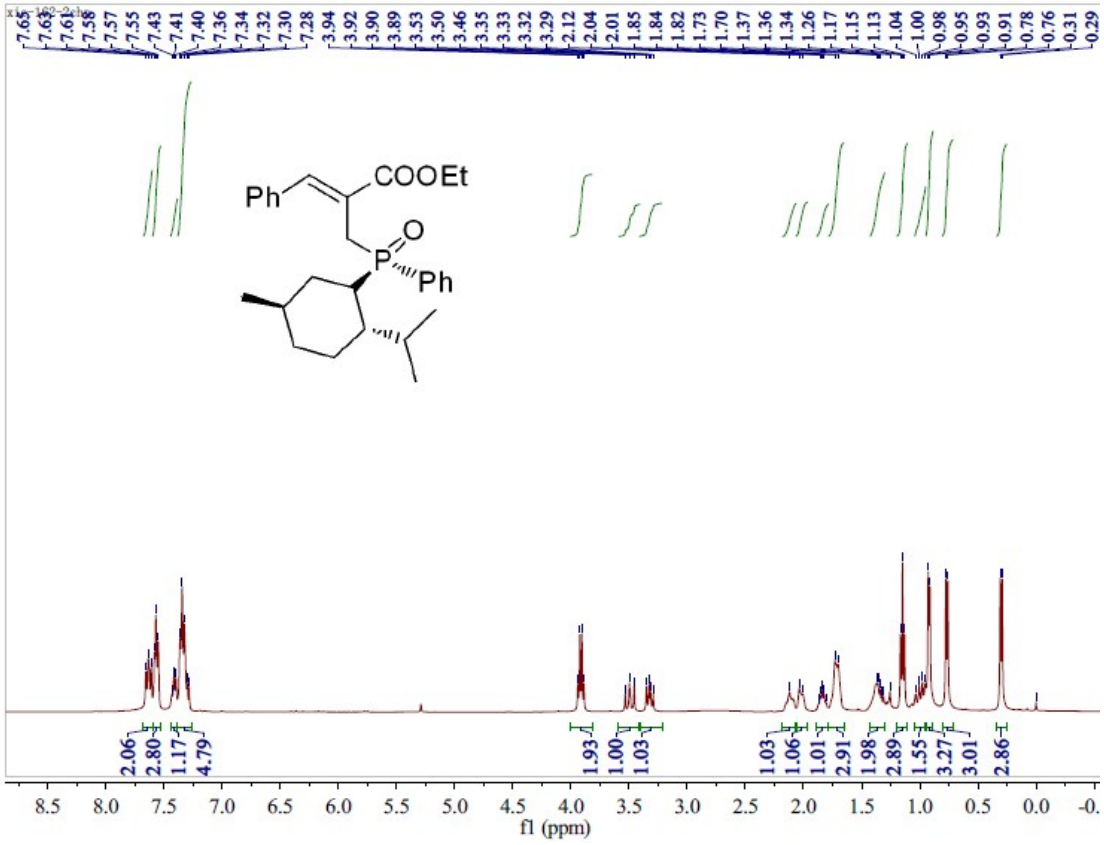

xie-178-1CHP
167.62
142.03
141.94
138.09
137.96
134.94
134.91
133.47
133.44
132.99
132.01
129.39
128.90
128.81
128.73
128.49
124.39
124.30
61.03
30.98
30.31
21.30
13.97
CO OEt
O
P
3w
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

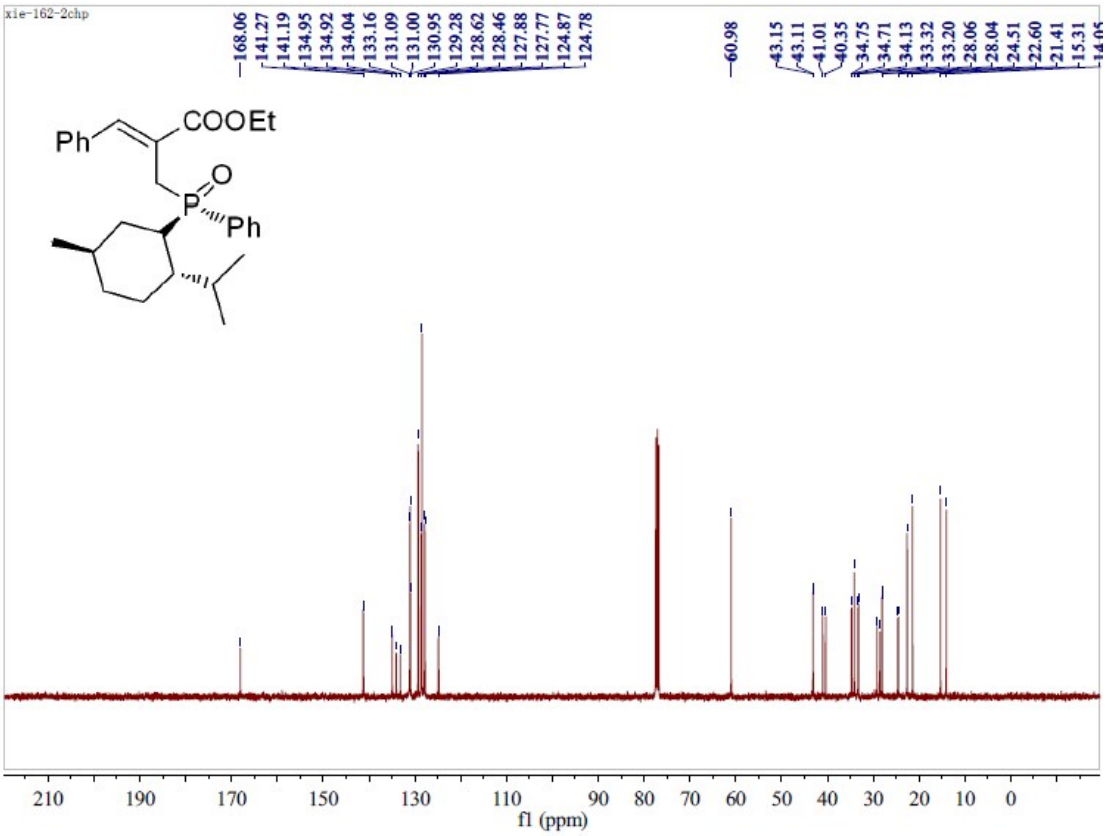

xie-178-1CHP
30.15
CO OEt
O
P
3w
100
50
0
-50
-100
-150
-200
f1 (ppm)

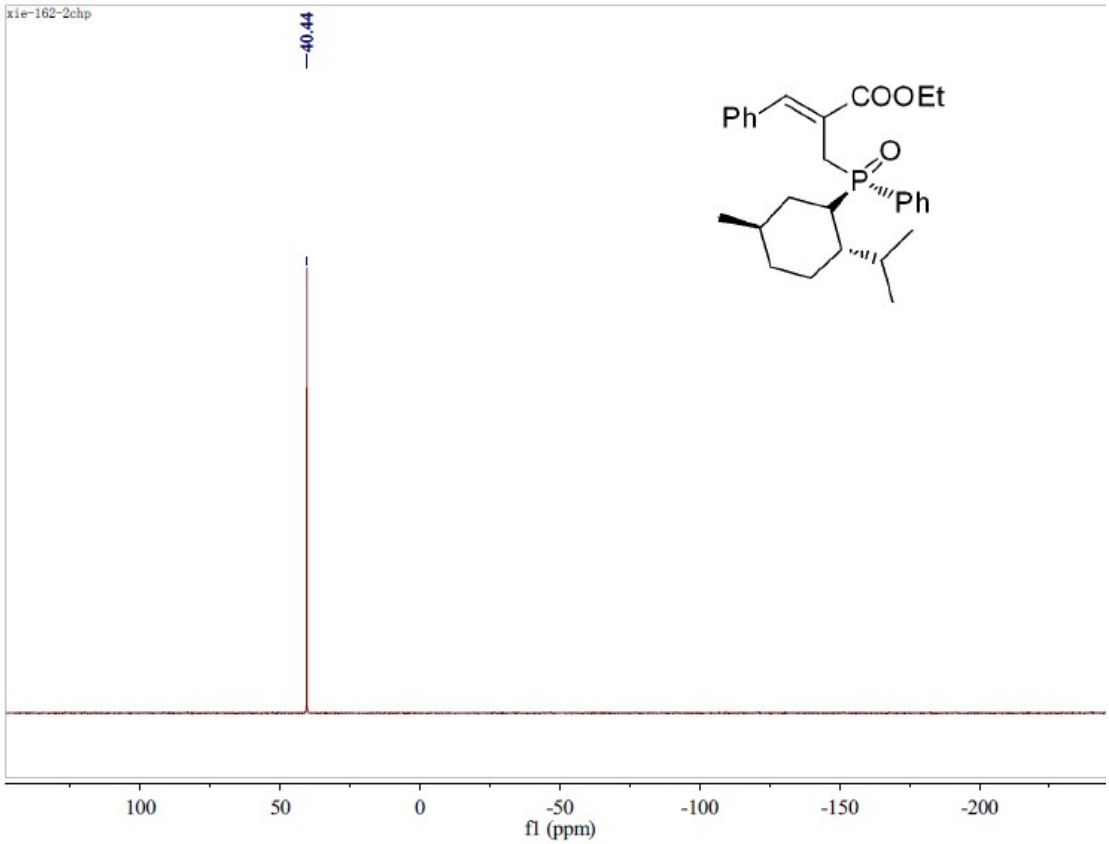

xie-182-1CHP
7.92
7.91
7.66
7.64
7.44
7.42
7.40
7.37
7.35
7.34
7.27
4.33
4.31
4.29
4.27
3.20
3.17
1.69
1.68
1.66
1.49
1.39
1.37
1.36
1.35
1.34
0.90
0.88
0.86
0.00
COOEt
O
P
3x
1.00
2.07
2.13
1.14
2.11
2.08
4.24
4.28
7.21
6.54
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

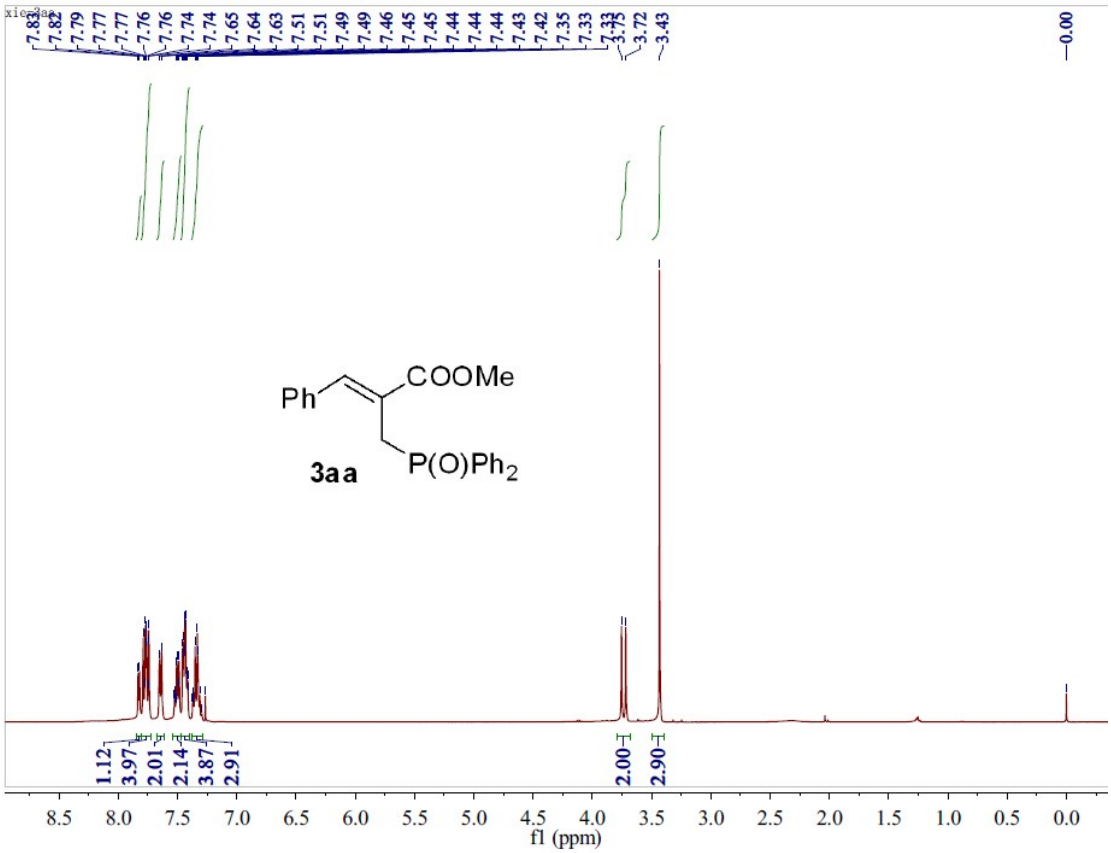

xie-182-1CHP
167.83
142.55
142.47
134.89
129.35
129.05
128.70
124.21
124.12
61.46
28.78
28.48
28.14
27.88
24.29
24.14
23.60
23.56
14.27
13.55
COOEt
O
P
3x
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

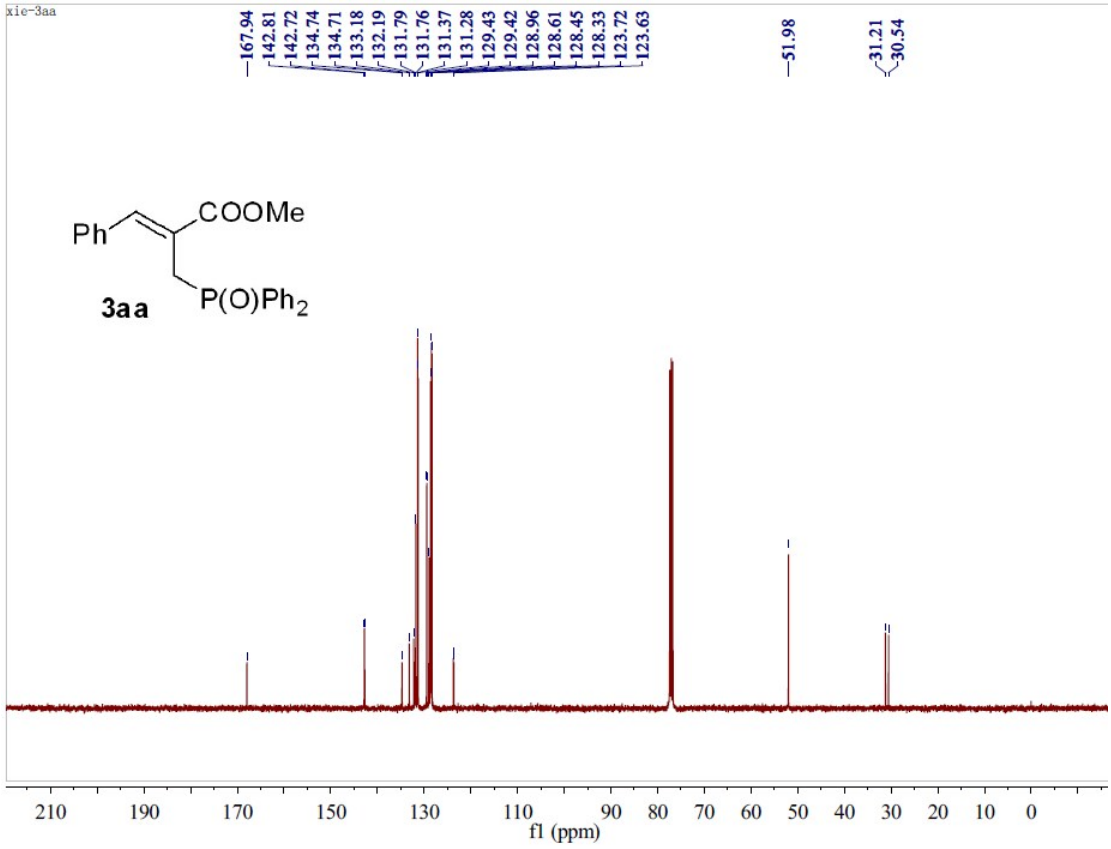

xie-182-1CHP
49.36
COOEt
O
P
3x
100
50
0
-50
-100
-150
-200
f1 (ppm)

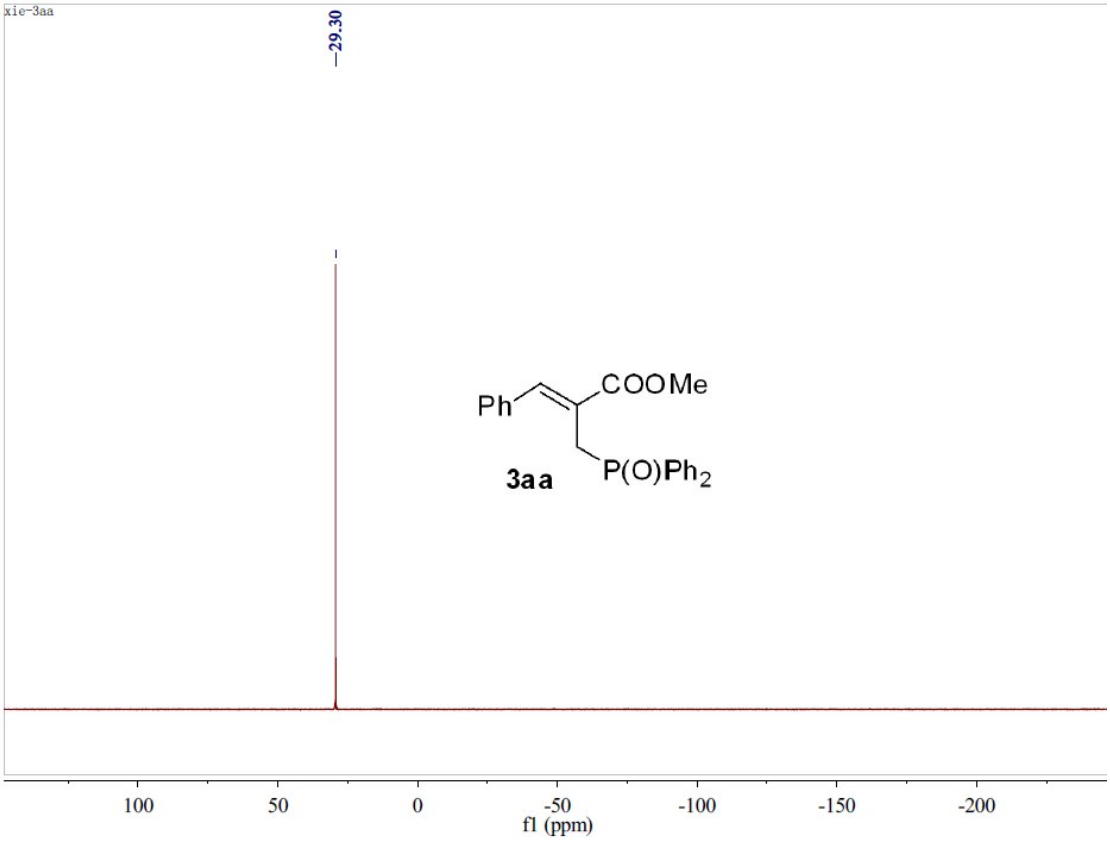

COOEt
Ph
O
P
Ph
2.06
2.80
1.17
4.79
1.93
1.00
1.03
1.03
1.06
1.01
2.91
1.98
2.89
1.55
3.27
3.01
2.86
f1 (ppm)


xie-162-2chp
168.06
141.27
141.19
134.95
134.92
134.04
133.16
131.09
131.00
130.95
129.28
128.62
128.46
127.88
127.77
124.87
124.78
60.98
43.15
43.11
41.01
40.35
34.75
34.71
34.13
33.32
33.20
28.06
28.04
24.51
22.60
21.41
15.31
COOEt
Ph
O
P
Ph
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


xie-162-2chp
40.44
COOEt
Ph
O
P
Ph
100
50
0
-50
-100
-150
-200
f1 (ppm)


7.83
7.82
7.79
7.77
7.77
7.76
7.76
7.74
7.74
7.65
7.64
7.63
7.51
7.51
7.49
7.49
7.46
7.45
7.45
7.44
7.44
7.44
7.43
7.42
7.35
7.33
3.75
3.72
3.43
0.00
Ph
COOMe
P(O)Ph2
3aa
1.12
3.97
2.01
2.14
3.87
2.91
2.00
2.90
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
f1 (ppm)


xie-3aa
167.94
142.81
142.72
134.74
134.71
133.18
132.19
131.79
131.76
131.37
131.28
129.43
129.42
128.96
128.61
128.45
128.33
123.72
123.63
51.98
31.21
30.54
Ph
COOMe
P(O)Ph2
3aa
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



9. Crystal Structure of 3j

CCDC-1484668 (3j) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.ac.uk/data_request/cif.