Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

$ZnCl_2$-Mediated Stereo- and Chemoselective Synthesis of Vinyl Phosphonates

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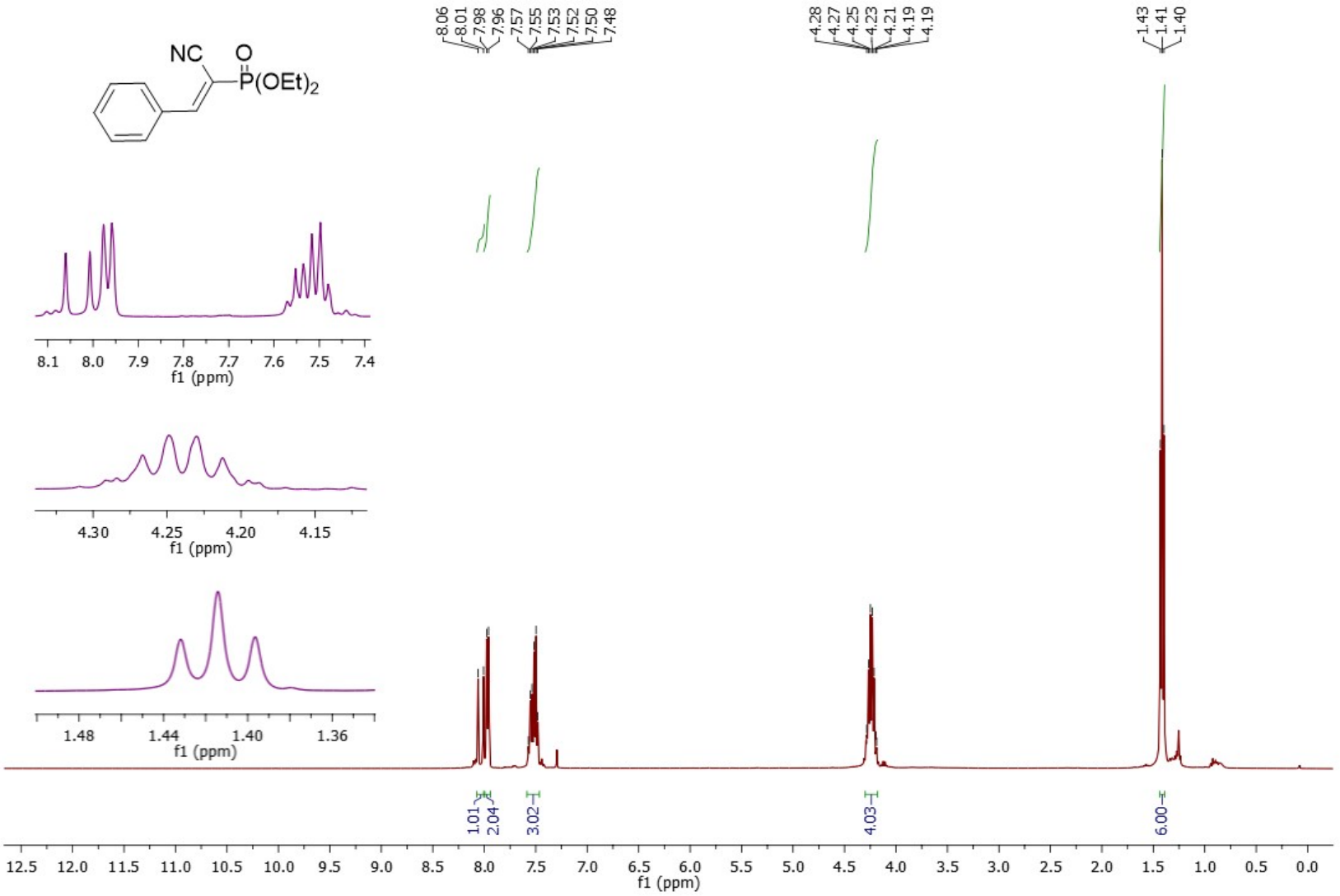


Figure S1: ^{1}H NMR Spectra of 2a

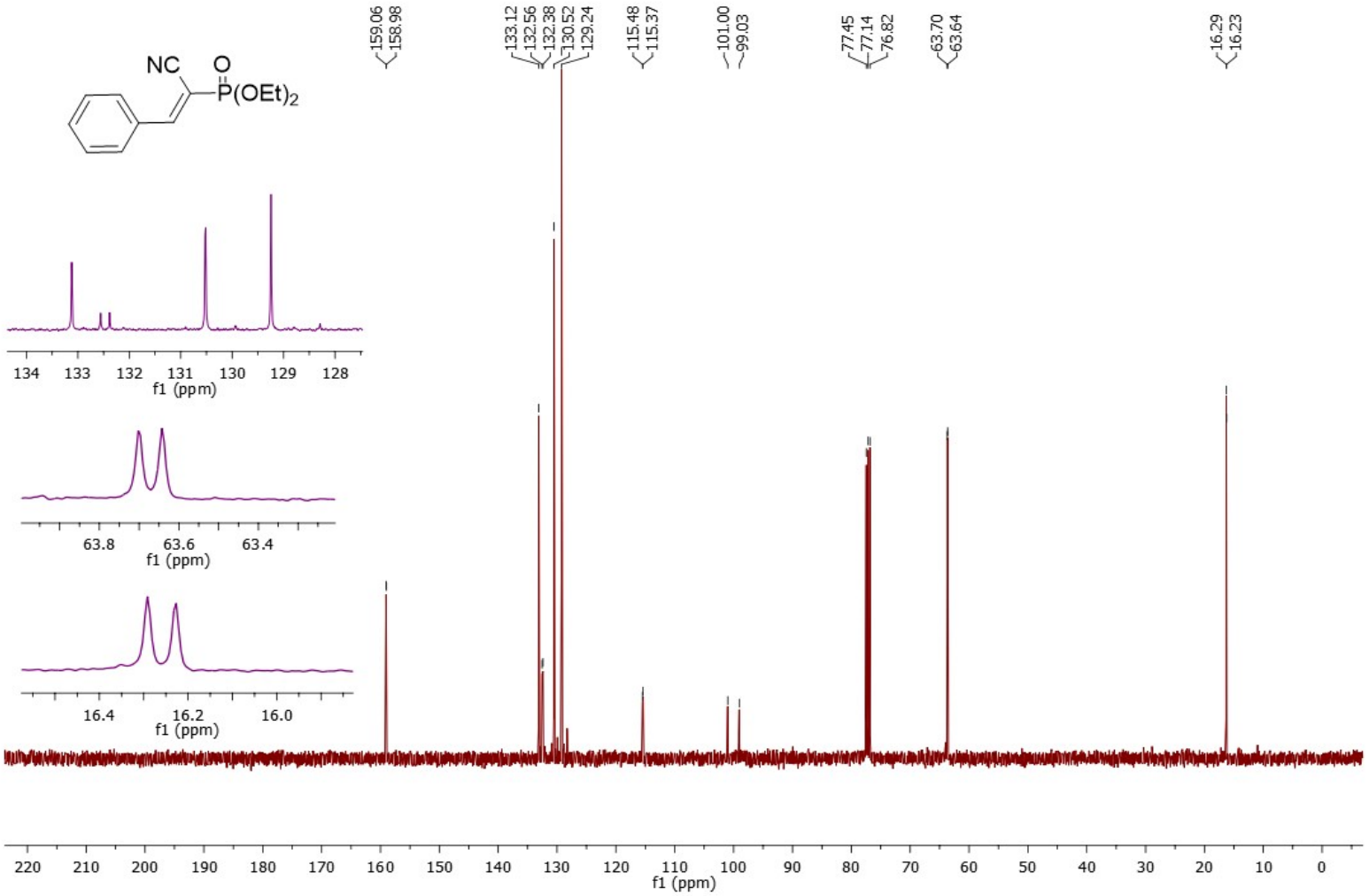


Figure S2: ^{13}C-NMR Spectra of 2a

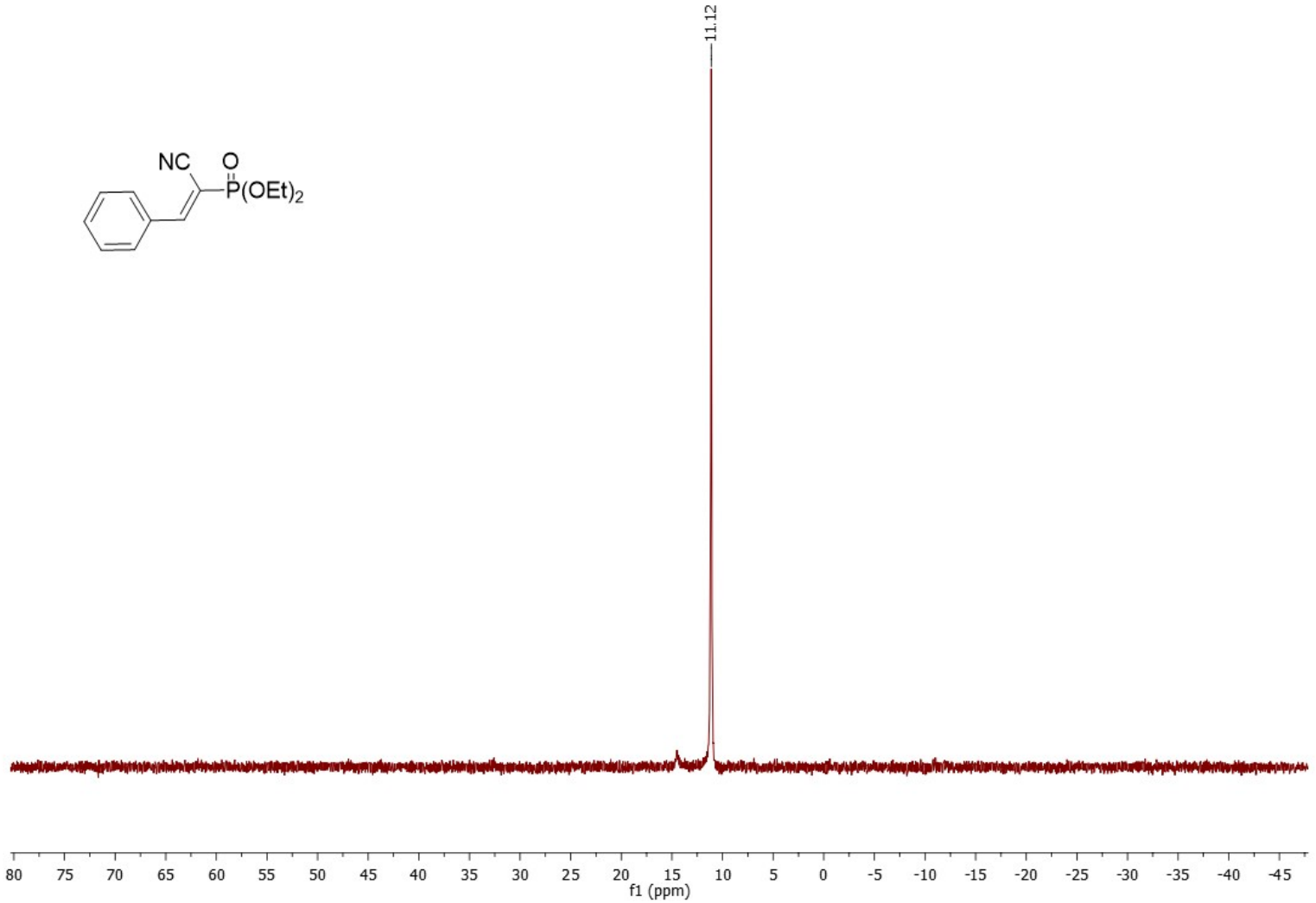


Figure S3: ^{31}PNMR Spectra of 2a

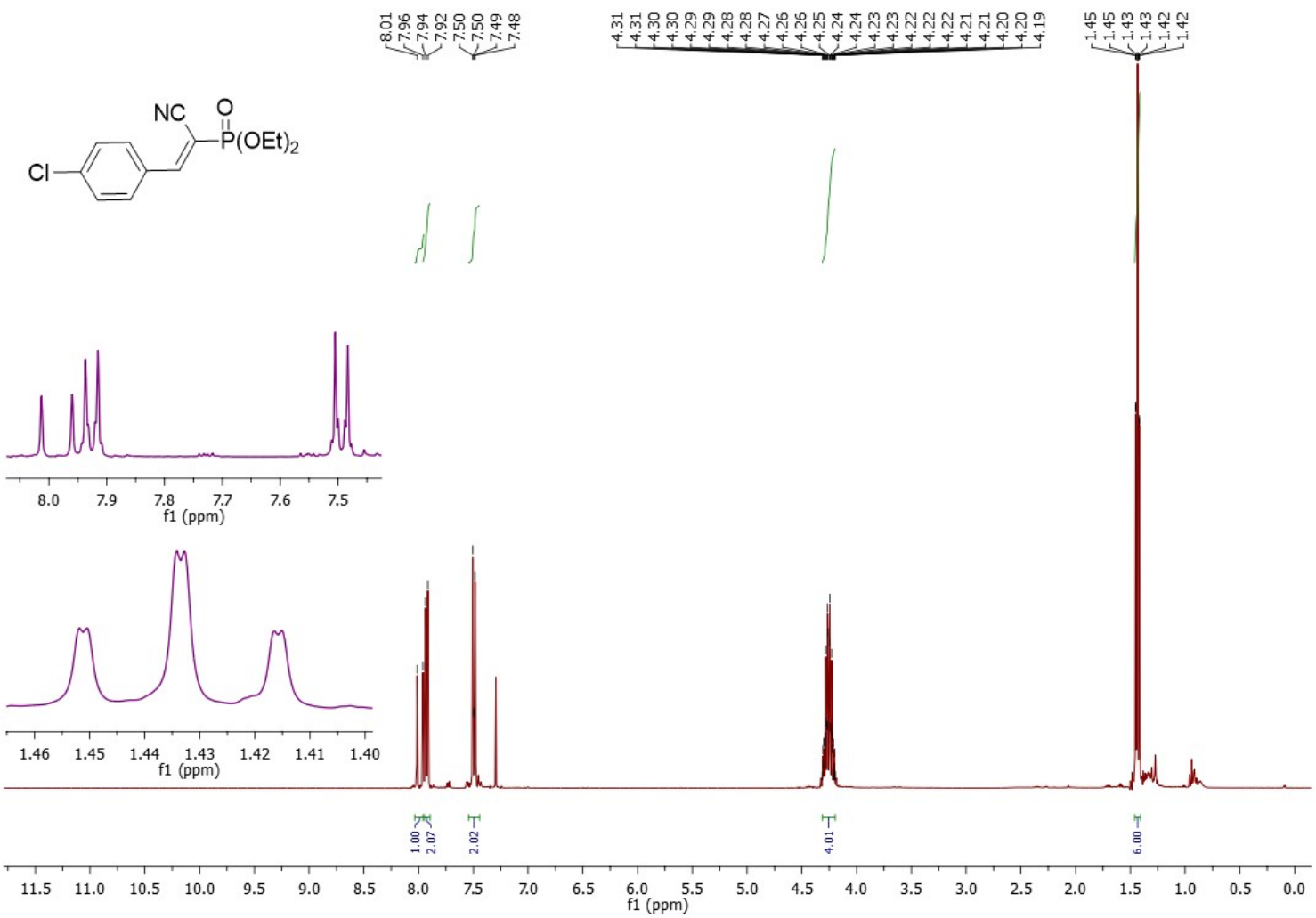


Figure S4: ^{1}HNMR Spectra of 2b

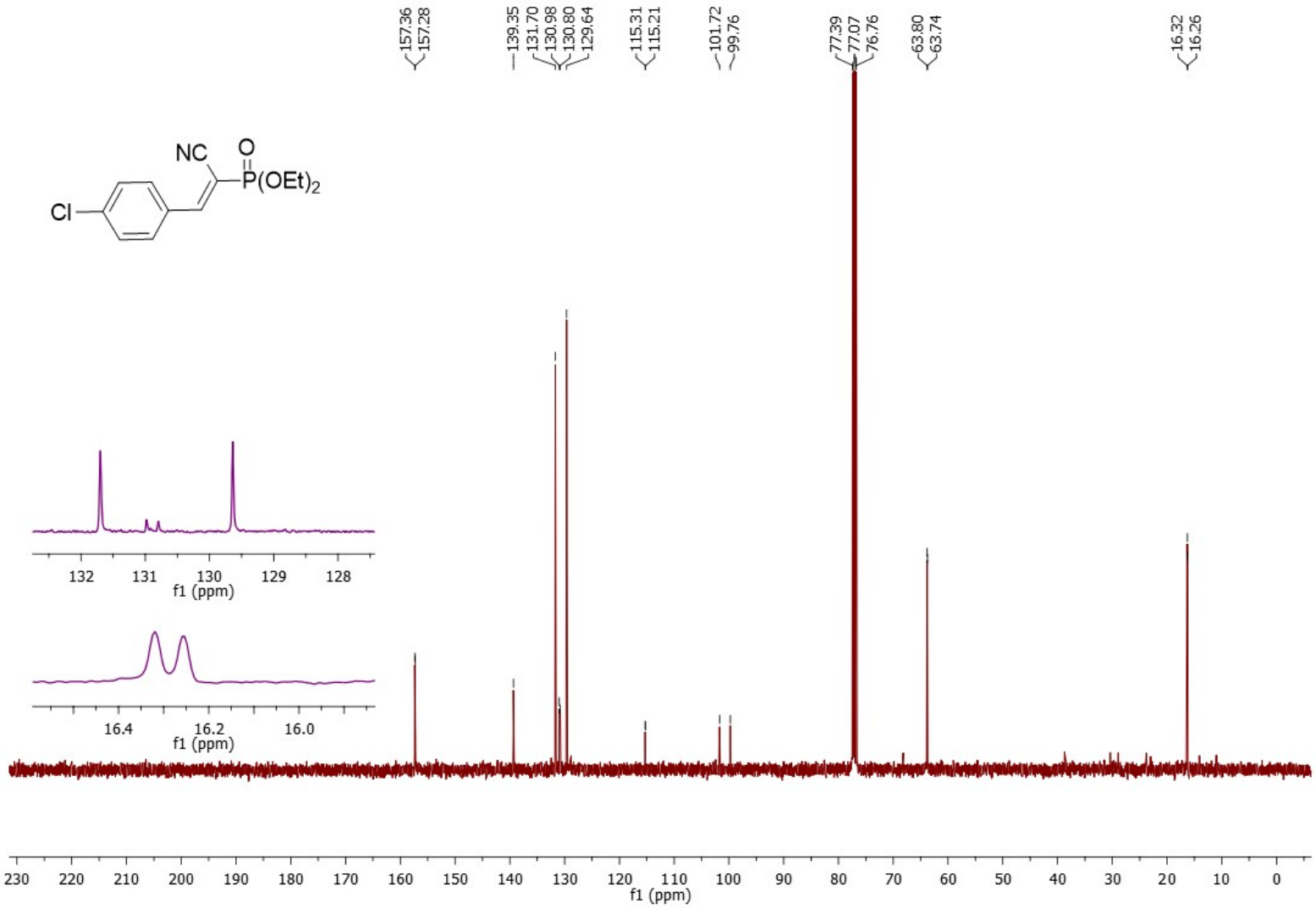


Figure S5: ^{13}CNMR Spectra of 2b

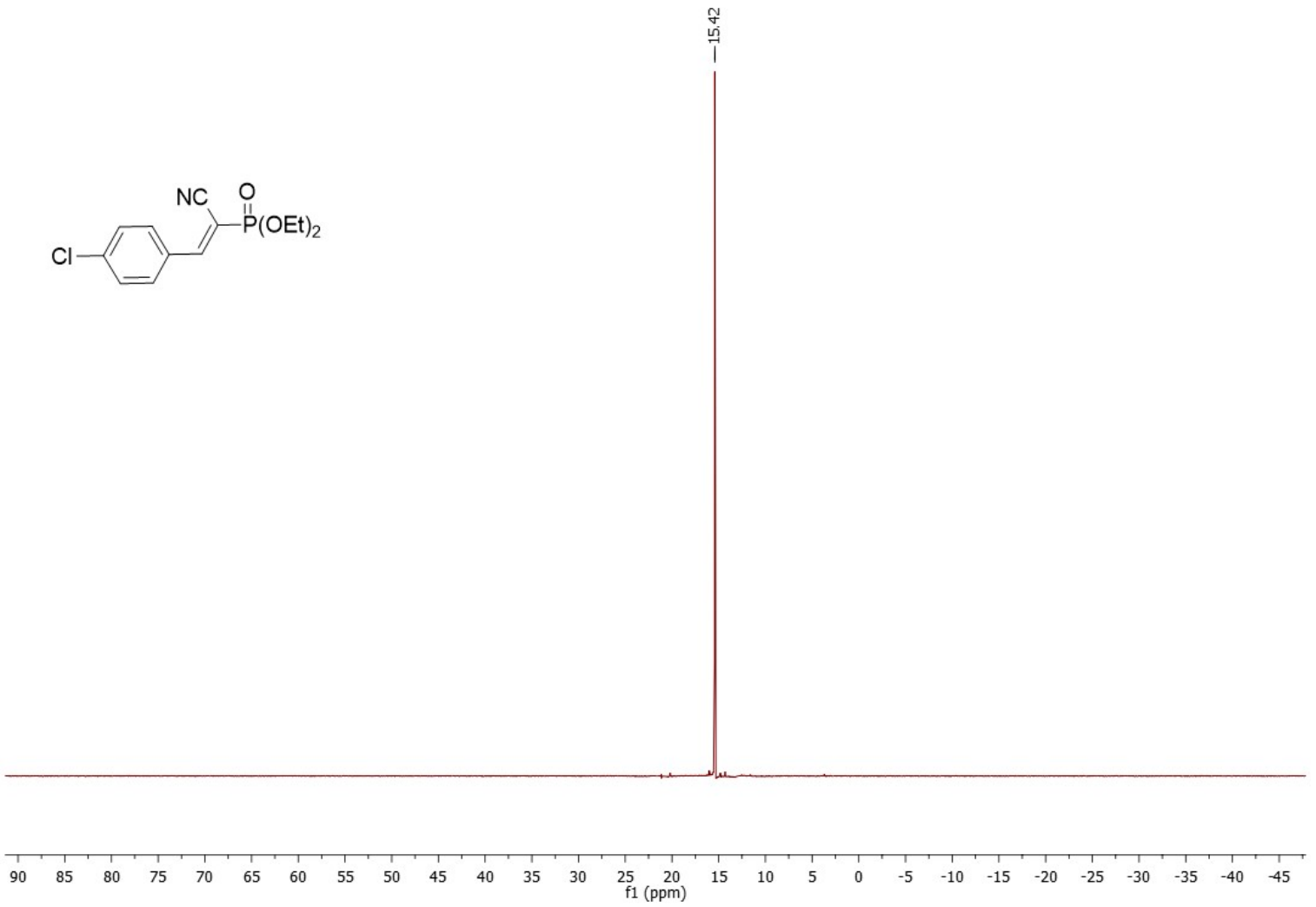


Figure S6: ^{31}P NMR Spectra of 2b

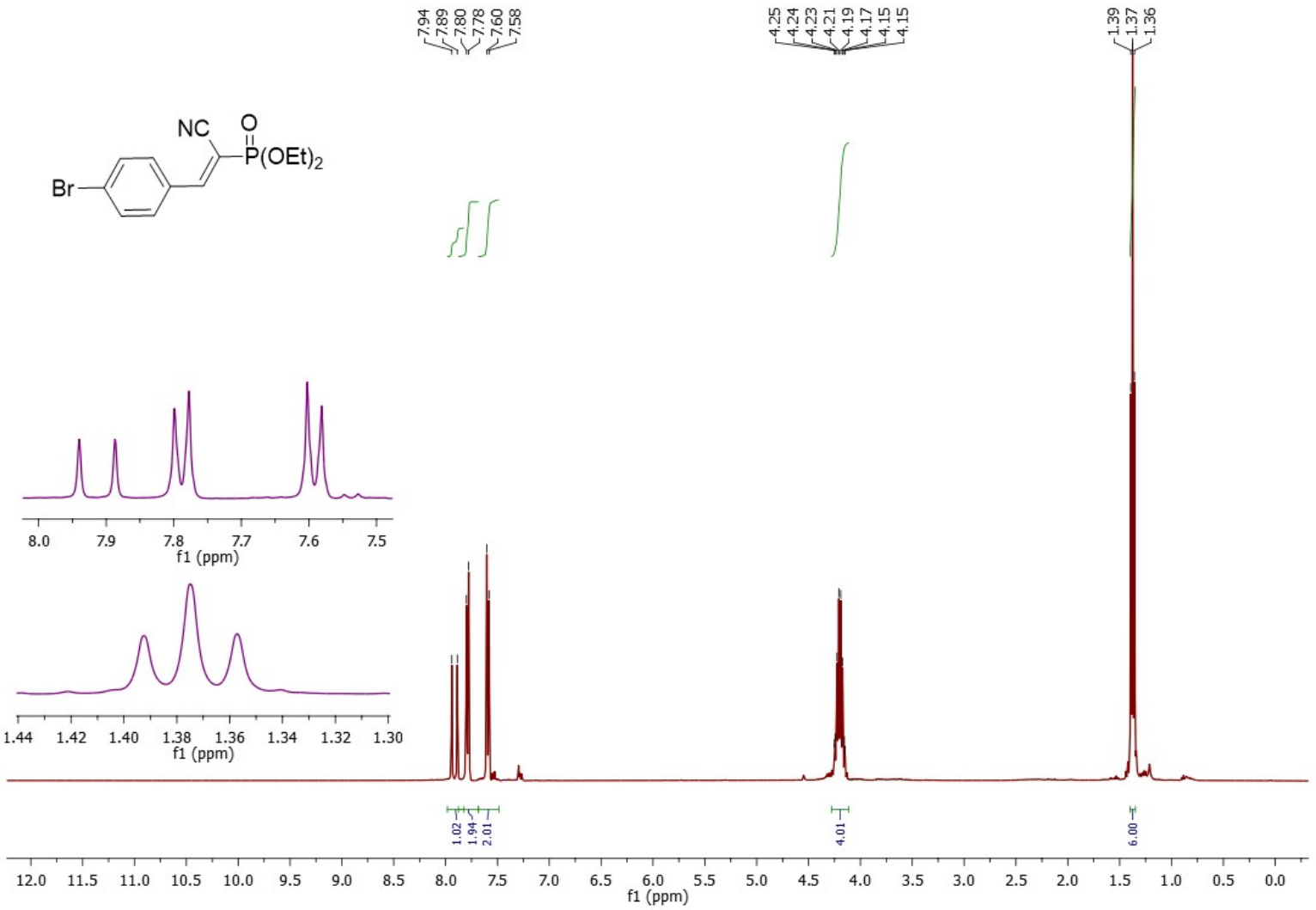


Figure S7: ^{1}HNMR Spectra of 2c

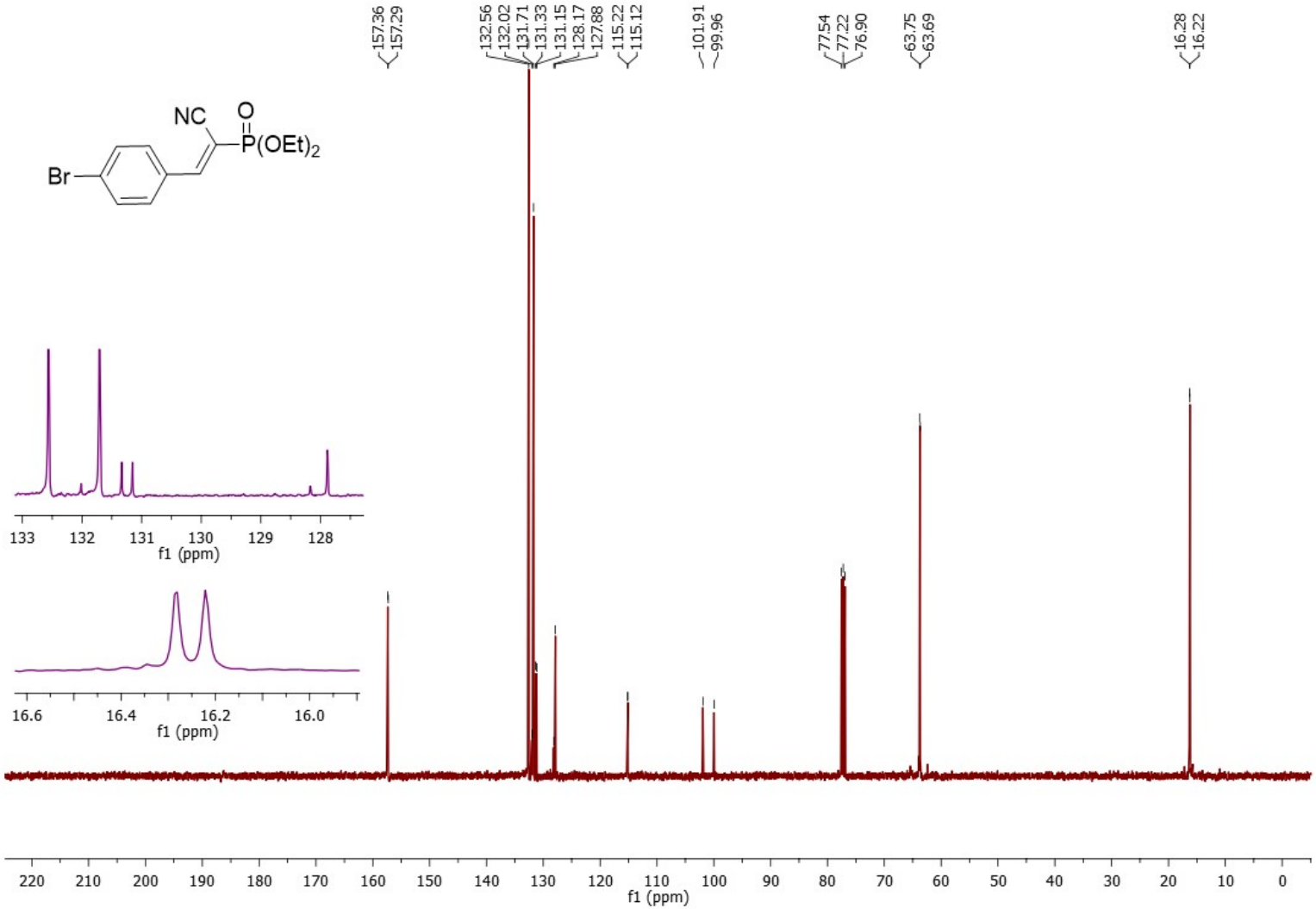


Figure S8: ^{13}C NMR Spectra of 2c

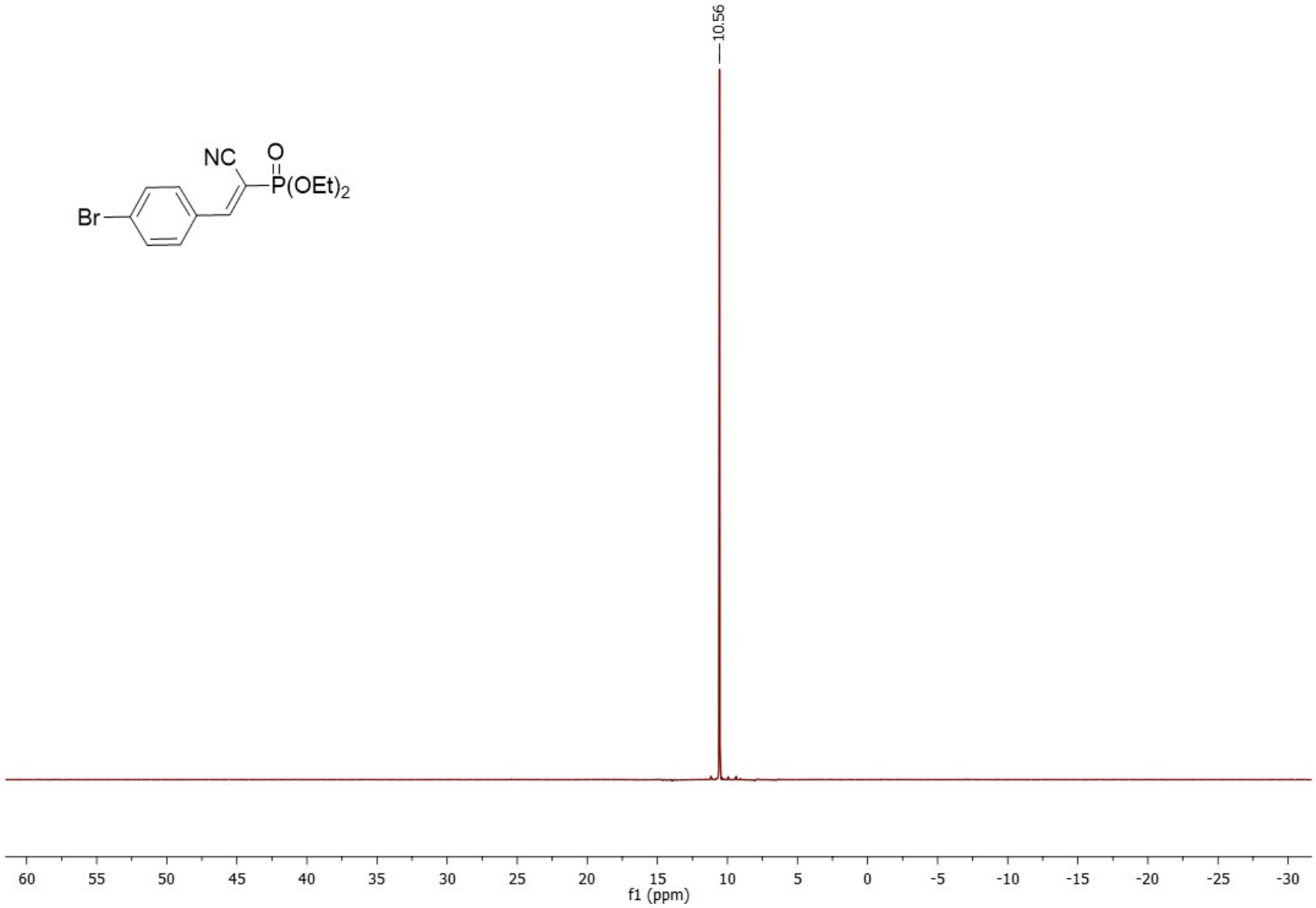


Figure S9: ^{31}P NMR Spectra of 2c

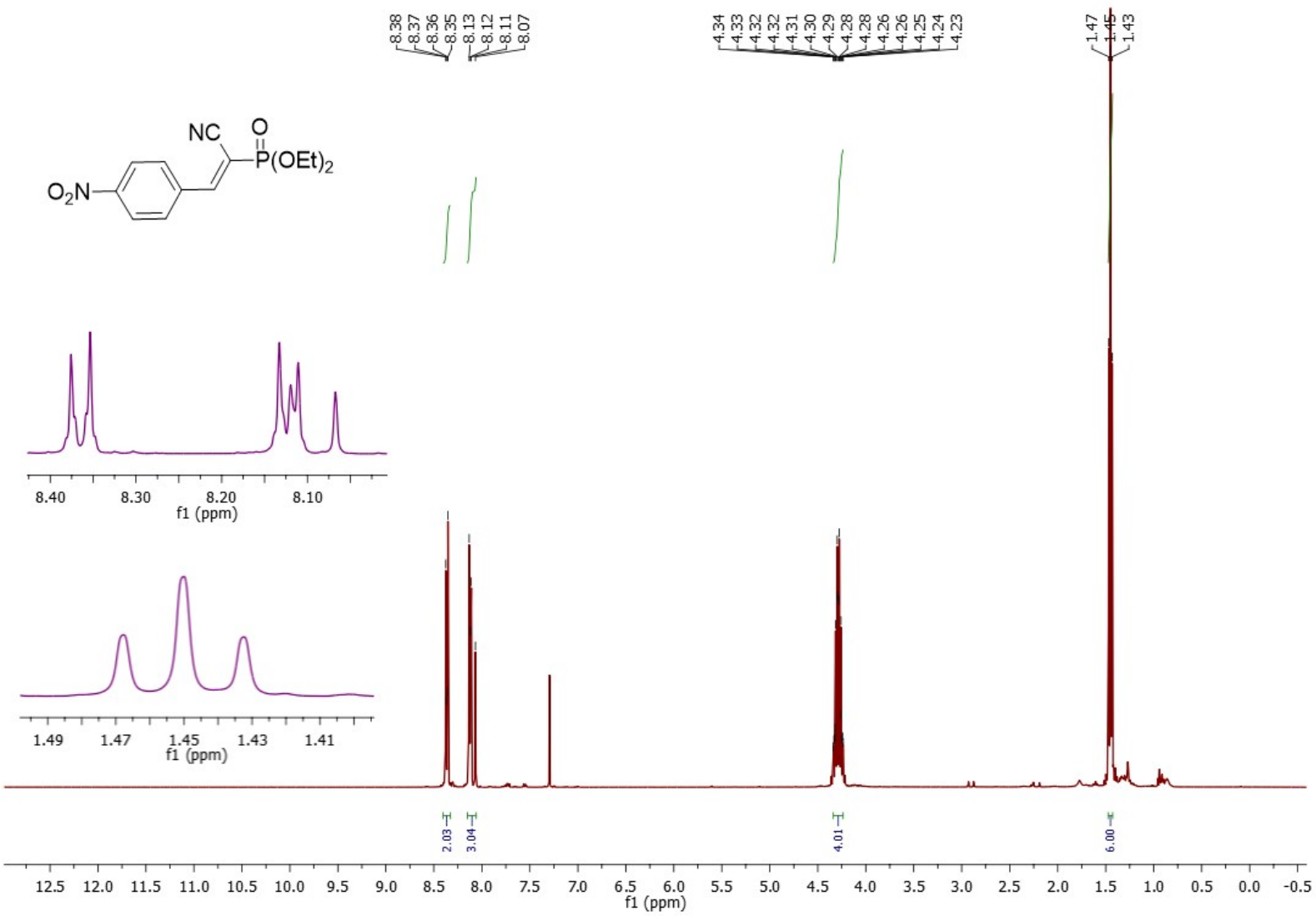


Figure S10:[1]HNMR Spectra of 2d

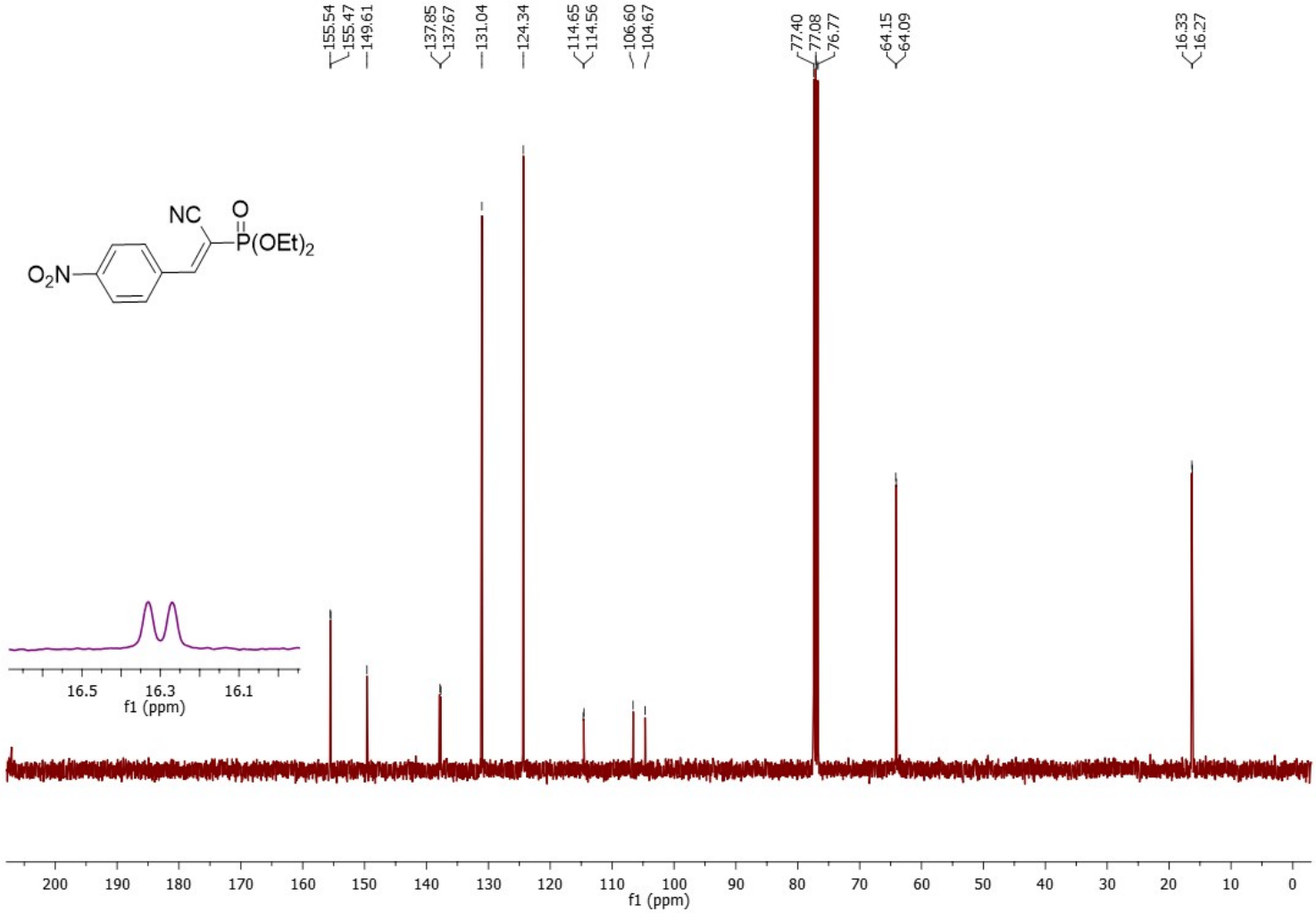


Figure S11: ^{13}C NMR Spectra of 2d

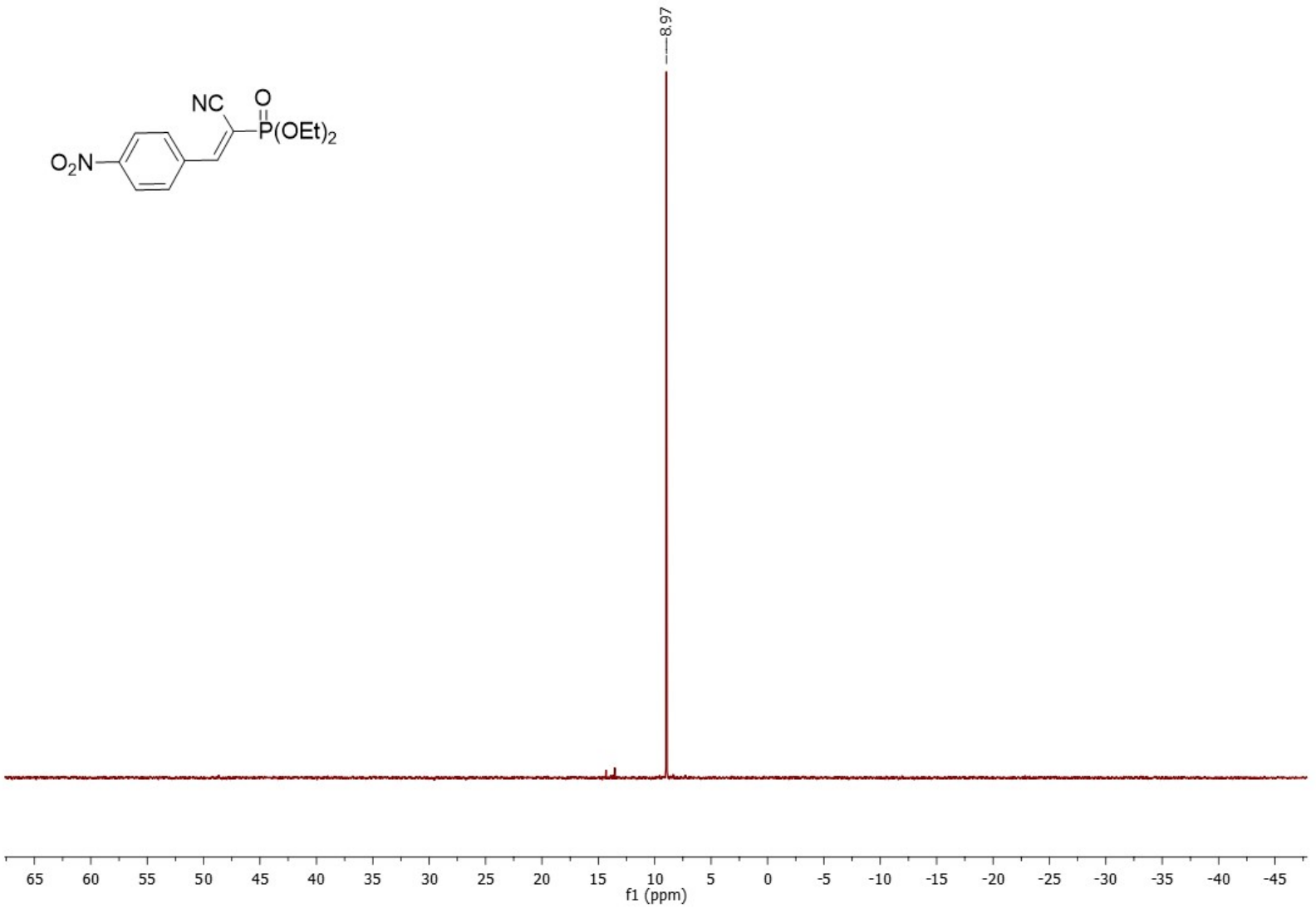


Figure S12: ^{31}P NMR Spectra of 2d

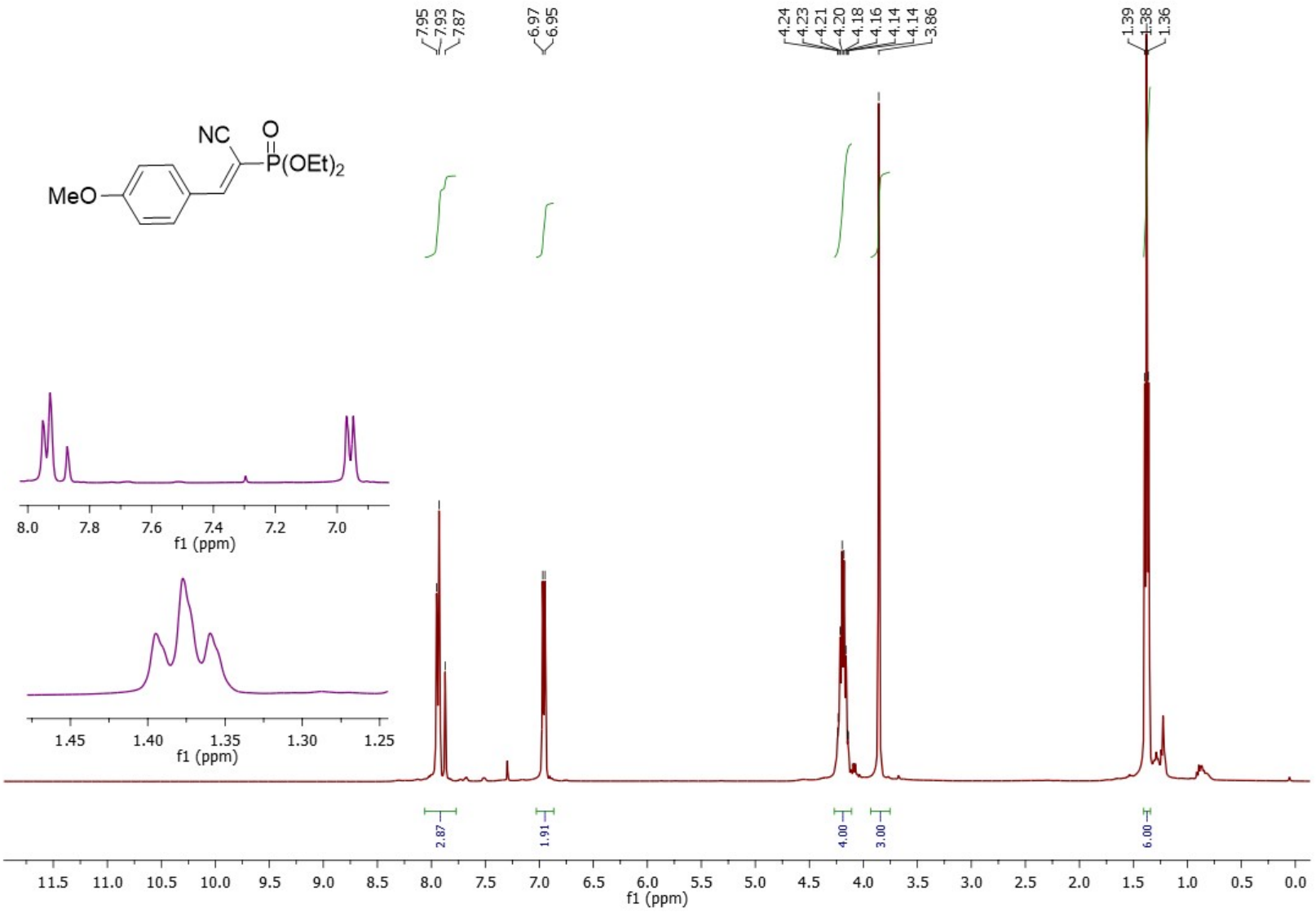


Figure S13: ^{1}HNMR Spectra of 2e

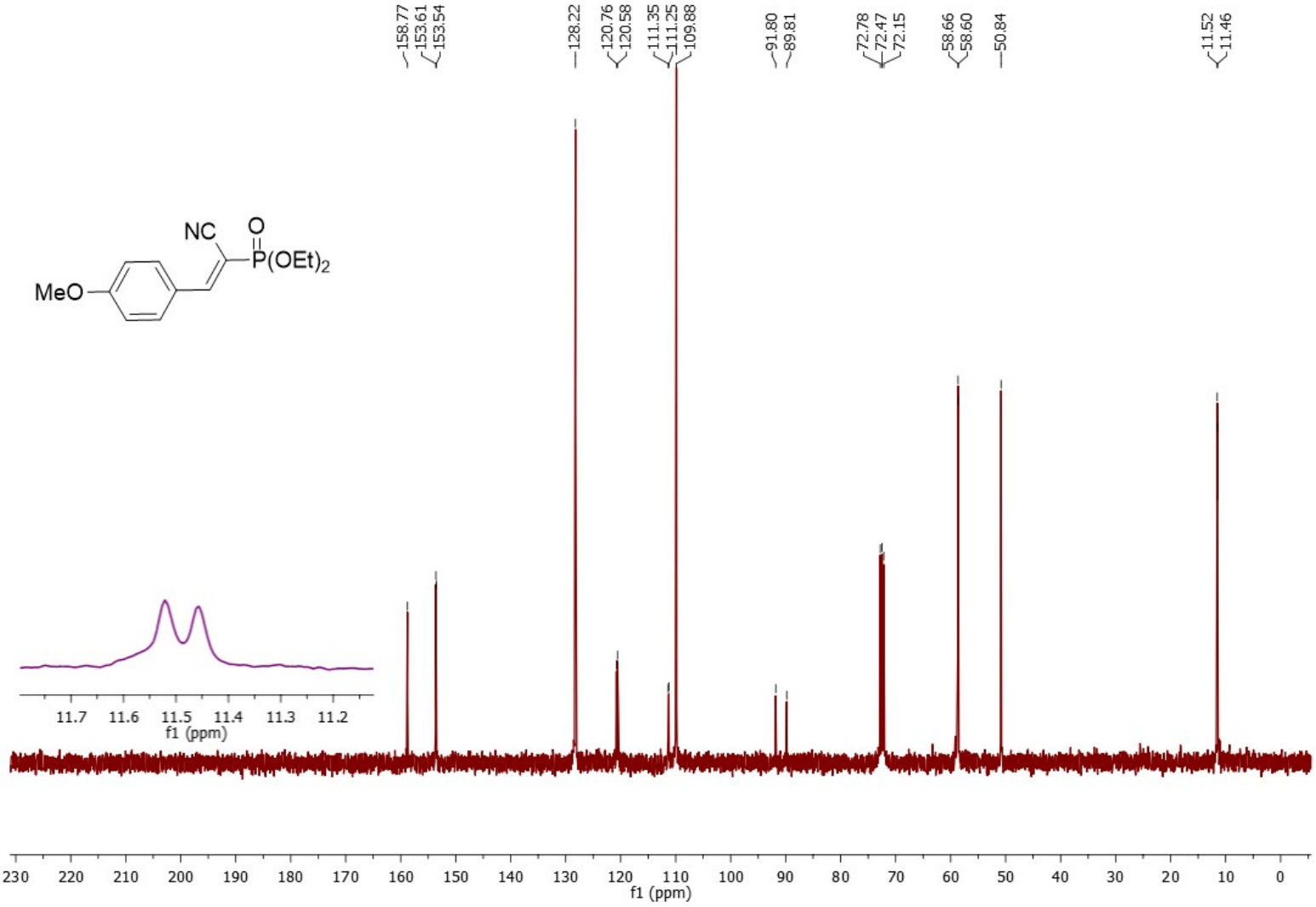


Figure S14: ^{13}C NMR Spectra of 2e

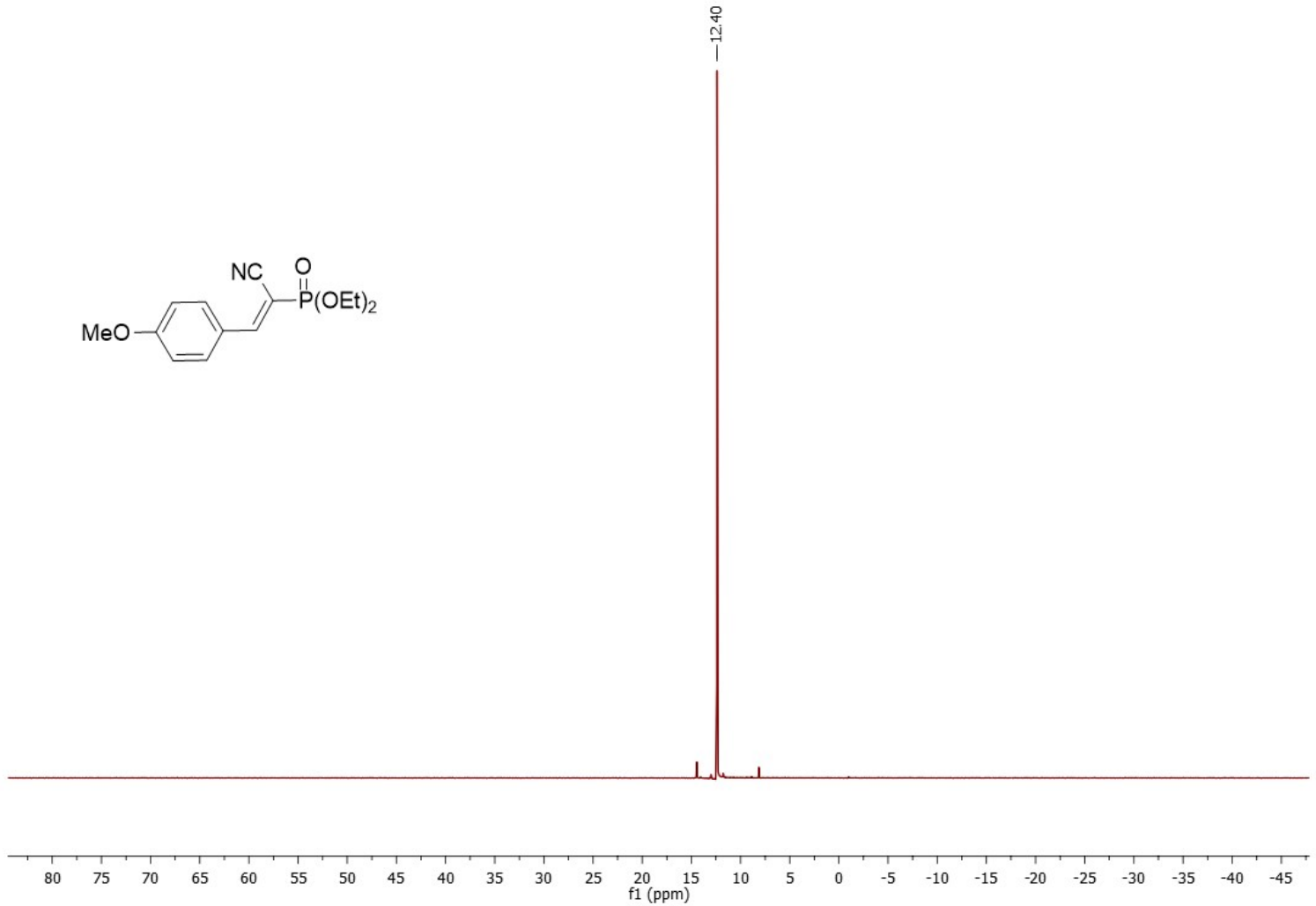


Figure S15: ^{31}P NMR Spectra of 2e

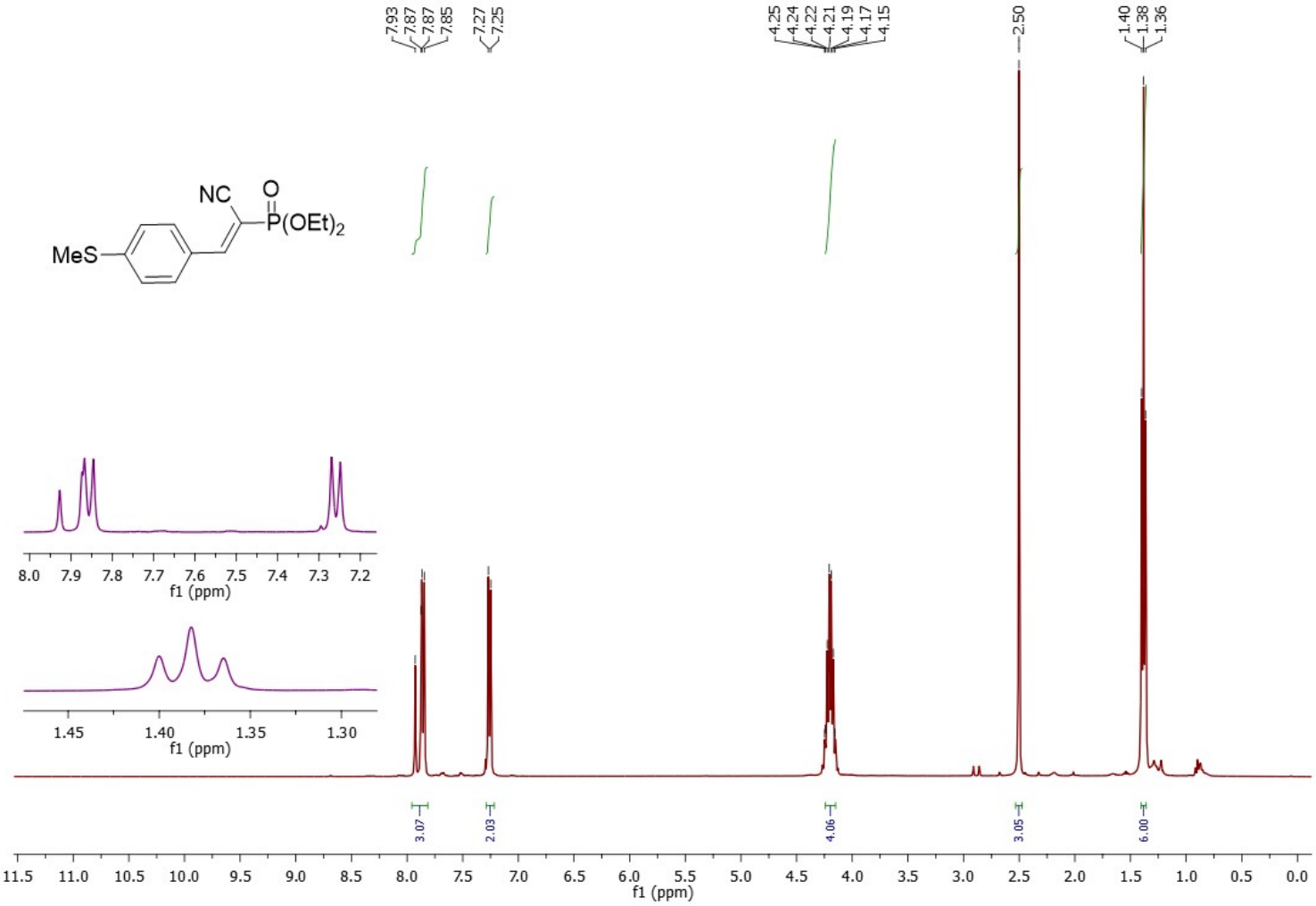


Figure S16: ^{1}HNMR Spectra of 2f

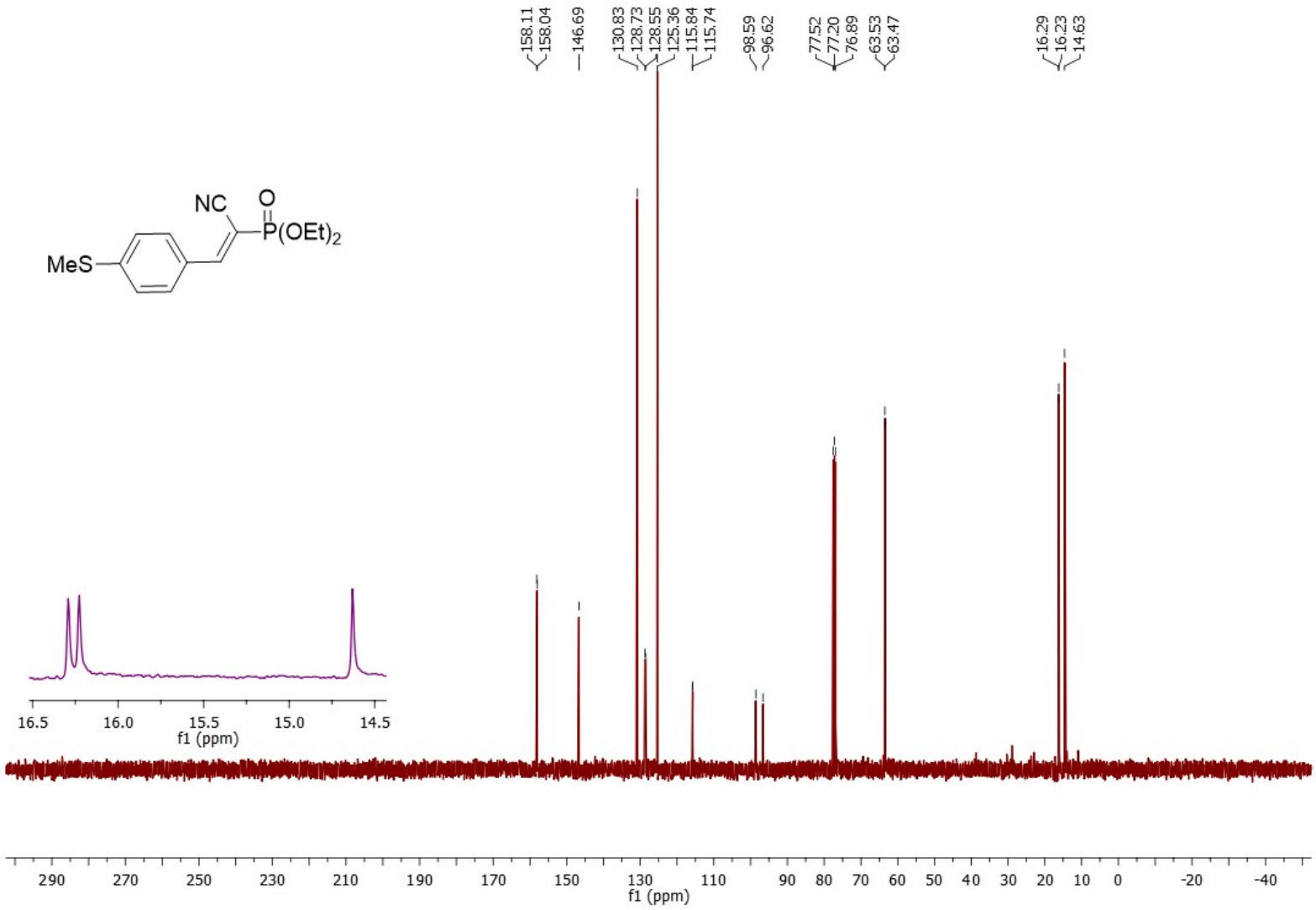


Figure S17: ^{13}C NMR Spectra of 2f

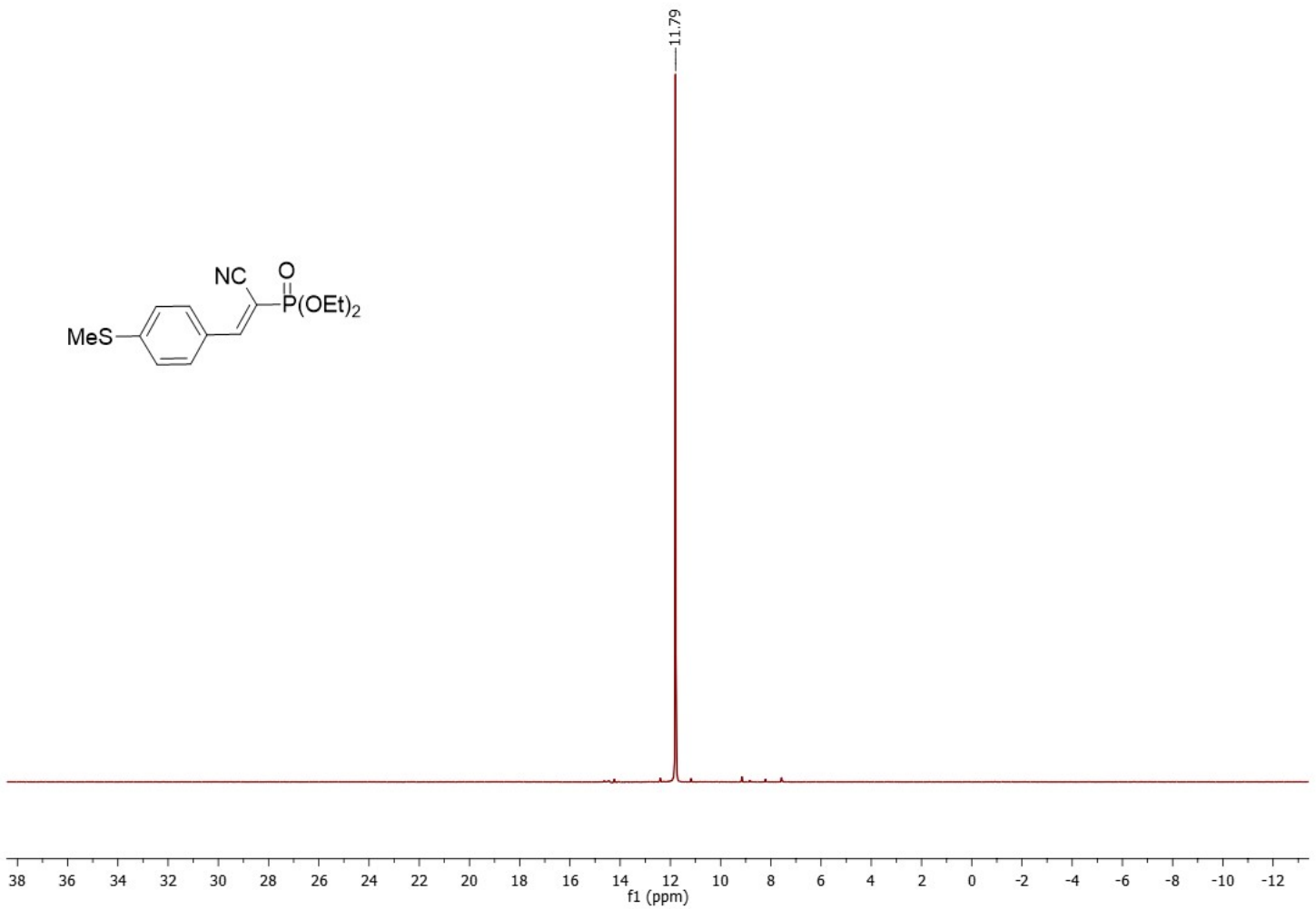


Figure S18: ^{31}P NMR Spectra of 2f

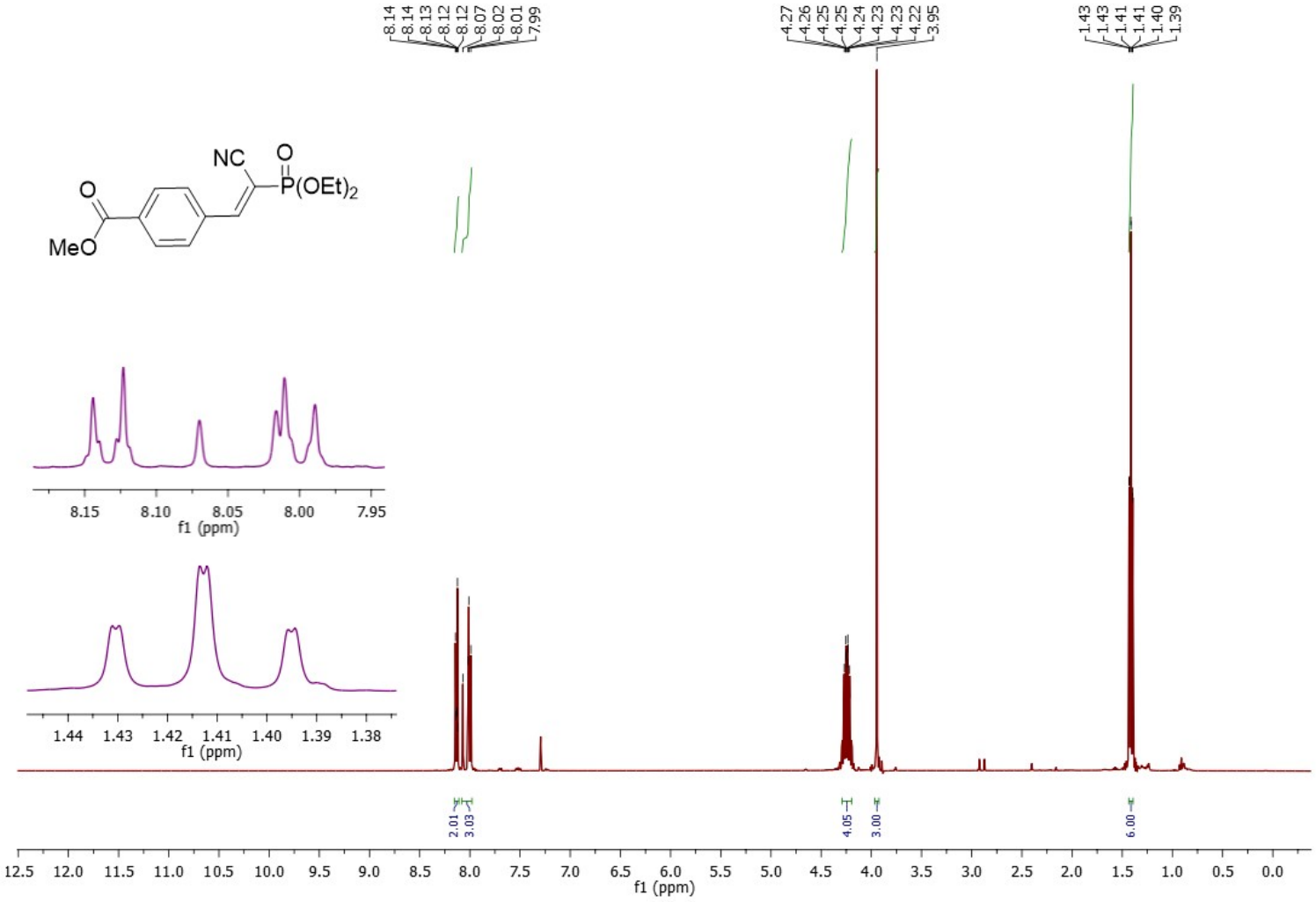


Figure S19: ^{1}HNMR Spectra of 2g

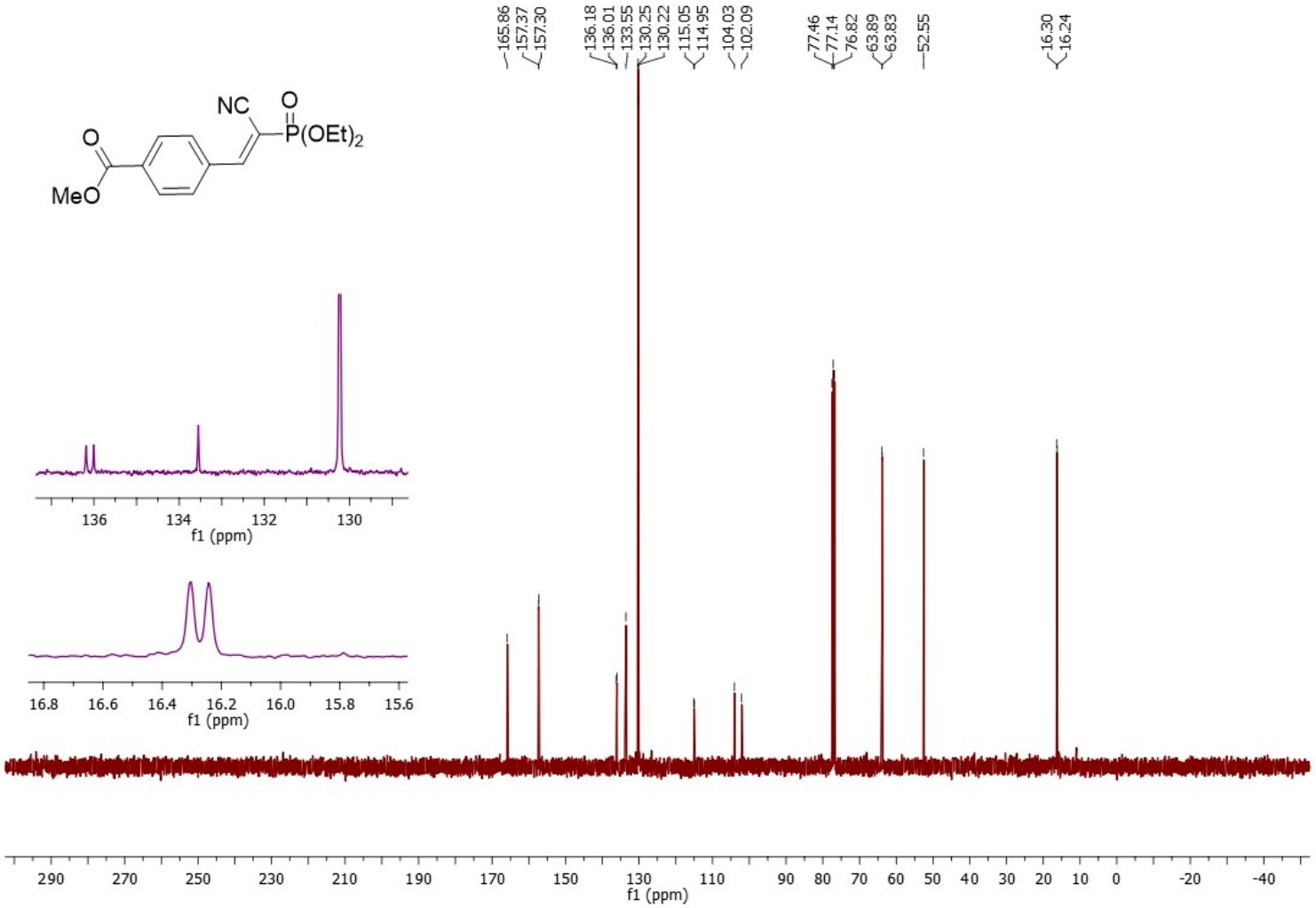


Figure S20: ^{13}C NMR Spectra of 2g

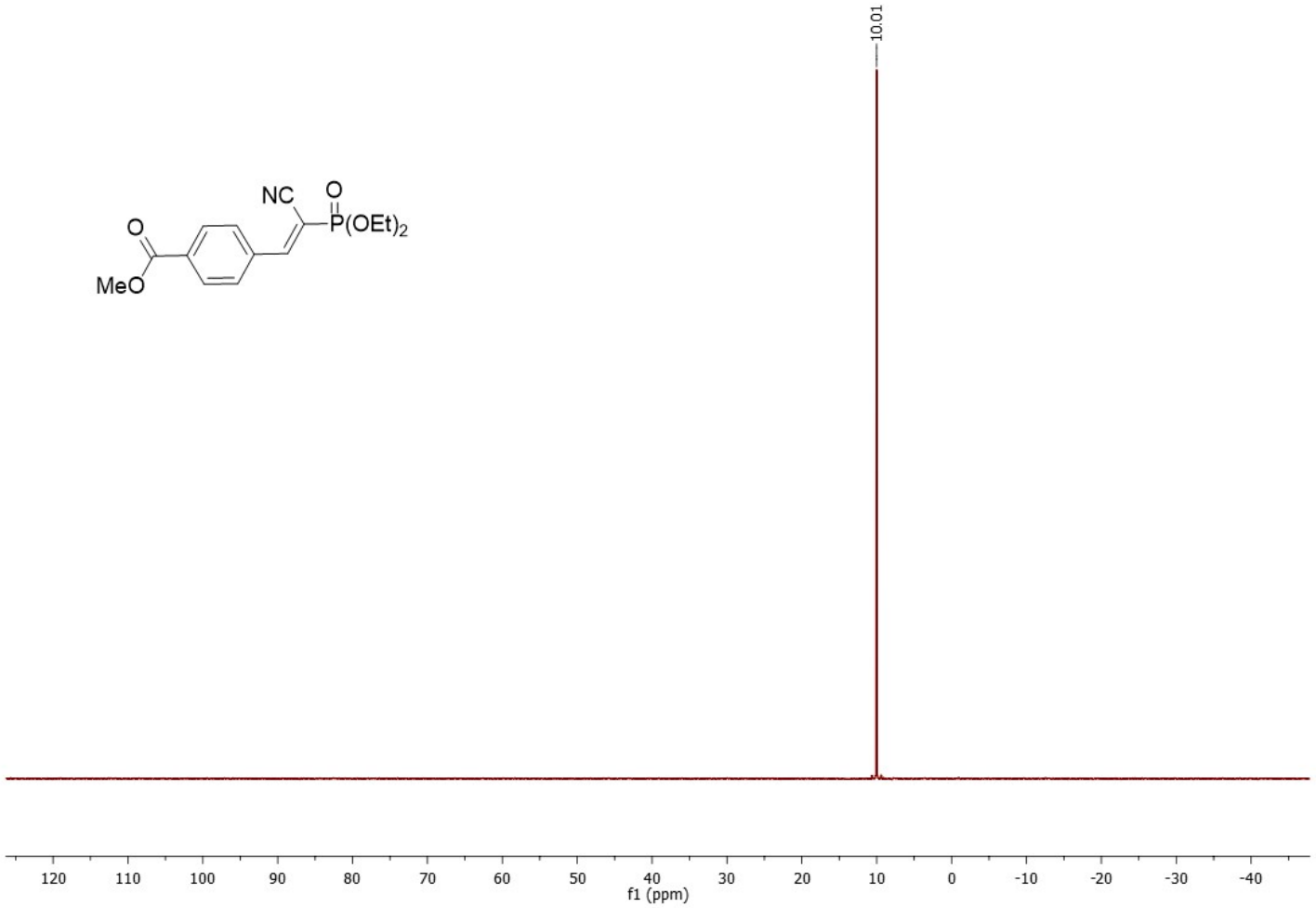


Figure S21: ^{31}P NMR Spectra of 2g

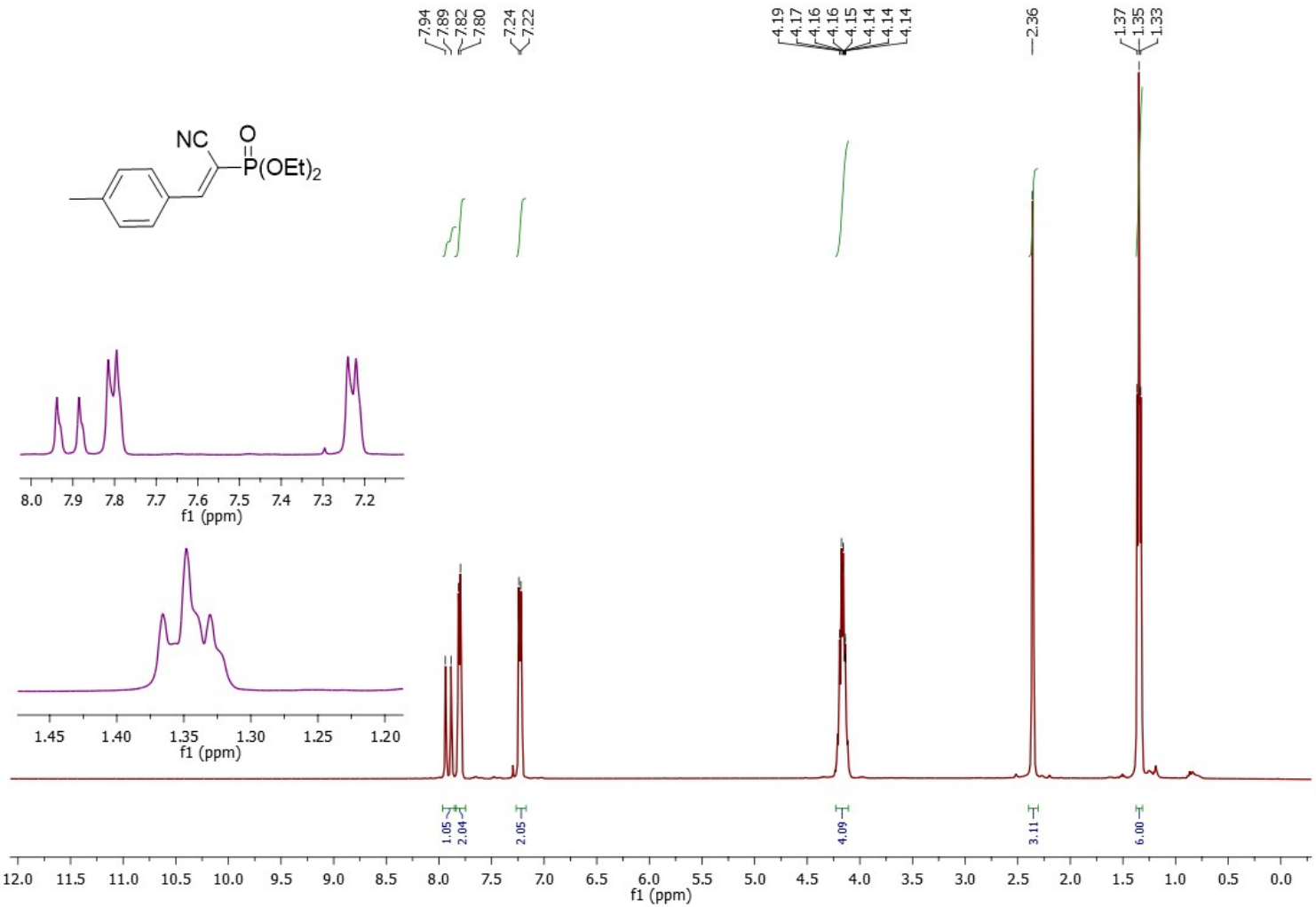


Figure S22: ^{1}HNMR Spectra of 2h

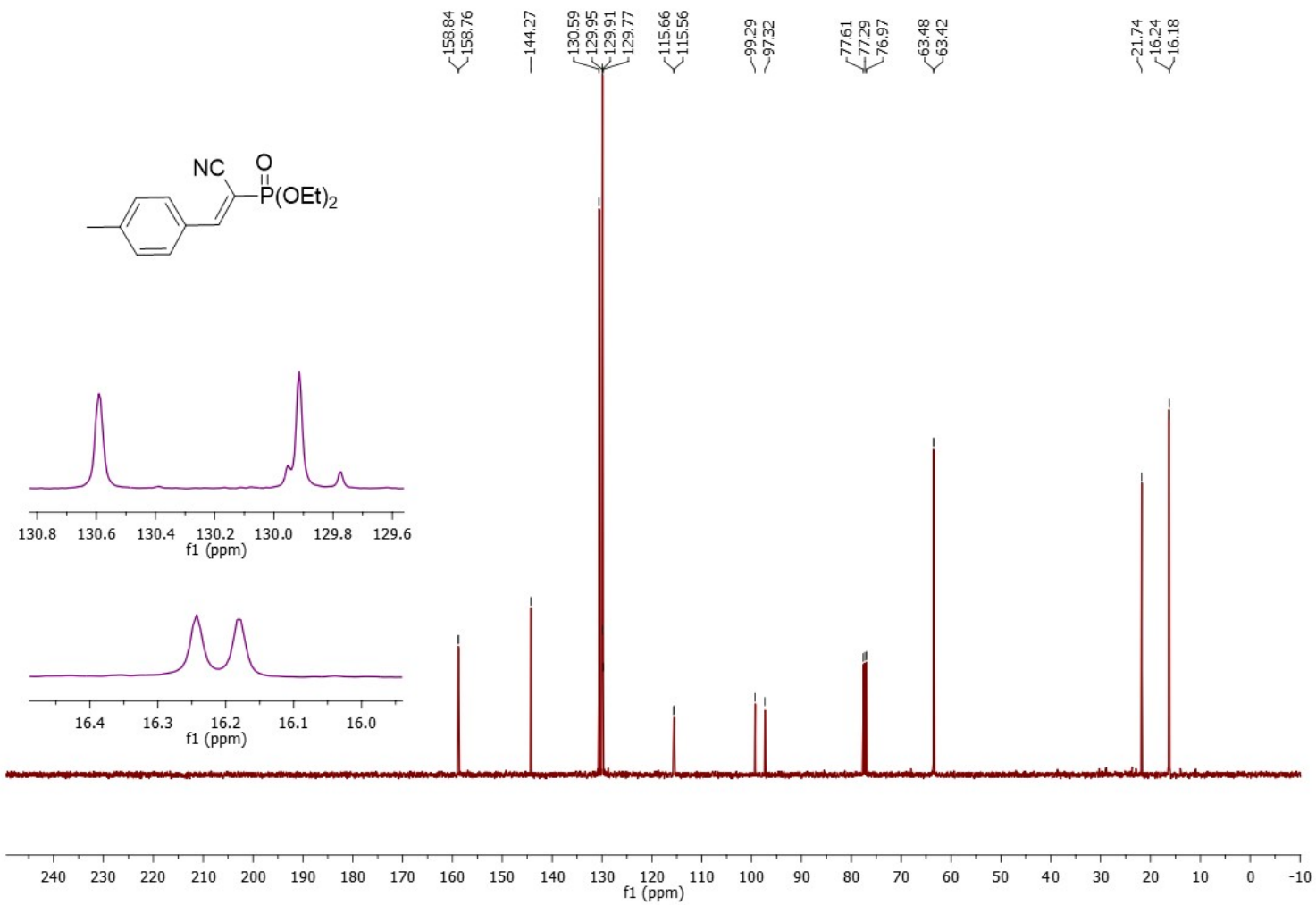


Figure S23: ^{13}C NMR Spectra of 2h

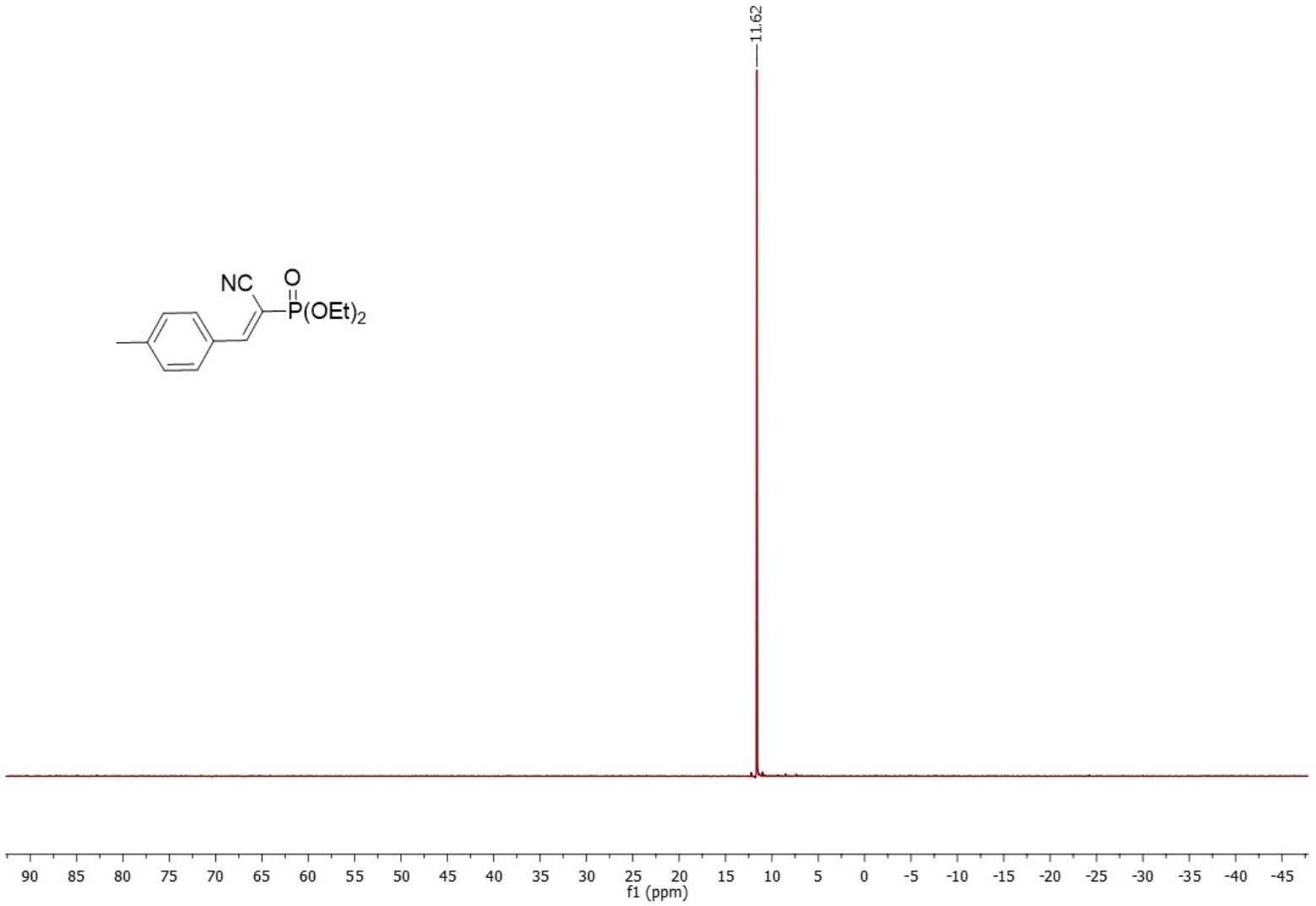


Figure S24: ^{31}P NMR Spectra of 2h

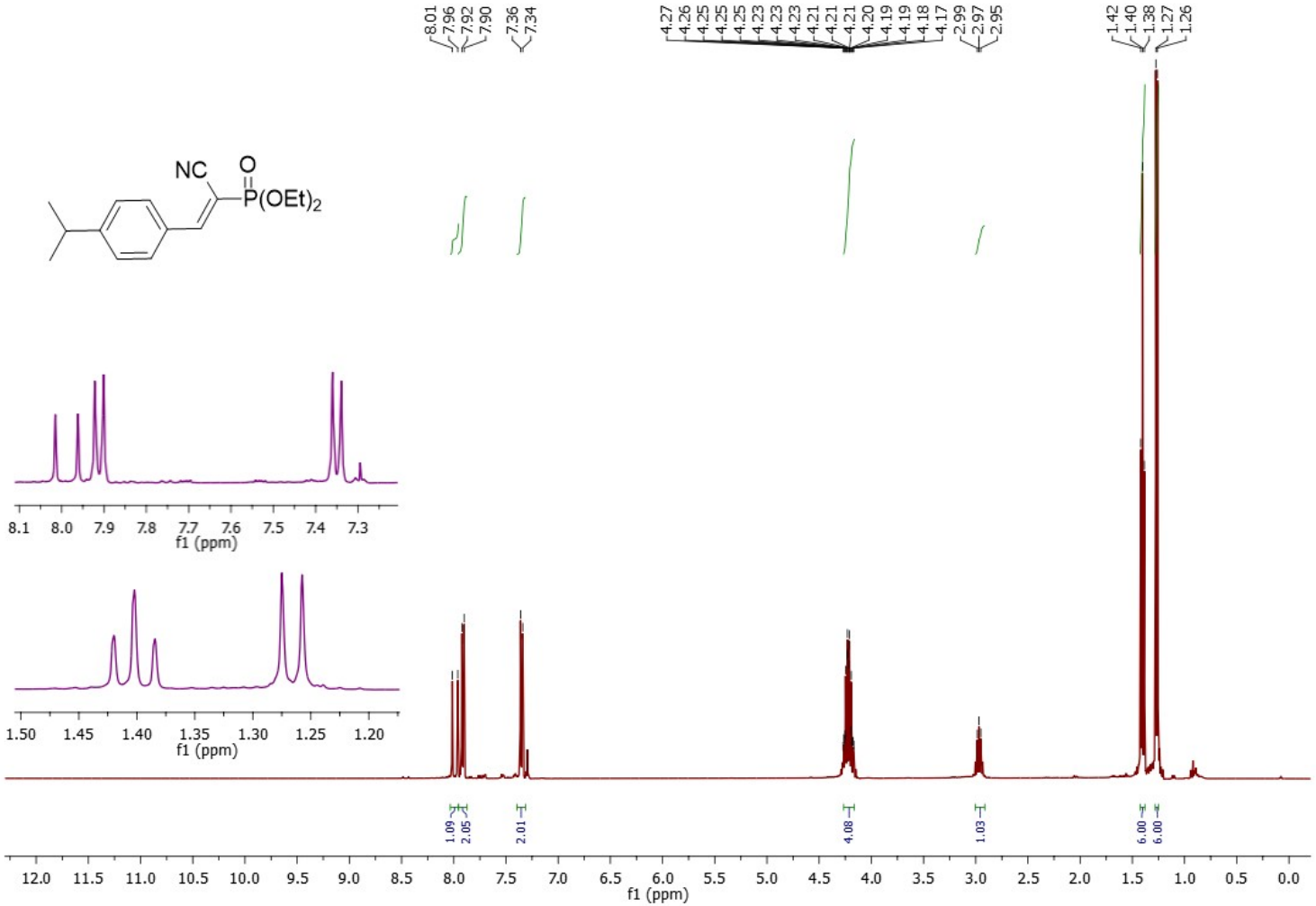


Figure S25: ^{1}HNMR Spectra of 2i

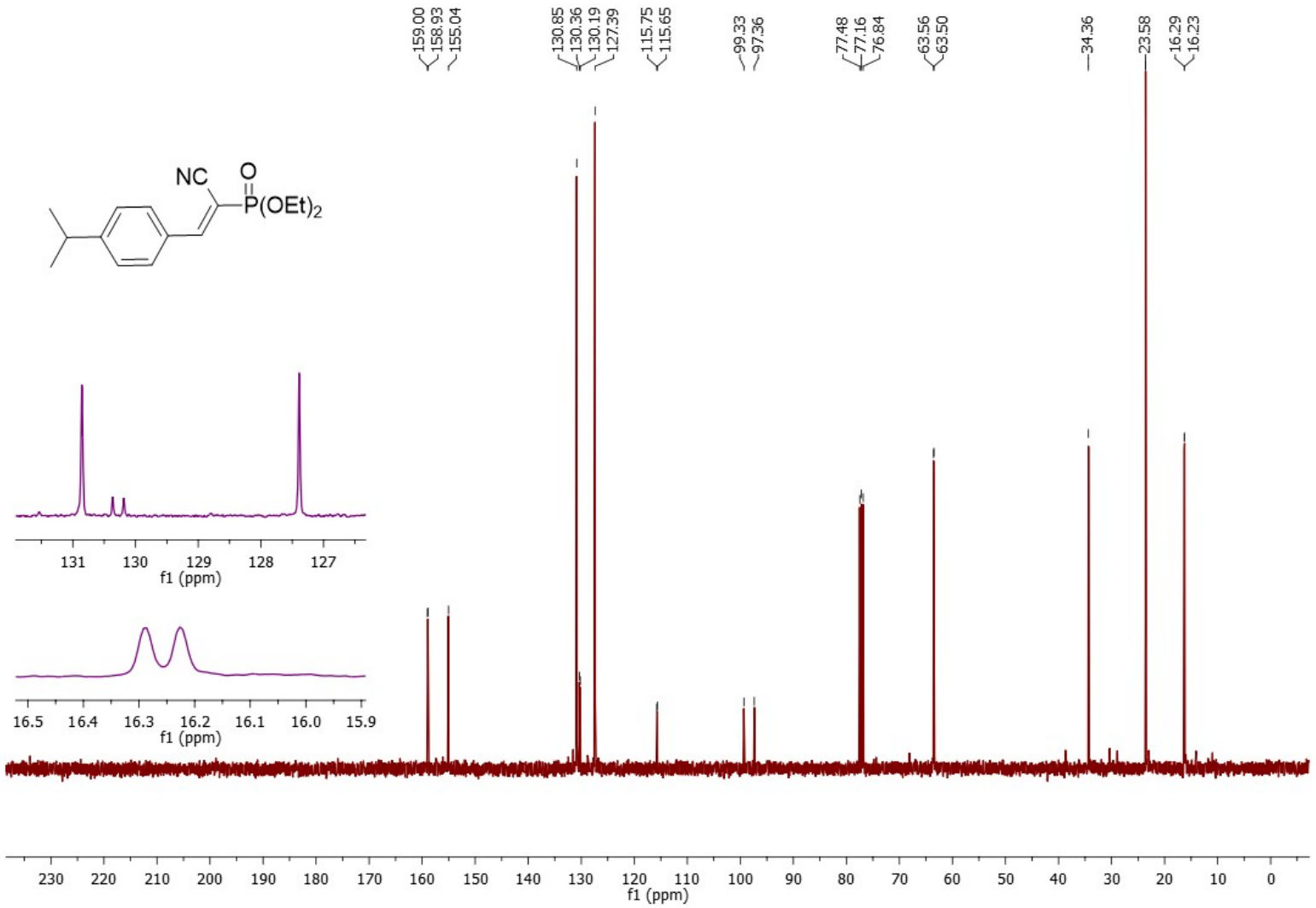


Figure S26: ^{13}C NMR Spectra of 2i

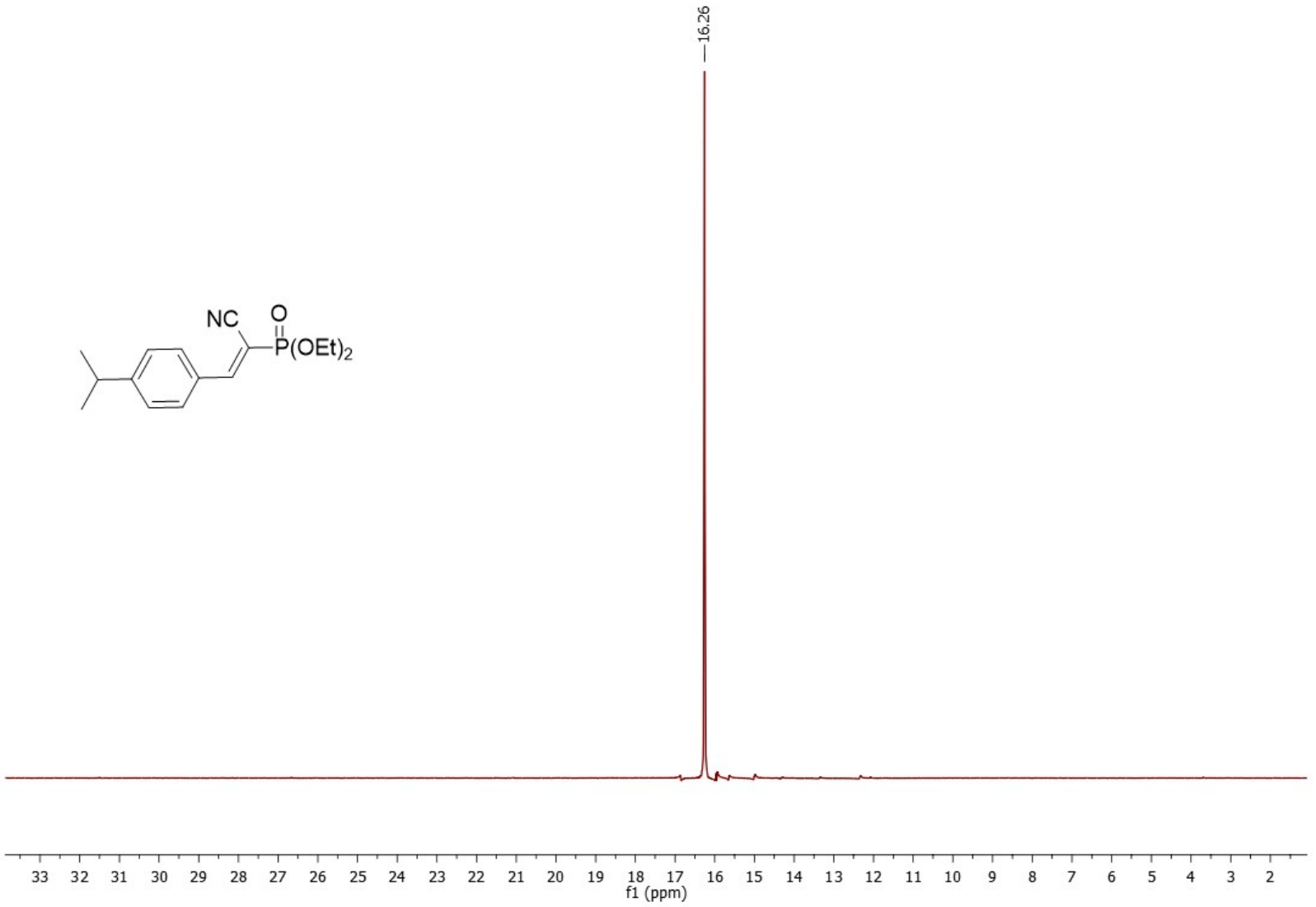


Figure S27: ^{31}P NMR Spectra of 2i

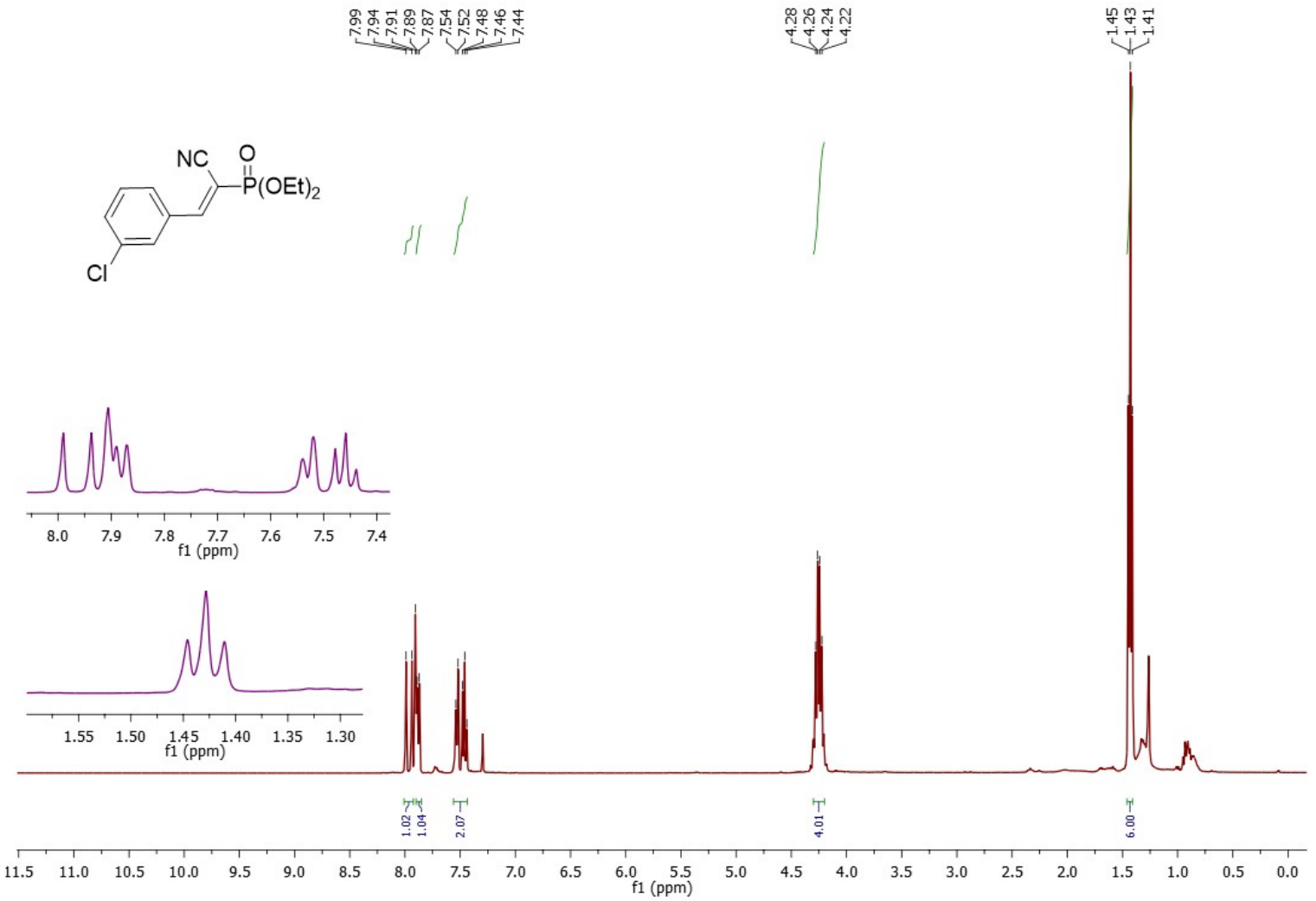


Figure S28: ^{1}HNMR Spectra of 2j

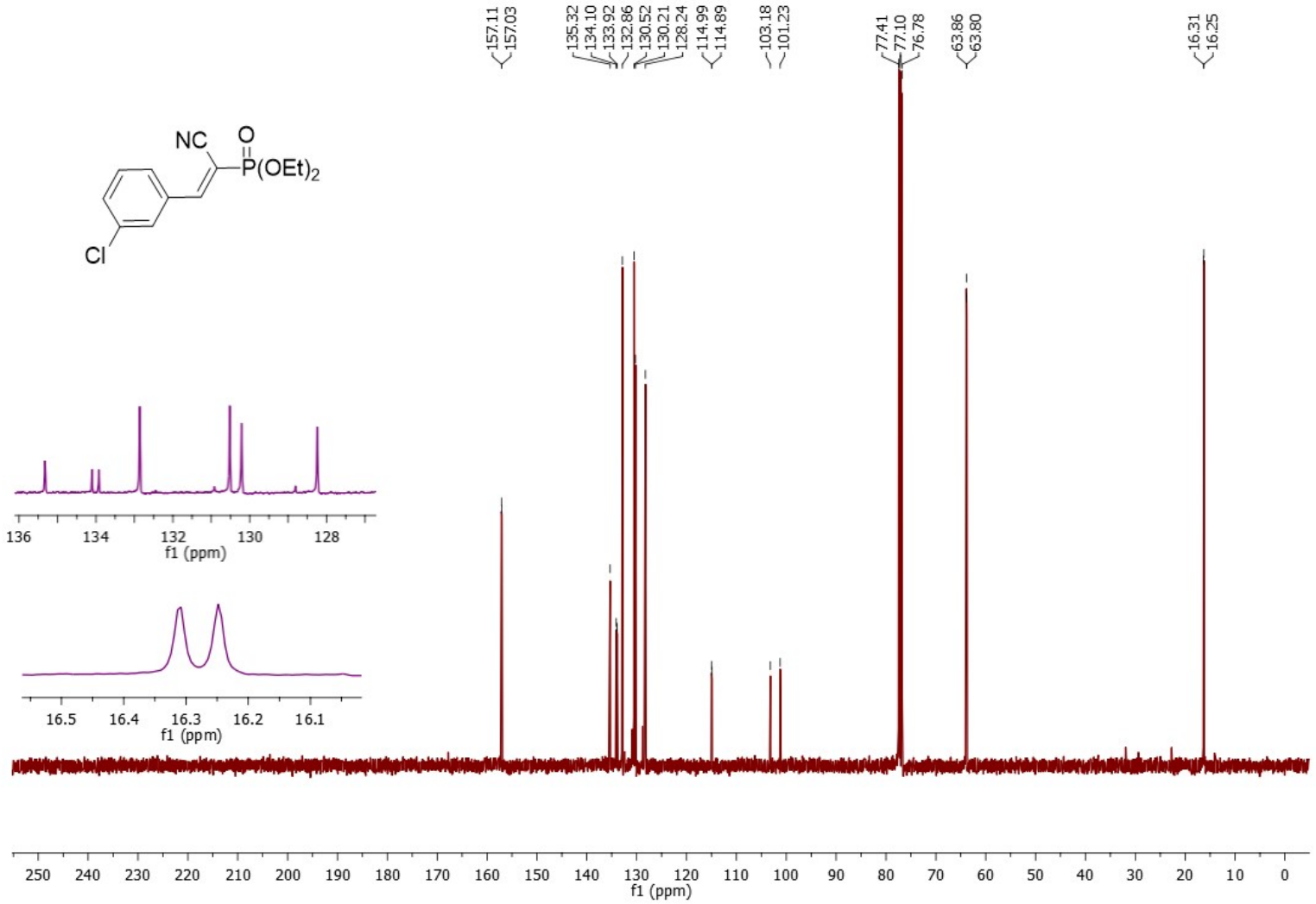


Figure S29: ^{13}C NMR Spectra of 2j

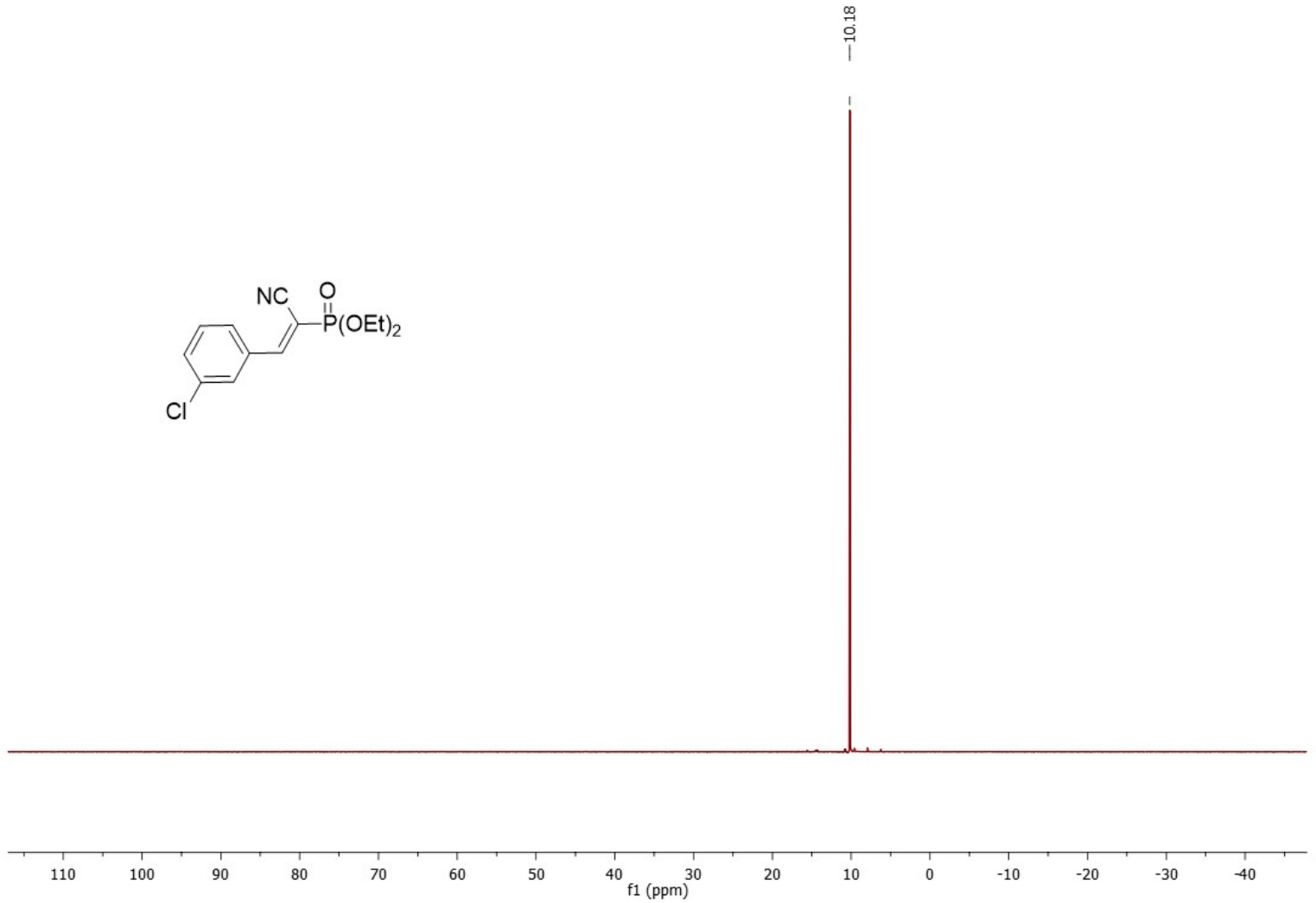


Figure S30: ^{31}P NMR Spectra of 2j

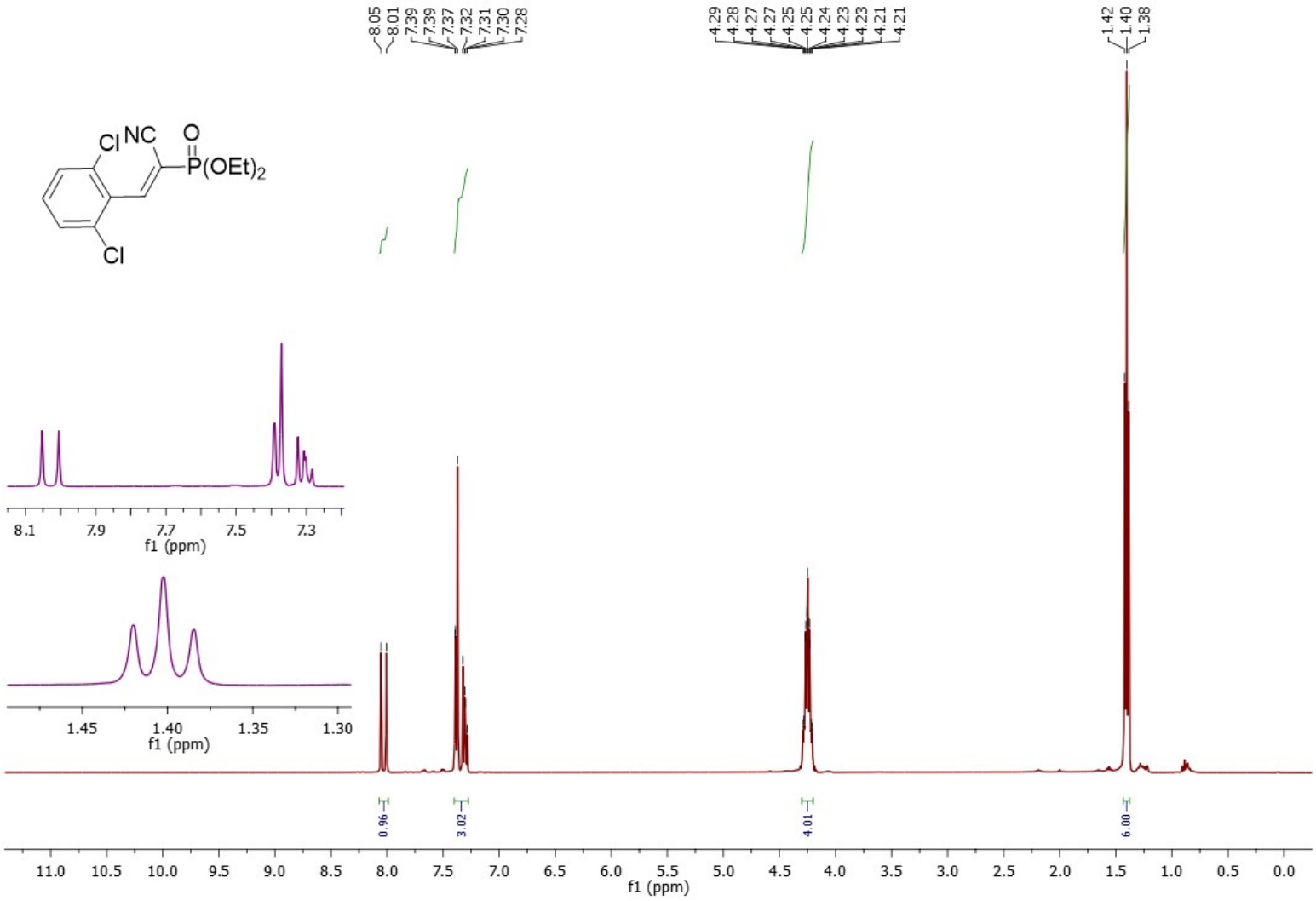


Figure S31: ^{1}HNMR Spectra of 2k

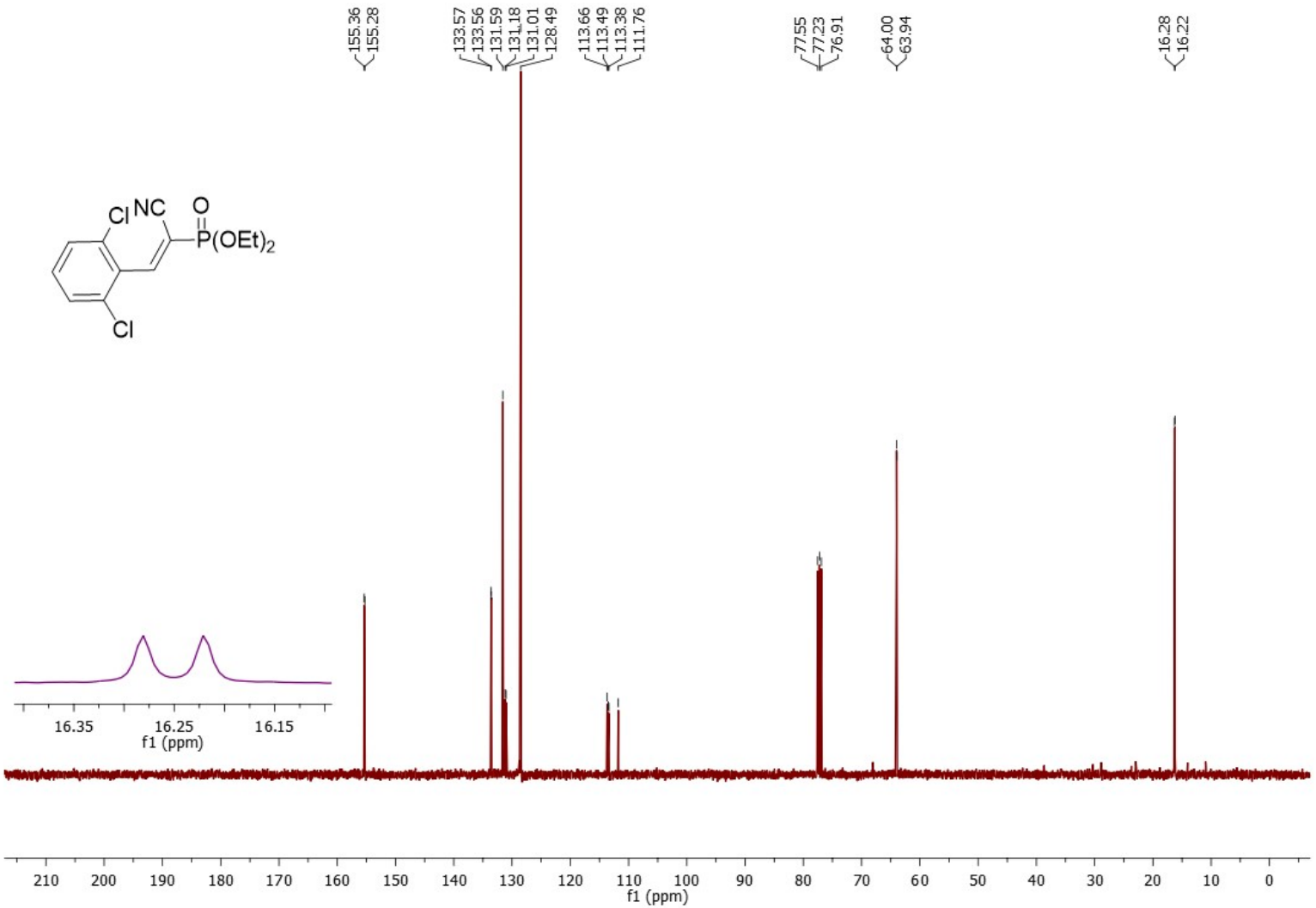


Figure S32: ^{13}C NMR Spectra of 2k

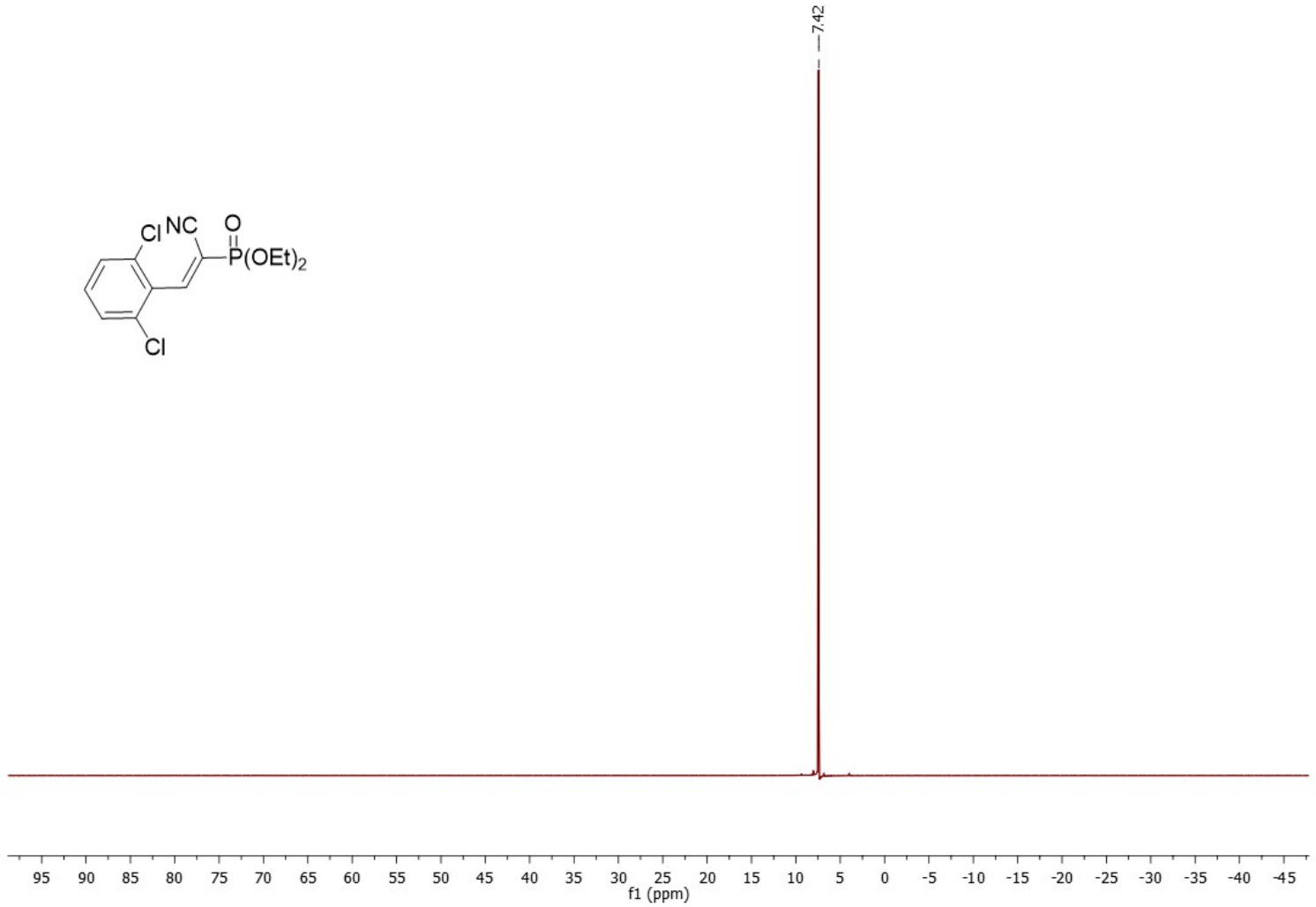


Figure S33: ^{31}P NMR Spectra of 2k

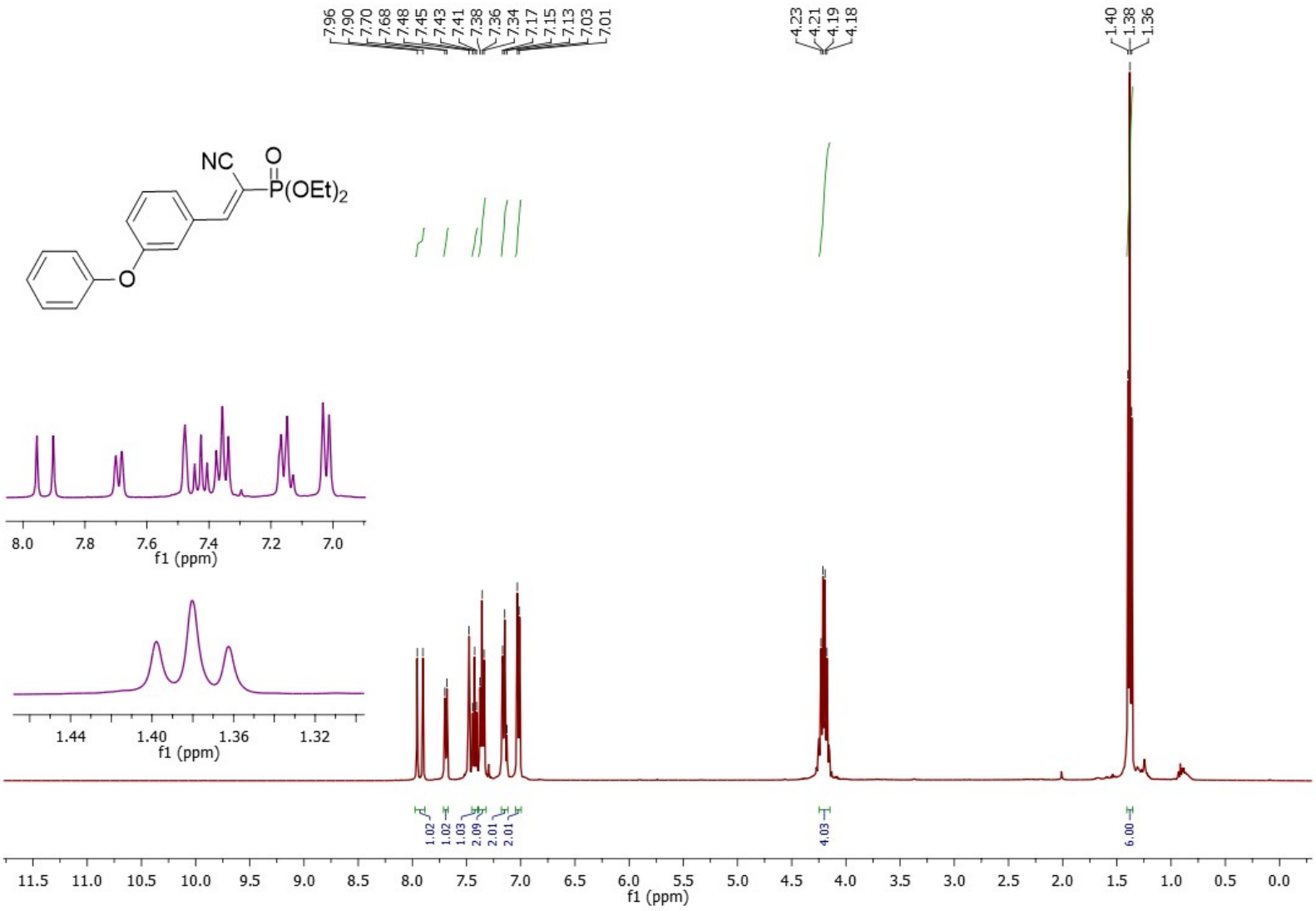


Figure S34: ^{1}HNMR Spectra of 2l

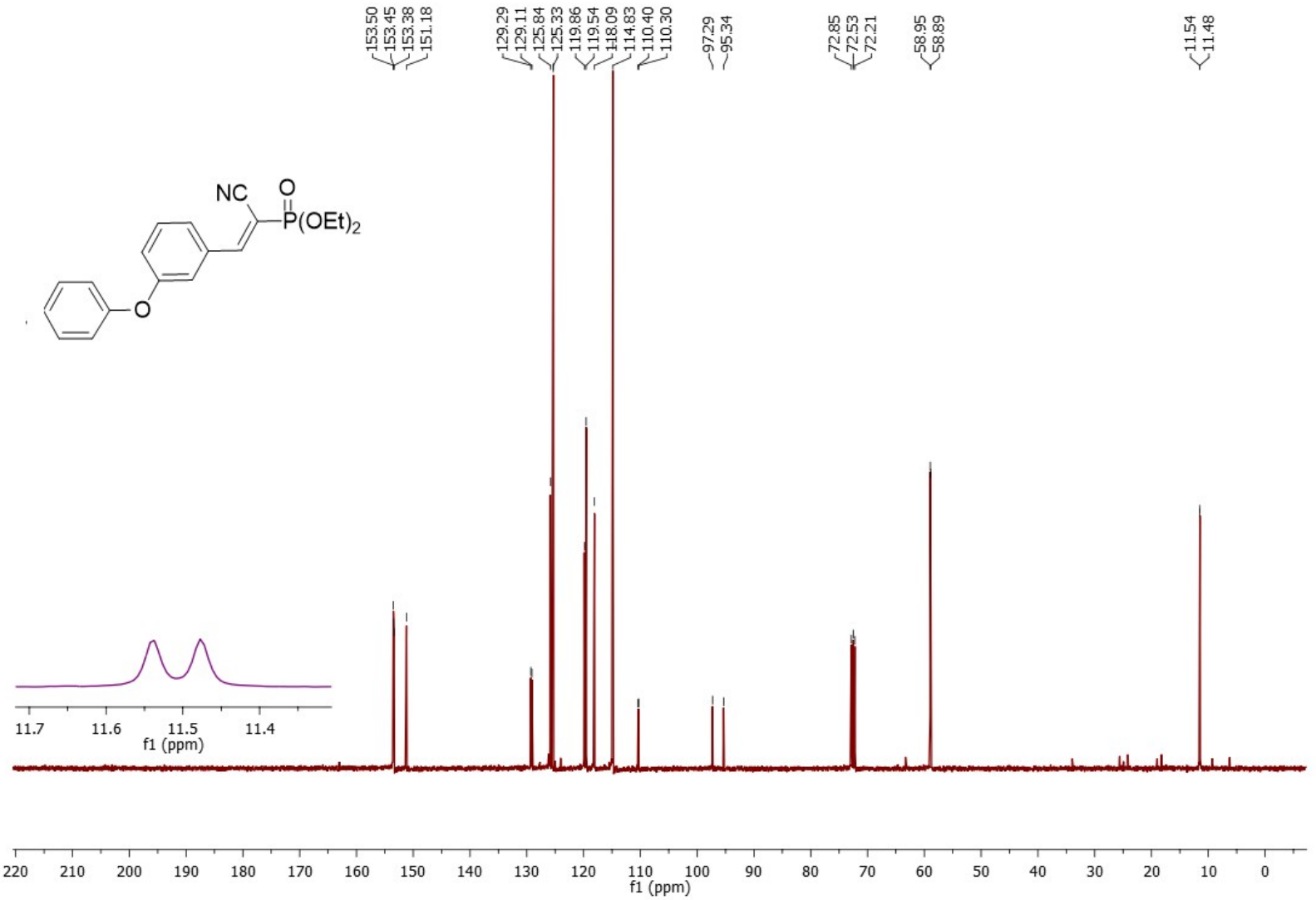


Figure S35: ^{13}C NMR Spectra of 2l

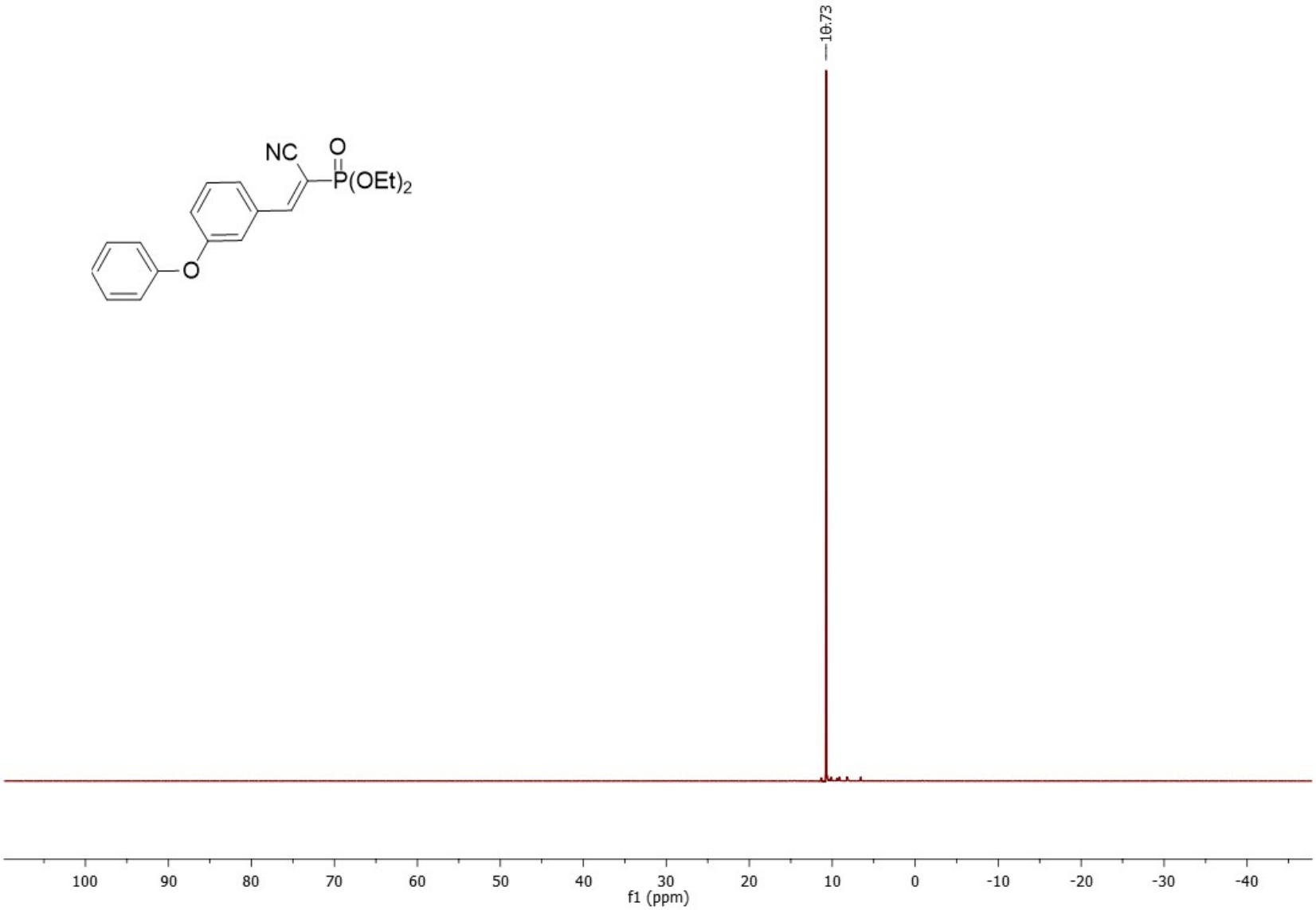


Figure S36: ^{31}PNMR Spectra of 2l

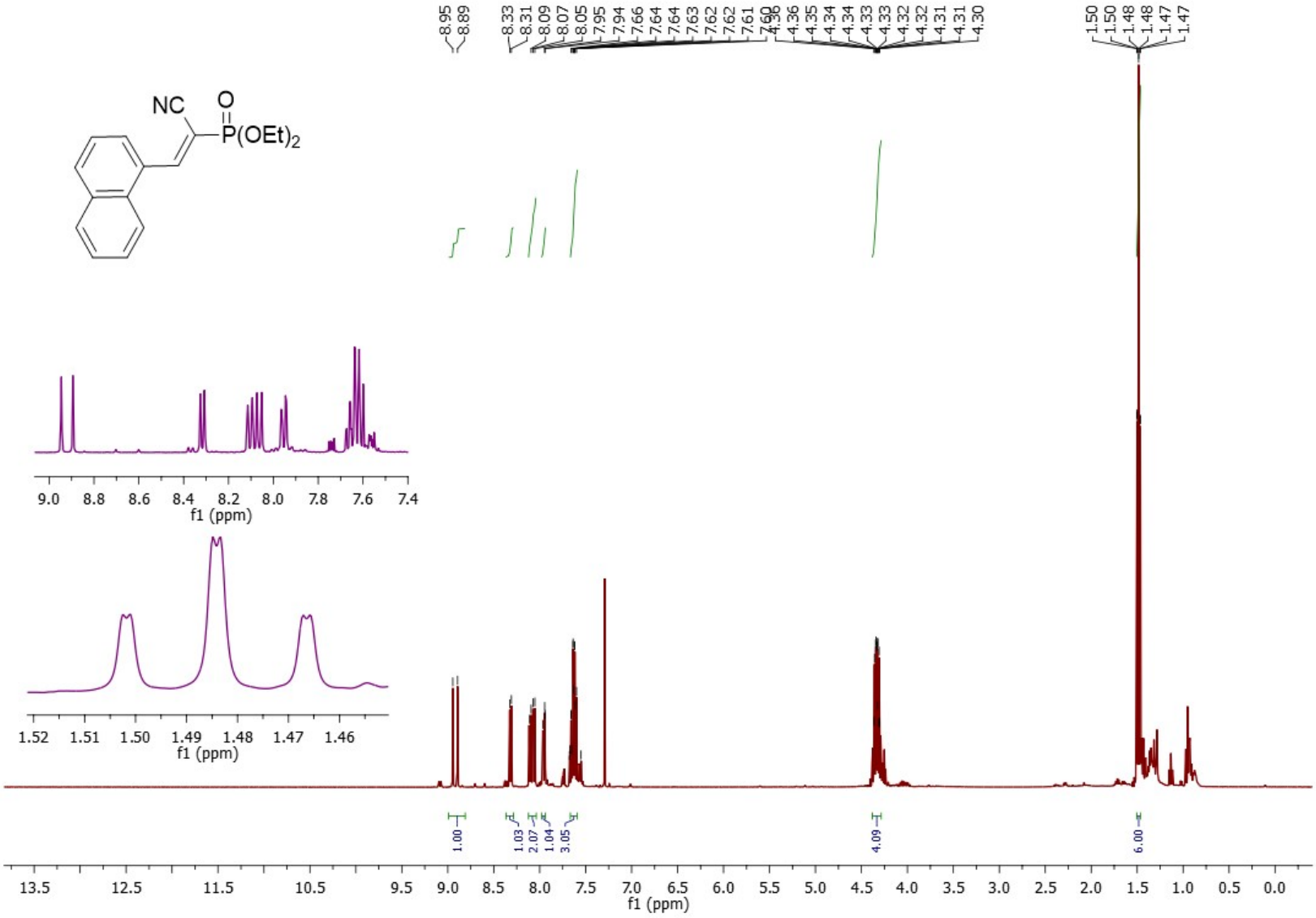


Figure S37: ^{1}HNMR Spectra of 2m

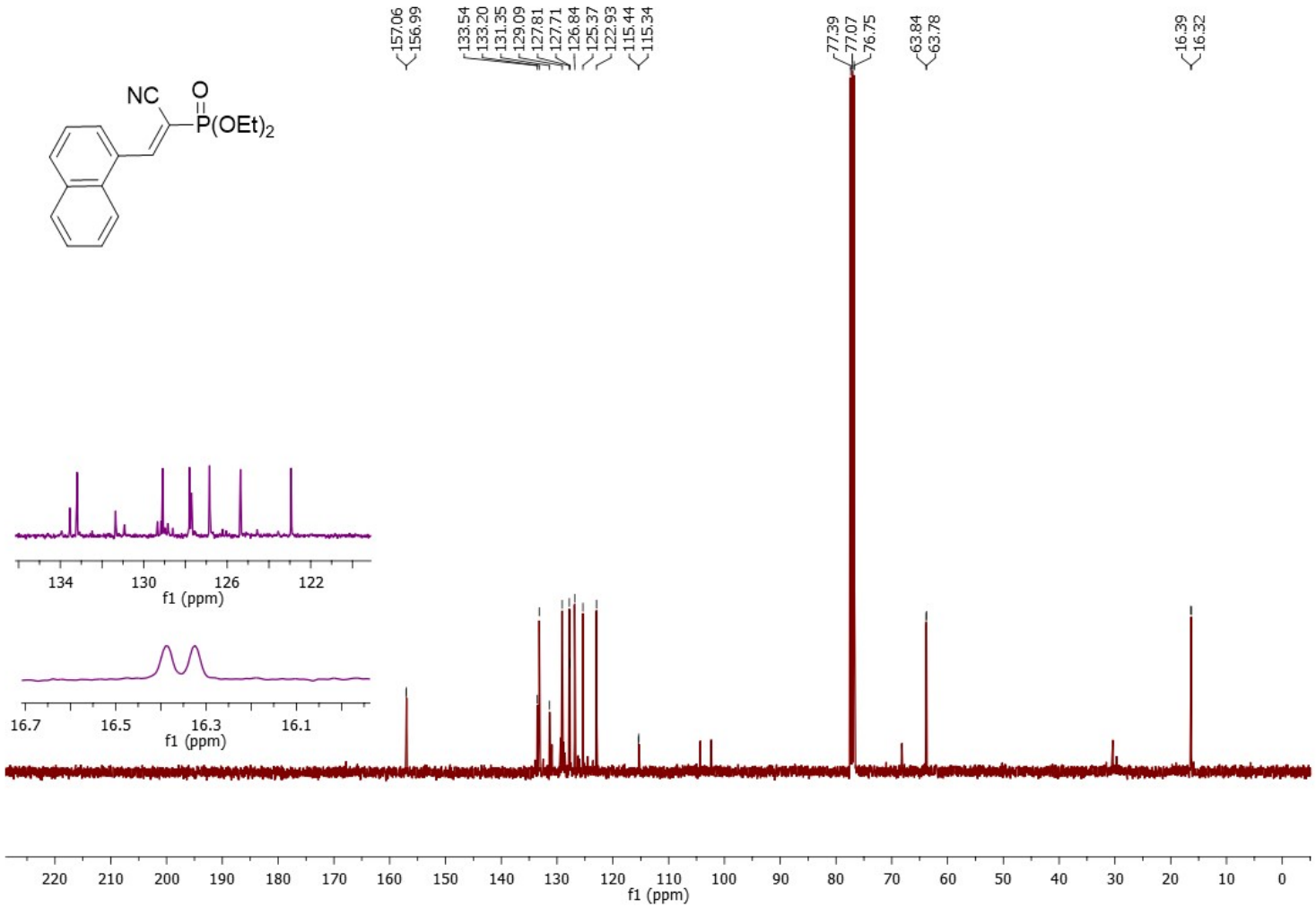


Figure S38: ^{13}C NMR Spectra of 2m

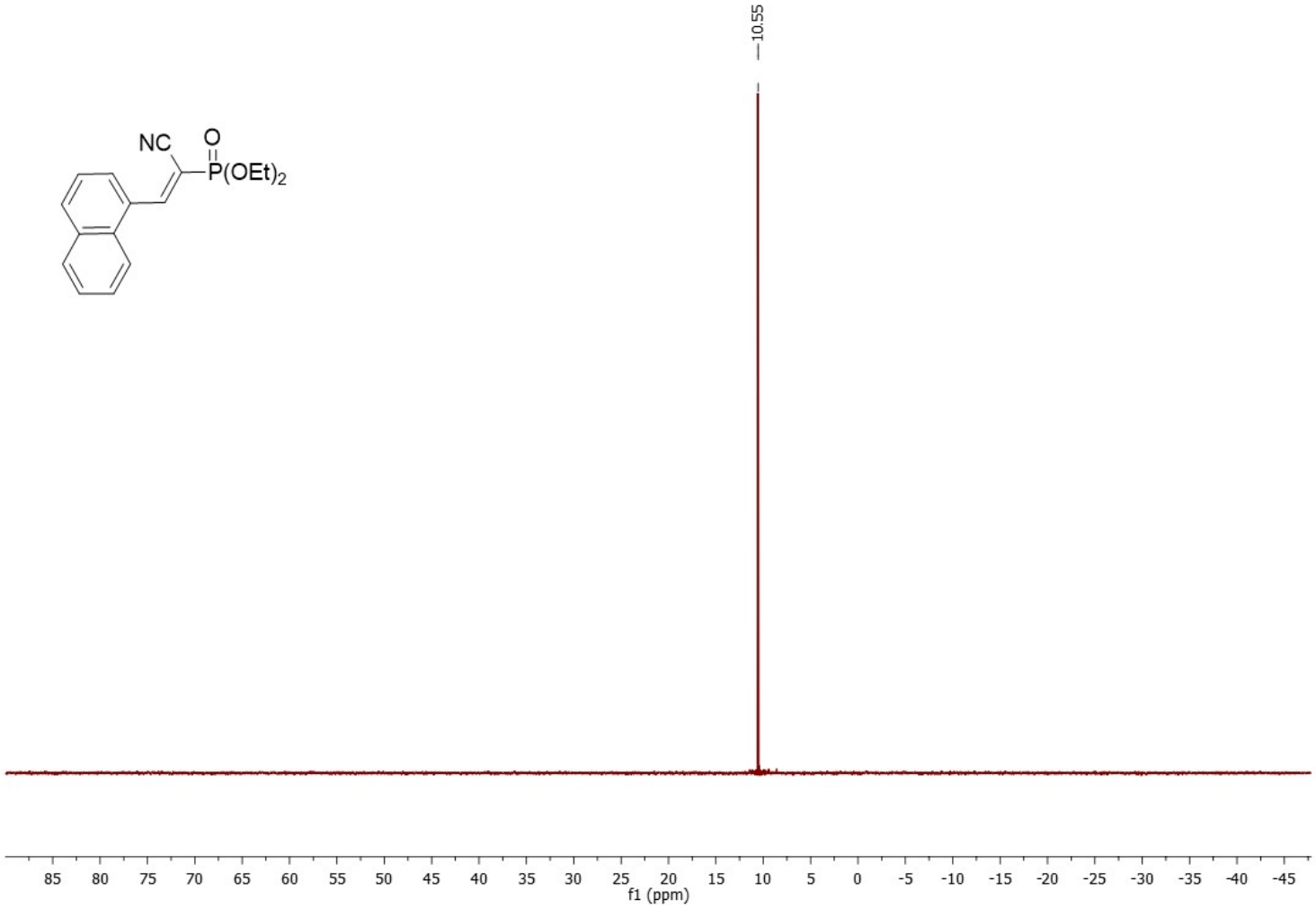


Figure S39: ^{31}P NMR Spectra of 2m

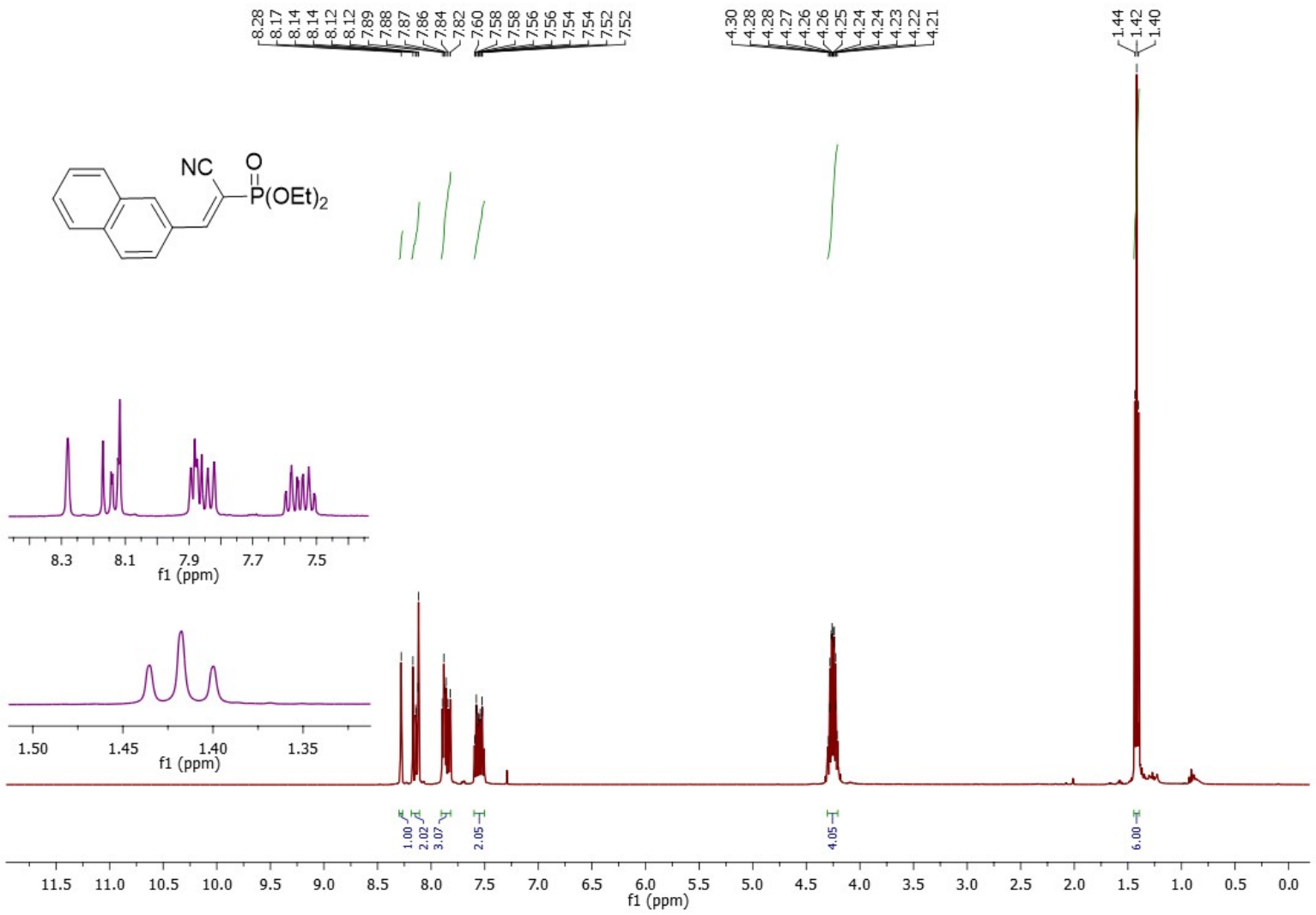


Figure S40: ^{1}HNMR Spectra of 2n

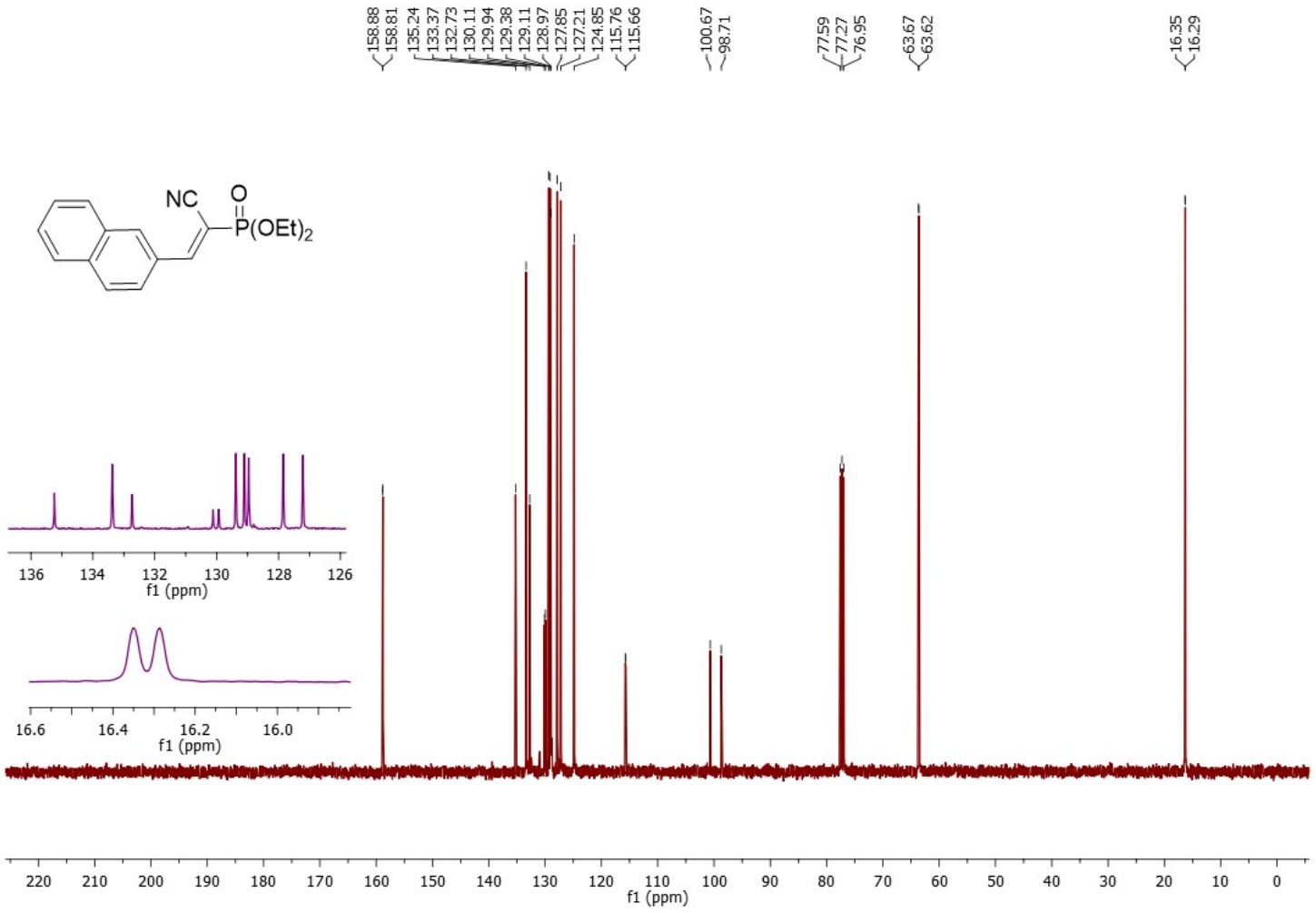


Figure S41: ^{13}C NMR Spectra of 2n

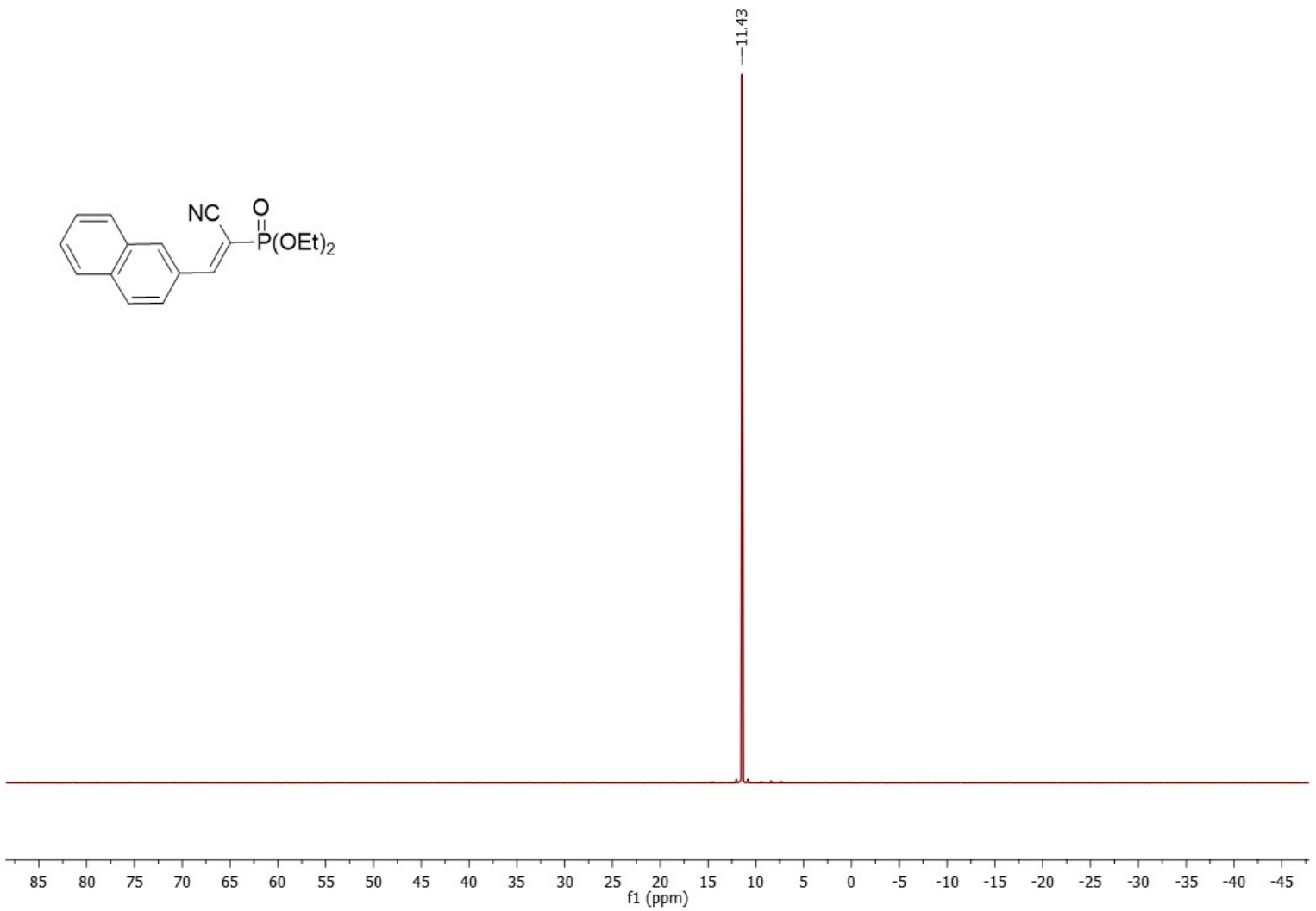


Figure S42: ^{31}P NMR Spectra of 2n

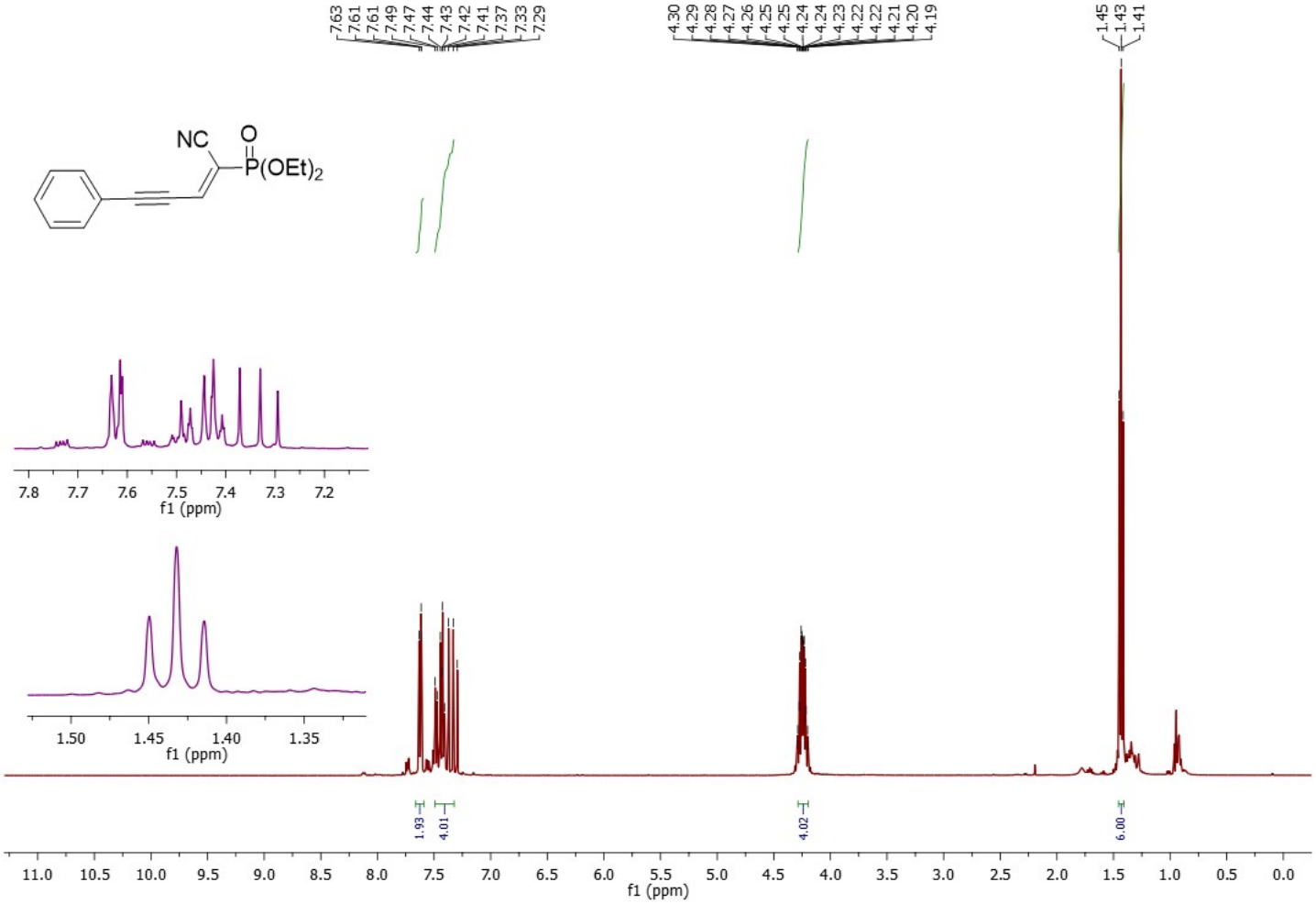


Figure S43: ^{1}HNMR Spectra of 2o

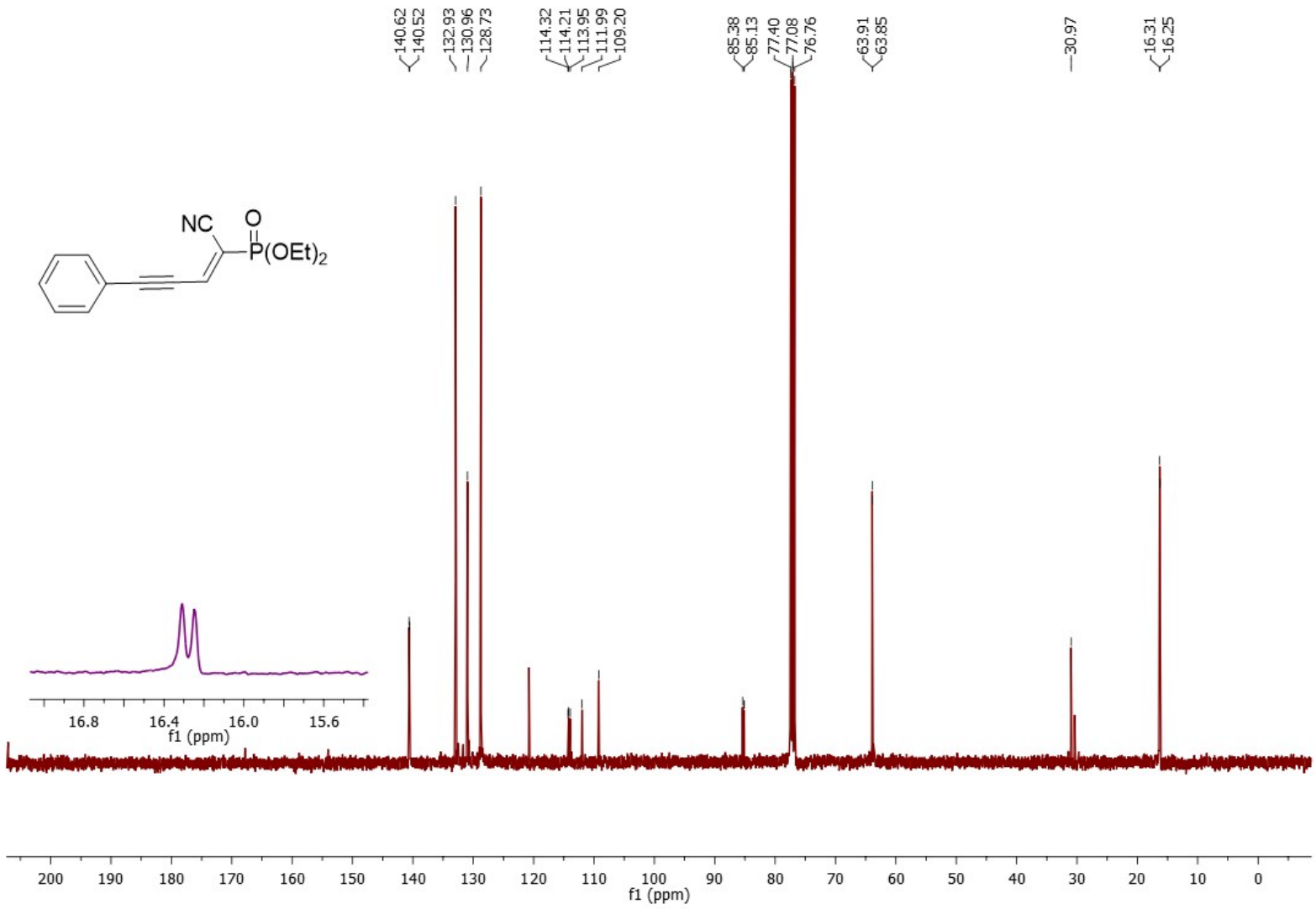


Figure S44: ^{13}C NMR Spectra of 2o

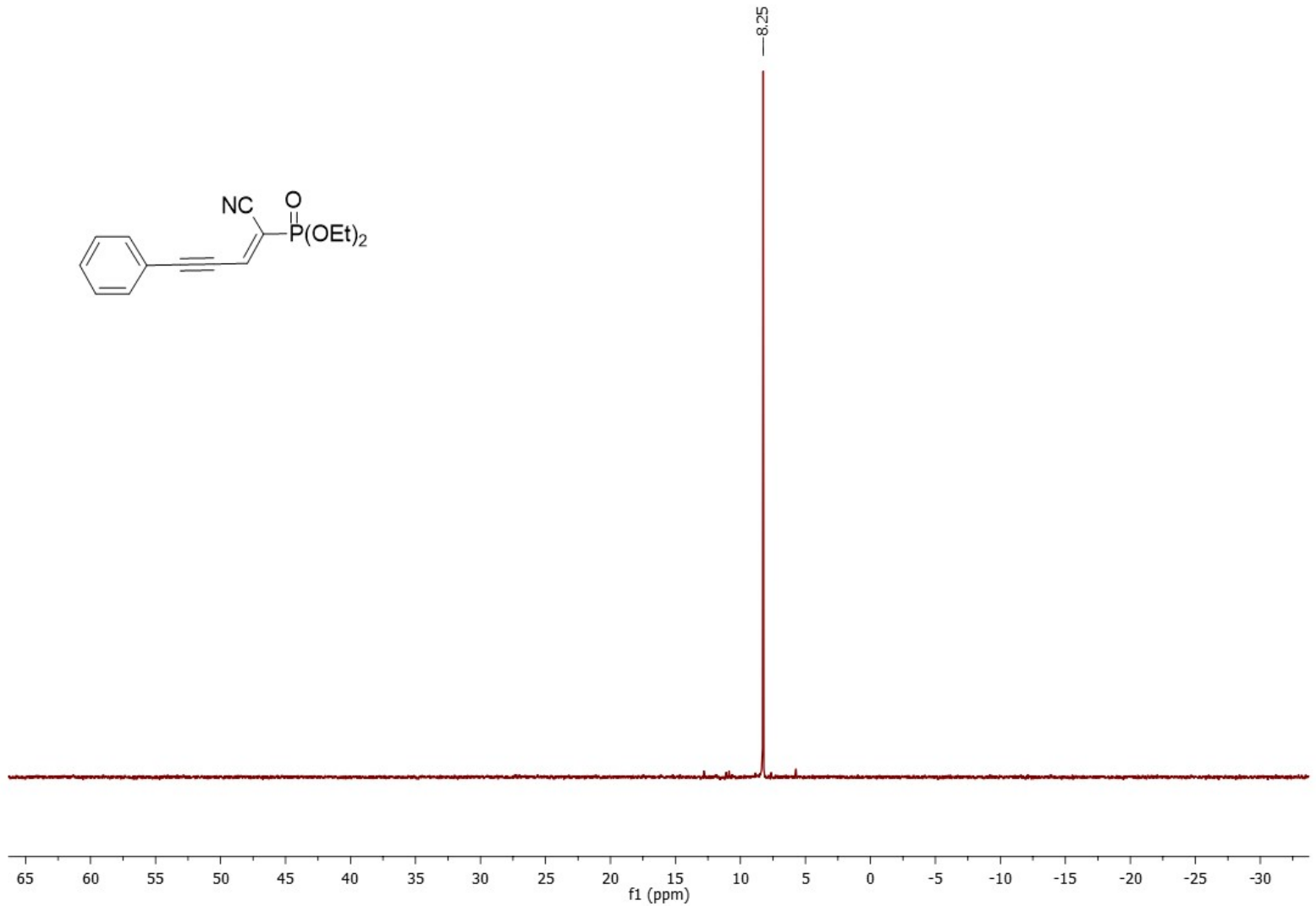


Figure S45: ^{31}P NMR Spectra of 2o

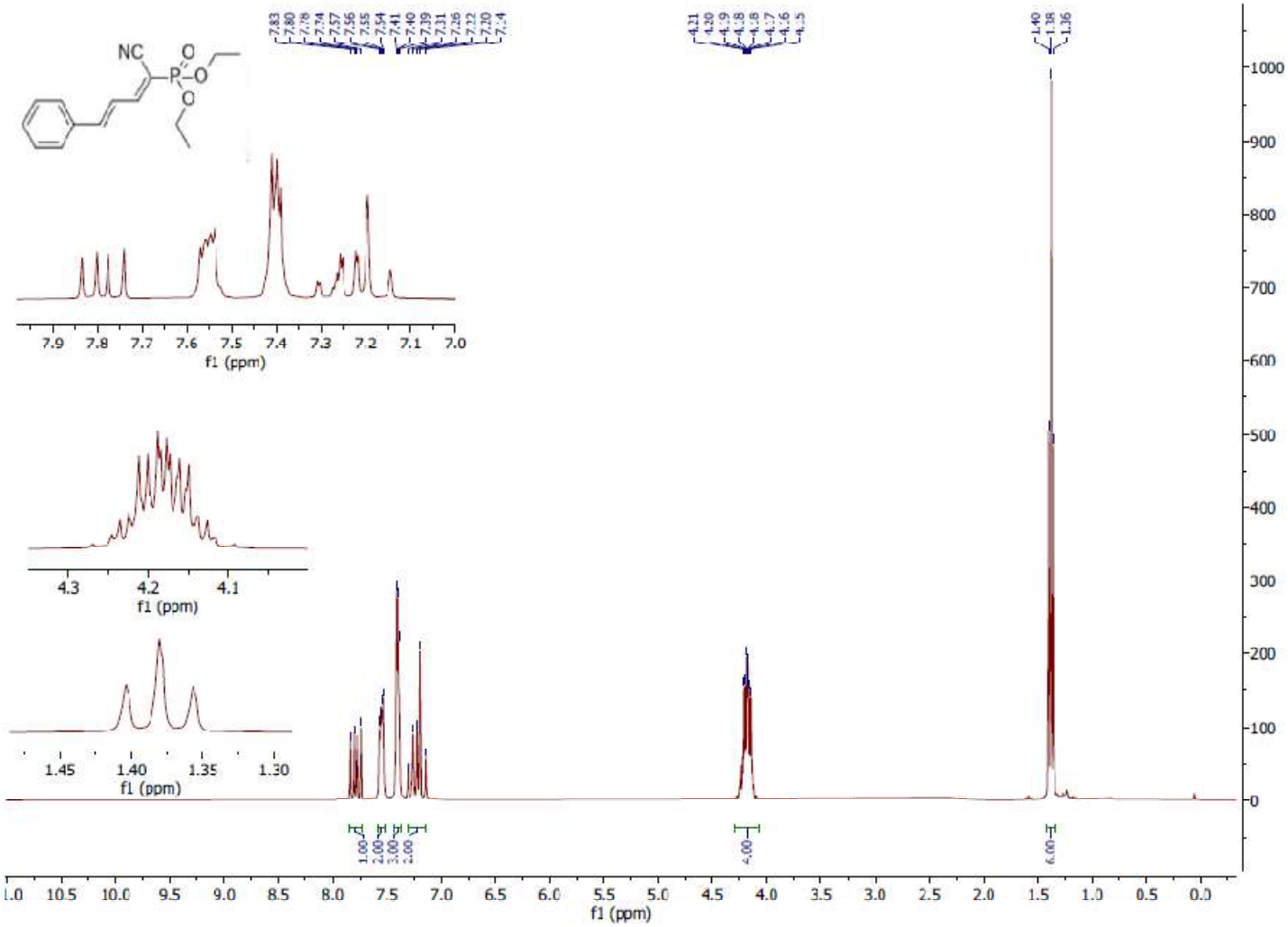


Figure S46: ^{1}HNMR Spectra of 2p

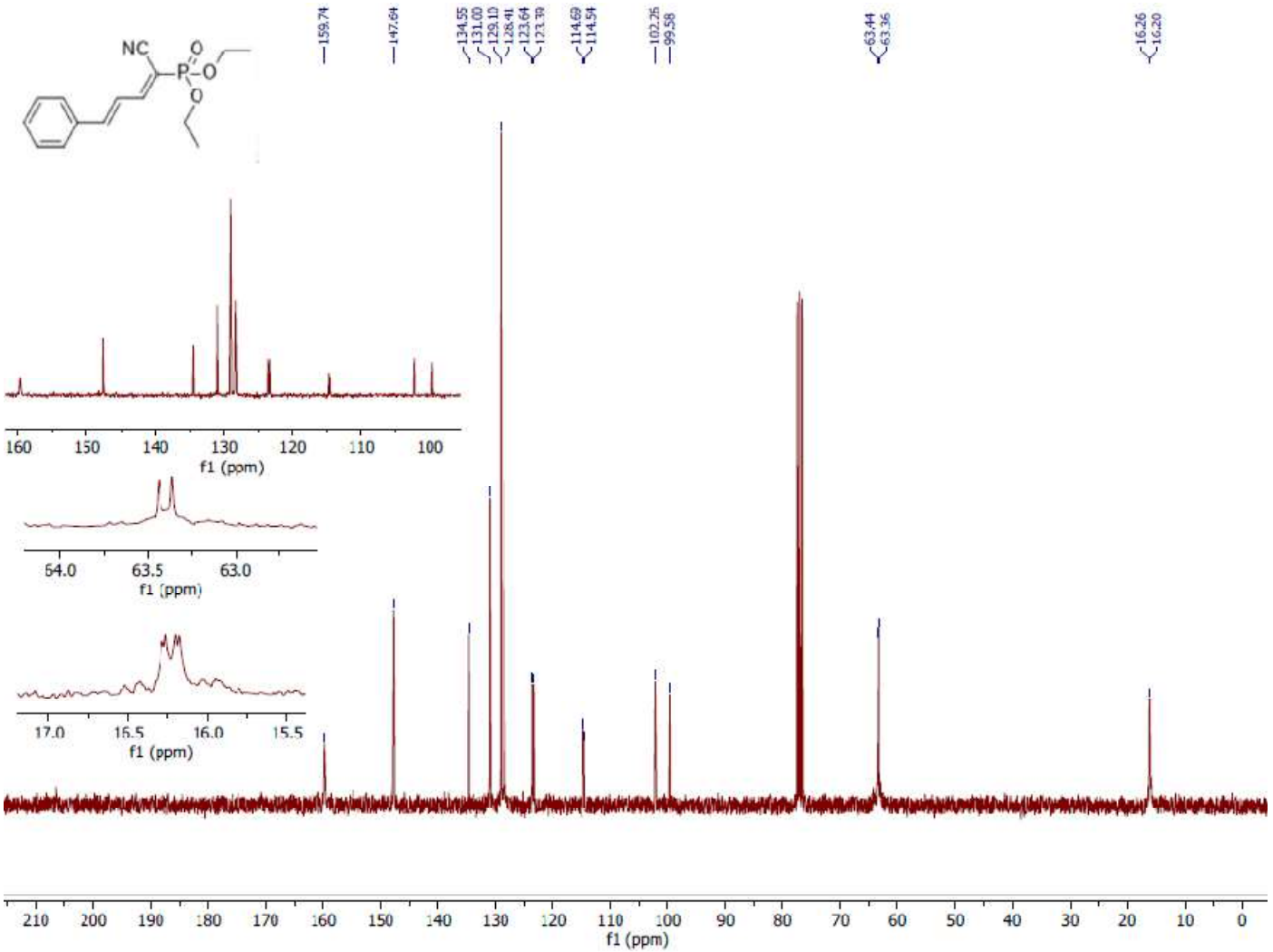


Figure S47: ^{13}C NMR Spectra of 2p

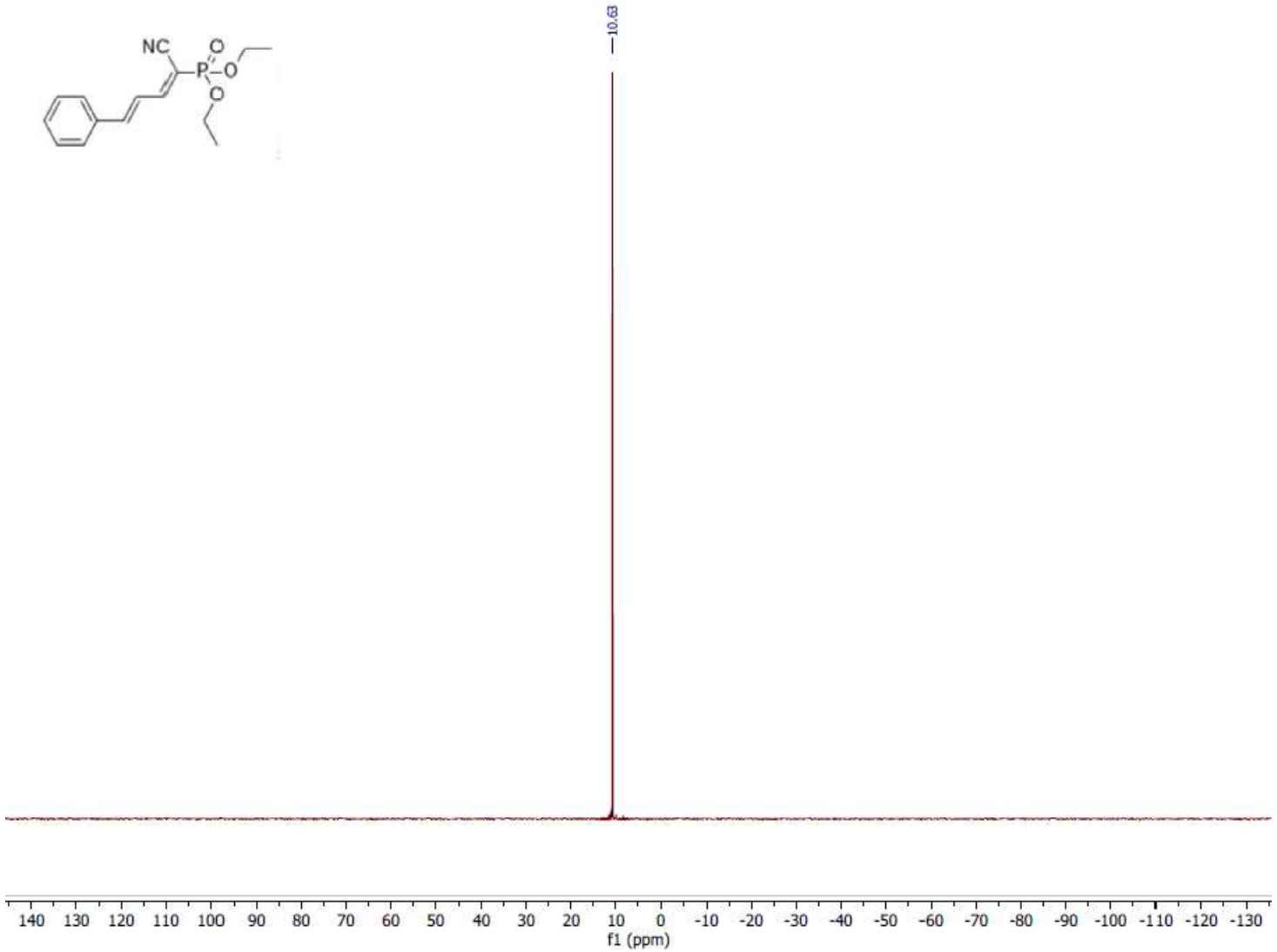


Figure S48: ^{31}P NMR Spectra of 2p

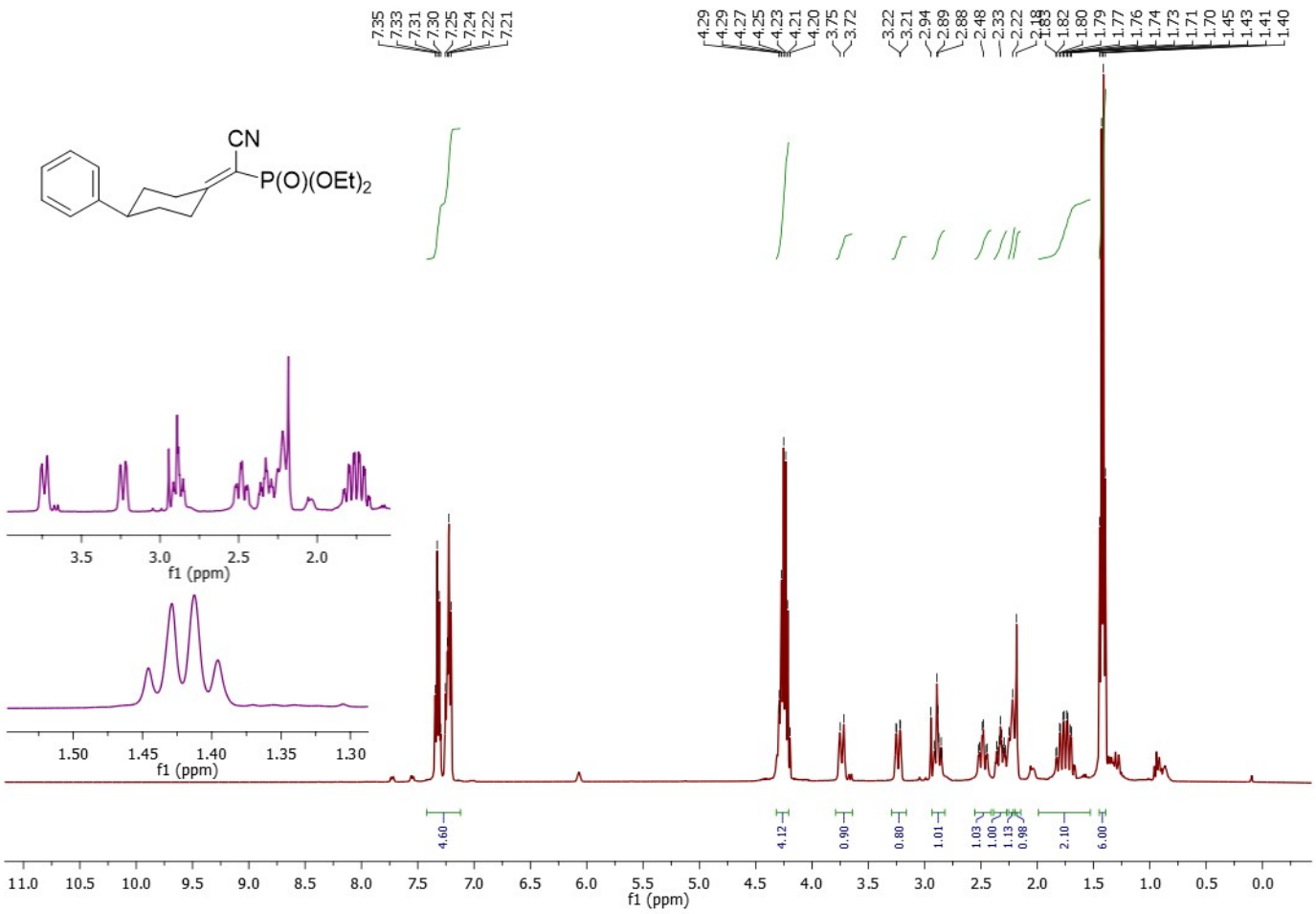


Figure S49: 1HNMR Spectra of 4a

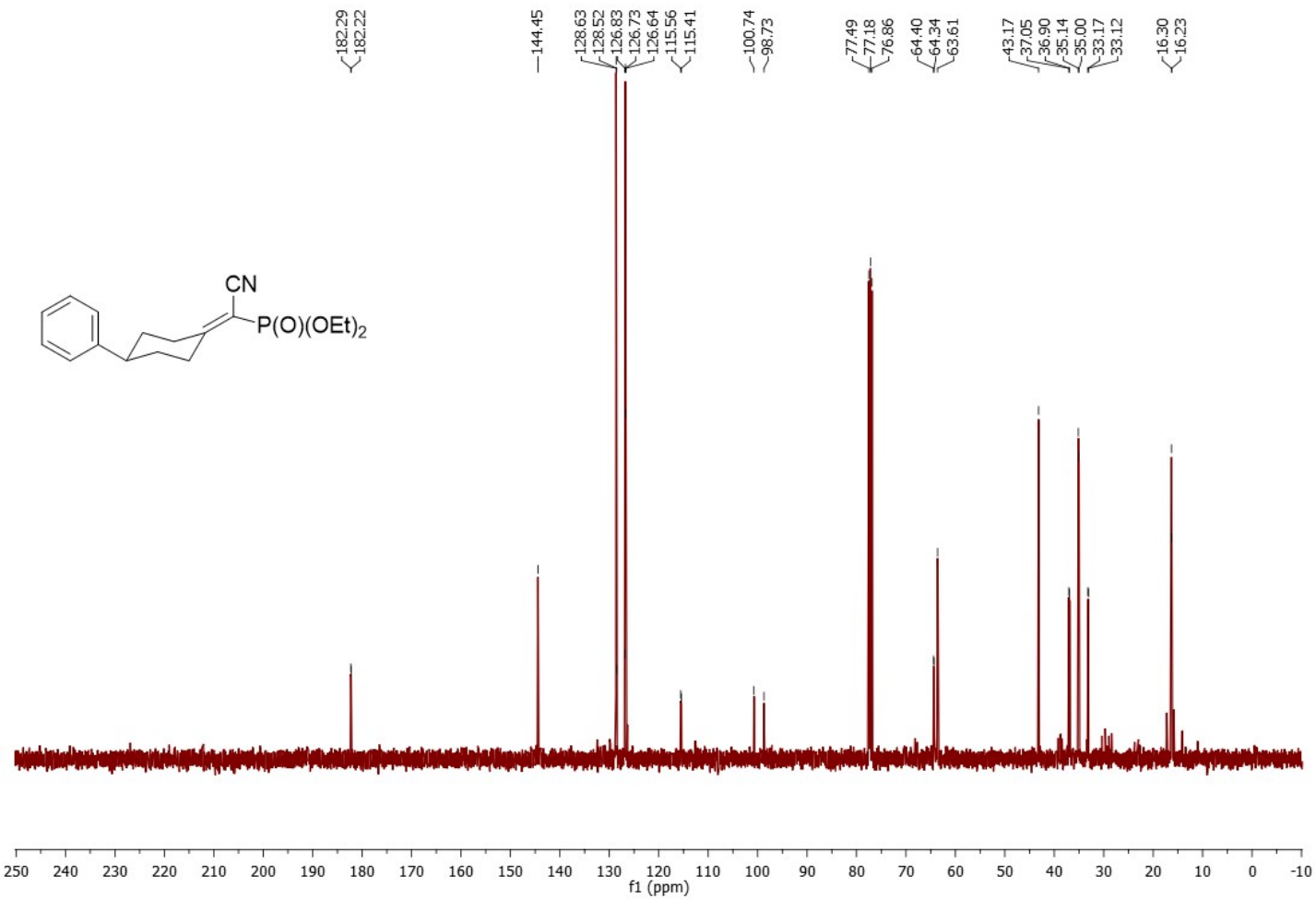


Figure S50: ^{13}CNMR Spectra of 4a

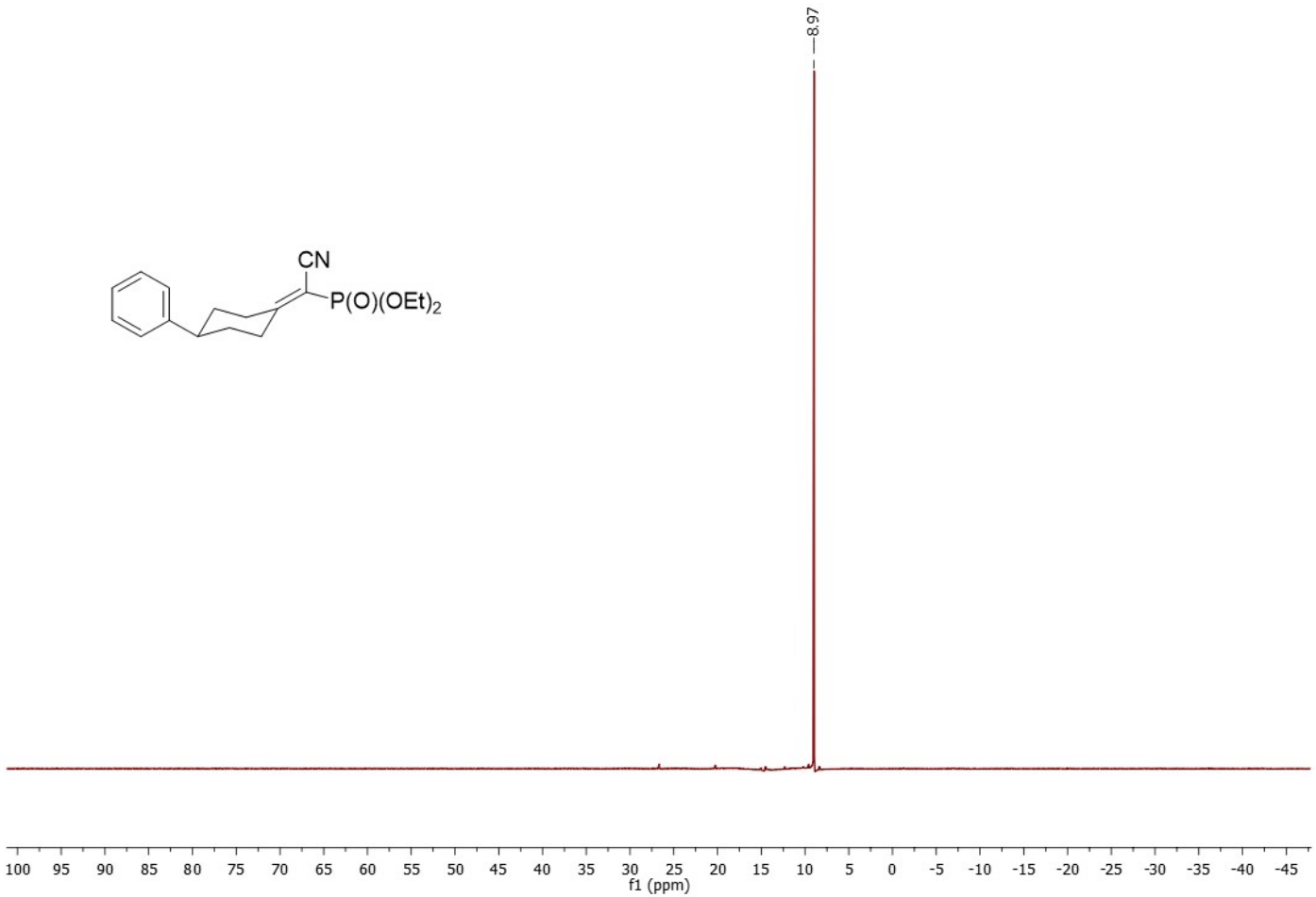


Figure S51: ^{31}P NMR Spectra of 4a

Elemental Composition Report

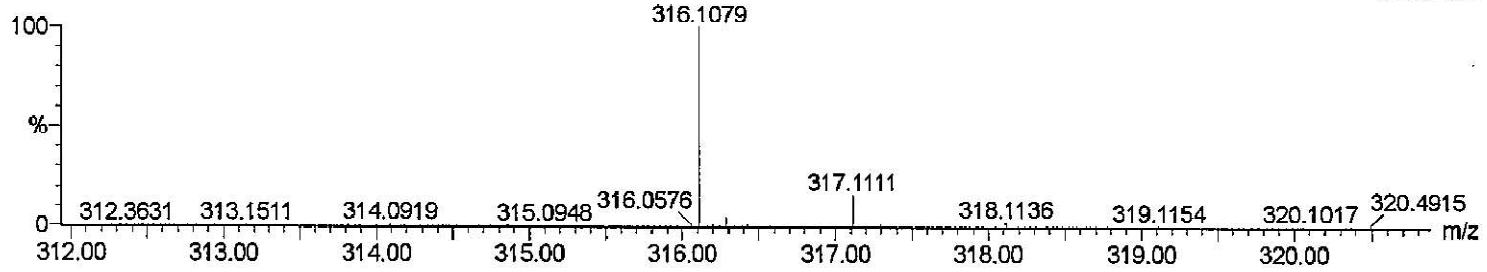
Single Mass Analysis

Tolerance = 10.0 mDa / DBE: min = -1.5, max = 300.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-300 H: 0-3000 N: 1-1 O: 3-3 Na: 1-1 P: 1-1

VNL17
M-18969 128 (1.298) AM2 (Ar,22000.0,0.00,0.00); ABS; Cm (120:149)

1: TOF MS ES+
8.58e+007



Minimum:				-1.5				
Maximum:		10.0	5.0	300.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
316.1079	316.1078	0.1	0.3	6.5	964.5	n/a	n/a	C15 H20 N O3 Na P

Figure S52: HR Mass data for the unstable compound 2q

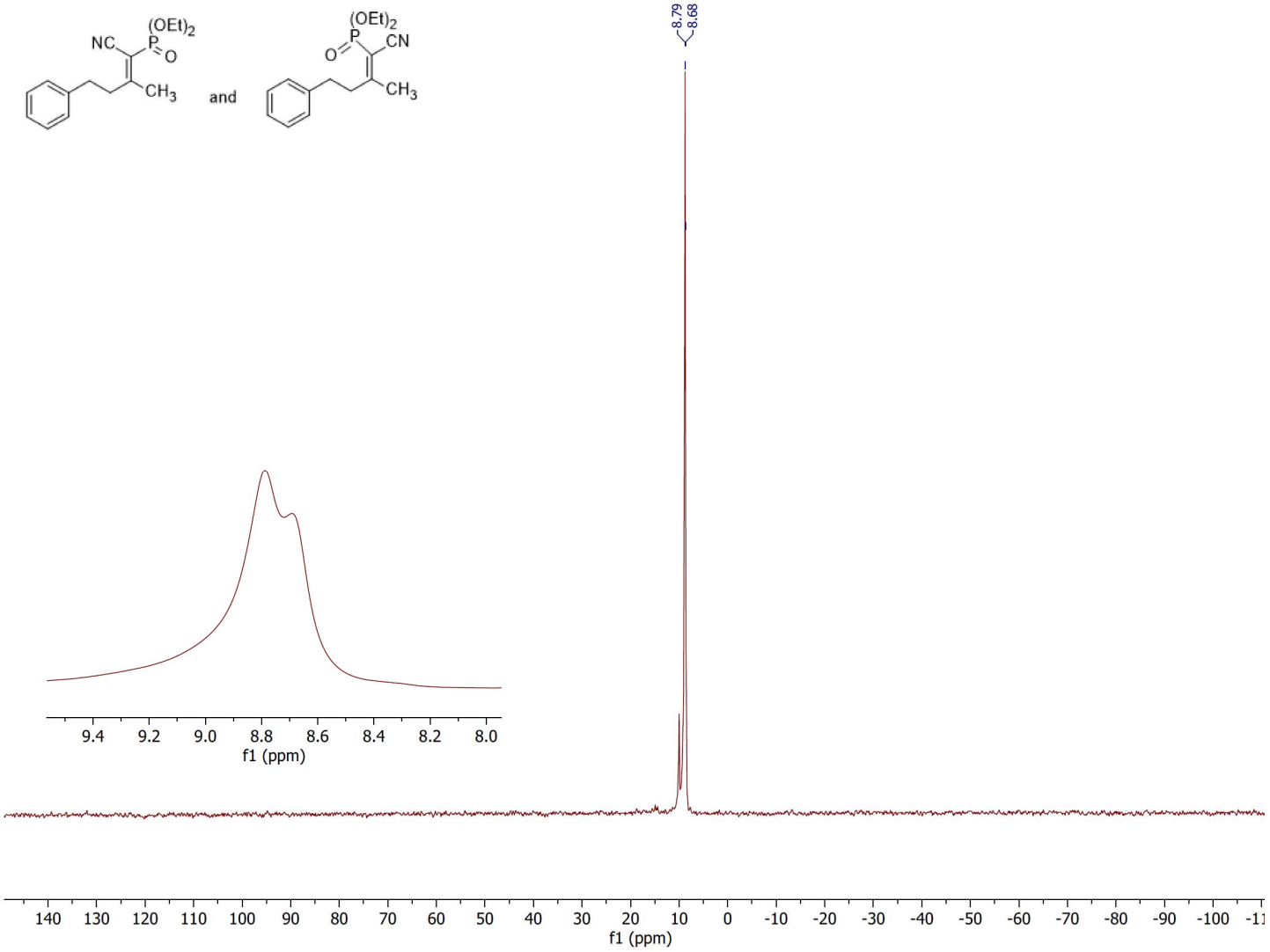


Figure S53: ^{31}P NMR Spectra of 4b (a mixture of E and Z ~50:50)

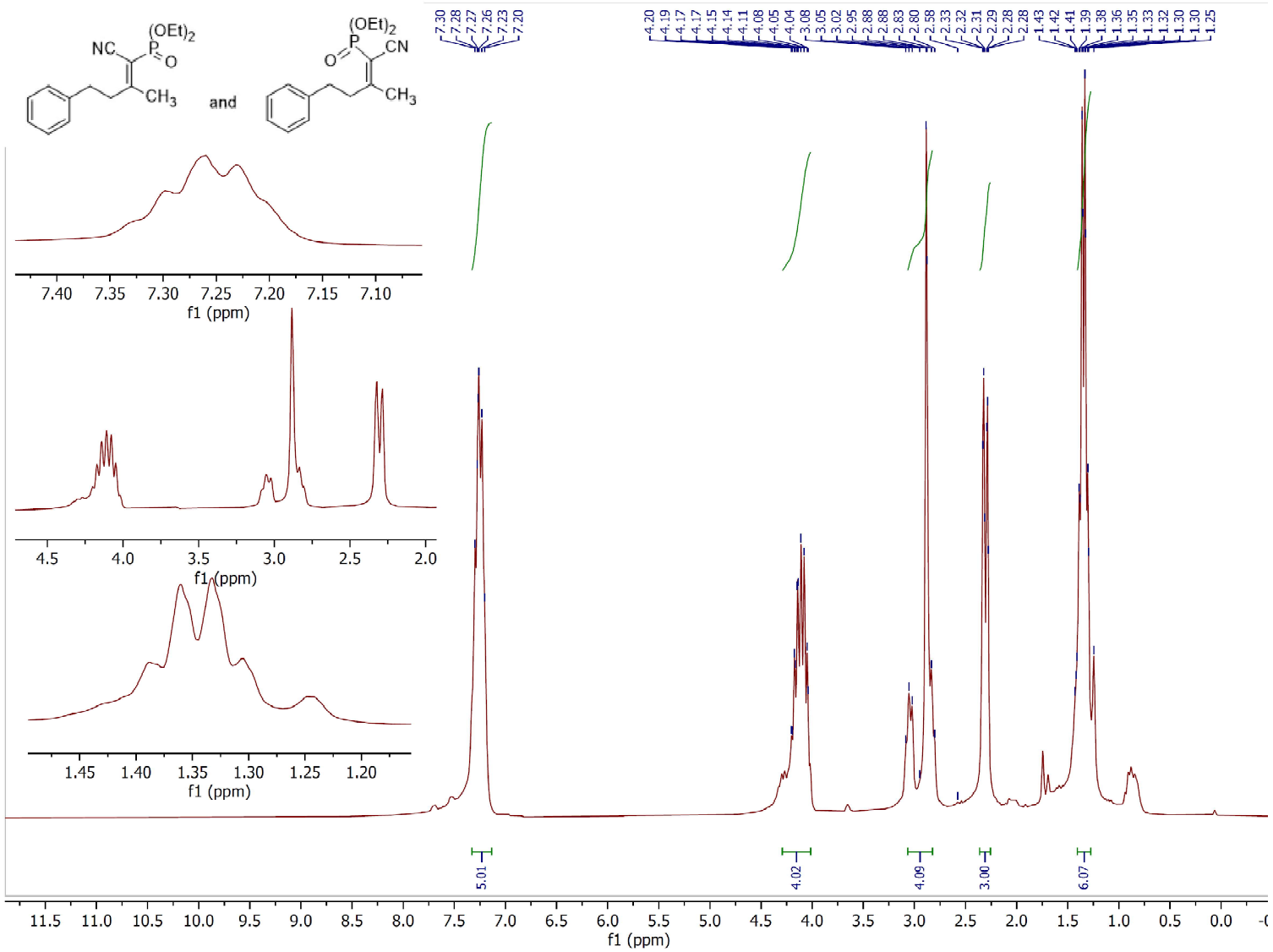


Figure S54: ^{1}H NMR Spectra of 4b (a mixture of E and Z ~50:50)

1. DFT calculations

All calculations were carried out by using *Gaussian 09* program, revision D.01.[1] Molecular geometries were optimized and characterized by frequency analysis using a hybrid density functional (M06).[2] Ahlrichs' SVP all–electron basis set[3] for Zn atom and 6-31+G(d) basis set for other atoms were used for all calculations. Single imaginary frequency was obtained in all transition states, which were supported by the intrinsic reaction coordinate (IRC) calculations using 'lqa' keyword. Each geometry of intermediates was obtained by geometry optimization of the IRC geometries. The geometries are visualized by using the *CYLview* program.[4] For bonding analysis, Bader's Quantum Theory of Atoms in Molecules (QTAIM) was applied by using *AIMAll* program.[5]

1. 1 For starting molecules

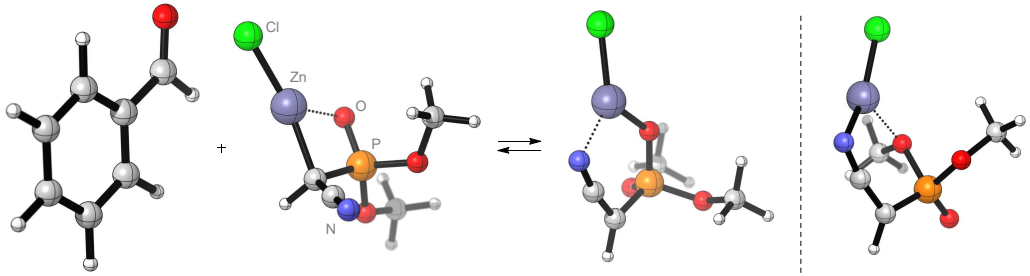


Table S1. Coordinates and energies for optimized geometry of **1a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.980841	0.464852	0.000108
2	8	0	-2.842811	-0.392077	-0.000232
3	1	0	-2.258824	1.544332	0.000427
4	6	0	-0.533033	0.205338	0.000113
5	6	0	0.352246	1.286655	0.000036
6	6	0	-0.040812	-1.105006	0.000113
7	6	0	1.725204	1.063734	-0.000087
8	1	0	-0.043731	2.303191	0.000103
9	6	0	1.328875	-1.326405	0.000042
10	1	0	-0.746995	-1.933879	0.000168
11	6	0	2.210543	-0.242404	-0.000086
12	1	0	2.416042	1.904669	-0.000191
13	1	0	1.717950	-2.342933	0.000091
14	1	0	3.284951	-0.419354	-0.000179

E(RM06) = -345.342780337

Zero-point correction= 0.109661 (Hartree/Particle)

Sum of electronic and thermal Energies= -345.225154

Sum of electronic and thermal Enthalpies= -345.224084

Sum of electronic and thermal Free Energies= -345.268827

Table S2. Coordinates and energies for optimized geometry of **INT1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	1.454010	-0.147284	-0.268157
2	8	0	-0.291835	-1.409112	0.353628
3	15	0	-1.212120	-0.286640	-0.077875
4	6	0	-0.173625	0.831436	-1.010345
5	17	0	3.466995	-0.675578	0.242792
6	8	0	-1.910249	0.463968	1.142894
7	6	0	-1.164725	0.751839	2.334892
8	1	0	-0.702504	-0.161087	2.725232
9	1	0	-0.400436	1.513634	2.134542
10	1	0	-1.882590	1.146514	3.056223

11	8	0	-2.439039	-0.708938	-0.986580
12	6	0	-3.360007	-1.708171	-0.514958
13	1	0	-2.829722	-2.645225	-0.311693
14	1	0	-3.868261	-1.351874	0.387413
15	1	0	-4.085374	-1.855491	-1.316639
16	6	0	-0.333050	2.229594	-0.771995
17	7	0	-0.440467	3.368322	-0.545156
18	1	0	-0.207834	0.582667	-2.078721

E(RM06) = -3017.53999763

Zero-point correction= 0.118728 (Hartree/Particle)

Sum of electronic and thermal Energies= -3017.403732

Sum of electronic and thermal Enthalpies= -3017.402661

Sum of electronic and thermal Free Energies= -3017.473486

Table S3. Coordinates and energies for optimized geometry of **INT1'**

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	30	0	-1.642173	-0.115256	-0.017101
2	8	0	0.195352	0.532764	0.326387
3	15	0	1.512208	-0.059897	-0.182983
4	6	0	1.256103	-1.586099	-0.946094
5	17	0	-3.431010	1.014434	0.391698
6	8	0	2.575471	-0.116346	1.016679
7	6	0	2.226448	-0.842473	2.197776
8	1	0	1.391231	-0.352452	2.711355
9	1	0	1.958985	-1.877206	1.945789
10	1	0	3.110582	-0.838350	2.838515
11	8	0	2.269749	0.912648	-1.188129
12	6	0	2.687380	2.211158	-0.740736
13	1	0	1.862796	2.724109	-0.231740
14	1	0	3.545917	2.118008	-0.067936
15	1	0	2.970514	2.767858	-1.636124
16	6	0	-0.077711	-1.872558	-0.968602
17	7	0	-1.262574	-1.909272	-0.858449
18	1	0	2.029335	-2.159000	-1.445369

E(RM06) = -3017.53811404

Zero-point correction= 0.118776 (Hartree/Particle)

Sum of electronic and thermal Energies= -3017.402218

Sum of electronic and thermal Enthalpies= -3017.401147

Sum of electronic and thermal Free Energies= -3017.469607

** QTAIM projection of **INT1'***

In QTAIM analysis, DI is regarded asa covalent bond order and ellipticityis an useful indicator for characterization of C-C single bond (0in ethane) and C=Cdouble bond (0.45 in ethylene).[6] DI values of Zn-O and Zn-N bonds exhibit highly polarized covalent bond characters.

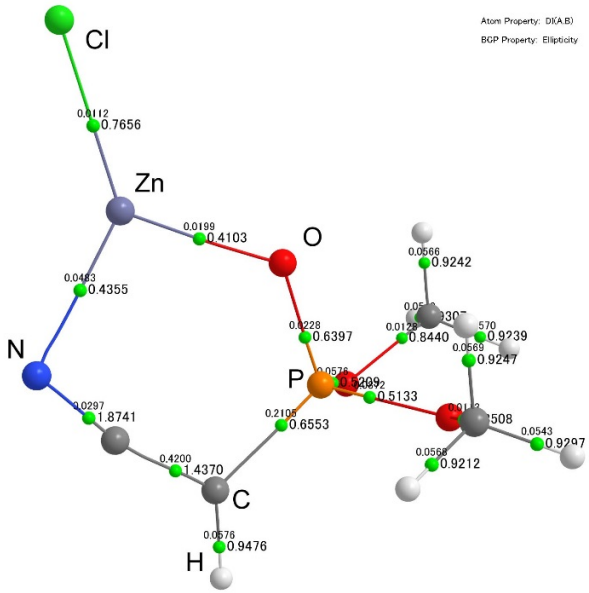


Fig S56. Bond critical points are shown by small spheres. Delocalisation index (DI) and ellipticity are shown by larger and smaller letters, respectively.

1.2 *Reaction pathways for the Knoevenagel reaction*

1.2.1 For (*Z*)-product

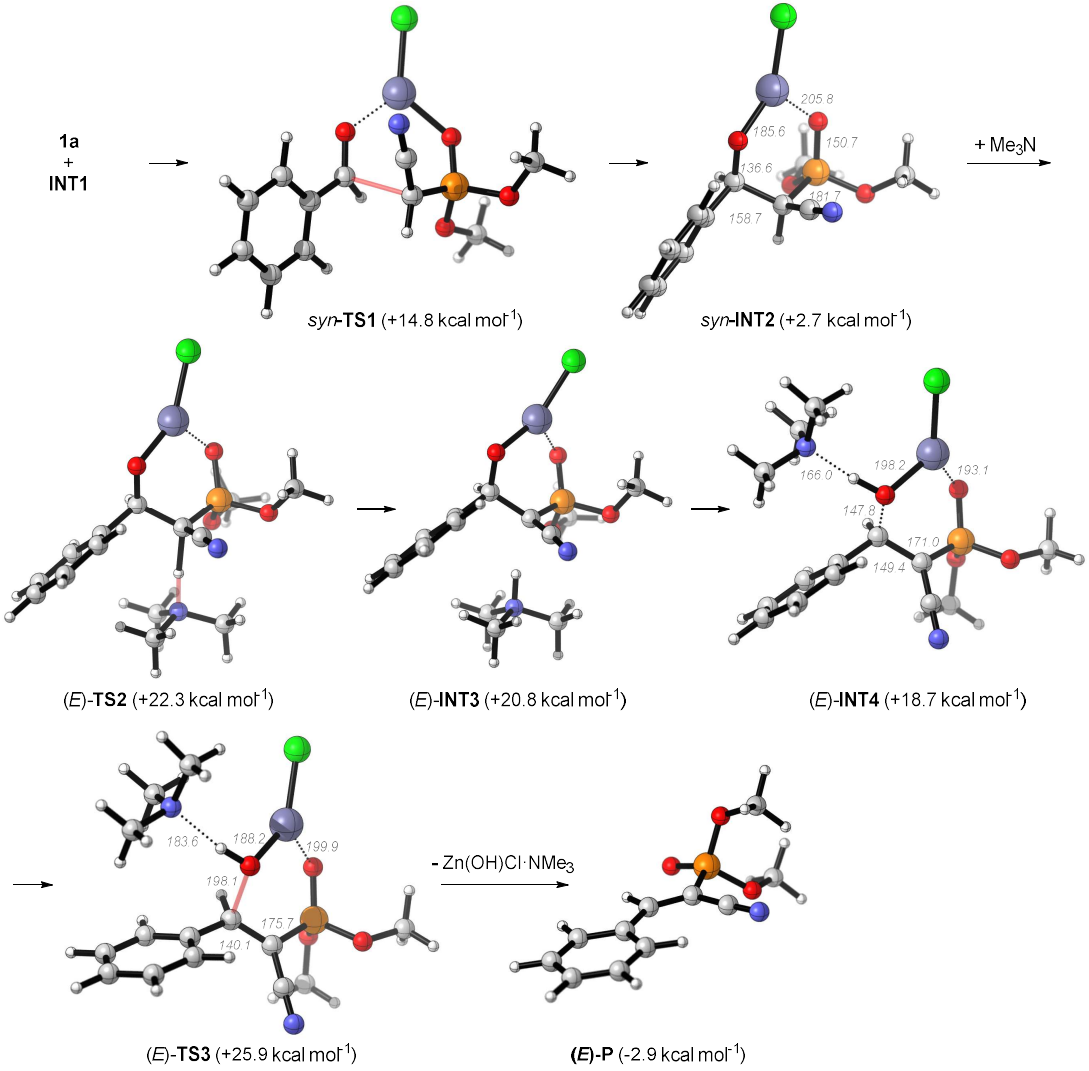


Table S4. Coordinates and energies for optimized geometry of *syn*-**TS1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	1.387176	1.520584	-0.465839
2	8	0	1.960187	-0.332281	-0.245184
3	15	0	1.132855	-1.567108	0.107821
4	6	0	-0.375992	-1.142127	0.843159
5	6	0	-1.195731	0.297443	-0.850570
6	8	0	-0.540128	1.366692	-0.689316
7	17	0	2.639407	3.265622	-0.272904
8	8	0	2.084418	-2.587875	0.897014
9	6	0	2.805047	-2.107331	2.040301
10	1	0	3.516514	-1.330842	1.739416
11	1	0	2.112405	-1.710694	2.793773
12	1	0	3.338435	-2.966109	2.452029
13	8	0	0.710623	-2.443757	-1.151473
14	6	0	1.705308	-3.133336	-1.921675
15	1	0	2.539665	-2.464861	-2.164846
16	1	0	2.070102	-4.003149	-1.366754
17	1	0	1.211630	-3.454914	-2.840863
18	6	0	-0.318455	-0.148049	1.831897
19	7	0	-0.247574	0.762193	2.567551

20	1	0	-1.114890	-1.936859	0.952106
21	1	0	-0.848722	-0.459309	-1.570973
22	6	0	-2.601402	0.214584	-0.454042
23	6	0	-3.362642	-0.886983	-0.863469
24	6	0	-3.185414	1.222439	0.320707
25	6	0	-4.700674	-0.980058	-0.505119
26	1	0	-2.890042	-1.673297	-1.455698
27	6	0	-4.524797	1.124137	0.680262
28	1	0	-2.579600	2.071465	0.632583
29	6	0	-5.281144	0.026147	0.269973
30	1	0	-5.293662	-1.836125	-0.822291
31	1	0	-4.982546	1.905519	1.284320
32	1	0	-6.329706	-0.046088	0.554715

E(RM06) = -3362.88489816

Zero-point correction = 0.229736 (Hartree/Particle)

Sum of electronic and thermal Energies = -3362.628926

Sum of electronic and thermal Enthalpies = -3362.627855

Sum of electronic and thermal Free Energies = -3362.718695

Table S5. Coordinates and energies for optimized geometry of *syn*-**INT2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	30	0	1.362789	1.646247	-0.189059
2	8	0	2.088685	-0.277180	-0.095538
3	15	0	1.170560	-1.472641	-0.091454
4	6	0	-0.551653	-1.062483	0.317868
5	6	0	-1.067563	0.170460	-0.537753
6	8	0	-0.468156	1.340877	-0.166453
7	17	0	2.926592	3.127689	-0.206841
8	8	0	1.686064	-2.619167	0.875890
9	6	0	2.464341	-2.327433	2.055296
10	1	0	3.328498	-1.710500	1.792914
11	1	0	1.843344	-1.819132	2.800565
12	1	0	2.793166	-3.293948	2.440180
13	6	0	2.143023	-2.640282	-2.217967
14	1	0	2.833243	-1.805766	-2.380922
15	1	0	2.640045	-3.447479	-1.669344
16	1	0	1.773005	-3.012014	-3.174517
17	6	0	-0.648198	-0.786428	1.741760
18	7	0	-0.684187	-0.551301	2.879243
19	1	0	-1.147105	-1.958100	0.080614
20	6	0	-2.574287	0.229778	-0.384410
21	6	0	-3.162665	1.122456	0.510232
22	6	0	-4.547050	1.141275	0.670063

23	6	0	-5.351435	0.273631	-0.065917
24	6	0	-4.767067	-0.615656	-0.967080
25	6	0	-3.384115	-0.634937	-1.123842
26	1	0	-2.524302	1.801592	1.072760
27	1	0	-4.999099	1.840476	1.372386
28	1	0	-6.433293	0.293765	0.057773
29	1	0	-5.390538	-1.288269	-1.554722
30	1	0	-2.927376	-1.323908	-1.838656
31	8	0	0.985280	-2.193334	-1.488226
32	1	0	-0.849387	-0.117975	-1.588724

E(RM06) = -3362.90798600

Zero-point correction = 0.232577 (Hartree/Particle)

Sum of electronic and thermal Energies = -3362.649373

Sum of electronic and thermal Enthalpies = -3362.648302

Sum of electronic and thermal Free Energies = -3362.737935

Table S6. Coordinates and energies for optimized geometry of (*E*)-**TS2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	-2.423299	-1.334336	-0.193251
2	8	0	-2.280636	0.660110	-0.558920
3	15	0	-1.012477	1.392852	-0.150783

4	6	0	0.333183	0.380952	0.365283
5	6	0	0.339061	-0.974107	-0.413968
6	8	0	-0.648208	-1.852386	-0.003755
7	17	0	-4.483293	-1.998697	-0.164164
8	8	0	-1.325053	2.525099	0.936886
9	6	0	-2.266243	2.272977	1.993467
10	1	0	-2.431786	3.232650	2.487302
11	1	0	-3.208992	1.896186	1.582511
12	1	0	-1.848307	1.556000	2.710392
13	8	0	-0.428818	2.252447	-1.370787
14	6	0	-1.346228	3.024609	-2.159339
15	1	0	-2.002573	2.361584	-2.732362
16	1	0	-1.945433	3.681126	-1.517157
17	1	0	-0.738748	3.628352	-2.837023
18	6	0	0.419302	0.276672	1.781128
19	7	0	0.565948	0.239421	2.942428
20	1	0	1.599000	1.163799	0.079037
21	7	0	2.625017	1.830830	-0.003703
22	6	0	2.312269	3.089261	0.693090
23	1	0	1.466127	3.575344	0.195505
24	1	0	2.040249	2.866136	1.730935
25	1	0	3.184696	3.756974	0.676891

26	6	0	2.924151	2.057855	-1.425228
27	1	0	3.116542	1.092994	-1.906954
28	1	0	2.059036	2.533918	-1.898174
29	1	0	3.810177	2.700392	-1.526833
30	6	0	3.709235	1.096725	0.672882
31	1	0	3.410946	0.883713	1.705137
32	1	0	3.886881	0.151820	0.146971
33	1	0	4.627369	1.701471	0.670704
34	1	0	0.215847	-0.680075	-1.481667
35	6	0	1.695811	-1.639322	-0.312628
36	6	0	2.091209	-2.274157	0.869042
37	6	0	2.564827	-1.647595	-1.404715
38	6	0	3.347714	-2.864016	0.966498
39	1	0	1.402008	-2.307263	1.711758
40	6	0	3.822666	-2.244330	-1.314116
41	1	0	2.244462	-1.194953	-2.346078
42	6	0	4.221006	-2.846105	-0.122766
43	1	0	3.646023	-3.349753	1.894827
44	1	0	4.484736	-2.250314	-2.179598
45	1	0	5.201057	-3.315371	-0.046296

E(RM06) = -3537.23957491

Zero-point correction = 0.351949 (Hartree/Particle)

Sum of electronic and thermal Energies= -3536.854287

Sum of electronic and thermal Enthalpies=-3536.853216

Sum of electronic and thermal Free Energies= -3536.957015

Table S7. Coordinates and energies for optimized geometry of (*E*)-**INT3**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	-2.455041	-1.288867	-0.315862
2	8	0	-2.205010	0.669279	-0.885715
3	15	0	-1.013967	1.338964	-0.210848
4	6	0	0.221621	0.241412	0.304760
5	6	0	0.272008	-1.056691	-0.532251
6	8	0	-0.727078	-1.968822	-0.214747
7	17	0	-4.552520	-1.687303	0.096069
8	8	0	-1.476673	2.299289	0.990656
9	6	0	-2.444896	1.787920	1.919143
10	1	0	-2.586747	2.562536	2.675482
11	1	0	-3.391837	1.585011	1.405662
12	1	0	-2.075144	0.873288	2.402434
13	8	0	-0.338423	2.402984	-1.213856
14	6	0	-1.197436	3.288099	-1.946077
15	1	0	-1.885987	2.714346	-2.575738
16	1	0	-1.764252	3.926482	-1.257674

17	1	0	-0.548094	3.905869	-2.570843
18	6	0	0.494997	0.188553	1.680679
19	7	0	0.810811	0.198942	2.813231
20	1	0	1.848881	1.176732	0.083413
21	7	0	2.713504	1.798182	0.164817
22	6	0	2.266954	3.002830	0.909594
23	1	0	1.466688	3.487012	0.341210
24	1	0	1.888916	2.688560	1.887534
25	1	0	3.117818	3.682359	1.029548
26	6	0	3.152330	2.138613	-1.208424
27	1	0	3.475564	1.222794	-1.712419
28	1	0	2.307152	2.581372	-1.744269
29	1	0	3.984748	2.848824	-1.151713
30	6	0	3.755441	1.047071	0.912218
31	1	0	3.360217	0.790021	1.899723
32	1	0	3.994343	0.131404	0.359943
33	1	0	4.645478	1.679947	1.004934
34	1	0	0.183396	-0.719456	-1.589774
35	6	0	1.642246	-1.689189	-0.412407
36	6	0	1.986190	-2.457892	0.703000
37	6	0	2.594777	-1.495005	-1.415197
38	6	0	3.266727	-2.991619	0.823601

39	1	0	1.237408	-2.639822	1.472862
40	6	0	3.877088	-2.032099	-1.301399
41	1	0	2.318142	-0.928397	-2.308262
42	6	0	4.218827	-2.777476	-0.174368
43	1	0	3.522836	-3.586043	1.699934
44	1	0	4.603572	-1.881473	-2.100069
45	1	0	5.216525	-3.204535	-0.080770

E(RM06) = -3537.24223737

Zero-point correction = 0.355600 (Hartree/Particle)

Sum of electronic and thermal Energies= -3536.852243

Sum of electronic and thermal Enthalpies= -3536.851172

Sum of electronic and thermal Free Energies= -3536.959463

Table S8. Coordinates and energies for optimized geometry of (*E*)-**INT4**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	0.717358	1.981057	-0.194260
2	8	0	2.171062	1.033868	0.652376
3	15	0	2.402931	-0.437170	0.271532
4	6	0	0.998717	-1.195781	-0.342503
5	6	0	-0.307492	-0.696018	0.183484
6	8	0	-0.651700	0.577856	-0.483345

7	17	0	0.241531	4.076711	-0.479854
8	8	0	3.017569	-1.059873	1.626688
9	6	0	3.175488	-2.480210	1.689560
10	1	0	2.200369	-2.976831	1.599998
11	1	0	3.839197	-2.839952	0.891406
12	1	0	3.618925	-2.700727	2.663001
13	8	0	3.554340	-0.627827	-0.819791
14	6	0	4.884031	-0.187768	-0.521760
15	1	0	4.876622	0.851194	-0.171010
16	1	0	5.341719	-0.831372	0.238363
17	1	0	5.447024	-0.258368	-1.454502
18	6	0	1.100136	-2.242558	-1.265688
19	7	0	1.194789	-3.130218	-2.027890
20	1	0	-1.597711	0.872249	-0.205386
21	7	0	-3.022372	1.500823	0.370258
22	6	0	-4.144582	0.568676	0.328994
23	1	0	-4.357061	0.293132	-0.710916
24	1	0	-3.895054	-0.344125	0.885279
25	1	0	-5.053397	1.019870	0.769467
26	6	0	-3.317719	2.694971	-0.417907
27	1	0	-2.454755	3.373069	-0.404804
28	1	0	-3.523211	2.407874	-1.456268

29	1	0	-4.198642	3.230899	-0.018397
30	6	0	-2.700842	1.860376	1.747293
31	1	0	-2.451102	0.955144	2.317091
32	1	0	-1.838532	2.541190	1.761211
33	1	0	-3.549356	2.364586	2.245676
34	1	0	-0.214052	-0.451107	1.256941
35	6	0	-1.445824	-1.662927	0.021109
36	6	0	-1.893943	-2.387350	1.126428
37	6	0	-2.047268	-1.866042	-1.222685
38	6	0	-2.932439	-3.306946	0.994460
39	1	0	-1.423403	-2.228997	2.099036
40	6	0	-3.087169	-2.781497	-1.354846
41	1	0	-1.696187	-1.304453	-2.088529
42	6	0	-3.533044	-3.502419	-0.247437
43	1	0	-3.273822	-3.868069	1.863170
44	1	0	-3.548504	-2.936938	-2.329081
45	1	0	-4.345175	-4.219972	-0.354440

E(RM06) = -3537.24640448

Zero-point correction = 0.354702 (Hartree/Particle)

Sum of electronic and thermal Energies= -3536.858534

Sum of electronic and thermal Enthalpies= -3536.857463

Sum of electronic and thermal Free Energies= -3536.962781

Table S9. Coordinates and energies for optimized geometry of (*E*)-**TS3**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	0.400291	1.992266	-0.219548
2	8	0	2.076345	1.144279	0.463659
3	15	0	2.500110	-0.293394	0.245278
4	6	0	1.176849	-1.383420	-0.138239
5	6	0	-0.085815	-1.035872	0.358306
6	8	0	-0.644487	0.516049	-0.738883
7	17	0	0.194659	4.135772	0.084765
8	8	0	3.286650	-0.713988	1.576481
9	6	0	3.734868	-2.069239	1.706158
10	1	0	2.876849	-2.750653	1.759963
11	1	0	4.375681	-2.352603	0.861074
12	1	0	4.305805	-2.117655	2.635361
13	8	0	3.532391	-0.494759	-0.951006
14	6	0	4.764945	0.239351	-0.941602
15	1	0	4.565119	1.316567	-0.920001
16	1	0	5.373184	-0.044606	-0.074382
17	1	0	5.285829	-0.024956	-1.863458
18	6	0	1.408686	-2.453195	-1.029504

19	7	0	1.644682	-3.351506	-1.739687
20	1	0	-1.600559	0.720663	-0.560462
21	7	0	-3.225407	1.391510	-0.029340
22	6	0	-4.288092	0.426415	-0.254959
23	1	0	-4.352470	0.187488	-1.324207
24	1	0	-4.070325	-0.500485	0.293424
25	1	0	-5.272001	0.812638	0.079569
26	6	0	-3.452739	2.611153	-0.788980
27	1	0	-2.624335	3.313533	-0.624783
28	1	0	-3.503797	2.375796	-1.859616
29	1	0	-4.397843	3.109586	-0.494034
30	6	0	-3.078645	1.682481	1.386620
31	1	0	-2.836712	0.760184	1.933353
32	1	0	-2.266181	2.406753	1.537204
33	1	0	-4.005357	2.109716	1.819633
34	1	0	-0.095474	-0.413710	1.255594
35	6	0	-1.277574	-1.885576	0.213865
36	6	0	-2.029446	-2.187294	1.354622
37	6	0	-1.671289	-2.403031	-1.025720
38	6	0	-3.139464	-3.023112	1.267050
39	1	0	-1.729498	-1.776119	2.319773
40	6	0	-2.788978	-3.224171	-1.113414

41	1	0	-1.110906	-2.140900	-1.921662
42	6	0	-3.520651	-3.542041	0.031622
43	1	0	-3.709514	-3.264322	2.162822
44	1	0	-3.092735	-3.619061	-2.081428
45	1	0	-4.392399	-4.190408	-0.041249

E(RM06) = -3537.23189944

Zero-point correction= 0.353193 (Hartree/Particle)

Sum of electronic and thermal Energies= -3536.844452

Sum of electronic and thermal Enthalpies= -3536.843381

Sum of electronic and thermal Free Energies= -3536.951357

Table S10. Coordinates and energies for optimized geometry of (*E*)-**P**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.03231	0.721563	-1.37996
2	15	0	2.540713	-0.44992	-0.63553
3	6	0	1.244056	-1.56451	-0.05271
4	6	0	-0.0064	-1.36016	-0.54275
5	8	0	3.565343	-1.28796	-1.54163
6	6	0	4.227446	-2.46215	-1.06466
7	1	0	3.534384	-3.31183	-1.04738
8	1	0	4.642453	-2.3041	-0.06127

9	1	0	5.036055	-2.66912	-1.76922
10	8	0	3.324156	-0.16861	0.733761
11	6	0	4.426677	0.747055	0.71074
12	1	0	4.09709	1.730147	0.356494
13	1	0	5.228441	0.367979	0.064342
14	1	0	4.787056	0.822726	1.738303
15	6	0	1.609327	-2.57465	0.87702
16	7	0	1.968616	-3.38704	1.631865
17	1	0	-0.08363	-0.51979	-1.23766
18	6	0	-1.25693	-2.055	-0.30176
19	6	0	-2.3853	-1.58309	-0.99556
20	6	0	-1.41009	-3.14863	0.568846
21	6	0	-3.62679	-2.18213	-0.83243
22	1	0	-2.27535	-0.73455	-1.67072
23	6	0	-2.65265	-3.74445	0.730552
24	1	0	-0.56054	-3.53833	1.123898
25	6	0	-3.76206	-3.26564	0.032646
26	1	0	-4.48879	-1.80411	-1.37846
27	1	0	-2.7581	-4.58986	1.407615
28	1	0	-4.73325	-3.73922	0.165344

E(RM06) = -1047.74374704

Zero-point correction= 0.214897 (Hartree/Particle)

Sum of electronic and thermal Energies = -1047.508536

Sum of electronic and thermal Enthalpies = -1047.507465

Sum of electronic and thermal Free Energies = -1047.582959

1.2.2 For (*E*)-product

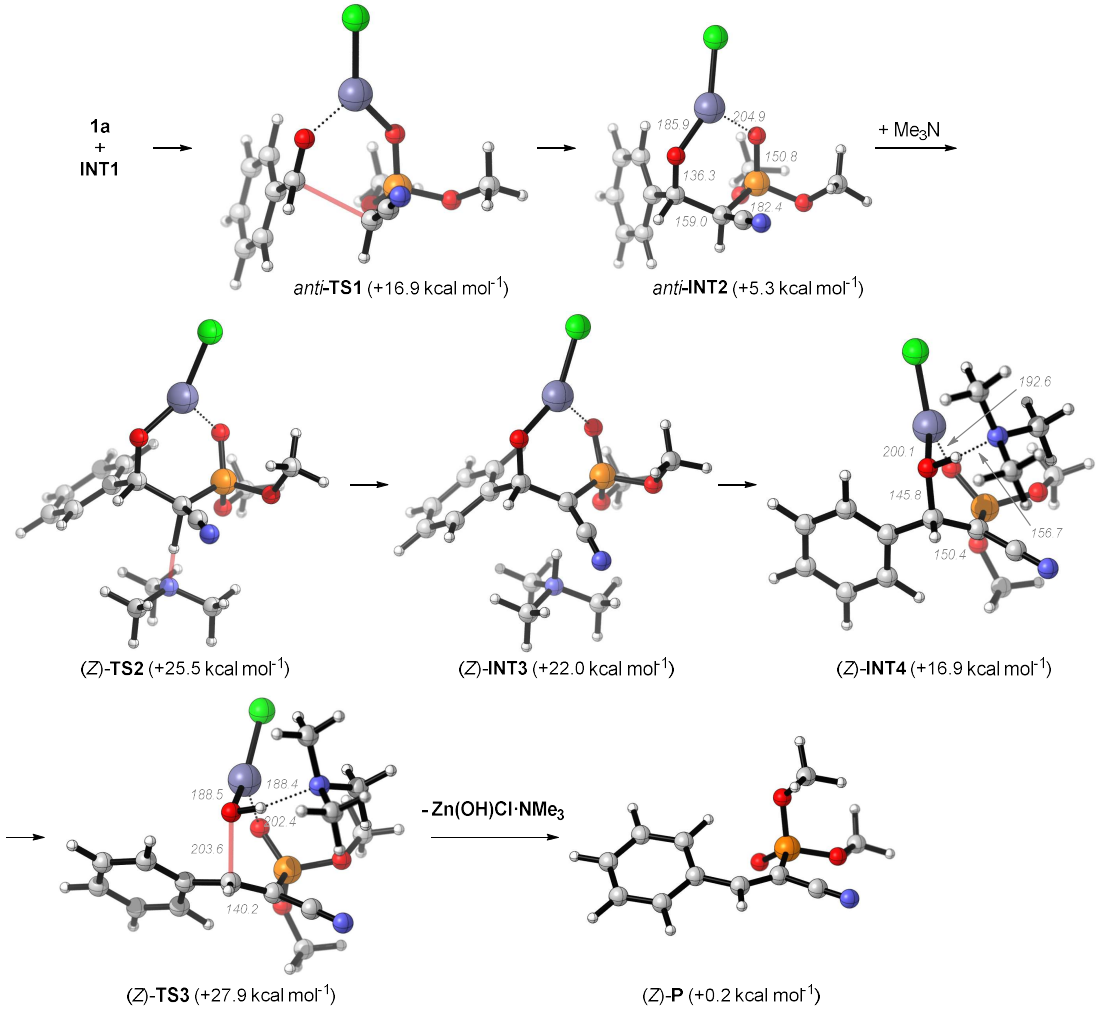


Table S11. Coordinates and energies for optimized geometry of*anti*-**TS1**

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	30	0	-1.699255	-1.114172	-0.183203
2	8	0	-1.040388	0.578436	-0.848169
3	15	0	-0.058726	1.601153	-0.270432
4	6	0	0.167005	1.419040	1.437047
5	6	0	0.627582	-0.952247	1.627156
6	8	0	-0.445468	-1.500629	1.265817
7	17	0	-3.225329	-2.469472	-0.871252
8	8	0	-0.523042	3.045813	-0.795403
9	6	0	-1.863668	3.485522	-0.548657
10	1	0	-2.585052	2.767984	-0.956125
11	1	0	-2.032888	3.619174	0.527161
12	1	0	-1.972130	4.447193	-1.054377
13	8	0	1.403119	1.511559	-0.881963
14	6	0	1.590980	1.540929	-2.301043
15	1	0	1.086824	0.685050	-2.765805
16	1	0	1.210780	2.479250	-2.719877
17	1	0	2.667687	1.467737	-2.466043
18	6	0	-1.009168	1.386628	2.206686
19	7	0	-2.003534	1.268644	2.816876
20	1	0	1.033756	1.930027	1.859623
21	1	0	0.736940	-0.690990	2.690953

22	6	0	1.870745	-1.016541	0.852162
23	6	0	1.929637	-1.667878	-0.384321
24	6	0	3.130955	-1.725815	-1.082144
25	6	0	4.276494	-1.134157	-0.550418
26	6	0	4.227418	-0.500652	0.692924
27	6	0	3.031009	-0.451295	1.393914
28	1	0	1.042212	-2.153550	-0.789455
29	1	0	3.177395	-2.238526	-2.041546
30	1	0	5.215651	-1.178182	-1.099935
31	1	0	5.125957	-0.053061	1.113991
32	1	0	2.979057	0.043620	2.365075

E(RM06) = -3362.88325132

Zero-point correction= 0.229897 (Hartree/Particle)

Sum of electronic and thermal Energies= -3362.627418

Sum of electronic and thermal Enthalpies= -3362.626347

Sum of electronic and thermal Free Energies= -3362.715339

Table S12. Coordinates and energies for optimized geometry of *anti*-**INT2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	1.382123	1.450134	0.217536
2	8	0	1.254051	-0.234512	-0.942351

3	15	0	0.382385	-1.404144	-0.560477
4	6	0	-0.131337	-1.372212	1.189674
5	6	0	-0.674352	0.041147	1.674431
6	8	0	0.294379	0.999896	1.655884
7	17	0	2.558278	2.995846	-0.724172
8	8	0	1.096538	-2.791734	-0.854042
9	6	0	2.532439	-2.918580	-0.890815
10	1	0	2.956153	-2.190175	-1.588068
11	1	0	2.951096	-2.776243	0.110902
12	1	0	2.730772	-3.934148	-1.236921
13	8	0	-0.997111	-1.511427	-1.319330
14	6	0	-1.077932	-1.211624	-2.723558
15	1	0	-0.709920	-0.197105	-2.911218
16	1	0	-0.498489	-1.942712	-3.298438
17	1	0	-2.135731	-1.279687	-2.982134
18	6	0	1.013351	-1.761055	1.999364
19	7	0	1.945439	-2.057232	2.626937
20	1	0	-0.915192	-2.137971	1.297836
21	1	0	-0.962462	-0.156492	2.726897
22	6	0	-1.953121	0.377015	0.920315
23	6	0	-2.035373	1.480702	0.075113
24	6	0	-3.204852	1.744282	-0.638355

25	6	0	-4.311540	0.912159	-0.498589
26	6	0	-4.251864	-0.172203	0.378035
27	6	0	-3.083745	-0.429073	1.086262
28	1	0	-1.187315	2.159535	-0.013194
29	1	0	-3.250828	2.611144	-1.296182
30	1	0	-5.225973	1.118618	-1.052817
31	1	0	-5.121397	-0.813513	0.514945
32	1	0	-3.051872	-1.273001	1.779275

E(RM06) = -3362.90667280

Zero-point correction = 0.233327 (Hartree/Particle)

Sum of electronic and thermal Energies= -3362.647889

Sum of electronic and thermal Enthalpies= -3362.646818

Sum of electronic and thermal Free Energies= -3362.733880

Table S13. Coordinates and energies for optimized geometry of (*Z*)-**TS2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	-2.468179	0.842436	-0.423755
2	8	0	-1.628049	-0.193467	1.115036
3	15	0	-0.457202	-1.093877	0.758860
4	6	0	0.372033	-0.737165	-0.760638
5	6	0	0.251687	0.714944	-1.333123

6	8	0	-1.038179	1.160700	-1.554187
7	17	0	-4.606920	1.048303	-0.121435
8	8	0	-0.884793	-2.636554	0.793896
9	6	0	-2.161547	-3.013266	0.249796
10	1	0	-2.967896	-2.508289	0.792850
11	1	0	-2.214449	-2.769988	-0.819340
12	1	0	-2.240513	-4.094339	0.378047
13	8	0	0.674084	-1.037592	1.888581
14	6	0	0.276552	-0.998394	3.265448
15	1	0	-0.284476	-0.079601	3.469722
16	1	0	-0.334546	-1.873833	3.515824
17	1	0	1.197697	-1.011905	3.852537
18	6	0	0.122145	-1.726315	-1.754008
19	7	0	0.008327	-2.539812	-2.588366
20	1	0	1.807058	-0.979767	-0.456717
21	1	0	0.752143	0.631652	-2.319556
22	6	0	1.092015	1.704097	-0.535731
23	6	0	0.771736	2.095067	0.769301
24	6	0	1.577103	2.993981	1.462410
25	6	0	2.711773	3.536910	0.858314
26	6	0	3.022991	3.183885	-0.451761
27	6	0	2.215023	2.276842	-1.137704

28	1	0	-0.118498	1.699921	1.258541
29	1	0	1.312431	3.279539	2.480178
30	1	0	3.336432	4.244524	1.401583
31	1	0	3.889126	3.622067	-0.946660
32	1	0	2.451378	2.022355	-2.173250
33	7	0	3.001486	-1.329062	-0.335002
34	6	0	2.927120	-2.756044	0.020048
35	1	0	2.420936	-2.860674	0.985305
36	1	0	2.351478	-3.286552	-0.747238
37	1	0	3.937432	-3.183907	0.084783
38	6	0	3.685815	-0.543697	0.703561
39	1	0	3.704910	0.510720	0.405083
40	1	0	3.135692	-0.640353	1.644062
41	1	0	4.715085	-0.909725	0.831529
42	6	0	3.629588	-1.143600	-1.652607
43	1	0	3.056344	-1.690795	-2.409209
44	1	0	3.632311	-0.076952	-1.901388
45	1	0	4.663590	-1.516217	-1.635417

E(RM06) = -3537.23662953

Zero-point correction= 0.352031 (Hartree/Particle)

Sum of electronic and thermal Energies=-3536.852288

Sum of electronic and thermal Enthalpies= -3536.851218

Sum of electronic and thermal Free Energies= -3536.951920

Table S14. Coordinates and energies for optimized geometry of (*Z*)-**INT3**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	-2.578463	0.809671	-0.287330
2	8	0	-1.670514	-0.376262	1.077084
3	15	0	-0.514112	-1.220173	0.557942
4	6	0	0.207367	-0.650746	-0.900122
5	6	0	0.069542	0.822293	-1.353874
6	8	0	-1.222626	1.316400	-1.439742
7	17	0	-4.718100	0.984326	0.054193
8	8	0	-0.915562	-2.770152	0.431077
9	6	0	-2.055434	-3.102108	-0.372835
10	1	0	-2.936928	-2.538721	-0.041058
11	1	0	-1.849538	-2.896324	-1.431207
12	1	0	-2.230532	-4.171277	-0.236519
13	8	0	0.622247	-1.323118	1.699695
14	6	0	0.229287	-1.559478	3.056296
15	1	0	-0.397677	-0.736129	3.416890
16	1	0	-0.314410	-2.508167	3.139463
17	1	0	1.150338	-1.609982	3.643896

18	6	0	0.558707	-1.613952	-1.850747
19	7	0	0.937239	-2.412320	-2.629280
20	1	0	2.120633	-0.804185	-0.220871
21	1	0	0.505913	0.820306	-2.373655
22	6	0	0.959391	1.750418	-0.533179
23	6	0	0.707212	2.033967	0.815835
24	6	0	1.532655	2.895420	1.531332
25	6	0	2.628512	3.501502	0.912839
26	6	0	2.881423	3.243136	-0.431454
27	6	0	2.047811	2.378590	-1.143576
28	1	0	-0.146827	1.579475	1.320325
29	1	0	1.315777	3.103481	2.578825
30	1	0	3.268345	4.181456	1.473635
31	1	0	3.717609	3.727929	-0.935015
32	1	0	2.234305	2.201767	-2.205476
33	7	0	3.138703	-1.055105	-0.115044
34	6	0	3.195078	-2.513093	0.174356
35	1	0	2.666894	-2.704475	1.111460
36	1	0	2.707440	-3.049061	-0.646132
37	1	0	4.245590	-2.811822	0.256177
38	6	0	3.705690	-0.246742	0.993882
39	1	0	3.597197	0.815769	0.748946

40	1	0	3.156343	-0.473588	1.911930
41	1	0	4.764346	-0.504260	1.108404
42	6	0	3.799052	-0.744893	-1.411904
43	1	0	3.288646	-1.301307	-2.204648
44	1	0	3.720814	0.330927	-1.594608
45	1	0	4.851279	-1.041735	-1.347012

E(RM06) = -3537.24115733

Zero-point correction= 0.356767 (Hartree/Particle)

Sum of electronic and thermal Energies= -3536.851073

Sum of electronic and thermal Enthalpies= -3536.850002

Sum of electronic and thermal Free Energies= -3536.957497

Table S15. Coordinates and energies for optimized geometry of (*Z*)-**INT4**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	0.769023	-1.040171	-1.246070
2	8	0	-0.569665	0.275478	-1.676980
3	15	0	-0.808829	1.447317	-0.715977
4	6	0	-0.501248	1.060745	0.923822
5	6	0	-0.424481	-0.381354	1.342670
6	8	0	0.723305	-1.061320	0.754699
7	17	0	2.320001	-2.179883	-2.228091

8	8	0	-2.299390	1.932018	-1.087712
9	6	0	-2.894785	2.945673	-0.274899
10	1	0	-2.995655	2.599282	0.762276
11	1	0	-2.295754	3.866453	-0.287187
12	1	0	-3.882870	3.141711	-0.696732
13	8	0	0.105105	2.720357	-1.062397
14	6	0	-0.008536	3.326150	-2.354925
15	1	0	0.138973	2.577488	-3.142756
16	1	0	-0.989366	3.800177	-2.479147
17	1	0	0.777099	4.082351	-2.412155
18	6	0	-0.132141	2.067706	1.817895
19	7	0	0.190640	2.898021	2.585493
20	1	0	1.593317	-0.590799	1.100920
21	7	0	2.967782	0.050497	1.494989
22	6	0	2.973528	0.443047	2.903110
23	1	0	2.230611	1.233009	3.068368
24	1	0	2.720383	-0.424013	3.526205
25	1	0	3.966802	0.819467	3.207635
26	6	0	3.210116	1.205028	0.632962
27	1	0	3.174787	0.895800	-0.420977
28	1	0	2.437665	1.964950	0.804480
29	1	0	4.201986	1.650366	0.830037

30	6	0	3.944918	-1.006279	1.242355
31	1	0	3.717310	-1.873454	1.874631
32	1	0	3.892515	-1.317744	0.190538
33	1	0	4.972261	-0.665213	1.463386
34	1	0	-0.248266	-0.392891	2.431620
35	6	0	-1.645933	-1.232683	1.056695
36	6	0	-1.530890	-2.589670	0.738631
37	6	0	-2.923497	-0.683146	1.190876
38	6	0	-2.668033	-3.367022	0.523603
39	1	0	-0.544869	-3.045843	0.663384
40	6	0	-4.059654	-1.460156	0.986613
41	1	0	-3.021543	0.368280	1.459495
42	6	0	-3.935964	-2.805517	0.643701
43	1	0	-2.557949	-4.419397	0.265261
44	1	0	-5.046141	-1.010865	1.092721
45	1	0	-4.823763	-3.412766	0.474387

E(RM06) = -3537.25055740

Zero-point correction= 0.354887 (Hartree/Particle)

Sum of electronic and thermal Energies= -3536.862034

Sum of electronic and thermal Enthalpies=-3536.860964

Sum of electronic and thermal Free Energies= -3536.965637

Table S16. Coordinates and energies for optimized geometry of (*Z*)-**TS3**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	0.476577	-1.277025	-1.002798
2	8	0	-0.536369	0.401388	-1.504673
3	15	0	-0.467605	1.596413	-0.580304
4	6	0	-0.485755	1.175290	1.133268
5	6	0	-0.969259	-0.070198	1.558505
6	8	0	0.321009	-1.483246	0.864400
7	17	0	1.682668	-1.978114	-2.676136
8	8	0	-1.637089	2.593100	-1.028174
9	6	0	-1.832034	3.799247	-0.277968
10	1	0	-2.101350	3.564426	0.760776
11	1	0	-0.925475	4.417112	-0.293393
12	1	0	-2.653133	4.332493	-0.760544
13	8	0	0.885731	2.432055	-0.719088
14	6	0	1.368374	2.753856	-2.031414
15	1	0	1.518758	1.836486	-2.613787
16	1	0	0.662546	3.415781	-2.548680
17	1	0	2.322019	3.265857	-1.888457
18	6	0	0.374440	1.897588	1.992867
19	7	0	1.069538	2.502408	2.713025

20	1	0	1.203186	-1.176974	1.200968
21	7	0	3.016574	-0.686145	1.339138
22	6	0	3.317526	-0.397891	2.733402
23	1	0	2.784199	0.508943	3.047457
24	1	0	2.992863	-1.236257	3.363401
25	1	0	4.403615	-0.242807	2.894372
26	6	0	3.405753	0.429883	0.490507
27	1	0	3.130020	0.224353	-0.554971
28	1	0	2.894154	1.343788	0.816256
29	1	0	4.499893	0.606625	0.526530
30	6	0	3.675410	-1.909888	0.907242
31	1	0	3.336209	-2.753084	1.523163
32	1	0	3.423518	-2.121317	-0.141261
33	1	0	4.778066	-1.834153	0.992214
34	1	0	-0.697763	-0.339071	2.581479
35	6	0	-2.193787	-0.725708	1.061157
36	6	0	-2.411588	-2.089150	1.314024
37	6	0	-3.205310	0.012781	0.436763
38	6	0	-3.595678	-2.699178	0.923434
39	1	0	-1.626984	-2.664205	1.801617
40	6	0	-4.391444	-0.600741	0.042659
41	1	0	-3.084597	1.082927	0.277692

42	6	0	-4.587865	-1.957681	0.279491
43	1	0	-3.747458	-3.759235	1.120414
44	1	0	-5.166355	-0.011354	-0.444305
45	1	0	-5.516253	-2.437314	-0.026619

E(RM06) = -3537.23005100

Zero-point correction= 0.353657 (Hartree/Particle)

Sum of electronic and thermal Energies= -3536.842421

Sum of electronic and thermal Enthalpies= -3536.841350

Sum of electronic and thermal Free Energies= -3536.948110

Table S17. Coordinates and energies for optimized geometry of (*Z*)-**P**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.744767	0.599723	-1.807847
2	15	0	-0.499810	1.624891	-0.773450
3	6	0	-0.404760	1.047085	0.941725
4	6	0	-1.188650	0.094326	1.516048
5	8	0	-1.642404	2.756600	-0.825322
6	6	0	-1.627202	3.843056	0.105125
7	1	0	-1.853555	3.484827	1.117864
8	1	0	-0.654010	4.350200	0.100899
9	1	0	-2.405765	4.538132	-0.215800

10	8	0	0.888099	2.415286	-0.857623
11	6	0	1.274574	2.977725	-2.118020
12	1	0	1.329973	2.195532	-2.882796
13	1	0	0.560155	3.751900	-2.425933
14	1	0	2.259214	3.423616	-1.966421
15	6	0	0.615205	1.620733	1.758700
16	7	0	1.428769	2.101605	2.439912
17	1	0	-0.894675	-0.181887	2.532698
18	6	0	-2.344336	-0.641506	1.034346
19	6	0	-2.660346	-1.828555	1.719105
20	6	0	-3.178505	-0.228411	-0.017607
21	6	0	-3.744431	-2.606279	1.337987
22	1	0	-2.033242	-2.143265	2.553344
23	6	0	-4.273034	-0.998804	-0.384619
24	1	0	-2.993670	0.705985	-0.540951
25	6	0	-4.553174	-2.191584	0.281739
26	1	0	-3.965058	-3.529710	1.869700
27	1	0	-4.915034	-0.664211	-1.197009
28	1	0	-5.411308	-2.791637	-0.016032

E(RM06) = -1047.73757857

Zero-point correction= 0.214398 (Hartree/Particle)

Sum of electronic and thermal Energies= -1047.502667

Sum of electronic and thermal Enthalpies= -1047.501597

Sum of electronic and thermal Free Energies= -1047.577891

1.3 *Reaction pathways for the Horner-Wadsworth-Emmons reaction*

The HWE path from intermediate *syn*-**INT2** was computed. Transition state**TS4** ($\Delta G_{338\ K}$ = +26.3 kcal mol^{-1}) was 4.0 kcal mol^{-1}less stable than transition state TS2 for the Me3N-mediated deprotonation.

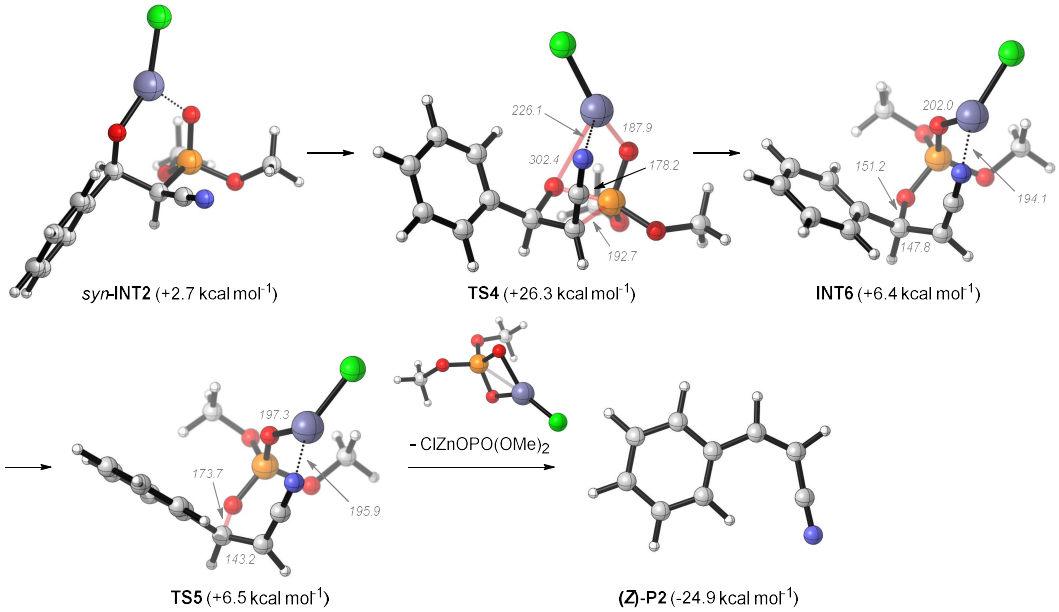


Table S18. Coordinates and energies for optimized geometry of **TS4**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	-0.314338	1.907383	-0.127333

2	17	0	1.084297	3.418446	0.482485
3	8	0	-1.845225	0.866486	0.191984
4	15	0	-1.764556	-0.686462	0.029308
5	8	0	-2.822373	-0.911577	-1.233789
6	6	0	-4.168046	-0.474337	-1.135672
7	1	0	-4.224384	0.548203	-0.739139
8	1	0	-4.583576	-0.489720	-2.148480
9	1	0	-4.752375	-1.146058	-0.494245
10	8	0	-2.716015	-1.496058	1.054333
11	6	0	-2.492928	-1.507808	2.462778
12	1	0	-1.632121	-2.133699	2.716364
13	1	0	-2.328731	-0.492997	2.844253
14	1	0	-3.404012	-1.922259	2.903524
15	6	0	-0.376085	-1.409543	-1.094056
16	1	0	-0.661954	-2.203938	-1.788028
17	6	0	0.130391	-0.224303	-1.718366
18	7	0	0.468506	0.865560	-1.975284
19	6	0	0.410321	-1.735005	0.193164
20	8	0	-0.315443	-0.879040	1.048749
21	1	0	0.228355	-2.798223	0.437843
22	6	0	1.887424	-1.462574	0.179905
23	6	0	2.432230	-0.385928	0.876520

24	6	0	3.800870	-0.127297	0.806634
25	6	0	4.630236	-0.943990	0.043490
26	6	0	4.089103	-2.028259	-0.648764
27	6	0	2.724459	-2.287424	-0.576747
28	1	0	1.781492	0.248589	1.477168
29	1	0	4.216365	0.720169	1.350091
30	1	0	5.698163	-0.738891	-0.012737
31	1	0	4.732674	-2.671705	-1.246984
32	1	0	2.300608	-3.136211	-1.118065

E(RM06) = -3362.87459325

Zero-point correction= 0.232901 (Hartree/Particle)

Sum of electronic and thermal Energies= -3362.617526

Sum of electronic and thermal Enthalpies= -3362.616455

Sum of electronic and thermal Free Energies= -3362.700380

Table S19. Coordinates and energies for optimized geometry of **INT6**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	-1.472086	-1.596679	-0.180782
2	17	0	-3.337623	-2.099408	-1.169461
3	8	0	-0.884601	0.292347	-0.586996
4	15	0	-0.643243	1.589123	0.140667

5	8	0	-1.635850	1.843440	1.345963
6	6	0	-3.052080	1.789775	1.106508
7	1	0	-3.330047	0.840993	0.631098
8	1	0	-3.529218	1.867608	2.084845
9	1	0	-3.354739	2.630221	0.472725
10	8	0	-0.917042	2.832680	-0.806094
11	6	0	-0.260821	2.928067	-2.076074
12	1	0	0.791253	3.199503	-1.929388
13	1	0	-0.339899	1.982111	-2.624320
14	1	0	-0.770319	3.720088	-2.628020
15	6	0	0.784904	-0.097291	2.262648
16	1	0	0.401755	0.254337	3.217630
17	6	0	0.260365	-1.205701	1.709471
18	7	0	-0.180846	-2.174584	1.148805
19	6	0	1.621639	0.802728	1.441334
20	8	0	0.803567	1.831166	0.692752
21	1	0	2.195496	1.472345	2.094733
22	6	0	2.556016	0.131823	0.458406
23	6	0	2.786668	0.643433	-0.820435
24	6	0	3.701635	0.033634	-1.676647
25	6	0	4.411780	-1.088787	-1.260810
26	6	0	4.198860	-1.597656	0.018890

27	6	0	3.278994	-0.993247	0.870201
28	1	0	2.248593	1.528416	-1.152980
29	1	0	3.860015	0.444112	-2.673052
30	1	0	5.127353	-1.564616	-1.929562
31	1	0	4.748203	-2.475120	0.356857
32	1	0	3.111938	-1.402182	1.866133

E(RM06) = -3362.90501973

Zero-point correction= 0.232792 (Hartree/Particle)

Sum of electronic and thermal Energies= -3362.647612

Sum of electronic and thermal Enthalpies= -3362.646541

Sum of electronic and thermal Free Energies= -3362.732142

Table S20. Coordinates and energies for optimized geometry of **TS5**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	-1.653894	-1.400820	-0.197301
2	8	0	-0.758339	0.324458	-0.533111
3	15	0	-0.447395	1.633714	0.166888
4	6	0	0.797294	-0.368424	2.424643
5	6	0	1.722345	0.432412	1.679750
6	8	0	0.909700	1.743392	0.881798
7	17	0	-3.503974	-1.824786	-1.242912

8	8	0	-1.565316	2.022000	1.229233
9	6	0	-2.934098	2.125926	0.818523
10	1	0	-3.291905	1.177843	0.396785
11	1	0	-3.506997	2.364669	1.716713
12	1	0	-3.049367	2.927258	0.080355
13	6	0	0.245315	2.750440	-2.080216
14	1	0	0.004778	3.638439	-2.668305
15	1	0	1.314968	2.750792	-1.835487
16	1	0	-0.009387	1.847295	-2.646815
17	6	0	0.078686	-1.341183	1.802991
18	7	0	-0.526263	-2.177000	1.204309
19	1	0	0.452411	-0.020183	3.395598
20	6	0	2.562286	-0.152791	0.589477
21	6	0	3.216927	0.688005	-0.321631
22	6	0	4.042835	0.162687	-1.307469
23	6	0	4.243993	-1.215329	-1.392134
24	6	0	3.625088	-2.056591	-0.473451
25	6	0	2.795017	-1.529330	0.514426
26	1	0	3.066452	1.763855	-0.253526
27	1	0	4.536997	0.831985	-2.010249
28	1	0	4.892151	-1.627897	-2.163772
29	1	0	3.789824	-3.131972	-0.517208

30	1	0	2.343541	-2.198870	1.243457
31	8	0	-0.538009	2.829416	-0.886062
32	1	0	2.277257	1.126992	2.313215

E(RM06) = -3362.90234711

Zero-point correction= 0.231979 (Hartree/Particle)

Sum of electronic and thermal Energies= -3362.645288

Sum of electronic and thermal Enthalpies= -3362.644217

Sum of electronic and thermal Free Energies=-3362.731985

Table S21. Coordinates and energies for optimized geometry of (*Z*)-**P2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.268586	1.008120	-0.000188
2	6	0	0.965796	1.363048	-0.000351
3	6	0	2.784865	-0.315375	0.000251
4	7	0	3.253098	-1.382704	0.000613
5	1	0	3.026167	1.790282	-0.000543
6	6	0	-0.250466	0.560340	-0.000173
7	6	0	-1.474871	1.249408	0.000268
8	6	0	-2.683635	0.564985	0.000443
9	6	0	-2.690514	-0.827741	0.000120
10	6	0	-1.483572	-1.526960	-0.000346

11	6	0	-0.274237	-0.844458	-0.000529
12	1	0	-1.469948	2.339656	0.000488
13	1	0	-3.620584	1.119003	0.000850
14	1	0	-3.634578	-1.369913	0.000180
15	1	0	-1.484284	-2.615315	-0.000615
16	1	0	0.652455	-1.413051	-0.000963
17	1	0	0.787382	2.440065	-0.000658

E(RM06) = -401.601503235

Zero-point correction= 0.132565 (Hartree/Particle)

Sum of electronic and thermal Energies= -401.458578

Sum of electronic and thermal Enthalpies= -401.457507

Sum of electronic and thermal Free Energies= -401.508809

Table S22. Coordinates and energies for optimized geometry of $ClZnOPO(OMe)_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	1.367022	0.011643	-0.034332
2	8	0	-0.336047	0.147801	1.089321
3	15	0	-1.168444	0.037953	-0.199704
4	8	0	-0.168045	-0.234323	-1.330059
5	17	0	3.493622	0.158121	0.158256
6	8	0	-1.997663	1.347475	-0.526153

7	6	0	-2.907696	1.864499	0.453094
8	1	0	-2.390533	2.021233	1.407290
9	1	0	-3.267251	2.819627	0.065685
10	1	0	-3.748719	1.175392	0.586825
11	6	0	-1.963870	-2.382493	0.331322
12	1	0	-2.892071	-2.956399	0.360201
13	1	0	-1.277022	-2.831565	-0.396331
14	1	0	-1.504810	-2.365539	1.326431
15	8	0	-2.318967	-1.056131	-0.073288

E(RM06) = -2961.32391280

Zero-point correction= 0.097712 (Hartree/Particle)

Sum of electronic and thermal Energies= -2961.211791

Sum of electronic and thermal Enthalpies= -2961.210720

Sum of electronic and thermal Free Energies= -2961.273210

References

1) For *Gaussian 09*, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W.

Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

2) Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*: 215.

3) A. Schäfer, H. Horn, R.Ahlrichs, *J. Chem. Phys.***1992**, *97*, 2571.

4) For *CYLview* (Ver. 1.0b), C. Y. Legault, Université de Sherbrooke, 2009.

5) a) *The Quantum Theory of Atoms in Molecules* (Eds.: C. F.Matta, R. J. Boyd), Wiley-VCH, Weinheim, 2007; b) R. F. W.Bader, *Atoms in Molecules: A Quantum Theory*, OxfordUniversity Press, Oxford, 1990.

6) a) R. F. W. Bader, M. E. Stephens, *J. Am. Chem. Soc.***1975**, *97*, 7391; b) X. Fradera, M. A. Austen, R. F. W. Bader, *J. Phys. Chem. A***1999**, *103*, 304; c) X. Fradera, J. Poater, S. Simon, M. Duran, M. Sol, *Theor. Chem. Acc.***2002**, *108*, 214