Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Supporting Information

Chemo-, Regio- and Stereoselective Synthesis of (*E*)-γ,γ-Diarylvinylphosphonates from α-Hydroxyallylphosphonates in TFA

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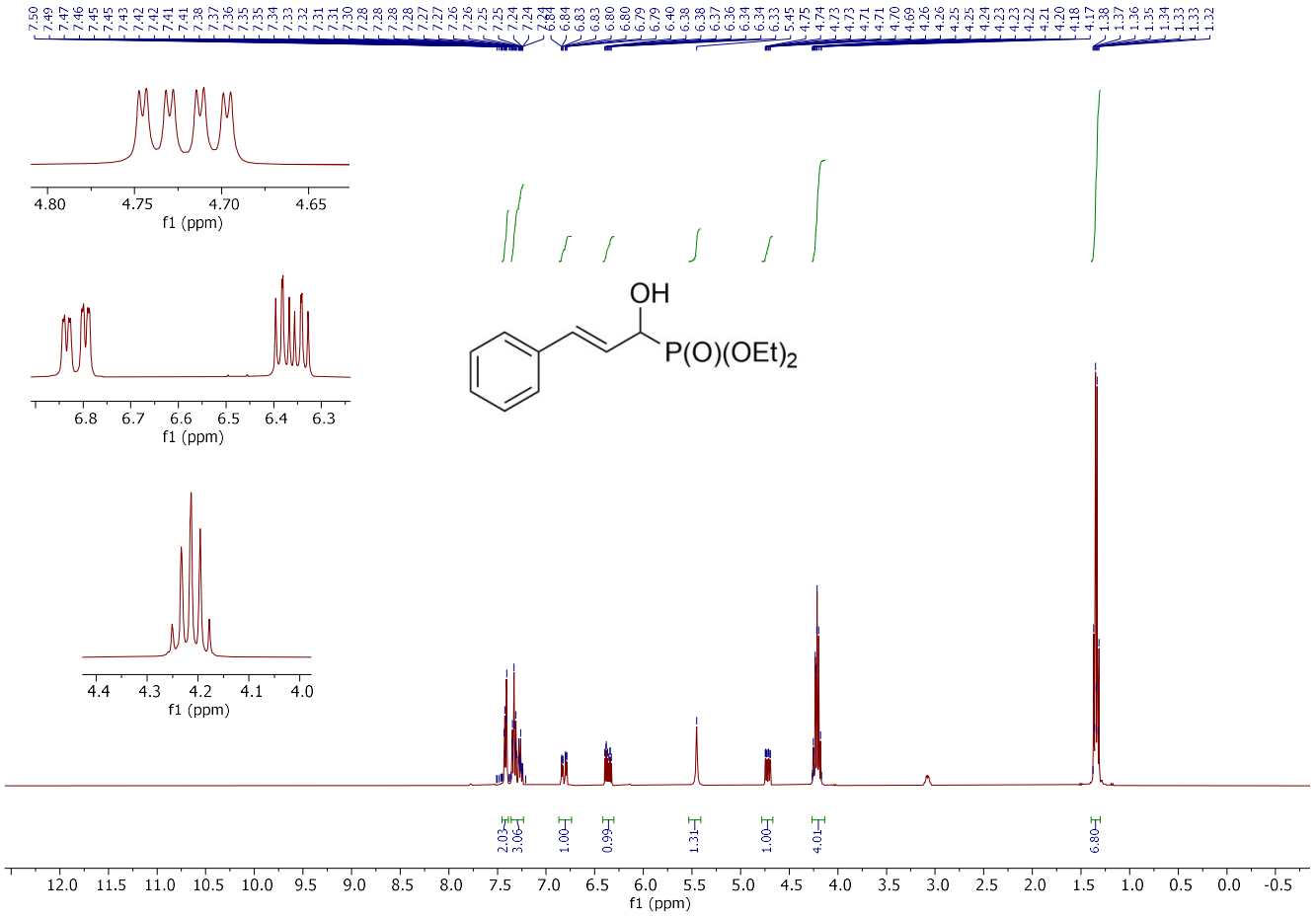


Figure S1: ^{1}H NMR Spectra of 1a in $CDCl_3$

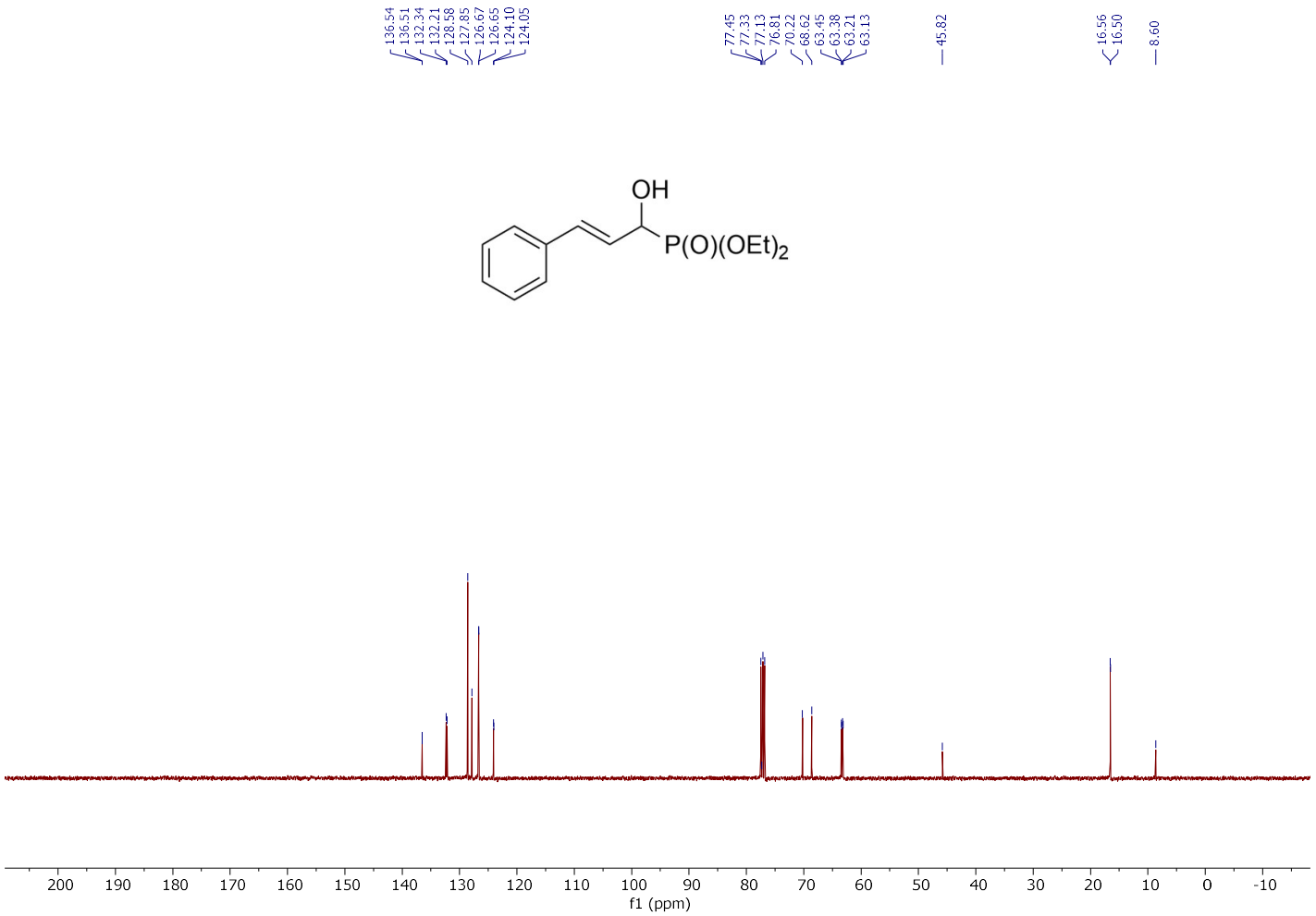


Figure S2: $^{13}C\{^{1}H\}$ NMR Spectra of 1a in $CDCl_3$

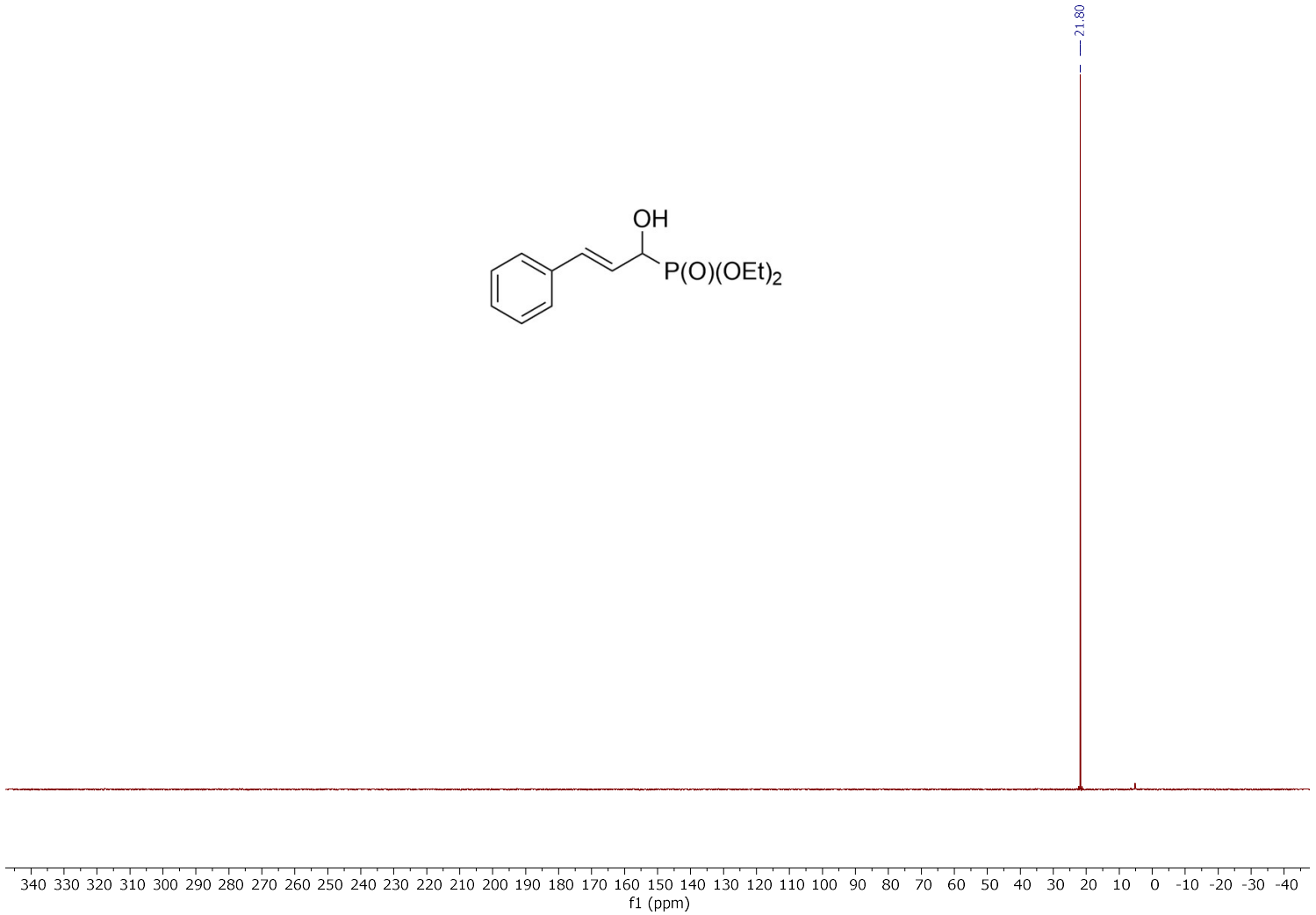


Figure S3: $^{31}P\{^{1}H\}$ NMR Spectra of 1a in $CDCl_3$

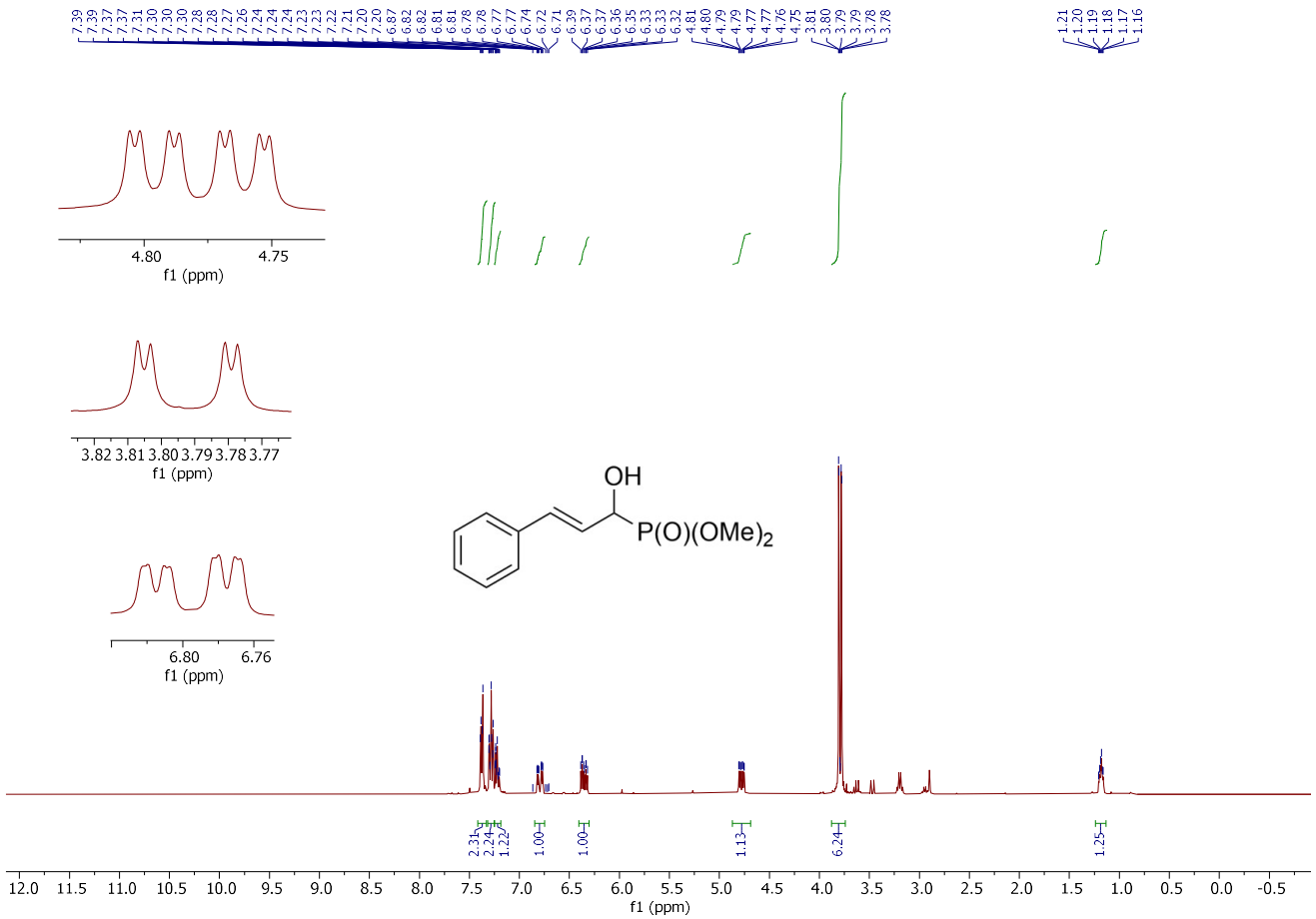


Figure S4: ^{1}H NMR Spectra of 1b in $CDCl_3$

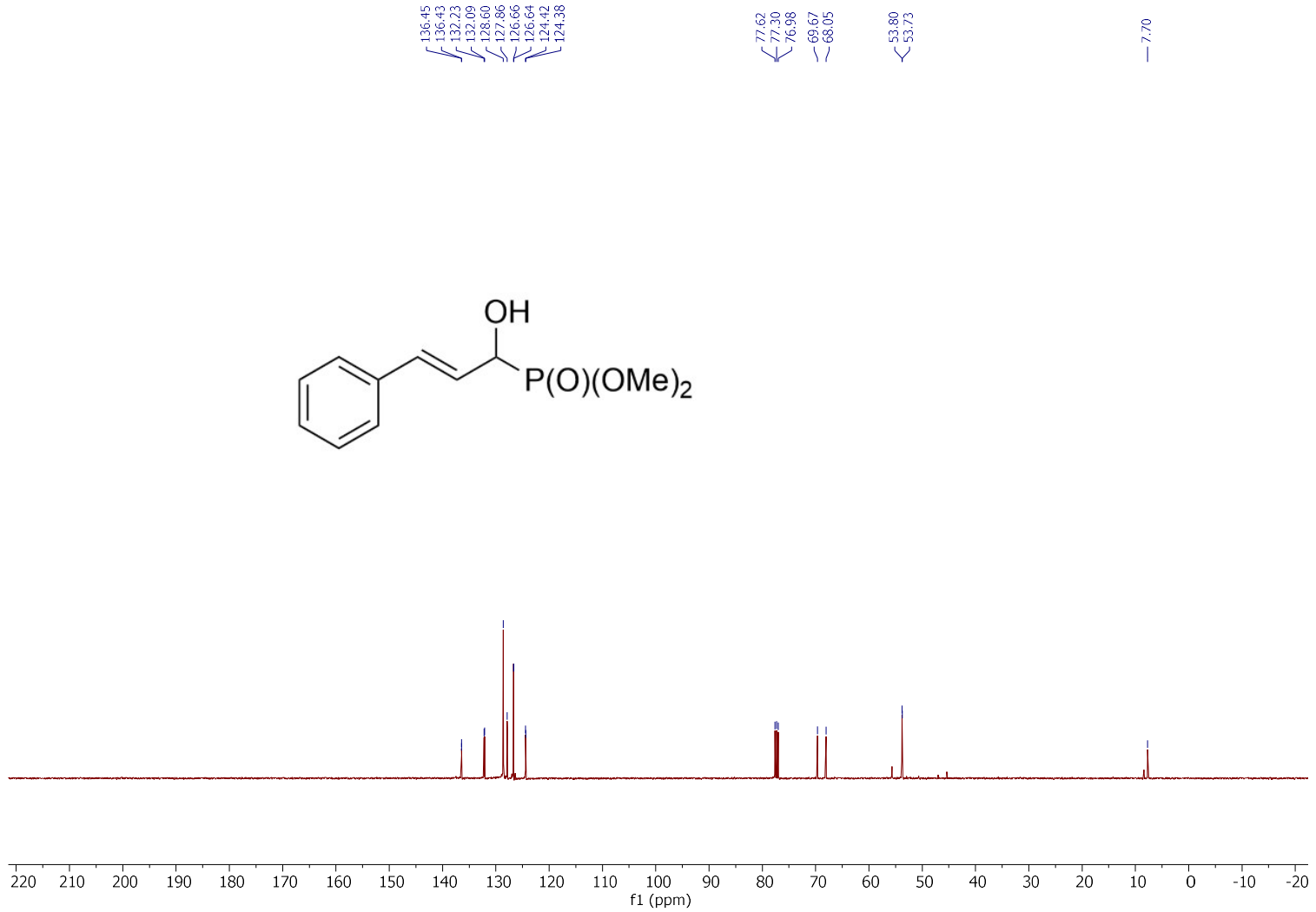


Figure S5: $^{13}C\{^{1}H\}$ NMR Spectra of 1b in $CDCl_3$

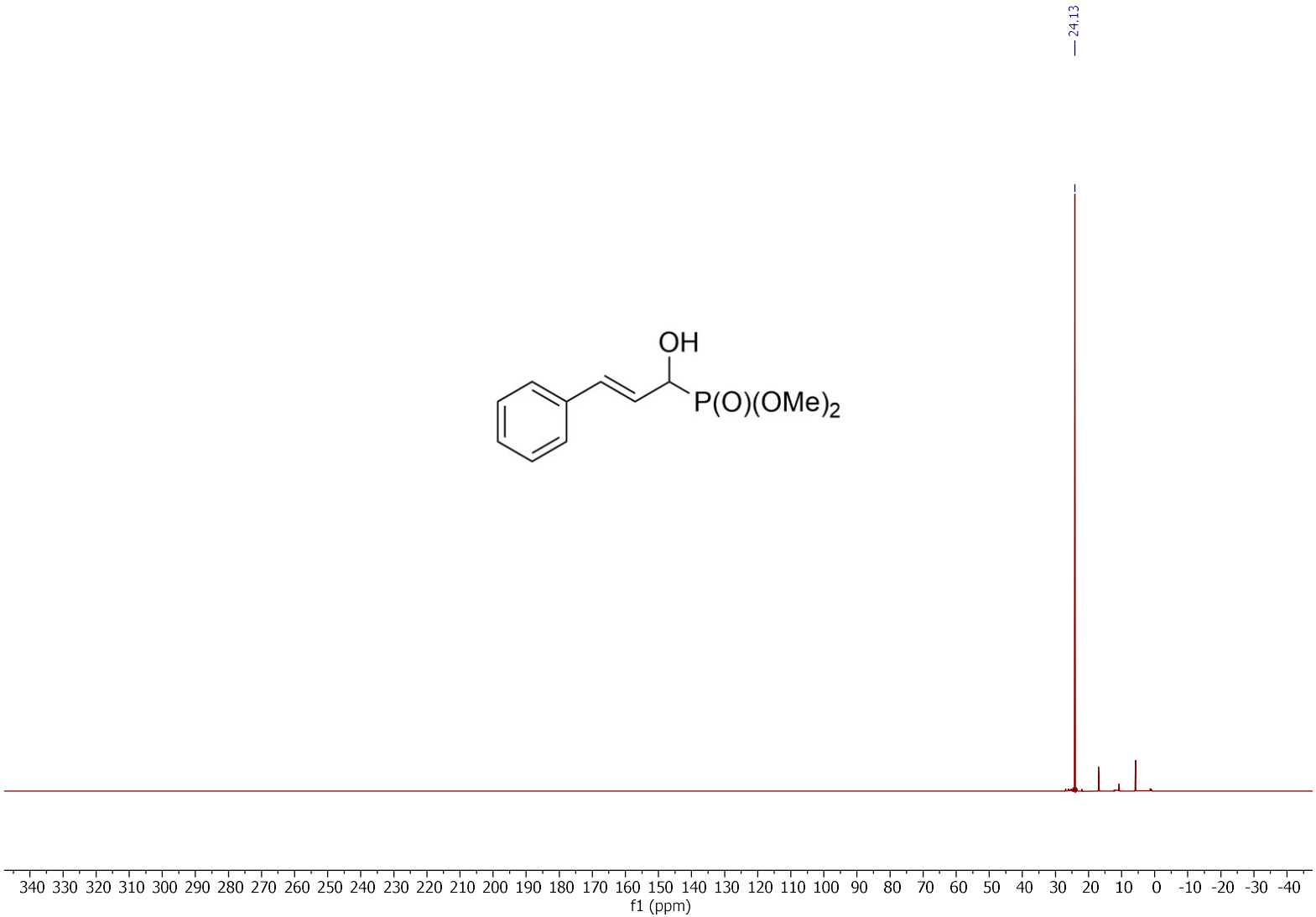


Figure S6: $^{31}P\{^{1}H\}$ NMR Spectra of 1b in $CDCl_3$

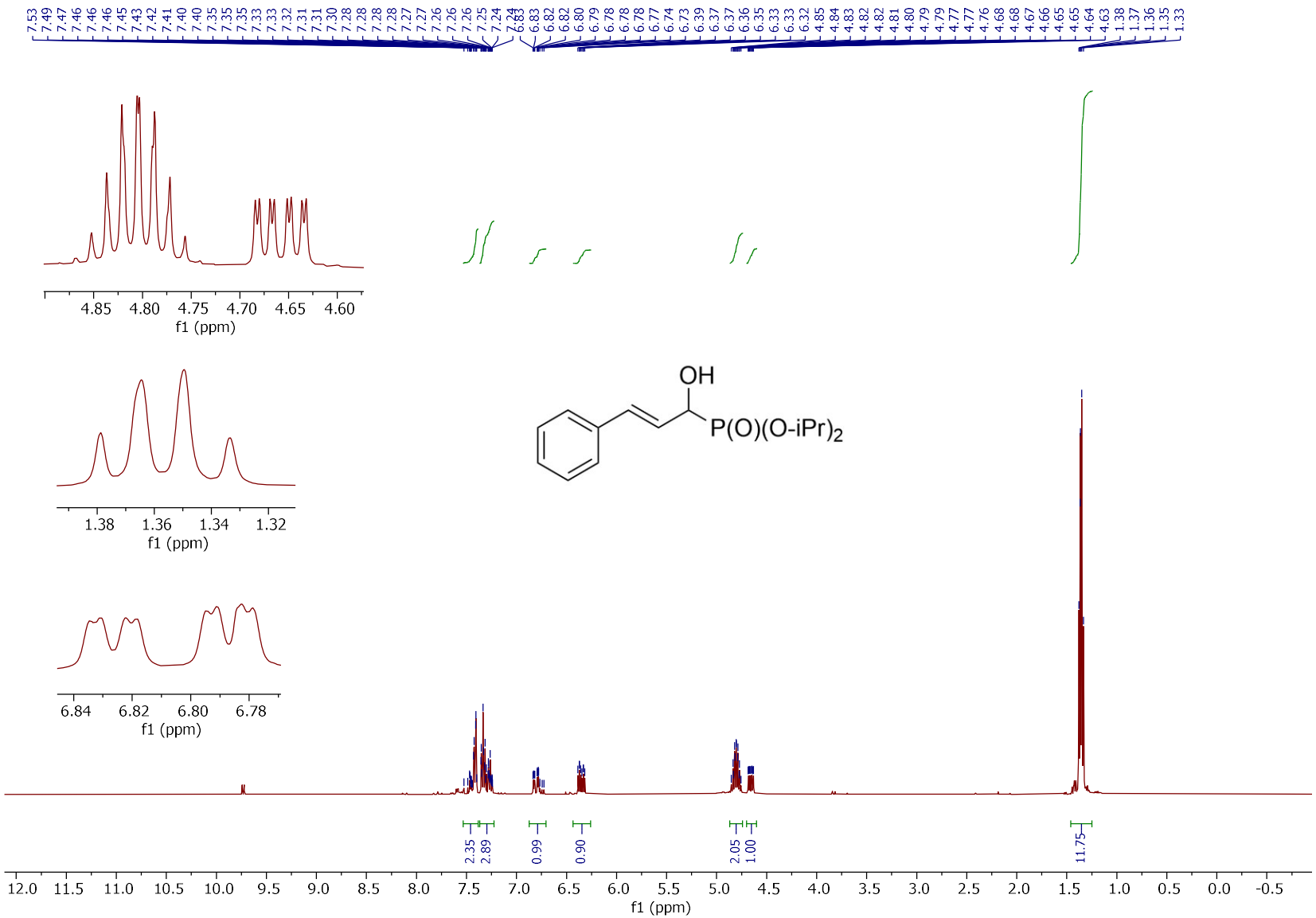


Figure S7: ^{1}H NMR Spectra of 1c in $CDCl_3$

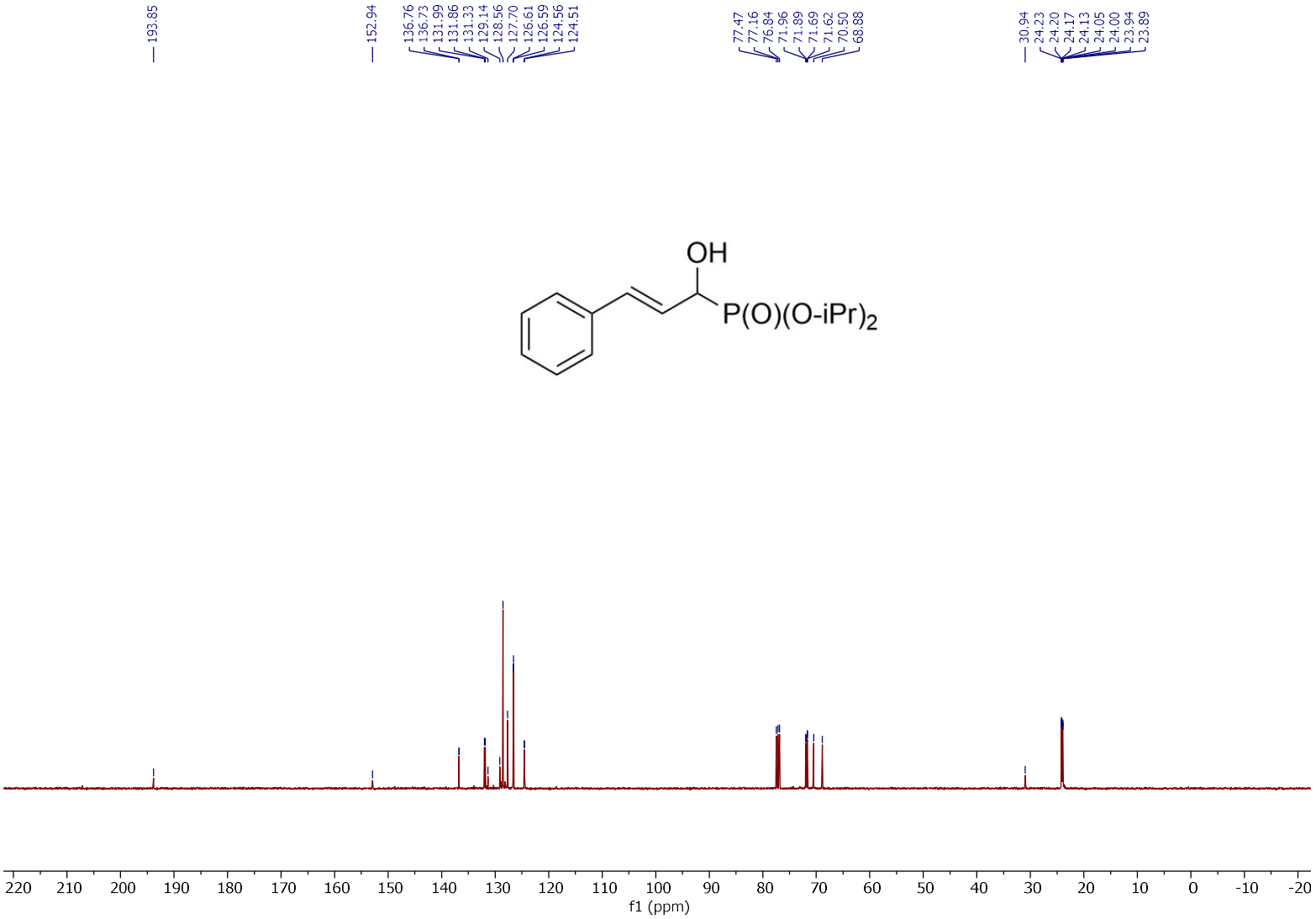


Figure S8: $^{13}C\{^{1}H\}$ NMR Spectra of 1c in $CDCl_3$

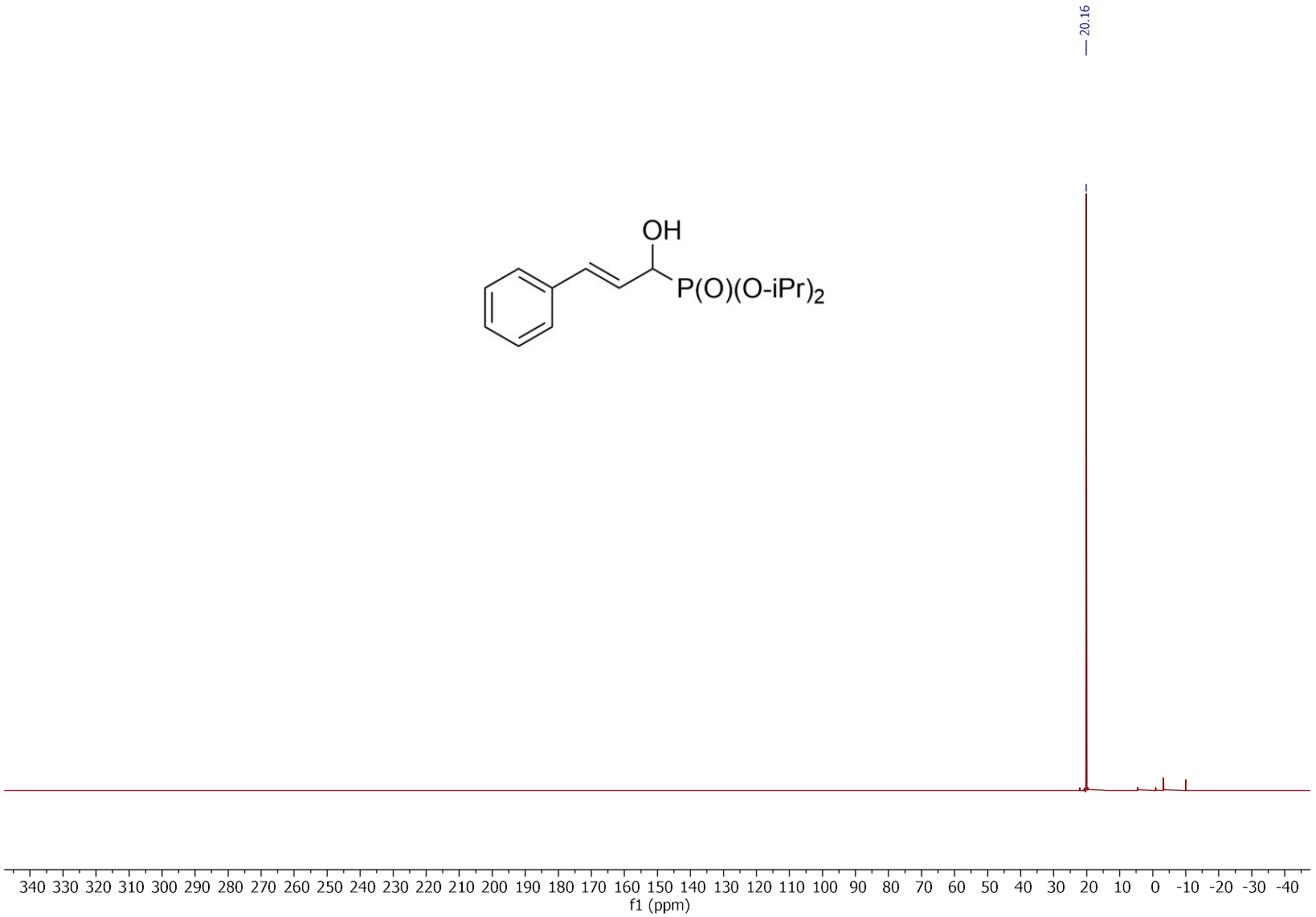


Figure S9: $^{31}P\{^{1}H\}$ NMR Spectra of 1c in $CDCl_3$

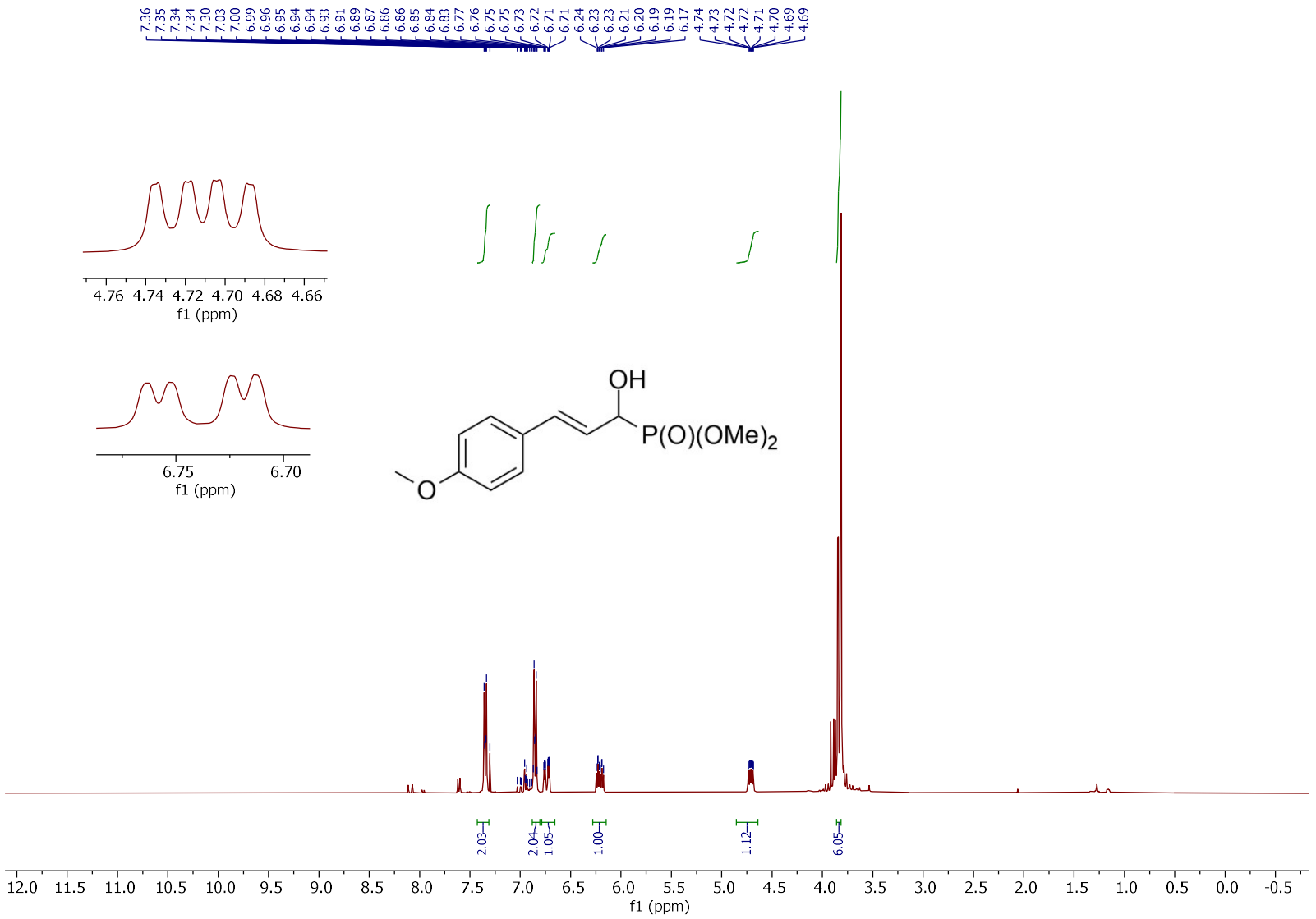


Figure S10: ^{1}H NMR Spectra of 1d in $CDCl_3$

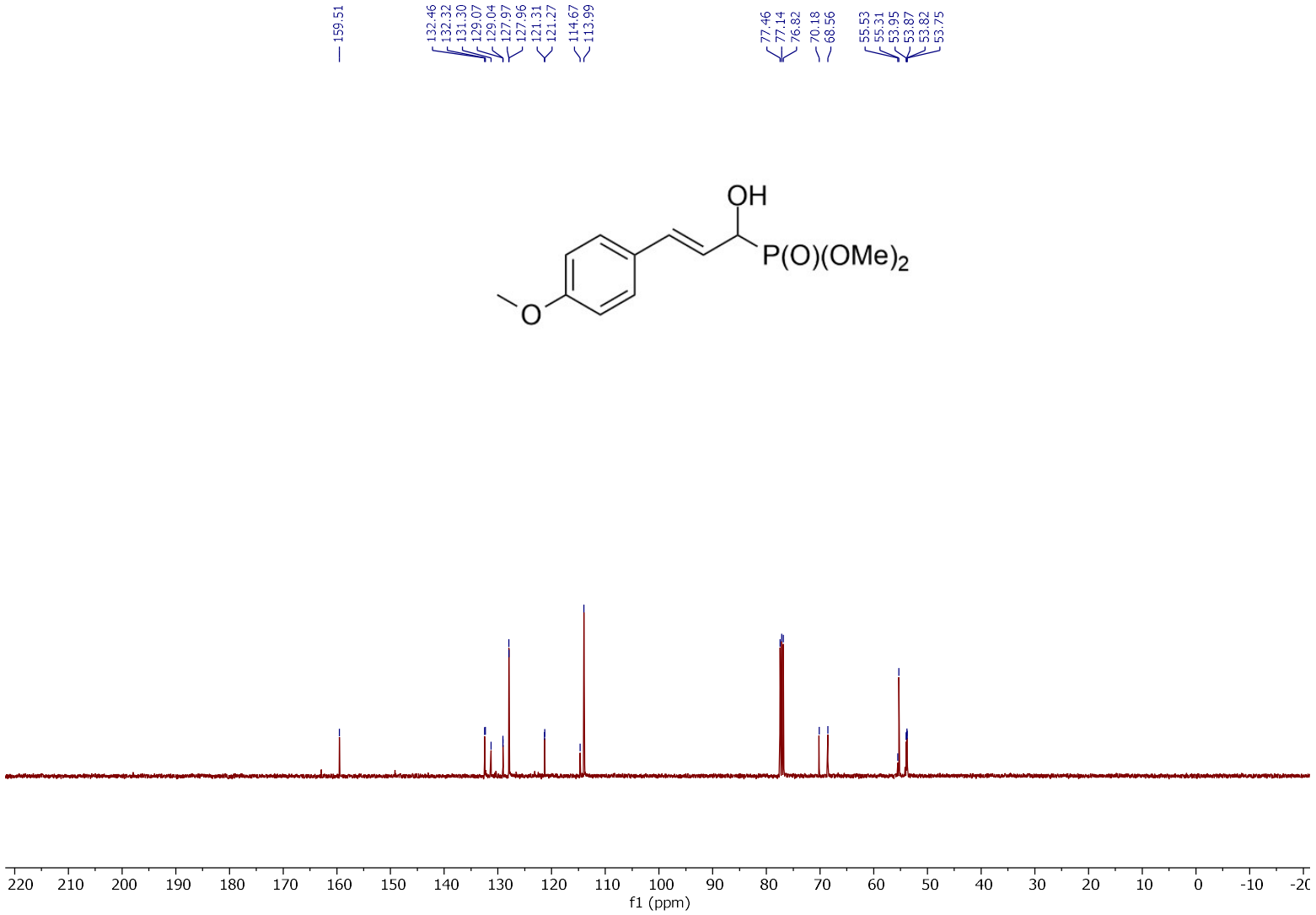
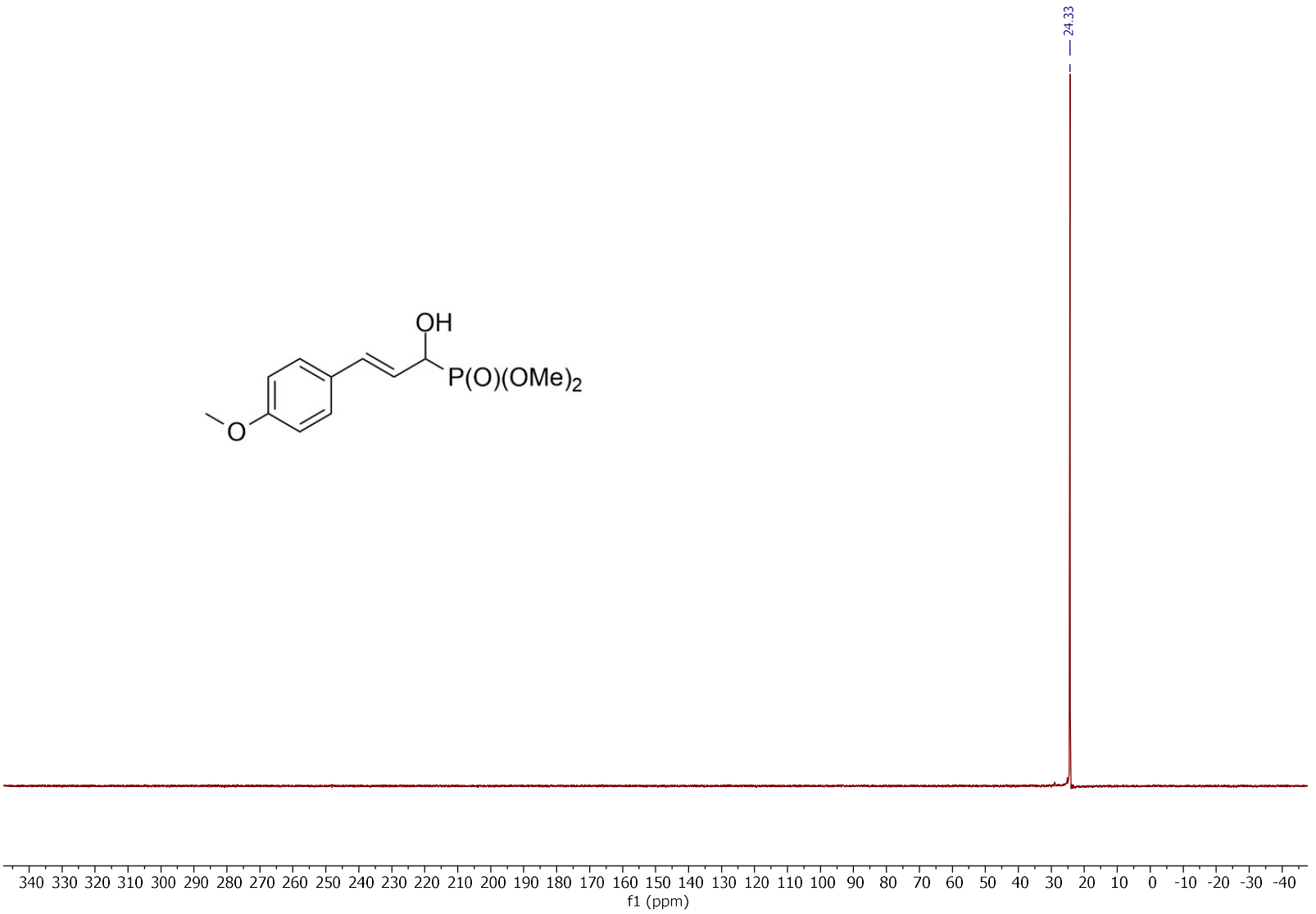


Figure S11: $^{13}C\{^{1}H\}$ NMR Spectra of 1d in $CDCl_3$



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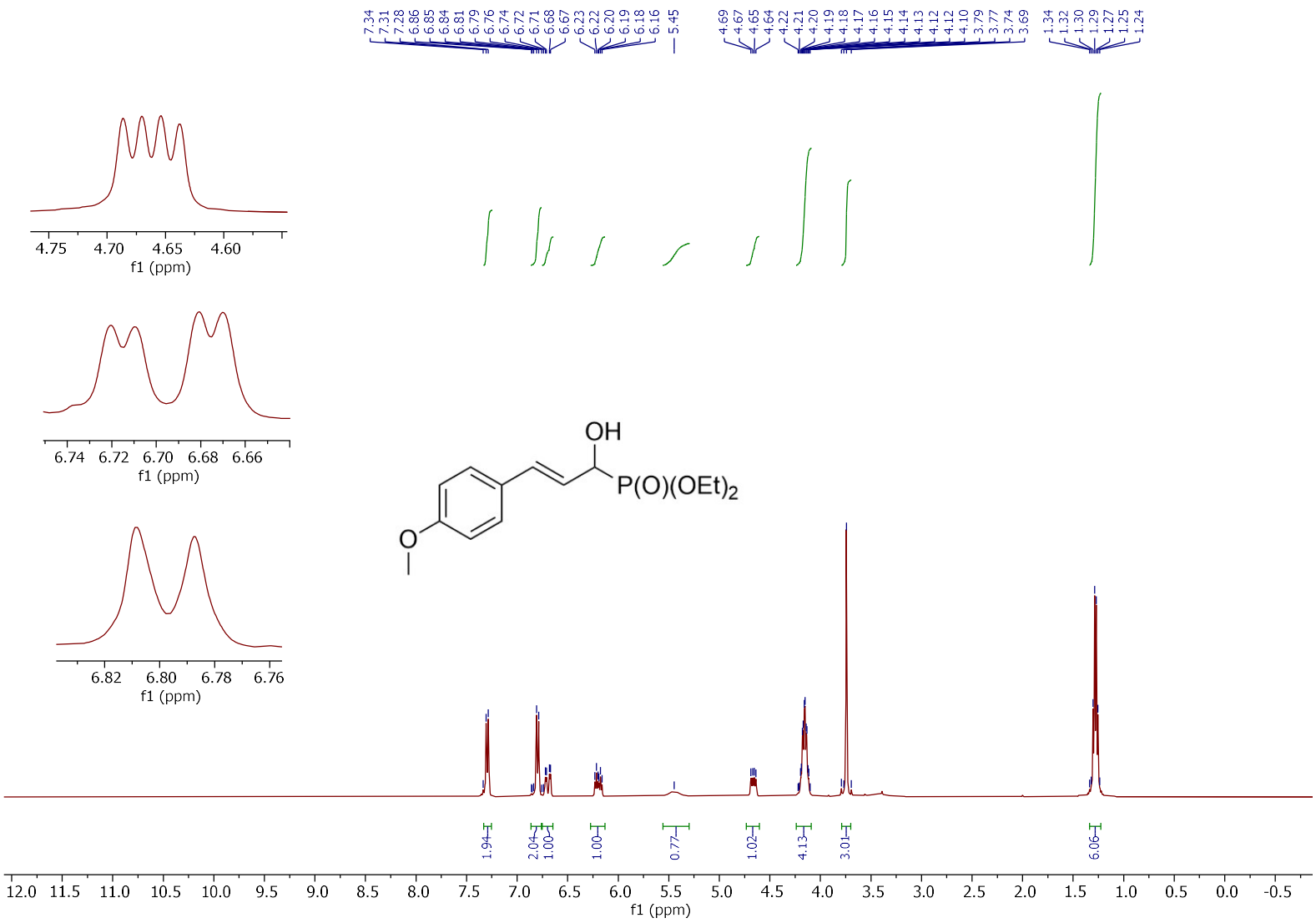


Figure S13: ^{1}H NMR Spectra of 1e in $CDCl_3$

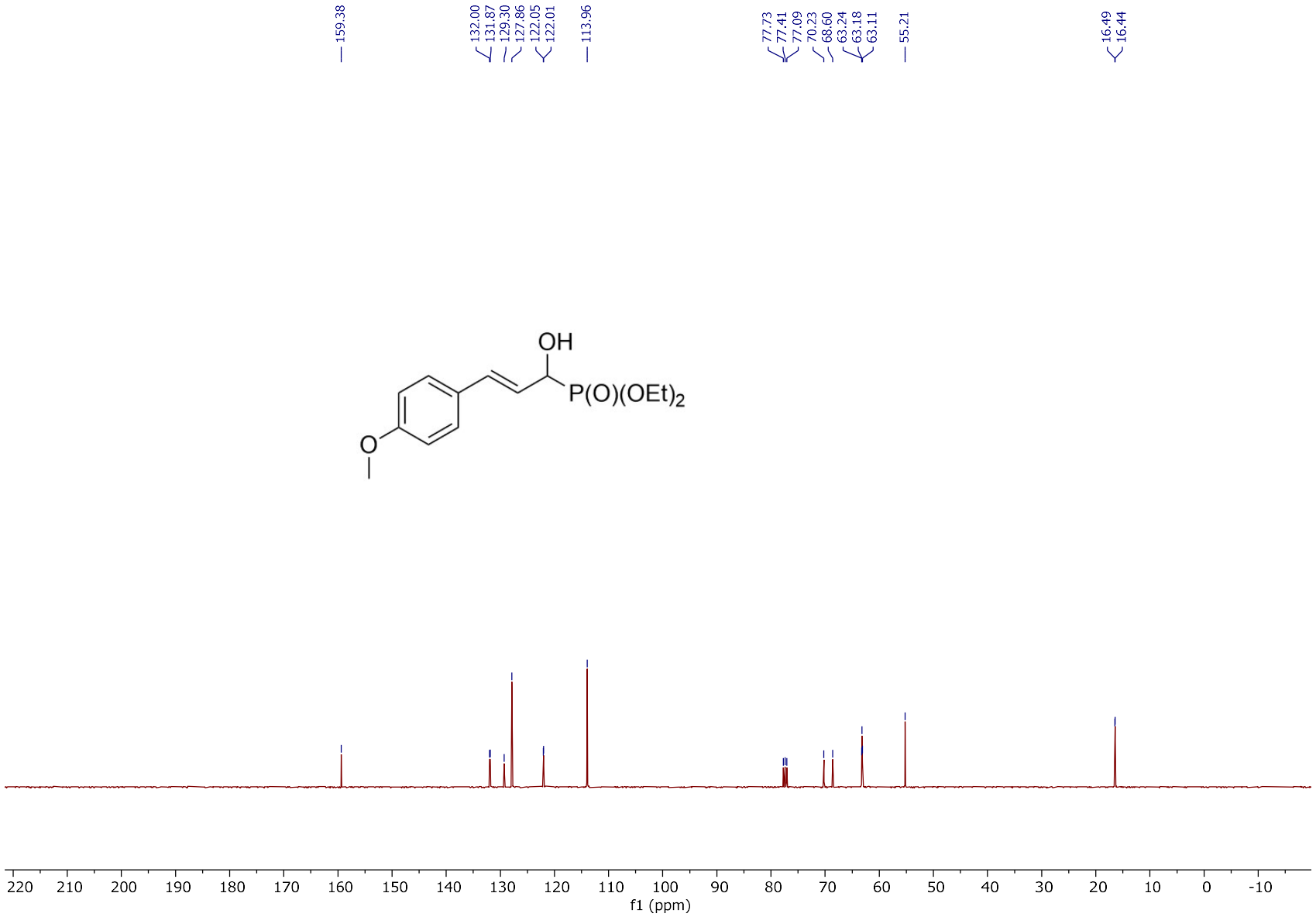


Figure S14: $^{13}C\{^{1}H\}$ MR Spectra of 1e in $CDCl_3$

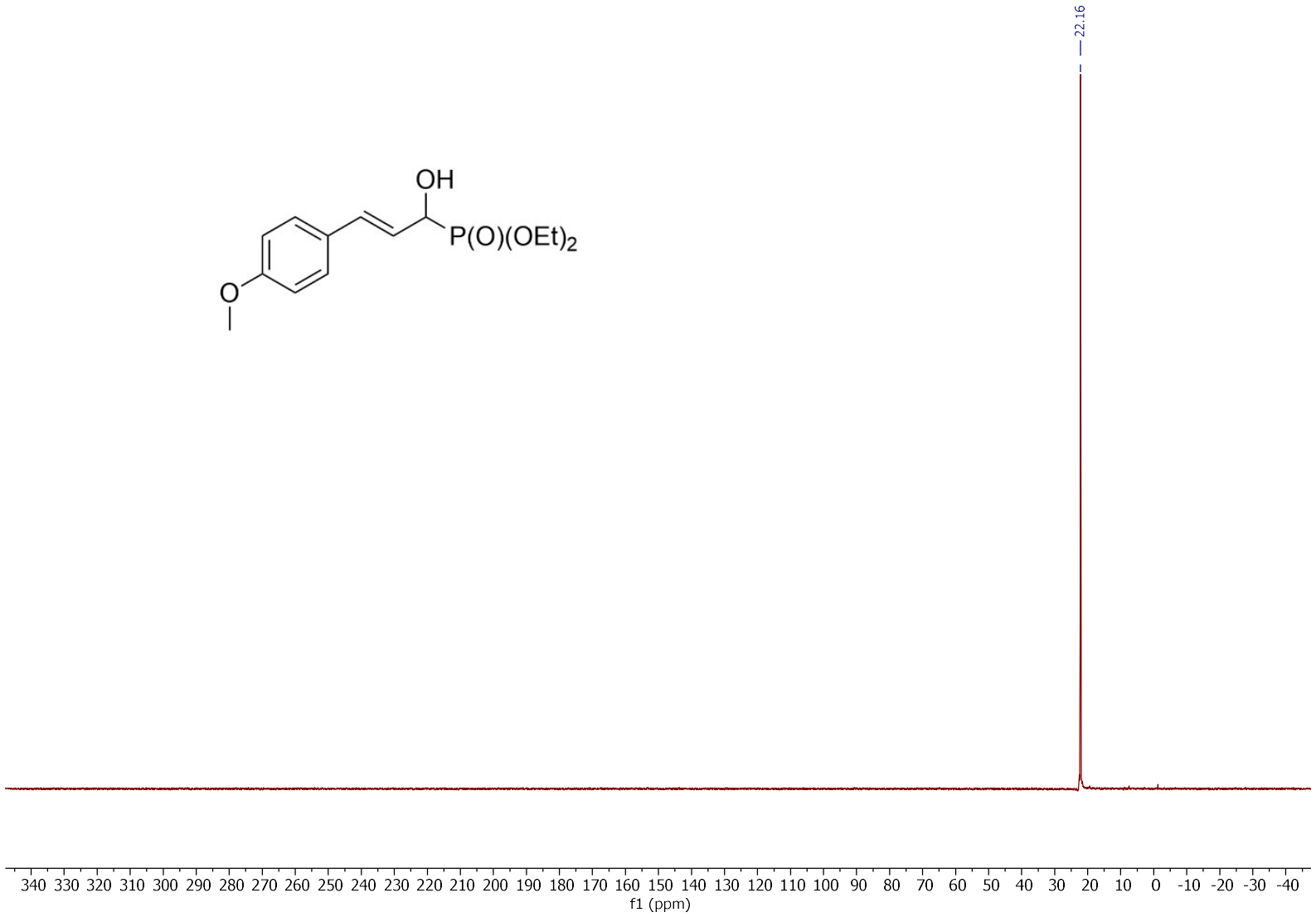


Figure S15: ^{31}P {^{1}H} MR Spectra of 1e in $CDCl_3$

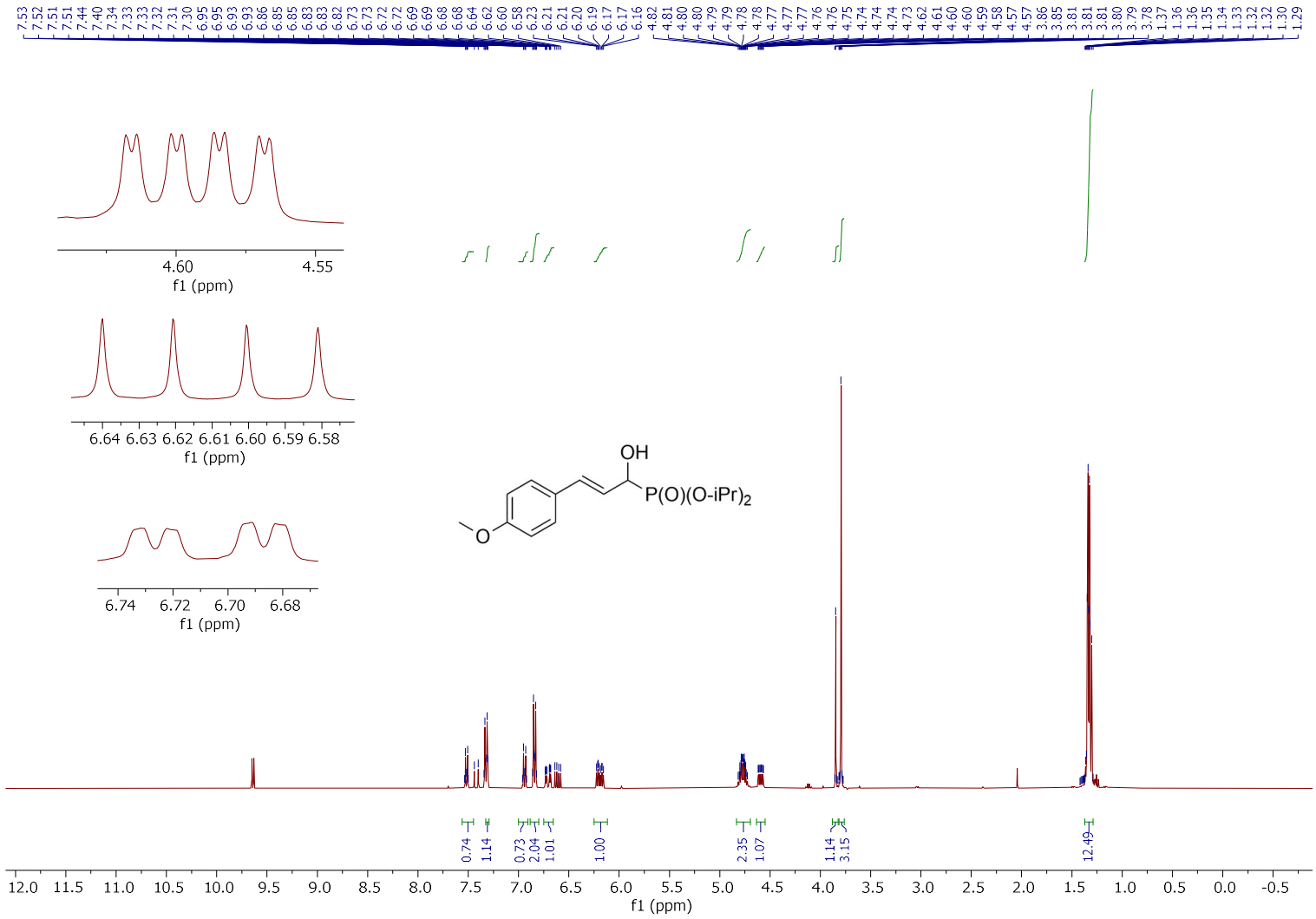
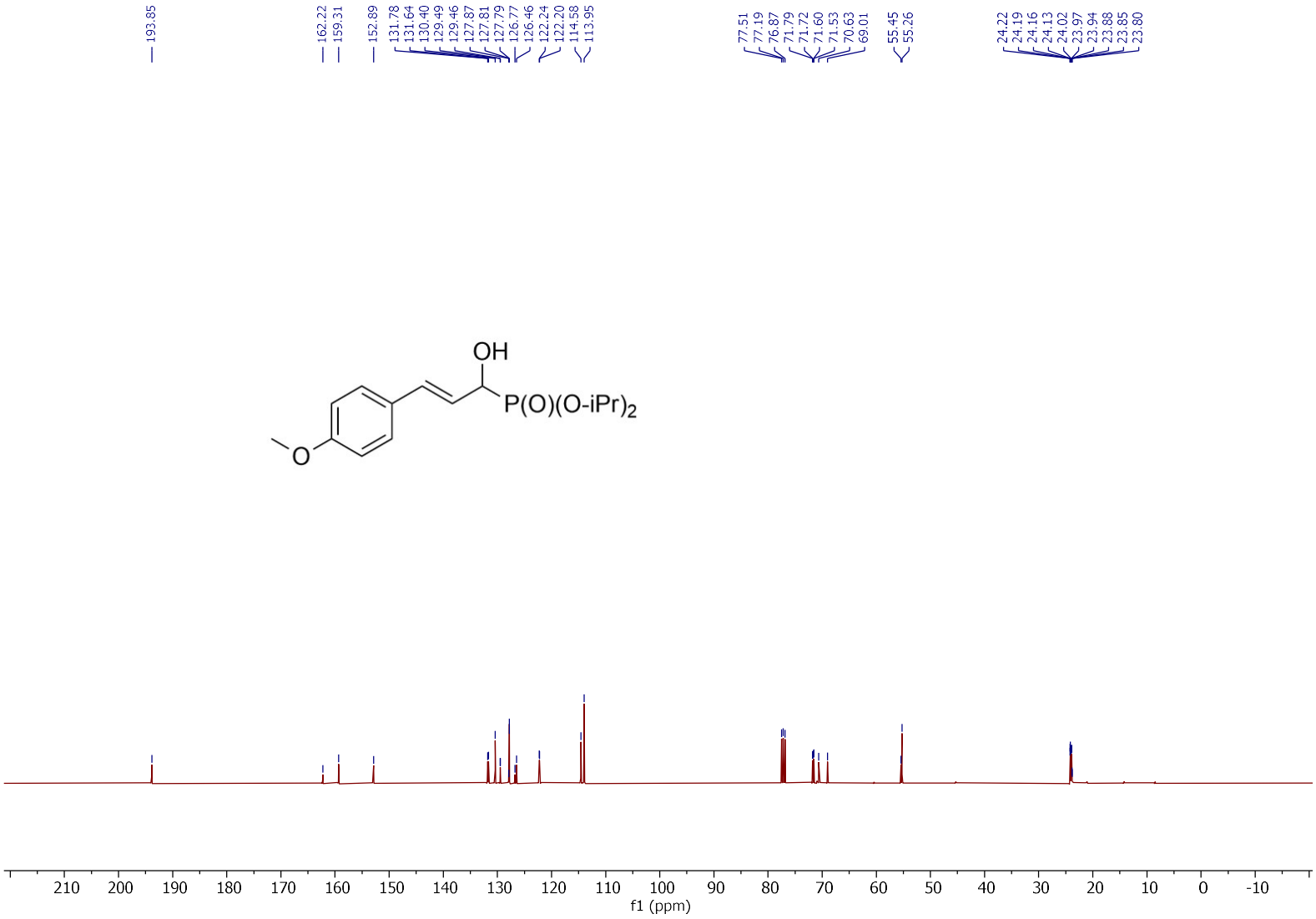


Figure S16: ^{1}H NMR Spectra of 1f in $CDCl_3$



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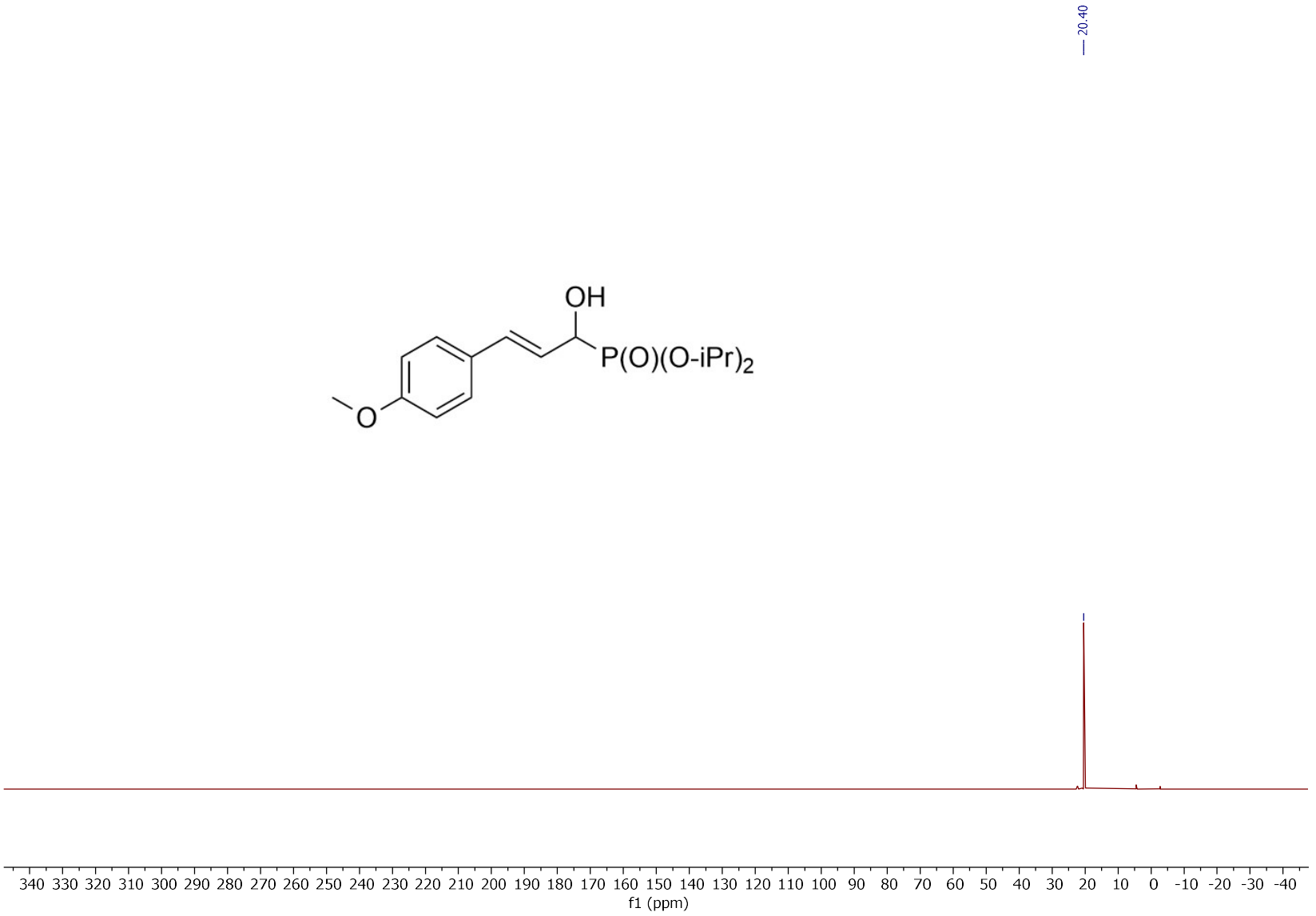

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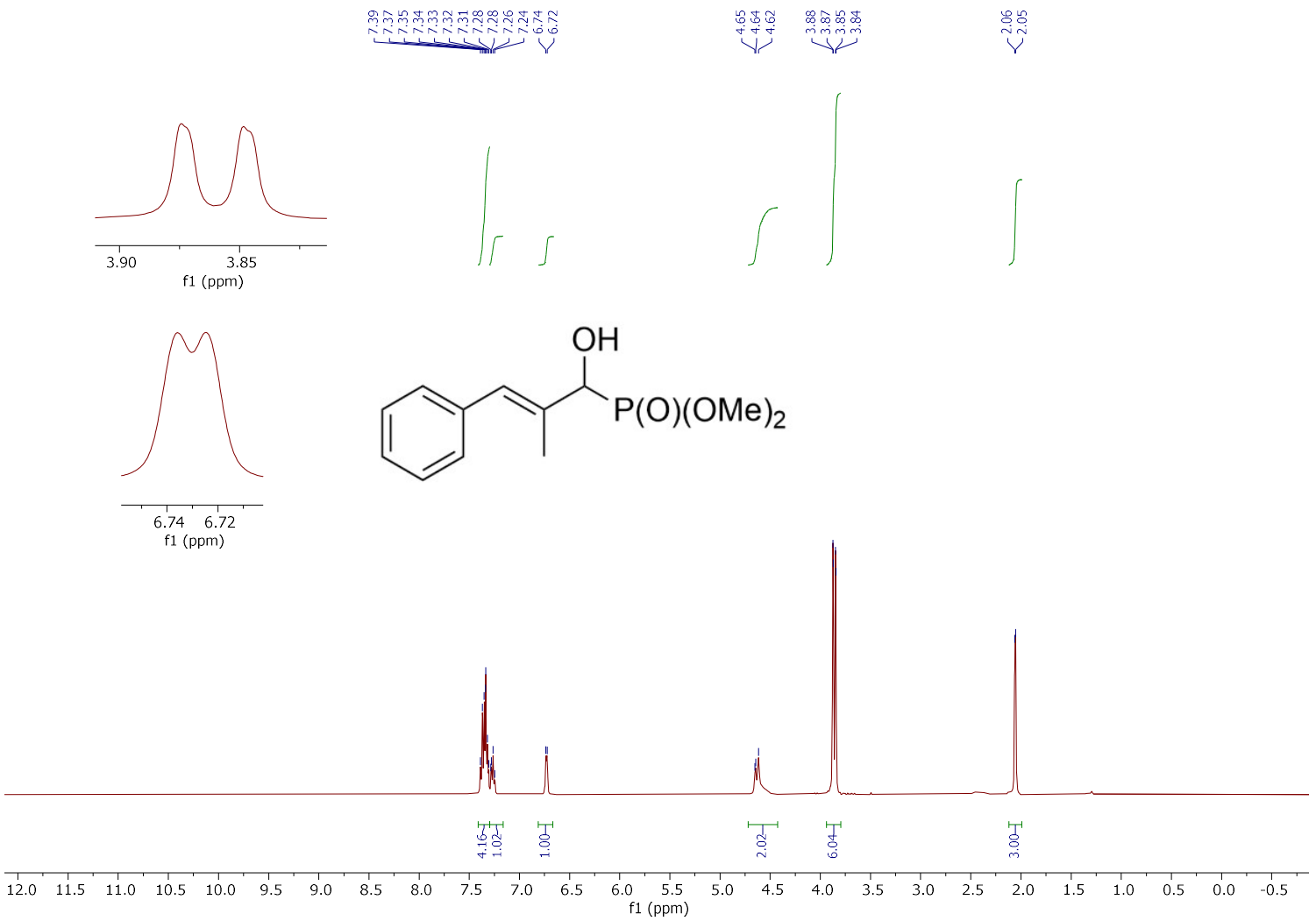

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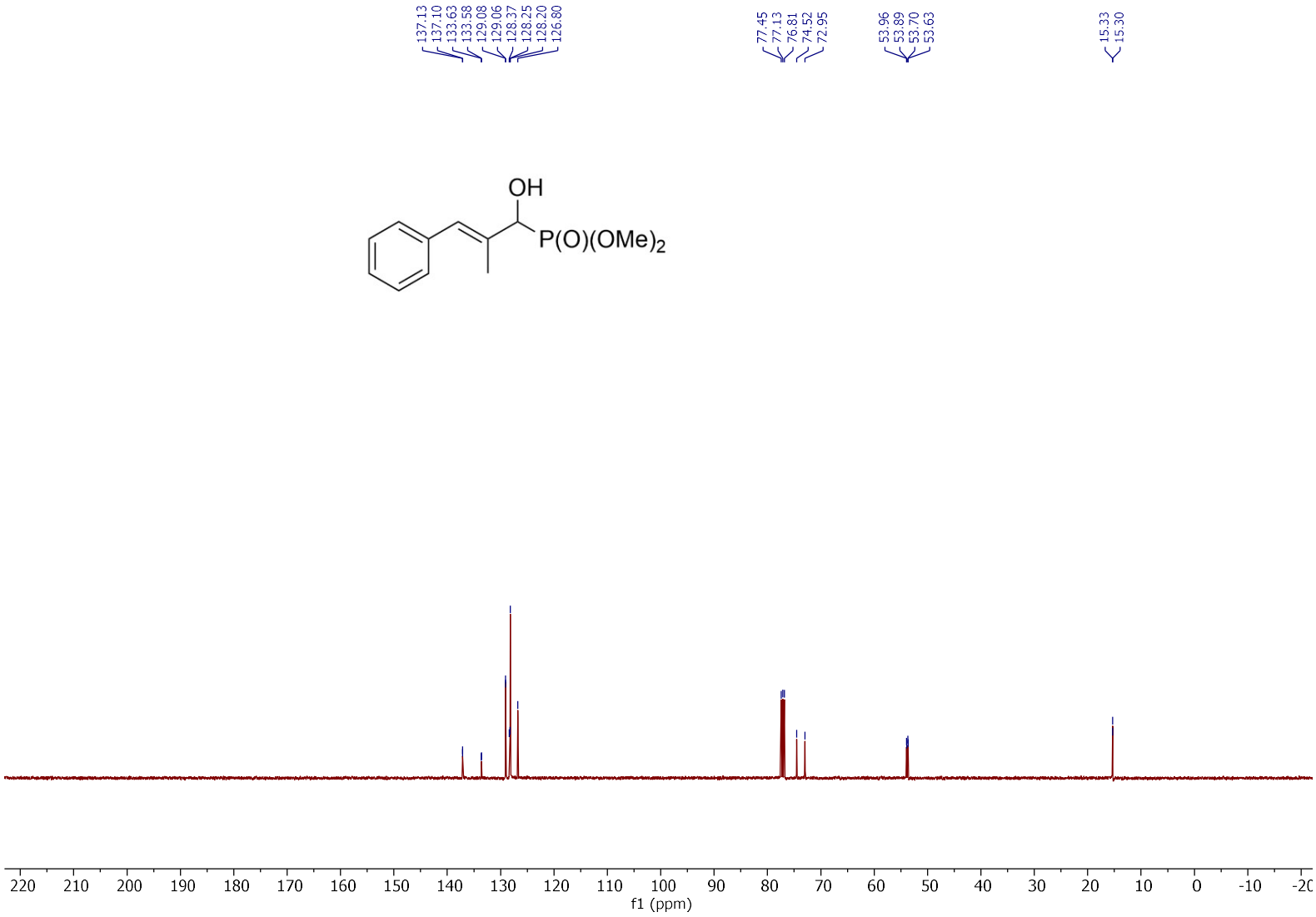


Figure S20: $^{13}C\{^{1}H\}$ NMR Spectra of 1g in $CDCl_3$

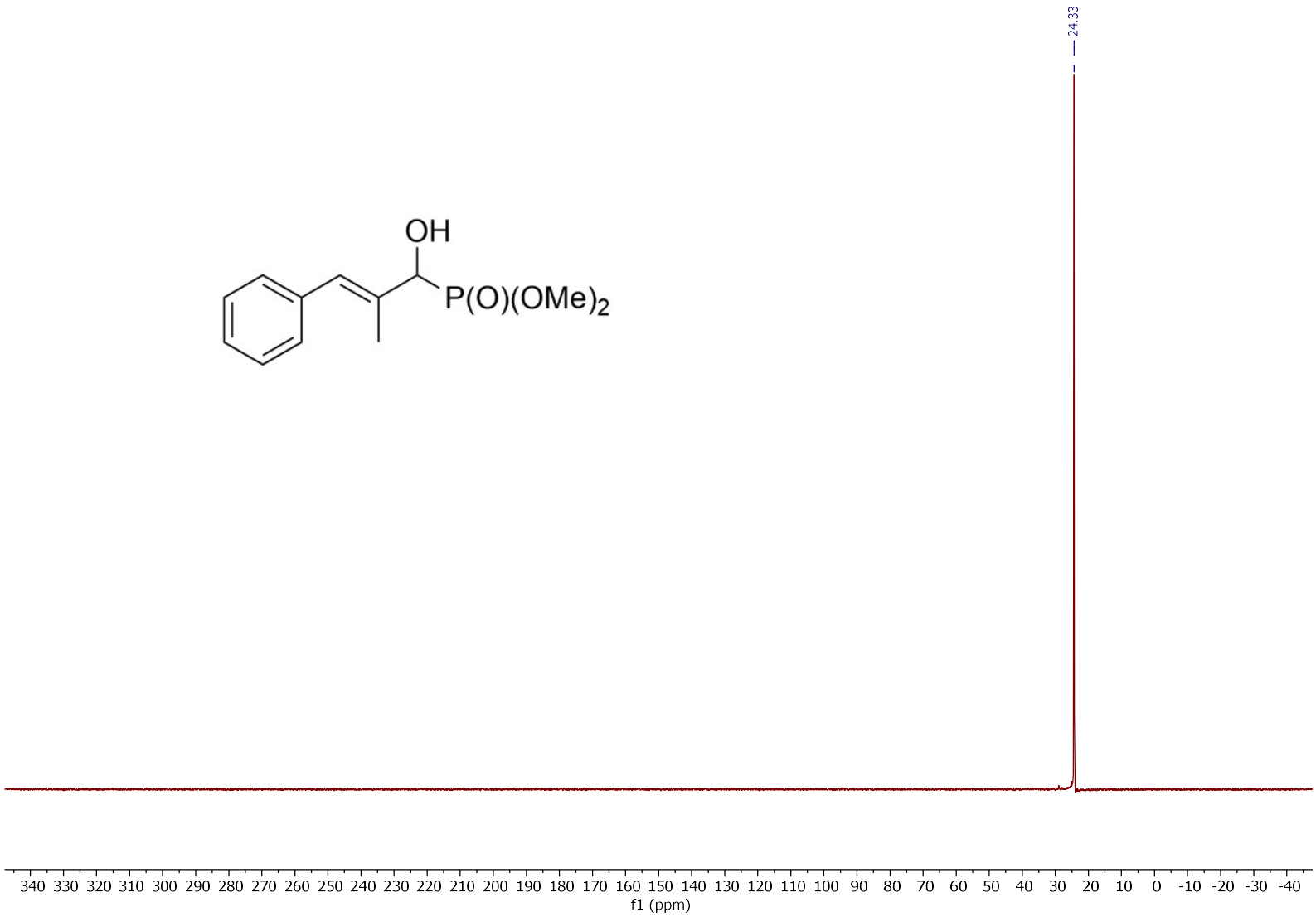


Figure S21: $^{31}P\{^{1}H\}$ NMR Spectra of 1g in $CDCl_3$

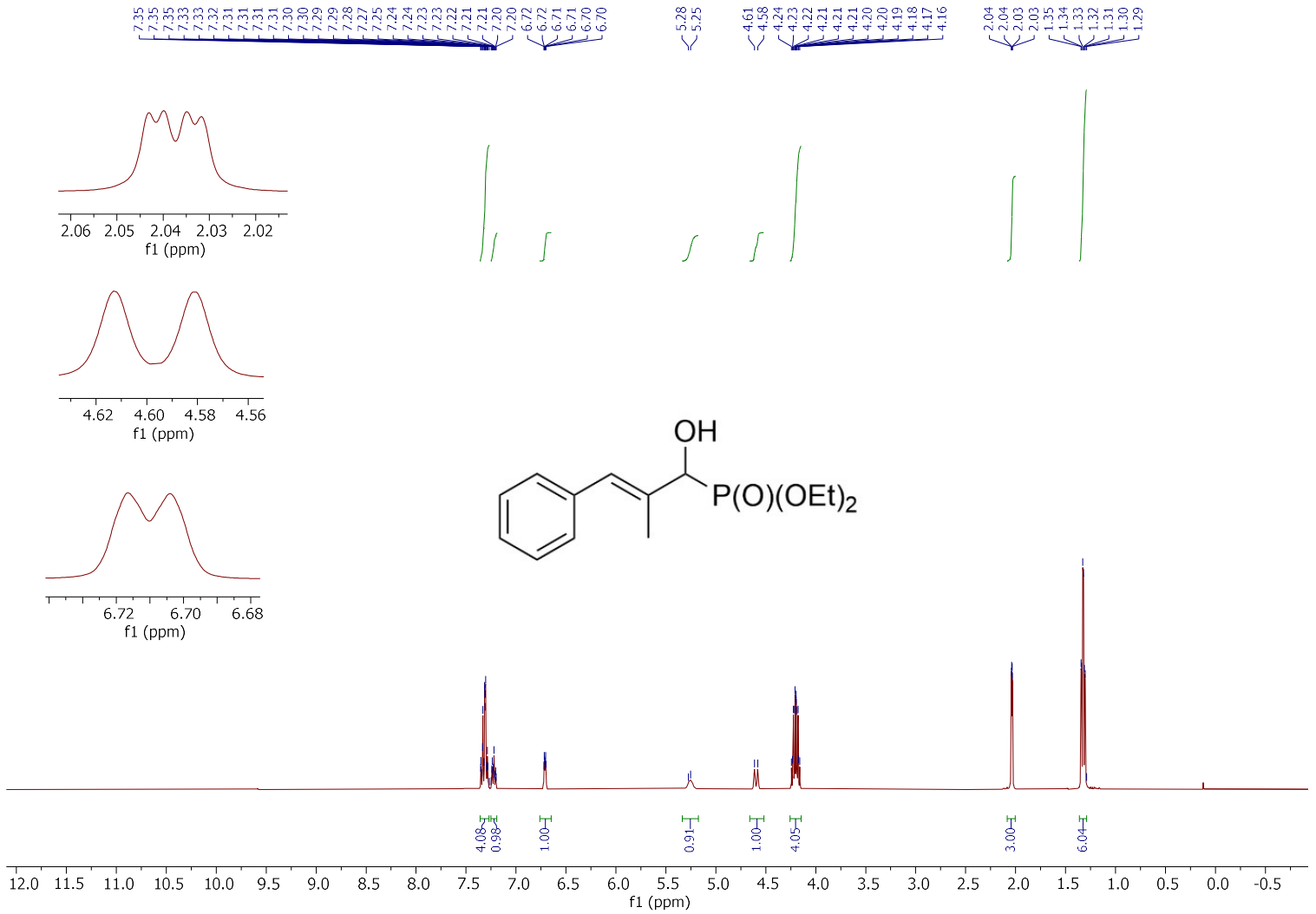
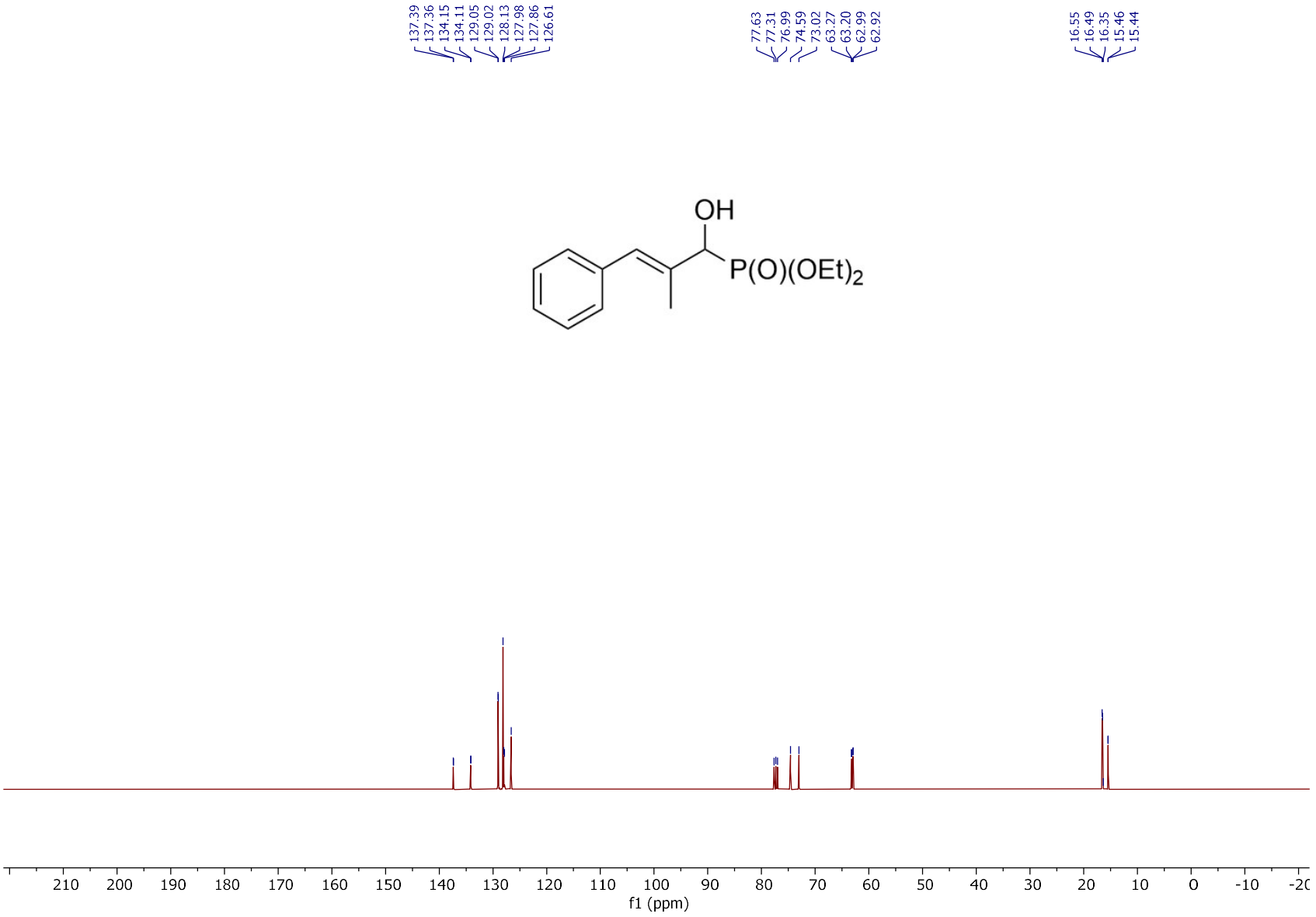


Figure S22: ^{1}H NMR Spectra of 1h in $CDCl_3$



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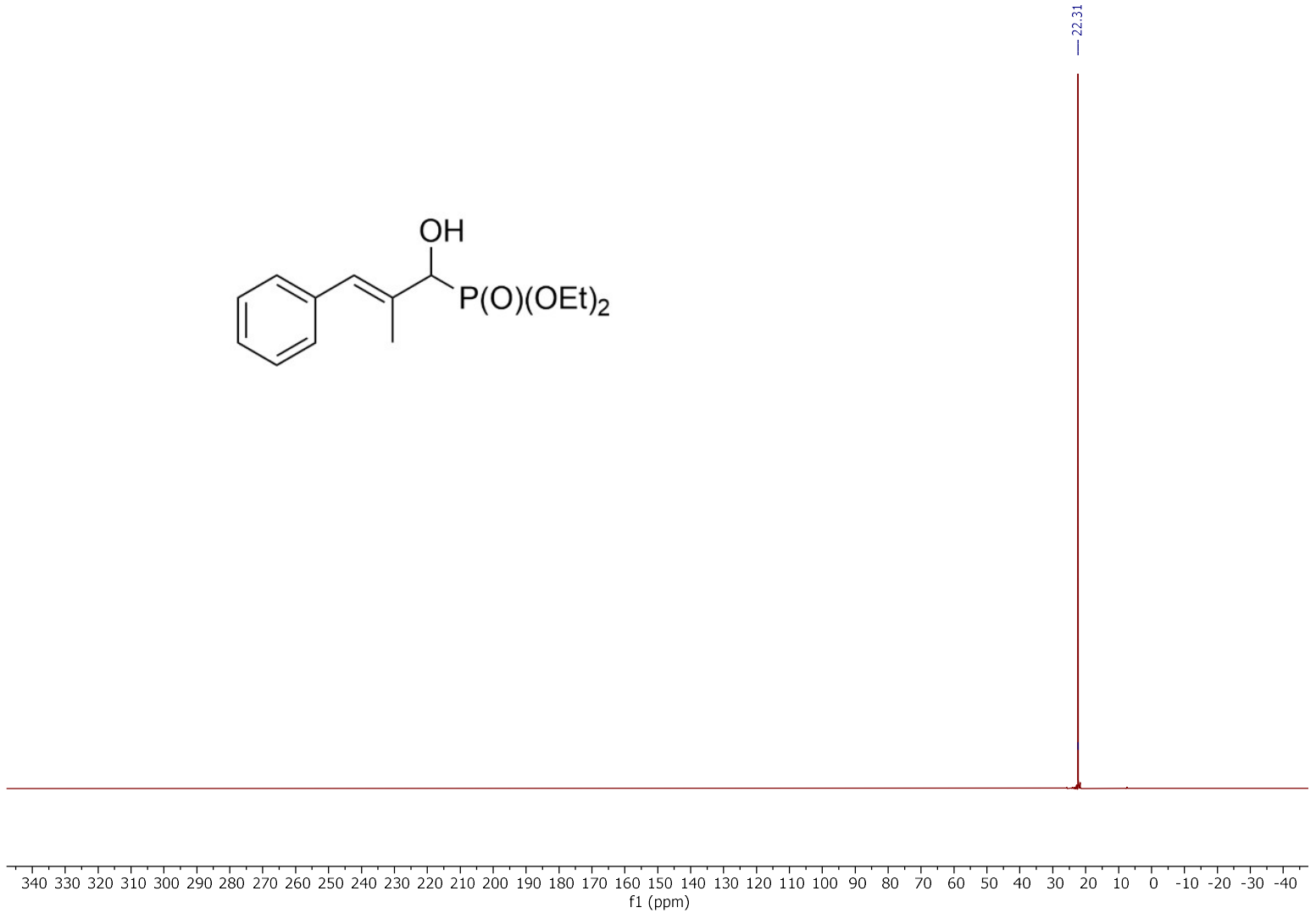


Figure S24: $^{31}P\{^{1}H\}$ NMR Spectra of 1h in $CDCl_3$

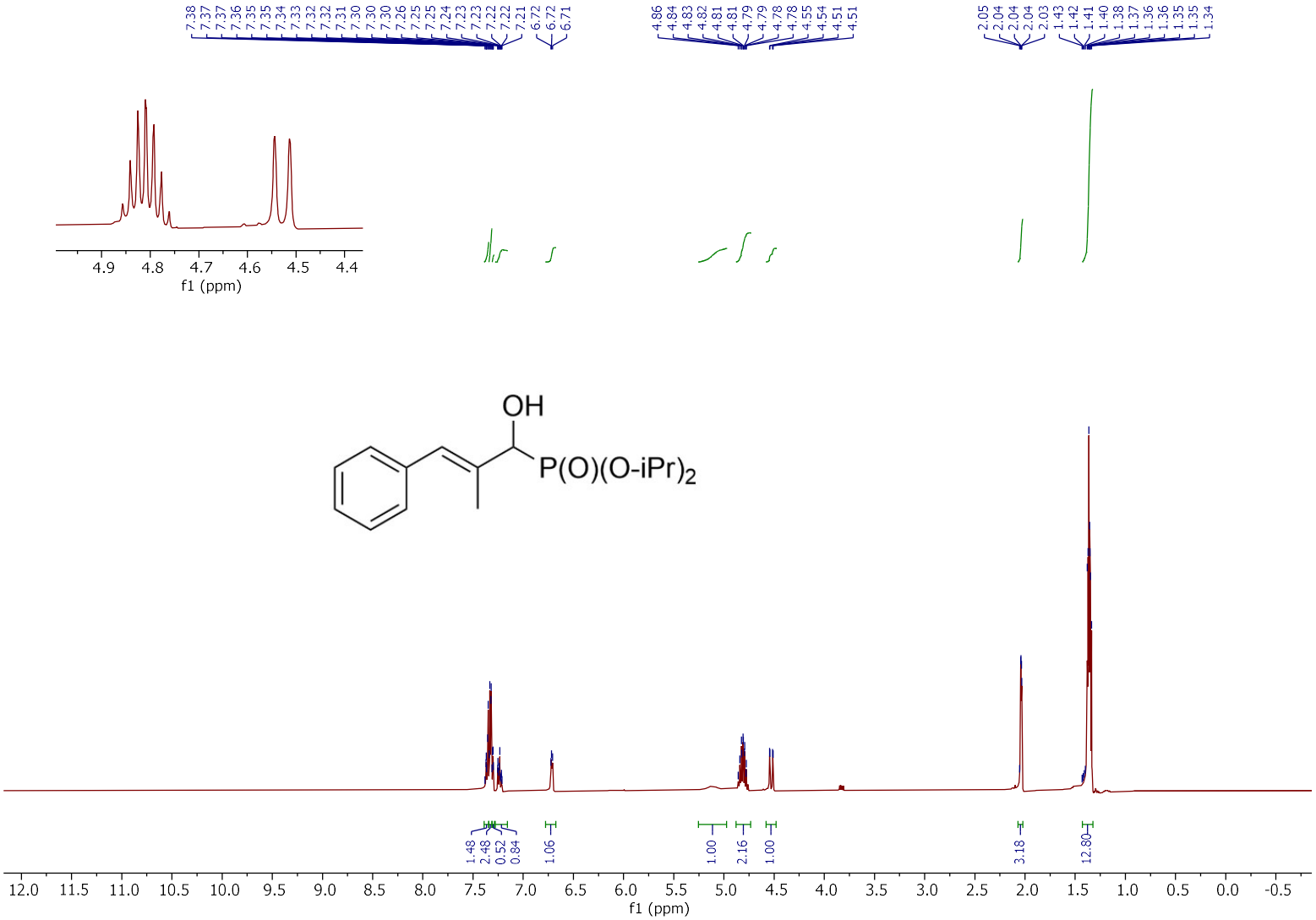
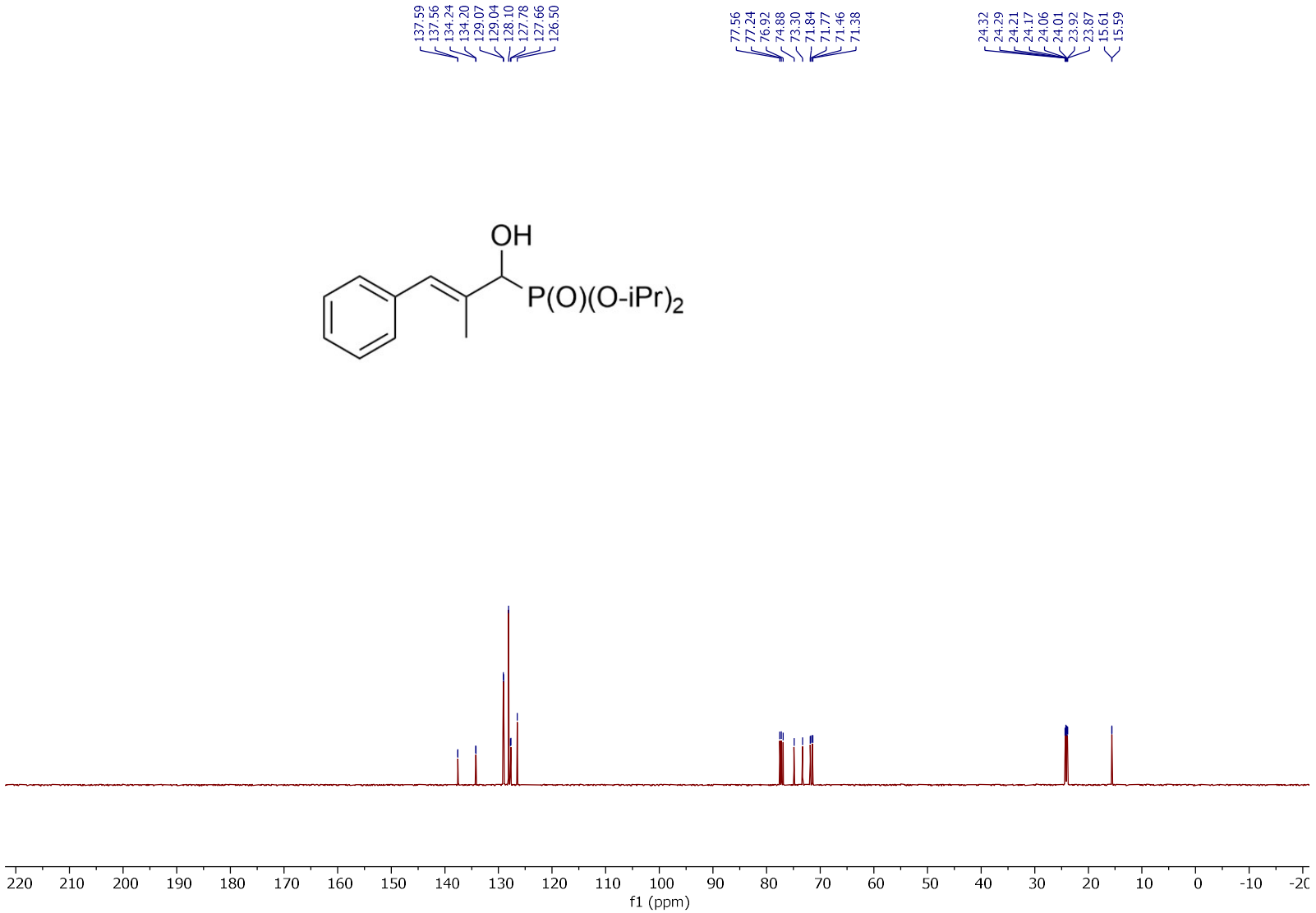


Figure S25: ^{1}H NMR Spectra of 1i in $CDCl_3$



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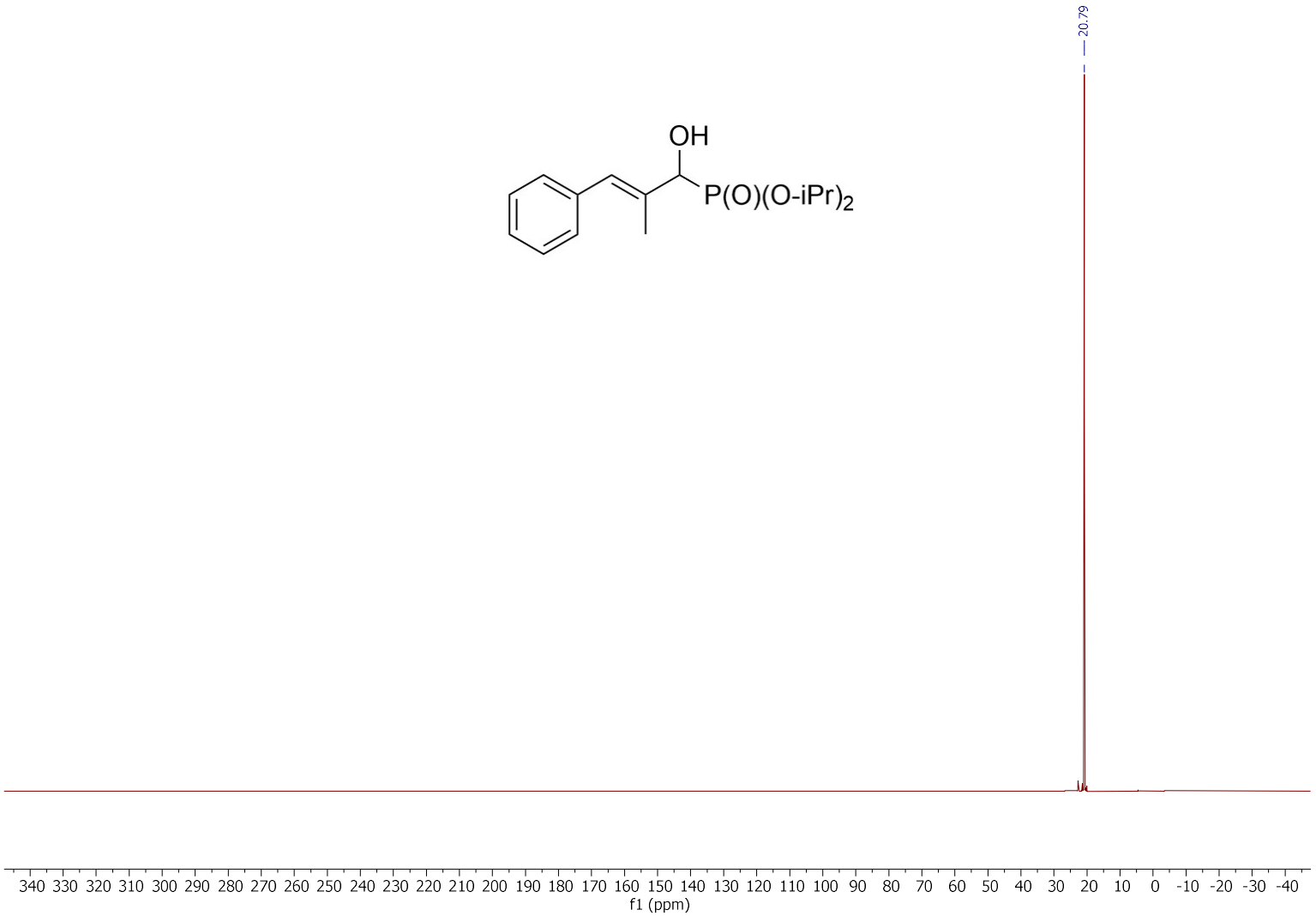

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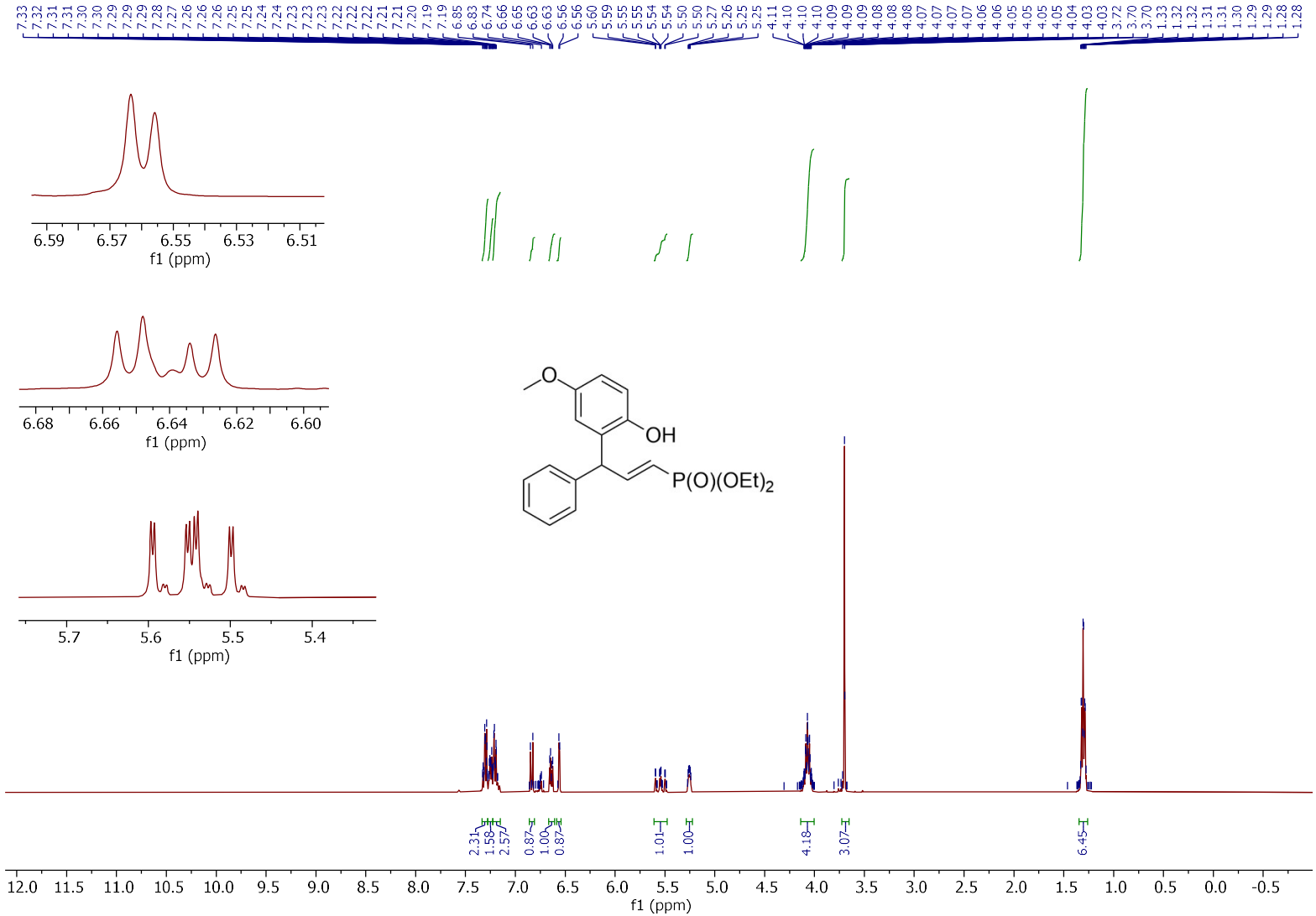


Figure S28: ^{1}H NMR Spectra of 3a in $CDCl_3$

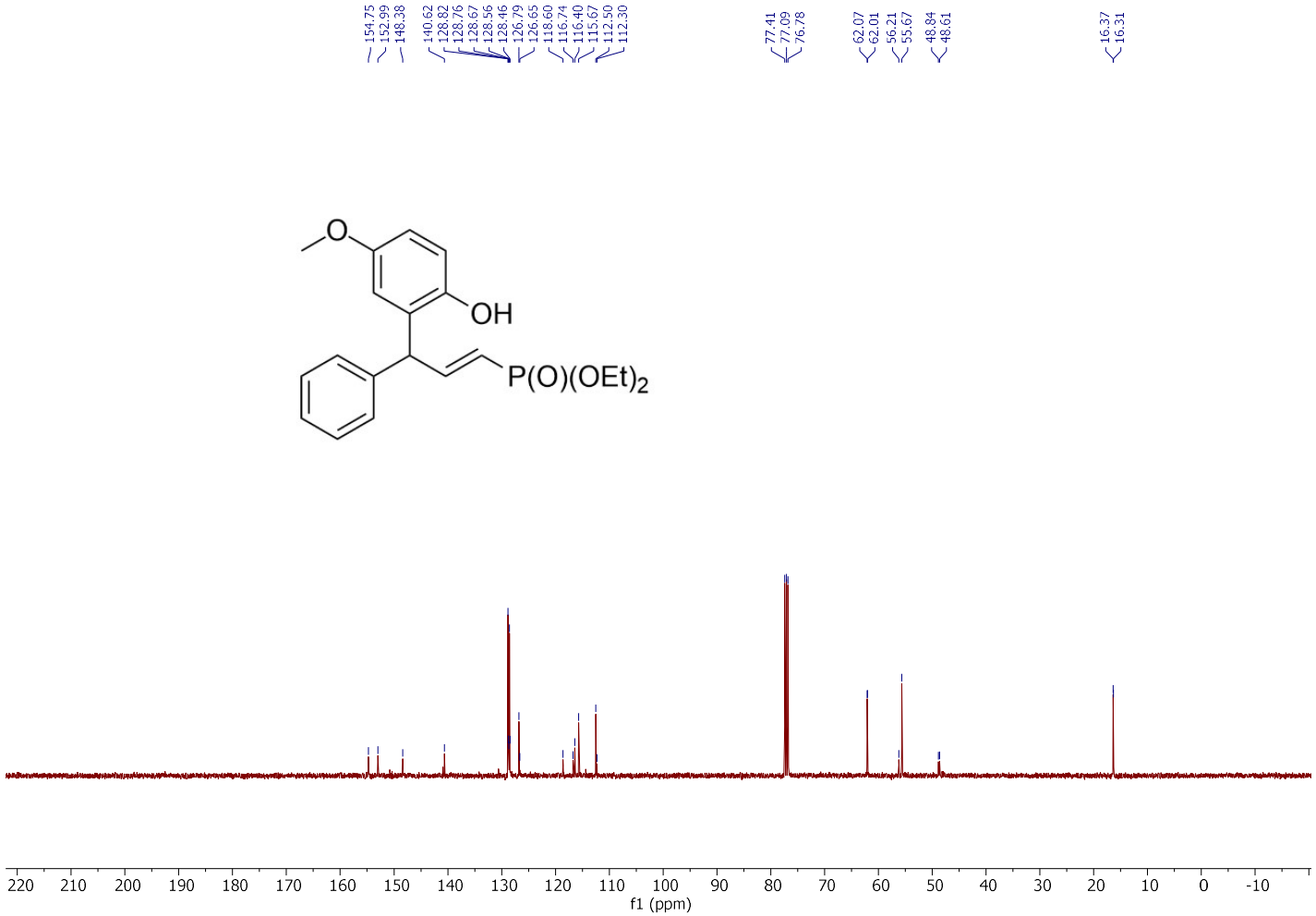


Figure S29: $^{13}C\{^{1}H\}$ NMR Spectra of 3a in $CDCl_3$

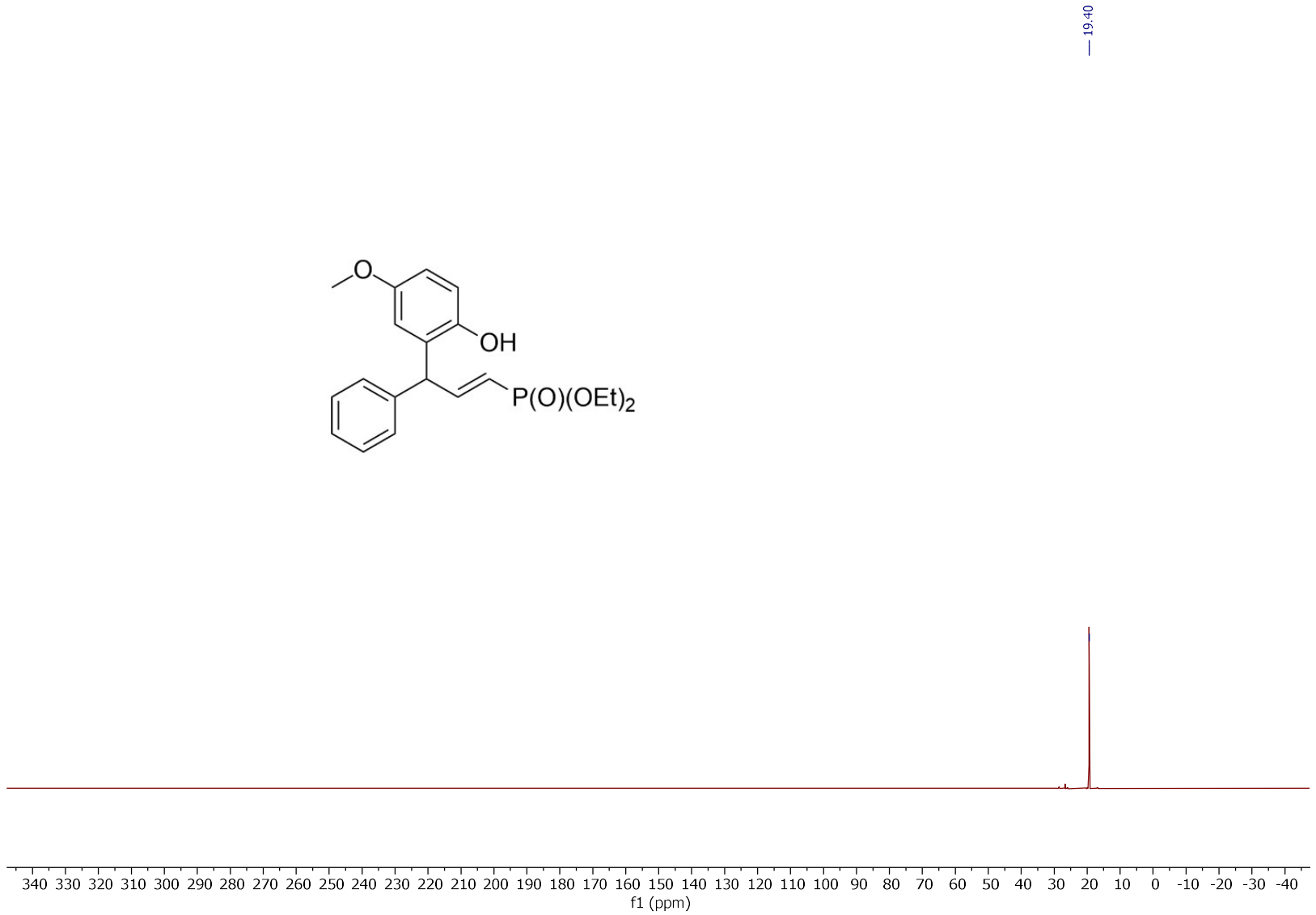


Figure S30: $^{31}P\{^{1}H\}$ NMR Spectra of 3a in $CDCl_3$

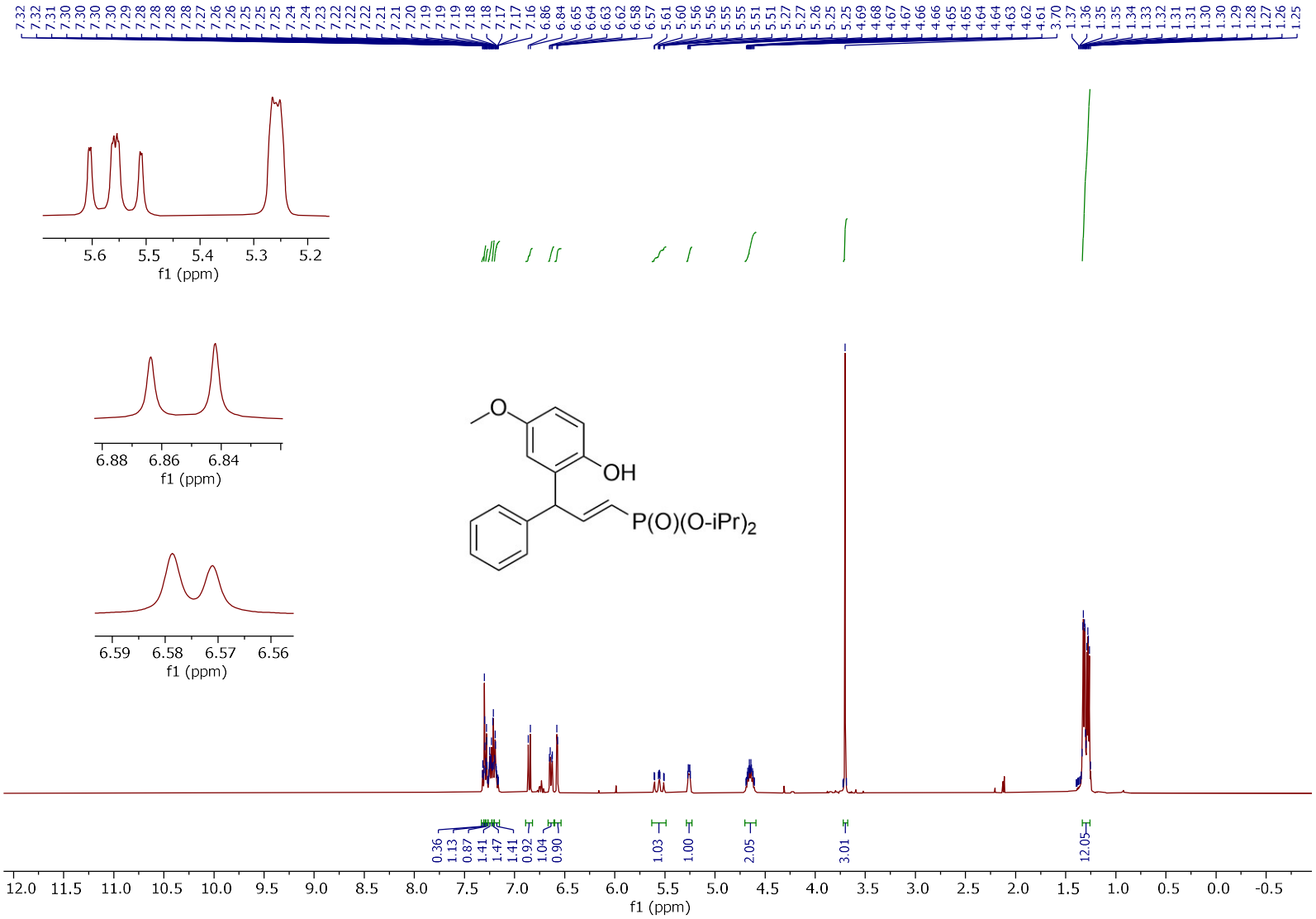


Figure S31: ^{1}H NMR Spectra of 3f in $CDCl_3$

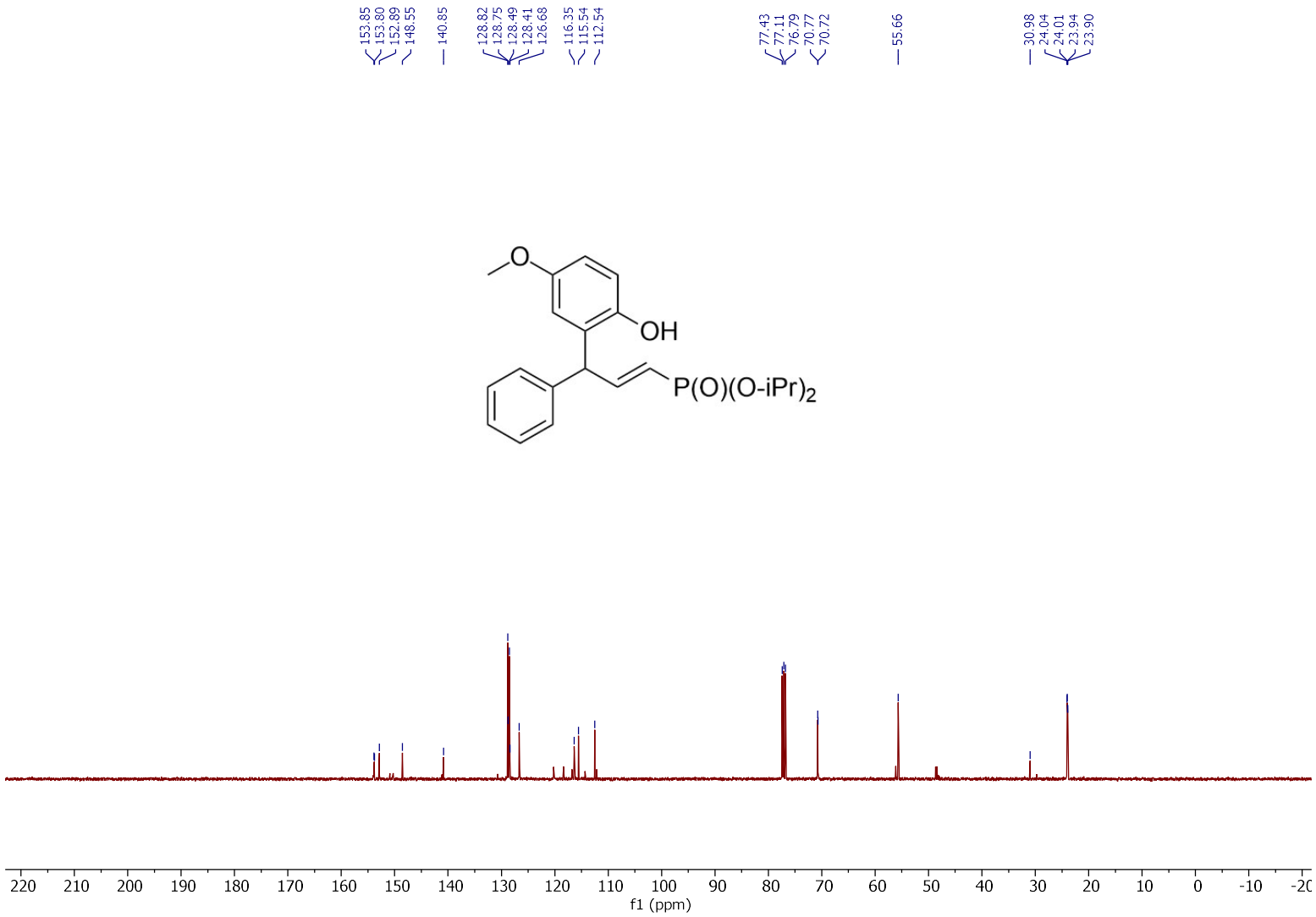


Figure S32: $^{13}C\{^{1}H\}$ NMR Spectra of 3f in $CDCl_3$

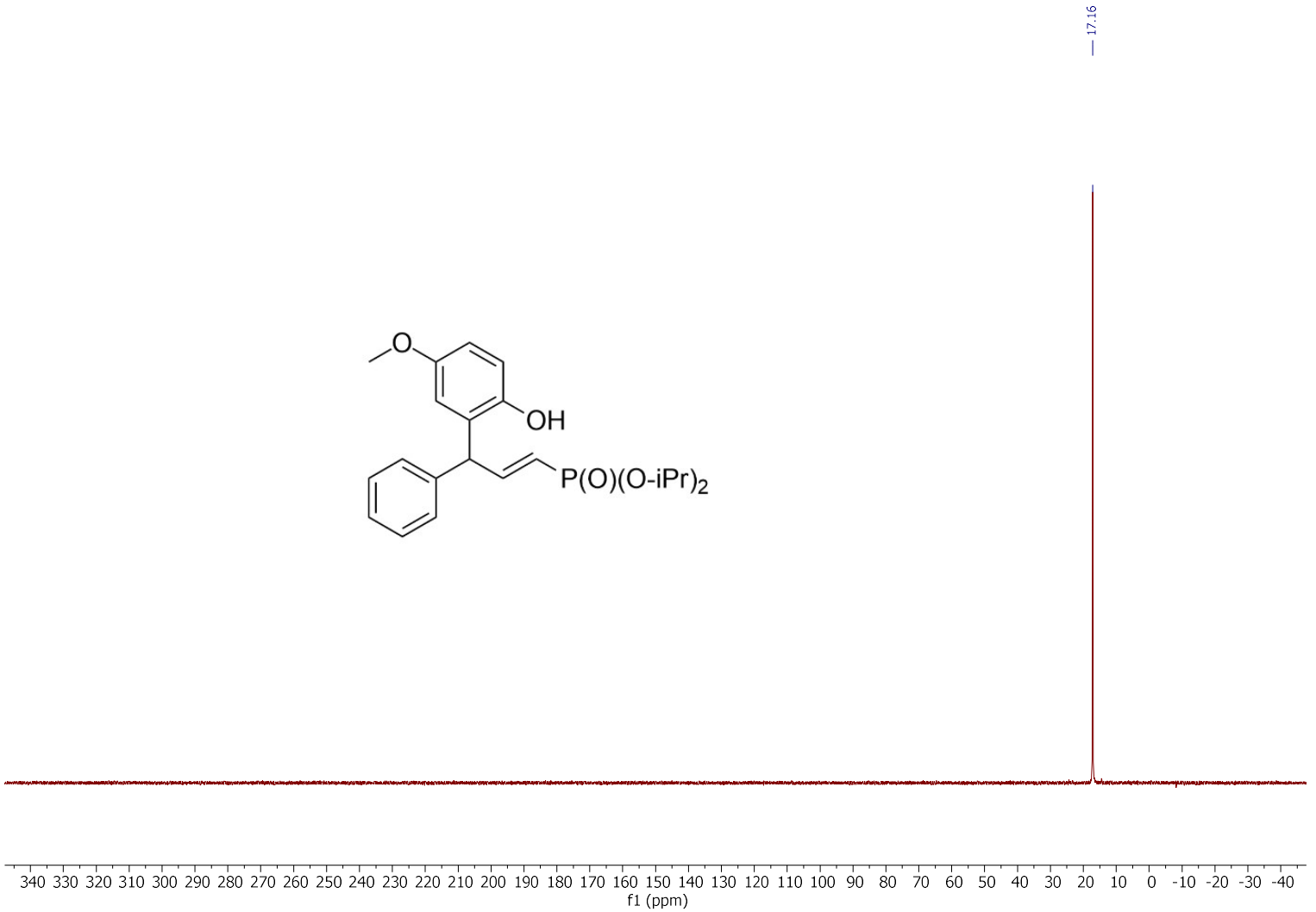


Figure S33: $^{31}P\{^{1}H\}$ NMR Spectra of 3f in $CDCl_3$

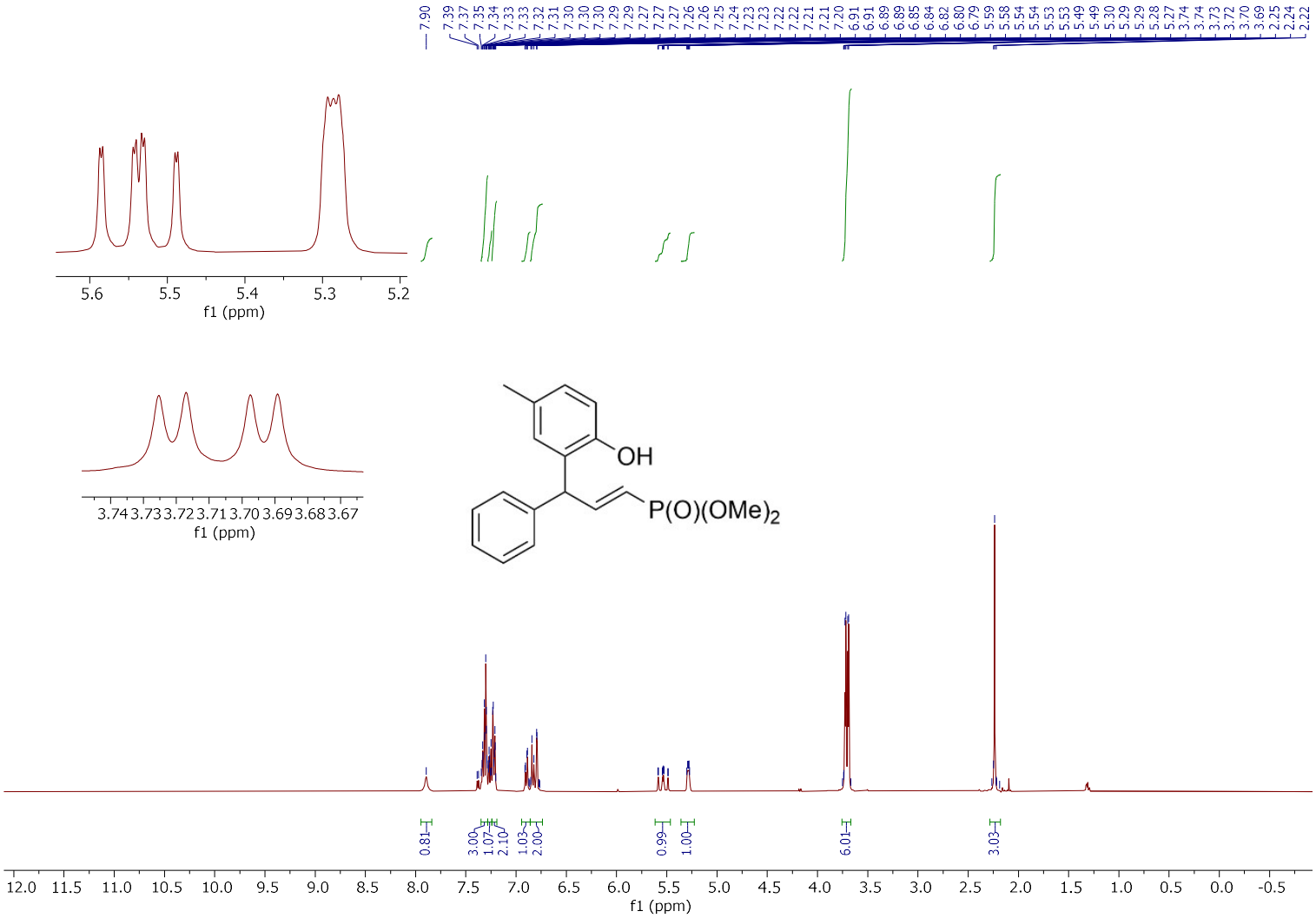


Figure S34: ^{1}H NMR Spectra of 3d in $CDCl_3$

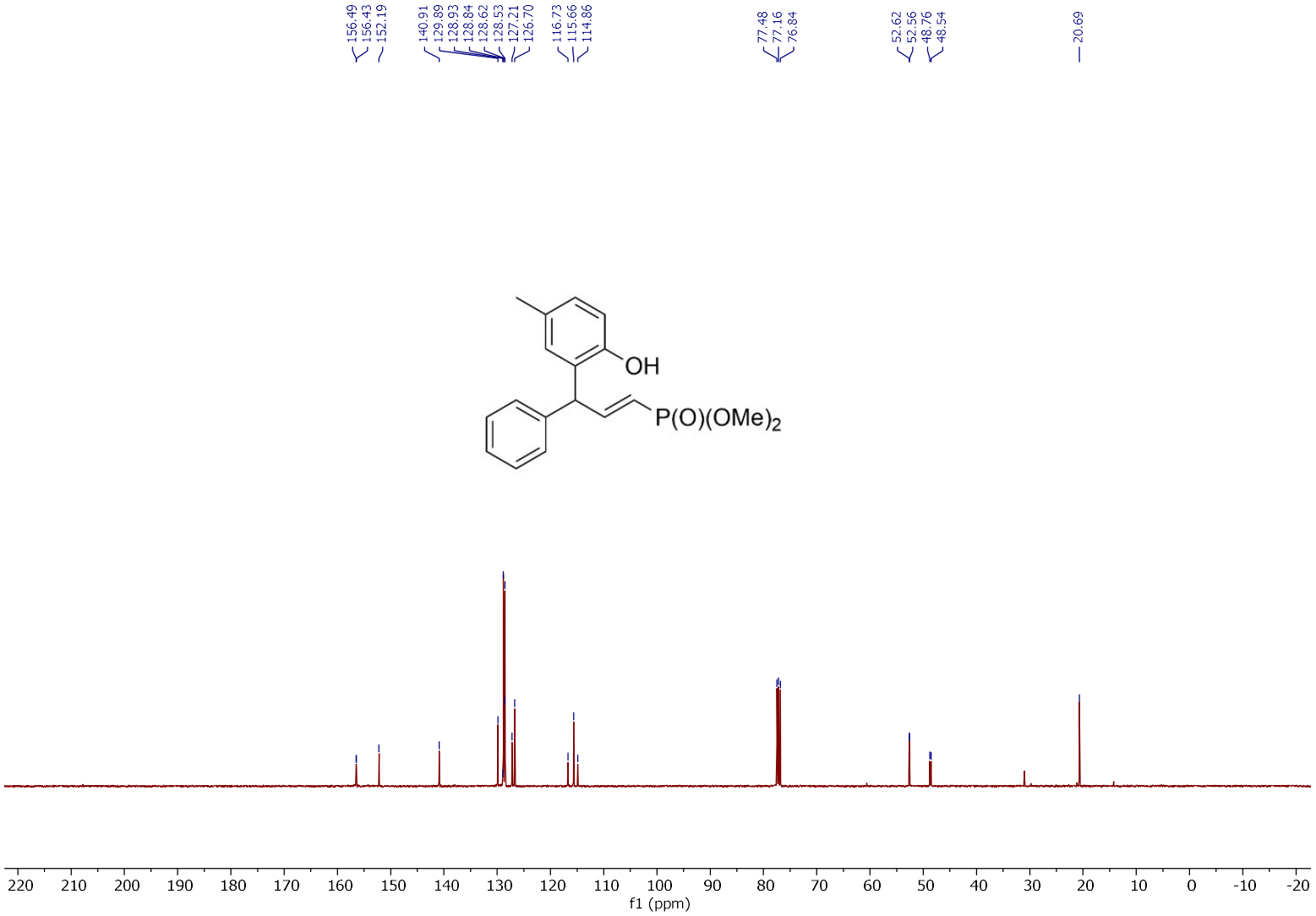


Figure S35: $^{13}C\{^{1}H\}$ NMR Spectra of 3d in $CDCl_3$

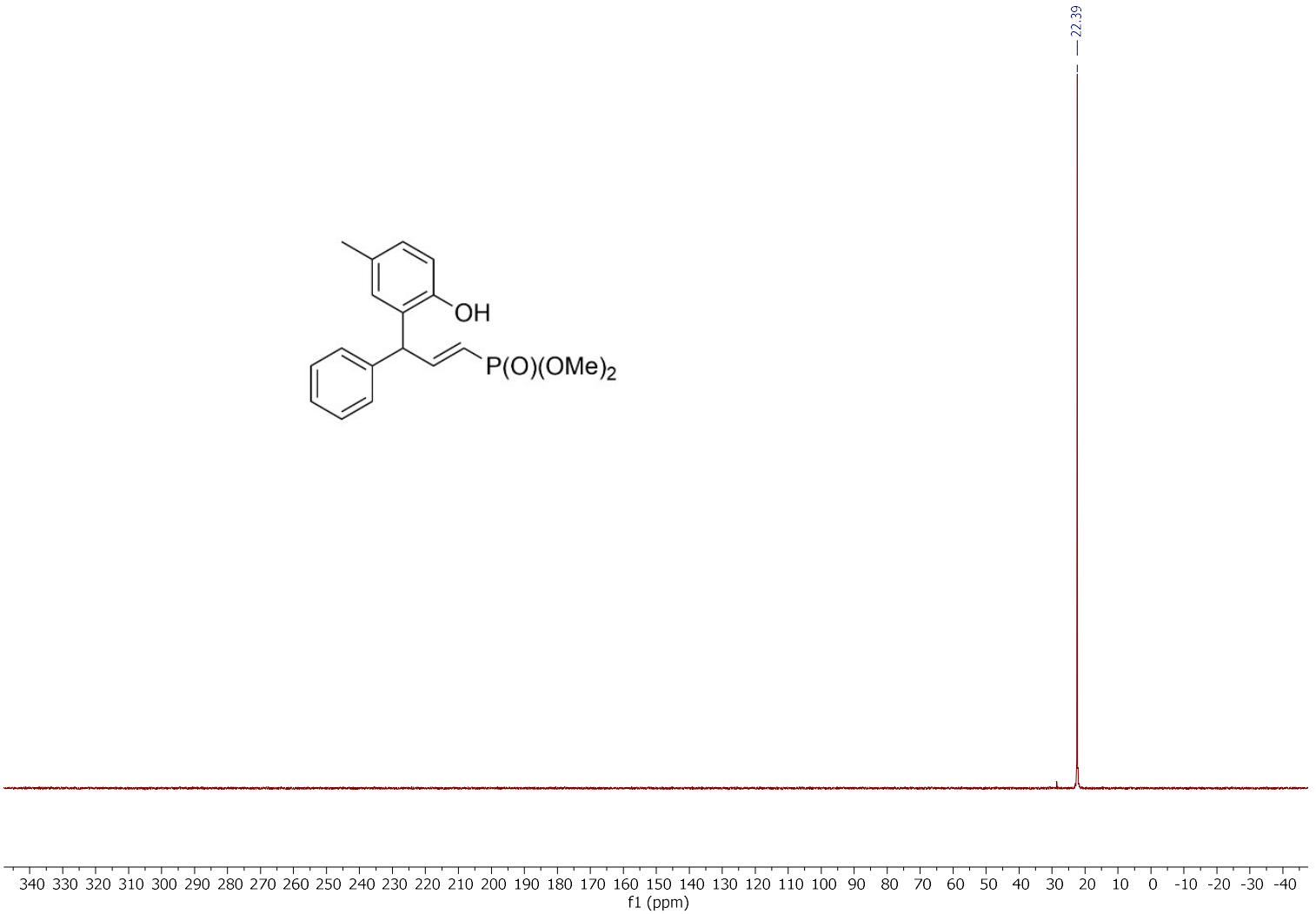


Figure S36: $^{31}P\{^{1}H\}$ NMR Spectra of 3d in $CDCl_3$

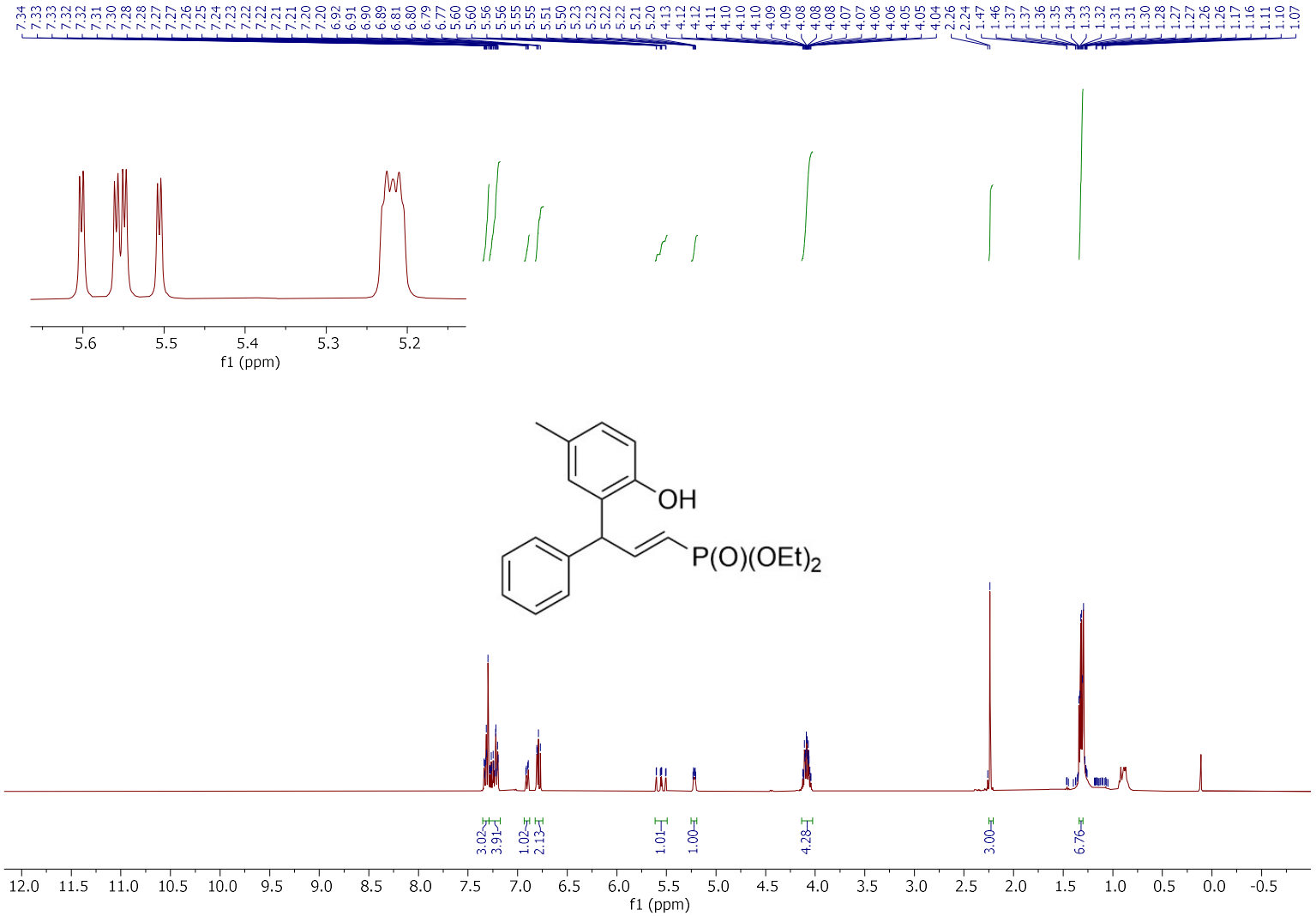


Figure S37: ^{1}H NMR Spectra of 3b in $CDCl_3$

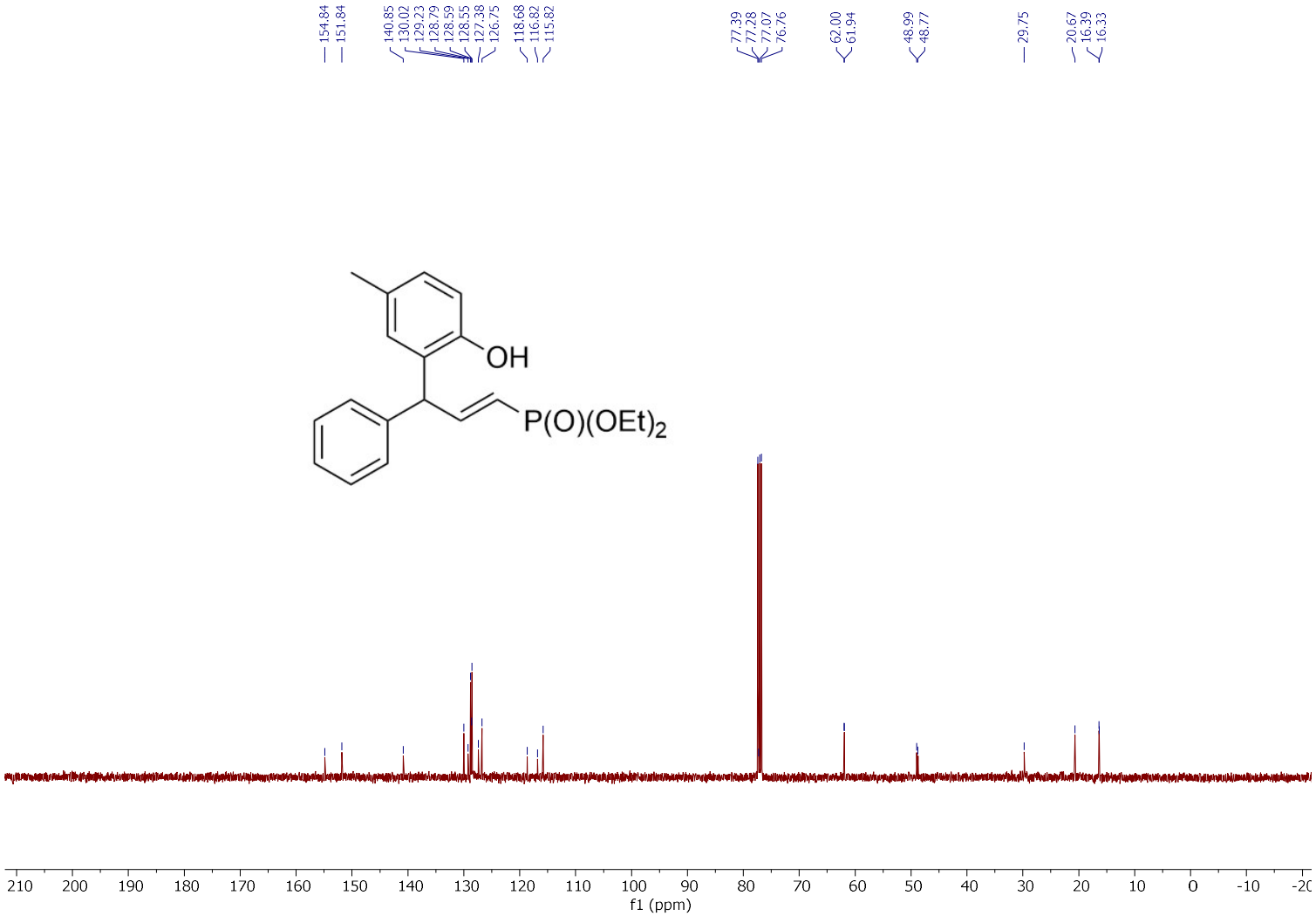


Figure S38: $^{13}C\{^{1}H\}$ NMR Spectra of 3b in $CDCl_3$

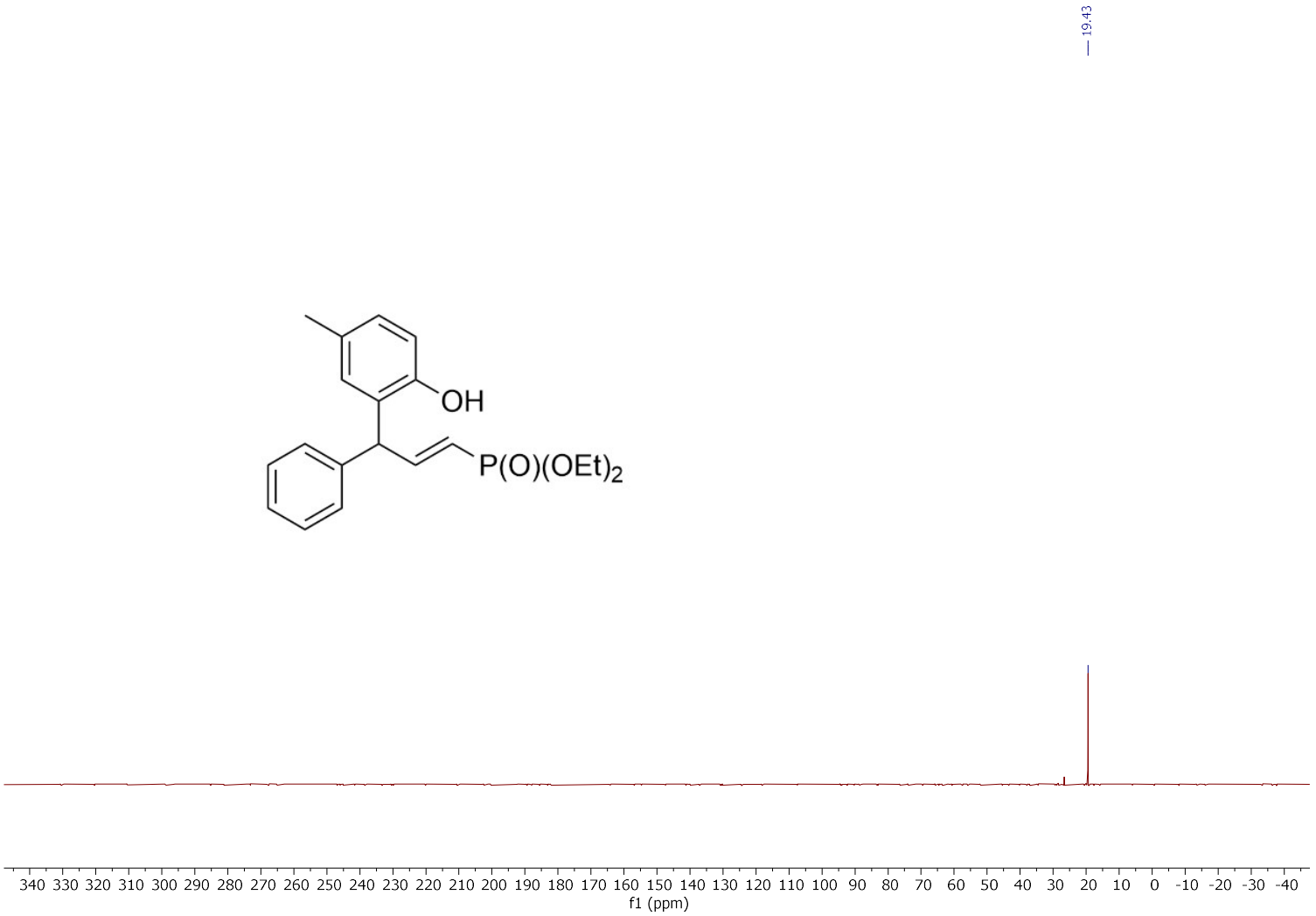


Figure S39: $^{31}P\{^{1}H\}$ NMR Spectra of 3b in $CDCl_3$

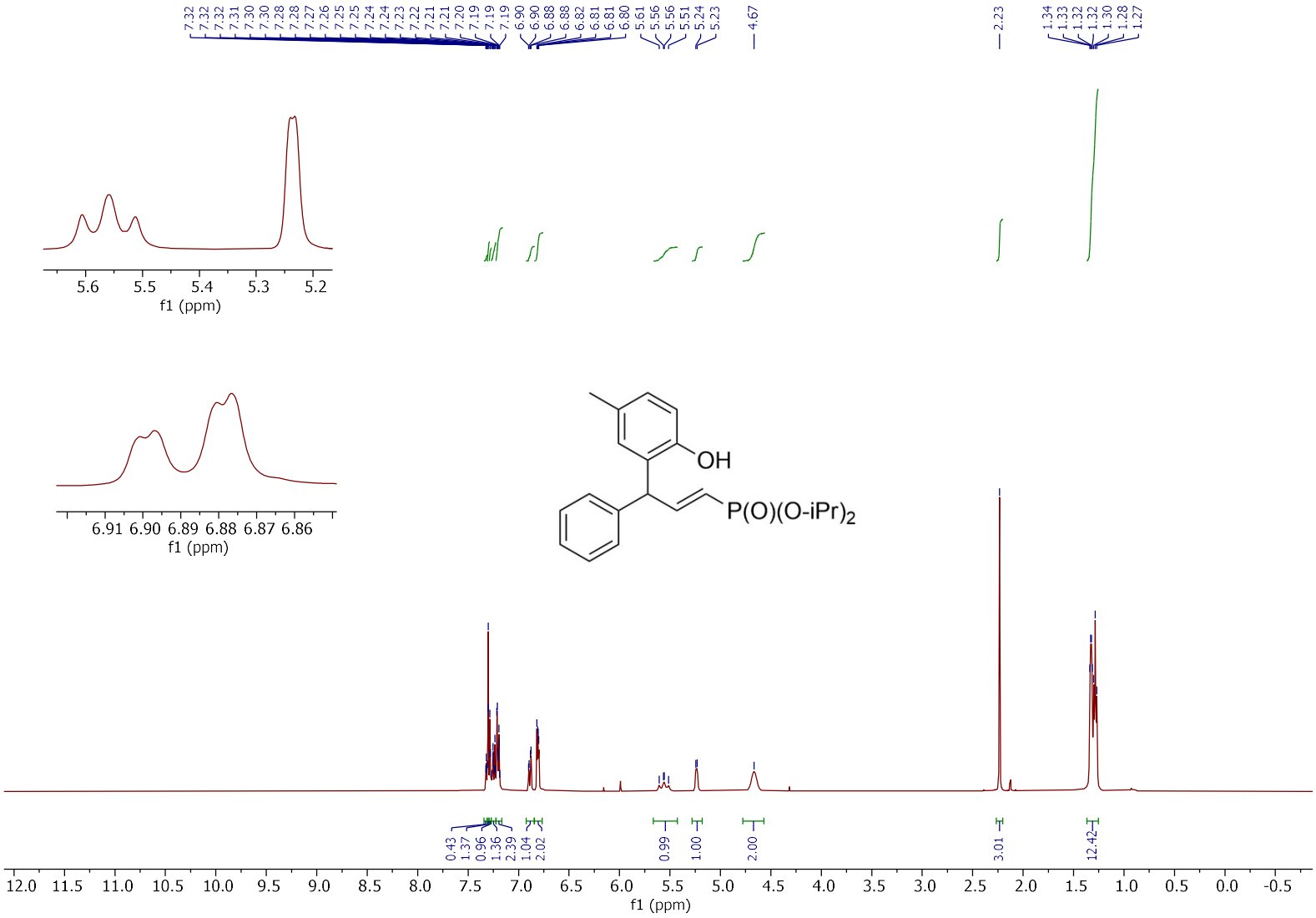


Figure S40: ^{1}H NMR Spectra of 3e in $CDCl_3$

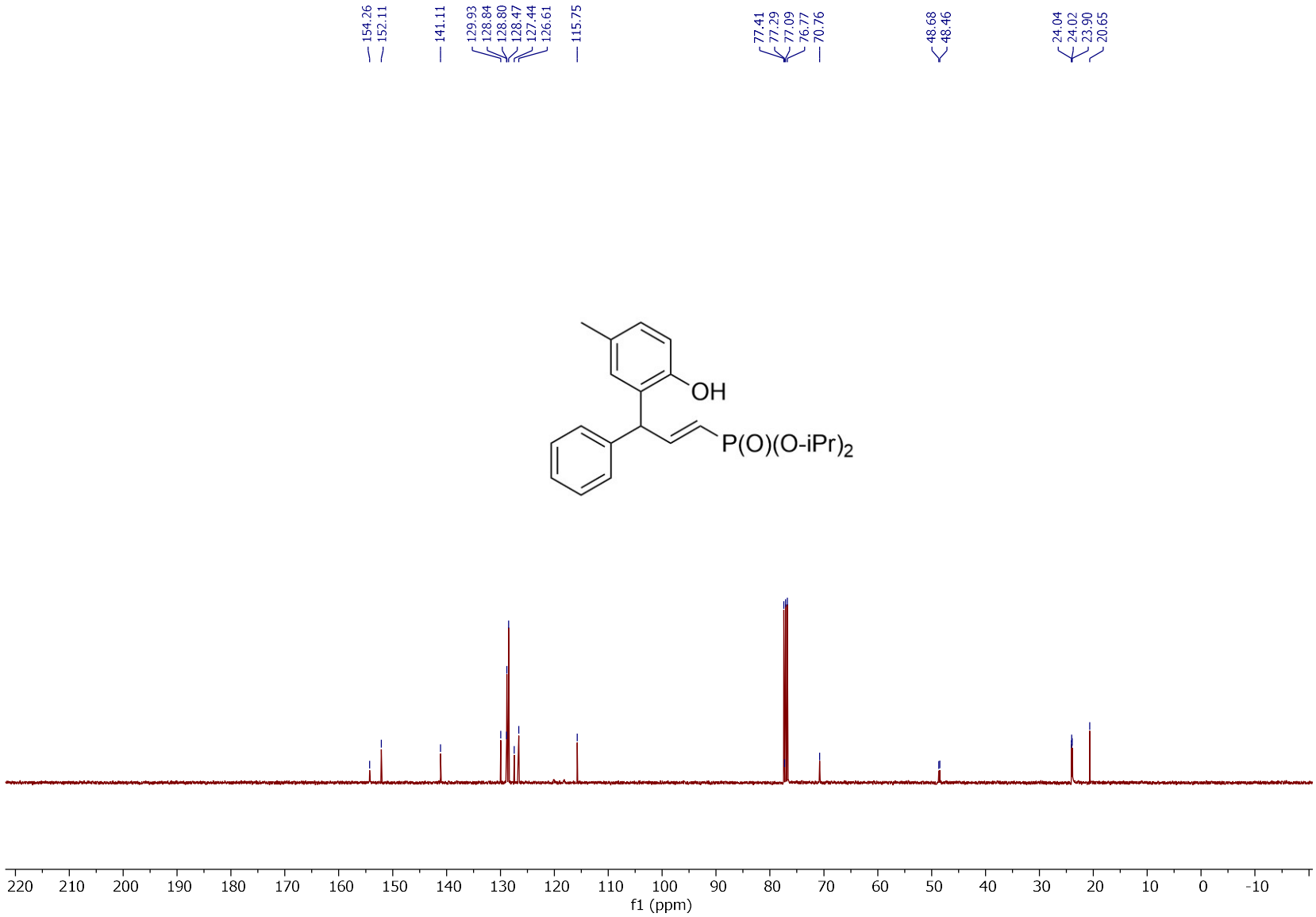


Figure S41: $^{13}C\{^{1}H\}$ NMR Spectra of 3e in $CDCl_3$

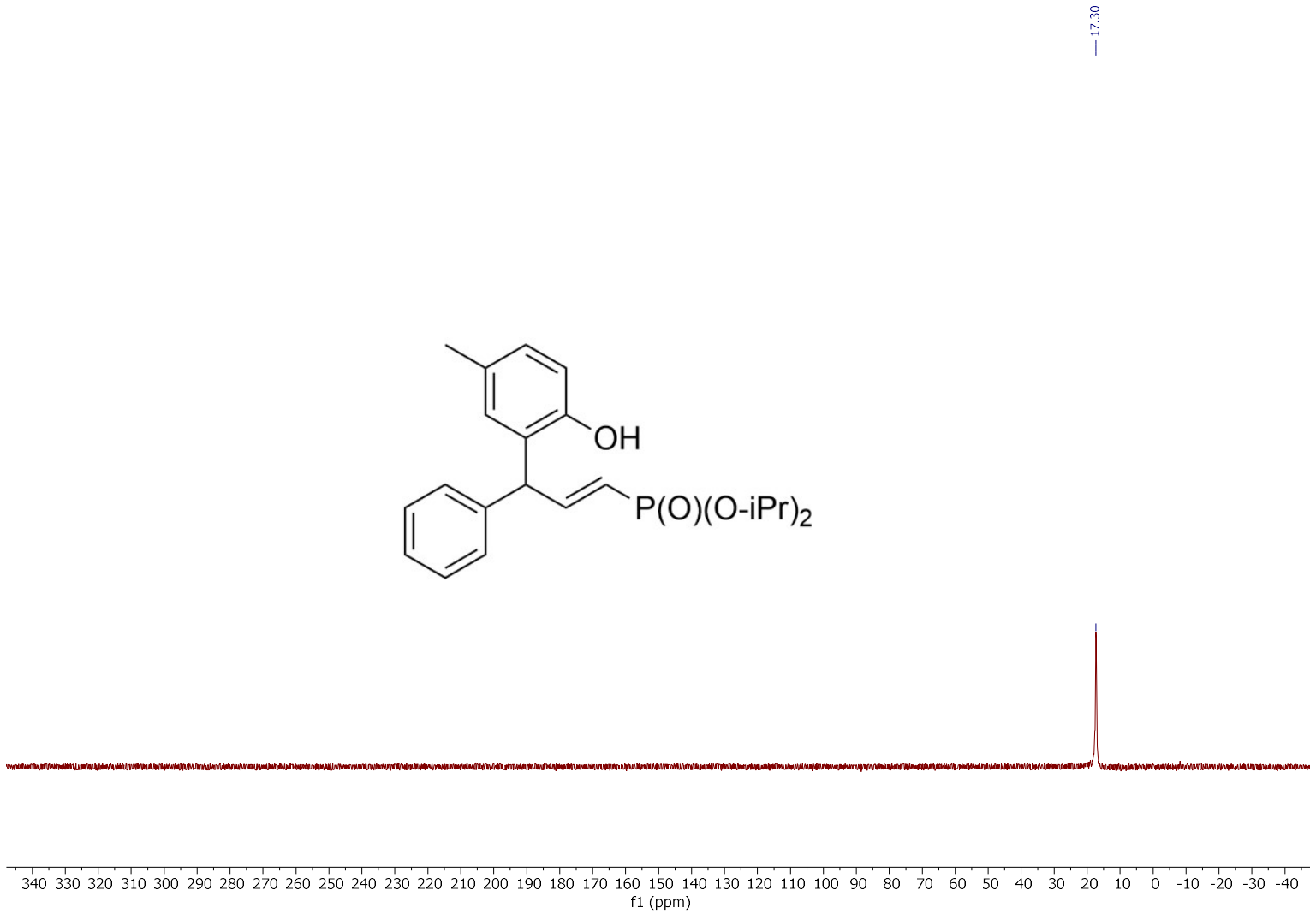


Figure S42: $^{31}P\{^{1}H\}$ NMR Spectra of 3e in $CDCl_3$

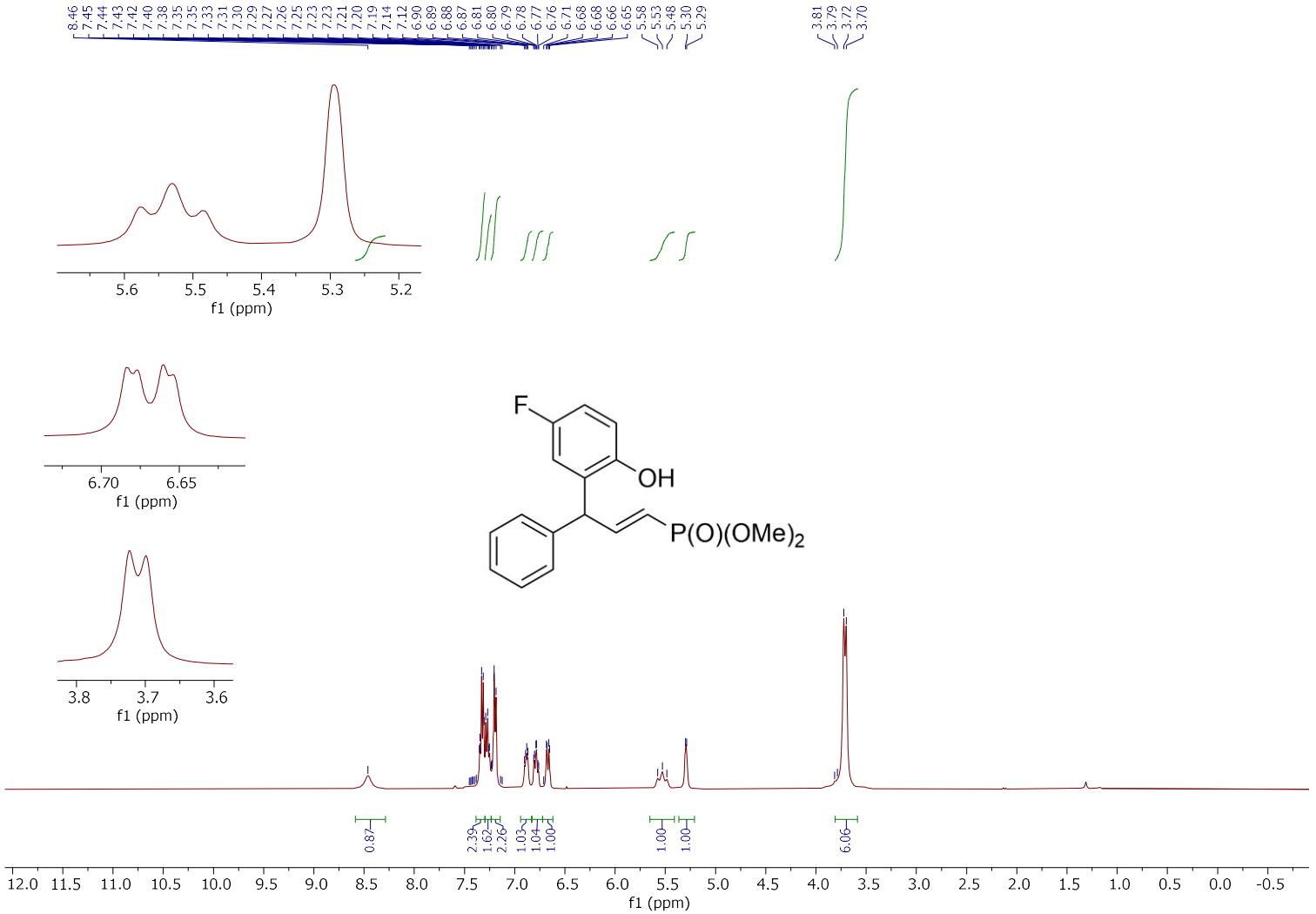


Figure S43: ^{1}H NMR Spectra of 3g in $CDCl_3$

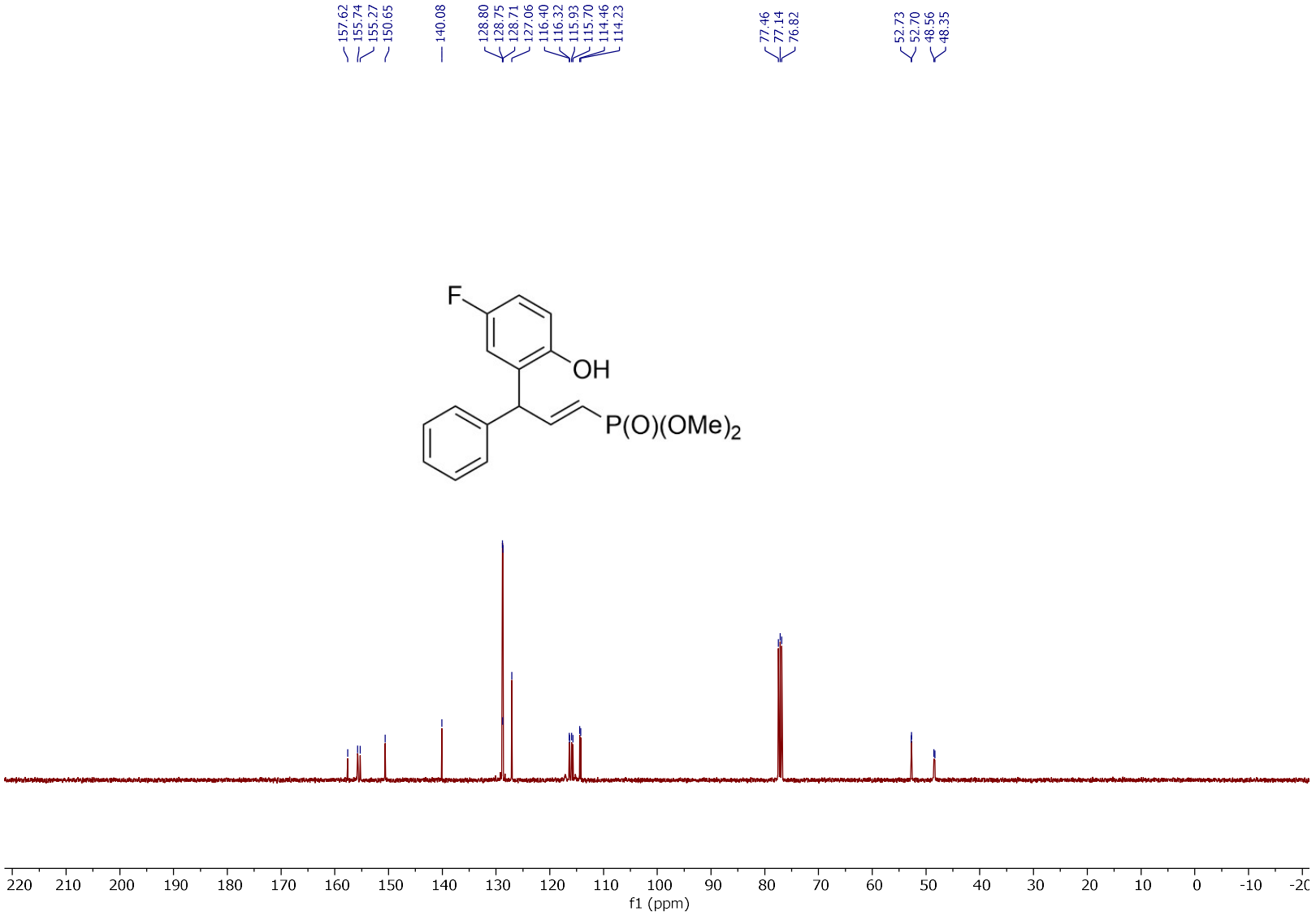


Figure S44: $^{13}C\{^{1}H\}$ NMR Spectra of 3g in $CDCl_3$

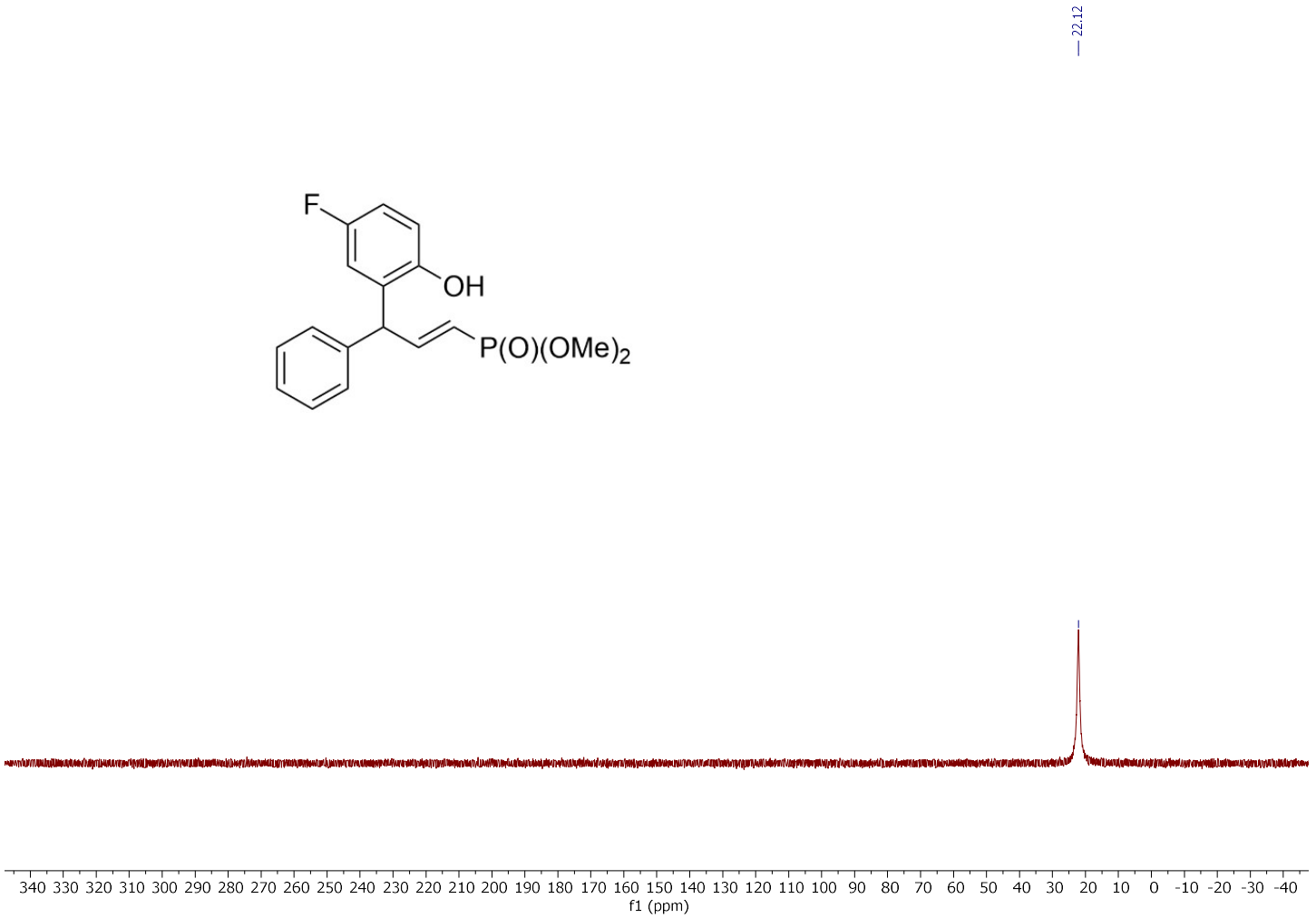


Figure S45: $^{31}P\{^{1}H\}$ NMR Spectra of 3g in $CDCl_3$

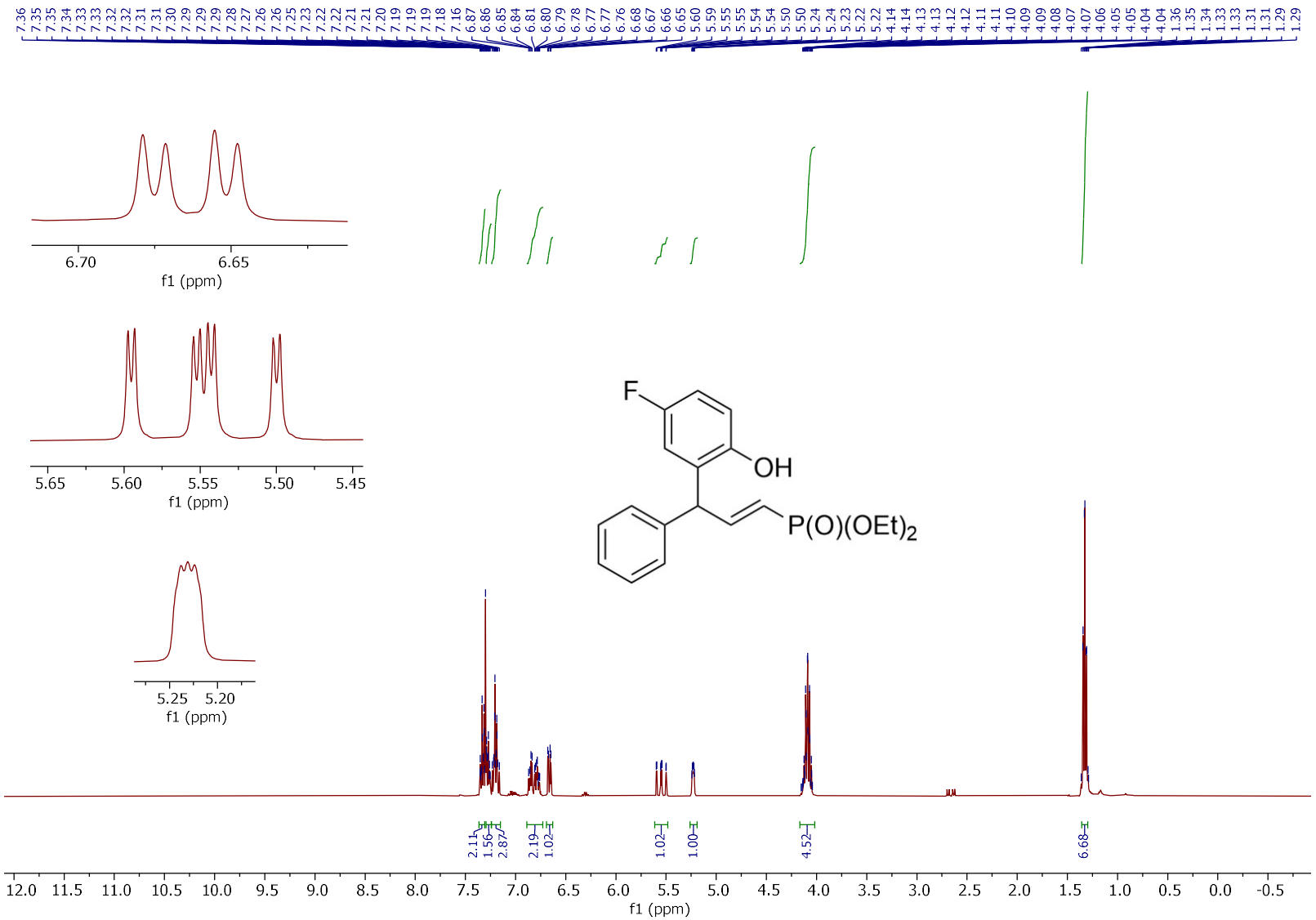


Figure S46: ^{1}H NMR Spectra of 3c in $CDCl_3$

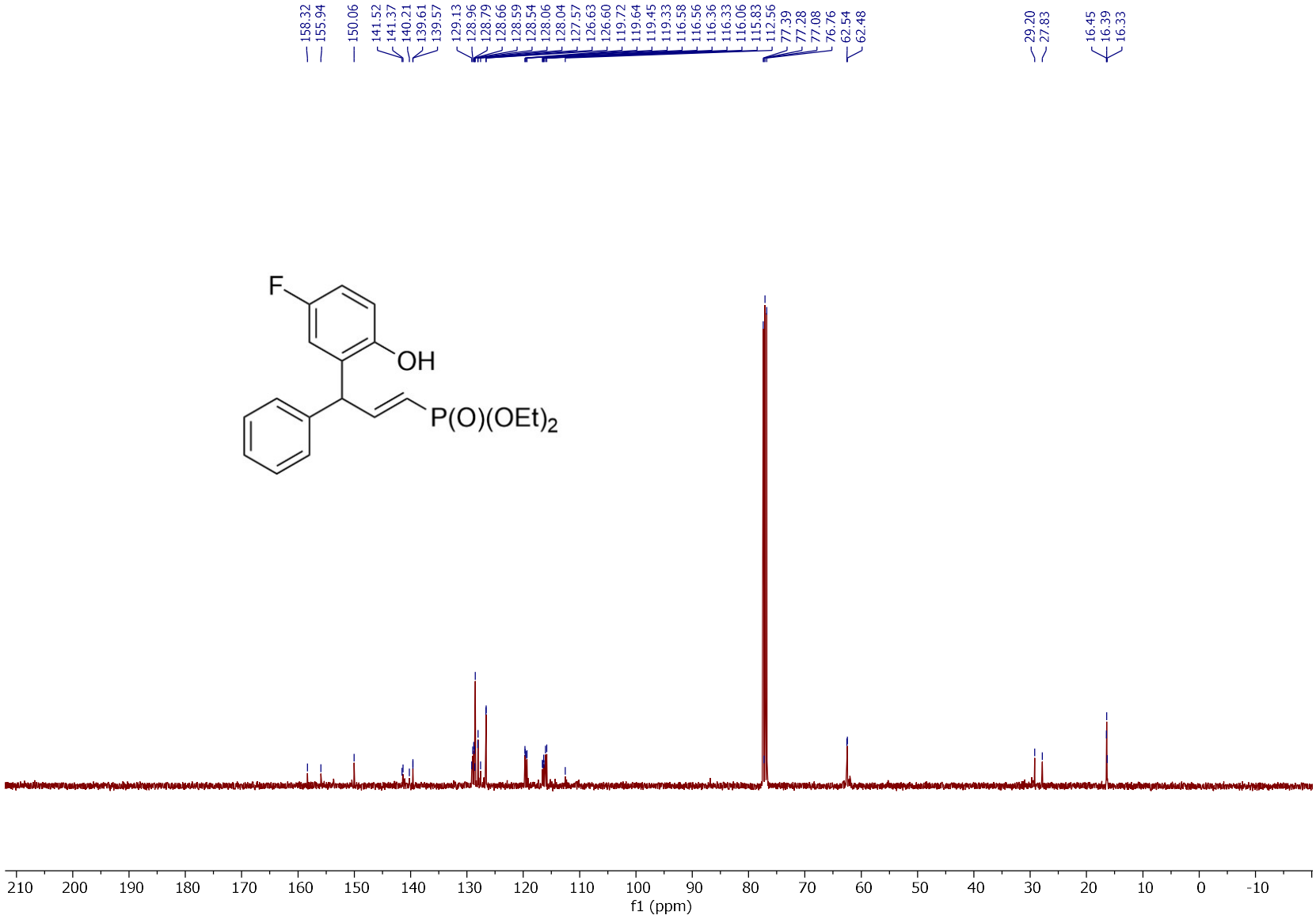


Figure S47: $^{13}C\{^{1}H\}$ NMR Spectra of 3c in $CDCl_3$

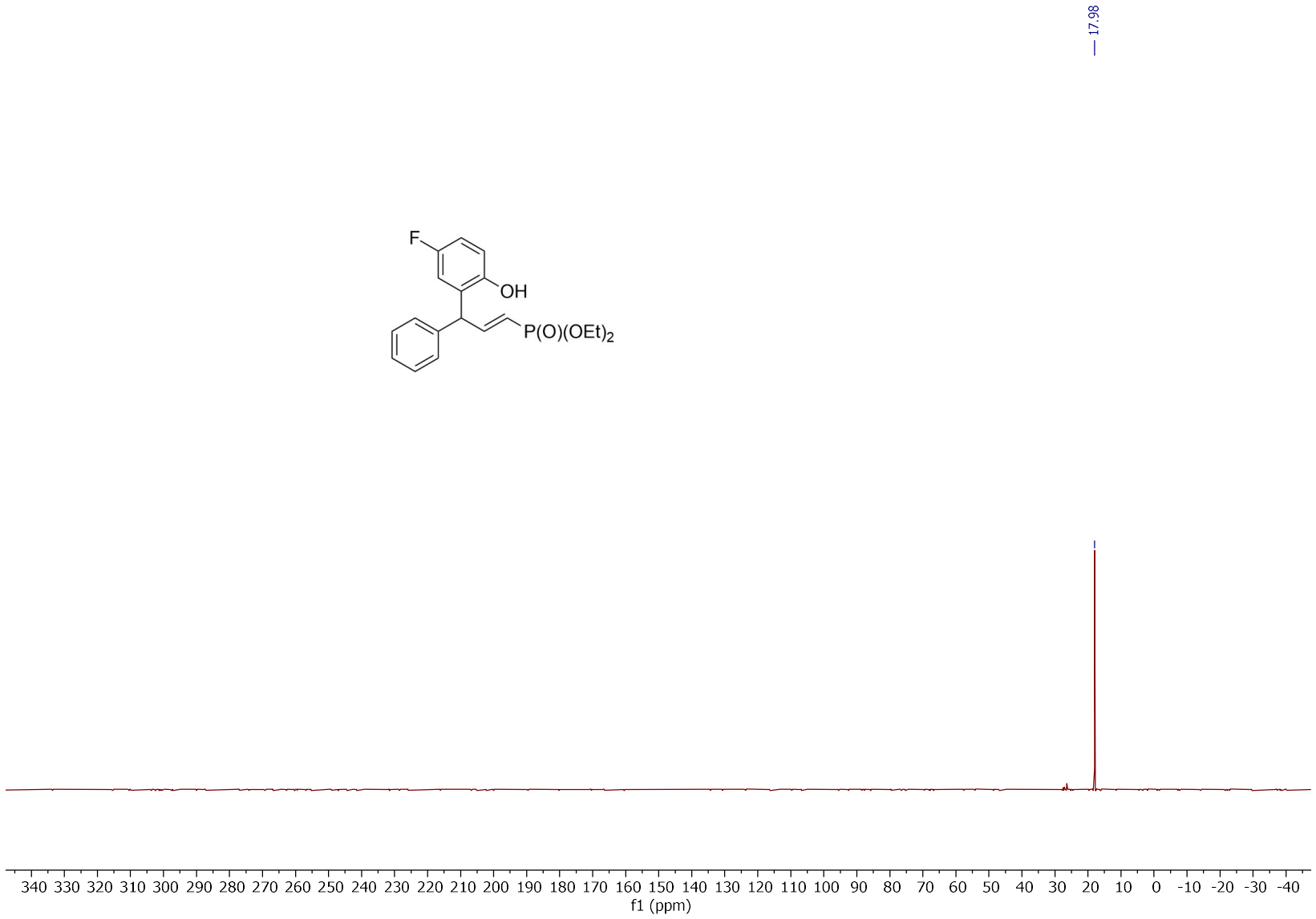


Figure S48: $^{31}P\{^{1}H\}$ NMR Spectra of 3c in $CDCl_3$

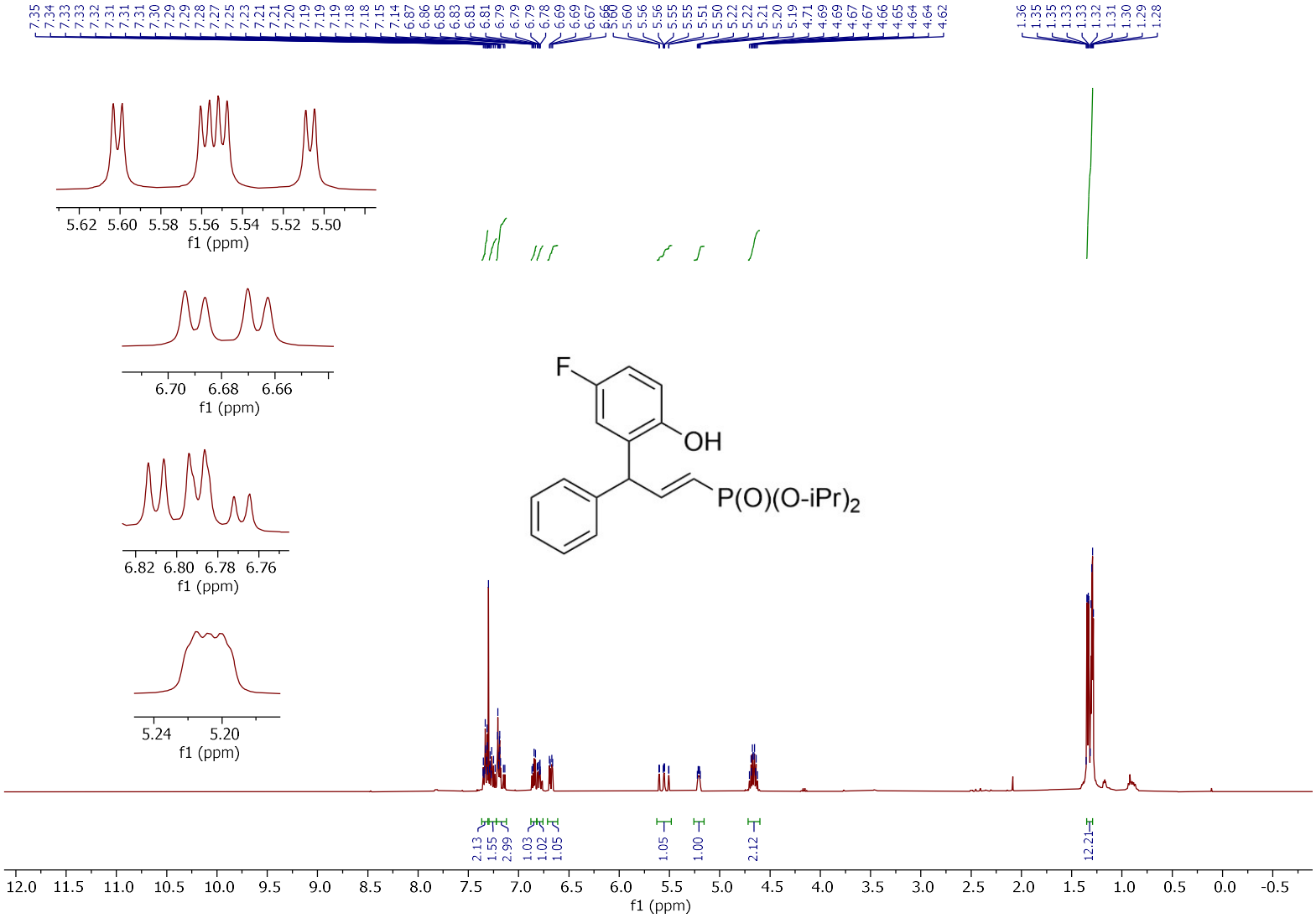


Figure S49: ^{1}H NMR Spectra of 3h in $CDCl_3$

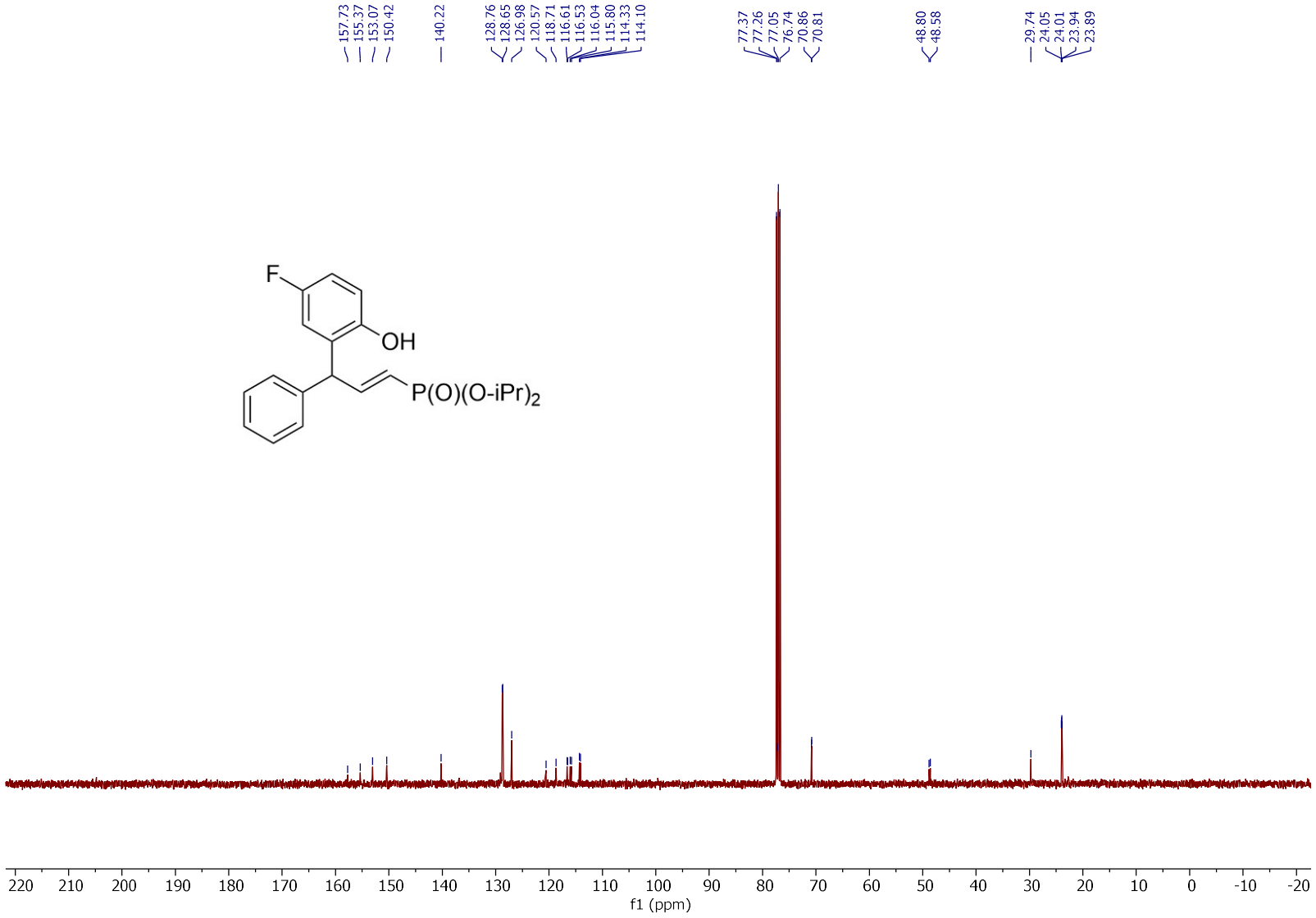


Figure S50: $^{13}C\{^{1}H\}$ NMR Spectra of 3h in $CDCl_3$

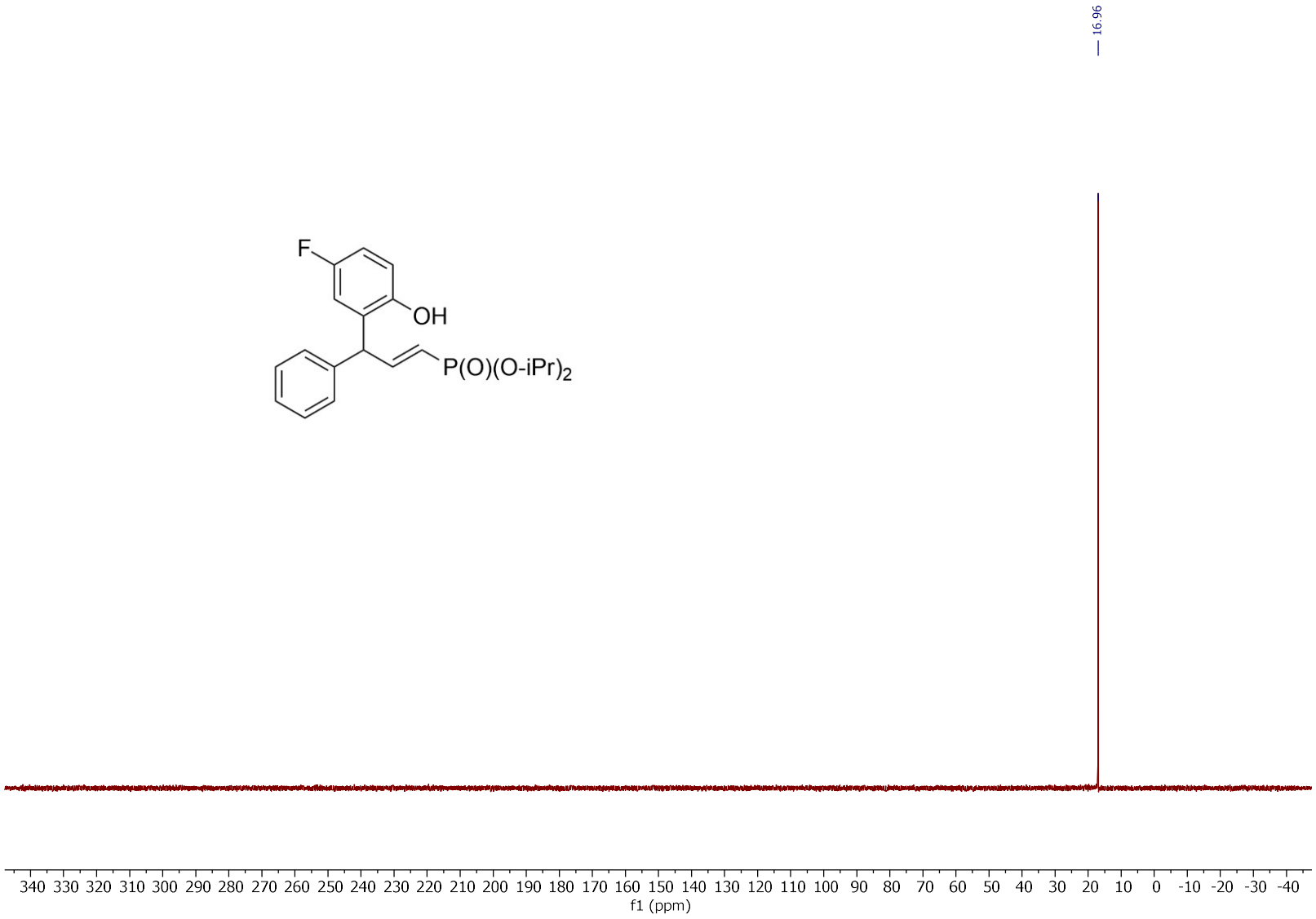


Figure S51: $^{31}P\{^{1}H\}$ NMR Spectra of 3h in $CDCl_3$

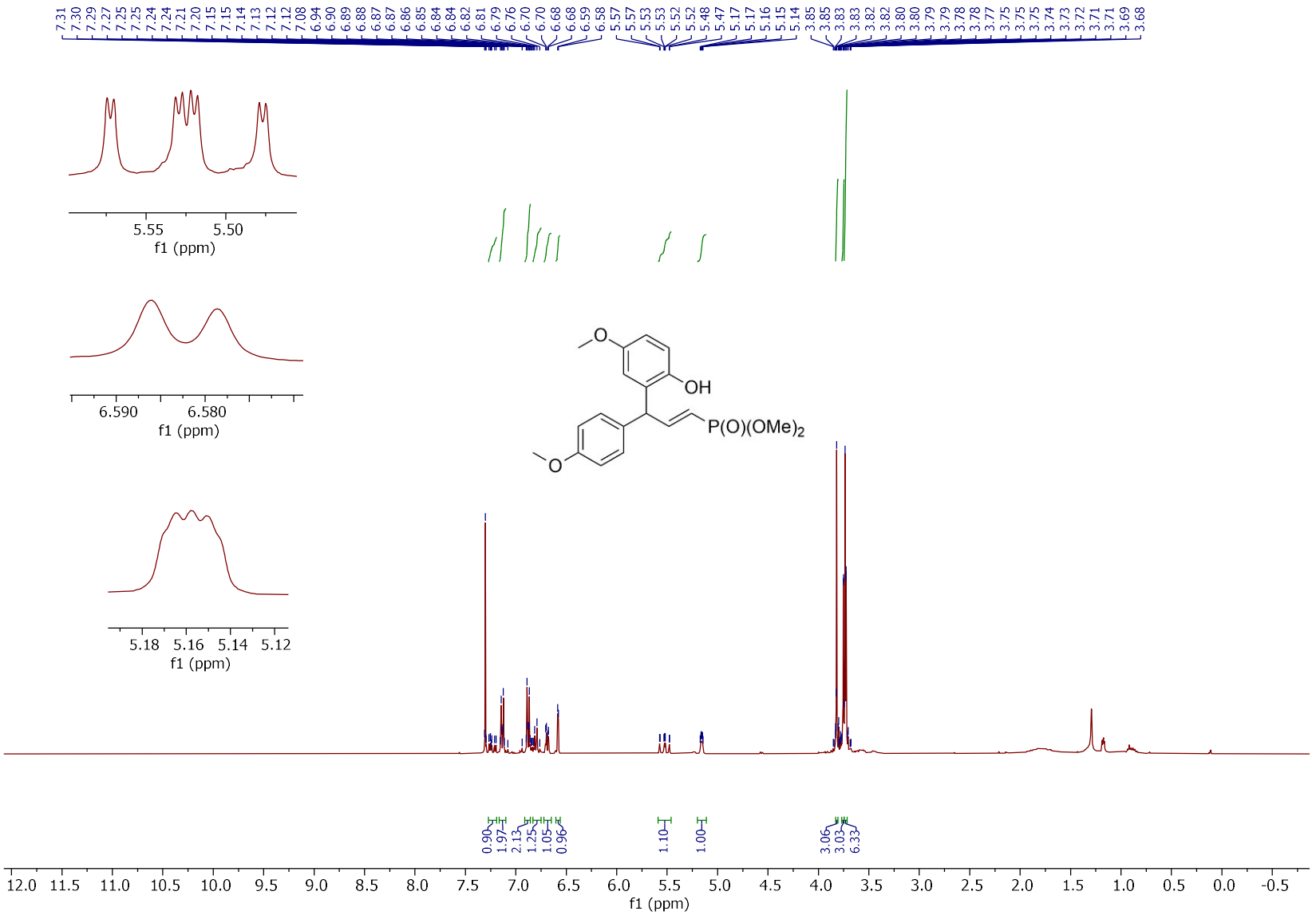


Figure S52: ^{1}H NMR Spectra of 3l in $CDCl_3$

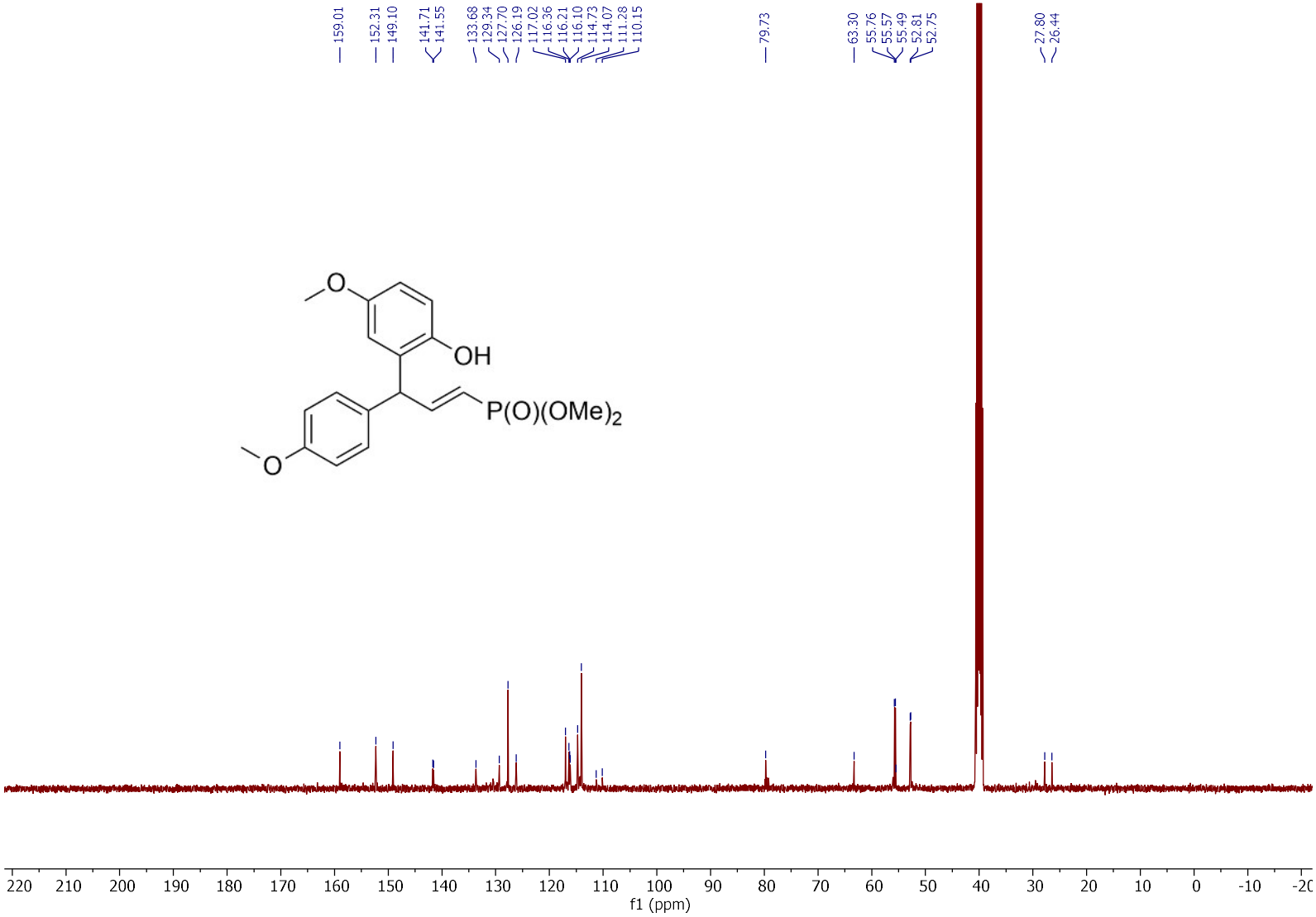


Figure S53: $^{13}C\{^{1}H\}$ NMR Spectra of 3l in $CDCl_3$

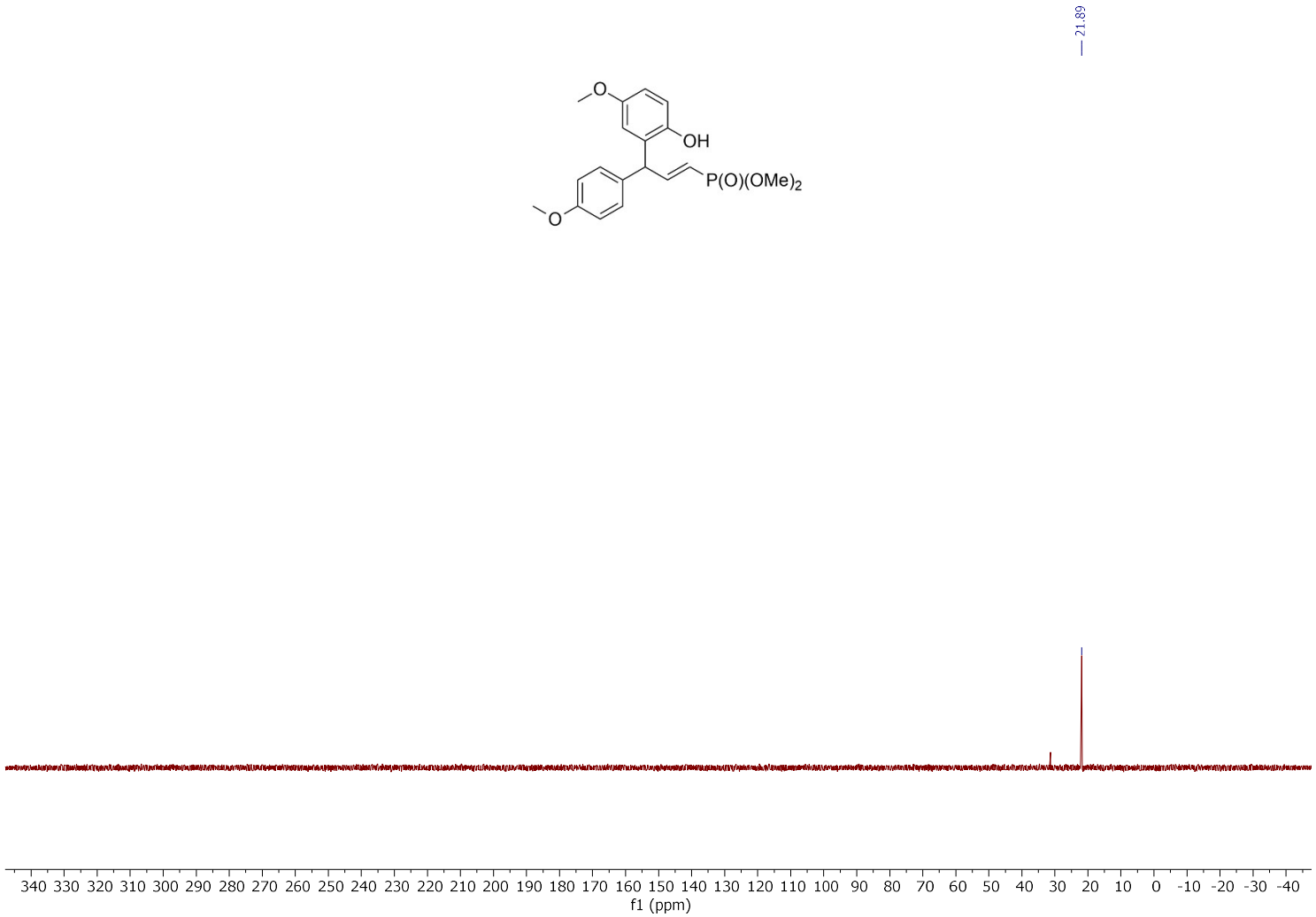


Figure S54: $^{31}P\{^{1}H\}$ NMR Spectra of 3l in $CDCl_3$

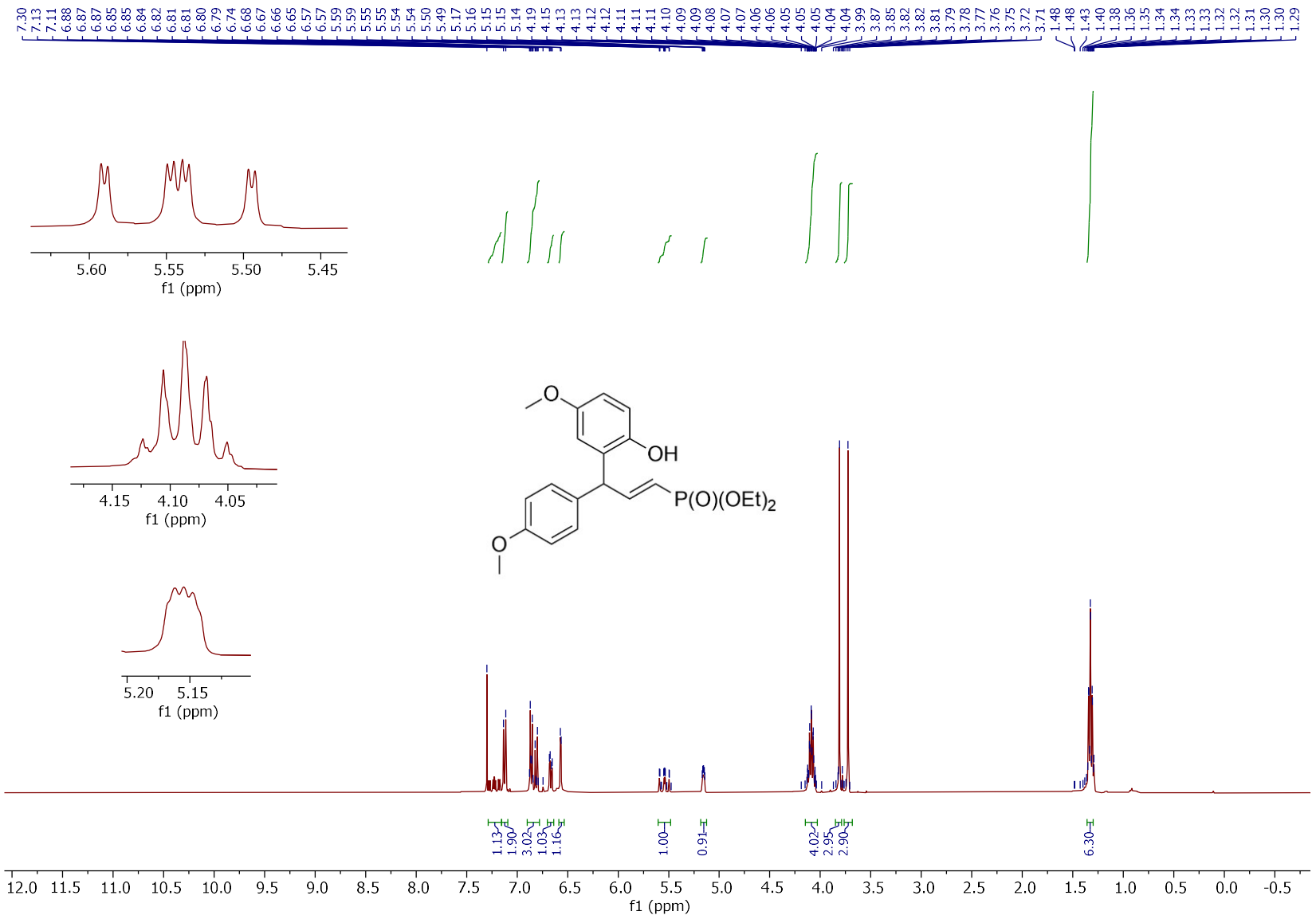


Figure S55: ^{1}H NMR Spectra of 3m in $CDCl_3$

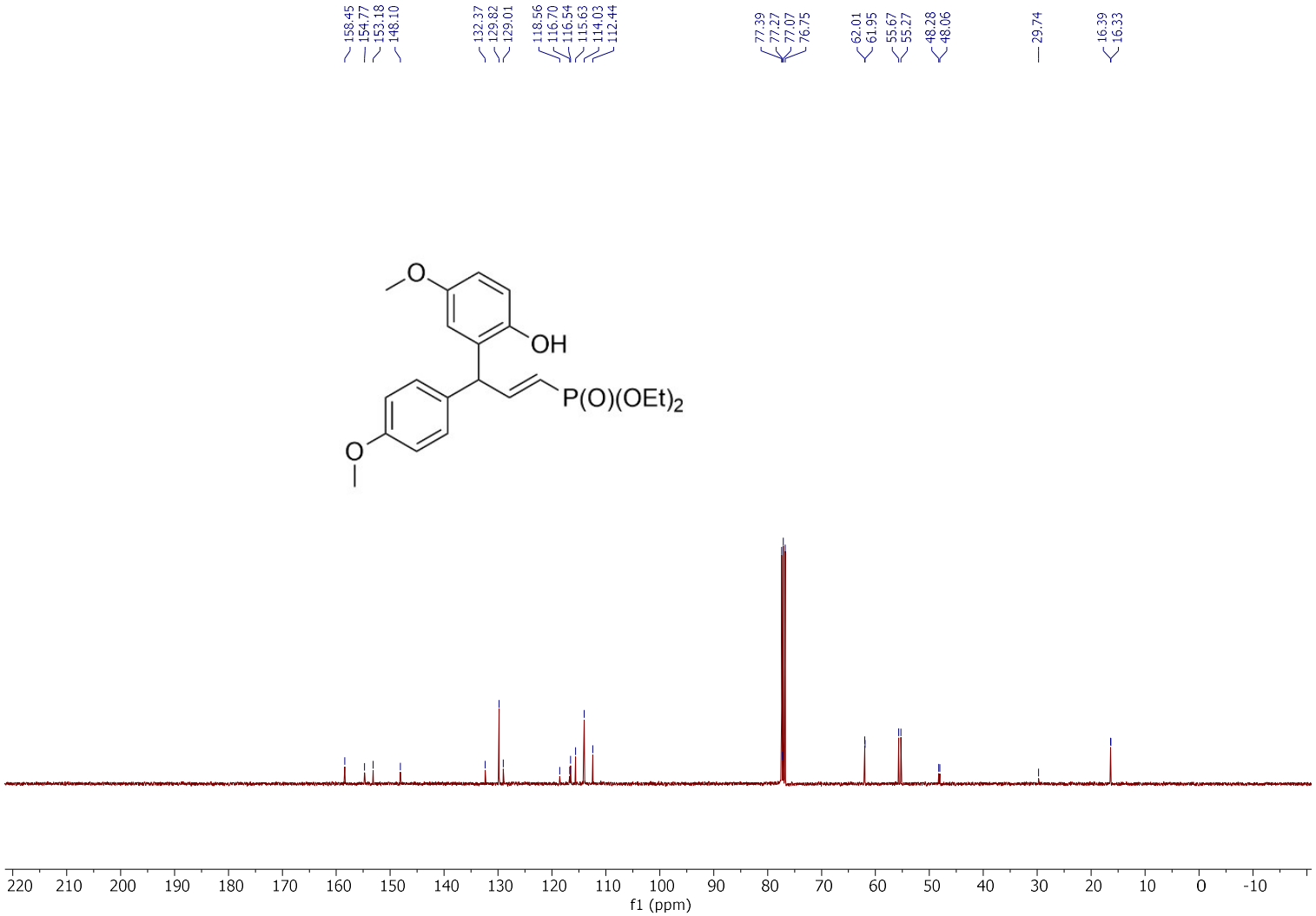


Figure S656: $^{13}C\{^{1}H\}$ NMR Spectra of 3m in $CDCl_3$

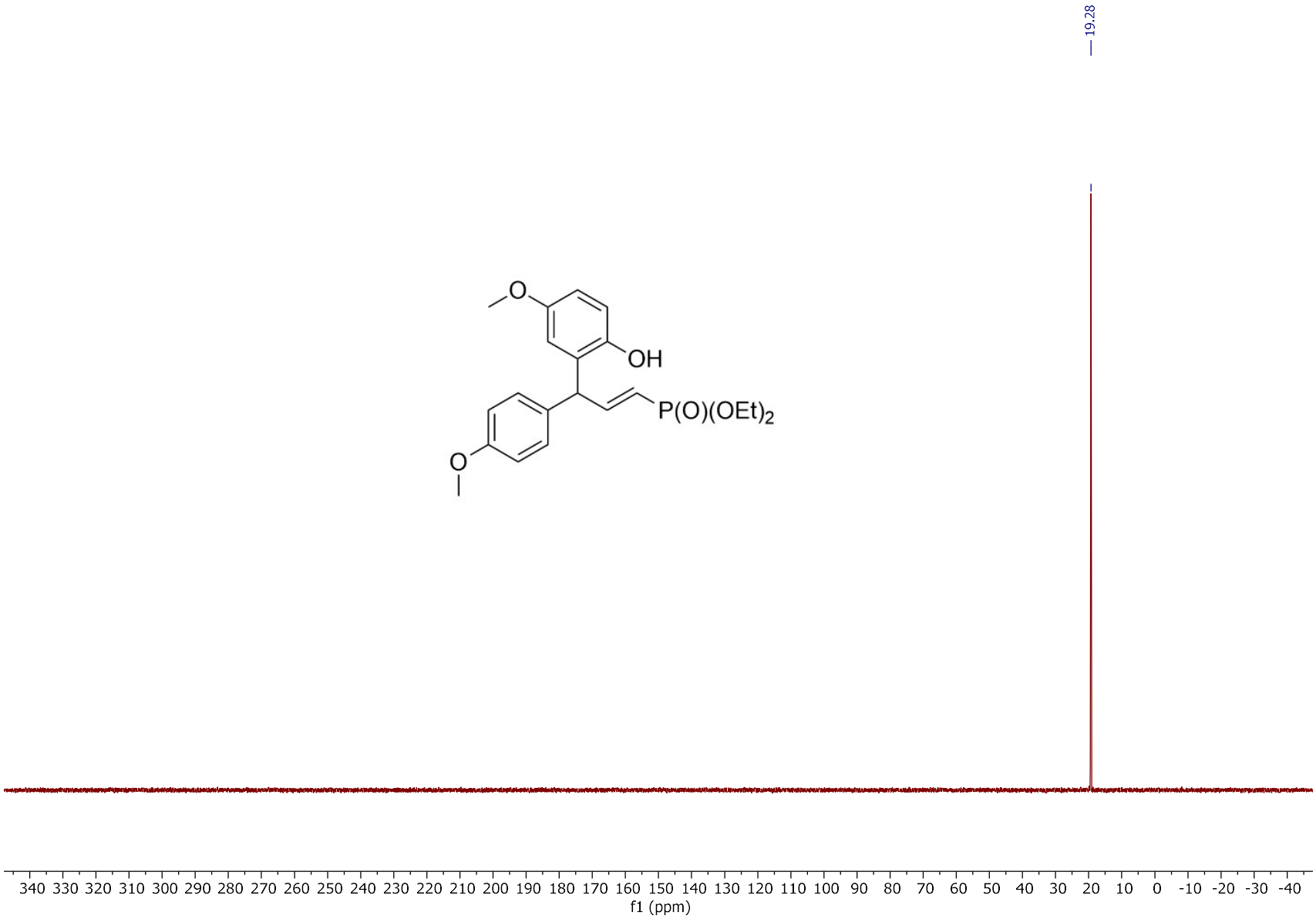


Figure S57: $^{31}P\{^{1}H\}$ NMR Spectra of 3m in $CDCl_3$

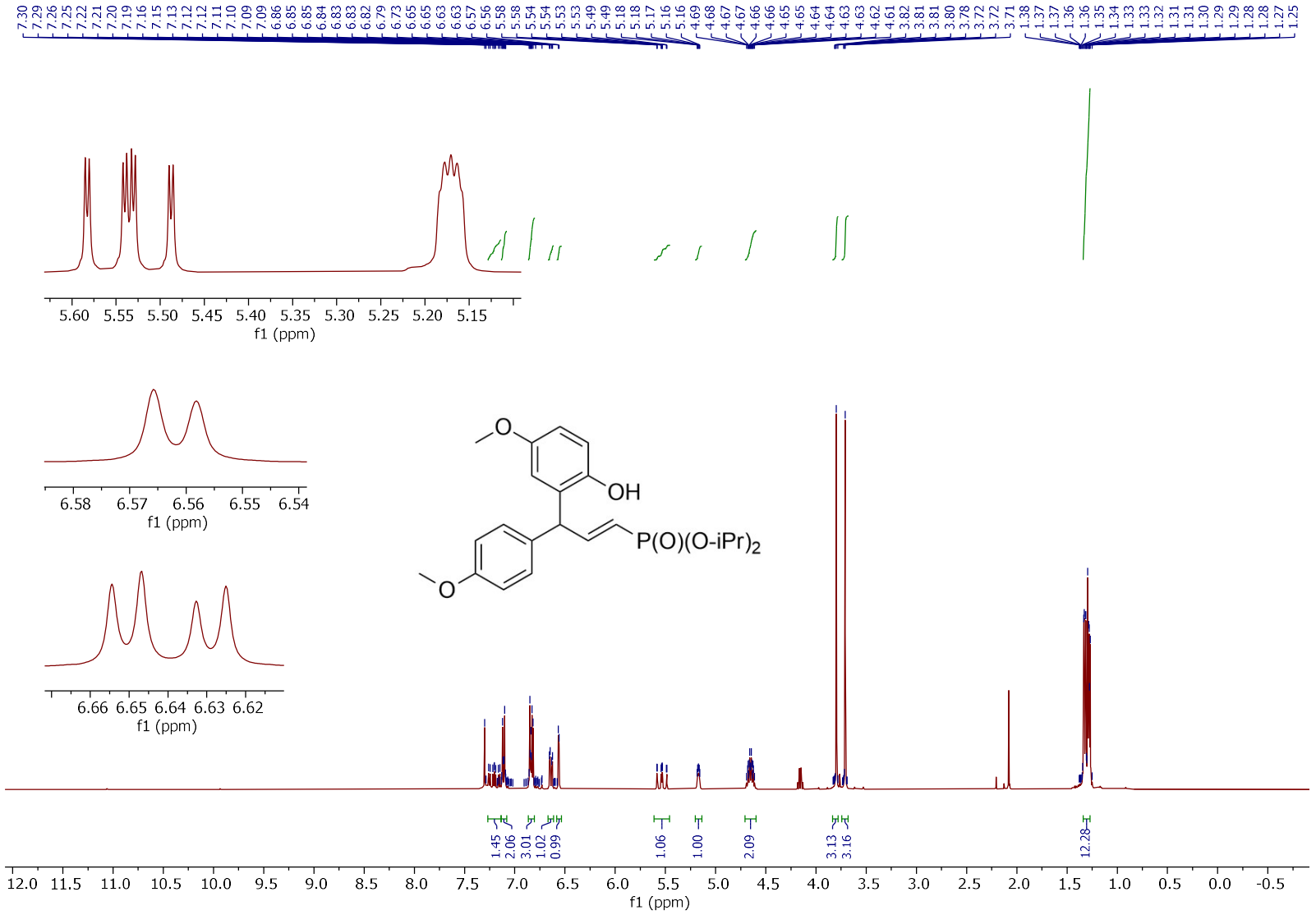


Figure S58: ^{1}H NMR Spectra of 3n in $CDCl_3$

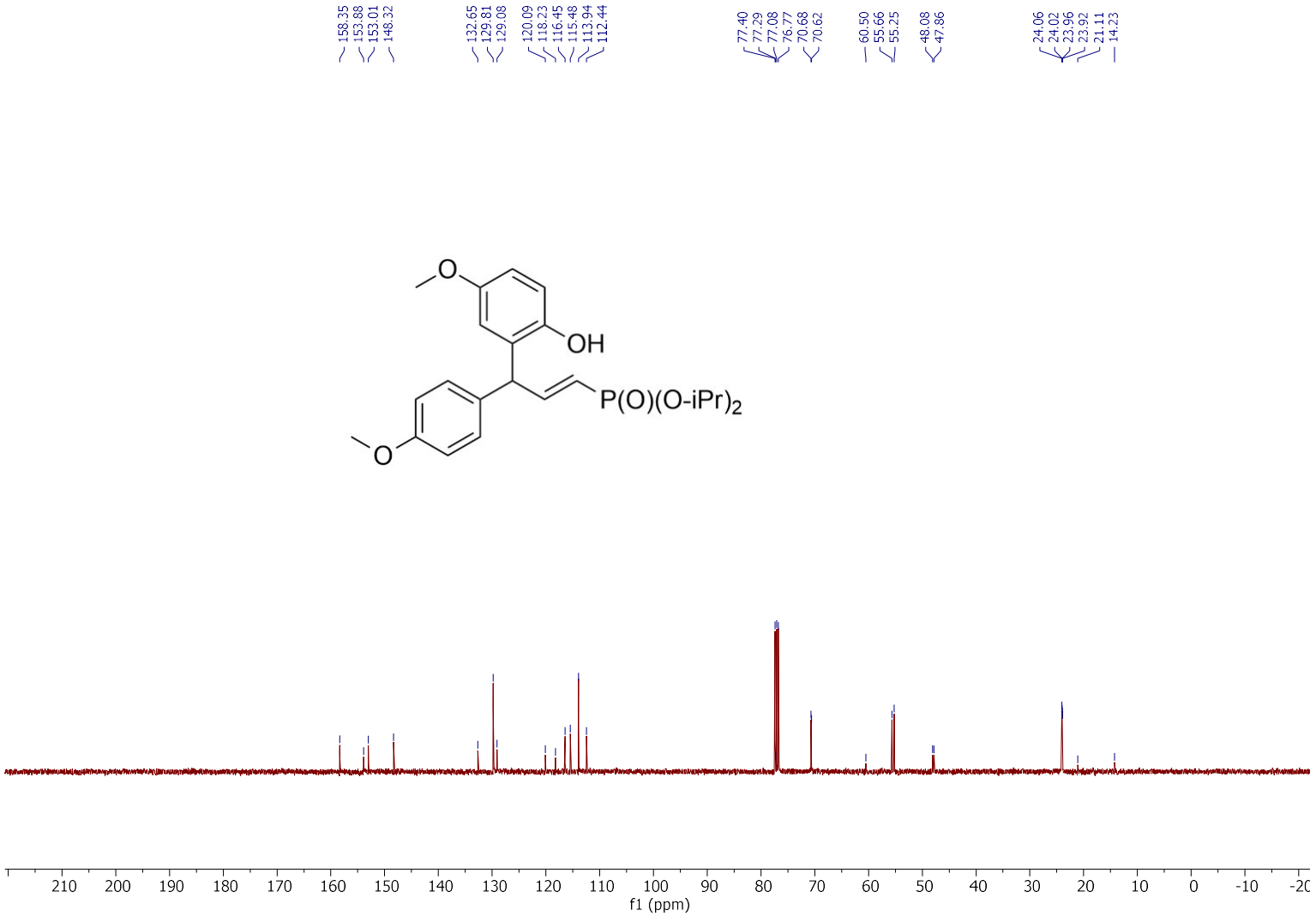


Figure S59: $^{13}C\{^{1}H\}$ NMR Spectra of 3n in $CDCl_3$

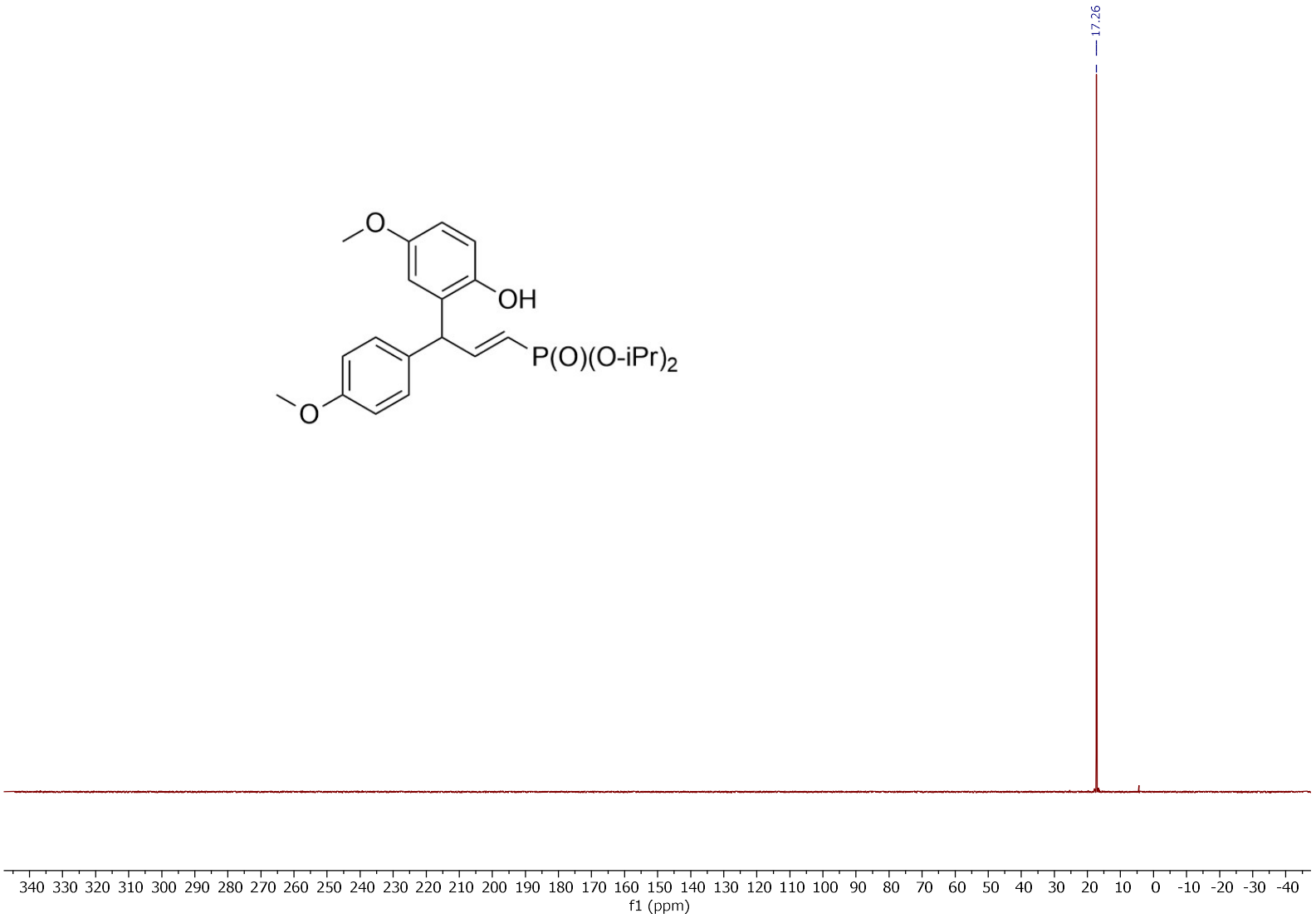


Figure S60: $^{31}P\{^{1}H\}$ NMR Spectra of 3n in $CDCl_3$

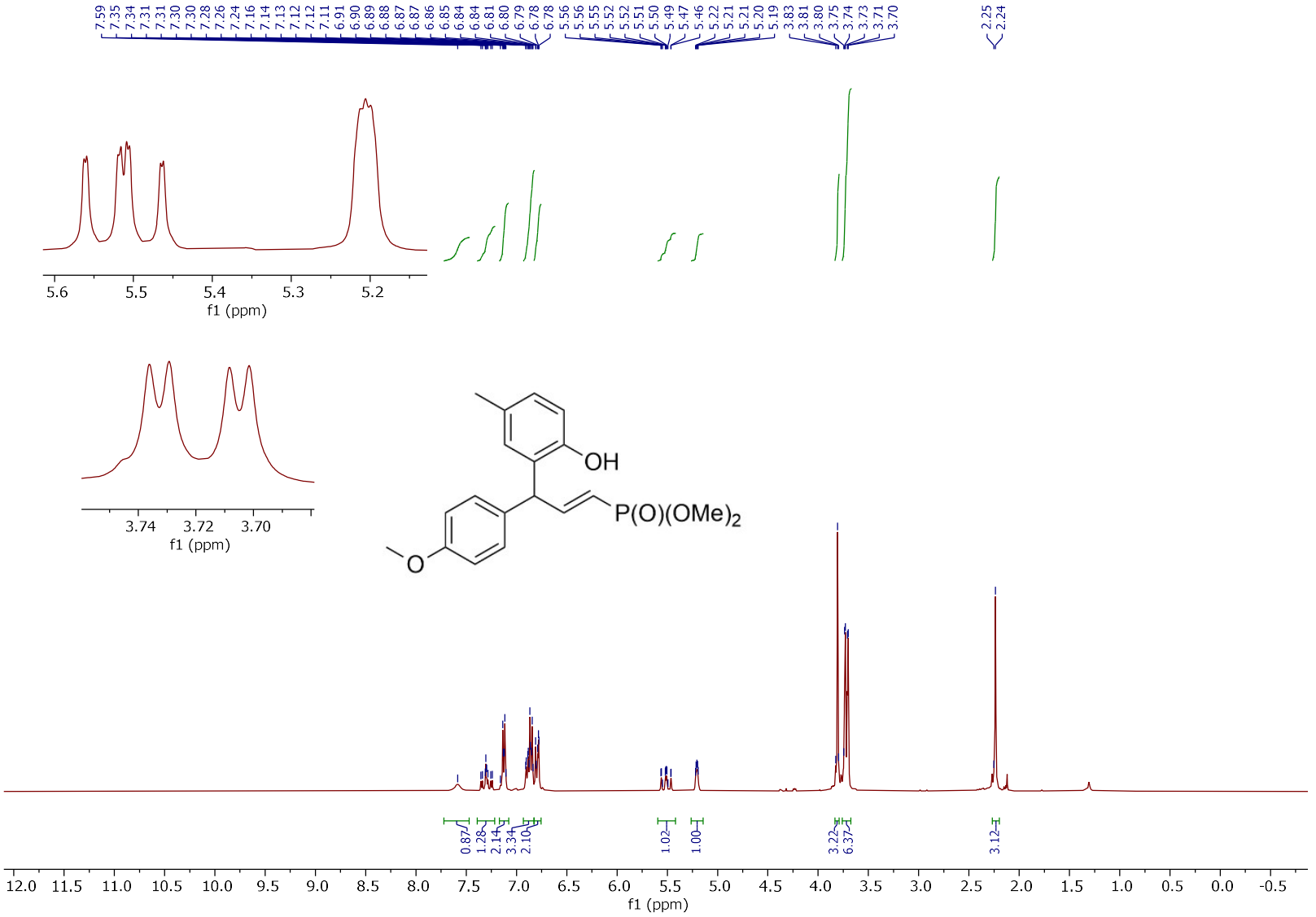


Figure S61: ^{1}H NMR Spectra of 3i in $CDCl_3$

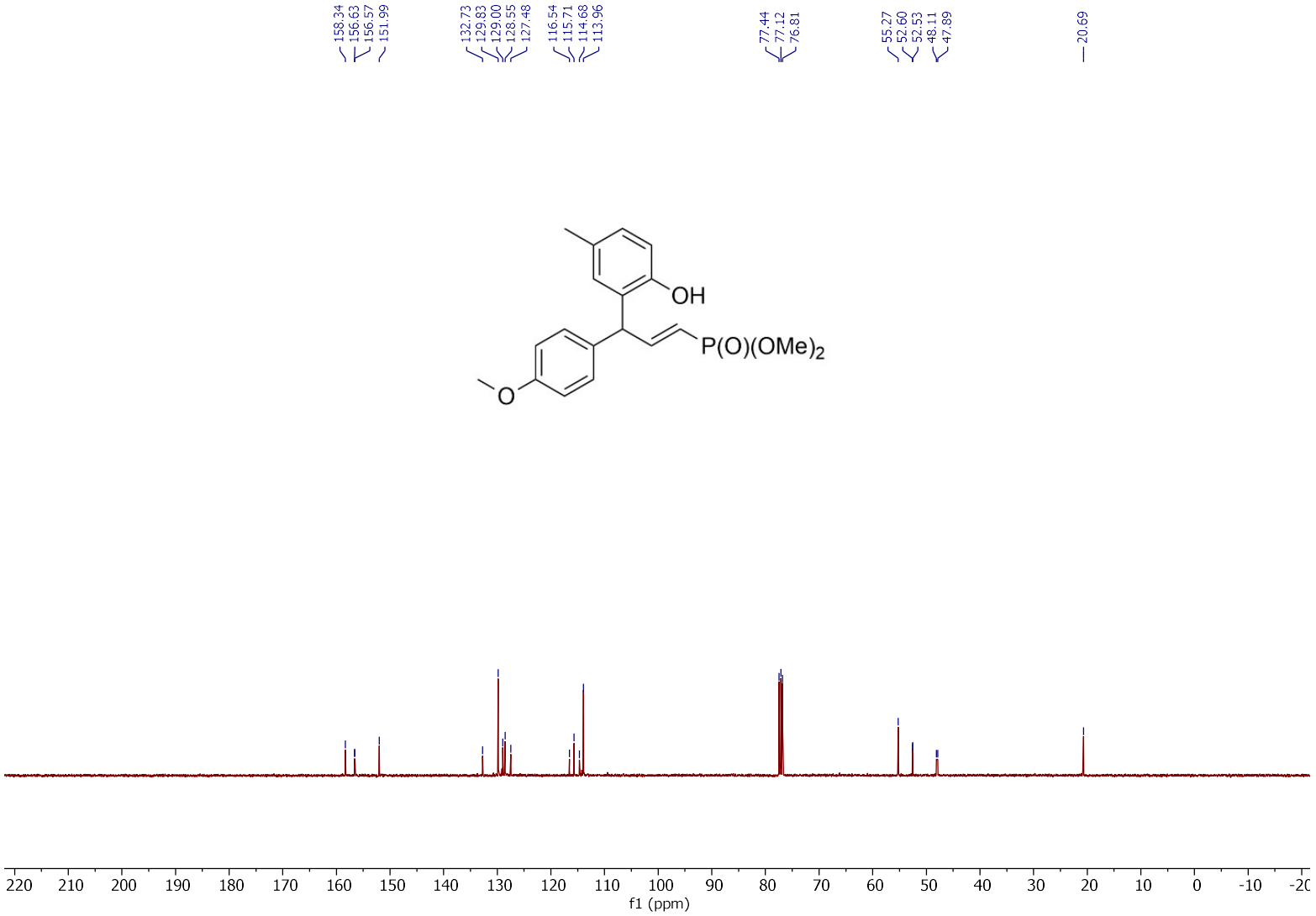


Figure S62: $^{13}C\{^{1}H\}$ NMR Spectra of 3i in $CDCl_3$

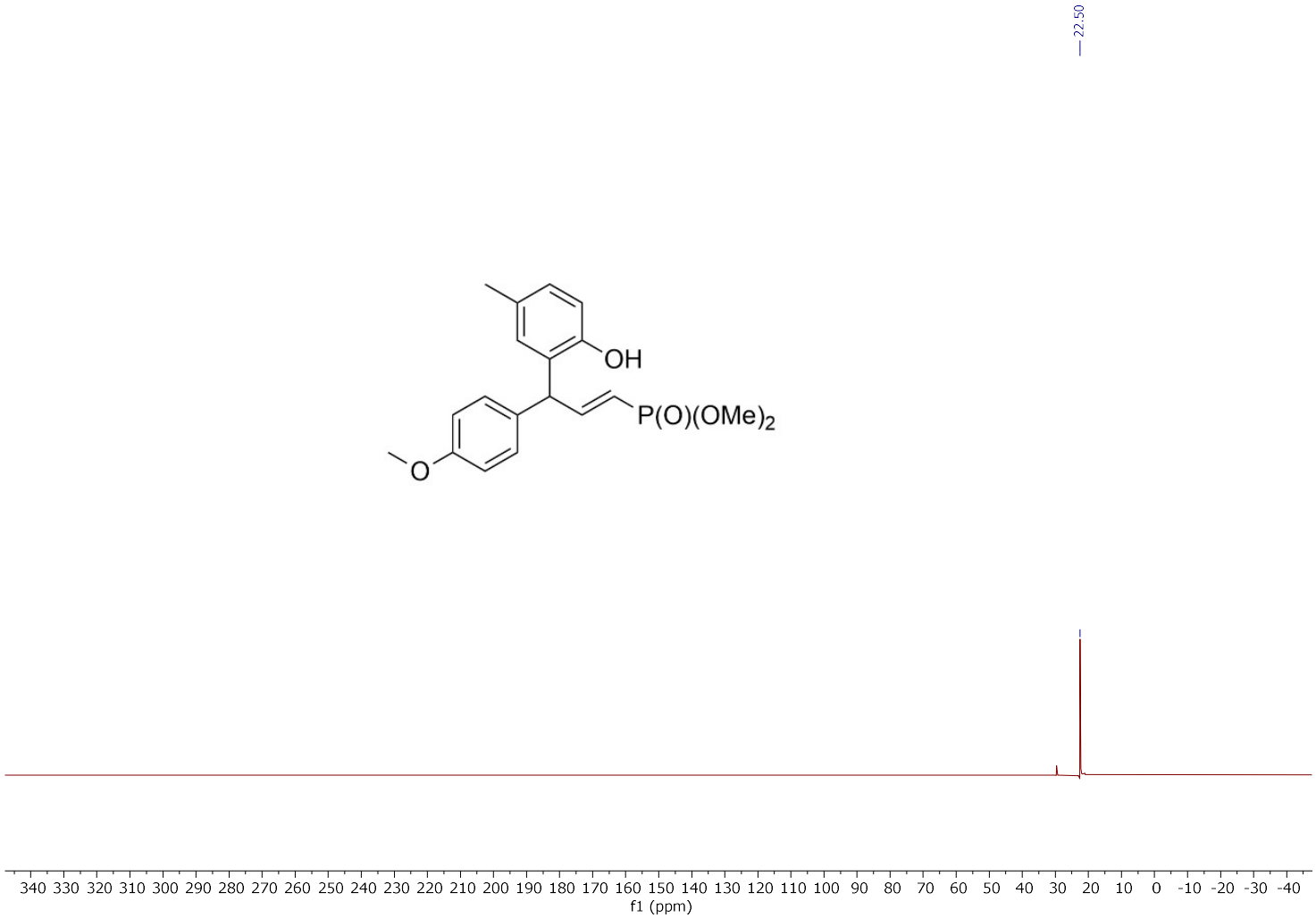


Figure S63: $^{31}P\{^{1}H\}$ NMR Spectra of 3i in $CDCl_3$

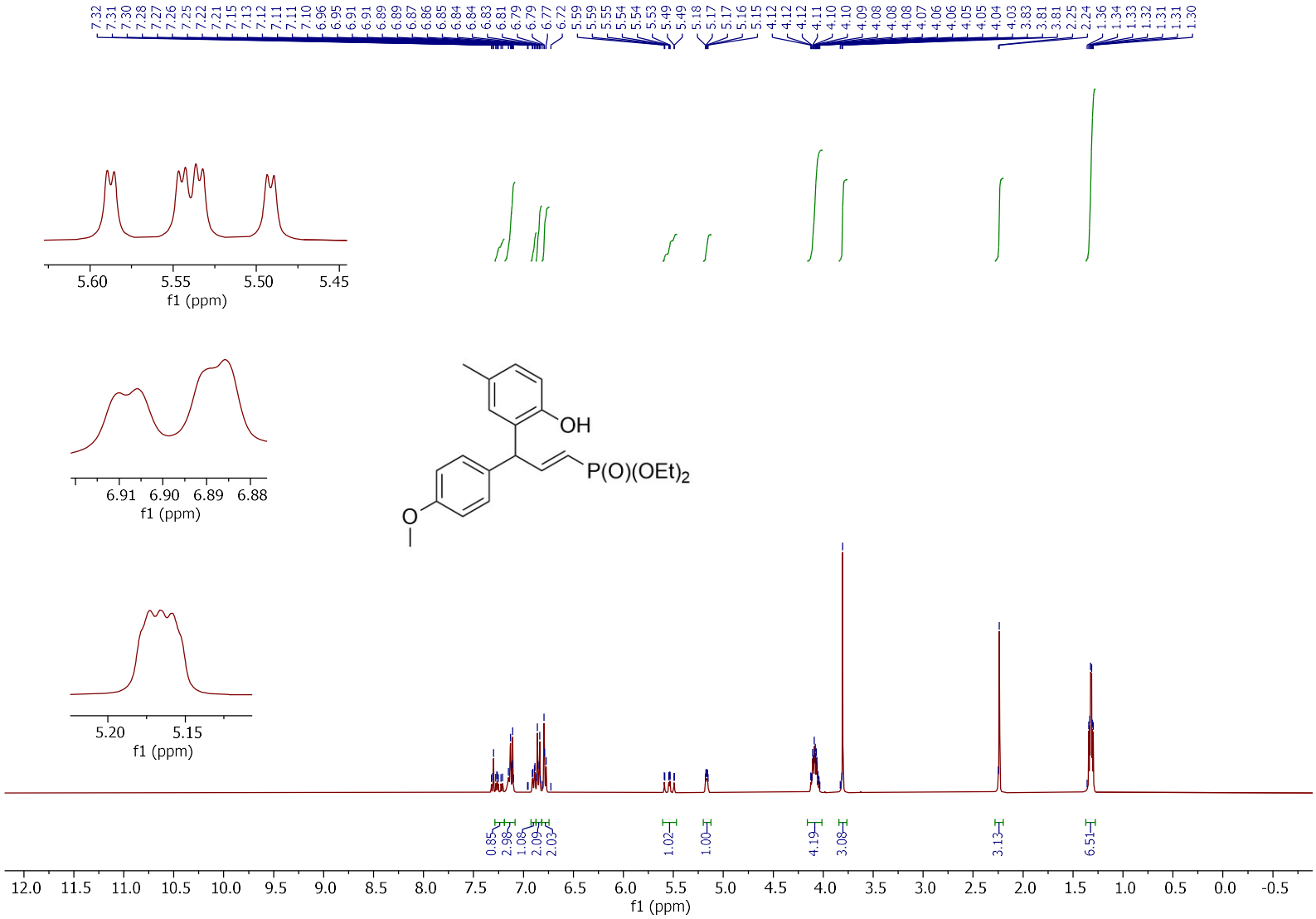


Figure S64: ^{1}H NMR Spectra of 3j in $CDCl_3$

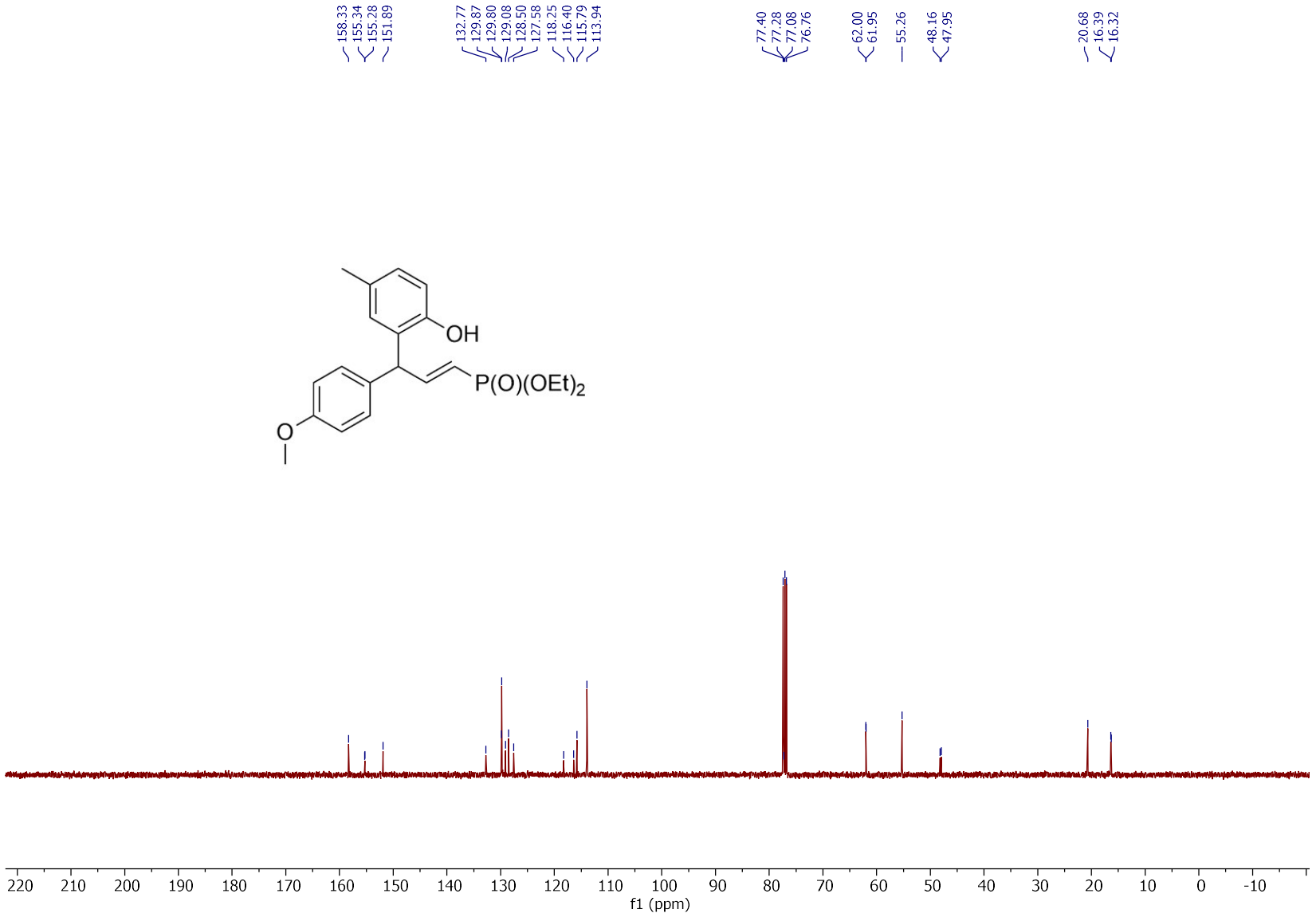


Figure S65: $^{13}C\{^{1}H\}$ NMR Spectra of 3j in $CDCl_3$

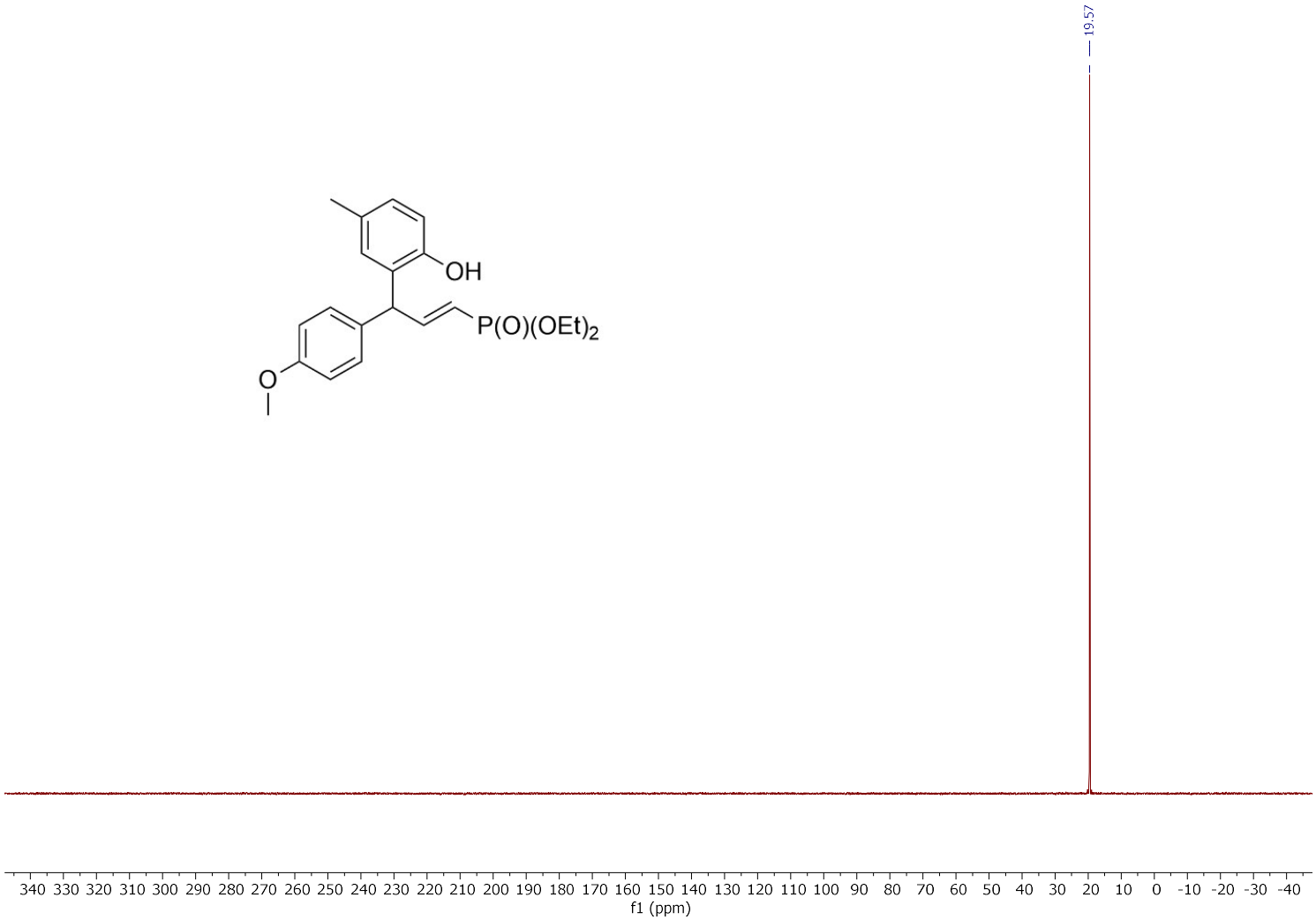


Figure S66: $^{31}P\{^{1}H\}$ NMR Spectra of 3j in $CDCl_3$

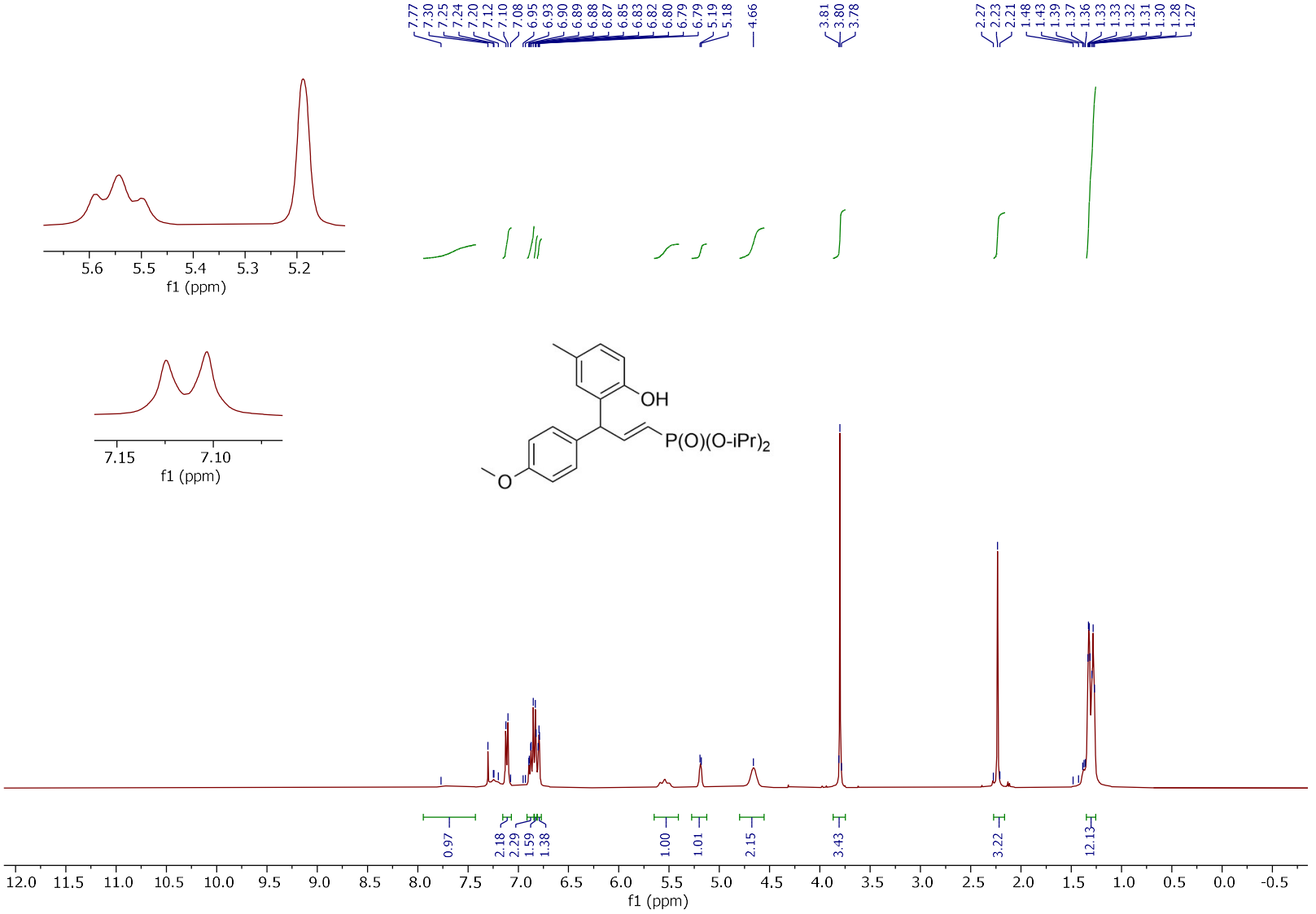


Figure S67: ^{1}H NMR Spectra of 3k in $CDCl_3$

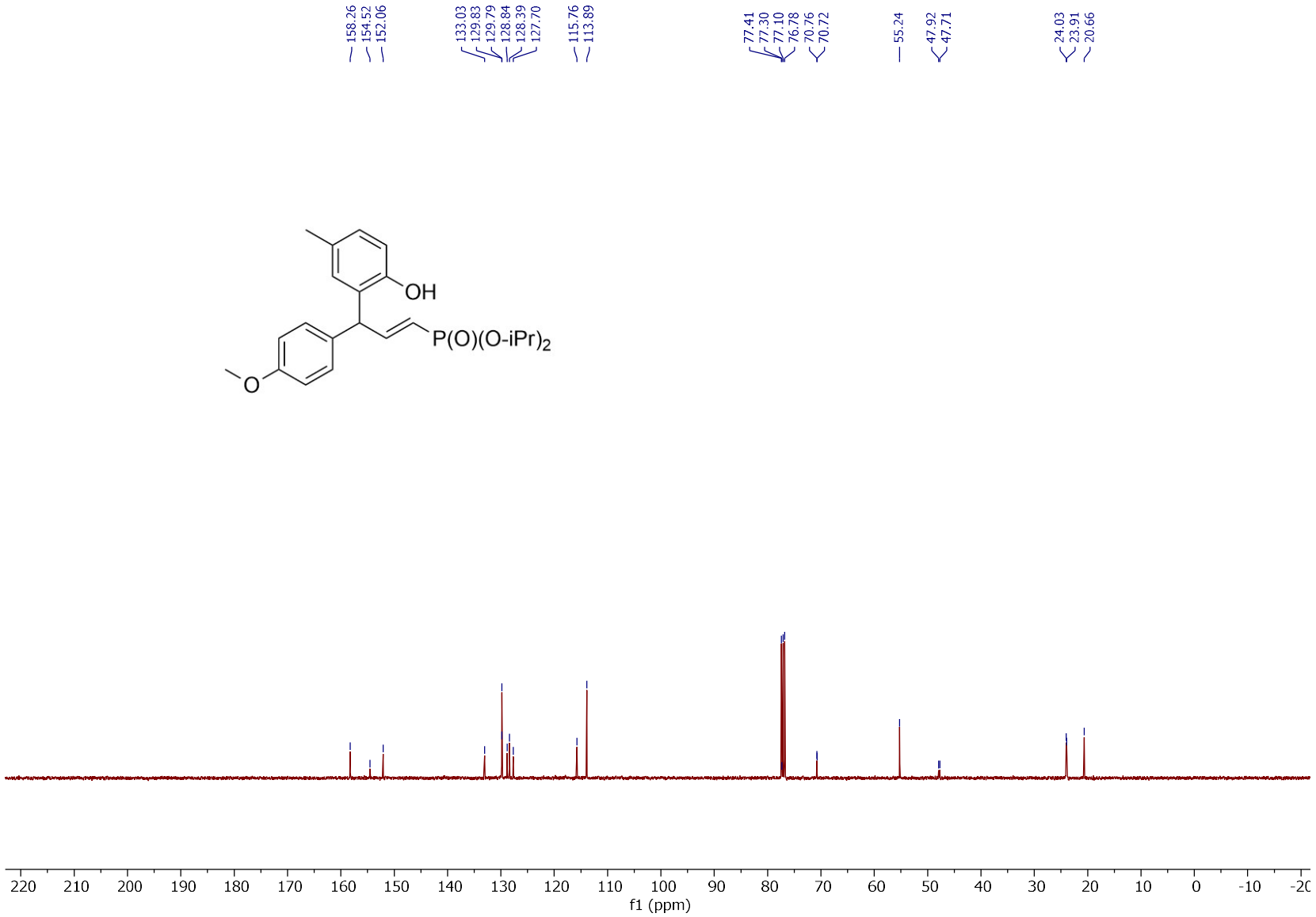


Figure S68: $^{13}C\{^{1}H\}$ NMR Spectra of 3k in $CDCl_3$

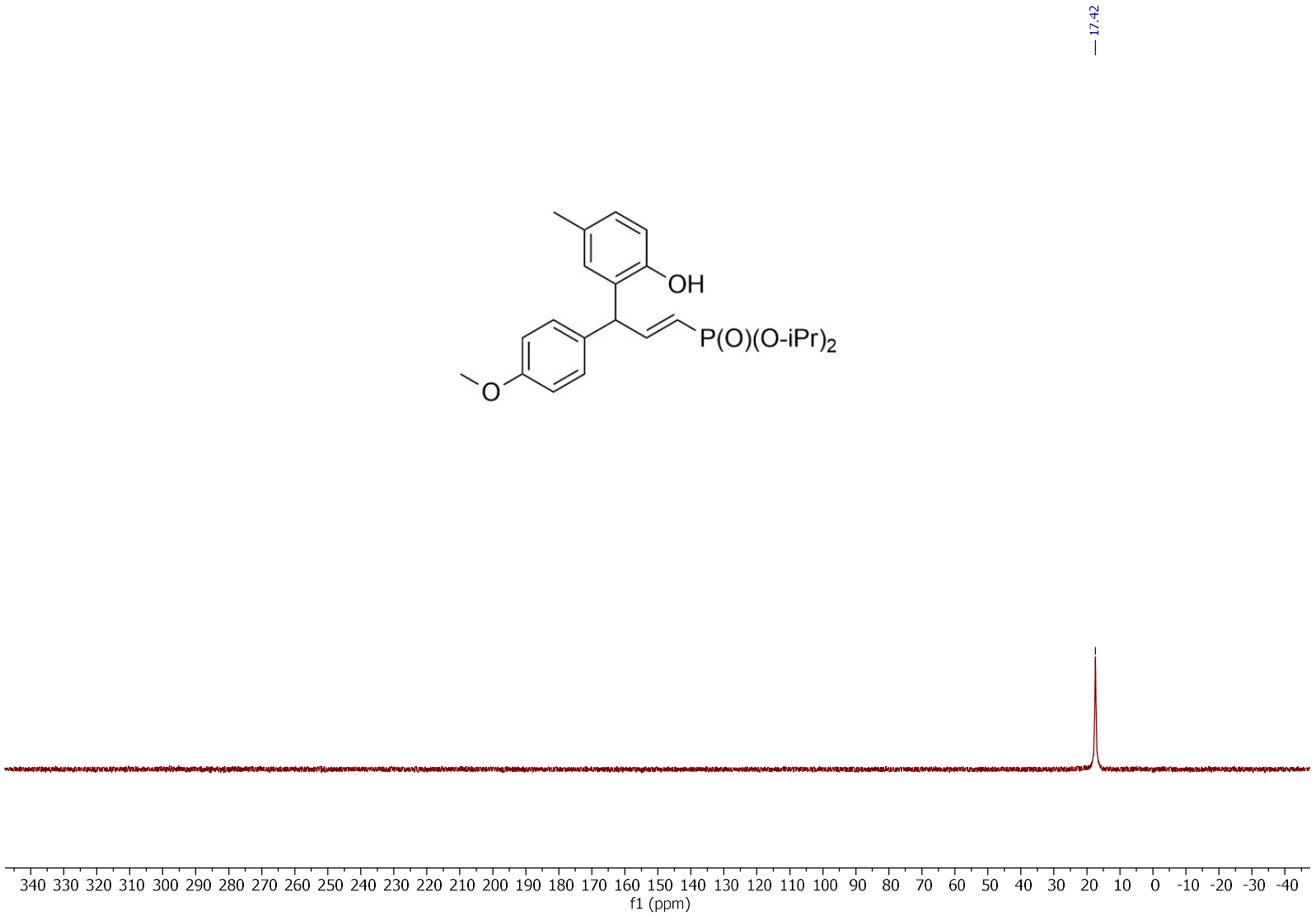


Figure S69: $^{31}P\{^{1}H\}$ NMR Spectra of 3k in $CDCl_3$

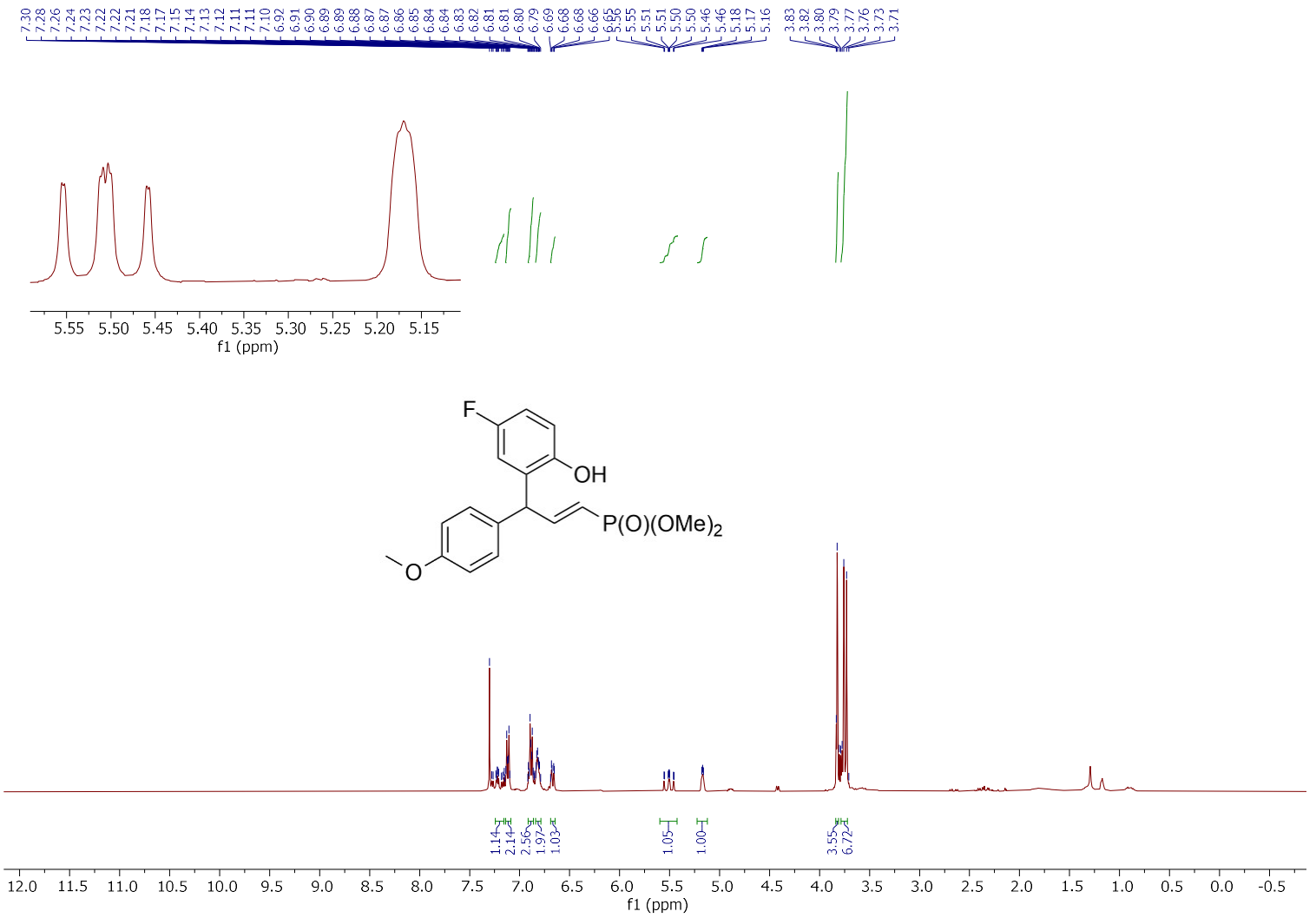


Figure S70: ^{1}H NMR Spectra of 3o in $CDCl_3$

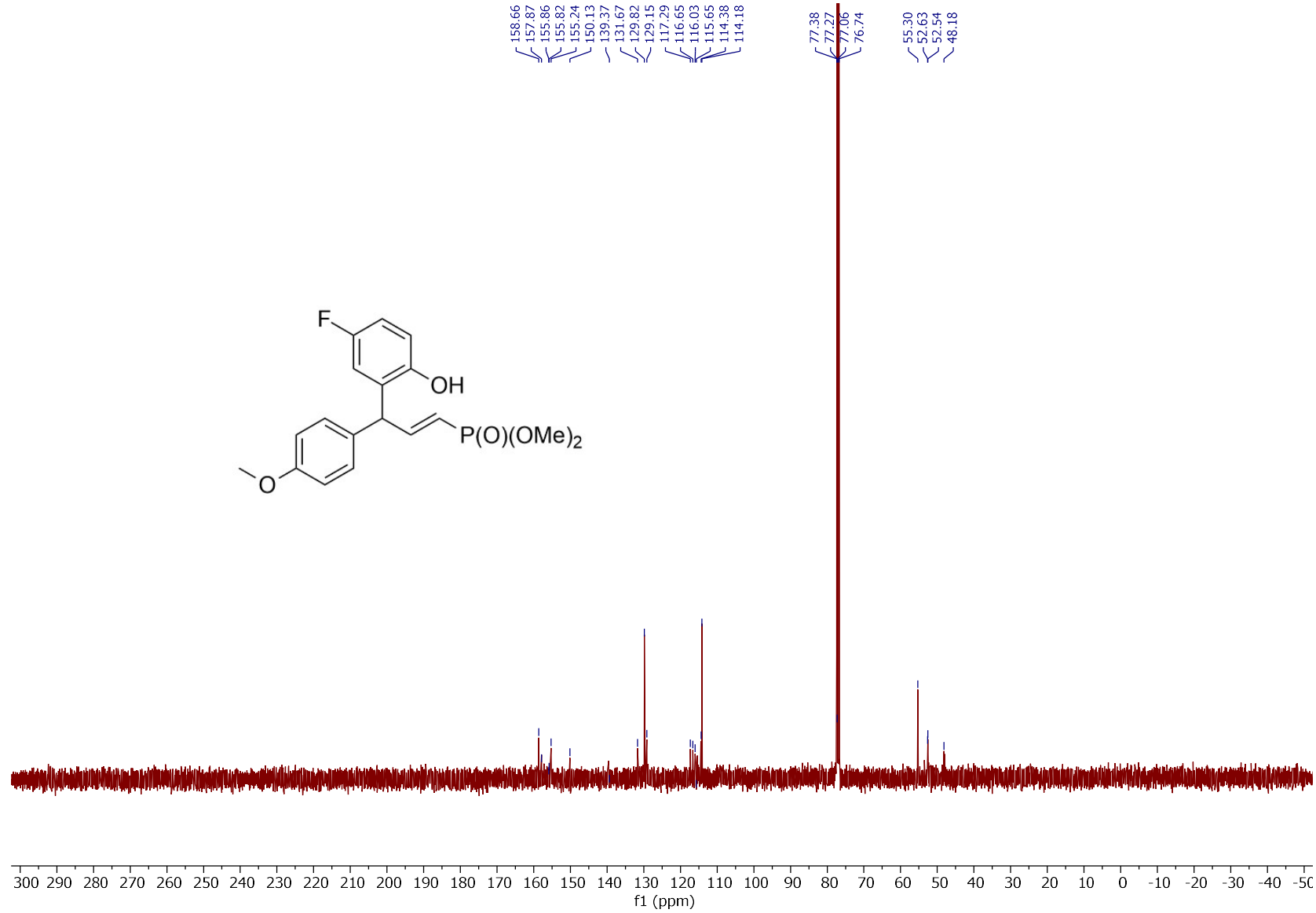


Figure S71: $^{13}C\{^{1}H\}$ NMR Spectra of 3o in $CDCl_3$

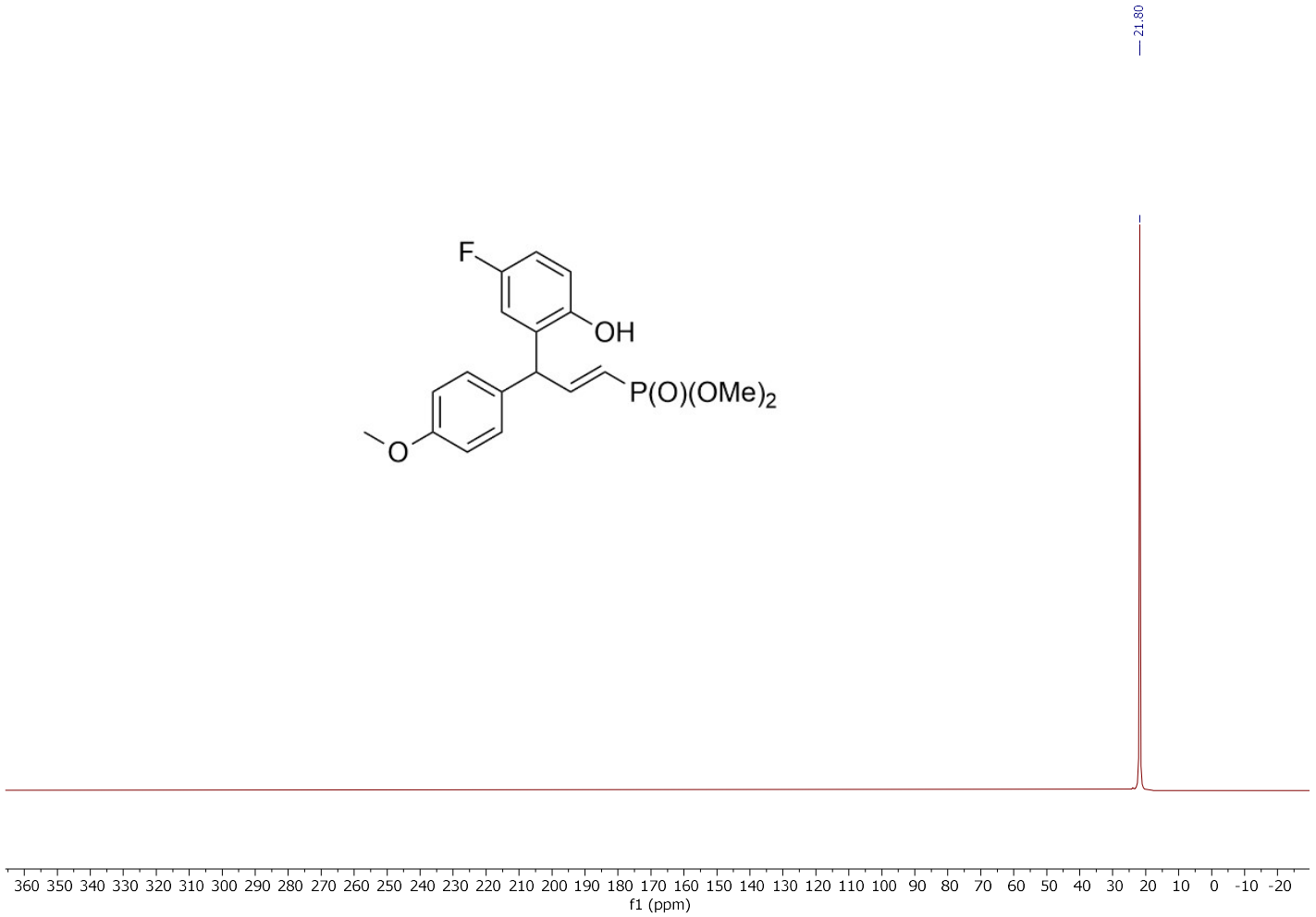


Figure S72: $^{31}P\{^{1}H\}$ NMR Spectra of 3o in $CDCl_3$

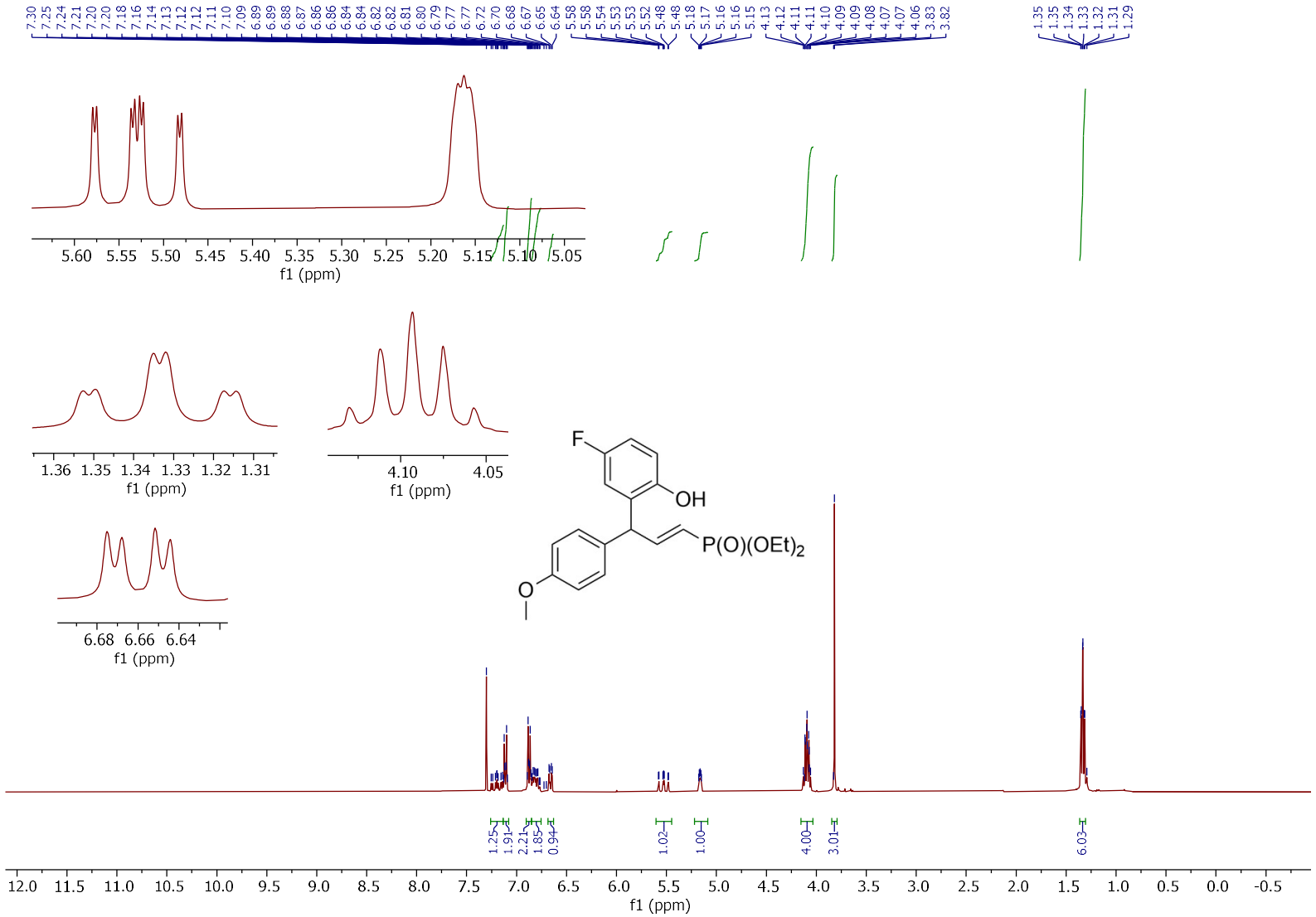


Figure S73: ^{1}H NMR Spectra of 3p in $CDCl_3$

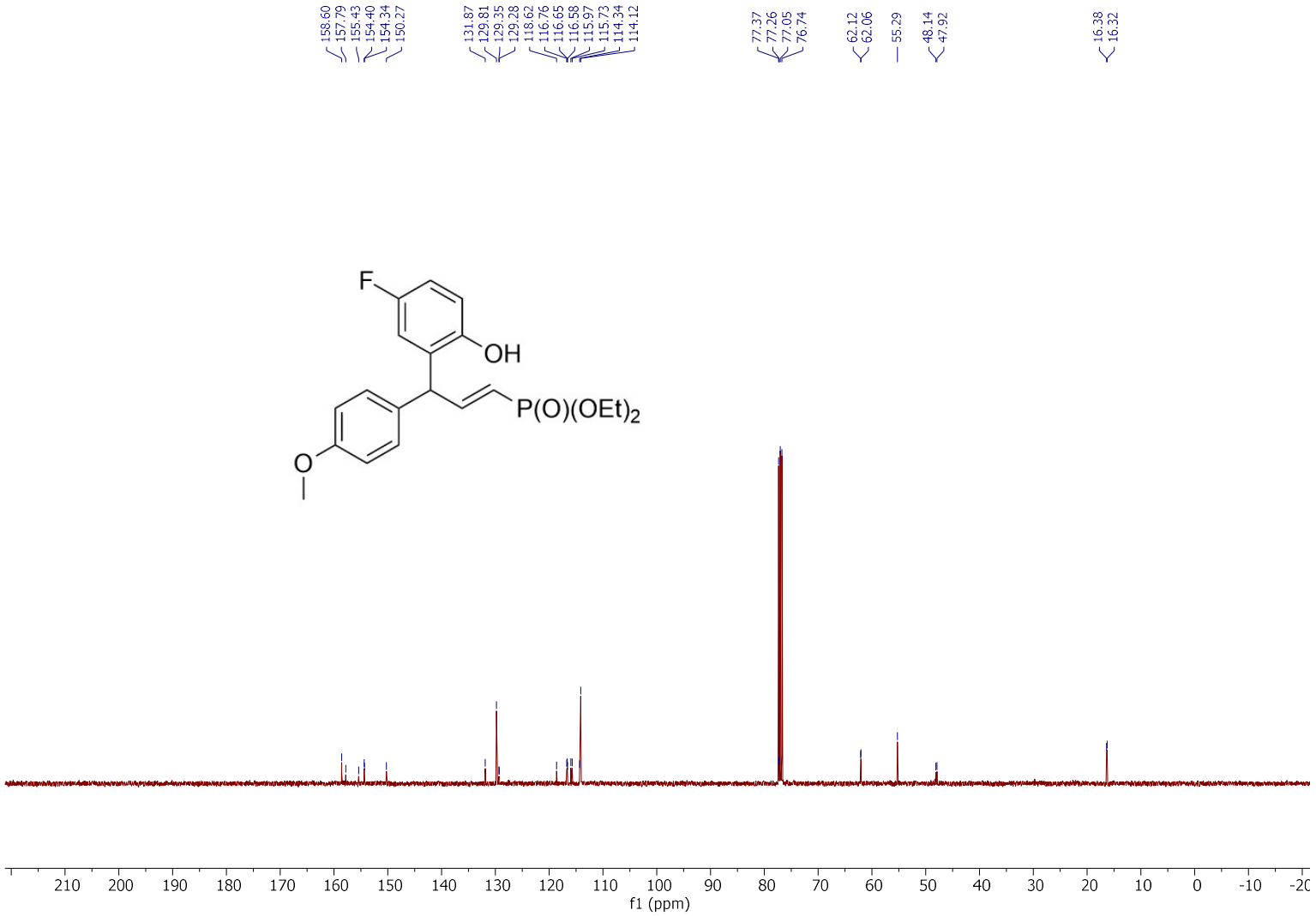


Figure S74: $^{13}C\{^{1}H\}$ NMR Spectra of 3p in $CDCl_3$

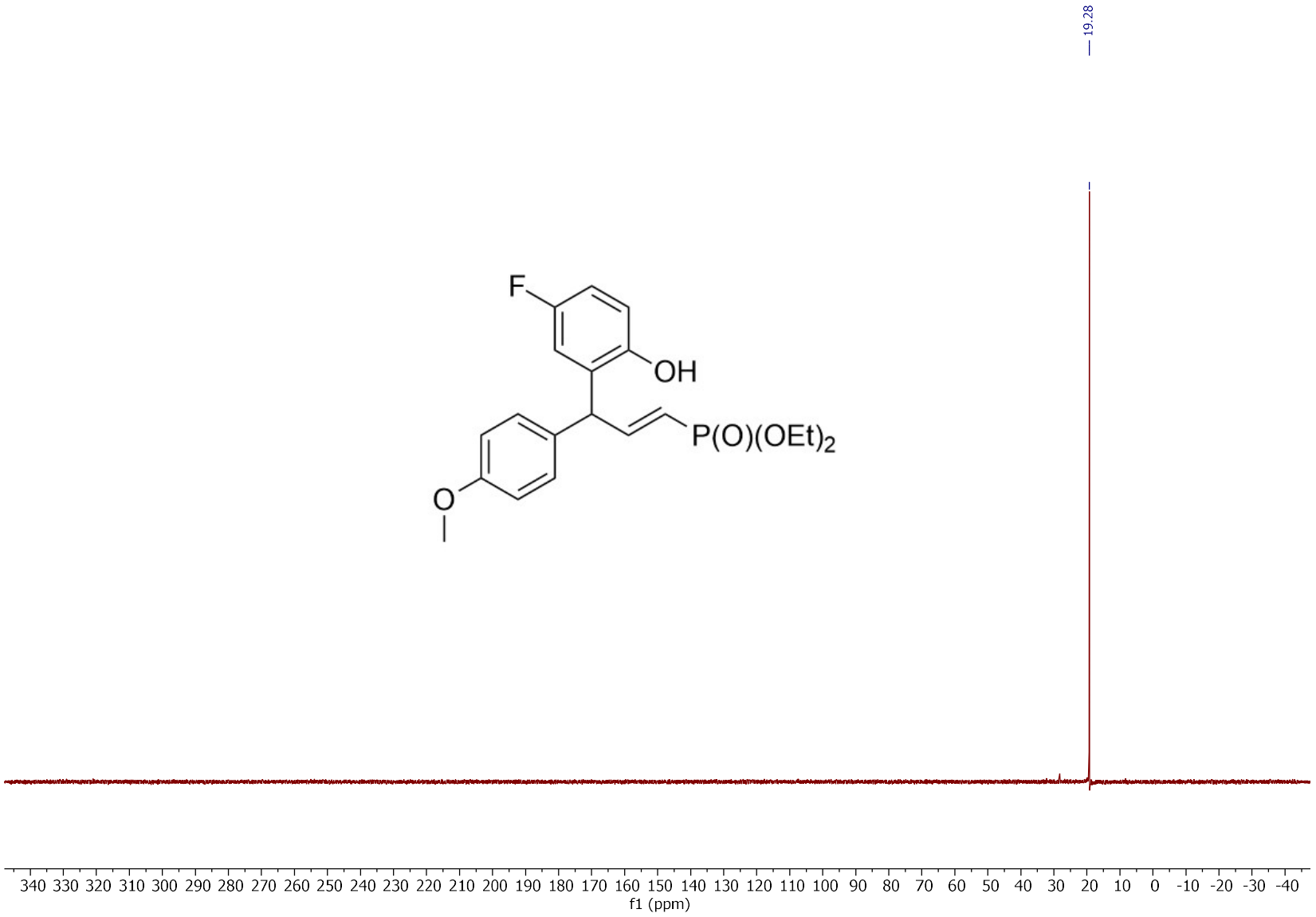


Figure S75: $^{31}P\{^{1}H\}$ NMR Spectra of 3p in $CDCl_3$

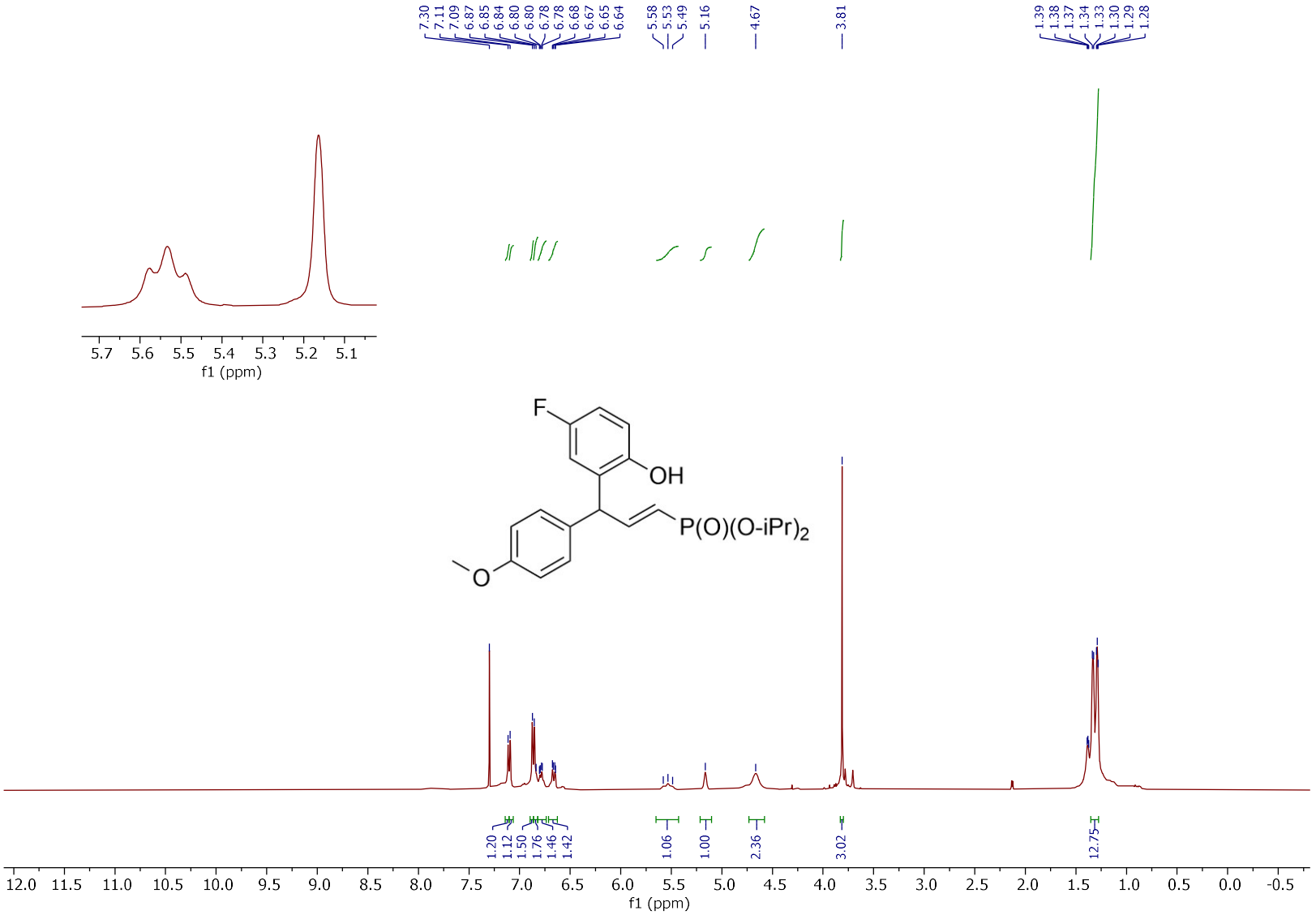


Figure S76: ^{1}H NMR Spectra of 3q in $CDCl_3$

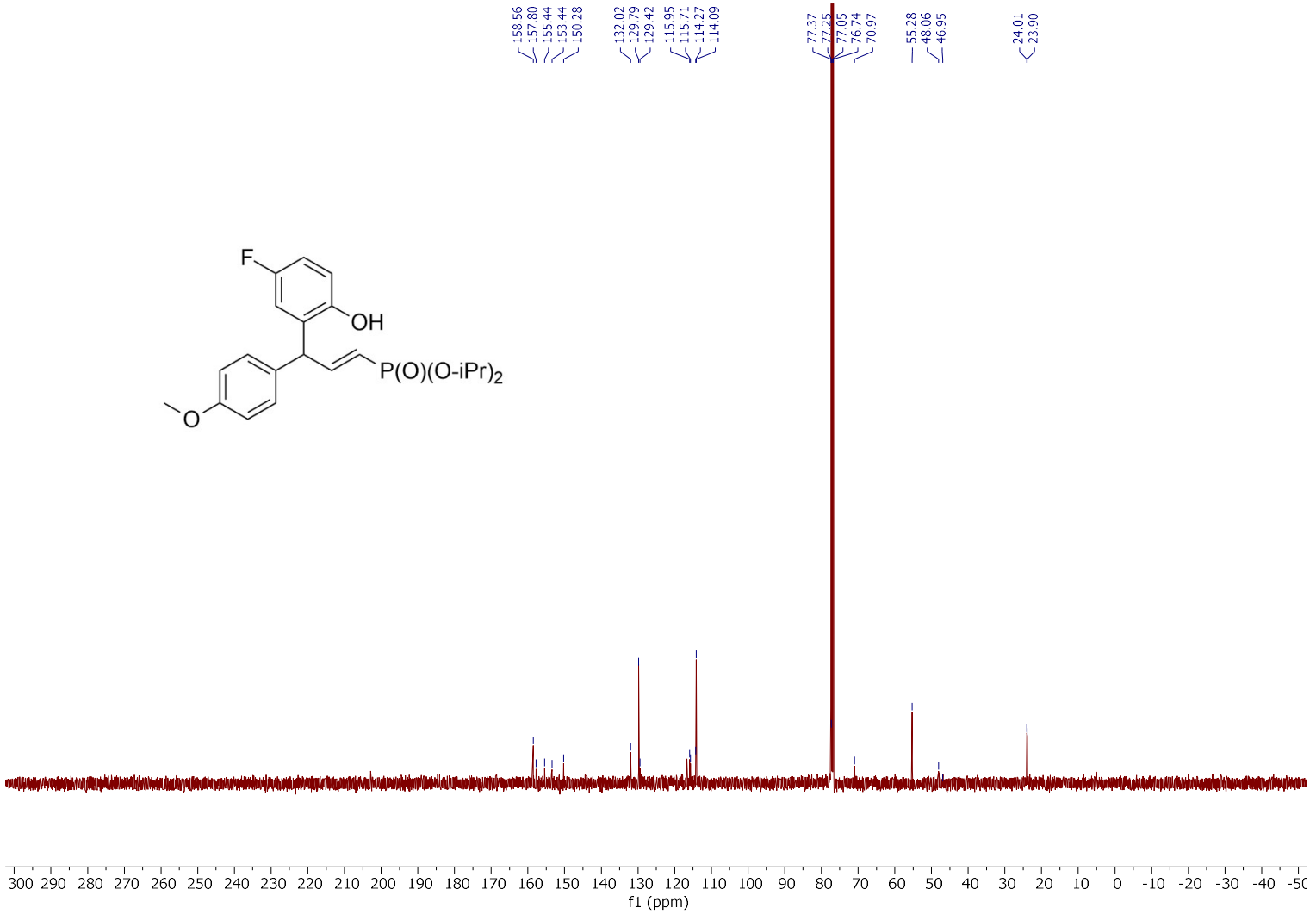


Figure S77: $^{13}C\{^{1}H\}$ NMR Spectra of 3q in $CDCl_3$

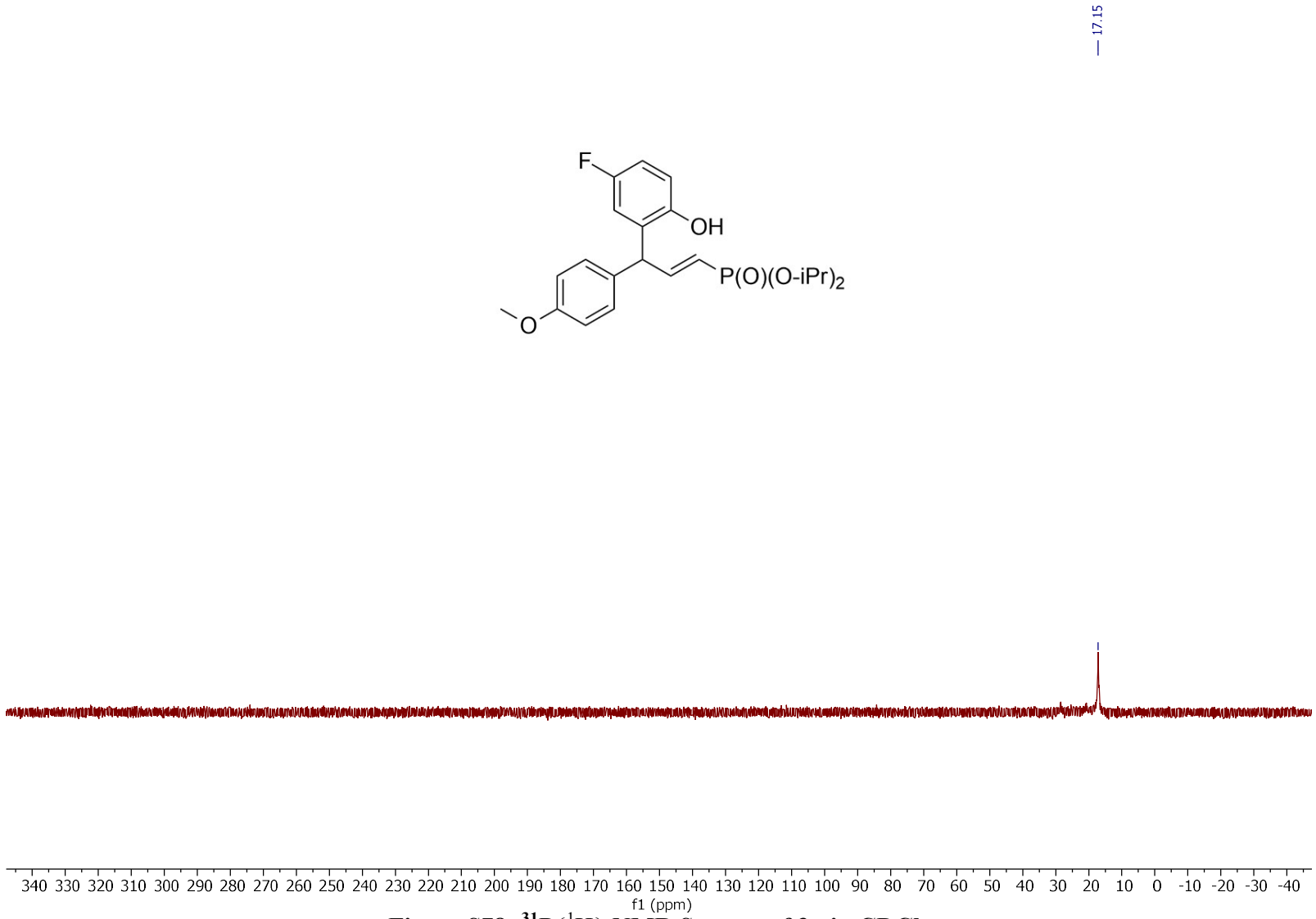


Figure S78: $^{31}P\{^{1}H\}$ NMR Spectra of 3q in $CDCl_3$

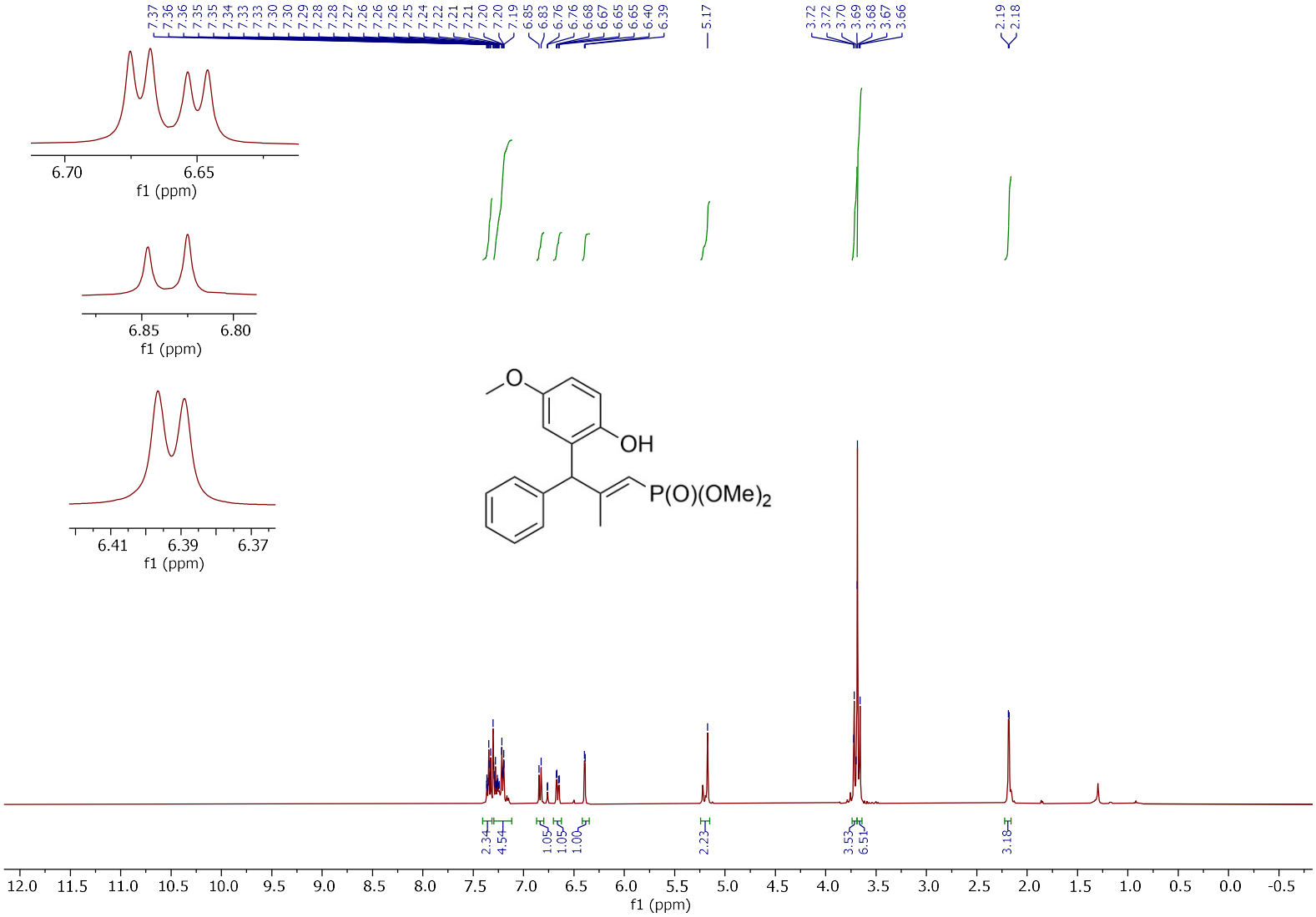


Figure S79: ^{1}H NMR Spectra of 3u in $CDCl_3$

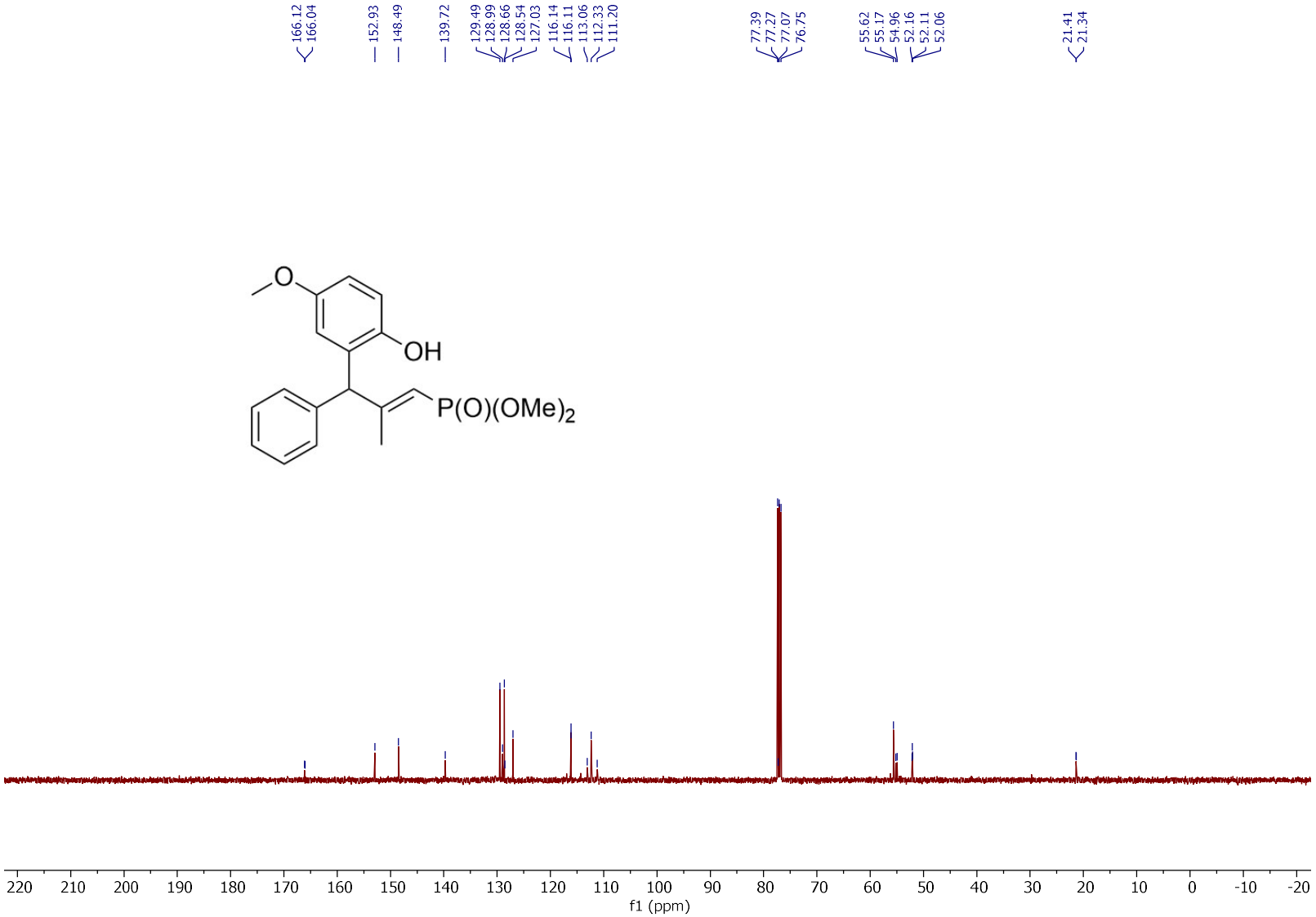


Figure S80: $^{13}C\{^{1}H\}$ NMR Spectra of 3u in $CDCl_3$

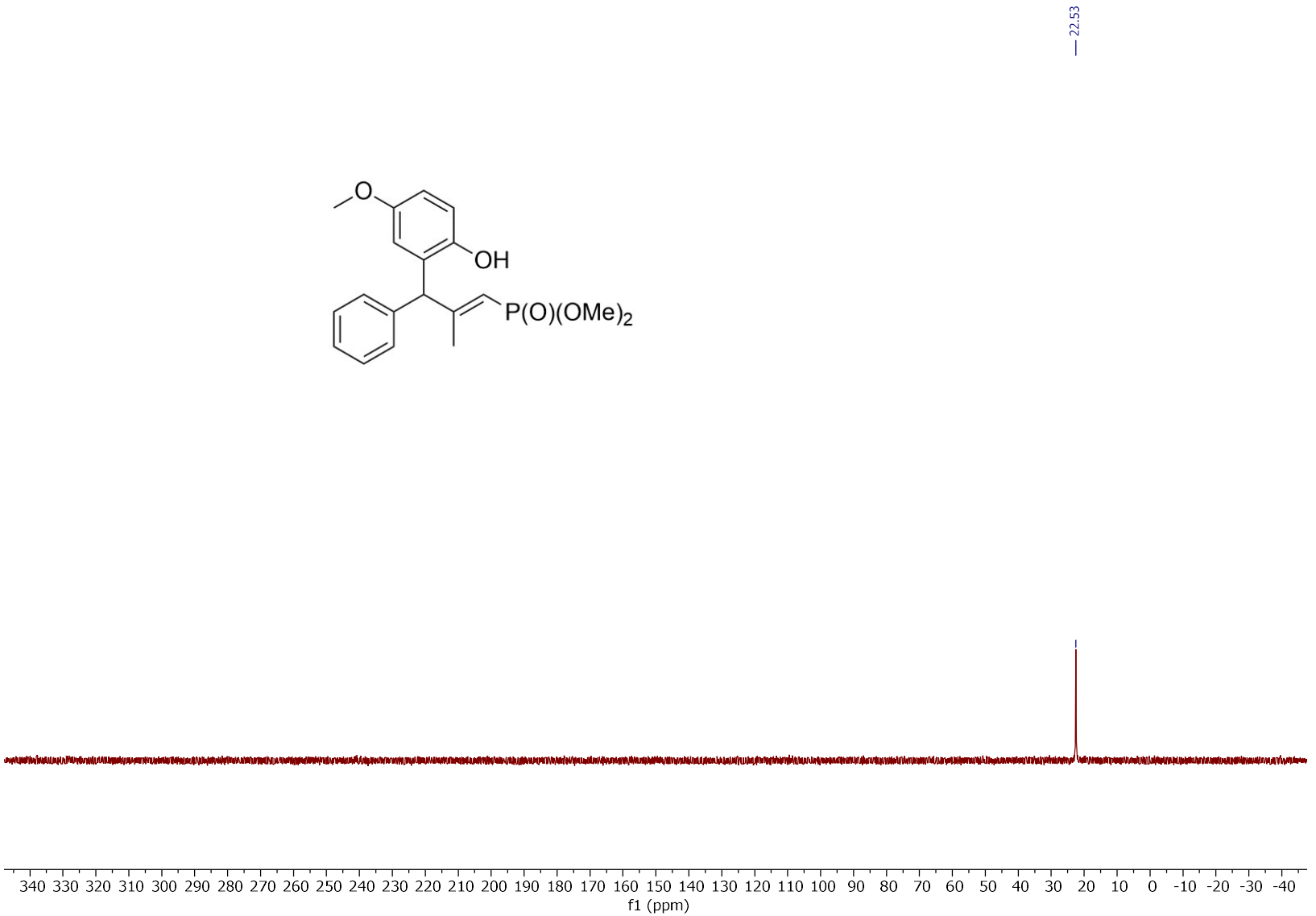


Figure S81: $^{31}P\{^{1}H\}$ NMR Spectra of 3u in $CDCl_3$

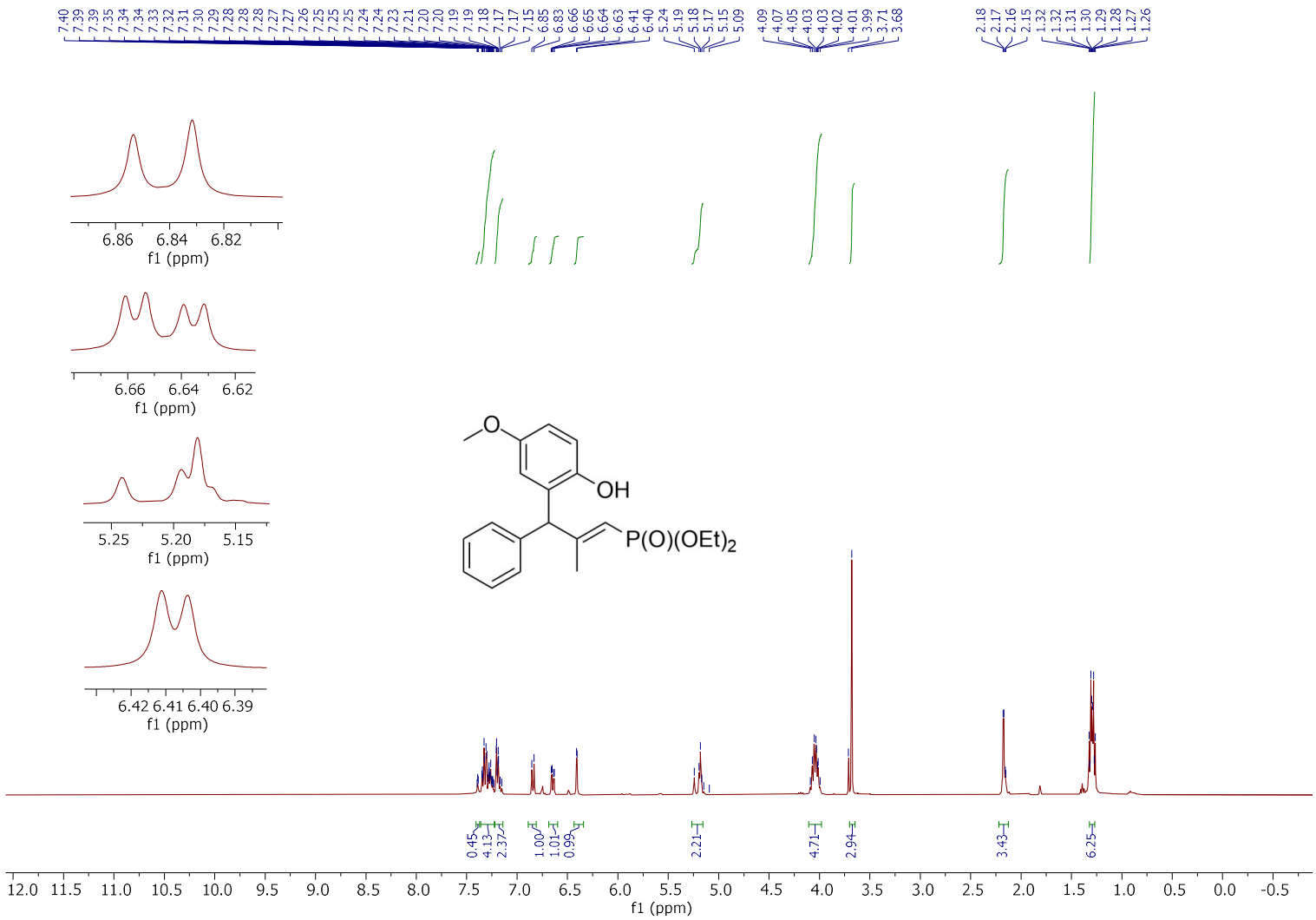


Figure S82: ^{1}H NMR Spectra of 3v in $CDCl_3$

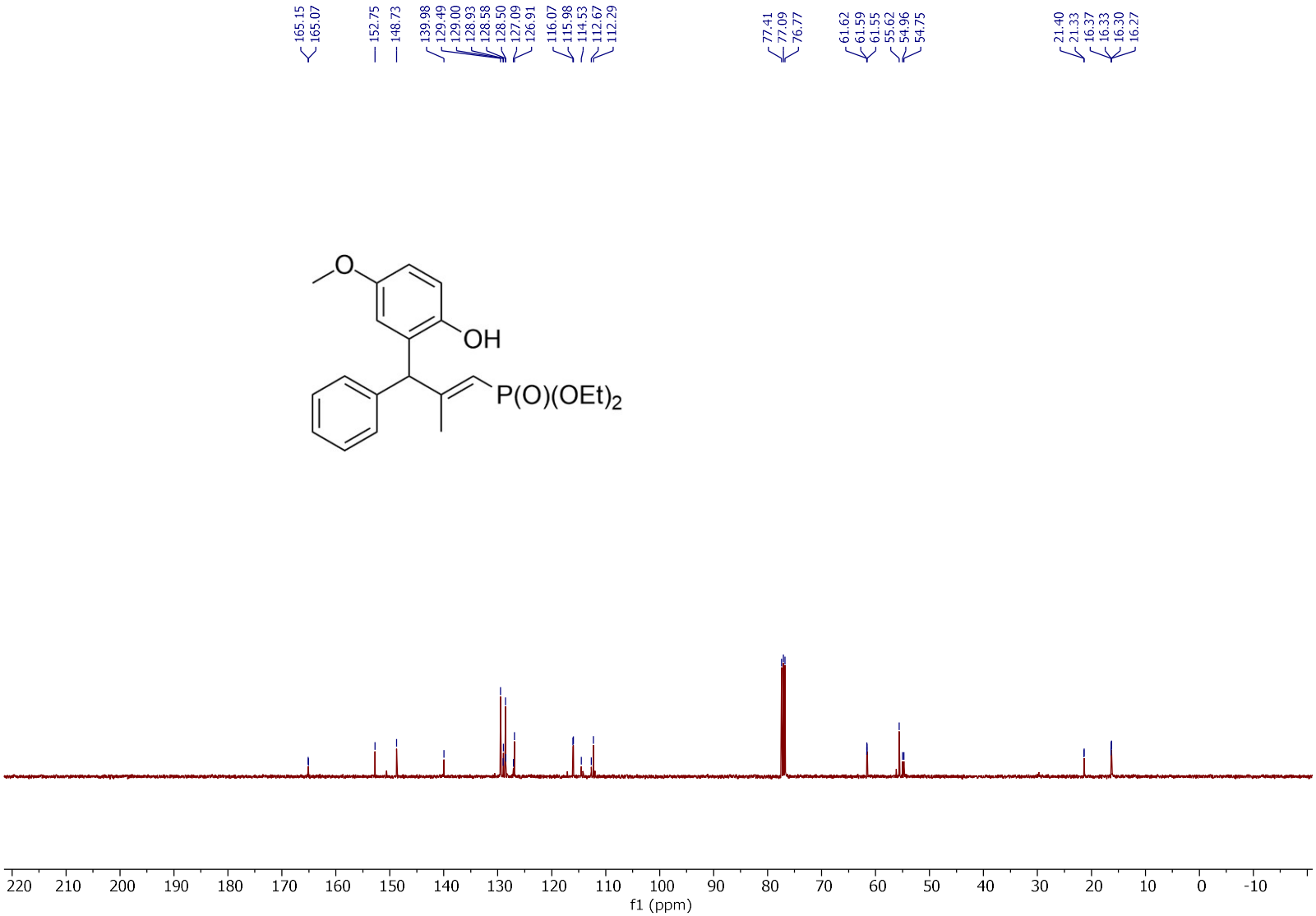


Figure S83: $^{13}C\{^{1}H\}$ NMR Spectra of 3v in $CDCl_3$

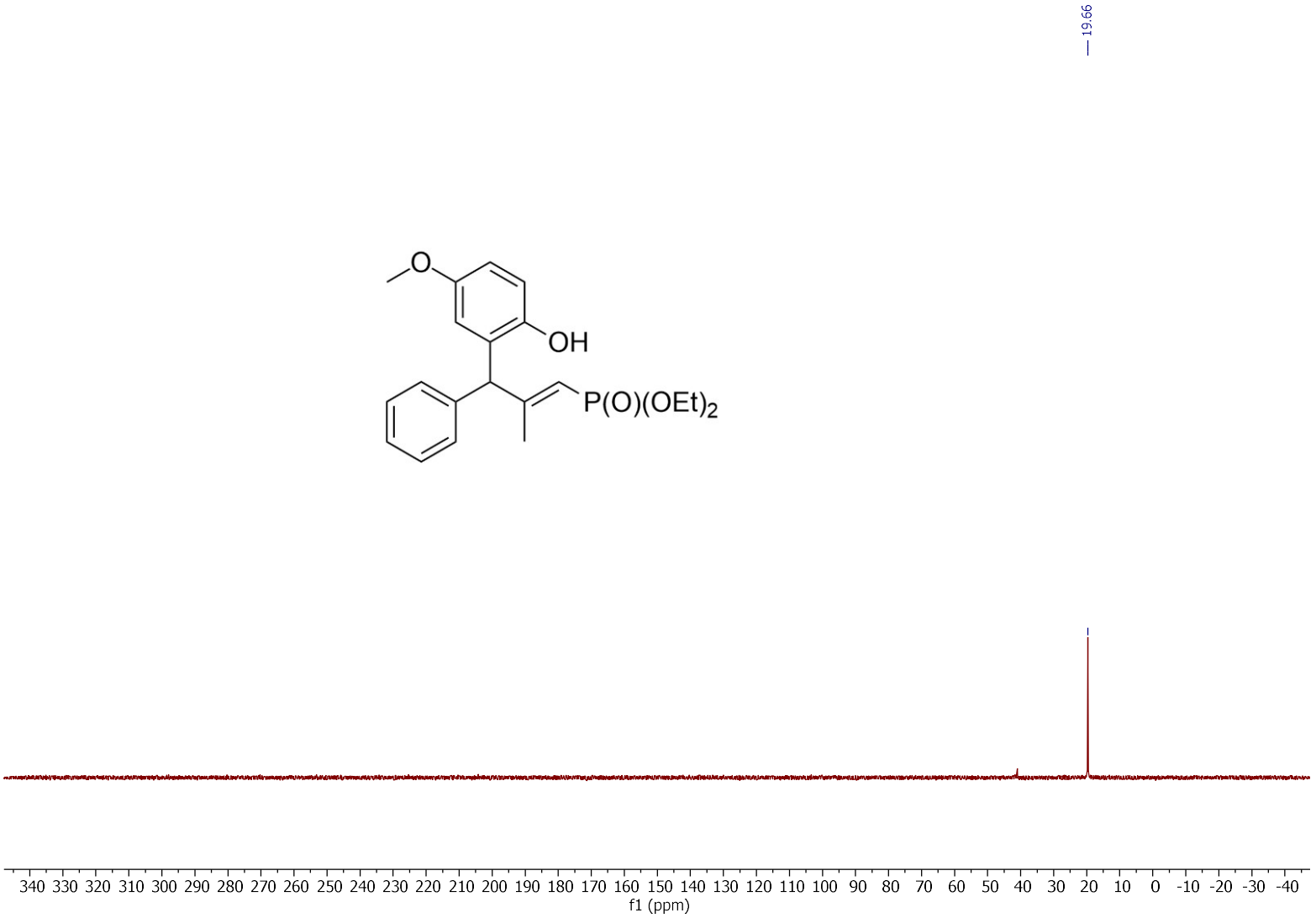


Figure S84: $^{31}P\{^{1}H\}$ NMR Spectra of 3v in $CDCl_3$

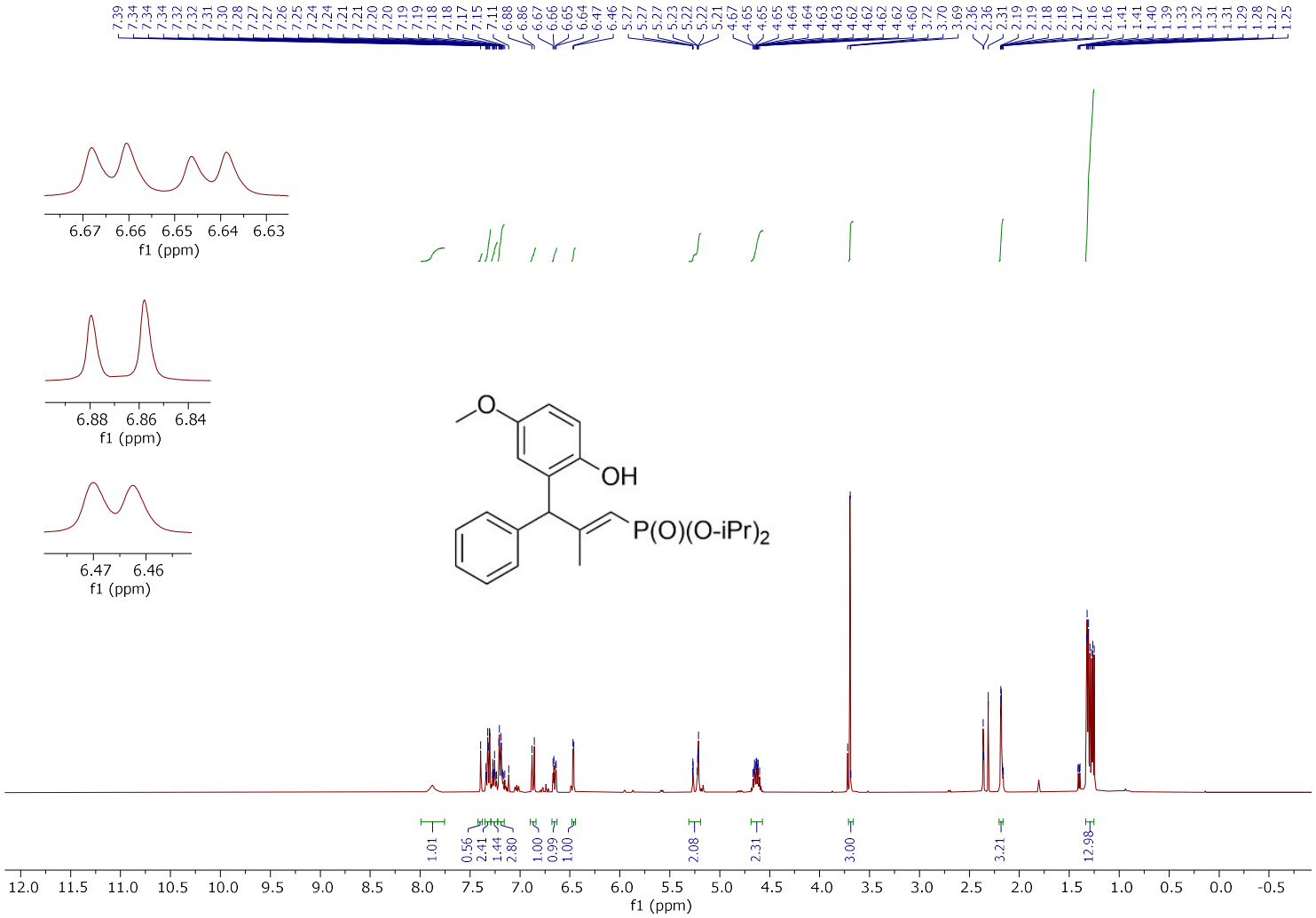


Figure S85: ^{1}H NMR Spectra of 3w in $CDCl_3$

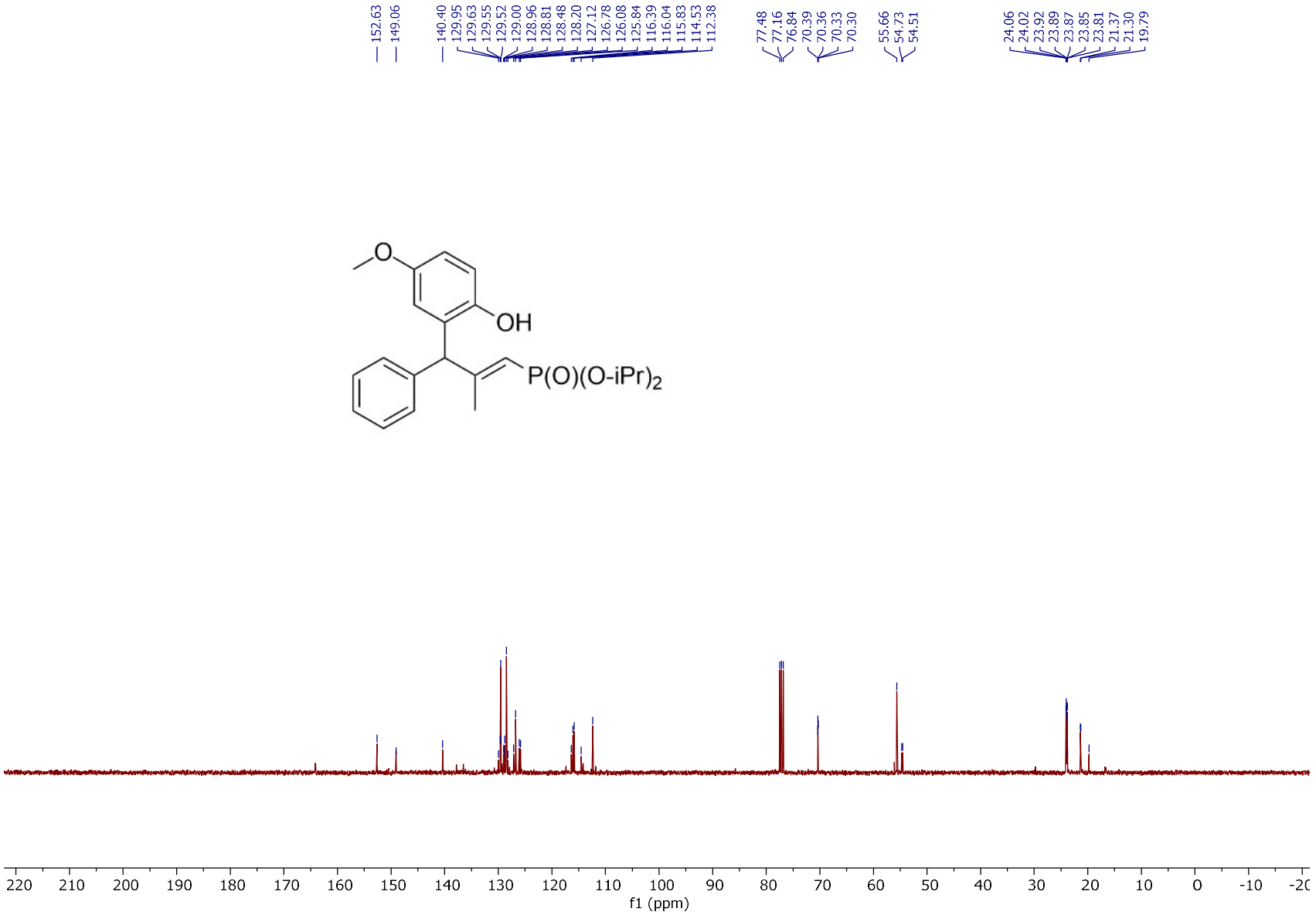


Figure S86: $^{13}C\{^{1}H\}$ NMR Spectra of 3w in $CDCl_3$

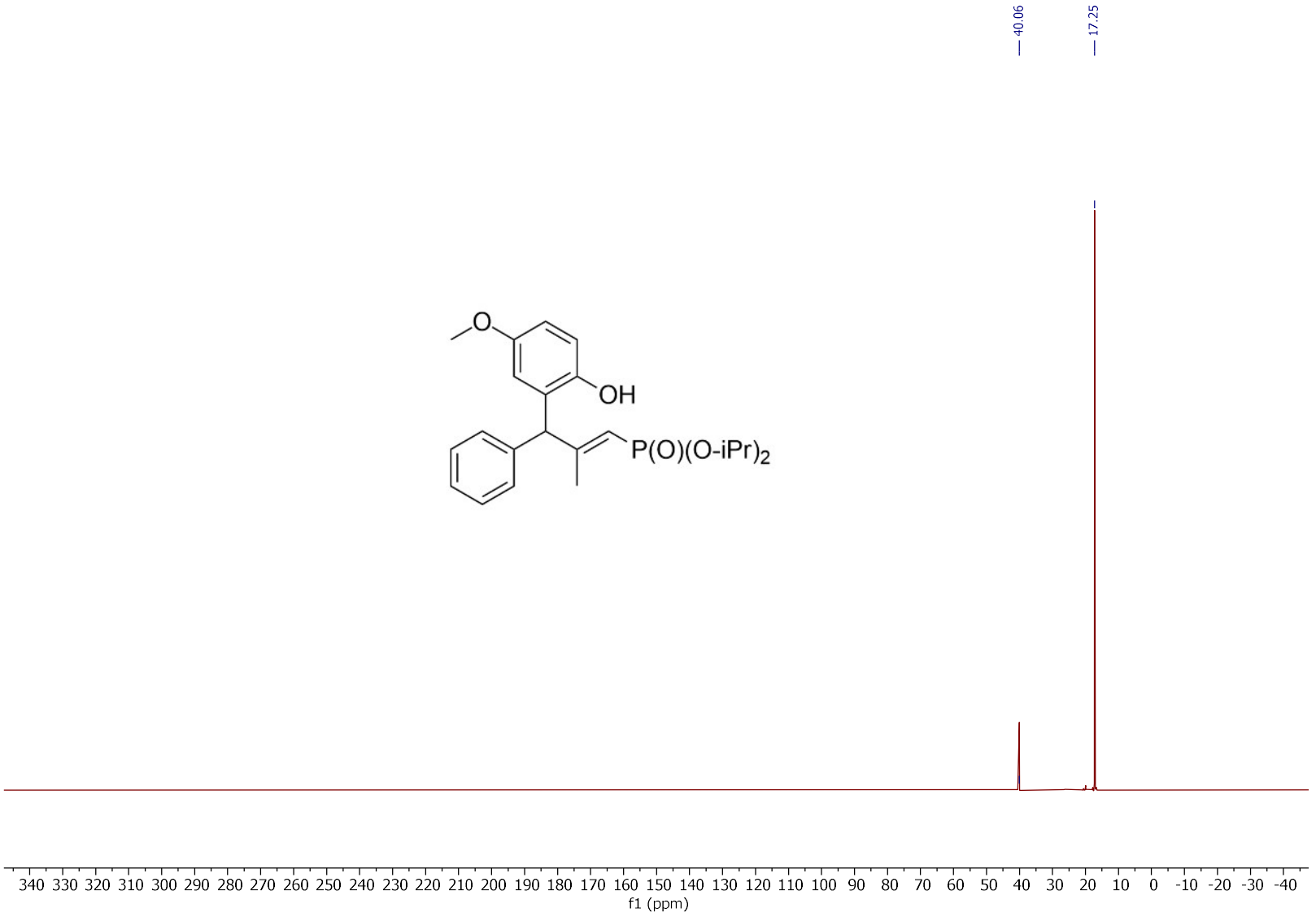


Figure S87: $^{31}P\{^{1}H\}$ NMR Spectra of 3w in $CDCl_3$

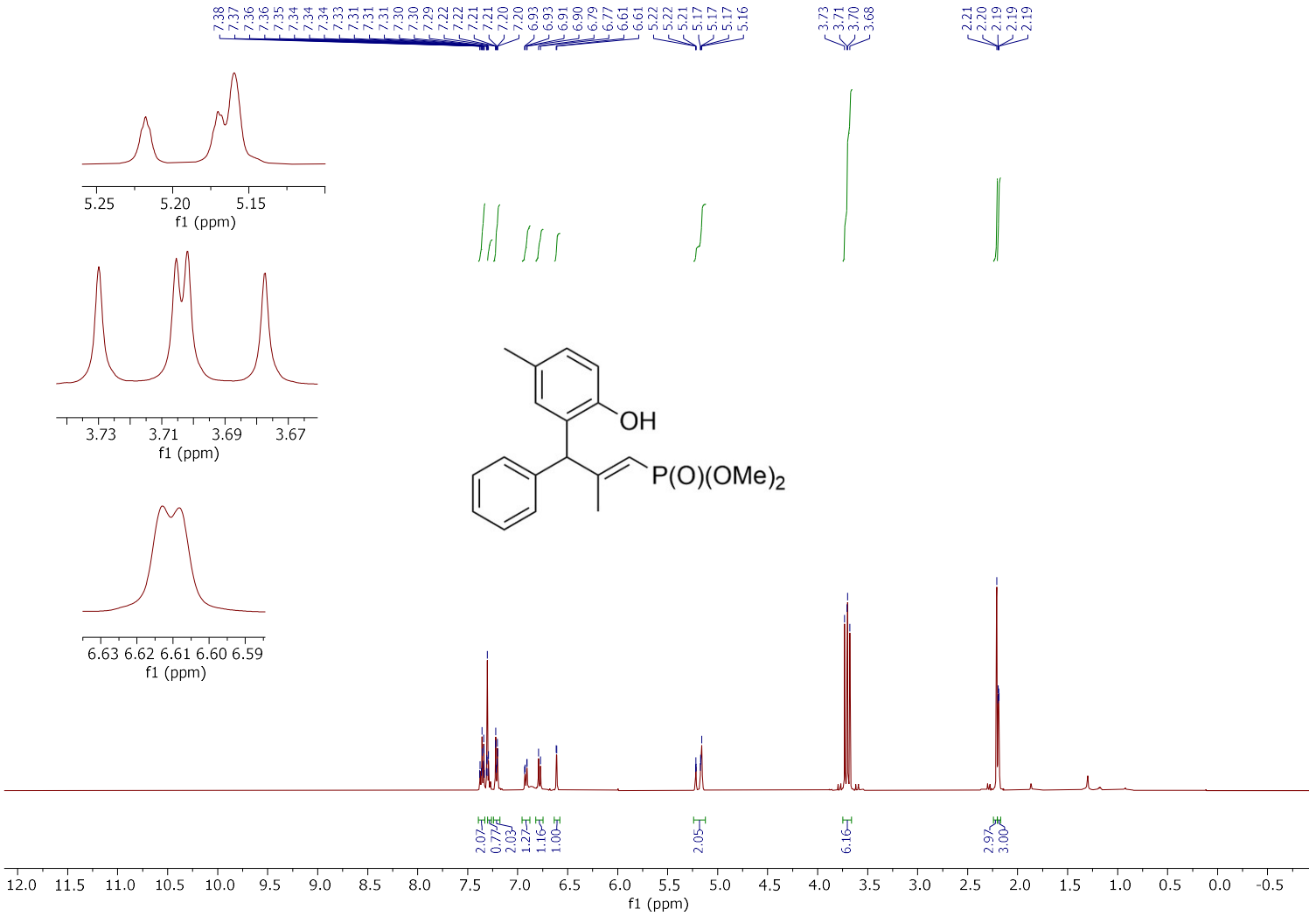


Figure S88: ^{1}H NMR Spectra of 3r in $CDCl_3$

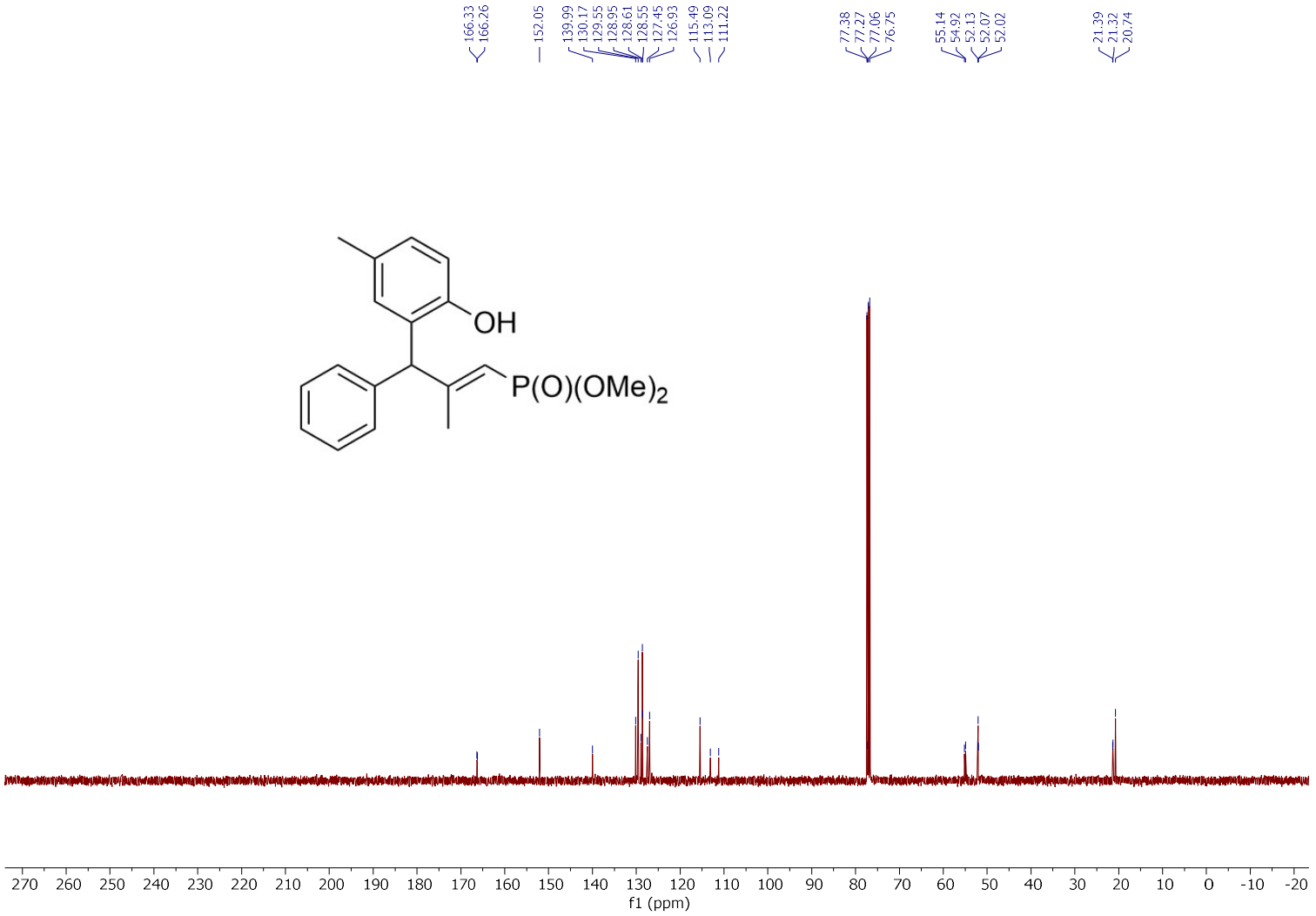


Figure S89: $^{13}C\{^{1}H\}$ NMR Spectra of 3r in $CDCl_3$

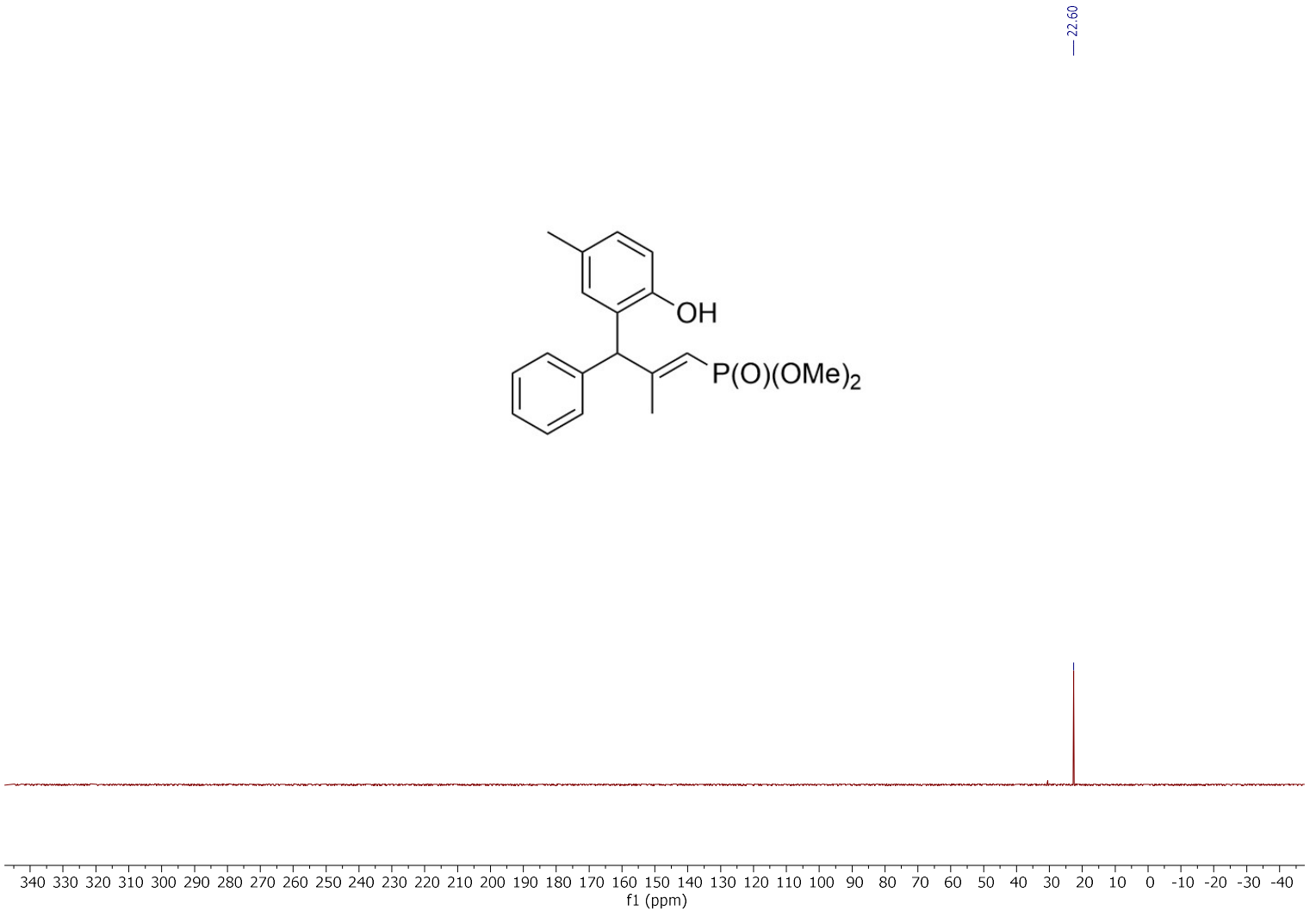


Figure S90: $^{31}P\{^{1}H\}$ NMR Spectra of 3r in $CDCl_3$

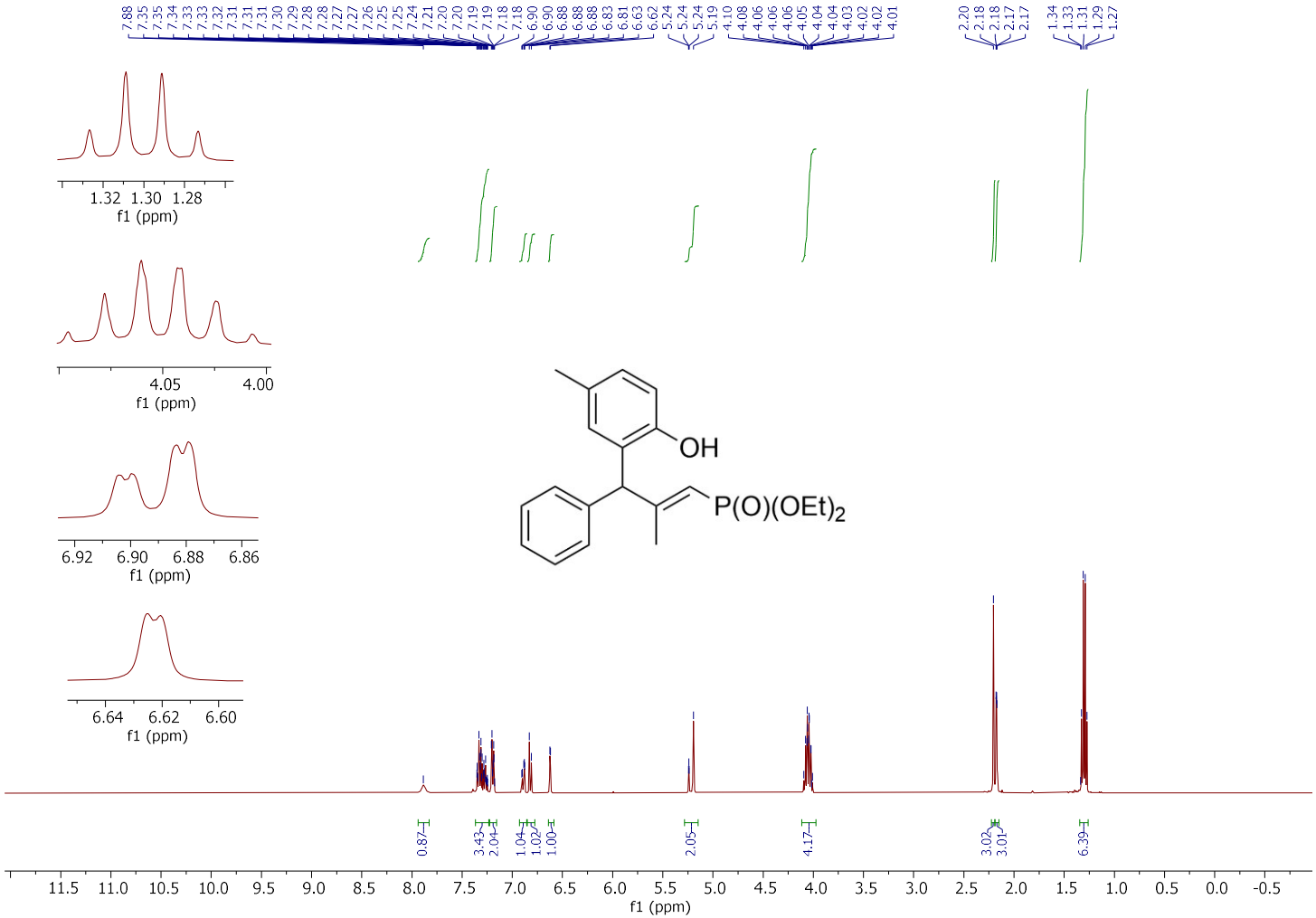


Figure S91: ^{1}H NMR Spectra of 3s in $CDCl_3$

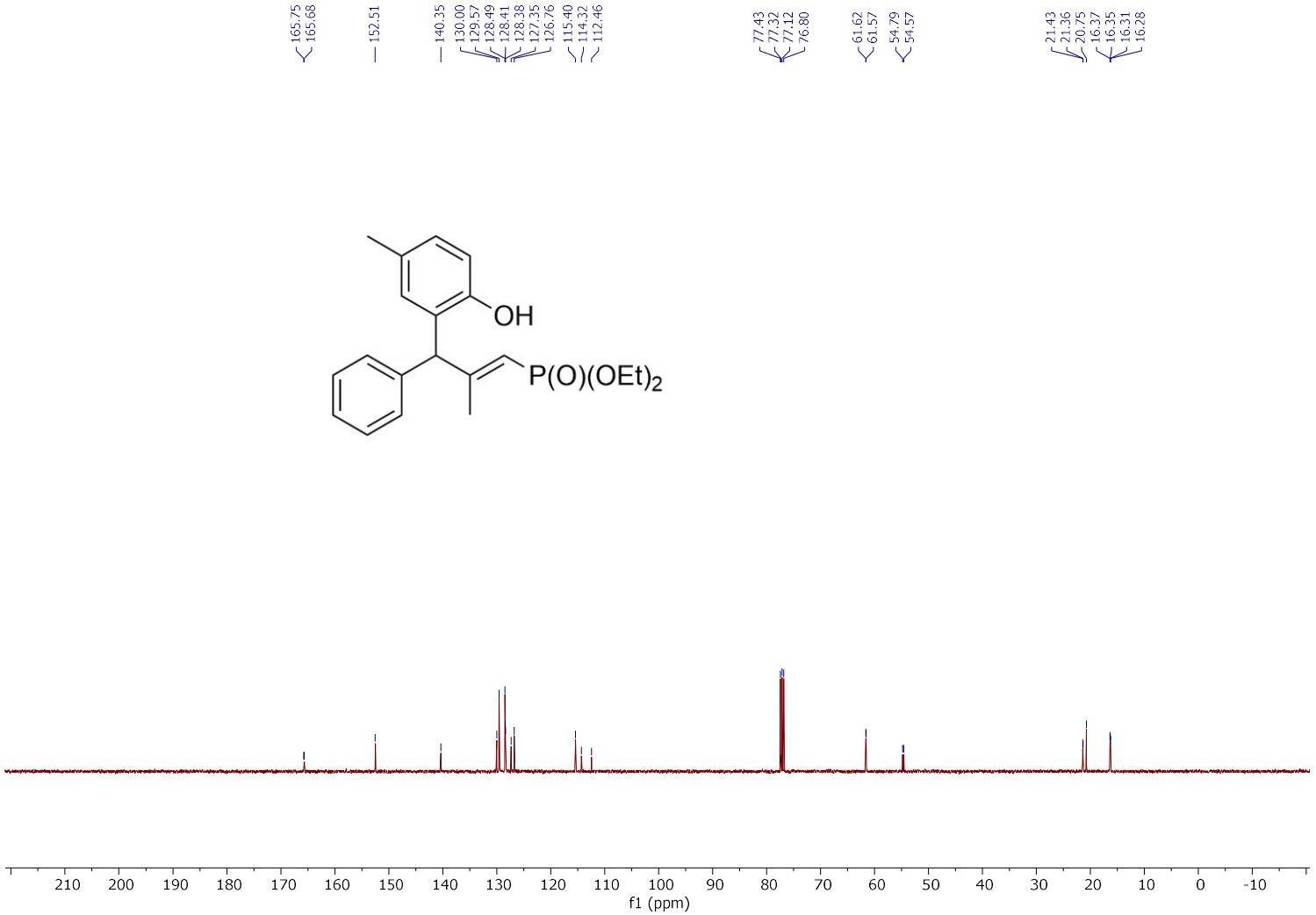


Figure S92: $^{13}C\{^{1}H\}$ NMR Spectra of 3s in $CDCl_3$

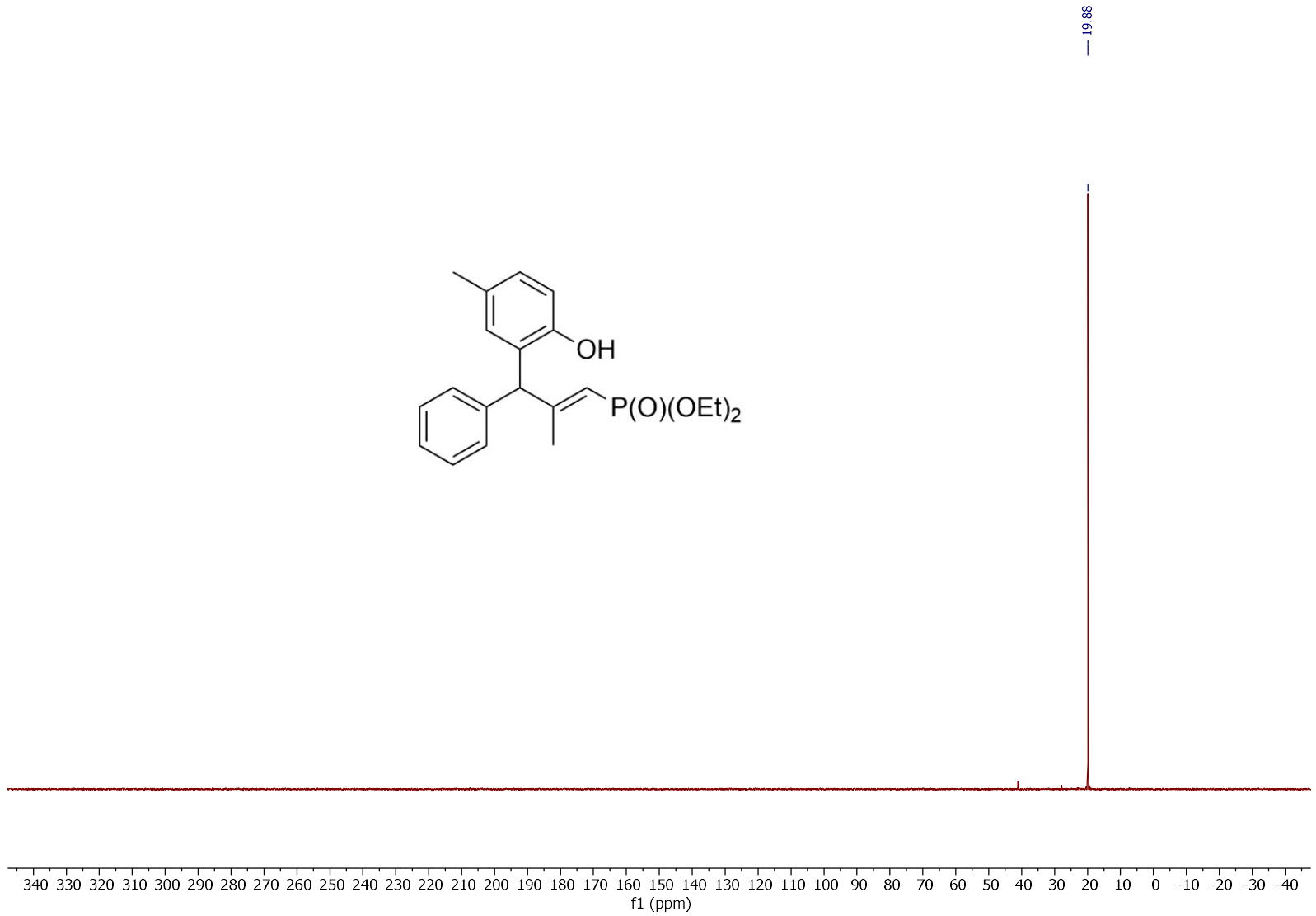


Figure S93: $^{31}P\{^{1}H\}$ NMR Spectra of 3s in $CDCl_3$

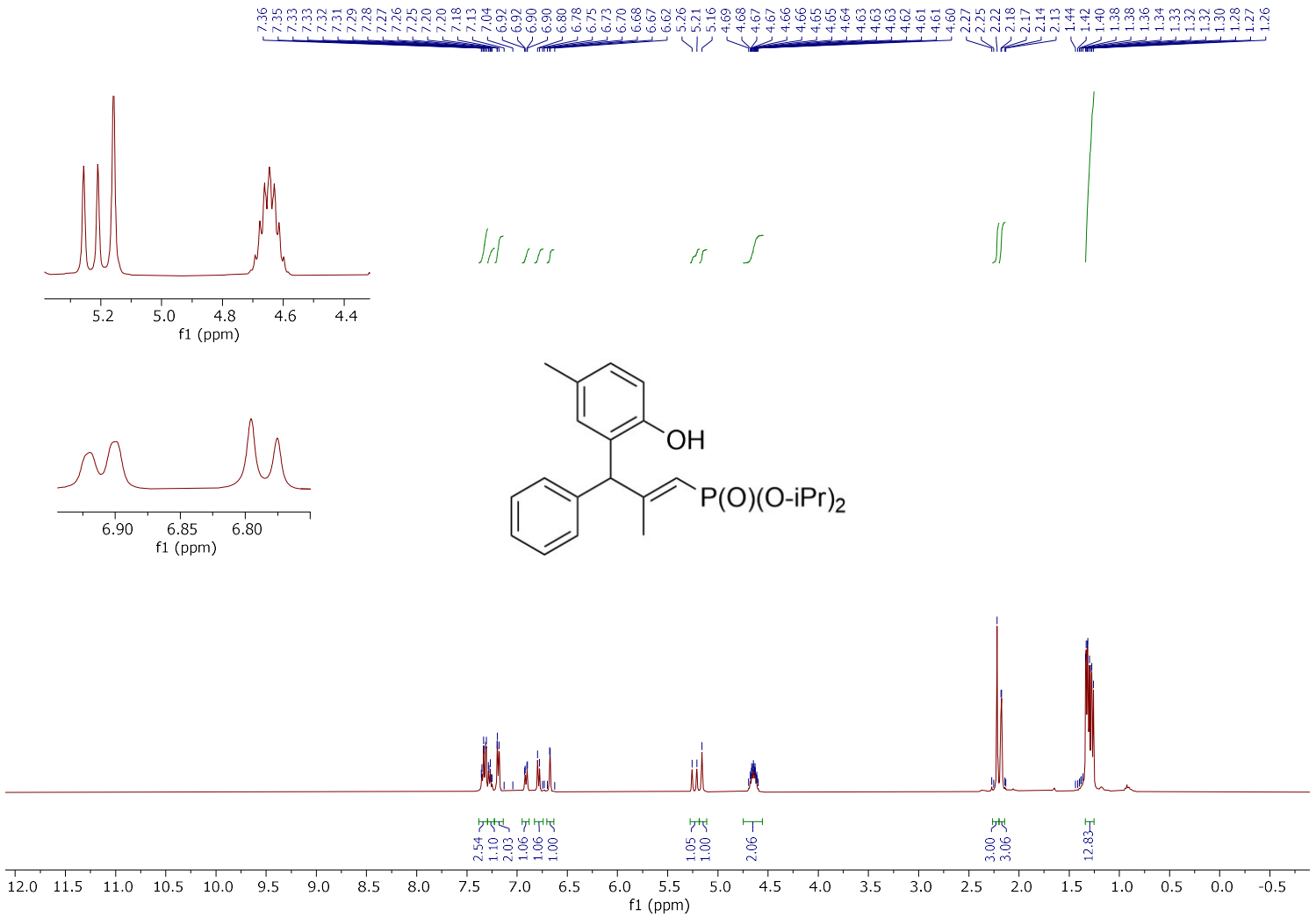


Figure S94: ^{1}H NMR Spectra of 3t in $CDCl_3$

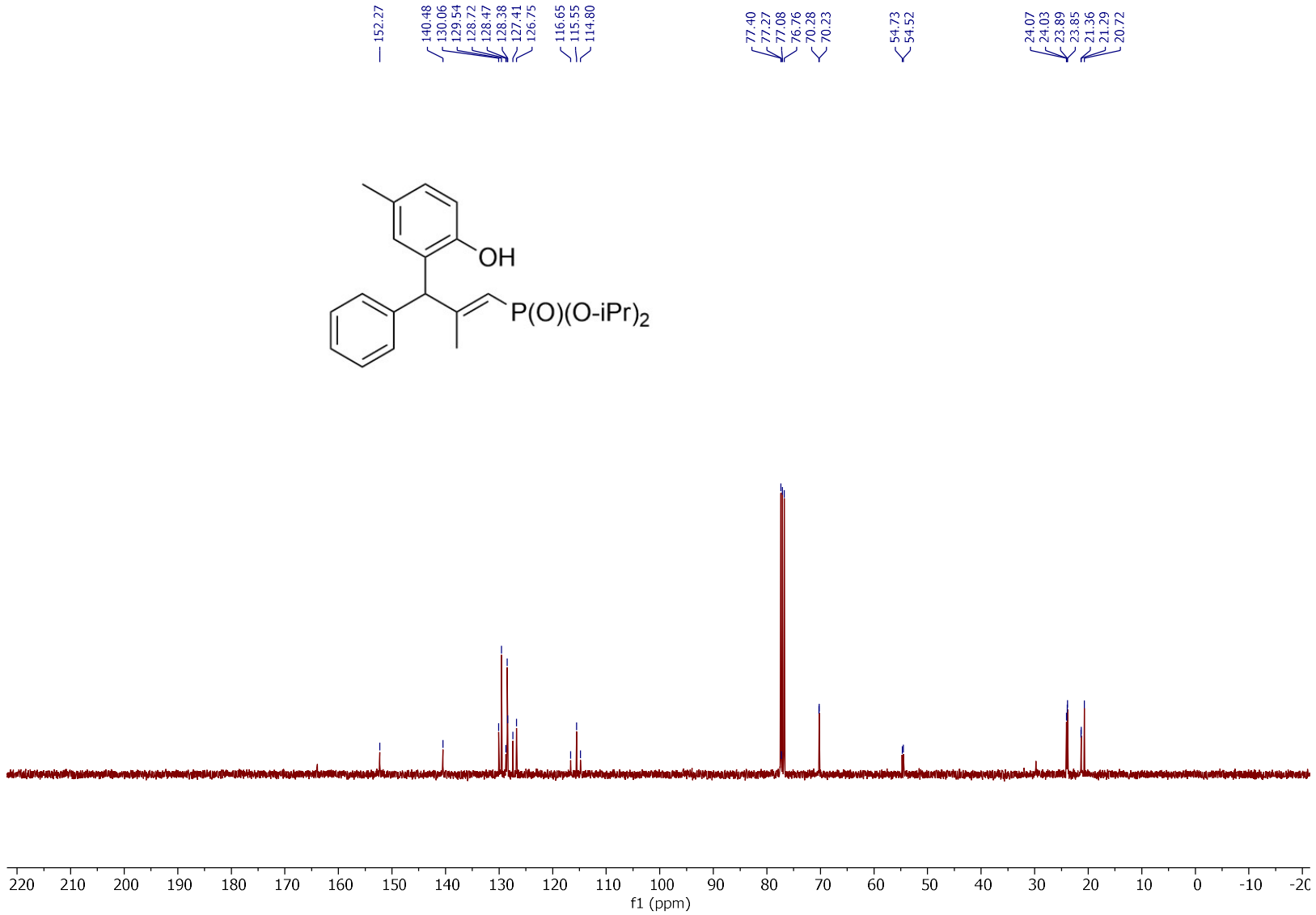


Figure S95: $^{13}C\{^{1}H\}$ NMR Spectra of 3t in $CDCl_3$

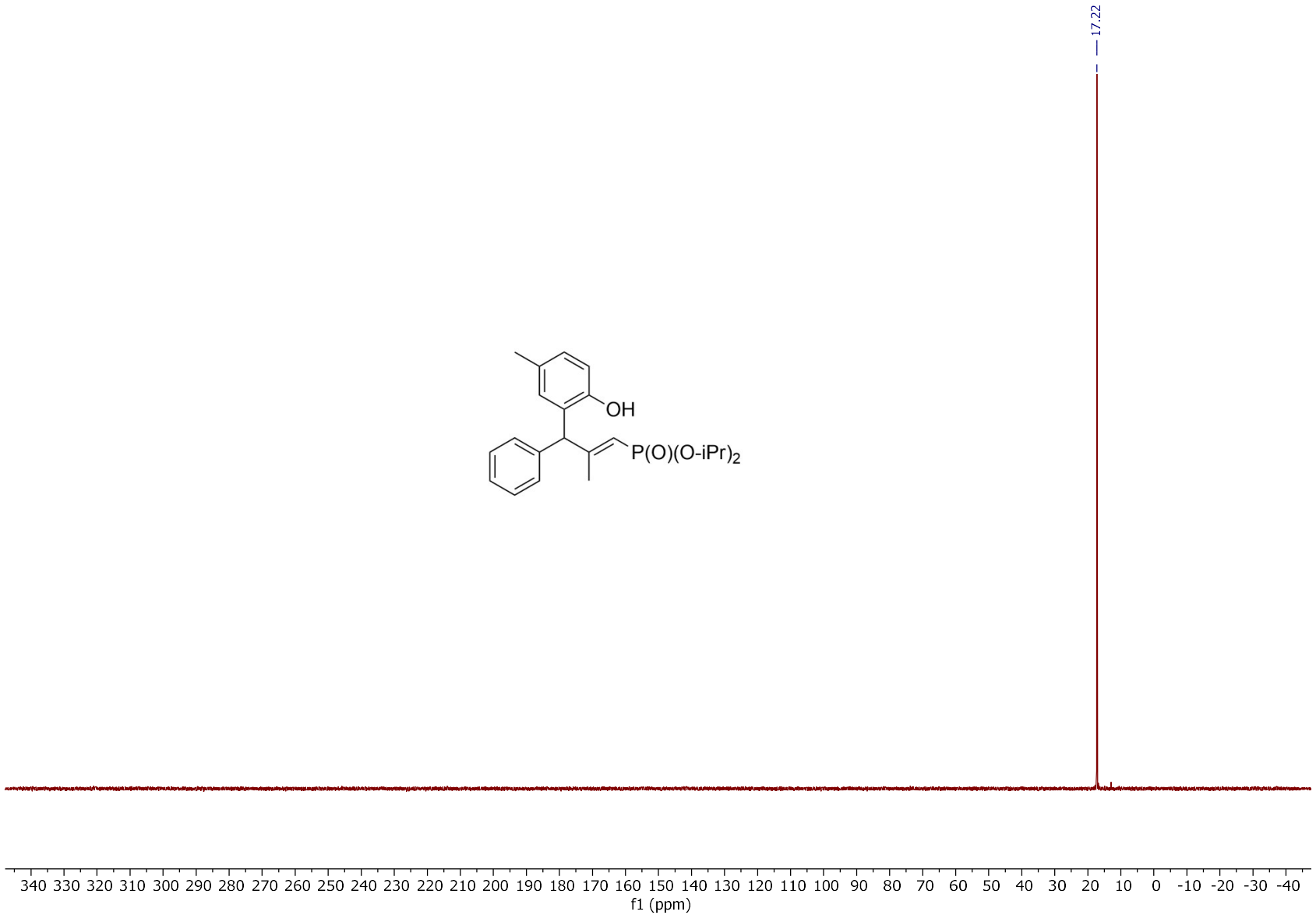


Figure S96: $^{31}P\{^{1}H\}$ NMR Spectra of 3t in $CDCl_3$

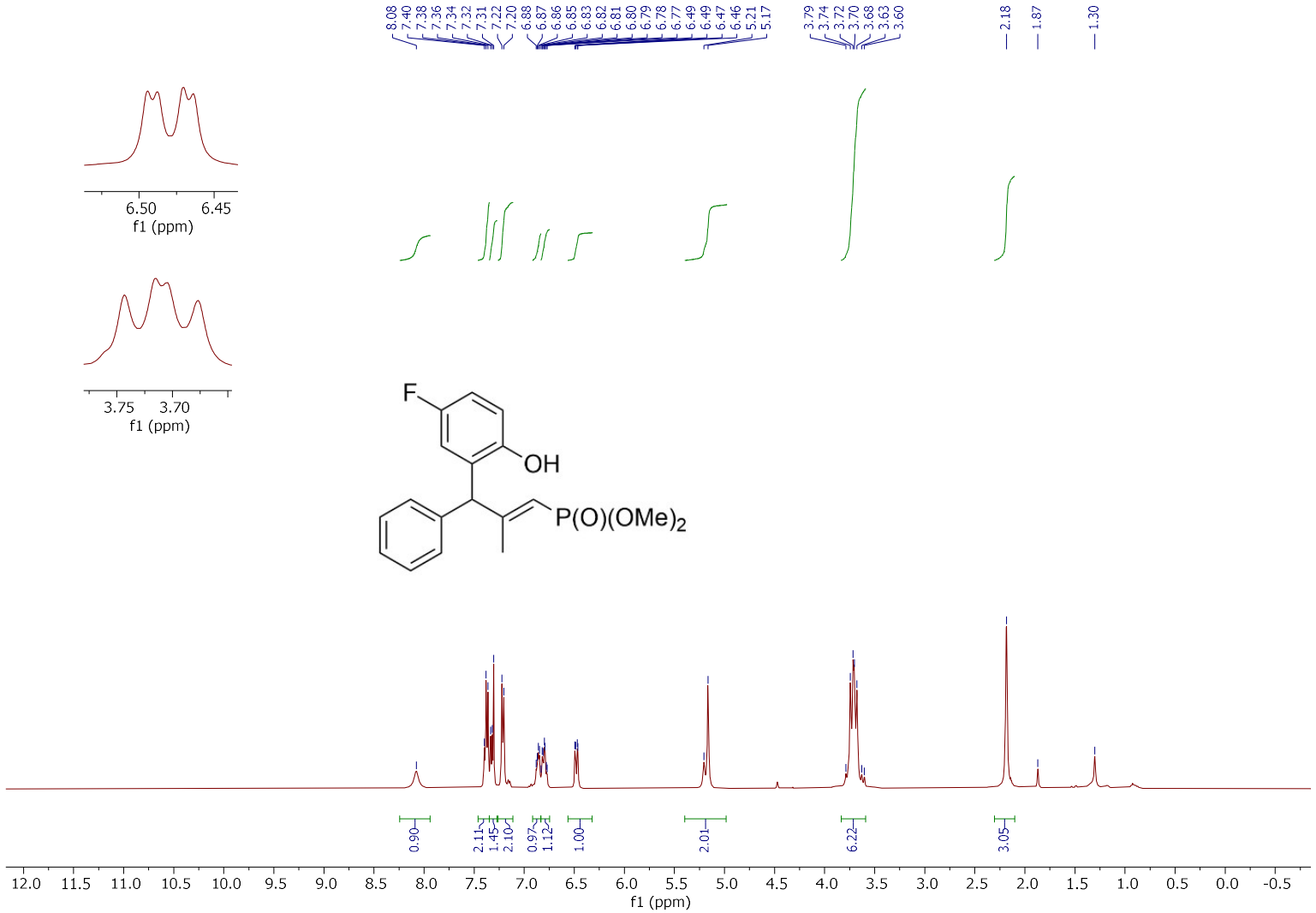


Figure S97: ^{1}H NMR Spectra of 3x in $CDCl_3$

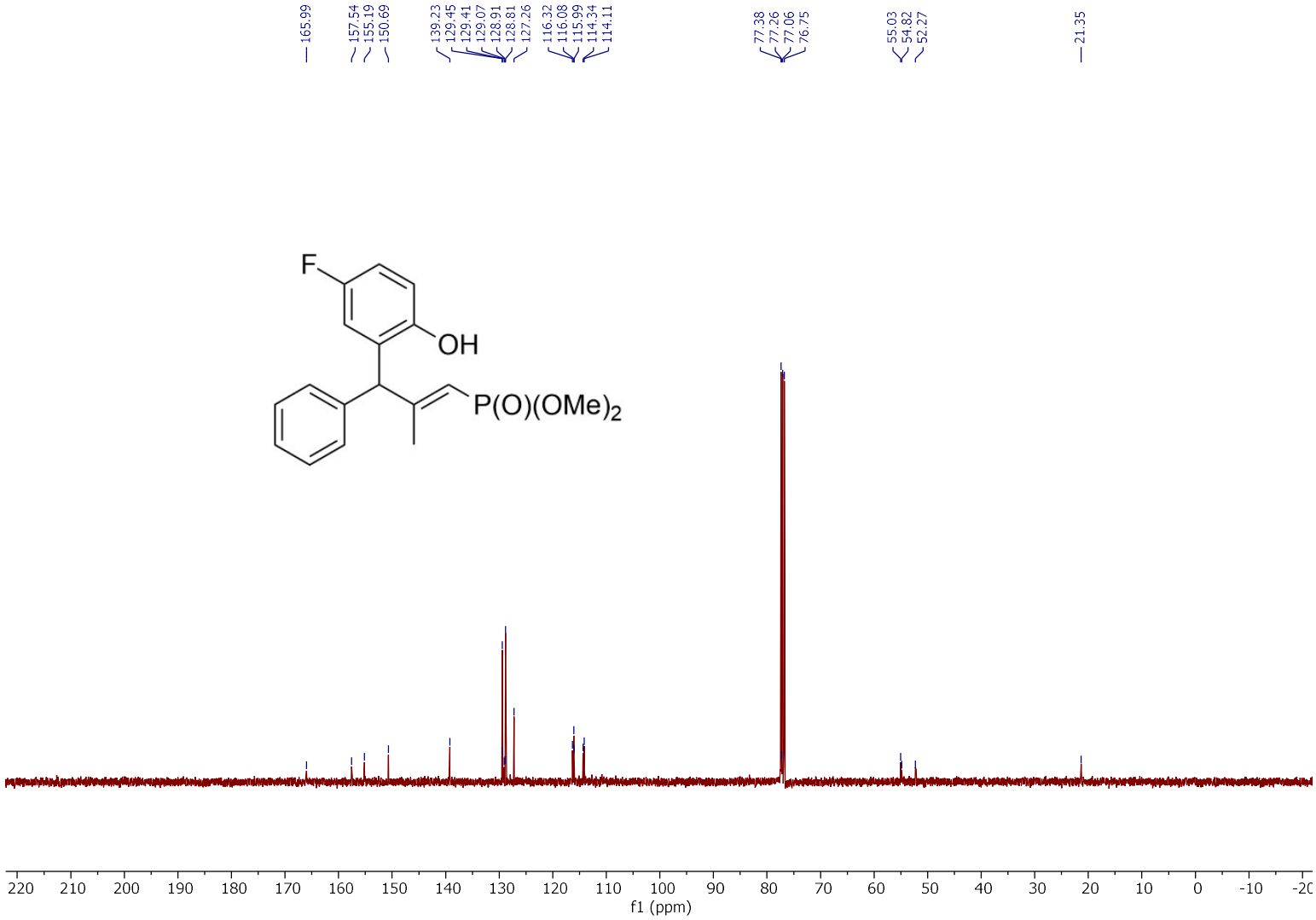


Figure S98: $^{13}C\{^{1}H\}$ NMR Spectra of 3x in $CDCl_3$

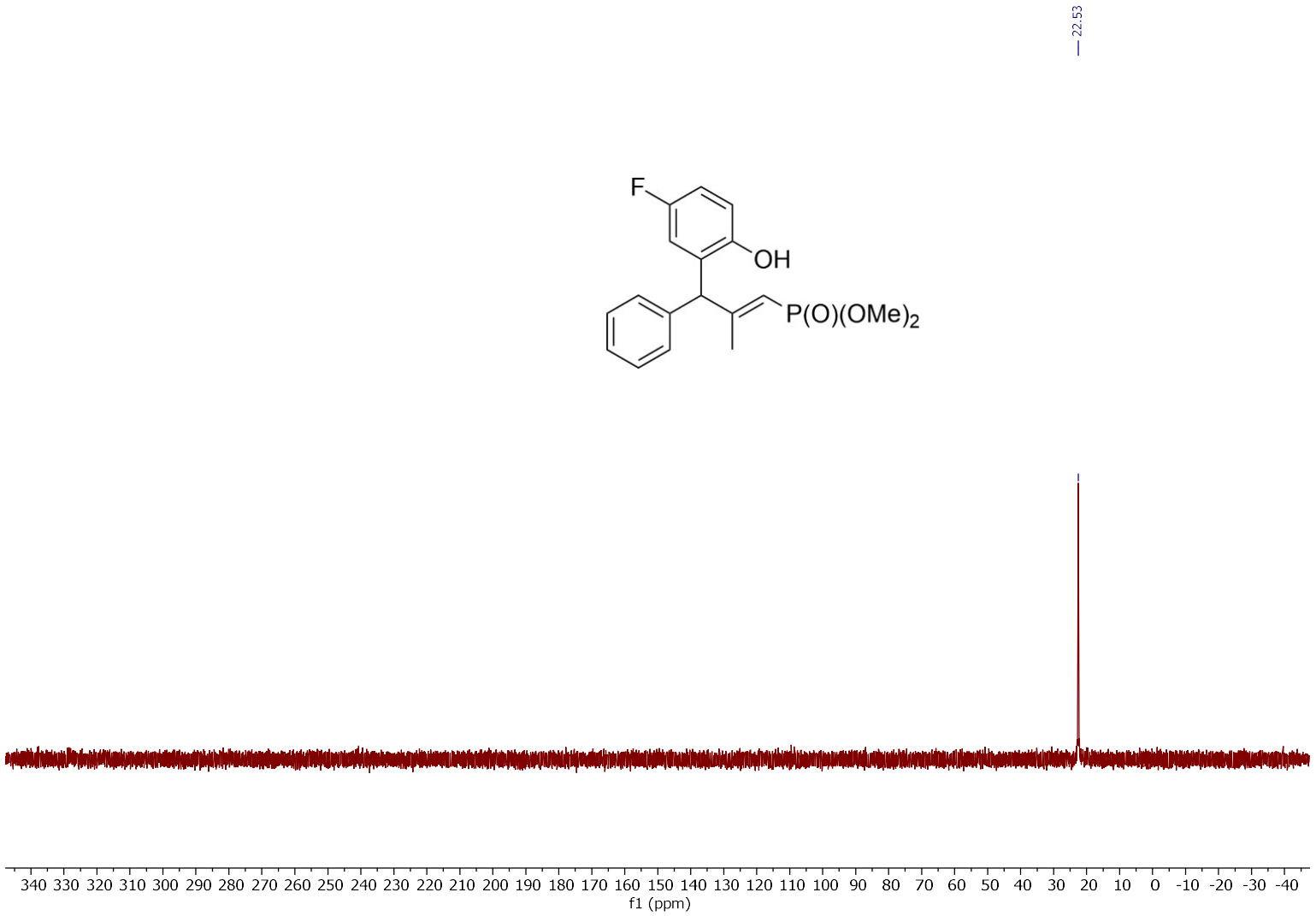


Figure S99: $^{31}P\{^{1}H\}$ NMR Spectra of 3x in $CDCl_3$

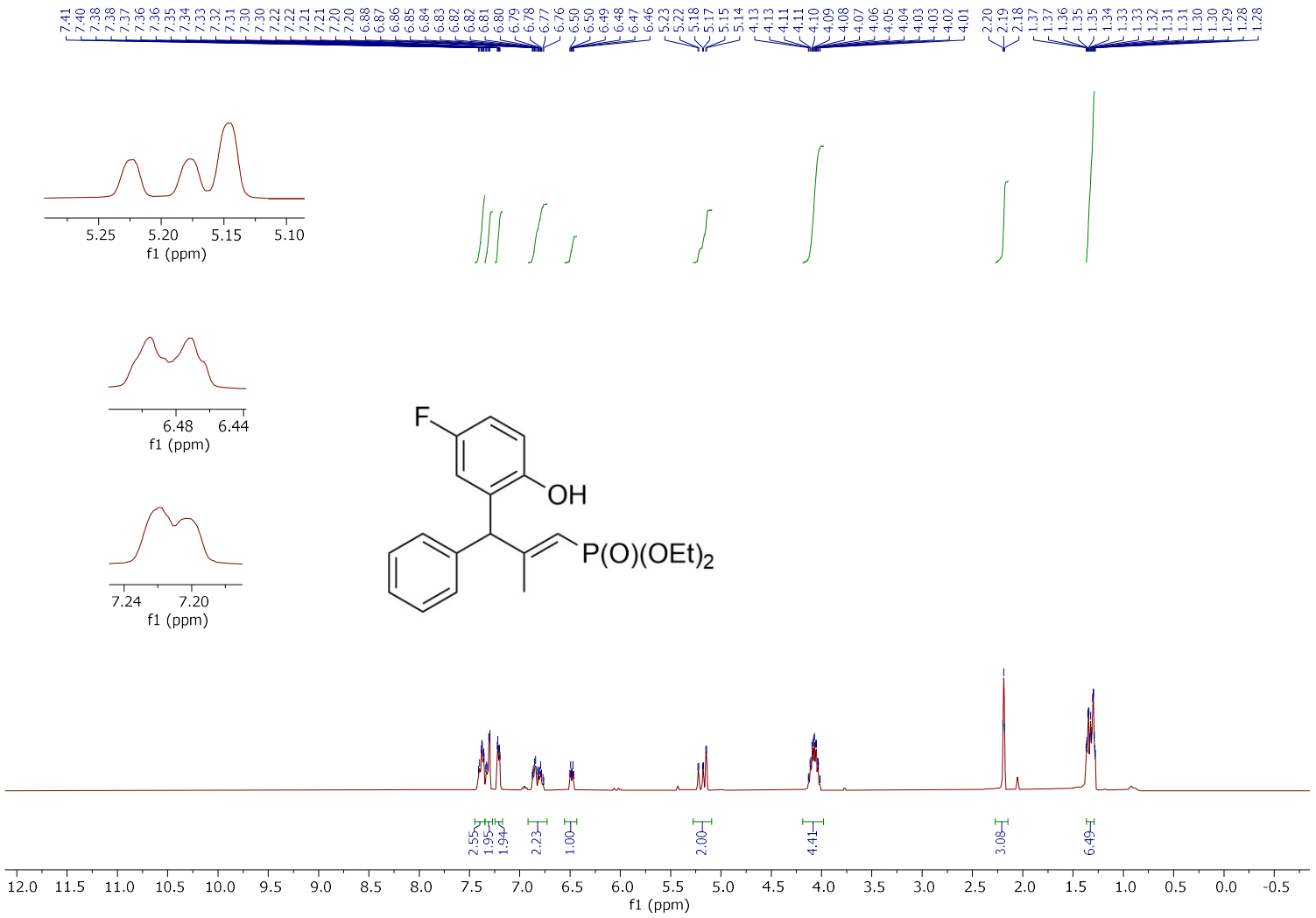


Figure S100: ^{1}H NMR Spectra of 3y in $CDCl_3$

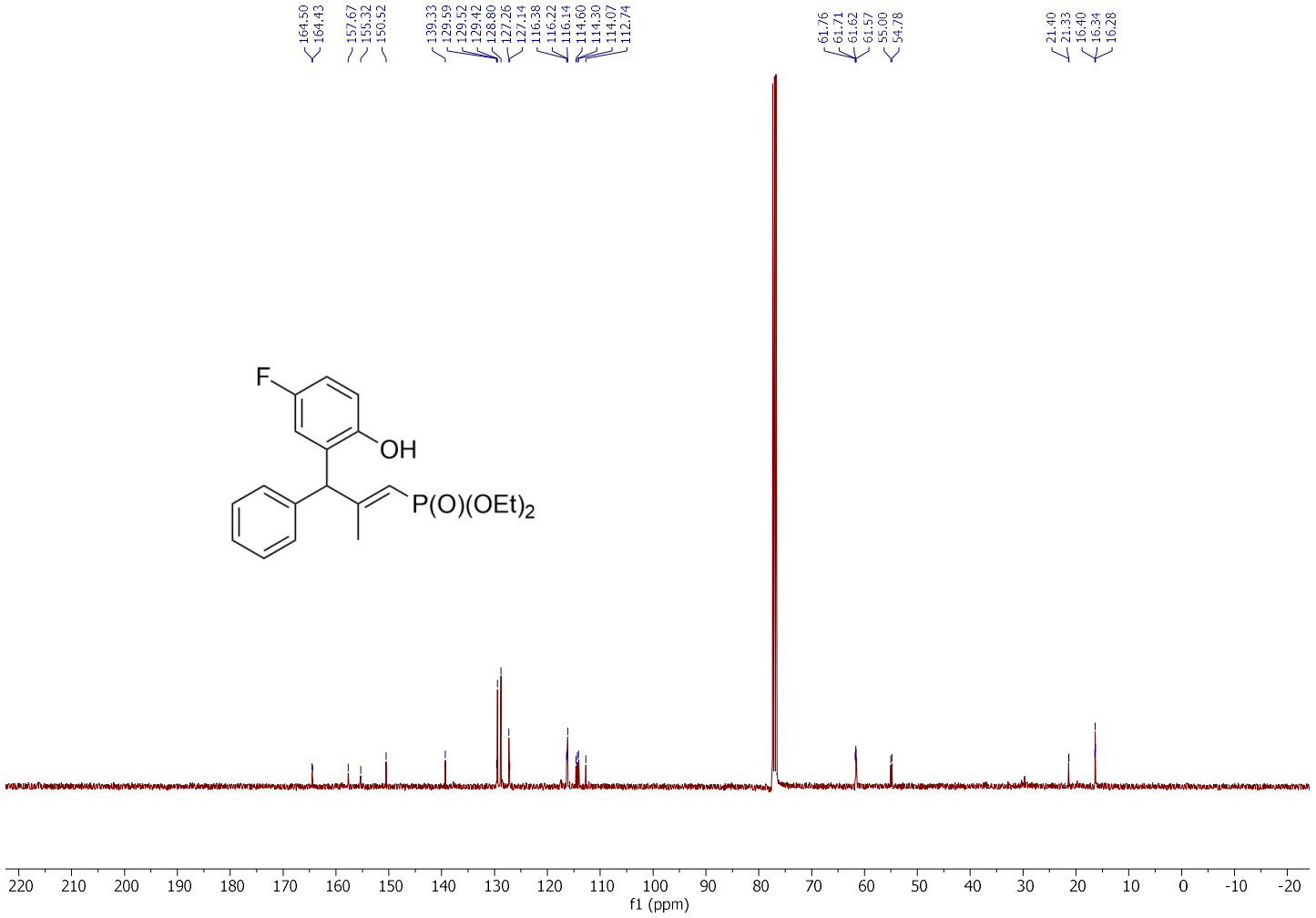


Figure S101: $^{13}C\{^{1}H\}$ NMR Spectra of 3y in $CDCl_3$

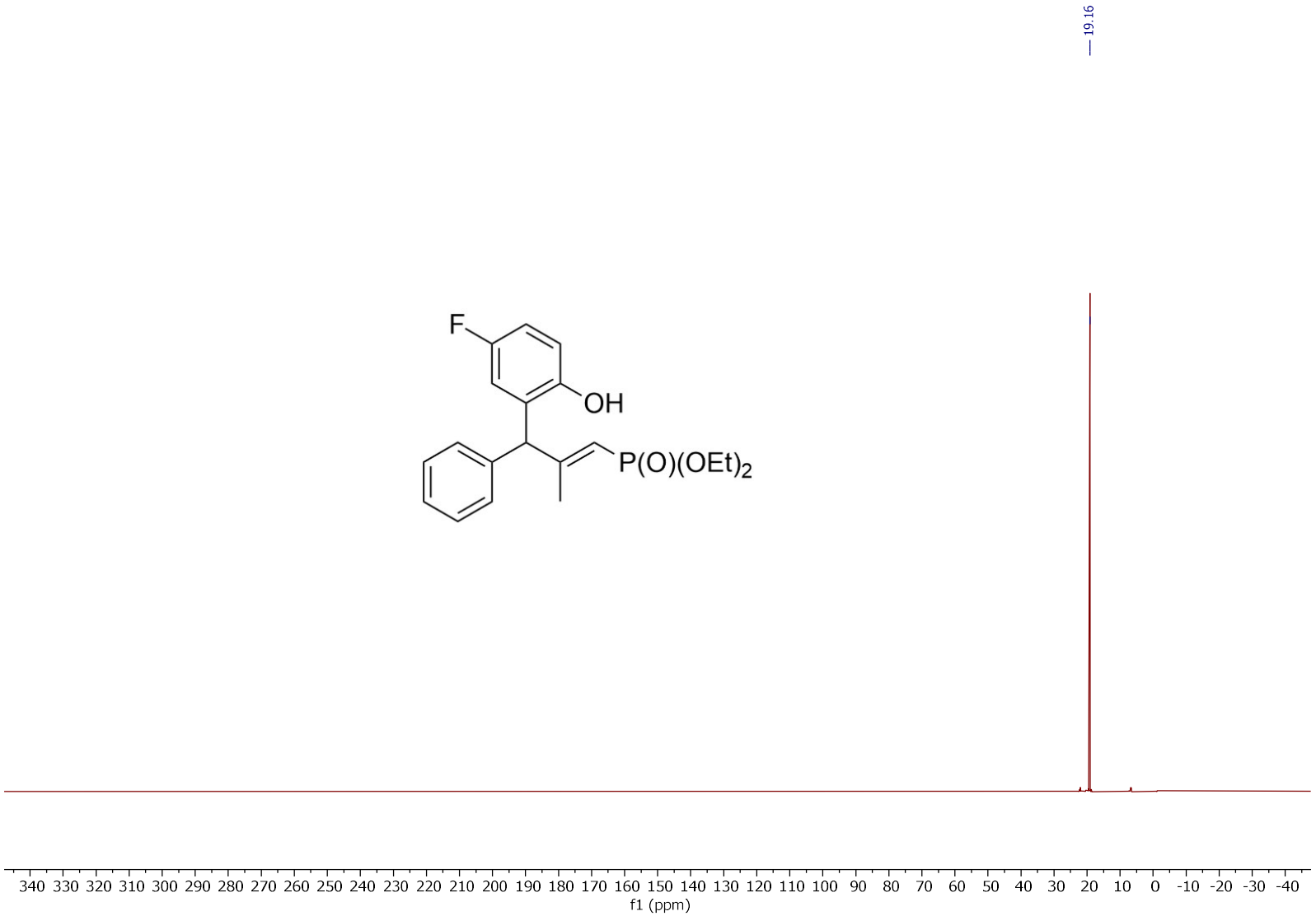


Figure S102: ^{31}P NMR Spectra of 3y in $CDCl_3$

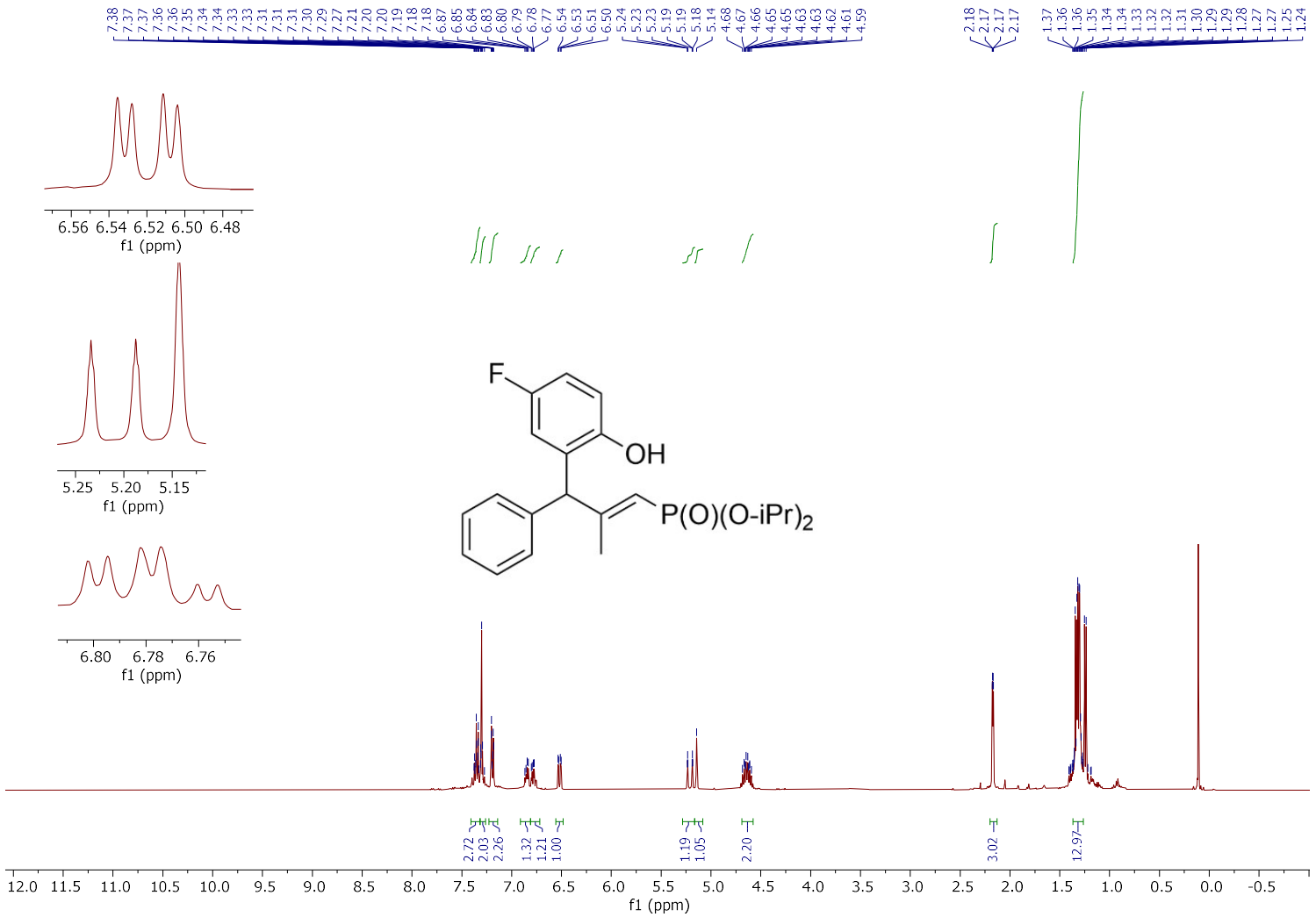


Figure S103: ^{1}H NMR Spectra of 3z in $CDCl_3$

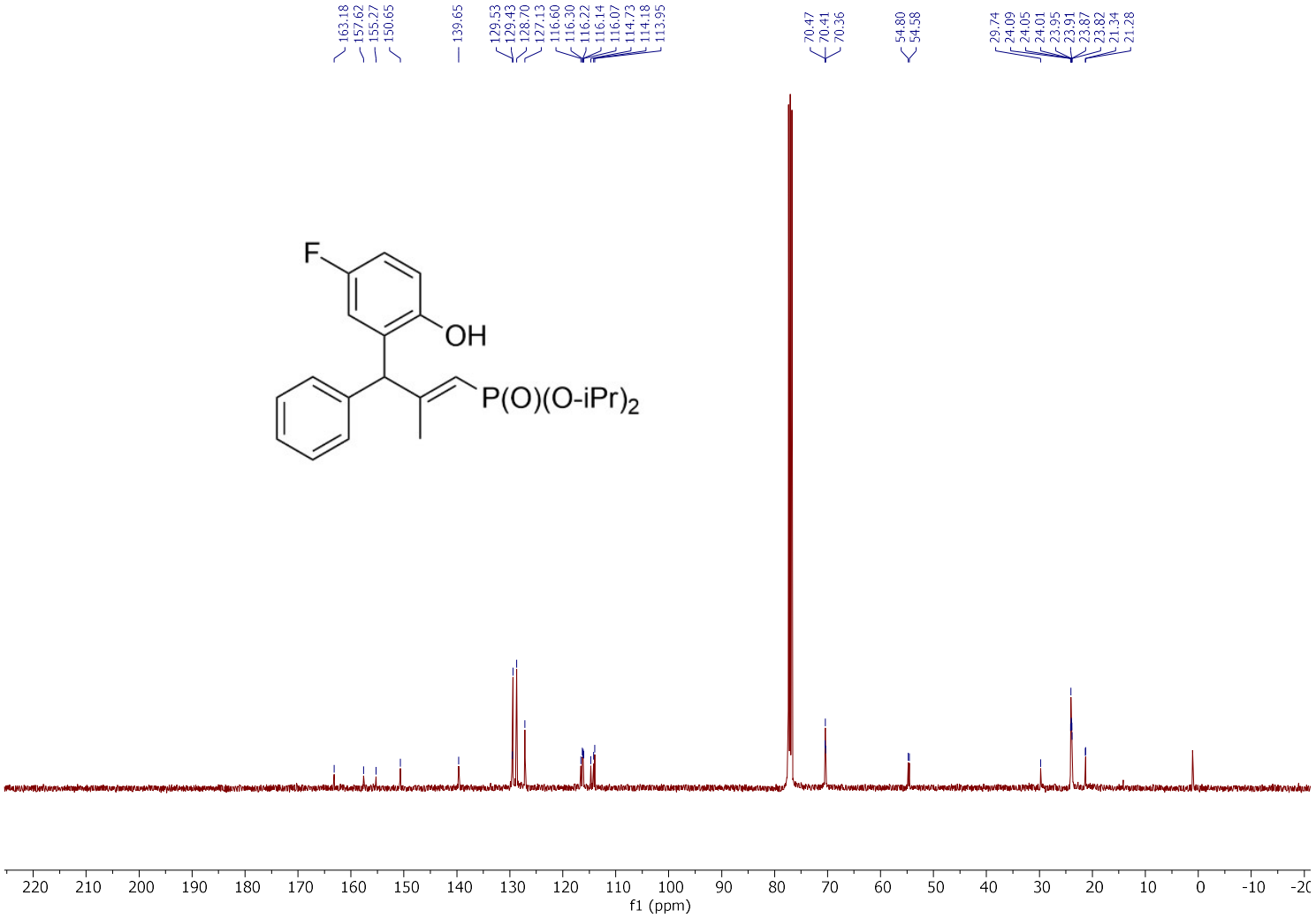


Figure S104: ^{13}C NMR Spectra of 3z in $CDCl_3$

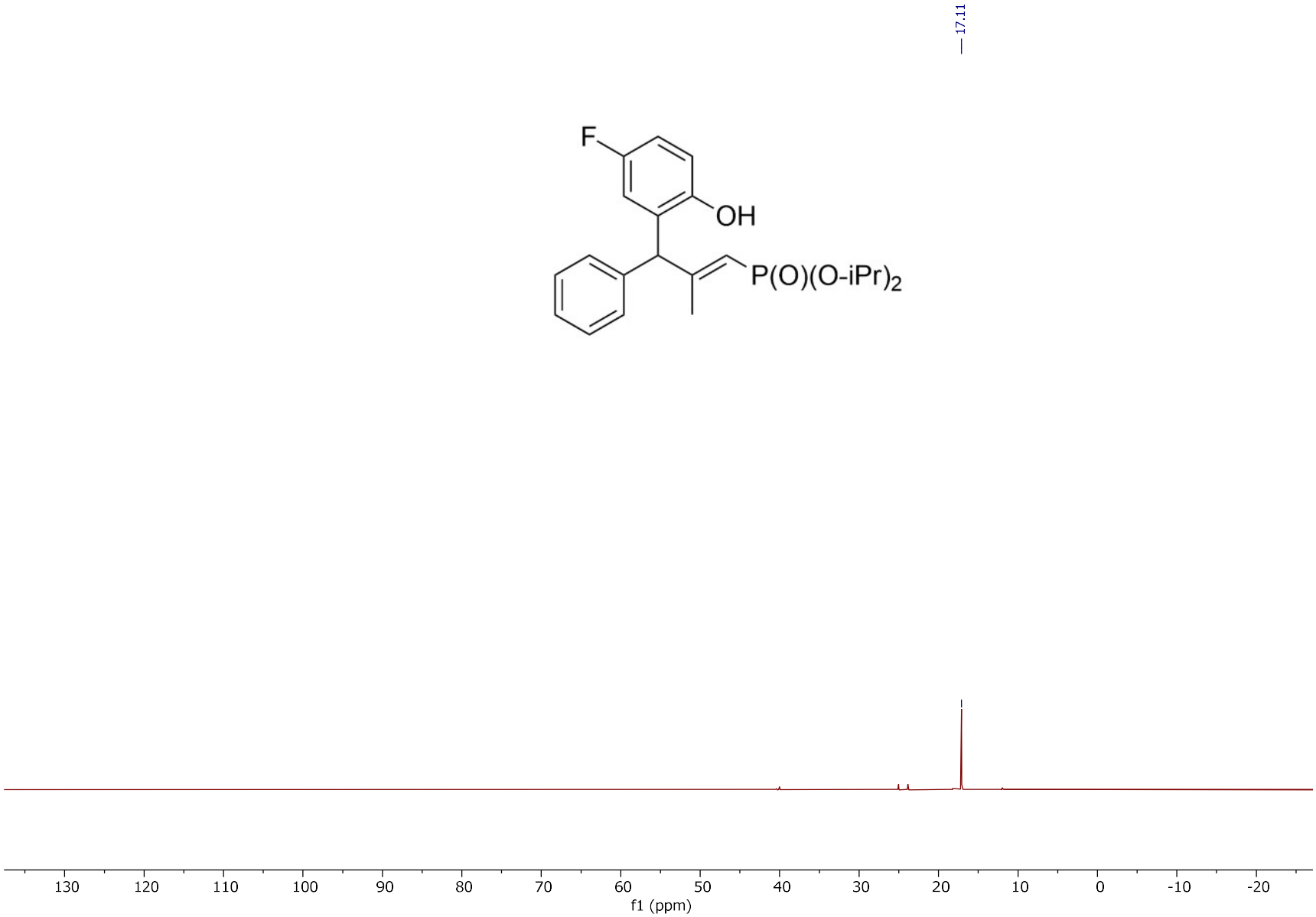


Figure S105: ^{31}P NMR Spectra of 3z in $CDCl_3$

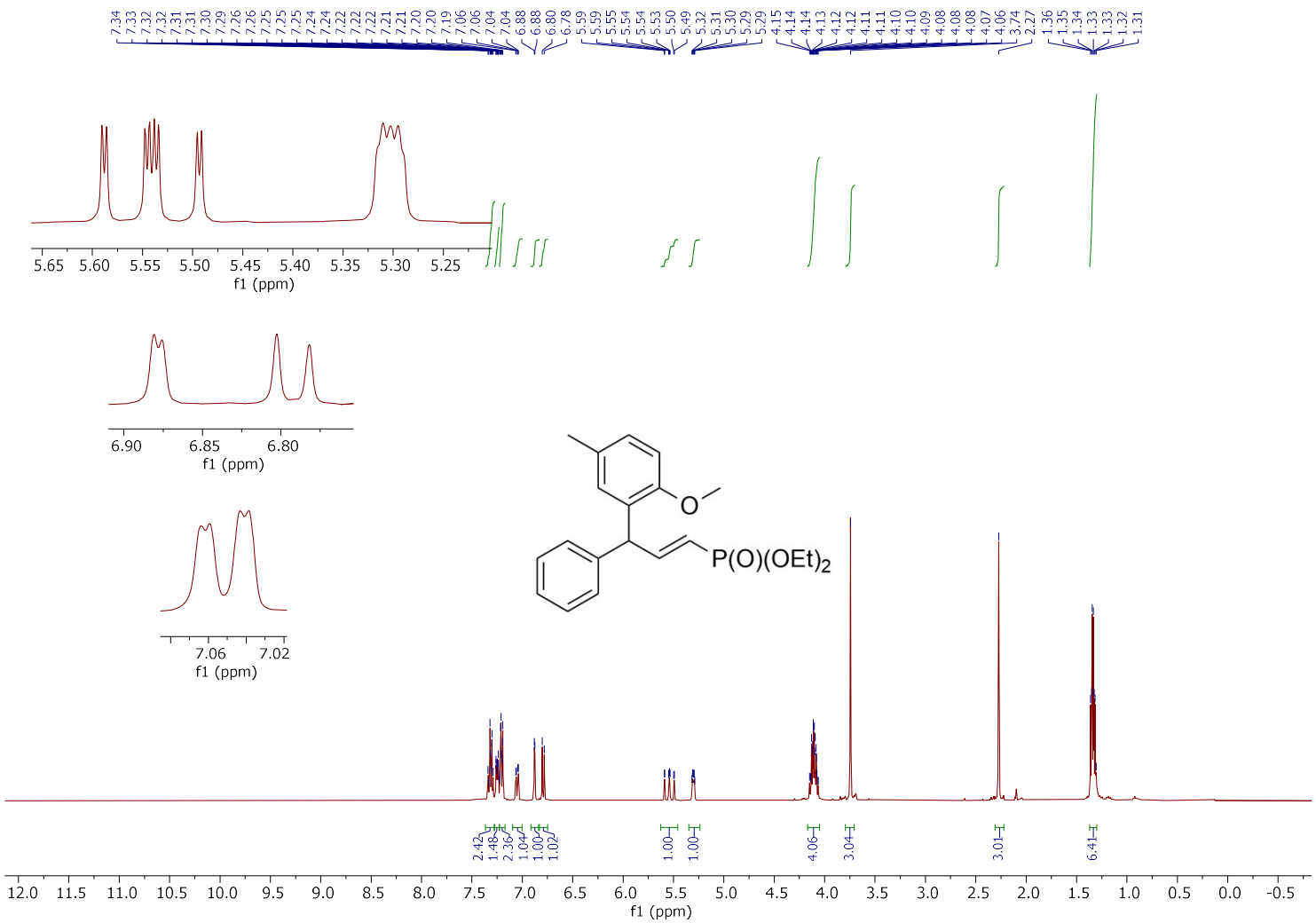


Figure S106: ^{1}H NMR Spectra of 5a in $CDCl_3$

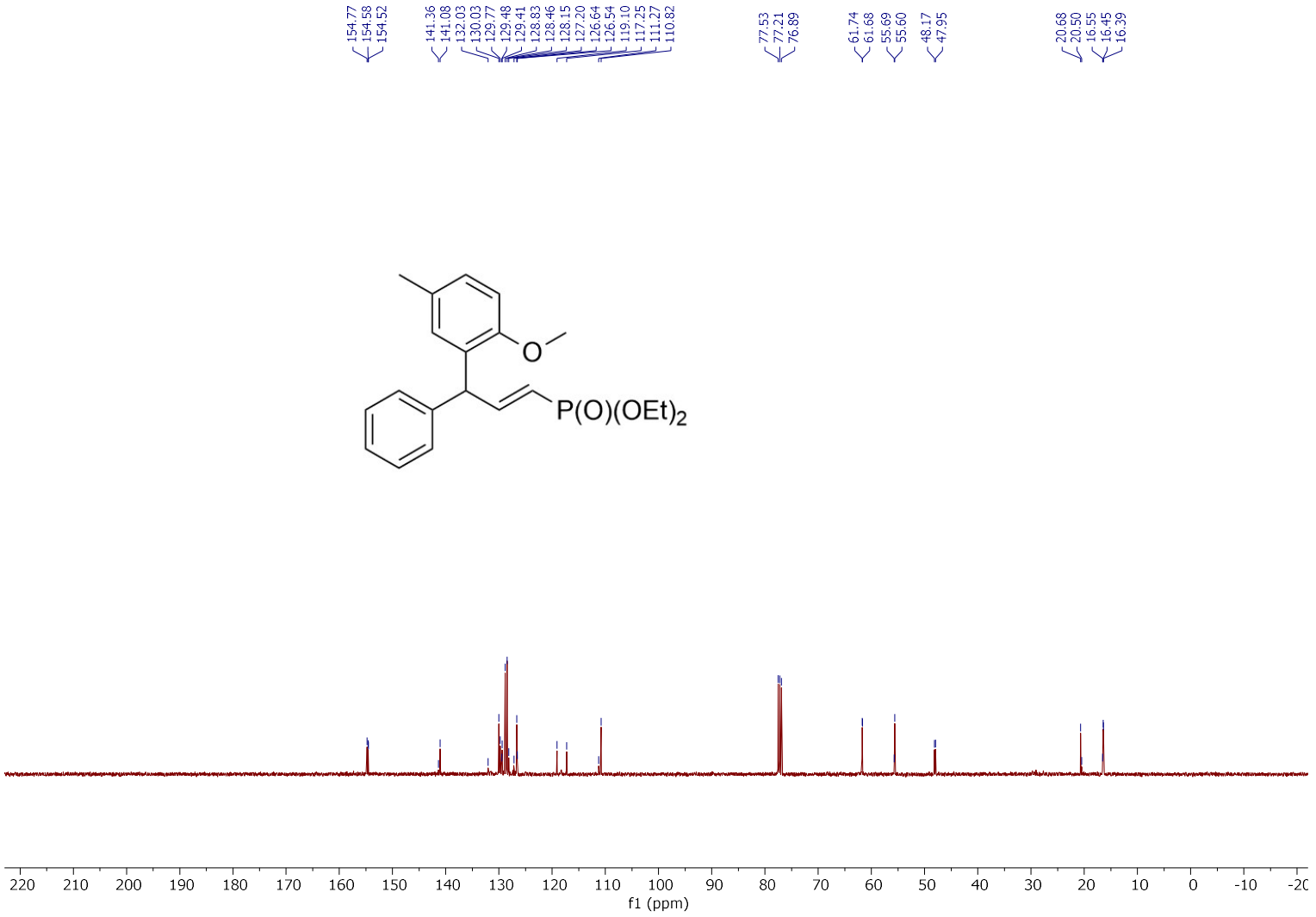


Figure S107: $^{13}C\{^{1}H\}$ NMR Spectra of 5a in $CDCl_3$

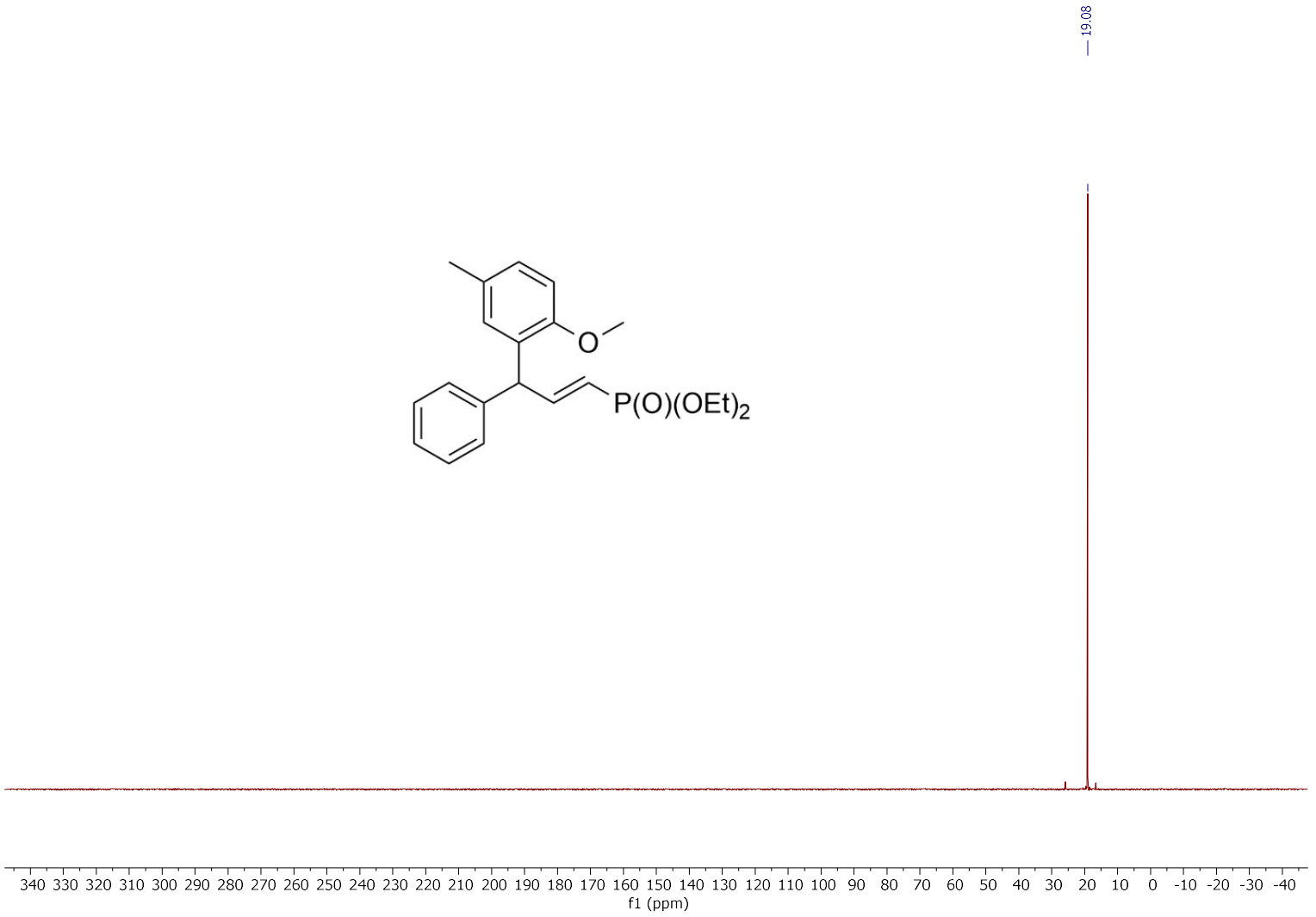


Figure S108: $^{31}P\{^{1}H\}$ NMR Spectra of 5a in $CDCl_3$

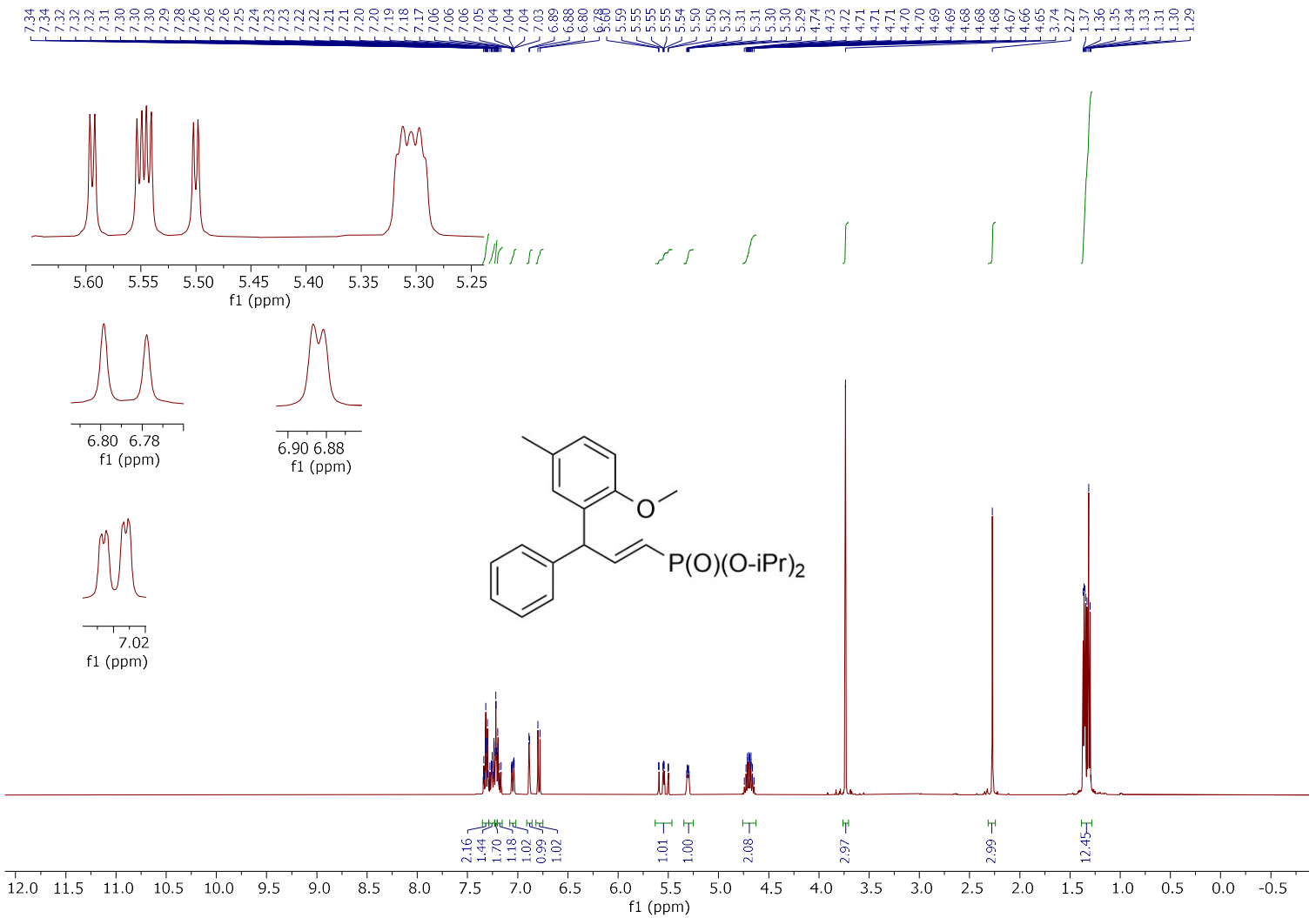


Figure S109: ^{1}H NMR Spectra of 5b in $CDCl_3$

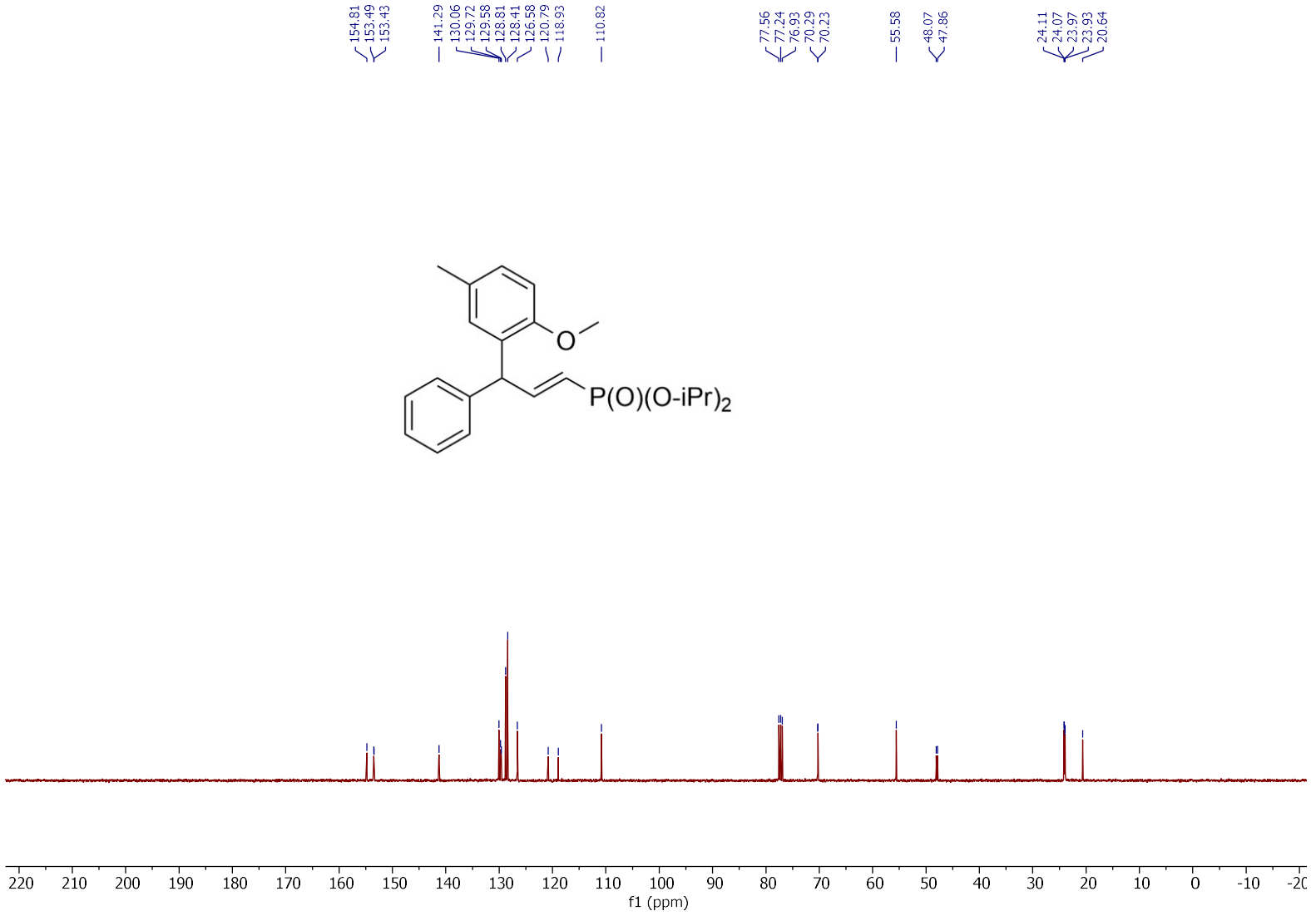


Figure S110: $^{13}C\{^{1}H\}$ NMR Spectra of 5b in $CDCl_3$

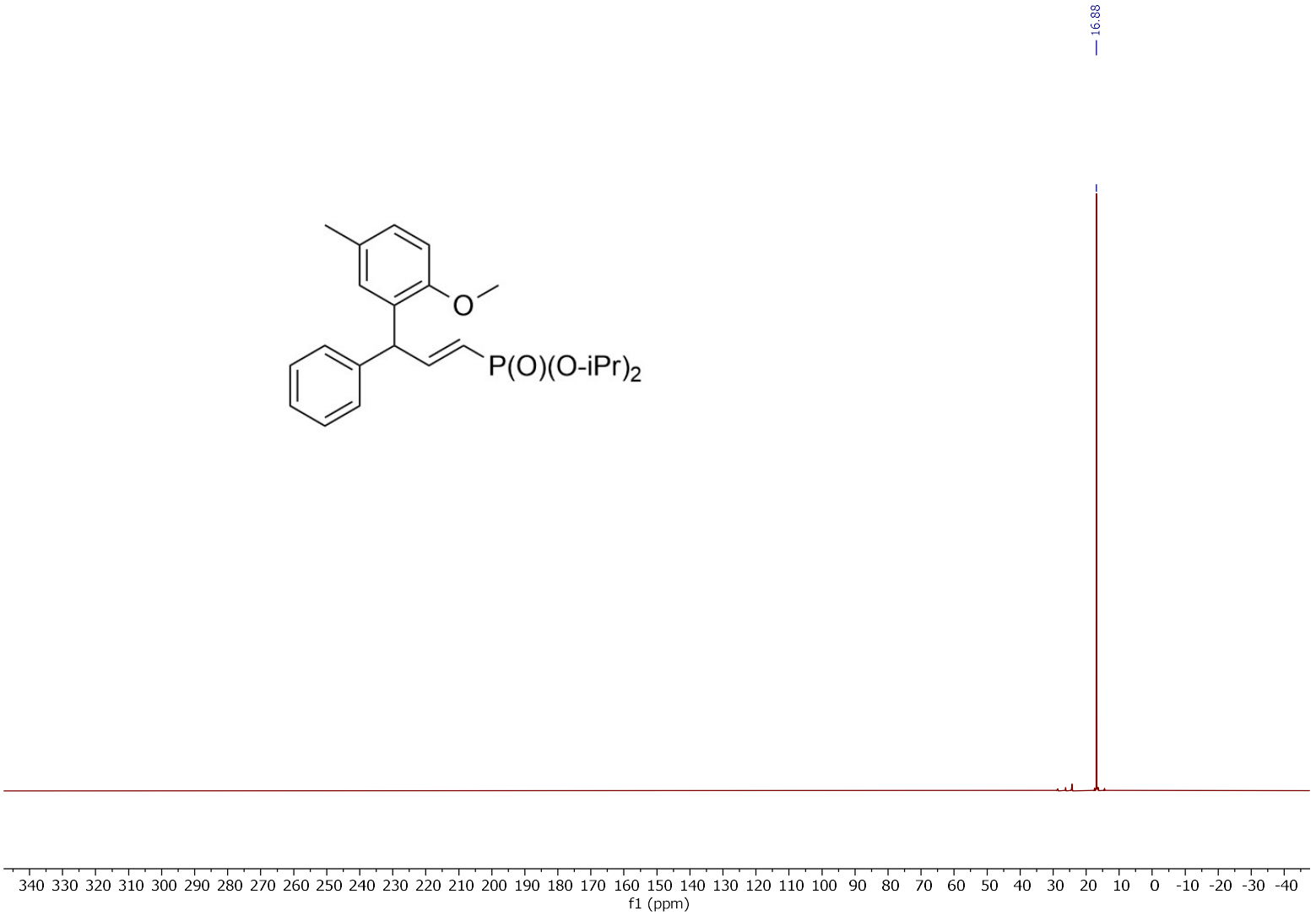


Figure S111: $^{31}P\{^{1}H\}$ NMR Spectra of 5b in $CDCl_3$

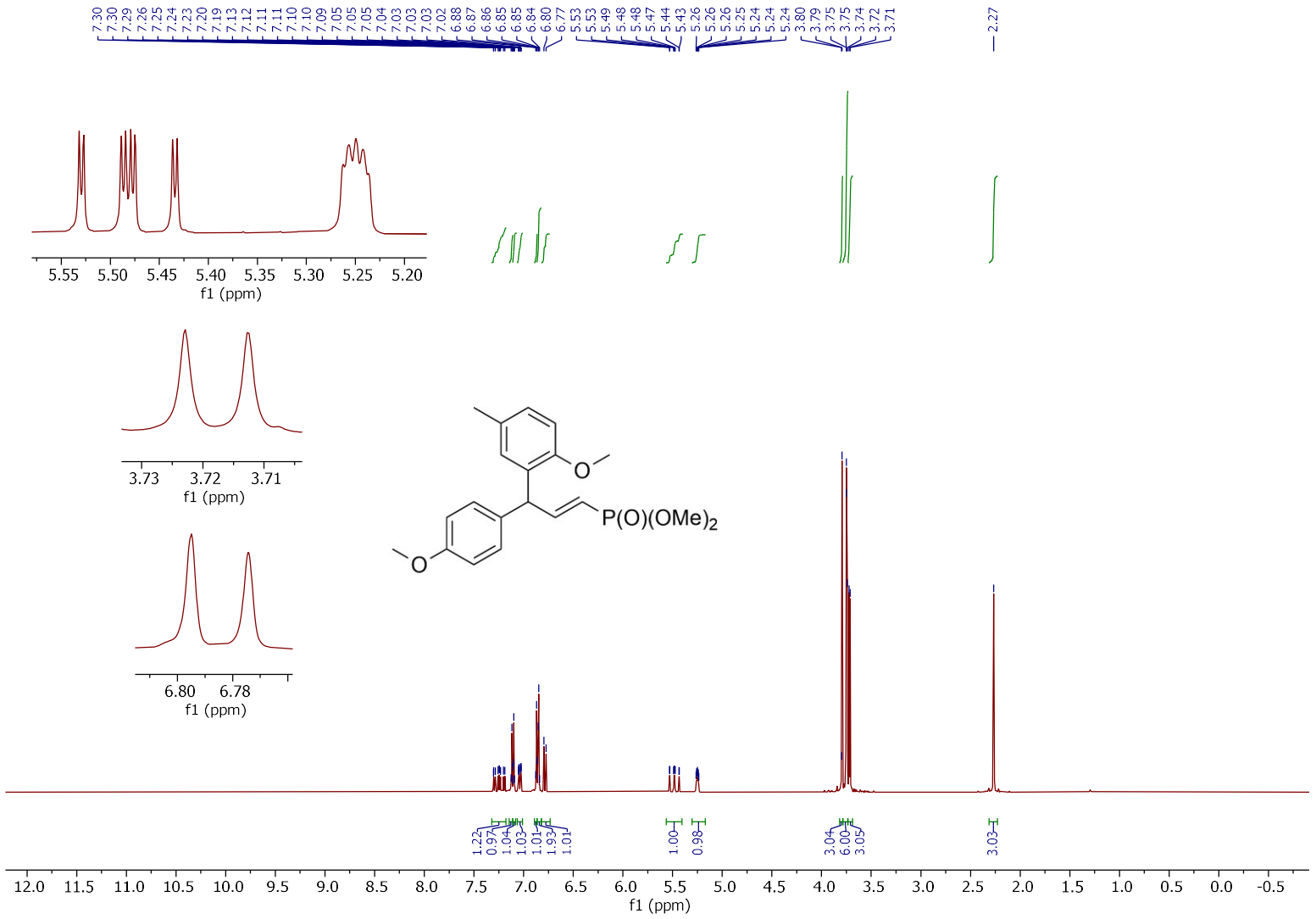


Figure S112: ^{1}H NMR Spectra of 5c in $CDCl_3$

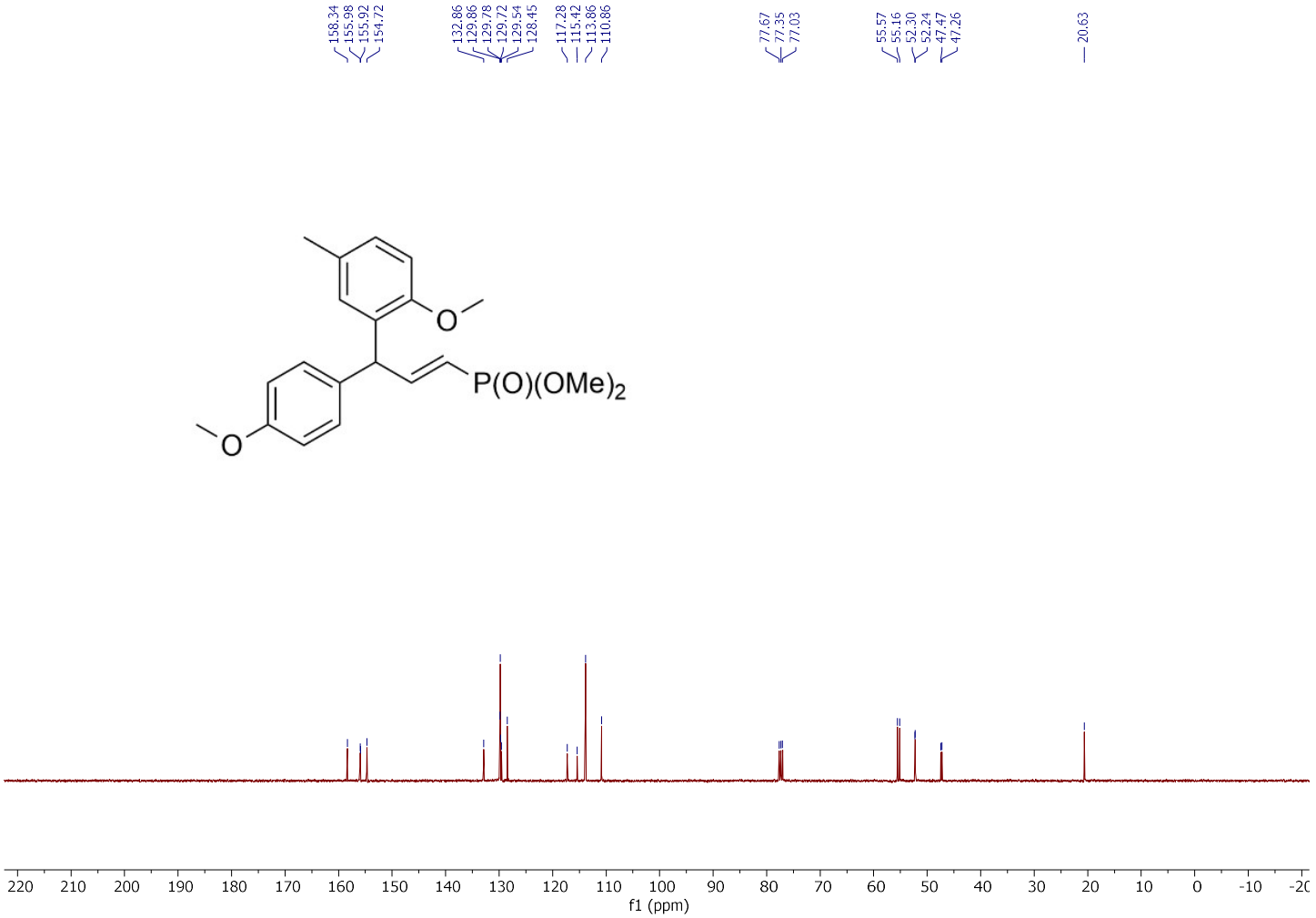


Figure S113: $^{13}C\{^{1}H\}$ NMR Spectra of 5c in $CDCl_3$

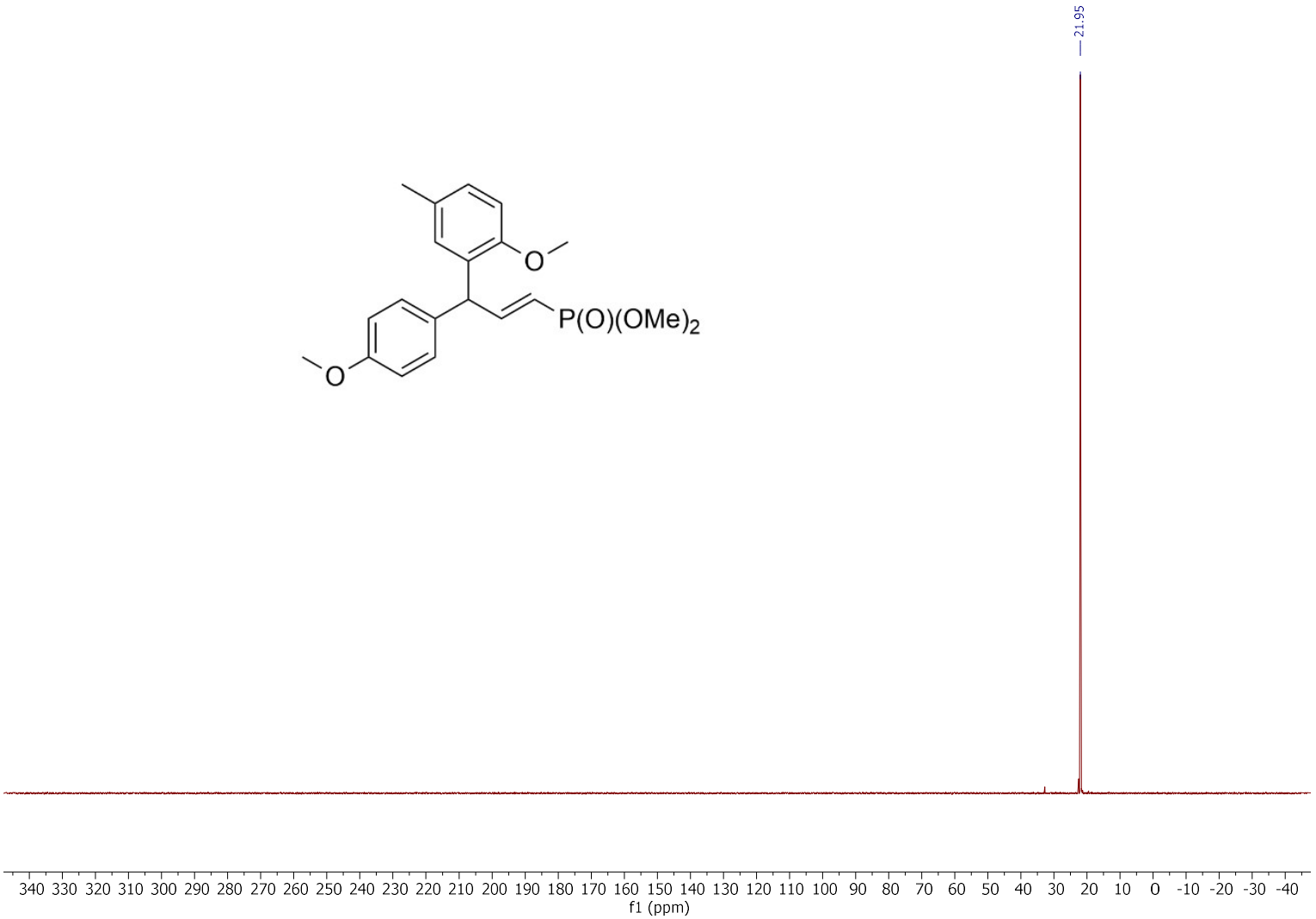


Figure S114: $^{31}P\{^{1}H\}$ NMR Spectra of 5c in $CDCl_3$

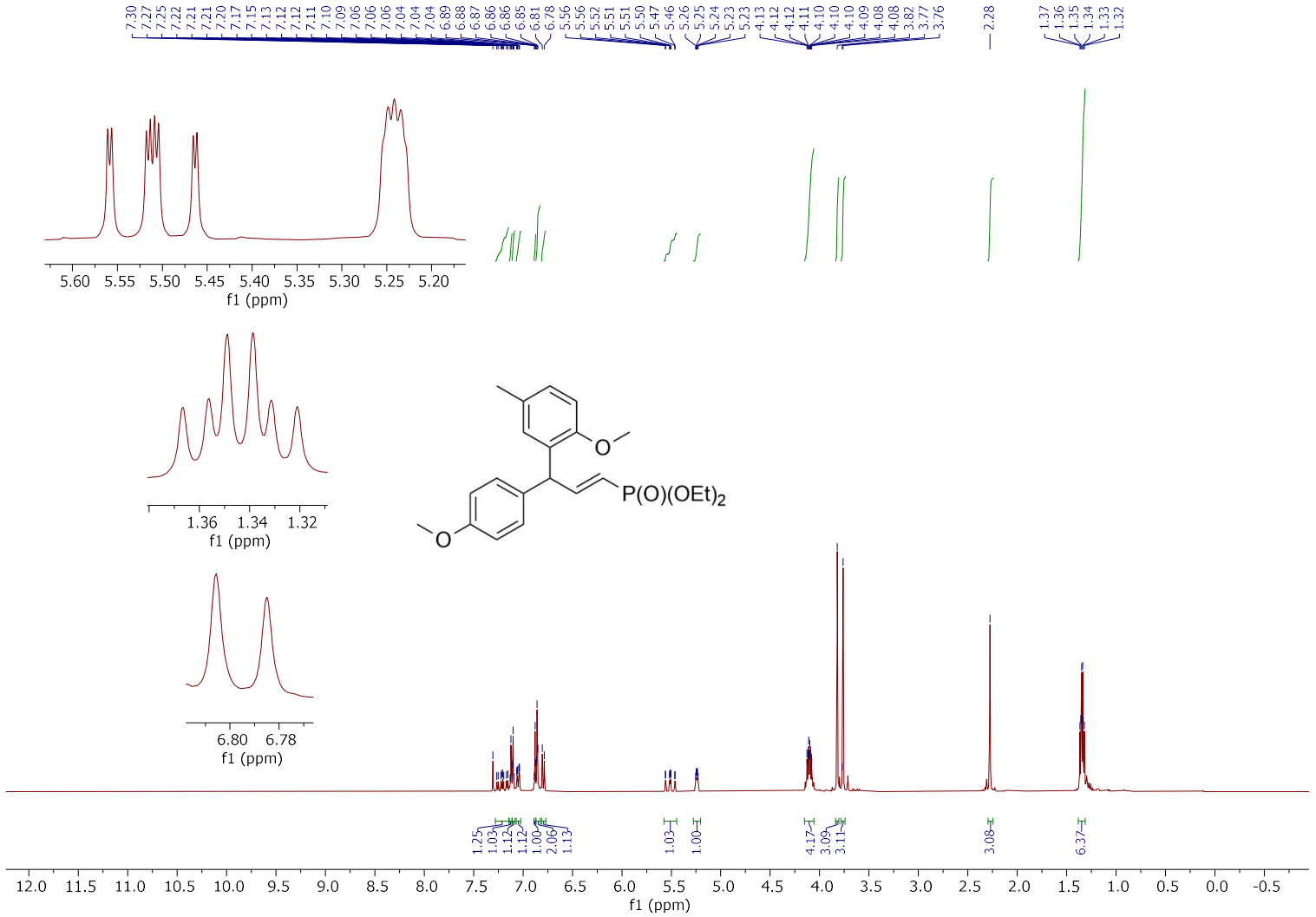


Figure S115: ^{1}H NMR Spectra of 5d in $CDCl_3$

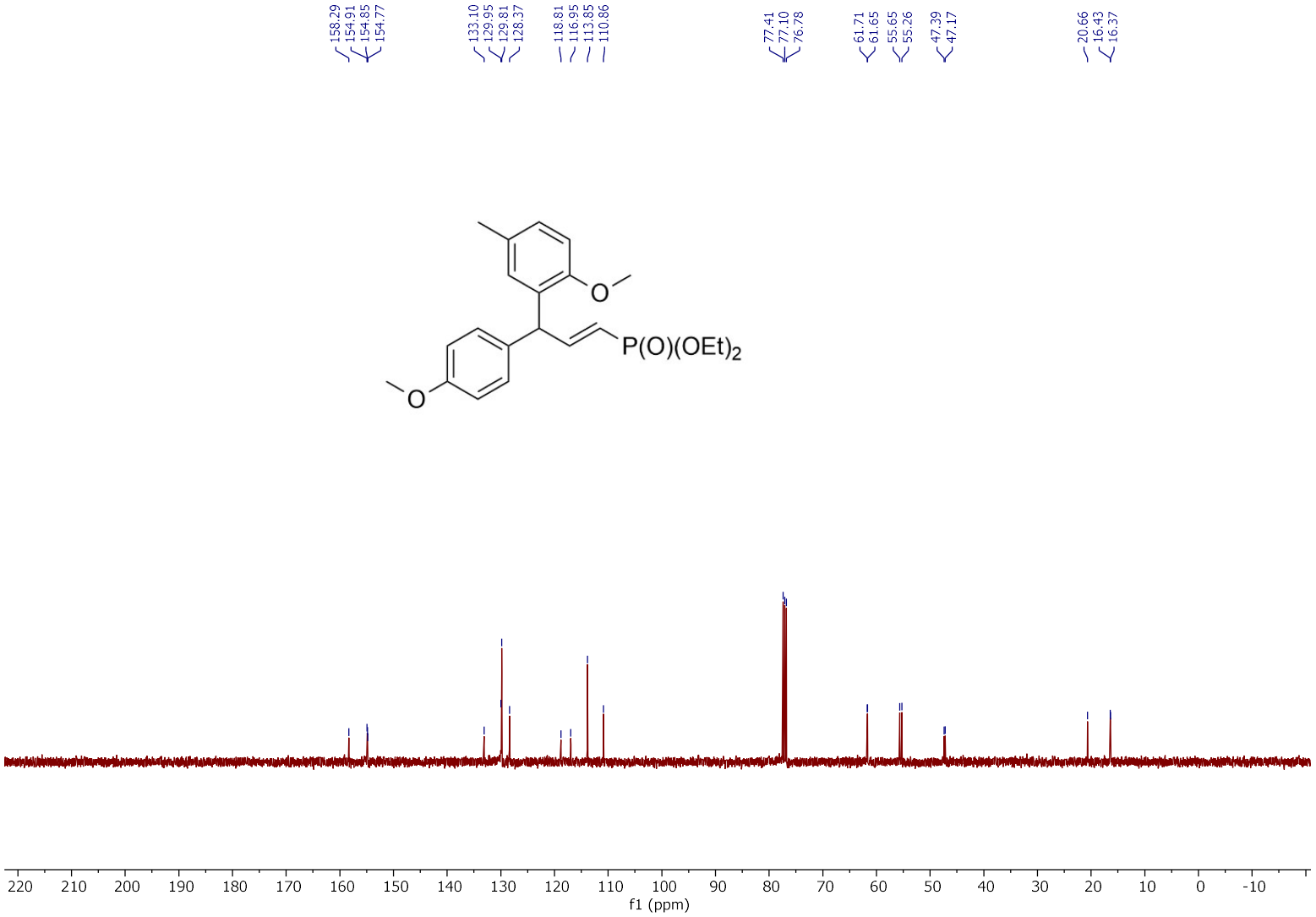


Figure S116: $^{13}C\{^{1}H\}$ NMR Spectra of 5d in $CDCl_3$

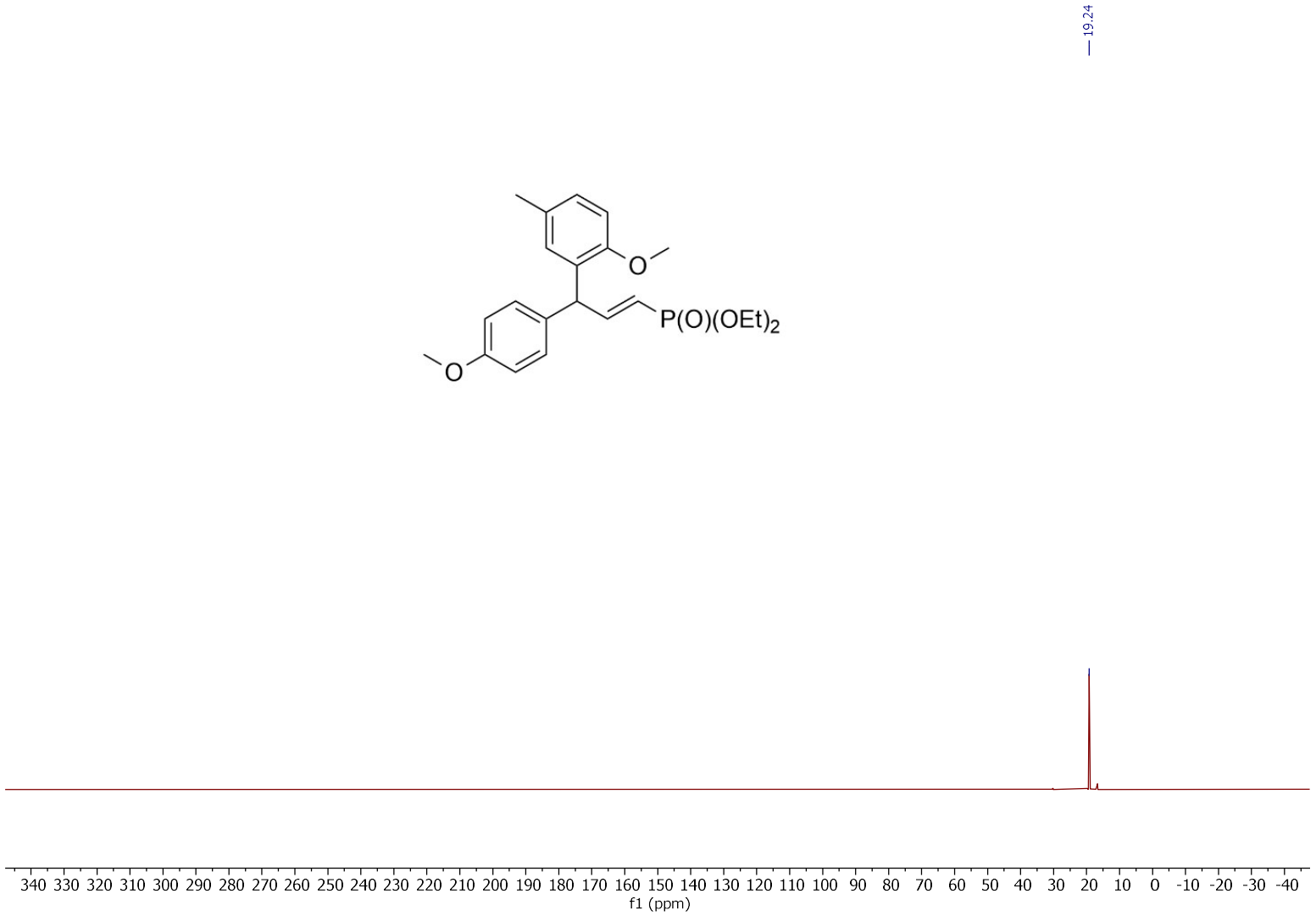


Figure S117: $^{31}P\{^{1}H\}$ NMR Spectra of 5d in $CDCl_3$

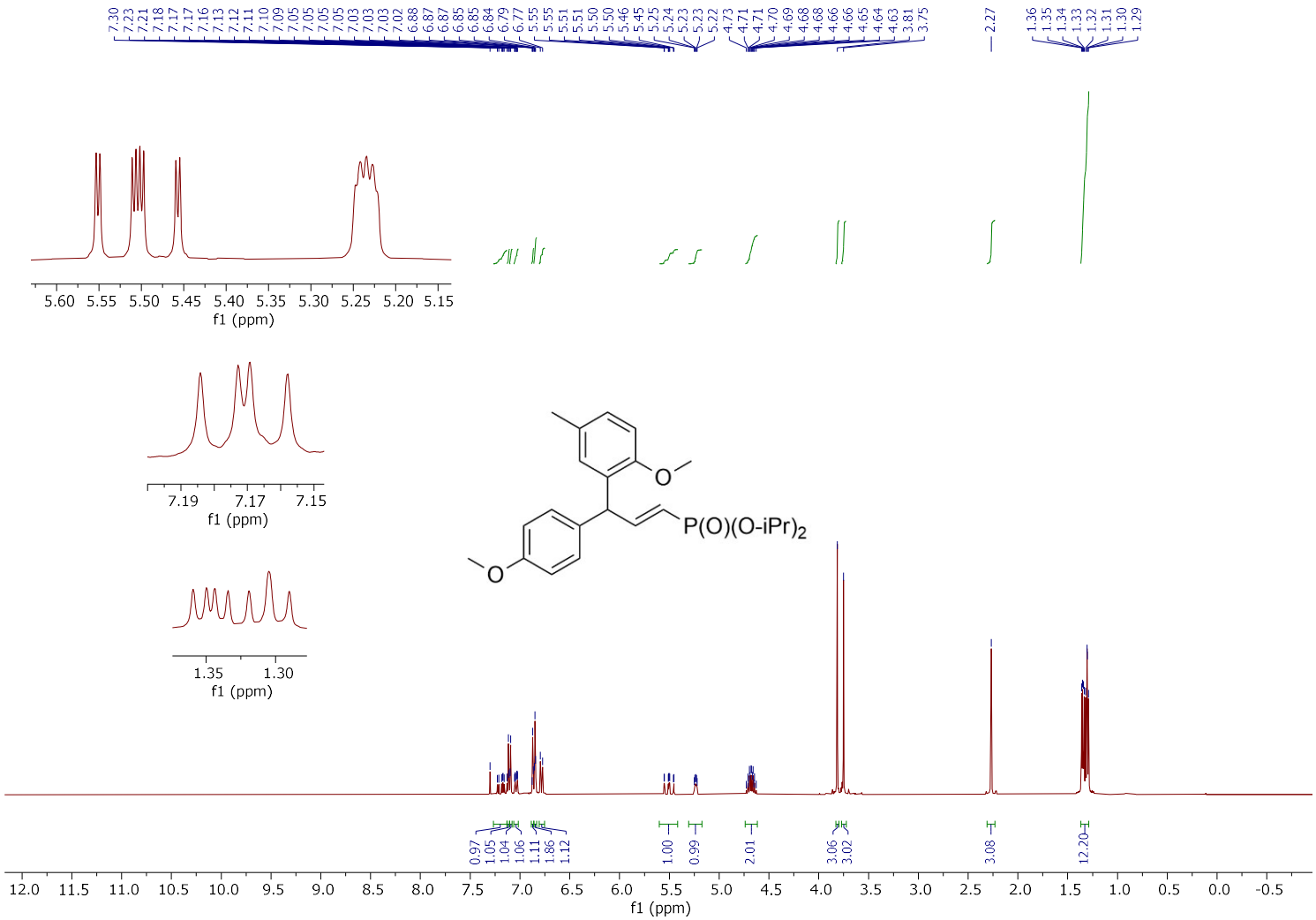


Figure S118: ^{1}H NMR Spectra of 5e in $CDCl_3$

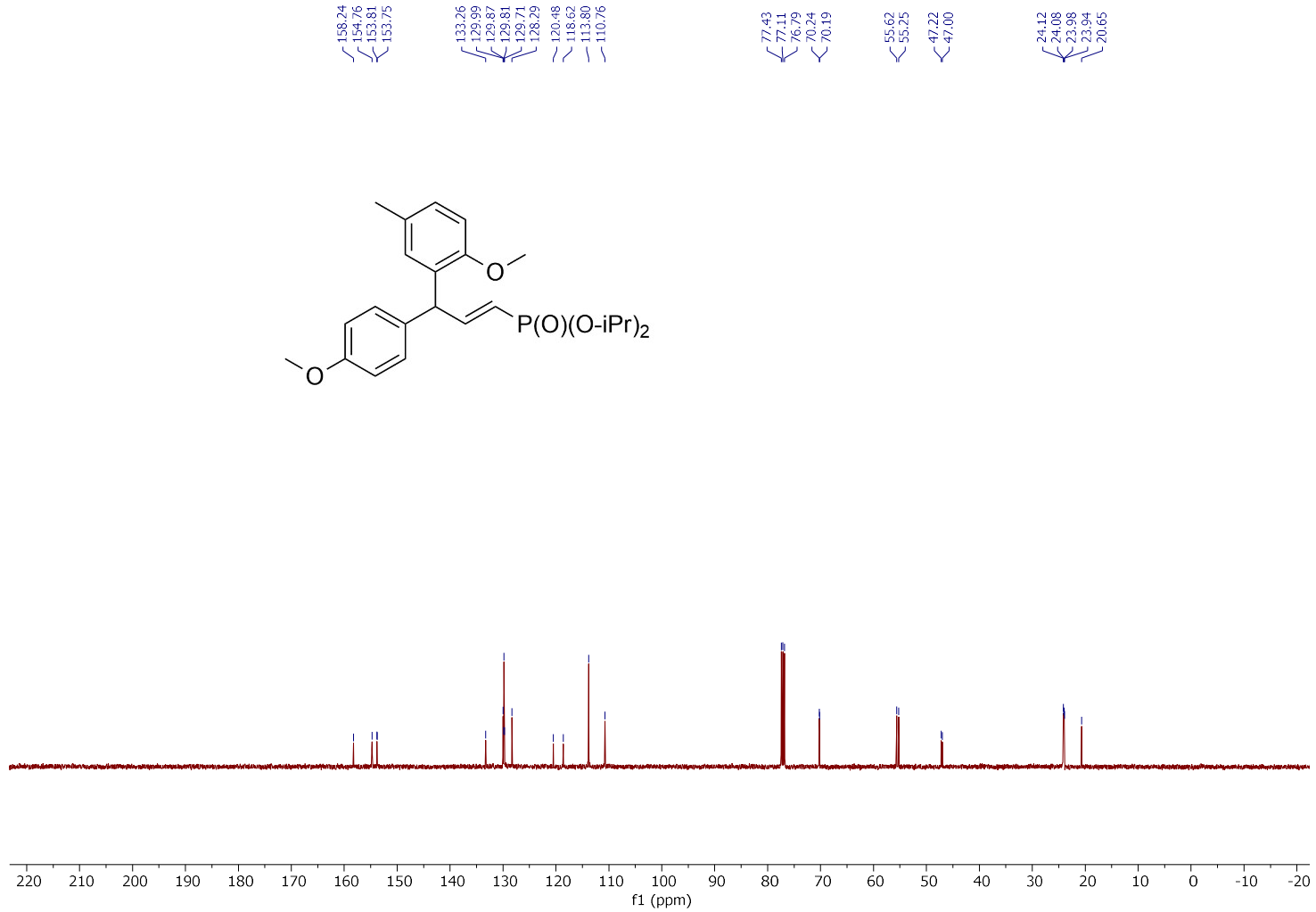


Figure S119: $^{13}C\{^{1}H\}$ NMR Spectra of 5e in $CDCl_3$

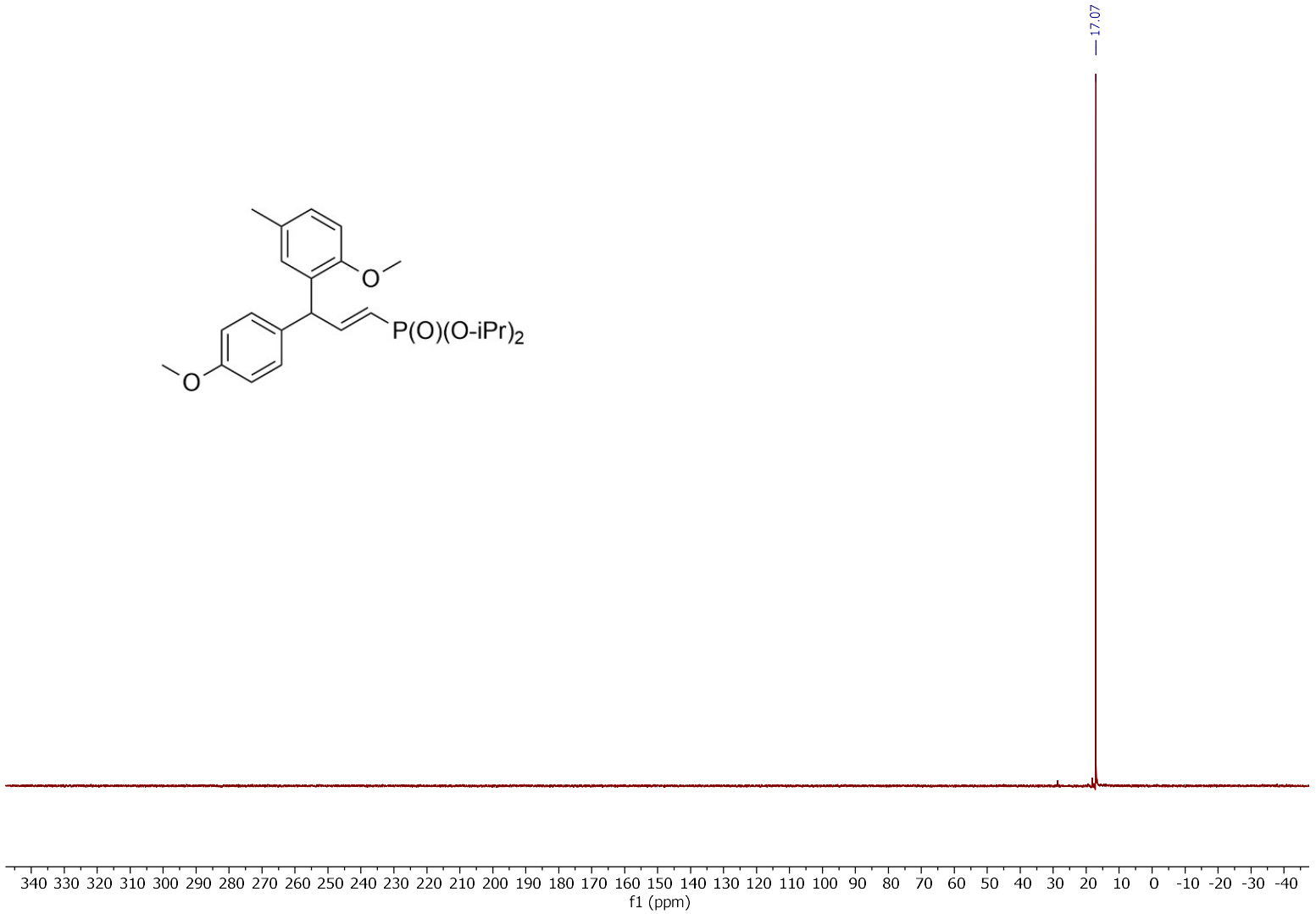


Figure S120: $^{31}P\{^{1}H\}$ NMR Spectra of 5e in $CDCl_3$

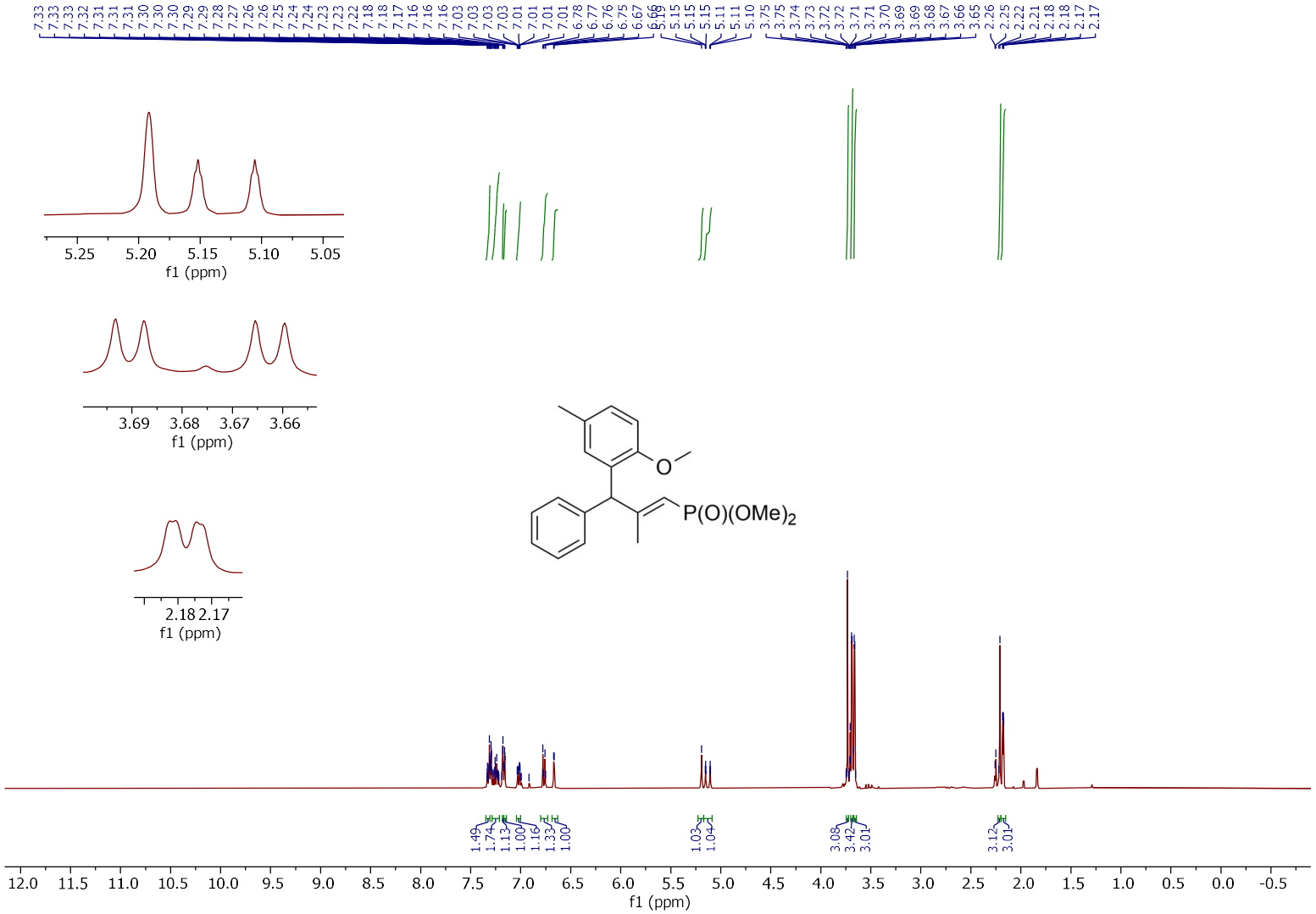


Figure S121: ^{1}H NMR Spectra of 5f in $CDCl_3$

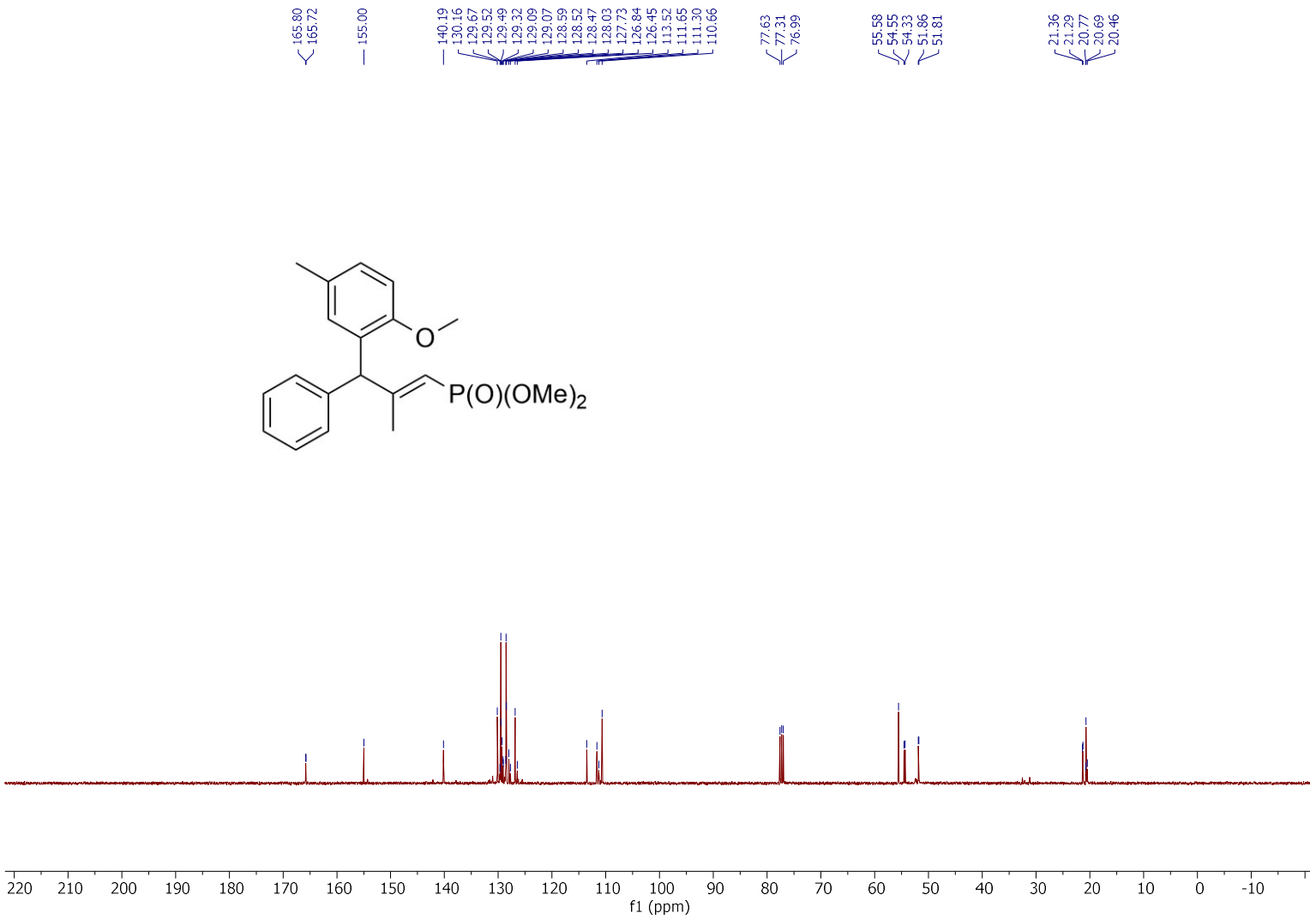


Figure S122: $^{13}C\{^{1}H\}$ NMR Spectra of 5f in $CDCl_3$

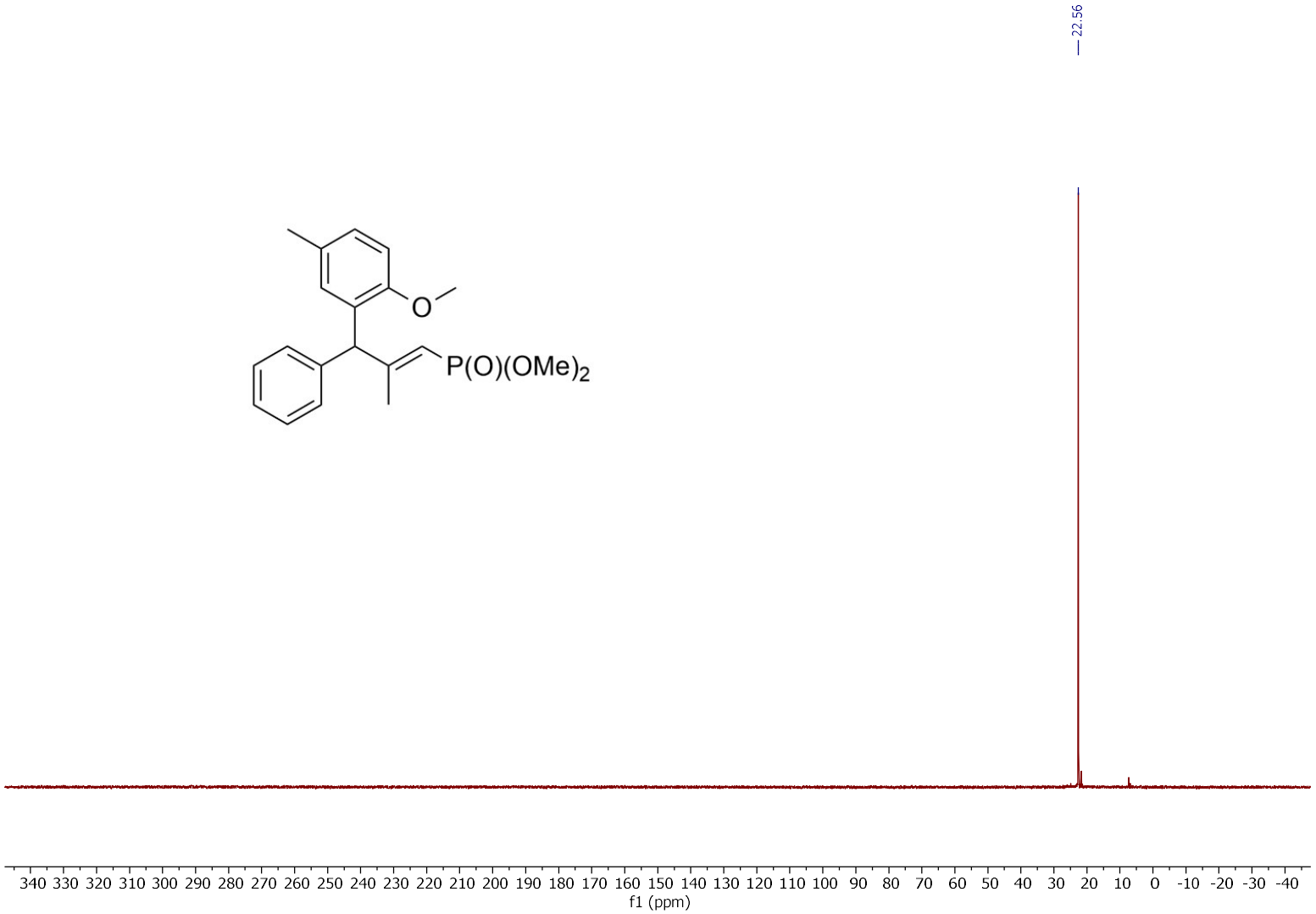


Figure S123: $^{31}P\{^{1}H\}$ NMR Spectra of 5f in $CDCl_3$

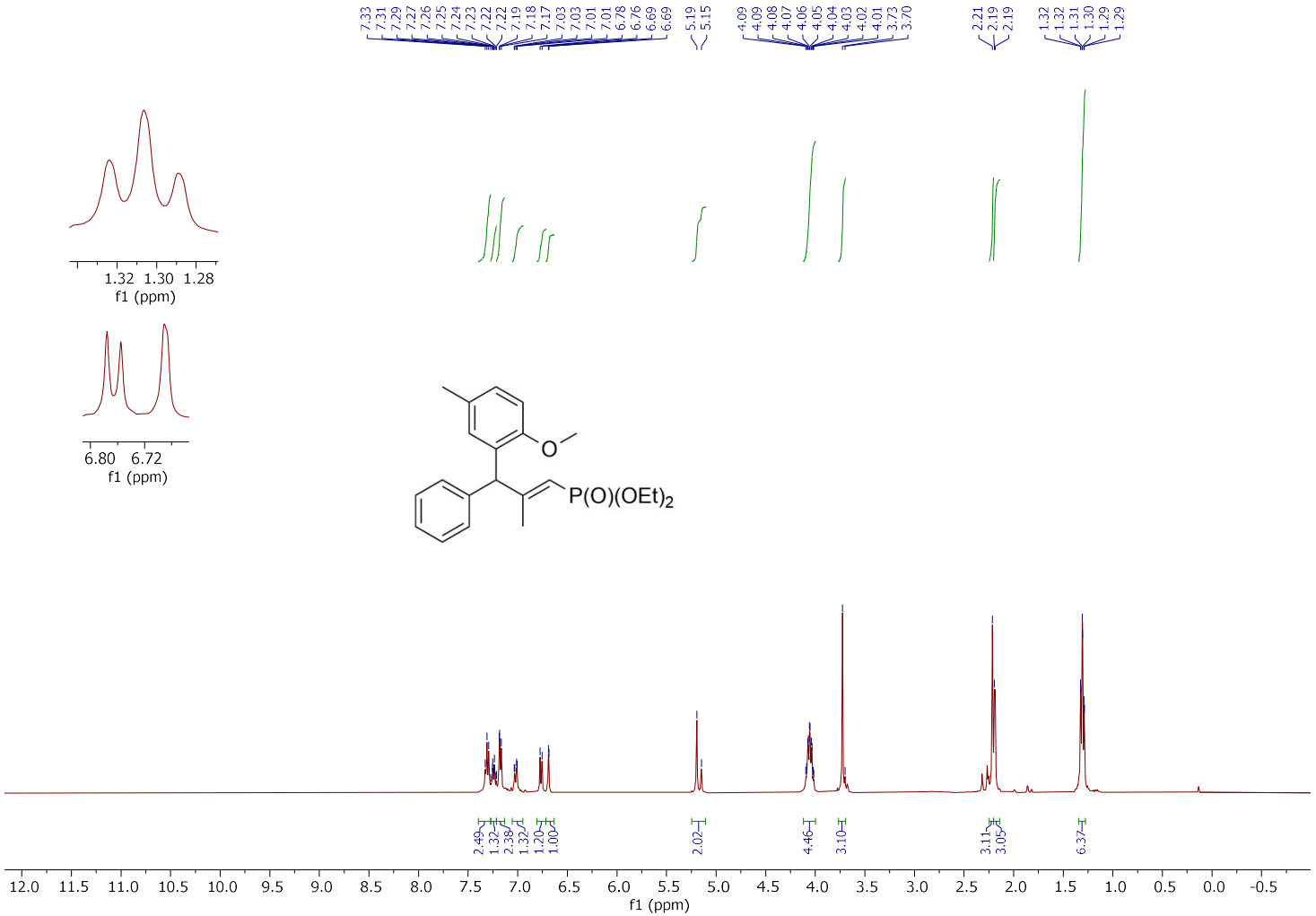


Figure S124: ^{1}H NMR Spectra of 5g in $CDCl_3$

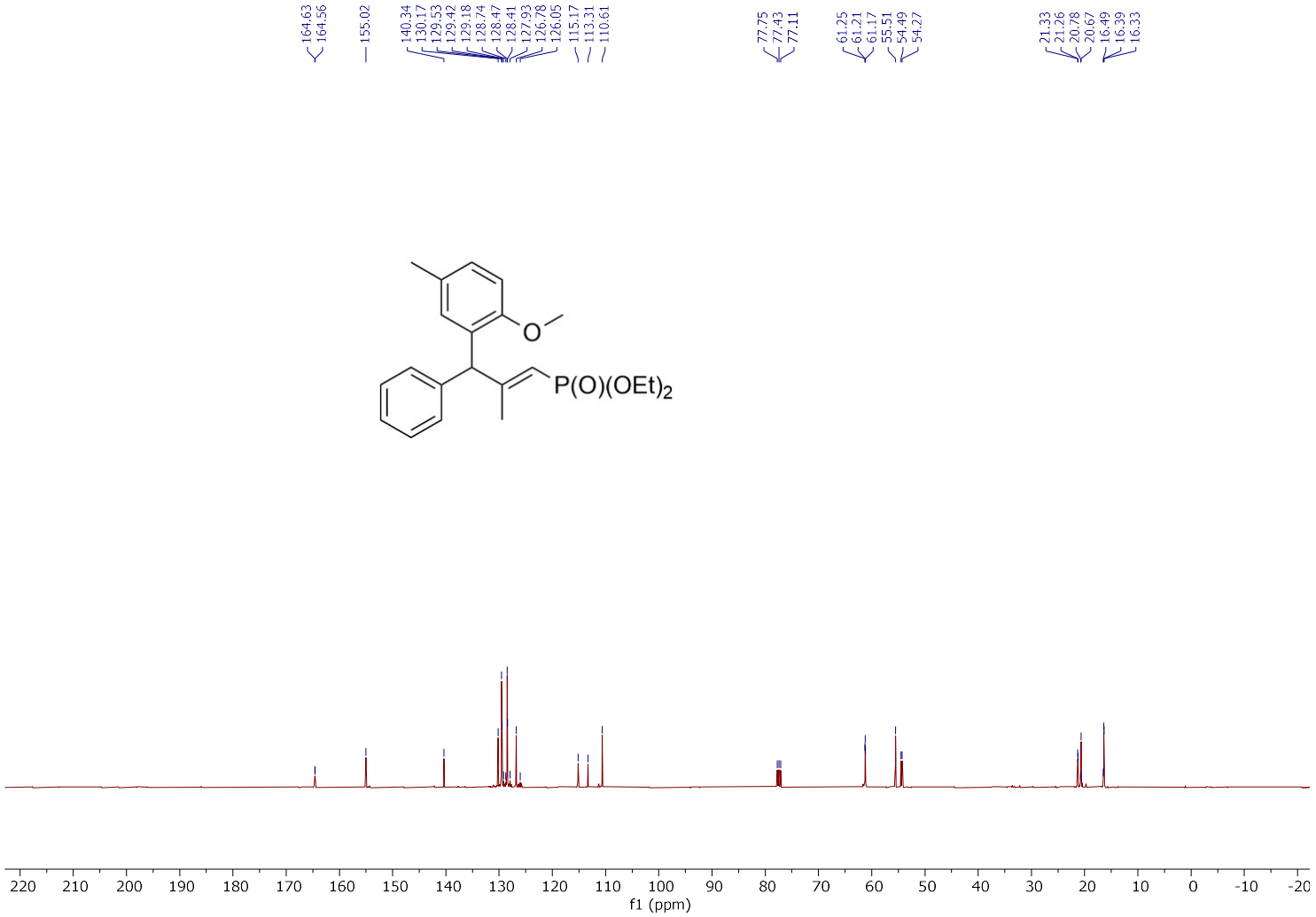


Figure S125: $^{13}C\{^{1}H\}$ NMR Spectra of 5g in $CDCl_3$

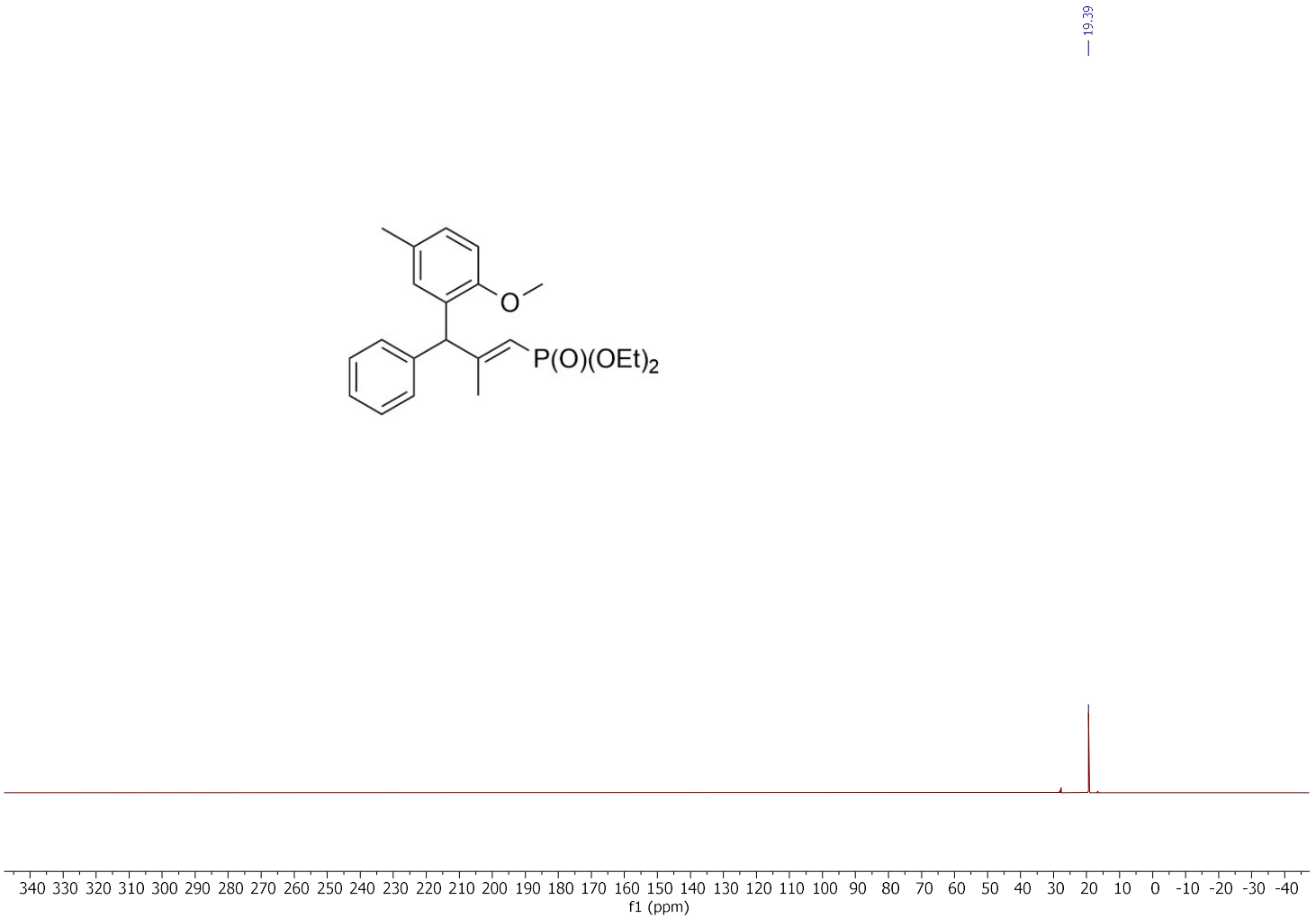


Figure S126: $^{31}P\{^{1}H\}$ NMR Spectra of 5g in $CDCl_3$

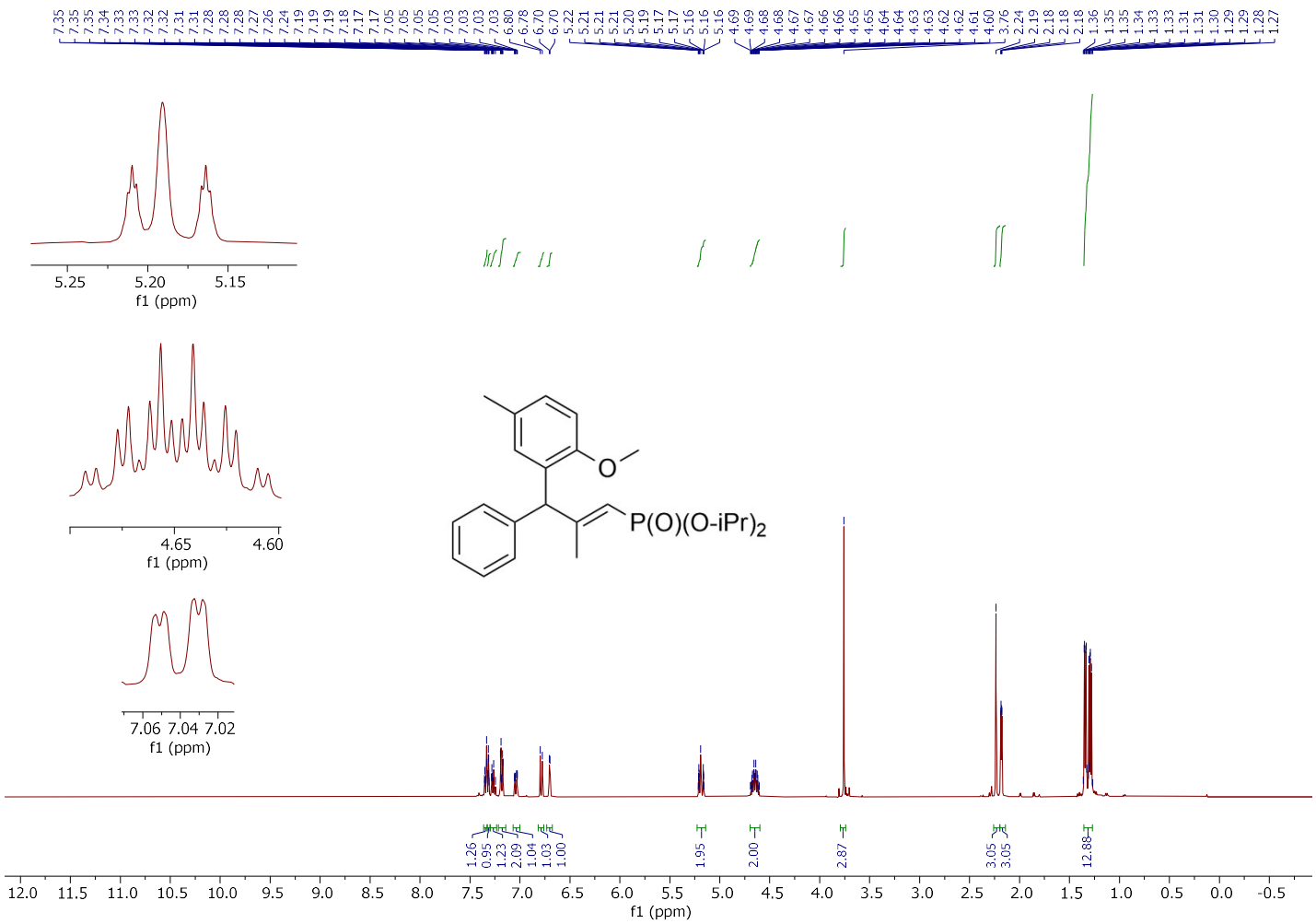


Figure S127: ^{1}H NMR Spectra of 5h in $CDCl_3$

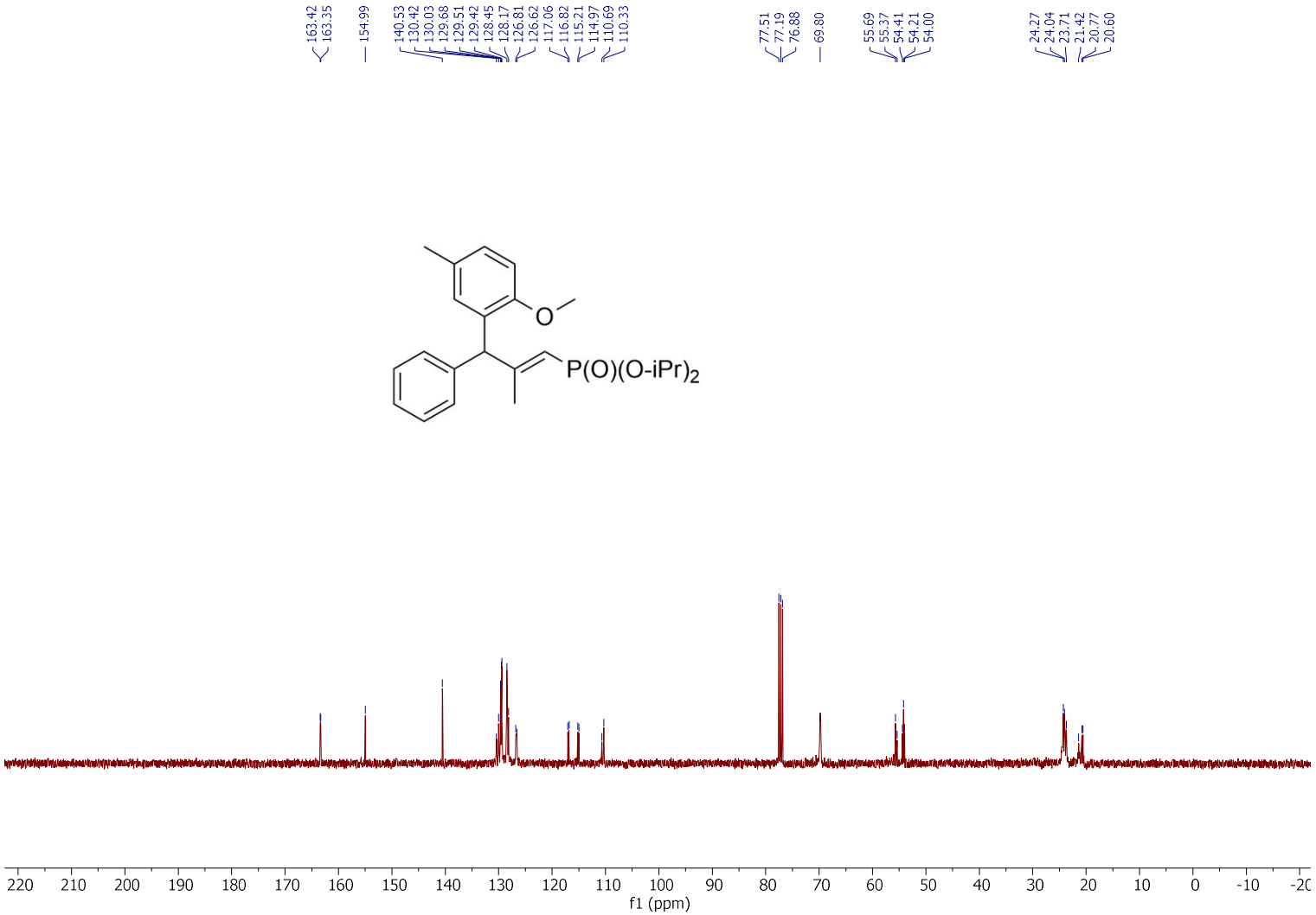


Figure S128: $^{13}C\{^{1}H\}$ NMR Spectra of 5h in $CDCl_3$

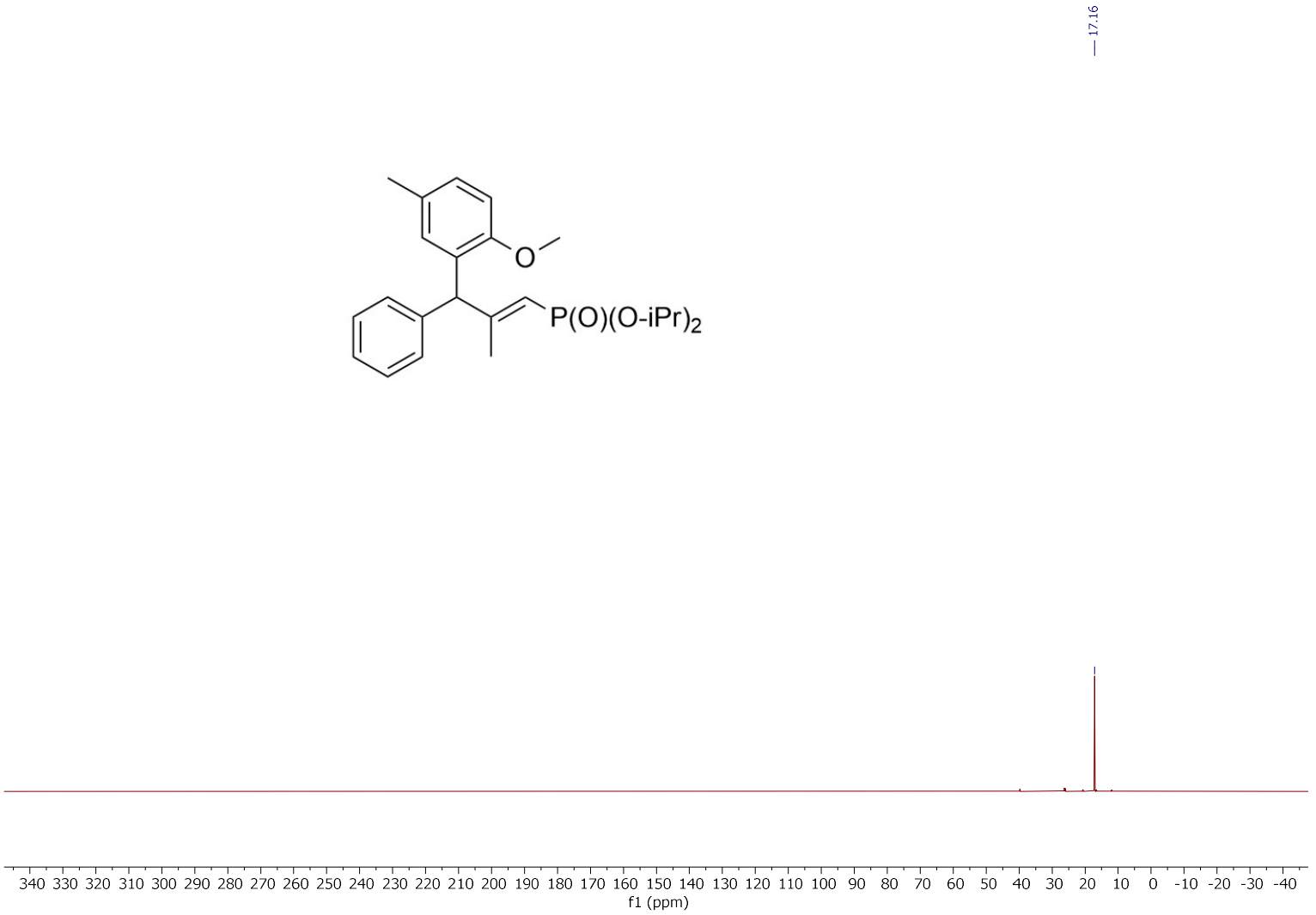


Figure S129: $^{31}P\{^{1}H\}$ NMR Spectra of 5h in $CDCl_3$

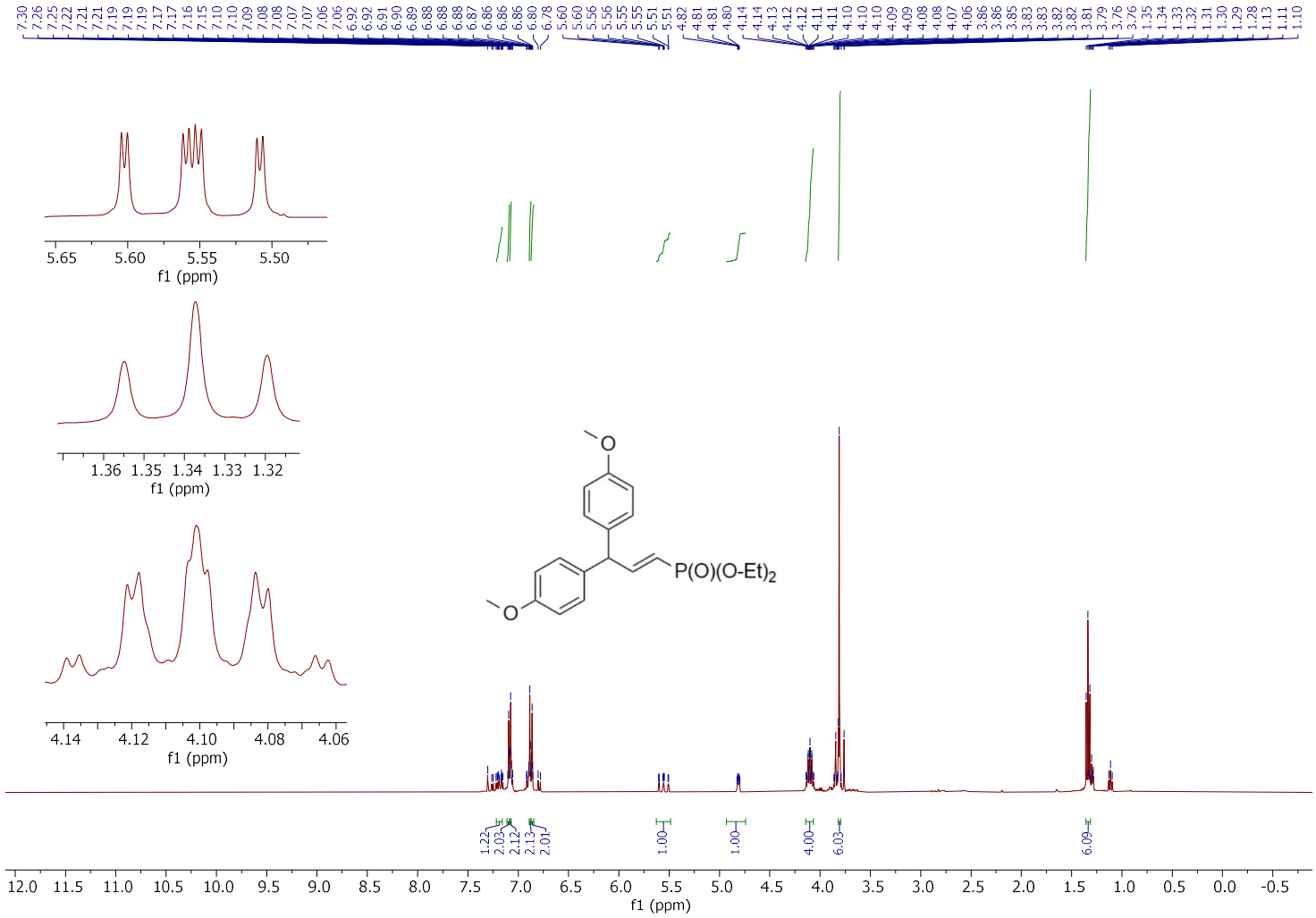


Figure S130: ^{1}H NMR Spectra of 7a in $CDCl_3$

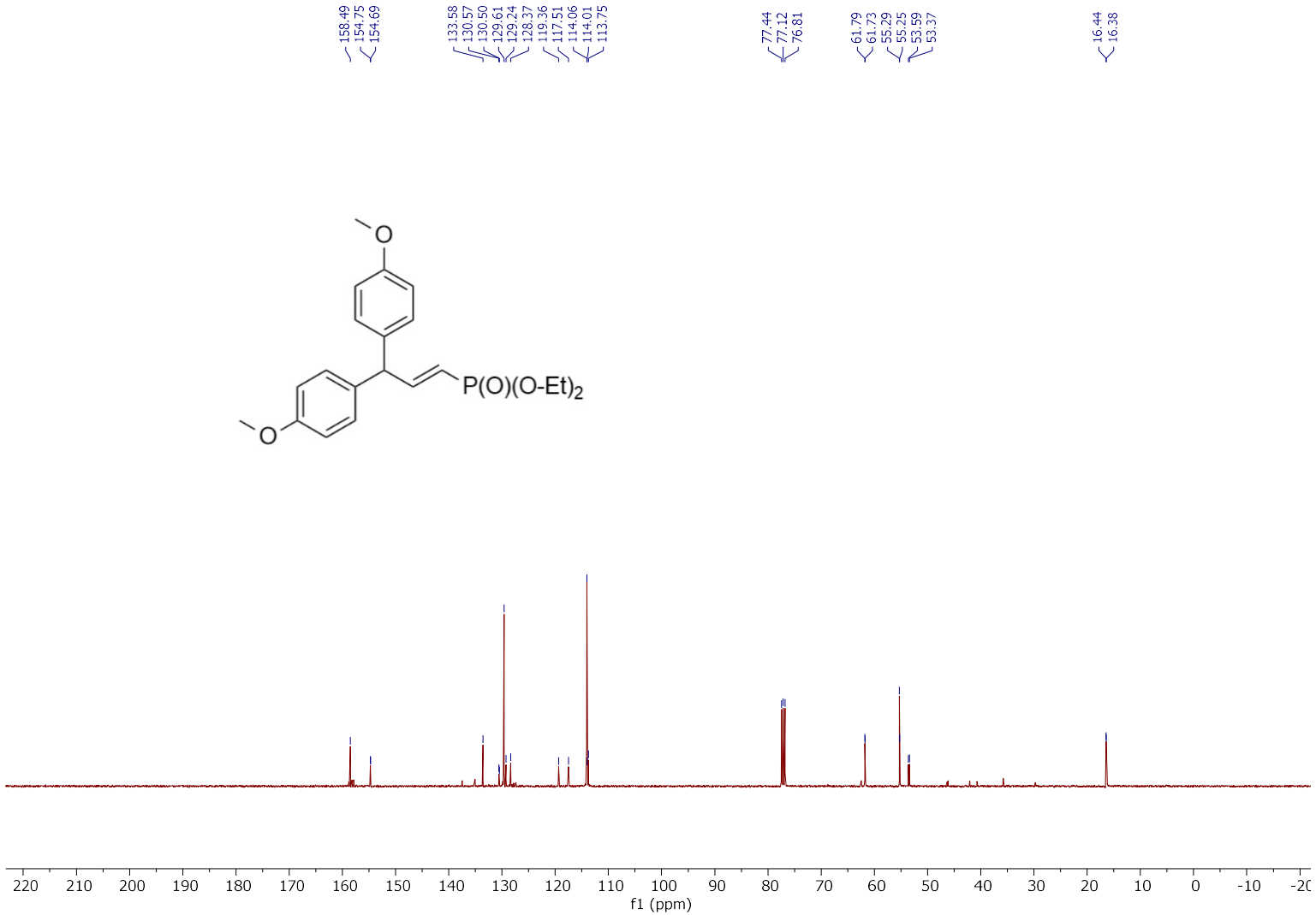


Figure S131: $^{13}C\{^{1}H\}$ NMR Spectra of 7a in $CDCl_3$

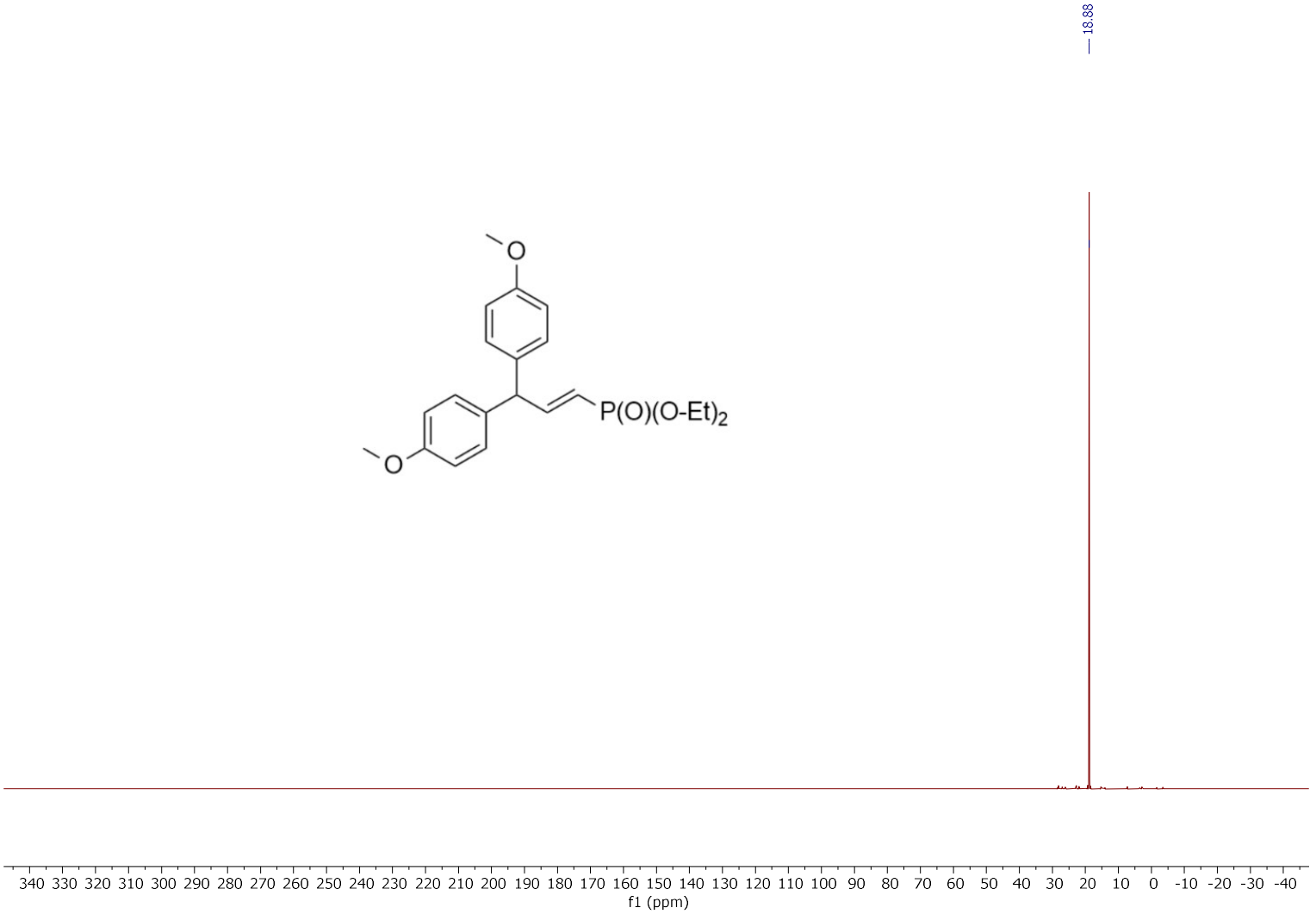


Figure S132: $^{31}P\{^{1}H\}$ NMR Spectra of 7a in $CDCl_3$

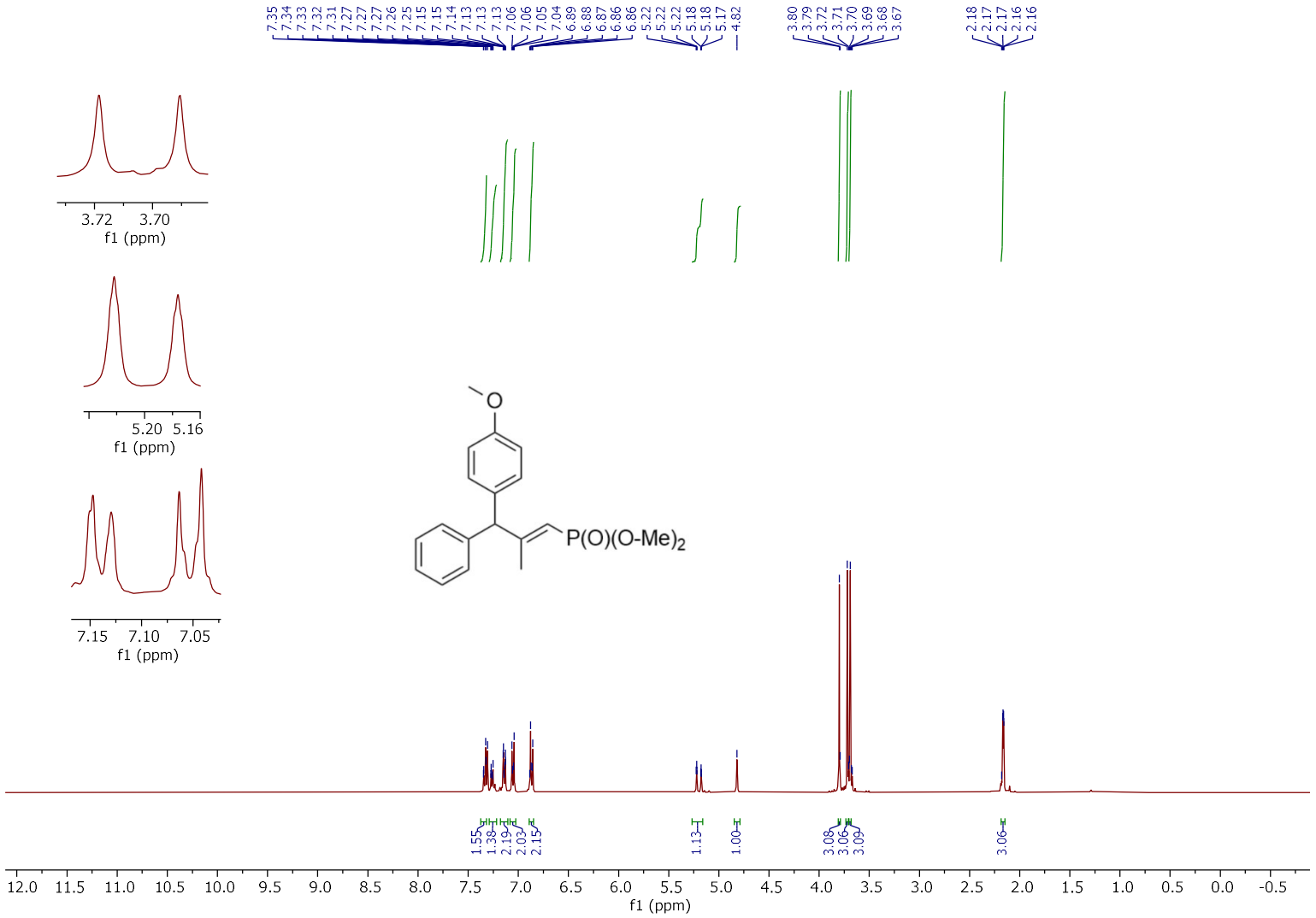


Figure S133: ^{1}H NMR Spectra of 7b in $CDCl_3$

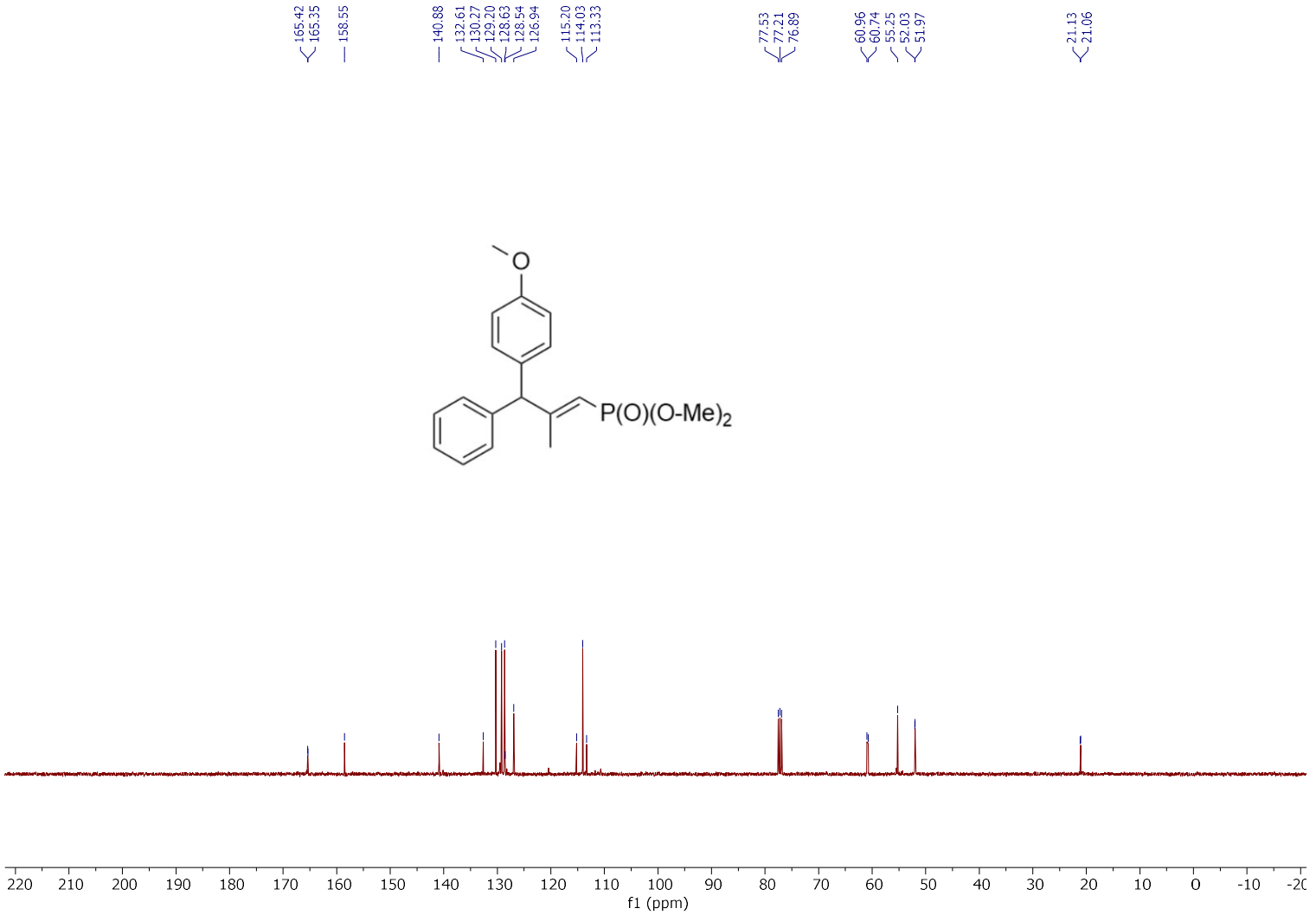


Figure S134: $^{13}C\{^{1}H\}$ NMR Spectra of 7b in $CDCl_3$

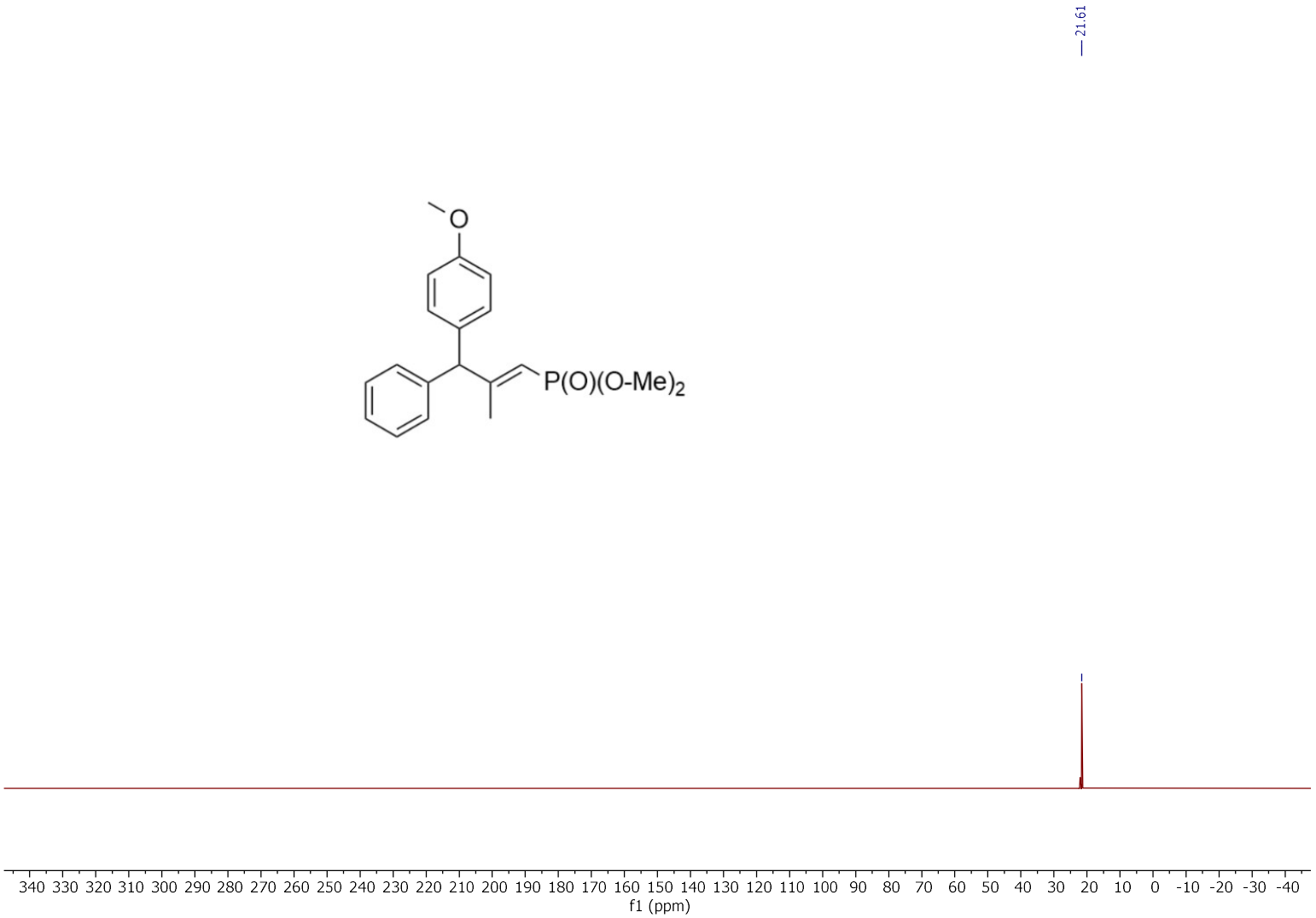


Figure S135: $^{31}P\{^{1}H\}$ NMR Spectra of 7b in $CDCl_3$

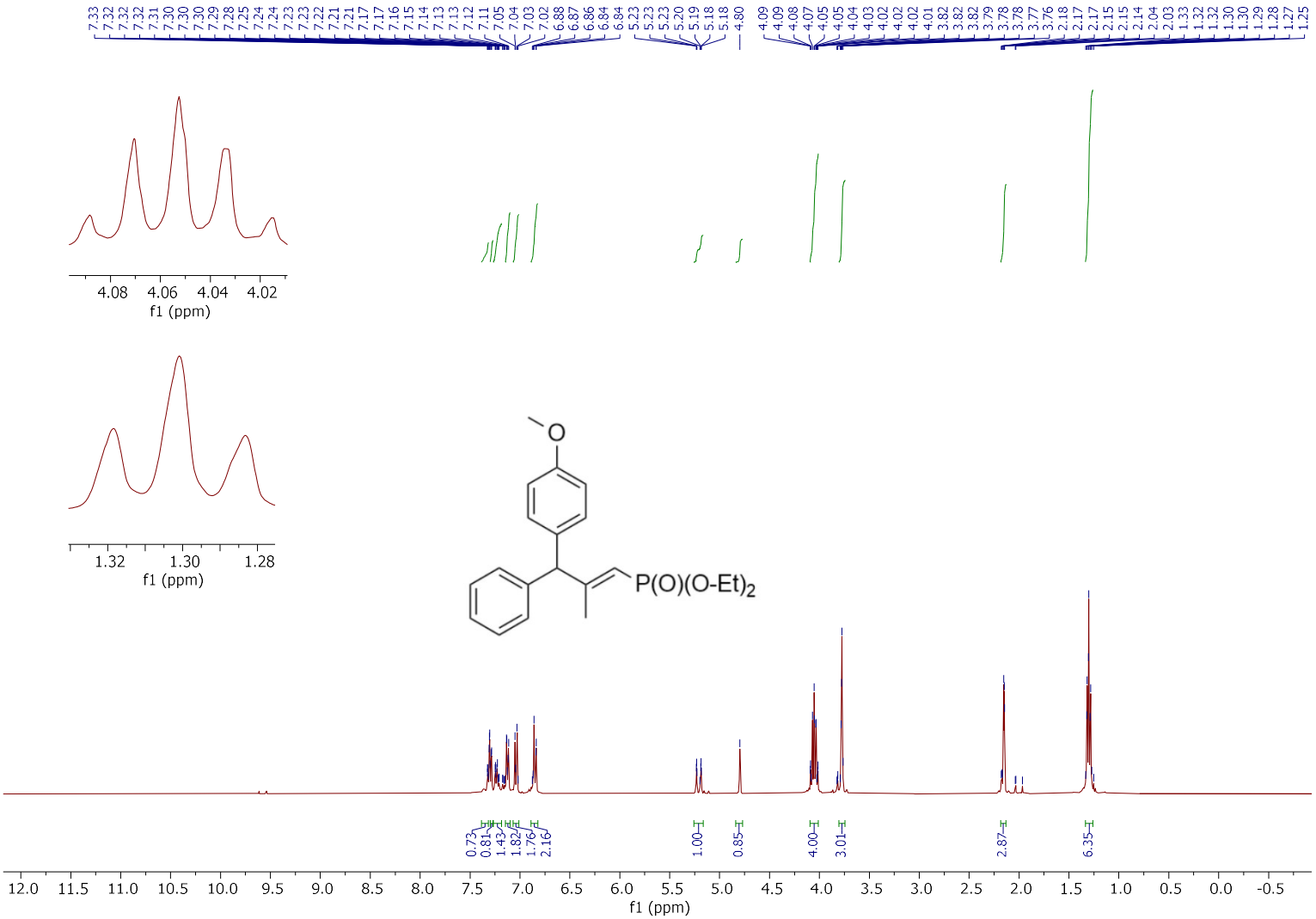


Figure S136: ^{1}H NMR Spectra of 7c in $CDCl_3$

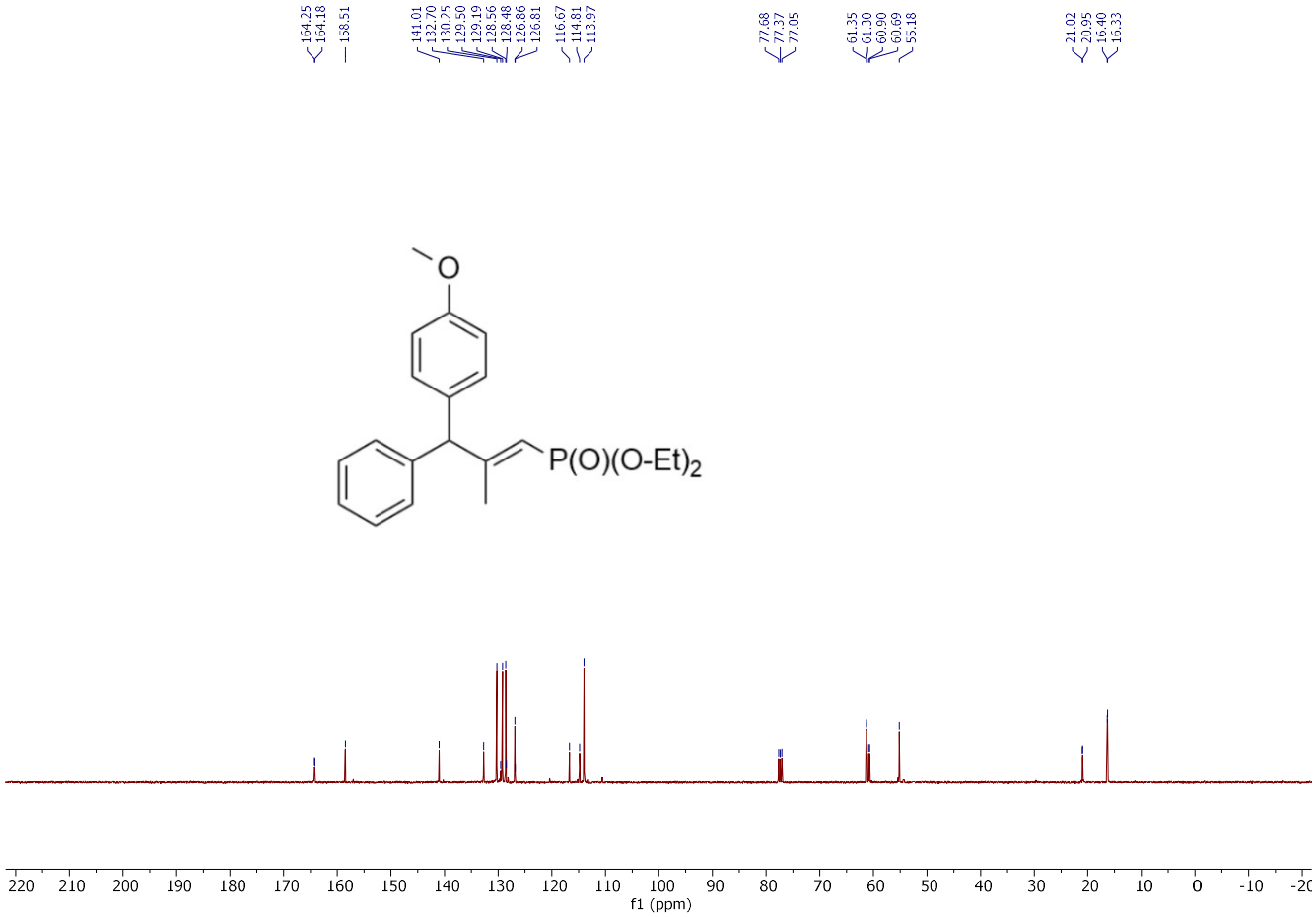


Figure S137: $^{13}C\{^{1}H\}$ NMR Spectra of 7c in $CDCl_3$

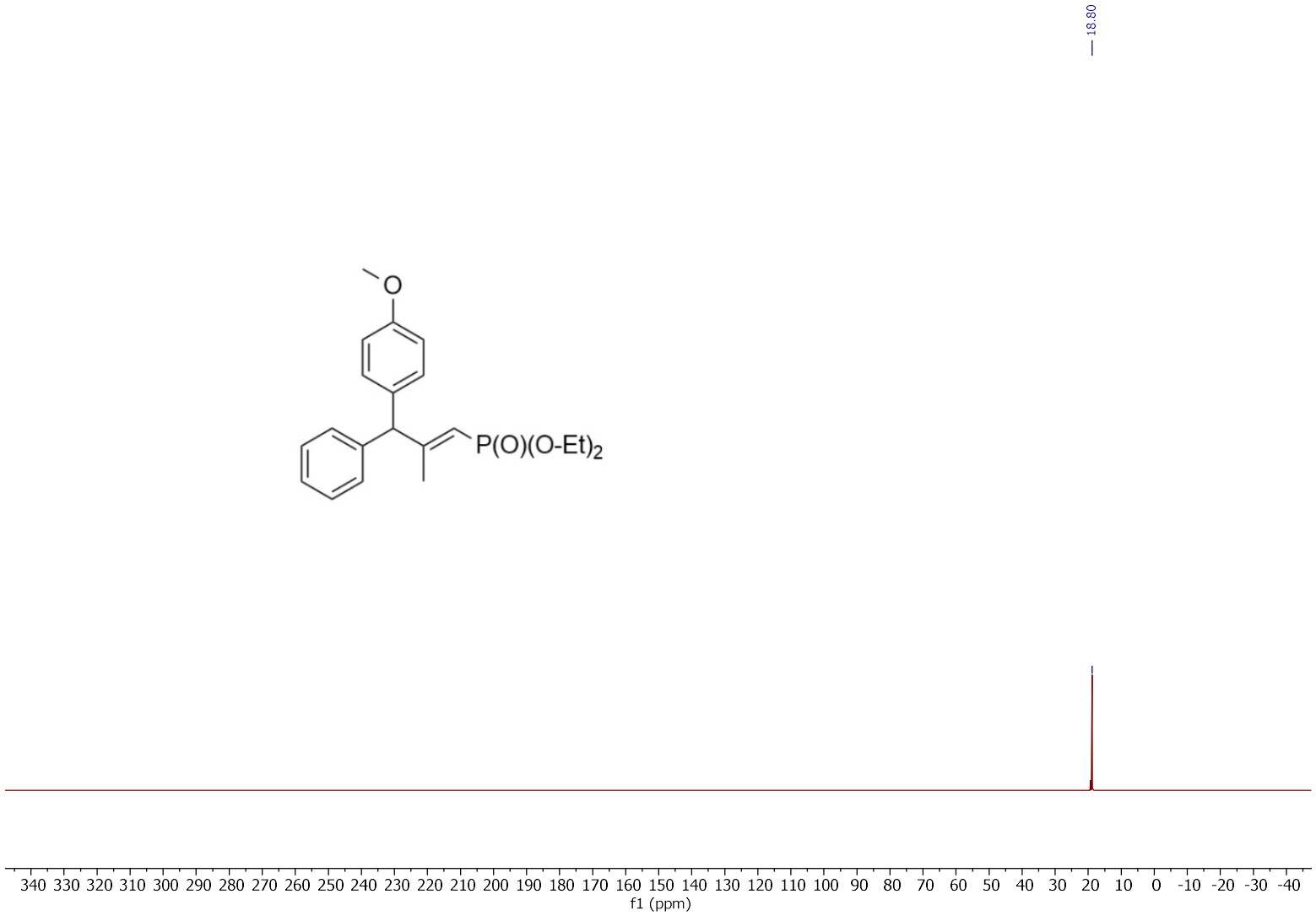


Figure S138: $^{31}P\{^{1}H\}$ NMR Spectra of 7c in $CDCl_3$

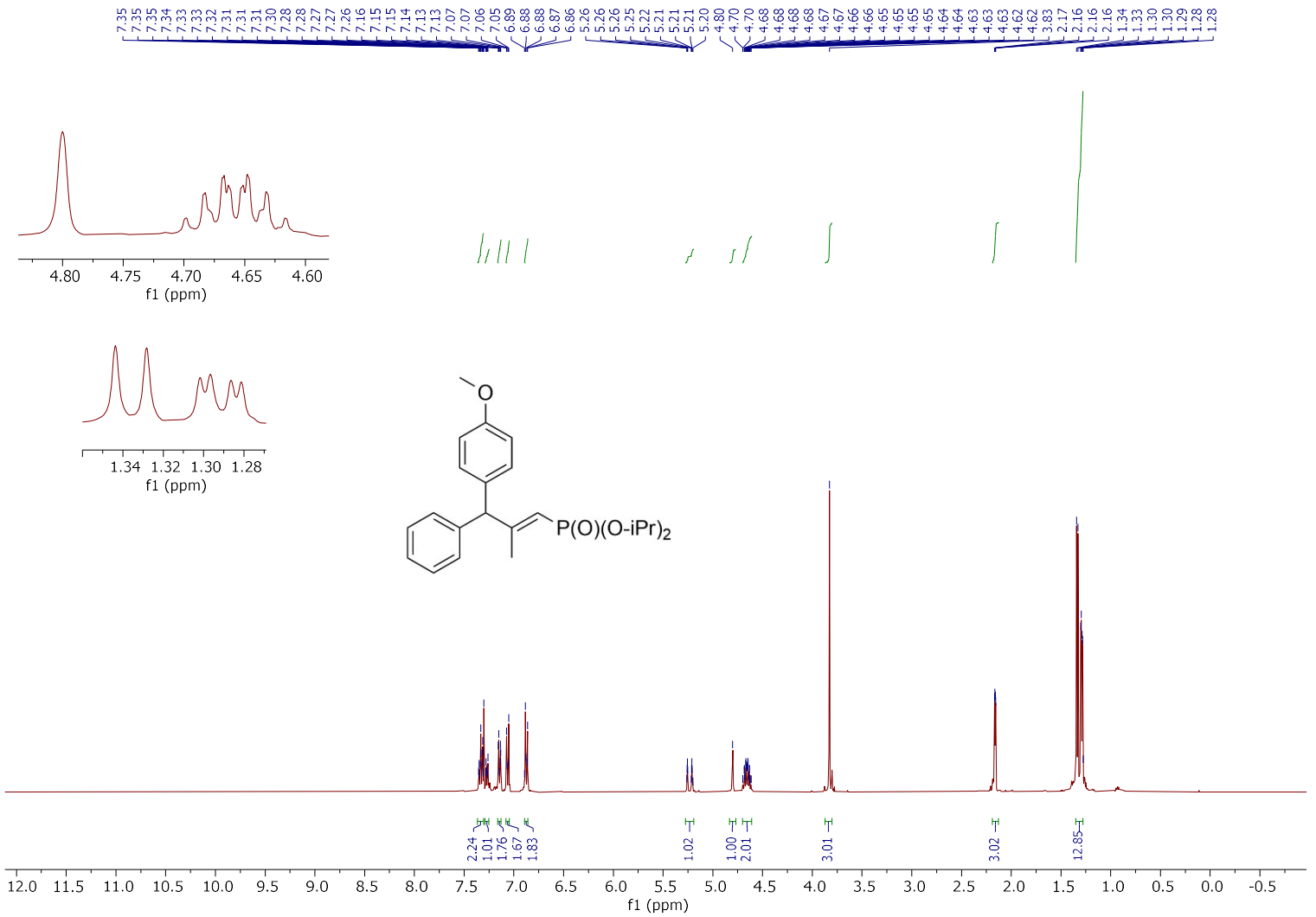


Figure S139: ^{1}H NMR Spectra of 7d in $CDCl_3$

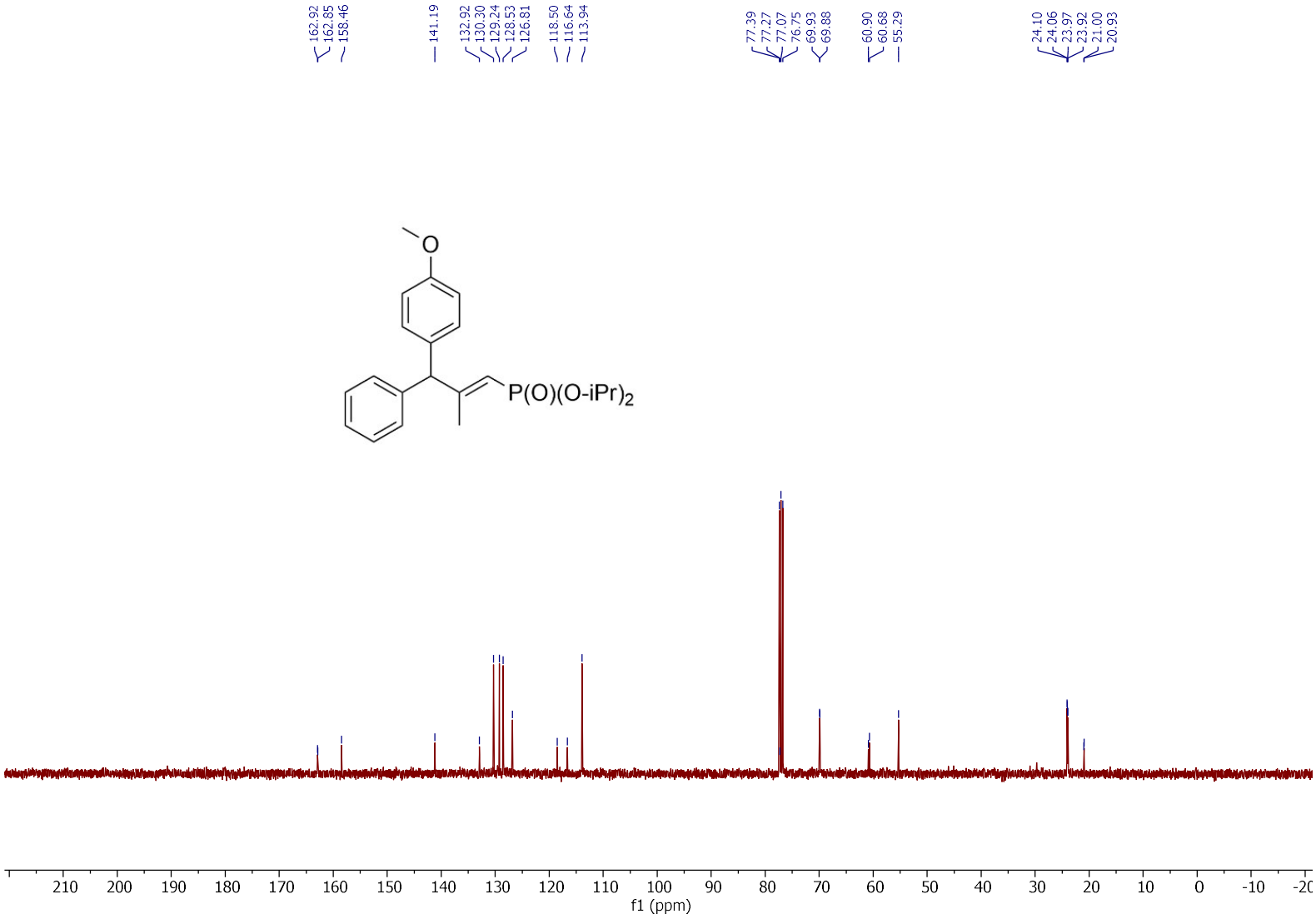


Figure S140: $^{13}C\{^{1}H\}$ NMR Spectra of 7d in $CDCl_3$

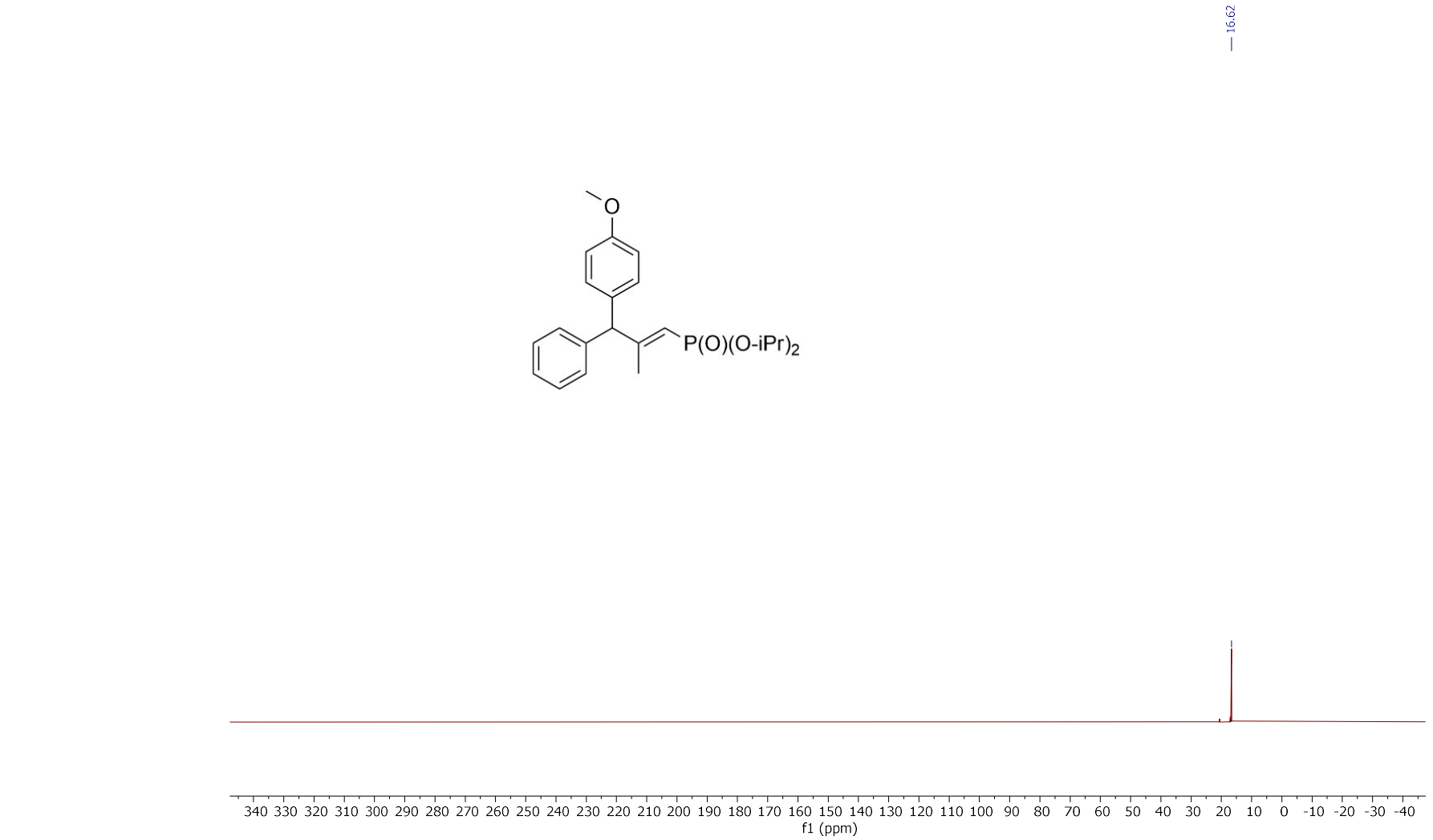


Figure S141: $^{31}P\{^{1}H\}$ NMR Spectra of 7d in $CDCl_3$

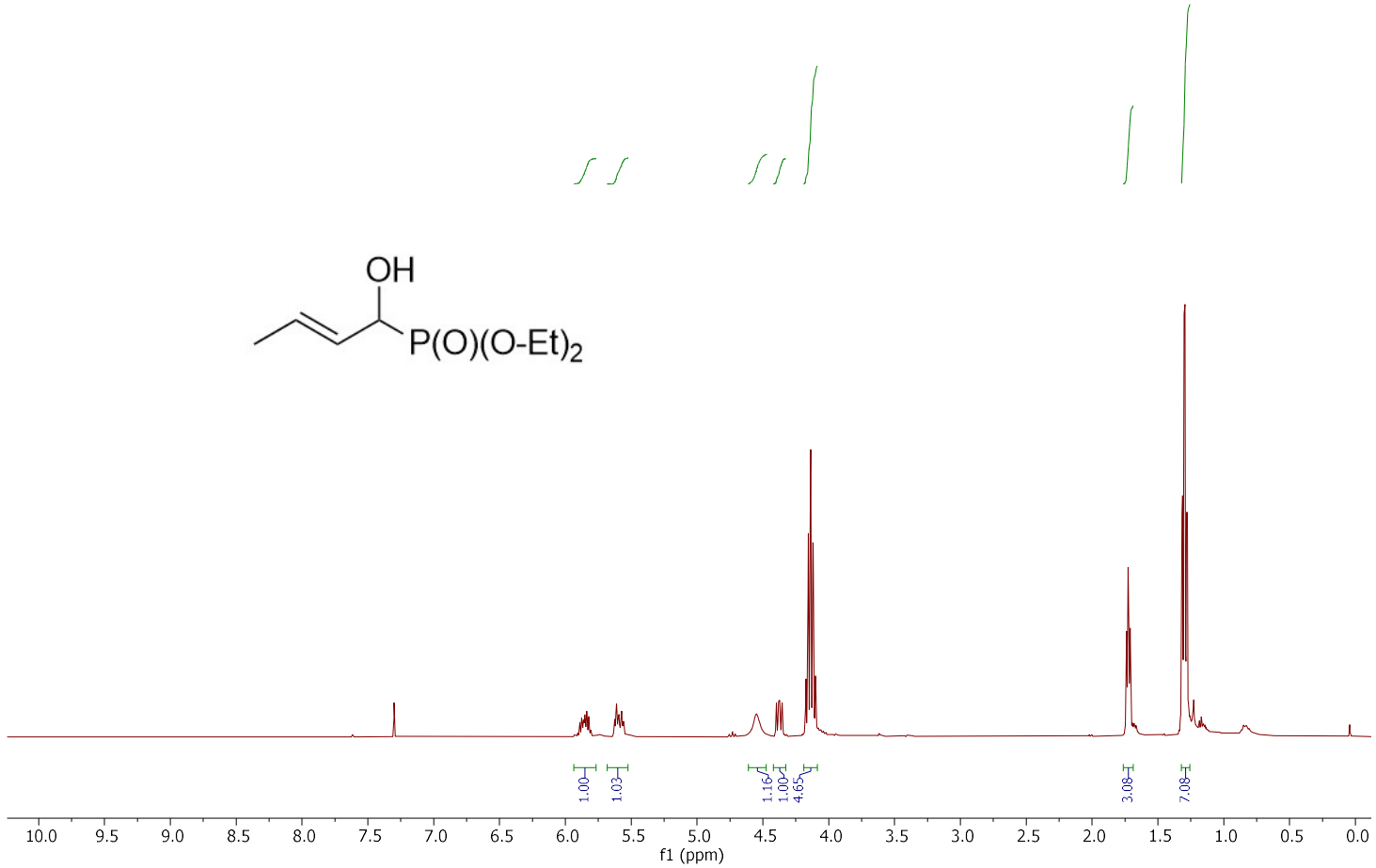


Figure S142: ^{1}H NMR Spectra of 1aa in $CDCl_3$

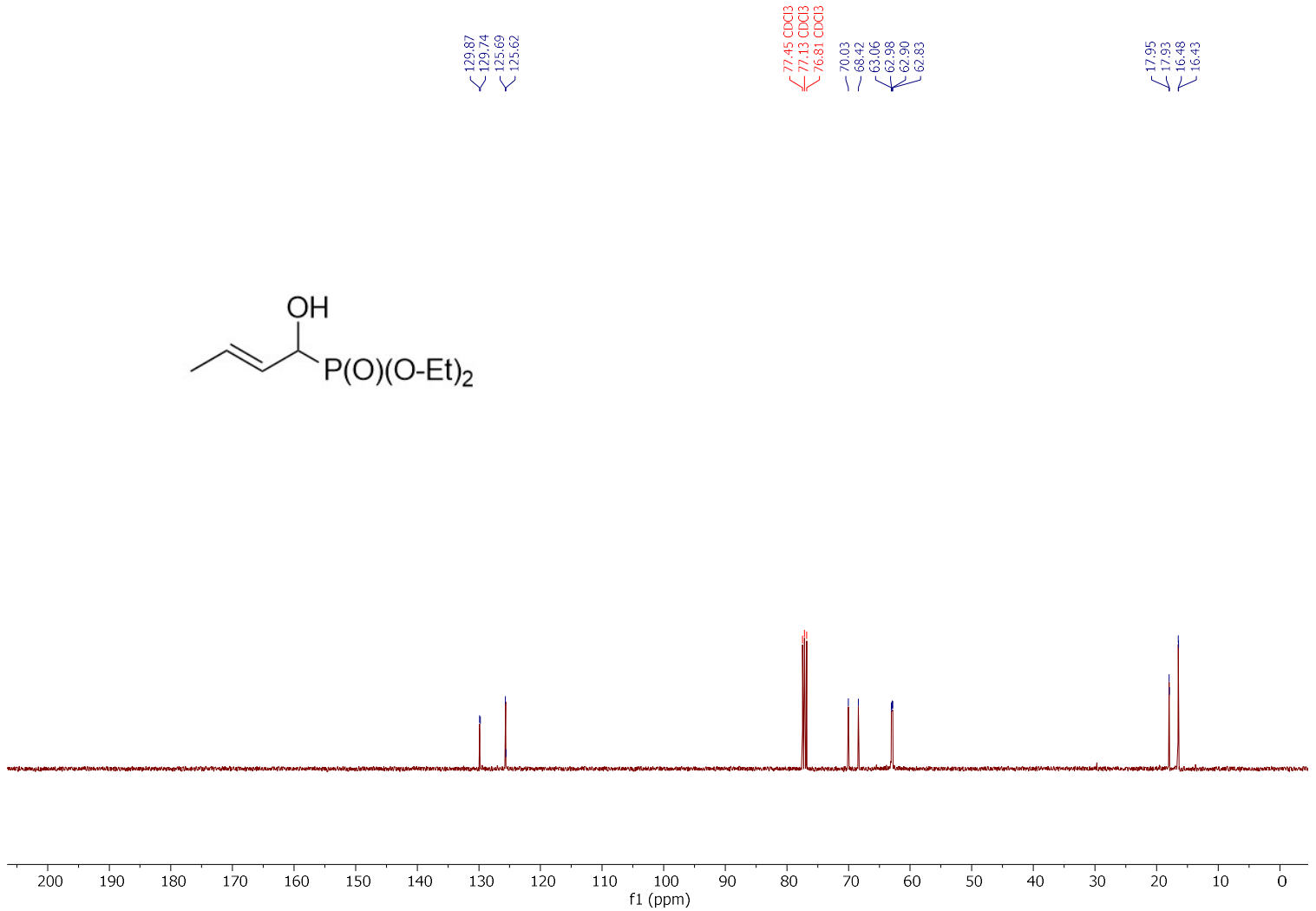


Figure S143: $^{13}C\{^{1}H\}$ NMR Spectra of 1aa in $CDCl_3$

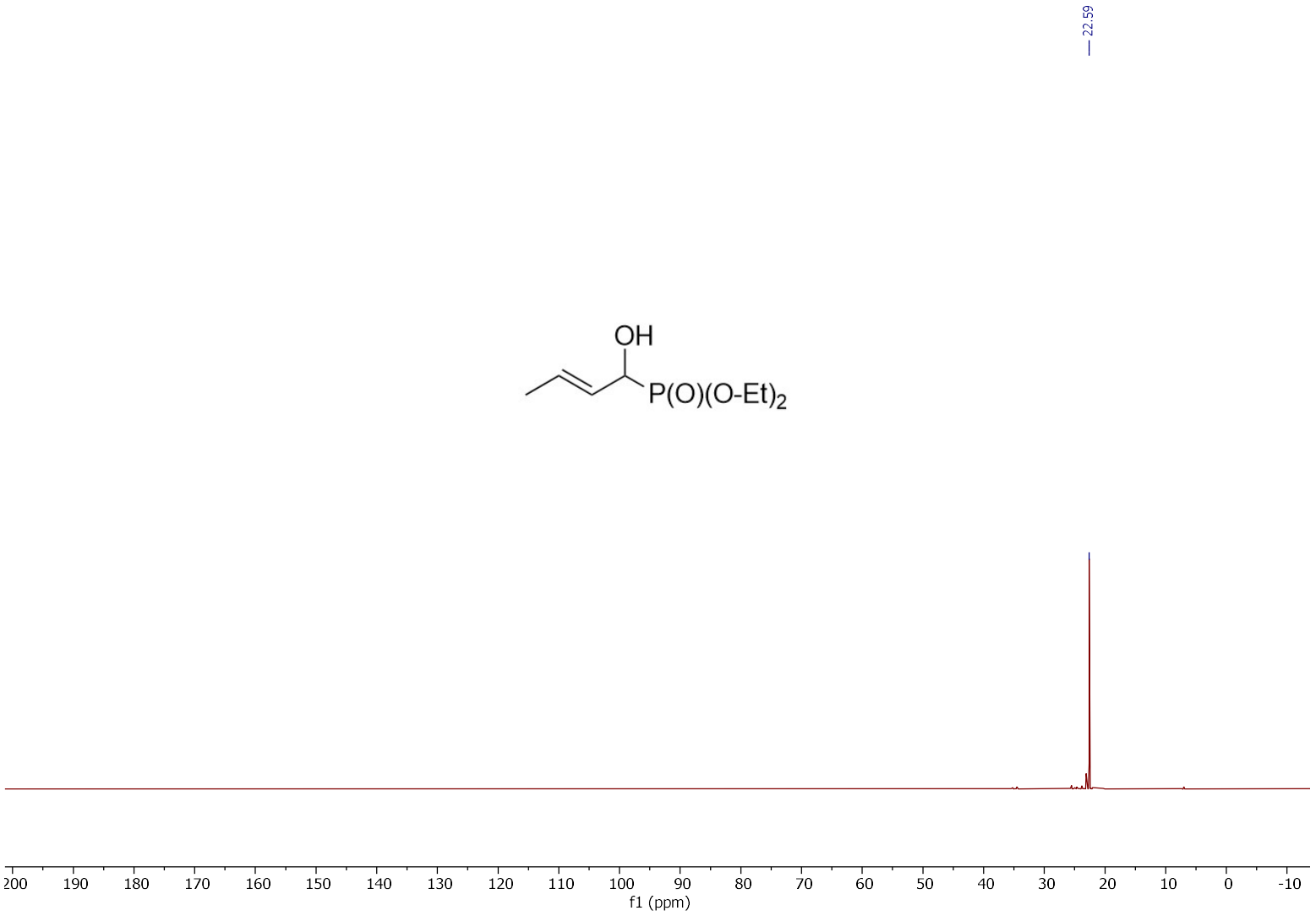


Figure S144: $^{31}P\{^{1}H\}$ NMR Spectra of 1aa in $CDCl_3$

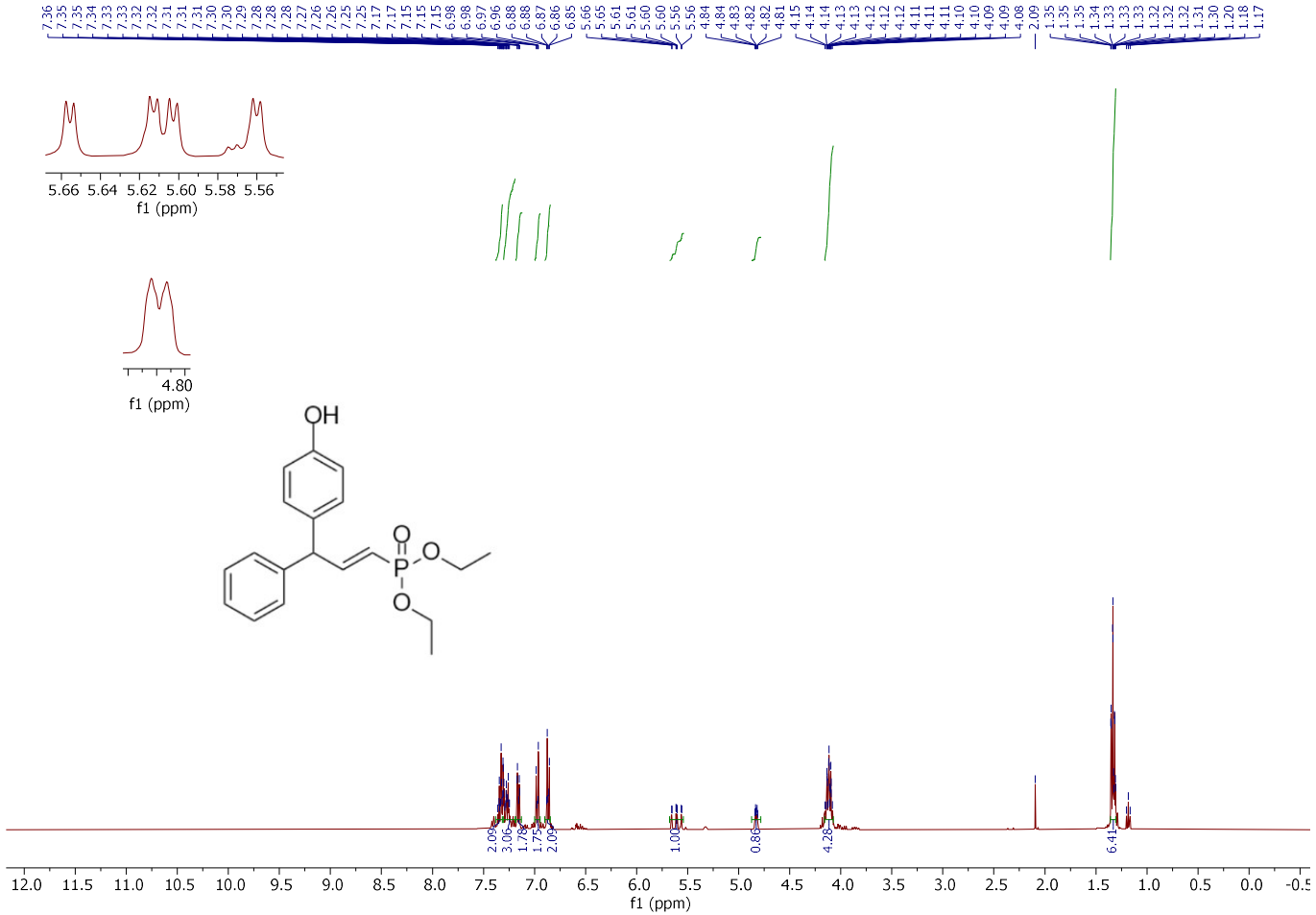


Figure S145: ^{1}H NMR Spectra of products of the reaction of Phenol with 1a in TFA in $CDCl_3$

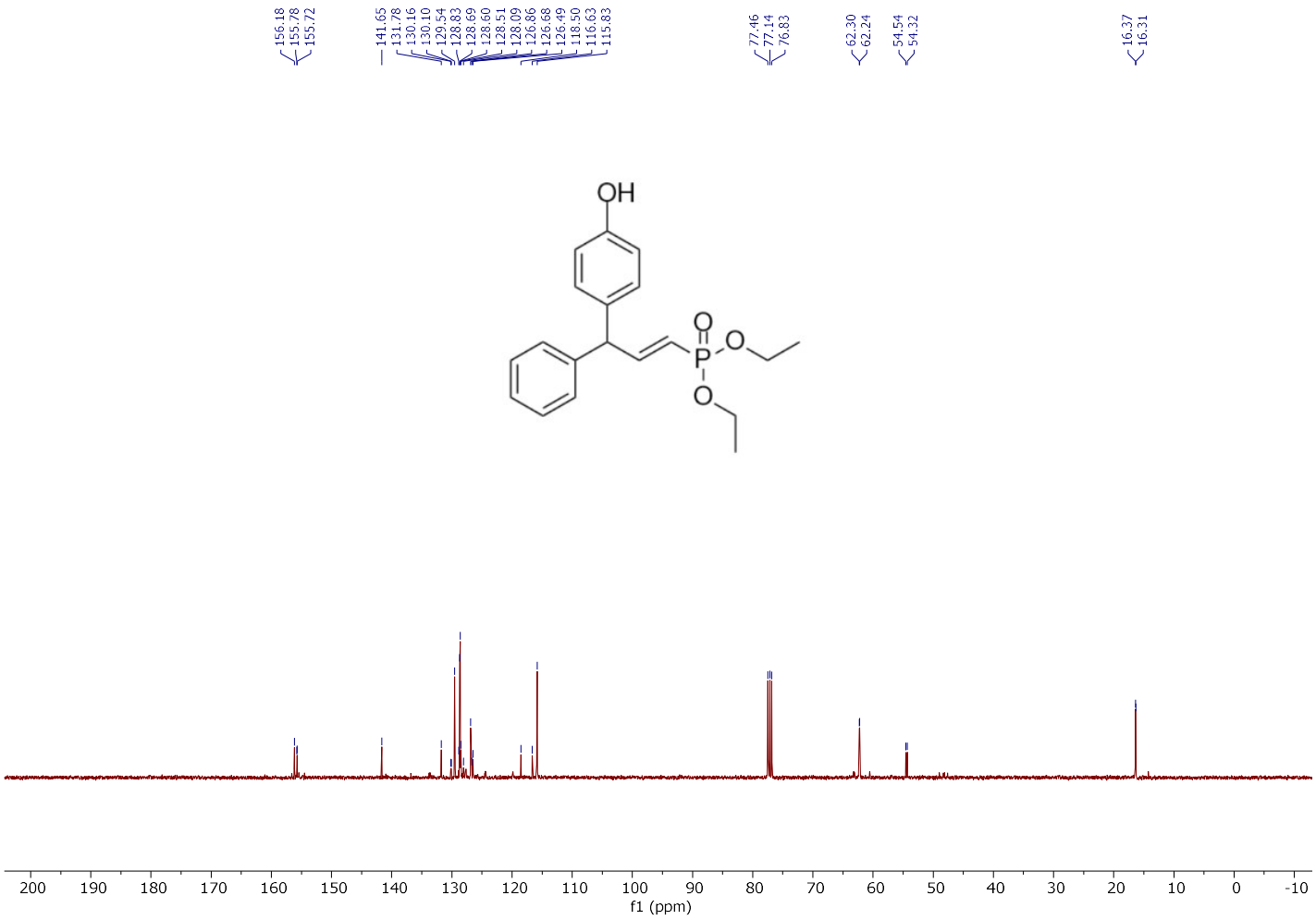


Figure S146: $^{13}C\{^{1}H\}$ NMR Spectra of products of the reaction of Phenol with 1a in TFA in $CDCl_3$

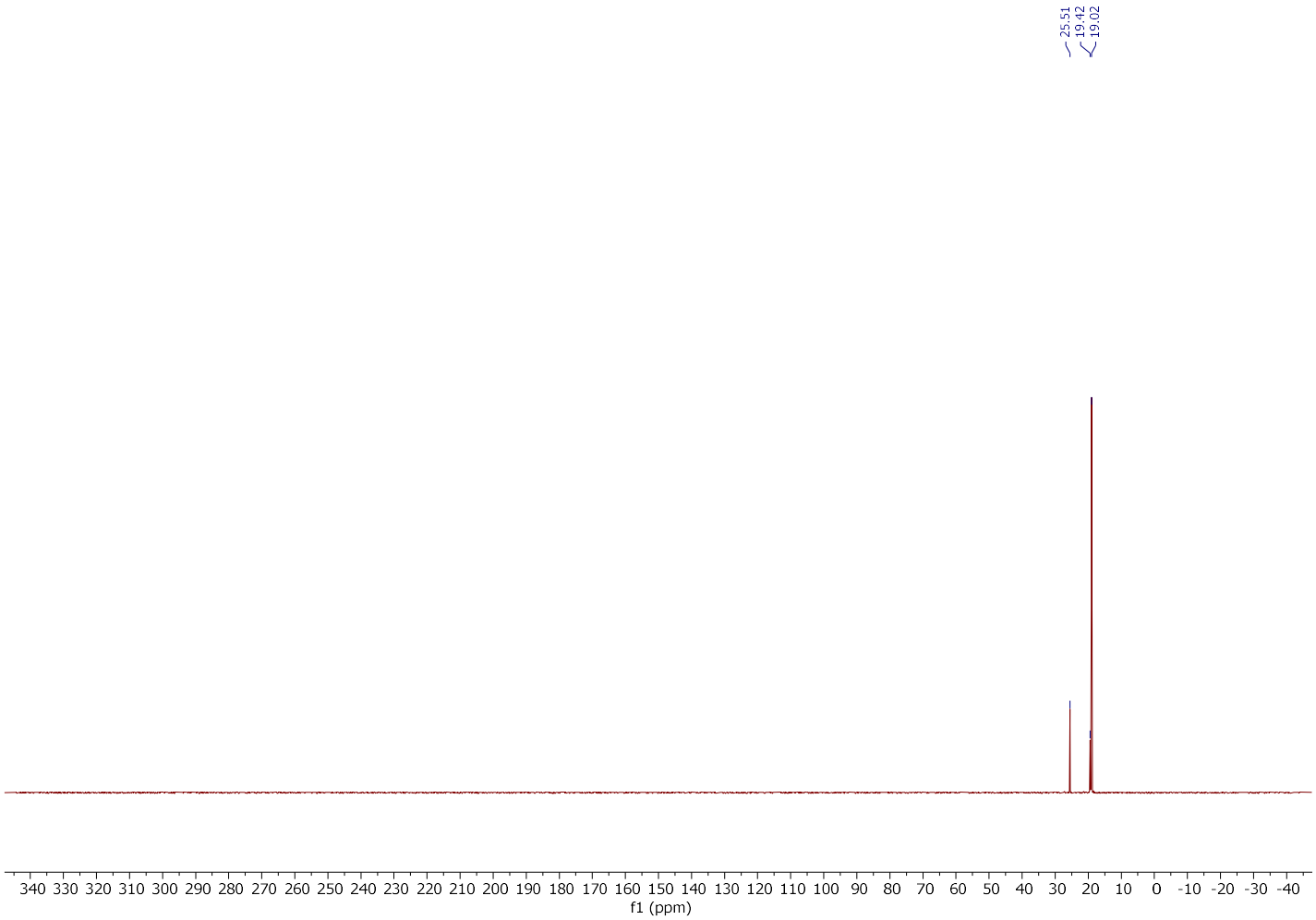


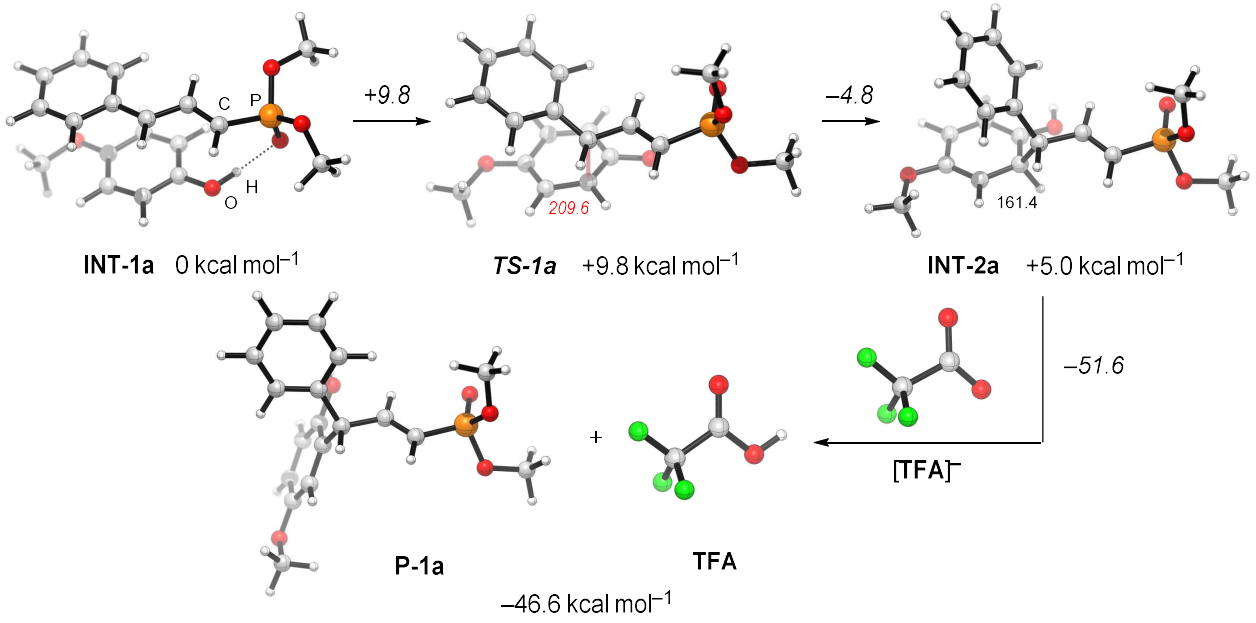
Figure S147: $^{31}P\{^{1}H\}$ NMR Spectra of products of the reaction of Phenol with 1a in TFA in $CDCl_3$

DFT calculations

All calculations were conducted by using a *Gaussian 09* program package, revision D.01.[1] Molecular geometries were optimized atPCM(AcOH)-M062X/6-31+G(d,p)level of theory. Thermochemical properties were obtained by single point calculations with frequency analysis. Free Gibbs energies Δ*G* are calculated as the values at 298 K.Single imaginary frequency was obtained in all transition states, which were supported by the intrinsic reaction coordinate (IRC) calculations using the local quadratic approximation (lqa) algorithm. Each geometry of reaction intermediates was obtained by structural optimization of the IRC geometries.

Simulated reaction paths for C-C and C-O bond forming reactions

Table S1. Molecular geometries and energies for the C-C bond forming reaction



INT-1a

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.578483	-0.591016	1.532869
2	1	1.171216	-1.385937	2.153983
3	6	0.805616	0.439576	1.121097
4	1	1.234527	1.219669	0.498387
5	6	-0.594853	0.444070	1.403657
6	1	-0.958161	-0.334166	2.074341
7	6	-1.536103	1.367374	0.923019
8	6	-2.896514	1.208168	1.313052
9	6	-1.200466	2.419124	0.022460
10	6	-3.865229	2.079546	0.855127
11	1	-3.158017	0.395726	1.985261
12	6	-2.178394	3.279583	-0.436290
13	1	-0.174695	2.555590	-0.301148
14	6	-3.507183	3.106410	-0.028340
15	1	-4.896787	1.965854	1.169460
16	1	-1.922056	4.078606	-1.122344
17	1	-4.271198	3.782345	-0.399784
18	6	-0.503276	-1.525175	-0.846982
19	6	-1.824367	-1.788546	-0.451654

TS-1a

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.054926	-0.686778	0.175723
2	1	1.561284	-1.329026	0.902831
3	6	1.389148	0.233713	-0.534104
4	1	1.939254	0.837284	-1.252816
5	6	-0.049207	0.453917	-0.383053
6	1	-0.490102	-0.069346	0.463301
7	6	-0.639394	1.760187	-0.646989
8	6	-1.813896	2.113155	0.046224
9	6	-0.086960	2.678356	-1.558286
10	6	-2.411915	3.348135	-0.154850
11	1	-2.243309	1.409849	0.755433
12	6	-0.687260	3.918286	-1.756229
13	1	0.810595	2.431297	-2.116303
14	6	-1.848590	4.252222	-1.060694
15	1	-3.312268	3.610397	0.390391
16	1	-0.250323	4.621306	-2.456871
17	1	-2.315807	5.218353	-1.221196
18	6	-0.125595	-0.663600	-2.778924
19	6	-0.953861	-0.946029	-1.653512

20	6	-0.241586	-0.459786	-1.729857	20	6	-0.535635	0.296490	-3.720502
21	6	-2.874189	-1.012761	-0.924334	21	6	-2.315119	-0.510926	-1.659122
22	1	-2.011030	-2.626195	0.212667	22	1	-0.678238	-1.809186	-1.055133
23	6	-1.281438	0.328211	-2.183664	23	6	-1.792169	0.838750	-3.600463
24	1	0.777234	-0.267951	-2.056180	24	1	0.120636	0.590613	-4.533096
25	6	-2.607902	0.068084	-1.779090	25	6	-2.711137	0.418084	-2.588620
26	1	-3.886474	-1.245298	-0.616415	26	1	-2.970083	-0.851088	-0.866150
27	1	-1.102378	1.151664	-2.867272	27	1	-2.135460	1.588322	-4.307324
28	15	3.215493	-0.834740	0.833394	28	15	3.826582	-0.854796	-0.061283
29	8	4.150635	-1.505511	1.930168	29	8	3.988638	-2.435011	-0.150230
30	8	3.764349	0.648059	0.724757	30	8	4.508216	-0.541440	1.356370
31	8	3.120583	-1.609004	-0.442163	31	8	4.351924	-0.038074	-1.184413
32	6	4.314952	-2.940052	1.976164	32	6	5.311568	-2.994173	-0.291115
33	1	3.395738	-3.410604	2.331221	33	1	5.900278	-2.779934	0.602766
34	1	4.575731	-3.316808	0.987033	34	1	5.175092	-4.067525	-0.402426
35	1	5.122740	-3.123713	2.680906	35	1	5.799021	-2.583979	-1.177639
36	6	5.055293	0.877811	0.114374	36	6	4.819223	0.823623	1.689133
37	1	5.191807	1.956452	0.101737	37	1	5.298512	0.796276	2.665635
38	1	5.834366	0.406254	0.715687	38	1	5.496056	1.246081	0.945249
39	1	5.060882	0.482824	-0.902797	39	1	3.902839	1.418408	1.744542
40	8	0.461846	-2.325683	-0.365283	40	8	1.026114	-1.316494	-2.847367
41	1	1.360907	-2.088643	-0.681598	41	1	1.582812	-1.013264	-3.581656

42	8	-3.546399	0.903571	-2.266277	42	8	-3.922752	0.998944	-2.664339
43	6	-4.914607	0.562679	-2.066895	43	6	-4.876188	0.646418	-1.669331
44	1	-5.165868	0.551951	-1.001934	44	1	-4.506653	0.915525	-0.673496
45	1	-5.489818	1.337329	-2.570477	45	1	-5.772814	1.218428	-1.897292
46	1	-5.133050	-0.413794	-2.510121	46	1	-5.097925	-0.424725	-1.709651

E(RM062X) = -1416.02667499	E(RM062X) = -1416.01044361
Zero-point correction= 0.376162 (Hartree/Particle)	Zero-point correction= 0.376299 (Hartree/Particle)
Sum of electronic and thermal Energies= -1415.625602	Sum of electronic and thermal Energies= -1415.609779
Sum of electronic and thermal Enthalpies= -1415.624658	Sum of electronic and thermal Enthalpies= -1415.608835
Sum of electronic and thermal Free Energies= -1415.705733	Sum of electronic and thermal Free Energies= -1415.690094

INT-2a

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.449793	-1.117987	1.206656
2	1	0.885240	-1.661561	1.961899
3	6	0.864132	-0.299920	0.329774
4	1	1.488067	0.218260	-0.394880
5	6	-0.620442	-0.052875	0.308920
6	1	-1.046040	-0.481399	1.220911
7	6	-0.988036	1.417905	0.246424
8	6	-1.985009	1.910713	1.093944

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Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.930680	-0.760813	1.324609
2	1	0.251367	-1.036817	2.129112
3	6	0.571810	0.086123	0.355698
4	1	1.282635	0.340749	-0.430108
5	6	-0.798493	0.707428	0.251867
6	1	-1.381230	0.366885	1.117317
7	6	-0.763183	2.235304	0.305528
8	6	0.322644	2.918855	0.857279

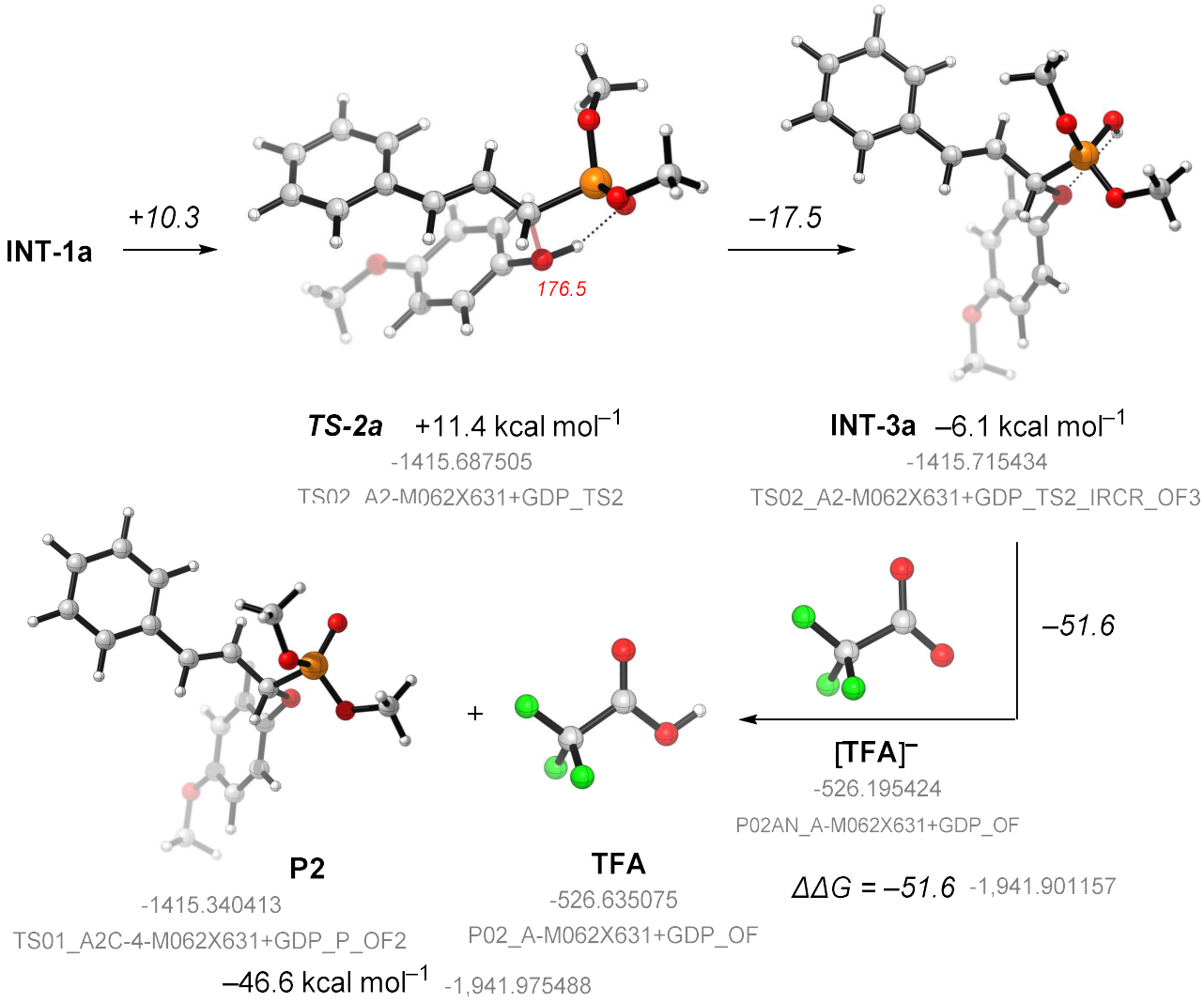
9	6	-0.365933	2.296252	-0.647650	9	6	-1.862008	2.973506	-0.147271
10	6	-2.362293	3.251303	1.044156	10	6	0.314980	4.311598	0.950316
11	1	-2.467884	1.240540	1.801314	11	1	1.185477	2.365537	1.217095
12	6	-0.742129	3.637409	-0.699847	12	6	-1.874092	4.363098	-0.051534
13	1	0.425381	1.948186	-1.307156	13	1	-2.712252	2.455751	-0.583868
14	6	-1.742211	4.117487	0.144522	14	6	-0.782868	5.039031	0.496410
15	1	-3.136139	3.618253	1.710480	15	1	1.170891	4.825522	1.377107
16	1	-0.248062	4.306962	-1.396287	16	1	-2.735525	4.919156	-0.408779
17	1	-2.032038	5.162402	0.105890	17	1	-0.789342	6.122132	0.567206
18	6	-0.889031	-0.445922	-2.188276	18	6	-1.016330	0.467792	-2.268796
19	6	-1.351709	-0.894313	-0.858257	19	6	-1.496868	0.173441	-0.989918
20	6	-1.735144	0.239409	-3.072137	20	6	-1.669425	-0.037811	-3.394374
21	6	-2.816685	-0.797688	-0.636412	21	6	-2.631696	-0.635097	-0.858169
22	1	-1.006475	-1.926509	-0.713040	22	6	-2.795715	-0.837083	-3.255827
23	6	-3.054410	0.382833	-2.727490	23	1	-1.290152	0.195406	-4.385566
24	1	-1.357428	0.628263	-4.011612	24	6	-3.284376	-1.141628	-1.982988
25	6	-3.620161	-0.153880	-1.517175	25	1	-2.992081	-0.855557	0.140692
26	1	-3.193249	-1.202415	0.296211	26	1	-3.307131	-1.234581	-4.126076
27	1	-3.731981	0.908686	-3.394886	27	15	2.573911	-1.448393	1.353083
28	15	3.228664	-1.308672	1.178379	28	8	2.299807	-3.015466	1.512867
29	8	3.392777	-2.892407	1.269406	29	8	3.190577	-1.112548	2.806364
30		3.767851	-0.859535	2.624810	30	8	3.453304	-1.032382	0.228969

31	8	3.895610	-0.614166	0.046914	31	6	3.425438	-3.903902	1.629189
32	6	4.719170	-3.450587	1.349500	32	1	3.965436	-3.702540	2.556934
33	1	5.193008	-3.147848	2.285290	33	1	3.017197	-4.912623	1.646485
34	1	4.595352	-4.531232	1.325040	34	1	4.089815	-3.785438	0.770543
35	1	5.316906	-3.123295	0.496350	35	6	3.785720	0.177804	3.002791
36	6	4.050800	0.532076	2.847919	36	1	4.157699	0.193967	4.025887
37	1	4.417856	0.608937	3.869626	37	1	4.607238	0.326608	2.299548
38	1	4.810047	0.878349	2.144953	38	1	3.037221	0.966055	2.873228
39	1	3.139626	1.127561	2.737857	39	8	0.096015	1.258439	-2.364025
40	8	0.359237	-0.704933	-2.456321	40	1	0.340485	1.381771	-3.289672
41	1	0.646711	-0.370366	-3.323833	41	8	-4.395524	-1.932356	-1.937587
42	8	-4.943273	0.058735	-1.402331	42	6	-4.905336	-2.273627	-0.660717
43	6	-5.567863	-0.412188	-0.212111	43	1	-5.214380	-1.379687	-0.107239
44	1	-5.119727	0.063751	0.666476	44	1	-5.772956	-2.906442	-0.841398
45	1	-6.615402	-0.131874	-0.292853	45	1	-4.163383	-2.828597	-0.075664
46	1	-5.477953	-1.500646	-0.137561					

E(RM062X) = -1416.01901457	E(RM062X) = -1415.64677720
Zero-point correction= 0.377970 (Hartree/Particle)	Zero-point correction= 0.364460 (Hartree/Particle)
Sum of electronic and thermal Energies= -1415.616513	Sum of electronic and thermal Energies= -1415.257440
Sum of electronic and thermal Enthalpies= -1415.615569	Sum of electronic and thermal Enthalpies= -1415.256496
Sum of electronic and thermal Free Energies= -1415.697763	Sum of electronic and thermal Free Energies= -1415.340413

[**TFA**]$^-$					**TFA**				
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z	Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.079837	-2.085665	-0.948991	1	6	-1.147908	-2.058617	-0.919631
2	6	-1.552364	-0.592583	-0.947476	2	6	-1.558242	-0.570332	-0.947569
3	8	-1.867190	-2.896615	-0.434134	3	8	-1.845186	-2.916258	-0.456505
4	8	0.037422	-2.236018	-1.475865	4	8	0.046456	-2.201262	-1.470738
5	9	-2.761992	-0.399334	-0.394220	5	1	0.306675	-3.138149	-1.456096
6	9	-0.690727	0.198552	-0.269875	6	9	-2.752487	-0.406718	-0.390864
7	9	-1.621293	-0.093005	-2.201371	7	9	-0.669680	0.172736	-0.279299
					8	9	-1.608933	-0.124217	-2.207327
E(RM062X) = -526.191000752					E(RM062X) = -526.643381074				
Zero-point correction= 0.026627 (Hartree/Particle)					Zero-point correction= 0.039659 (Hartree/Particle)				
Sum of electronic and thermal Energies= -526.158437					Sum of electronic and thermal Energies= -526.597519				
Sum of electronic and thermal Enthalpies= -526.157493					Sum of electronic and thermal Enthalpies= -526.596575				
Sum of electronic and thermal Free Energies= -526.195424					Sum of electronic and thermal Free Energies= -526.635075				

Table S2. Molecular geometries and energies for the C-O bond forming reaction



TS-2a

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.775525	-0.573795	1.020557
2	1	1.670002	-1.160506	1.931216
3	6	1.052009	0.663521	0.944455
4	1	1.331006	1.389776	0.186639
5	6	-0.097599	0.792933	1.658006
6	1	-0.302088	0.045707	2.425638
7	6	-1.133290	1.796778	1.477184
8	6	-2.232564	1.784682	2.352271
9	6	-1.111957	2.720844	0.417173
10	6	-3.278822	2.685456	2.185729
11	1	-2.259667	1.062038	3.163465
12	6	-2.157989	3.618867	0.252493
13	1	-0.286699	2.729660	-0.287767
14	6	-3.241817	3.602648	1.135083
15	1	-4.121604	2.670769	2.868612
16	1	-2.137364	4.327408	-0.568620
17	1	-4.059168	4.303438	0.998868
18	6	-0.296088	-1.348155	-0.486202

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Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.811020	-0.488674	0.066013
2	1	0.419656	-1.030096	0.937971
3	6	0.380551	0.944248	0.067534
4	1	0.634071	1.519752	-0.821905
5	6	-0.274153	1.485266	1.103783
6	1	-0.543520	0.838698	1.939655
7	6	-0.684002	2.891074	1.231437
8	6	-1.608777	3.233979	2.227035
9	6	-0.176396	3.902233	0.400581
10	6	-2.037705	4.550791	2.375906
11	1	-1.998163	2.459307	2.882007
12	6	-0.602999	5.216987	0.550981
13	1	0.564347	3.667628	-0.358423
14	6	-1.537172	5.544726	1.536562
15	1	-2.758965	4.800057	3.147223
16	1	-0.201621	5.990475	-0.095689
17	1	-1.866236	6.572294	1.652473
18	6	-0.818657	-1.529228	-1.300027

19	6	-1.371516	-1.726479	0.300256	19	6	-1.283555	-2.700171	-0.722361
20	6	-0.444589	-0.480585	-1.567872	20	6	-1.663427	-0.711141	-2.047337
21	6	-2.643423	-1.236854	0.004040	21	6	-2.618632	-3.074570	-0.887963
22	1	-1.214017	-2.389508	1.145126	22	1	-0.604803	-3.326965	-0.151600
23	6	-1.706409	0.000217	-1.868305	23	6	-2.989575	-1.080255	-2.217532
24	1	0.420149	-0.176214	-2.151824	24	1	-1.277445	0.199865	-2.492924
25	6	-2.808945	-0.357722	-1.071924	25	6	-3.473812	-2.261138	-1.637558
26	1	-3.480259	-1.531790	0.624177	26	1	-2.969206	-3.994166	-0.436408
27	1	-1.863888	0.678855	-2.699369	27	1	-3.671029	-0.466638	-2.796763
28	15	3.430821	-0.675805	0.230809	28	15	2.626945	-0.618666	0.115169
29	8	4.305109	-1.266818	1.399389	29	8	2.965088	-2.058073	0.598627
30	8	3.978398	0.793922	0.019520	30	8	3.340079	0.371901	1.080763
31	8	3.278913	-1.466504	-1.032971	31	8	3.179202	-0.299011	-1.326912
32	6	5.744467	-1.376387	1.257861	32	6	4.338559	-2.531123	0.742690
33	1	6.095110	-1.840161	2.176001	33	1	4.250447	-3.566780	1.057466
34	1	5.983969	-2.006429	0.400099	34	1	4.846658	-2.462261	-0.219095
35	1	6.174393	-0.380525	1.144828	35	1	4.841092	-1.934489	1.502942
36	6	4.033049	1.399991	-1.295022	36	6	3.542440	1.794718	0.831716
37	1	4.190415	2.461874	-1.121975	37	1	4.423604	2.063929	1.407739
38	1	4.865260	0.973731	-1.854324	38	1	3.710819	1.963547	-0.231919
39	1	3.097924	1.234568	-1.831767	39	1	2.663969	2.332186	1.186555
40	8	0.975168	-1.724943	-0.051608	40	8	0.525233	-1.174653	-1.150867

41	1	1.672569	-1.839504	-0.773452	41	1	2.626004	-0.640829	-2.054460
42	8	-3.985781	0.200281	-1.421741	42	8	-4.783978	-2.533151	-1.860230
43	6	-5.115104	-0.048719	-0.593822	43	6	-5.320804	-3.720533	-1.297025
44	1	-4.925540	0.294724	0.428829	44	1	-5.247269	-3.703727	-0.204474
45	1	-5.933532	0.522323	-1.027512	45	1	-6.368415	-3.744449	-1.591494
46	1	-5.370417	-1.112980	-0.591229	46	1	-4.809238	-4.606039	-1.688770

E(RM062X) = -1416.00784106	E(RM062X) = -1416.03455818
Zero-point correction= 0.375726 (Hartree/Particle)	Zero-point correction= 0.376991 (Hartree/Particle)
Sum of electronic and thermal Energies= -1415.608038	Sum of electronic and thermal Energies= -1415.632861
Sum of electronic and thermal Enthalpies= -1415.607094	Sum of electronic and thermal Enthalpies= -1415.631916
Sum of electronic and thermal Free Energies= -1415.687505	Sum of electronic and thermal Free Energies= -1415.715434

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Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	0.914808	-0.488625	-0.063847
2	1	0.564086	-1.021701	0.831817
3	6	0.414211	0.924180	-0.064954
4	1	0.650273	1.506349	-0.954772
5	6	-0.254197	1.451421	0.967872
6	1	-0.494958	0.804745	1.812495
7	6	-0.712772	2.846091	1.084550

8	6	-1.674351	3.165252	2.052984
9	6	-0.213922	3.872852	0.268042
10	6	-2.146701	4.469010	2.188216
11	1	-2.058105	2.380008	2.699084
12	6	-0.684531	5.174997	0.403147
13	1	0.557231	3.657272	-0.465718
14	6	-1.654729	5.477737	1.361194
15	1	-2.895753	4.696687	2.939977
16	1	-0.286992	5.958835	-0.233853
17	1	-2.017204	6.495327	1.466463
18	6	-0.783989	-1.522013	-1.327592
19	6	-1.289639	-2.593546	-0.604252
20	6	-1.616829	-0.783451	-2.168267
21	6	-2.638531	-2.941606	-0.712101
22	1	-0.627186	-3.167482	0.037251
23	6	-2.956696	-1.126258	-2.284286
24	1	-1.203727	0.049693	-2.727837
25	6	-3.474065	-2.204616	-1.555235
26	1	-3.013974	-3.784195	-0.144478
27	1	-3.623000	-0.569197	-2.934575
28	15	2.744017	-0.490584	-0.002751
29	8	3.052524	-2.038170	0.231486

30	8	3.092284	0.151368	1.428638
31	8	3.432455	0.170509	-1.140313
32	6	4.425306	-2.471541	0.254516
33	1	4.401063	-3.551290	0.386939
34	1	4.913773	-2.219694	-0.688604
35	1	4.950628	-2.004929	1.091279
36	6	3.489053	1.531154	1.524045
37	1	3.894679	1.661578	2.526010
38	1	4.248763	1.758007	0.774691
39	1	2.620196	2.179951	1.386625
40	8	0.562423	-1.200624	-1.247528
41	8	-4.799110	-2.460618	-1.734368
42	6	-5.362143	-3.547970	-1.020116
43	1	-5.276159	-3.395130	0.061309
44	1	-6.413782	-3.580023	-1.300457
45	1	-4.880502	-4.492094	-1.297174

E(RM062X) = -1415.62892204

Zero-point correction= 0.364475 (Hartree/Particle)

Sum of electronic and thermal Energies= -1415.239813

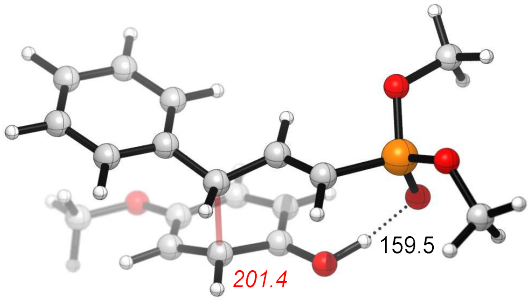
Sum of electronic and thermal Enthalpies= -1415.238869

Sum of electronic and thermal Free Energies= -1415.323685

Energetic impact of H-bonding or non-H-bonding transition states

As shown in Table S3, the H-bonding between phenolic hydroxy group and phosphoryl group slightly destabilized the transition state for the C-C bond formation step ($\Delta\Delta G$ = +0.3 kcal mol^{-1}by the H-bonding). In contrast, this H-bonding highly stabilized the transition state for the C-O bond formation step ($\Delta\Delta G$ = +1.1 kcal mol^{-1}bylack of the H-bonding).

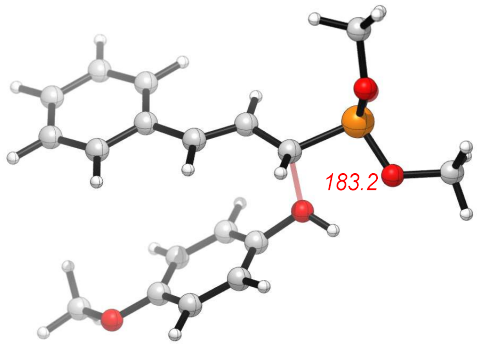
Table S3. Molecular geometries and energies



TS-1a' +10.1 kcal mol^{-1}

H-bond-assisted version of ***TS-1a***

($\Delta\Delta G$ = +0.3 kcal mol^{-1})



TS-2a' +12.5 kcal mol^{-1}

non H-bonding version of ***TS-2a***

($\Delta\Delta G$ = +1.1 kcal mol^{-1})

TS-1a'

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.019763	-0.265267	0.602942
2	1	1.691810	-1.071857	1.255270

TS-2a'

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.555898	-0.361830	0.514528
2	1	1.209191	-0.861228	1.419651

3	6	1.151265	0.589061	0.042496	3	6	0.936995	0.871022	0.169197
4	1	1.529054	1.361117	-0.624865	4	1	1.399577	1.481658	-0.600500
5	6	-0.306896	0.455341	0.163596	5	6	-0.294132	1.151668	0.689133
6	1	-0.616543	-0.144868	1.017895	6	1	-0.695497	0.460749	1.432189
7	6	-1.134261	1.657029	-0.046918	7	6	-1.169829	2.250876	0.336256
8	6	-2.340555	1.773439	0.661194	8	6	-2.477180	2.240705	0.853566
9	6	-0.778267	2.661594	-0.959376	9	6	-0.777184	3.289704	-0.528363
10	6	-3.165367	2.876136	0.475987	10	6	-3.378230	3.243109	0.510594
11	1	-2.624191	0.992246	1.361662	11	1	-2.781094	1.436526	1.518790
12	6	-1.614534	3.758863	-1.154869	12	6	-1.675863	4.293142	-0.859672
13	1	0.144419	2.597403	-1.527123	13	1	0.229971	3.318205	-0.931335
14	6	-2.804820	3.870103	-0.437935	14	6	-2.976667	4.269321	-0.344140
15	1	-4.088226	2.962297	1.039874	15	1	-4.386612	3.227199	0.909886
16	1	-1.332560	4.528797	-1.865139	16	1	-1.368956	5.097045	-1.519932
17	1	-3.450331	4.729371	-0.587777	17	1	-3.675134	5.056460	-0.609278
18	6	0.283600	-1.071252	-1.879052	18	6	-0.521253	-1.626464	-0.644231
19	6	-0.955763	-0.916428	-1.160192	19	6	-1.202337	-2.329880	0.349656
20	6	0.532639	-0.248878	-3.010134	20	6	-1.181979	-0.819271	-1.555911
21	6	-2.072375	-0.316960	-1.847921	21	6	-2.581550	-2.230251	0.405143
22	1	-1.171712	-1.707983	-0.448307	22	1	-0.662573	-2.940961	1.067759
23	6	-0.512999	0.454486	-3.539840	23	6	-2.570633	-0.710422	-1.493757
24	1	1.513056	-0.246406	-3.474848	24	1	-0.613473	-0.272957	-2.301335

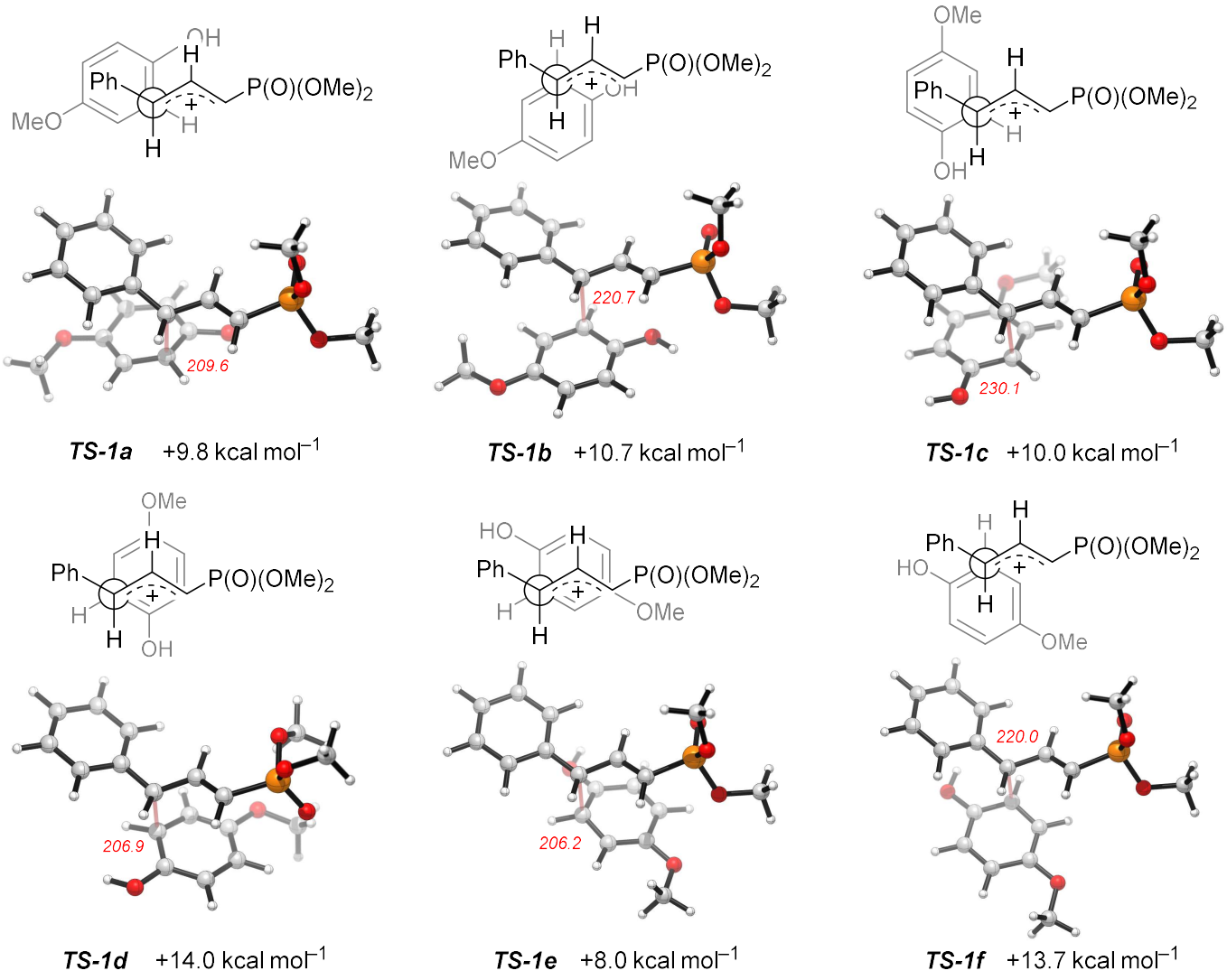
25	6	-1.842101	0.396642	-2.988273	25	6	-3.271315	-1.409245	-0.505010
26	1	-3.048229	-0.358399	-1.380810	26	1	-3.150164	-2.767275	1.156045
27	1	-0.371119	1.064251	-4.427583	27	1	-3.081087	-0.073526	-2.204851
28	15	3.664753	-0.373865	-0.087997	28	15	3.328393	-0.591348	0.136379
29	8	4.701958	-0.916266	0.983832	29	8	3.351663	-2.185622	0.095002
30	8	4.090529	1.135764	-0.301453	30	8	4.069769	-0.251222	1.501205
31	8	3.614875	-1.216103	-1.338998	31	8	3.793056	0.150508	-1.053757
32	6	4.992674	-2.325835	1.102916	32	6	4.598728	-2.874502	-0.170996
33	1	4.181714	-2.825612	1.635838	33	1	5.305557	-2.667258	0.633660
34	1	5.128975	-2.764029	0.113836	34	1	4.355792	-3.933754	-0.196470
35	1	5.912490	-2.392634	1.679524	35	1	4.997891	-2.551797	-1.133334
36	6	5.347190	1.431099	-0.953530	36	6	4.718891	1.027638	1.691716
37	1	5.383915	2.513163	-1.053594	37	1	5.375179	0.901450	2.549722
38	1	6.172643	1.081383	-0.331431	38	1	5.294151	1.289762	0.803827
39	1	5.376657	0.957781	-1.936393	39	1	3.968764	1.792141	1.901320
40	8	1.149675	-1.907317	-1.396150	40	8	0.876879	-1.589070	-0.663527
41	1	2.126053	-1.714162	-1.618407	41	1	1.301905	-2.447254	-0.463465
42	8	-2.753253	1.091999	-3.692371	42	8	-4.609306	-1.354688	-0.341871
43	6	-4.064175	1.175153	-3.143066	43	6	-5.352329	-0.498512	-1.201489
44	1	-4.027490	1.623213	-2.143484	44	1	-5.258379	-0.817118	-2.244242
45	1	-4.631566	1.813327	-3.816905	45	1	-6.389375	-0.585925	-0.884047
46	1	-4.524894	0.183343	-3.094649	46	1	-5.018607	0.539254	-1.096049

E(RM062X) = -1416.00923982	E(RM062X) = -1416.00486883
Zero-point correction= 0.375113 (Hartree/Particle)	Zero-point correction= 0.376148 (Hartree/Particle)
Sum of electronic and thermal Energies= -1415.610034	Sum of electronic and thermal Energies= -1415.604164
Sum of electronic and thermal Enthalpies= -1415.609090	Sum of electronic and thermal Enthalpies= -1415.603220
Sum of electronic and thermal Free Energies= -1415.689633	Sum of electronic and thermal Free Energies= -1415.685735

Conformational flexibility of the transition states and Eyringkinetic analysis

To consider conformational influence to the reaction outcome, approaching direction of *p*-methoxyphenol was examined. Conformational varieties of *p*-methoxyphenol and dimethyl phosphonate moiety havebeen fixed. As shown in Table S4, six possibilities were considered for the transition states of the C-C bond forming step. Gibbs energies differences were calculated from the value of **INT-1a**. For the C-O bond forming reaction, two possibilities keeping the H-boning was computed (Table S5).

Table S4. Considered transition states, molecular geometries and energies



TS-1b

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.612698	-0.065992	0.501442
2	1	1.178792	-0.692726	1.280679
3	6	0.858445	0.806849	-0.186456
4	1	1.313637	1.414060	-0.965152
5	6	-0.565395	0.902728	0.065545
6	1	-0.932654	0.333613	0.920154
7	6	-1.327907	2.099363	-0.254190
8	6	-2.467097	2.383648	0.521409
9	6	-0.958261	2.978126	-1.288632
10	6	-3.211926	3.530637	0.280614
11	1	-2.750467	1.705696	1.322340
12	6	-1.713863	4.116897	-1.533681
13	1	-0.092746	2.768580	-1.909294
14	6	-2.837755	4.395080	-0.750319
15	1	-4.080851	3.752069	0.890781
16	1	-1.429139	4.790816	-2.334097
17	1	-3.421858	5.288711	-0.944372
18	6	-0.647752	-1.650162	-0.901342

TS-1c

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.385824	-0.384617	0.302560
2	1	0.953383	-1.012001	1.079659
3	6	0.651098	0.501097	-0.387106
4	1	1.129834	1.106331	-1.153303
5	6	-0.765688	0.698481	-0.107084
6	1	-1.186446	0.085628	0.690755
7	6	-1.445652	1.928407	-0.387401
8	6	-2.602413	2.239397	0.366625
9	6	-1.010231	2.829697	-1.383791
10	6	-3.277201	3.427082	0.153807
11	1	-2.939299	1.544504	1.131418
12	6	-1.703147	4.015668	-1.601268
13	1	-0.134465	2.607849	-1.984248
14	6	-2.827812	4.314970	-0.833907
15	1	-4.150294	3.671998	0.748275
16	1	-1.364816	4.704747	-2.366857
17	1	-3.360734	5.245253	-1.001729
18	6	-2.851751	-0.581763	-1.311590

19	6	-1.217391	-2.481034	0.085651	19	6	-3.584231	0.337671	-2.073335
20	6	-1.377959	-0.539655	-1.394039	20	6	-1.507671	-0.846243	-1.642178
21	6	-2.529997	-2.286766	0.441544	21	6	-2.980824	0.946097	-3.154029
22	1	-0.636560	-3.285773	0.525086	22	1	-4.604700	0.588984	-1.801598
23	6	-2.766219	-0.427052	-1.090852	23	6	-0.939141	-0.304210	-2.824005
24	1	-0.973167	-0.012609	-2.252757	24	1	-1.000052	-1.648734	-1.117183
25	6	-3.328125	-1.269951	-0.161384	25	6	-1.655958	0.619930	-3.553719
26	1	-2.997941	-2.921304	1.187620	26	1	-3.518536	1.686649	-3.738351
27	1	-3.330223	0.371667	-1.556849	27	1	0.071617	-0.589485	-3.090947
28	15	3.339673	-0.333666	0.087052	28	15	3.145246	-0.527399	-0.045148
29	8	3.286651	-1.909429	-0.190435	29	8	3.315250	-2.107226	-0.101302
30	8	4.173707	-0.279487	1.450334	30	8	3.911251	-0.162664	1.313344
31	8	3.846107	0.545023	-0.992867	31	8	3.574074	0.265426	-1.223687
32	6	4.520431	-2.605019	-0.481283	32	6	4.628938	-2.664798	-0.320399
33	1	4.243445	-3.634241	-0.698089	33	1	4.493937	-3.742973	-0.367561
34	1	5.004691	-2.155706	-1.350070	34	1	5.038972	-2.295707	-1.262259
35	1	5.177520	-2.566152	0.389058	35	1	5.284510	-2.403405	0.512262
36	6	4.787875	0.959230	1.859178	36	6	4.285528	1.205882	1.559905
37	1	4.020359	1.685903	2.136343	37	1	3.392973	1.828990	1.662697
38	1	5.399896	0.719002	2.726000	38	1	4.842093	1.202984	2.494768
39	1	5.407211	1.353430	1.052790	39	1	4.909910	1.575653	0.745668
40	8	0.586643	-1.805332	-1.361812	40	8	-3.338084	-1.174767	-0.209066

41	1	1.098219	-2.493176	-0.902714	41	1	-4.258164	-0.921025	-0.047022
42	8	-4.609335	-1.234216	0.257930	42	8	-1.212969	1.269845	-4.650675
43	6	-5.454530	-0.244606	-0.316910	43	6	0.111988	0.987418	-5.085423
44	1	-5.535769	-0.389368	-1.399057	44	1	0.215430	-0.069648	-5.349860
45	1	-6.429034	-0.376172	0.148093	45	1	0.276171	1.605180	-5.965654
46	1	-5.073604	0.760785	-0.104291	46	1	0.840298	1.248616	-4.309184

E(RM062X) = -1416.00646923	E(RM062X) = -1416.00888716
Zero-point correction= 0.375189 (Hartree/Particle)	Zero-point correction= 0.375705 (Hartree/Particle)
Sum of electronic and thermal Energies=-1415.606526	Sum of electronic and thermal Energies= -1415.608573
Sum of electronic and thermal Enthalpies= -1415.605581	Sum of electronic and thermal Enthalpies= -1415.607628
Sum of electronic and thermal Free Energies= -1415.688686	Sum of electronic and thermal Free Energies= -1415.689816

TS-1d

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.866712	-0.739488	0.440709
2	1	1.437269	-1.568159	1.000802
3	6	1.100535	0.238875	-0.065102
4	1	1.565029	1.056960	-0.609276
5	6	-0.351712	0.236944	0.069248
6	1	-0.737449	-0.461997	0.810949
7	6	-1.106778	1.495394	-0.005282

TS-1e

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.605284	-0.105940	0.423376
2	1	1.166391	-0.782083	1.154861
3	6	0.877792	0.828400	-0.208165
4	1	1.375007	1.474109	-0.927966
5	6	-0.562148	0.948032	-0.014535
6	1	-0.940773	0.409612	0.852086
7	6	-1.276061	2.193959	-0.296746

8	6	-2.265848	1.623214	0.776694	8	6	-2.531173	2.393972	0.306365
9	6	-0.700792	2.565662	-0.819441	9	6	-0.752478	3.195573	-1.132304
10	6	-2.997092	2.806258	0.759594	10	6	-3.241384	3.565501	0.086751
11	1	-2.580375	0.797327	1.409567	11	1	-2.941063	1.625358	0.957120
12	6	-1.438042	3.742293	-0.838921	12	6	-1.464458	4.370763	-1.346420
13	1	0.183045	2.481989	-1.444654	13	1	0.213703	3.071257	-1.610097
14	6	-2.584955	3.865082	-0.049410	14	6	-2.707695	4.556221	-0.742120
15	1	-3.884149	2.902807	1.376035	15	1	-4.205200	3.712467	0.561764
16	1	-1.121042	4.566261	-1.468908	16	1	-1.049138	5.142294	-1.985618
17	1	-3.156010	4.787466	-0.066761	17	1	-3.260767	5.473997	-0.913093
18	6	-1.018291	-2.030511	-0.998694	18	6	-0.833918	0.039746	-2.456817
19	6	-1.032392	-0.743508	-1.620303	19	6	0.363692	-0.508935	-2.957884
20	6	0.094018	-2.858707	-1.160821	20	6	-1.399716	-0.474118	-1.250380
21	6	-0.056028	-0.450562	-2.624320	21	6	0.876334	-1.629548	-2.355087
22	1	-1.980097	-0.215068	-1.667333	22	1	0.857188	-0.066432	-3.816855
23	6	1.107346	-2.476903	-2.020705	23	6	-0.929659	-1.724949	-0.740316
24	1	0.145447	-3.796795	-0.619972	24	1	-2.419071	-0.174419	-1.028104
25	6	1.026316	-1.278807	-2.791676	25	6	0.214917	-2.276593	-1.260602
26	1	-0.135954	0.463269	-3.203989	26	1	1.796707	-2.077839	-2.717502
27	1	1.977477	-3.117516	-2.111239	27	1	-1.461937	-2.175085	0.088846
28	15	3.635401	-0.804971	0.123663	28	15	3.359817	-0.250946	0.071532
29	8	4.221126	-0.769130	1.600880	29	8	3.482787	-1.813311	-0.205941

30	8	4.024219	0.627081	-0.476510	30	8	4.129849	-0.109715	1.470435
31	8	4.043003	-1.945881	-0.737953	31	8	3.829774	0.679042	-0.986132
32	6	5.650751	-0.847553	1.785639	32	6	4.781803	-2.384574	-0.461765
33	1	5.816587	-0.831122	2.860355	33	1	4.609009	-3.434031	-0.690995
34	1	6.031438	-1.777071	1.358989	34	1	5.249744	-1.886709	-1.313409
35	1	6.132418	0.014538	1.319292	35	1	5.408801	-2.291286	0.426926
36	6	4.352167	0.767180	-1.874336	36	6	4.493203	1.203906	1.933578
37	1	4.705327	1.789319	-1.996133	37	1	3.595593	1.796534	2.131178
38	1	5.136186	0.060097	-2.149183	38	1	5.047686	1.056944	2.858218
39	1	3.465775	0.597861	-2.492128	39	1	5.117102	1.703603	1.191279
40	8	-1.987299	-2.434669	-0.177677	40	8	-1.463360	1.057780	-3.016991
41	1	-2.784178	-1.887122	-0.245408	41	1	-0.989980	1.410242	-3.787326
42	8	1.973844	-0.908165	-3.679270	42	8	0.793067	-3.421797	-0.863839
43	6	3.033273	-1.824651	-3.970878	43	6	0.210101	-4.101449	0.241567
44	1	2.630766	-2.759172	-4.373821	44	1	-0.815737	-4.405283	0.010552
45	1	3.638615	-1.332356	-4.729833	45	1	0.826816	-4.981227	0.410834
46	1	3.634970	-2.016461	-3.076950	46	1	0.220442	-3.464785	1.132848

E(RM062X) = -1416.00696121	E(RM062X) = -1416.01387813
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Sum of electronic and thermal Enthalpies= -1415.605008	Sum of electronic and thermal Enthalpies= -1415.612289
Sum of electronic and thermal Free Energies= -1415.683443	Sum of electronic and thermal Free Energies= -1415.692955

TS-1f

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.593336	-0.201846	0.424868
2	1	1.203979	-0.794791	1.250828
3	6	0.807534	0.602037	-0.304439
4	1	1.241599	1.172934	-1.121719
5	6	-0.609864	0.773757	0.018175
6	1	-0.963781	0.197217	0.872986
7	6	-1.271634	2.037941	-0.212328
8	6	-2.350655	2.391635	0.623353
9	6	-0.867287	2.927892	-1.231261
10	6	-2.975335	3.622942	0.482163
11	1	-2.680388	1.696078	1.390851
12	6	-1.516336	4.142959	-1.387033
13	1	-0.056062	2.667905	-1.903233
14	6	-2.561306	4.495680	-0.525098
15	1	-3.790597	3.896948	1.142135
16	1	-1.207456	4.823224	-2.172837
17	1	-3.057044	5.453234	-0.646434
18	6	-0.826115	-1.857305	-1.035241
19	6	-1.426358	-2.664351	-0.094343

20	6	-1.441431	-0.645138	-1.442856
21	6	-2.705076	-2.303280	0.417299
22	6	-2.772471	-0.377992	-1.027447
23	1	-1.039508	-0.114541	-2.303008
24	6	-3.366952	-1.184862	-0.043353
25	1	-3.185533	-2.916536	1.170649
26	15	3.350808	-0.295967	0.057249
27	8	3.581009	-1.869440	0.072496
28	8	4.115749	0.159983	1.389623
29	8	3.740367	0.456214	-1.160663
30	6	4.913989	-2.384593	-0.131962
31	1	4.818691	-3.467919	-0.148642
32	1	5.311033	-2.027726	-1.084118
33	1	5.559202	-2.075522	0.692457
34	6	4.433625	1.553129	1.566165
35	1	3.517411	2.148514	1.608785
36	1	4.963662	1.624638	2.513718
37	1	5.066596	1.898902	0.748086
38	8	-3.476914	0.658244	-1.476188
39	1	-3.024647	1.134604	-2.188773
40	8	-0.753605	-3.769688	0.292947
41	1	-4.357098	-0.930594	0.317658

42	1	0.153346	-2.122650	-1.417778
43	6	-1.389331	-4.675614	1.188934
44	1	-2.327585	-5.048742	0.766583
45	1	-0.692396	-5.501500	1.314588
46	1	-1.573405	-4.203576	2.159011

E(RM062X) = -1416.00171605

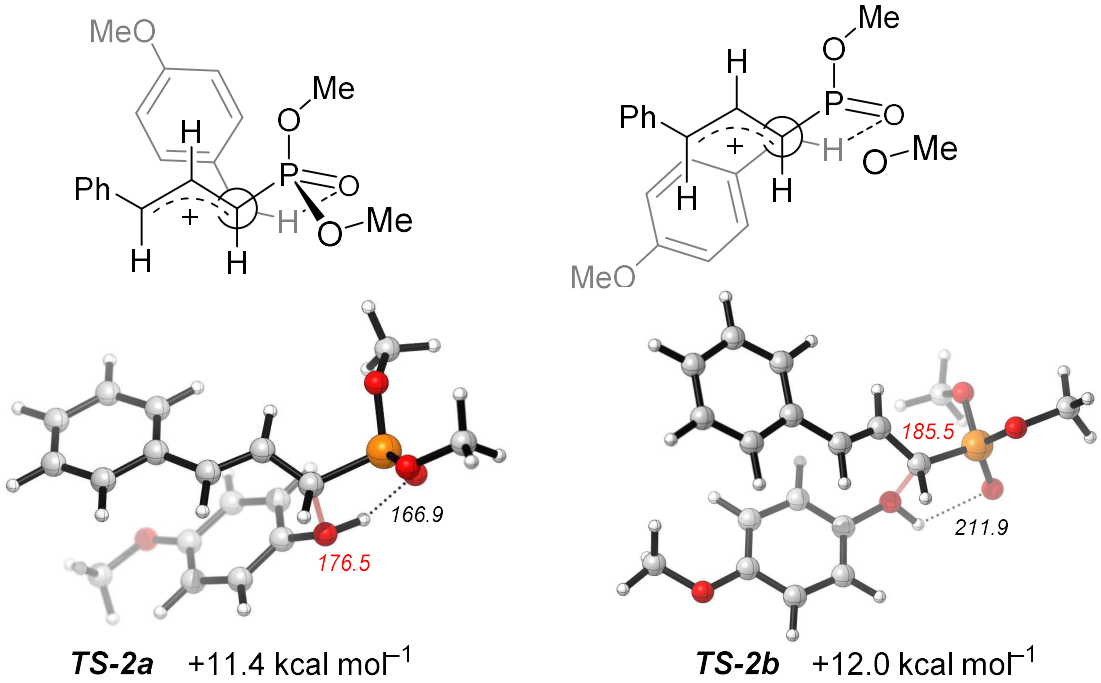
Zero-point correction= 0.375626 (Hartree/Particle)

Sum of electronic and thermal Energies= -1415.601350

Sum of electronic and thermal Enthalpies= -1415.600406

Sum of electronic and thermal Free Energies= -1415.683872

Table S5. Considered transition states, molecular geometries and energies



TS-2b

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.252806	-0.962805	0.934992
2	1	2.212846	-1.697762	1.739395
3	6	1.266789	0.056521	0.933684
4	1	1.395935	0.910171	0.275124

5	6	0.117124	-0.157273	1.640998
6	1	0.069163	-1.056697	2.257085
7	6	-1.080648	0.657235	1.643375
8	6	-2.219065	0.149389	2.293957
9	6	-1.155669	1.902200	0.990786
10	6	-3.412157	0.863744	2.285434
11	1	-2.160898	-0.812006	2.797740
12	6	-2.344727	2.616374	0.993839
13	1	-0.284270	2.314522	0.492288
14	6	-3.473999	2.096832	1.636677
15	1	-4.288200	0.464522	2.785026
16	1	-2.398630	3.578954	0.496958
17	1	-4.401809	2.659706	1.632565
18	6	0.456654	-2.645408	-0.226724
19	6	-0.588285	-1.937590	-0.800004
20	6	0.232299	-3.735275	0.616121
21	6	-1.903526	-2.322722	-0.542885
22	1	-0.372223	-1.085481	-1.436428
23	6	-1.072457	-4.125861	0.861224
24	1	1.062482	-4.268656	1.070499
25	6	-2.146612	-3.414126	0.297082
26	1	-2.714381	-1.761157	-0.989090

27	1	-1.289538	-4.973868	1.501131
28	15	3.926044	-0.713931	0.245370
29	8	4.658665	-0.111915	1.505038
30	8	3.830548	0.512675	-0.760769
31	8	4.415194	-1.985503	-0.347736
32	6	6.048480	0.291627	1.421346
33	1	6.151436	1.096964	0.692899
34	1	6.313247	0.643248	2.415160
35	1	6.664082	-0.565373	1.145207
36	6	3.560889	0.287937	-2.163943
37	1	3.801120	1.221603	-2.667181
38	1	4.187027	-0.521931	-2.539100
39	1	2.504097	0.047029	-2.299992
40	8	1.738024	-2.127883	-0.414213
41	1	2.459481	-2.787600	-0.501607
42	8	-3.377374	-3.856832	0.628403
43	6	-4.500726	-3.143621	0.125831
44	1	-4.527833	-3.180583	-0.967647
45	1	-5.377111	-3.645294	0.530965
46	1	-4.480552	-2.102033	0.464009

E(RM062X) = -1416.00578811

Zero-point correction=0.376086 (Hartree/Particle)

Sum of electronic and thermal Energies= -1415.605272

Sum of electronic and thermal Enthalpies= -1415.604327

Sum of electronic and thermal Free Energies= -1415.686608

Based on all the transition states, the total kinetic constant k_{total} for each C-C and C-O bond forming step was calculated according to the Eyringequation (Eqns. 1 and 2).

$$k_{total} = k_a + k_b \cdots + k_n \quad \cdots \quad \text{(Eqn. 1)}$$

$$\Delta G^{\ddagger}_{total} = RT \cdot \ln\left(\frac{k_B \cdot T}{k_{total} \cdot h}\right) \quad \cdots \quad \text{(Eqn. 1)}$$

where k_B is Boltzmann constant (1.38065 x 10^{-23} J K^{-1}), T is temperature (298.15 K), h is Planck's constant (6.62607 x 10^{-34} J s), and R is gas constant (8.31447 J K^{-1} mol^{-1}).

Table S7. ΔG_{298} of transition states and their Boltzmann weights

TS-1	$\Delta G^{\ddagger}$ (kcal mol^{-1})	k(x 10^4 s^{-1})	**TS-2**	$\Delta G^{\ddagger}$ (kcal mol^{-1})	k (x 10^4 s^{-1})
TS-1a	10.7	8.96	**TS-2a**	11.4	2.56
TS-1b	9.8	39.8	**TS-2b**	12.0	0.992
TS-1c	10.0	29.6			
TS-1d	14.0	0.0347			
TS-1e	8.0	824			
TS-1f	13.7	0.0547			
Total	7.96	902		11.2	3.56

Natural bond orbital (NBO) calculation

To study atomic charges of each atom in the allyl cation intermediate, NBO calculation was conducted by using *NBO7.0* package program. As shown in Figure S148, NPA (natural population analysis) charges of C3 and C1 atoms were +0.10 *e* and –0.43 *e*, respectively. Interatomic distances and NLMO (natural localization molecular orbital)/NPA bond orders, which is a covalent bond order in the NBO theory, clearly demonstrate a pronounced double bond character of the C1–C2 bond rather than the C2–C3 bond. From these theoretical results, we have concluded that the larger positive charge of C3 atom also contributes to the γ-selectivity observed in the experiments.

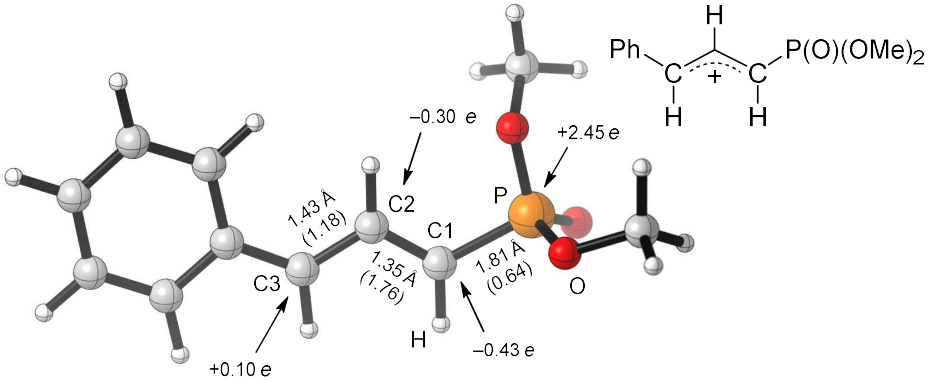


Figure S148. Considered transition states, molecular geometries and energies

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