

Electronic Supplementary Information

for

Azetidines-derived dinuclear zinc catalyzed asymmetric phospha-Michael addition of dialkyl phosphite to α,β -unsaturated carbonyl compounds

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1. Materials

L1–L4 were synthesized according to literature procedures respectively.¹ Diethylzinc was prepared from EtI with Zn and then diluted with toluene to 1.0 mol/L. Diethyl phosphite and dimethyl phosphite were purchased from *Alfa Aesar* or *TCI*. Chalcone and its derivatives were synthesized according to literature procedures.² α,β -Unsaturated acylpyrroles were prepared according to the known method.³ All the racemic γ -oxo phosphonates were obtained according to literature procedure.⁴

2. Non-linear Effects Experiments

Table S1. Non-linear effects experiments

$\text{Ph}-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{Ph} + \text{EtO}-\text{P}(=\text{O})(\text{EtO})-\text{H} \xrightarrow[\text{toluene (0.5 M), 17 }^\circ\text{C, 30 h}]{\text{L1 (20 mol\%), Et}_2\text{Zn (40 mol\%)}} \text{Ph}-\text{CH}(\text{P}(=\text{O})(\text{EtO})_2)-\text{CH}_2-\text{C}(=\text{O})-\text{Ph}$

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

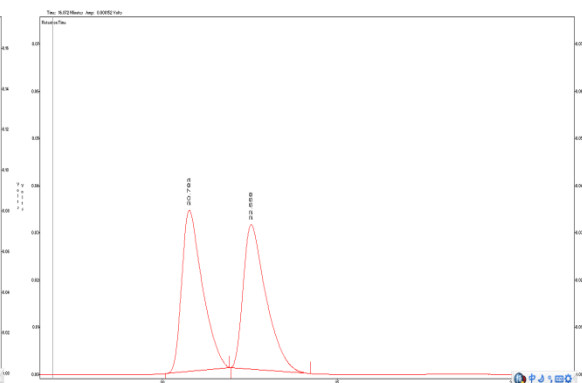
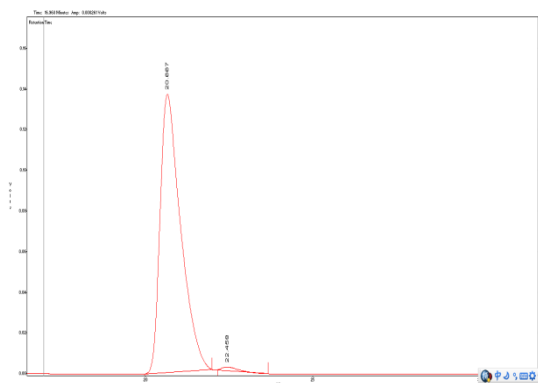
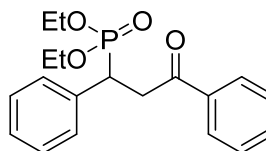
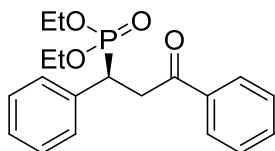
Entry	ee of L1 (%)	Yield (%)	ee of product (%)
1	0	72	0
2	20	68	33
3	40	69	58
4	60	59	87
5	80	62	94
6	100	63	96

^a Reaction conditions: **1a** (0.5 mmol), **2a** (2.0 equiv), **L1** (20 mol%), Et₂Zn (40 mol%) in toluene. All reactions were processed under argon for indicated reaction time. Isolated yield reported. The ee values were determined by HPLC analysis. In all cases, the product chromatogram was compared against a known racemic mixture. The absolute configuration was assigned by comparison to literature values.

When nonenantiopure **L1** was employed as chiral ligand, there exhibited a positive non-linear effect. The phosphonate **3aa** was generated in 33% ee using 20% ee **L1** (Table S1). Using >60% ee **L1** provided moderate reactivity (nearly 60% yield) with high enantioselectivity (96% ee).

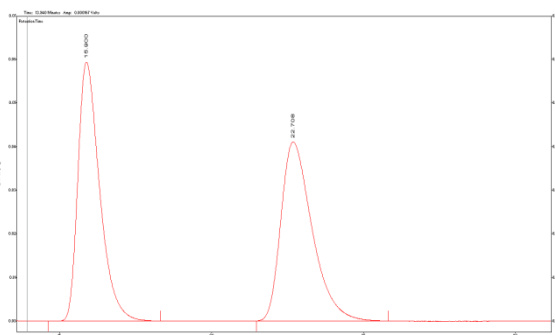
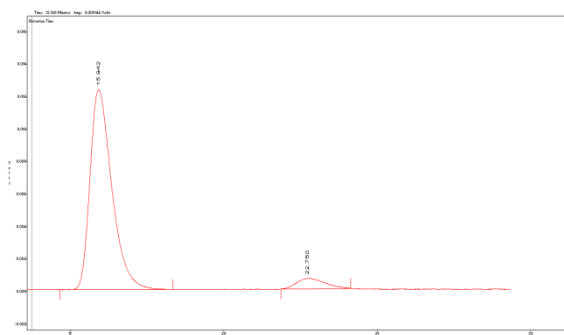
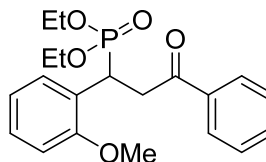
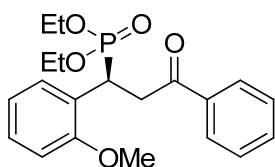
3. Chiral HPLC Spectra of the Phospha-Michael Addition Products

(S)-Diethyl 3-oxo-1,3-diphenylpropylphosphonate (3aa):

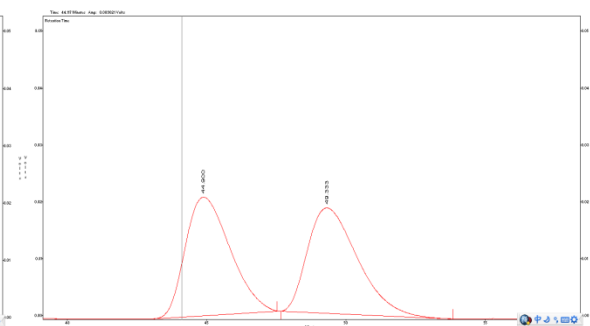
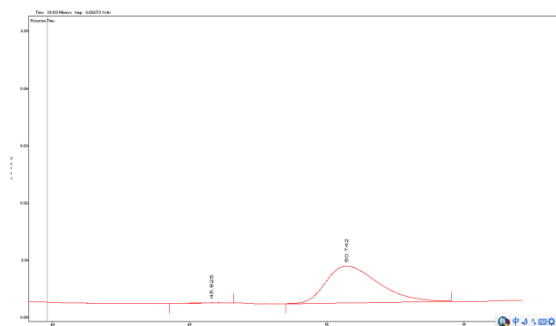
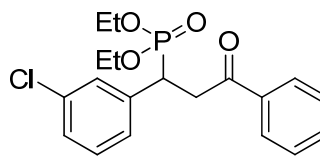
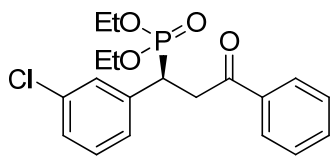


Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
20.667	5815624	99.845	20.783	1409089	50.287
22.458	9022	0.155	22.558	1392997	49.713

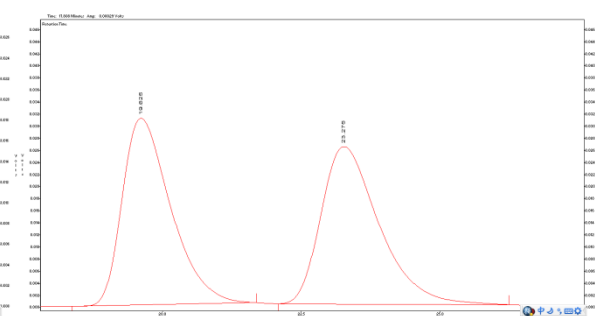
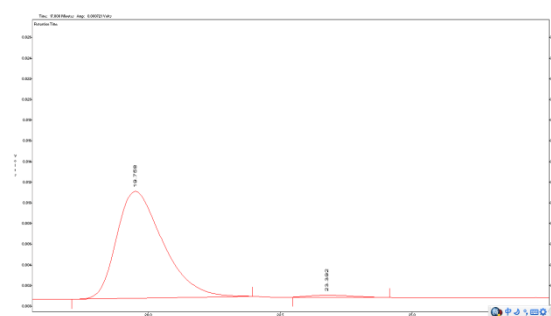
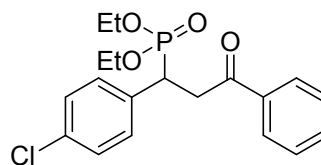
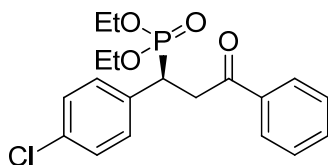
(S)-Diethyl 1-(2-methoxyphenyl)-3-oxo-3-phenylpropylphosphonate (3ba):



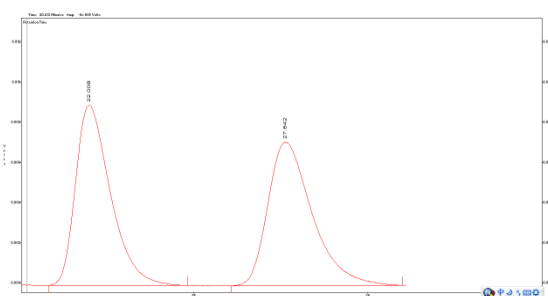
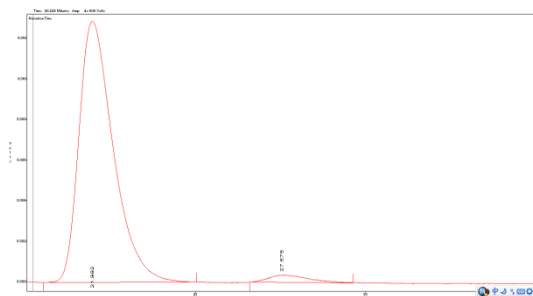
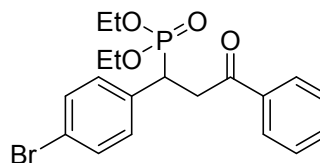
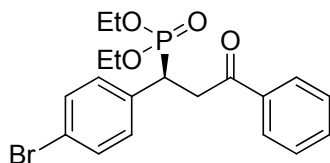
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
15.942	608045	93.515	15.900	2941298	50.062
22.750	42168	6.485	22.708	2934070	49.938

(S)-Diethyl 1-(3-chlorophenyl)-3-oxo-3-phenylpropylphosphonate (3ca):

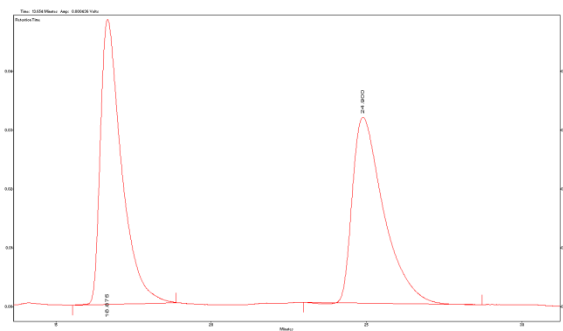
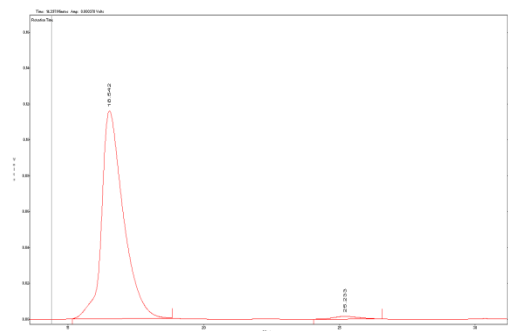
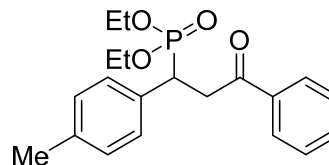
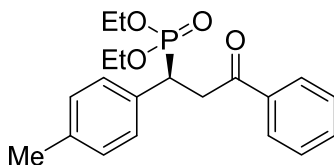
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
44.850	1015	0.123	44.900	2317268	50.061
50.742	824963	99.877	49.333	2311657	49.939

(S)-Diethyl 1-(4-chlorophenyl)-3-oxo-3-phenylpropylphosphonate (3da):

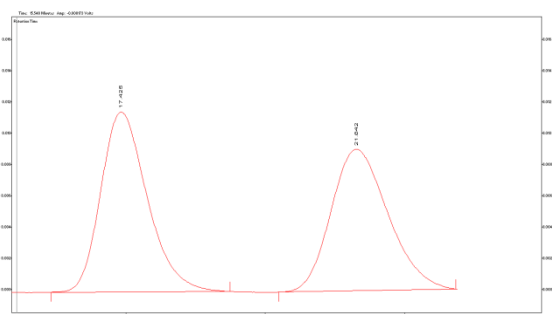
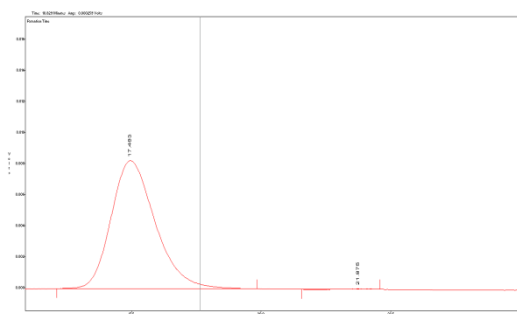
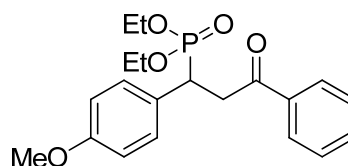
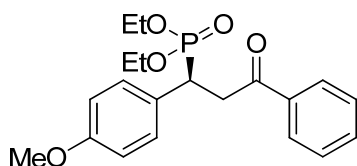
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
19.758	633486	98.694	19.625	1880888	49.808
23.392	8383	1.306	23.275	1895426	50.192

(S)-Diethyl 1-(4-bromophenyl)-3-oxo-3-phenylpropylphosphonate (3ea):

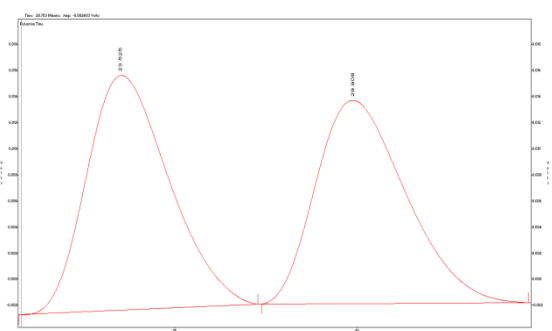
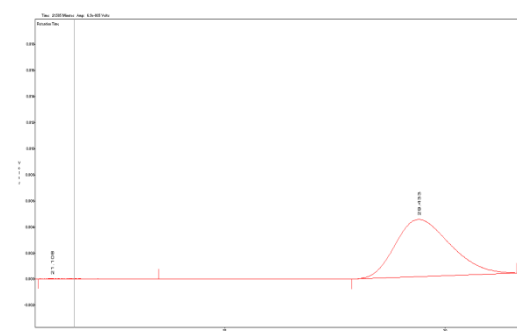
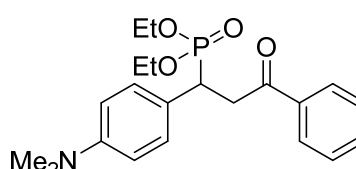
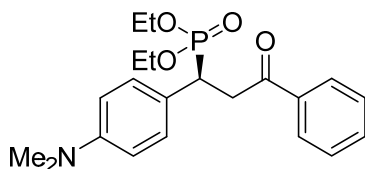
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
21.992	900837	97.512	22.008	625884	49.759
27.575	22985	2.488	27.642	631954	50.241

(S)-Diethyl 3-oxo-3-phenyl-1-p-tolylpropylphosphonate (3fa):

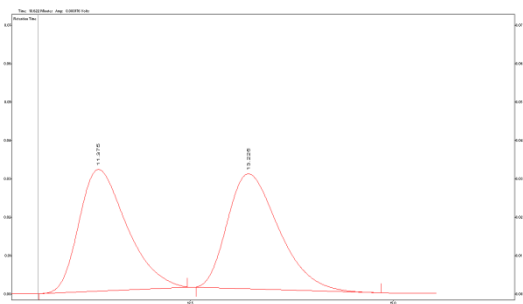
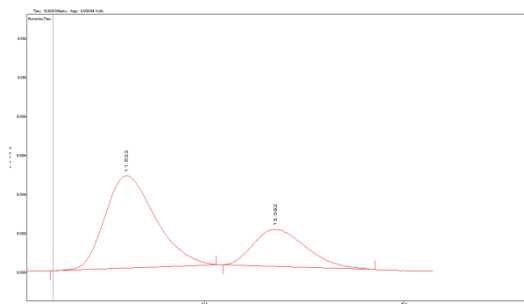
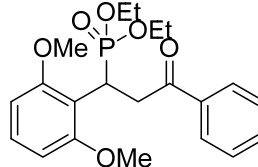
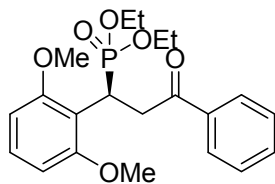
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
16.542	6537997	98.563	16.675	2283513	50.994
25.233	95334	1.437	24.900	2194470	49.006

(S)-Diethyl 1-(4-methoxyphenyl)-3-oxo-3-phenylpropylphosphonate (3ga):

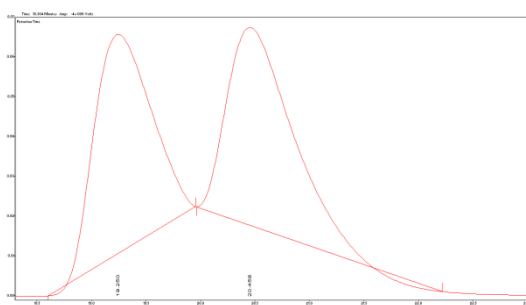
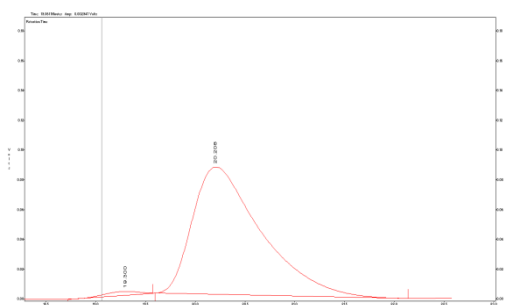
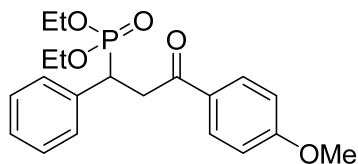
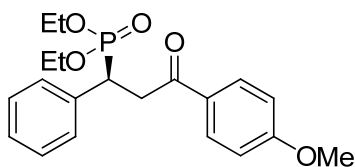
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
17.488	488609	99.645	17.425	666841	50.927
21.875	1741	0.355	21.642	642556	49.073

(S)-Diethyl 1-(4-dimethylamino)-3-oxo-3-phenylpropylphosphonate (3ha):

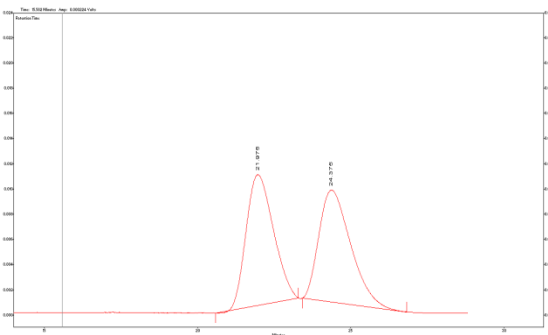
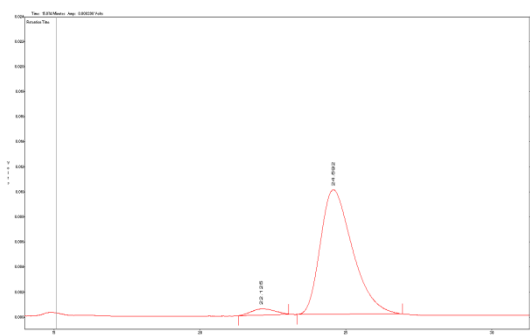
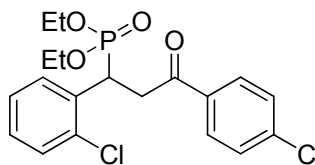
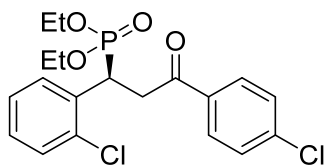
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
23.475	683	0.176	23.525	2828030	51.409
29.433	387282	99.824	29.908	2672974	48.591

(S)-Diethyl 1-(2,6-dimethoxyphenyl)-3-oxo-3-phenylpropylphosphonate (3ia):

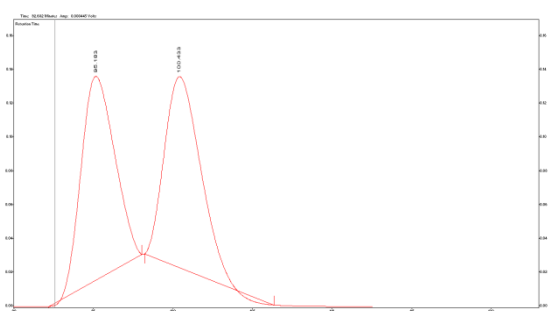
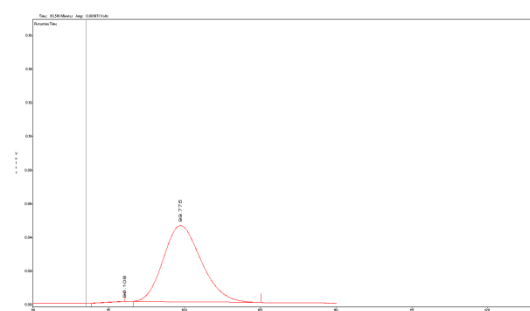
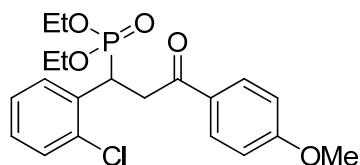
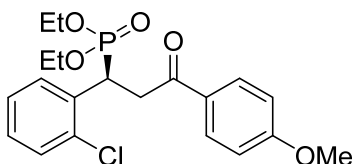
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
11.533	208527	73.860	11.375	1296395	49.568
13.392	77675	27.140	13.225	1318965	50.432

(S)-Diethyl 3-(4-methoxyphenyl)-3-oxo-1-phenylpropylphosphonate (3ja):

Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
19.300	43062	1.042	19.250	1985167	48.862
20.208	4089078	98.958	20.458	2077615	51.138

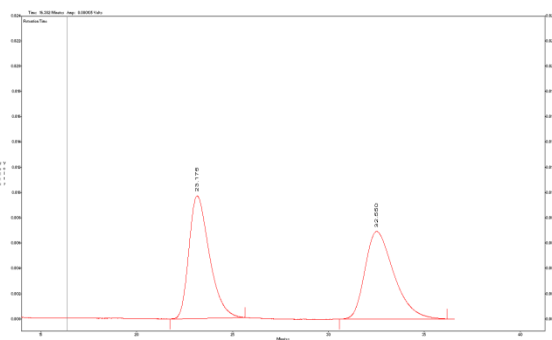
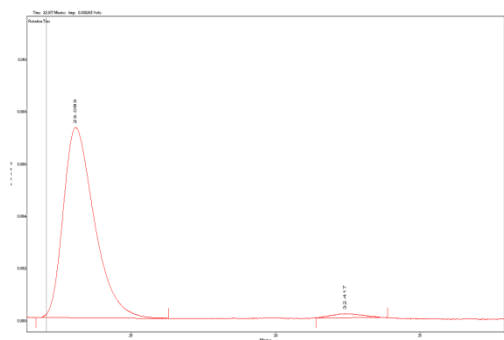
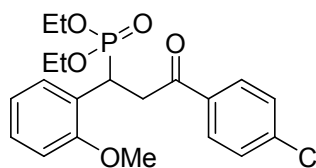
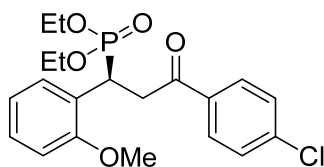
(S)-Diethyl 1-(2-chlorophenyl)-3-(4-chlorophenyl)-3-oxopropylphosphonate (3ka):

Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
22.125	26522	3.346	21.975	640982	50.027
24.592	766081	96.654	24.375	640298	49.973

(S)-Diethyl 1-(2-chlorophenyl)-3-(4-methoxyphenyl)-3-oxopropylphosphonate (3la):

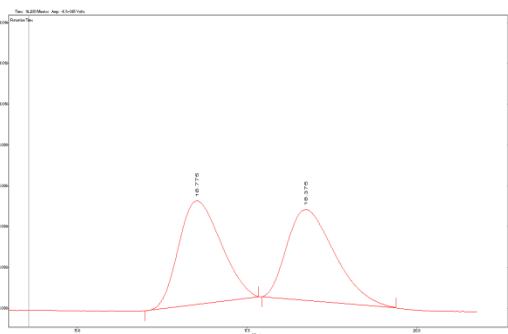
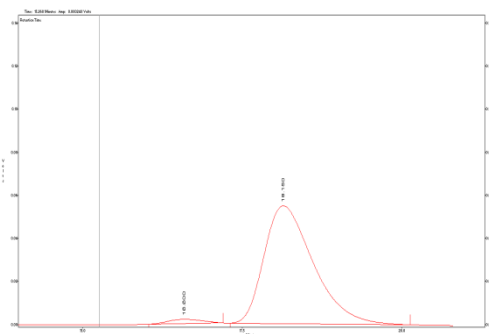
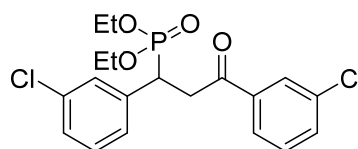
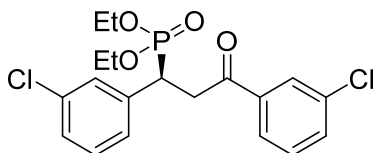
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
96.192	14938	0.189	95.183	17680952	49.881
99.775	7902311	99.811	100.433	17765228	50.119

(S)-Diethyl 3-(4-chlorophenyl)-1-(2-methoxyphenyl)-3-oxopropylphosphonate (3ma):

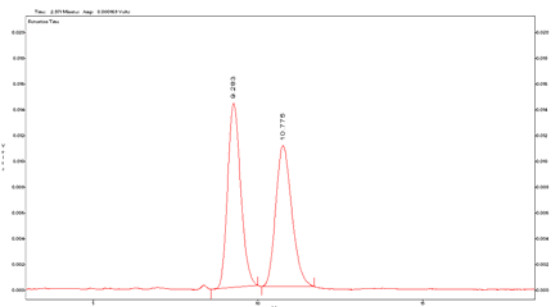
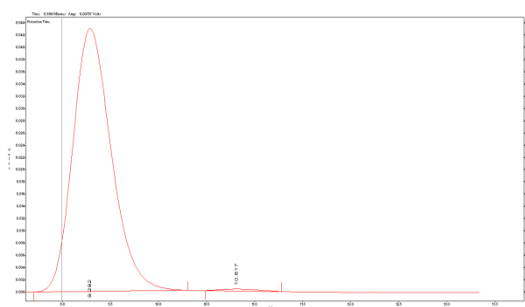
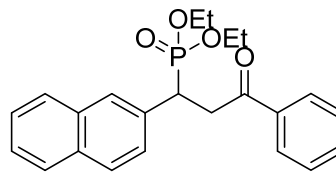
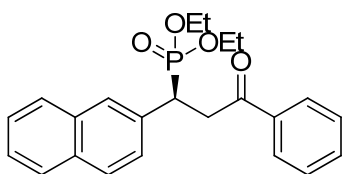


Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
23.083	544231	97.746	23.175	717875	49.737
32.417	12551	2.254	32.550	725397	50.263

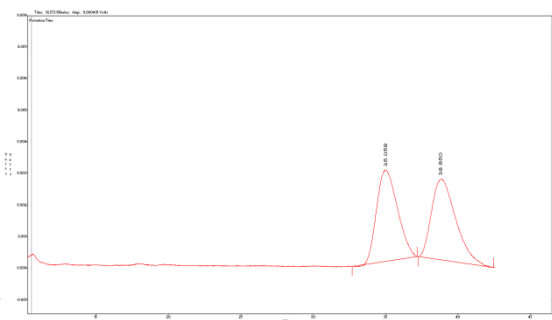
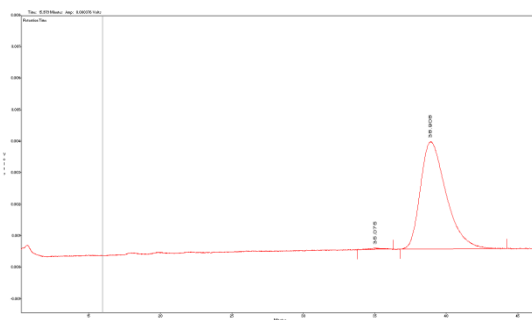
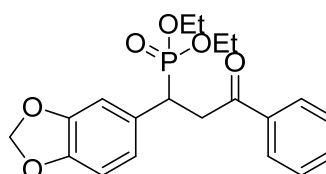
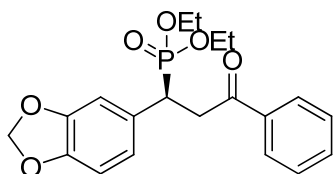
(S)-Diethyl 1,3-bis(3-chlorophenyl)-3-oxopropylphosphonate (3na):



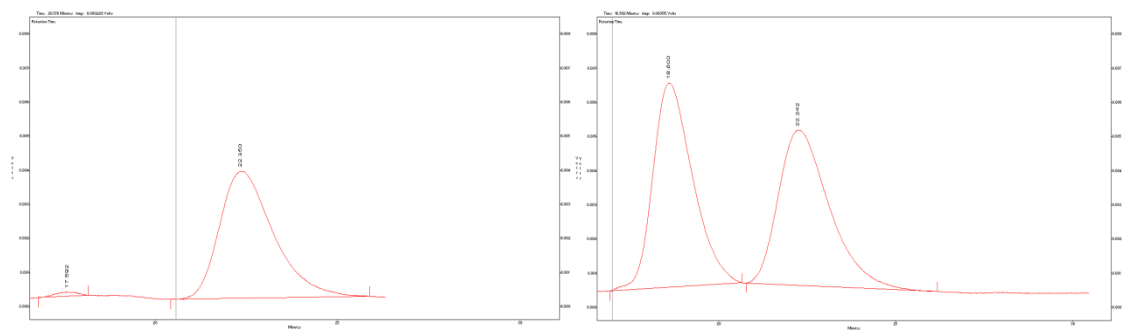
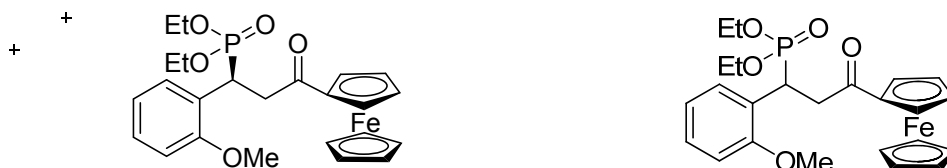
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
16.600	78333	2.597	16.775	219548	50.173
18.150	2938054	97.403	18.375	218032	49.827

(S)-Diethyl 1-(naphthalen-3-yl)-3-oxo-3-phenylpropylphosphonate (3oa):

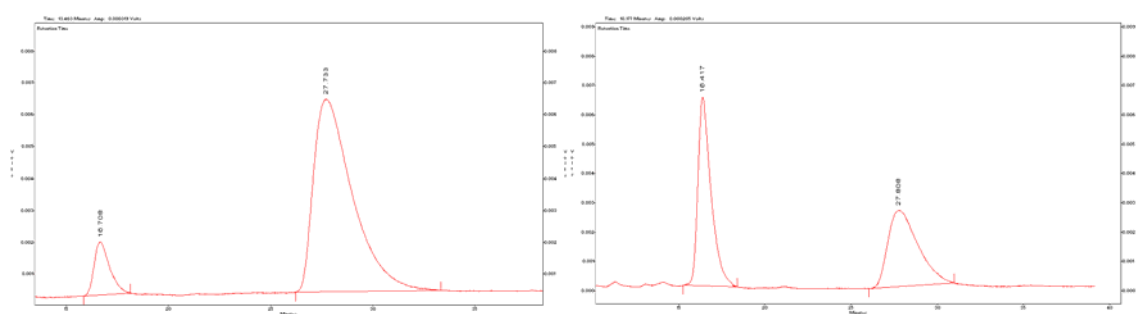
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
9.292	1178776	99.494	9.283	393737	50.981
10.817	597	0.506	10.775	378583	49.019

(S)-Diethyl 1-(benzo[d][1,3]dioxol-6-yl)-3-oxo-3-phenylpropylphosphonate (3pa):

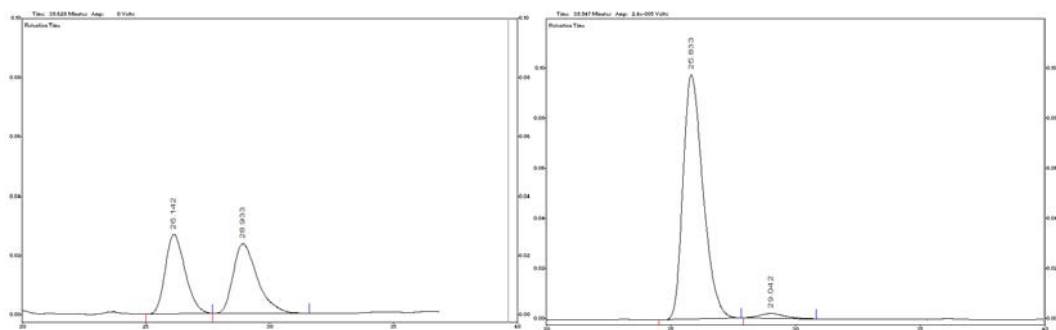
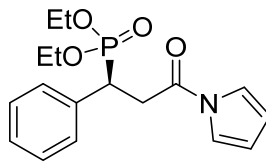
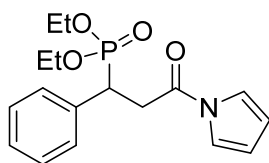
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
35.075	719	0.175	35.058	288549	49.424
38.908	409907	99.825	38.850	295278	50.567

(S)-Diethyl 3-(ferrocene)-1-(2-methoxyphenyl)-3-oxopropylphosphonate (3qa):

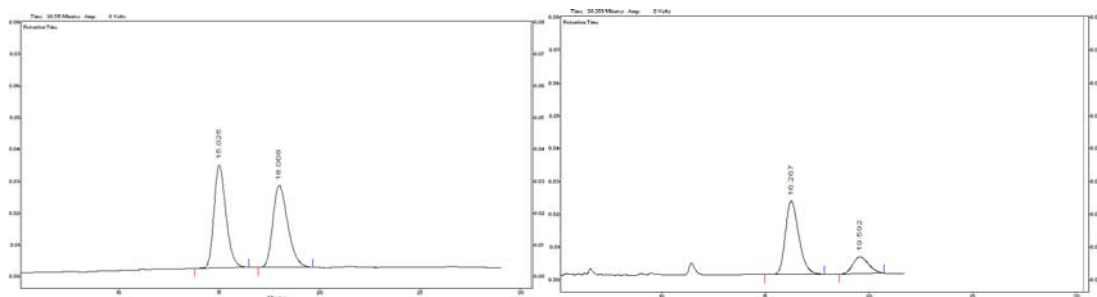
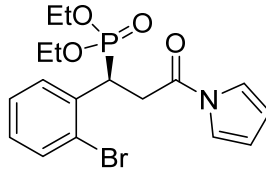
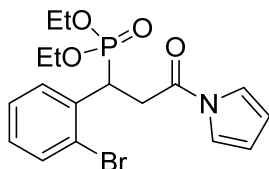
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
17.592	5585	1.472	18.600	466178	50.689
22.350	373771	98.528	22.242	453501	49.311

(S)-Diethyl 3-(ferrocene)-1-(2-pyridinyl)-3-oxopropylphosphonate (3ra):

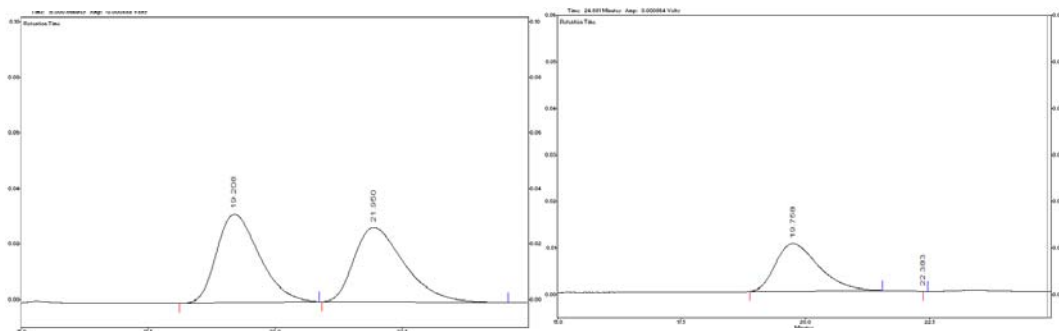
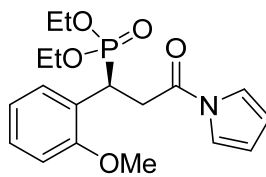
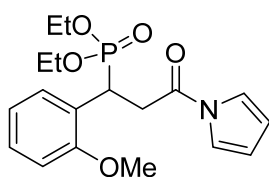
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
16.708	90761	10.062	16.417	355447	50.943
27.733	811219	89.938	27.808	332655	49.057

(S)-Diethyl 1-phenyl-3-oxo-3-pyrrol-1-yl-propylphosphonate (5aa):

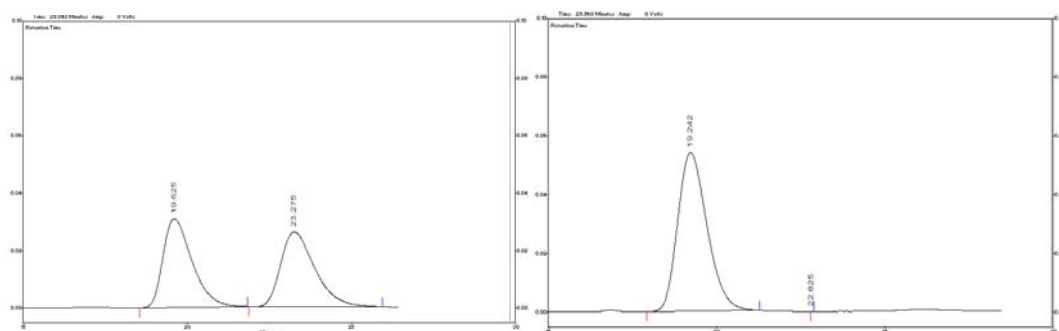
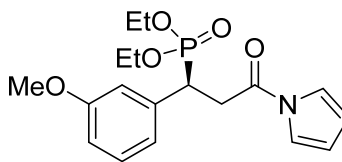
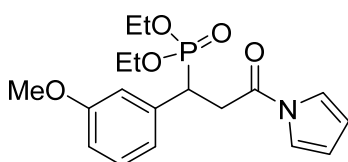
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
26.142	1504260	48.532	25.833	5440417	98.005
28.933	1595289	51.468	29.042	110735	1.995

(S)-Diethyl 1-(2-bromophenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ba):

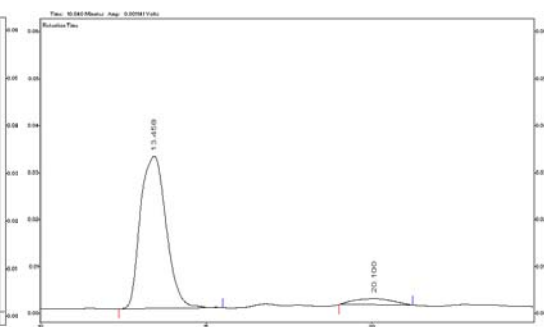
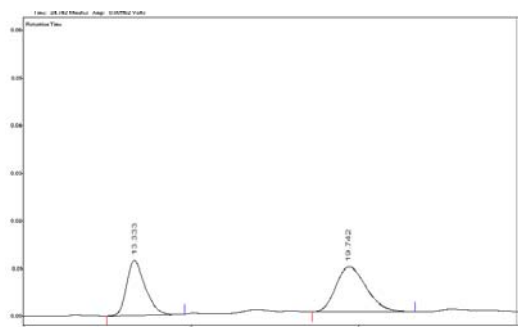
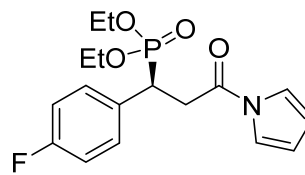
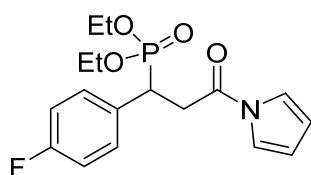
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
15.025	635178	50.530	16.267	985398	79.143
18.008	621839	49.470	19.592	259685	20.857

(S)-Diethyl 1-(2-methoxyphenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ca):

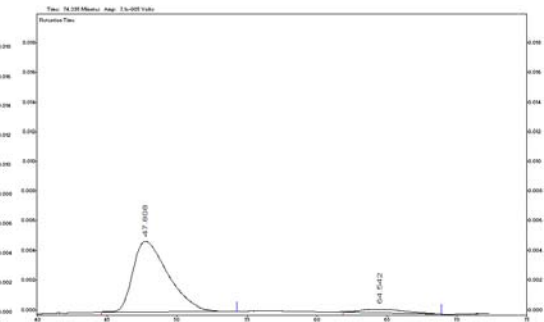
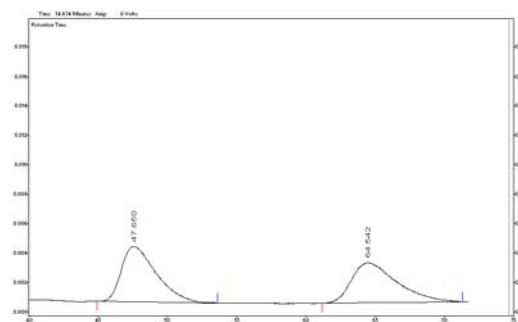
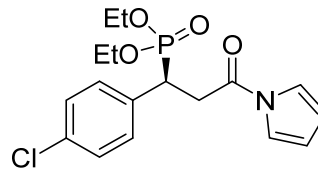
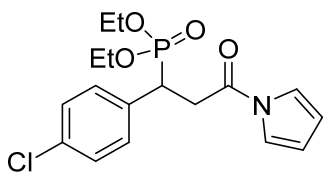
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
19.208	1841598	51.358	19.758	614303	100.000
21.950	1815395	49.642	22.375	2	0.000

(S)-Diethyl 1-(3-methoxyphenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5da):

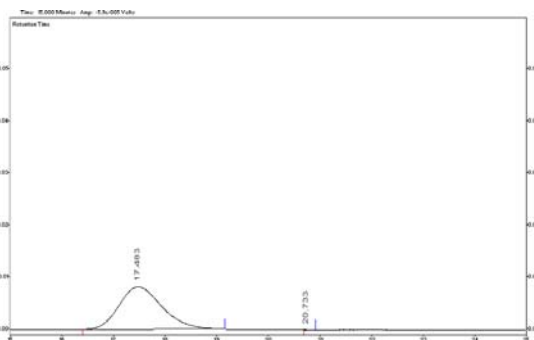
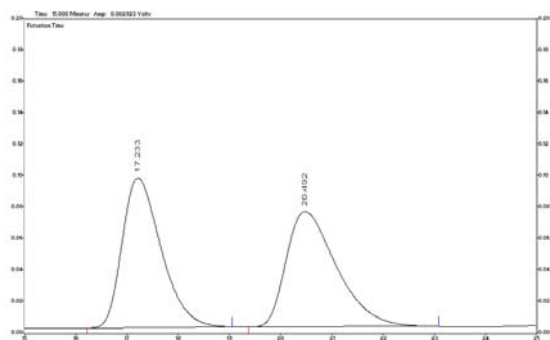
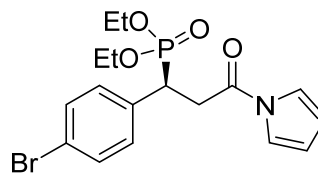
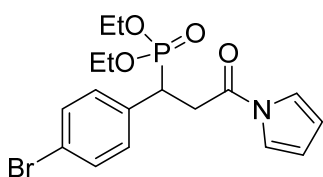
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
19.625	1887469	49.904	19.242	3273751	99.998
23.275	1894701	50.096	22.767	78	0.002

(S)-Diethyl 1-(4-fluorophenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ea):

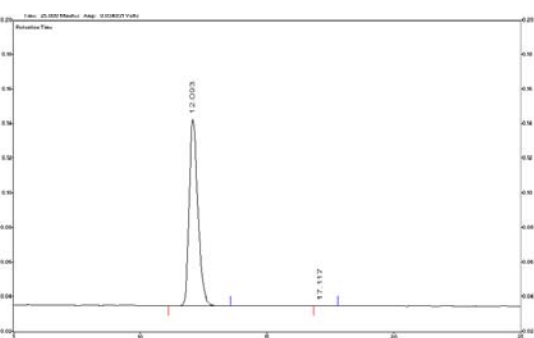
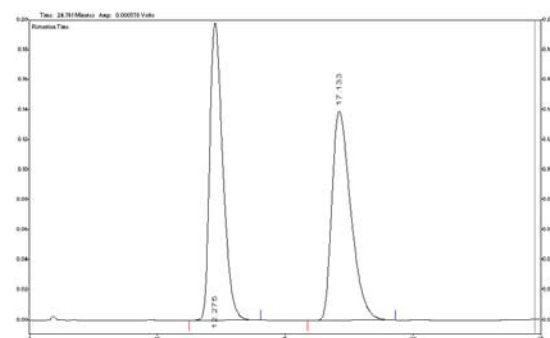
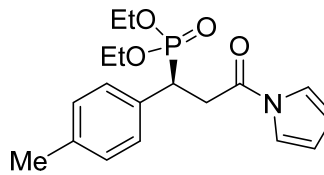
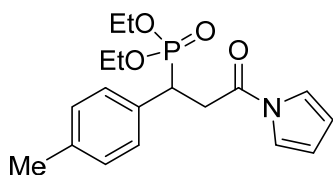
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
13.333	429299	42.837	13.458	1702266	91.871
19.742	586219	57.163	20.100	150619	8.129

(S)-Diethyl 1-(4-chlorophenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5fa):

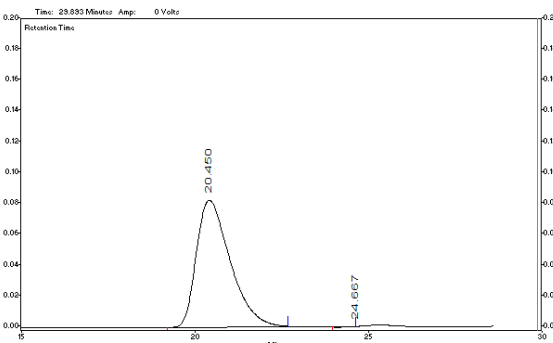
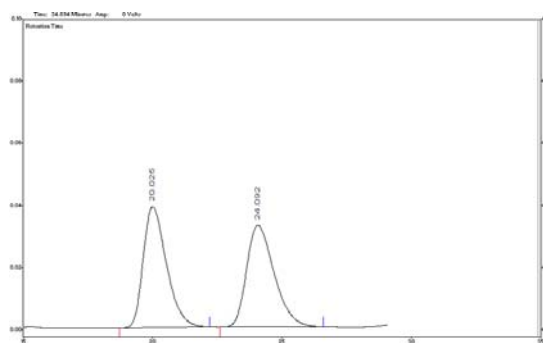
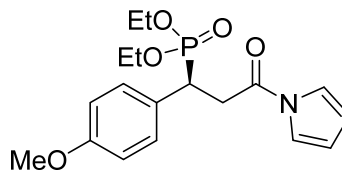
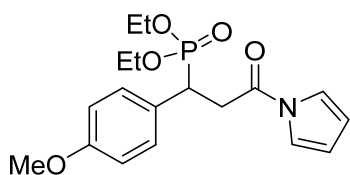
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
47.650	646560	51.876	47.808	820036	95.021
64.542	599795	48.124	64.542	42973	4.979

(S)-Diethyl 1-(4-bromophenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ga):

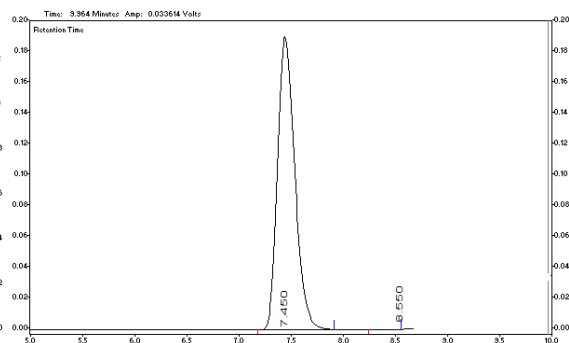
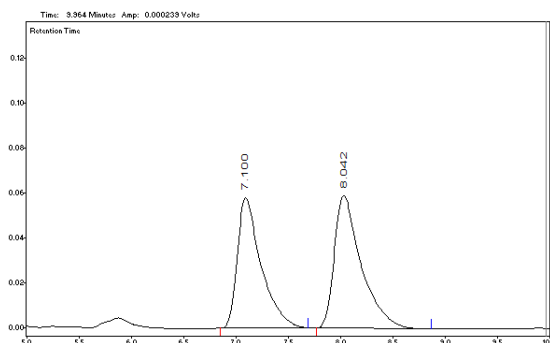
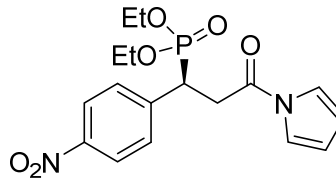
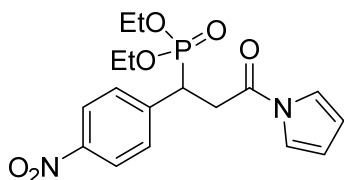
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
17.233	5040932	50.002	17.483	464780	99.997
20.492	5040527	49.998	20.608	13	0.003

(S)-Diethyl 1-(4-methylphenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ha):

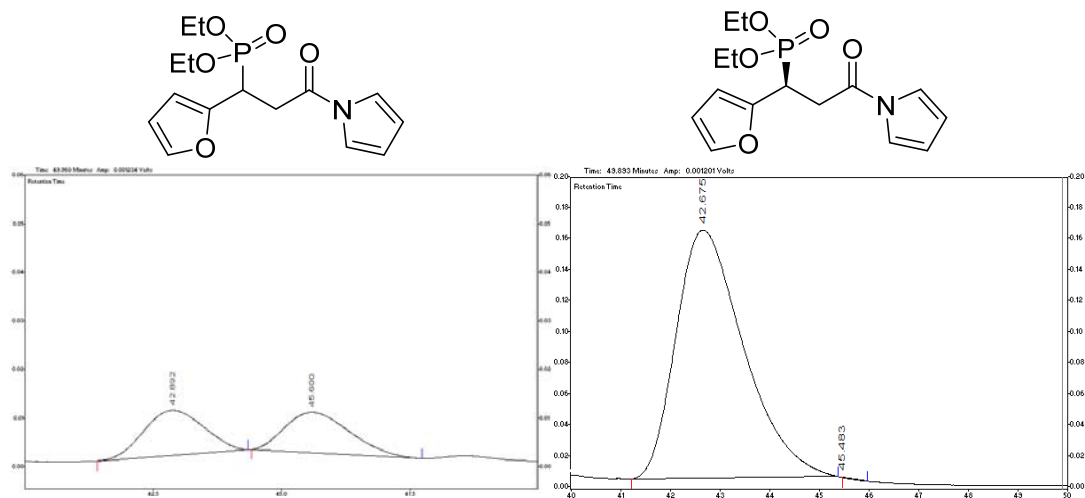
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
12.275	7058130	49.668	12.093	2565012	99.998
17.133	7152411	50.332	17.117	43	0.002

(S)-Diethyl 1-(4-methoxyphenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ia):

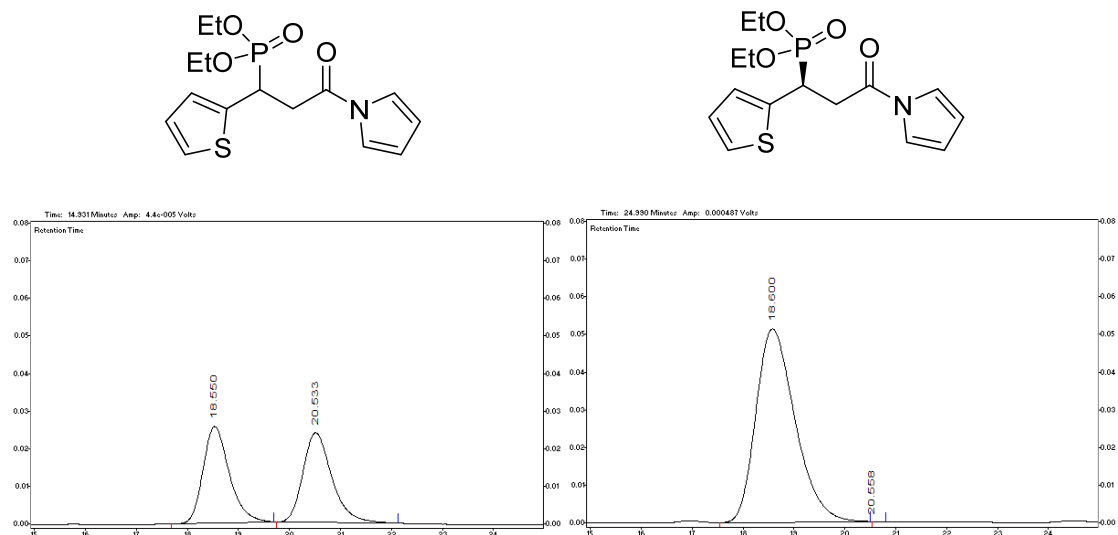
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
20.025	2424056	50.172	20.450	5600105	98.378
24.092	2407902	49.828	25.375	92335	1.622

(S)-Diethyl 1-(4-nitrophenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ja):

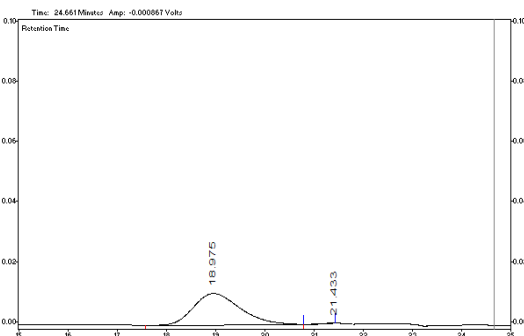
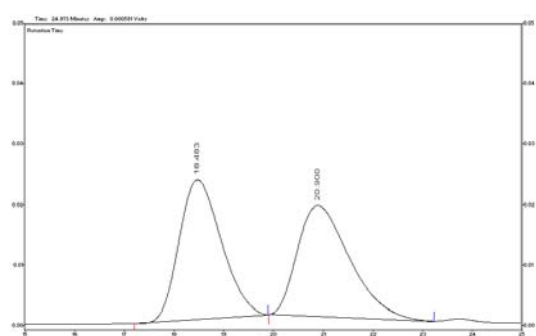
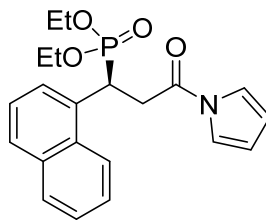
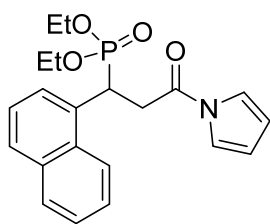
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
7.100	193322	48.002	7.450	2547478	99.992
8.042	209418	51.998	8.550	200	0.008

(S)-Diethyl 1-(furan-2-yl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ka):

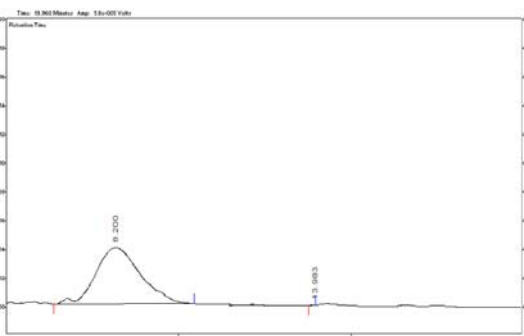
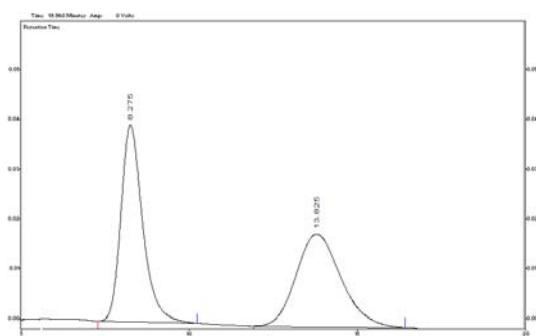
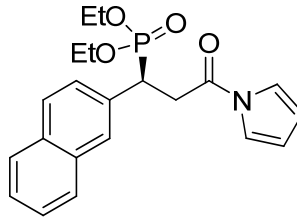
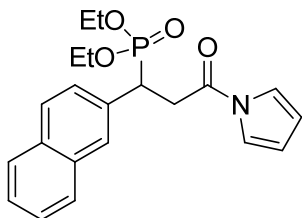
Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
42.892	741165	50.231	41.492	84450	1.272
45.600	734335	49.769	43.892	6552660	98.728

(S)-Diethyl 1-(thiophen-2-yl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5la):

Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
18.550	1011333	50.278	18.600	9501	0.346
20.533	1000143	49.722	20.558	2732858	99.654

(S)-Diethyl 1-(1-naphthyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ma):

Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
18.483	1363788	50.351	18.975	674955	92.855
20.900	1344748	49.649	21.842	51937	7.145

(S)-Diethyl 1-(2-naphthyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5na):

Ret. Time (min)	Area	Area (%)	Ret. Time (min)	Area	Area (%)
8.275	1788386	51.146	8.200	329275	99.952
13.825	1708212	48.854	13.908	158	0.048

4. NMR Data of the Phospha-Michael Addition Products

(S)-Diethyl 3-oxo-1,3-diphenylpropylphosphonate (3aa): ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.97 – 7.91 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (d, J = 7.8 Hz, 4H), 7.32 – 7.27 (m, 2H), 7.22 (dd, J = 7.3, 1.7 Hz, 1H), 4.07 (ddd, J = 7.7, 7.2, 2.8 Hz, 2H), 4.03 – 3.87 (m, 2H), 3.76 – 3.67 (m, 3H), 1.28 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*): δ = 16.3 (d, J = 5.5 Hz), 16.5 (d, J = 6.2 Hz), 39.1 (d, J = 140.0 Hz), 39.1, 62.1 (d, J = 7.3 Hz), 63.1 (d, J = 6.9 Hz), 127.4 (d, J = 3.0 Hz), 128.2, 128.6 (d, J = 2.3 Hz), 128.7, 129.3 (d, J = 6.6 Hz), 133.4, 136.0 (d, J = 6.9 Hz), 136.0, 196.5 (d, J = 14.8 Hz) ppm.

(S)-Diethyl 1-(2-methoxyphenyl)-3-oxo-3-phenylpropylphosphonate (3ba): ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.92 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.7 Hz, 3H), 7.17 (t, J = 7.6 Hz, 1H), 6.93 – 6.82 (m, 2H), 4.60 (dt, J = 7.7, 6.9 Hz, 1H), 4.13 – 4.03 (m, 2H), 3.85 – 3.92 (m, 4H), 3.79 – 3.66 (m, 3H), 1.26 (t, J = 6.8 Hz, 3H), 1.07 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*): δ = 16.3 (d, J = 6.0 Hz), 16.4 (d, J = 6.2 Hz), 30.6 (d, J = 141.0 Hz), 39.1, 56.0, 62.0 (d, J = 7.0 Hz), 62.7 (d, J = 7.1 Hz), 111.1 (d, J = 2.2 Hz), 120.8 (d, J = 3.1 Hz), 124.7 (d, J = 7.1 Hz), 128.2, 128.3 (d, J = 3.4 Hz), 128.6, 128.8 (d, J = 5.0 Hz), 133.2, 136.8, 157.5 (d, J = 7.1 Hz), 196.7 (d, J = 14.9 Hz) ppm.

(S)-Diethyl 1-(3-chlorophenyl)-3-oxo-3-phenylpropylphosphonate (3ca): ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.93 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.32 (d, J = 8.6 Hz, 1H), 7.20 (q, J = 9.9, 8.9 Hz, 2H), 4.07 (td, J = 7.7, 7.3, 3.0 Hz, 2H), 3.98 – 3.89 (m, 2H), 3.84 – 3.76 (m, 1H), 3.68 (t, J = 5.5 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*): δ = 196.1 (d, J = 15.0 Hz), 138.3 (d, J = 6.8 Hz), 136.4, 134.3 (d, J = 2.3 Hz), 133.5, 129.7 (d, J = 2.3 Hz), 129.4 (d, J = 6.8 Hz), 128.7, 128.1, 127.6 (d, J = 2.3 Hz), 127.5, 63.0 (d, J = 7.5 Hz), 62.2 (d, J = 7.5 Hz), 39.0, 38.7 (d, J = 140.0 Hz), 16.4 (d, J = 6.0 Hz), 16.3 (d, J = 6.0 Hz) ppm.

(S)-Diethyl 1-(4-chlorophenyl)-3-oxo-3-phenylpropylphosphonate (3da): ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.93 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.38 (dd, J = 8.5, 2.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 4.09 (td, J = 7.8, 7.3, 2.7 Hz, 2H), 3.98 – 3.89 (m, 2H), 3.76 – 3.82 (m, 1H), 3.73 – 3.64 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*): δ = 196.1 (d, J = 15.0 Hz), 136.4, 134.6 (d, J = 6.8 Hz), 133.4, 133.1 (d, J = 3.8 Hz), 130.5 (d, J = 6.8 Hz), 128.6, 128.0, 63.0 (d, J = 7.5 Hz), 62.1 (d, J = 7.5 Hz), 39.0, 38.4 (d, J = 140.0 Hz), 16.3 (d, J = 6.0 Hz), 16.2 (d, J = 6.0 Hz) ppm.

(S)-Diethyl 1-(4-bromophenyl)-3-oxo-3-phenylpropylphosphonate (3ea): ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.91 (d, J = 7.3 Hz, 2H), 7.53 (d, J = 7.2 Hz, 1H), 7.42 (dd, J = 13.6, 7.8 Hz, 4H), 7.30 (d, J = 6.5 Hz, 2H), 4.13 – 4.03 (m, 2H), 3.93 (d, J = 9.2 Hz, 2H), 3.82 – 3.75 (m, 1H), 3.67 (t, J = 9.1 Hz, 2H), 1.27 (t, J = 7.0 Hz, 3H), 1.11 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*): δ = 196.1 (d, J = 15.0 Hz), 136.4, 135.2 (d, J = 6.8 Hz), 133.5, 133.6 (d, J = 2.3 Hz), 130.9 (d, J = 6.8 Hz), 128.7, 128.1, 121.3 (d, J = 3.8 Hz), 63.1 (d, J = 7.5 Hz), 62.2 (d, J = 7.5 Hz), 38.9, 38.6 (d, J = 140.0 Hz), 16.4 (d, J = 6.0 Hz), 16.3 (d, J = 6.0 Hz) ppm.

(S)-Diethyl 3-oxo-3-phenyl-1-*p*-tolylpropylphosphonate (3fa): ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.94 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 6.2 Hz, 2H), 7.09 (d, J = 7.7 Hz, 2H), 4.14 – 4.02 (m, 2H), 3.92 (dd, J = 15.0, 8.4 Hz, 2H), 3.78 – 3.67 (m, 3H), 2.28 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*): δ = 196.4 (d, J = 15.0 Hz), 136.9 (d, J = 3.0 Hz), 136.5, 133.1, 132.7 (d, J = 7.5 Hz), 129.1 (d, J = 2.3 Hz), 129.0 (d, J = 6.0 Hz), 128.6, 128.1, 63.0 (d, J = 7.5 Hz), 61.9 (d, J = 7.5 Hz), 39.0, 37.9 (d, J = 140.0 Hz), 21.0, 16.3 (d, J = 6.0 Hz), 16.1 (d, J = 6.0 Hz) ppm.

(S)-Diethyl 1-(4-methoxyphenyl)-3-oxo-3-phenylpropylphosphonate (3ga): ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.92 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 6.8 Hz, 1H), 7.41 (d, J

= 7.4 Hz, 2H), 7.33 (dd, J = 8.8, 2.3 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 4.10 – 4.01 (m, 2H), 3.95 – 3.85 (m, 2H), 3.74 (s, 3H), 3.71 – 3.60 (m, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.09 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d): δ = 196.5 (d, J = 15.8 Hz), 158.6 (d, J = 3.0 Hz), 136.5, 133.2, 130.2 (d, J = 6.8 Hz), 128.5, 128.0, 127.7 (d, J = 6.8 Hz), 113.8 (d, J = 2.3 Hz), 62.8 (d, J = 6.8 Hz), 61.9 (d, J = 6.8 Hz), 55.2, 39.2, 37.6 (d, J = 140.3 Hz), 16.3 (d, J = 6.0 Hz), 16.2 (d, J = 5.3 Hz) ppm.

(S)-Diethyl 3-(4-methoxyphenyl)-3-oxo-1-phenylpropylphosphonate (3ja): ^1H NMR (400 MHz, Chloroform- d): δ = 7.92 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 7.2 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 7.21 (d, J = 6.7 Hz, 1H), 6.90 (d, J = 8.5 Hz, 2H), 4.12 – 4.03 (m, 2H), 3.96 – 3.88 (m, 2H), 3.84 (s, 3H), 3.76 – 3.66 (m, 2H), 3.63 (dd, J = 15.8, 3.7 Hz, 1H), 1.28 (t, J = 7.0 Hz, 3H), 1.08 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d): δ = 194.8 (d, J = 15.8 Hz), 163.6 (d, J = 3.0 Hz), 136.5, 133.2, 130.2 (d, J = 6.8 Hz), 128.6, 128.1, 127.7 (d, J = 6.8 Hz), 113.7 (d, J = 2.3 Hz), 62.8 (d, J = 6.8 Hz), 61.8 (d, J = 6.8 Hz), 55.5, 38.6, 38.0 (d, J = 140.3 Hz), 16.3 (d, J = 6.0 Hz), 16.2 (d, J = 5.3 Hz) ppm.

(S)-Diethyl 1-(naphthalen-3-yl)-3-oxo-3-phenylpropylphosphonate (3oa): ^1H NMR (400 MHz, Chloroform- d): δ = 7.99 – 7.87 (m, 3H), 7.79 (d, J = 8.1 Hz, 3H), 7.62 – 7.50 (m, 2H), 7.43 (t, J = 7.4 Hz, 4H), 4.21 – 4.04 (m, 4H), 3.80 – 3.78 (m, 3H), 1.29 (d, J = 14.1 Hz, 3H), 1.06 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d): δ = 196.2 (d, J = 15.0 Hz), 136.5, 133.5 (d, J = 7.5 Hz), 133.3, 132.5 (d, J = 2.3 Hz), 128.6, 128.1 (d, J = 3.0 Hz), 128.0, 127.8, 127.5, 127.4 (d, J = 5.3 Hz), 126.0, 125.8, 62.9 (d, J = 6.8 Hz), 62.0 (d, J = 7.5 Hz), 39.3, 39.1 (d, J = 140.0 Hz), 16.4 (d, J = 6.0 Hz), 16.2 (d, J = 6.0 Hz) ppm.

(S)-Diethyl 1-phenyl-3-oxo-3-pyrrol-1-yl-propylphosphonate (5aa): ^1H NMR (400 MHz, Chloroform- d): δ = 7.56 – 7.28 (m, 7H), 6.27 (s, 2H), 4.09 (d, J = 4.5 Hz, 2H), 3.91 – 3.88 (m, 2H), 3.74 – 3.47 (m, 3H), 1.36 – 1.24 (m, 3H), 1.07 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d): δ = 167.7 (d, J = 18.0 Hz), 135.2 (d, J = 6.8 Hz), 129.1 (d, J = 6.0 Hz), 128.7 (d, J = 2.3 Hz), 127.6 (d, J = 3.0 Hz), 119.1, 113.4, 63.2 (d, J = 7.5 Hz),

62.1 (d, $J = 7.5$ Hz), 39.5 (d, $J = 140.3$ Hz), 35.5, 16.3 (d, $J = 6.0$ Hz), 16.1 (d, $J = 5.3$ Hz) ppm.

(S)-Diethyl 1-(2-bromophenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ba): ^1H NMR (400 MHz, Chloroform- d): $\delta = 7.56$ (d, $J = 28.7$ Hz, 2H), 7.31 – 7.29 (m, 3H), 7.11 – 7.08 (m, 1H), 6.29 – 6.27 (m, 2H), 4.60 (s, 1H), 4.13 (s, 2H), 3.93 – 3.89 (m, 1H), 3.66 (d, $J = 37.8$ Hz, 3H), 1.34 – 1.32 (m, 3H), 1.09 – 1.07 (m, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d): $\delta = 167.3$ (d, $J = 18.2$ Hz), 135.1 (d, $J = 6.4$ Hz), 133.3 (d, $J = 6.8$ Hz), 129.2, 128.9, 127.7, 126.3 (d, $J = 9.2$ Hz), 119.1, 113.4, 63.3 (d, $J = 7.1$ Hz), 62.4 (d, $J = 7.2$ Hz), 38.1 (d, $J = 140.3$ Hz), 35.8, 16.3 (d, $J = 6.0$ Hz), 16.1 (d, $J = 6.0$ Hz) ppm.

(S)-Diethyl 1-(2-methoxyphenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ca): ^1H NMR (400 MHz, Chloroform- d): $\delta = 7.42$ (dt, $J = 7.6, 2.0$ Hz, 1H), 7.33 – 7.28 (m, 2H), 7.26 – 7.16 (m, 1H), 7.00 – 6.81 (m, 2H), 6.29 – 6.20 (m, 2H), 4.59 (d, $J = 4.7$ Hz, 1H), 4.14 – 4.04 (m, 2H), 3.77 – 3.85 (m, 1H), 3.87 (s, 3H), 3.73 (d, $J = 10.1$ Hz, 1H), 3.64 – 3.44 (m, 2H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.08 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d): $\delta = 167.9$ (d, $J = 18.0$ Hz), 157.4 (d, $J = 7.5$ Hz), 128.7 (d, $J = 5.3$ Hz), 128.6 (d, $J = 3.0$ Hz), 123.8 (d, $J = 6.8$ Hz), 120.8 (d, $J = 3.0$ Hz), 119.1, 113.2, 111.1 (d, $J = 2.3$ Hz), 62.9 (d, $J = 6.8$ Hz), 62.1 (d, $J = 6.8$ Hz), 55.9, 35.4, 31.2 (d, $J = 141.0$ Hz), 16.3 (d, $J = 6.0$ Hz), 16.2 (d, $J = 6.0$ Hz) ppm.

(S)-Diethyl 1-(3-methoxyphenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5da): ^1H NMR (400 MHz, Chloroform- d): $\delta = 7.31$ (s, 2H), 7.23 (t, $J = 7.9$ Hz, 1H), 7.05 – 6.95 (m, 2H), 6.80 (d, $J = 8.2$ Hz, 1H), 6.32 – 6.24 (m, 2H), 4.06 (s, 2H), 3.98 – 3.82 (m, 2H), 3.79 (s, 3H), 3.76–3.68 (m, 1H), 3.47 (s, 2H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.10 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform- d): $\delta = 167.7$ (d, $J = 18.0$ Hz), 159.6 (d, $J = 3.0$ Hz), 136.7 (d, $J = 6.8$ Hz), 129.5 (d, $J = 2.3$ Hz), 121.5 (d, $J = 6.8$ Hz), 119.0, 114.9 (d, $J = 6.0$ Hz), 113.4, 113.1 (d, $J = 3.0$ Hz), 63.2 (d, $J = 6.8$ Hz), 62.1 (d, $J = 7.5$ Hz), 55.2, 39.6 (d, $J = 140.3$ Hz), 35.5, 16.4 (d, $J = 6.0$ Hz), 16.2 (d, $J = 6.0$ Hz) ppm.

(S)-Diethyl 1-(4-fluorophenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ea): ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.40 (ddd, J = 7.6, 5.2, 2.3 Hz, 2H), 7.29 (s, 2H), 7.01 (t, J = 8.5 Hz, 2H), 6.33 – 6.22 (m, 2H), 4.14 – 4.03 (m, 2H), 3.97 – 3.80 (m, 2H), 3.75 – 3.67 (m, 1H), 3.48 (s, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.09 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*): δ = 167.6 (d, J = 18.8 Hz), 162.1 (dd, J = 245.3, 3.8 Hz), 130.9 (dd, J = 6.8, 3.8 Hz), 130.7 (dd, J = 7.5, 6.8 Hz), 119.0, 115.6 (dd, J = 21.0, 2.3 Hz), 113.4, 63.2 (d, J = 7.5 Hz), 63.1 (d, J = 7.5 Hz), 39.3 (d, J = 141.0 Hz), 35.6, 16.4 (d, J = 6.0 Hz), 16.2 (d, J = 6.0 Hz) ppm.

(S)-Diethyl 1-(4-chlorophenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5fa): ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.37 (d, J = 8.3 Hz, 2H), 7.29 (s, 4H), 6.28 (s, 2H), 4.15 – 4.02 (m, 2H), 3.95 – 3.73 (m, 3H), 3.62 – 3.41 (m, 2H), 1.29 (t, J = 7.0 Hz, 3H), 1.11 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*): δ = 167.4 (d, J = 18.8 Hz), 133.7 (d, J = 6.8 Hz), 133.4 (d, J = 3.8 Hz), 130.4 (d, J = 6.8 Hz), 128.8 (d, J = 3.0 Hz), 119.0, 113.5, 63.4 (d, J = 6.8 Hz), 62.2 (d, J = 6.8 Hz), 39.4 (d, J = 141.0 Hz), 35.4, 16.3 (d, J = 6.0 Hz), 16.2 (d, J = 6.0 Hz) ppm.

(S)-Diethyl 1-(4-bromophenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ga): ^1H NMR (400 MHz, Chloroform-*d*): δ = 8.35 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 3.8 Hz, 1H), 7.45 (d, J = 8.3 Hz, 2H), 7.36 (dd, J = 8.6, 2.2 Hz, 2H), 7.29 – 7.25 (m, 1H), 6.65 (d, J = 3.8 Hz, 1H), 4.16 – 4.06 (m, 2H), 3.98 – 3.88 (m, 2H), 3.83 – 3.72 (m, 1H), 3.71 – 3.61 (m, 1H), 3.60 – 3.49 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*): δ = 168.1 (d, J = 18.8 Hz), 134.3 (d, J = 7.5 Hz), 131.7 (d, J = 2.3 Hz), 130.9 (d, J = 6.8 Hz), 123.9, 120.9, 116.6, 63.2 (d, J = 7.5 Hz), 62.2 (d, J = 6.8 Hz), 39.0 (d, J = 140.3 Hz), 35.3, 16.3 (d, J = 6.0 Hz), 16.1 (d, J = 5.3 Hz) ppm.

(S)-Diethyl 1-(4-methylphenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ha): ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.39 – 7.22 (m, 4H), 7.12 (d, J = 7.7 Hz, 2H), 6.27 (s, 2H), 4.13 – 4.01 (m, 2H), 3.99 – 3.79 (m, 2H), 3.76 – 3.66 (m, 1H), 3.53 (dd, J = 14.1, 7.0 Hz, 2H), 2.30 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H), 1.09 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100

MHz, Chloroform-*d*): δ = 167.7 (d, *J* = 18.0 Hz), 137.2 (d, *J* = 3.0 Hz), 131.9 (d, *J* = 6.8 Hz), 129.3 (d, *J* = 2.3 Hz), 128.9 (d, *J* = 6.8 Hz), 119.0, 113.2, 63.1 (d, *J* = 6.8 Hz), 62.0 (d, *J* = 6.8 Hz), 39.1 (d, *J* = 140.3 Hz), 35.5, 21.0, 16.3 (d, *J* = 6.0 Hz), 16.1 (d, *J* = 6.0 Hz) ppm.

(S)-Diethyl 1-(4-methoxyphenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ia): ¹H NMR (400 MHz, Chloroform-*d*): δ = 7.38 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 6.90 – 6.80 (m, 2H), 6.30 – 6.23 (m, 2H), 4.07 (ddd, *J* = 10.9, 7.0, 3.0 Hz, 2H), 3.96 – 3.84 (m, 2H), 3.77 (s, 3H), 3.74 – 3.65 (m, 1H), 3.58 – 3.42 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*): δ = 167.8 (d, *J* = 18.0 Hz), 158.9 (d, *J* = 3.0 Hz), 130.2 (d, *J* = 6.8 Hz), 126.9 (d, *J* = 6.8 Hz), 119.1, 114.1 (d, *J* = 2.3 Hz), 113.4, 63.2 (d, *J* = 6.8 Hz), 62.1 (d, *J* = 7.5 Hz), 55.2, 38.7 (d, *J* = 141.0 Hz), 35.7, 16.4 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 6.0 Hz) ppm.

(S)-Diethyl 1-(4-nitrophenyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ja): ¹H NMR (400 MHz, Chloroform-*d*): δ = 8.19 (d, *J* = 8.7 Hz, 2H), 7.62 (dd, *J* = 8.9, 2.2 Hz, 2H), 7.28 (d, *J* = 4.0 Hz, 2H), 6.30 (d, *J* = 4.7 Hz, 2H), 4.19 – 4.08 (m, 2H), 4.06 – 3.92 (m, 2H), 3.89 – 3.78 (m, 1H), 3.64 – 3.54 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (100 MHz, Chloroform-*d*): δ = 167.0 (d, *J* = 18.0 Hz), 147.2 (d, *J* = 3.8 Hz), 143.1 (d, *J* = 6.8 Hz), 130.0 (d, *J* = 6.0 Hz), 123.7 (d, *J* = 3.0 Hz), 118.9, 113.7, 63.3 (d, *J* = 6.8 Hz), 62.5 (d, *J* = 6.8 Hz), 39.6 (d, *J* = 139.5 Hz), 35.1, 16.3 (d, *J* = 6.0 Hz), 16.1 (d, *J* = 5.3 Hz) ppm.

(S)-Diethyl 1-(furan-2-yl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ka): ¹H NMR (400 MHz, Chloroform-*d*): δ = 7.41 – 7.29 (m, 3H), 6.30 (dt, *J* = 8.9, 2.1 Hz, 4H), 4.12 – 4.03 (m, 4H), 3.96 – 3.89 (m, 1H), 3.60 – 3.42 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (100 MHz, Chloroform-*d*): δ = 167.6 (d, *J* = 17.3 Hz), 148.4 (d, *J* = 9.0 Hz), 142.2 (d, *J* = 3.8 Hz), 119.0, 113.5, 110.9 (d, *J* = 3.0 Hz), 108.5 (d, *J* = 7.5 Hz), 63.2 (d, *J* = 6.8 Hz), 62.6 (d, *J* = 6.8 Hz), 33.8 (d, *J* = 144.0 Hz), 33.6, 16.4 (d, *J* = 3.8 Hz), 16.3 (d, *J* = 4.5 Hz) ppm.

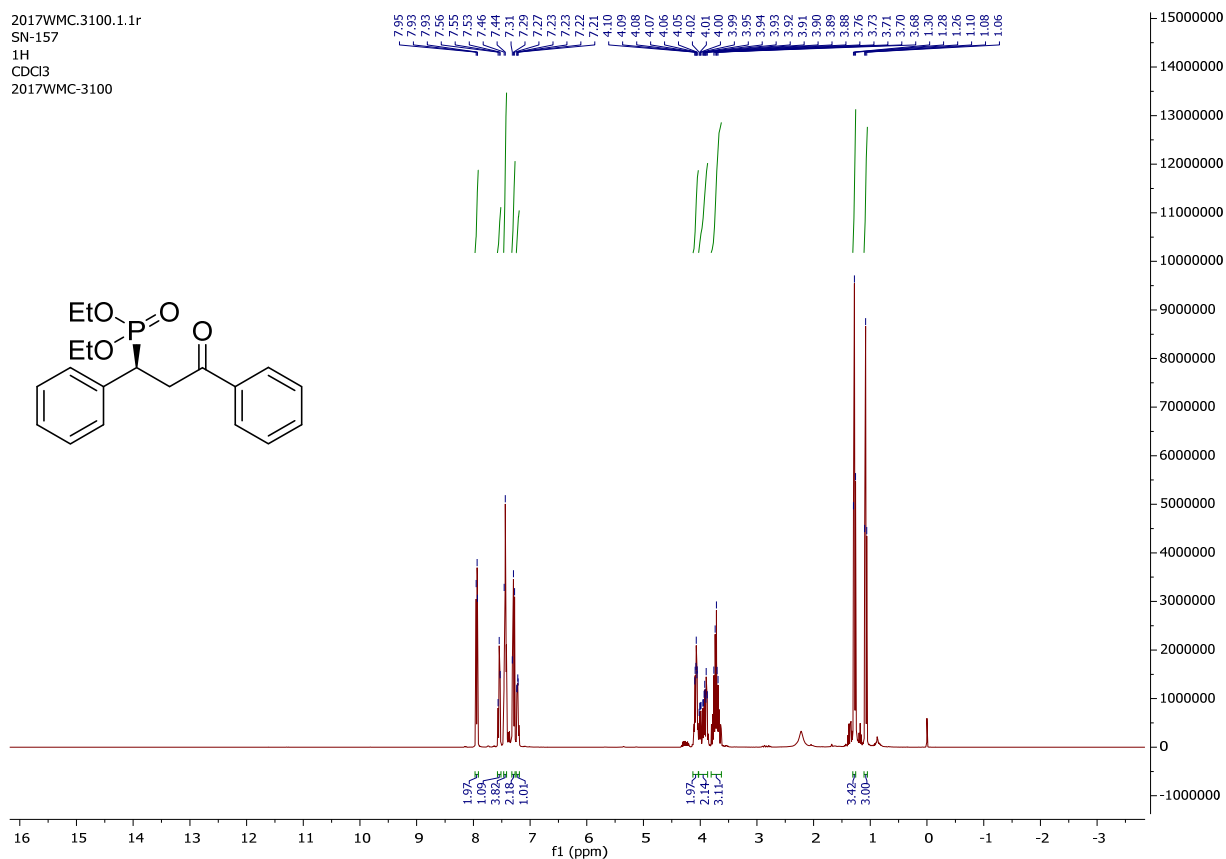
(S)-Diethyl 1-(thiophen-2-yl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5la): ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.31 (s, 2H), 7.20 (d, J = 5.1 Hz, 1H), 7.11 (t, J = 3.1 Hz, 1H), 6.99 – 6.90 (m, 1H), 6.36 – 6.23 (m, 2H), 4.21 (ddd, J = 22.3, 9.7, 4.0 Hz, 1H), 4.10 (p, J = 7.1, 6.5 Hz, 2H), 4.05 – 3.96 (m, 1H), 3.91 – 3.80 (m, 1H), 3.65 – 3.40 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*): δ = 167.4 (d, J = 18.0 Hz), 135.0 (d, J = 6.8 Hz), 128.1 (d, J = 4.5 Hz), 125.8, 123.4 (d, J = 9.0 Hz), 119.0, 113.4, 63.2 (d, J = 6.8 Hz), 62.2 (d, J = 6.8 Hz), 34.9 (d, J = 143.3 Hz), 35.8, 16.3 (d, J = 6.0 Hz), 16.1 (d, J = 6.0 Hz) ppm.

(S)-Diethyl 1-(1-naphthyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5ma): ^1H NMR (400 MHz, Chloroform-*d*): δ = 8.32 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.65 – 7.40 (m, 4H), 7.34 – 7.19 (m, 2H), 6.30 – 6.22 (m, 1H), 4.99 – 4.83 (m, 1H), 4.08 (td, J = 7.6, 7.1, 3.5 Hz, 2H), 3.75 – 3.72 (m, 3H), 3.42 – 3.28 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H), 0.76 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*): δ = 167.8 (d, J = 16.5 Hz), 133.8, 132.0 (d, J = 6.8 Hz), 131.7 (d, J = 6.8 Hz), 128.8, 128.1 (d, J = 3.8 Hz), 126.4, 125.7, 125.1 (d, J = 3.8 Hz), 123.3, 119.0, 116.5, 113.3, 63.2 (d, J = 6.8 Hz), 62.1 (d, J = 7.5 Hz), 36.3, 33.2 (d, J = 140.3 Hz), 16.2 (d, J = 6.0 Hz), 15.8 (d, J = 5.3 Hz) ppm.

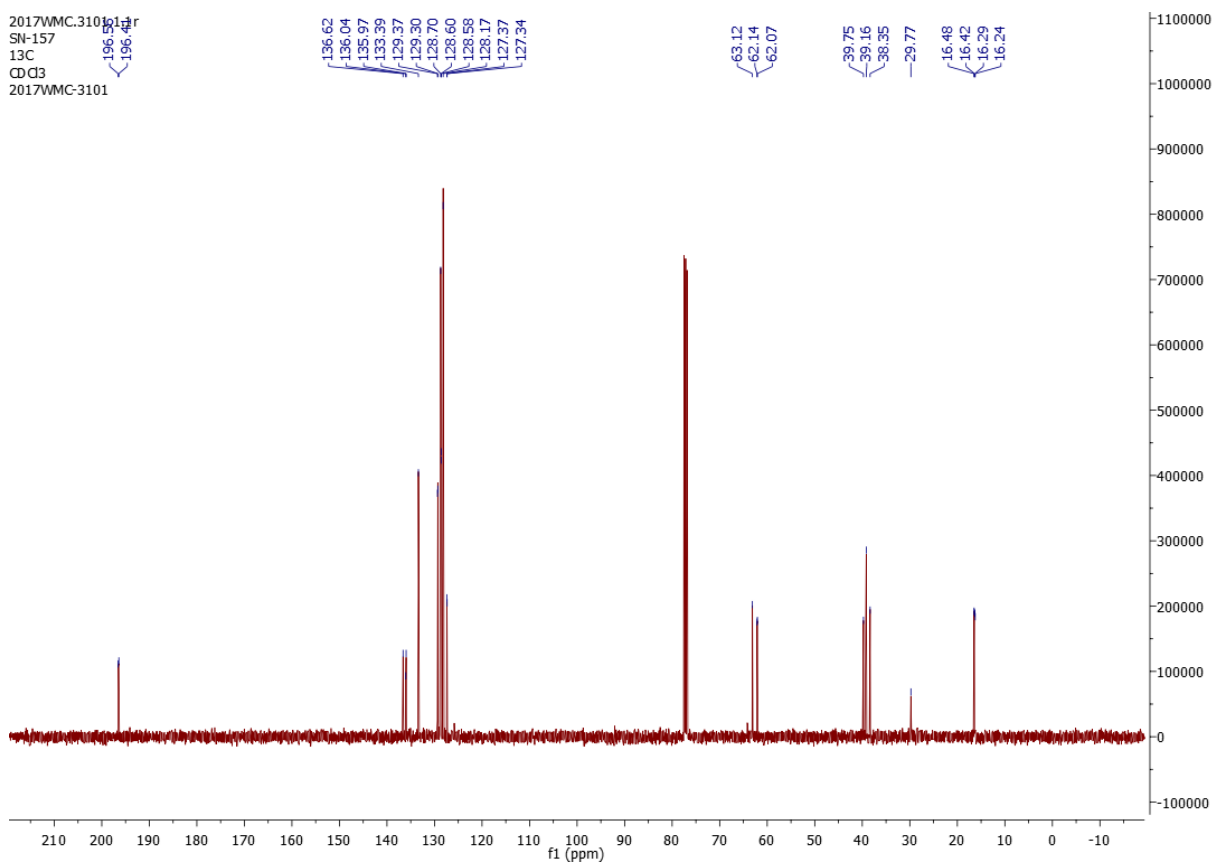
(S)-Diethyl 1-(2-naphthyl)-3-oxo-3-pyrrol-1-yl-propylphosphonate (5na): ^1H NMR (400 MHz, Chloroform-*d*): δ = 7.91 (d, J = 16.5 Hz, 1H), 7.80 (t, J = 8.0 Hz, 3H), 7.67 – 7.49 (m, 2H), 7.44 (d, J = 6.4 Hz, 2H), 7.34 – 7.16 (m, 2H), 6.25 (s, 1H), 4.10 (d, J = 5.9 Hz, 3H), 3.93 – 3.85 (m, 1H), 3.80 – 3.59 (m, 3H), 1.29 (t, J = 6.0 Hz, 3H), 1.03 (t, J = 6.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*): δ = 167.6 (d, J = 18.8 Hz), 133.2 (d, J = 3.0 Hz), 132.7 (d, J = 2.3 Hz), 132.6 (d, J = 7.5 Hz), 128.3 (d, J = 1.5 Hz), 128.1 (d, J = 8.3 Hz), 127.9, 127.6, 127.0 (d, J = 5.3 Hz), 126.2, 126.0, 119.0, 113.4, 63.3 (d, J = 6.8 Hz), 62.3 (d, J = 6.8 Hz), 39.6 (d, J = 141.0 Hz), 35.6, 16.3 (d, J = 6.0 Hz), 16.1 (d, J = 6.0 Hz) ppm.

5. NMR Spectra for All Compounds

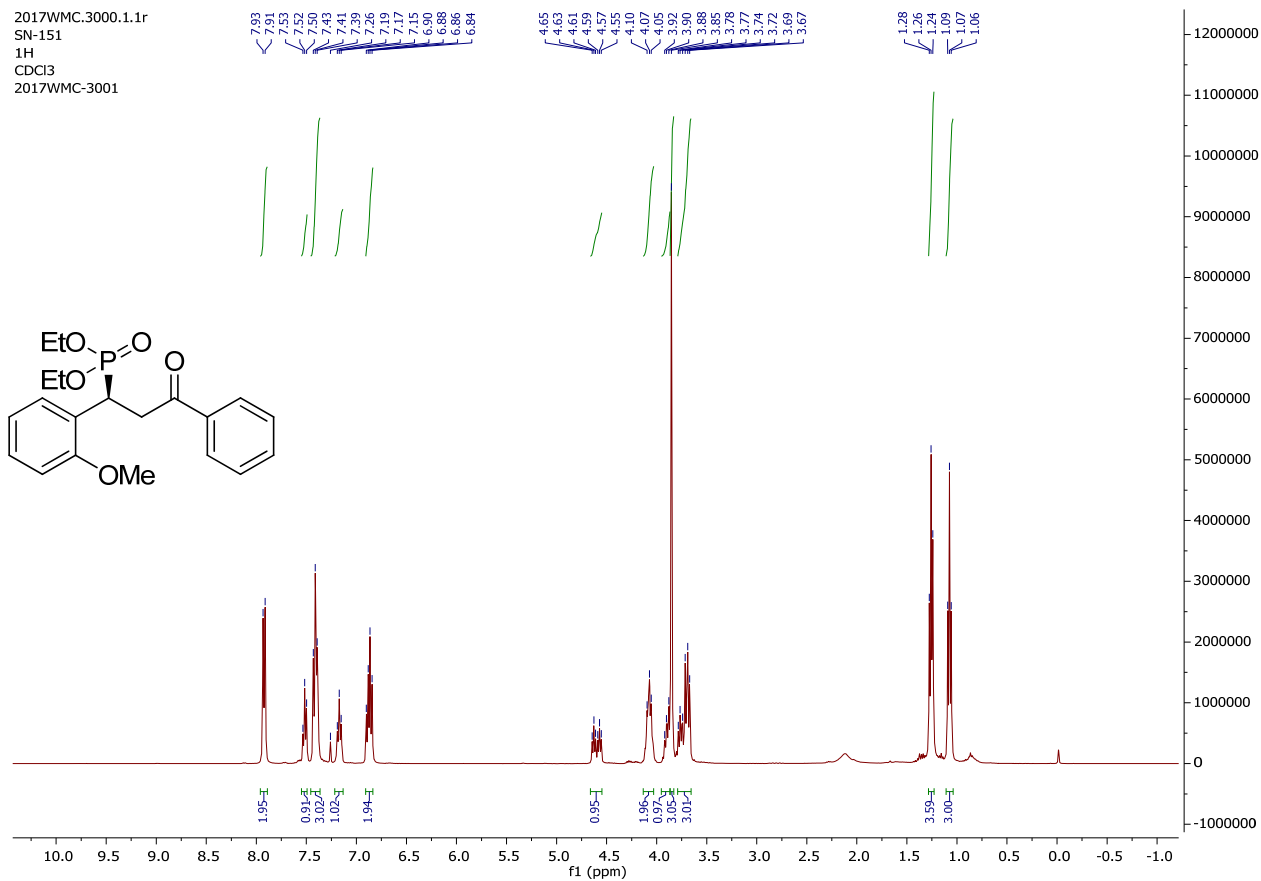
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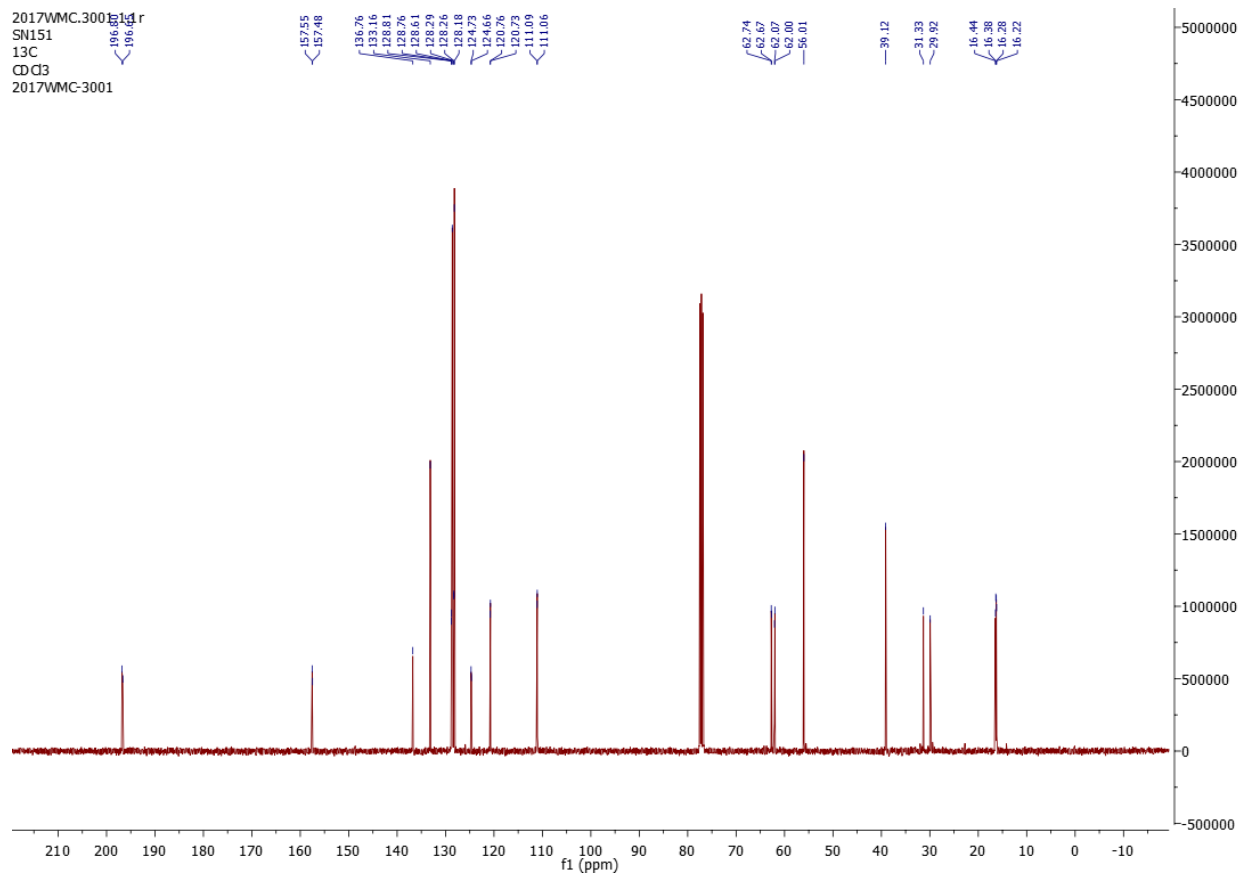
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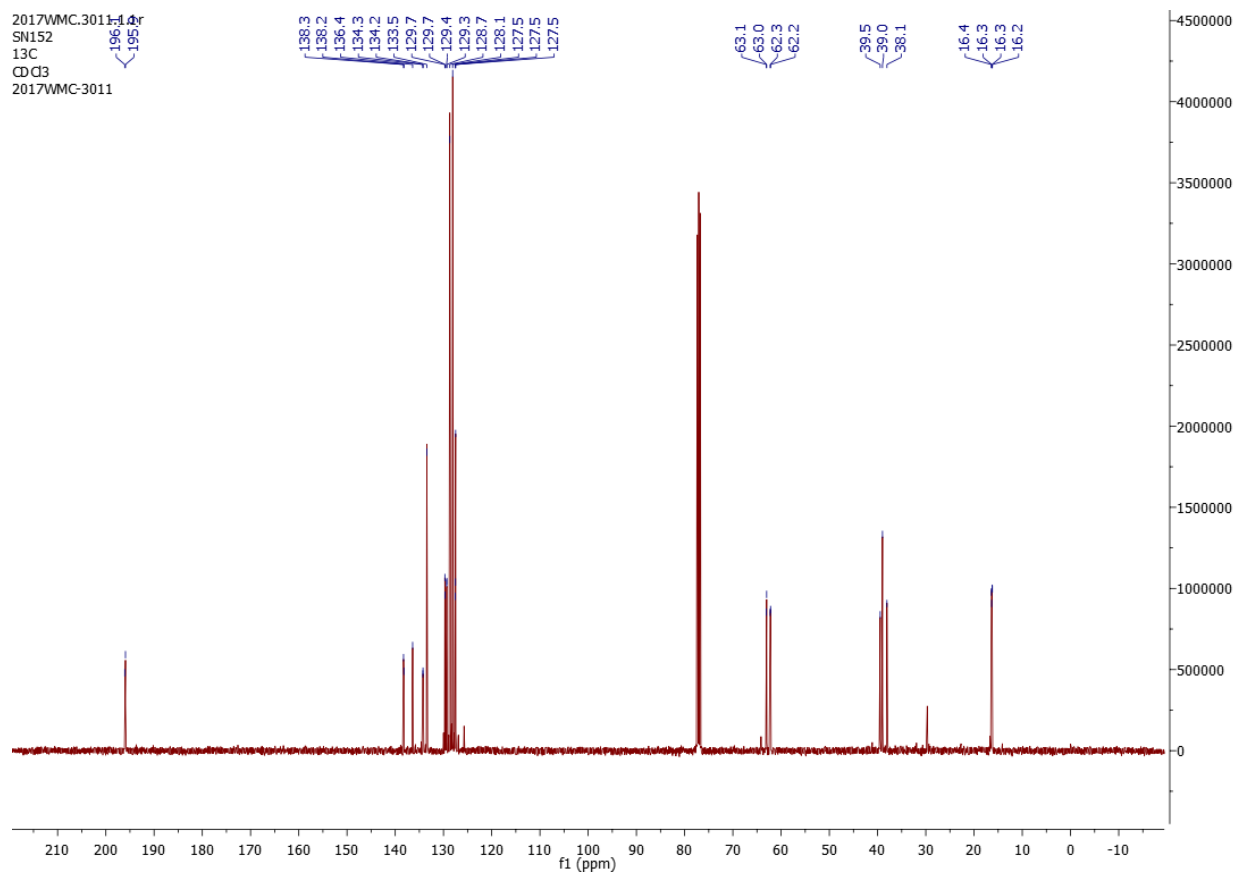
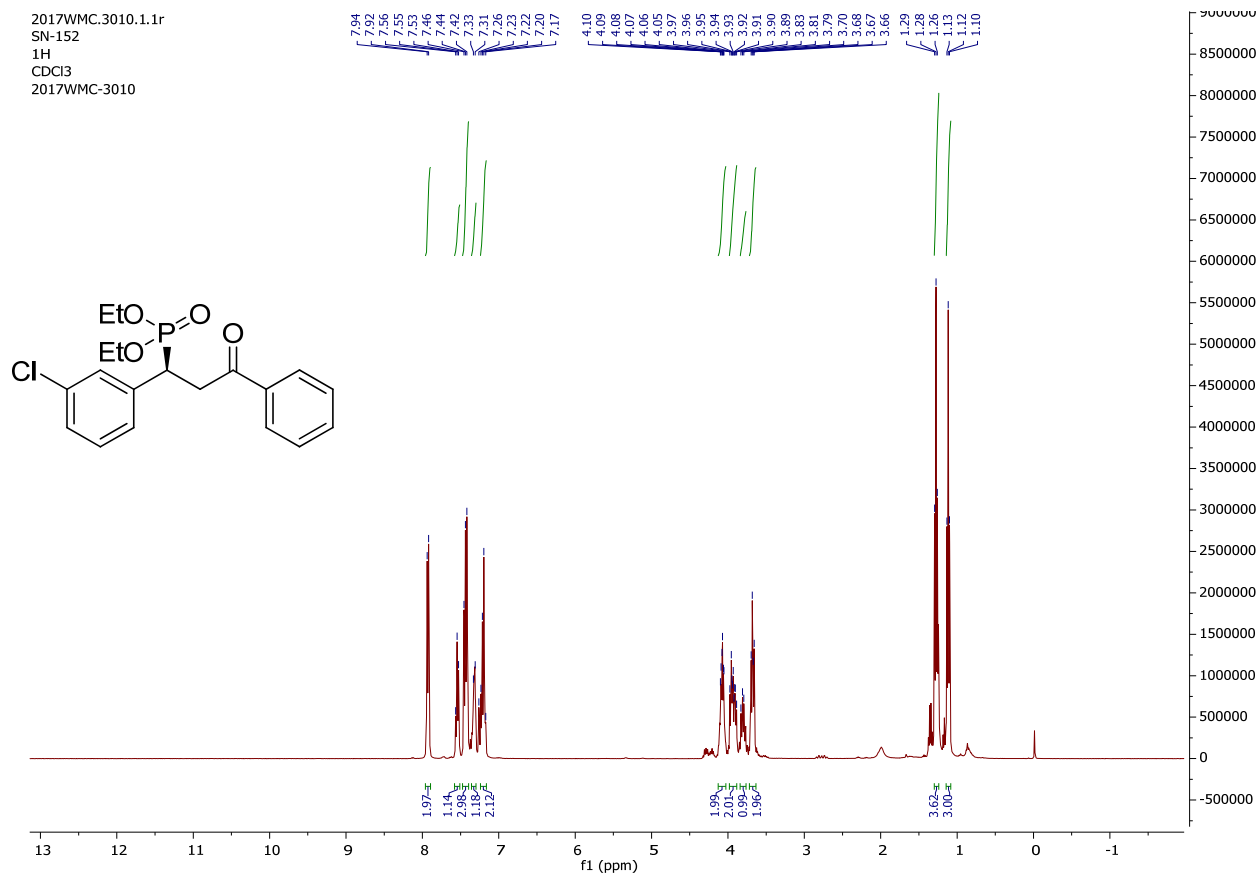


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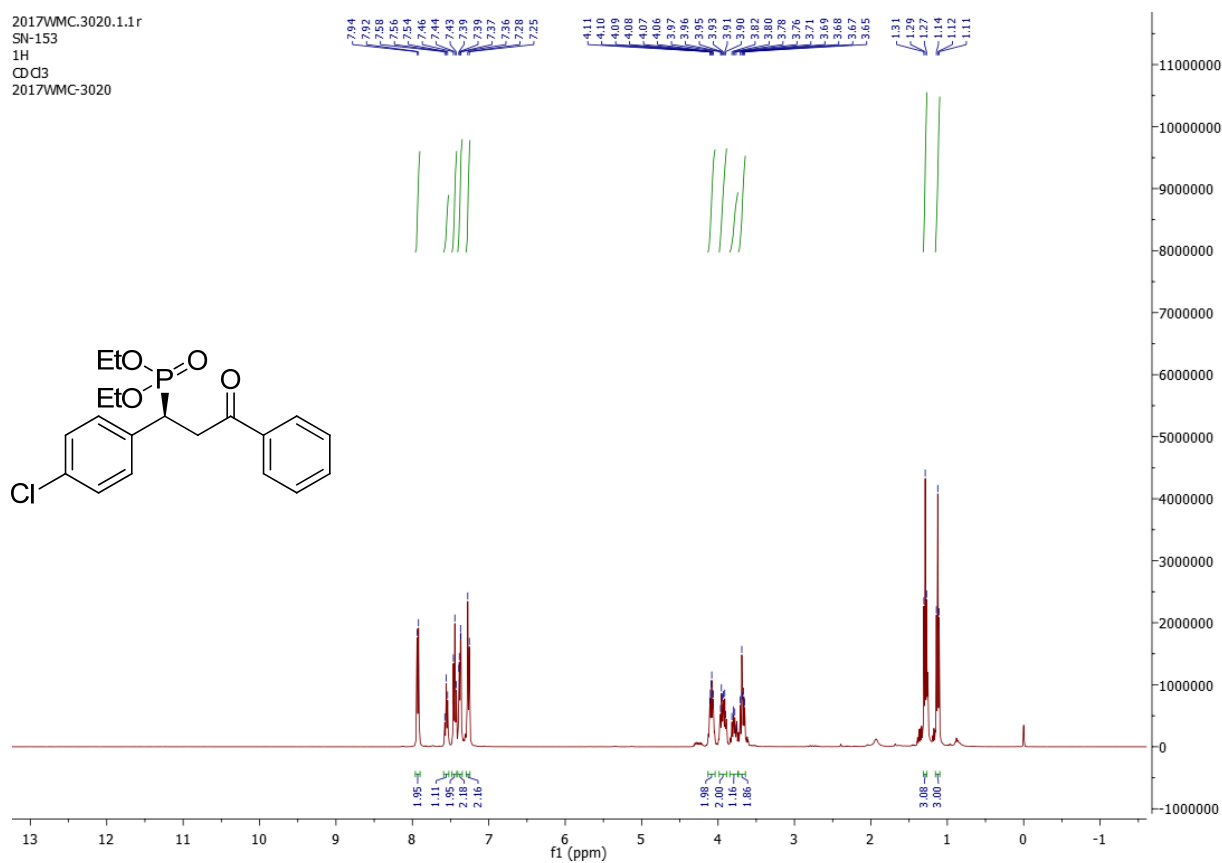


2017WMC.3000.1.1r
SN151
13C
CDCl3
2017WMC-3001

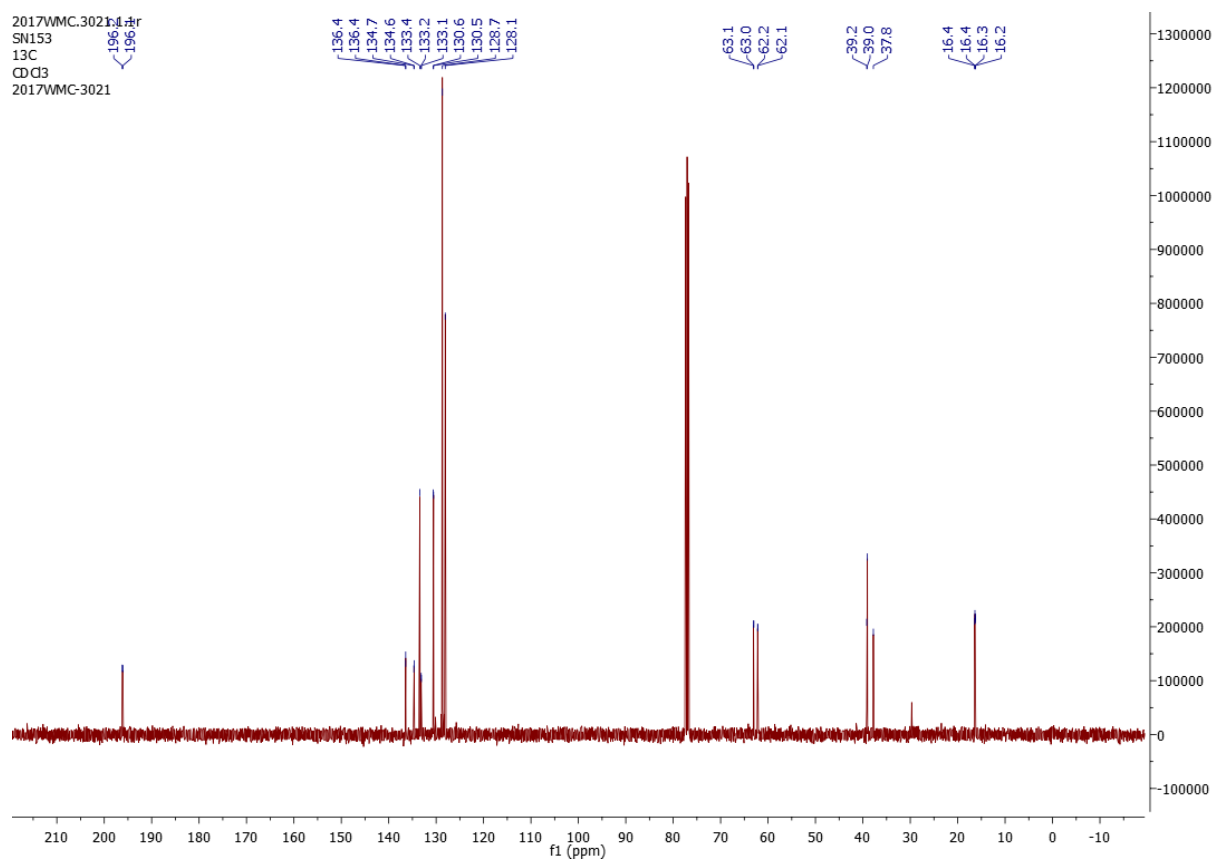




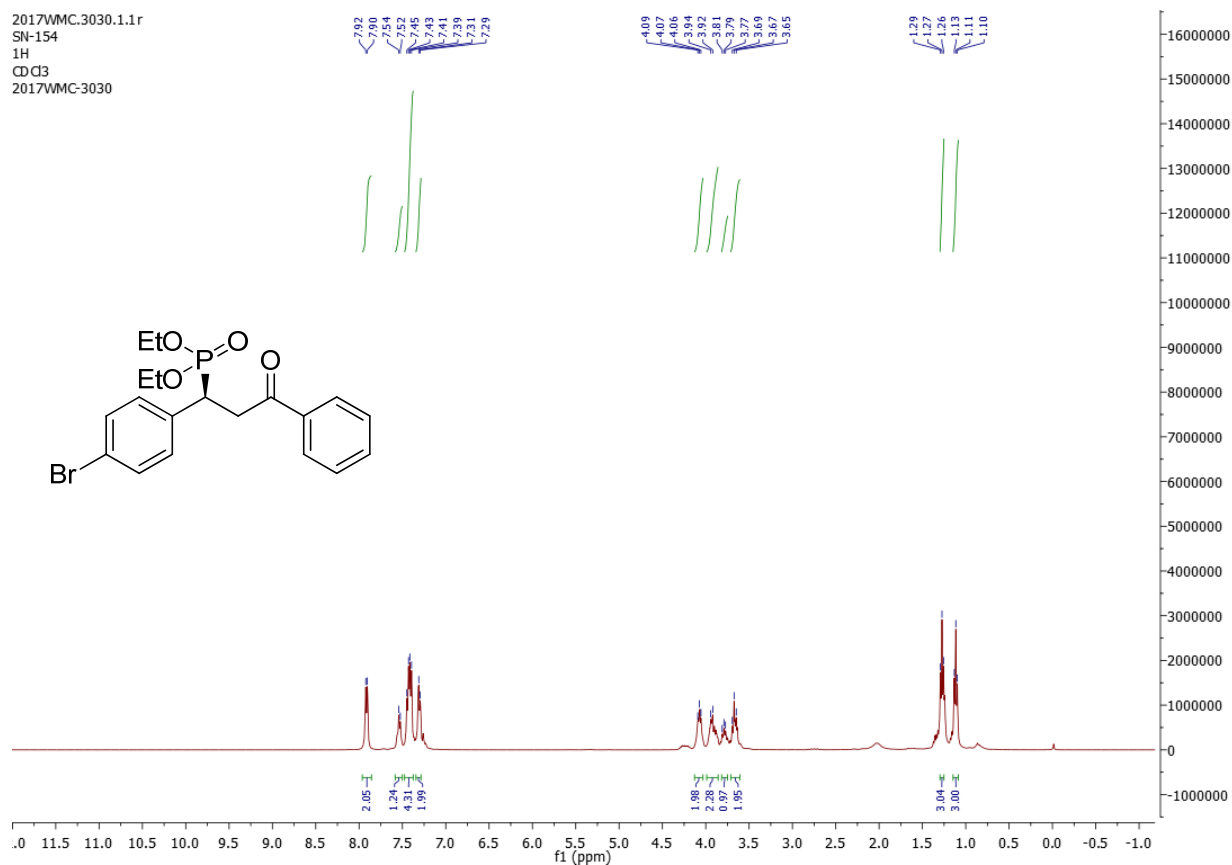
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SN-153
1H
CDCl₃
2017WMC-3020



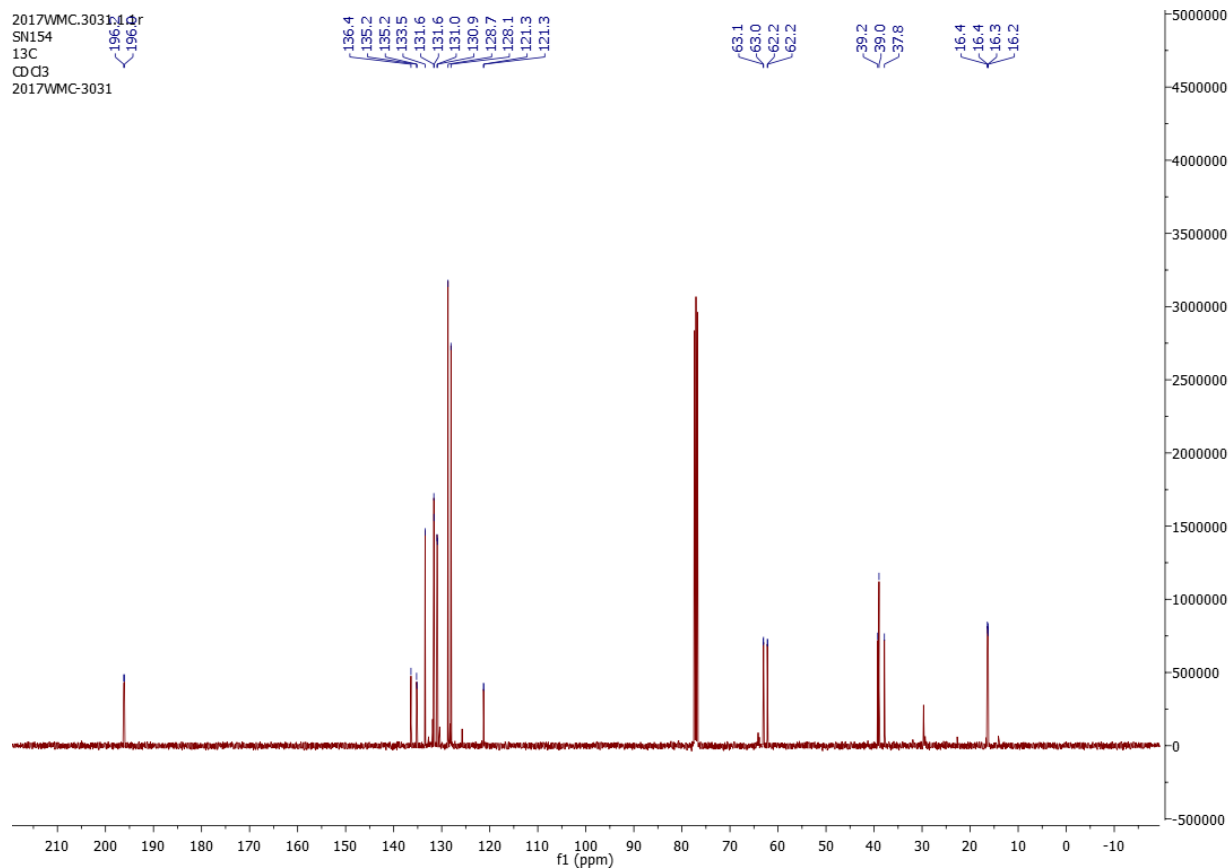
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SN153
13C
CDCl₃
2017WMC-3021

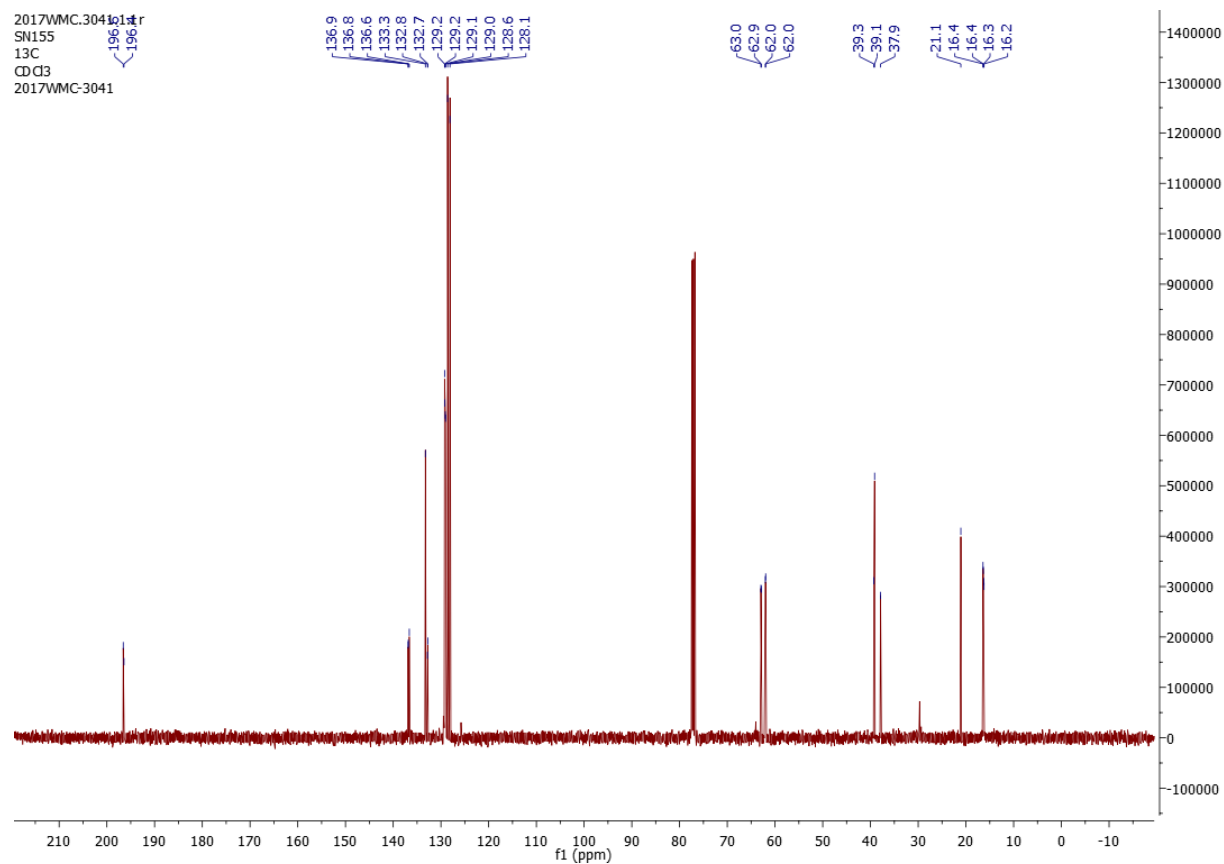
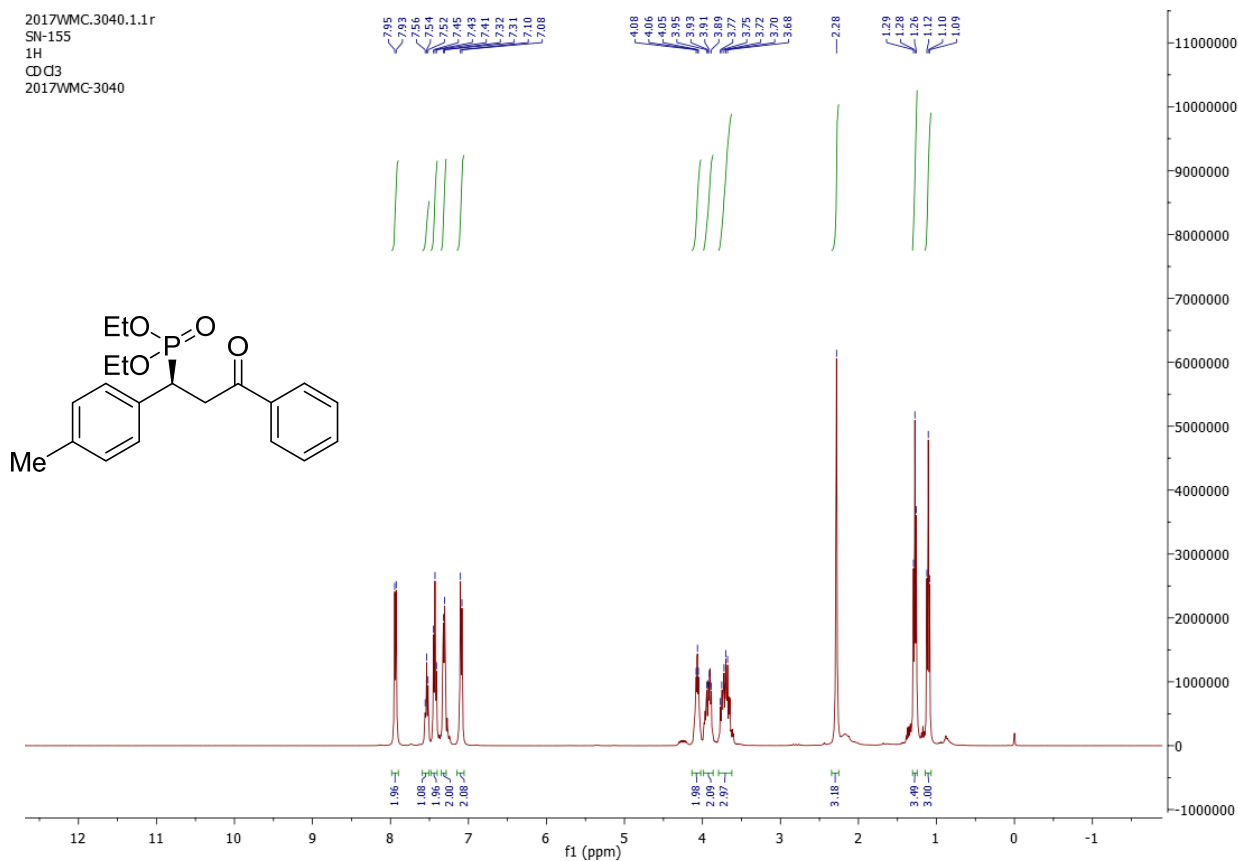


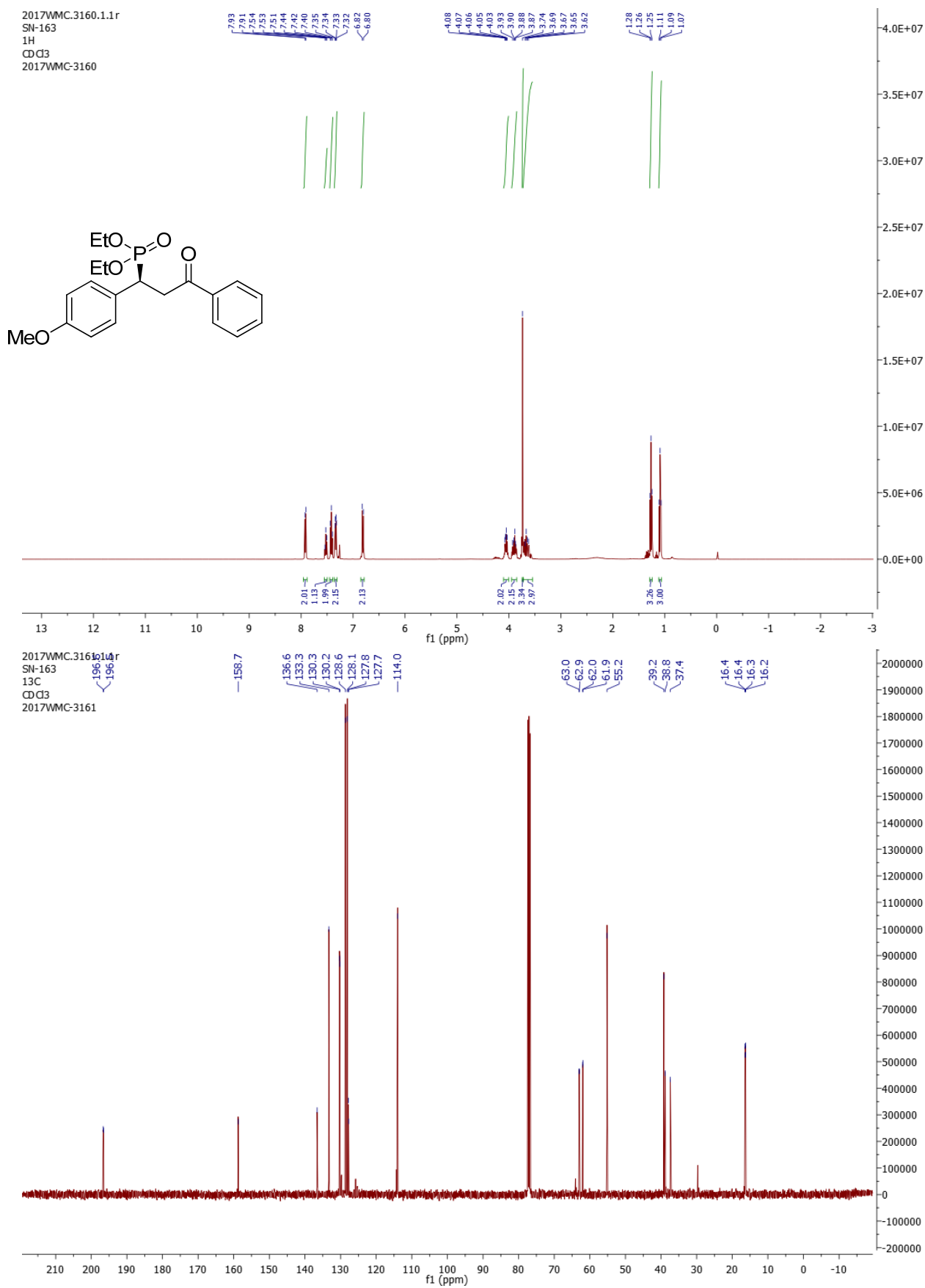
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SN-154
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CDCl₃
2017WMC-3030

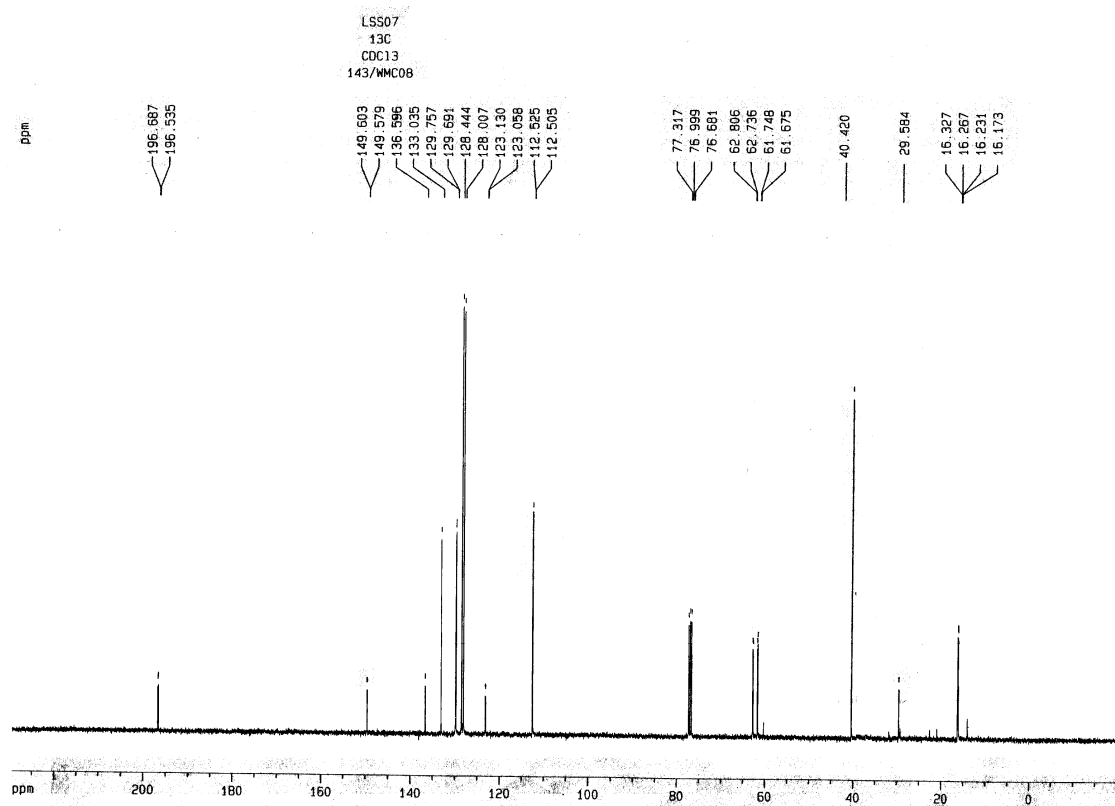
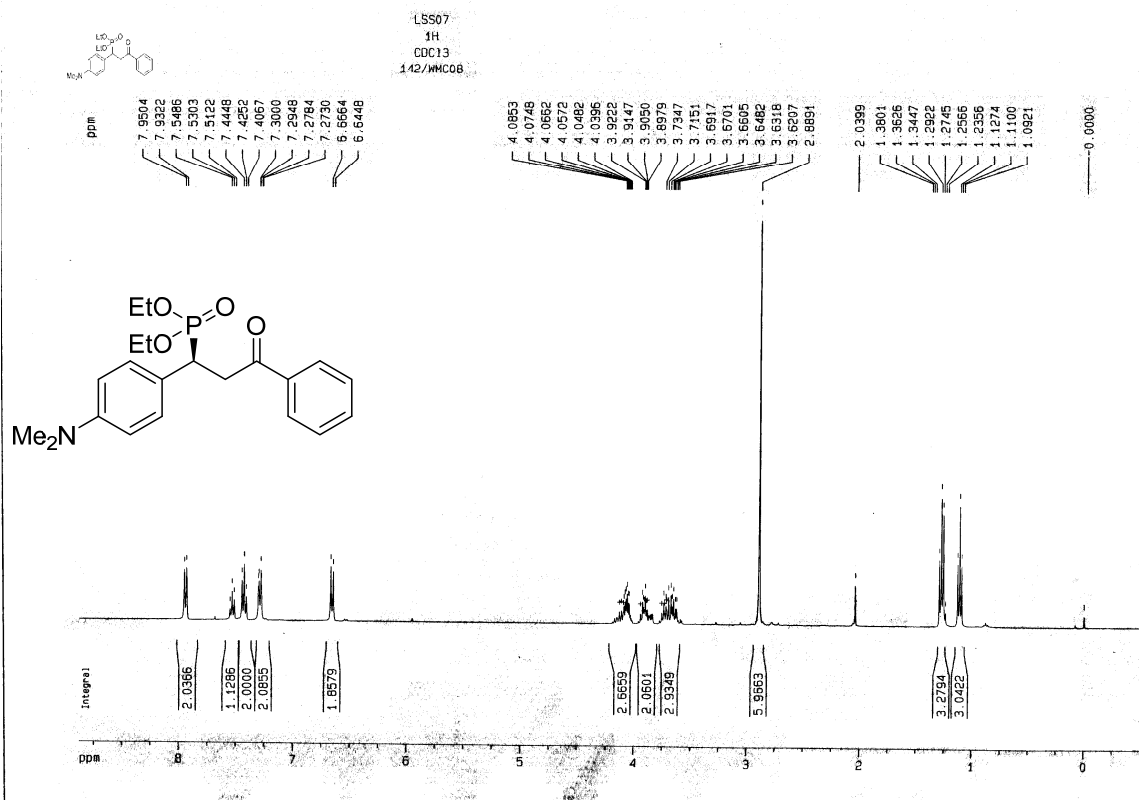


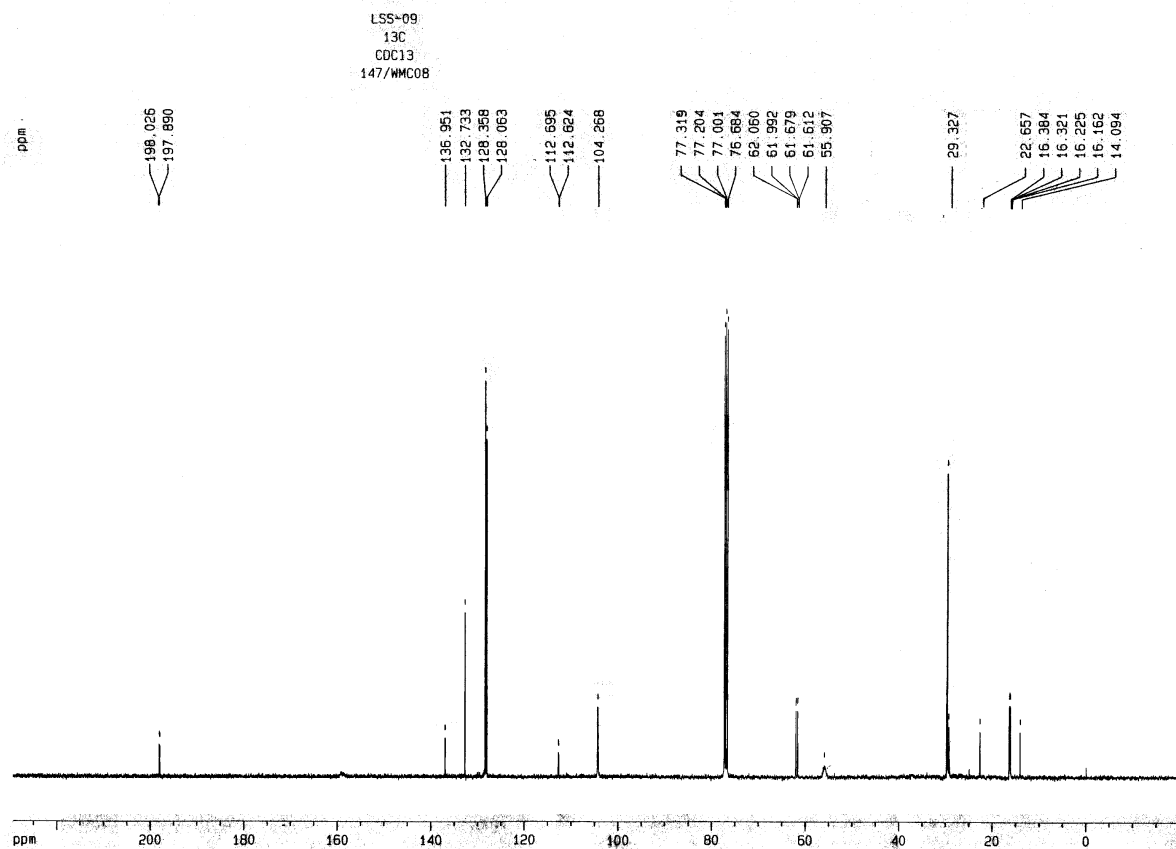
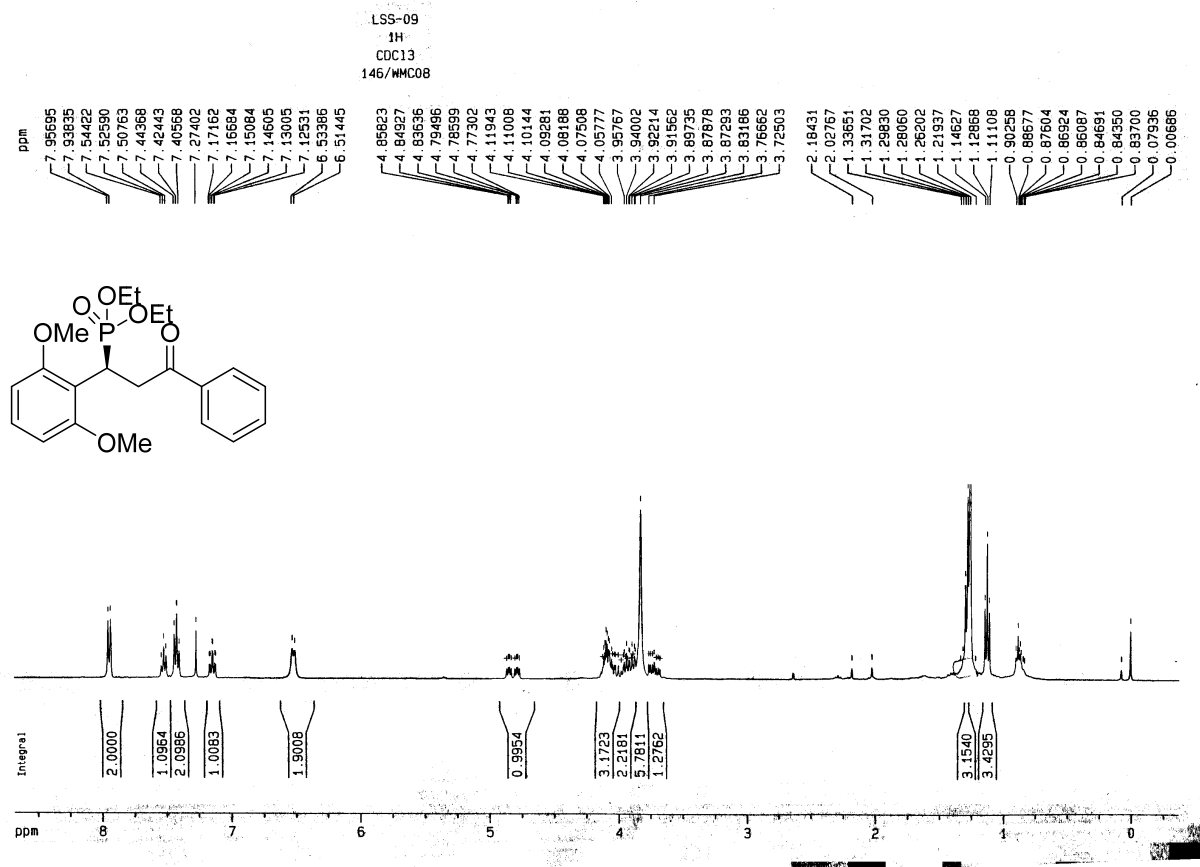
2017WMC.3030.1.1dr
SN154
13C
CDCl₃
2017WMC-3031



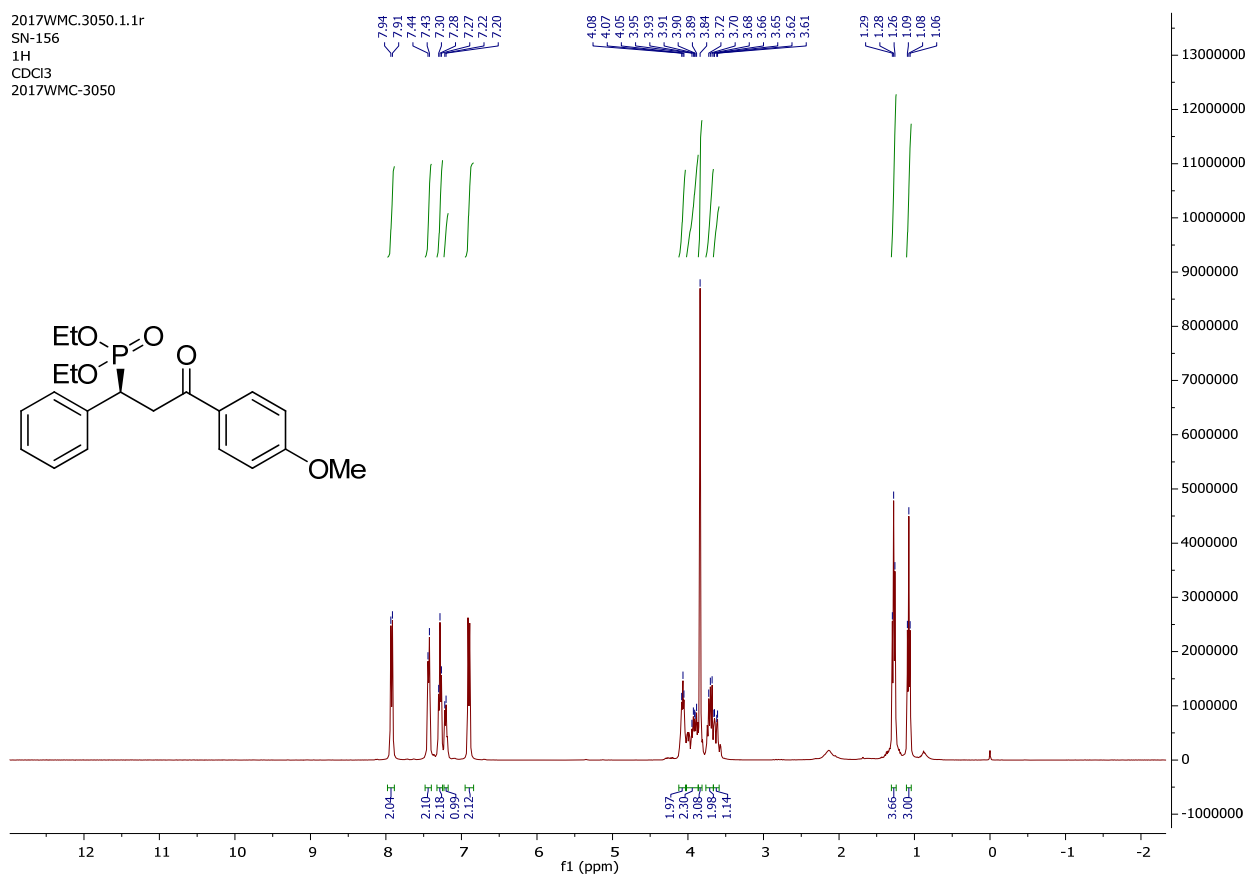




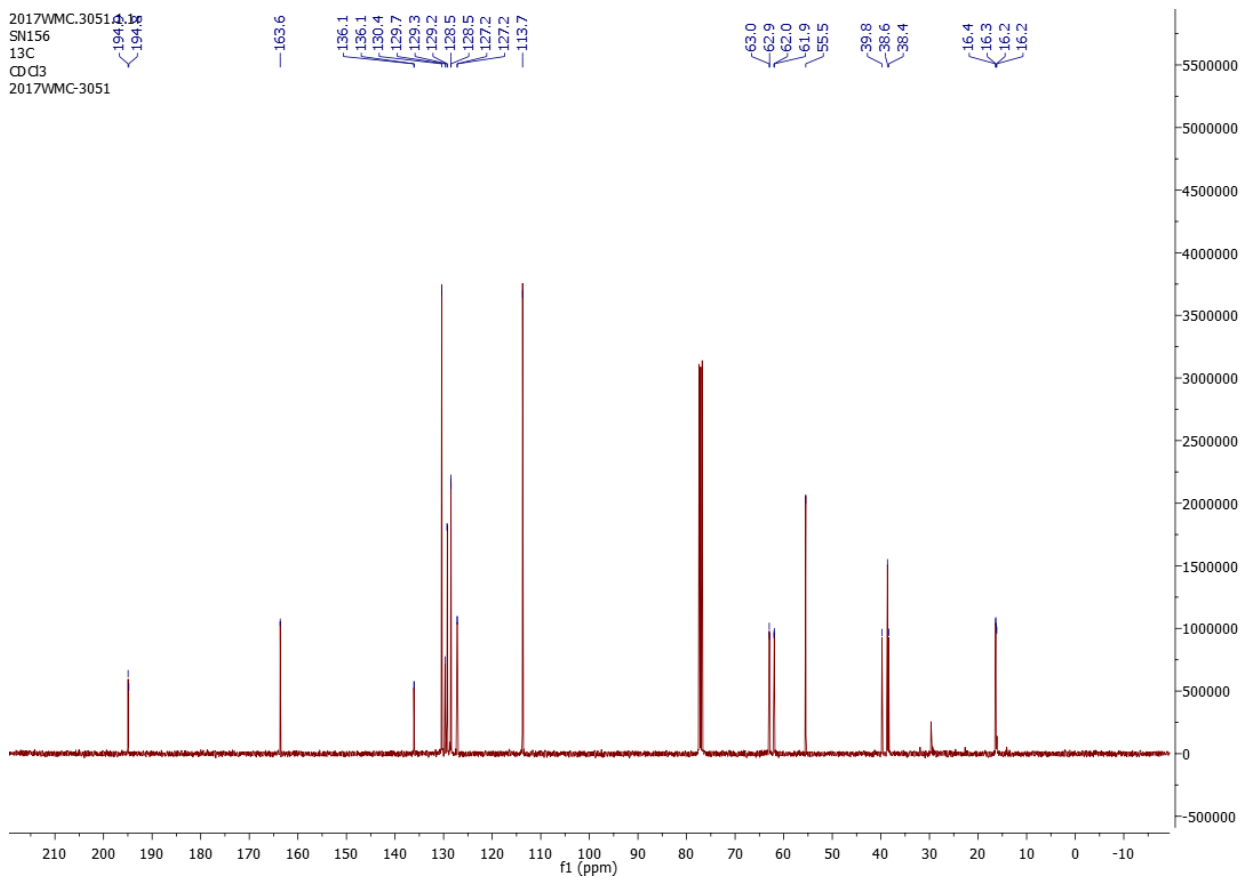


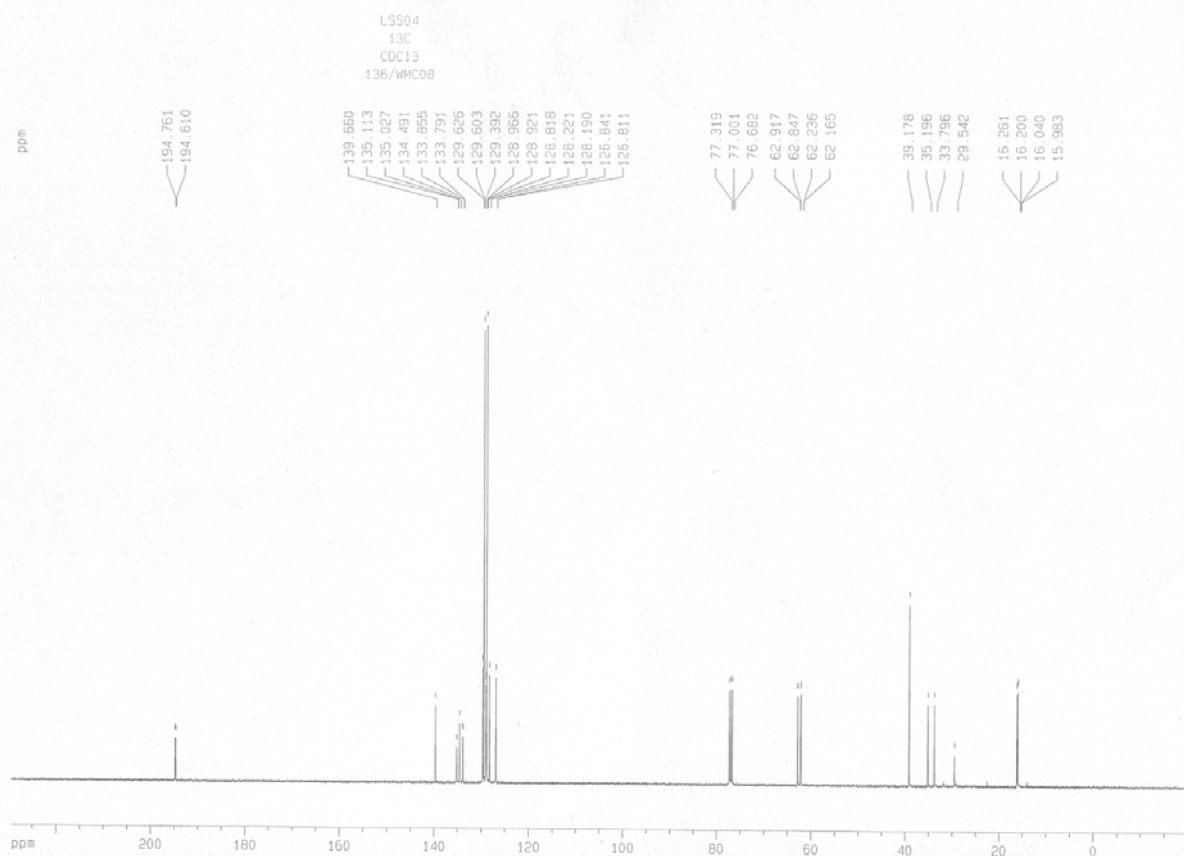
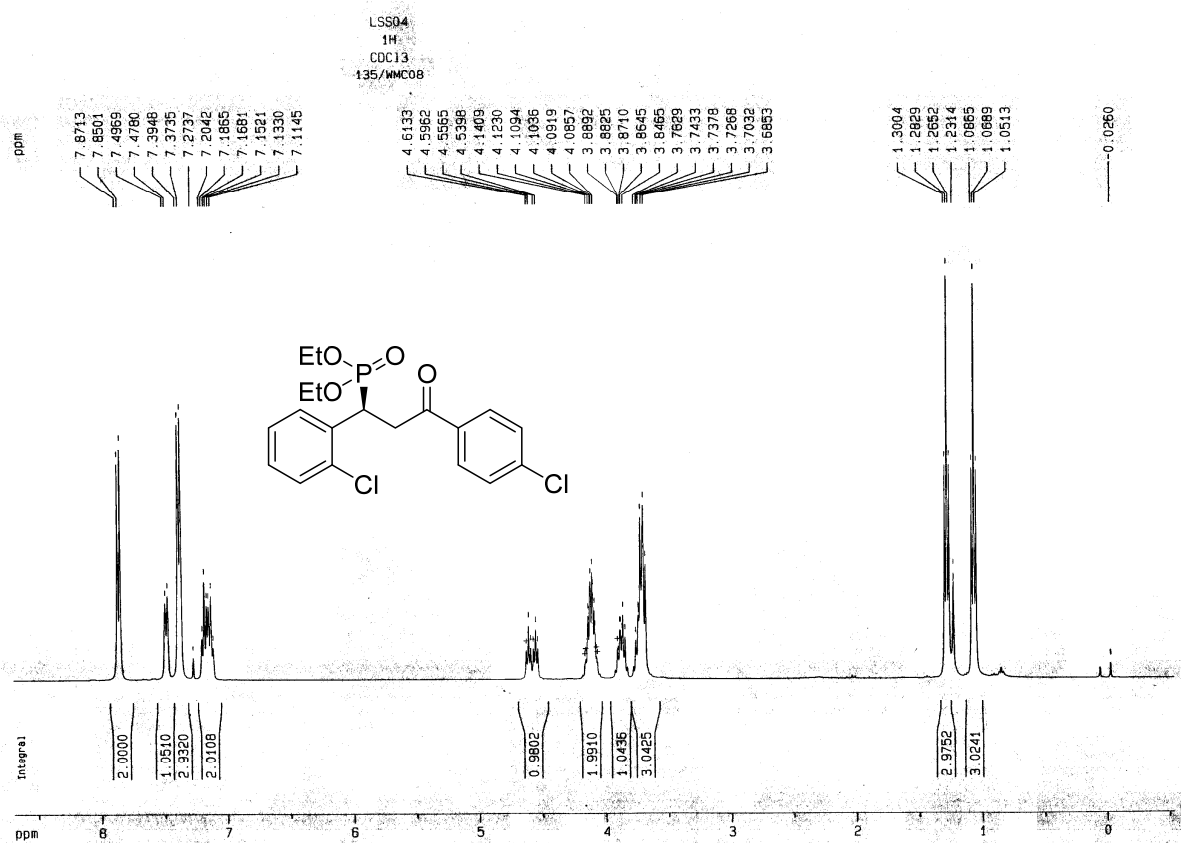


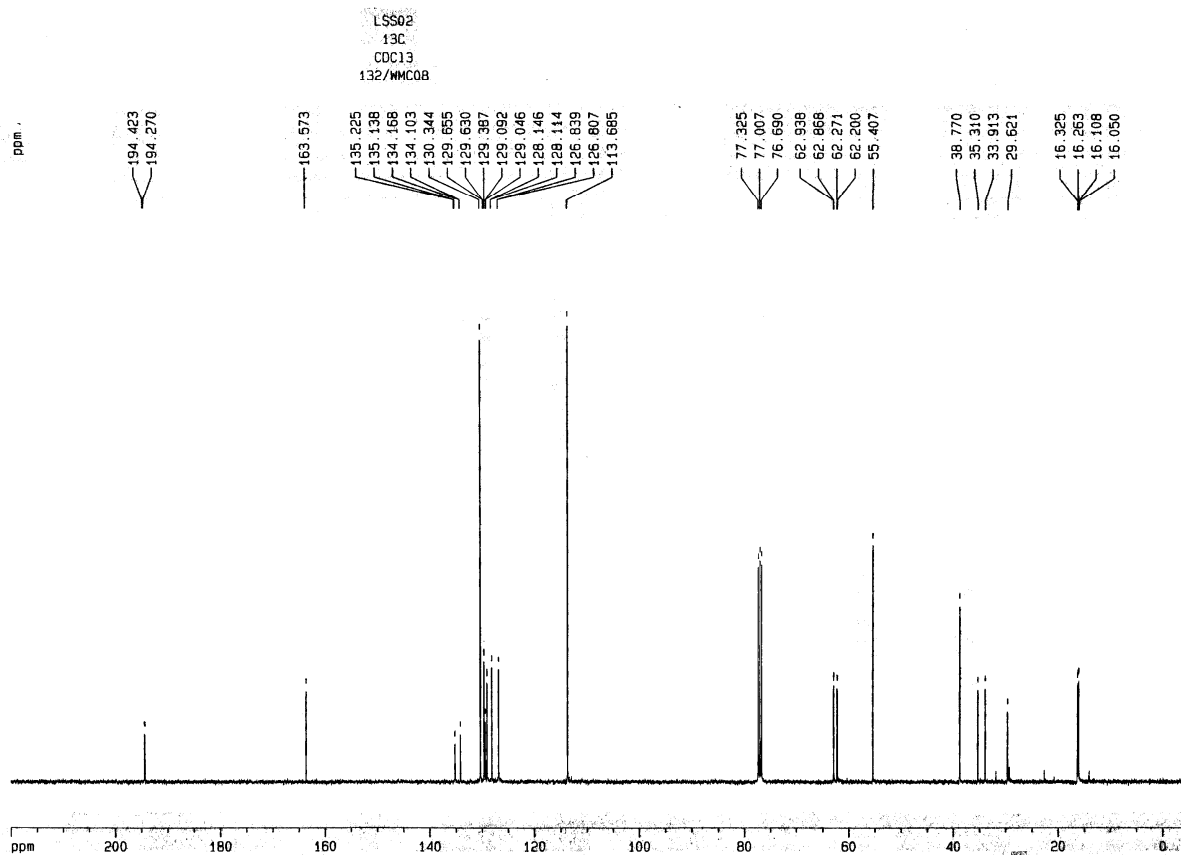
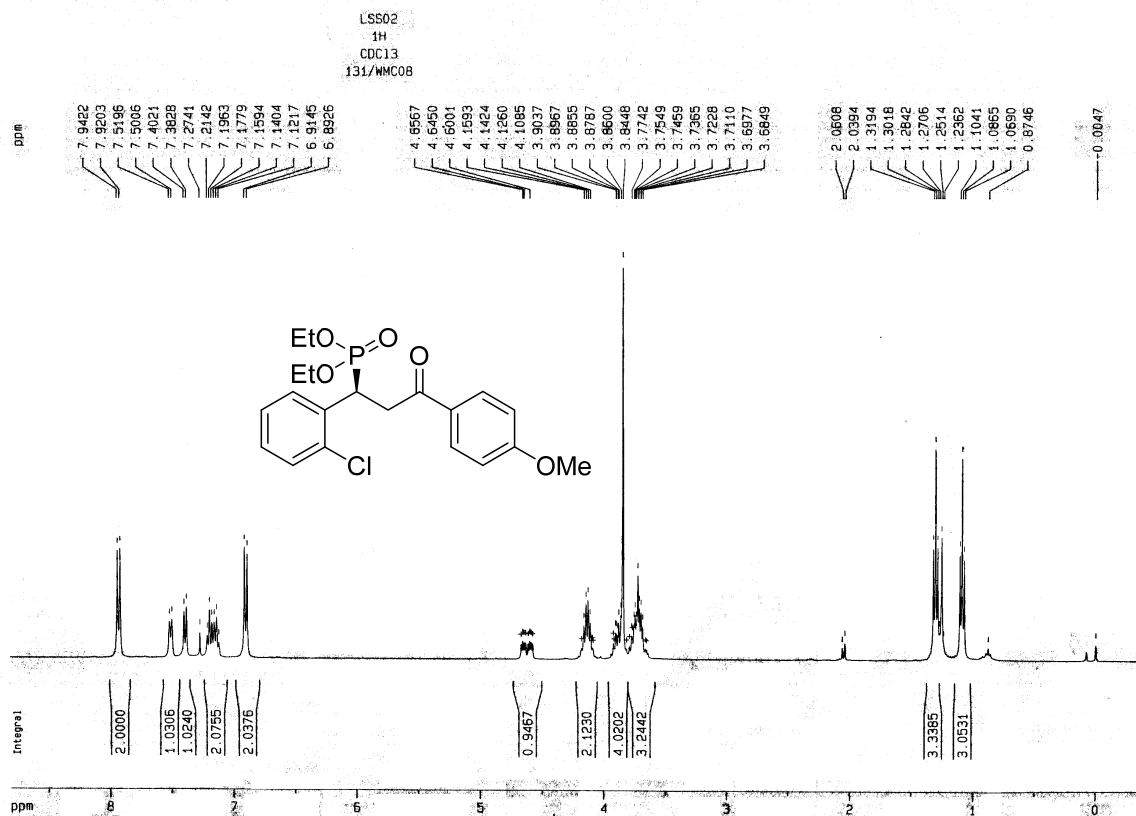
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SN-156
1H
CDCl3
2017WMC-3050

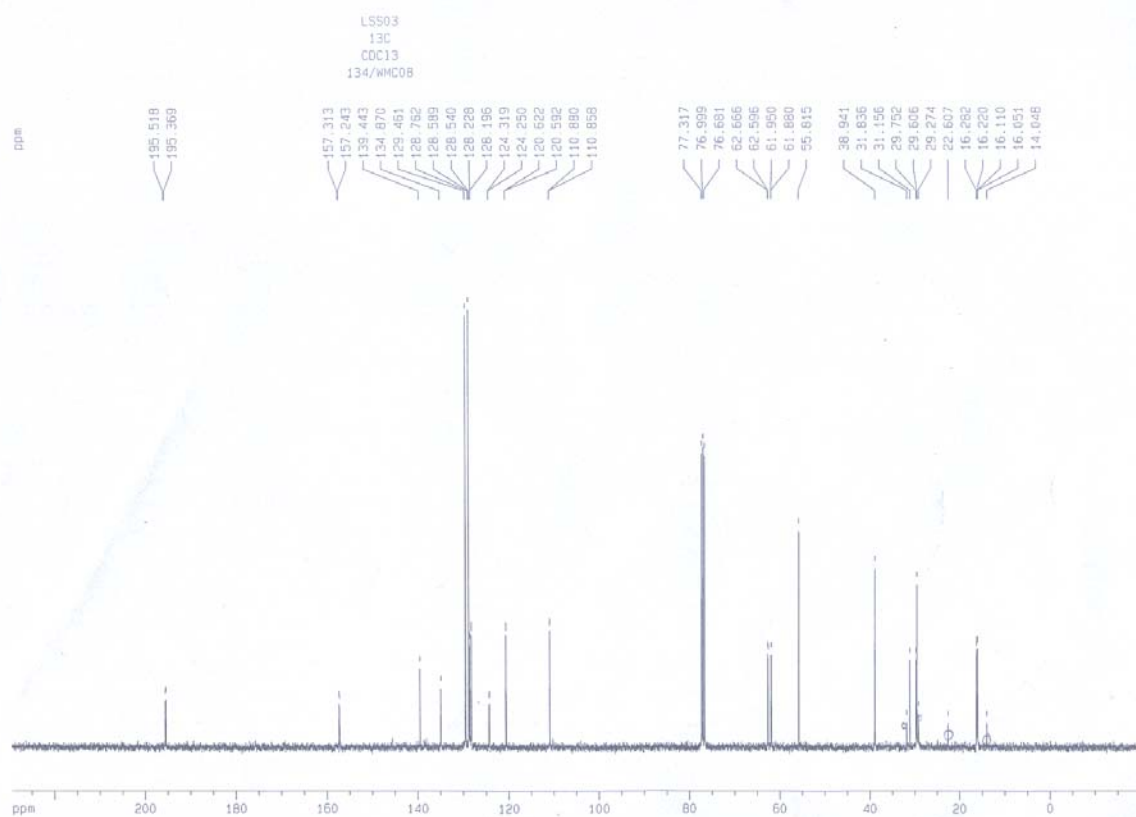
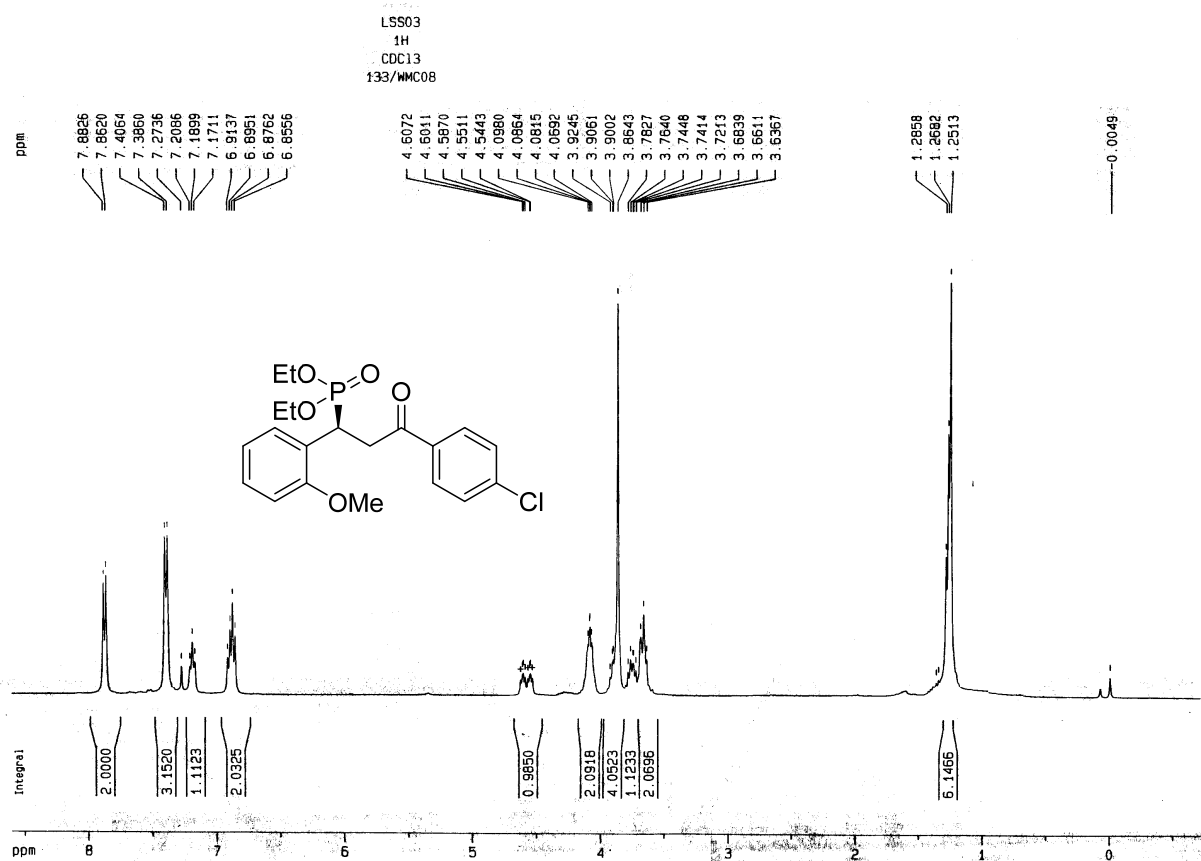


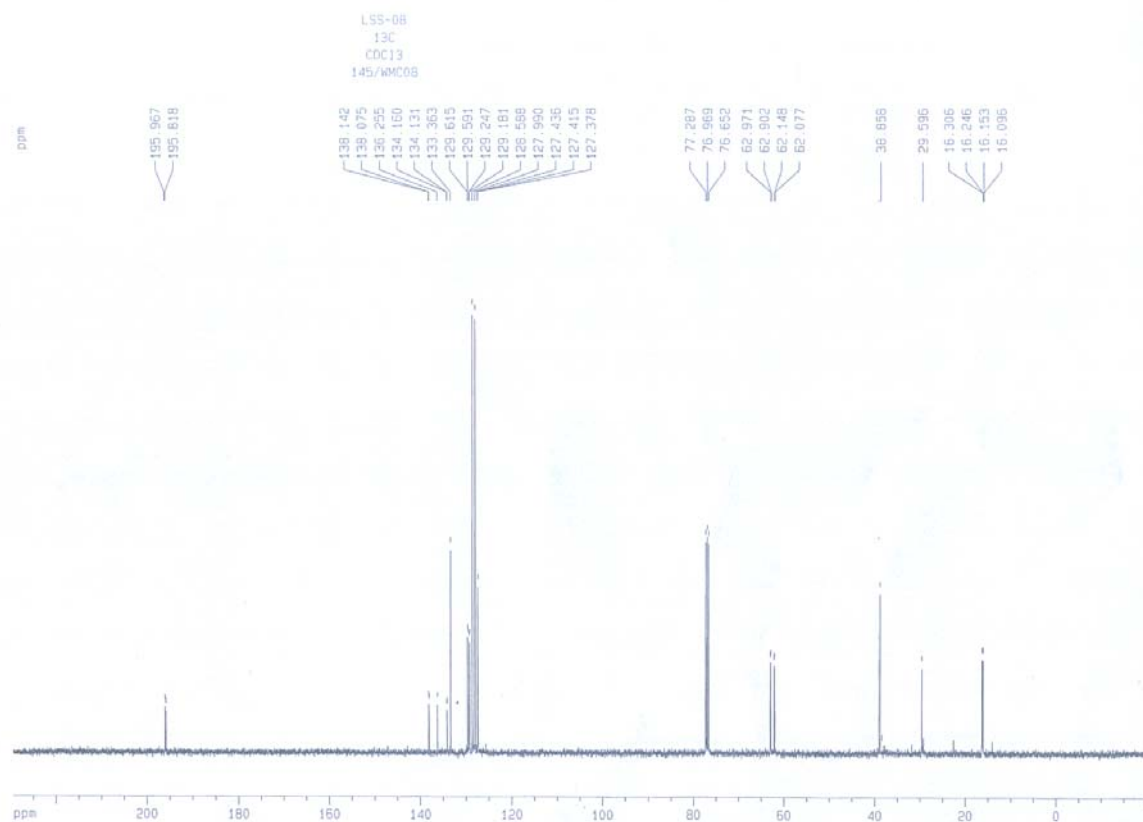
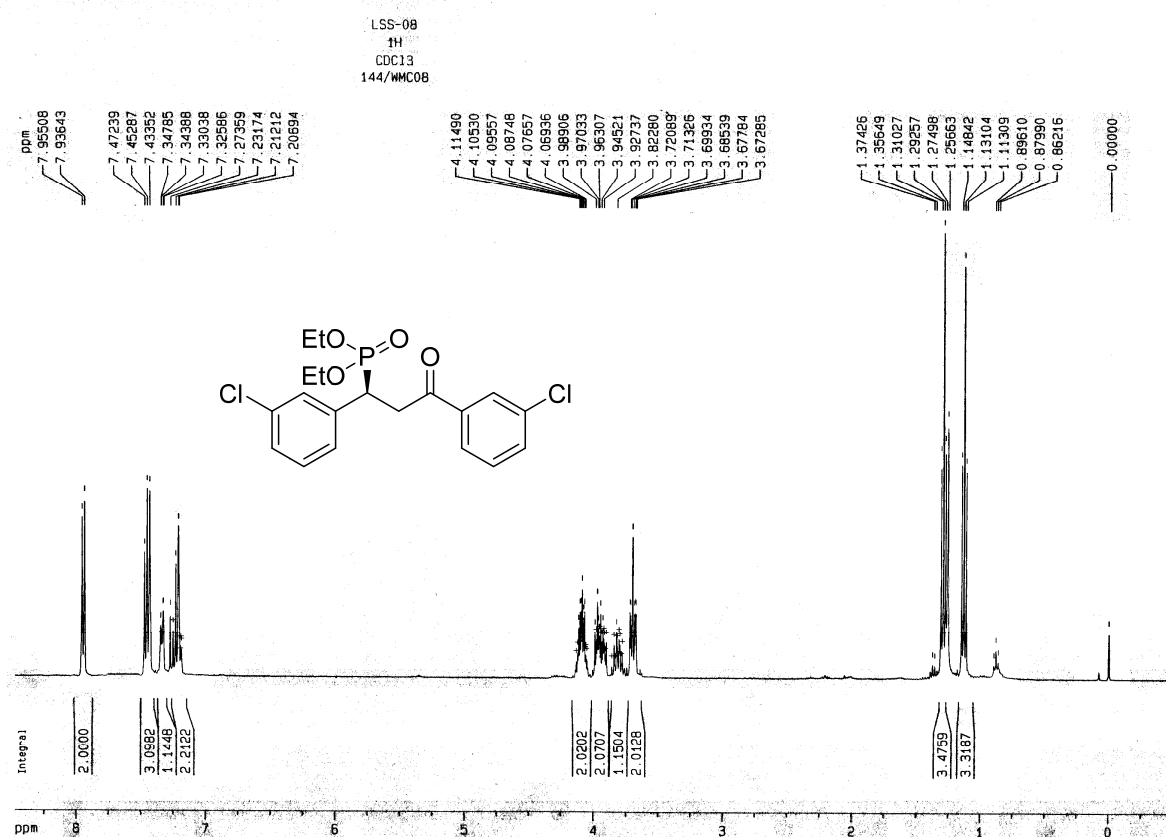
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13C
CDCl3
2017WMC-3051

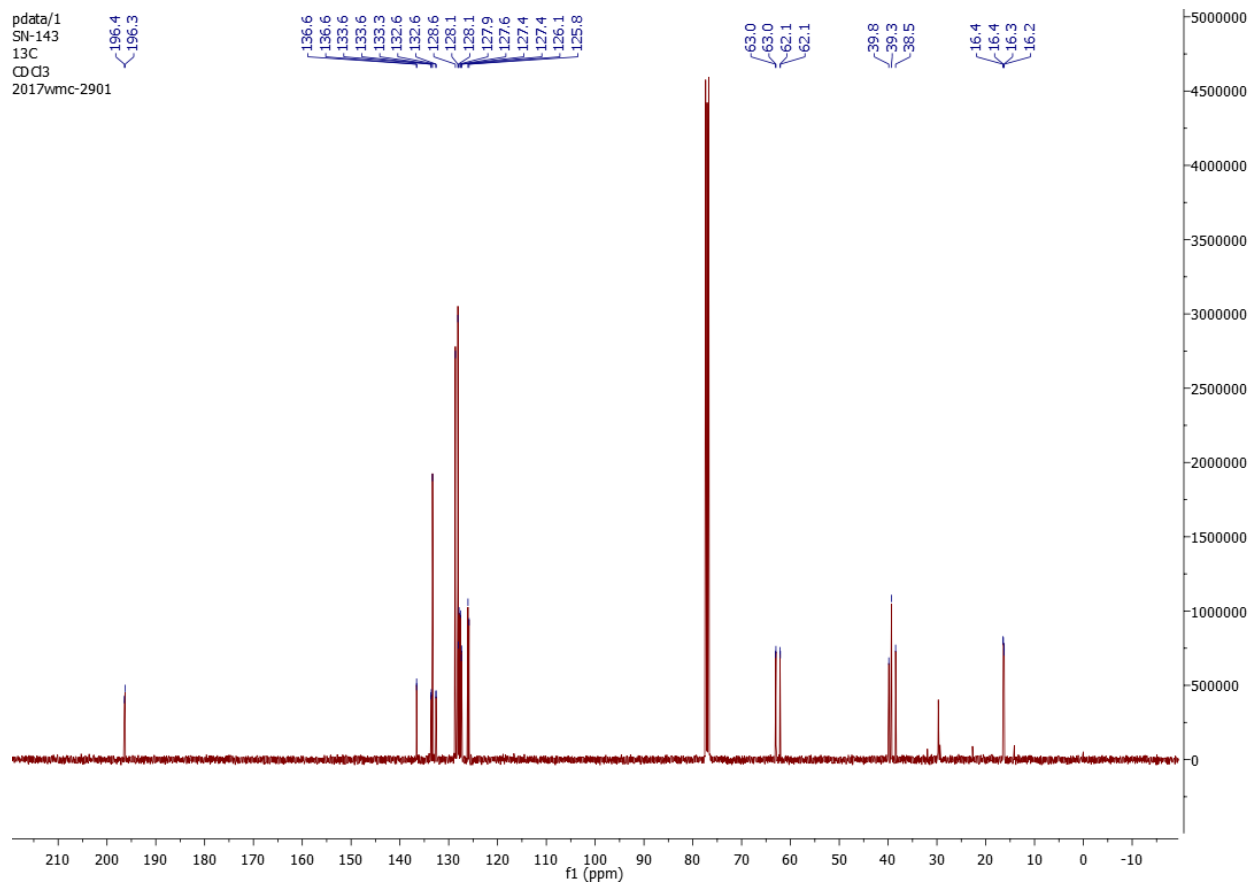
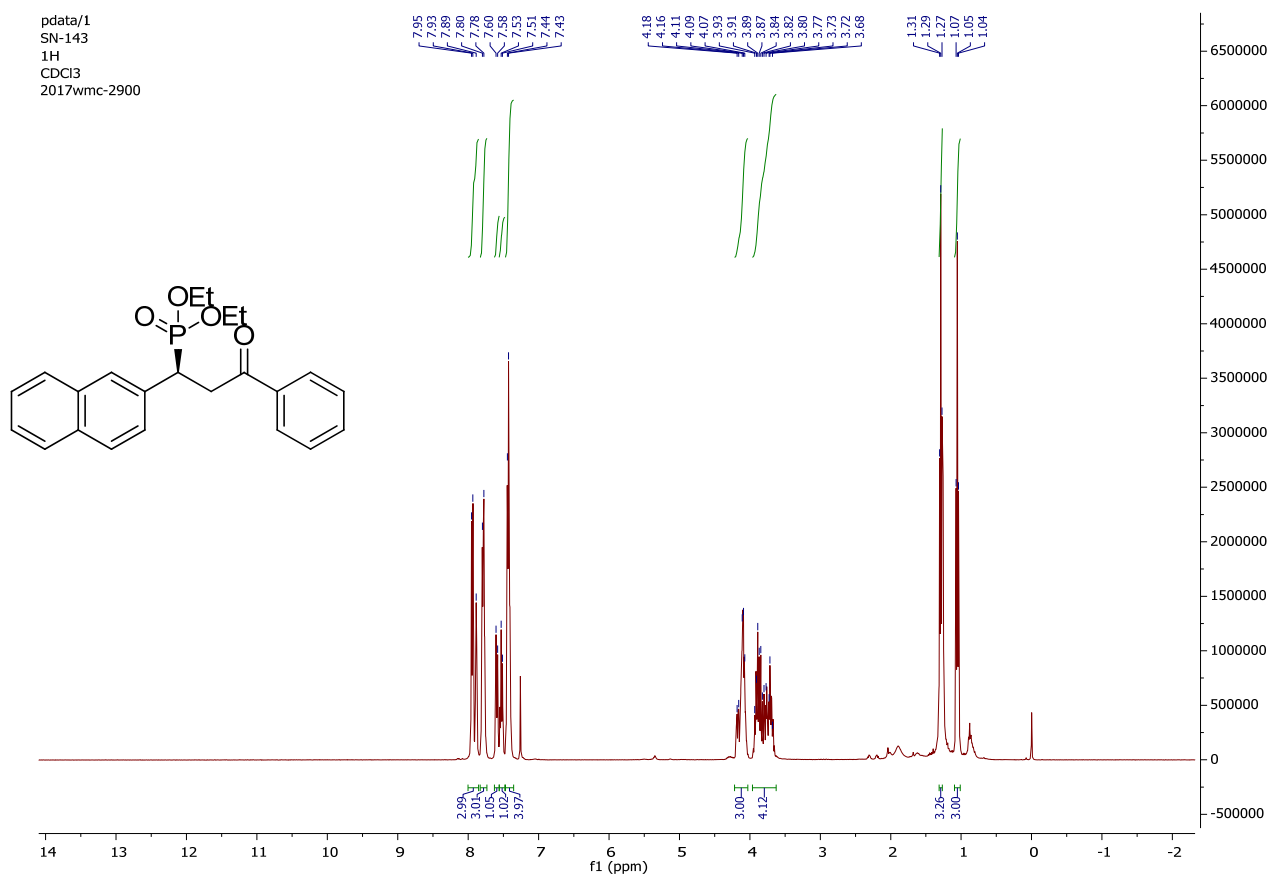




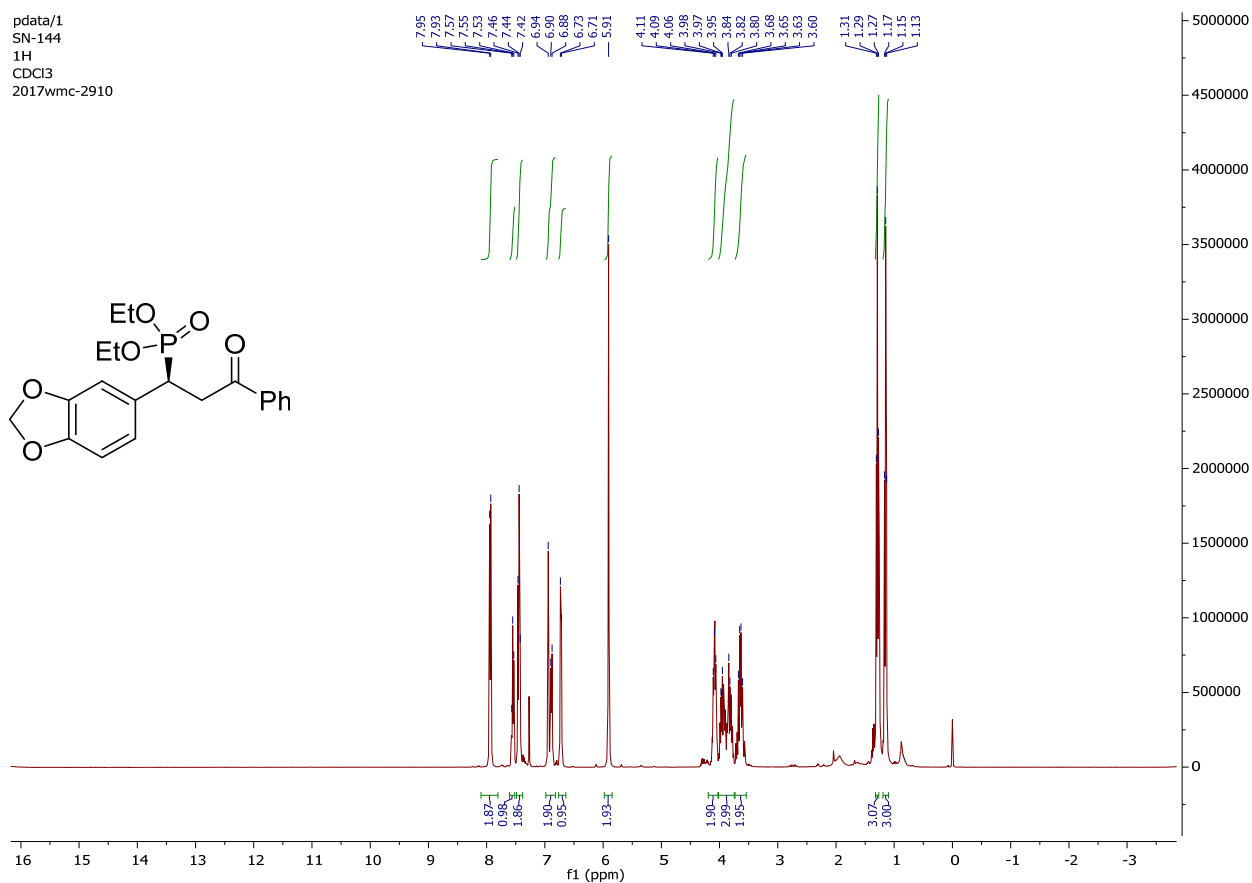




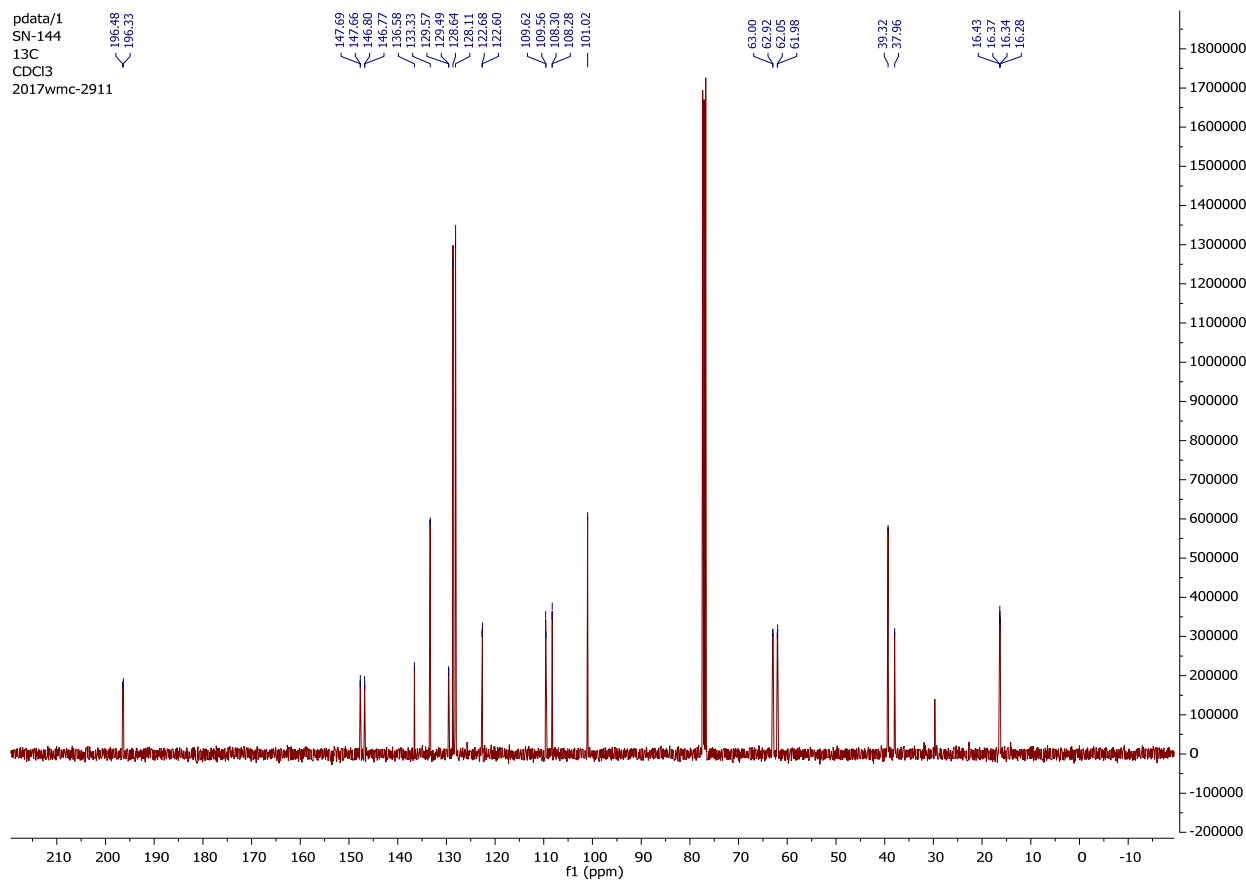


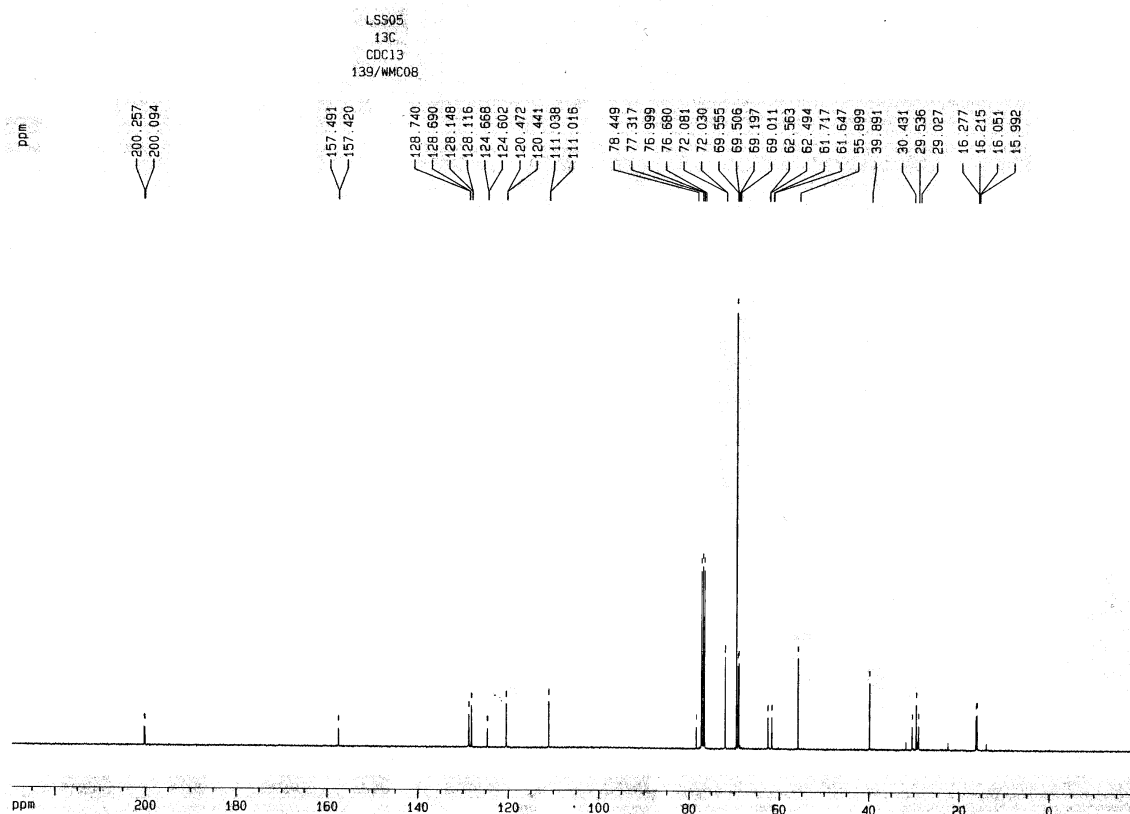
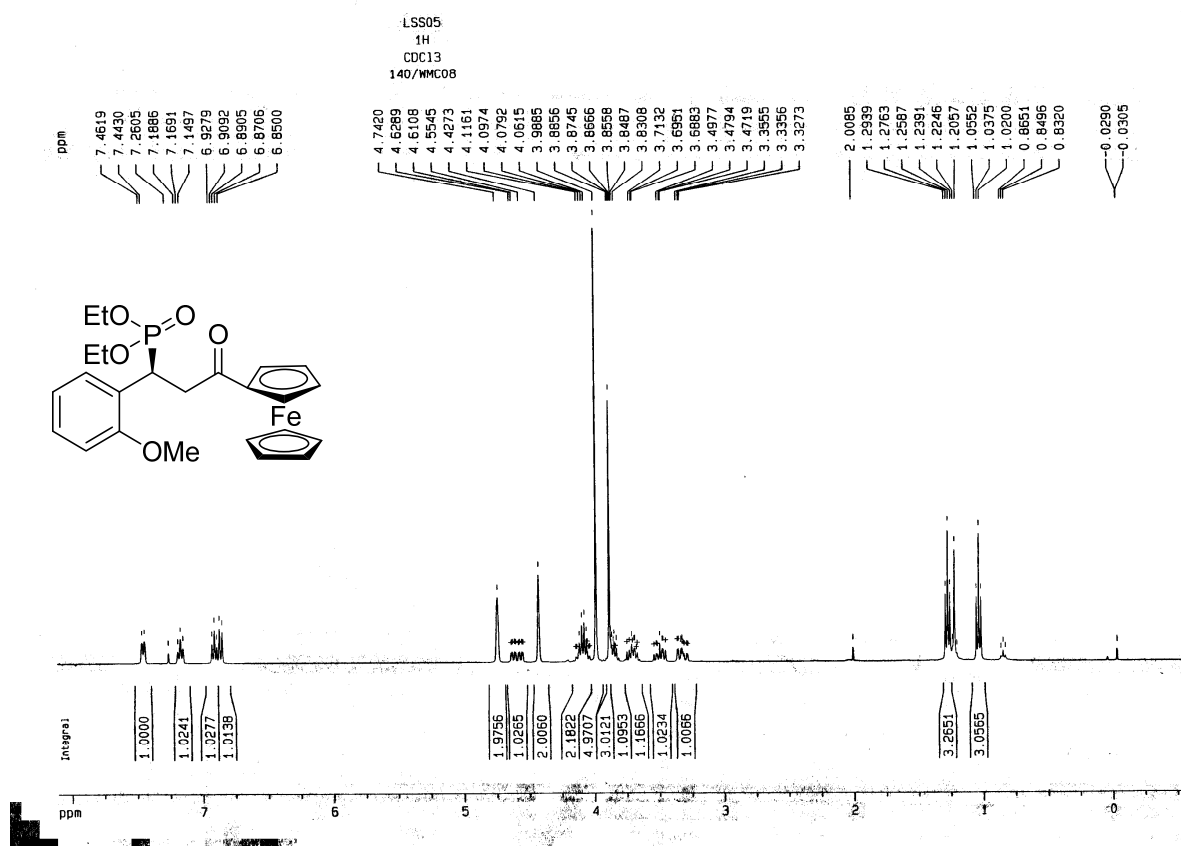


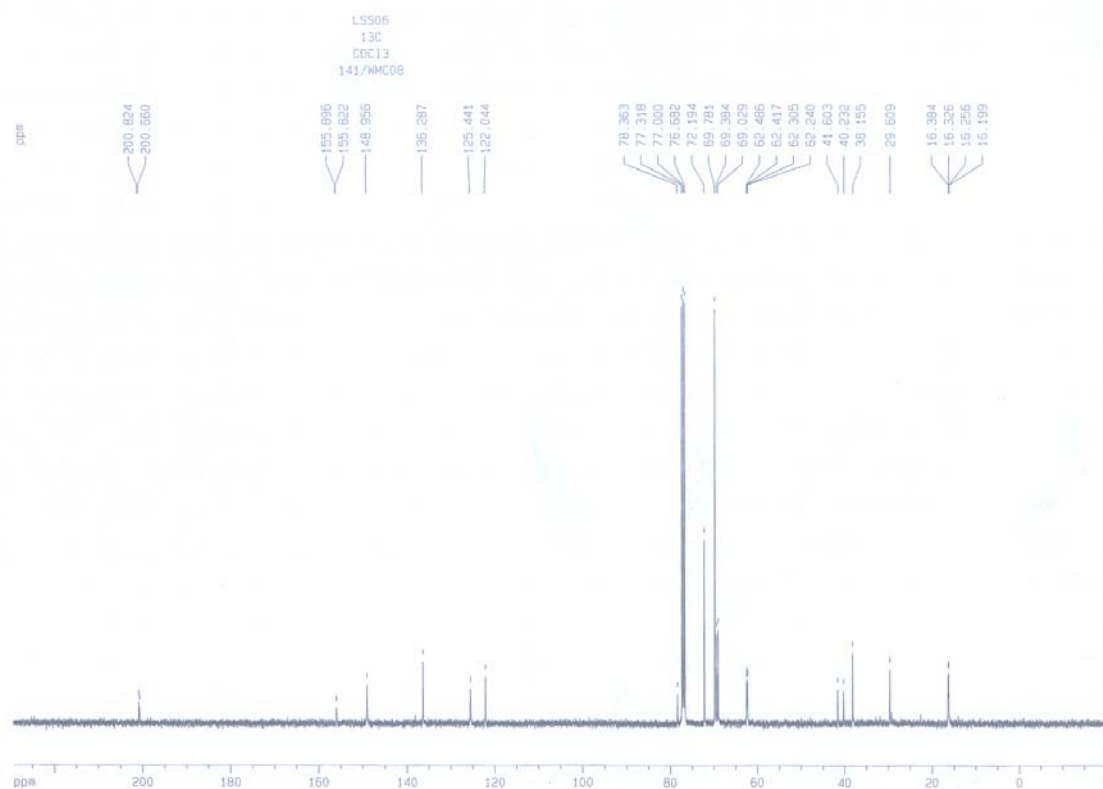
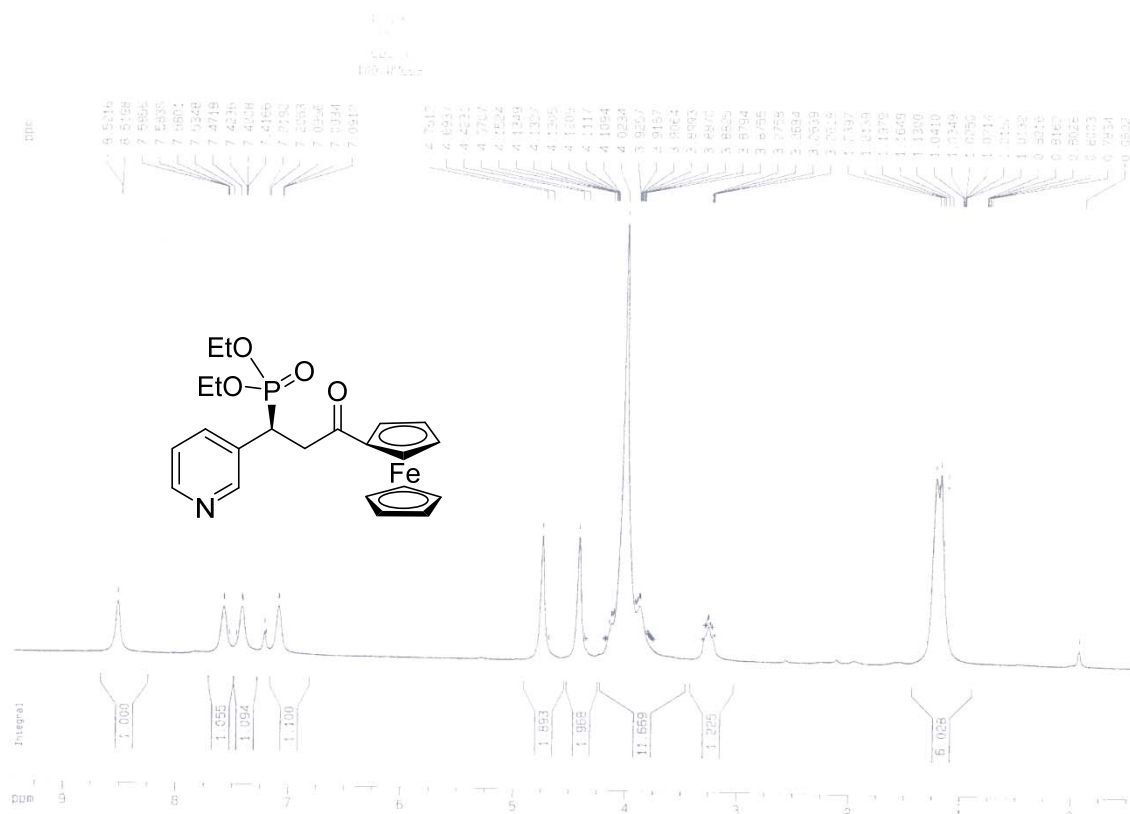
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SN-144
1H
CDCl3
2017wmc-2910



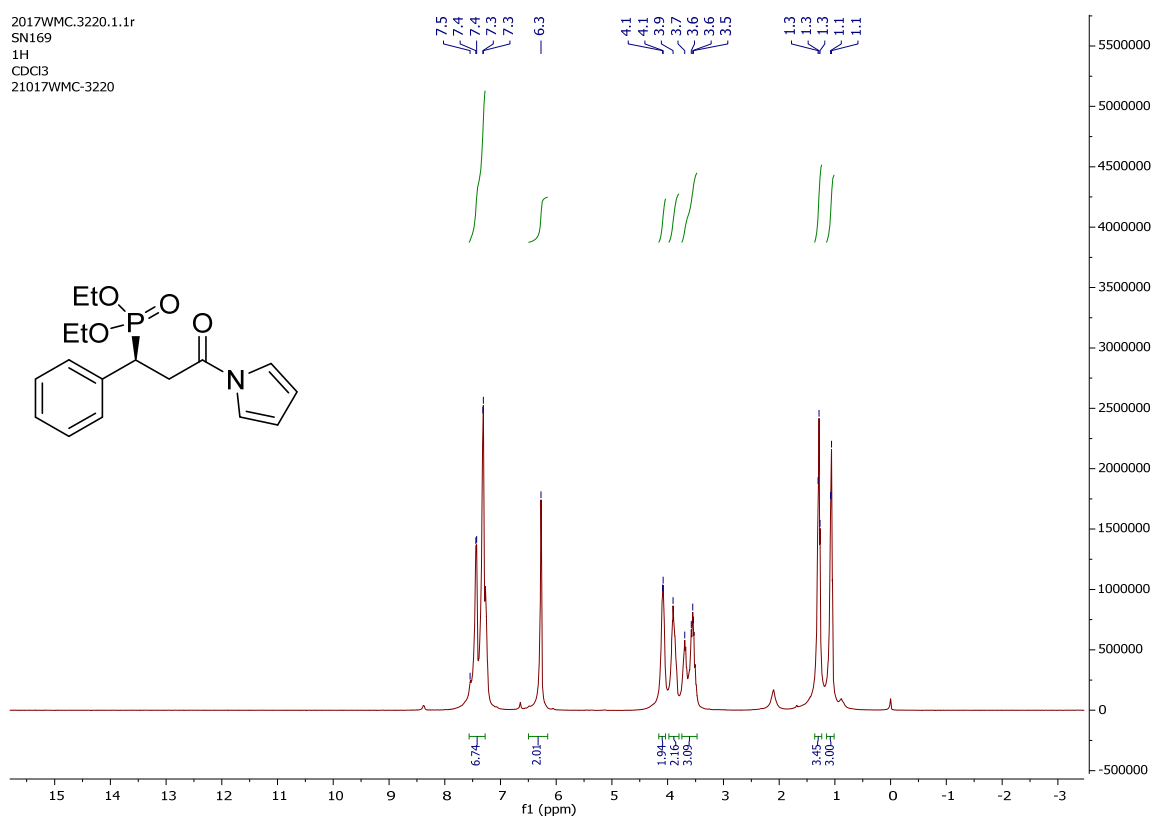
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13C
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2017wmc-2911



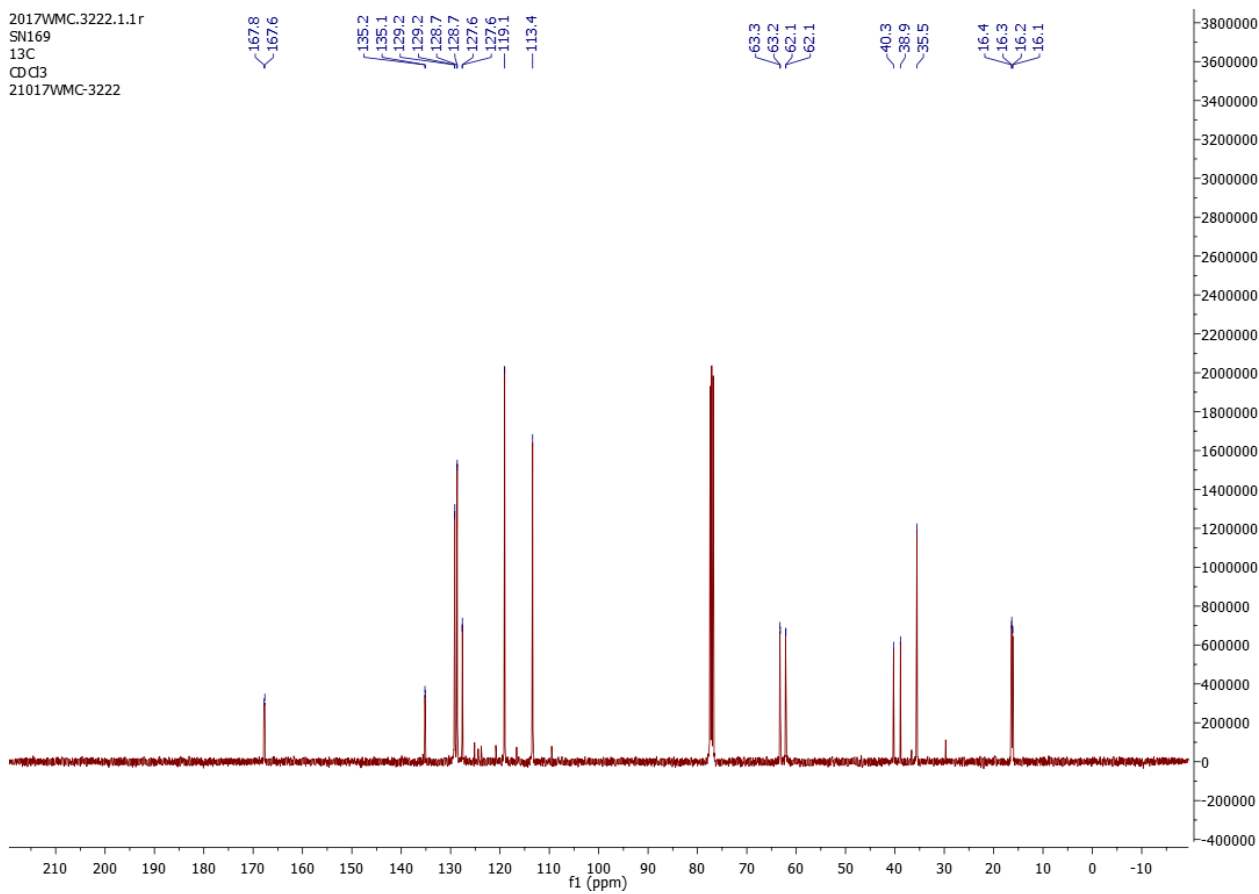


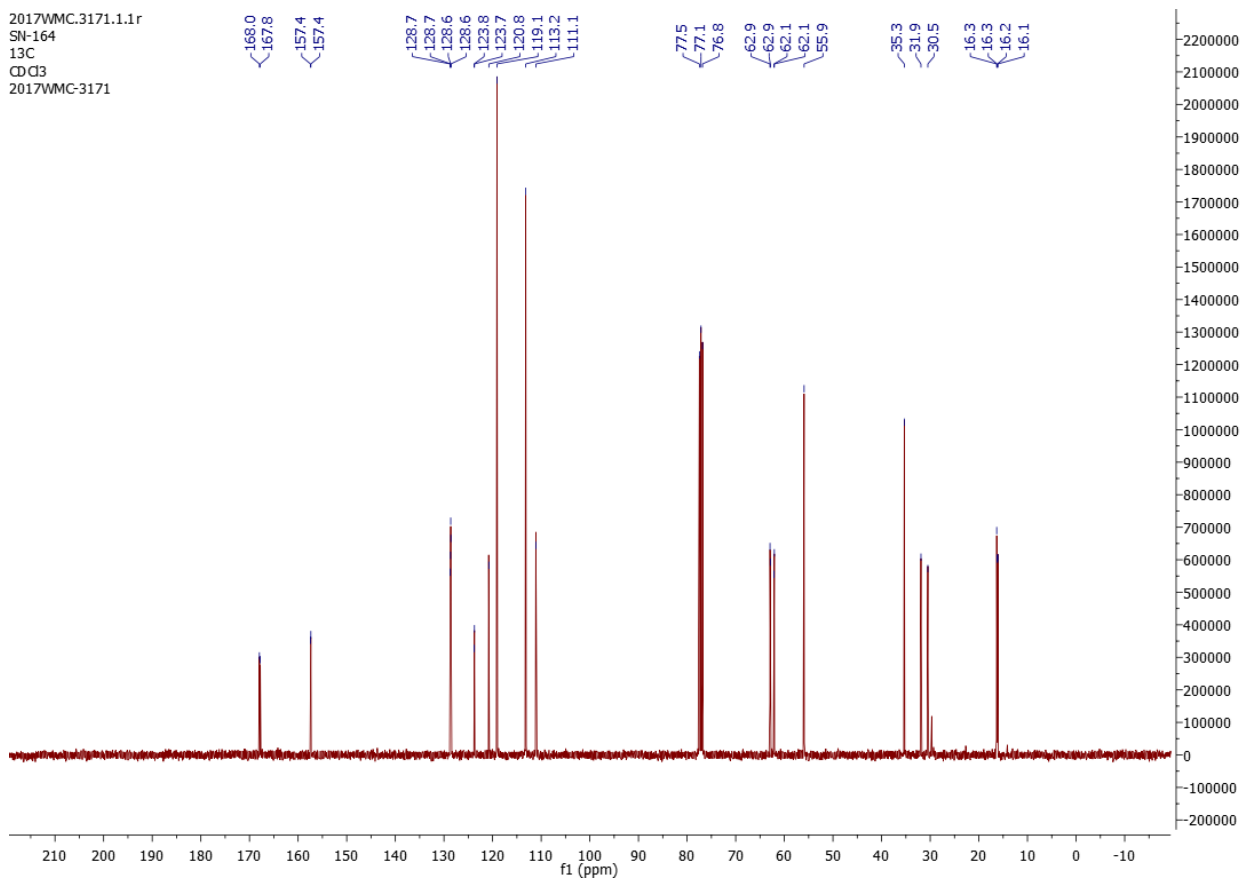
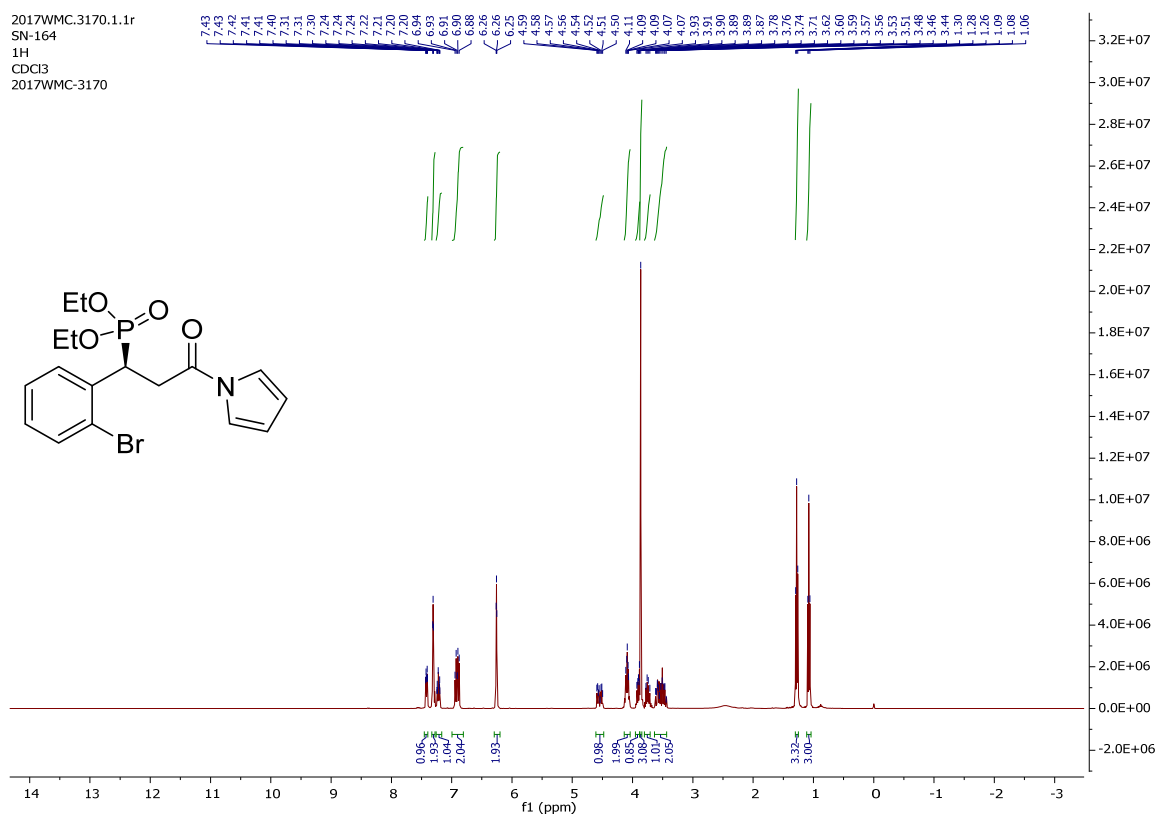


2017WMC.3220.1.1r
SN169
1H
CDCl3
21017WMC-3220

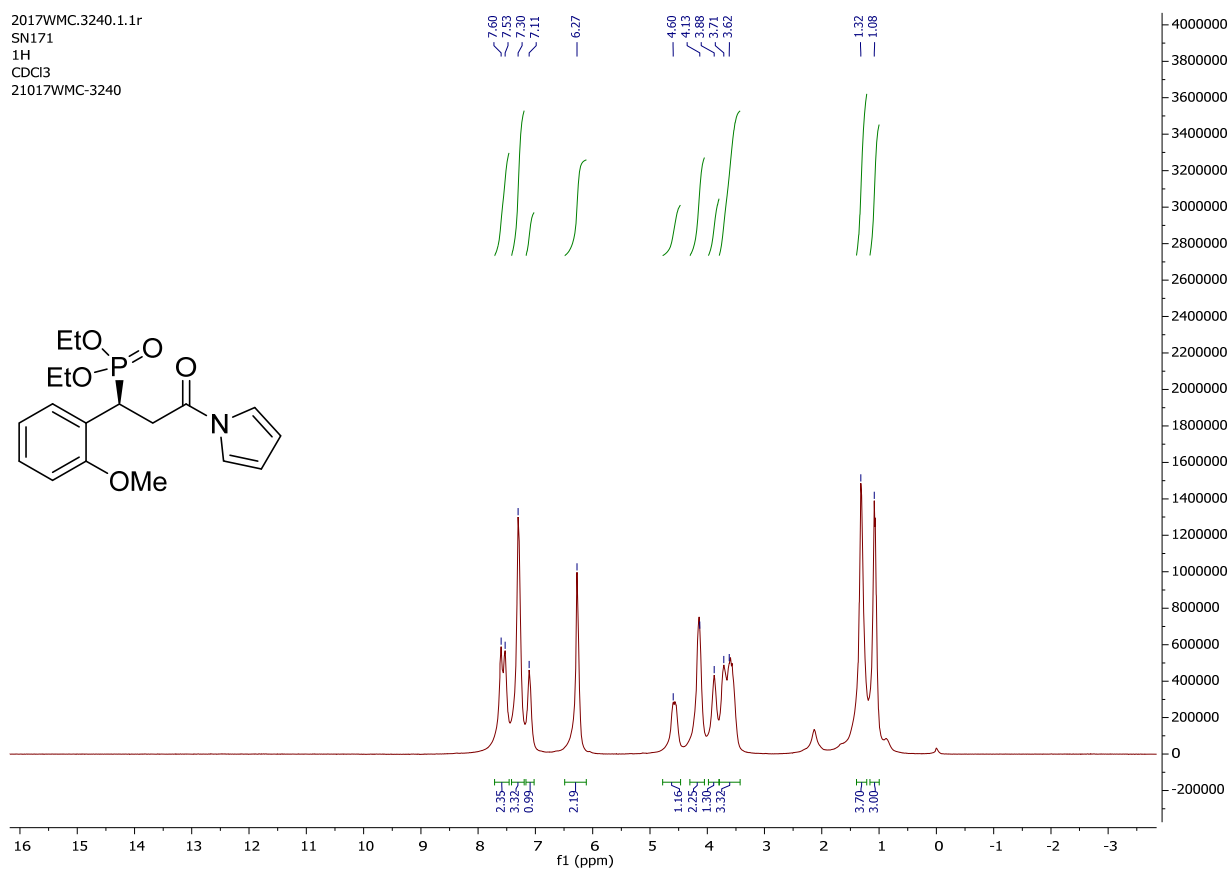


2017WMC.3222.1.1r
SN169
13C
CDCl3
21017WMC-3222

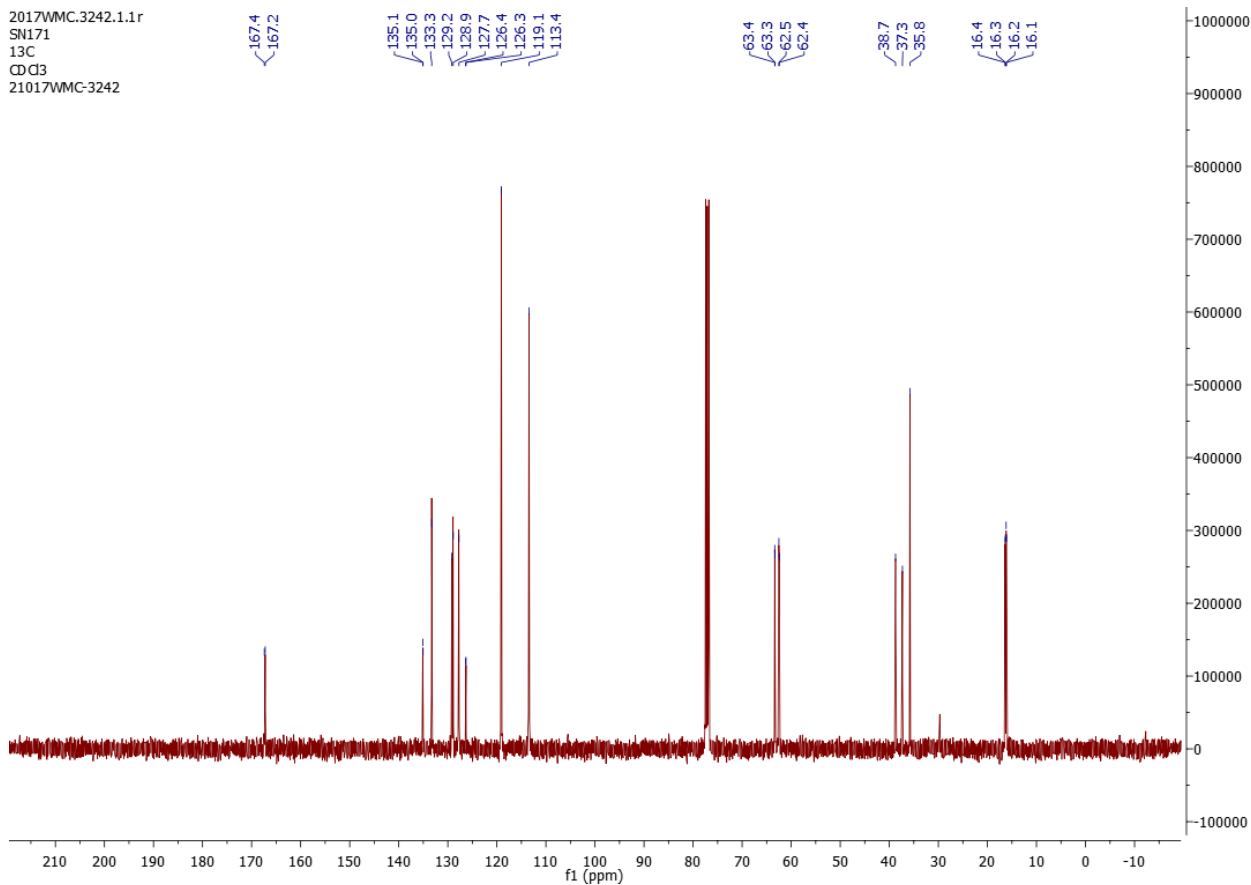




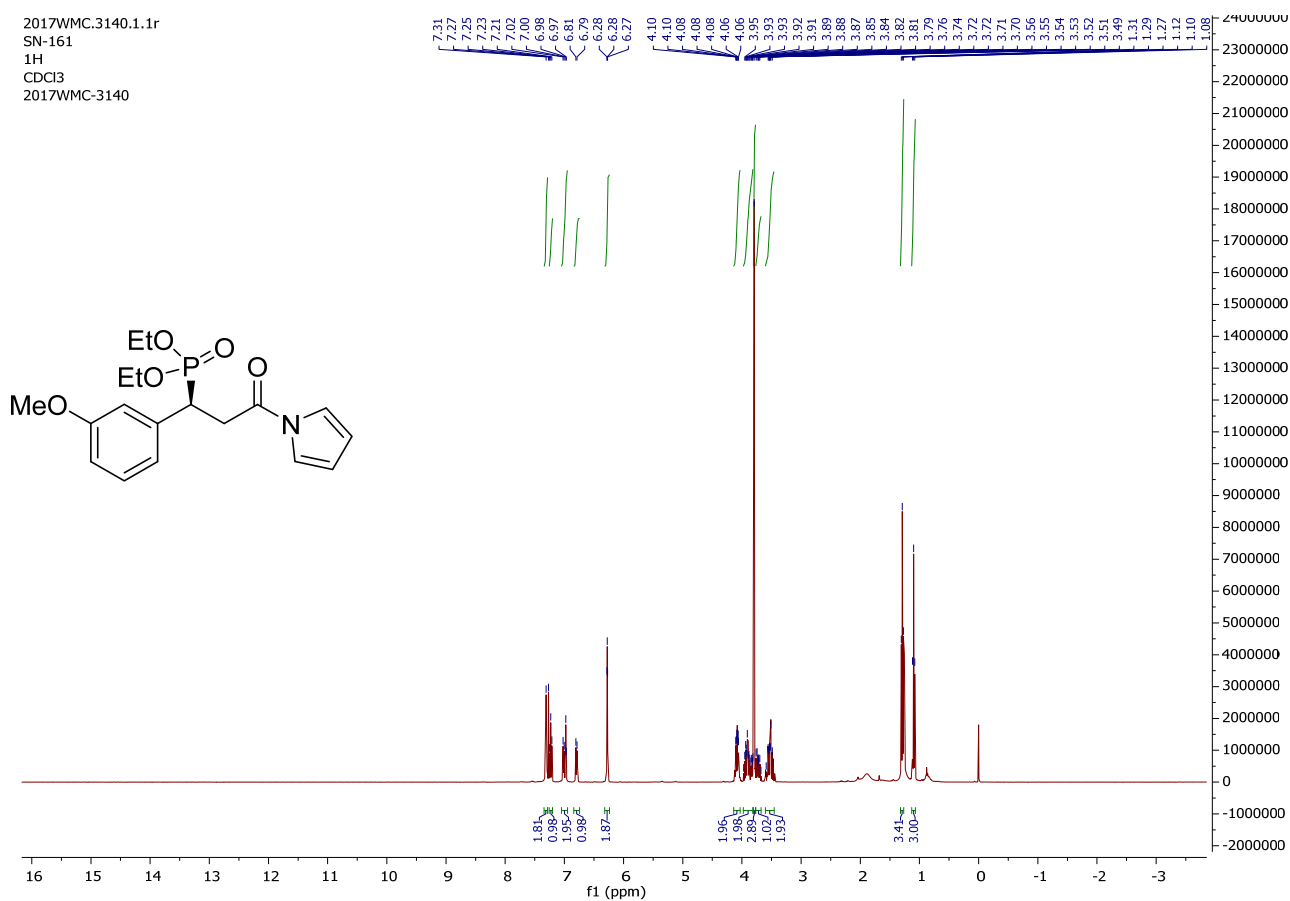
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SN171
1H
CDCl3
21017WMC-3240



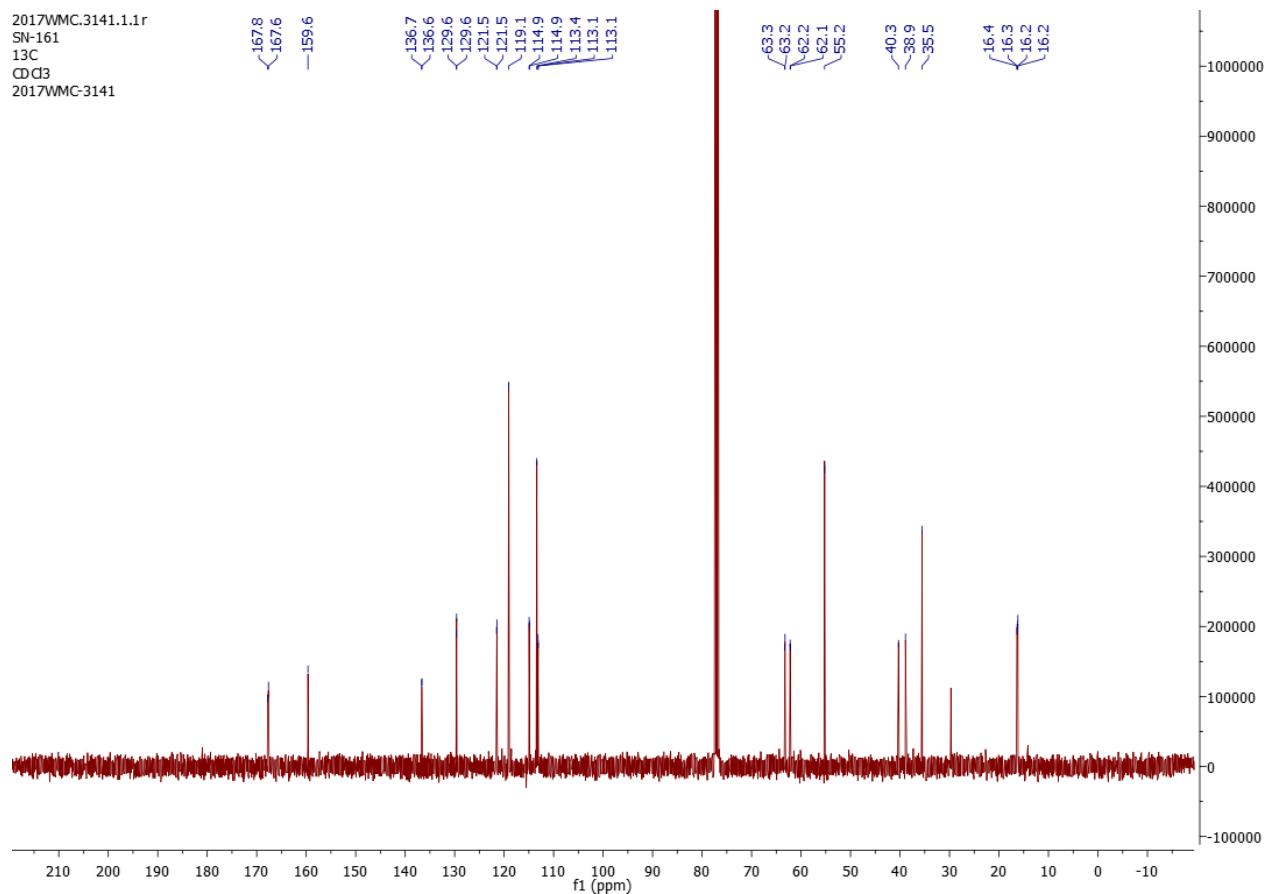
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SN171
13C
CDCl3
21017WMC-3242

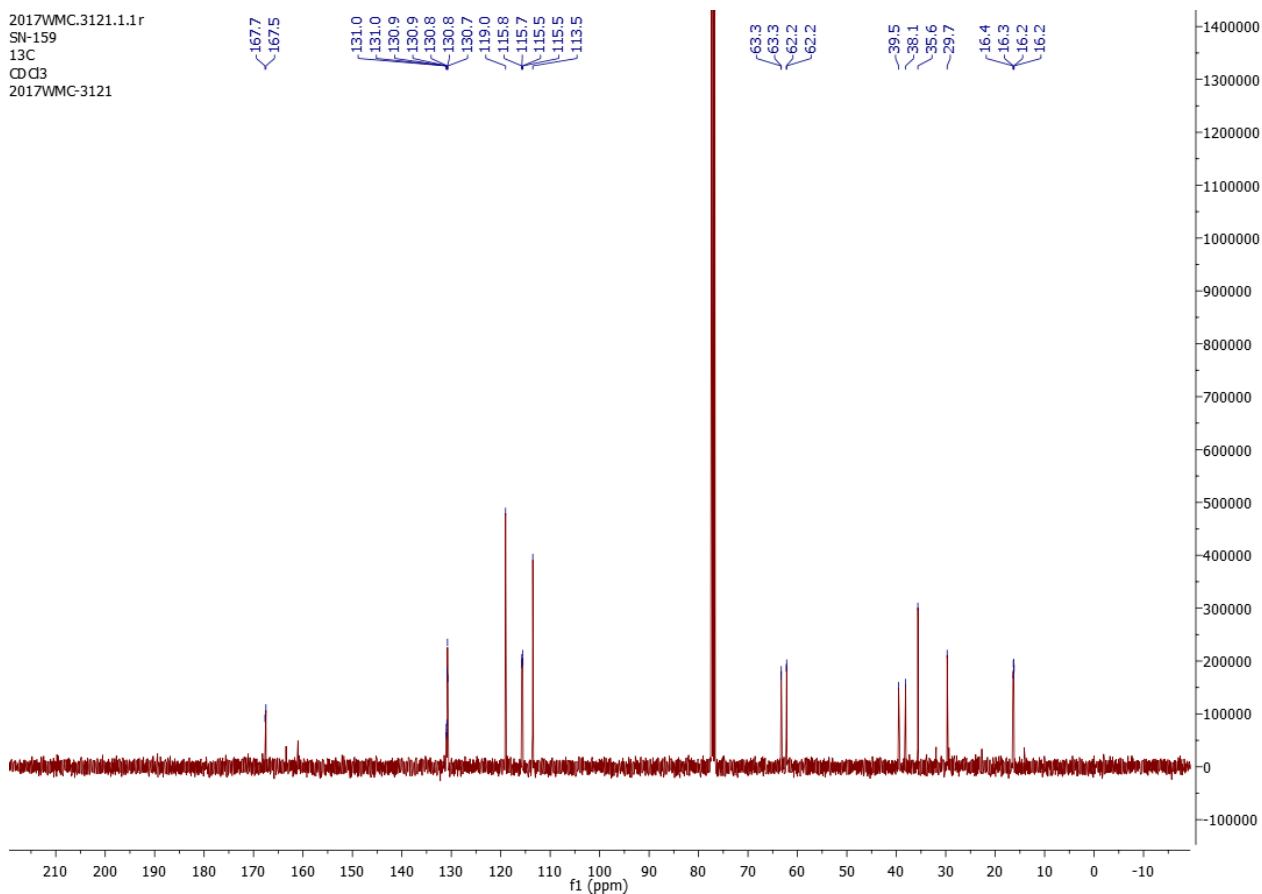
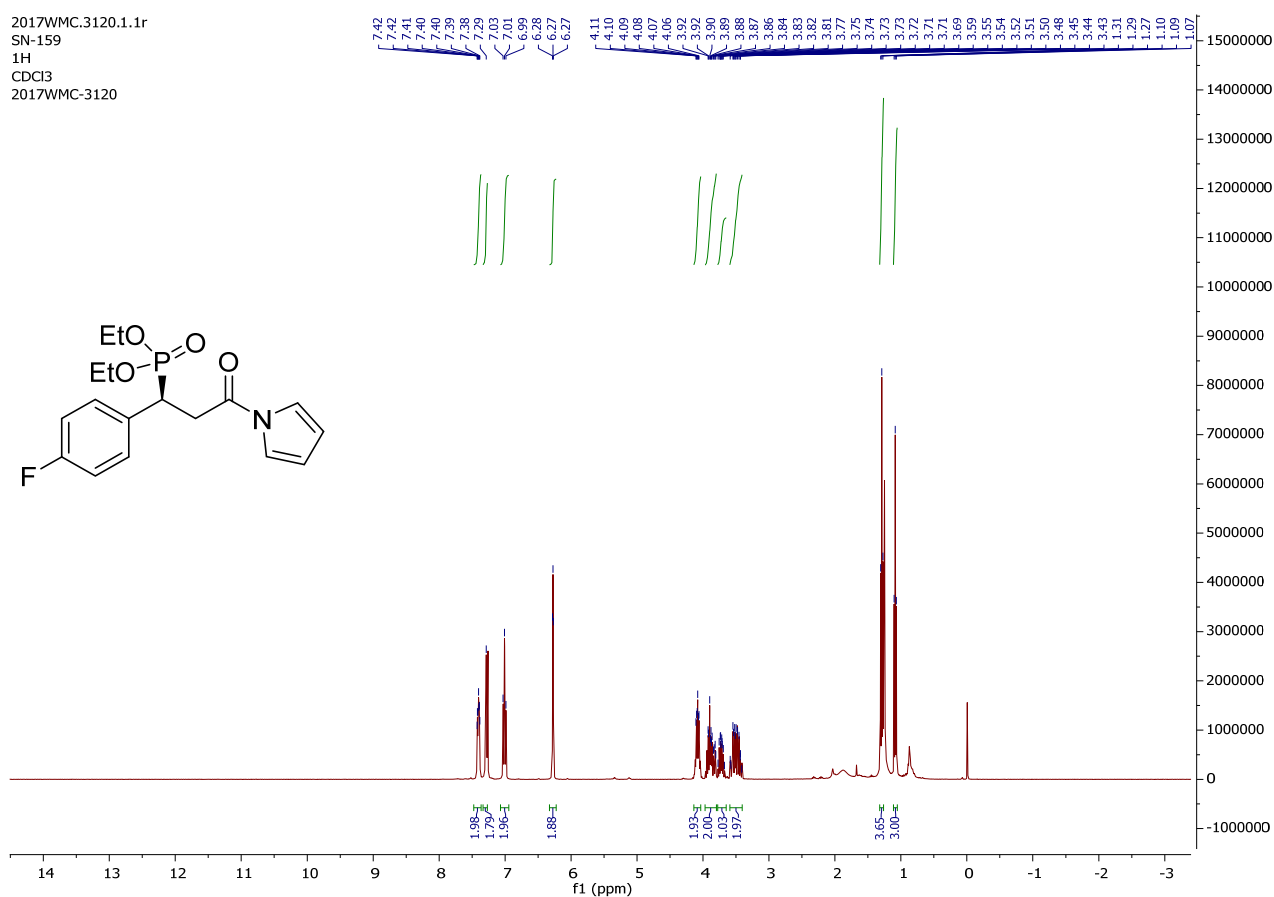


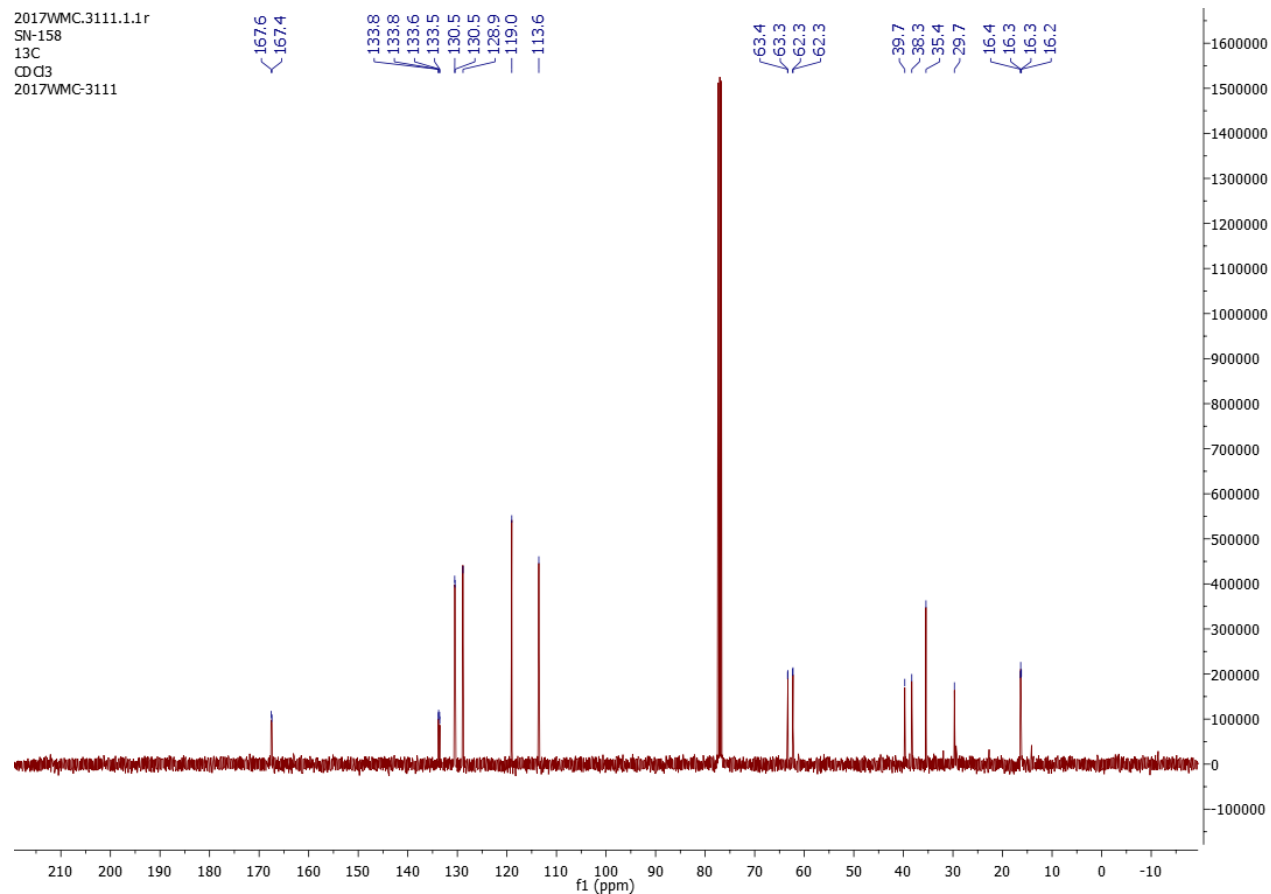
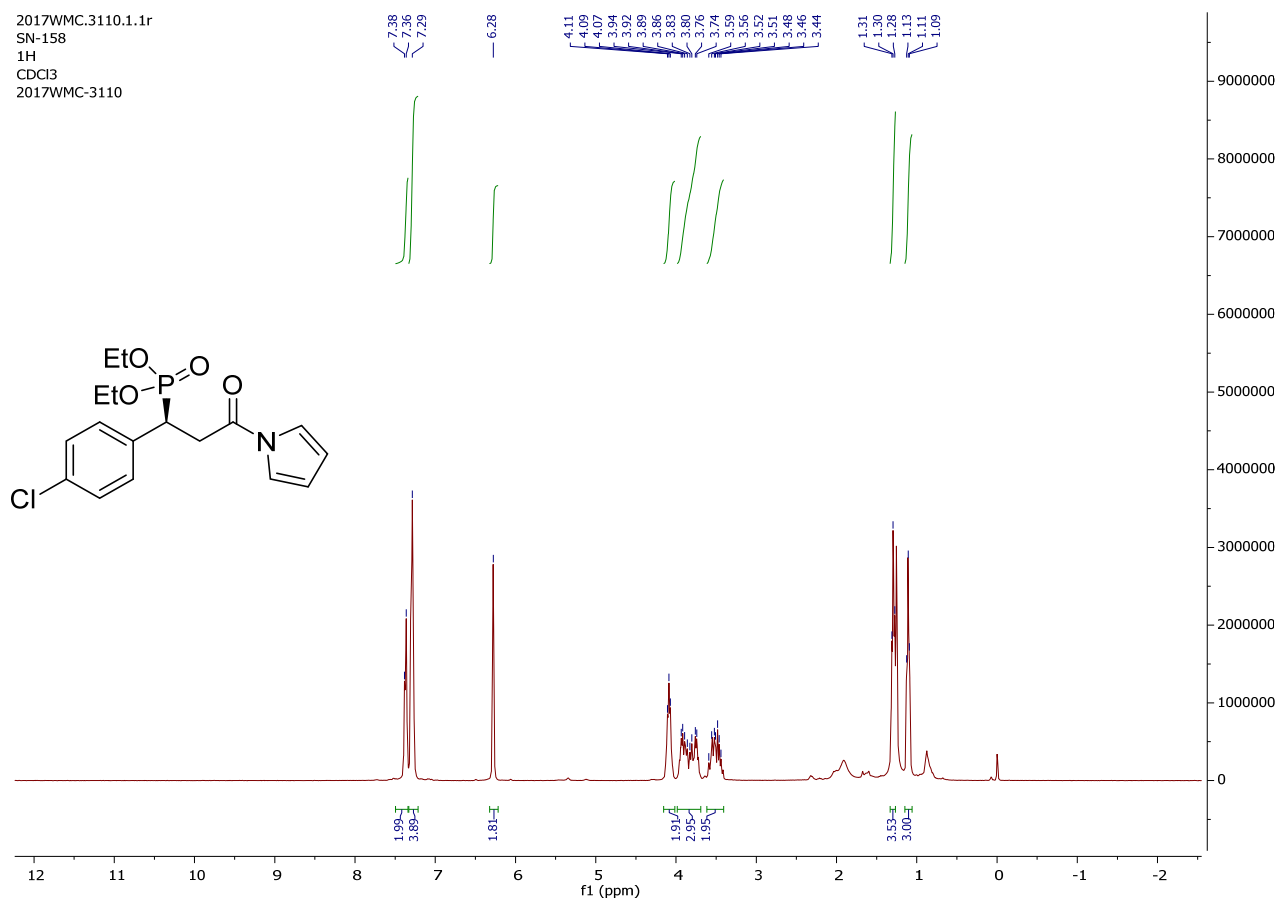
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SN-161
1H
CDCl3
2017WMC-3140



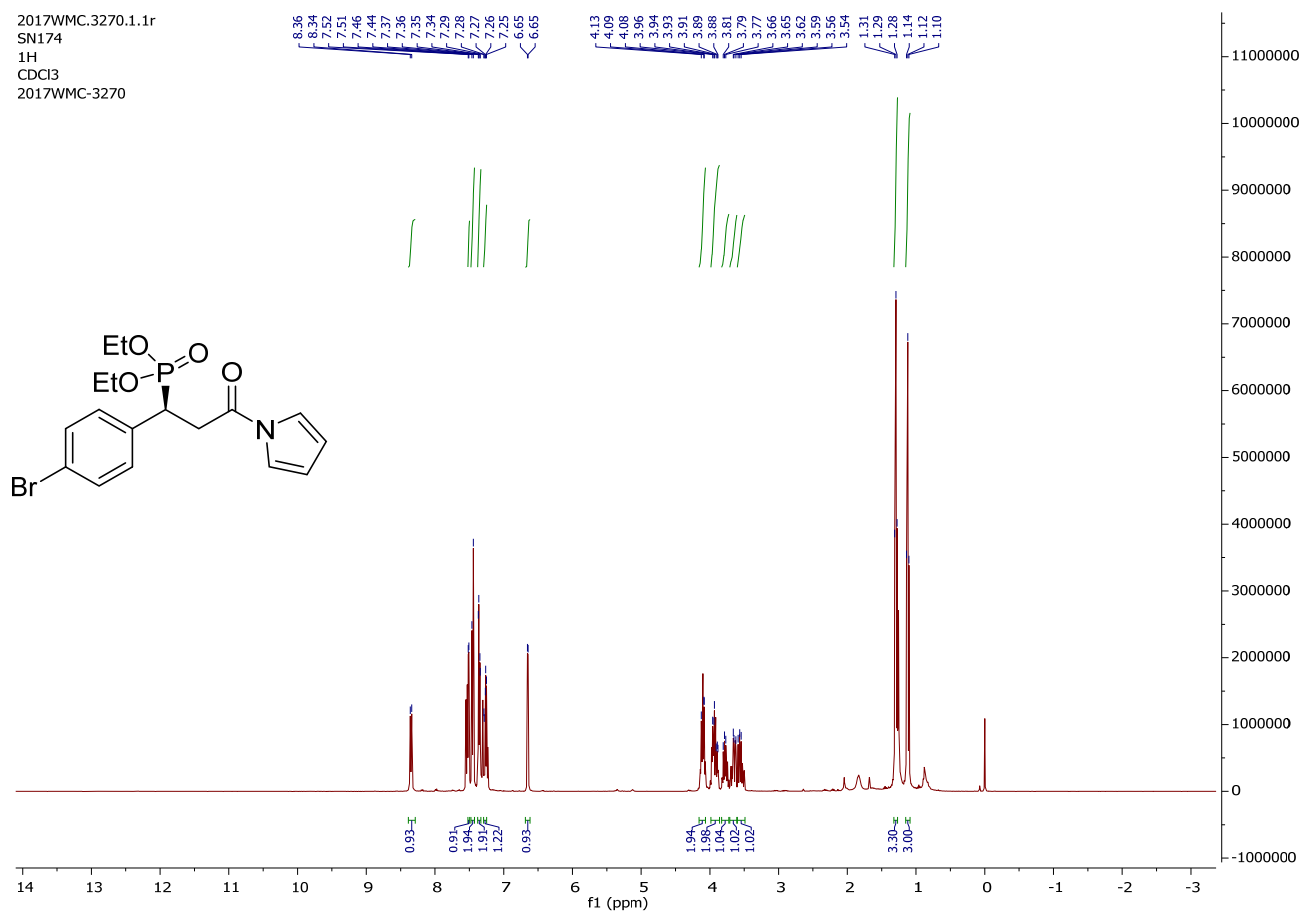
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SN-161
13C
CDCl3
2017WMC-3141



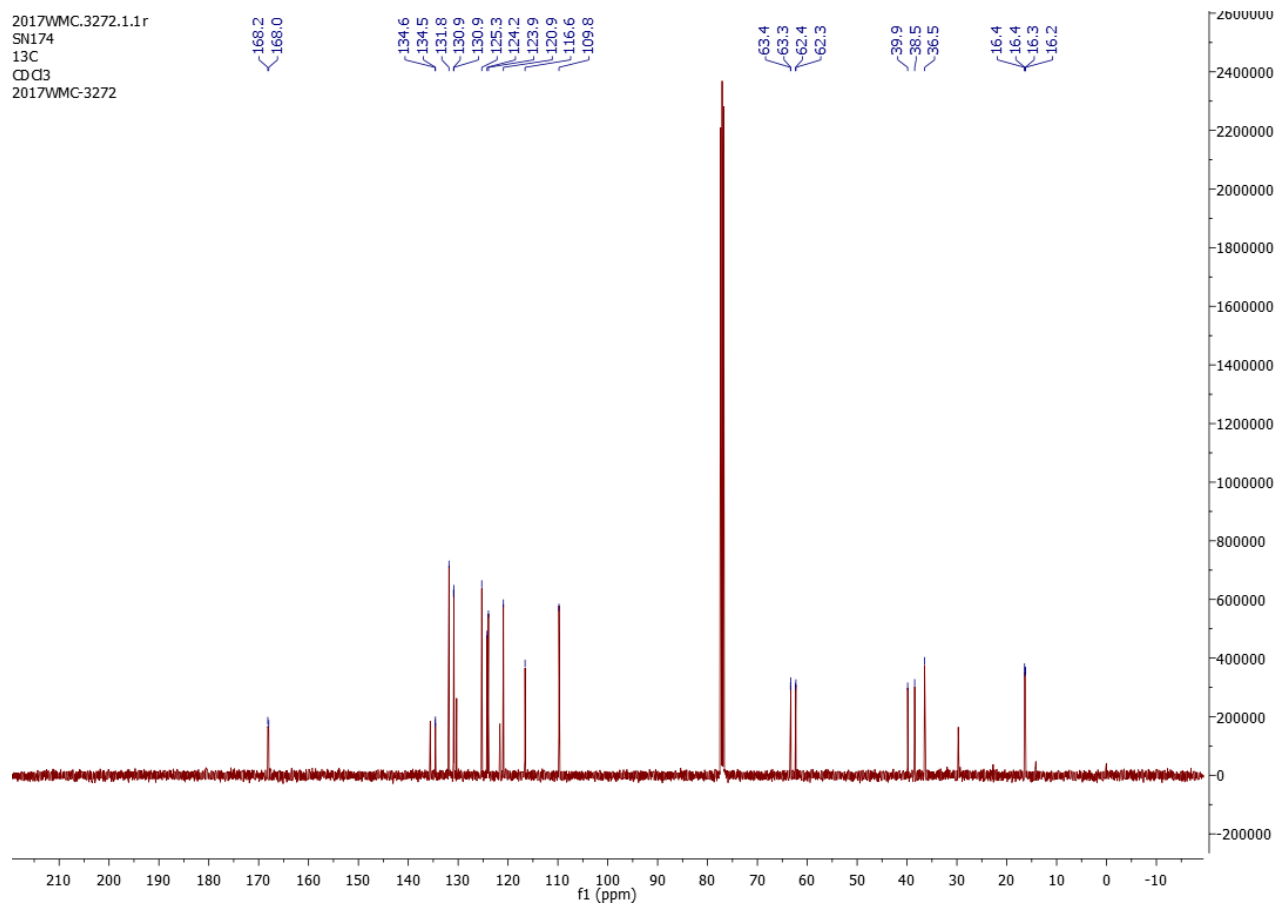




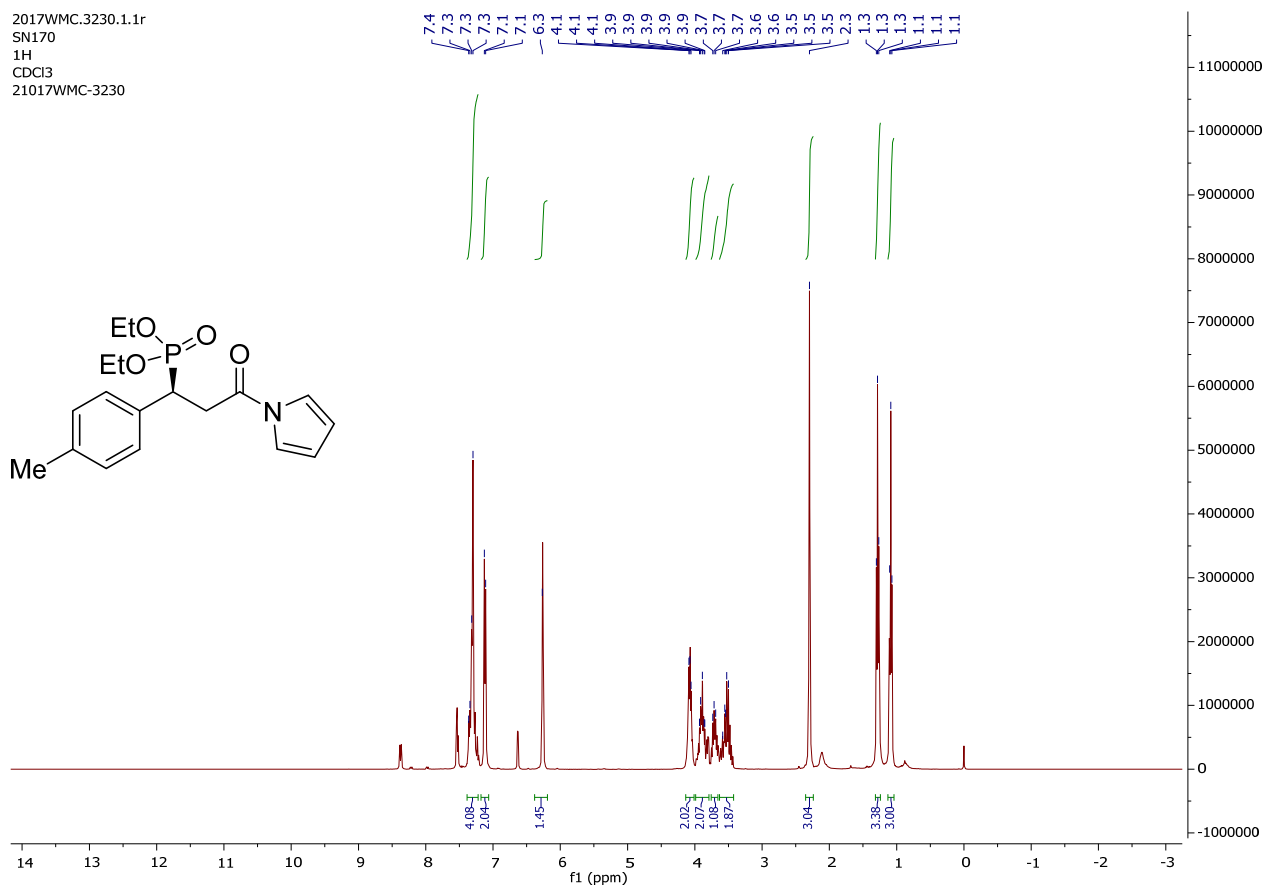
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SN174
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CDCl3
2017WMC-3270



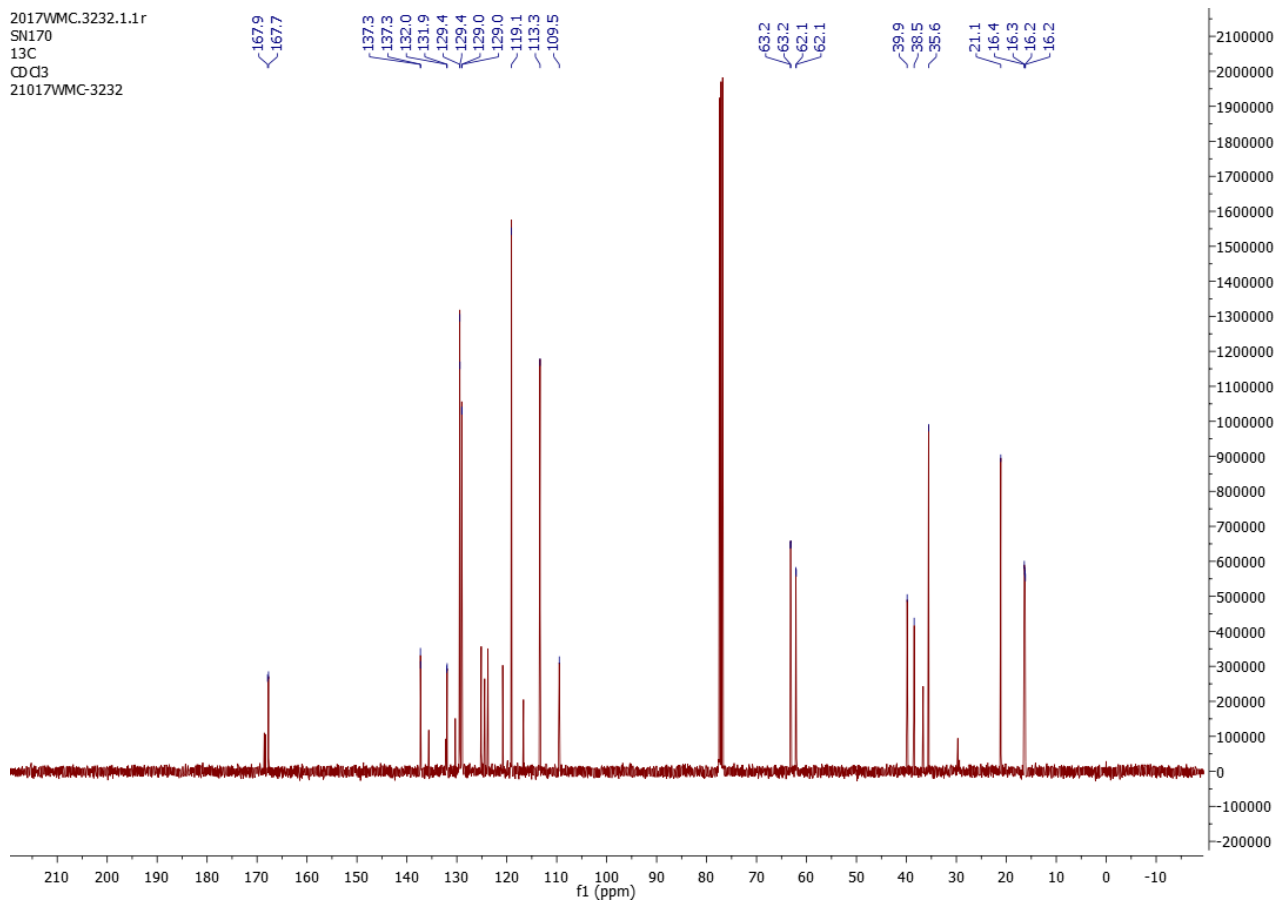
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SN174
13C
CDCl3
2017WMC-3272



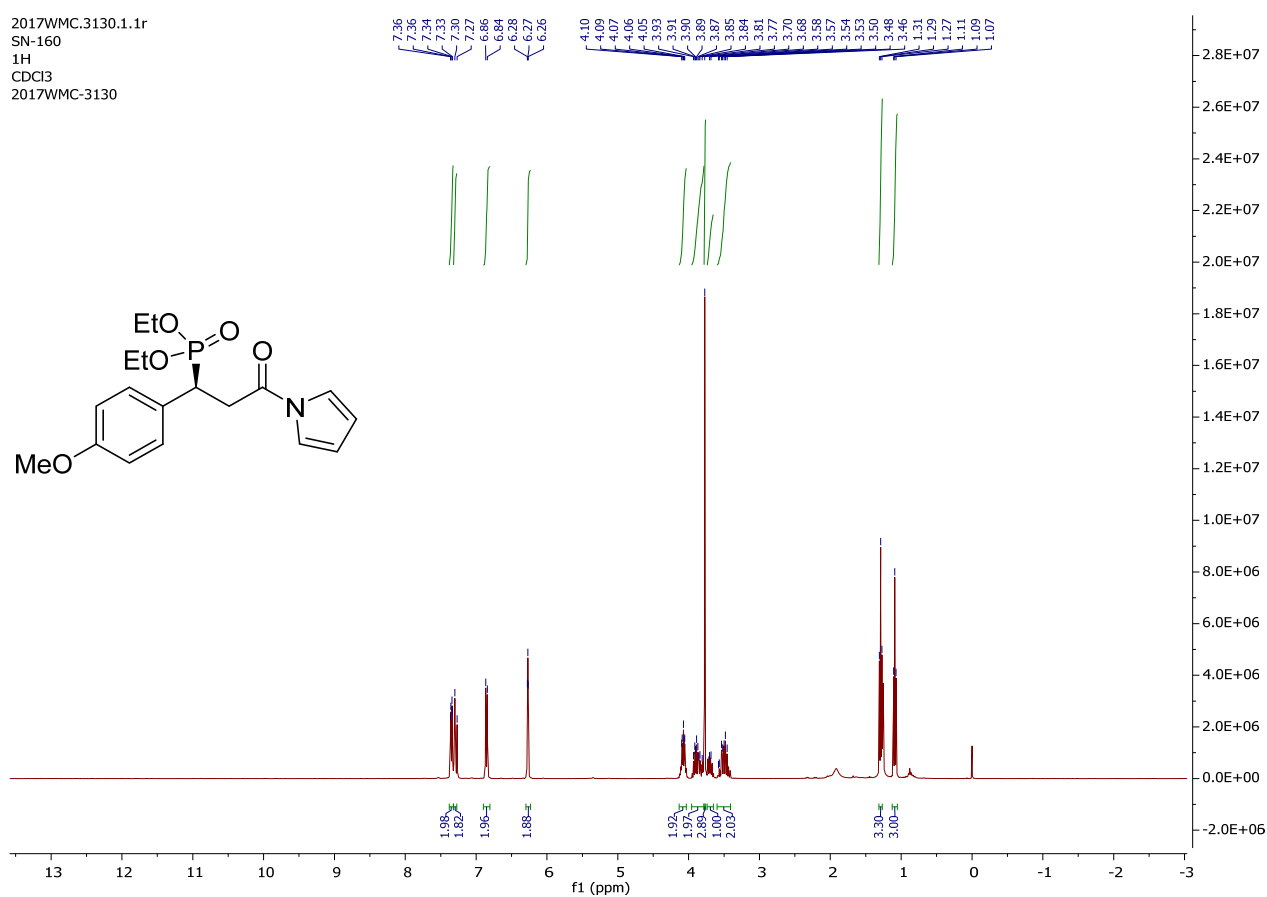
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SN170
1H
CDCl3
21017WMC-3230



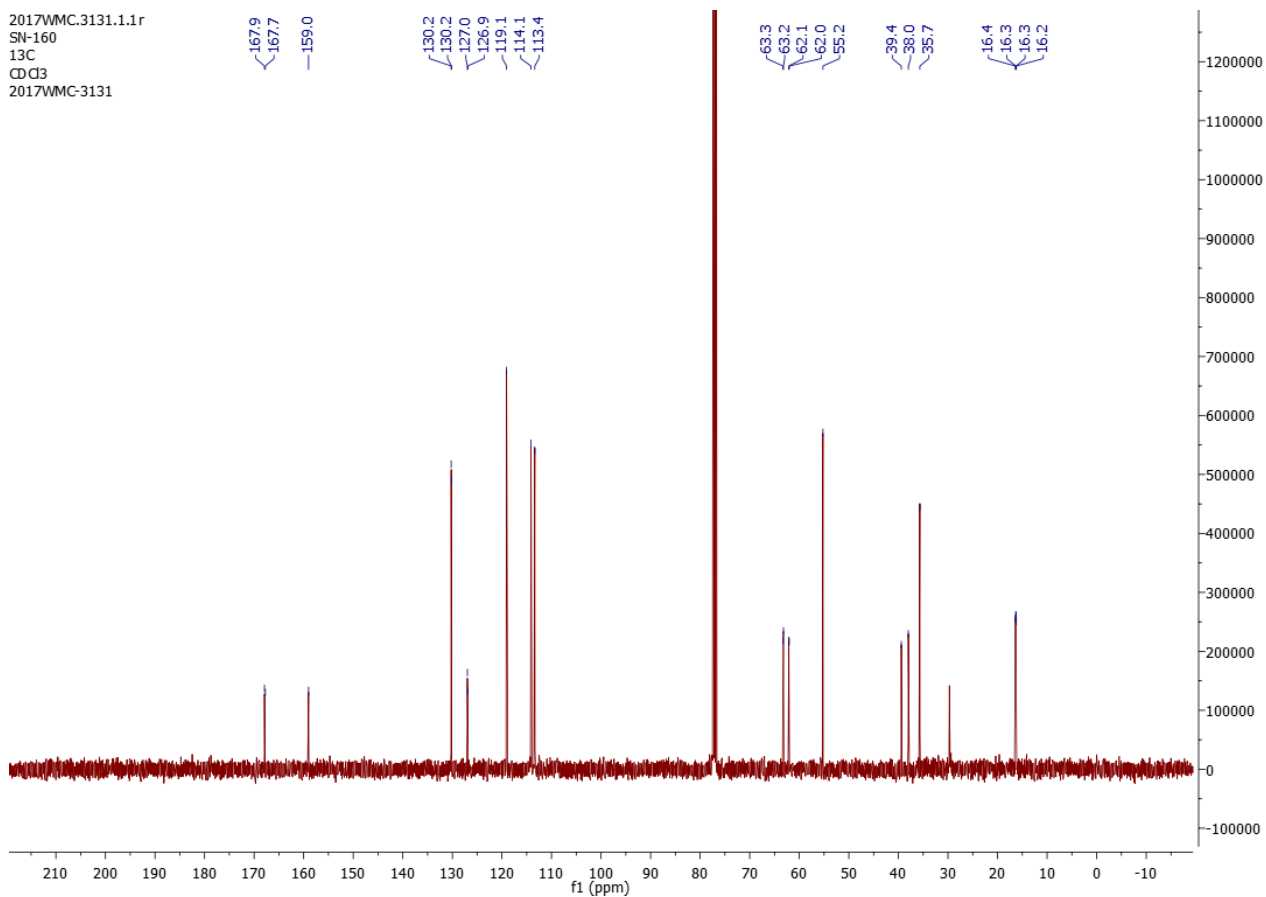
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SN170
13C
CDCl3
21017WMC-3232



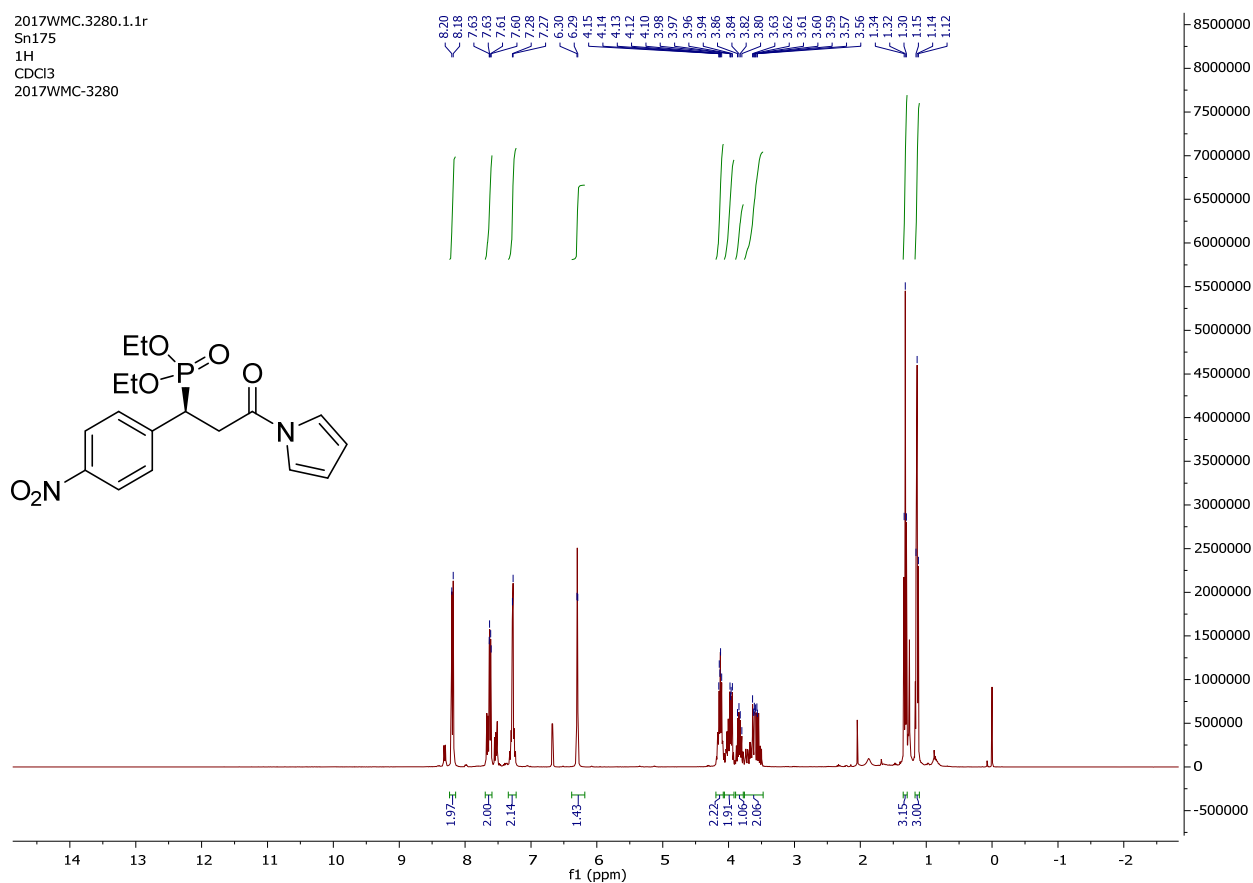
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SN-160
1H
CDCl3
2017WMC-3130



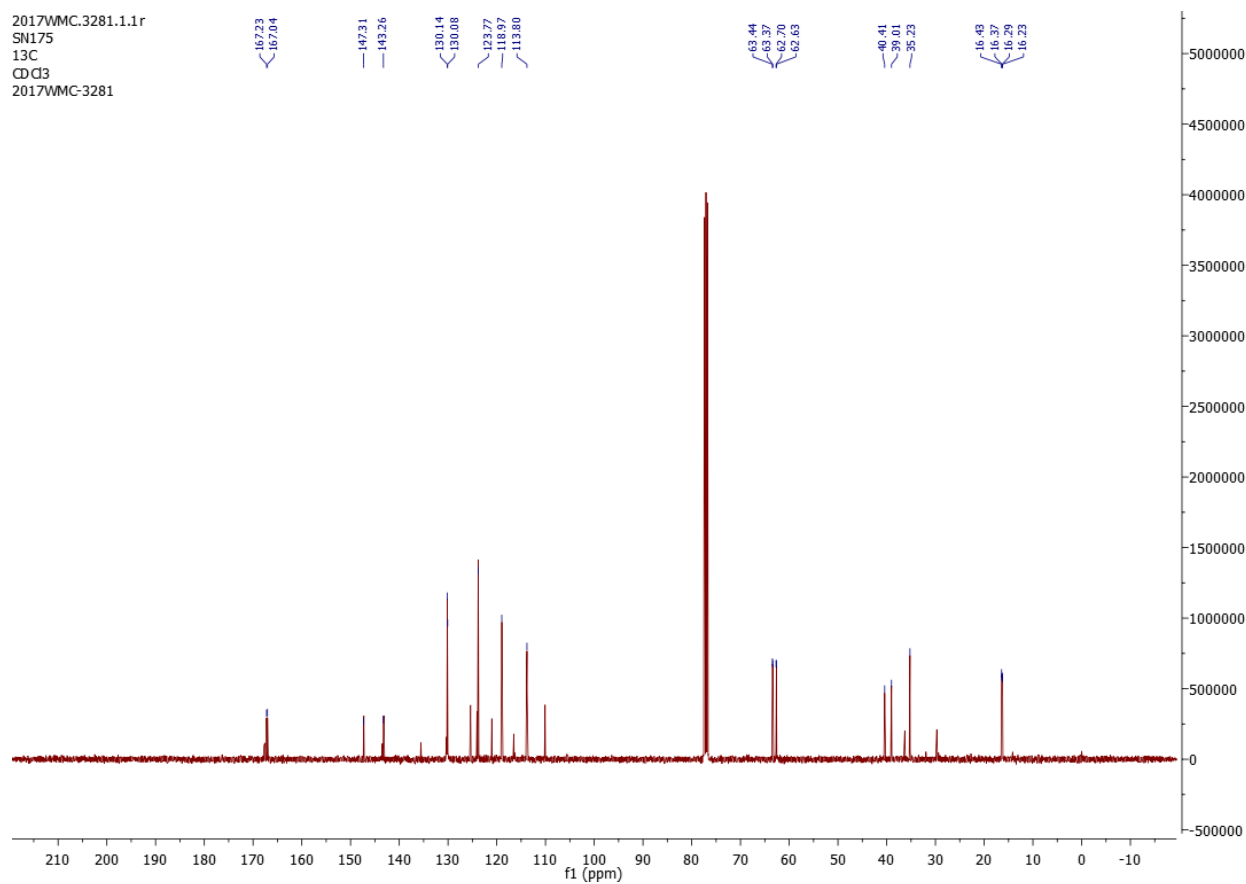
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SN-160
13C
CDCl3
2017WMC-3131



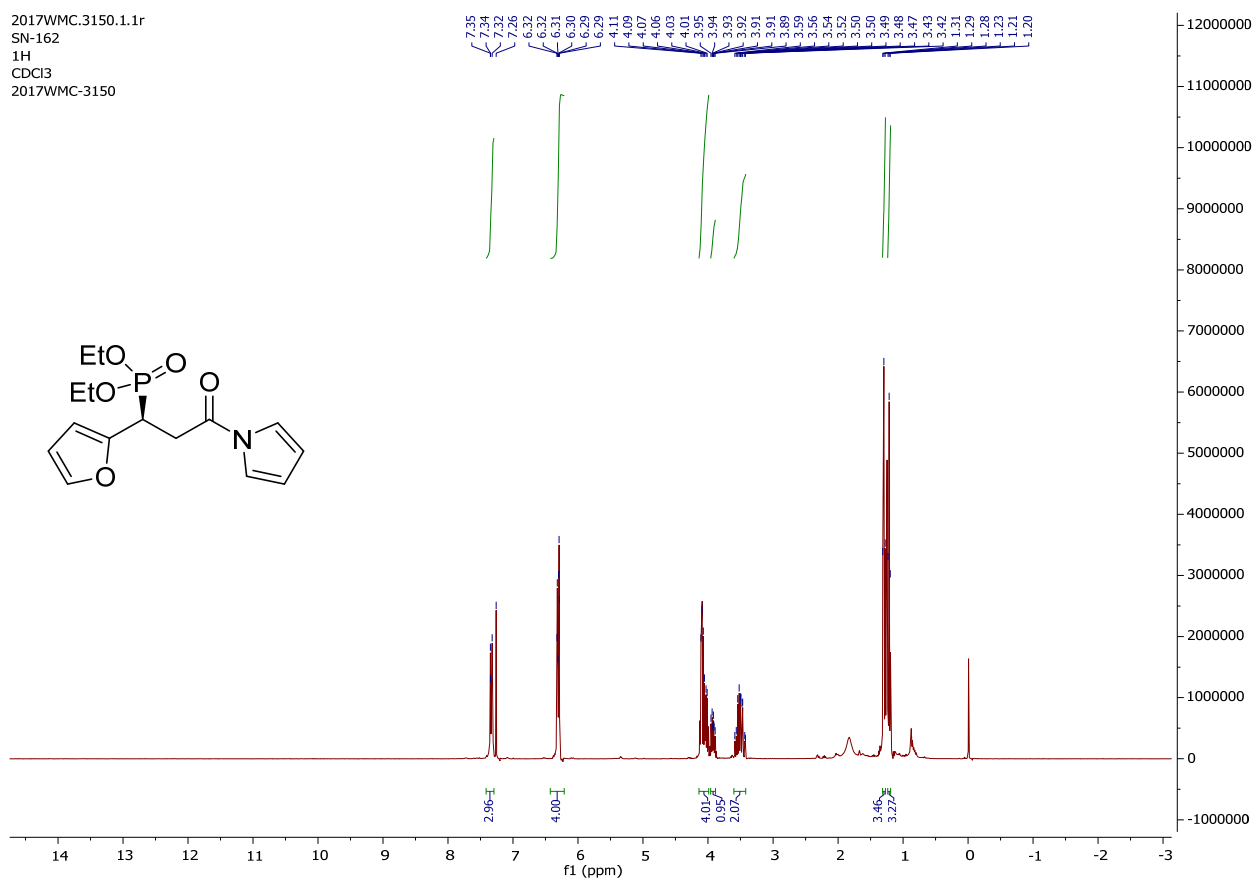
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Sn175
1H
CDCl3
2017WMC-3280



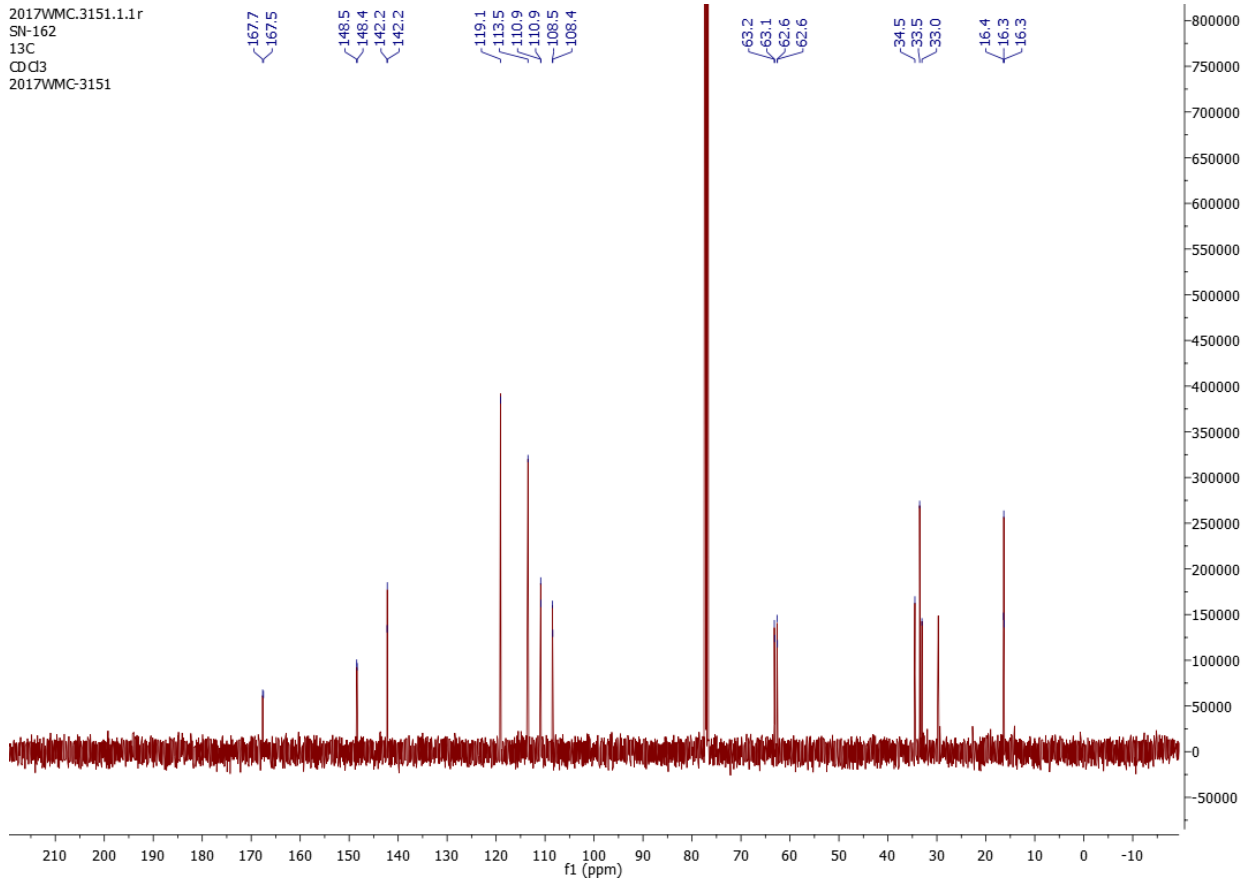
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SN175
13C
CDCl3
2017WMC-3281



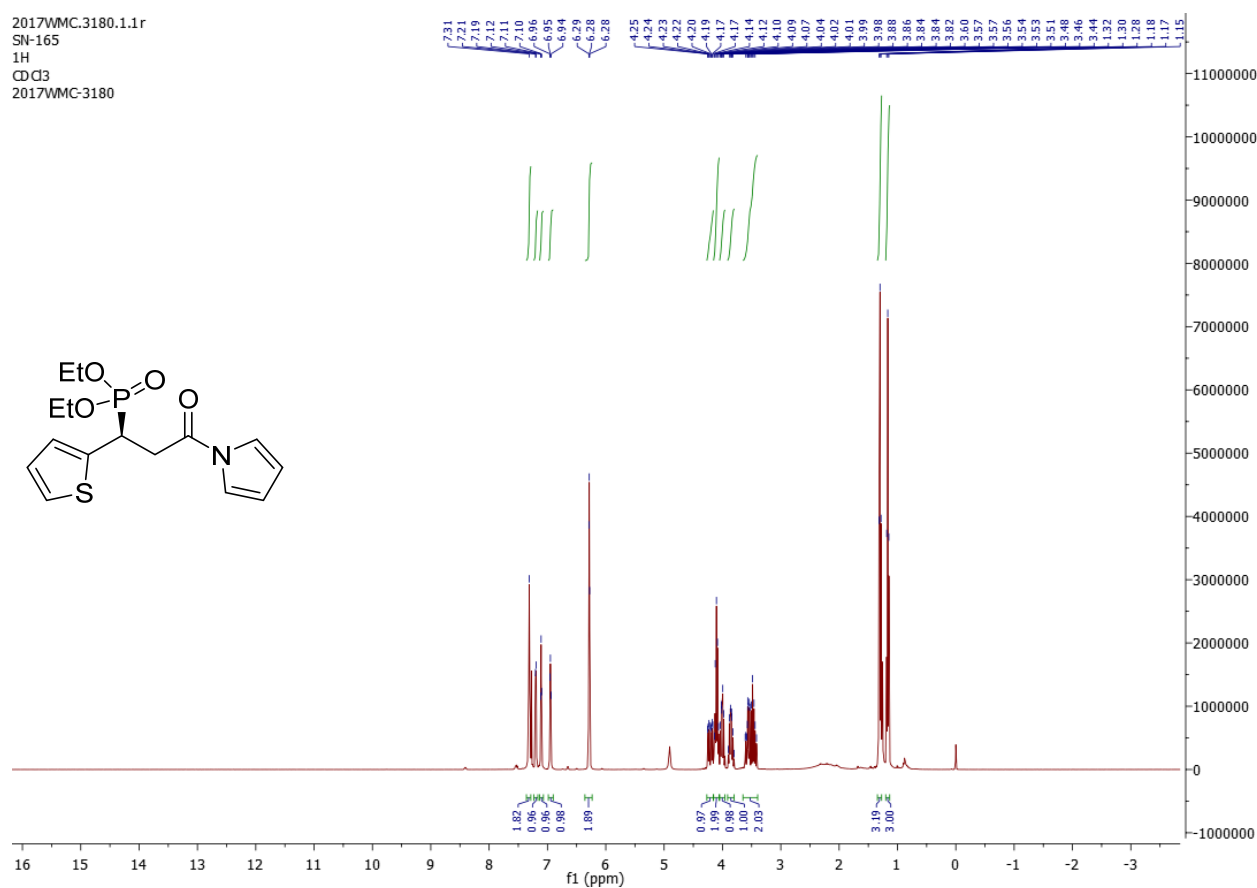
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SN-162
1H
CDCl3
2017WMC-3150



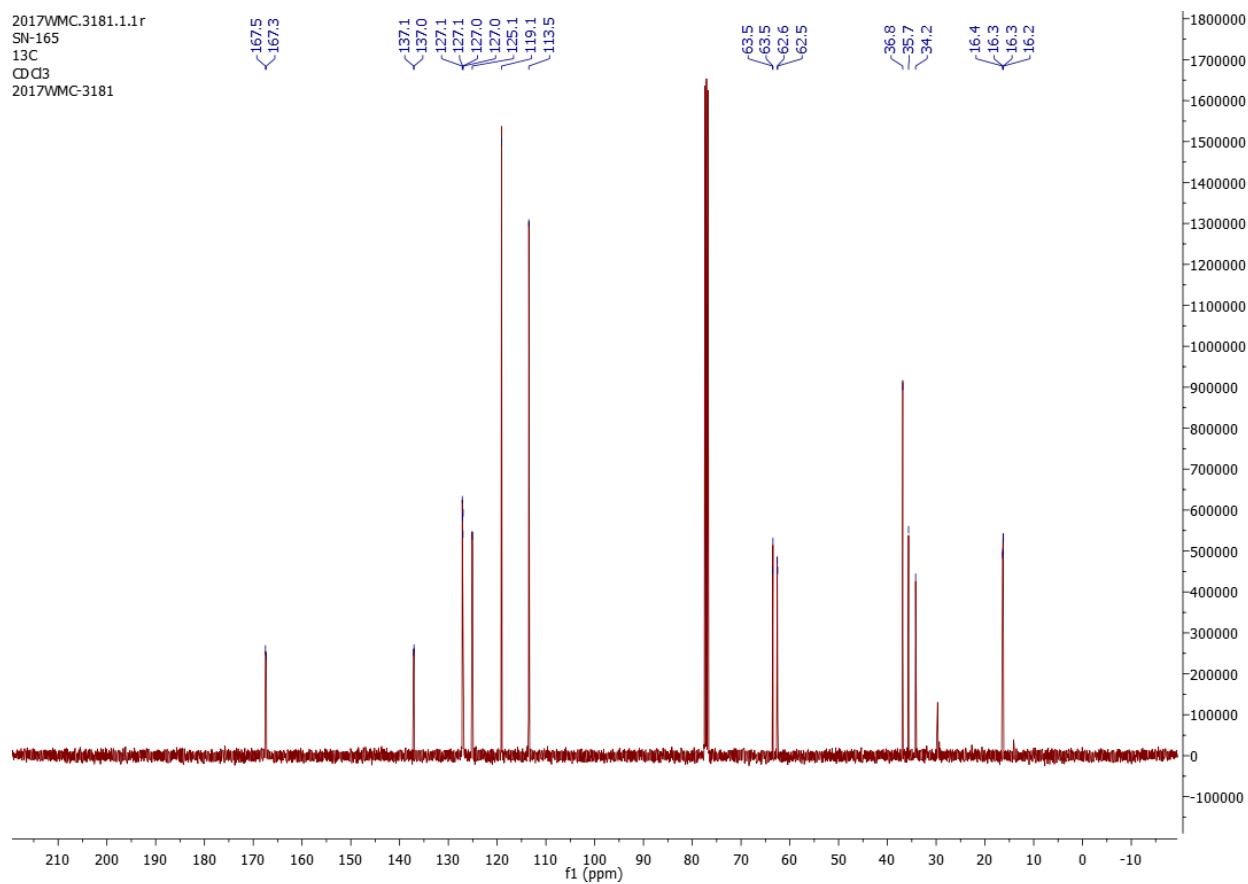
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SN-162
13C
CDCl3
2017WMC-3151

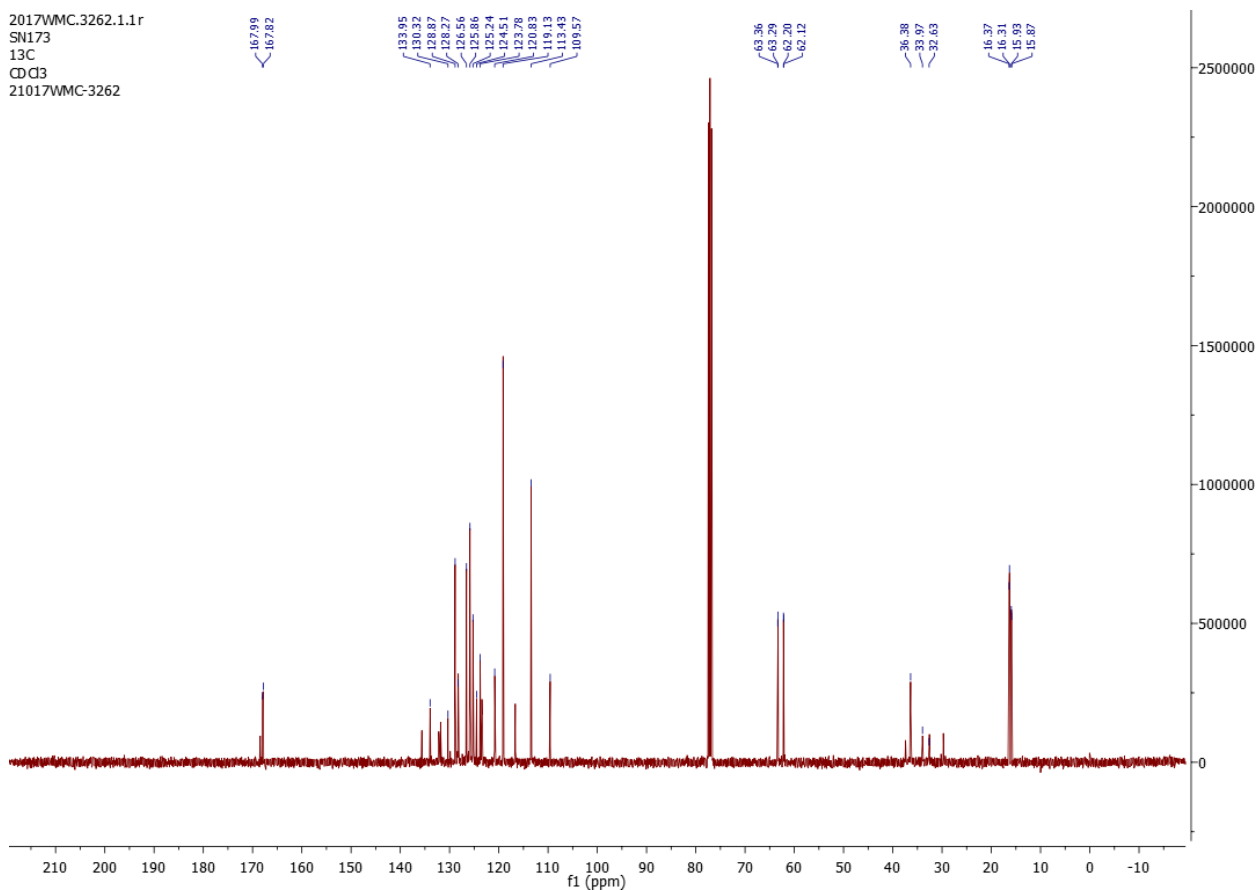
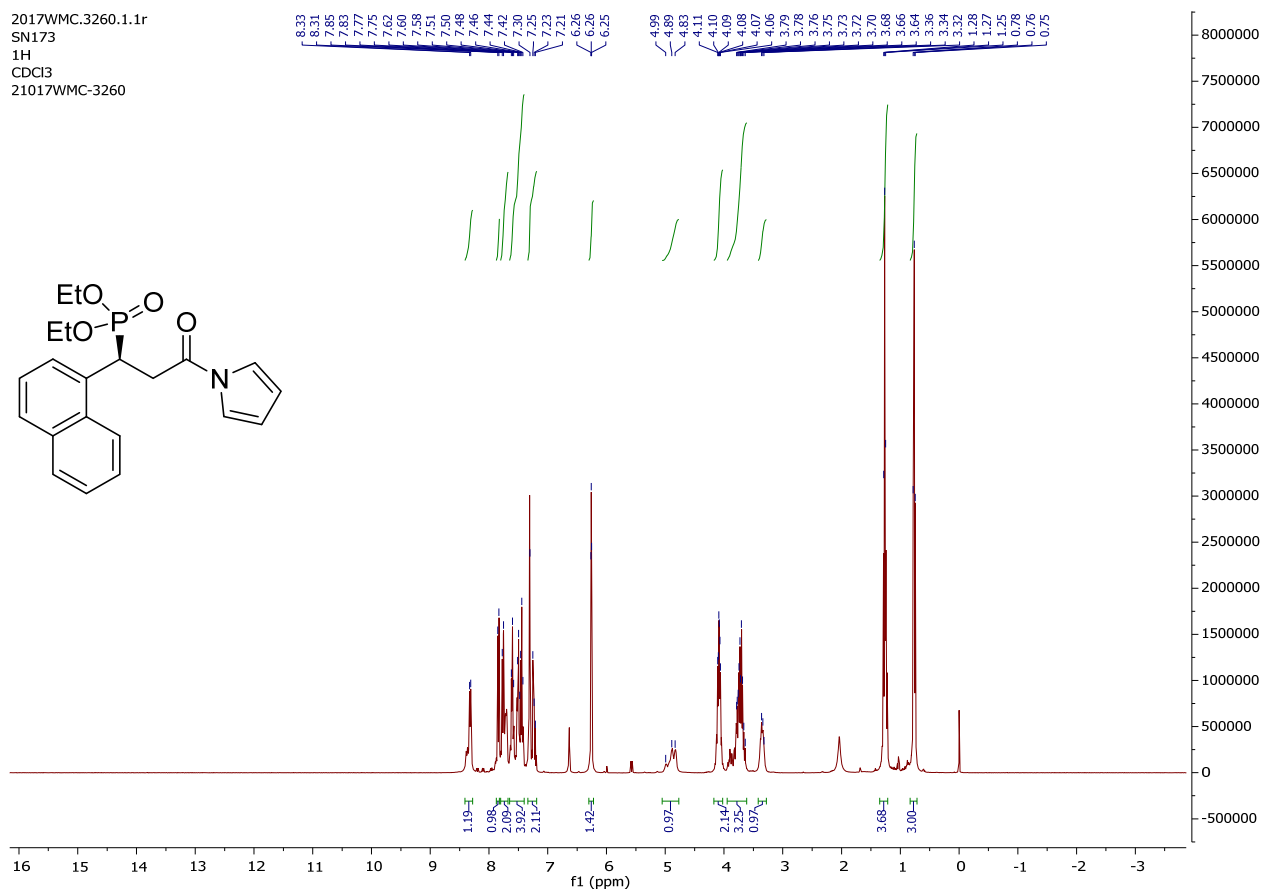


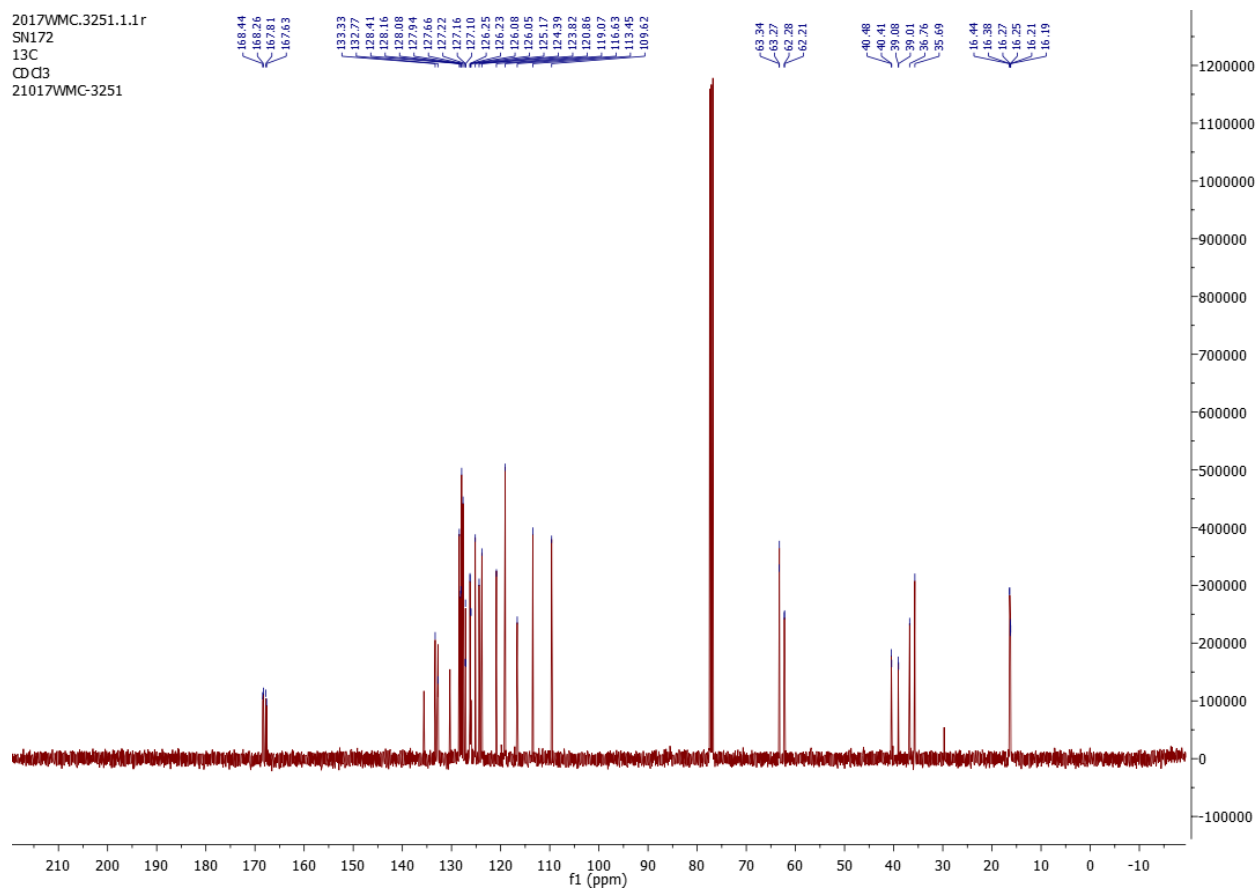
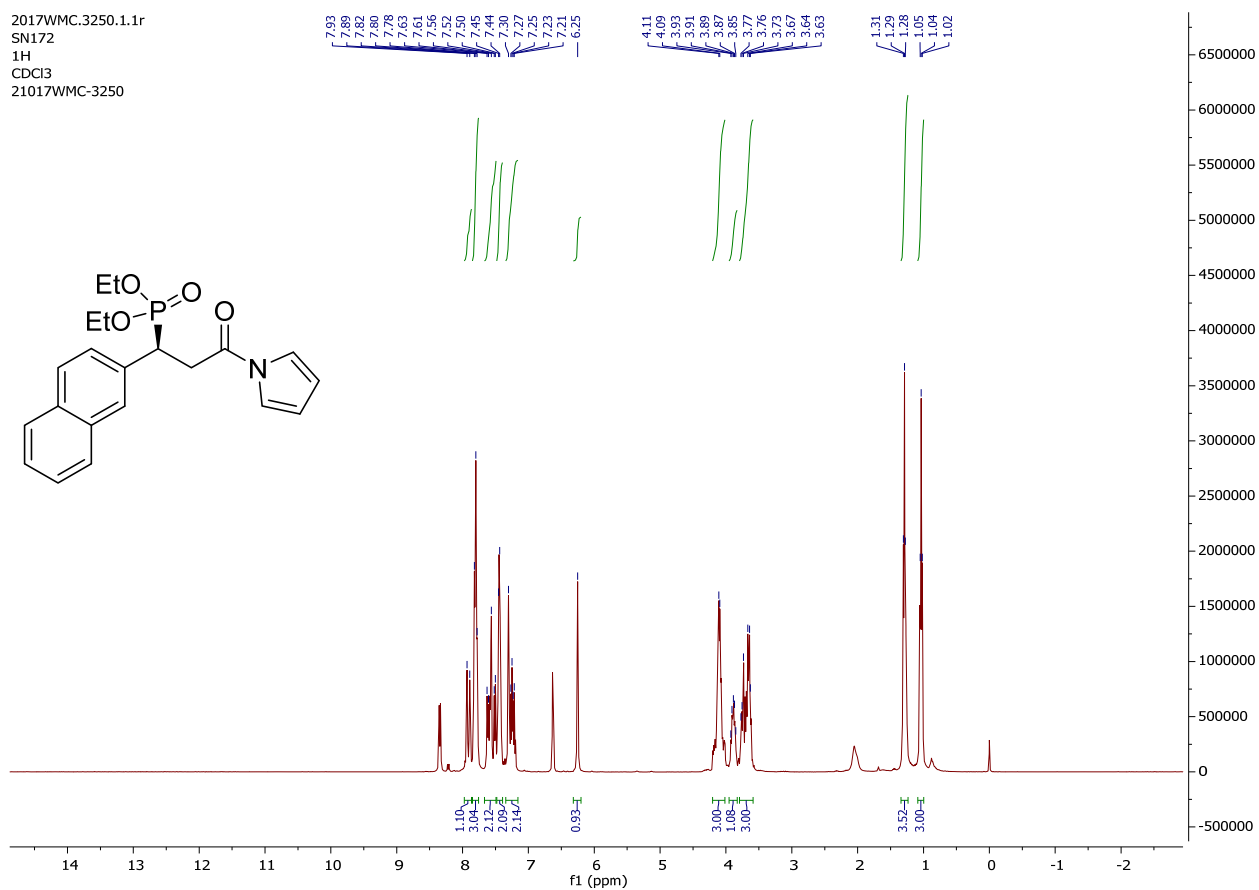
2017WMC.3180.1.1r
SN-165
1H
CDCl₃
2017WMC-3180



2017WMC.3181.1.1r
SN-165
13C
CDCl₃
2017WMC-3181







6. References

- 1 For the preparation of ligands **L1** and **L3**: see (a) Y.-Z. Hua, X.-W. Han, X.-C. Yang, X. Song, M.-C. Wang, J.-B. Chang, *J. Org. Chem.*, 2014, **79**, 11690; (b) Y.-Z. Hua, L.-J. Lu, P.-J. Huang, D.-H. Wei, M.-S. Tang, M.-C. Wang, J.-B. Chang, *Chem.–Eur. J.*, 2014, **20**, 12394; for the preparation of ligand **L2**: see (c) M.-C. Wang, Y.-H. Wang, G.-W. Li, P.-P. Sun, J.-X. Tian, H.-J. Lu, *Tetrahedron: Asymmetry*, 2011, **22**, 761; for the preparation of ligand **L4**: see (d) X. Song, A.-X. Liu, S.-S. Liu, W.-C. Gao, M.-C. Wang, J. Chang, *Tetrahedron*, 2014, **70**, 1464.
- 2 (a) Y. Tanaka, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.*, 2010, **132**, 8862; (b) S.-M. Lu, C. Bolm, *Chem.–Eur. J.*, 2008, **14**, 7513; (c) Y. Tsuchiya, Y. Hamashima, M. Sodeoka, *Org. Lett.*, 2006, **8**, 4851.
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- 4 D. Zhao, Y. Yuan, A. S. C. Chan, R. Wang, *Chem.–Eur. J.*, 2009, **15**, 2738.