Supplementary Material (ESI) for Chemical Communications

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Supporting Information

Reduction of Activated Carbonyl Groups by Alkyl Phosphines: Formation of α-Hydroxy Esters and Ketones

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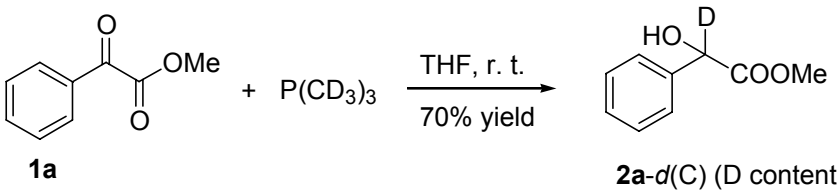
Deuterium and ^{18}O Labeling Experiments.

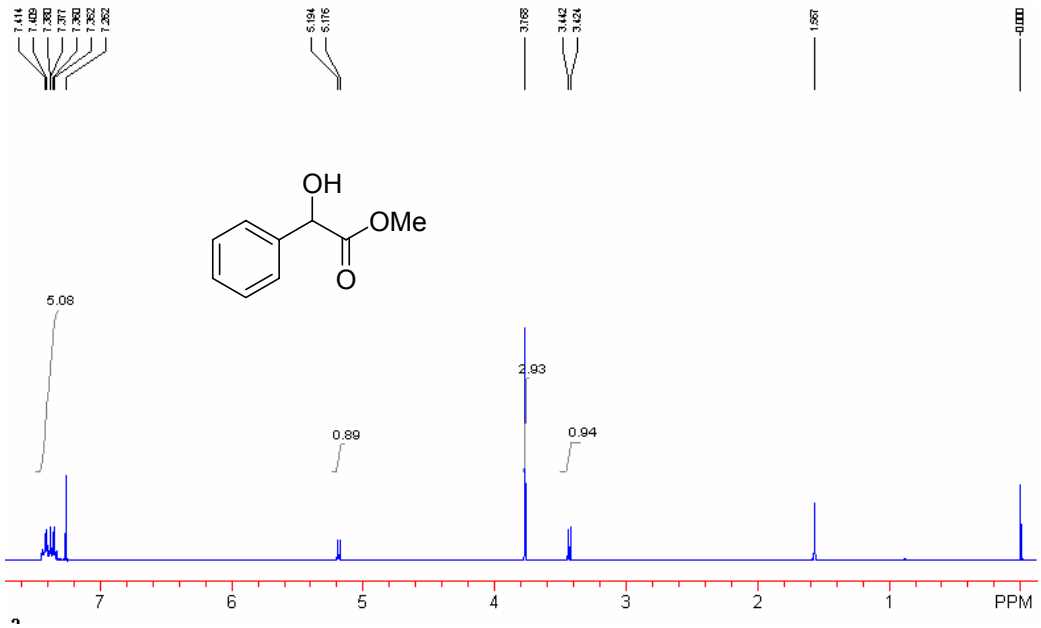
1. The effect of $P(CD_3)_3$[1] in the reduction reaction.

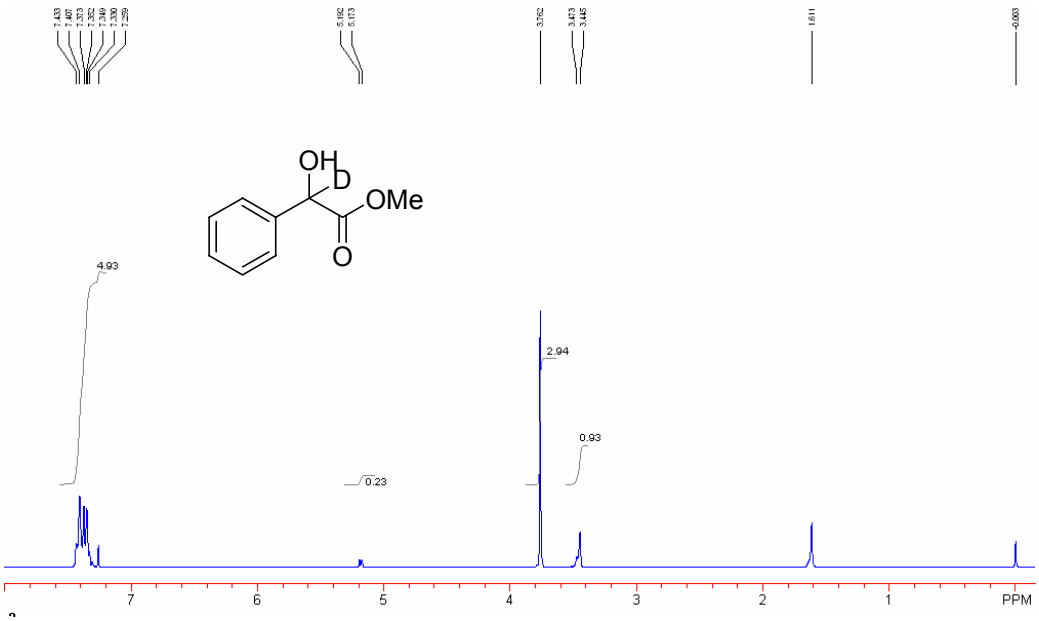
Scheme SI-1. Reduction of α-keto ester **1a** (0.3 mmol) with trimethylphosphine-d_9 in THF.



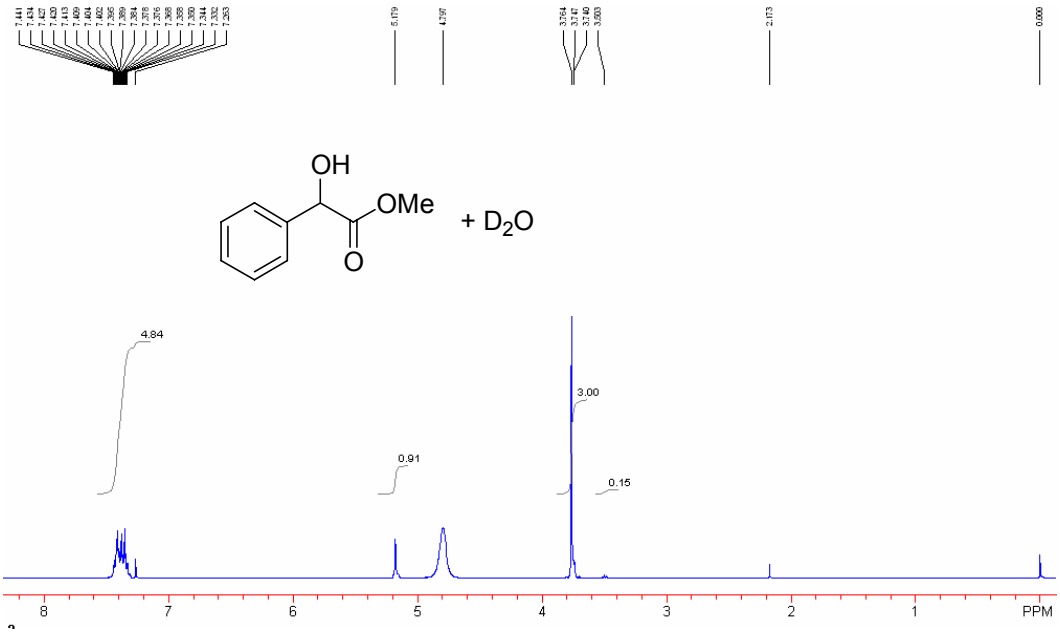
1a **2a**-*d*(C) (D content 80%)

^1H NMR spectrum of the corresponding products **2a** and **2a**-*d*(C).



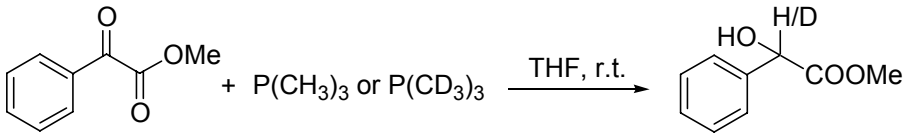


Determination of hydroxy proton (OH) by addition of D_2O.



2. Isotopic effect.

Table SI-1. Phosphine reduction of α-keto ester **1a** (0.3 mmol) in THF.[a)]



1a **2a**

entry	time/min.	**2a**/%[b)]	**2a**/%[c)]
1	0	0	0
2	10	73.45	41.57
3	20	83.01	42.87
4	30	85.85	43.82
5	40	87.30	43.83
6	50	88.83	44.09
7	60	90.79	44.37
8	80	92.10	44.47
9	100	93.15	45.28
10	120	93.71	45.34
11	150	94.44	45.48
12	180	95.18	45.82
13	210	95.51	45.87
14	390	95.40	46.18

[a)] **1a** (0.3 mmol), PMe_3 or $P(CD_3)_3$ (0.3 mmol), THF (0.3 mL). The yield of **2a** was determined by GLC analysis. [b)] In the presence of PMe_3. [c)] In the presence of $P(CD_3)_3$.

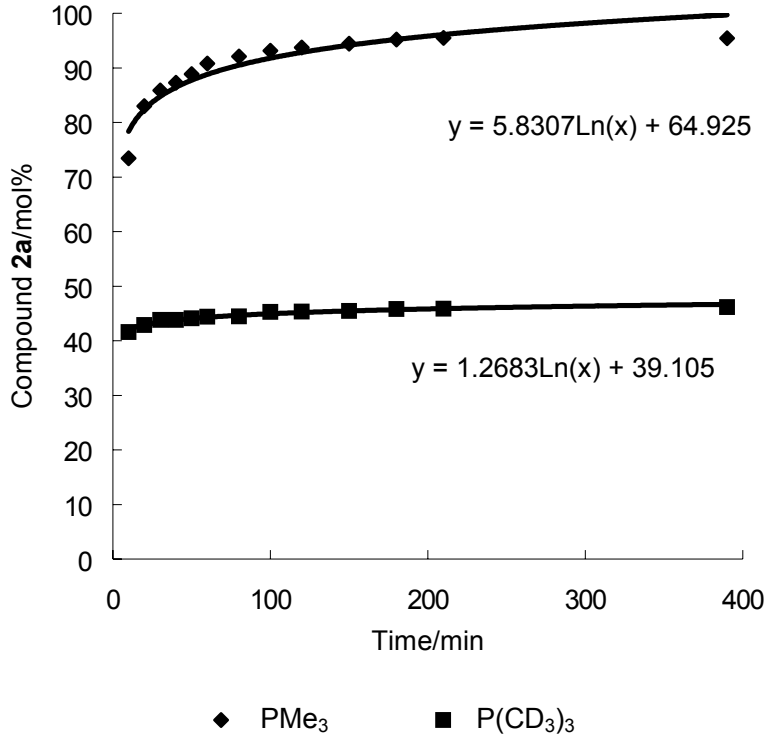


Figure SI-1. Rate profile for the reduction of α-keto ester **1a** (0.3 mmol) in the presence of trimethylphosphine (PMe_3) (0.3 mmol) or trimethylphosphine-d^9 [$P(CD_3)_3$] (0.3 mmol) in THF (0.3 mL).

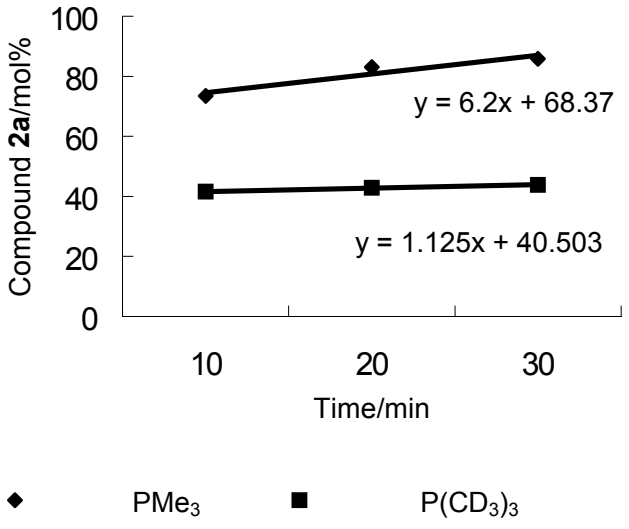
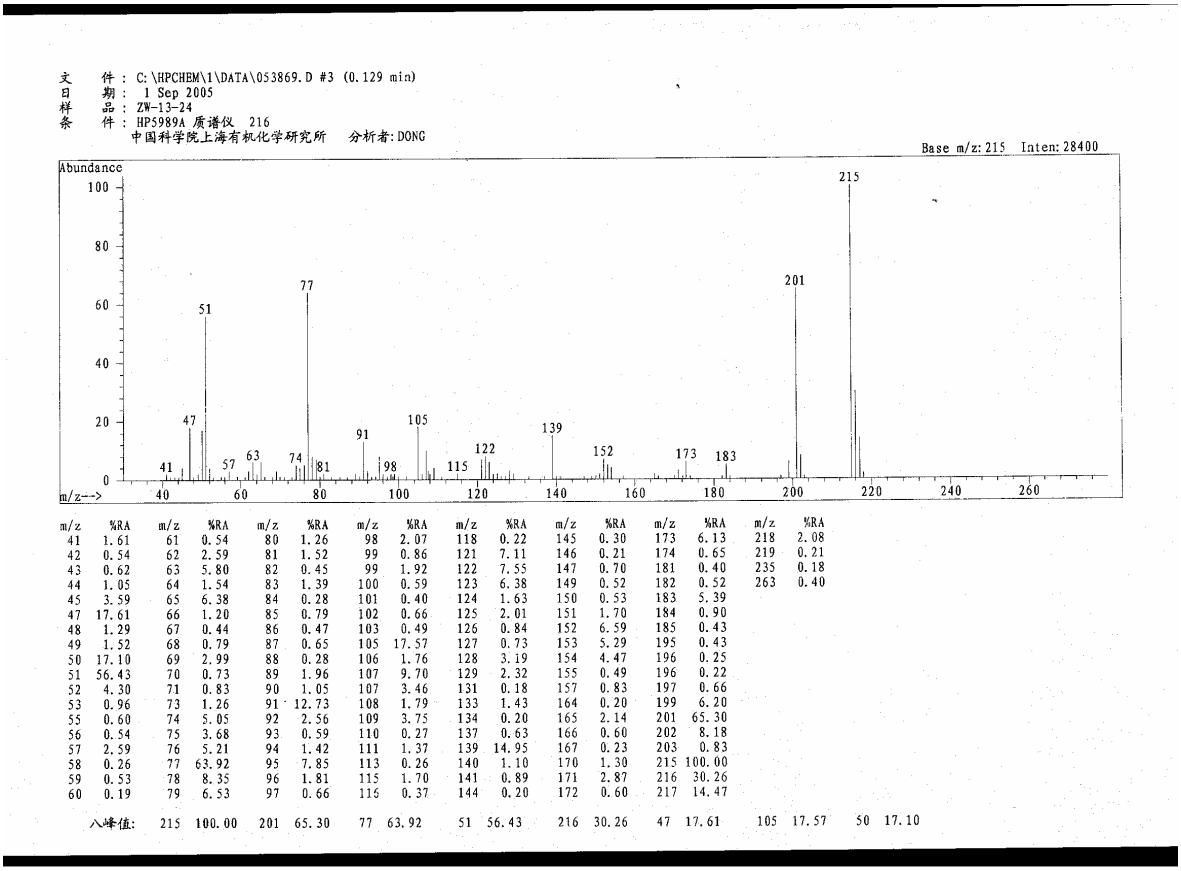


Figure SI-2. k(PMe_3) and k[$P(CD_3)_3$] at initial stage within 40 minutes.
k(PMe_3)/ k[$P(CD_3)_3$] = 5.5

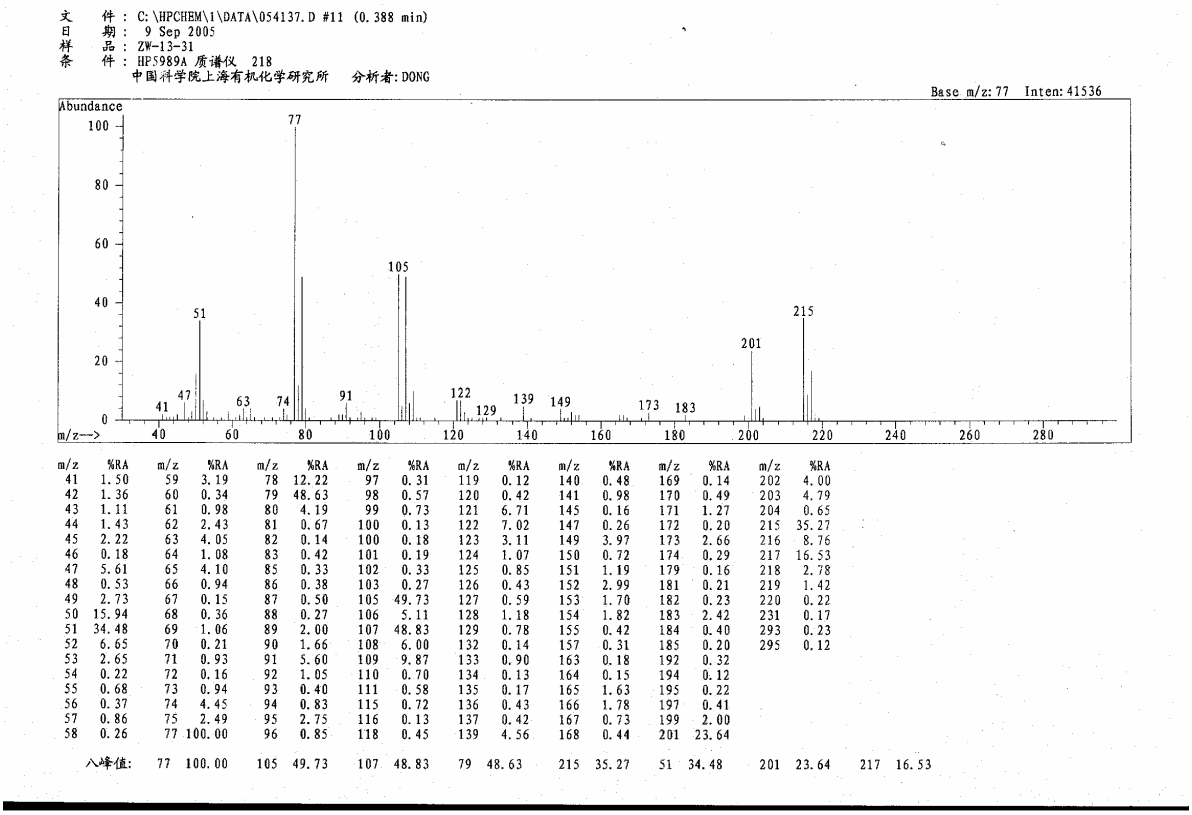
3. EI-MS, ^{1}H NMR and ^{31}P NMR spectroscopic data for phosphine oxides.



m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA
41	1.61	61	0.54	80	1.26	98	2.07	118	0.22	145	0.30	173	6.13	218	2.08
42	0.54	62	2.59	81	1.52	99	0.86	121	7.11	146	0.21	174	0.65	219	0.21
43	0.62	63	5.80	82	0.45	99	1.92	122	7.55	147	0.70	181	0.40	235	0.18
44	1.05	64	1.54	83	1.39	100	0.59	123	6.38	149	0.52	182	0.52	263	0.40
45	3.59	65	6.38	84	0.28	101	0.40	124	1.63	150	0.53	183	5.39		
47	17.61	66	1.20	85	0.79	102	0.66	125	2.01	151	1.70	184	0.90		
48	1.29	67	0.44	86	0.47	103	0.49	126	0.84	152	6.59	185	0.43		
49	1.52	68	0.79	87	0.65	105	17.57	127	0.73	153	5.29	195	0.43		
50	17.10	69	2.99	88	0.28	106	1.76	128	3.19	154	4.47	196	0.25		
51	56.43	70	0.73	89	1.96	107	9.70	129	2.32	155	0.49	196	0.22		
52	4.30	71	0.83	90	1.05	107	3.46	131	0.18	157	0.83	197	0.66		
53	0.96	73	1.26	91	12.73	108	1.79	133	1.43	164	0.20	199	6.20		
55	0.60	74	5.05	92	2.56	109	3.75	134	0.20	165	2.14	201	65.30		
56	0.54	75	3.68	93	0.59	110	0.27	137	0.63	166	0.60	202	8.18		
57	2.59	76	5.21	94	1.42	111	1.37	139	14.95	167	0.23	203	0.83		
58	0.26	77	63.92	95	7.85	113	0.26	140	1.10	170	1.30	215	100.00		
59	0.53	78	8.35	96	1.81	115	1.70	141	0.89	171	2.87	216	30.26		
60	0.19	79	6.53	97	0.66	116	0.37	144	0.20	172	0.60	217	14.47		

八峰值: 215 100.00 201 65.30 77 63.92 51 56.43 216 30.26 47 17.61 105 17.57 50 17.10

Figure SI-3. EI-MS spectrum of phosphine oxide under identical conditions.



m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA
41	1.50	59	3.19	78	12.22	97	0.31	119	0.12	140	0.48	169	0.14	202	4.00
42	1.36	60	0.34	79	48.63	98	0.57	120	0.42	141	0.98	170	0.49	203	4.79
43	1.11	61	0.98	80	4.19	99	0.73	121	6.71	145	0.16	171	1.27	204	0.65
44	1.43	62	2.43	81	0.67	100	0.13	122	7.02	147	0.26	172	0.20	215	35.27
45	2.22	63	4.05	82	0.14	100	0.18	123	3.11	149	3.97	173	2.66	216	8.76
46	0.18	64	1.08	83	0.42	101	0.19	124	1.07	150	0.72	174	0.29	217	16.53
47	5.61	65	4.10	85	0.33	102	0.33	125	0.85	151	1.19	179	0.16	218	2.78
48	0.53	66	0.94	86	0.38	103	0.27	126	0.43	152	2.99	181	0.21	219	1.42
49	2.73	67	0.15	87	0.50	105	49.73	127	0.59	153	1.70	182	0.23	220	0.22
50	15.94	68	0.36	88	0.27	106	5.11	128	1.18	154	1.82	183	2.42	231	0.17
51	34.48	69	1.06	89	2.00	107	48.83	129	0.78	155	0.42	184	0.40	293	0.23
52	6.65	70	0.21	90	1.66	108	6.00	132	0.14	157	0.31	185	0.20	295	0.12
53	2.65	71	0.93	91	5.60	109	9.87	133	0.90	163	0.18	192	0.32		
54	0.22	72	0.16	92	1.05	110	0.70	134	0.13	164	0.15	194	0.12		
55	0.68	73	0.94	93	0.40	111	0.58	135	0.17	165	1.63	195	0.22		
56	0.37	74	4.45	94	0.83	115	0.72	136	0.43	166	1.78	197	0.41		
57	0.86	75	2.49	95	2.75	116	0.13	137	0.42	167	0.73	199	2.00		
58	0.26	77	100.00	96	0.85	118	0.45	139	4.56	168	0.44	201	23.64		

八峰值: 77 100.00 105 49.73 107 48.83 79 48.63 215 35.27 51 34.48 201 23.64 217 16.53

Figure SI-4. EI-MS spectrum of phosphine oxide under identical conditions by addition of $H_2{}^{18}O$.

On the basis of EI-MS spectrum, P(^{18}O)Ph$_2$Me (^{18}O content 25%) can be calculated.

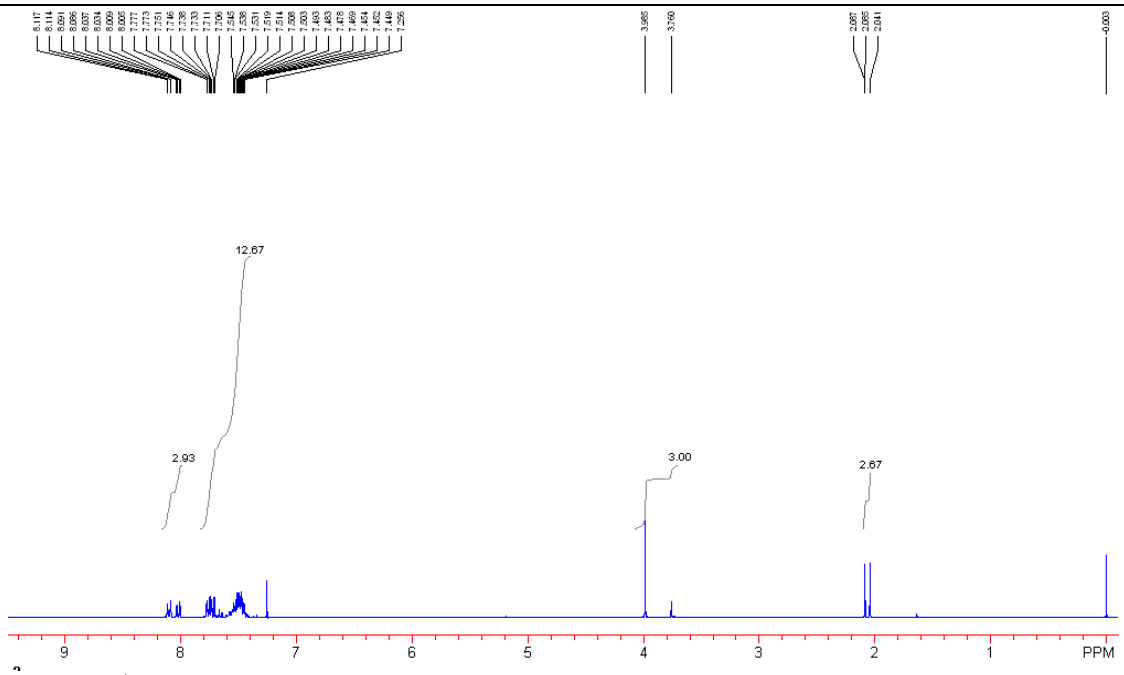


Figure SI-5. ^{1}H NMR spectrum of the reaction system under identical conditions by addition of D_2O (1.0 equiv.). On the basis of this ^{1}H NMR spectrum, D content of $P(O)Ph_2CH_2D$ is 33% and the yield of **2a** is 31%.

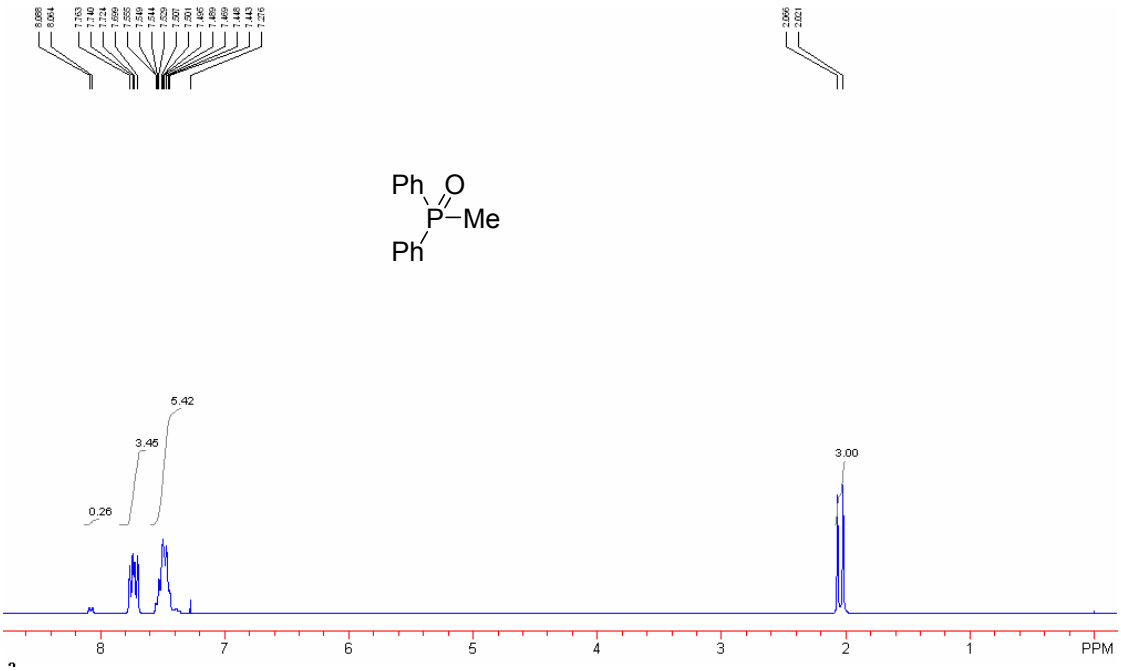


Figure SI-6. ^{1}H NMR spectrum of $P(O)Ph_2Me$ isolated from the reaction mixture in $CDCl_3$.

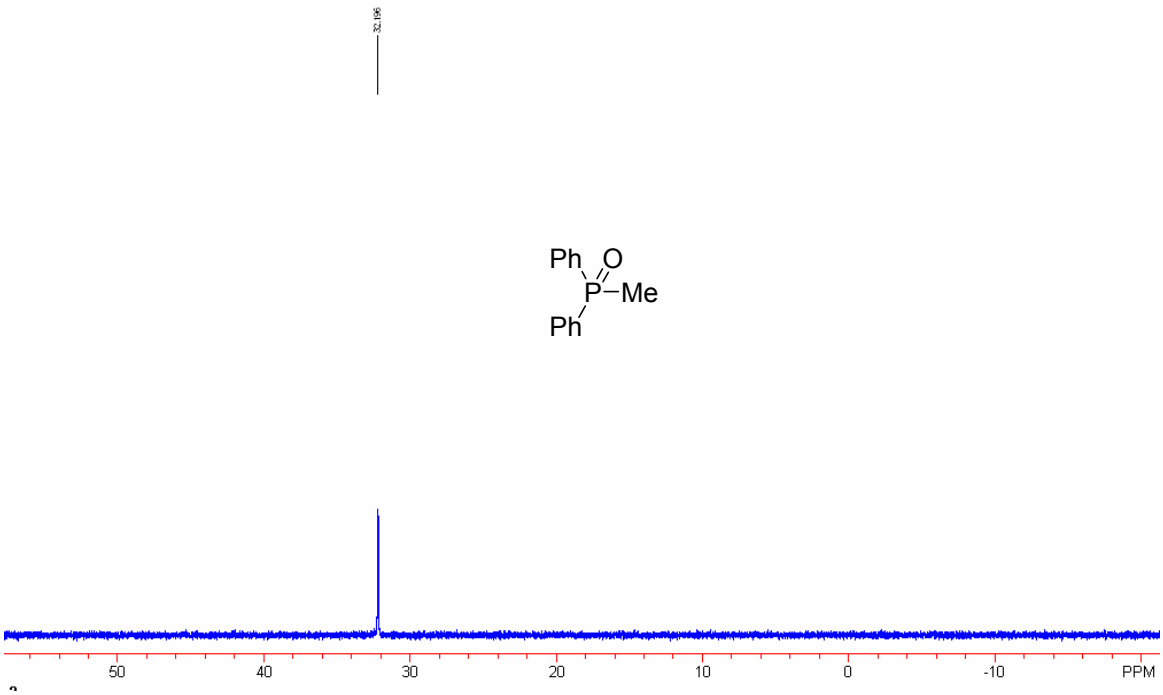


Figure SI-7. ^{31}P NMR spectrum of $P(O)Ph_2Me$ isolated from the reaction mixture in $CDCl_3$.

^{1}H and ^{31}P NMR spectroscopic trace in C_6D_6 for the reduction system under identical conditions.

The reduction using PPh_2Me in benzene is sluggish. Therefore, the spectrum change can be clearly observed. The formation of $P(O)Ph_2Me$ is due to the ambient moisture during the measurement.

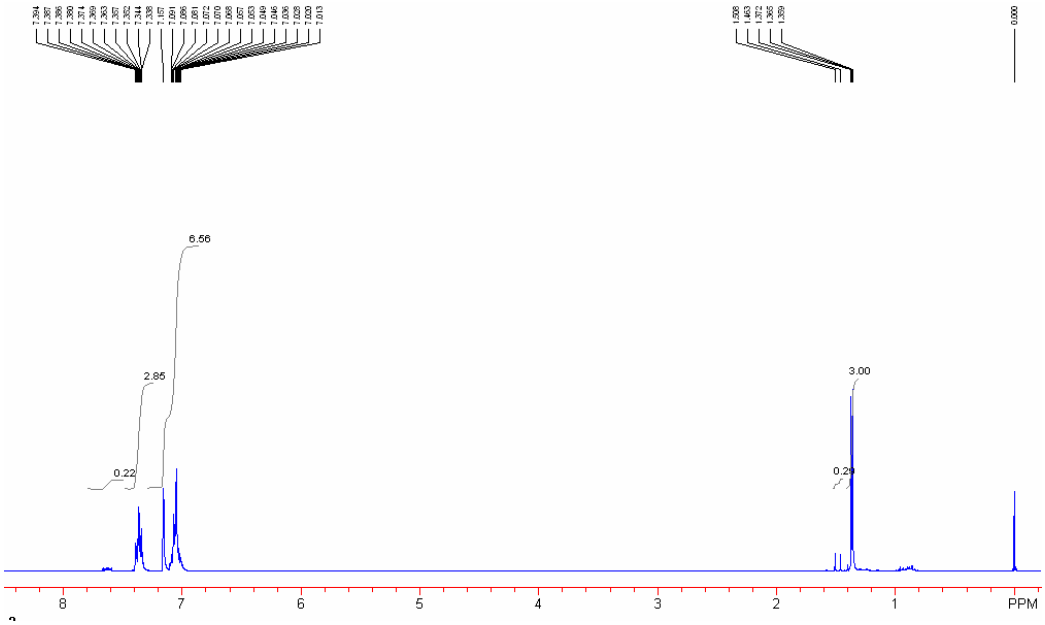


Figure SI-8. ^{1}H NMR spectrum of PPh_2Me in C_6D_6.

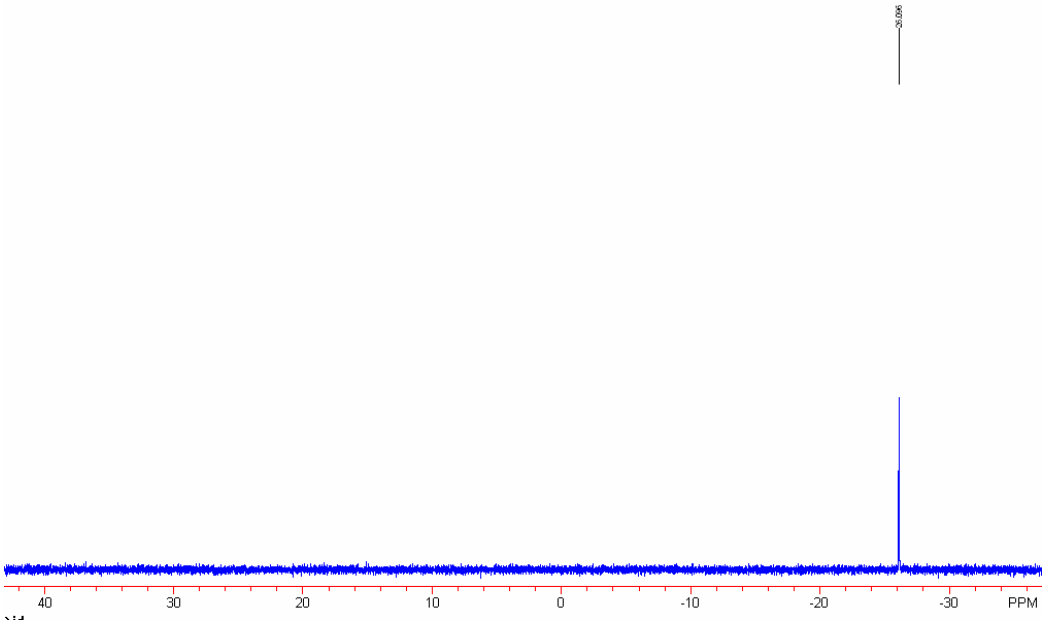


Figure SI-9. ^{31}P NMR spectrum of PPh_2Me in C_6D_6.

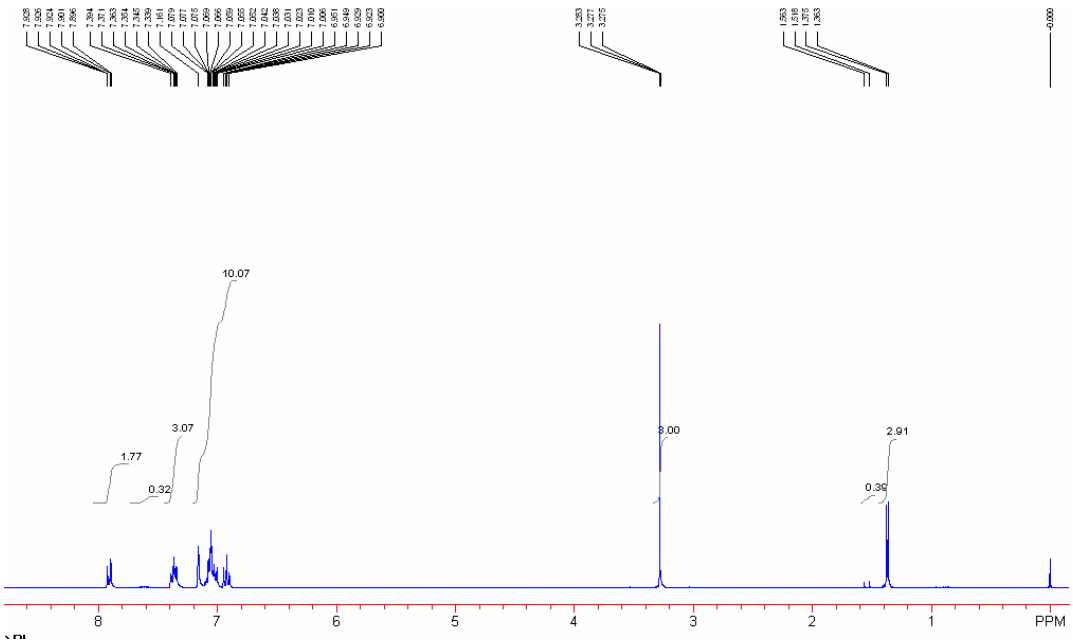


Figure SI-10. ^{1}H NMR spectrum by addition of **1a** (1.0 equiv) to PPh_2Me in C_6D_6 after 5 minutes.

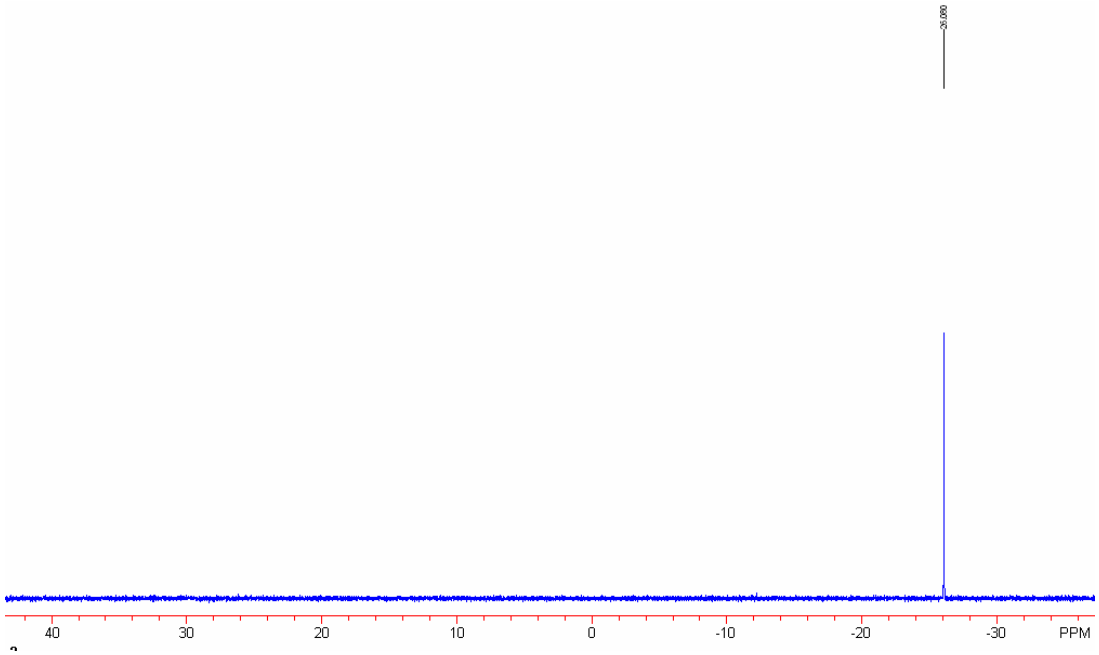


Figure SI-11. ^{31}P NMR spectrum by addition of **1a** (1.0 equiv) to PPh_2Me in C_6D_6 after 5 minutes.

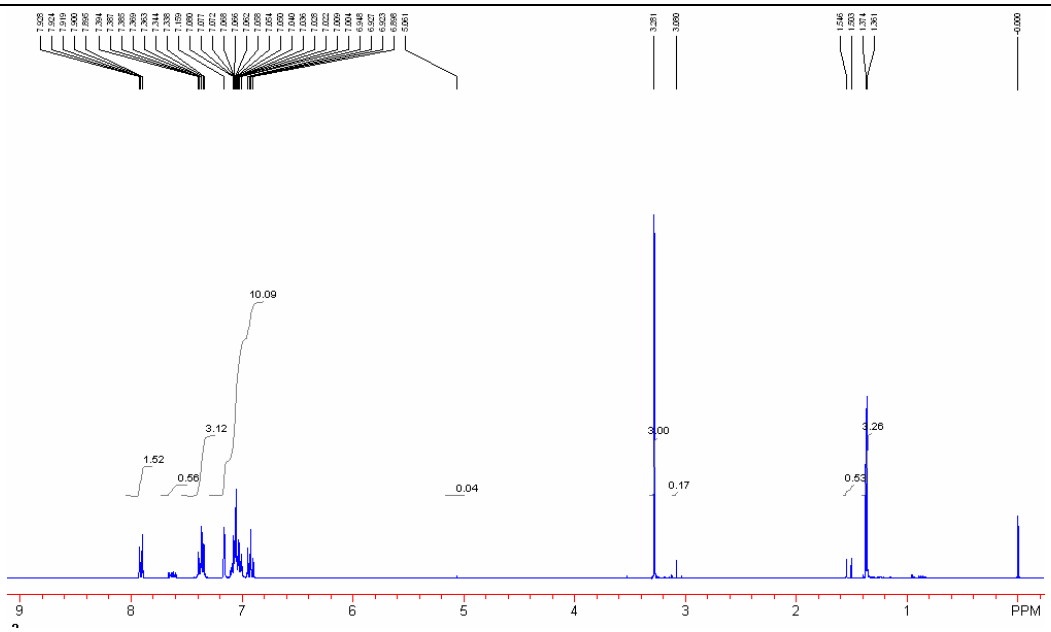


Figure SI-12. ^{1}H NMR spectrum by addition of **1a** (1.0 equiv) to PPh_2Me in C_6D_6 after 5 hours.

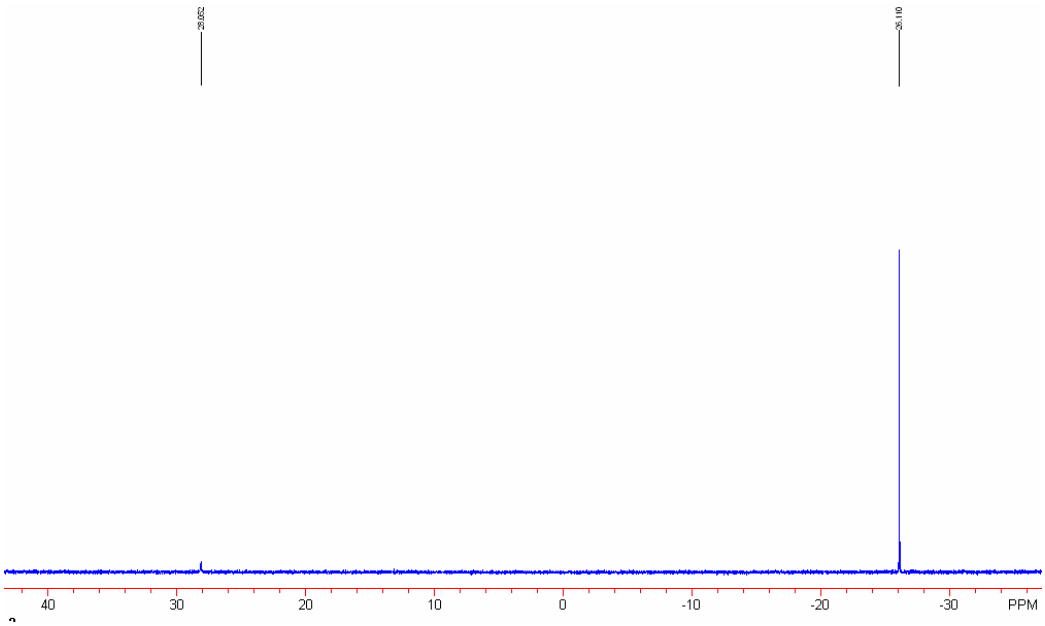


Figure SI-13. ^{31}P NMR spectrum by addition of **1a** (1.0 equiv) to PPh_2Me in C_6D_6 after 5 hours.

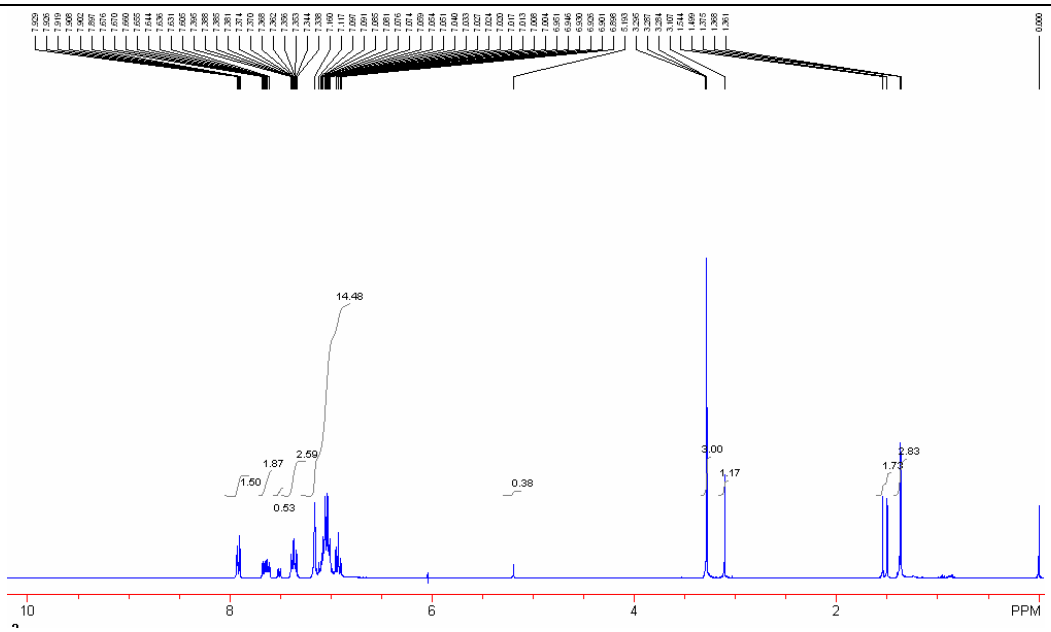


Figure SI-14. ^{1}H NMR spectrum by addition of **1a** (1.0 equiv) to PPh_2Me in C_6D_6 after 2 days.

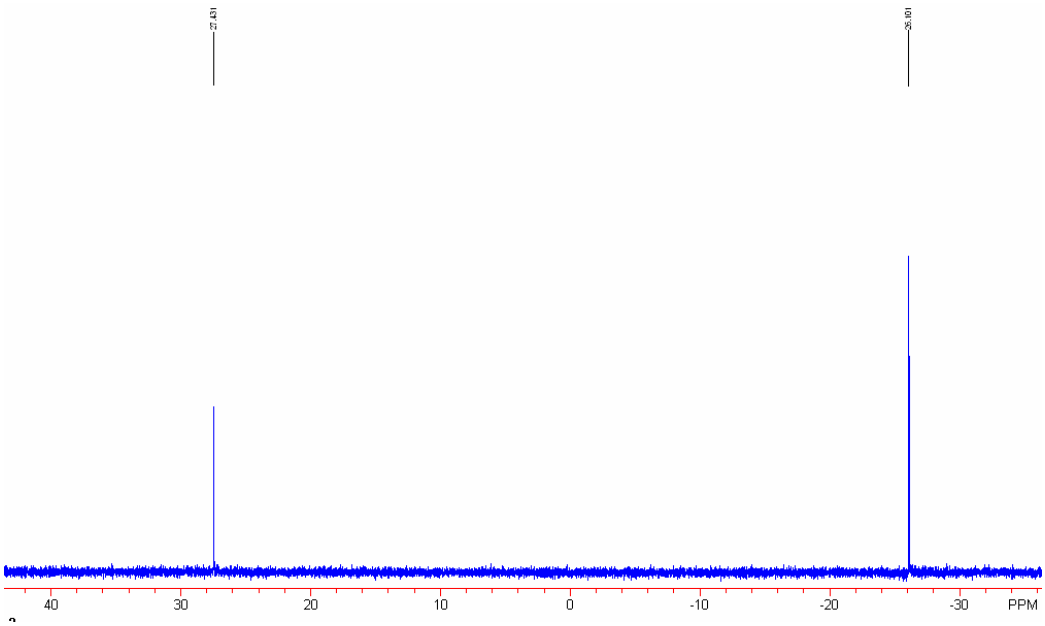


Figure SI-15. ^{31}P NMR spectrum by addition of **1a** (1.0 equiv) to PPh_2Me in C_6D_6 after 2 days.

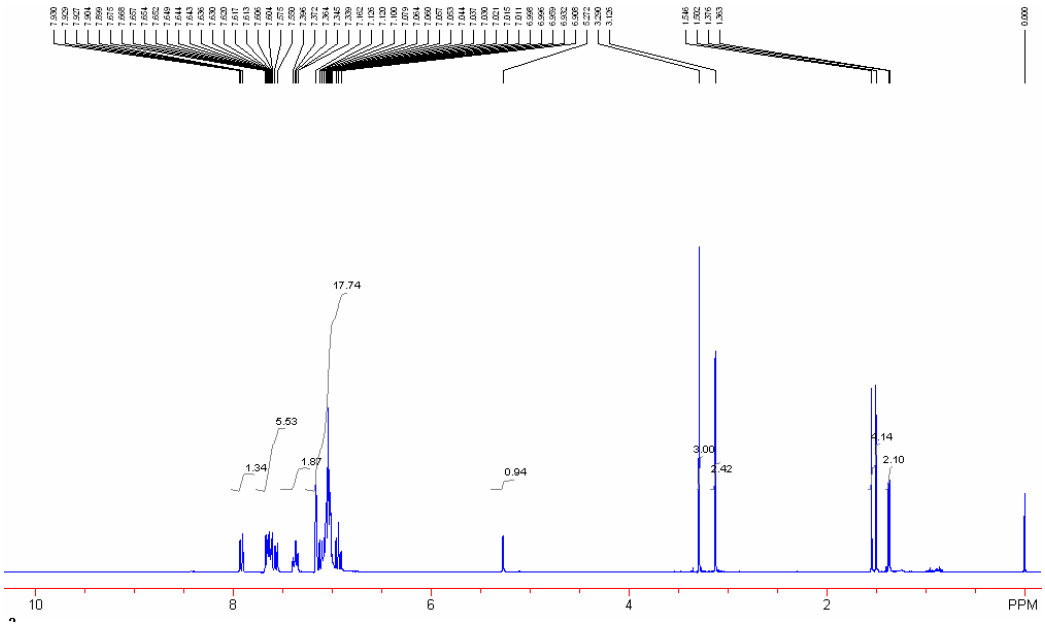


Figure SI-16. ^{1}H NMR spectrum by addition of **1a** (1.0 equiv) to PPh_2Me in C_6D_6 after 5 days.

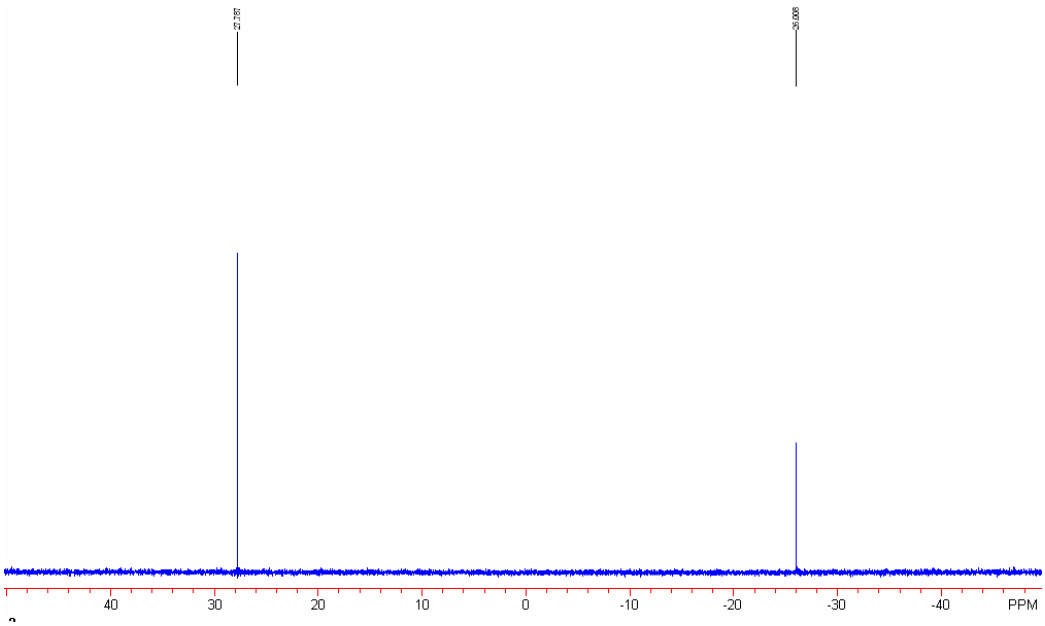


Figure SI-17. ^{31}P NMR spectrum by addition of **1a** (1.0 equiv) to PPh_2Me in C_6D_6 after 5 days.

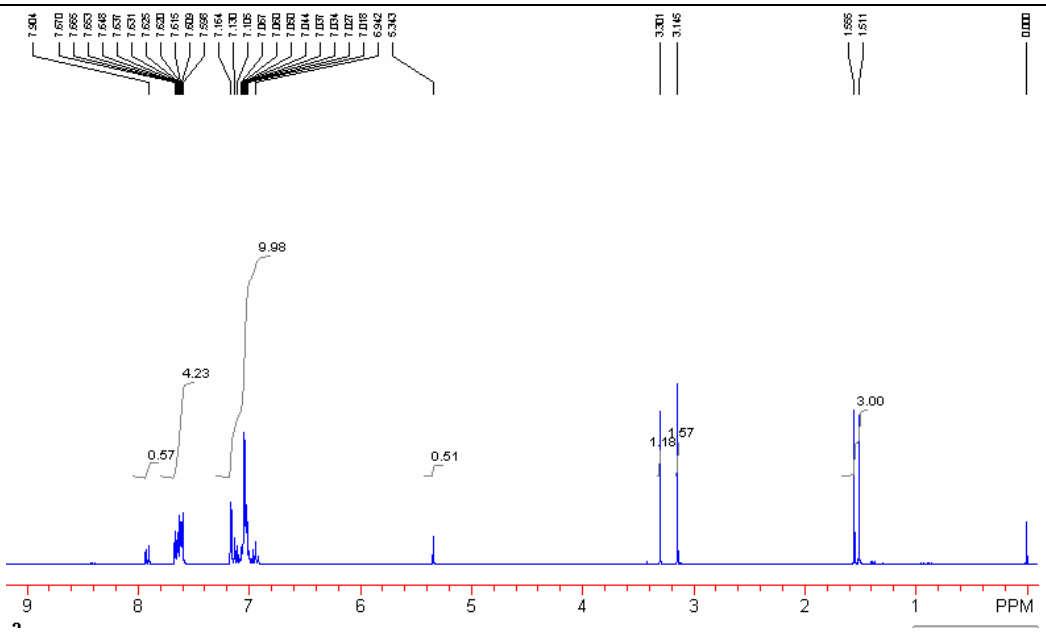


Figure SI-18. ^{1}H NMR spectrum by addition of **1a** (1.0 equiv) to PPh_2Me in C_6D_6 after 7 days.

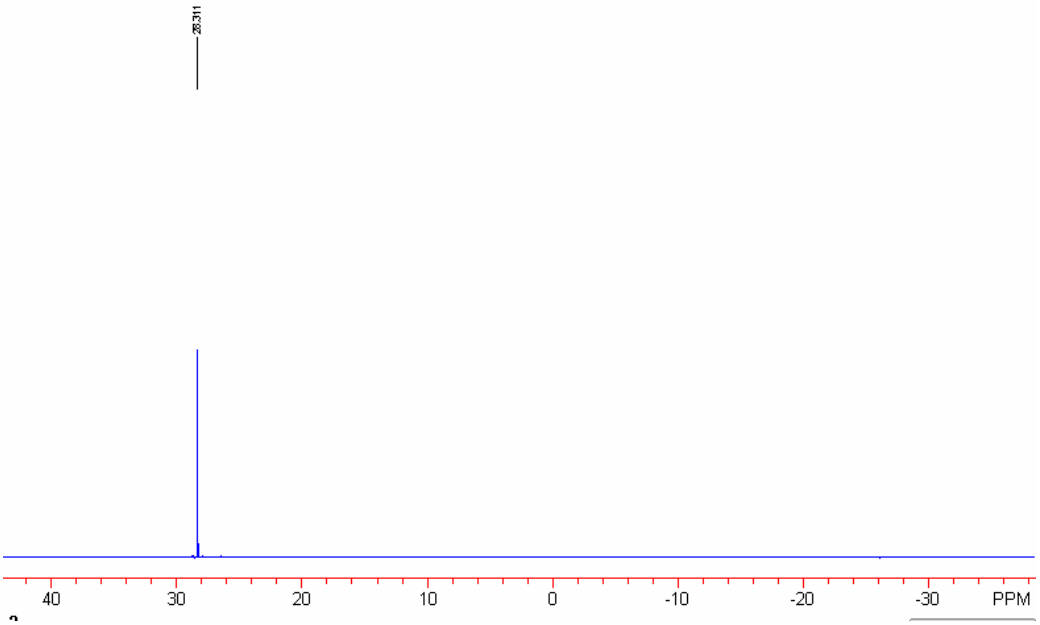


Figure SI-19. ^{31}P NMR spectrum by addition of **1a** (1.0 equiv) to PPh_2Me in C_6D_6 after 7 days.

General Reaction Procedure and Spectra Charts of Compounds Reported in the Main Text.

General Remarks.

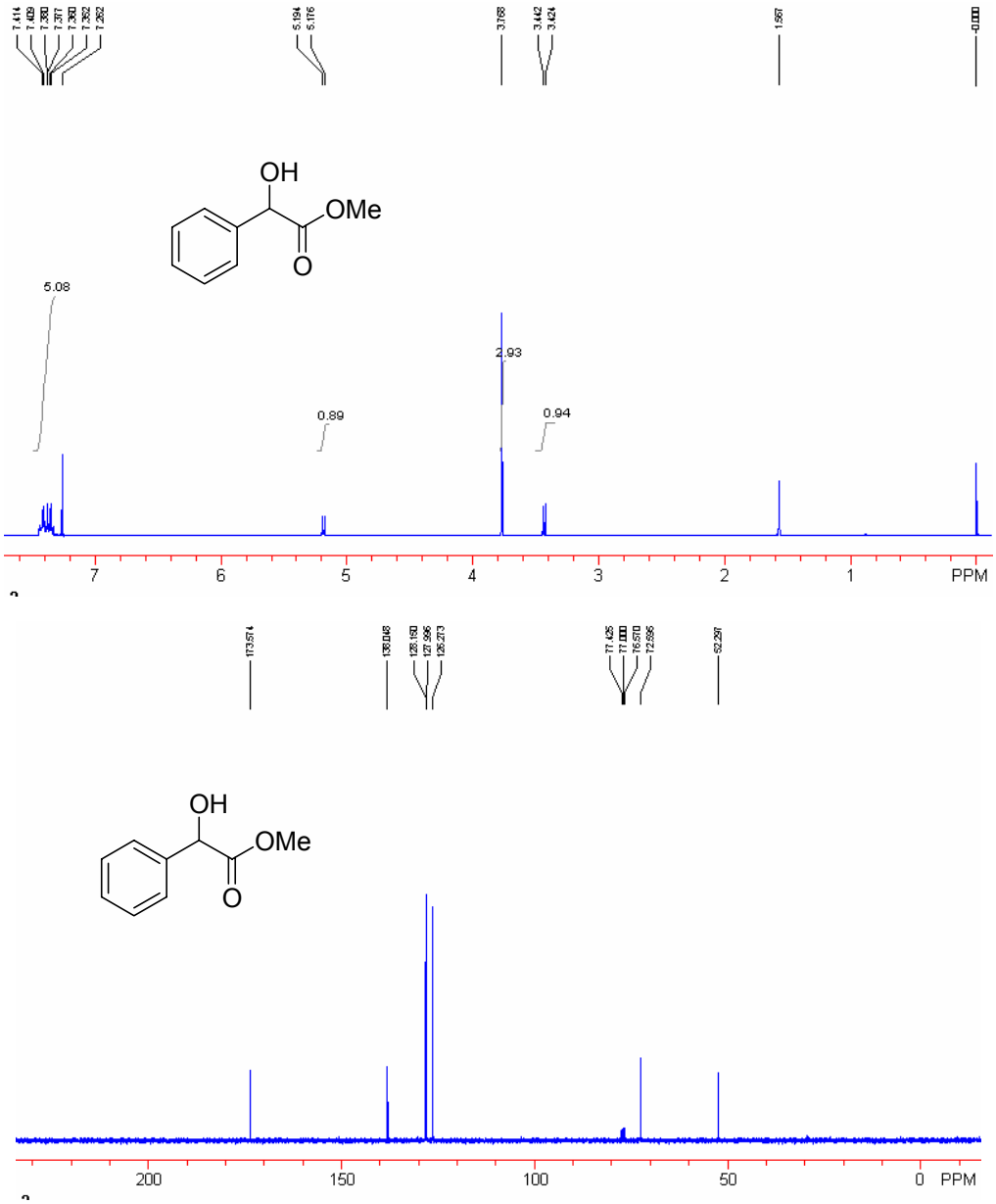
^{1}H NMR and ^{13}C NMR spectra were recorded for a solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure. Reaction experiments were performed under argon atmosphere using standard Schlenk techniques. The starting materials **1b**-**1j**,[2] **3b**-**3c**,[3] **5**-**7**[4] were synthesis according to the previous literature.

General Reaction Procedure.

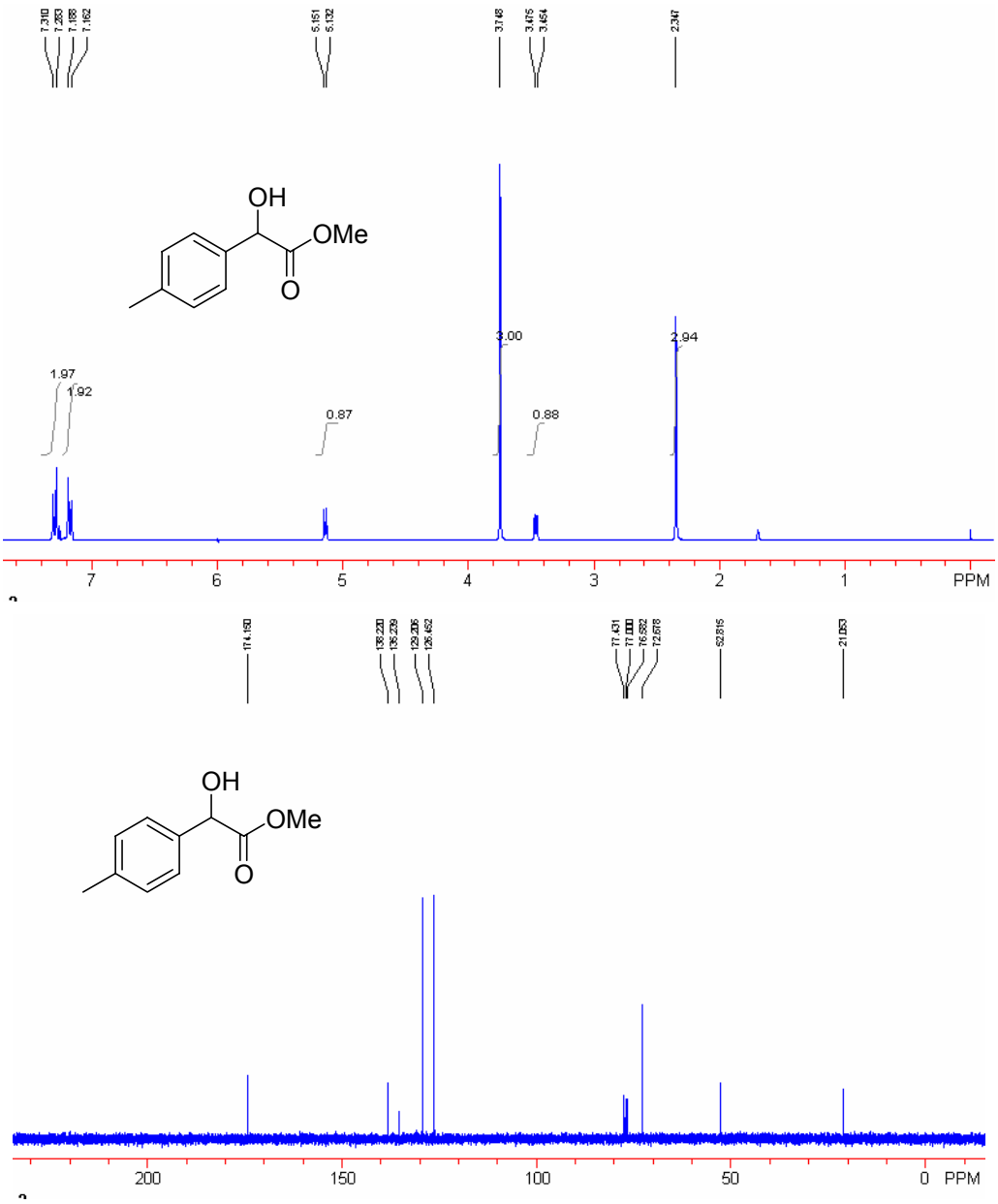
To a mixture of α-keto ester compound (0.3 mmol), phosphine (0.3 mmol) and solvent (0.3 mL) were stirred under argon at room temperature for the required time indicated in the Tables. After the reaction solution was concentrated under reduced pressure, the residue was purified by flash chromatography on silica gel (Eluent: EtOAc/petroleum = 1/10) to afford pure products **2**.

^{1}H NMR and ^{13}C NMR spectra.

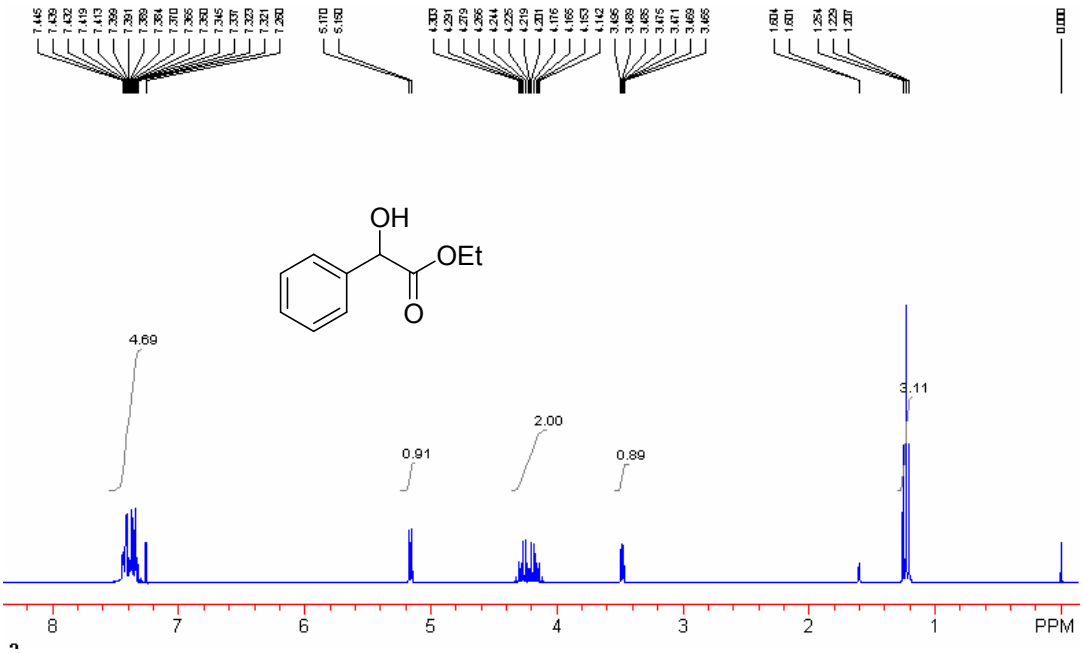
Hydroxy-phenyl-acetic acid methyl ester (2a) (a known compound).[5] A white solid: 37 mg, 75% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 3.43 (d, J = 5.4 Hz, 1H, OH), 3.77 (s, 3H, CH_3), 5.18 (d, J = 5.4 Hz, 1H, OH), 7.35-7.42 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 52.3, 72.6, 126.3, 128.0, 136.1, 173.6.

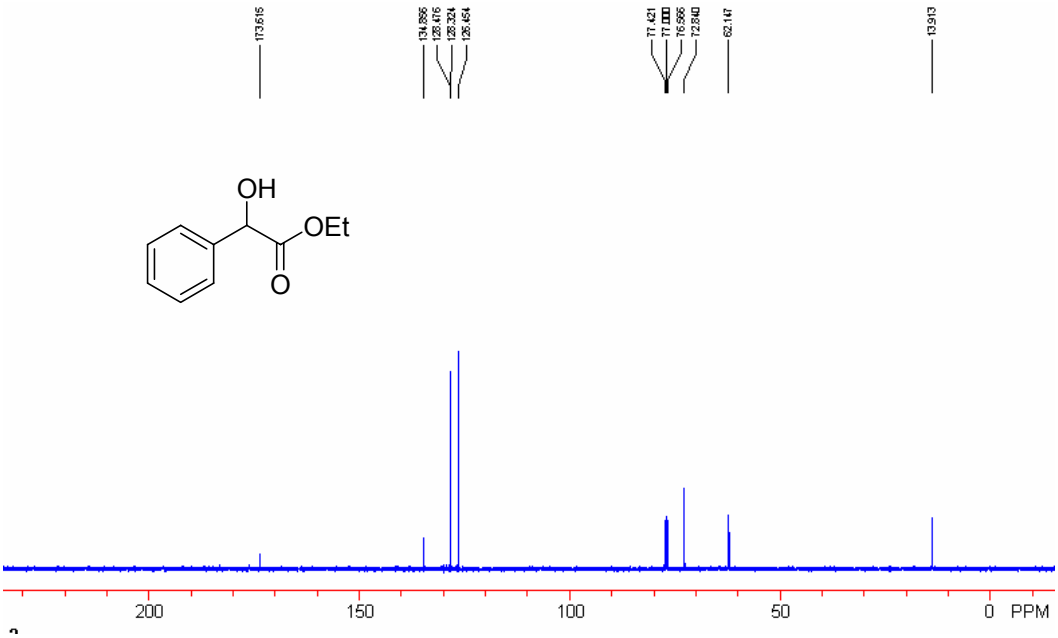


Hydroxy-p-tolyl-acetic acid methyl ester (2b) (a known compound).[6] A white solid: 44 mg, 81% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.35 (s, 3H, CH_3), 3.46 (d, J = 6.3 Hz, 1H, OH), 3.75 (s, 3H, CH_3), 5.14 (d, J = 5.7 Hz, 1H, CH), 7.17 (d, J = 7.8 Hz, 2H, Ar), 7.30 (d, J = 8.1 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.1, 52.6, 72.7, 126.5, 129.2, 135.2, 138.2, 174.2.

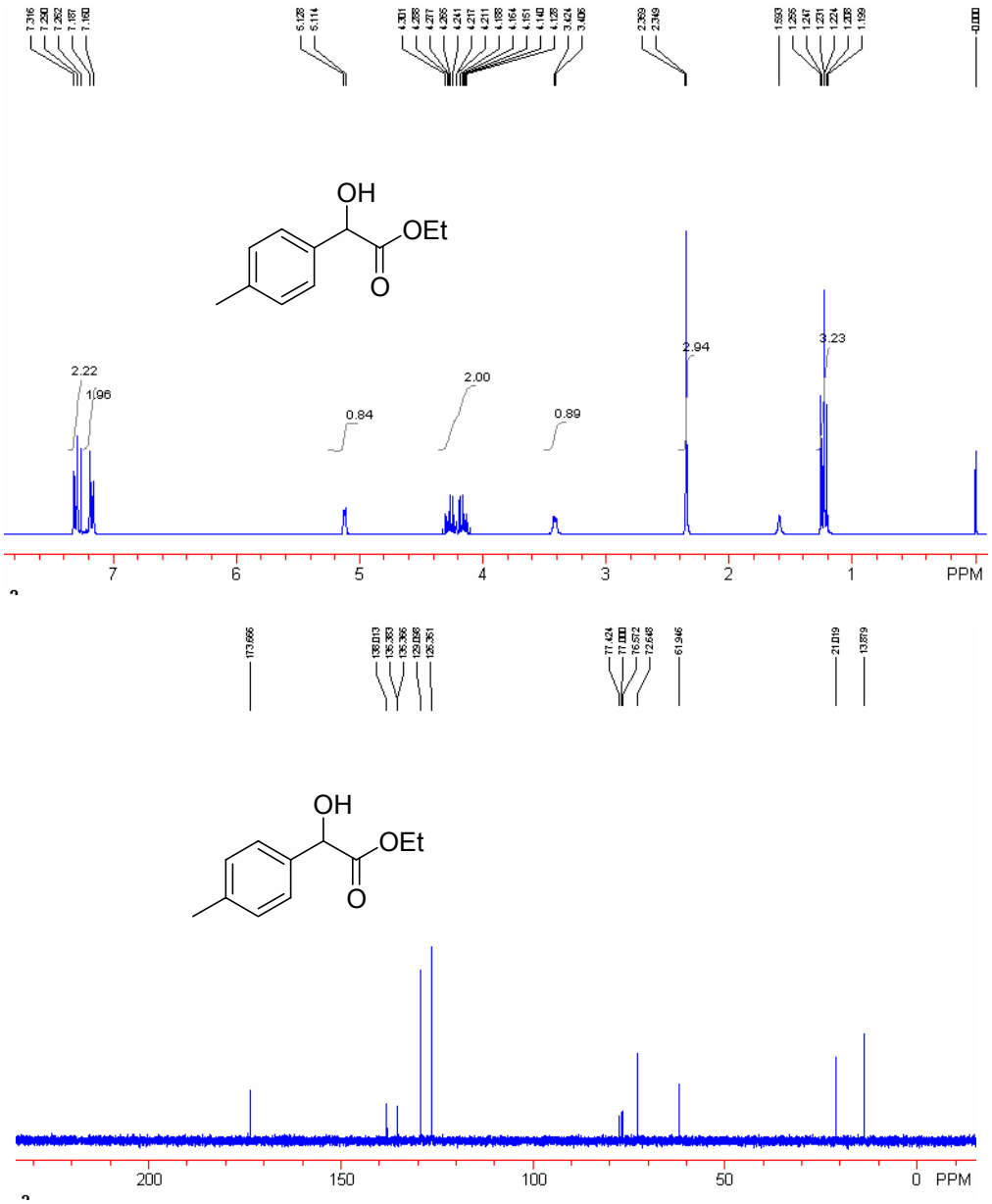


Hydroxy-phenyl-acetic acid ethyl ester (2c) (a known compound).[5] A colorless oil: 42 mg, 81% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.23 (t, J = 6.6 Hz, 3H, CH_3), 3.47 (d, J = 6.0 Hz, 1H, OH), 4.14-4.30 (m, 2H, CH_2), 5.16 (d, J = 6.0 Hz, 1H, CH), 7.32-7.45 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 62.2, 72.8, 126.5, 128.3, 128.5, 134.9, 173.8.

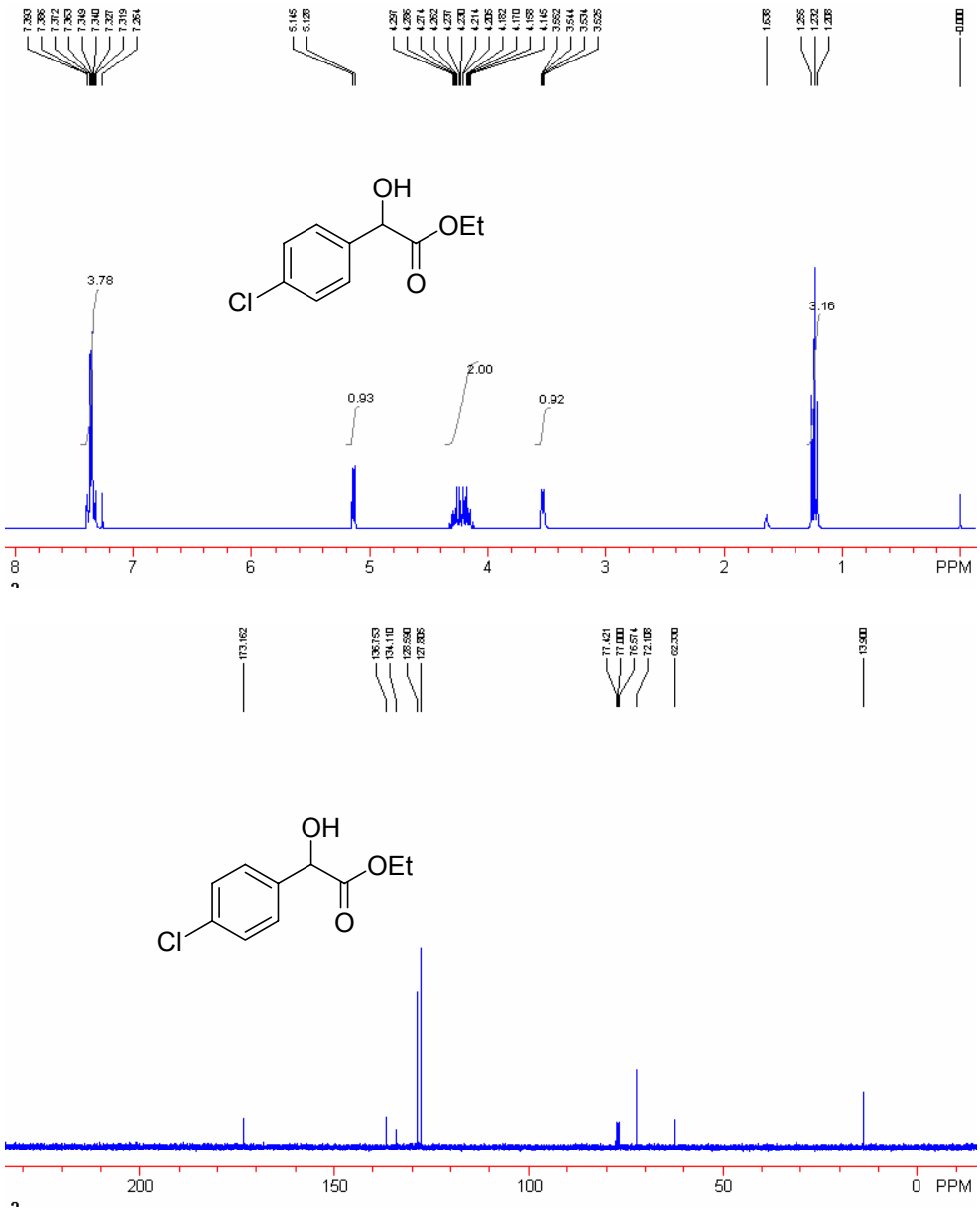




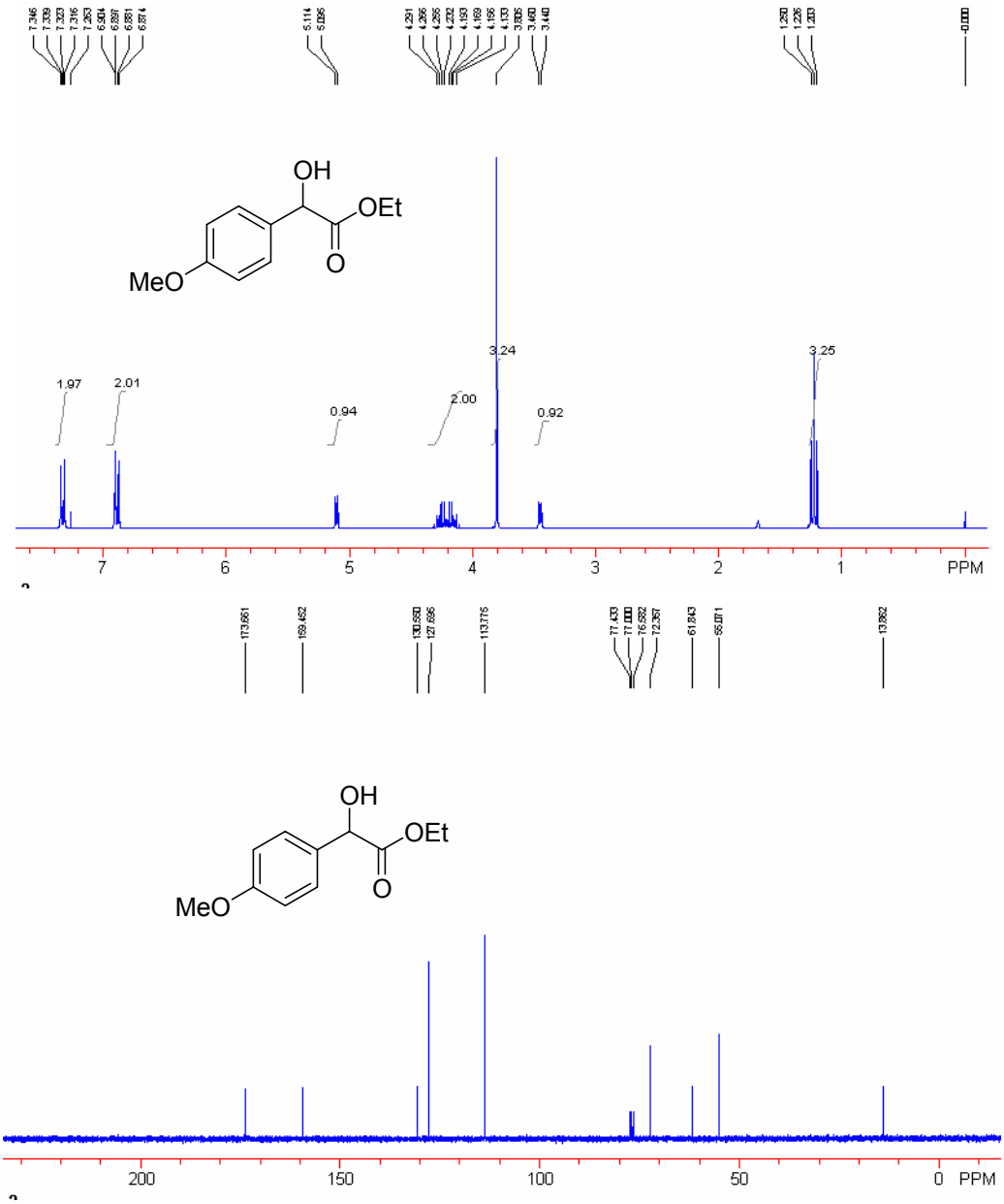
Hydroxy-p-tolyl-acetic acid ethyl ester (2d) (a known compound).[7] A white solid: 47 mg, 85% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.23 (t, J = 7.2 Hz, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.41 (d, J = 5.4 Hz, 1H, OH), 4.13-4.30 (m, 2H, CH_2), 5.12 (d, J = 4.2 Hz, 1H, CH), 7.17 (d, J = 8.1 Hz, 2H, Ar), 7.30 (d, J = 7.8 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 21.0, 62.0, 72.7, 126.4, 129.1, 135.4, 138.0, 173.7.



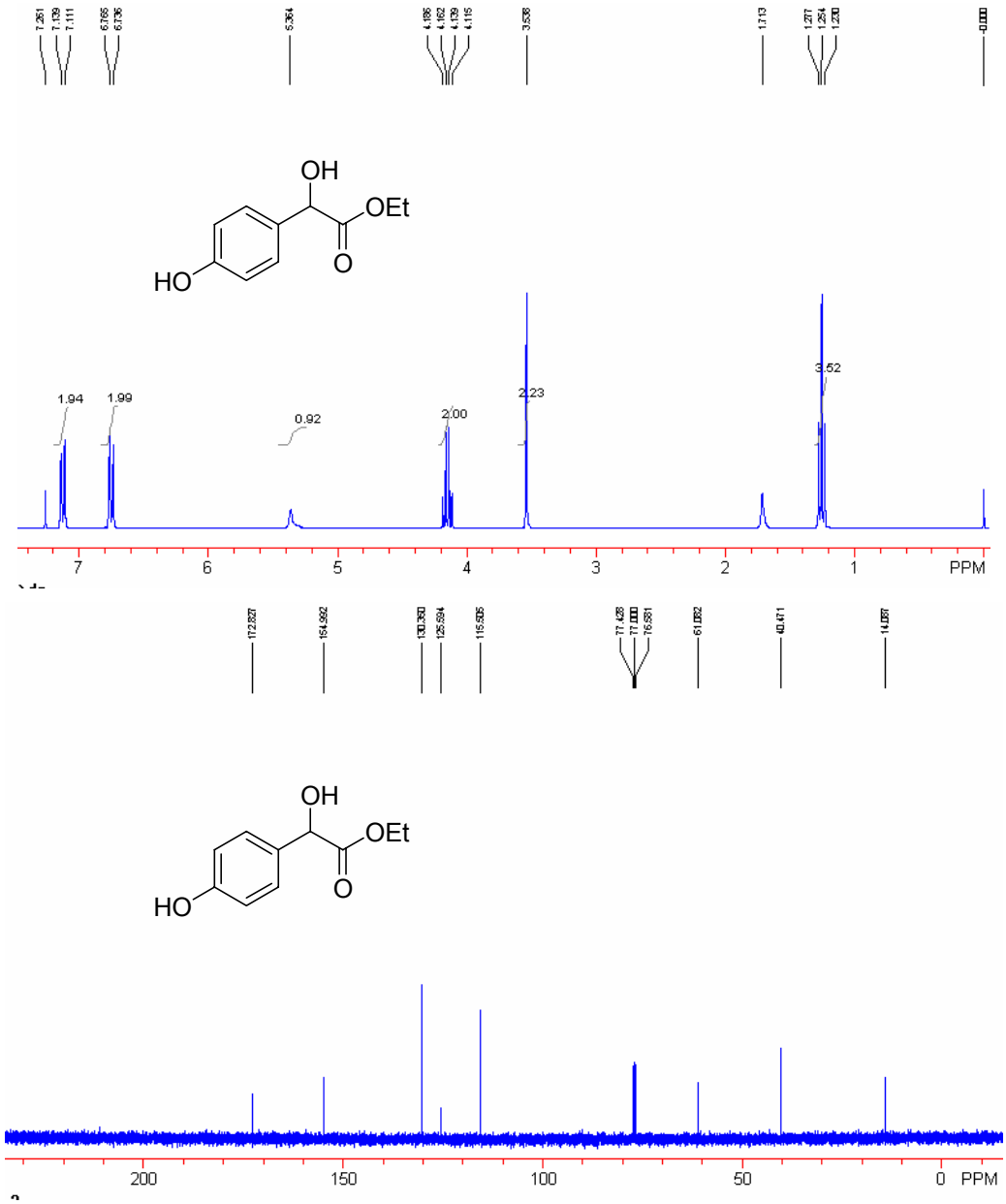
(4-Chlorophenyl)-hydroxy-acetic acid ethyl ester (2e) (a known compound).[8] A white solid: 52 mg, 81% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.23 (t, J = 6.9 Hz, 3H, CH_3), 3.53 (d, J = 5.7 Hz, 1H, OH), 4.15-4.30 (m, 2H, CH_2), 5.13 (d, J = 5.1 Hz, 1H, CH), 7.32-7.39 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 62.3, 72.1, 127.8, 128.6, 134.1, 136.8, 173.2.



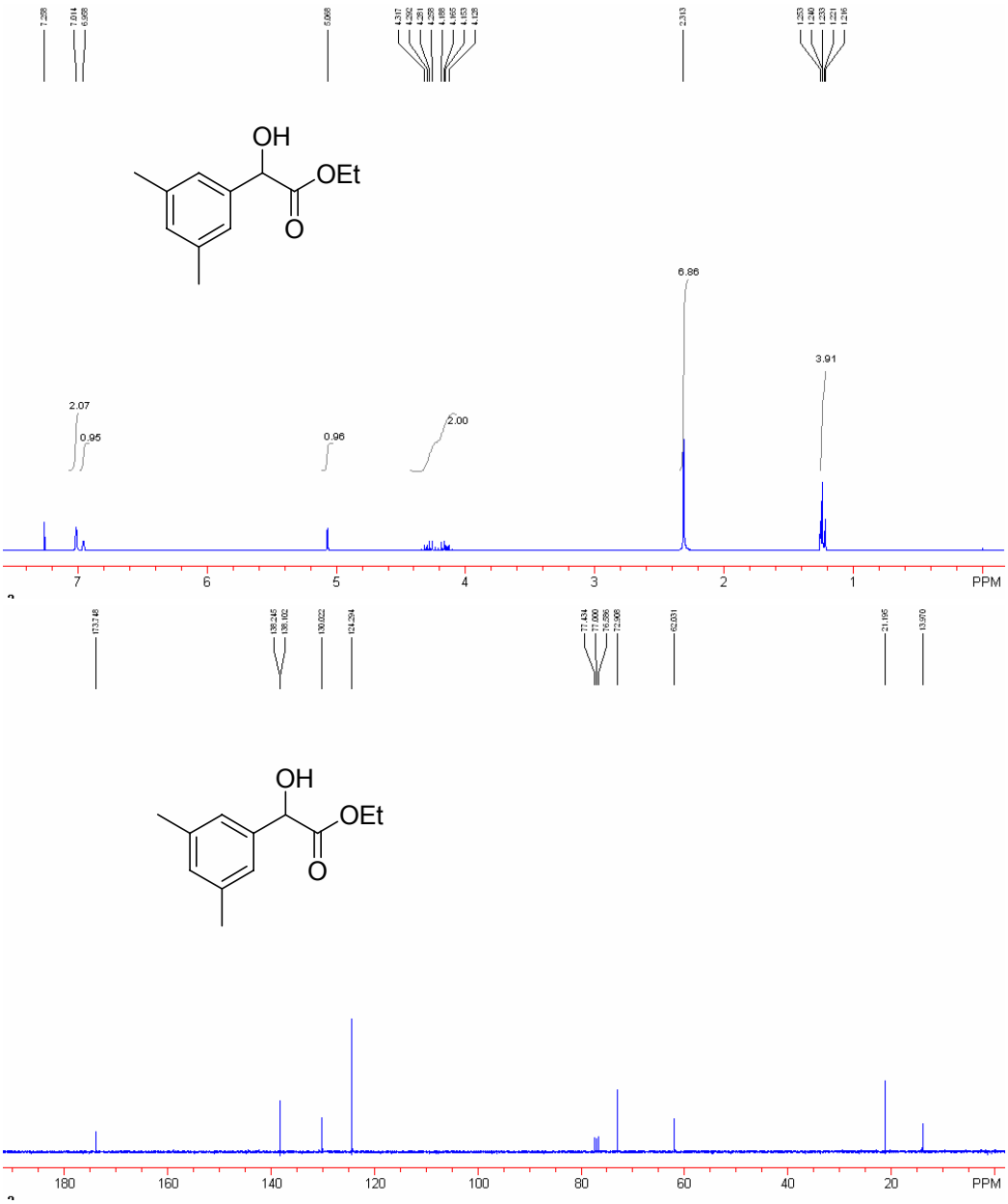
Hydroxy-(4-methoxyphenyl)-acetic acid ethyl ester (2f) (a known compound).[9] A white solid: 53 mg, 85% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.23 (t, J = 6.9 Hz, 3H, CH_3), 3.45 (d, J = 6.0 Hz, 1H, OH), 3.81 (s, 3H, CH_3), 4.13-4.29 (m, 2H, CH_2), 5.10 (d, J = 6.0 Hz, 1H, CH), 6.89 (d, J = 6.9 Hz, 2H, Ar), 7.33 (d, J = 6.9 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9, 55.1, 61.8, 72.4, 113.8, 127.7, 130.6, 159.5, 173.7.



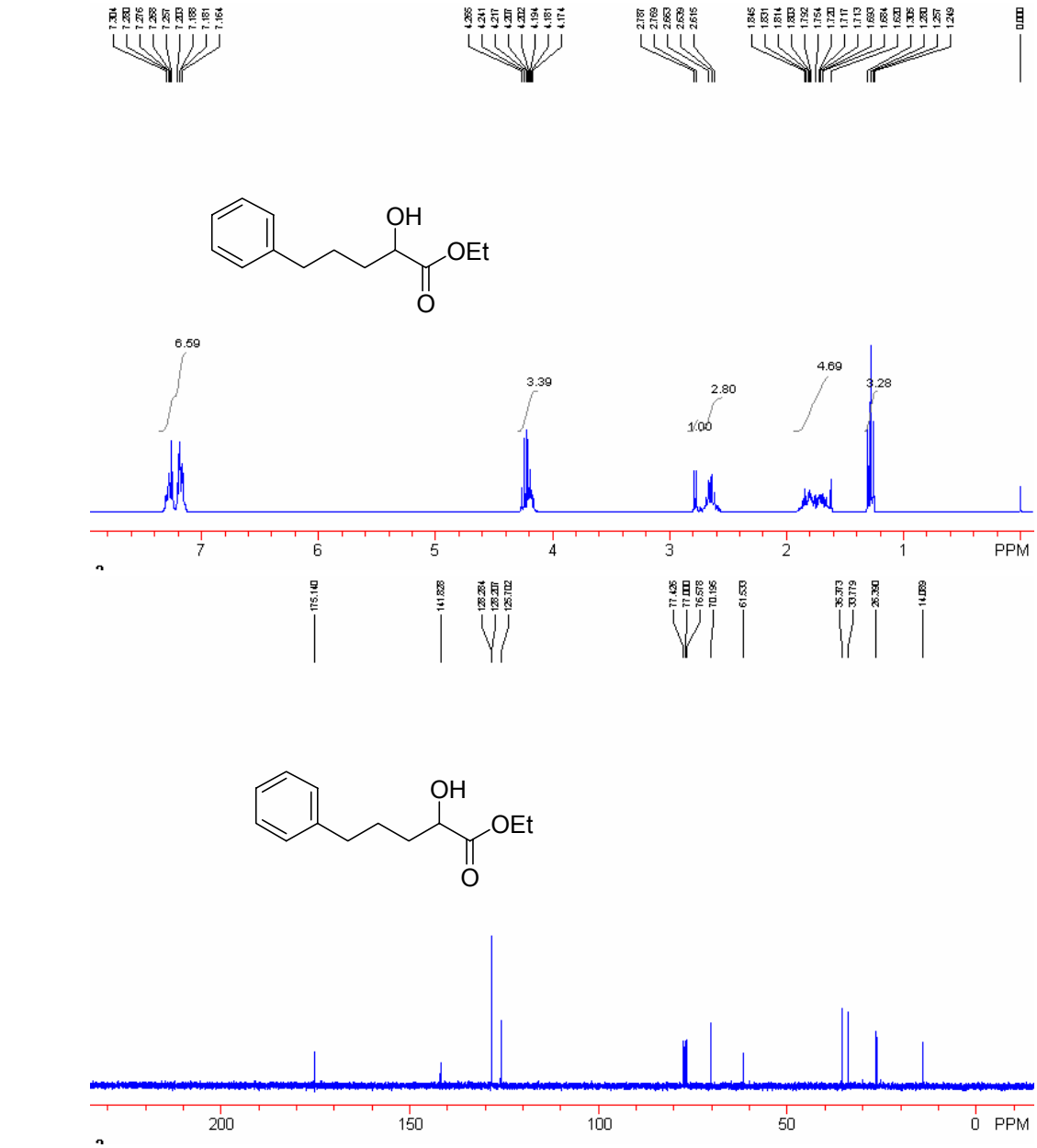
Hydroxy-(4-hydroxyphenyl)-acetic acid ethyl ester (2g) (a known compound).[10] A white solid: 39 mg, 71% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.25 (t, J = 6.9 Hz, 3H, CH_3), 3.54 (s, 2H, OH), 4.15 (q, J = 7.2 Hz, 2H, CH_2), 5.36 (s, 1H, CH), 6.75 (d, J = 8.7 Hz, 2H, Ar), 7.12 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 40.5, 61.1, 115.5, 125.6, 130.4, 155.0, 172.8.



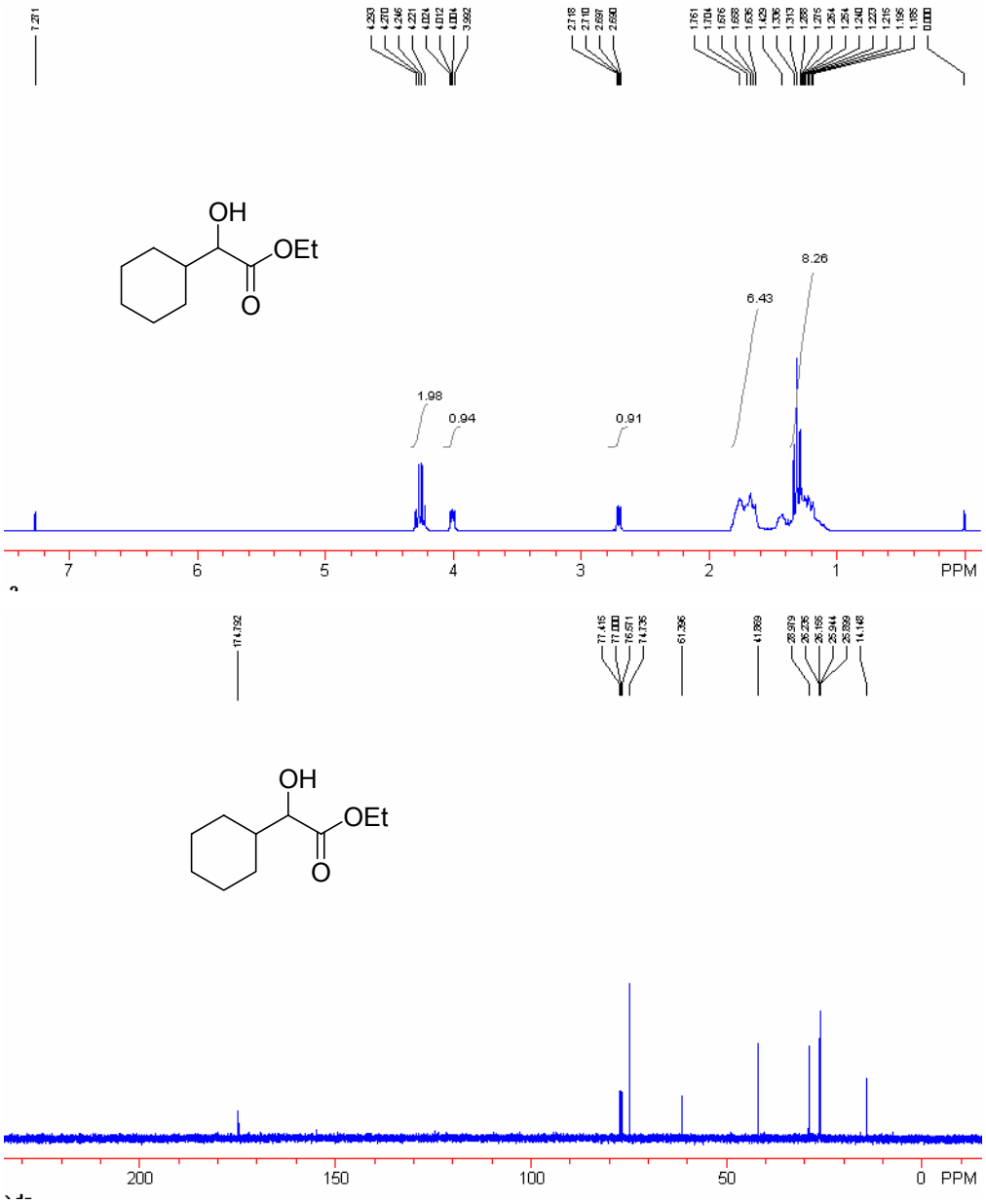
Hydroxy-(3,5-dimethylphenyl)-acetic acid ethyl ester (2h) (a known compound).[11] A colorless oil: 89 mg, 71% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.24 (t, J = 7.5 Hz, 3H, CH_3), 2.32 (s, 3H, CH_3), 4.15-4.32 (m, 2H, CH_2), 5.07 (s, 1H, CH), 6.96 (s, 1H, Ar), 7.02 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ14.0, 21.2, 62.0, 72.9, 124.3, 130.0, 138.1, 138.2, 173.7.



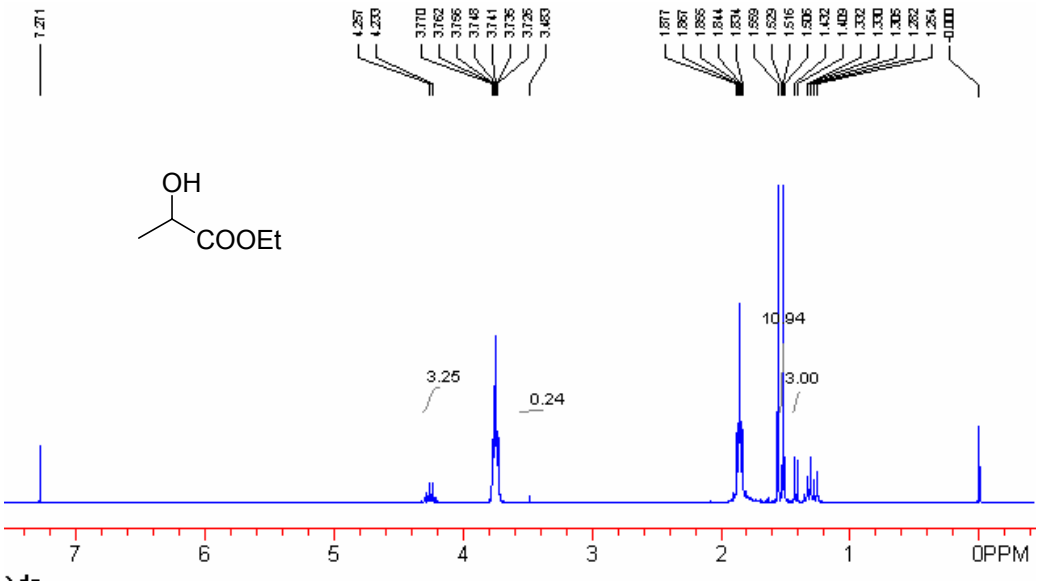
Hydroxy-5-phenyl-pentanoic acid ethyl ester (2i) (a known compound).[12] A colorless oil: 54 mg, 80% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.28 (t, J = 6.9 Hz, 3H, CH_3), 1.62-1.85 (m, 4H, CH_2), 2.62-2.66 (m, 2H, CH_2), 2.78 (d, J = 5.4 Hz, 1H, OH), 4.17-4.27 (m, 3H, CH_2 and CH), 7.16-7.30 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 26.4, 33.8, 35.4, 61.5, 70.2, 125.7, 128.2, 128.3, 141.8, 175.1.



Cyclohexyl-hydroxy-acetic acid ethyl ester (2j) (a known compound).[7] A colorless oil: 54 mg, 96% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.31 (t, 3H, J = 7.5 Hz, CH_3), 1.18-1.76 (m, 11H, Cy), 2.70 (dd, J = 2.1, 6.0 Hz, 1H, OH), 4.00 (dd, J = 3.6, 6.0 Hz, 1H, CH), 4.26 (q, J = 7.5 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.2, 25.9, 25.9, 26.2, 26.2, 29.0, 41.9, 61.4, 74.7, 174.8.



2-Hydroxy-propionic acid ethyl ester (2k) (a known compound).[13] A colorless oil, 97% GC yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.31-1.33 (m, 3H, CH_3), 1.41-1.43 (m, 3H, CH_3), 3.48 (s, 1H, OH), 4.23-4.26 (m, 3H, CH_2 and CH). GC analysis condition Chiraldex HP-1 column, 20 m x 0.25 mm, 60 ^{o}C (10 min), 60-150 ^{o}C, 5 ^{o}C/min, 150 ^{o}C (2.0 min), 10.0 psi N_2, t = 5.830 min.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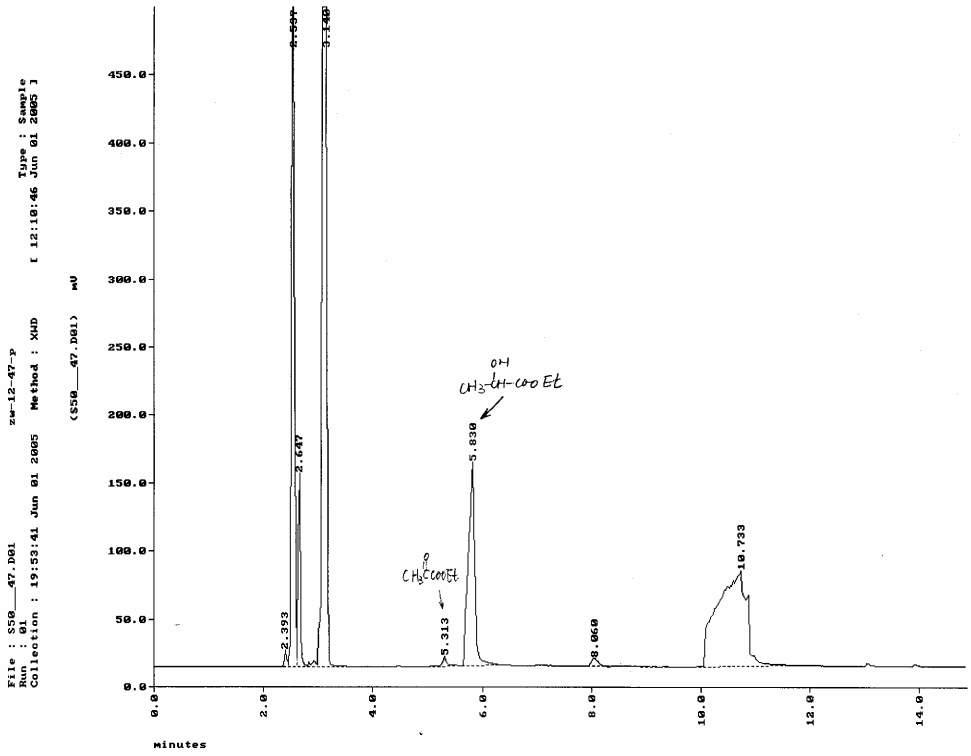
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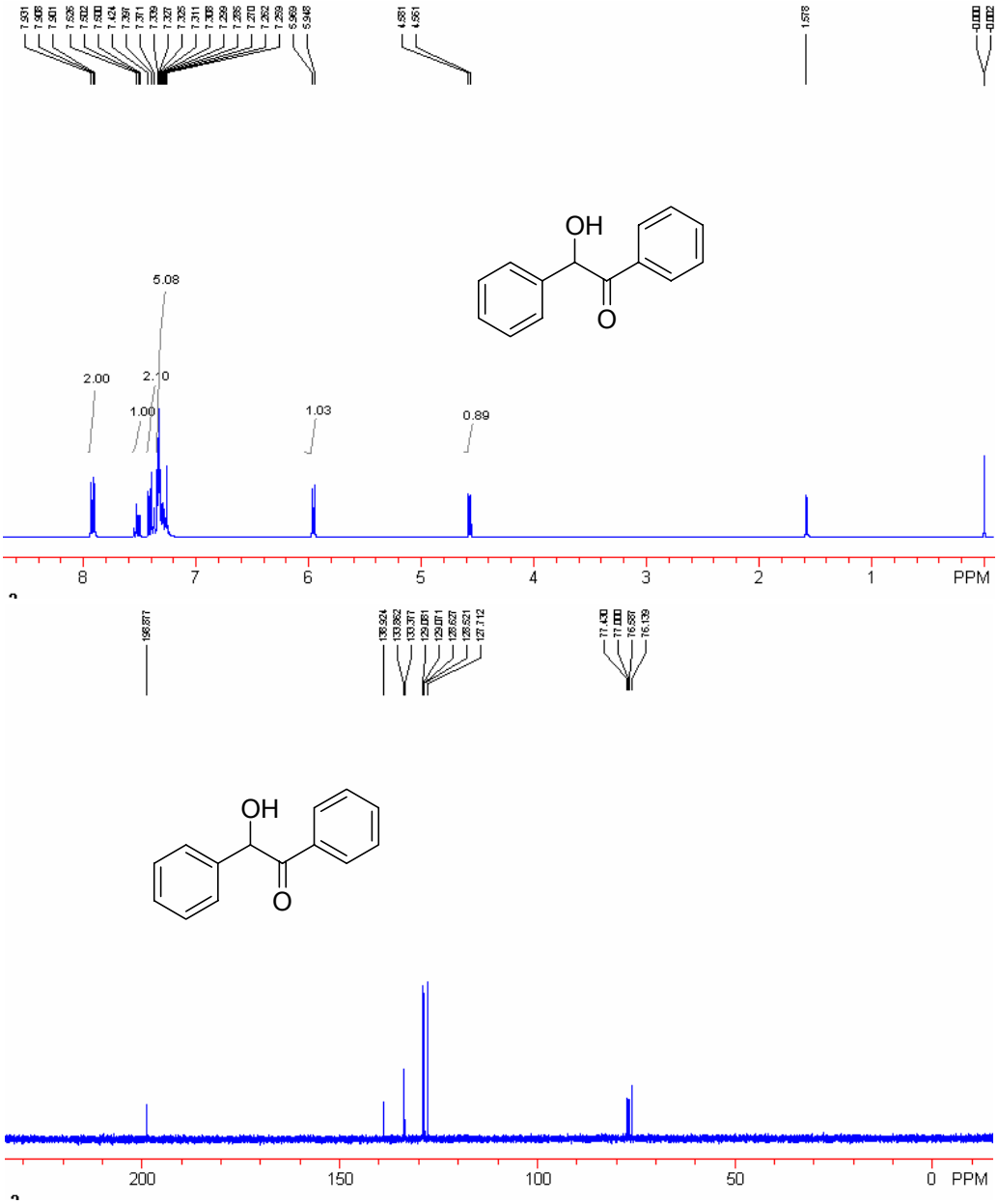
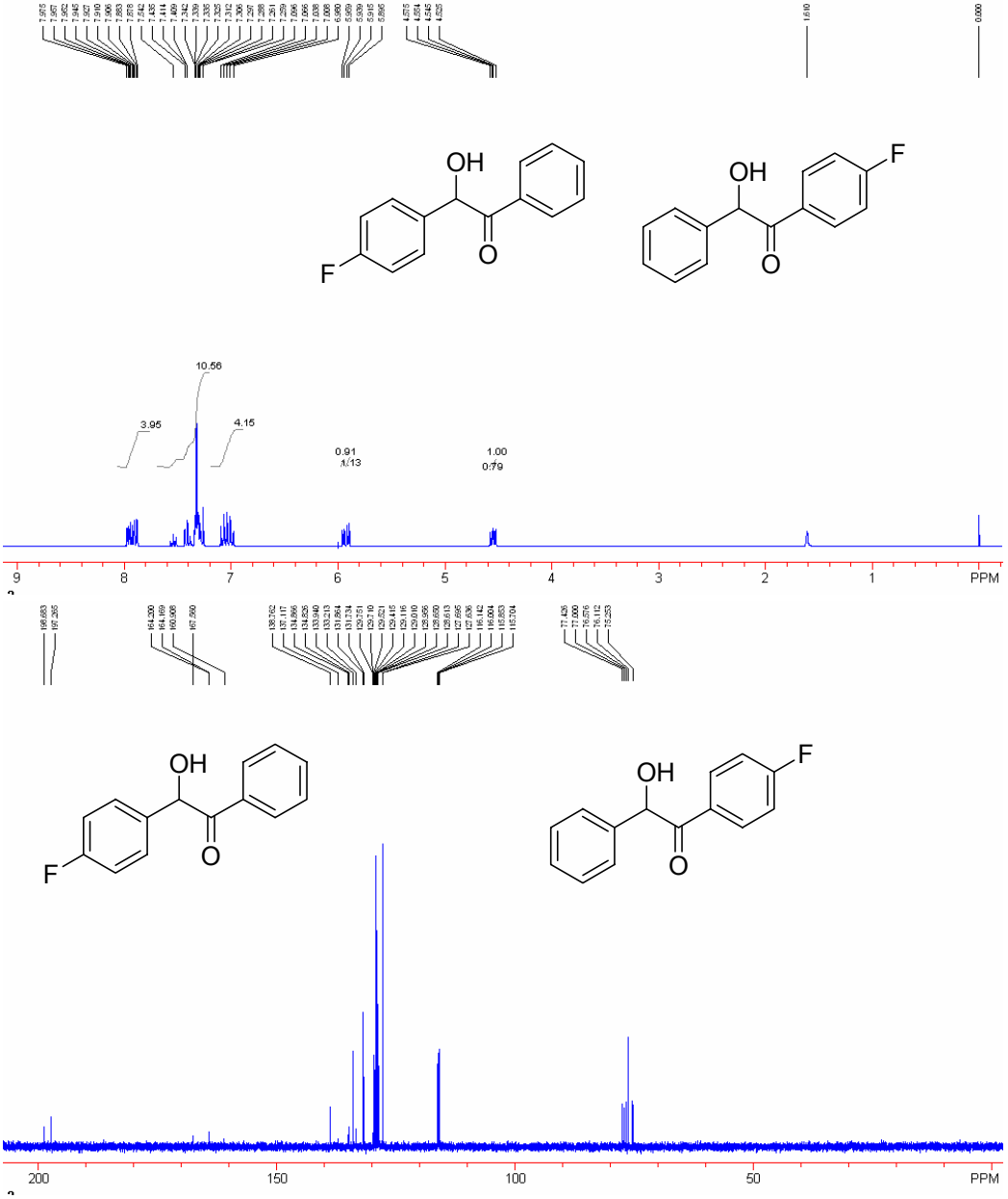
2-Hydroxy-1,2-diphenyl-ethanone (4a) (a known compound).[14] A white solid: 54 mg, 84%

yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 4.57 (d, J = 6.0 Hz, 1H, OH), 5.96 (d, J = 6.3 Hz, 1H, CH), 7.26-7.53 (m, 8H, Ar), 7.91 (d, J = 6.9 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 76.1, 127.7, 128.5, 128.6, 129.1, 129.1, 133.4, 133.9, 138.9, 198.9.



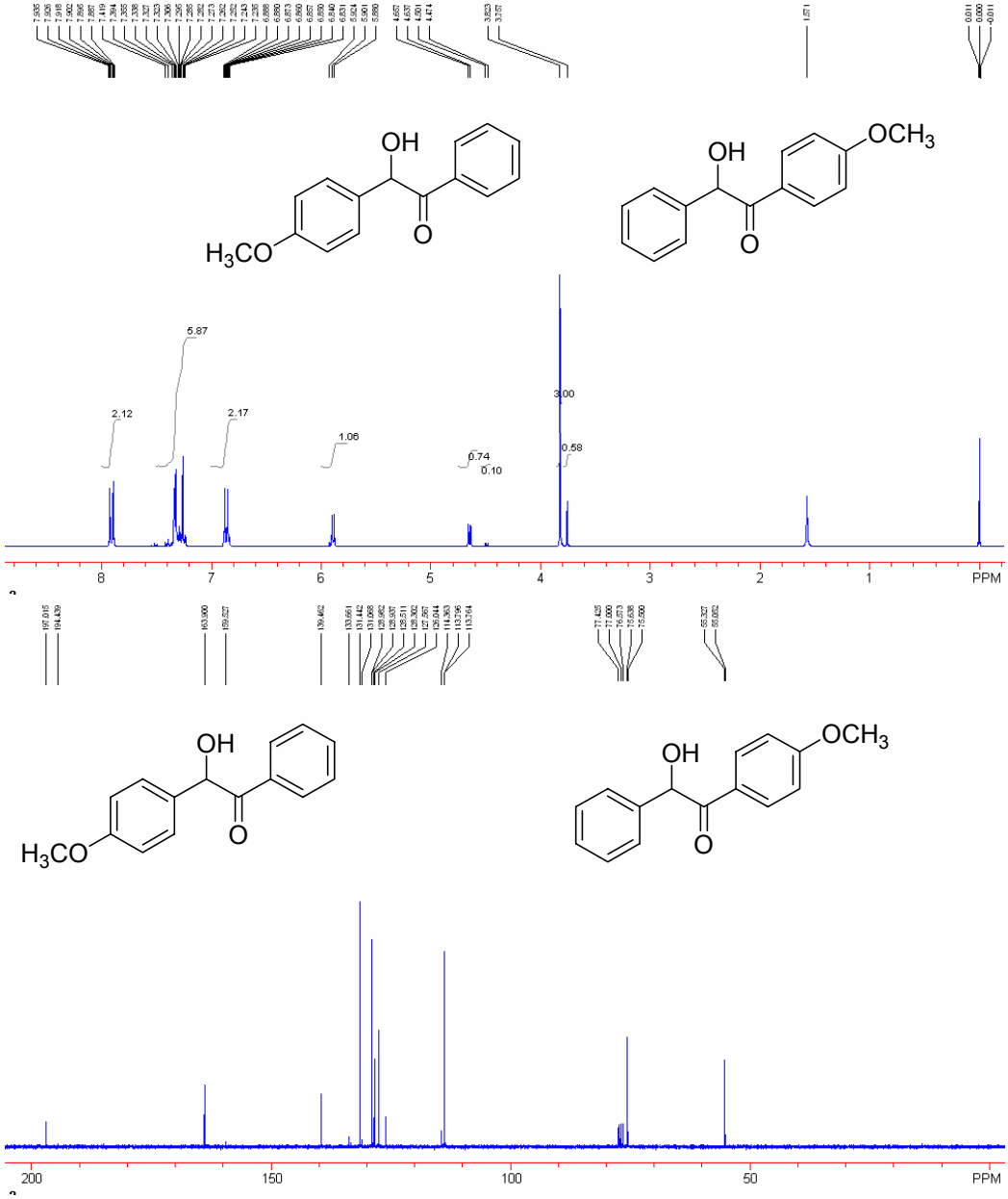
4-Fluorobenzoin/4'-fluorobenzoin (4b/4b') (a known compound).[16] A white solid: 58 mg, 85% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 4.54 (d, J = 6.0 Hz, 1H, OH), 4.56 (d, J = 6.3 Hz, OH), 5.91 (d, J = 6.0 Hz, 1H, CH), 5.95 (d, J = 6.0 Hz, CH), 6.98-7.10 (m, 4H, Ar), 7.26-7.54 (m, 10H, Ar), 7.88-7.98 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 75.3, 76.1, 115.9 (d, J = 22.5 Hz), 116.0 (d, J = 21.7 Hz), 127.6, 128.6 (d, J = 2.8 Hz), 129.1 (d, J = 8.0

Hz), 129.5 (d, J = 8.0 Hz), 129.7 (d, J = 3.1 Hz), 131.7, 131.9, 133.2, 133.9, 134.8, 134.9, 138.8, 162.6 (d, J = 246.9 Hz), 165.9 (d, J = 254.3 Hz), 197.3, 198.7.



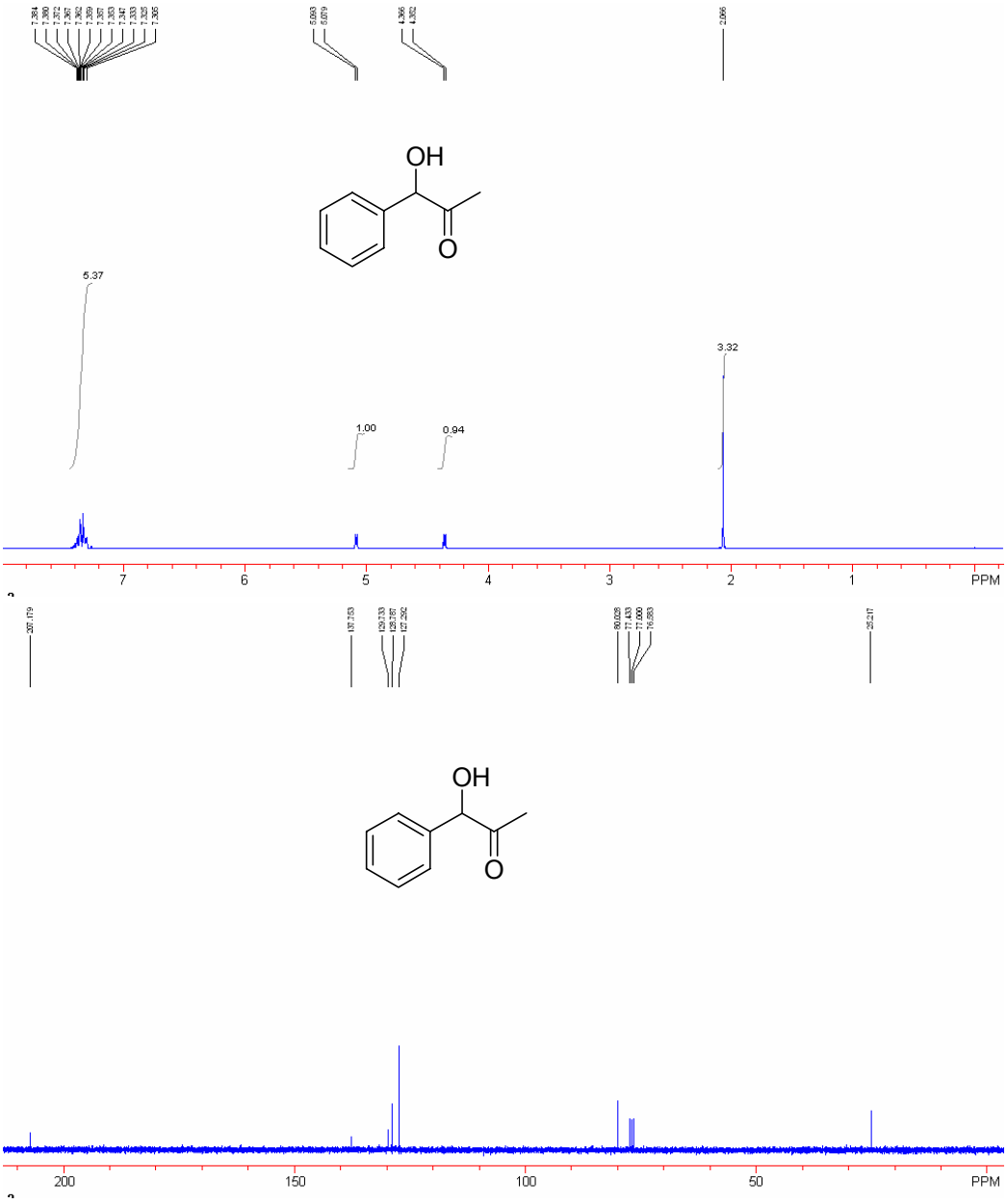
4-Methoxybenzoin/4'-methoxybenzoin (4c/4c') (a known compound).[17] A white solid: 65 mg, 93% yield. **4c**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 3.82, 4.64 (d, J = 6.0 Hz, OH), 5.89 (d, J = 6.3 Hz, 1H, CH), 6.83-6.89 (m, 2H, Ar), 7.24-7.89 (m, 5H, Ar), 7.90-7.94 (m, 2H, Ar). **4c**: ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.3, 75.6, 113.8, 126.0, 127.6, 128.3, 129.0, 131.4, 139.5, 163.9, 197.0. **4c'**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 3.76, 4.49 (d, J = 6.0 Hz, OH), 5.91 (d, J = 6.3 Hz, 1H, CH), 6.83-6.89 (m, 2H, Ar), 7.24-7.89 (m, 5H, Ar), 7.90-7.94 (m, 2H, Ar). **4c'**:

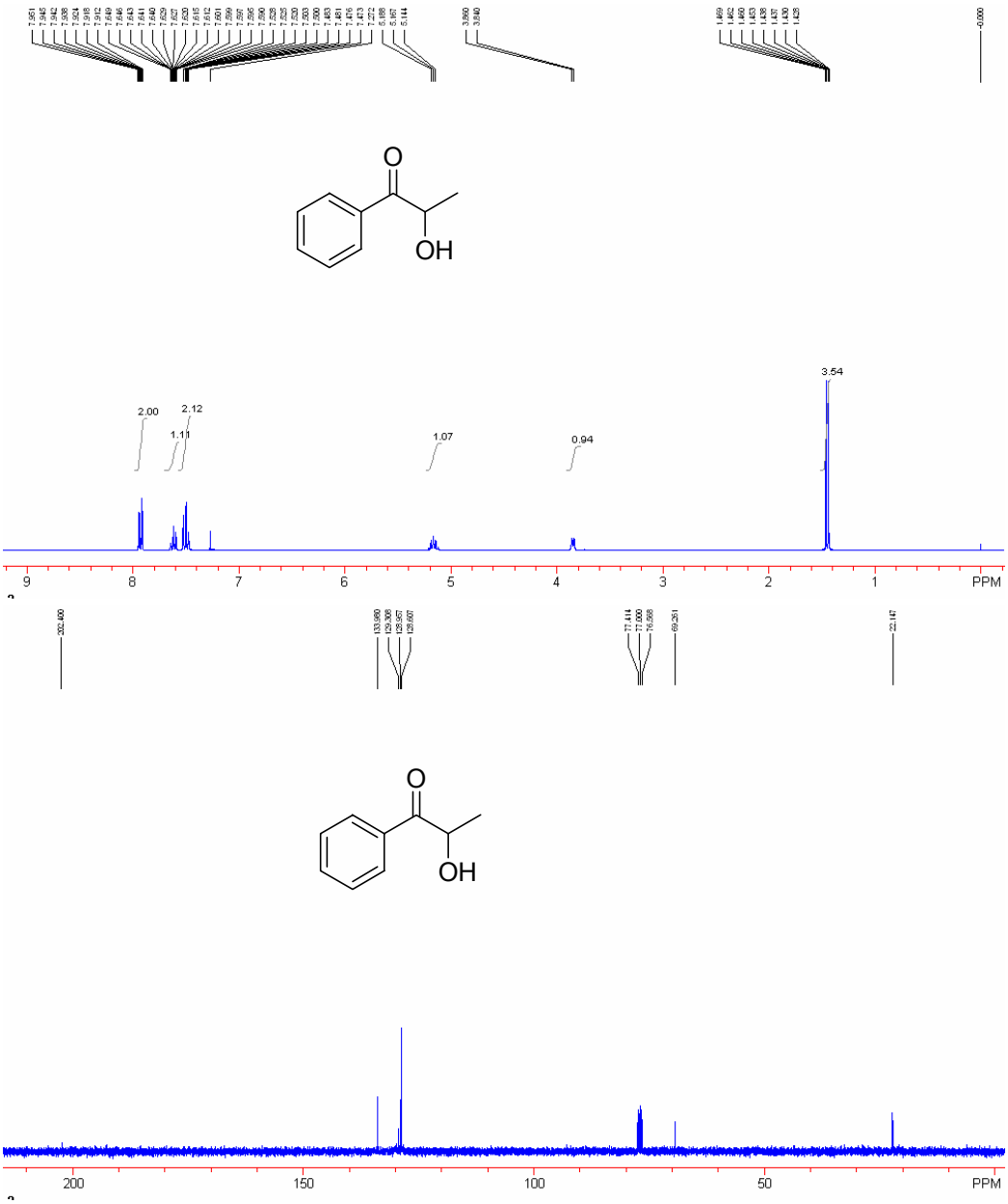
^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.0, 75.0, 114.4, 128.5, 128.9, 130.0, 131.1, 133.4, 133.7, 159.6, 194.4.



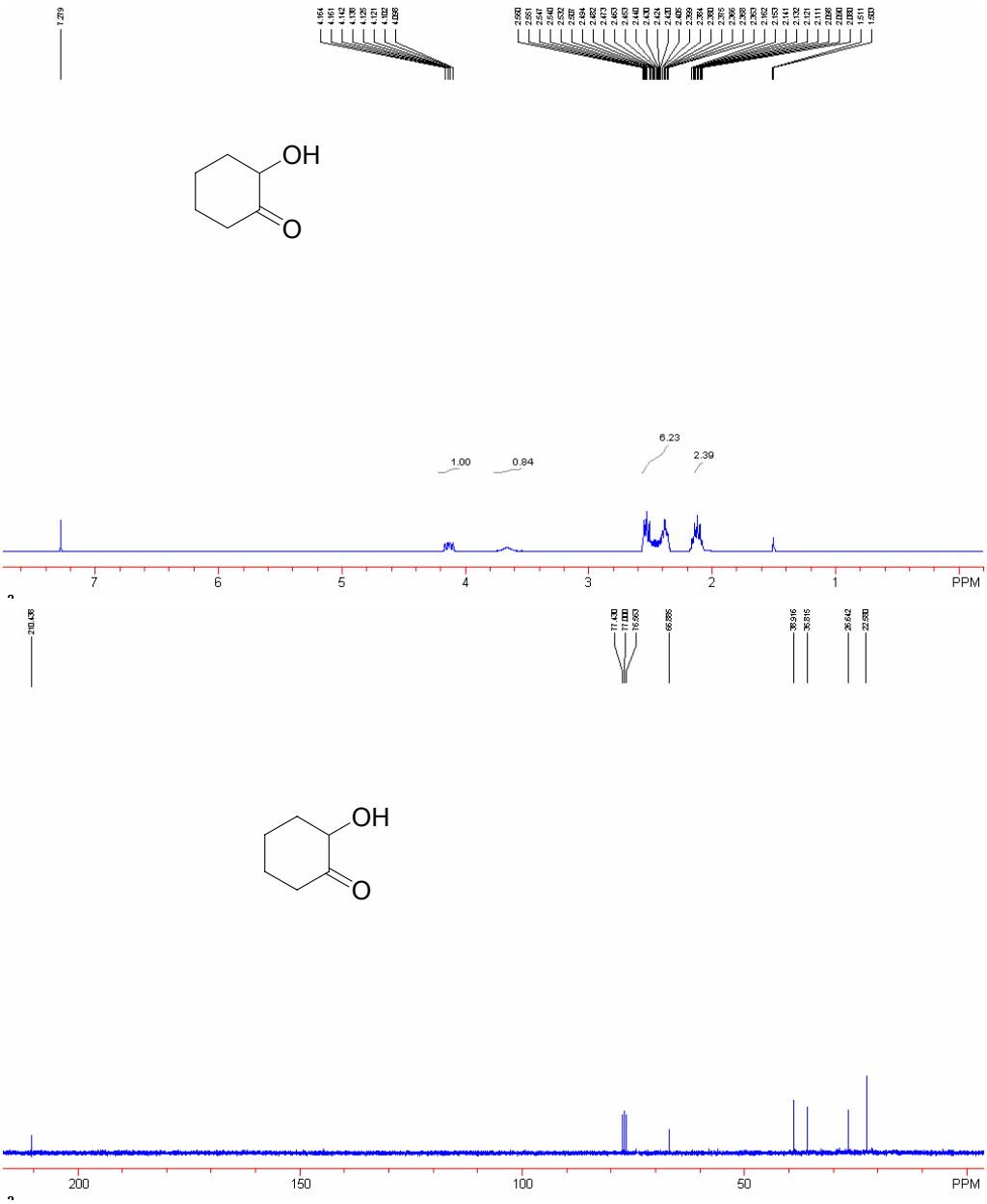
1-Hydroxy-1-phenylpropan-2-one/2-hydroxy-1-phenylpropan-1-one (4d/4d') (a known compound).[17] A white solid: 33 mg, 73% yield. **4d**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.08 (s, 3H, Me), 4.36 (d, J = 4.5 Hz, 1H, OH), 5.10 (d, J = 4.2 Hz, 1H, CH), 7.27-7.41 (m, 5H, Ar). **4d**: ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.2, 80.0, 127.3, 128.8, 129.7, 137.7, 207.2. **4d'**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.45 (d, J = 6.3 Hz, 1H, OH), 3.85 (d, J = 6.0 Hz, 1H, CH), 5.15 (q, J = 6.3 Hz, 1H, CH), 7.47-7.62 (m, 3H, Ar), 7.91-7.95 (m, 2H, Ar). **4d'**: ^{13}C NMR

($CDCl_3$, 75 MHz): δ 22.1, 69.3, 128.6, 129.0, 129.3, 134.0, 202.3.

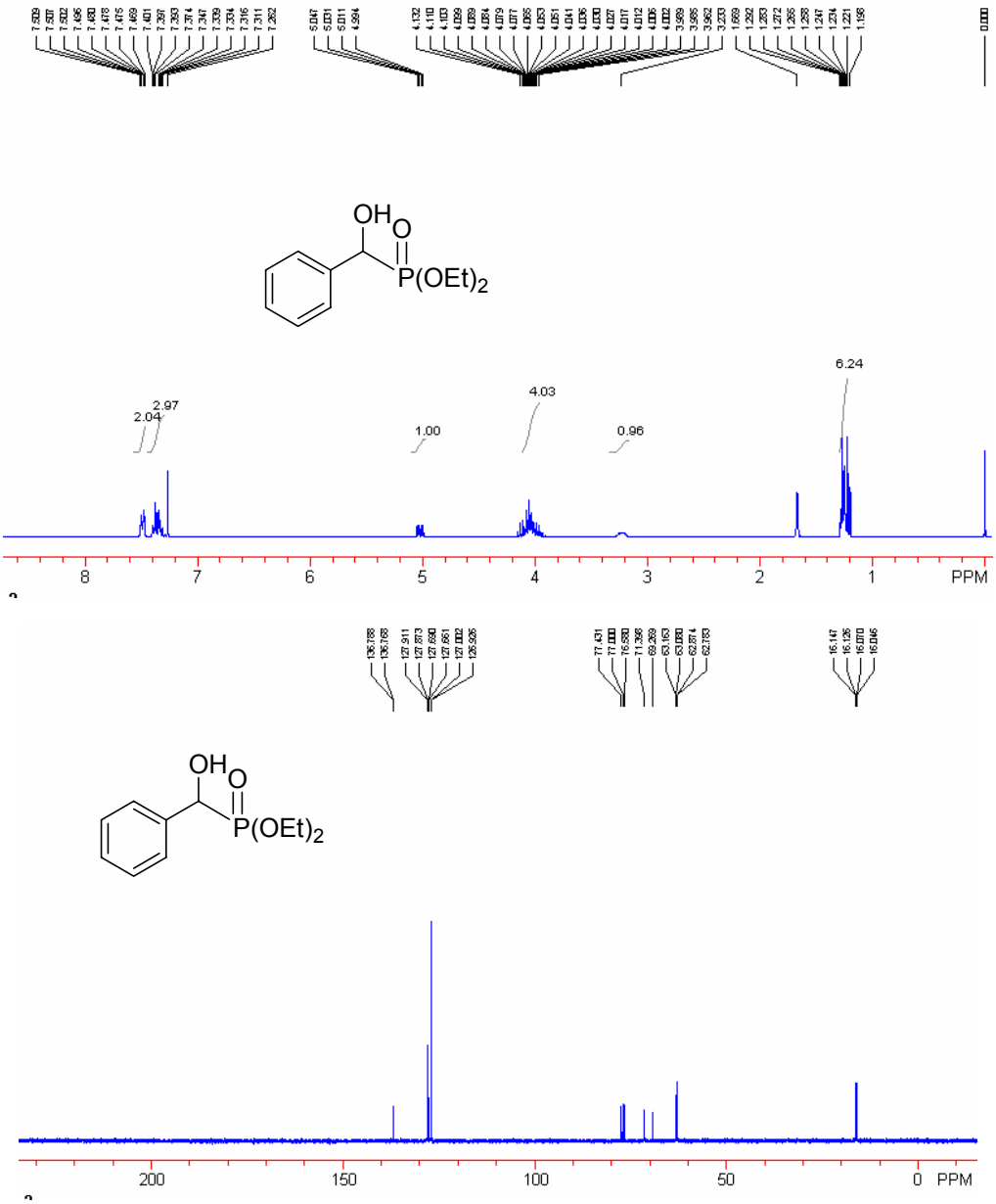




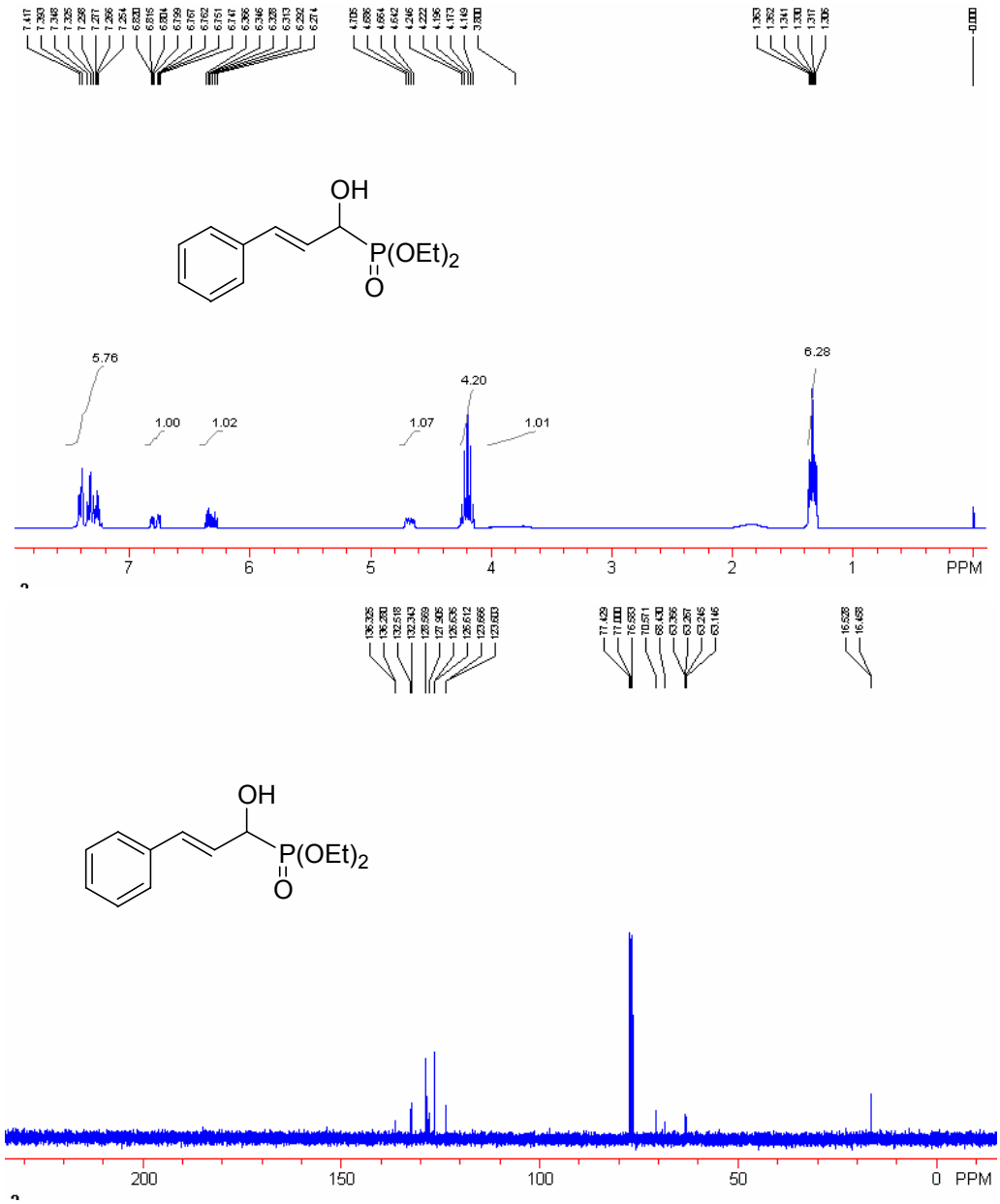
2-Hydroxycyclohexanone (4e) (a known compound).[18] A white solid: 27 mg, 80% yield. **4d**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.08-2.16 (m, 2H), 2.36-2.57 (m, 6H), 3.65 (br, 1H, OH), 4.11 (ddd, J = 0.9, 6.6, 11.7 Hz, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.5, 26.6, 35.8, 38.9, 66.9, 210.4.



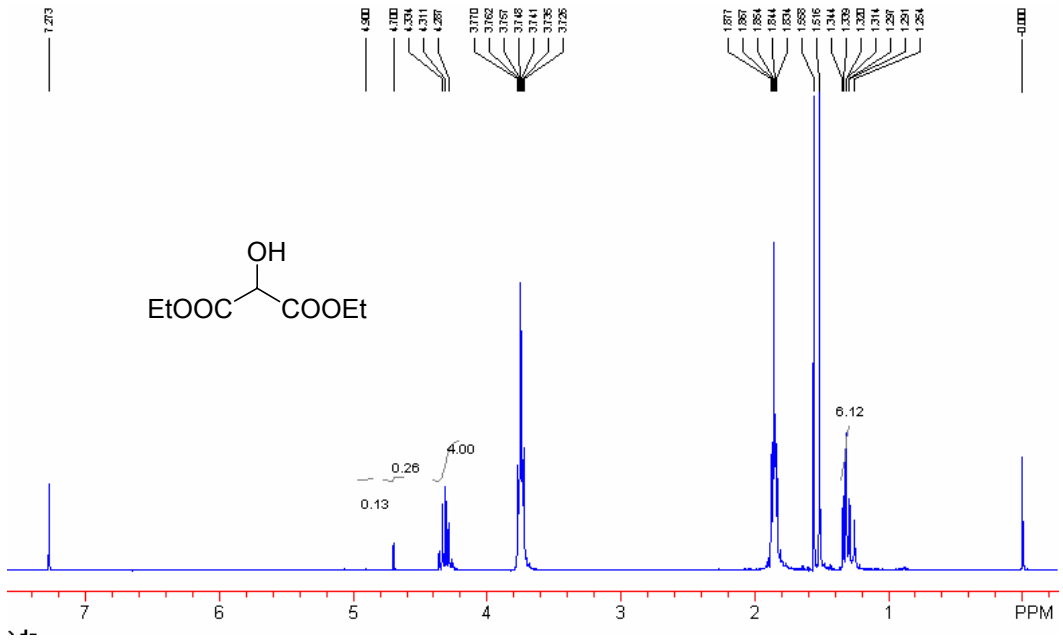
(Hydroxy-phenylmethyl)-phosphonic acid diethyl ester (6) (a known compound).[19] A white solid: 63 mg, 86% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.20-1.29 (m, 6H, $2CH_3$), 3.23 (br, 1H, OH), 3.96-4.13 (m, 4H, $2CH_2$), 5.02 (dd, J = 5.1, 11.1 Hz, 1H, CH), 7.31-7.40 (m, 3H, Ar), 7.47-7.51 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.1 (d, J = 1.8 Hz), 16.1 (d, J = 1.6 Hz), 62.8 (d, J = 6.8 Hz), 63.1 (d, J = 6.2 Hz), 70.3 (d, J = 159.7 Hz), 127.0 (d, J = 5.8 Hz), 127.7 (d, J = 2.2 Hz), 127.9 (d, J = 2.9 Hz), 136.8 (d, J = 1.5 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ 21.99.



(1-Hydroxy-3-phenyl-allyl)-phosphonic acid diethyl ester (8) (a known compound).[20] A white solid: 52 mg, 65% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.34 (dt, 6H, J = 3.3, 7.2 Hz, $2CH_3$), 3.80 (br, 1H, OH), 4.12-4.25 (m, 4H, $2CH_2$), 4.67 (dd, J = 6.6, 13.2 Hz, 1H, CH), 6.27-6.37 (m, 1H, CH), 6.75-6.82 (m, 1H, CH), 7.25-7.42 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.5, 16.5, 62.2 (d, J = 7.4 Hz), 63.3 (d, J = 6.7 Hz), 69.5 (d, J = 160.6 Hz), 123.6 (d, J = 4.7 Hz), 126.6 (d, J = 1.7 Hz), 127.9, 128.6 (d, J = 6.0 Hz), 132.4 (d, J = 13.1 Hz), 136.3 (d, J = 3.4 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4): δ 22.66.



2-Hydroxy-malonic acid diethyl ester (10) (a known compound).[21] A colorless oil: 84% GC yield. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.31 (dt, J = 1.8, 6.9 Hz, 6H, $2CH_3$), 4.29-4.33 (m, 4H, $2CH_2$), 4.70 (s, 1H, CH), 4.90 (br, 1H, OH). GC analysis condition Chiraldex HP-1 column, 20 m x 0.25 mm, 80 ^{o}C (10 min), 80-150 ^{o}C, 5 ^{o}C/min, 150 ^{o}C (2 min), 10.0 psi N_2, t = 16.468 min. GC-MS: 177 (M^++1).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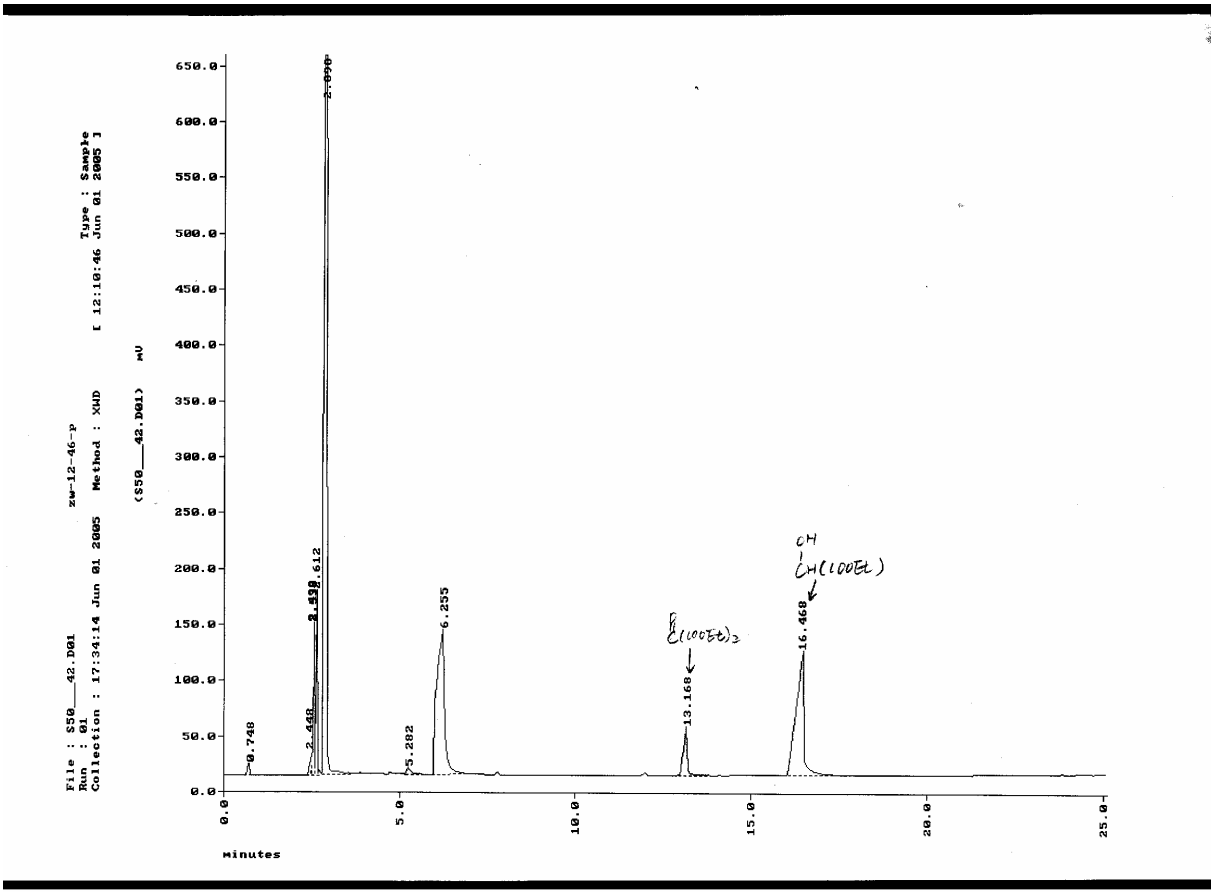
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Reference:

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