Supporting Information:

n-BuLi as a Highly Efficient Precatalyst for Hydrophosphonylation of Aldehydes and Unactivated Ketones

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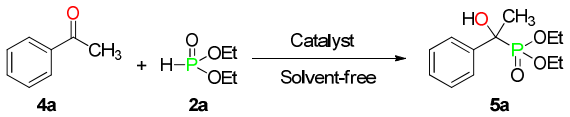
Content

General procedure for hydrophosphonylation reactions: A 5.0 mL Schlenk tube was charged with *n*-BuLi (17 μL, 0.005 mmol) and diethyl phosphite (0.77 mL, 6 mmol) under dry argon. The mixture was stirred for 5 min before aldehyde or ketone (5 mmol) was added. The resulting mixture was allowed to stir at room temperature (for aldehyde) or 10 °C (for ketone) for 5 min. The reaction was quenched by adding ethyl acetate (3 mL). All volatiles were removed under reduced pressure, and products were obtained by washing the crude product from aldehydes with *n*-hexane. The crude product from ketones was purified by column chromatography on a short silica gel column (petroleum ether/ethyl acetate 5:1- petroleum ether/ethyl acetate 10:1).

Table S1. Hydrophosphonylation of Acetophenone Catalyzed by Organic Alkali Metal Compounds[a]



4a **2a** **5a**

entry	cat. (mol %)	time (min)	yield (%)[b]	TOF (h^{-1})
1	2,6-$^{i}Pr_2$PhNHLi (0.1)	20	74	2220
2	2,6-Me_2PhNHLi (0.1)	20	78	2340
3	PhNHLi (0.1)	20	71	2130
4	4-FPhNHLi (0.1)	20	67	2010
5	4-MeOPhNHLi (0.1)	20	66	1980
6	$(Me_3Si)_2$NLi (0.1)	20	56	1680
7	$^{i}Pr_2$NLi (0.1)	20	66	1980
8	2,6-$^{i}Pr_2$PhNHNa (0.1)	20	76	2280
9	2,6-$^{i}Pr_2$PhNHK (0.1)	20	71	2130
10	*n*-BuLi (0.1)	20	75	2250
11	*n*-BuLi (0.05)	20	28	1680

[a] Reaction conditions: acetophenone **4a** (5.0 mmol), diethyl phosphite **2a** (6.0 mmol), catalyst (required amount), room temperature, 20 min. [b] Isolated yields.

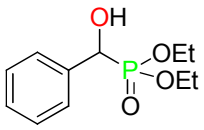
Table S2. Hydrophosphonylation and Retro-hydrophosphonylation Reactions Catalyzed by *n*-BuLi

entry	catalyst loading (mol %)	time (min)	temp (°C)	yield (%)	
				5a[a]	**4a**[b]
1	0.1	**5**	25	75	
2	0.1	**10**	25	77	
3	0.1	**15**	25	74	
4	0.1	**60**	25	78	
5	0.1	**120**	25	78	

[a] Reaction conditions: acetophenone **4a** (5.0 mmol), diethyl phosphite **2a** (6.0 mmol), *n*-BuLi (required amount). Isolated yields. [b] Reaction conditions: α-hydroxy phosphonates **5a** (5.0 mmol), *n*-BuLi (required amount), *n*-hexane (2 mL). Isolated yields.

Characterizations of α-hydroxyphosphonates:

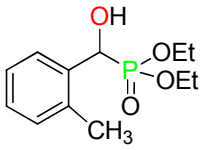
All compounds have been reported except for **5k**, **5o**, **5p**, **5q**, and **5w**. ^{1}H NMR spectra of all known compounds are consistent with reported data, and full characterization of unpublished compounds (including ^{1}H, ^{13}C NMR spectra and HRMS) is provided.



3a

Diethyl hydroxy(phenyl)methylphosphonate (3a).[1]

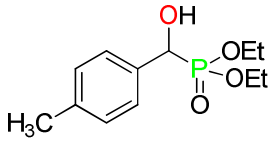
>99% yield (1.209 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.49-7.47 (2H, m), 7.37-7.28 (3H, m), 5.03-5.00 (1H, d, J = 10.8 Hz), 4.08-3.94 (4H, m), 3.63 (1H, s), 1.28-1.24 (3H, t, J = 7.1 Hz), 1.23-1.19 (3H, t, J = 7.1 Hz).



3b

Diethyl hydroxy(2-methylphenyl)methylphosphonate (3b).[2]

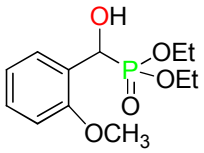
>99% yield (1.278 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.65-7.63 (1H, d, J = 7.6 Hz), 7.24-7.13 (3H, m), 5.27-5.24 (1H, d, J = 10.9 Hz), 4.09-3.87 (4H, m), 3.68 (1H, s), 2.37 (3H, s), 1.28-1.25 (3H, t, J = 7.0 Hz), 1.21-1.17 (3H, t, J = 7.1 Hz).



3c

Diethyl hydroxy(4-methylphenyl)methylphosphonate (3c).[3]

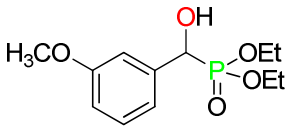
>99% yield (1.278 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.37-7.35 (2H, m), 7.17-7.15 (2H, d, J = 8.0 Hz), 4.98-4.95 (1H, d, J = 10.5 Hz), 4.09-3.92 (4H, m), 3.89 (1H, s), 2.34 (3H, s), 1.28-1.25 (3H, t, J = 7.1 Hz), 1.23-1.19 (3H, t, J = 7.1 Hz).



3d

Diethyl hydroxy(2-methoxyphenyl)methylphosphonate (3d).[2]

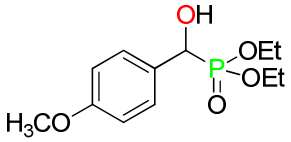
90% yield (1.234 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.54-7.51 (1H, m), 7.29-7.25 (1H, m), 7.00-6.96 (1H, t, J = 7.4 Hz), 6.89-6.86 (1H, d, J = 8.1 Hz), 5.43-5.40 (1H, d, J = 12.0 Hz), 4.15-3.87 (4H, m), 3.84 (3H, s), 3.68 (1H, s), 1.30-1.27 (3H, t, J = 7.1 Hz), 1.18-1.15 (3H, t, J = 7.1 Hz).



3e

Diethyl hydroxy(3-methoxyphenyl)methylphosphonate (3e).[2]

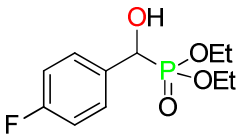
>99% yield (1.358 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.54-7.51 (1H, m), 7.30-7.25 (1H, m), 7.00-6.96 (1H, t, J = 7.5 Hz), 6.88-6.86 (1H, d, J = 8.3 Hz), 5.43-5.40 (1H, d, J = 12.0 Hz), 4.15-3.87 (4H, m), 3.84 (3H, s), 1.31-1.27 (3H, t, J = 7.1 Hz), 1.18-1.15 (3H, t, J = 7.0 Hz).



3f

Diethyl hydroxy(4-methoxyphenyl)methylphosphonate (3f).[2]

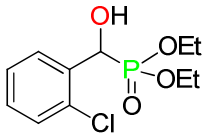
>99% yield (1.358 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.42-7.39 (2H, m), 6.90-6.88 (2H, d, J = 8.6 Hz), 4.95-4.93 (1H, d, J = 9.9 Hz), 4.09-3.91 (4H, m), 3.80 (3H, s), 3.03 (1H, s), 1.29-1.25 (3H, t, J = 7.0 Hz), 1.23-1.20 (3H, t, J = 7.0 Hz).



3g

Diethyl hydroxy(4-fluorophenyl)methylphosphonate (3g).[4]

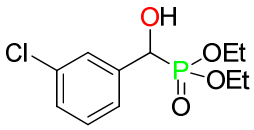
>99% yield (1.298 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.47-7.43 (2H, m), 7.05-7.01 (2H, t, J = 8.6 Hz), 5.00-4.98 (1H, d, J = 10.4 Hz), 4.53 (1H, s), 4.10-3.94 (4H, m), 1.27-1.24 (3H, t, J = 7.1 Hz), 1.23-1.20 (3H, t, J = 7.1 Hz).



3h

Diethyl hydroxy(2-chlorophenyl)methylphosphonate (3h).[5]

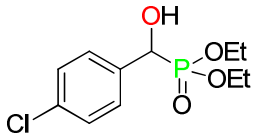
>99% yield (1.379 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.76-7.74 (1H, d, J = 7.8 Hz), 7.36-7.30 (2H, m), 7.24-7.22 (1H, d, J = 7.4 Hz), 5.57-5.54 (1H, d, J = 11.6 Hz), 4.22-3.92 (4H, m), 3.55 (1H, s), 1.32-1.29 (3H, t, J = 7.1 Hz), 1.22-1.18 (3H, t, J = 7.0 Hz).



3i

Diethyl hydroxy(3-chlorophenyl)methylphosphonate (3i).[6]

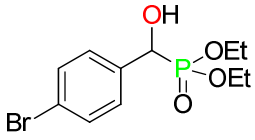
>99% yield (1.379 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.47 (1H, s), 7.33-7.30 (1H, m), 7.24-7.23 (2H, d, J = 5.0 Hz), 4.98-4.95 (1H, d, J = 11.3 Hz), 4.10-3.95 (4H, m), 1.26-1.22 (3H, t, J = 7.1 Hz), 1.22-1.18 (3H, t, J = 7.0 Hz).



3j

Diethyl hydroxy(4-chlorophenyl)methylphosphonate (3j).[6]

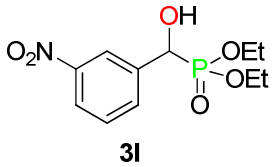
>99% yield (1.379 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.41-7.39 (2H, d, J = 6.4 Hz), 7.32-7.28 (2H, m), 4.99-4.96 (1H, d, J = 11.1 Hz), 4.78 (1H, s), 4.05-3.96 (4H, m), 1.27-1.24 (3H, t, J = 6.9 Hz), 1.22-1.19 (3H, t, J = 6.8 Hz).



3k

Diethyl hydroxy(4-bromophenyl)methylphosphonate (3k).[7]

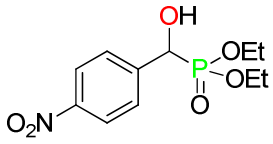
>99% yield (1.599 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.49-7.47 (2H, d, J = 8.4 Hz), 7.37-7.34 (2H, m), 4.99-4.96 (1H, d, J = 10.9 Hz), 4.47 (1H, s), 4.10-3.99 (4H, m), 1.28-1.25 (3H, t, J = 7.0 Hz), 1.25-1.21 (3H, t, J = 7.1 Hz).



3l

Diethyl hydroxy(3-nitrophenyl)methylphosphonate (3l).[8]

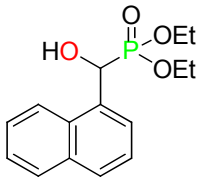
>99% yield (1.432 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.41-8.40 (1H, d, J = 1.9 Hz), 8.16-8.14 (1H, d, J = 7.6 Hz), 7.81-7.80 (1H, d, J = 7.4 Hz), 7.54-7.50 (1H, t, J = 8.0 Hz), 5.18-5.15 (1H, d, J = 11.4 Hz), 4.18-4.06 (4H, m), 1.31-1.27 (3H, t, J = 7.1 Hz), 1.27-1.23 (3H, t, J = 7.0 Hz).



3m

Diethyl hydroxy(4-nitrophenyl)methylphosphonate (3m).[5]

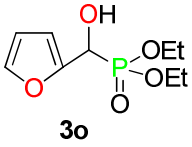
>99% yield (1.432 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.22-8.20 (2H, d, J = 8.7 Hz), 7.67-7.65 (2H, m), 5.18-5.15 (1H, d, J = 12.3 Hz), 4.48 (1H, s), 4.16-4.02 (4H, m), 1.30-1.27 (3H, t, J = 7.1 Hz), 1.26-1.23 (3H, t, J = 7.0 Hz).



3n

Diethyl hydroxy(1-naphthyl)methylphosphonate (3n).[9]

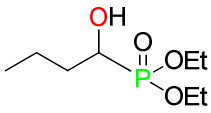
>99% yield (1.457 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.09-8.07 (1H, d, J = 8.3 Hz), 7.90-7.81 (3H, m), 7.54-7.46 (3H, m), 5.88-5.85 (1H, d, J = 11.5 Hz), 4.10-3.73 (4H, m), 1.22-1.18 (3H, t, J = 7.1 Hz), 1.06-1.03 (3H, t, J = 7.1 Hz).



3o

Diethyl hydroxy(furan-2-yl)methylphosphonate (3o).[10]

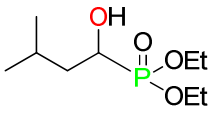
90% yield (1.054 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.38 (1H, s), 6.47 (1H, s), 6.33 (1H, s), 4.99-4.96 (1H, d, J = 13.5 Hz), 4.38 (1H, s), 4.16-3.98 (4H, m), 1.29-1.25 (3H, t, J = 7.1 Hz), 1.22-1.19 (3H, t, J = 7.1 Hz).



3p

Diethyl 1-hydroxybutylphosphonate (3p).[11]

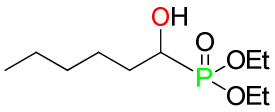
97% yield (1.020 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.14-4.04 (4H, m), 3.82-3.77 (1H, m), 1.67-1.31 (4H, m), 1.28-1.24 (6H, m), 0.89-0.85 (3H, t, J = 7.2 Hz).



3q

Diethyl 1-hydroxy-3-methyl-butylphosphonate (3q).[12]

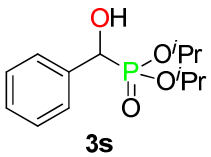
94% yield (1.054 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.78 (1H, s), 4.15-4.06 (4H, m), 3.91-3.86 (1H, m), 1.87 (1H, s), 1.70-1.60 (1H, m), 1.41-1.33 (1H, m), 1.28-1.25 (6H, m), 0.90-0.89 (3H, d, J = 6.7 Hz), 0.85-0.84 (3H, d, J = 6.5 Hz).



3r

Diethyl 1-hydroxyhexanylphosphonate (3r).[13]

91% yield (1.084 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.13-4.05 (4H, m), 3.88 (1H, s), 3.79-3.75 (1H, m), 1.68-1.55 (3H, m), 1.35-1.18 (11H, m), 0.83-0.80 (3H, d, J = 6.6 Hz).

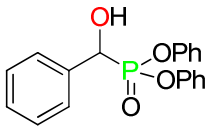


3s

Diisopropyl hydroxyphenylmethylphosphonate (3s).[2]

99% yield (1.348 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.50-7.48 (2H, m), 7.35-7.26 (3H, m), 4.97-4.93 (1H, dd, J_1 = 11.0 Hz, J_2 = 5.4 Hz), 4.67-4.57 (2H, m),

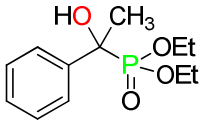
4.46-4.43 (1H, dd, J_1 = 8.3 Hz, J_2 = 5.6 Hz), 1.27-1.25 (9H, m), 1.14-1.13 (3H, d, J = 6.2 Hz).



3t

Diphenyl hydroxy(phenyl)methylphosphonate (3t).[2]

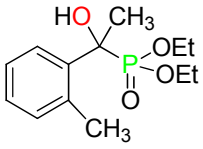
50% yield (0.851 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.58-7.56 (3H, m), 7.38-7.36 (3H, m), 7.29-7.22 (4H, m), 7.17-7.11 (2H, m), 7.06-6.99 (3H, m), 5.33-5.30 (1H, d, J = 9.12 Hz).



5a

Diethyl 1-hydroxy-1-phenyl-ethylphosphonate (5a).[14]

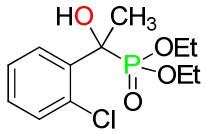
95% yield (1.227 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.62-7.58 (2H, m), 7.37-7.33 (2H, m), 7.30-7.27 (1H, m), 4.15-3.84 (4H, m), 3.45 (1H, s), 1.84-1.80 (3H, d, J = 15.4 Hz), 1.27-1.24 (3H, t, J = 7.1 Hz), 1.21-1.17 (3H, t, J = 7.1 Hz).



5b

Diethyl 1-hydroxy-1-(2-methyl)phenyl-ethylphosphonate (5b).[15]

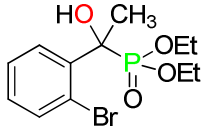
35% yield (0.477 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.58-7.55 (1H, m), 7.19-7.12 (3H, m), 4.13-3.85 (4H, m), 3.15 (1H, s), 2.64 (3H, s), 1.92-1.88 (3H, d, J = 15.4 Hz), 1.28-1.24 (3H, t, J = 7.1 Hz), 1.23-1.19 (3H, t, J = 7.1 Hz).



5c

Diethyl 1-hydroxy-1-(2-chloro)phenyl-ethylphosphonate (5c).[15]

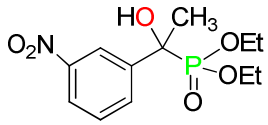
79% yield (1.156 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.74-7.71 (1H, m), 7.37-7.35 (1H, d, J = 7.6 Hz), 7.29-7.19 (2H, m), 4.19-3.95 (4H, m), 3.14 (1H, s), 2.00-1.97 (3H, d, J = 15.2 Hz), 1.31-1.27 (3H, t, J = 7.1 Hz), 1.24-1.20 (3H, t, J = 7.1 Hz).



5d

Diethyl 1-hydroxy-1-(2-bromo)phenyl-ethylphosphonate (5d).[15]

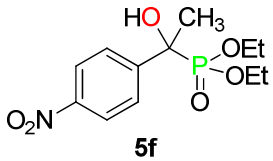
59% yield (0.995 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.74-7.71 (1H, m), 7.60-7.58 (1H, d, J = 8.0 Hz), 7.32-7.29 (1H, t, J = 7.7 Hz), 7.14-7.10 (1H, m), 4.17-3.97 (4H, m), 2.00-1.97 (3H, d, J = 15.2 Hz), 1.31-1.28 (3H, t, J = 7.1 Hz), 1.26-1.23 (3H, t, J = 7.1 Hz).



5e

Diethyl 1-hydroxy-1-(3-nitro)phenyl-ethylphosphonate (5e).[15]

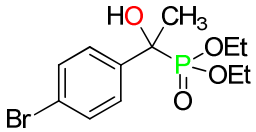
99% yield (1.501 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.51-8.49 (1H, m), 8.16-8.13 (1H, m), 7.96-7.93 (1H, m), 7.55-7.51 (1H, t, J = 8.0 Hz), 4.25 (1H, s), 4.19-4.04 (4H, m), 1.88-1.84 (3H, d, J = 15.3 Hz), 1.29-1.25 (6H, m).



5f

Diethyl 1-hydroxy-1-(4-nitro)phenyl-ethylphosphonate (5f).[16]

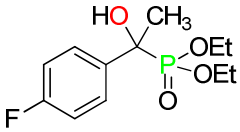
99% yield (1.501 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.21-8.19 (2H, d, J = 9.0 Hz), 7.81-7.77 (2H, m), 4.29 (1H, s), 4.18-4.01 (4H, m), 1.87-1.83 (3H, d, J = 15.4 Hz), 1.28-1.24 (6H, m).



5g

Diethyl 1-hydroxy-1-(4-bromo)phenyl-ethylphosphonate (5g).[15]

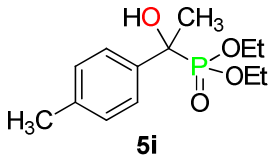
99% yield (1.669 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.48 (4H, s), 4.14-3.89 (4H, m), 3.48 (1H, s), 1.81-1.77 (3H, d, J = 15.4 Hz), 1.28-1.25 (3H, t, J = 7.0 Hz), 1.24-1.20 (3H, t, J = 7.1 Hz).



5h

Diethyl 1-hydroxy-1-(4-fluro)phenyl-ethylphosphonate (5h).[15]

99% yield (1.367 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.60-7.55 (2H, m), 7.05-7.01 (2H, t, J = 8.7 Hz) 4.14-3.88 (4H, m), 3.66 (1H, s), 1.82-1.78 (3H, d, J = 15.3 Hz), 1.27-1.24 (3H, t, J = 7.1 Hz), 1.23-1.19 (3H, t, J = 7.1 Hz).

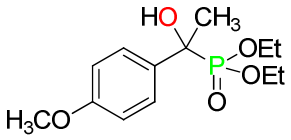


5i

Diethyl 1-hydroxy-1-(4-methyl)phenyl-ethylphosphonate (5i).[15]

84% yield (1.144 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.49-7.46 (2H, m),

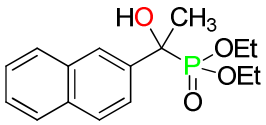
7.17-7.15 (2H, d, J = 8.2 Hz), 4.13-3.85 (4H, m), 2.34 (3H, s), 1.82-1.78 (3H, d, J = 15.4 Hz), 1.28-1.24 (3H, t, J = 7.1 Hz), 1.22-1.19 (3H, t, J = 7.1 Hz).



5j

Diethyl 1-hydroxy-1-(4-methoxy)phenyl-ethylphosphonate (5j).[15]

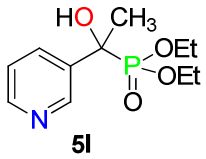
72% yield (1.038 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.52-7.50 (2H, m), 6.89-6.87 (2H, d, J = 8.8 Hz), 4.14-3.85 (4H, m), 3.80 (3H, s), 3.28 (1H, s), 1.81-1.77 (3H, d, J = 15.4 Hz), 1.28-1.24 (3H, t, J = 7.1 Hz), 1.22-1.19 (3H, t, J = 7.1 Hz).



5k

Diethyl 1-hydroxy-1-naphthyl-ethylphosphonate (5k).

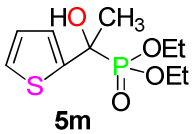
99% yield (1.526 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.10 (1H, s), 7.87-7.82 (3H, m), 7.74 (1H, d, J = 8.7 Hz), 7.48-7.46 (2H, m), 4.16-3.86 (4H, m), 3.72 (1H, s), 1.92 (3H, d, J = 15.4 Hz), 1.26 (3H, t, J = 7.1 Hz), 1.19 (3H, t, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 138.4, 132.7 (d, J = 3 Hz), 132.3 (d, J = 2 Hz), 128.1 (d, J = 1 Hz), 127.2, 125.7, 124.5 (d, J = 6 Hz), 123.9 (d, J = 3 Hz) (Ar-C), 73.4 (d, J = 158 Hz, CP), 63.2 (d, J = 7 Hz), 63.0 (d, J = 7 Hz) (OCH_2), 25.8 (d, J = 3 Hz), 16.14, 16.08 (d, J = 5 Hz) (CH_3). HRMS (ESI) Calcd. for $C_{16}H_{21}O_4P$ $[M+H]^+$: 308.1180, found 308.1177.



5l

Diethyl 1-hydroxy-1-(pyridin-3-yl)-ethylphosphonate (5l).[17]

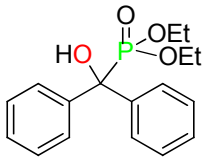
96% yield (1.244 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.79 (1H, s), 8.48 (1H, s), 7.94-7.91 (1H, m), 7.26 (1H, s), 4.15-3.98 (4H, m), 2.42 (1H, s), 1.84-1.81 (3H, d, J = 15.5 Hz), 1.25-1.21 (6H, m).



5m

Diethyl 1-hydroxy-1-(thiophen-2-yl)-ethylphosphonate (5m).[17]

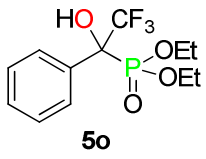
69% yield (0.912 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.26-7.24 (1H, m), 7.14-7.12 (1H, m), 6.99-6.97 (1H, m), 4.17-4.01 (4H, m), 3.96 (1H, s), 1.87-1.84 (3H, d, J = 14.9 Hz), 1.29-1.25 (6H, m).



5n

Diethyl hydroxy-diphenyl-methylphosphonate (5n).[17]

97% yield (1.554 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.69-7.67 (4H, d, J = 7.4 Hz), 7.34-7.24 (6H, m), 3.99-3.85 (4H, m), 1.17-1.14 (6H, t, J = 6.9 Hz).

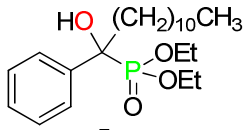


5o

Diethyl 2,2,2-trifluoro-1-hydroxy-1-phenyl-ethylphosphonate (5o).

90% yield (1.405 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.78-7.77 (2H, m),

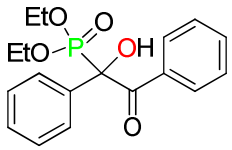
7.41-7.40 (3H, m), 4.18-3.97 (4H, m), 1.24 (3H, t, J = 7.1 Hz), 1.19 (3H, t, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 132.2, 129.1, 128.3, 126.8, 125.4 (d, J = 11 Hz), 112.5 (d, J = 10 Hz) (Ar-C), 75.7 (d, J = 29 Hz, CP), 64.9 (d, J = 7 Hz), 64.5 (d, J = 7 Hz) (OCH_2), 16.3 (d, J = 6 Hz), 16.2 (d, J = 6 Hz) (CH_3). HRMS (ESI) Calcd. for $C_{12}H_{16}F_3O_4PNa$ $[M+Na]^+$: 335.0630, found 335.0624.



5p

Diethyl 1-hydroxy-1-phenyl- dodecenylphosphonate (5p).

40% yield (0.797 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.58-7.56 (2H, m), 7.37-7.33 (2H, m), 7.28-7.25 (1H, m), 4.14-4.07 (2H, m), 3.99-3.89 (1H, m), 3.84-3.75 (1H, m), 3.29-3.24 (1H, m) , 2.30-2.20 (1H, m), 2.15-2.06 (1H, m), 1.42-1.33 (2H, m), 1.28-1.14 (22H, m), 0.89-0.85 (3H, t, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 138.9, 128.1 (d, J = 4 Hz), 127.2 (d, J = 3 Hz), 126.2 (d, J = 4 Hz) (Ar-C), 76.5 (d, J = 160 Hz, CP), 63.4 (d, J = 7 Hz), 63.2 (d, J = 7 Hz) (OCH_2), 37.4 (d, J = 4 Hz), 32.0, 29.9, 29.7, 29.67, 29.6, 29.4, 22.8, 22.0, 21.9 (CH_2), 16.5 (d, J = 5 Hz), 16.4 (d, J = 5 Hz) (OCH_2CH_3), 14.2 (CH_3). HRMS (ESI) Calcd. for $C_{22}H_{39}O_4PNa$ $[M+Na]^+$: 421.2478, found 421.2487.

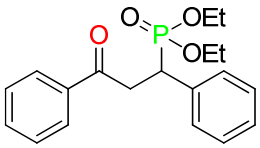


5q

Diethyl-3-hydroxy-2-oxoindolin-3-ylphosphonate (5q).

55% yield (0.958 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.94-7.92 (2H, m), 7.51-7.49 (3H, m), 7.41-7.32 (5H, m), 6.64-6.62 (1H, d, J = 8.0 Hz), 4.23-4.14 (2H, m), 3.96-3.86 (2H, m), 1.34-1.30 (3H, t, J = 7.1 Hz), 1.16-1.12 (3H, t, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 193.6 (d, J = 4 Hz, CO), 134.9 (d, J = 6 Hz), 134.3, 133.5, 129.3, 129.1, 129.0, 128.6, 128.1 (Ar-C), 80.1 (d, J = 5 Hz, CP), 64.3 (d, J = 6

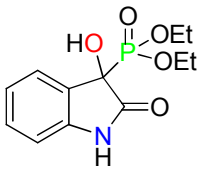
Hz), 63.9 (d, J = 6 Hz) (OCH_2), 16.0 (d, J = 7 Hz), 16.8 (d, J = 7 Hz) (CH_3). HRMS (ESI) Calcd. for $C_{18}H_{21}O_5PNa$ $[M+Na]^+$: 371.1018, found 371.1017.



5r

Diethyl 3-oxo-1,3-diphenyl-propylphosphonate (5r).[18]

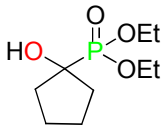
86% yield (1.489 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.95-7.93 (2H, m), 7.56-7.52 (1H, m), 7.45-7.41 (4H, m), 7.31-7.27 (2H, m), 7.23-7.20 (1H, m), 4.12-3.86 (4H, m), 3.80-3.63 (3H, m), 1.30-1.26 (3H, t, J = 7.1 Hz), 1.10-1.06 (3H, t, J = 7.0 Hz).



5s

Diethyl 3-hydroxy-2-oxoindolin-3-ylphosphonate (5s).[19]

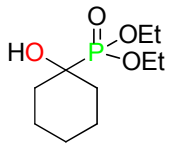
93% yield (1.326 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.15 (1H, s), 7.54-7.52 (1H, d, J = 7.4 Hz), 7.33-7.26 (1H, m), 7.08-7.04 (1H, m), 6.86-6.75 (1H, m), 5.56-5.55 (1H, d, J = 3.7 Hz), 4.31-4.11 (4H, m), 1.40-1.30 (6H, m).



5t

Diethyl 1-hydroxy-cyclopentanylphosphonate (5t).[20]

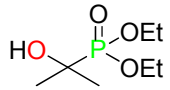
96% yield (1.067 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.06-3.97 (4H, m), 3.79 (1H, s),1.87-1.50 (8H, m), 1.18-1.15 (6H, t, J = 7.1 Hz).



5u

Diethyl 1-hydroxy-cyclohexanylphosphonate (5u).[21]

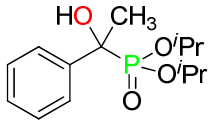
95% yield (1.122 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.20-4.13 (4H, m), 1.86-1.54 (10H, m), 1.35-1.31 (6H, t, J = 7.0 Hz).



5v

Diethyl 1-hydroxy-1-methyl-ethylphosphonate (5v).[21]

92% yield (0.902 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.15-4.08 (4H, m), 1.39-1.35 (6H, d, J = 15.9 Hz), 1.29-1.25 (6H, t, J = 7.1 Hz).

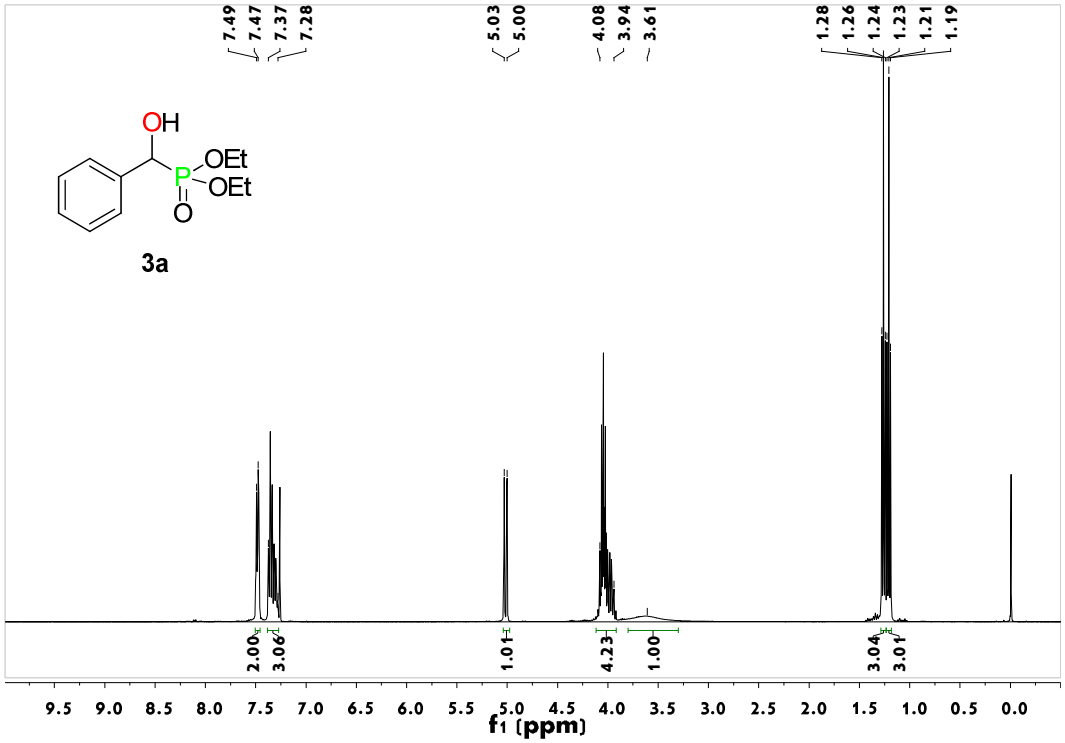


5w

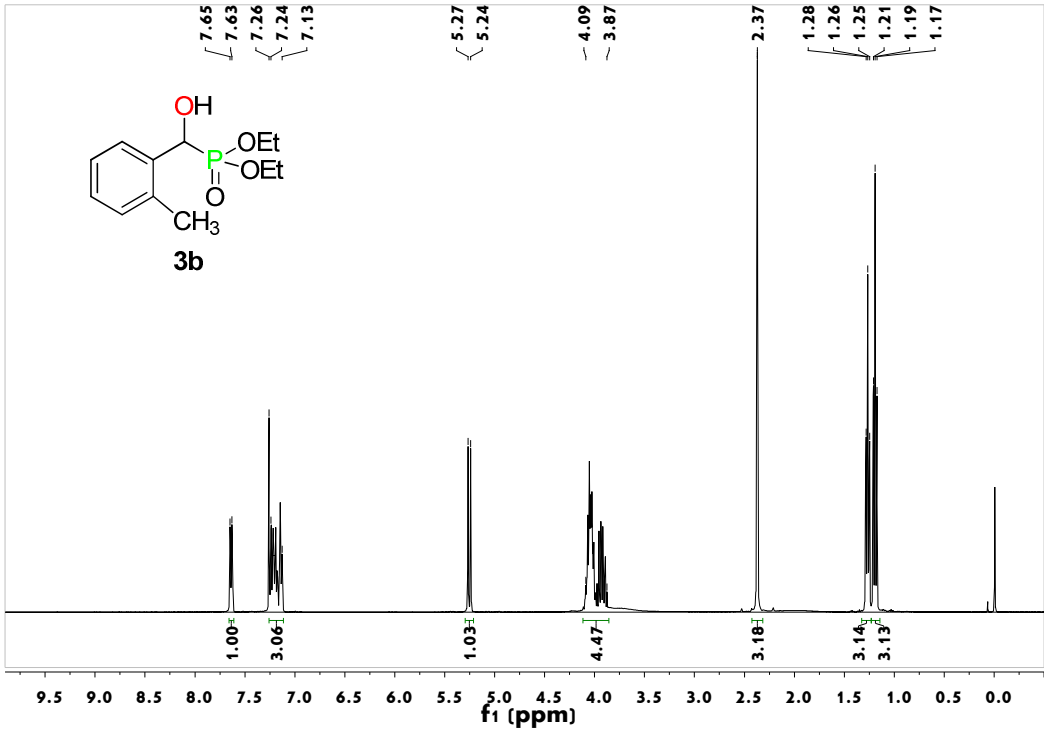
Diisopropyl 1-hydroxy-1-phenyl-ethylphosphonate (5w).

85% yield (1.217 g); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.64-7.62 (2H, m), 7.38-7.34 (2H, m), 7.30-7.26 (1H, m), 4.76-4.65 (1H, m), 4.56-4.48 (1H, m), 3.43-3.35 (1H, m), 1.83-1.79 (3H, d, J = 15.4 Hz), 1.32-1.30 (3H, d, J = 6.2 Hz), 1.27-1.24 (6H, m), 1.12-1.10 (3H, d, J = 6.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 141.2, 128.0, 127.3, 126.0 (d, J = 1 Hz) (Ar-C), 73.5 (d, J = 1 Hz, CP), 72.0 (d, J = 7 Hz), 71.8 (d, J = 7 Hz) (OCH), 26.4 (d, J = 4 Hz, CH_3), 24.3 (d, J = 3 Hz), 24.2 (d, J = 3 Hz), 23.8 (d, J = 6 Hz), 23.6 (d, J = 5 Hz) ($OCH(CH_3)_2$). HRMS (ESI) Calcd. for $C_{14}H_{23}O_4PNa$ $[M+Na]^+$: 309.1226, found 309.1227.

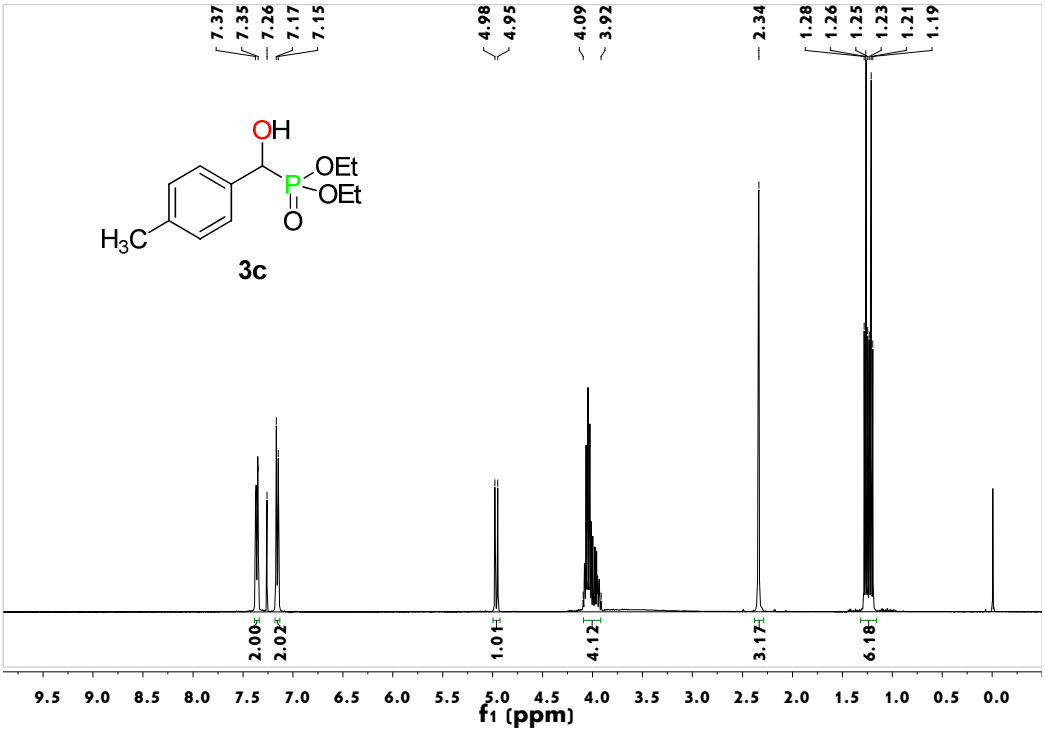
^{1}H NMR spectrum of 3a



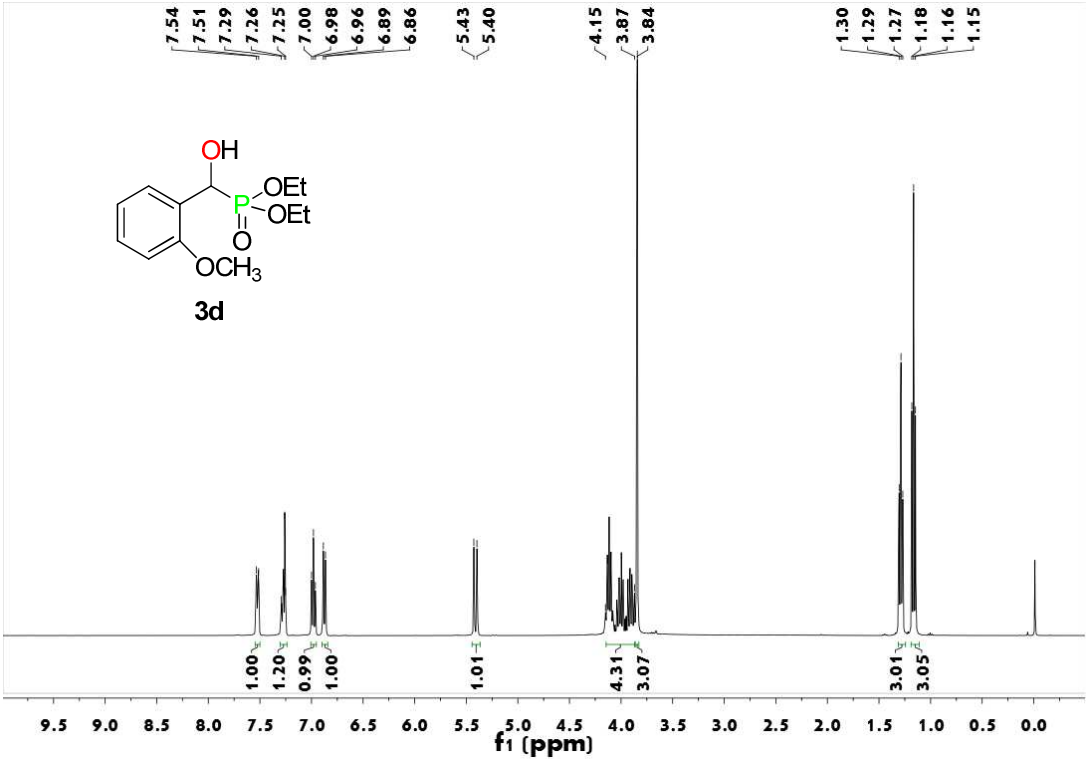
^{1}H NMR spectrum of 3b



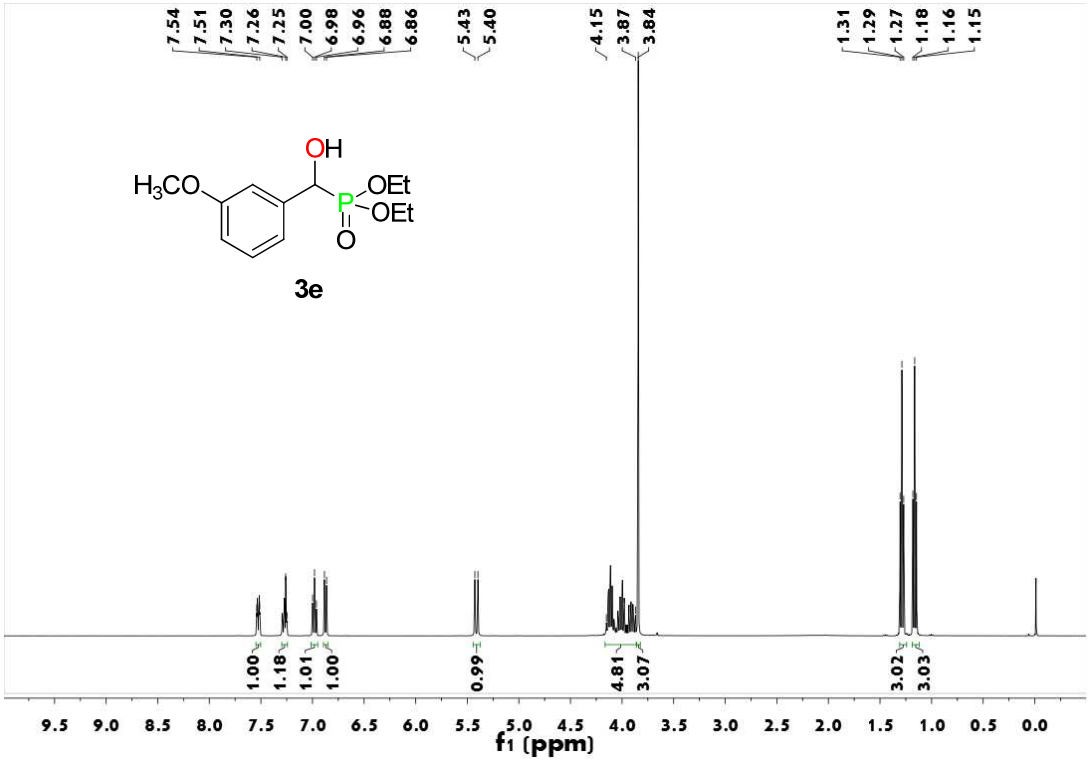
^{1}H NMR spectrum of 3c



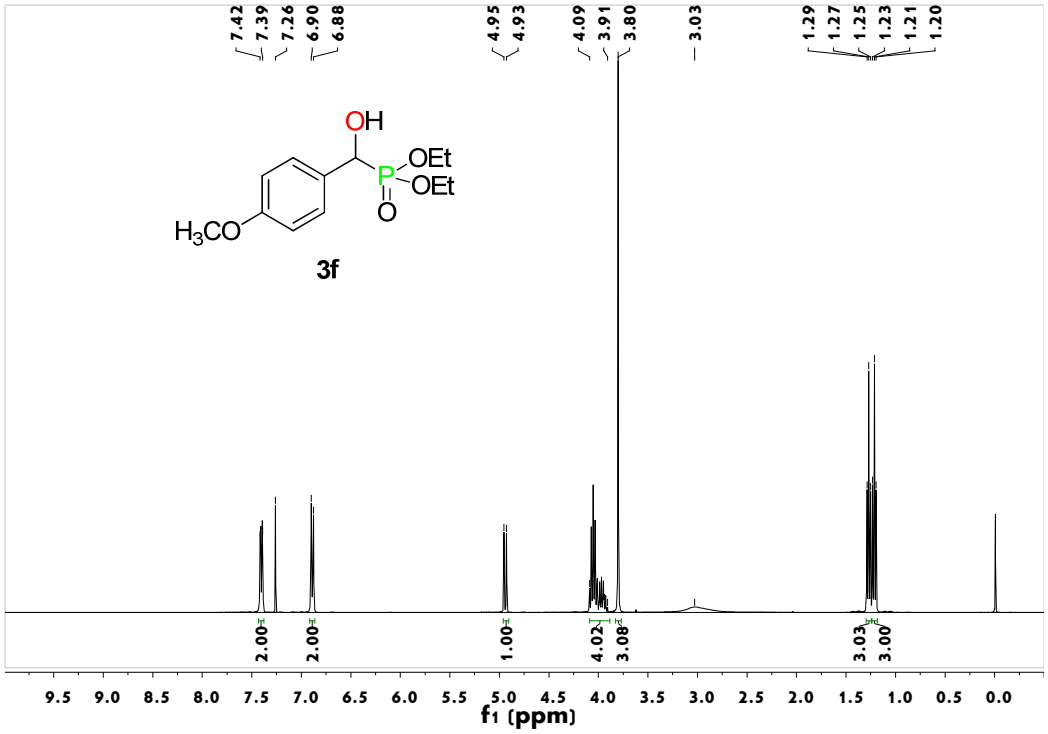
^{1}H NMR spectrum of 3d



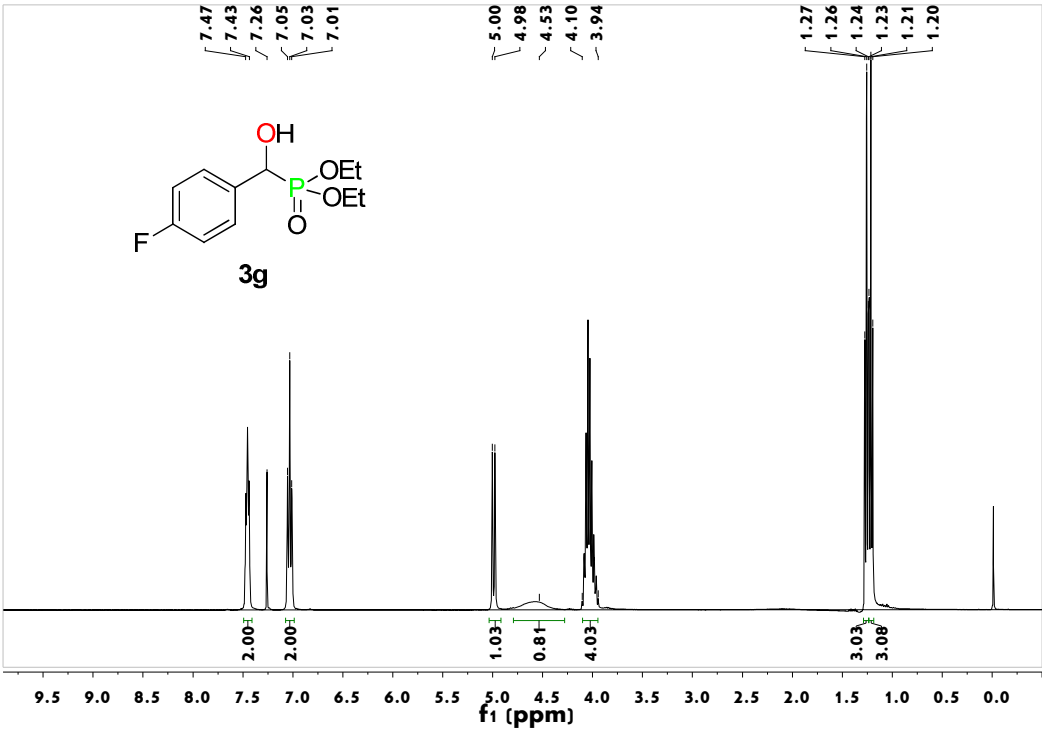
^{1}H NMR spectrum of 3e



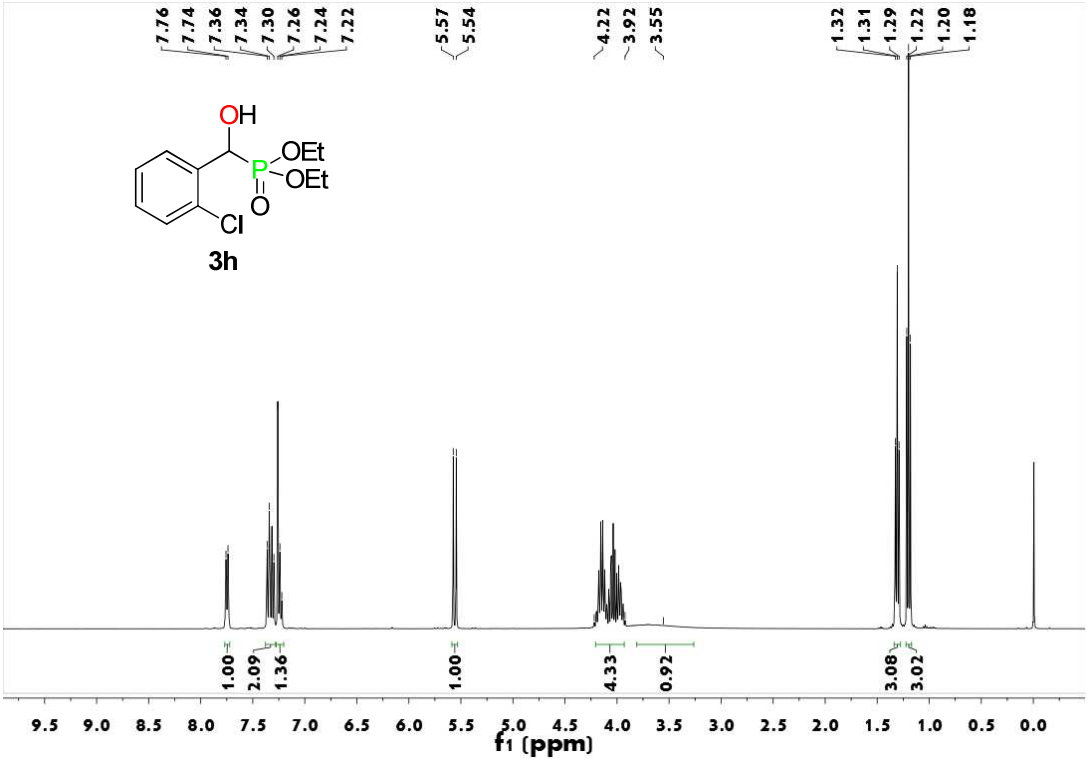
^{1}H NMR spectrum of 3f



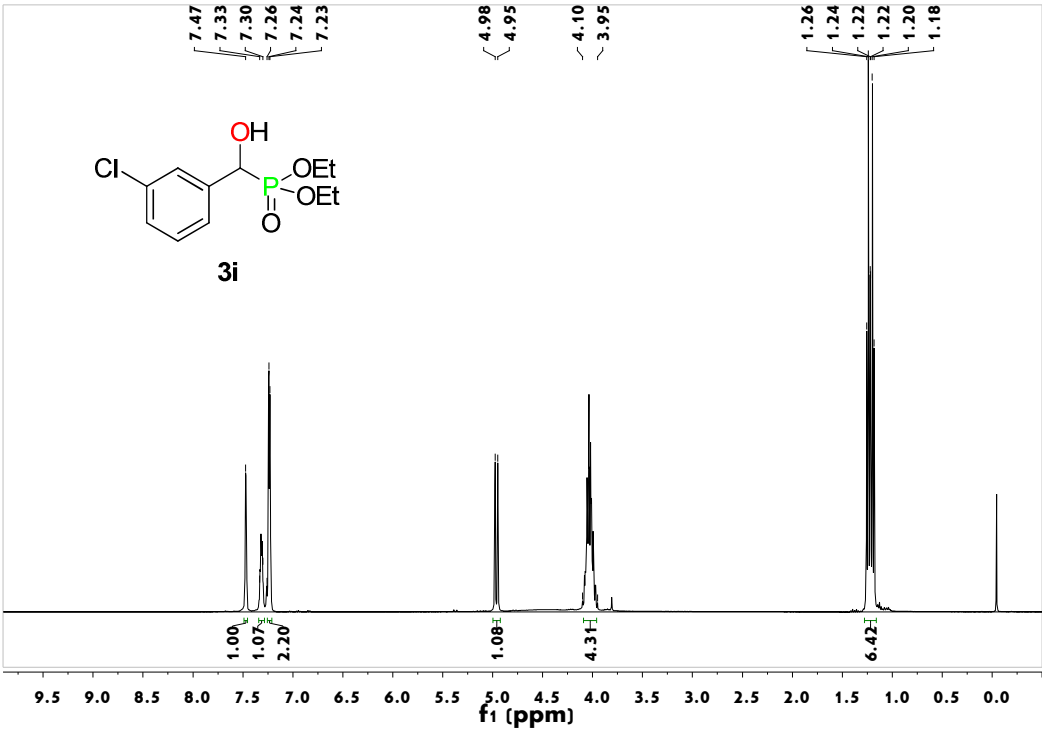
^{1}H NMR spectrum of 3g



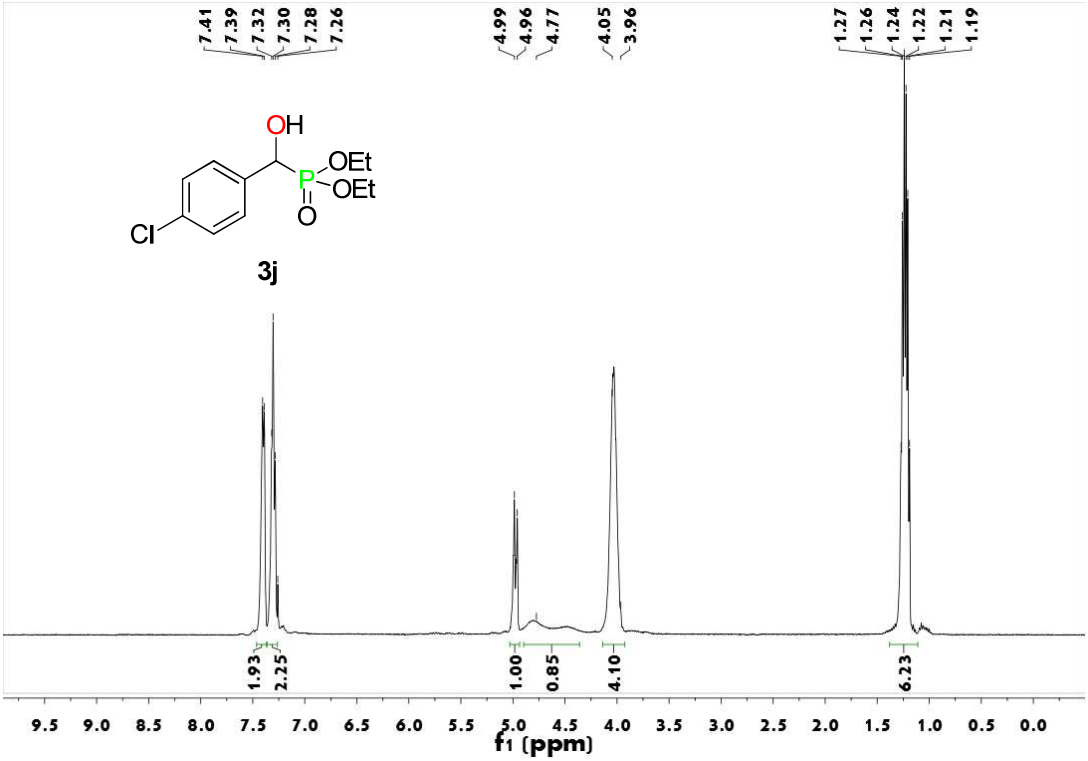
^{1}H NMR spectrum of 3h



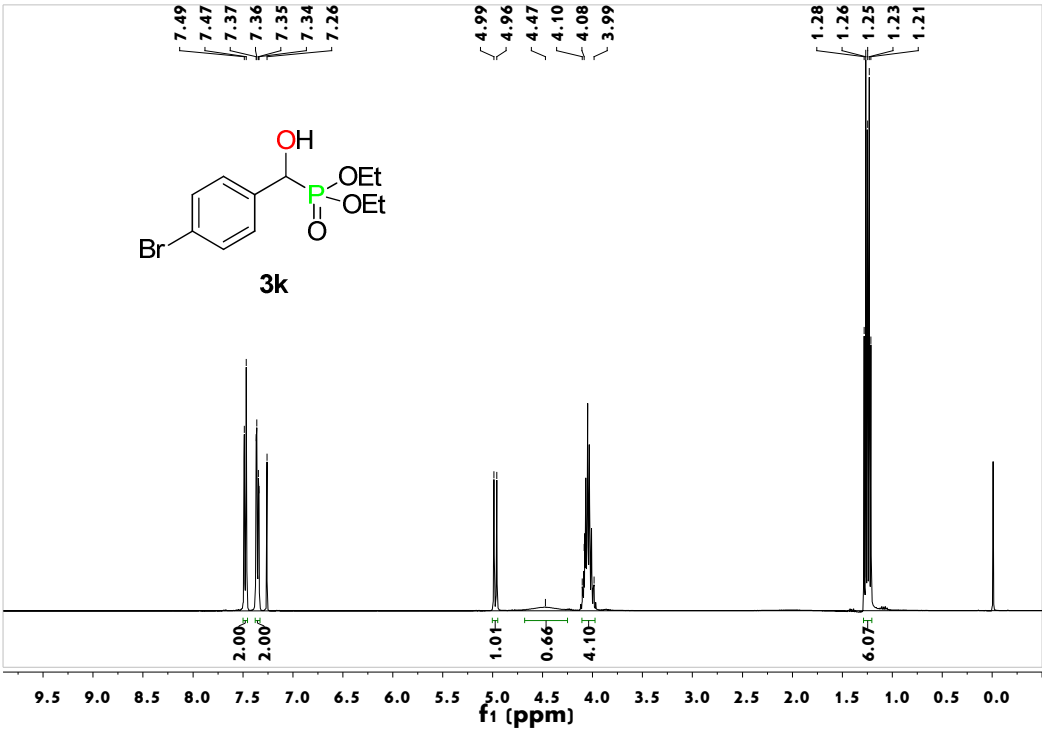
^{1}H NMR spectrum of 3i



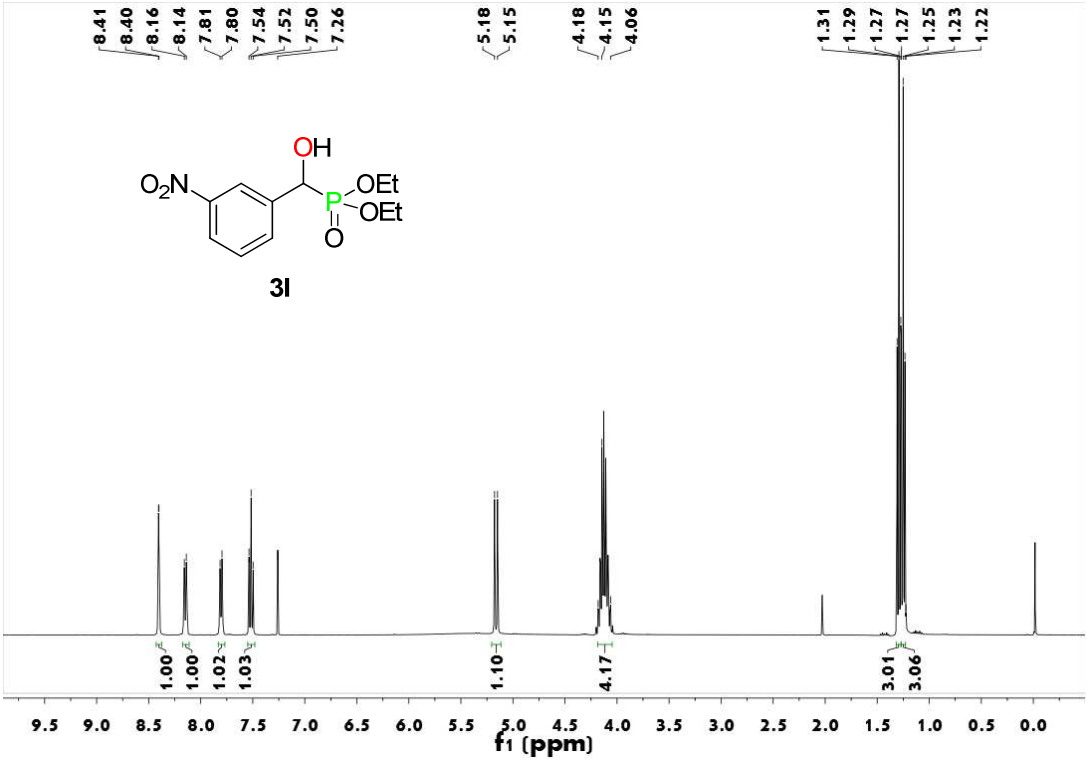
^{1}H NMR spectrum of 3j



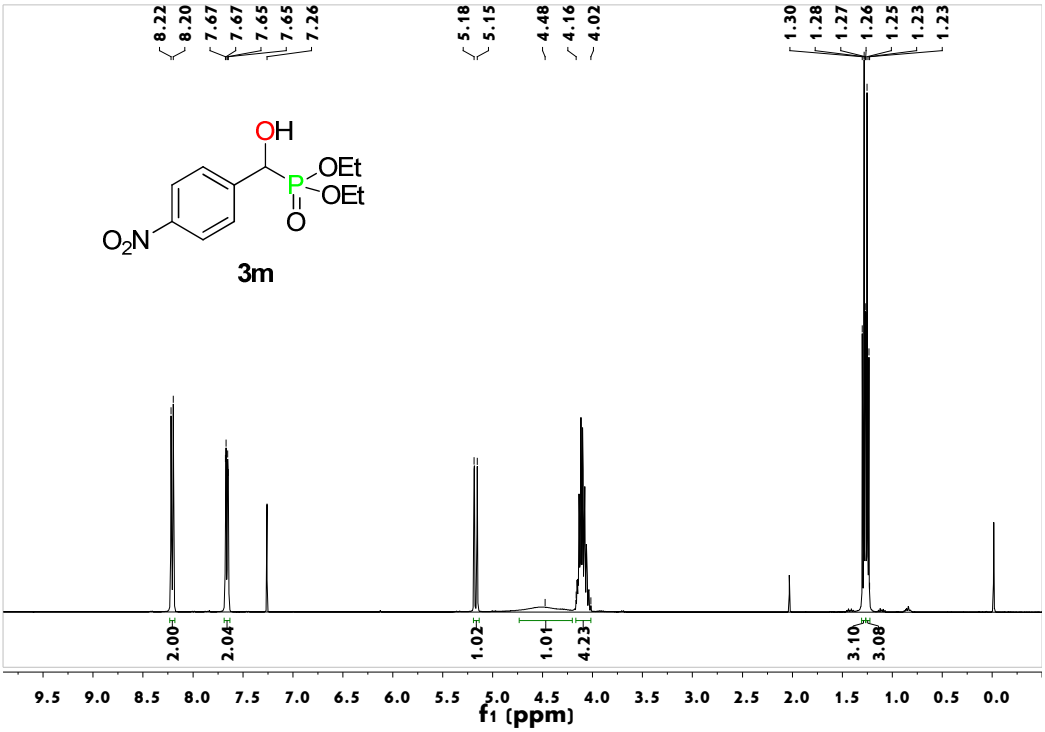
^{1}H NMR spectrum of 3k



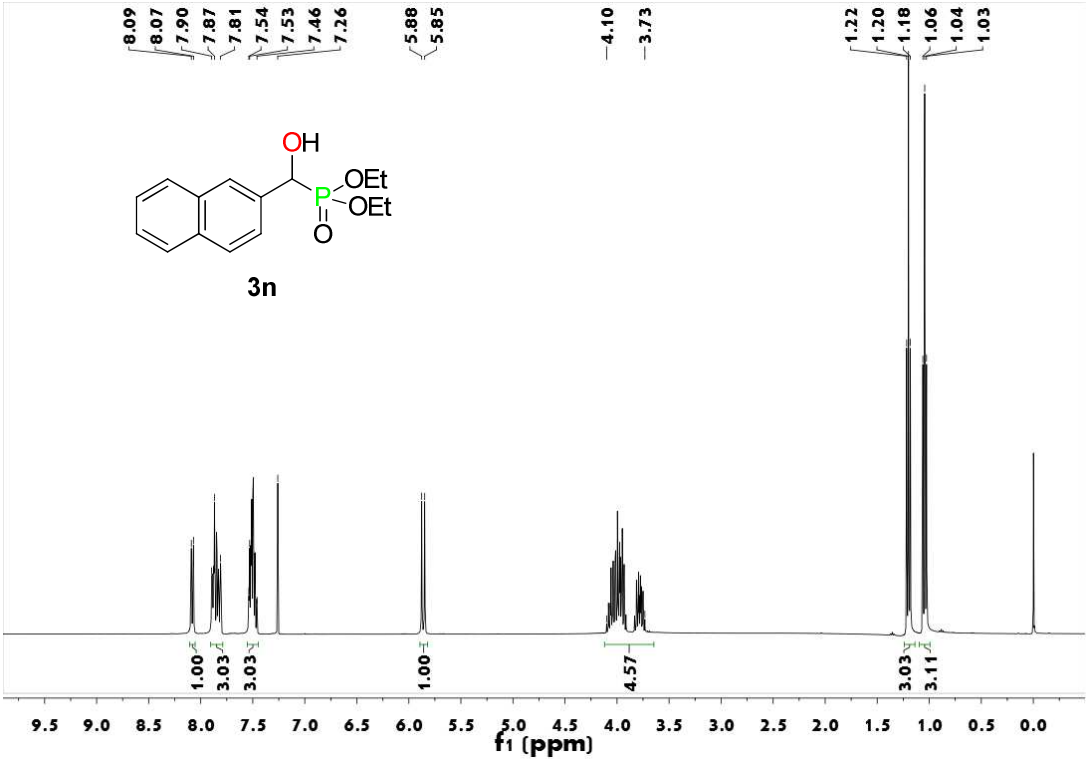
^{1}H NMR spectrum of 3l



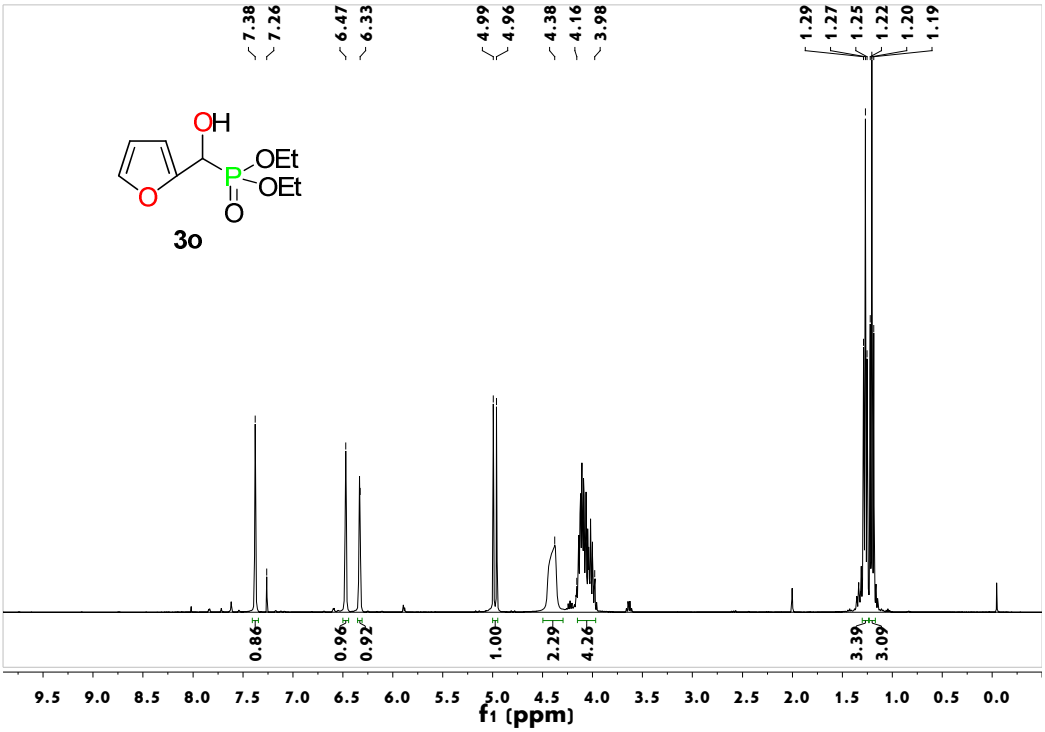
^{1}H NMR spectrum of 3m



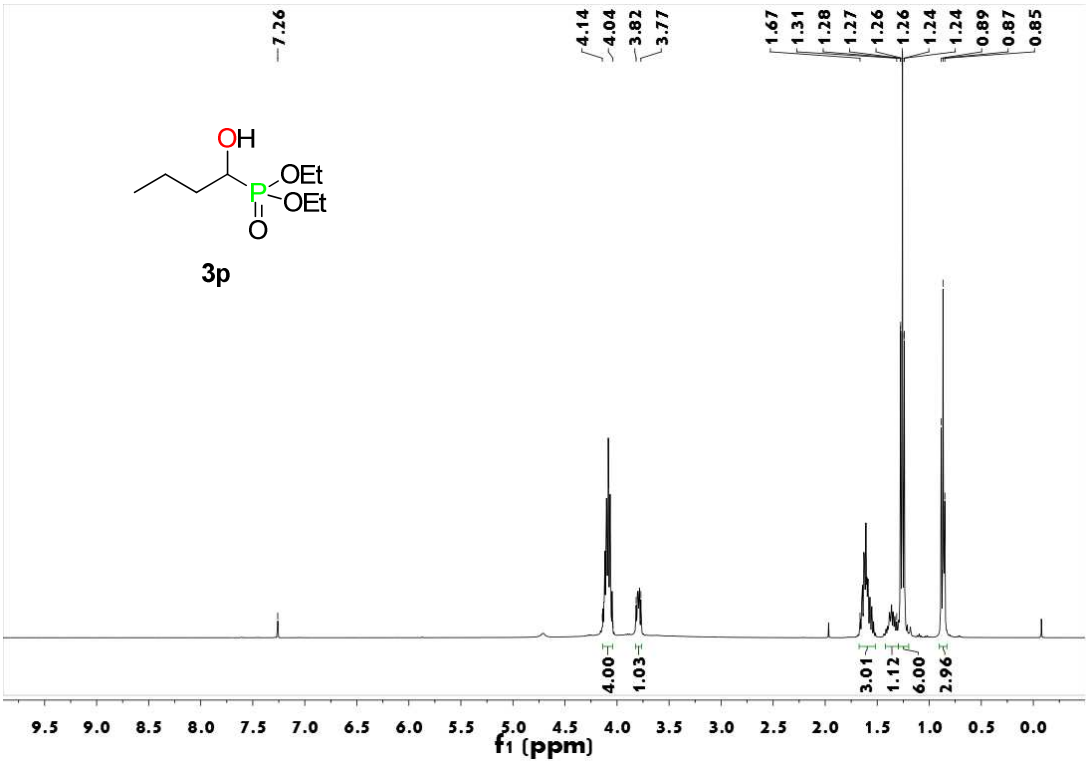
^{1}H NMR spectrum of 3n



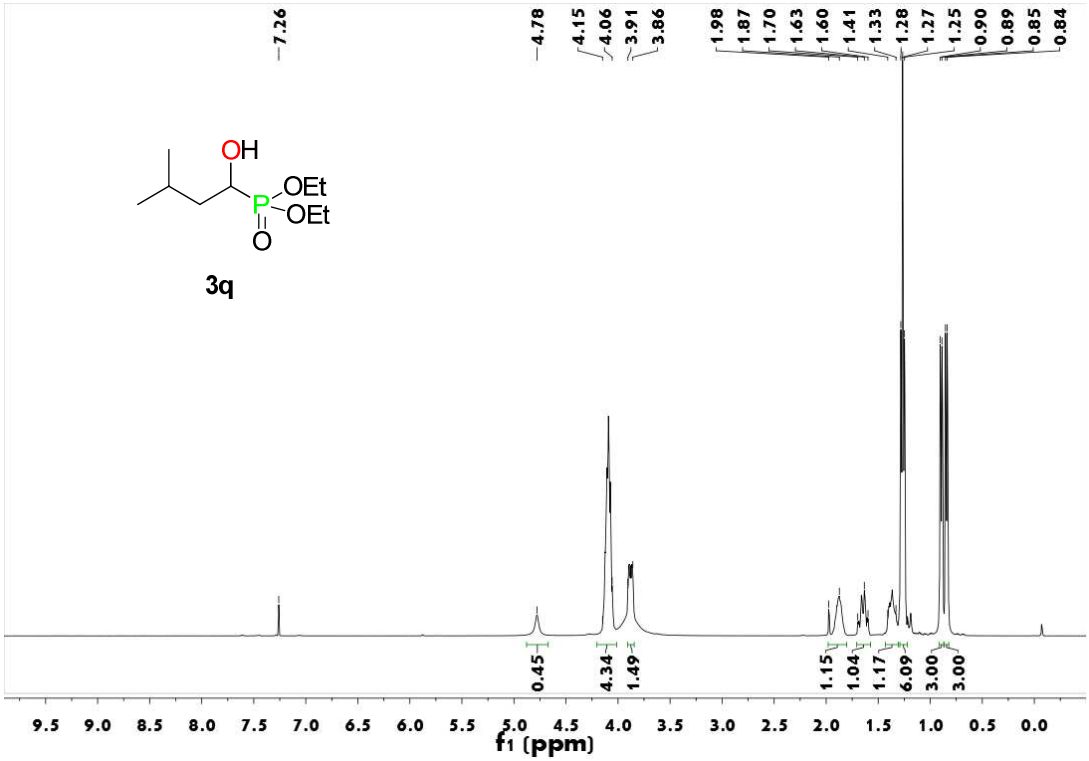
^{1}H NMR spectrum of 3o



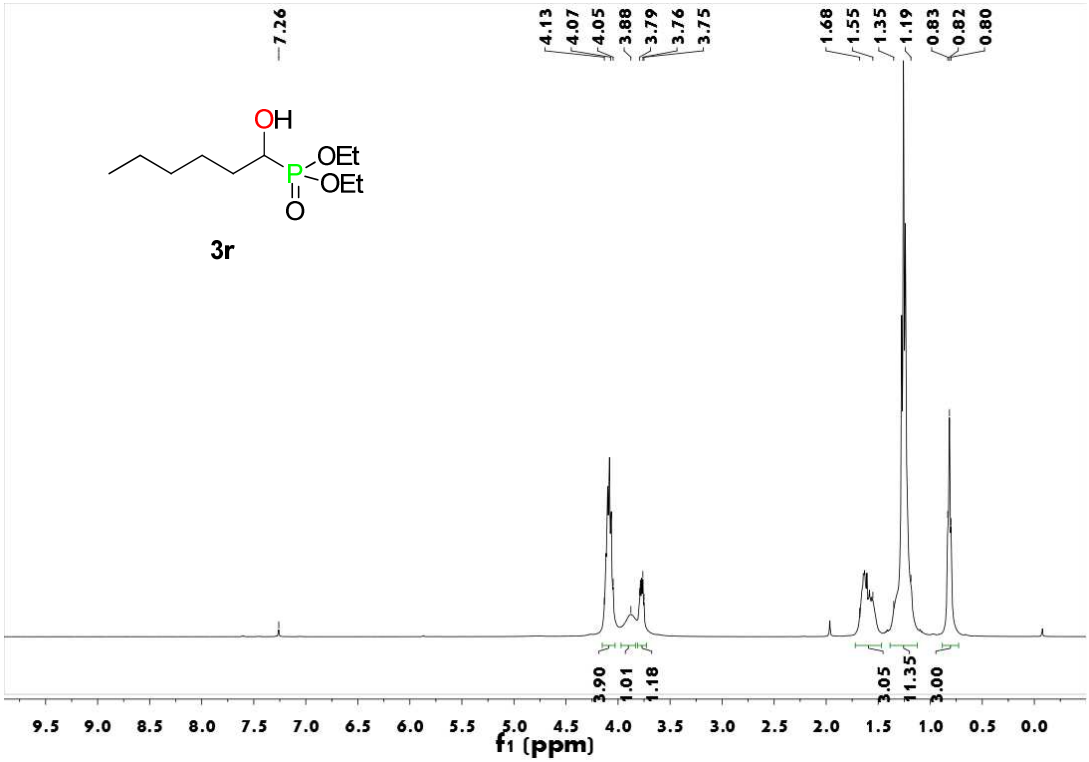
^{1}H NMR spectrum of 3p



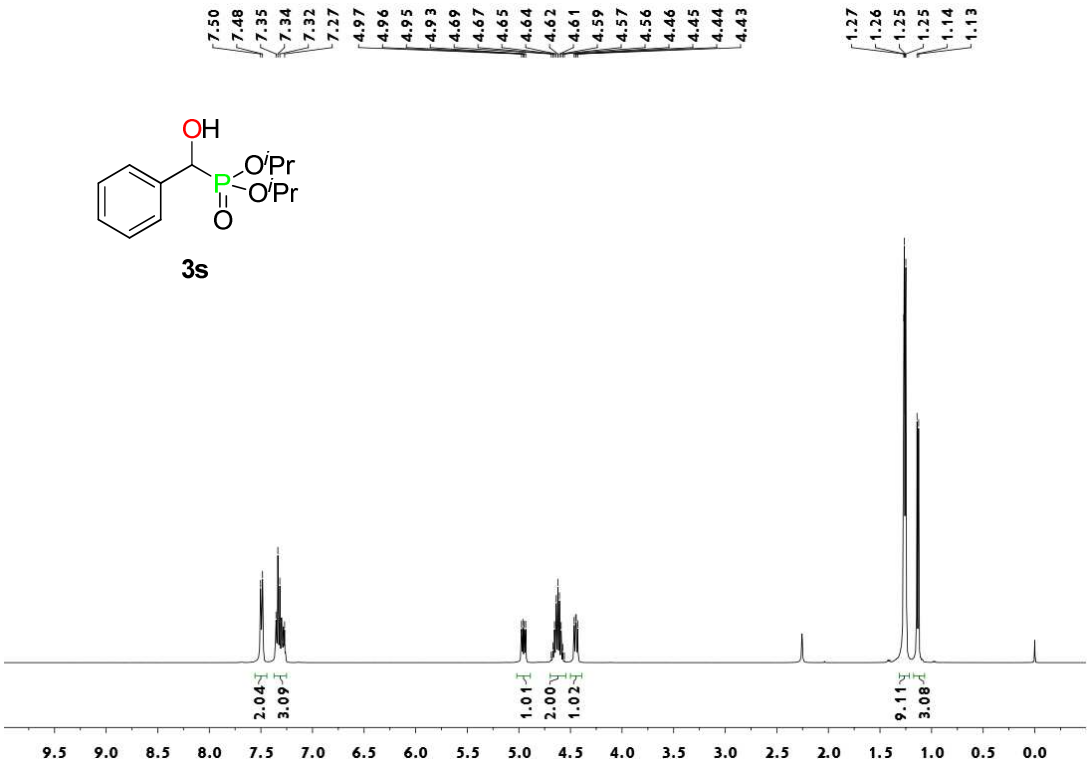
^{1}H NMR spectrum of 3q



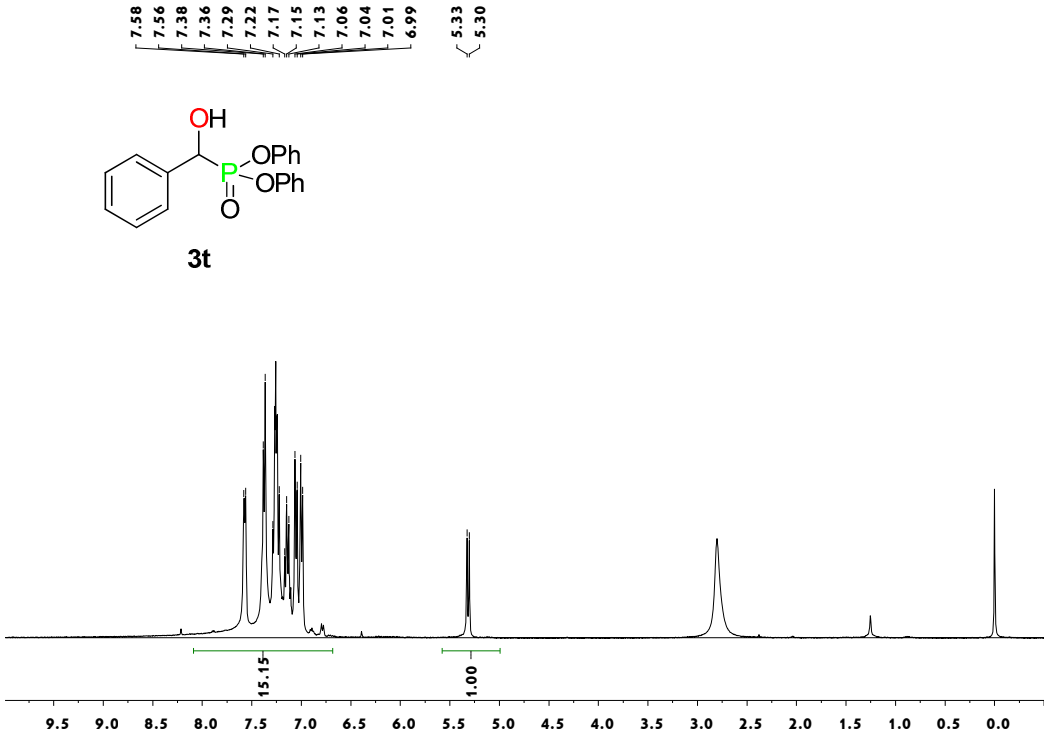
^{1}H NMR spectrum of 3r



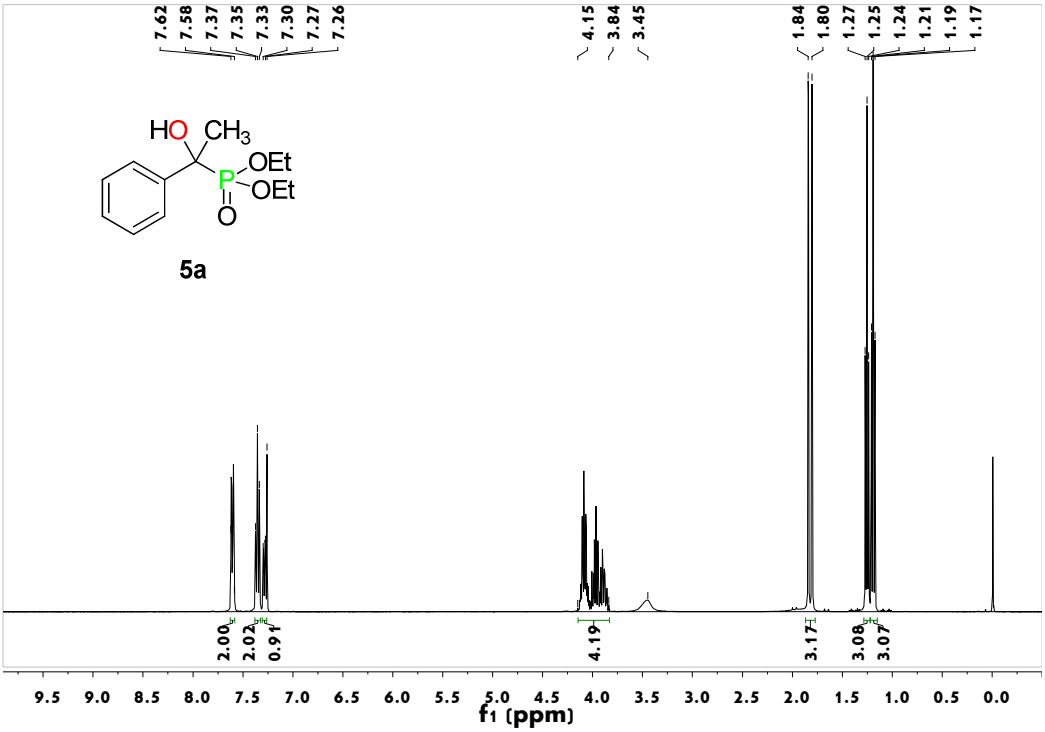
^{1}H NMR spectrum of 3s



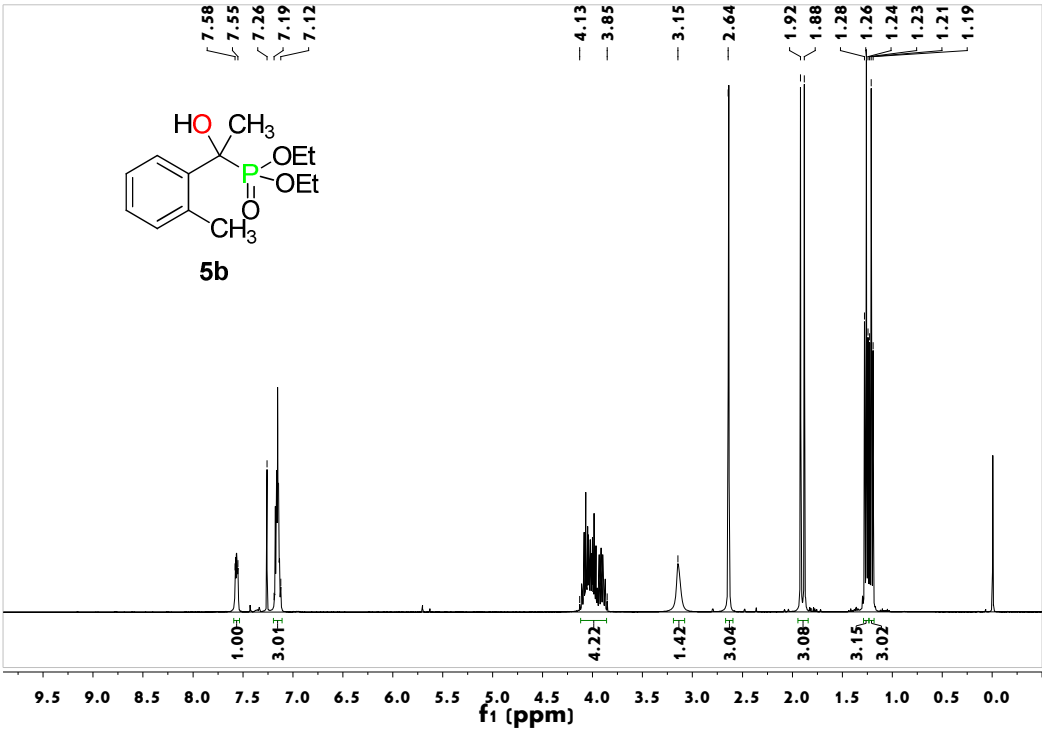
^{1}H NMR spectrum of 3t



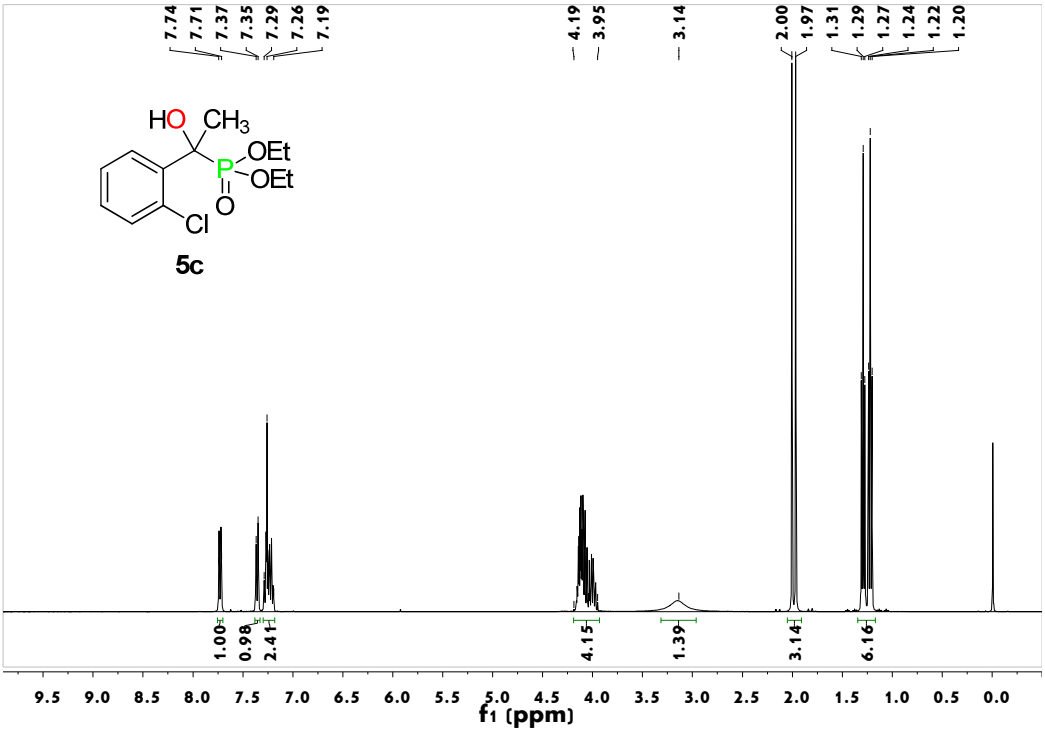
^{1}H NMR spectrum of 5a



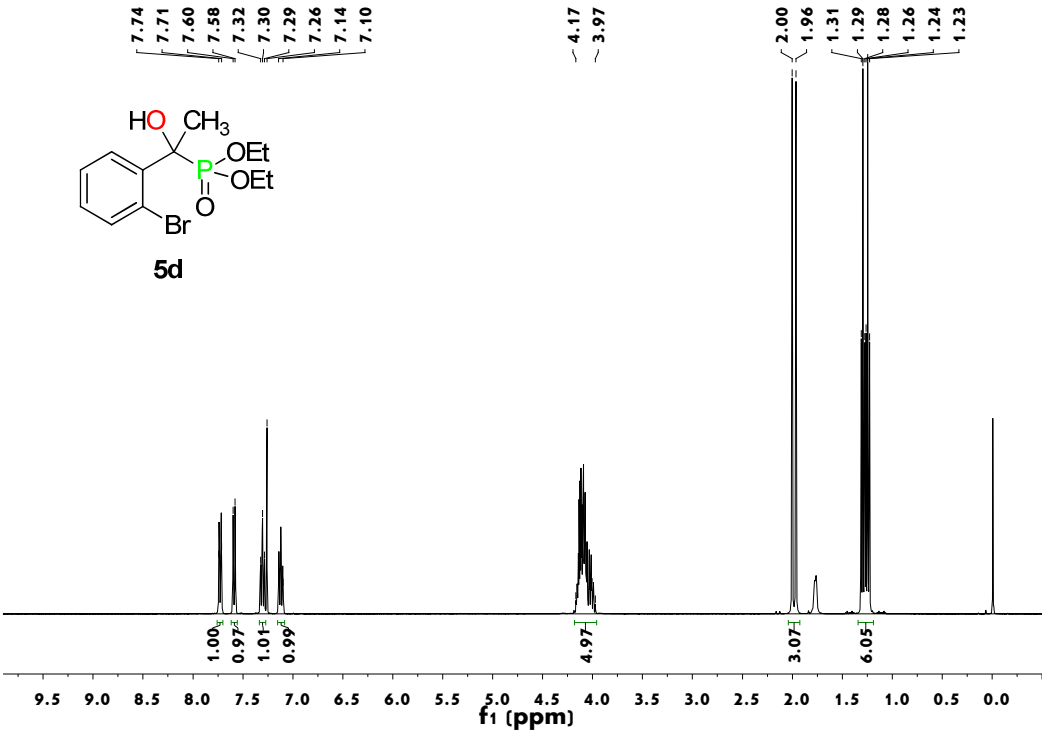
^{1}H NMR spectrum of 5b



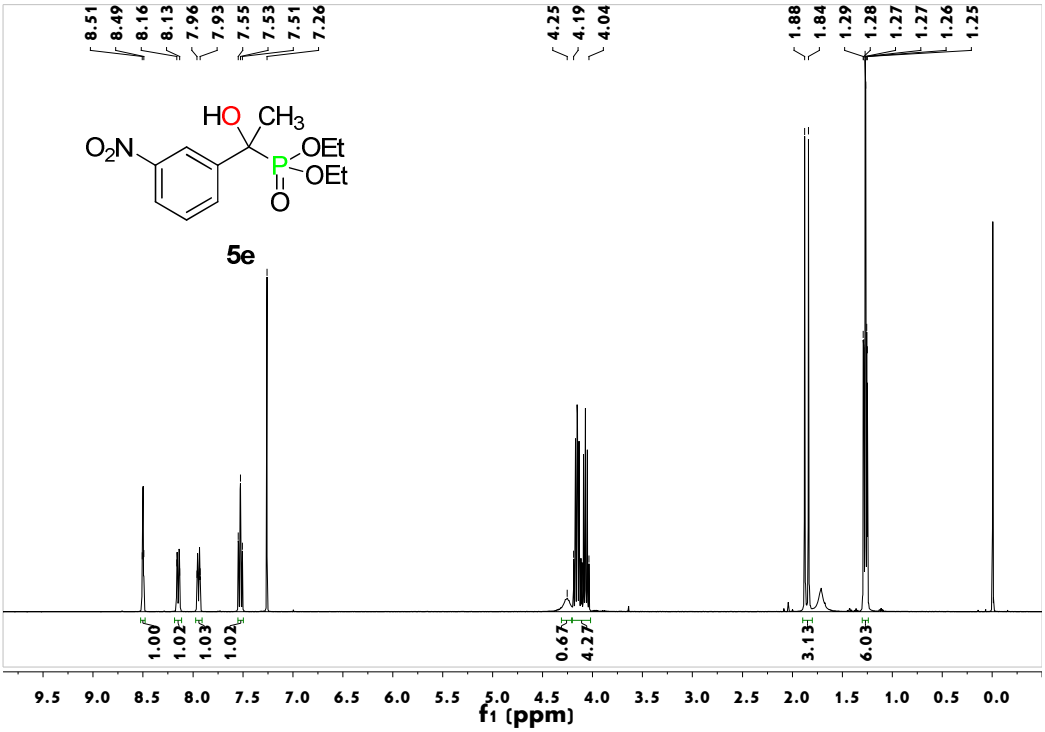
^{1}H NMR spectrum of 5c



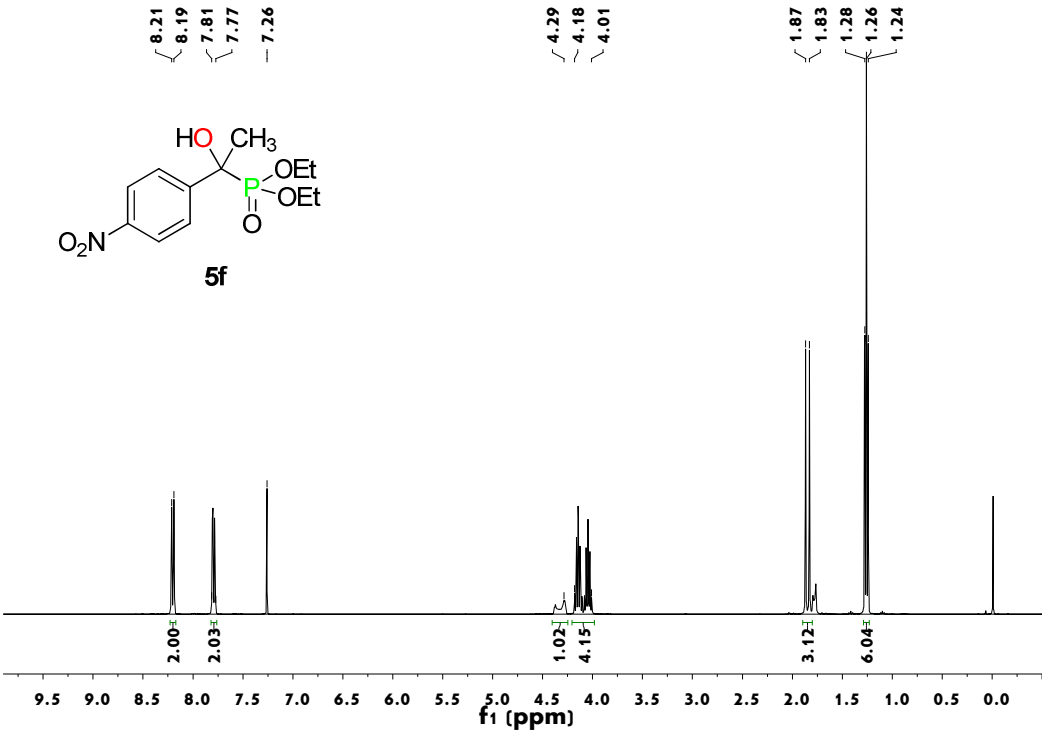
^{1}H NMR spectrum of 5d



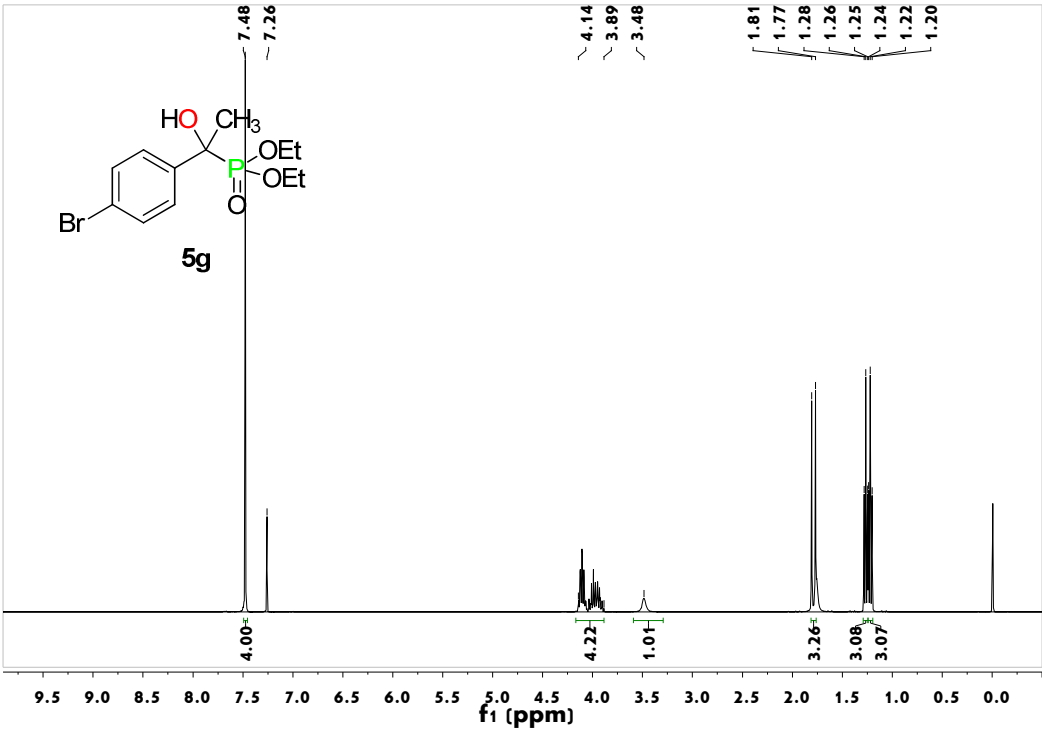
^{1}H NMR spectrum of 5e



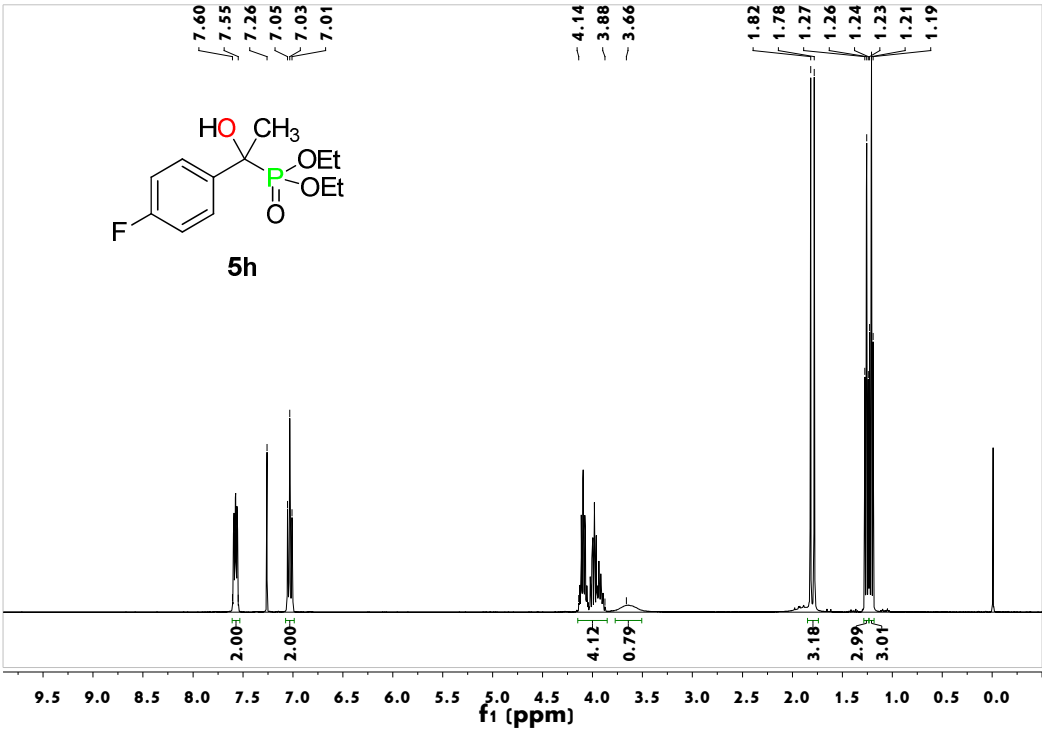
^{1}H NMR spectrum of 5f



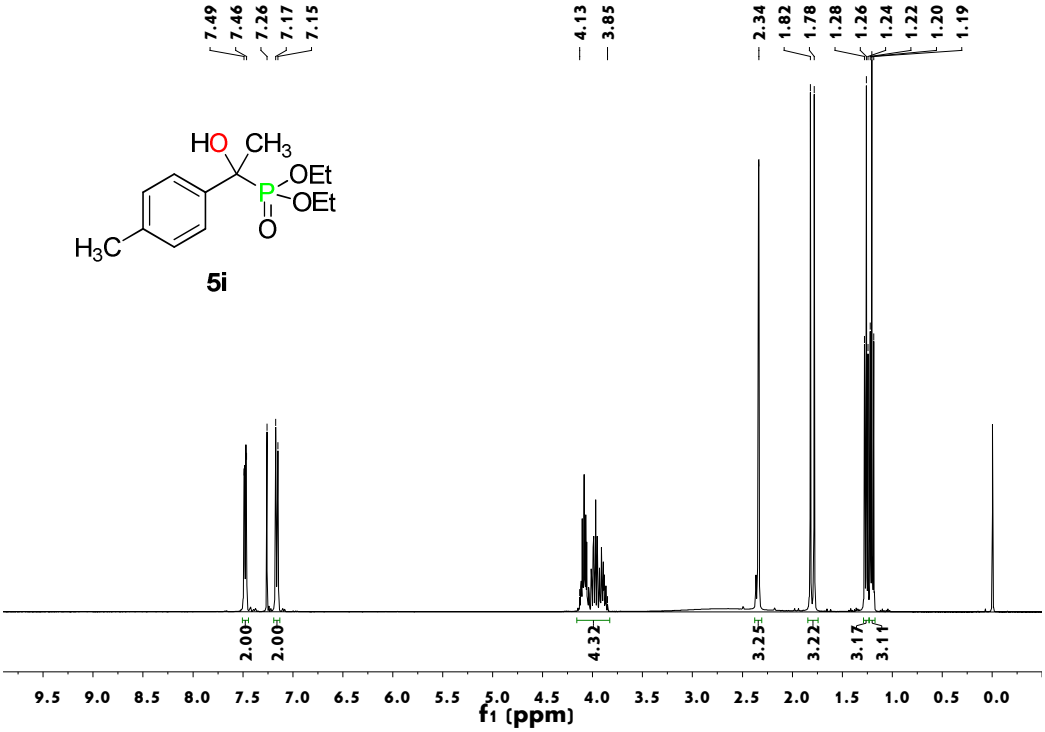
^{1}H NMR spectrum of 5g



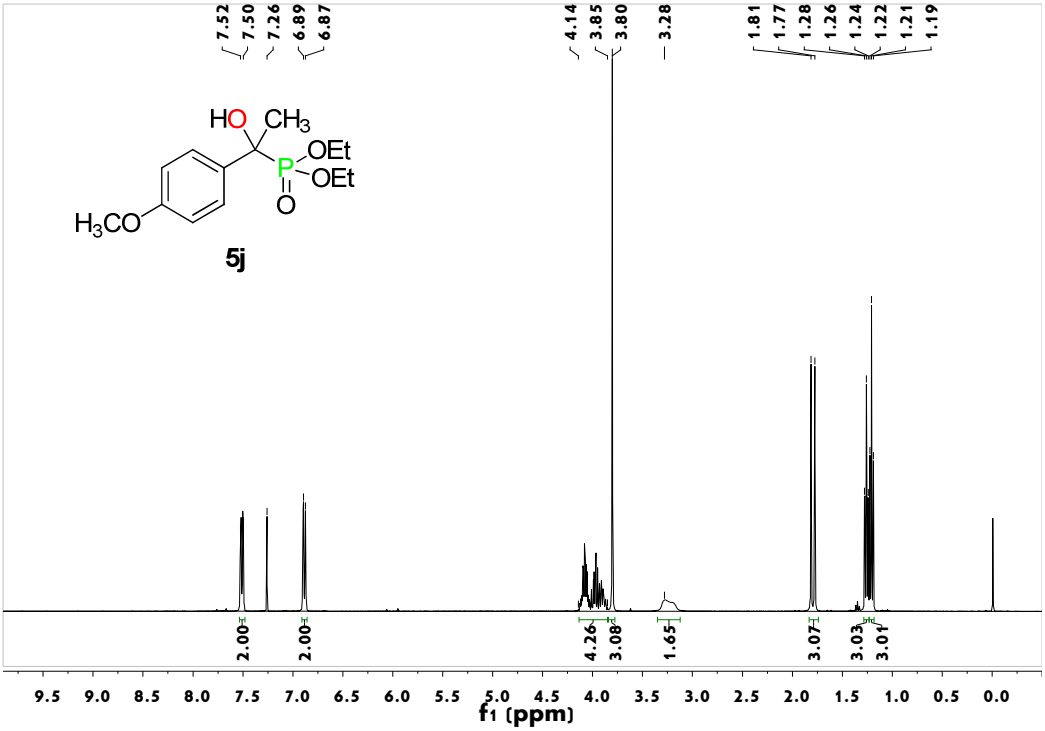
^{1}H NMR spectrum of 5h



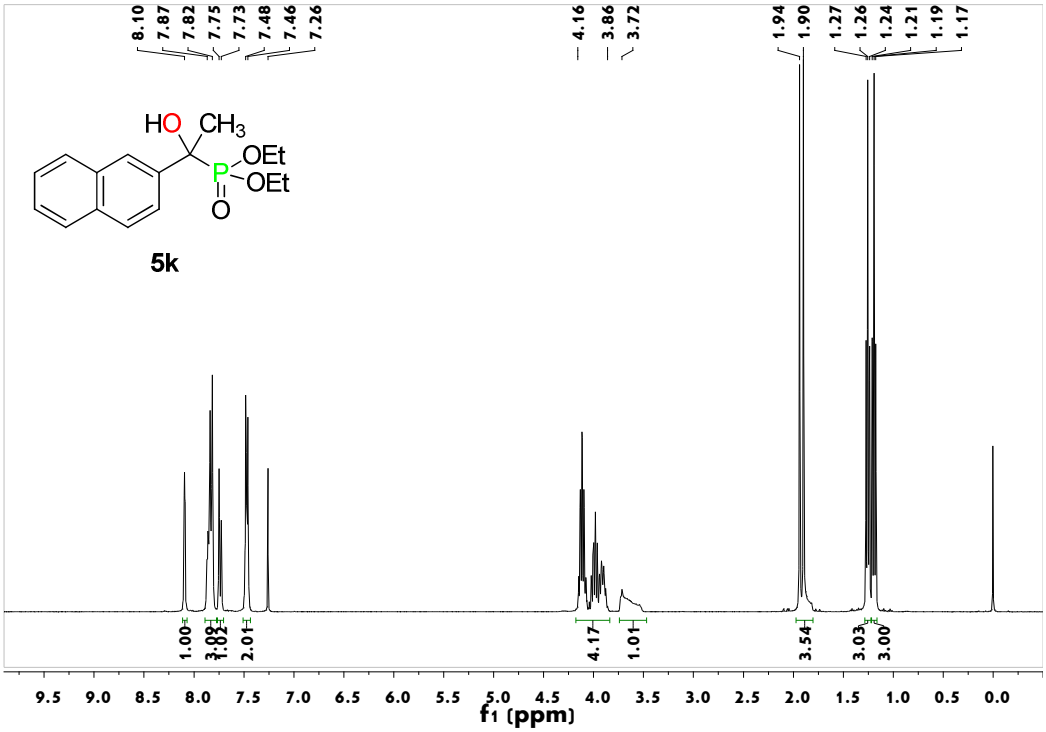
^{1}H NMR spectrum of 5i



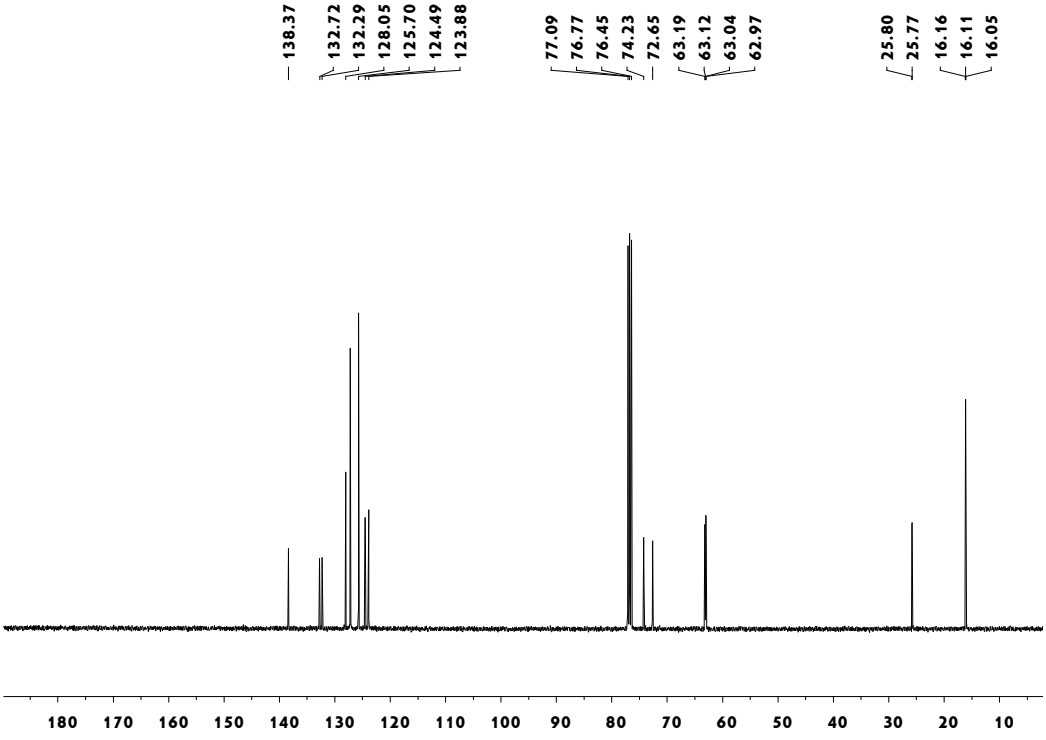
^{1}H NMR spectrum of 5j



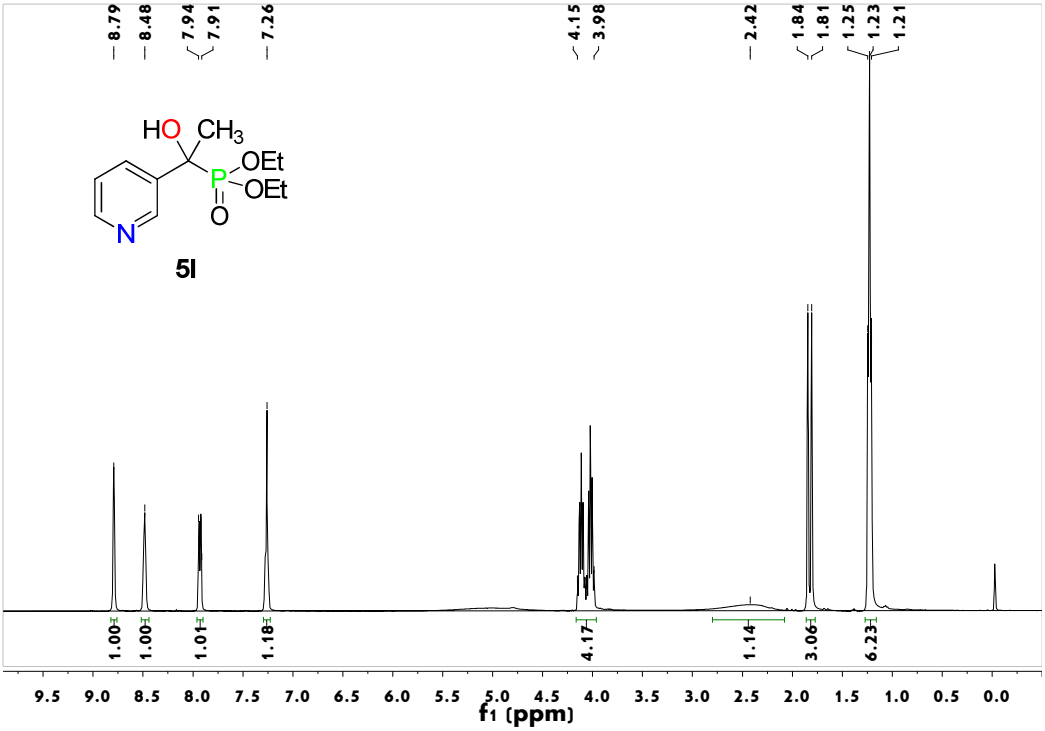
^{1}H NMR spectrum of 5k



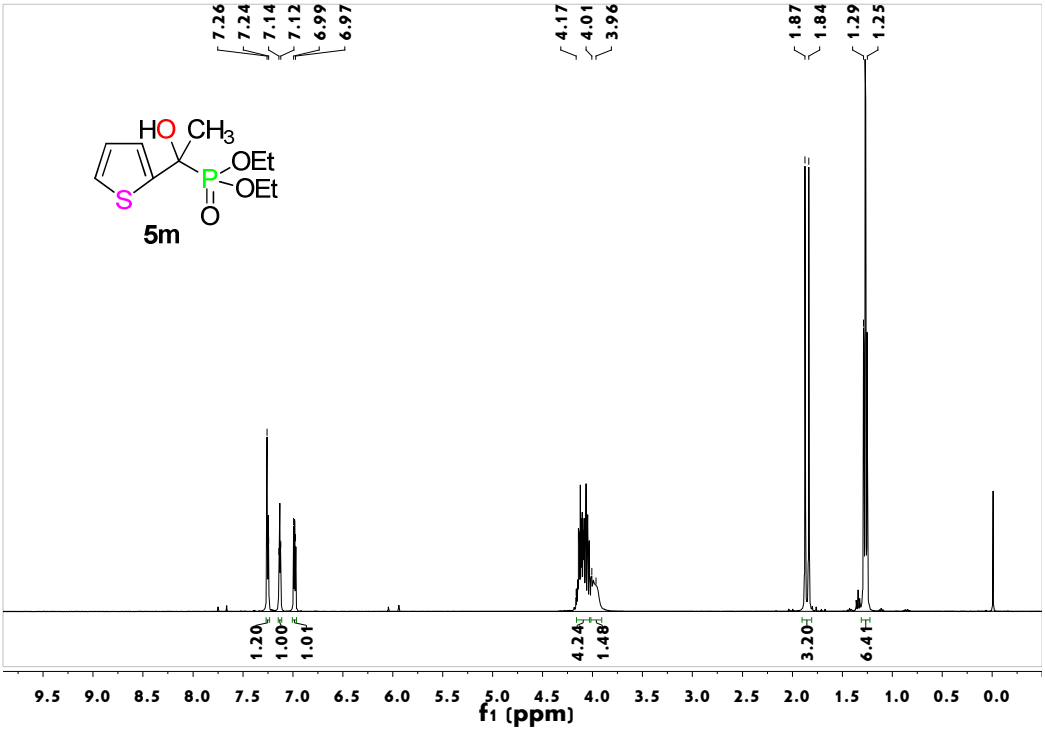
^{13}C NMR spectrum of 5k



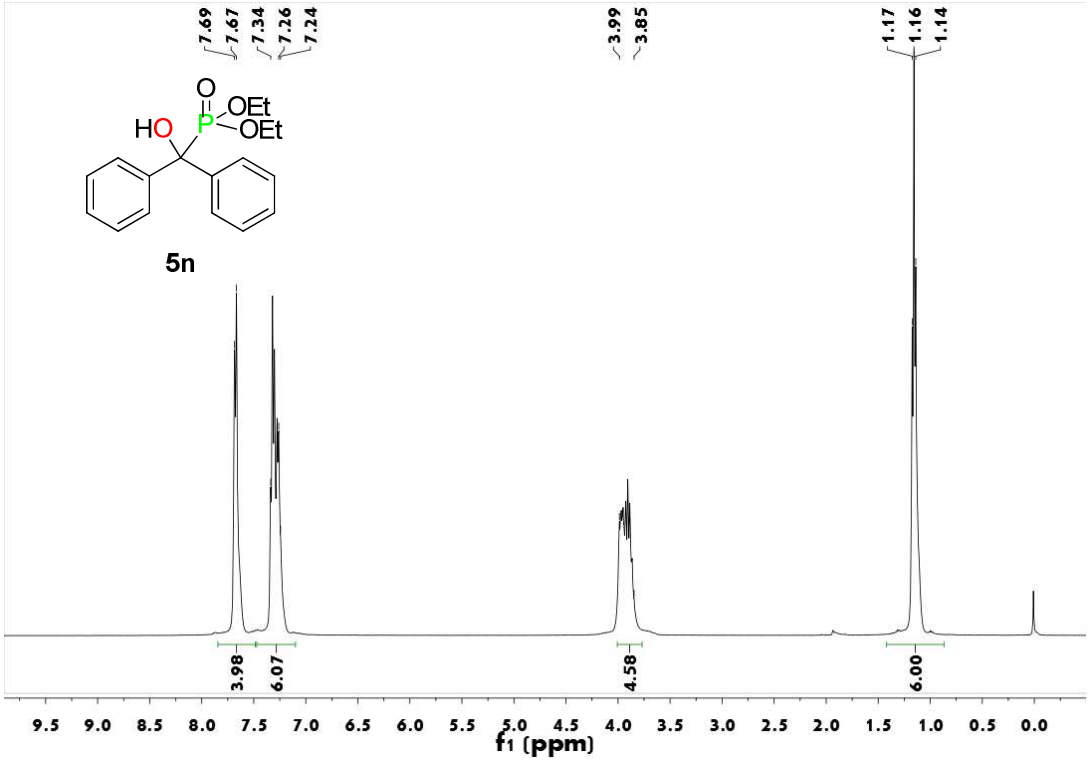
^{1}H NMR spectrum of 5l



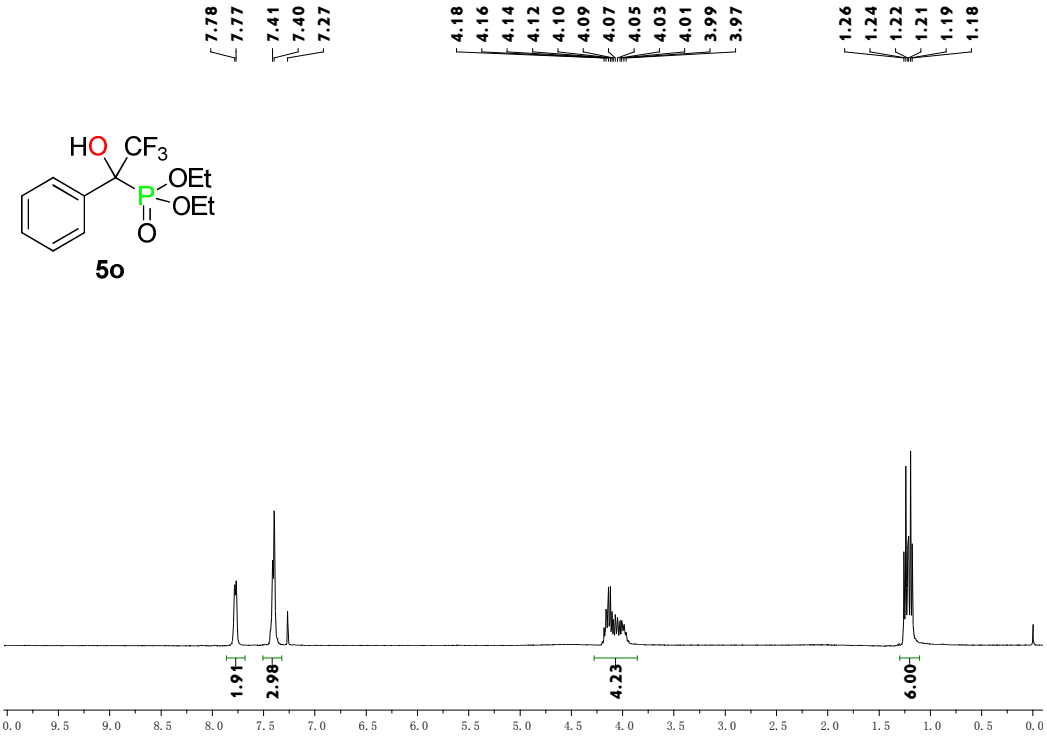
^{1}H NMR spectrum of 5m



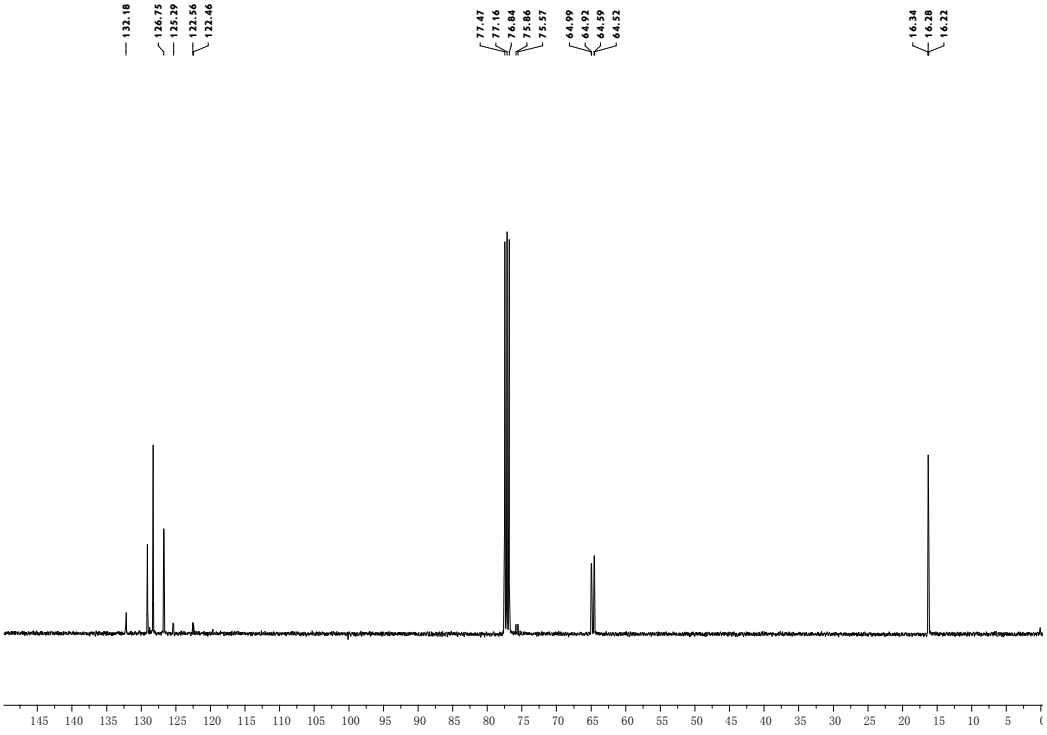
^{1}H NMR spectrum of 5n



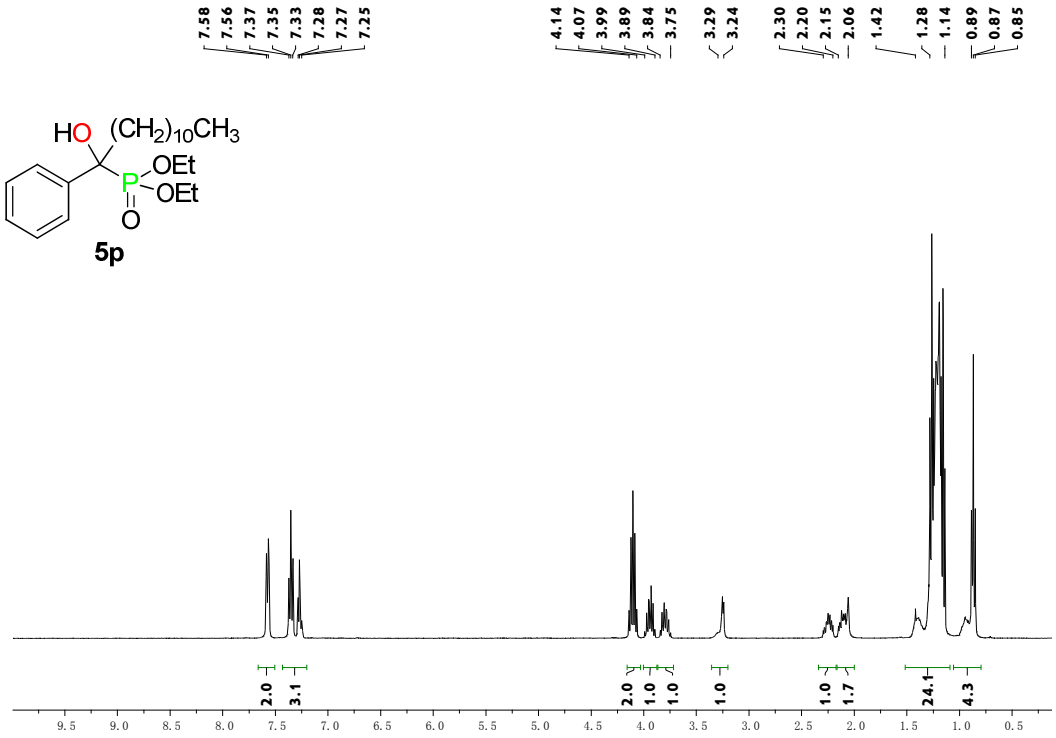
^{1}H NMR spectrum of 5o



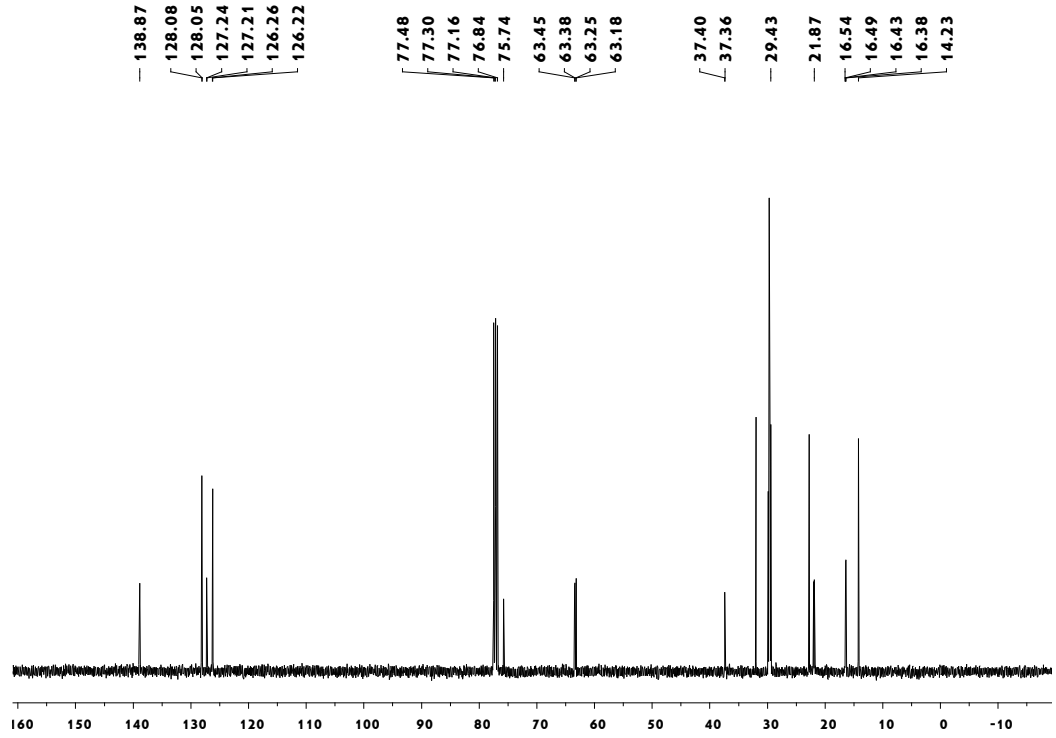
^{13}C NMR spectrum of 5o



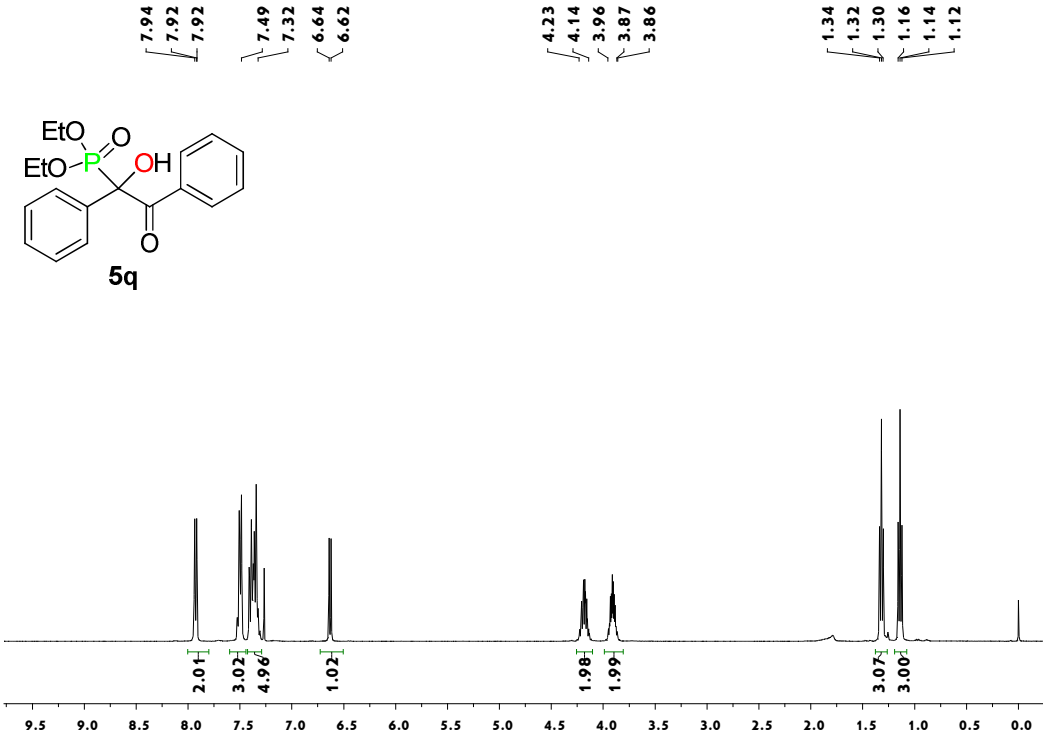
^{1}H NMR spectrum of 5p



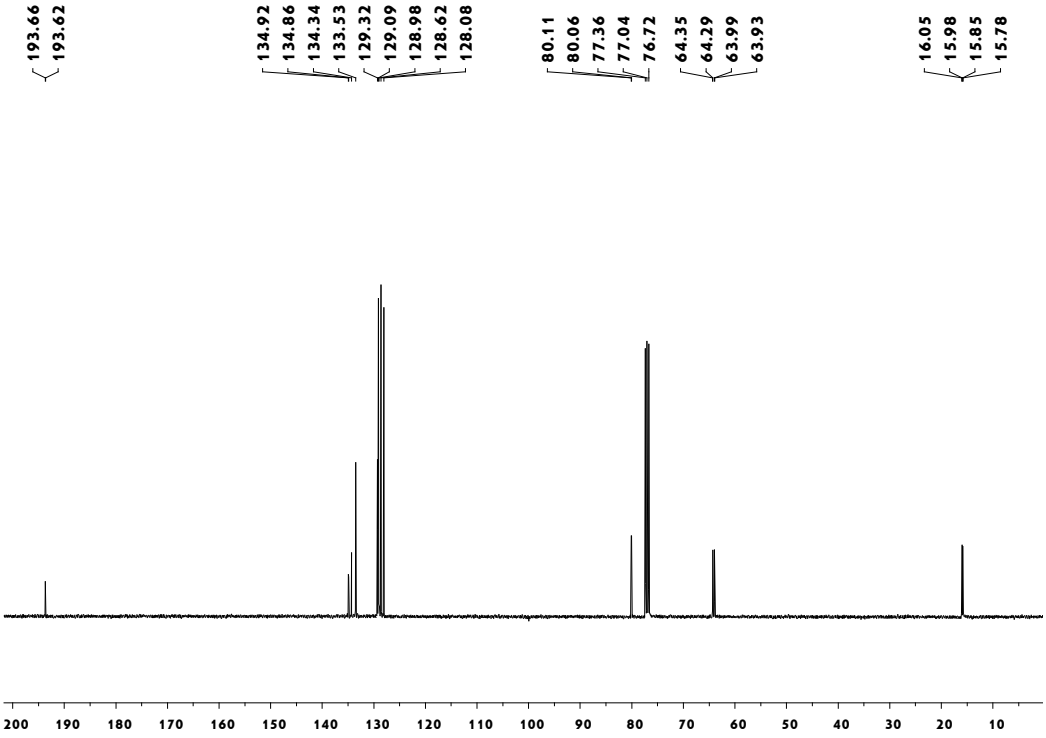
^{13}C NMR spectrum of 5p



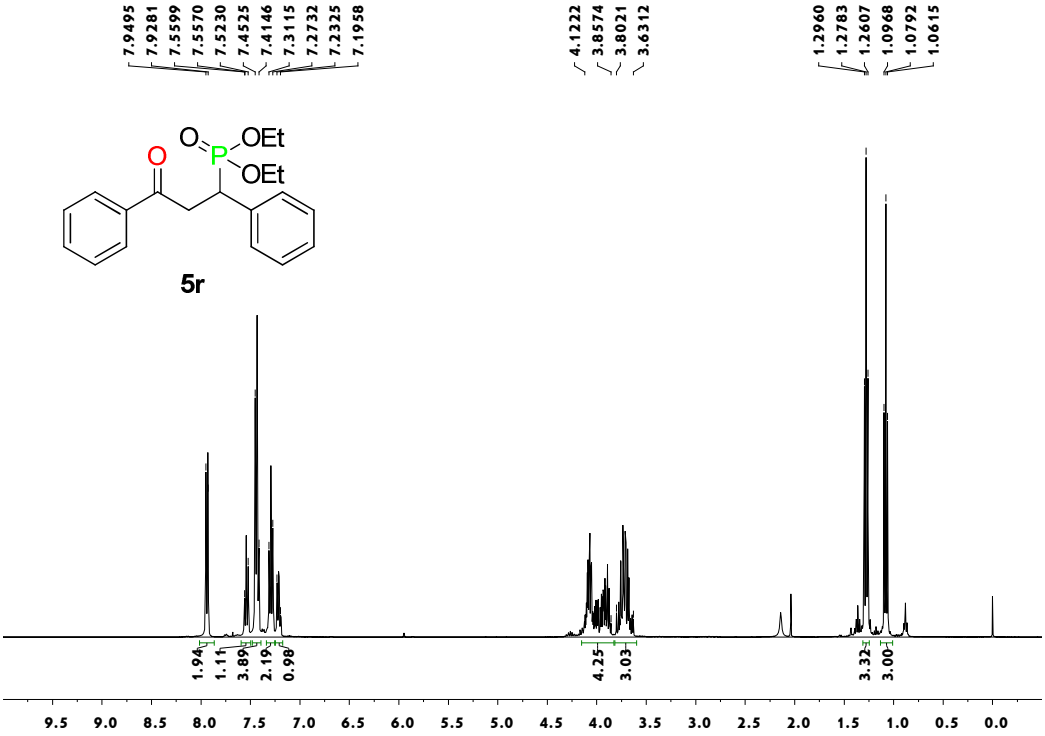
^{1}H NMR spectrum of 5q



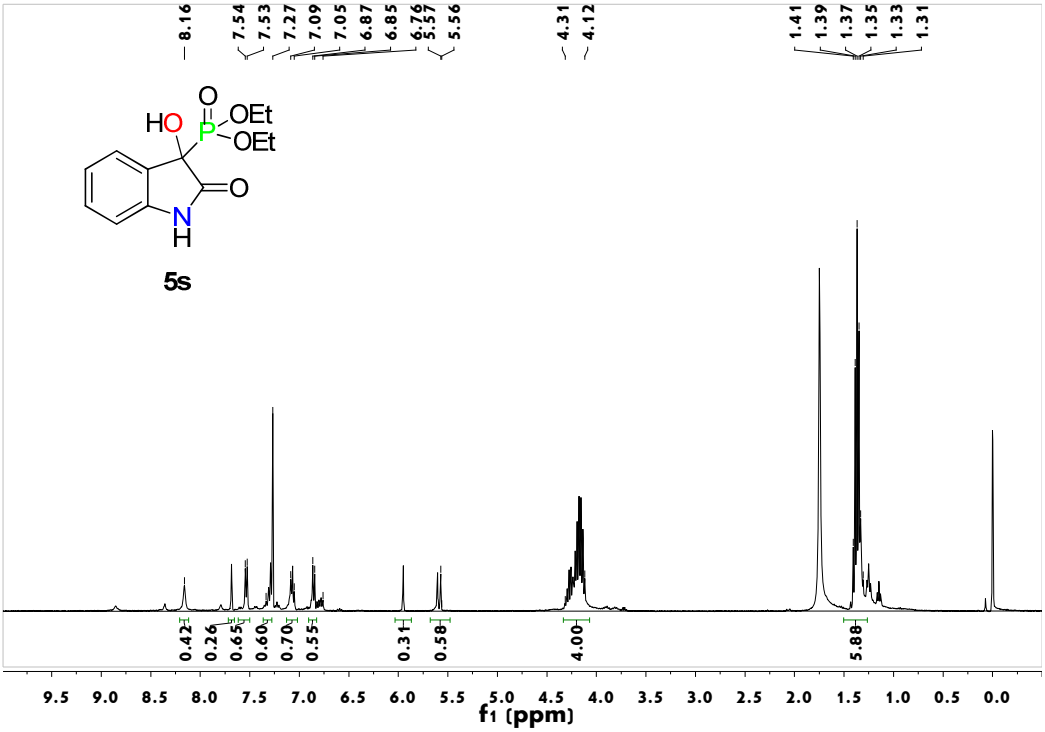
^{13}C NMR spectrum of 5q



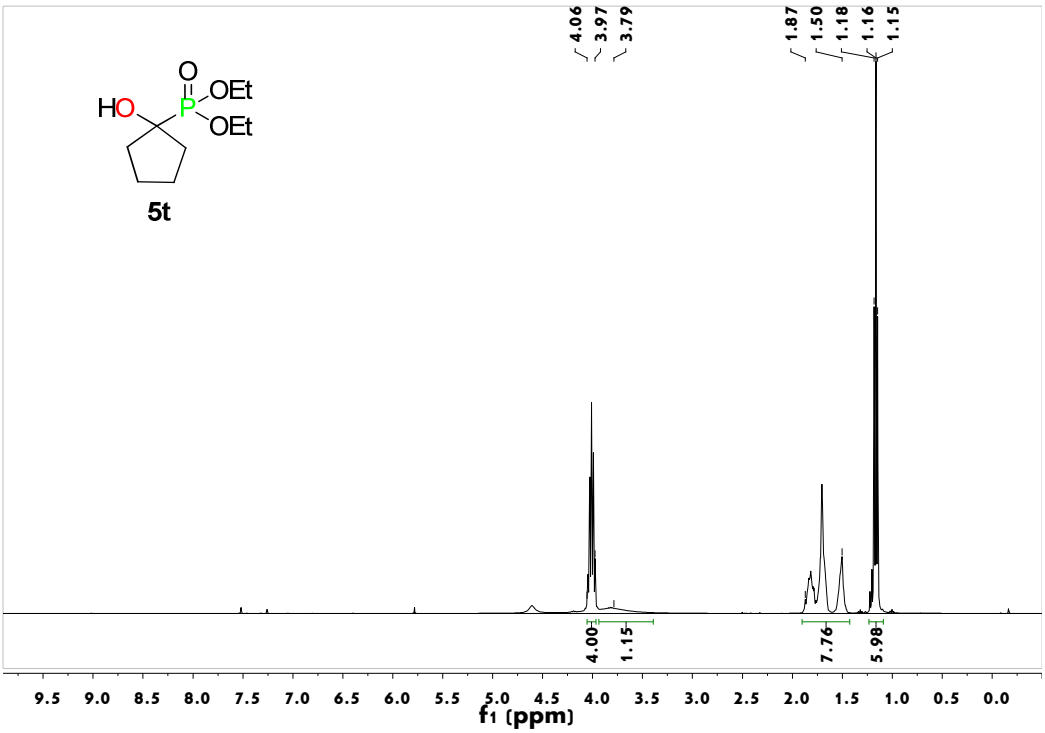
^{1}H NMR spectrum of 5r



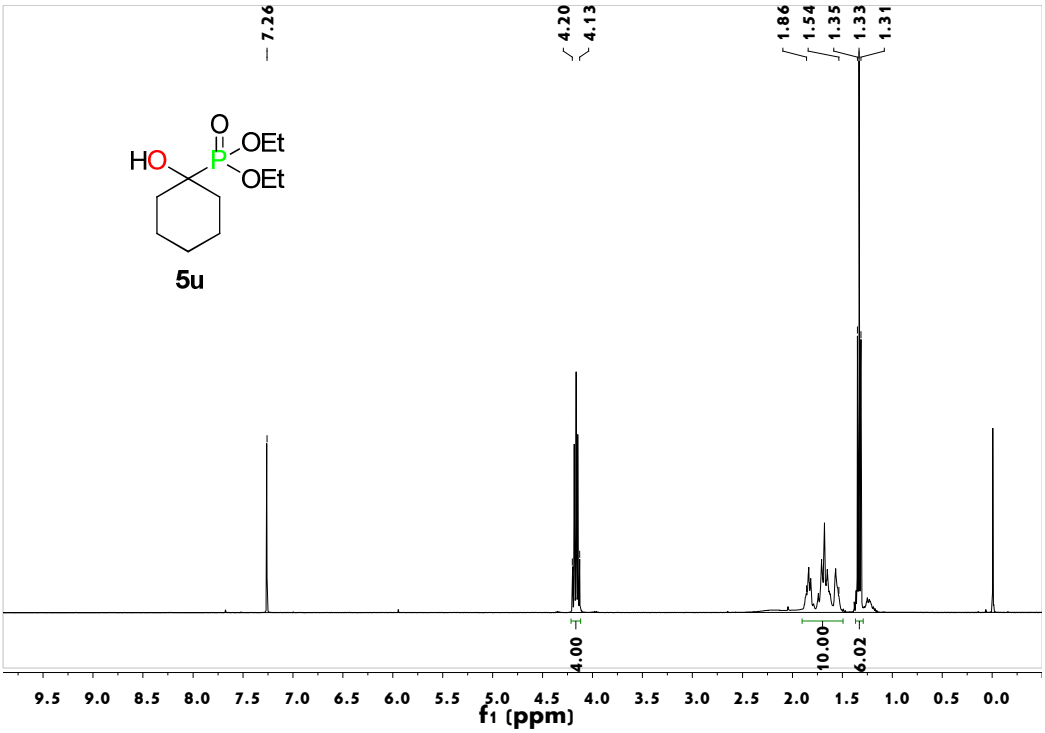
^{1}H NMR spectrum of 5s



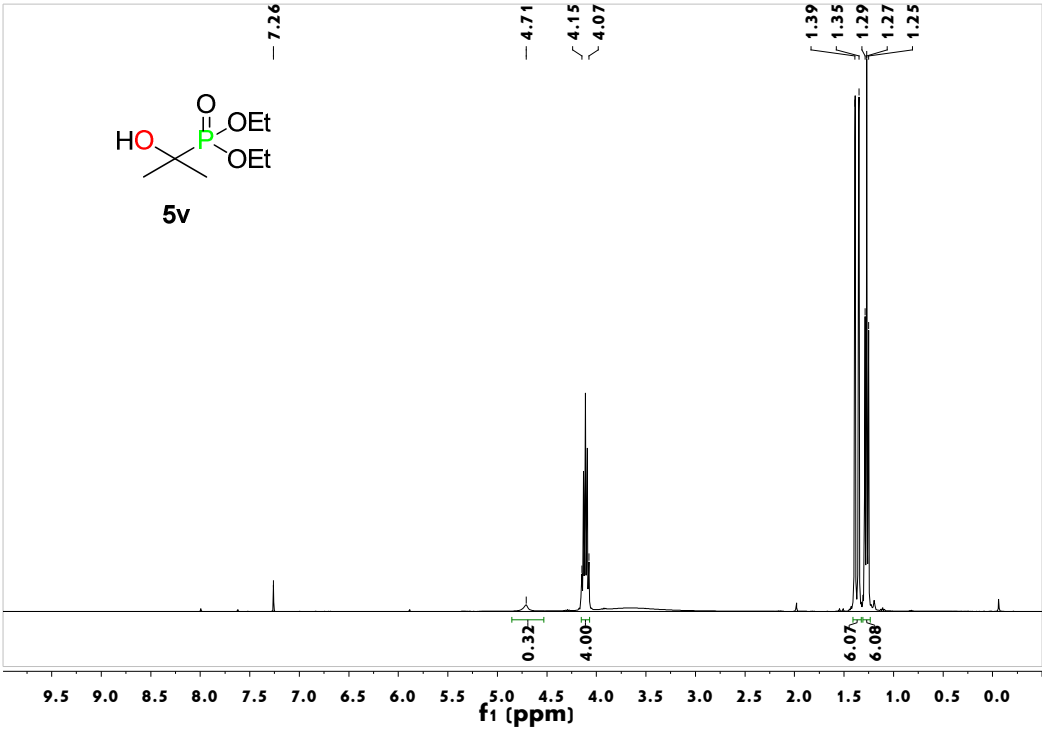
^{1}H NMR spectrum of 5t



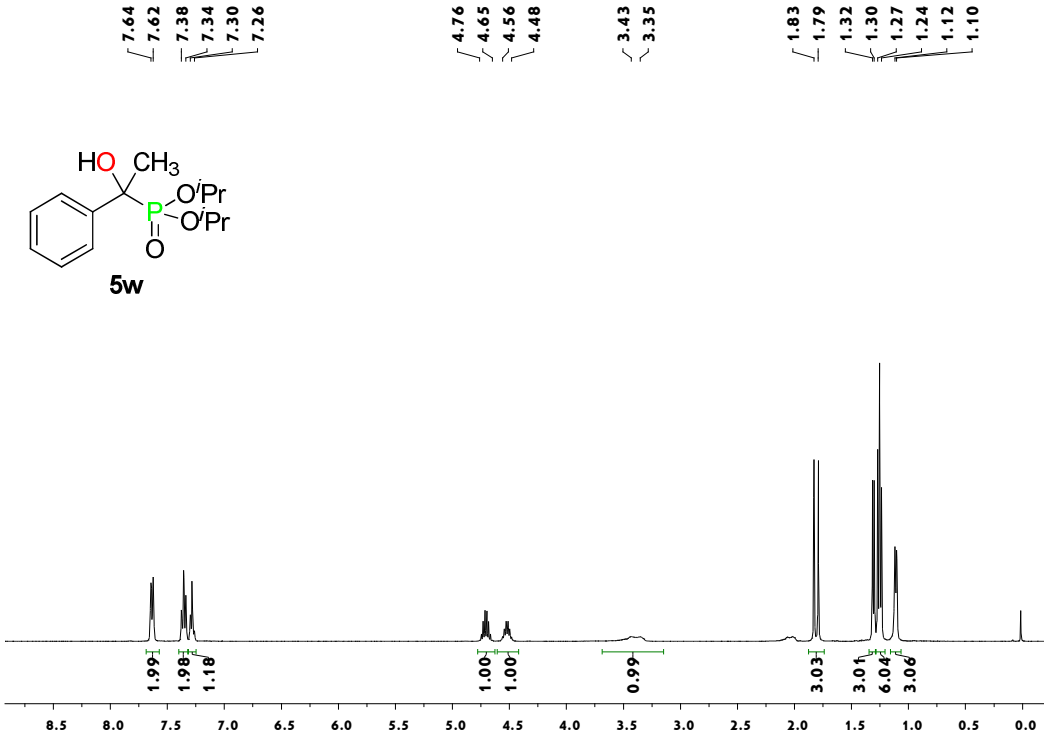
^{1}H NMR spectrum of 5u



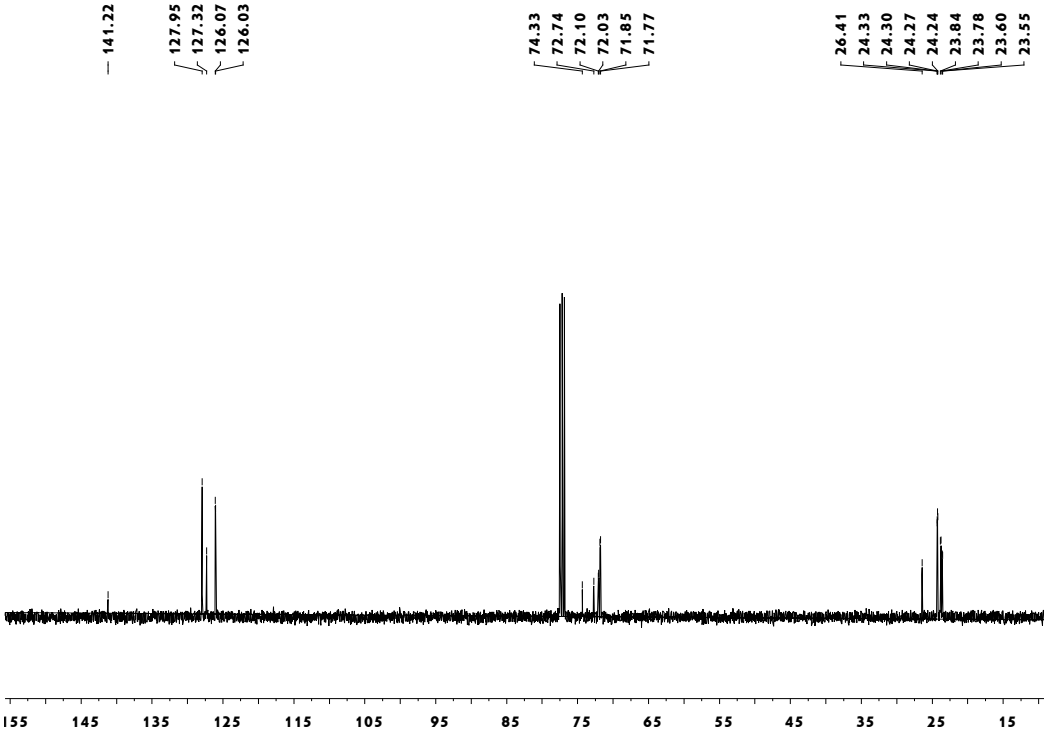
^{1}H NMR spectrum of 5v



^{1}H NMR spectrum of 5w



^{13}C NMR spectrum of 5w



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