Supporting Information

Electrochemical-induced Markovnikov-type Selective Hydro/deuterophosphonylation of Electron-rich Alkenes

*Weijie Deng,‡ Yunfei Hu,‡ Jinhui Hu, Xinling Li, Yibiao Li and Yubing Huang**

School of Biotechnology and Health Sciences, Wuyi University, Jiangmen, 529090, P. R. China.

E-mail: wyuchemhyb@126.com

‡These authors contributed equally to this work

List of Contents

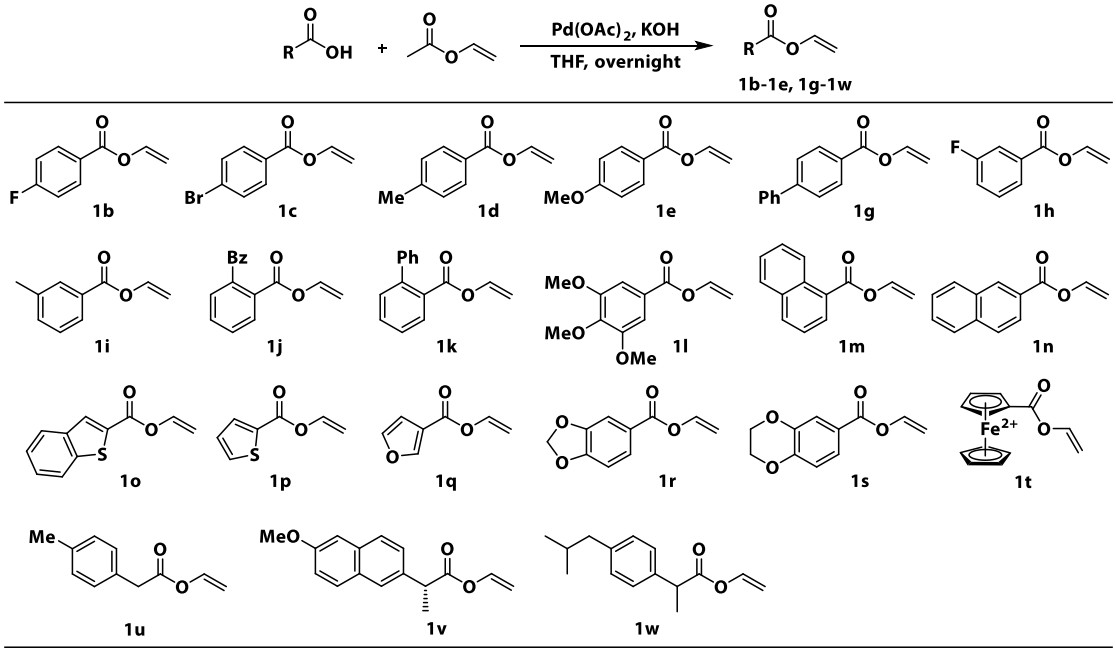
1. General Methods

Unless otherwise stated, all the reagents were purchased from commercial sources (Energy chemical, J&K Chemic, TCI, Fluka, Acros, SCRC), used without further purification. Technical grade petroleum ether (40-60°C bp.) and ethyl acetate were used for chromatography column. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker Advance III 500 spectrometers. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm) or $(CD_3)_2CO$ (2.05 ppm), and ^{13}C NMR spectra were referenced to $CDCl_3$ (77.16 ppm) or $(CD_3)_2CO$ (29.84 ppm). Chemical shift (δ) and coupling constants (J) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: s, singlet, d, doublet, t, triplet, q, quartet, m, multiplet. The chemical shift signals at 1.28 and 0.92 ppm in ^{1}H NMR are the signal peaks of impurities. Electrolysis reactions were conducted using ElectraSyn 2.0 Package supply purchased from IKA Instruments. Cyclic voltammetry (CV) analysis was performed on ElectraSyn 2.0 Package, using a glassy carbon electrode as working electrode, a platinum plated electrode as counter electrode and Ag/AgCl electrode as a reference electrode. Cyclic voltammogram was recorded at 0.2 V/s scan rate. GC yield and mass spectra were recorded on an Agilent GCMS-5977B gas chromatograph-mass spectrometer, where *n*-dodecane was used as the internal standard when determining the yield by GC analysis. High resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI) and time-of-flight (TOF) mass analysis. TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was affected at 254 nm.

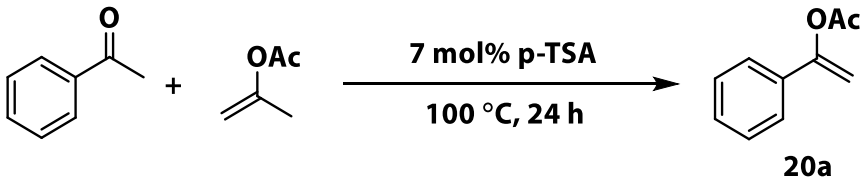
2. Preparation of Starting Materials

General Procedure A for Preparation of 1b-1e and 1g-1w:[1-2] A mixture of the appropriate carboxylic acids (2 mmol), vinyl acetate (4 ml), $Pd(OAc)_2$ (5 mol%, 22.4 mg), and KOH (10 mol%, 11.2 mg) was stirred overnight. After stirring overnight, the mixture was purified by column chromatography with petroleum ether to achieve the target products in moderate to good yields. Of these, the NMR spectra data for

alkenes (**1b**, **1d**, **1e**, and **1n**) are available in the literature and are referenced accordingly.

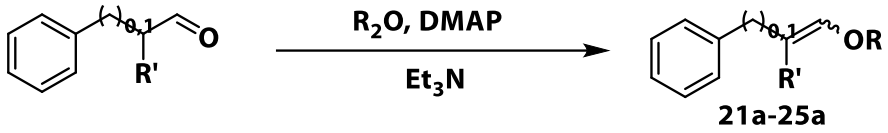


Experimental Procedure B for Preparation of 1-Phenylvinyl Acetate 20a:[3a] To a solution of acetophenone (1.2 g, 10 mmol) in isopropenyl acetate (5.0 g, 5.0 mL, 50 mmol) was added *p*-Toluenesulfonic acid (120.0 mg, 7 mol %). The reaction mixture was refluxed at 100 °C for 24 h, and the remaining isopropenyl acetate was then removed under reduced pressure. The brown oily residue was diluted with ethyl acetate (50 mL), washed with water (15 mL × 3), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by silica gel column to give vinyl acetates.

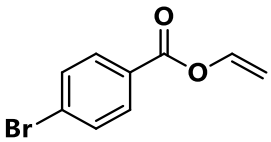


General Procedure C for Preparation of 21a-25a:[3a-b] To a solution of aldehyde (10.0 mmol), anhydride (50.0 mmol), and triethylamine (2.02 g, 20.0 mmol) was added dimethylaminopyridine (122 mg, 1.0 mmol). The reaction mixture was stirred at room temperature for 72 hours, and then poured into ice. The resulting mixture was stirred for 1 hour. The aqueous phase was separated and extracted twice with diethyl

ether. The extract was washed with saturated aqueous solution of Na_2CO_3, water, brine, and dried over anhydrous Na_2SO_4. Diethyl ether was removed under vacuum and the residue was purified by distillation to afford **21a-25a**.



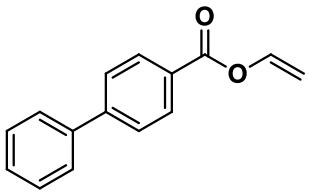
3. Characterization of Starting Materials



Vinyl 4-bromobenzoate (1c)

The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a gray solid, mp 50-51 ºC, 271 mg (60% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.94 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.49 (dd, *J* = 13.9, 6.2 Hz, 1H), 5.08 (dd, *J* = 13.9, 1.8 Hz, 1H), 4.72 (dd, *J* = 6.2, 1.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 162.9, 141.3, 131.9, 131.5, 128.9, 127.8, 98.6.

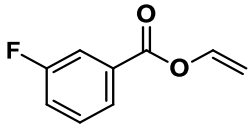
The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.[4a]



Vinyl [1,1'-biphenyl]-4-carboxylate (1g)

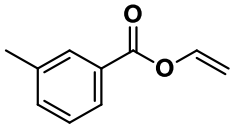
The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a yellow oil, 314 mg (70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.20 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 6.6 Hz, 2H), 7.58 (dd, *J* = 14.0, 6.2 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 5.13 (dd, *J* = 13.9, 1.8 Hz, 1H), 4.75 (dd, *J* = 6.3, 1.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 163.6, 146.4, 141.5, 139.8, 130.6, 129.0, 128.4,

127.6, 127.4, 127.2, 98.3. **HRMS** (ESI) (m/z): calcd for $C_{15}H_{12}O_2Na$ $[M+Na]^+$: 247.0730, found: 247.0728.



Vinyl 3-fluorobenzoate (1h)

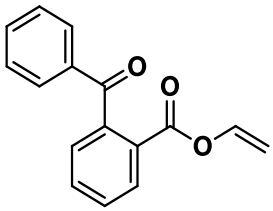
The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a yellow oil, 299 mg (90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.90 (ddt, *J* = 7.7, 2.6, 1.3 Hz, 1H), 7.77 (ddt, *J* = 7.8, 2.7, 1.5 Hz, 1H), 7.54-7.48 (m, 1H), 7.47-7.40 (m, 1H), 7.34-7.26 (m, 1H), 5.10 (dd, *J* = 13.9, 1.8 Hz, 1H), 4.74 (dd, *J* = 6.3, 1.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 162.5 (d, *J* = 247.3 Hz), 162.5 (t, *J* = 3.3 Hz), 141.2, 131.1 (d, *J* = 7.5 Hz), 130.2 (d, *J* = 7.8 Hz), 125.7 (d, *J* = 3.0 Hz), 120.7 (d, *J* = 21.3 Hz), 116.8 (d, *J* = 23.2 Hz), 98.7. **HRMS** (ESI) (m/z): calcd for $C_9H_7FO_2K$ $[M+K]^+$: 205.0062, found: 205.0070.



Vinyl 3-methylbenzoate (1i)

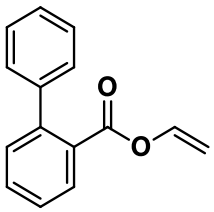
The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a yellow oil, 292 mg (90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.90 (d, *J* = 9.3 Hz, 2H), 7.52 (dd, *J* = 14.0, 6.2 Hz, 1H), 7.39 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.37-7.28 (m, 1H), 5.07 (dd, *J* = 14.0, 1.7 Hz, 1H), 4.70 (dt, *J* = 6.3, 1.5 Hz, 1H), 2.40 (d, *J* = 2.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 163.8, 141.5, 138.4, 134.4, 130.5, 128.8, 128.4, 127.2, 98.1, 21.3.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.[4a]



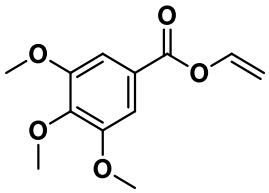
Vinyl 2-benzoylbenzoate (1j)

The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a yellow solid. mp 69-70 ºC, 454 mg (90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.15 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.81-7.73 (m, 2H), 7.69 (td, *J* = 7.5, 1.1 Hz, 1H), 7.63-7.54 (m, 2H), 7.44 (t, *J* = 6.8 Hz, 3H), 7.19 (dd, *J* = 13.9, 6.2 Hz, 1H), 4.76 (dd, *J* = 13.9, 1.8 Hz, 1H), 4.53 (dd, *J* = 6.3, 1.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 196.8, 162.9, 142.3, 140.8, 136.9, 133.3, 133.1, 130.6, 129.7, 129.4, 128.6, 127.9, 127.7, 98.7. **HRMS** (ESI) (m/z): calcd for $C_{16}H_{13}O_3$ $[M+H]^+$: 253.0859, found: 253.0869.



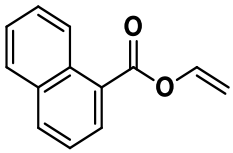
Vinyl [1,1'-biphenyl]-2-carboxylate (1k)

The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a yellow solid. mp 45-46 ºC, 358 mg (80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.07-7.97 (m, 1H), 7.62 (td, *J* = 7.6, 1.4 Hz, 1H), 7.53-7.31 (m, 8H), 4.60 (dt, *J* = 13.9, 2.0 Hz, 1H), 4.54 (dt, *J* = 6.2, 1.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.3, 143.5, 141.3, 141.1, 132.1, 131.1, 130.6, 129.2, 128.5, 128.1, 127.4, 127.3, 98.3. **HRMS** (ESI) (m/z): calcd for $C_{15}H_{12}O_2Na$ $[M+Na]^+$: 247.0730, found: 247.0726.



Vinyl 3,4,5-trimethoxybenzoate (1l)

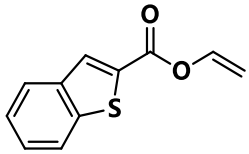
The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a white solid. mp 75-76 ºC, 381 mg (80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.51 (dd, *J* = 13.9, 6.2 Hz, 1H), 7.37 (s, 2H), 5.11 (dd, *J* = 14.0, 1.8 Hz, 1H), 4.74 (dd, *J* = 6.3, 1.8 Hz, 1H), 3.95 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 164.2, 153.0, 142.8, 141.6, 123.8, 107.2, 98.3, 61.0, 56.3. **HRMS** (ESI) (m/z): calcd for $C_{12}H_{15}O_5$ $[M+H]^+$: 239.0914, found: 239.0915.



Vinyl 1-naphthoate (1m)

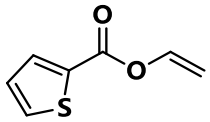
The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a yellow oil, 317 mg (80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 9.00 (d, *J* = 8.7 Hz, 1H), 8.35 (d, *J* = 7.2 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.67 (dt, *J* = 11.9, 7.0 Hz, 2H), 7.57 (dt, *J* = 17.4, 7.8 Hz, 2H), 5.15 (dd, *J* = 14.0, 1.8 Hz, 1H), 4.79 (dd, *J* = 6.2, 1.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 164.2, 141.5, 134.3, 133.9, 131.6, 131.1, 128.7, 128.2, 126.4, 125.7, 125.4, 124.5, 98.3.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.[4a]



Vinyl benzo[b]thiophene-2-carboxylate (1o)

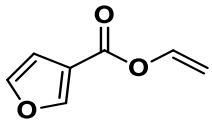
The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a yellow oil, 204 mg (50% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.19 (s, 1H), 7.92 (t, *J* = 9.0 Hz 2H), 7.51 (dd, *J* = 14.0, 6.3 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 5.14 (dd, *J* = 13.9, 1.9 Hz, 1H), 4.77 (dd, *J* = 6.2, 1.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 159.9, 142.6, 141.1, 138.6, 132.1, 131.8, 127.4, 125.8, 125.1, 122.8, 98.7. **HRMS** (ESI) (m/z): calcd for $C_{11}H_9O_2S$ $[M+H]^+$: 205.0318, found: 205.0325.



Vinyl thiophene-2-carboxylate (1p)

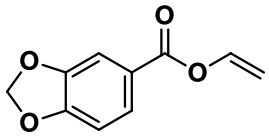
The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a yellow oil, 154 mg (50% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.91 (dt, *J* = 3.8, 1.0 Hz, 1H), 7.65 (dt, *J* = 4.8, 1.0 Hz, 1H), 7.46 (dd, *J* = 13.9, 6.2 Hz, 1H), 7.22-7.09 (m, 1H), 5.07 (dd, *J* = 13.9, 1.7 Hz, 1H), 4.71 (dd, *J* = 6.3, 1.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 159.3, 141.1, 134.6, 133.7, 132.3, 128.1, 98.3.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.[4b]



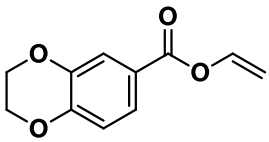
Vinyl furan-3-carboxylate (1q)

The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a yellow oil, 138 mg (50% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.11 (s, 1H), 7.46 (s, 1H), 7.43 (t, *J* = 6.8 Hz, 1H), 6.80 (d, *J* = 1.8 Hz, 1H), 5.00 (dd, *J* = 13.9, 1.6 Hz, 1H), 4.66 (dd, *J* = 6.3, 1.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 160.1, 148.7, 144.1, 140.9, 118.3, 109.8, 98.0. **HRMS** (ESI) (m/z): calcd for $C_7H_6O_3Na$ $[M+Na]^+$: 161.0209, found: 161.0210.



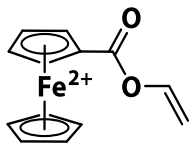
Vinyl benzo[d][1,3]dioxole-5-carboxylate (1r)

The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield an orange oil, 307 mg (80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.75-7.65 (m, 1H), 7.61-7.42 (m, 2H), 6.85 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.04 (t, *J* = 2.6 Hz, 2H), 5.03 (dd, *J* = 14.0, 1.7 Hz, 1H), 4.67 (dd, *J* = 6.3, 1.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 162.9, 152.2, 147.9, 141.4, 126.1, 122.7, 109.7, 108.1, 102.0, 97.9. **HRMS** (ESI) (m/z): calcd for $C_{10}H_9O_4$ $[M+H]^+$: 193.0495, found: 193.0499.



Vinyl 2,3-dihydrobenzo[b][1,4]dioxine-6-carboxylate (1s)

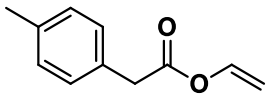
The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a white soild, mp 67-68 ºC, 165 mg (40% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.84-7.55 (m, 2H), 7.47 (dd, *J* = 14.0, 6.3 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 5.02 (dd, *J* = 14.0, 1.6 Hz, 1H), 4.65 (dd, *J* = 6.3, 1.6 Hz, 1H), 4.35-4.29 (m, 2H), 4.29-4.24 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 163.1, 148.4, 143.3, 141.5, 124.0, 122.0, 119.4, 117.3, 97.8, 64.7, 64.1. **HRMS** (ESI) (m/z): calcd for $C_{11}H_{11}O_4$ $[M+H]^+$: 207.0652, found: 207.0652.



Vinyl terrocenecarboxylate (1t)

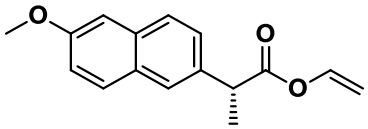
The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE/EA = 10:1) to yield an orange oil, 458 mg (80%

yield). **^{1}H NMR** (500 MHz, $(CD_3)_2CO$, ppm) δ = 7.44 (dd, *J* = 14.0, 6.3 Hz, 1H), 4.96 (dd, *J* = 14.0, 1.4 Hz, 1H), 4.88-4.83 (m, 2H), 4.63 (dd, *J* = 6.3, 1.4 Hz, 1H), 4.57-4.52 (m, 2H), 4.25 (s, 4H). **^{13}C NMR** (126 MHz, $(CD_3)_2CO$, ppm) δ = 169.1, 142.2, 97.2, 72.8, 71.0, 70.7, 70.3, 68.6. **HRMS** (ESI) (m/z): calcd for $C_{13}H_{11}FeO_2$ $[M-H]^+$: 255.0306, found: 255.0306.



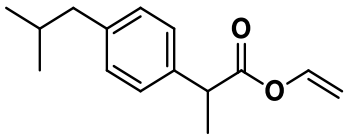
Vinyl 2-(p-tolyl)acetate (1u)

The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a yellow oil, 317 mg (90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.31 (dd, *J* = 14.0, 6.3 Hz, 1H), 7.24-7.15 (m, 4H), 4.93 (dd, *J* = 14.0, 1.5 Hz, 1H), 4.61 (dd, *J* = 6.3, 1.7 Hz, 1H), 3.68 (s, 2H), 2.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 168.9, 141.4, 137.0, 130.1, 129.4, 129.2, 98.0, 40.5, 21.1. **HRMS** (ESI) (m/z): calcd for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0910, found: 177.0909.



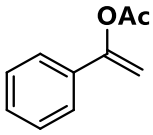
(R)-vinyl 2-(6-methoxynaphthalen-2-yl)propanoate (1v)

The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a colorless oil, 410 mg (80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.76-7.67 (m, 3H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.29 (dd, *J* = 14.0, 6.3 Hz, 1H), 7.16 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.13 (d, *J* = 1.9 Hz, 1H), 4.87 (d, *J* = 14.0 Hz, 1H), 4.56 (d, *J* = 6.2 Hz, 1H), 3.93 (d, *J* = 8.4 Hz, 4H), 1.63 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 171.8, 157.8, 141.4, 134.8, 133.8, 129.3, 128.9, 127.3, 126.1, 119.1, 105.6, 98.0, 55.3, 45.2, 18.5. **HRMS** (ESI) (m/z): calcd for $C_{16}H_{17}O_3$ $[M+H]^+$: 257.1172, found: 257.1170.



Vinyl 2-(4-isobutylphenyl)propanoate (1w)

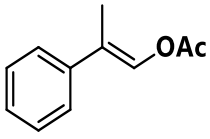
The title compound was synthesized following **General Procedure A** and purified by flash chromatography on silica gel (PE) to yield a colorless oil, 348 mg (75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.36-7.26 (m, 3H), 7.18 (dd, *J* = 8.2, 3.2 Hz, 2H), 4.91 (dt, *J* = 14.0, 1.6 Hz, 1H), 4.59 (dd, *J* = 6.3, 1.6 Hz, 1H), 3.82 (qd, *J* = 7.1, 3.1 Hz, 1H), 2.52 (dd, *J* = 7.2, 3.7 Hz, 2H), 1.97-1.86 (m, 1H), 1.59 (dd, *J* = 7.2, 2.8 Hz, 3H), 0.97 (dd, *J* = 6.8, 4.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 171.8, 141.5, 140.8, 137.0, 129.5, 127.3, 97.8, 45.1, 44.9, 30.2, 22.4, 18.5. **HRMS** (ESI) (m/z): calcd for $C_{15}H_{21}O_2$ $[M+H]^+$: 233.1536, found: 233.1545.



1-Phenylvinyl acetate (20a)

The title compound was synthesized following **Procedure B** and purified by flash chromatography on silica gel (PE/EA = 10:1) to yield a yellow oil, 697 mg (43% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.51 (dd, *J* = 7.0, 1.2 Hz, 2H), 7.42-7.33 (m, 3H), 5.52 (d, *J* = 2.1 Hz, 1H), 5.07 (d, *J* = 2.2 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 169.2, 153.0, 134.3, 129.0, 128.6, 124.9, 102.2, 21.0.

The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.[3a]

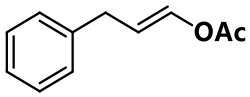


(E)-2-Phenylprop-1-en-1-yl acetate (21a, E/Z= 6.9:1)

The title compound was synthesized following **General Procedure C** and purified by flash chromatography on silica gel (PE/EA = 10:1) to yield a yellow oil, 881 mg (50%

yield). The Z/E ratio was determined by ^{1}H NMR in comparison to related compounds in the literature.[3b] **^{1}H NMR** (500 MHz, $CDCl_3$, E/Z mixture) δ = 7.57 (q, *J* = 1.5 Hz, 1H), 7.45-7.41 (m, 2H), 7.40-7.32 (m, 2H), 7.32-7.26 (m, 1H), 2.25 (s, 2.62H), 2.16 (s, 0.38H), 2.14 (d, *J* = 1.6 Hz, 2.62H), 2.06 (d, *J* = 1.5 Hz, 0.38H). **^{13}C NMR** (126 MHz, $CDCl_3$, E/Z mixture) δ = 168.1, 139.1, 137.5, 132.6, 130.7, 128.5, 128.1, 128.0, 127.3, 127.3, 125.8, 121.6, 119.7, 28.1, 20.9, 19.0, 13.6.

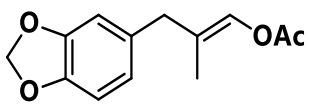
The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.[3b]



(E)-3-Phenylprop-1-en-1-yl acetate (22a, E/Z= 1.3:1)

The title compound was synthesized following **General Procedure C** and purified by flash chromatography on silica gel (PE/EA = 10:1) to yield a yellow oil, 634 mg (36% yield). The Z/E ratio was determined by ^{1}H NMR in comparison to related compounds in the literature.[3a] **^{1}H NMR** (500 MHz, $CDCl_3$, E/Z mixture) δ = 7.37-7.30 (m, 2H), 7.25 (ddt, *J* = 6.9, 5.4, 1.7 Hz, 3H), 5.63 (dt, *J* = 12.4, 7.6 Hz, 0.42H), 5.13 (td, *J* = 7.6, 6.3 Hz, 0.58H), 3.55 (d, *J* = 7.6 Hz, 1.14H), 3.38 (d, *J* = 7.5 Hz, 0.86H), 2.22 (s, 1.7H), 2.16 (s, 1.3H). **^{13}C NMR** (126 MHz, $CDCl_3$, E/Z mixture) δ =168.2, 168.1, 140.1, 139.8, 136.4, 134.7, 128.6, 128.5, 128.4, 128.3, 126.4, 126.2, 113.8, 112.5, 33.6, 30.7, 20.8, 20.7.

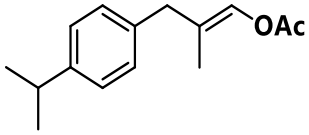
The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.[3a]



(E)-3-(Benzo[d][1,3]dioxol-5-yl)-2-methylprop-1-en-1-yl acetate (23a, E/Z= 1.4:1)

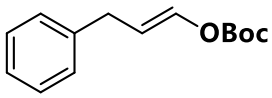
The title compound was synthesized following **General Procedure C** and purified by flash chromatography on silica gel (PE/EA = 10:1) to yield a yellow oil, 539 mg (23% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, E/Z mixture) δ = 7.07-6.98 (m, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.70-6.63 (m, 2H), 5.93 (s, 2H), 3.38 (s, 0.82H), 3.19 (s, 1.18H), 2.18 (s, 1.24H), 2.16 (s, 1.76H), 1.61 (d, *J* = 1.5 Hz, 1.76H), 1.58 (d, *J* = 1.6 Hz, 1.24H). **^{13}C**

NMR (126 MHz, $CDCl_3$, E/Z mixture) δ = 168.3, 147.7, 146.1, 145.9, 132.9, 132.8, 131.2, 130.4, 121.7, 121.5, 121.3, 121.0, 109.1, 109.0, 108.1, 108.1, 100.9, 100.8, 40.0, 35.5, 20.8, 20.8, 17.2, 13.4. **HRMS** (ESI) (m/z): calcd for $C_{13}H_{14}O_4Na$ $[M+Na]^+$: 257.0784, found: 257.0787.



(E)-3-(4-Isopropylphenyl)-2-methylprop-1-en-1-yl acetate (24a, E/Z= 1.8:1)

The title compound was synthesized following **General Procedure C** and purified by flash chromatography on silica gel (PE/EA = 10:1) to yield a yellow oil, 1417 mg (61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, E/Z mixture) δ = 7.21-7.11 (m, 4H), 7.11-6.97 (m, 1H), 3.47 (s, 0.72H), 3.27 (s, 1.28H), 2.92 (ddd, *J* = 11.8, 7.9, 5.8 Hz, 1H), 2.18 (dd, *J* = 6.3, 1.3 Hz, 3H), 1.63 (dd, *J* = 14.9, 1.6 Hz, 3H), 1.28 (dt, *J* = 7.0, 1.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, E/Z mixture) δ = 168.4, 168.3, 146.9, 146.7, 136.4, 136.3, 131.2, 130.5, 128.7, 128.6, 126.5, 126.4, 121.4, 121.1, 40.0, 35.4, 33.7, 24.1, 24.1, 20.8, 20.8, 17.4, 13.6. **HRMS** (ESI) (m/z): calcd for $C_{15}H_{20}O_2Na$ $[M+Na]^+$: 255.1356, found: 255.1358.



(E)-tert-Butyl (3-phenylprop-1-en-1-yl) carbonate (25a, E/Z= 2.1:1)

The title compound was synthesized following **General Procedure C** and purified by flash chromatography on silica gel (PE/EA = 10:1) to yield a yellow oil, 1874 mg (80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, E/Z mixture) δ = 7.33 (ddd, *J* = 8.2, 5.8, 1.5 Hz, 2H), 7.27-7.19 (m, 3H), 7.04-6.94 (m, 1H), 5.61 (dt, *J* = 12.3, 7.5 Hz, 0.32H), 5.05 (td, *J* = 7.5, 6.3 Hz, 0.68H), 3.58-3.54 (m, 1.35H), 3.39-3.35 (m, 0.65H), 1.57 (s, 6.06H), 1.55 (s, 2.94H). **^{13}C NMR** (126 MHz, $CDCl_3$, E/Z mixture) δ = 151.1, 151.1, 140.2, 139.7, 137.6, 135.9, 128.5, 128.5, 128.4, 128.4, 126.3, 126.1, 113.0, 111.8, 83.3, 83.2,

33.4, 30.5, 27.7, 27.7. **HRMS** (ESI) (m/z): calcd for $C_{14}H_{18}O_3Na$ $[M+Na]^+$: 257.1148, found: 257.1151.

4. General Procedures of Electrochemical Reaction

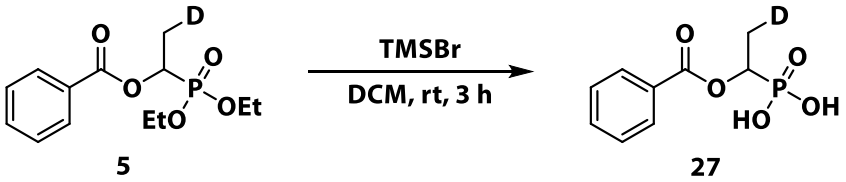
General Procedure D for Preparation of Desired Products 3: A mixture of alkenes **1** (0.4 mmol), **2** (0.48 mmol), Et_4NPF_6 (1 equiv.), Et_3N (2.5 equiv.) in 4 mL DMF/NMP (1:1 *v/v*) was added to an electrolytic cell (30 mL). The electrolytic cell was equipped with graphite rod (ϕ 6 mm) as an anode and Al plate (1 cm×1 cm×0.2 cm) as a cathode. The solution was electrolyzed at ambient temperature under a constant current (j = 10 mA/cm^2) for 6-10 h. After electrolysis, the mixture was poured into water and extracted with ethyl acetate twice. The combined organic layer was washed with brine (10 mL) and dried over $MgSO_4$, filtered and concentrated. The resulting mixture was purified by silica gel column chromatography (eluted with petroleum ether/ethyl acetate/ethanol) to afford the desired products.

General Procedure E for Preparation of Monodeuterated Organophosphorus Compounds: A mixture of alkenes **1** (0.4 mmol), **2** (0.48 mmol), Et_4NPF_6 (0.1 M), Et_3N (2.5 equiv.), D_2O (25 equiv.) in 4 mL dry DMF/NMP (1:1 *v/v*) was added to an electrolytic cell (30 mL). The electrolytic cell was equipped with graphite rod (ϕ 6 mm) as an anode and Al plate (1 cm×1 cm×0.2 cm) as a cathode. The solution was electrolyzed at ambient temperature under a constant current (j = 10 mA/cm^2) for 6 h. After electrolysis, the mixture was poured into water and extracted with ethyl acetate twice. The combined organic layer was washed with brine (10 mL) and dried over $MgSO_4$, filtered and concentrated. The resulting mixture was purified by silica gel column chromatography (eluted with petroleum ether/ethyl acetate/ethanol) to afford the desired products.

Experimental Procedure for the Scale-up Synthesis of 3aa and 3fa: A mixture of **1a** (8 mmol, 1.184 g) or **1f** (8 mmol, 1.633 g), **2a** (9.6 mmol, 1.325 g), Et_4NPF_6 (8 mmol, 2.202 g), Et_3N (20 mmol, 2.024 g) in 80 mL DMF/NMP (1:1 *v/v*) was added to

a beaker (100 mL). The electrolytic cell was equipped with graphite rod (ϕ 20 mm) as an anode and Al plate (3 cm×3 cm×0.2 cm) as a cathode. The solution was electrolyzed at ambient temperature under a constant current (j = 8.89 mA/cm^2) for 15 h. After electrolysis, the mixture was poured into water and extracted with ethyl acetate three times. The combined organic layer was washed with brine (30 mL) and dried over $MgSO_4$, filtered and concentrated. The resulting mixture was purified by silica gel column chromatography (eluted with petroleum ether/ethyl acetate/ethanol) to afford **3aa** (1.922 g, 84%) and **3fa** (2.217 g, 81%).

Experimental Procedure for the Scale-up Synthesis of 5 and 16: A mixture of **1a** (5 mmol, 0.740 g), **2a** (6 mmol, 0.828 g) or **2h** (6 mmol, 1.212 g), Et_4NPF_6 (5 mmol, 1.376 g), Et_3N (12.5 mmol, 1.265 g), D_2O (125 mmol, 2.500 g) in 50 mL dry DMF/NMP (1:1 *v/v*) was added to a beaker (100 mL). The electrolytic cell was equipped with graphite rod (ϕ 20 mm) as an anode and Al plate (3 cm×3 cm×0.2 cm) as a cathode. The solution was electrolyzed at ambient temperature under a constant current (j = 5.56 mA/cm^2) for 10 h. After electrolysis, the mixture was poured into water and extracted with ethyl acetate three times. The combined organic layer was washed with brine (30 mL) and dried over $MgSO_4$, filtered and concentrated. The resulting mixture was purified by silica gel column chromatography (eluted with petroleum ether/ethyl acetate/ethanol) to afford **5** (1.134 g, 79%) and **16** (1.492 g, 85%).



5 27

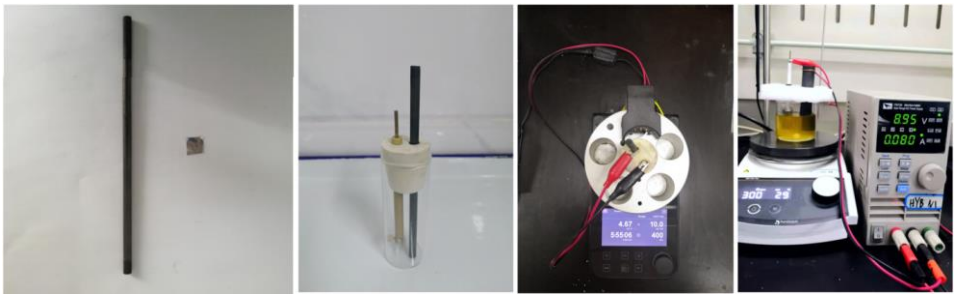
Experimental Procedure F for Preparation of Phosphoric Acid 27：5 (299 mg, 1.04 mmol) and bromotrimethylsilane (0.270 mL, 2.08 mmol) were dissolved in 10 mL dry dichloromethane at room temperature under an N_2 atmosphere and the resulting mixture was stirred for 36 h. Upon completion, the reaction mixture was

evaporated to dryness, and the residue was purified by column chromatographically (silica; dichloromethane/methanol; 10:1, *v*/*v*) to obtain **27** in 73% yield (175 mg).

5. Photographic Guide for Electrochemical Reaction

5.1 Overview of Materials Used

From left to right: 1) graphite rod (ϕ 6 mm) and Al plate (1 cm×1 cm×0.1 cm). 2) electrolysis device. 3) electrolysis reaction using ElectraSyn 2.0 Package. 4) scale-up experiment device.



5.2 CV Analysis Device

From left to right: 1) Pt plate electrode (1 cm×1 cm×0.1 cm). 2) glassy carbon electrode (ϕ = 6 mm). 3) Ag/AgCl (saturated KCl) reference electrode.

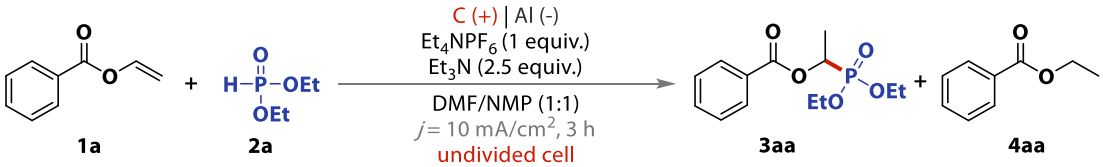
Fig. 5.2.1

Fig. 5.2.2

Fig. 5.2.3

6. Optimization of the Reaction Conditions

6.1 Table S1. Optimization of the Reaction Conditions



Entry	Variation from standard conditions	Yield of 3aa/4aa (%)[b]
1	***none***	***95/<5***
2	DMSO, DMF or NMP as solvent	54/38; 75/10; 64/33
3	DMF/NMP (3:1or 1:3) as solvent	88/<5; 84/11
4	NaOAc or DBU as base	75/16; 52/43
5	Et_3N (4 or 0 equiv.)	61/36; 21/43
6	$^nBu_4NPF_6$ or $^nBu_4NBF_4$ as electrolyte	86/8; 64/30
7	graphite rod cathode (ϕ 6 mm)	<5/90
8	Ni plate cathode (1 cm×1 cm)	31/65
9	j = 12 mA/cm^2	85/12
10	dry DMF/NMP	32/<5
11	no electricity	0/0

[a] Reaction conditions: undivided cell, graphite rod anode (ϕ 6 mm), Al plate cathode (1 cm×1 cm), constant current (j = 10 mA/cm^2), **1a** (0.2 mmol), **2a** (0.24 mmol), Et_4NPF_6 (1 equiv.), Et_3N (2.5 equiv.), DMF/NMP = (1:1, *v/v*, 2 mL), air, 3 h. [b] Yields were by GC analysis with *n*-dodecane as the internal standard.

We began our exploration through the electrochemical hydrophosphonylation of vinyl benzoate **1a** with diethyl phosphonate **2a** (**Table S1**). Initially, electrolysis was performed in an undivided cell equipped with graphite rod anode and Al cathode in a mixed solvent of DMF/NMP (1:1) under a constant current (j = 10 mA/cm^2), using Et_4NPF_6 as electrolyte, and Et_3N as base. Gratifyingly, the reaction provided phosphonate **3aa** in an excellent yield of 95% through Markovnikov's rule, as well as a trace amount of hydrogenation by-product **4aa** (Entry 1). After the subsequent solvent screening, single solvents, such as DMSO, DMF, and NMP, resulted in decreased yields (Entry 2). Changing the ratio of DMF and NMP to 3:1 or 1:3 led to a slight decrease in yield (Entry 3). Replacing Et_3N with other bases of varying strength, including NaOAc and DBU, did not show an increase in yield (Entry 4). Increasing the amount of Et_3N resulted in a slight decrease in **3aa**, while no addition of base resulted in a rapid decrease in **3aa** and an increase in **4aa** (Entry 5). The use of other electrolytes, such as $^nBu_4NPF_6$, and $^nBu_4NBF_4$, did not give satisfactory results (Entry 6). By comparison with graphite rod and Ni plate, Al plate was considered the most suitable cathode, among which the use of graphite rod cathode was beneficial to the generation of **4aa** (Entries 7-8). When the current (j = 12 mA/cm^2) increased, a

slightly decreased yield was obtained (Entry 9). Using anhydrous solvent mixtures resulted in a rapid drop in yield (Entry 10). In addition, no **3aa** and **4aa** were obtained in the absence of electricity (Entry 11).

7. D_2O Dosage Screening

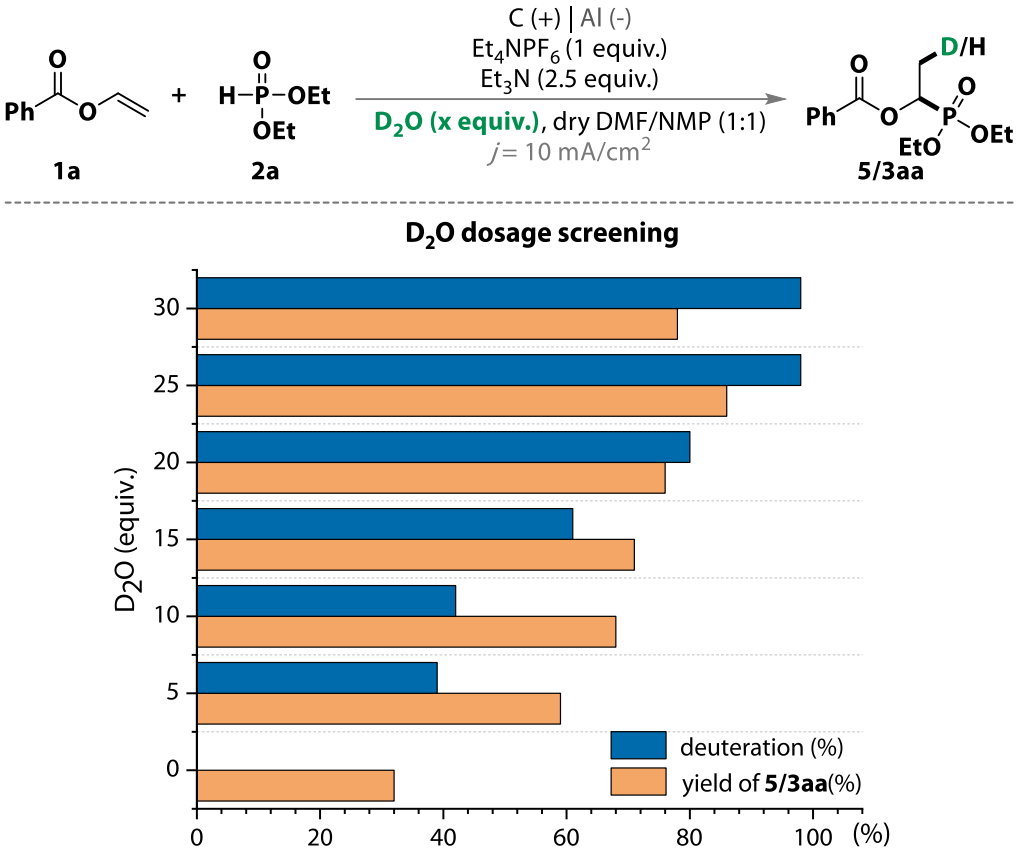


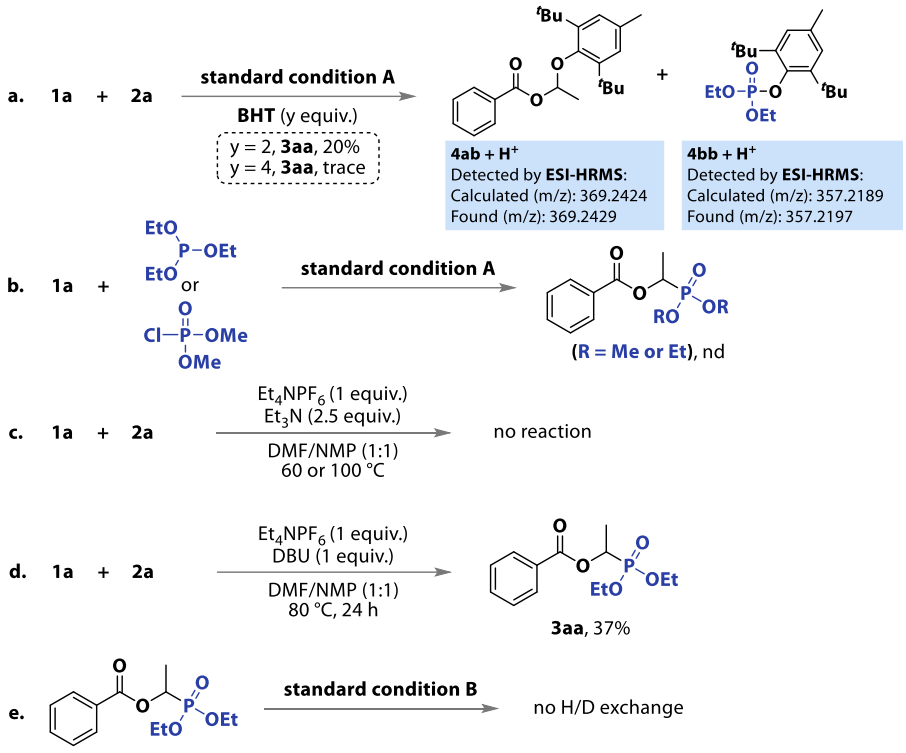
Figure S1. D_2O dosage screening. Yields and D-incorporation were determined by ^1H NMR analysis with CH_2Br_2 as the internal standard.

To obtain monodeuterated products efficiently through the established electrochemical-induced Markovnikov-type hydrophosphonylation strategy, we subsequently investigated the changes in yield and D-incorporation of organophosphorus products under different D_2O dosages (**Figure S1**). With the increase in the amount of D_2O, the yield and D-incorporation of organophosphorus products were increasing, accompanied by the increase in the proportion of the monodeuterated product **5**. When D_2O was increased to 25 equiv., the yield and

D-incorporation reached the maximum. When using 30 equivalents of D_2O, the yield dropped slightly. Therefore, the use of 25 equivalents of D_2O was considered to be the most suitable for the synthesis of monodeuterated products.

8. Mechanistic Investigations

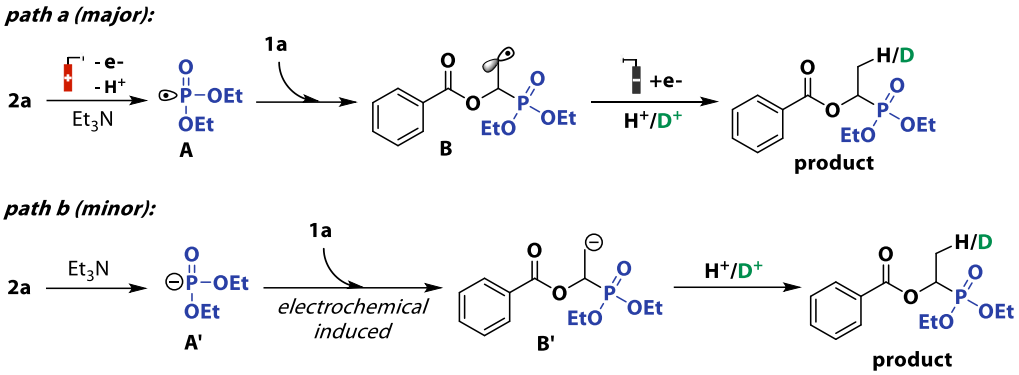
To investigate the reaction mechanism in-depth, several control experiments were performed (**Scheme S1**). Radical scavenger addition experiments showed that the reaction could be effectively inhibited when BHT (2,2,6,6-tetramethylpiperidine-1-oxyl) was gradually increased to 4 equivalents. Notably, the free radical trapping products, **4ab** ($[M + H]^+$ = 369.2429) and **4bb** ($[M + H]^+$ = 357.2197), had been detected by ESI-HRMS analysis of the reaction solution, indicating that the electrochemical hydrophosphonylation might undergo a radical process (**Scheme S1a**). When nucleophilic triethyl phosphite or electrophilic dimethyl phosphorochloridate was used instead of **2a**, no hydrophosphonylation products were detected under standard electrochemical conditions (**Scheme S1b**), suggesting that the reaction was not *via* a simple electrophilic or nucleophilic addition. The reaction couldn't proceed when heated to 60 or 100 ℃ without electricity and the raw material were retained (**Scheme S1c**). When the multifunctional base DBU was used, 37% of the expected product could be detected after performing the reaction at 80 °C for 24 h. It was speculated that part of the products could be obtained by the nucleophilic addition process (**Scheme S1d**). Meanwhile, it was proved that no H/D exchange occurred (**Scheme S1e**).



Scheme S1. Control experiments.

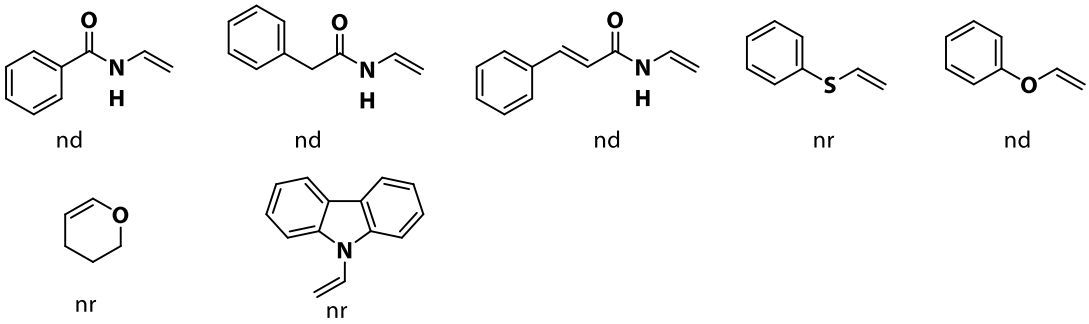
9. Proposed Mechanism

A possible mechanism is then proposed based on the above experimental results (**Scheme S2**). With the assistance of Et_3N, **2a** is first converted to a phosphonyl radical intermediate **A** by electrochemical induction, which then attacks alkene **1a** to generate radical intermediate **B**. Radical intermediate **B** can be converted to the product by further reduction and protonation processes (*path a*). In addition, a few products may also be obtained by electrochemically induced nucleophilic addition (*path b*). Under the action of base, **2a** is first converted into a phosphonyl anion, which then attacks alkene **1a** by electrochemically induced nucleophilic addition to form intermediate **B'**. Subsequently, the protonation of intermediate **B'** leads to the formation of the product.



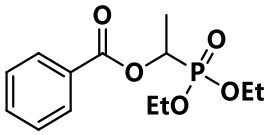
Scheme S2. Proposed mechanism

10. Other Alkene Compounds Examined



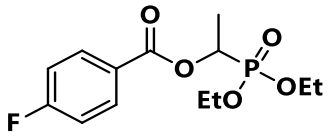
We had tried several amide substrates, but no corresponding product was observed in the reaction. The alkene substrates were either retained or decomposed by C-N bond cleavage. Phenyl(vinyl)sulfane was stable in electrolysis and retained completely. The reaction of (vinyloxy)benzene with diethyl phosphite yielded the homocoupling byproduct without the expected product formation. The use of 3,4-dihydro-2*H*-pyran and 9-vinyl-9*H*-carbazole did not obtain the expected product, and the starting material remained.

11. Characterization of Products



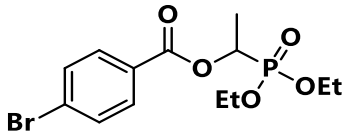
1-(Diethoxyphosphoryl)ethyl benzoate (3aa)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 102 mg (89% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.02 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 5.49 (quint, *J* = 7.2 Hz, 1H), 4.15 (quint, *J* = 7.2 Hz, 4H), 1.55 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.3 (d, *J* = 7.6 Hz), 133.4, 129.8, 129.5, 128.5, 64.9 (d, *J* = 171.2 Hz), 62.9 (d, *J* = 6.9 Hz), 62.7 (d, *J* = 6.4 Hz), 16.5 (d, *J* = 5.6 Hz), 16.4 (d, *J* = 5.8 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.37. **HRMS** (ESI) (m/z): calcd for $C_{13}H_{20}O_5P$ $[M+H]^+$: 287.1046, found: 287.1043.



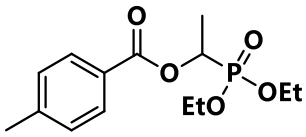
1-(Diethoxyphosphoryl)ethyl 4-fluorobenzoate (3ba)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 92 mg (76% yeld). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.08 (ddt, *J* = 8.8, 5.4, 2.7 Hz, 2H), 7.13 (td, *J* = 8.8, 2.8 Hz, 2H), 5.50 (m, 1H), 4.18 (m, 4H), 1.58 (ddd, *J* = 16.7, 7.1, 2.8 Hz, 3H), 1.32 (tt, *J* = 7.0, 2.8 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 166.0 (d, *J* = 254.6 Hz), 164.4 (d, *J* = 7.7 Hz), 132.4 (d, *J* = 9.4 Hz), 125.8 (d, *J* = 2.9 Hz), 115.7 (d, *J* = 22.1 Hz), 65.1 (d, *J* = 171.5 Hz), 63.0 (d, *J* = 6.9 Hz), 62.8 (d, *J* = 6.5 Hz), 16.5 (d, *J* = 5.6 Hz), 16.5 (d, *J* = 5.7 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.34. **HRMS** (ESI) (m/z): calcd for $C_{13}H_{19}FO_5P$ $[M+H]^+$: 305.0949, found: 305.0948.



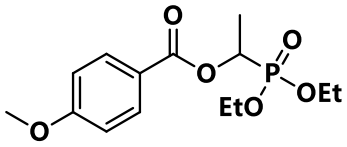
1-(Diethoxyphosphoryl)ethyl 4-bromobenzoate (3ca)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 66 mg (45% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.94 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.62 (dd, *J* = 8.5, 1.5 Hz, 2H), 5.52 (quint, *J* = 8.3, 7.7 Hz, 1H), 4.20 (quint, *J* = 7.1 Hz, 4H), 1.60 (ddd, *J* = 16.7, 7.1, 1.6 Hz, 3H), 1.36-1.31 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 164.7 (d, *J* = 7.6 Hz), 131.9, 131.3, 128.6, 128.4, 65.2 (d, *J* = 171.5 Hz), 63.0 (d, *J* = 6.9 Hz), 62.8 (d, *J* = 6.4 Hz), 16.5 (d, *J* = 5.6 Hz), 16.5 (d, *J* = 5.8 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.16. **HRMS** (ESI) (m/z): calcd for $C_{13}H_{19}BrO_5P$ $[M+H]^+$: 365.0149, found: 365.0149.



1-(Diethoxyphosphoryl)ethyl 4-methylbenzoate (3da)

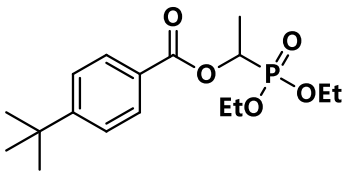
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 103 mg (86% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.91 (d, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 5.47 (quint, *J* = 7.2 Hz, 1H), 4.14 (quint, *J* = 7.0 Hz, 4H), 2.36 (s, 3H), 1.53 (dd, *J* = 16.3, 6.6 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.4 (d, *J* = 7.7 Hz), 144.1, 129.8, 129.2, 126.7, 64.7 (d, *J* = 171.3 Hz), 63.0 (d, *J* = 6.9 Hz), 62.7 (d, *J* = 6.4 Hz), 21.7, 16.5 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 5.8 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.56. **HRMS** (ESI) (m/z): calcd for $C_{14}H_{22}O_5P$ $[M+H]^+$: 301.1199, found: 301.1198.



1-(Diethoxyphosphoryl)ethyl 4-methoxybenzoate (3ea)

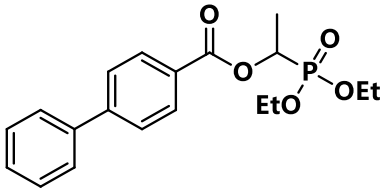
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 95 mg (75% yield). $\mathbf{R_f}$ = 0.4

(PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.96 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.44 (quint, *J* = 7.1 Hz, 1H), 4.16-4.09 (m, 4H), 3.80 (s, 3H), 1.51 (dd, *J* = 16.8, 7.1 Hz, 3H), 1.26 (td, *J* = 7.0, 3.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.0 (d, *J* = 7.9 Hz), 163.7, 131.9, 121.8, 113.7, 64.5 (d, *J* = 171.3 Hz), 63.0 (d, *J* = 6.9 Hz), 62.7 (d, *J* = 6.4 Hz), 55.4, 16.5 (d, *J* = 5.6 Hz), 16.4 (d, *J* = 5.8 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.70. **HRMS** (ESI) (m/z): calcd for $C_{14}H_{22}O_6P$ $[M+H]^+$: 317.1149, found: 317.1149.



1-(Diethoxyphosphoryl)ethyl 4-(tert-butyl)benzoate (3fa)

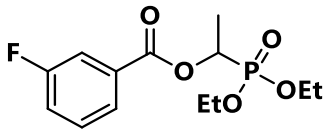
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 118 mg (86% yield). **R_f** = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.98 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 5.51 (quint, *J* = 7.1 Hz, 1H), 4.18 (quint, *J* = 7.4 Hz, 4H), 1.57 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.36-1.26 (m, 15H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.3 (d, *J* = 7.7 Hz), 157.1, 129.7, 126.7, 125.4, 64.7 (d, *J* = 171.1 Hz), 63.0 (d, *J* = 6.9 Hz), 62.7 (d, *J* = 6.4 Hz), 35.1, 31.1, 16.5 (d, *J* = 5.6 Hz), 16.4 (d, *J* = 5.6 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.55. **HRMS** (ESI) (m/z): calcd for $C_{17}H_{28}O_5P$ $[M+H]^+$: 343.1669, found: 343.1669.



1-(Diethoxyphosphoryl)ethyl [1,1'-biphenyl]-4-carboxylate (3ga)

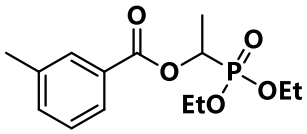
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 127 mg (88% yield). **R_f** = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.12 (d, *J* = 8.4

Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.60 (dd, *J* = 7.1, 1.4 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.38 (q, *J* = 7.5, 6.7 Hz, 1H), 5.62-5.46 (m, 1H), 4.18 (quint, *J* = 6.9 Hz, 4H), 1.59 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.3 (d, *J* = 7.7 Hz), 146.1, 139.8, 130.4, 129.0, 128.3, 128.2, 127.3, 127.2, 65.0 (d, *J* = 171.2 Hz), 63.0 (d, *J* = 6.9 Hz), 62.8 (d, *J* = 6.5 Hz), 16.6 (d, *J* = 5.5 Hz), 16.5 (d, *J* = 5.8 Hz), 15.3. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.49. **HRMS** (ESI) (m/z): calcd for $C_{19}H_{24}O_5P$ $[M+H]^+$: 363.1356, found: 363.1355.



1-(Diethoxyphosphoryl)ethyl 3-fluorobenzoate (3ha)

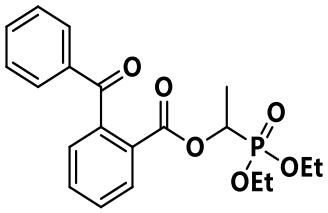
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 88 mg (72% yield). **R_f** = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.81 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.39 (q, *J* = 7.8, 6.9 Hz, 1H), 7.24 (t, *J* = 8.2 Hz, 1H), 5.46 (quint, *J* = 7.1 Hz, 1H), 4.14 (quint, *J* = 7.0 Hz, 4H), 1.54 (ddd, *J* = 17.0, 7.0, 1.5 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 164.2 (dd, *J* = 7.5, 3.3 Hz), 162.5 (d, *J* = 247.4 Hz), 131.6 (d, *J* = 7.6 Hz), 130.2 (d, *J* = 7.8 Hz), 125.5 (d, *J* = 3.0 Hz), 120.4 (d, *J* = 21.2 Hz), 116.6 (d, *J* = 23.1 Hz), 65.3 (d, *J* = 171.3 Hz), 62.9 (d, *J* = 6.9 Hz), 62.8 (d, *J* = 6.4 Hz), 16.5 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 5.8 Hz), 15.1. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.03. **HRMS** (ESI) (m/z): calcd for $C_{13}H_{19}FO_5P$ $[M+H]^+$: 305.0949, found: 305.0947.



1-(Diethoxyphosphoryl)ethyl 3-methylbenzoate (3ia)

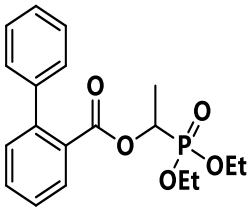
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 108 mg (84% yield). **R_f** = 0.6

(PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.86 (d, *J* = 9.3 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 5.52 (quint, *J* = 7.2 Hz, 1H), 4.18 (quint, *J* = 7.1, 6.2 Hz, 4H), 2.40 (s, 3H), 1.58 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.31 (td, *J* = 7.1, 3.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.5 (d, *J* = 7.5 Hz), 138.3, 134.2, 130.3, 129.4, 128.4, 127.0, 64.8 (d, *J* = 171.2 Hz), 63.0 (d, *J* = 6.9 Hz), 62.7 (d, *J* = 6.4 Hz), 21.3, 16.5 (d, *J* = 5.6 Hz), 16.5 (d, *J* = 5.7 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.54. **HRMS** (ESI) (m/z): calcd for $C_{14}H_{22}O_5P$ $[M+H]^+$: 301.1199, found: 301.1199.



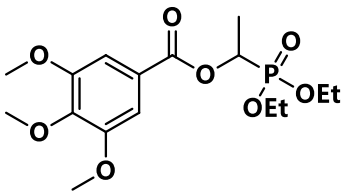
1-(Diethoxyphosphoryl)ethyl 2-benzoylbenzoate (3ja)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 101 mg (65% yield). **R_f** = 0.4 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.08 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.57 (dtd, *J* = 14.7, 7.6, 1.5 Hz, 2H), 7.45-7.41 (m, 2H), 7.39 (d, *J* = 7.5 Hz, 1H), 5.29 (quint, *J* = 7.1 Hz, 1H), 4.06 (m, 4H), 1.30-1.21 (m, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 196.6, 164.7 (d, *J* = 7.4 Hz), 142.0, 136.9, 133.3, 132.7, 130.4, 129.6, 129.6, 128.5, 127.8, 65.5 (d, *J* = 170.7 Hz), 62.9 (d, *J* = 7.0 Hz), 62.8 (d, *J* = 6.3 Hz), 16.5 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 5.8 Hz), 14.5. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 20.75, 20.75. **HRMS** (ESI) (m/z): calcd for $C_{20}H_{24}O_6P$ $[M+H]^+$: 391.1305, found: 391.1305.



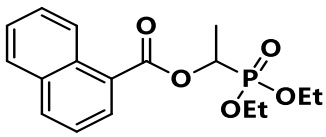
1-(Diethoxyphosphoryl)ethyl [1,1'-biphenyl]-2-carboxylate (3ka)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 94mg (65% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.83 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.53 (td, *J* = 7.6, 1.3 Hz, 1H), 7.47-7.34 (m, 5H), 7.30 (dd, *J* = 7.8, 1.6 Hz, 2H), 5.32 (quint, *J* = 7.1 Hz, 1H), 4.07 (dq, *J* = 13.8, 7.0 Hz, 4H), 1.30-1.23 (m, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 167.2 (d, *J* = 7.6 Hz), 142.7, 141.1, 131.5, 130.9, 130.2, 129.9, 128.5, 128.1, 127.4, 127.2, 64.9 (d, *J* = 170.3 Hz), 62.8 (d, *J* = 6.5 Hz), 62.8 (d, J = 6.5 Hz), 16.5 (d, *J* = 5.9 Hz), 16.4 (d, *J* = 6.0 Hz), 14.6. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.14. **HRMS** (ESI) (m/z): calcd for $C_{19}H_{24}O_5P$ $[M+H]^+$: 363.1356, found: 363.1354.



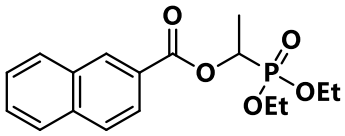
1-(Diethoxyphosphoryl)ethyl 3,4,5-trimethoxybenzoate (3la)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 105 mg (70% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 6:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.31 (s, 2H), 5.54-5.44 (m, 1H), 4.23-4.14 (m, 4H), 3.90 (s, 3H), 3.90 (s, 6H), 1.58 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.32 (q, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.0 (d, *J* = 7.9 Hz), 153.0, 142.5, 124.5, 107.0, 65.1 (d, *J* = 171.5 Hz), 63.0 (d, *J* = 7.2 Hz), 62.7 (d, *J* = 6.4 Hz), 61.0, 56.3, 16.6 (d, *J* = 5.7 Hz), 16.5 (d, *J* = 5.8 Hz), 15.3. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.45. **HRMS** (ESI) (m/z): calcd for $C_{16}H_{26}O_8P$ $[M+H]^+$: 377.1360, found: 377.1367.



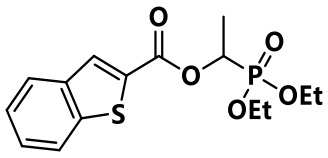
1-(Diethoxyphosphoryl)ethyl 1-naphthoate (3ma)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 105 mg (78% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.91 (d, *J* = 8.6 Hz, 1H), 8.22 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.61 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H), 7.51 (dt, *J* = 15.5, 8.1 Hz, 2H), 5.72-5.58 (m, 1H), 4.21 (quint, *J* = 7.1 Hz, 4H), 1.65 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.32 (td, *J* = 7.1, 1.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 166.1 (d, *J* = 7.7 Hz), 133.8, 133.8, 131.3, 130.6, 128.6, 127.9, 126.3, 125.6, 124.5, 64.8 (d, *J* = 170.9 Hz), 62.9 (d, *J* = 6.9 Hz), 62.8 (d, *J* = 6.4 Hz), 16.6 (d, *J* = 5.8 Hz), 16.5 (d, *J* = 5.7 Hz), 15.3. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.65. **HRMS** (ESI) (m/z): calcd for $C_{17}H_{22}O_5P$ $[M+H]^+$: 337.1199, found: 337.1198.



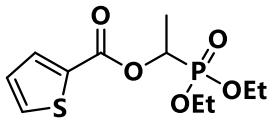
1-(Diethoxyphosphoryl)ethyl 2-naphthoate(3na)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 102 mg (77% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.66 (s, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.92 – 7.88 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 5.62 (quint, *J* = 7.5 Hz, 1H), 4.26 – 4.20 (m, 4H), 1.66 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.35 (q, *J* = 7.2 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.6 (d, *J* = 7.5 Hz), 135.7, 132.4, 131.5, 129.4, 128.5, 128.3, 127.8, 126.8, 126.7, 125.2, 65.1 (d, *J* = 171.4 Hz), 63.1 (d, *J* = 7.0 Hz), 62.8 (d, *J* = 6.5 Hz), 16.6 (d, *J* = 5.6 Hz), 16.5 (d, *J* = 5.8 Hz), 15.3. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.53. **HRMS** (ESI) (m/z): calcd for $C_{17}H_{22}O_5P$ $[M+H]^+$: 337.1199, found: 337.1198.



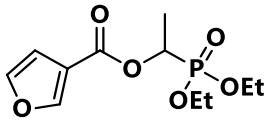
1-(Diethoxyphosphoryl)ethyl benzo[b]thiophene-2-carboxylate (3oa)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 99 mg (72% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.12 (s, 1H), 7.88 (dd, *J* = 11.7, 8.1 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 5.59-5.45 (m, 1H), 4.22 (dt, *J* = 15.2, 7.3 Hz, 4H), 1.62 (dd, *J* = 16.6, 7.1 Hz, 3H), 1.37-1.32 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 161.6 (d, *J* = 8.2 Hz), 142.4, 138.6, 132.6, 131.3, 127.2, 125.7, 125.1, 122.8, 65.7 (d, *J* = 171.0 Hz), 63.2 (d, *J* = 7.0 Hz), 62.9 (d, *J* = 6.5 Hz), 16.6 (d, *J* = 5.7 Hz), 16.5 (d, *J* = 5.8 Hz), 15.3. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 20.69. **HRMS** (ESI) (m/z): calcd for $C_{15}H_{20}O_5PS$ $[M+H]^+$: 343.0764, found: 343.0768.



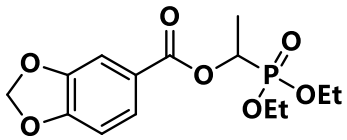
1-(Diethoxyphosphoryl)ethyl thiophene-2-carboxylate (3pa)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 54 mg (46% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.81 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.57 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.08 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.49-5.34 (m, 1H), 4.16 (dt, *J* = 14.2, 7.1 Hz, 4H), 1.54 (dd, *J* = 16.6, 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 160.9 (d, *J* = 8.2 Hz), 134.1, 133.1, 132.8, 127.9, 65.3 (d, *J* = 171.1 Hz), 63.1 (d, *J* = 6.9 Hz), 62.9 (d, *J* = 6.4 Hz), 16.5 (d, *J* = 5.7 Hz), 16.4 (d, *J* = 5.8 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.24. **HRMS** (ESI) (m/z): calcd for $C_{11}H_{18}O_5PS$ $[M+H]^+$: 293.0607, found: 293.0607.



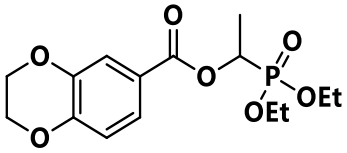
1-(Diethoxyphosphoryl)ethyl furan-3-carboxylate (3qa)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 47 mg (42% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.03 (s, 1H), 7.40 (m, 1H), 6.72 (s, 1H), 5.40 (quint, *J* = 7.2 Hz, 1H), 4.13 (quint, *J* = 7.2, 6.8 Hz, 4H), 1.50 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.28 (td, *J* = 7.0, 2.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 161.7 (d, *J* = 8.0 Hz), 148.2, 143.9, 118.6, 109.8, 64.4 (d, *J* = 171.5 Hz), 63.0 (d, *J* = 6.9 Hz), 62.7 (d, *J* = 6.5 Hz), 16.5 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 5.7 Hz), 15.1. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.30. **HRMS** (ESI) (m/z): calcd for $C_{11}H_{18}O_6P$ $[M+H]^+$: 277.0836, found: 277.0839.



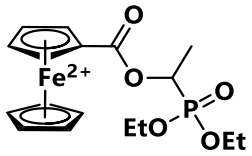
1-(Diethoxyphosphoryl)ethyl benzo[d][1,3]dioxole-5-carboxylate (3ra)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a brown oil, 79 mg (59% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.66 (dt, *J* = 8.5, 1.2 Hz, 1H), 7.46 (t, *J* = 1.5 Hz, 1H), 6.83 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.03 (s, 2H), 5.46 (quint, *J* = 7.2 Hz, 1H), 4.16 (quint, *J* = 7.0 Hz, 4H), 1.55 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 164.7 (d, *J* = 7.8 Hz), 152.0, 147.8, 125.8, 123.4, 109.6, 108.1, 101.9, 64.8 (d, *J* = 171.3 Hz), 63.0 (d, *J* = 6.9 Hz), 62.7 (d, *J* = 6.4 Hz), 16.5 (d, *J* = 5.6 Hz), 16.5 (d, *J* = 5.8 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.57. **HRMS** (ESI) (m/z): calcd for $C_{14}H_{20}O_7P$ $[M+H]^+$: 331.0941, found: 331.0946.



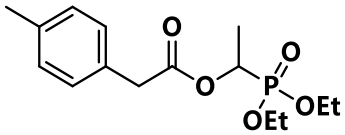
1-(Diethoxyphosphoryl)ethyl 2,3-dihydrobenzo[b][1,4]dioxine-6-carboxylate (3sa)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 83 mg (62% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.62-7.48 (m, 2H), 6.87 (dd, *J* =7.0, 2.5 Hz, 1H), 5.52-5.40 (m, 1H), 4.27 (ddd, *J* = 19.6, 5.9, 2.6 Hz, 4H), 4.16 (quint, *J* = 7.5 Hz, 4H), 1.54 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.30 (td, *J* = 7.1, 2.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 164.8 (d, *J* = 7.5 Hz), 148.2, 143.2, 123.7, 122.6, 119.2, 117.2, 64.7 (d, *J* = 176.4 Hz), 64.6, 64.1, 63.0 (d, *J* = 6.9 Hz), 62.7 (d, *J* = 6.4 Hz), 16.5 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 5.6 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.53. **HRMS** (ESI) (m/z): calcd for $C_{15}H_{22}O_7P$ $[M+H]^+$: 345.1098, found: 345.1096.



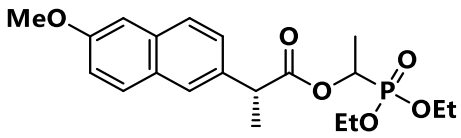
1-(Diethoxyphosphoryl)ethyl terrocenecarboxylate (3ta)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a brown oil, 123 mg (78% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 5.46-5.35 (m, 1H), 4.80 (dq, *J* = 12.5, 2.2 Hz, 2H), 4.39 (t, *J* = 1.8 Hz, 2H), 4.25-4.13 (m, 9H), 1.51 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.34 (td, *J* = 7.1, 4.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 170.6 (d, *J* = 8.0 Hz), 71.6 (d, *J* = 6.2 Hz), 70.2 (d, *J* = 12.7 Hz), 70.0, 69.9, 63.9 (d, *J* = 171.1 Hz), 62.8 (d, *J* = 3.8 Hz), 62.8 (d, *J* = 4.6 Hz), 16.6 (d, *J* = 4.2 Hz), 16.5 (d, *J* = 4.3 Hz), 15.4. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.72. **HRMS** (ESI) (m/z): calcd for $C_{17}H_{22}FeO_5P$ $[M-H]^+$: 393.0752, found: 393.0754.



1-(Diethoxyphosphoryl)ethyl 2-(p-tolyl)acetate (3ua)

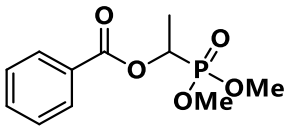
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 107 mg (85% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.15 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 5.25 (quint, *J* = 7.6 Hz, 1H), 4.12-3.98 (m, 4H), 3.61 (s, 2H), 2.30 (s, 3H), 1.43 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.24 (q, *J* = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 170.6 (d, *J* = 7.6 Hz), 136.8, 130.4, 129.3, 129.1, 64.8 (d, *J* = 170.9 Hz), 62.9 (d, *J* = 7.0 Hz), 62.7 (d, *J* = 6.2 Hz), 40.8, 21.1, 16.4 (d, *J* = 5.6 Hz), 16.3 (d, *J* = 5.8 Hz), 15.1. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.11. **HRMS** (ESI) (m/z): calcd for $C_{15}H_{24}O_5P$ $[M+H]^+$: 315.1353, found: 315.1356.



(2R)-1-(Diethoxyphosphoryl)ethyl 2-(6-methoxynaphthalen-2-yl)propanoate (3va)

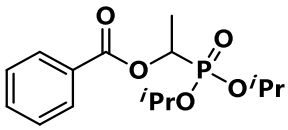
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 88 mg (56% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.72-7.65 (m, 3H), 7.39 (dt, *J* = 8.5, 1.7 Hz, 1H), 7.14-7.07 (m, 2H), 5.30-5.20 (m, 1H), 4.09-4.01 (m, 2H), 3.95-3.82 (m, 5H), 3.82-3.50 (m, 1H), 1.58 (dd, *J* = 7.3, 3.5 Hz, 3H), 1.45 (dd, *J* = 16.6, 7.1 Hz, 1H), 1.35-1.30 (m, 2H), 1.26-1.20 (m, 3H), 1.01 (dt, *J* = 45.9, 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 173.5 (d, *J* = 7.9 Hz), 173.4 (d, *J* = 7.4 Hz), 157.7, 135.1, 135.0, 133.8, 129.3, 129.2, 128.9, 128.9, 127.2, 127.1, 126.2, 126.2, 126.2, 126.0, 119.0, 105.5, 105.5, 64.8 (d, *J* = 170.4 Hz), 64.7 (d, *J* = 170.9 Hz), 62.8 (d, *J* = 7.6 Hz), 62.8 (d, *J* = 6.8 Hz), 62.8 (d, *J* = 7.2 Hz), 62.5 (d, *J* = 6.4 Hz), 55.3, 45.4, 18.4, 18.3, 16.4 (d, *J* = 5.8 Hz), 16.3 (d, *J* = 5.7 Hz), 16.2 (d, *J* = 5.7 Hz), 15.1, 14.9. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.25, 20.75.

HRMS (ESI) (m/z): calcd for $C_{20}H_{27}O_6PK$ $[M+K]^+$: 433.1177, found: 433.1170.



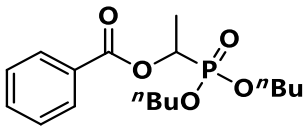
1-(Dimethoxyphosphoryl)ethyl benzoate (3ab)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 93 mg (90% yield). $\mathbf{R_f}$ = 0.5 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.03 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 5.58-5.40 (m, 1H), 3.79 (dd, *J* = 10.6, 5.1 Hz, 6H), 1.56 (dd, *J* = 16.8, 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.3 (d, *J* = 7.5 Hz), 133.5, 129.8, 129.3, 128.5, 64.5 (d, *J* = 170.9 Hz), 53.6 (d, *J* = 7.0 Hz), 53.3 (d, *J* = 6.4 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 23.90. **HRMS** (ESI) (m/z): calcd for $C_{11}H_{16}O_5P$ $[M+H]^+$: 259.0726, found: 259.0730.



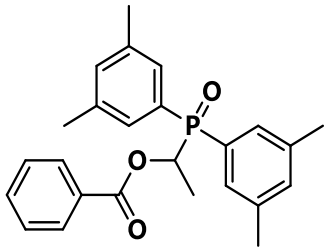
1-(Diisopropoxyphosphoryl)ethyl benzoate (3ac)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 114 mg (91% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.03 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.57-7.51 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 5.43 (dq, *J* = 8.9, 7.1 Hz, 1H), 4.75 (ddtd, *J* = 12.4, 7.4, 6.2, 2.9 Hz, 2H), 1.53 (dd, *J* = 16.7, 7.1 Hz, 3H), 1.34-1.27 (m, 9H), 1.24 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 65.4 (d, *J* = 8.3 Hz), 133.3, 129.7, 129.6, 128.4, 71.6 (d, *J* = 7.2 Hz), 71.4 (d, *J* = 6.7 Hz), 65.4 (d, *J* = 173.7 Hz), 24.1 (d, *J* = 3.0 Hz), 24.1 (t, *J* = 3.3 Hz), 23.9 (d, *J* = 2.4 Hz), 23.9 (d, *J* = 2.3 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 19.37. **HRMS** (ESI) (m/z): calcd for $C_{15}H_{24}O_5P$ $[M+H]^+$: 315.1353, found: 315.1356.



1-(Dibutoxyphosphoryl)ethyl benzoate (3ad)

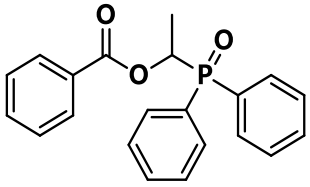
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 126 mg (92% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.03 (dd, *J* = 7.3, 1.1 Hz, 2H), 7.55 (td, *J* = 7.5, 1.2 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 5.50 (quint, *J* = 7.2 Hz, 1H), 4.12-4.05 (m, 4H), 1.63-1.53 (m, 7H), 1.37-1.30 (m, 4H), 0.85 (q, *J* = 7.8 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.3 (d, *J* = 7.7 Hz), 133.3, 129.8, 129.5, 128.4, 66.6 (d, *J* = 7.2 Hz), 66.4 (d, *J* = 6.6 Hz), 64.9 (d, *J* = 171.4 Hz), 32.6 (d, *J* = 5.8 Hz), 32.5 (d, *J* = 5.8 Hz), 18.6, 15.3, 13.5. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.33. **HRMS** (ESI) (m/z): calcd for $C_{17}H_{28}O_5P$ $[M+H]^+$: 343.1669, found: 343.1669.



1-(Bis(3,5-dimethylphenyl)phosphoryl)ethyl benzoate (3ae)

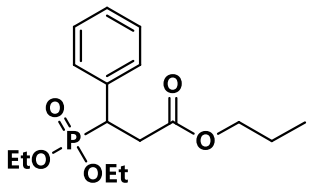
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 135 mg (83% yield). $\mathbf{R_f}$ = 0.5 (PE/EA/EtOH = 6:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.93 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 6.9 Hz, 1H), 7.51 (d, *J* = 11.6 Hz, 2H), 7.40-7.45 (m, 4H), 7.15 (d, *J* = 5.0 Hz, 2H), 6.06 (q, *J* = 7.0 Hz, 1H), 2.31 (s, 12H), 1.61 (dd, *J* = 14.0, 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.4 (d, *J* = 7.0 Hz), 138.5 (d, *J* = 12.4 Hz), 138.2 (d, *J* = 12.4 Hz), 134.1 (d, *J* = 2.8 Hz), 134.0 (d, *J* = 3.1 Hz), 133.3, 130.0 (d, *J* = 98.1 Hz), 129.7, 129.5, 129.4 (d, *J* = 9.2 Hz), 128.9 (d, *J* = 9.1 Hz), 128.9 (d, *J* = 98.3 Hz), 128.4, 68.2, 67.5, 21.3 (d, *J* = 2.4 Hz), 14.2. **^{31}P NMR** (202 MHz, $CDCl_3$,

ppm) δ = 31.45. **HRMS** (ESI) (m/z): calcd for $C_{25}H_{28}O_3P$ $[M+H]^+$: 407.1771, found: 407.1771.



1-(diphenylphosphoryl)ethyl benzoate (3af)

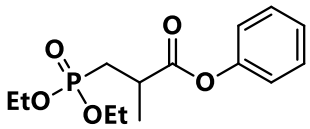
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 119 mg (85% yield). $\mathbf{R_f}$ = 0.5 (PE/EA/EtOH = 6:1:1, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.97 – 7.92 (m, 2H), 7.88 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.85 – 7.80 (mm, 2H), 7.59 – 7.50 (m, 5H), 7.47 (ddt, *J* = 6.7, 5.4, 2.2 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 6.12 (qd, *J* = 7.0, 2.2 Hz, 1H), 1.63 (dd, *J* = 14.2, 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.4 (d, *J* = 7.0 Hz), 133.4, 132.4 (d, *J* = 2.9 Hz), 132.4 (d, *J* = 3.1 Hz), 131.9 (d, *J* = 9.2 Hz), 131.3 (d, *J* = 9.3 Hz), 130.3 (d, *J* = 99.0 Hz), 129.6, 129.2, 128.9 (d, *J* = 99.7 Hz), 128.8 (d, *J* = 11.6 Hz), 128.6 (d, *J* = 11.8 Hz), 128.5, 67.7 (d, *J* = 88.7 Hz), 14.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 31.40. **HRMS** (ESI) (m/z): calcd for $C_{21}H_{20}O_3P$ $[M+H]^+$: 351.1145, found: 351.1148.



Propyl-3-(diethoxyphosphoryl)-3-phenylpropanoate (3wa)

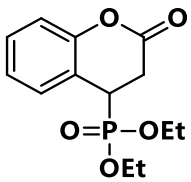
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 114 mg (87% yield). $\mathbf{R_f}$ = 0.5 (PE/EA/EtOH = 4:0.5:0.5, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) *δ* = 7.3-7.3 (m, 2H), 7.2 (t, *J* = 7.5 Hz, 2H), 7.2 (dt, *J* = 7.5, 3.5 Hz, 1H), 4.0 (pd, *J* = 7.2, 2.4 Hz, 2H), 3.9-3.8 (m, 3H), 3.7-3.7 (m, 1H), 3.6 (ddd, *J* = 22.5, 10.6, 4.7 Hz, 1H), 3.0 (ddd, *J* = 14.6, 9.8, 4.7 Hz, 1H), 2.9 (dt, *J* = 16.3, 10.5 Hz, 1H), 1.5-1.4 (m, 2H), 1.2 (t, *J* = 7.1

Hz, 3H), 1.0 (t, *J* = 7.1 Hz, 3H), 0.7 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 171.1 (d, *J* = 19.7 Hz), 135.2 (d, *J* = 7.0 Hz), 129.1 (d, *J* = 6.3 Hz), 128.5 (d, *J* = 2.7 Hz), 127.4 (d, *J* = 3.2 Hz), 66.4, 62.8 (d, *J* = 6.9 Hz), 62.2 (d, *J* = 7.3 Hz), 40.5 (d, *J* = 140.2 Hz), 35.2, 21.8, 16.4 (d, *J* = 6.0 Hz), 16.2 (d, *J* = 5.7 Hz), 10.3. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 27.20. **HRMS** (ESI) (m/z): calcd for $C_{16}H_{26}O_5P$ $[M+H]^+$: 329.1512, found: 329.1512.



Phenyl 3-(diethoxyphosphoryl)-2-methylpropanoate (3ax)

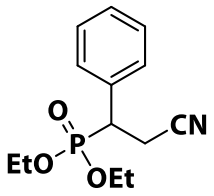
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 77 mg (64% yield). **R_f** = 0.5 (PE/EA/EtOH = 4:0.5:0.5, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.37 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.18-6.93 (m, 2H), 4.22-4.07 (m, 4H), 3.08 (dq, *J* = 13.7, 7.0 Hz, 1H), 2.46-2.37 (m, 1H), 1.93 (ddd, *J* = 18.1, 15.5, 6.5 Hz, 1H), 1.46 (d, *J* = 7.1 Hz, 3H), 1.32 (td, *J* = 7.1, 5.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 173.8 (d, *J* = 11.7 Hz), 150.7, 129.4, 125.9, 121.4, 62.0 (d, *J* = 6.1 Hz), 62.0 (d, *J* = 6.1 Hz), 34.8 (d, *J* = 3.5 Hz), 29.2 (d, *J* = 142.7 Hz), 18.8 (d, *J* = 10.4 Hz), 16.5 (d, *J* = 1.9 Hz), 16.4 (d, *J* = 1.5 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 29.08. **HRMS** (ESI) (m/z): calcd for $C_{14}H_{22}O_5P$ $[M+H]^+$: 301.1199, found: 301.1202.



Diethyl (2-oxochroman-4-yl)phosphonate (3ya)

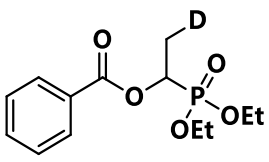
The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 61 mg (54% yield). **R_f** = 0.6 (PE/EA/EtOH = 2:0.5:0.5, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.35 (d, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.2

Hz, 1H), 4.20-4.07 (m, 2H), 3.96 (dt, *J* = 8.7, 6.3 Hz, 2H), 3.44 (ddd, *J* = 21.8, 8.1, 1.7 Hz, 1H), 3.20 (ddd, *J* = 16.6, 10.2, 1.8 Hz, 1H), 2.94 (ddd, *J* = 36.0, 16.6, 8.2 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 166.1 (d, *J* = 3.2 Hz), 151.8 (d, *J* = 5.9 Hz), 129.8 (d, *J* = 5.0 Hz), 129.5 (d, *J* = 3.6 Hz), 124.6 (d, *J* = 3.3 Hz), 117.4 (d, *J* = 5.3 Hz), 117.4 (d, *J* = 5.3 Hz), 63.4 (d, *J* = 7.3 Hz), 62.9 (d, *J* = 7.0 Hz), 34.6 (d, *J* = 143.2 Hz), 29.6 (d, *J* = 5.6 Hz), 16.4 (d, *J* = 5.7 Hz), 16.2 (d, *J* = 5.6 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 28.19. **HRMS** (ESI) (m/z): calcd for $C_{13}H_{18}O_5P$ $[M+H]^+$: 285.0886, found: 285.0895.



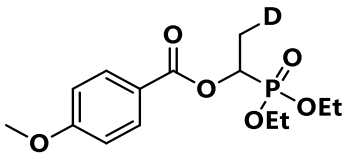
Diethyl (2-cyano-1-phenylethyl)phosphonate (3za)

The title compound was synthesized following **General Procedure D** and purified by using silica gel chromatography to yield a yellow oil, 75 mg (70% yield). **R_f** = 0.6 (PE/EA/EtOH = 4:0.5:0.5, *v*/*v*/*v*). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.41-7.32 (d, *J* = 4.5 Hz, 4H), 7.33-7.27 (m, 1H), 4.11-4.01 (m, 2H), 3.90 (dt, *J* = 10.1, 7.2 Hz, 1H), 3.76-3.65 (m, 1H), 3.34 (ddd, *J* = 22.0, 10.5, 5.2 Hz, 1H), 3.07 (ddd, *J* = 17.1, 9.2, 5.2 Hz, 1H), 3.01-2.91 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 133.2 (d, *J* = 6.6 Hz), 129.0 (d, *J* = 2.4 Hz), 128.8 (d, *J* = 6.4 Hz), 128.4 (d, *J* = 2.9 Hz), 117.4 (d, *J* = 20.0 Hz), 63.5 (d, *J* = 7.1 Hz), 62.5 (d, *J* = 7.2 Hz), 40.9 (d, *J* = 141.8 Hz), 19.6, 16.3 (d, *J* = 5.9 Hz), 16.2 (d, *J* = 5.8 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 24.13. **HRMS** (ESI) (m/z): calcd for $C_{13}H_{19}NO_3P$ $[M+H]^+$: 268.1097, found: 268.1105.



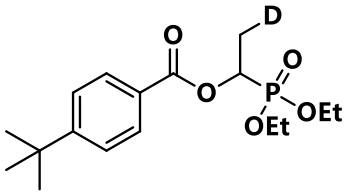
1-(Diethoxyphosphoryl)ethyl-2-d benzoate (5)

The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 99 mg (86% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). 98% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.06 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.56 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 5.57-5.45 (m, 1H), 4.23-4.12 (m, 4H), 1.60-1.52 (m, 2.02H), 1.30 (td, *J* = 7.1, 1.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.4 (d, *J* = 7.7 Hz), 133.4, 129.8, 129.5, 128.5, 64.9 (dd, *J* = 171.3, 5.7 Hz), 63.0 (d, *J* = 6.9 Hz), 62.8 (d, *J* = 6.4 Hz), 16.5 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 5.9 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.43. **HRMS** (ESI) (m/z): calcd for $C_{13}H_{19}DO_5P$ $[M+H]^+$: 288.1106, found: 288.1101.



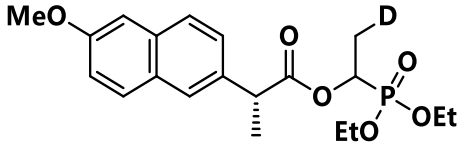
1-(Diethoxyphosphoryl)ethyl-2-d 4-methoxybenzoate (6)

The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 109 mg (90% yield). $\mathbf{R_f}$ = 0.4 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). 95% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.01 (dt, *J* = 9.0, 2.5 Hz, 2H), 6.92 (dt, *J* = 9.0, 2.5 Hz, 2H), 5.49 (quint, *J* = 6.7 Hz, 1H), 4.23-4.12 (m, 4H), 3.86 (s, 3H), 1.59-1.52 (m, 2.05H), 1.31 (td, *J* = 7.1, 3.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.1 (d, *J* = 7.8 Hz), 163.7, 131.9, 121.9, 113.7, 64.6 (dd, *J* = 171.3, 5.5 Hz), 63.0 (d, *J* = 7.0 Hz), 62.7 (d, *J* = 6.3 Hz), 55.5, 16.5 (d, *J* = 5.6 Hz), 16.4 (d, *J* = 5.8 Hz), 15.3. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.73. **HRMS** (ESI) (m/z): calcd for $C_{14}H_{21}DO_6P$ $[M+H]^+$: 318.1211, found: 318.1209.



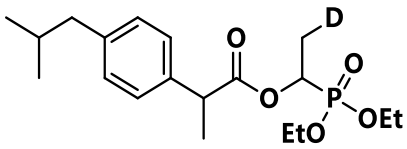
1-(Diethoxyphosphoryl)ethyl-2-d 4-(tert-butyl)benzoate (7)

The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 125 mg (91% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). 97% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.97 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 5.49 (quint, *J* = 6.8 Hz, 1H), 4.16 (quint, *J* = 7.6 Hz, 4H), 1.58-1.51 (m, 2.05H), 1.35-1.24 (m, 15H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.3 (d, *J* = 7.7 Hz), 157.1, 129.7, 126.7, 125.4, 64.6 (ddd, *J* = 171.2, 11.7, 5.9 Hz), 62.9 (d, *J* = 6.9 Hz), 62.7 (d, *J* = 6.3 Hz), 35.1, 31.1, 16.5 (d, *J* = 5.6 Hz), 16.4 (d, *J* = 5.8 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.52. **HRMS** (ESI) (m/z): calcd for $C_{17}H_{27}O_5PD$ $[M+H]^+$: 344.1732, found: 344.1725.



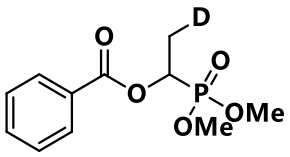
1-(Diethoxyphosphoryl)ethyl-2-d (2R)-2-(6-methoxynaphthalen-2-yl)propanoate (8)

The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 93 mg (59% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). 77% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.69 (ddd, *J* = 8.3, 4.8, 2.1 Hz, 3H), 7.40 (dt, *J* = 8.3, 1.7 Hz, 1H), 7.15-7.09 (m, 2H), 5.27 (ddd, *J* = 8.6, 7.2, 3.7 Hz, 1H), 4.10-4.04 (m, 2H), 3.97-3.81 (m, 5H), 3.80-3.61 (m, 1H), 1.62-1.58 (m, 3H), 1.46 (dd, *J* = 16.7, 7.2 Hz, 0.74H), 1.34 (dd, *J* = 16.7, 7.2 Hz, 1.49H), 1.27-1.23 (m, 3H), 1.02 (dt, *J* = 47.9, 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 173.5 (d, *J* = 7.7 Hz), 173.4 (d, *J* = 7.3 Hz), 157.7, 157.7, 135.1, 135.0, 133.7, 129.3, 129.2, 128.9, 128.9, 127.2, 127.1, 126.2, 126.2, 126.0, 119.0, 105.5, 105.5, 64.8 (d, *J* = 170.6 Hz), 64.7 (d, *J* = 170.5 Hz), 62.8 (d, *J* = 6.8 Hz), 62.8 (d, *J* = 6.9 Hz), 62.8 (d, *J* = 6.7 Hz), 62.5 (d, *J* = 6.4 Hz), 55.3, 45.4, 18.4, 18.3, 16.4 (d, *J* = 5.6 Hz), 16.3 (d, *J* = 5.9 Hz), 16.2 (d, *J* = 5.8 Hz), 15.2, 14.9. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.26, 20.76. **HRMS** (ESI) (m/z): calcd for $C_{20}H_{27}DO_6P$ $[M+H]^+$: 396.1681, found: 396.1690.



1-(Diethoxyphosphoryl)ethyl-2-d 2-(4-isobutylphenyl)propanoate (9)

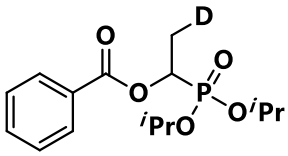
The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 99 mg (67% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.20 (dd, *J* = 8.2, 2.6 Hz, 2H), 7.09 (dd, *J* = 8.2, 2.4 Hz, 2H), 5.30-5.21 (m, 1H), 4.14-3.69 (m, 5H), 2.44 (dd, *J* = 7.1, 4.3 Hz, 2H), 1.83 (dq, *J* = 13.3, 6.7 Hz, 1H), 1.50 (dd, *J* = 7.2, 5.8 Hz, 3H), 1.47-1.42 (m, 1.01H), 1.35 (dd, *J* = 16.7, 7.1 Hz, 1.00H), 1.28 (dt, *J* = 16.2, 7.1 Hz, 3H), 1.16 (dt, *J* = 10.8, 7.0 Hz, 3H), 0.89 (s, 3H), 0.88 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ =173.5 (d, *J* = 10.8 Hz), 173.4 (d, *J* = 10.2 Hz), 140.7, 137.2, 137.1, 129.3, 129.3, 127.3, 127.2, 64.6 (dd, *J* = 170.5, 5.8 Hz), 64.3 (dd, *J* = 169.7, 5.2 Hz), 62.9 (d, *J* = 7.1 Hz), 62.8 (d, *J* = 7.2 Hz), 62.8 (d, *J* = 6.4 Hz), 62.5 (d, *J* = 6.2 Hz), 45.0, 45.0, 30.2, 30.2, 22.3, 18.4, 18.4, 16.4 (d, *J* = 5.6 Hz), 16.3 (d, *J* = 6.0 Hz), 16.2 (d, *J* = 5.7 Hz), 15.1, 14.8. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.33, 20.87. **HRMS** (ESI) (m/z): calcd for $C_{19}H_{31}DO_5P$ $[M+H]^+$: 372.2045, found: 372.2040.



1-(Dimethoxyphosphoryl)ethyl-2-d benzoate (10)

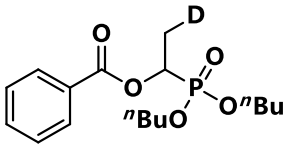
The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 89 mg (86% yield). $\mathbf{R_f}$ = 0.5 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). 96% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.13-8.00 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 5.55 (quint, *J* = 6.7, 6.3 Hz, 1H), 3.82 (dd, *J* = 10.6, 5.1 Hz, 6H), 1.62-1.54 (m, 2.04H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.3 (d, *J* =

7.4 Hz), 133.5, 129.9, 129.4, 128.5, 64.5 (dd, *J* = 170.9, 5.6 Hz), 53.6 (d, *J* = 7.2 Hz), 53.3 (d, *J* = 6.4 Hz), 15.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 23.91. **HRMS** (ESI) (m/z): calcd for $C_{11}H_{15}DO_5P$ $[M+H]^+$: 260.0793, found: 260.0789.



1-(Dimethoxyphosphoryl)ethyl-2-d benzoate (11)

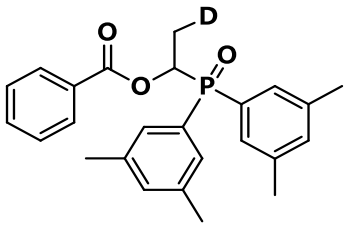
The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 116 mg (92% yield). **R_f** = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). 95% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.03 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 5.43 (quint, *J* = 7.1 Hz, 1H), 4.76 (dt, *J* = 12.7, 6.3 Hz, 2H), 1.56-1.48 (m, 2.10H), 1.35-1.27 (m, 9H), 1.24 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.4 (d, *J* = 8.5 Hz), 133.3, 129.7, 129.7, 128.4, 71.5 (d, *J* = 7.1 Hz), 71.4 (d, *J* = 6.7 Hz), 65.4 (dd, *J* = 173.8, 5.5 Hz), 24.1 (d, *J* = 2.9 Hz), 24.1 (d, *J* = 3.1 Hz), 23.9 (d, *J* = 2.4 Hz), 23.9 (d, *J* = 2.3 Hz), 15.3. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 19.36. **HRMS** (ESI) (m/z): calcd for $C_{15}H_{23}DO_5P$ $[M+H]^+$: 316.1419, found: 316.1413.



1-(Dibutoxyphosphoryl)ethyl-2-d benzoate (12)

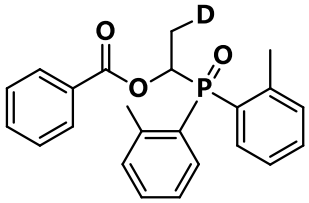
The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 123 mg (90% yield). **R_f** = 0.6 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.05 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.0 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 5.52 (quint, *J* = 6.2 Hz, 1H), 4.16-4.06 (m, 4H), 1.67-1.60 (m, 4H), 1.59-1.51 (m, 2.09H), 1.36 (h, *J* = 7.5, 6.8 Hz, 4H), 0.87 (q, *J* =

7.8 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.3 (d, *J* = 7.9 Hz), 133.3, 129.8, 129.5, 128.4, 66.6 (d, *J* = 7.2 Hz), 66.4 (d, *J* = 6.6 Hz), 64.9 (dd, *J* = 171.3, 5.5 Hz), 32.6 (d, *J* = 5.7 Hz), 32.5 (d, *J* = 5.8 Hz), 18.7, 18.6, 15.3, 13.6, 13.5. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 21.35. **HRMS** (ESI) (m/z): calcd for $C_{17}H_{27}DO_5P$ $[M+H]^+$: 344.1747, found: 344.1740.



1-(Bis(3,5-dimethylphenyl)phosphoryl)ethyl-2-d benzoate (13)

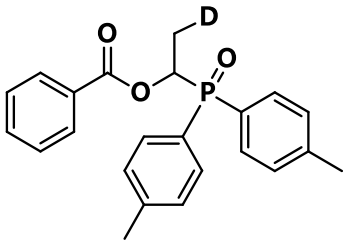
The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 133 mg (82% yield). **R_f** = 0.5 (PE/EA/EtOH = 6:1:1, *v*/*v*/*v*). 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.91 (d, *J* = 8.2 Hz, 2H), 7.54 (t, *J* = 6.9 Hz, 1H), 7.48 (d, *J* = 11.6 Hz, 2H), 7.40 (dd, *J* = 9.2, 5.5 Hz, 4H), 7.12 (d, *J* = 5.0 Hz, 2H), 6.07-5.99 (m, 1H), 2.29 (s, 12H), 1.67-1.46 (m, 2.01H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.4 (d, *J* = 7.0 Hz), 138.5 (d, *J* = 12.4 Hz), 138.2 (d, *J* = 12.4 Hz), 134.1 (d, *J* = 2.8 Hz), 134.0 (d, *J* = 3.1 Hz), 133.3, 130.0 (d, *J* = 98.4 Hz), 129.7, 129.4, 129.3 (d, *J* = 9.2 Hz), 128.9 (d, *J* = 9.1 Hz), 128.9 (d, *J* = 98.4 Hz), 128.4, 68.2, 67.5, 21.3 (d, *J* = 2.4 Hz), 14.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 31.39. **HRMS** (ESI) (m/z): calcd for $C_{25}H_{27}DO_3P$ $[M+H]^+$: 408.1833, found: 408.1840.



1-(Di-o-tolylphosphoryl)ethyl-2-d benzoate (14)

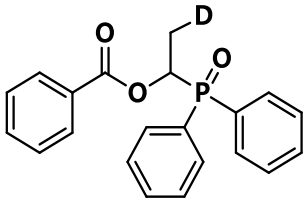
The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 130 mg (86% yield). **R_f** = 0.5

(PE/EA/EtOH = 6:1:1, *v*/*v*/*v*). 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.85 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.75 (dd, *J* = 12.7, 7.7 Hz, 1H), 7.55-7.50 (m, 2H), 7.37 (dt, *J* = 15.6, 7.6 Hz, 4H), 7.21 (dq, *J* = 13.0, 8.2, 5.8 Hz, 4H), 6.26 – 6.21 (m, 1H), 2.45 (s, 3H), 2.43 (s, 3H), 1.76-1.63 (m, 2.01H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.5 (d, *J* = 7.3 Hz), 143.0 (d, *J* = 8.2 Hz), 142.7 (d, *J* = 8.1 Hz), 133.4, 132.3 (d, *J* = 1.3 Hz), 132.2 (d, *J* = 2.6 Hz), 132.1, 132.1 (d, *J* = 2.6 Hz), 131.6 (d, *J* = 11.1 Hz), 129.8, 129.5 (d, *J* = 97.0 Hz), 129.2, 128.4 (d, *J* = 97.2 Hz), 128.4, 125.7 (d, *J* = 12.0 Hz), 125.5 (d, *J* = 12.1 Hz), 67.2 (ddd, *J* = 87.9, 10.7, 5.3 Hz), 21.5 (d, *J* = 4.0 Hz), 21.3 (d, *J* = 4.1 Hz), 14.8. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 35.07. **HRMS** (ESI) (m/z): calcd for $C_{23}H_{23}DO_3P$ $[M+H]^+$: 380.1520, found: 380.1517.



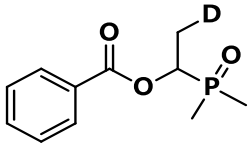
1-(Di-p-tolylphosphoryl)ethyl-2-d benzoate (15)

The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 114 mg (75% yield). **R_f** = 0.5 (PE/EA/EtOH = 6:1:1, *v*/*v*/*v*). 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.89 (d, *J* = 8.3 Hz, 2H), 7.83-7.78 (m, 2H), 7.71-7.65 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.11-6.03 (m, 1H), 2.37 (d, *J* = 14.9 Hz, 6H), 1.63-1.54 (m, 2.06H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.4 (d, *J* = 7.2 Hz), 142.9 (d, *J* = 2.8 Hz), 142.8 (d, *J* = 2.8 Hz), 133.3, 131.9 (d, *J* = 9.4 Hz), 131.3 (d, *J* = 9.6 Hz), 129.7, 129.5 (d, *J* = 12.1 Hz), 129.3 (d, *J* = 11.9 Hz), 128.4, 127.2 (d, *J* = 101.7 Hz), 125.7 (d, *J* = 102.3 Hz), 67.7 (ddd, *J* = 88.3, 11.2, 5.7 Hz), 14.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 31.56. **HRMS** (ESI) (m/z): calcd for $C_{23}H_{23}DO_3P$ $[M+H]^+$: 380.1520, found: 380.1519.



1-(Diphenylphosphoryl)ethyl-2-d benzoate (16)

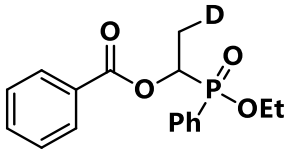
The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 126 mg (90% yield). $\mathbf{R_f}$ = 0.5 (PE/EA/EtOH = 6:1:1, *v*/*v*/*v*). 98% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.94-7.89 (m, 2H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.82-7.74 (m, 2H), 7.64-7.47 (m, 5H), 7.47-7.40 (m, 3H), 7.37 (t, *J* = 7.8 Hz, 2H), 6.09 (dt, *J* = 10.4, 5.2 Hz, 1H), 1.70-1.51 (m, 2.02H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.4 (d, *J* = 7.1 Hz), 133.4, 132.4 (d, *J* = 2.5 Hz), 132.4 (d, *J* = 2.5 Hz), 131.9 (d, *J* = 9.1 Hz), 131.3 (d, *J* = 9.2 Hz), 130.3 (d, *J* = 99.0 Hz), 129.6, 129.2, 128.9 (d, *J* = 99.3 Hz), 128.8 (d, *J* = 11.6 Hz), 128.6 (d, *J* = 11.7 Hz), 128.4, 67.6 (ddd, *J* = 89.6, 11.4, 5.7 Hz), 14.2. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 31.19. **HRMS** (ESI) (m/z): calcd for $C_{21}H_{19}DO_3P$ $[M+H]^+$: 352.1207, found: 352.1203.



1-(Dimethylphosphoryl)ethyl-2-d benzoate (17)

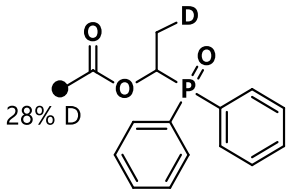
The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 80 mg (88% yield). $\mathbf{R_f}$ = 0.6 (PE/EA/EtOH = 6:1:1, *v*/*v*/*v*). 97% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.08-7.98 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 5.48 (dd, *J* = 6.9, 3.7 Hz, 1H), 1.67-1.59 (m, 2.03H), 1.55 (dd, *J* = 26.5, 12.8 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.4 (d, *J* = 6.3 Hz), 133.7, 129.7, 129.1, 128.7, 67.8 (ddd, *J* = 84.9, 11.3, 5.9 Hz), 14.2 (d, *J* =

68.4 Hz), 13.7, 12.2 (d, *J* = 68.1 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 44.98. **HRMS** (ESI) (m/z): calcd for $C_{11}H_{15}DO_3P$ $[M+H]^+$: 228.0894, found: 228.0894.



1-(Ethoxy(phenyl)phosphoryl)ethyl-2-d benzoate (18)

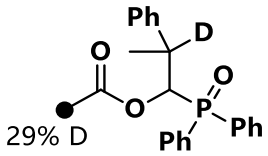
The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 70 mg (55% yield). **R_f** = 0.5 (PE/EA/EtOH = 6:1:1, *v*/*v*/*v*). 99% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 8.03-8.00 (m, 1H), 7.93 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.90- 7.83 (m, 2H), 7.57 (dddt, *J* = 9.2, 7.5, 5.8, 1.5 Hz, 2H), 7.50-7.42 (m, 4H), 5.72 (q, *J* = 7.4 Hz, 0.45H) (*minor diastereomer*), 5.59-5.55 (m, 0.55H), 4.24-4.18 (m, 0.9H) (*minor diastereomer*), 4.10 (ddt, *J* = 11.2, 7.2, 3.5 Hz, 1.1H), 1.60-1.48 (m, 2.01H), 1.37-1.31 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 165.3 (d, *J* = 7.0 Hz), 165.2 (d, *J* = 6.9 Hz), 133.3 (d, *J* = 2.4 Hz), 132.9 (d, *J* = 2.3 Hz), 132.6 (d, *J* = 9.6 Hz), 132.4 (d, *J* = 9.7 Hz), 131.7, 131.7, 129.8, 129.7, 129.6, 129.4, 128.7 (d, *J* = 12.5 Hz), 128.5 (d, *J* = 12.9 Hz), 128.4, 128.4 (d, *J* = 73.8 Hz), 127.4 (d, *J* = 75.8 Hz), 67.7 (dd, *J* = 120.8, 5.3 Hz), 66.6 (dd, *J* = 121.8, 5.5 Hz), 61.7 (d, *J* = 6.9 Hz), 61.6 (d, *J* = 6.9 Hz), 16.6 (d, *J* = 5.9 Hz), 16.5 (d, *J* = 6.2 Hz), 14.4, 14.1. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 37.80, 36.84. **HRMS** (ESI) (m/z): calcd for $C_{17}H_{19}DO_4P$ $[M+H]^+$: 320.1156, found: 320.1159.



1-(Diphenylphosphoryl)ethyl-2-d acetate-2-d (19)

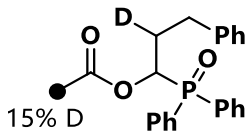
The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 106 mg (92% yield). **R_f** = 0.6 (PE/EA/EtOH = 6:1:1, *v*/*v*/*v*). 98% and 28% Deuterium incorporation were

determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.89-7.83 (m, 2H), 7.78-7.71 (m, 2H), 7.57-7.44 (m, 6H), 5.83 (dtt, *J* = 7.0, 3.6, 1.7 Hz, 1H), 1.90-1.85 (m, 2.26H), 1.50-1.38 (m, 2.04H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 169.6 (d, *J* = 6.7 Hz), 132.4 (d, *J* = 2.6 Hz), 132.4 (d, *J* = 2.6 Hz), 131.8 (d, *J* = 9.0 Hz), 131.3 (d, *J* = 9.2 Hz), 130.3 (d, *J* = 98.7 Hz), 128.8 (d, *J* = 98.7 Hz), 128.8 (d, *J* = 11.8 Hz), 128.6 (d, *J* = 11.8 Hz), 67.2 (dd, *J* = 88.8, 5.5 Hz), 20.8, 14.0. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 30.98. **HRMS** (ESI) (m/z): calcd for $C_{16}H_{16}D_2O_3P$ $[M+H]^+$: 291.1114, found: 291.1110.



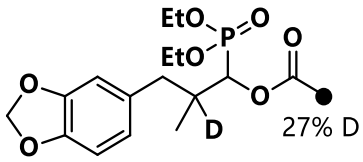
1-(Diphenylphosphoryl)-2-phenylpropyl-2-d acetate (21)

The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 53 mg (35% yield). **R_f** = 0.6 (PE/EA/EtOH = 6:1:1, *v*/*v*/*v*). 81% and 29% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.92-7.63 (m, 4H), 7.57-7.42 (m, 5H), 7.32 (dt, *J* = 7.5, 3.8 Hz, 1H), 7.22-7.00 (m, 5H), 6.03 (d, *J* = 2.1 Hz, 0.59H), 5.96 (d, *J* = 1.4 Hz, 0.32H) (*minor diastereomer*), 3.72-3.52 (m, 0.19H), 1.79 (s, 1.37H), 1.42 (s, 0.75H) (*minor diastereomer*), 1.36 (d, *J* = 8.8 Hz, 1.94H), 1.31 (d, *J* = 4.5 Hz, 1.06H) (*minor diastereomer*). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 169.8 (d, *J* = 4.2 Hz), 168.8 (d, *J* = 3.5 Hz), 141.8 (d, *J* = 5.7 Hz), 132.2 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 2.7 Hz), 131.9 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 9.1 Hz), 131.6 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 9.2 Hz), 131.2 (d, *J* = 9.2 Hz), 130.9 (d, *J* = 9.1 Hz), 130.4, 130.3, 129.5 (d, *J* = 98.5 Hz), 128.7 (d, *J* = 11.6 Hz), 128.4 (d, *J* = 11.9 Hz), 128.4, 128.4 (d, *J* = 99.5 Hz), 128.3, 128.3, 128.2, 128.1 (d, *J* = 2.2 Hz), 127.9 (d, *J* = 2.9 Hz), 127.0, 126.8, 74.7 (dd, *J* = 83.9, 8.1 Hz), 74.3 (dd, *J* = 82.9, 8.9 Hz), 40.9 (d, *J* = 2.5 Hz), 39.5 (d, *J* = 2.2 Hz), 20.3, 19.9, 18.8 (d, *J* = 13.3 Hz), 17.4 (d, *J* = 6.4 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 30.77, 28.93. **HRMS** (ESI) (m/z): calcd for $C_{23}H_{23}DO_3P$ $[M+H]^+$: 380.1520, found: 380.1520.



1-(Diphenylphosphoryl)-3-phenylpropyl-2-d acetate (22)

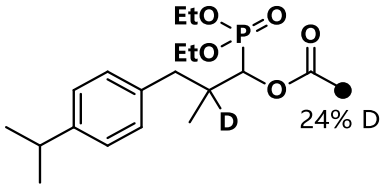
The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 82 mg (54% yield). $\mathbf{R_f}$ = 0.5 (PE/EA/EtOH = 6:1:1, *v*/*v*/*v*). 73% and 15% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.93-7.86 (m, 2H), 7.76-7.70 (m, 2H), 7.58-7.44 (m, 6H), 7.25 (t, *J* = 7.4 Hz, 2H), 7.20-7.16 (m, 1H), 7.14-7.07 (m, 2H), 5.93 (ddd, *J* = 9.1, 3.7, 1.7 Hz, 1H), 2.75-2.62 (m, 2H), 2.20 (ddt, *J* = 14.8, 10.6, 3.4 Hz, 1.27H), 1.84 (s, 2.54H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 169.8 (d, *J* = 4.5 Hz), 140.4, 132.4 (d, *J* = 2.6 Hz), 132.4 (d, *J* = 2.5 Hz), 131.8 (d, *J* = 9.0 Hz), 131.3 (d, *J* = 9.2 Hz), 130.2 (d, *J* = 98.1 Hz), 129.0 (d, *J* = 106.8 Hz), 128.8 (d, *J* = 11.6 Hz), 128.6 (d, *J* = 11.8 Hz), 128.4, 128.4, 126.2, 70.4 (dd, *J* = 86.2, 6.8 Hz), 32.2 (t, *J* = 12.0 Hz), 30.4 (d, *J* = 2.5 Hz), 20.5. **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 30.38. **HRMS** (ESI) (m/z): calcd for $C_{23}H_{23}DO_3P$ $[M+H]^+$: 380.1520, found: 380.1519.



3-(Benzo[d][1,3]dioxol-5-yl)-1-(diethoxyphosphoryl)-2-methylpropyl-2-d acetate (23)

The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 67 mg (46% yield). $\mathbf{R_f}$ = 0.5 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). 87% and 27% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 6.74 (d, *J* = 7.9 Hz, 1H), 6.68 (dd, *J* = 3.9, 1.7 Hz, 1H), 6.62 (ddd, *J* = 7.9, 4.2, 1.7 Hz, 1H), 5.94 (s, 2H), 5.23 (dd, *J* = 19.9, 9.8 Hz, 1H), 4.22-4.11 (m, 4H), 3.03 (d, *J* = 13.8 Hz, 0.46H) (*minor*

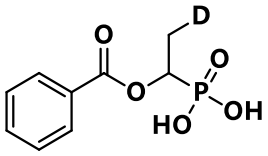
diastereomer), 2.76 (d, *J* = 13.5 Hz, 0.54H), 2.36 (d, *J* = 13.4 Hz, 0.54H), 2.25 (d, *J* = 13.6 Hz, 0.46H) (*minor diastereomer*), 2.17 (d, *J* = 7.5 Hz, 2.18H), 1.48 (dd, *J* = 16.6, 7.2 Hz, 0.13H), 1.40-1.29 (m, 6H), 1.04 (d, *J* = 7.0 Hz, 1.62H), 0.97 (d, *J* = 6.7 Hz, 1.38H) (*minor diastereomer*). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 170.0 (d, *J* = 7.6 Hz), 170.0 (d, *J* = 7.3 Hz), 147.6, 147.6, 145.9, 145.8, 133.7, 133.4, 122.2, 122.1, 109.5, 109.4, 108.1, 108.1, 100.8, 100.8, 71.8 (dd, *J* = 165.4, 7.3 Hz), 70.2 (dd, *J* = 166.0, 6.9 Hz), 62.7 (d, *J* = 6.7 Hz), 62.7 (d, *J* = 6.9 Hz), 62.6 (d, *J* = 6.4 Hz), 39.8, 39.8, 38.2 (d, *J* = 7.5 Hz), 36.2 (d, *J* = 10.4 Hz), 20.7, 20.7, 16.4 (d, *J* = 14.6 Hz), 16.4 (d, *J* = 14.8 Hz), 15.9 (d, *J* = 7.6 Hz), 15.8 (d, *J* = 6.9 Hz), 14.8 (d, *J* = 4.6 Hz), 14.7 (d, *J* = 4.5 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 20.44 (q, *J* = 7.9 Hz), 20.17 (q, *J* = 8.2 Hz). **HRMS** (ESI) (m/z): calcd for $C_{17}H_{25}DO_7P$ $[M+H]^+$: 374.1473, found: 374.1478.



1-(Diethoxyphosphoryl)-3-(4-isopropylphenyl)-2-methylpropyl-2-d acetate (24)

The title compound was synthesized following **General Procedure E** and purified by using silica gel chromatography to yield a yellow oil, 65 mg (48% yield). **R_f** = 0.5 (PE/EA/EtOH = 8:1:1, *v*/*v*/*v*). 94% and 24% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ = 7.16 (d, *J* = 7.9 Hz, 2H), 7.10 (dd, *J* = 8.1, 2.0 Hz, 2H), 5.26 (dd, *J* = 23.7, 9.8 Hz, 1H), 4.24-4.07 (m, 4H), 3.06 (d, *J* = 13.7 Hz, 0.46H) (*minor diastereomer*), 2.96-2.85 (m, 1H), 2.81 (d, *J* = 13.4 Hz, 0.54H), 2.42 (d, *J* = 13.3 Hz, 0.46H) (*minor diastereomer*), 2.32 (dd, *J* = 13.2, 6.3 Hz, 0.54H), 2.17 (d, *J* = 15.8 Hz, 2.27H), 1.50-1.42 (m, 0.06H), 1.34 (dq, *J* = 19.4, 7.1 Hz, 6H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.06 (d, *J* = 7.4 Hz, 1.62H), 0.99 (d, *J* = 6.7 Hz, 1.38H) (*minor diastereomer*). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ = 170.0 (d, *J* = 8.2 Hz), 169.9 (d, *J* = 8.1 Hz), 146.7, 146.6, 137.2, 137.0, 129.1, 129.1, 126.4, 126.3, 72.0 (dd, *J* = 165.2, 7.3 Hz), 70.4 (dd, *J* = 165.6, 7.1 Hz), 62.7 (d, *J* = 2.4 Hz), 62.7 (d, *J* = 2.4

Hz), 62.6 (d, *J* = 6.5 Hz), 39.8, 39.7, 38.2 (d, *J* = 7.9 Hz), 36.1 (d, *J* = 8.8 Hz), 33.7, 24.1, 24.0, 20.7, 16.4 (d, *J* = 14.7 Hz), 16.4 (d, *J* = 13.0 Hz), 16.1 (d, *J* = 7.0 Hz), 16.0 (d, *J* = 7.2 Hz), 15.0 (d, *J* = 4.4 Hz), 14.8 (d, *J* = 4.4 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$, ppm) δ = 20.54 (q, *J* = 8.5 Hz), 20.30 (q, *J* = 8.3 Hz). **HRMS** (ESI) (m/z): calcd for $C_{19}H_{31}DO_5P$ $[M+H]^+$: 372.2045, found: 372.2047.



(1-(benzoyloxy)ethyl-2-d)phosphonic acid (27)

The title compound was synthesized following **Experimental Procedure F** and purified by using silica gel chromatography to yield a yellow oil, 175 mg (73% yield). **R_f** = 0.2 (DCM/MeOH = 10:1, *v*/*v*). 98% Deuterium incorporation was determined by ^{1}H NMR. **^{1}H NMR** (500 MHz, DMSO-d_6/D_2O = 1:3, ppm) δ = 8.01 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.15 (s, 1H), 1.41 (dd, *J* = 14.5, 6.4 Hz, 1.98H). **^{13}C NMR** (126 MHz, DMSO-d_6/D_2O = 1:3, ppm) δ = 166.0, 133.5, 130.7, 129.9, 128.9, 16.2. **^{31}P NMR** (202 MHz, DMSO-d_6/D_2O = 1:2, ppm) δ = 15.15. **HRMS** (ESI) (m/z): calcd for $C_9H_9DO_5P$ $[M-H]^+$: 230.0323, found: 230.0322.

References

1. K. Holthusen, W. Leitner, G. Franciò, *J. Org. Chem.* **2016**, *81*, 4823–4828.

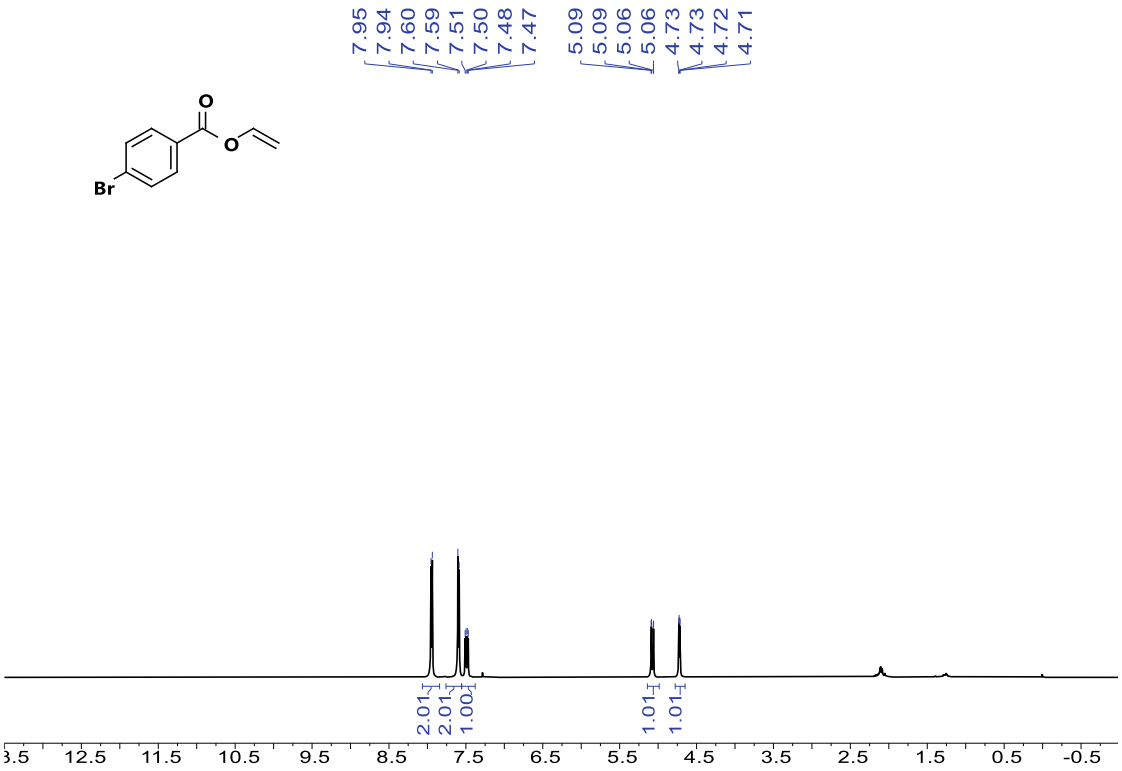
2. S. Martínez-Montero, S. Fernández, Y. S. Sanghvi, V. Gotor, M. Ferrero, *Org. Biomol. Chem.* **2011**, *9*, 5960–5966.

3. (a) R.-D. He, C.-L. Li, Q.-Q. Pan, P. Guo, X.-Y. Liu, X.-Z. Shu, *J. Am. Chem. Soc.* **2019**, *141*, 12481–12486. (b) C. Liu, J. Yuan, J. Zhang, Z. Wang, Z. Zhang, W. Zhang, *Org. Lett.* **2018**, *20*, 108–111.

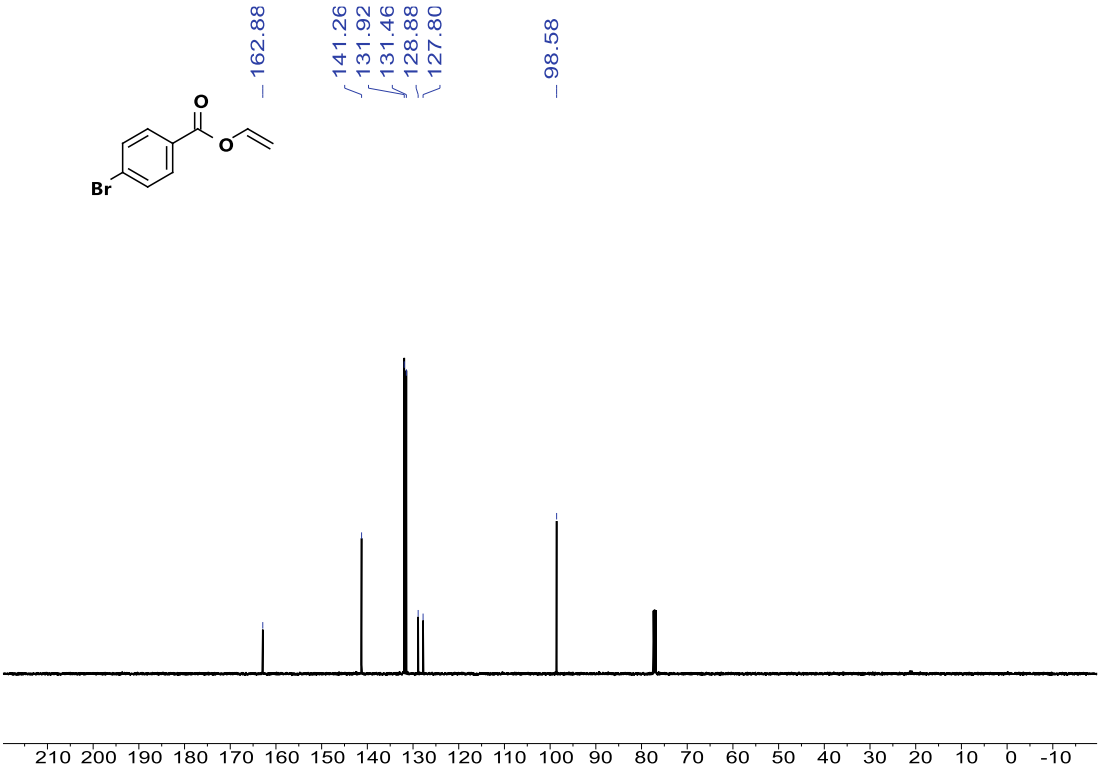
4. (a) R. Jiang, Z. Chen, K. Zhan, L. Liu, J. Zhou, Y. Ai, S. Li, H. Bao, Z. Hu, L. Qi, J. Wang, H.-B. Sun, *Tetrahedron Lett.* **2018**, *59*, 3279–3282. (b) L. Steemers, L. Wijsman, J. H. van Maarseveen, *Adv. Synth. Catal.* **2018**, *360*, 4241-4245.

12. NMR Spectra

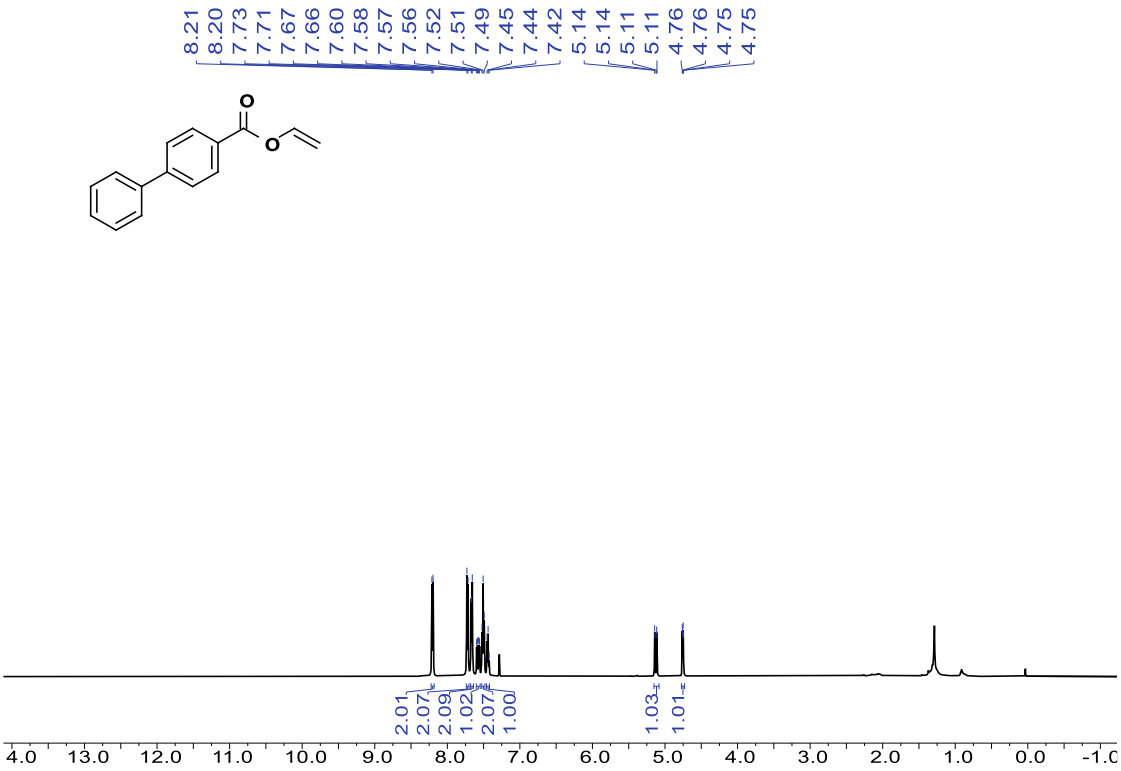
^{1}H NMR spectra of 1c (500 MHz, $CDCl_3$)



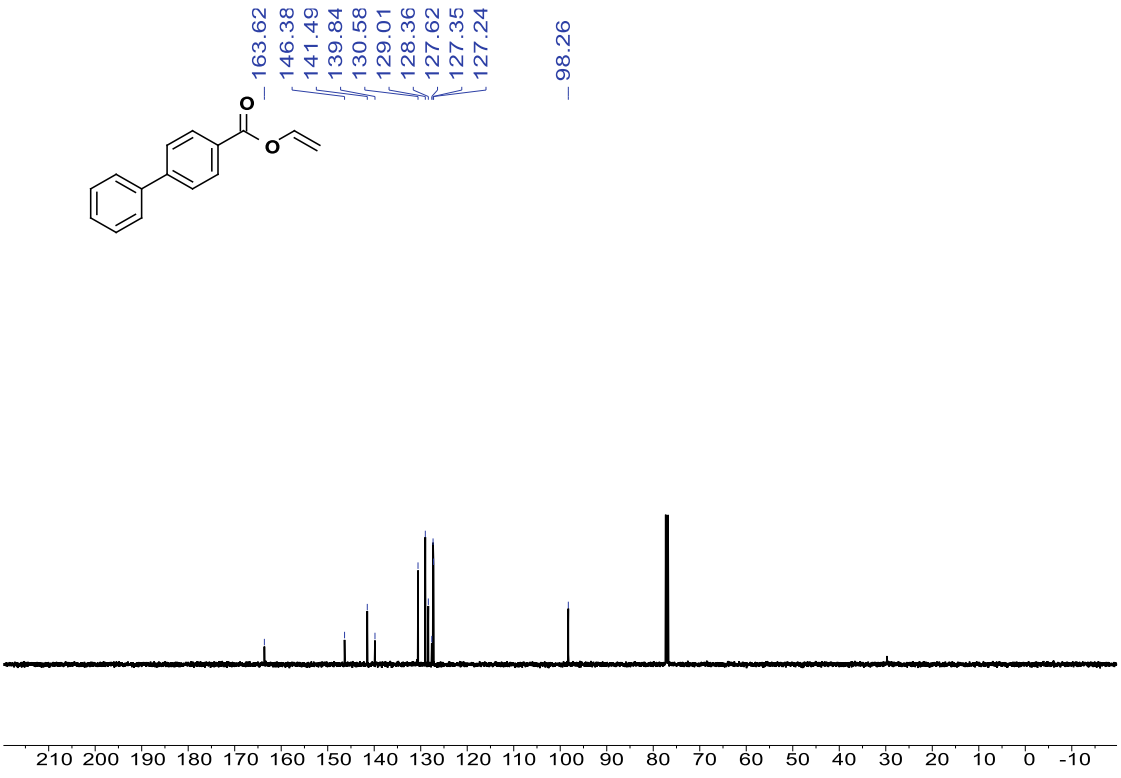
^{13}C NMR spectra of 1c (126 MHz, $CDCl_3$)



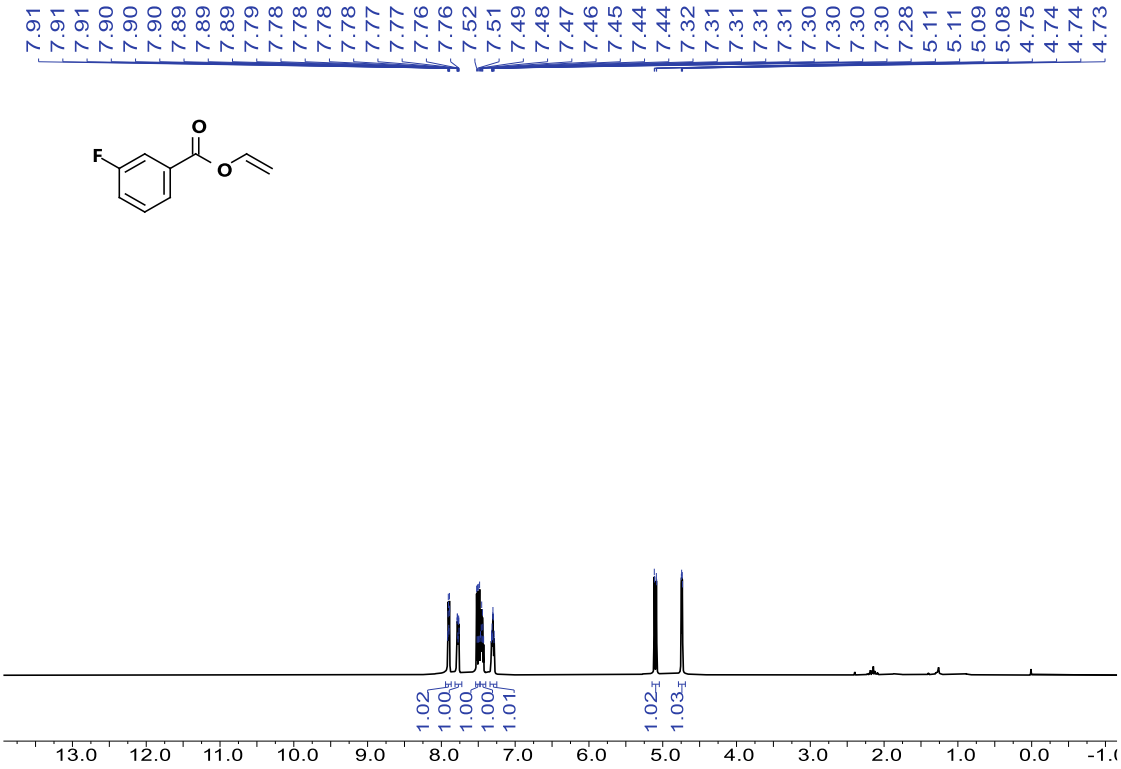
^{1}H NMR spectra of 1g (500 MHz, $CDCl_3$)



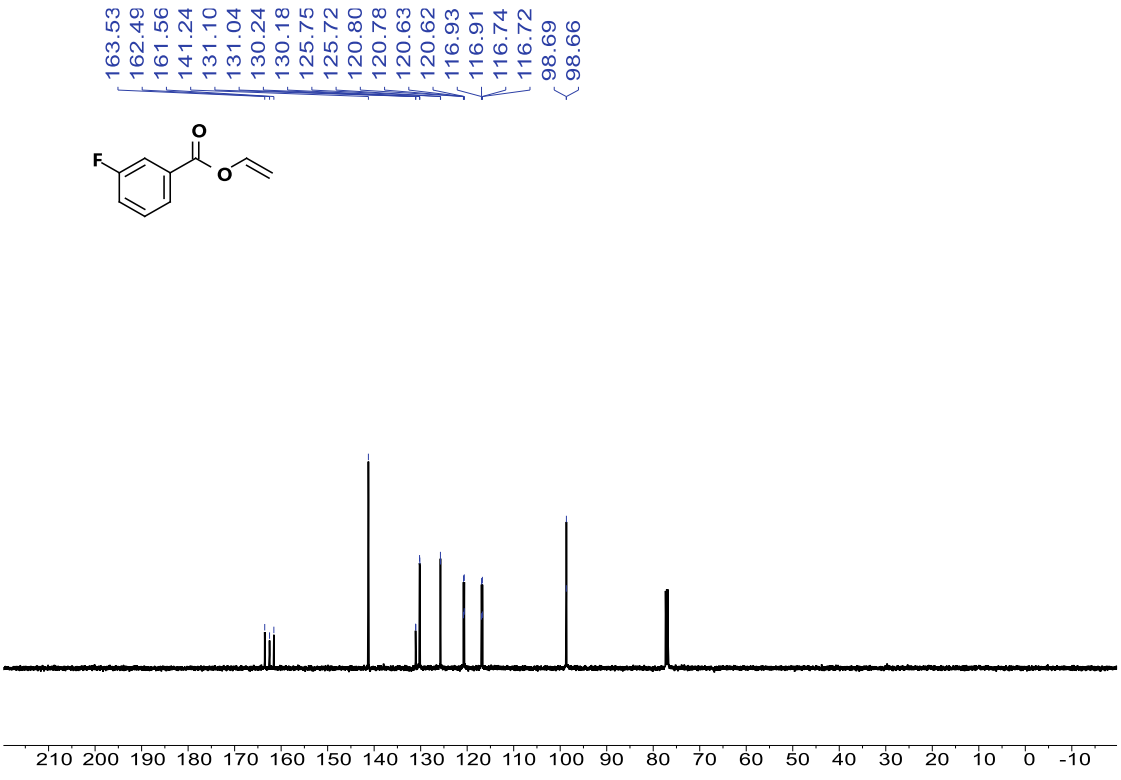
^{13}C NMR spectra of 1g (126 MHz, $CDCl_3$)



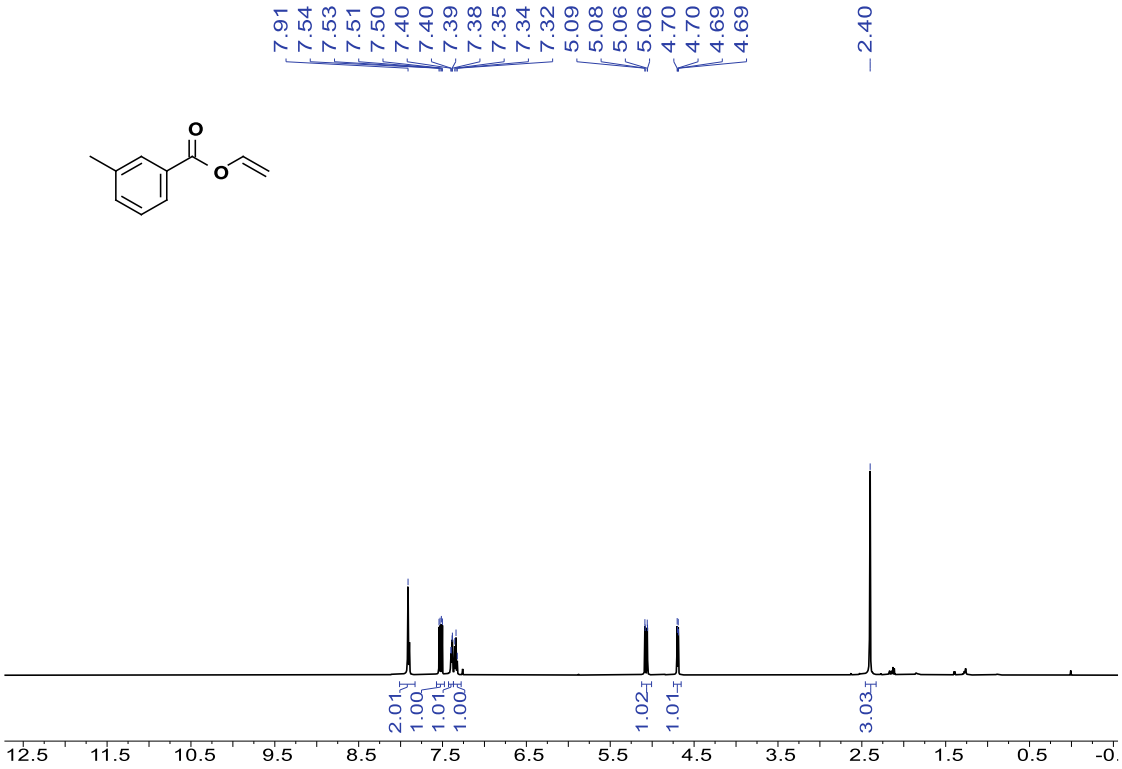
^{1}H NMR spectra of 1h (500 MHz, $CDCl_3$)



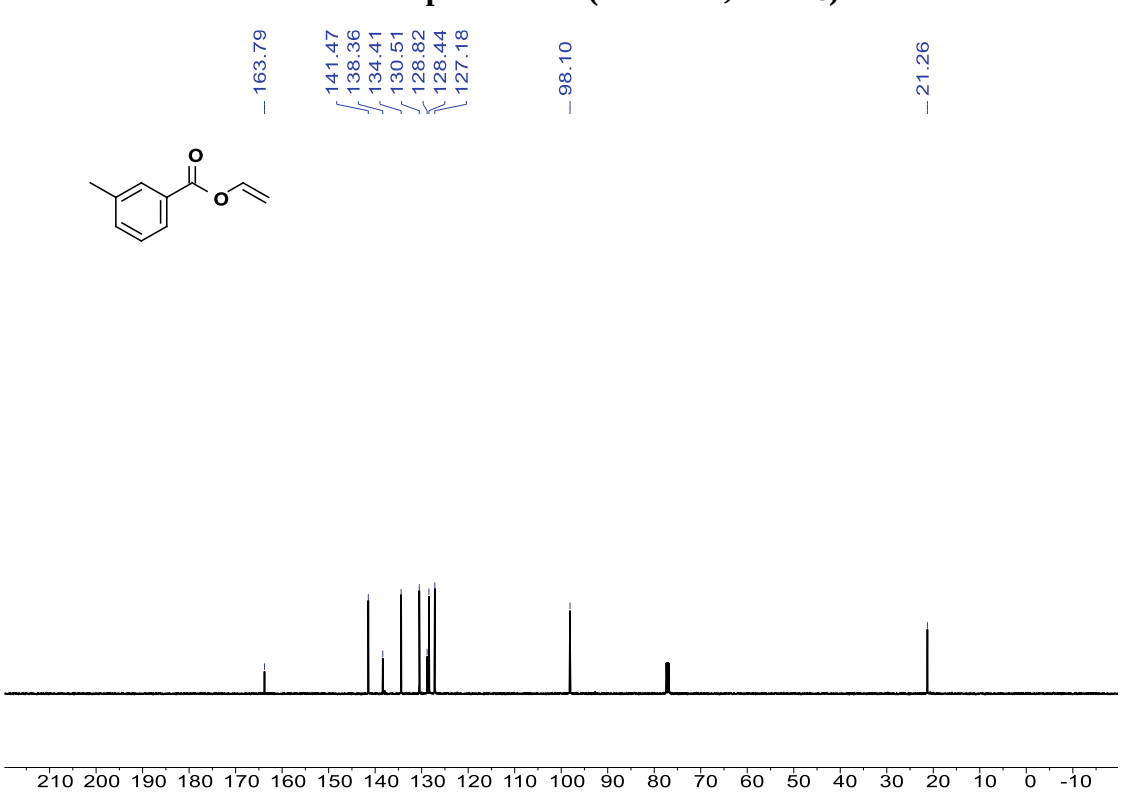
^{13}C NMR spectra of 1h (126 MHz, $CDCl_3$)



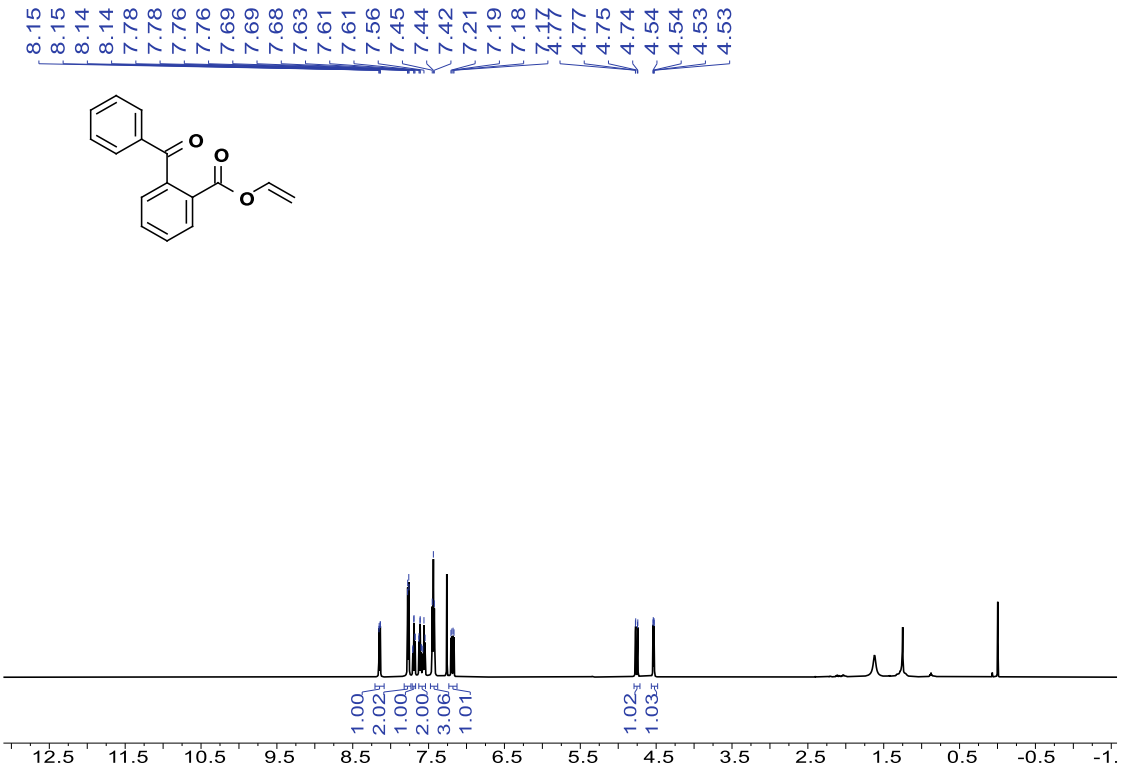
^{1}H NMR spectra of 1i (500 MHz, $CDCl_3$)



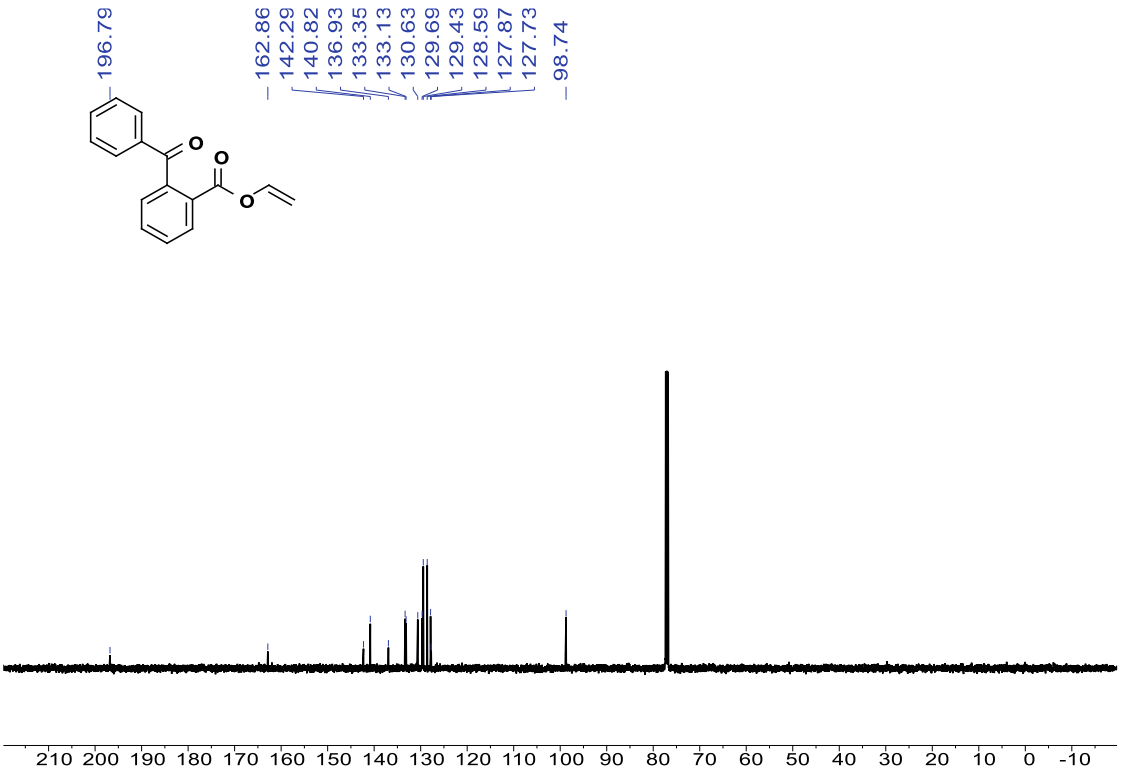
^{13}C NMR spectra of 1i (126 MHz, $CDCl_3$)



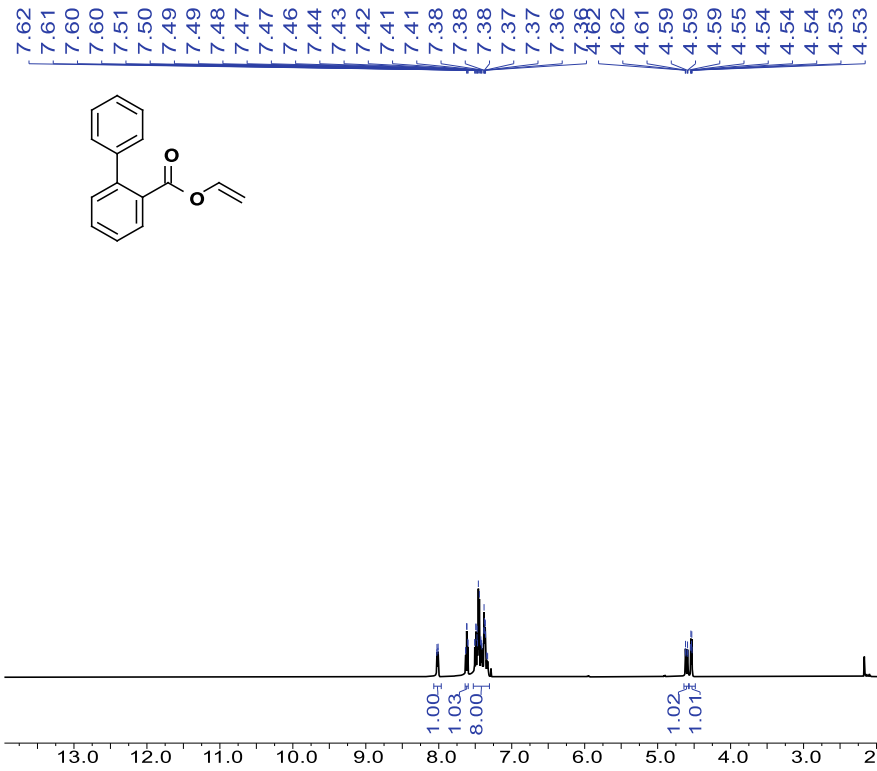
^{1}H NMR spectra of 1j (500 MHz, $CDCl_3$)



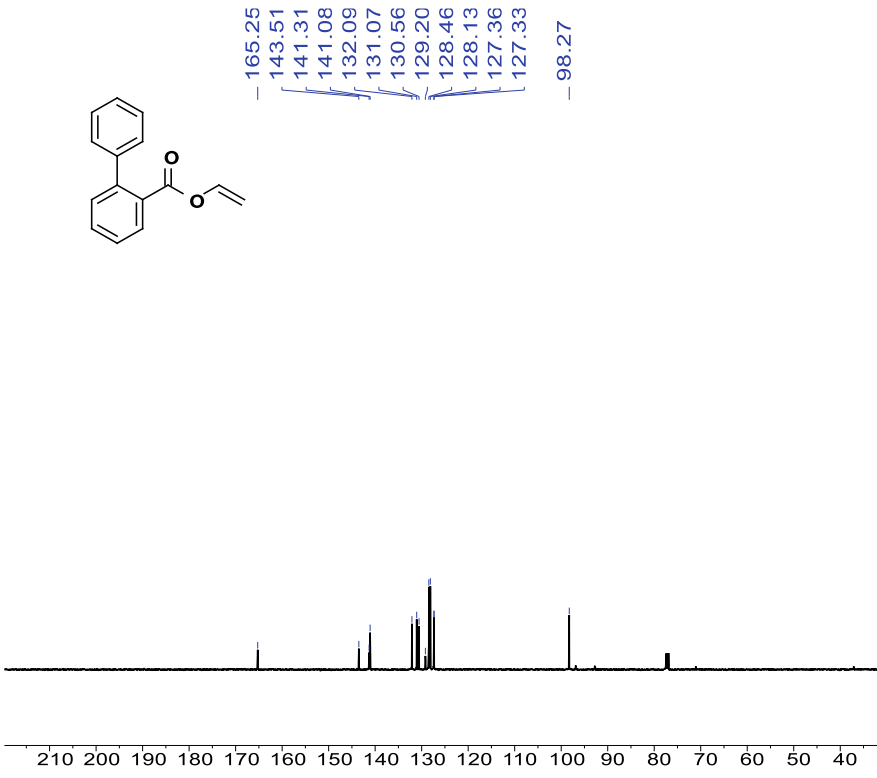
^{13}C NMR spectra of 1j (126 MHz, $CDCl_3$)



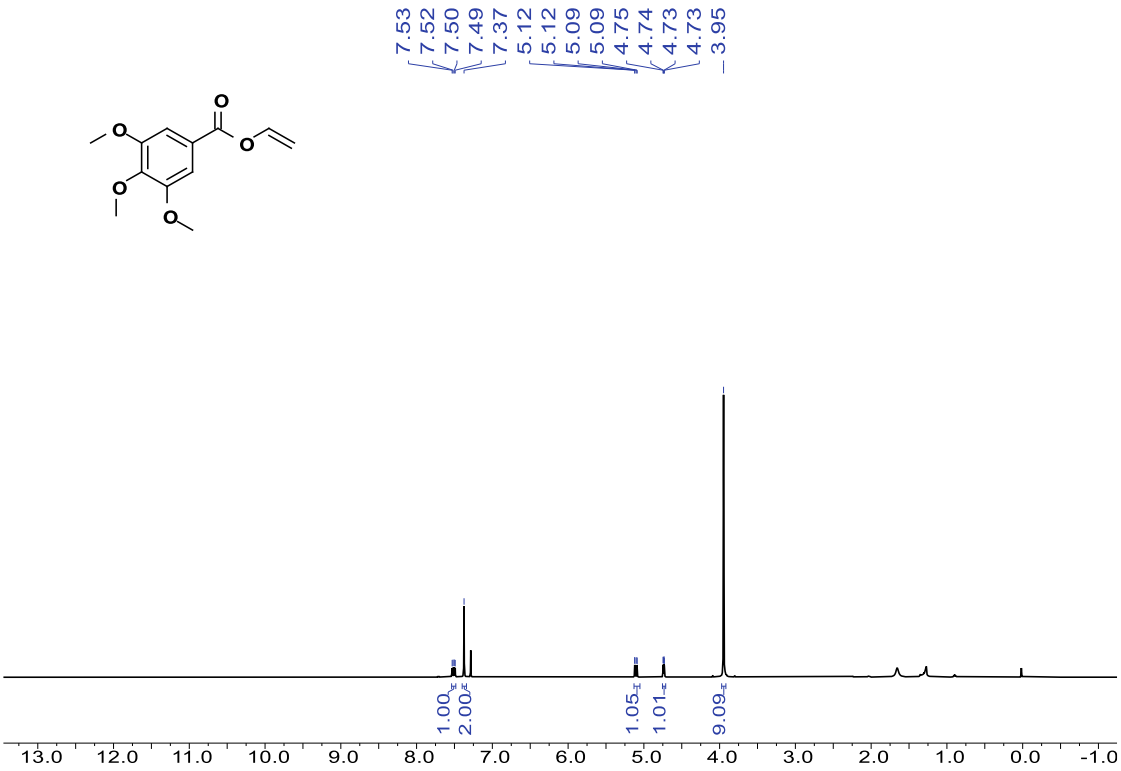
^{1}H NMR spectra of 1k (500 MHz, $CDCl_3$)



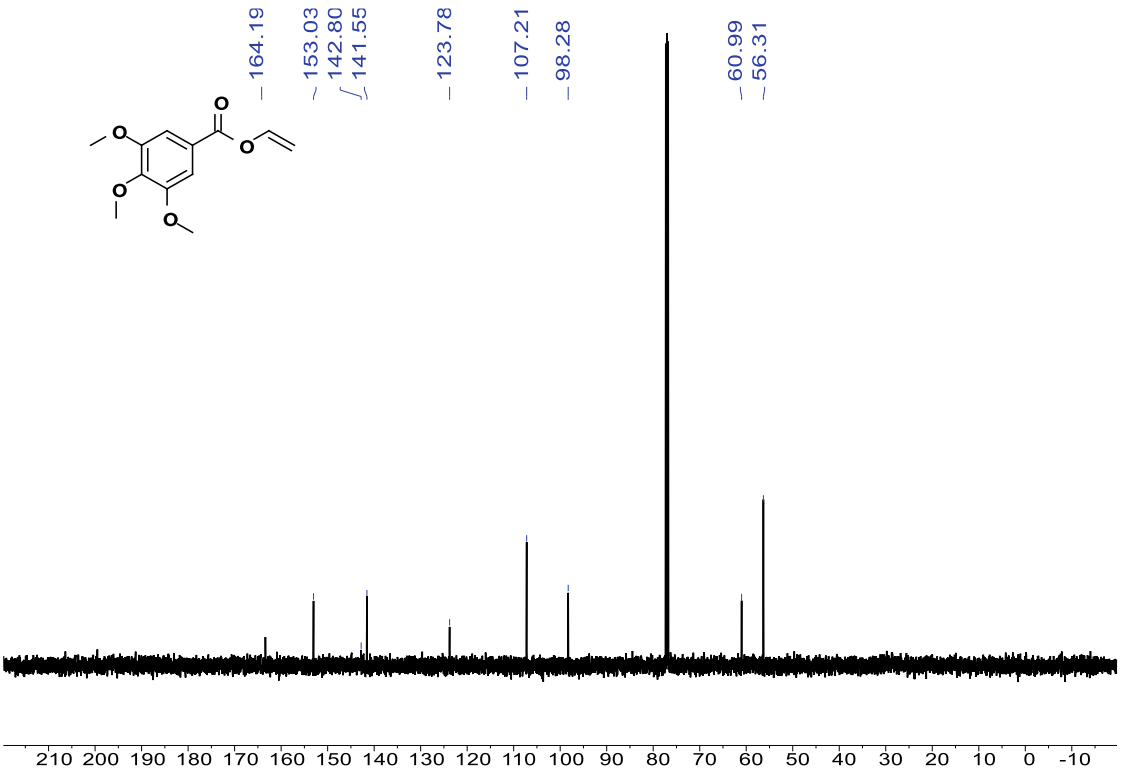
^{13}C NMR spectra of 1k (126 MHz, $CDCl_3$)



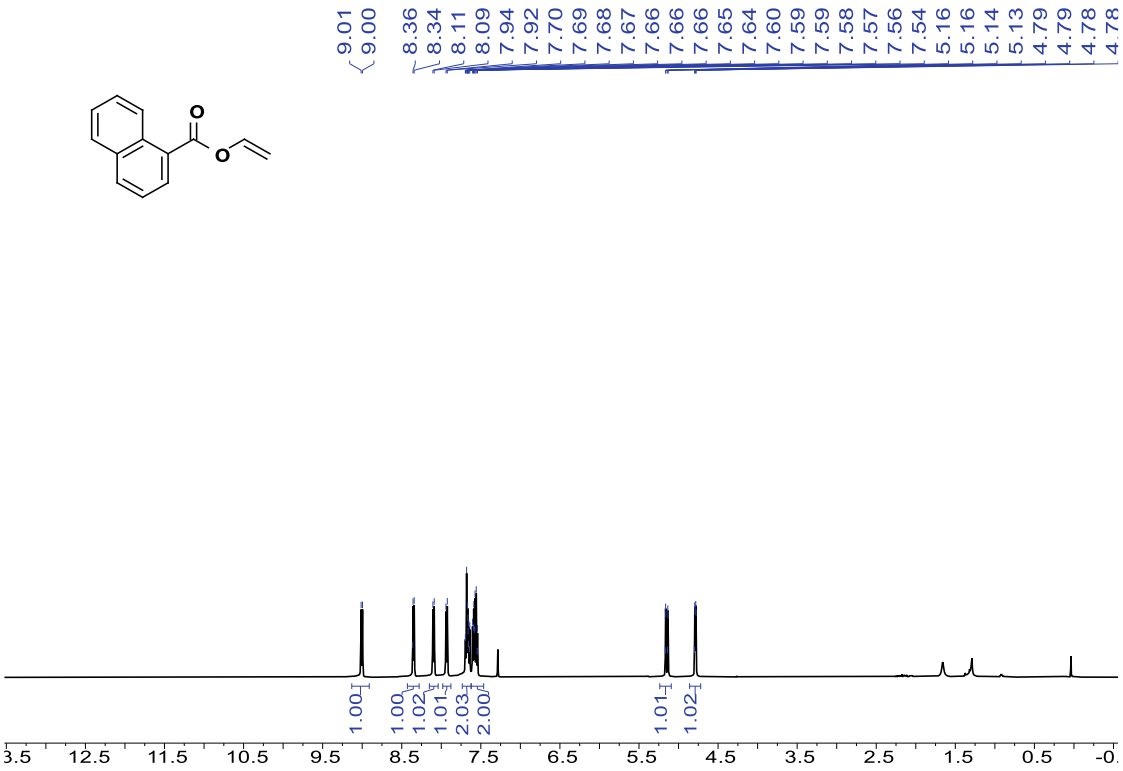
^{1}H NMR spectra of 1l (500 MHz, $CDCl_3$)



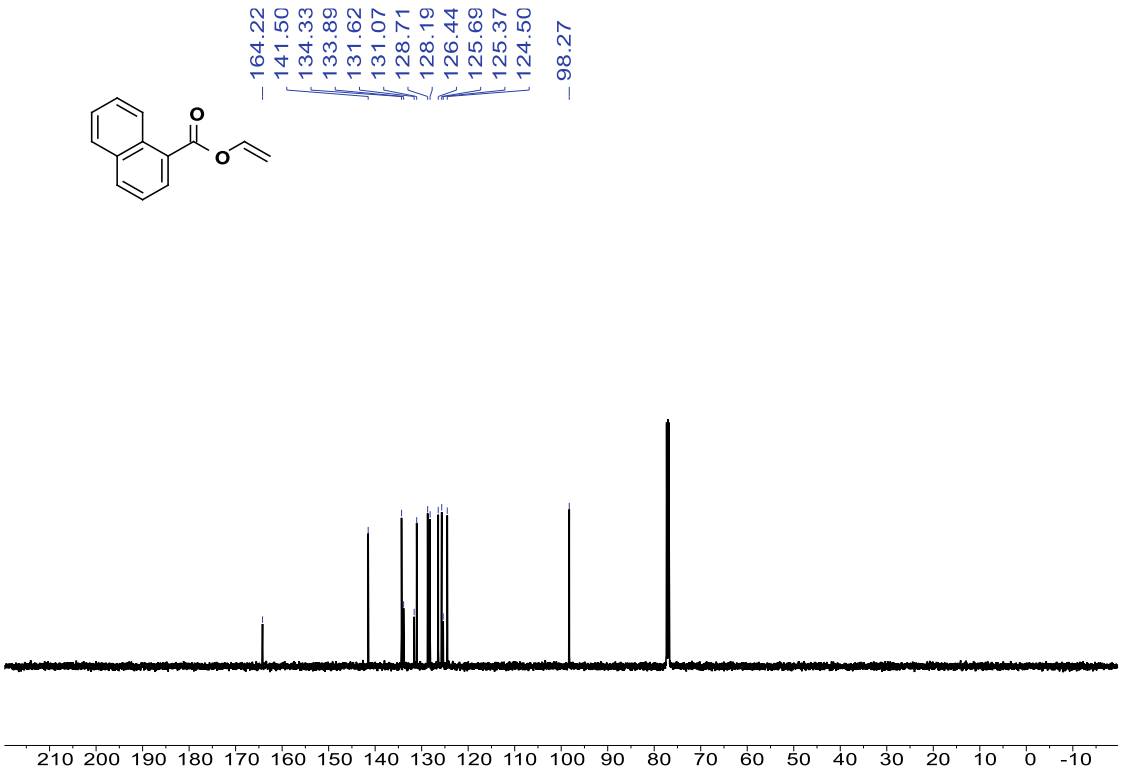
^{13}C NMR spectra of 1l (126 MHz, $CDCl_3$)



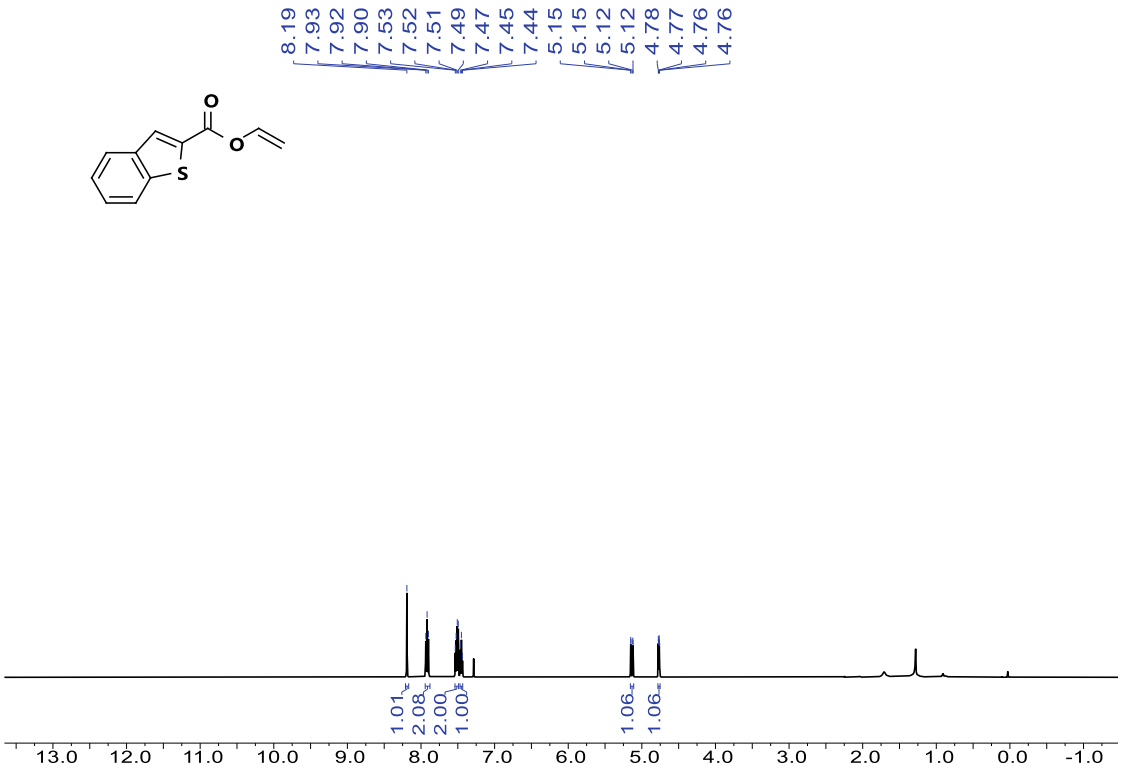
^{1}H NMR spectra of 1m (500 MHz, $CDCl_3$)



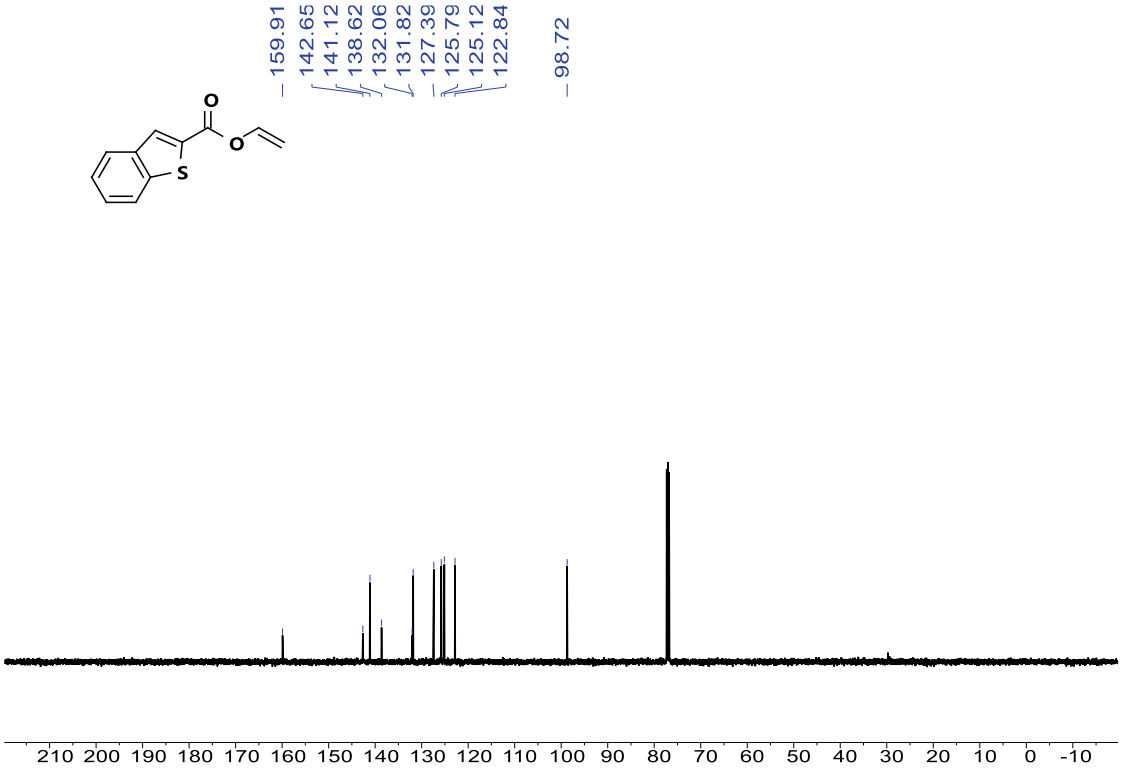
^{13}C NMR spectra of 1m (126 MHz, $CDCl_3$)



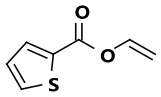
^{1}H NMR spectra of 1o (500 MHz, $CDCl_3$)

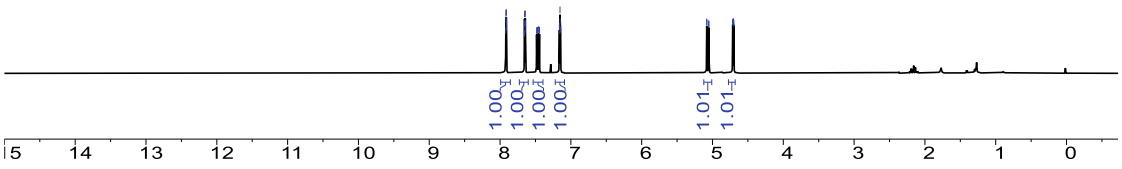


^{13}C NMR spectra of 1o (126 MHz, $CDCl_3$)

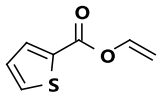


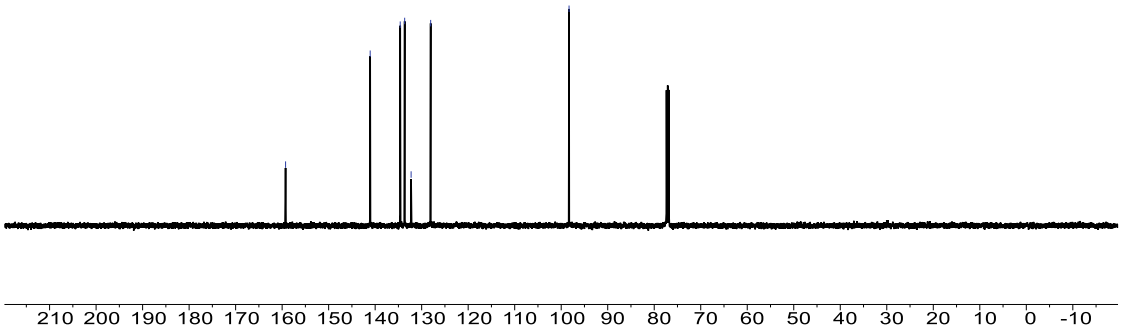
^{1}H NMR spectra of 1p (500 MHz, $CDCl_3$)



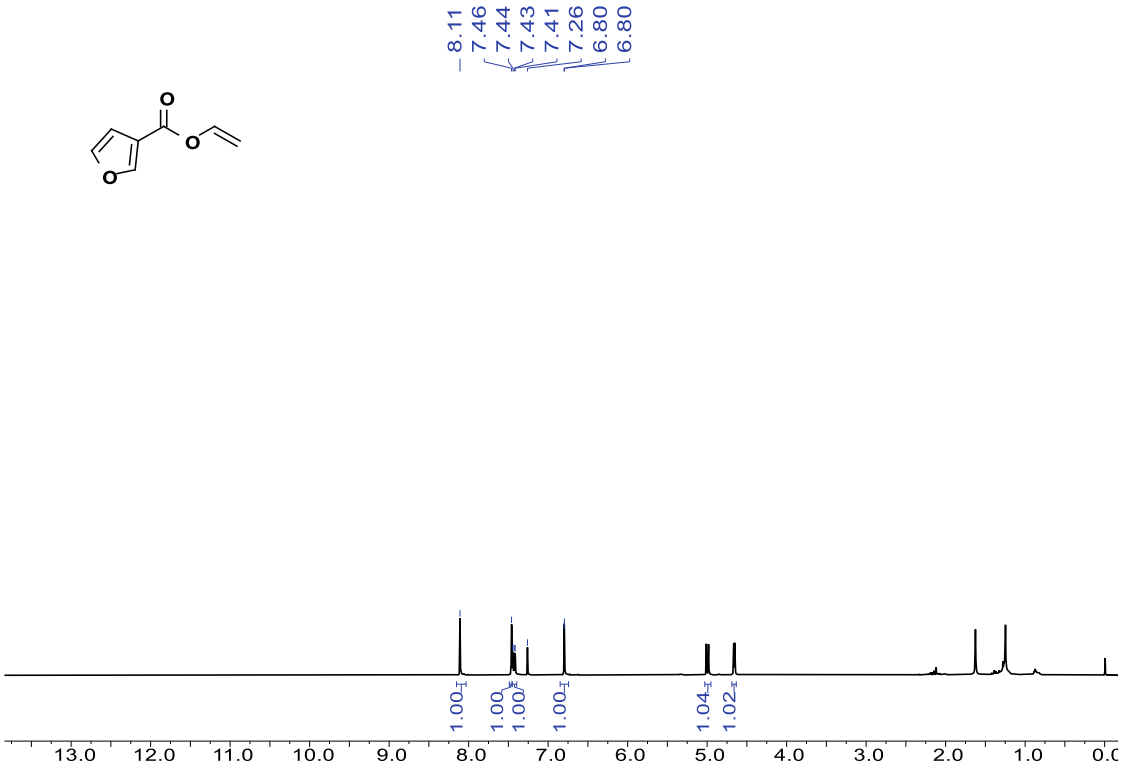


^{13}C NMR spectra of 1p (126 MHz, $CDCl_3$)

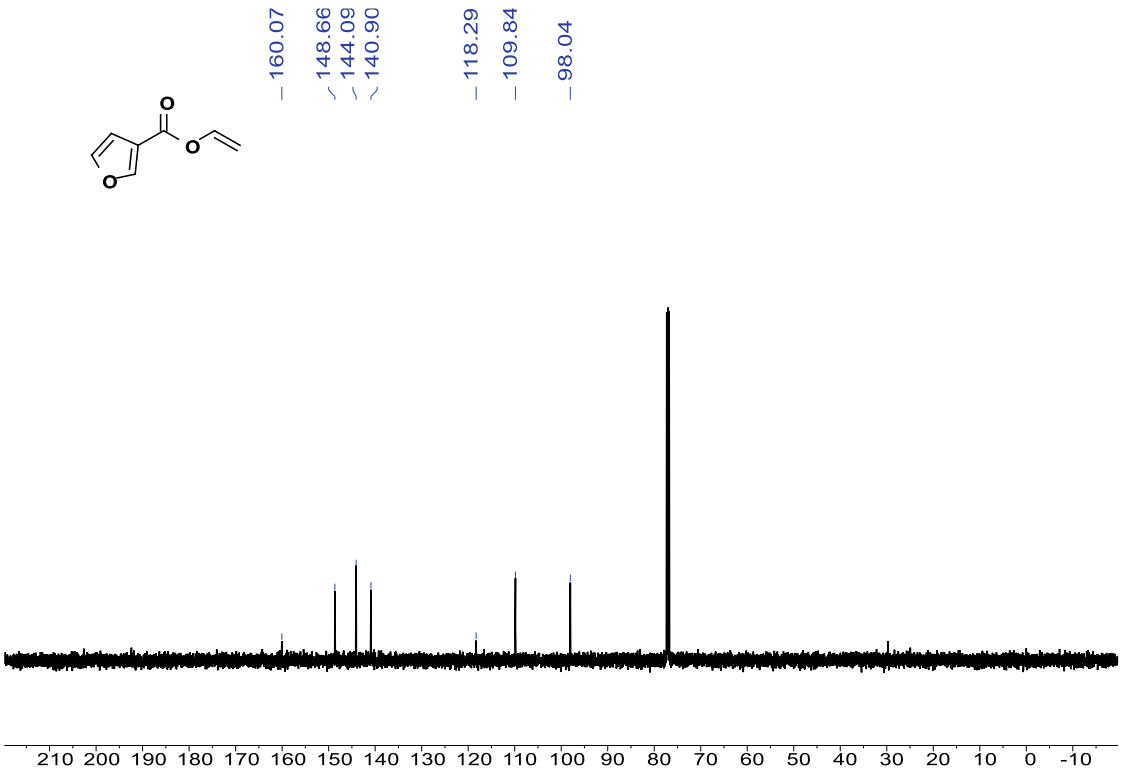




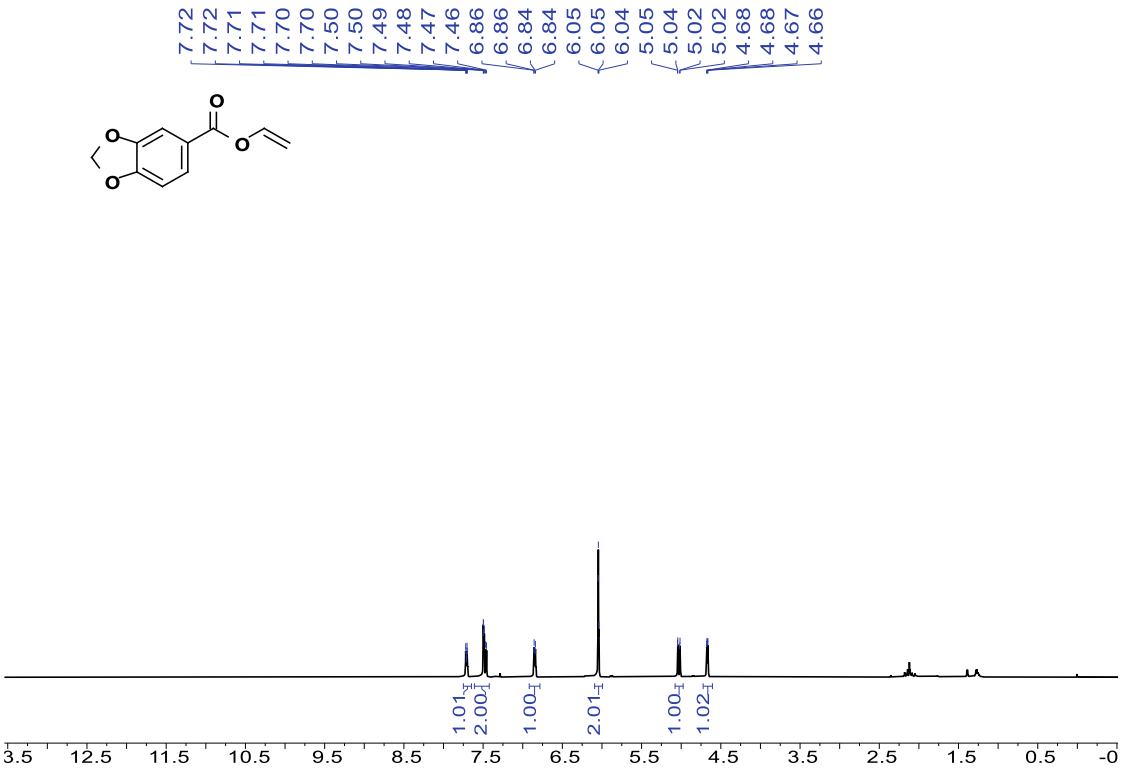
^{1}H NMR spectra of 1q (500 MHz, $CDCl_3$)



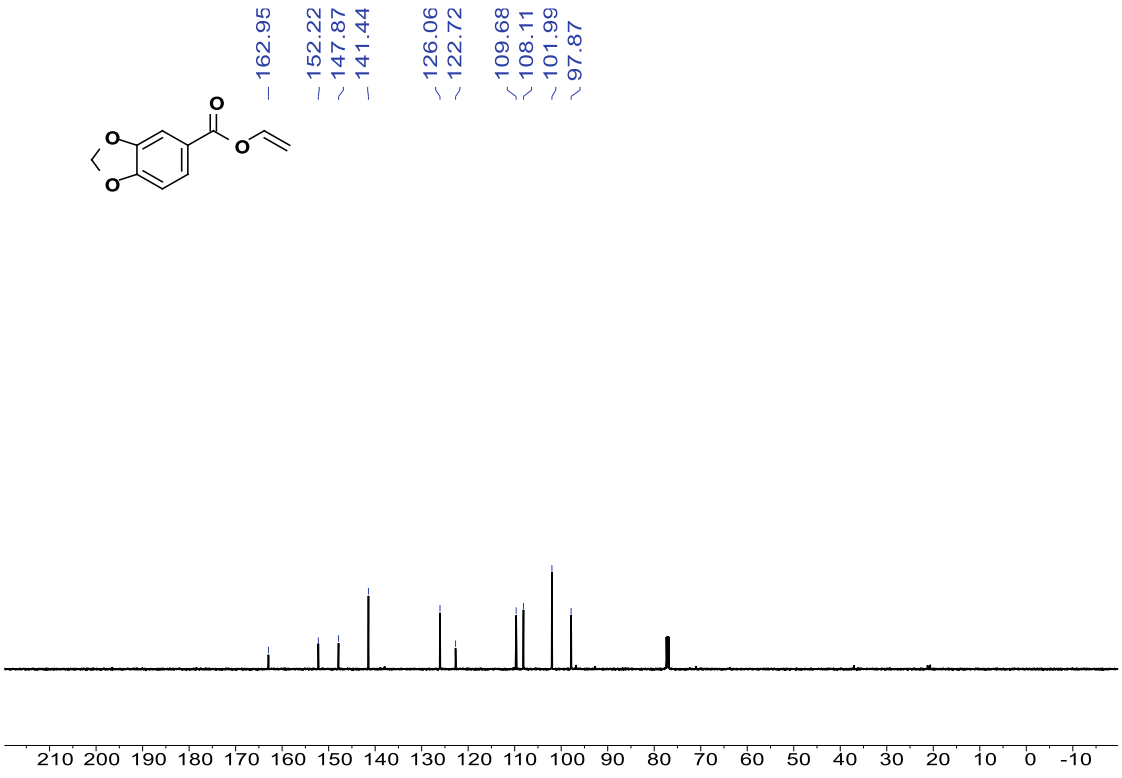
^{13}C NMR spectra of 1q (126 MHz, $CDCl_3$)



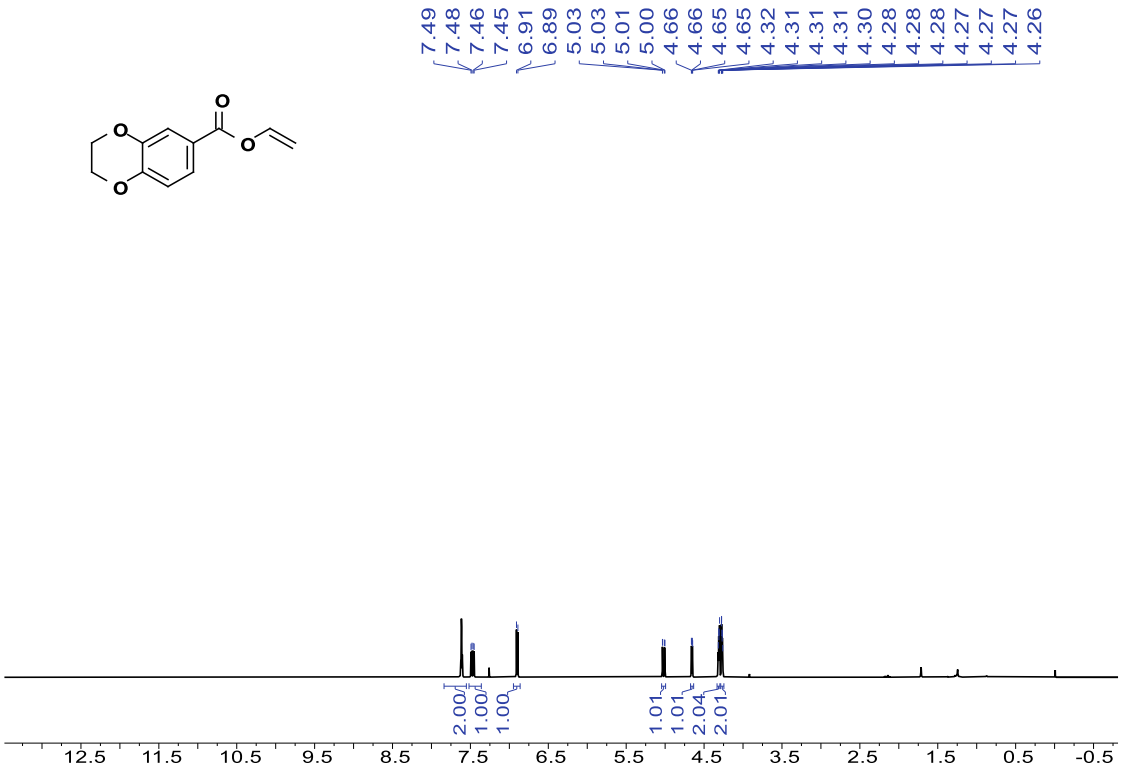
^{1}H NMR spectra of 1r (500 MHz, $CDCl_3$)



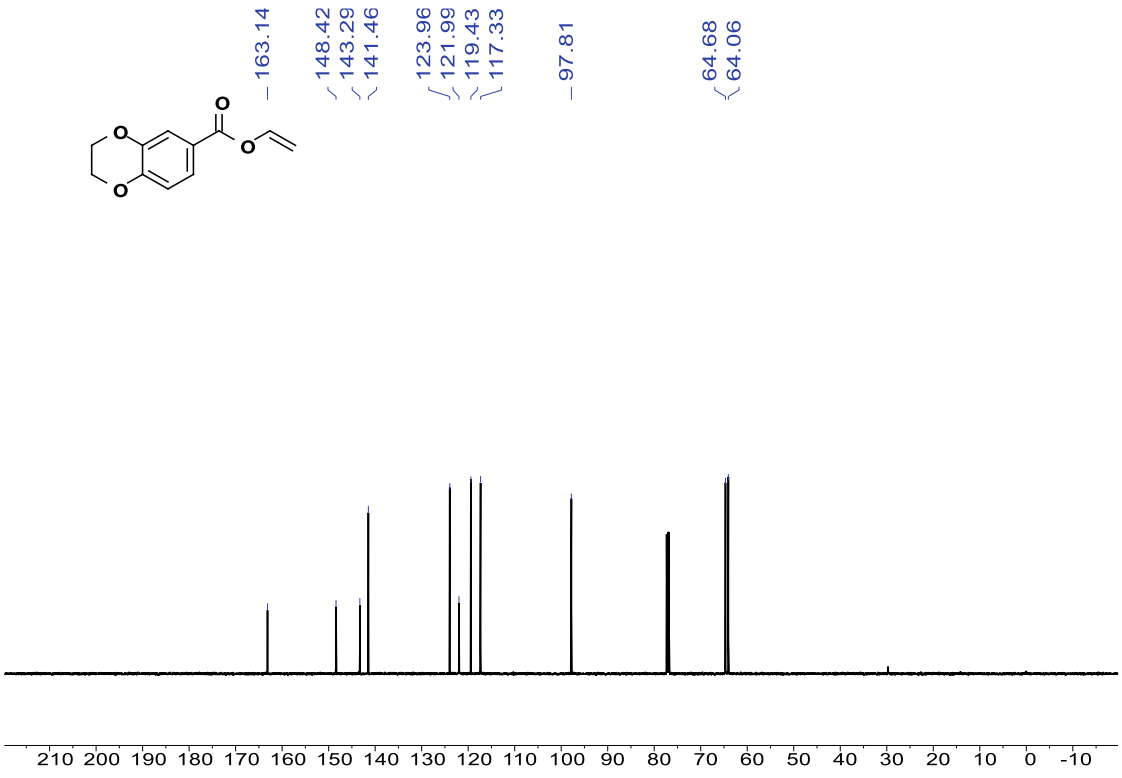
^{13}C NMR spectra of 1r (126 MHz, $CDCl_3$)



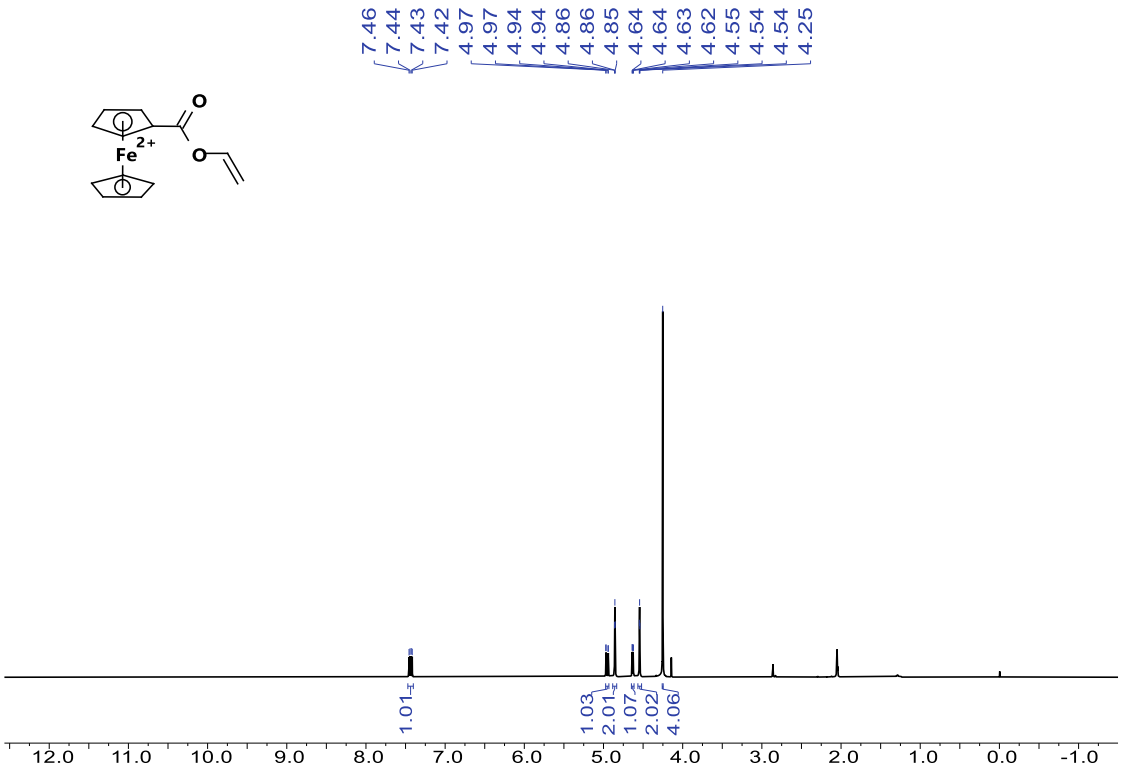
^{1}H NMR spectra of 1s (500 MHz, $CDCl_3$)



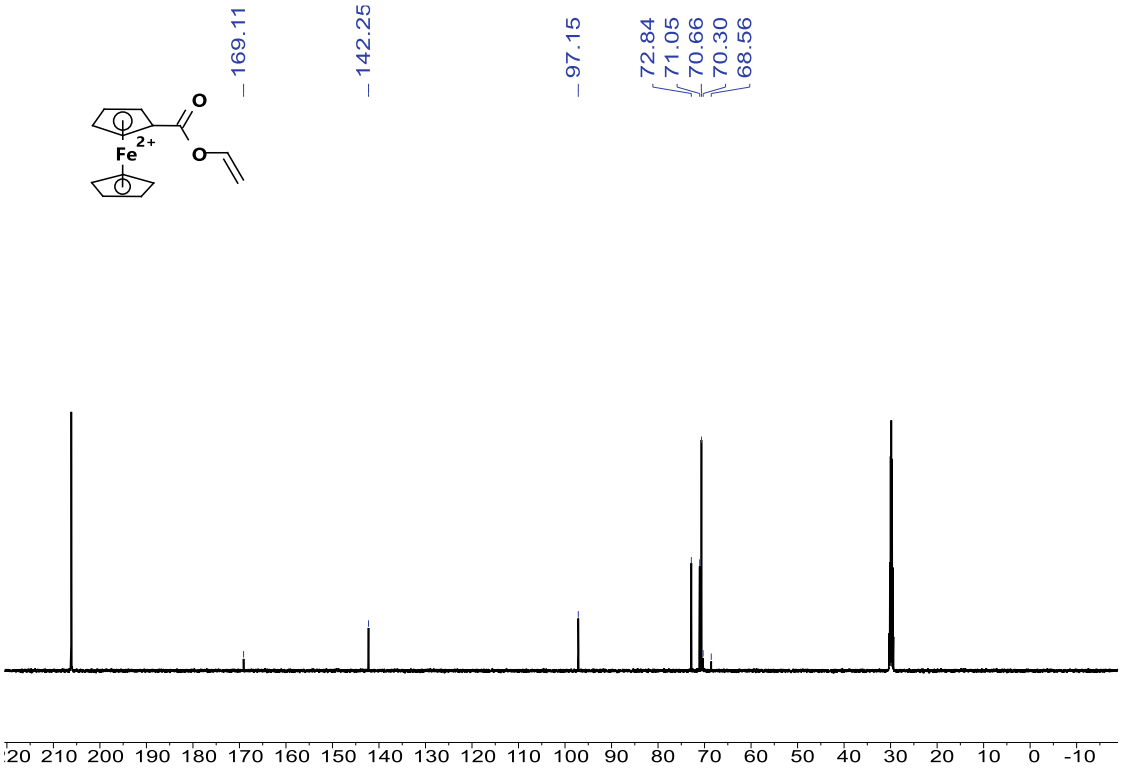
^{13}C NMR spectra of 1s (126 MHz, $CDCl_3$)



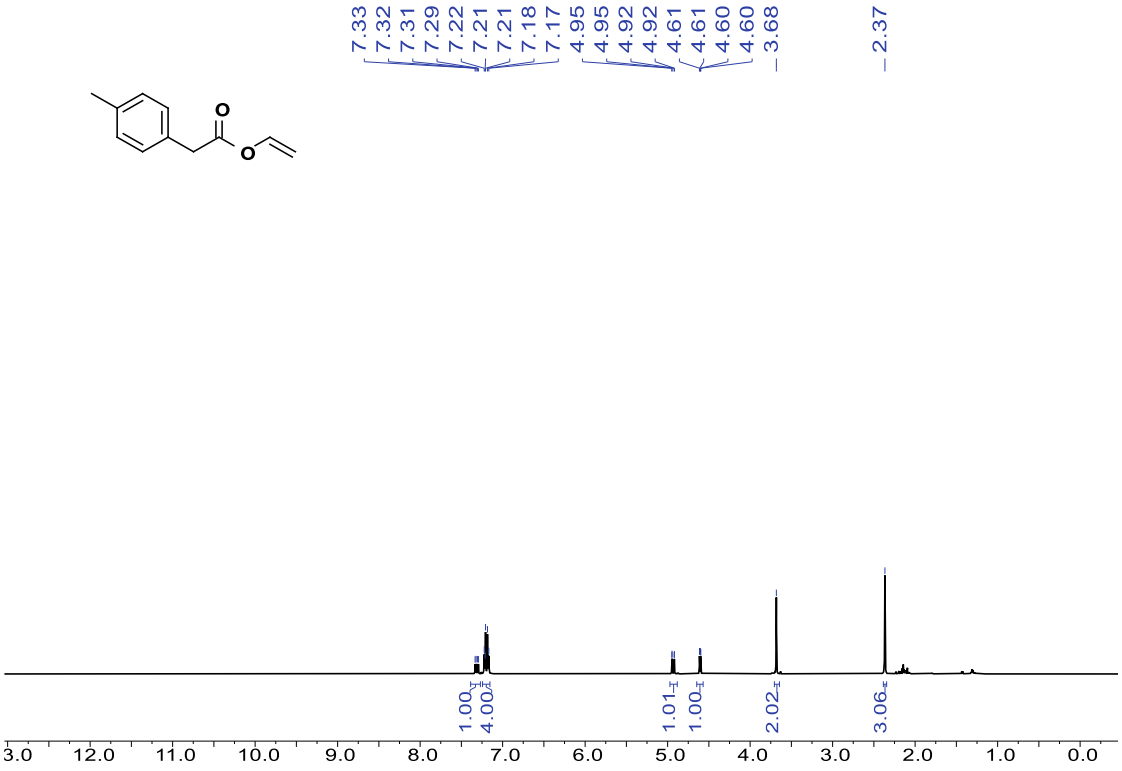
^{1}H NMR spectra of 1t (500 MHz, $(CD_3)_2CO$)



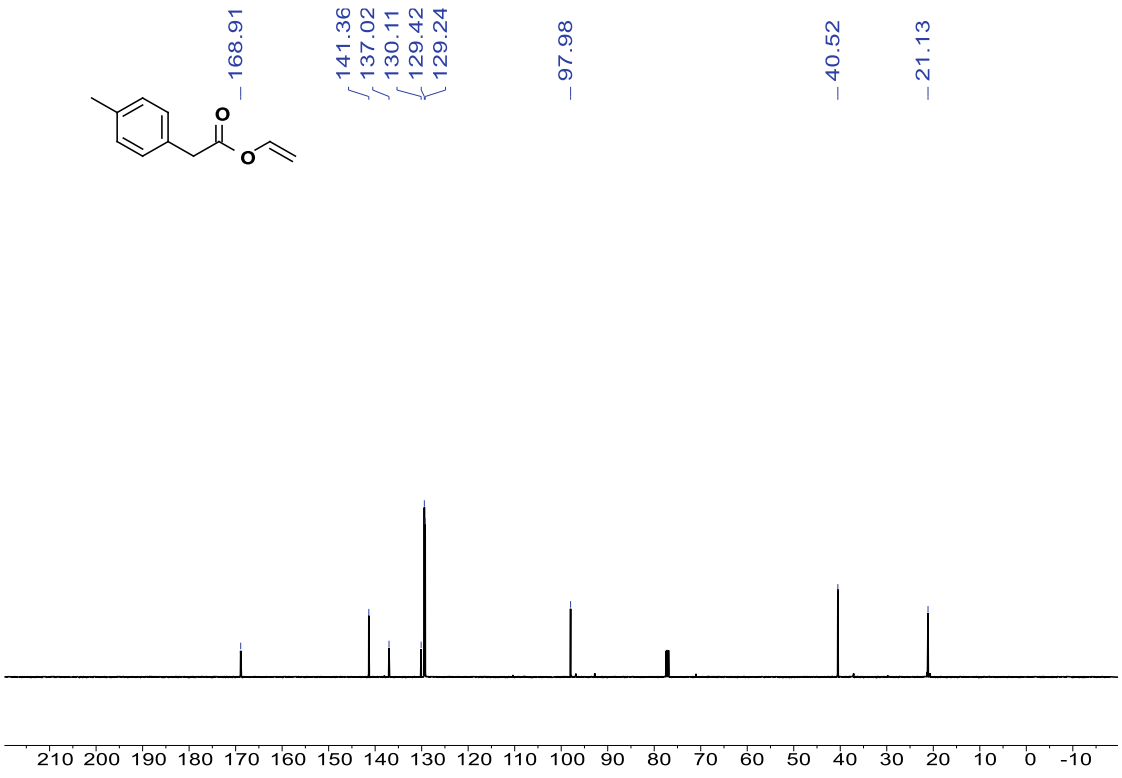
^{13}C NMR spectra of 1t (126 MHz, $(CD_3)_2CO$)



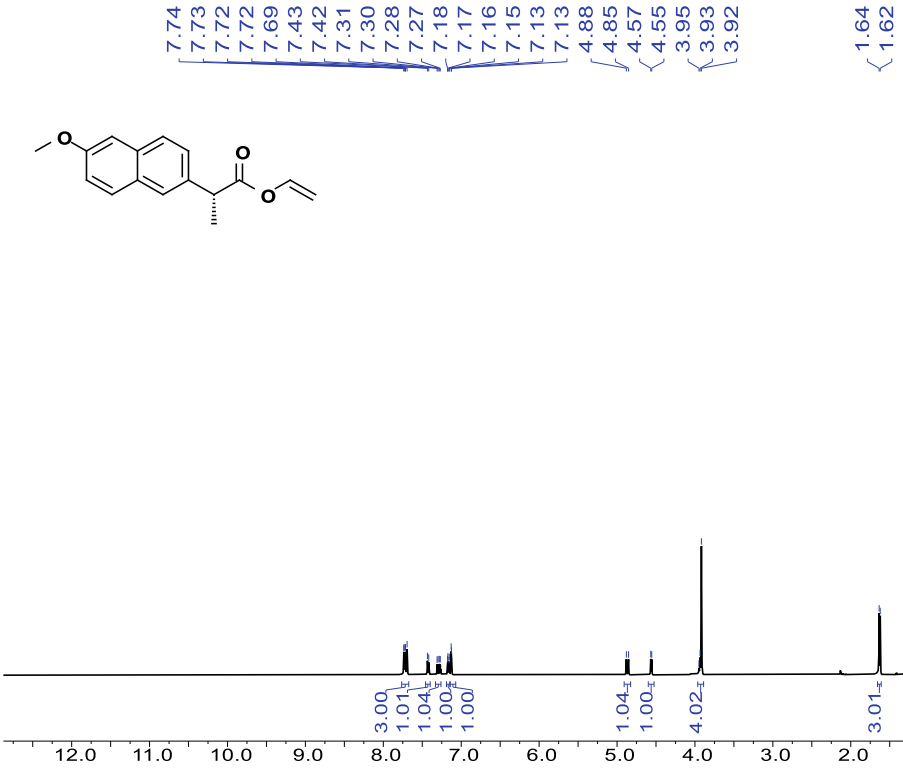
^{1}H NMR spectra of 1u (500 MHz, $CDCl_3$)



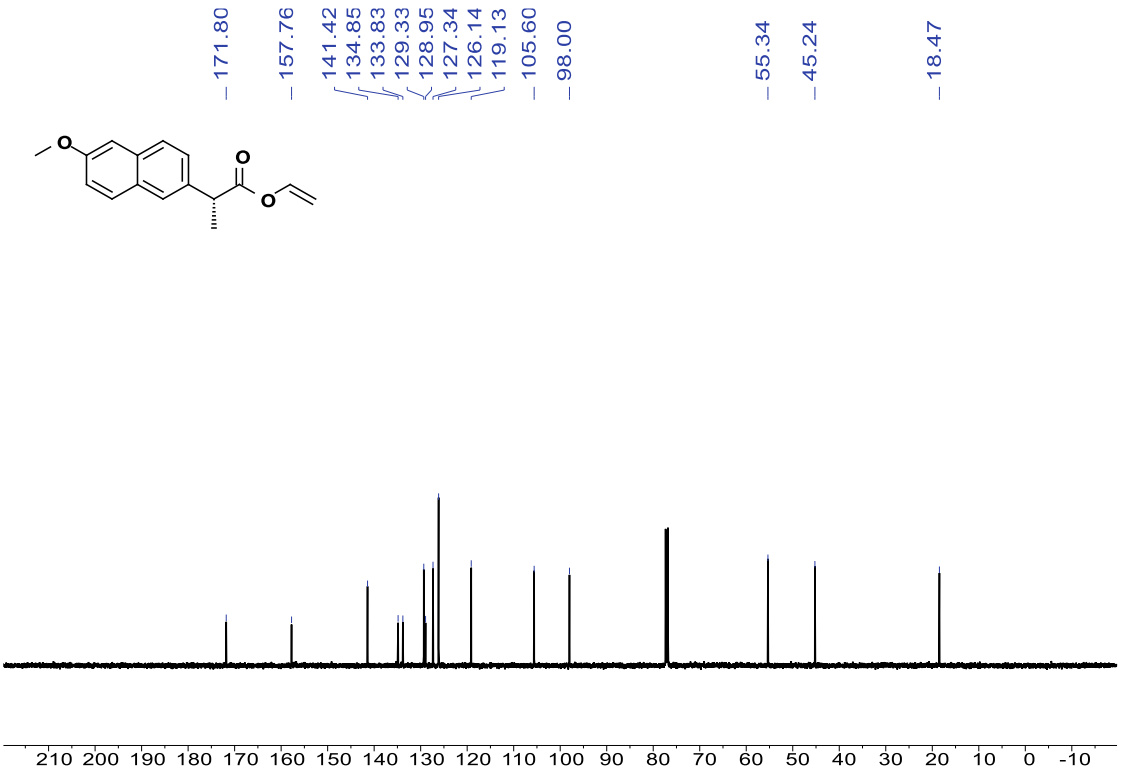
^{13}C NMR spectra of 1u (126 MHz, $CDCl_3$)



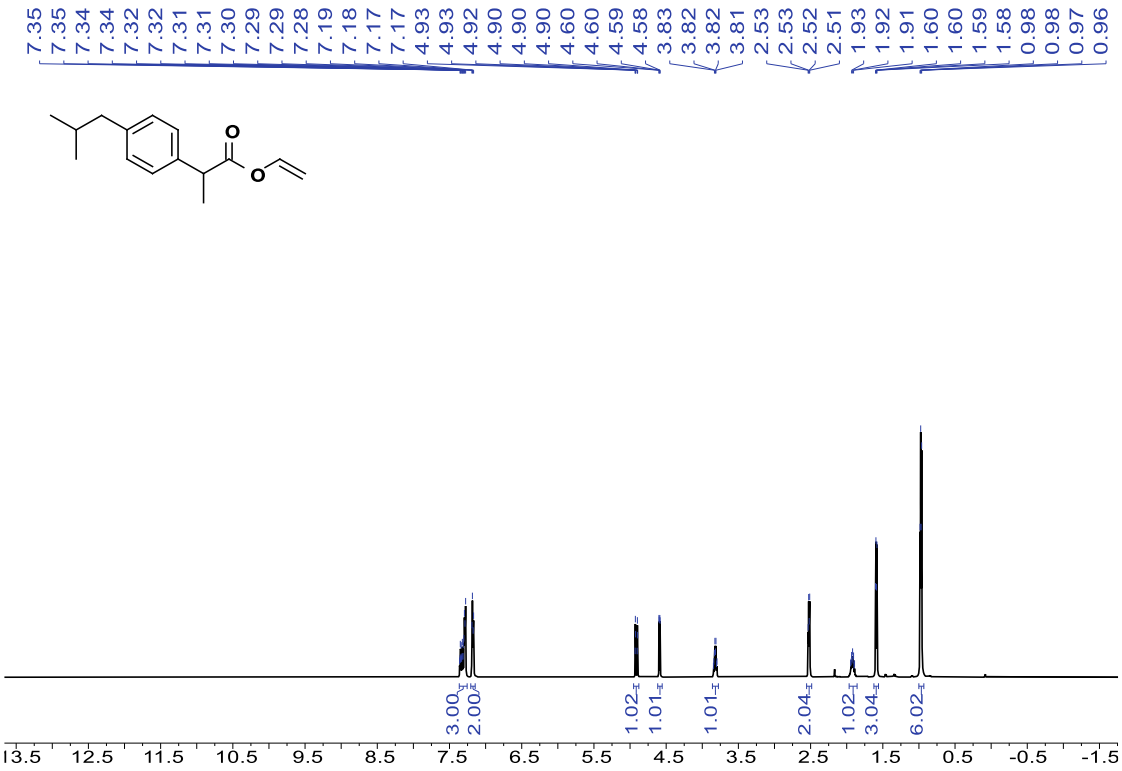
^{1}H NMR spectra of 1v (500 MHz, $CDCl_3$)



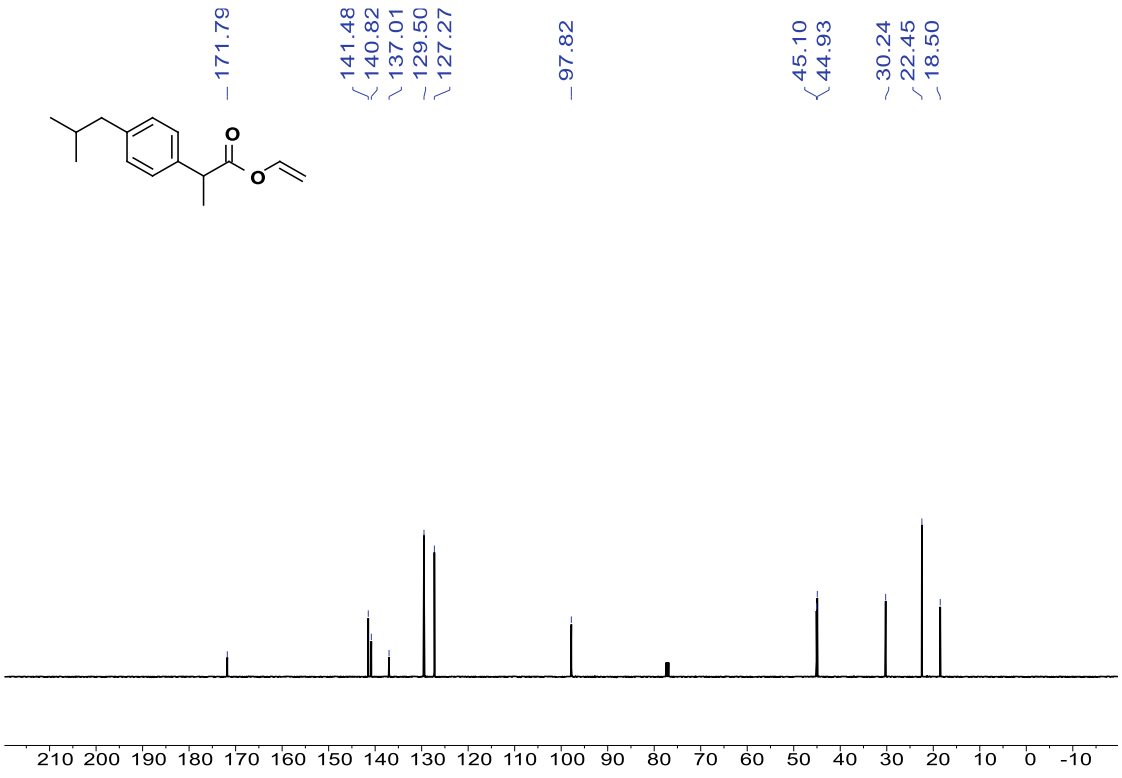
^{13}C NMR spectra of 1v (126 MHz, $CDCl_3$)



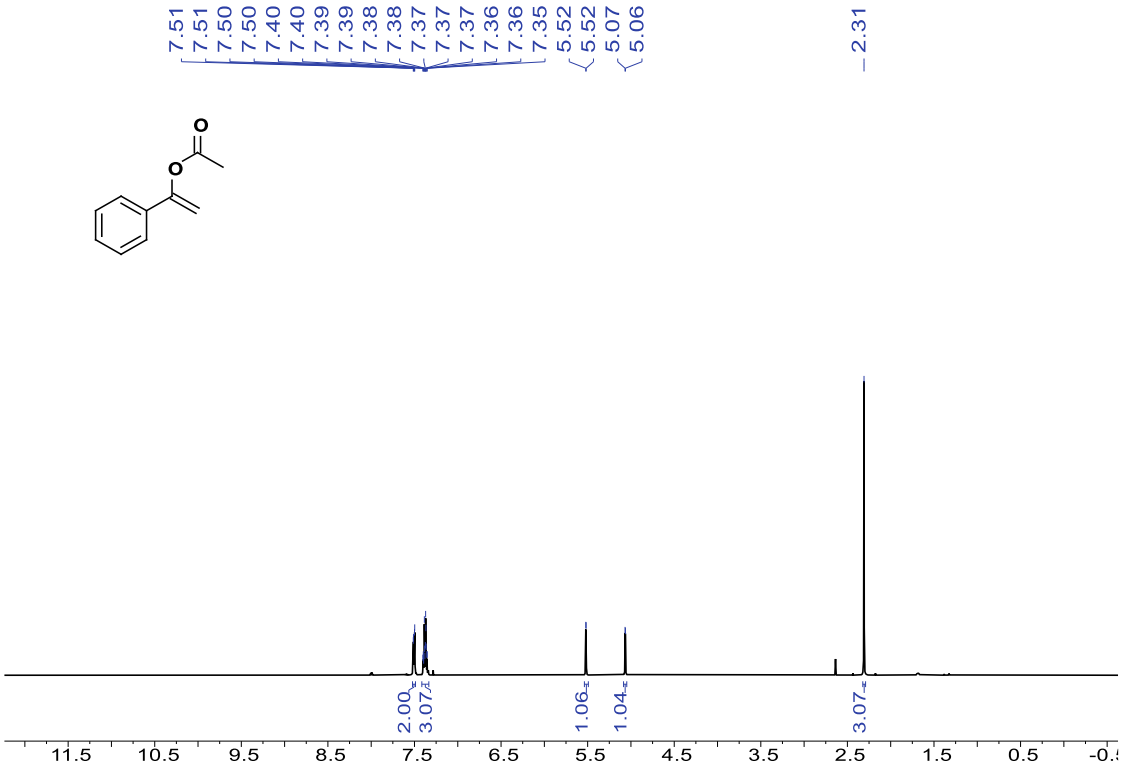
^{1}H NMR spectra of 1w (500 MHz, $CDCl_3$)



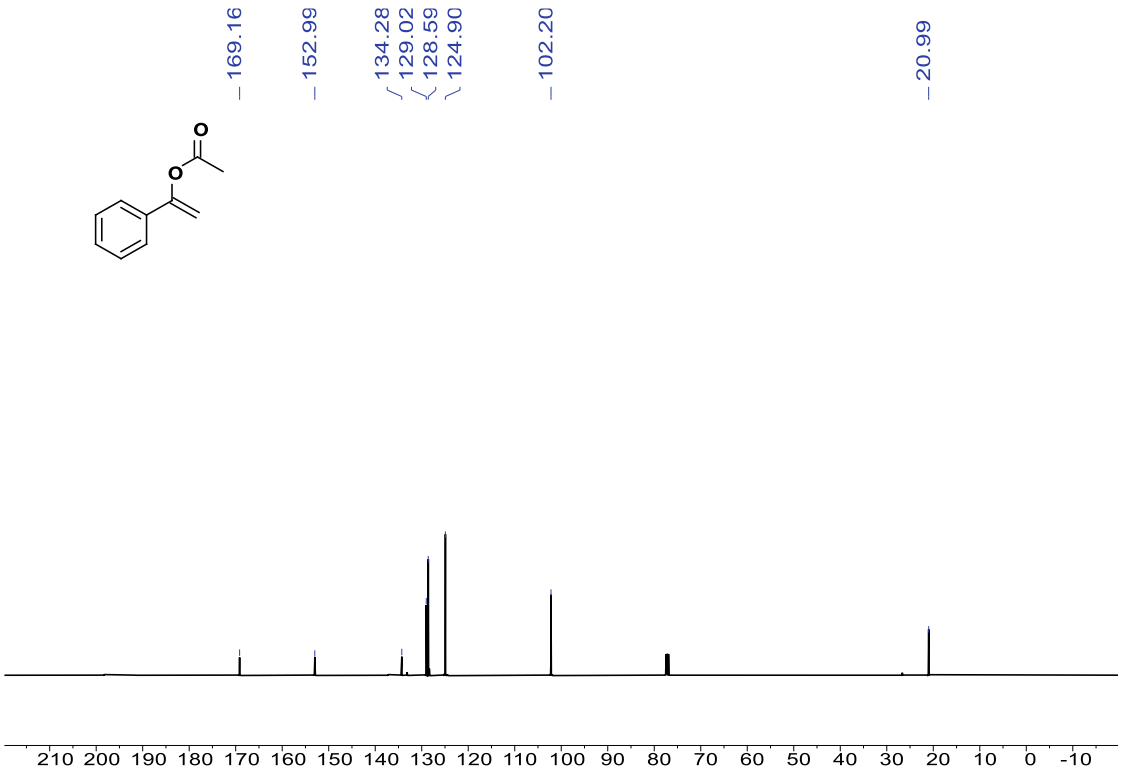
^{13}C NMR spectra of 1w (126 MHz, $CDCl_3$)



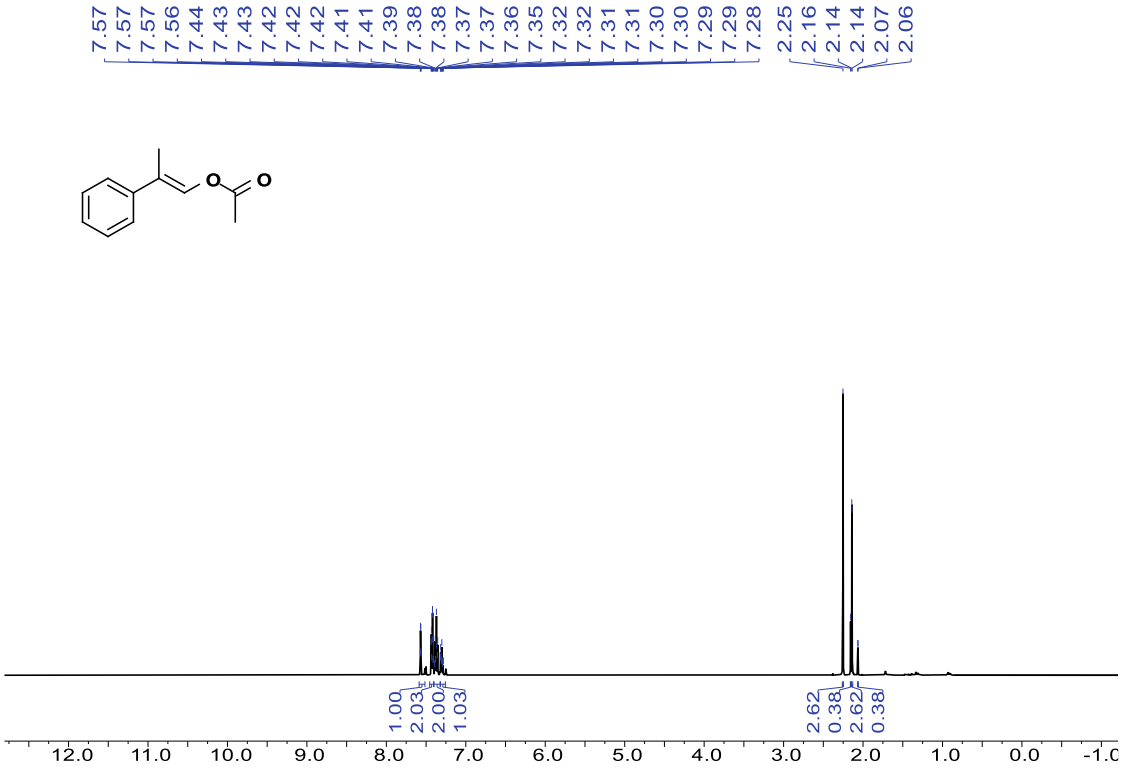
^{1}H NMR spectra of 20a (500 MHz, $CDCl_3$)



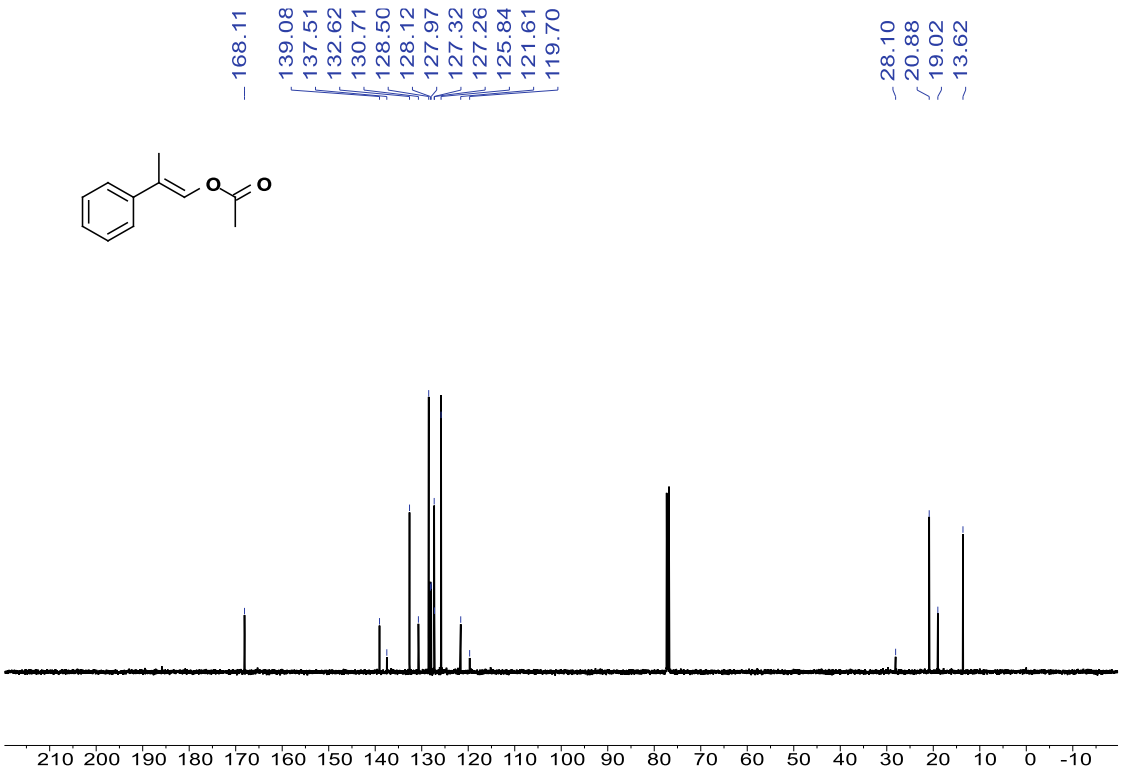
^{13}C NMR spectra of 20a (126 MHz, $CDCl_3$)



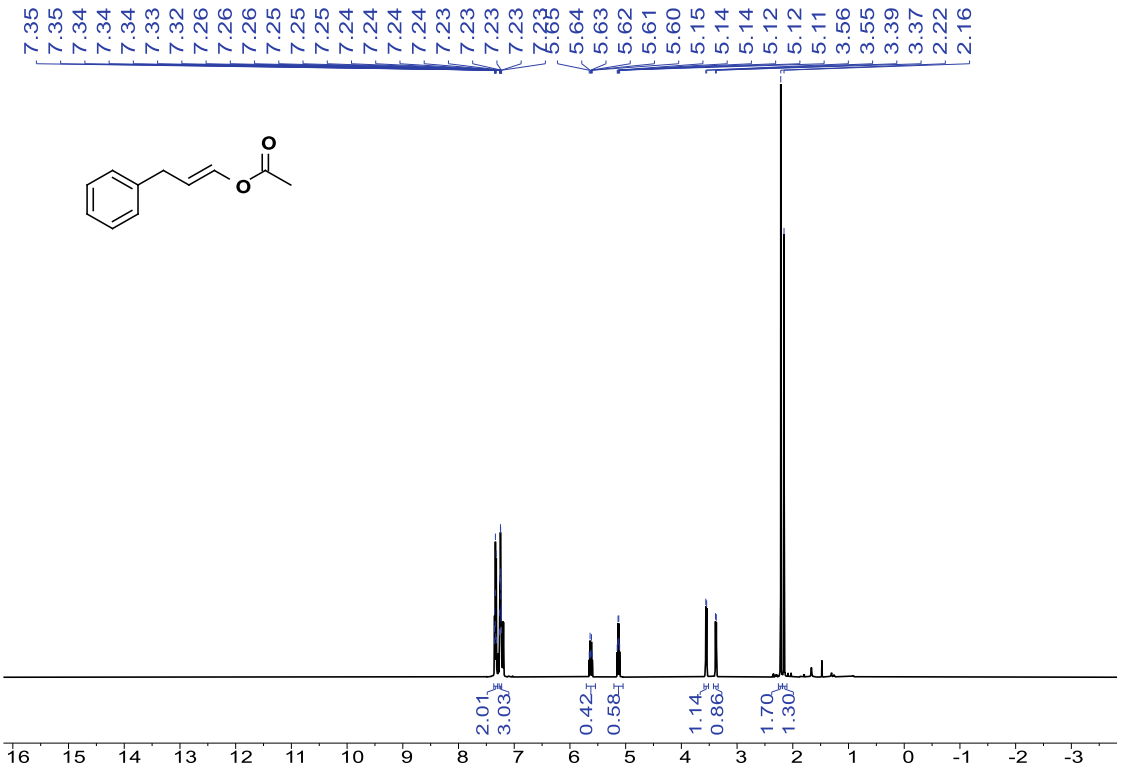
^{1}H NMR spectra of 21a (500 MHz, $CDCl_3$)



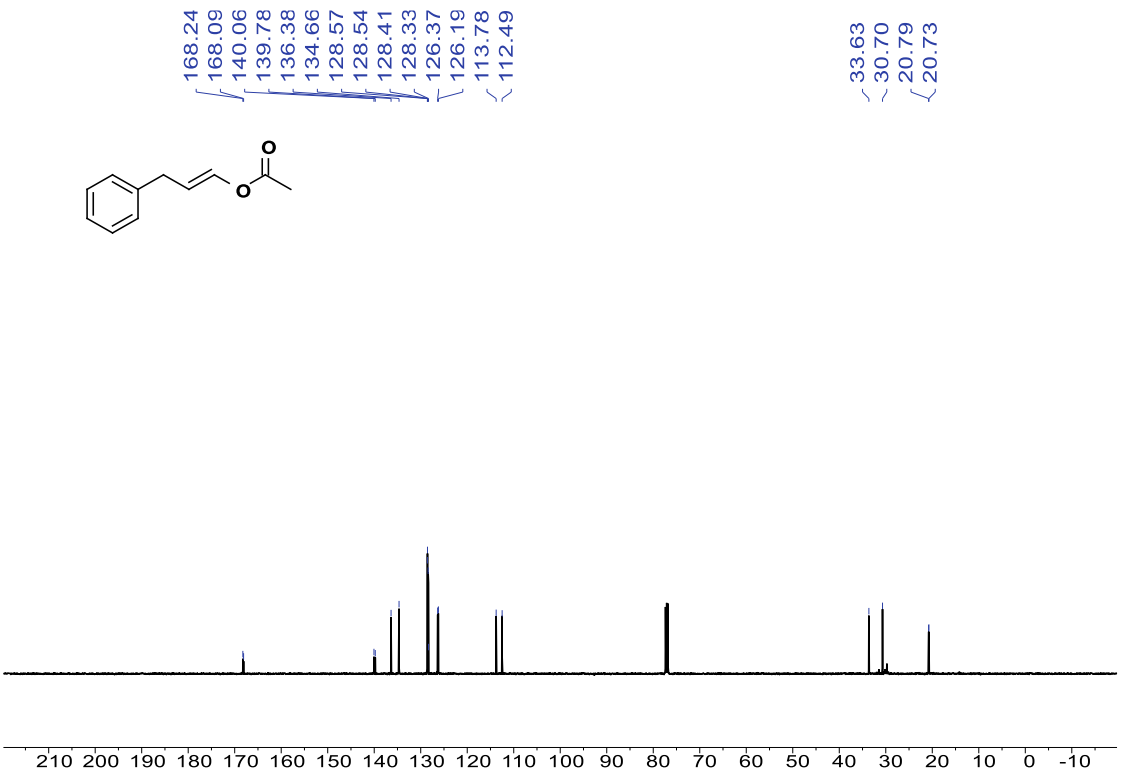
^{13}C NMR spectra of 21a (126 MHz, $CDCl_3$)



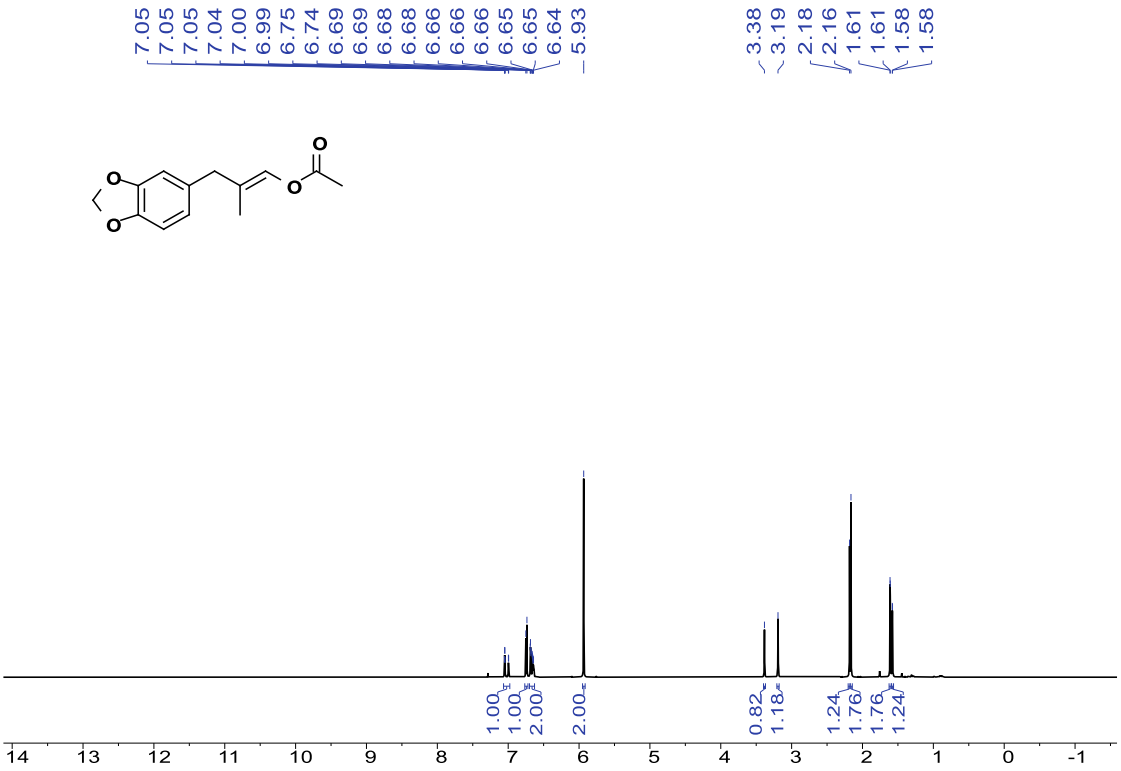
^{1}H NMR spectra of 22a (500 MHz, $CDCl_3$)



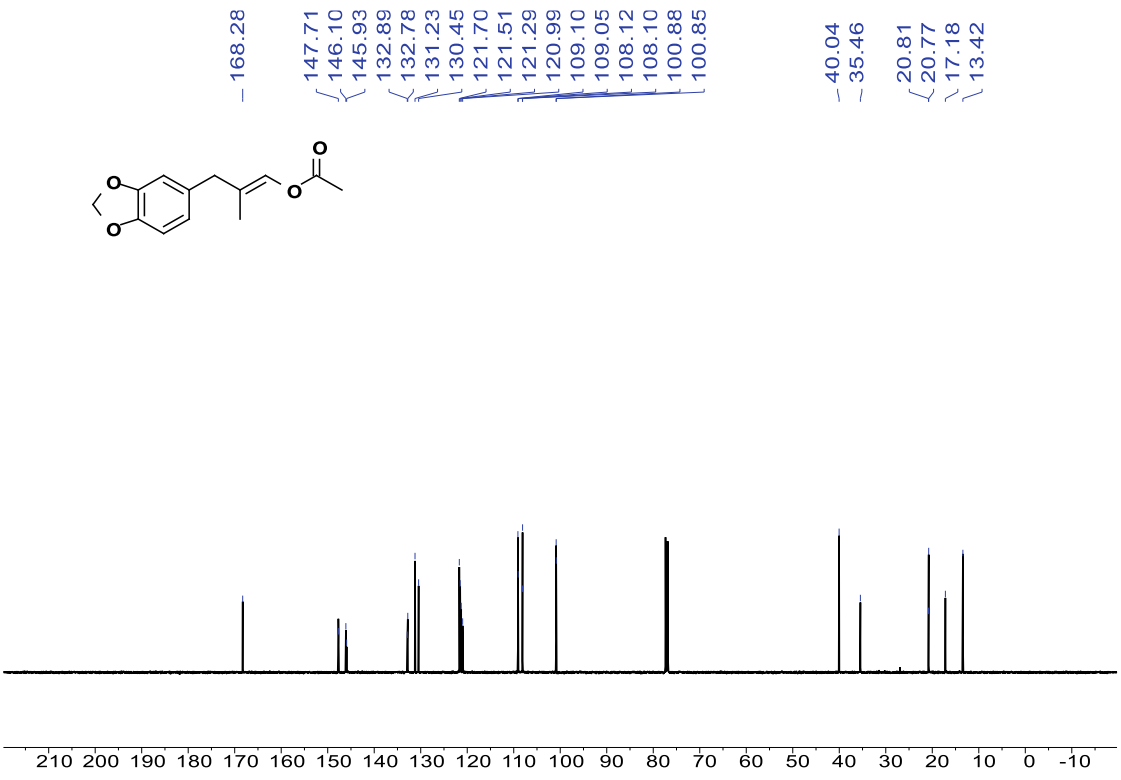
^{13}C NMR spectra of 22a (126 MHz, $CDCl_3$)



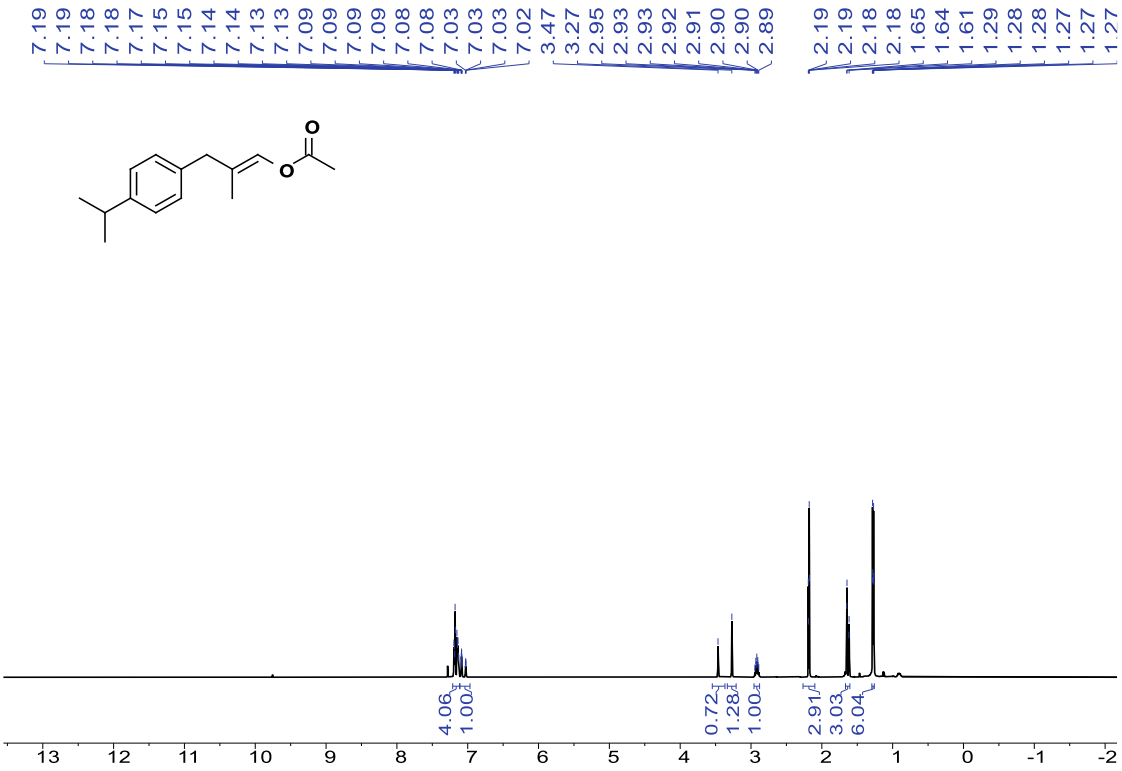
^{1}H NMR spectra of 23a (500 MHz, $CDCl_3$)



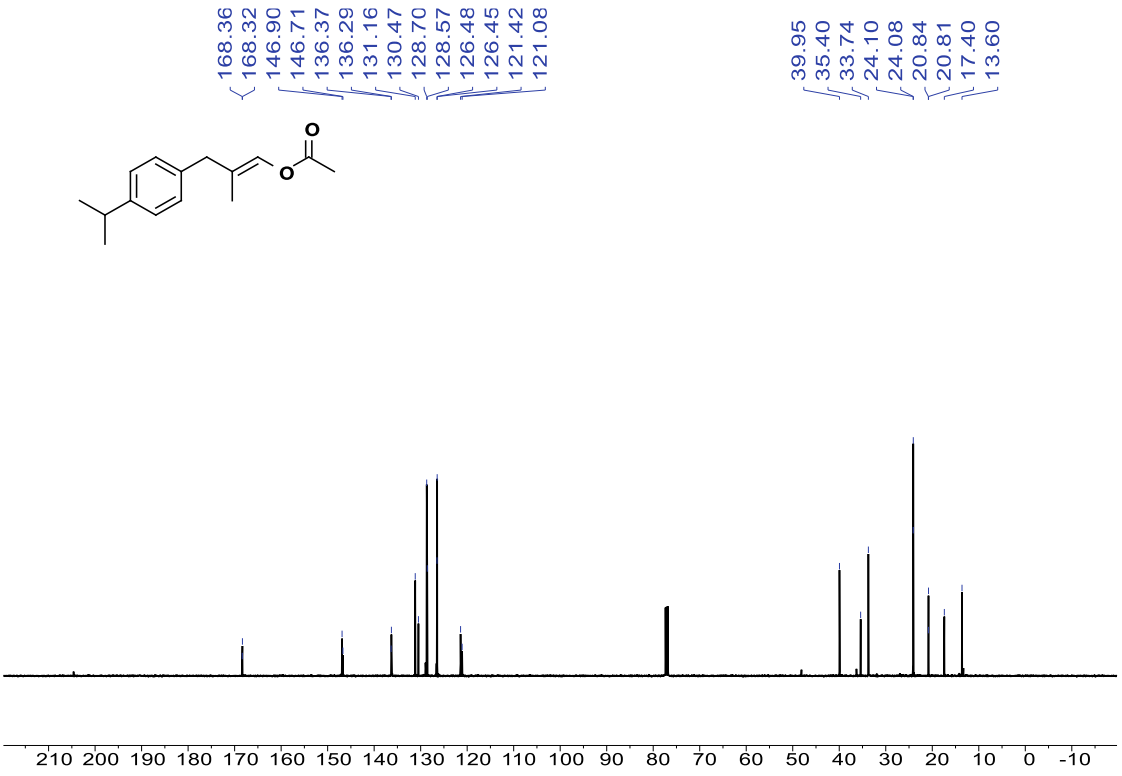
^{13}C NMR spectra of 23a (126 MHz, $CDCl_3$)



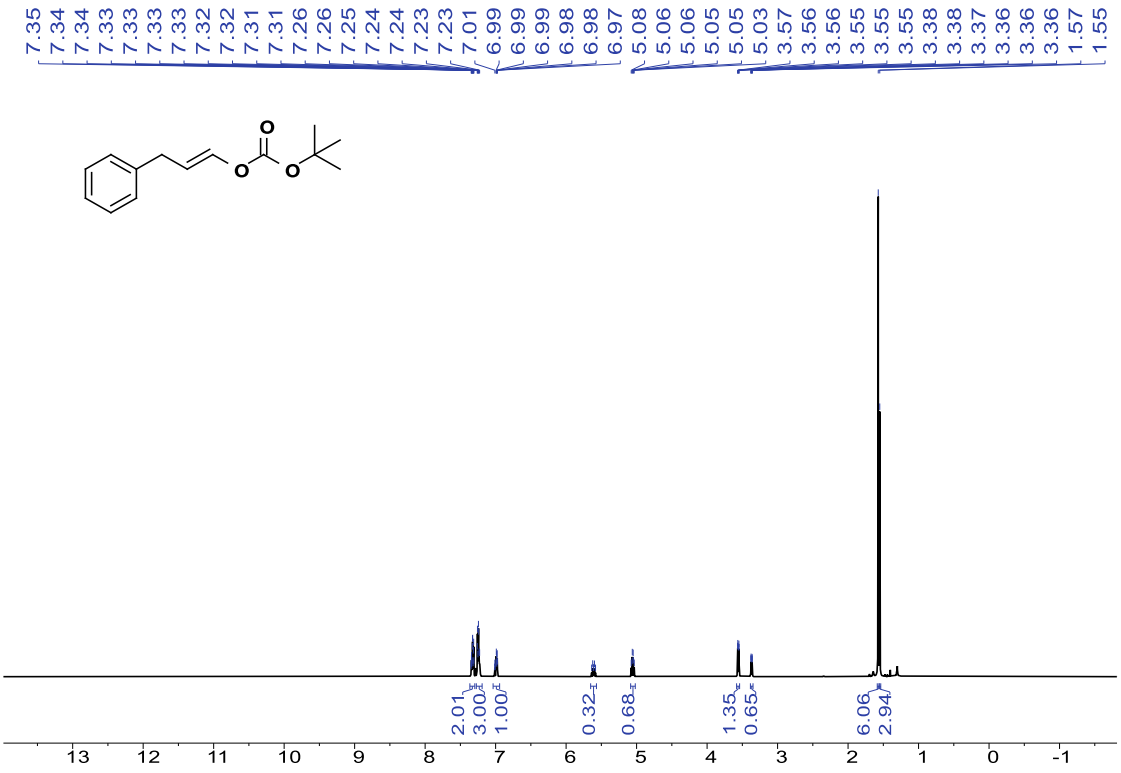
^{1}H NMR spectra of 24a (500 MHz, $CDCl_3$)



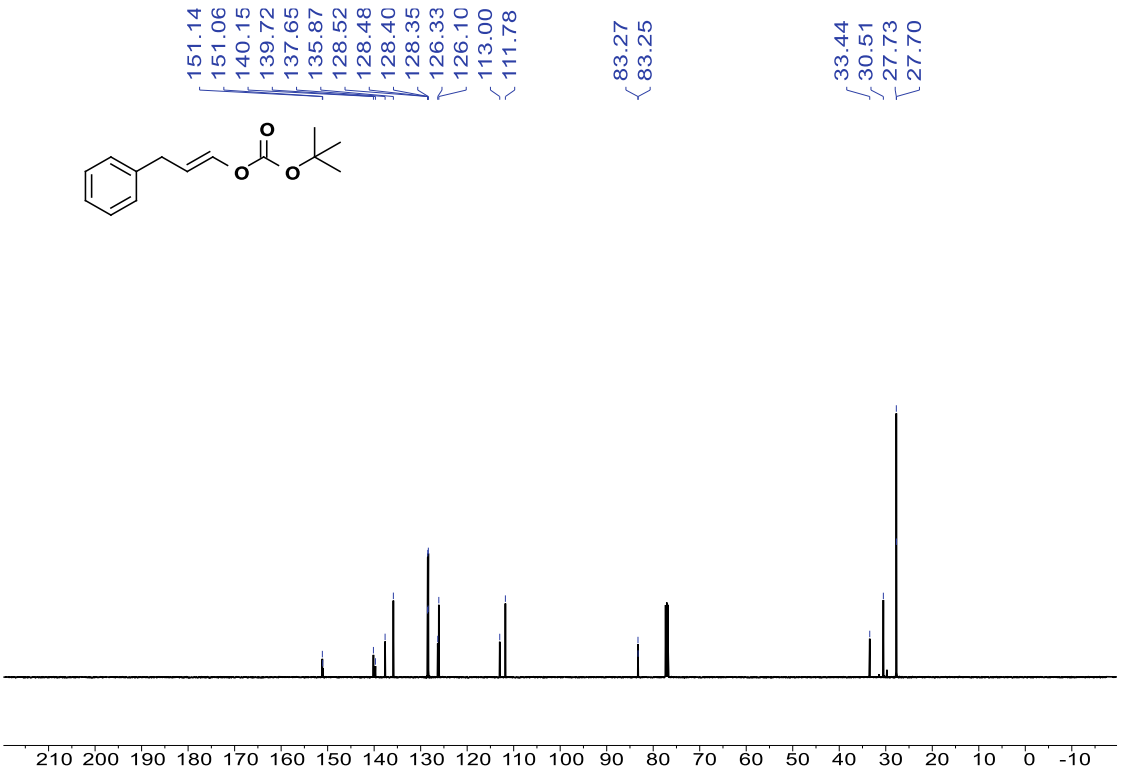
^{13}C NMR spectra of 24a (126 MHz, $CDCl_3$)



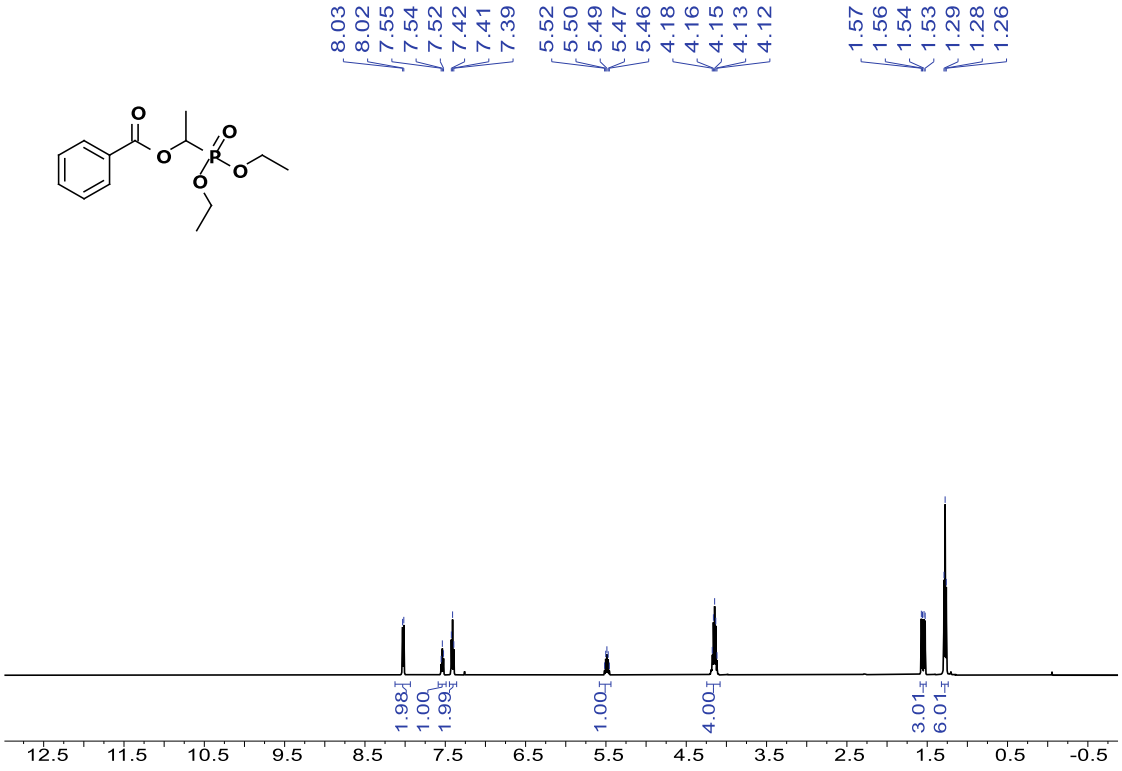
^{1}H NMR spectra of 25a (500 MHz, $CDCl_3$)



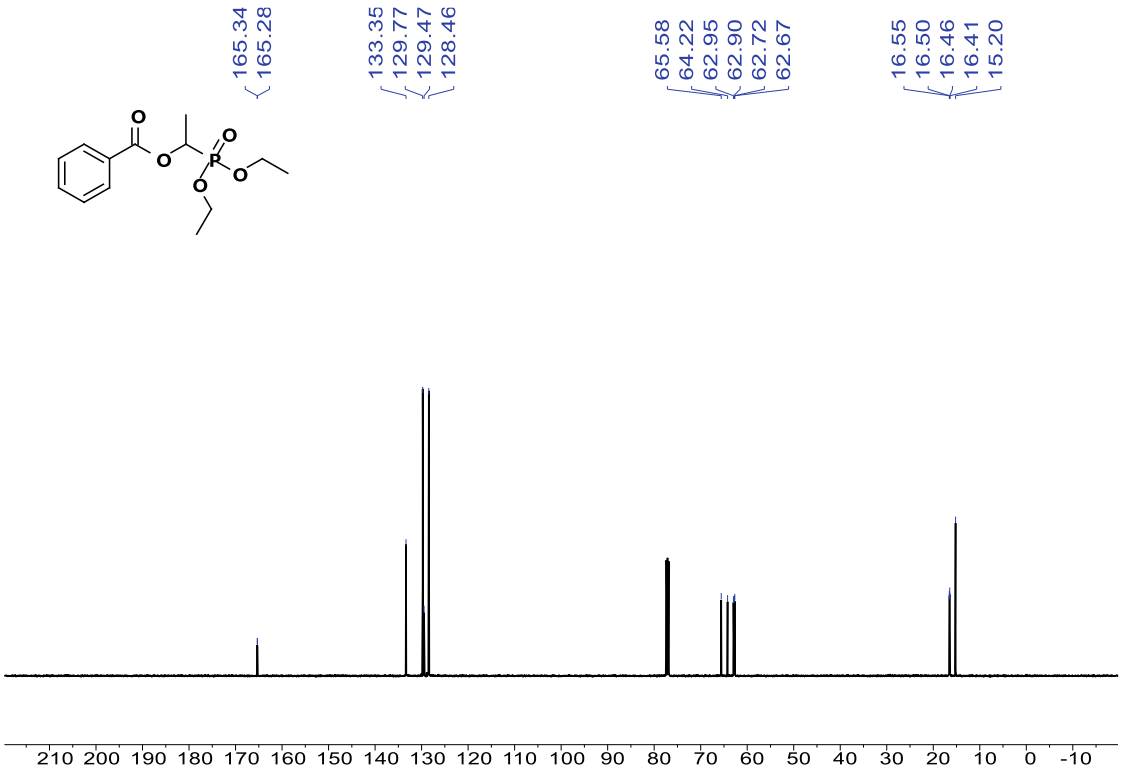
^{13}C NMR spectra of 25a (126 MHz, $CDCl_3$)



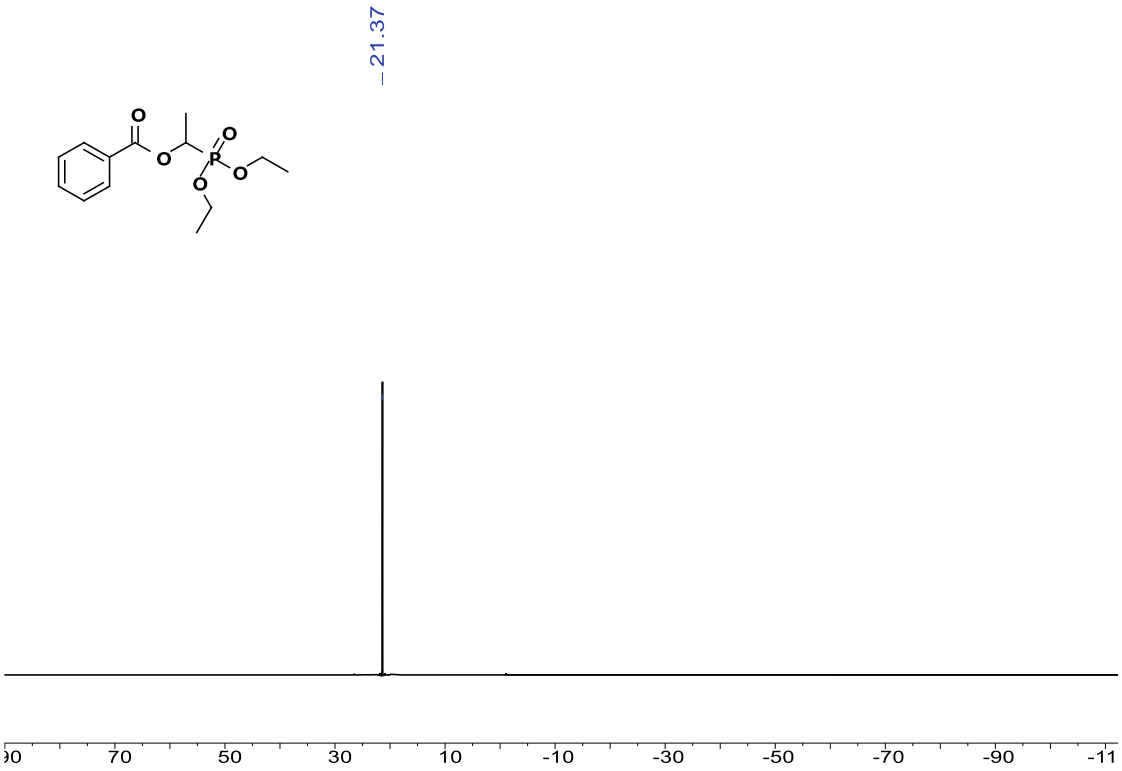
^{1}H NMR spectra of 3aa (500 MHz, $CDCl_3$)



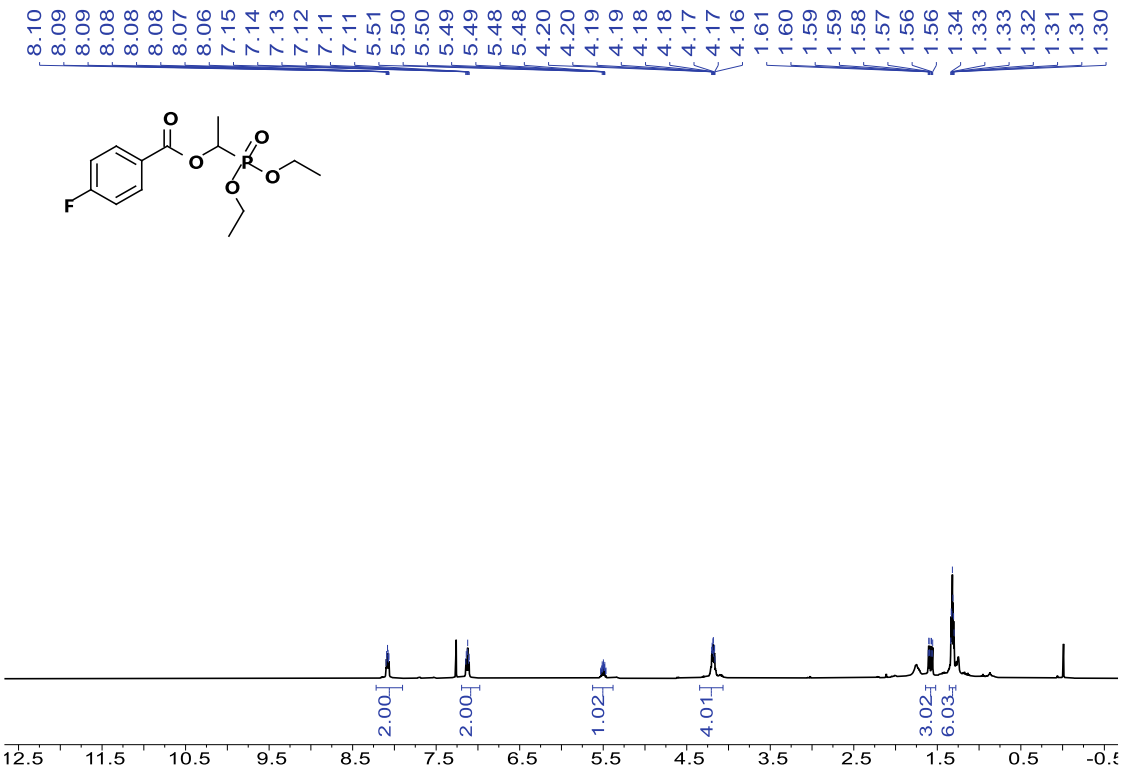
^{13}C NMR spectra of 3aa (126 MHz, $CDCl_3$)



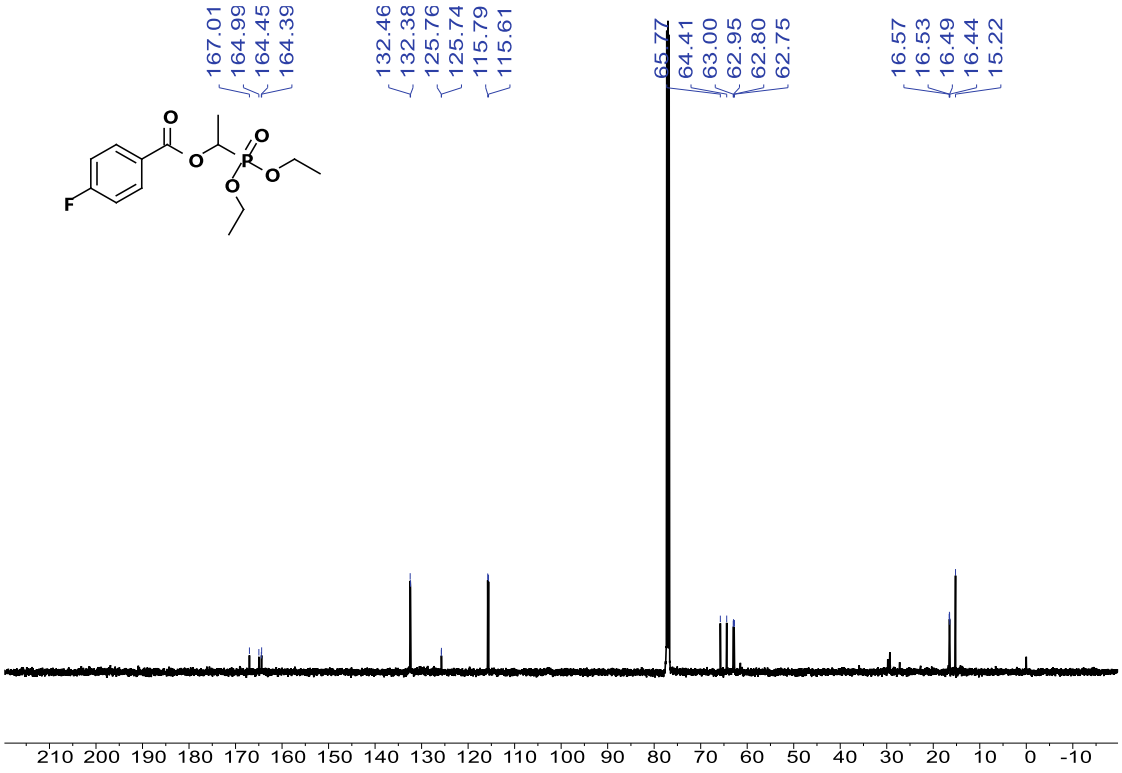
^{31}P NMR spectra of 3aa (202 MHz, $CDCl_3$)



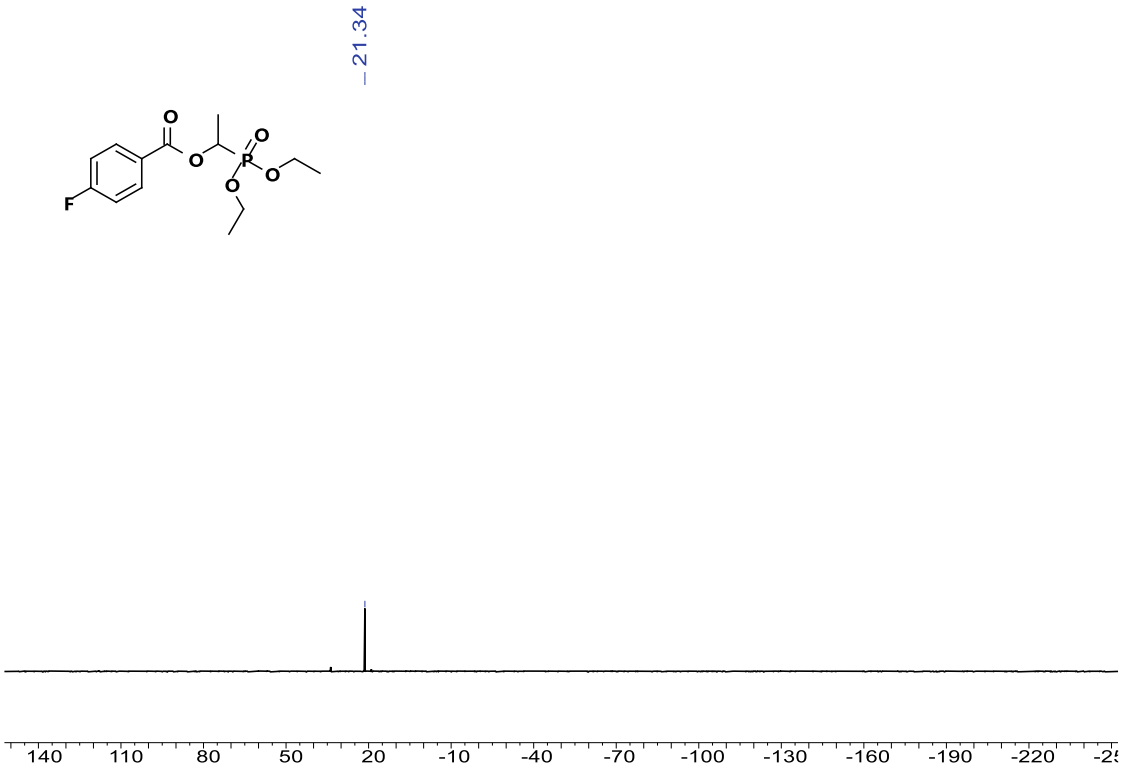
^{1}H NMR spectra of 3ba (500 MHz, $CDCl_3$)



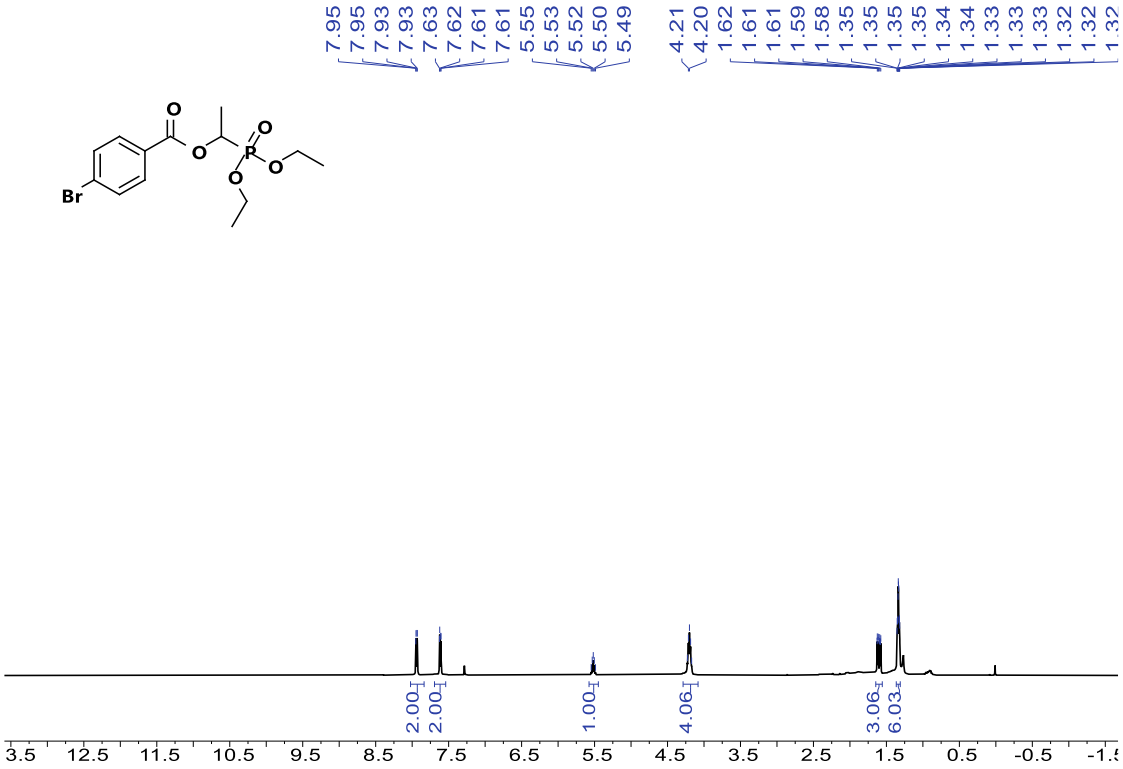
^{13}C NMR spectra of 3ba (126 MHz, $CDCl_3$)



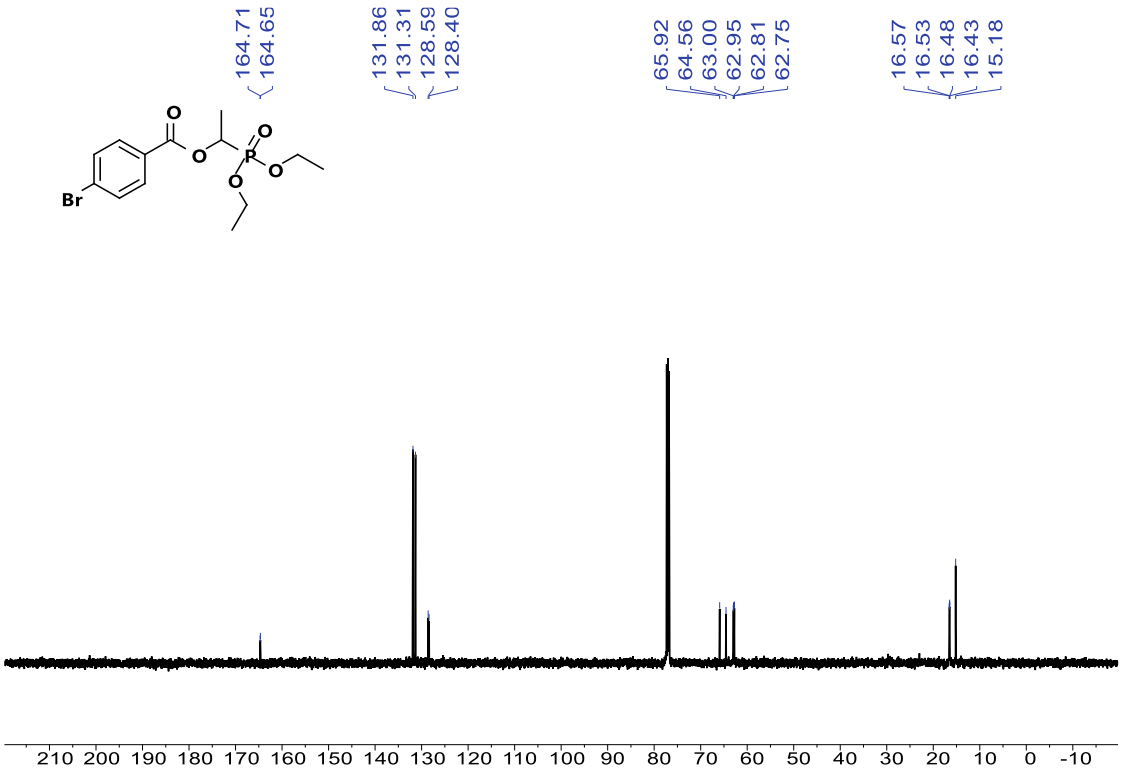
^{31}P NMR spectra of 3ba (202 MHz, $CDCl_3$)



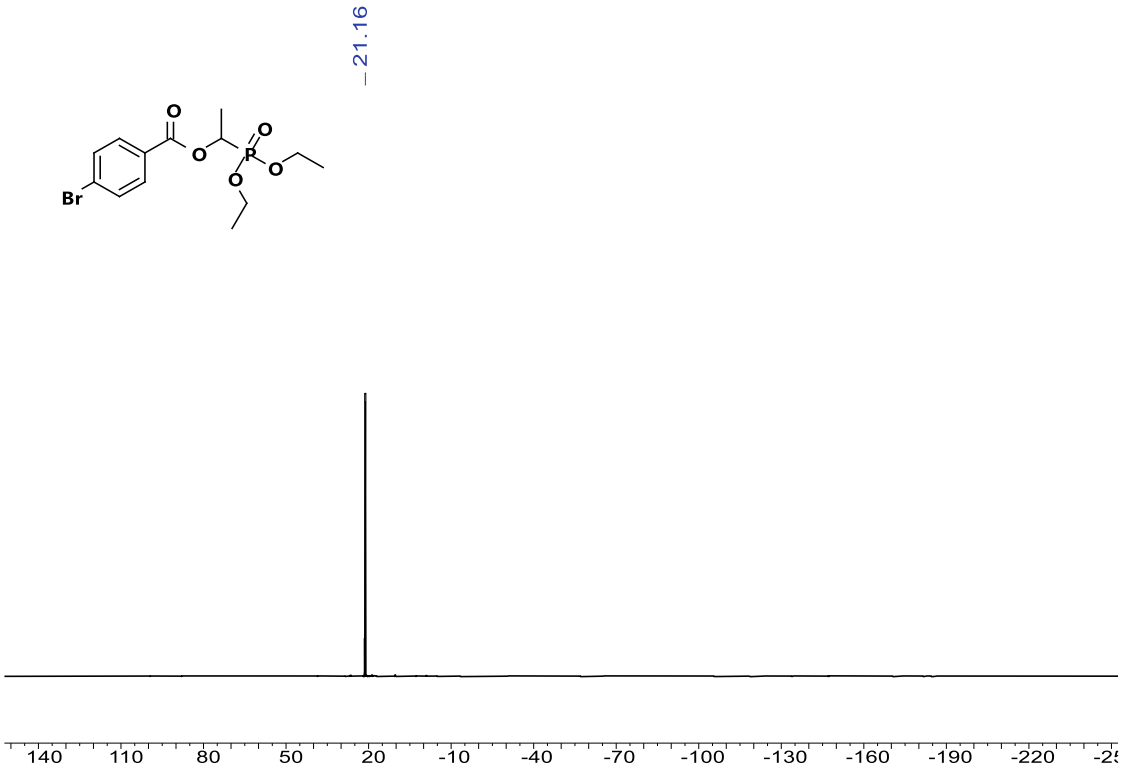
^{1}H NMR spectra of 3ca (500 MHz, $CDCl_3$)



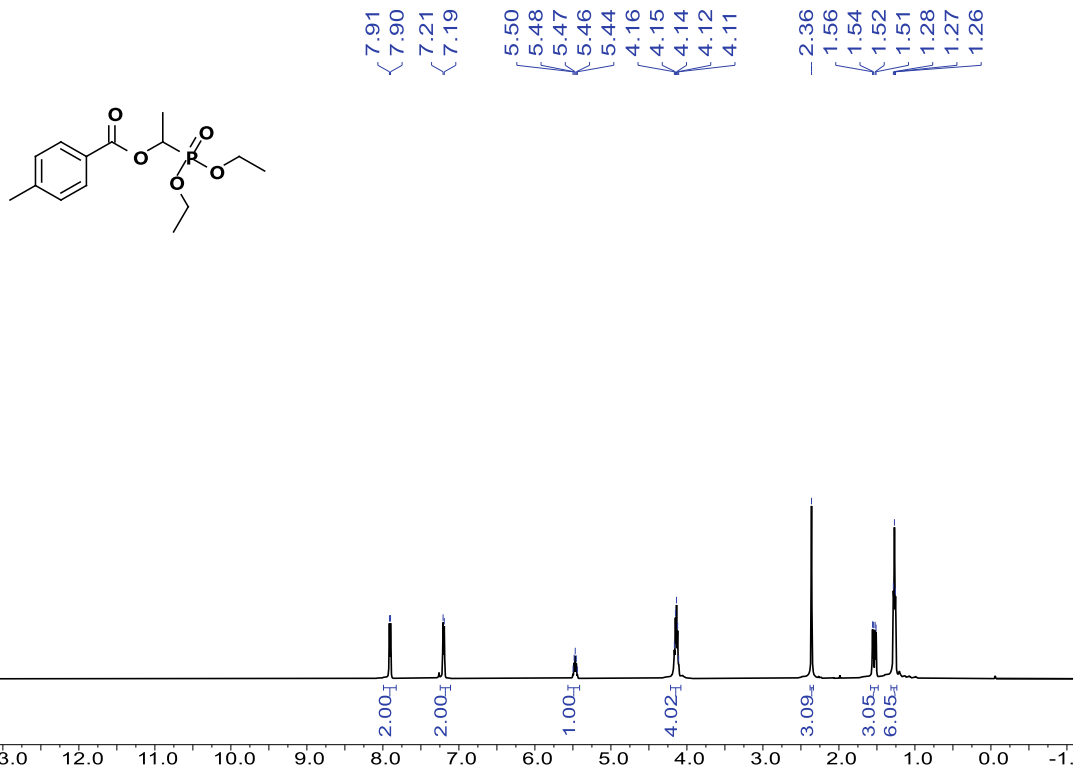
^{13}C NMR spectra of 3ca (126 MHz, $CDCl_3$)



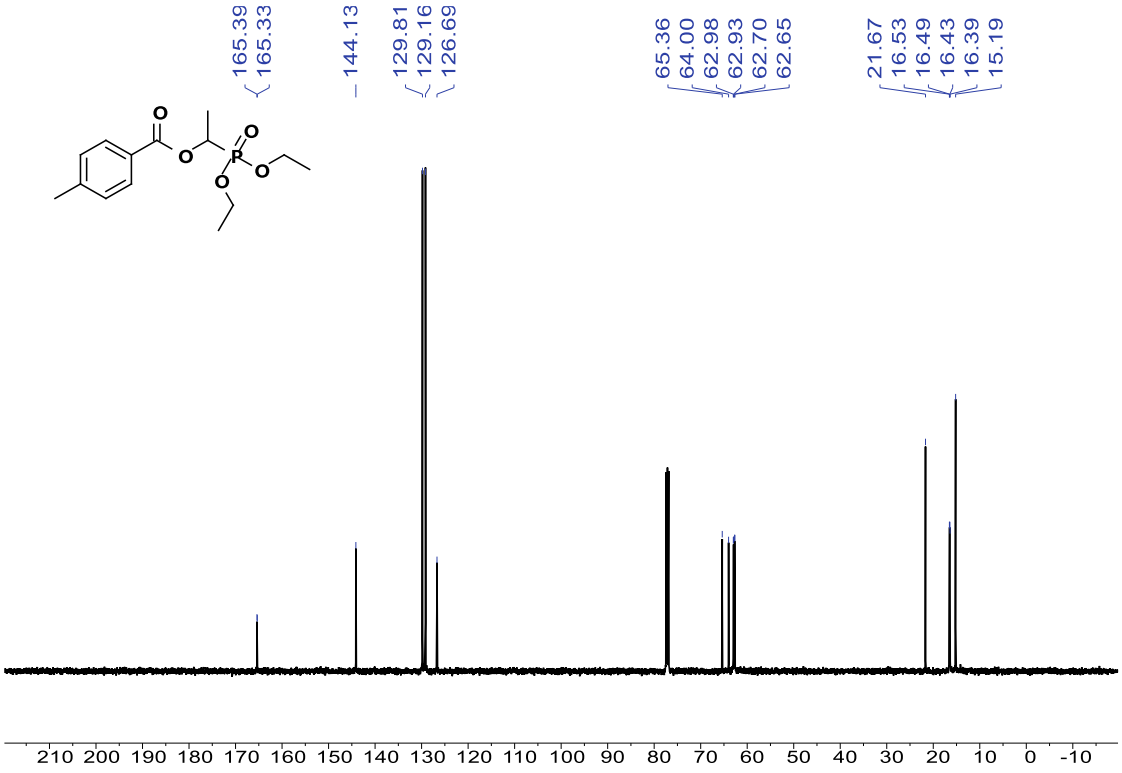
^{31}P NMR spectra of 3ca (202 MHz, $CDCl_3$)



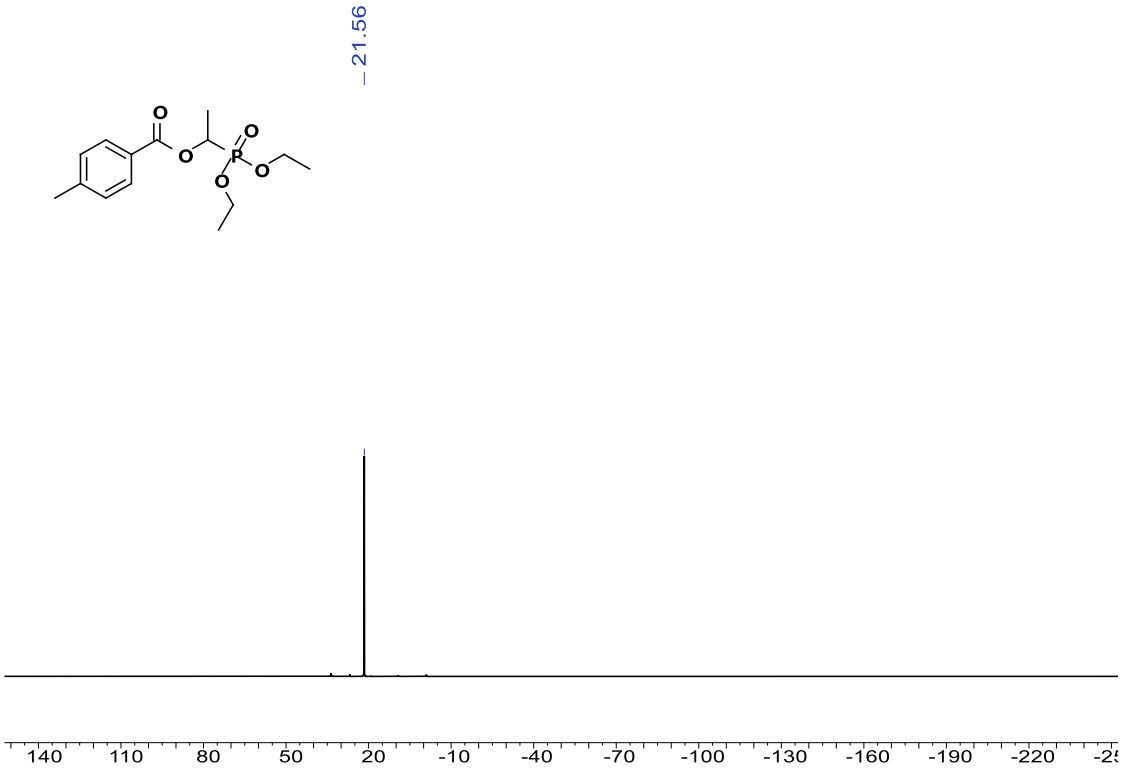
^{1}H NMR spectra of 3da (500 MHz, $CDCl_3$)



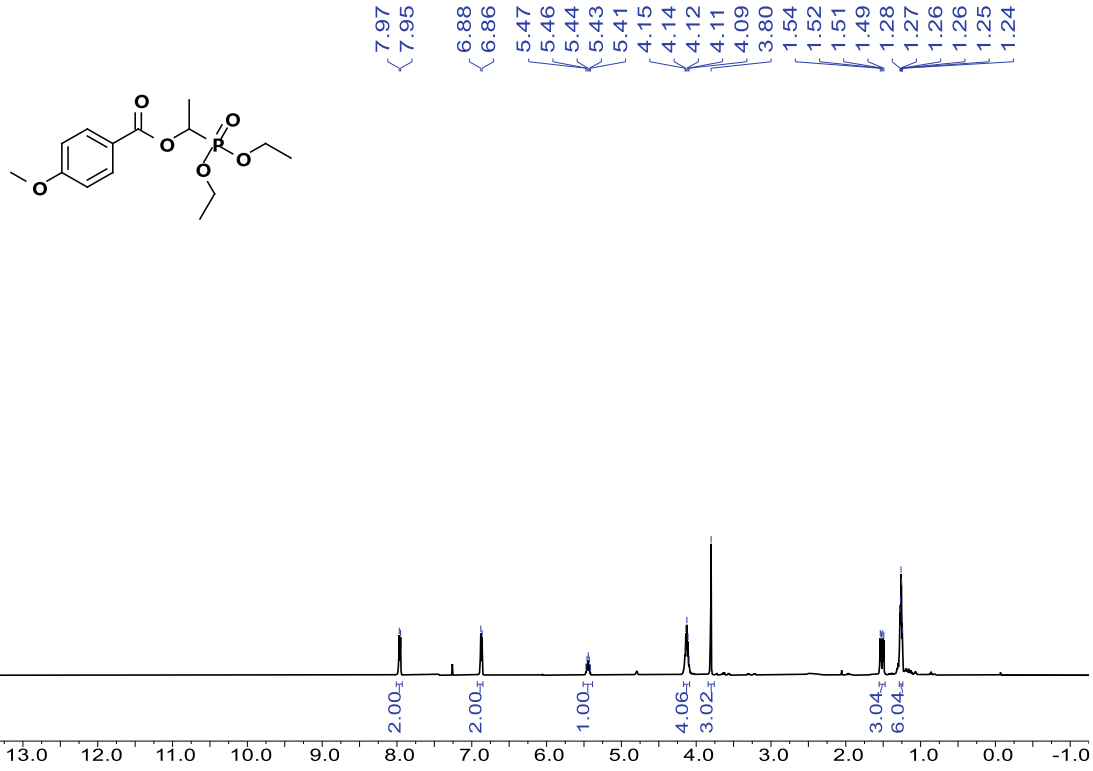
^{13}C NMR spectra of 3da (126 MHz, $CDCl_3$)



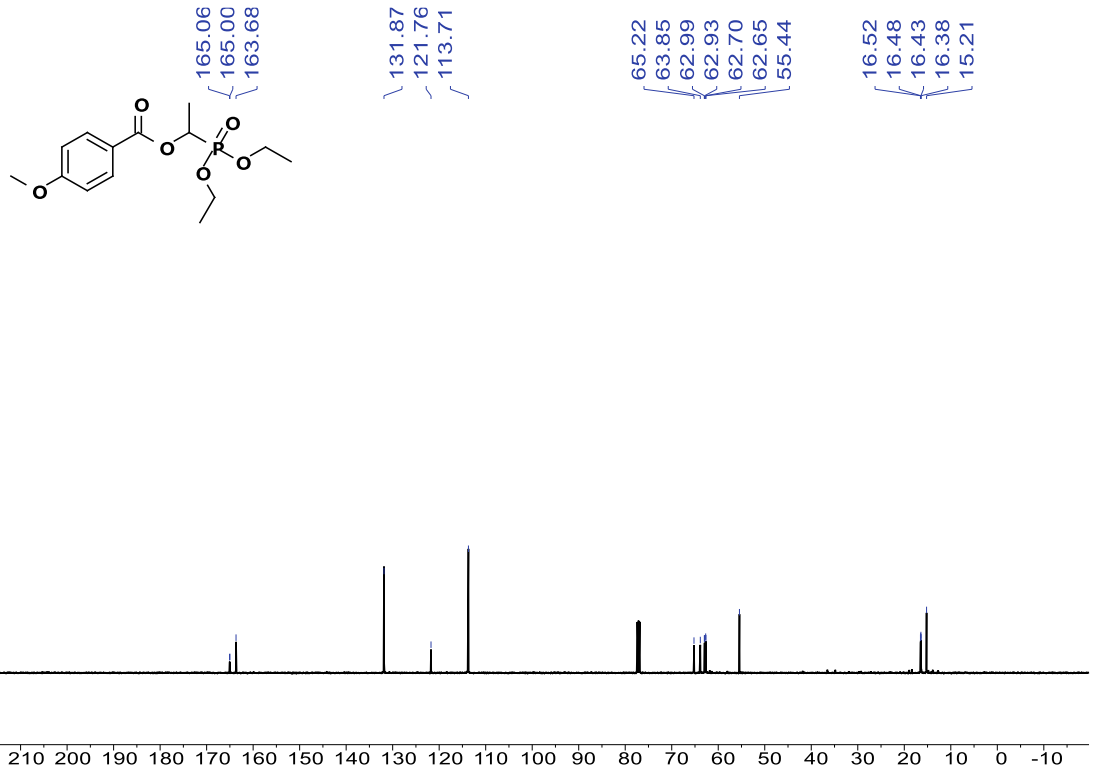
^{31}P NMR spectra of 3da (202 MHz, $CDCl_3$)



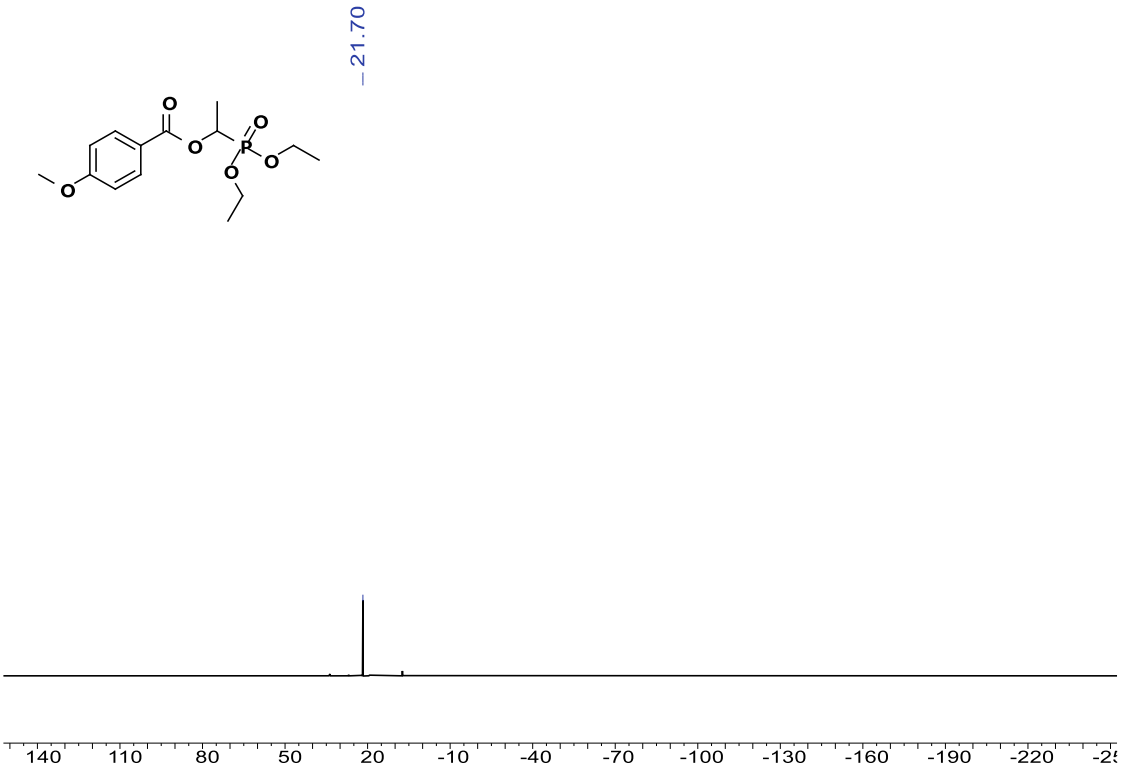
^{1}H NMR spectra of 3ea (500 MHz, $CDCl_3$)



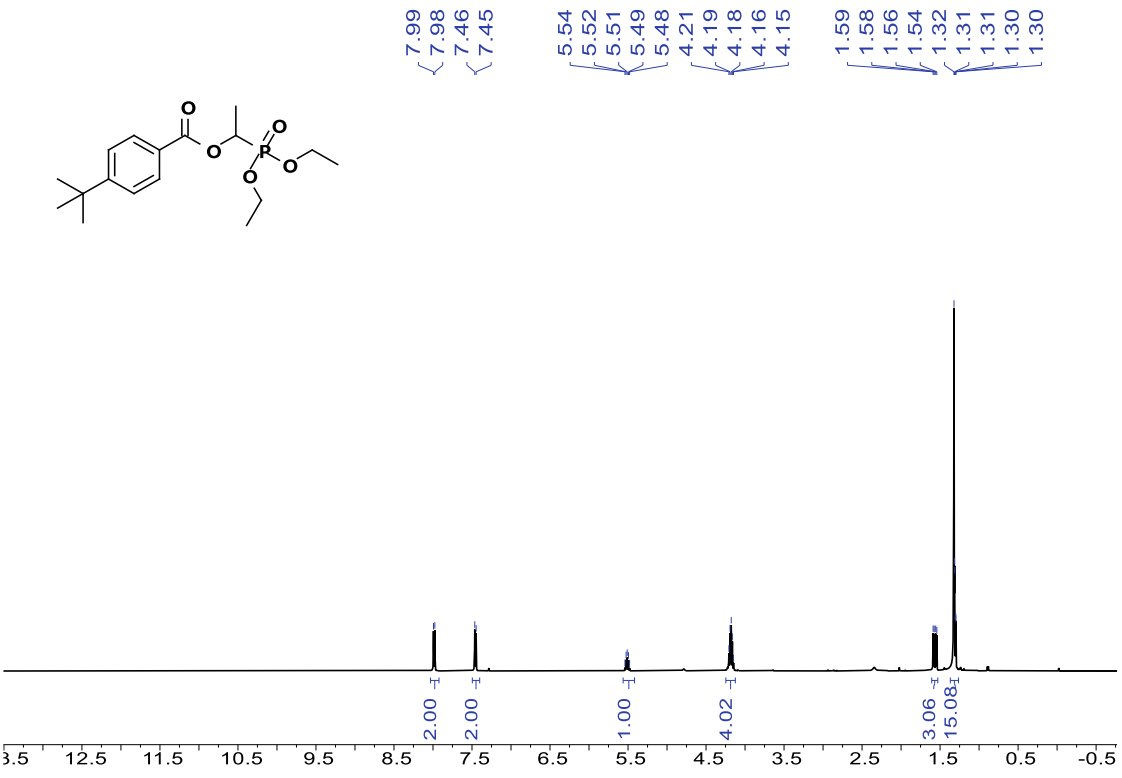
^{13}C NMR spectra of 3ea (126 MHz, $CDCl_3$)



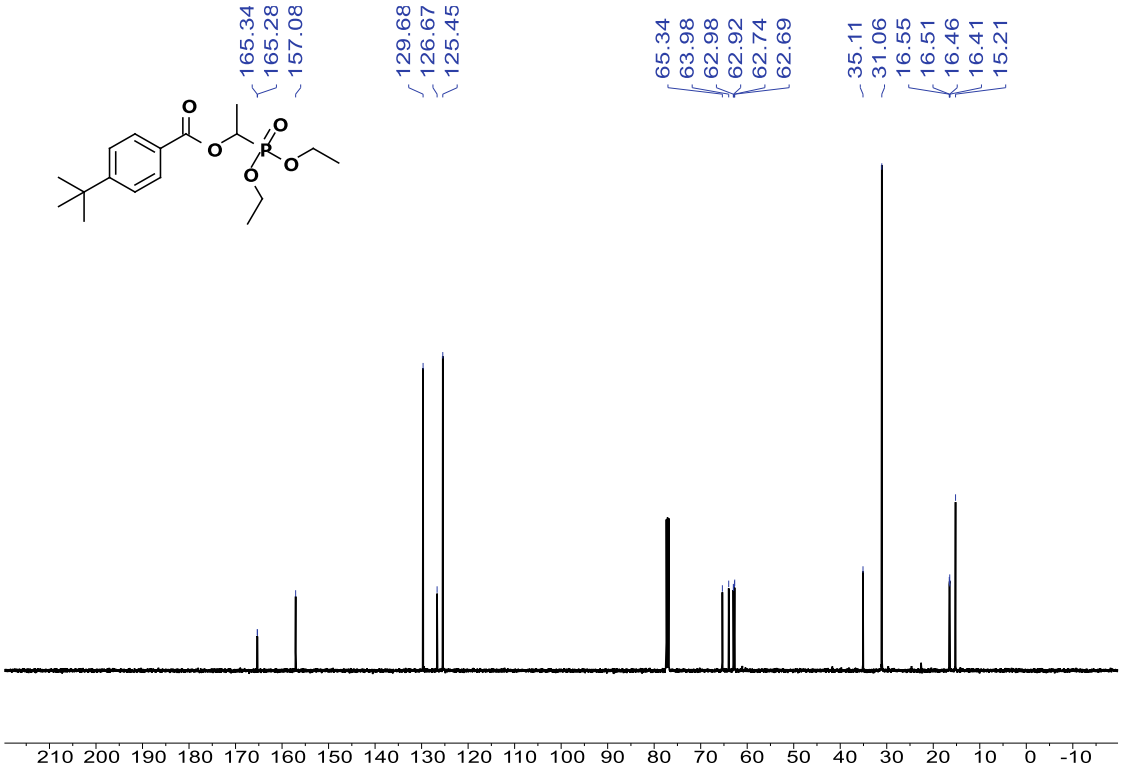
^{31}P NMR spectra of 3ea (202 MHz, $CDCl_3$)



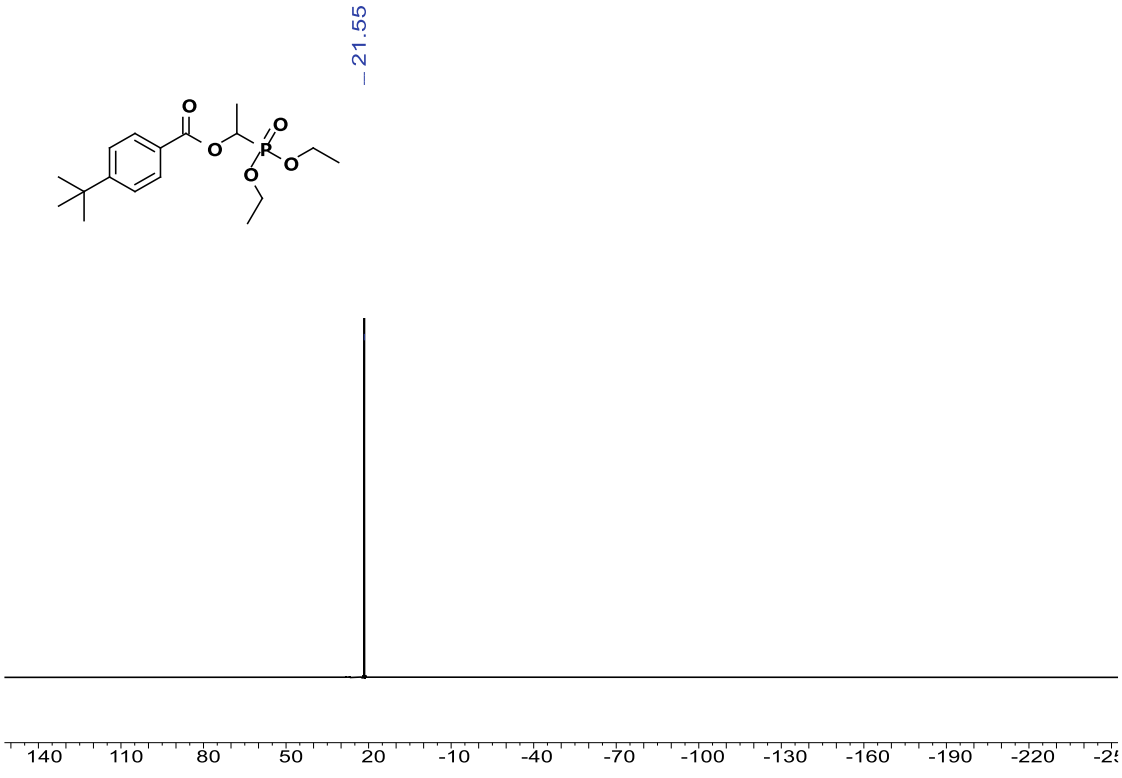
^{1}H NMR spectra of 3fa (500 MHz, $CDCl_3$)



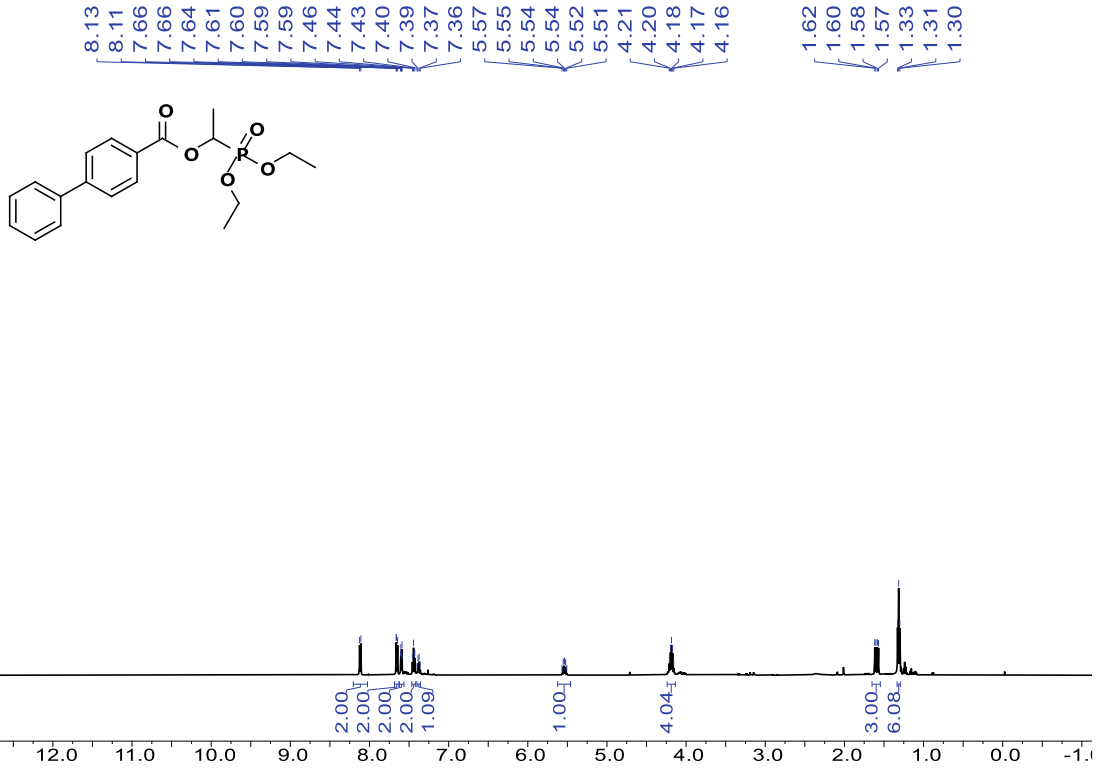
^{13}C NMR spectra of 3fa (126 MHz, $CDCl_3$)



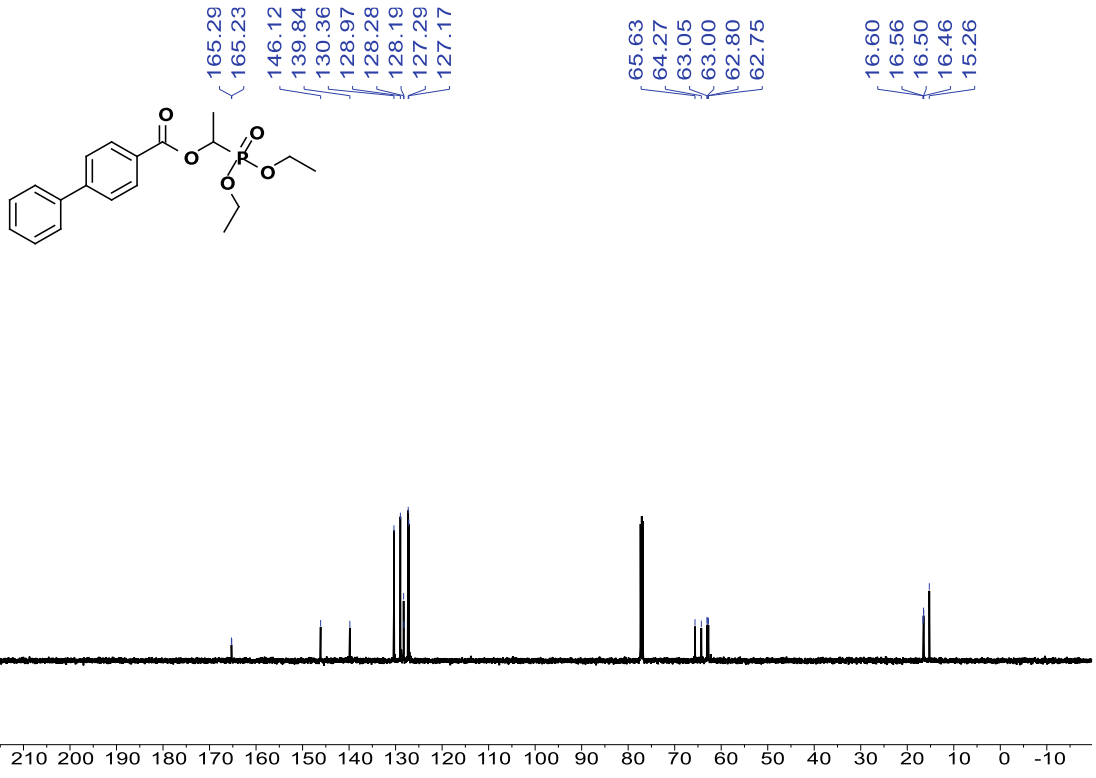
^{31}P NMR spectra of 3fa (202 MHz, $CDCl_3$)



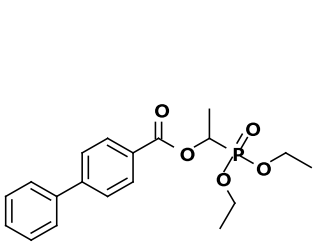
^{1}H NMR spectra of 3ga (500 MHz, $CDCl_3$)



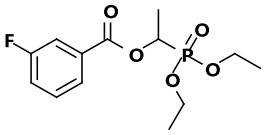
^{13}C NMR spectra of 3ga (126 MHz, $CDCl_3$)



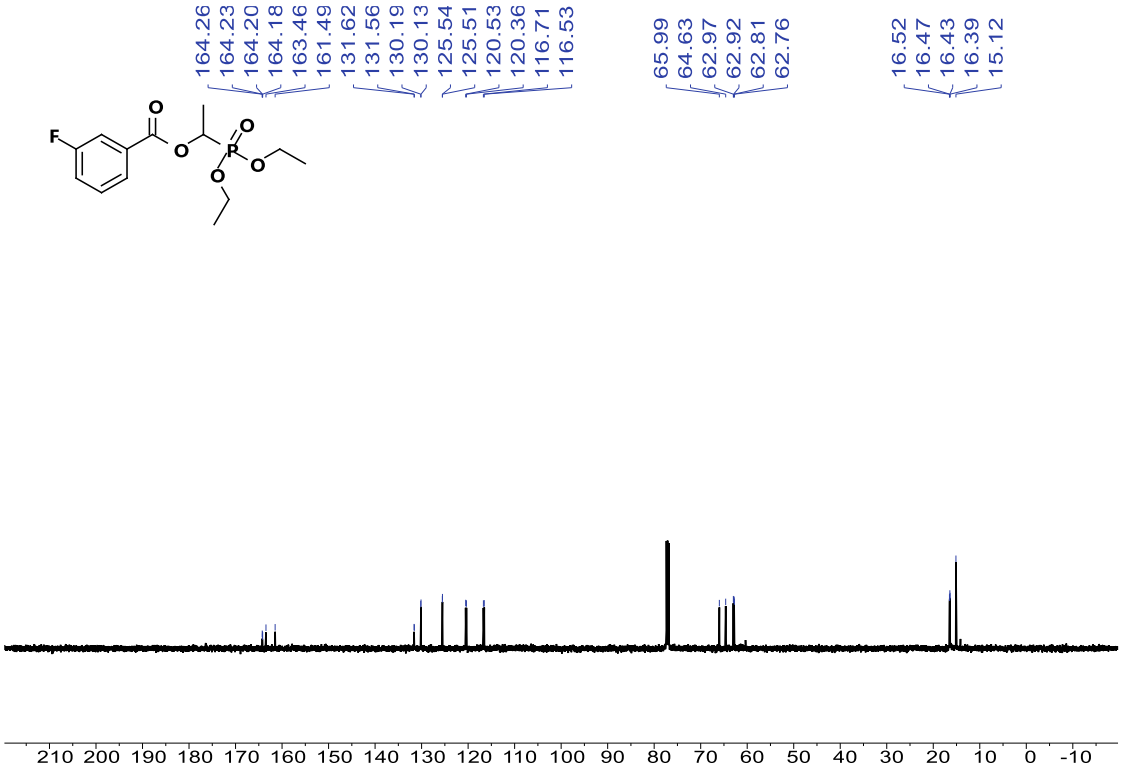
^{31}P NMR spectra of 3ga (202 MHz, $CDCl_3$)



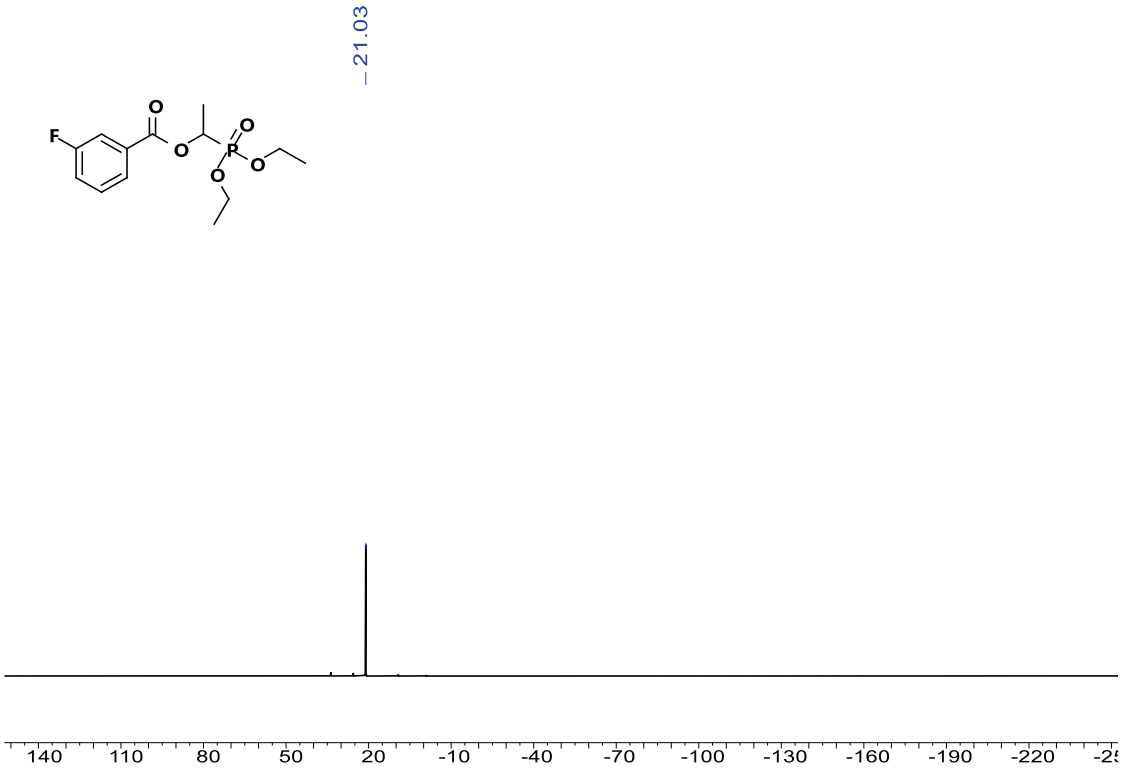
^{1}H NMR spectra of 3ha (500 MHz, $CDCl_3$)



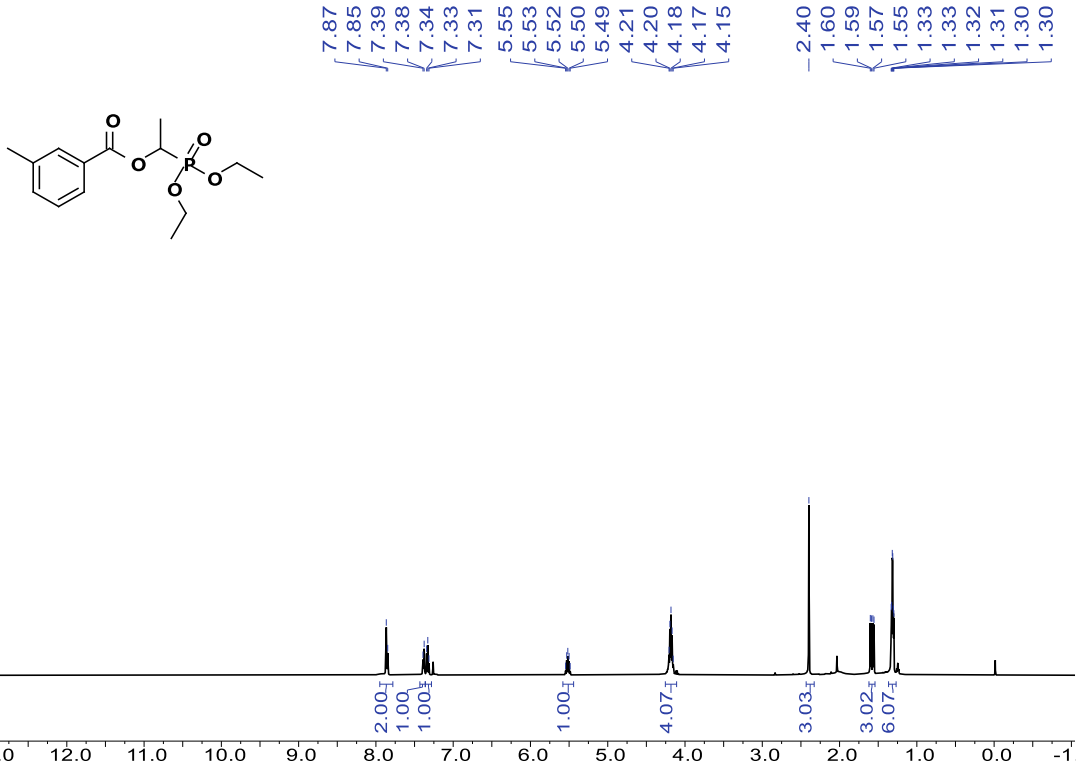
^{13}C NMR spectra of 3ha (126 MHz, $CDCl_3$)



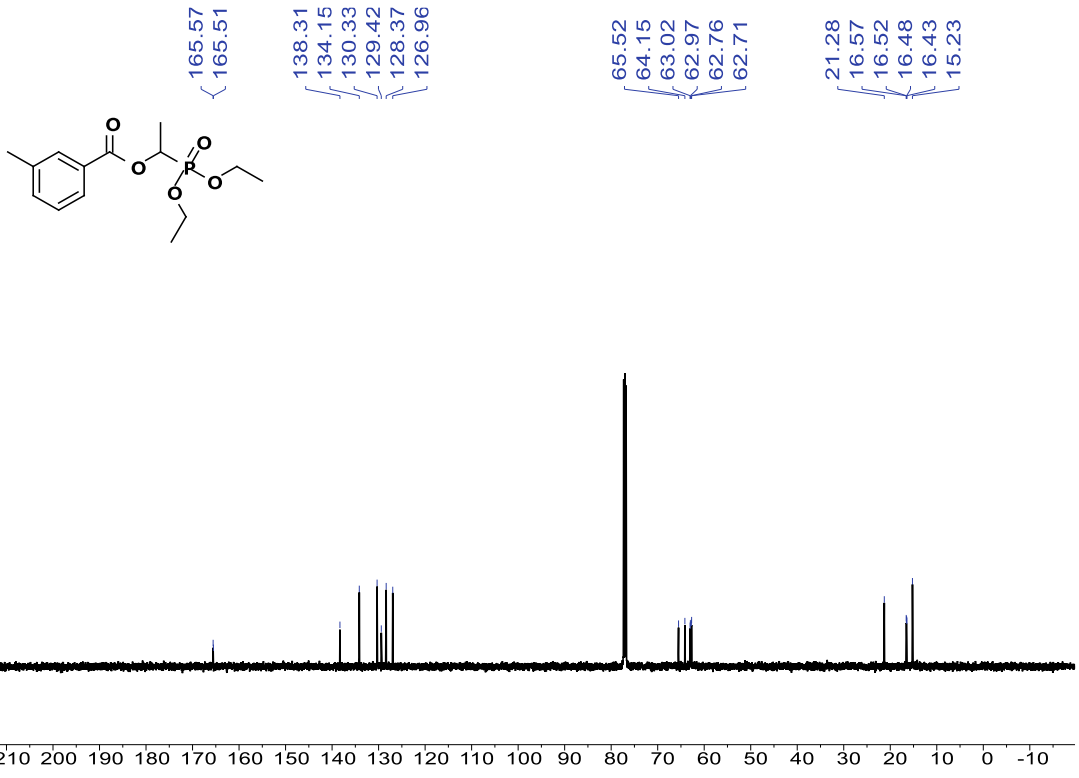
^{31}P NMR spectra of 3ha (202 MHz, $CDCl_3$)



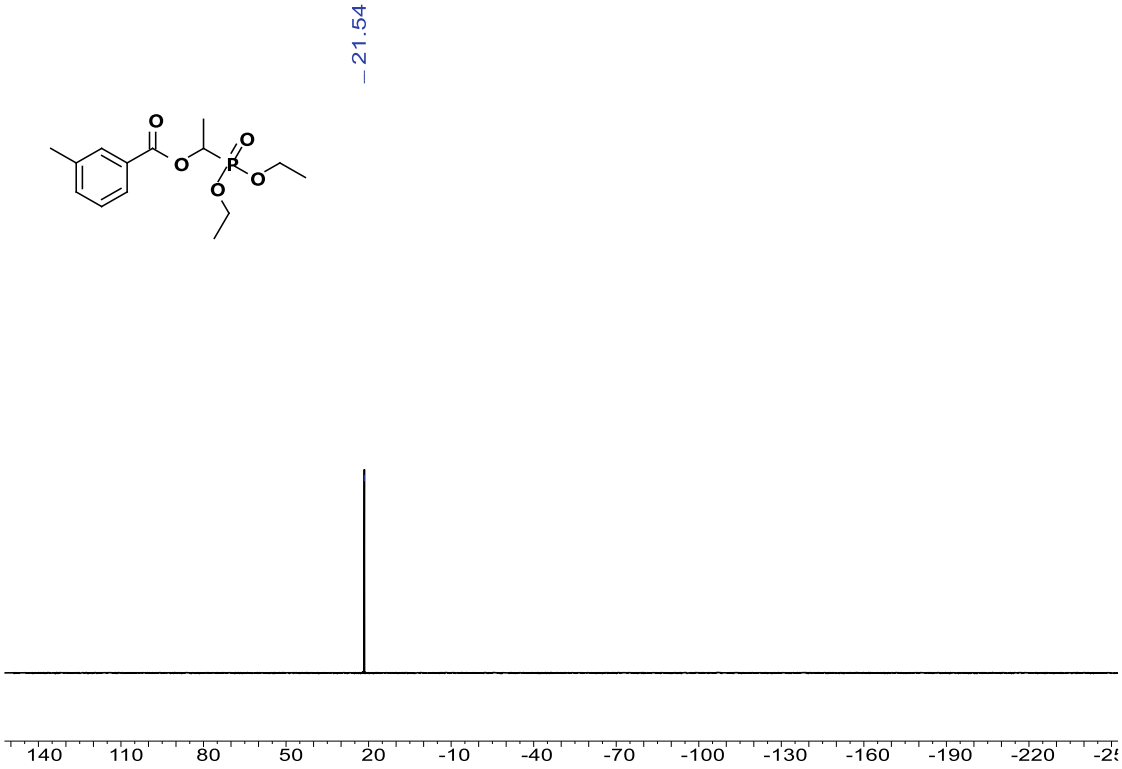
^{1}H NMR spectra of 3ia (500 MHz, $CDCl_3$)



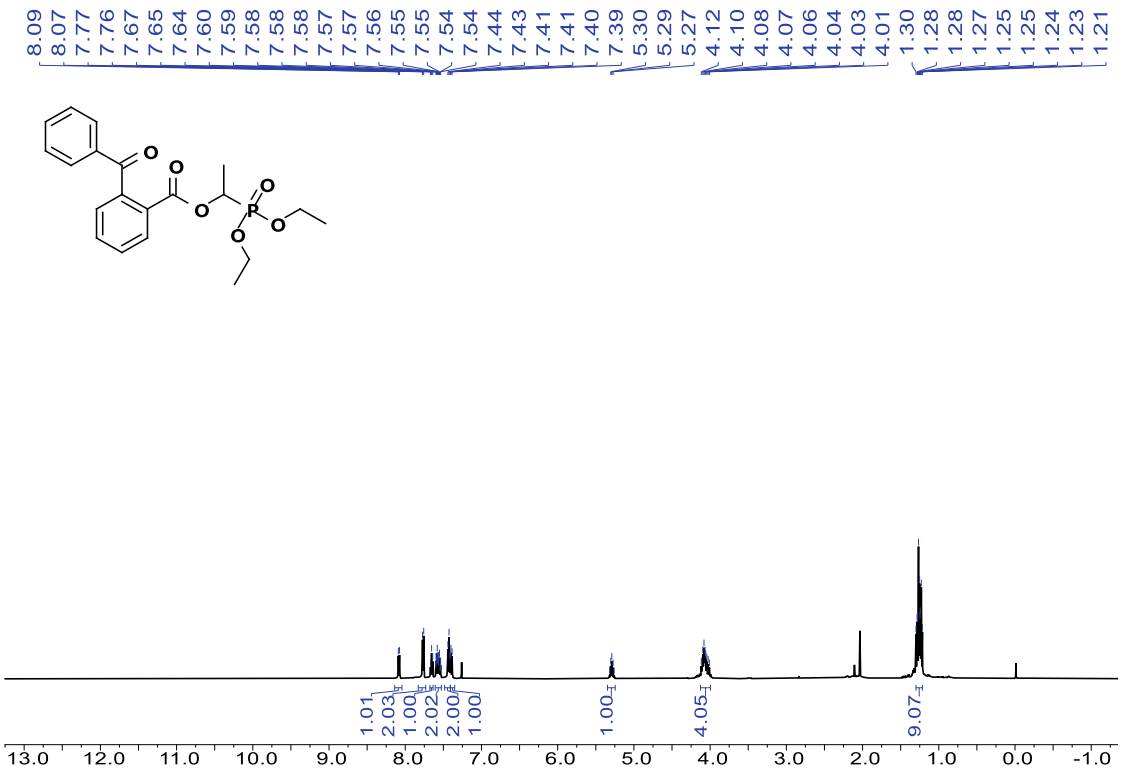
^{13}C NMR spectra of 3ia (126 MHz, $CDCl_3$)



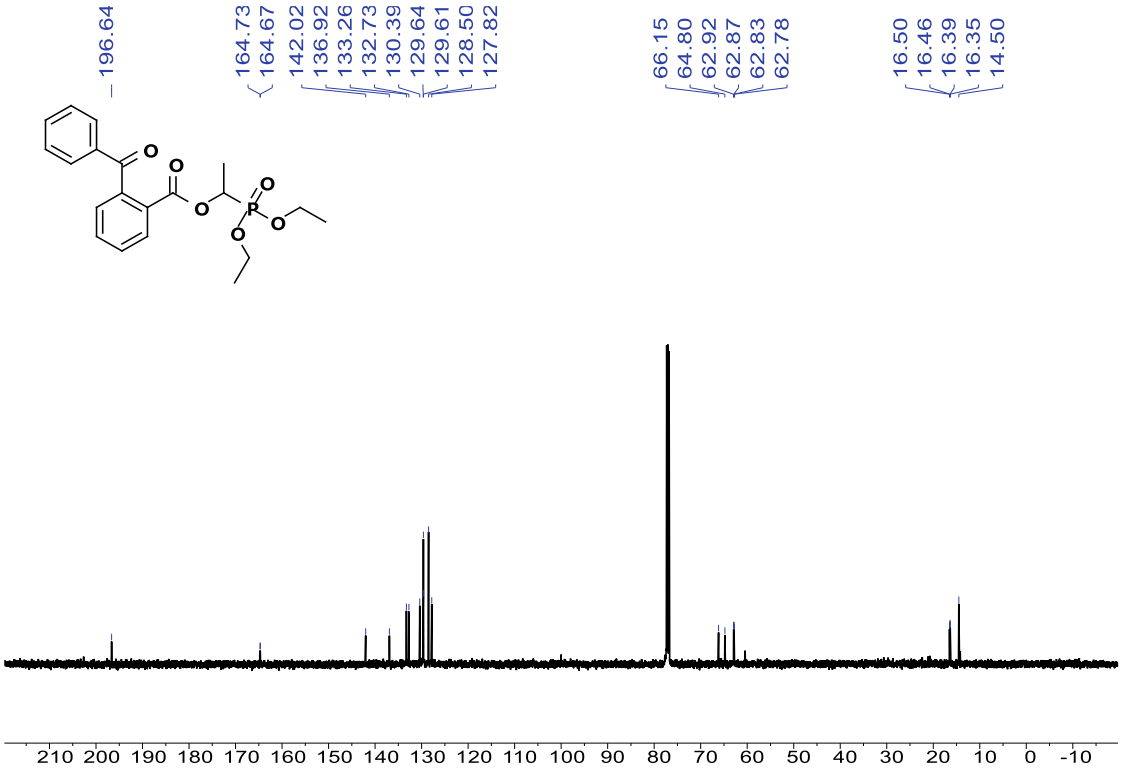
^{31}P NMR spectra of 3ia (202 MHz, $CDCl_3$)



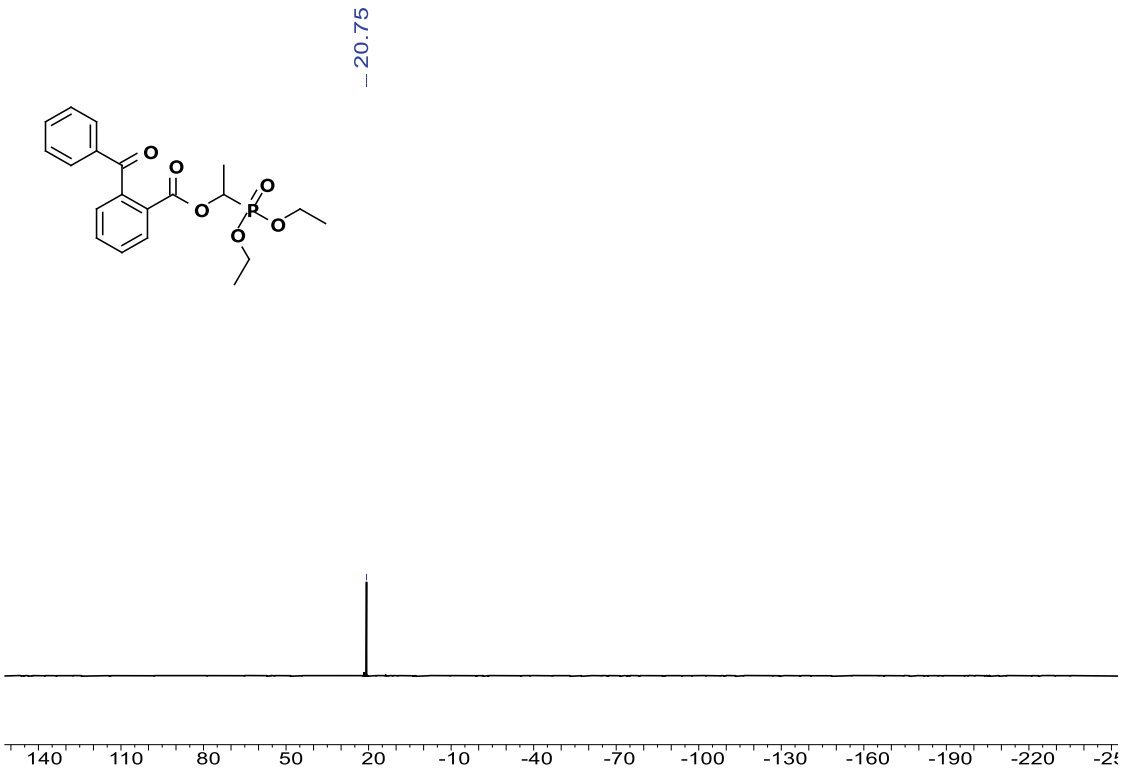
^{1}H NMR spectra of 3ja (500 MHz, $CDCl_3$)



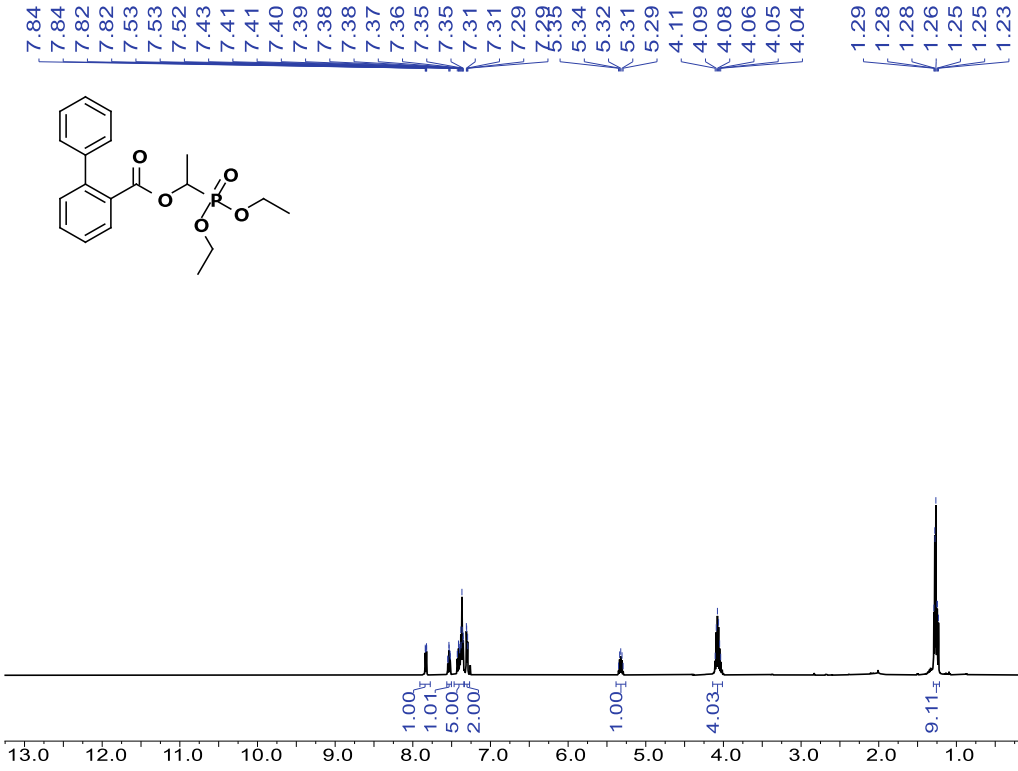
^{13}C NMR spectra of 3ja (126 MHz, $CDCl_3$)



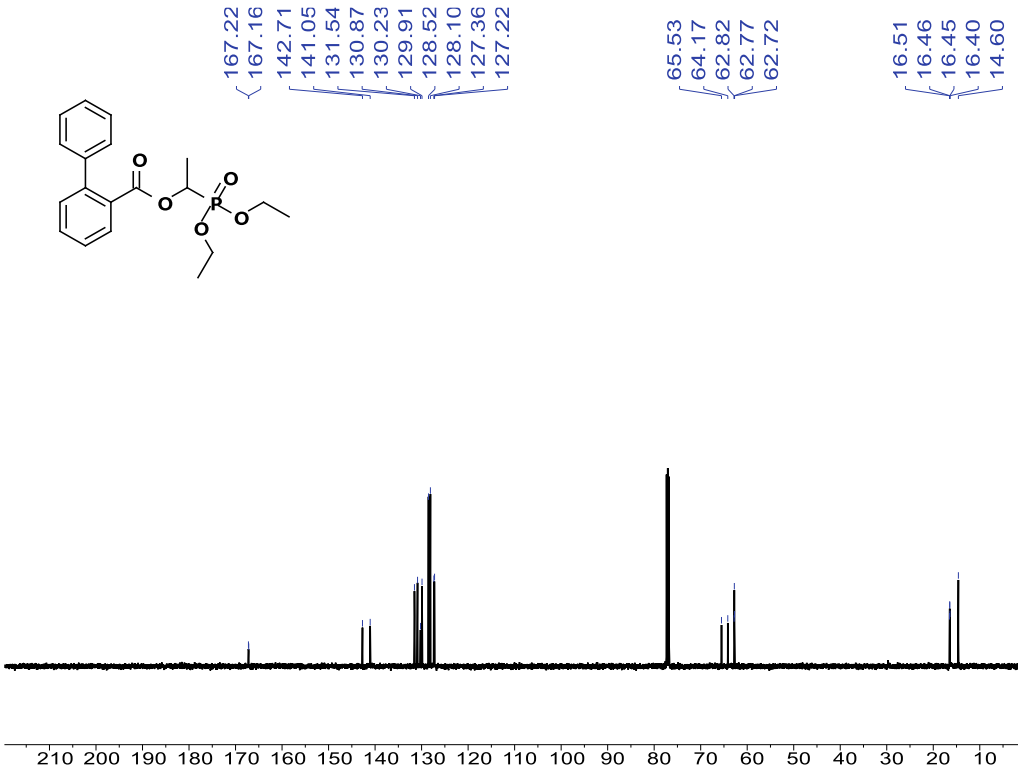
^{31}P NMR spectra of 3ja (202 MHz, $CDCl_3$)



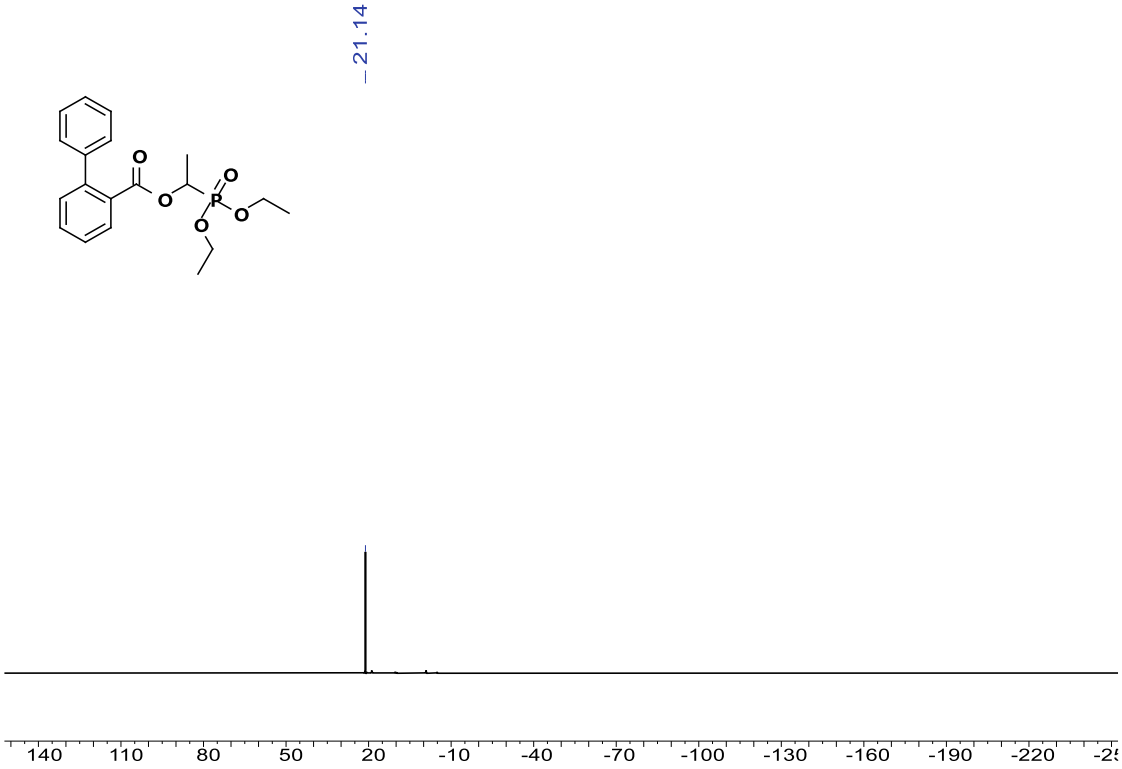
^{1}H NMR spectra of 3ka (500 MHz, $CDCl_3$)



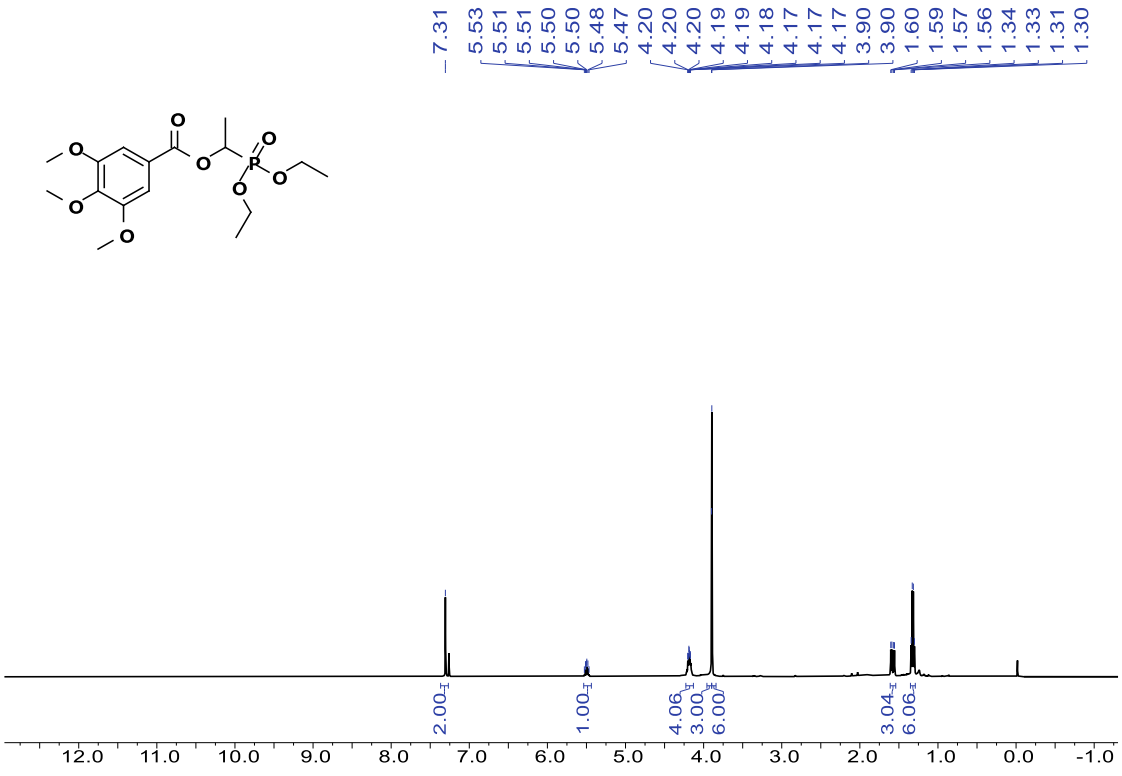
^{13}C NMR spectra of 3ka (126 MHz, $CDCl_3$)



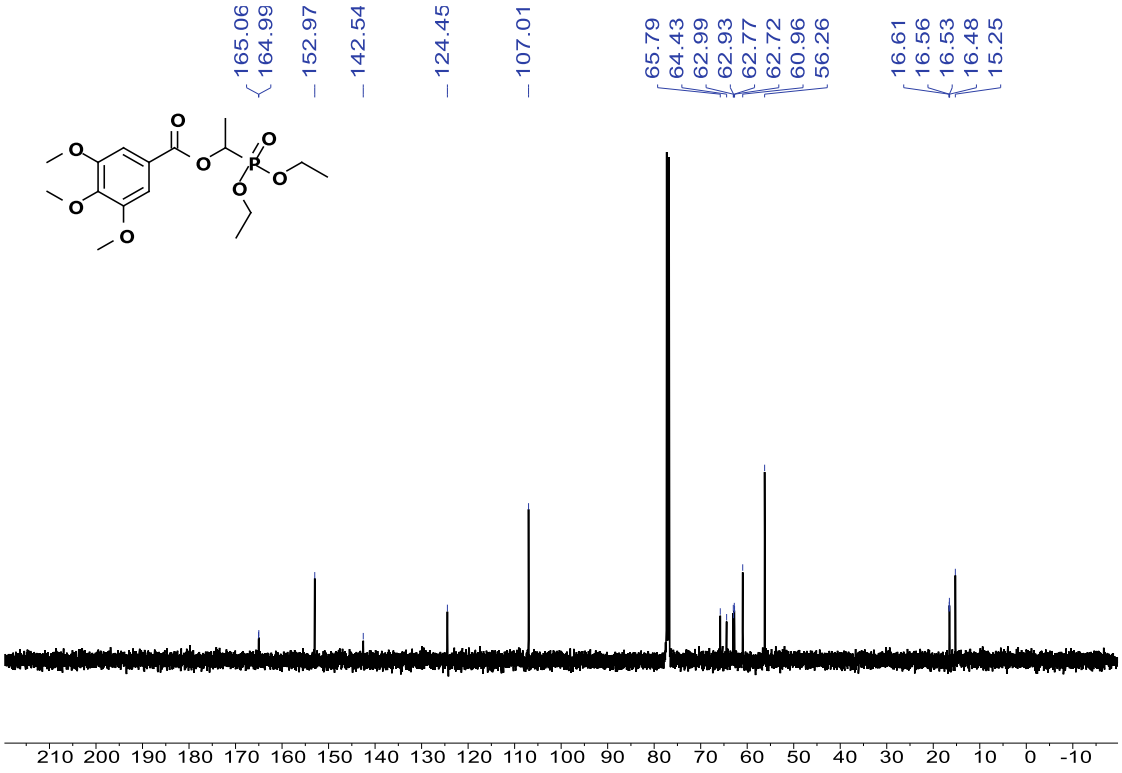
^{31}P NMR spectra of 3ka (202 MHz, $CDCl_3$)



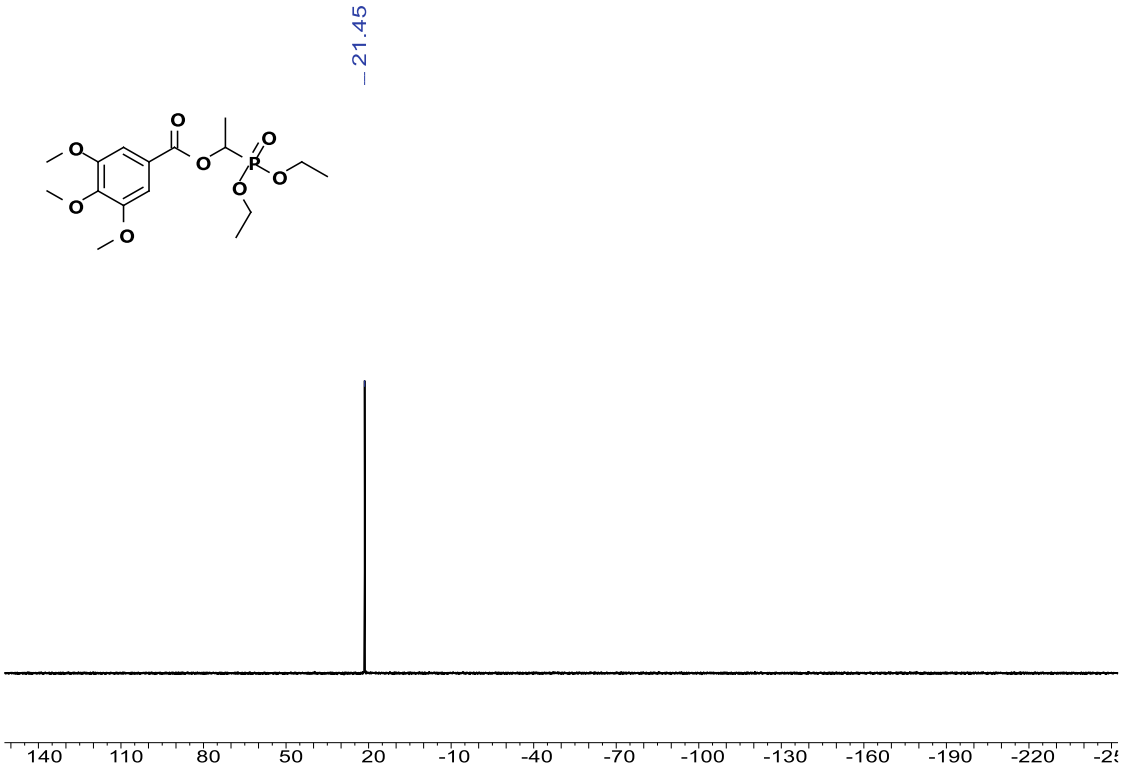
^{1}H NMR spectra of 3la (500 MHz, $CDCl_3$)



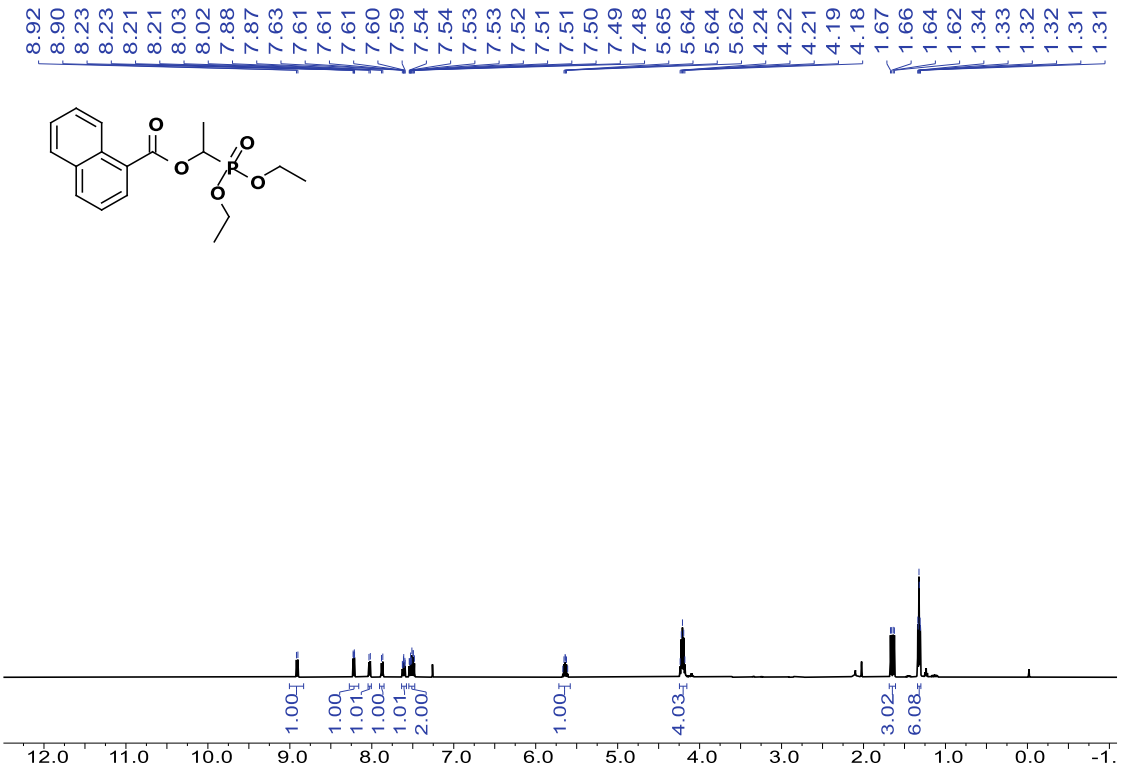
^{13}C NMR spectra of 3la (126 MHz, $CDCl_3$)



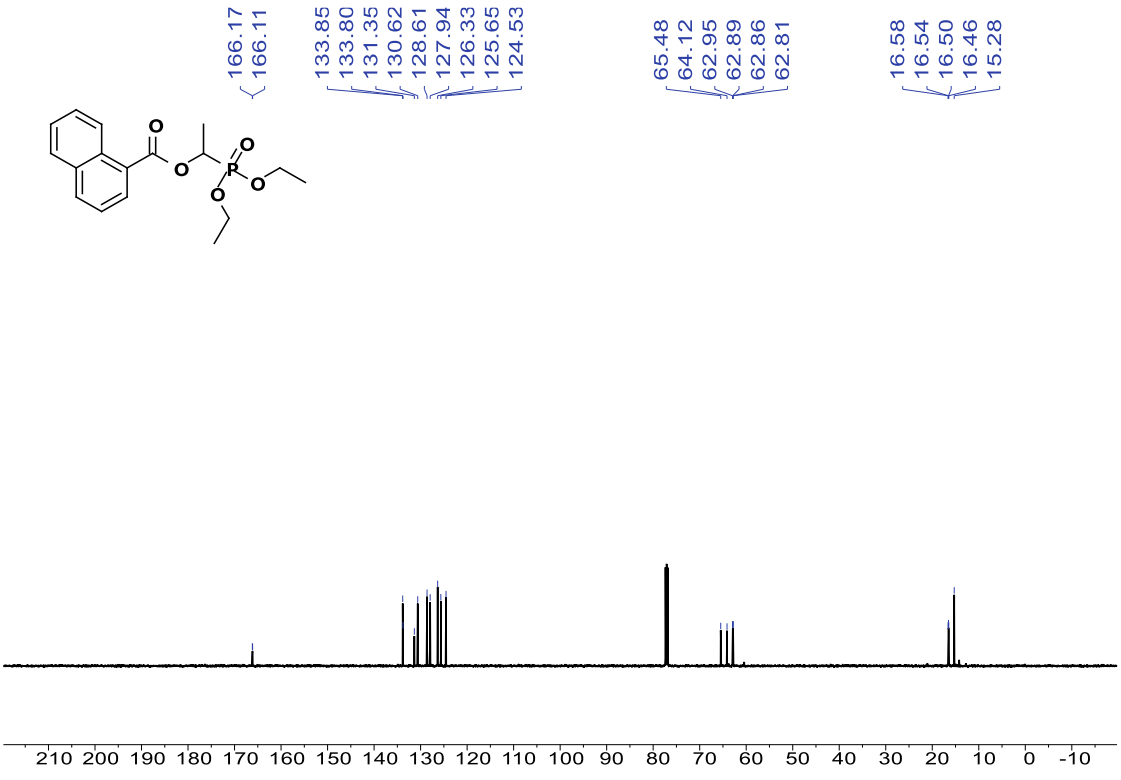
^{31}P NMR spectra of 3la (202 MHz, $CDCl_3$)



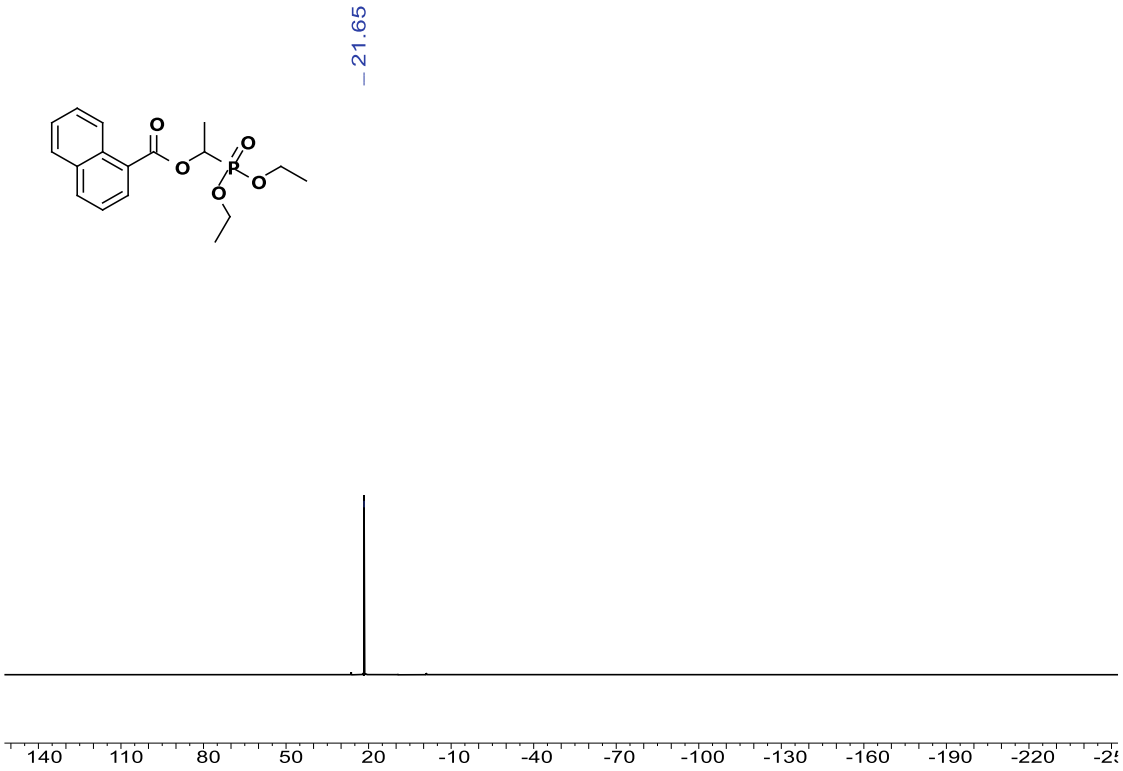
^{1}H NMR spectra of 3ma (500 MHz, $CDCl_3$)



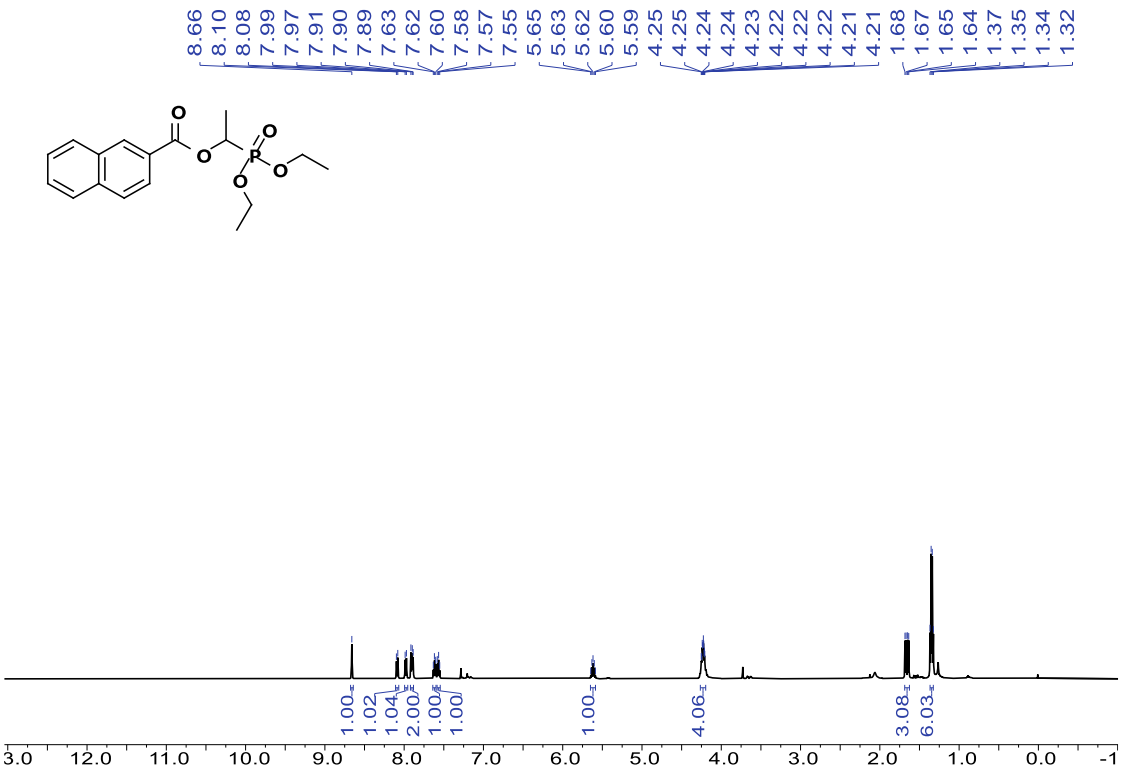
^{13}C NMR spectra of 3ma (126 MHz, $CDCl_3$)



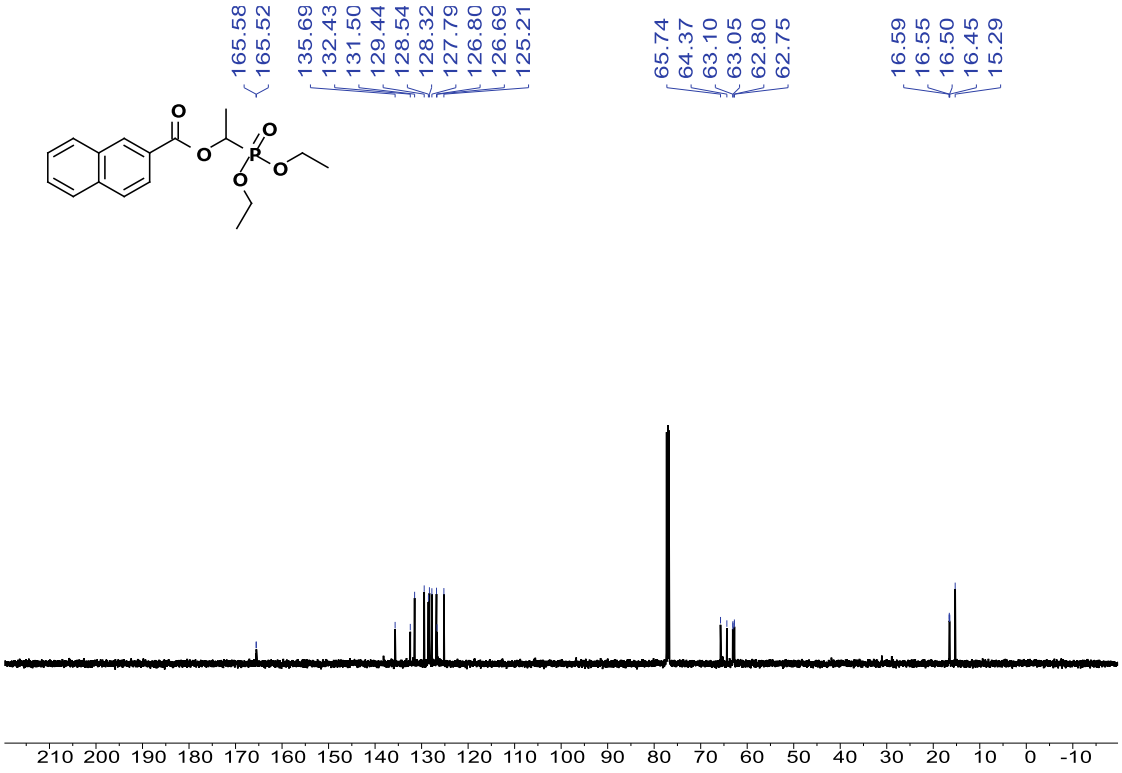
^{31}P NMR spectra of 3ma (202 MHz, $CDCl_3$)



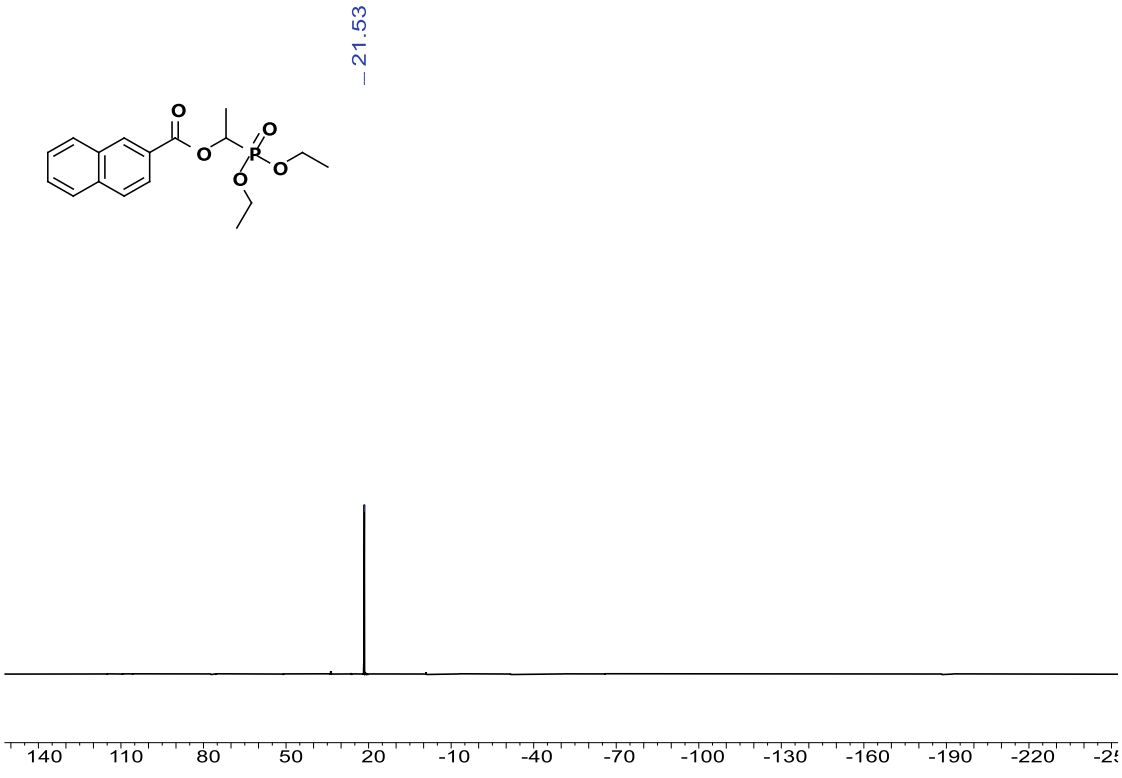
^{1}H NMR spectra of 3na (500 MHz, $CDCl_3$)



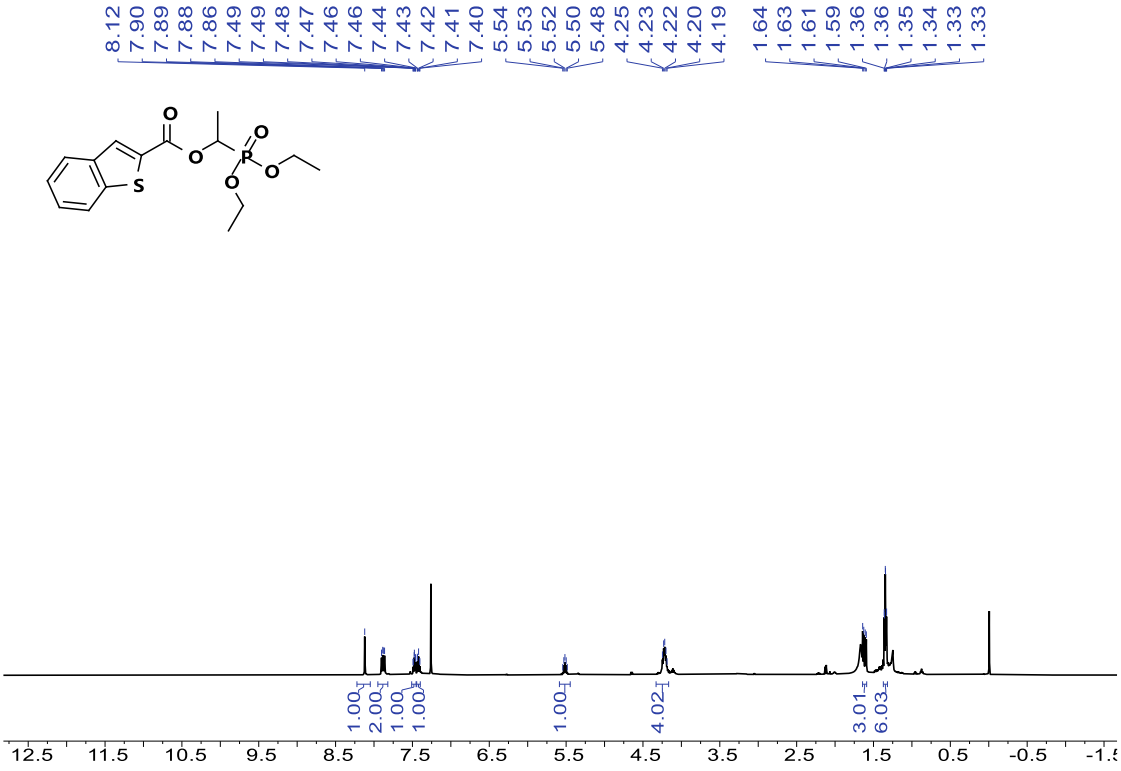
^{13}C NMR spectra of 3na (126 MHz, $CDCl_3$)



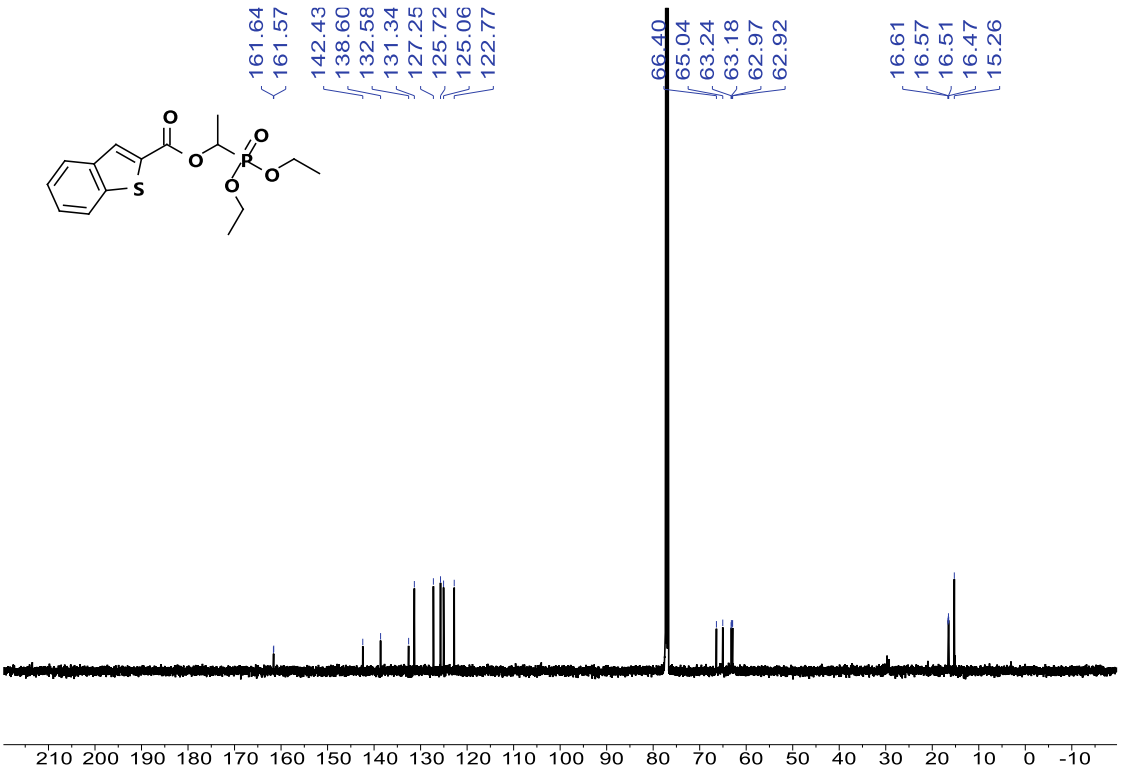
^{31}P NMR spectra of 3na (202 MHz, $CDCl_3$)



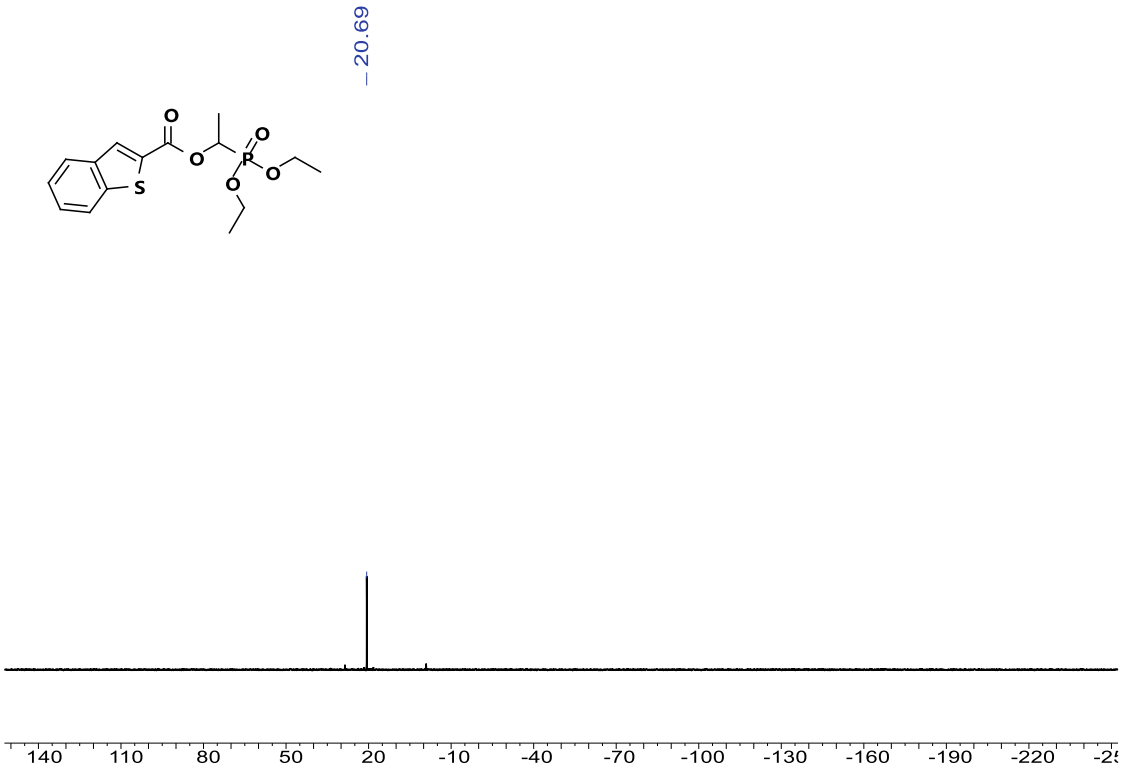
^{1}H NMR spectra of 3oa (500 MHz, $CDCl_3$)



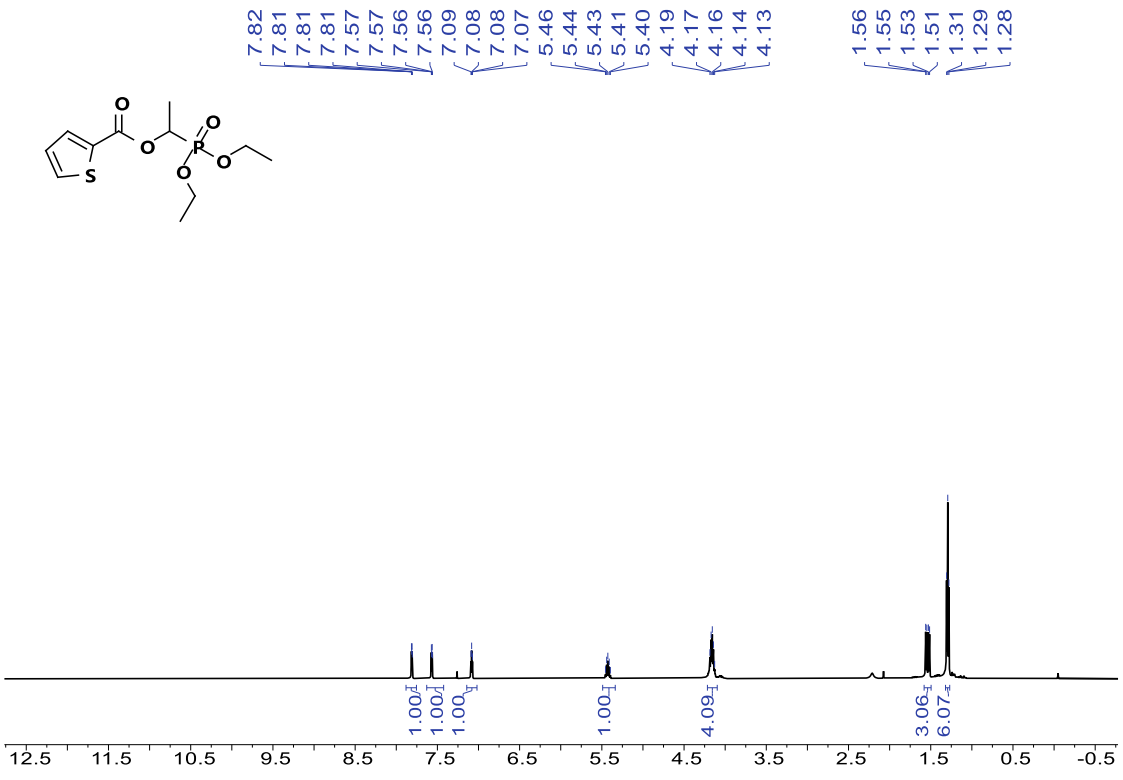
^{13}C NMR spectra of 3oa (126 MHz, $CDCl_3$)



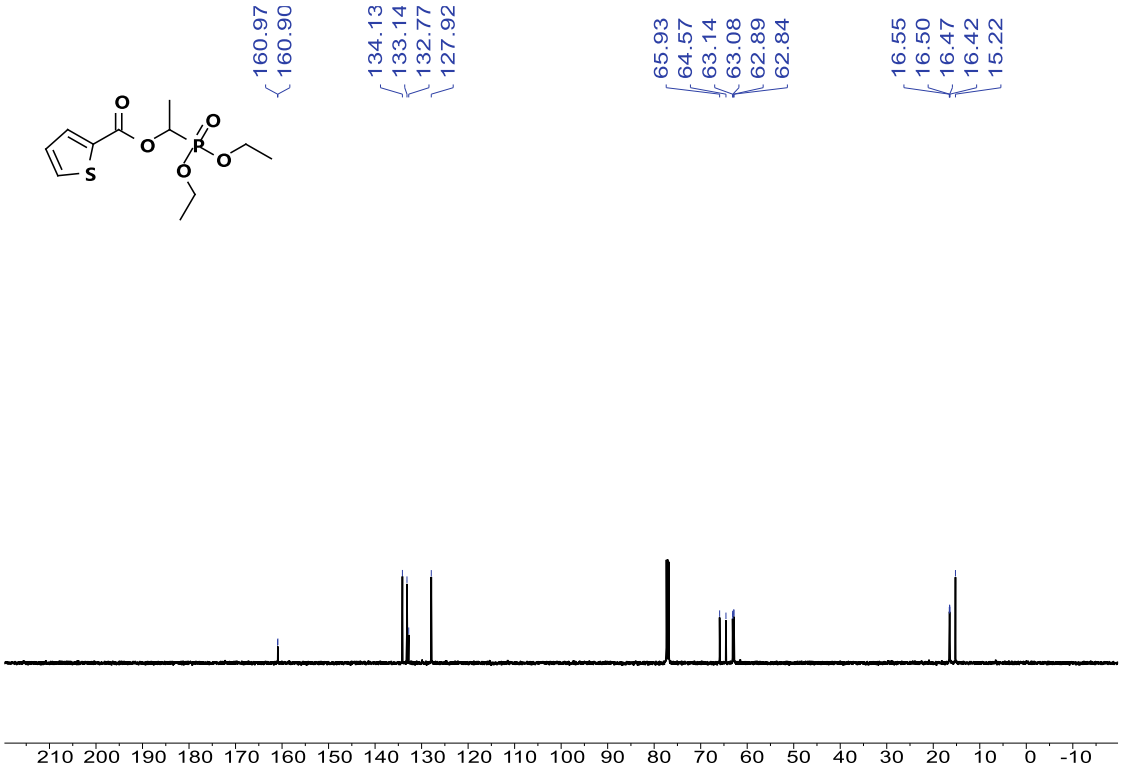
^{31}P NMR spectra of 3oa (202 MHz, $CDCl_3$)



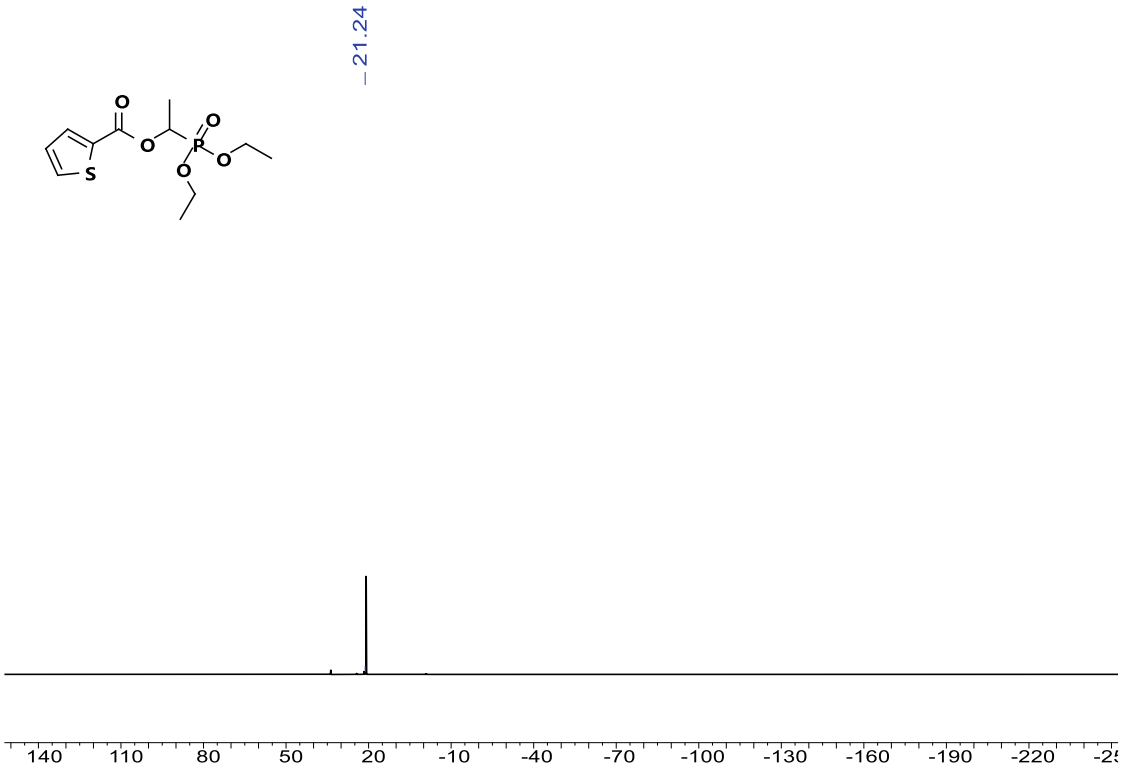
^{1}H NMR spectra of 3pa (500 MHz, $CDCl_3$)



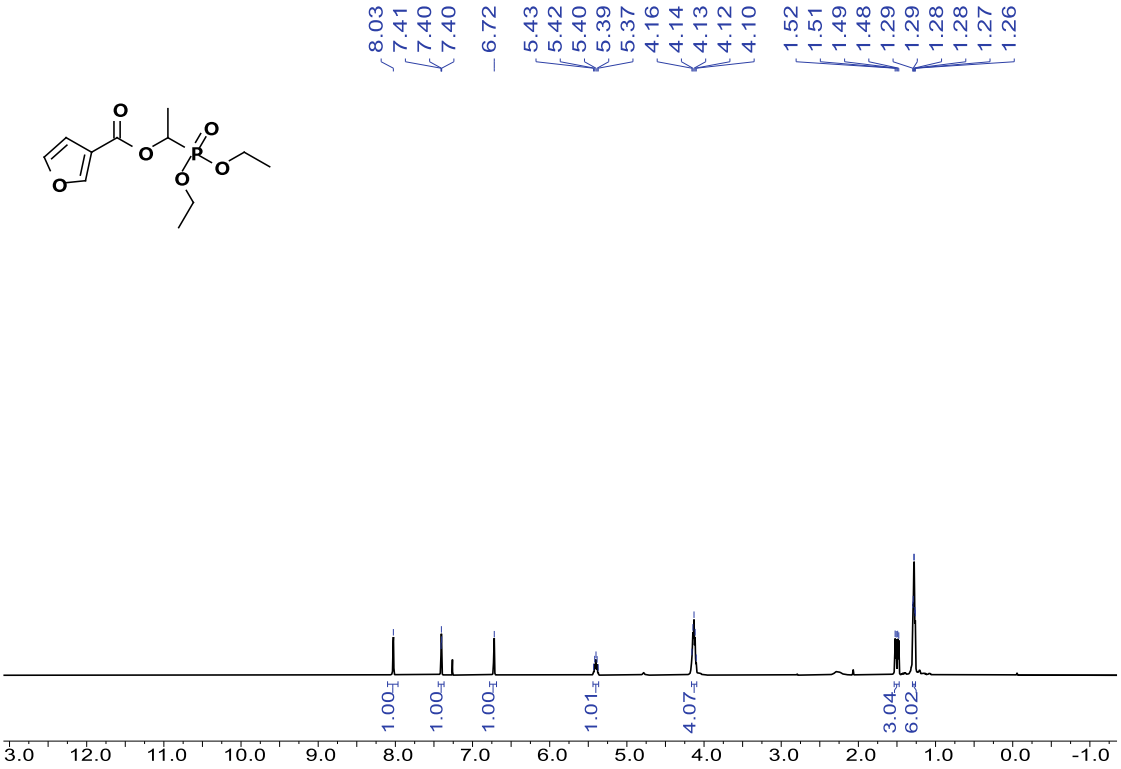
^{13}C NMR spectra of 3pa (126 MHz, $CDCl_3$)



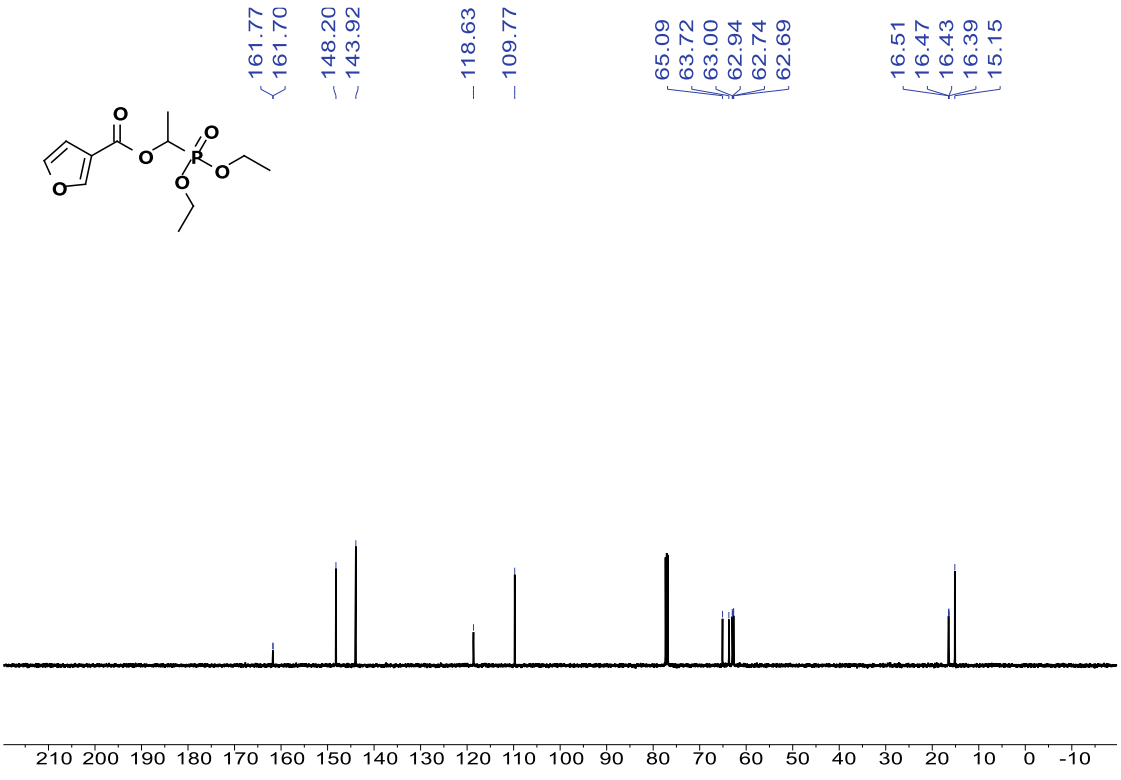
^{31}P NMR spectra of 3pa (202 MHz, $CDCl_3$)



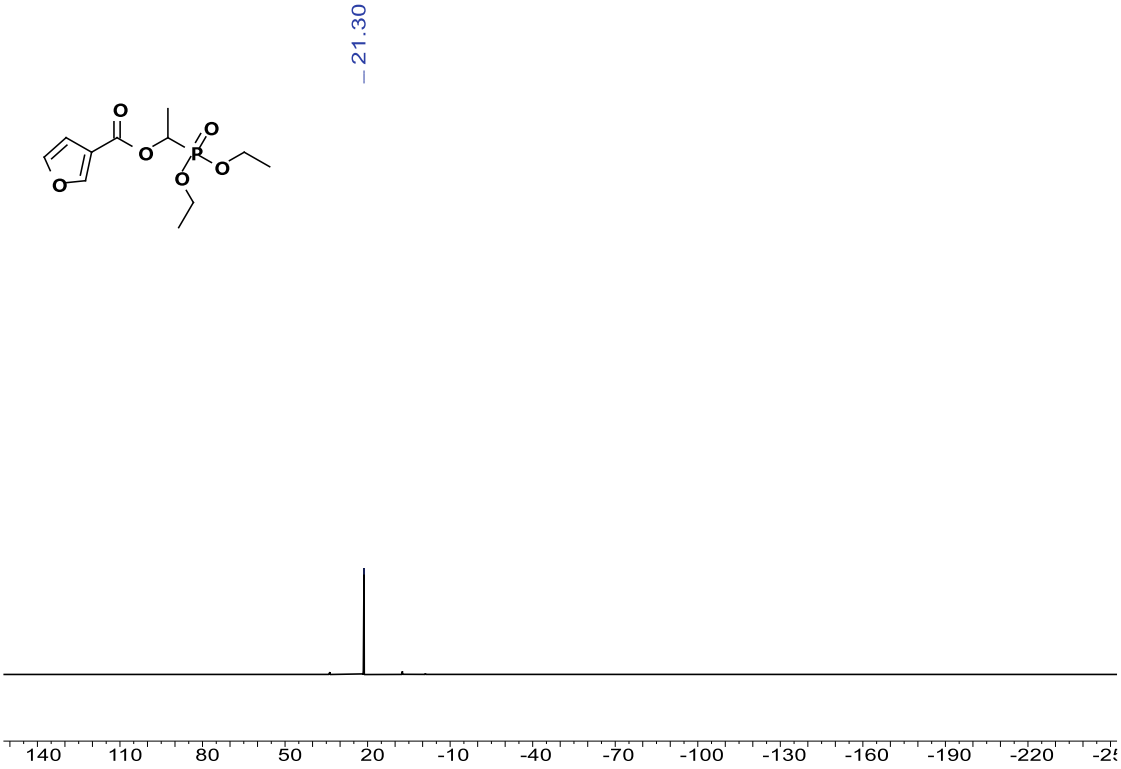
^{1}H NMR spectra of 3qa (500 MHz, $CDCl_3$)



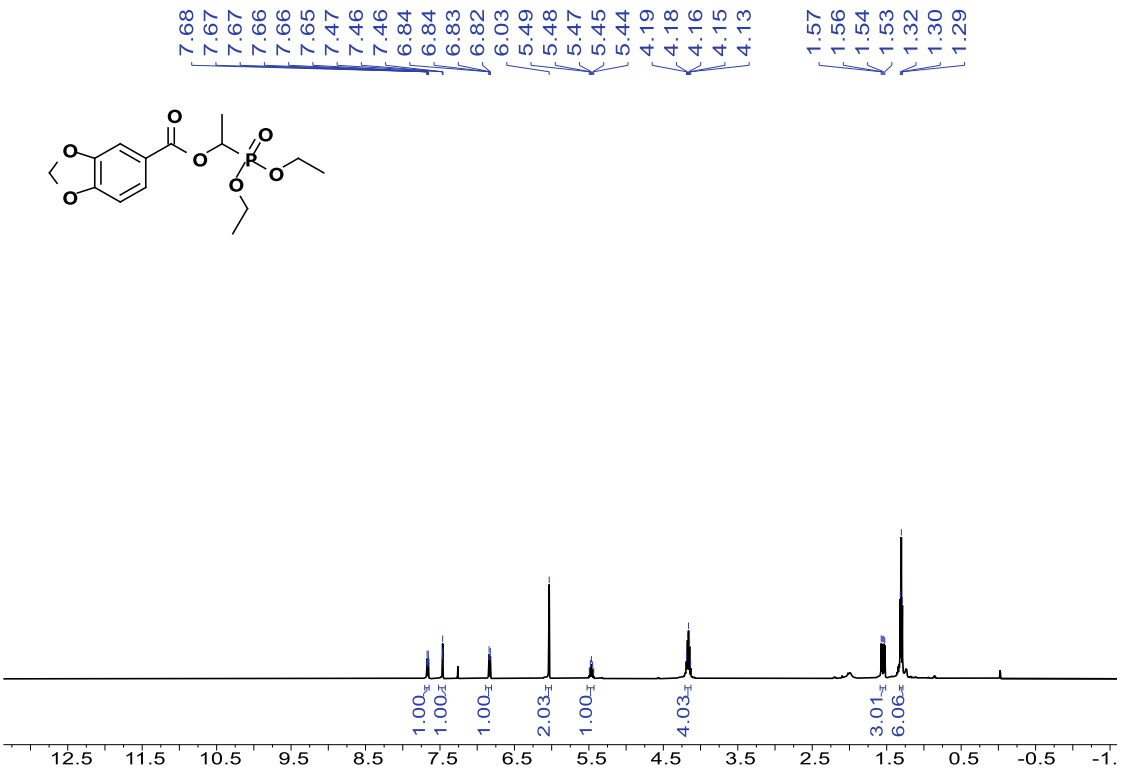
^{13}C NMR spectra of 3qa (126 MHz, $CDCl_3$)



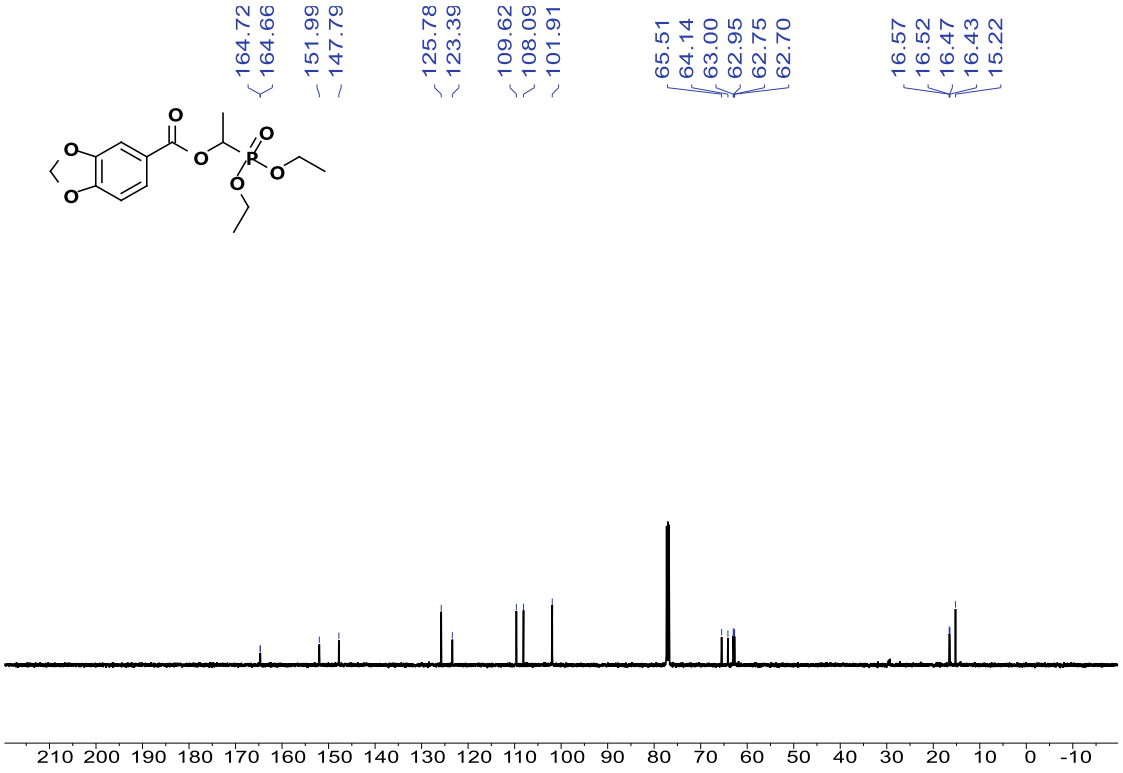
^{31}P NMR spectra of 3qa (202 MHz, $CDCl_3$)



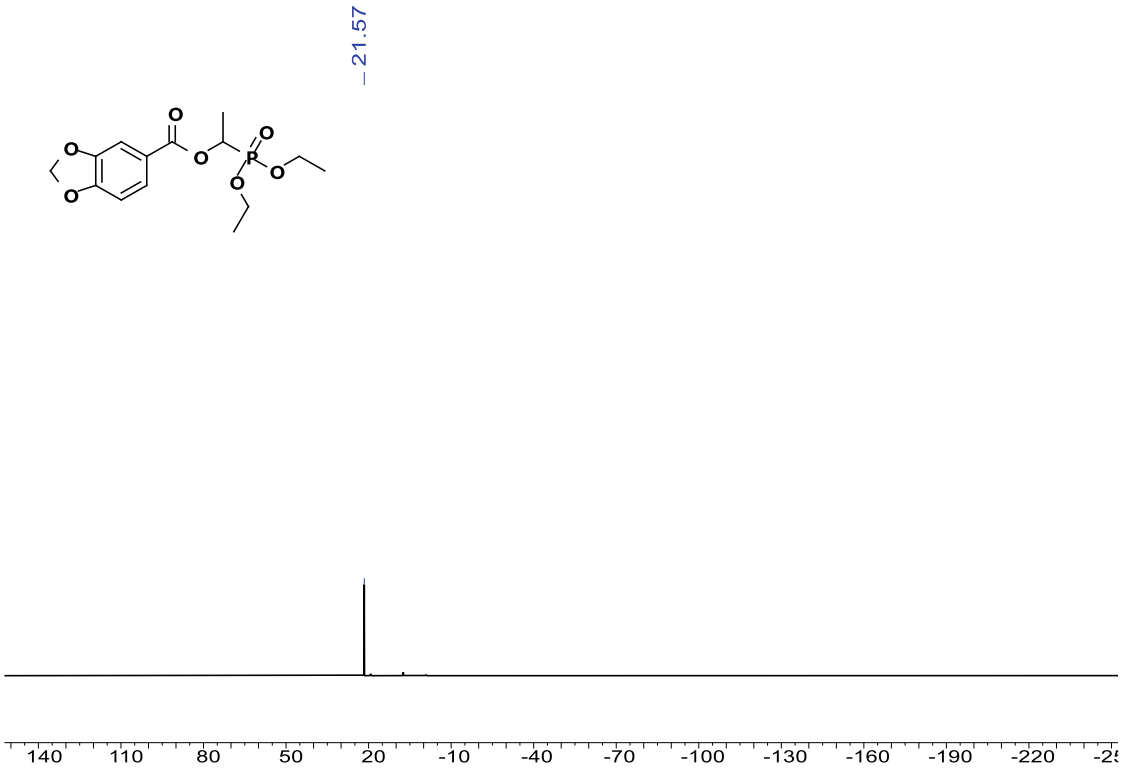
^{1}H NMR spectra of 3ra (500 MHz, $CDCl_3$)



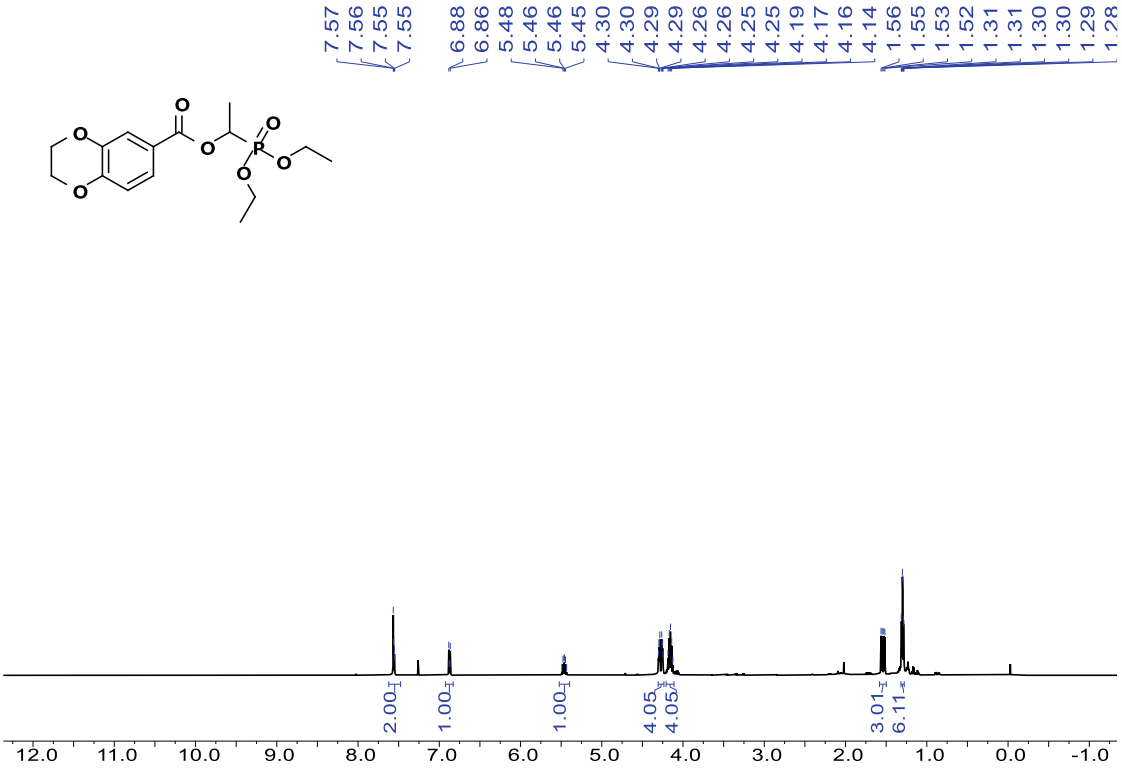
^{13}C NMR spectra of 3ra (126 MHz, $CDCl_3$)



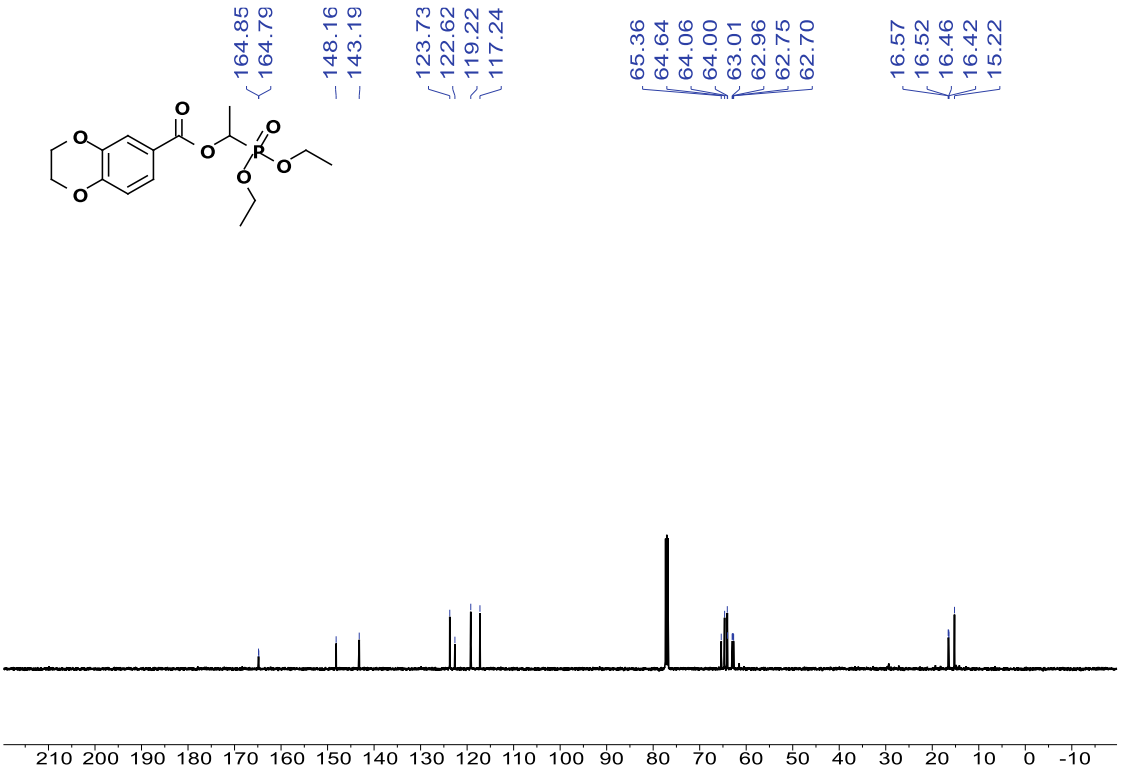
^{31}P NMR spectra of 3ra (202 MHz, $CDCl_3$)



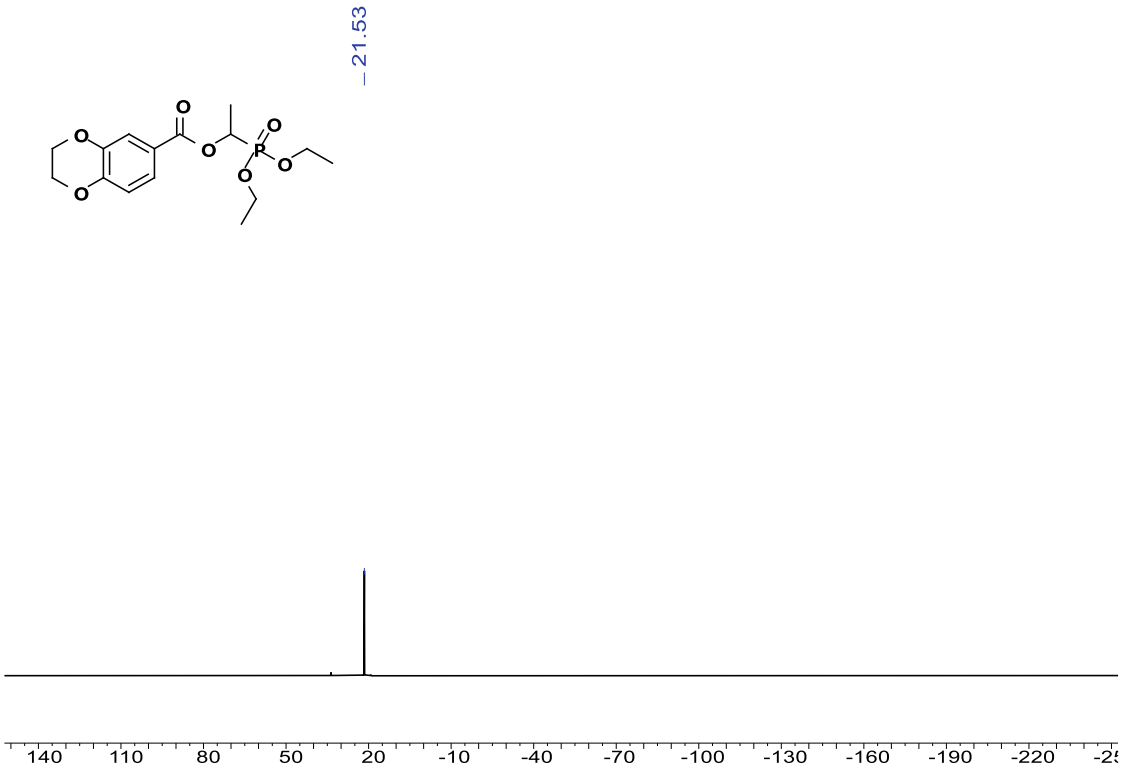
^{1}H NMR spectra of 3sa (500 MHz, $CDCl_3$)



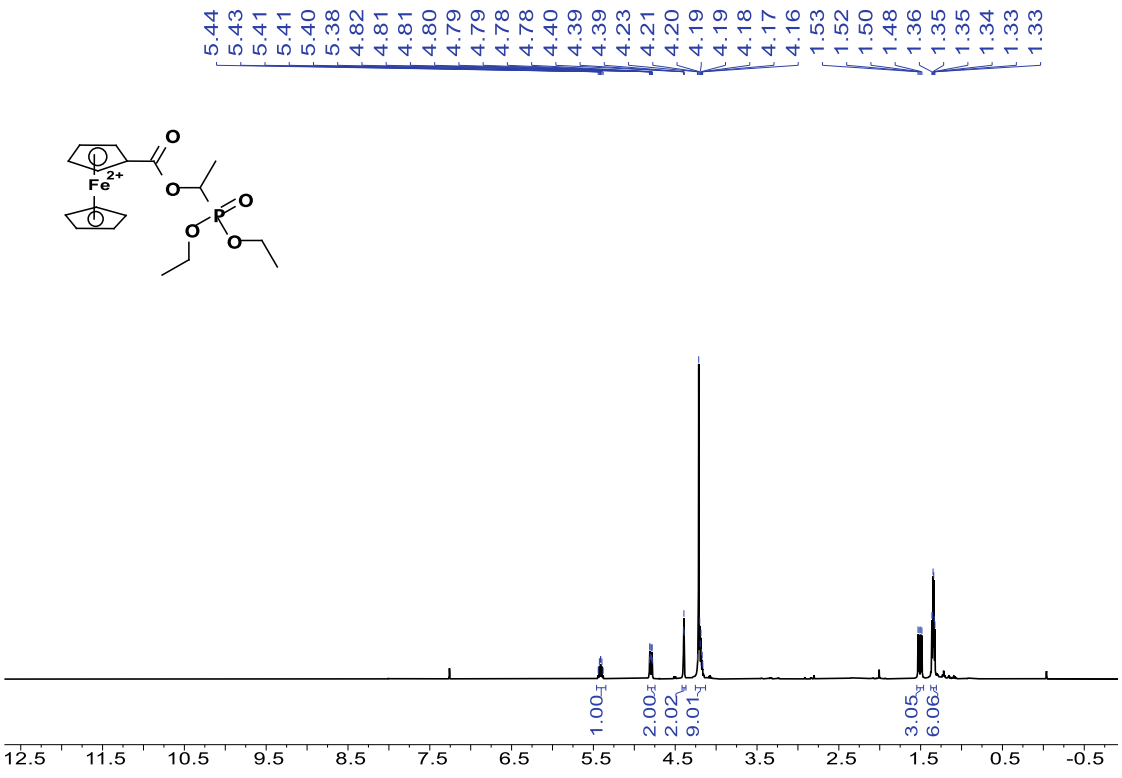
^{13}C NMR spectra of 3sa (126 MHz, $CDCl_3$)



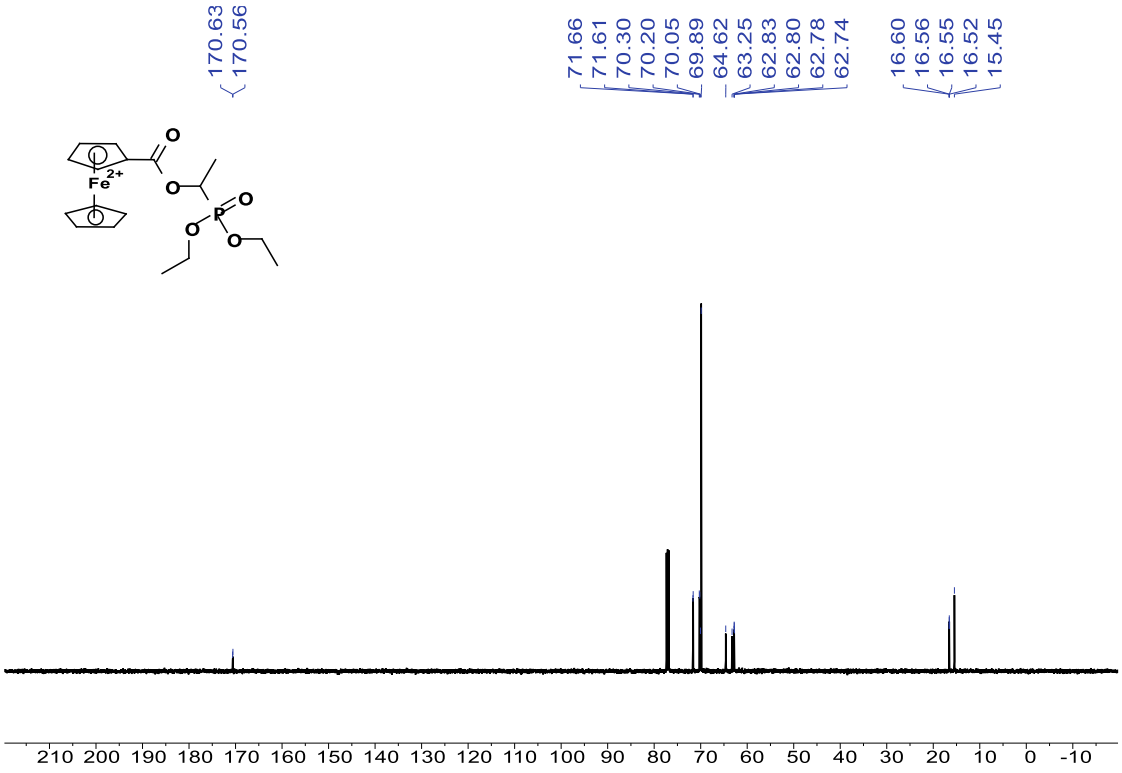
^{31}P NMR spectra of 3sa (202 MHz, $CDCl_3$)



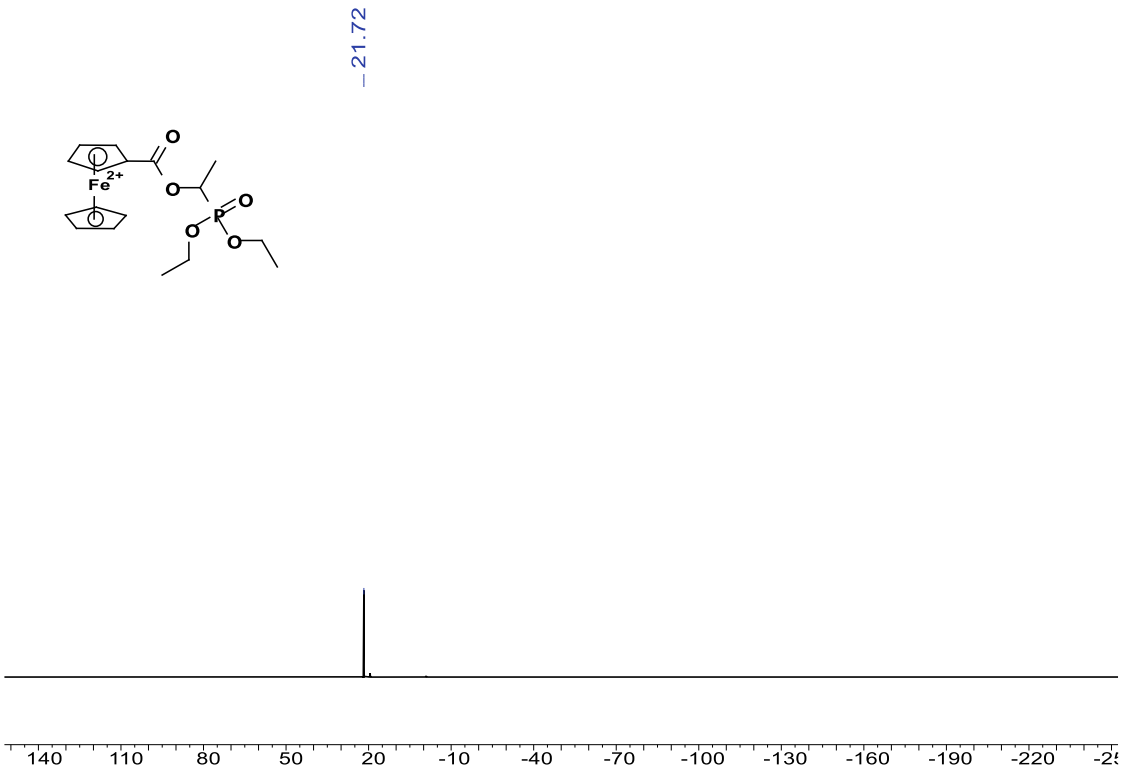
^{1}H NMR spectra of 3ta (500 MHz, $CDCl_3$)



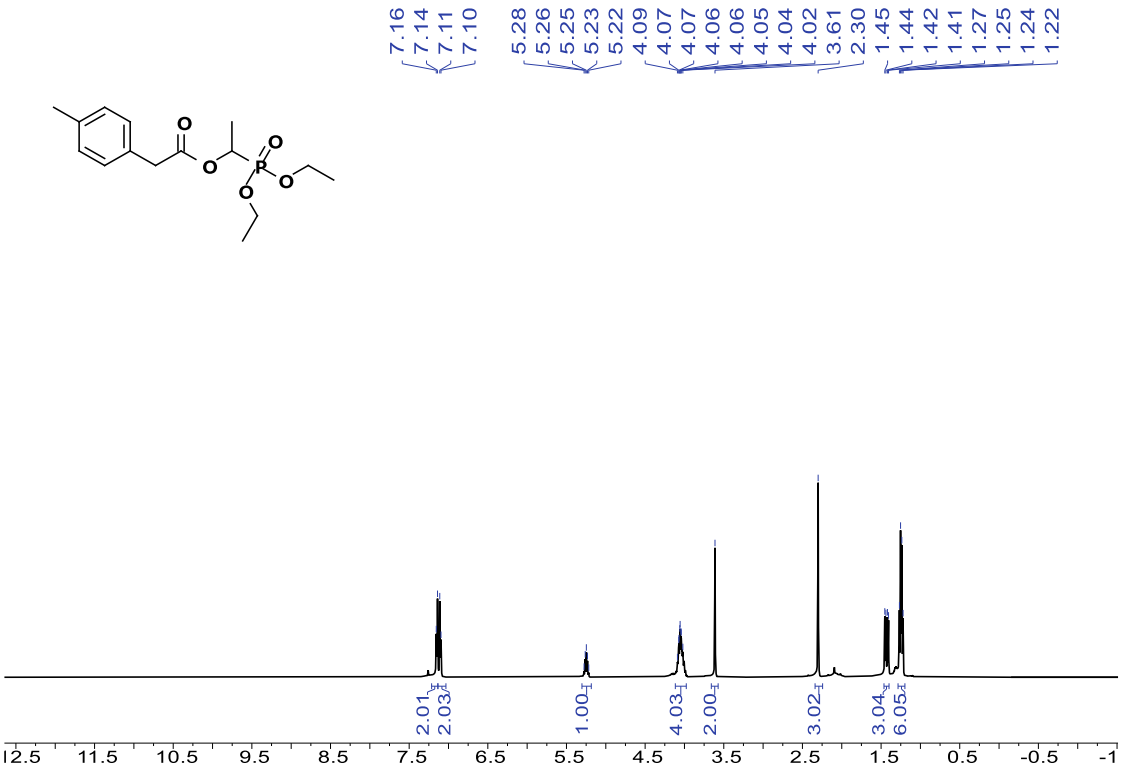
^{13}C NMR spectra of 3ta (126 MHz, $CDCl_3$)



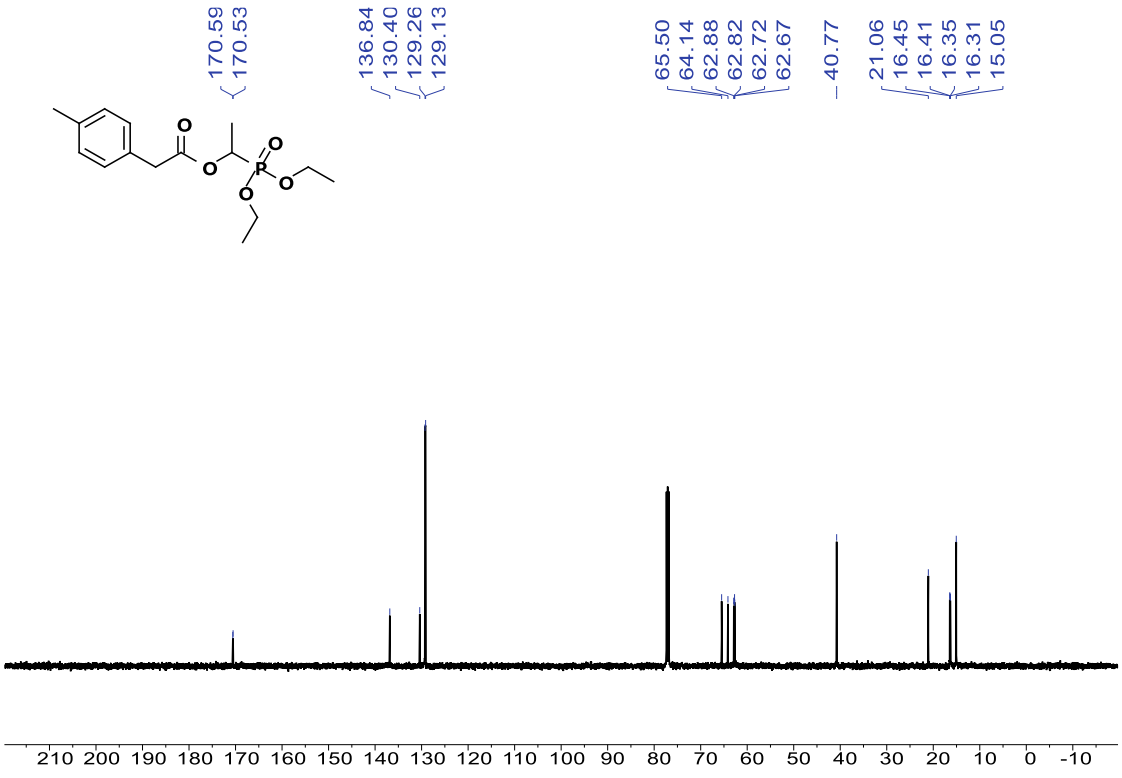
^{31}P NMR spectra of 3ta (202 MHz, $CDCl_3$)



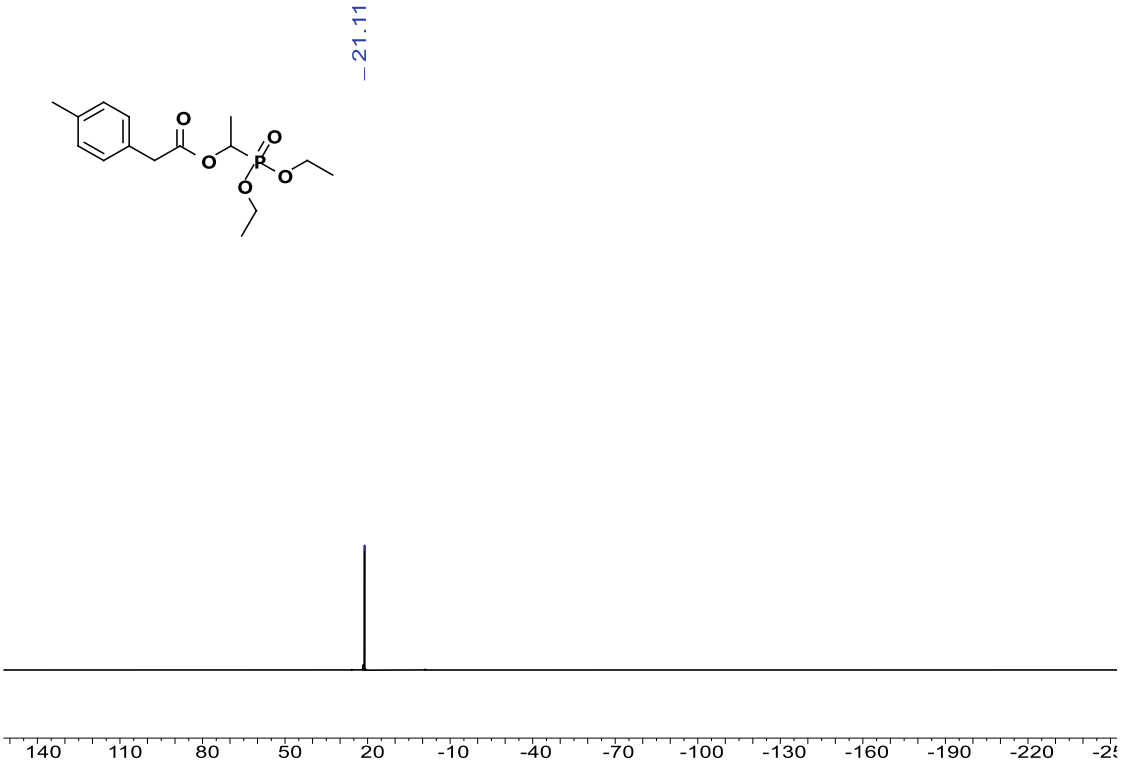
^{1}H NMR spectra of 3ua (500 MHz, $CDCl_3$)



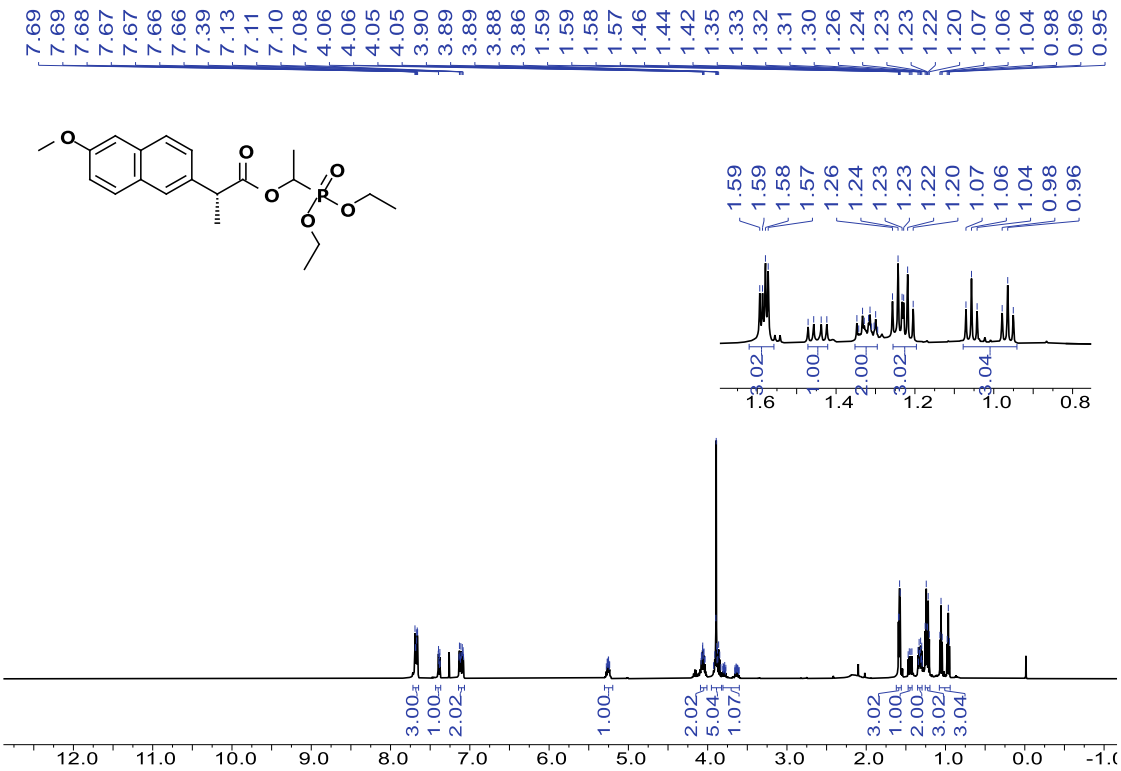
^{13}C NMR spectra of 3ua (126 MHz, $CDCl_3$)



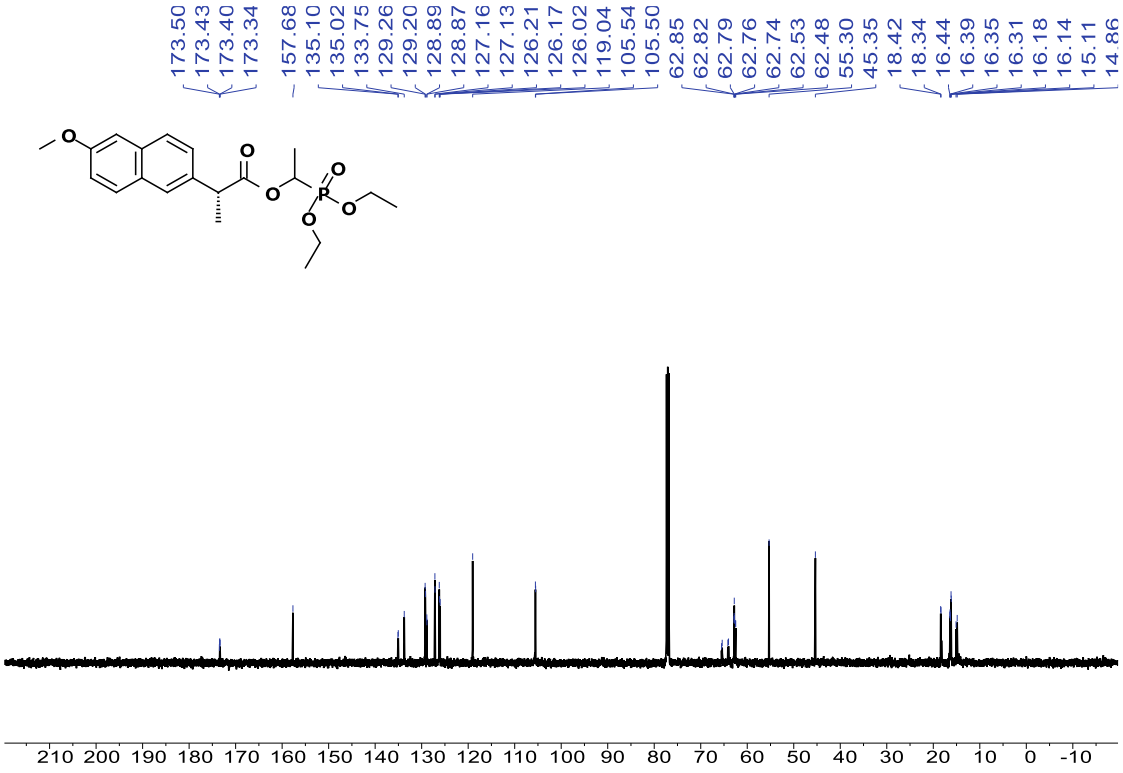
^{31}P NMR spectra of 3ua (202 MHz, $CDCl_3$)



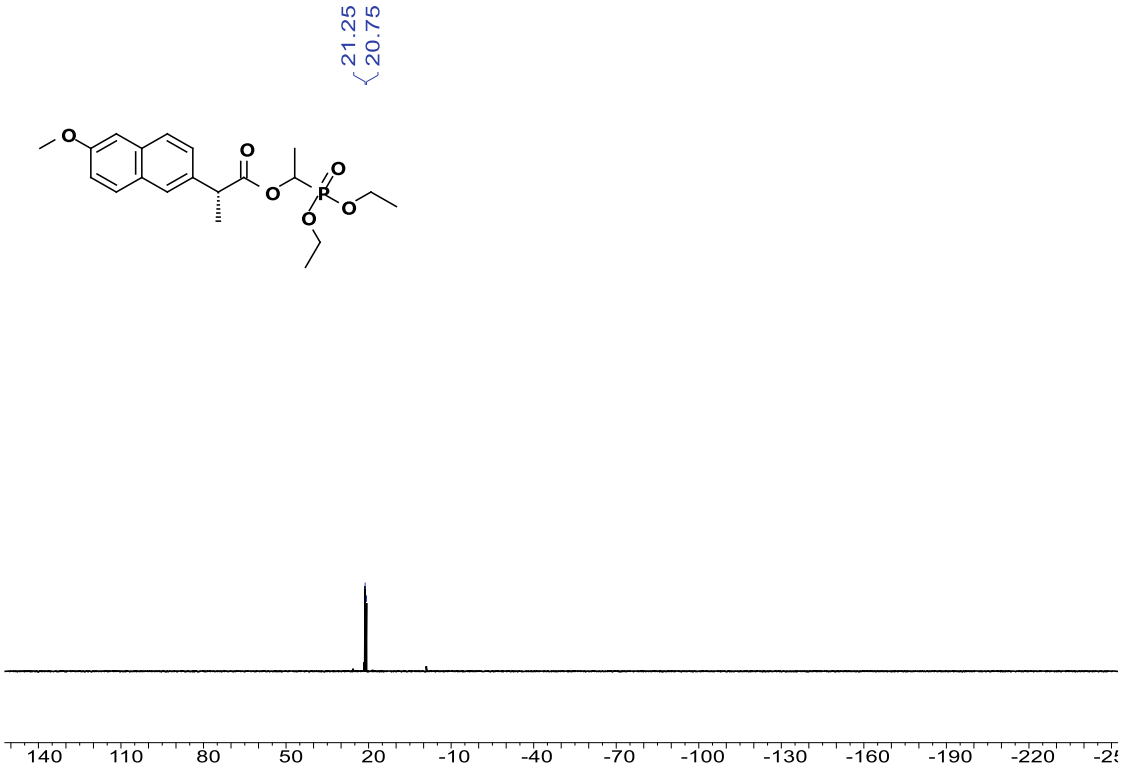
^{1}H NMR spectra of 3va (500 MHz, $CDCl_3$)



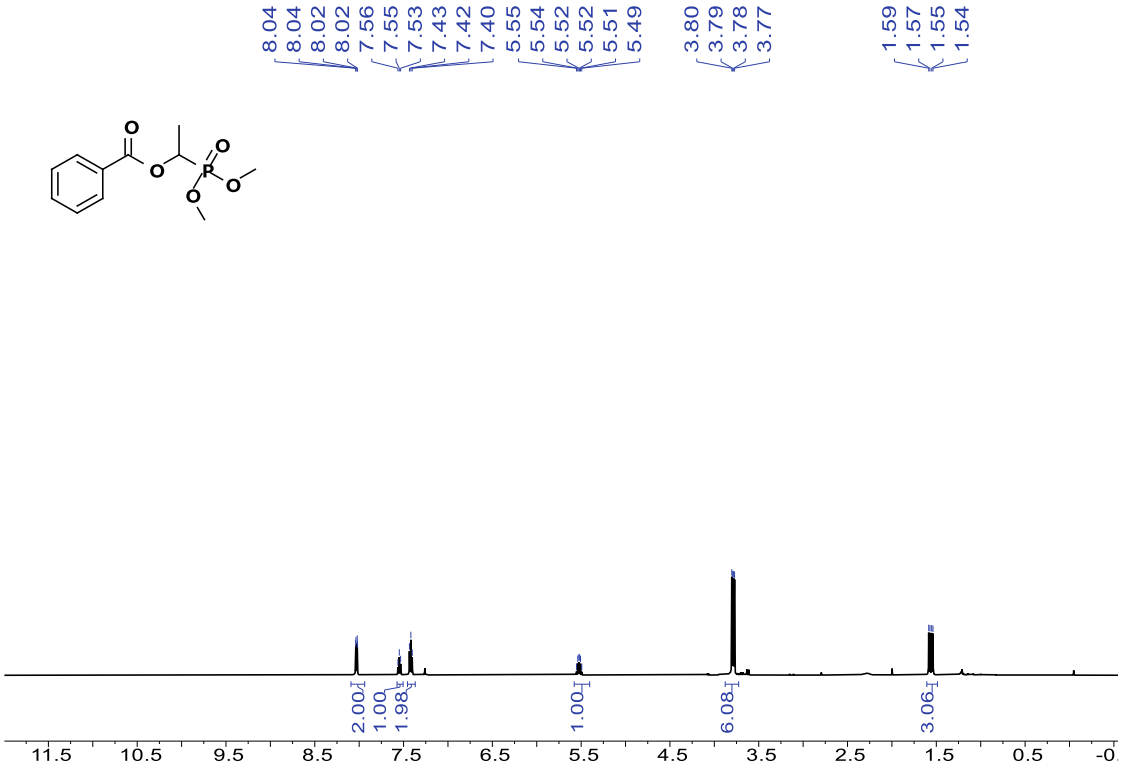
^{13}C NMR spectra of 3va (126 MHz, $CDCl_3$)



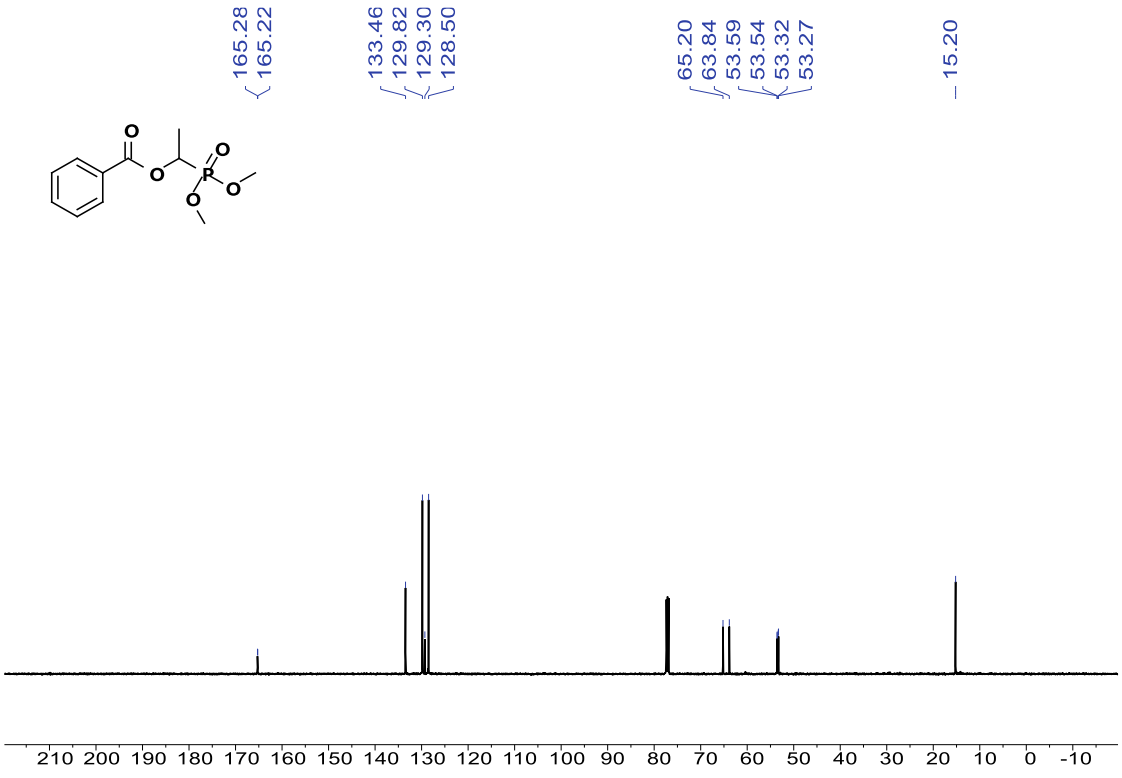
^{31}P NMR spectra of 3va (202 MHz, $CDCl_3$)



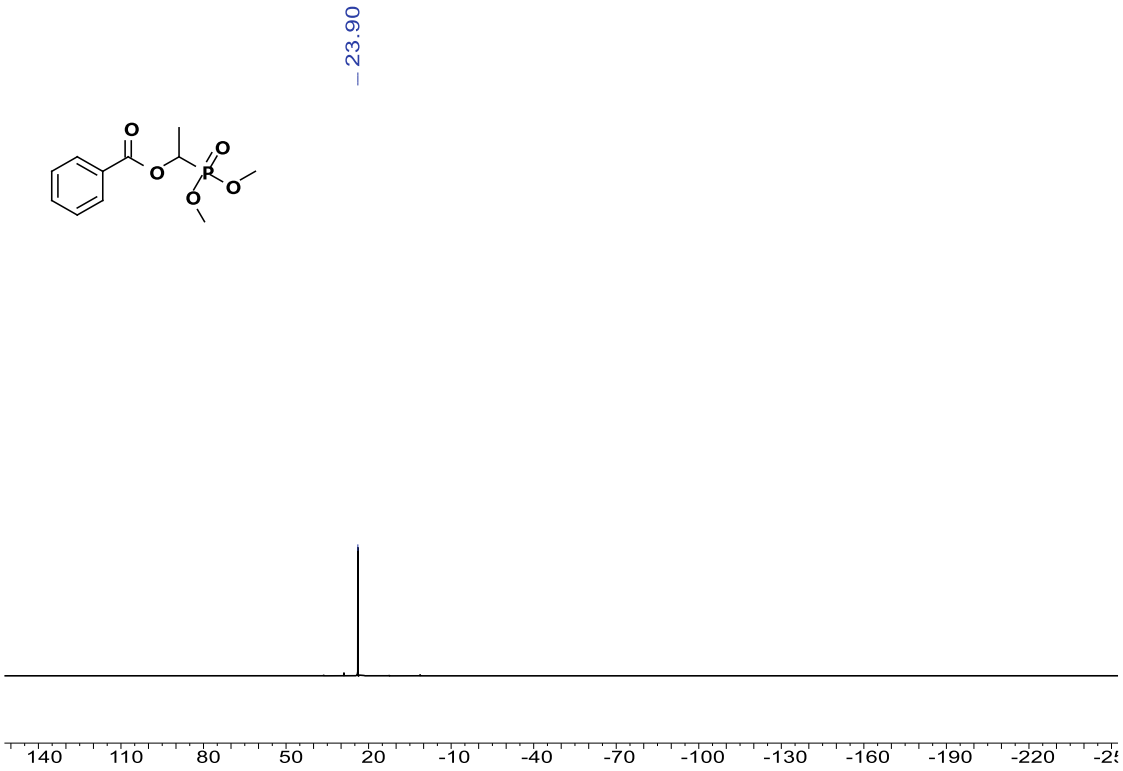
^{1}H NMR spectra of 3ab (500 MHz, $CDCl_3$)



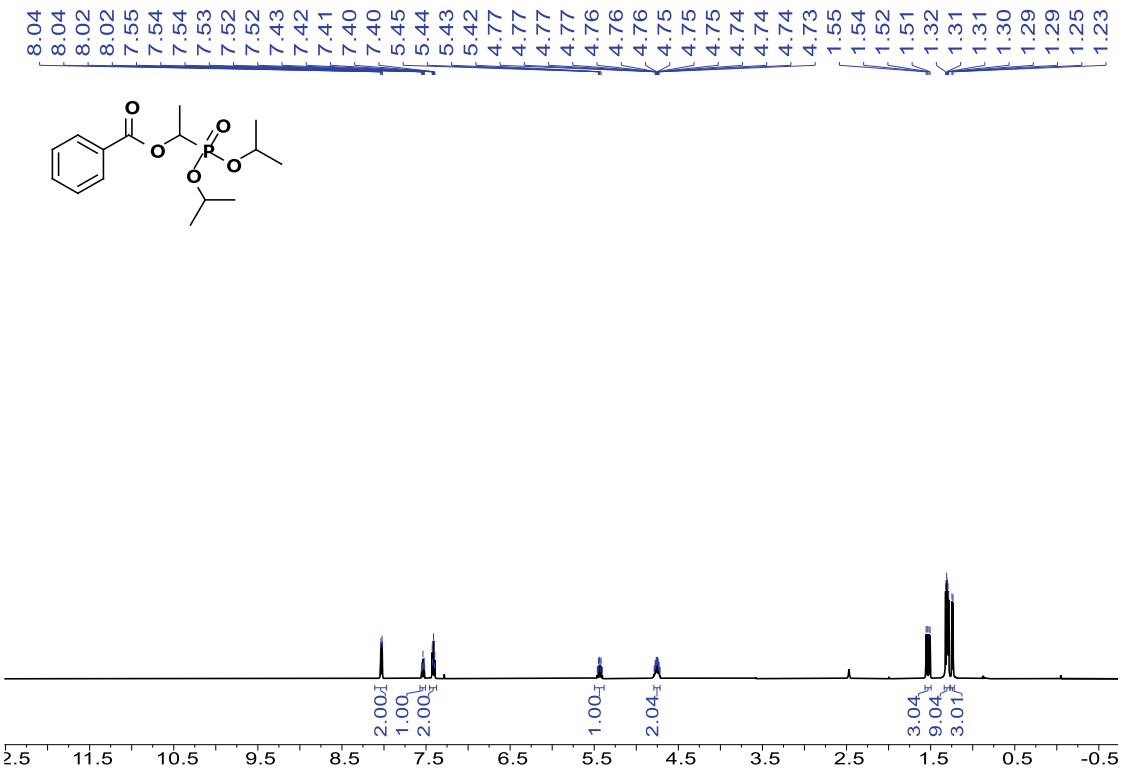
^{13}C NMR spectra of 3ab (126 MHz, $CDCl_3$)



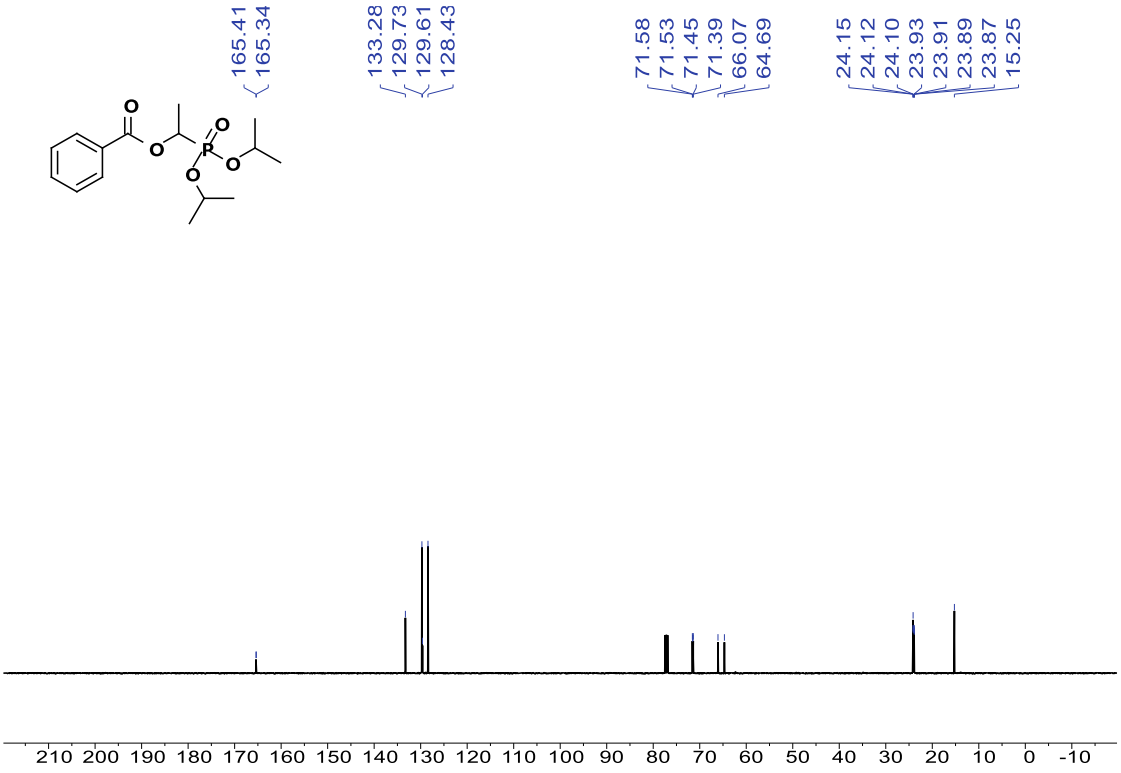
^{31}P NMR spectra of 3ab (202 MHz, $CDCl_3$)



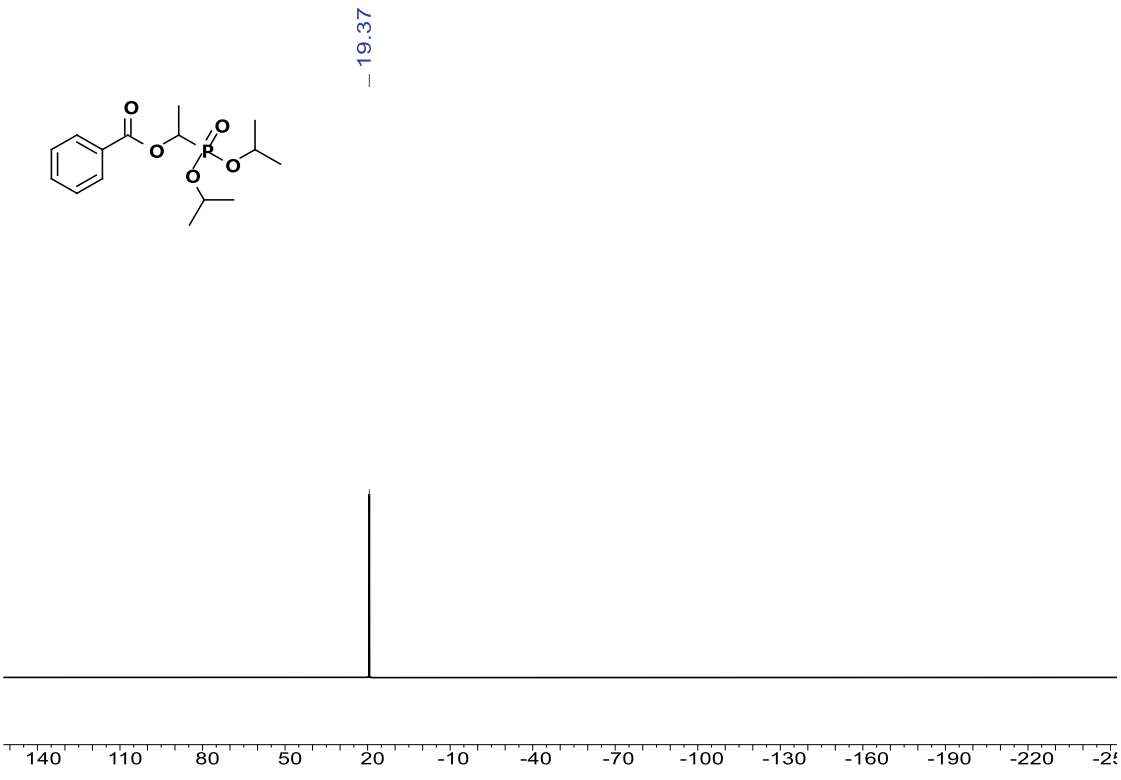
^{1}H NMR spectra of 3ac (500 MHz, $CDCl_3$)



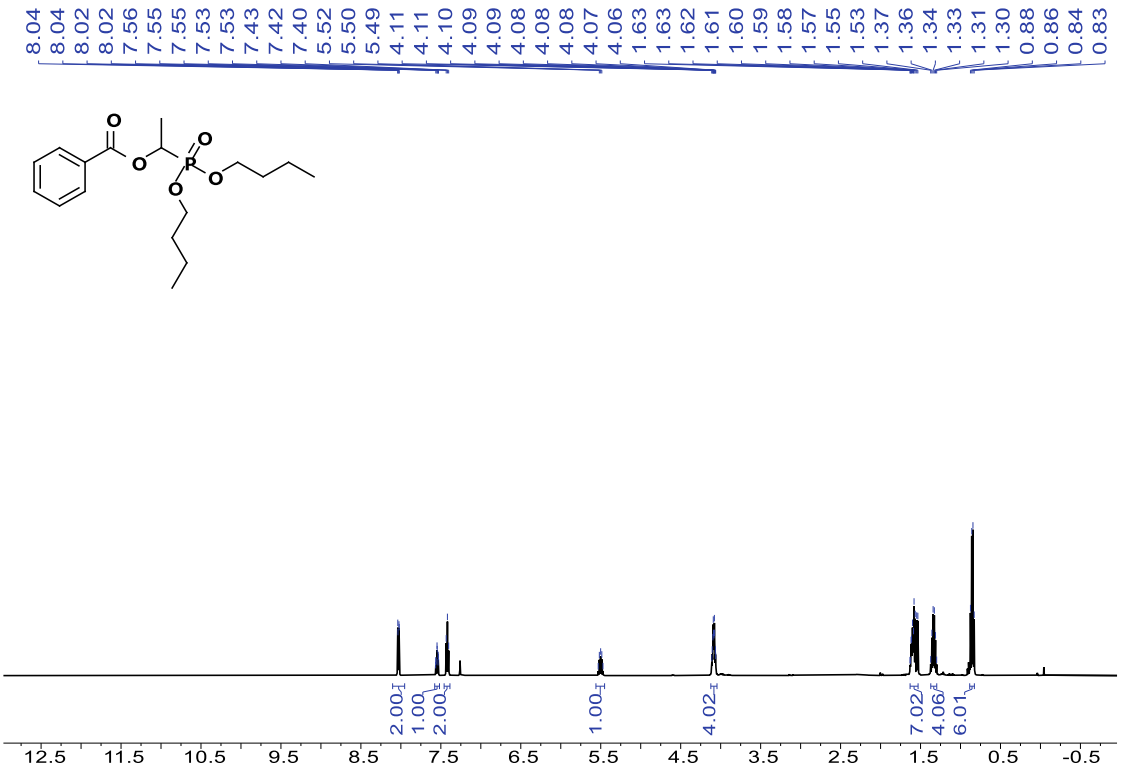
^{13}C NMR spectra of 3ac (126 MHz, $CDCl_3$)



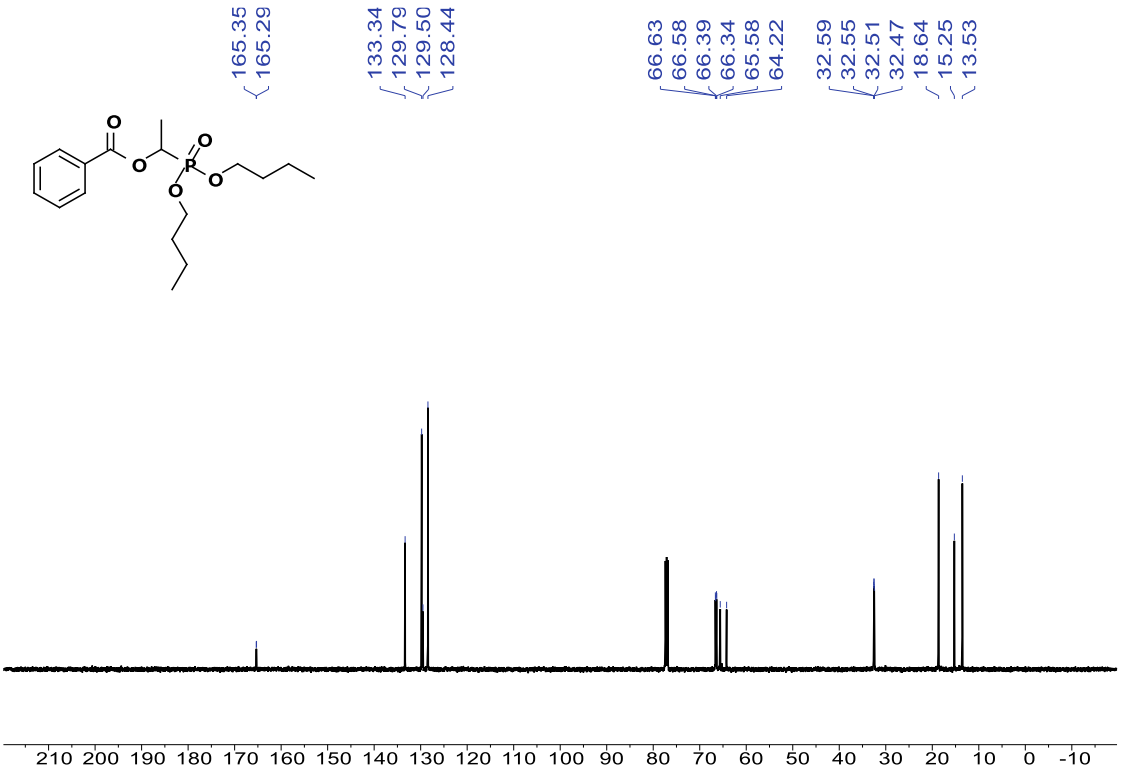
^{31}P NMR spectra of 3ac (202 MHz, $CDCl_3$)



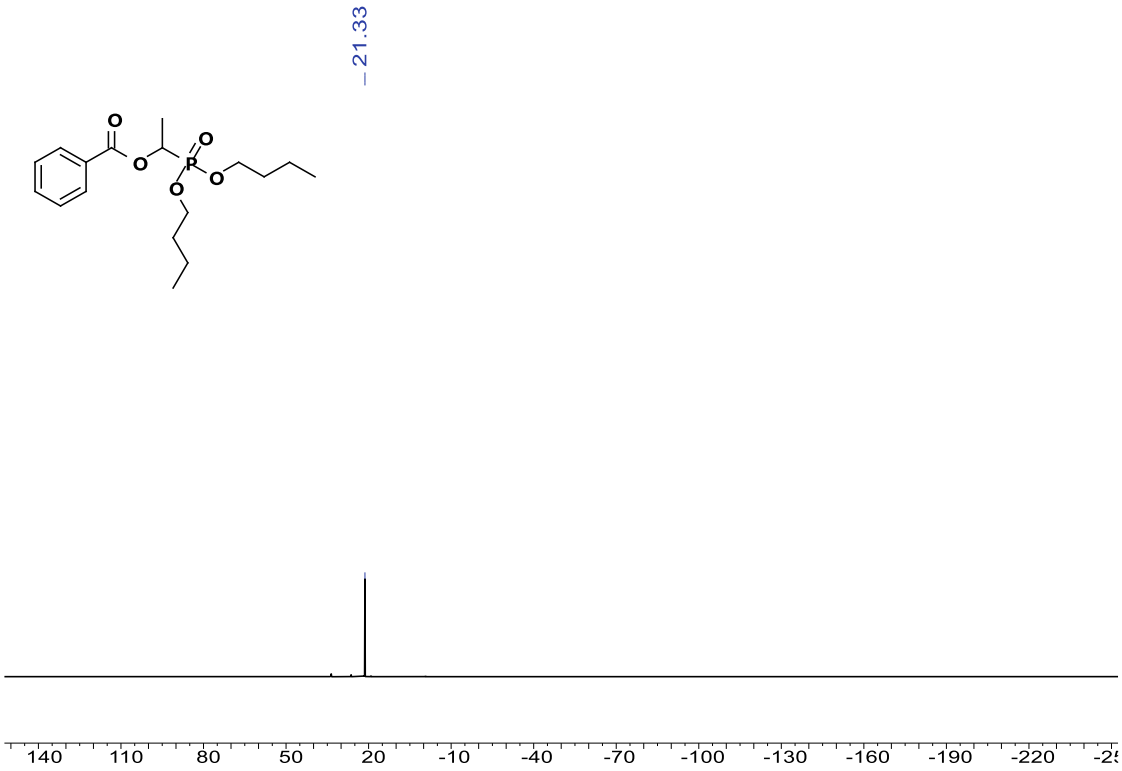
^{1}H NMR spectra of 3ad (500 MHz, $CDCl_3$)



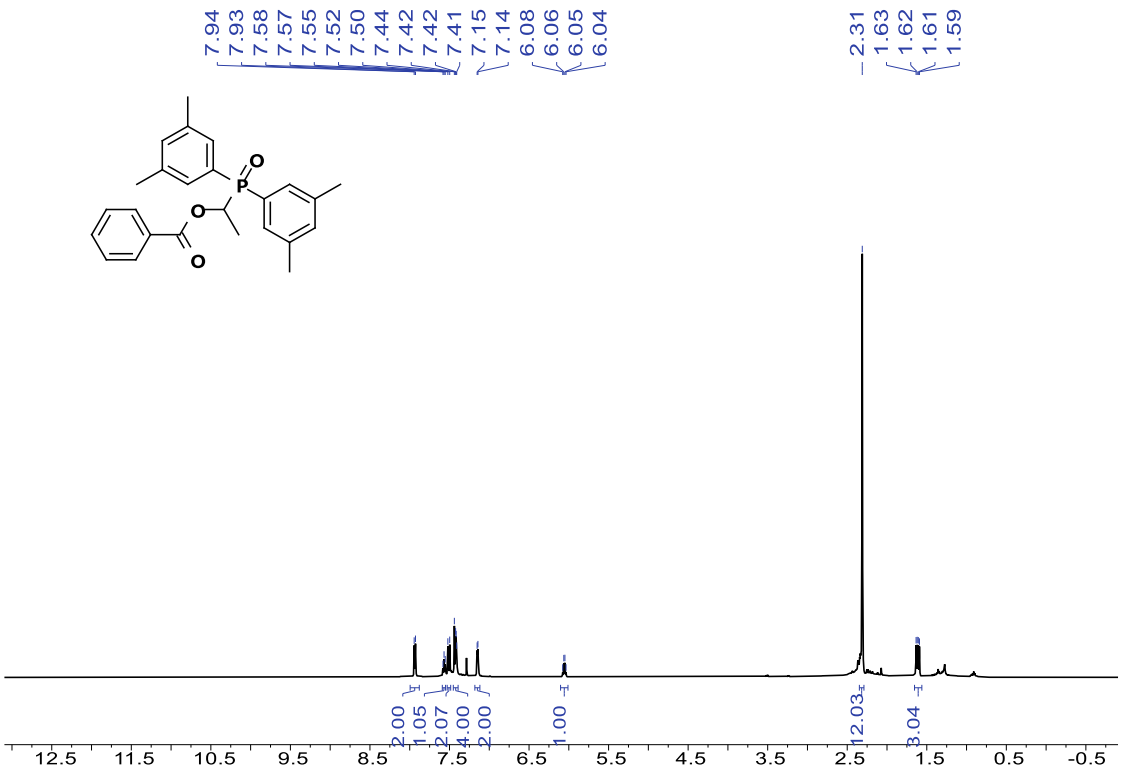
^{13}C NMR spectra of 3ad (126 MHz, $CDCl_3$)



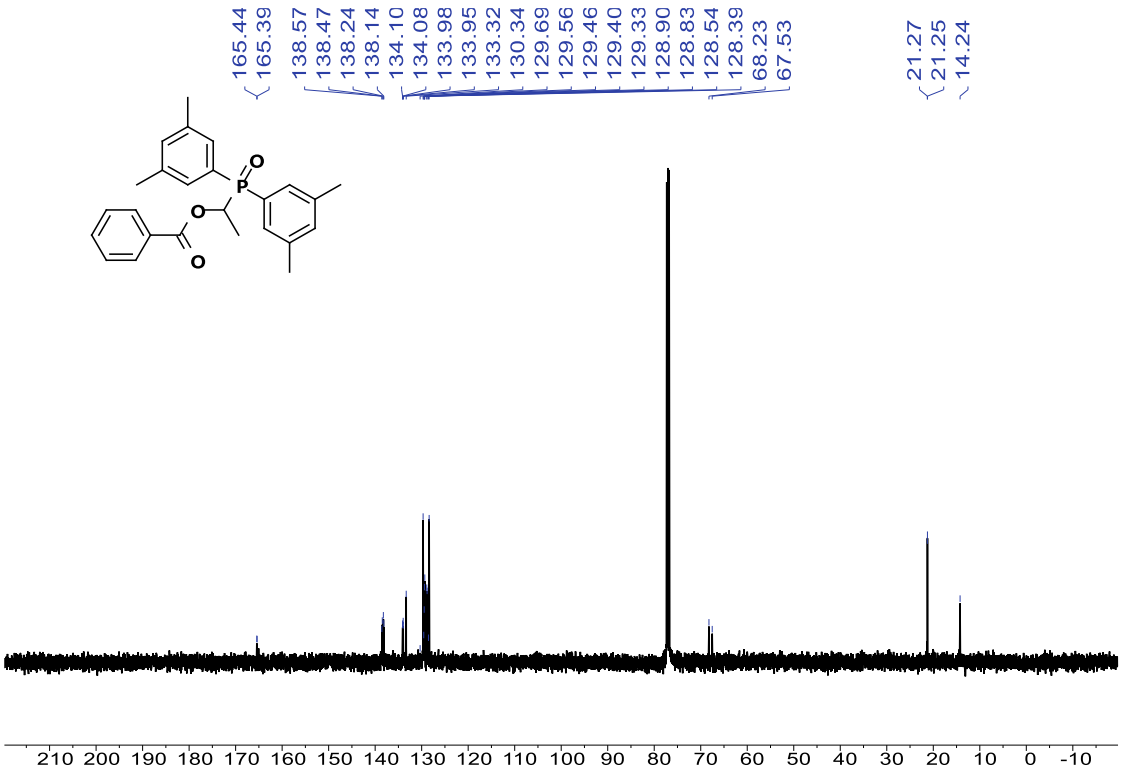
^{31}P NMR spectra of 3ad (202 MHz, $CDCl_3$)



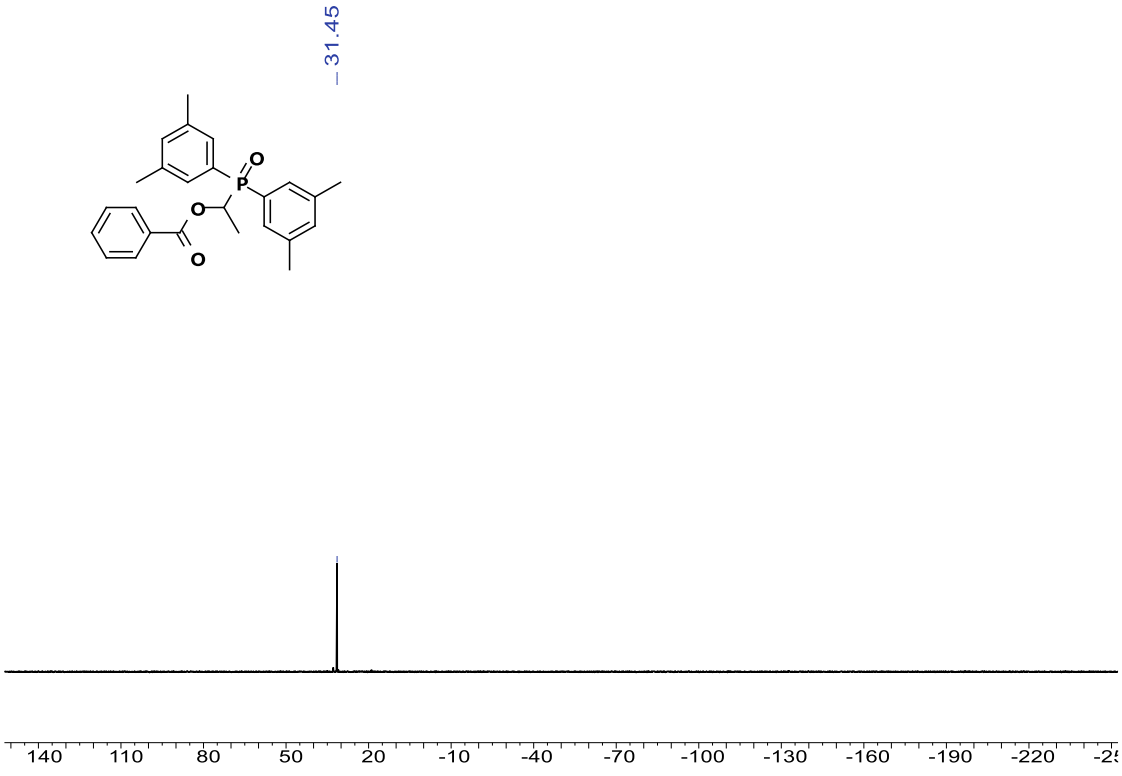
^{1}H NMR spectra of 3ae (500 MHz, $CDCl_3$)



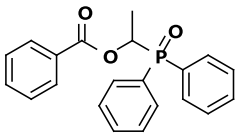
^{13}C NMR spectra of 3ae (126 MHz, $CDCl_3$)

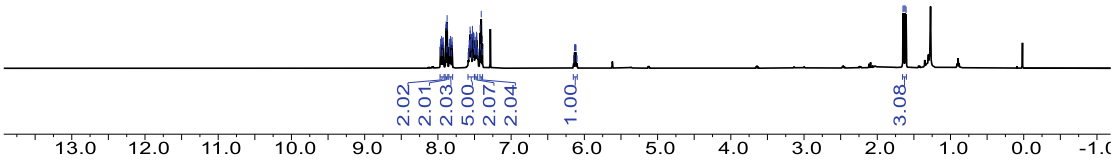


^{31}P NMR spectra of 3ae (202 MHz, $CDCl_3$)

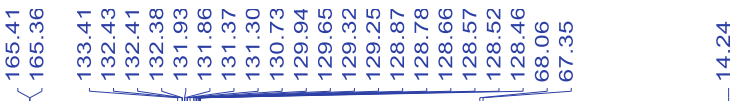


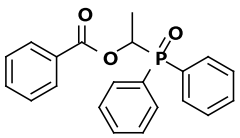
^{1}H NMR spectra of 3af (500 MHz, $CDCl_3$)

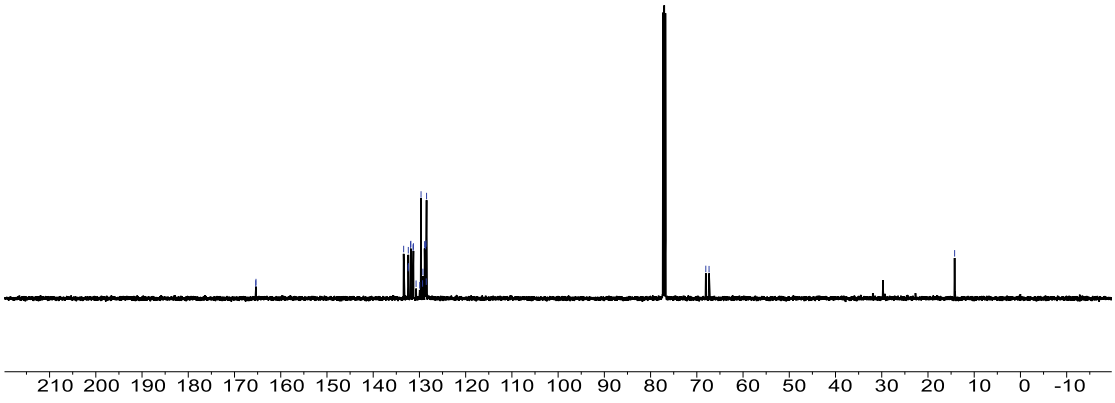




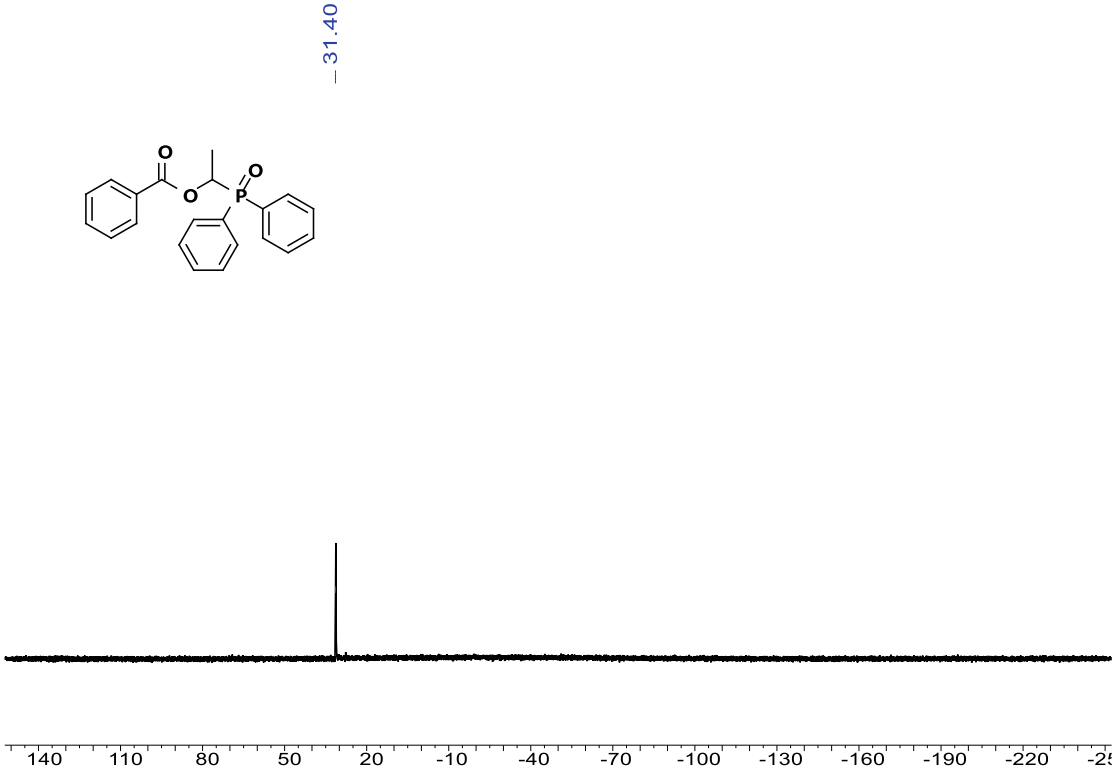
^{13}C NMR spectra of 3af (126 MHz, $CDCl_3$)



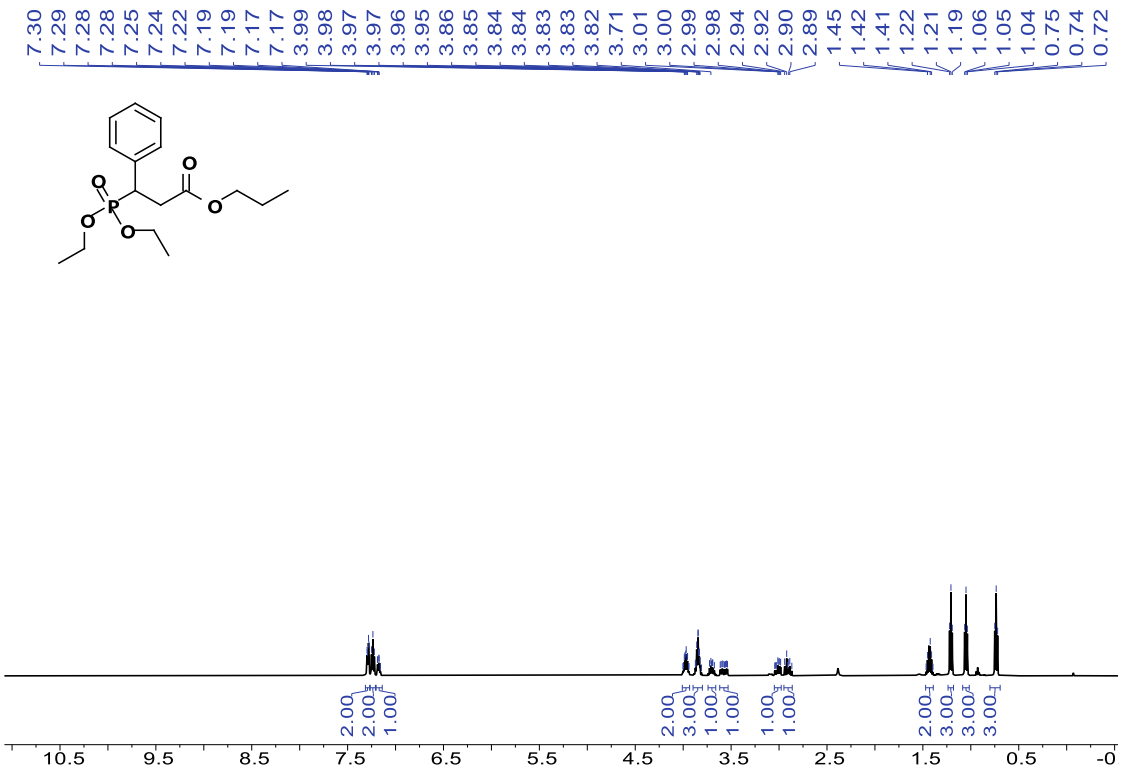




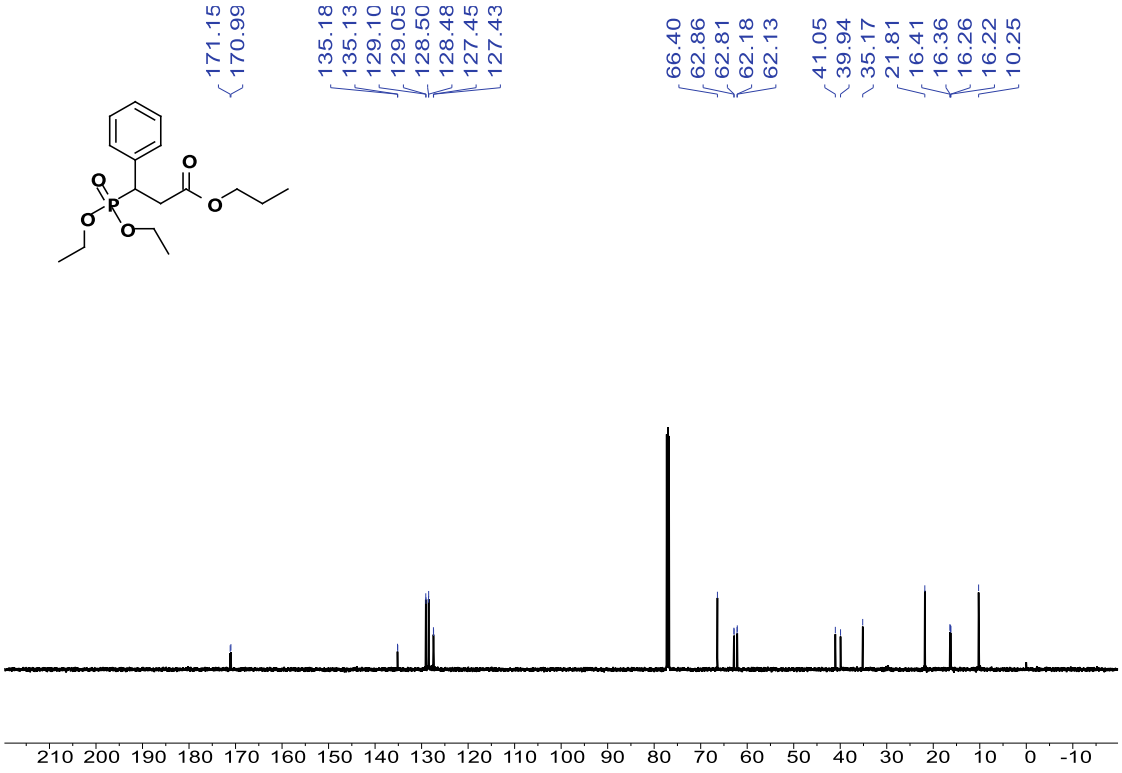
^{31}P NMR spectra of 3af (202 MHz, $CDCl_3$)



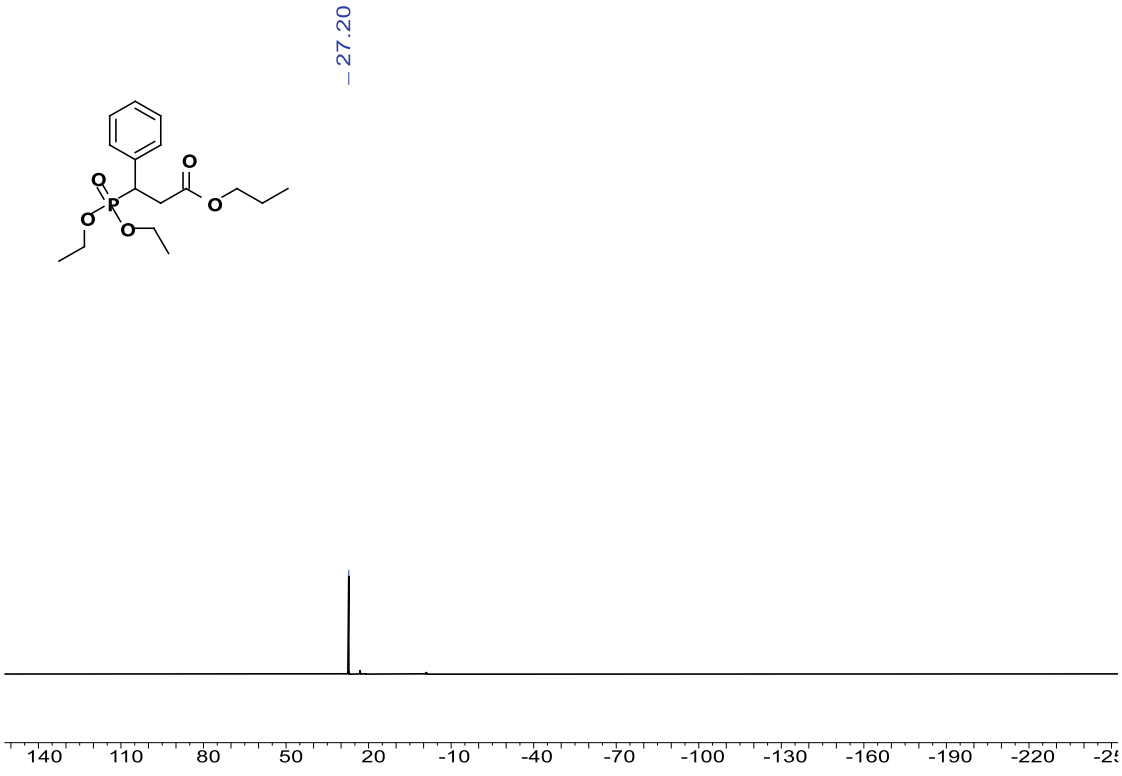
^{1}H NMR spectra of 3wa (500 MHz, $CDCl_3$)



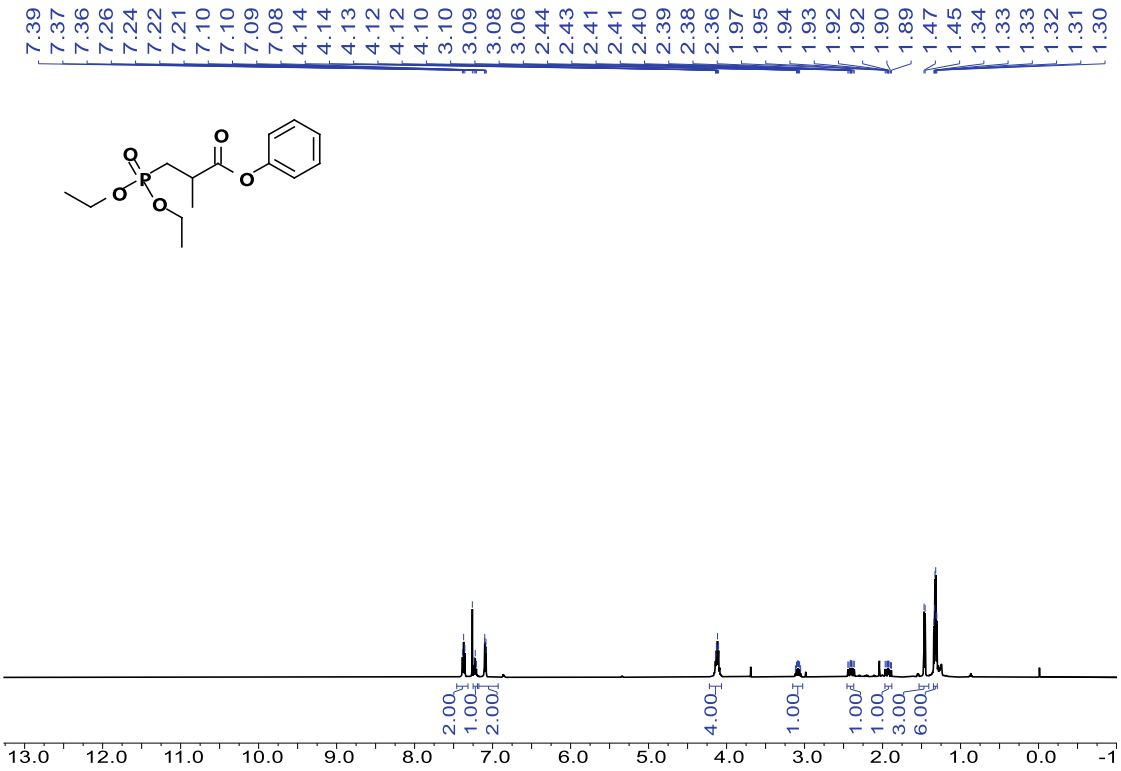
^{13}C NMR spectra of 3wa (126 MHz, $CDCl_3$)



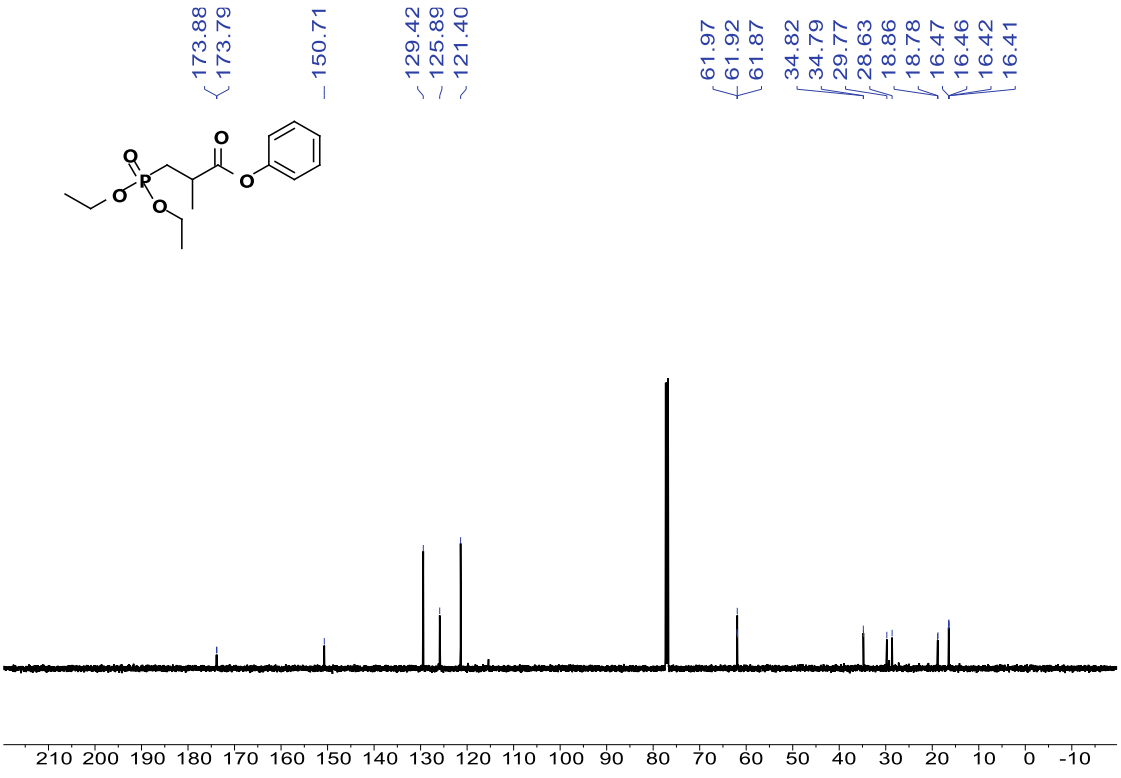
^{31}P NMR spectra of 3wa (202 MHz, $CDCl_3$)



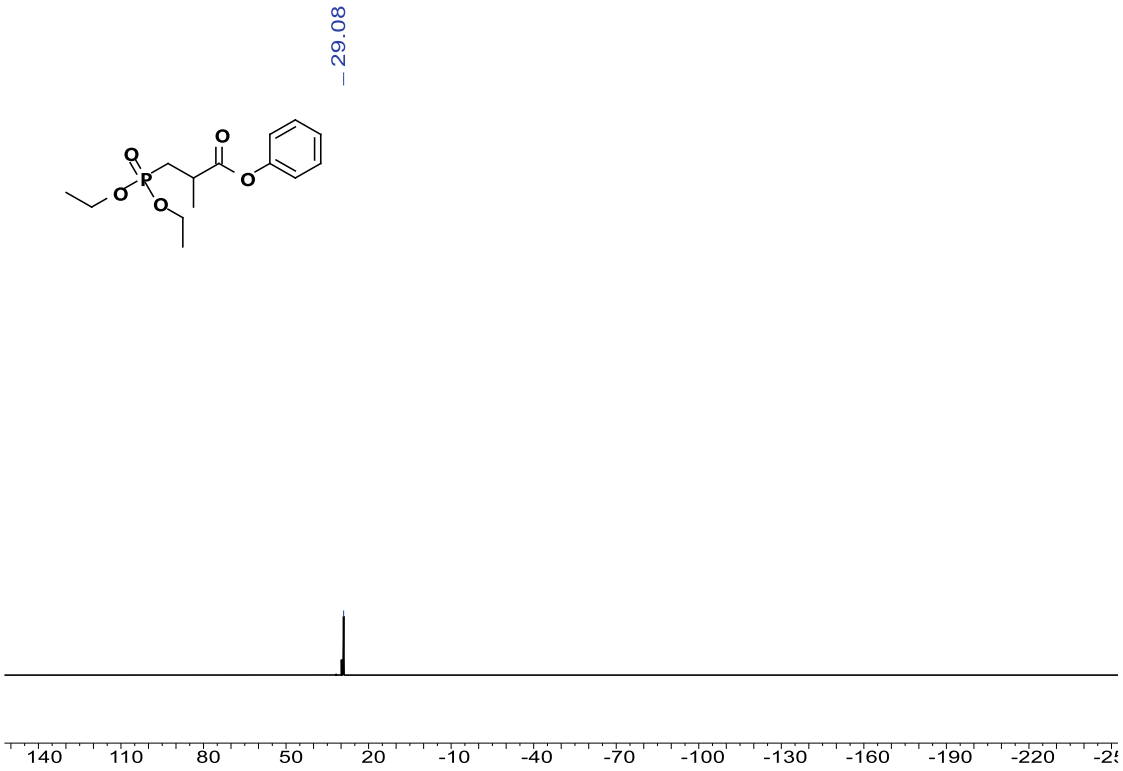
^{1}H NMR spectra of 3xa (500 MHz, $CDCl_3$)



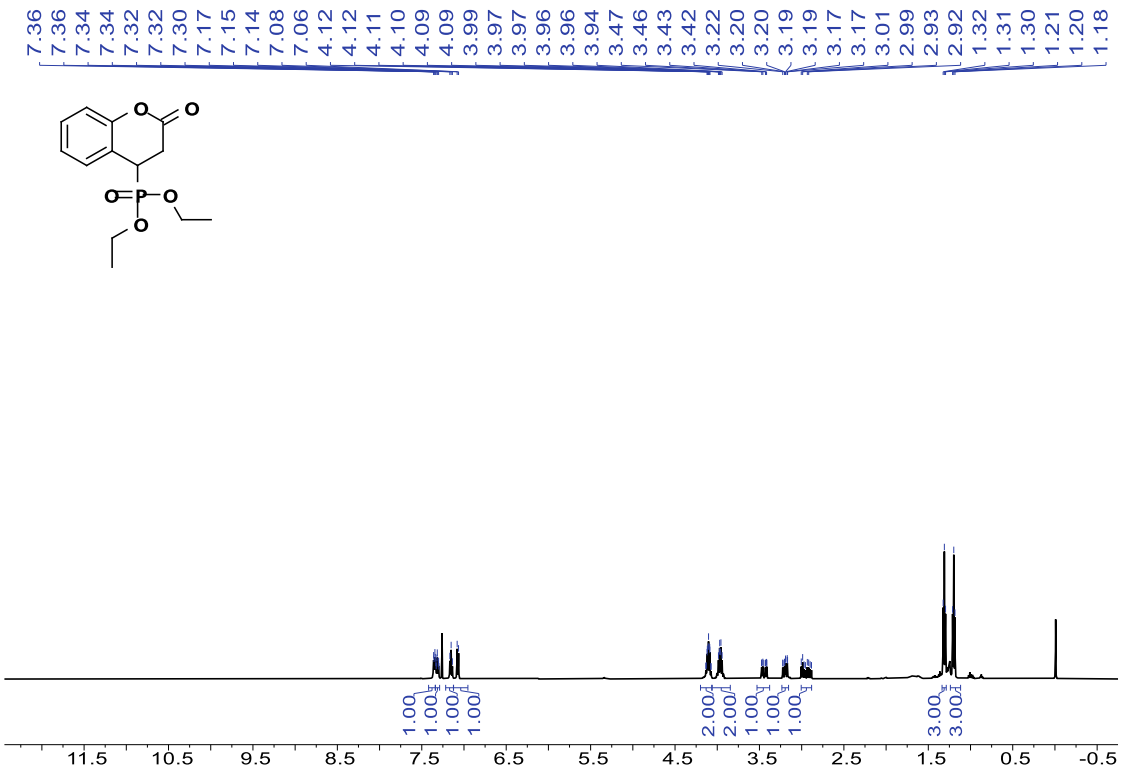
^{13}C NMR spectra of 3xa (126 MHz, $CDCl_3$)



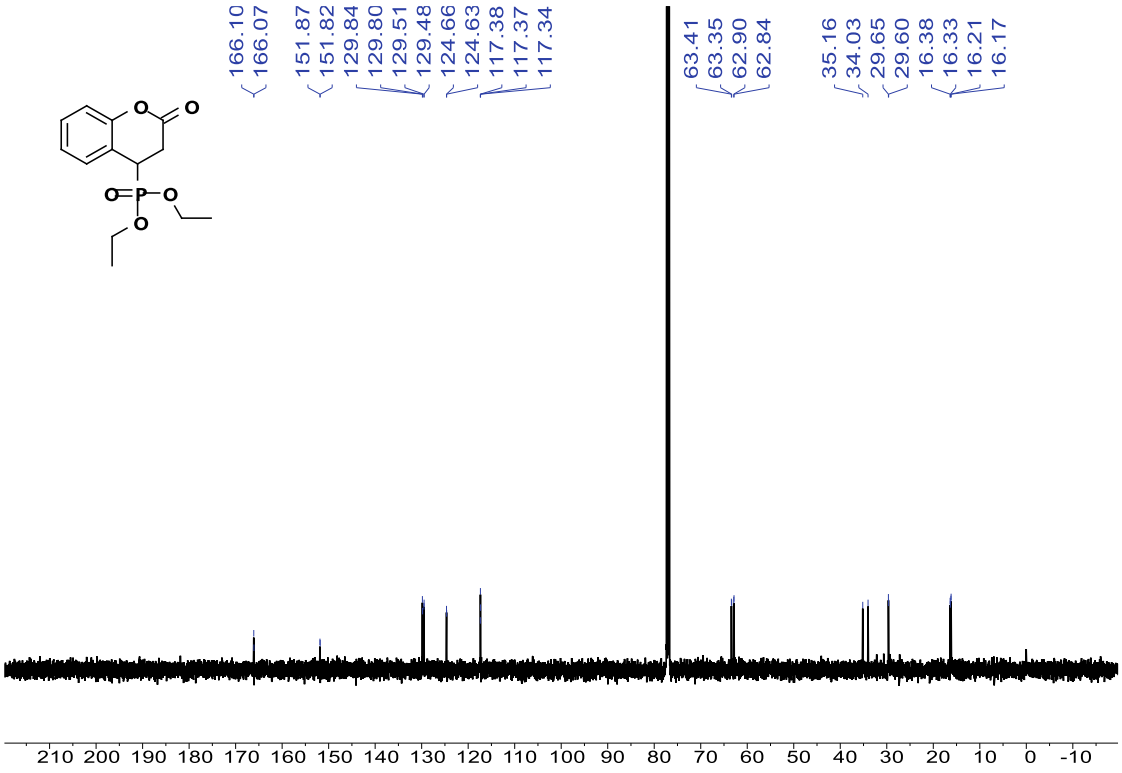
^{31}P NMR spectra of 3xa (202 MHz, $CDCl_3$)



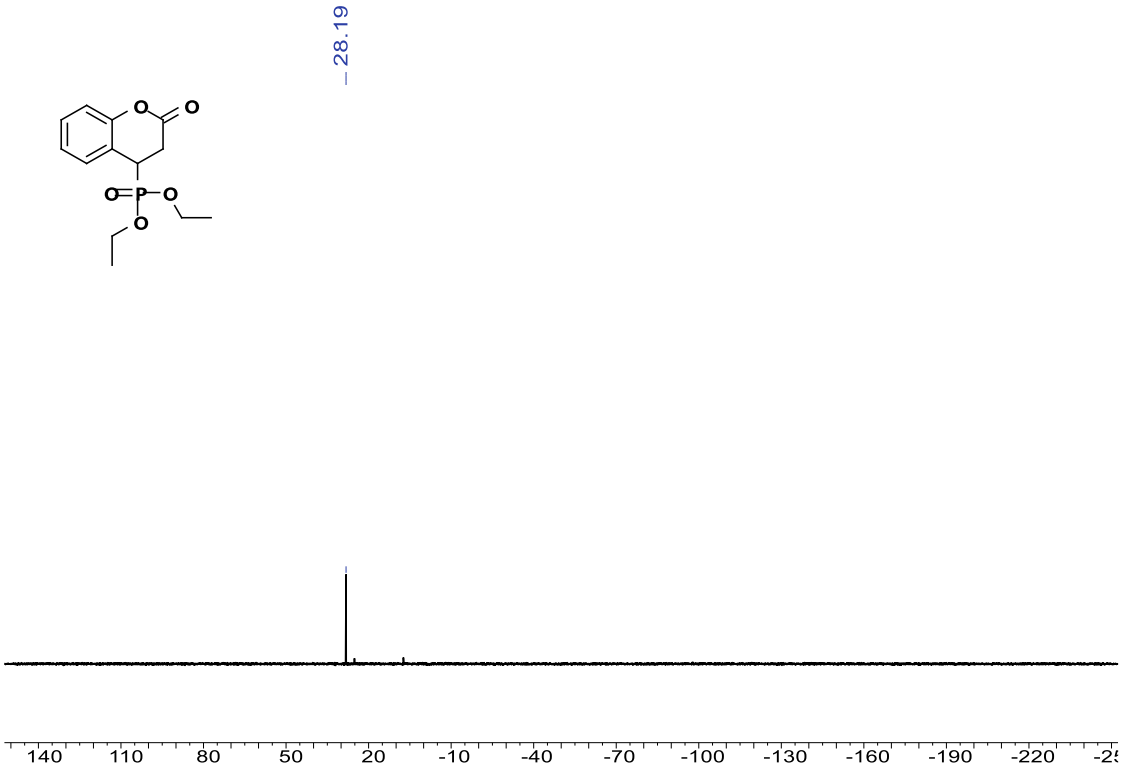
^{1}H NMR spectra of 3ya (500 MHz, $CDCl_3$)



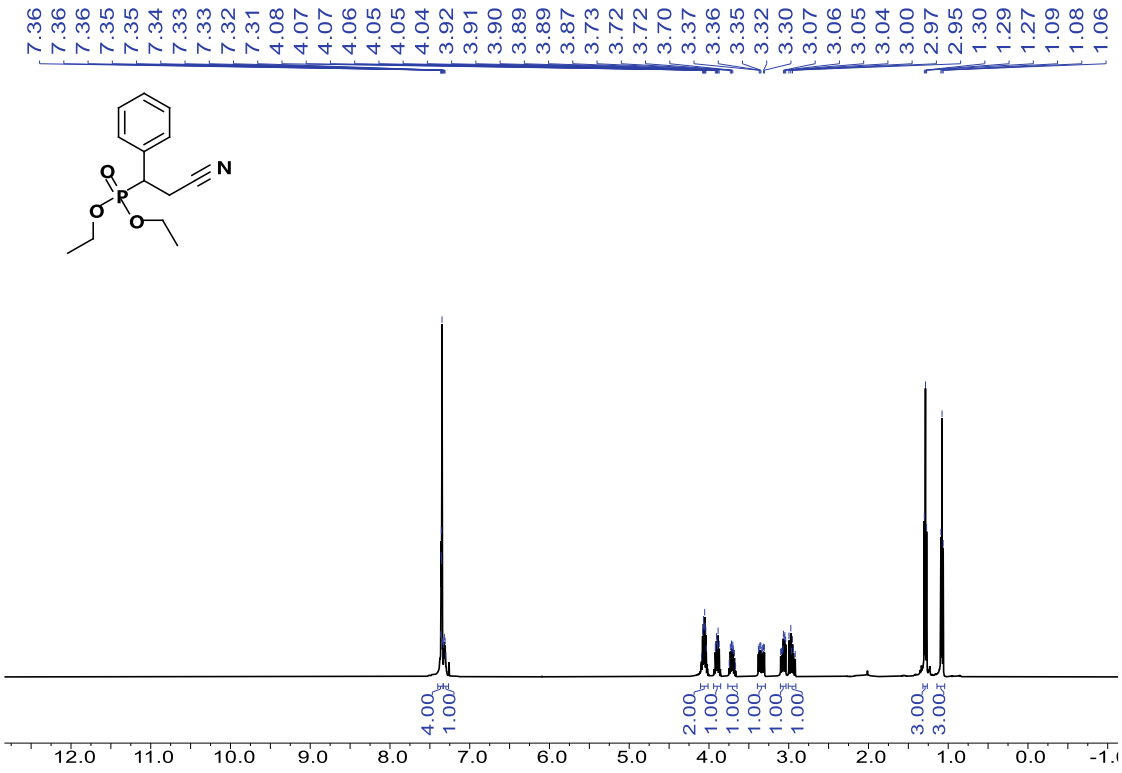
^{13}C NMR spectra of 3ya (126 MHz, $CDCl_3$)



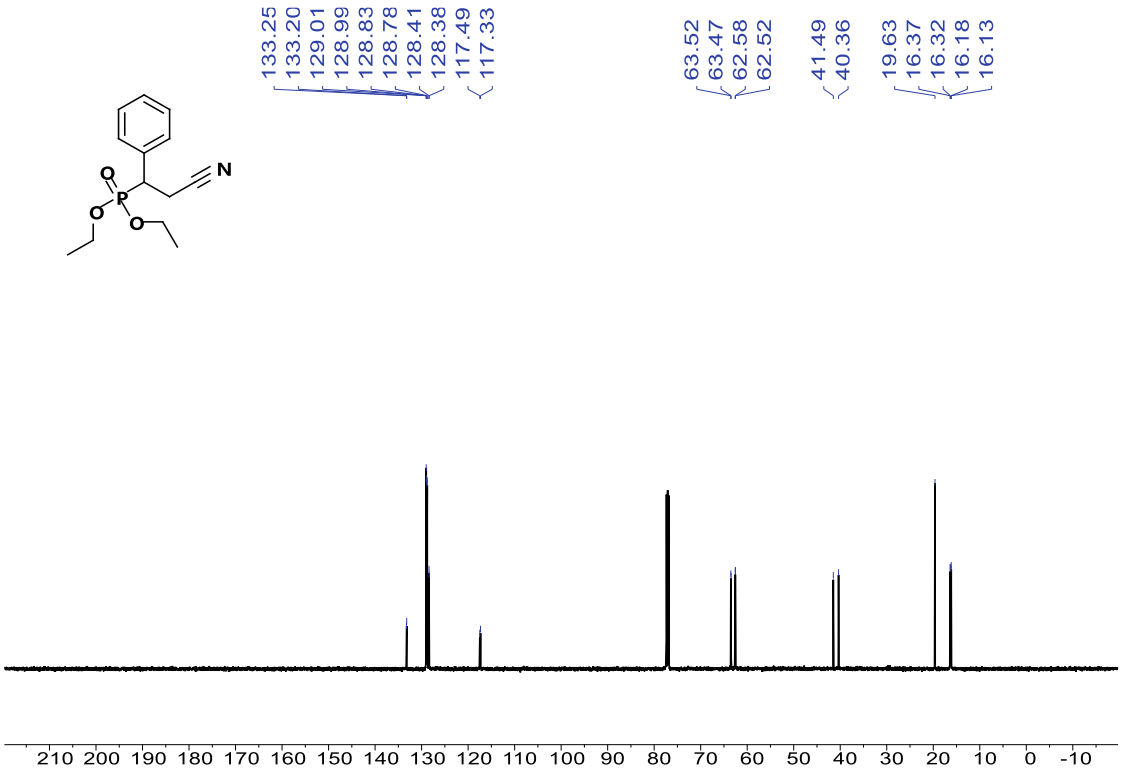
^{31}P NMR spectra of 3ya (202 MHz, $CDCl_3$)



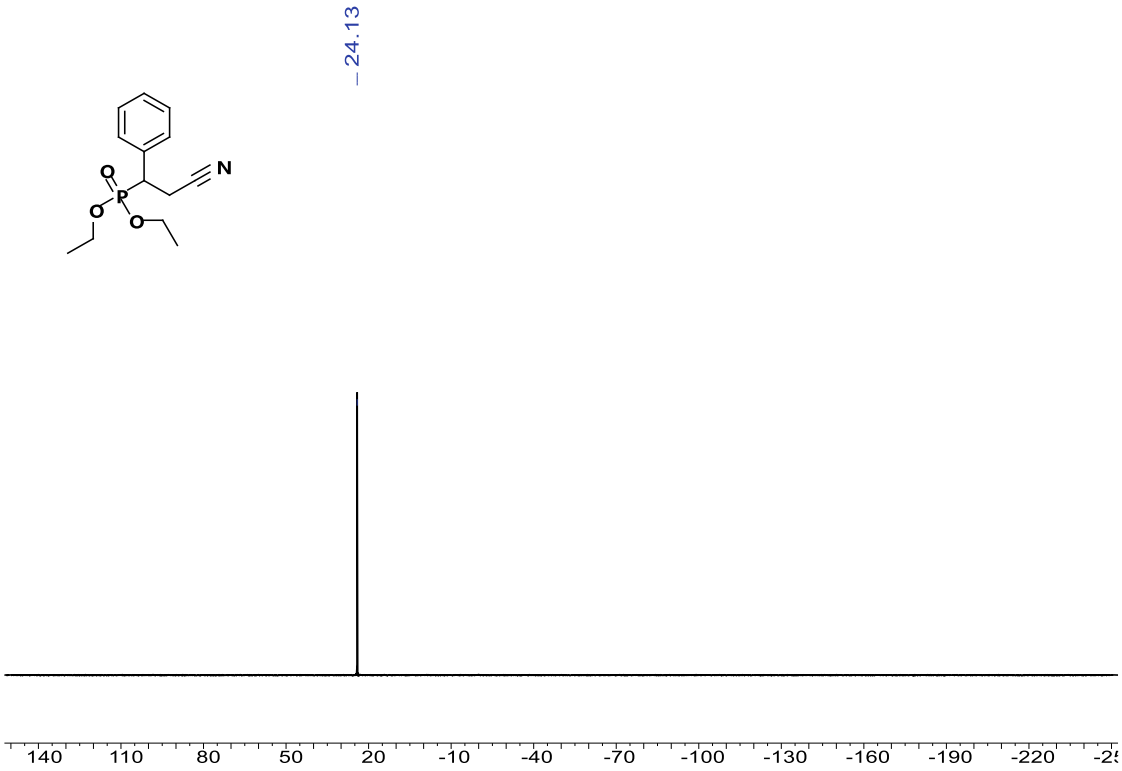
^{1}H NMR spectra of 3za (500 MHz, $CDCl_3$)



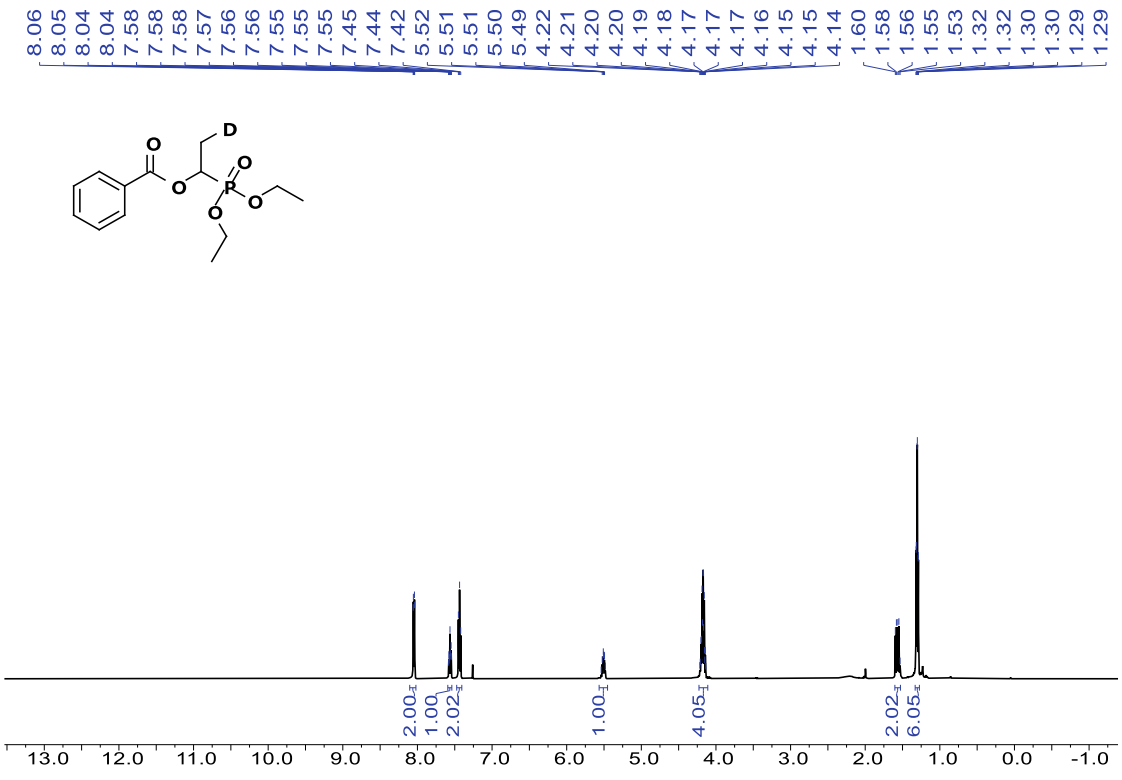
^{13}C NMR spectra of 3za (126 MHz, $CDCl_3$)



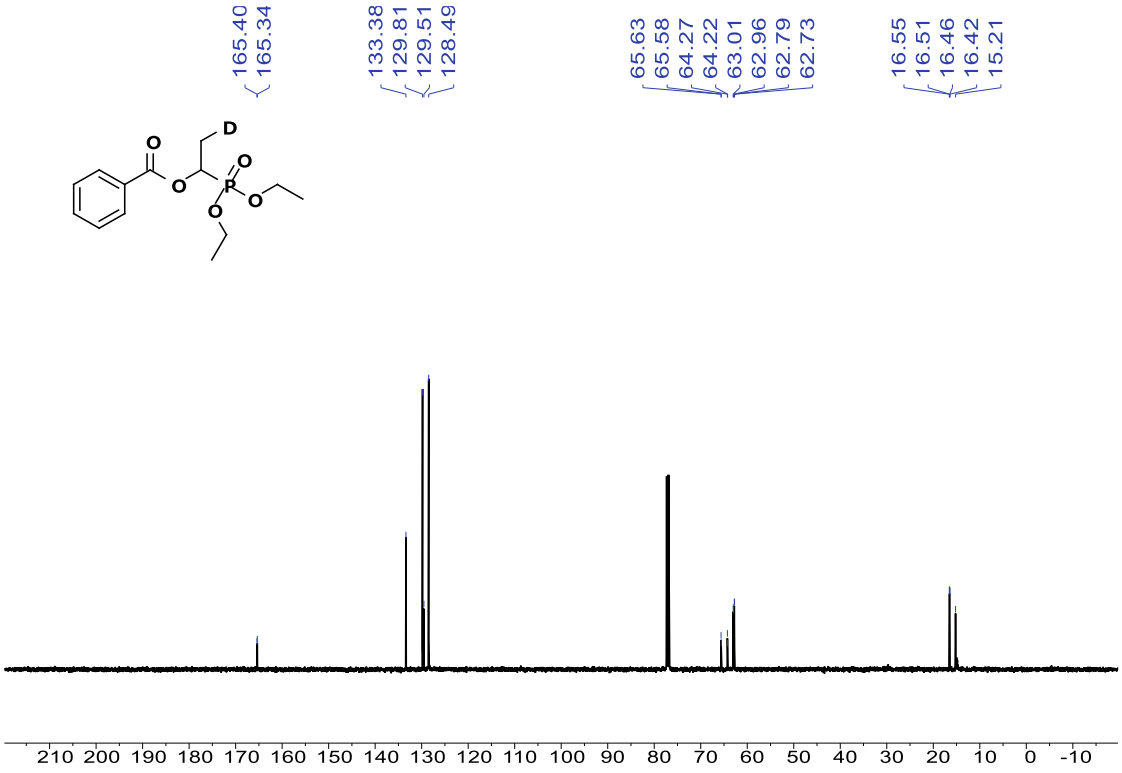
^{31}P NMR spectra of 3za (202 MHz, $CDCl_3$)



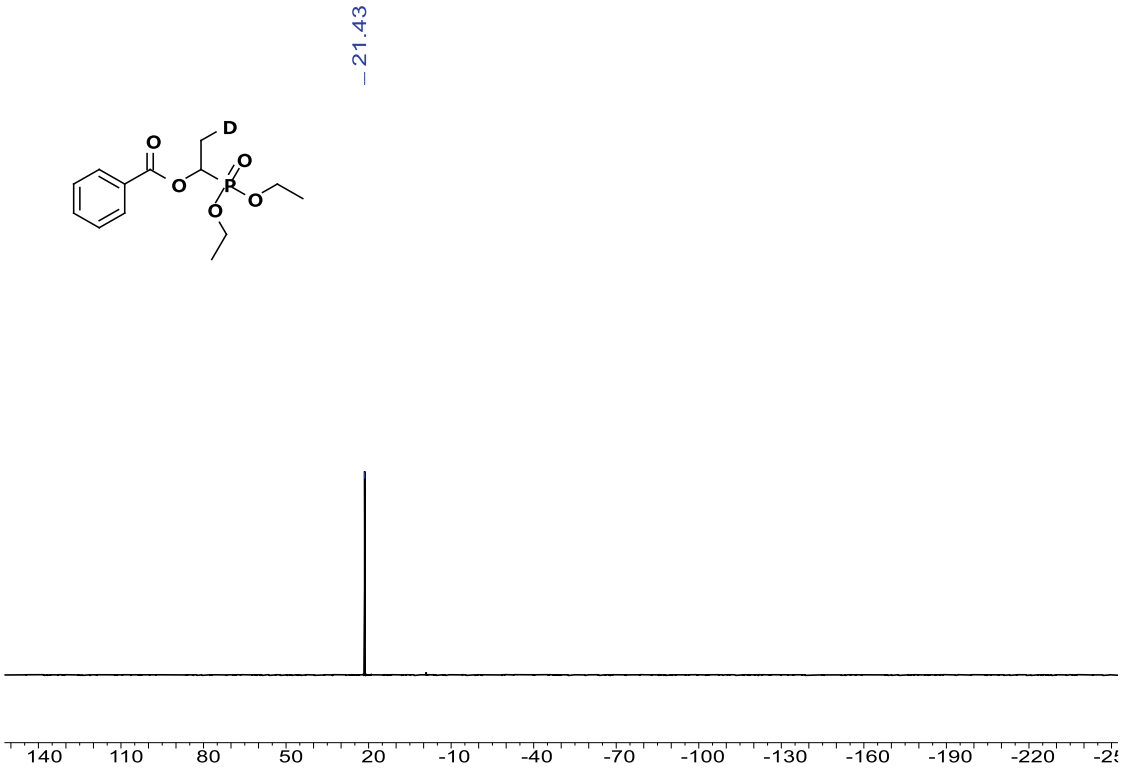
^{1}H NMR spectra of 5 (500 MHz, $CDCl_3$)



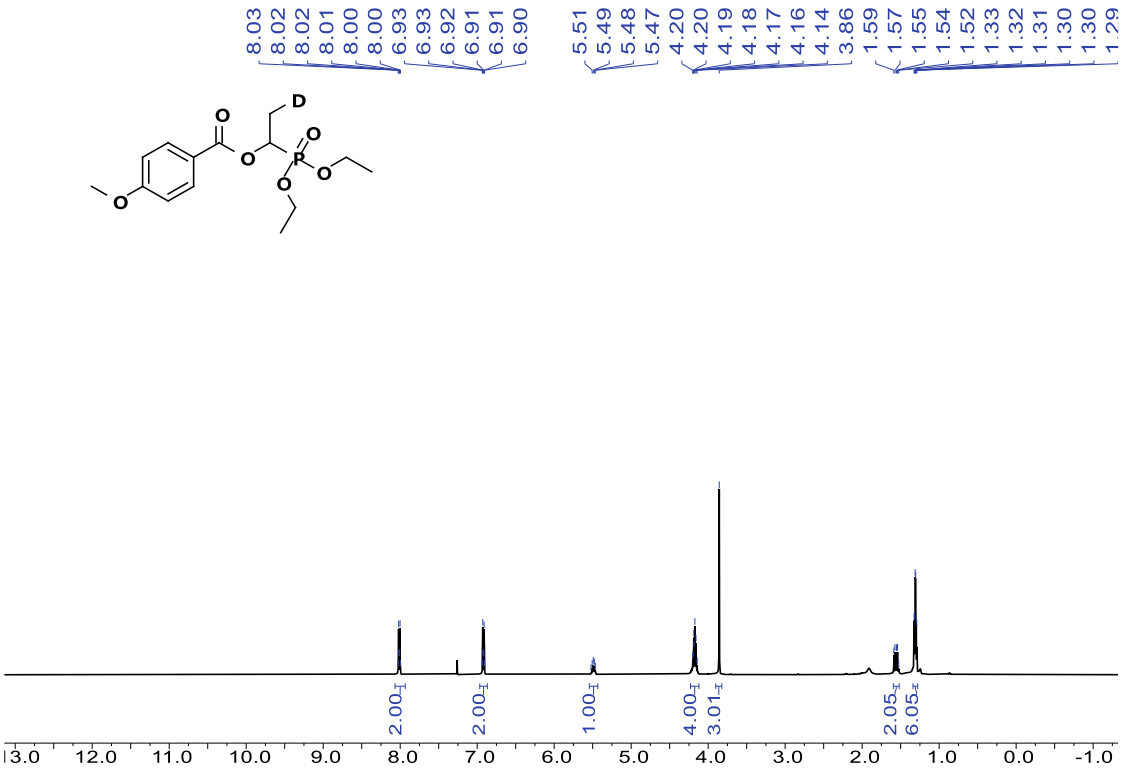
^{13}C NMR spectra of 5 (126 MHz, $CDCl_3$)



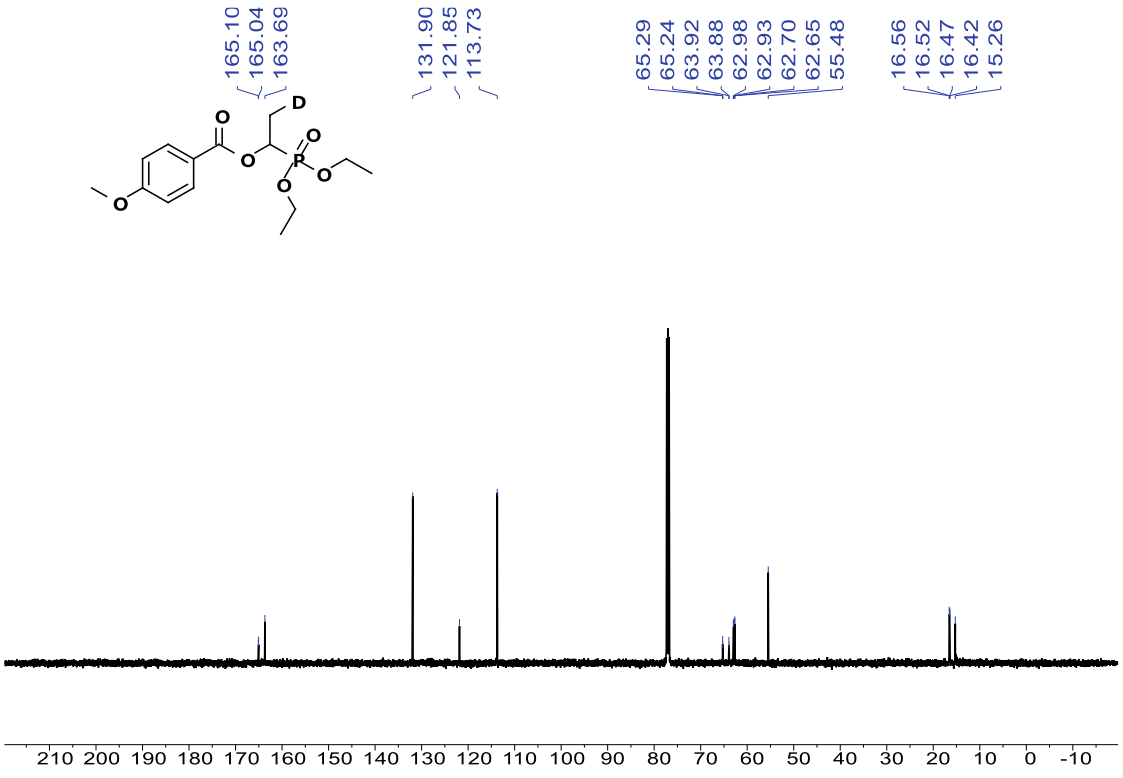
^{31}P NMR spectra of 5 (202 MHz, $CDCl_3$)



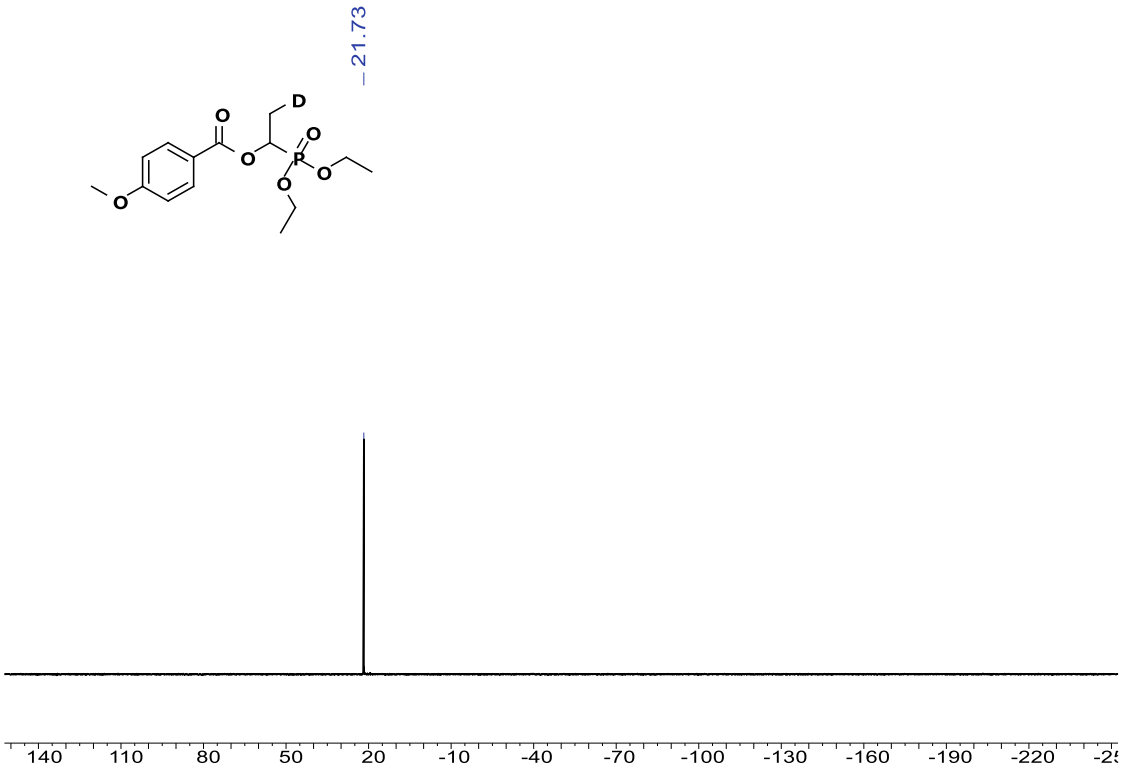
^{1}H NMR spectra of 6 (500 MHz, $CDCl_3$)



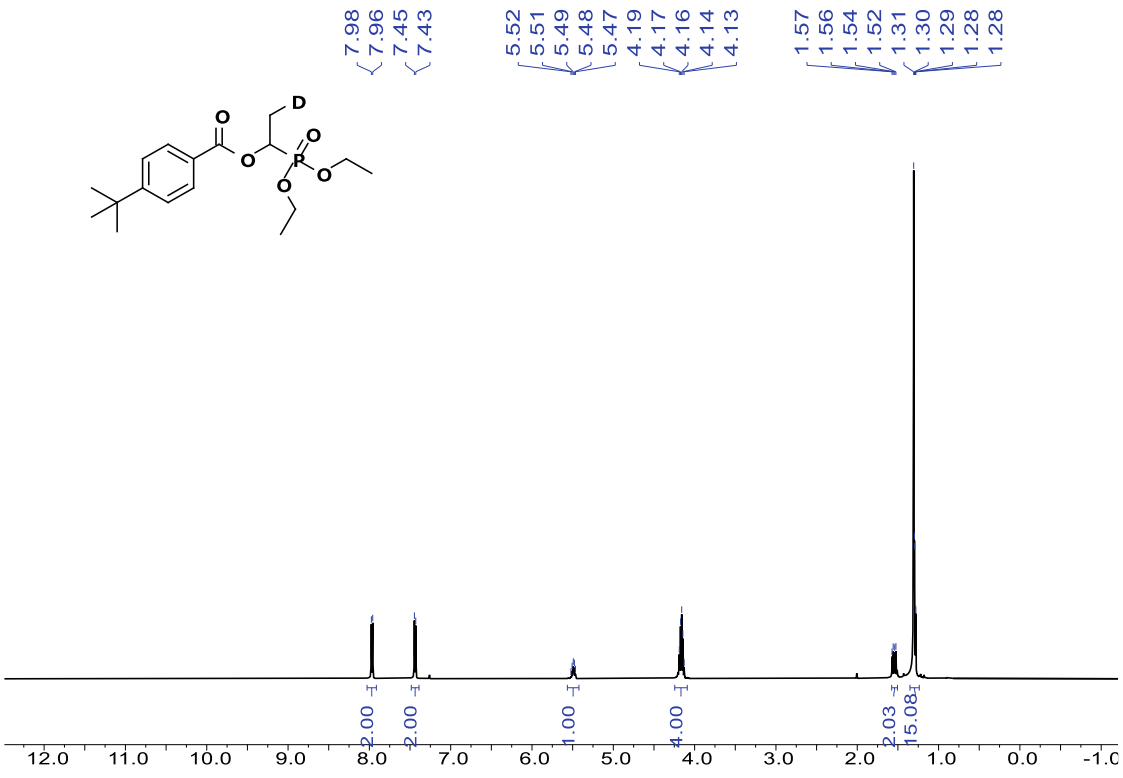
^{13}C NMR spectra of 6 (126 MHz, $CDCl_3$)



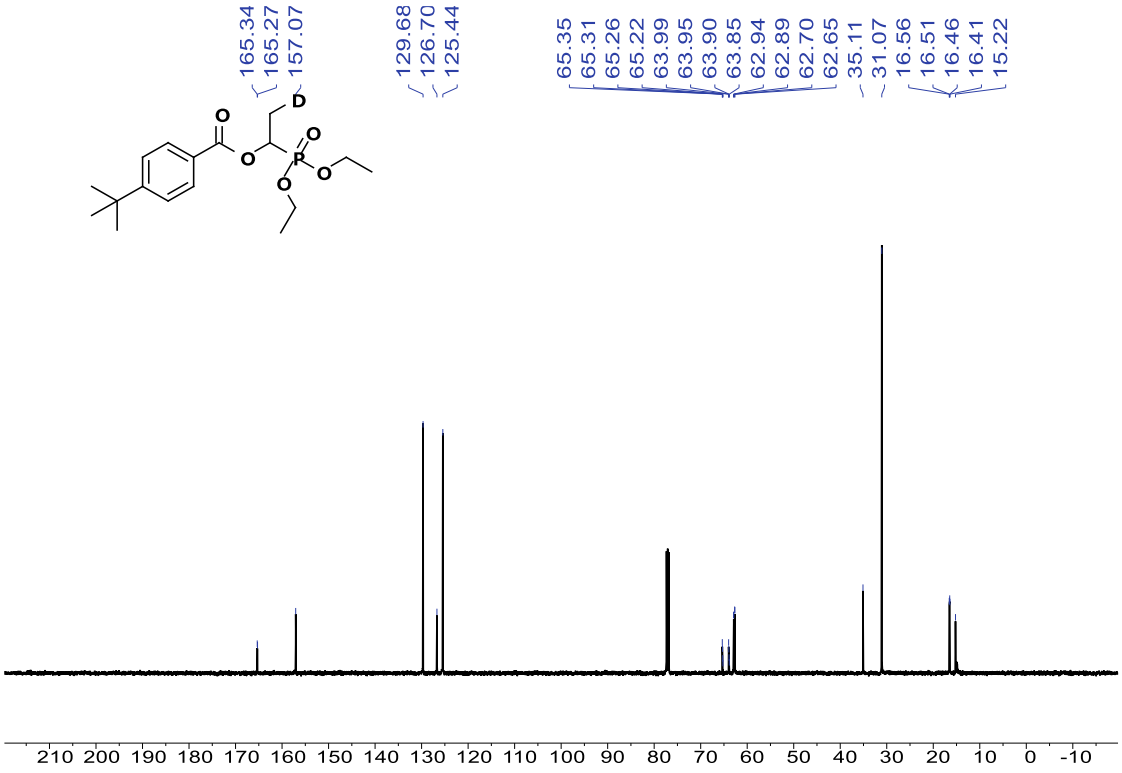
^{31}P NMR spectra of 6 (202 MHz, $CDCl_3$)



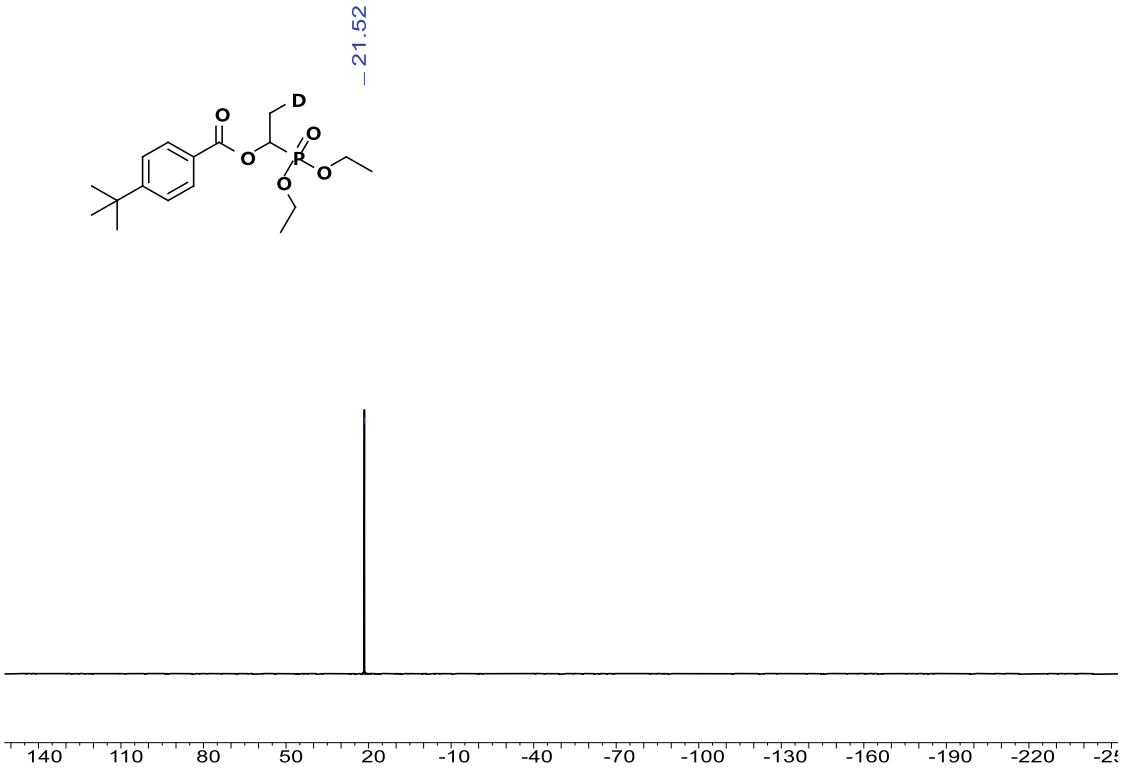
^{1}H NMR spectra of 7 (500 MHz, $CDCl_3$)



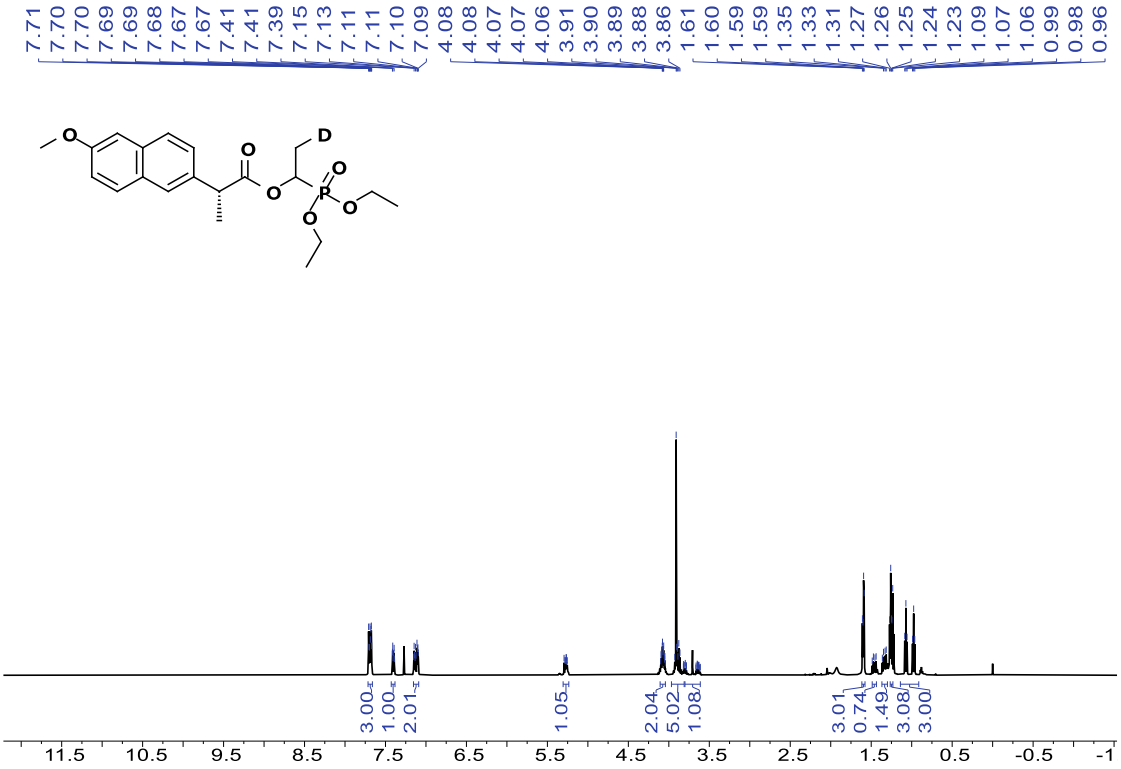
^{13}C NMR spectra of 7 (126 MHz, $CDCl_3$)



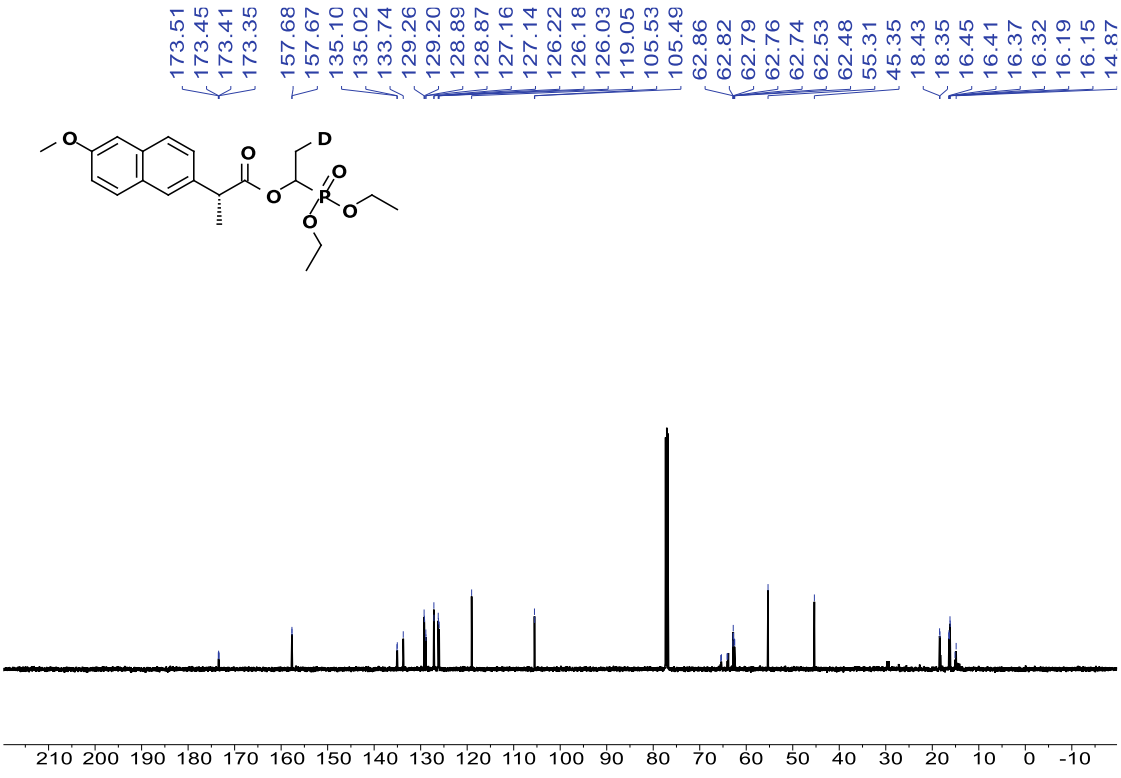
^{31}P NMR spectra of 7 (202 MHz, $CDCl_3$)



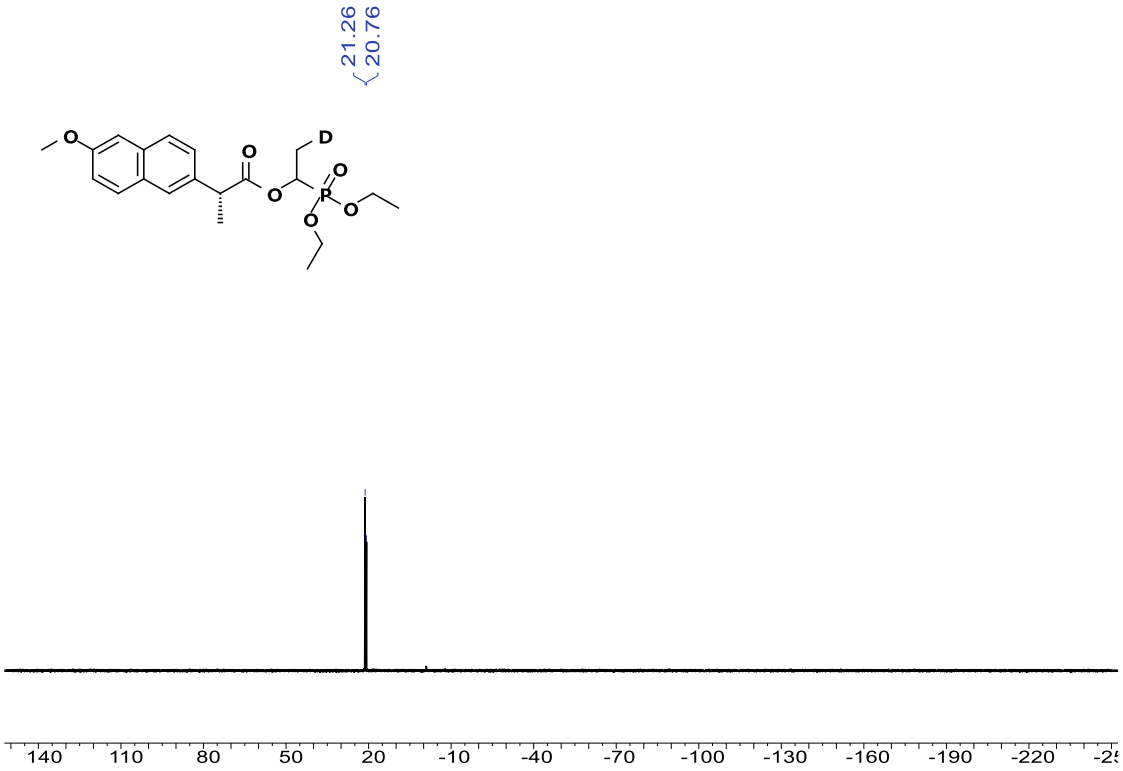
^{1}H NMR spectra of 8 (500 MHz, $CDCl_3$)



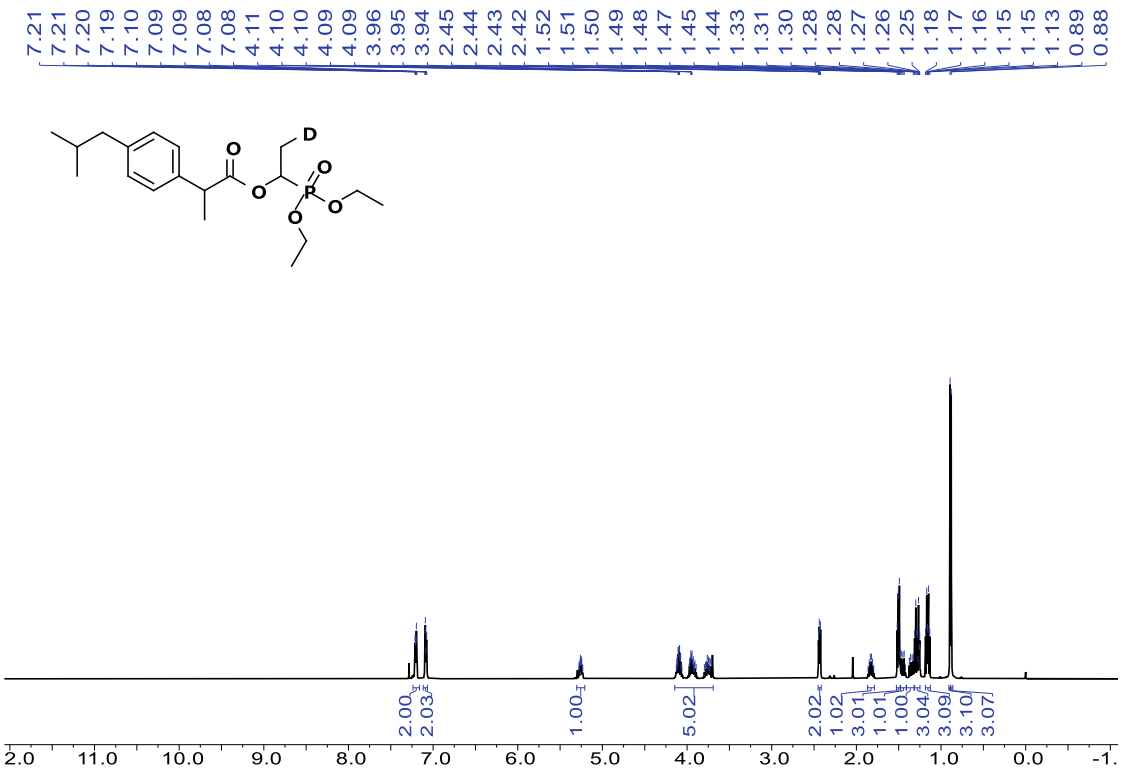
^{13}C NMR spectra of 8 (126 MHz, $CDCl_3$)



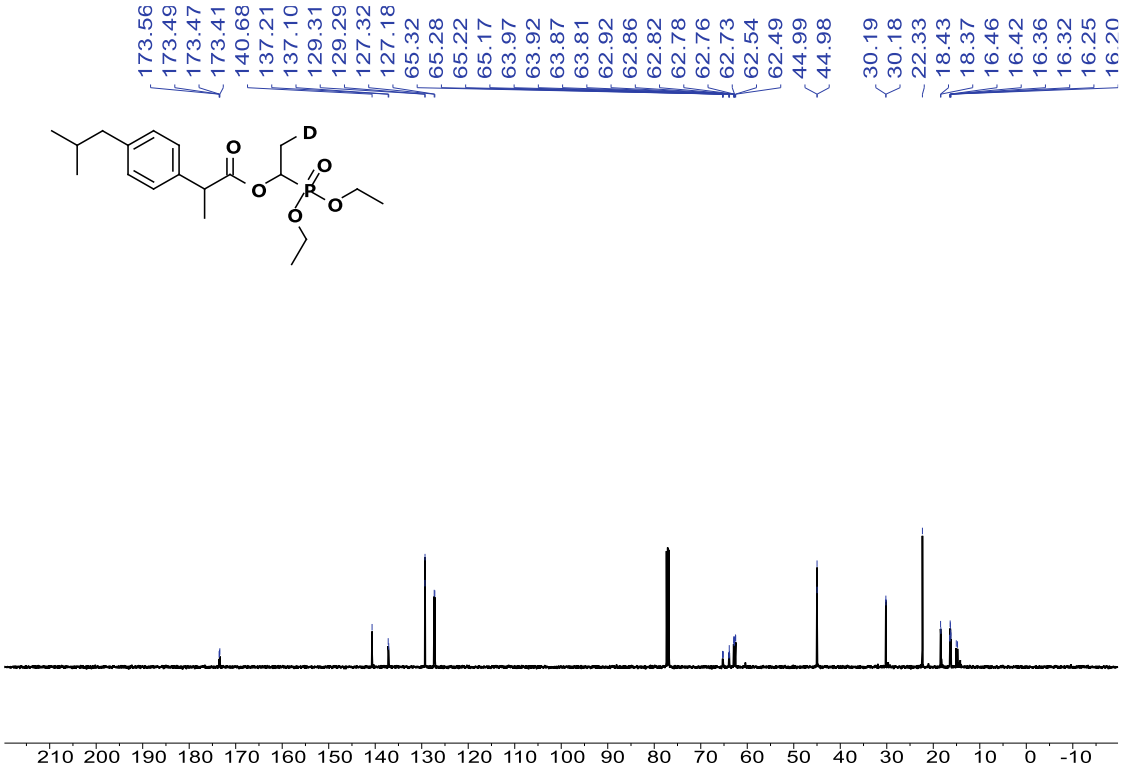
^{31}P NMR spectra of 8 (202 MHz, $CDCl_3$)



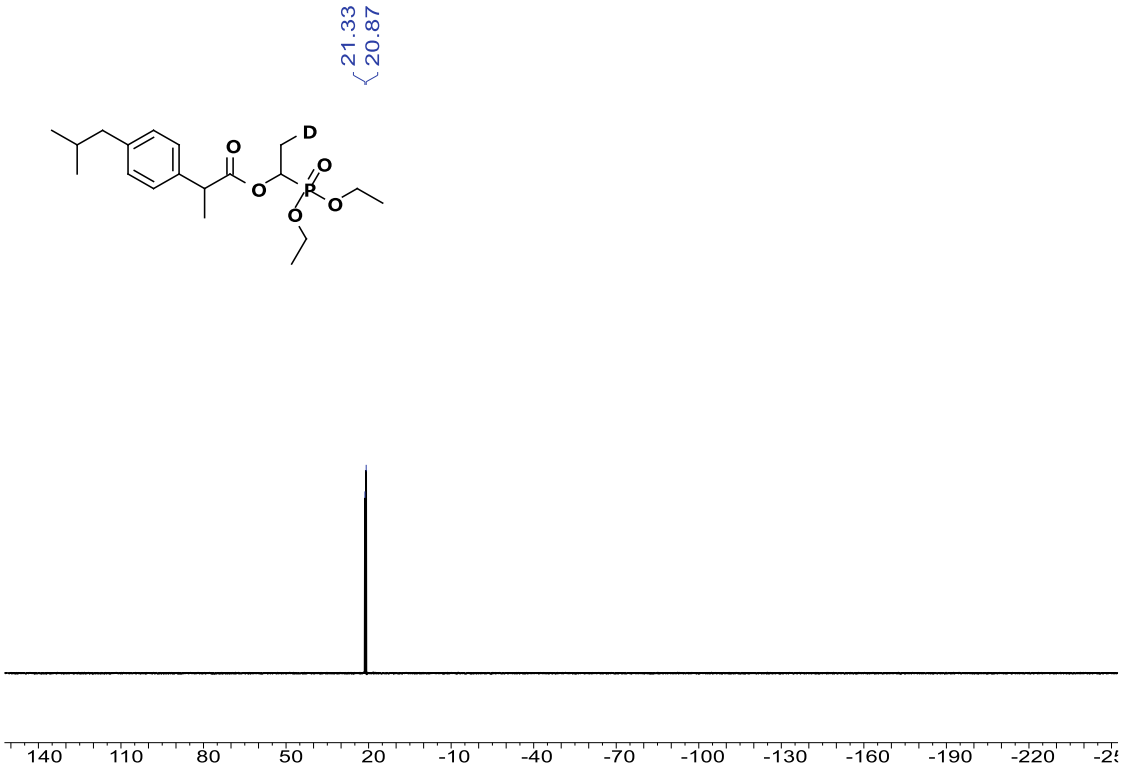
^{1}H NMR spectra of 9 (500 MHz, $CDCl_3$)



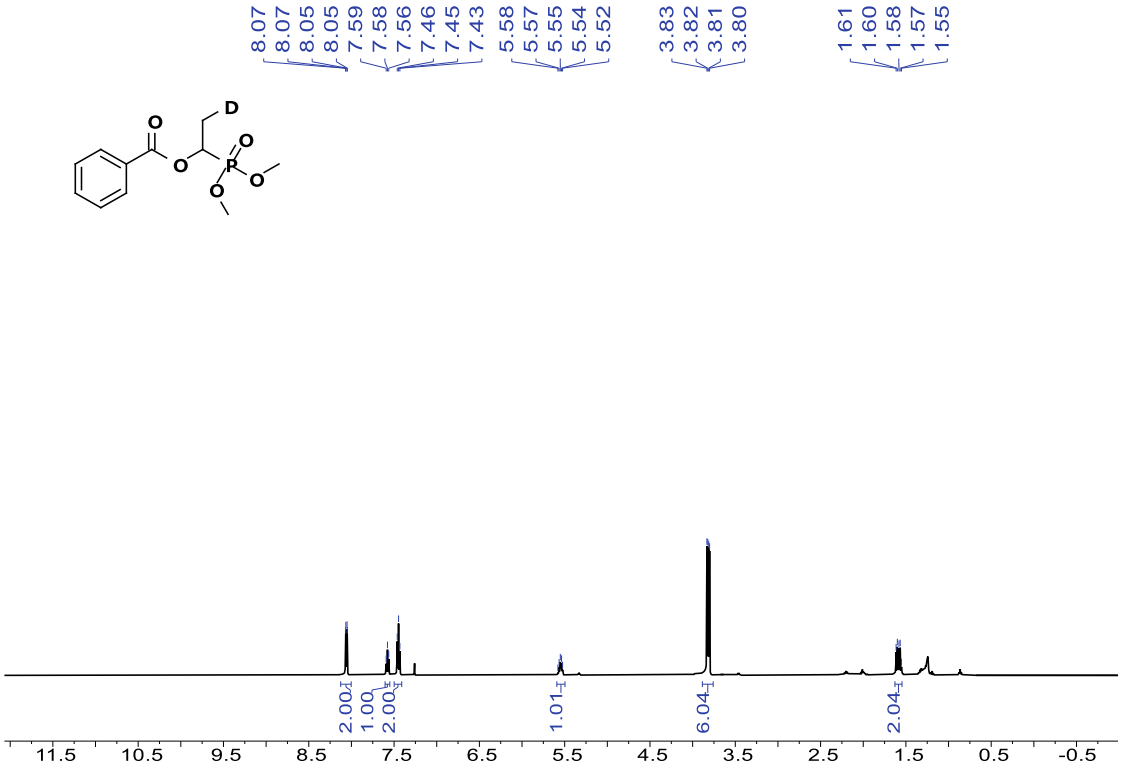
^{13}C NMR spectra of 9 (126 MHz, $CDCl_3$)



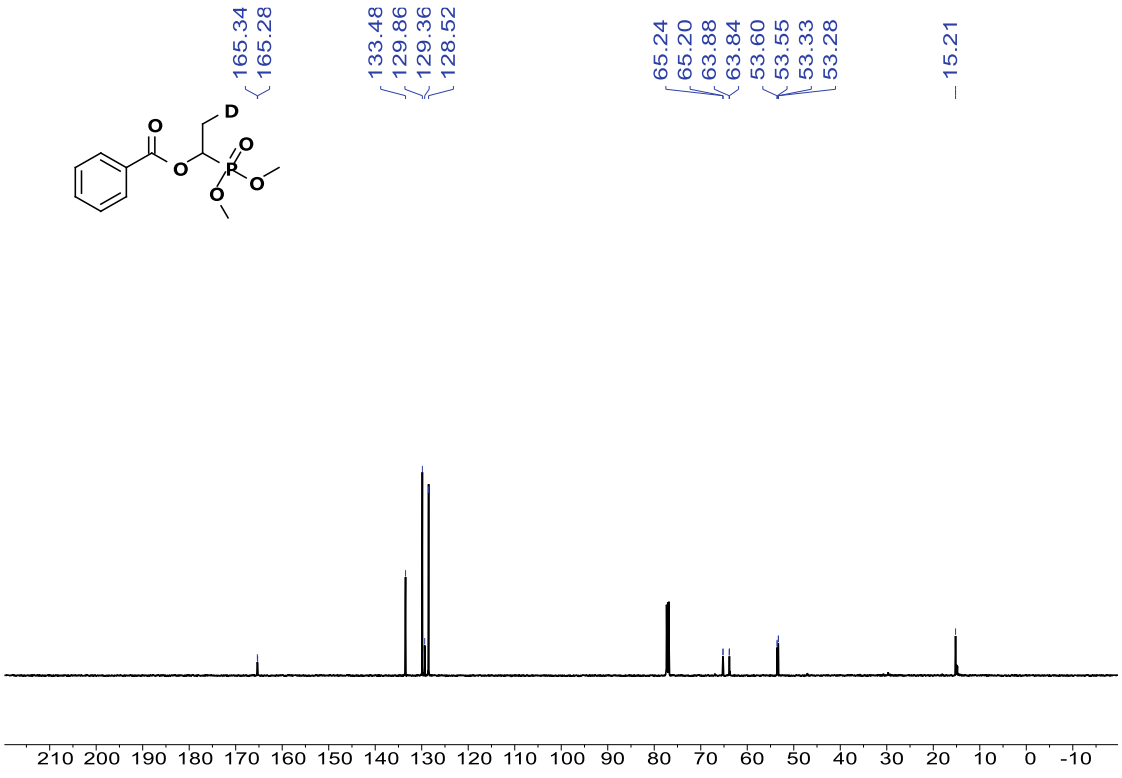
^{31}P NMR spectra of 9 (202 MHz, $CDCl_3$)



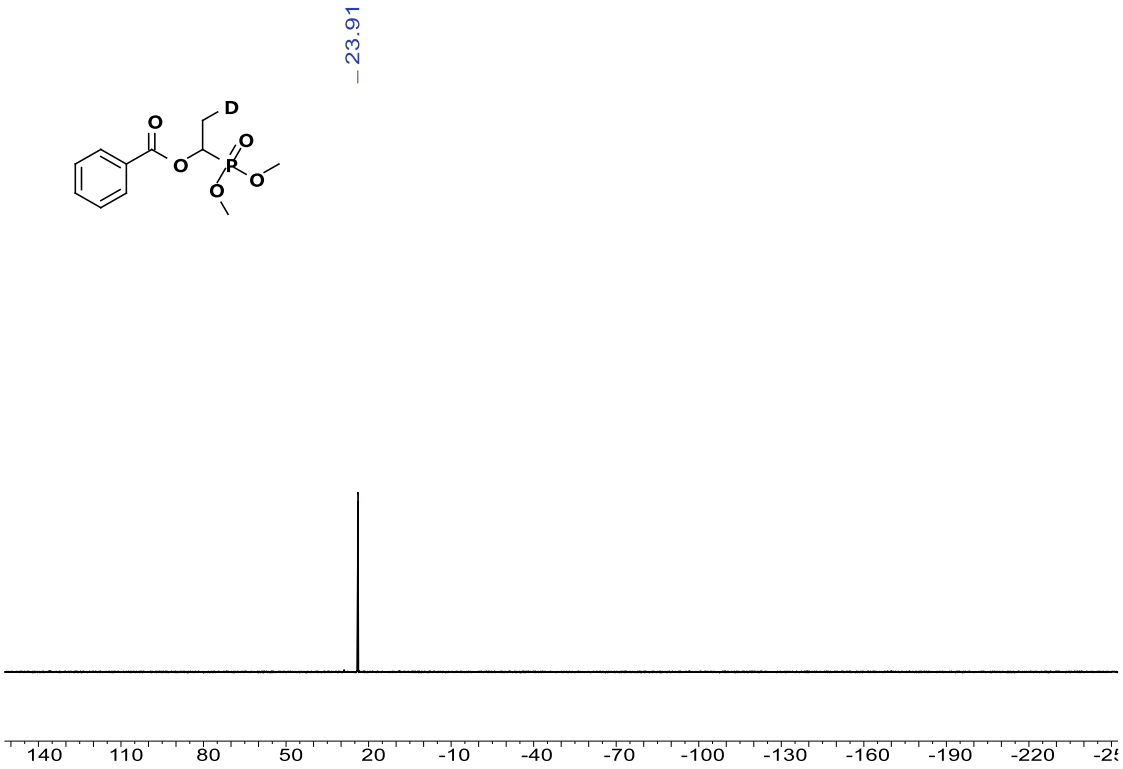
^{1}H NMR spectra of 10 (500 MHz, $CDCl_3$)



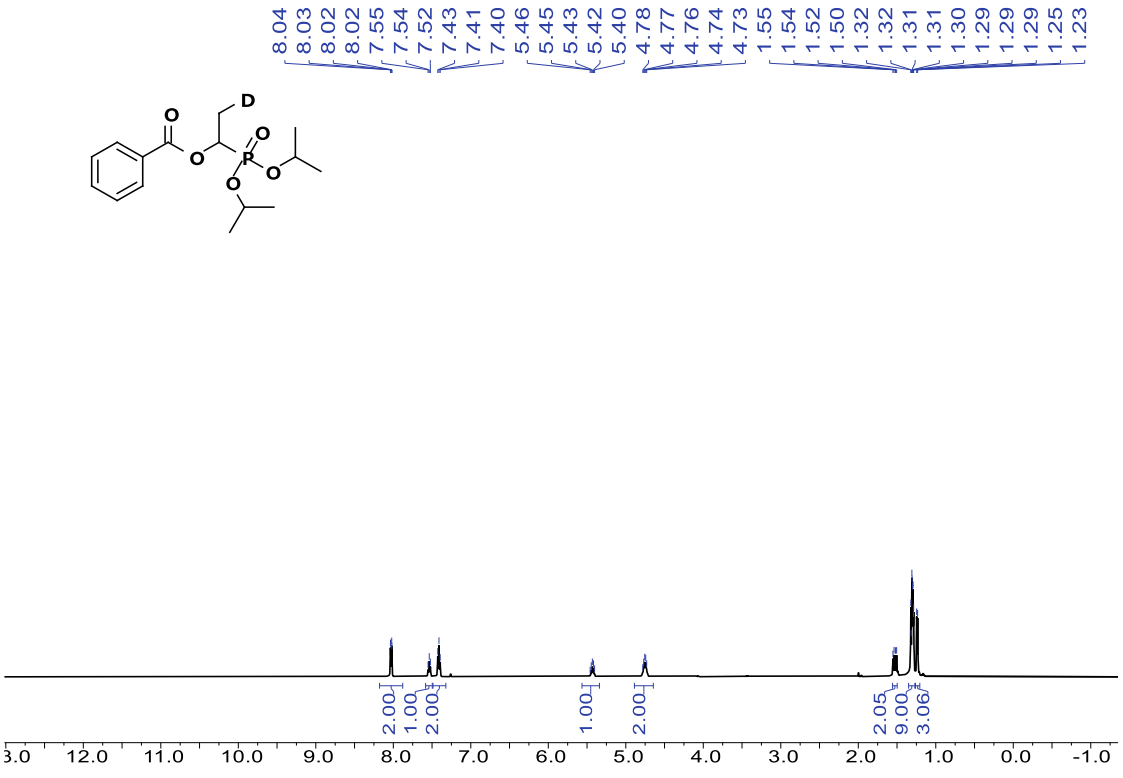
^{13}C NMR spectra of 10 (126 MHz, $CDCl_3$)



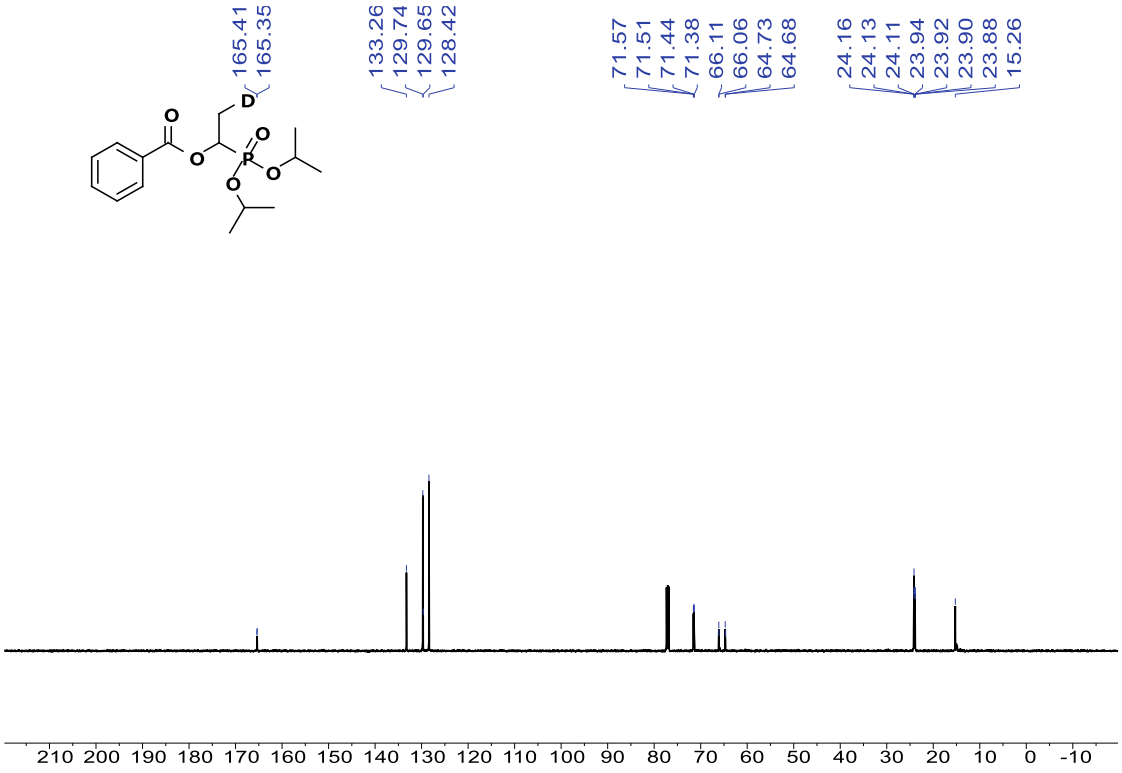
^{31}P NMR spectra of 10 (202 MHz, $CDCl_3$)



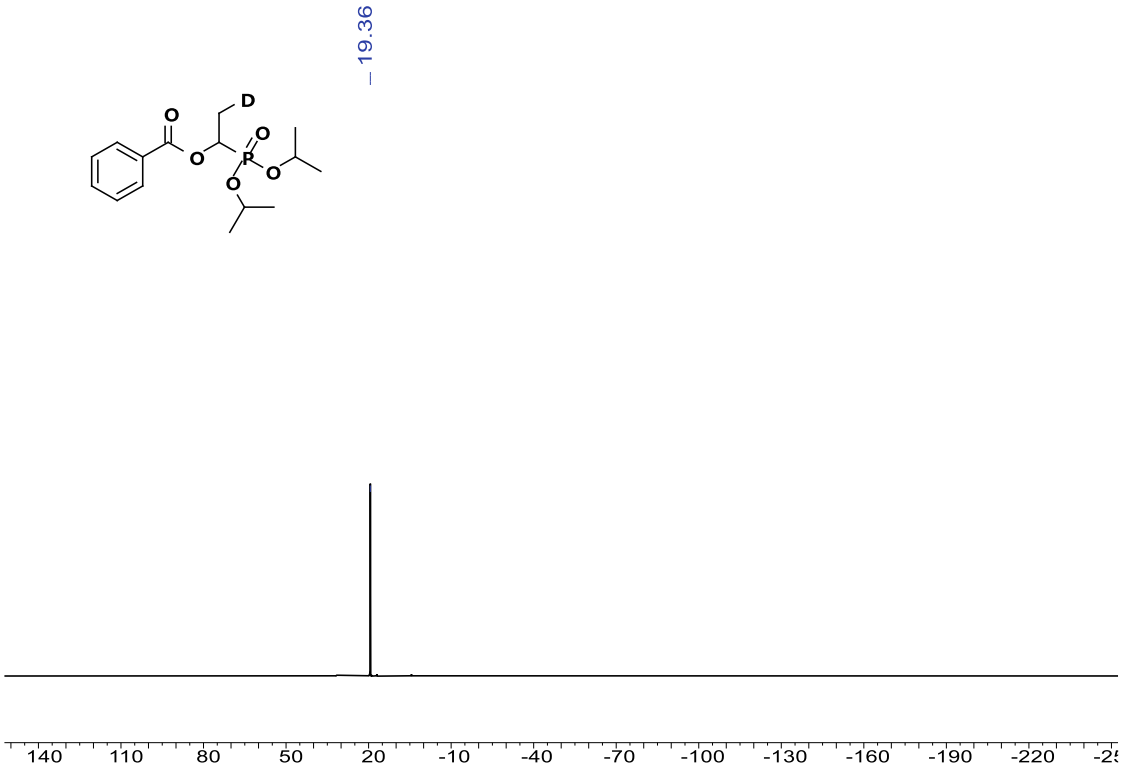
^{1}H NMR spectra of 11 (500 MHz, $CDCl_3$)



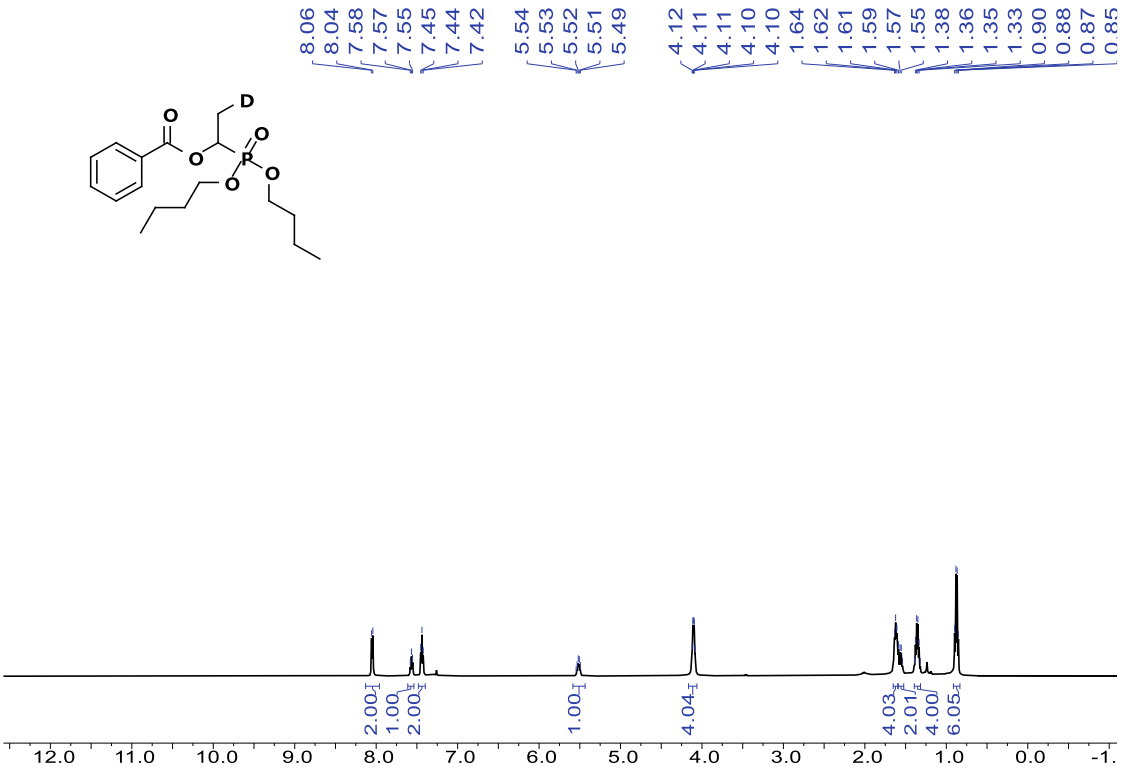
^{13}C NMR spectra of 11 (126 MHz, $CDCl_3$)



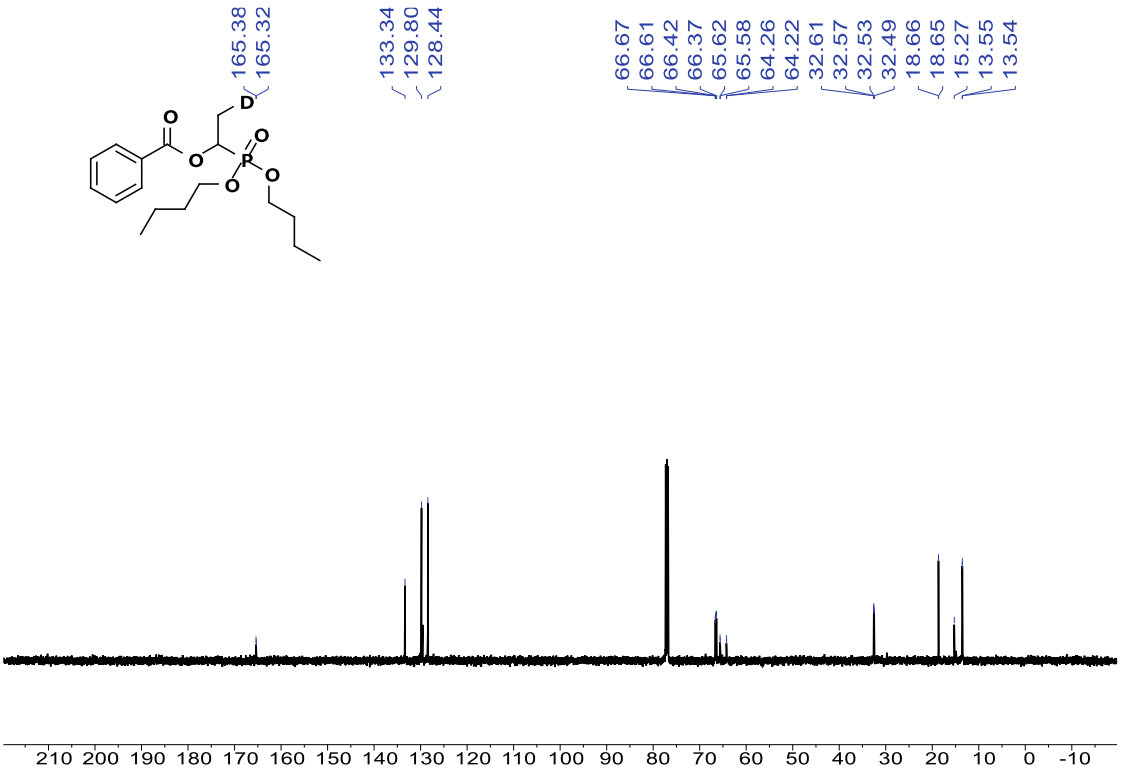
^{31}P NMR spectra of 11 (202 MHz, $CDCl_3$)



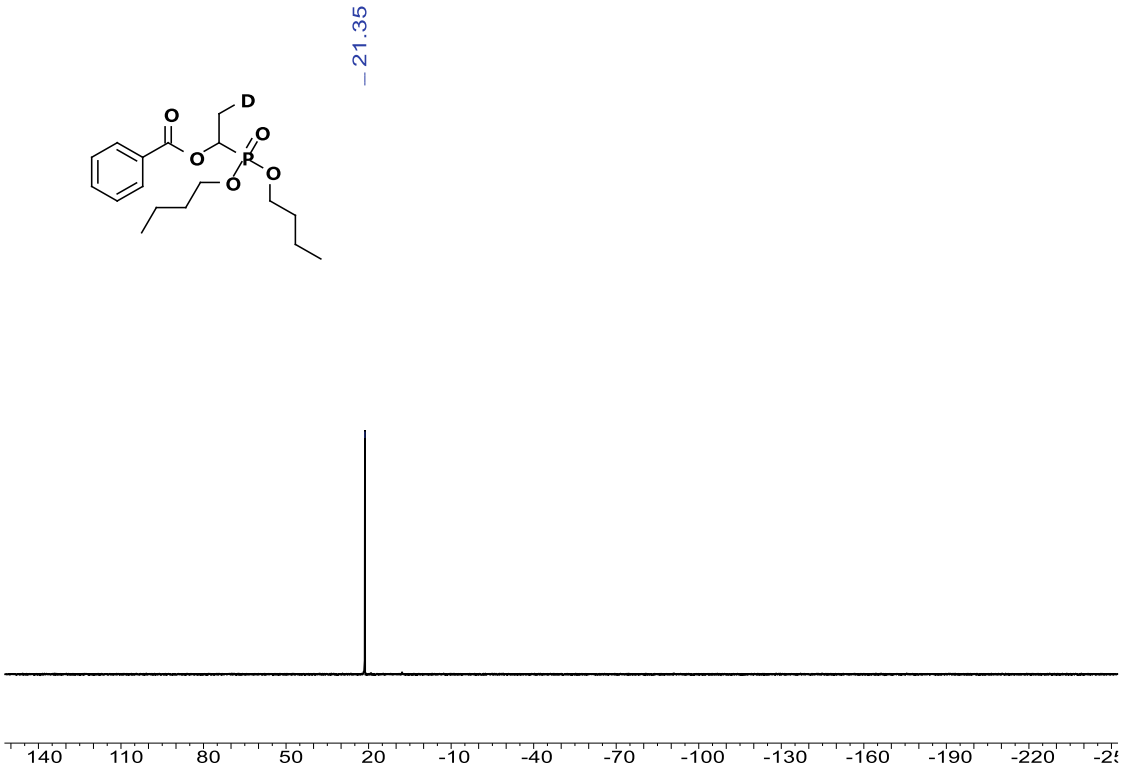
^{1}H NMR spectra of 12 (500 MHz, $CDCl_3$)



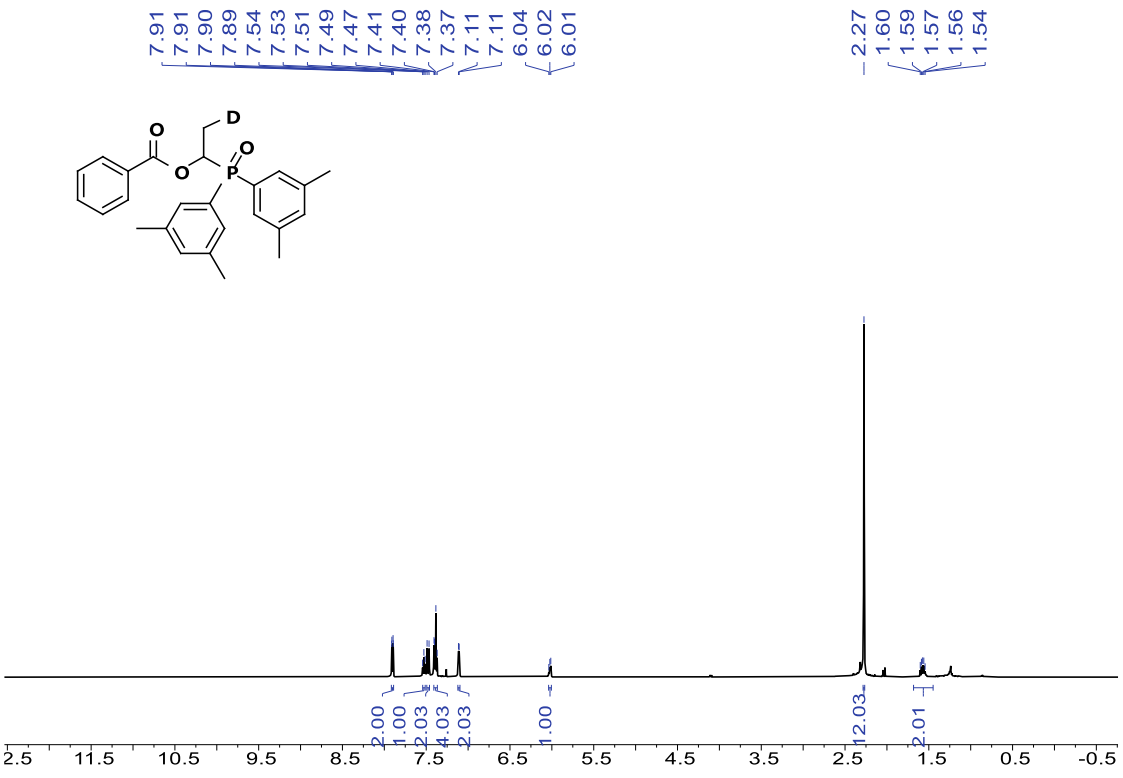
^{13}C NMR spectra of 12 (126 MHz, $CDCl_3$)



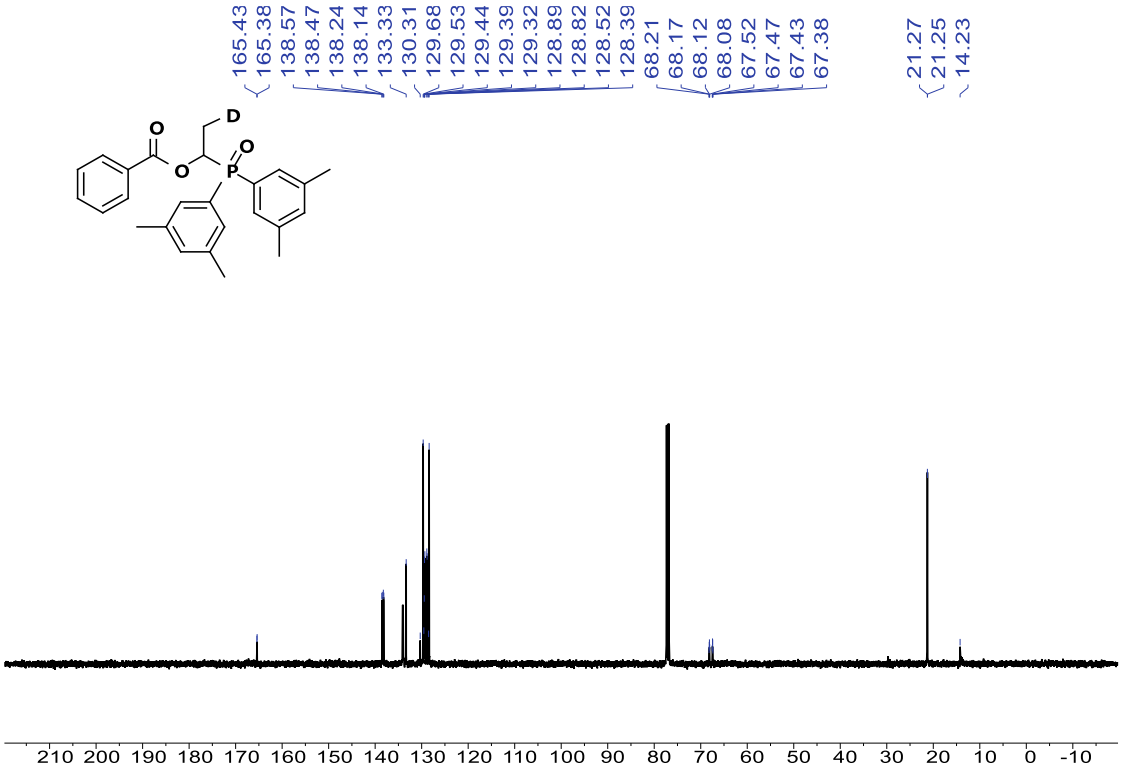
^{31}P NMR spectra of 12 (202 MHz, $CDCl_3$)



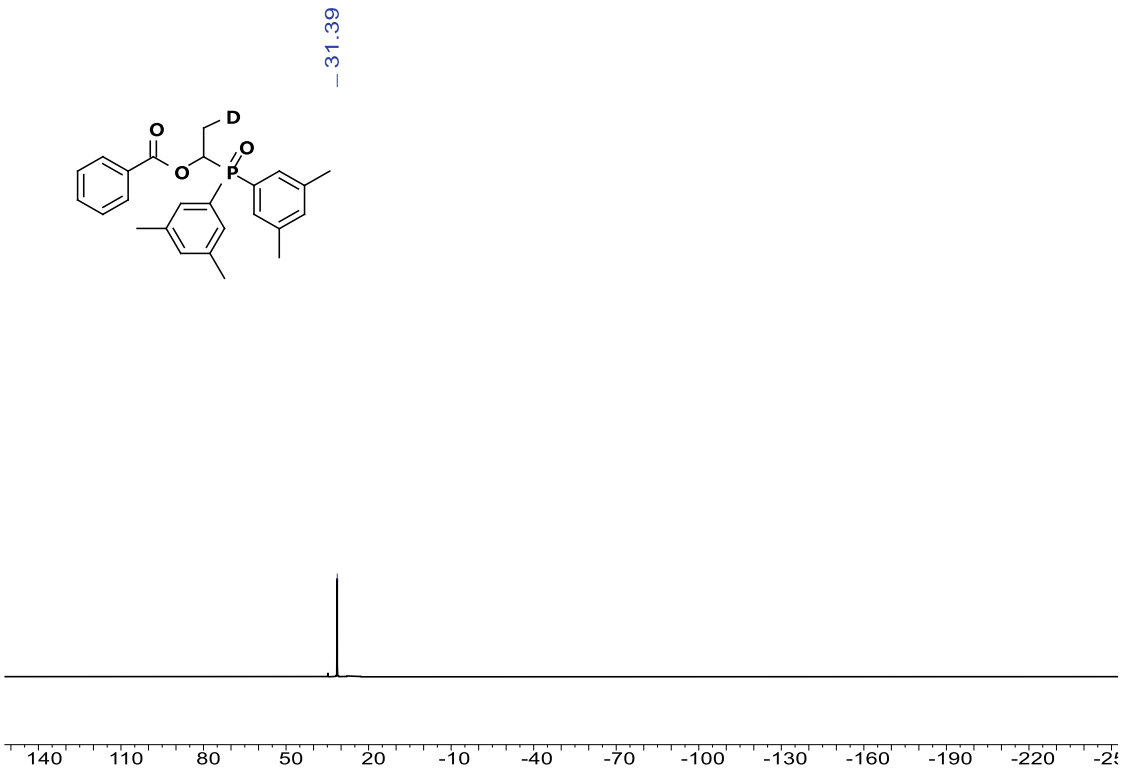
^{1}H NMR spectra of 13 (500 MHz, $CDCl_3$)



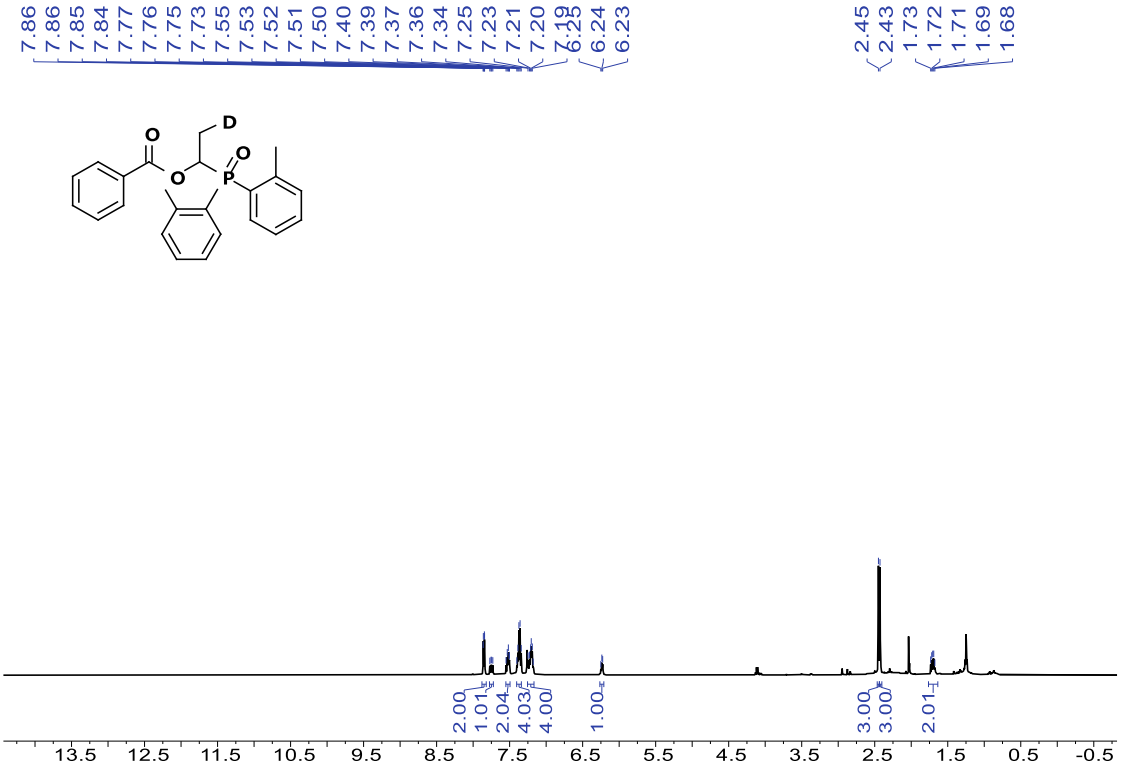
^{13}C NMR spectra of 13 (126 MHz, $CDCl_3$)



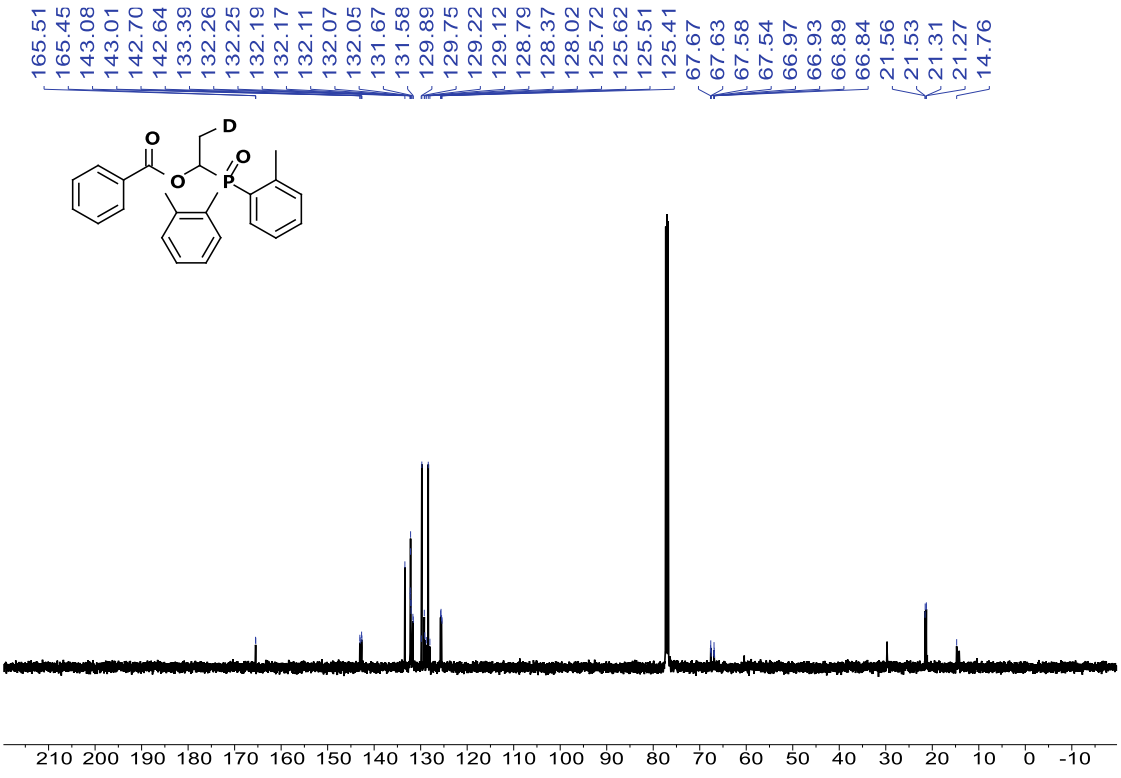
^{31}P NMR spectra of 13 (202 MHz, $CDCl_3$)



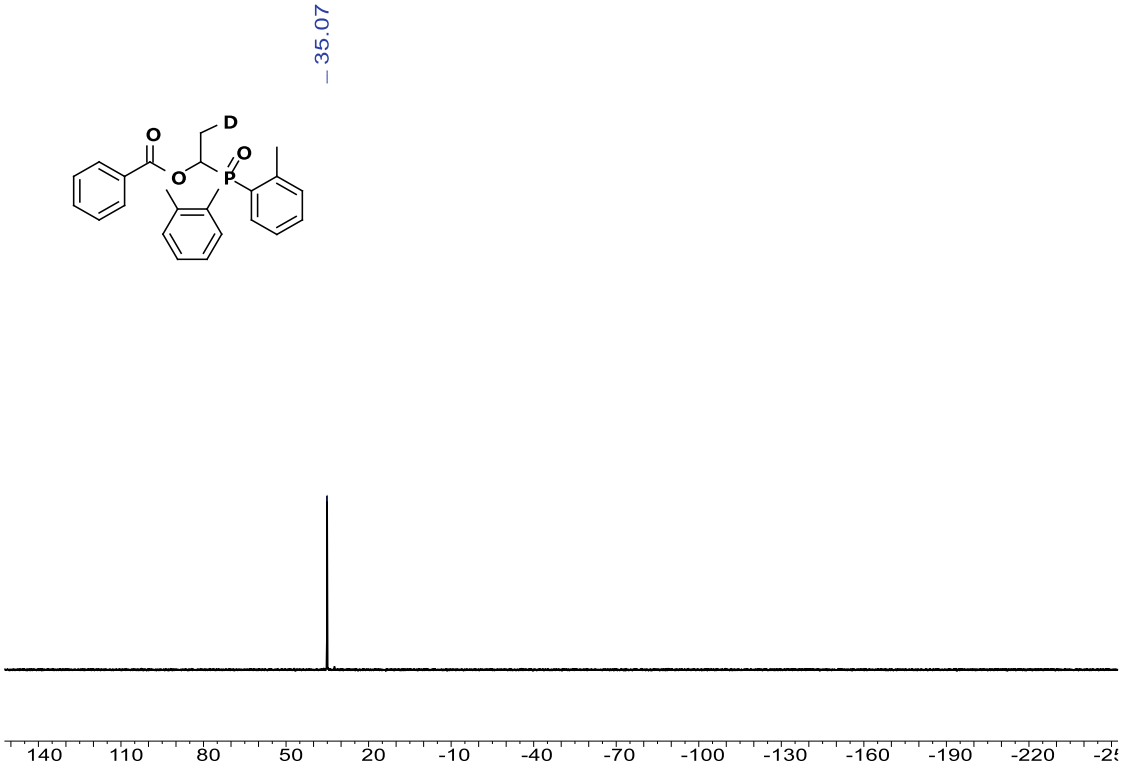
^{1}H NMR spectra of 14 (500 MHz, $CDCl_3$)



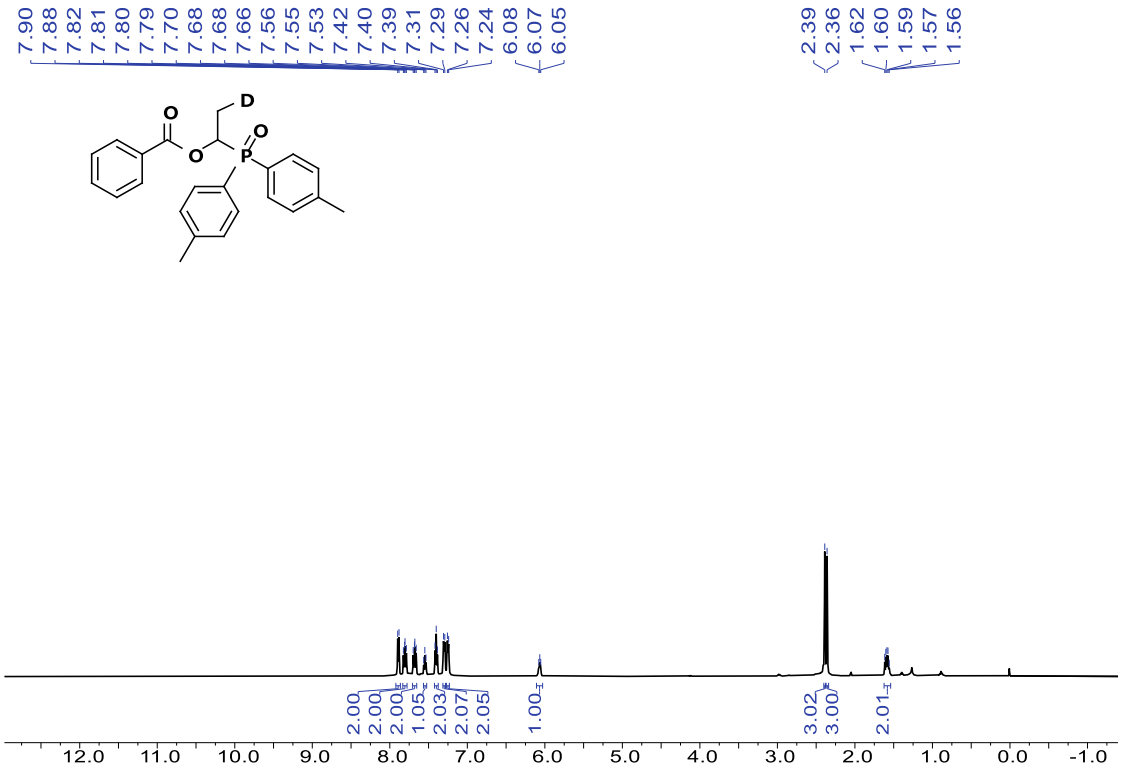
^{13}C NMR spectra of 14 (126 MHz, $CDCl_3$)



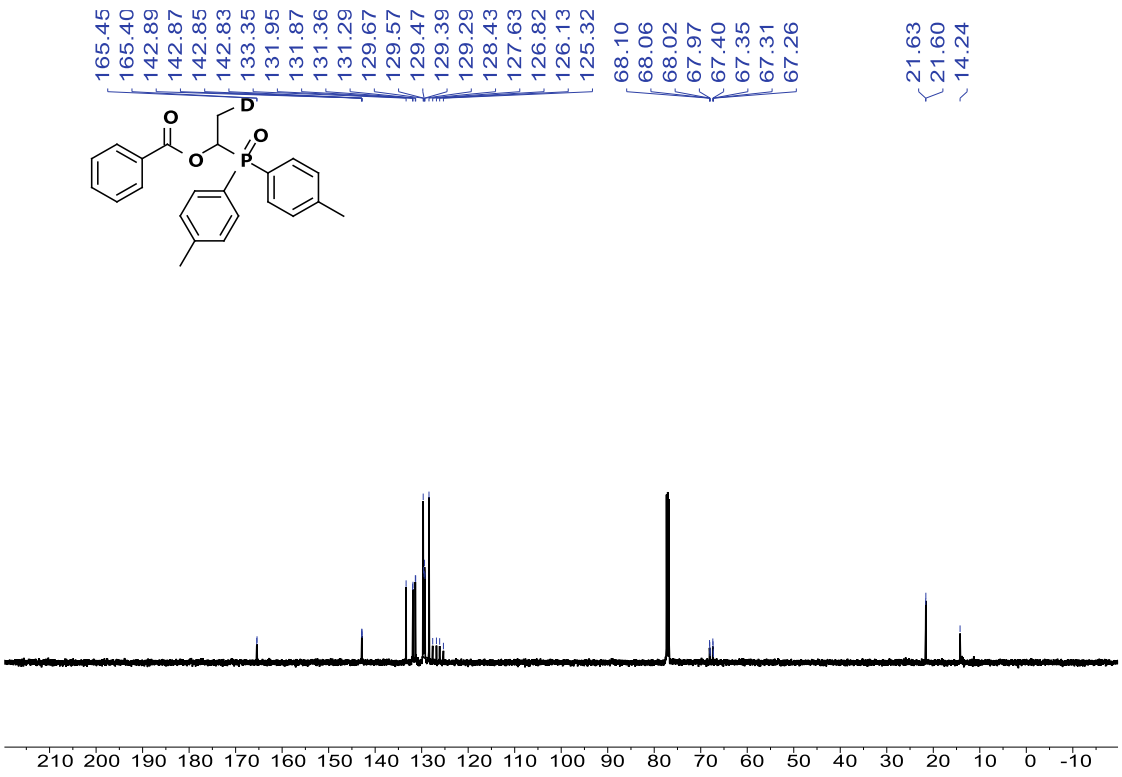
^{31}P NMR spectra of 14 (202 MHz, $CDCl_3$)



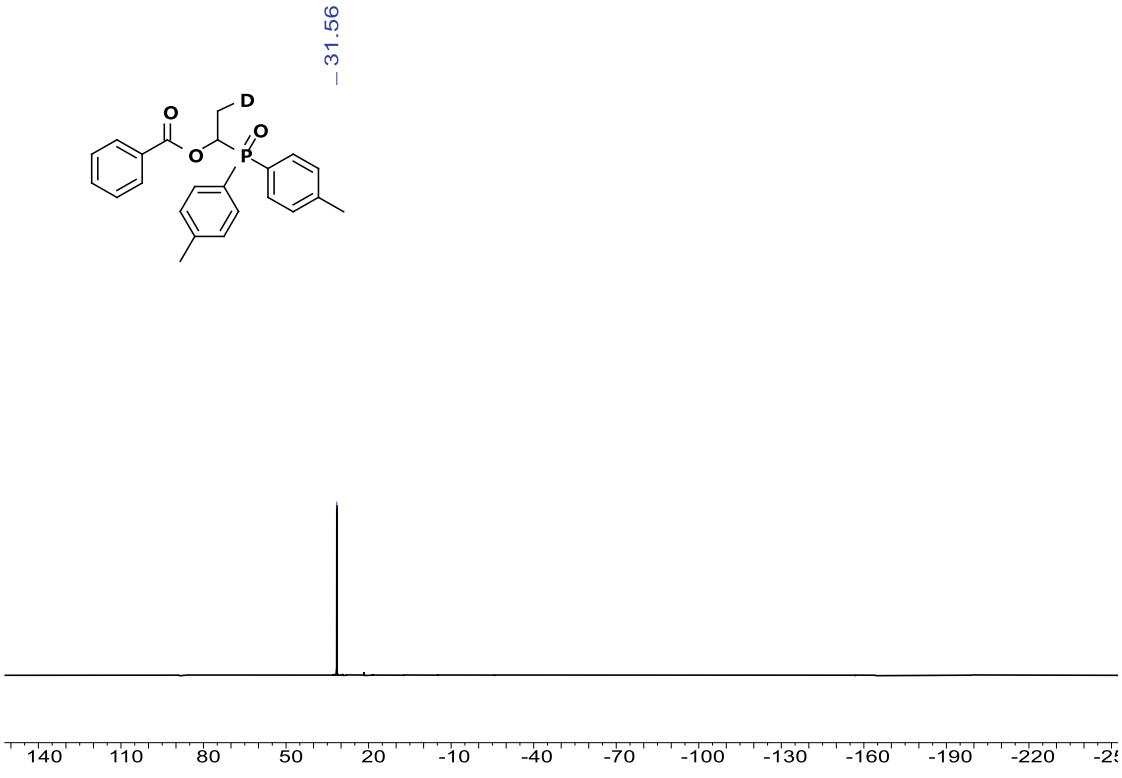
^{1}H NMR spectra of 15 (500 MHz, $CDCl_3$)



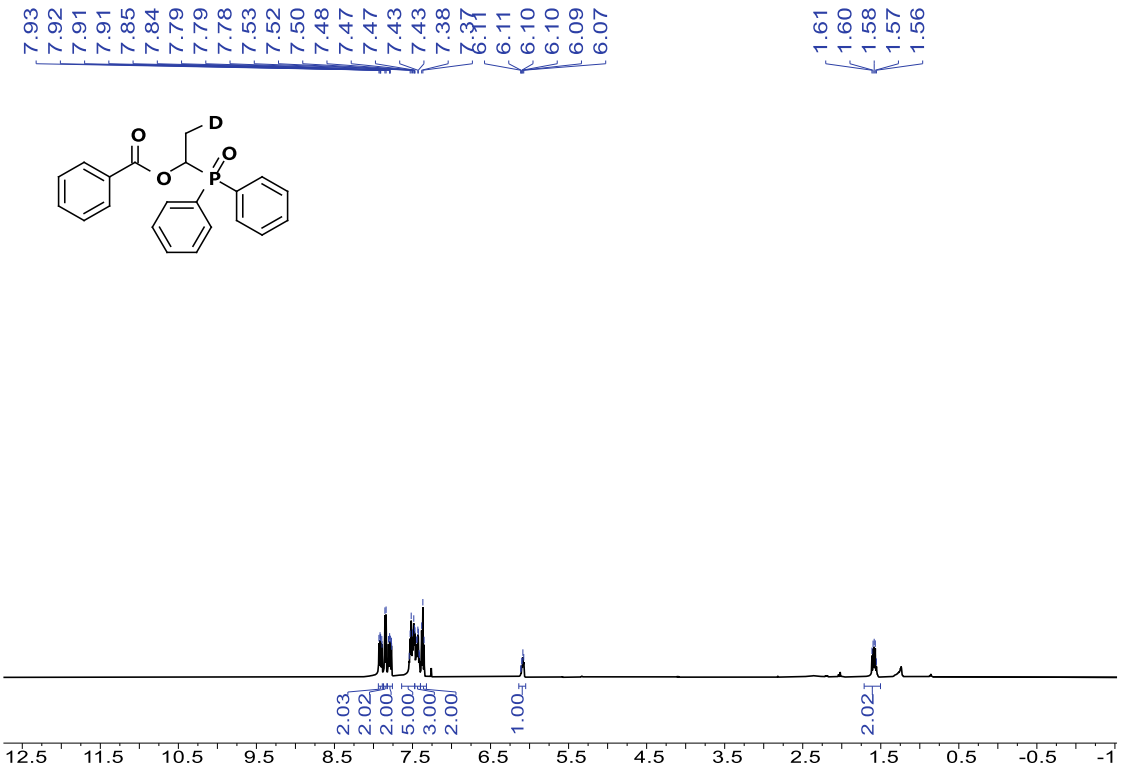
^{13}C NMR spectra of 15 (126 MHz, $CDCl_3$)



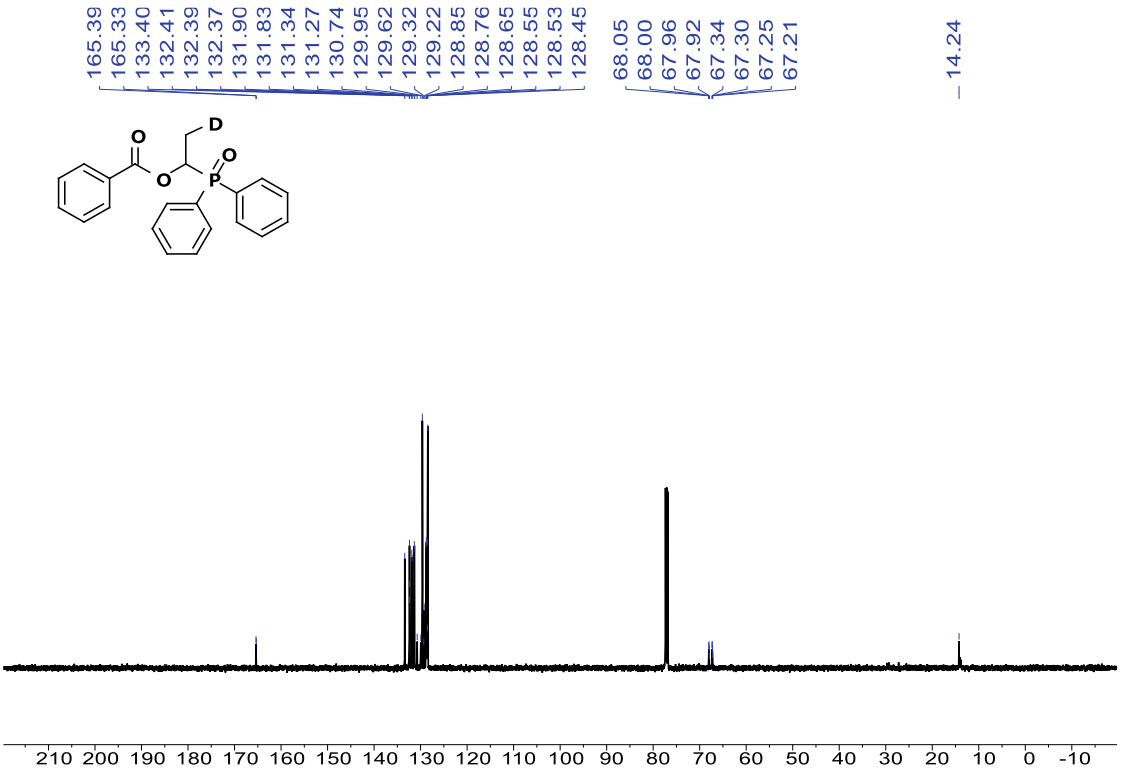
^{31}P NMR spectra of 15 (202 MHz, $CDCl_3$)



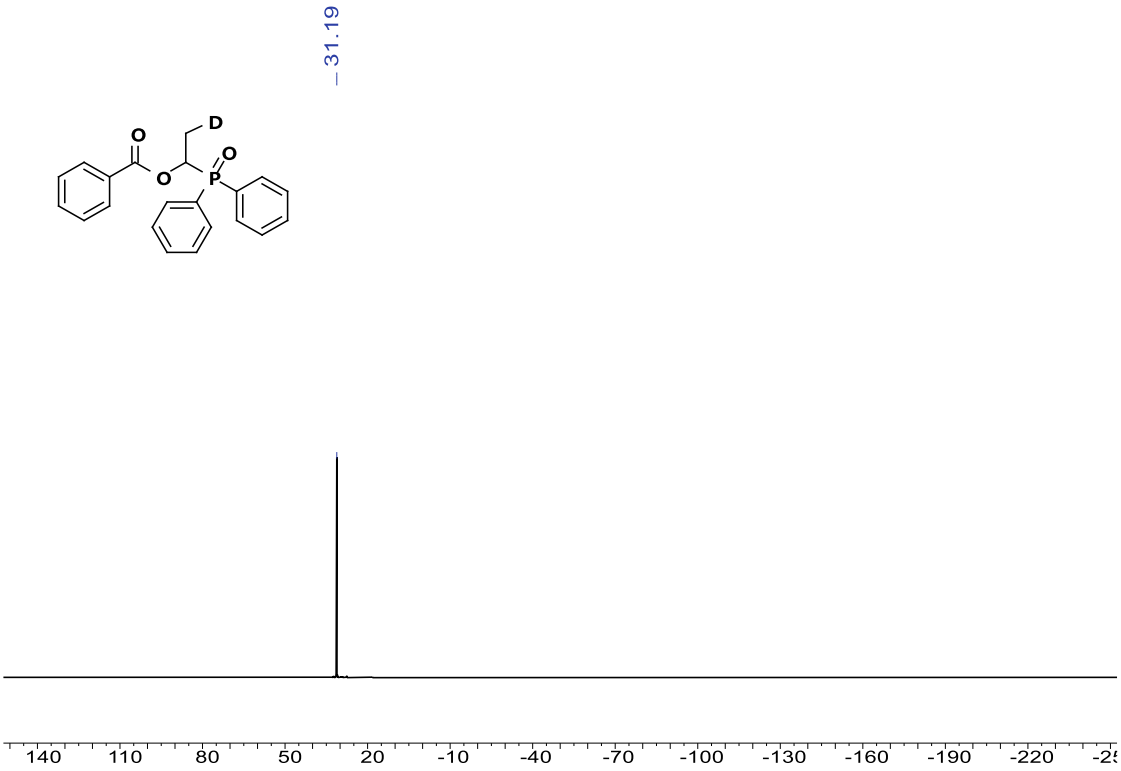
^{1}H NMR spectra of 16 (500 MHz, $CDCl_3$)



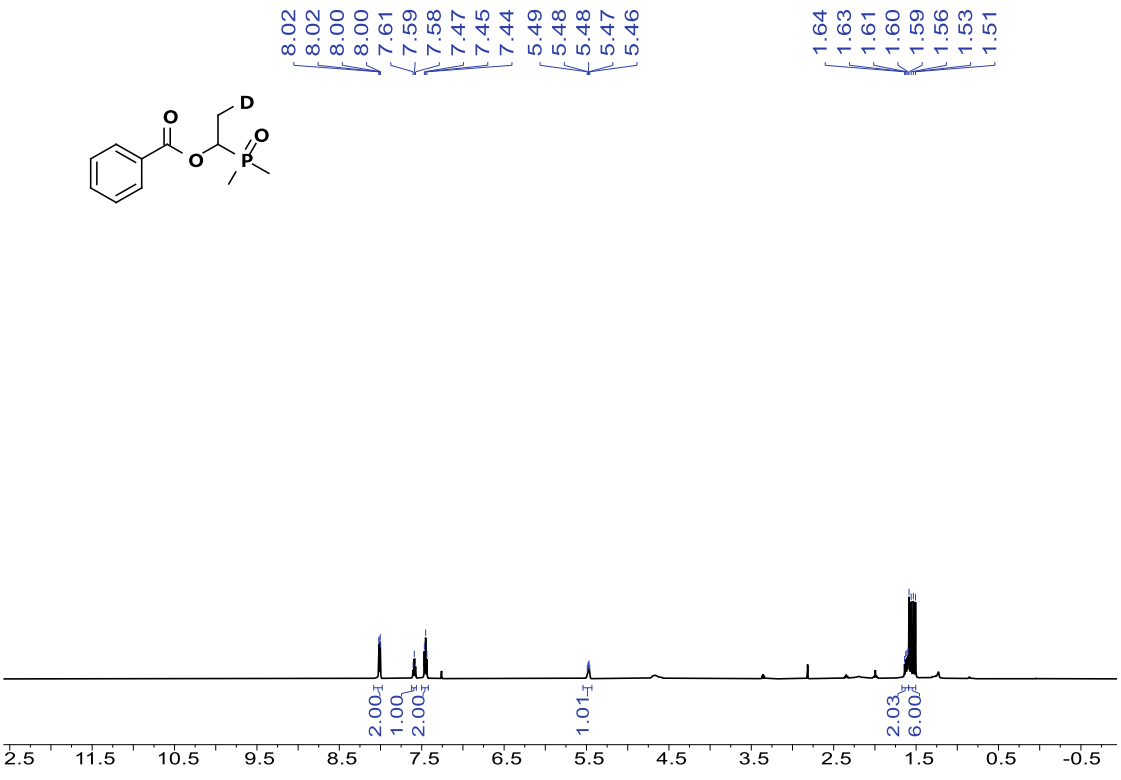
^{13}C NMR spectra of 16 (126 MHz, $CDCl_3$)



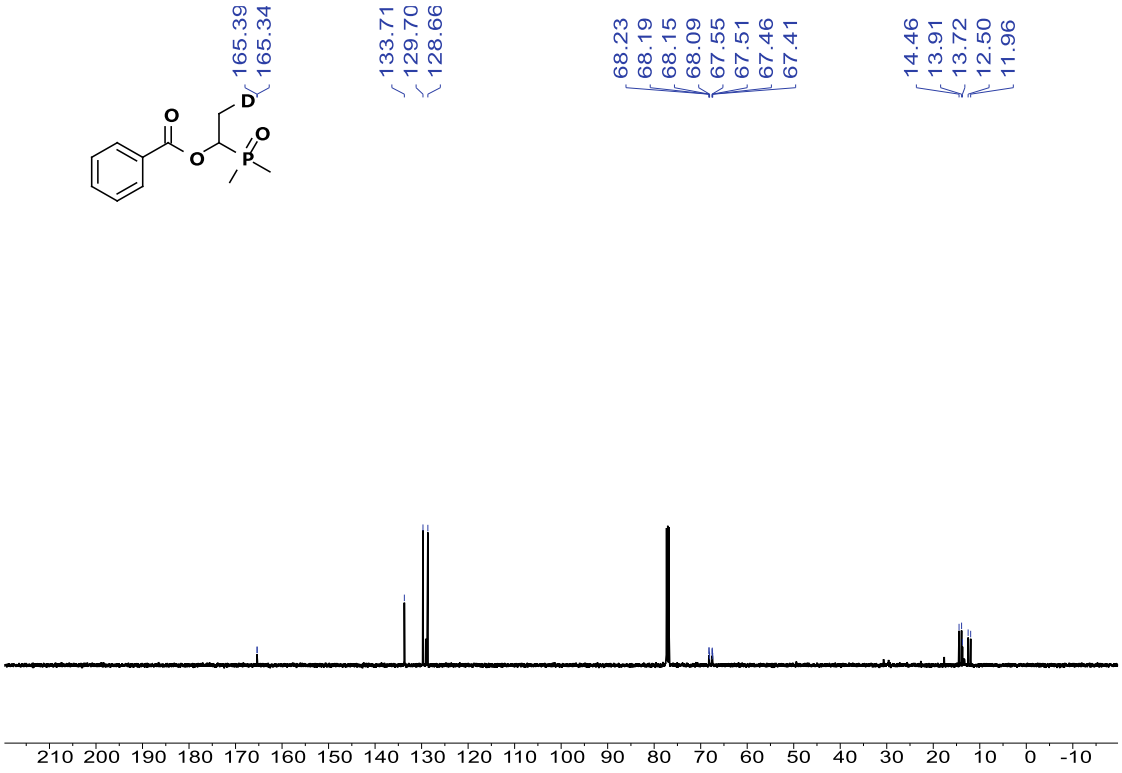
^{31}P NMR spectra of 16 (202 MHz, $CDCl_3$)



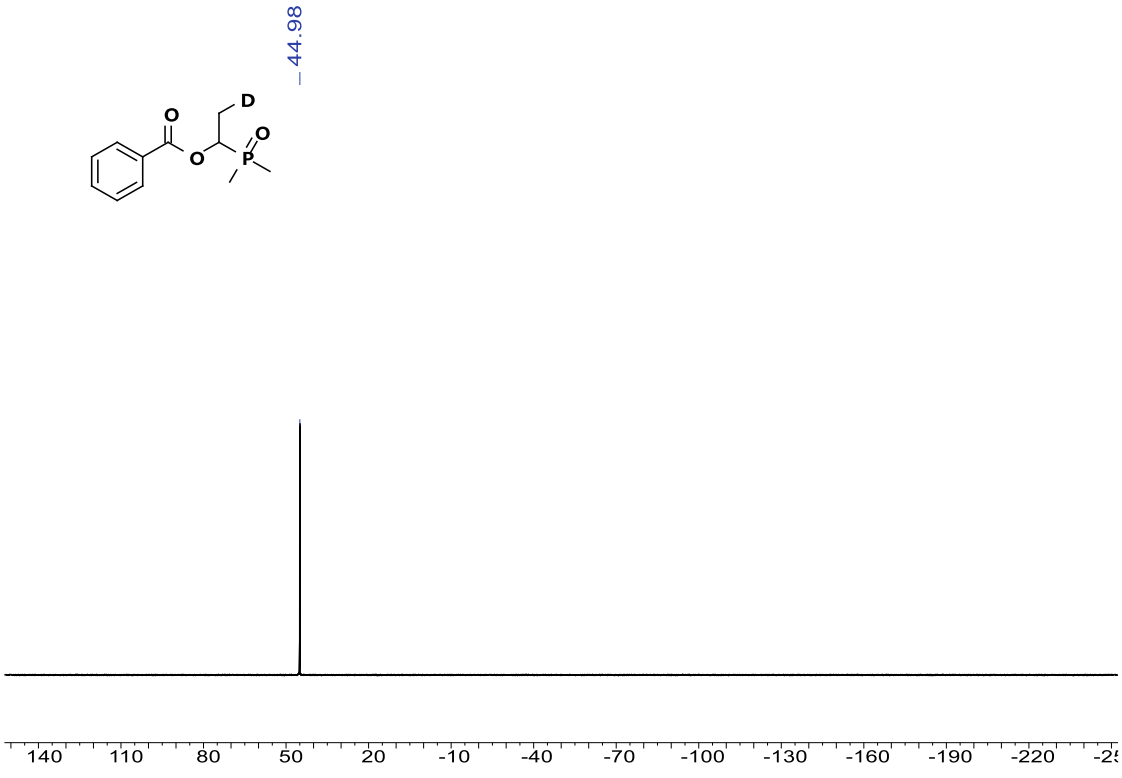
^{1}H NMR spectra of 17 (500 MHz, $CDCl_3$)



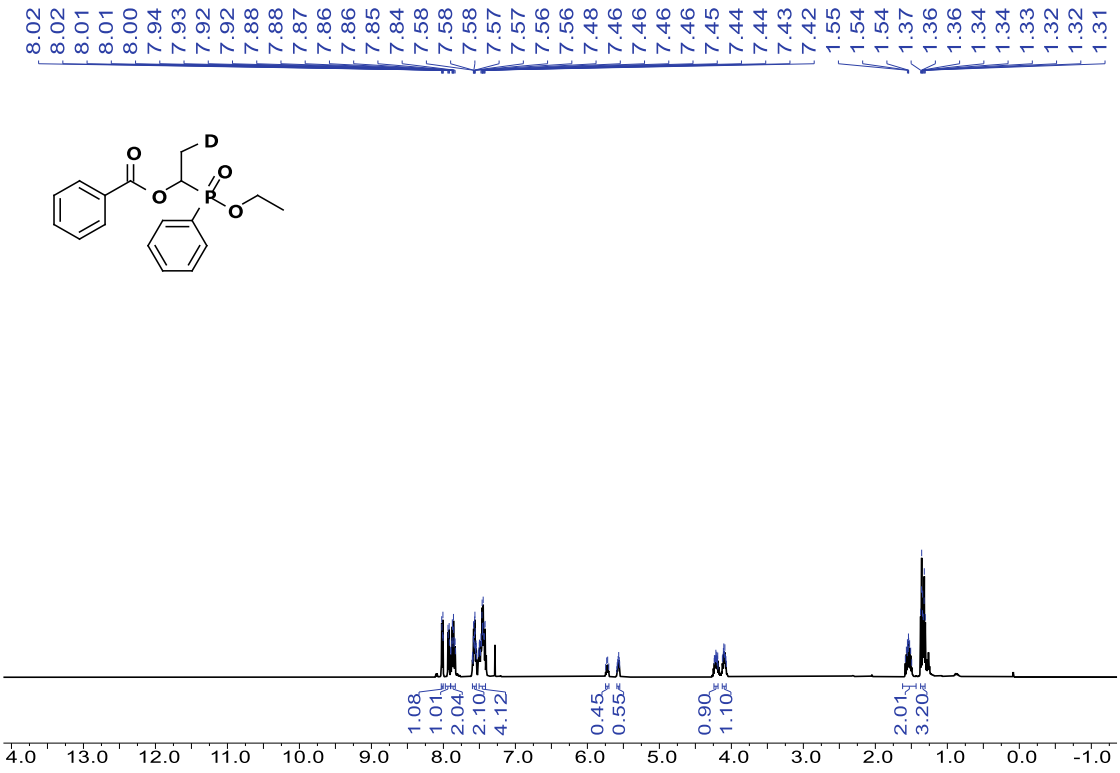
^{13}C NMR spectra of 17 (126 MHz, $CDCl_3$)



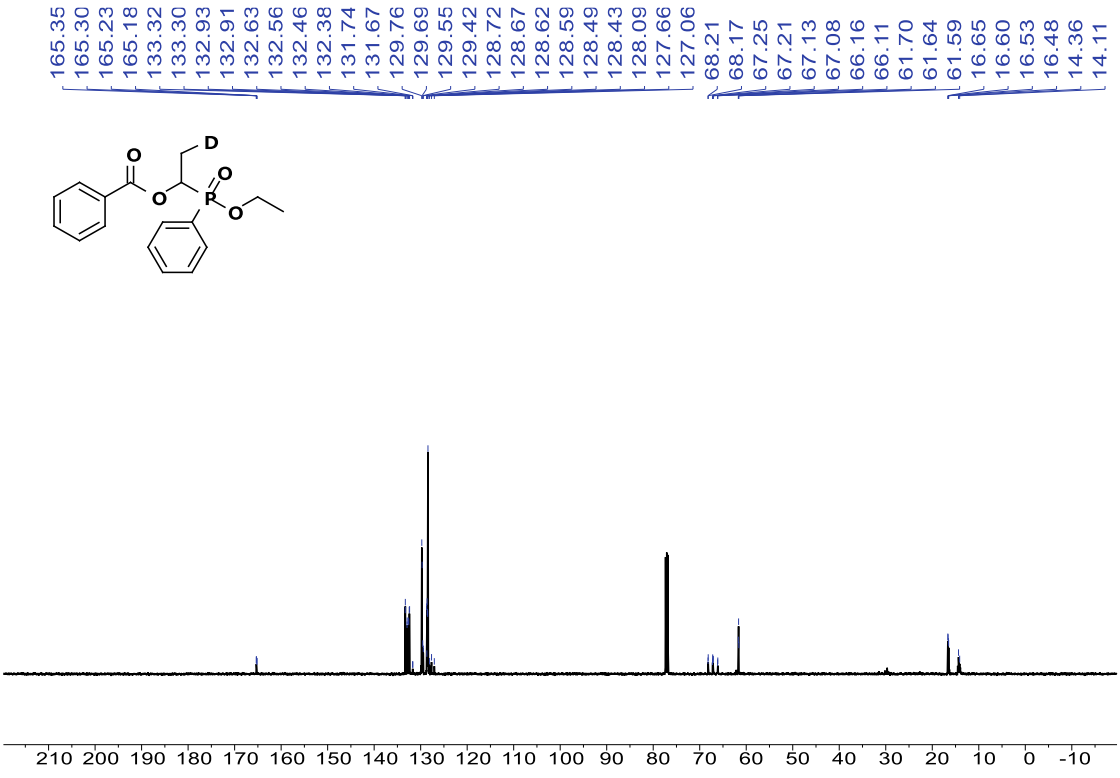
^{31}P NMR spectra of 17 (202 MHz, $CDCl_3$)



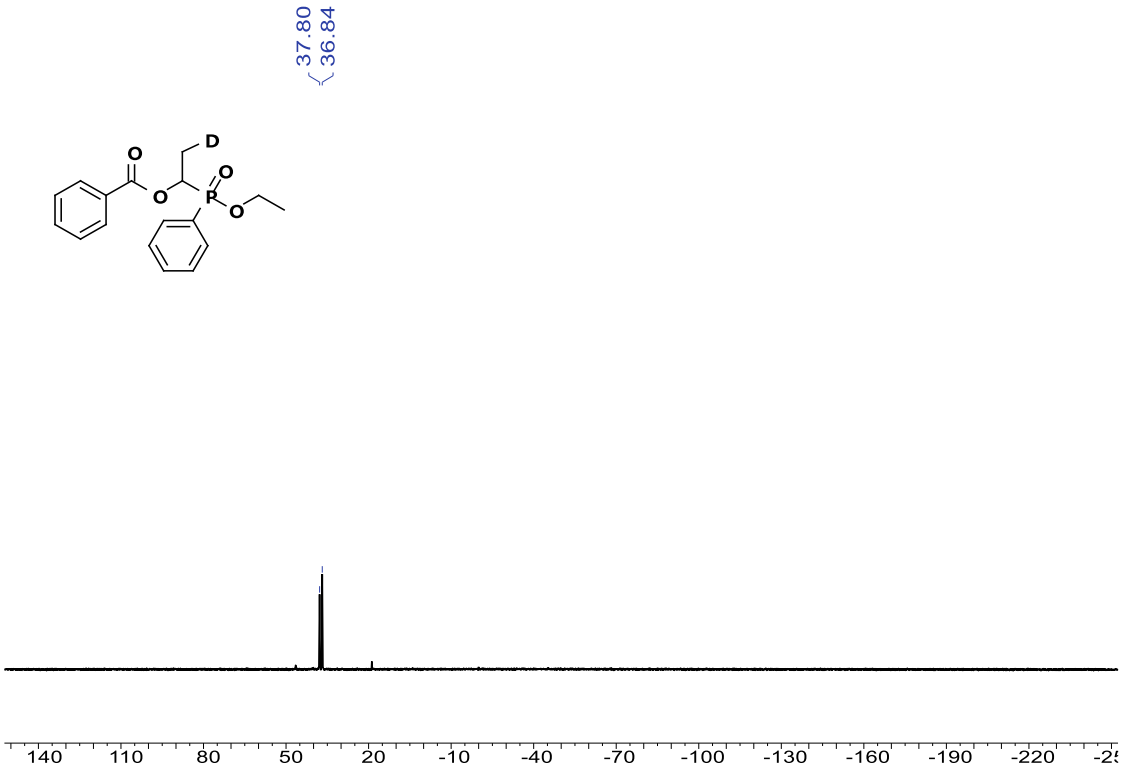
^{1}H NMR spectra of 18 (500 MHz, $CDCl_3$)



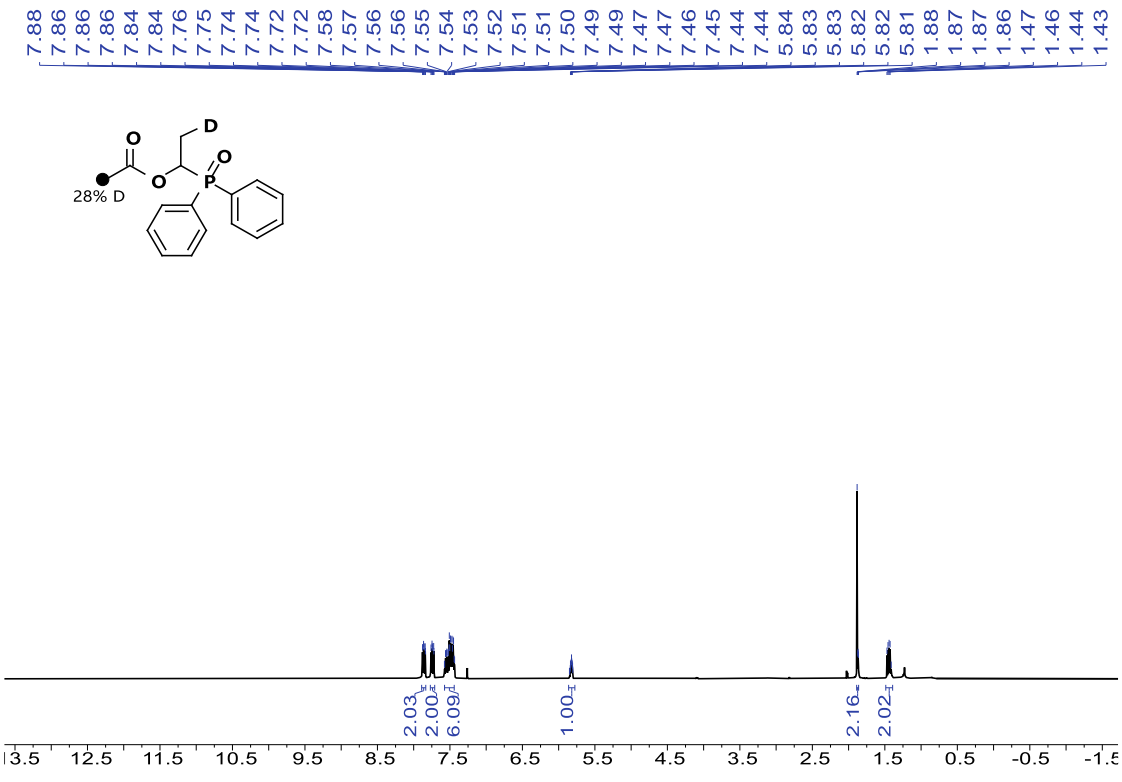
^{13}C NMR spectra of 18 (126 MHz, $CDCl_3$)



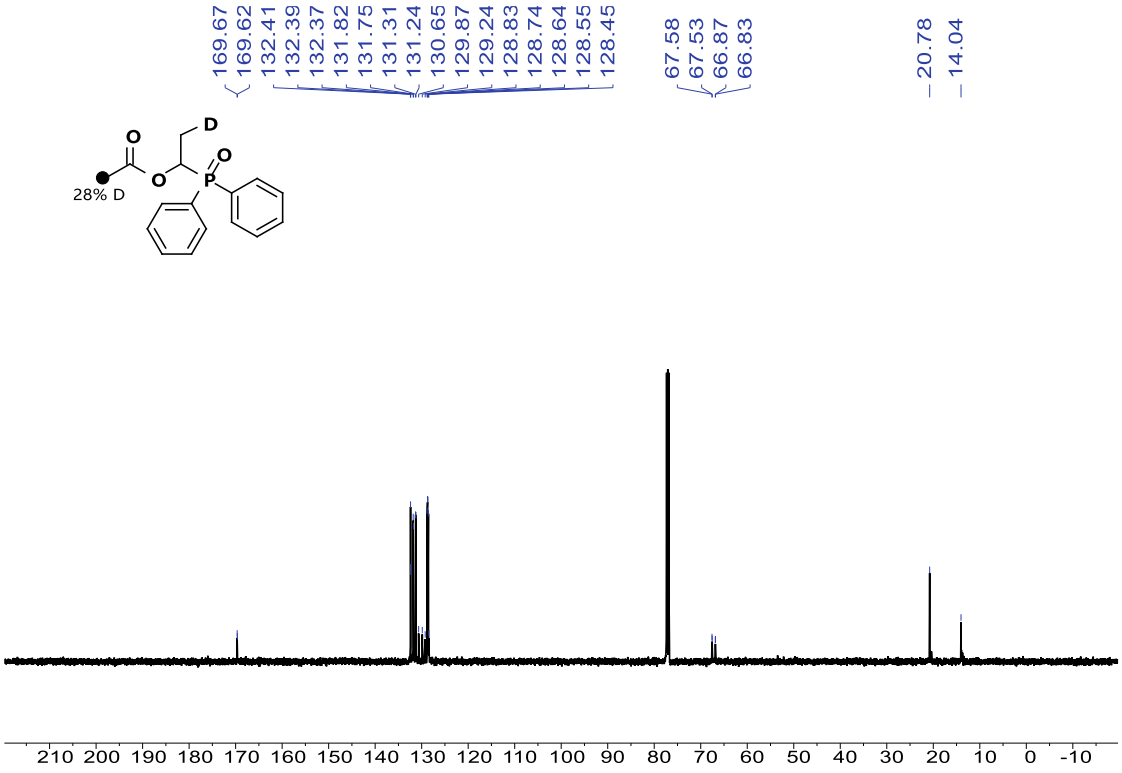
^{31}P NMR spectra of 18 (202 MHz, $CDCl_3$)



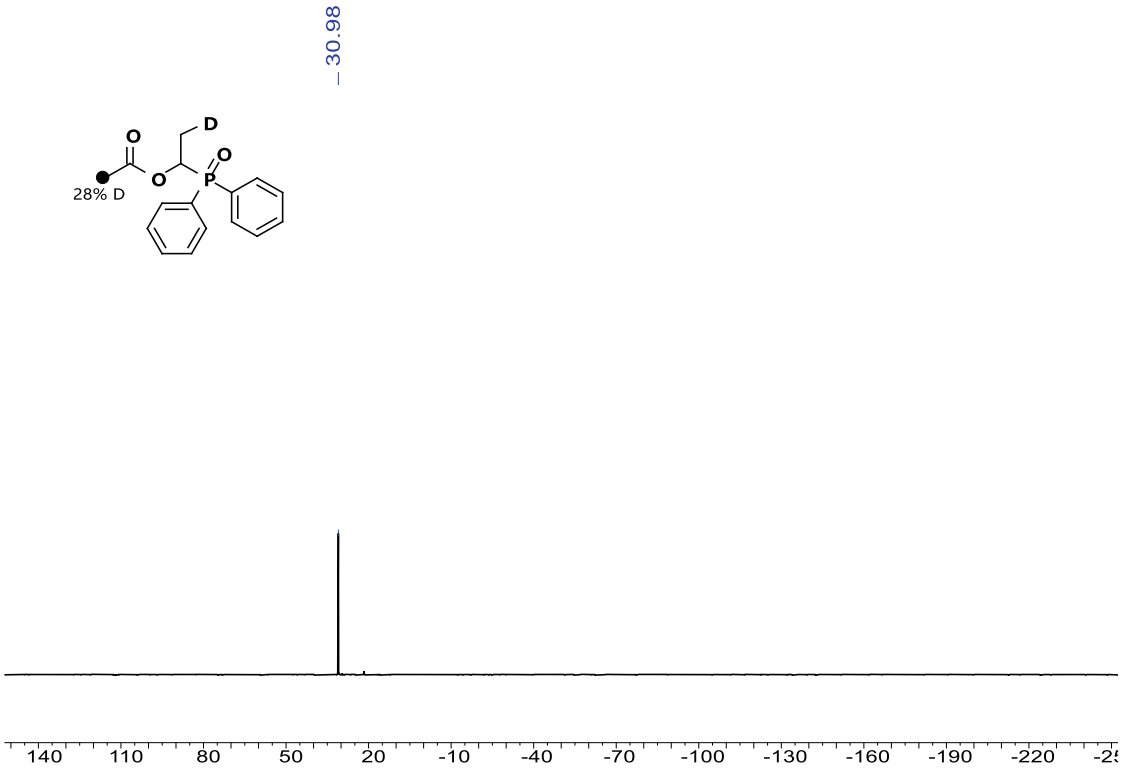
^{1}H NMR spectra of 19 (500 MHz, $CDCl_3$)



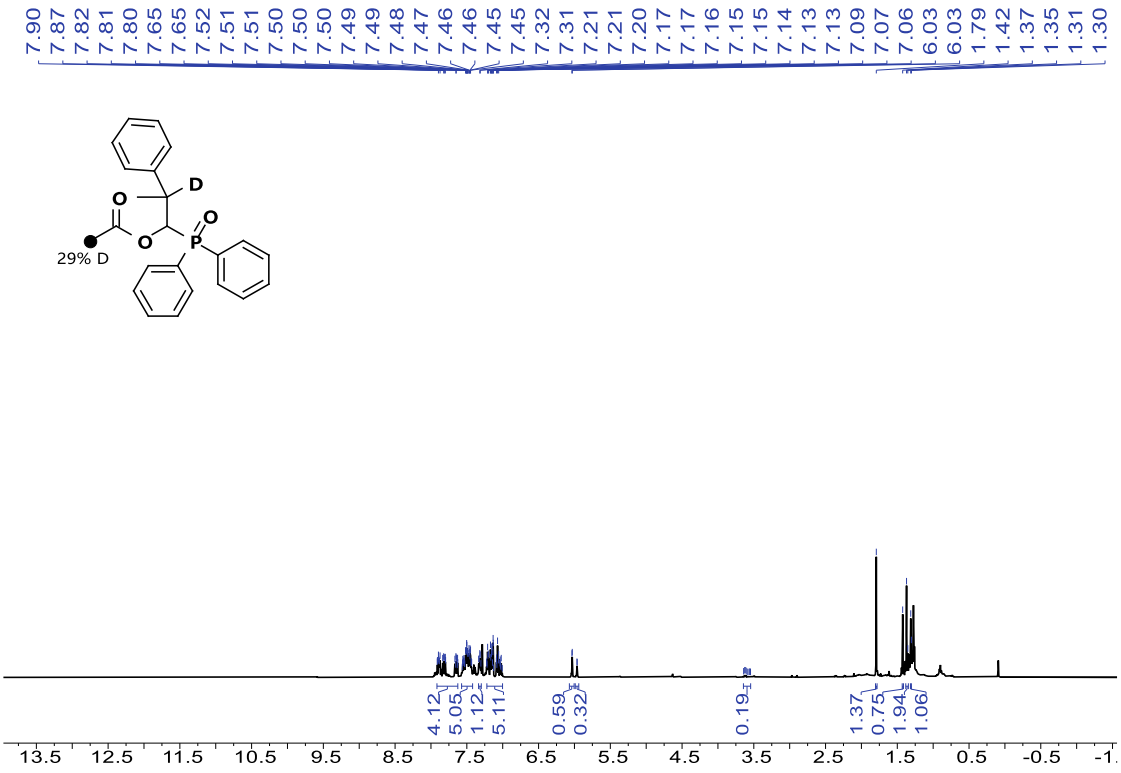
^{13}C NMR spectra of 19 (126 MHz, $CDCl_3$)



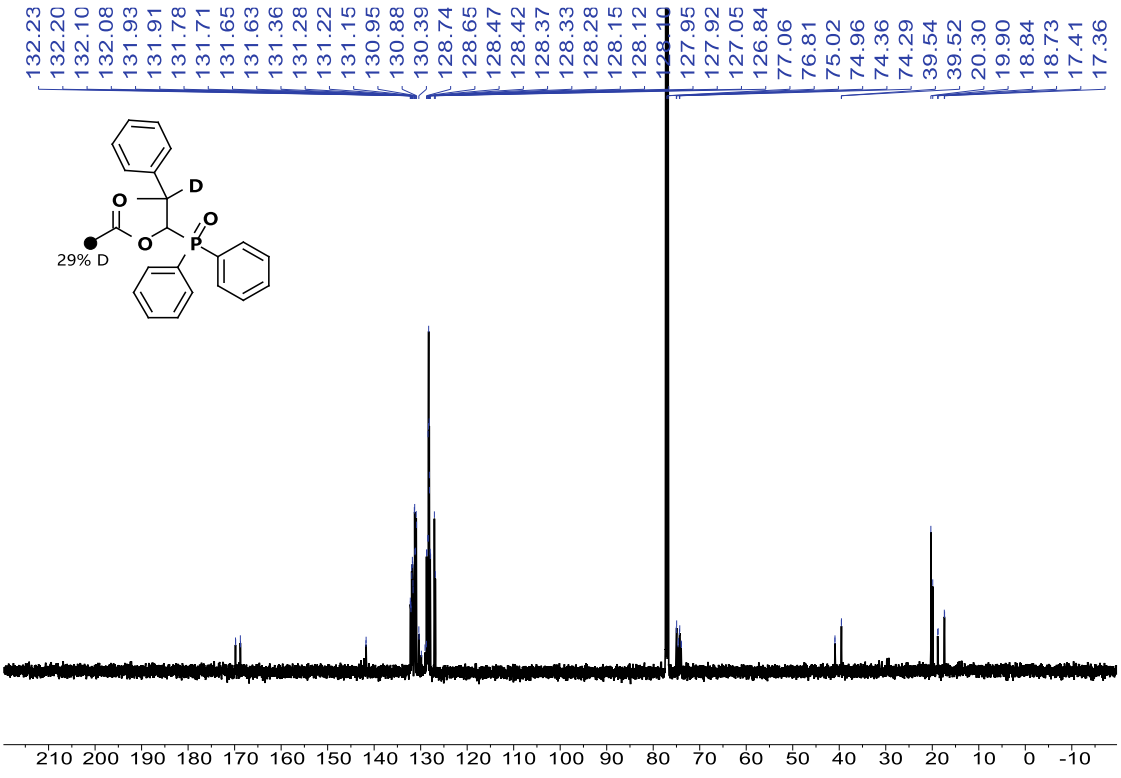
^{31}P NMR spectra of 19 (202 MHz, $CDCl_3$)



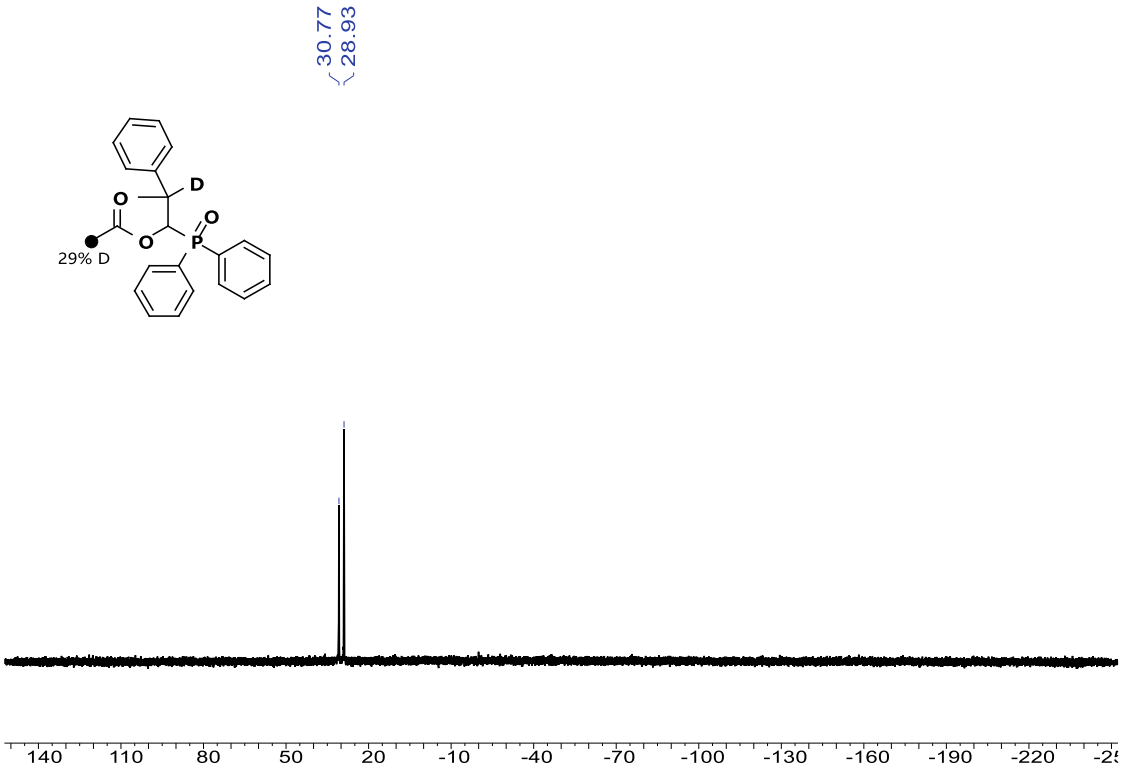
^{1}H NMR spectra of 21 (500 MHz, $CDCl_3$)



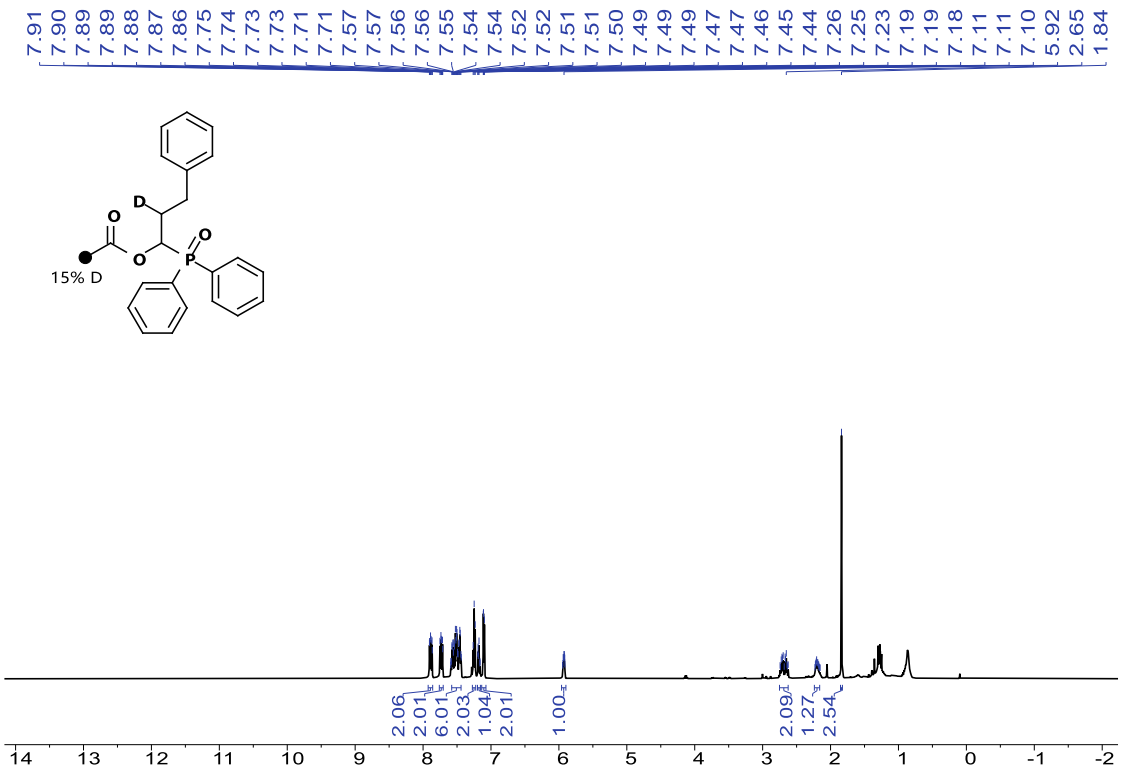
^{13}C NMR spectra of 21 (126 MHz, $CDCl_3$)



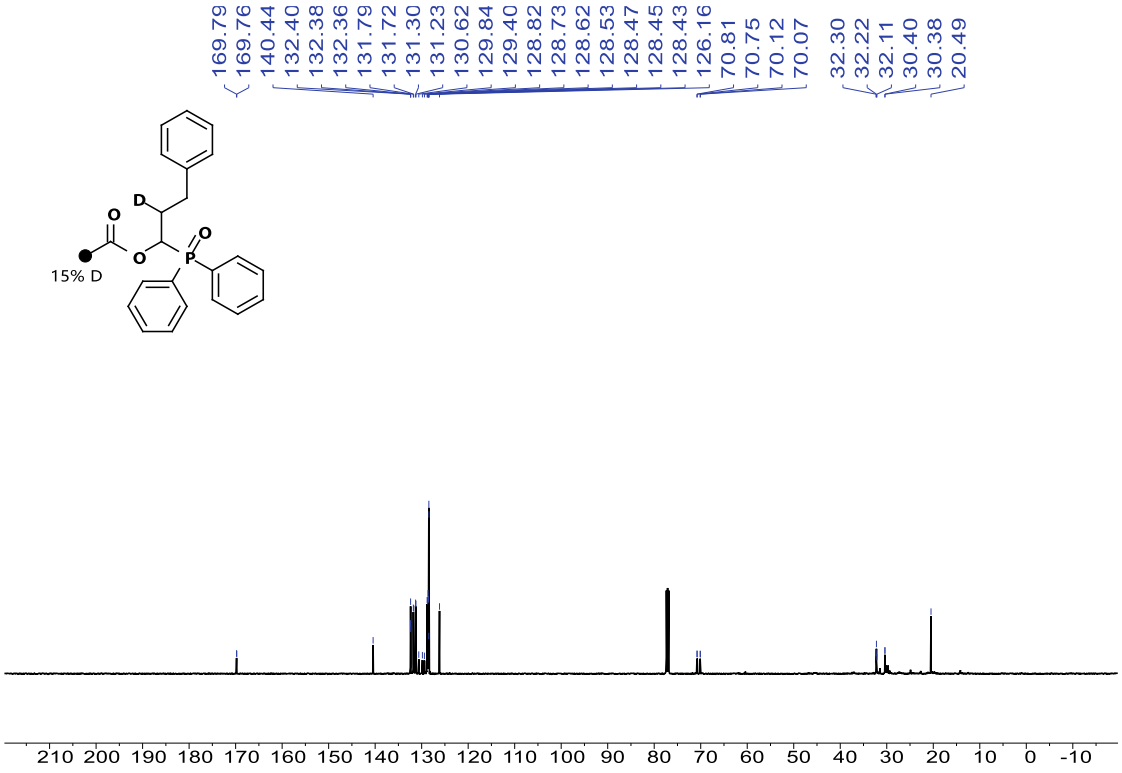
^{31}P NMR spectra of 21 (202 MHz, $CDCl_3$)



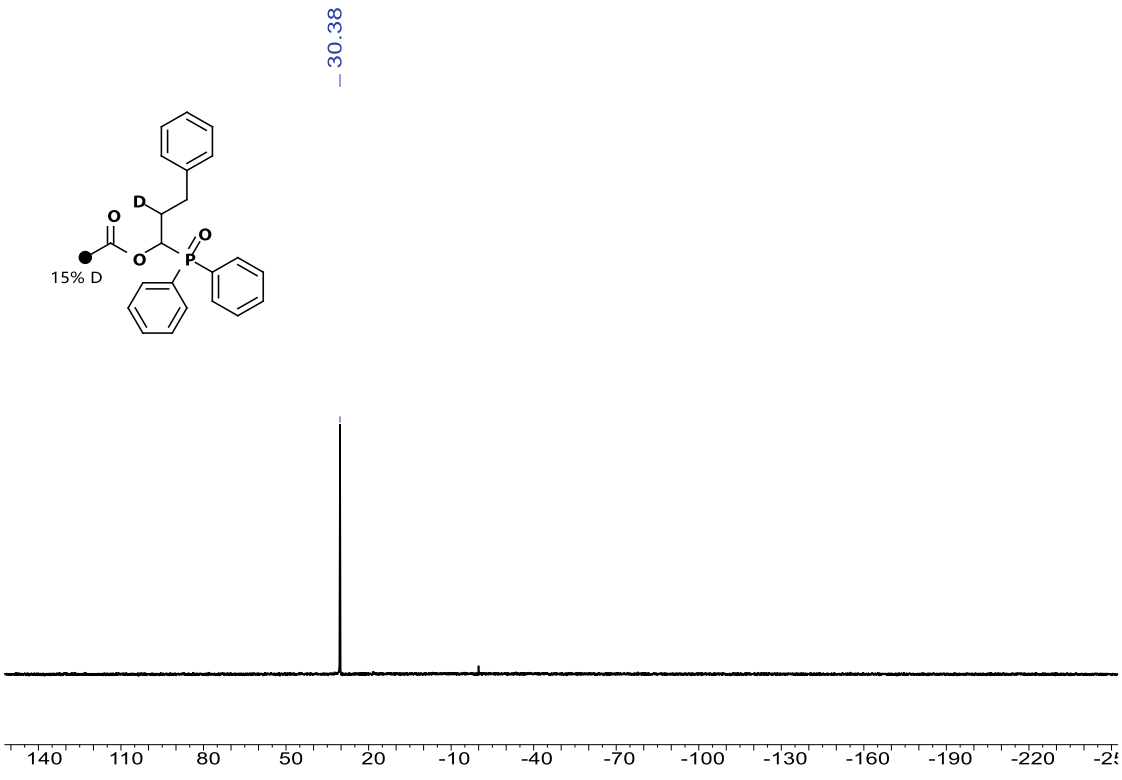
^{1}H NMR spectra of 22 (500 MHz, $CDCl_3$)



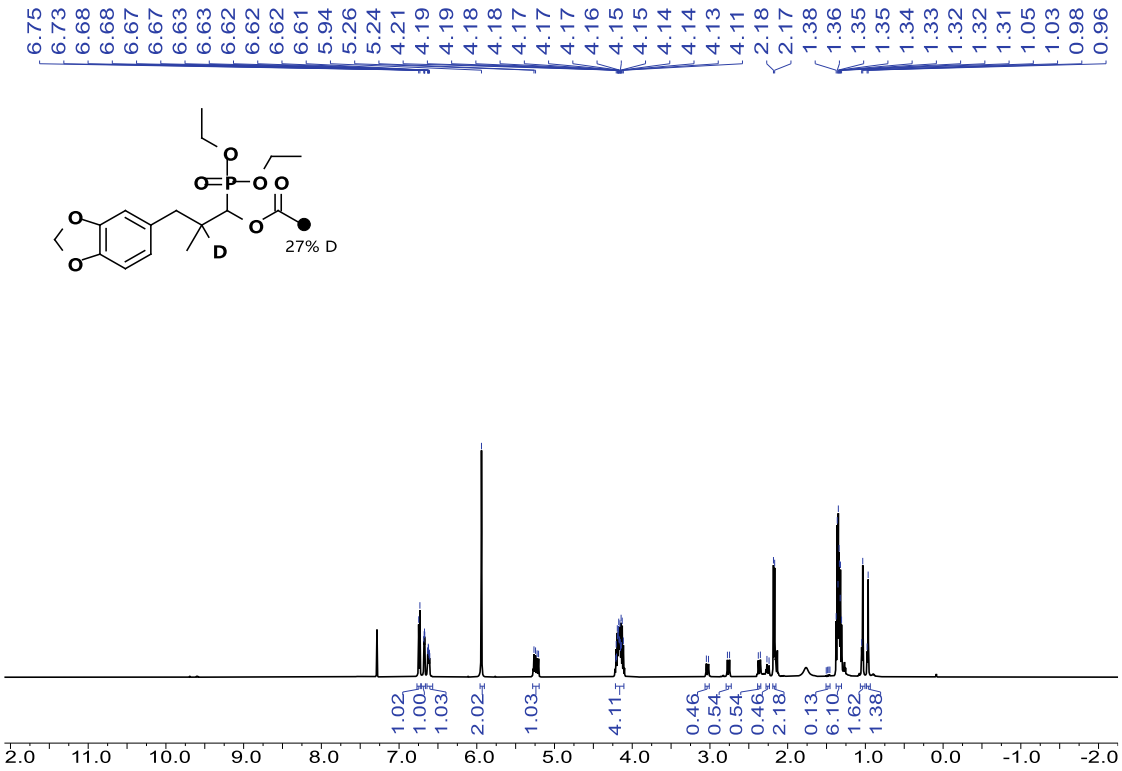
^{13}C NMR spectra of 22 (126 MHz, $CDCl_3$)



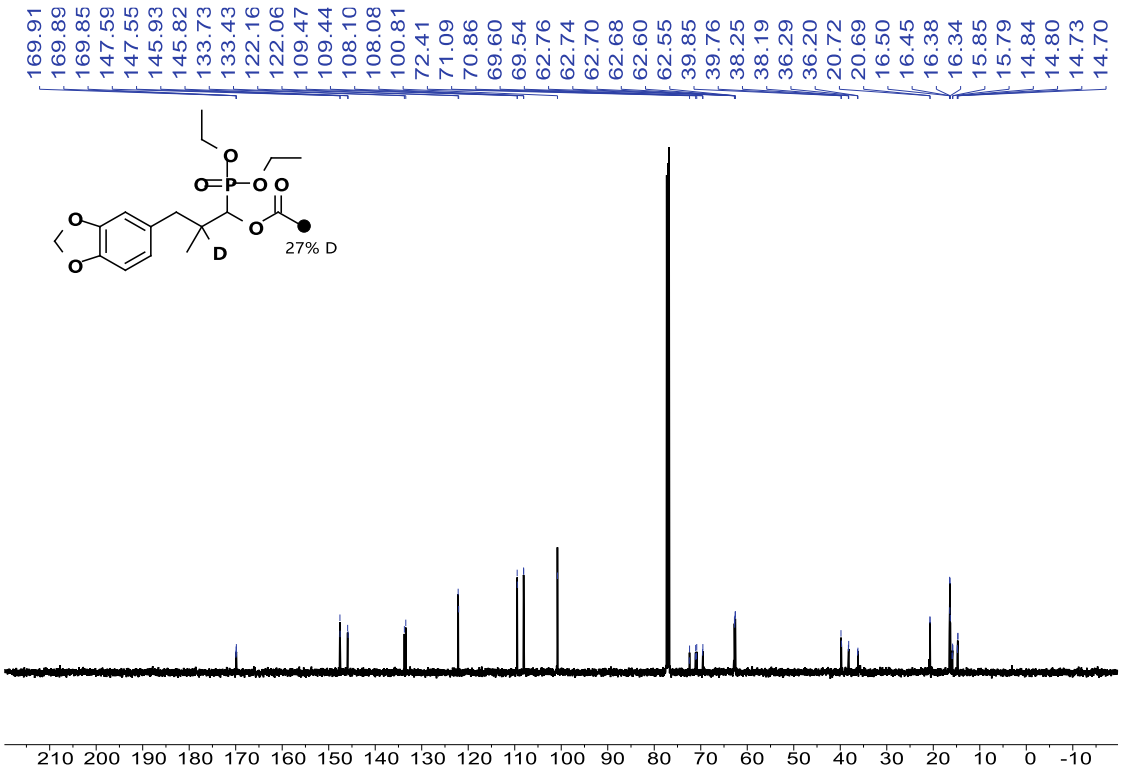
^{31}P NMR spectra of 22 (202 MHz, $CDCl_3$)



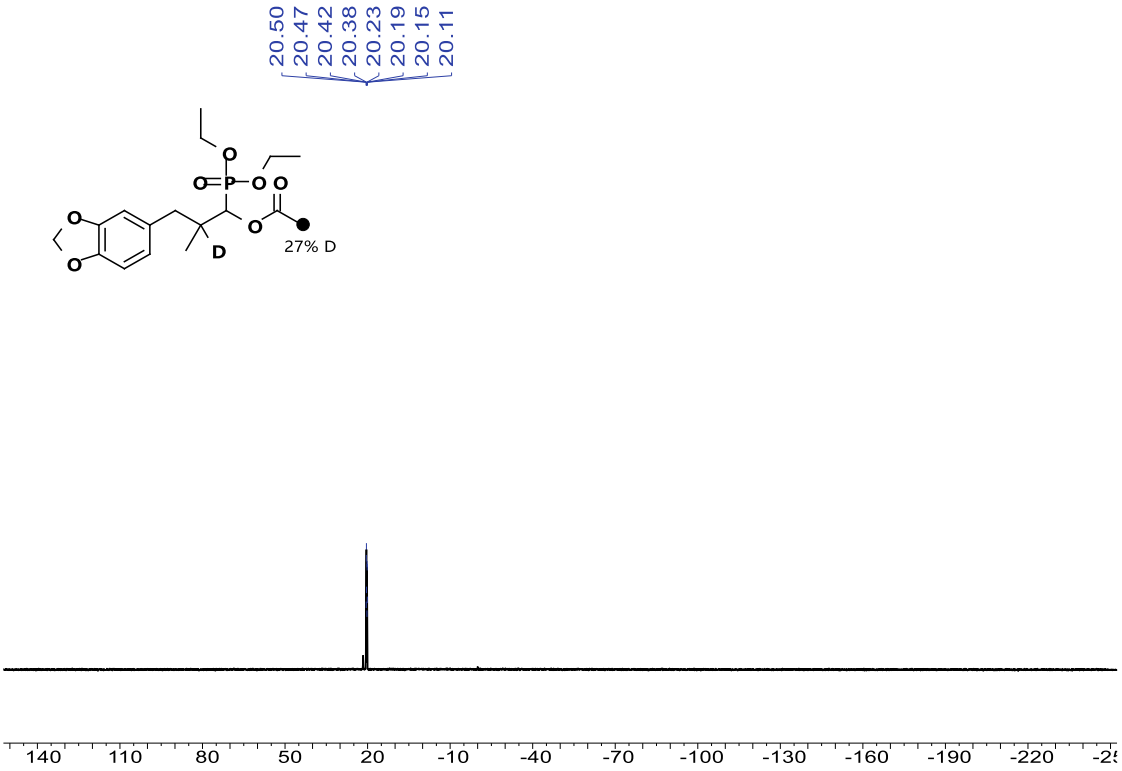
^{1}H NMR spectra of 23 (500 MHz, $CDCl_3$)



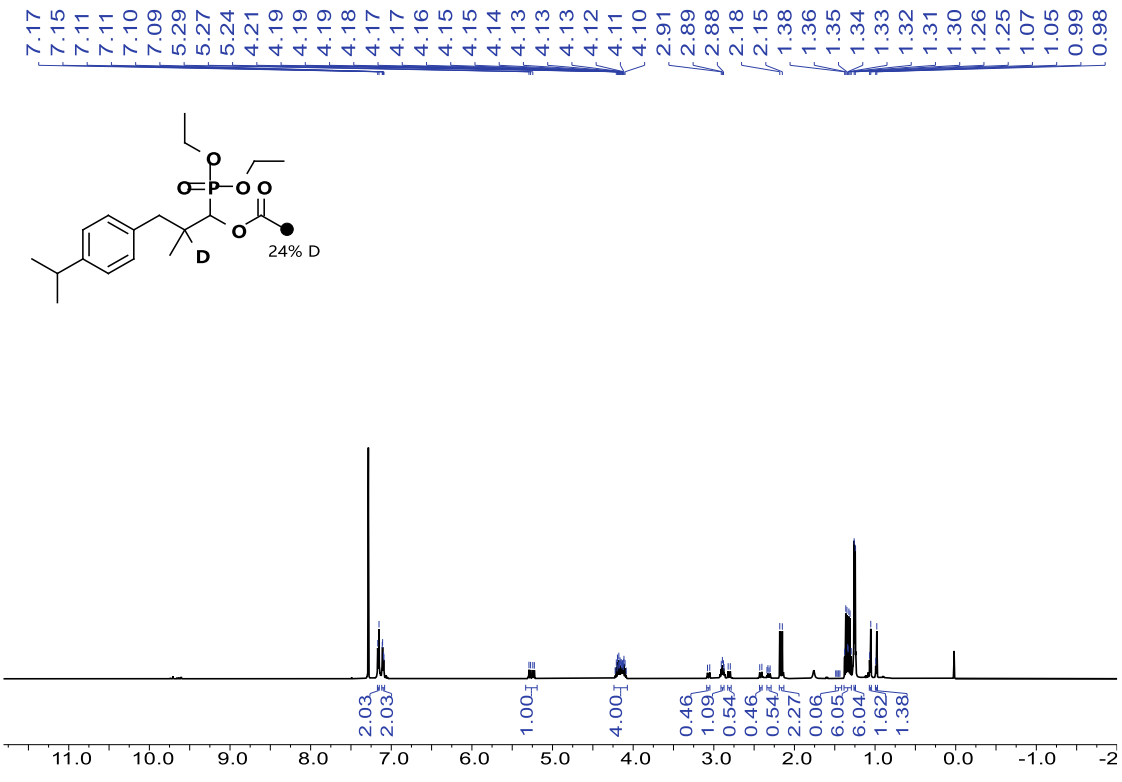
^{13}C NMR spectra of 23 (126 MHz, $CDCl_3$)



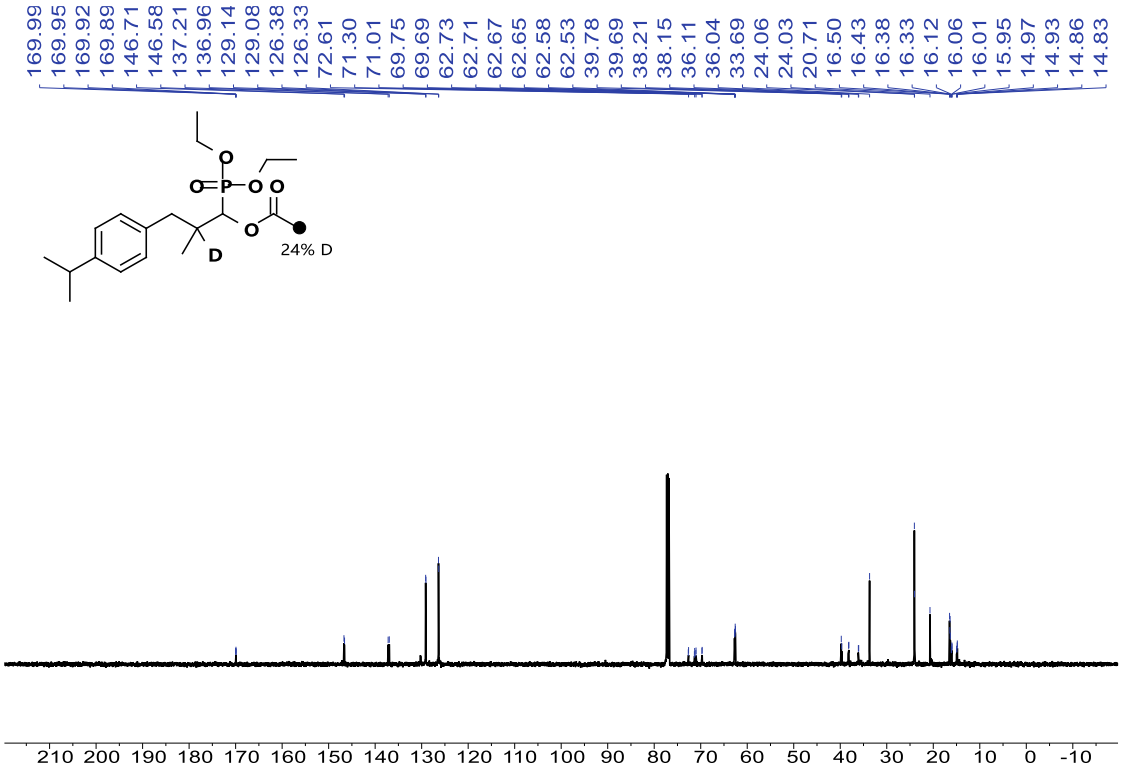
^{31}P NMR spectra of 23 (202 MHz, $CDCl_3$)



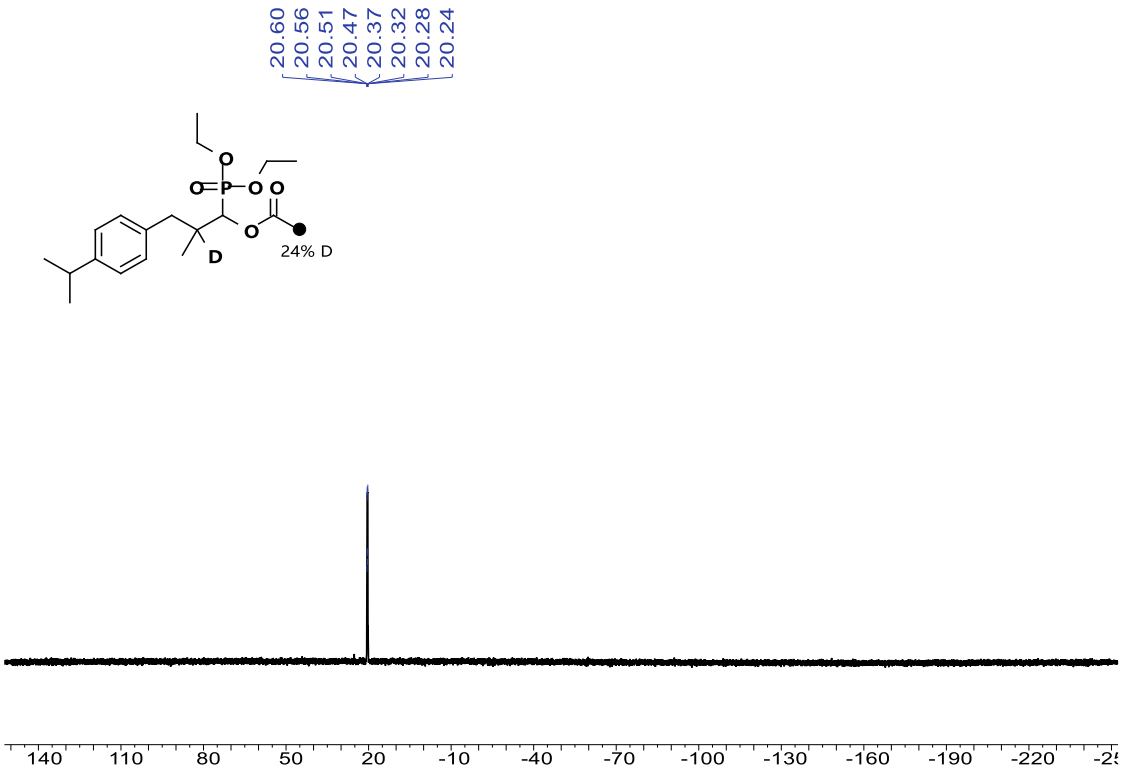
^{1}H NMR spectra of 24 (500 MHz, $CDCl_3$)



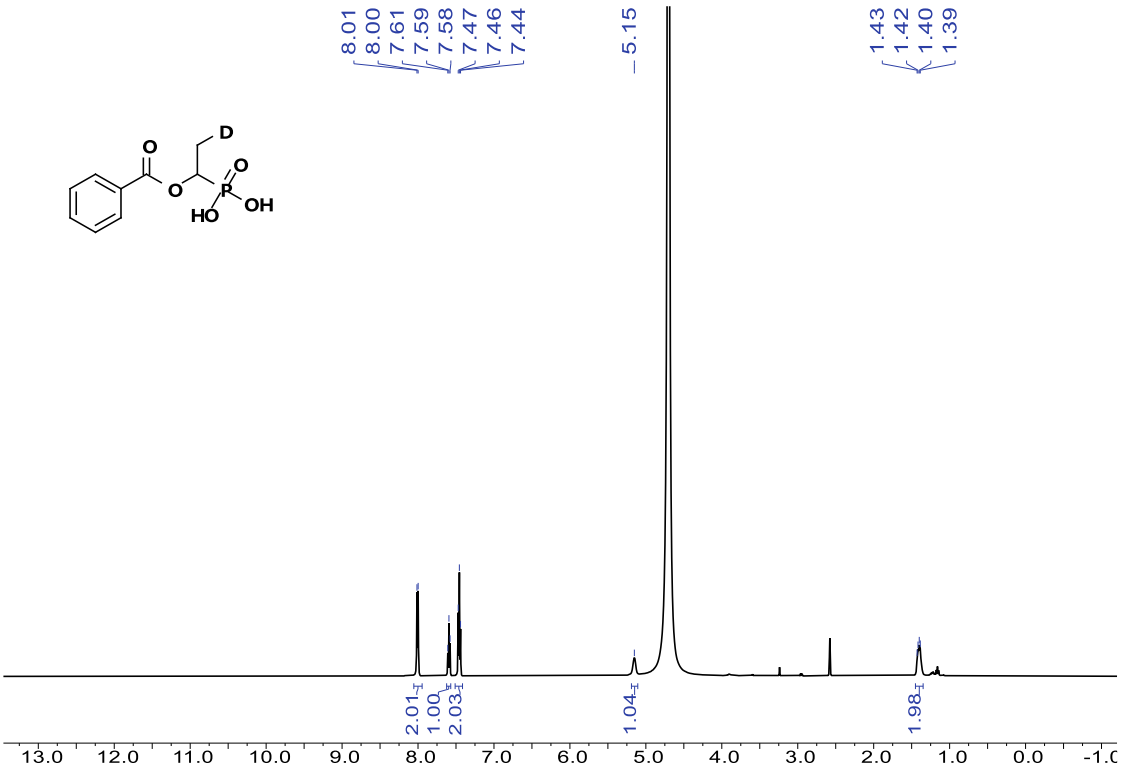
^{13}C NMR spectra of 24 (126 MHz, $CDCl_3$)



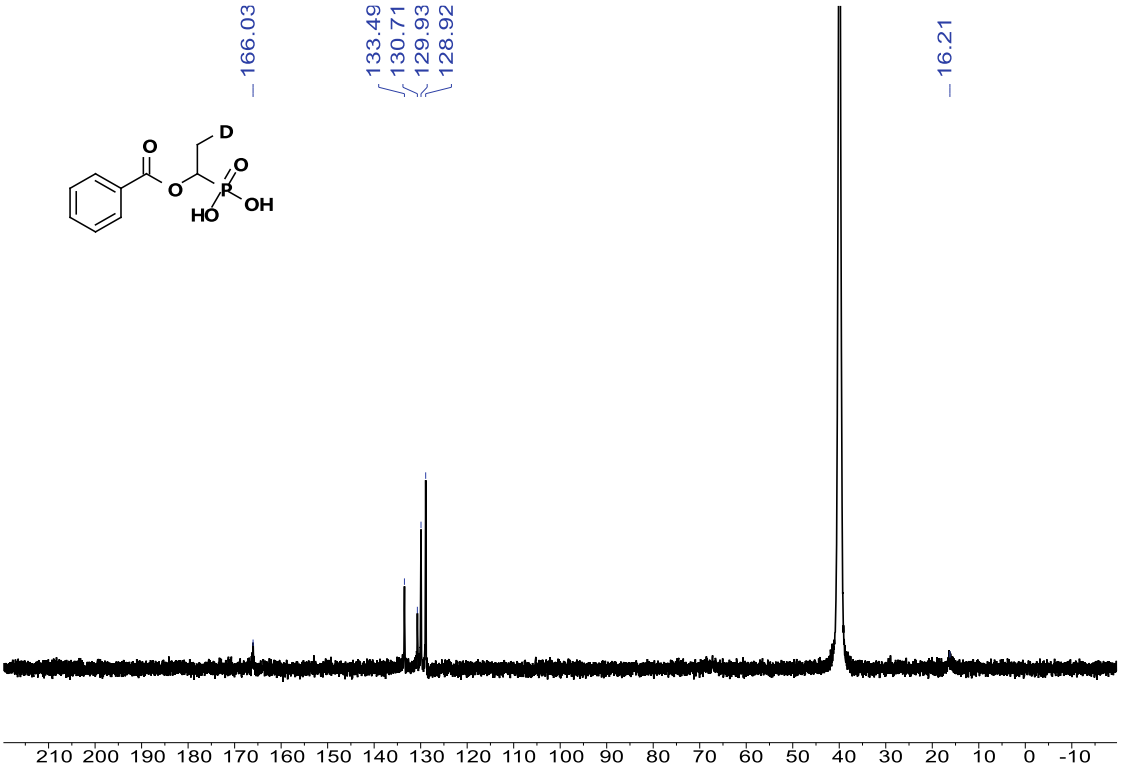
^{31}P NMR spectra of 24 (202 MHz, $CDCl_3$)



^{1}H NMR spectra of 27 (500 MHz, DMSO-d_6/D_2O = 1:3)



^{13}C NMR spectra of 27 (126 MHz, DMSO-d_6/D_2O = 1:3)



^{31}P NMR spectra of 27 (202 MHz, DMSO-d_6/D_2O = 1:3)