Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Nickel/Photoredox-Catalyzed Carbonylative Transformations of *α*-Phosphorus-, *α*-Sulfur-, *α*-Boron-Substituted Alkyl Halides

Le-Cheng Wang [a,b] and Xiao-Feng Wu *[a,b]

[a.] *Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 116023 Dalian, Liaoning, China. E-mail: xwu2020@dicp.ac.cn*

[b.] *Leibniz-Institut für Katalyse e.V., 18059 Rostock, Germany. E-mail: Xiao-Feng.Wu@catalysis.de*

Contents

1. General Information

Reagents, solvents, and analytical methods:

Unless otherwise noted, all reactions were carried out under carbon monoxide or nitrogen atmosphere. The reagents were ordered from Adamas-beta®, Energy Chemical, Sigma-Aldrich, Bidepharm and used without purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C), dichloromethane and ethyl acetate as eluent. All NMR spectra were recorded at ambient temperature using Bruker Avance III 400 MHz NMR (^{1}H, 400 MHz; ^{13}C {1H}, 101 MHz, ^{19}F 376 MHz), Bruker AVANCE III HD 700 MHz NMR spectrometers (^{1}H, 700 MHz; ^{13}C{1H}, 176 MHz). 1H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm; d_6-DMSO: 2.50 ppm) whereas 13C{1H} NMR spectra are reported relative to TMS via the carbon signals of the deuterated solvent ($CDCl_3$: 77.0 ppm; d_6-DMSO: 39.5 ppm. Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad), coupling constant (Hz), and integration. All ^{13}C NMR spectra were broad-band ^{1}H decoupled. All reactions were monitored by GC-FID or NMR analysis. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI-TOF) or Agilent 6540 Accurate-MS spectrometer (Q-TOF).

NOTE: Carbon monoxide should only be handled in a well-ventilated fume hood. The laboratory should be well-equipped with a CO detector and alarm system.

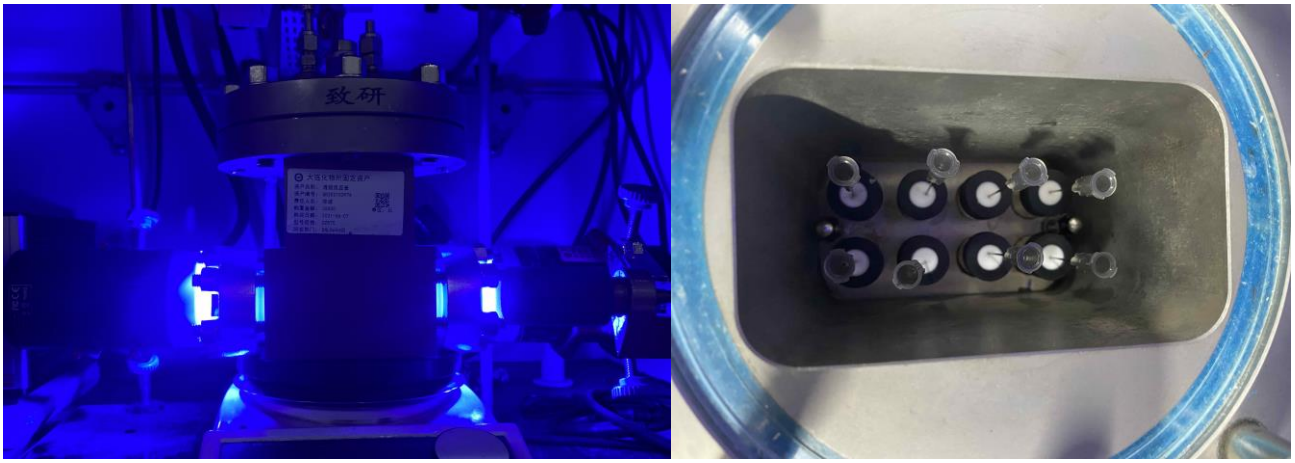
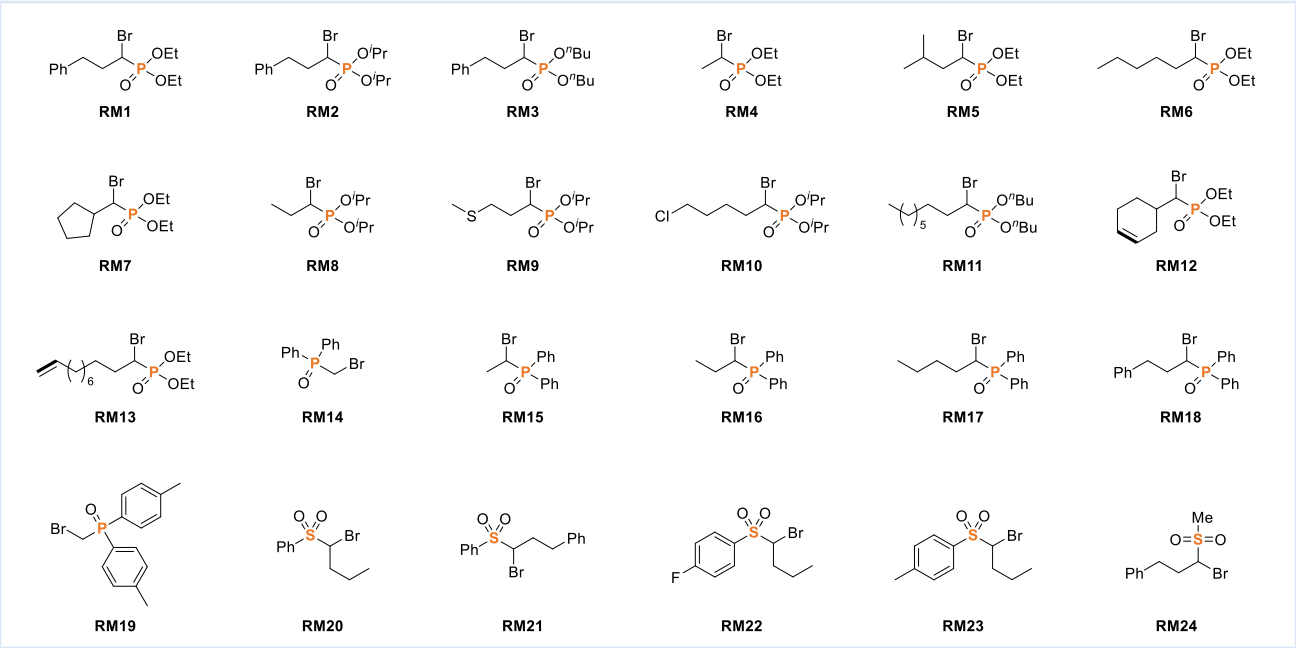
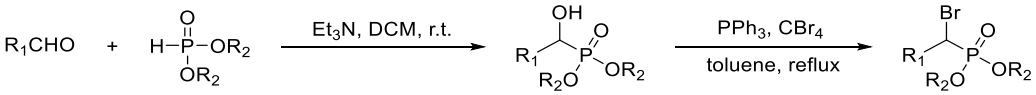


Figure S1. Photochemical Setup

2. Synthesis of the Starting Materials

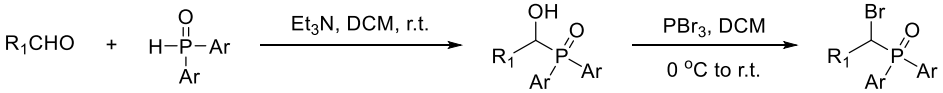


List of α-Heteroatom Phosphorus and Sulfur Alkyl Halides



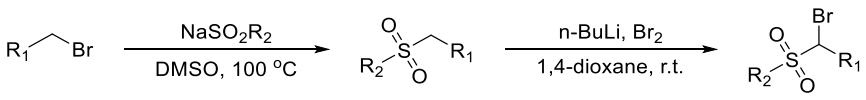
Preparation of α-Bromophosphonates

According to the reported literature, α-bromophosphonates (**RM1**-**RM13**) were conveniently synthesized in gram scale.[1-3]



Preparation of α-Bromoalkyldiarylphosphine Oxides

According to the reported literature, α-bromoalkyldiarylphosphine oxides (**RM14**-**RM19**) were conveniently synthesized in gram scale.[2-3]

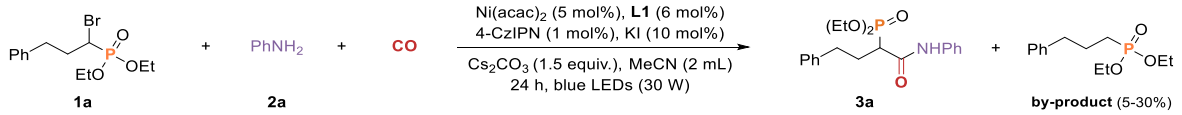


Preparation of α-Bromosulfones

According to the reported literature, α-bromosulfones (**RM20**-**RM24**) were conveniently synthesized in gram scale.[4]

3. Optimization of the Reaction Conditions

Table S1. Optimization of the Reaction Conditions



Entry	**1a** eq.	**2a** eq.	Catlyst	Ligand	PC	Base	Solcent	Yield %
1	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	MeCN	68
2	1.2	1	$NiBr_2$·DME	**L1**	4-CzIPN	Cs_2CO_3	MeCN	17
3	1.2	1	$Ni(TMHD)_2$	**L1**	4-CzIPN	Cs_2CO_3	MeCN	36
4	1.2	1	$Ni(OTf)_2$	**L1**	4-CzIPN	Cs_2CO_3	MeCN	10
5	1.2	1	NiI_2	**L1**	4-CzIPN	Cs_2CO_3	MeCN	8
6	1.2	1	$Ni(hfac)_2$	**L1**	4-CzIPN	Cs_2CO_3	MeCN	13
7	1.2	1	CuBr·DME	**L1**	4-CzIPN	Cs_2CO_3	MeCN	0
8	1.2	1	$Co(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	MeCN	0
9	1.2	1	$Ni(acac)_2$	**L2-L18**	4-CzIPN	Cs_2CO_3	MeCN	0-20
10	1.2	1	$Ni(acac)_2$	**L1**	Acr-$Mes^+ClO_4^-$	Cs_2CO_3	MeCN	2
11	1.2	1	$Ni(acac)_2$	**L1**	fac-$Ir(ppy)_3$	Cs_2CO_3	MeCN	59
12	1.2	1	$Ni(acac)_2$	**L1**	$Ru(bpy)_3Cl_2$ $6H_2O$	Cs_2CO_3	MeCN	17
13	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	Na_2CO_3	MeCN	53
14	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	K_3PO_4	MeCN	62
15	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	K_2HPO_4	MeCN	24
16	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	KOMe	MeCN	4

17	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	DiPEA	MeCN	0
18	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	NEt_3	MeCN	0
19	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	$PhCF_3$	62
20	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	THF	10
21	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	DMAc	0
22	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	DCE	0
23	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	Toluene	5
23	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	Dioxane	8
23	1.5	1	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	MeCN	75
23	1	1.2	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	MeCN	54
23	1	1.5	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	MeCN	60
24[b]	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	MeCN	60
25[c]	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	MeCN	87
26[d]	1.2	1	$Ni(acac)_2$	**L1**	4-CzIPN	Cs_2CO_3	MeCN	93

Reaction conditions: **1a** (1.2 mL), **2a** (0.2 mmol), $Ni(acac)_2$ (5 mol%), **L1** (6 mol%), 4-CzIPN (1 mol%), Cs_2CO_3 (1.5 equiv.), CO (10 bar), 30W blue LEDs, 18-25 °C, 24 h. isolated yields. [b]1 bar CO. [c]KI (1 equiv.). [d]KI (10 mol%).

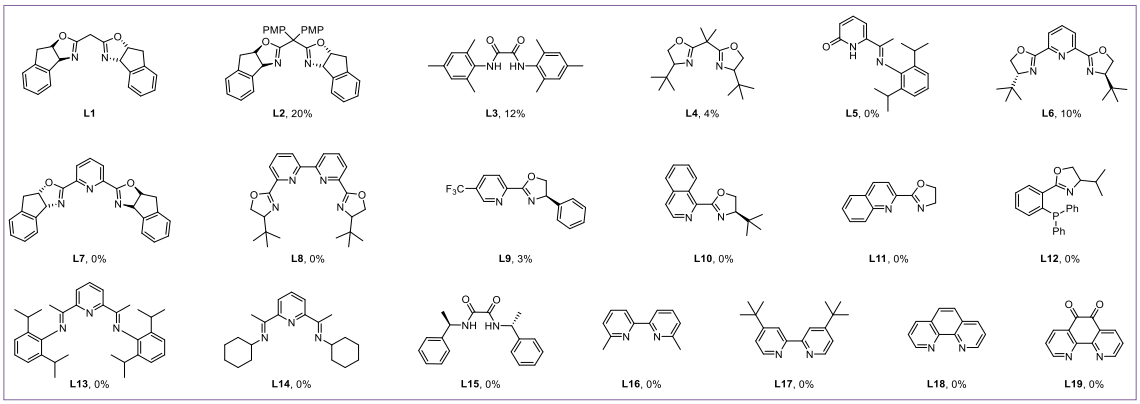
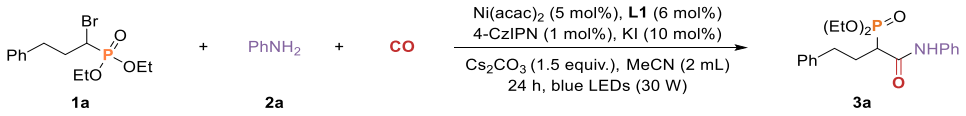


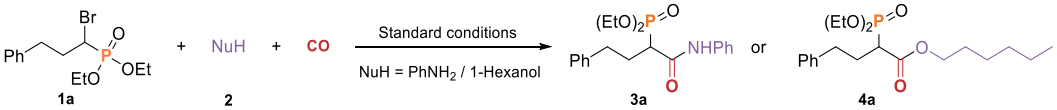
Table S2. Control reactions



Entry	Variation from standard conditions	Yield %
1	none	93
2	Without $Ni(acac)_2$	0
3	Without **L1**	0
4	Without 4-CzIPN	0
5	Without Cs_2CO_3	0
6	Without light	0

Reaction conditions: **1a** (1.2 mL), **2a** (0.2 mmol), $Ni(acac)_2$ (5 mol%), **L1** (6 mol%), 4-CzIPN (1 mol%), Cs_2CO_3 (1.5 equiv.), CO (10 bar), 30W blue LEDs, 18-25 °C, 24 h. isolated yields.

Table S3. Research on other methods and alkyl halides

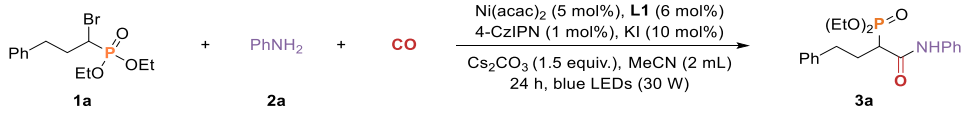


Entry	standard conditions	Yield %
1	none	93 (**3a**)
2	**1a** (2.5 equiv), NuH = $PhNH_2$ (0.3 mmol), $Pd(OAc)_2$ (5 mol%), Xantphos (5 mol%), Na_2CO_3 (1.5 equiv.), MeCN (1.5 mL), CO (6 bar), 50 °C, 18 h.[5]	0
3	**1a** (3 equiv), NuH = 1-hexanol (0.2 mmol), $Fe_3(CO)_{12}$ (7.5 mol%), 1,10-Phen (9 mol%), Cs_2CO_3 (3 equiv.), toliene (0.3 mL), CO (6 bar), 90 °C, 12 h.[6]	0
4	**1a** (0.25 mmol), NuH = 1-hexanol (0.25 mL), $Pd(PPh_3)_2Cl_2$ (5 mol%), IMes (10 mol%), Cs_2CO_3 (2 equiv.), *n*-heptane (0.25 mL), CO (2 bar), 50 °C, 24 h.[7]	0
5	**1a** (1.5 equiv), NuH = $PhNH_2$ (0.2 mmol), $CuBr(Me_2S)$ (10 mol%), bpy (10 mol%), Cs_2CO_3 (2 equiv.), 1,4-dioxane (2 mL), CO (40 bar), 110 °C, 15 h, w or w/o KI (1 equiv.).[8]	0

Reaction conditions: **1a** (1.2 mL), **2a** (0.2 mmol), $Ni(acac)_2$ (5 mol%), **L1** (6 mol%), 4-CzIPN (1 mol%), Cs_2CO_3 (1.5 equiv.), CO (10 bar), 30W blue LEDs, 18-25 °C, 24 h. isolated yields.

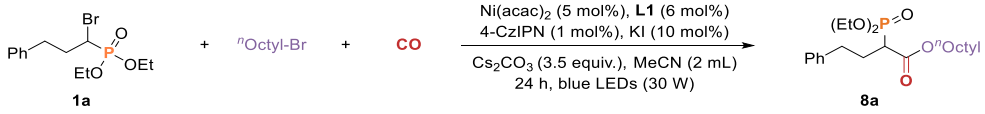
4. General Procedure

General procedure for carbonylation of *α*-bromo alkyl phosphates with nucleophiles



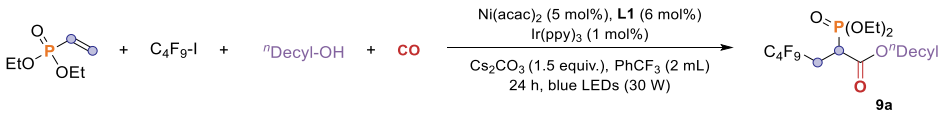
A 4 mL screw-cap vial was charged with $Ni(acac)_2$ (2.6 mg, 5 mol%), **L1** (4.0 mg, 6 mol%), 4-CzIPN (1.6 mg, 1 mol%), KI (3.3 mg, 10 mol%), Cs_2CO_3 (97.7 mg, 1.5 equiv.), and a stirring bar. The vial was closed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was evacuated under vacuum and recharged with nitrogen for three times. After MeCN (2 mL), *α*-bromo alkyl phosphate (1.2 equiv.), and nucleophiles (0.2 mmol) were added with a syringe under nitrogen atmosphere. The vials (usually 8) were placed on an alloy plate, which was transferred into an autoclave with two inserted quartz-glass windows. After the autoclave was flushed three times, it was pressurised with 10 bar of CO and then irradiated with 30 W blue LEDs at 18-25 °C for 24 h. After completed, the reaction mixture was directly purified by column chromatographyon silica gel using petroleum ether and ethyl acetate to afford the corresponding product.

General procedure for carbonylation of *α*-bromo alkyl phosphates with alkyl bromides



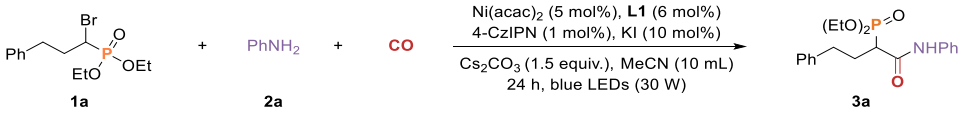
A 4 mL screw-cap vial was charged with $Ni(acac)_2$ (2.6 mg, 5 mol%), **L1** (4.0 mg, 6 mol%), 4-CzIPN (1.6 mg, 1 mol%), KI (3.3 mg, 10 mol%), Cs_2CO_3 (228.0 mg, 1.5 equiv.), and a stirring bar. The vial was closed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was evacuated under vacuum and recharged with nitrogen for three times. After MeCN (2 mL), *α*-bromo alkyl phosphate (1.2 equiv.), and alkyl bromides (0.2 mmol) were added with a syringe under nitrogen atmosphere. The vials (usually 8) were placed on an alloy plate, which was transferred into an autoclave with two inserted quartz-glass windows. After the autoclave was flushed three times, it was pressurised with 10 bar of CO and then irradiated with 30 W blue LEDs at 18-25 °C for 24 h. After completed, the reaction mixture was directly purified by column chromatographyon silica gel using petroleum ether and ethyl acetate to afford the corresponding product.

General procedure for four-component carbonylation of vinyl phosphonate



A 4 mL screw-cap vial was charged with $Ni(acac)_2$ (2.6 mg, 5 mol%), **L1** (4.0 mg, 6 mol%), 4-$Ir(ppy)_3$ (1.3 mg, 1 mol%), Cs_2CO_3 (97.7 mg, 1.5 equiv.), and a stirring bar. The vial was closed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was evacuated under vacuum and recharged with nitrogen for three times. After MeCN (2 mL), vinyl phosphonate (1.5 equiv.), alcohols (0.2 mmol) and alkyl iodides (2.5 equiv.) were added with a syringe under nitrogen atmosphere. The vials (usually 8) were placed on an alloy plate, which was transferred into an autoclave with two inserted quartz-glass windows. After the autoclave was flushed three times, it was pressurised with 10 bar of CO and then irradiated with 30 W blue LEDs at 18-25 ^oC for 24 h. After completed, the reaction mixture was directly purified by column chromatographyon silica gel using petroleum ether and ethyl acetate to afford the corresponding product.

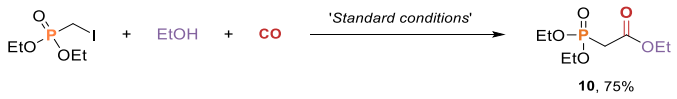
General procedure for 1 mmol scale synthesis



A 20 mL screw-cap vial was charged with $Ni(acac)_2$ (13 mg, 5 mol%), **L1** (20 mg, 6 mol%), 4-CzIPN (8 mg, 1 mol%), KI (16.5 mg, 10 mol%), Cs_2CO_3 (488.5 mg, 1.5 equiv.), and a stirring bar. The vial was closed by PTFE/white rubber septum and phenolic cap and connected with atmosphere with a needle. The vial was evacuated under vacuum and recharged with nitrogen for three times. After MeCN (10 mL), *α*-bromo alkyl phosphate (400.8 mg, 1.2 equiv.), and aniline (93.1 mg, 1 mmol) were added with a syringe under nitrogen atmosphere. The vial was placed on an alloy plate, which was transferred into an autoclave with two inserted quartz-glass windows. After the autoclave was flushed three times, it was pressurised with 10 bar of CO and then irradiated with 30 W blue LEDs at 18-25 ^oC for 24 h. After completed, the reaction mixture was directly purified by column chromatographyon silica gel using petroleum ether and ethyl acetate to afford the corresponding product (0.27 g).

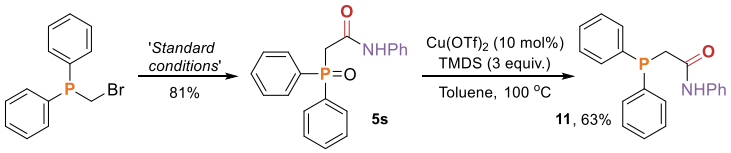
5. Synthetic applications.

Synthesis of Wittig-Horner reagent



A 4 mL screw-cap vial was charged with $Ni(acac)_2$ (2.6 mg, 5 mol%), **L1** (4.0 mg, 6 mol%), 4-CzIPN (1.6 mg, 1 mol%), Cs_2CO_3 (97.7 mg, 1.5 equiv.), and a stirring bar. The vial was closed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was evacuated under vacuum and recharged with nitrogen for three times. After $PhCF_3$ (2 mL), α-iodide alkyl phosphate (1.2 equiv.) and ethanol (0.2 mmol) were added with a syringe under nitrogen atmosphere. The vial was placed on an alloy plate, which was transferred into an autoclave with two inserted quartz-glass windows. After the autoclave was flushed three times, it was pressurised with 10 bar of CO and then irradiated with 30 W blue LEDs at 18-25 ^oC for 24 h. After completed, the reaction mixture was directly purified by column chromatographyon silica gel using petroleum ether and ethyl acetate to afford the corresponding Wittig-Horner reagent **10**.

Synthesis of P-ligand

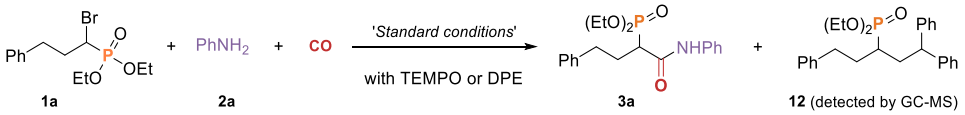


A 4 mL screw-cap vial was charged with $Ni(acac)_2$ (2.6 mg, 5 mol%), **L1** (4.0 mg, 6 mol%), 4-CzIPN (1.6 mg, 1 mol%), KI (3.3 mg, 10 mol%), Cs_2CO_3 (97.7 mg, 1.5 equiv.), and a stirring bar. The vial was closed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was evacuated under vacuum and recharged with nitrogen for three times. After MeCN (2 mL), α-bromo alkyl phosohine oxide (1.2 equiv.) and aniline (0.2 mmol) were added with a syringe under nitrogen atmosphere. The vials were placed on an alloy plate, which was transferred into an autoclave with two inserted quartz-glass windows. After the autoclave was flushed three times, it was pressurised with 10 bar of CO and then irradiated with 30 W blue LEDs at 18-25 ^oC for 24 h. After completed, the reaction mixture was directly purified by column chromatographyon silica gel using petroleum ether and ethyl acetate to afford the corresponding product **5s**.

According to the reported literature,[9] the diphenylphosphine oxide (83.8 mg, 0.25 mmol) and $Cu(OTf)_2$ (9 mg, 10 mol%) were added in a 10 mL schlenk tube at room temperature. TMDS (66.7 mg, 0.5 mmol) and toluene (2 mL) were added under argon flow. The reaction mixture was stirred for 2 h at 100 ^oC. After completed, the reaction mixture was directly purified by column chromatographyon silica gel using petroleum ether and ethyl acetate to afford the corresponding ligand **11**.

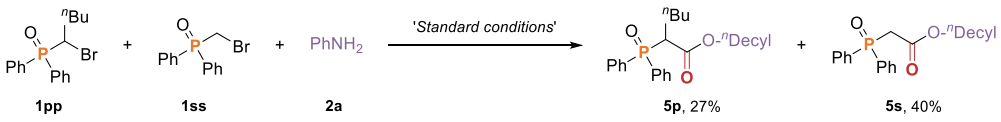
6. Mechanism Studies

Radical chain mechanism studies



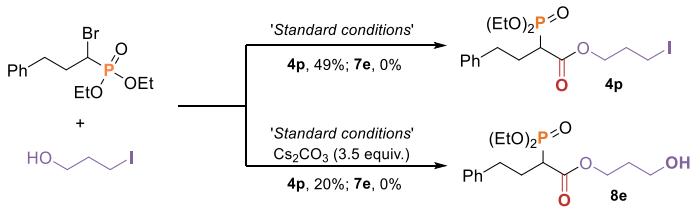
A 4 mL screw-cap vial was charged with $Ni(acac)_2$ (2.6 mg, 5 mol%), **L1** (4.0 mg, 6 mol%), 4-CzIPN (1.6 mg, 1 mol%), KI (3.3 mg, 10 mol%), Cs_2CO_3 (97.7 mg, 1.5 equiv.), TEMPO (2 equiv.) / DPE (2 equiv.), and a stirring bar. The vial was closed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was evacuated under vacuum and recharged with nitrogen for three times. After MeCN (2 mL), *α*-bromo alkyl phosphate (1.2 equiv.), and aniline (0.2 mmol) were added with a syringe under nitrogen atmosphere. The vials were placed on an alloy plate, which was transferred into an autoclave with two inserted quartz-glass windows. After the autoclave was flushed three times, it was pressurised with 10 bar of CO and then irradiated with 30 W blue LEDs at 18-25 °C for 24 h. After completed, the reaction results were detected by GC and GC-MS analysis.

7. Competition between primary and second α-phosphate halides



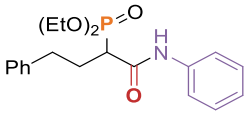
A 4 mL screw-cap vial was charged with $Ni(acac)_2$ (2.6 mg, 5 mol%), **L1** (4.0 mg, 6 mol%), 4-CzIPN (1.6 mg, 1 mol%), KI (3.3 mg, 10 mol%), Cs_2CO_3 (97.7 mg, 1.5 equiv.), and a stirring bar. The vial was closed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was evacuated under vacuum and recharged with nitrogen for three times. After MeCN (2 mL), *α*-bromo alkyl phosohine oxide **1pp** (1.2 equiv.) and **1ss** (1.2 equiv.), and aniline (0.2 mmol) were added with a syringe under nitrogen atmosphere. The vials were placed on an alloy plate, which was transferred into an autoclave with two inserted quartz-glass windows. After the autoclave was flushed three times, it was pressurised with 10 bar of CO and then irradiated with 30 W blue LEDs at 18-25 °C for 24 h. After completed, the reaction mixture was directly purified by column chromatographyon silica gel using petroleum ether and ethyl acetate to afford the corresponding products.

8. Testing the reactivity of 3-iodopropanol



A 4 mL screw-cap vial was charged with $Ni(acac)_2$ (2.6 mg, 5 mol%), **L1** (4.0 mg, 6 mol%), 4-CzIPN (1.6 mg, 1 mol%), KI (3.3 mg, 10 mol%), Cs_2CO_3 (condition a: 97.7 mg, 1.5 equiv. condition b: 228.0 mg, 3.5 equiv.), and a stirring bar. The vial was closed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was evacuated under vacuum and recharged with nitrogen for three times. After MeCN (2 mL), *α*-bromo alkyl phosphate (1.2 equiv.), and 3-iodopropanol (0.2 mmol) were added with a syringe under nitrogen atmosphere. The vials were placed on an alloy plate, which was transferred into an autoclave with two inserted quartz-glass windows. After the autoclave was flushed three times, it was pressurised with 10 bar of CO and then irradiated with 30 W blue LEDs at 18-25 °C for 24 h. After completed, the reaction mixture was directly purified by column chromatographyon silica gel using petroleum ether and ethyl acetate to afford the corresponding product.

9. Spectroscopic Data of Products



Diethyl (1-oxo-4-phenyl-1-(phenylamino)butan-2-yl)phosphonate (3a)

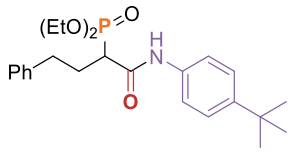
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (64.5 mg, 86% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.31 – 7.24 (m, 4H), 7.22 – 7.15 (m, 3H), 7.06 (t, *J* = 7.4 Hz, 1H), 4.27 – 3.93 (m, 4H), 3.01 – 2.93 (m, 1H), 2.93 – 2.84 (m, 1H), 2.72 – 2.54 (m, 1H), 2.54 – 2.30 (m, 1H), 2.20 – 2.02 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 140.7, 138.0, 128.8, 128.6, 128.5, 126.2, 124.2, 119.8, 63.2 (d, *J* = 6.7 Hz), 62.6 (d, *J* = 6.7 Hz), 45.8 (d, *J* = 129.0 Hz), 34.1 (d, *J* = 14.6 Hz), 28.5 (d, *J* = 4.3 Hz), 16.4 (d, *J* = 6.5 Hz), 16.3. (d, *J* = 6.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.42.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{27}NO_4P^+$ 376.1672; Found: 376.1678.



Diethyl (1-((4-(tert-butyl)phenyl)amino)-1-oxo-4-phenylbutan-2-yl)phosphonate (3b)

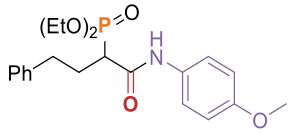
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (63.8 mg, 74% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.24 (m, 4H), 7.23 – 7.12 (m, 3H), 4.84 – 3.90 (m, 4H), 3.05 – 2.76 (m, 2H), 2.73 – 2.54 (m, 1H), 2.52 – 2.28 (m, 1H), 2.25 – 1.98 (m, 1H), 1.41 – 1.19 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 147.1, 140.8, 135.3, 128.6, 128.4, 126.1, 125.6, 119.6, 63.1 (d, *J* = 6.5 Hz), 62.6 (d, *J* = 6.4 Hz), 45.8 (d, *J* = 128.7 Hz), 34.3, 34.0 (d, *J* = 14.5 Hz), 31.3, 28.5 (d, *J* = 4.3 Hz), 16.4 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 6.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.49.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{35}NO_4P^+$ 432.2298; Found: 432.2305.



Diethyl (1-((4-methoxyphenyl)amino)-1-oxo-4-phenylbutan-2-yl)phosphonate (3c)

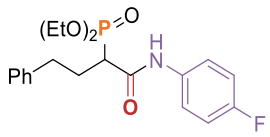
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:2) to afford the title compound as a brown liquid (34.0 mg, 42% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.38 – 7.22 (m, 2H), 7.22 – 6.91 (m, 3H), 6.81 (d, J = 9.0 Hz, 2H), 4.30 – 3.91 (m, 4H), 3.77 (s, 3H), 3.12 – 2.80 (m, 2H), 2.74 – 2.55 (m, 1H), 2.53 – 2.30 (m, 1H), 2.25 – 2.05 (m, 1H), 1.50 – 1.10 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 156.3, 140.8, 131.2, 128.6, 128.4, 126.1, 121.5, 114.0, 63.1 (d, *J* = 6.7 Hz), 62.6 (d, *J* = 6.8 Hz), 55.4, 45.7 (d, *J* = 129.0 Hz), 34.1 (d, *J* = 14.5 Hz), 28.5 (d, *J* = 4.4 Hz), 16.4 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 6.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.59.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{29}NO_5P^+$ 406.1778; Found: 406.1787.



Diethyl (1-((4-fluorophenyl)amino)-1-oxo-4-phenylbutan-2-yl)phosphonate (3d)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (55.0 mg, 70% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ^{31}P NMR, and HRMS.

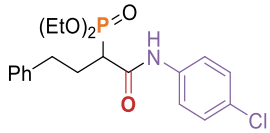
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.50 – 7.42 (m, 2H), 7.37 – 7.23 (m, 2H), 7.23 – 7.08 (m, 3H), 6.90 (t, *J* = 8.7 Hz, 2H), 4.26 – 4.09 (m, 2H), 4.08 – 3.88 (m, 2H), 3.07 – 2.92 (m, 1H), 2.89 – 2.73 (m, 1H), 2.73 – 2.54 (m, 1H), 2.54 – 2.29 (m, 1H), 2.18 – 1.96 (m, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4 (d, *J* = 2.5 Hz), 159.2 (d, *J* = 243.1 Hz), 140.7, 134.2 (d, *J* = 2.8 Hz), 128.6, 128.4, 126.2, 121.3 (d, *J* = 7.8 Hz), 115.3 (d, *J* = 22.4 Hz), 63.4 (d, *J* = 6.6 Hz), 62.4 (d, *J* = 6.8 Hz), 45.7 (d, *J* = 129.1 Hz), 34.1 (d, *J* = 15.0 Hz), 28.5 (d, *J* = 4.7 Hz), 16.4 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 6.0 Hz).

^{19}F NMR (**376 MHz, $CDCl_3$**) δ -118.54.

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.33.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{26}FNO_4P^+$ 394.1578; Found: 394.1582.



Diethyl (1-((4-chlorophenyl)amino)-1-oxo-4-phenylbutan-2-yl)phosphonate (3e)

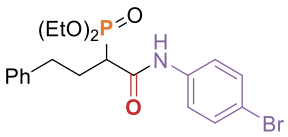
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (67.9 mg, 83% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 3H), 7.12 (d, *J* = 8.9 Hz, 2H), 4.28 – 4.09 (m, 2H), 4.09 – 3.75 (m, 2H), 3.35 – 2.94 (m, 1H), 2.94 – 2.75 (m, 1H), 2.69 – 2.51 (m, 1H), 2.51 – 2.31 (m, 1H), 2.26 – 1.96 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (d, *J* = 2.8 Hz), 140.7, 136.8, 128.8, 128.61, 128.56, 128.4, 126.1, 120.7, 63.5 (d, *J* = 6.6 Hz), 62.2 (d, *J* = 6.9 Hz), 45.9 (d, *J* = 129.4 Hz), 34.1 (d, *J* = 15.2 Hz), 28.5 (d, *J* = 4.8 Hz), 16.4 (d, *J* = 5.9 Hz), 16.2 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.14.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{26}ClNO_4P^+$ 410.1282; Found: 410.1286.



Diethyl (1-((4-bromophenyl)amino)-1-oxo-4-phenylbutan-2-yl)phosphonate (3f)

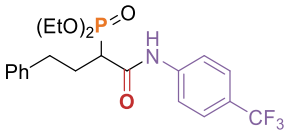
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (73.4 mg, 81% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.38 (d, *J* = 8.9 Hz, 2H), 7.33 – 7.23 (m, 4H), 7.23 – 7.11 (m, 3H), 4.33 – 4.08 (m, 2H), 4.06 – 3.84 (m, 2H), 3.28 – 2.92 (m, 1H), 2.91 – 2.73 (m, 1H), 2.62 – 2.52 (m, 1H), 2.51 – 2.37 (m, 1H), 2.26 – 1.95 (m, 1H), 1.34 (t, *J* = 7.0 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (d, *J* = 2.7 Hz), 140.7, 137.2, 131.6, 128.6, 128.4, 126.1, 121.0, 116.5, 63.5 (d, *J* = 6.7 Hz), 62.3 (d, *J* = 6.9 Hz), 45.9 (d, *J* = 129.0 Hz), 34.1 (d, *J* = 15.1 Hz), 28.5 (d, *J* = 4.8 Hz), 16.4 (d, *J* = 5.8 Hz), 16.3 (d, *J* = 6.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.16.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{26}BrNO_4P^+$ 454.0777; Found: 454.0781.



Diethyl (1-oxo-4-phenyl-1-((4-(trifluoromethyl)phenyl)amino)butan-2-yl)phosphonate (3g)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (61.1 mg, 69% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ^{31}P NMR, and HRMS.

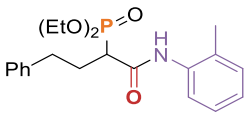
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.23 (m, 2H), 7.23 – 6.98 (m, 3H), 4.28 – 4.10 (m, 2H), 4.06 – 3.80 (m, 2H), 3.17 – 2.94 (m, 1H), 2.91 – 2.75 (m, 1H), 2.66 – 2.54 (m, 1H), 2.53 – 2.38 (m, 1H), 2.20 – 1.96 (m, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 141.2, 140.6, 128.6, 128.5, 127.2 (q, *J* = 271.4 Hz), 126.2, 125.9, 125.4, 119.0, 63.5 (d, *J* = 6.7 Hz), 62.3 (d, *J* = 6.9 Hz), 45.9 (d, *J* = 129.0 Hz), 34.1 (d, *J* = 15.1 Hz), 28.5 (d, *J* = 4.8 Hz), 16.4 (d, *J* = 5.8 Hz), 16.3 (d, *J* = 6.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.25.

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.01.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{26}F_3NO_4P^+$ 444.1546; Found: 444.1549.



Diethyl (1-oxo-4-phenyl-1-(*o*-tolylamino)butan-2-yl)phosphonate (3h)

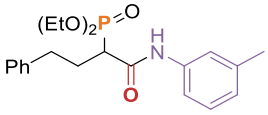
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (51.3 mg, 66% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.25 – 7.16 (m, 5H), 7.07 (t, *J* = 7.5 Hz, 1H), 4.53 – 3.98 (m, 4H), 3.01 – 2.86 (m, 2H), 2.83 – 2.60 (m, 1H), 2.48 – 2.35 (m, 1H), 2.33 (s, 3H), 2.27 – 2.06 (m, 1H), 1.34 – 1.26 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (d, *J* = 1.9 Hz), 140.7, 135.8, 130.5, 129.0, 128.6, 128.5, 126.6, 126.2, 125.0, 122.5, 63.0 (d, *J* = 6.9 Hz), 62.8 (d, *J* = 6.8 Hz), 45.6 (d, *J* = 128.5 Hz), 34.1 (d, *J* = 14.2 Hz), 28.7 (d, *J* = 4.3 Hz), 16.4 (d, *J* = 4.3 Hz), 16.3 (d, *J* = 4.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.89.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{29}NO_4P^+$ 390.1829; Found: 390.1834.



Diethyl (1-oxo-4-phenyl-1-(m-tolylamino)butan-2-yl)phosphonate (3i)

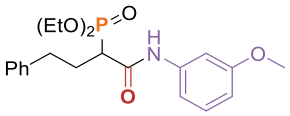
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (63.8 mg, 82% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.38 – 7.31 (m, 2H), 7.31 – 7.24 (m, 2H), 7.23 – 7.15 (m, 3H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 4.28 – 4.11 (m, 2H), 4.11 – 3.90 (m, 2H), 3.17 – 2.91 (m, 1H), 2.91 – 2.75 (m, 1H), 2.74 – 2.55 (m, 1H), 2.56 – 2.35 (m, 1H), 2.28 (s, 3H), 2.19 – 1.99 (m, 1H), 1.32 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (d, *J* = 2.5 Hz), 140.8, 138.6, 137.9, 128.62, 128.57, 128.4, 126.1, 124.9, 120.3, 116.8, 63.2 (d, *J* = 6.8 Hz), 62.5 (d, *J* = 6.7 Hz), 45.8 (d, J = 128.8 Hz), 34.1 (d, *J* = 14.9 Hz), 28.5 (d, *J* = 4.7 Hz), 21.4, 16.4 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.43.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{29}NO_4P^+$ 390.1829; Found: 390.1835.



Diethyl (1-((3-methoxyphenyl)amino)-1-oxo-4-phenylbutan-2-yl)phosphonate (3j)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:2) to afford the title compound as a brown liquid

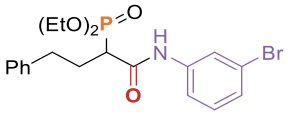
(64.0 mg, 79% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 7.31 – 7.24 (m, 2H), 7.24 – 7.13 (m, 4H), 7.13 – 6.99 (m, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 4.23 – 4.09 (m, 2H), 4.09 – 3.89 (m, 2H), 3.75 (s, 3H), 3.10 – 2.95 (m, 1H), 2.94 – 2.77 (m, 1H), 2.70 – 2.55 (m, 1H), 2.53 – 2.29 (m, 1H), 2.21 – 2.00 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4 (d, *J* = 2.8 Hz), 159.8, 140.7, 139.3, 129.3, 128.6, 128.4, 126.1, 111.8, 110.2, 104.9, 63.3 (d, *J* = 6.7 Hz), 62.3 (d, *J* = 6.8 Hz), 55.1, 45.9 (d, *J* = 129.2 Hz), 34.0 (d, *J* = 15.0 Hz), 28.5 (d, *J* = 4.6 Hz), 16.4 (d, *J* = 5.9 Hz), 16.2 (d, *J* = 6.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.31.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{29}NO_5P^+$ 406.1778; Found: 406.1781.



Diethyl (1-((3-bromophenyl)amino)-1-oxo-4-phenylbutan-2-yl)phosphonate(3k)

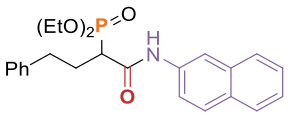
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (59.8 mg, 66% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.76 (t, *J* = 2.0 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.24 (m, 2H), 7.23 – 7.15 (m, 3H), 7.10 (d, *J* = 8.9 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 4.35 – 4.14 (m, 3H), 4.09 – 3.82 (m, 2H), 3.11 – 2.95 (m, 1H), 2.91 – 2.76 (m, 1H), 2.68 – 2.52 (m, 1H), 2.20 – 1.96 (m, 1H), 1.36 (t, *J* = 7.0 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 140.7, 139.4, 129.9, 128.64, 128.60, 128.4, 126.8, 126.1, 122.3, 117.8, 63.6 (d, *J* = 6.5 Hz), 62.3 (d, *J* = 6.7 Hz), 45.8 (d, *J* = 129.0 Hz), 34.0 (d, *J* = 15.2 Hz), 28.5 (d, *J* = 5.0 Hz), 16.4 (d, *J* = 5.8 Hz), 16.3 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.14.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{26}BrNO_4P^+$ 454.0777; Found: 454.0782



Diethyl (1-(naphthalen-2-ylamino)-1-oxo-4-phenylbutan-2-yl)phosphonate (3l)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (73.1 mg, 86% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

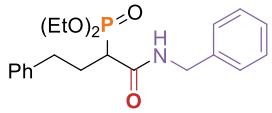
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.19 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.42 (d, *J* = 8.9 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.23 (m, 3H), 7.22 – 7.14 (m, 3H), 4.33 – 4.14 (m, 2H), 4.12 – 3.94 (m, 2H), 3.17 – 2.99 (m, 1H), 2.96 – 2.82 (m,

1H), 2.76 – 2.59 (m, 1H), 2.57 – 2.43 (m, 1H), 2.29 – 2.03 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ165.6 (d, *J* = 2.8 Hz), 140.8, 135.6, 133.6, 130.4, 128.6, 128.4, 128.3, 127.5, 127.3, 126.10, 126.09, 124.6, 119.6, 116.3, 63.4 (d, *J* = 6.7 Hz), 62.4 (d, *J* = 6.9 Hz), 46.0 (d, *J* = 128.9 Hz), 34.1 (d, *J* = 15.0 Hz), 28.6 (d, *J* = 4.7 Hz), 16.4 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.39.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{29}NO_4P^+$ 426.1829; Found: 426.1833.



Diethyl (1-(benzylamino)-1-oxo-4-phenylbutan-2-yl)phosphonate (3m)

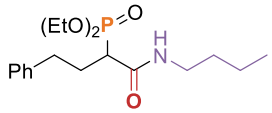
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (48.2 mg, 62% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 4.4 Hz, 4H), 7.30 – 7.24 (m, 3H), 7.23 – 7.14 (m, 3H), 6.79 (s, 1H), 4.60 – 4.41 (m, 2H), 4.19 – 3.90 (m, 4H), 2.87 – 2.78 (m, 1H), 2.77 – 2.69 (m, 1H), 2.68 – 2.54 (m, 1H), 2.45 – 2.22 (m, 1H), 2.18 – 2.00 (m, 1H), 1.30 – 1.19 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1 (d, *J* = 2.3 Hz), 140.7, 138.1, 128.58, 128.56, 128.4, 127.7, 127.4, 126.1, 62.7 (d, *J* = 6.8 Hz), 62.6 (d, *J* = 6.7 Hz), 45.1 (d, *J* = 129.5 Hz), 43.8, 34.0 (d, *J* = 14.8 Hz), 28.5 (d, *J* = 4.4 Hz), 16.3 (d, *J* = 2.2 Hz), 16.2 (d, *J* = 2.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.43.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{29}NO_4P^+$ 390.1829; Found: 390.1834.



Diethyl (1-(butylamino)-1-oxo-4-phenylbutan-2-yl)phosphonate (3n)

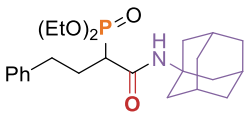
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:3) to afford the title compound as a brown liquid (59.6 mg, 84% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.23 – 7.12 (m, 3H), 6.49 (s, 1H), 4.20 – 3.92 (m, 4H), 3.47 – 3.07 (m, 2H), 3.00 – 2.77 (m, 1H), 2.77 – 2.52 (m, 2H), 2.41 – 2.19 (m, 1H), 2.15 – 2.00 (m, 1H), 1.57 – 1.47 (m, 2H), 1.45 – 1.34 (m, 2H), 1.34 – 1.23 (m, 6H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0 (d, *J* = 2.3 Hz), 140.8, 128.5, 128.4, 126.1, 62.7 (d, *J* = 6.8 Hz), 62.5 (d, *J* = 6.8 Hz), 45.1 (d, *J* = 129.4 Hz), 39.5, 34.0 (d, *J* = 14.7 Hz), 31.5, 28.6 (d, *J* = 4.4 Hz), 19.9, 16.34 (d, *J* = 3.1 Hz), 16.28 (d, *J* = 3.0 Hz), 13.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.83.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{31}NO_4P^+$ 356.1985; Found: 356.1991.



Diethyl (1-(((3s,5s,7s)-adamantan-1-yl)amino)-1-oxo-4-phenylbutan-2-yl)phosphonate (3o)

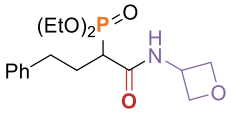
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:3) to afford the title compound as a brown liquid (66.7 mg, 77% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.24 – 7.14 (m, 3H), 6.03 (s, 1H), 4.36 – 3.87 (m, 4H), 2.86 – 2.75 (m, 1H), 2.72 – 2.48 (m, 2H), 2.39 – 2.17 (m, 1H), 2.15 – 1.99 (m, 10H), 1.77 – 1.62 (m, 6H), 1.33 – 1.23 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (d, *J* = 2.3 Hz), 141.0, 128.6, 128.4, 126.1, 62.6 (d, *J* = 6.7 Hz), 62.5 (d, *J* = 6.7 Hz), 52.3, 46.0 (d, *J* = 128.5 Hz), 41.4, 36.3, 34.0 (d, *J* = 14.9 Hz), 29.4, 28.7 (d, *J* = 4.3 Hz), 16.43 (d, *J* = 1.7 Hz), 16.57 (d, *J* = 1.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 26.04.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{37}NO_4P^+$ 434.2455; Found: 434.2460



Diethyl (1-(oxetan-3-ylamino)-1-oxo-4-phenylbutan-2-yl)phosphonate (3p)

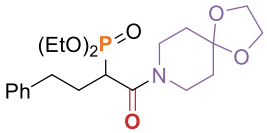
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/^{i}PrOH = 4:1) to afford the title compound as a brown liquid (44.7 mg, 63% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.38 – 7.24 (m, 2H), 7.24 – 7.00 (m, 3H), 5.09 – 4.96 (m, 1H), 4.96 – 4.84 (m, 2H), 4.53 (t, *J* = 6.4 Hz, 2H), 4.33 – 3.97 (m, 4H), 2.97 – 2.69 (m, 2H), 2.69 – 2.43 (m, 1H), 2.42 – 2.24 (m, 1H), 2.16 – 1.95 (m, 1H), 1.36 – 1.26 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0 (d, *J* = 2.5 Hz), 140.6, 128.5, 128.4, 126.2, 78.2, 78.0, 63.0 (d, *J* = 6.7 Hz), 62.5 (d, *J* = 6.7 Hz), 45.1, 44.8 (d, *J* = 129.9 Hz), 34.0 (d, *J* = 14.5 Hz), 28.2 (d, *J* = 4.7 Hz), 16.31 (d, *J* = 3.8 Hz), 16.26 (d, *J* = 3.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 24.99.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{27}NO_5P^+$ 356.1621; Found: 356.1625.



Diethyl (1-oxo-4-phenyl-1-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)butan-2-yl)phosphonate (3q)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/^{i}PrOH = 7:3) to afford the title compound as a brown liquid

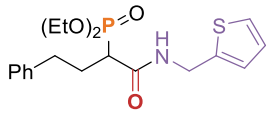
(62.1 mg, 73% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 6.8 Hz, 2H), 4.19 – 4.04 (m, 4H), 3.97 (s, 4H), 3.90 – 3.68 (m, 2H), 3.57 – 3.35 (m, 2H), 3.32 – 3.13 (m, 1H), 3.00 – 2.70 (m, 1H), 2.59 – 2.40 (m, 2H), 2.31 – 2.08 (m, 1H), 1.87 – 1.73 (m, 1H), 1.69 (q, *J* = 5.6, 5.2 Hz, 2H), 1.61 – 1.51 (m, 1H), 1.37 – 1.17 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (d, *J* = 4.5 Hz), 140.5, 128.6, 128.4, 126.2, 106.8, 64.4, 62.6 (d, *J* = 4.2 Hz), 62.5 (d, *J* = 4.4 Hz), 44.4, 40.4, 40.1 (d, *J* = 132.9 Hz), 35.2, 34.8, 33.8 (d, *J* = 15.7 Hz), 28.8 (d, *J* = 4.4 Hz), 16.41 (d, *J* = 2.8 Hz), 16.35 (d, *J* = 3.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 24.11.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{33}NO_6P^+$ 426.2040; Found: 426.2044.



Diethyl (1-oxo-4-phenyl-1-((thiophen-2-ylmethyl)amino)butan-2-yl)phosphonate (3r)

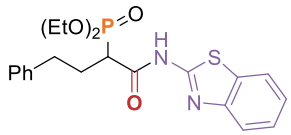
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (59.3 mg, 75% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.23 – 7.14 (m, 4H), 7.03 – 6.98 (m, 1H), 6.97 – 6.90 (m, 1H), 6.83 (s, 1H), 4.65 (d, *J* = 5.7 Hz, 2H), 4.36 – 3.89 (m, 4H), 2.87 – 2.67 (m, 2H), 2.67 – 2.54 (m, 1H), 2.43 – 2.22 (m, 1H), 2.18 – 1.97 (m, 1H), 1.35 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0 (d, *J* = 2.3 Hz), 140.72, 140.68, 128.6, 128.4, 126.8, 126.1, 126.1, 125.1, 62.8 (d, *J* = 6.8 Hz), 62.7 (d, *J* = 6.8 Hz), 45.0 (d, *J* = 129.6 Hz), 38.5, 34.0 (d, *J* = 14.5 Hz), 28.5 (d, *J* = 4.3 Hz), 16.32 (d, *J* = 2.6 Hz), 16.26 (d, *J* = 2.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.25.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{27}NO_4SP^+$ 396.1393; Found: 396.1401.

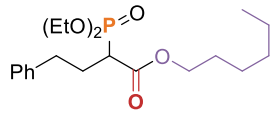


Diethyl (1-(benzo[d]thiazol-2-ylamino)-1-oxo-4-phenylbutan-2-yl)phosphonate (3s)

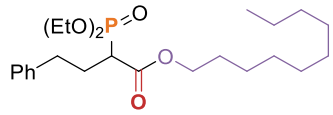
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:3) to afford the title compound as a brown liquid (63.1 mg, 73% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.36 (s, 1H), 7.74 – 7.55 (m, 2H), 7.38 – 7.28 (m, 1H), 7.28 – 7.21 (m, 2H), 7.21 – 7.09 (m, 4H), 4.34 – 4.13 (m, 2H), 4.16 – 3.79 (m, 2H), 3.35 – 3.10 (m, 1H), 3.00 – 2.68 (m, 1H), 2.68 – 2.43 (m, 2H), 2.31 – 2.05 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

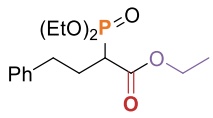
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4 (d, *J* = 3.7 Hz), 157.6, 148.4, 140.3, 132.1, 128.6, 128.5, 126.2, 125.8, 123.6, 121.0 (d, *J* = 2.3 Hz), 63.8 (d, *J* = 6.5 Hz), 62.8 (d, *J*= 6.6 Hz), 45.4 (d, *J* = 128.9 Hz), 34.0 (d, *J* = 14.6 Hz), 28.1 (d, *J* = 4.6 Hz), 16.4 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 5.9 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 22.98.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{26}N_2O_4SP^+$ 433.1345; Found: 433.1347.



Hexyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4a)
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (70.7 mg, 92% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and HRMS.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.24 – 7.12 (m, 3H), 4.32 – 3.99 (m, 6H), 3.03 – 2.85 (m, 1H), 2.84 – 2.65 (m, 1H), 2.65 – 2.52 (m, 1H), 2.44 – 2.24 (m, 1H), 2.24 – 2.00 (m, 1H), 1.75 – 1.61 (m, 2H), 1.44 – 1.21 (m, 12H), 1.05 – 0.80 (t, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1 (d, *J* = 5.0 Hz), 140.4, 128.5, 128.4, 126.2, 65.6, 62.7 (d, *J* = 6.2 Hz), 62.6 (d, *J* = 6.7 Hz), 45.0 (d, *J* = 130.9 Hz), 34.3 (d, *J* = 15.4 Hz), 31.4, 28.6 (d, *J* = 4.5 Hz), 28.5, 25.5, 22.5, 16.4 (d, *J* = 2.0 Hz), 16.3 (d, *J* = 2.1 Hz), 14.0.
^{31}P NMR (162 MHz, $CDCl_3$) δ 22.61.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{34}O_5P^+$ 385.2138; Found: 385.2145.



Decyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4b)
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (85.4 mg, 97% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and HRMS.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.24 – 7.07 (m, 3H), 4.17 – 4.03 (m, 6H), 3.03 – 2.89 (m, 1H), 2.79 – 2.68 (m, 1H), 2.64 – 2.52 (m, 1H), 2.40 – 2.24 (m, 1H), 2.22 – 2.08 (m, 1H), 1.72 – 1.62 (m, 2H), 1.46 – 1.16 (m, 20H), 0.92 – 0.84 (t, *J* = 6.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1 (d, *J* = 5.1 Hz), 140.4, 128.5, 128.4, 126.2, 65.6, 62.7 (d, *J* = 6.4 Hz), 62.6 (d, *J* = 6.7 Hz), 45.1 (d, *J* = 130.9 Hz), 34.3 (d, *J* = 15.3 Hz), 31.8, 29.5, 29.3, 29.2, 28.62 (d, *J* = 4.5 Hz), 28.56, 25.8, 22.6, 16.4 (d, *J* = 1.8 Hz), 16.3 (d, *J* = 2.0 Hz), 14.1.
^{31}P NMR (162 MHz, $CDCl_3$) δ 22.61.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{42}O_5P^+$ 441.2764; Found: 441.2770.



Ethyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4c)

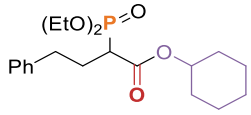
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (43.3 mg, 66% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.14 (m, 3H), 4.27 – 4.18 (m, 2H), 4.16 – 4.05 (m, 4H), 3.02 – 2.89 (m, 1H), 2.79 – 2.67 (m, 1H), 2.65 – 2.53 (m, 1H), 2.40 – 2.24 (m, 1H), 2.22 – 2.07 (m, 1H), 1.34 – 1.27 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0 (d, *J* = 5.1 Hz), 140.4, 128.5, 128.4, 126.2, 62.7 (d, *J* = 6.5 Hz), 62.6 (d, *J* = 6.8 Hz), 61.4, 45.0 (d, *J* = 130.9 Hz), 34.3 (d, *J* = 15.3 Hz), 28.6 (d, *J* = 4.7 Hz), 16.34 (d, *J* = 2.1 Hz), 16.28 (d, *J* = 2.3 Hz), 14.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.55.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{26}O_5P^+$ 329.1512; Found: 329.1512.



Cyclohexyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4d)

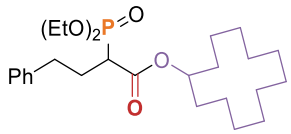
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (47.4 mg, 62% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.2 Hz, 2H), 7.25 – 7.14 (m, 3H), 5.00 – 4.80 (m, 1H), 4.26 – 4.02 (m, 4H), 3.04 – 2.86 (m, 1H), 2.83 – 2.68 (m, 1H), 2.64 – 2.52 (m, 1H), 2.41 – 2.23 (m, 1H), 2.23 – 2.06 (m, 1H), 1.99 – 1.84 (m, 2H), 1.80 – 1.72 (m, 2H), 1.65 – 1.23 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4 (d, *J* = 5.1 Hz), 140.5, 128.5, 128.4, 126.2, 73.7, 62.6 (d, *J* = 6.8 Hz), 62.5 (d, *J* = 7.4 Hz), 45.3 (d, *J* = 130.7 Hz), 34.3 (d, *J* = 15.6 Hz), 31.5, 31.4, 28.7 (d, *J* = 4.6 Hz), 25.3, 23.60, 23.58, 16.36 (d, *J* = 2.2 Hz), 16.30 (d, *J* = 2.3 Hz)

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.61.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{32}O_5P^+$ 383.1982; Found: 383.1983.



Cyclododecyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4e)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid

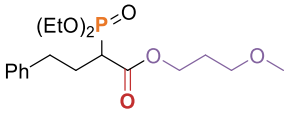
(81.1 mg, 87% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.14 (m, 3H), 5.23 – 5.07 (m, 1H), 4.21 – 4.03 (m, 4H), 2.99 – 2.86 (m, 1H), 2.80 – 2.68 (m, 1H), 2.63 – 2.51 (m, 1H), 2.39 – 2.23 (m, 1H), 2.21 – 2.06 (m, 1H), 1.81 – 1.68 (m, 2H), 1.58 – 1.51 (m, 2H), 1.49 – 1.21 (m, 24H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7 (d, *J* = 5.1 Hz), 140.5, 128.5, 128.4, 126.2, 73.5, 62.6 (d, *J* = 6.1 Hz), 62.5 (d, *J* = 6.4 Hz), 45.2 (d, *J* = 130.8 Hz), 34.3 (d, *J* = 15.8 Hz), 29.2, 29.1, 28.7 (d, *J* = 4.4 Hz), 23.9, 23.7, 23.44, 23.41, 23.26, 23.24, 21.03, 20.98, 16.4 (d, *J* = 2.6 Hz), 16.3 (d, *J* = 2.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.87.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{44}O_5P^+$ 467.2921; Found: 467.2926.



3-Methoxypropyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4f)

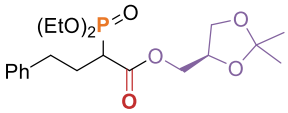
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:1) to afford the title compound as a colorless liquid (36.5 mg, 49% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 2H), 7.24 – 7.14 (m, 3H), 4.29 – 4.20 (m, 2H), 4.17 – 3.97 (m, 4H), 3.47 (t, *J* = 6.4 Hz, 2H), 3.34 (s, 3H), 3.03 – 2.89 (m, 1H), 2.79 – 2.66 (m, 1H), 2.65 – 2.53 (m, 1H), 2.40 – 2.24 (m, 1H), 2.23 – 2.07 (m, 1H), 1.99 – 1.86 (m, 2H), 1.36 – 1.23 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0 (d, *J* = 4.9 Hz), 140.4, 128.5, 128.4, 126.2, 68.9, 62.70 (d, *J* = 6.5 Hz), 62.58 (d, *J* = 6.4 Hz), 62.57, 58.7, 45.0 (d, *J* = 130.9 Hz), 34.3 (d, *J* = 15.2 Hz), 28.9, 28.6 (d, *J* = 4.5 Hz), 16.4, 16.3 (d, *J* = 1.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.52.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{30}O_6P^+$ 373.1775; Found:373.1777.



((R)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4g)

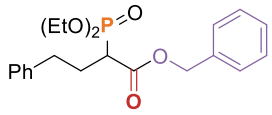
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a colorless liquid (35.6 mg, 43% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 2H), 7.25 – 7.13 (m, 3H), 4.38 – 4.28 (m, 1H), 4.27 – 4.00 (m, 7H), 3.83 – 3.73 (m, 1H), 3.07 – 2.93 (m, 1H), 2.79 – 2.66 (m, 1H), 2.66 – 2.54 (m, 1H), 2.40 – 2.24 (m, 1H), 2.24 – 2.08 (m, 1H), 1.44 (s, 3H), 1.37 (s, 3H), 1.35 – 1.26 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9 (d, *J* = 5.1 Hz), 140.3, 128.6, 128.5, 126.3, 109.8, 73.3, 66.4, 65.5, 65.4, 62.8 (d, *J* = 6.7 Hz), 62.7 (d, *J* = 7.7 Hz), 44.9 (d, *J* = 130.9 Hz), 34.3 (d, *J* = 15.1 Hz), 28.6 (d, *J* = 4.6 Hz), 26.8, 25.3, 16.31, 16.27.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.11.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{32}O_7P^+$ 415.1880; Found: 415.1885.



Benzyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4h)

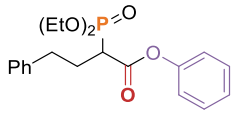
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (53.8 mg, 69% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H), 7.25 (t, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 6.7 Hz, 2H), 5.20 (s, 2H), 4.62 – 3.87 (m, 4H), 3.07 – 2.91 (m, 1H), 2.75 – 2.63 (m, 1H), 2.61 – 2.49 (m, 1H), 2.41 – 2.25 (m, 1H), 2.24 – 2.08 (m, 1H), 1.38 – 1.21 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9 (d, *J* = 5.1 Hz), 140.3, 135.5, 128.53, 128.50, 128.4, 128.3, 126.2, 67.1, 62.72 (d, *J* = 6.4 Hz), 62.67 (d, *J* = 6.8 Hz) , 45.0 (d, *J* = 130.9 Hz), 34.2 (d, *J* = 15.1 Hz), 28.6 (d, *J* = 4.6 Hz), 16.3 (d, *J* = 5.6 Hz), 16.2 (d, *J* = 5.7 Hz)

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.26.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{28}O_5P^+$ 391.1669; Found: 391.1672.



Phenyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4j)

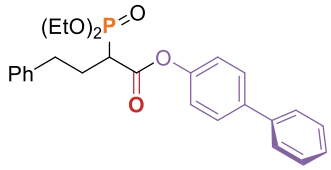
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (63.2 mg, 84% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.15 (m, 4H), 7.11 (d, *J* = 7.3 Hz, 2H), 4.28 – 4.09 (m, 4H), 3.46 – 3.10 (m, 1H), 2.92 – 2.80 (m, 1H), 2.78 – 2.66 (m, 1H), 2.52 – 2.36 (m, 1H), 2.34 – 2.19 (m, 1H), 1.38 – 1.29 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 (d, *J* = 5.4 Hz), 150.6, 140.2, 129.5, 128.58, 128.56, 126.4, 126.1, 121.3, 63.0 (d, *J* = 6.4 Hz), 62.9 (d, *J* = 6.7 Hz), 45.1 (d, *J* = 129.9 Hz), 34.3 (d, *J* = 15.0 Hz), 28.6 (d, *J* = 4.5 Hz), 16.4 (d, *J* = 1.4 Hz), 16.4 (d, *J* = 1.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 21.77.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{26}O_5P^+$ 377.1512; Found: 377.1513.



[1,1'-Biphenyl]-4-yl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4k)

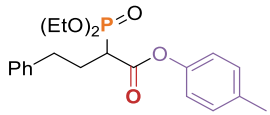
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (56.0 mg, 62% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.49 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.29 (m, 3H), 7.27 – 7.16 (m, 5H), 4.27 – 4.10 (m, 4H), 3.37 – 3.11 (m, 1H), 2.99 – 2.82 (m, 1H), 2.79 – 2.67 (m, 1H), 2.59 – 2.38 (m, 1H), 2.38 – 2.19 (m, 1H), 1.41 – 1.21 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9 (d, *J* = 5.5 Hz), 150.0, 140.3, 140.2, 139.3, 128.8, 128.59, 128.57, 128.2, 127.4, 127.1, 126.4, 121.6, 63.1 (d, *J* = 6.4 Hz), 62.9 (d, *J* = 6.8 Hz), 45.2 (d, *J* = 130.0 Hz), 34.4 (d, *J* = 15.0 Hz), 28.6 (d, *J* = 4.5 Hz), 16.42, 16.36.

^{31}P NMR (162 MHz, $CDCl_3$) δ 21.73.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{30}O_5P^+$ 453.1825; Found: 453.1828.



***p*-Tolyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4l)**

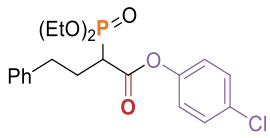
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (53.8 mg, 69% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.16 (m, 5H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.28 – 4.02 (m, 4H), 3.28 – 3.12 (m, 1H), 2.91 – 2.79 (m, 1H), 2.78 – 2.66 (m, 1H), 2.56 – 2.37 (m, 1H), 2.35 (s, 3H), 2.31 – 2.15 (m, 1H), 1.44 – 1.24 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0 (d, *J* = 5.3 Hz), 148.4, 140.2, 135.7, 129.9, 128.6, 128.5, 126.3, 121.0, 63.0 (d, *J* = 6.5 Hz), 62.9 (d, *J* = 6.9 Hz), 45.1 (d, *J* = 129.9 Hz), 34.3 (d, *J* = 15.0 Hz), 28.6 (d, *J* = 4.5 Hz), 20.8, 16.4 (d, *J* = 1.7 Hz), 16.3 (d, *J* = 1.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 21.83.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{28}O_5P^+$ 391.1669; Found: 391.1675.



4-Chlorophenyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4m)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid

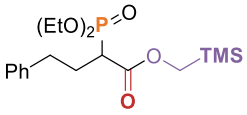
(49.2 mg, 60% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 4H), 7.26 – 7.19 (m, 3H), 7.04 (d, *J* = 8.9 Hz, 2H), 4.27 – 4.09 (m, 4H), 3.25 – 3.12 (m, 1H), 2.97 – 2.78 (m, 1H), 2.76 – 2.65 (m, 1H), 2.54 – 2.35 (m, 1H), 2.32 – 2.14 (m, 1H), 1.48 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7 (d, *J* = 5.5 Hz), 149.1, 140.1, 131.5, 129.5, 128.6, 126.4, 122.7, 63.1 (d, *J* = 6.4 Hz), 62.9 (d, *J* = 6.9 Hz), 45.1 (d, J = 129.8 Hz), 34.3 (d, *J* = 14.8 Hz), 28.5 (d, *J* = 4.7 Hz), 16.4, 16.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ 21.53.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{25}ClO_5P^+$ 411.1123; Found: 411.1128.



(Trimethylsilyl)methyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4n)

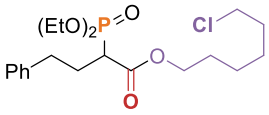
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 5:2) to afford the title compound as a colorless liquid (47.9 mg, 62% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.12 (m, 2H), 7.12 – 7.01 (m, 3H), 4.12 – 3.91 (m, 4H), 3.75 (d, *J* = 3.2 Hz, 2H), 2.92 – 2.78 (m, 1H), 2.67 – 2.55 (m, 1H), 2.51 – 2.39 (m, 1H), 2.28 – 2.13 (m, 1H), 2.10 – 1.95 (m, 1H), 1.33 – 0.99 (m, 6H), 0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7 (d, *J* = 5.1 Hz), 140.4, 128.5, 128.4, 126.2, 62.6 (d, J = 4.0 Hz), 62.5 (d, *J* = 4.3 Hz), 59.0, 45.0 (d, *J* = 131.3 Hz), 34.3 (d, *J* = 15.5 Hz), 28.7 (d, J = 4.4 Hz), 16.4, 16.3, -3.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.90.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{32}O_5PSi^+$ 387.1751; Found: 387.1756.



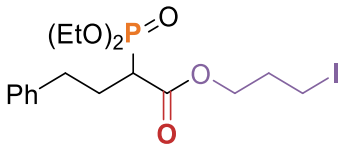
6-Chlorohexyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4o)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (63.6 mg, 76% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and HRMS.

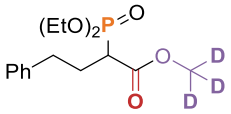
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.13 (m, 3H), 4.24 – 4.02 (m, 6H), 3.53 (t, *J* = 6.6 Hz, 2H), 3.03 – 2.89 (m, 1H), 2.79 – 2.67 (m, 1H), 2.65 – 2.53 (m, 1H), 2.40 – 2.23 (m, 1H), 2.23 – 2.07 (m, 1H), 1.83 – 1.63 (m, 4H), 1.55 – 1.37 (m, 4H), 1.40 – 1.23 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1 (d, *J* = 4.9 Hz), 140.4, 128.5, 128.4, 126.2, 65.3, 62.7 (d, *J* = 6.5 Hz), 62.6 (d, *J* = 6.8 Hz), 45.0 (d, *J* = 131.0 Hz), 44.9, 34.3 (d, *J* = 15.1 Hz), 32.4, 28.6 (d, *J* = 4.7 Hz), 28.4, 26.4, 25.2, 16.4, 16.3.

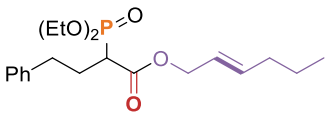
^{31}P NMR (162 MHz, $CDCl_3$) δ 22.55.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{33}ClO_5P^+$ 419.1749; Found: 419.1750.



3-Iodopropyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4p)
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (45.9 mg, 49% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 2H), 7.25 – 7.12 (m, 3H), 4.52 – 4.17 (m, 2H), 4.17 – 3.94 (m, 4H), 3.27 (t, *J* = 6.8 Hz, 2H), 3.11 – 2.83 (m, 1H), 2.78 – 2.64 (m, 1H), 2.65 – 2.53 (m, 1H), 2.48 – 2.24 (m, 1H), 2.22 – 2.09 (m, 3H), 1.39 – 1.10 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9 (d, *J* = 5.1 Hz), 140.2, 128.53, 128.48, 126.3, 64.8, 62.8 (d, *J* = 6.5 Hz), 62.7 (d, *J* = 6.8 Hz), 44.9 (d, *J* = 130.9 Hz), 34.3 (d, *J* = 15.1 Hz), 32.2, 28.4 (d, *J* = 4.6 Hz), 16.41, 16.35, 1.5.
^{31}P NMR (162 MHz, $CDCl_3$) δ 22.37.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{27}IO_5P^+$ 469.0635; Found:469.0642.



Methyl-d3 2-(diethoxyphosphoryl)-4-phenylbutanoate (4q)
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (43.7 mg, 69% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.24 – 7.14 (m, 3H), 4.22 – 4.02 (m, 4H), 3.05 – 2.91 (m, 1H), 2.78 – 2.67 (m, 1H), 2.64 – 2.52 (m, 1H), 2.41 – 2.24 (m, 1H), 2.23 – 2.07 (m, 1H), 1.35 – 1.22 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5 (d, *J* = 5.0 Hz), 140.3, 128.5, 128.4, 126.2, 62.8 (d, *J* = 6.4 Hz), 62.7 (d, *J* = 6.7 Hz), 44.9 (d, *J* = 131.0 Hz), 34.3 (d, *J* = 15.0 Hz), 28.6 (d, *J* = 4.6 Hz), 16.3 (d, *J* = 2.0 Hz), 16.3 (d, *J* = 2.2 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 22.51.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{21}D_3O_5P^+$ 318.1544; Found: 318.1545.



(*E*)-Hex-2-en-1-yl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4r)

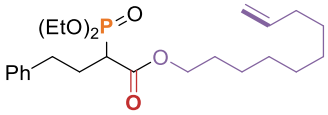
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (53.5 mg, 70% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 2H), 7.23 – 7.13 (m, 3H), 5.87 – 5.76 (m, 1H), 5.64 – 5.53 (m, 1H), 4.60 (d, *J* = 6.5 Hz, 2H), 4.18 – 4.02 (m, 4H), 3.04 – 2.90 (m, 1H), 2.81 – 2.67 (m, 1H), 2.64 – 2.52 (m, 1H), 2.40 – 2.24 (m, 1H), 2.22 – 2.09 (m, 1H), 2.09 – 1.98 (m, 2H), 1.51 – 1.37 (m, 2H), 1.36 – 1.23 (m, 6H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8 (d, *J* = 5.0 Hz), 140.5, 136.9, 128.6, 128.4, 126.2, 123.5, 66.1, 62.72 (d, *J* = 5.7 Hz), 62.66 (d, *J* = 6.5 Hz), 45.0 (d, *J* = 130.9 Hz), 34.3, 34.3 (d, *J* = 15.2 Hz), 28.7 (d, *J* = 4.7 Hz), 22.0, 16.3 (d, *J* = 3.1 Hz), 16.3 (d, *J* = 3.4 Hz), 13.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.43.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{32}O_5P^+$ 383.1982; Found: 383.1985.



Dec-9-en-1-yl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4s)

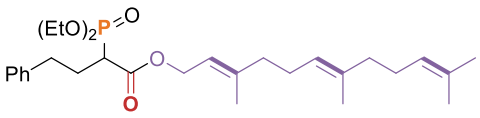
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (71.0 mg, 81% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.24 – 7.15 (m, 3H), 5.88 – 5.73 (m, 1H), 5.03 – 4.96 (m, 1H), 4.96 – 4.89 (m, 1H), 4.23 – 4.01 (m, 6H), 3.04 – 2.89 (m, 1H), 2.81 – 2.67 (m, 1H), 2.64 – 2.52 (m, 1H), 2.40 – 2.23 (m, 1H), 2.22 – 2.10 (m, 1H), 2.12 – 1.99 (m, 2H), 1.73 – 1.62 (m, 2H), 1.42 – 1.22 (m, 16H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1 (d, *J* = 5.0 Hz), 140.4, 139.1, 128.5, 128.4, 126.2, 114.2, 65.6, 62.7 (d, *J* = 6.6 Hz), 62.6 (d, *J* = 6.9 Hz), 45.1 (d, *J* = 131.0 Hz), 34.3 (d, *J* = 15.3 Hz), 33.7, 29.3, 29.2, 29.0, 28.9, 28.6 (d, *J* = 4.5 Hz), 28.6, 25.8, 16.4 (d, *J* = 1.7 Hz), 16.3 (d, *J* = 1.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.61.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{40}O_5P^+$ 439.2608; Found: 439.2612.



(*2E*,*6E*)-3,7,11-Trimethyldodeca-2,6,10-trien-1-yl 2-(diethoxyphosphoryl)-4-phenylbutanoate (4t)

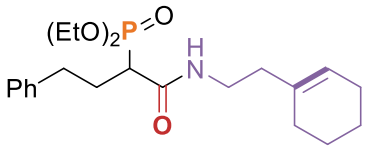
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (58.5 mg, 58% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.23 – 7.13 (m, 3H), 5.39 (t, *J* = 6.5 Hz, 1H), 5.27 – 5.00 (m, 2H), 4.68 (d, *J* = 6.3 Hz, 2H), 4.42 – 3.83 (m, 4H), 3.03 – 2.89 (m, 1H), 2.79 – 2.67 (m, 1H), 2.64 – 2.52 (m, 1H), 2.40 – 2.23 (m, 1H), 2.22 – 2.01 (m, 7H), 2.01 – 1.87 (m, 2H), 1.73 (s, 3H), 1.71 – 1.54 (m, 9H), 1.42 – 1.15 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0 (d, *J* = 4.9 Hz), 142.8, 140.5, 135.5, 131.3, 128.6, 128.4, 126.2, 124.3, 123.5, 117.9, 62.7 (d, *J* = 5.2 Hz), 62.64 (d, *J* = 5.9 Hz), 62.3, 45.0 (d, *J* = 130.9 Hz), 39.7, 39.5, 34.3 (d, *J* = 15.3 Hz), 28.7 (d, *J* = 4.5 Hz), 26.7, 26.3, 25.7, 17.7, 16.5, 16.4 (d, *J* = 3.4 Hz), 16.3 (d, *J* = 3.6 Hz), 16.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.52.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{46}O_5P^+$ 505.3077; Found: 505.3079.



Diethyl (1-((2-(cyclohex-1-en-1-yl)ethyl)amino)-1-oxo-4-phenylbutan-2-yl)phosphonate (4u)

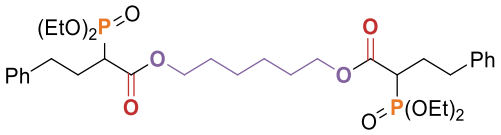
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:3) to afford the title compound as a brown liquid (47.2 mg, 58% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.24 – 7.14 (m, 3H), 6.31 (s, 1H), 5.49 (s, 1H), 4.22 – 3.97 (m, 5H), 3.65 – 3.30 (m, 2H), 2.94 – 2.75 (m, 1H), 2.75 – 2.54 (m, 2H), 2.33 – 2.21 (m, 1H), 2.16 (t, *J* = 7.0 Hz, 2H), 2.03 – 1.90 (m, 4H), 1.68 – 1.58 (m, 2H), 1.58 – 1.49 (m, 2H), 1.40 – 1.20 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0 (d, *J* = 2.4 Hz), 140.8, 134.5, 128.6, 128.4, 126.1, 123.5, 62.7 (d, *J* = 6.8 Hz), 62.5 (d, *J* = 6.6 Hz), 61.4 (d, *J* = 6.5 Hz), 45.2 (d, *J* = 129.7 Hz), 37.8, 37.6, 34.0 (d, *J* = 14.7 Hz), 28.7 (d, *J* = 4.3 Hz), 27.9, 25.2, 22.8, 22.3, 16.4 (d, J = 2.1 Hz), 16.3 (d, *J* = 2.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.60.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{35}NO_4P^+$ 408.2298; Found: 408.2302.



Hexane-1,6-diyl bis(2-(diethoxyphosphoryl)-4-phenylbutanoate) (4v)

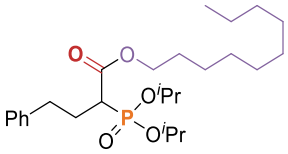
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:1) to afford the title compound as a brown liquid (85.9 mg, 63% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 4H), 7.24 – 7.14 (m, 6H), 4.18 – 4.05 (m, 12H), 3.07 – 2.90 (m, 2H), 2.79 – 2.65 (m, 2H), 2.64 – 2.49 (m, 2H), 2.43 – 2.25 (m, 2H), 2.22 – 2.07 (m, 2H), 1.72 – 1.64 (m, 4H), 1.47 – 1.36 (m, 4H), 1.35 – 1.23 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0 (d, *J* = 4.9 Hz), 140.3, 128.44, 128.38, 126.2, 65.2, 62.64 (d, *J* = 6.3 Hz), 62.55 (d, *J* = 6.7 Hz), 45.0 (d, *J* = 131.0 Hz), 34.2 (d, *J* = 15.2 Hz), 28.5 (d, *J* = 4.4 Hz), 28.4, 25.5, 16.3, 16.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.65.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{34}H_{53}O_{10}P_2^+$ 683.3108; Found: 683.3110.



Decyl 2-(diisopropoxyphosphoryl)-4-phenylbutanoate (5a)

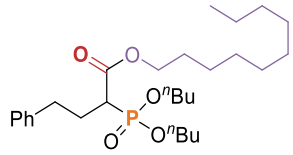
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (83.3 mg, 89% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.3 Hz, 2H), 7.23 – 7.13 (m, 3H), 4.77 – 4.62 (m, 2H), 4.21 – 4.07 (m, 2H), 2.96 – 2.82 (m, 1H), 2.78 – 2.67 (m, 1H), 2.63 – 2.51 (m, 1H), 2.38 – 2.22 (m, 1H), 2.20 – 2.06 (m, 1H), 1.72 – 1.62 (m, 2H), 1.42 – 1.23 (m, 26H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2 (d, *J* = 5.1 Hz), 140.5, 128.5, 128.4, 126.1, 71.3 (d, *J* = 6.8 Hz), 71.1 (d, *J* = 7.0 Hz), 65.4, 45.8 (d, *J* = 132.3 Hz), 34.3 (d, *J* = 15.5 Hz), 31.8, 29.5, 29.2 (d, *J* = 4.8 Hz), 28.8 (d, *J* = 4.7 Hz), 28.6, 25.8, 24.1 (d, *J* = 3.5 Hz), 24.0 (d, *J* = 3.7 Hz), 23.73 (d, *J* = 5.2 Hz), 23.70 (d, *J* = 5.3 Hz), 22.6, 14.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.60.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{46}O_5P^+$ 469.3077; Found: 469.3083.



Decyl 2-(dibutoxyphosphoryl)-4-phenylbutanoate (5b)

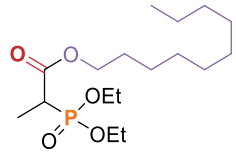
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (81.7 mg, 82% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.13 (m, 3H), 4.24 – 4.11 (m, 2H), 4.11 – 3.94 (m, 4H), 3.03 – 2.87 (m, 1H), 2.79 – 2.68 (m, 1H), 2.64 – 2.52 (m, 1H), 2.40 – 2.24 (m, 1H), 2.22 – 2.08 (m, 1H), 1.71 – 1.57 (m, 6H), 1.42 – 1.21 (m, 18H), 0.97 – 0.84 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1 (d, *J* = 5.1 Hz), 140.4, 128.5, 128.4, 126.2, 66.34 (d, J = 6.9 Hz), 66.27 (d, *J* = 7.3 Hz), 65.6, 45.0 (d, *J* = 131.0 Hz), 34.3 (d, *J* = 15.4 Hz), 32.5 (d, *J* = 6.2 Hz), 31.9, 29.5, 29.3 (d, *J* = 3.4 Hz), 25.9, 22.6, 18.6 (d, *J* = 2.3 Hz), 14.1, 13.6 (d, *J* = 1.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.51.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{50}O_5P^+$ 497.3390; Found: 497.3394.



Decyl 2-(diethoxyphosphoryl)propanoate (5c)

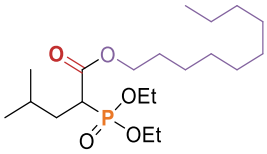
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:1) to afford the title compound as a colorless liquid (58.8 mg, 84% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29 – 3.86 (m, 6H), 3.14 – 2.83 (m, 1H), 1.80 – 1.51 (m, 2H), 1.50 – 1.37 (m, 3H), 1.36 – 1.10 (m, 20H), 0.92 – 0.68 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.78 (d, *J* = 4.5 Hz), 65.5, 62.5 (d, *J* = 6.6 Hz), 39.3 (d, *J* = 133.5 Hz), 31.8, 29.43, 29.42, 29.2 (d, *J* = 6.6 Hz), 28.5, 25.7, 22.6, 16.3 (d, *J* = 3.1 Hz), 16.3 (d, *J* = 3.4 Hz), 14.0, 11.7, 11.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 23.89.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{36}O_5P^+$ 351.2295; Found: 351.2299.



Decyl 2-(diethoxyphosphoryl)-4-methylpentanoate (5d)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid

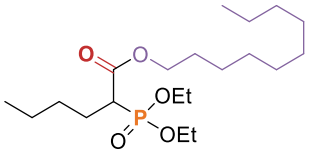
(69.0 mg, 88% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 – 3.94 (m, 6H), 3.12 – 2.88 (m, 1H), 2.13 – 1.83 (m, 1H), 1.72 – 1.50 (m, 4H), 1.43 – 1.07 (m, 20H), 1.03 – 0.73 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5 (d, *J* = 5.1 Hz), 65.4, 62.6 (d, *J* = 5.8 Hz), 62.5 (d, *J* = 6.3 Hz), 44.0 (d, *J* = 131.2 Hz), 35.5 (d, *J* = 5.1 Hz), 31.8, 29.5, 29.2, 29.1, 28.5, 26.9 (d, *J* = 14.8 Hz), 25.8, 22.9, 22.6, 21.1, 16.33 (d, *J* = 2.3 Hz), 16.28 (d, *J* = 2.6 Hz), 14.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ 23.49.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{42}O_5P^+$ 393.2764; Found: 393.2772.



Decyl 2-(diethoxyphosphoryl)hexanoate (5e)

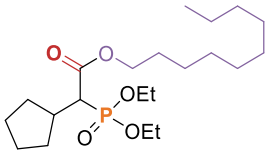
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (72.9 mg, 93% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 – 3.86 (m, 6H), 3.09 – 2.71 (m, 1H), 2.05 – 1.88 (m, 1H), 1.87 – 1.74 (m, 1H), 1.73 – 1.54 (m, 2H), 1.43 – 1.11 (m, 24H), 1.04 – 0.67 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4 (d, *J* = 4.8 Hz), 65.4, 62.6 (d, *J* = 4.8 Hz), 62.5 (d, *J* = 5.2 Hz), 45.8 (d, *J* = 131.2 Hz), 31.8, 30.5 (d, *J* = 14.9 Hz), 29.5, 29.2, 29.1, 28.5, 26.6 (d, *J* = 4.9 Hz), 25.8, 22.6, 22.2, 16.3 (d, *J* = 2.9 Hz), 16.3 (d, *J* = 2.9 Hz), 14.0, 13.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 23.11.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{42}O_5P^+$ 393.2764; Found: 393.2770.



Decyl 2-cyclopentyl-2-(diethoxyphosphoryl)acetate (5f)

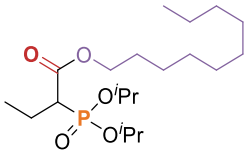
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (51.7 mg, 64% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 – 3.90 (m, 6H), 2.90 – 2.65 (m, 1H), 2.46 – 2.33 (m, 1H), 2.01 – 1.89 (m, 1H), 1.84 – 1.72 (m, 1H), 1.72 – 1.47 (m, 6H), 1.46 – 1.10 (m, 22H), 0.85 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5 (d, *J* = 4.1 Hz), 65.3, 62.33 (d, *J* = 6.6 Hz), 62.32 (d, *J* = 7.6 Hz), 51.4 (d, *J* = 132.5 Hz), 38.9 (d, *J* = 5.0 Hz), 31.9 (d, *J* = 15.8 Hz), 31.4 (d, *J* = 2.4 Hz), 29.5, 29.2, 29.1, 28.5, 25.8, 24.9, 24.2, 22.6, 16.4, 16.3, 14.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.45.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{42}O_5P^+$ 405.2764; Found: 405.2767.



Decyl 2-(diisopropoxyphosphoryl)butanoate (5g)

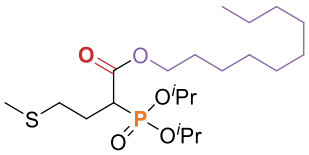
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (72.1 mg, 92% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 – 4.53 (m, 2H), 4.26 – 3.97 (m, 2H), 2.94 – 2.63 (m, 1H), 2.01 – 1.79 (m, 2H), 1.75 – 1.54 (m, 2H), 1.47 – 1.20 (m, 26H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ169.4 (d, *J* = 4.8 Hz), 71.2 (d, *J* = 6.7 Hz), 71.0 (d, *J* = 7.2 Hz), 65.3, 48.3 (d, *J* = 132.8 Hz), 31.8, 29.48, 29.46, 29.2 (d, *J* = 6.9 Hz), 28.5, 25.8, 24.1 (d, *J* = 3.4 Hz), 24.0 (d, *J* = 3.7 Hz), 23.8 (d, *J* = 5.2 Hz), 23.7 (d, *J* = 5.4 Hz), 22.6, 20.8 (d, *J* = 5.1 Hz), 14.1, 13.1, 12.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 20.75.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{42}O_5P^+$ 393.2764; Found: 393.2761.



Decyl 2-(diisopropoxyphosphoryl)-4-(methylthio)butanoate (5h)

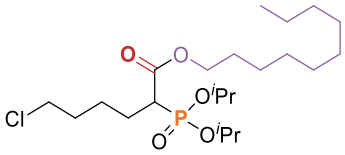
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (66.6 mg, 76% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 – 4.50 (m, 2H), 4.28 – 3.95 (m, 2H), 3.33 – 2.99 (m, 1H), 2.73 – 2.52 (m, 1H), 2.50 – 2.38 (m, 1H), 2.34 – 2.20 (m, 1H), 2.18 – 2.08 (m, 1H), 2.06 (s, 3H), 1.85 – 1.49 (m, 2H), 1.53 – 1.13 (m, 26H), 0.86 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0 (d, *J* = 5.2 Hz), 71.5 (d, *J* = 6.7 Hz), 71.3 (d, *J* = 7.0 Hz), 65.5, 45.1 (d, *J* = 132.5 Hz), 32.5 (d, *J* = 16.3 Hz), 31.8, 29.50, 29.47, 29.2 (d, *J* = 6.2 Hz), 28.5, 26.3 (d, *J* = 4.2 Hz), 25.8, 24.1 (d, *J* = 3.6 Hz), 24.0 (d, *J* = 3.8 Hz), 23.8 (d, *J* = 5.1 Hz), 23.7 (d, *J* = 5.2 Hz), 22.6, 15.1, 14.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 20.27.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{44}O_5PS^+$ 439.2642; Found: 439.2647.



Decyl 6-chloro-2-(diisopropoxyphosphoryl)hexanoate (5i)

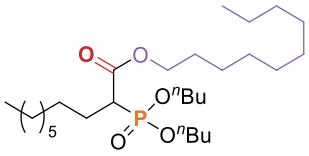
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (64.5 mg, 71% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 – 4.63 (m, 2H), 4.16 – 4.06 (m, 2H), 3.54 – 3.45 (m, 2H), 2.93 – 2.71 (m, 1H), 2.08 – 1.71 (m, 4H), 1.68 – 1.58 (m, 2H), 1.50 – 1.37 (m, 2H), 1.39 – 1.16 (m, 26H), 0.85 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2 (d, *J* = 5.0 Hz), 71.4 (d, *J* = 6.7 Hz), 71.2 (d, *J* = 7.1 Hz), 65.4, 46.5 (d, *J* = 132.8 Hz), 44.4, 32.0, 31.8, 29.48, 29.46, 29.2 (d, *J* = 6.1 Hz), 28.5, 26.4 (d, *J* = 4.9 Hz), 25.8, 25.6, 24.1 (d, *J* = 3.6 Hz), 24.0 (d, *J* = 3.8 Hz), 23.8 (d, *J* = 5.2 Hz), 23.7 (d, *J* = 5.3 Hz), 22.6, 14.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ 20.45.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{45}O_5PCl^+$ 455.2688; Found: 455.2690.



Decyl 2-(dibutoxyphosphoryl)decanoate (5j)

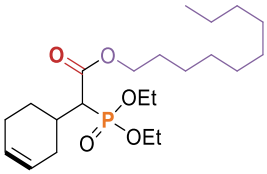
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (51.4 mg, 51% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 – 3.88 (m, 7H), 1.79 – 1.48 (m, 14H), 1.48 – 1.18 (m, 24H), 0.92 (t, *J* = 7.4 Hz, 6H), 0.87 (t, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 65.2 (d, *J* = 5.0 Hz), 65.1 (d, *J* = 4.8 Hz), 64.2, 45.5, 32.6 (d, *J* = 6.1 Hz), 32.2, 31.8 (d, *J* = 3.8 Hz), 30.6 (d, J = 16.8 Hz), 29.5 (d, *J* = 3.6 Hz), 29.3 (d, *J* = 3.4 Hz), 29.2, 29.1, 28.7, 26.1 (d, *J* = 27.3 Hz), 24.8, 22.6 (d, *J* = 1.9 Hz), 22.6, 22.4 (d, *J* = 5.1 Hz), 18.8, 14.1, 13.9, 13.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 20.64.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{58}O_5P^+$ 505.4016; Found: 505.4020.



Decyl 2-(cyclohex-3-en-1-yl)-2-(diethoxyphosphoryl)acetate (5k)

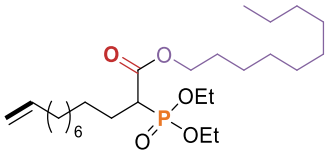
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (39.1 mg, 47% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.42 (m, 2H), 4.25 – 3.86 (m, 6H), 3.04 – 2.77 (m, 1H), 2.42 – 2.32 (m, 1H), 2.12 – 1.93 (m, 4H), 1.68 – 1.60 (m, 4H), 1.44 – 1.12 (m, 20H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3 (d, *J* = 4.4 Hz), 169.2 (d, *J* = 4.4 Hz), 126.8, 126.5, 125.6, 125.2, 65.4, 62.5 (d, *J* = 12.4 Hz), 62.4 (d, *J* = 12.4 Hz), 51.7 (d, *J* = 132.3 Hz), 51.5 (d, *J* = 132.3 Hz), 33.3, 33.2, 31.9, 30.2, 30.1 (d, *J* = 17.6 Hz), 30.2, 29.5, 29.23 (d, *J* = 17.6 Hz), 28.51, 28.49, 27.54, 27.46, 27.10, 27.07, 25.84, 25.83, 24.74, 24.71, 22.7, 16.39 (d, J = 5.5 Hz), 16.36 (d, J = 5.5 Hz), 14.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.43, 22.36.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{42}O_5P^+$ 417.2764; Found: 417.2767.



Decyl 2-(diethoxyphosphoryl)dodec-11-enoate (5l)

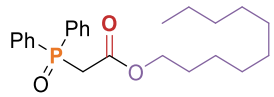
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (52.1 mg, 55% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 – 5.59 (m, 1H), 5.23 – 4.76 (m, 2H), 4.46 – 3.80 (m, 6H), 3.23 – 2.76 (m, 1H), 2.41 – 1.98 (m, 2H), 1.95 (d, *J* = 8.3 Hz, 1H), 1.89 – 1.77 (m, 1H), 1.76 – 1.56 (m, 4H), 1.48 – 1.14 (m, 30H), 0.87 (t, *J* = 6.5 Hz 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4 (d, *J* = 4.7 Hz), 139.2, 114.1, 65.5, 62.62 (d, *J* = 7.1 Hz), 62.58 (d, *J* = 7.3 Hz), 45.9 (d, *J* = 131.3 Hz), 33.8, 31.9, 29.5, 29.3 (d, *J* = 7.8 Hz), 29.2 (d, *J* = 2.9 Hz), 29.1, 29.0, 28.9, 28.6, 28.4 (d, *J* = 15.1 Hz), 27.0 (d, *J* = 4.7 Hz), 25.8, 22.7, 16.39 (d, *J* = 5.7 Hz), 16.36 (d, *J* = 5.8 Hz), 14.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 23.06.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{52}O_5P^+$ 475.3547; Found: 475.3555.



Decyl 2-(diphenylphosphoryl)acetate (5m)

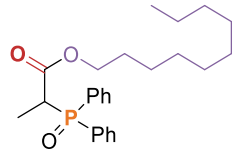
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (61.6 mg, 77% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.68 (m, 4H), 7.68 – 7.35 (m, 6H), 3.92 (t, *J* = 6.7 Hz, 2H), 3.49 (d, *J* = 14.9 Hz, 2H), 1.56 – 1.32 (m, 2H), 1.32 – 1.01 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 166.3, 132.3 (d, *J* = 3.0 Hz), 131.8 (d, *J* = 104.1 Hz), 131.1 (d, *J* = 10.0 Hz), 128.6 (d, *J* = 12.3 Hz), 65.8, 39.2 (d, *J* = 60.6 Hz), 31.9, 29.53, 29.45, 29.3, 29.2, 28.3, 25.7, 22.7, 14.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 26.85.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{34}O_3P^+$ 401.2240; Found: 401.2243.



Decyl 2-(diphenylphosphoryl)propanoate (5n)

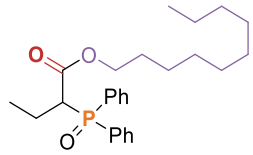
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (58.8 mg, 71% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.74 (m, 4H), 7.61 – 7.37 (m, 6H), 3.93 – 3.83 (m, 1H), 3.83 – 3.73 (m, 1H), 3.66 – 3.50 (m, 1H), 1.55 – 1.38 (m, 3H), 1.37 – 1.11 (m, 14H), 1.11 – 0.99 (m, 2H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 132.0 (d, *J* = 2.6 Hz), 132.0 (d, *J* = 2.7 Hz), 131.6 (d, *J* = 9.2 Hz), 131.2 (d, *J* = 9.2 Hz), 130.5 (d, *J* = 94.4 Hz), 128.6 (d, *J* = 11.8 Hz), 128.4 (d, *J* = 11.9 Hz), 65.5, 42.5 (d, J = 60.6 Hz), 31.8, 29.5, 29.4, 29.2, 29.1, 28.1, 25.6, 22.6, 14.1, 11.0 (d, *J* = 3.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 31.06.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{36}O_3P^+$ 415.2397; Found: 415.2403.



Decyl 2-(diphenylphosphoryl)butanoate (5o)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid

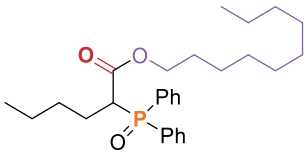
(59.9 mg, 70% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.84 – 7.75 (m, 2H), 7.57 – 7.36 (m, 6H), 3.93 – 3.82 (m, 1H), 3.80 – 3.70 (m, 1H), 3.43 – 3.31 (m, 1H), 2.14 – 1.96 (m, 1H), 1.93 – 1.79 (m, 1H), 1.41 – 1.07 (m, 16H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 132.0 (d, *J* = 2.7 Hz), 132.0 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 9.2 Hz), 131.2 (d, *J* = 9.2 Hz), 130.5 (d, *J* = 100.1 Hz), 128.5 (d, *J* = 12.0 Hz), 128.3 (d, *J* = 12.1 Hz), 65.4, 51.2 (d, *J* = 59.8 Hz), 31.8, 29.5, 29.4, 29.2, 29.1, 28.1, 25.7, 22.6, 20.2 (d, *J* = 2.4 Hz), 14.1, 13.3 (d, *J* = 13.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.18.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{38}O_3P^+$ 429.2553; Found: 429.2560.



Decyl 2-(diphenylphosphoryl)hexanoate (5p)

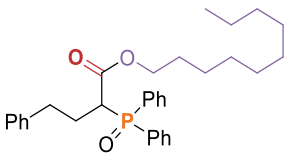
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (56.7 mg, 62% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.84 (m, 2H), 7.84 – 7.75 (m, 2H), 7.61 – 7.39 (m, 6H), 3.97 – 3.82 (m, 1H), 3.81 – 3.63 (m, 1H), 3.55 – 3.32 (m, 1H), 2.08 – 1.95 (m, 1H), 1.89 – 1.74 (m, 1H), 1.44 – 1.12 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.81 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0 (d, *J* = 2.3 Hz), 132.0 (d, *J* = 3.3 Hz), 132.0 (d, *J* = 3.3 Hz), 131.7 (d, *J* = 9.3 Hz), 131.2 (d, *J* = 9.3 Hz), 130.5 (d, *J* = 100.0 Hz), 128.6 (d, *J* = 11.9 Hz), 128.3 (d, *J* = 12.0 Hz), 65.4, 49.5 (d, *J* = 59.7 Hz), 31.8, 30.9 (d, *J* = 12.3 Hz), 29.5, 29.4, 29.3, 29.1, 28.1, 26.2 (d, *J* = 2.6 Hz), 25.7, 22.6, 22.2, 14.1, 13.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.26.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{42}O_3P^+$ 457.2866; Found: 457.2873.



Decyl 2-(diphenylphosphoryl)-4-phenylbutanoate (5q)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (57.5 mg, 57% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

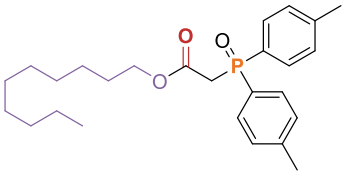
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 2H), 7.74 – 7.63 (m, 2H), 7.59 – 7.47 (m, 2H), 7.48 – 7.38 (m, 4H), 7.31 – 7.19 (m, 3H), 7.07 (d, J = 7.0 Hz, 2H), 3.96 – 3.83 (m, 1H), 3.80 – 3.69 (m, 1H),

3.46 (t, *J* = 11.3 Hz, 1H), 2.83 – 2.71 (m, 1H), 2.62 – 2.50 (m, 1H), 2.50 – 2.31 (m, 1H), 2.19 – 2.00 (m, 1H), 1.58 – 1.01 (m, 16H), 0.89 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 132.0 (d, *J* = 3.1 Hz), 132.0 (d, *J* = 3.3 Hz), 131.6 (d, *J* = 9.3 Hz), 131.4 (d, *J* = 100.6 Hz), 131.2 (d, *J* = 9.1 Hz), 130.5 (d, *J* = 100.8 Hz), 128.6, 128.5 (d, *J* = 12.0 Hz), 128.4, 128.3, 126.2, 65.5, 48.2 (d, *J* = 59.4 Hz), 34.5 (d, *J* = 12.7 Hz), 31.8, 29.5, 29.4, 29.3, 29.1, 28.2, 28.1, 25.7, 22.6, 14.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.55.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{32}H_{42}O_3P^+$ 505.2866; Found: 505.2869.



Decyl 2-(di-p-tolylphosphoryl)acetate (5r)

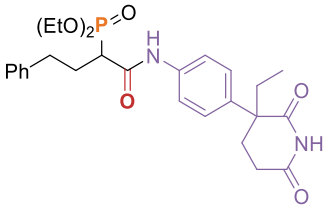
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (63.3 mg, 74% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 4H), 7.28 (d, *J* = 8.7 Hz, 4H), 3.93 (t, *J* = 6.7 Hz, 2H), 3.45 (d, *J* = 14.8 Hz, 2H), 2.40 (s, 6H), 1.58 – 1.34 (m, 2H), 1.34 – 1.03 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ166.5, 142.7 (d, *J* = 2.6 Hz), 131.2 (d, *J* = 10.0 Hz), 129.3 (d, *J* = 12.8 Hz), 128.8 (d, *J* = 106.5 Hz), 65.7, 39.3 (d, *J* = 60.5 Hz), 31.9, 29.6, 29.5, 29.3, 29.2, 28.3, 25.7, 22.7, 21.6, 14.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.32.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{38}O_3P^+$ 429.2553; Found: 429. 2560.



Diethyl (1-((4-(3-ethyl-2,6-dioxopiperidin-3-yl)phenyl)amino)-1-oxo-4-phenylbutan-2-yl)phosphonate (6a)

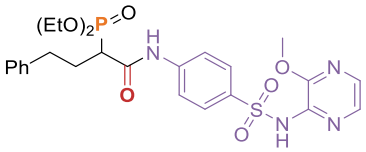
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:2) to afford the title compound as a brown liquid (70.9 mg, 69% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 9.01 (s, 1H), 7.50 (d, *J* = 14.5 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.23 – 7.12 (m, 5H), 4.23 – 3.85 (m, 4H), 3.27 – 2.91 (m, 1H), 2.91 – 2.78 (m, 1H), 2.76 – 2.51 (m, 2H), 2.52 – 2.27 (m, 3H), 2.27 – 2.16 (m, 1H), 2.14 – 1.99 (m, 2H), 1.95 – 1.82 (m, 1H), 1.44 – 1.20 (m, 6H), 0.99 – 0.75 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7 (d, *J* = 34.5 Hz), 172.9 (d, *J* = 46.0 Hz), 165.5 (d, *J* = 2.8 Hz), 140.7, 137.5, 134.5 (d, *J* = 4.6 Hz), 128.6, 128.4, 126.7 (d, *J* = 2.2 Hz), 126.2, 120.2 (d, J = 12.6 Hz), 63.3 (d, J = 6.9 Hz), 62.7 (d, J = 5.8 Hz), 50.7 (d, J = 5.8 Hz), 46.1 (d, *J* = 128.6 Hz), 34.1 (d, *J* = 15.8 Hz), 32.7, 29.3 (d, *J* = 5.1 Hz), 28.3, 27.2 (d, *J* = 15.2 Hz), 16.4 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 6.1 Hz), 9.1 (d, *J* = 7.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 24.88.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{36}N_2O_6P^+$ 515.2305; Found: 505.2311.



Diethyl (1-((4-(N-(3-methoxypyrazin-2-yl)sulfamoyl)phenyl)amino)-1-oxo-4-phenylbutan-2-yl)phosphonate (6b)

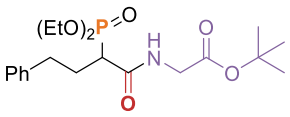
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:2) to afford the title compound as a brown liquid (60.7 mg, 54% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.75 (d, *J* = 9.0 Hz, 4H), 7.70 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.22 (m, 2H), 7.21 – 7.12 (m, 3H), 4.25 – 4.12 (m, 2H), 4.07 – 3.84 (m, 5H), 3.15 – 2.93 (m, 1H), 2.92 – 2.70 (m, 1H), 2.63 – 2.48 (m, 1H), 2.48 – 2.35 (m, 1H), 2.19 – 1.94 (m, 1H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 142.7, 140.5, 133.7, 129.3, 128.6, 128.4, 126.2, 118.6, 63.7, 62.5, 54.1, 46.0 (d, *J* = 129.2 Hz), 34.0 (d, *J* = 14.8 Hz), 27.5, 16.4 (d, *J* = 5.8 Hz), 16.2 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 24.70.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{32}N_4O_7PS^+$ 563.1724; Found: 563.1727.



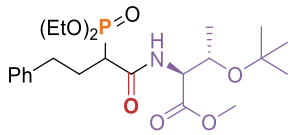
Tert-butyl (2-(diethoxyphosphoryl)-4-phenylbutanoyl)glycinate (6c)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:2) to afford the title compound as a brown liquid (66.9 mg, 81% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

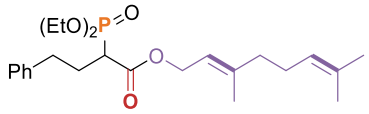
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.24 – 7.14 (m, 3H), 6.81 (s, 1H), 4.19 – 4.01 (m, 4H), 3.96 (t, *J* = 5.5 Hz, 2H), 2.90 – 2.72 (m, 2H), 2.72 – 2.53 (m, 1H), 2.41 – 2.27 (m, 1H), 2.18 – 2.04 (m, 1H), 1.48 (s, 9H), 1.34 – 1.18 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 167.4 (d, *J* = 2.6 Hz), 140.8, 128.6, 128.4, 126.1, 82.1, 62.8 (d, *J* = 6.7 Hz), 62.7 (d, *J* = 6.7 Hz), 45.1 (d, *J* = 130.1 Hz), 42.4, 34.0 (d, *J* = 14.5 Hz), 28.6 (d, *J* = 4.4 Hz), 28.0, 16.31 (d, *J* = 2.1 Hz), 16.27 (d, *J* = 2.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 24.88.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{33}NO_6P^+$ 414.2040; Found: 414.2031.



Methyl *O*-(tert-butyl)-*N*-(2-(diethoxyphosphoryl)-4-phenylbutanoyl)-*L*-allothreoninate (6d)
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:2) to afford the title compound as a brown liquid (72.5 mg, 77% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.08 (m, 5H), 6.74 (s, 1H), 4.61 – 4.50 (m, 1H), 4.31 – 4.23 (m, 1H), 4.20 – 4.03 (m, 5H), 3.73 (s, 3H), 2.92 – 2.72 (m, 2H), 2.70 – 2.52 (m, 1H), 2.48 – 2.26 (m, 1H), 1.37 – 1.27 (m, 6H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.13 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 167.8 (d, *J* = 3.9 Hz), 140.9, 128.6, 128.4, 126.0, 74.0, 67.3, 62.6 (d, *J* = 1.7 Hz), 62.5 (d, *J* = 1.8 Hz), 58.2, 52.1, 45.4 (d, *J* = 131.4 Hz), 33.8 (d, *J* = 15.7 Hz), 28.6 (d, *J* = 4.2 Hz), 28.3, 28.3, 20.9, 16.3 (d, *J* = 6.0 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 24.30.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{39}NO_7P^+$ 472.2459; Found: 472.2461.



(E)-3,7-Dimethylocta-2,6-dien-1-yl 2-(diethoxyphosphoryl)-4-phenylbutanoate (6e)
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (51.5 mg, 59% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.23 – 7.13 (m, 3H), 5.49 – 5.27 (m, 1H), 5.28 – 5.02 (m, 1H), 4.84 – 4.55 (m, 2H), 4.37 – 3.96 (m, 5H), 3.31 – 2.86 (m, 1H), 2.80 – 2.66 (m, 1H), 2.65 – 2.52 (m, 1H), 2.32 – 2.31 (m, 1H), 2.24 – 2.01 (m, 4H), 1.77 – 1.53 (m, 9H), 1.41 – 1.20 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0 (d, *J* = 4.9 Hz), 142.7, 140.5, 131.9, 128.5, 128.4, 126.2, 123.6, 117.9, 62.7 (d, *J* = 4.2 Hz), 62.6 (d, *J* = 4.8 Hz), 62.3, 45.0 (d, *J* = 130.9 Hz), 39.5, 34.3 (d, *J* = 15.4 Hz), 28.7 (d, *J* = 4.6 Hz), 26.3, 25.6, 17.6, 16.5, 16.33 (d, *J* = 3.3 Hz), 16.29 (d, *J* = 3.5 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 22.54.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{38}O_5P^+$ 437.2451; Found: 437.2460.

(*7R,11R,E*)-3,7,11,15-Tetramethylhexadec-2-en-1-yl 2-(diethoxyphosphoryl)-4-phenylbutanoate (6f)

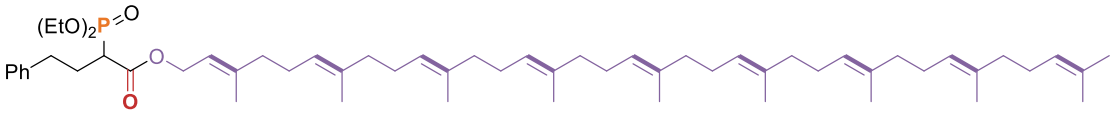
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (78.7 mg, 68% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.23 – 7.13 (m, 3H), 5.37 (t, *J* = 7.0 Hz, 1H), 4.68 (d, *J* = 7.0 Hz, 2H), 4.36 – 3.92 (m, 4H), 3.03 – 2.89 (m, 1H), 2.78 – 2.67 (m, 1H), 2.64 – 2.52 (m, 1H), 2.40 – 2.23 (m, 1H), 2.22 – 2.09 (m, 1H), 2.13 – 1.93 (m, 2H), 1.72 (s, 3H), 1.61 – 1.47 (m, 1H), 1.46 – 1.19 (m, 19H), 1.17 – 1.11 (m, 2H), 1.11 – 0.99 (m, 3H), 0.95 – 0.60 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0 (d, *J* = 5.0 Hz), 142.7, 140.5, 132.2, 128.5, 128.4, 126.2, 123.5, 118.8, 62.7 (d, *J* = 2.8 Hz), 62.6 (d, *J* = 3.3 Hz), 62.0, 45.0 (d, *J* = 130.9 Hz), 34.3 (d, *J* = 15.3 Hz), 32.2, 28.7 (d, *J* = 4.5 Hz), 26.6, 25.7, 23.5, 17.6, 16.31 (d, *J* = 4.0 Hz), 16.28 (d, *J* = 4.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.54.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{34}H_{60}O_5P^+$ 579.4173; Found: 579.4174.



(2E,6E,10E,14E,18E,22E,26E,30E)-3,7,11,15,19,23,27,31,35-Nonamethylhexatriaconta-2,6,10,14,18,22,26,30,34-nonaen-1-yl 2-(diethoxyphosphoryl)-4-phenylbutanoate (6g)

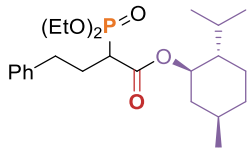
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (93.0 mg, 51% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.23 – 7.13 (m, 3H), 5.43 – 5.35 (m, 1H), 5.12 (d, *J* = 6.8 Hz, 8H), 4.68 (d, *J* = 7.0 Hz, 2H), 4.18 – 4.06 (m, 4H), 3.04 – 2.86 (m, 1H), 2.78 – 2.67 (m, 1H), 2.64 – 2.52 (m, 1H), 2.40 – 2.23 (m, 1H), 2.21 – 1.94 (m, 33H), 1.73 (s, 3H), 1.70 – 1.56 (m, 27H), 1.39 – 1.24 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0 (d, *J* = 4.9 Hz), 142.9, 140.5, 135.6, 135.0, 134.92, 134.90, 134.87, 131.2, 128.6, 128.4, 126.2, 124.4, 124.23, 124.19, 124.1, 123.5, 117.9, 62.7 (d, *J* = 4.9 Hz), 62.6, 62.2, 45.0 (d, *J* = 130.8 Hz), 39.73, 39.67, 39.6, 34.3 (d, *J* = 15.3 Hz), 29.7, 28.7 (d, *J* = 4.5 Hz), 26.73, 26.68 (d, *J* = 2.0 Hz), 26.7, 26.3, 25.7, 17.7, 16.5, 16.4 (d, *J* = 3.4 Hz), 16.3 (d, *J* = 3.5 Hz), 16.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.53.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{59}H_{94}O_5P^+$ 913.6833; Found: 913.6824.



(*1R,2S,5R*)-2-Isopropyl-5-methylcyclohexyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (6h)

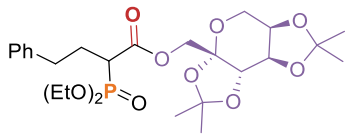
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (75.3 mg, 86% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.22 – 7.14 (m, 3H), 4.85 – 4.73 (m, 1H), 4.20 – 4.02 (m, 4H), 3.02 – 2.86 (m, 1H), 2.80 – 2.68 (m, 1H), 2.63 – 2.49 (m, 1H), 2.39 – 2.24 (m, 1H), 2.26 – 2.11 (m, 1H), 2.11 – 1.90 (m, 2H), 1.70 (d, *J* = 11.4 Hz, 2H), 1.64 – 1.39 (m, 2H), 1.39 – 1.17 (m, 6H), 1.17 – 1.00 (m, 2H), 0.97 – 0.85 (m, 7H), 0.79 (t, *J* = 6.7 Hz, 3H).

13C NMR (101 MHz, Chloroform-d) δ 168.5 (d, *J* = 5.0 Hz), 140.5, 128.5, 128.4, 126.2, 75.5, 62.6 (d, *J* = 2.6 Hz), 46.8 (d, *J* = 8.4 Hz), 44.6, 45.25 (d, *J* = 131.6 Hz), 40.6, 34.1 (d, *J* = 2.2 Hz), 31.3 (d, *J* = 3.4 Hz), 28.9 (d, *J* = 4.4 Hz), 25.4, 22.8, 22.0, 20.8, 16.3 (d, *J* = 2.7 Hz), 16.2 (d, *J* = 2.6 Hz), 15.9, 15.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.91.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{40}O_5P^+$ 439.2608; Found: 439.2608.



((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (6i)

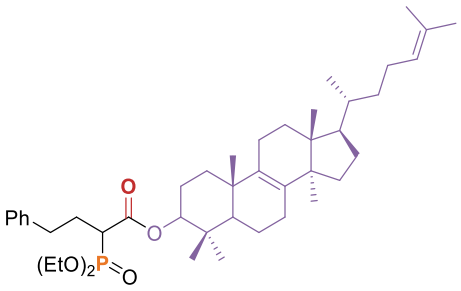
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 1:2) to afford the title compound as a colorless liquid (75.9 mg, 70% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 4.61 (t, *J* = 10.0 Hz, 1H), 4.42 – 4.27 (m, 2H), 4.24 (d, *J* = 7.7 Hz, 1H), 4.19 – 4.08 (m, 5H), 3.93 (d, *J* = 13.0 Hz, 1H), 3.77 (d, *J* = 13.1 Hz, 1H), 3.07 – 2.94 (m, 1H), 2.85 – 2.68 (m, 1H), 2.69 – 2.55 (m, 1H), 2.43 – 2.27 (m, 1H), 2.27 – 2.10 (m, 1H), 1.55 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.35 – 1.28 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5 (d, *J* = 5.2 Hz), 140.4, 128.6, 128.5, 126.2, 109.1, 108.8, 101.3, 70.8, 70.2, 70.0, 66.1, 62.9 (d, *J* = 6.6 Hz), 62.8 (d, *J* = 6.5 Hz), 61.2, 44.9 (d, *J* = 130.8 Hz), 34.2 (d, *J* = 14.7 Hz), 28.6 (d, *J* = 4.5 Hz), 26.5, 25.9, 25.3, 24.1, 16.32 (d, *J* = 5.9 Hz), 16.27 (d, *J* = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.17.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{40}O_{10}P^+$ 543.2354; Found: 543.2362.



(10*S*,13*R*,14*R*,17*R*)-4,4,10,13,14-Pentamethyl-17-((*R*)-6-methylhept-5-en-2-yl)-2,3,4,5,6,7,10,11,12,13,14,15,16,17-tetradecahydro-*1H*-cyclopenta[a]phenanthren-3-yl 2-(diethoxyphosphoryl)-4-phenylbutanoate (6j)

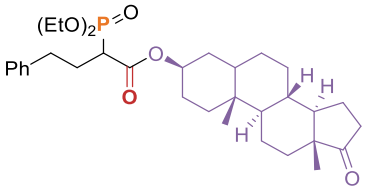
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (82.1 mg, 58% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.15 (m, 3H), 5.10 (t, *J* = 7.0 Hz, 1H), 4.64 – 4.43 (m, 1H), 4.41 – 3.98 (m, 4H), 3.04 – 2.87 (m, 1H), 2.85 – 2.66 (m, 1H), 2.65 – 2.52 (m, 1H), 2.44 – 2.26 (m, 1H), 2.22 – 2.11 (m, 1H), 2.12 – 1.99 (m, 4H), 1.96 – 1.83 (m, 2H), 1.80 – 1.64 (m, 8H), 1.63 – 1.43 (m, 6H), 1.42 – 1.24 (m, 10H), 1.22 – 1.10 (m, 3H), 1.02 (s, 3H), 1.00 – 0.81 (m, 14H), 0.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6 (d, *J* = 18.4 Hz), 140.5 (d, *J* = 3.6 Hz), 134.6 (d, *J* = 1.7 Hz), 134.1, 130.9, 128.5 (d, *J* = 3.1 Hz), 128.5 (d, *J* = 1.9 Hz), 126.2, 125.2, 82.3 (d, *J* = 13.5 Hz), 62.6 (d, *J* = 3.3 Hz), 62.5 (d, J = 3.5 Hz), 50.6 (d, *J* = 6.3 Hz), 50.4 (d, *J* = 11.8 Hz), 49.8, 46.1 (d, *J* = 8.2 Hz), 44.8 (d, *J* = 9.1 Hz), 44.4 (d, *J* = 2.2 Hz), 39.5, 37.9 (d, J = 8.8 Hz), 36.9, 36.4, 36.3 (d, *J* = 8.9 Hz), 35.2 (d, *J* = 3.1 Hz), 34.4 (d, *J* = 7.6 Hz), 34.3, 30.9 (d, *J* = 13.6 Hz), 28.9, 28.5, 28.2, 28.0, 27.8 (d, *J* = 3.3 Hz), 26.3, 25.7, 24.9, 24.2 (d, *J* = 1.8 Hz), 24.0 (d, *J* = 11.4 Hz), 22.8, 22.5, 21.0, 19.2, 18.6 (d, *J* = 8.6 Hz), 18.1, 17.6, 16.6, 16.4 (d, *J* = 5.6 Hz), 15.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ 23.07, 22.97.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{44}H_{70}O_5P^+$ 709.4955; Found: 709.4960.



(*3R*,*8S*,*9R*,*10R*,*13R*,*14R*)-10,13-Dimethyl-17-oxohexadecahydro-*1H*-cyclopenta[a]phenanthren-3-yl 2-(diethoxyphosphoryl)-4-phenylbutanoate (6k)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (88.1 mg, 77% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

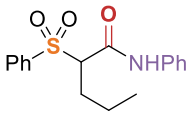
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.24 – 7.14 (m, 3H), 4.87 – 4.74 (m, 1H), 4.19 – 4.02 (m, 4H), 2.99 – 2.85 (m, 1H), 2.79 – 2.67 (m, 1H), 2.63 – 2.51 (m, 1H), 2.49 – 2.32 (m, 1H), 2.35

– 2.22 (m, 1H), 2.20 – 1.99 (m, 2H), 1.98 – 1.84 (m, 2H), 1.84 – 1.72 (m, 3H), 1.73 – 1.62 (m, 2H), 1.62 – 1.48 (m, 3H), 1.48 – 1.39 (m, 1H), 1.37 – 1.18 (m, 12H), 1.13 – 0.94 (m, 2H), 0.86 (s, 6H), 0.77 – 0.67 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.1, 168.5 (d, *J* = 4.9 Hz), 140.5, 128.5, 128.4, 126.2, 74.6, 62.6 (d, *J* = 6.3 Hz), 62.5 (d, *J* = 2.8 Hz), 62.5 (d, *J* = 2.7 Hz), 54.2, 51.3, 47.7, 45.8 (d, *J* = 2.4 Hz), 44.6 (d, *J* = 3.4 Hz), 44.5, 36.6 (d, *J* = 3.1 Hz), 35.8, 35.6, 35.0, 34.2 (d, *J* = 14.6 Hz), 33.7 (d, *J* = 21.4 Hz), 31.5, 30.7, 28.7 (d, *J* = 3.7 Hz), 28.2 (d, *J* = 3.0 Hz), 27.3, 27.2, 21.7, 20.4, 16.3 (d, *J* = 5.9 Hz), 13.8, 12.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.79.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{33}H_{50}O_6P^+$ 573.3340; Found: 573.3348.



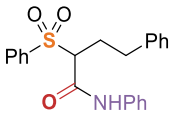
***N*-Phenyl-2-(phenylsulfonyl)pentanamide (7a)**

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (49.5 mg, 78% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.88 (d, *J* = 7.1 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.60 – 7.44 (m, 4H), 7.46 – 7.21 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.39 – 3.60 (m, 1H), 2.57 – 1.86 (m, 2H), 1.59 – 1.30 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 137.2, 136.2, 134.4, 129.2, 129.1, 129.0, 124.9, 120.1, 72.1, 28.7, 20.2, 13.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{20}NO_3S^+$ 318.1158; Found: 318.1159.



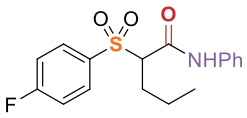
***N*,4-Diphenyl-2-(phenylsulfonyl)butanamide (7b)**

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (45.5 mg, 60% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.82 (d, *J* = 7.1 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.60 – 7.42 (m, 4H), 7.39 – 7.30 (m, 2H), 7.30 – 7.22 (m, 2H), 7.22 – 7.10 (m, 4H), 4.07 – 3.70 (m, 1H), 3.06 – 2.77 (m, 1H), 2.75 – 2.58 (m, 1H), 2.51 – 2.25 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 139.5, 137.1, 136.0, 134.5, 129.2, 129.1, 129.1, 128.6, 128.5, 126.5, 125.1, 120.1, 71.2, 32.7, 28.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{22}NO_3S^+$ 380.1315; Found: 380.1318.



2-((4-Fluorophenyl)sulfonyl)-*N*-phenylpentanamide (7c)

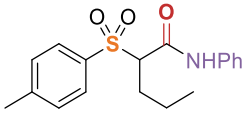
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (46.9 mg, 70% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.42 (s, 1H), 8.21 – 7.75 (m, 2H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.21 (t, *J* = 8.5 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 4.12 – 3.80 (m, 1H), 2.16 – 1.86 (m, 2H), 1.59 – 1.31 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 166.4 (d, *J* = 257.8 Hz), 162.2, 137.2, 132.2 (d, *J* = 9.8 Hz), 129.1, 125.2, 120.1, 116.7 (d, *J* = 22.8 Hz), 72.3, 28.9, 20.3, 13.6.

^{19}F NMR (376 MHz, CDCl$_3$) δ -101.85.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{19}FNO_3S^+$ 336.1064; Found: 336.1069.



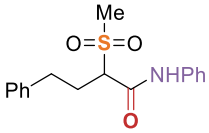
***N*-Phenyl-2-tosylpentanamide (7d)**

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (52.3 mg, 79% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.50 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.41 – 7.22 (m, 4H), 7.13 (t, *J* = 7.4 Hz, 1H), 4.90 – 3.60 (m, 1H), 2.42 (s, 3H), 2.22 – 1.85 (m, 2H), 1.70 – 1.28 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 162.4, 145.6, 137.3, 133.2, 129.9, 129.1, 129.0, 124.9, 120.1, 72.1, 28.7, 21.7, 20.3, 13.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{22}NO_3S^+$ 332.1315; Found: 332.1322.

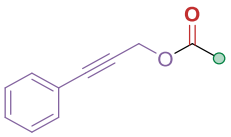


2-(Methylsulfonyl)-*N*,4-diphenylbutanamide (7e)

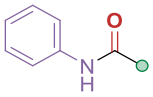
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (39.3 mg, 62% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.33 (s, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.44 – 7.25 (m, 4H), 7.24 – 7.07 (m, 4H), 3.90 – 3.57 (m, 1H), 2.98 (s, 3H), 2.94 – 2.79 (m, 1H), 2.75 – 2.61 (m, 1H), 2.58 – 2.36 (m, 2H).

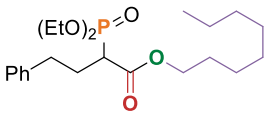
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 139.3, 137.1, 129.1, 128.8, 128.6, 126.7, 125.3, 120.3, 70.5, 37.8, 32.9, 28.7.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{20}NO_3S^+$ 318.1158; Found: 318.1161.



3-Phenylprop-2-yn-1-yl acetate (7f)[10]
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 10:1) to afford the title compound as a colorless liquid (27.1 mg, 78% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.41 (m, 2H), 7.41 – 7.24 (m, 3H), 4.90 (s, 2H), 2.13 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 131.9, 128.7, 128.3, 122.1, 86.4, 82.9, 52.8, 20.8.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{11}H_{11}O_2^+$ 175.0754; Found: 175.0759.



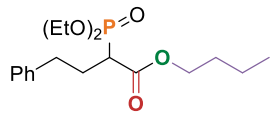
***N*-Phenylacetamide (7g)**[11]
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (22.1 mg, 82% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 2.13 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 138.0, 128.8, 124.2, 120.1, 24.3.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_8H_{10}NO_2^+$ 136.0757; Found: 136.0758.



Octyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (8a)
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (47.8 mg, 58% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.24 – 7.13 (m, 3H), 4.19 – 4.04 (m, 6H), 3.09 – 2.88 (m, 1H), 2.85 – 2.67 (m, 1H), 2.64 – 2.51 (m, 1H), 2.41 – 2.25 (m, 1H), 2.23 – 2.07 (m, 1H), 1.72 – 1.60 (m, 2H), 1.40 – 1.25 (m, 16H), 0.87 (t, *J* = 6.9 Hz 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1 (d, *J* = 5.0 Hz), 140.4, 128.5, 128.4, 126.2, 65.6, 62.7 (d, *J* = 13.0 Hz), 62.7, 45.1 (d, *J* = 130.9 Hz), 34.3 (d, *J* = 15.4 Hz), 31.8, 29.2, 28.6 (d, *J* = 4.5 Hz), 28.6, 25.8, 22.6, 16.4 (d, *J* = 1.9 Hz), 16.3 (d, *J* = 2.1 Hz), 14.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.67.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{38}O_5P^+$ 413.2451; Found: 413.2458.



Butyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (8b)

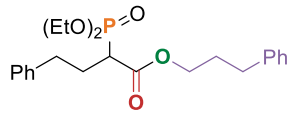
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (37.7 mg, 53% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.0 Hz, 2H), 4.26 – 3.99 (m, 6H), 3.16 – 2.87 (m, 1H), 2.81 – 2.69 (m, 1H), 2.66 – 2.54 (m, 1H), 2.45 – 2.26 (m, 1H), 2.23 – 2.07 (m, 1H), 1.81 – 1.59 (m, 2H), 1.47 – 1.37 (m, 2H), 1.31 – 1.23 (m, 6H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1 (d, *J* = 4.9 Hz), 140.4, 128.5, 128.4, 126.2, 65.2, 62.6 (d, *J* = 6.4 Hz), 62.6 (d, *J* = 7.0 Hz), 45.0 (d, *J* = 130.9 Hz), 34.3 (d, *J* = 15.4 Hz), 30.5, 28.6 (d, *J* = 4.5 Hz), 19.0, 16.3 (d, *J* = 3.7 Hz), 16.3 (d, *J* = 3.9 Hz), 13.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.65.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{30}O_5P^+$ 357.1825; Found: 357.1826.



3-Phenylpropyl 2-(diethoxyphosphoryl)-4-phenylbutanoate (8c)

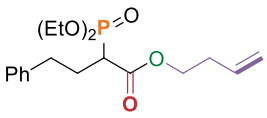
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (50.2 mg, 60% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 4H), 7.24 – 7.00 (m, 6H), 4.33 – 3.94 (m, 6H), 3.02 – 2.94 (m, 1H), 2.80 – 2.66 (m, 3H), 2.65 – 2.50 (m, 1H), 2.46 – 2.27 (m, 1H), 2.24 – 2.09 (m, 1H), 2.09 – 1.94 (m, 2H), 1.51 – 1.15 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0 (d, *J* = 5.0 Hz), 141.0, 140.3, 128.5, 128.4, 128.4, 128.4, 126.2, 126.0, 64.6, 62.7 (d, *J* = 6.4 Hz), 62.6 (d, *J* = 6.6 Hz), 45.0 (d, *J* = 131.0 Hz), 34.3 (d, *J* = 15.4 Hz), 32.0, 30.2, 28.6 (d, *J* = 4.5 Hz), 16.3 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.63.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{32}O_5P^+$ 419.1928; Found: 419.1933.



But-3-en-1-yl 2-(diethoxyphosphoryl)-4-phenylbutanoate (8d)

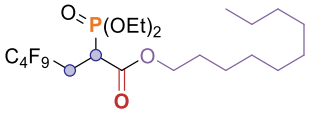
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (22.7 mg, 32% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.14 (m, 3H), 5.95 – 5.59 (m, 1H), 5.31 – 4.77 (m, 2H), 4.29 – 4.18 (m, 2H), 4.18 – 4.03 (m, 4H), 3.03 – 2.89 (m, 1H), 2.81 – 2.67 (m, 1H), 2.64 – 2.52 (m, 1H), 2.48 – 2.40 (m, 2H), 2.35 – 2.23 (m, 1H), 2.22 – 2.06 (m, 1H), 1.47 – 1.23 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0 (d, *J* = 4.9 Hz), 140.4, 133.8, 128.5, 128.4, 126.2, 117.4, 64.5, 62.7 (d, *J* = 6.3 Hz), 62.6 (d, *J* = 6.9 Hz), 45.0 (d, *J* = 131.0 Hz), 34.3 (d, *J* = 15.3 Hz), 32.9, 28.6 (d, *J* = 4.7 Hz), 16.3 (d, *J* = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 22.46.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{28}O_5P^+$ 355.1669; Found: 355.1670.



Decyl 2-(diethoxyphosphoryl)-4,4,5,5,6,6,7,7,7-nonafluoroheptanoate (9a)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (71.6 mg, 63% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, ^{19}F NMR and HRMS.

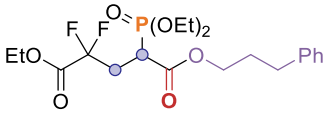
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 – 3.98 (m, 6H), 3.48 – 3.22 (m, 1H), 3.12 – 2.79 (m, 1H), 2.76 – 2.42 (m, 1H), 1.77 – 1.57 (m, 2H), 1.42 – 1.20 (m, 20H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 167.6 (d, *J* = 6.3 Hz), 66.4, 63.6 (d, *J* = 6.4 Hz), 63.3 (d, *J* = 6.9 Hz), 38.1 (d, *J* = 131.8 Hz), 31.8, 29.5 (d, *J* = 3.3 Hz), 29.3, 29.2, 28.8 (t, *J* = 21.5 Hz), 28.4, 25.7, 22.6, 16.3 (d, *J* = 5.9 Hz), 14.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 19.95.

^{19}F NMR (176 MHz, $CDCl_3$) δ -80.53 – -81.71 (m, 3F), -112.58 – -116.50 (m, 2F), -121.97 – -125.15 (m, 2F), -125.15 – -127.65 (m, 2F).

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{35}F_9O_5P^+$ 569.2073; Found: 569.2069.



1-Ethyl 5-(3-phenylpropyl) 4-(diethoxyphosphoryl)-2,2-difluoropentanedioate (9b)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid

(43.2 mg, 48% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, ^{19}F NMR and HRMS.

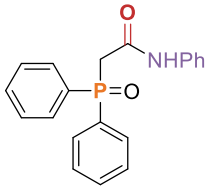
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 2H), 7.24 – 7.04 (m, 3H), 4.52 – 4.25 (m, 2H), 4.24 – 3.99 (m, 6H), 3.51 – 3.16 (m, 1H), 3.07 – 2.81 (m, 1H), 2.90 – 2.66 (m, 2H), 2.67 – 2.49 (m, 1H), 2.23 – 1.81 (m, 2H), 1.56 – 1.13 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0 (d, *J* = 5.9 Hz), 163.3 (t, *J* = 32.2 Hz), 141.1, 128.5, 128.4, 126.0, 114.6 (d, *J* = 16.8 Hz), 65.3, 63.5 (d, *J* = 6.5 Hz), 63.3, 63.2 (d, *J* = 6.8 Hz), 62.6 (d, *J* = 5.8 Hz), 39.0 (d, *J* = 131.6 Hz), 32.1 (d, *J* = 3.8 Hz), 31.9, 30.1, 16.3 (d, *J* = 5.4 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 20.57.

^{19}F NMR (176 MHz, $CDCl_3$) δ -95.15 – -118.30 (m, 2F)

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{30}F_2O_7P^+$ 451.1692; Found: 451.1699.



2-(Diphenylphosphoryl)-*N*-phenylacetamide (5s)

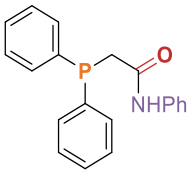
This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a colorless liquid (54.3 mg, 81% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.82 – 7.68 (m, 4H), 7.62 – 7.40 (m, 8H), 7.21 (t, *J* = 7.9 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 3.53 (d, *J* = 12.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5 (d, *J* = 8.6 Hz), 137.7, 136.8 (d, *J* = 13.0 Hz), 132.7 (d, *J* = 19.4 Hz), 130.7 (d, *J* = 10.1 Hz), 128.9 (d, *J* = 2.9 Hz), 128.8, 124.3, 119.9, 38.7 (d, *J* = 22.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.13.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{19}NO_2P^+$ 336.1148; Found: 336.1150.



2-(Diphenylphosphanyl)-*N*-phenylacetamide (11)

This reaction was conducted on a 0.2 mmol scale with the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 5:1) to afford the title compound as a colorless liquid (40.2 mg, 63% yield). The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and HRMS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 4H), 7.40 – 7.35 (m, 6H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.9 Hz, 3H), 7.06 (t, *J* = 7.2 Hz, 1H), 3.17 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, *J* = 4.9 Hz), 138.0, 132.6 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 103.6 Hz), 130.8 (d, *J* = 10.0 Hz), 129.0 (d, *J* = 12.3 Hz), 128.8, 124.2, 120.1, 39.7 (d, *J* = 59.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ -17.08.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{19}NOP^+$ 320.1199; Found: 320.1203.

10. References

[1] J.-P. Fu, Y.-H. He, J. Zhong, Y. Yang, X. Deng and Z. J. Guan, An Efficient and General Route to the Synthesis of Diethyl α,α-Bromofluorophosphonates, *Fluor. Chem.* **2011**, *132*, 636−640.

[2] S.-J. He, J.-W. Wang, Y. Li, Z.-Y. Xu, X.-X. Wang, X. Lu and Y. Fu, Nickel-Catalyzed Enantioconvergent Reductive Hydroalkylation of Olefins with α-Heteroatom Phosphorus or Sulfur Alkyl Electrophiles, *J. Am. Chem. Soc.* **2020**, *142*, 214−221.

[3] H. Wang, P. Zheng, X. Wu, Y. Li and T. XU, Modular and Facile Access to Chiral α-Aryl Phosphates via Dual Nickel- and Photoredox-Catalyzed Reductive Cross-Coupling, *J. Am. Chem. Soc.* **2022**, *144*, 3989−3997.

[4] L. Qi, X. Pang, K. Yin, Q.-Q. Pan, X.-X. Wei and X.-Z. Shu, Mn-Mediated Reductive C(sp^3)–Si Coupling of Activated Secondary Alkyl Bromides with Chlorosilanes, *Chinese Chemical Letters* **2022**, *33*, 5061–5064.

[5] Z.-P. Bao and X.-F. Wu, Palladium-Catalyzed Direct Carbonylation of Bromoacetonitrile to Synthesize 2-Cyano-*N*-acetamide and 2-Cyanoacetate Compounds, *Angew. Chem. Int. Ed.* **2023**, e202301671.

[6] H.-J. Ai, B. N. Leidecker, P. Dam, C. Kubis, J. Rabeah and X.-F. Wu, Iron-Catalyzed Alkoxycarbonylation of Alkyl Bromides via a Two-Electron Transfer Process, *Angew. Chem. Int. Ed.* **2022**, *61*, e202211939.

[7] B. T. Sargent and E. J. Alexanian, Palladium-Catalyzed Alkoxycarbonylation of Unactivated Secondary Alkyl Bromides at Low Pressure, *J. Am. Chem. Soc.* **2016**, *138*, 7520−7523.

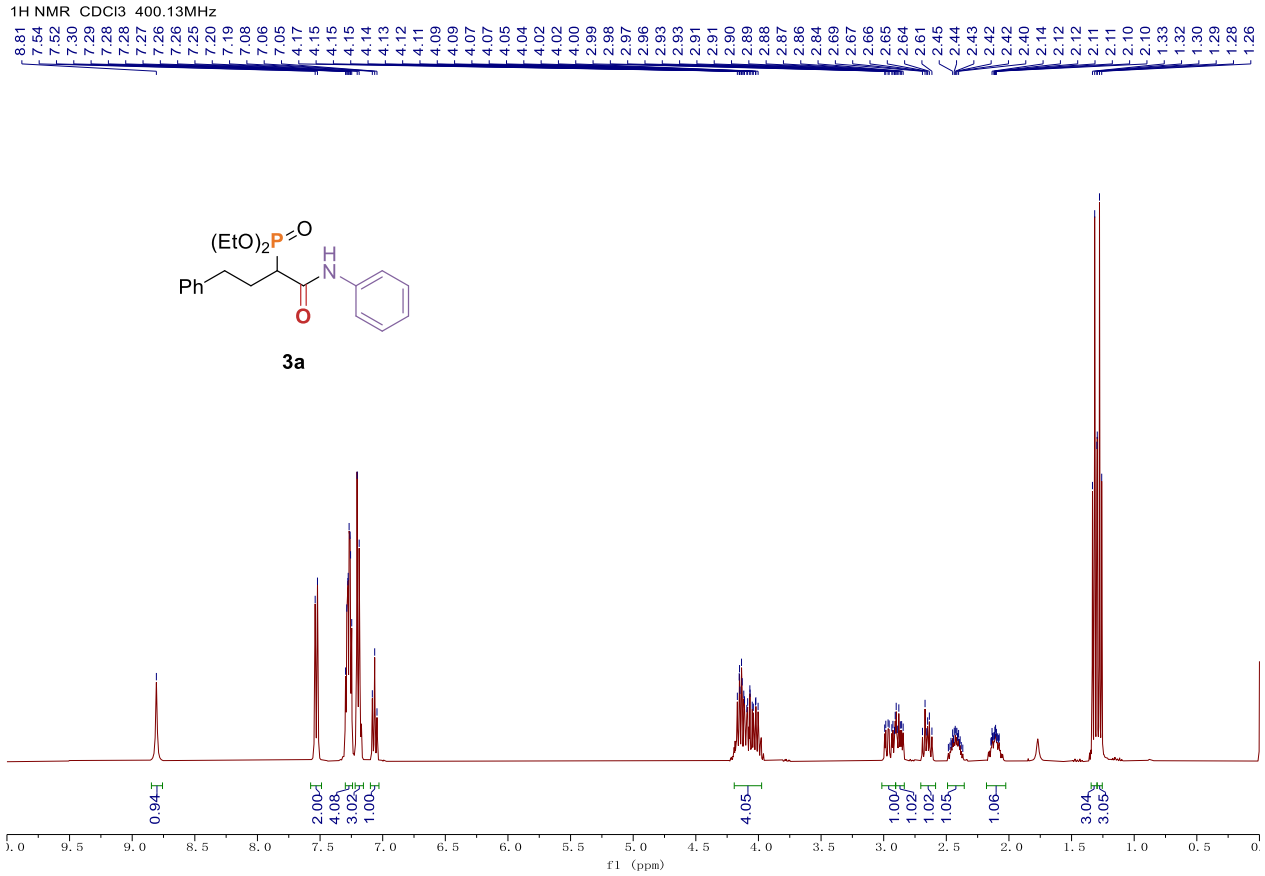
[8] F. Zhao, H.-J. Ai and X.-F. Wu, Copper-Catalyzed Substrate-Controlled Carbonylative Synthesis of α-Keto Amides and Amides from Alkyl Halides, *Angew. Chem. Int. Ed.* **2022**, *61*, e202200062.

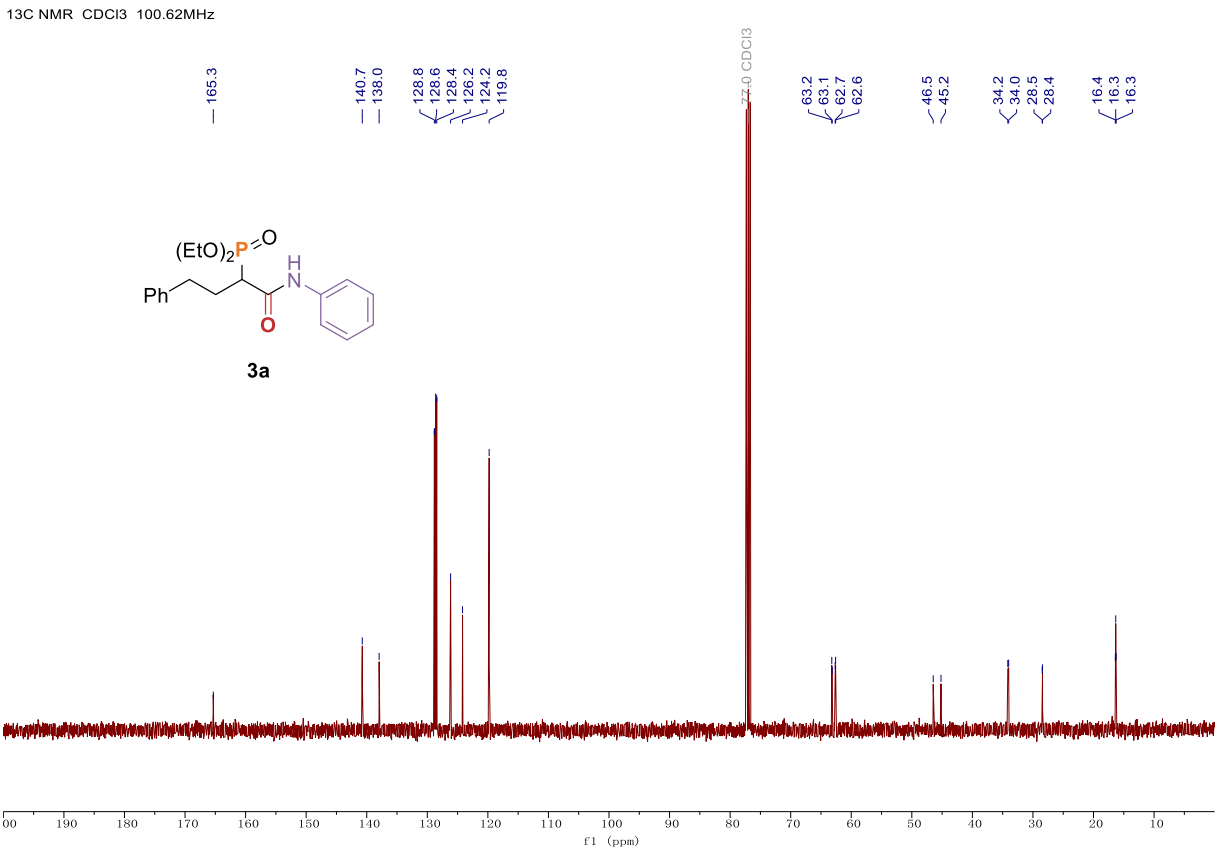
[9] Y. Li, S. Das, S. Zhou, K. Junge and M. Beller, General and Selective Copper-Catalyzed Reduction of Tertiary and Secondary Phosphine Oxides: Convenient Synthesis of Phosphines, *J. Am. Chem. Soc.* **2012**, *134*, 9727−9732.

[10] Y. Nishimoto, A. Okita, M. Yasuda and A. Baba, Synthesis of a Wide Range of Thioethers by Indium Triiodide Catalyzed Direct Coupling between Alkyl Acetates and Thiosilanes, *Org. Lett.* **2012**, *14*, 1846–1849.

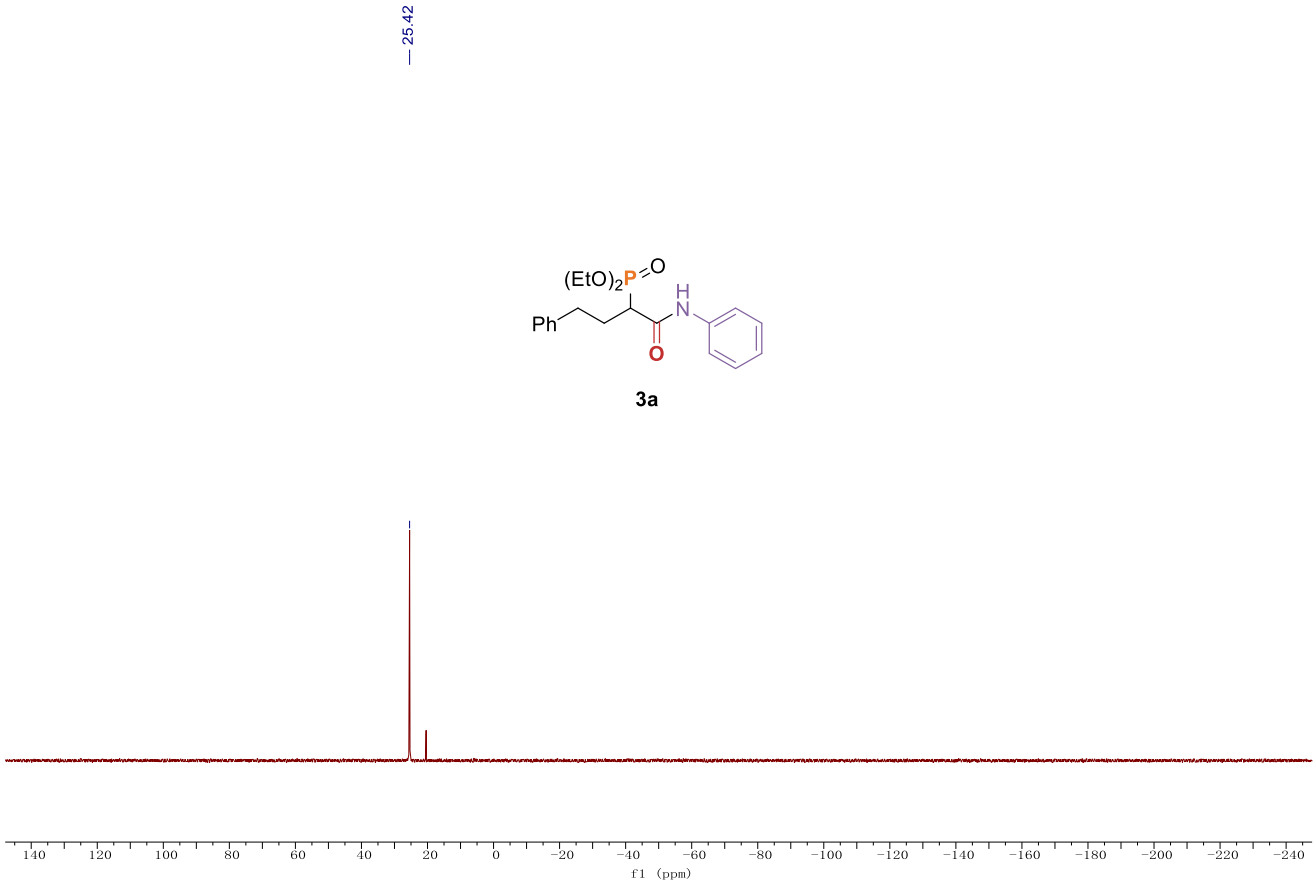
[11] Y. Gao, Y. Mao, B. Zhang, Y. Zhan and Y. Huo, Regioselective Nitration of Anilines with $Fe(NO_3)_3{\cdot}9H_2O$ as A Promoter and A Nitro Source, *Org. Biomol. Chem.*, **2018**, *16*, 3881-3884.

11. Spectra Data for the Compounds



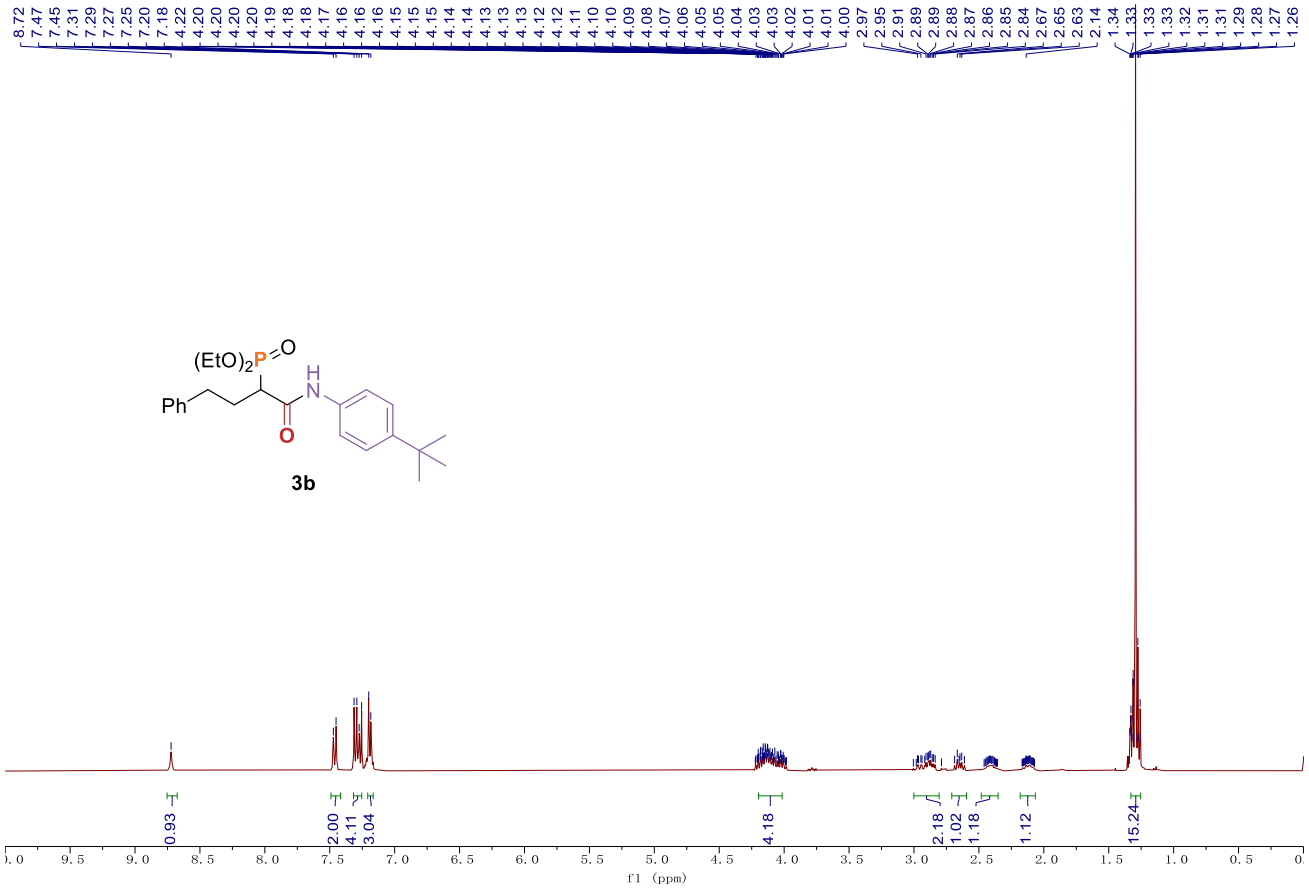


31P NMR CDCl3 161.97MHz



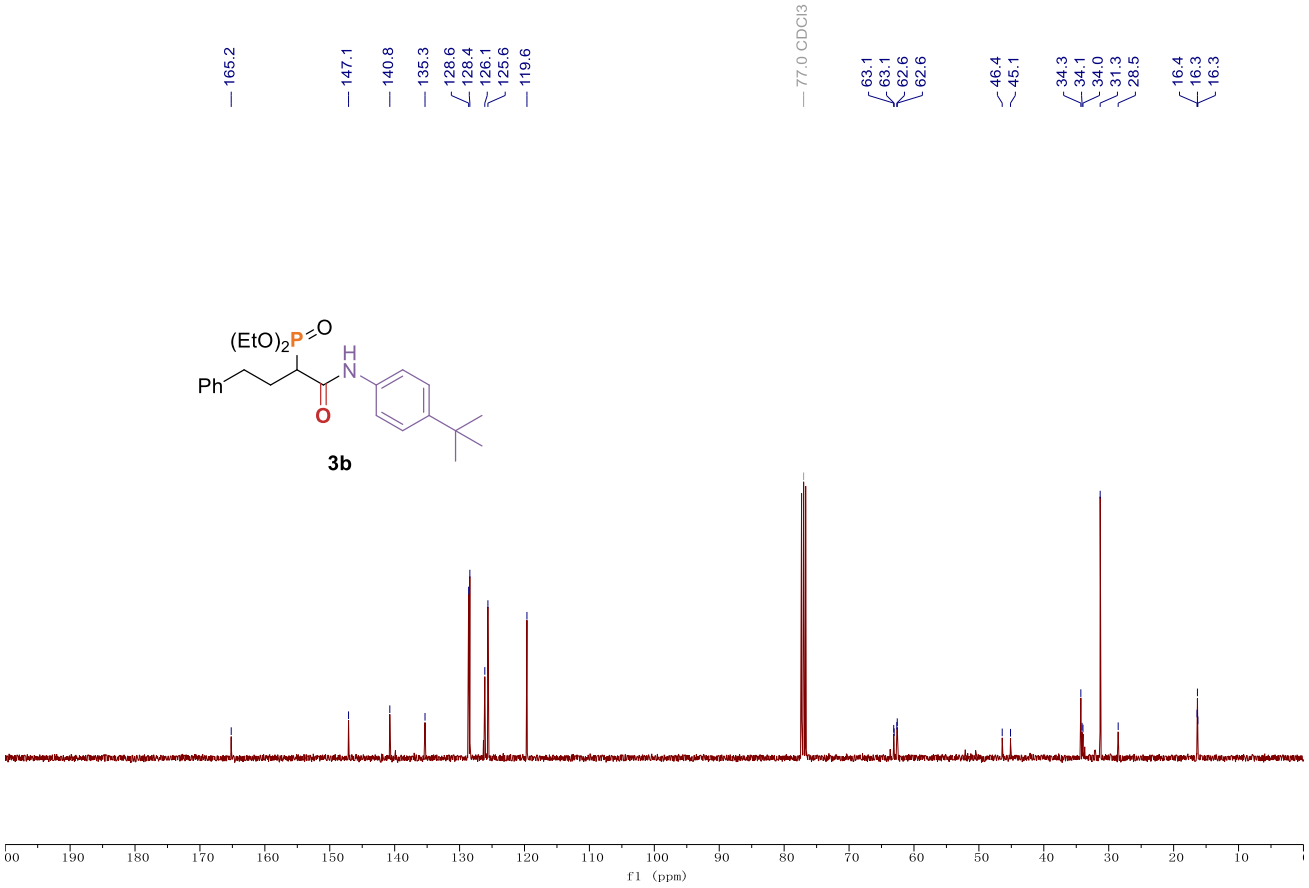
3a

1H NMR CDCl3 400.13MHz



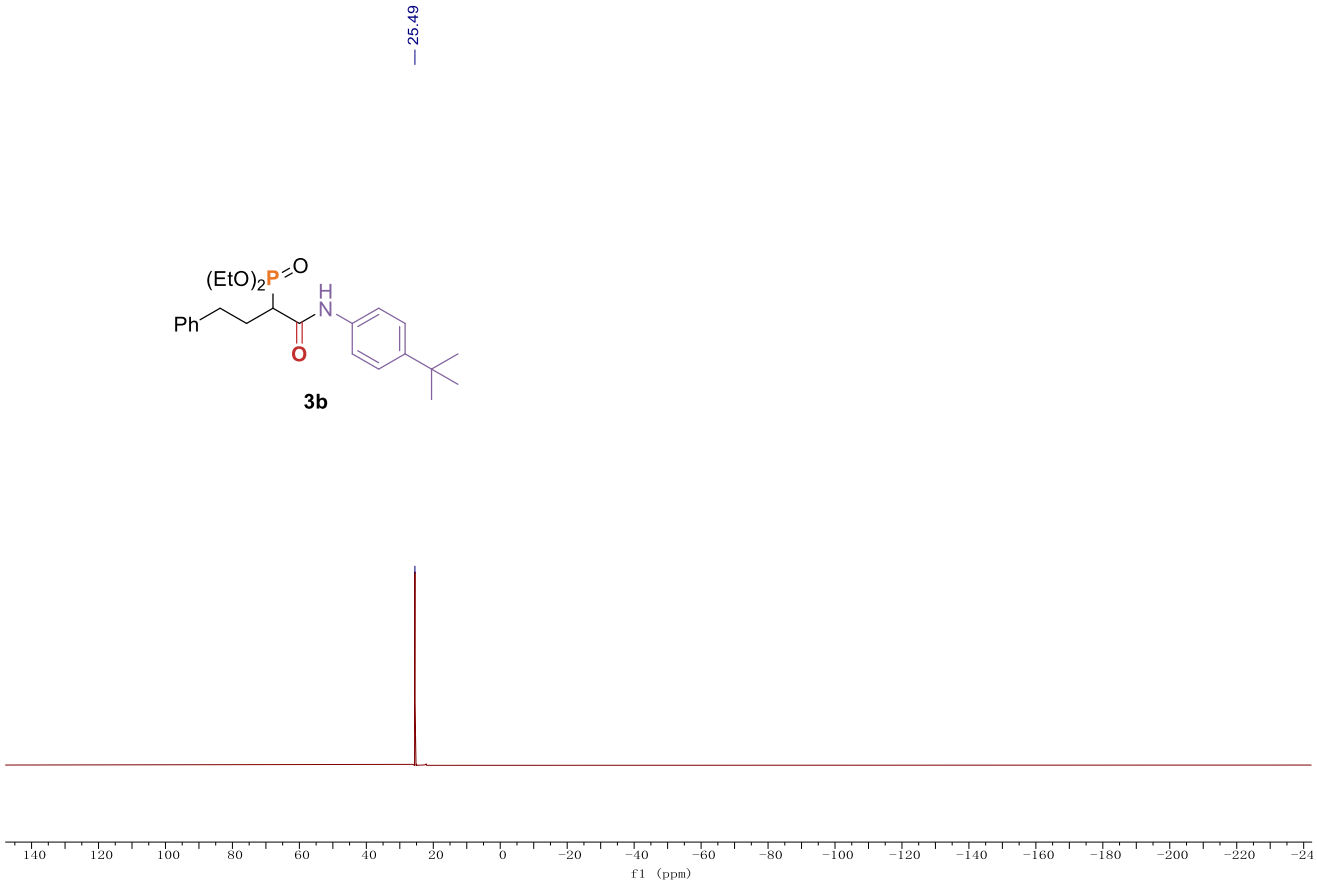
3b

13C NMR CDCl3 100.62MHz

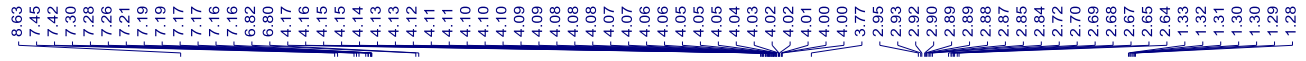


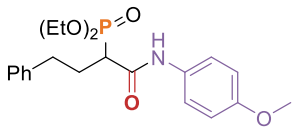
3b

31P NMR CDCl3 161.97MHz

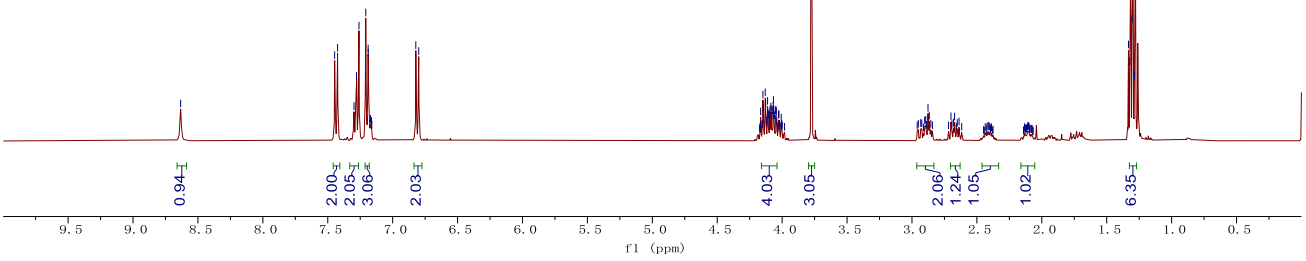


1H NMR CDCl3 400.13MHz



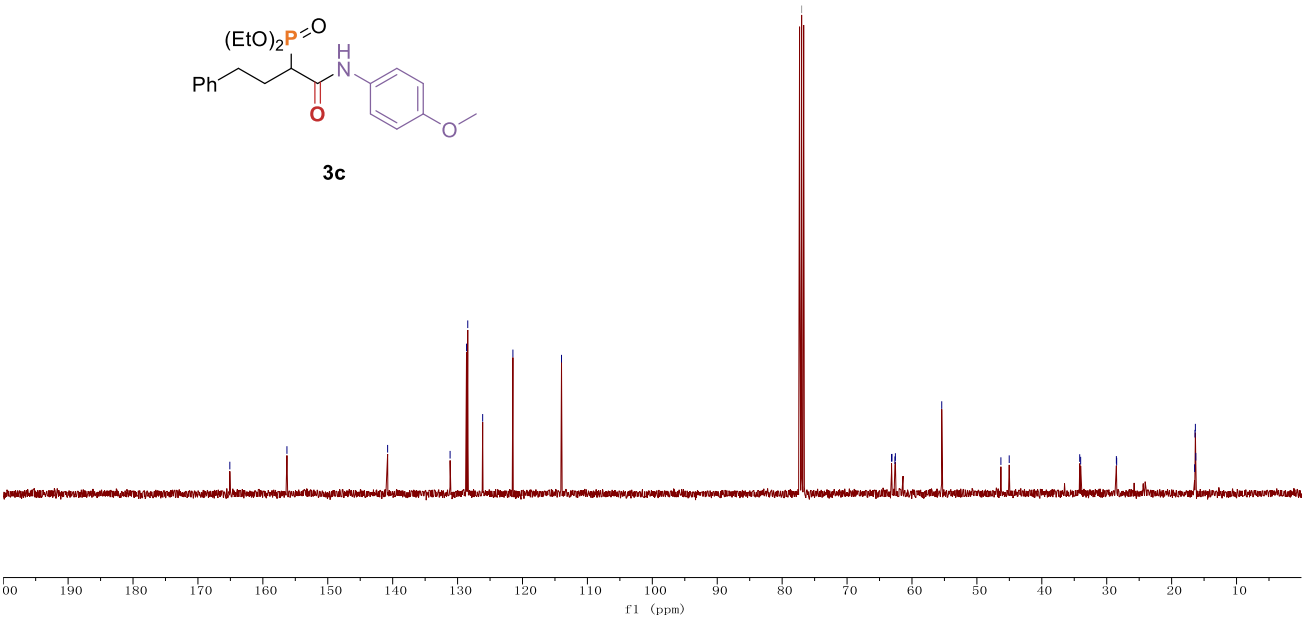


3c

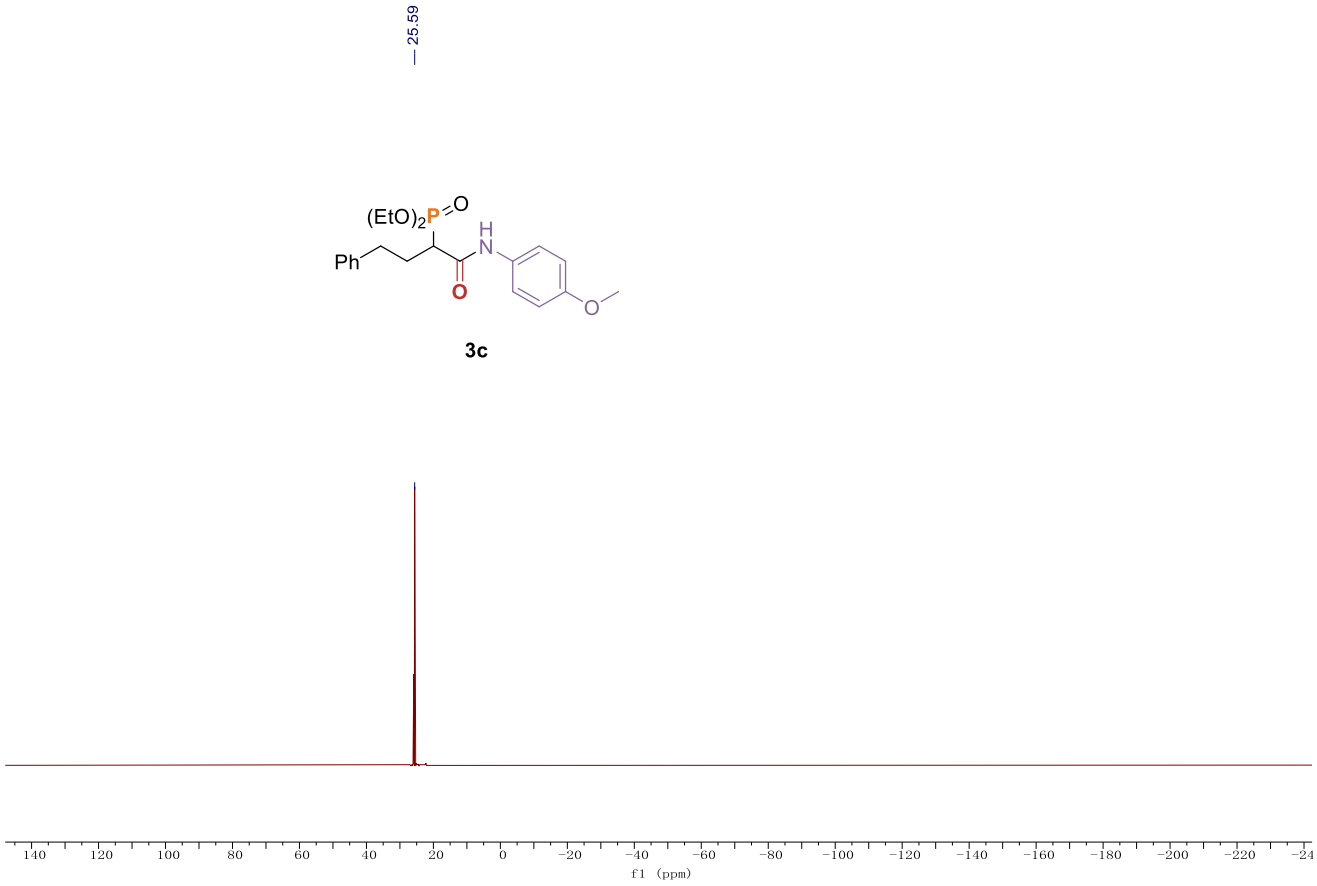


13C NMR CDCl3 100.62MHz

3c



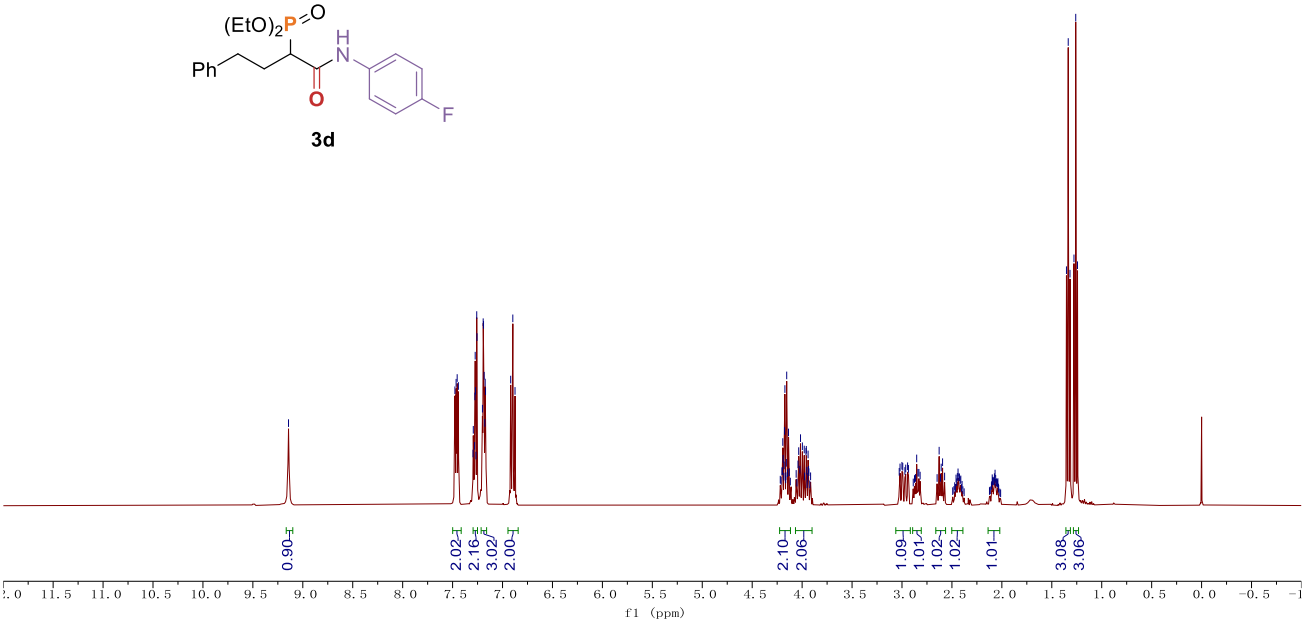
31P NMR CDCl3 161.97MHz



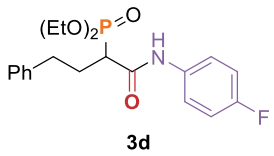
3c

1H NMR CDCl3 400.13MHz

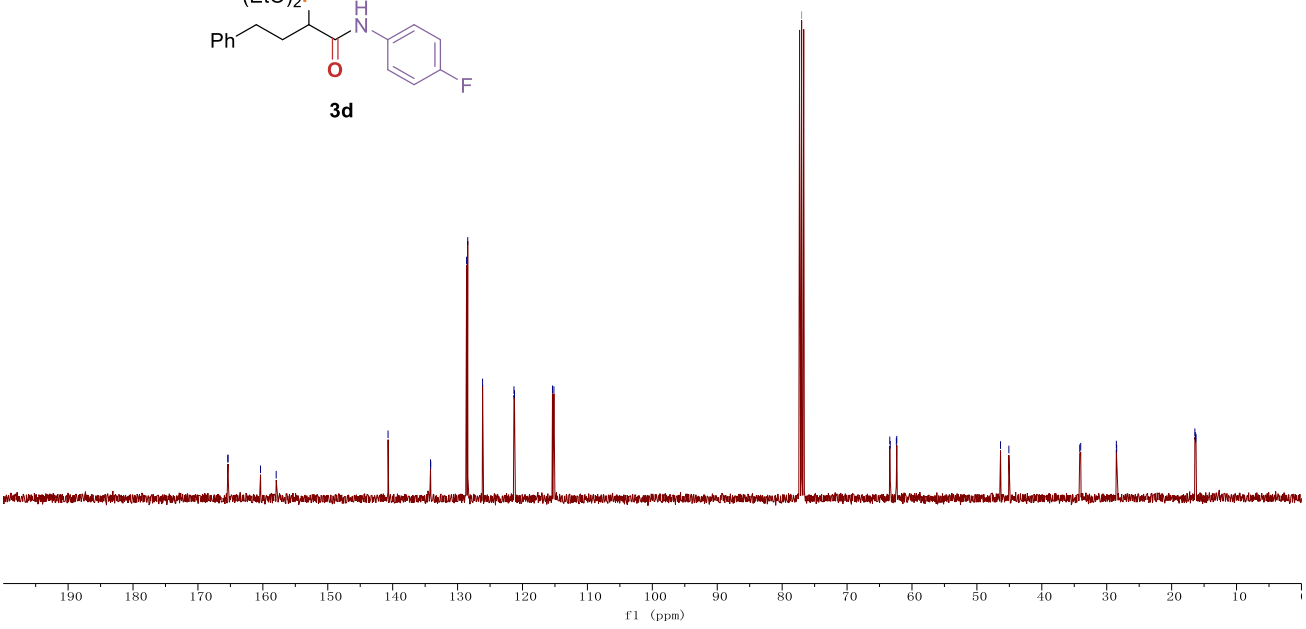
3d



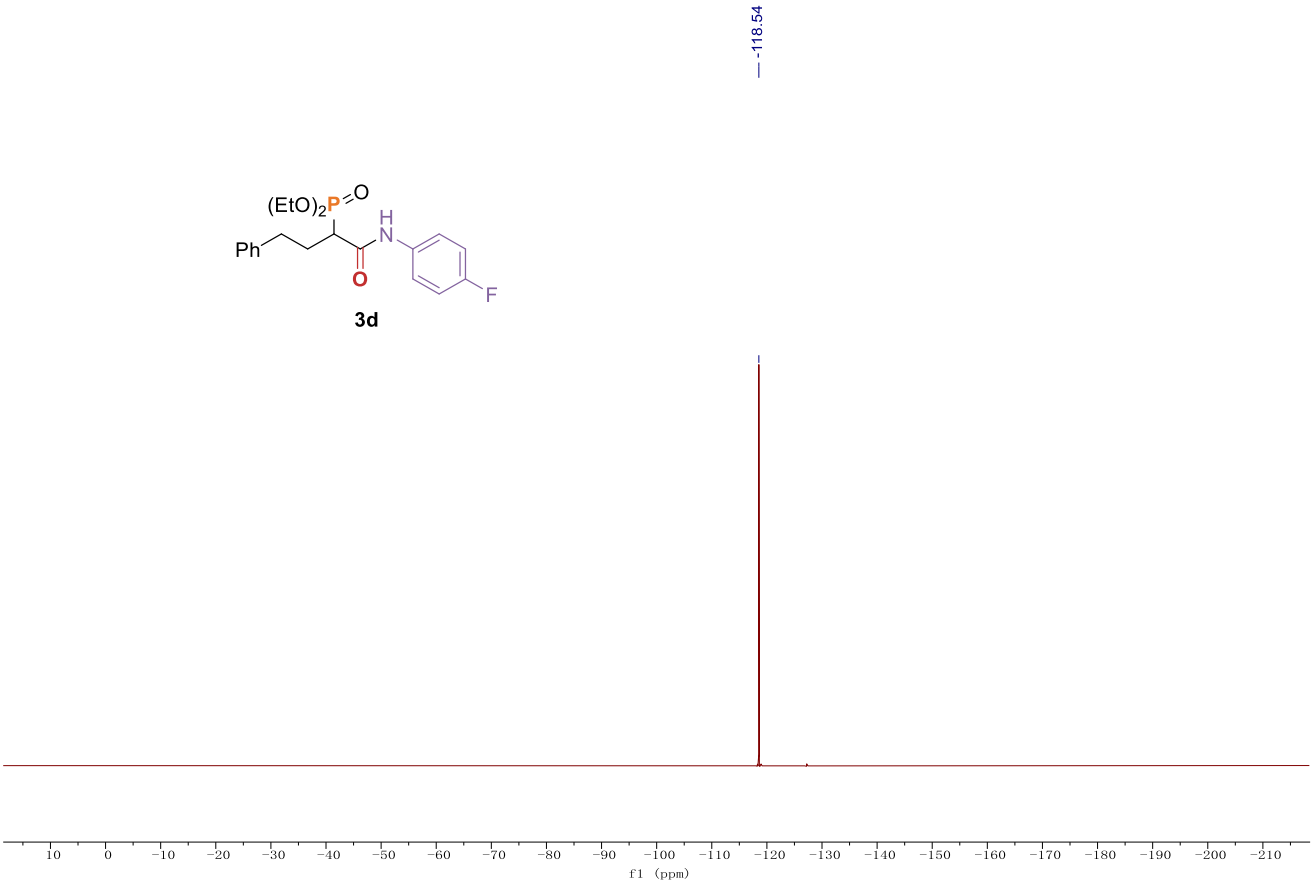
13C NMR CDCl3 100.62MHz



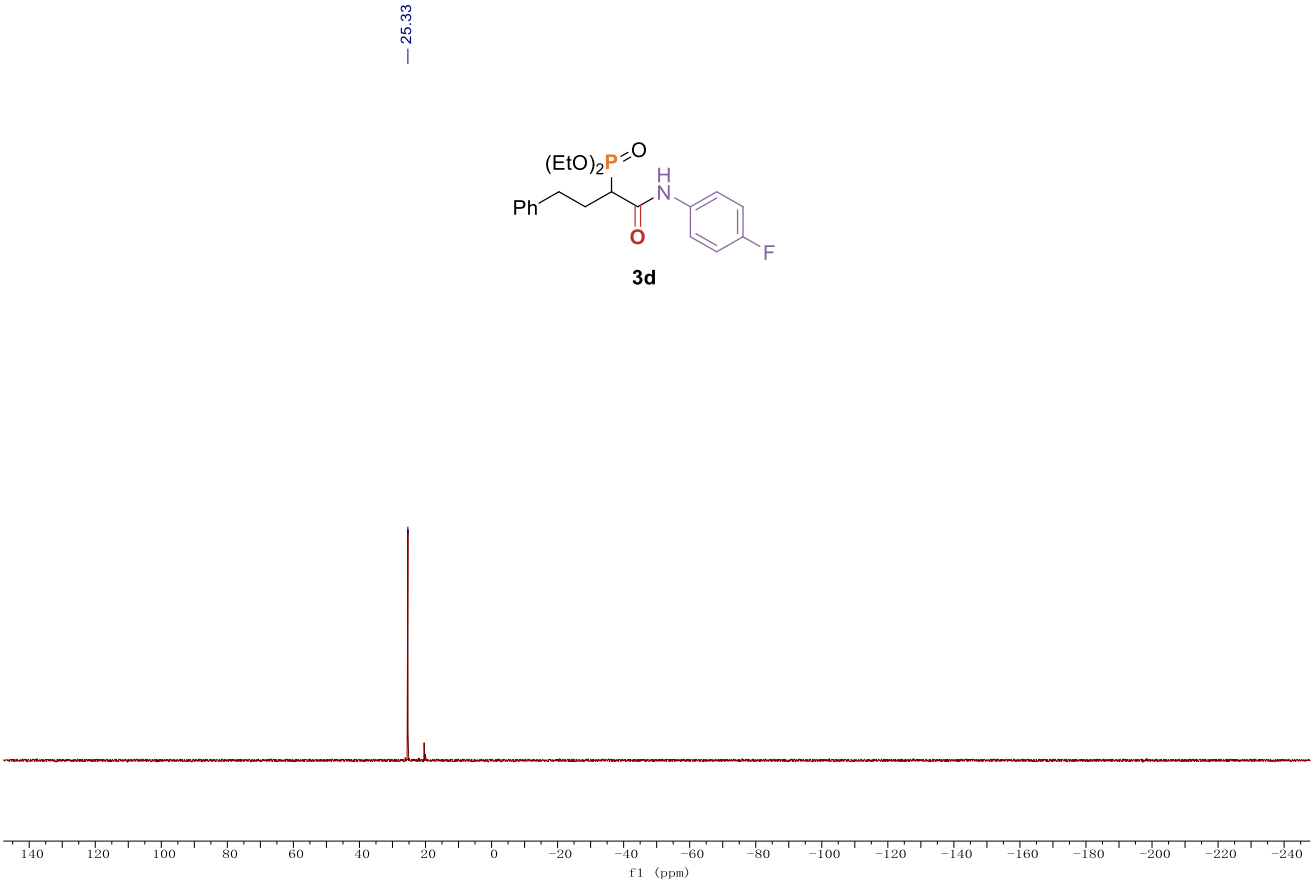
3d



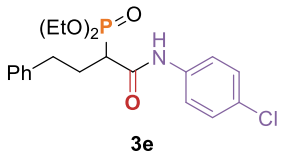
19F NMR CDCl3 376.46MHz



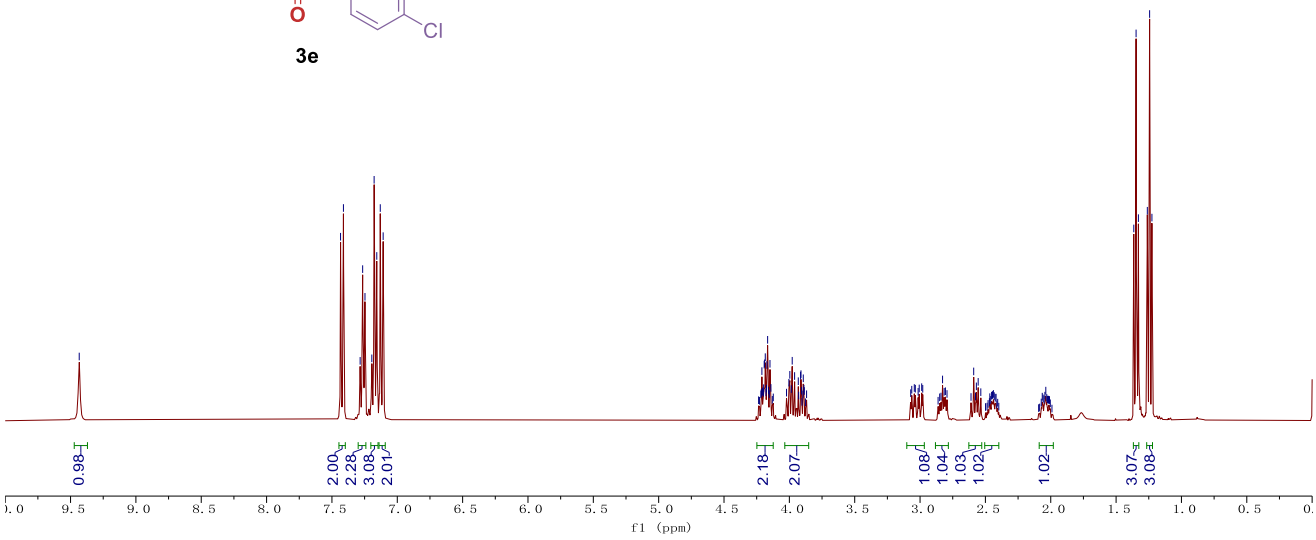
31P NMR CDCl3 161.97MHz



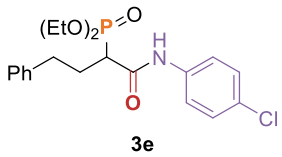
1H NMR CDCl3 400.13MHz



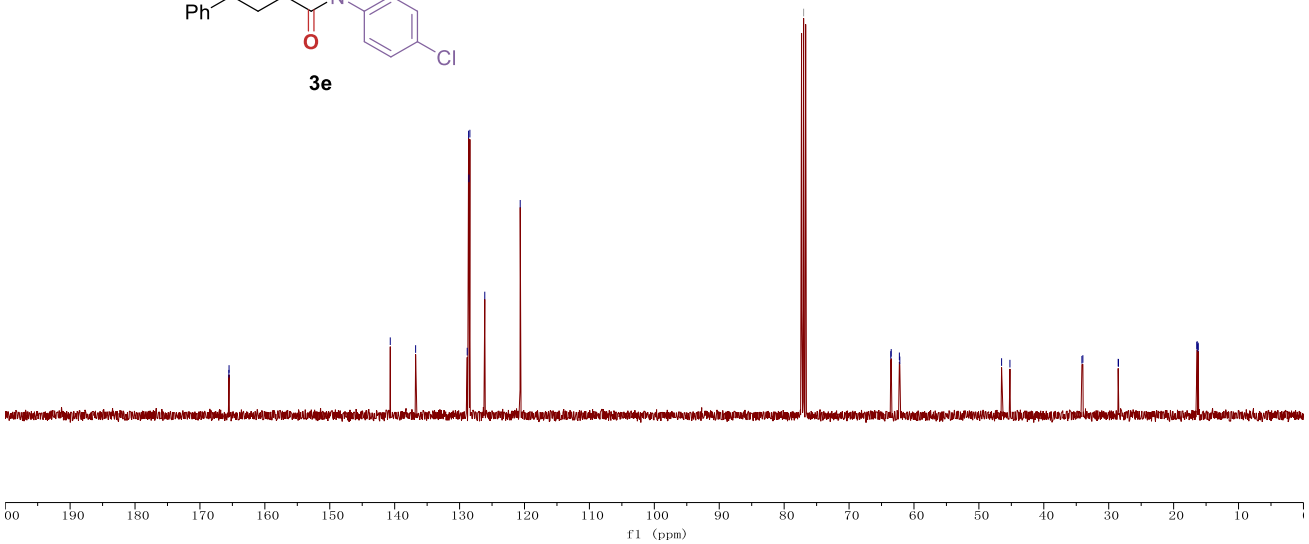
3e



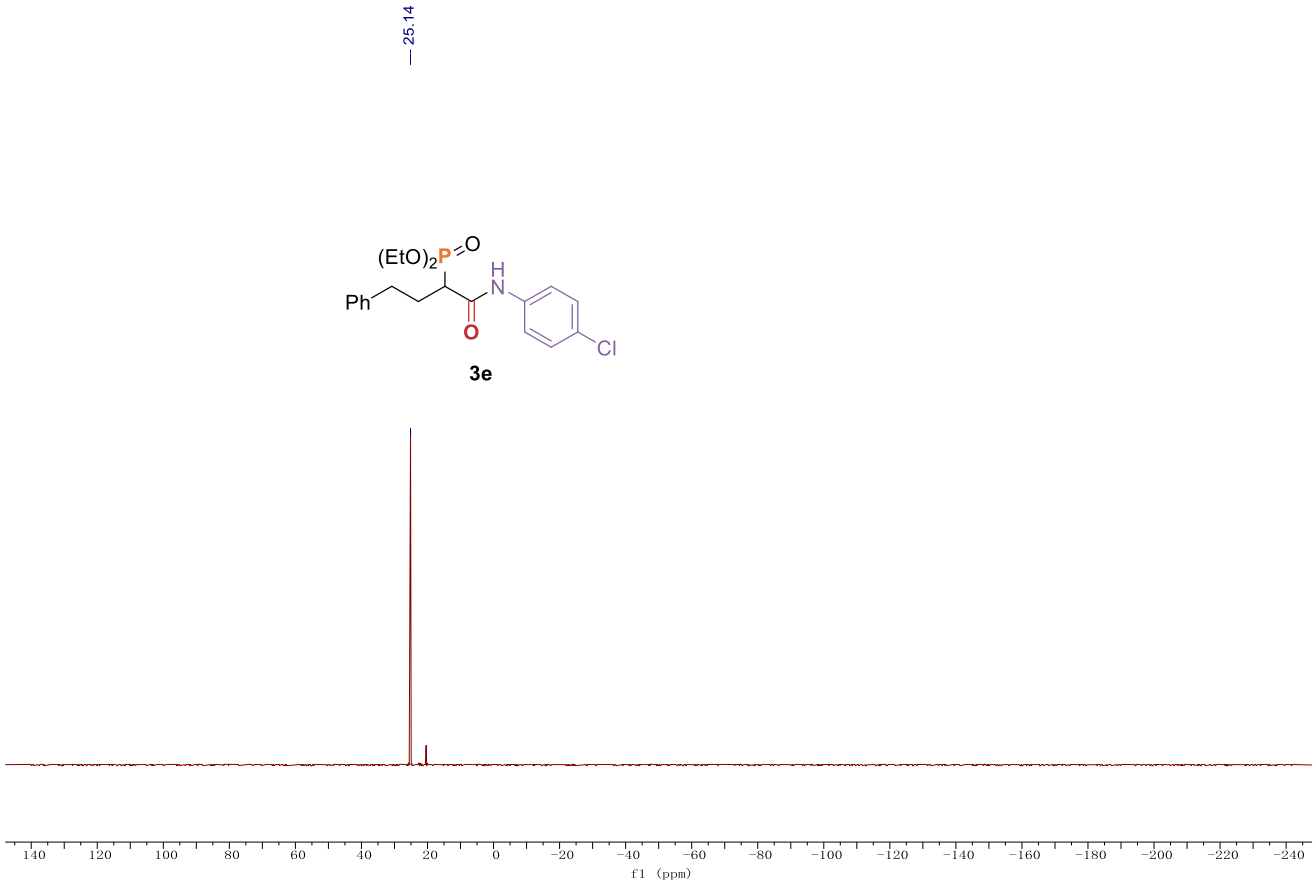
13C NMR CDCl3 100.62MHz



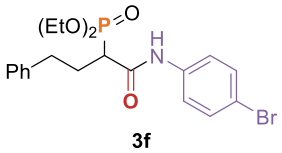
3e



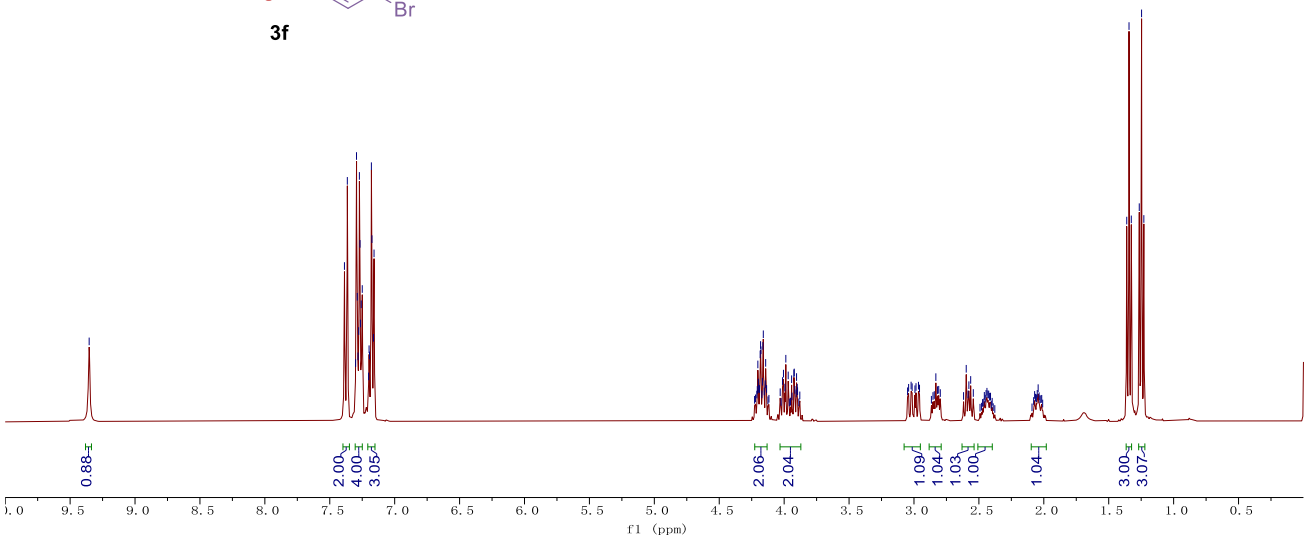
31P NMR CDCl3 161.97MHz



1H NMR CDCl3 400.13MHz

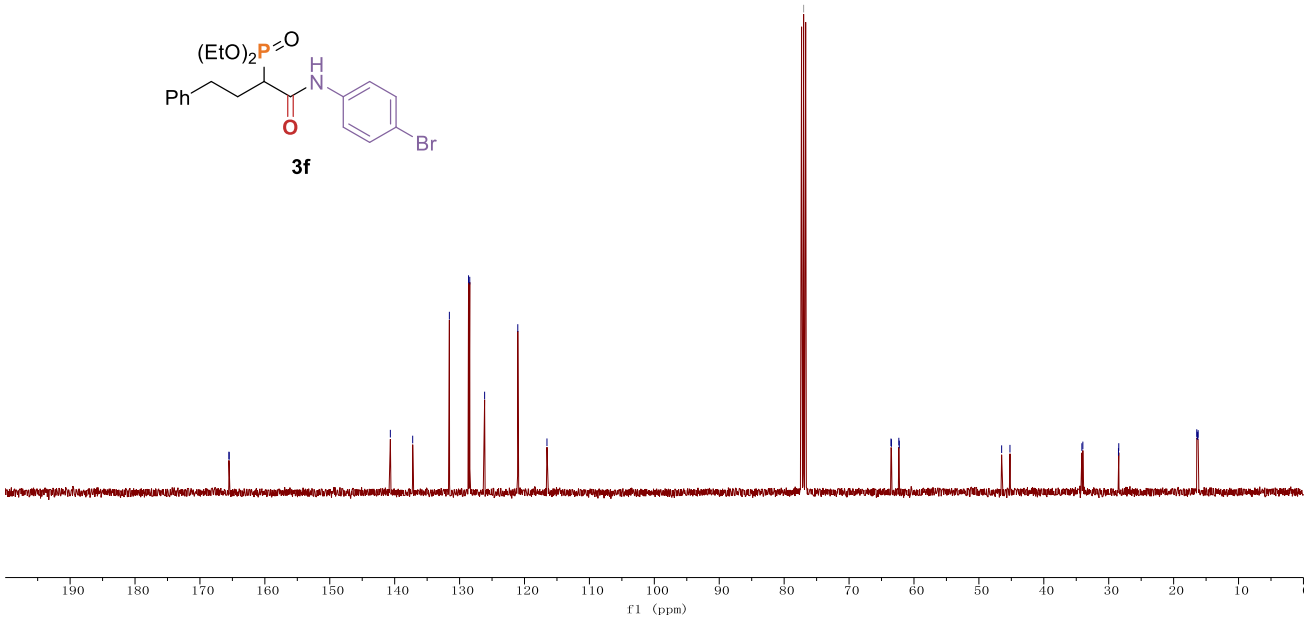


3f

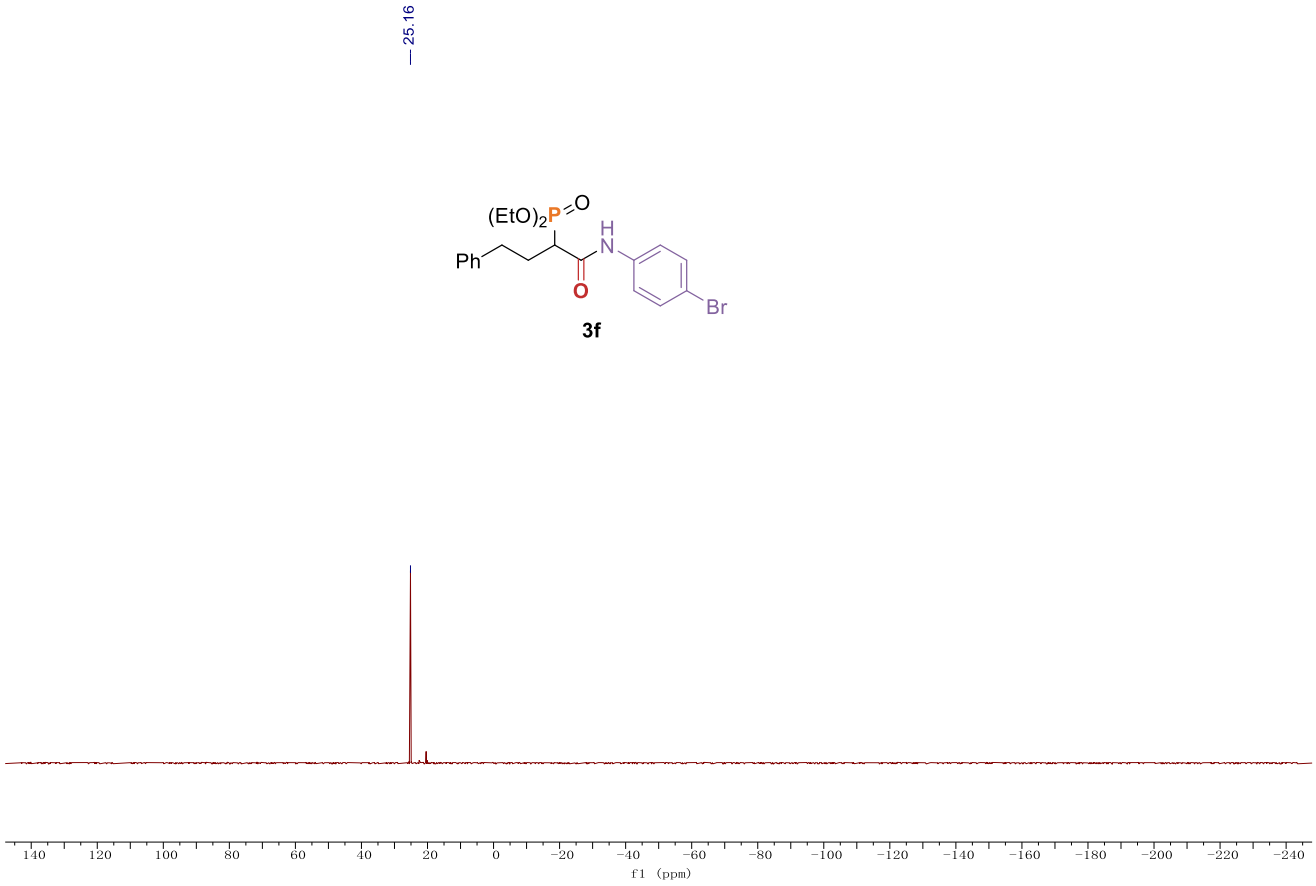


13C NMR CDCl3 100.62MHz

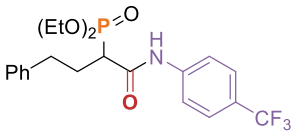
3f



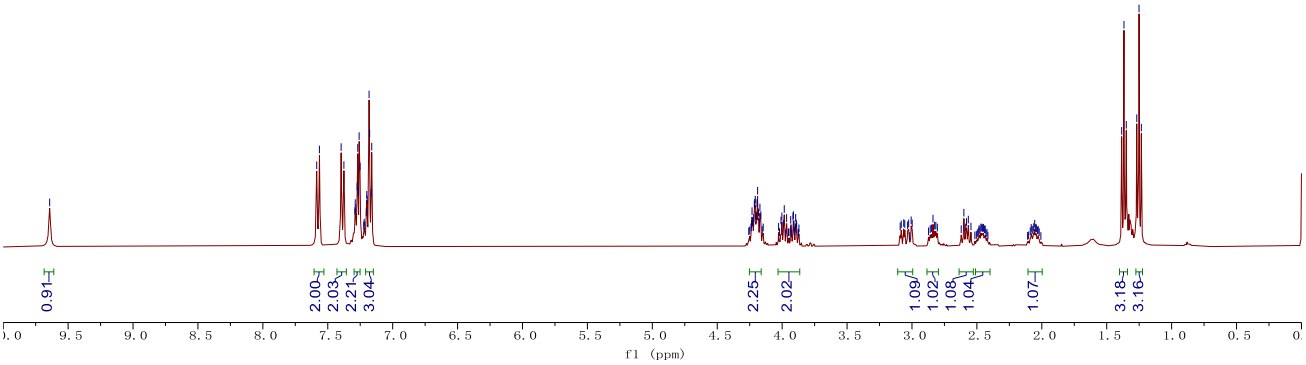
31P NMR CDCl3 161.97MHz



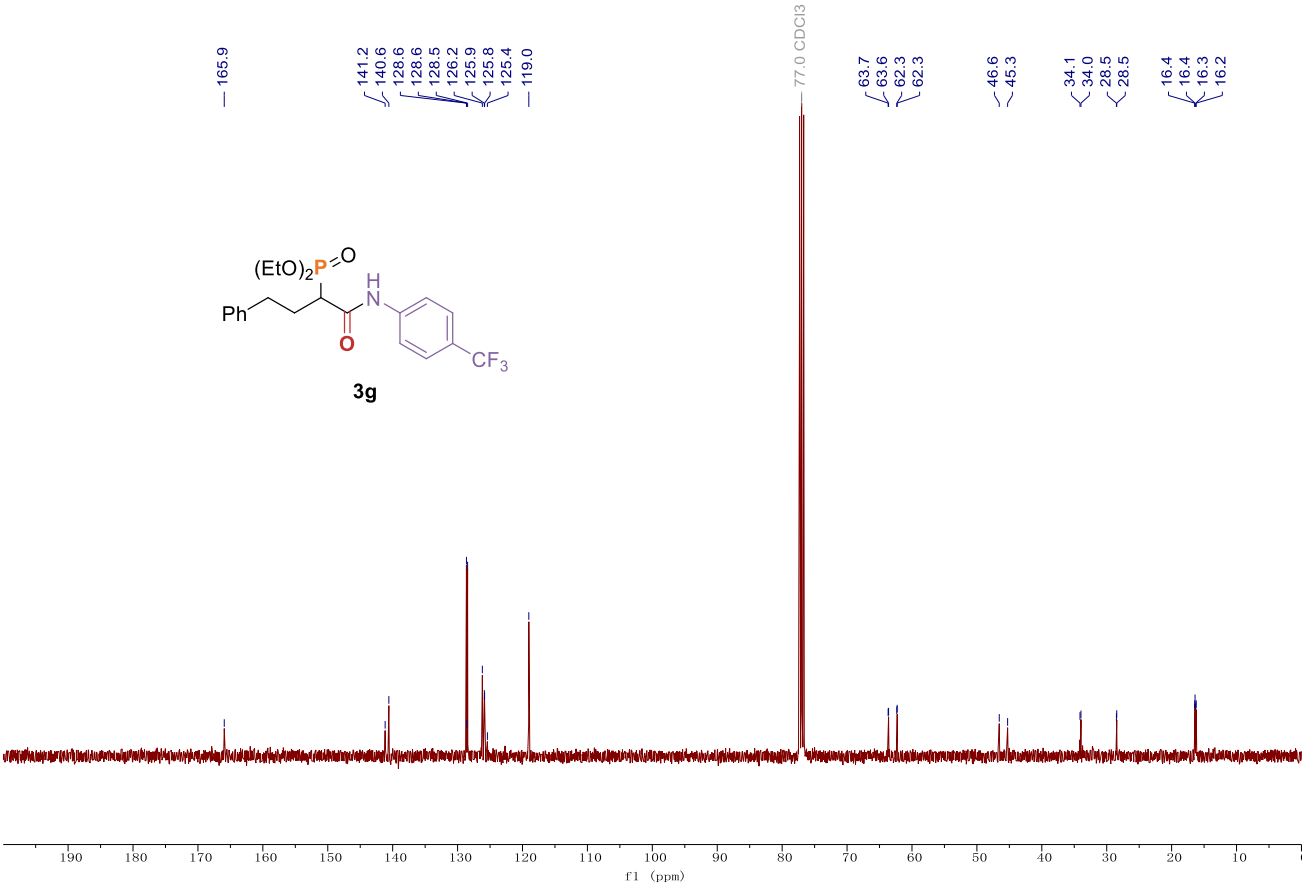
1H NMR CDCl3 400.13MHz



3g

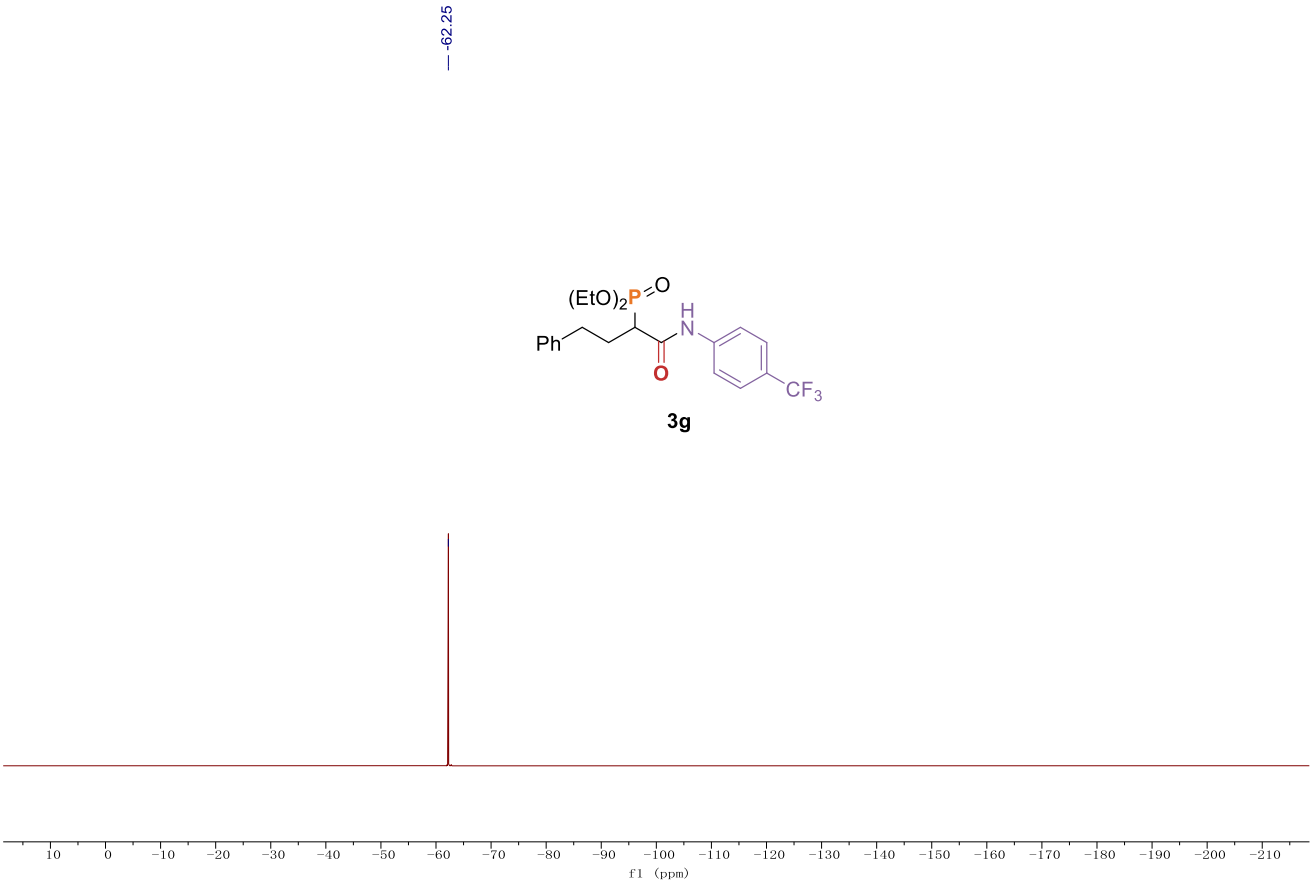


13C NMR CDCl3 100.62MHz



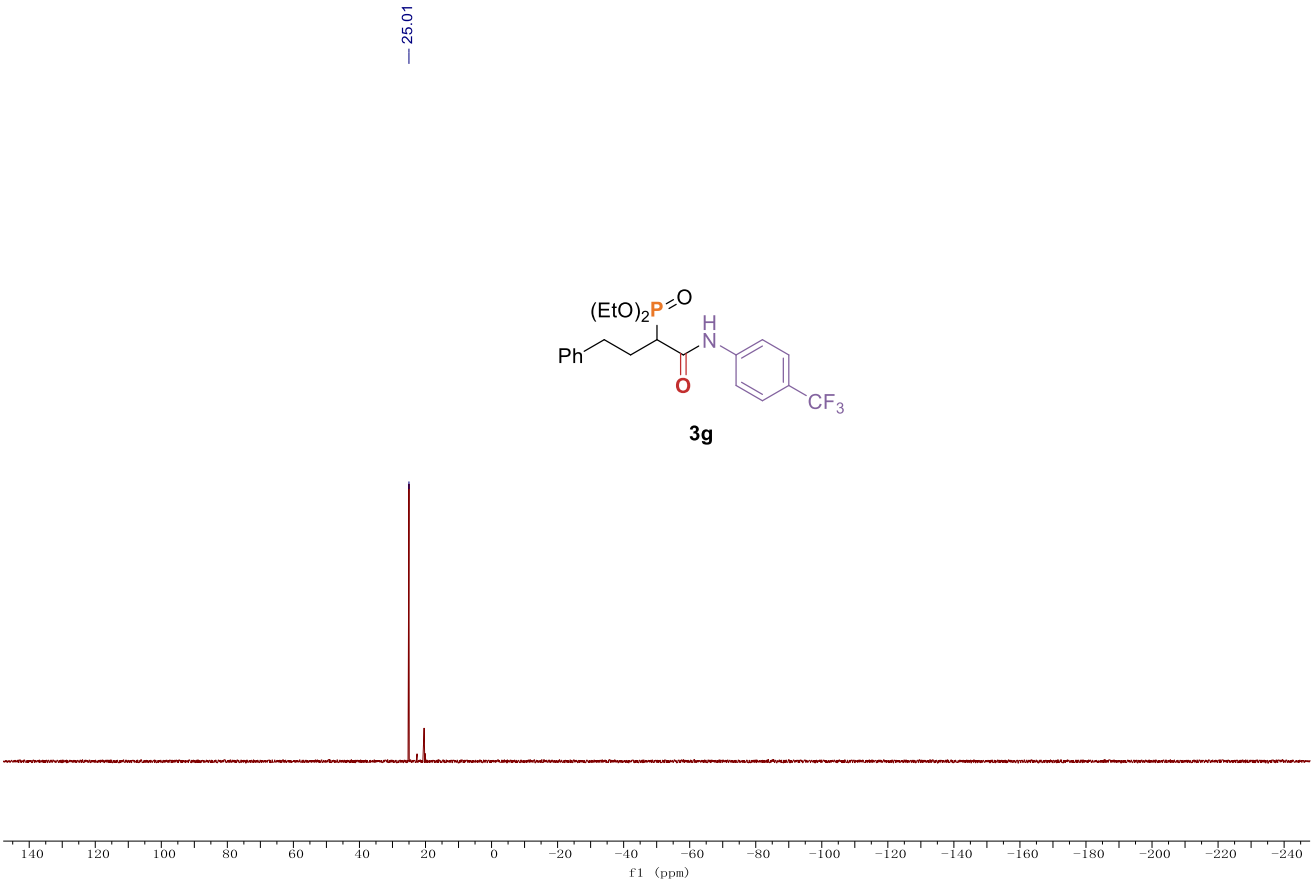
3g

19F NMR DMSO-d6 376.46MHz



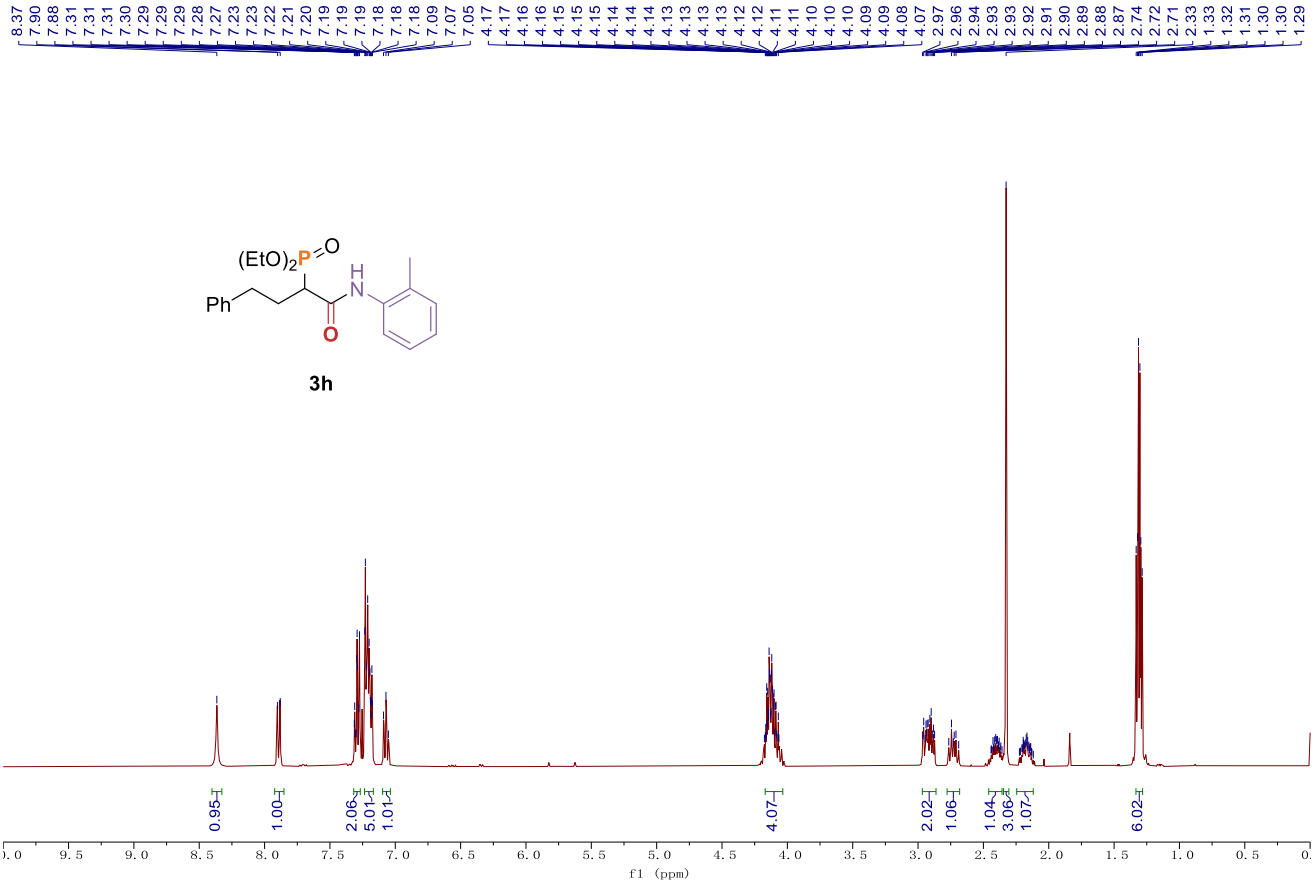
3g

31P NMR CDCl3 161.97MHz

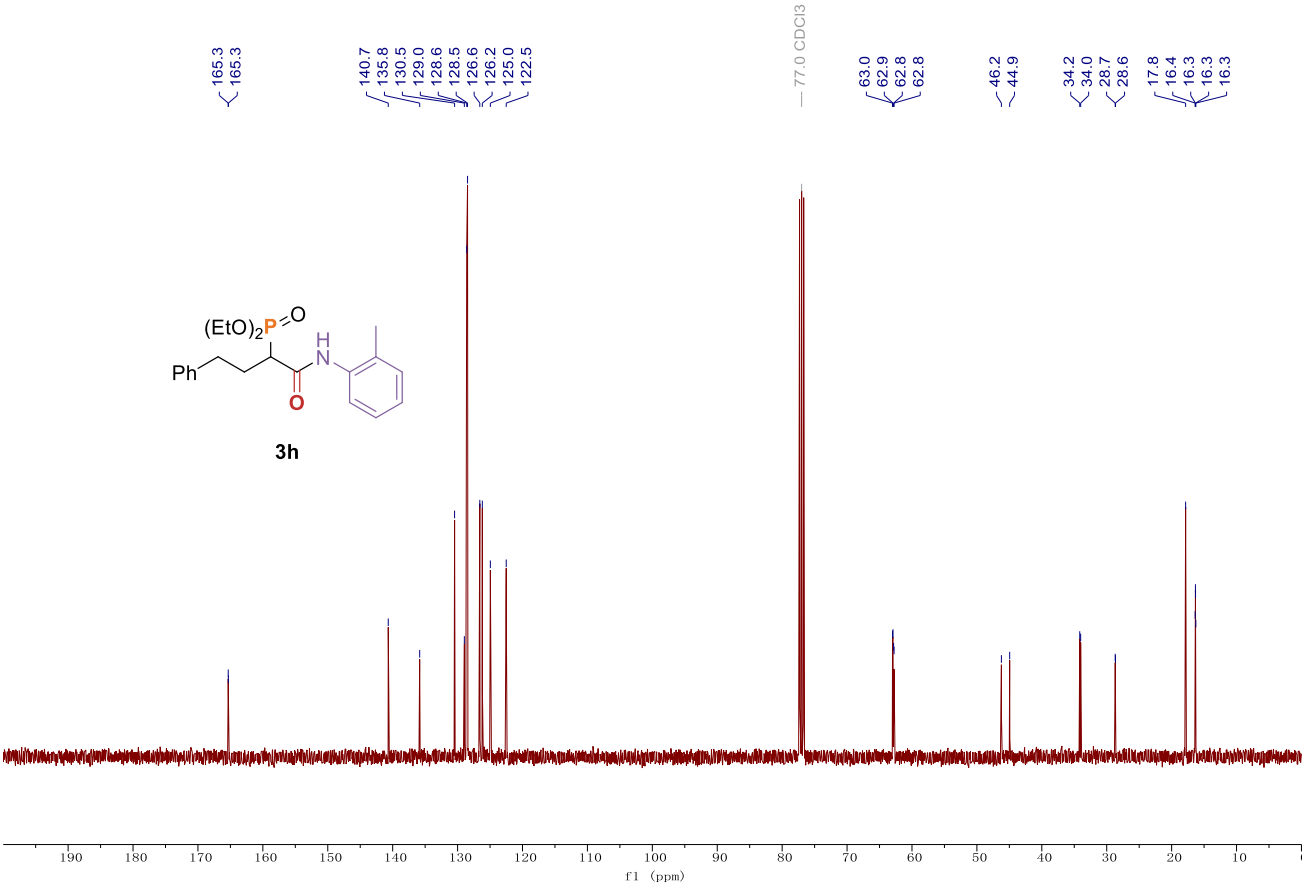


3g

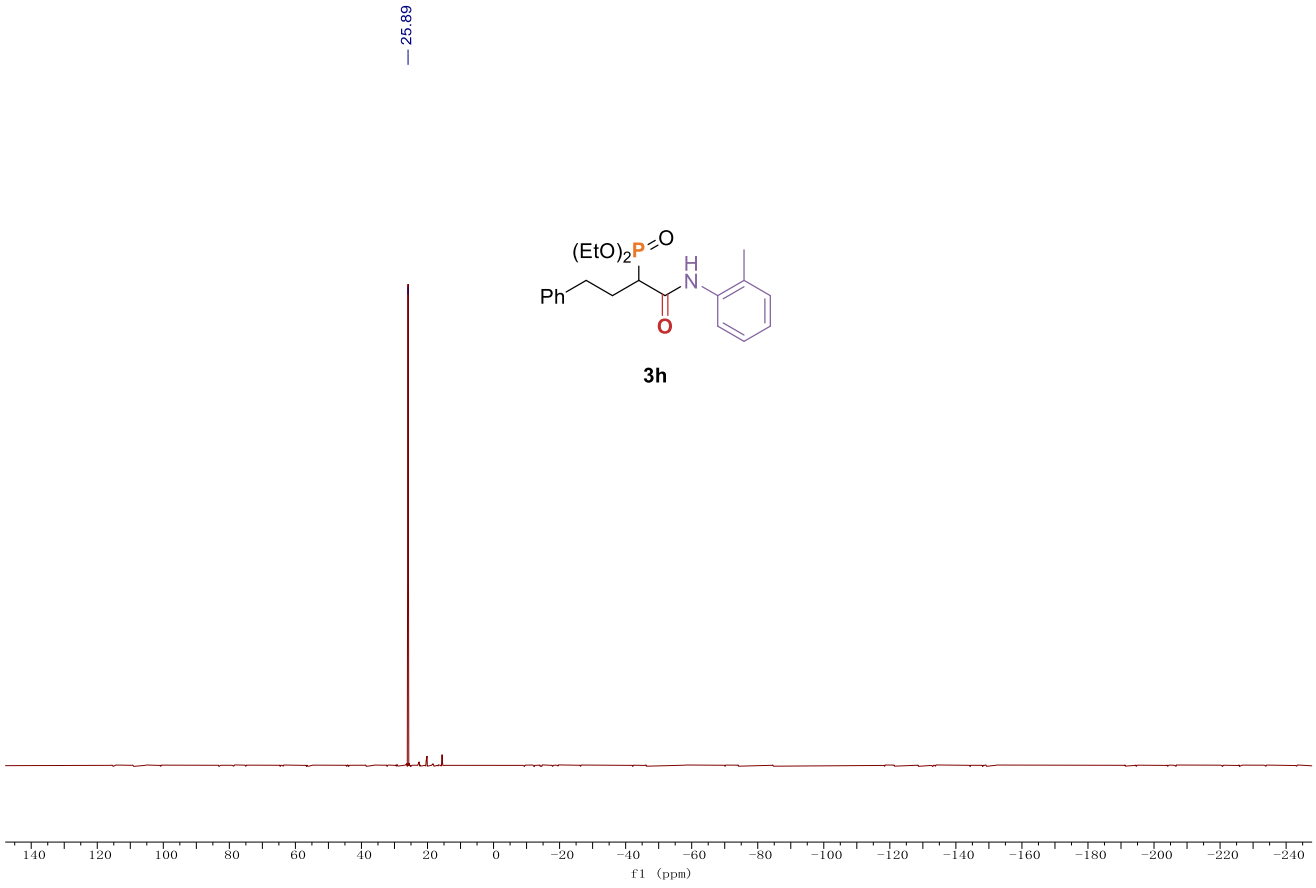
1H NMR CDCl3 400.13MHz



13C NMR CDCl3 100.62MHz

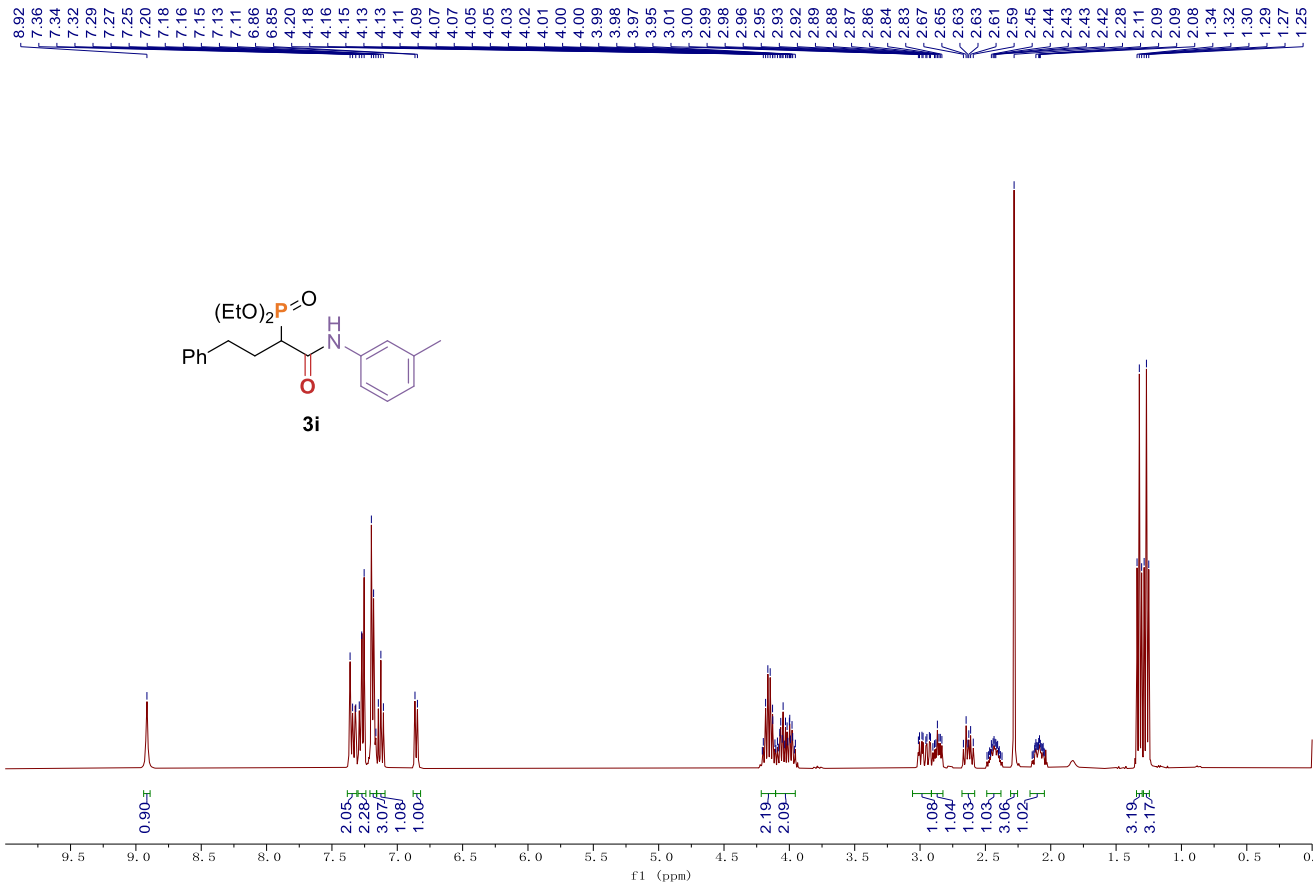


31P NMR CDCl3 161.97MHz

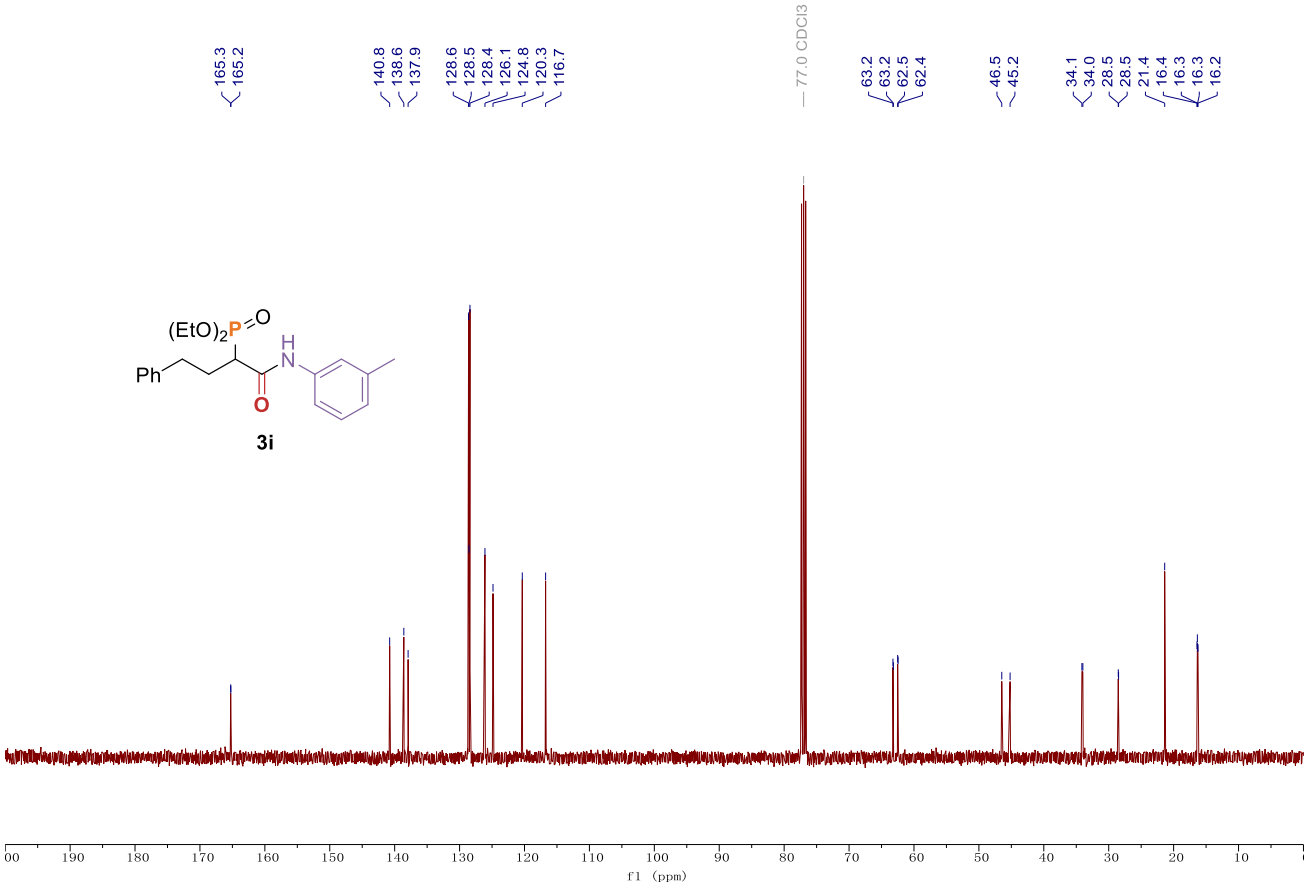


3h

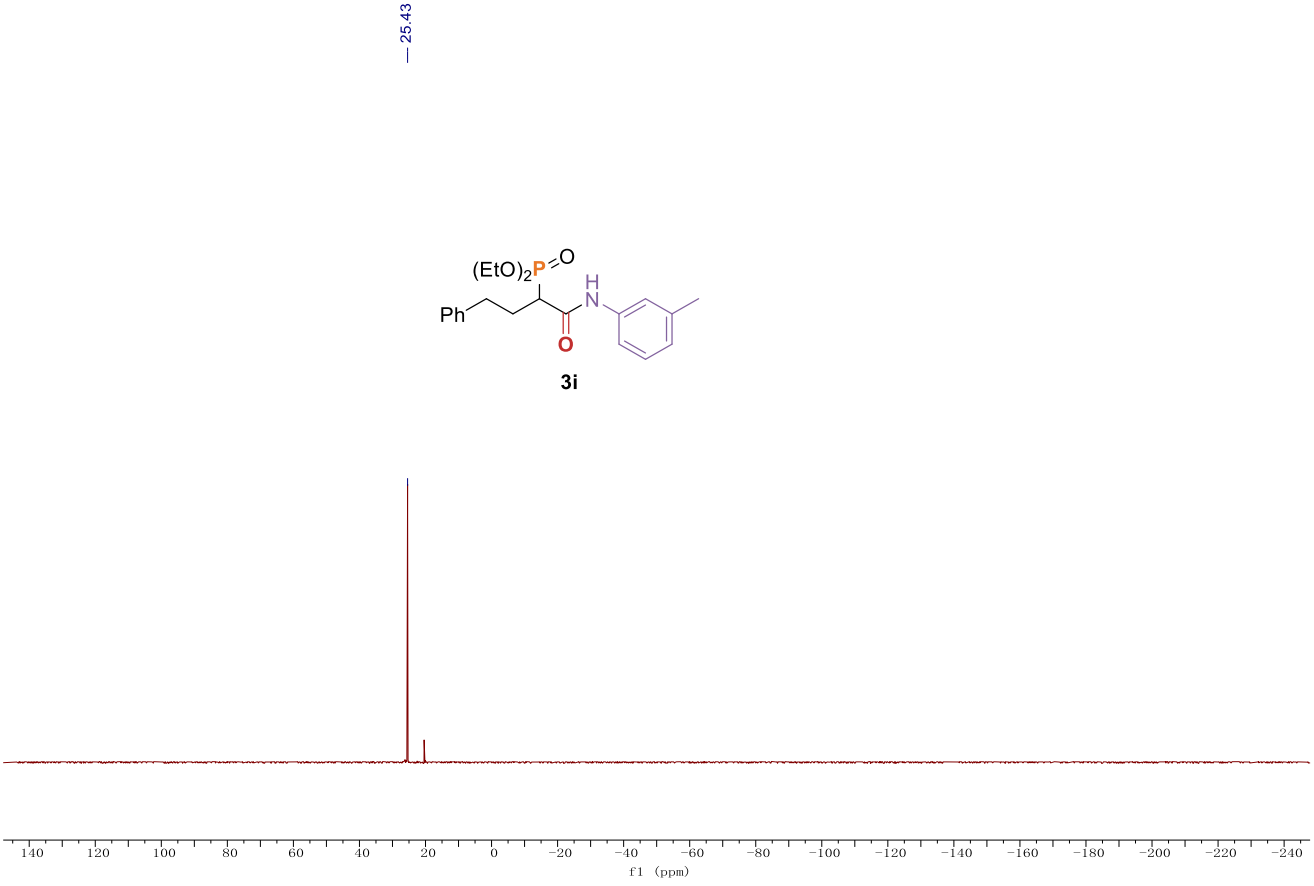
1H NMR CDCl3 400.13MHz



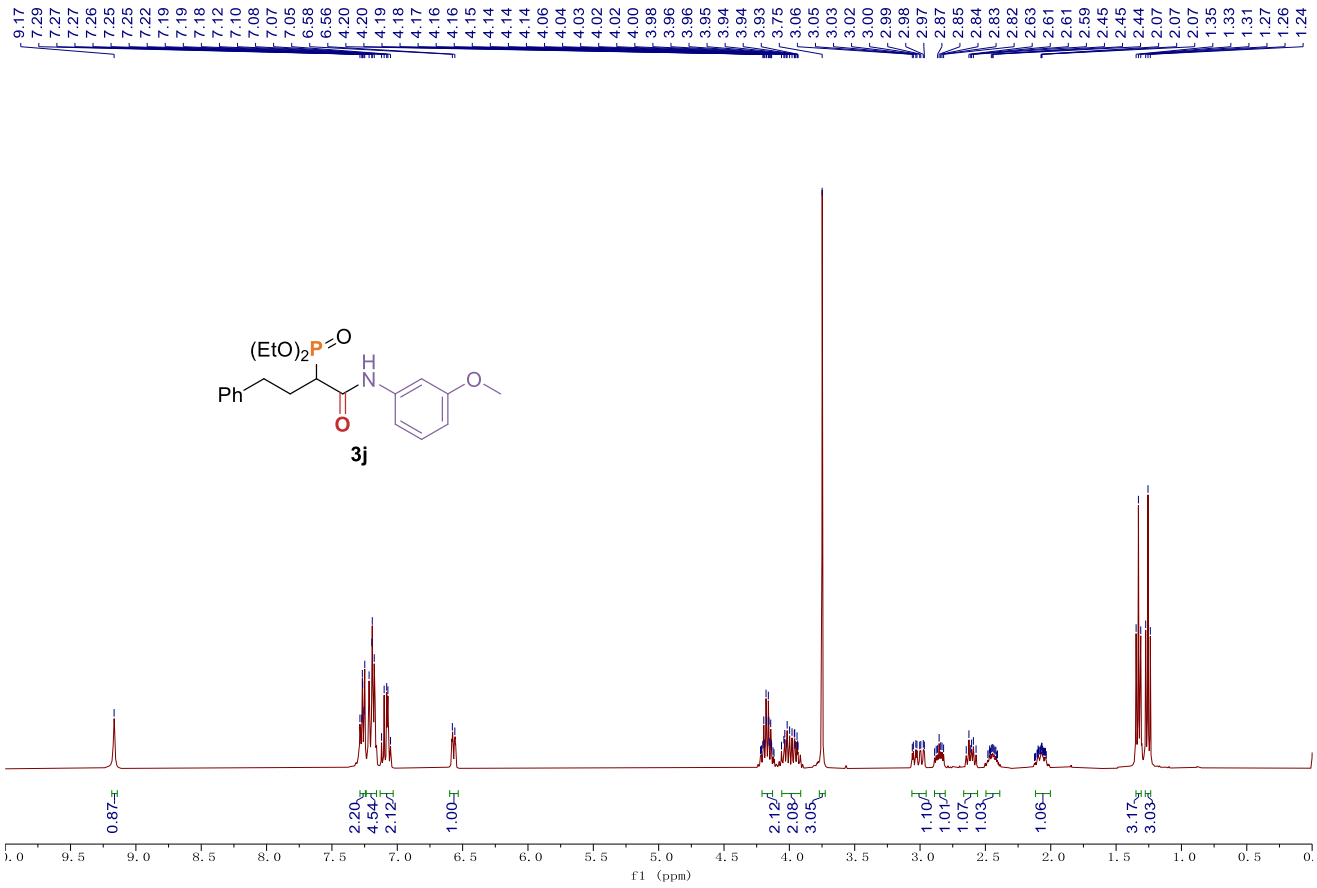
13C NMR CDCl3 100.62MHz



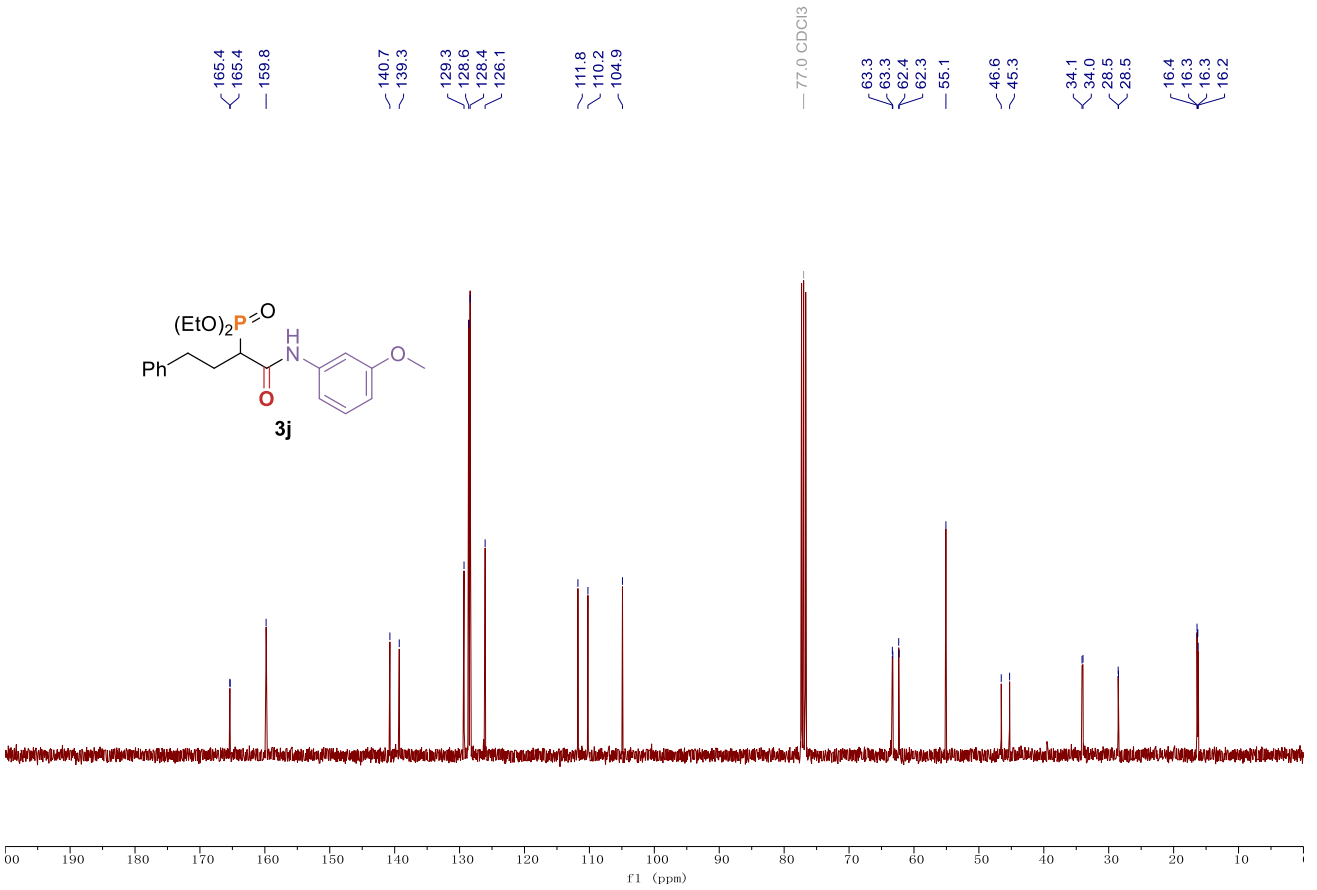
31P NMR CDCl3 161.97MHz



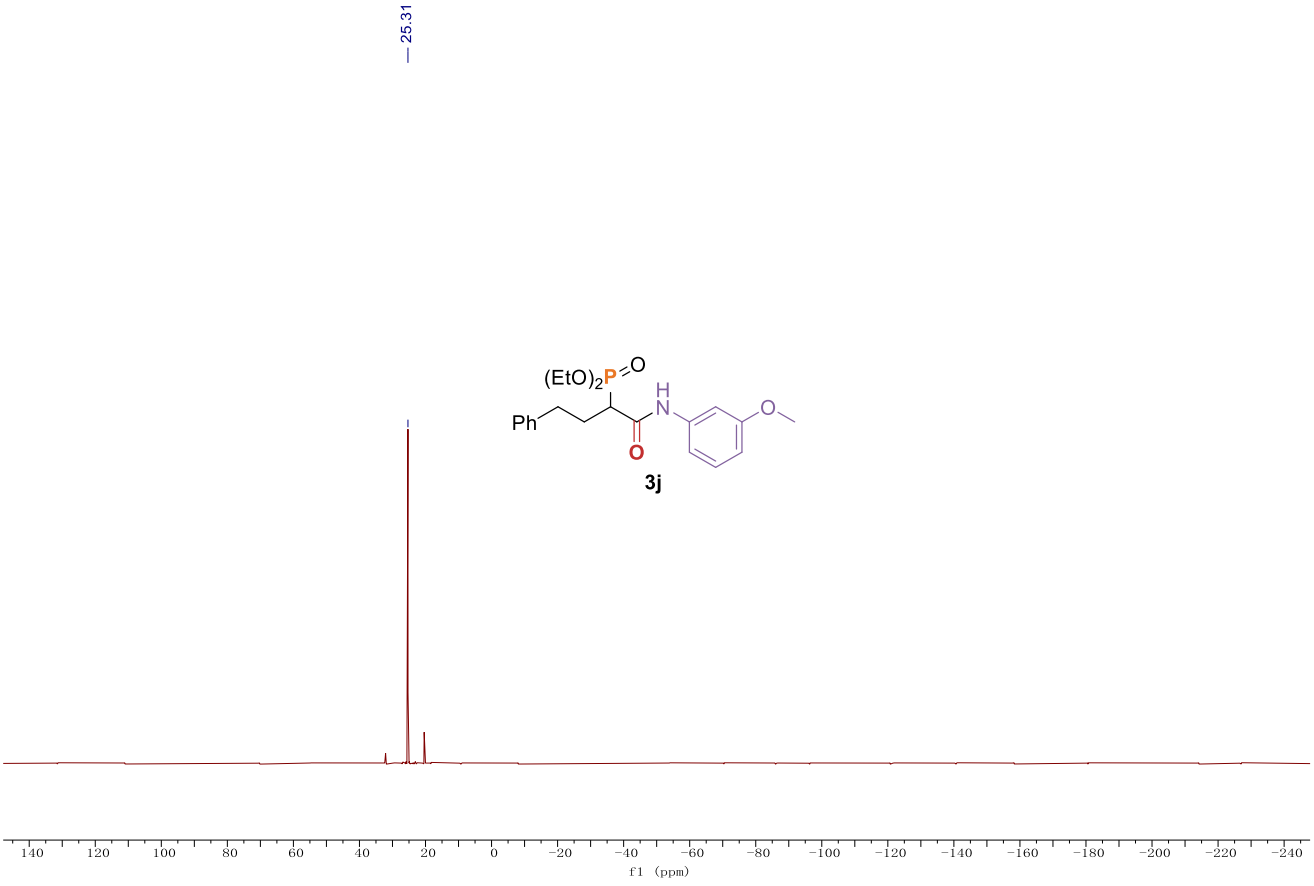
1H NMR CDCl3 400.13MHz



13C NMR CDCl3 100.62MHz



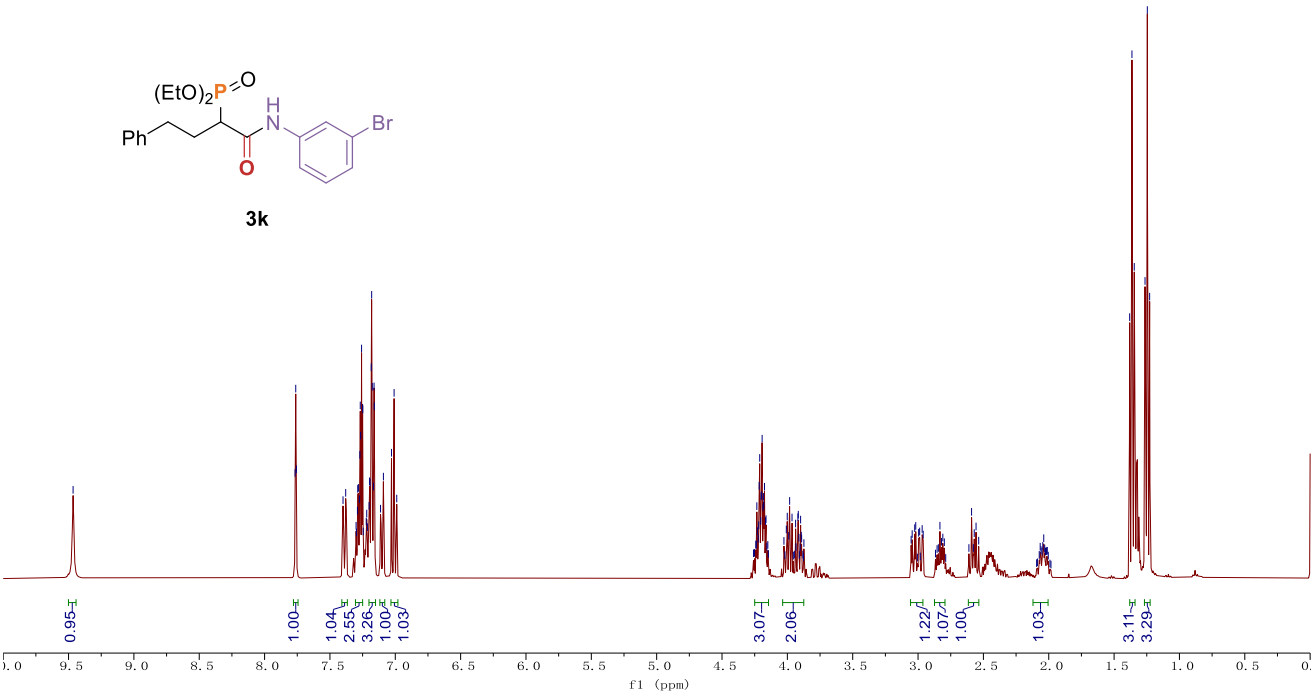
31P NMR CDCl3 161.97MHz



1H NMR CDCl3 400.13MHz

9.47 7.77 7.76 7.76 7.40 7.38 7.30 7.29 7.29 7.28 7.27 7.27 7.27 7.27 7.26 7.25 7.25 7.25 7.22 7.22 7.21 7.20 7.20 7.19 7.18 7.18 7.18 7.17 7.16 7.16 7.11 7.09 7.03 7.01 6.99 4.23 4.23 4.22 4.22 4.21 4.20 4.20 4.20 4.19 4.19 4.18 4.18 4.17 4.17 4.16 4.01 4.00 3.98 3.96 3.94 3.92 3.92 3.90 3.03 3.02 2.99 2.97 2.83 2.59 2.56 1.38 1.36 1.35 1.26 1.25 1.23

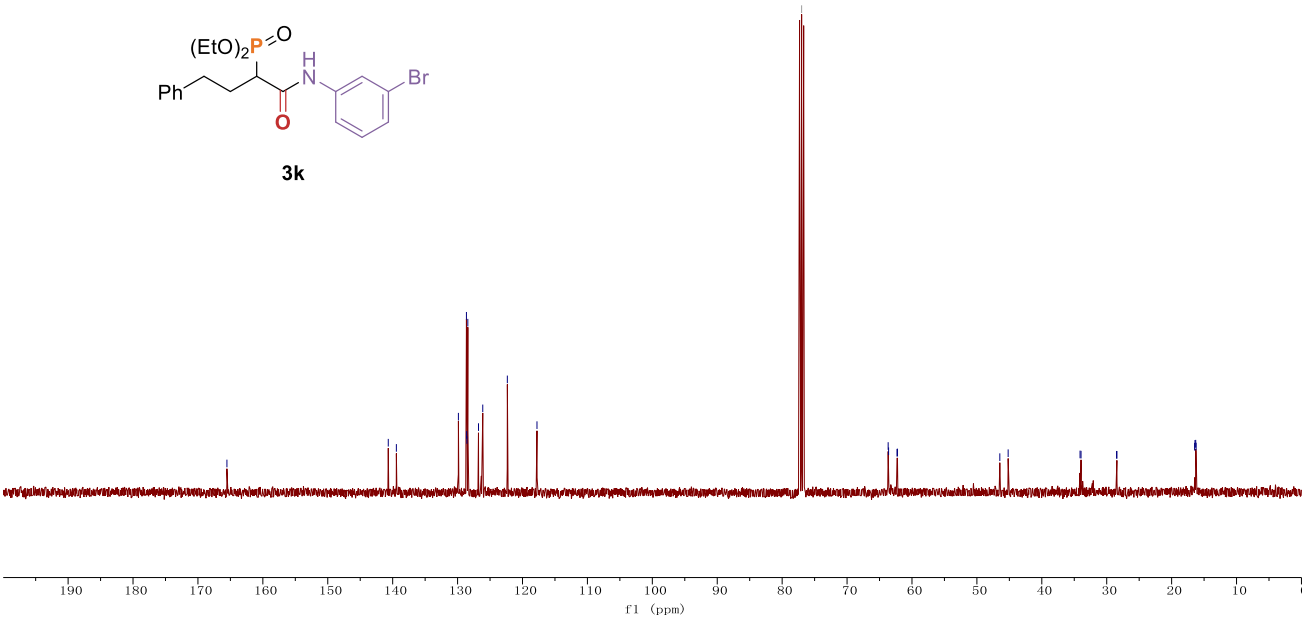
3k



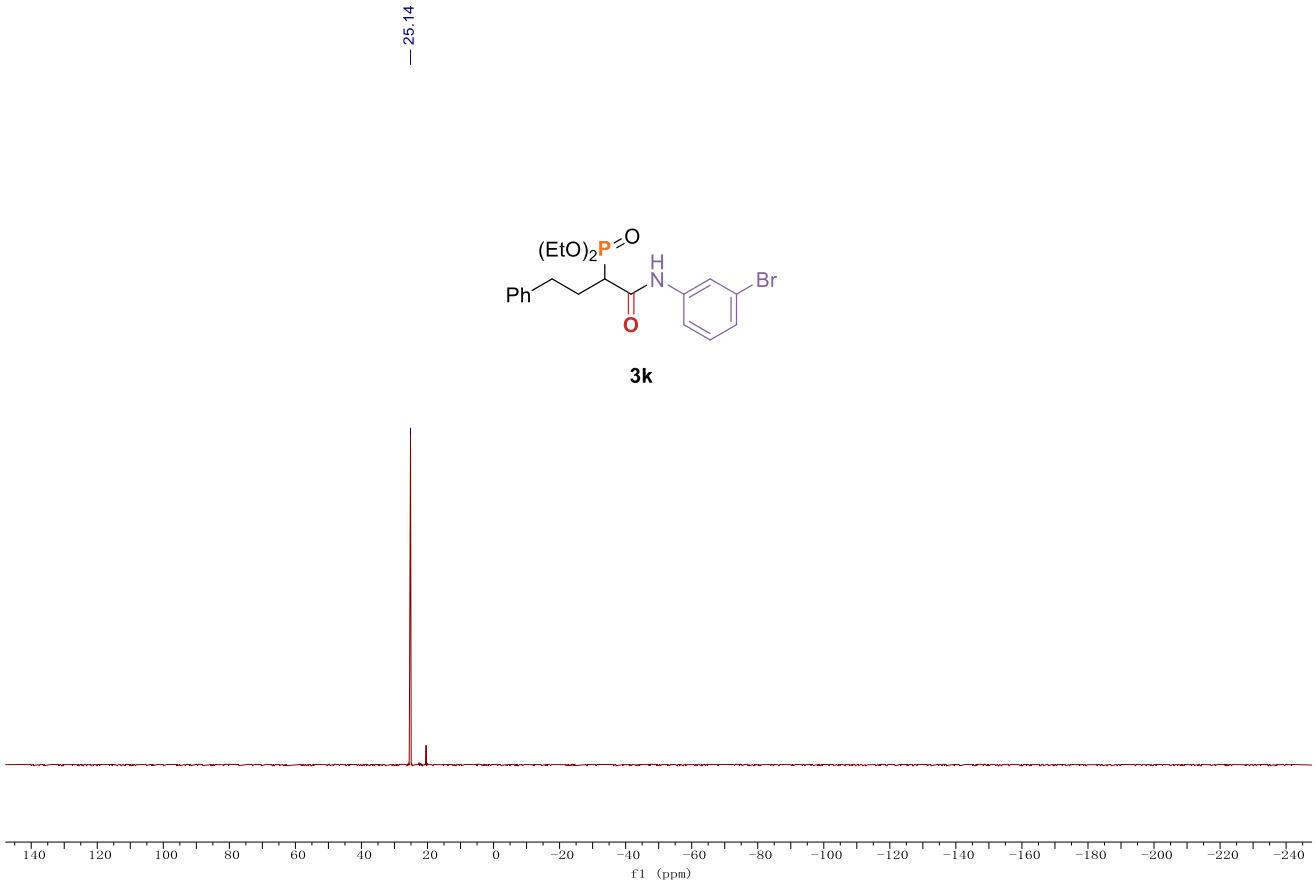
13C NMR CDCl3 100.62MHz

165.5 140.7 139.4 129.9 128.6 128.6 128.6 128.4 126.8 126.1 122.3 117.8 77.0 CDCl3 63.7 63.6 62.3 62.2 46.5 45.2 34.1 34.0 28.5 28.4 16.5 16.4 16.3 16.2

3k

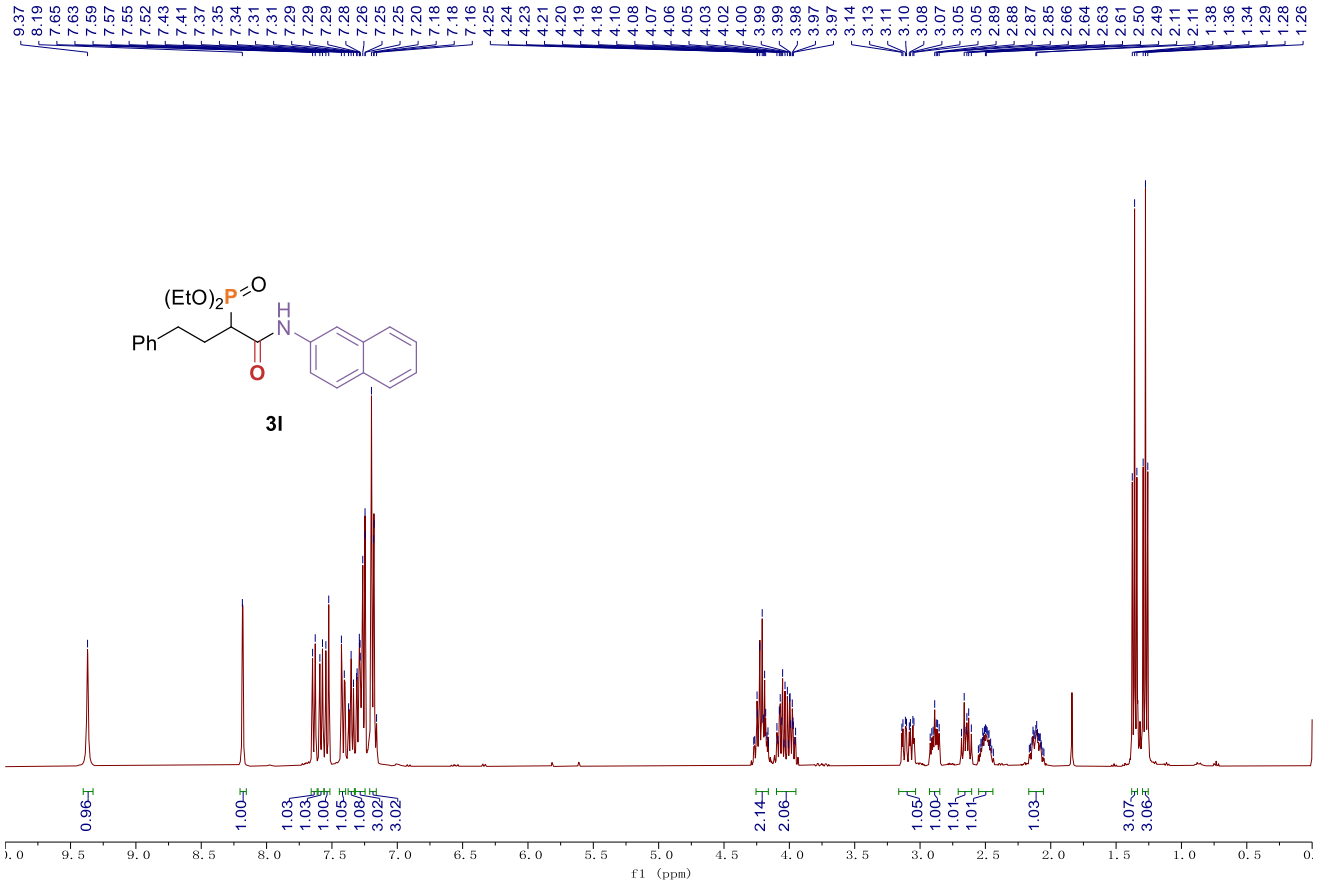


31P NMR CDCl3 161.97MHz

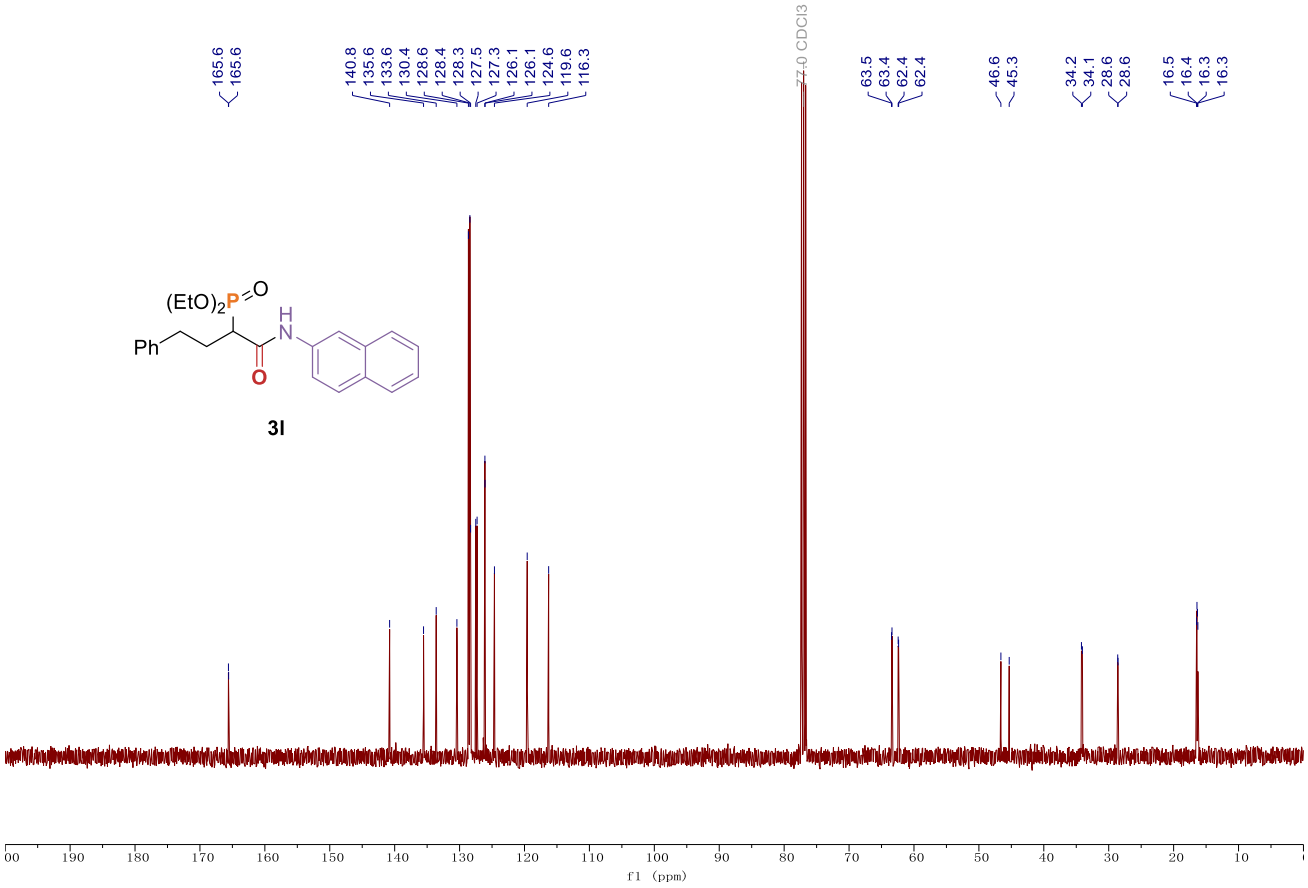


3k

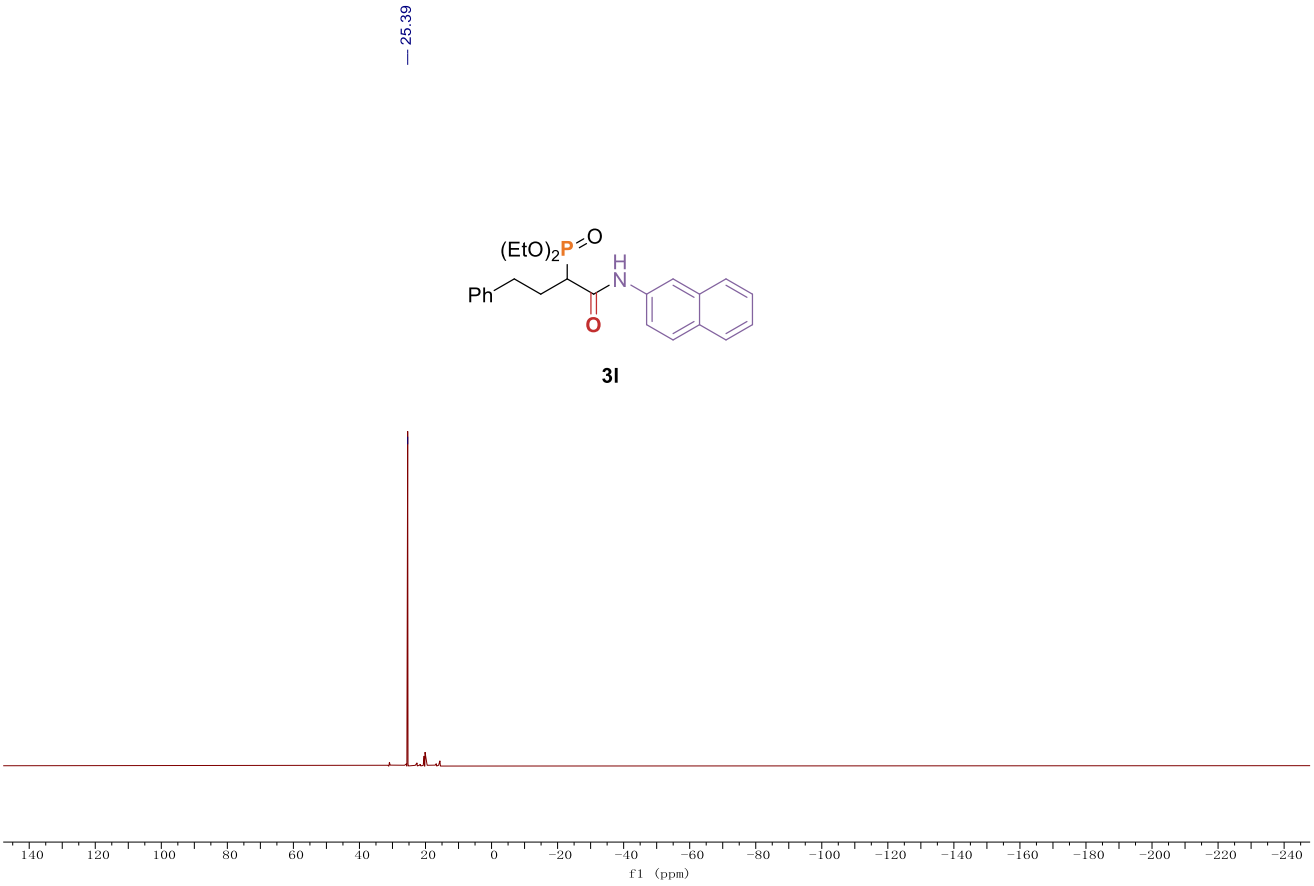
1H NMR CDCl3 400.13MHz



13C NMR CDCl3 100.62MHz

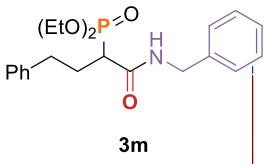


31P NMR CDCl3 161.97MHz

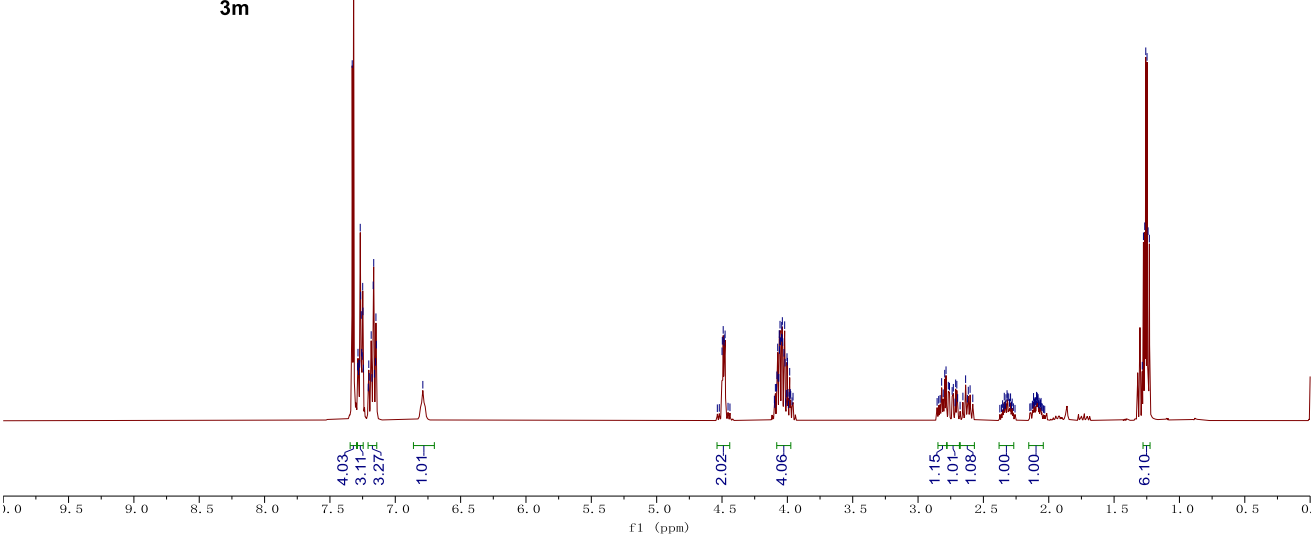


3l

1H NMR CDCl3 400.13MHz

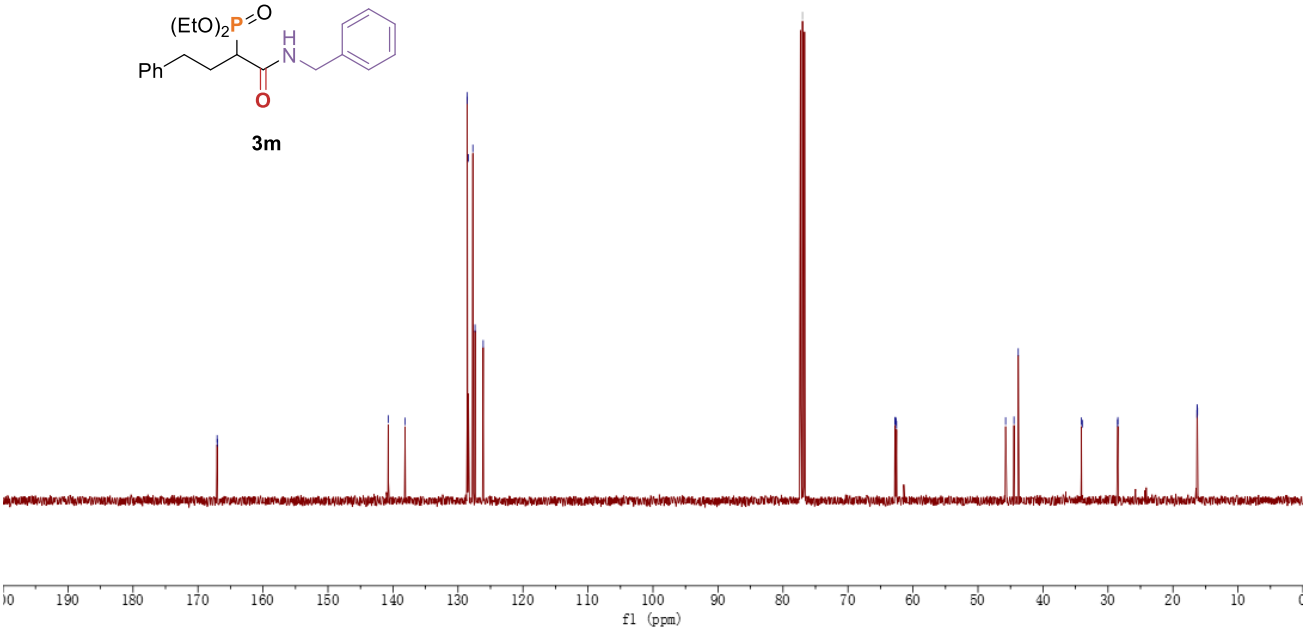


3m

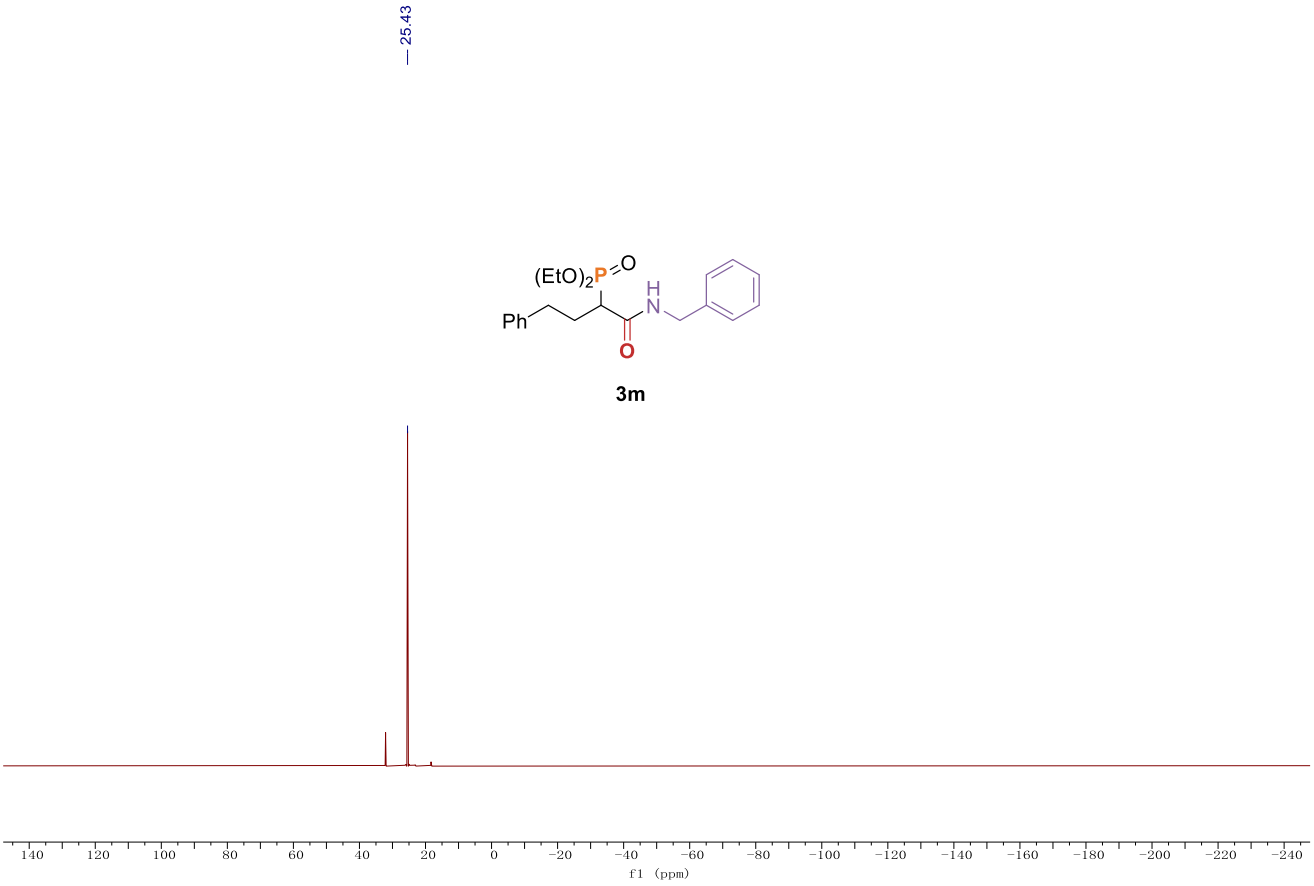


13C NMR CDCl3 100.62MHz

3m

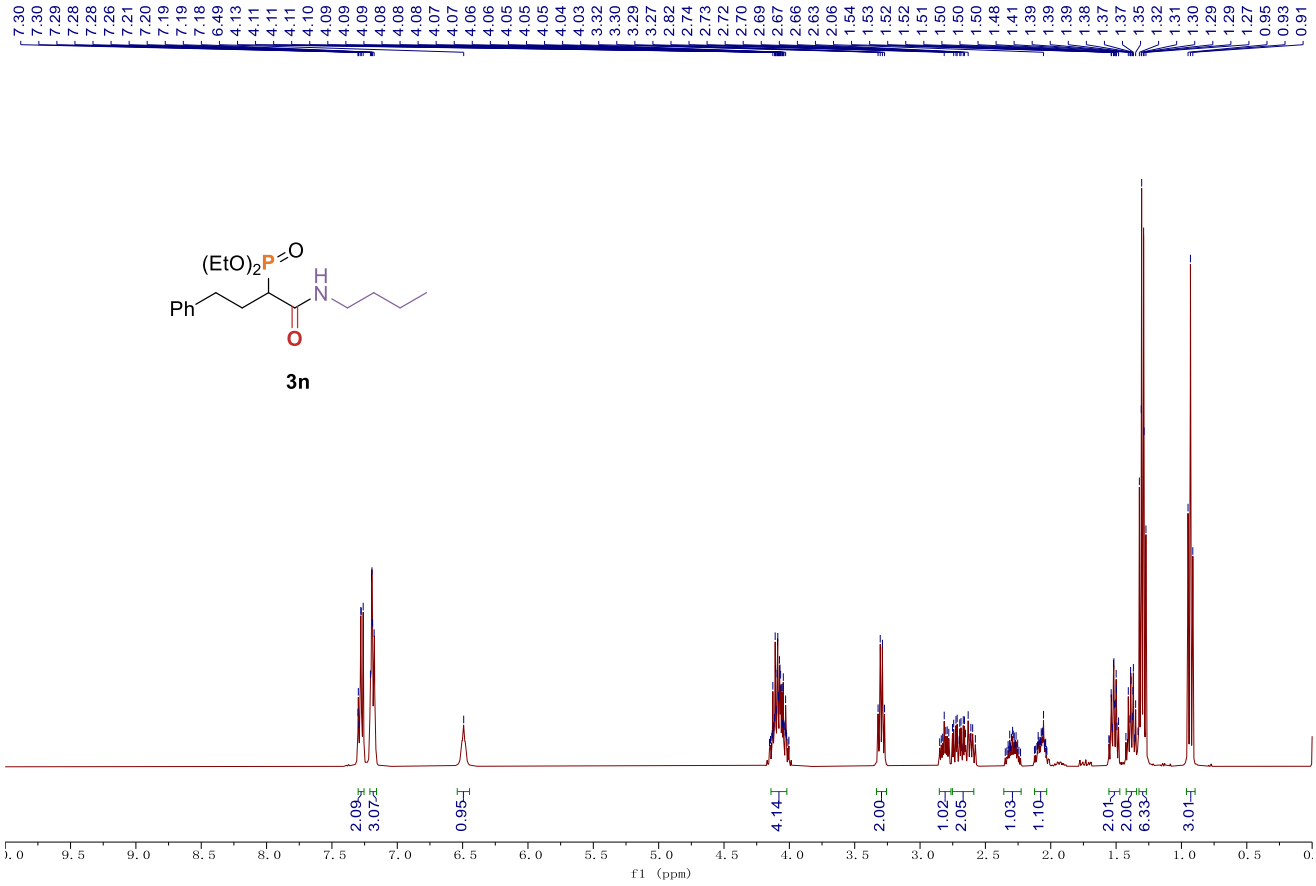


31P NMR CDCl3 161.97MHz

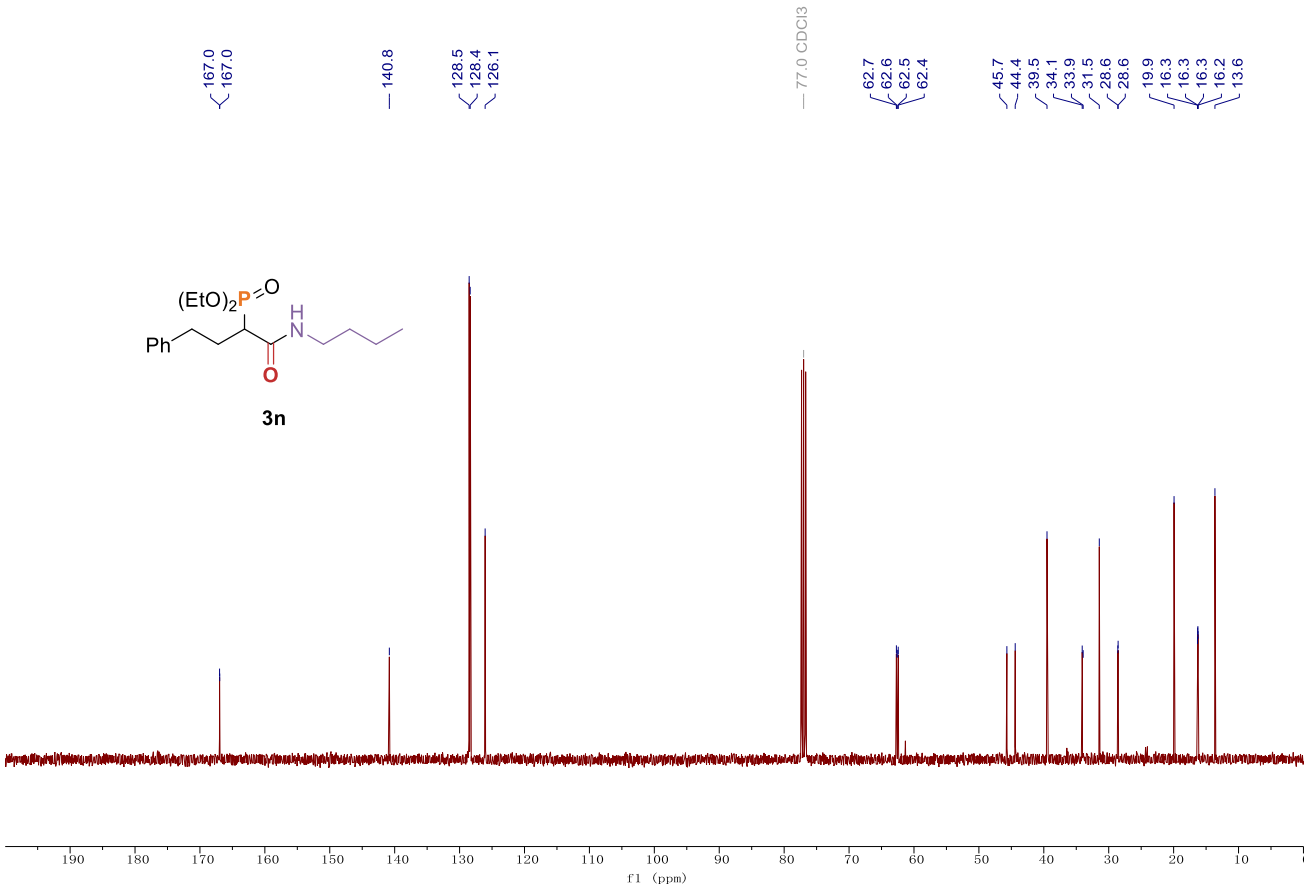


3m

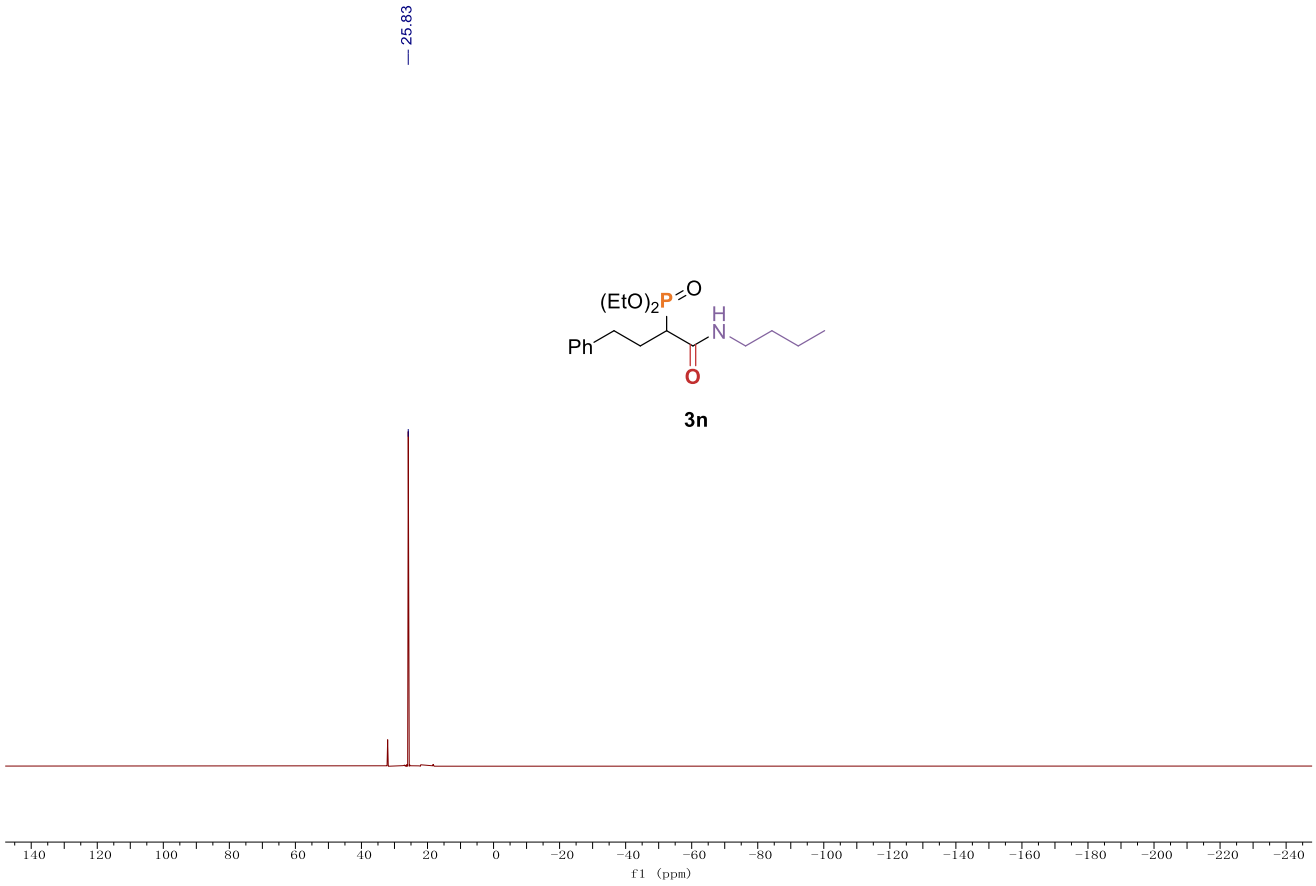
1H NMR CDCl3 400.13MHz



13C NMR CDCl3 100.62MHz



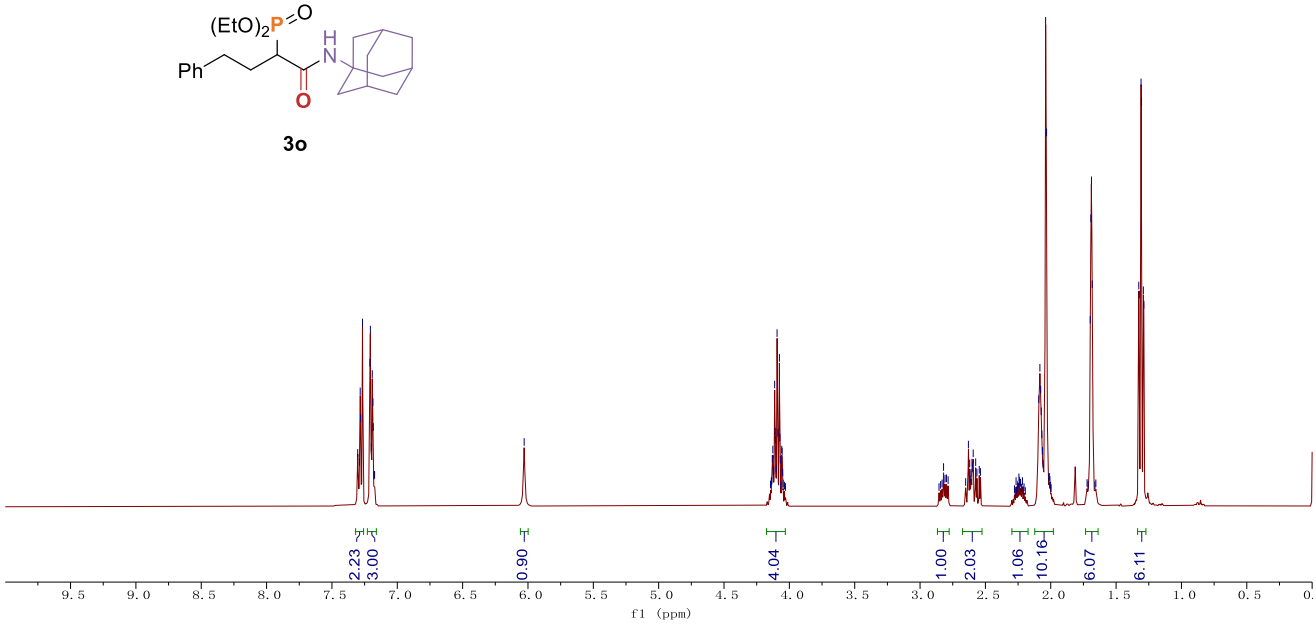
31P NMR CDCl3 161.97MHz



3n

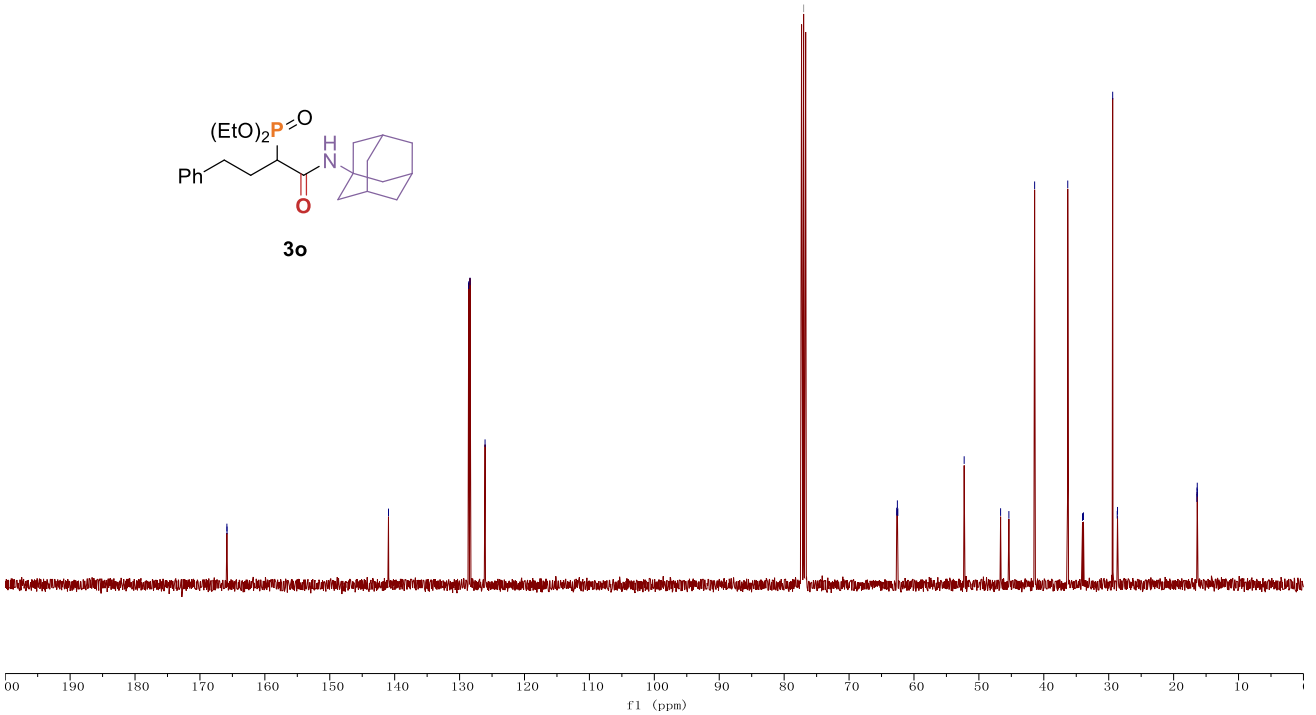
1H NMR CDCl3 400.13MHz

3o

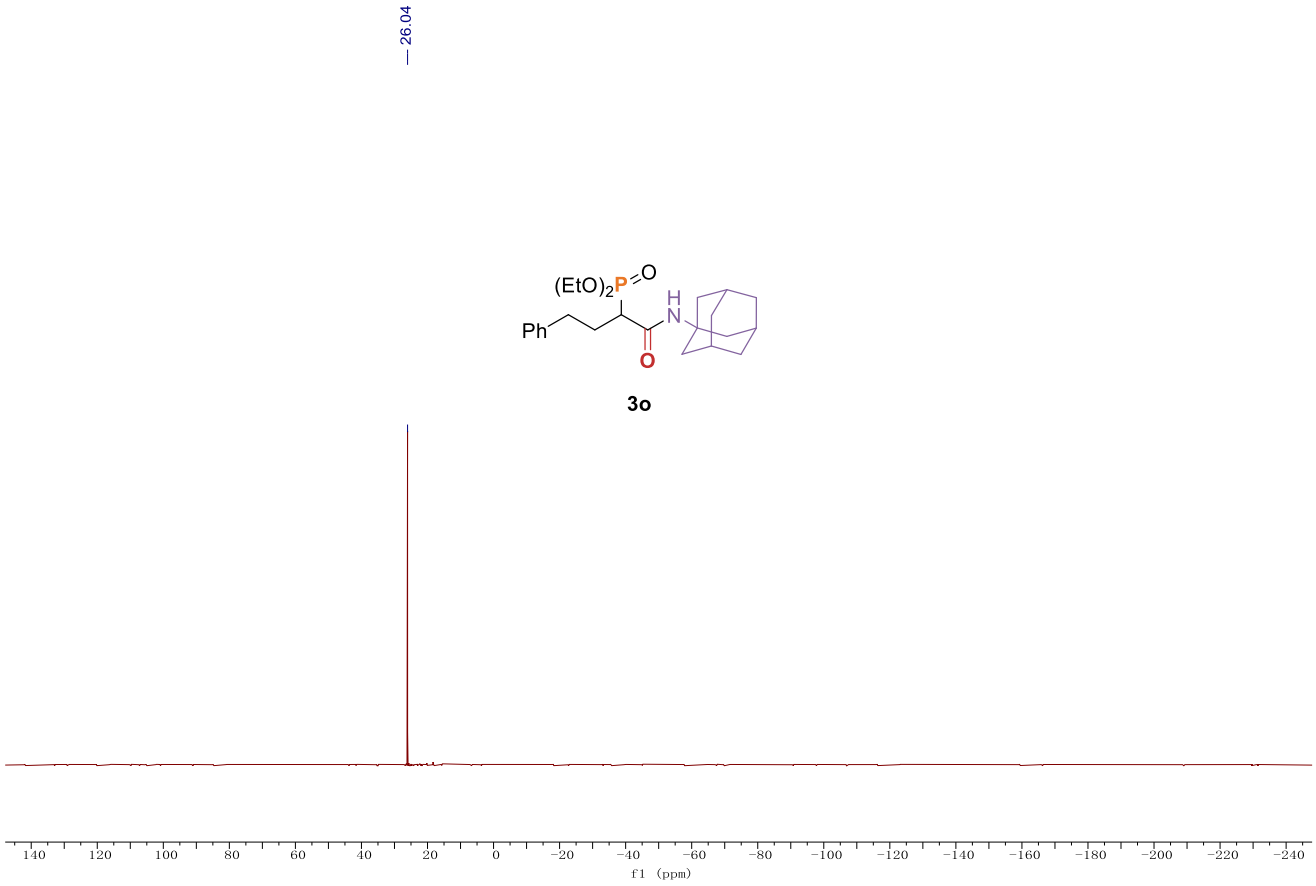


13C NMR CDCl3 100.62MHz

3o

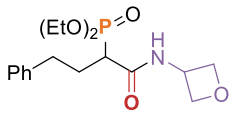


31P NMR CDCl3 161.97MHz

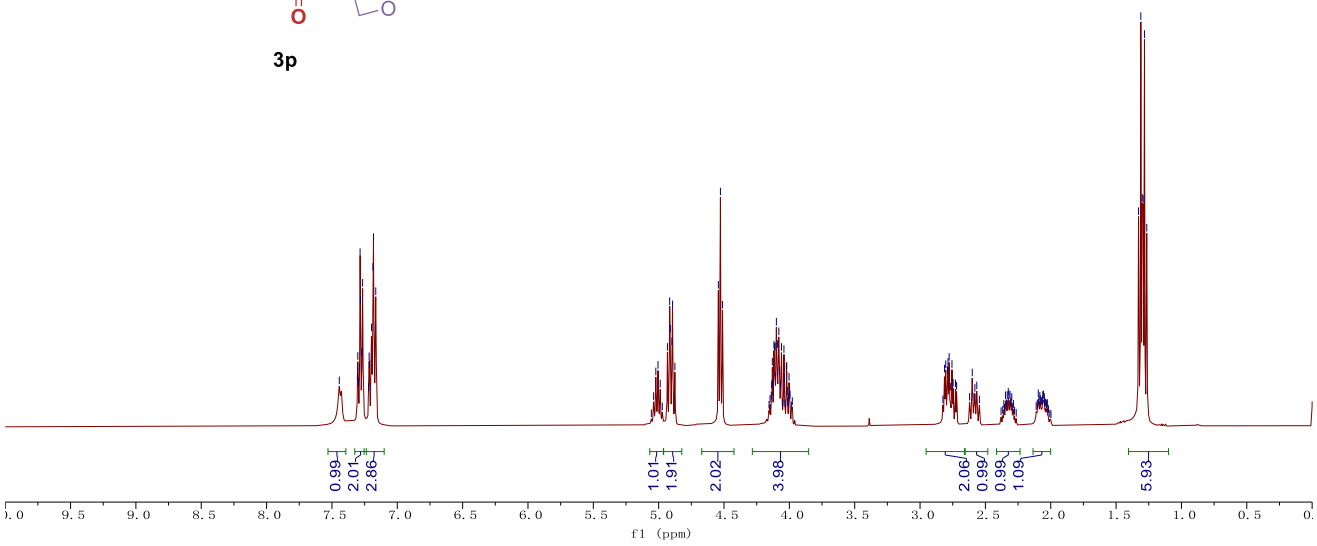


3o

1H NMR CDCl3 400.13MHz

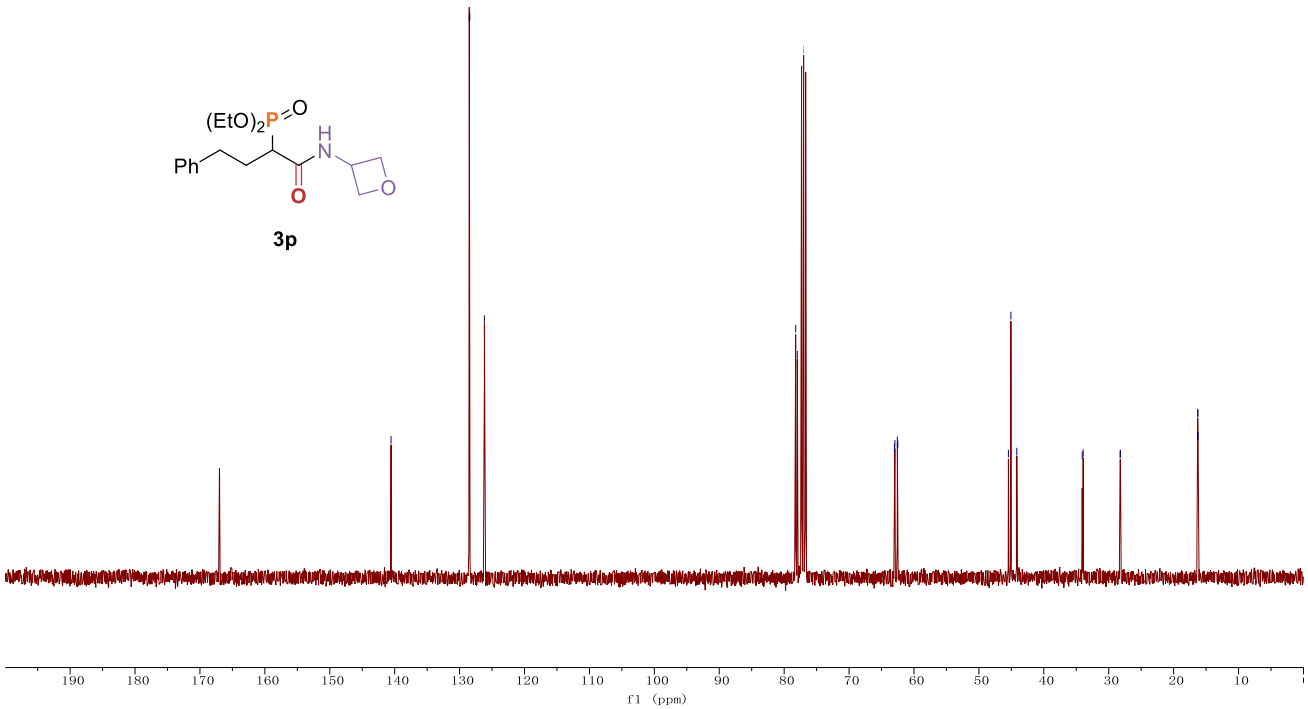


3p

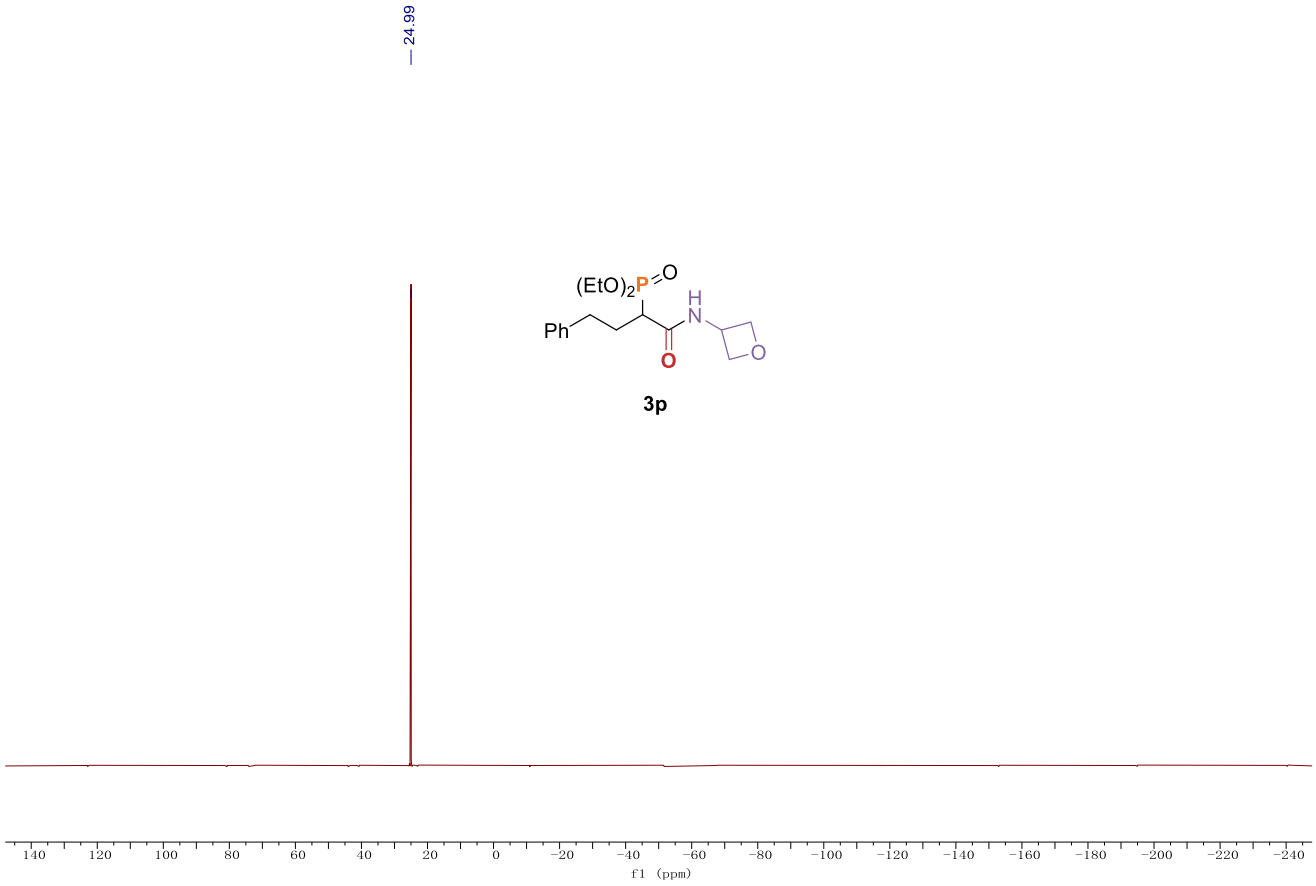


13C NMR CDCl3 100.62MHz

3p



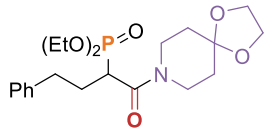
31P NMR CDCl3 161.97MHz



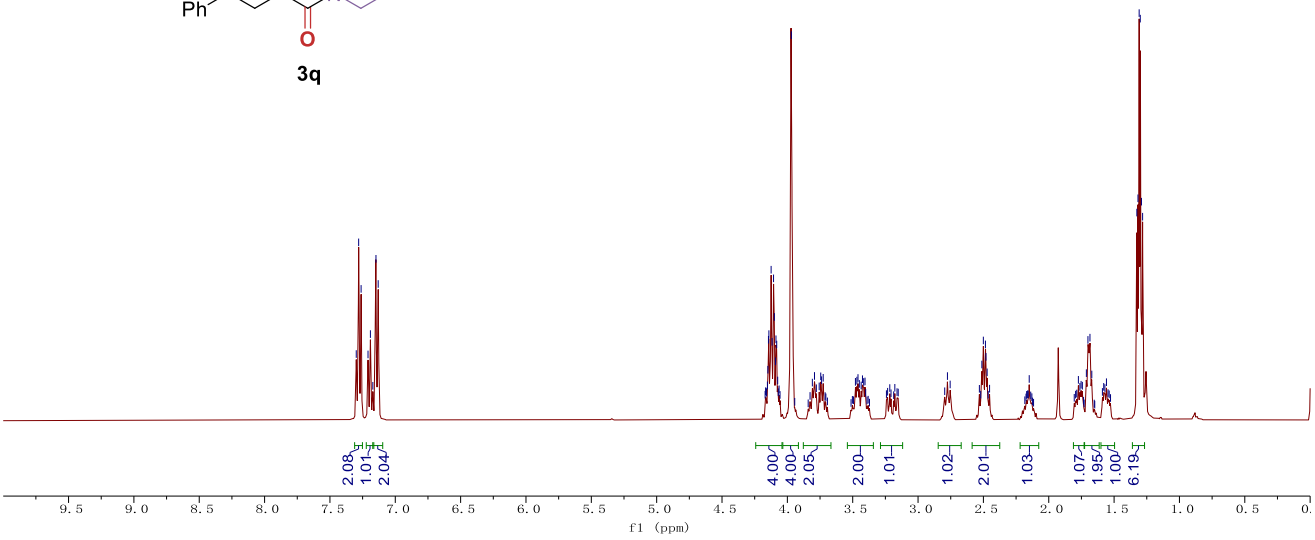
3p

1H NMR CDCl3 400.13MHz

7.30 7.28 7.26 7.21 7.19 7.17 7.15 7.13 4.17 4.16 4.15 4.15 4.14 4.14 4.12 4.12 4.11 4.10 4.09 4.09 4.08 4.07 4.06 3.97 3.81 3.79 3.78 3.76 3.74 3.74 3.73 3.48 3.47 3.46 3.45 3.44 3.43 3.42 3.41 3.23 3.22 3.18 3.16 2.80 2.78 2.75 2.53 2.51 2.50 2.48 2.48 2.47 2.45 2.15 1.77 1.76 1.75 1.74 1.71 1.70 1.68 1.67 1.59 1.58 1.57 1.56 1.33 1.32 1.31 1.30 1.29 1.28



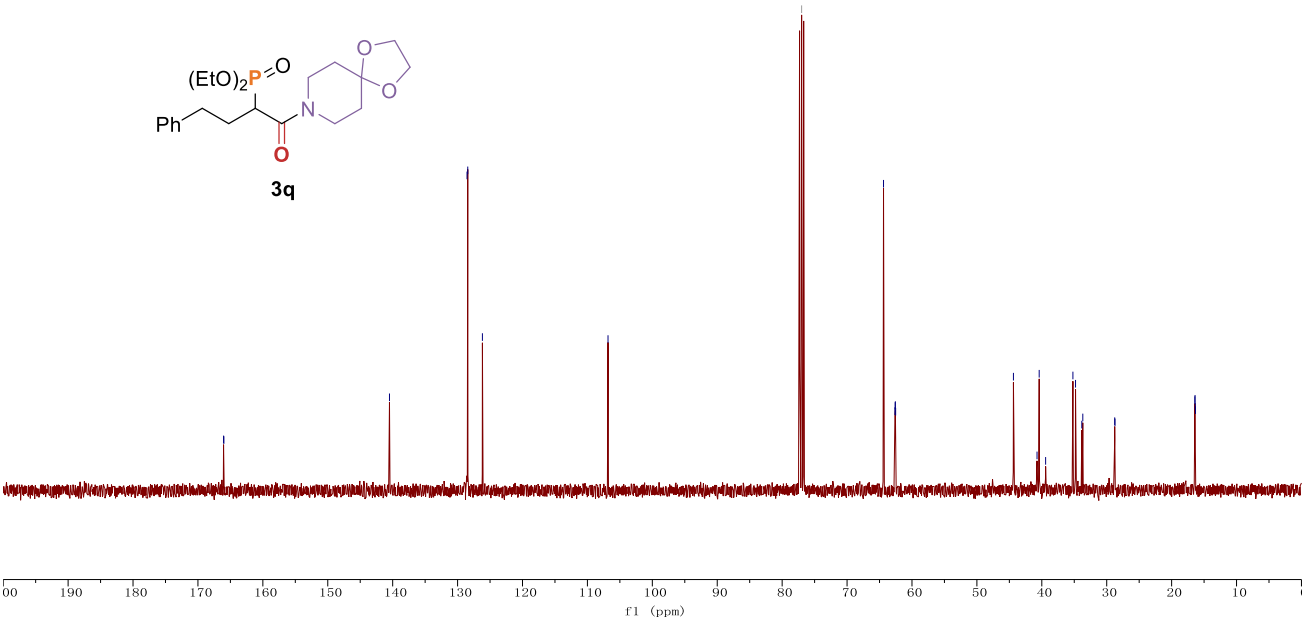
3q



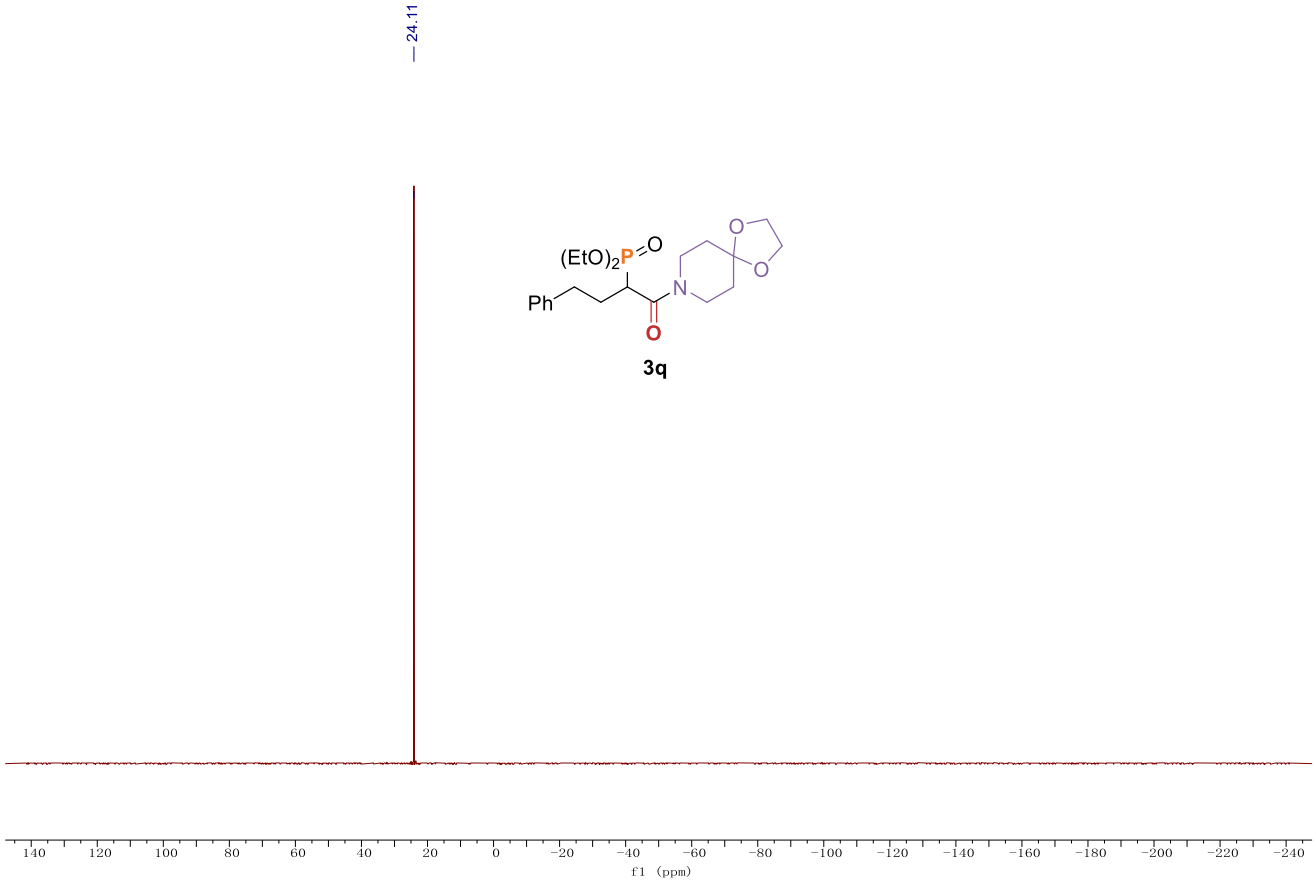
13C NMR CDCl3 100.62MHz

166.1 166.0 140.5 128.5 128.4 126.2 106.8 77.0 CDCl3 64.4 62.6 62.6 62.6 62.5 44.4 40.7 40.4 39.4 35.2 34.8 33.8 33.7 28.8 28.7 16.4 16.4 16.4 16.3

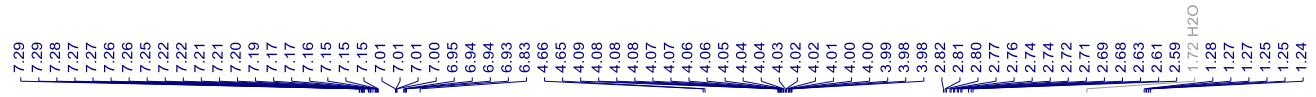
3q

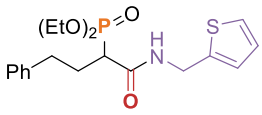


31P NMR CDCl3 161.97MHz

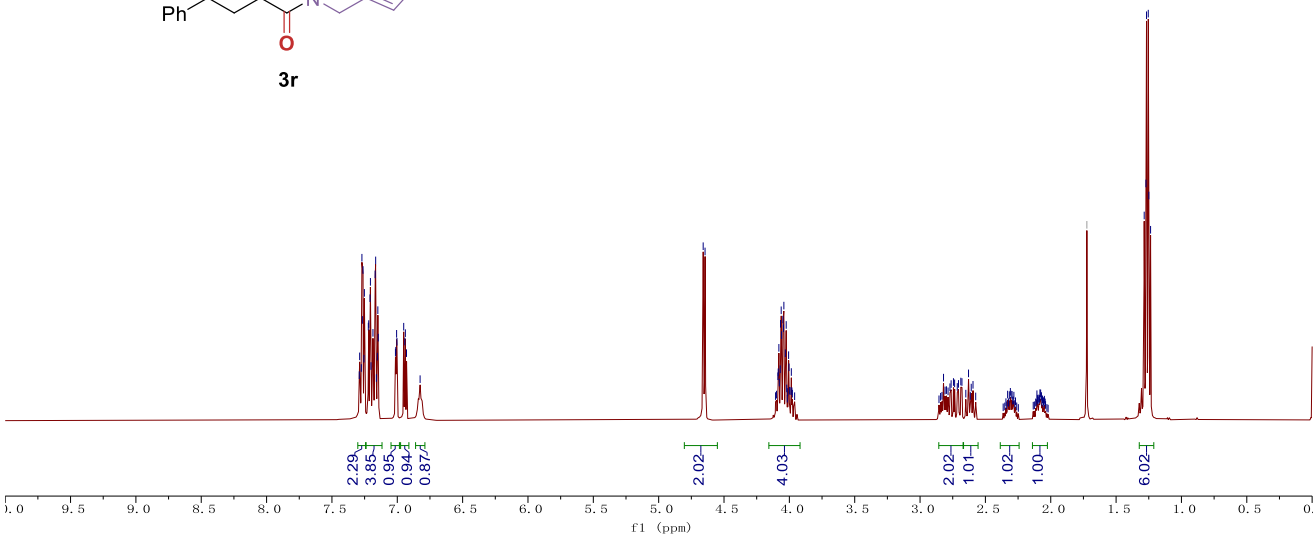


1H NMR CDCl3 400.13MHz

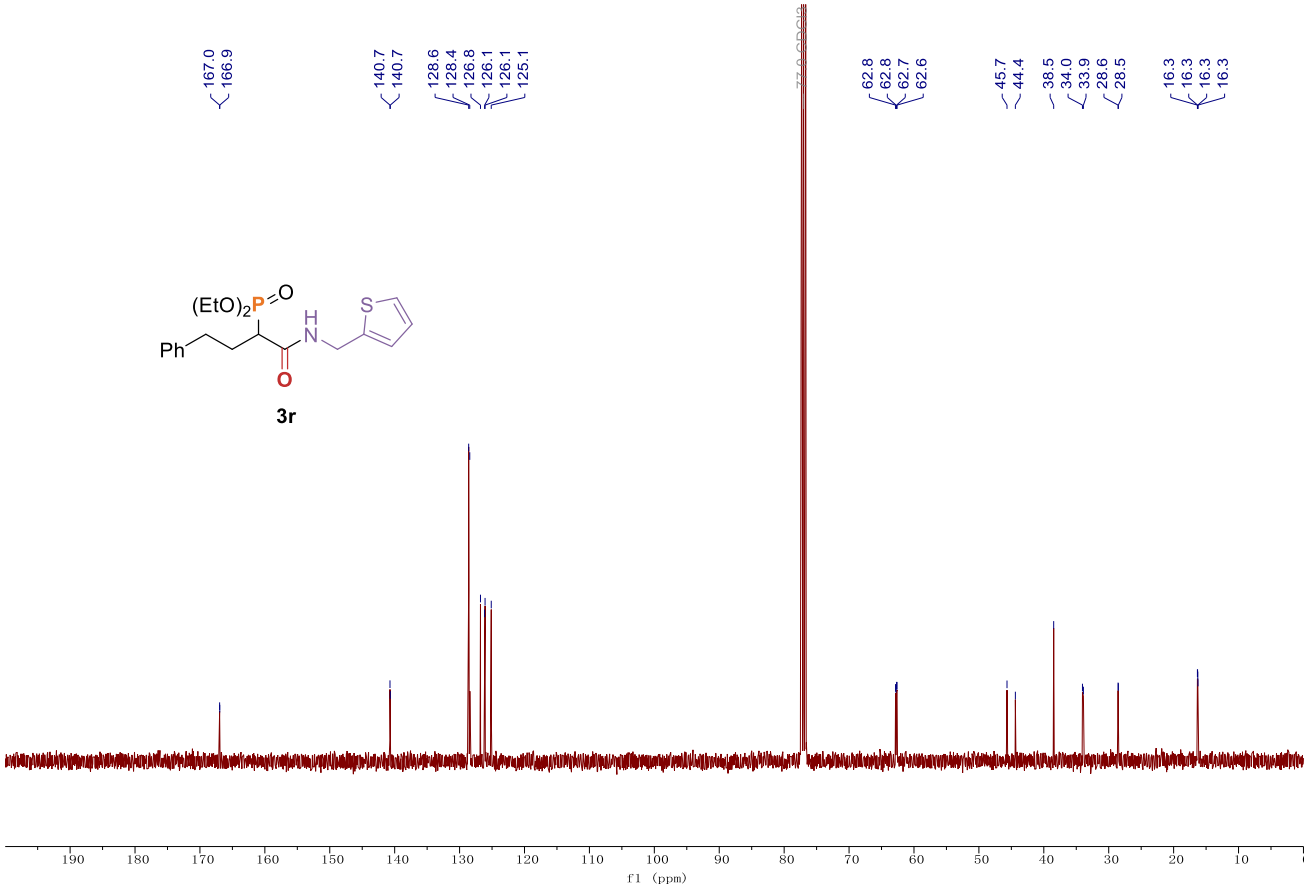




3r

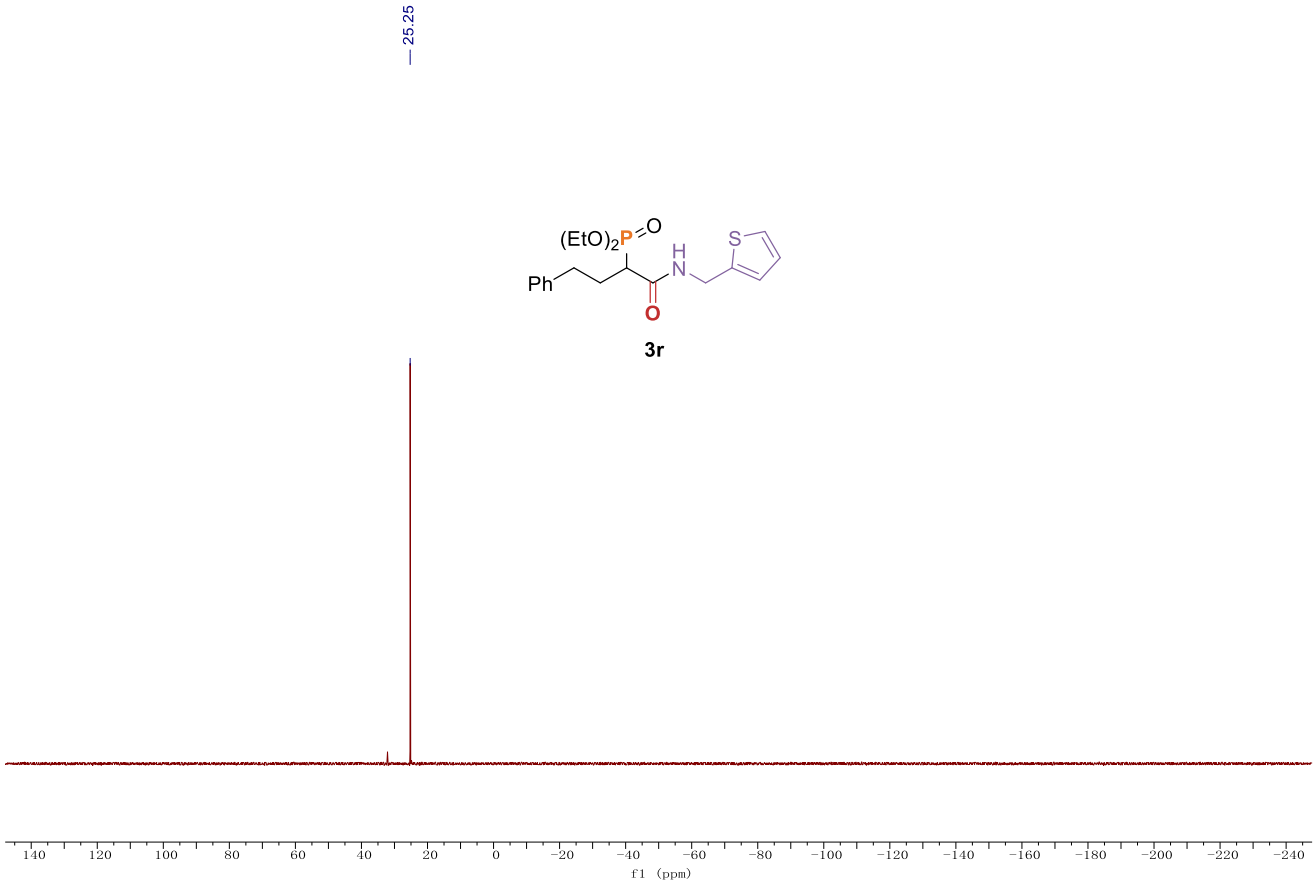


13C NMR CDCl3 100.62MHz



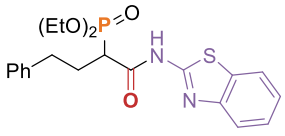
3r

31P NMR CDCl3 161.97MHz

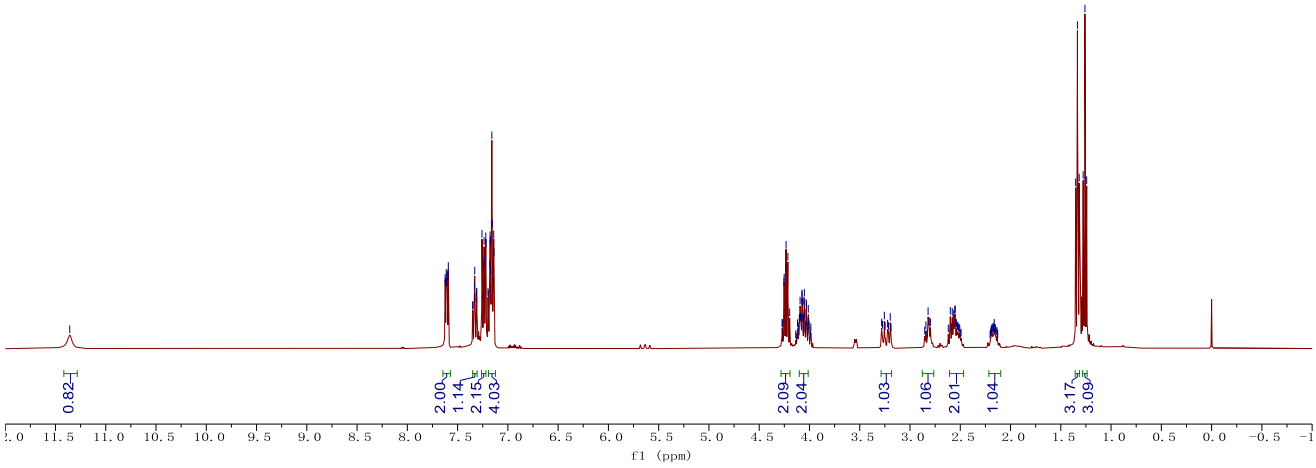


3r

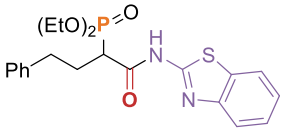
1H NMR CDCl3 400.13MHz



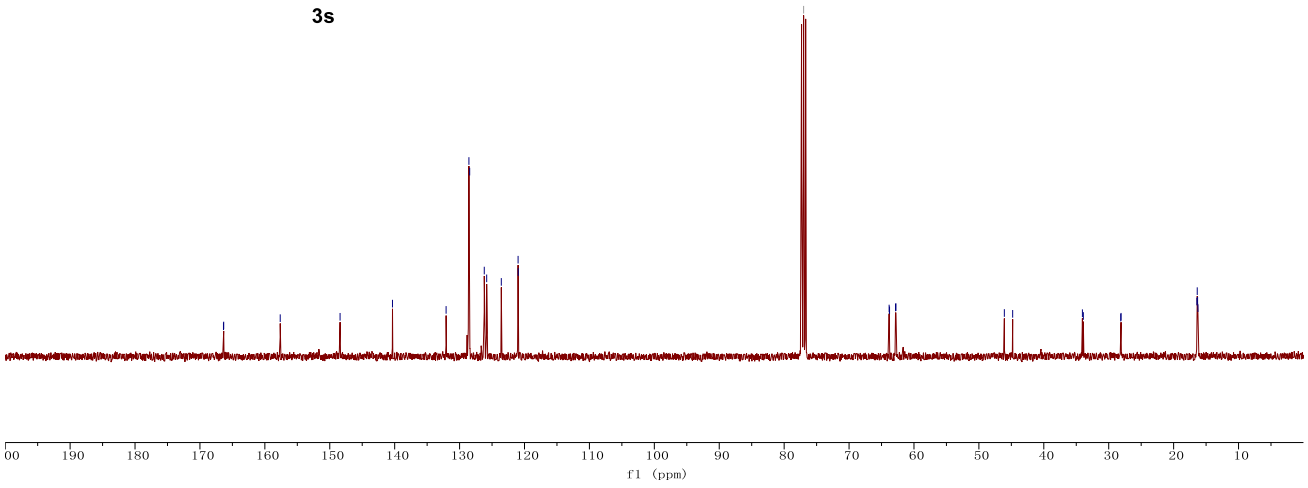
3s



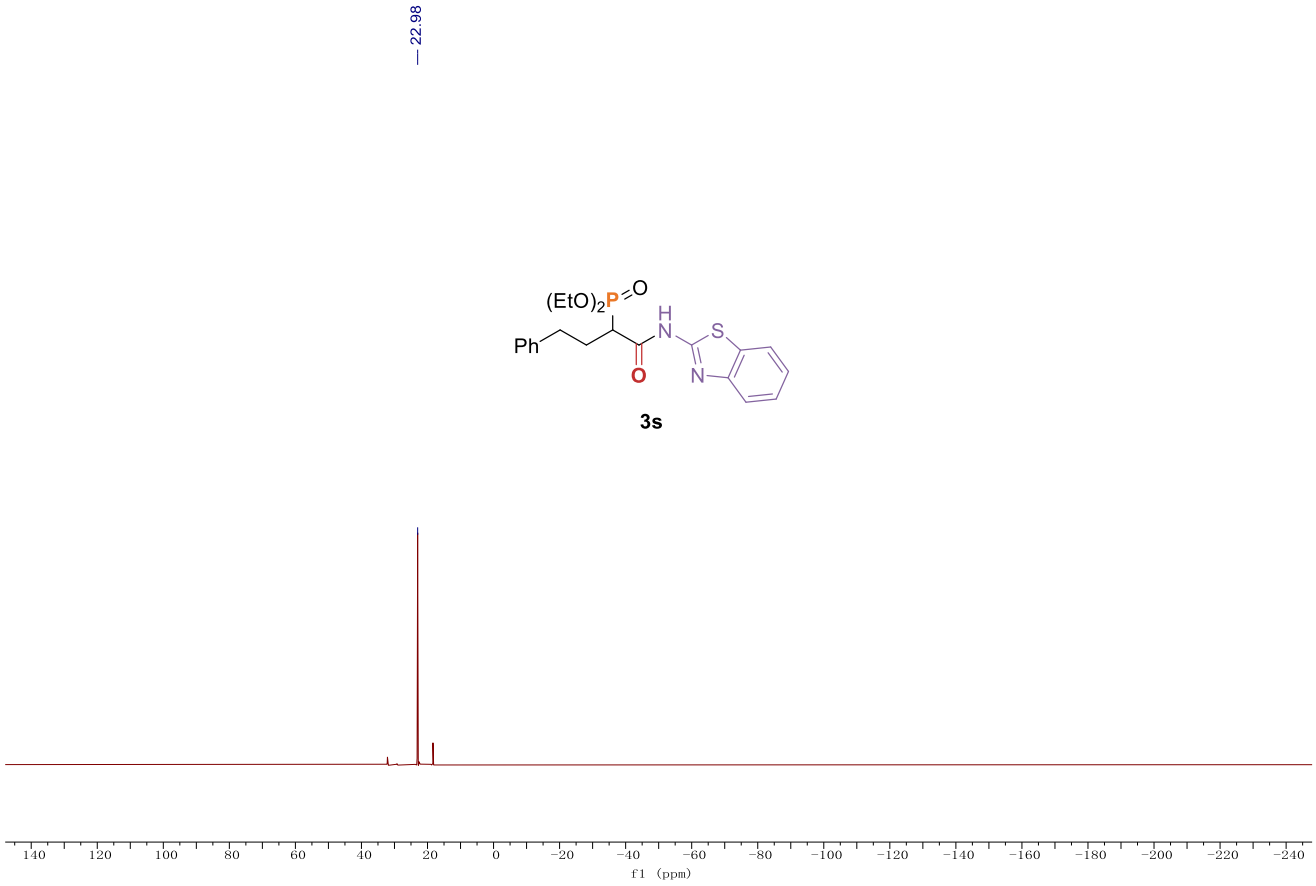
13C NMR CDCl3 100.62MHz



3s

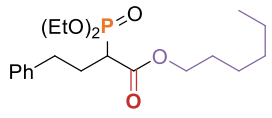


31P NMR CDCl3 161.97MHz

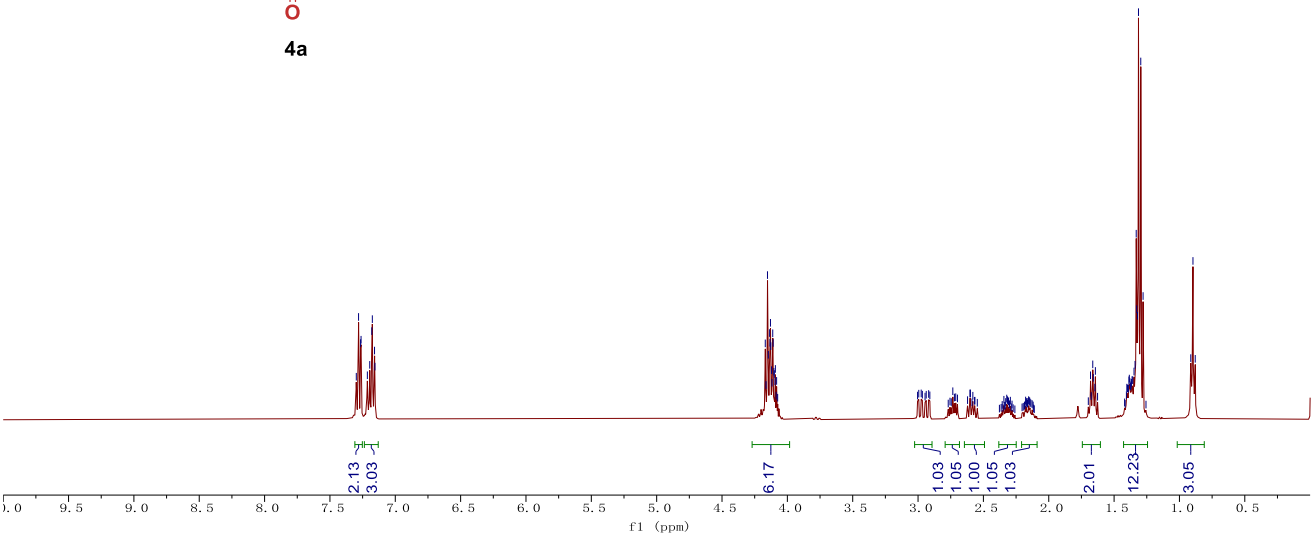


1H NMR CDCl3 400.13MHz

7.30 7.28 7.27 7.26 7.21 7.20 7.18 7.18 7.16 7.16 4.17 4.16 4.15 4.15 4.14 4.13 4.13 4.13 4.12 4.12 4.11 4.11 4.10 4.10 4.09 4.09 4.09 4.08 3.00 2.99 2.98 2.97 2.95 2.94 2.92 2.91 2.73 2.72 2.71 2.60 2.60 2.58 1.68 1.68 1.66 1.66 1.65 1.64 1.63 1.41 1.40 1.40 1.39 1.39 1.38 1.38 1.37 1.37 1.37 1.36 1.36 1.35 1.34 1.33 1.33 1.32 1.31 1.30 1.28 0.91 0.90 0.88



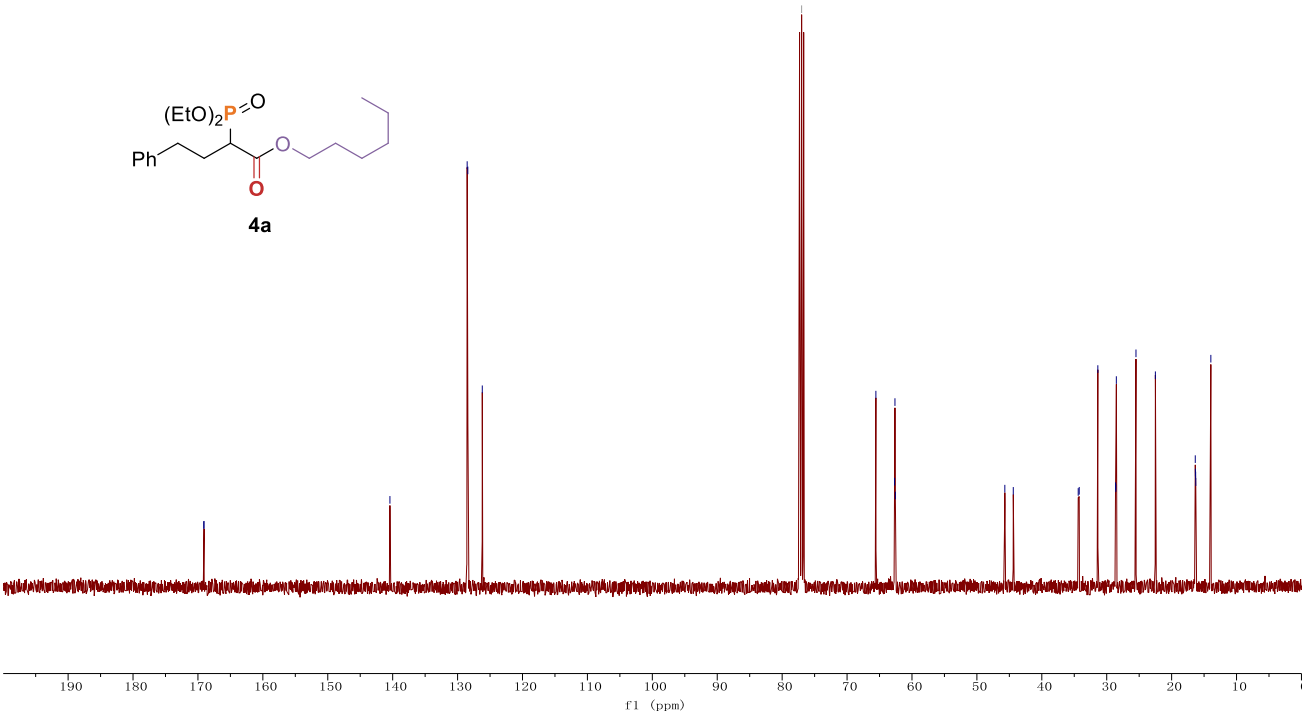
4a



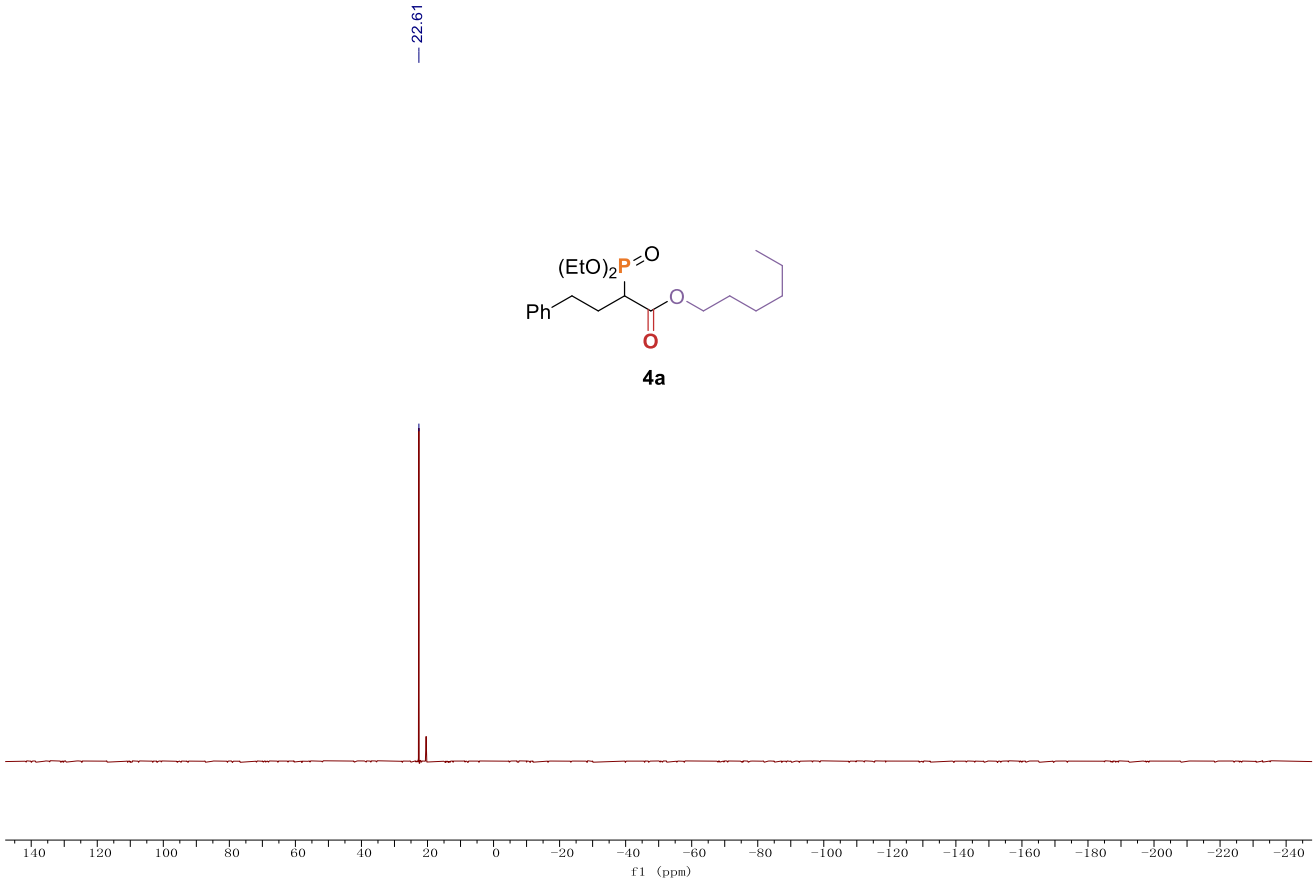
13C NMR CDCl3 100.62MHz

169.1 169.1 140.4 128.5 128.4 126.2 77.0 CDCl3 65.6 62.7 62.6 62.6 45.7 44.4 34.4 34.2 31.4 28.6 28.6 28.5 25.5 22.5 16.4 16.3 16.3 16.3 14.0

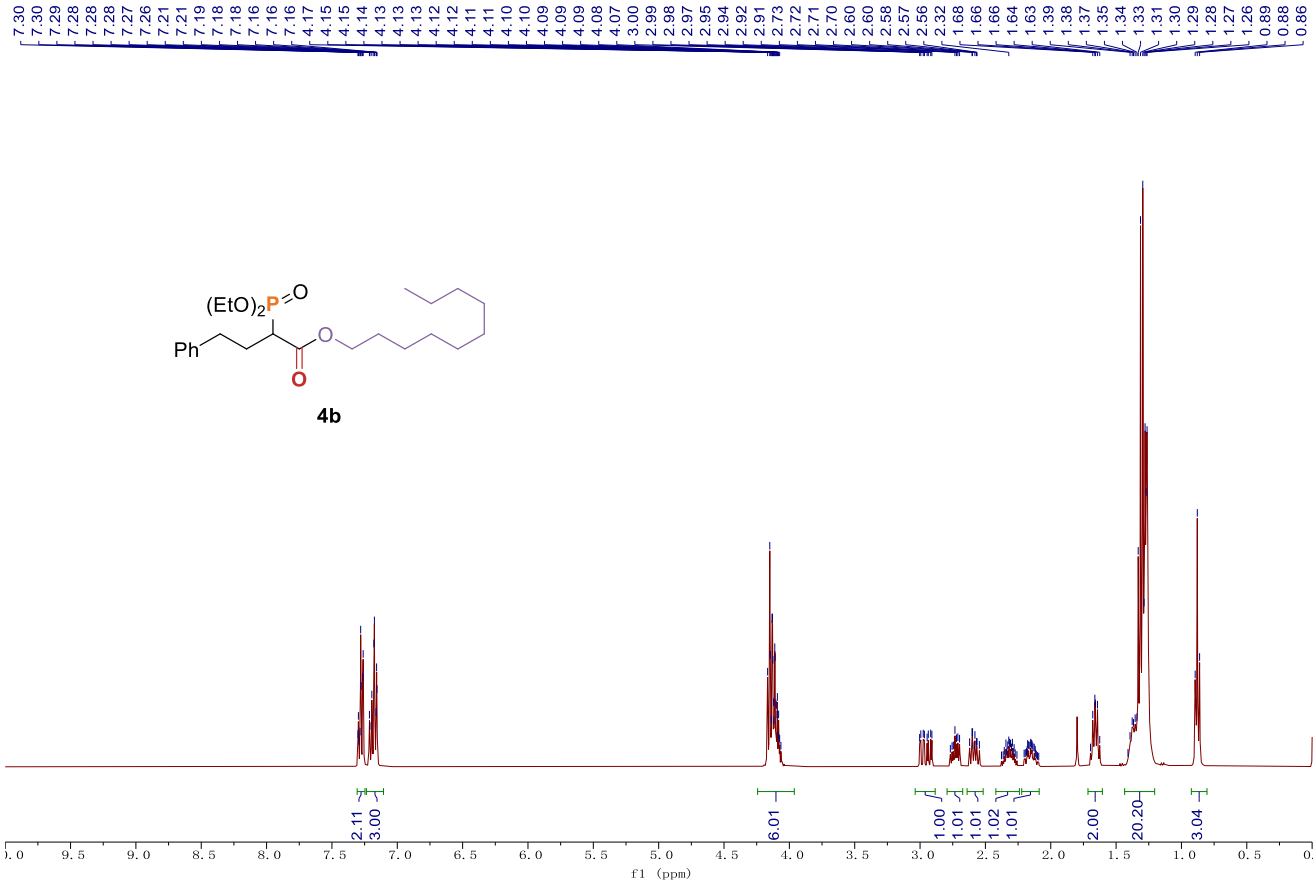
4a



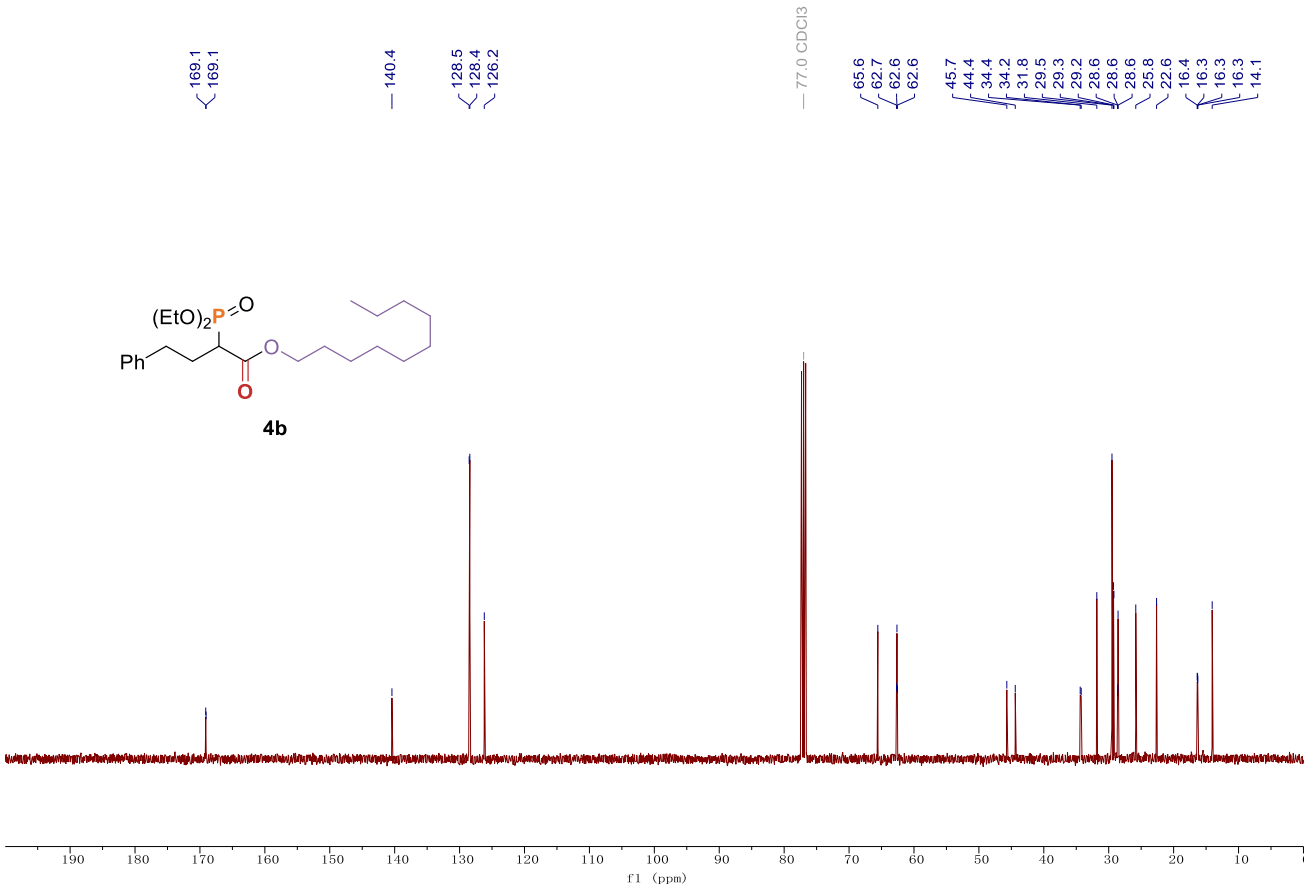
1H NMR CDCl3 161.97MHz



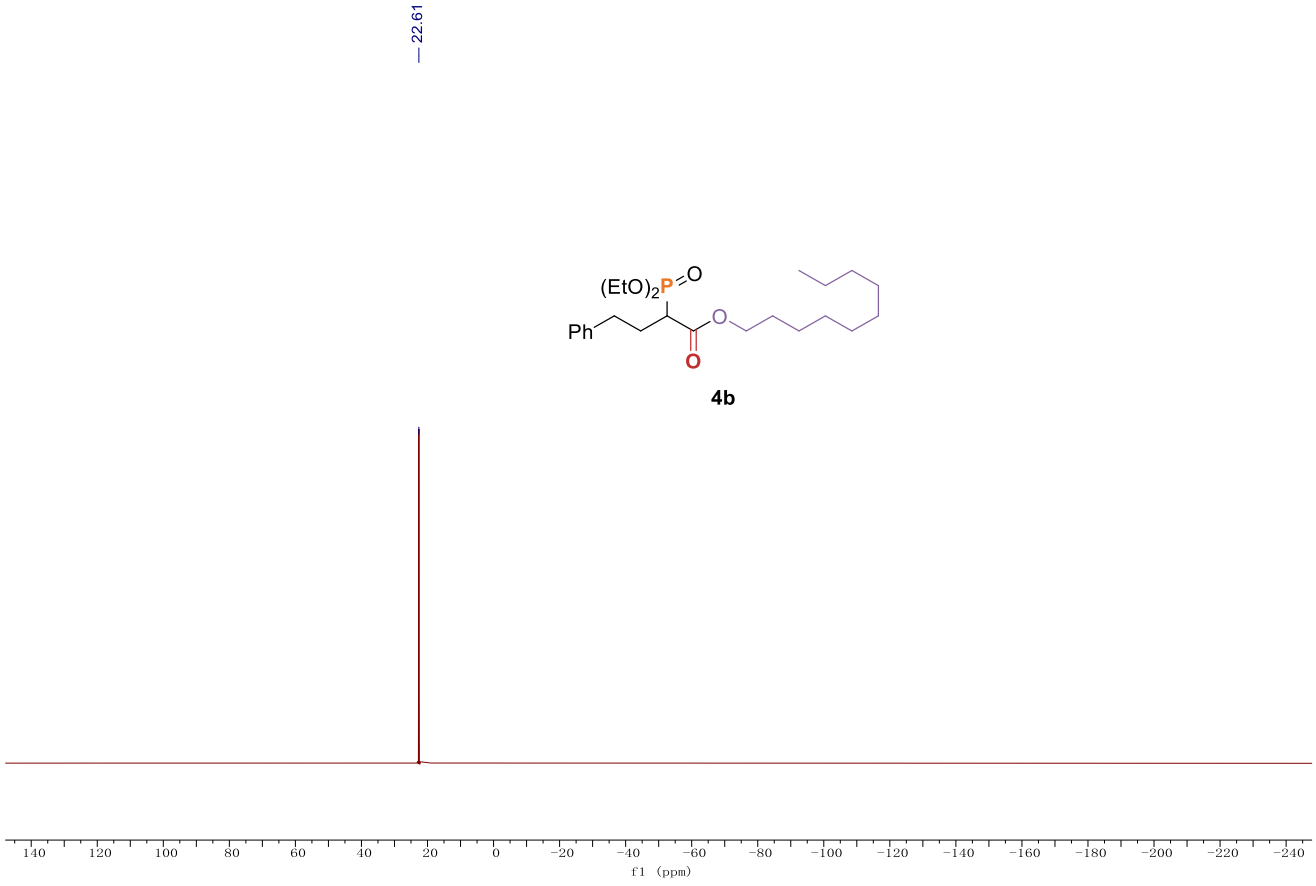
1H NMR CDCl3 400.13MHz



13C NMR CDCl3 100.62MHz

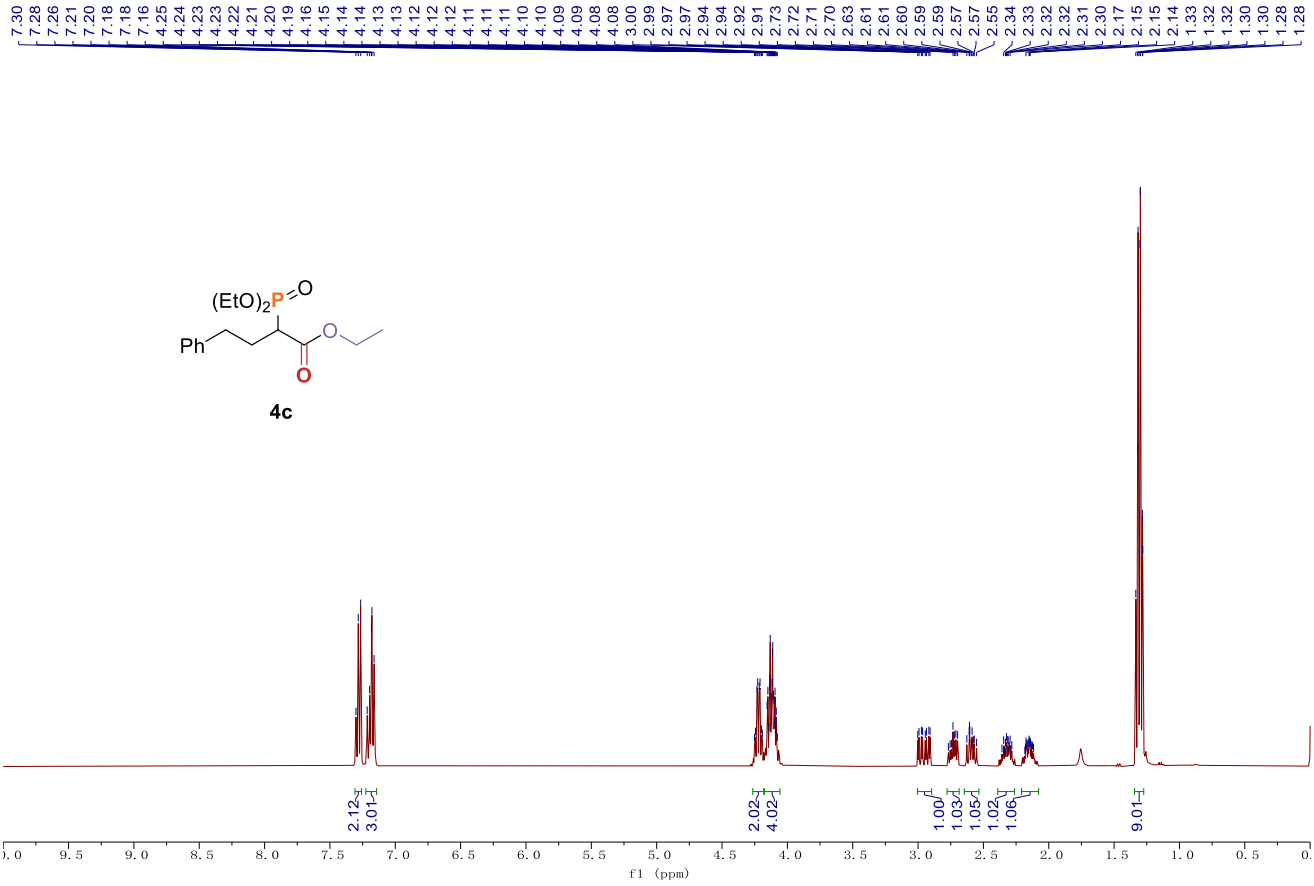


31P NMR CDCl3 161.97MHz

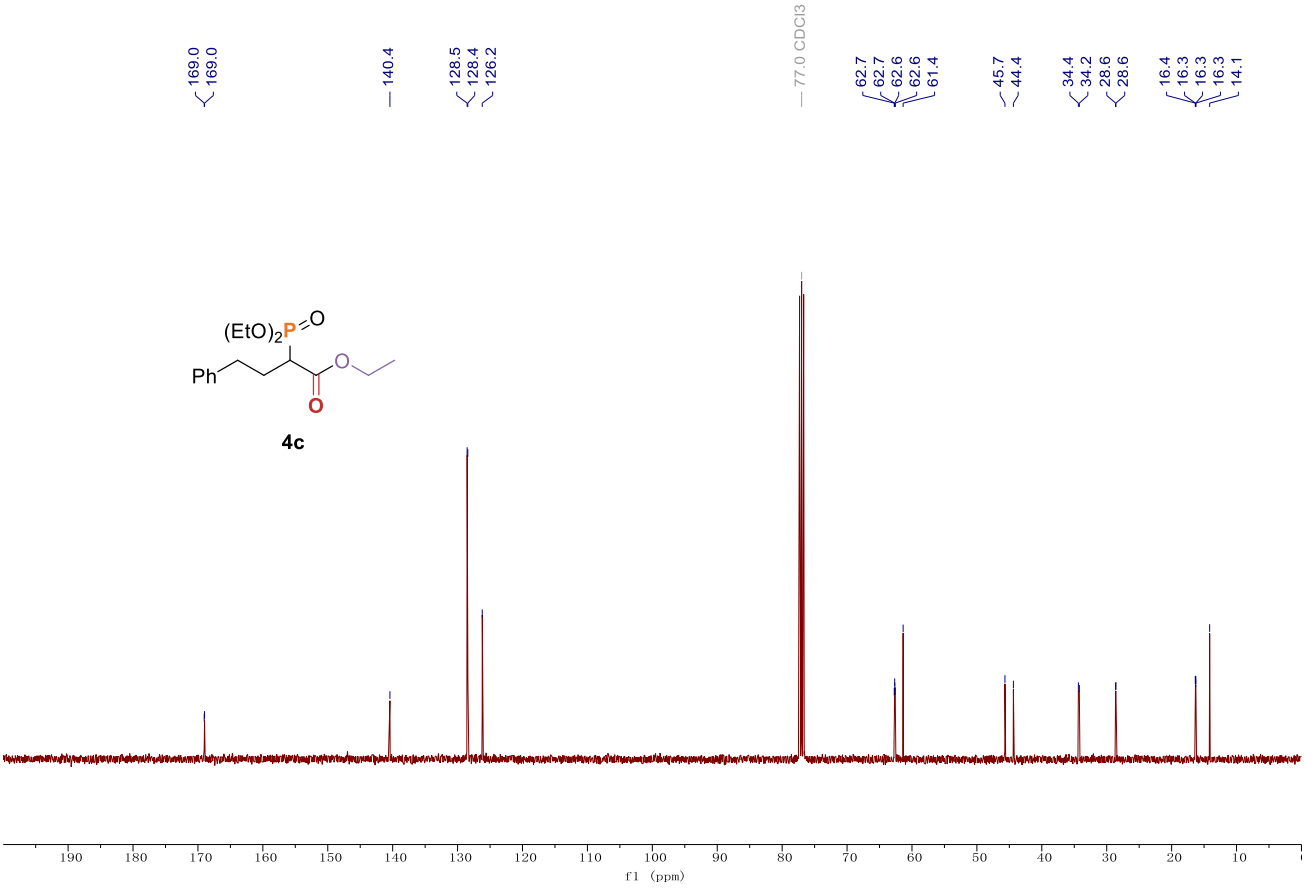


4b

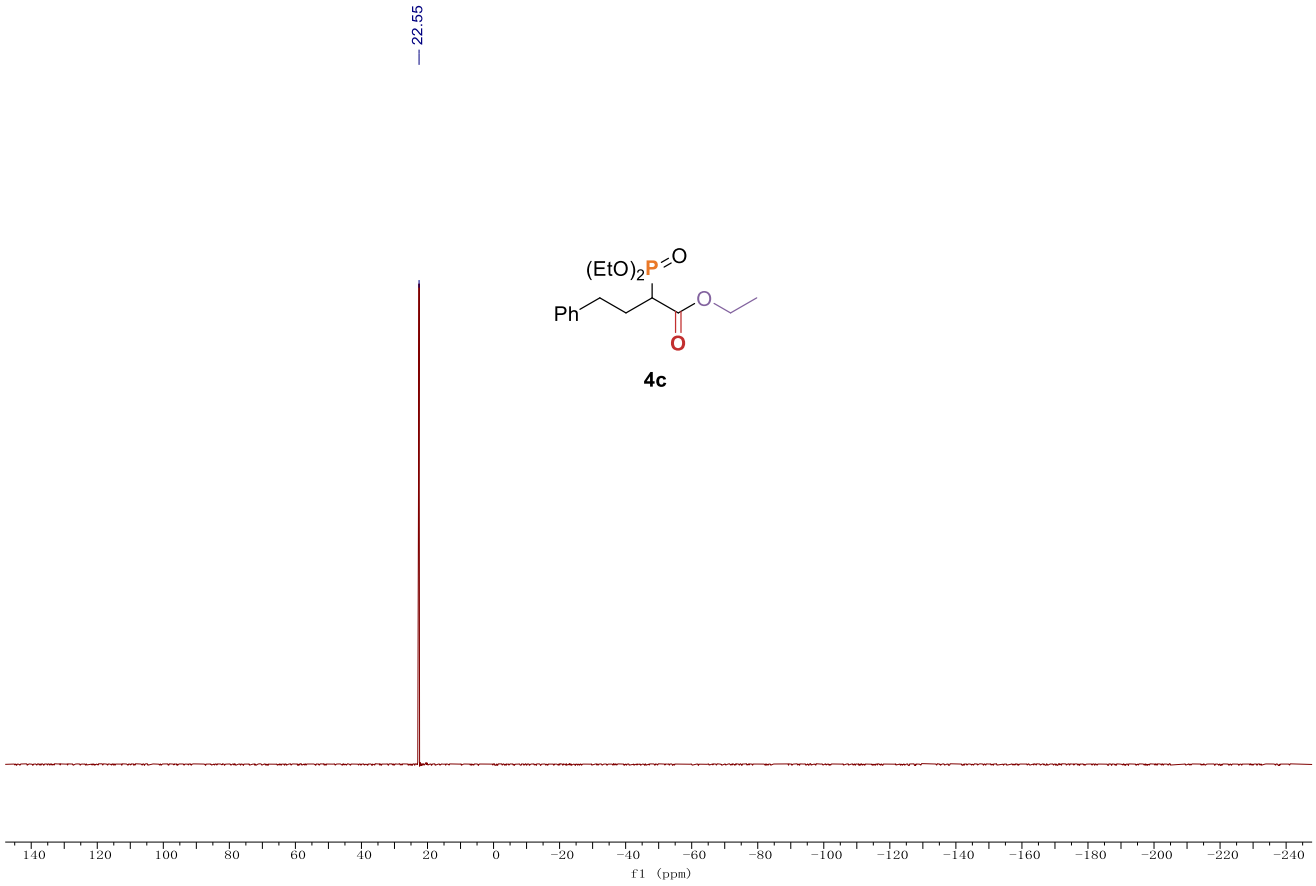
1H NMR CDCl3 400.13MHz



13C NMR CDCl3 100.62MHz

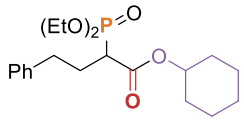


31P NMR CDCl3 161.97MHz

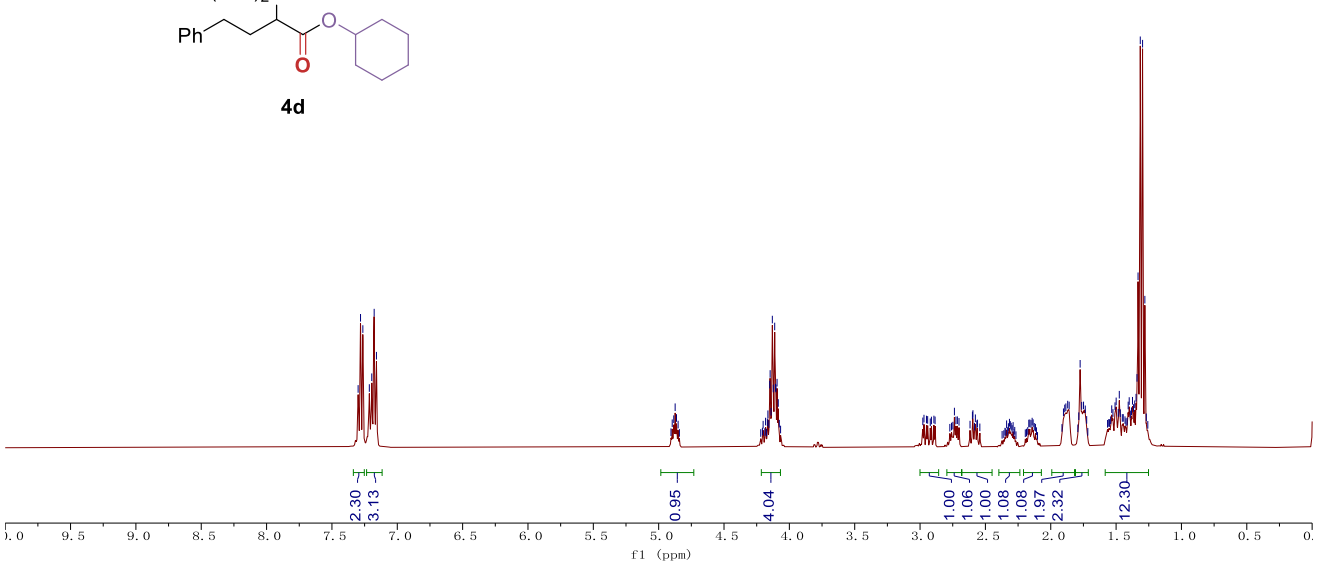


1H NMR CDCl3 400.13MHz

7.30 7.28 7.26 7.21 7.20 7.18 7.16 4.88 4.87 4.86 4.18 4.16 4.15 4.14 4.13 4.12 4.11 4.11 4.10 4.09 4.08 2.98 2.97 2.95 2.94 2.91 2.89 2.89 2.74 2.73 2.71 2.60 2.60 2.58 1.90 1.89 1.88 1.87 1.86 1.79 1.78 1.76 1.75 1.74 1.73 1.54 1.53 1.52 1.51 1.50 1.48 1.48 1.47 1.45 1.45 1.43 1.42 1.41 1.40 1.39 1.38 1.37 1.37 1.36 1.35 1.34 1.33 1.31 1.30 1.28 1.27

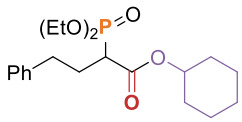


4d

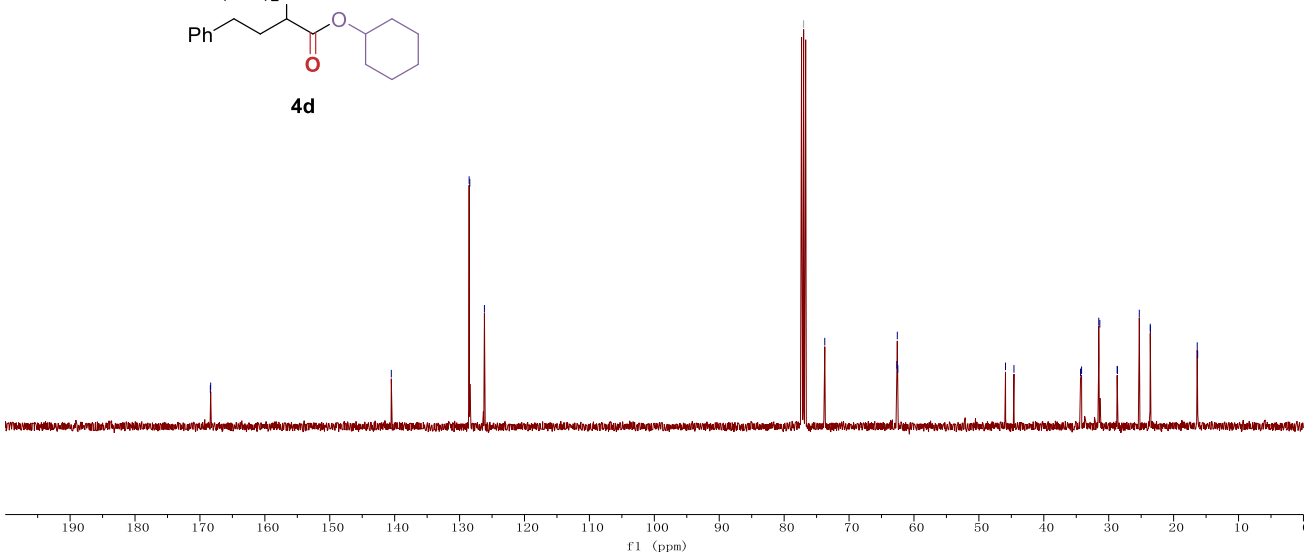


13C NMR CDCl3 100.62MHz

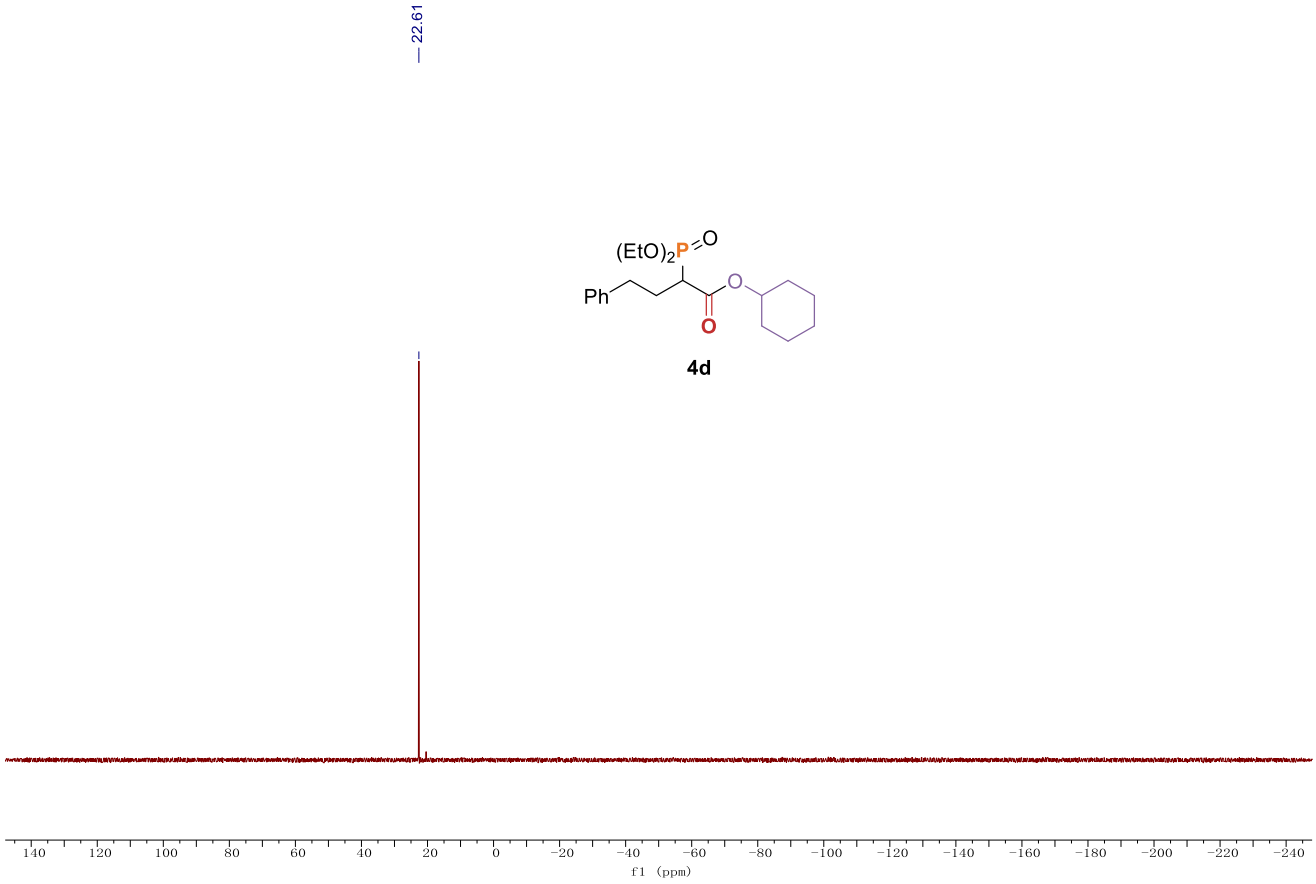
168.4 168.3 140.5 128.5 128.4 126.2 77.0 CDCl3 73.7 62.6 62.6 62.5 45.9 44.6 34.3 34.2 31.5 31.4 28.7 28.7 25.3 23.6 23.6 16.4 16.3



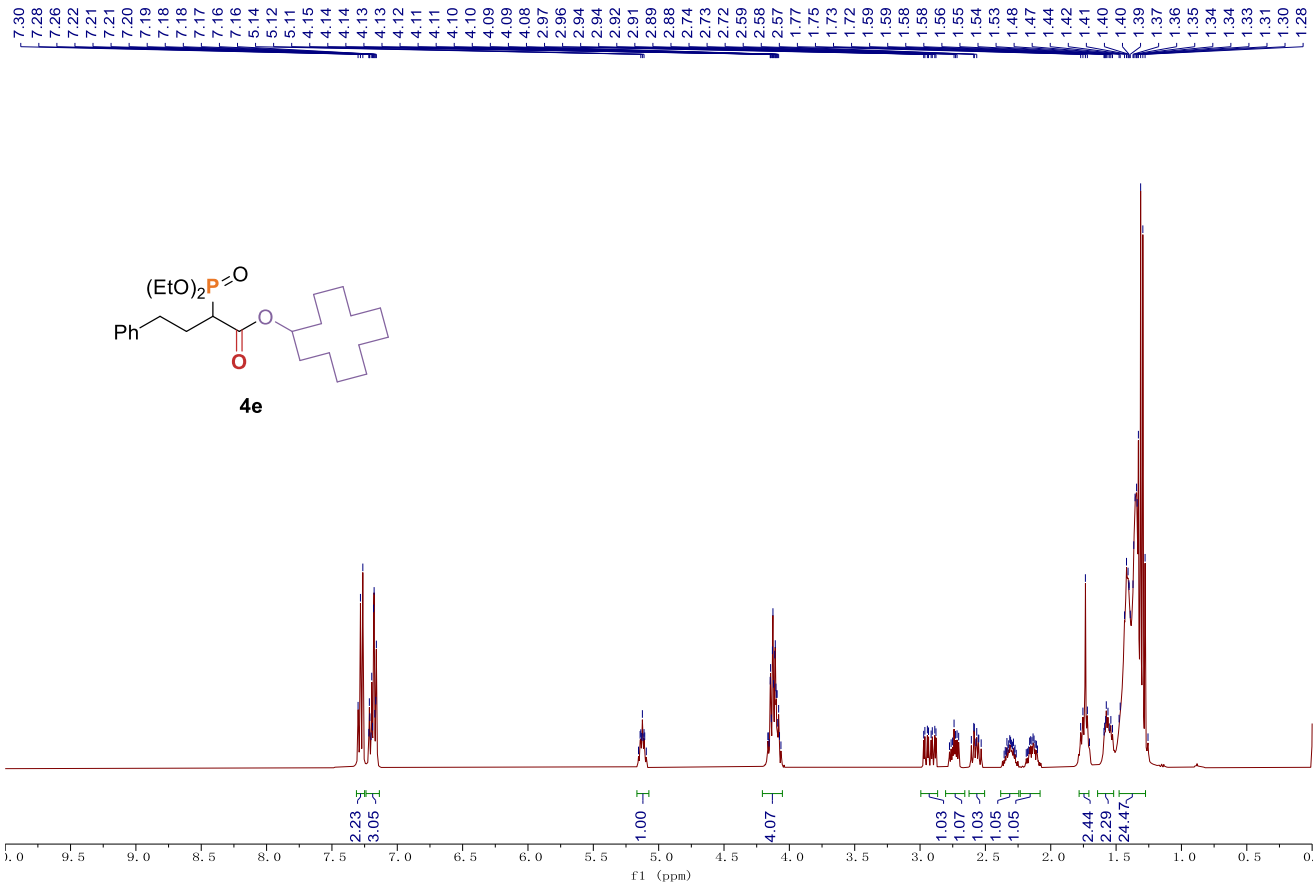
4d



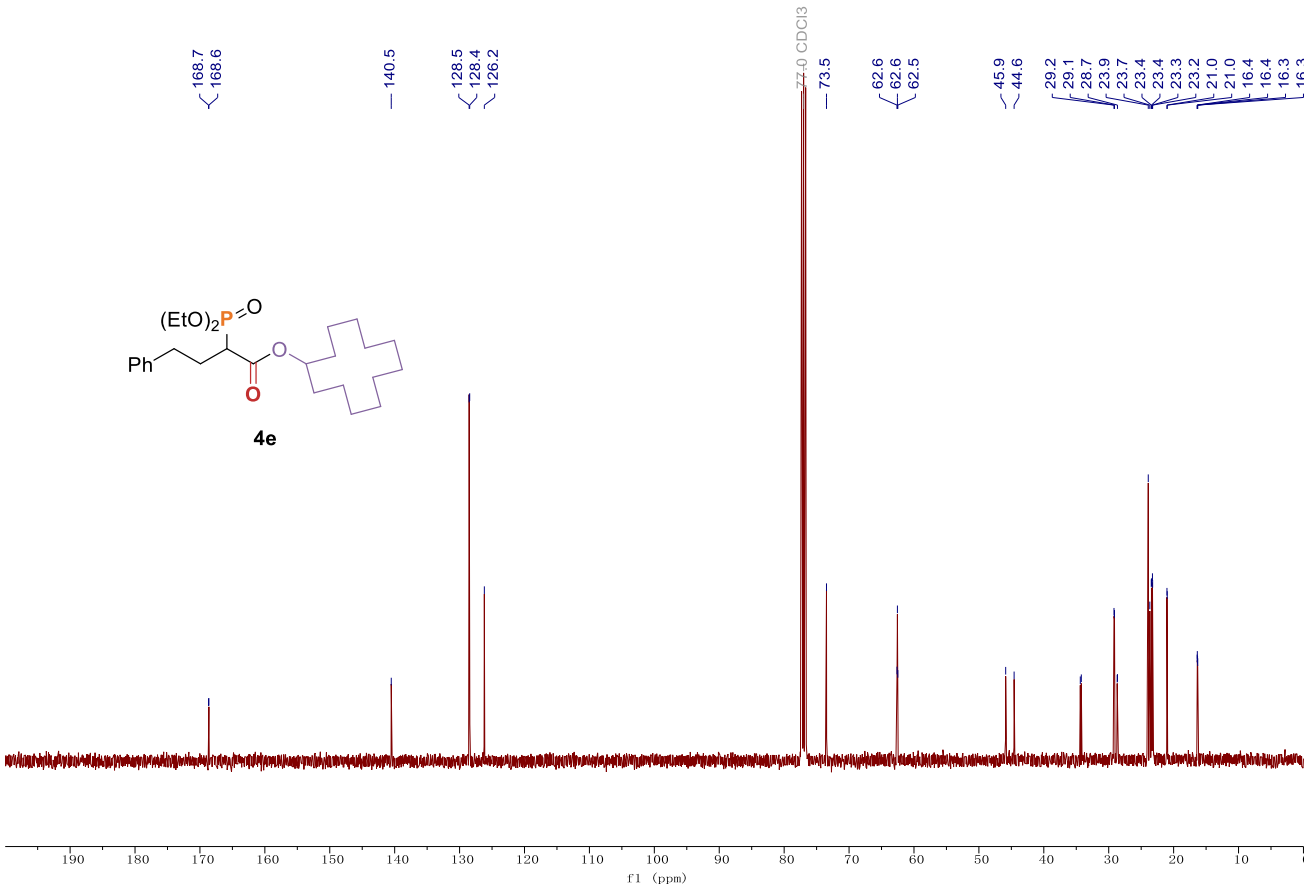
31P NMR CDCl3 161.97MHz



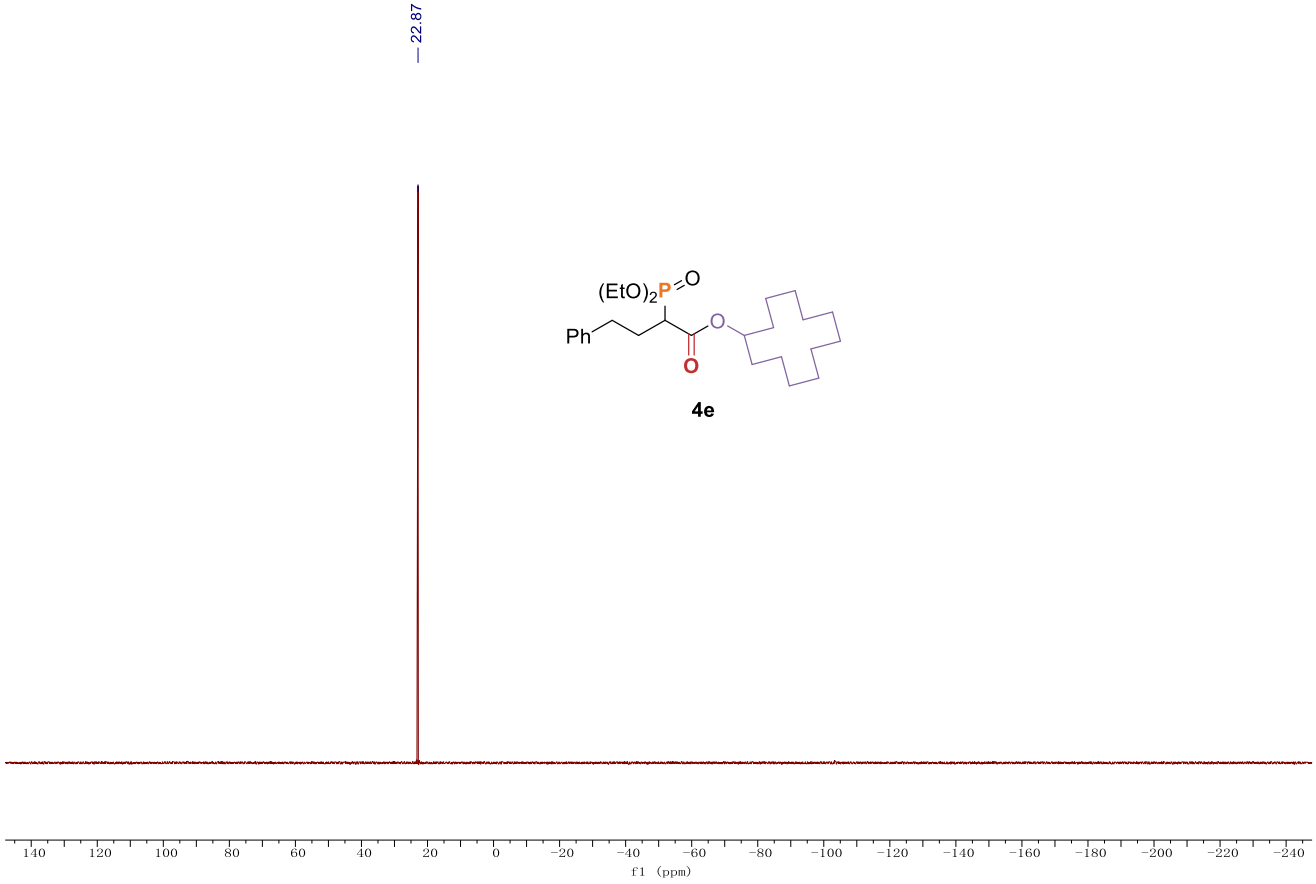
1H NMR CDCl3 400.13MHz



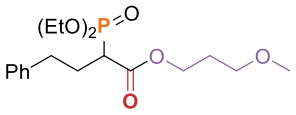
13C NMR CDCl3 100.62MHz



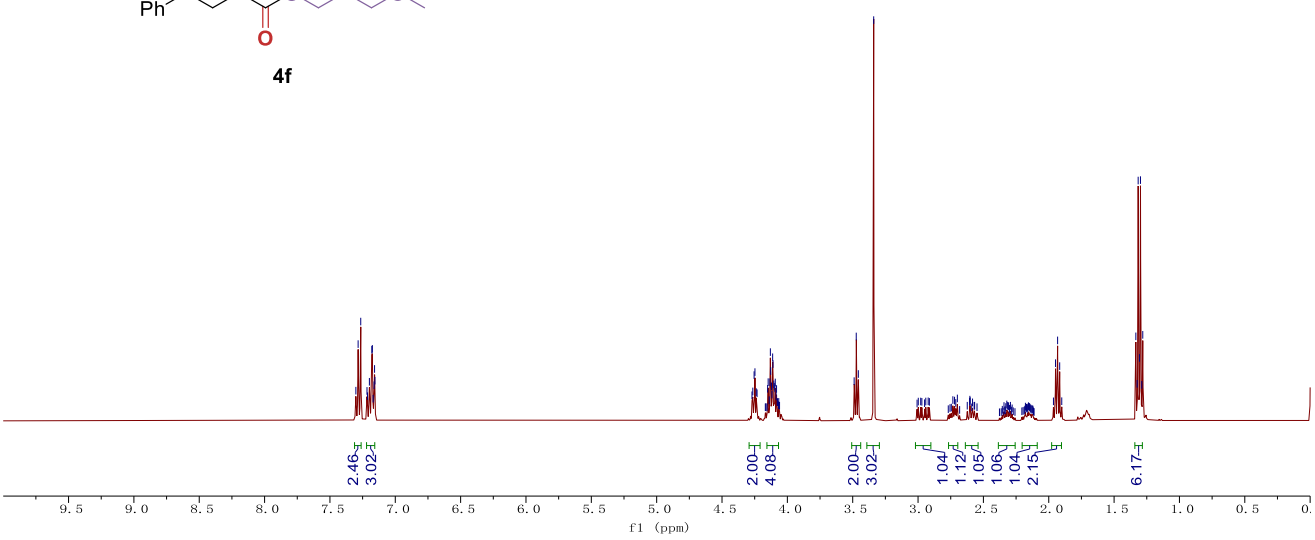
31P NMR CDCl3 161.97MHz



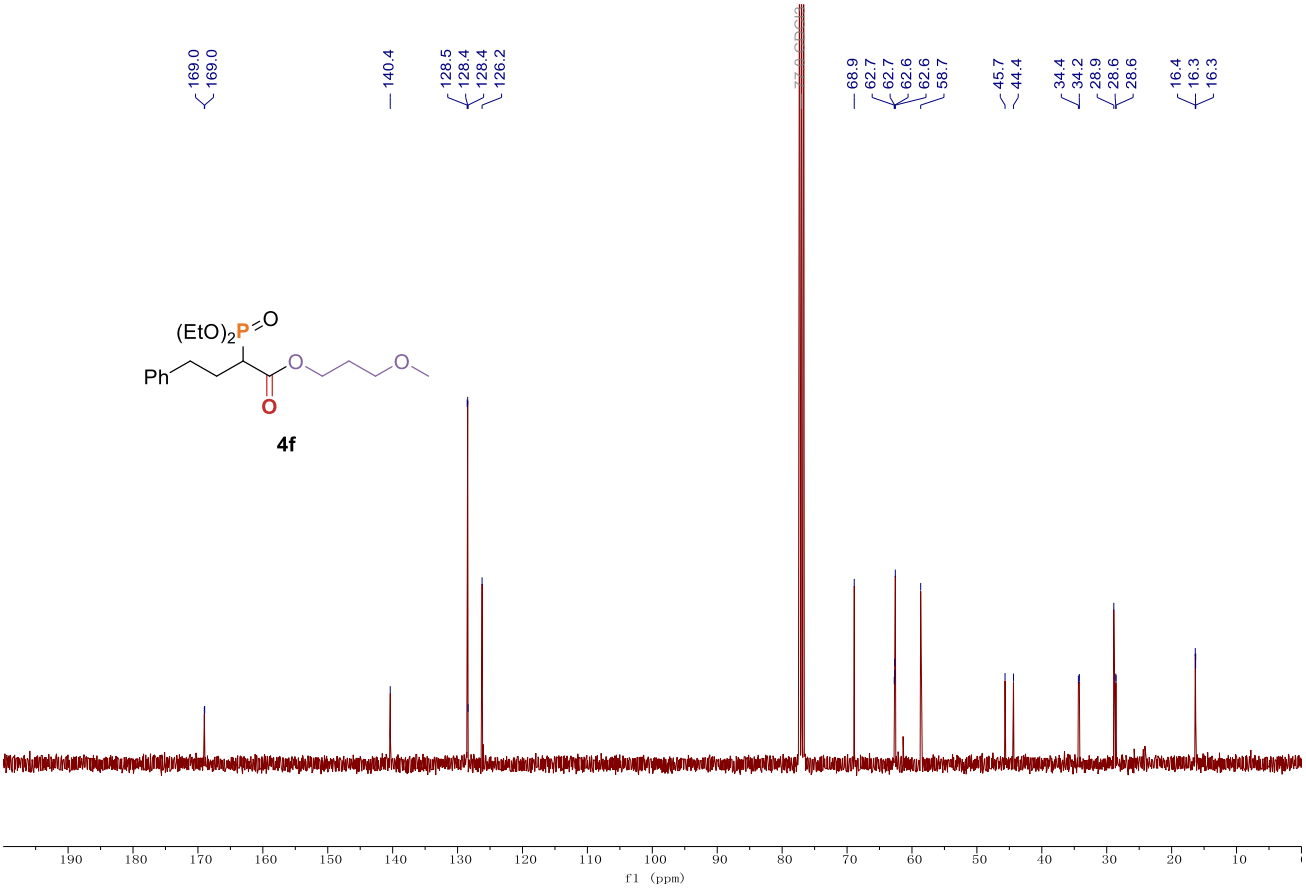
1H NMR CDCl3 400.13MHz



4f

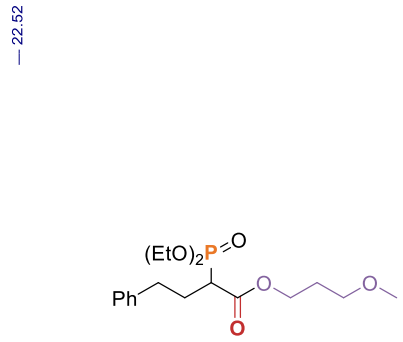


13C NMR CDCl3 100.62MHz

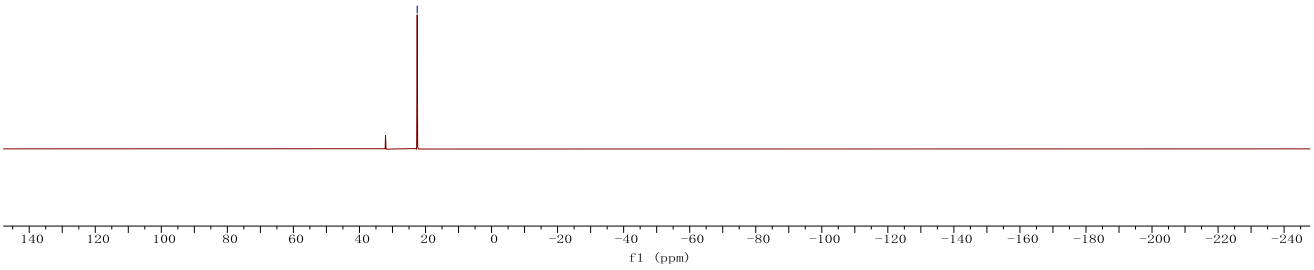


4f

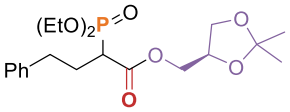
31P NMR CDCl3 161.97MHz



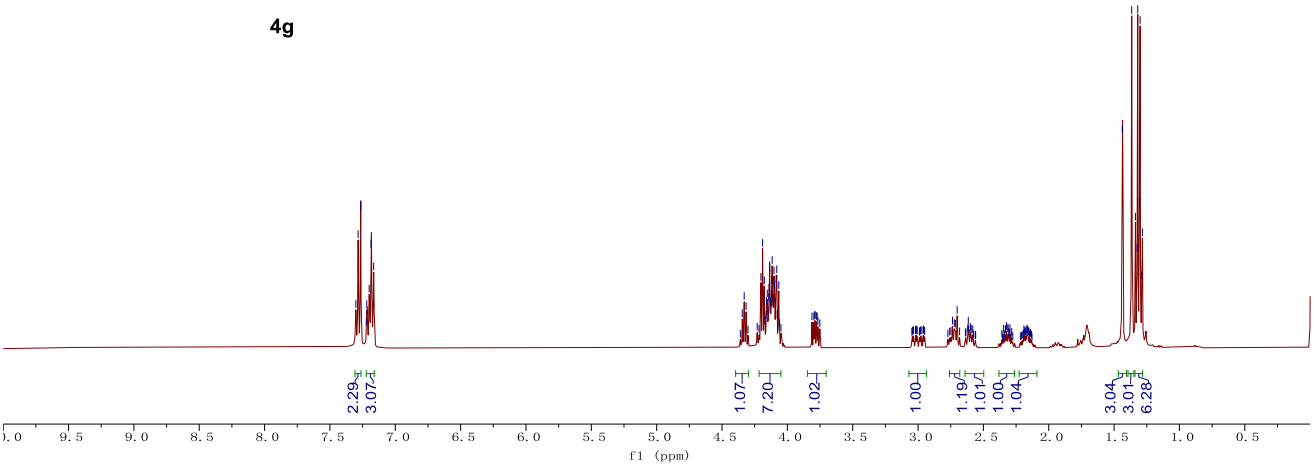
4f



1H NMR CDCl3 400.13MHz

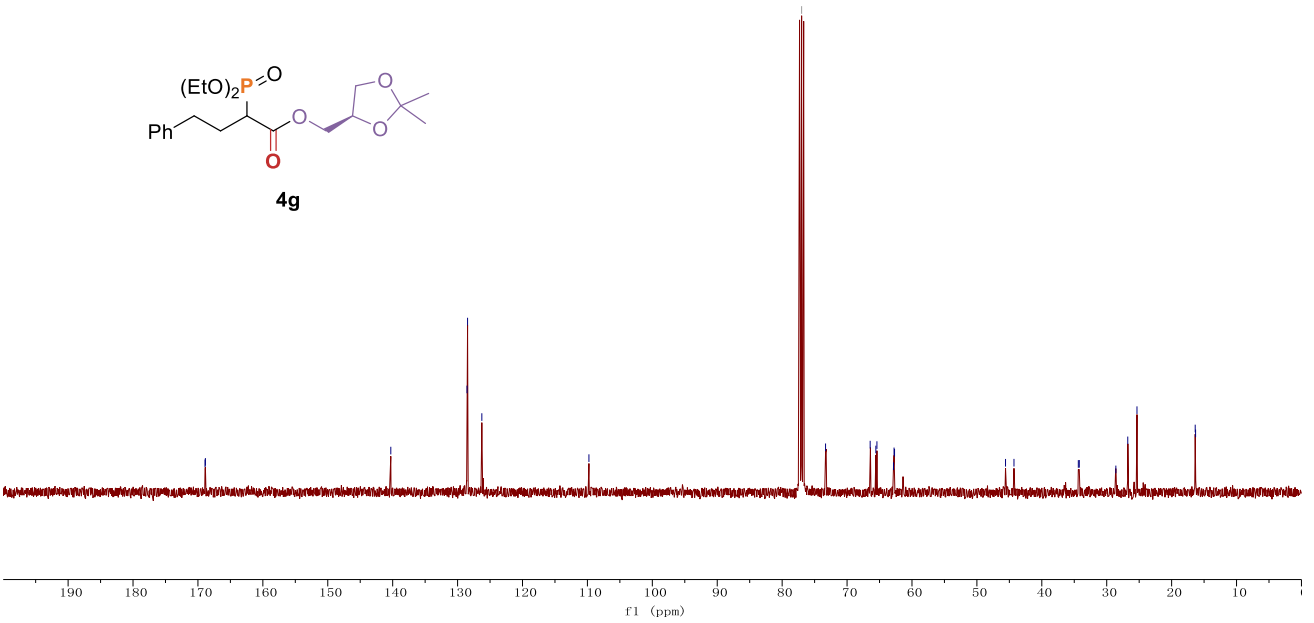


4g

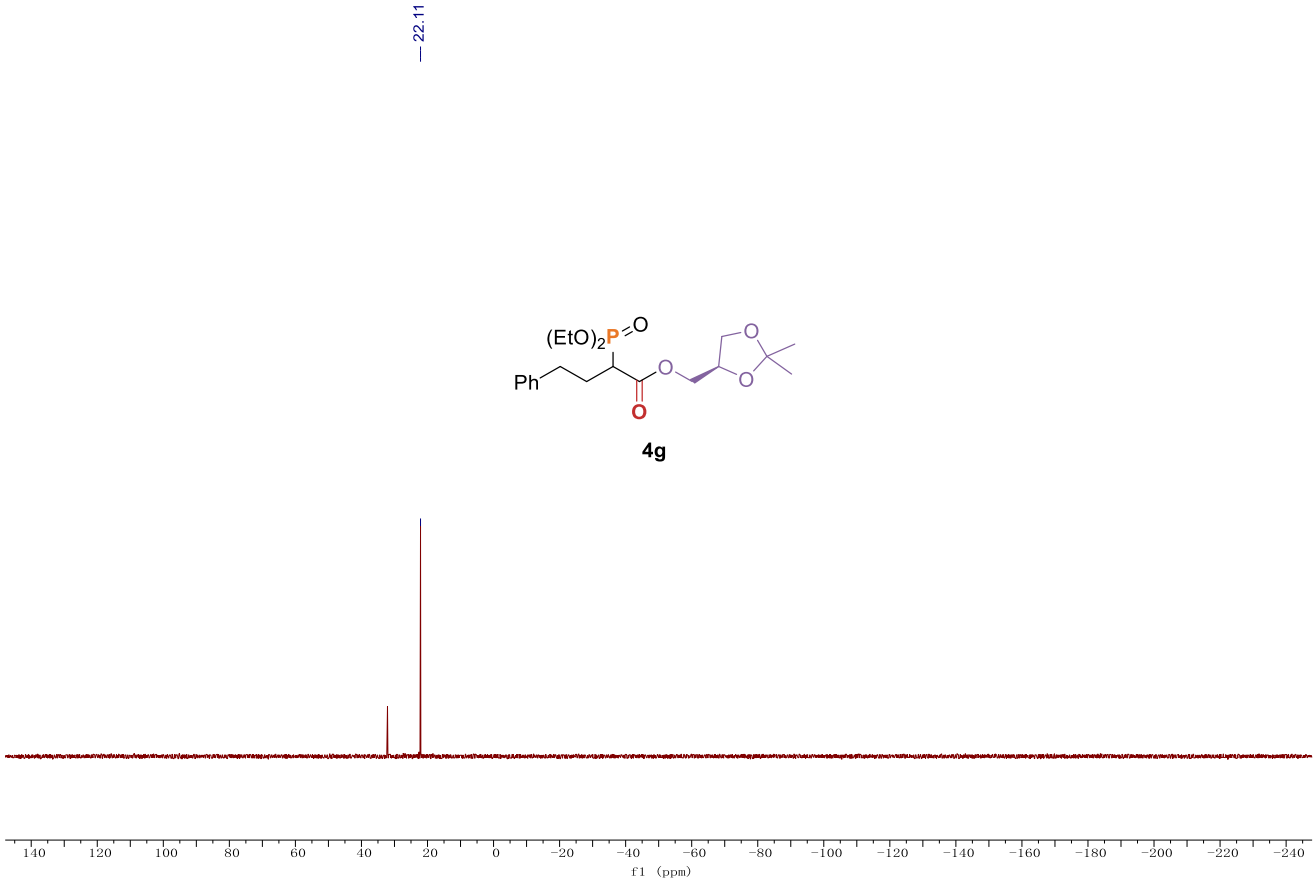


13C NMR CDCl3 100.62MHz

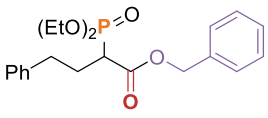
4g



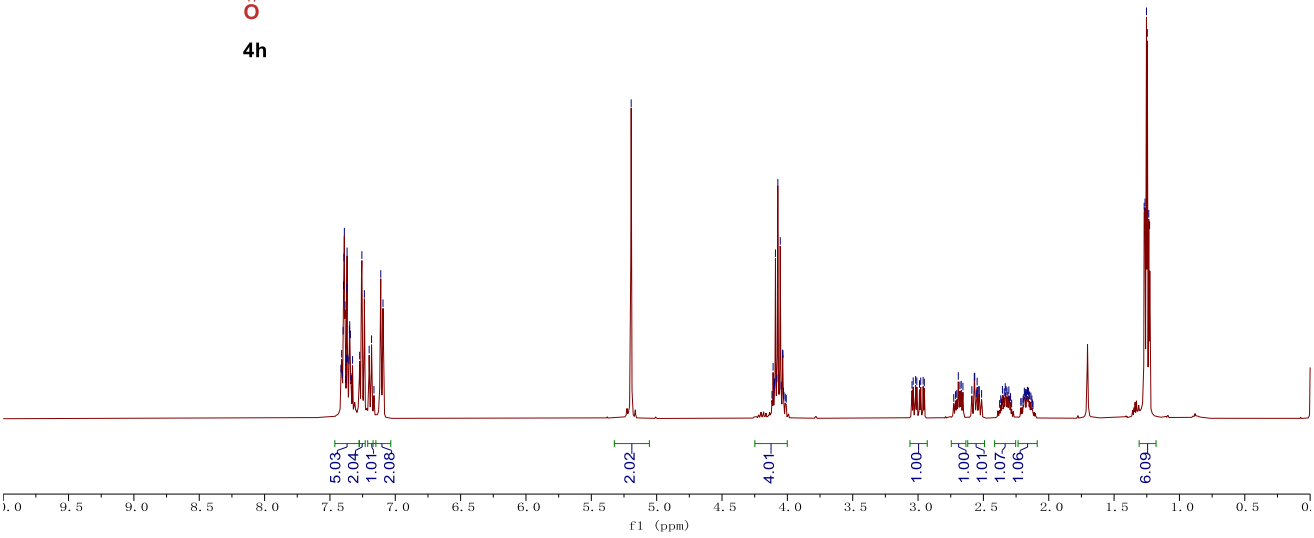
31P NMR CDCl3 161.97MHz



1H NMR CDCl3 400.13MHz

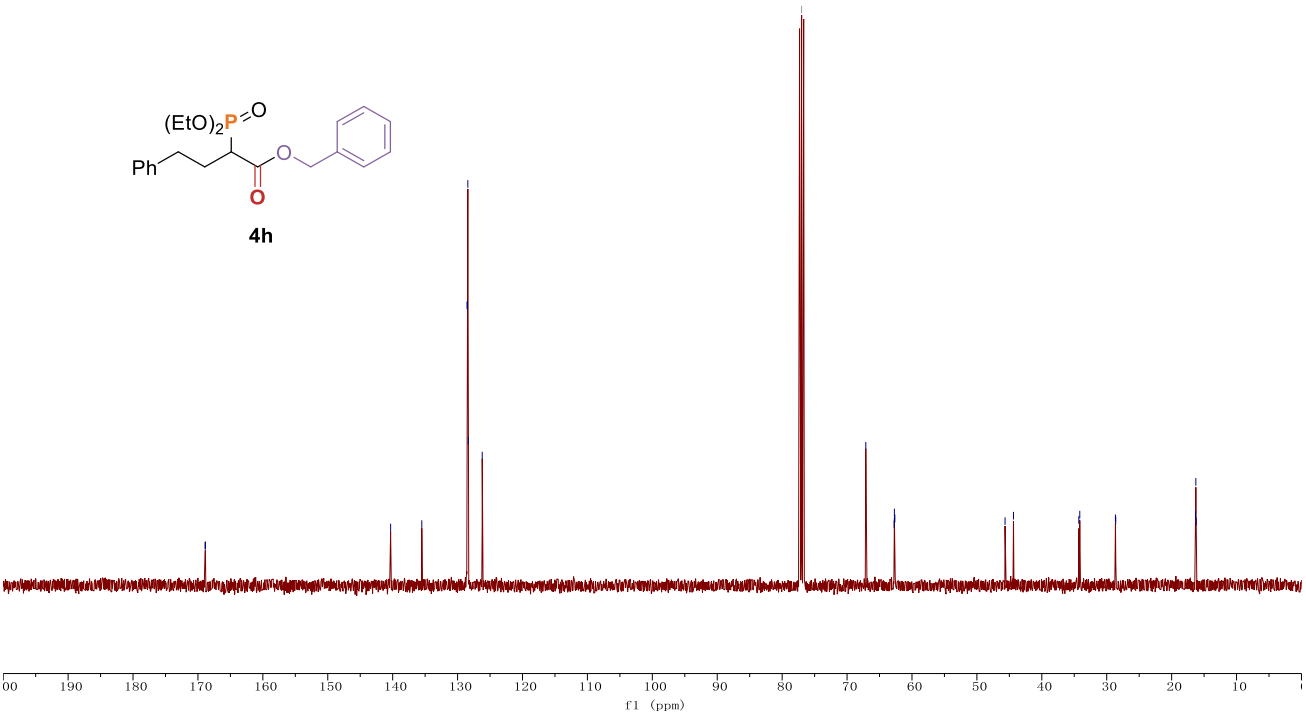


4h

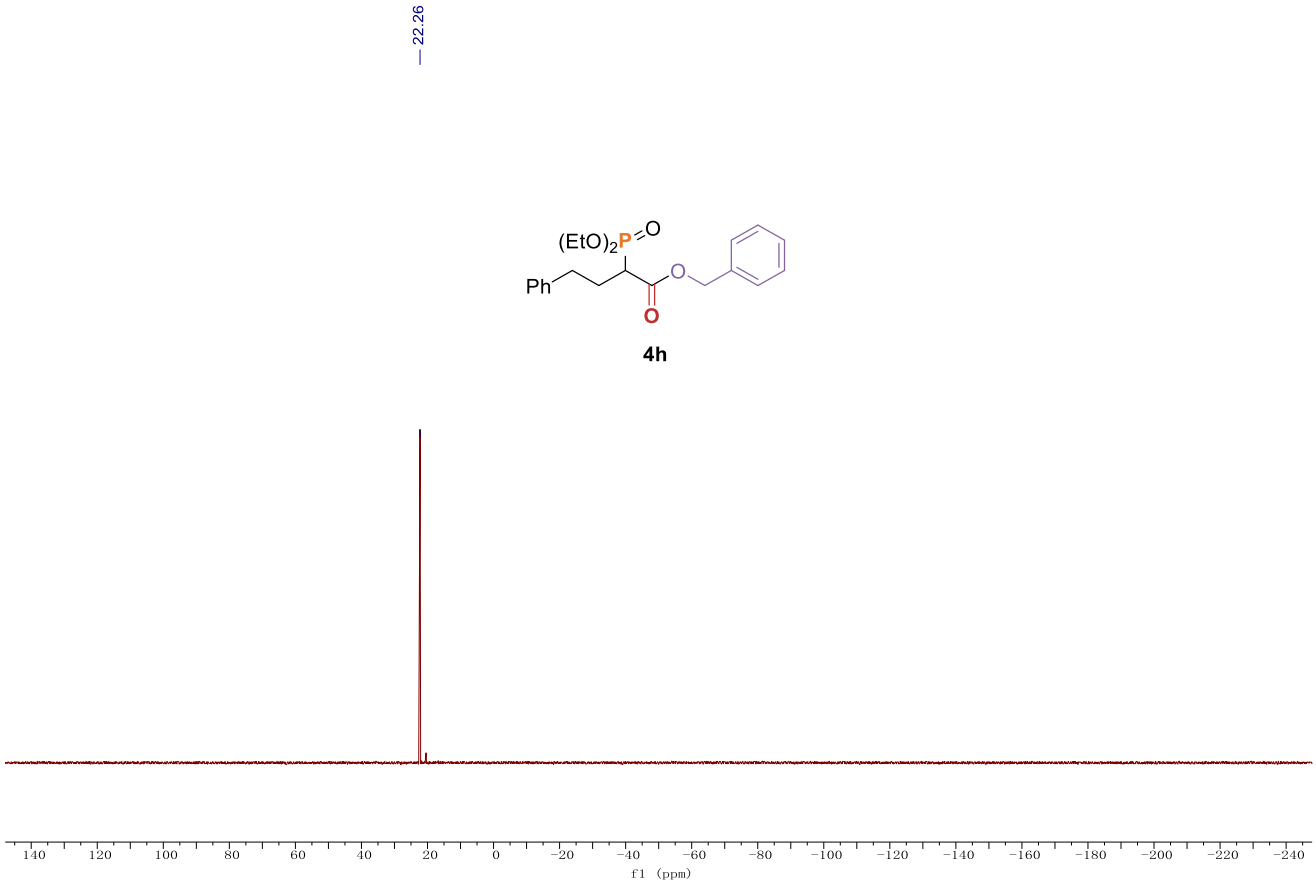


13C NMR CDCl3 100.62MHz

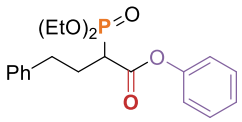
4h



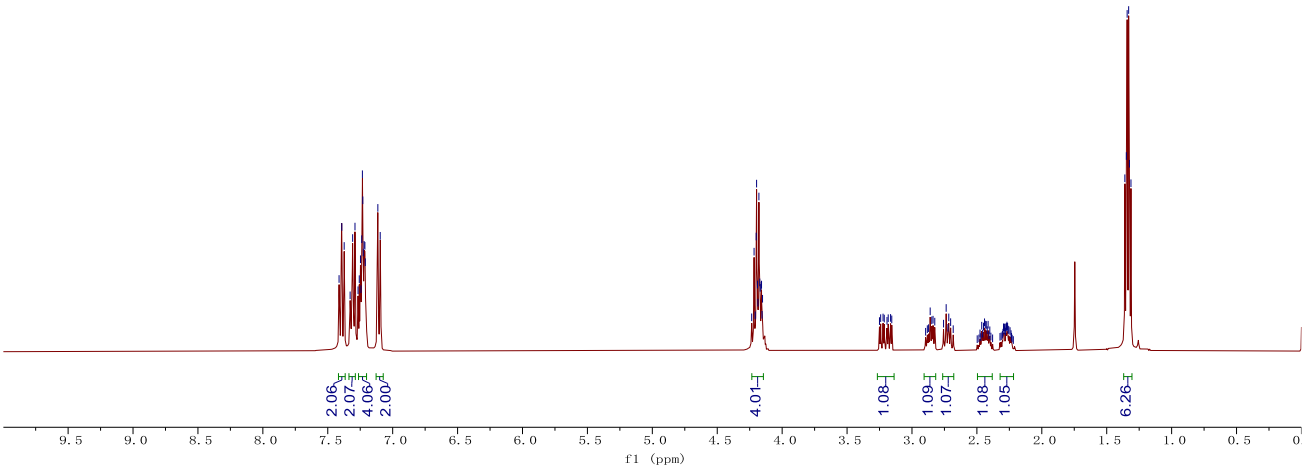
31P NMR CDCl3 161.97MHz



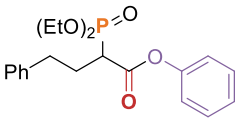
1H NMR CDCl3 400.13MHz



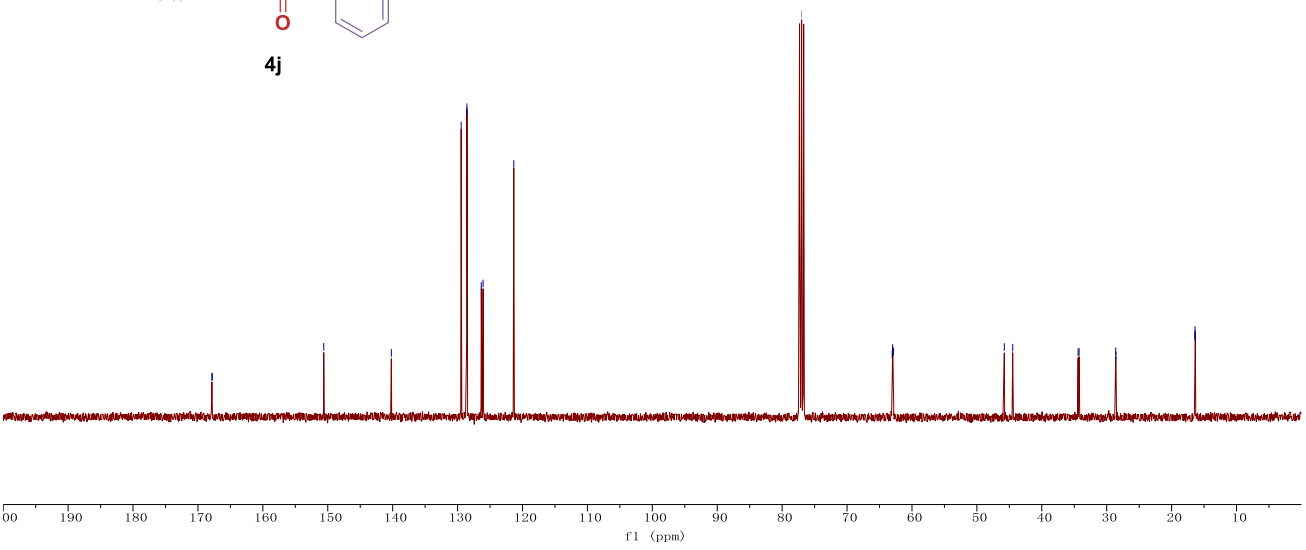
4j



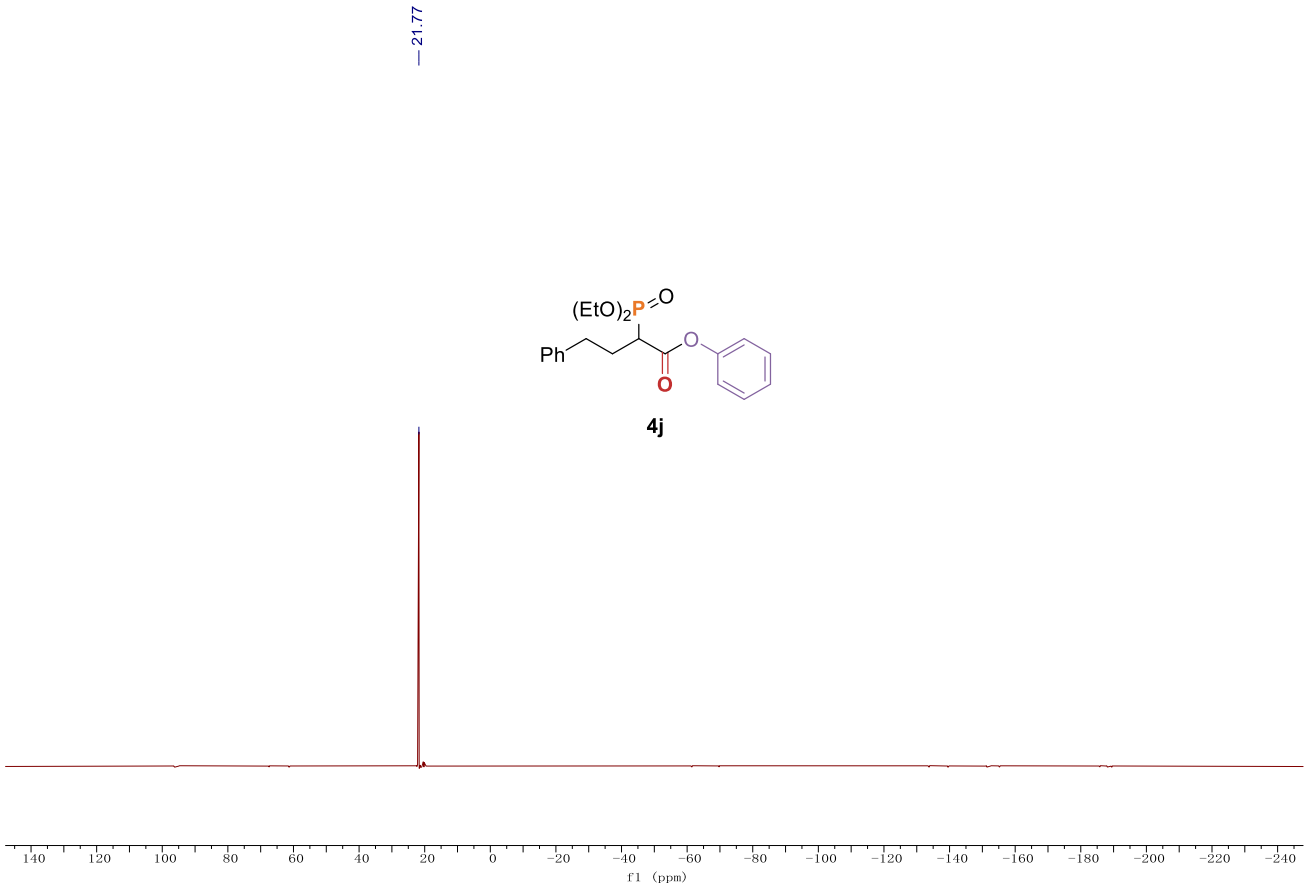
13C NMR CDCl3 100.62MHz



4j

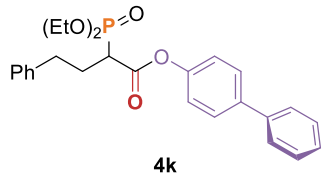


31P NMR CDCl3 161.97MHz

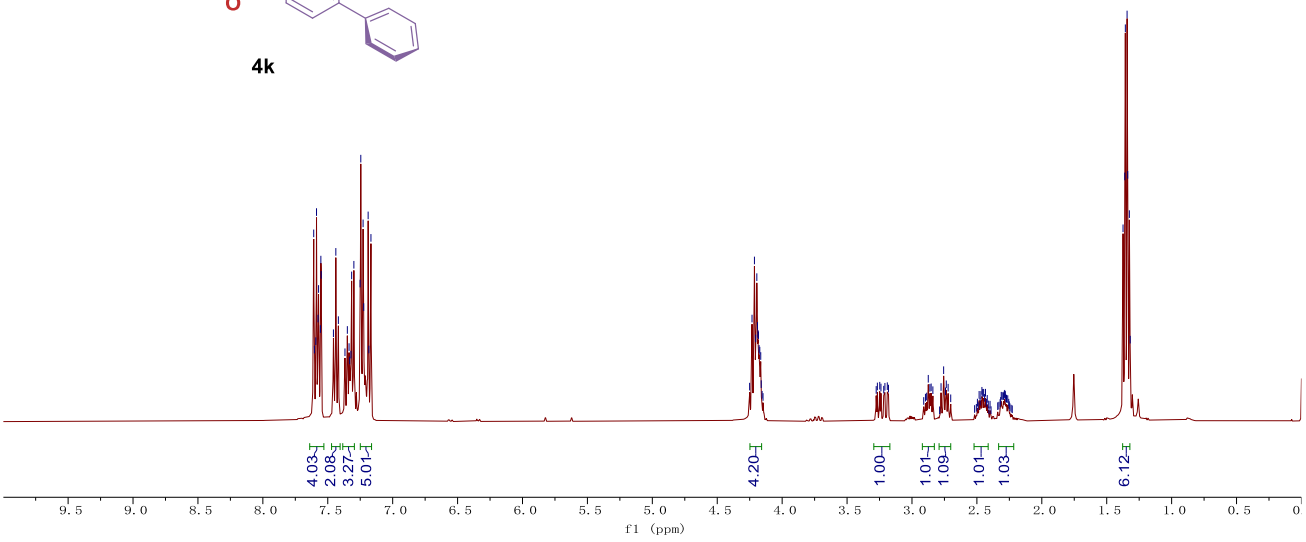


1H NMR CDCl3 400.13MHz

7.61 7.60 7.59 7.59 7.57 7.57 7.56 7.55 7.55 7.46 7.44 7.42 7.37 7.35 7.34 7.33 7.32 7.32 7.30 7.25 7.25 7.23 7.22 7.19 7.18 7.17 4.25 4.23 4.21 4.20 4.20 4.19 4.19 4.18 4.18 4.17 4.16 4.16 4.15 3.28 3.27 3.25 3.24 3.22 3.21 3.19 3.18 2.87 2.86 2.85 2.84 2.78 2.76 2.74 2.74 2.72 2.48 2.47 2.46 2.46 2.45 2.43 2.29 2.29 2.28 1.37 1.36 1.36 1.34 1.34 1.33 1.32

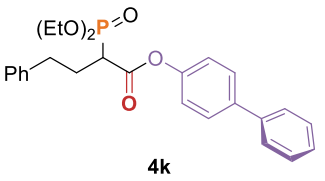


4k

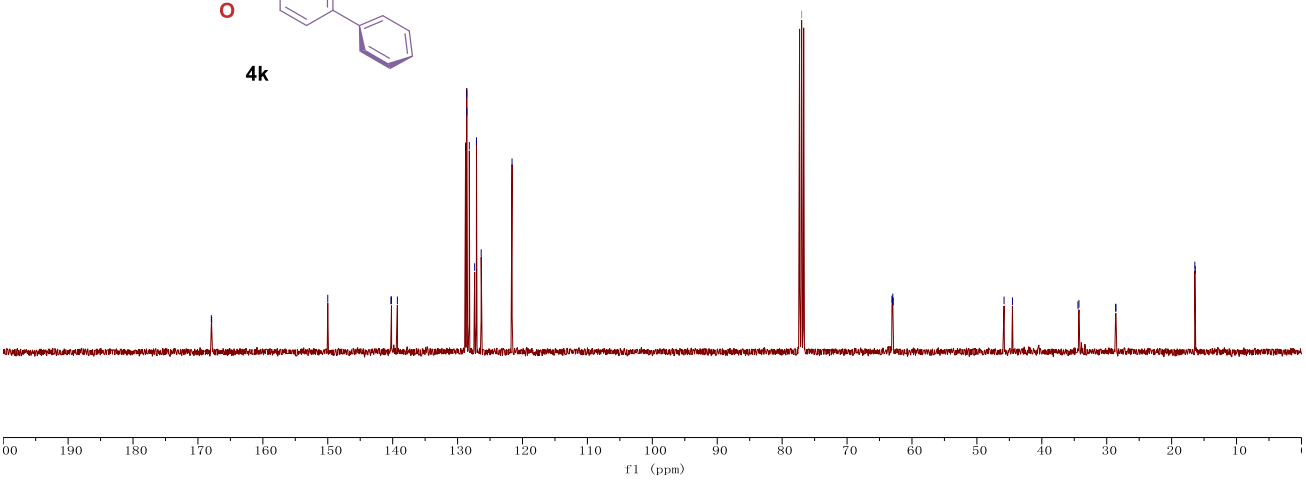


13C NMR CDCl3 100.62MHz

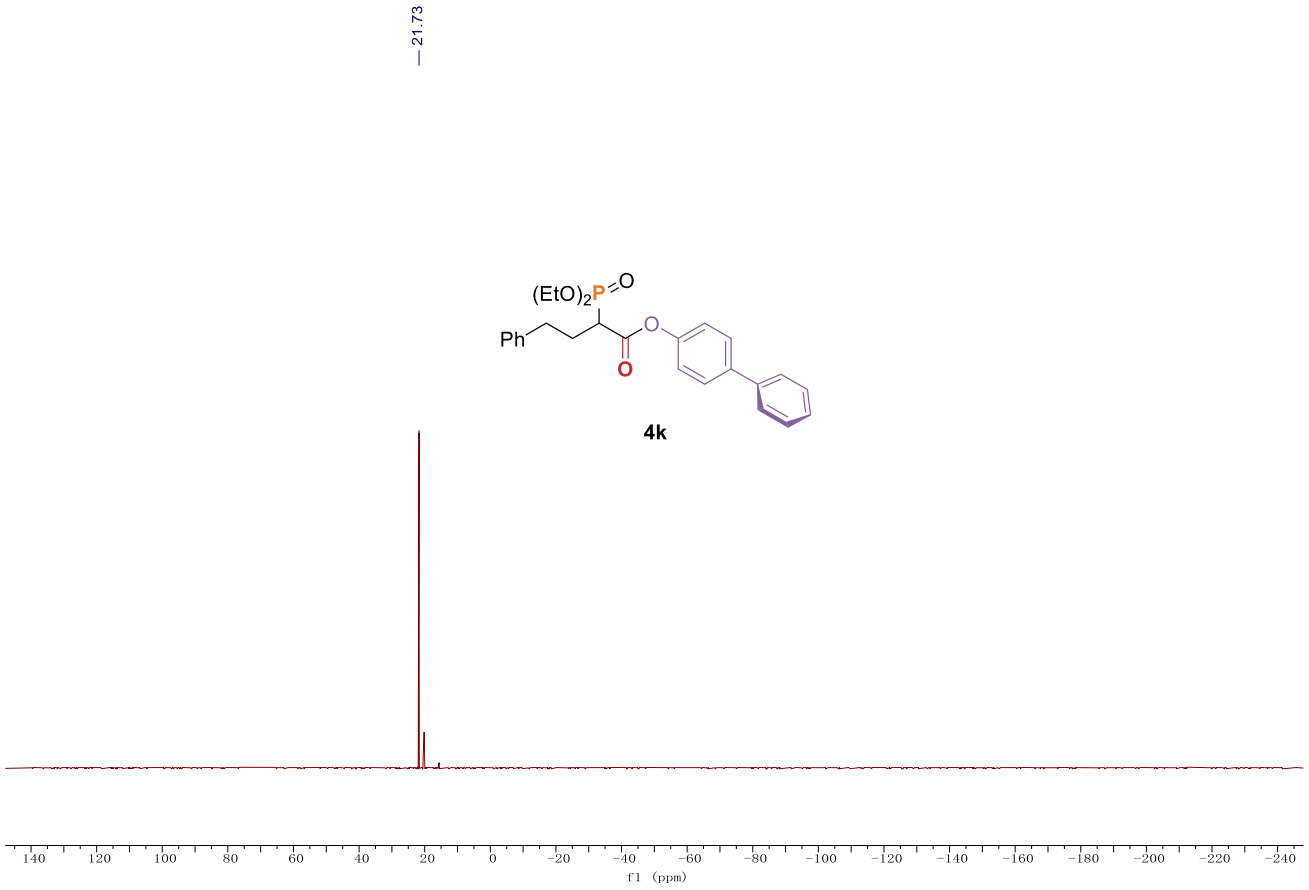
167.9 167.9 150.0 140.3 140.2 139.3 128.8 128.6 128.6 128.2 127.4 127.1 126.4 121.6 77.0 CDCl3 63.1 63.0 63.0 62.9 45.8 44.5 34.4 34.3 28.6 28.6 16.4 16.4



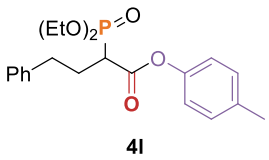
4k



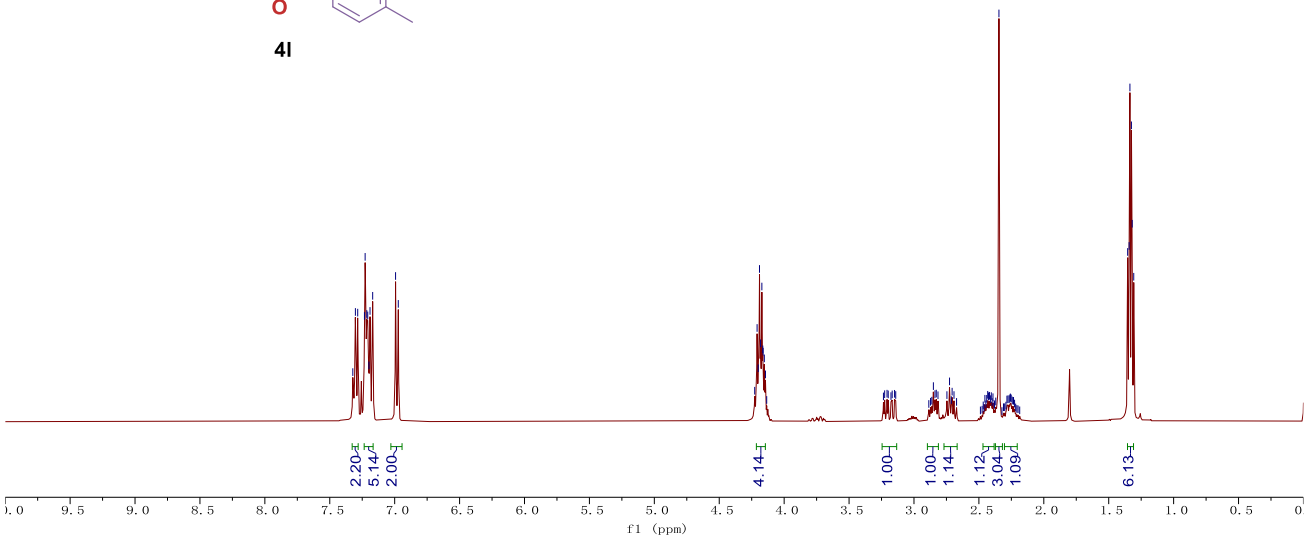
31P NMR CDCl3 161.97MHz



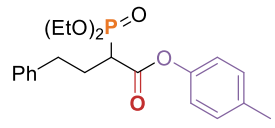
1H NMR CDCl3 400.13MHz



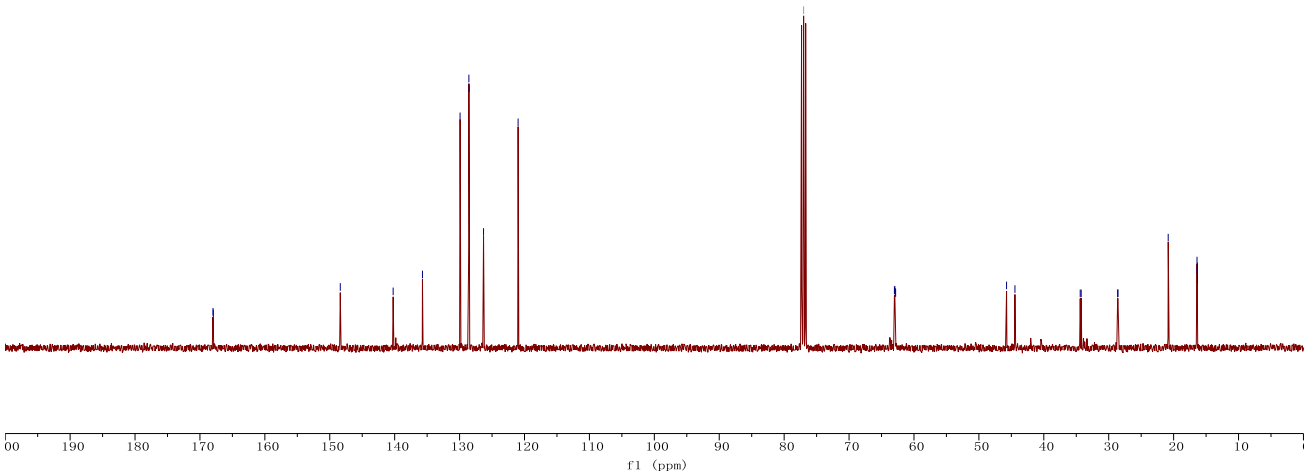
4l



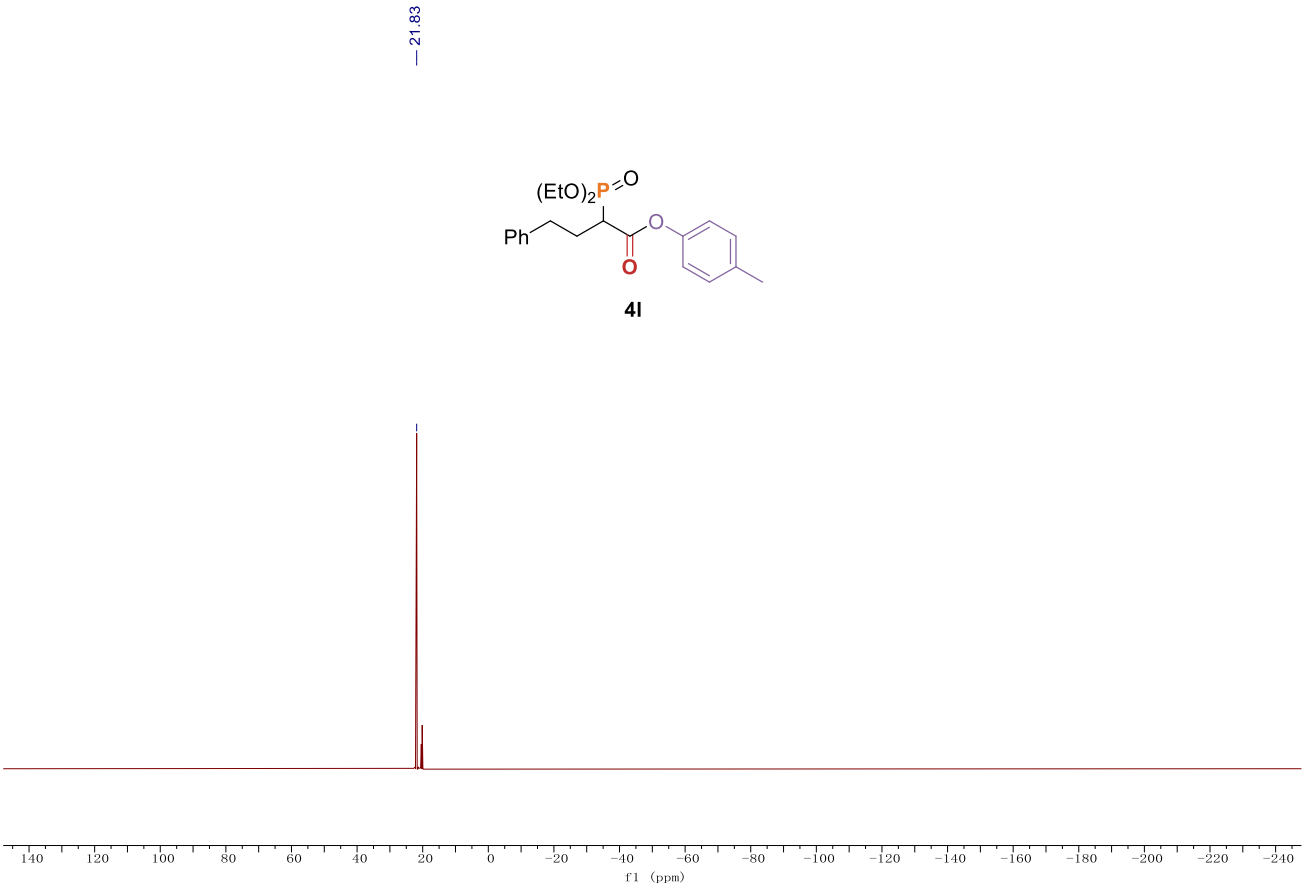
13C NMR CDCl3 100.62MHz



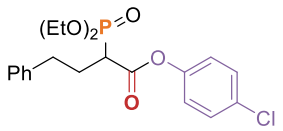
4l



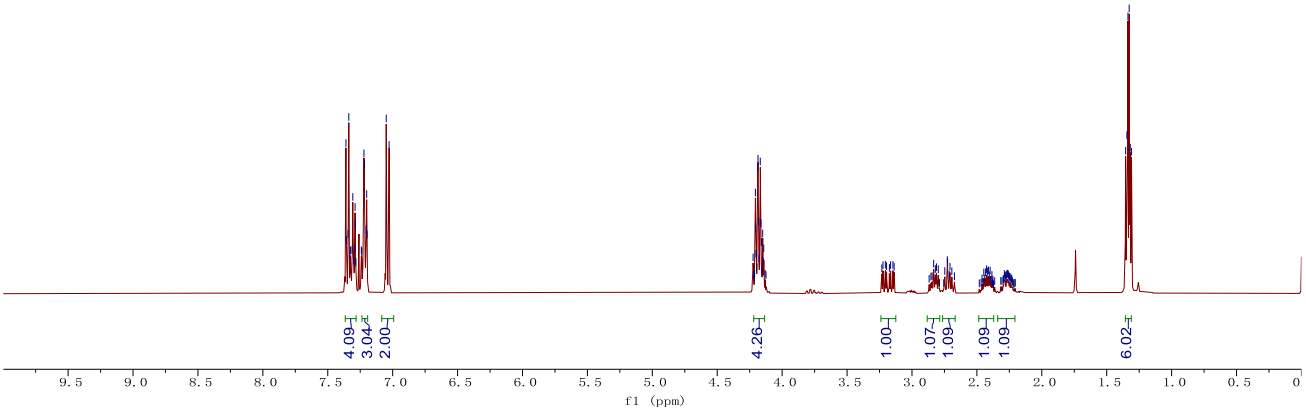
31P NMR CDCl3 161.97MHz



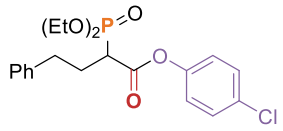
1H NMR CDCl3 400.13MHz



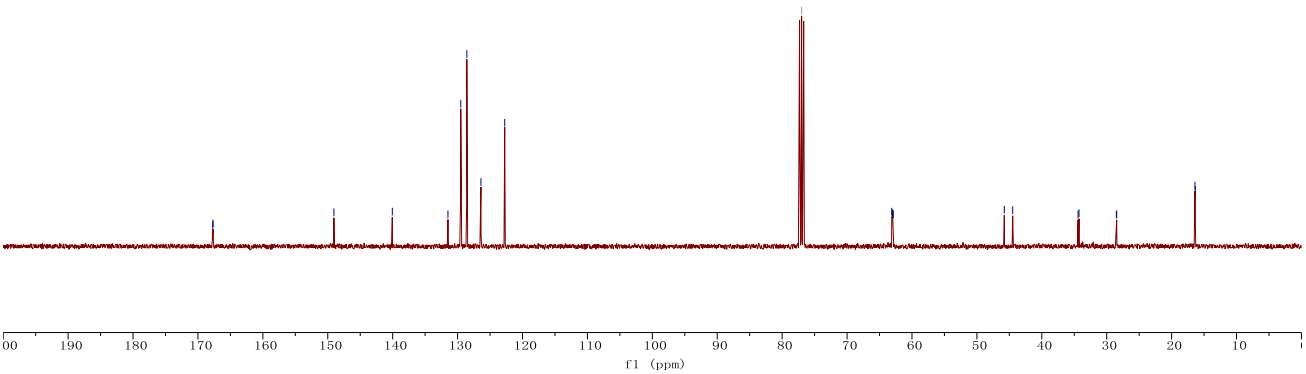
4m



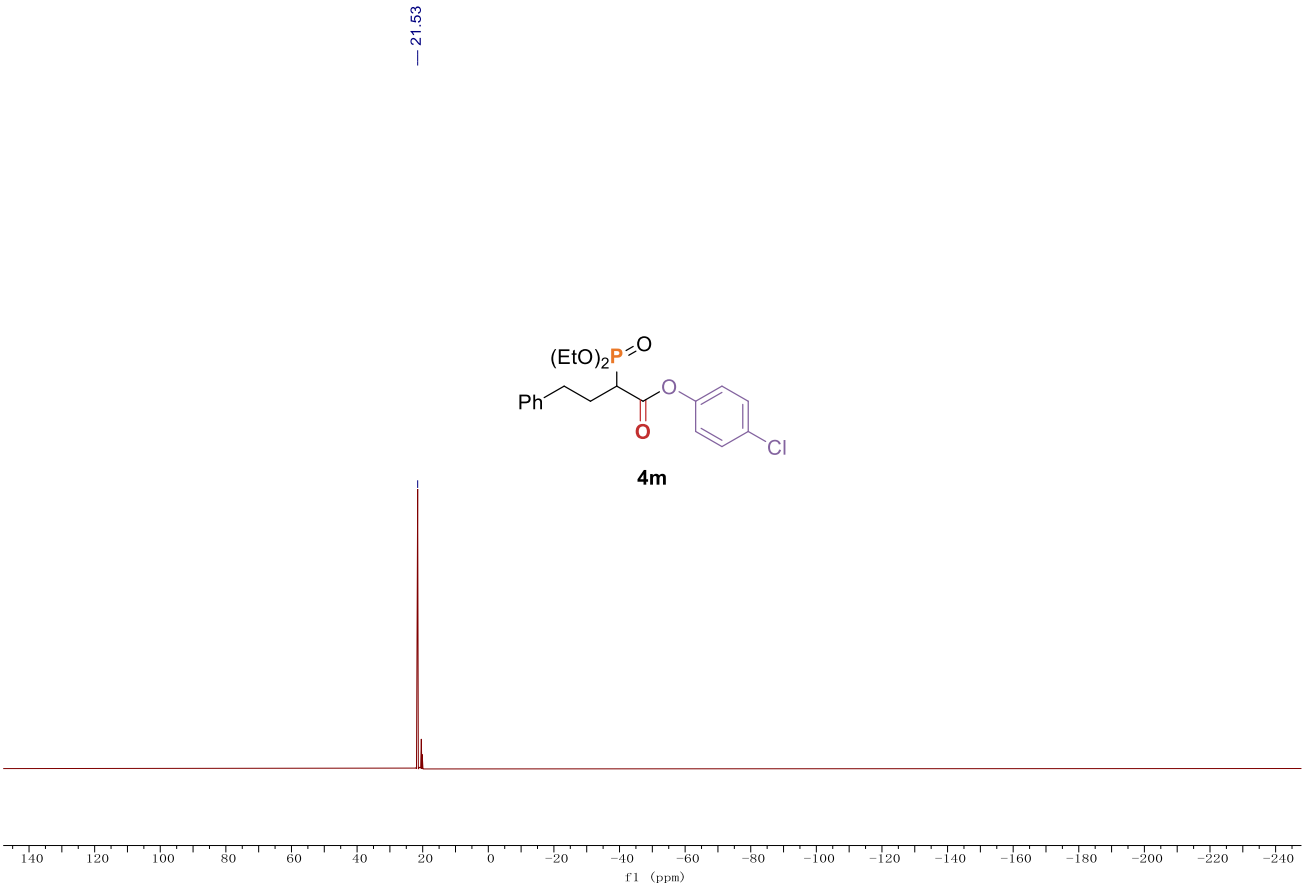
13C NMR CDCl3 100.62MHz



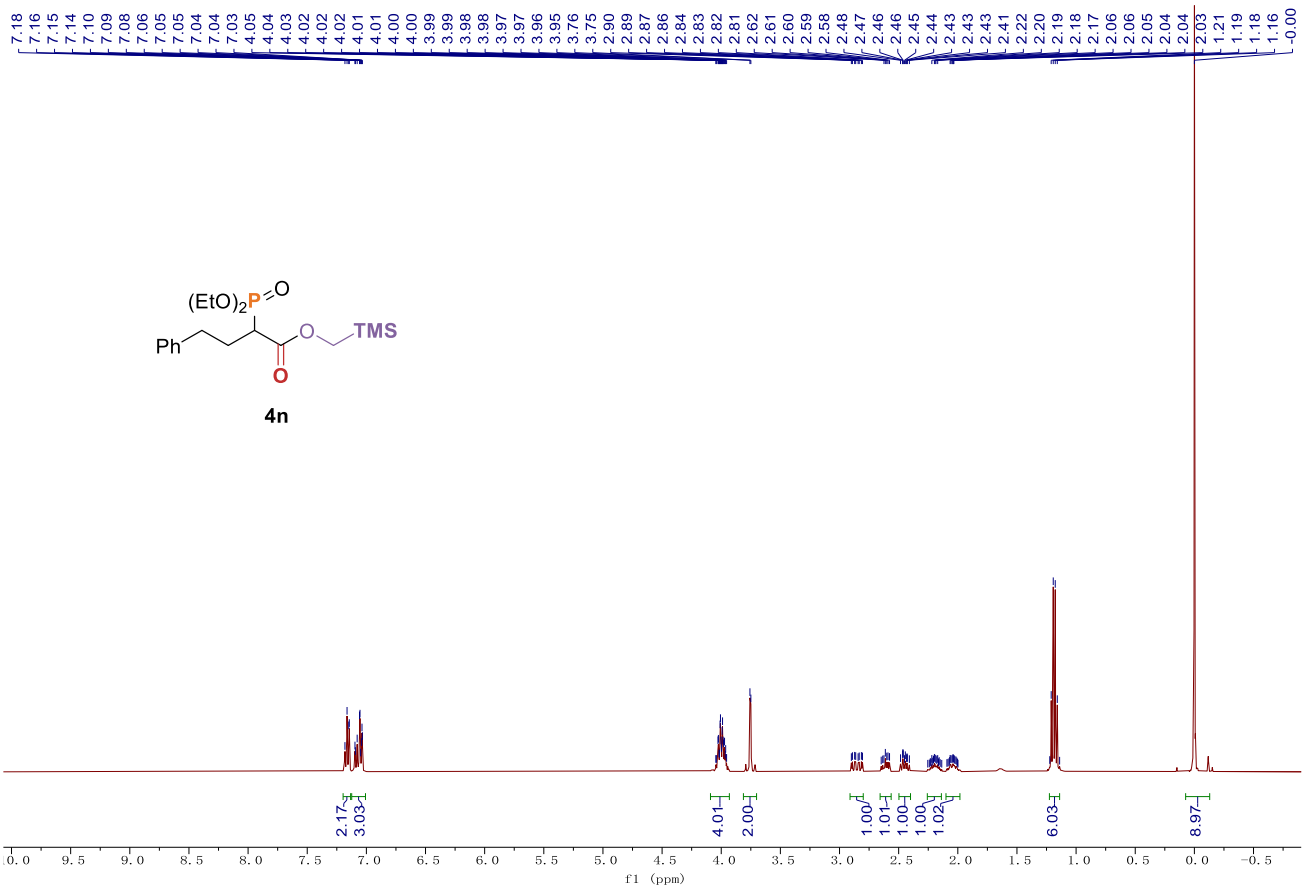
4m



31P NMR CDCl3 161.97MHz

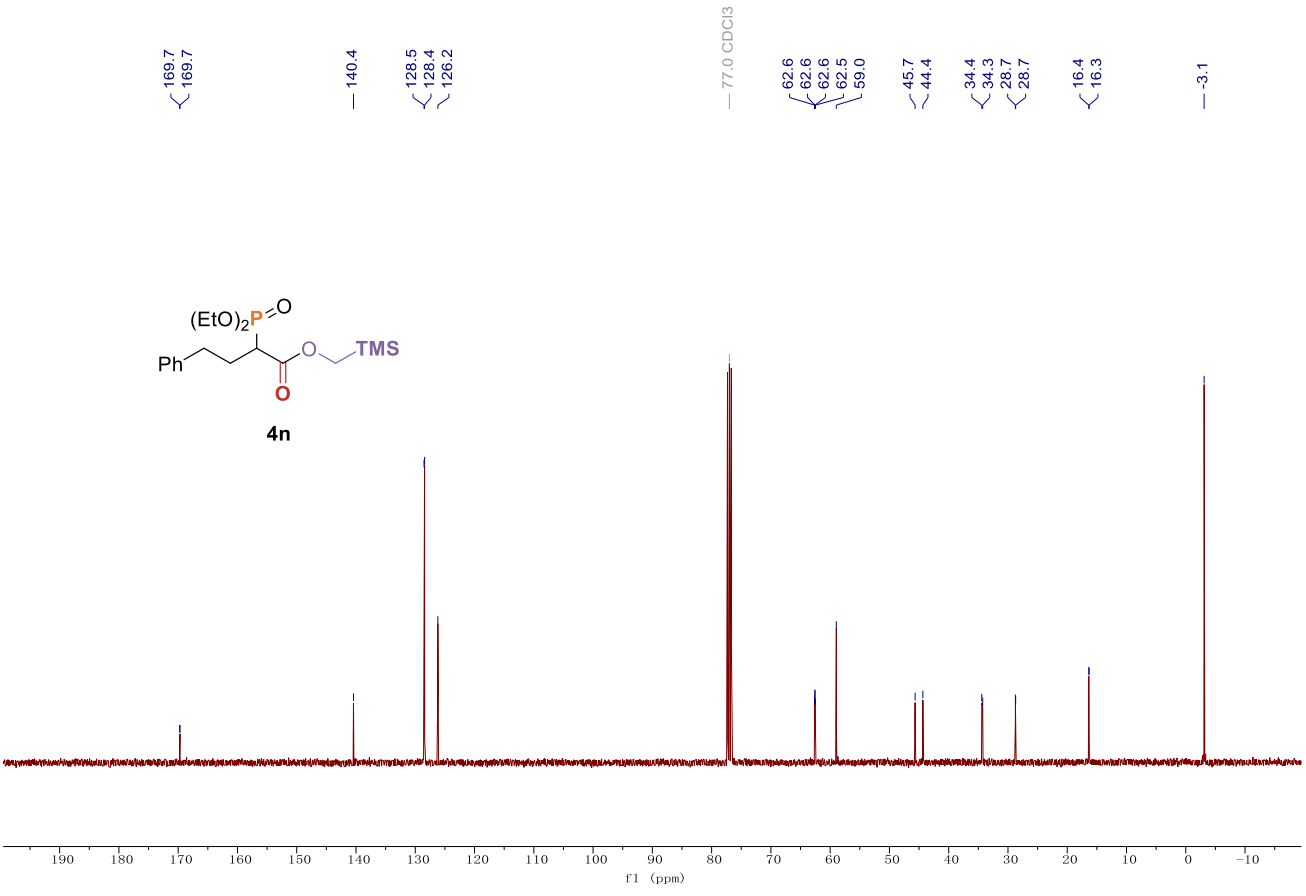


1H NMR CDCl3 400.13MHz



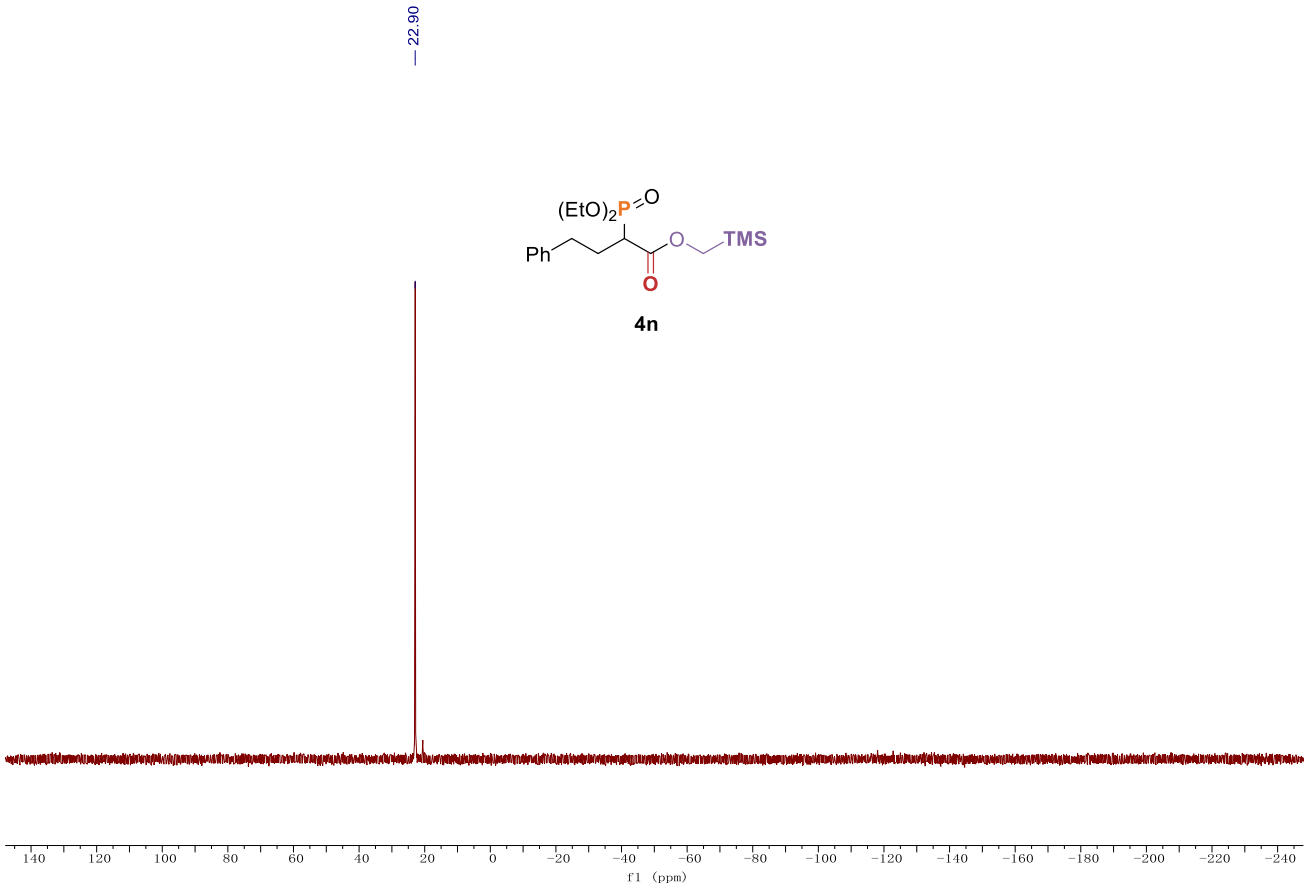
4n

13C NMR CDCl3 100.62MHz

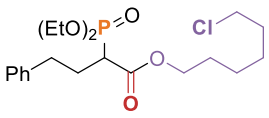


4n

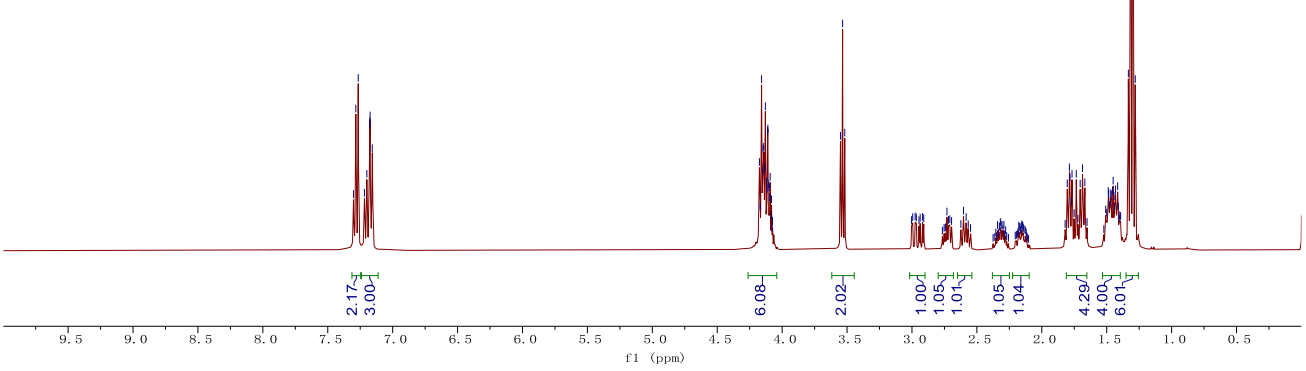
31P NMR CDCl3 161.97MHz



1H NMR CDCl3 400.13MHz

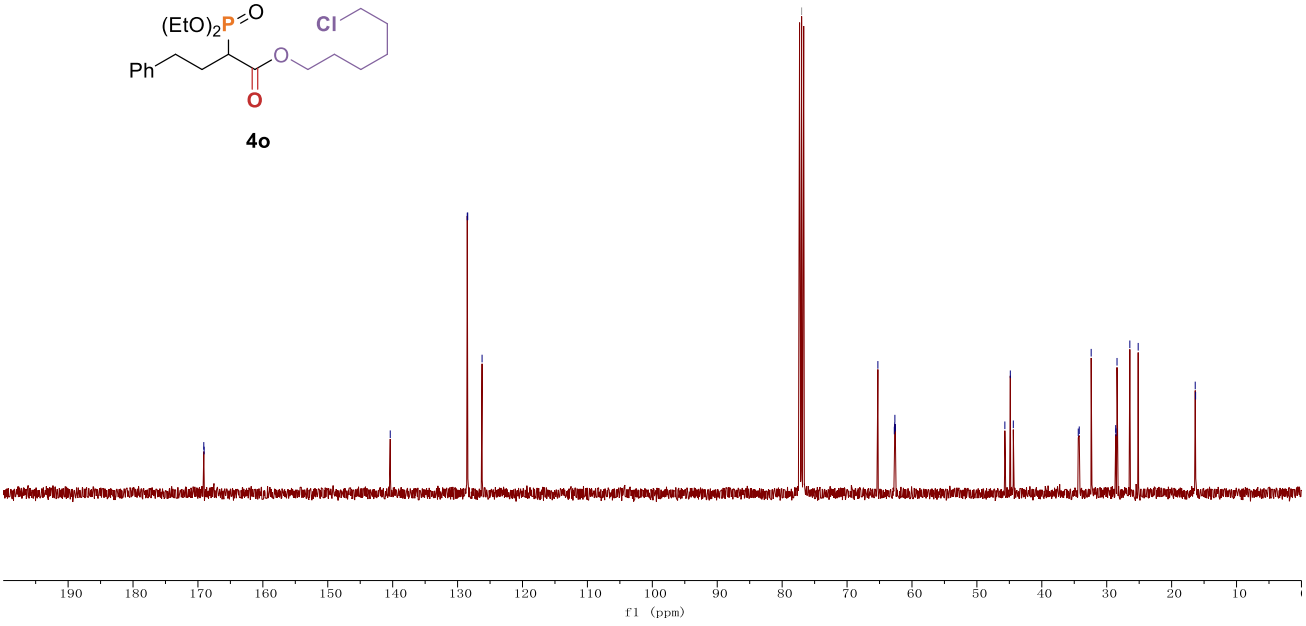


4o

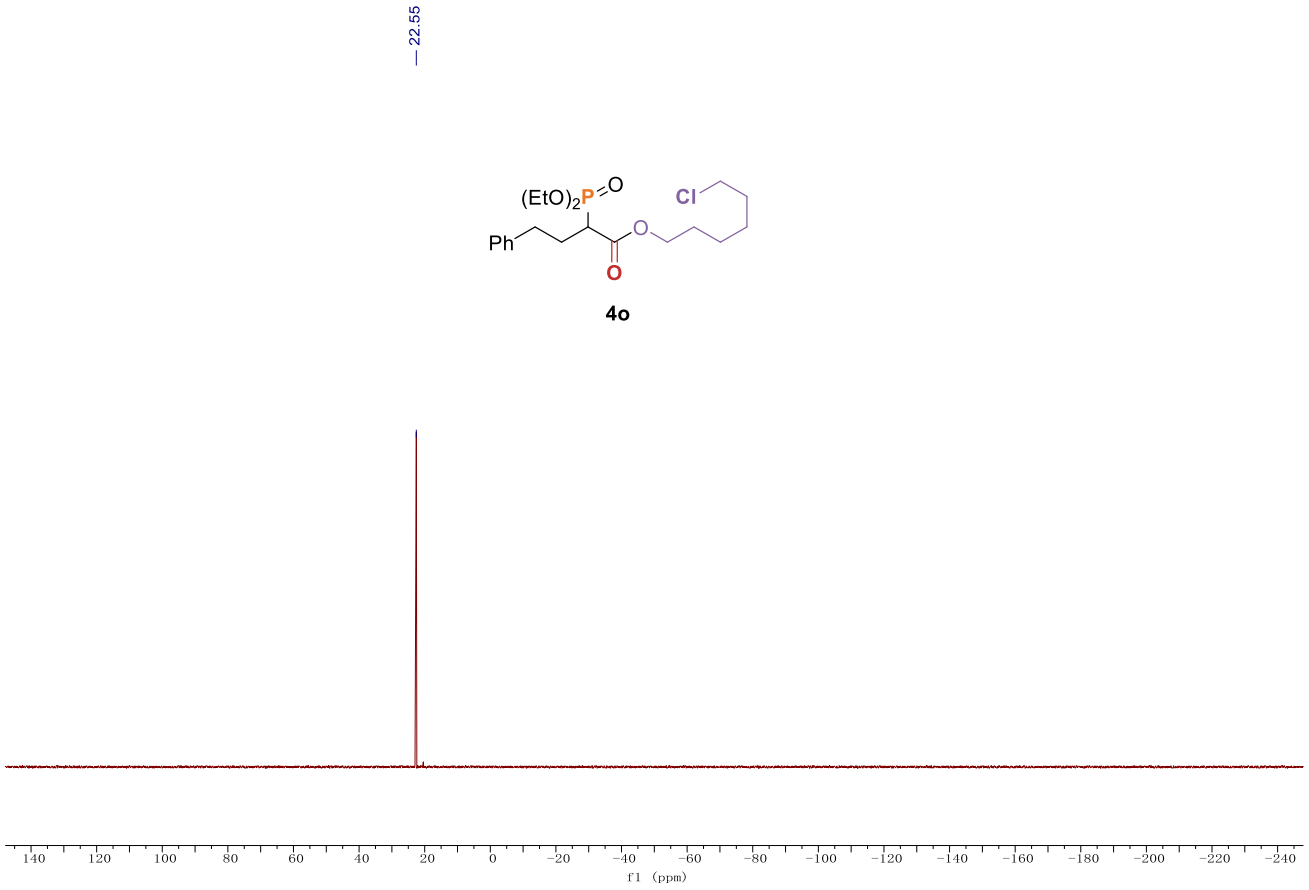


13C NMR CDCl3 100.62MHz

4o

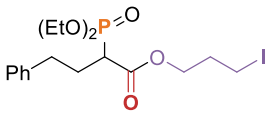


1H NMR CDCl3 161.97MHz

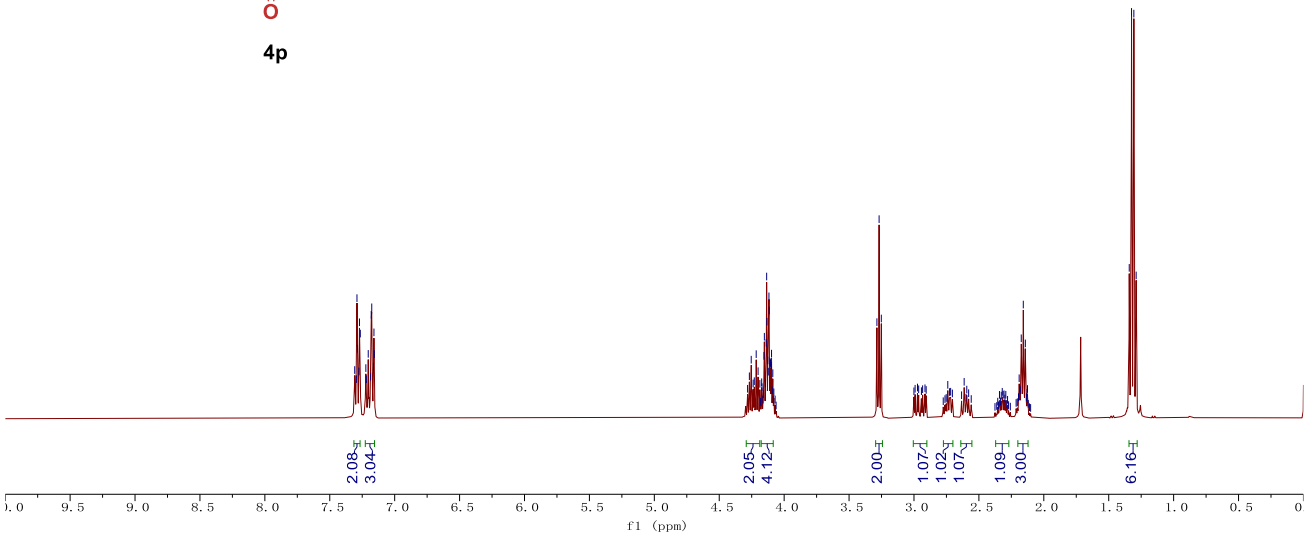


4o

1H NMR CDCl3 400.13MHz

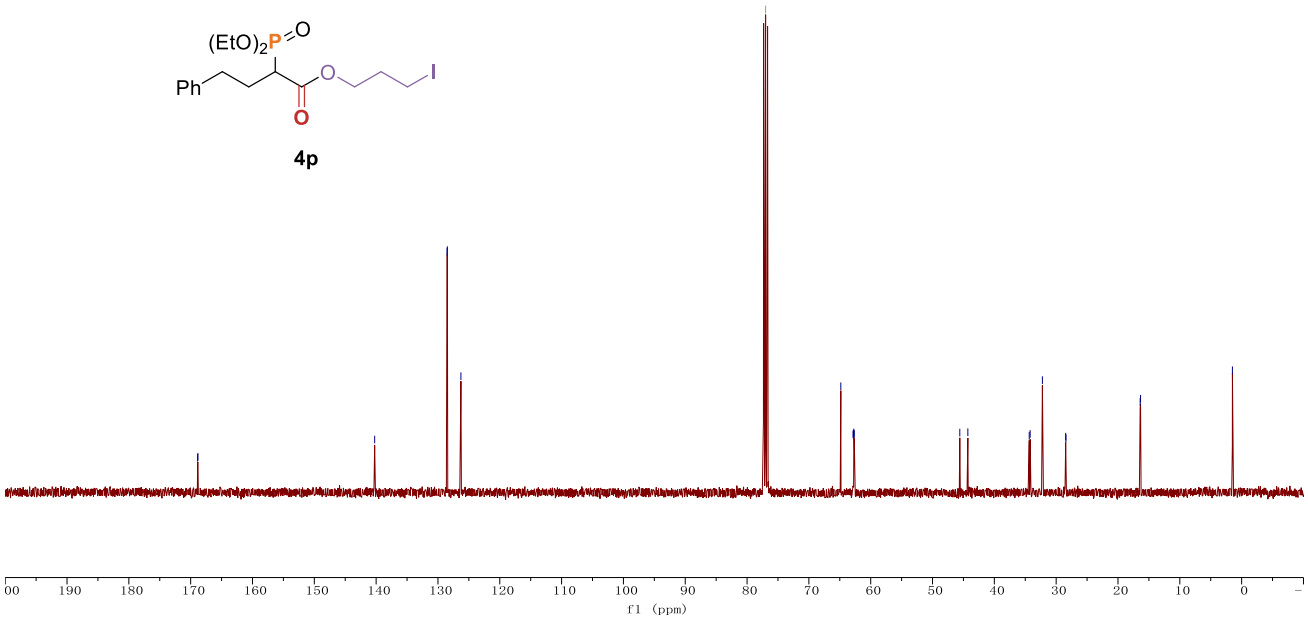


4p

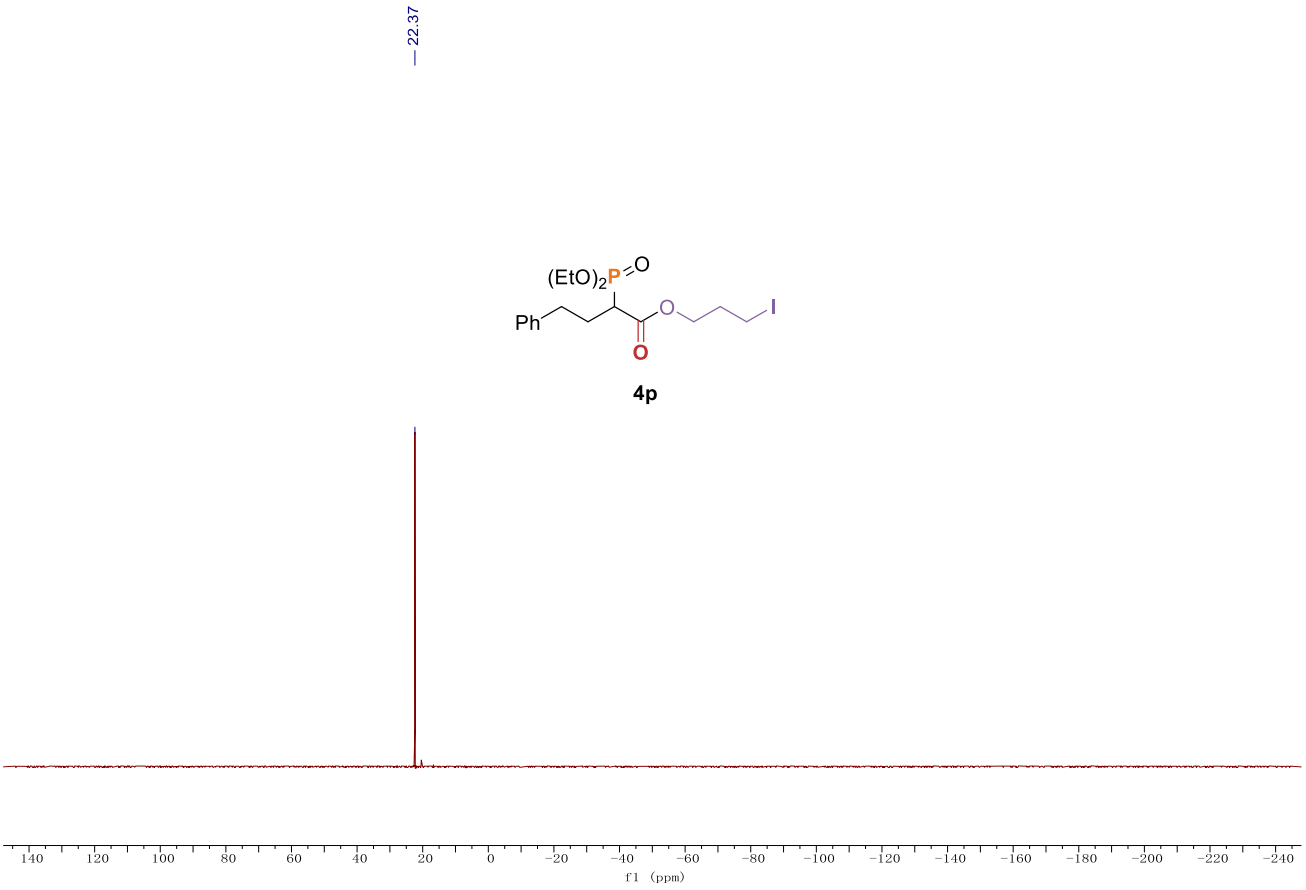


13C NMR CDCl3 100.62MHz

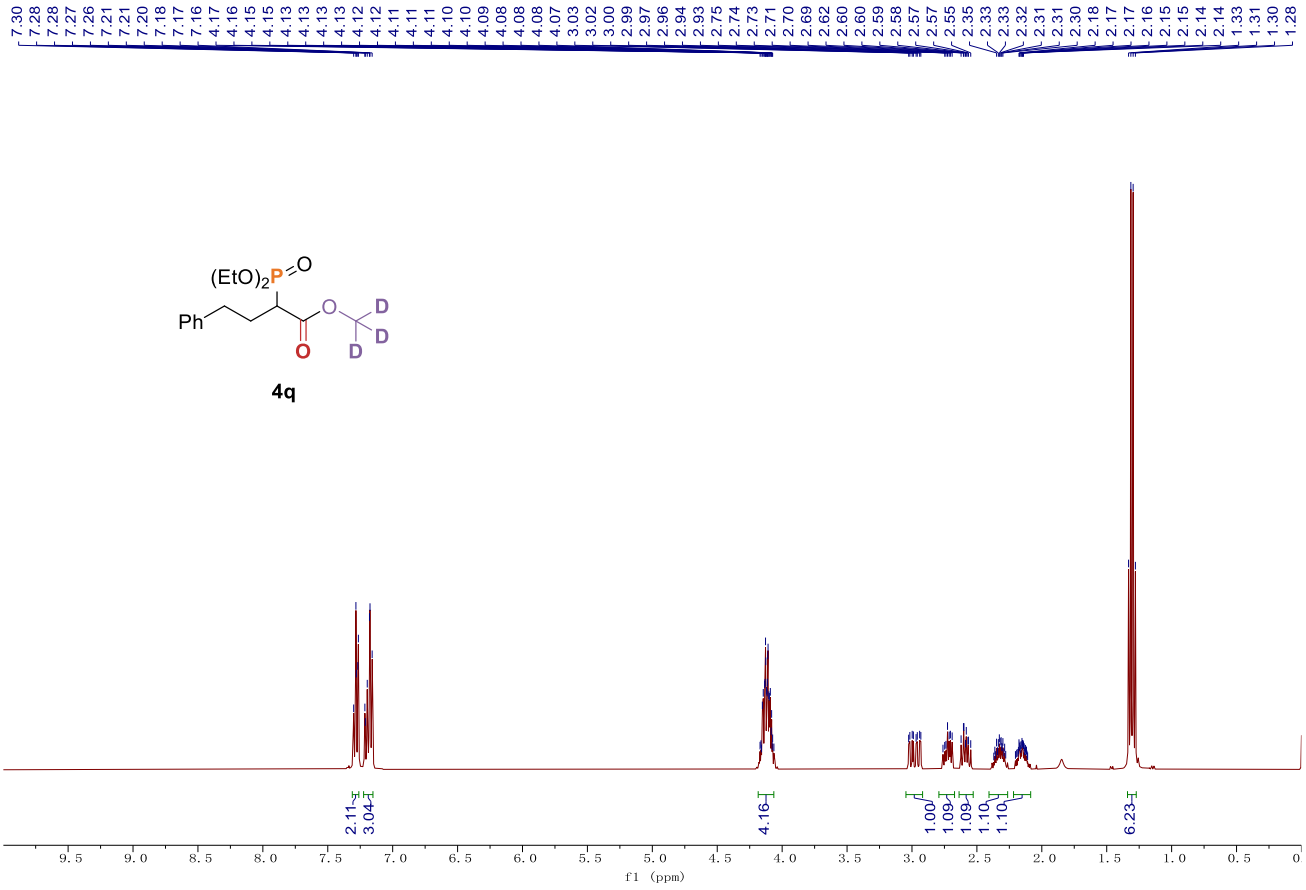
4p



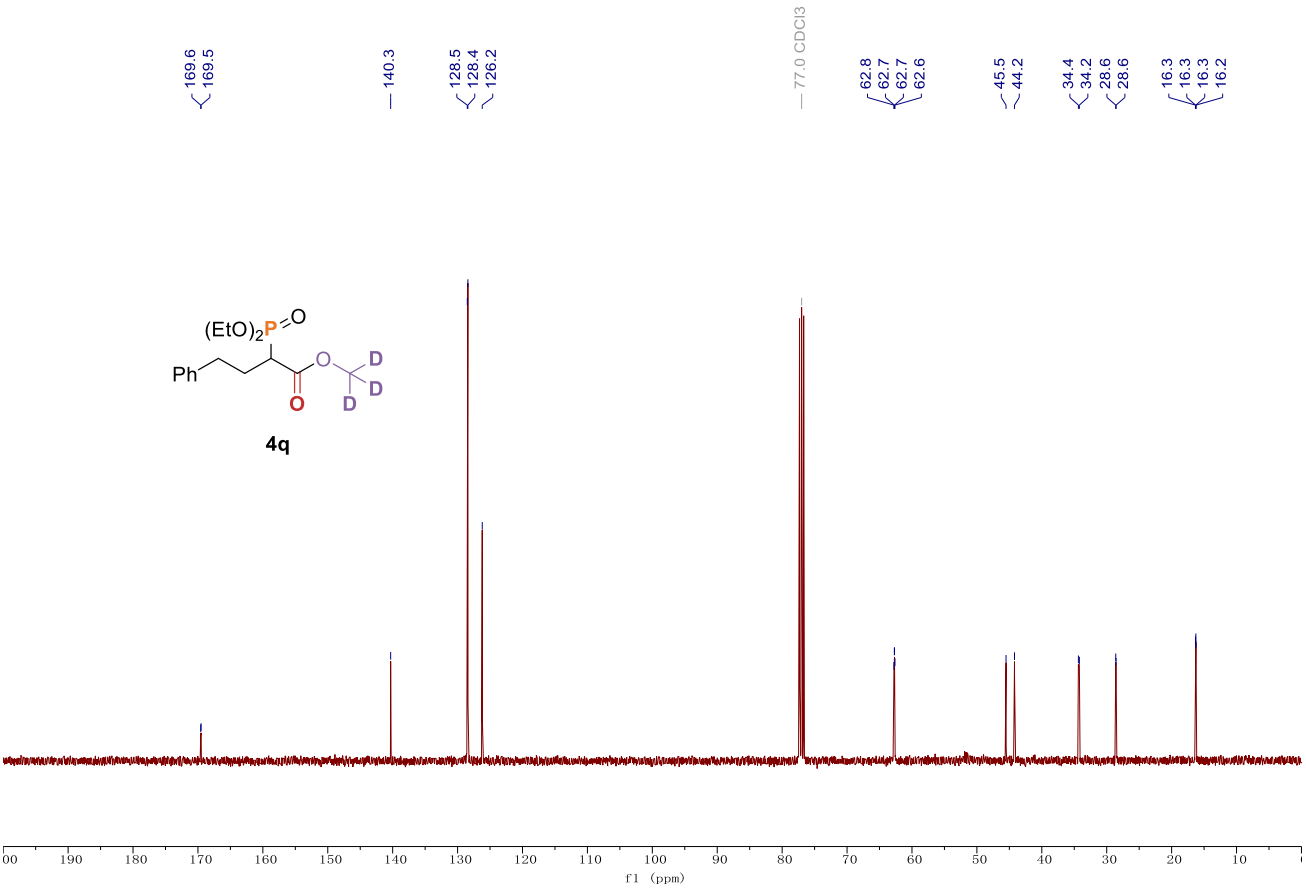
31P NMR CDCl3 161.97MHz



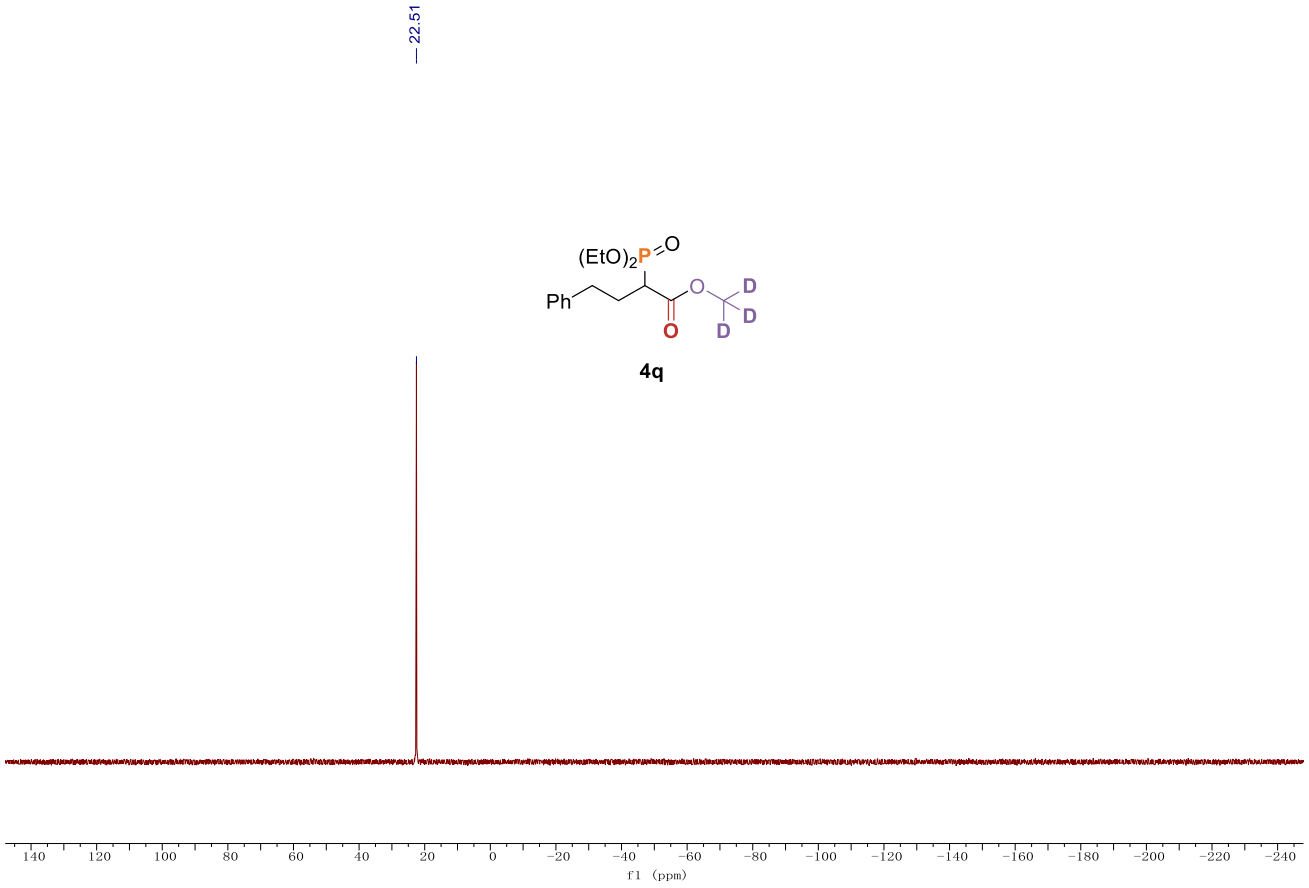
1H NMR CDCl3 400.13MHz



13C NMR CDCl3 100.62MHz

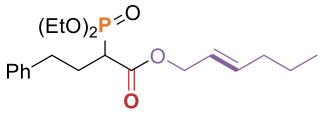


31P NMR CDCl3 161.97MHz

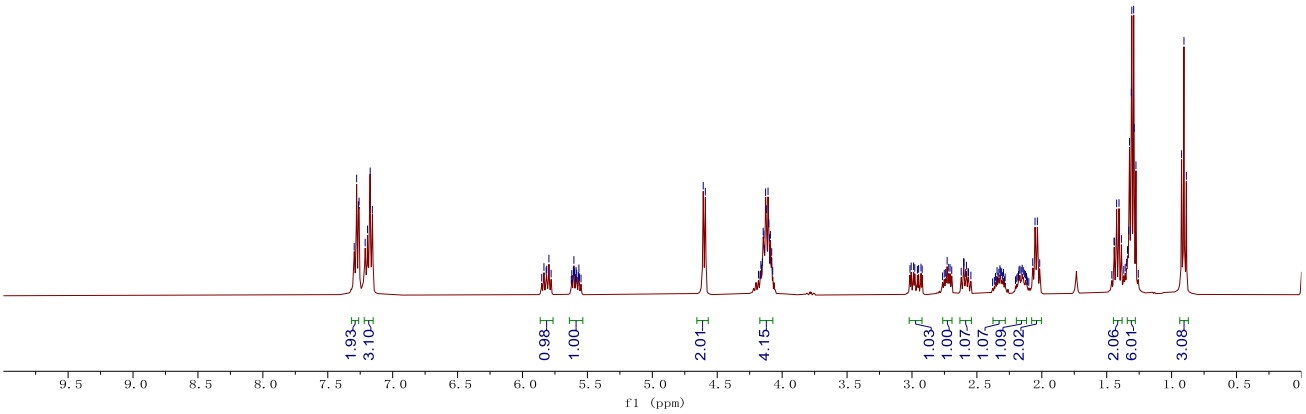


4q

1H NMR CDCl3 400.13MHz

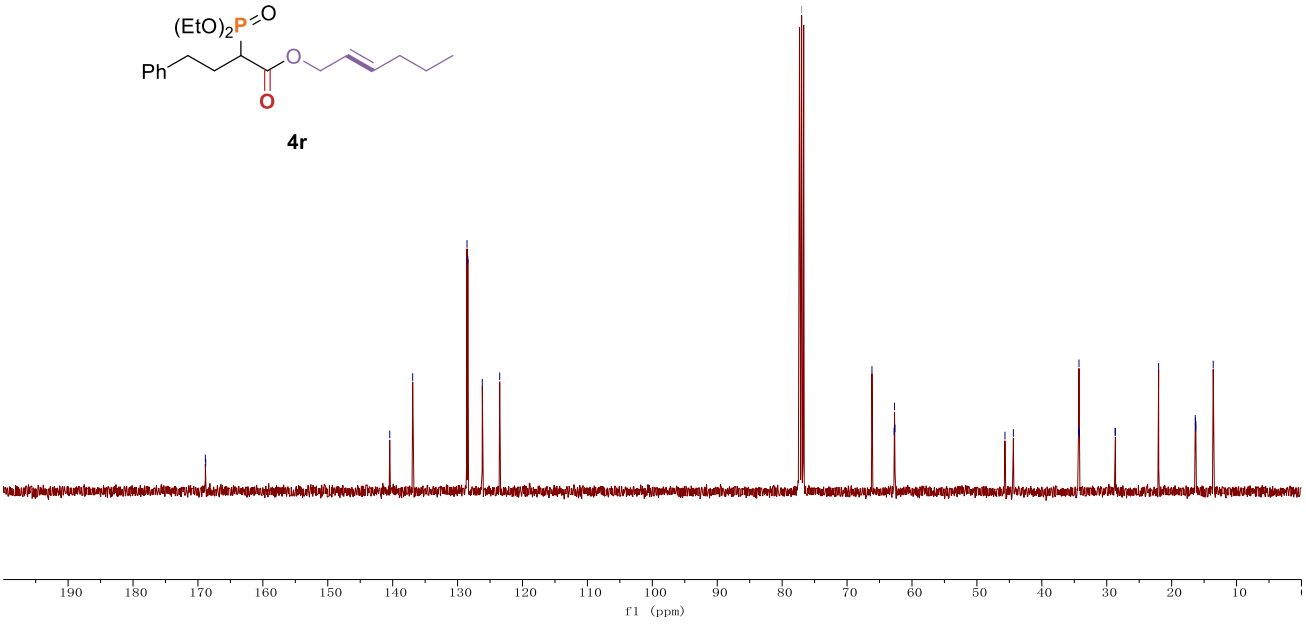


4r

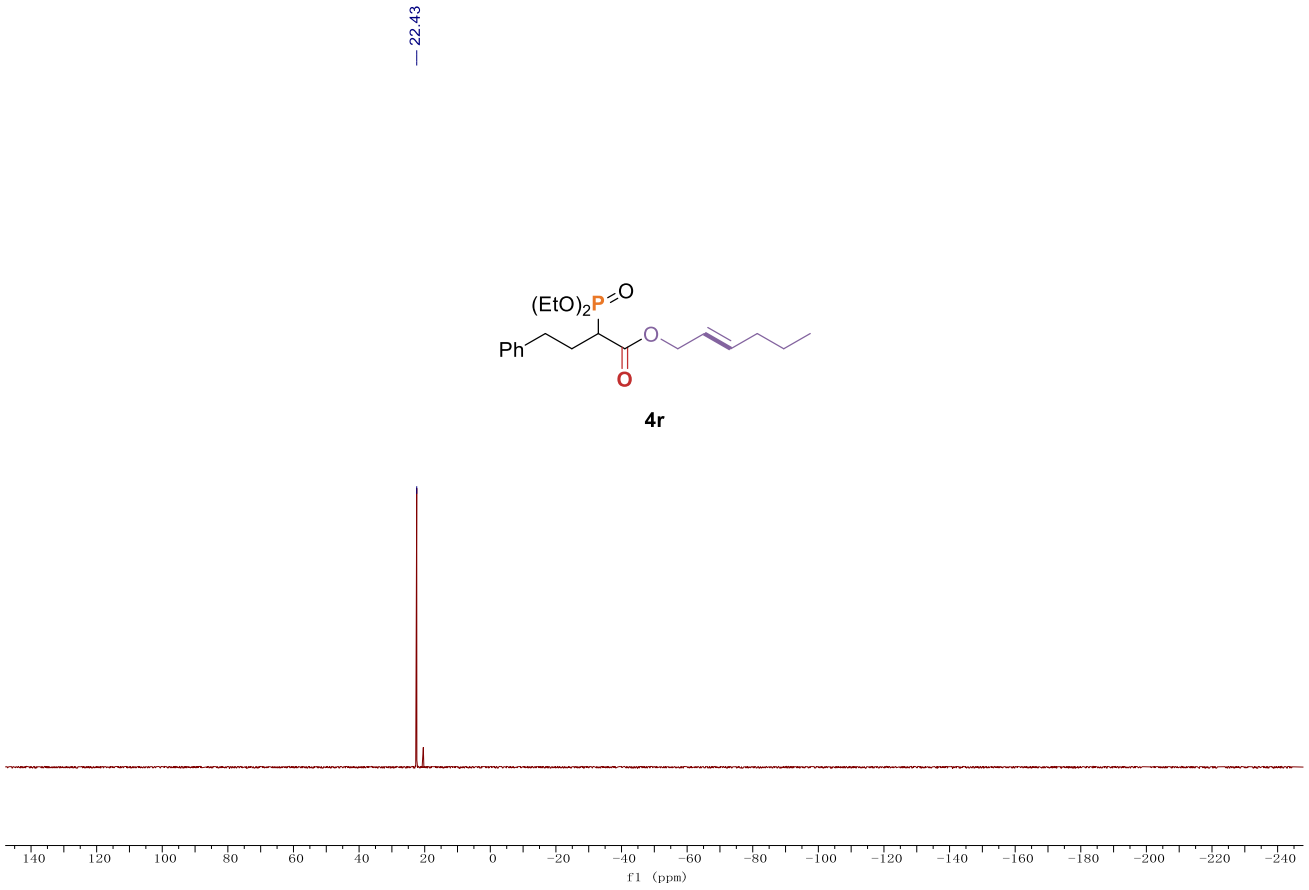


13C NMR CDCl3 100.62MHz

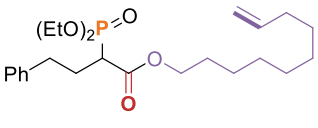
4r



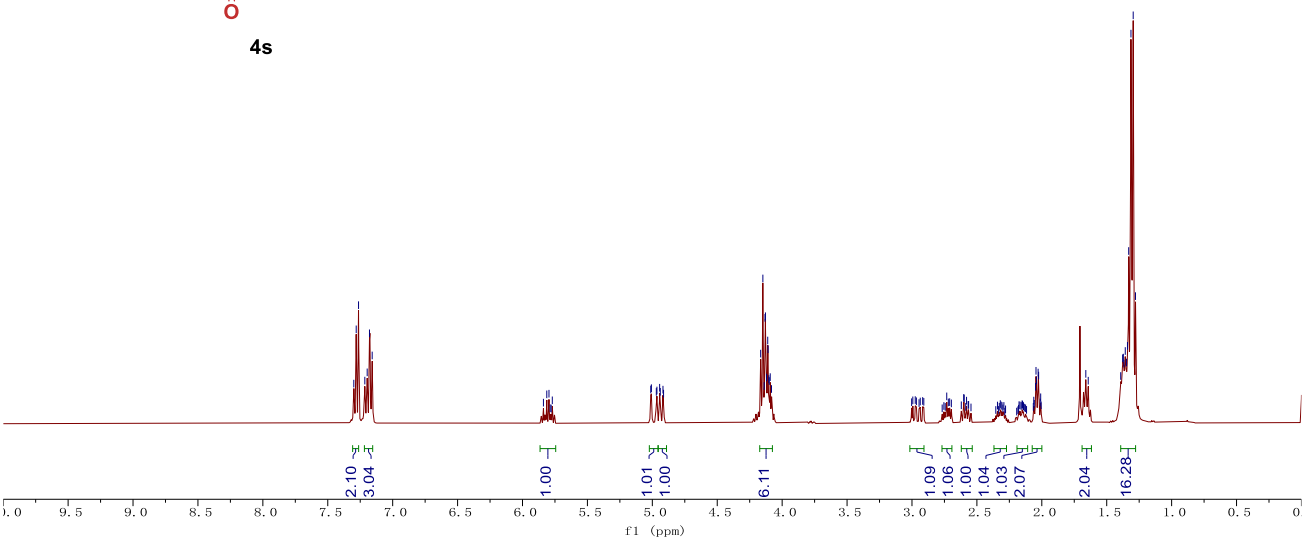
31P NMR CDCl3 161.97MHz



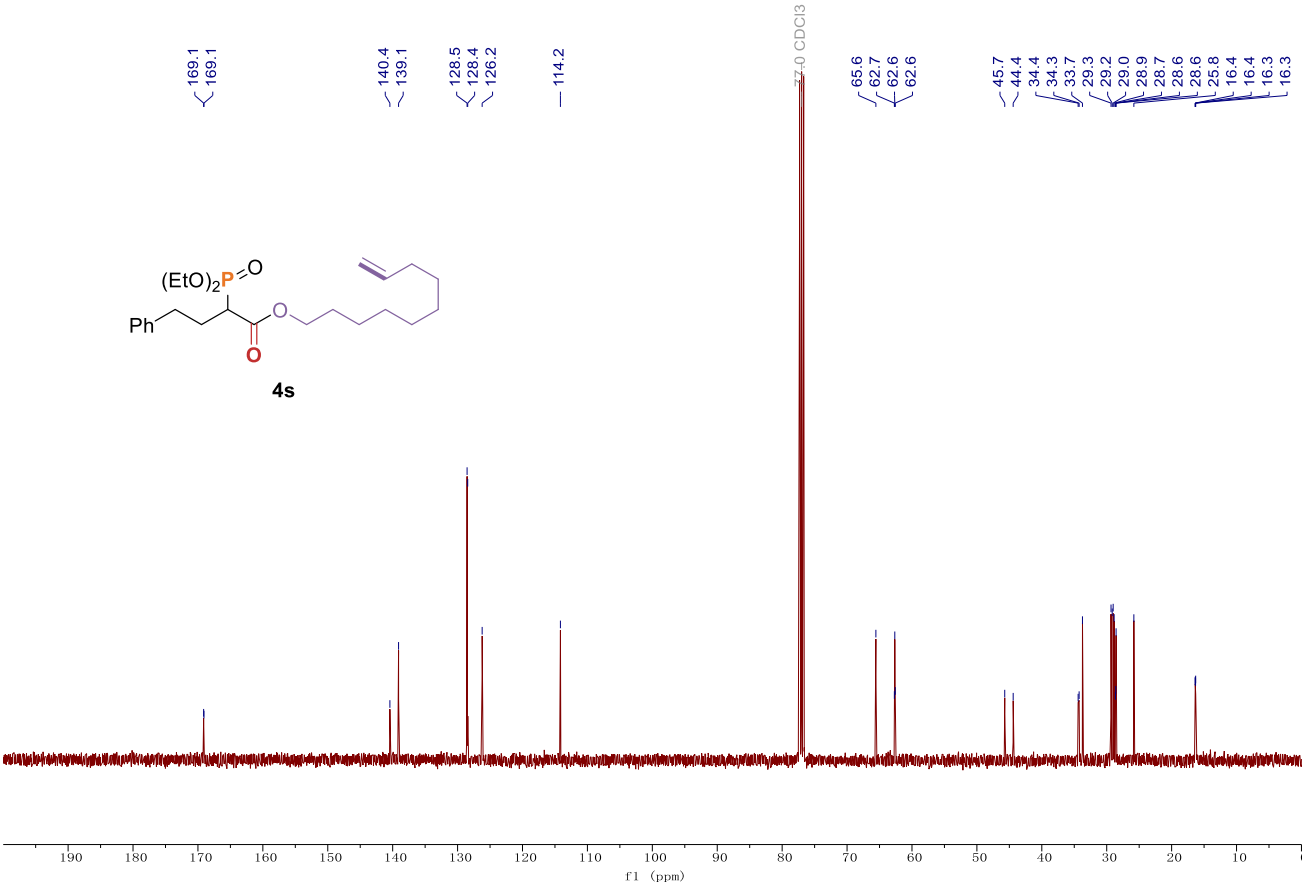
1H NMR CDCl3 400.13MHz



4s

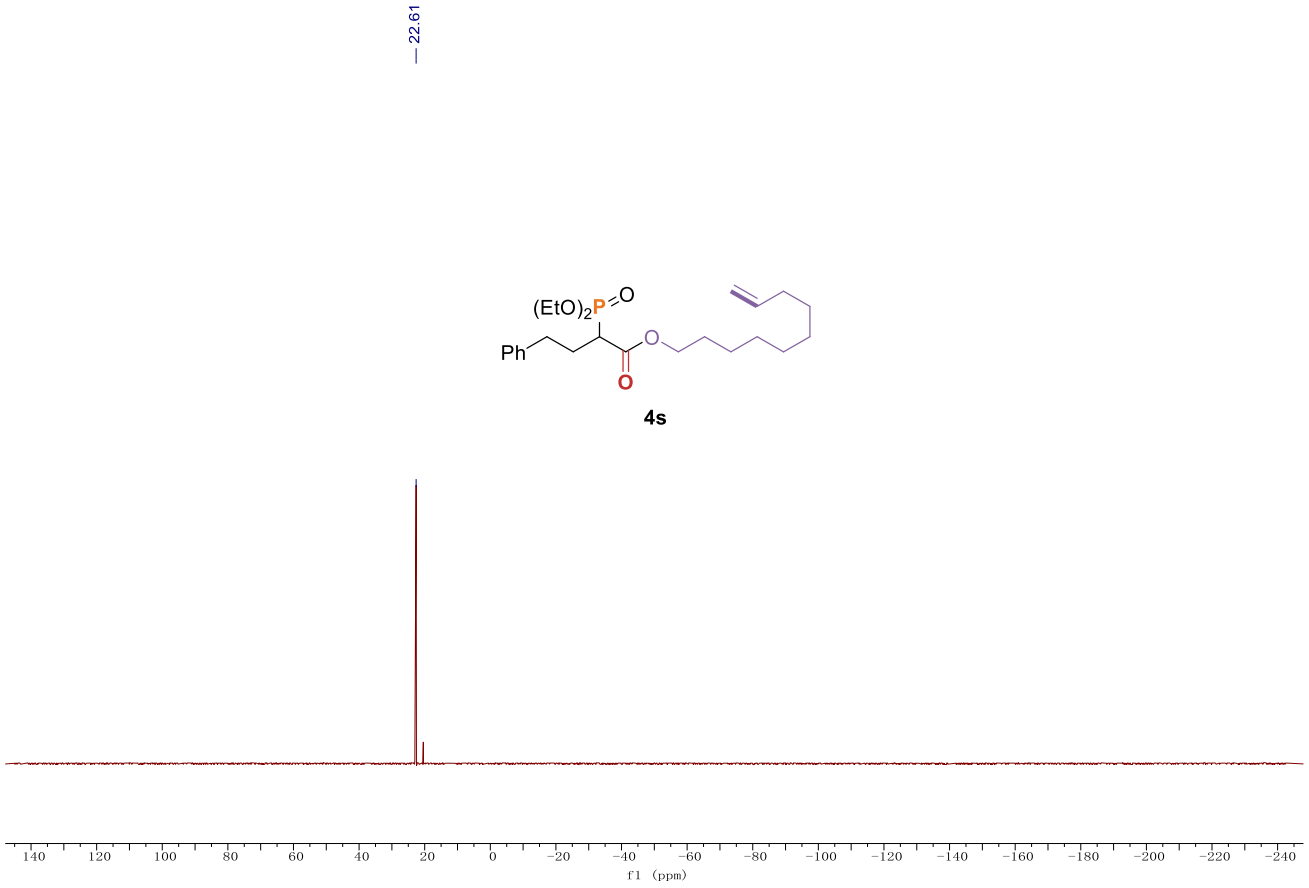


13C NMR CDCl3 100.62MHz

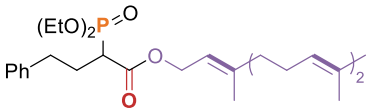


4s

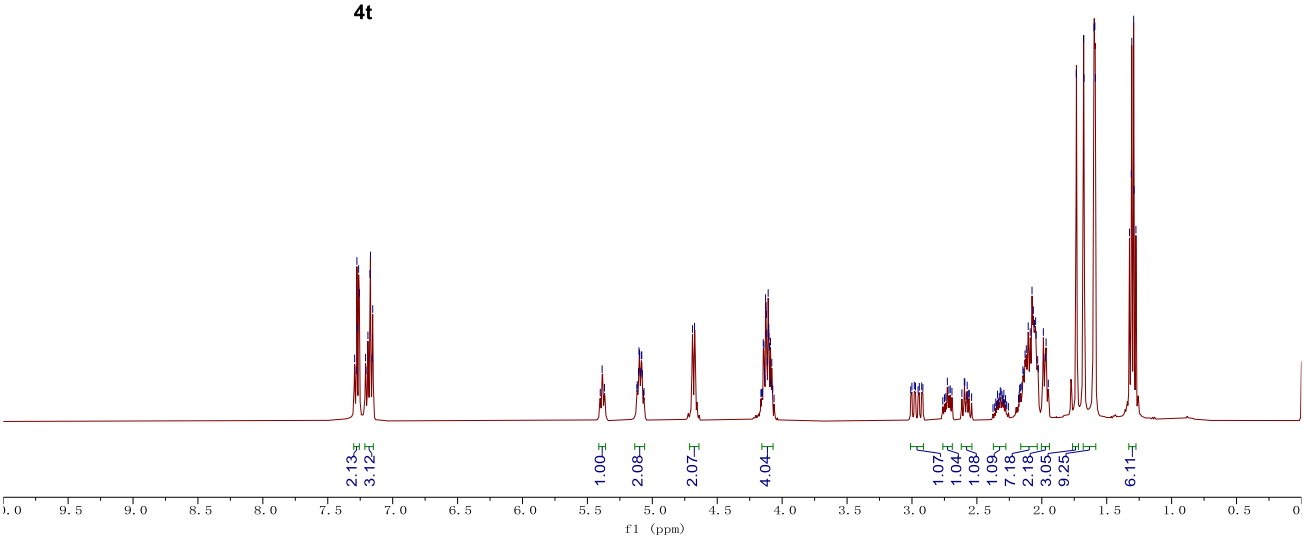
31P NMR CDCl3 161.97MHz



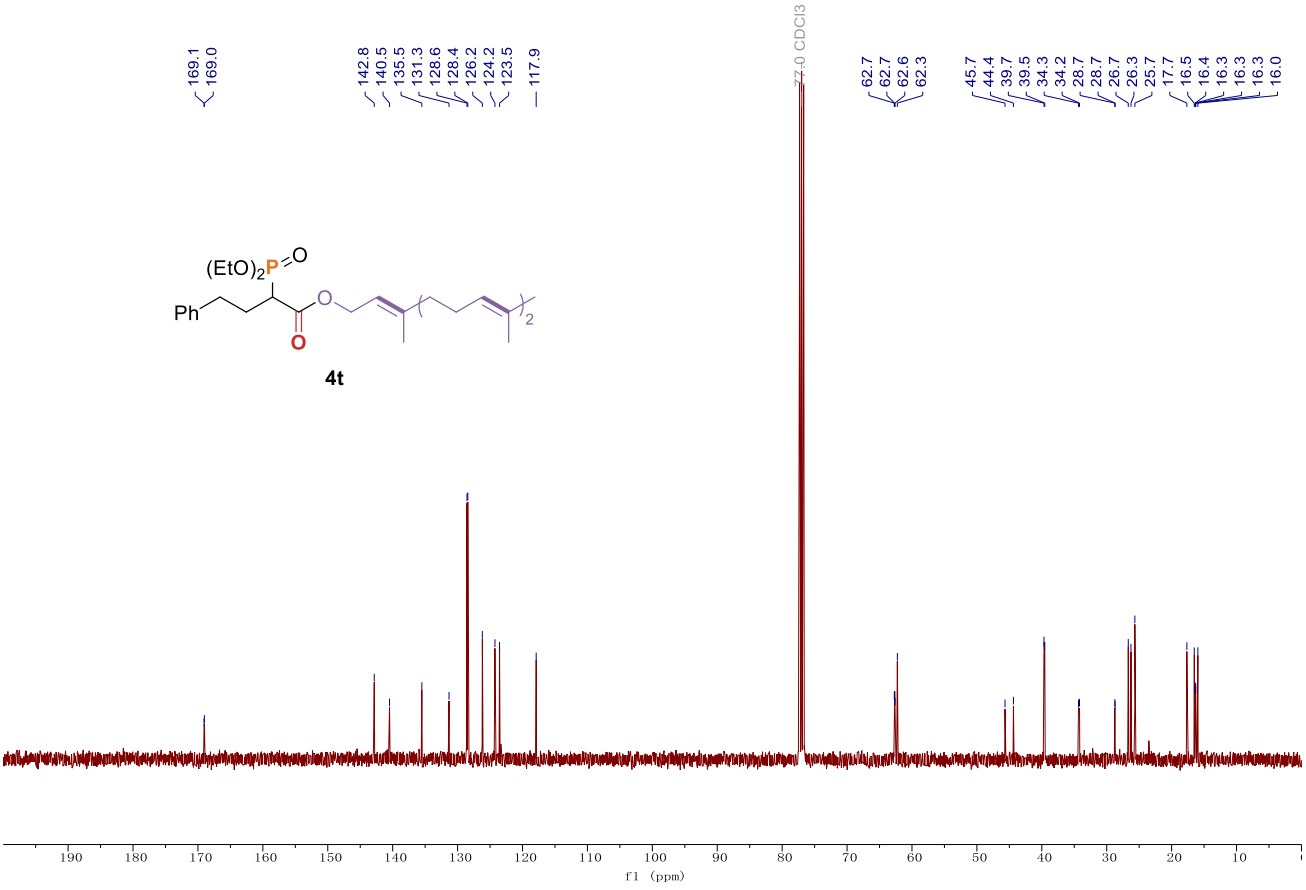
1H NMR CDCl3 400.13MHz



4t

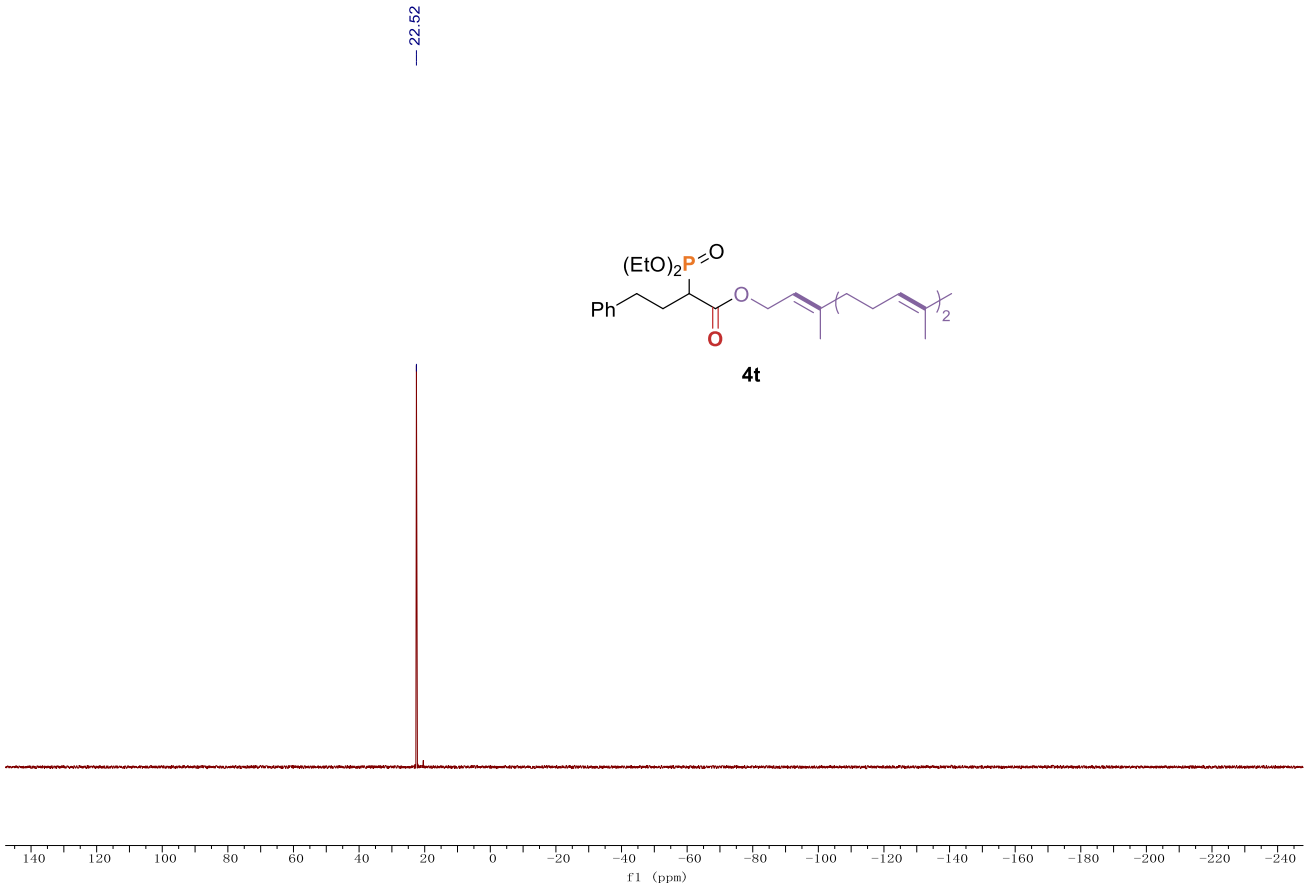


13C NMR CDCl3 100.62MHz



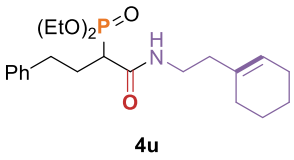
4t

31P NMR CDCl3 161.97MHz

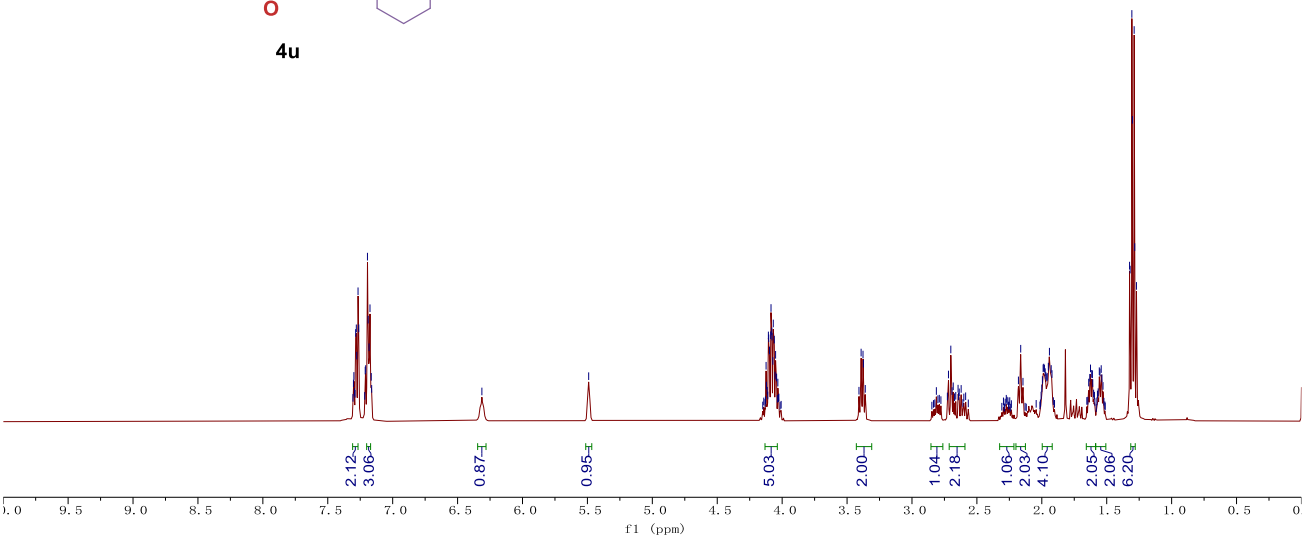


4t

1H NMR CDCl3 400.13MHz

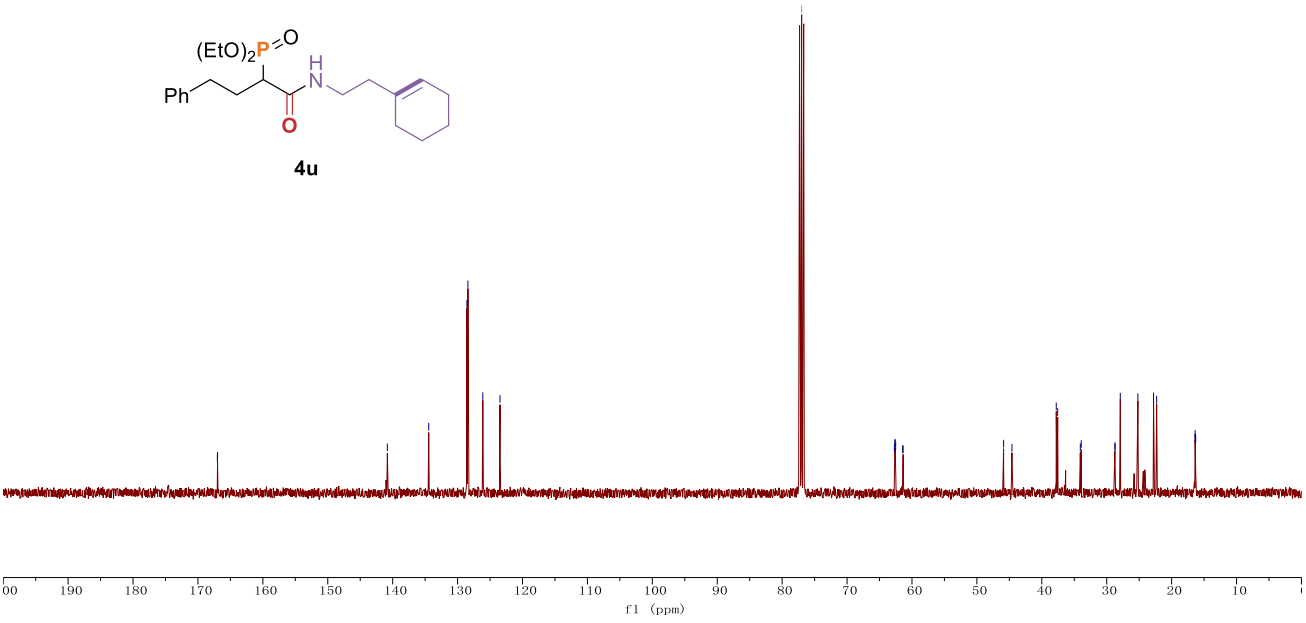


4u

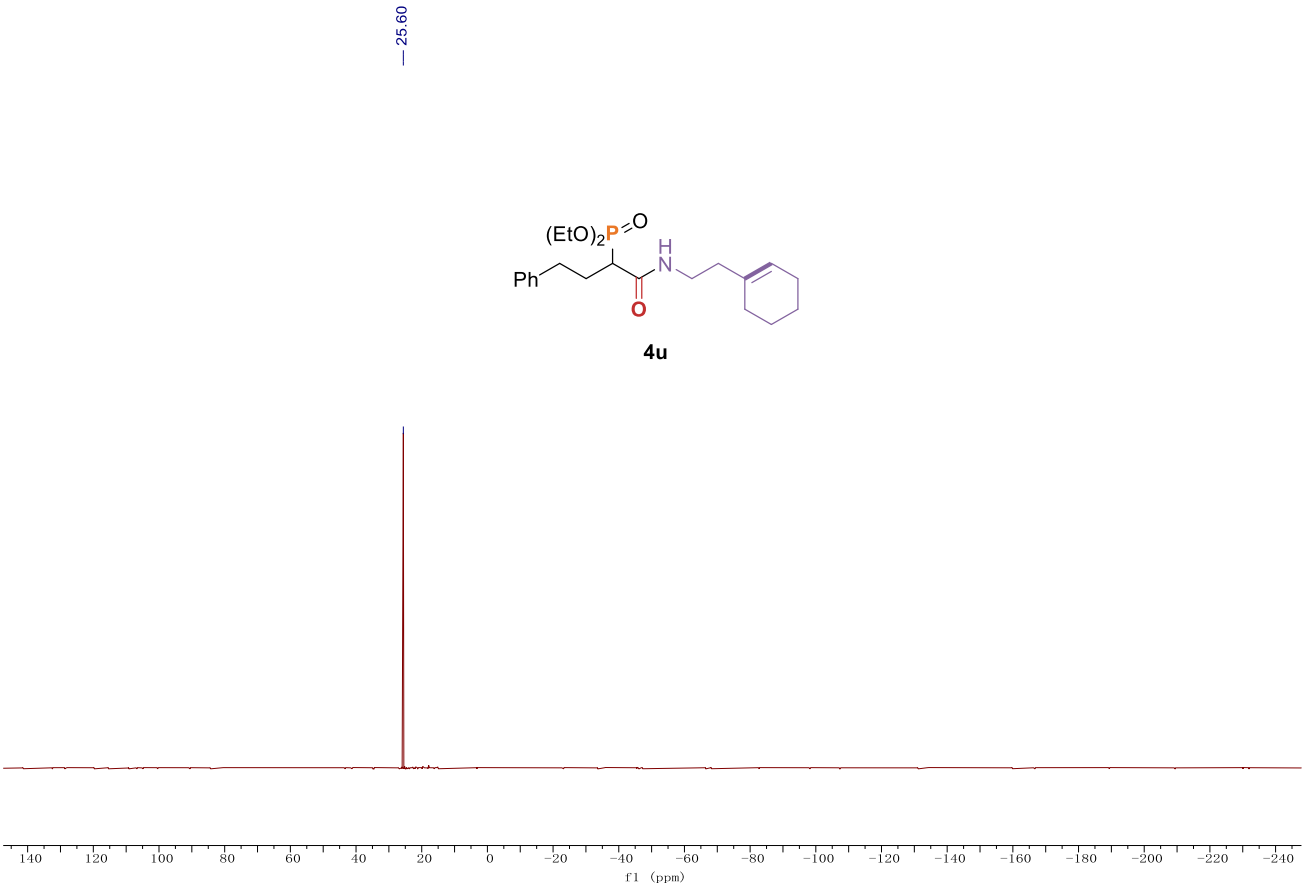


13C NMR CDCl3 100.62MHz

4u

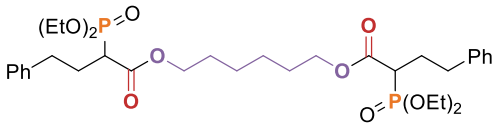


31P NMR CDCl3 161.97MHz

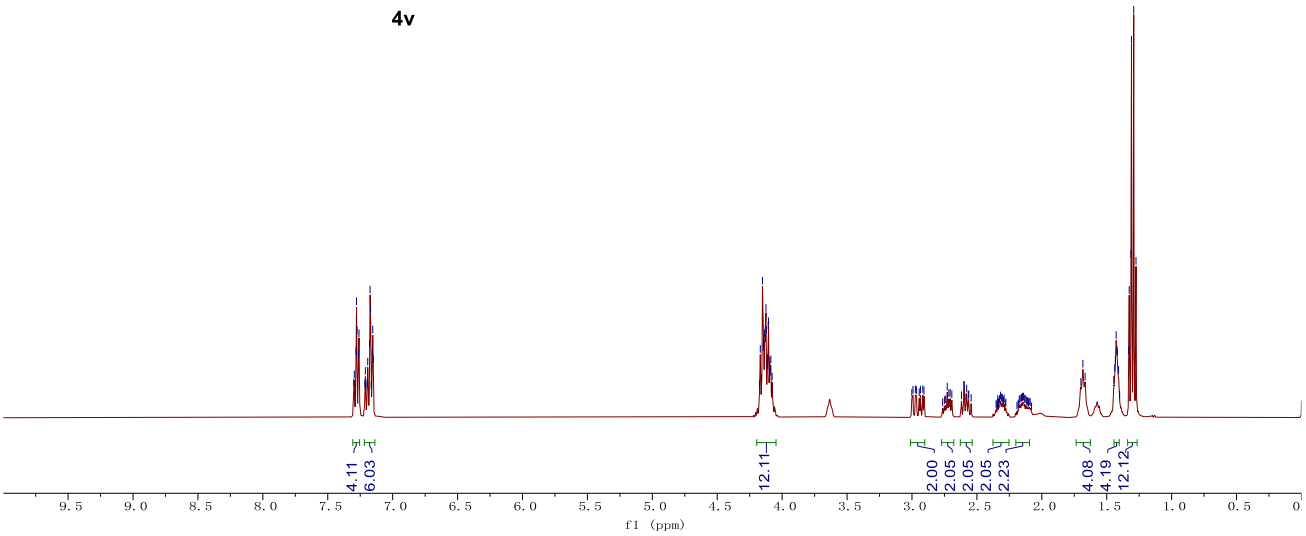


4u

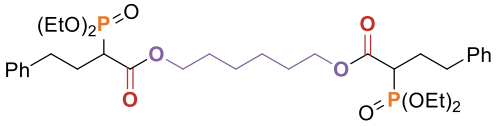
1H NMR CDCl3 400.13MHz



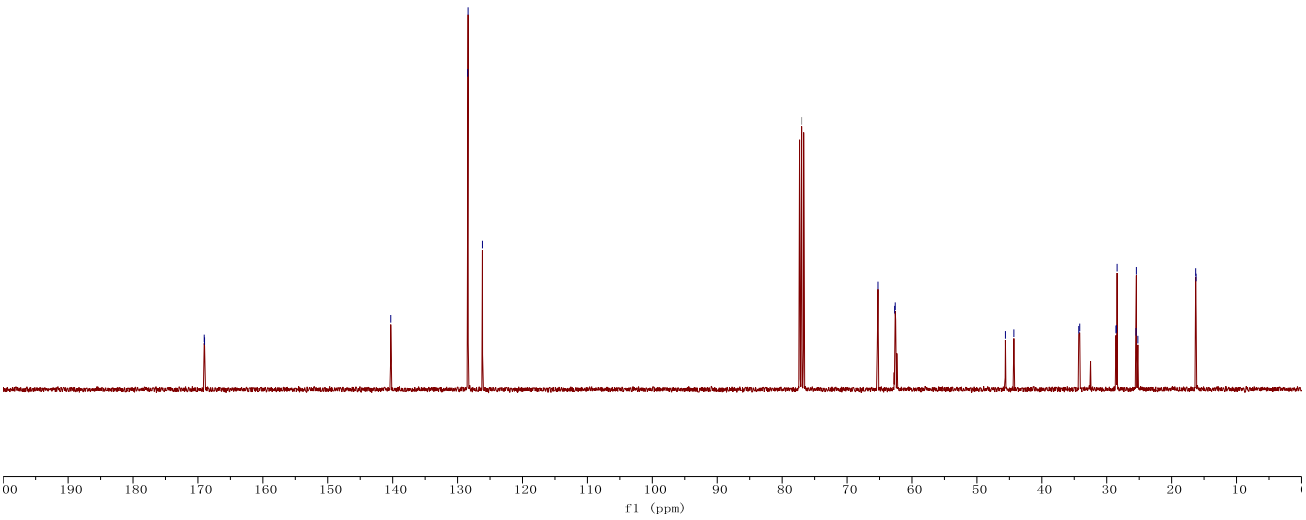
4v



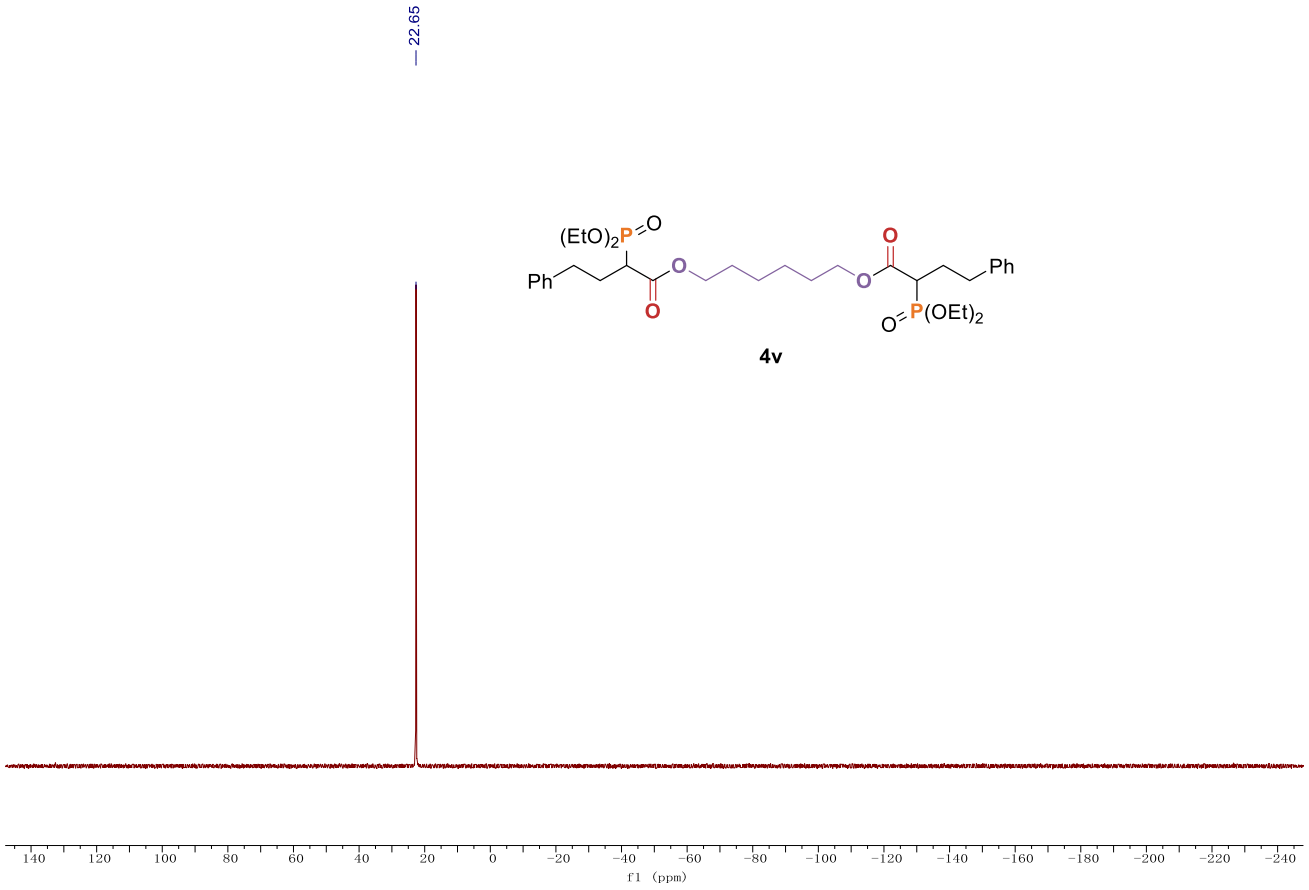
13C NMR CDCl3 100.62MHz



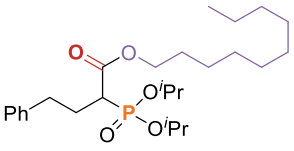
4v



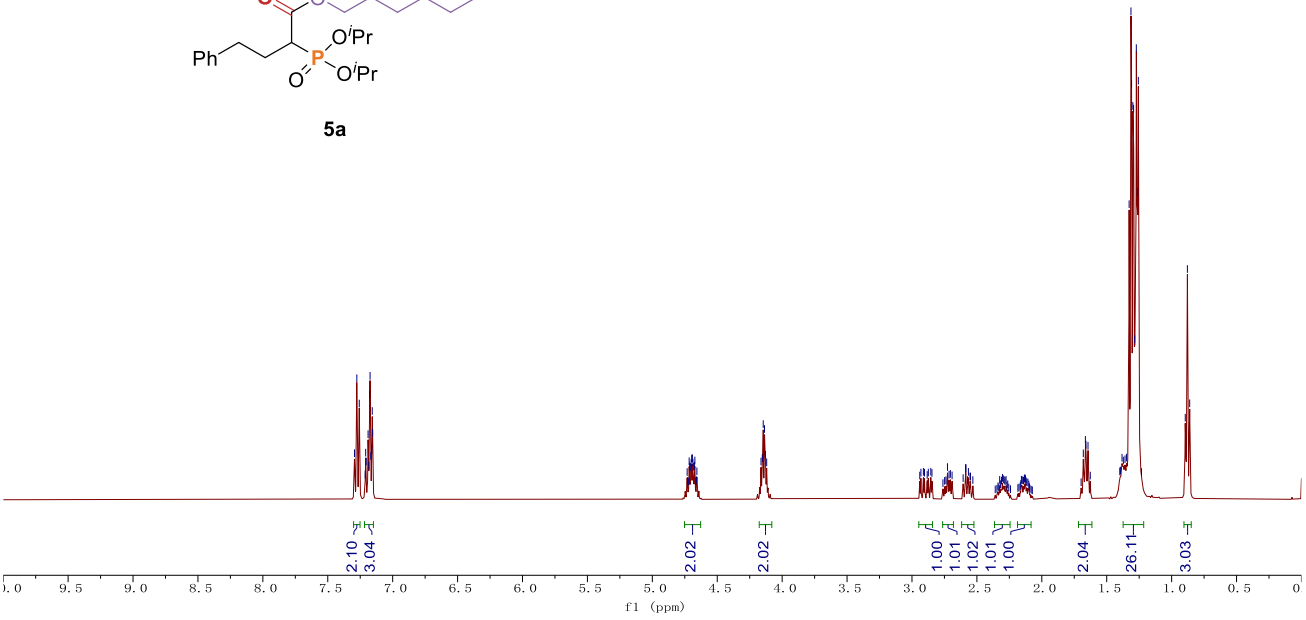
31P NMR CDCl3 161.97MHz



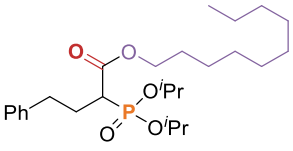
1H NMR CDCl3 400.13MHz



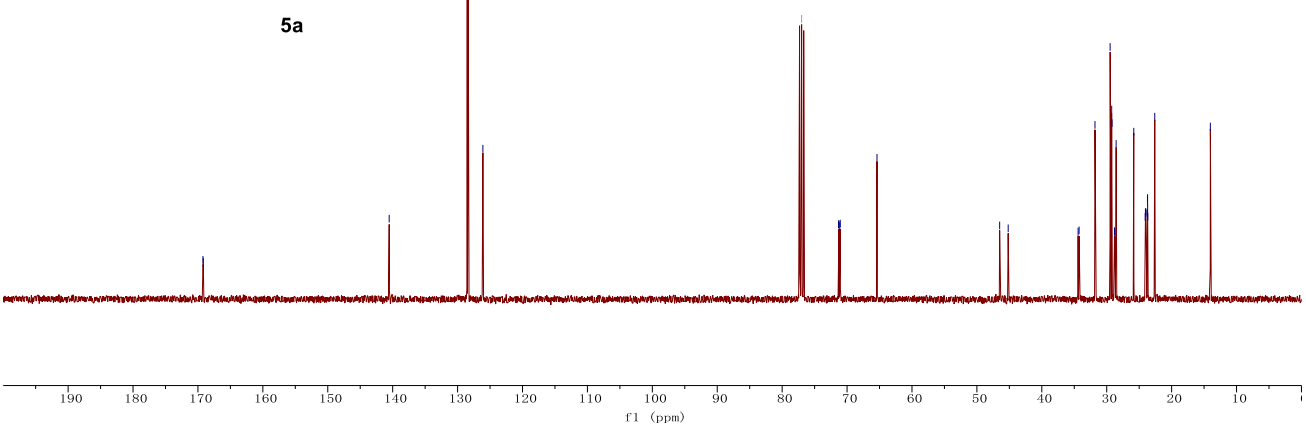
5a



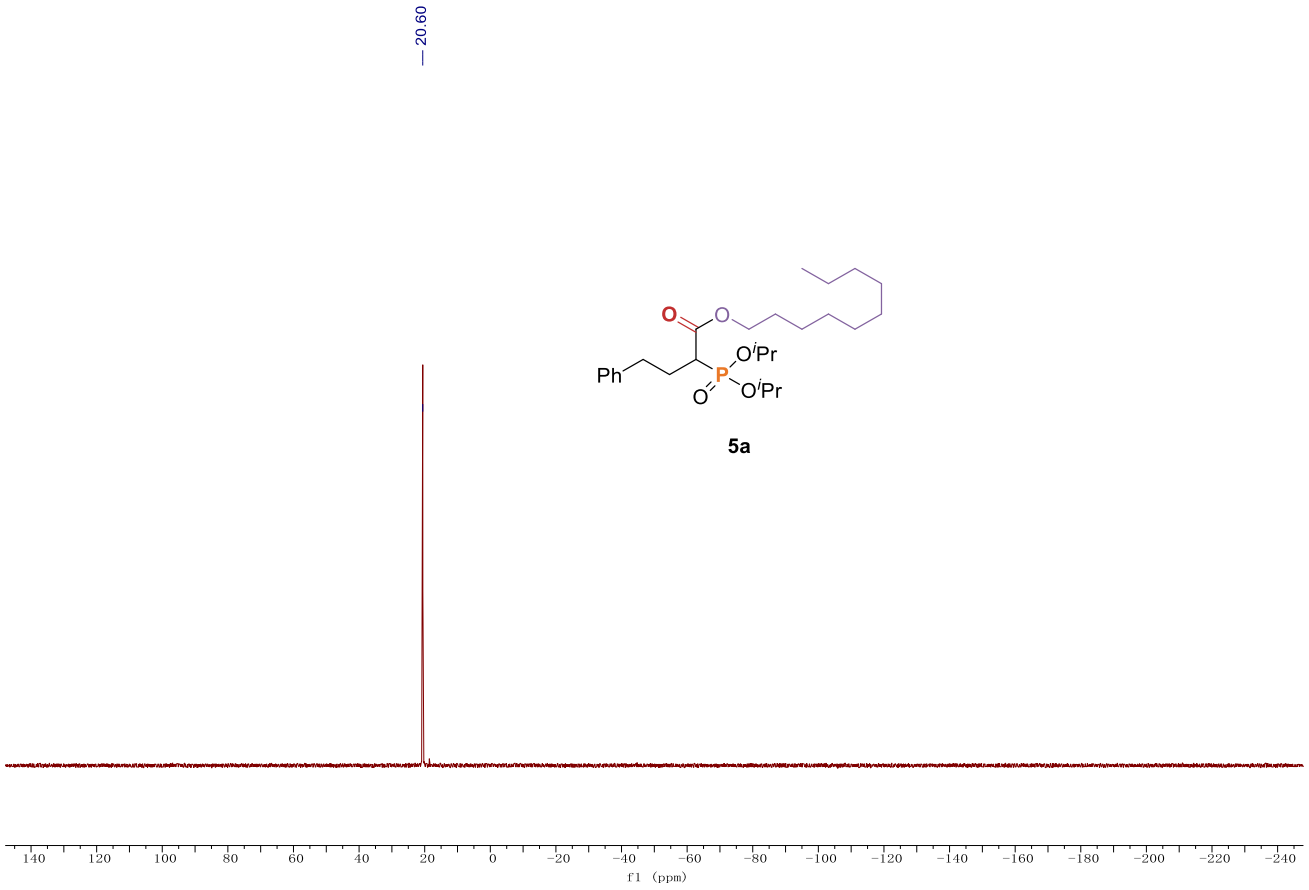
13C NMR CDCl3 100.62MHz



5a

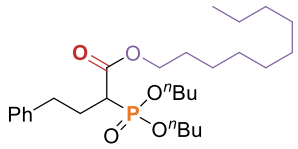


31P NMR CDCl3 161.97MHz

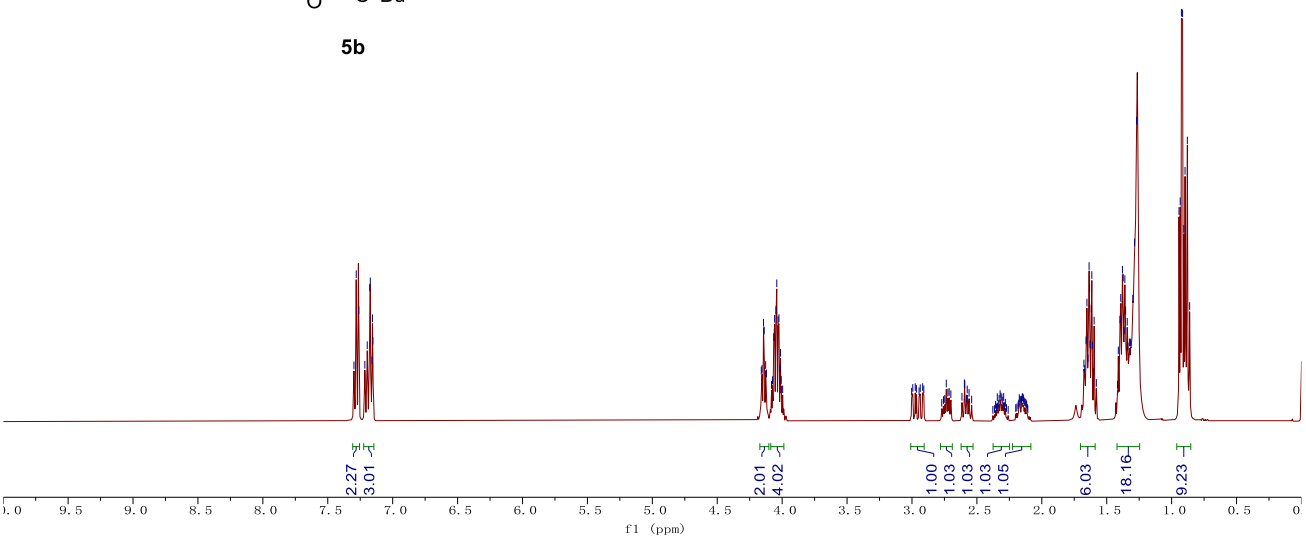


5a

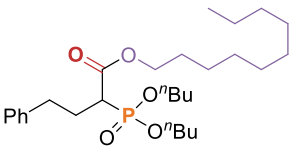
1H NMR CDCl3 400.13MHz



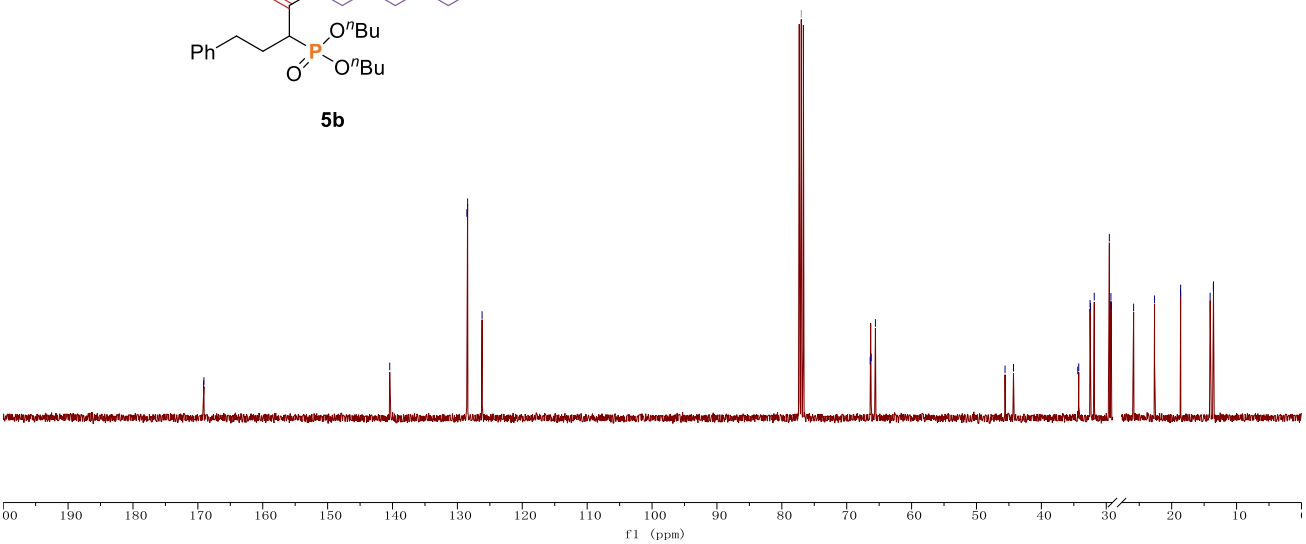
5b



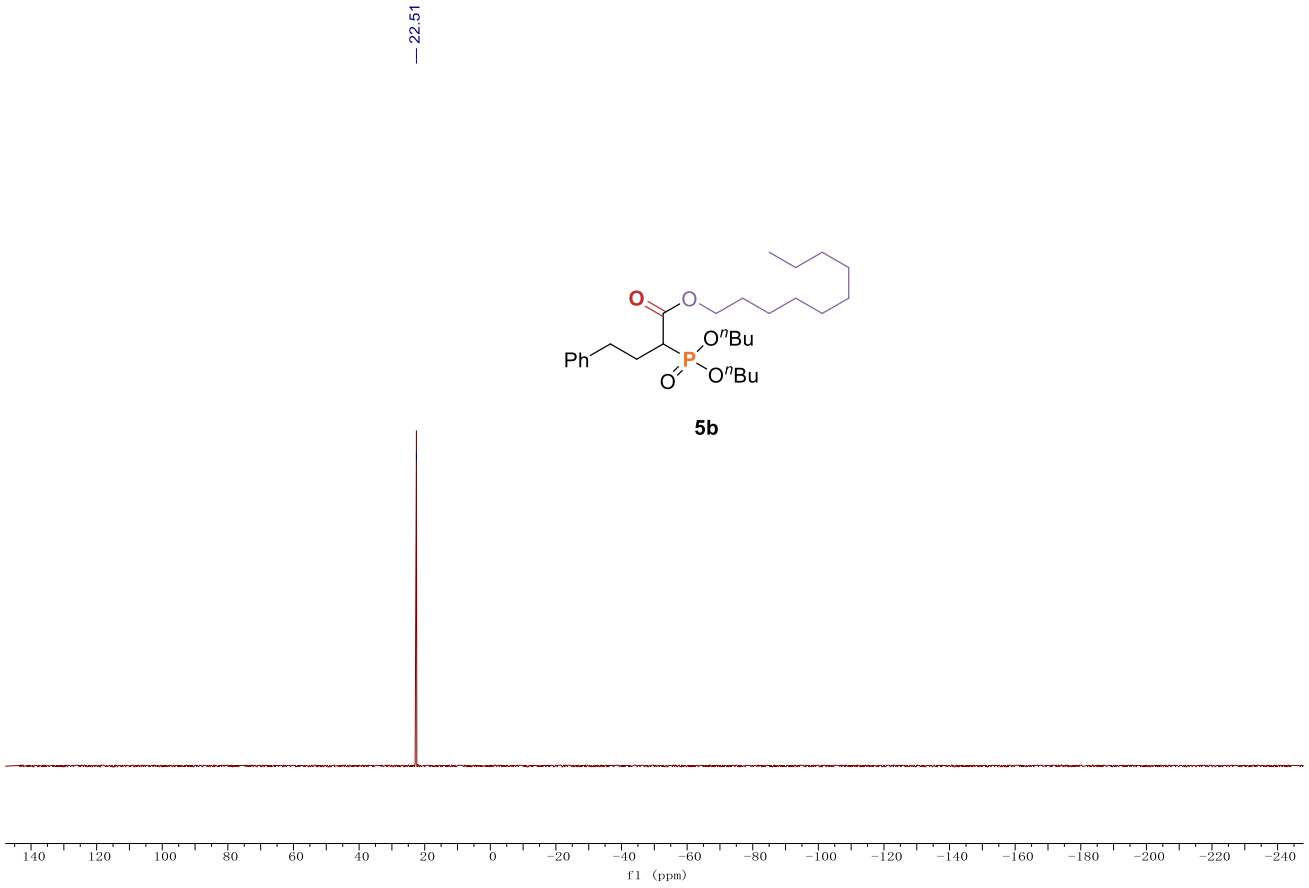
13C NMR CDCl3 100.62MHz



5b

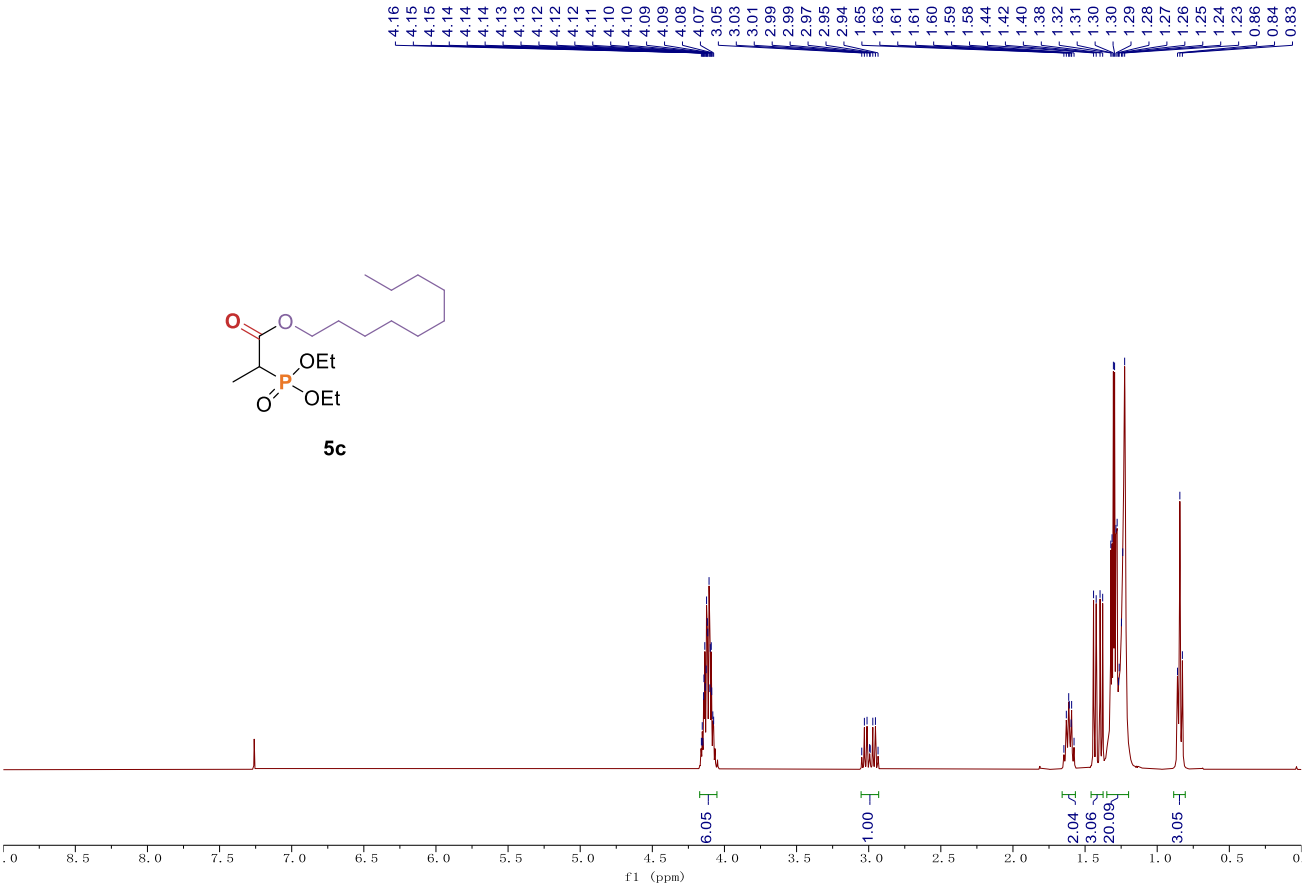


31P NMR CDCl3 161.97MHz



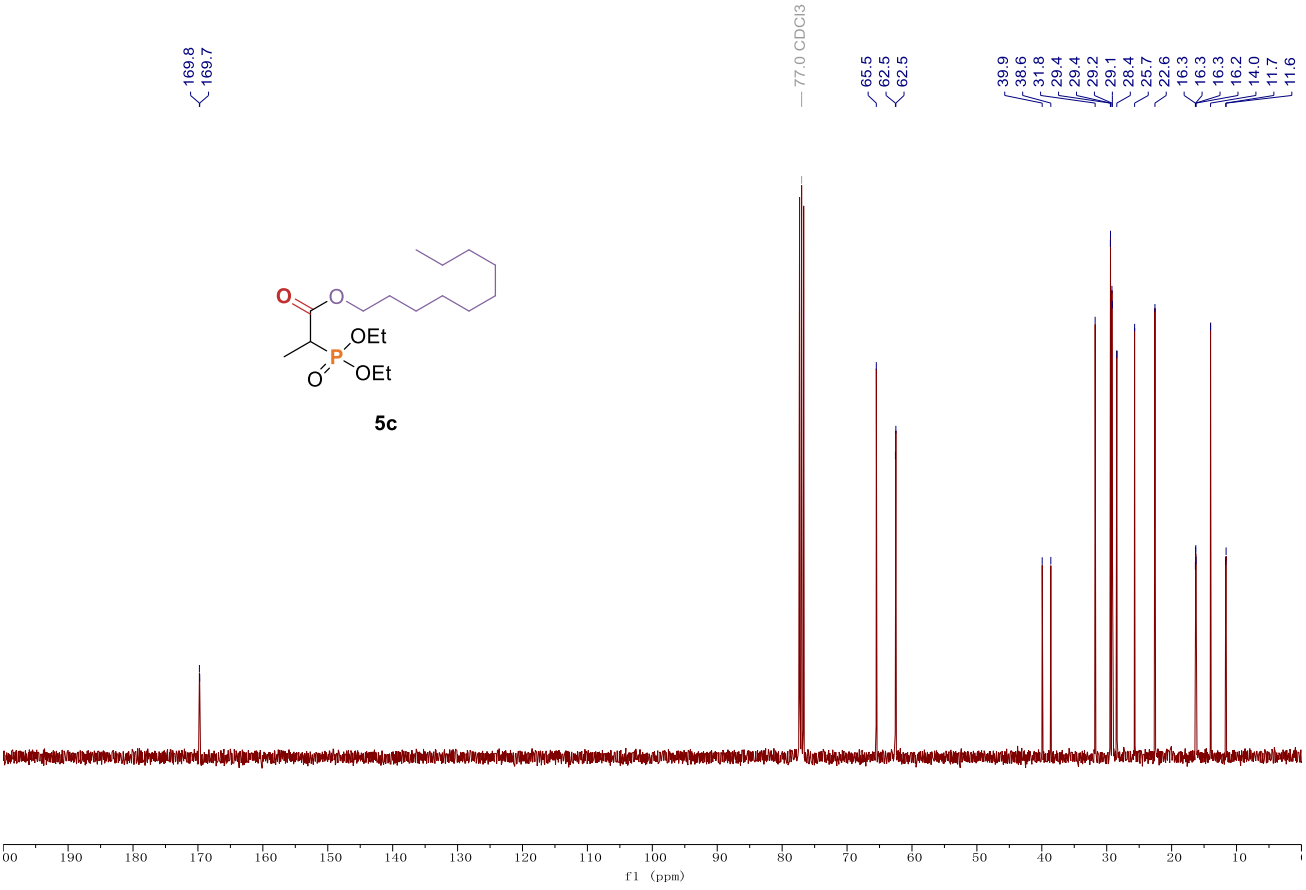
5b

1H NMR CDCl3 400.13MHz



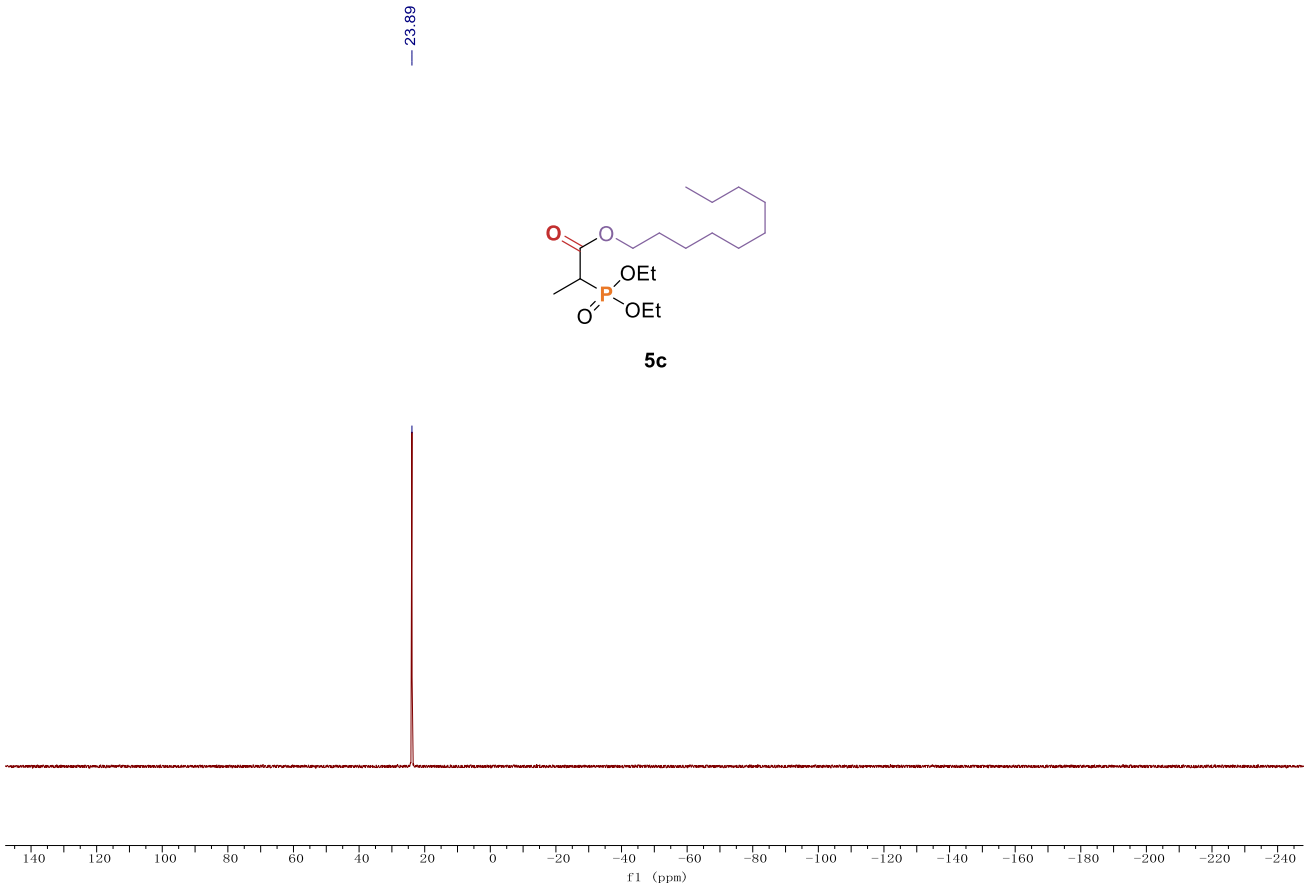
5c

13C NMR CDCl3 100.62MHz



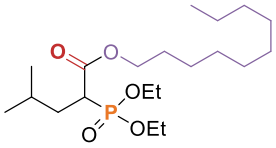
5c

31P NMR CDCl3 161.97MHz

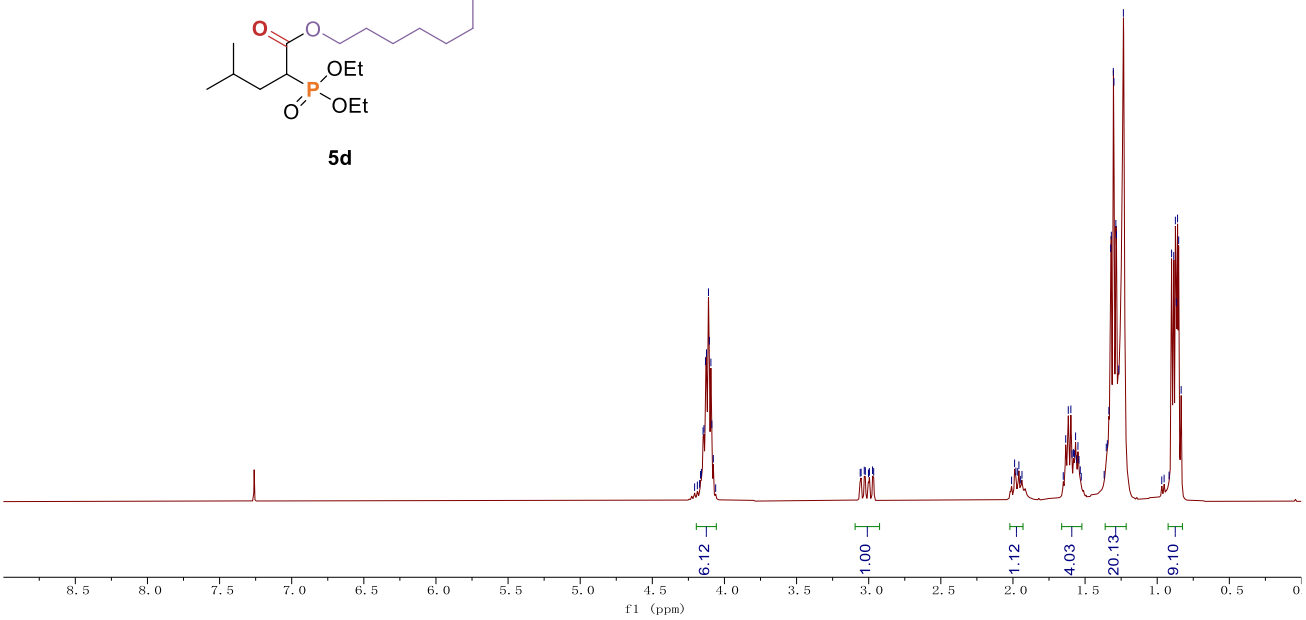


5c

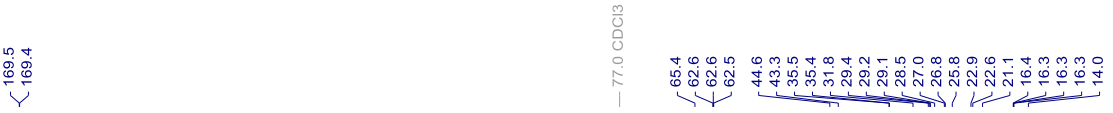
1H NMR CDCl3 400.13MHz

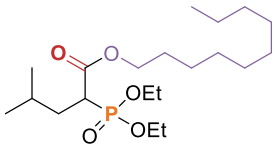


5d

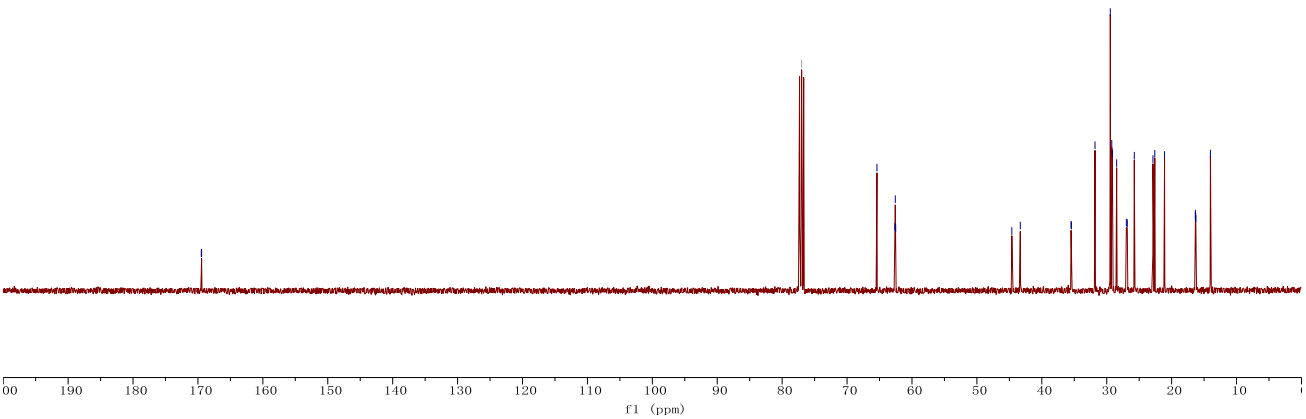


13C NMR CDCl3 100.62MHz

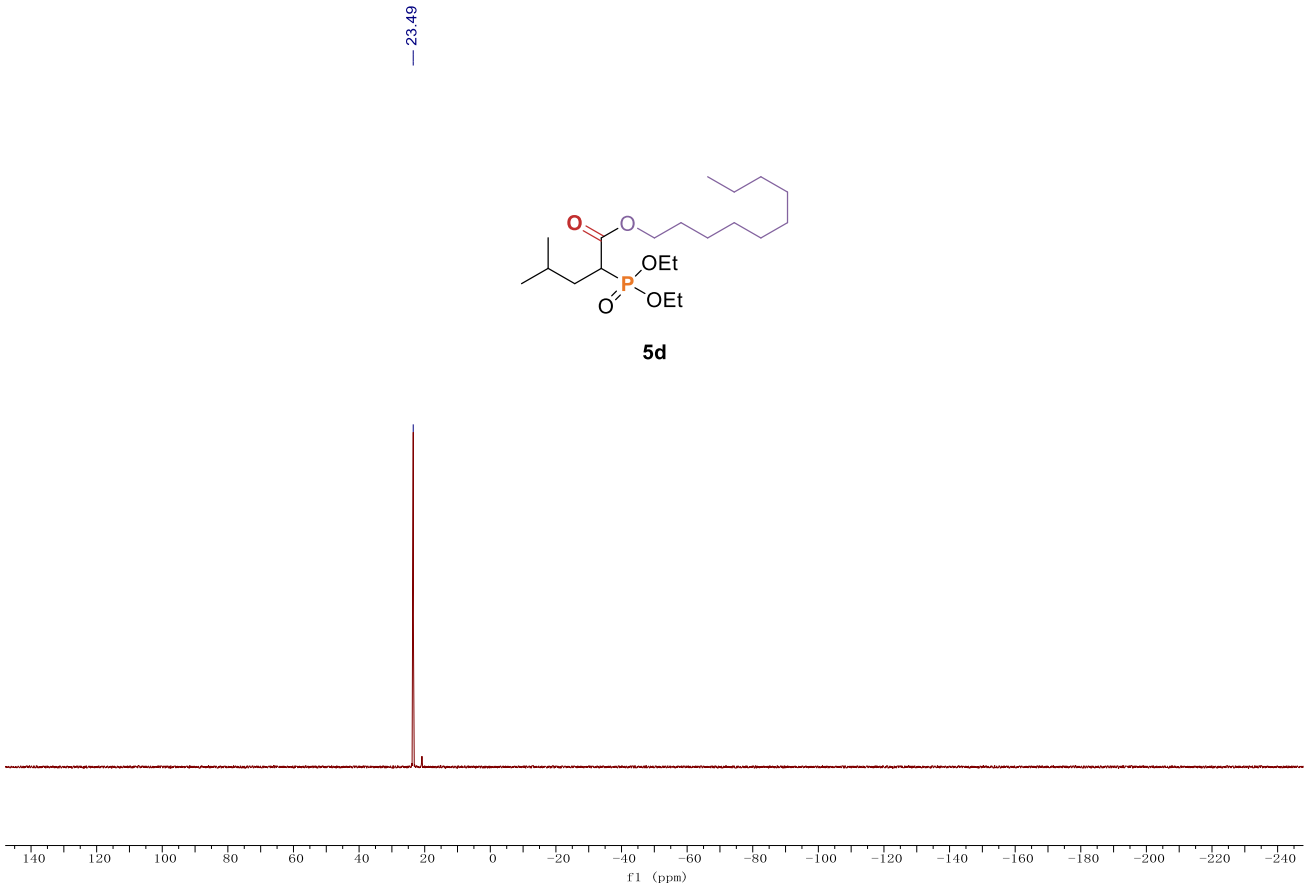




5d

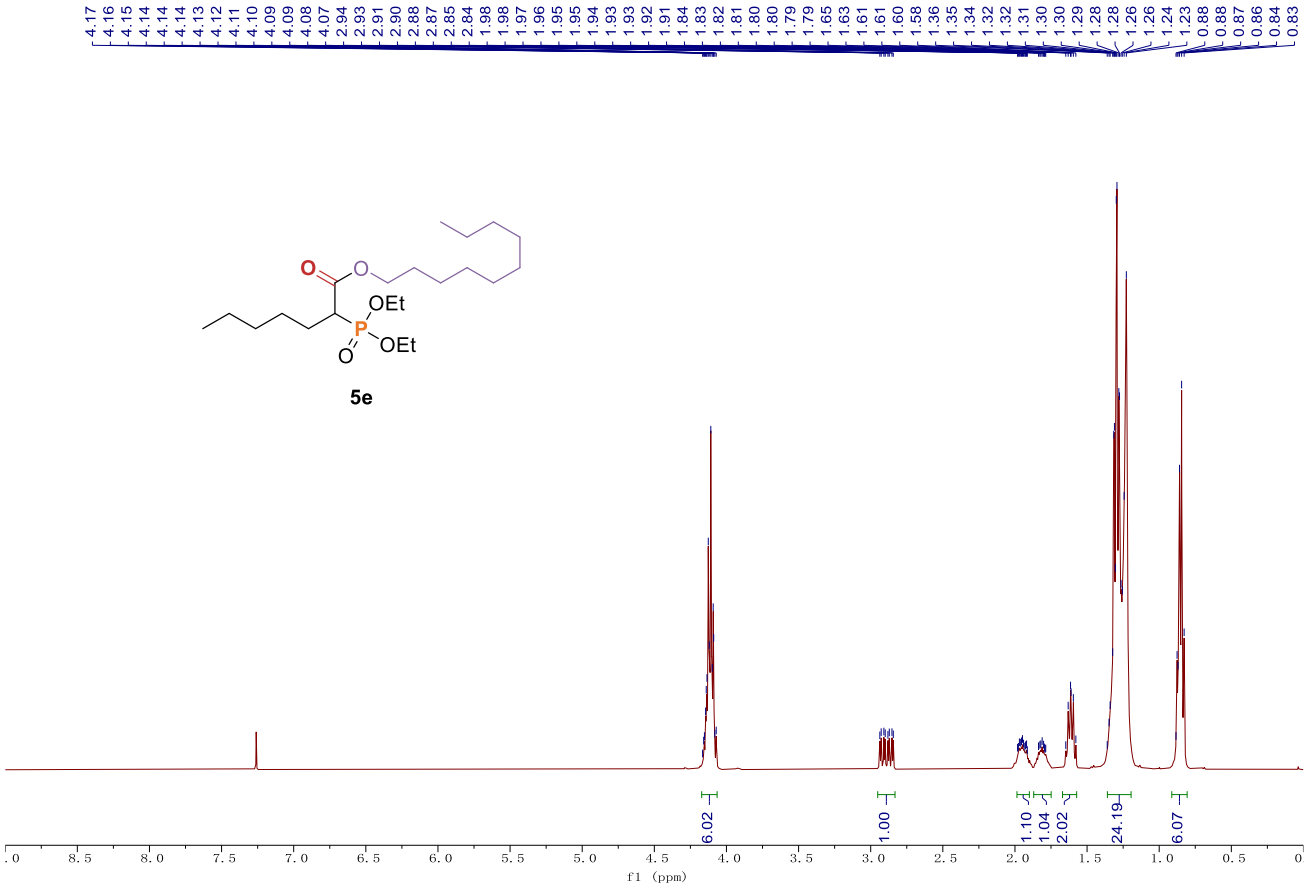


31P NMR CDCl3 161.97MHz



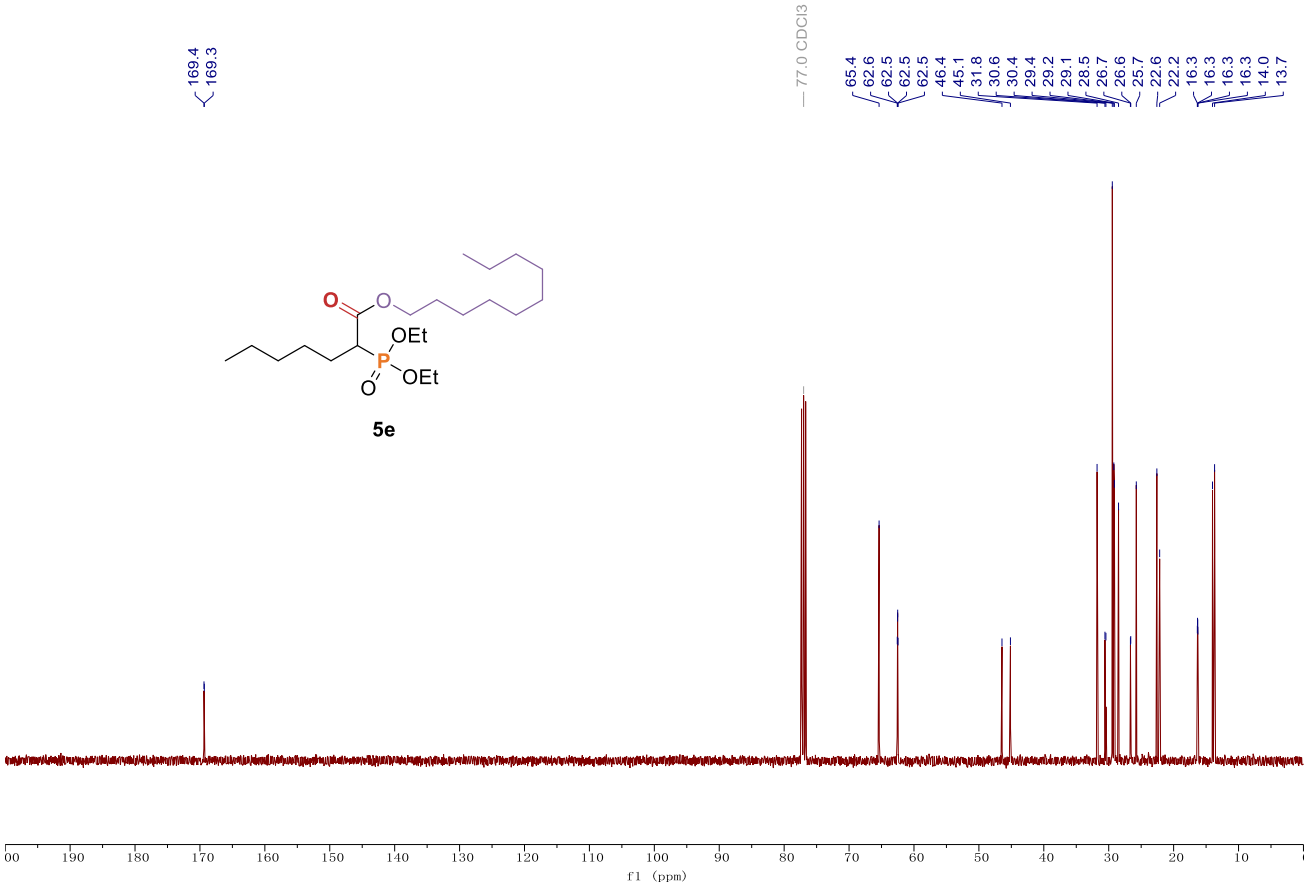
5d

1H NMR CDCl3 400.13MHz



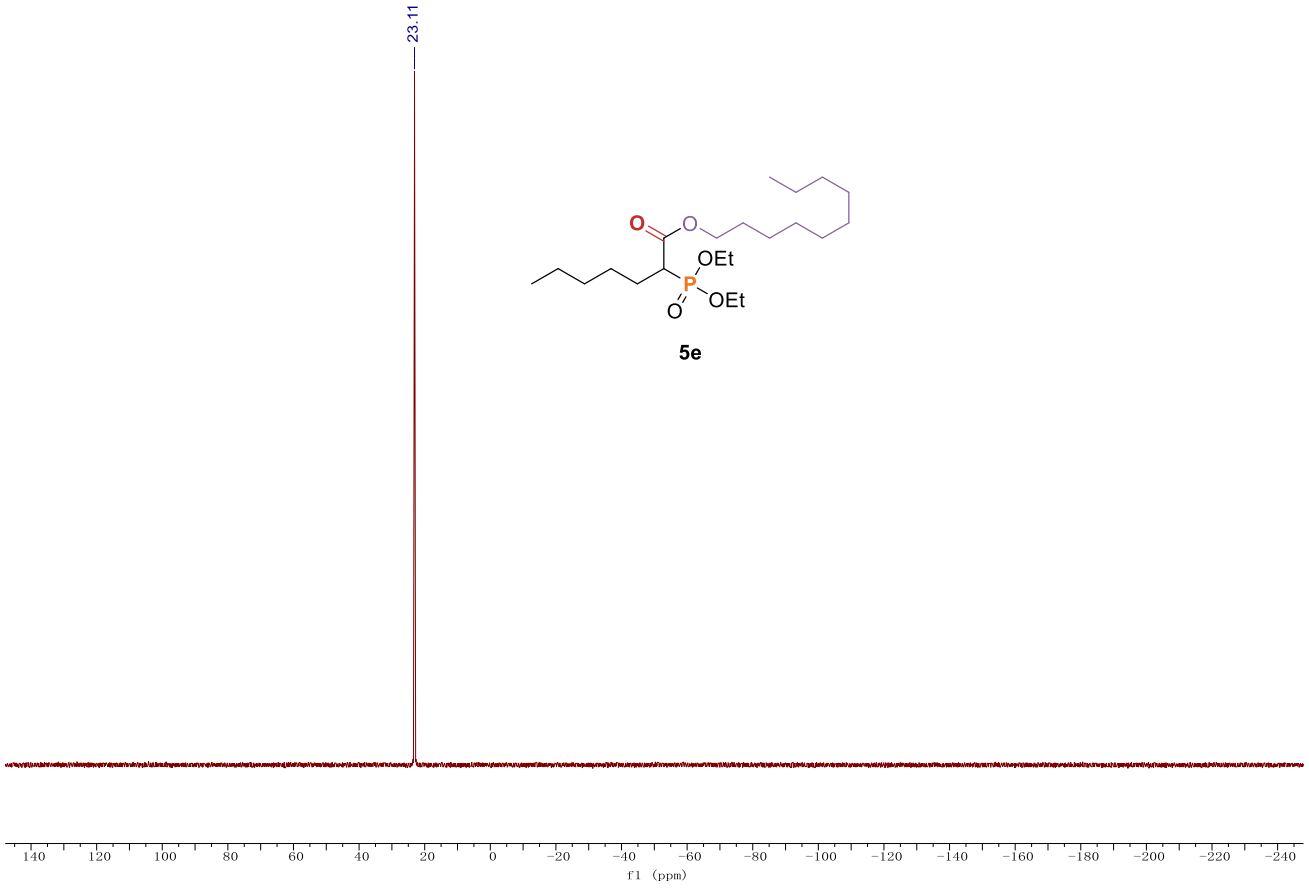
5e

13C NMR CDCl3 100.62MHz



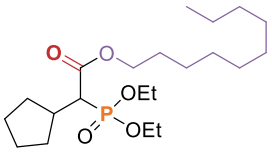
5e

31P NMR CDCl3 161.97MHz

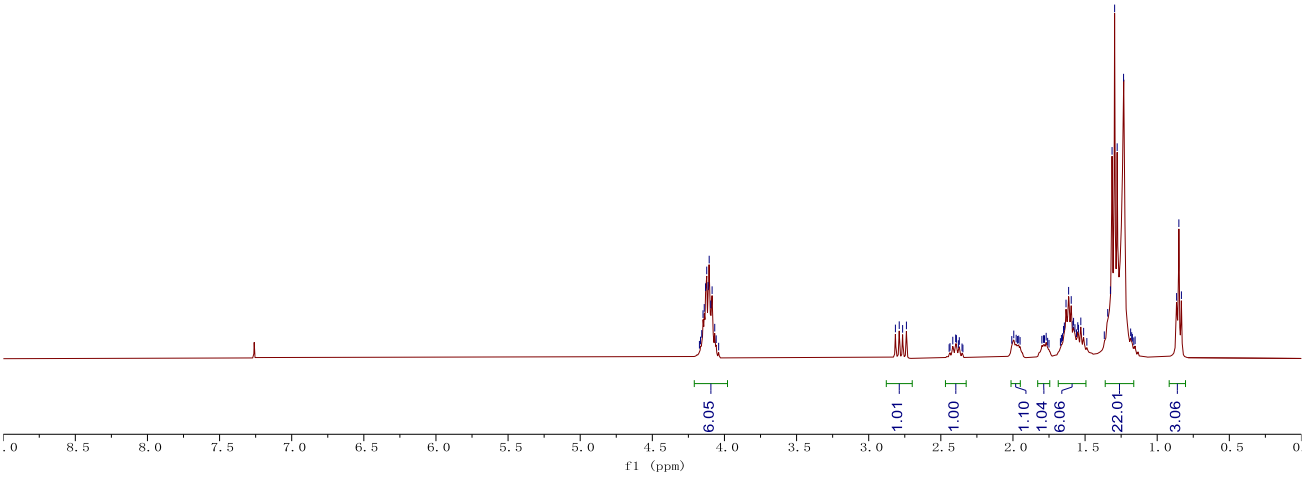


5e

1H NMR CDCl3 400.13MHz

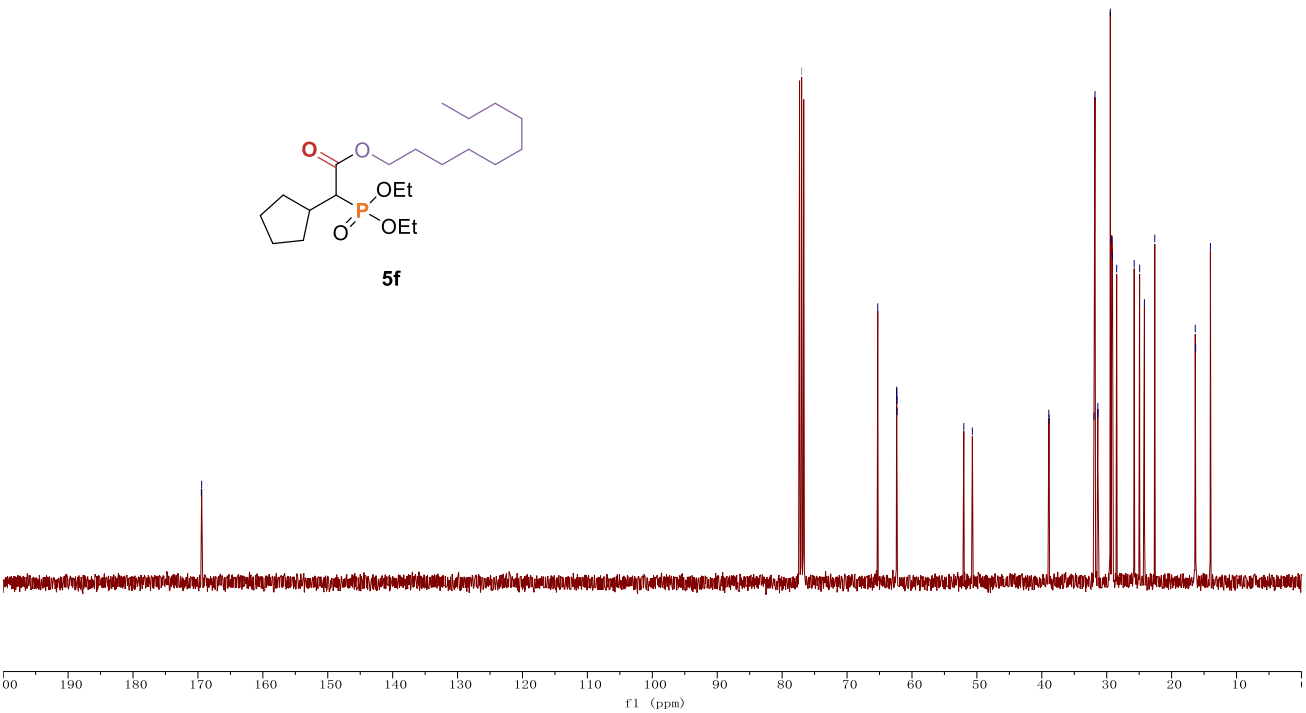


5f

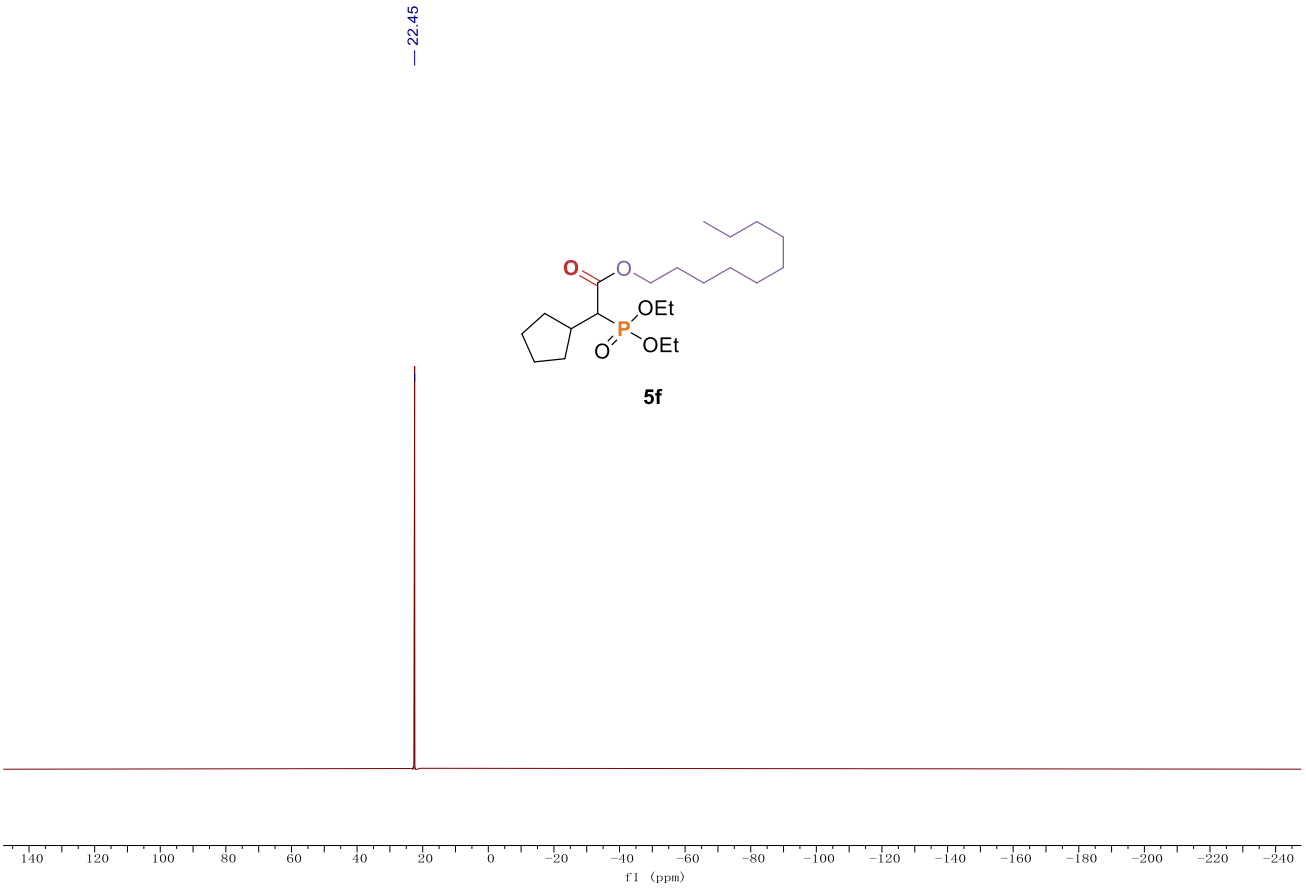


13C NMR CDCl3 100.62MHz

5f



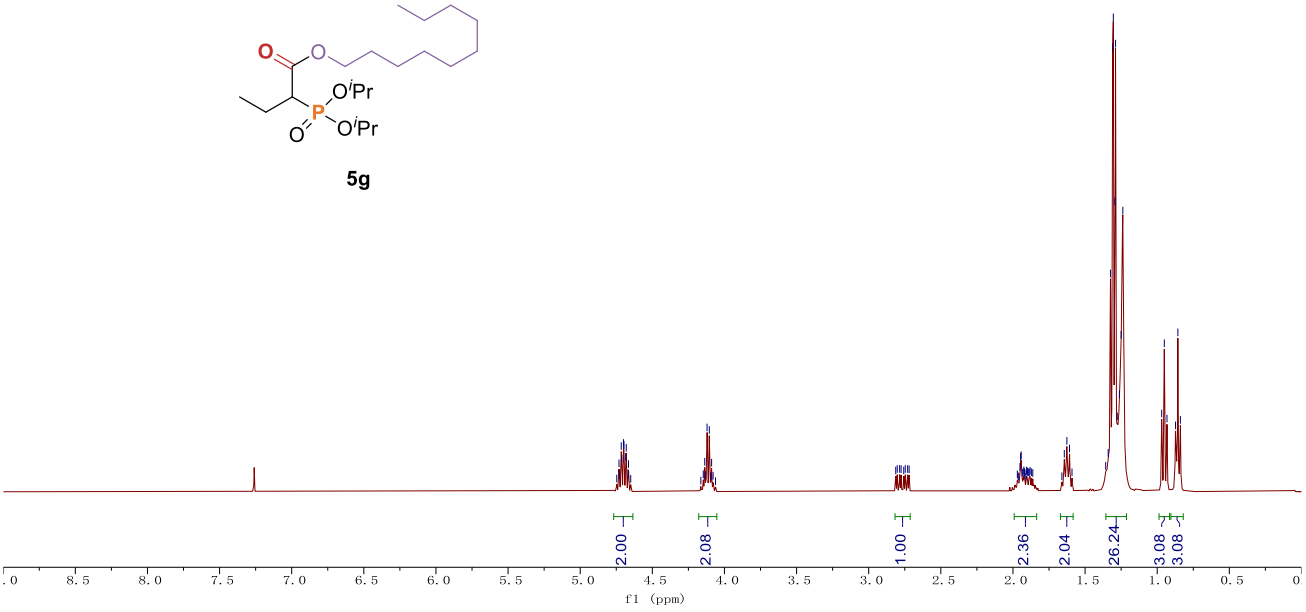
31P NMR CDCl3 161.97MHz



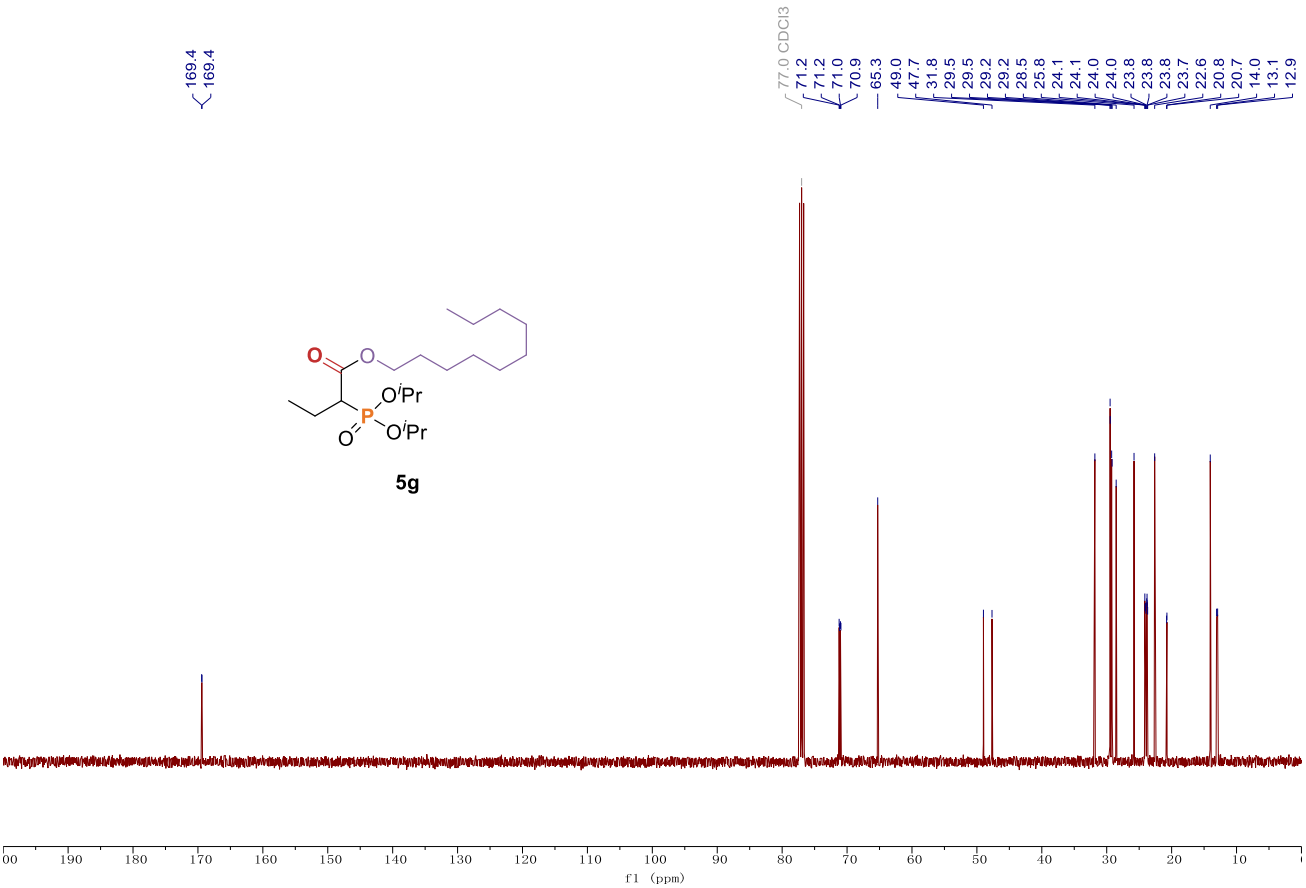
5f

1H NMR CDCl3 400.13MHz

5g

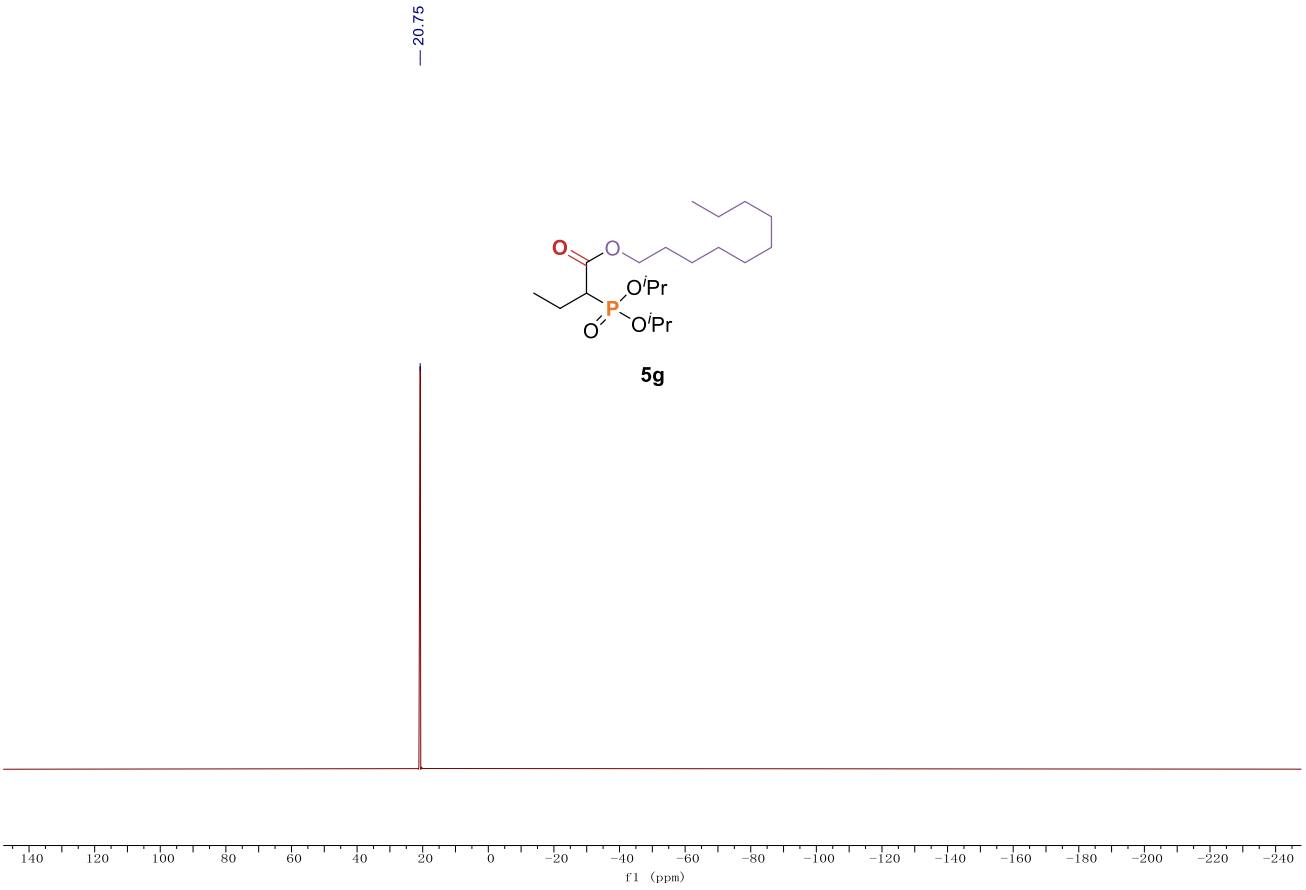


13C NMR CDCl3 100.62MHz



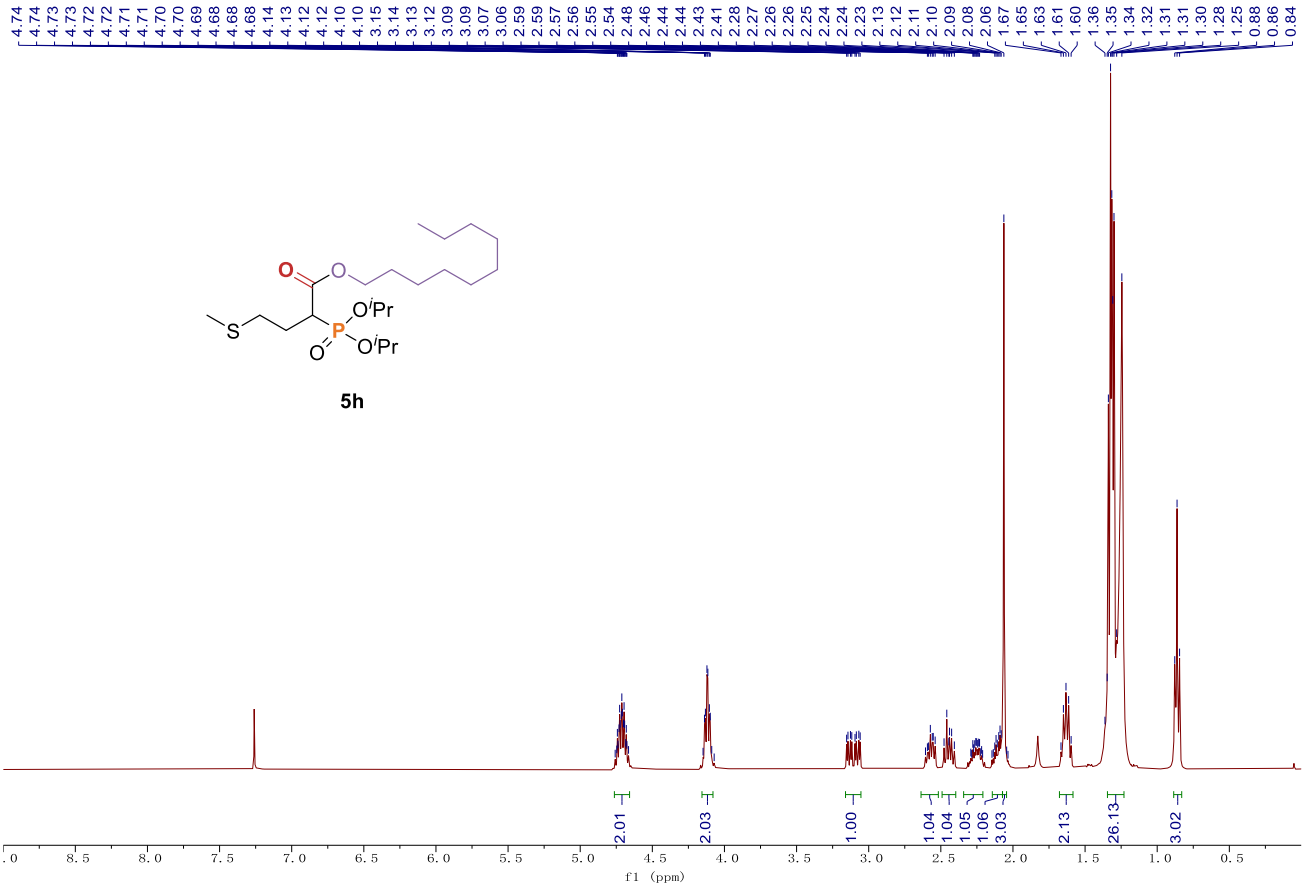
5g

31P NMR CDCl3 161.97MHz



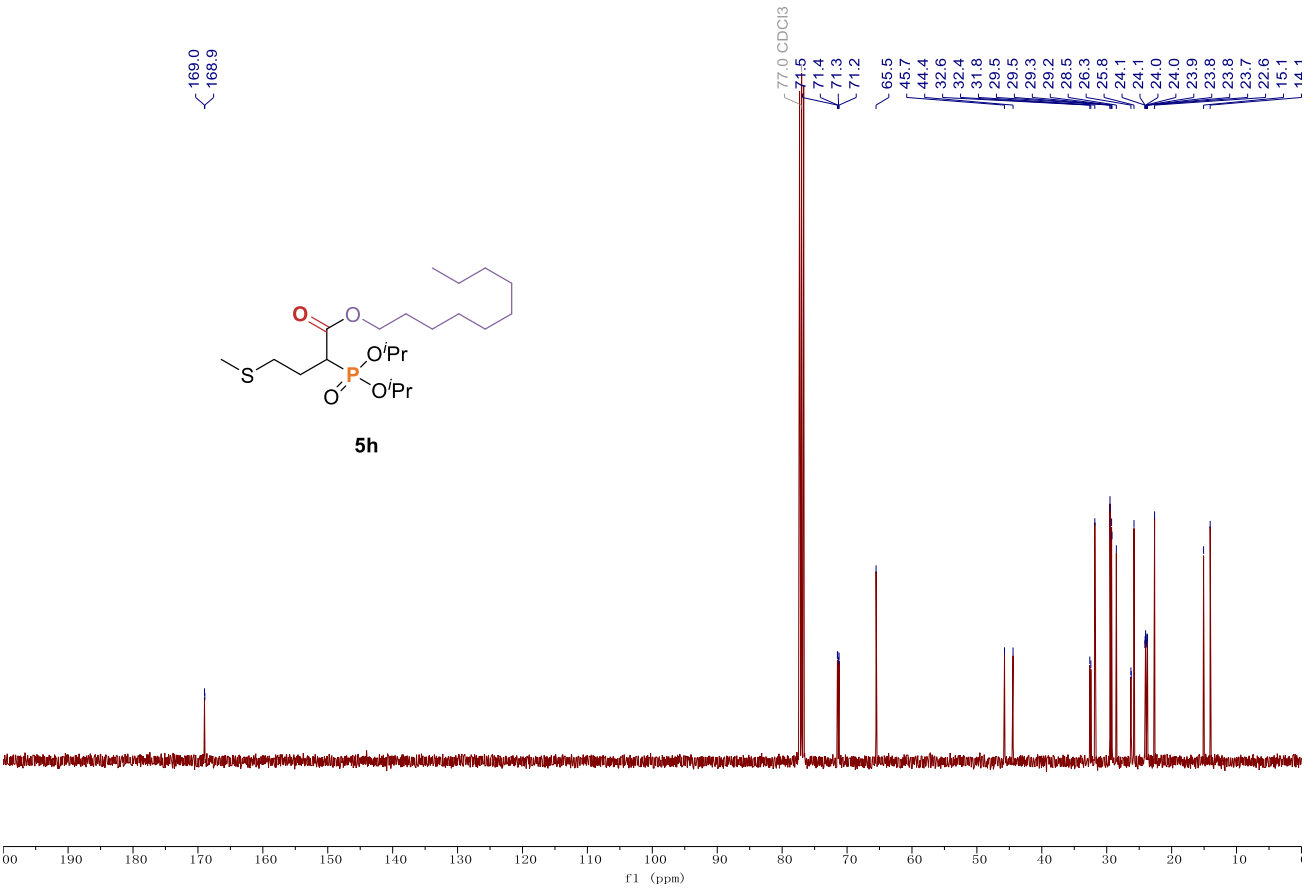
5g

1H NMR CDCl3 400.13MHz



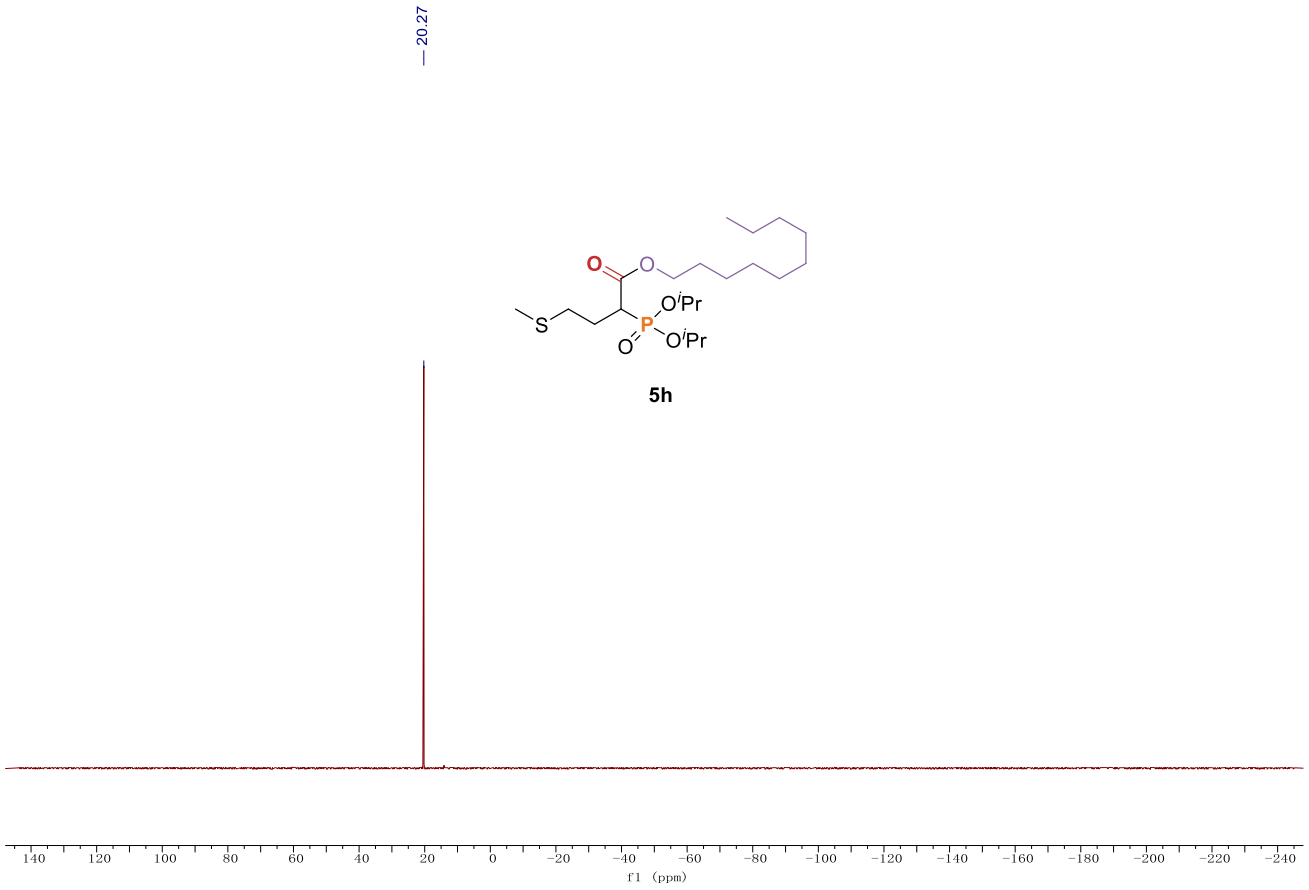
5h

13C NMR CDCl3 100.62MHz



5h

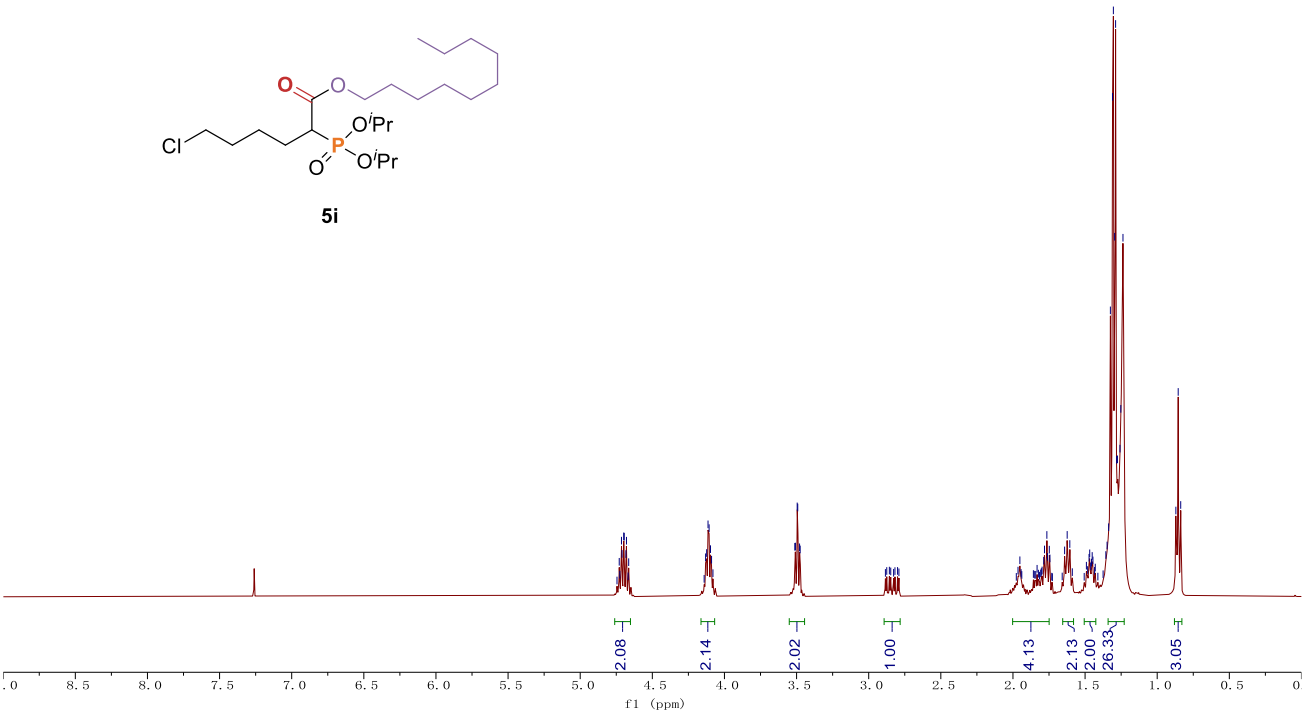
31P NMR CDCl3 161.97MHz



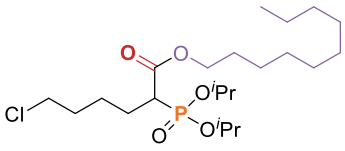
5h

1H NMR CDCl3 400.13MHz

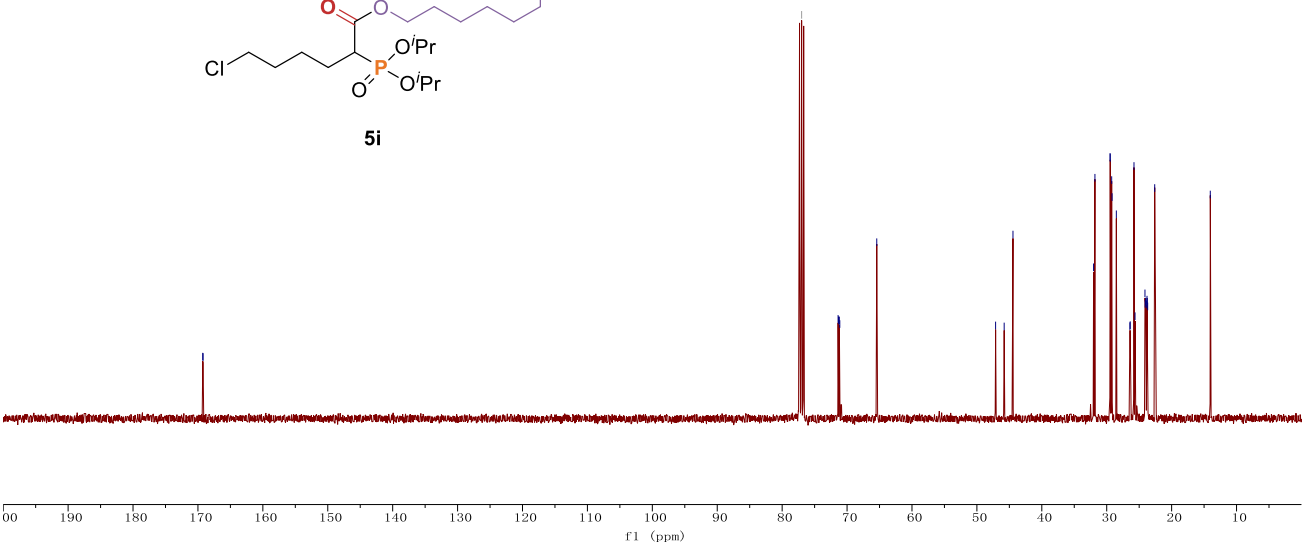
5i



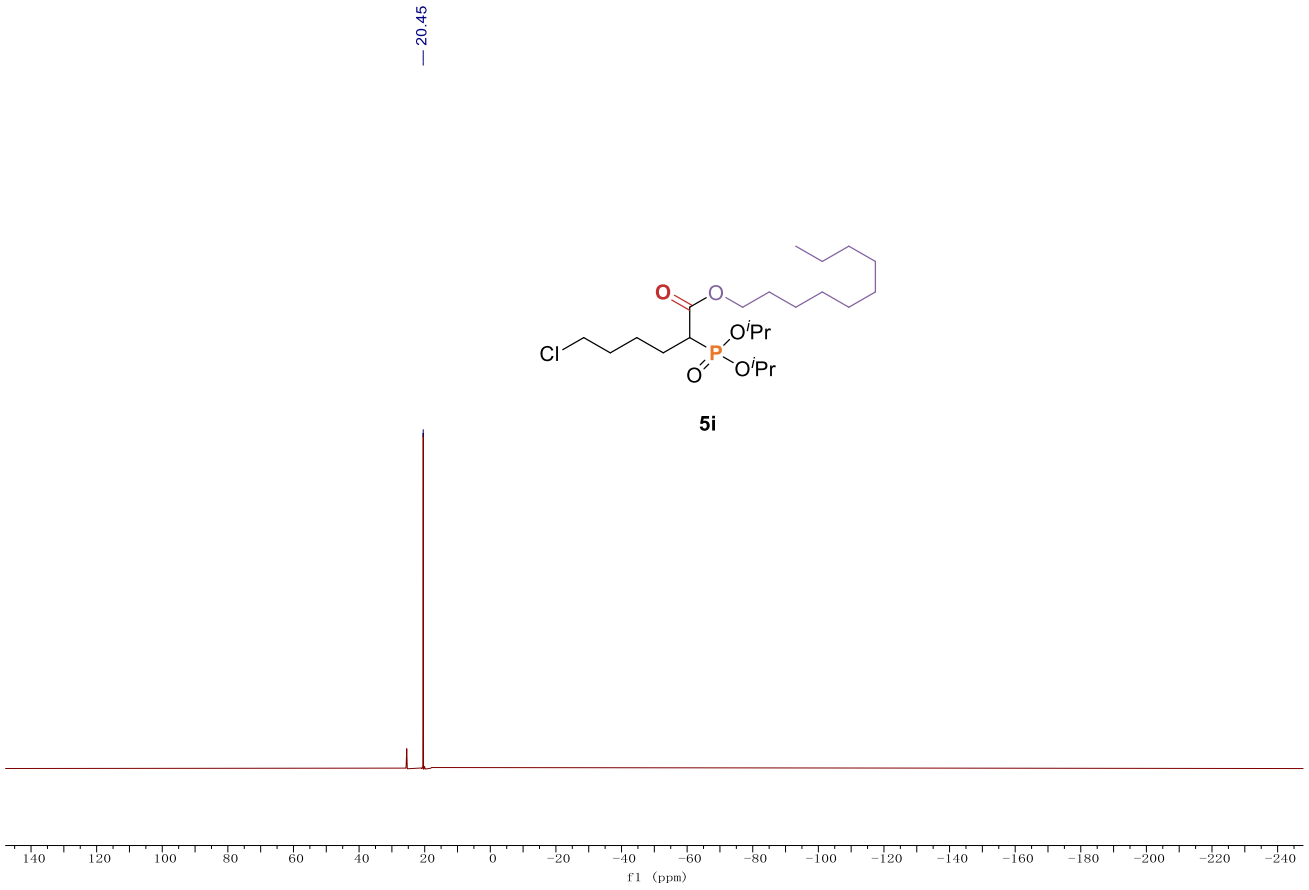
13C NMR CDCl3 100.62MHz



5i

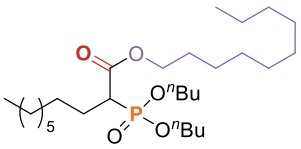


31P NMR CDCl3 161.97MHz

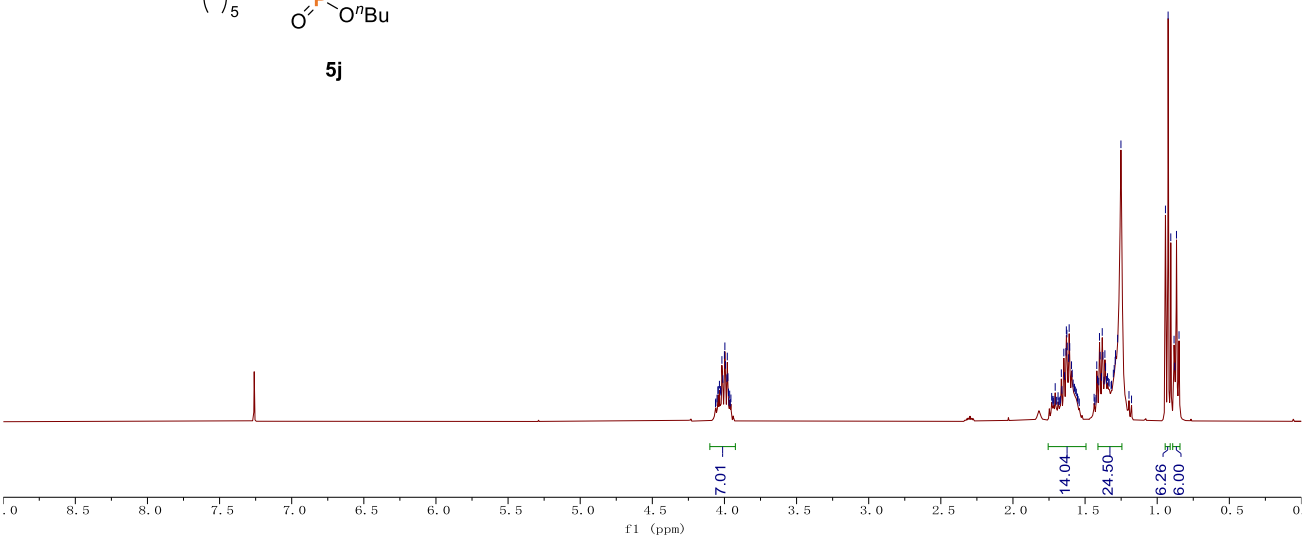


5i

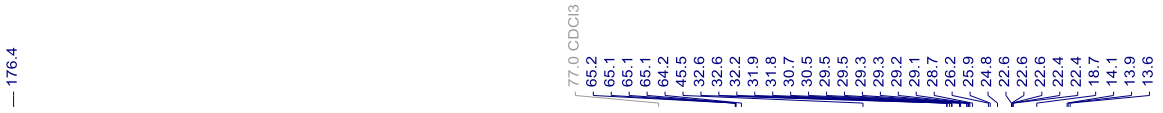
1H NMR CDCl3 400.13MHz



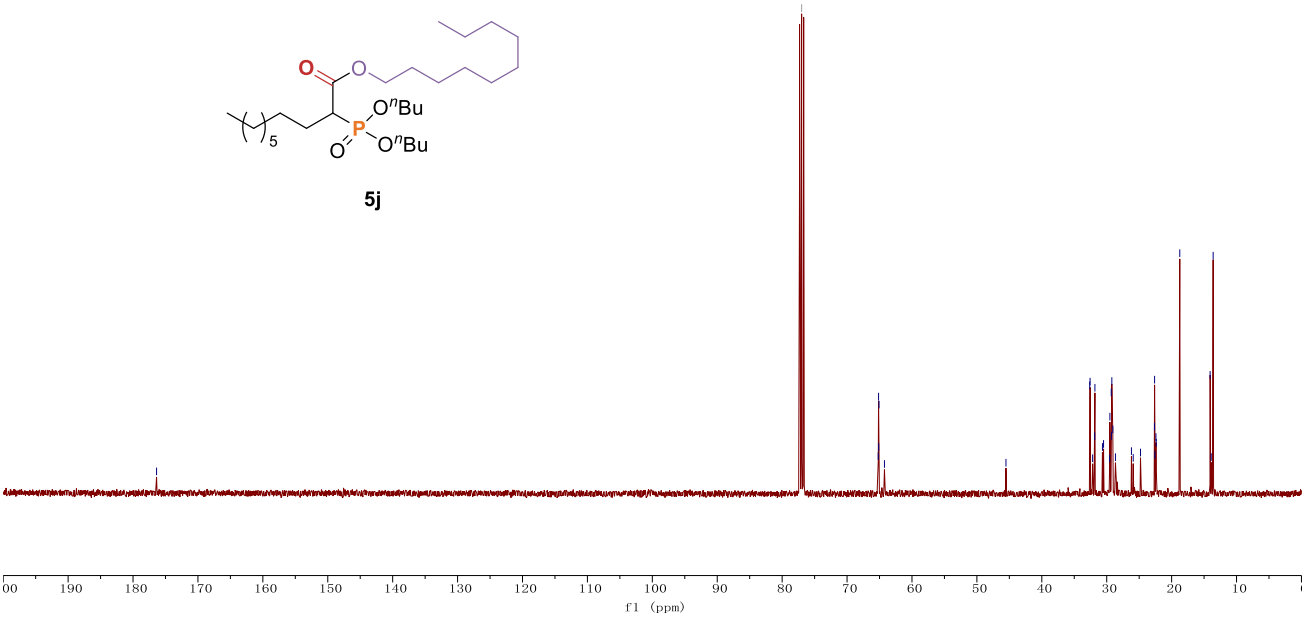
5j



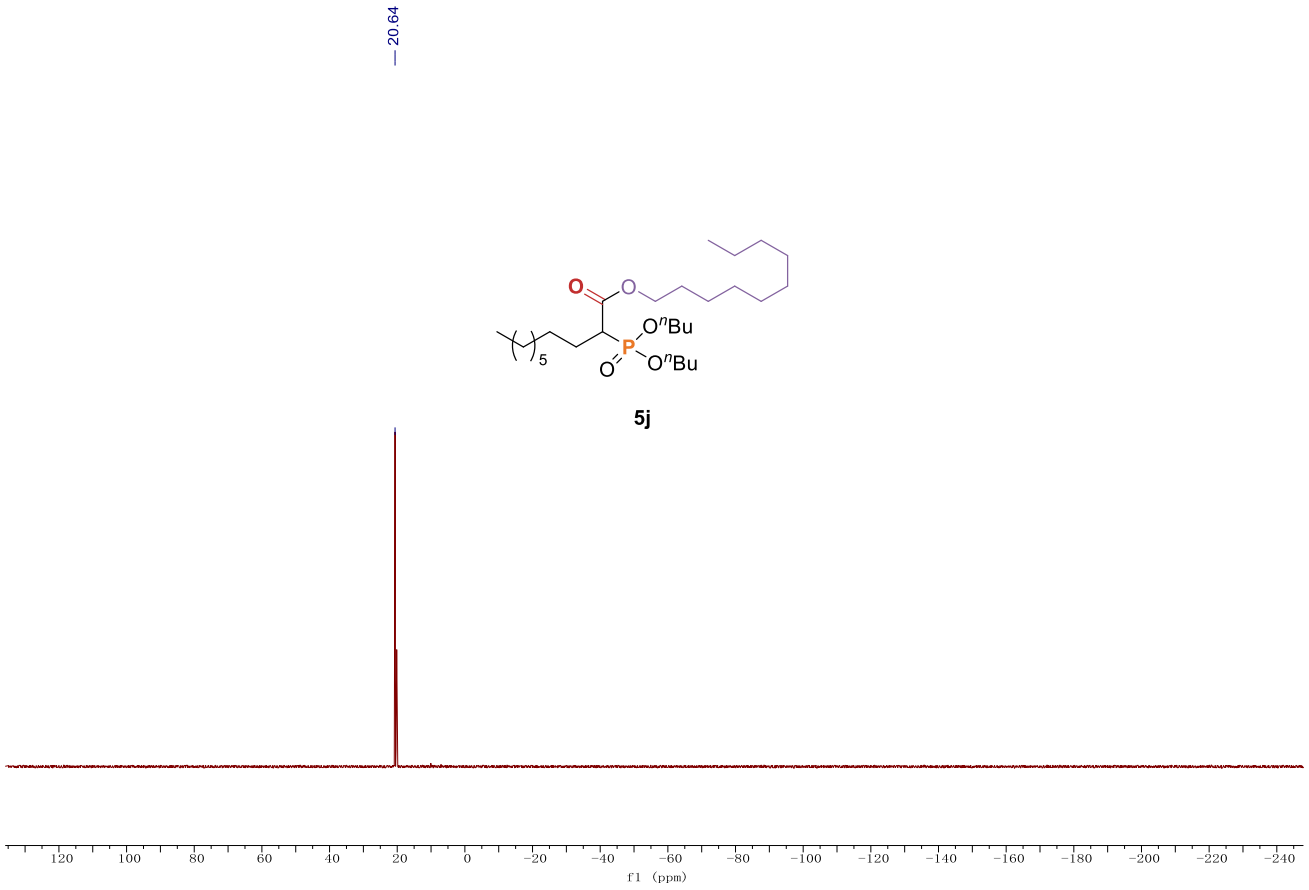
13C NMR CDCl3 100.62MHz



5j

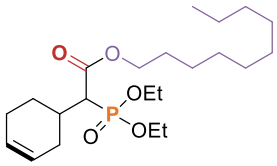


31P NMR CDCl3 161.97MHz

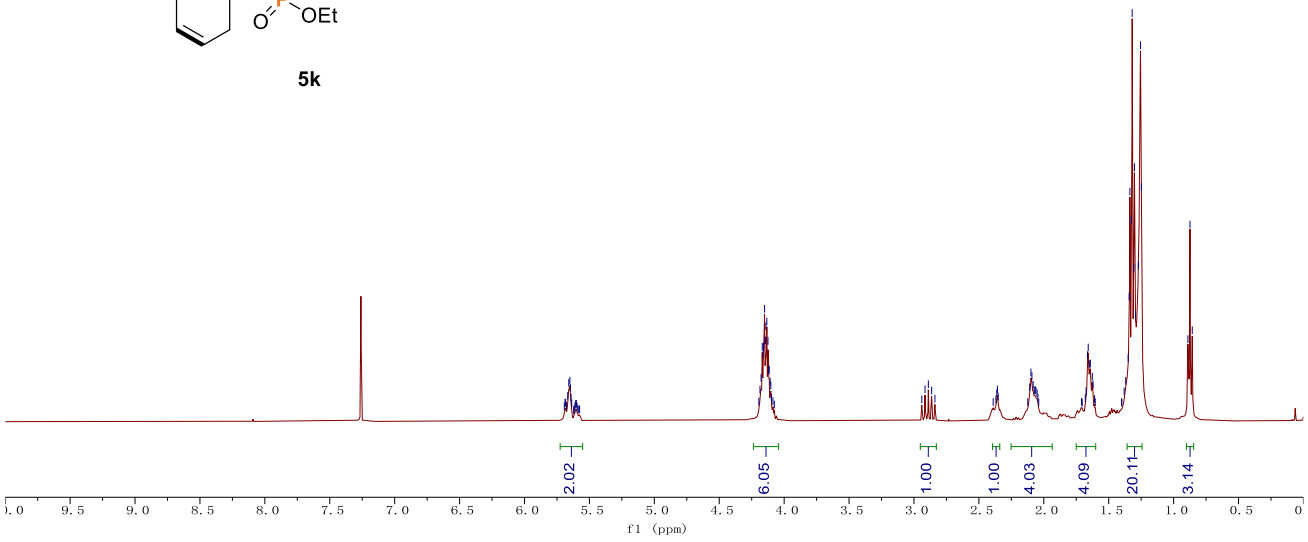


5j

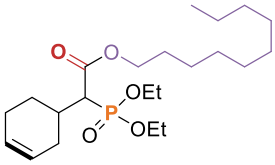
1H NMR CDCl3 400.13MHz



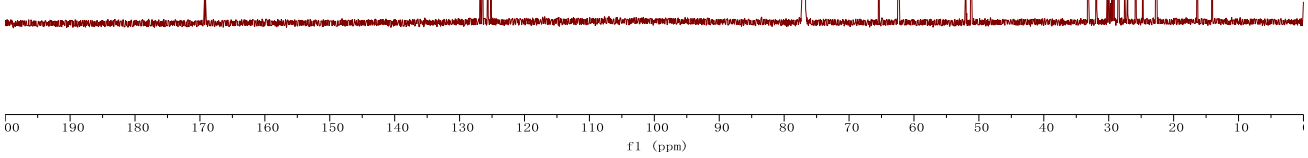
5k



13C NMR CDCl3 176.08MHz

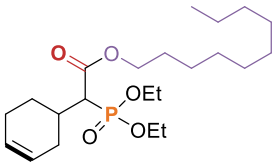


5k

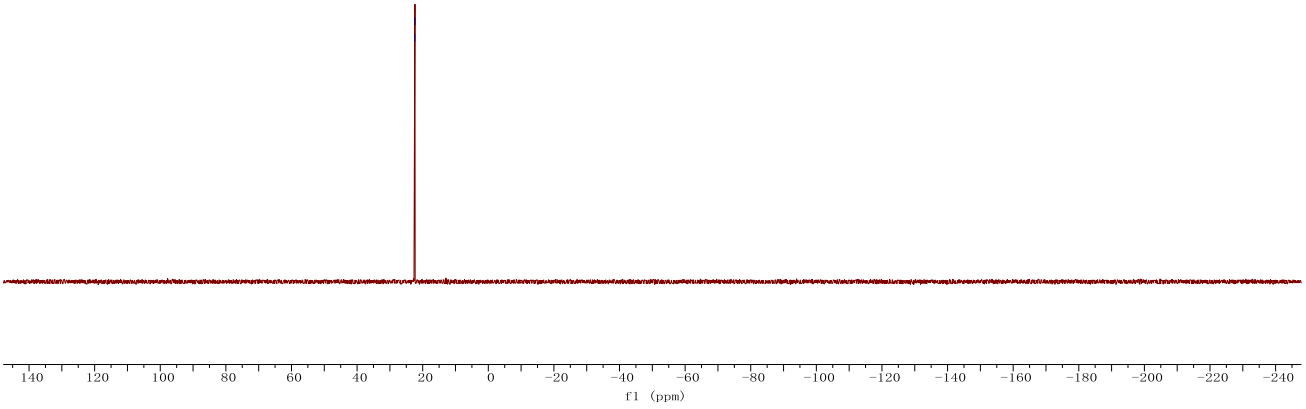


31P NMR CDCl3 161.97MHz

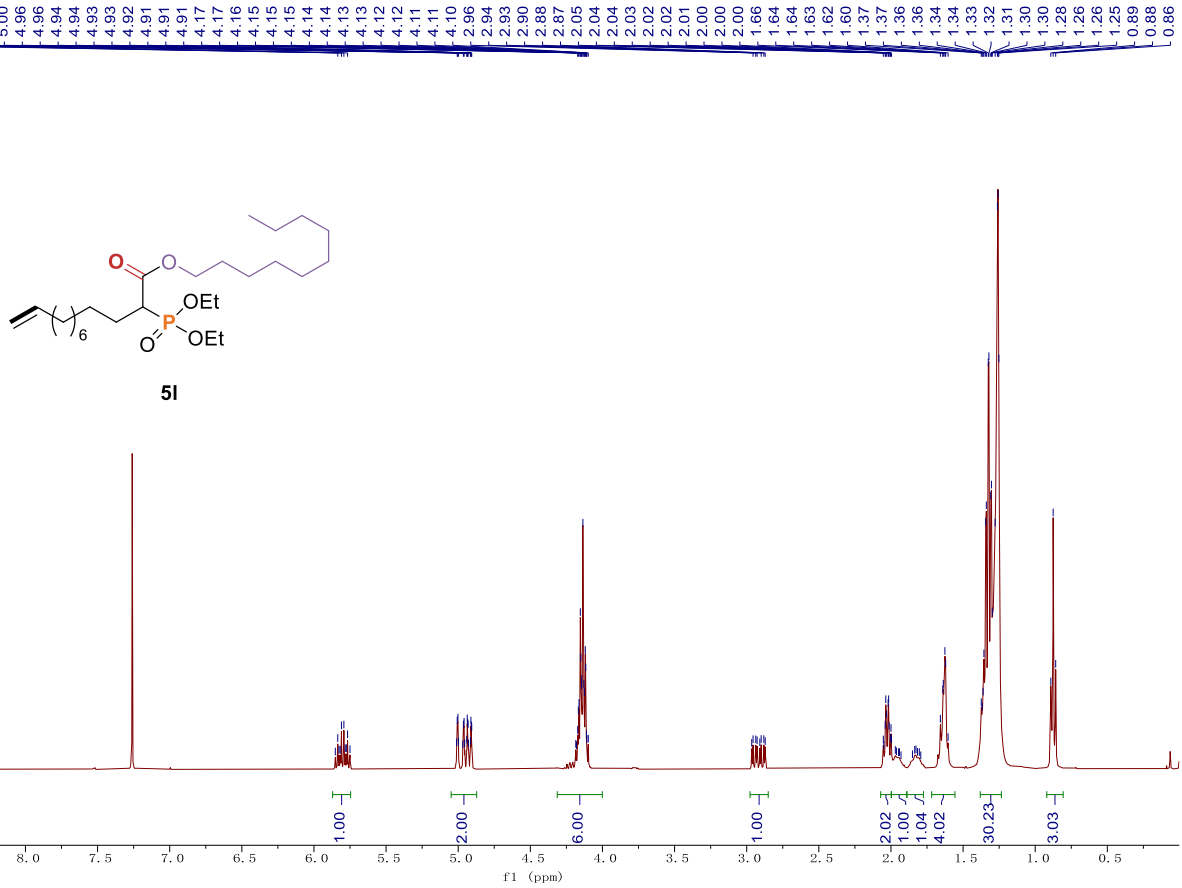
22.43
22.36



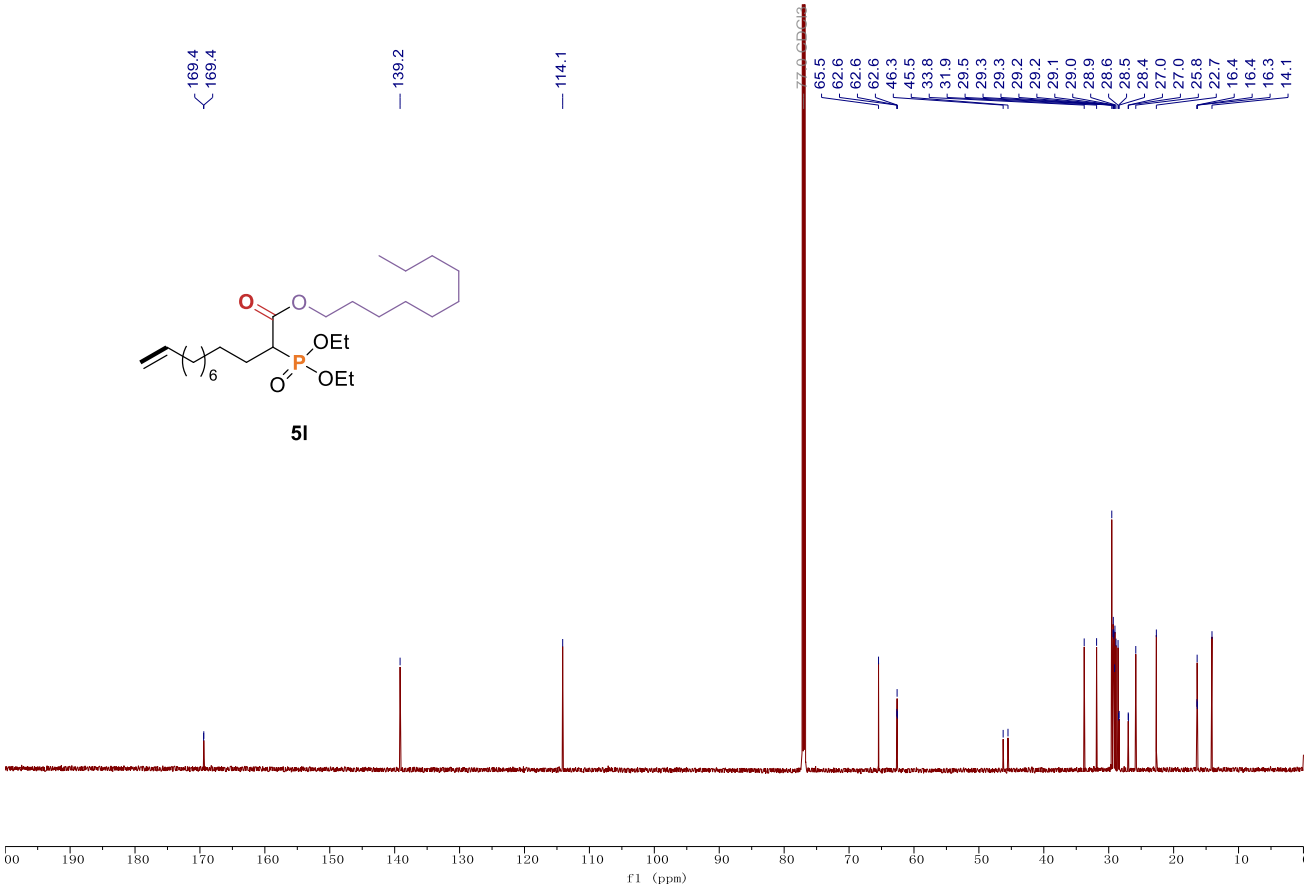
5k



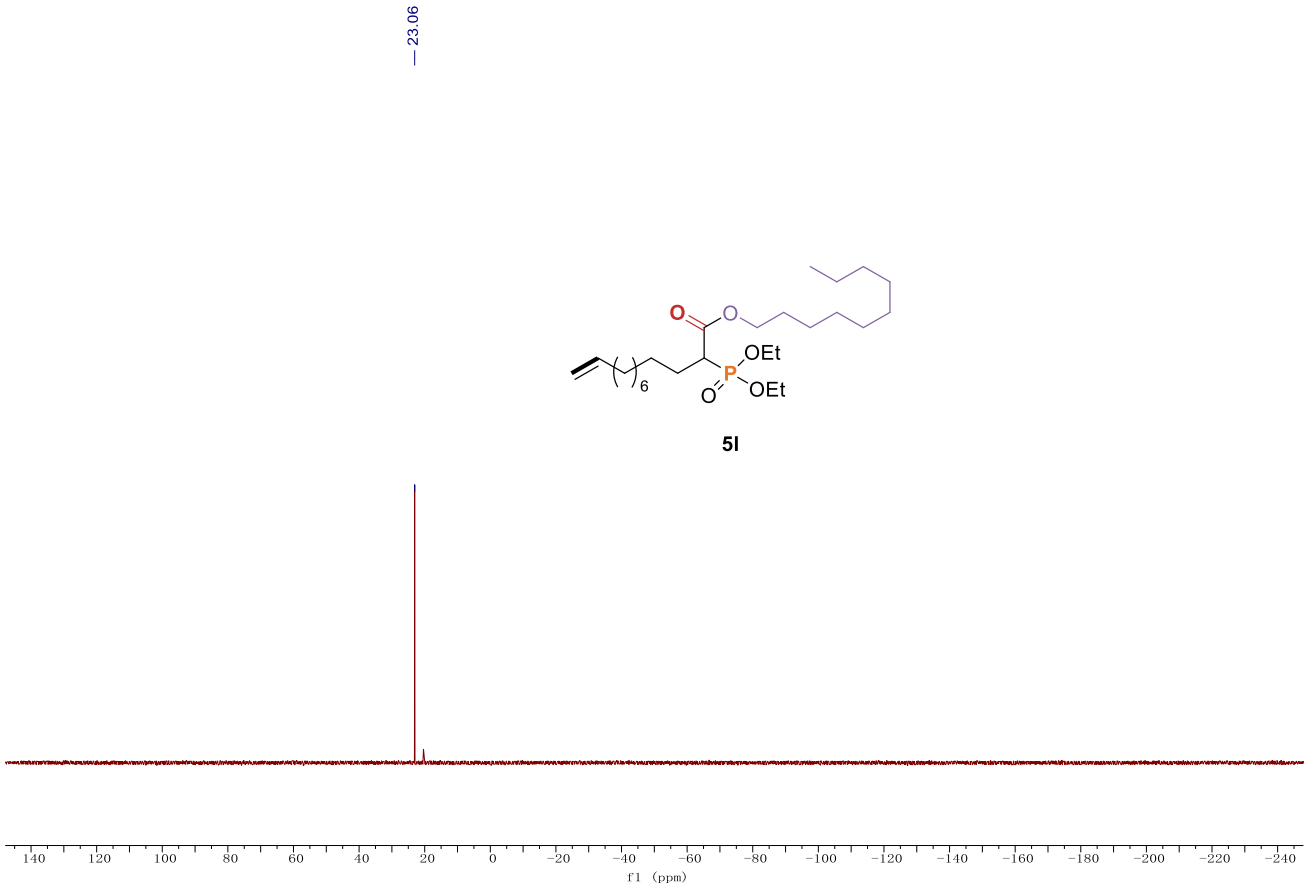
1H NMR CDCl3 400.13MHz



13C NMR CDCl3 176.08MHz

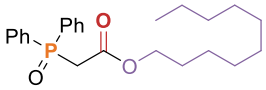


31P NMR CDCl3 161.97MHz

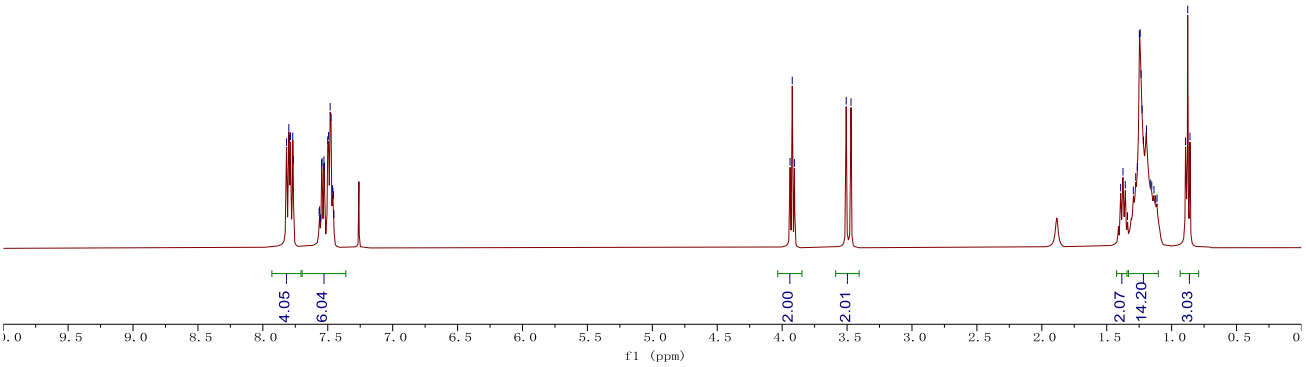


5l

1H NMR CDCl3 400.13MHz

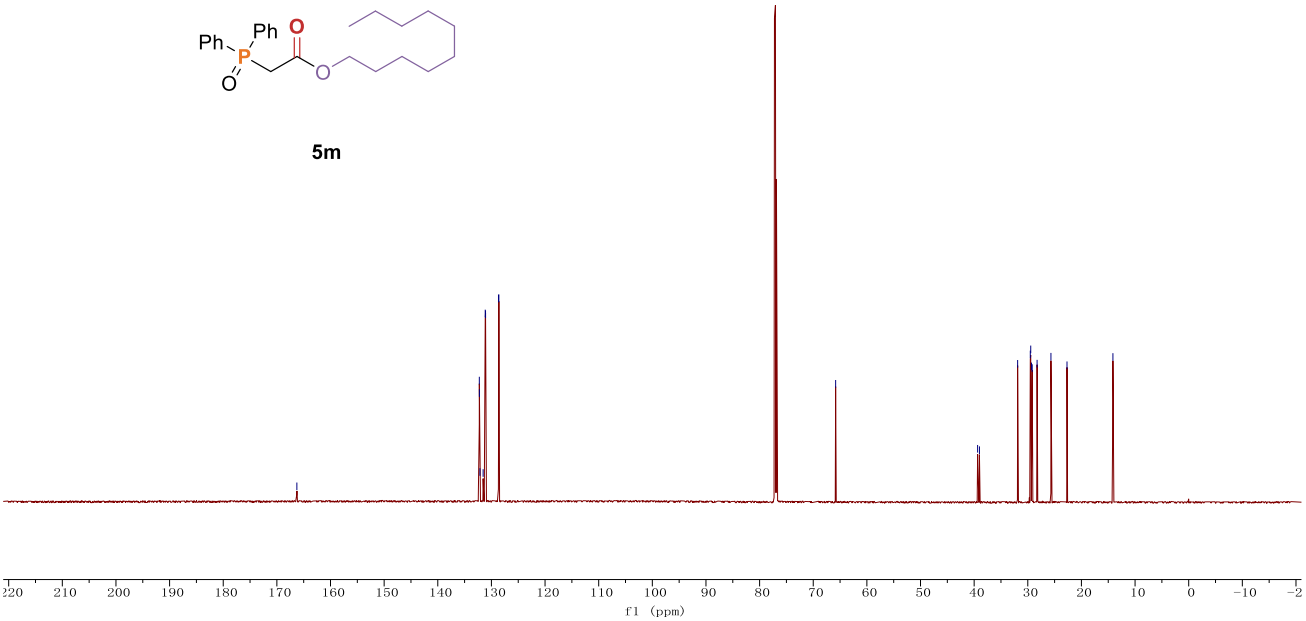


5m

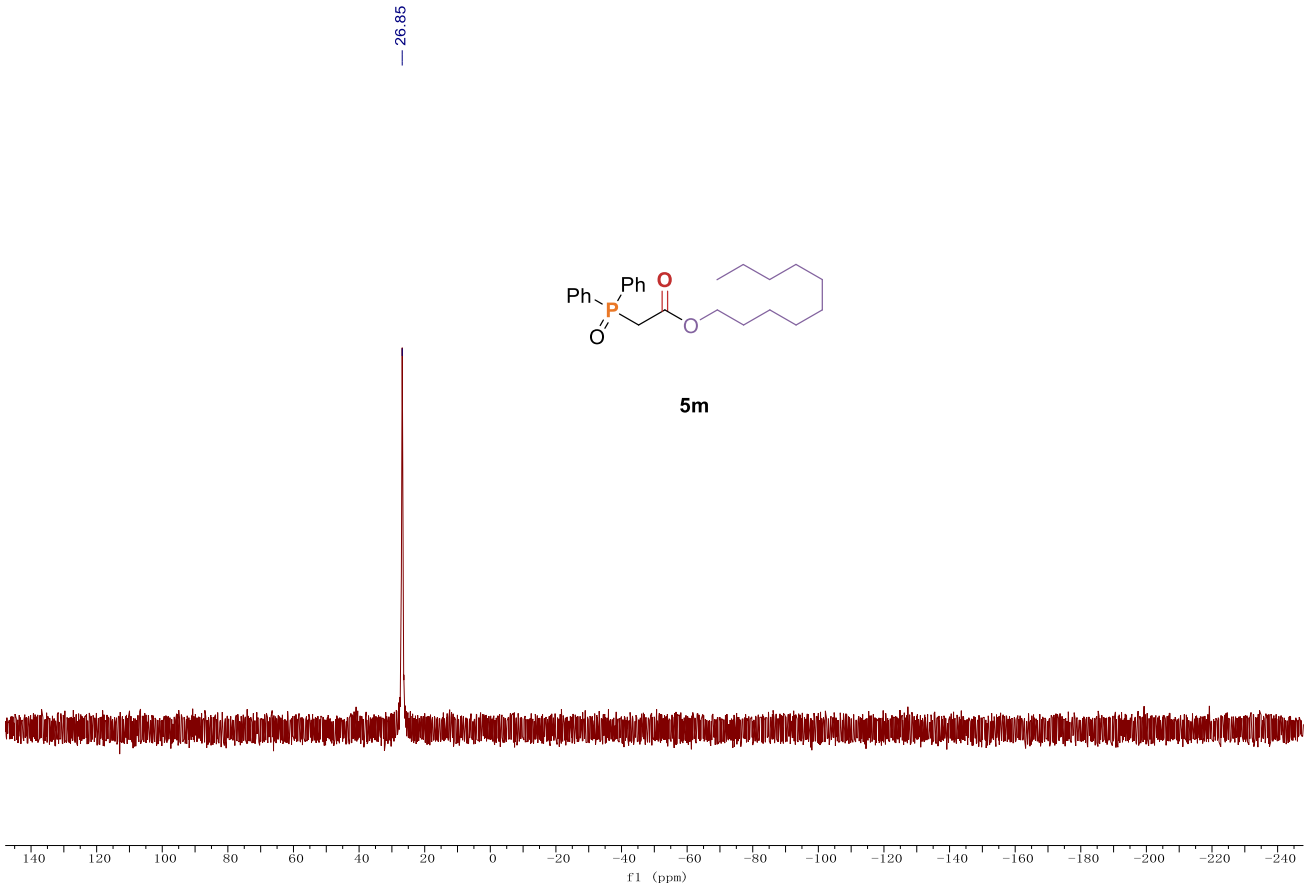


13C NMR CDCl3 176.08MHz

5m

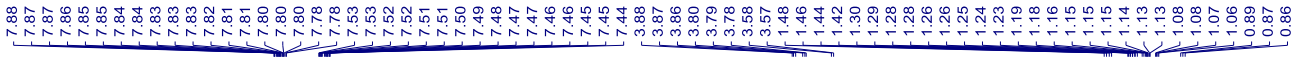


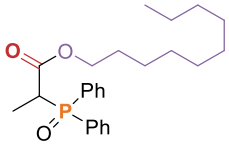
31P NMR CDCl3 161.97MHz



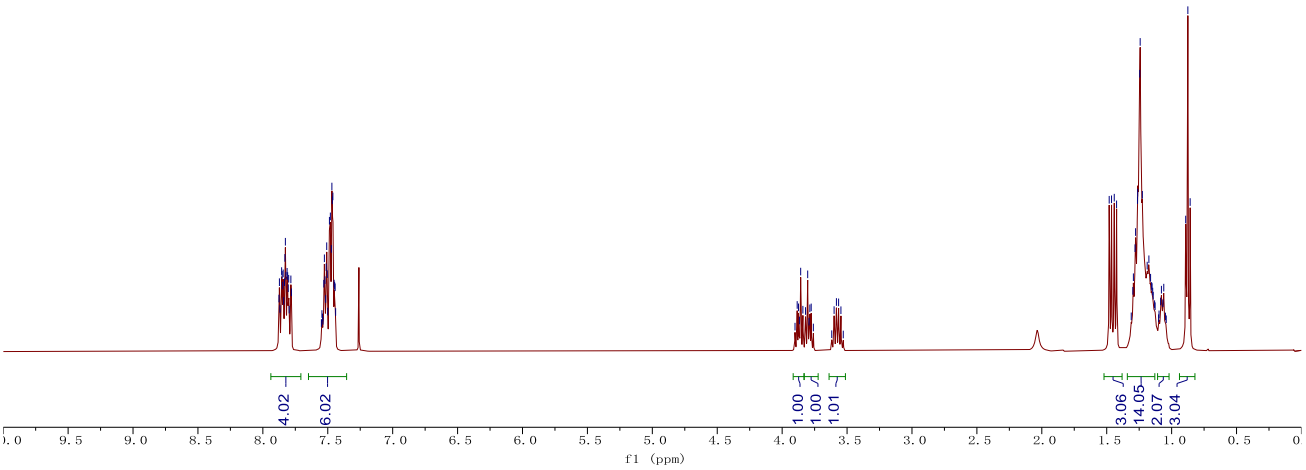
5m

1H NMR CDCl3 400.13MHz

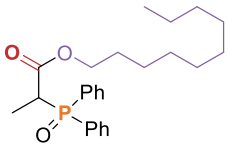




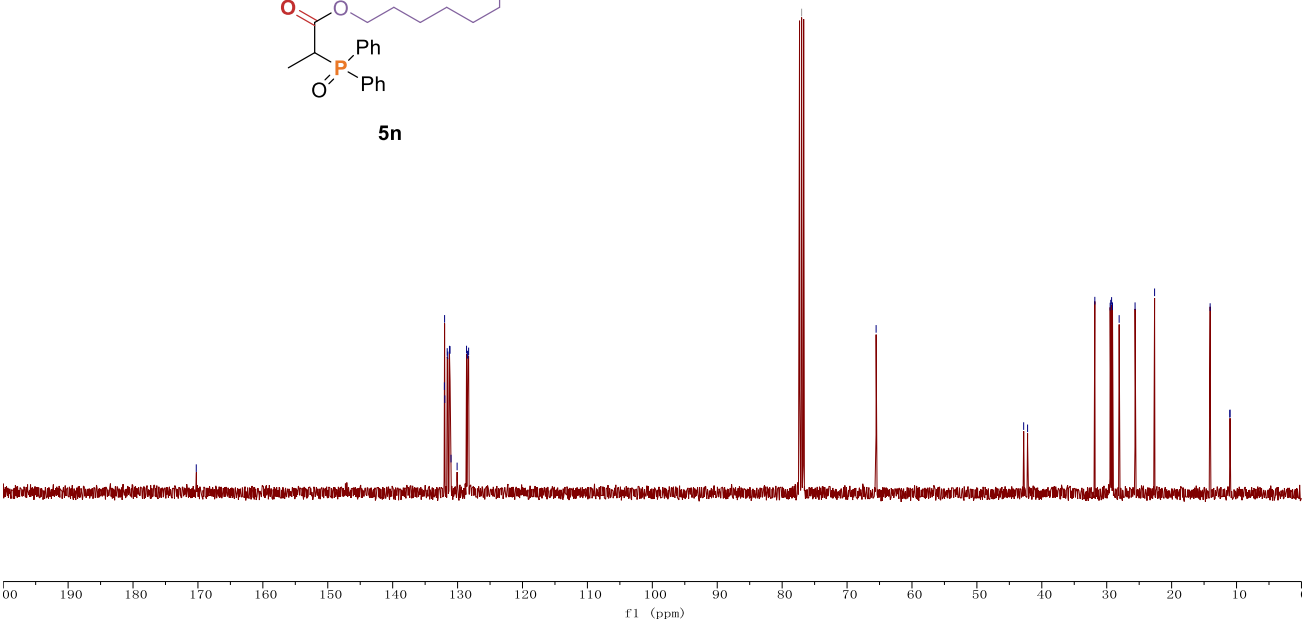
5n



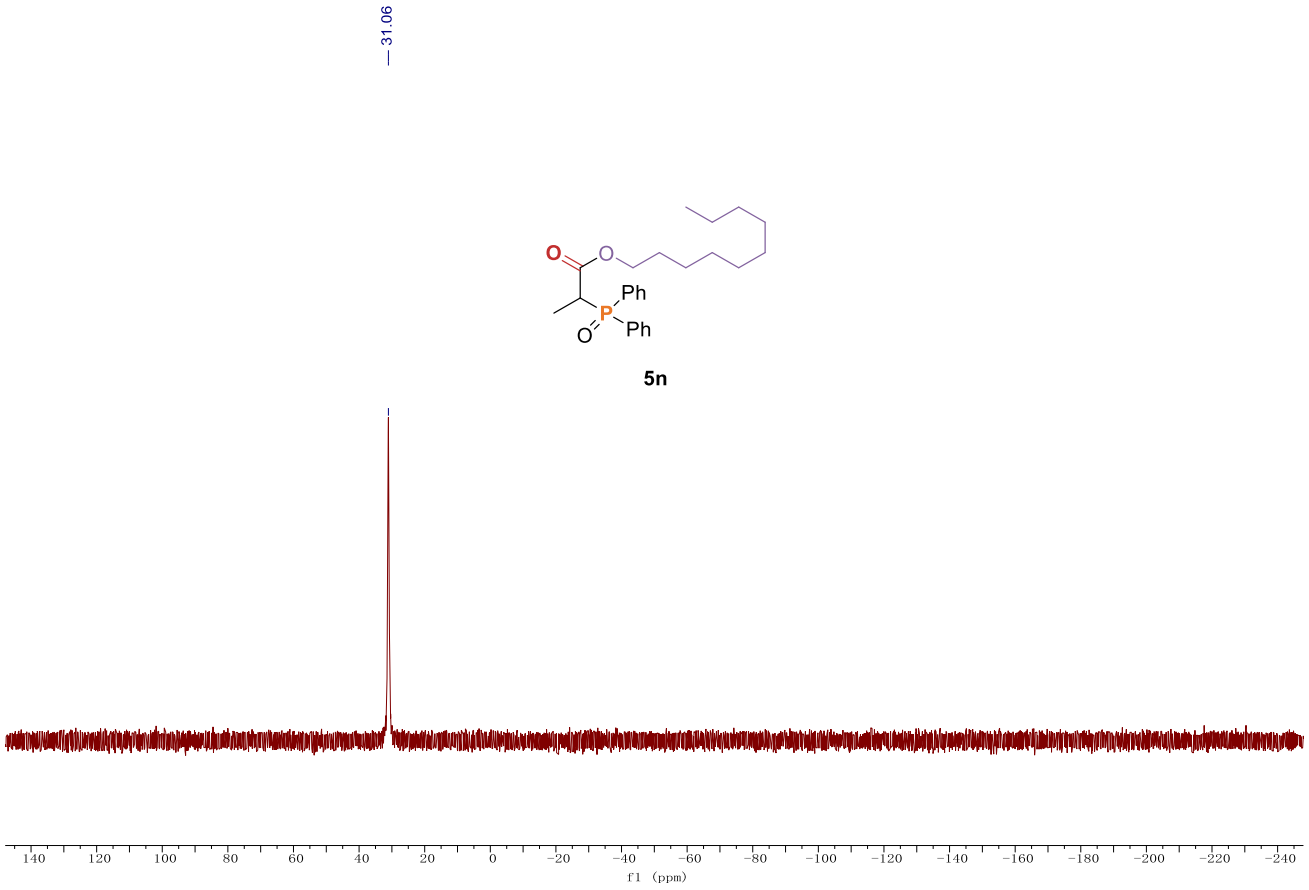
13C NMR CDCl3 100.62MHz



5n

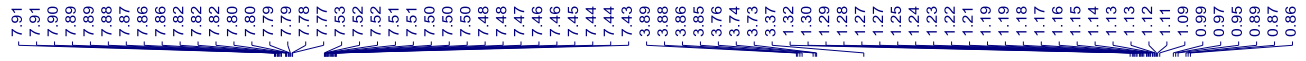


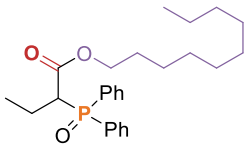
31P NMR CDCl3 161.97MHz



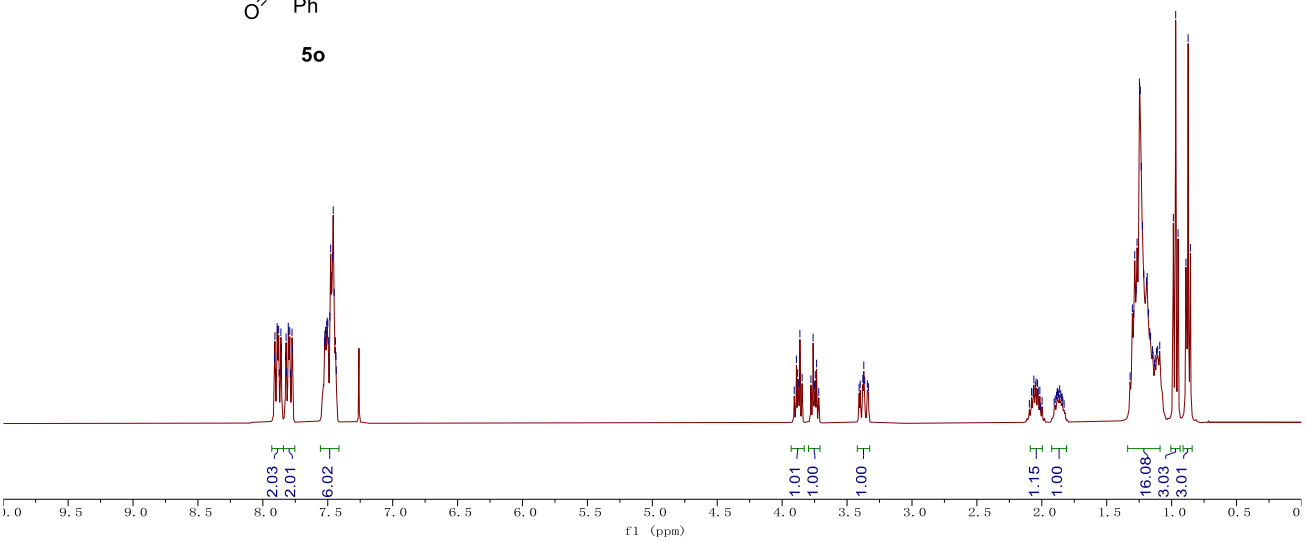
5n

1H NMR CDCl3 400.13MHz

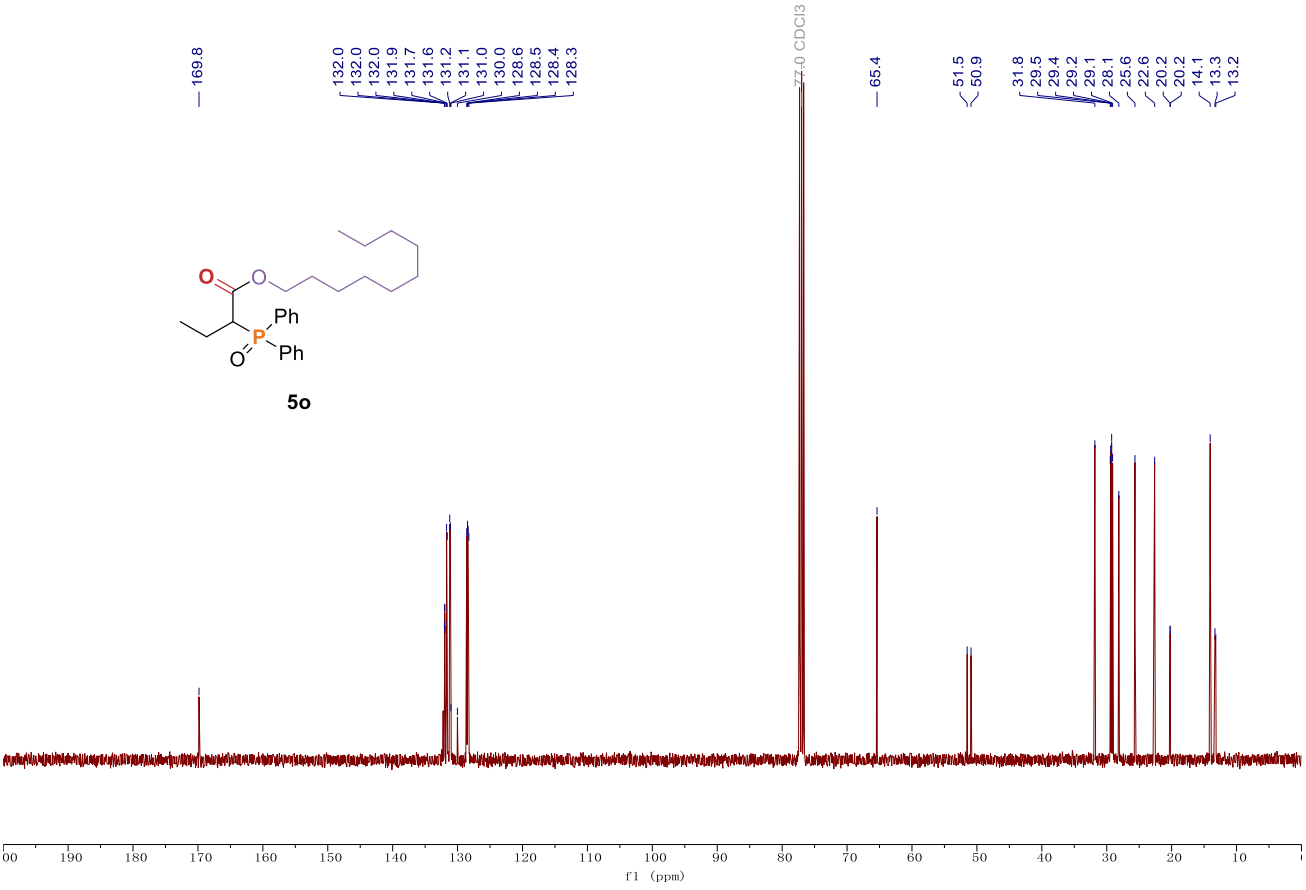




5o

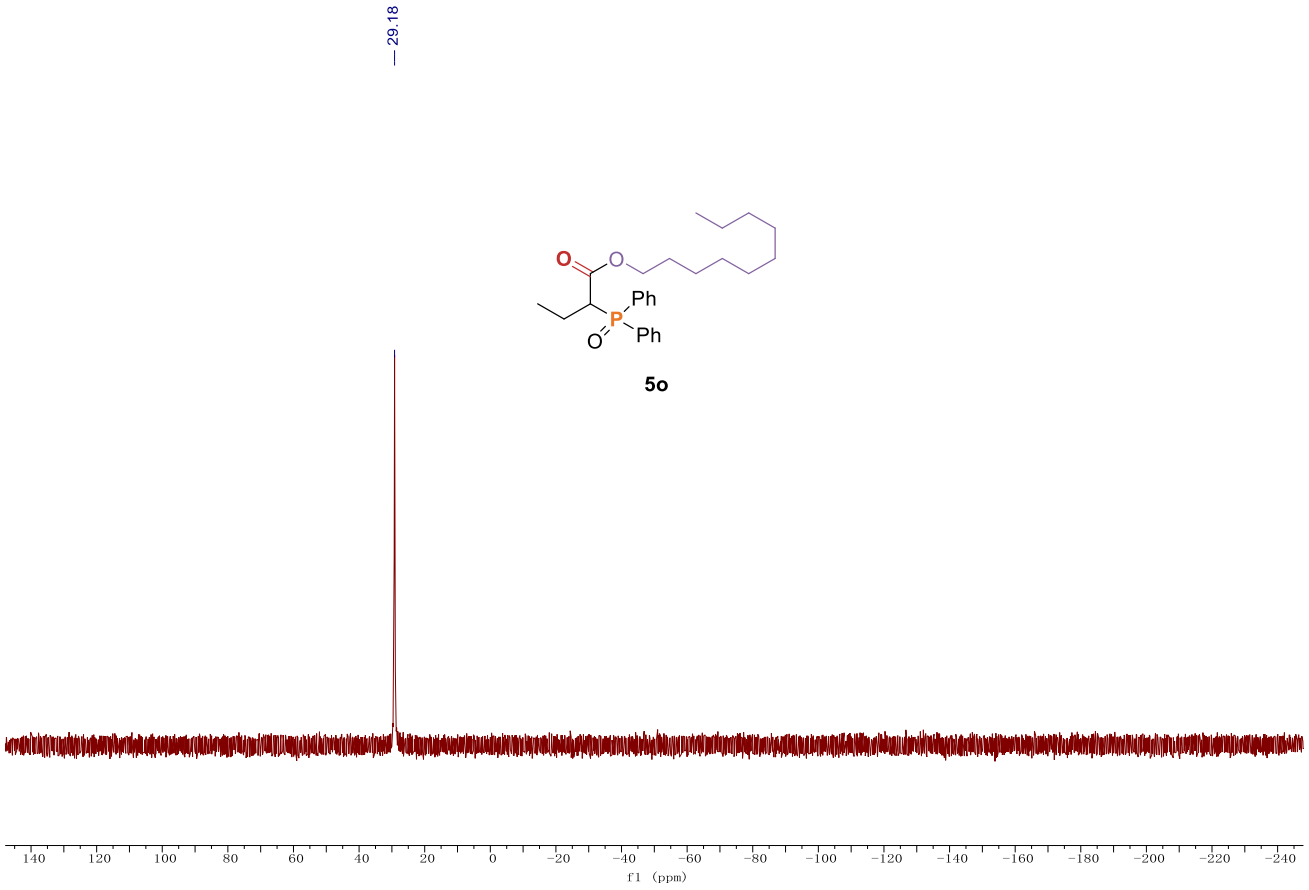


13C NMR CDCl3 100.62MHz



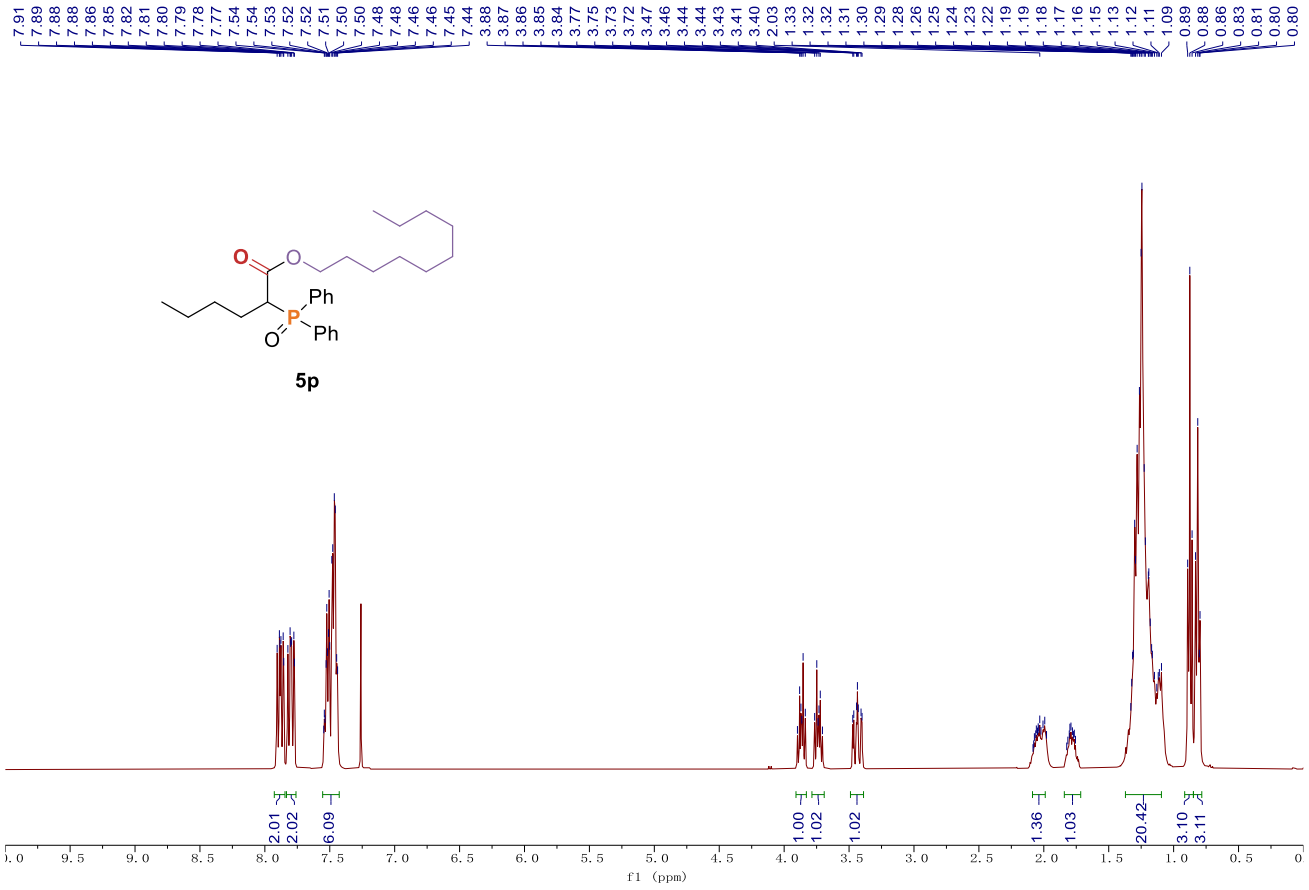
5o

31P NMR CDCl3 161.97MHz

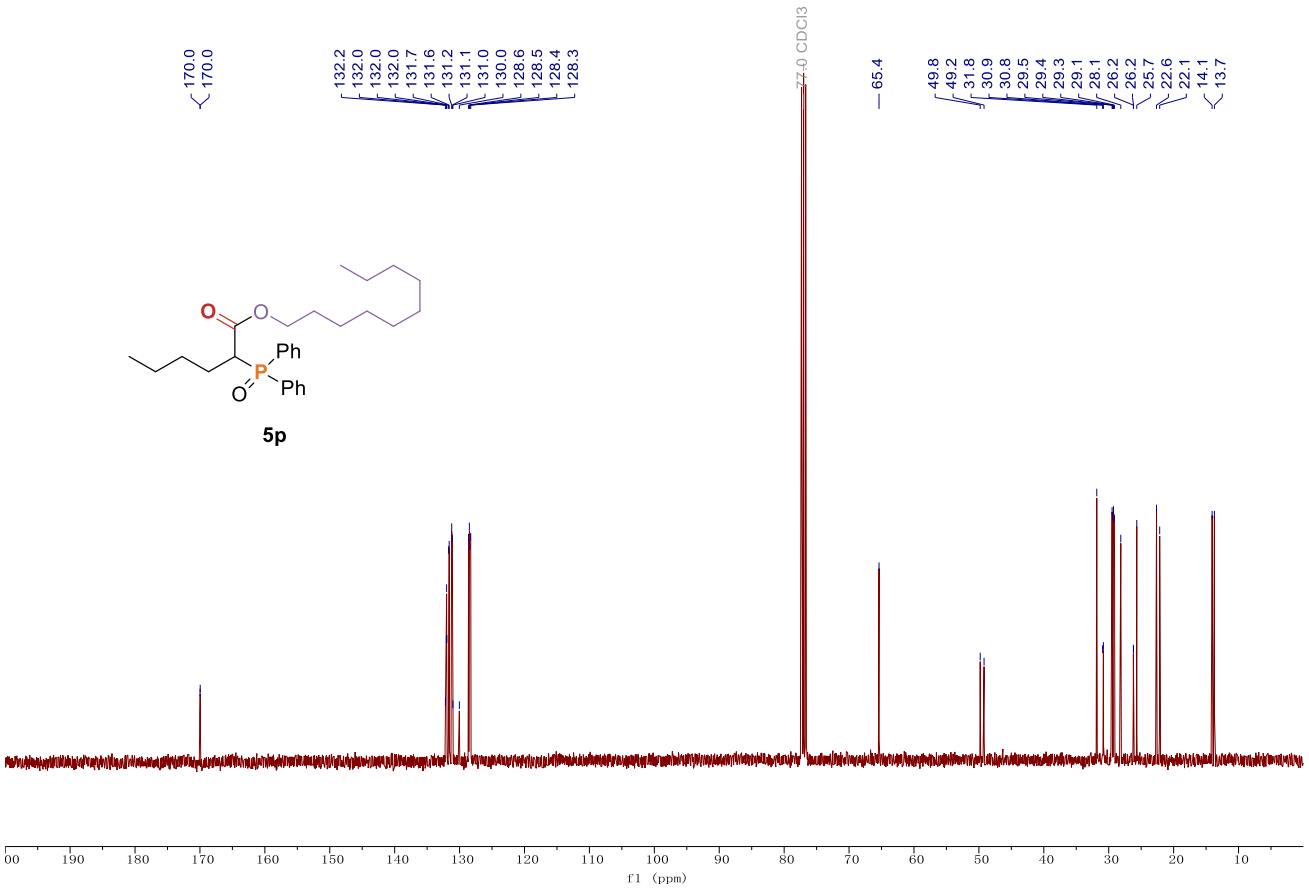


5o

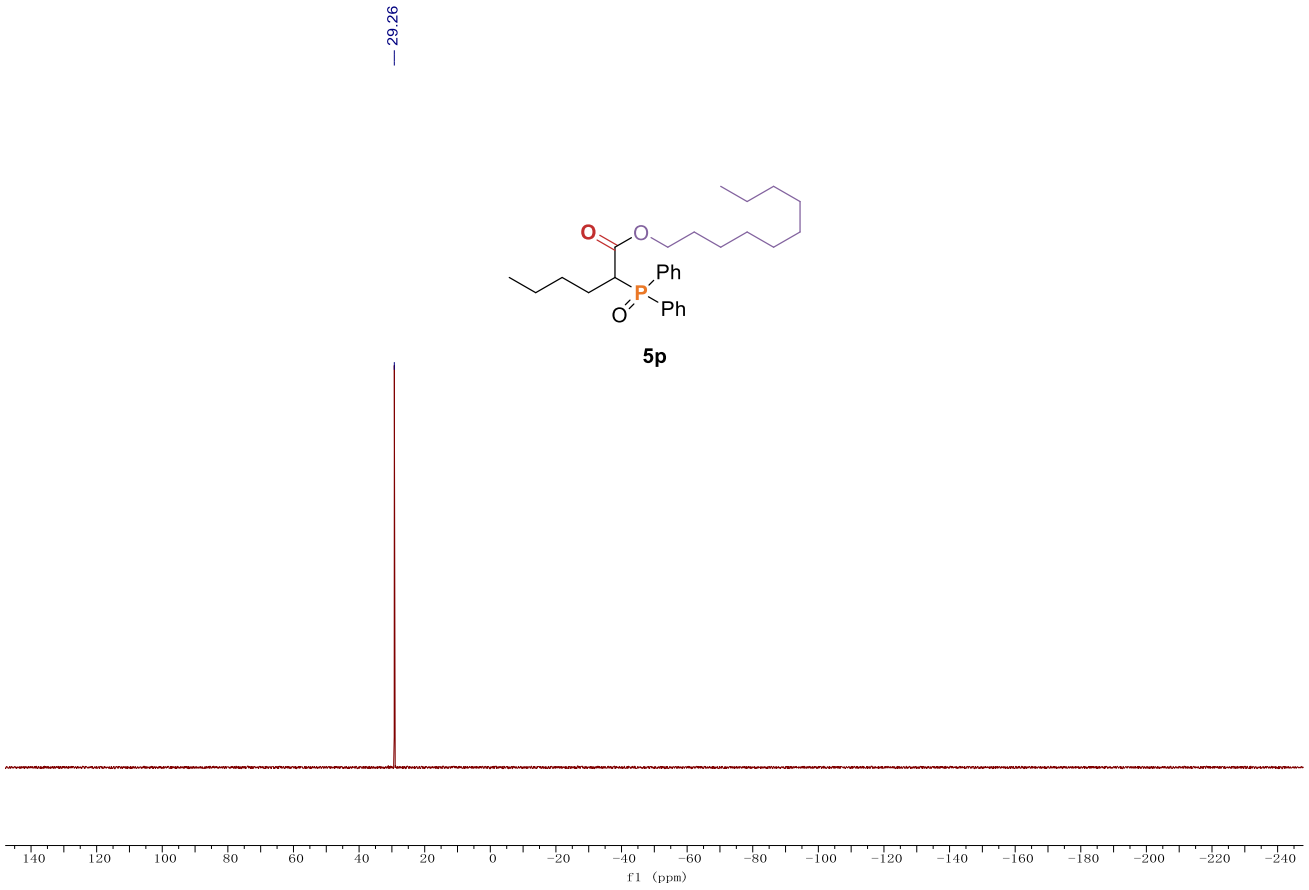
1H NMR CDCl3 400.13MHz



13C NMR CDCl3 100.62MHz

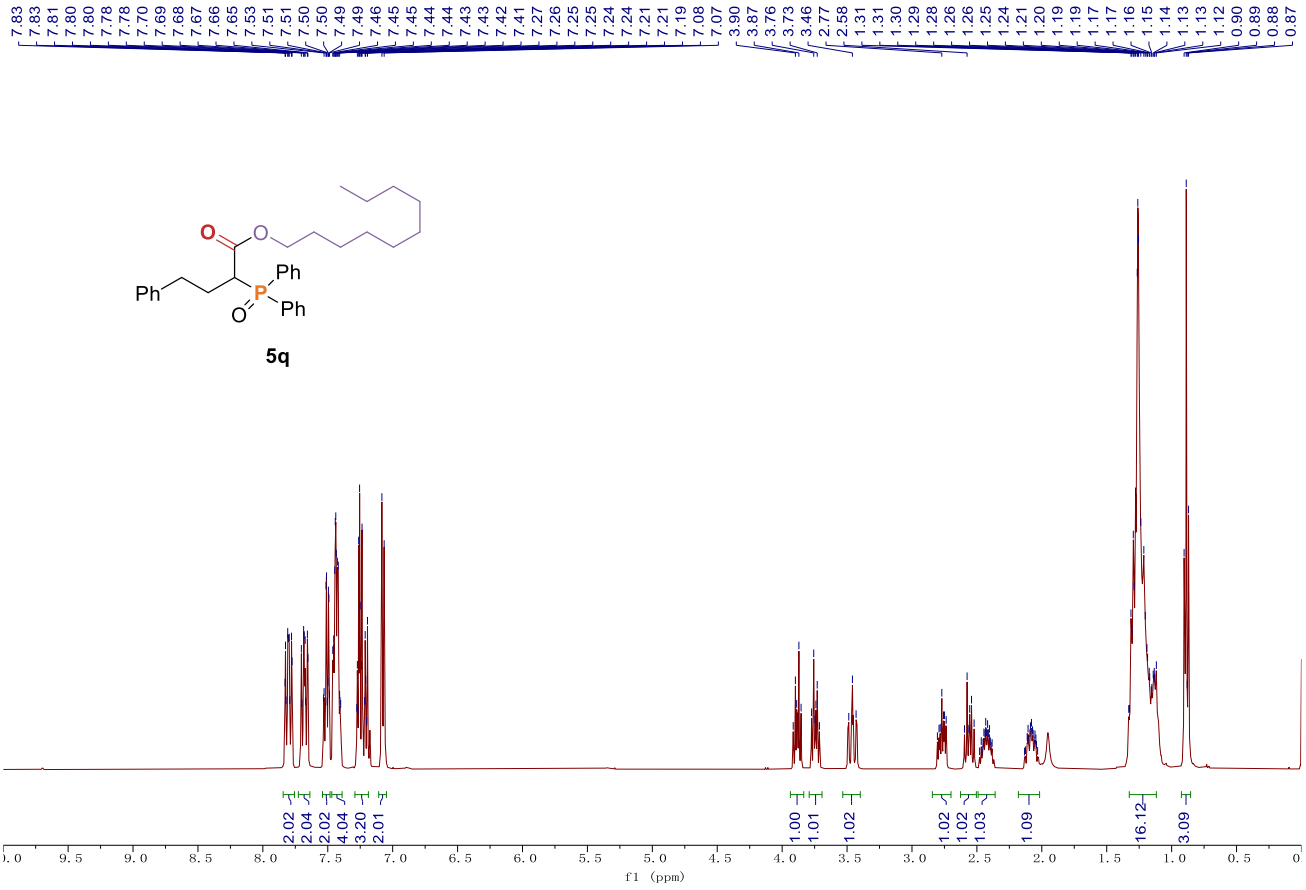


31P NMR CDCl3 161.97MHz



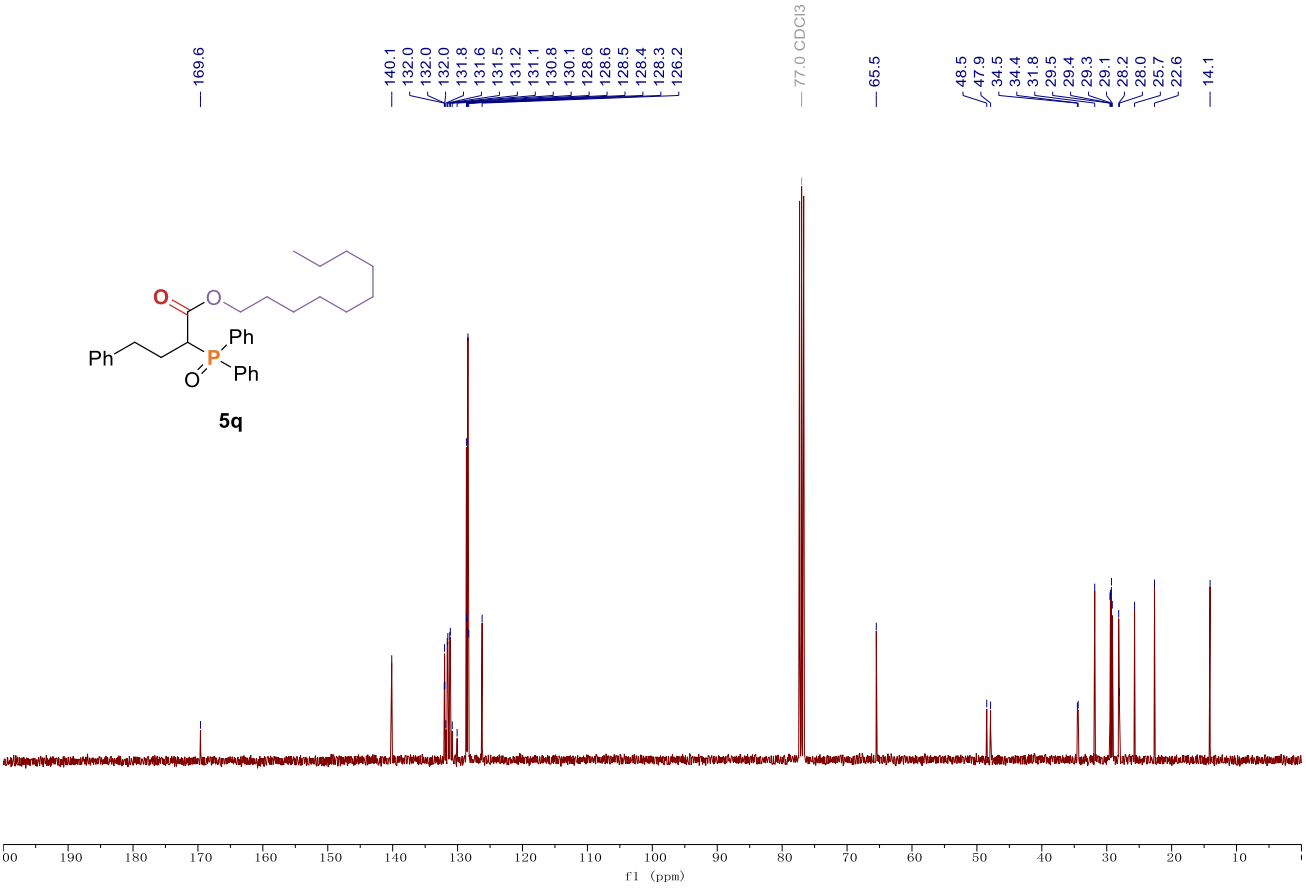
5p

1H NMR CDCl3 400.13MHz



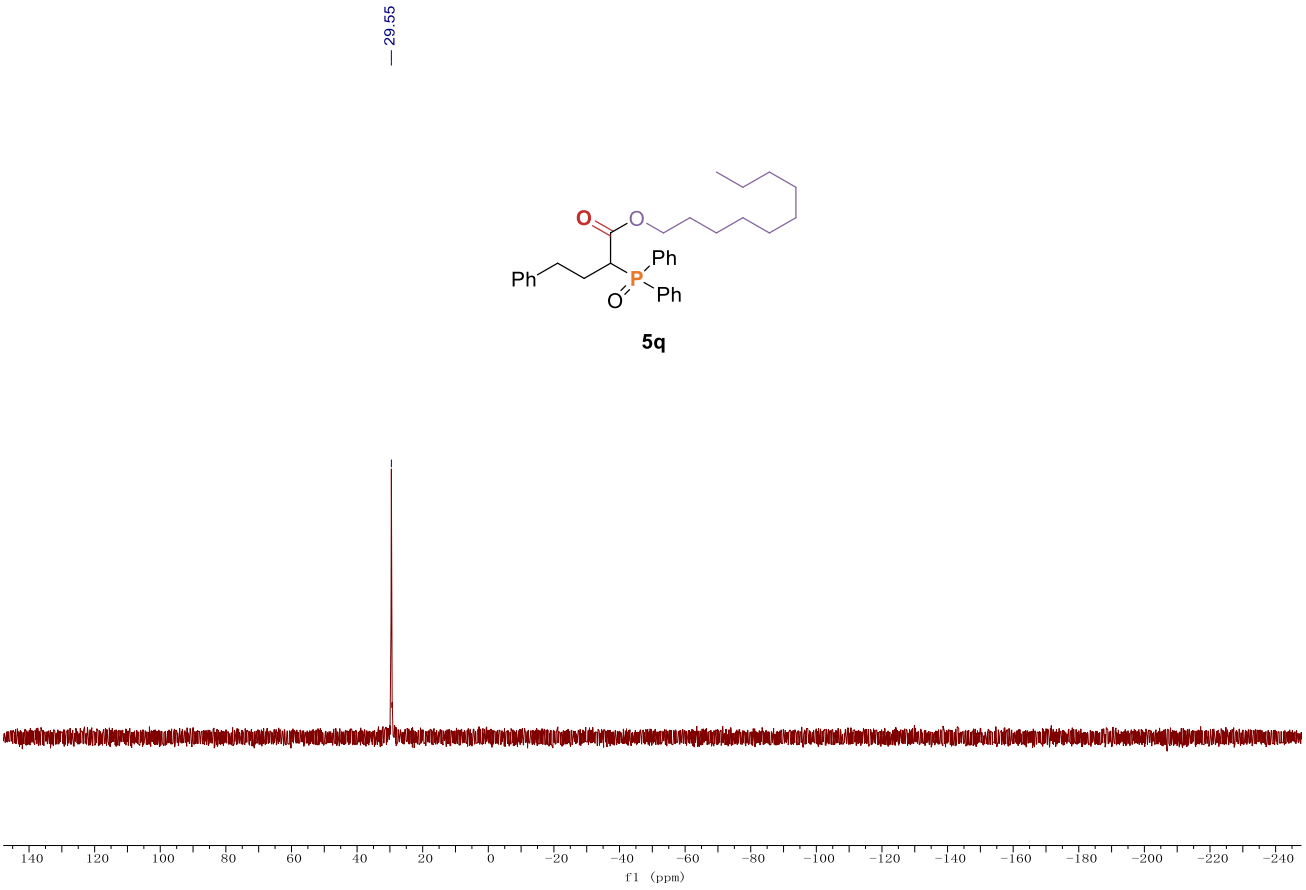
5q

13C NMR CDCl3 100.62MHz



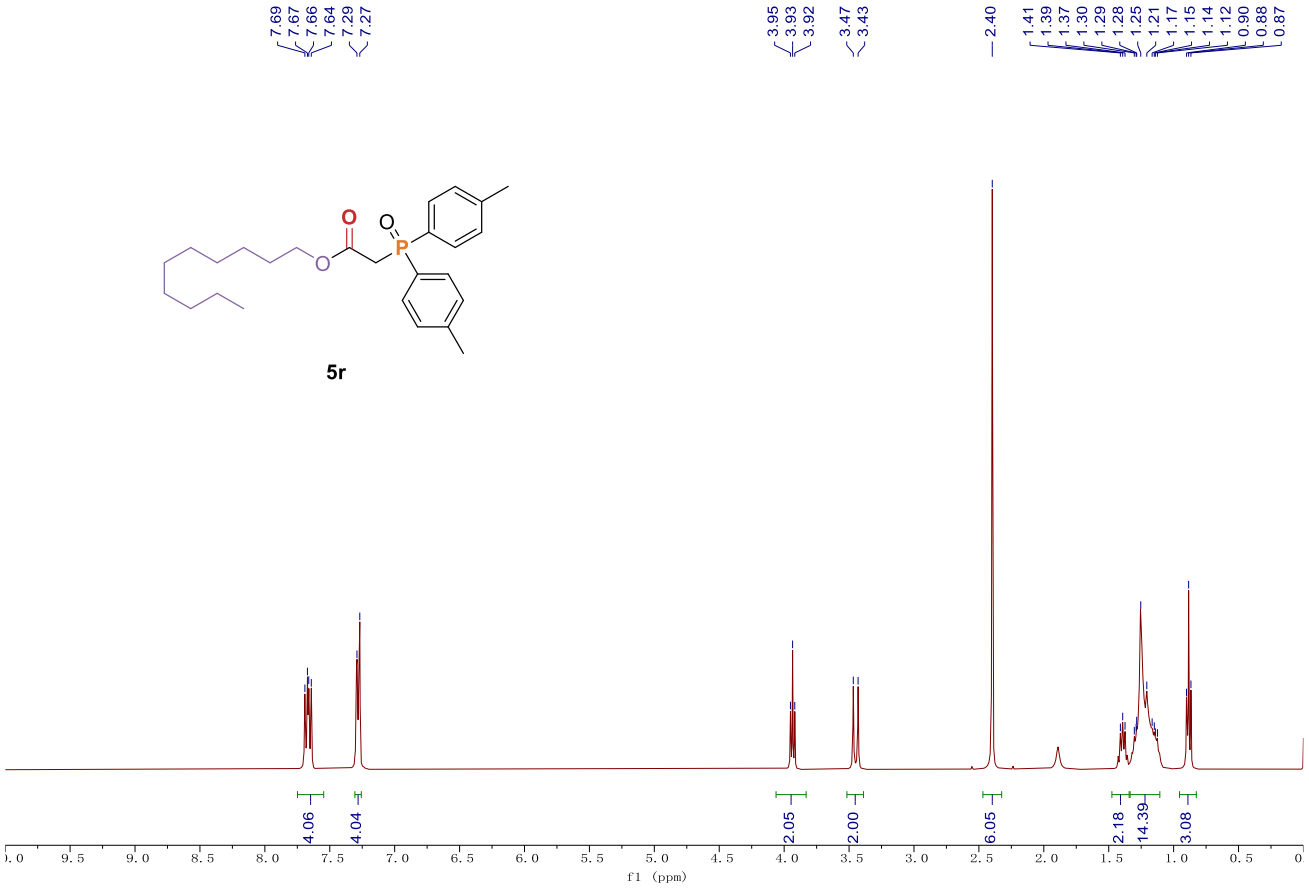
5q

31P NMR CDCl3 161.97MHz



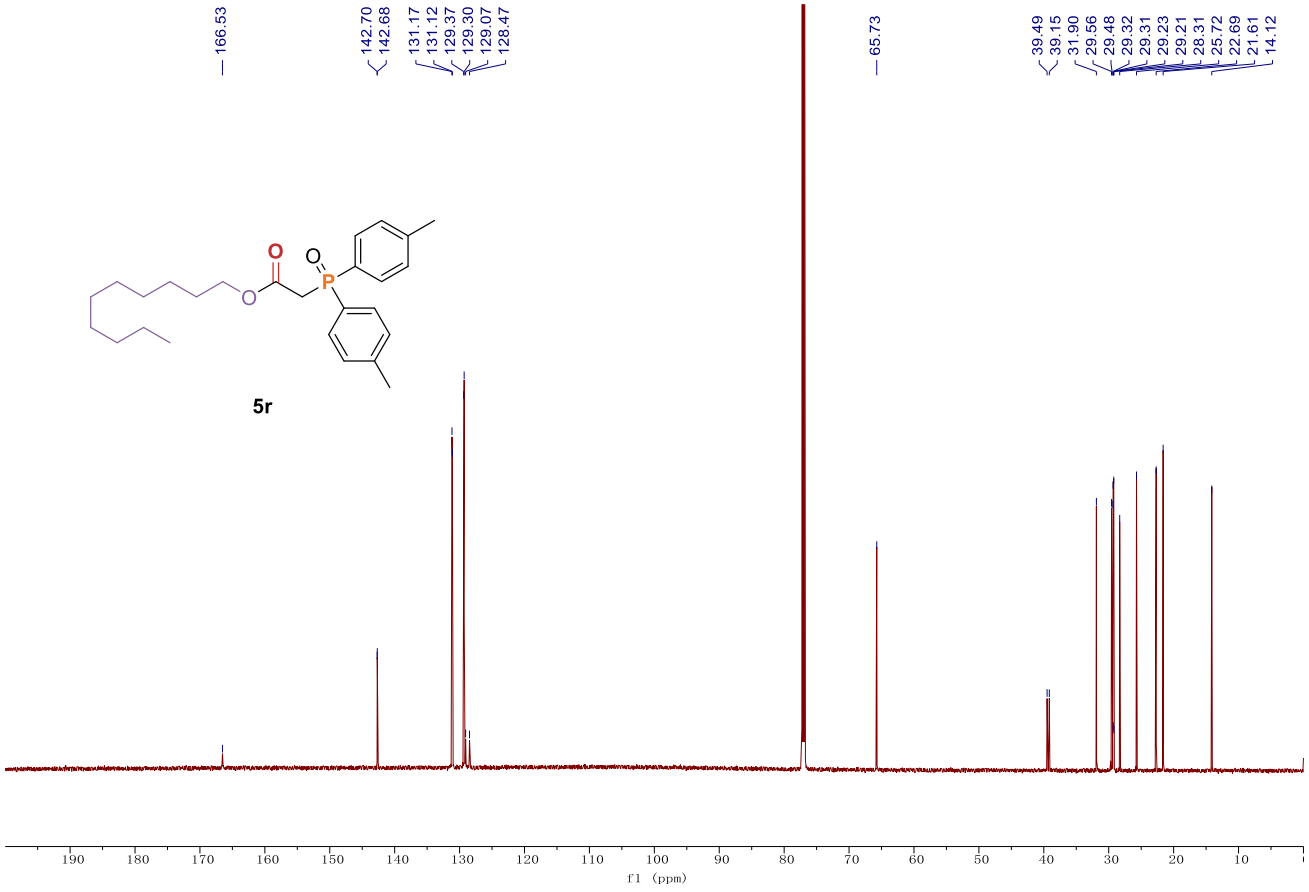
5q

1H NMR CDCl3 400.13MHz



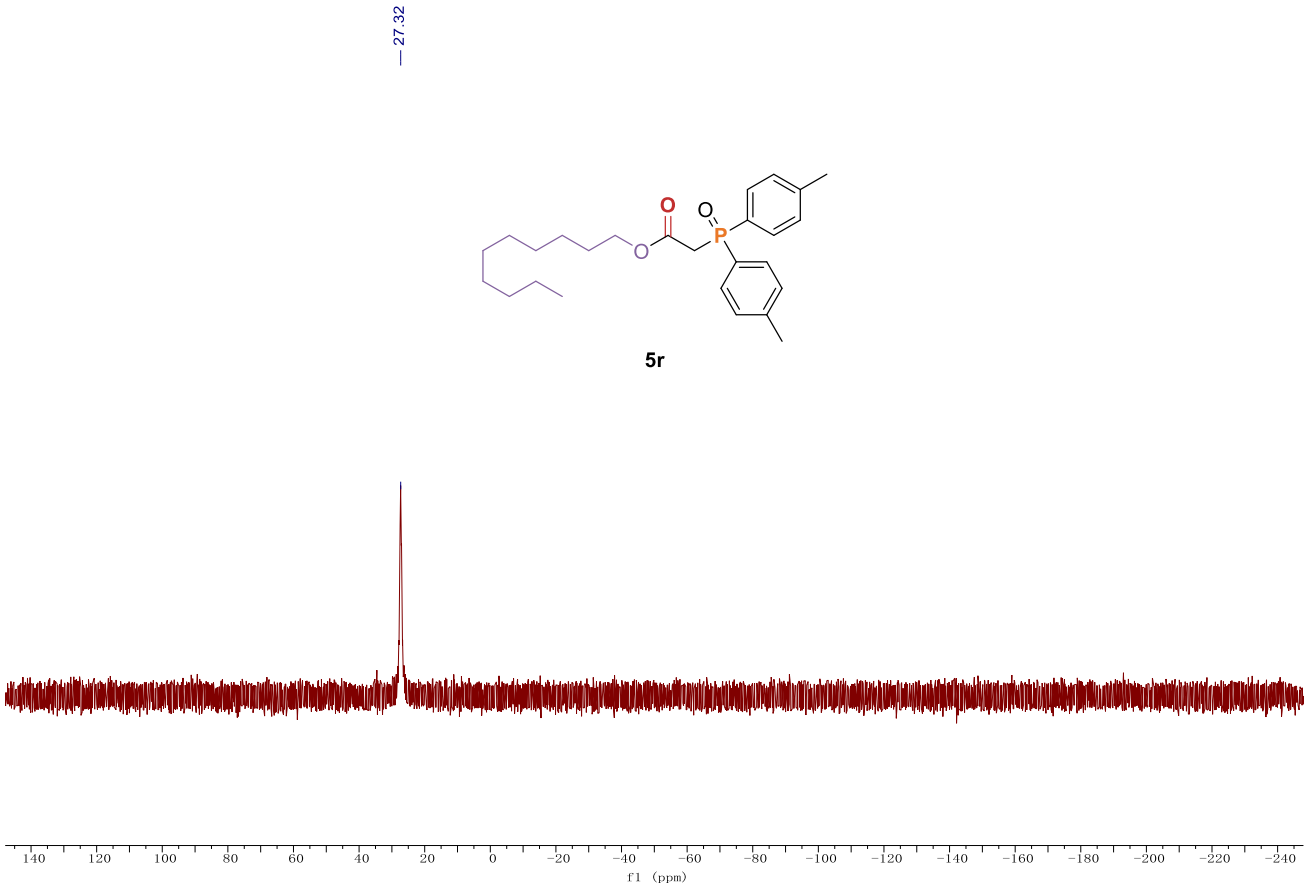
5r

13C NMR CDCl3 176.08MHz



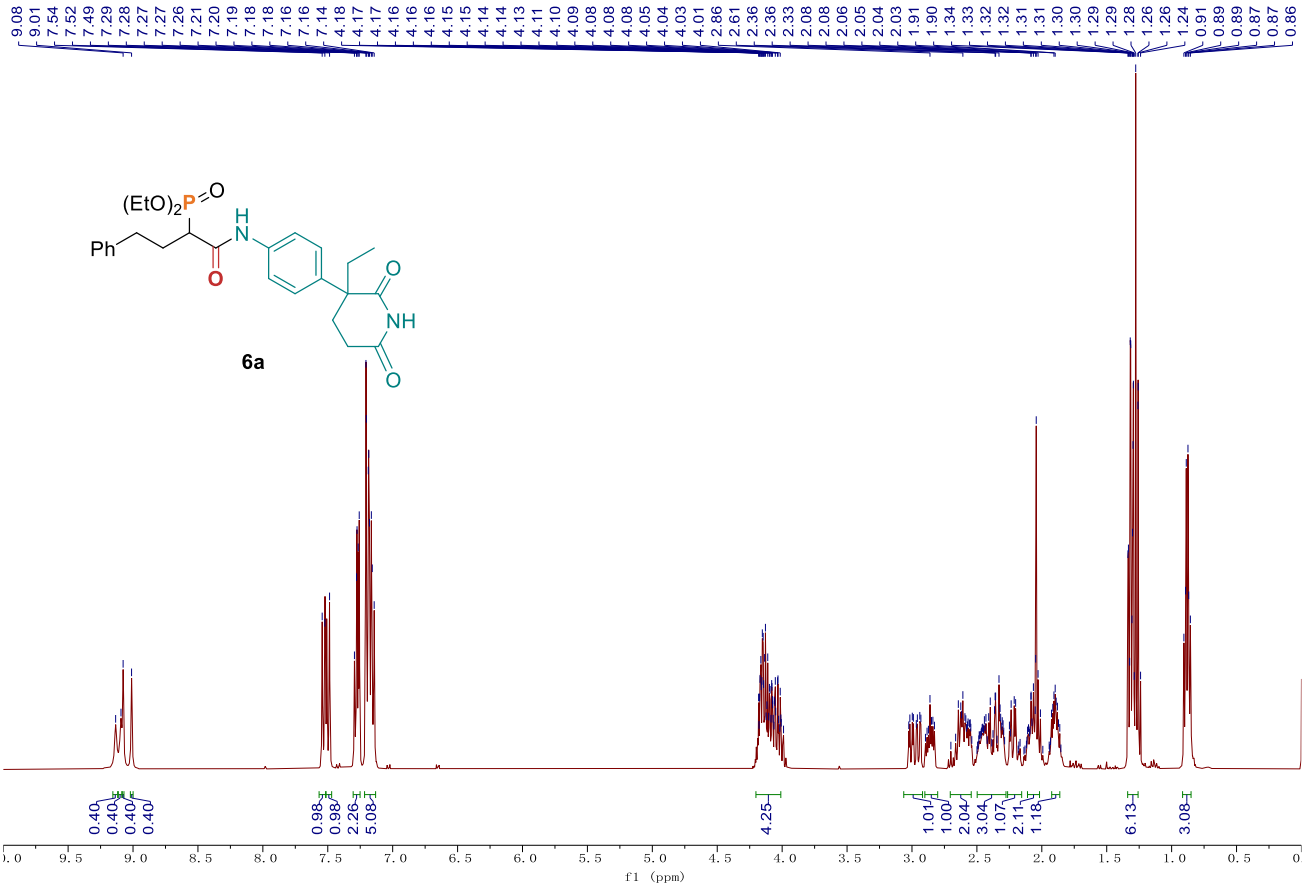
5r

31P NMR CDCl3 161.97MHz

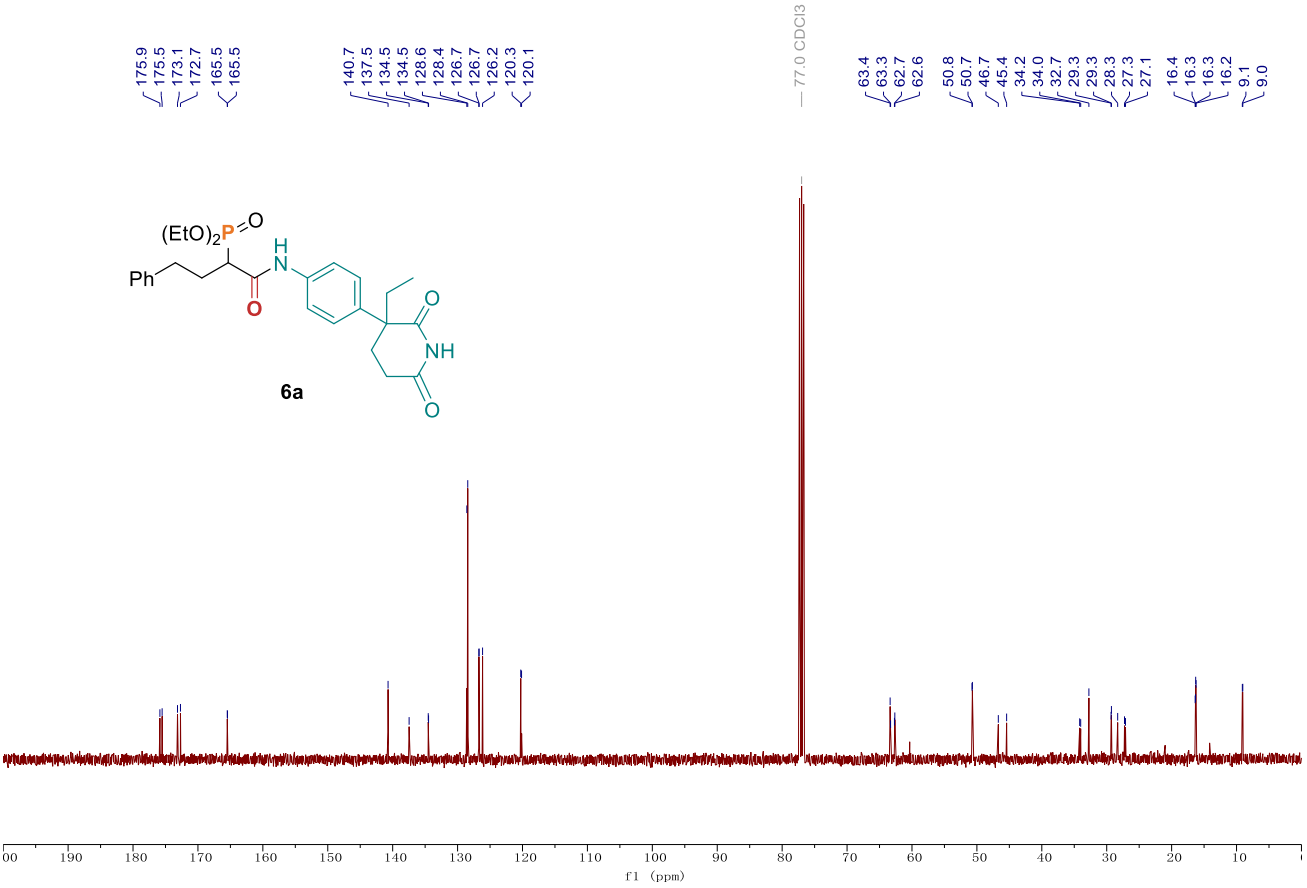


5r

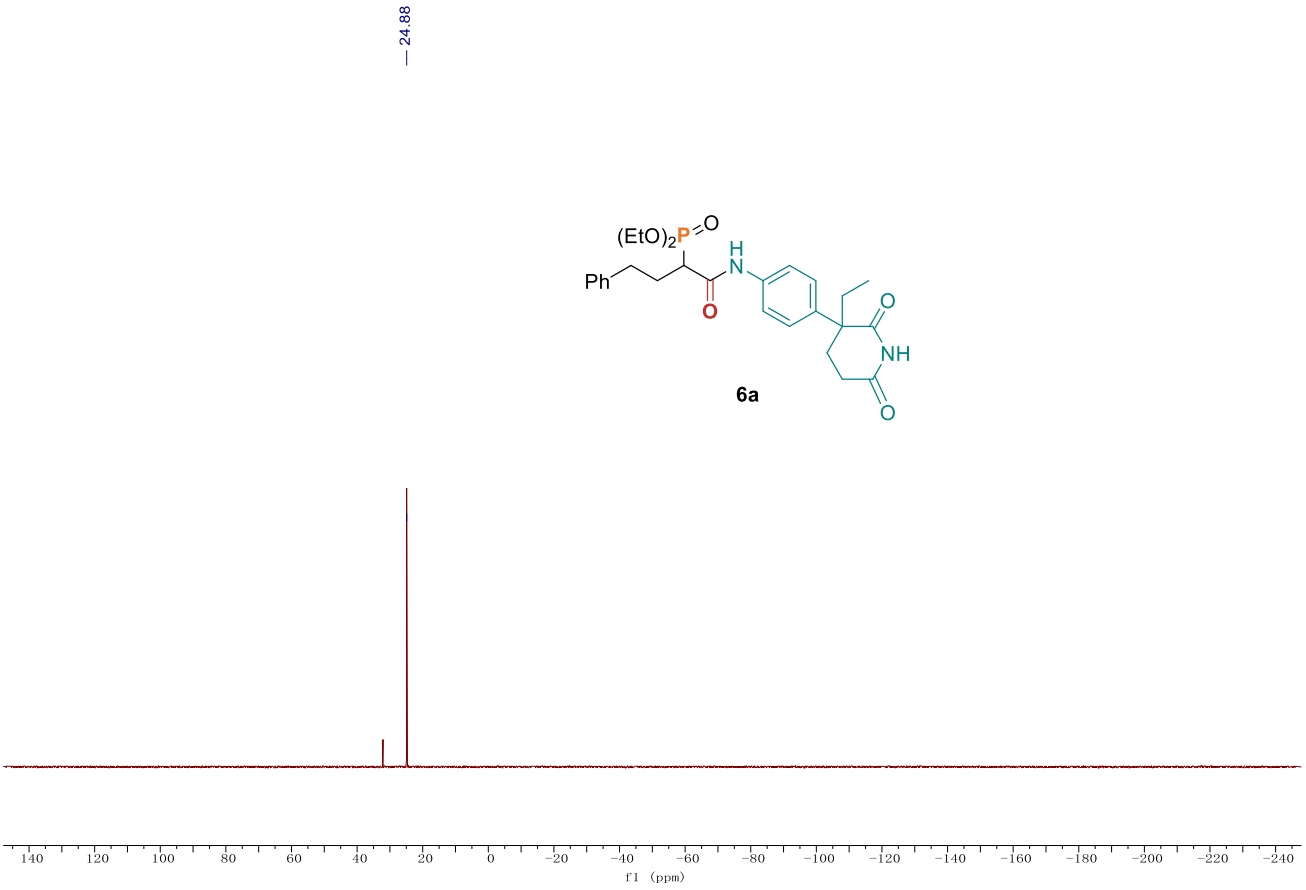
1H NMR CDCl3 400.13MHz



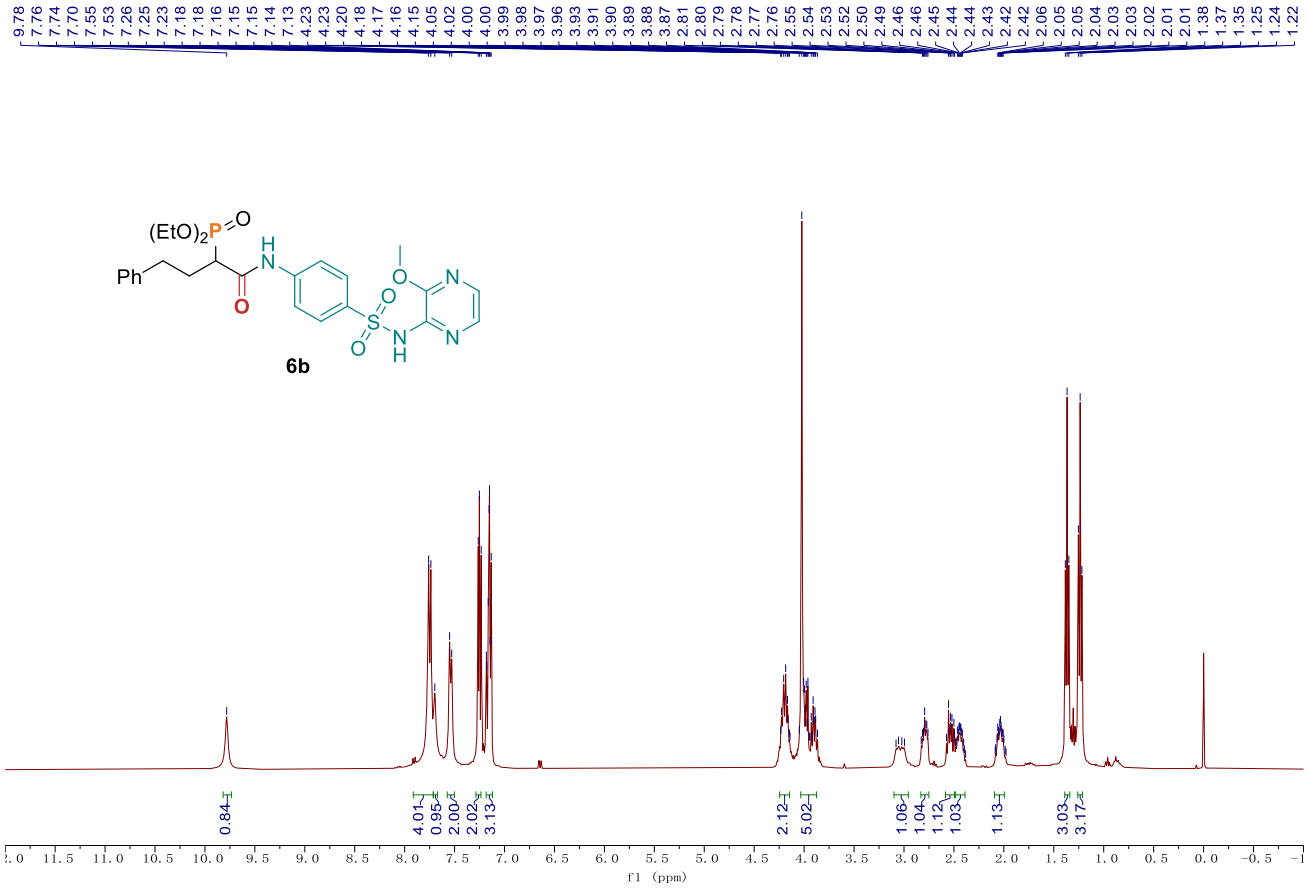
13C NMR CDCl3 100.62MHz



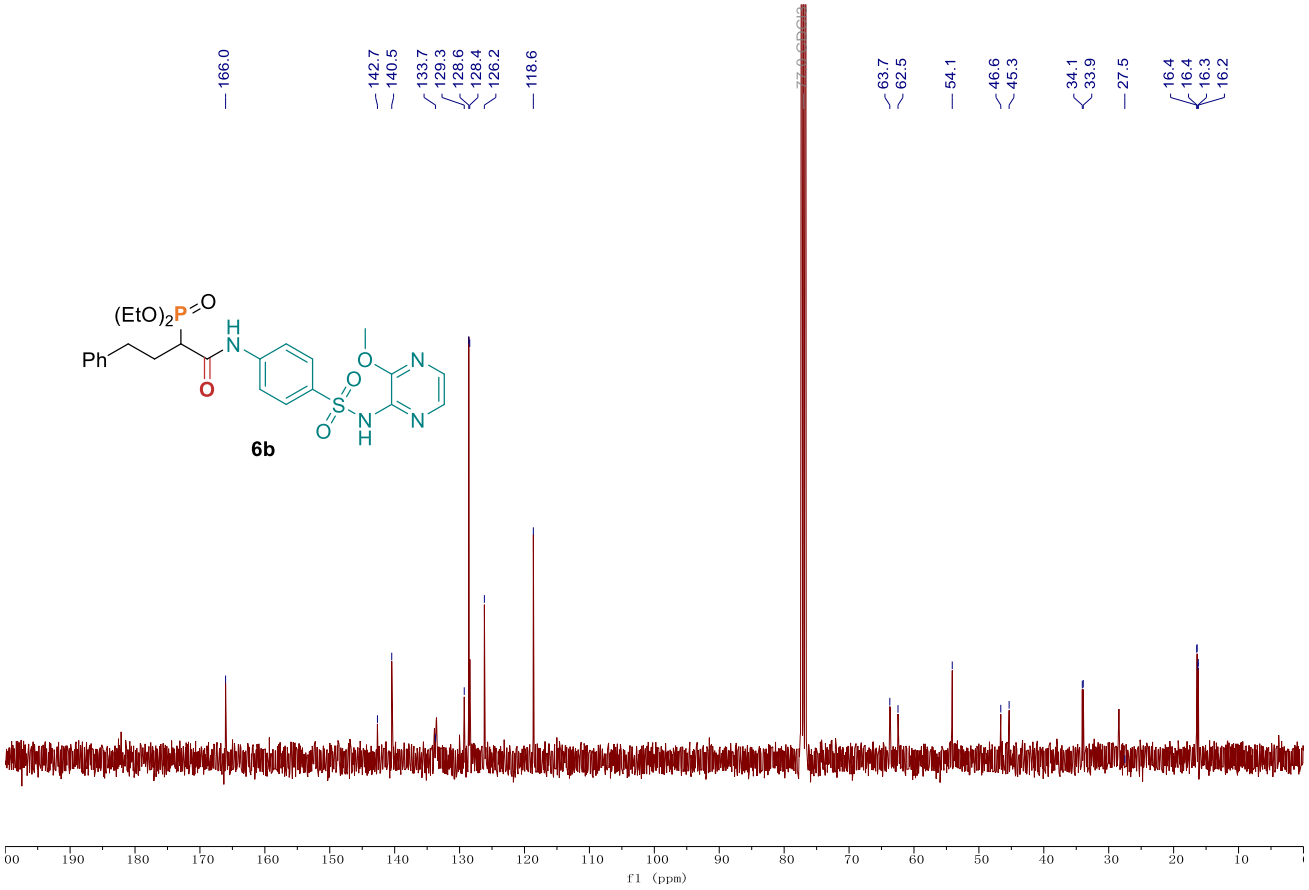
31P NMR CDCl3 161.97MHz



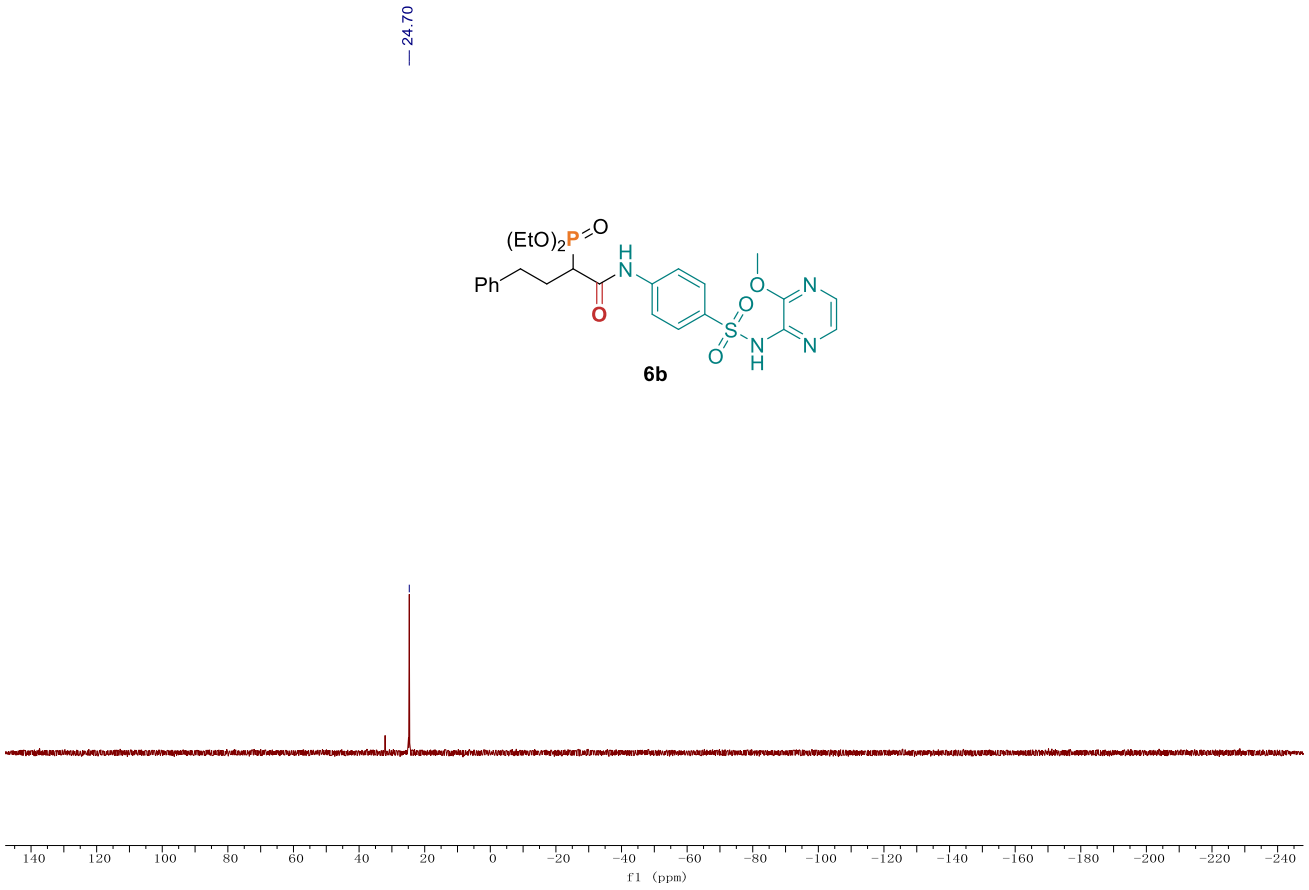
1H NMR CDCl3 400.13MHz



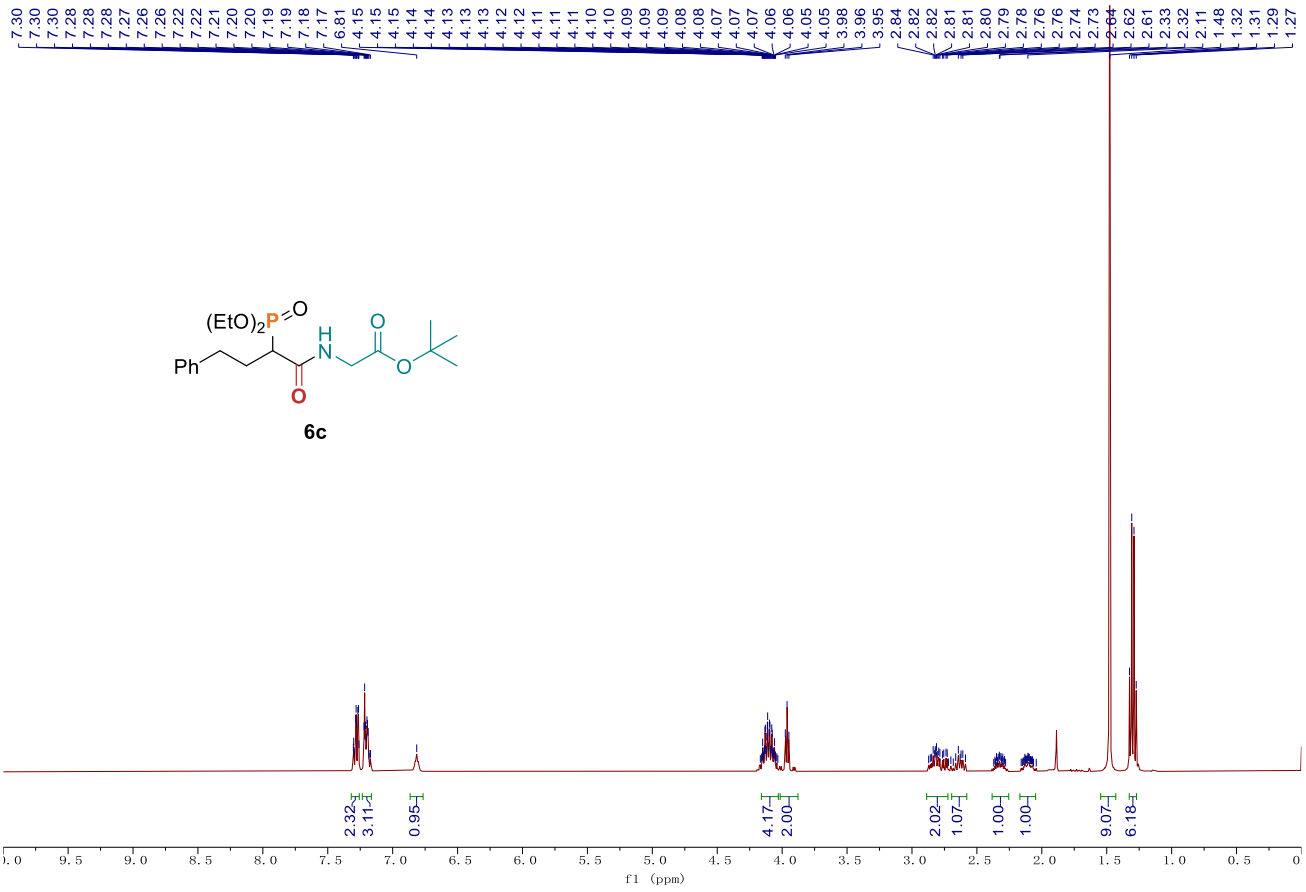
13C NMR CDCl3 100.62MHz



31P NMR CDCl3 161.97MHz

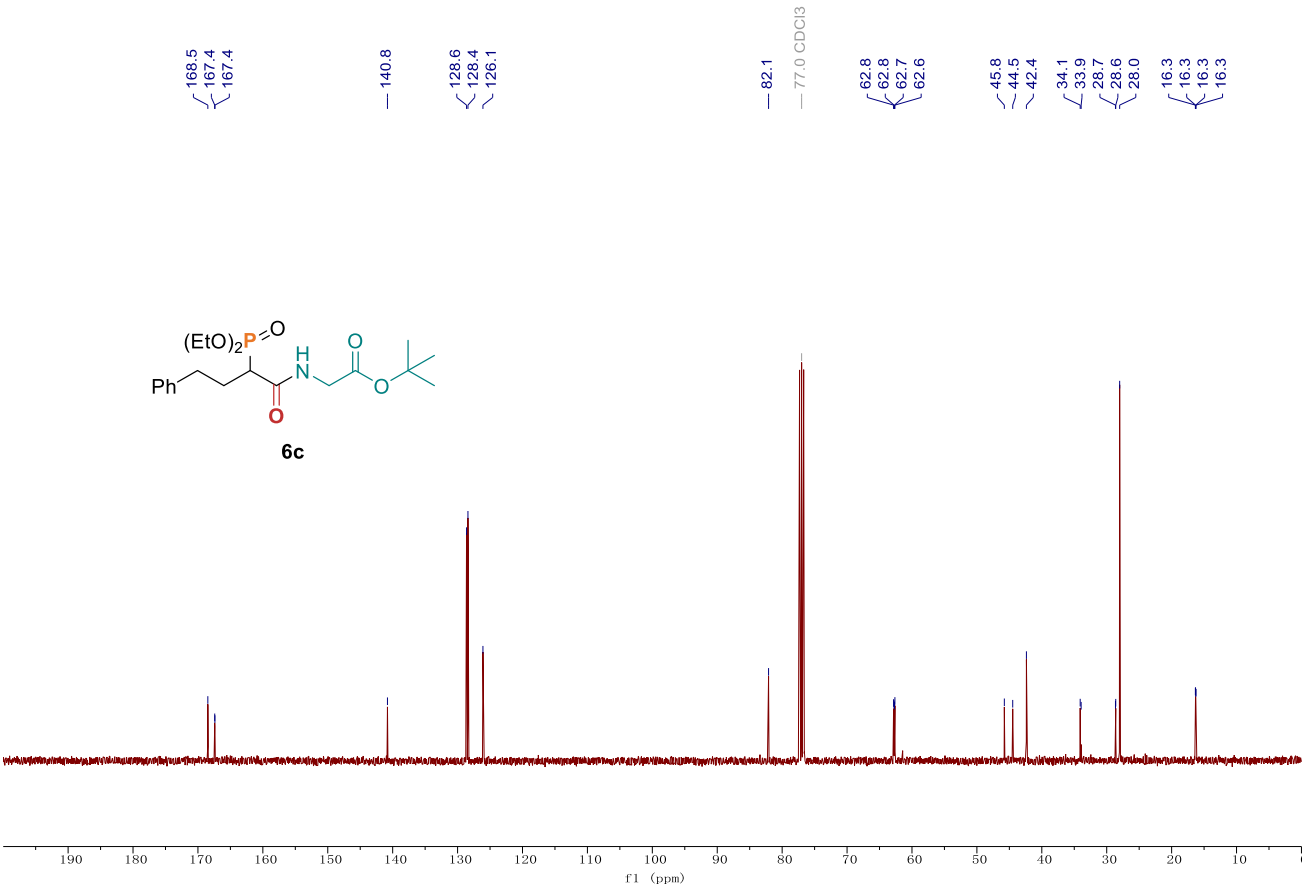


1H NMR CDCl3 400.13MHz



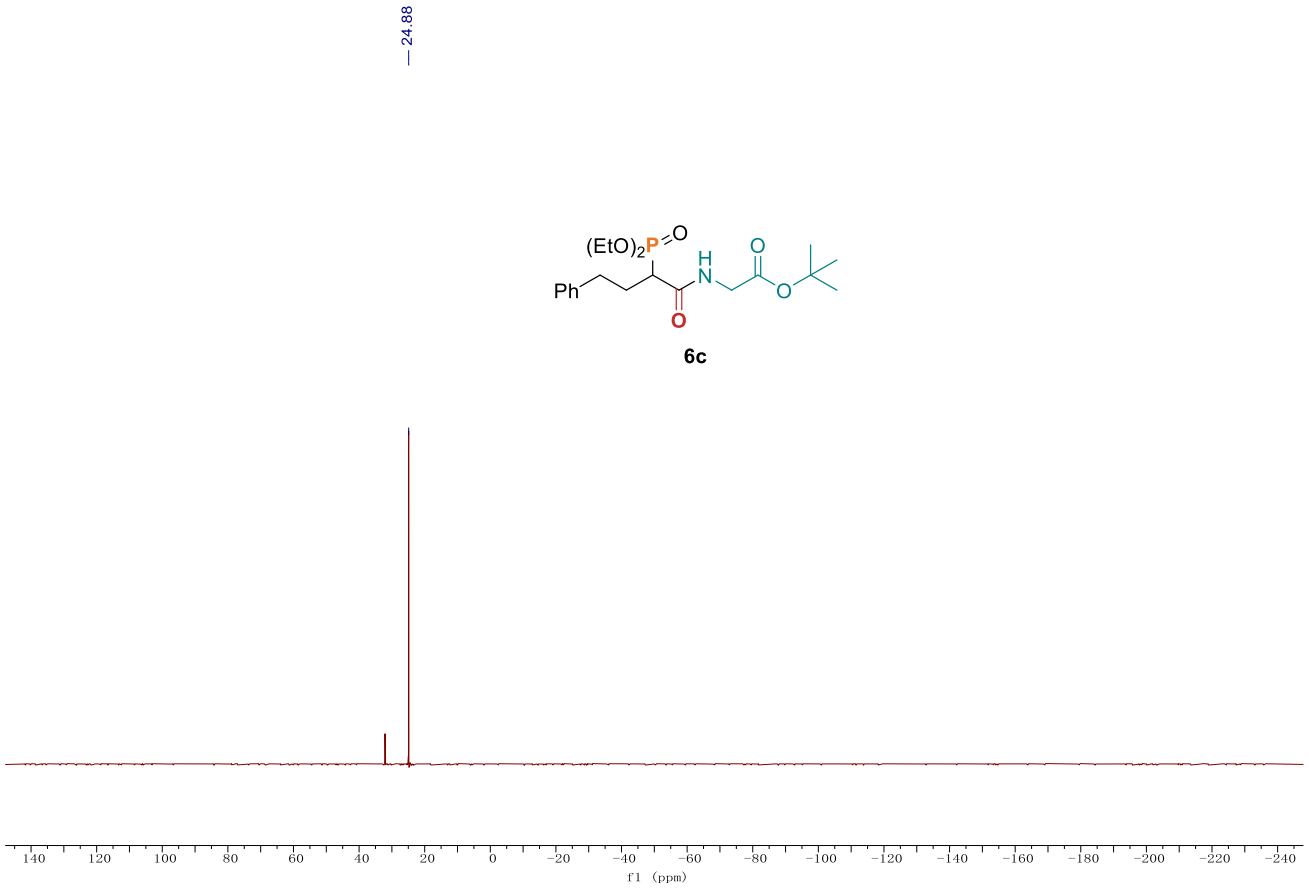
6c

13C NMR CDCl3 100.62MHz



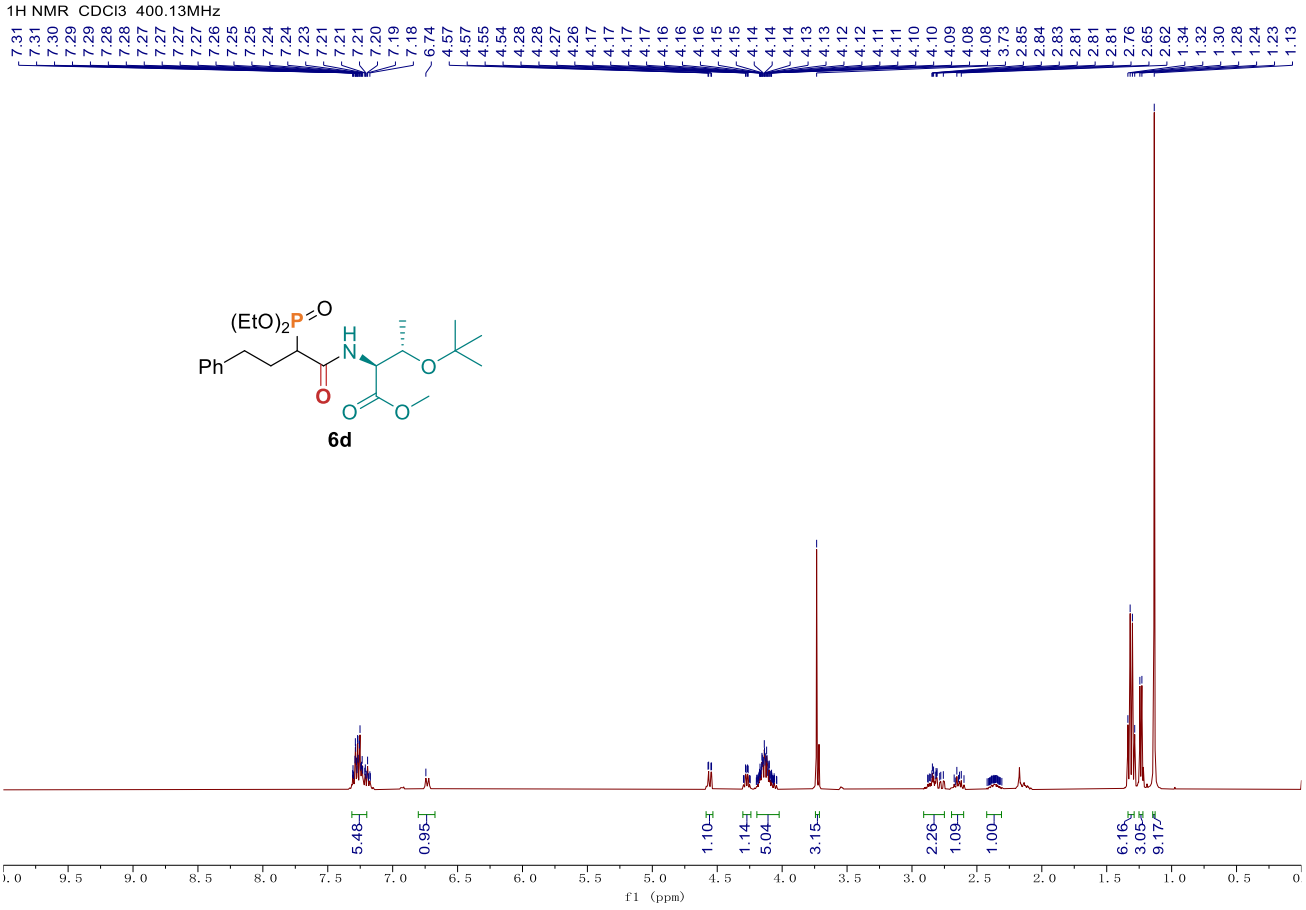
6c

31P NMR CDCl3 161.97MHz

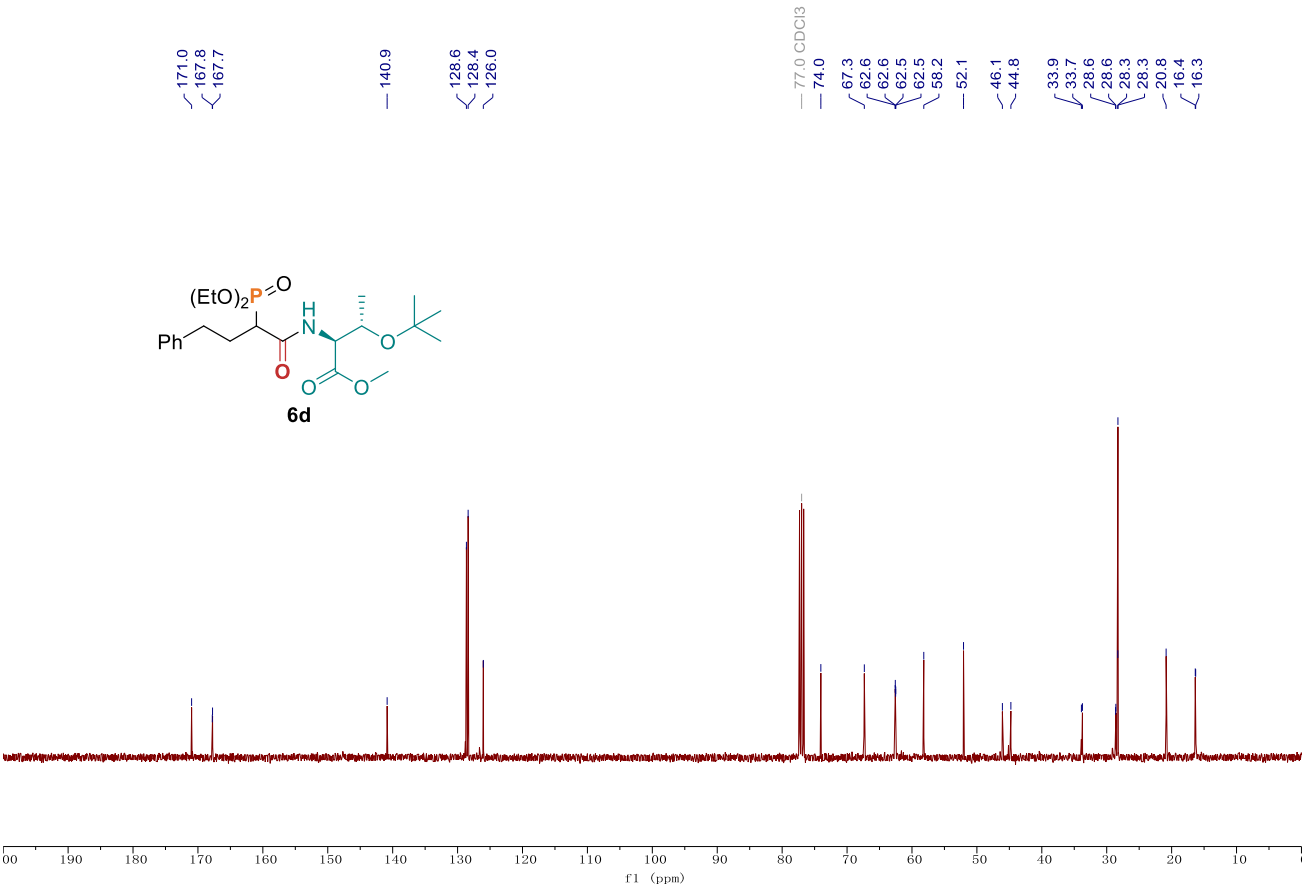


6c

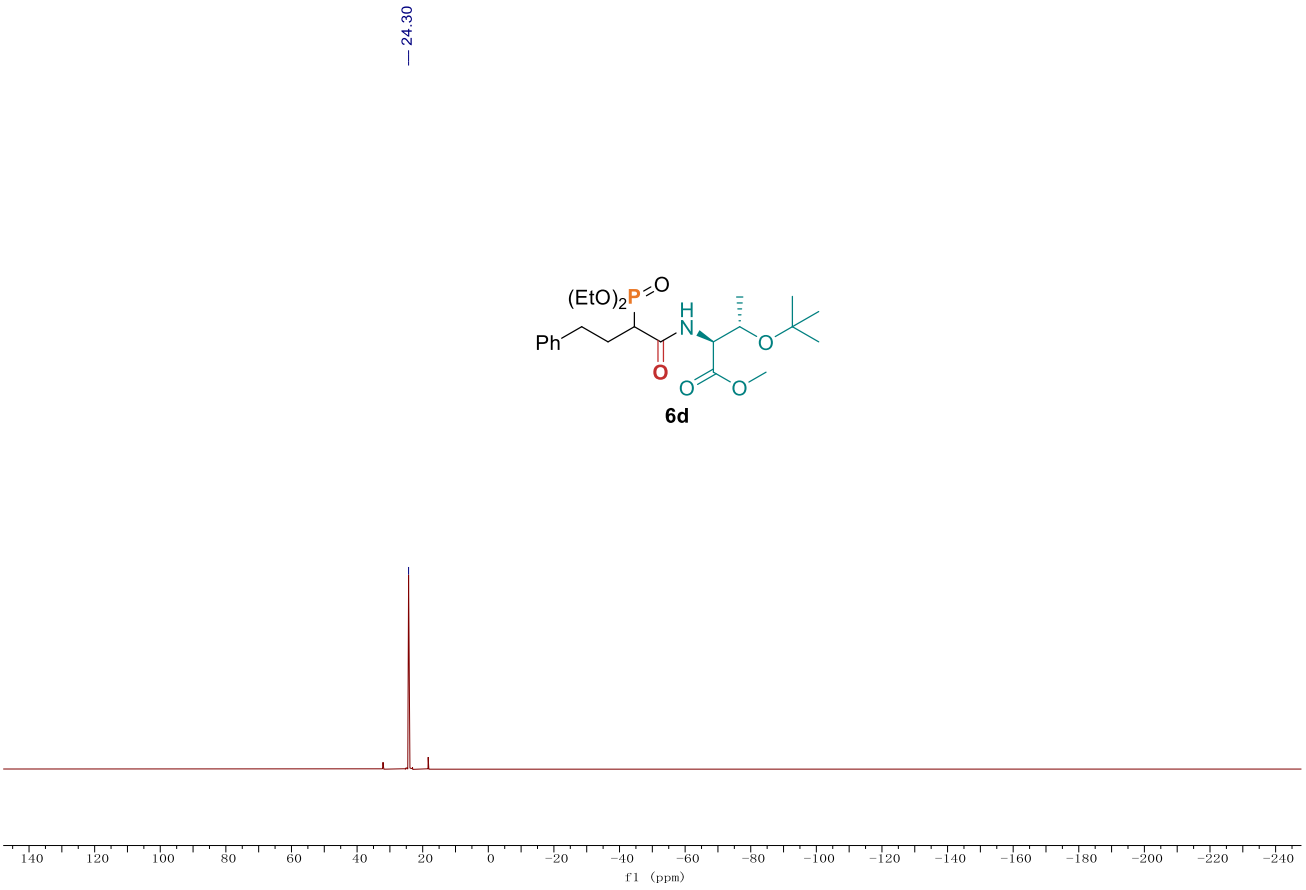
1H NMR CDCl3 400.13MHz



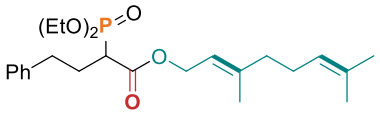
13C NMR CDCl3 100.62MHz



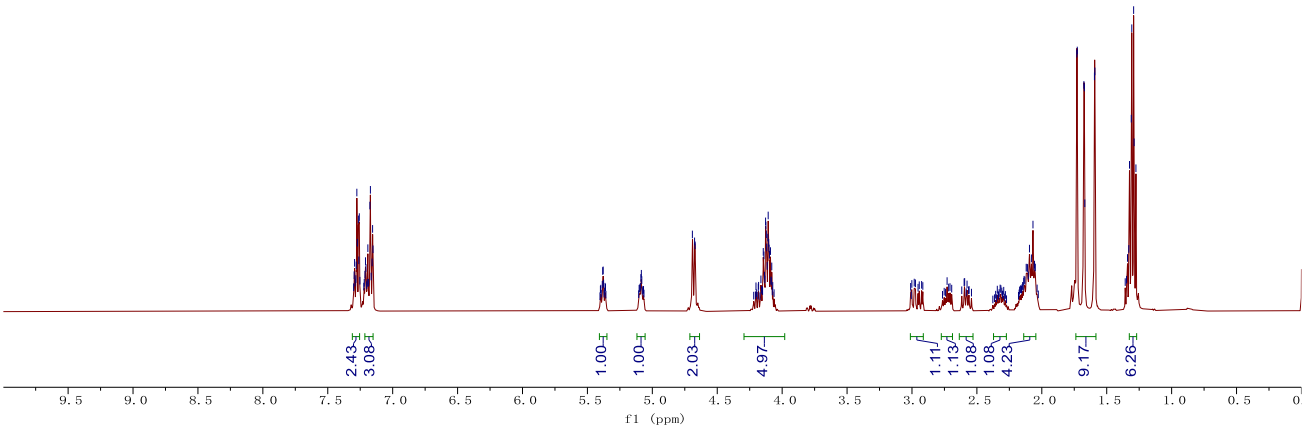
31P NMR CDCl3 161.97MHz



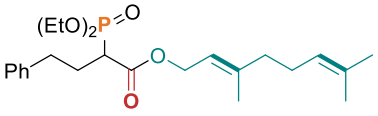
1H NMR CDCl3 400.13MHz



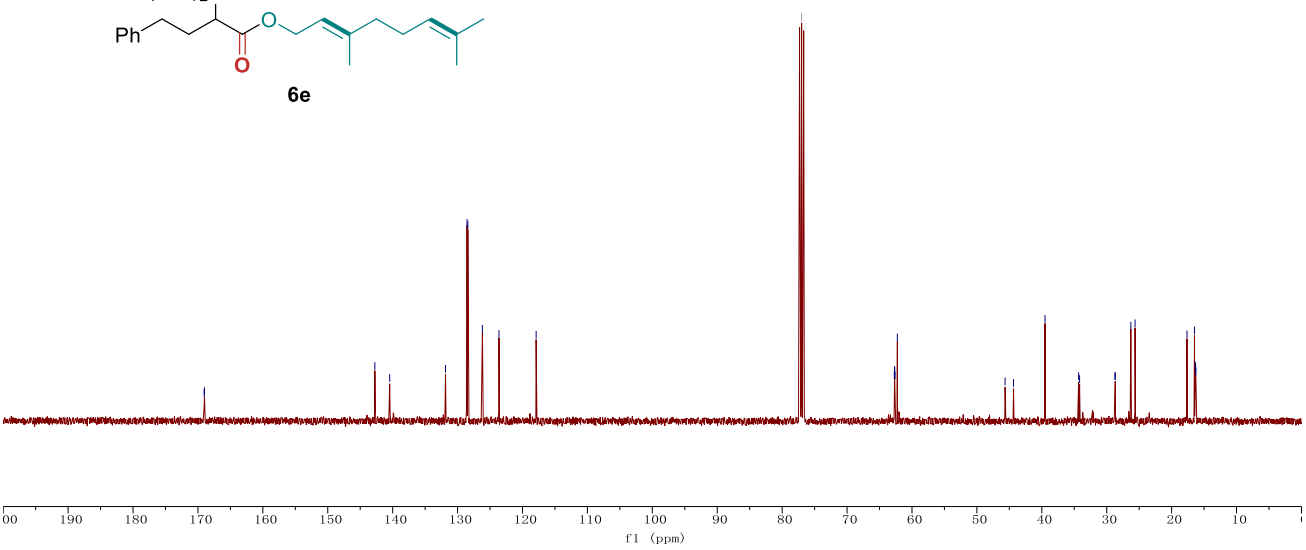
6e



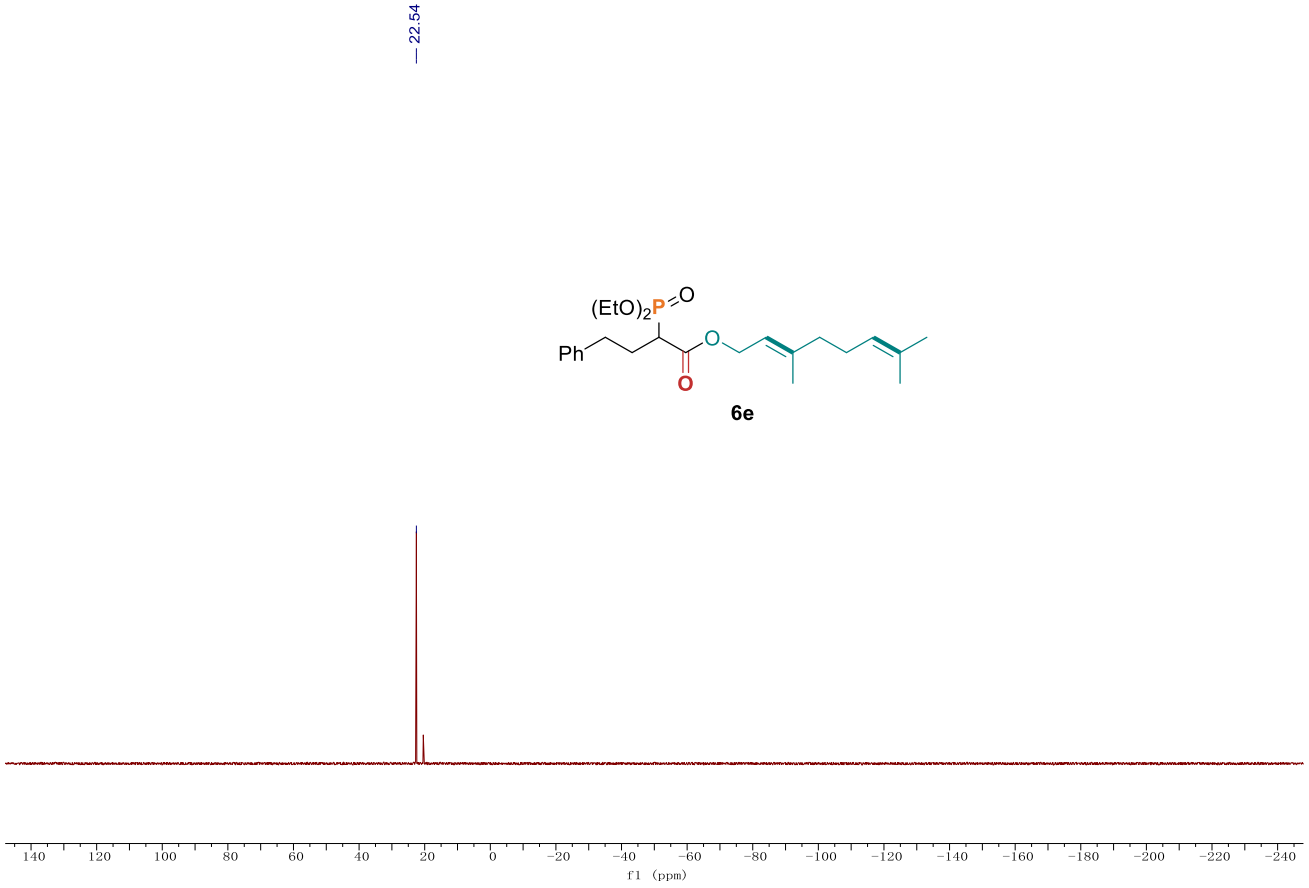
13C NMR CDCl3 100.62MHz



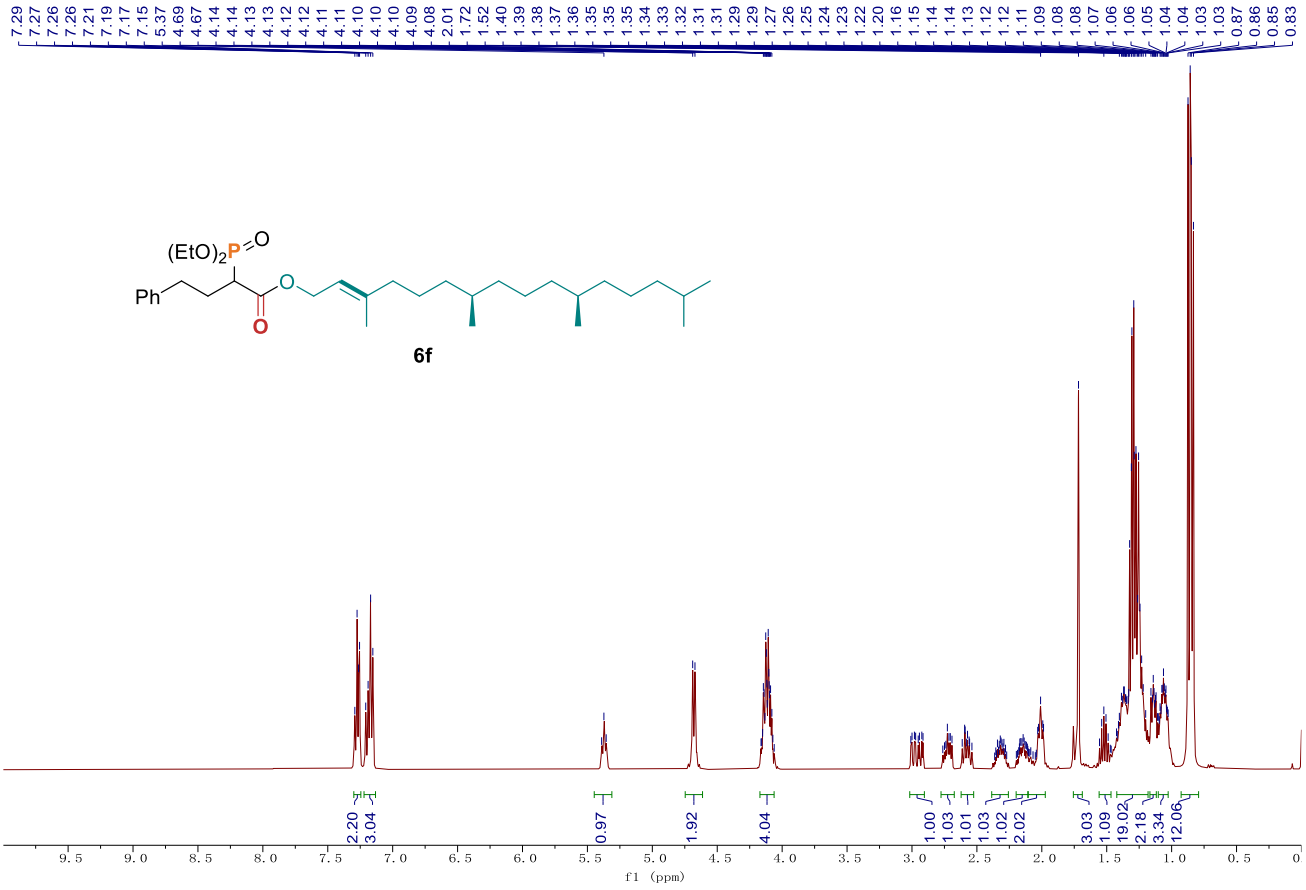
6e



31P NMR CDCl3 161.97MHz

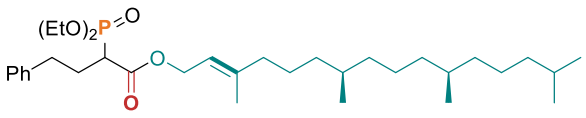


1H NMR CDCl3 400.13MHz

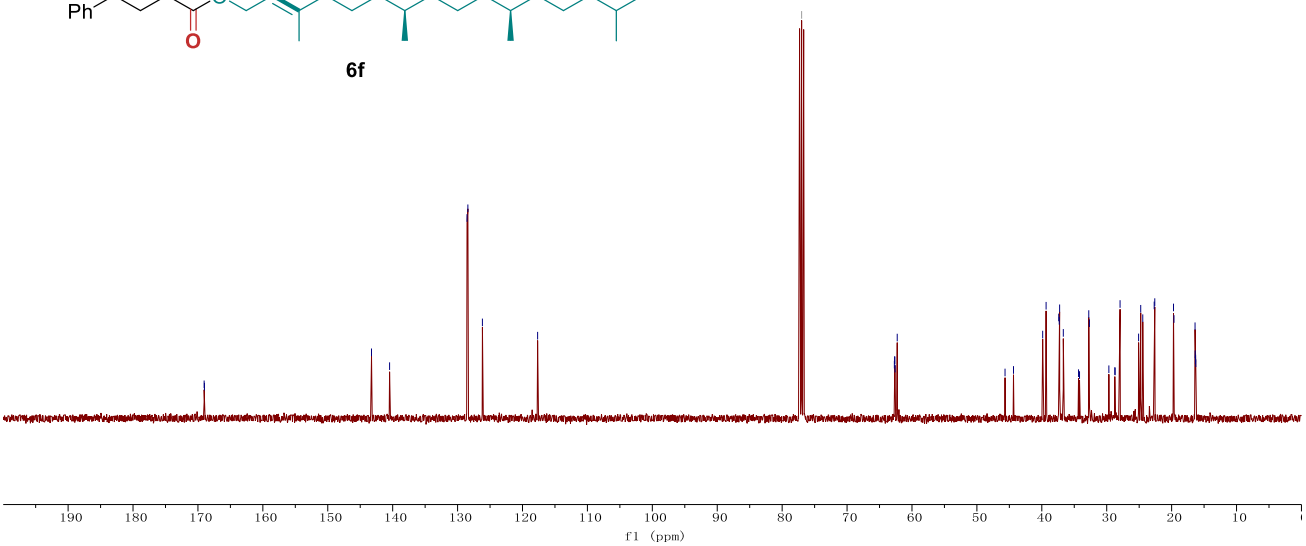


6f

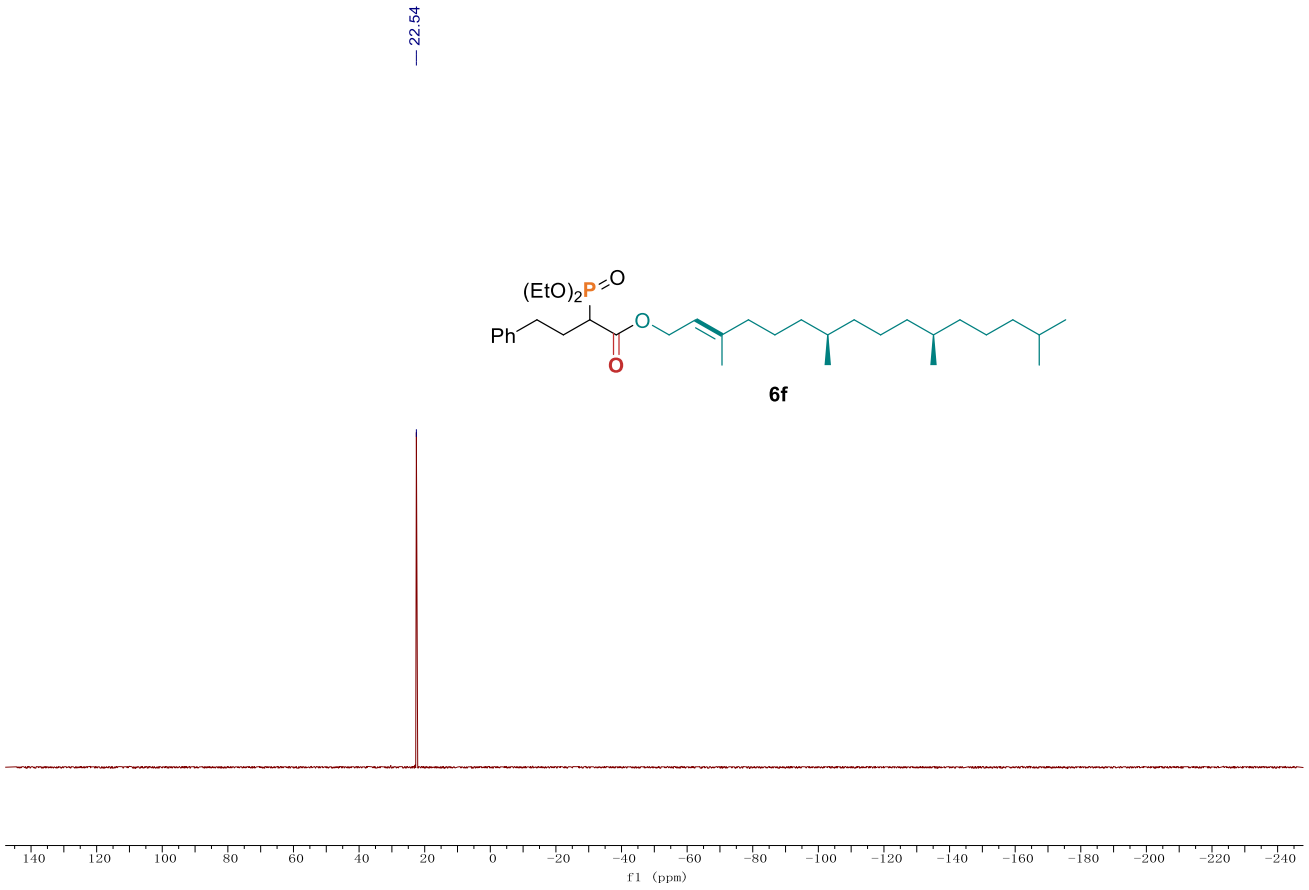
13C NMR CDCl3 100.62MHz



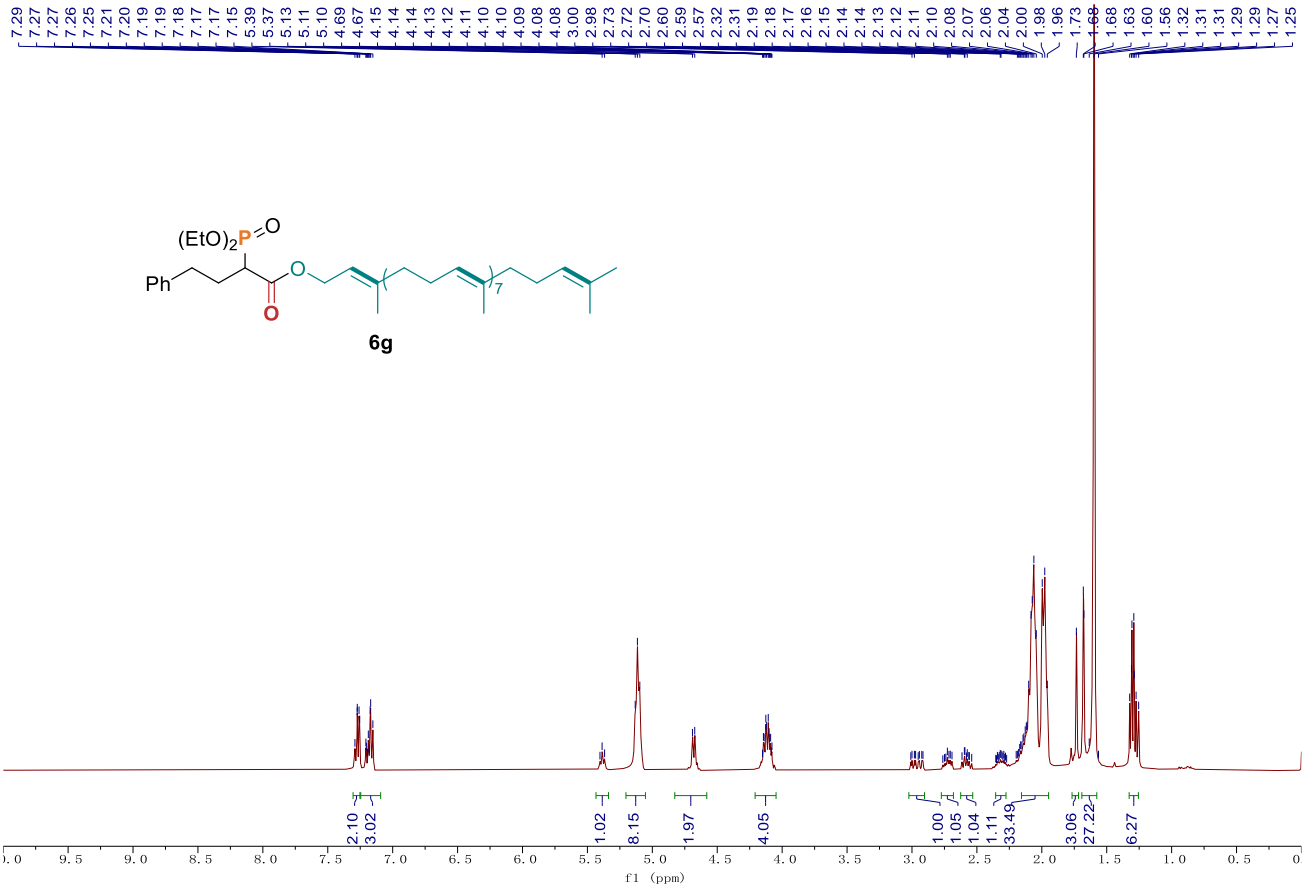
6f



31P NMR CDCl3 161.97MHz

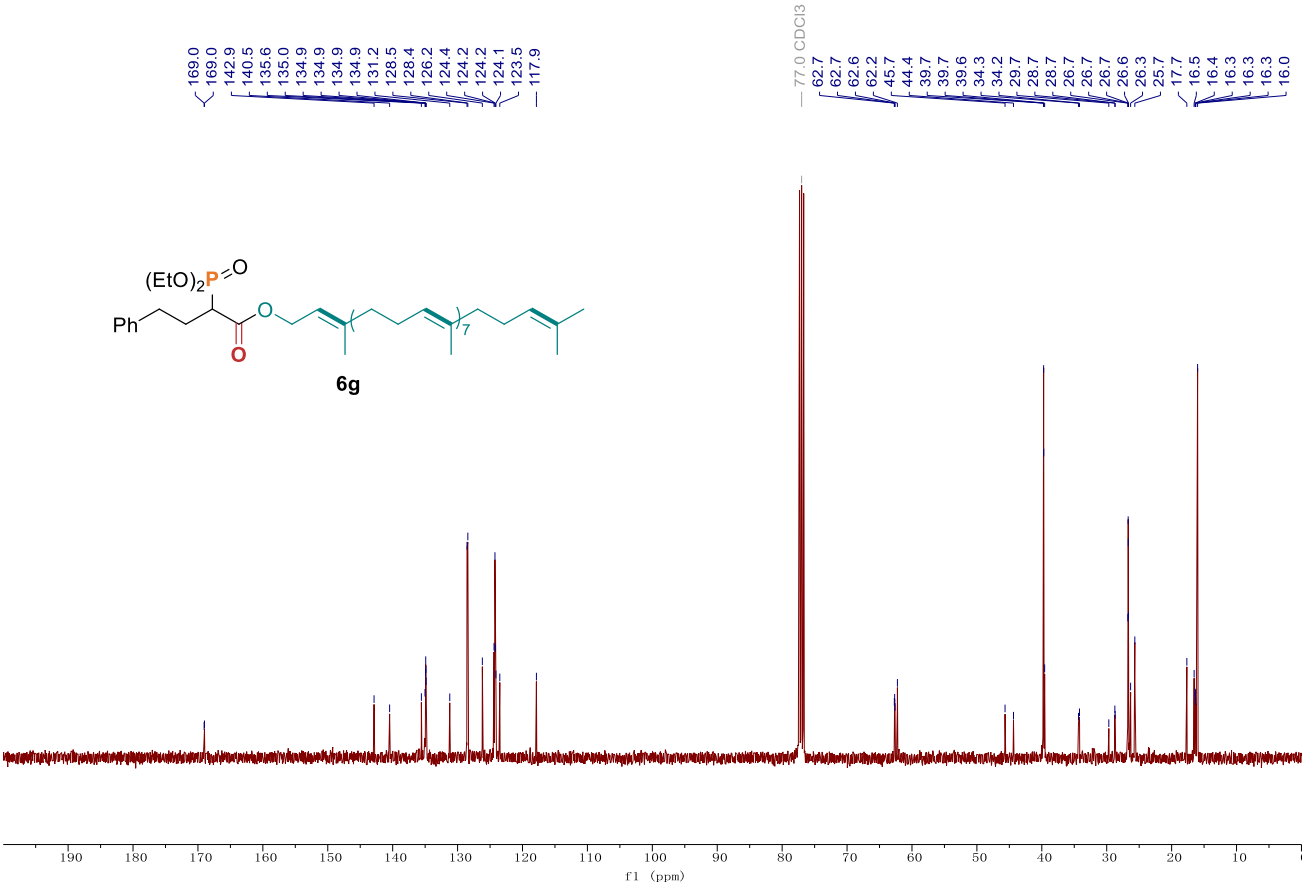


1H NMR CDCl3 400.13MHz



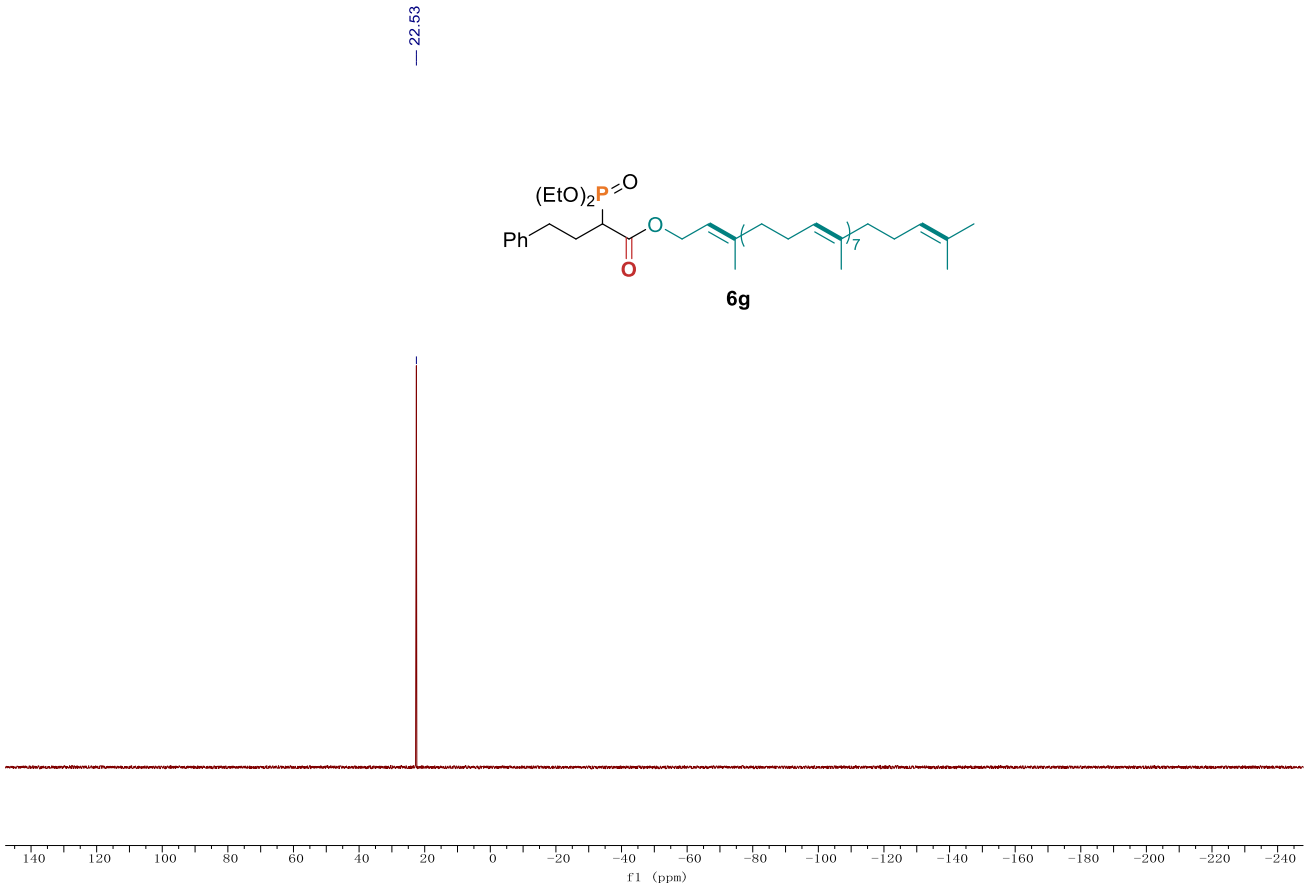
6g

13C NMR CDCl3 100.62MHz



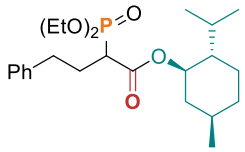
6g

31P NMR CDCl3 161.97MHz

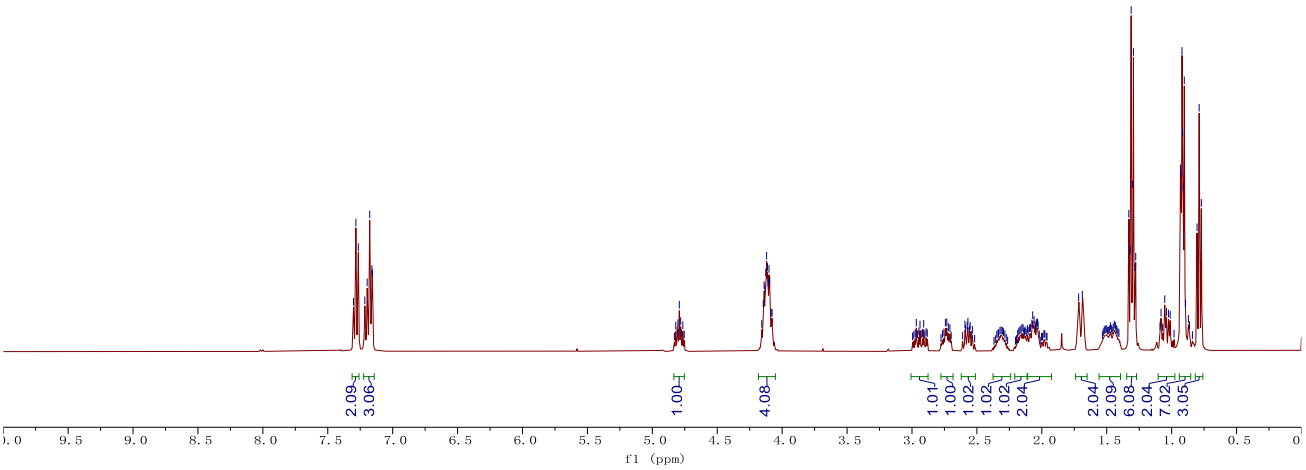


6g

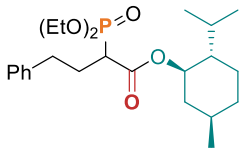
1H NMR CDCl3 400.13MHz



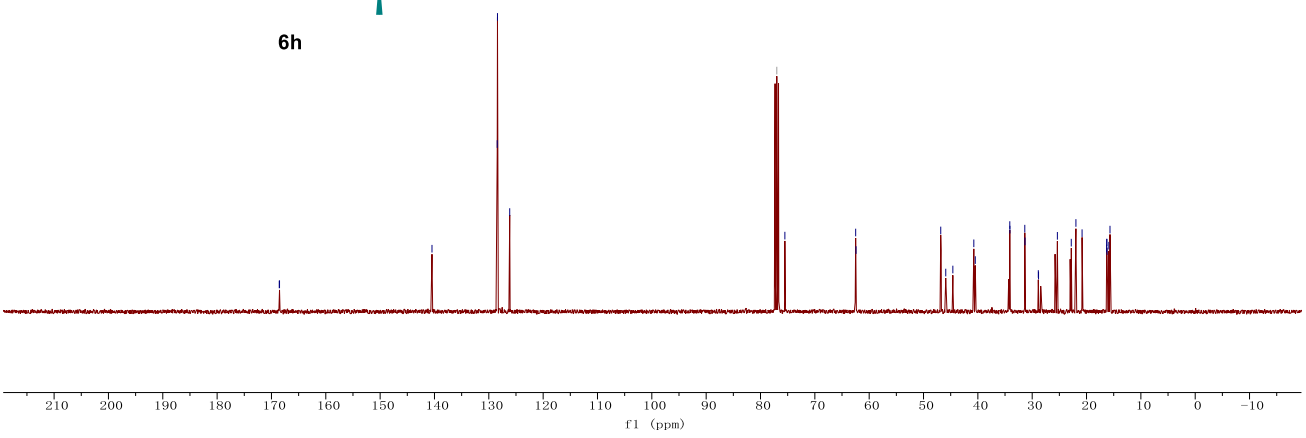
6h



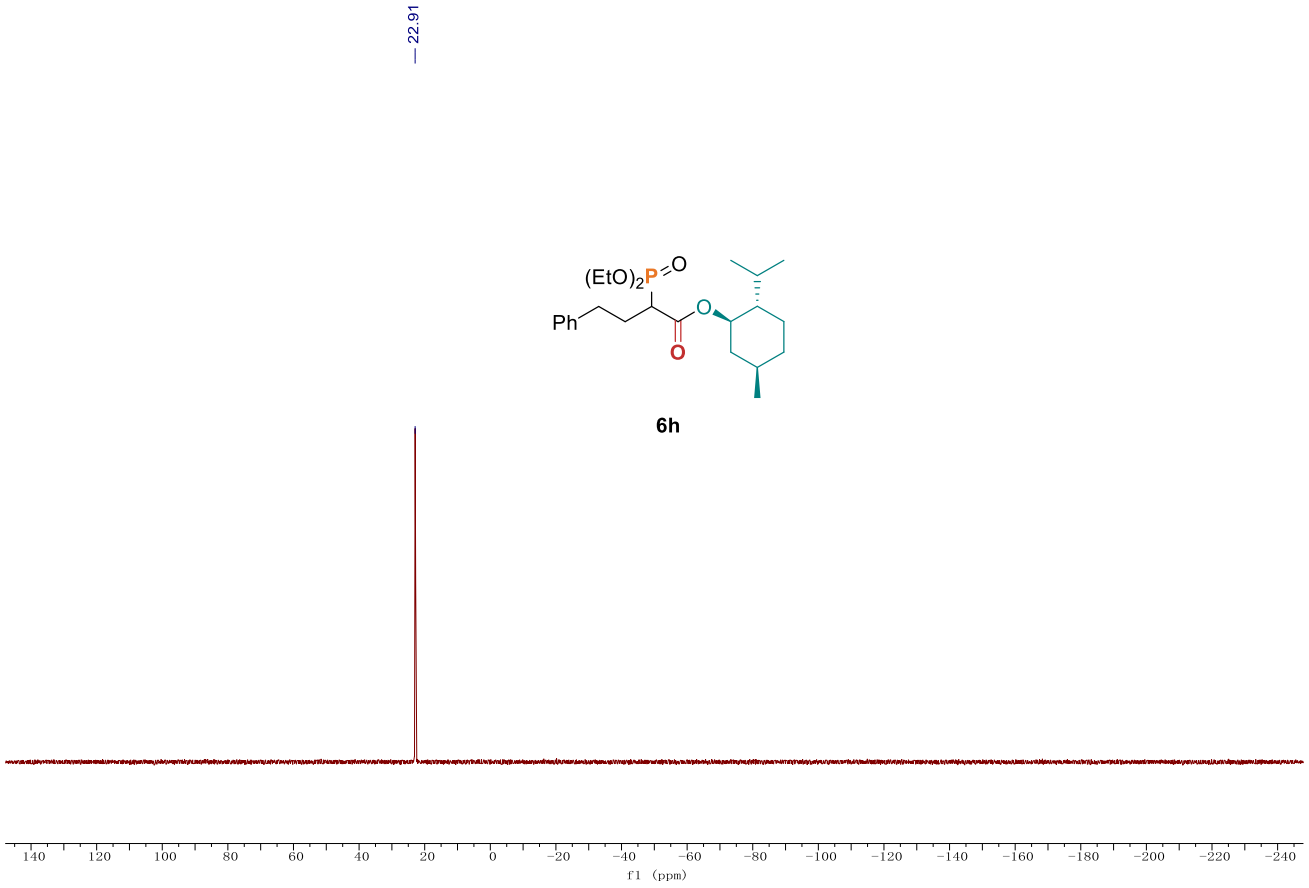
13C NMR CDCl3 100.62MHz



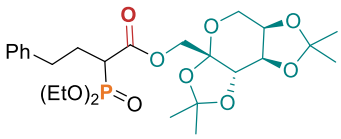
6h



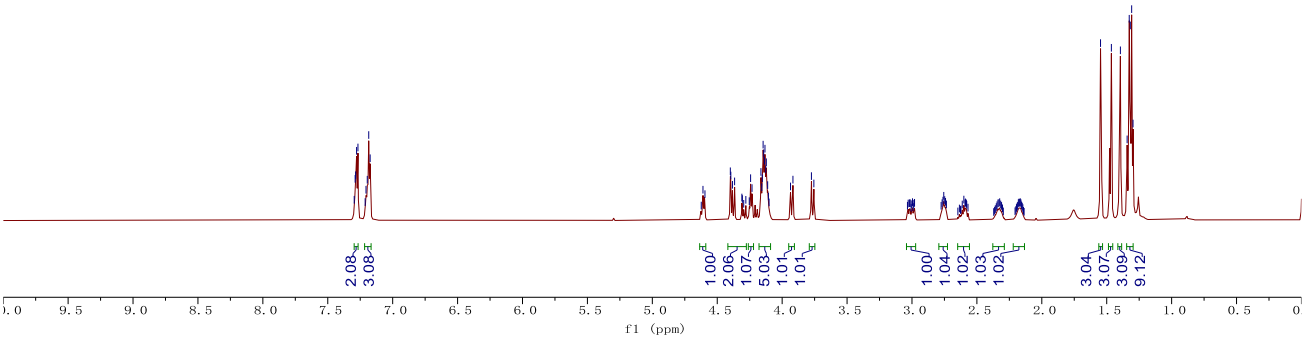
31P NMR CDCl3 161.97MHz



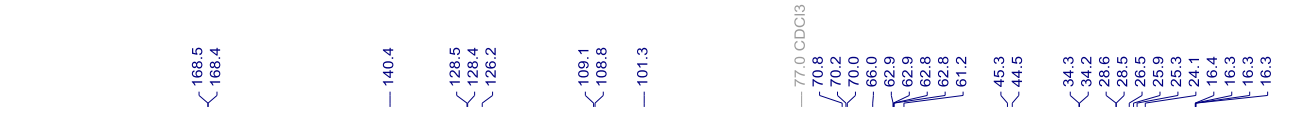
1H NMR CDCl3 700.17MHz

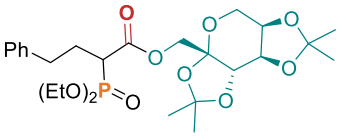


6i

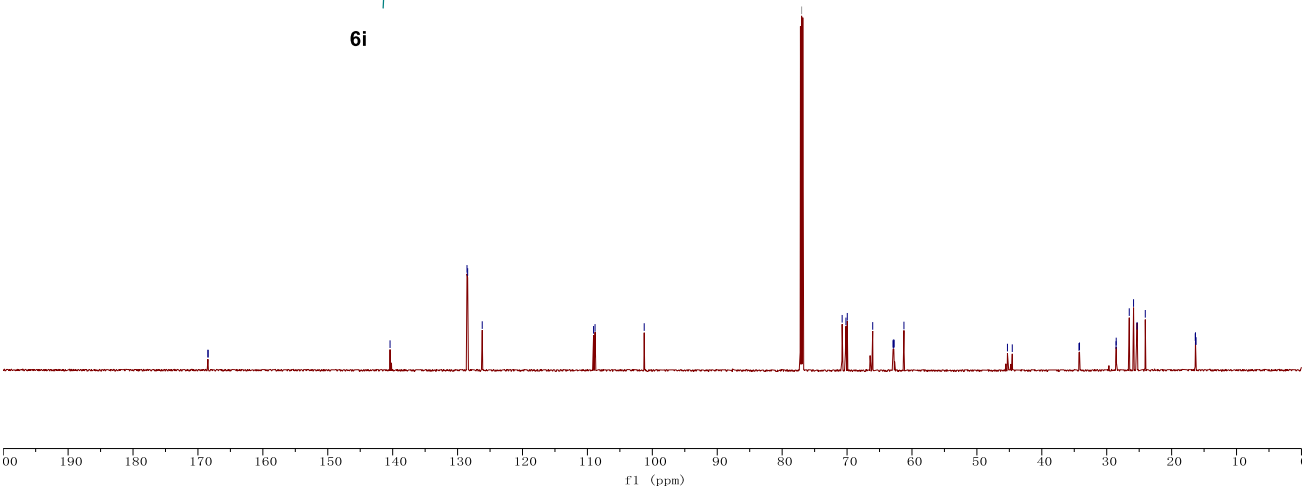


13C NMR CDCl3 176.08MHz

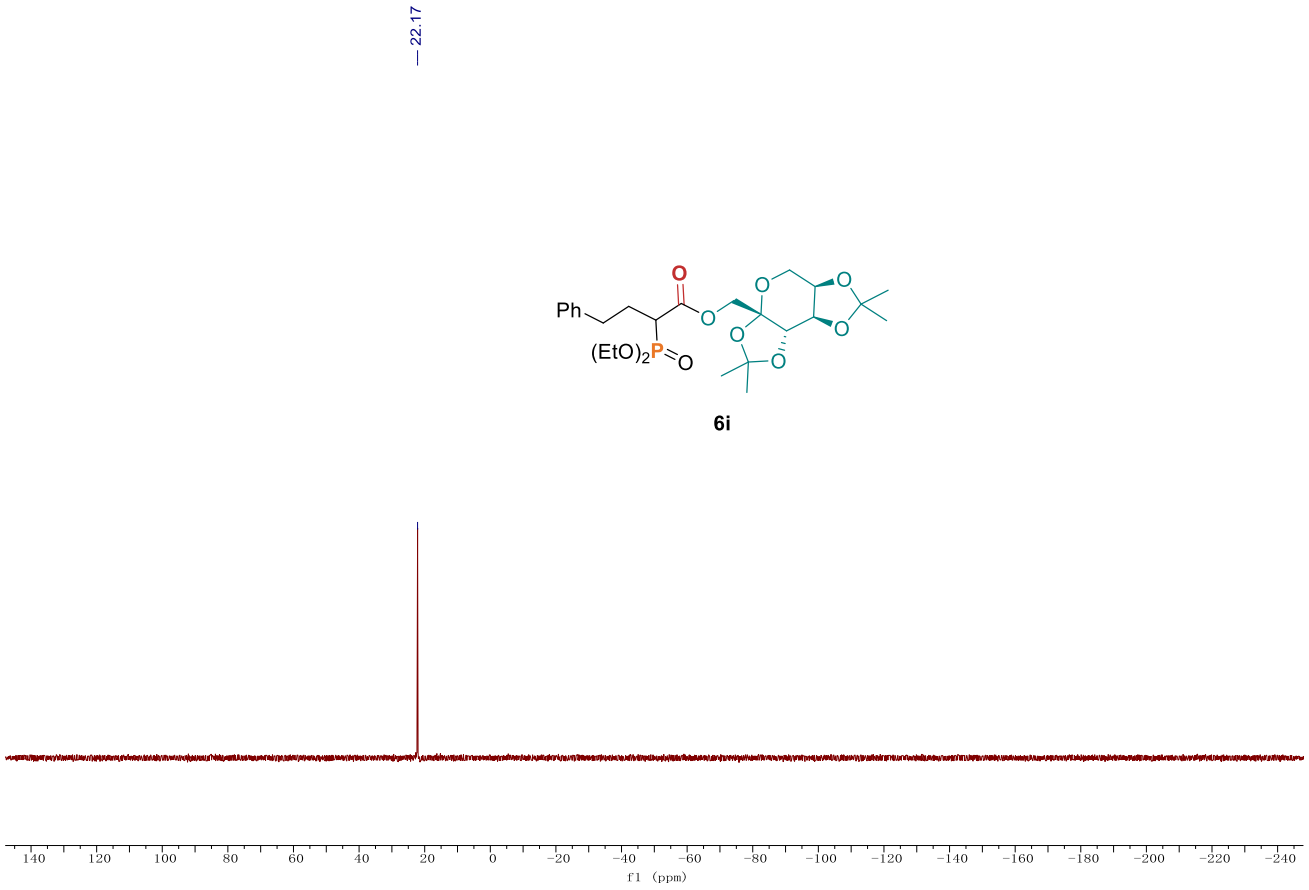




6i

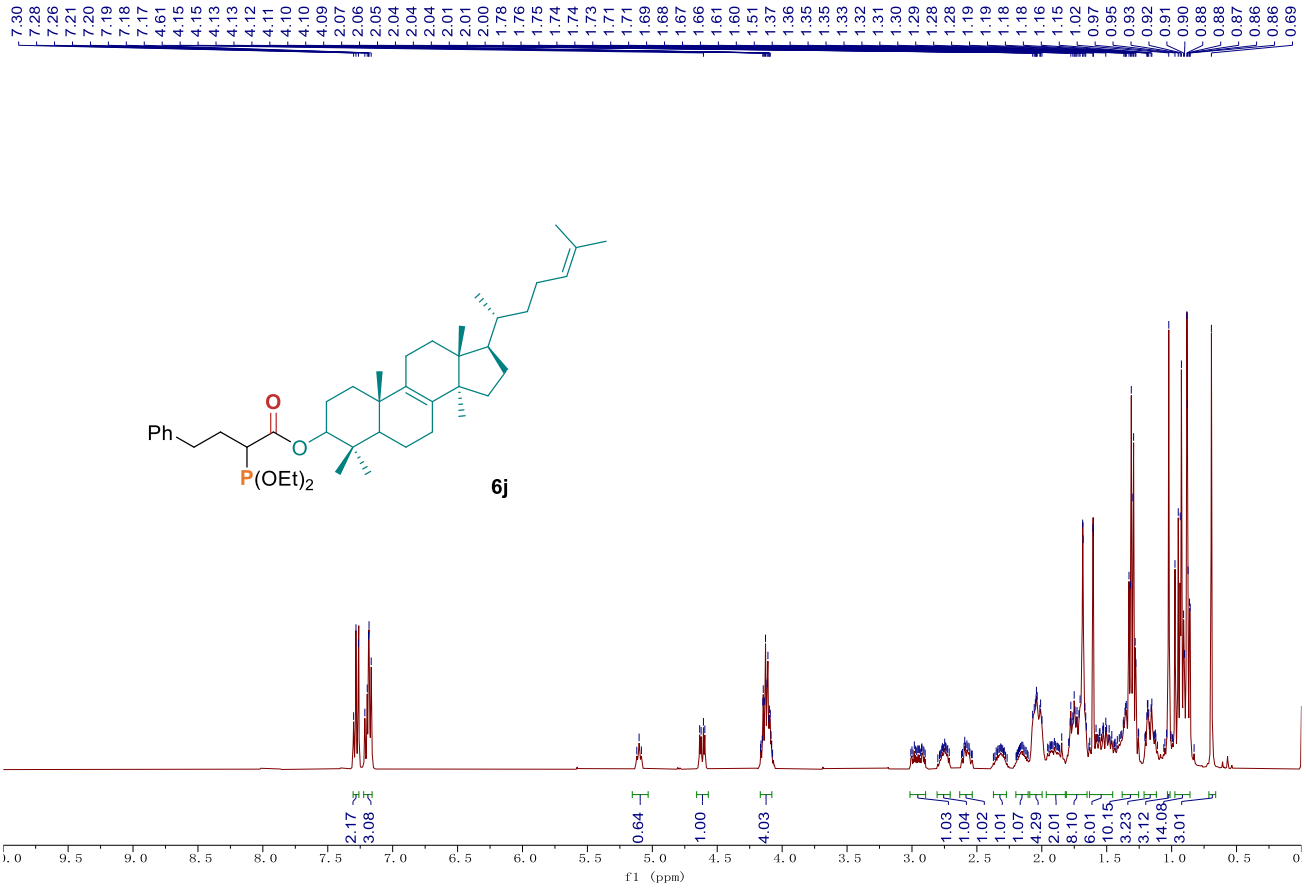


31P NMR CDCl3 161.97MHz

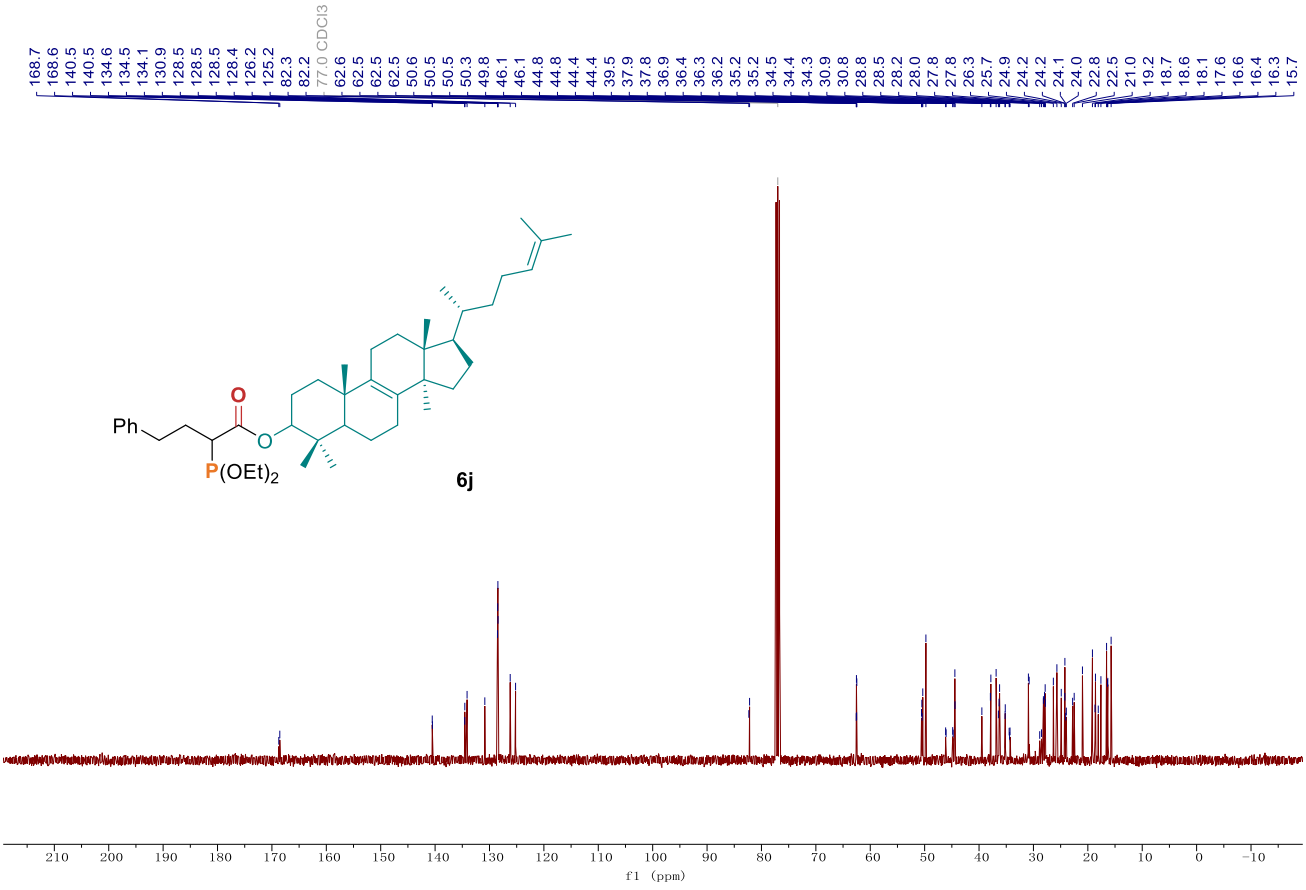


6i

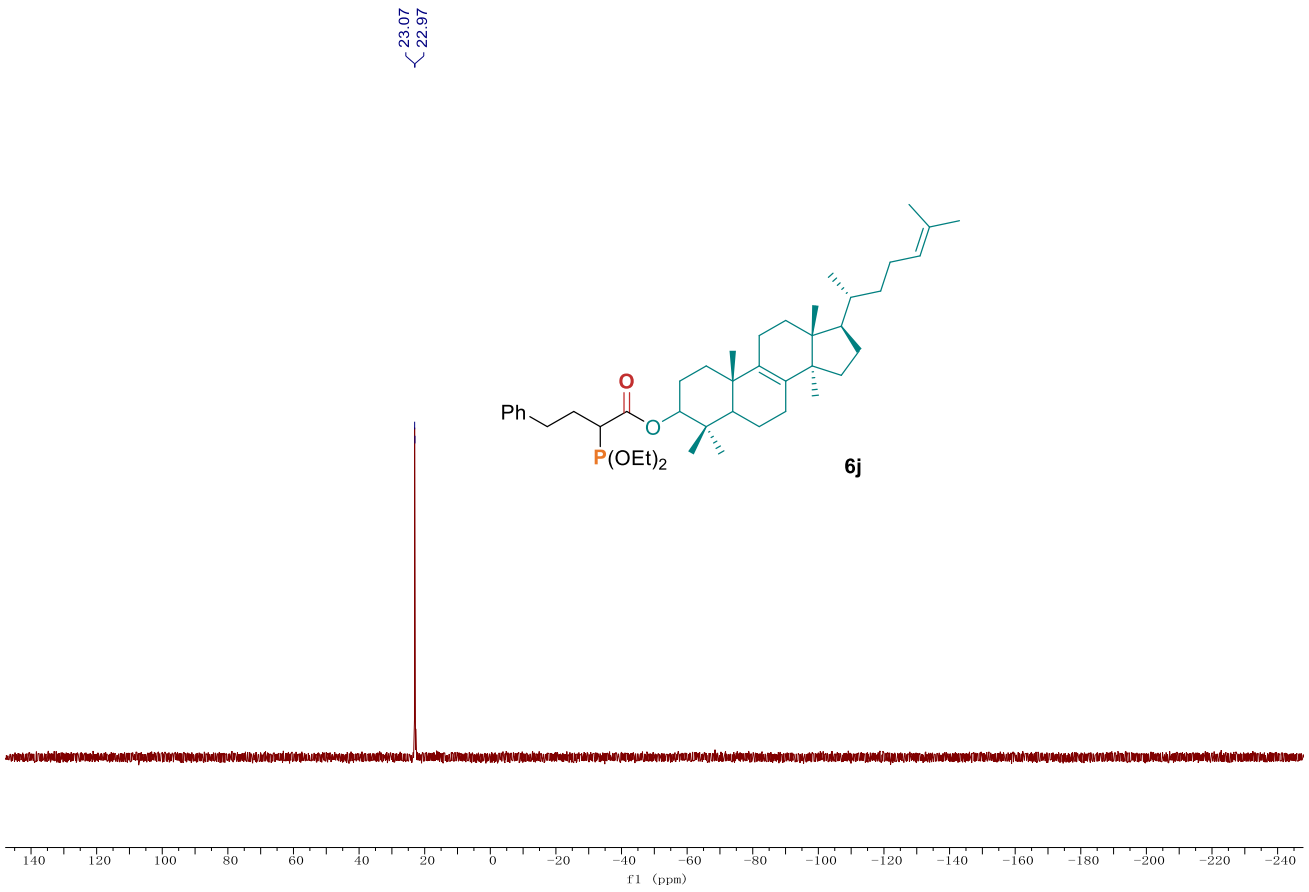
1H NMR CDCl3 400.13MHz



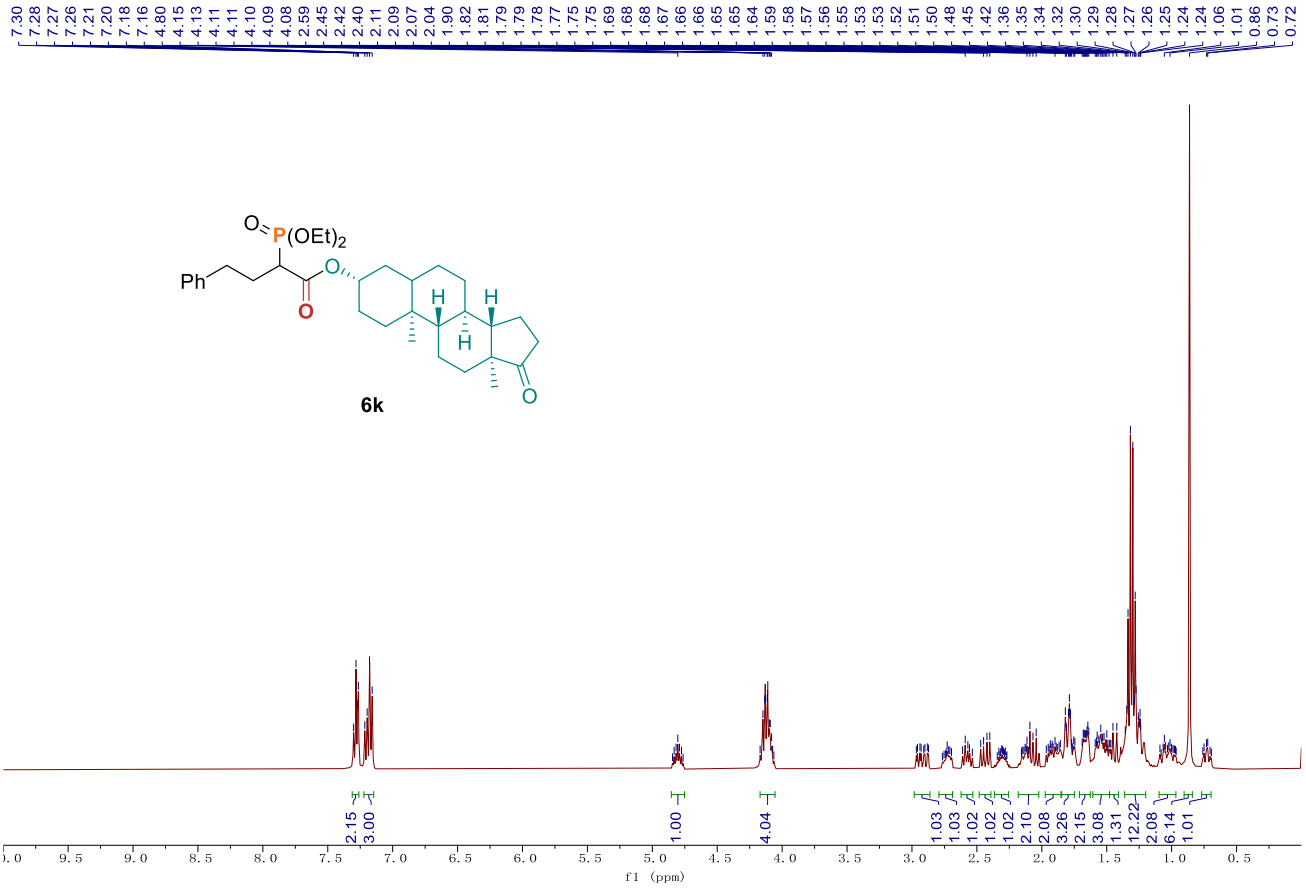
13C NMR CDCl3 100.62MHz



31P NMR CDCl3 161.97MHz

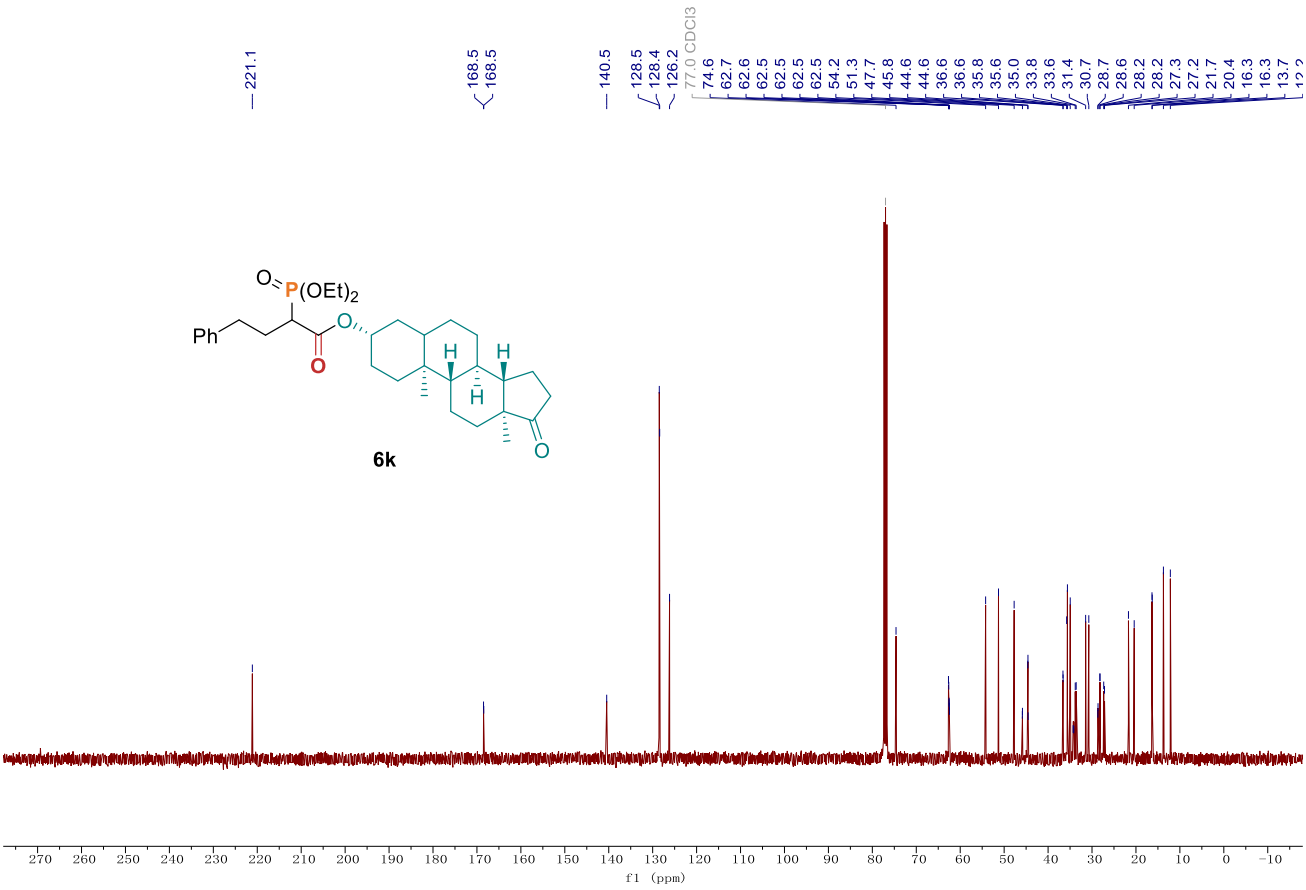


1H NMR CDCl3 400.13MHz



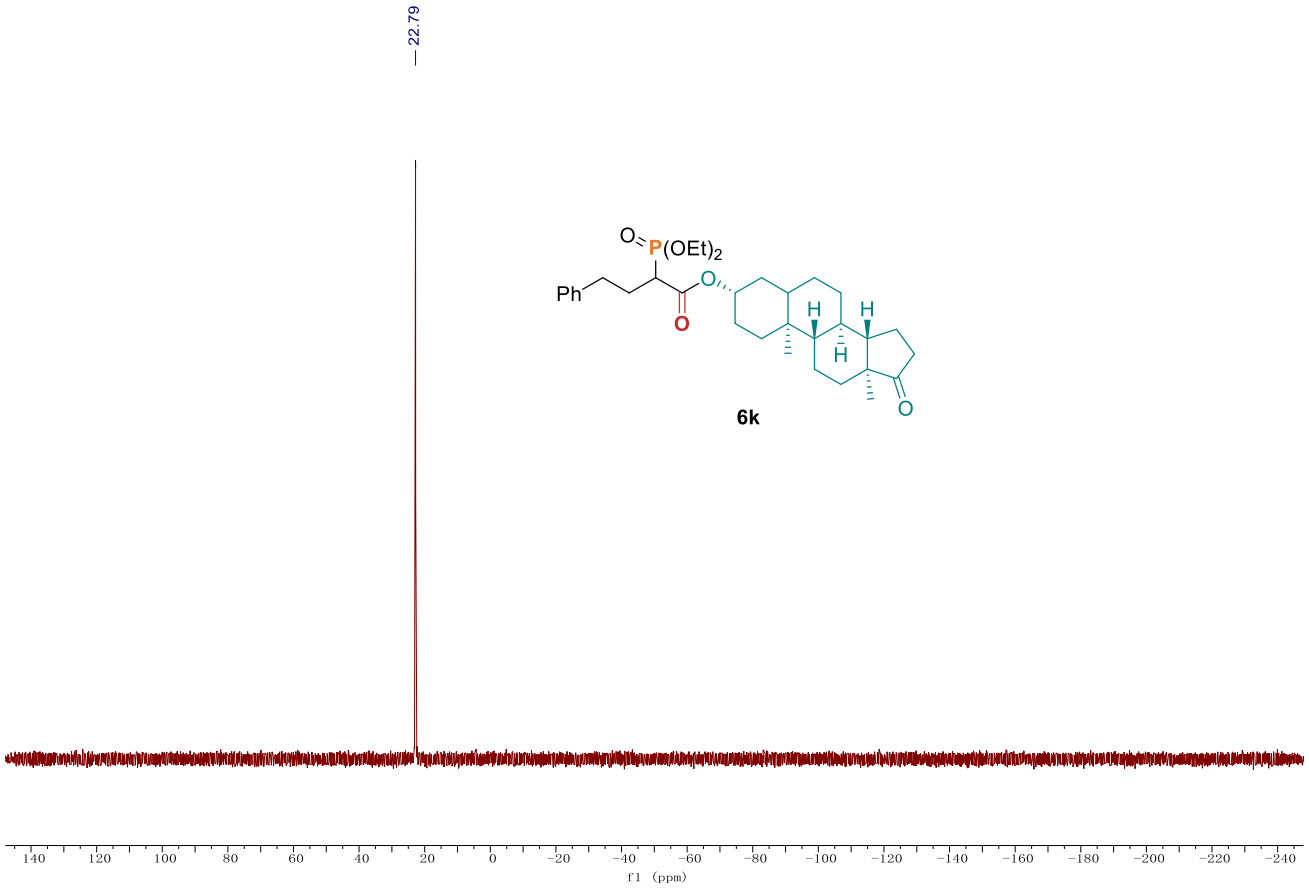
6k

13C NMR CDCl3 100.63MHz



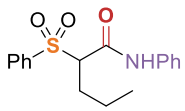
6k

31P NMR CDCl3 161.97MHz

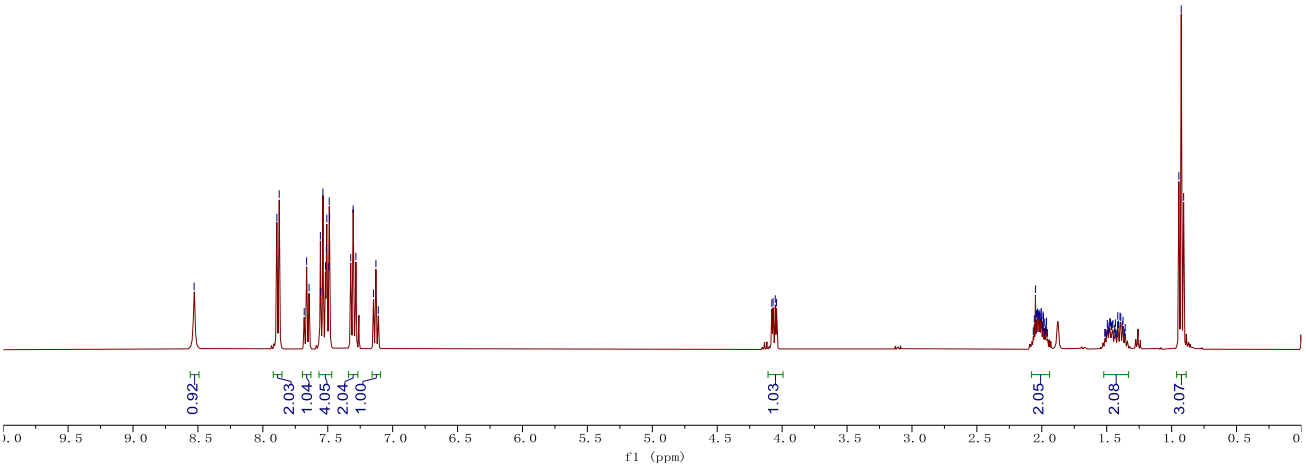


6k

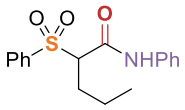
1H NMR CDCl3 400.13MHz



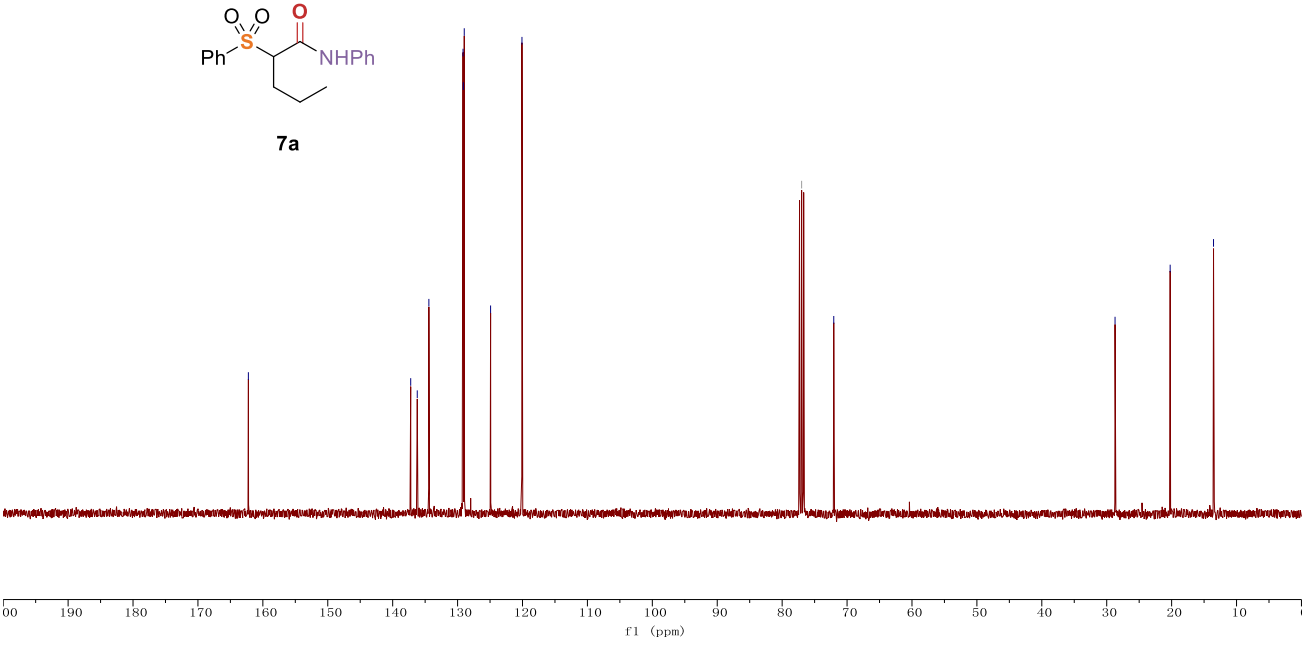
7a



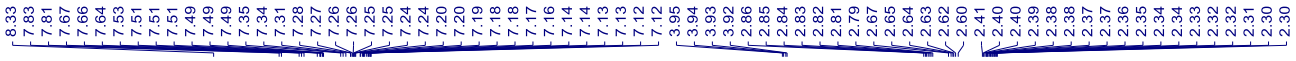
13C NMR CDCl3 100.62MHz

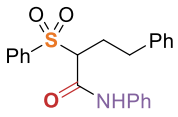


7a

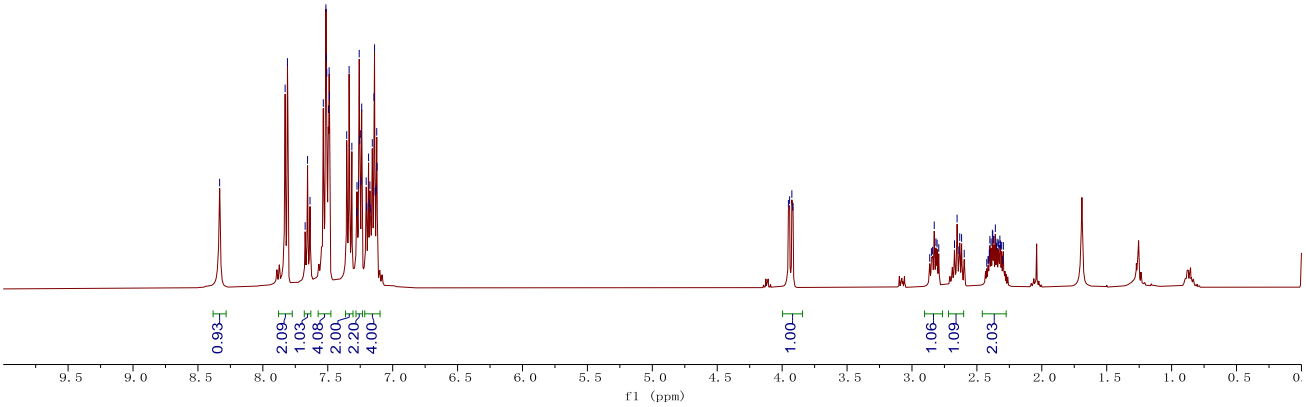


1H NMR CDCl3 400.13MHz

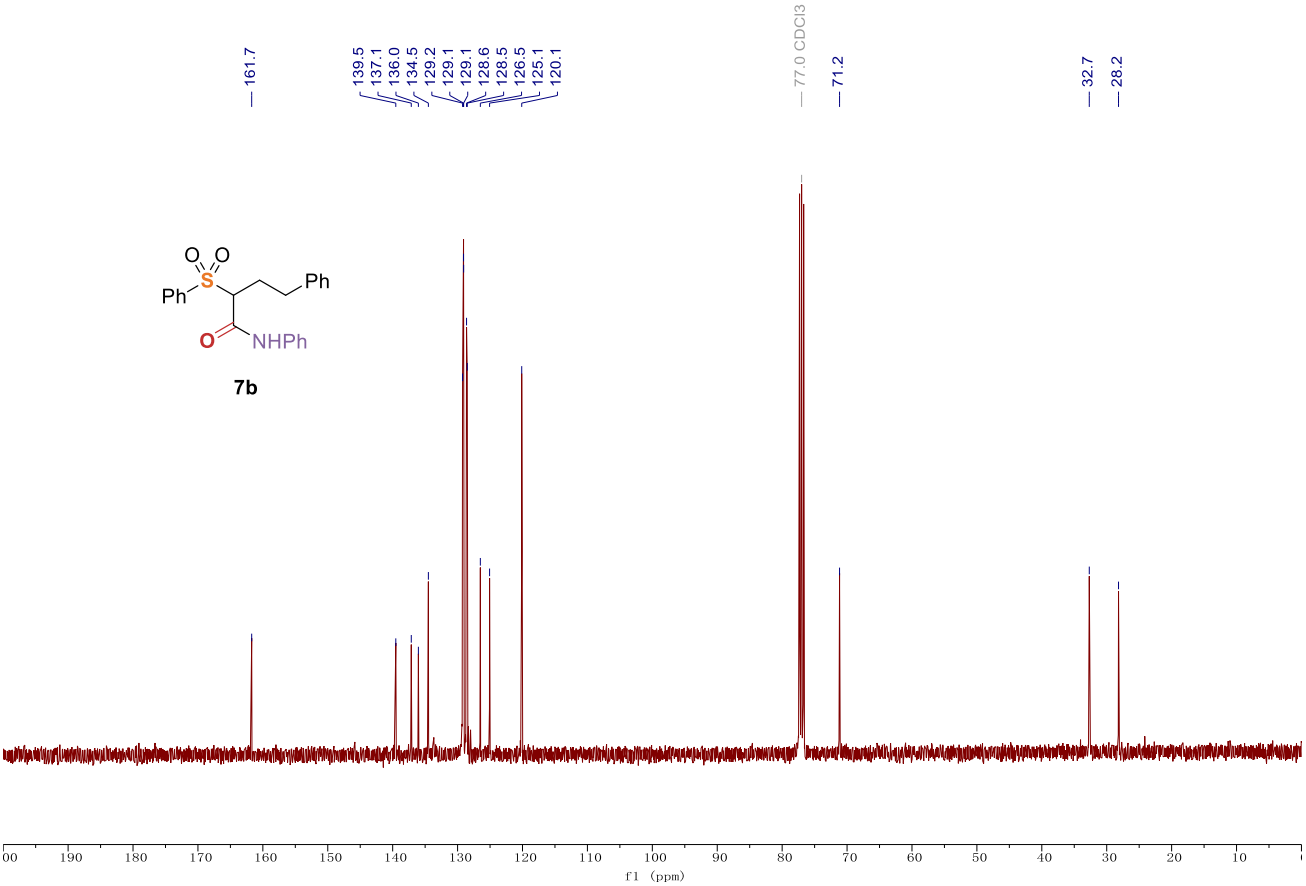




7b

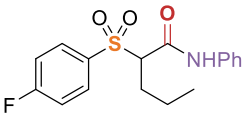


13C NMR CDCl3 100.62MHz

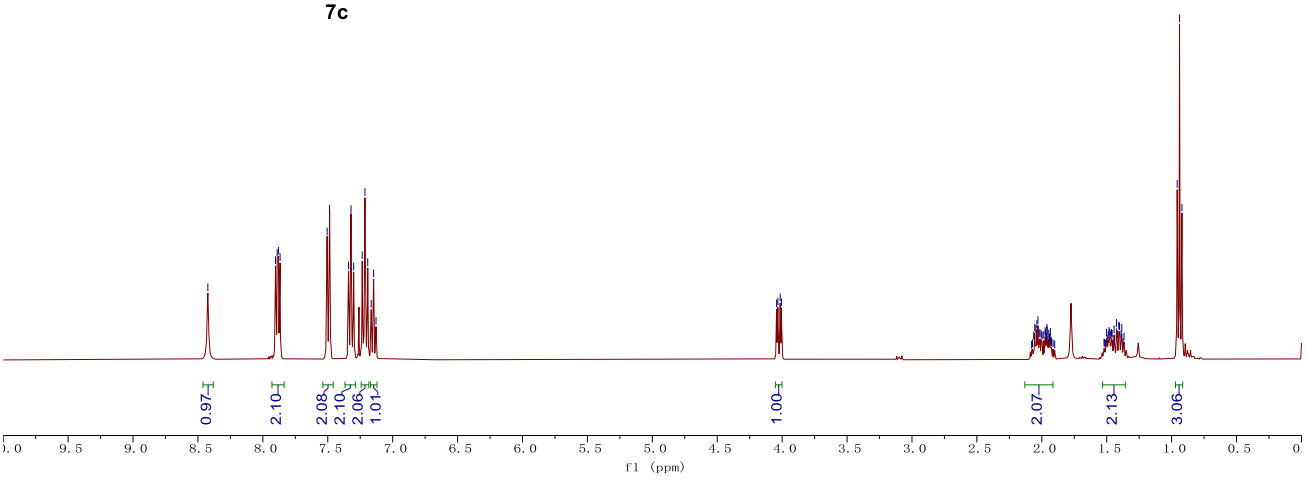


7b

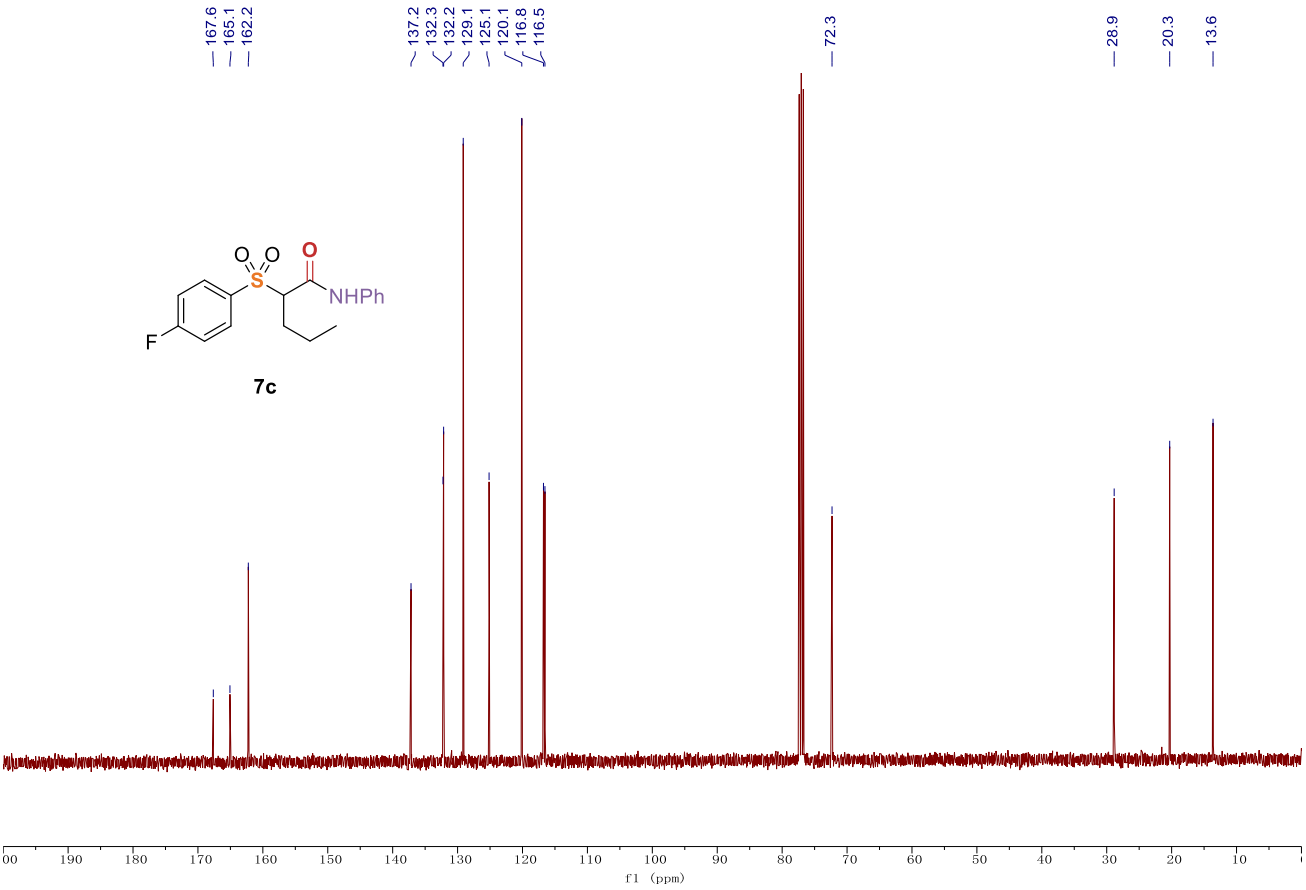
1H NMR CDCl3 400.13MHz



7c

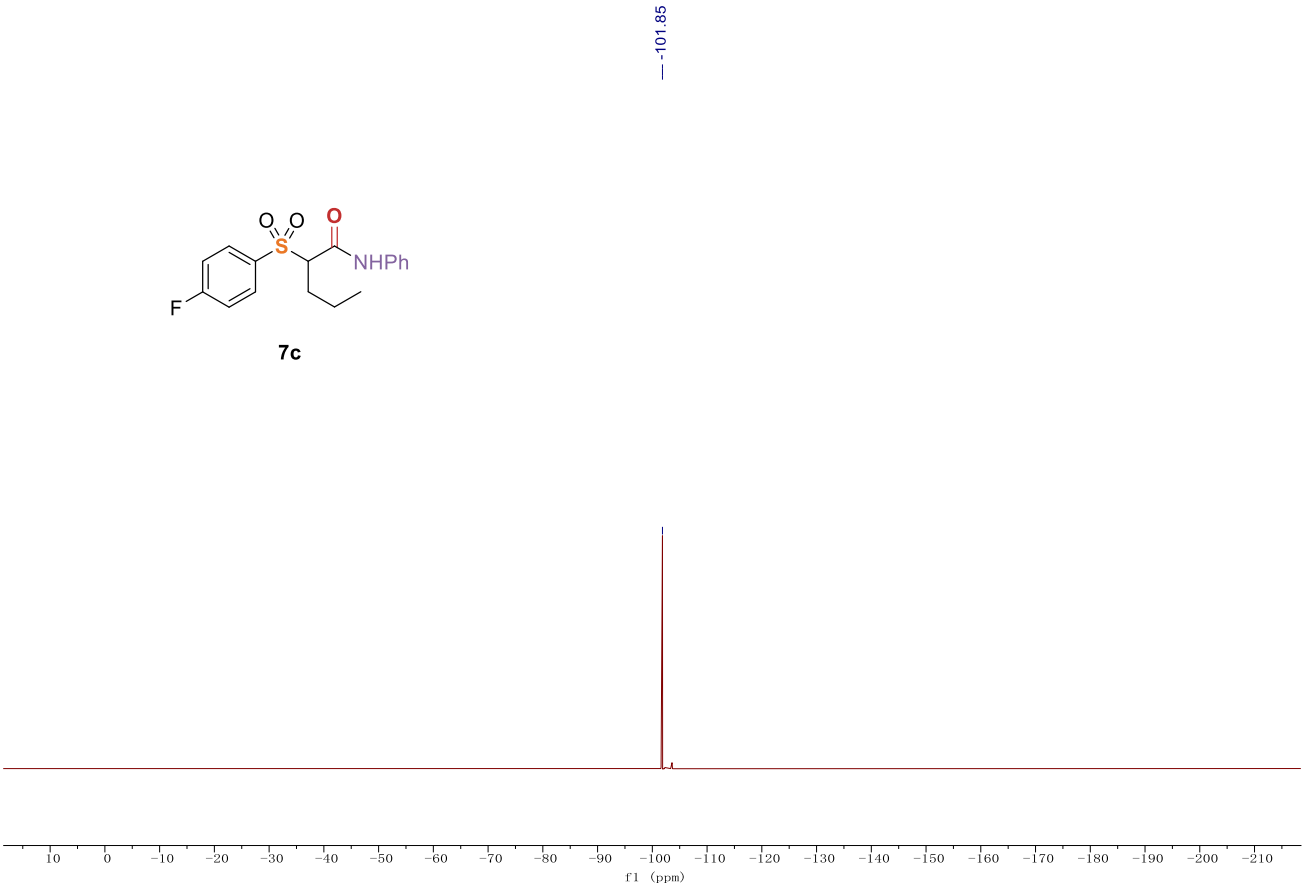


13C NMR CDCl3 100.62MHz



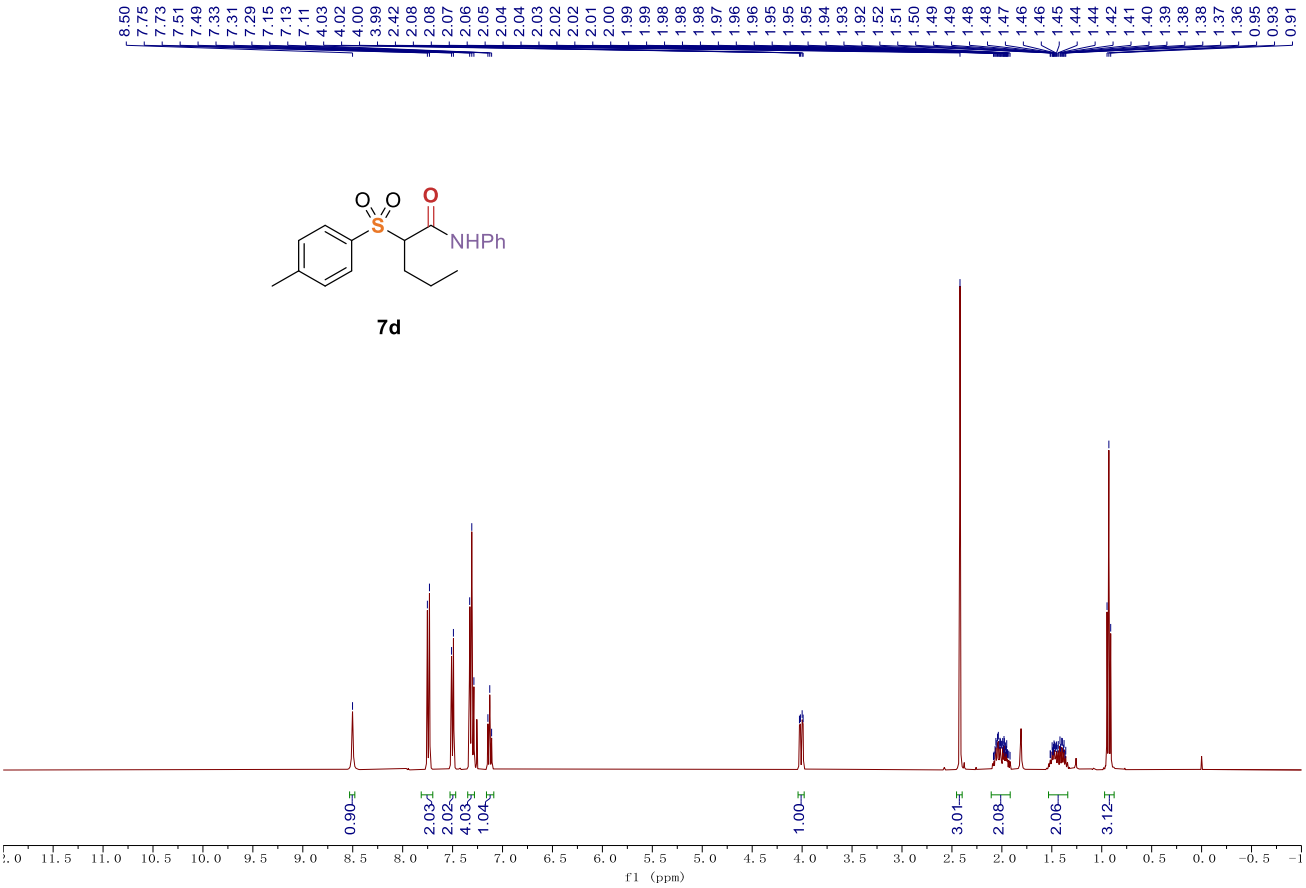
7c

19F NMR CDCl3 376.46MHz

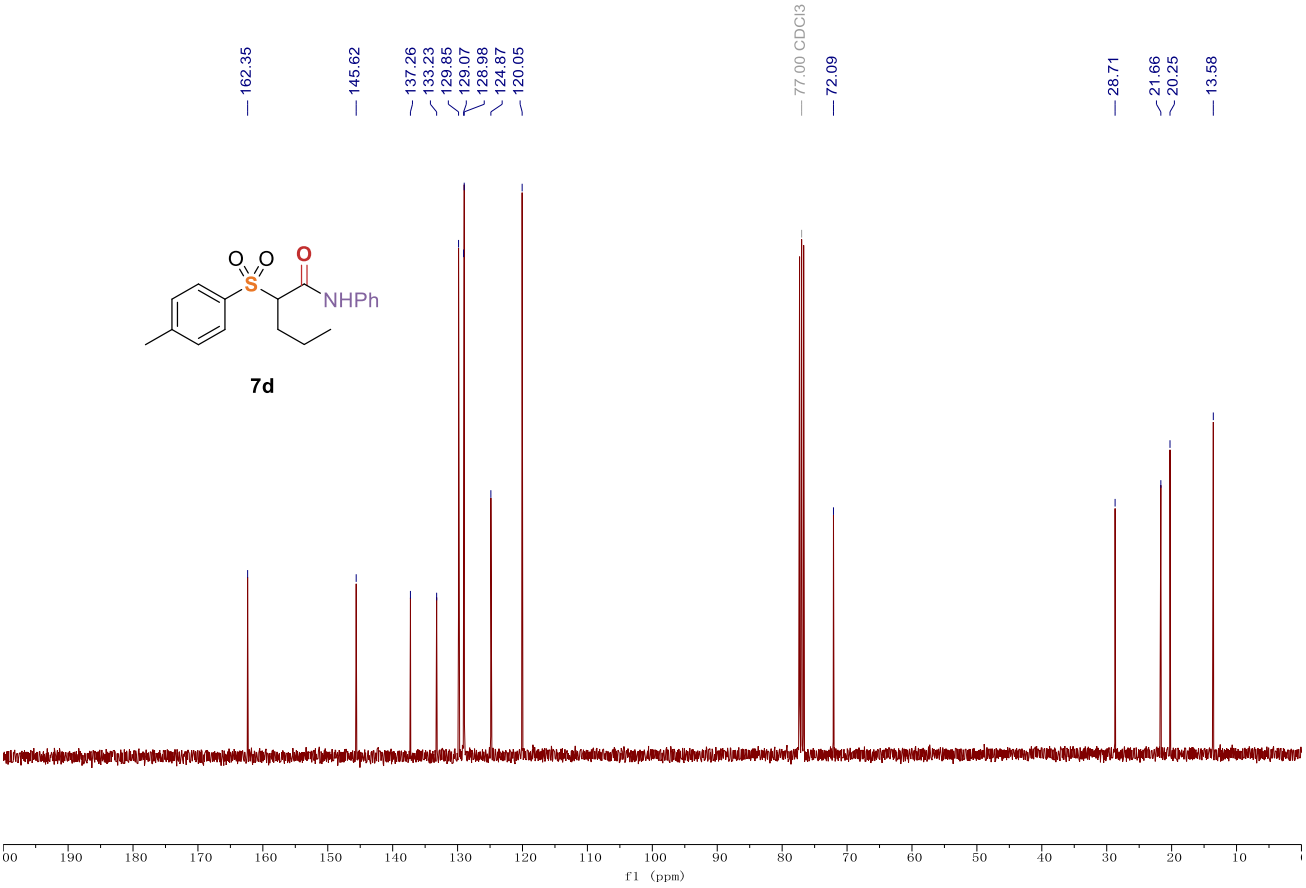


7c

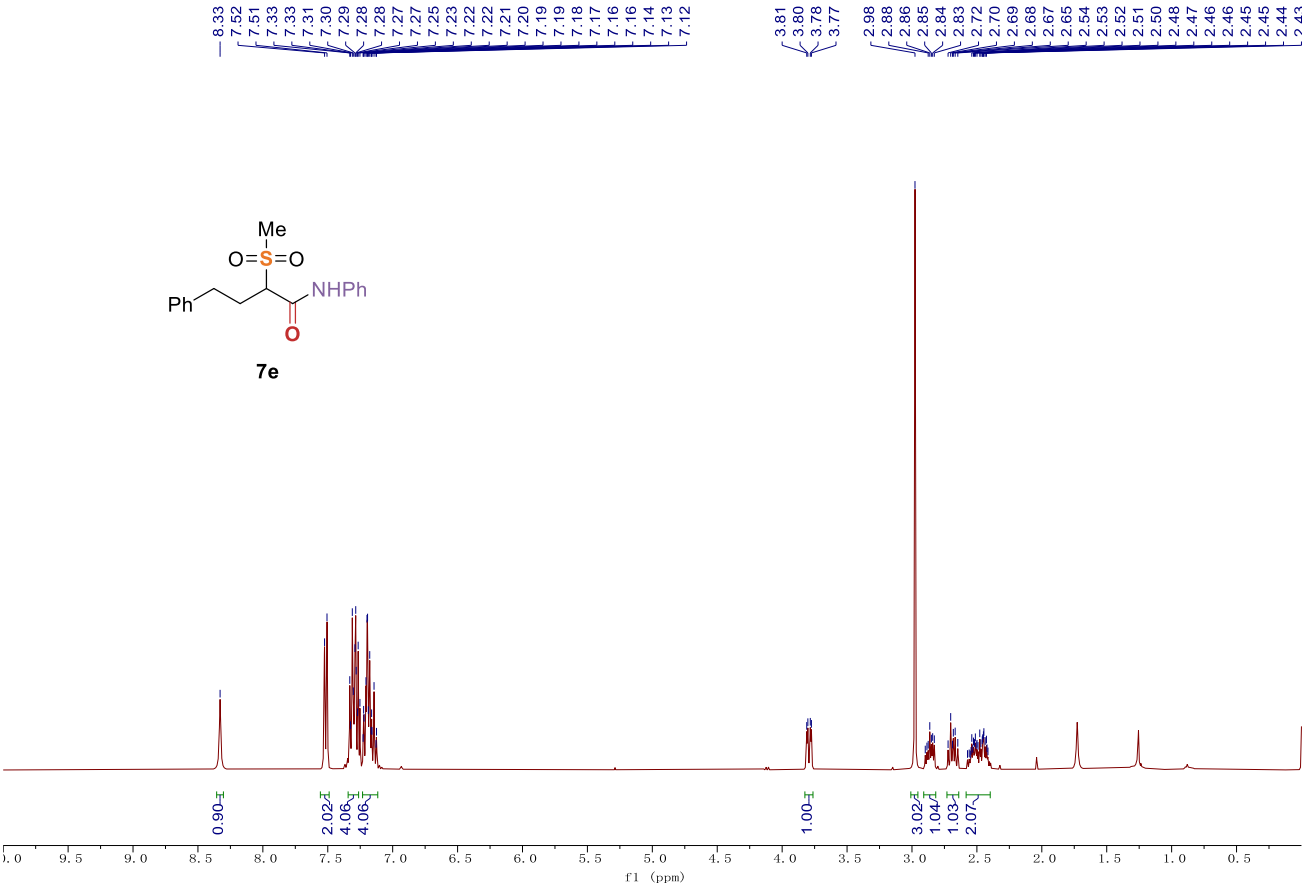
1H NMR CDCl3 400.13MHz



13C NMR CDCl3 100.62MHz

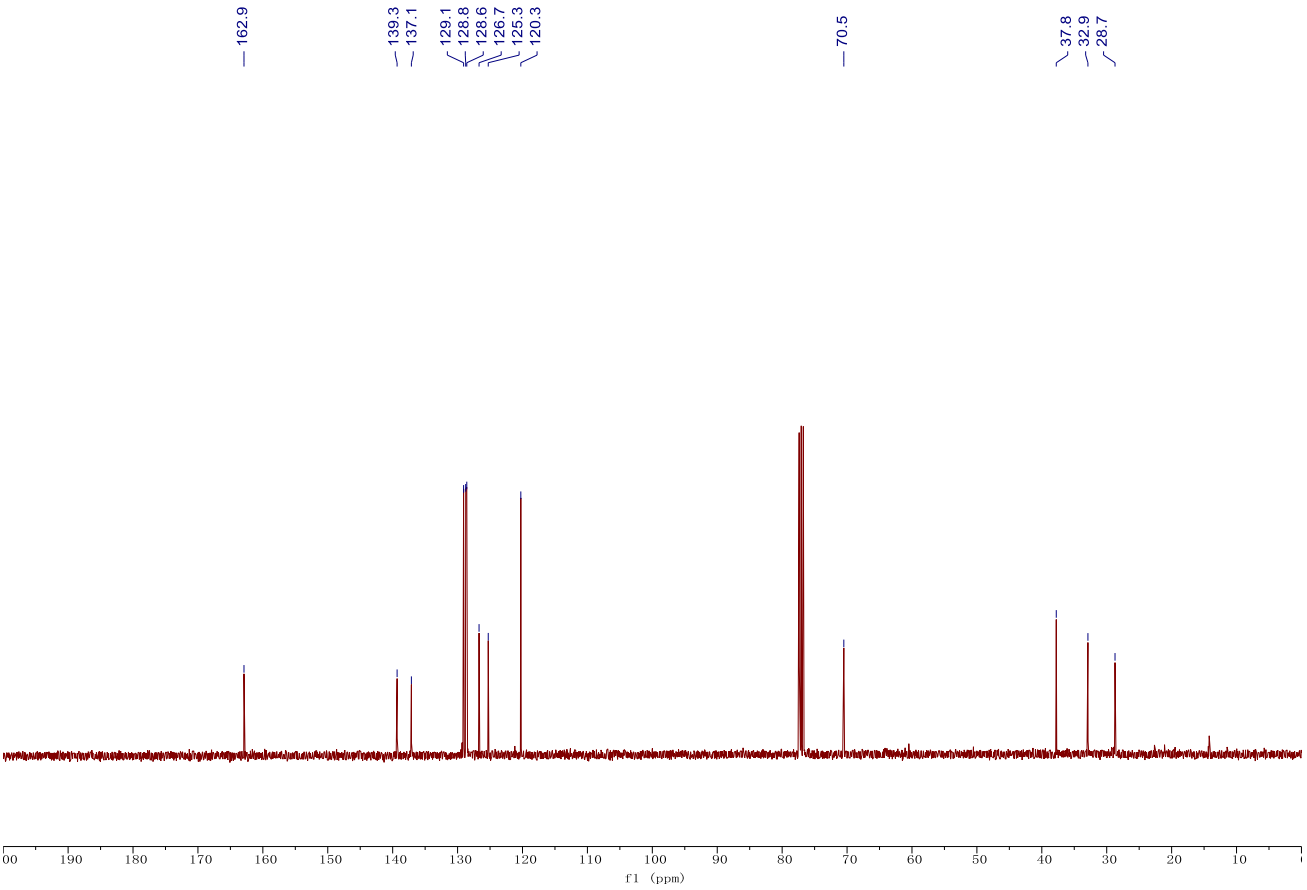


1H NMR CDCl3 400.13MHz

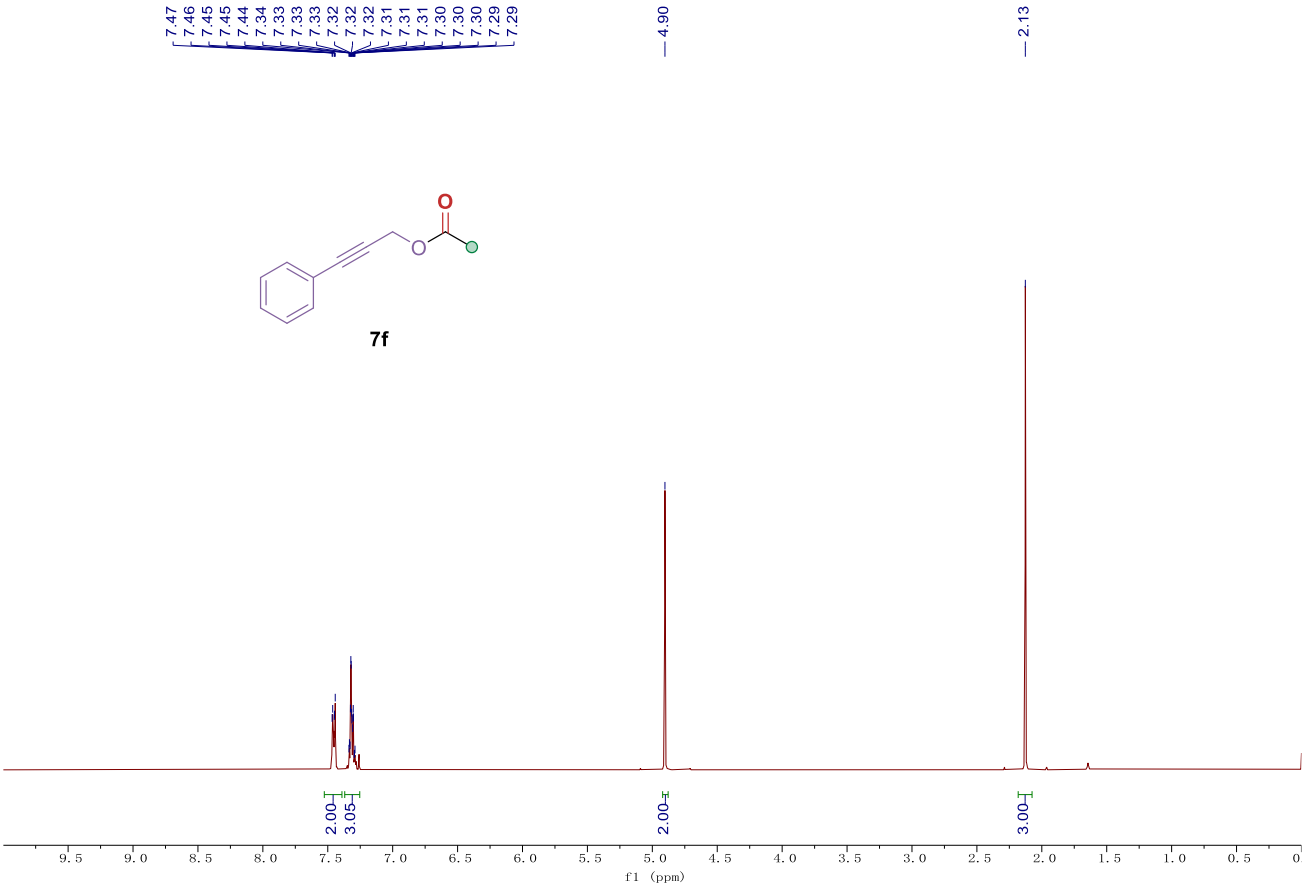


7e

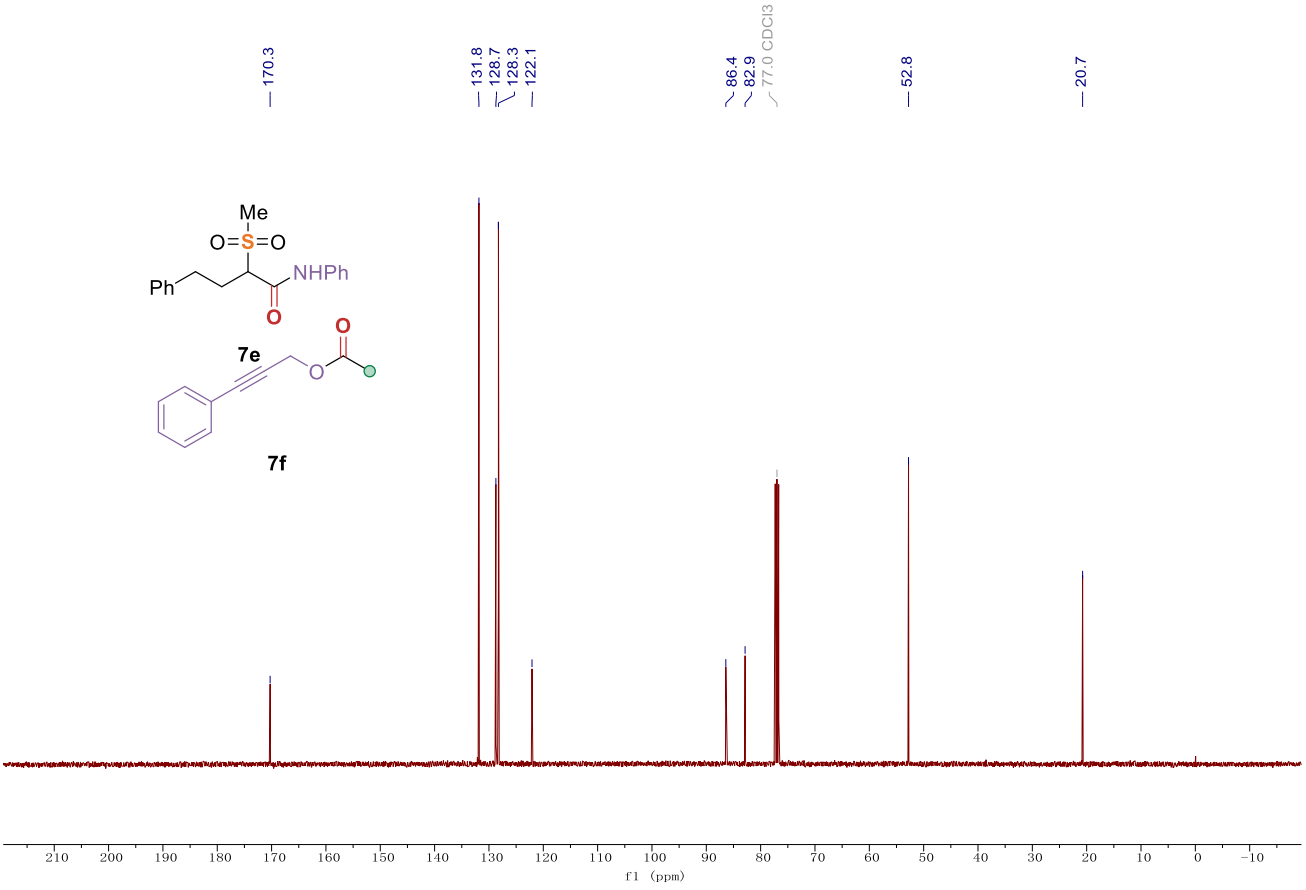
13C NMR CDCl3 100.62MHz



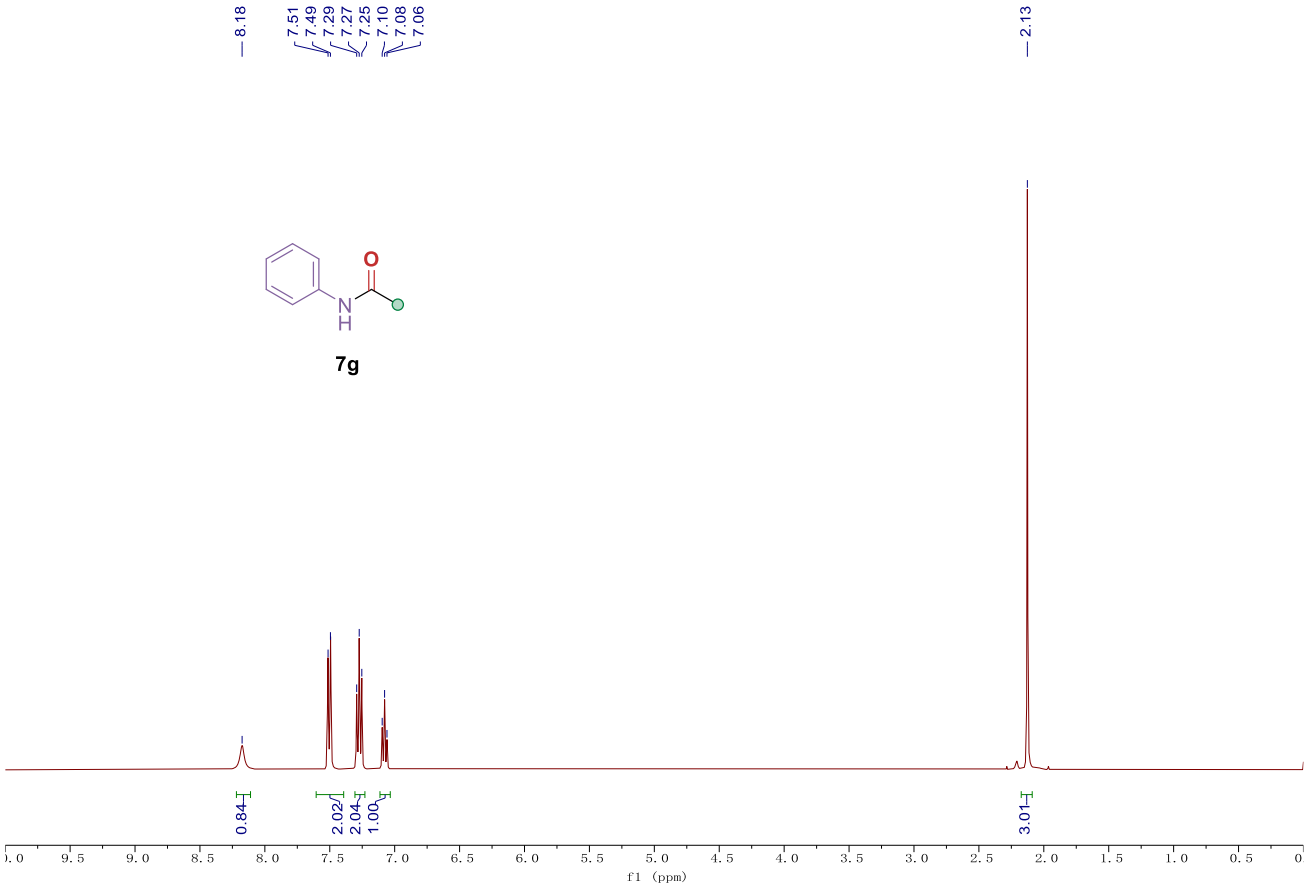
1H NMR CDCl3 400.13MHz



13C NMR CDCl3 100.62MHz

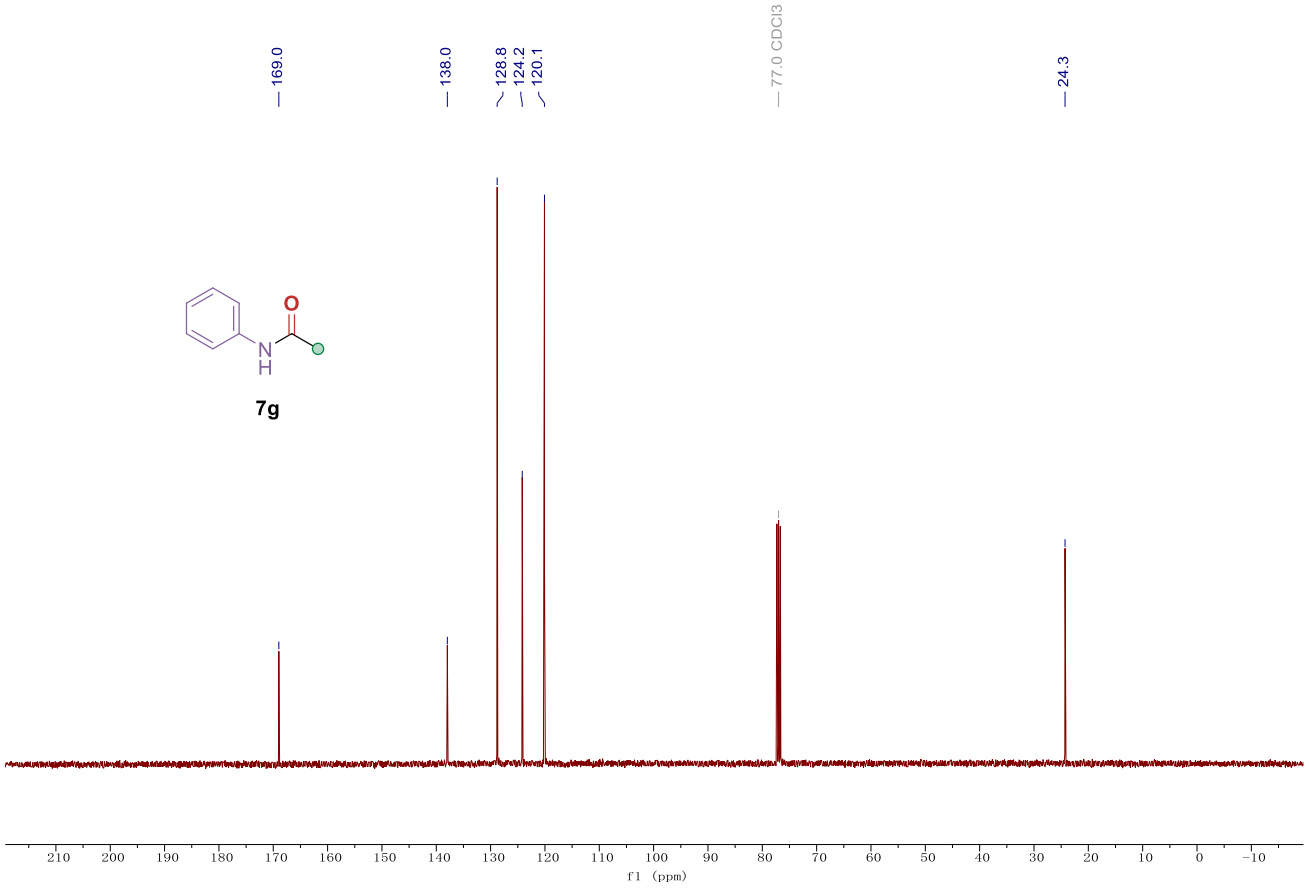


1H NMR CDCl3 400.13MHz



7g

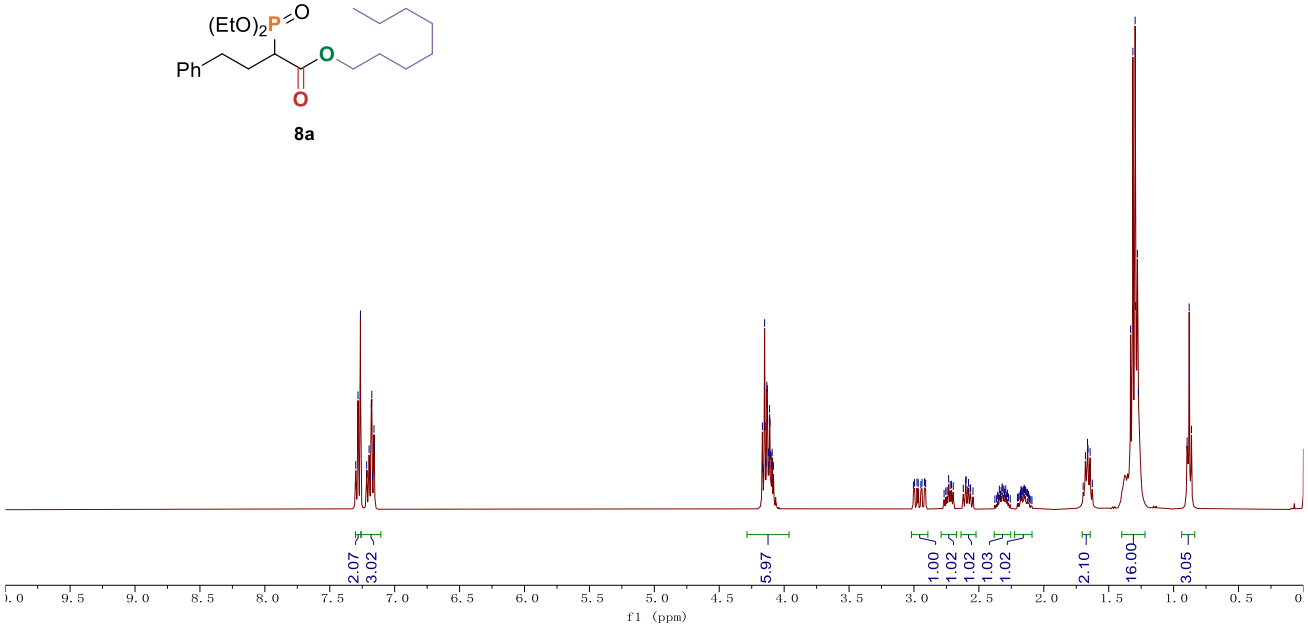
13C NMR CDCl3 100.62MHz



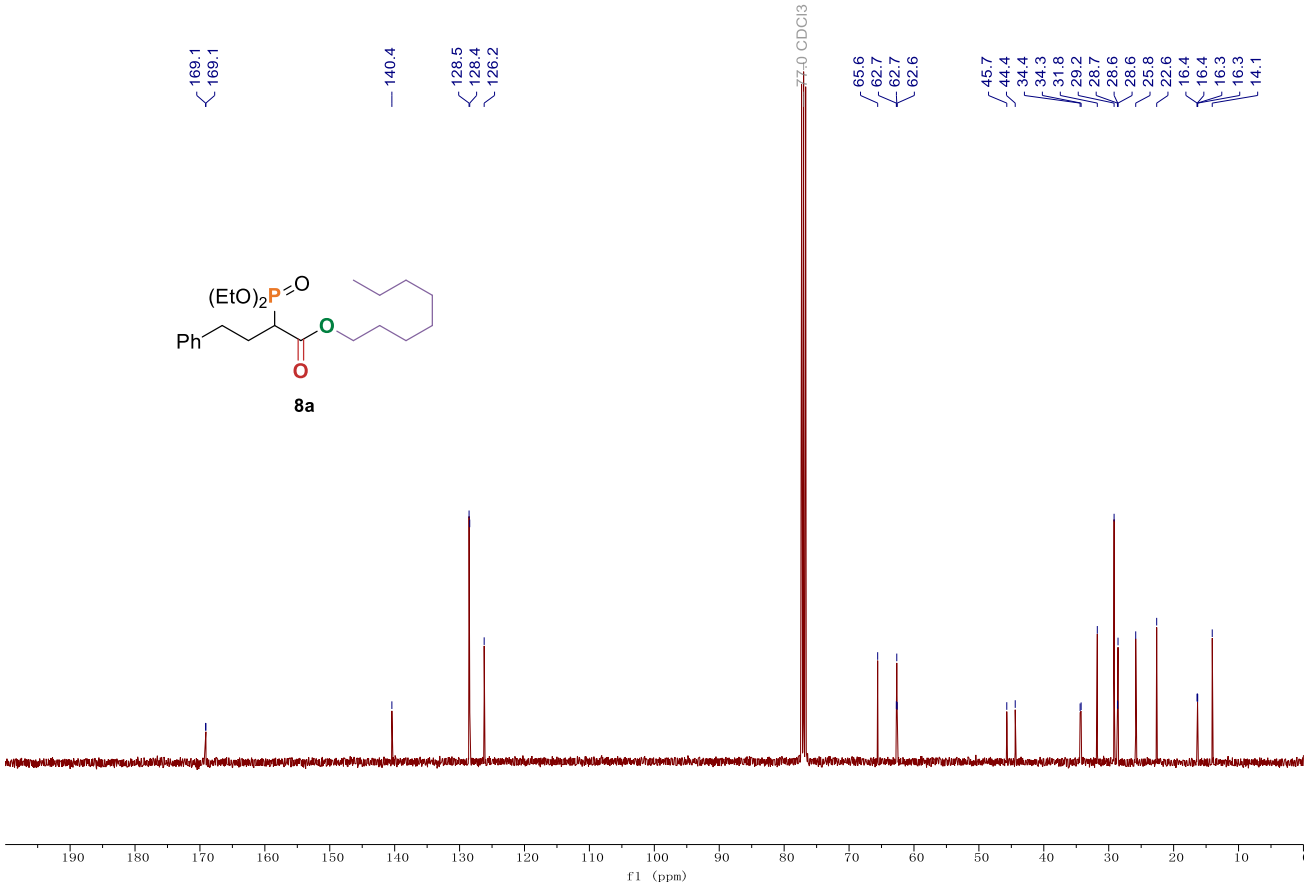
7g

1H NMR CDCl3 400.13MHz

8a

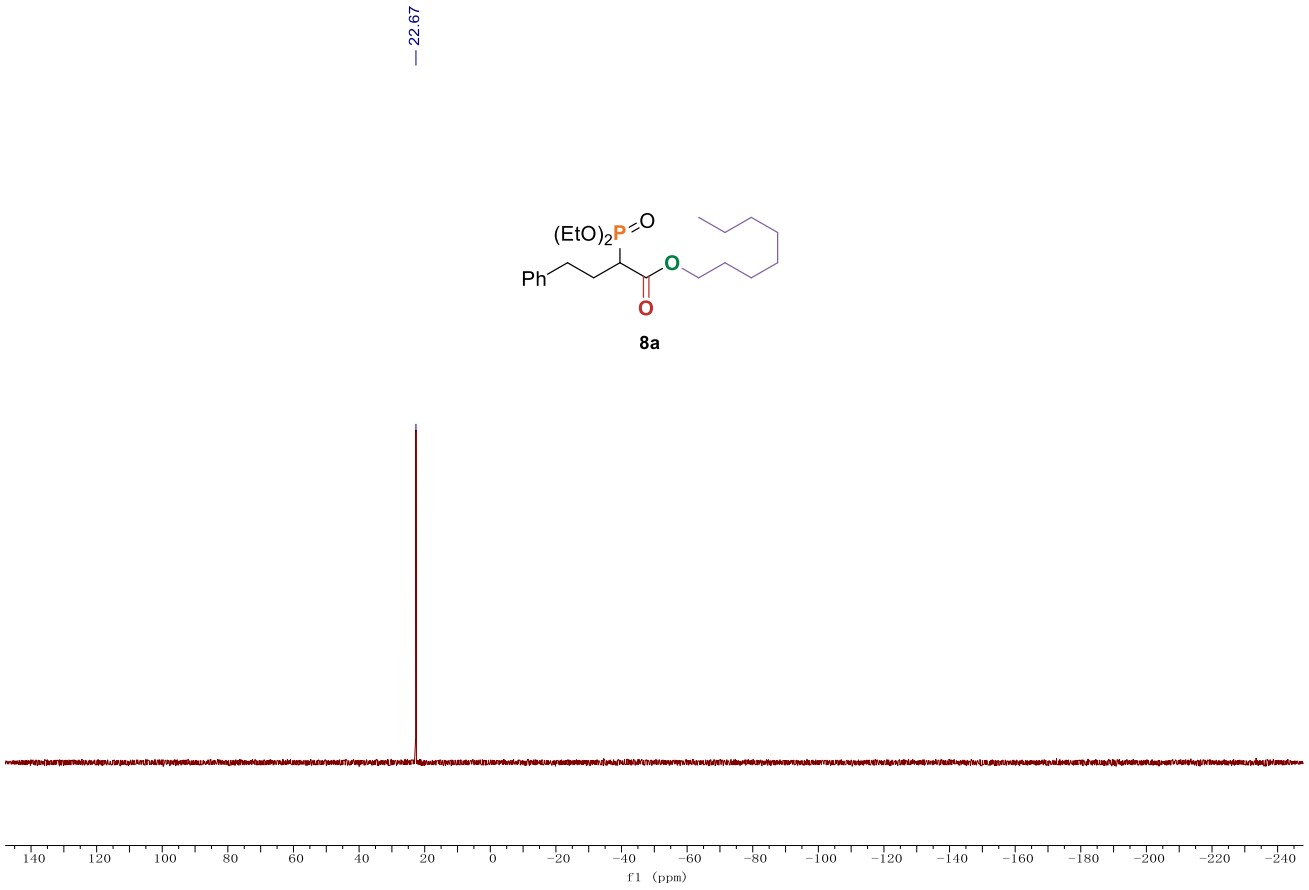


13C NMR CDCl3 100.62MHz

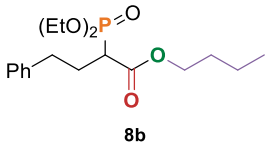


8a

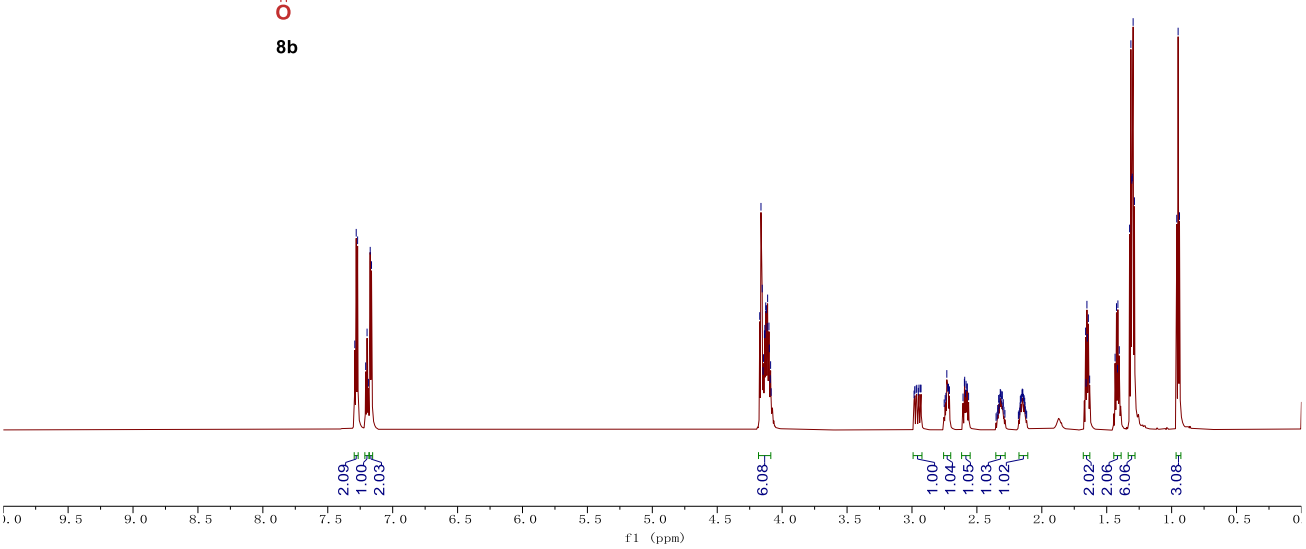
31P NMR CDCl3 161.97MHz



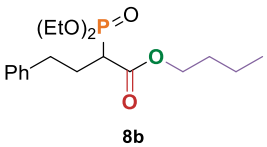
1H NMR CDCl3 700.17MHz



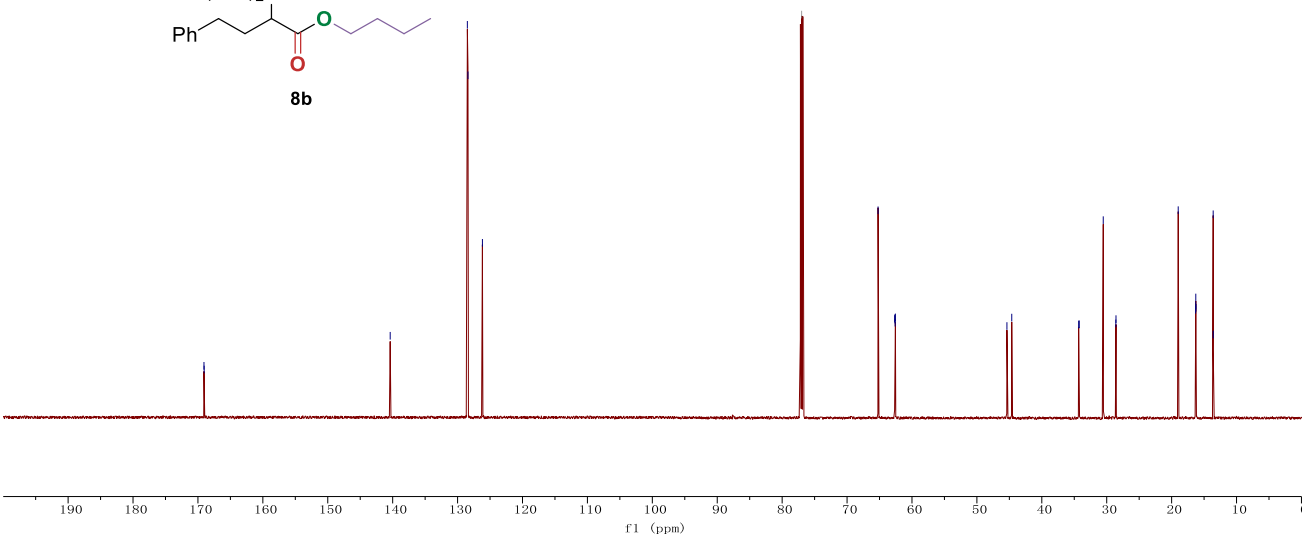
8b



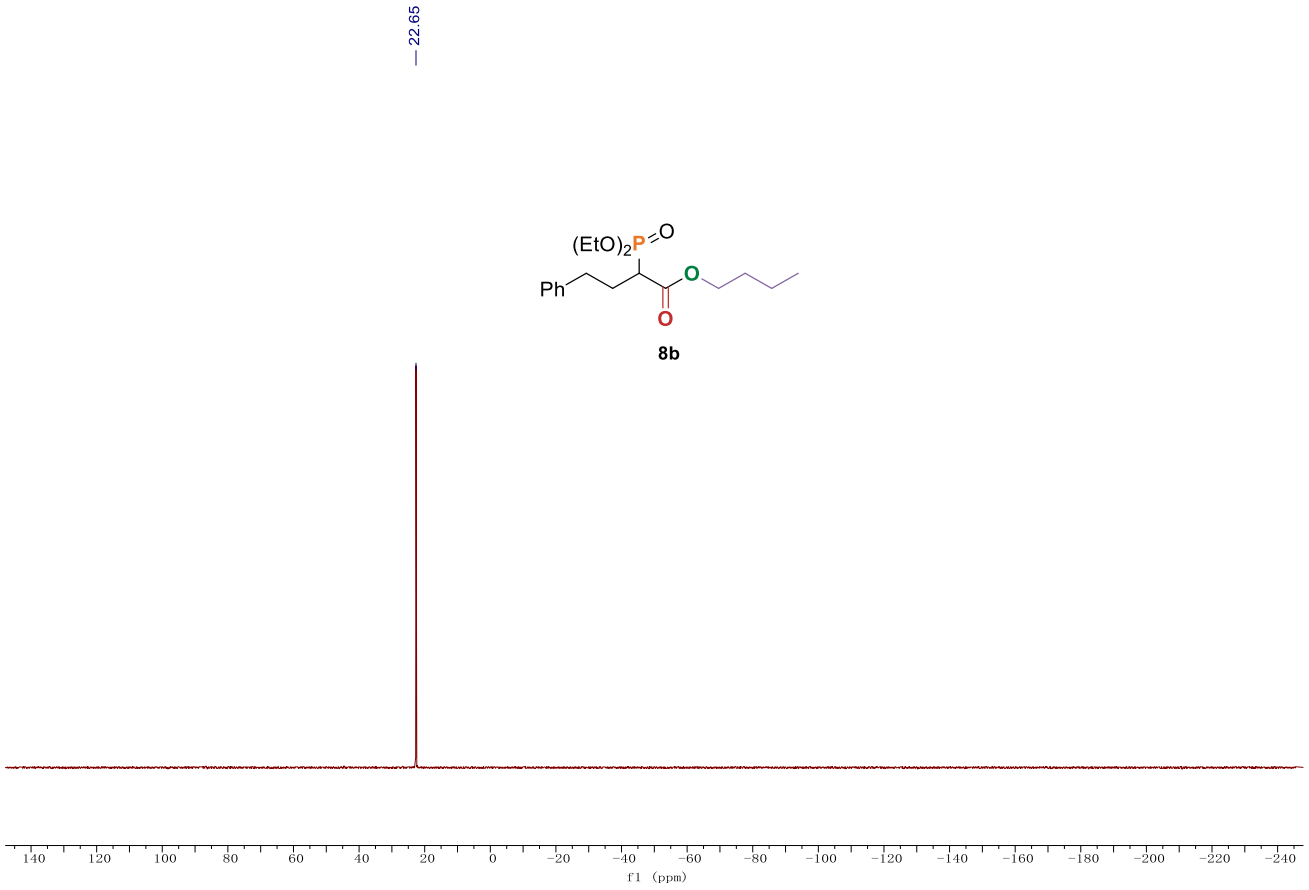
13C NMR CDCl3 176.08MHz



8b



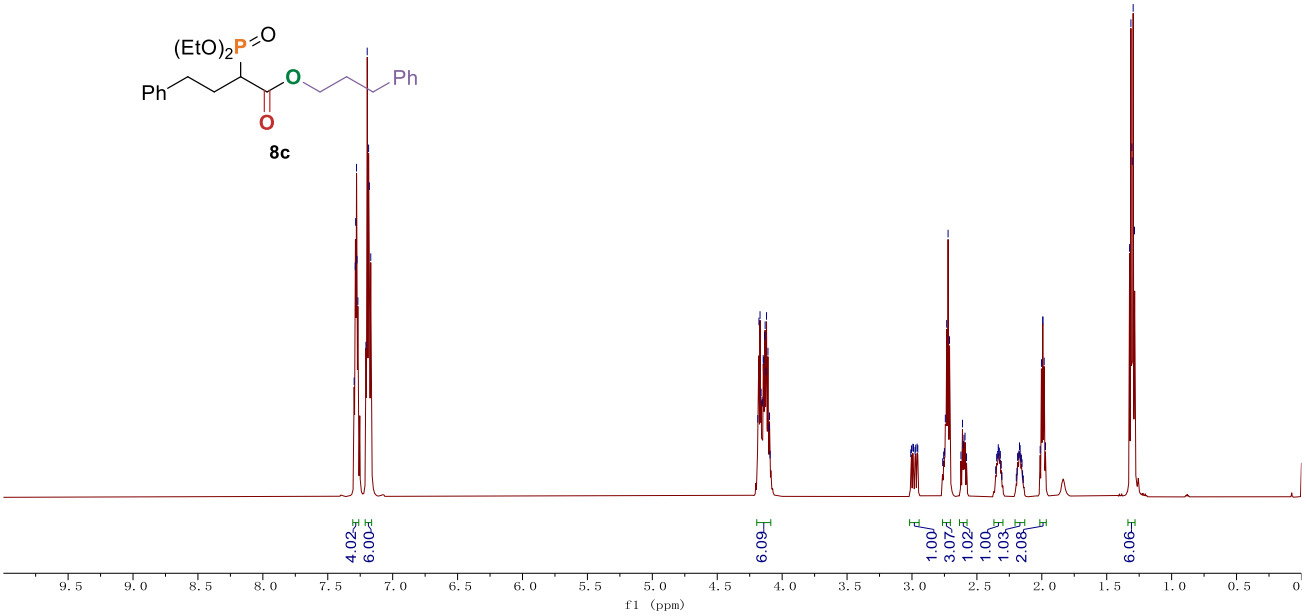
31P NMR CDCl3 161.97MHz



8b

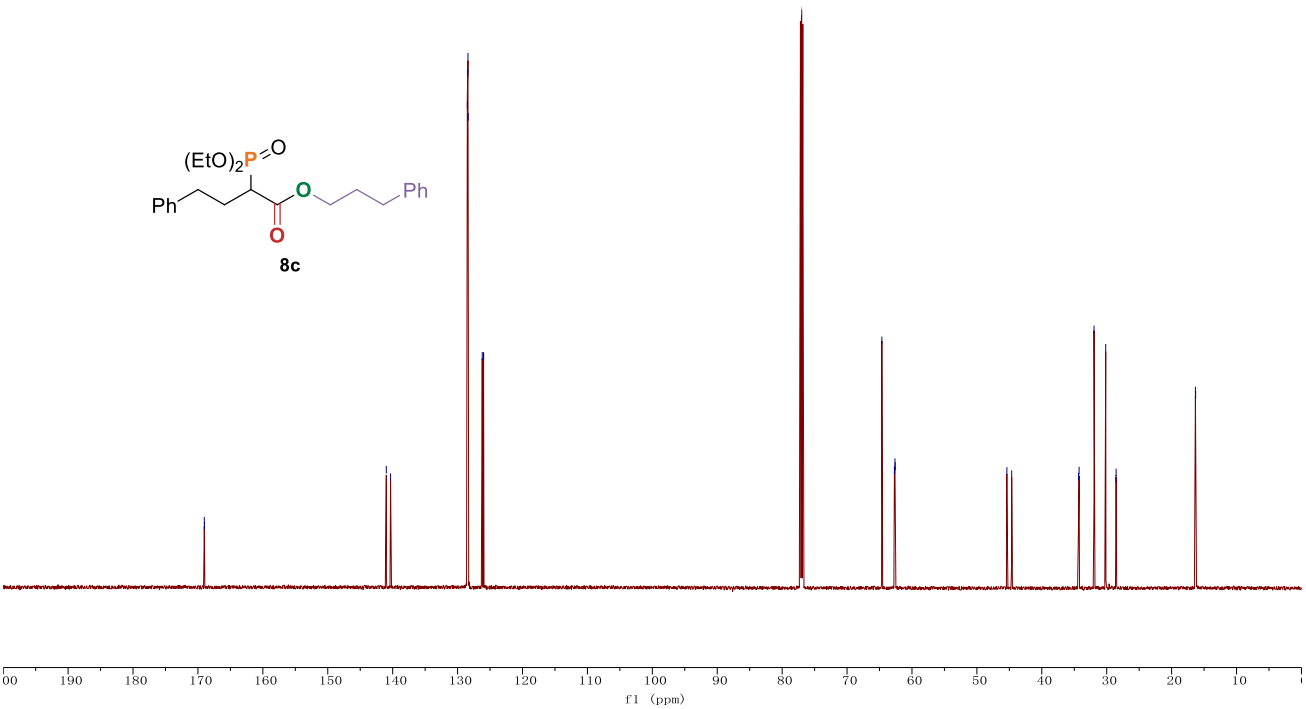
1H NMR CDCl3 700.17MHz

8c

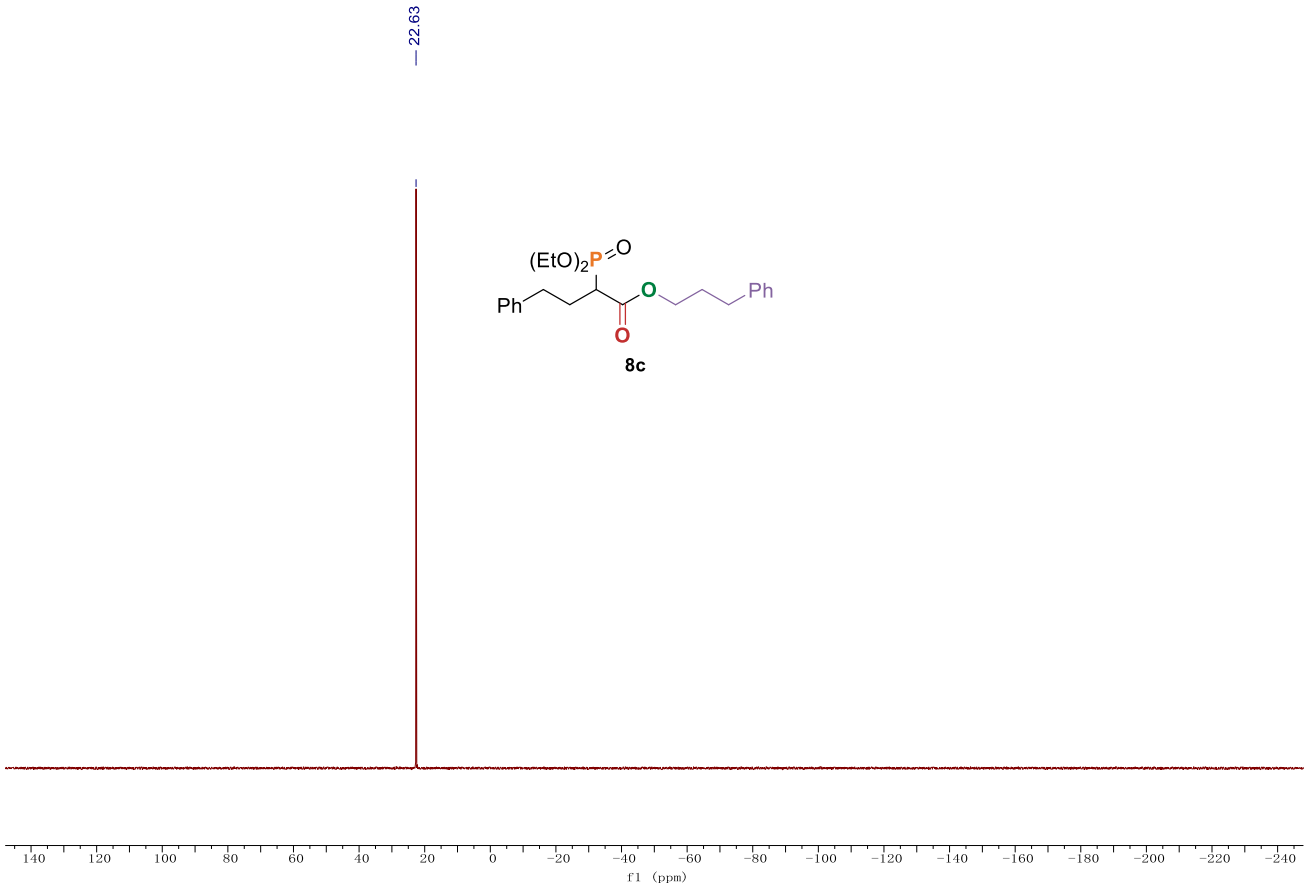


13C NMR CDCl3 176.08MHz

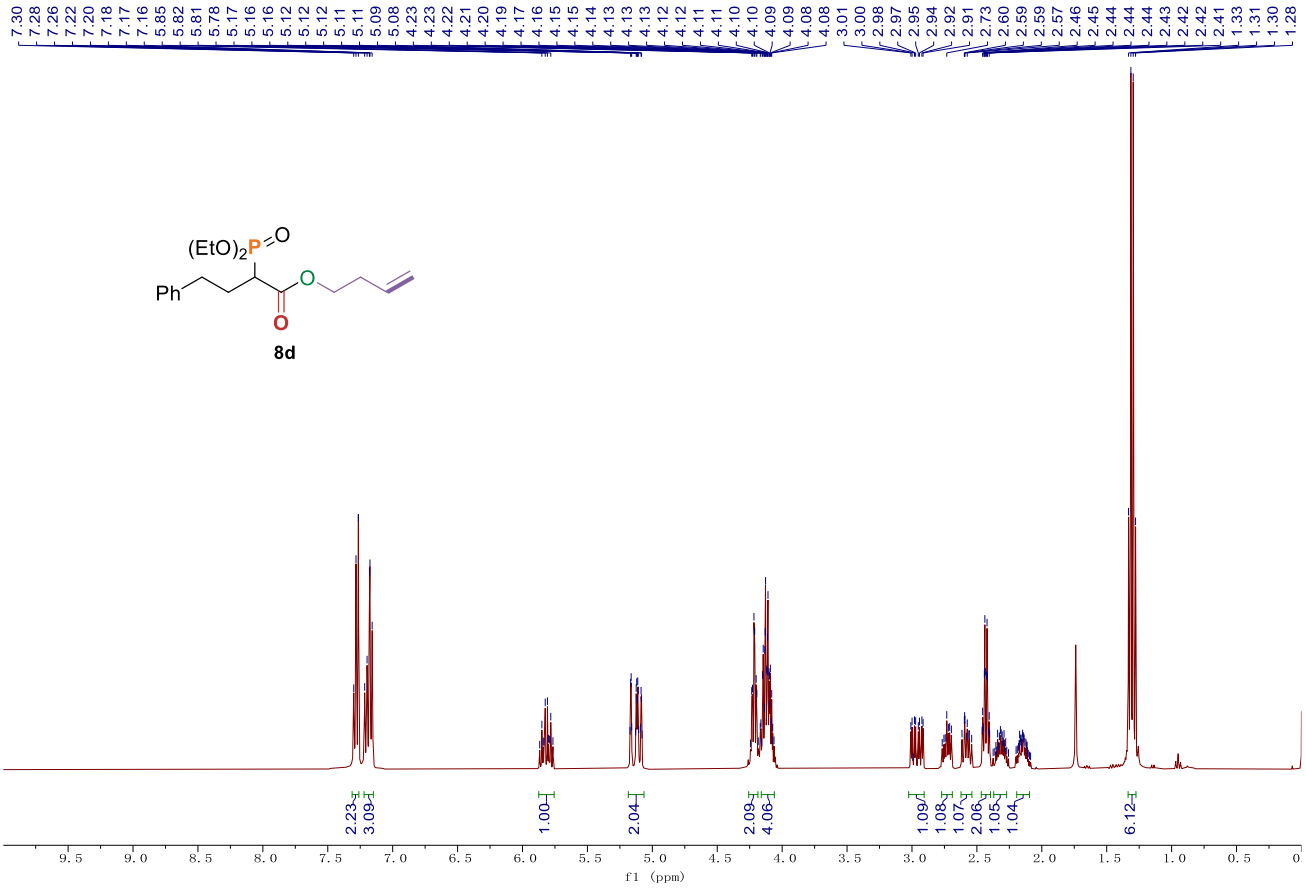
8c



31P NMR CDCl3 161.97MHz

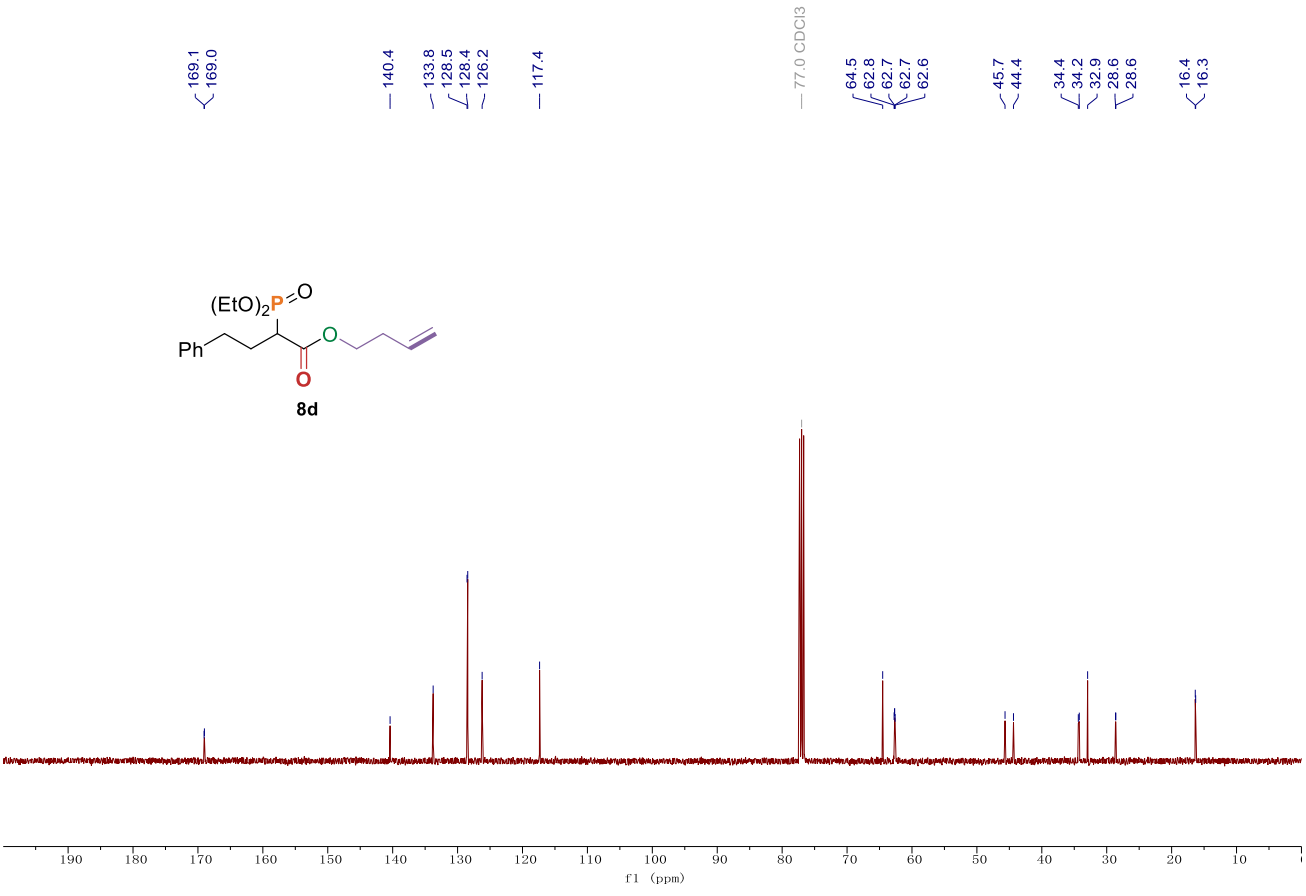


1H NMR CDCl3 400.13MHz



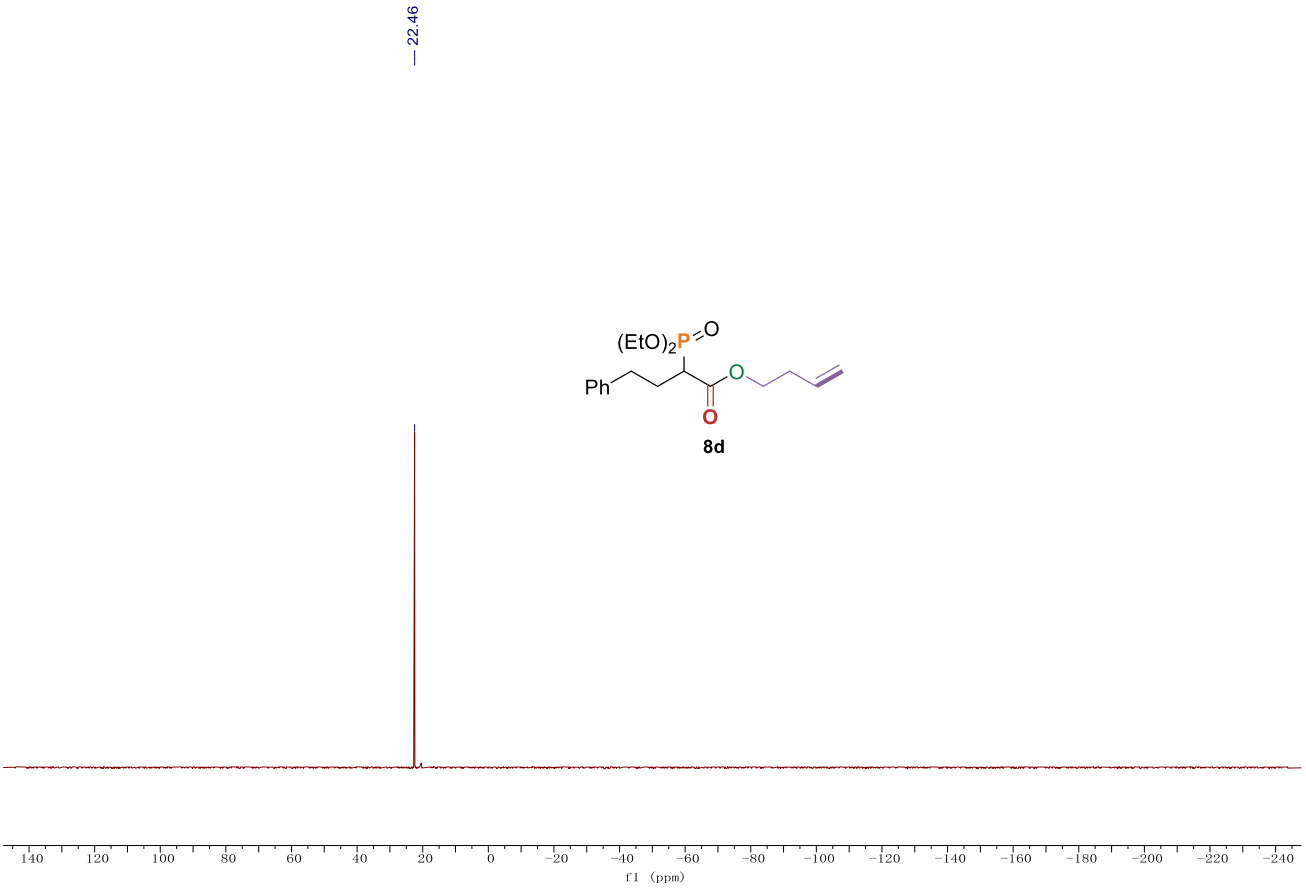
8d

13C NMR CDCl3 100.62MHz

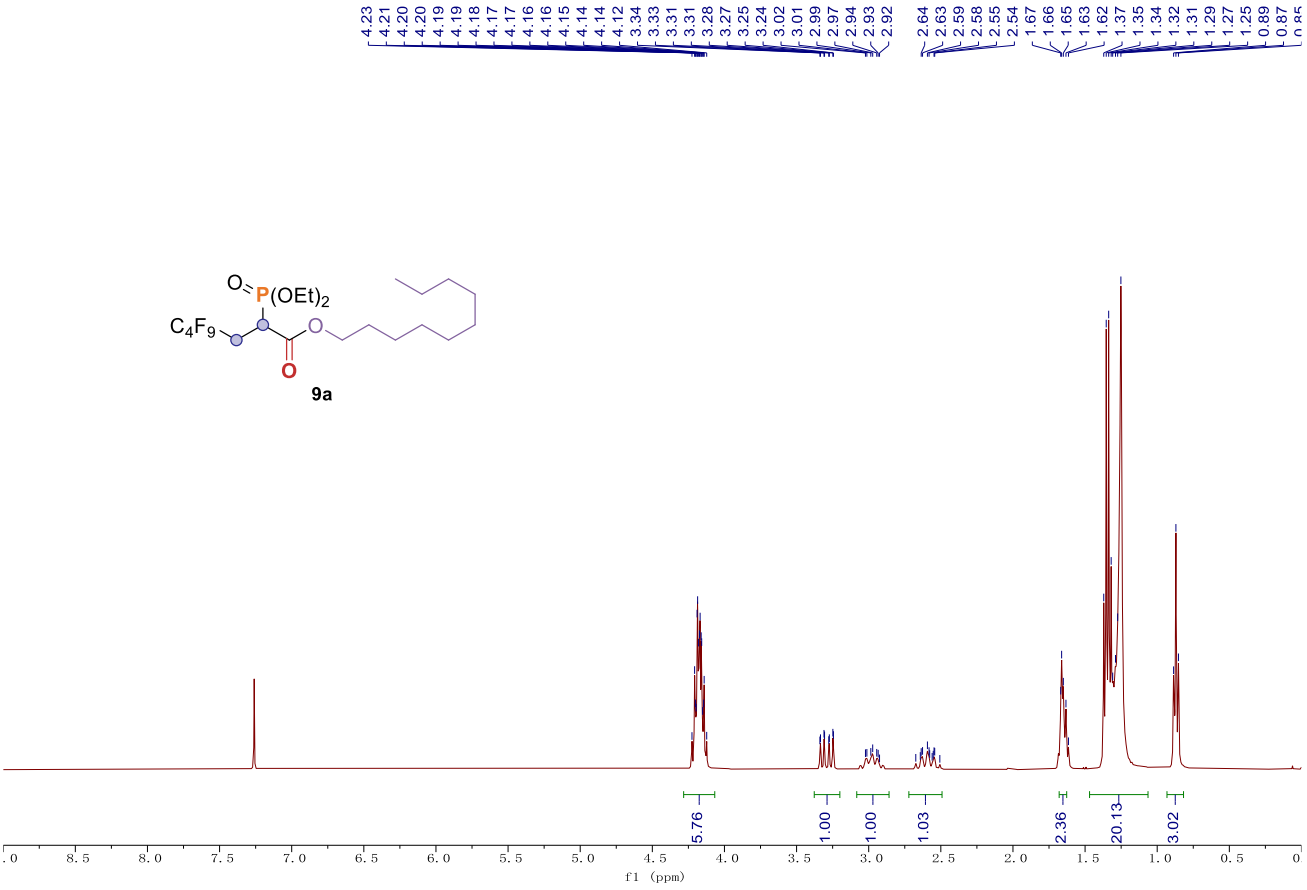


8d

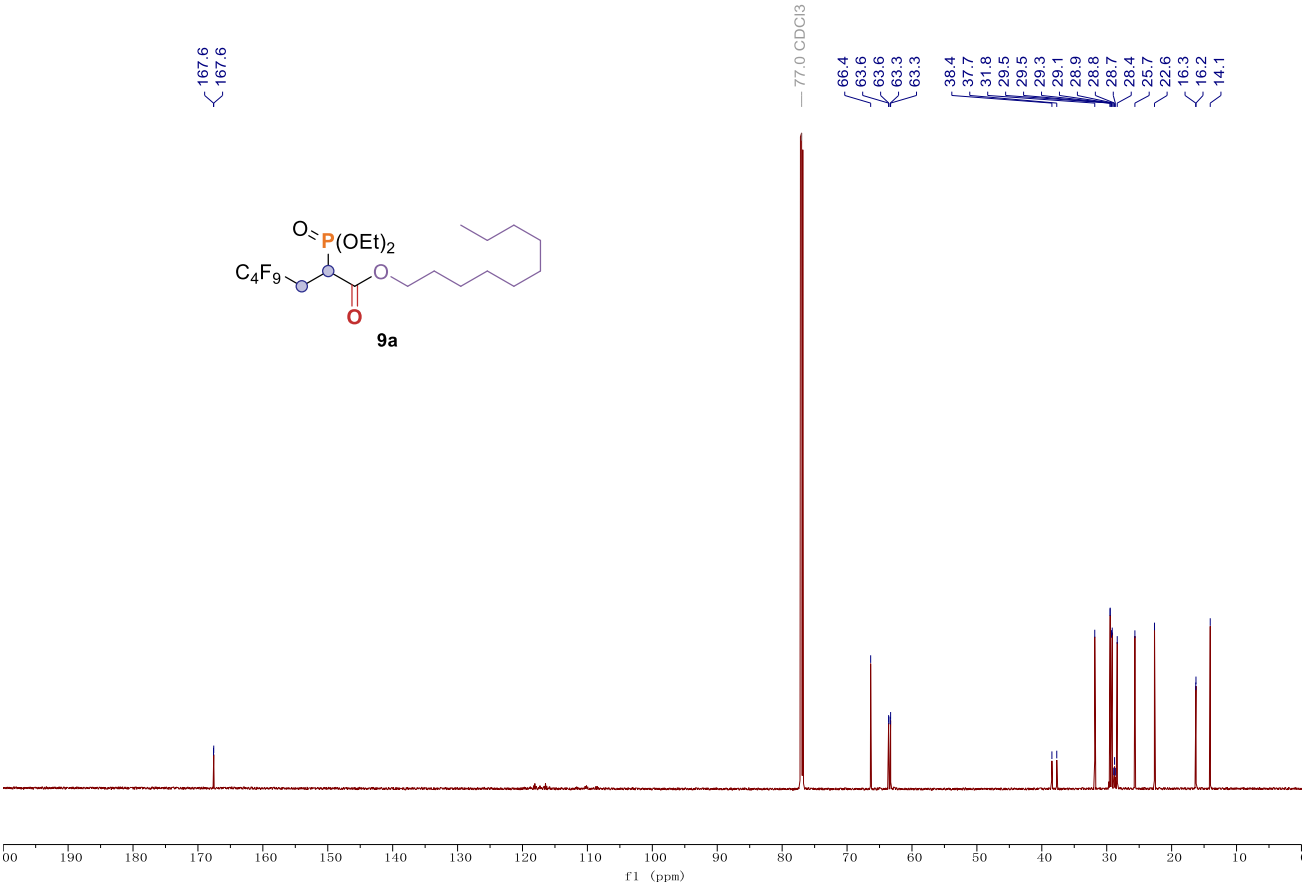
31P NMR CDCl3 161.97MHz



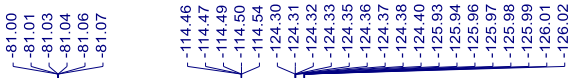
1H NMR CDCl3 400.13MHz

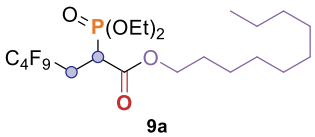


13C NMR CDCl3 176.08MHz

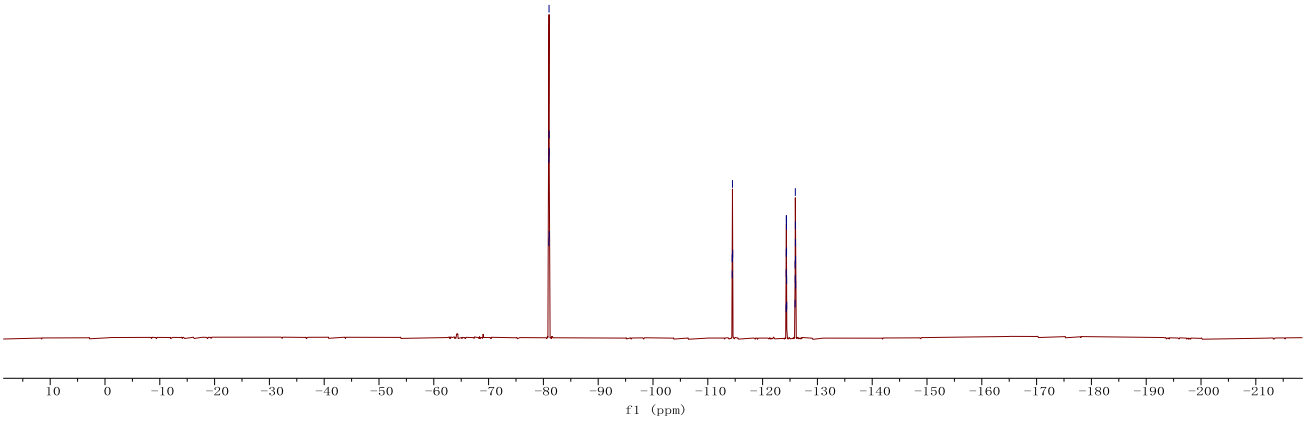


19F NMR CDCl3 376.46MHz

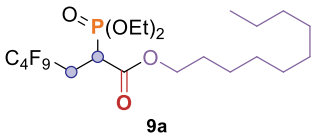




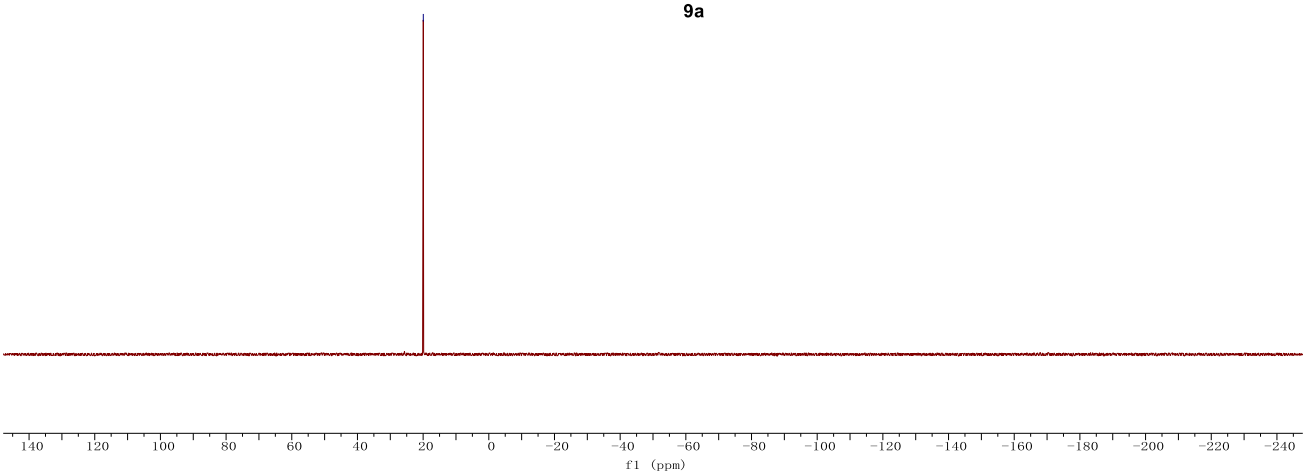
9a



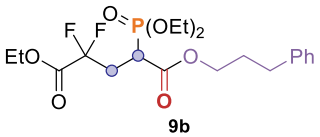
31P NMR CDCl3 161.97MHz



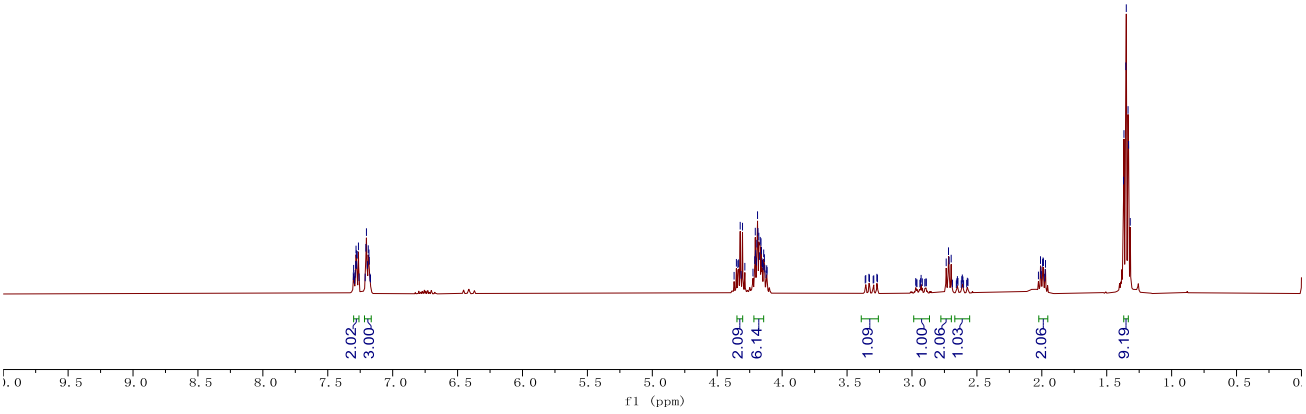
9a



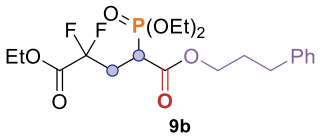
1H NMR CDCl3 400.13MHz



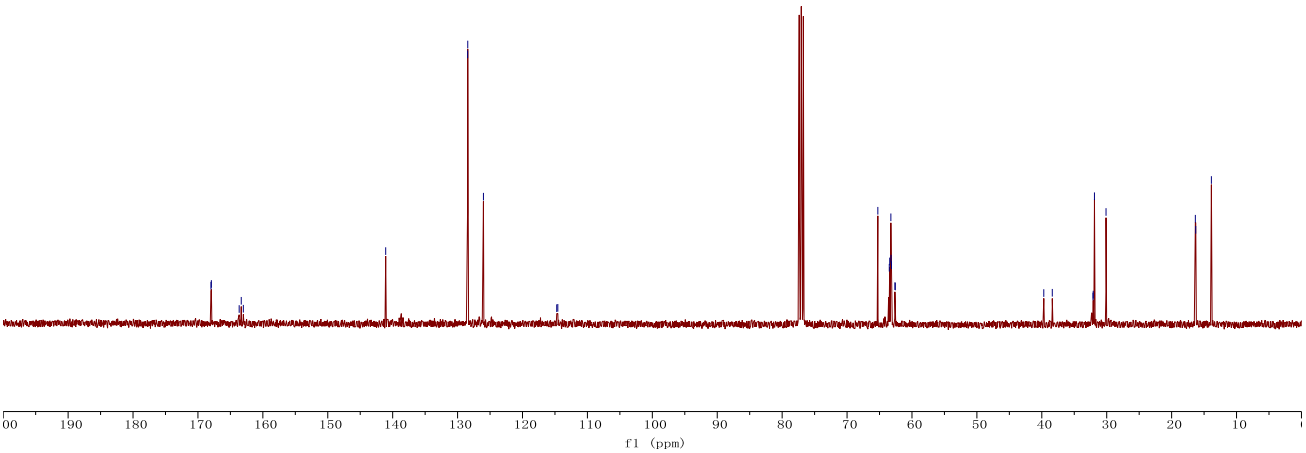
9b



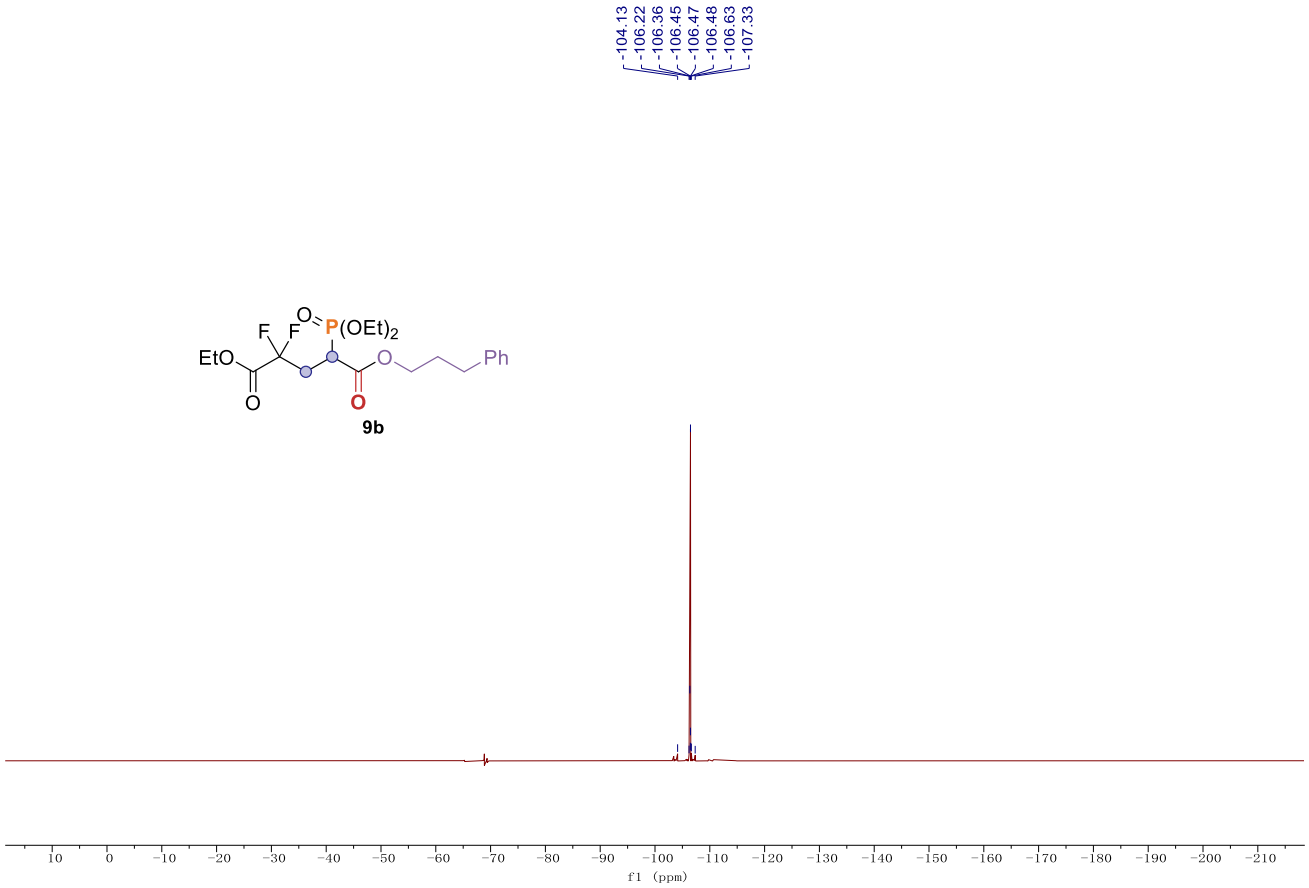
1H NMR CDCl3 100.62MHz



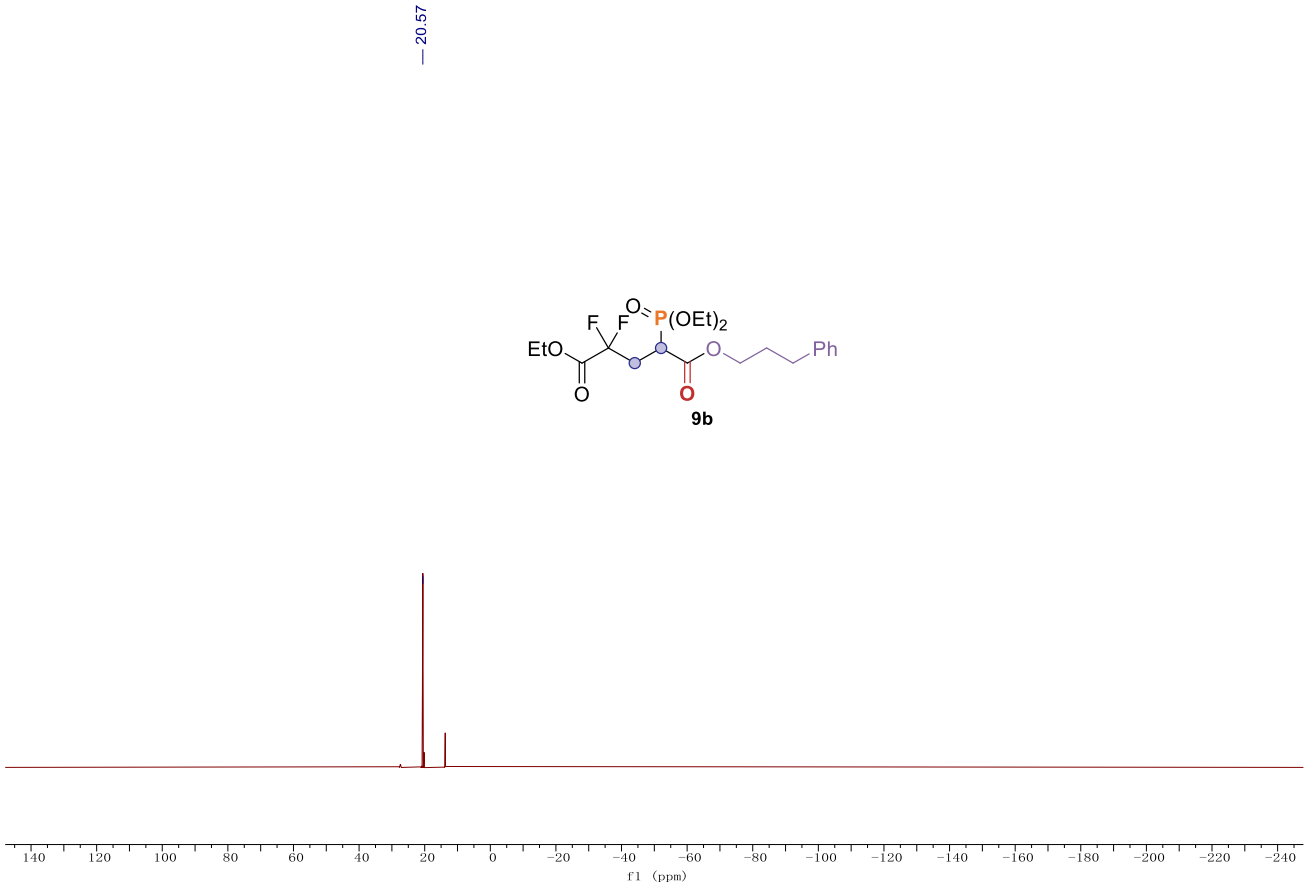
9b



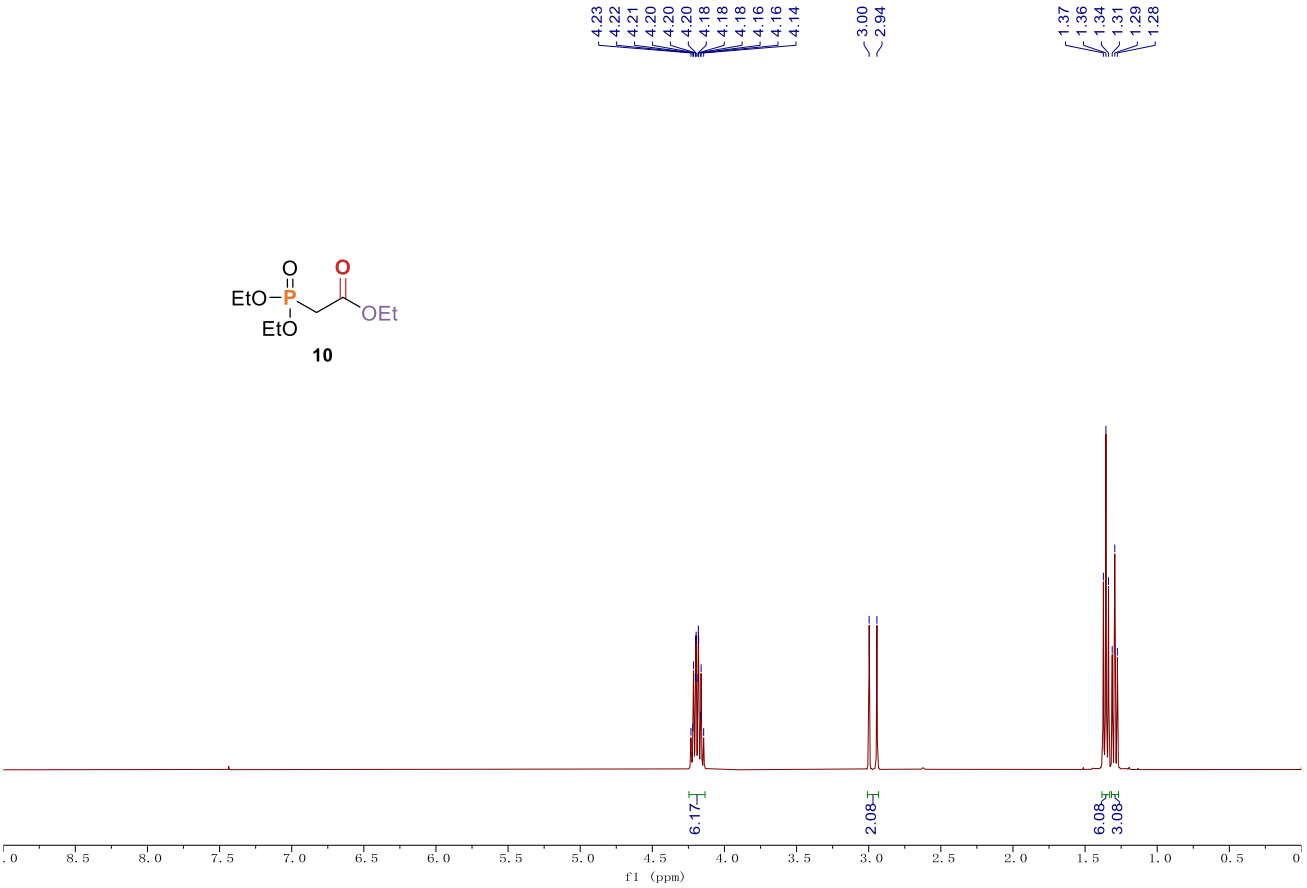
19F NMR CDCl3 376.46MHz



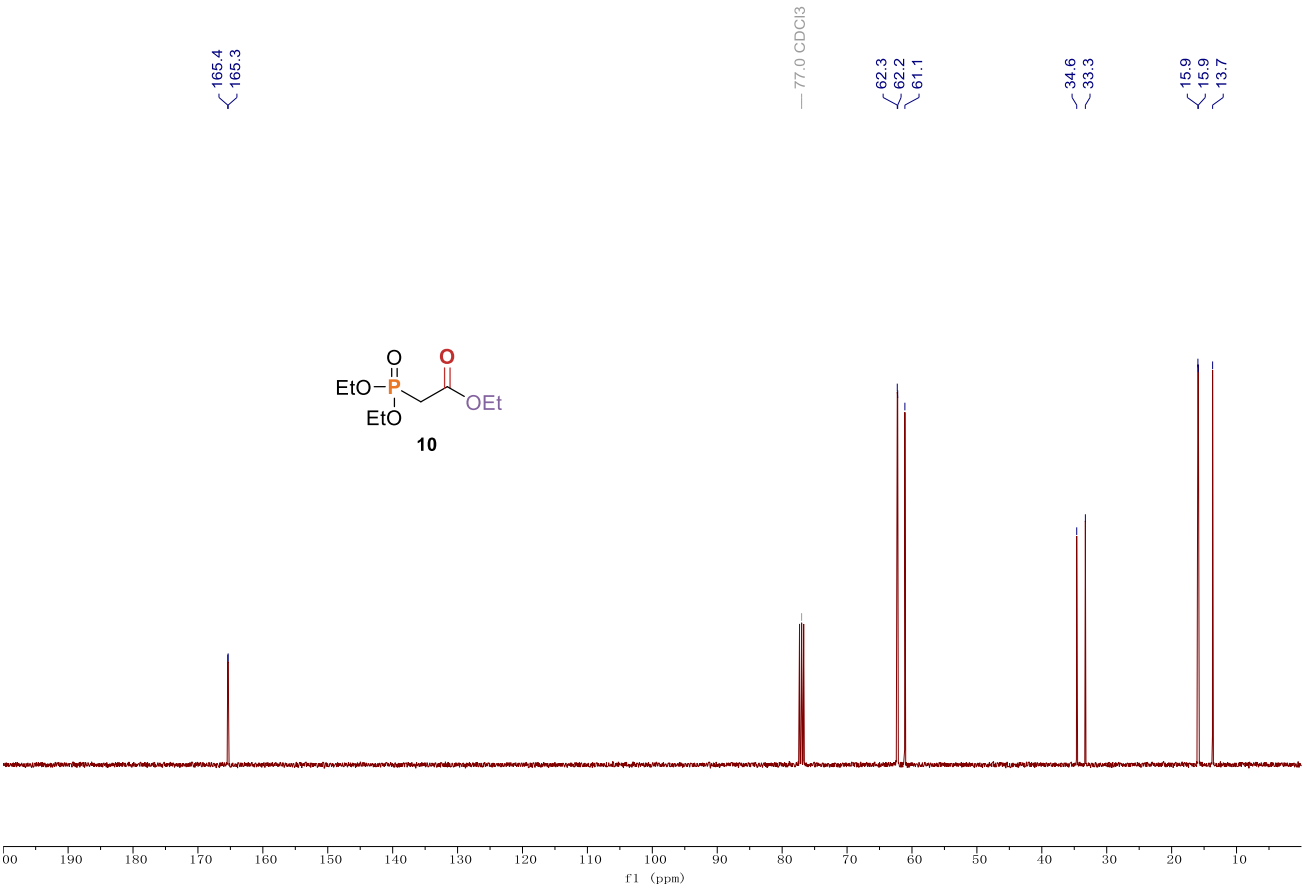
31P NMR CDCl3 161.97MHz



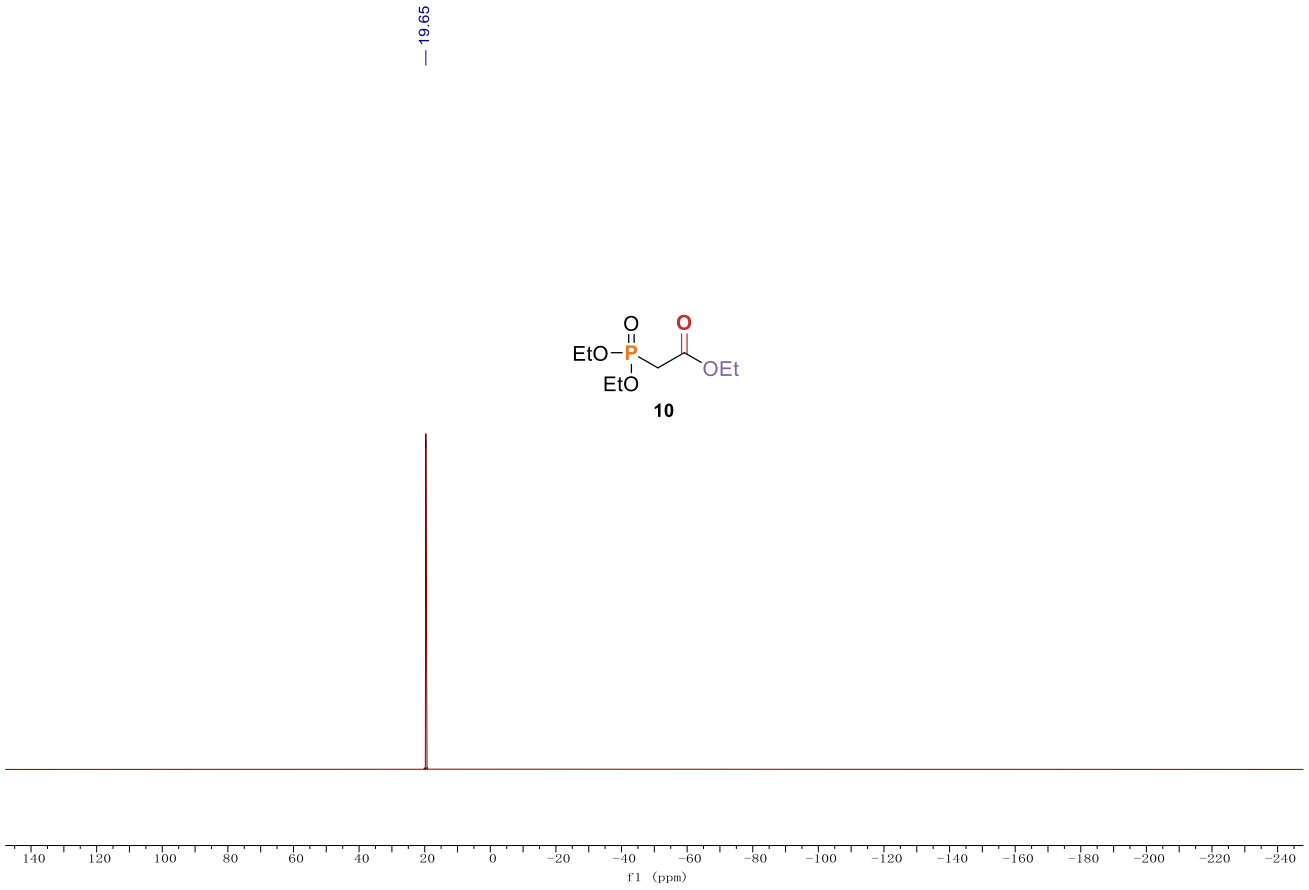
1H NMR CDCl3 400.13MHz



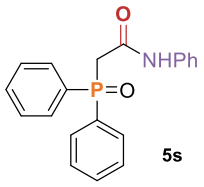
13C NMR CDCl3 100.62MHz



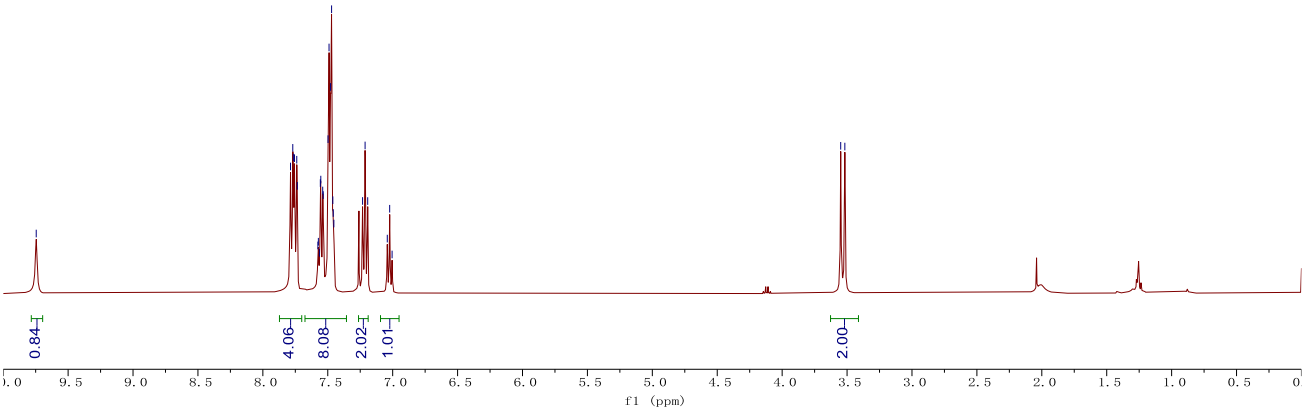
31P NMR CDCl3 161.97MHz



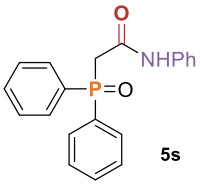
1H NMR CDCl3 400.13MHz



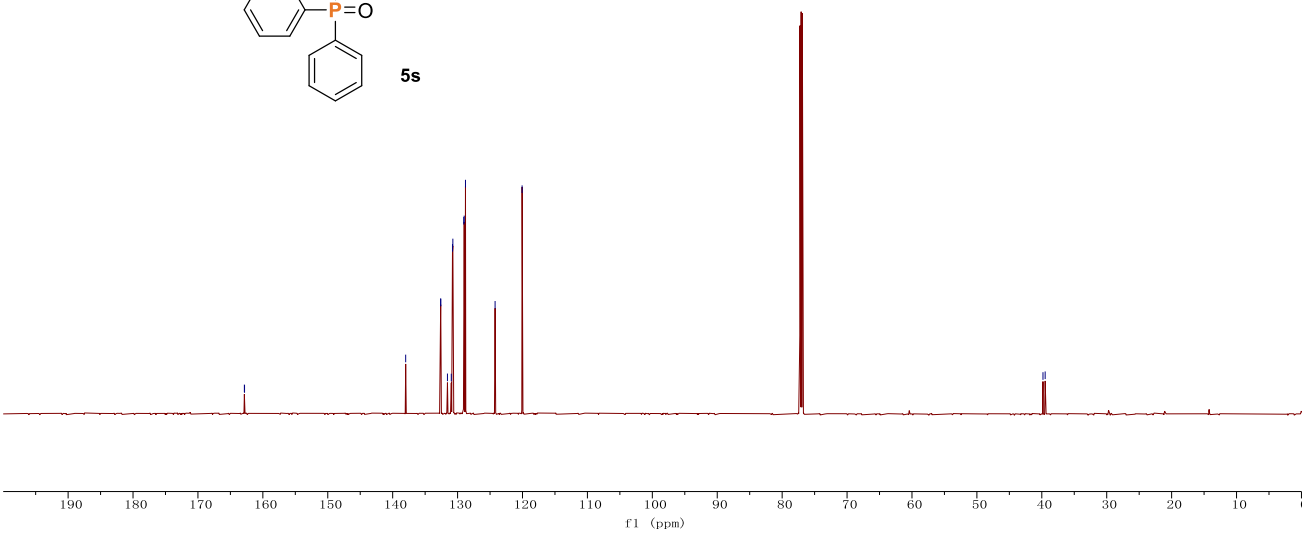
5s



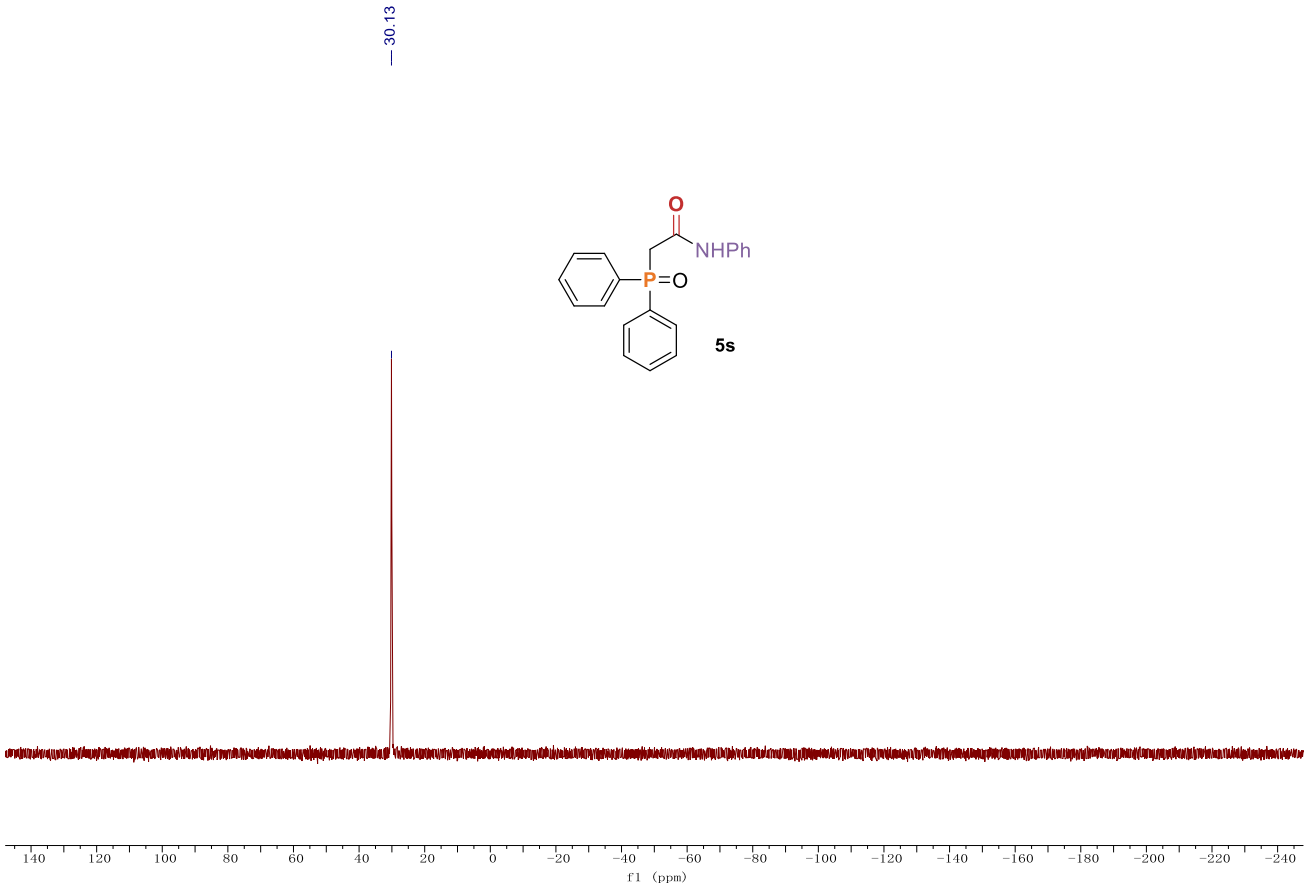
13C NMR CDCl3 176.08MHz



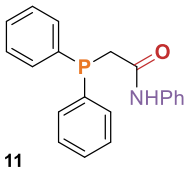
5s



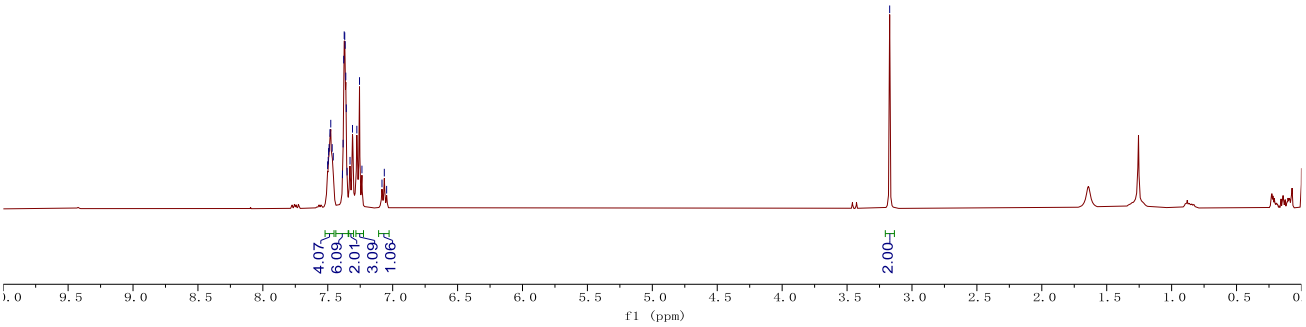
31P NMR CDCl3 161.97MHz



1H NMR CDCl3 400.13MHz

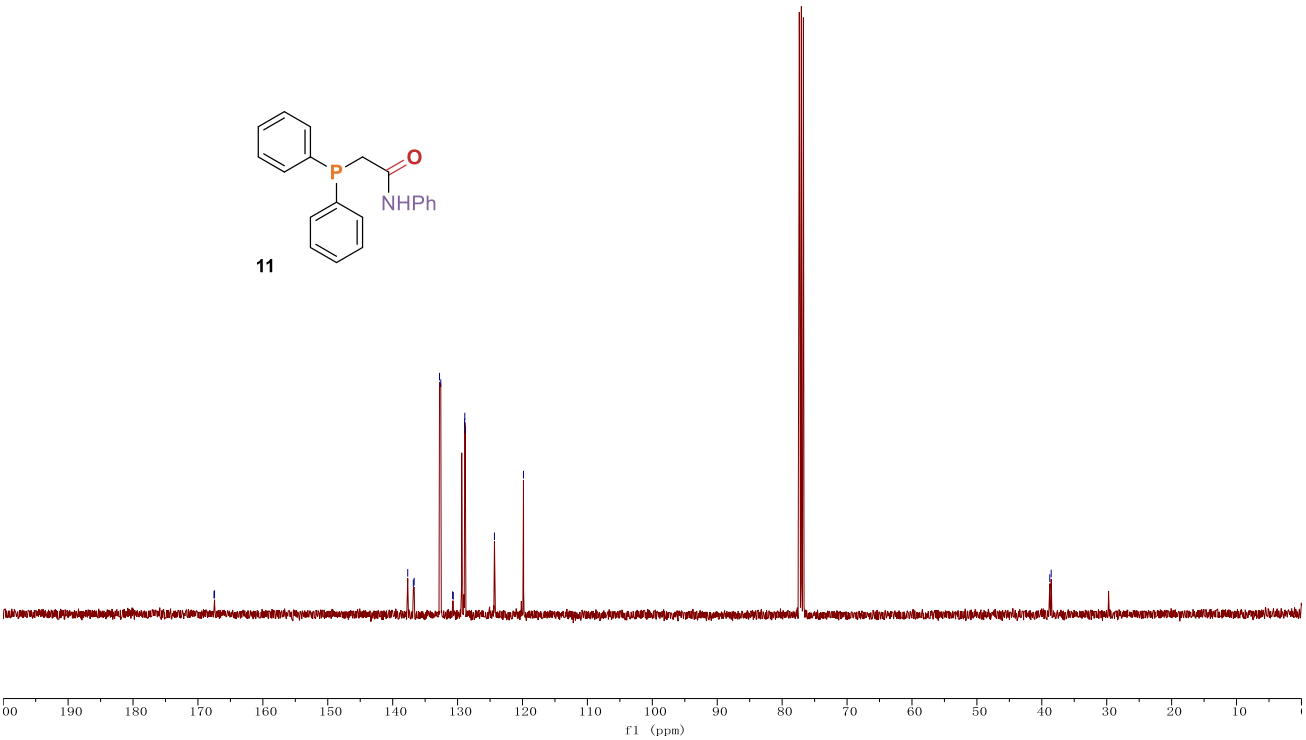


11



13C NMR CDCl3 100.62MHz

11



31P NMR CDCl3 161.97MHz