Supporting Information for

Copper-Catalyzed Chemo- and Enantioselective Radical 1,2-Carbophosphonylation of Styrenes

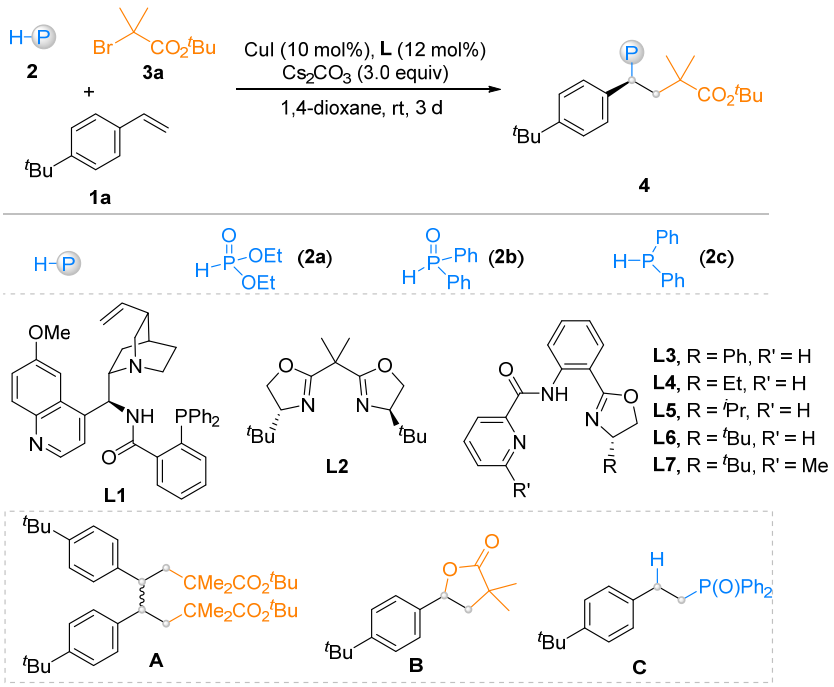
Huan Zhou,[a],+ Li-Wen Fan,[a],+ Yang-Qing Ren,[a] Li-Lei Wang,[a] Chang-Jiang Yang,[a,c] Qiang-Shuai Gu,[b] Zhong-Liang Li,[b],* and Xin-Yuan Liu[a],*

[a]Shenzhen Grubbs Institute and Department of Chemistry, Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen 518055, China
*E-mail: liuxy3@sustech.edu.cn
[b]Academy for Advanced Interdisciplinary Studies and Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China
*E-mail: lizl@sustech.edu.cn
[c]School of Science and Institute of Scientific Research, Great Bay University, Dongguan 523000, China
[+]These authors contributed equally to this work.

Table of Contents

Supplementary tables for experiments

Table S1. Screening of reaction conditions.[a]

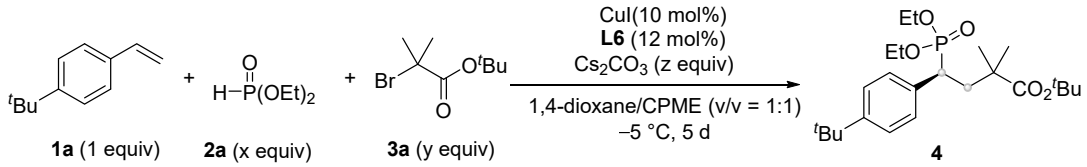


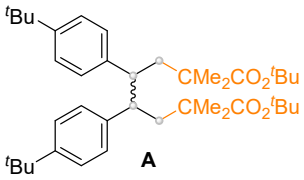
Entry	2	L	[Cu] salt	Base	yield of **4** (%)	yield of **A** (%)	yield of **B** (%)	Ee of **4** (%)
1	**2a**	**L1**	CuI	Cs_2CO_3	<5	38	<5	N.D
2	**2a**	**L2**	CuI	Cs_2CO_3	0	0	0	N.D
3	**2a**	**L3**	CuI	Cs_2CO_3	32	14	<5	80
4	**2a**	**L4**	CuI	Cs_2CO_3	46	12	<5	71
5	**2a**	**L5**	CuI	Cs_2CO_3	48	12	<5	82
6	**2a**	**L6**	CuI	Cs_2CO_3	54	14	<5	92
7	**2a**	**L7**	CuI	Cs_2CO_3	7	27	0	98
8	**2a**	**L6**	CuCl	Cs_2CO_3	50	18	7	92
9	**2a**	**L6**	$CuBr{\cdot}SMe_2$	Cs_2CO_3	48	20	9	91
10	**2a**	**L6**	$Cu(OTf)_2$	Cs_2CO_3	38	12	14	92
11	**2a**	**L6**	CuI	Na_2CO_3	0	<5	78	N.D
12	**2a**	**L6**	CuI	K_2CO_3	12	14	4	82
13	**2a**	**L6**	CuI	DIPEA	<5	6	62	N.D
14	**2a**	**L6**	CuI	DABCO	0	<5	44	N.D
15[b]	**2a**	**L6**	CuI	Cs_2CO_3	**70**	**6**	**<5**	**93**
16[c]	**2a**	**L6**	CuI	Cs_2CO_3	21	19	13	86
17[d]	**2a**	**L6**	CuI	Cs_2CO_3	63	8	5	92

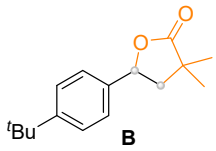
18	**2b**	**L6**	CuI	Cs_2CO_3	0	34	20	N.D
19[e]	**2c**	**L6**	CuI	Cs_2CO_3	0	0	<5	N.D
20	-	**L6**	CuI	Cs_2CO_3	0	0	13	N.D

[a] Reaction conditions: **1a** (0.10 mmol), **2** (0.20 mmol), **3a** (0.25 mmol), CuI (10 mol%), **L** (12 mol%), and Cs_2CO_3 (3.0 equiv) in 1,4-dioxane (1.0 mL) at room temperature. Yield was based on ^1H NMR analysis of the crude product using CH_2Br_2 as an internal standard; ee values were determined by HPLC analysis. [b] Conducted at –5 °C in a mixed solvent of 1,4-dioxane and CPME (v/v = 1:1) for 5 d. [c] Conducted at 60 °C in 1,4-dioxane for 1 d. [d] Conducted at –5 °C in a mixed solvent of 1,4-dioxane and CPME (v/v = 1:1) for 0.5 d, then 5 °C for 1 d, and then rt for another day. [e] Hydrophosphinoylation product **C** was obtained owing to the easy oxidation of hydrophosphinylation product. CPME, cyclopentyl methyl ether. N.D, no detected.

Table S2. The investigatin of substrate/base ratio.[a]



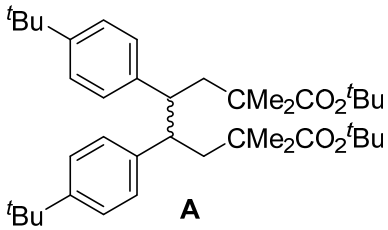




entry	x	y	z	yield of **4** (%)	yield of **A** (%)	Yield of **B** (%)	Ee of **4** (%)
1	1.2	1.5	3	52	8	5	92
2	1.5	2.0	3	59	8	<5	92
3	**2**	**2.5**	**3**	**70**	**6**	**<5**	**93**
4	2	2.5	2	31	<5	8	92
5	2	2.5	1	19	<5	26	93

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (x equiv), **3a** (y equiv), CuI (10 mol%), **L6** (12 mol%), and Cs_2CO_3 (z equiv) conducted at –5 °C in a mixed solvent of 1,4-dioxane and CPME (1 mL, v/v = 1:1) for 5 d. Yield was based on ^{1}H NMR analysis of the crude product using CH_2Br_2 as an internal standard; ee values were determined by HPLC analysis.

Di-tert-butyl 4,5-bis(4-(tert-butyl)phenyl)-2,2,7,7-tetramethyloctanedioate (A)

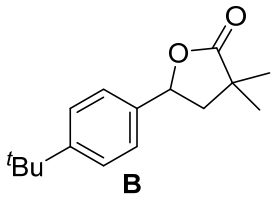


(**A** diastereomeric mixture ca. 4:1) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.3 Hz, 3.2H), 7.03 (d, *J* = 8.2 Hz, 0.8H), 6.97 (d, *J* = 8.2 Hz, 3.2H), 6.77 (d, *J* = 8.3 Hz, 0.8H), 2.68 – 2.58 (m, 2H), 2.02 – 1.94 (m, 0.4H), 1.88 – 1.79 (m, 1.6H), 1.52 – 1.47 (m, 2H), 1.28 (s, 14.4H), 1.24 (s, 3.6H), 1.20 (s, 3.6H), 1.17 (s, 14.4H), 0.98 (s, 1.2H), 0.81 (s, 6H), 0.70 (s, 4.8H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.1, 177.0, 149.0, 148.4, 141.0, 140.4, 129.2, 129.0, 124.9, 124.2, 79.6, 79.3, 49.7, 49.5, 43.2, 43.1, 42.4, 42.3, 34.4, 34.3, 31.6, 31.5, 27.9, 27.8, 26.8, 26.3, 26.2, 25.3.

HRMS (ESI) *m/z* calcd. for $[C_{40}H_{63}O_4]^+$ ($[M + H]^+$) 607.4721, found 607.4724.

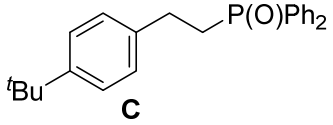
5-(4-(tert-butyl)phenyl)-3,3-dimethyldihydrofuran-2(3H)-one (B)[1]



B

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 9.9 Hz, 2H), 5.46 (dd, *J* = 10.1, 6.2 Hz, 1H), 2.48 (dd, *J* = 12.9, 6.2 Hz, 1H), 2.12 (dd, *J* = 12.9, 10.1 Hz, 1H), 1.39 (s, 3H), 1.33 (m, 12H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 181.9, 151.6, 136.5, 125.8, 125.4, 77.8, 46.1, 41.0, 34.8, 31.4, 25.1, 24.4.

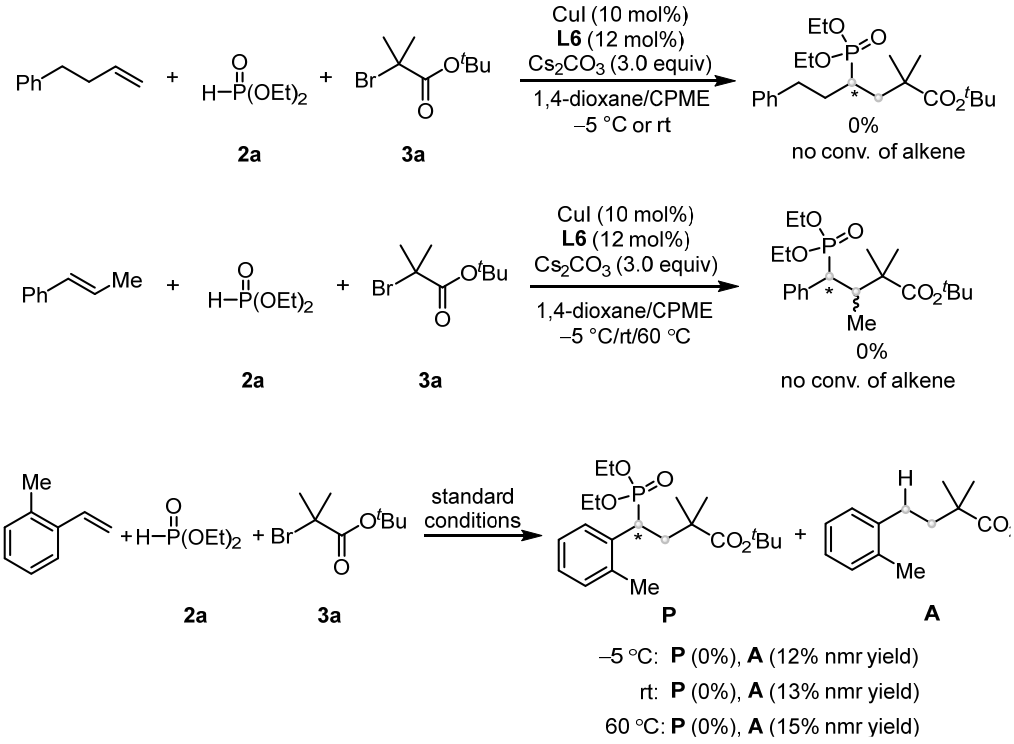
(4-(tert-butyl)phenethyl)diphenylphosphine oxide (C)[2]



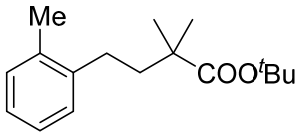
C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 4H), 7.55 – 7.43 (m, 6H), 7.30 – 7.25 (m, 2H), 7.12 – 7.07 (m, 2H), 2.96 – 2.86 (m, 2H), 2.64 – 2.53 (m, 2H), 1.29 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 138.2 (d, *J* = 15.3 Hz), 132.9 (d, *J* = 98.3 Hz), 131.9 (d, *J* = 2.7 Hz), 130.9 (d, *J* = 9.4 Hz), 128.8 (d, *J* = 11.6 Hz), 127.9, 125.6, 34.5, 31.9 (d, *J* = 69.9 Hz), 31.5, 27.1 (d, *J* = 3.2 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.02.

Scheme S1. Unsuccessful alkenes



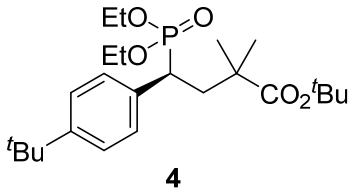
Tert-butyl 2,2-dimethyl-4-(*o*-tolyl)butanoate



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.06 (m, 4H), 2.59 – 2.49 (m, 2H), 2.31 (s, 3H), 1.75 – 1.67 (m, 2H), 1.48 (s, 9H), 1.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 140.8, 135.9, 130.3, 129.0, 126.2, 126.1, 80.0, 42.9, 41.8, 29.1, 28.2, 25.4, 19.3.

HRMS (ESI) *m/z* calcd. for $[C_{17}H_{26}O_2Na]^+$ ($[M + Na]^+$) 285.1825, found 285.1820.



4

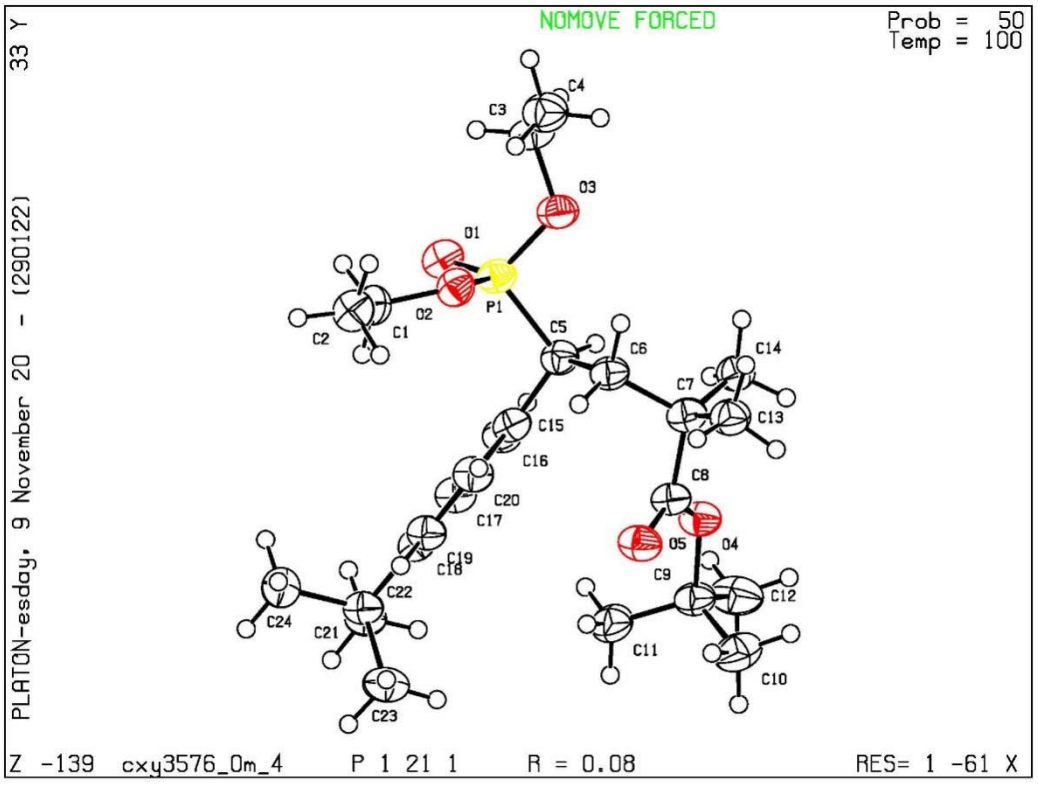
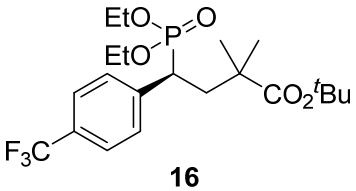


Figure S1. The X-ray structure of **4**.



16

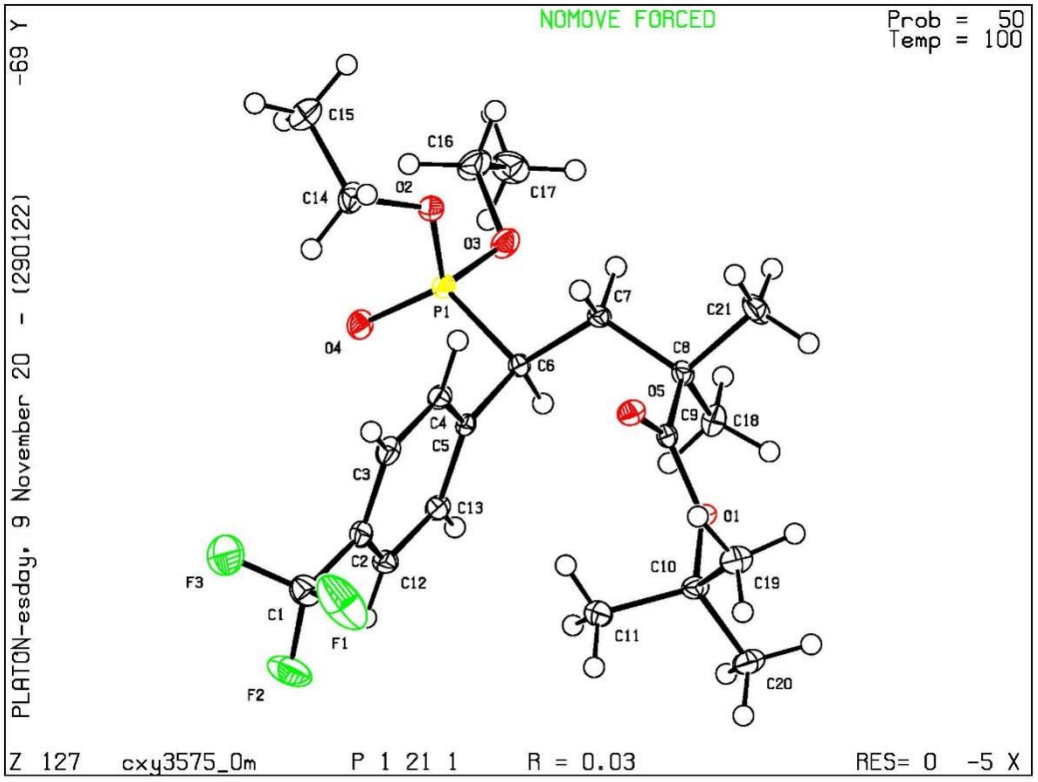
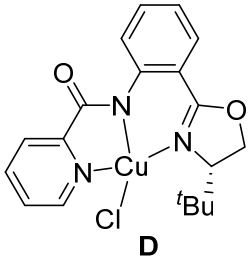


Figure S2. The X-ray structure of **16**.



D

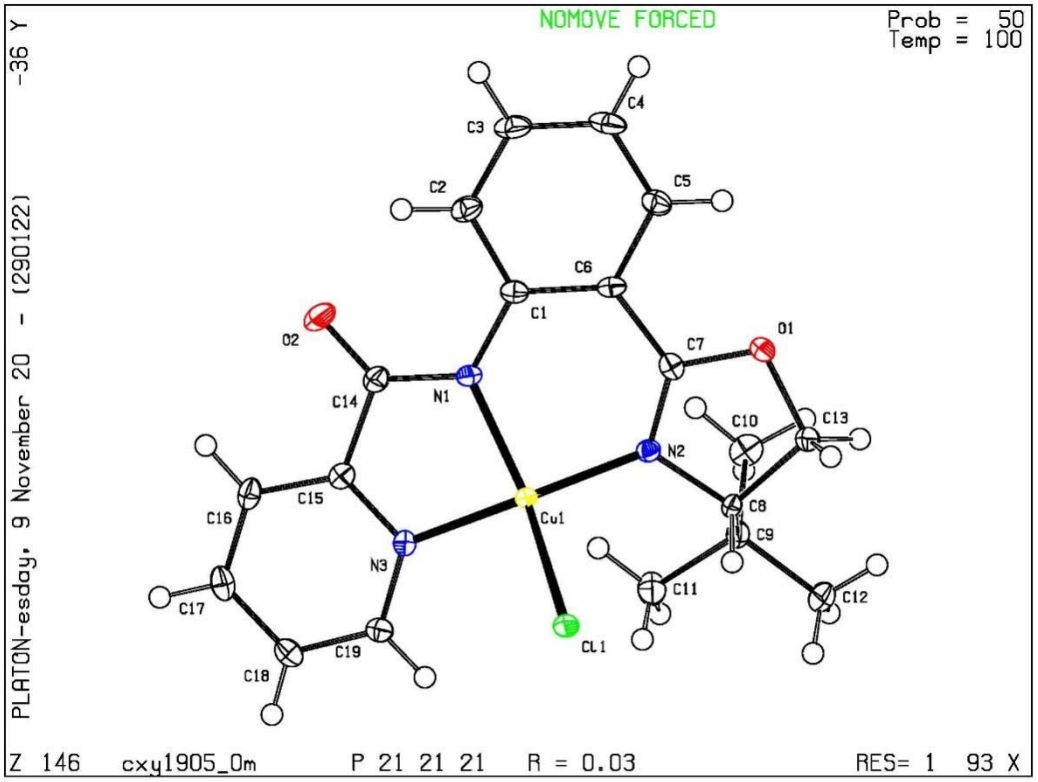


Figure S3. The X-ray structure of complex **D** in Scheme 3.

General information

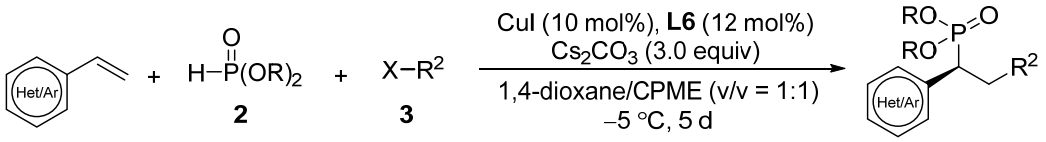
Reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Cuprous iodide (99.999%) was purchased from Sigma-Aldrich. Cesium carbonate (Cs_2CO_3) was purchased from Bide Pharmatech Ltd., which was directly used without further treatment. Anhydrous 1,4-dioxane and cyclopentyl methyl ether were purchased from J&K. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). As the eluent, the petroleum ether (PE), hexane, ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2) and methanol were purchased from Shanghai Titan Scientific Co. Ltd without further purification. Visualization on TLC was achieved by use of UV light (254 nm), iodine or basic $KMnO_4$ indicator. NMR spectra were recorded on Bruker DRX-400 and DPX-600 spectrometers at 400 or 600 MHz for ^1H NMR, 100 or 150 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR and 162 MHz or 243 MHz for ^{31}P NMR, respectively, in $CDCl_3$ and DMSO-d_6 with tetramethylsilane (TMS) as internal standard. The chemical shifts were expressed in ppm and coupling constants were given in Hz. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; dd = doublet of doublets; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm), multiplicity (d, doublet), coupling constant (Hz), integration. High-resolution mass spectroscopy (HRMS) was obtained on Thermo Scientific Q Exactive mass spectrometer using ESI ion source. Enantiomeric excess (e.e.) was determined using SHIMADZU LC-20AD with SPD-20AV detector or Agilent high-performance liquid chromatography (HPLC) with Hatachi detector (at appropriate wavelength). Column conditions were reported in the experimental section below.

The synthesis of substrates

Most of alkenes, dialkyl phosphites, and radical precursors were purchased from commercial sources. The alkenes for the product **10**[3], **18–24**[3], **25**[4], **26**[3], **29–31**[3] were synthesized according to the reported literature. The radical precursors for the product **46**[5] were synthesized according to the reported literature. All the characterization data are consistent with those in the reported literature.

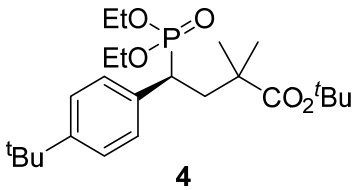
Copper-Catalyzed Chemo- and Enantioselective Radical 1,2-Carbophosphonylation of Styrenes

General procedure A



An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.02 mmol, 10 mol%), **L6** (7.8 mg, 0.024 mmol, 12 mol%), and anhydrous Cs_2CO_3 (195.5 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Then 1,4-dioxane/CPME (2.0 mL, (v/v = 1:1) was added by syringe under argon atmosphere. Finally, alkene (0.20 mmol, 1.0 equiv), radical precursor (0.50 mmol, 2.5 equiv) and dialkyl phosphite (0.40 mmol, 2.0 equiv) were sequentially added into the mixture and the reaction mixture was stirred at –5 °C for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

Tert-butyl (S)-4-(4-(tert-butyl)phenyl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (4)



4

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **4** as a colorless oil (60.7 mg, 69% yield, 93% ee). The reaction was performed on 5 mmol scale for 4-tert-butylstyrene to yield the product **4** as a colorless oil (1.76 g, 80% yield, 93% ee), which was crystallized when it was placed in the refrigerator.

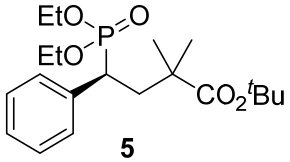
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 214 nm), t_R (minor) = 16.11 min, t_R (major) = 17.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 4H), 4.14 – 3.97 (m, 2H), 3.87 – 3.75 (m, 1H), 3.61 – 3.50 (m, 1H), 3.10 (ddd, *J* = 25.0, 10.6, 2.0 Hz, 1H), 2.40 – 2.20 (m, 2H), 1.32 – 1.26 (m, 12H), 1.24 (s, 9H), 1.10 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H), 0.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 150.1 (d, *J* = 3.8 Hz), 133.2 (d, *J* = 8.0 Hz), 129.5 (d, *J* = 7.0 Hz), 125.4 (d, *J* = 3.0 Hz), 80.0, 62.9 (d, *J* = 7.0 Hz), 61.8 (d, *J* = 7.5 Hz), 43.1 (d, *J* = 16.3 Hz), 41.3 (d, *J* = 136.5 Hz), 39.5 (d, *J* = 2.4 Hz), 34.5, 31.4, 27.8, 26.6, 25.3, 16.5 (d, *J* = 6.0 Hz), 16.2 (d, *J* = 5.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.31.
HRMS (ESI) *m/z* calcd. for $[C_{24}H_{42}O_5P]^+$ ($[M + H]^+$) 441.2764, found 441.2760.

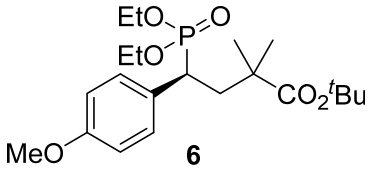
Tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-phenylbutanoate (5)



5

According to the **general procedure A**, styrene (20.8 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **5** as a colorless oil (46.9 mg, 61% yield, 90% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 96/4, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 19.21 min, t_R (minor) = 21.22 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.31 – 7.26 (m, 2H), 7.26 – 7.20 (m, 1H), 4.16 – 3.98 (m, 2H), 3.89 – 3.77 (m, 1H), 3.63 – 3.49 (m, 1H), 3.20 – 3.07 (m, 1H), 2.40 – 2.26 (m, 2H), 1.33 – 1.29 (m, 12H), 1.10 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H), 0.91 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 136.8 (d, *J* = 8.0 Hz), 129.9 (d, *J* = 7.0 Hz), 128.5 (d, *J* = 2.9 Hz), 127.2 (d, *J* = 3.6 Hz), 80.2, 62.9 (d, *J* = 7.0 Hz), 61.9 (d, *J* = 7.4 Hz), 43.3 (d, *J* = 16.1 Hz), 41.9 (d, *J* = 136.2 Hz), 39.6 (d, *J* = 2.7 Hz), 27.9, 26.0, 25.9, 16.5 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.90.
HRMS (ESI) *m/z* calcd. for $[C_{20}H_{34}O_5P]^+$ ($[M + H]^+$) 385.2138, found 385.2138.

Tert-butyl (S)-4-(diethoxyphosphoryl)-4-(4-methoxyphenyl)-2,2-dimethylbutanoate (6)

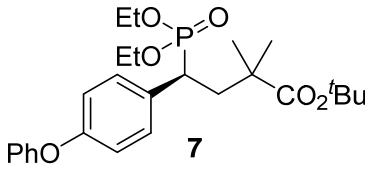


6

According to the **general procedure A**, 1-methoxy-4-vinylbenzene (26.8 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **6** as a colorless oil (49.7 mg, 60% yield, 88% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 37.46 min, t_R (minor) = 40.76 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 6.86 – 6.77 (m, 2H), 4.13 – 3.97 (m, 2H), 3.87 – 3.78 (m, 1H), 3.77 (s, 3H), 3.61 – 3.50 (m, 1H), 3.06 (ddd, *J* = 25.0, 10.0, 2.9 Hz, 1H), 2.33 – 2.18 (m, 2H), 1.32 – 1.26 (m, 12H), 1.09 – 1.02 (m, 6H), 0.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 158.9 (d, *J* = 3.4 Hz), 130.8 (d, *J* = 7.0 Hz), 128.5 (d, *J* = 8.2 Hz), 114.0 (d, *J* = 2.9 Hz), 80.1, 62.9 (d, *J* = 7.2 Hz), 61.8 (d, *J* = 7.5 Hz), 55.5, 43.3 (d, *J* = 16.4 Hz), 41.0 (d, *J* = 137.0 Hz), 39.6 (d, *J* = 2.1 Hz), 27.9, 26.0, 25.9, 16.6 (d, *J* = 5.9 Hz), 16.4 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 29.16.
HRMS (ESI) *m/z* calcd. for $[C_{21}H_{36}O_6P]^+$ ($[M + H]^+$) 415.2244, found 415.2248.

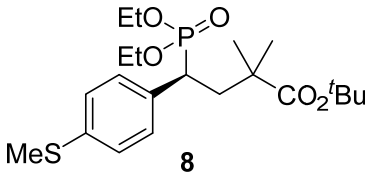
Tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-(4-phenoxyphenyl)butanoate (7)



7

According to the **general procedure A**, 1-phenoxy-4-vinylbenzene (39.3 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **7** as a colorless oil (63.8 mg, 67% yield, 91% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 13.19 min, t_R (minor) = 14.36 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.11 – 7.05 (m, 1H), 6.99 – 6.90 (m, 4H), 4.15 – 3.98 (m, 2H), 3.92 – 3.79 (m, 1H), 3.70 – 3.58 (m, 1H), 3.11 (ddd, *J* = 25.1, 9.5, 3.2 Hz, 1H), 2.36 – 2.21 (m, 2H), 1.34 – 1.27 (m, 12H), 1.11 – 1.05 (m, 6H), 0.92 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 157.1, 156.4 (d, *J* = 3.7 Hz), 131.4 (d, *J* = 8.1 Hz), 131.1 (d, *J* = 7.0 Hz), 129.7, 123.3, 118.8, 118.7, 80.1, 62.8 (d, *J* = 7.2 Hz), 61.8 (d, *J* = 7.6 Hz), 43.2 (d, *J* = 16.1 Hz), 41.1 (d, *J* = 137.1 Hz), 39.5 (d, *J* = 2.5 Hz), 27.8, 26.0, 25.8, 16.4 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.82.
HRMS (ESI) *m/z* calcd. for $[C_{26}H_{38}O_6P]^+$ ($[M + H]^+$) 477.2401, found 477.2409.

Tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-(4-(methylthio)phenyl)butanoate (8)

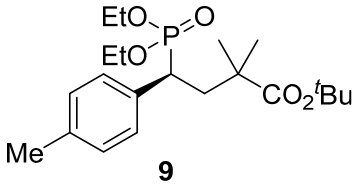


8

According to the **general procedure A**, methyl(4-vinylphenyl)sulfane (30.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **8** as a colorless oil (59.3 mg, 69% yield, 92% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 43.09 min, t_R (minor) = 45.39 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 4.15 – 3.99 (m, 2H), 3.91 – 3.79 (m, 1H), 3.68 – 3.55 (m, 1H), 3.09 (ddd, *J* = 25.1, 9.5, 3.2 Hz, 1H), 2.46 (s, 3H), 2.35 – 2.21 (m, 2H), 1.34 – 1.27 (m, 12H), 1.13 – 1.04 (m, 6H), 0.90 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 137.2 (d, *J* = 4.0 Hz), 133.5 (d, *J* = 8.3 Hz), 130.3 (d, *J* = 7.0 Hz), 126.7 (d, *J* = 2.9 Hz), 80.2, 62.9 (d, *J* = 7.1 Hz), 61.9 (d, *J* = 7.3 Hz), 43.3 (d, *J* = 16.1 Hz), 41.4 (d, *J* = 136.6 Hz), 39.5 (d, *J* = 2.5 Hz), 27.9, 26.1, 25.9, 16.5 (d, *J* = 5.9 Hz), 16.4 (d, *J* = 5.8 Hz), 16.0.
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.65.
HRMS (ESI) *m/z* calcd. for $[C_{21}H_{36}O_5PS]^+$ ($[M + H]^+$) 431.2016, found 431.2022.

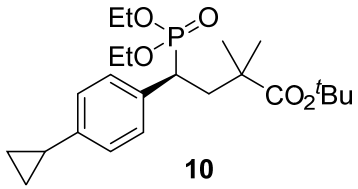
Tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-(p-tolyl)butanoate (9)



9

According to the **general procedure A**, 1-methyl-4-vinylbenzene (23.6 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **9** as a colorless oil (54.2 mg, 68% yield, 89% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 10.96 min, t_R (minor) = 11.66 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 4.11 – 3.95 (m, 2H), 3.86 – 3.74 (m, 1H), 3.61 – 3.49 (m, 1H), 3.06 (ddd, *J* = 25.0, 9.3, 3.4 Hz, 1H), 2.33 – 2.19 (m, 5H), 1.32 – 1.24 (m, 12H), 1.08 – 1.00 (m, 6H), 0.87 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 136.8 (d, *J* = 3.8 Hz), 133.4 (d, *J* = 8.1 Hz), 129.6 (d, *J* = 7.0 Hz), 129.2 (d, *J* = 2.9 Hz), 80.1, 62.8 (d, *J* = 7.1 Hz), 61.9 (d, *J* = 7.4 Hz), 43.3 (d, *J* = 16.4 Hz), 41.4 (d, *J* = 136.4 Hz), 39.5 (d, *J* = 2.5 Hz), 27.8, 26.0, 25.9, 21.2 (d, *J* = 1.3 Hz), 16.5 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 29.13.
HRMS (ESI) *m/z* calcd. for $[C_{21}H_{36}O_5P]^+$ ($[M + H]^+$) 399.2295, found 399.2299.

Tert-butyl (S)-4-(4-cyclopropylphenyl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (10)

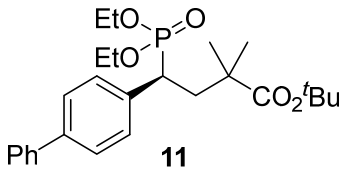


10

According to the **general procedure A**, 1-cyclopropyl-4-vinylbenzene (28.8 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **10** as a colorless oil (60.2 mg, 71% yield, 93% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 96/4, flow rate 0.6 mL/min, λ = 230 nm), t_R (minor) = 25.11 min, t_R (major) = 26.72 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.14 (m, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 4.12 – 3.93 (m, 2H), 3.87 – 3.73 (m, 1H), 3.61 – 3.47 (m, 1H), 3.05 (ddd, *J* = 25.0, 8.0, 4.8 Hz, 1H), 2.31 – 2.21 (m, 2H), 1.88 – 1.76 (m, 1H), 1.31 – 1.23 (m, 12H), 1.07 – 0.98 (m, 6H), 0.94 – 0.85 (m, 5H), 0.66 – 0.57 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 143.0 (d, *J* = 3.7 Hz), 133.4 (d, *J* = 8.2 Hz), 129.7 (d, *J* = 7.1 Hz), 125.7 (d, *J* = 3.1 Hz), 80.1, 62.9 (d, *J* = 7.1 Hz), 61.9 (d, *J* = 7.4 Hz), 43.2 (d, *J* = 16.3 Hz), 41.4 (d, *J* = 136.4 Hz), 39.5 (d, *J* = 2.4 Hz), 27.9, 26.1, 25.8, 16.5 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.8 Hz), 15.2 (d, *J* = 1.4 Hz), 9.3 (d, *J* = 3.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 29.12.
HRMS (ESI) *m/z* calcd. for $[C_{23}H_{38}O_5P]^+$ ($[M + H]^+$) 425.2451, found 425.2455.

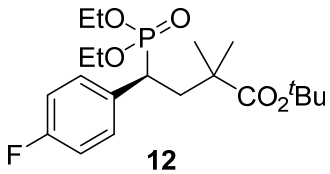
Tert-butyl (S)-4-([1,1'-biphenyl]-4-yl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (11)



11

According to the **general procedure A**, 1-phenyl-4-vinylbenzene (59.8 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **11** as a colorless oil (59.8 mg, 65% yield, 93% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 13.76 min, t_R (minor) = 14.81 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 4H), 7.46 – 7.37 (m, 4H), 7.35 – 7.30 (m, 1H), 4.16 – 3.99 (m, 2H), 3.93 – 3.80 (m, 1H), 3.70 – 3.56 (m, 1H), 3.17 (ddd, *J* = 25.0, 9.2, 3.4 Hz, 1H), 2.43 – 2.26 (m, 2H), 1.34 – 1.26 (m, 12H), 1.11 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.95 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 140.9 (d, *J* = 1.5 Hz), 140.0 (d, *J* = 3.8 Hz), 135.8 (d, *J* = 8.1 Hz), 130.3 (d, *J* = 7.0 Hz), 128.9, 127.4, 127.2 (d, *J* = 3.0 Hz), 127.1, 80.2, 62.9 (d, *J* = 7.0 Hz), 62.0 (d, *J* = 7.4 Hz), 43.3 (d, *J* = 16.1 Hz), 41.6 (d, *J* = 136.3 Hz), 39.6 (d, *J* = 2.6 Hz), 27.9, 26.3, 25.7, 16.6 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 5.9 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.78.
HRMS (ESI) *m/z* calcd. for $[C_{26}H_{38}O_5P]^+$ ($[M + H]^+$) 461.2451, found 461.2455.

Tert-butyl (S)-4-(diethoxyphosphoryl)-4-(4-fluorophenyl)-2,2-dimethylbutanoate (12)



12

According to the **general procedure A**, 1-fluoro-4-vinylbenzene (24.4 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **12** as a colorless oil (54.7 mg, 68% yield, 89% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 11.15 min, t_R (minor) = 11.97 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 6.99 (t, *J* = 8.5 Hz, 2H), 4.16 – 3.99 (m, 2H), 3.91 – 3.78 (m, 1H), 3.68 – 3.54 (m, 1H), 3.12 (ddd, *J* = 25.1, 10.0, 2.7 Hz, 1H), 2.36 – 2.20 (m, 2H), 1.36 – 1.26 (m, 12H), 1.12 – 1.03 (m, 6H), 0.90 (s, 3H).

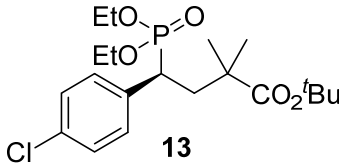
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 162.1 (dd, *J* = 245.6, 3.9 Hz), 132.5 (dd, *J* = 7.9, 3.2 Hz), 131.3 (t, *J* = 7.5 Hz), 115.4 (dd, *J* = 21.3, 2.9 Hz), 80.2, 62.9 (d, *J* = 7.1 Hz), 62.0 (d, *J* = 7.4 Hz), 43.2 (d, *J* = 16.1 Hz), 41.1 (d, *J* = 137.3 Hz), 39.7 (d, *J* = 2.5 Hz), 27.9, 26.1, 25.8, 16.5 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.65 (d, *J* = 5.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.54 (d, *J* = 5.2 Hz).

HRMS (ESI) *m/z* calcd. for $[C_{20}H_{33}FO_5P]^+$ ($[M + H]^+$) 403.2044, found 403.2047.

Tert-butyl (S)-4-(4-chlorophenyl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (13)



13

According to the **general procedure A**, 1-chloro-4-vinylbenzene (27.7 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **13** as a colorless oil (59.4 mg, 71% yield, 91% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 10.26 min, t_R (minor) = 12.39 min.

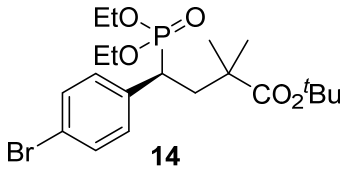
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 4H), 4.16 – 3.99 (m, 2H), 3.92 – 3.80 (m, 1H), 3.71 – 3.57 (m, 1H), 3.23 – 3.01 (m, 1H), 2.38 – 2.18 (m, 2H), 1.35 – 1.27 (m, 12H), 1.12 – 1.03 (m, 6H), 0.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 135.4 (d, *J* = 8.1 Hz), 133.1 (d, *J* = 4.3 Hz), 131.1 (d, *J* = 7.0 Hz), 128.6 (d, *J* = 3.1 Hz), 80.3, 62.9 (d, *J* = 7.1 Hz), 62.1 (d, *J* = 7.4 Hz), 43.2 (d, *J* = 16.0 Hz), 41.3 (d, *J* = 136.9 Hz), 39.5 (d, *J* = 2.6 Hz), 27.8, 26.1, 25.8, 16.5 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.17.

HRMS (ESI) *m/z* calcd. for $[C_{20}H_{33}ClO_5P]^+$ ($[M + H]^+$) 419.1749, found 419.1751.

Tert-butyl (S)-4-(4-bromophenyl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (14)



14

According to the **general procedure A**, 1-bromo-4-vinylbenzene (36.6 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **14** as a colorless oil (61.9 mg, 67% yield, 90% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 6.62 min, t_R (minor) = 7.85 min.

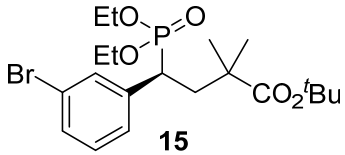
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.17 (m, 2H), 4.16 – 3.96 (m, 2H), 3.92 – 3.79 (m, 1H), 3.70 – 3.56 (m, 1H), 3.09 (ddd, *J* = 25.0, 10.2, 2.5 Hz, 1H), 2.37 – 2.16 (m, 2H), 1.33 – 1.26 (m, 12H), 1.12 – 1.03 (m, 6H), 0.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 136.0 (d, *J* = 8.0 Hz), 131.6 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 7.0 Hz), 121.2 (d, *J* = 4.4 Hz), 80.4, 63.0 (d, *J* = 7.1 Hz), 62.1 (d, *J* = 7.4 Hz), 43.3 (d, *J* = 16.0 Hz), 41.4 (d, *J* = 136.8 Hz), 39.5 (d, *J* = 2.7 Hz), 27.9, 26.2, 25.9, 16.6 (d, *J* = 5.9 Hz), 16.4 (d, *J* = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.01.

HRMS (ESI) *m/z* calcd. for $[C_{20}H_{33}BrO_5P]^+$ ($[M + H]^+$) 463.1244, found 463.1249.

Tert-butyl (S)-4-(3-bromophenyl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (15)



15

According to the **general procedure A**, 1-bromo-3-vinylbenzene (36.6 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **15** as a colorless oil (62.8 mg, 68% yield, 90% ee).

HPLC analysis: Chiralcel INA (hexane/*i*-PrOH = 96/4, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 7.84 min, t_R (major) = 10.76 min.

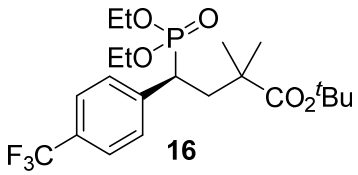
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.40 – 7.34 (m, 1H), 7.32 – 7.26 (m, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 4.16 – 3.99 (m, 2H), 3.94 – 3.83 (m, 1H), 3.74 – 3.61 (m, 1H), 3.10 (ddd, *J* = 25.1, 9.0, 3.5 Hz, 1H), 2.37 – 2.19 (m, 2H), 1.33 – 1.28 (m, 12H), 1.13 – 1.06 (m, 6H), 0.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 139.4 (d, *J* = 7.9 Hz), 132.7 (d, *J* = 7.1 Hz), 130.4 (d, *J* = 3.6 Hz), 130.0 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 6.8 Hz), 122.4 (d, *J* = 3.4 Hz), 80.3, 62.9 (d, *J* = 7.1 Hz), 62.2 (d, *J* = 7.3 Hz), 43.2 (d, *J* = 15.6 Hz), 41.6 (d, *J* = 136.5 Hz), 39.5 (d, *J* = 2.9 Hz), 27.9, 26.3, 25.7, 16.5 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.95.

HRMS (ESI) *m/z* calcd. for $[C_{20}H_{33}BrO_5P]^+$ ($[M + H]^+$) 463.1244, found 463.1251.

Tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-(4-(trifluoromethyl)phenyl)butanoate (16)



16

According to the **general procedure A**, 1-(trifluoromethyl)-4-vinylbenzene (34.4 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **16** as a white solid (m.p.: 97.2-99.5 °C) (56.1 mg, 62% yield, 91% ee).

HPLC analysis: Chiralcel INA (hexane/*i*-PrOH = 96/4, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 8.61 min, t_R (minor) = 9.59 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.35 (m, 2H), 4.04 – 3.90 (m, 2H), 3.83 – 3.70 (m, 1H), 3.65 – 3.51 (m, 1H), 3.18 – 3.04 (m, 1H), 2.30 – 2.16 (m, 2H), 1.22 – 1.15 (m, 12H), 1.00 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H), 0.80 (s, 3H).

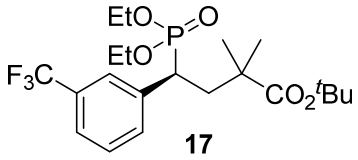
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 141.2 (d, *J* = 8.7 Hz), 130.0 (d, *J* = 6.9 Hz), 129.3 (qd, *J* = 32.5, 3.8 Hz), 125.1 (p, *J* = 3.7 Hz), 124.0 (q, *J* = 270.1 Hz), 80.0, 62.6 (d, *J* = 7.0 Hz), 62.0 (d, *J* = 7.3 Hz), 43.0 (d, *J* = 15.7 Hz), 41.7 (d, *J* = 136.3 Hz), 39.3 (d, *J* = 3.1 Hz), 27.5, 26.1, 25.4, 16.2 (d, *J* = 6.0 Hz), 16.0 (d, *J* = 5.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.70.

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.57.

HRMS (ESI) *m/z* calcd. for $[C_{21}H_{33}F_3O_5P]^+$ ($[M + H]^+$) 453.2012, found 453.2018.

Tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-(3-(trifluoromethyl)phenyl)butanoate (17)



17

According to the **general procedure A**, 1-(trifluoromethyl)-3-vinylbenzene (34.6 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **17** as a colorless oil (58.8 mg, 65% yield, 90% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.75 min, t_R (major) = 7.70 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 4.13 – 3.96 (m, 2H), 3.89 – 3.78 (m, 1H), 3.73 – 3.59 (m, 1H), 3.18 (ddd, *J* = 25.2, 8.4, 4.3 Hz, 1H), 2.36 – 2.23 (m, 2H), 1.28 – 1.21 (m, 12H), 1.09 – 1.01 (m, 6H), 0.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 138.2 (d, *J* = 8.0 Hz), 133.2 (d, *J* = 6.5 Hz), 130.6 (td, *J* = 32.3, 3.1 Hz), 128.9 (d, *J* = 2.9 Hz), 127.4 – 126.3 (m), 124.1 (q, *J* =

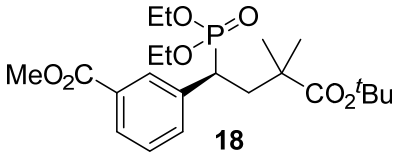
272.4 Hz), 124.2 – 123.9 (m), 80.3, 62.9 (d, J = 7.1 Hz), 62.2 (d, J = 7.4 Hz), 43.2 (d, J = 15.4 Hz), 41.7 (d, J = 136.7 Hz), 39.5 (d, J = 2.9 Hz), 27.7, 26.3, 25.6, 16.4 (d, J = 5.9 Hz), 16.2 (d, J = 5.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.67.

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.68.

HRMS (ESI) *m/z* calcd. for $[C_{21}H_{33}F_3O_5P]^+$ ($[M + H]^+$) 453.2012, found 453.2019.

Methyl (S)-3-(4-(tert-butoxy)-1-(diethoxyphosphoryl)-3,3-dimethyl-4-oxobutyl)benzoate (18)



18

According to the **general procedure A**, methyl 3-vinylbenzoate (32.4 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **18** as a colorless oil (58.3 mg, 66% yield, 87% ee).

HPLC analysis: Chiralcel IH (hexane/*i*-PrOH = 93/7, flow rate 1.0 mL/min, λ = 230 nm), t_R (minor) = 5.44 min, t_R (major) = 10.94 min.

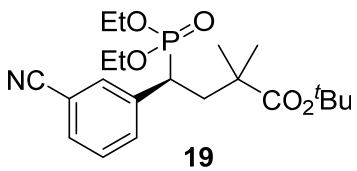
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 4.13 – 3.97 (m, 2H), 3.89 (s, 3H), 3.86 – 3.78 (m, 1H), 3.70 – 3.57 (m, 1H), 3.18 (ddd, J = 25.1, 9.2, 3.3 Hz, 1H), 2.38 – 2.23 (m, 2H), 1.30 – 1.23 (m, 12H), 1.09 – 1.01 (m, 6H), 0.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 167.0, 137.6 (d, J = 8.0 Hz), 134.4 (d, J = 6.6 Hz), 130.9 (d, J = 7.2 Hz), 130.3 (d, J = 2.8 Hz), 128.6 (d, J = 2.9 Hz), 128.5 (d, J = 3.4 Hz), 80.3, 62.8 (d, J = 7.1 Hz), 62.2 (d, J = 7.4 Hz), 52.2, 43.3 (d, J = 15.8 Hz), 41.7 (d, J = 136.5 Hz), 39.4 (d, J = 2.8 Hz), 27.9, 26.1, 25.9, 16.5 (d, J = 5.9 Hz), 16.3 (d, J = 5.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.10.

HRMS (ESI) *m/z* calcd. for $[C_{22}H_{36}O_7P]^+$ ($[M + H]^+$) 443.2193, found 443.2193.

Tert-butyl (S)-4-(3-cyanophenyl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (19)



19

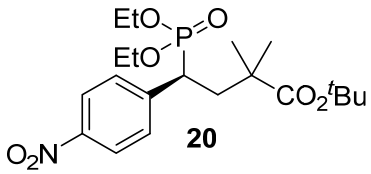
According to the **general procedure A**, 3-vinylbenzonitrile (25.8 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **19** as a colorless oil (55.7 mg, 68% yield, 90% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), t_R (minor) = 7.39 min, t_R (major) = 9.02 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 4.14 – 3.98 (m, 2H), 3.94 – 3.82 (m, 1H), 3.77 – 3.65 (m, 1H), 3.15 (ddd, *J* = 25.0, 10.1, 2.4 Hz, 1H), 2.37 – 2.18 (m, 2H), 1.31 – 1.24 (m, 12H), 1.11 – 1.05 (m, 6H), 0.88 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 139.0 (d, *J* = 7.8 Hz), 134.4 (d, *J* = 6.8 Hz), 133.2 (d, *J* = 7.1 Hz), 130.9 (d, *J* = 3.5 Hz), 129.3 (d, *J* = 2.9 Hz), 118.7, 112.6 (d, *J* = 3.0 Hz), 80.5, 62.9 (d, *J* = 7.1 Hz), 62.3 (d, *J* = 7.4 Hz), 43.2 (d, *J* = 15.4 Hz), 41.6 (d, *J* = 137.0 Hz), 39.4 (d, *J* = 3.0 Hz), 27.9, 26.4, 25.7, 16.5 (d, *J* = 5.8 Hz), 16.3 (d, *J* = 5.7 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 27.26.
HRMS (ESI) *m/z* calcd. for $[C_{21}H_{33}NO_5P]^+$ ($[M + H]^+$) 410.2091, found 410.2095.

Methyl (S)-3-(4-(tert-butoxy)-1-(diethoxyphosphoryl)-3,3-dimethyl-4-oxobutyl)benzoate

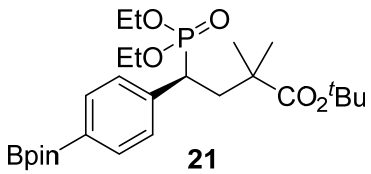
tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-(4-nitrophenyl)butanoate (20)



20

According to the **general procedure A**, 1-nitro-4-vinylbenzene (29.8 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **20** as a white solid (m.p.: 96.8-98.6 °C) (68.7 mg, 80% yield, 88% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 21.48 min, t_R (major) = 26.87 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.48 (m, 2H), 4.16 – 4.02 (m, 2H), 3.96 – 3.84 (m, 1H), 3.79 – 3.67 (m, 1H), 3.27 (ddd, *J* = 25.2, 10.4, 2.2 Hz, 1H), 2.43 – 2.23 (m, 2H), 1.33 – 1.27 (m, 12H), 1.13 – 1.05 (m, 6H), 0.88 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 147.2 (d, *J* = 4.3 Hz), 145.3 (d, *J* = 8.0 Hz), 130.7 (d, *J* = 6.8 Hz), 123.6 (d, *J* = 2.9 Hz), 80.6, 63.0 (d, *J* = 7.2 Hz), 62.5 (d, *J* = 7.4 Hz), 43.4 (d, *J* = 15.2 Hz), 42.2 (d, *J* = 135.9 Hz), 39.6 (d, *J* = 3.3 Hz), 27.9, 26.2, 25.9, 16.6 (d, *J* = 5.8 Hz), 16.4 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 26.82.
HRMS (ESI) *m/z* calcd. for $[C_{21}H_{33}NO_7P]^+$ ($[M + H]^+$) 430.1989, found 430.1994.

Tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butanoate (21)



21

According to the **general procedure A**, 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (46.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **21** as a colorless oil (63.3 mg, 62% yield, 89% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 96/4, flow rate 1.0 mL/min, λ = 230 nm), t_R (minor) = 7.61 min, t_R (majnor) = 8.30 min.

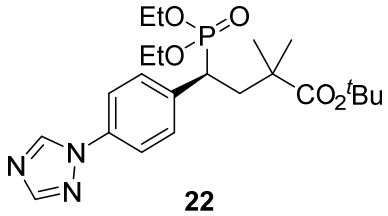
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.33 (m, 2H), 4.15 – 3.98 (m, 2H), 3.90 – 3.78 (m, 1H), 3.63 – 3.51 (m, 1H), 3.16 (ddd, *J* = 25.0, 10.6, 2.0 Hz, 1H), 2.43 – 2.24 (m, 2H), 1.37 – 1.28 (m, 24H), 1.10 – 1.03 (m, 6H), 0.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 140.3 (d, *J* = 8.0 Hz), 134.9 (d, *J* = 2.9 Hz), 129.2 (d, *J* = 6.9 Hz), 83.9, 80.2, 63.0 (d, *J* = 7.1 Hz), 62.0 (d, *J* = 7.3 Hz), 43.5 (d, *J* = 16.1 Hz), 42.3 (d, *J* = 135.6 Hz), 39.4 (d, *J* = 2.9 Hz), 27.9, 26.4, 25.5, 25.1, 24.9, 24.8, 16.6 (d, *J* = 6.0 Hz), 16.4 (d, *J* = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.46.

HRMS (ESI) *m/z* calcd. for $[C_{26}H_{45}BO_7P]^+$ ($[M + H]^+$) 511.2991, found 511.3005.

Tert-butyl (S)-4-(4-(1H-1,2,4-triazol-1-yl)phenyl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (22)



22

According to the **general procedure A**, 1-(4-vinylphenyl)-1H-1,2,4-triazole (34.2 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **22** as a colorless oil (43.3 mg, 48% yield, 88% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 13.95 min, t_R (minor) = 16.15 min.

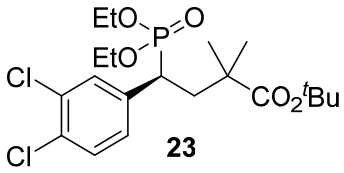
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.12 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.46 (m, 2H), 4.18 – 4.06 (m, 2H), 3.98 – 3.86 (m, 1H), 3.80 – 3.66 (m, 1H), 3.23 (ddd, *J* = 25.1, 10.5, 2.2 Hz, 1H), 2.45 – 2.22 (m, 2H), 1.37 – 1.30 (m, 12H), 1.16 – 1.08 (m, 6H), 0.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 152.6, 137.5 (d, *J* = 8.2 Hz), 136.0 (d, *J* = 5.2 Hz), 131.2 (d, *J* = 6.9 Hz), 120.0 (d, *J* = 3.0 Hz), 80.4, 63.0 (d, *J* = 7.2 Hz), 62.3 (d, *J* = 7.3 Hz), 43.3 (d, *J* = 15.7 Hz), 41.5 (d, *J* = 136.8 Hz), 39.5 (d, *J* = 2.9 Hz), 27.9, 26.2, 25.7, 16.5 (d, *J* = 5.8 Hz), 16.4 (d, *J* = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.92.

HRMS (ESI) *m/z* calcd. for $[C_{22}H_{35}N_3O_5P]^+$ ($[M + H]^+$) 452.2309, found 452.2304.

Tert-butyl (S)-4-(3,4-dichlorophenyl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (23)



23

According to the **general procedure A**, 1,2-dichloro-4-vinylbenzene (34.6 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **23** as a white solid (m.p.: 81.7-84.3 °C) (59.7 mg, 66% yield, 90% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 15.06 min, t_R (major) = 20.46 min.

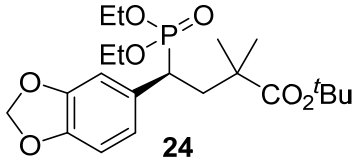
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.16 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.14 – 3.97 (m, 2H), 3.95 – 3.82 (m, 1H), 3.79 – 3.66 (m, 1H), 3.06 (ddd, *J* = 25.0, 10.3, 2.3 Hz, 1H), 2.34 – 2.13 (m, 2H), 1.33 – 1.24 (m, 12H), 1.10 (t, *J* = 7.0 Hz, 3H), 1.07 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 137.4 (d, *J* = 8.0 Hz), 132.4 (d, *J* = 3.3 Hz), 131.6 (d, *J* = 7.2 Hz), 131.3 (d, *J* = 4.3 Hz), 130.3 (d, *J* = 3.0 Hz), 129.2 (d, *J* = 6.9 Hz), 80.4, 62.9 (d, *J* = 7.1 Hz), 62.3 (d, *J* = 7.3 Hz), 43.2 (d, *J* = 15.5 Hz), 41.2 (d, *J* = 137.0 Hz), 39.4 (d, *J* = 2.9 Hz), 27.8, 26.4, 25.6, 16.5 (d, *J* = 5.9 Hz), 16.4 (d, *J* = 5.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.39.

HRMS (ESI) *m/z* calcd. for $[C_{20}H_{32}Cl_2O_5P]^+$ ($[M + H]^+$) 453.1359, found 453.1363.

Tert-butyl (S)-4-(benzo[d][1,3]dioxol-5-yl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (24)



24

According to the **general procedure A**, 5-vinylbenzo-[d]-[1,3]dioxole (29.6 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **24** as a colorless oil (57.4 mg, 67% yield, 91% ee).

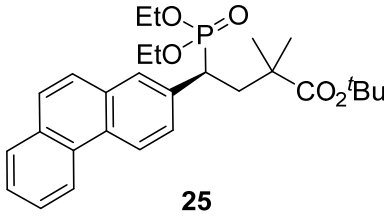
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), t_R (minor) = 9.13 min, t_R (major) = 13.85 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.84 (m, 1H), 6.78 – 6.69 (m, 2H), 5.92 (s, 2H), 4.14 – 3.97 (m, 2H), 3.93 – 3.81 (m, 1H), 3.73 – 3.60 (m, 1H), 3.04 (ddd, *J* = 25.0, 10.4, 2.5 Hz, 1H), 2.32 – 2.14 (m, 2H), 1.35 – 1.27 (m, 12H), 1.13 – 1.05 (m, 6H), 0.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 147.7 (d, *J* = 2.9 Hz), 146.9 (d, *J* = 3.6 Hz), 130.3 (d, *J* = 8.3 Hz), 123.3 (d, *J* = 8.4 Hz), 110.0 (d, *J* = 6.1 Hz), 108.3 (d, *J* = 2.9 Hz), 101.1, 80.2, 62.9 (d, *J* = 7.2 Hz), 62.0 (d, *J* = 7.4 Hz), 43.3 (d, *J* = 16.5 Hz), 41.6 (d, *J* = 137.2 Hz), 39.6 (d, *J* = 2.3 Hz), 27.9, 26.0, 25.9 (d, *J* = 5.4 Hz), 16.6 (d, *J* = 5.9 Hz), 16.4 (d, *J* = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.83.
HRMS (ESI) *m/z* calcd. for $[C_{21}H_{34}O_7P]^+$ ($[M + H]^+$) 429.2037, found 429.2035.

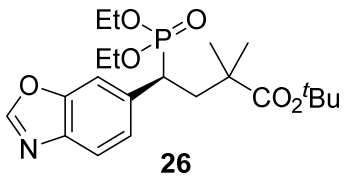
Tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-(phenanthren-2-yl)butanoate (25)



25

According to the **general procedure A**, 2-vinylphenanthrene (40.8 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **25** as a colorless oil (48.4 mg, 50% yield, 93% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 17.35 min, t_R (minor) = 21.31 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.58 (m, 2H), 7.91 – 7.83 (m, 2H), 7.73 – 7.55 (m, 5H), 4.18 – 4.01 (m, 2H), 3.86 – 3.73 (m, 1H), 3.55 – 3.44 (m, 1H), 3.36 (ddd, *J* = 24.9, 8.4, 4.1 Hz, 1H), 2.53 – 2.39 (m, 2H), 1.31 (t, *J* = 7.0 Hz, 3H), 1.24 (s, 9H), 1.12 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 3H).
^{13}C NMR (100 MHz,$CDCl_3$) δ 176.3, 135.2 (d, *J* = 8.0 Hz), 132.1 (d, *J* = 2.9 Hz), 132.0, 130.2 (d, *J* = 1.6 Hz), 129.5 (d, *J* = 5.4 Hz), 129.4, 128.6, 128.3 (d, *J* = 6.0 Hz), 127.2, 127.0, 126.7, 126.6, 122.9 (d, *J* = 2.6 Hz), 122.7, 80.2, 63.0 (d, *J* = 7.1 Hz), 62.0 (d, *J* = 7.4 Hz), 43.4 (d, *J* = 16.1 Hz), 41.9 (d, *J* = 136.2 Hz), 39.7 (d, *J* = 2.6 Hz), 27.8, 26.1, 26.0, 16.6 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 5.7 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.67.
HRMS (ESI) *m/z* calcd. for $[C_{28}H_{38}O_5P]^+$ ($[M + H]^+$) 485.2451, found 485.2462.

Tert-butyl (S)-4-(benzo[d]oxazol-6-yl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (26)

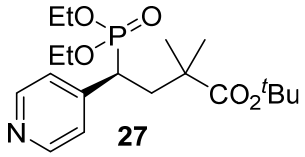


26

According to the **general procedure A**, 6-vinylbenzo-[d]-oxazole (29.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **26** as a colorless oil (40.8 mg, 48% yield, 90% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.34 min, t_R (major) = 14.22 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.37 – 7.29 (m, 1H), 4.14 – 3.99 (m, 2H), 3.88 – 3.76 (m, 1H), 3.65 – 3.52 (m,

1H), 3.27 (ddd, *J* = 25.1, 9.0, 3.8 Hz, 1H), 2.41 – 2.27 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 9H), 1.08 (s, 3H), 1.02 (t, *J* = 7.0 Hz, 3H), 0.87 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 152.9, 150.2 (d, *J* = 3.0 Hz), 139.4 (d, *J* = 3.2 Hz), 135.1 (d, *J* = 8.0 Hz), 126.8 (d, *J* = 7.0 Hz), 120.2 (d, *J* = 2.7 Hz), 112.1 (d, *J* = 7.2 Hz), 80.2, 62.9 (d, *J* = 7.2 Hz), 62.1 (d, *J* = 7.3 Hz), 43.2 (d, *J* = 15.9 Hz), 42.0 (d, *J* = 136.9 Hz), 40.0 (d, *J* = 2.6 Hz), 27.8, 26.2, 25.8, 16.5 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 5.7 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.18.
HRMS (ESI) *m/z* calcd. for $[C_{21}H_{33}NO_6P]^+$ ($[M + H]^+$) 426.2040, found 426.2040.

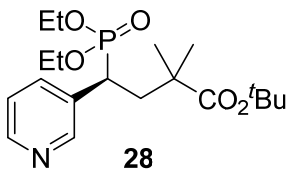
Tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-(pyridin-4-yl)butanoate (27)



27

According to the **general procedure A**, 4-vinylpyridine (21.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **27** as a colorless oil (53.9 mg, 70% yield, 84% ee).
HPLC analysis: Chiralcel AS-H (hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 11.04 min, t_R (major) = 12.56 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 2H), 7.37 – 7.26 (m, 2H), 4.14 – 3.99 (m, 2H), 3.94 – 3.82 (m, 1H), 3.77 – 3.64 (m, 1H), 3.11 (ddd, *J* = 25.1, 9.6, 2.8 Hz, 1H), 2.38 – 2.21 (m, 2H), 1.32 – 1.23 (m, 12H), 1.13 – 1.04 (m, 6H), 0.89 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 149.7 (d, *J* = 3.0 Hz), 147.1 (d, *J* = 7.0 Hz), 125.2, 80.5, 63.1 (d, *J* = 7.1 Hz), 62.4 (d, *J* = 7.3 Hz), 43.3 (d, *J* = 15.1 Hz), 41.7 (d, *J* = 135.5 Hz), 39.0 (d, *J* = 3.5 Hz), 27.8, 26.2, 25.7, 16.5 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 26.82.
HRMS (ESI) *m/z* calcd. for $[C_{19}H_{33}NO_5P]^+$ ($[M + H]^+$) 386.2091, found 386.2097.

Tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-(pyridin-3-yl)butanoate (28)

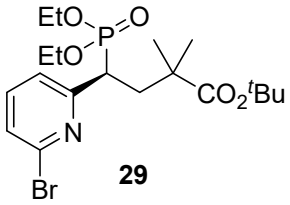


28

According to the **general procedure A**, 3-vinylpyridine (21.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **28** as a colorless oil (41.6 mg, 54% yield, 91% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 91/9, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 11.43 min, t_R (minor) = 15.63 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (brs, 2H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 4.14 – 4.01 (m, 2H), 3.93 – 3.82 (m, 1H), 3.79 – 3.66 (m, 1H), 3.16 (ddd, *J* = 25.1, 8.7, 3.9 Hz, 1H), 2.39 – 2.24 (m, 2H), 1.32 – 1.26 (m, 12H), 1.11 – 1.05 (m, 6H), 0.93 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 157.4 (d, *J* = 7.7 Hz), 149.2 (d, *J* = 2.7 Hz), 136.4 (d, *J* = 2.8 Hz), 124.8 (d, *J* = 5.3 Hz), 122.1 (d, *J* = 3.3 Hz), 80.2, 62.5 (d, *J* = 7.4 Hz), δ 62.4 (d, *J* = 7.5 Hz), 44.5 (d, *J* = 133.2 Hz), 43.4 (d, *J* = 15.4 Hz), 38.4 (d, *J* = 3.3 Hz), 28.0, 25.9, 25.3, 16.5 (d, *J* = 5.9 Hz), 16.4 (d, *J* = 5.9 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 27.58.
HRMS (ESI) *m/z* calcd. For $[C_{19}H_{33}NO_5P]^+$ ($[M + H]^+$) 386.2091, found 386.2092.

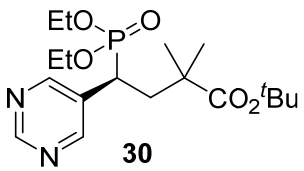
Tert-butyl (S)-4-(6-bromopyridin-2-yl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (29)



29

According to the **general procedure A**, 2-bromo-6-vinylpyridine (36.8 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **29** as a colorless oil (54.9 mg, 59% yield, 91% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 10.72 min, t_R (minor) = 14.67 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (t, *J* = 2.7 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 4.14 – 3.99 (m, 2H), 3.97 – 3.86 (m, 1H), 3.85 – 3.74 (m, 1H), 3.11 (ddd, *J* = 25.1, 9.8, 3.0 Hz, 1H), 2.33 – 2.18 (m, 2H), 1.31 – 1.24 (m, 12H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.08 (s, 3H), 0.93 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 151.2 (d, *J* = 8.3 Hz), 140.8 (d, *J* = 4.3 Hz), 139.6 (d, *J* = 5.7 Hz), 132.5 (d, *J* = 8.0 Hz), 127.8 (d, *J* = 2.9 Hz), 80.6, 63.0 (d, *J* = 7.1 Hz), 62.5 (d, *J* = 7.3 Hz), 43.0 (d, *J* = 15.3 Hz), 39.0 (d, *J* = 2.9 Hz), 38.7 (d, *J* = 138.1 Hz), 27.8, 26.8, 25.3, 16.5 (d, *J* = 5.8 Hz), 16.4 (d, *J* = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 26.85.
HRMS (ESI) *m/z* calcd. for $[C_{19}H_{32}BrNO_5P]^+$ ($[M + H]^+$) 466.1176, found 466.1177.

Tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-(pyrimidin-5-yl)butanoate (30)



30

According to the **general procedure A**, 5-vinylpyrimidine (21.2 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-

methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **30** as a colorless oil (40.2 mg, 52% yield, 91% ee).

HPLC analysis: Chiralcel AS-H (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 21.33 min, t_R (minor) = 30.72 min.

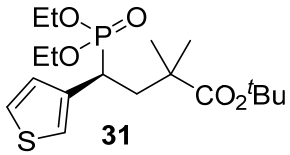
^{1}H NMR (600 MHz, DMSO) δ 9.05 (d, *J* = 2.1 Hz, 1H), 8.76 (d, *J* = 2.4 Hz, 2H), 4.09 – 3.98 (m, 2H), 3.96 – 3.83 (m, 2H), 3.28 (ddd, *J* = 25.3, 11.0, 1.9 Hz, 1H), 2.40 – 2.31 (m, 1H), 2.20 – 2.10 (m, 1H), 1.24 – 1.18 (m, 12H), 1.09 (t, *J* = 7.0 Hz, 3H), 1.05 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (150 MHz, DMSO) δ 175.6, 157.9 (d, *J* = 6.6 Hz), 157.3 (d, *J* = 3.7 Hz), 131.7 (d, *J* = 7.8 Hz), 80.2, 62.6 (d, *J* = 7.2 Hz), 62.5 (d, *J* = 7.2 Hz), 42.9 (d, *J* = 15.1 Hz), 38.1 (d, *J* = 2.9 Hz), 36.5 (d, *J* = 136.2 Hz), 27.8, 27.2, 24.7, 16.6 (d, *J* = 5.6 Hz), 16.5 (d, *J* = 5.4 Hz).

^{31}P NMR (243 MHz, DMSO) δ 31.69.

HRMS (ESI) *m/z* calcd. for $[C_{18}H_{32}N_2O_5P]^+$ ($[M + H]^+$) 387.2043, found 387.2048.

Tert-butyl (S)-4-(diethoxyphosphoryl)-2,2-dimethyl-4-(thiophen-3-yl)butanoate (31)



31

According to the **general procedure A**, 3-vinylthiophene (22.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **31** as a colorless oil (33.6 mg, 43% yield, 86% ee).

HPLC analysis: Chiralcel INA (hexane/*i*-PrOH = 98.5/1.5, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 24.70 min, t_R (minor) = 26.88 min.

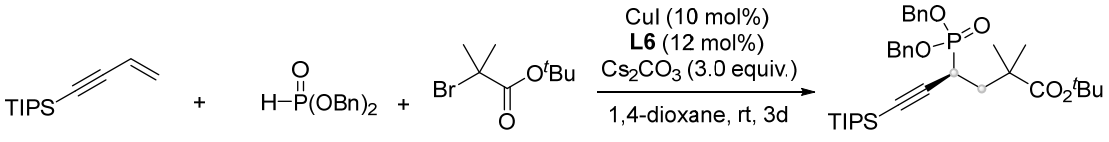
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 1H), 7.12 – 7.02 (m, 2H), 4.12 – 3.93 (m, 2H), 3.89 – 3.76 (m, 1H), 3.66 – 3.52 (m, 1H), 3.33 – 3.20 (m, 1H), 2.30 – 2.12 (m, 2H), 1.32 – 1.22 (m, 12H), 1.08 – 1.01 (m, 6H), 0.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 136.8 (d, *J* = 8.4 Hz), 128.8 (d, *J* = 4.5 Hz), 125.3 (d, *J* = 2.0 Hz), 123.2 (d, *J* = 10.2 Hz), 80.1, 62.8 (d, *J* = 7.0 Hz), 61.9 (d, *J* = 7.4 Hz), 43.1 (d, *J* = 15.9 Hz), 39.8 (d, *J* = 2.5 Hz), 37.0 (d, *J* = 139.1 Hz), 27.9, 25.8, 25.6, 16.5 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.10.

HRMS (ESI) *m/z* calcd. for $[C_{18}H_{32}O_5PS]^+$ ($[M + H]^+$) 391.1703, found 391.1709.

General procedure B

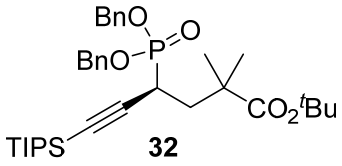


1c **2b** **3a** **32**

An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged

with CuI (3.8 mg, 0.02 mmol, 10 mol%), **L6** (7.8 mg, 0.024 mmol, 12 mol%), and anhydrous Cs_2CO_3 (195.5 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Then 1,4-dioxane (2.0 mL) was added by syringe under argon atmosphere. Finally, but-3-en-1-yn-1-yltriisopropylsilane (41.6 mg, 0.20 mmol, 1.0 equiv), dibenzyl phosphite (104.8 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were sequentially added into the mixture and the reaction mixture was stirred at rt for 3 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product **32** as a colorless oil (73.5 mg, 60% yield, 51% ee).

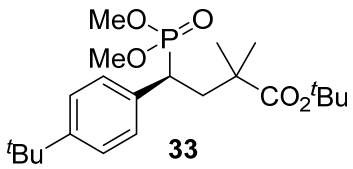
Tert-butyl (S)-4-(bis(benzyloxy)phosphoryl)-2,2-dimethyl-6-(triisopropylsilyl)hex-5-ynoate (32)



32

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 210 nm), t_R (minor) = 11.29 min, t_R (major) = 13.20 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, *J* = 3.2, 2.7 Hz, 10H), 5.11 – 5.00 (m, 4H), 2.98 (ddd, *J* = 27.1, 10.7, 1.7 Hz, 1H), 2.38 – 2.22 (m, 1H), 1.82 – 1.77 (m, 1H), 1.39 (s, 9H), 1.26 (s, 3H), 1.20 (s, 3H), 1.08 – 0.99 (m, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 136.4 (d, *J* = 6.2 Hz), 136.2 (d, *J* = 5.9 Hz), 128.5 (d, *J* = 2.1 Hz), 128.3 (d, *J* = 5.3 Hz), 127.9 (d, *J* = 9.9 Hz), 103.5 (d, *J* = 14.1 Hz), 85.5 (d, *J* = 9.2 Hz), 80.4, 68.4 (d, *J* = 7.1 Hz), 68.2 (d, *J* = 6.8 Hz), 43.4 (d, *J* = 14.9 Hz), 38.8 (d, *J* = 3.8 Hz), 28.8 (d, *J* = 142.6 Hz), 27.9, 27.0, 23.8, 18.6, 11.3.
^{31}P NMR (162 MHz, $CDCl_3$) δ 25.23.
HRMS (ESI) *m/z* calcd. for $[C_{35}H_{54}O_5PSi]^+$ ($[M + H]^+$) 613.3473, found 613.3469.

Tert-butyl (S)-4-(4-(tert-butyl)phenyl)-4-(dimethoxyphosphoryl)-2,2-dimethylbutanoate (33)

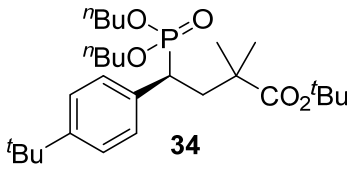


33

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), dimethyl phosphite (44.0 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **33** as a colorless oil (53.6 mg, 65% yield, 92% ee).
HPLC analysis: Chiralcel IH (hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 230 nm), t_R (minor) = 11.82 min, t_R (major) = 14.50 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.22 (m, 2H), 3.69 (d, *J* = 10.7 Hz, 3H), 3.36 (d, *J* = 10.4 Hz, 3H), 3.13 (ddd, *J* = 25.1, 10.3, 2.2 Hz, 1H), 2.39 – 2.19 (m, 2H), 1.27 (s, 9H), 1.25 (s, 9H), 1.09 (s, 3H), 0.92 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 150.2 (d, *J* = 3.9 Hz), 132.9 (d, *J* = 8.2 Hz), 129.4 (d, *J* = 7.0 Hz), 125.5 (d, *J* = 2.9 Hz), 80.1, 53.7 (d, *J* = 7.0 Hz), 52.7 (d, *J* = 7.4 Hz), 43.1 (d, *J* = 16.1 Hz), 40.9 (d, *J* = 136.1 Hz), 39.4 (d, *J* = 2.5 Hz), 34.5, 31.4, 27.8, 26.4, 25.5.
^{31}P NMR (162 MHz, $CDCl_3$) δ 31.48.
HRMS (ESI) *m/z* calcd. for $[C_{22}H_{38}O_5P]^+$ ($[M + H]^+$) 413.2451, found 413.2460.

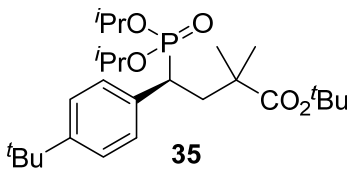
Tert-butyl (S)-4-(4-(tert-butyl)phenyl)-4-(dibutoxyphosphoryl)-2,2-dimethylbutanoate (34)



34

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), dibutyl phosphite (77.6 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **34** as a white solid (m.p.: 80.1-82.5 °C) (59.6 mg, 60% yield, 90% ee).
HPLC analysis: Chiralcel IH (hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 230 nm), t_R (minor) = 9.72 min, t_R (major) = 13.27 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 4H), 4.07 – 3.90 (m, 2H), 3.80 – 3.68 (m, 1H), 3.53 – 3.39 (m, 1H), 3.12 (ddd, *J* = 25.0, 10.8, 1.9 Hz, 1H), 2.39 (ddd, *J* = 14.4, 10.8, 3.8 Hz, 1H), 2.30 – 2.15 (m, 1H), 1.67 – 1.57 (m, 2H), 1.41 – 1.30 (m, 4H), 1.28 (s, 9H), 1.23 (s, 9H), 1.20 – 1.13 (m, 2H), 1.10 (s, 3H), 0.97 (s, 3H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.80 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 150.0 (d, *J* = 3.8 Hz), 133.3 (d, *J* = 8.0 Hz), 129.5 (d, *J* = 7.0 Hz), 125.4 (d, *J* = 2.9 Hz), 80.0, 66.6 (d, *J* = 7.2 Hz), 65.5 (d, *J* = 7.6 Hz), 43.0 (d, *J* = 16.4 Hz), 41.2 (d, *J* = 136.6 Hz), 39.6 (d, *J* = 2.4 Hz), 34.5, 32.7 (d, *J* = 6.0 Hz), 32.4 (d, *J* = 6.0 Hz), 31.5, 27.8, 26.8, 25.2, 18.8, 18.6, 13.8, 13.7.
^{31}P NMR (162 MHz, $CDCl_3$) δ 29.12.
HRMS (ESI) *m/z* calcd. for $[C_{28}H_{50}O_5P]^+$ ($[M + H]^+$) 497.3390, found 497.3405.

Tert-butyl (S)-4-(4-(tert-butyl)phenyl)-4-(diisopropoxyphosphoryl)-2,2-dimethylbutanoate (35)



35

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), diisopropyl phosphite (66.4 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-

2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **35** as a colorless oil (48.7 mg, 52% yield, 92% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 8.28 min, t_R (minor) = 11.30 min.

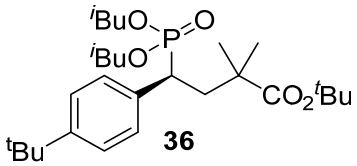
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 4H), 4.72 – 4.60 (m, 1H), 4.29 – 4.16 (m, 1H), 3.03 (ddd, *J* = 25.1, 10.9, 1.8 Hz, 1H), 2.37 (ddd, *J* = 14.5, 10.9, 3.7 Hz, 1H), 2.20 (td, *J* = 14.4, 1.9 Hz, 1H), 1.33 – 1.26 (m, 15H), 1.22 (s, 9H), 1.18 (d, *J* = 6.1 Hz, 3H), 1.09 (s, 3H), 0.96 (s, 3H), 0.67 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 150.0 (d, *J* = 3.6 Hz), 133.5 (d, *J* = 7.7 Hz), 129.7 (d, *J* = 7.2 Hz), 125.3 (d, *J* = 2.9 Hz), 79.9, 71.5 (d, *J* = 7.3 Hz), 70.0 (d, *J* = 7.7 Hz), 43.0 (d, *J* = 16.6 Hz), 41.8 (d, *J* = 138.6 Hz), 39.8 (d, *J* = 2.2 Hz), 34.5, 31.5, 27.8, 26.9, 25.1, 24.5 (d, *J* = 2.7 Hz), 24.1 (d, *J* = 4.4 Hz), 22.8 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.97.

HRMS (ESI) *m/z* calcd. for $[C_{26}H_{46}O_5P]^+$ ($[M + H]^+$) 469.3077, found 469.3092.

Tert-butyl (S)-4-(4-(tert-butyl)phenyl)-4-(diisobutoxyphosphoryl)-2,2-dimethylbutanoate (36)



36

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), diisobutyl phosphite (77.6 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **36** as a colorless oil (42.7 mg, 43% yield, 89% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98.5/1.5, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 21.17 min, t_R (minor) = 22.68 min.

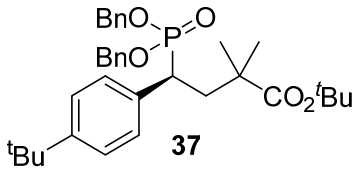
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 4H), 3.81 – 3.66 (m, 2H), 3.56 – 3.44 (m, 1H), 3.25 – 3.08 (m, 2H), 2.42 (ddd, *J* = 14.5, 10.9, 3.7 Hz, 1H), 2.23 (td, *J* = 14.4, 1.8 Hz, 1H), 1.93 – 1.84 (m, 1H), 1.66 – 1.54 (m, 1H), 1.27 (s, 9H), 1.22 (s, 9H), 1.10 (s, 3H), 0.99 (s, 3H), 0.91 (d, *J* = 6.7 Hz, 6H), 0.74 (d, *J* = 6.7 Hz, 3H), 0.71 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 150.1 (d, *J* = 3.8 Hz), 133.3 (d, *J* = 8.1 Hz), 129.6 (d, *J* = 7.0 Hz), 125.3 (d, *J* = 2.9 Hz), 80.0, 72.7 (d, *J* = 7.4 Hz), 71.7 (d, *J* = 7.8 Hz), 42.9 (d, *J* = 16.2 Hz), 41.2 (d, *J* = 136.8 Hz), 39.6 (d, *J* = 2.4 Hz), 34.5, 31.4, 29.4 (d, *J* = 6.3 Hz), 29.1 (d, *J* = 6.4 Hz), 27.8, 27.0, 25.0, 18.9, 18.8, 18.7, 18.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.69.

HRMS (ESI) *m/z* calcd. for $[C_{28}H_{50}O_5P]^+$ ($[M + H]^+$) 497.3390, found 497.3406.

Tert-butyl (S)-4-(bis(benzyloxy)phosphoryl)-4-(4-(tert-butyl)phenyl)-2,2-dimethylbutanoate (37)



37

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), dibenzyl phosphite (104.8 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **37** as a white solid (m.p.: 84.3-87.2 °C) (45.1 mg, 40% yield, 94% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 230 nm), t_R (minor) = 27.40 min, t_R (major) = 31.61 min.

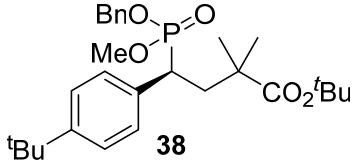
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 12H), 7.09 – 7.00 (m, 2H), 5.13 – 4.91 (m, 2H), 4.76 – 4.70 (m, 1H), 4.47 – 4.33 (m, 1H), 3.23 (dd, *J* = 25.1, 10.5 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.33 – 2.18 (m, 1H), 1.32 (s, 9H), 1.20 (s, 9H), 1.07 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 150.2 (d, *J* = 3.8 Hz), 136.6 (d, *J* = 5.2 Hz), 132.9 (d, *J* = 8.0 Hz), 129.6 (d, *J* = 7.1 Hz), 128.5 (d, *J* = 14.8 Hz), 128.3 (d, *J* = 17.4 Hz), 128.0 (d, *J* = 27.9 Hz), 125.5 (d, *J* = 2.9 Hz), 80.0, 68.2 (d, *J* = 6.9 Hz), 67.4 (d, *J* = 7.5 Hz), 43.0 (d, *J* = 16.5 Hz), 41.4 (d, *J* = 135.8 Hz), 39.4, 34.5, 31.5, 27.8, 26.7, 25.2.

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

HRMS (ESI) *m/z* calcd. for $[C_{34}H_{46}O_5P]^+$ ($[M + H]^+$) 565.3077, found 565.3069.

Tert-butyl 4-((benzyloxy)(methoxy)phosphoryl)-4-(4-(tert-butyl)phenyl)-2,2-dimethylbutanoate (38)



38

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), benzyl methyl phosphite (74.5 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **38** as a colorless oil (39.1 mg, 40% yield, 1.4:1 dr, 95% ee (major), 90% ee (minor)).

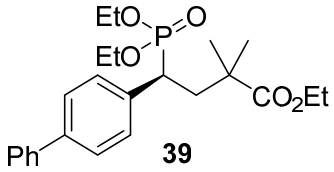
HPLC analysis: Chiralcel IB (hexane/*i*-PrOH = 97/3, flow rate 0.5 mL/min, λ = 214 nm), t_R (major$_1$) = 13.15 min, t_R (minor$_2$) = 14.84 min, t_R (major$_2$) = 21.16 min, t_R (minor$_1$) = 26.54 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.17 (m, 8H), 7.14 – 7.04 (m, 1H), 5.09 – 4.93 (m, 1.27H), 4.80 (dd, *J* = 11.7, 6.3 Hz, 0.40H), 4.33 (dd, *J* = 11.7, 7.4 Hz, 0.37H), 3.66 (d, *J* = 10.8 Hz, 1.23H), 3.34 (d, *J* = 10.5 Hz, 1.77H), 3.25 – 3.05 (m, 1H), 2.46 – 2.14 (m, 2H), 1.31 – 1.26 (m, 9H), 1.24 (s, 3.72H), 1.19 (s, 5.28H), 1.09 (s, 1.20H), 1.06 (s, 1.80H), 0.93 (s, 1.10H), 0.91 (s, 1.74H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 176.2, 150.3 (d, *J* = 3.8 Hz), 150.2 (d, *J* = 3.9 Hz), 136.6 (d, *J* = 1.2 Hz), 136.5 (d, *J* = 1.8 Hz), 132.9 (d, *J* = 8.1 Hz), 132.8 (d, *J* = 8.1 Hz), 129.5 (d, *J* = 7.0 Hz), 129.4 (d, *J* = 7.1 Hz), 128.7, 128.5(4), 128.4(6), 128.3, 128.1, 127.9, 125.6(1) (d, *J* = 2.9 Hz), 125.5(5) (d, *J* = 3.0 Hz), 80.1, 80.0, 68.4 (d, *J* = 6.8 Hz), 67.5 (d, *J* = 7.2 Hz), 53.5 (d, *J* = 7.1 Hz), 52.5 (d, *J* = 7.7 Hz), 43.1 (d, *J* = 16.4 Hz), 43.0 (d, *J* = 16.4 Hz), 42.9 (d, *J* = 9.5 Hz), 41.2 (d, *J* = 135.7 Hz), 41.1 (d, *J* = 136.0 Hz), 39.5 (d, *J* = 3.0 Hz), 39.4 (d, *J* = 2.5 Hz), 34.5, 31.5, 31.4, 27.8, 27.7, 26.6, 26.5, 25.5, 25.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.88, 30.78.
HRMS (ESI) *m/z* calcd. for $[C_{34}H_{46}O_5P]^+$ ($[M + H]^+$) 565.3077, found 565.3069.

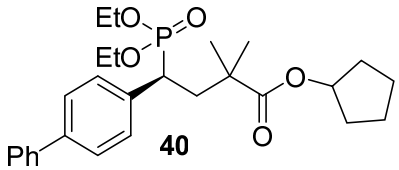
Ethyl (S)-4-([1,1'-biphenyl]-4-yl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (39)



39

According to the **general procedure A**, 1-phenyl-4-vinyl-benzene (36.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and ethyl 2-bromo-2-methylpropanoate (97.5 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **39** as a colorless oil (52.9 mg, 61% yield, 94% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 17.05 min, t_R (minor) = 20.38 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.46 – 7.36 (m, 4H), 7.33 (t, *J* = 7.3 Hz, 1H), 4.16 – 3.98 (m, 2H), 3.94 – 3.82 (m, 1H), 3.75 – 3.61 (m, 2H), 3.51 – 3.40 (m, 1H), 3.16 (ddd, *J* = 24.9, 11.1, 1.9 Hz, 1H), 2.47 (ddd, *J* = 14.6, 11.0, 3.8 Hz, 1H), 2.24 (td, *J* = 14.2, 1.9 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.18 (s, 3H), 1.11 – 1.04 (m, 6H), 1.02 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 140.7 (d, *J* = 1.6 Hz), 140.0 (d, *J* = 3.7 Hz), 135.1 (d, *J* = 7.9 Hz), 130.3 (d, *J* = 7.0 Hz), 128.9, 127.4, 127.0, 126.9 (d, *J* = 3.0 Hz), 62.9 (d, *J* = 7.1 Hz), 62.0 (d, *J* = 7.4 Hz), 60.4, 42.0 (d, *J* = 7.4 Hz), 41.3 (d, *J* = 128.3 Hz), 40.2 (d, *J* = 2.5 Hz), 27.1, 24.3, 16.5 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 5.8 Hz), 13.9.
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.50.
HRMS (ESI) *m/z* calcd. for $[C_{24}H_{34}O_5P]^+$ ($[M + H]^+$) 433.2138, found 433.2127.

Cyclopentyl (S)-4-([1,1'-biphenyl]-4-yl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (40)



40

According to the **general procedure A**, 1-phenyl-4-vinyl-benzene (36.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and cyclopentyl 2-bromo-2-methylpropanoate (117.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **40** as a colorless oil (62.3 mg, 66% yield, 93% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.97 min, t_R (minor) = 10.39 min.

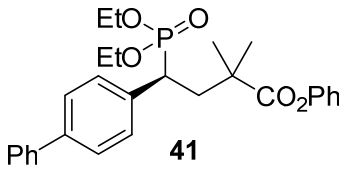
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.45 – 7.36 (m, 4H), 7.32 (t, *J* = 7.5 Hz, 1H), 4.66 – 4.54 (m, 1H), 4.17 – 3.99 (m, 2H), 3.93 – 3.79 (m, 1H), 3.71 – 3.57 (m, 1H), 3.23 – 3.08 (m, 1H), 2.42 (ddd, *J* = 14.7, 10.6, 4.0 Hz, 1H), 2.32 – 2.21 (m, 1H), 1.71 – 1.36 (m, 8H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.14 (s, 3H), 1.06 (t, *J* = 7.0 Hz, 3H), 1.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 140.8 (d, *J* = 1.6 Hz), 140.0 (d, *J* = 3.7 Hz), 135.2 (d, *J* = 8.0 Hz), 130.3 (d, *J* = 7.1 Hz), 128.9, 127.4, 127.0, 126.9 (d, *J* = 3.0 Hz), 77.2, 62.3 (d, *J* = 7.0 Hz), 62.0 (d, *J* = 7.5 Hz), 42.2 (d, *J* = 15.9 Hz), 41.3 (d, *J* = 136.8 Hz), 40.0 (d, *J* = 2.7 Hz), 32.7, 32.3, 26.8, 24.7, 23.8, 23.7, 16.5 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.64.

HRMS (ESI) *m/z* calcd. for $[C_{27}H_{38}O_5P]^+$ ($[M + H]^+$) 473.2451, found 473.2446.

Phenyl (S)-4-([1,1'-biphenyl]-4-yl)-4-(diethoxyphosphoryl)-2,2-dimethylbutanoate (41)



41

According to the **general procedure A**, 1-phenyl-4-vinyl-benzene (36.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and phenyl 2-bromo-2-methylpropanoate (121.6 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **41** as a colorless oil (57.6 mg, 60% yield, 92% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 11.76 min, t_R (minor) = 12.93 min.

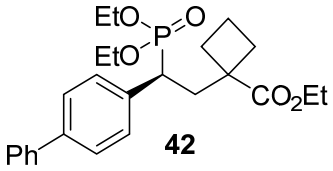
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.41 (m, 4H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.18 – 4.02 (m, 2H), 3.96 – 3.83 (m, 1H), 3.74 – 3.61 (m, 1H), 3.29 (ddd, *J* = 25.1, 10.8, 1.9 Hz, 1H), 2.63 (ddd, *J* = 14.5, 10.7, 3.9 Hz, 1H), 2.46 (td, *J* = 14.6, 1.9 Hz, 1H), 1.34 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.24 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 150.8, 140.7 (d, *J* = 1.5 Hz), 140.3 (d, *J* = 3.7 Hz), 135.2 (d, *J* = 8.0 Hz), 130.4 (d, *J* = 7.0 Hz), 129.2, 128.9, 127.5, 127.3 (d, *J* = 2.9 Hz), 127.1, 125.6, 121.4, 63.1 (d, *J* = 7.0 Hz), 62.1 (d, *J* = 7.4 Hz), 42.7 (d, *J* = 15.9 Hz), 41.4 (d, *J* = 136.9 Hz), 40.1 (d, *J* = 2.4 Hz), 27.0, 24.8, 16.5 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.36.

HRMS (ESI) *m/z* calcd. for $[C_{28}H_{34}O_5P]^+$ ($[M + H]^+$) 481.2138, found 481.2135.

Ethyl (S)-1-(2-([1,1'-biphenyl]-4-yl)-2-(diethoxyphosphoryl)ethyl)cyclobutane-1-carboxylate (42)



42

According to the **general procedure A**, 1-phenyl-4-vinyl-benzene (36.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and ethyl 1-bromocyclobutane-1-carboxylate (103.5 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **42** as a colorless oil (73.7 mg, 83% yield, 91% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.88 min, t_R (minor) = 11.98 min.

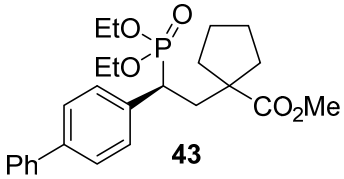
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 4.18 – 4.00 (m, 2H), 3.95 – 3.83 (m, 1H), 3.80 – 3.63 (m, 2H), 3.58 – 3.45 (m, 1H), 3.03 (ddd, *J* = 24.0, 7.8, 5.3 Hz, 1H), 2.61 – 2.52 (m, 2H), 2.50 – 2.40 (m, 1H), 2.12 – 2.04 (m, 1H), 2.00 – 1.92 (m, 1H), 1.87 – 1.77 (m, 2H), 1.74 – 1.65 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.10 – 0.99 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 140.7 (d, *J* = 1.5 Hz), 140.0 (d, *J* = 3.5 Hz), 134.8 (d, *J* = 7.5 Hz), 130.3 (d, *J* = 7.3 Hz), 128.8, 127.3, 127.0, 126.8 (d, *J* = 2.6 Hz), 62.9 (d, *J* = 7.1 Hz), 61.9 (d, *J* = 7.3 Hz), 60.3, 47.5 (d, *J* = 16.3 Hz), 41.4 (d, *J* = 137.5 Hz), 38.1 (d, *J* = 2.6 Hz), 31.6, 29.3, 16.5 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 5.9 Hz), 15.7, 14.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.22.

HRMS (ESI) *m/z* calcd. for $[C_{25}H_{34}O_5P]^+$ ($[M + H]^+$) 445.2138, found 445.2137.

Methyl (S)-1-(2-([1,1'-biphenyl]-4-yl)-2-(diethoxyphosphoryl)ethyl)cyclopentane-1-carboxylate (43)



43

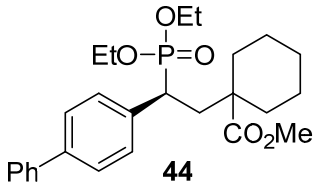
According to the **general procedure A**, 1-phenyl-4-vinyl-benzene (36.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and methyl 1-bromocyclopentane-1-carboxylate (103.5 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **43** as a colorless oil (56.9 mg, 64% yield, 92% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.73 min, t_R (minor) = 11.60 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.35 (m, 4H), 7.34 – 7.28 (m, 1H), 4.15 – 3.98 (m, 2H), 3.93 – 3.80 (m, 1H), 3.72 – 3.60 (m, 1H), 3.15 – 3.01 (m, 4H), 2.52 (ddd, *J* = 14.4, 10.8, 3.5 Hz, 1H), 2.38 – 2.21

(m, 2H), 1.90 – 1.80 (m, 1H), 1.67 – 1.47 (m, 5H), 1.42 – 1.34 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.06 (t, J = 7.1 Hz, 3H).
^{13}C NMR (100 MHz,$CDCl_3$) δ 177.0, 140.6 (d, J = 1.5 Hz), 139.9 (d, J = 3.6 Hz), 134.8 (d, J = 7.8 Hz), 130.4 (d, J = 7.1 Hz), 128.8, 127.4, 126.9, 126.8 (d, J = 2.9 Hz), 62.9 (d, J = 7.1 Hz), 62.0 (d, J = 7.4 Hz), 53.9 (d, J = 15.7 Hz), 51.3, 42.2 (d, J = 137.0 Hz), 38.8 (d, J = 2.6 Hz), 37.8, 34.4, 24.5, 24.3, 16.5 (d, J = 6.1 Hz), 16.3 (d, J = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.35.
HRMS (ESI) *m/z* calcd. for $[C_{25}H_{34}O_5P]^+$ ($[M + H]^+$) 445.2138, found 445.2135.

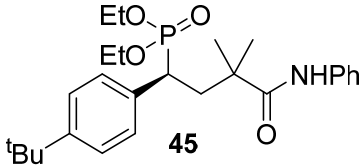
Methyl (S)-1-(2-([1,1'-biphenyl]-4-yl)-2-(diethoxyphosphoryl)ethyl)cyclohexane-1-carboxylate (44)



44

According to the **general procedure A**, 1-phenyl-4-vinyl-benzene (36.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and methyl 1-bromocyclohexane-1-carboxylate (110.5 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **44** as a colorless oil (77.0 mg, 84% yield, 91% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.64 min, t_R (minor) = 10.65 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.56 – 7.51 (m, 2H), 7.45 – 7.40 (m, 2H), 7.39 – 7.30 (m, 3H), 4.14 – 3.98 (m, 2H), 3.91 – 3.80 (m, 1H), 3.69 – 3.57 (m, 1H), 3.18 (ddd, J = 25.0, 10.6, 1.8 Hz, 1H), 3.10 (s, 3H), 2.43 – 2.33 (m, 1H), 2.31 – 2.14 (m, 2H), 1.96 – 1.77 (m, 2H), 1.63 – 1.56 (m, 1H), 1.55 – 1.45 (m, 2H), 1.43 – 1.34 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.24 – 1.12 (m, 3H), 1.06 (t, J = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 140.7 (d, J = 1.5 Hz), 139.8 (d, J = 3.7 Hz), 135.1 (d, J = 8.0 Hz), 130.4 (d, J = 6.9 Hz), 128.9, 127.4, 127.0, 126.8 (d, J = 3.0 Hz), 63.0 (d, J = 7.0 Hz), 62.0 (d, J = 7.3 Hz), 51.2, 46.4 (d, J = 14.8 Hz), 40.0 (d, J = 136.7 Hz), 39.9, 36.0, 33.1, 25.8, 23.2, 23.0, 16.5 (d, J = 6.0 Hz), 16.3 (d, J = 5.8 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.58.
HRMS (ESI) *m/z* calcd. for $[C_{26}H_{36}O_5P]^+$ ($[M + H]^+$) 459.2295, found 459.2294.

Diethyl (S)-(1-(4-(tert-butyl)phenyl)-3-methyl-3-(phenylamino)butyl)phosphonate (45)

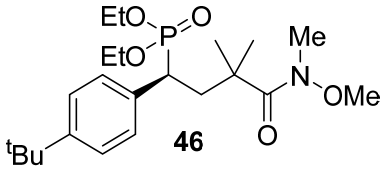


45

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and 2-bromo-2-methyl-N-phenylpropanamide (121.1 mg, 0.50 mmol, 2.5 equiv) were employed to yield the

product **45** as a colorless oil (65.2 mg, 71% yield, 88% ee).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 94/6, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 43.15 min, t_R (minor) = 49.07 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.17 (m, 6H), 7.03 (t, *J* = 7.5 Hz, 1H), 4.10 – 3.95 (m, 2H), 3.92 – 3.81 (m, 1H), 3.75 – 3.63 (m, 1H), 3.26 – 3.11 (m, 1H), 2.52 – 2.39 (m, 2H), 1.28 (s, 3H), 1.27 – 1.18 (m, 12H), 1.11 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 150.1 (d, *J* = 3.7 Hz), 138.2, 132.8 (d, *J* = 8.1 Hz), 129.2 (d, *J* = 6.8 Hz), 128.7, 125.4 (d, *J* = 2.9 Hz), 123.9, 120.1, 62.9 (d, *J* = 7.1 Hz), 62.2 (d, *J* = 7.3 Hz), 43.7 (d, *J* = 15.2 Hz), 41.3 (d, *J* = 135.9 Hz), 40.3 (d, *J* = 2.5 Hz), 34.4, 31.3, 26.6, 26.3, 16.4 (d, *J* = 5.9 Hz), 16.2 (d, *J* = 5.9 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.93.
HRMS (ESI) *m/z* calcd. for $[C_{26}H_{39}NO_4P]^+$ ($[M + H]^+$) 460.2611, found 460.2610.

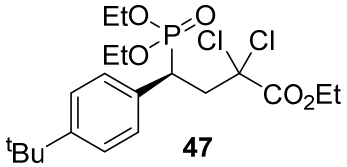
Diethyl (S)-(1-(4-(tert-butyl)phenyl)-4-(methoxy(methyl)amino)-3,3-dimethyl-4-oxobutyl)phosphonate (46)



46

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and 2-bromo-N-methoxy-N,2-dimethylpropanamide (105.0 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **46** as a colorless oil (43.6 mg, 51% yield, 86% ee).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 92/8, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 11.66 min, t_R (major) = 12.80 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.22 (m, 2H), 4.11 – 3.98 (m, 2H), 3.87 – 3.77 (m, 1H), 3.59 – 3.50 (m, 4H), 3.17 – 3.05 (m, 1H), 2.72 (ddd, *J* = 14.4, 11.1, 3.4 Hz, 1H), 2.51 (s, 3H), 2.18 – 2.09 (m, 1H), 1.32 – 1.26 (m, 12H), 1.22 (s, 4H), 1.20 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 149.8 (d, *J* = 3.7 Hz), 132.4 (d, *J* = 8.0 Hz), 129.7 (d, *J* = 7.1 Hz), 125.1 (d, *J* = 2.9 Hz), 62.9 (d, *J* = 7.0 Hz), 61.8 (d, *J* = 7.4 Hz), 60.4, 42.5 (d, *J* = 16.2 Hz), 40.7 (d, *J* = 136.6 Hz), 38.3 (d, *J* = 2.2 Hz), 34.5, 33.1, 31.4, 26.7, 25.9, 16.5 (d, *J* = 6.0 Hz), 16.2 (d, *J* = 6.0 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 29.47.
HRMS (ESI) *m/z* calcd. for $[C_{22}H_{39}NO_5P]^+$ ($[M + H]^+$) 428.2560, found 428.2558.

Ethyl (S)-4-(4-(tert-butyl)phenyl)-2,2-dichloro-4-(diethoxyphosphoryl)butanoate (47)



47

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and ethyl 2,2,2-trichloroacetate (95.7 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **47** as a colorless oil (52.4 mg, 58% yield, 91% ee) at –10 °C.

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 230 nm), t_R (minor) = 14.84 min, t_R (major) = 17.58 min.

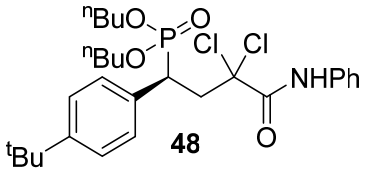
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 7.25 – 7.21 (m, 2H), 4.16 – 4.02 (m, 2H), 3.92 – 3.81 (m, 1H), 3.76 – 3.59 (m, 2H), 3.49 – 3.24 (m, 3H), 3.14 – 3.05 (m, 1H), 1.31 (t, *J* = 7.0 Hz, 3H), 1.26 (s, 9H), 1.07 – 0.99 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 150.8 (d, *J* = 3.3 Hz), 130.3 (d, *J* = 7.6 Hz), 129.8 (d, *J* = 7.0 Hz), 125.3 (d, *J* = 2.6 Hz), 84.6 (d, *J* = 23.1 Hz), 63.7, 63.3 (d, *J* = 6.9 Hz), 62.3 (d, *J* = 7.4 Hz), 45.9, 41.5 (d, *J* = 139.4 Hz), 34.6, 31.4, 16.5 (d, *J* = 6.0 Hz), 16.2 (d, *J* = 5.8 Hz), 13.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 26.32.

HRMS (ESI) *m/z* calcd. for $[C_{20}H_{32}Cl_2O_5P]^+$ ($[M + H]^+$) 453.1359, found 453.1356.

Dibutyl (S)-(1-(4-(tert-butyl)phenyl)-3,3-dichloro-3-(phenylamino)propyl)phosphonate (48)



48

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), dibutyl phosphite (77.6 mg, 0.40 mmol, 2.0 equiv), and 2,2,2-trichloro-N-phenylacetamide (119.2 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **48** as a colorless oil (68.8 mg, 62% yield, 81% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 14.87 min, t_R (major) = 17.94 min.

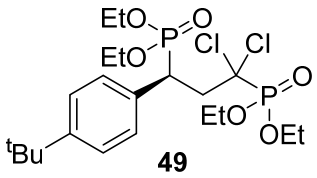
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.28 – 7.22 (m, 6H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.14 – 7.08 (m, 1H), 4.07 – 3.94 (m, 2H), 3.88 – 3.79 (m, 1H), 3.67 – 3.47 (m, 3H), 3.24 – 3.13 (m, 1H), 1.66 – 1.57 (m, 2H), 1.44 – 1.33 (m, 4H), 1.26 – 1.19 (m, 2H), 1.14 (s, 9H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.81 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 150.6 (d, *J* = 3.6 Hz), 136.5, 130.4 (d, *J* = 7.9 Hz), 129.7 (d, *J* = 6.8 Hz), 129.0, 125.4, 125.3 (d, *J* = 2.6 Hz), 120.1, 87.0 (d, *J* = 22.7 Hz), 66.9 (d, *J* = 7.3 Hz), 66.2 (d, *J* = 7.6 Hz), 44.7, 42.1 (d, *J* = 139.1 Hz), 34.4, 32.6 (d, *J* = 5.9 Hz), 32.4 (d, *J* = 6.1 Hz), 31.3, 18.8, 18.7, 13.7, 13.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 26.13.

HRMS (ESI) *m/z* calcd. for $[C_{28}H_{41}Cl_2NO_4P]^+$ ($[M + H]^+$) 556.2145, found 556.2145.

Tetraethyl (3-(4-(tert-butyl)phenyl)-1,1-dichloropropane-1,3-diyl)(S)-bis(phosphonate) (49)



49

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and diethyl (trichloromethyl)phosphonate (127.5 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **49** as a colorless oil (41.3 mg, 40% yield, 93% ee).

HPLC analysis: Chiralcel IH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm), t_R (minor) = 14.69 min, t_R (major) = 17.74 min.

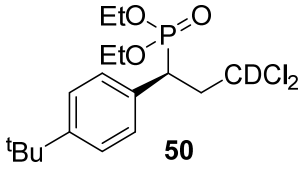
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 4H), 4.37 – 4.17 (m, 4H), 4.14 – 4.02 (m, 2H), 3.90 – 3.79 (m, 1H), 3.72 (ddd, *J* = 25.3, 8.9, 2.2 Hz, 1H), 3.66 – 3.55 (m, 1H), 3.19 – 2.99 (m, 2H), 1.38 – 1.29 (m, 9H), 1.28 (s, 9H), 1.02 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4 (d, *J* = 3.7 Hz), 132.7 (d, *J* = 7.9 Hz), 129.5 (d, *J* = 6.7 Hz), 125.4 (d, *J* = 2.9 Hz), 82.5 (dd, *J* = 179.1, 18.4 Hz), 65.8 (d, *J* = 7.2 Hz), 65.7 (d, *J* = 7.3 Hz), 63.3 (d, *J* = 7.0 Hz), 62.3 (d, *J* = 7.4 Hz), 42.4 (d, *J* = 3.6 Hz), 40.3 (dd, *J* = 138.8, 7.8 Hz), 34.5, 31.5, 16.7 – 16.4 (m), 16.2 (d, *J* = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.03 (d, *J* = 4.0 Hz), 11.60 (d, *J* = 4.2 Hz).

HRMS (ESI) *m/z* calcd. for $[C_{21}H_{37}Cl_2O_6P_2]^+$ ($[M + H]^+$) 517.1437, found 517.1437.

Diethyl (S)-(1-(4-(tert-butyl)phenyl)-3,3-dichloropropyl-3-d)phosphonate (50)



50

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and chloroform-*d* (60.2 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **50** as a colorless oil (39.6 mg, 52% yield, 70% ee) at –10 °C .

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), t_R (major) = 12.45 min, t_R (minor) = 13.93 min.

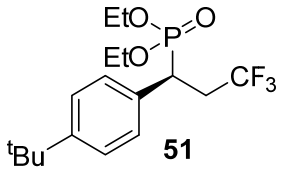
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.25 (m, 2H), 4.19 – 4.04 (m, 2H), 3.99 – 3.88 (m, 1H), 3.82 – 3.70 (m, 1H), 3.37 (ddd, *J* = 23.0, 9.1, 6.3 Hz, 1H), 2.91 – 2.79 (m, 2H), 1.37 – 1.31 (m, 12H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1 (d, *J* = 5.7 Hz), 130.3 (d, *J* = 7.3 Hz), 128.9 (d, *J* = 6.6 Hz), 126.0 (d, *J* = 2.5 Hz), 63.2 (d, *J* = 6.9 Hz), 62.3 (d, *J* = 7.2 Hz), 43.8, 41.8 (d, *J* = 140.5 Hz), 34.7, 31.4, 16.5 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 26.61.

HRMS (ESI) *m/z* calcd. for $[C_{17}H_{27}DCl_2O_3P]^+$ ($[M + H]^+$) 382.1210, found 382.1209.

Diethyl (S)-(1-(4-(tert-butyl)phenyl)-3,3,3-trifluoropropyl)phosphonate (51)



51

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole (165.0 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **51** as a colorless oil (31.5 mg, 43% yield, 74% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 9.58 min, t_R (minor) = 14.69 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.29 – 7.23 (m, 2H), 4.16 – 3.99 (m, 2H), 3.94 – 3.82 (m, 1H), 3.73 – 3.61 (m, 1H), 3.31 (ddd, *J* = 24.4, 10.6, 3.4 Hz, 1H), 2.94 – 2.71 (m, 2H), 1.34 – 1.27 (m, 12H), 1.05 (t, *J* = 7.1 Hz, 3H).

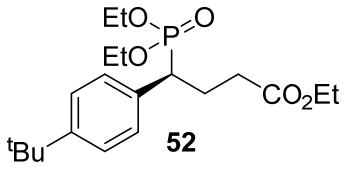
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9 (d, *J* = 3.5 Hz), 131.0 (d, *J* = 8.0 Hz), 128.7 (d, *J* = 6.8 Hz), 126.37 (qd, *J* = 276.2 Hz), 125.7 (d, *J* = 2.6 Hz), 63.5 (d, *J* = 7.0 Hz), 62.4 (d, *J* = 7.4 Hz), 38.47 (dq, *J* = 142.2, 2.6 Hz), 35.4 – 34.3 (m), 34.6, 31.4, 16.5 (d, *J* = 6.1 Hz), 16.2 (d, *J* = 5.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.39.

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.96.

HRMS (ESI) *m/z* calcd. for $[C_{17}H_{27}F_3O_3P]^+$ ($[M + H]^+$) 367.1650, found 367.1642.

Ethyl (S)-4-(4-(tert-butyl)phenyl)-4-(diethoxyphosphoryl)butanoate (52)



52

According to the **general procedure A**, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and ethyl 2-bromoacetate (83.5 mg, 0.50 mmol, 2.5 equiv) were employed to yield the product **52** as a colorless oil (61.6 mg, 80% yield, 29% ee).

HPLC analysis: Chiralcel OD-H (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 12.55 min, t_R (minor) = 14.77 min.

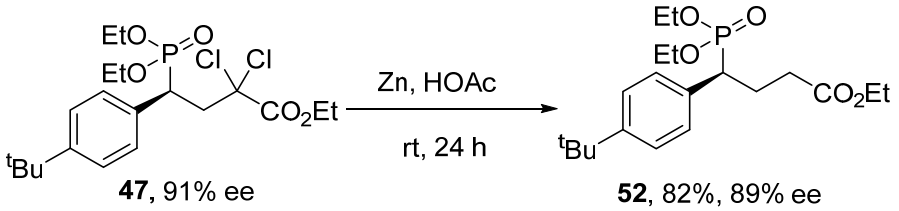
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.19 (m, 2H), 4.12 – 3.99 (m, 4H), 3.95 – 3.85 (m, 1H), 3.79 – 3.68 (m, 1H), 3.05 (ddd, *J* = 22.4, 10.3, 4.1 Hz, 1H), 2.47 – 2.34 (m, 1H), 2.30 – 2.16 (m, 3H), 1.31 – 1.27 (m, 12H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 150.4 (d, *J* = 4.0 Hz), 132.0 (d, *J* = 6.8 Hz), 129.0 (d, *J* = 6.8 Hz), 125.7 (d, *J* = 2.6 Hz), 62.7 (d, *J* = 7.1 Hz), 62.0 (d, *J* = 7.4 Hz), 60.5, 43.4 (d, *J* = 138.5 Hz), 34.6, 32.4 (d, *J* = 15.7 Hz), 31.5, 25.3 (d, *J* = 4.0 Hz), 16.6 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 6.0 Hz), 14.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.42.

HRMS (ESI) *m/z* calcd. for $[C_{20}H_{34}O_5P]^+$ ($[M + H]^+$) 385.2138, found 385.2130.

The transformation of product

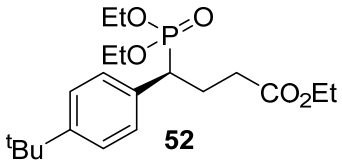


47, 91% ee

52, 82%, 89% ee

Under an argon atmosphere, HOAc (1.0 mL) was added to a mixture of **47** (45.3 mg, 0.10 mmol, 1.0 equiv, 91% ee) and Zn powder (52.3 mg, 0.80 mmol, 8.0 equiv) in an oven-dried Schlenk tube. The reaction mixture was then stirred at room temperature overnight. After completion of the reaction (monitored by TLC), the saturated Na_2CO_3 solution was added to the reaction mixture. Then EtOAc was used to extract the product from the aqueous layer (3 × 5.0 mL). The combined organic layer was washed by brine, dried over Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product **52** as a colorless oil (31.5 mg, 82% yield, 89% ee).

Ethyl (S)-4-(4-(tert-butyl)phenyl)-4-(diethoxyphosphoryl)butanoate (52)

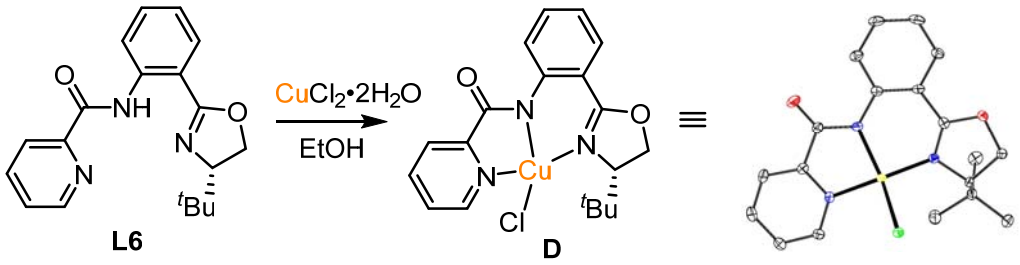


52

HPLC analysis: Chiralcel OD-H (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 12.55 min, t_R (minor) = 14.48 min.

Mechanistic investigation

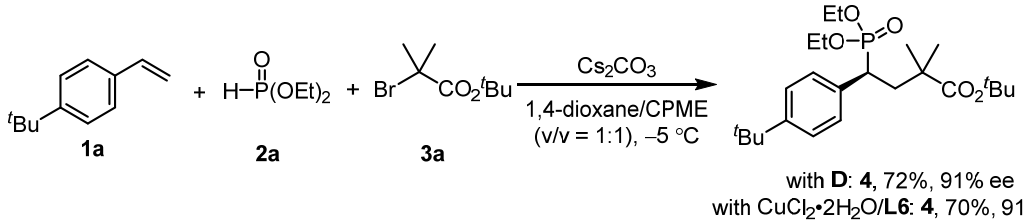
A. Preparation of CuL complex[6]



L6 **D**

In a 50 mL round-bottomed flask containing 10 mL of 95% EtOH, was placed compound **L6** (161.5 mg, 0.30 mmol); stirring was then initiated until complete dissolution of all solids. The resulting colorless mixture was then treated with $CuCl_2$•H_2O (67.2 mg, 0.40 mmol) at room temperature and stirring was continued for overnight. The resulting mixture was concentrated to afford the green-colored precipitate which was washed with diethyl ether (3 × 5.0 mL) and dried on a rotary evaporator. The powdered product was crystallized from a sealed vial by dissolving 0.2 g of the powder in 2.0 mL of CH_2Cl_2 and then layering with hexane (5.0 mL) and leaving undisturbed for approximately 48 h.

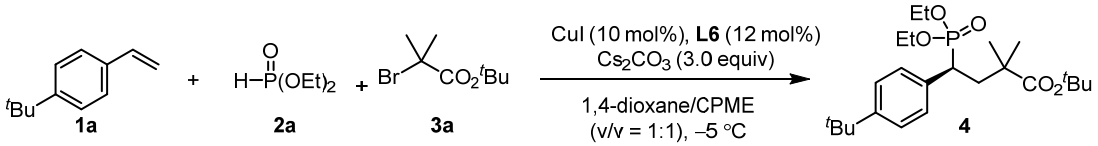
B. Reaction of CuL complex



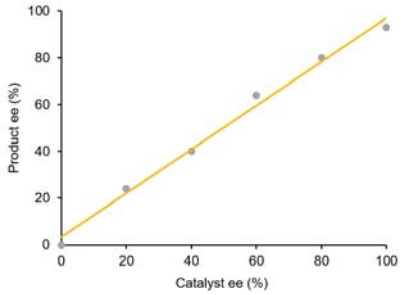
An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with complex **D** (8.4 mg, 0.02 mmol, 10 mol%) above mentioned, and anhydrous Cs_2CO_3 (195.5 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Then 1,4-dioxane/CPME (2.0 mL, v/v = 1:1) was added by syringe under argon. Finally, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were sequentially added into the mixture and the reaction mixture was stirred at –5 °C for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was diluted with EtOAc. The mixture was then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the product **4** (62.5 mg, 72%, 91% ee).

The reaction with $CuCl_2•2H_2O$ (3.4 mg, 0.02 mmol, 10 mol%) and **L6** (7.8 mg, 0.024 mmol, 12 mol%) followed the **general procedure** to afford **4** in 70% yield with 91% ee.

C. The nonlinear effect



entry	ee of **L6** (%)[b]	yield[c]	ee[d]
1	20	73	24
2	40	74	40
3	60	77	64
4	80	71	80
5	>98	75	93

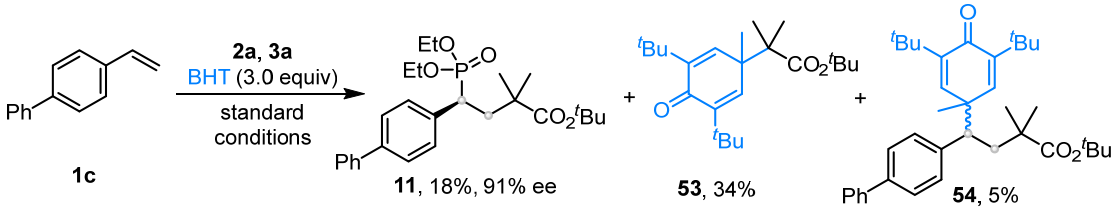


[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), **3a** (0.50 mmol), CuI (10 mol%), **L6** (12 mol%), and Cs_2CO_3 (3.0 equiv) in 1,4-dioxane/CPME (1.0 mL/1.0 mL) at –5°C for 5 d.
[b] the ee of ligand was calculated by mixing dufferent amounts of ligand (R)-L and ligand (S)-L, ee = [m((S)-L)-m((R)-L)]/[m((S)-L)+m((R)-L)]
[c] ^{1}H NMR yield.
[d] ee values determined by chiral HPLC analysis.

An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.02 mmol, 10 mol%), **L6** with different ee (7.8 mg, 0.024 mmol, 12

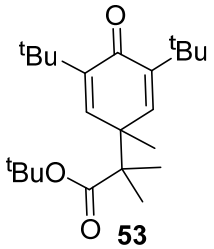
mol%), and anhydrous Cs_2CO_3 (195.5 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Then 1,4-dioxane/CPME (2.0 mL, (v/v = 1:1) was added by syringe under argon atmosphere. Finally, 4-tert-butylstyrene (32.0 mg, 0.20 mmol, 1.0 equiv), diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), and tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were sequentially added into the mixture and the reaction mixture was stirred at –5 °C for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product. The e.e. values of products were then determined by HPLC, which indicated a linear relationship between e.e. values of products and corresponding catalysts. The catalyst **L6** with different e.e. values were prepared by mixing (*S*)-**L6** (99% e.e.) and (*R*)-**L6** (99% e.e.) in appropriate ratios.

D. Radical inhibiting experiment



An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.02 mmol, 10 mol%), **L6** (7.8 mg, 0.024 mmol, 12 mol%), and anhydrous Cs_2CO_3 (195.5 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Then 1,4-dioxane/CPME (2.0 mL, (v/v = 1:1)) was added by syringe under argon. Finally, 1-phenyl-4-vinyl-benzene (59.8 mg, 0.20 mmol, 1.0 equiv) and diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv), tert-butyl 2-bromo-2-methylpropanoate (111.6 mg, 0.50 mmol, 2.5 equiv) were sequentially added into the mixture. To this solution was added BHT (132.0 mg, 0.60 mmol, 3.0 equiv), and the reaction mixture was stirred at –5 °C for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was diluted with EtOAc. The mixture was then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product (16.6 mg, 18% yield, 91% ee), **53** (61.5 mg, 34% yield), **54** (5.4 mg, 5% yield).

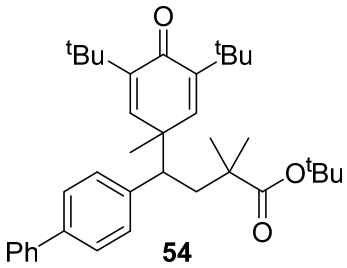
Tert-butyl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (53)



53

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 2H), 1.48 (s, 9H), 1.25 – 1.21 (m, 21H), 1.08 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 186.5, 174.9, 147.0, 144.1, 81.1, 49.3, 43.2, 35.1, 29.7, 28.2, 22.2, 22.0.
HRMS (ESI) *m/z* calcd. for $[C_{23}H_{39}O_3]^+$ ($[M + H]^+$) 363.2894, found 363.2893.

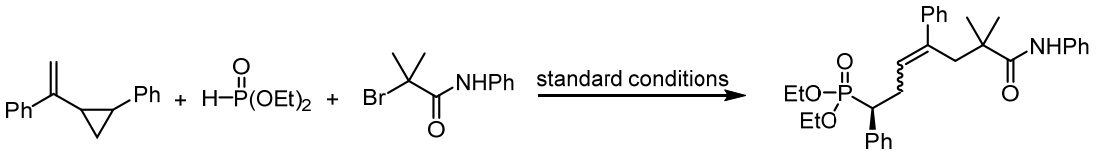
Tert-butyl 4-([1,1'-biphenyl]-4-yl)-4-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2,2-dimethylbutanoate (54)



54

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.46 – 7.38 (m, 4H), 7.35 – 7.30 (m, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.57 (d, *J* = 2.9 Hz, 1H), 6.42 (d, *J* = 2.9 Hz, 1H), 2.87 – 2.79 (m, 1H), 1.95 (dd, *J* = 14.2, 10.6 Hz, 1H), 1.83 (dd, *J* = 14.2, 1.5 Hz, 1H), 1.28 (s, 9H), 1.26 (s, 9H), 1.11 (s, 3H), 1.09 (s, 9H), 1.01 (s, 3H), 0.92 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 186.3, 176.8, 147.6, 146.4, 145.4, 145.3, 141.1, 140.4, 139.9, 128.9, 127.3, 127.1, 126.6, 80.1, 51.7, 43.5, 42.9, 40.1, 35.0, 34.8, 29.6, 29.4, 27.9, 26.3, 25.8, 25.2.
HRMS (ESI) *m/z* calcd. for $[C_{37}H_{50}NaO_3]^+$ ($[M + Na]^+$) 565.3652, found 565.3656.

E. Radical clock experiment

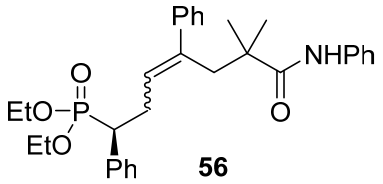


55 **2a** **3b** **56**, 53%, E/Z = 9/1 (19% ee_{major})

An oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.02 mmol, 10 mol%), **L6** (7.8 mg, 0.024 mmol, 12 mol%), and anhydrous Cs_2CO_3 (195.5 mg, 0.60 mmol, 3.0 equiv). The tube was evacuated and backfilled with argon three times. Then 1,4-dioxane/CPME (2.0 mL, (v/v = 1:1)) was added by syringe under argon. Finally, (1-(2-phenylcyclopropyl)vinyl)benzene **55** (44.1 mg, 0.20 mmol, 1.0 equiv) and diethyl phosphite (55.2 mg, 0.40 mmol, 2.0 equiv),

2-bromo-2-methyl-N-phenylpropanamide (121.0 mg, 0.50 mmol, 2.5 equiv) were sequentially added into the mixture and the reaction mixture was stirred at –5 °C for 5 d. Upon completion of the reaction (monitored by TLC), the reaction mixture was diluted with EtOAc. The mixture was then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the product **56** as a colorless oil (55.0 mg, 53% yield, E/Z = 9/1, 19% ee_{major}).

Diethyl (6,6-dimethyl-7-oxo-1,4-diphenyl-7-(phenylamino)hept-3-en-1-yl)phosphonate (56)



56

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 9H), 7.13 (d, *J* = 4.2 Hz, 5H), 7.09 – 6.99 (m, 2H), 5.47 (t, *J* = 6.9 Hz, 1H), 4.14 – 3.98 (m, 2H), 3.95 – 3.82 (m, 1H), 3.76 – 3.64 (m, 1H), 3.14 – 2.98 (m, 2H), 2.92 – 2.73 (m, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.16 (s, 3H), 1.13 (s, 3H), 1.08 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 143.9, 139.3 (d, *J* = 1.7 Hz), 137.8, 135.8 (d, *J* = 6.6 Hz), 130.2 (d, *J* = 15.9 Hz), 129.4 (d, *J* = 6.8 Hz), 128.7, 128.5 (d, *J* = 2.5 Hz), 128.2, 127.3 (d, *J* = 3.1 Hz), 126.8, 126.8, 124.0, 120.0, 62.8 (d, *J* = 7.0 Hz), 61.9 (d, *J* = 7.3 Hz), 44.8 (d, *J* = 137.2 Hz), 43.9, 40.0, 29.7 (d, *J* = 2.5 Hz), 25.9, 25.8, 16.5 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.24.

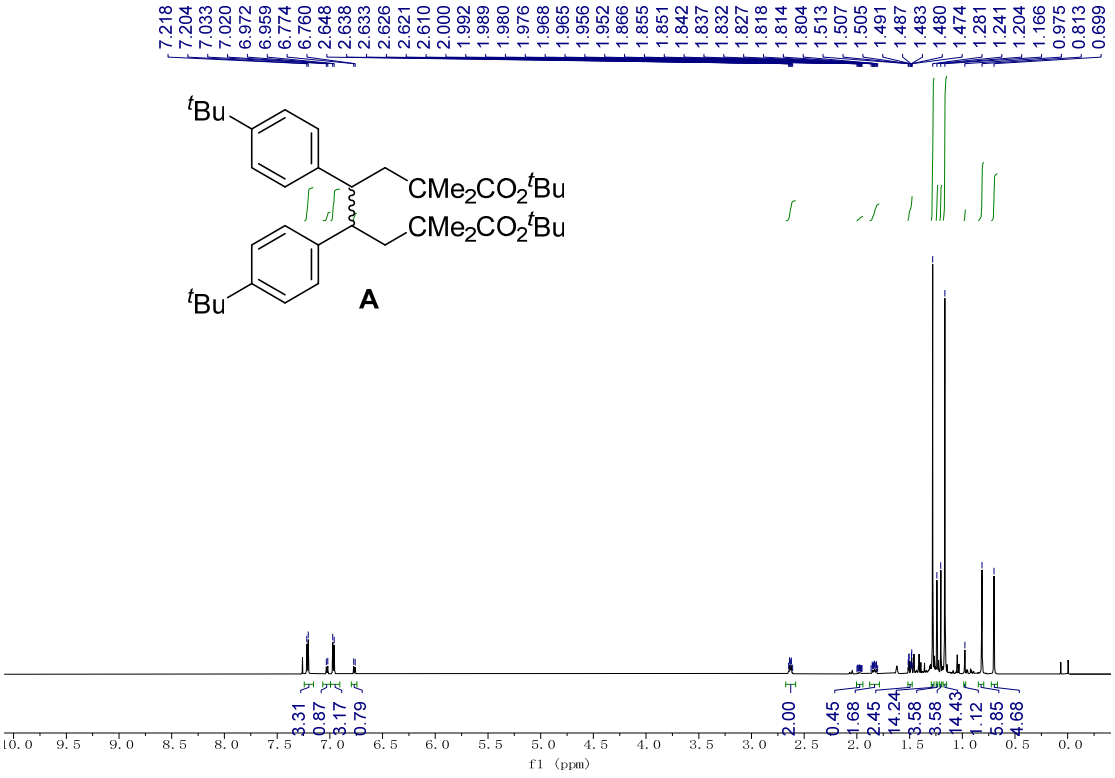
HRMS (ESI) *m/z* calcd. for $[C_{31}H_{39}NO_4P]^+$ ($[M + H]^+$) 520.2611, found 520.2609.

References

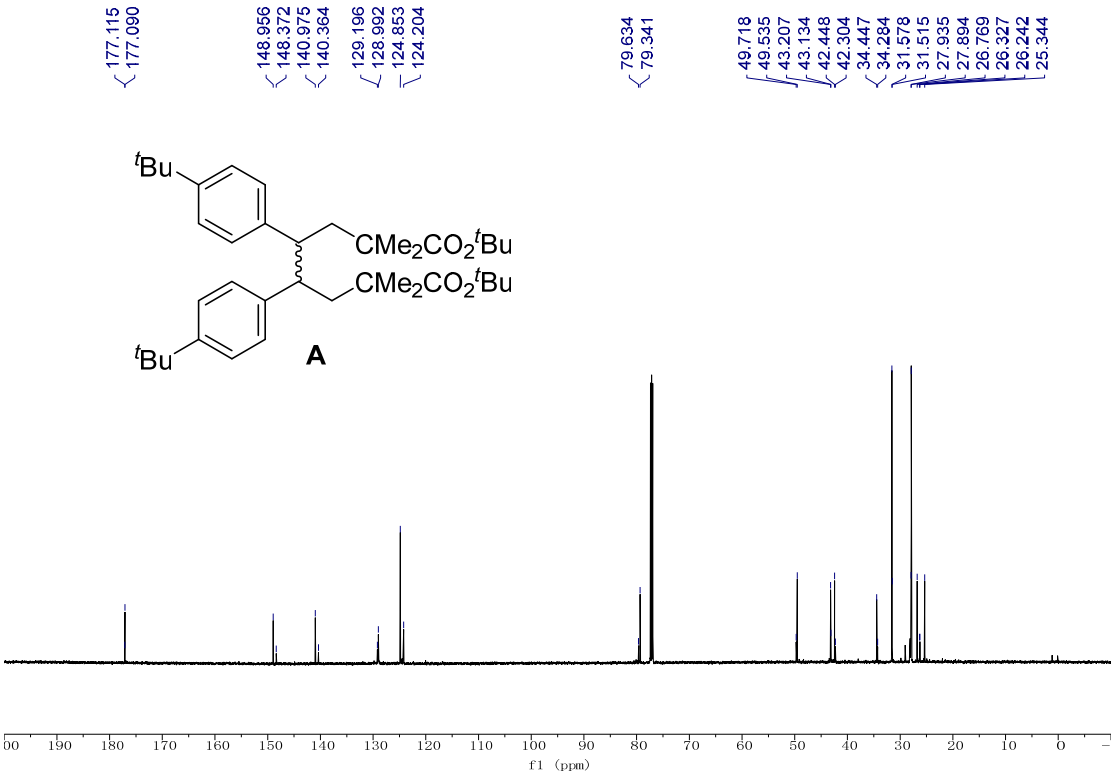
[1] Y. Lv, W. Pu, S. Mao, X. Ren, Y. Wu, H. Cui, *RSC Adv*. **2017**, *7*, 41723–41726.
[2] J. Zhang, J. Zhang, T. Chen, L. Han, *Org. Biomol. Chem.* **2017**, *15*, 5462–5467.
[3] X.-Y. Dong, J.-T. Cheng, Y.-F. Zhang, Z.-L. Li, T.-Y. Zhan, J.-J. Chen, F.-L. Wang, N.-Y. Yang, L. Ye, Q.-S. Gu, X.-Y. Liu, *J. Am. Chem. Soc*. **2020**, *142*, 9501–9509.
[4] C. C. Price, B. D. Halpern, *J. Am. Chem. Soc.* **1951**, *73*, 818–820.
[5] A. A. S. Gietter, P. G. Gildner, A. P. Cinderella, D. A. Watson, *Org. Lett.* **2014**, *16*, 3166–3169.
[6] M. Taghvaee, M. J. Rodríguez-Álvarez, J. García-Álvarez, I. del Río, A. J. Lough, R. A. Gossage, *J. Organomet. Chem.* **2017**, *845*, 107–114.

NMR spectra

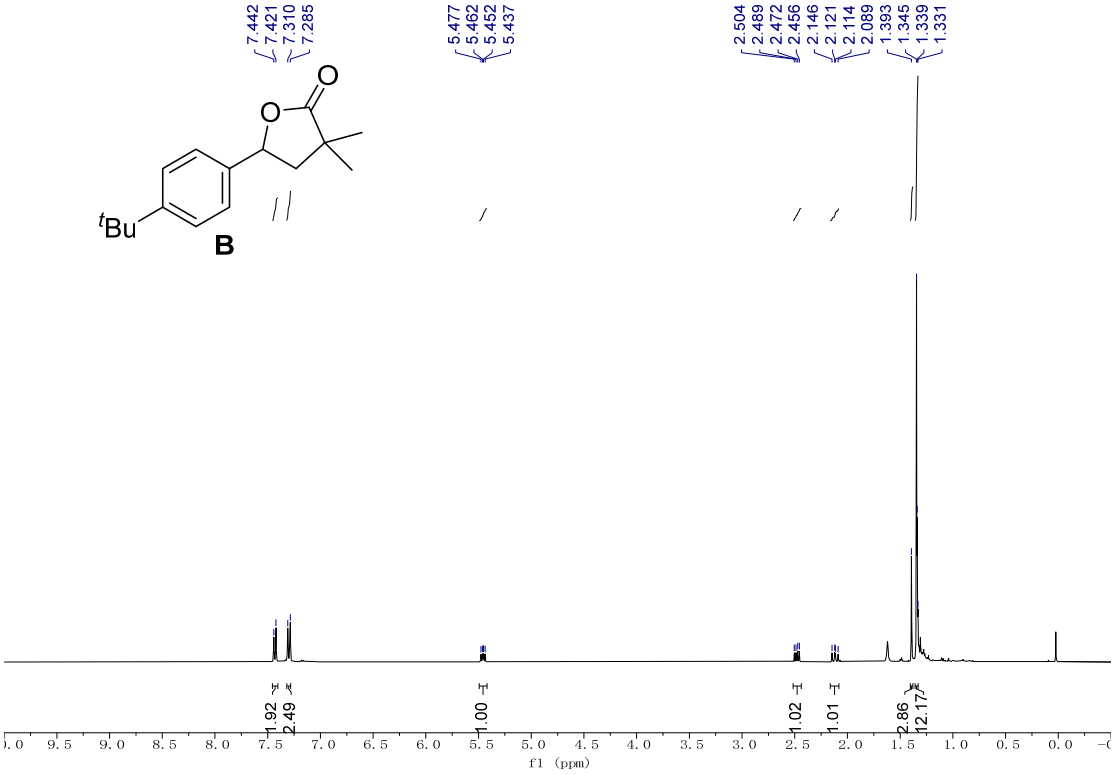
^{1}H NMR, 600 MHz, $CDCl_3$



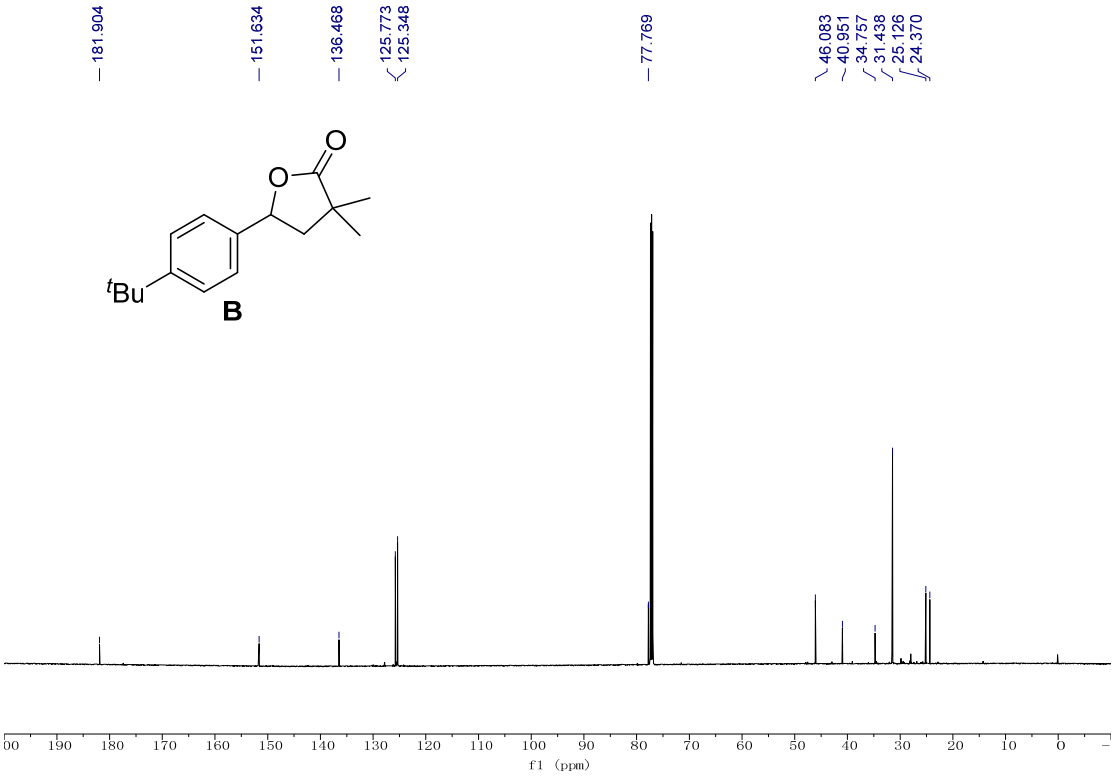
^{13}C NMR, 150 MHz, $CDCl_3$



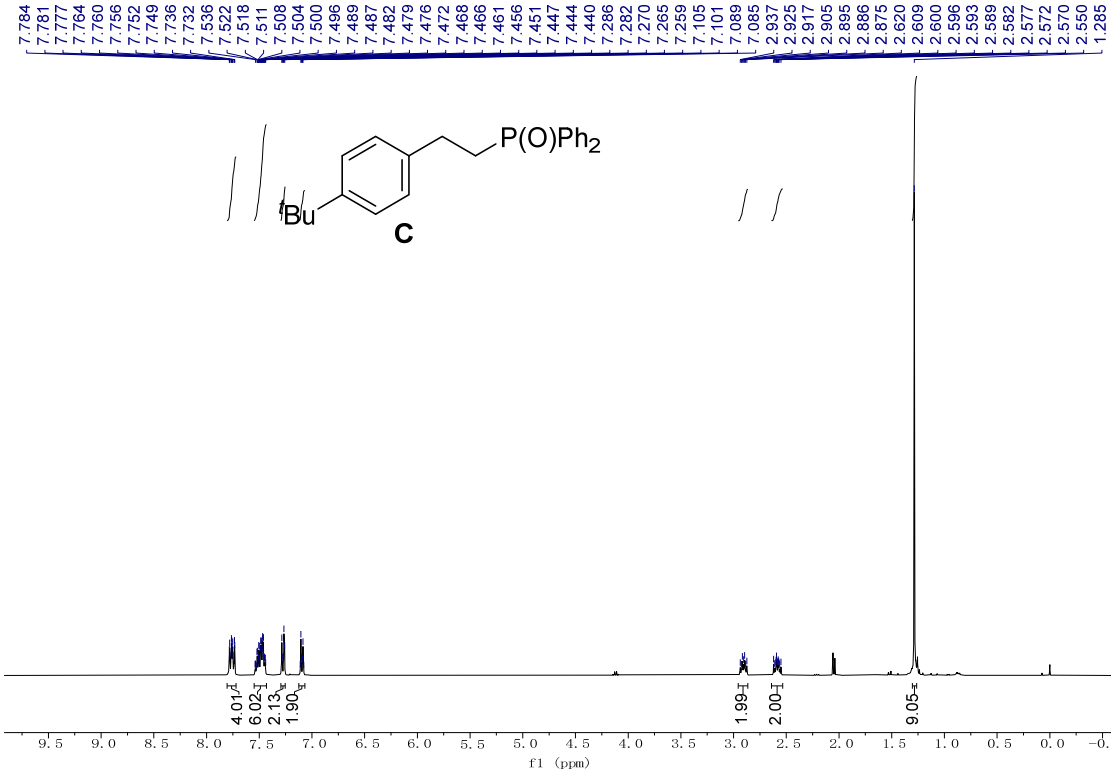
^{1}H NMR, 600 MHz, $CDCl_3$



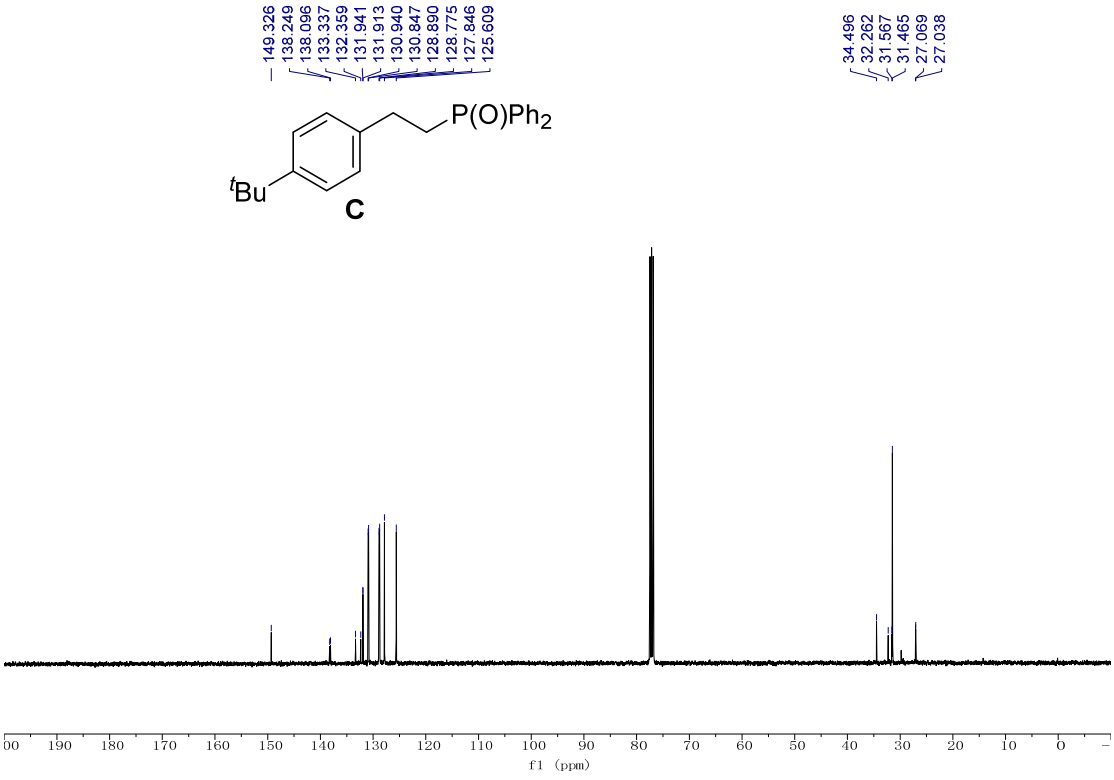
^{13}C NMR, 150 MHz, $CDCl_3$



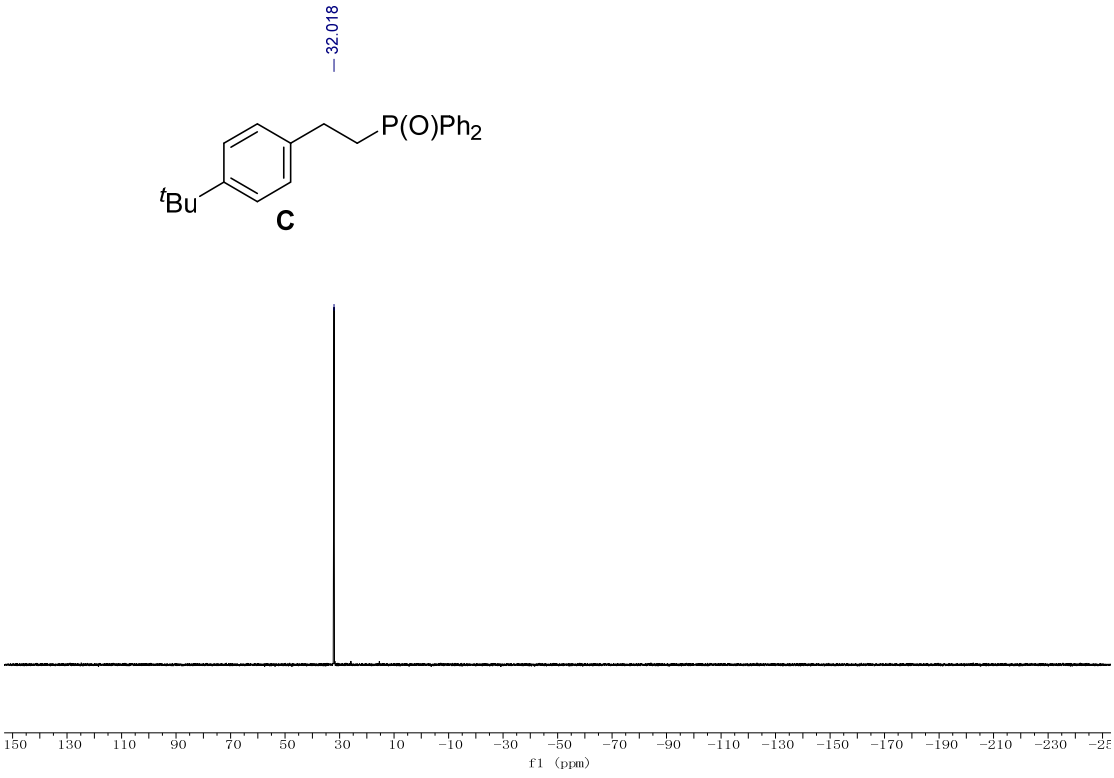
^{1}H NMR, 400 MHz, $CDCl_3$



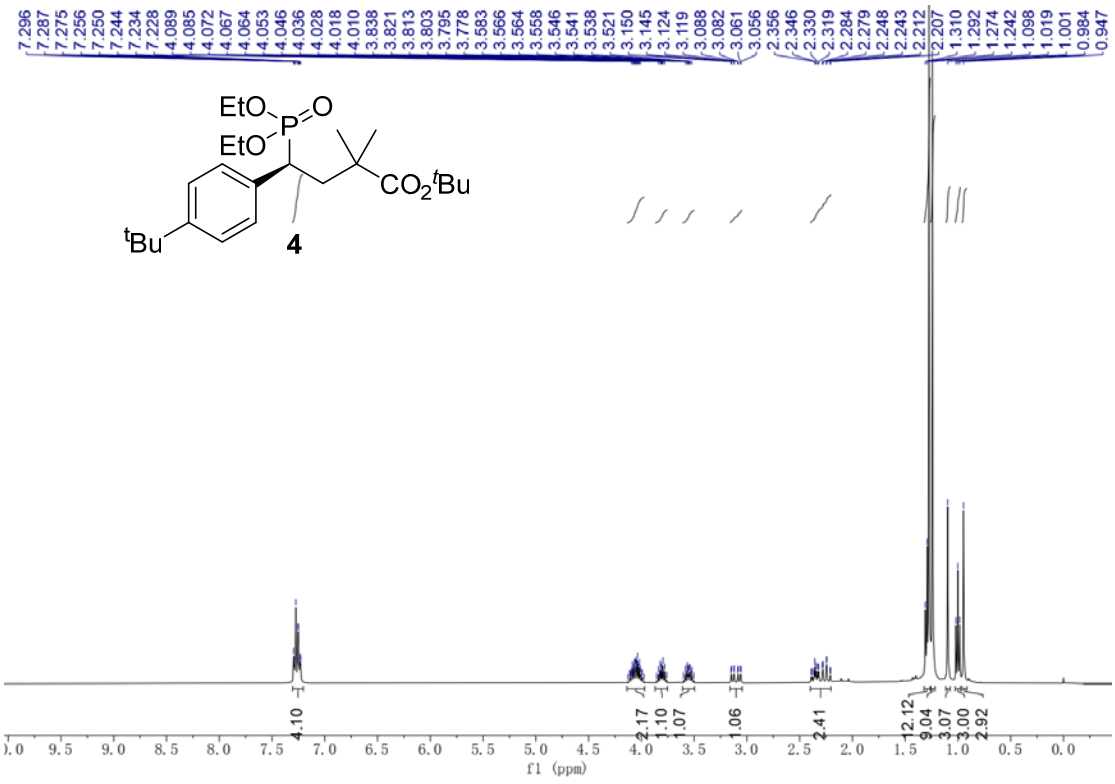
^{13}C NMR, 100 MHz, $CDCl_3$



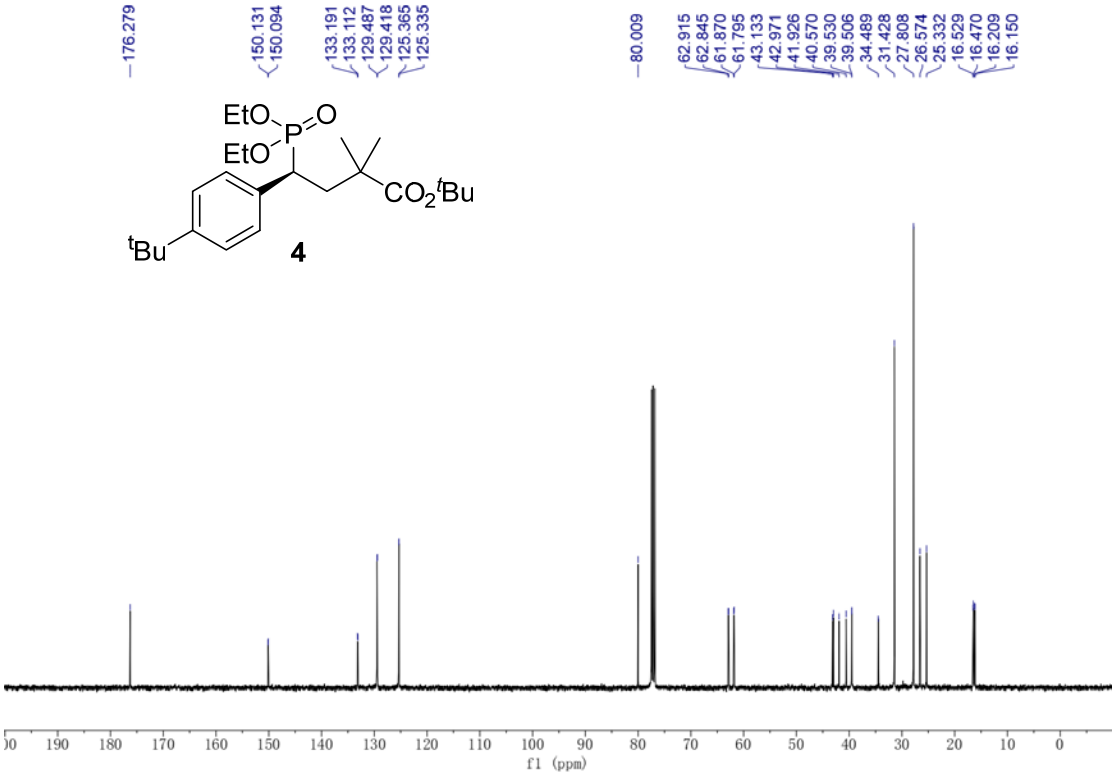
^{31}P NMR, 162 MHz, $CDCl_3$



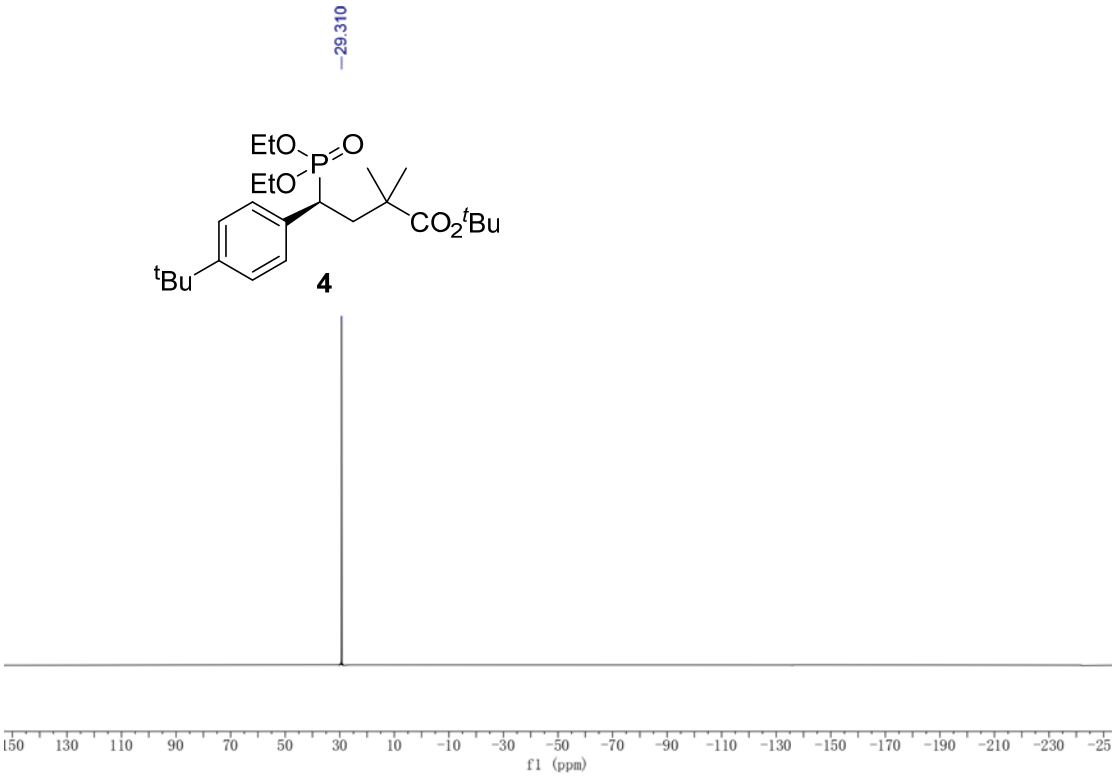
^{1}H NMR, 400 MHz, $CDCl_3$



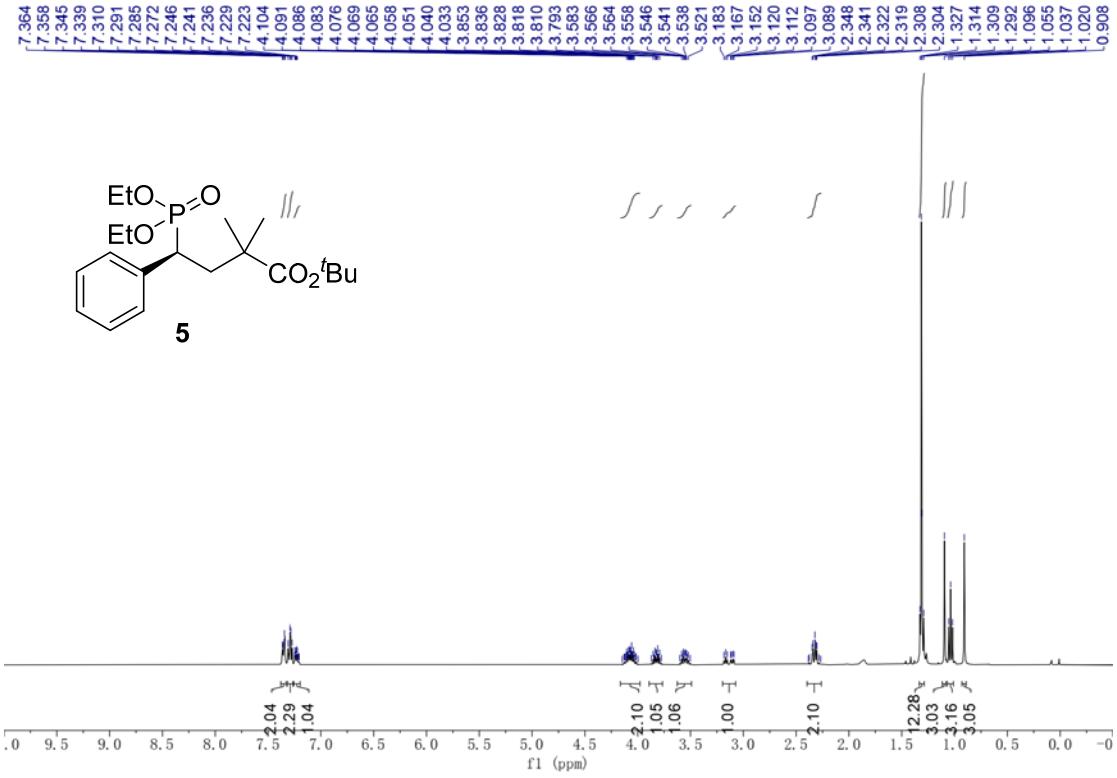
^{13}C NMR, 100 MHz, $CDCl_3$



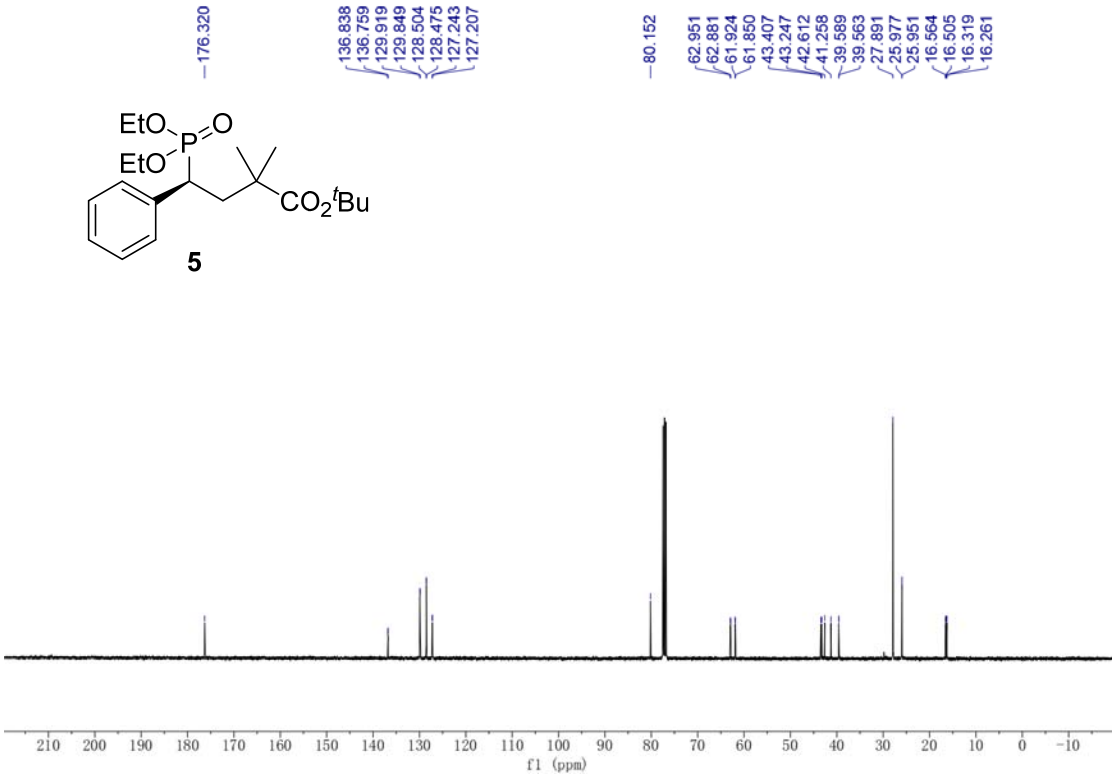
^{31}P NMR, 162 MHz, $CDCl_3$



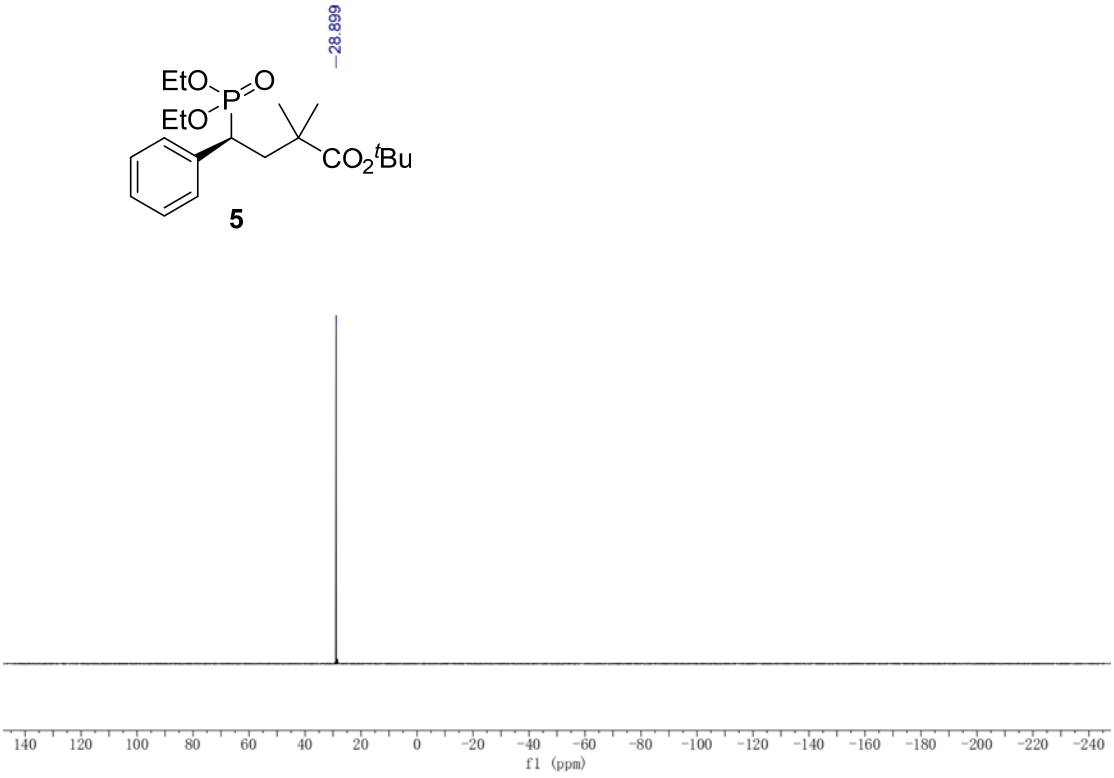
^{1}H NMR, 400 MHz, $CDCl_3$



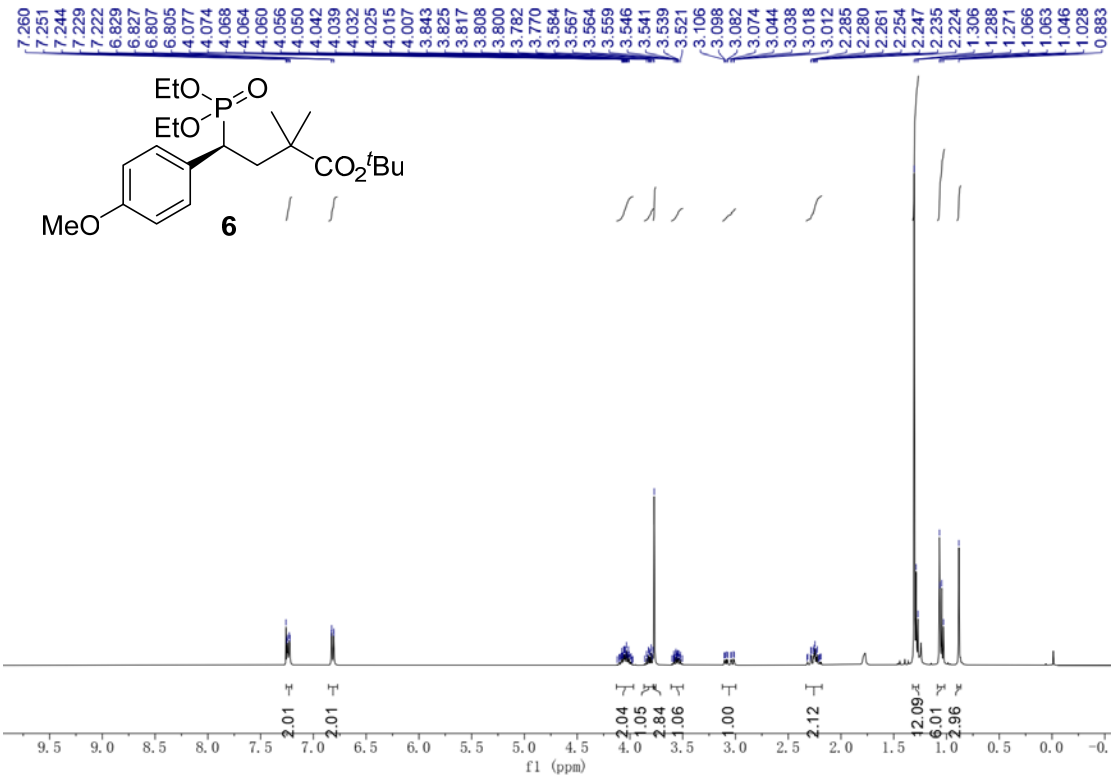
^{13}C NMR, 100 MHz, $CDCl_3$



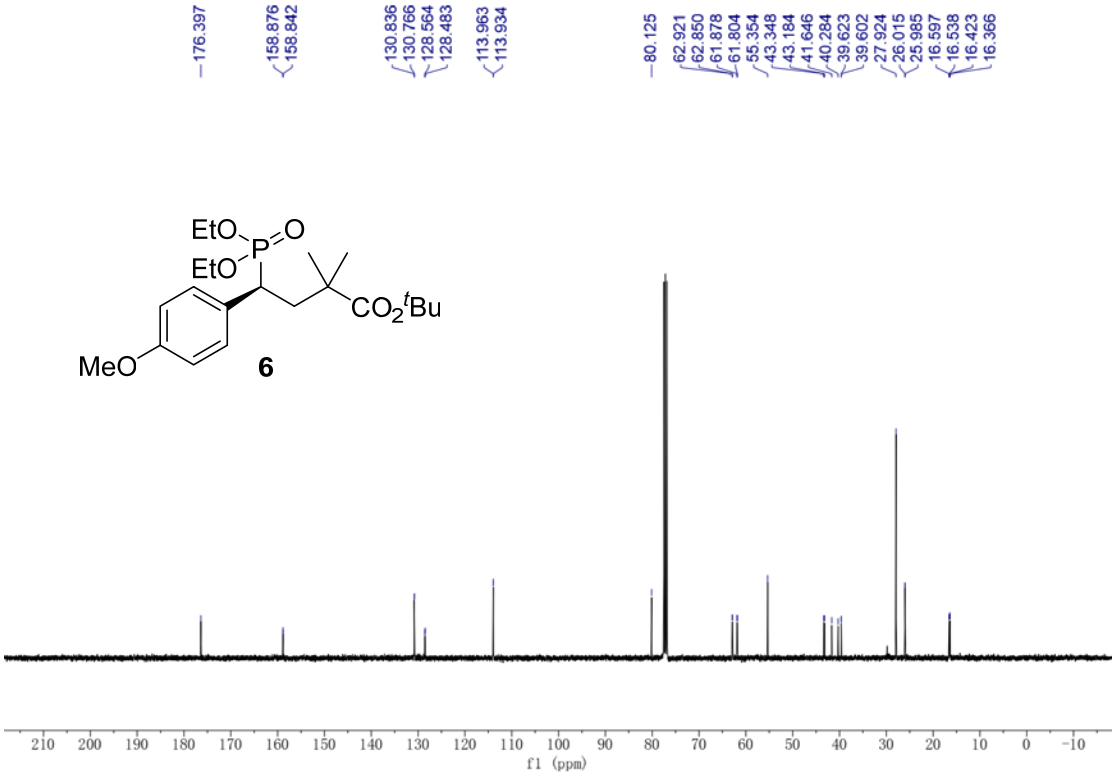
^{31}P NMR, 162 MHz, $CDCl_3$



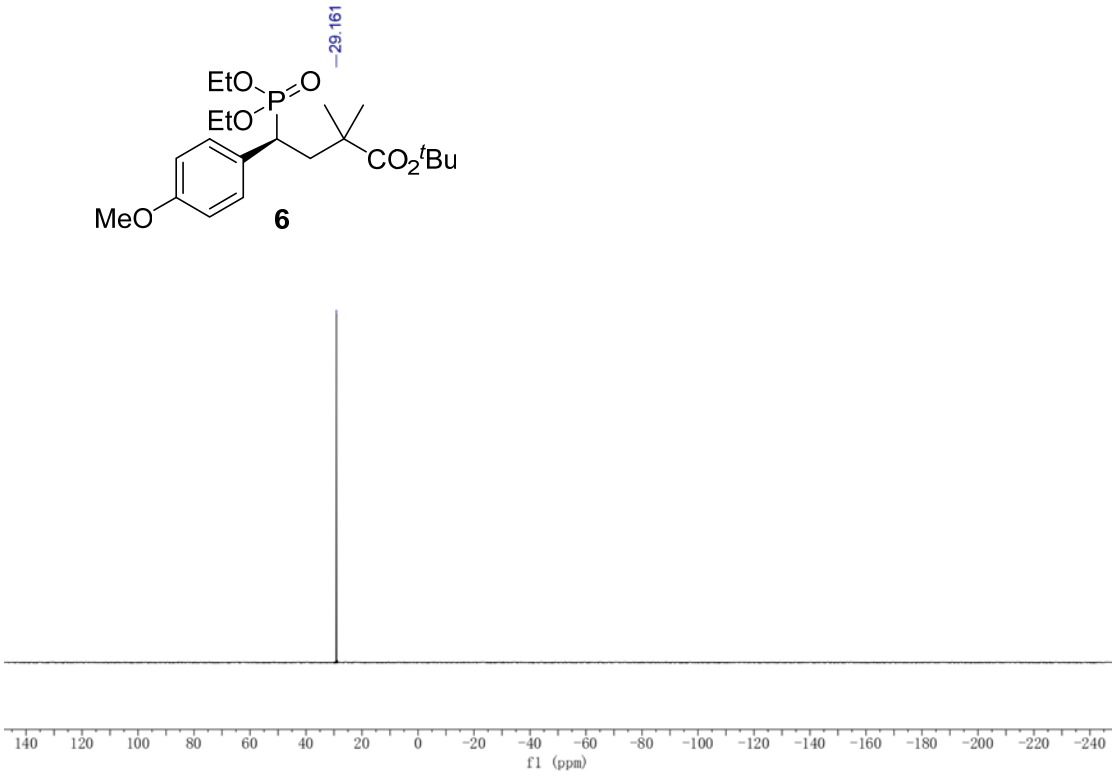
^{1}H NMR, 400 MHz, $CDCl_3$



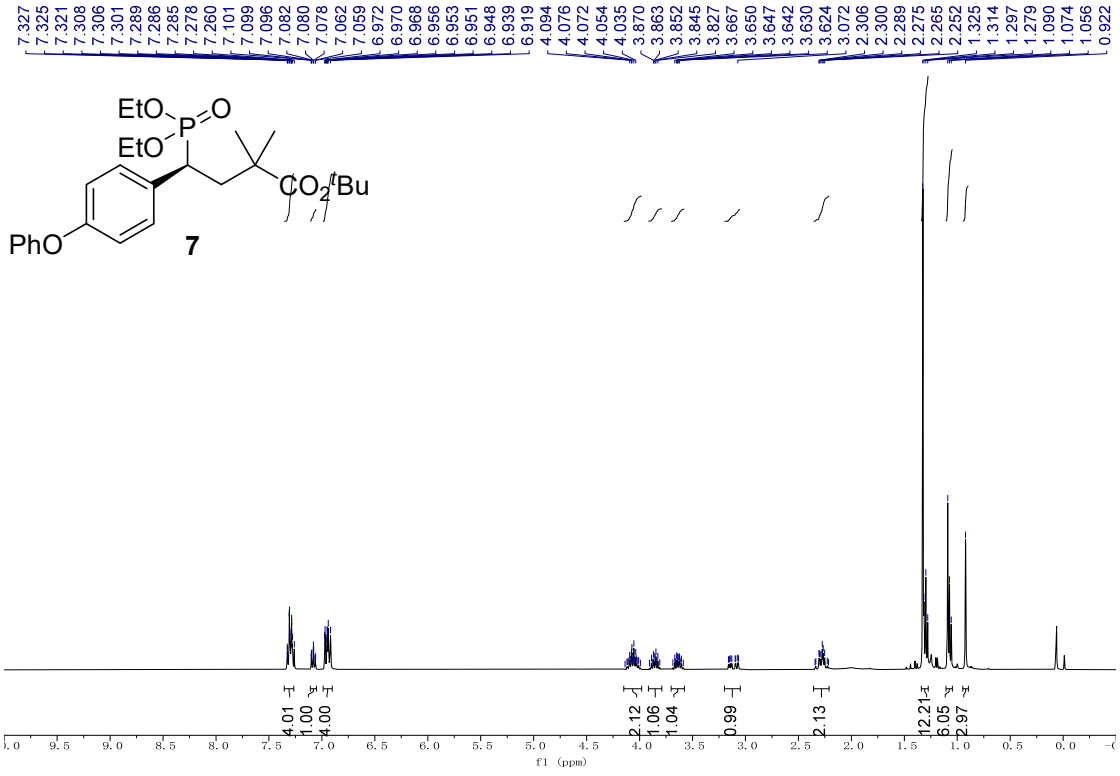
^{13}C NMR, 100 MHz, $CDCl_3$



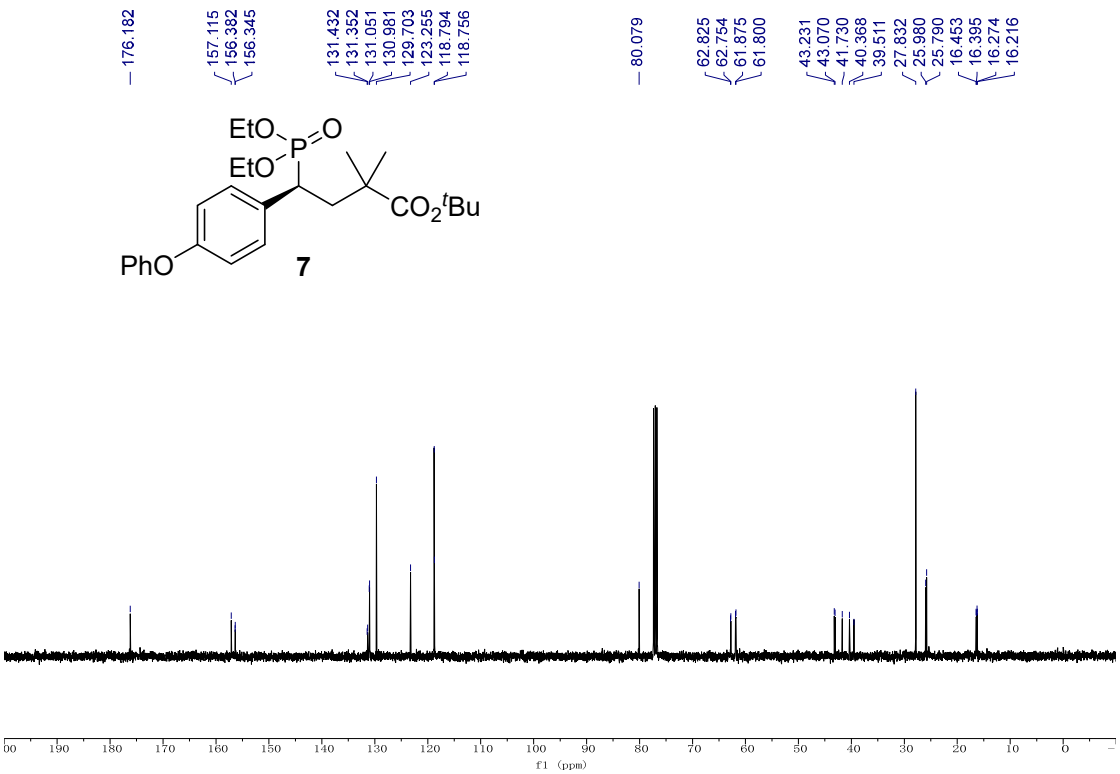
^{31}P NMR, 162 MHz, $CDCl_3$



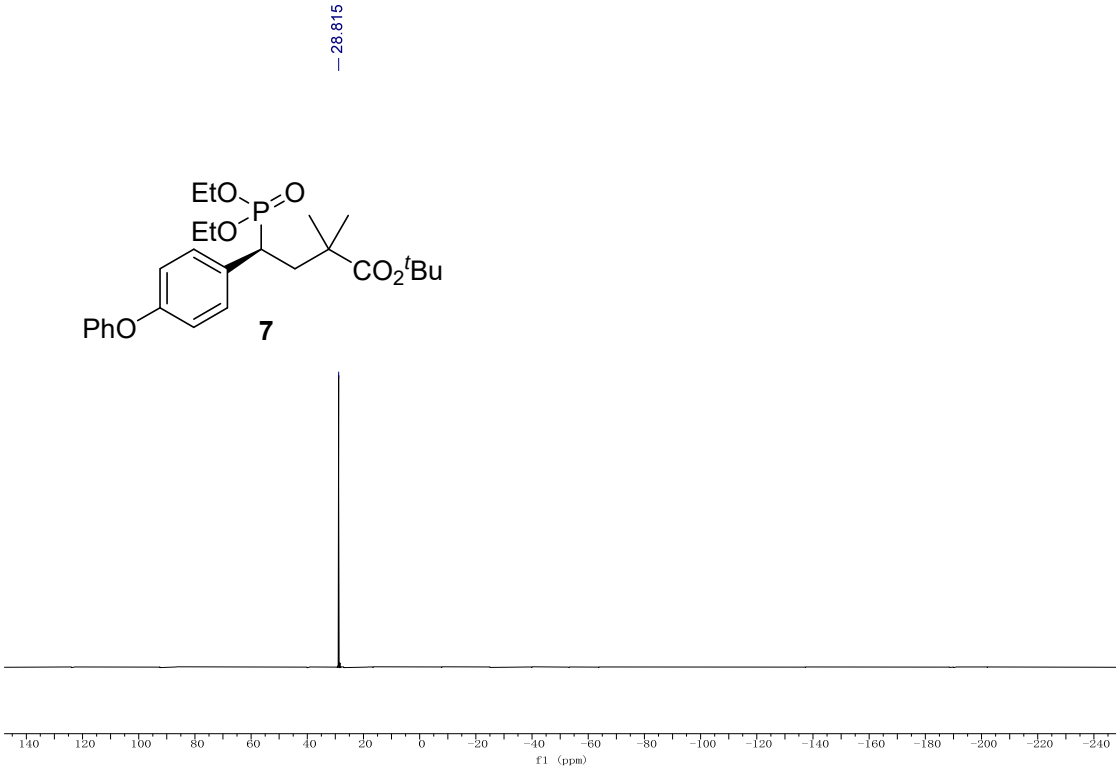
^{1}H NMR, 400 MHz, $CDCl_3$



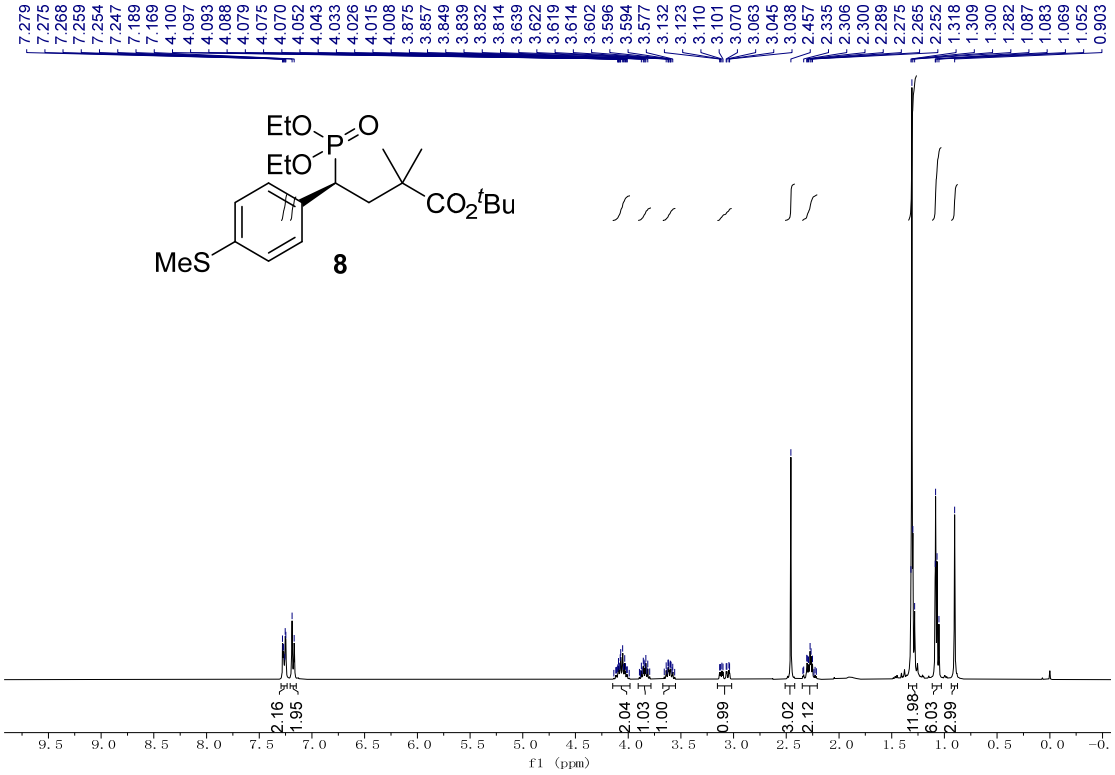
^{13}C NMR, 100 MHz, $CDCl_3$



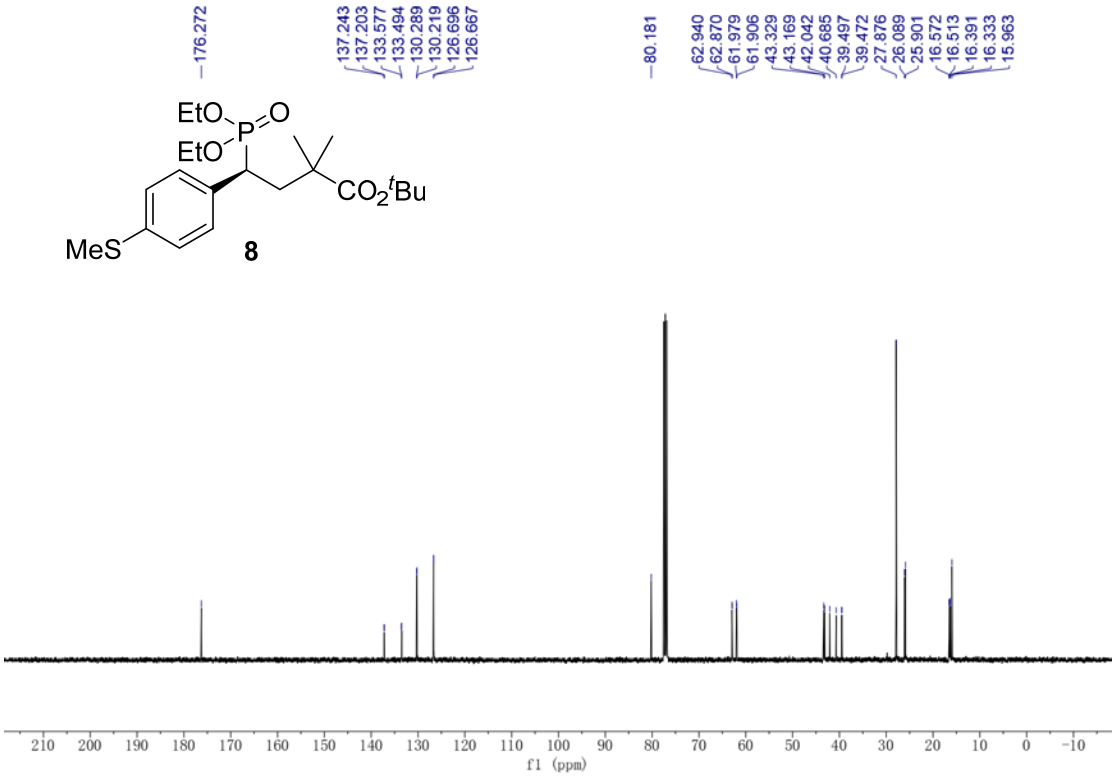
^{31}P NMR, 162 MHz, $CDCl_3$



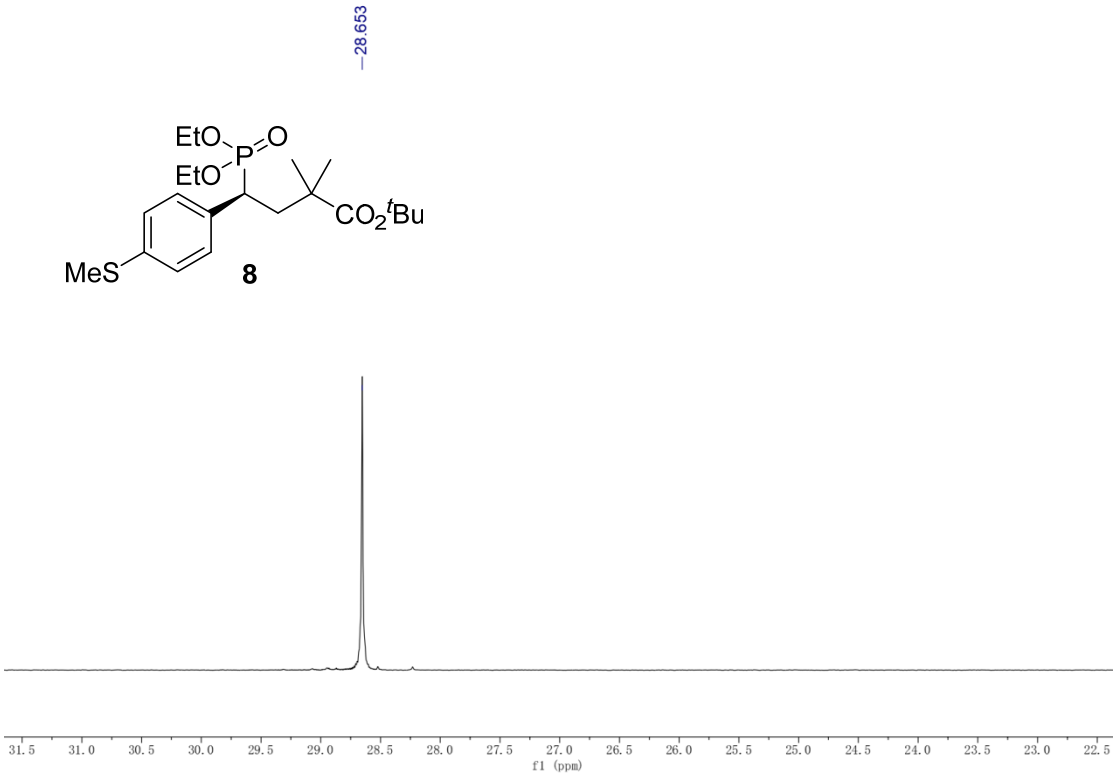
^{1}H NMR, 400 MHz, $CDCl_3$



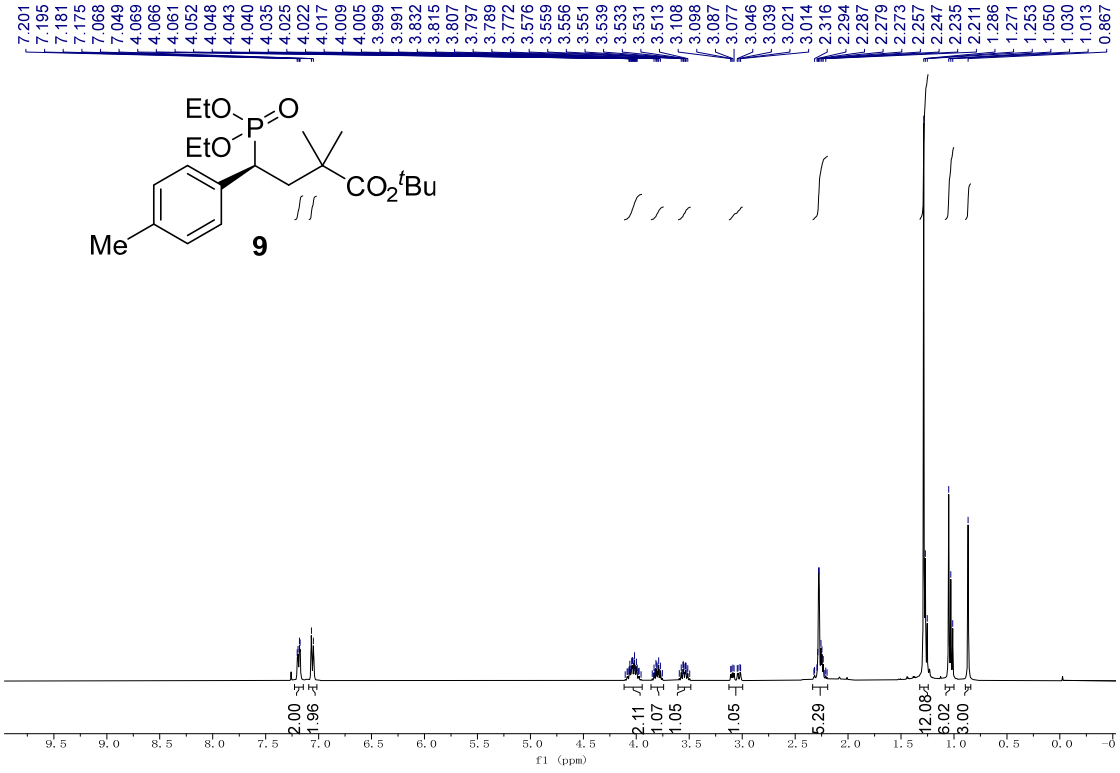
^{13}C NMR, 100 MHz, $CDCl_3$



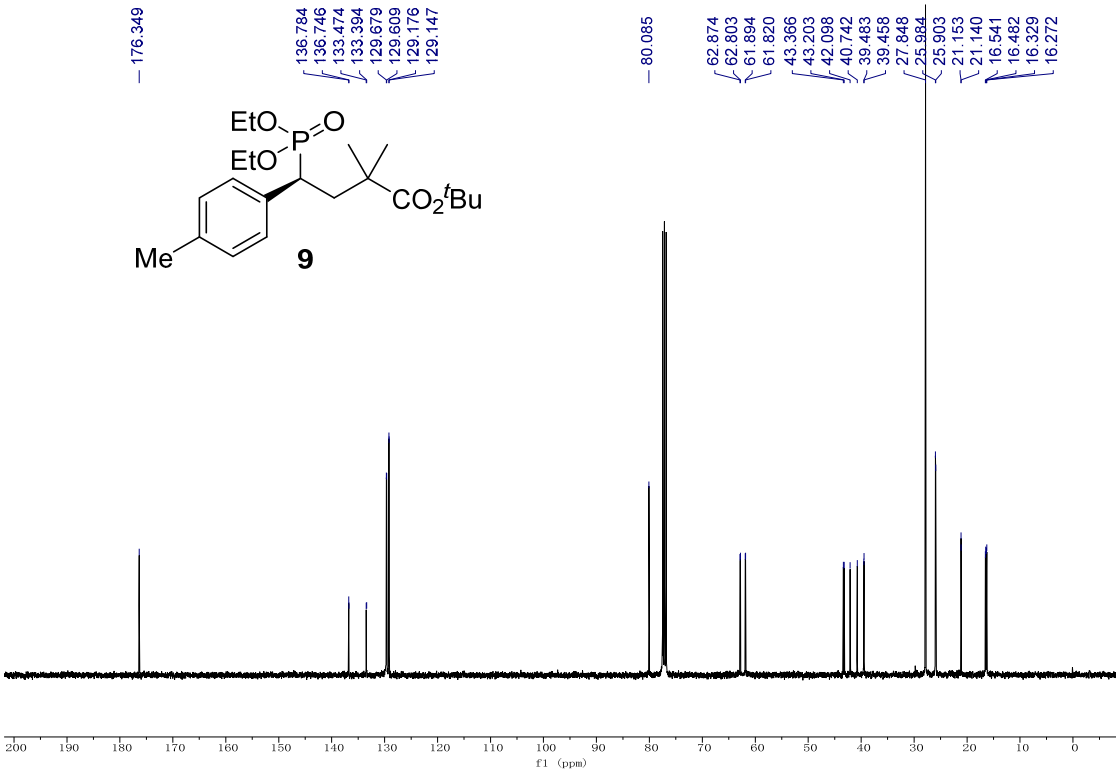
^{31}P NMR, 162 MHz, $CDCl_3$



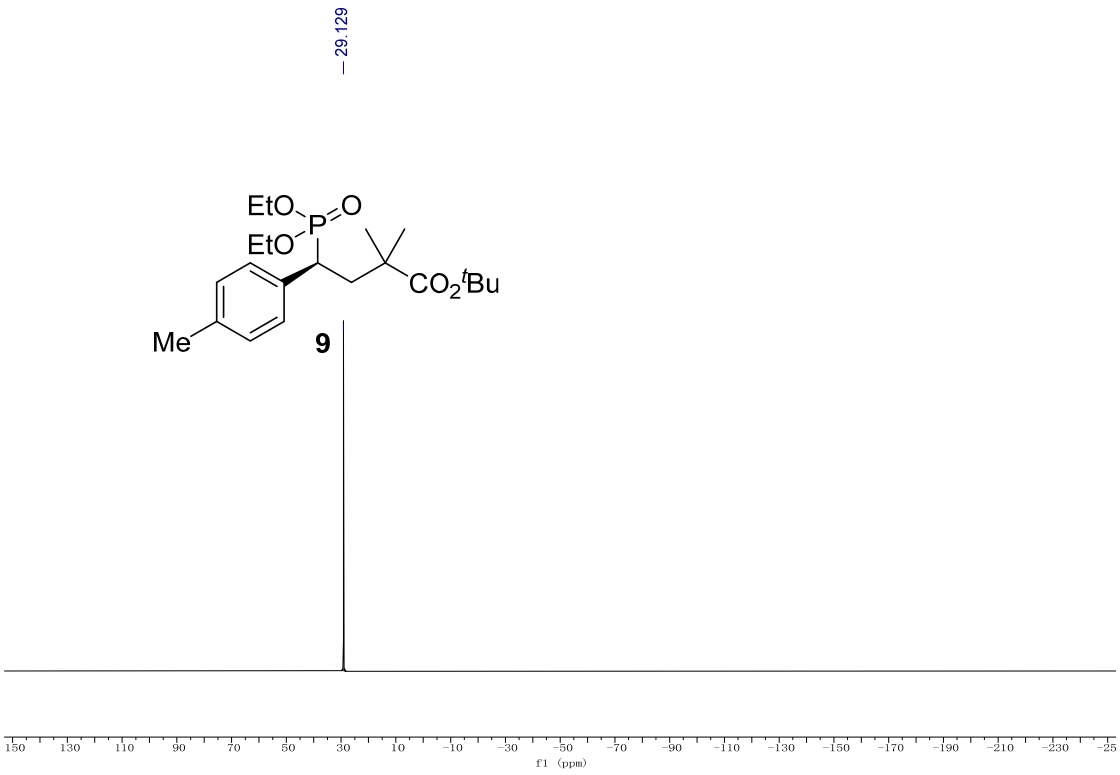
^{1}H NMR, 400 MHz, $CDCl_3$



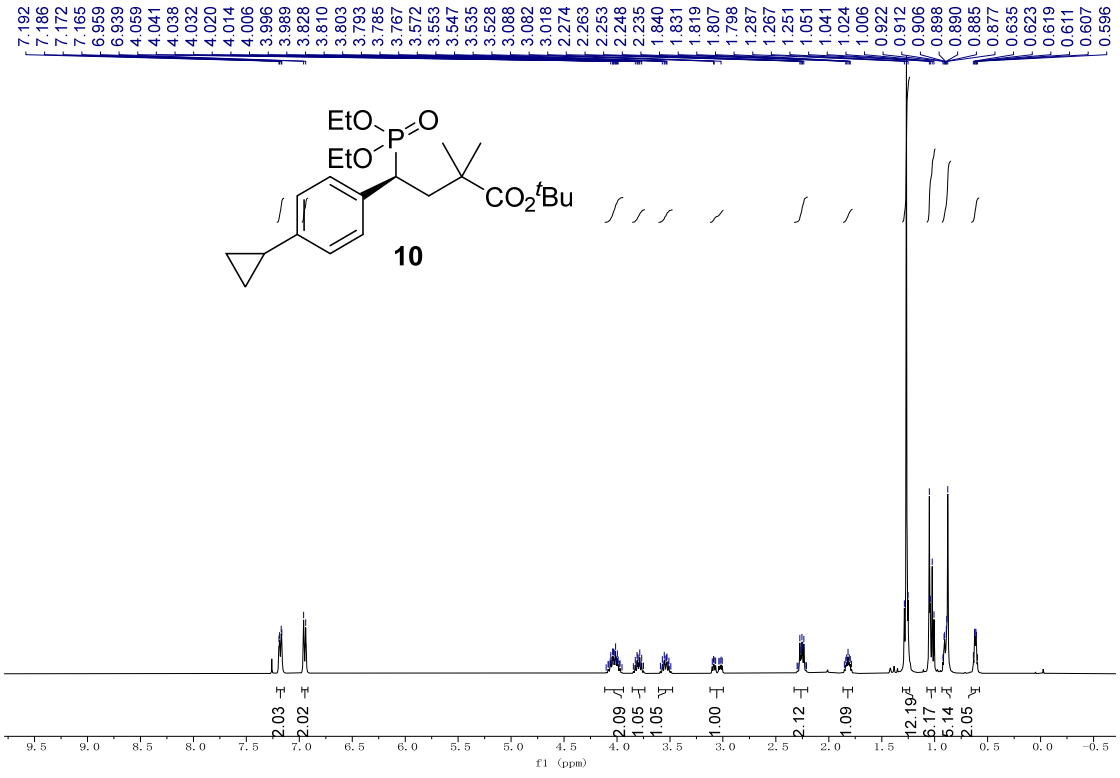
^{13}C NMR, 100 MHz, $CDCl_3$



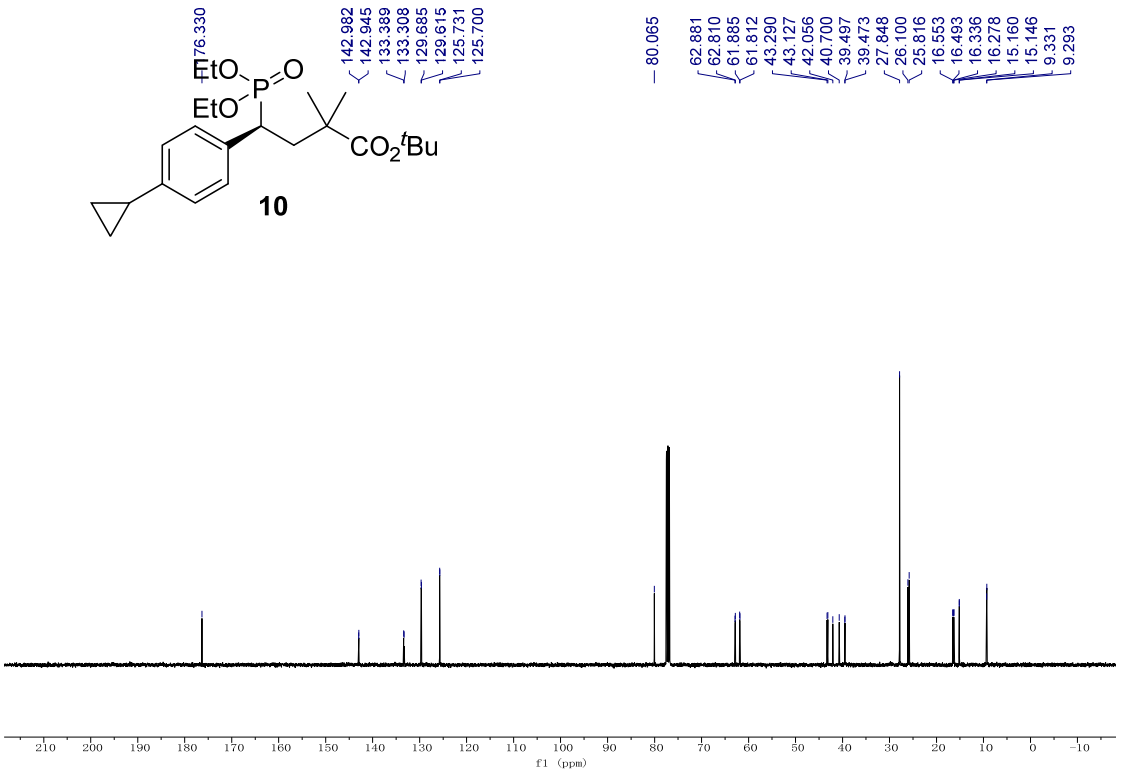
^{31}P NMR, 162 MHz, $CDCl_3$



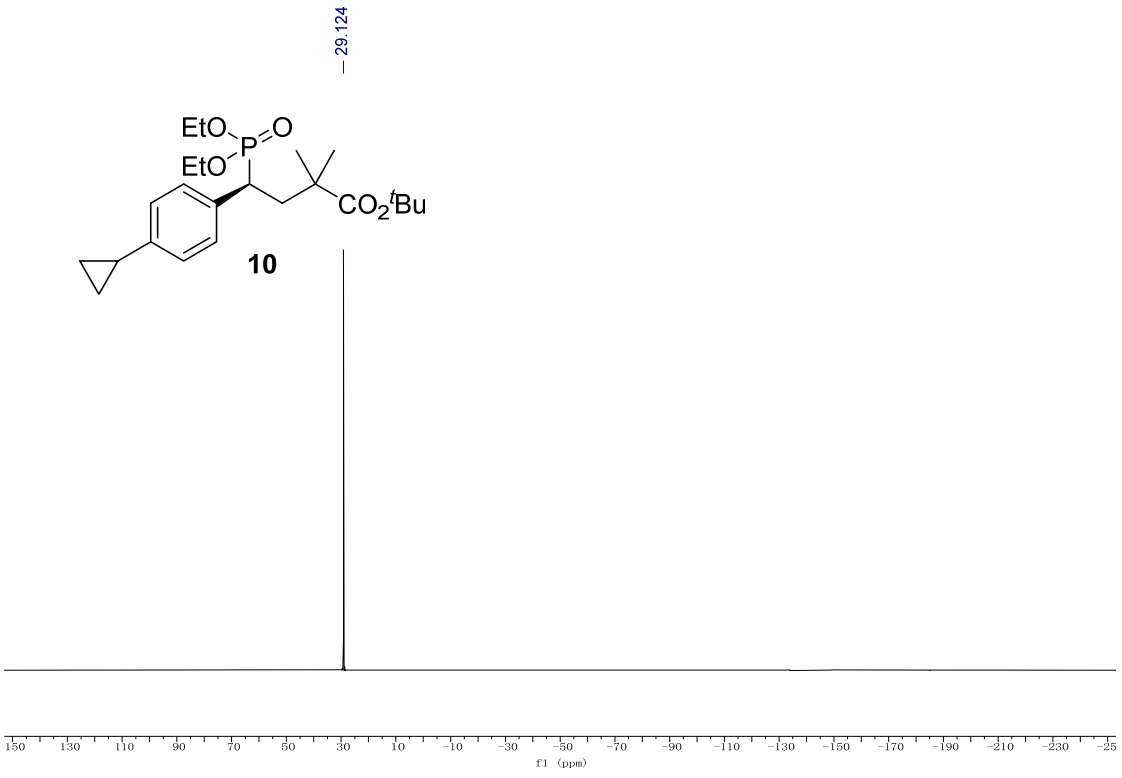
^{1}H NMR, 400 MHz, $CDCl_3$



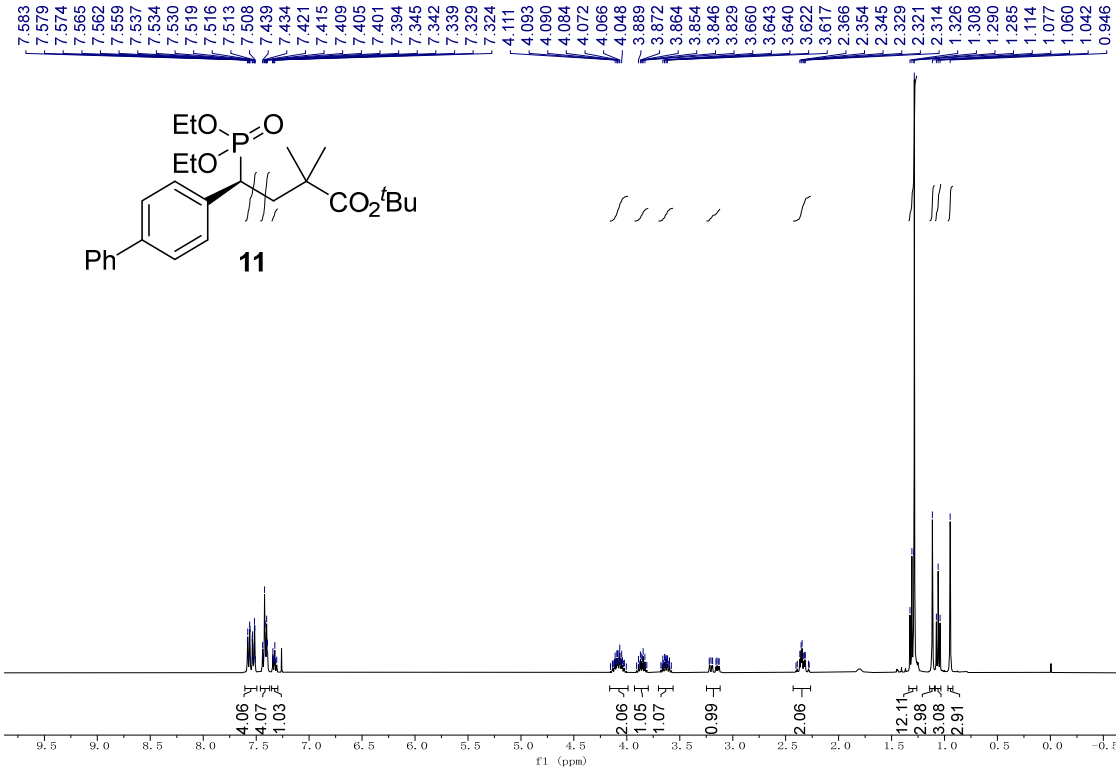
^{13}C NMR, 100 MHz, $CDCl_3$



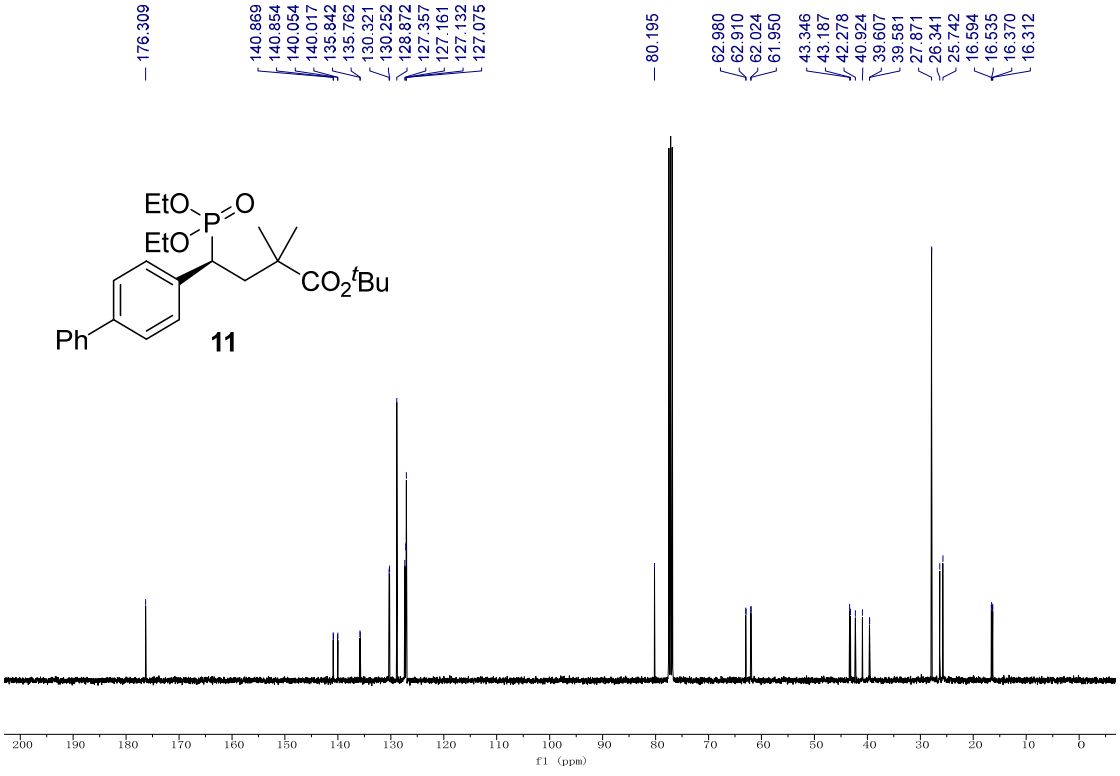
^{31}P NMR, 162 MHz, $CDCl_3$



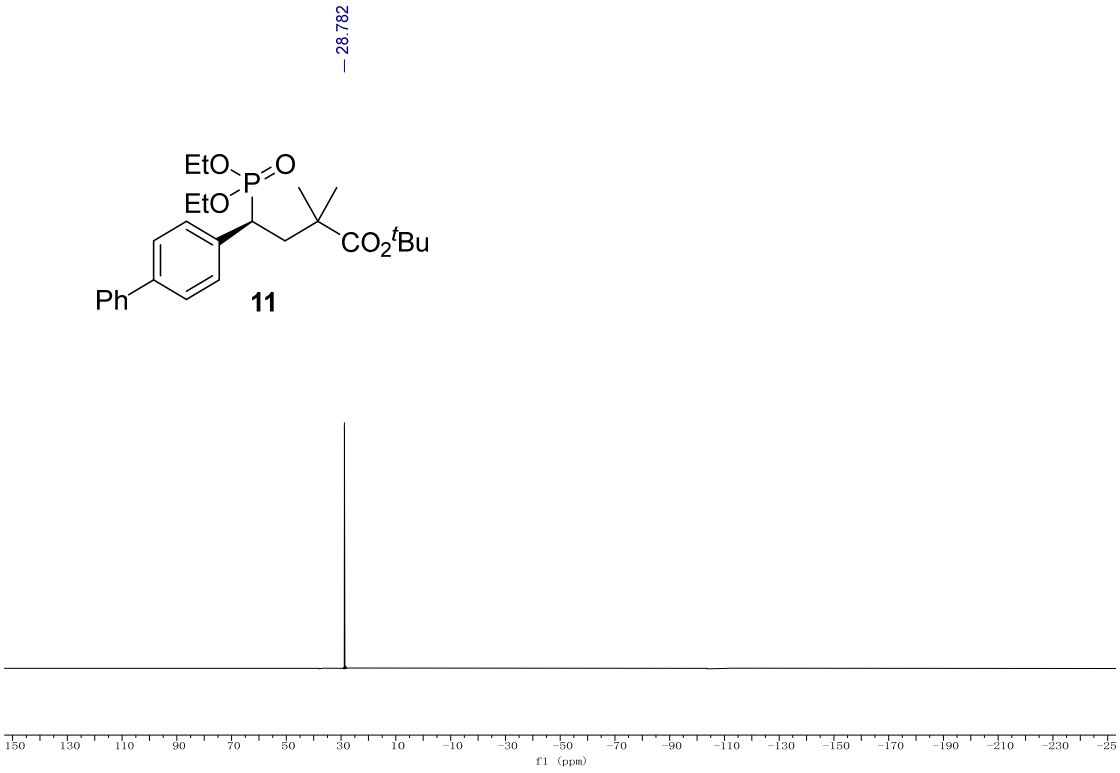
^{1}H NMR, 400 MHz, $CDCl_3$



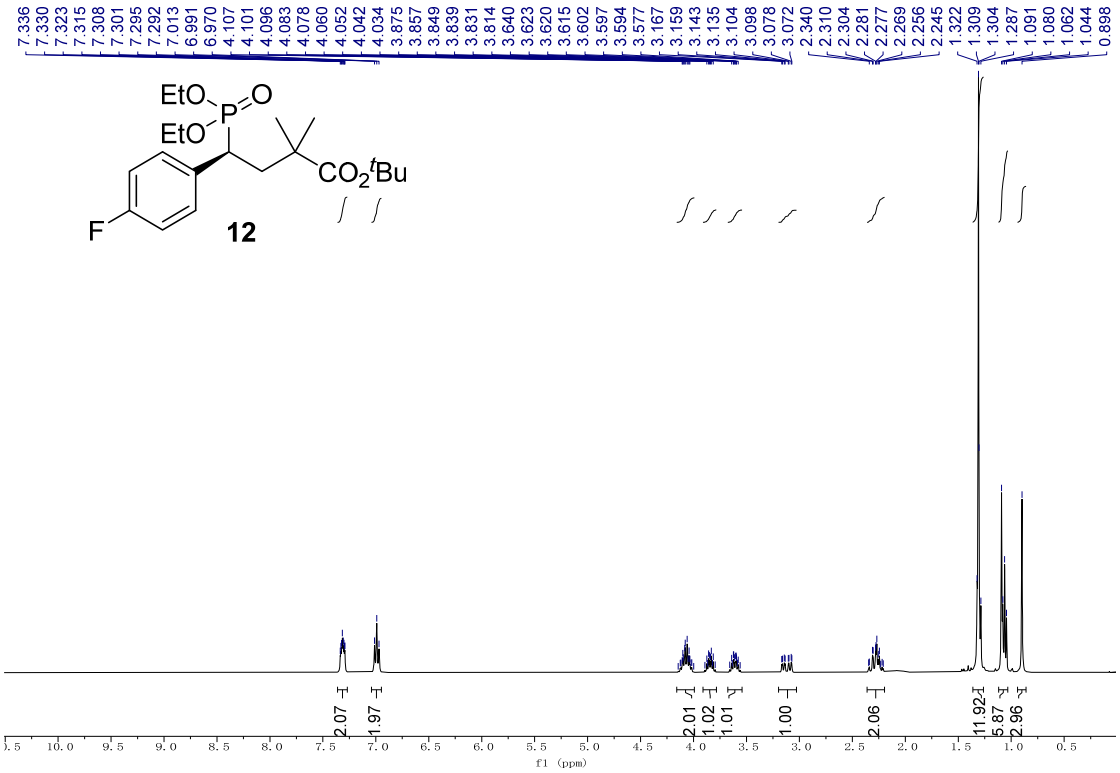
^{13}C NMR, 100 MHz, $CDCl_3$



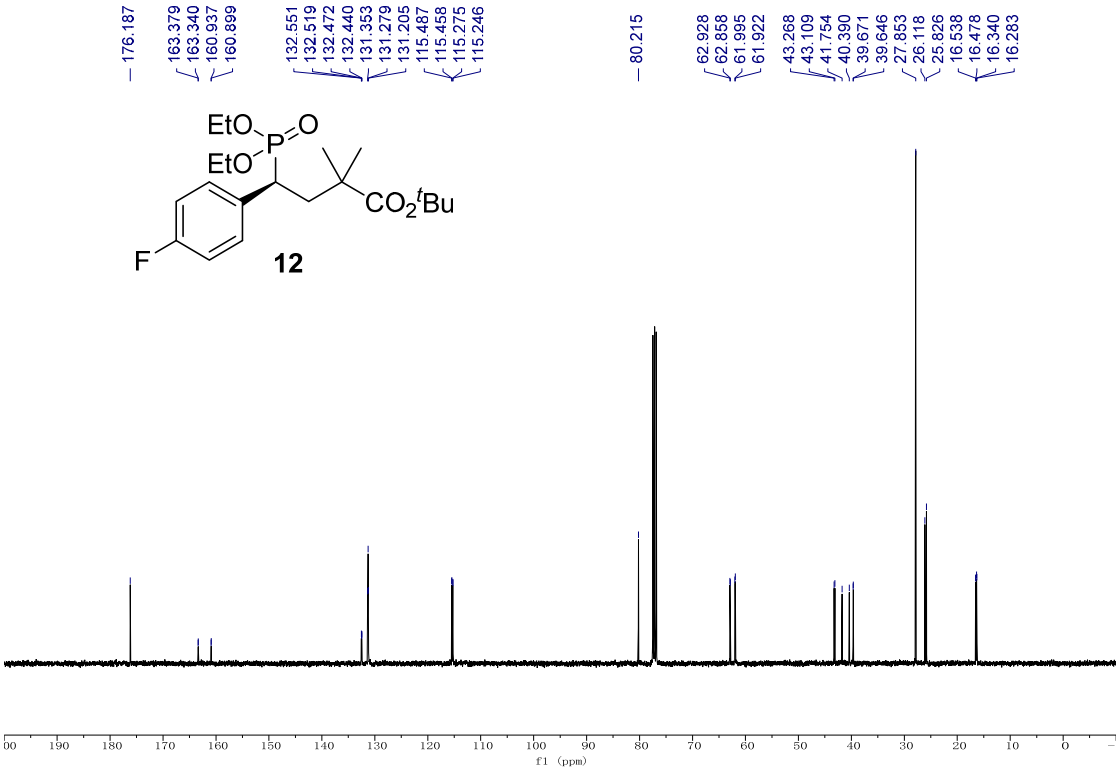
^{31}P NMR, 162 MHz, $CDCl_3$



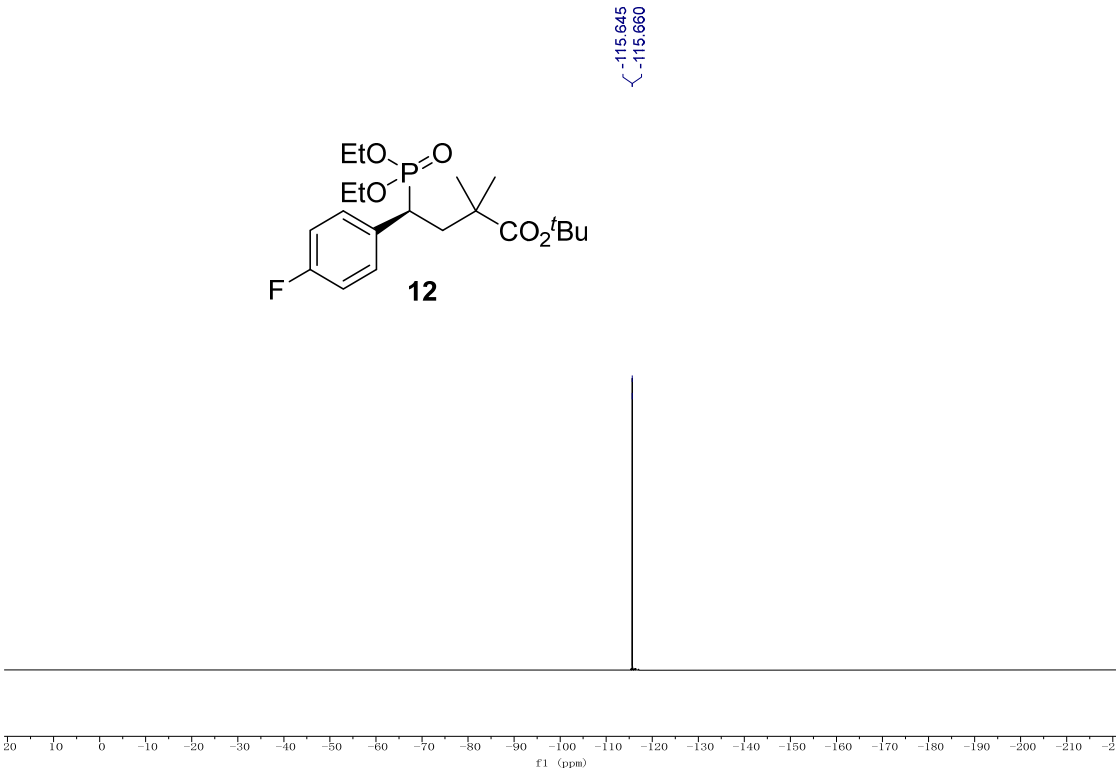
^{1}H NMR, 400 MHz, $CDCl_3$



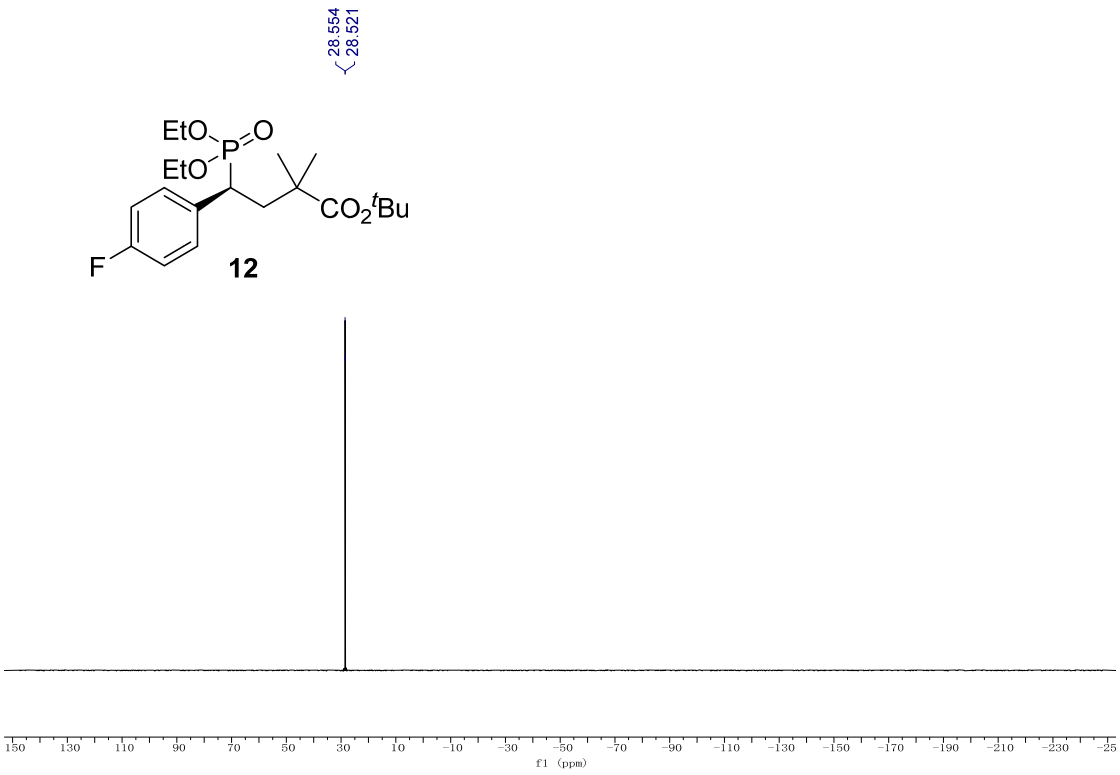
^{13}C NMR, 100 MHz, $CDCl_3$



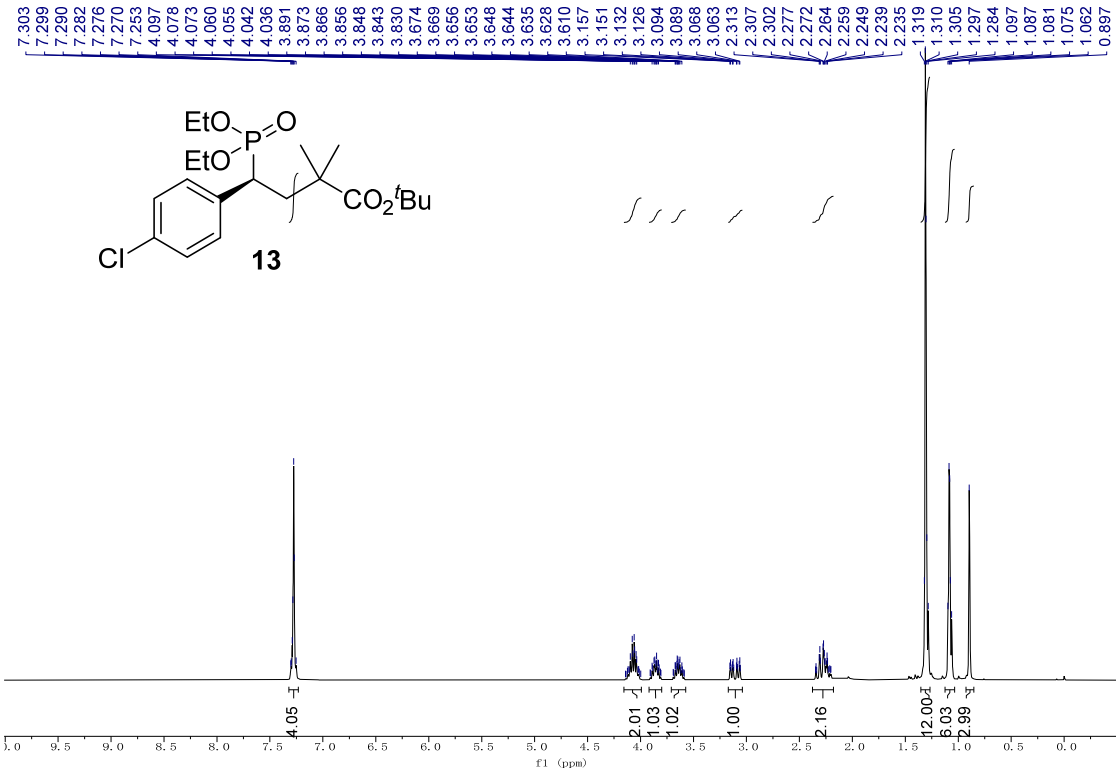
^{19}F NMR, 376 MHz, $CDCl_3$



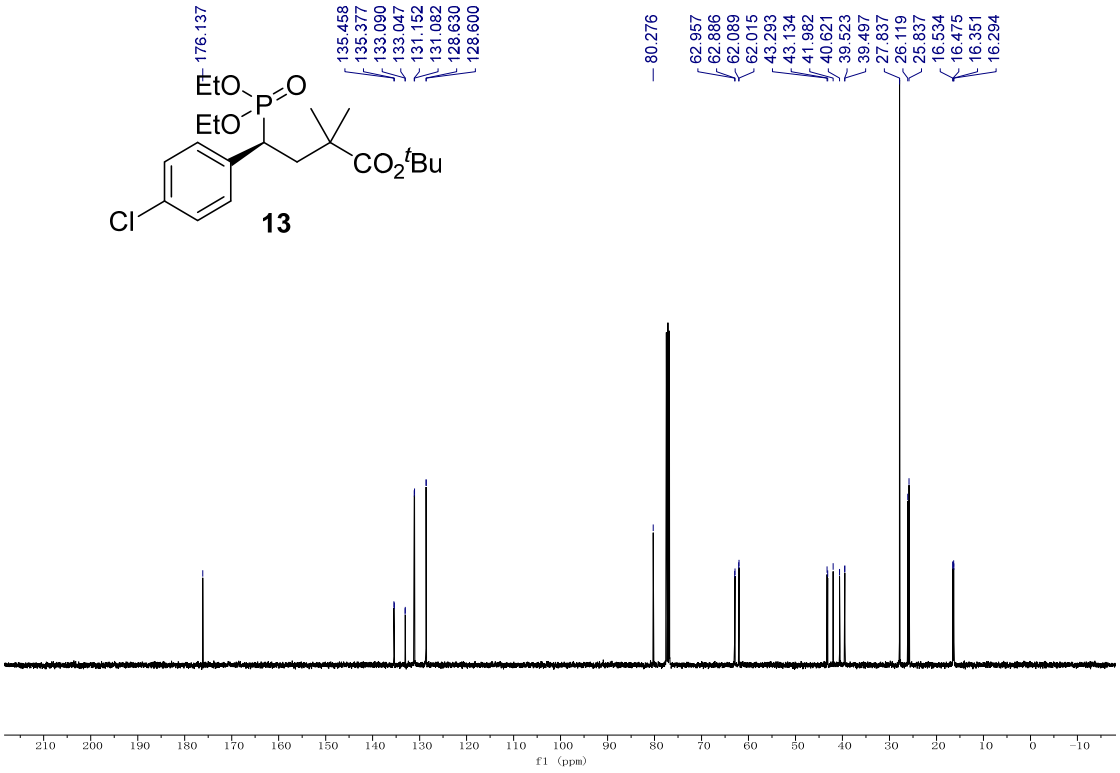
^{31}P NMR, 162 MHz, $CDCl_3$



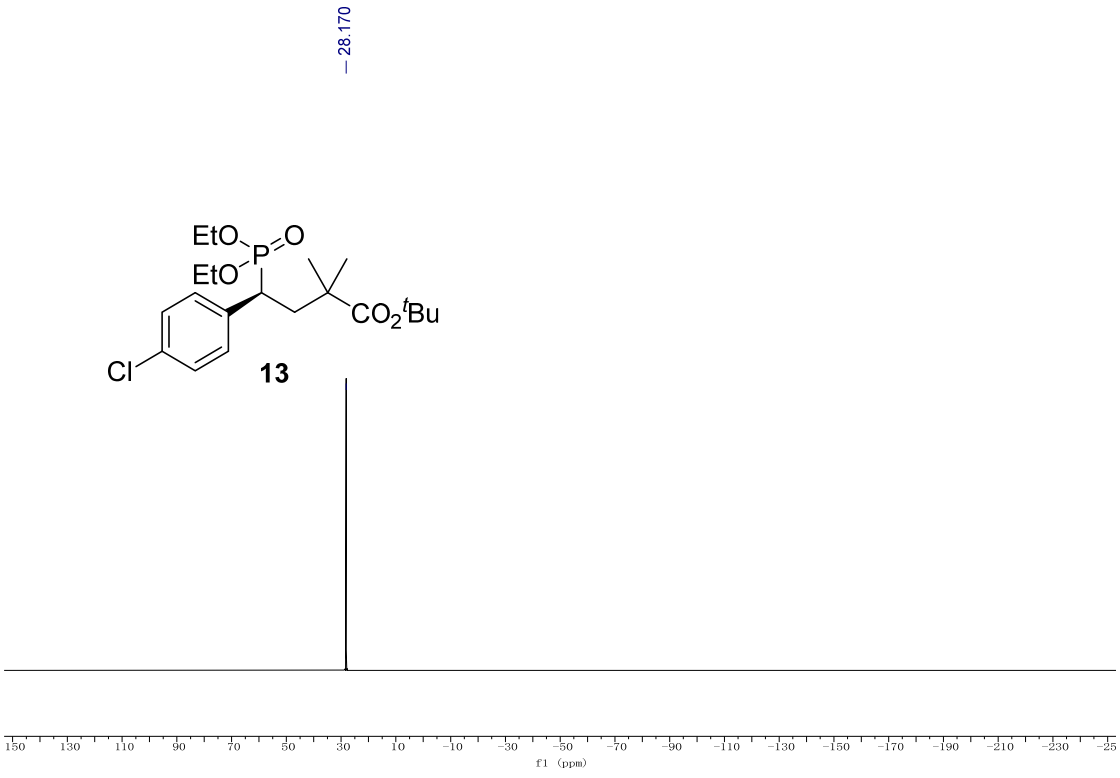
^{1}H NMR, 400 MHz, $CDCl_3$



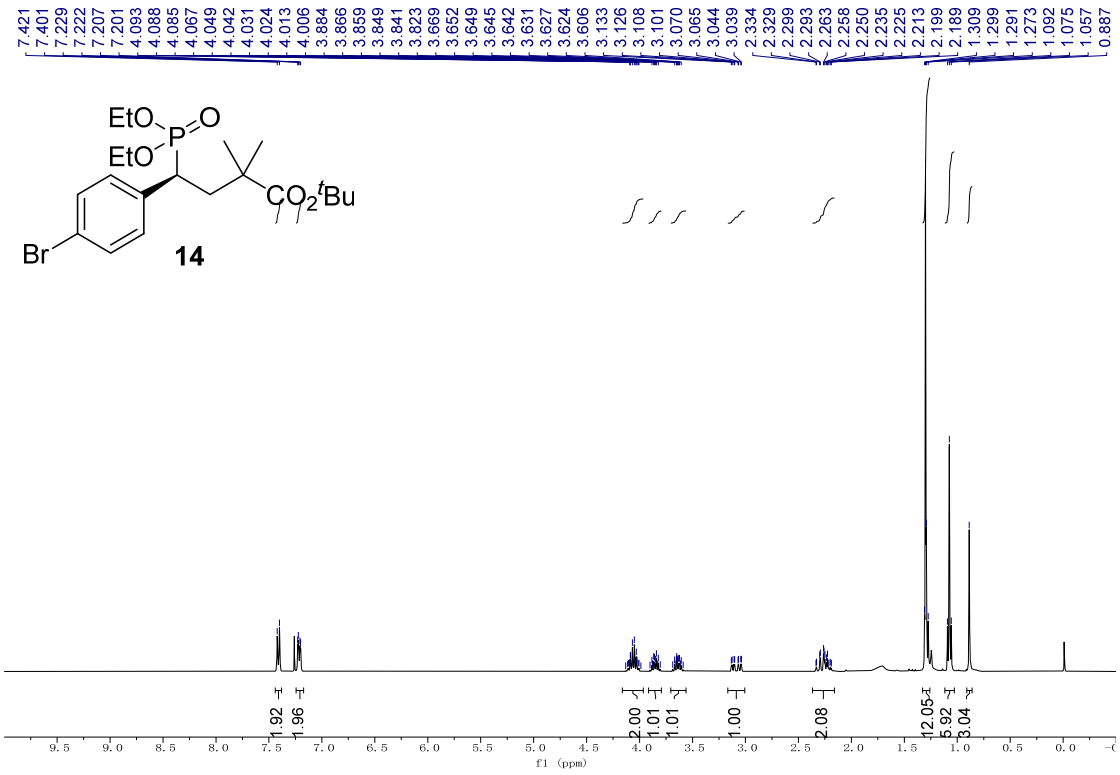
^{13}C NMR, 100 MHz, $CDCl_3$



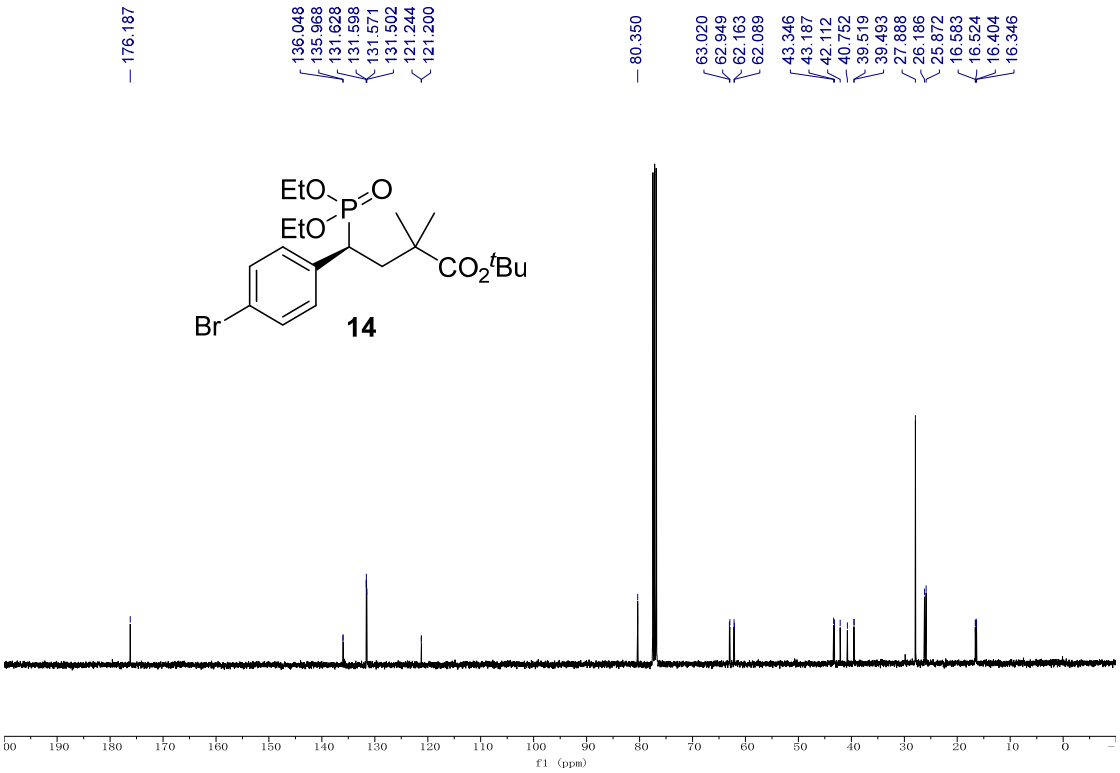
^{31}P NMR, 162 MHz, $CDCl_3$



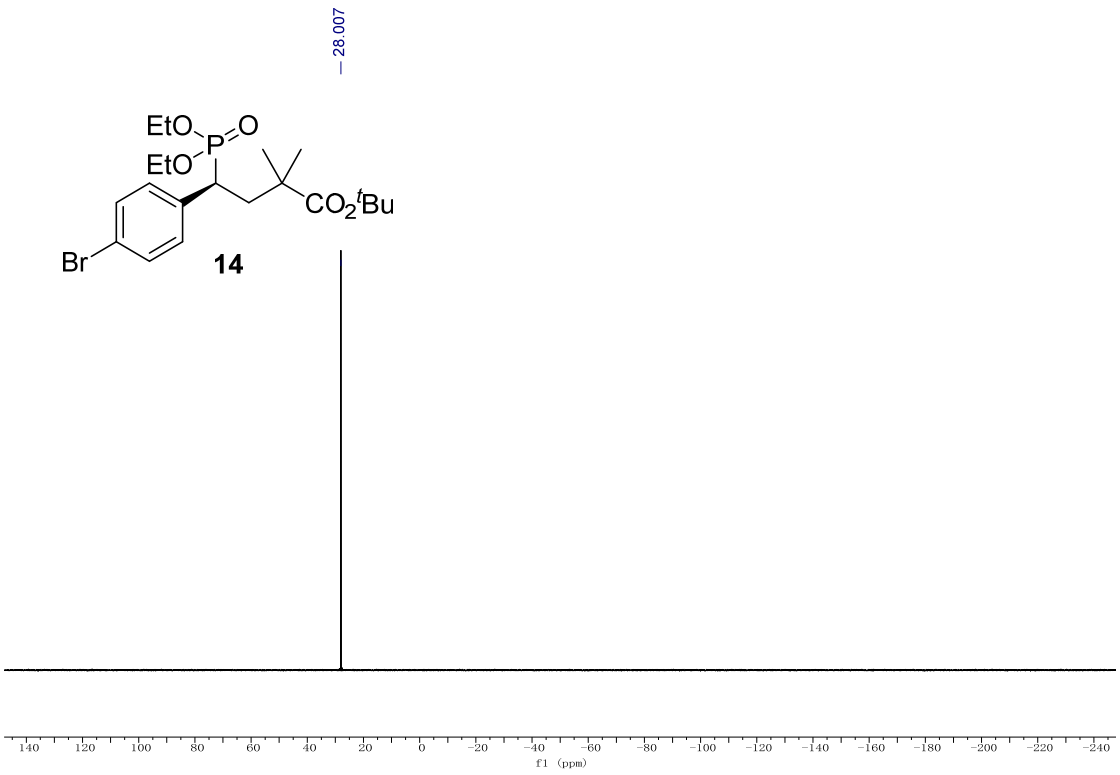
^{1}H NMR, 400 MHz, $CDCl_3$



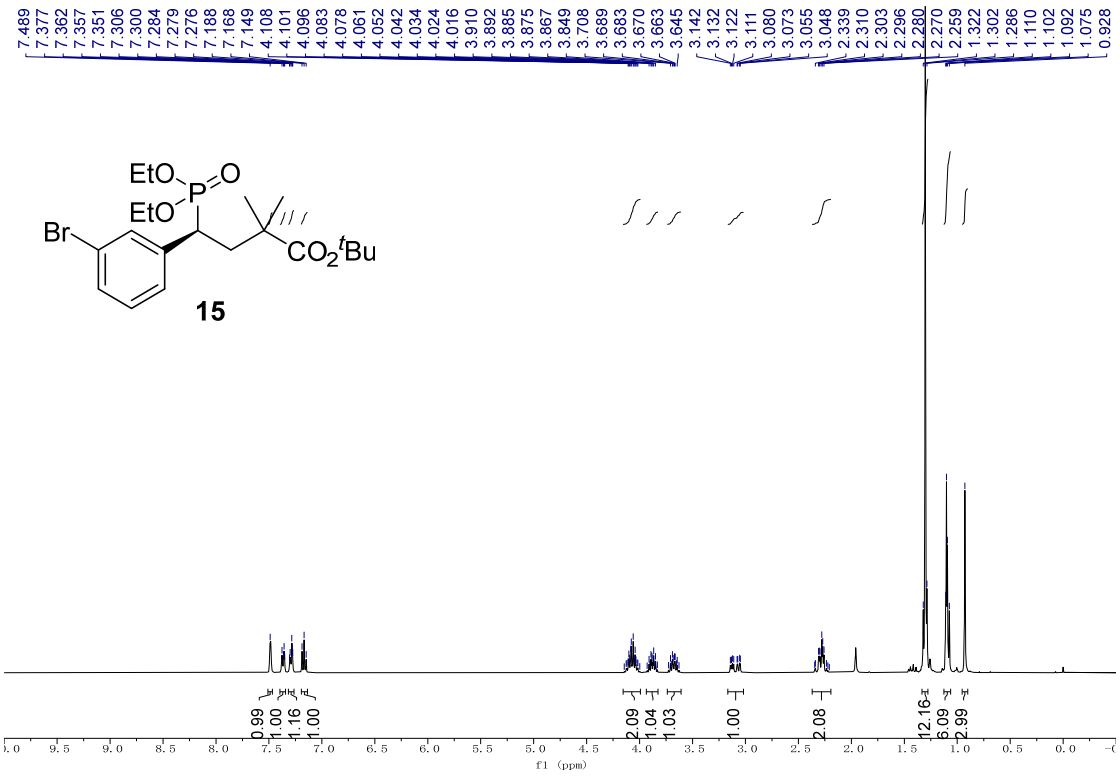
^{13}C NMR, 100 MHz, $CDCl_3$



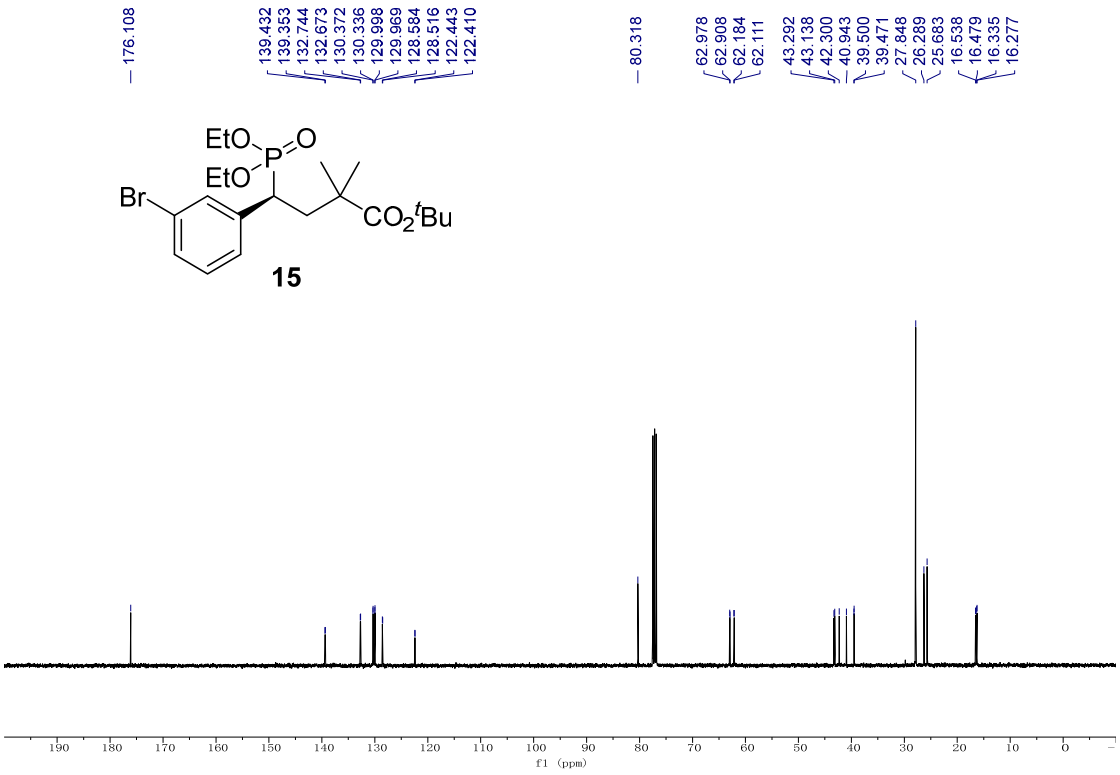
^{31}P NMR, 162 MHz, $CDCl_3$



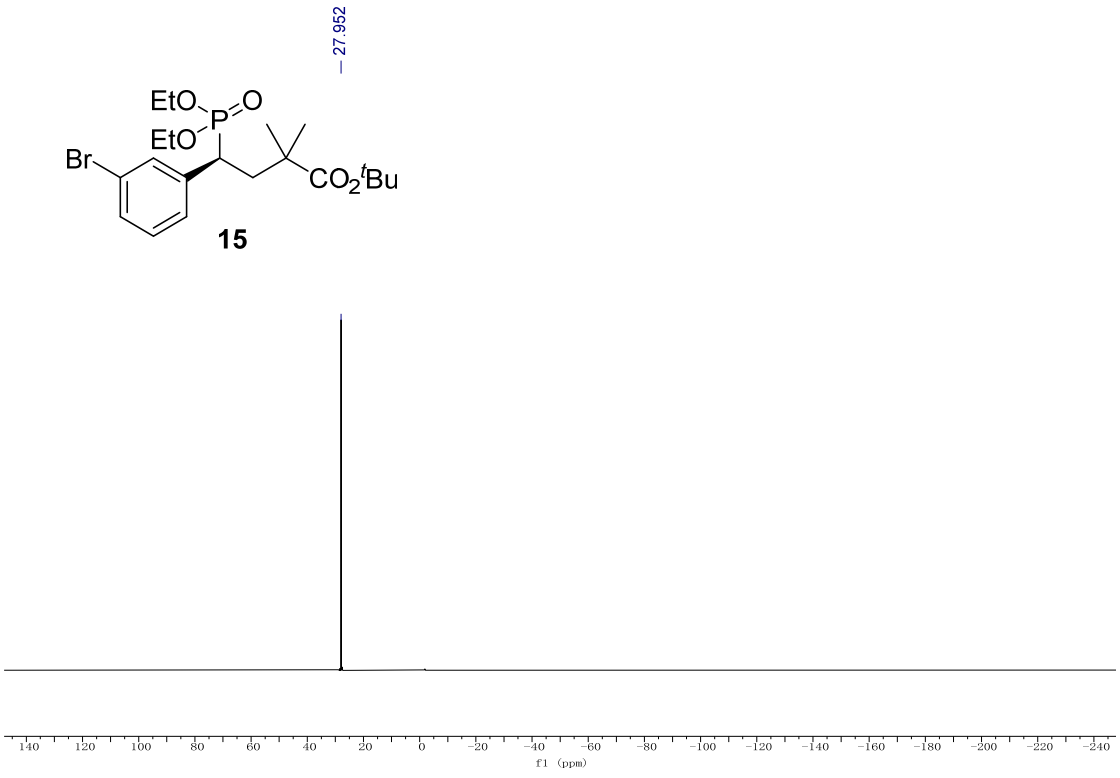
^{1}H NMR, 400 MHz, $CDCl_3$



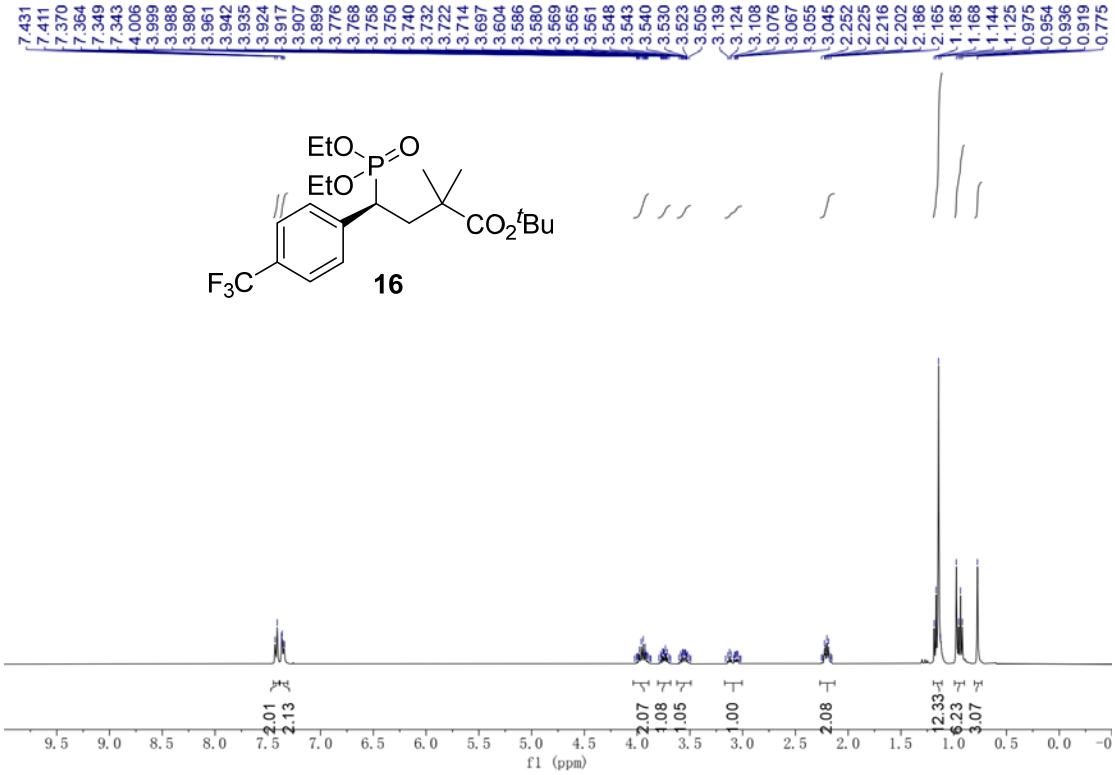
^{13}C NMR, 100 MHz, $CDCl_3$



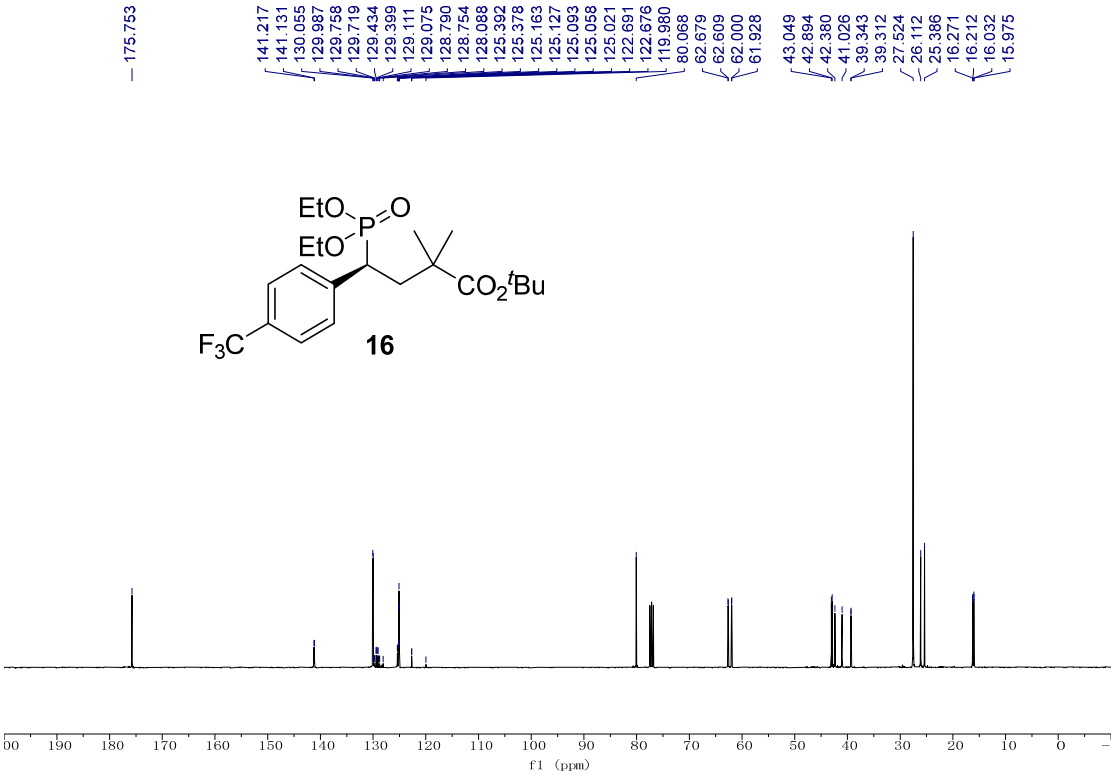
^{31}P NMR, 162 MHz, $CDCl_3$



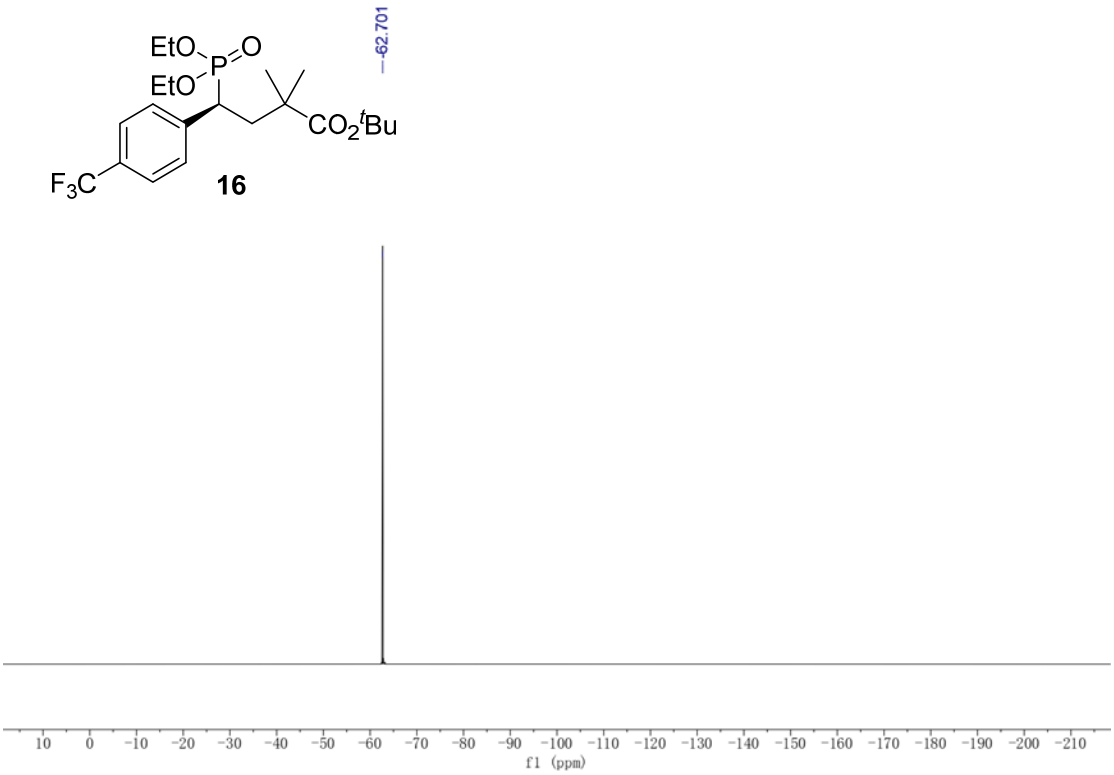
^{1}H NMR, 400 MHz, $CDCl_3$



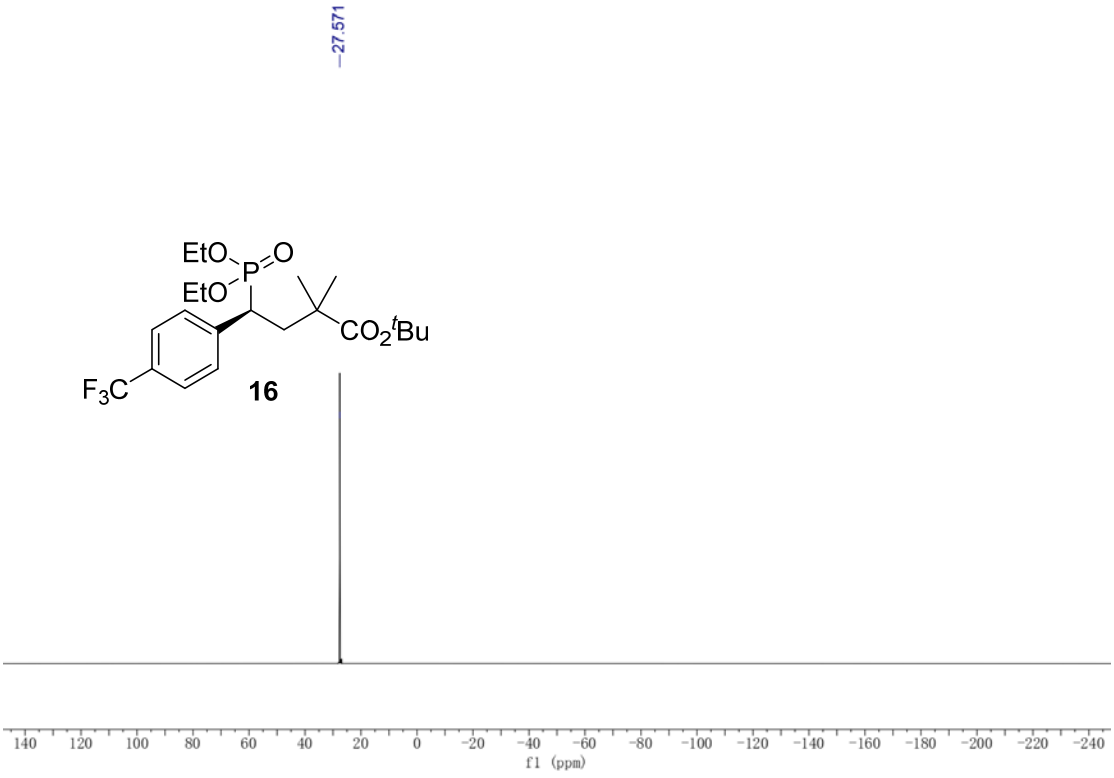
^{13}C NMR, 100 MHz, $CDCl_3$



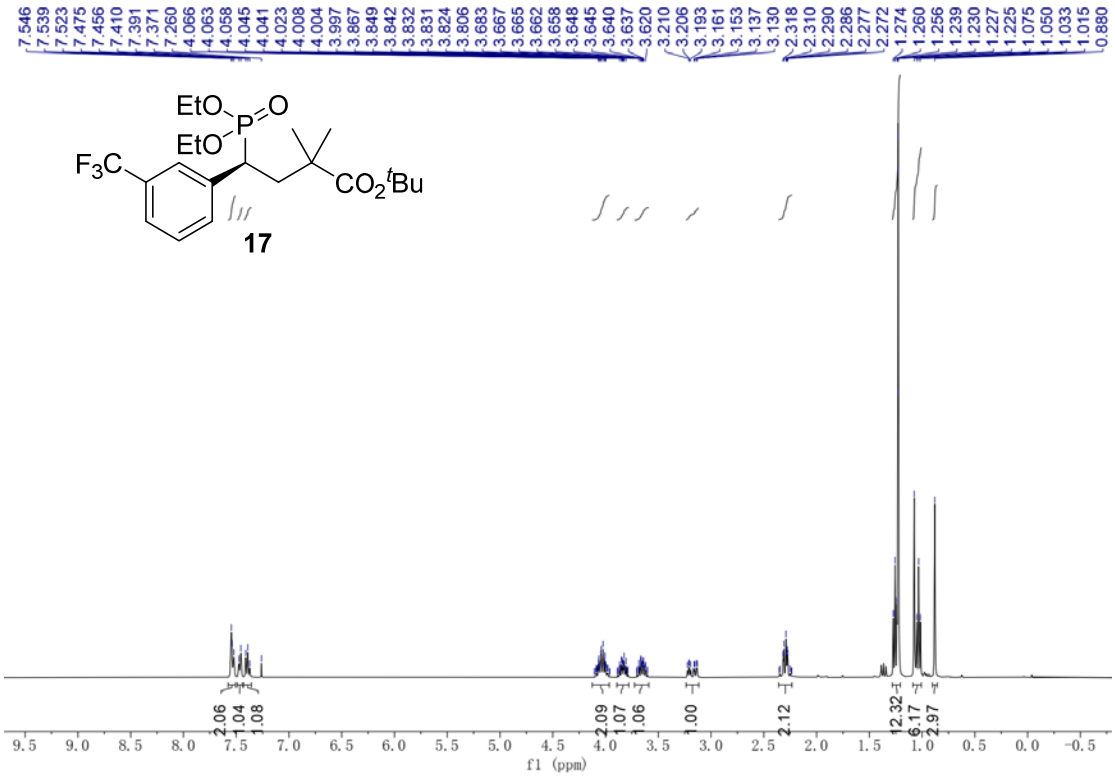
^{19}F NMR, 376 MHz, $CDCl_3$



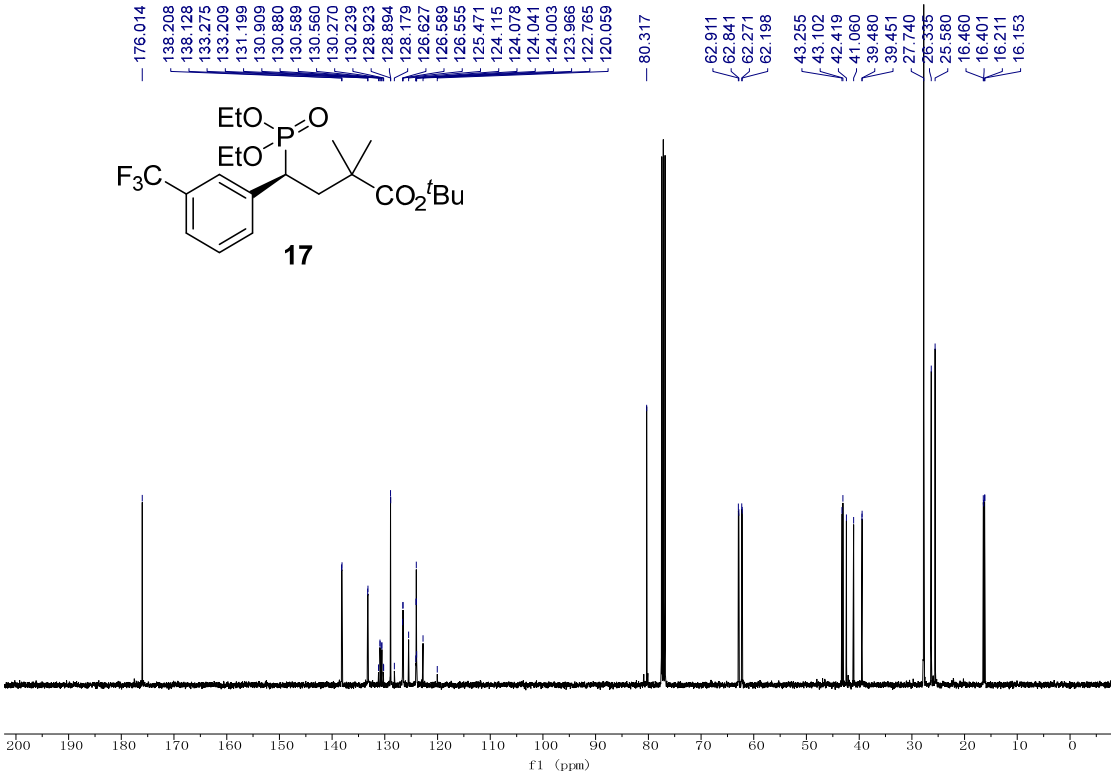
^{31}P NMR, 162 MHz, $CDCl_3$



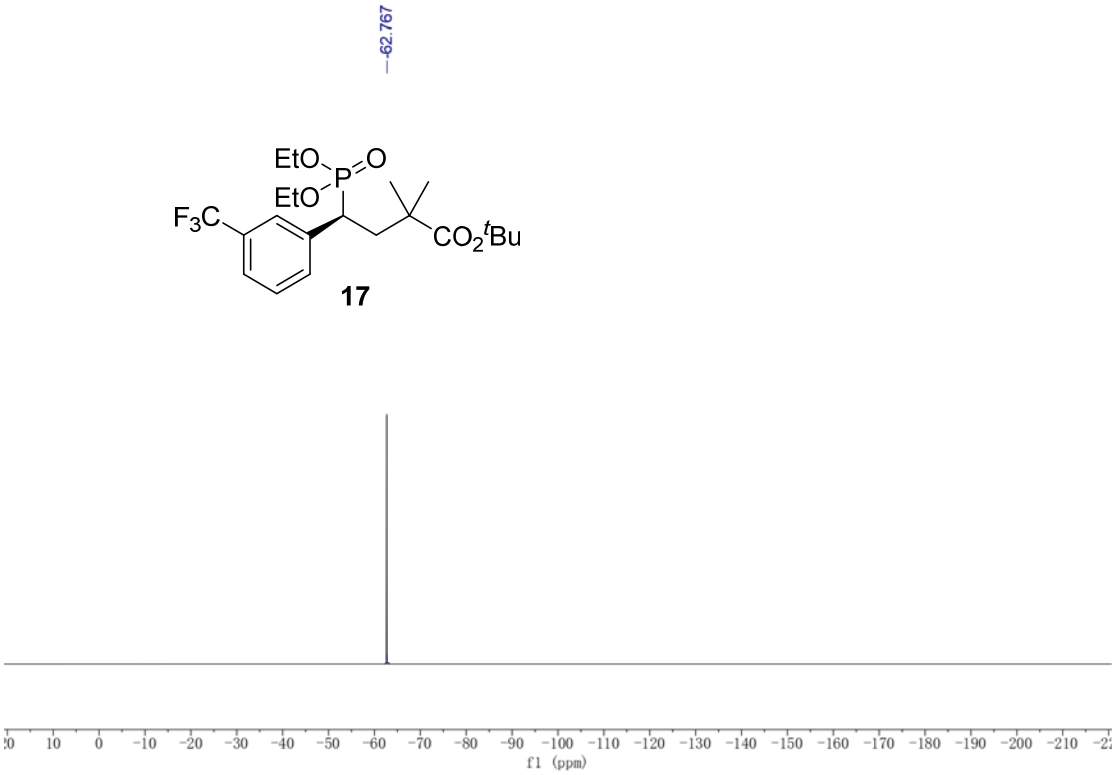
^{1}H NMR, 400 MHz, $CDCl_3$



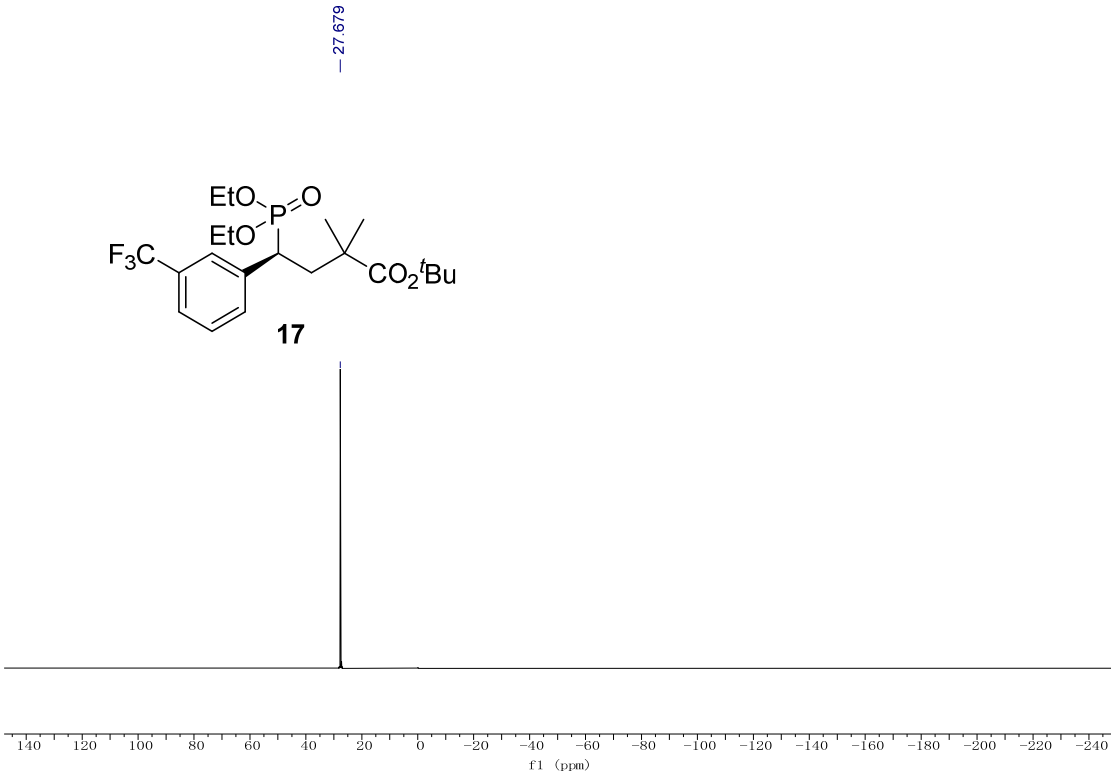
^{13}C NMR, 100 MHz, $CDCl_3$



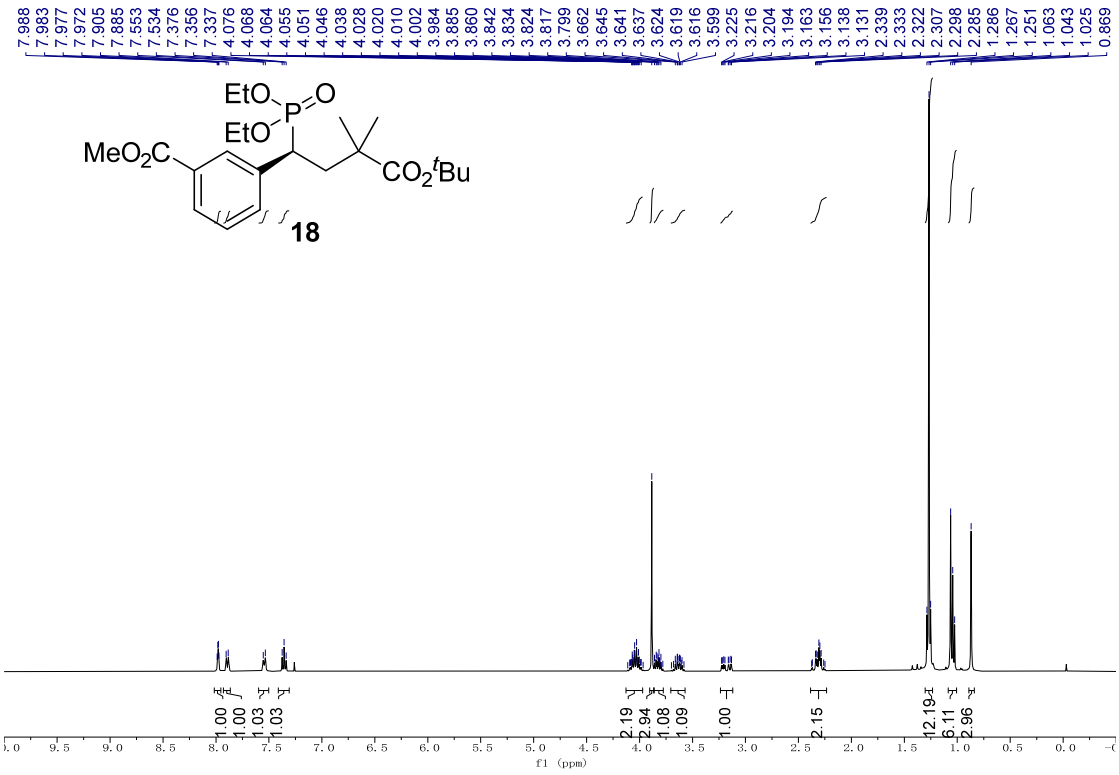
^{19}F NMR, 376 MHz, $CDCl_3$



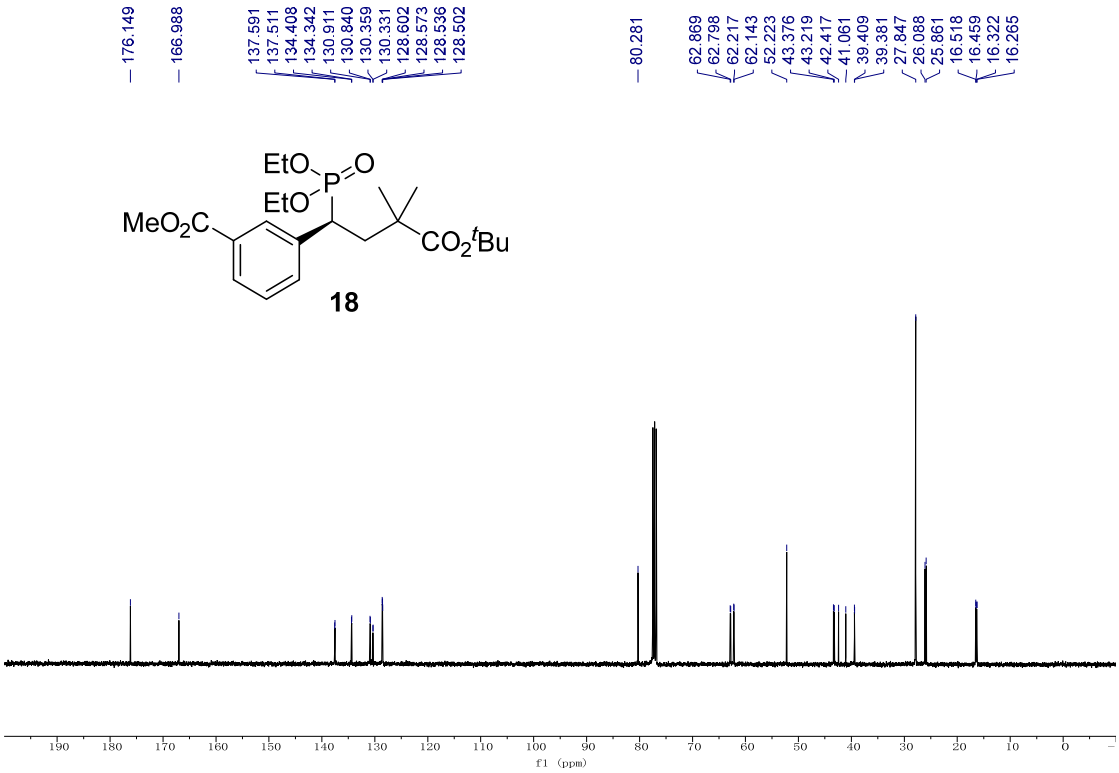
^{31}P NMR, 162 MHz, $CDCl_3$



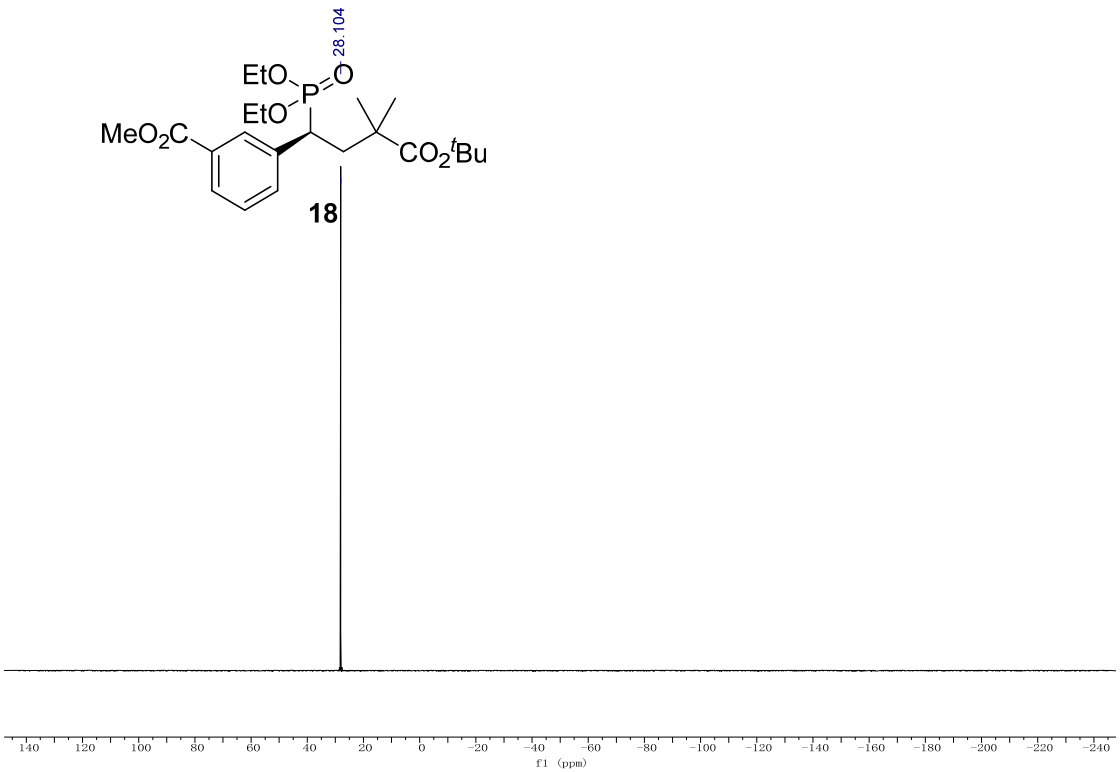
^{1}H NMR, 400 MHz, $CDCl_3$



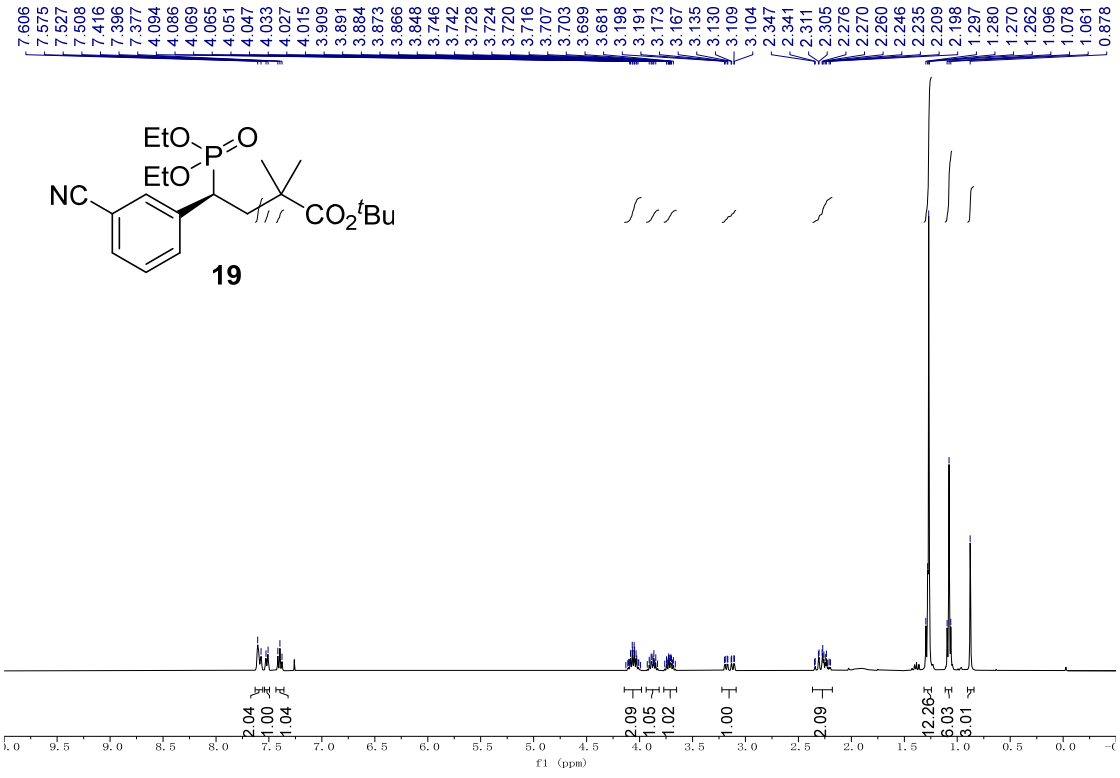
^{13}C NMR, 100 MHz, $CDCl_3$



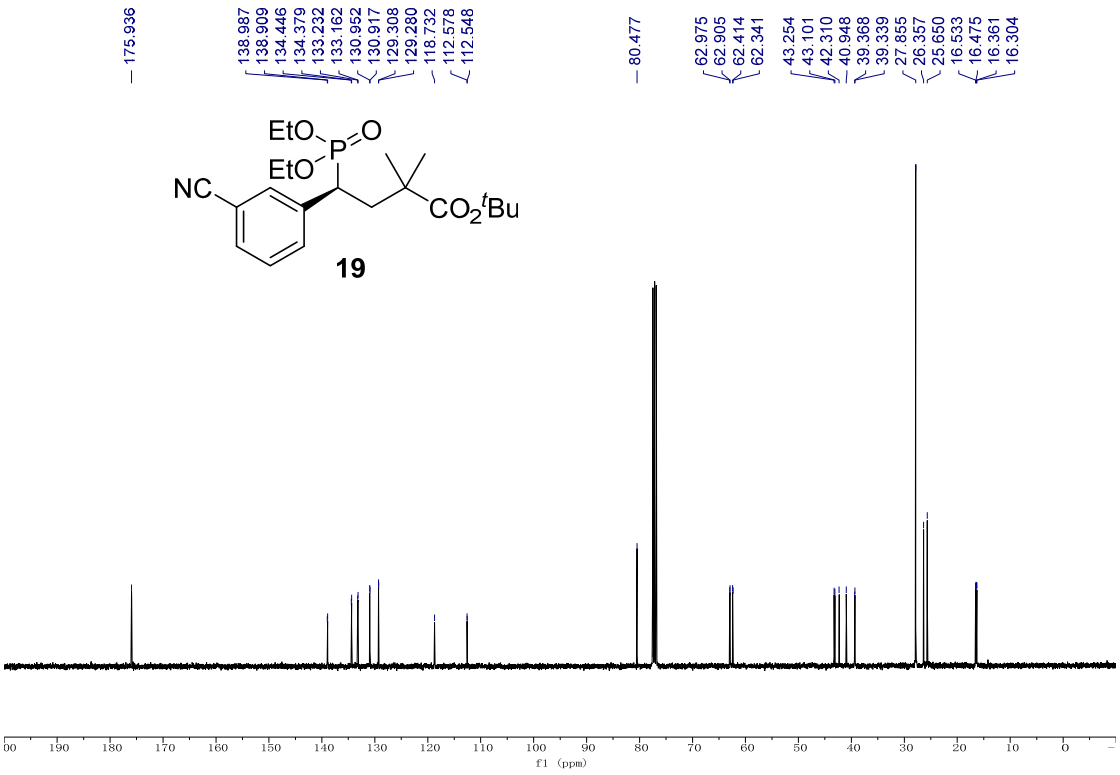
^{31}P NMR, 162 MHz, $CDCl_3$



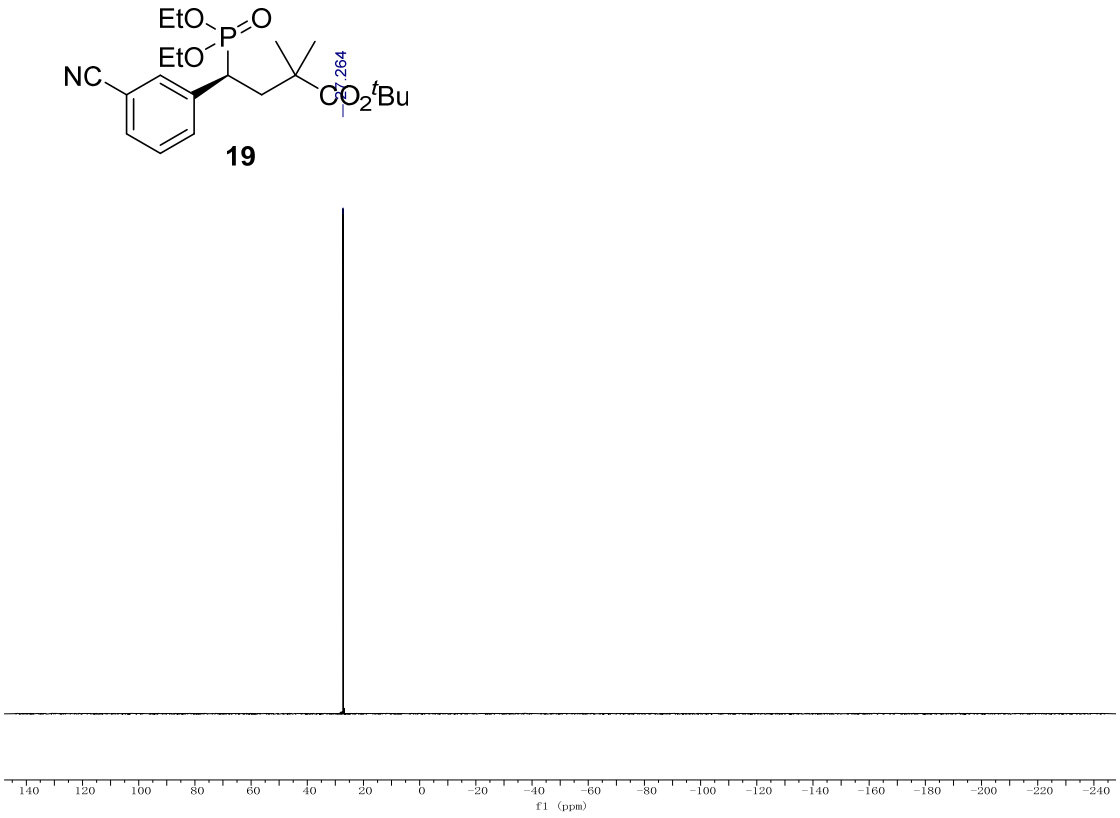
^{1}H NMR, 400 MHz, $CDCl_3$



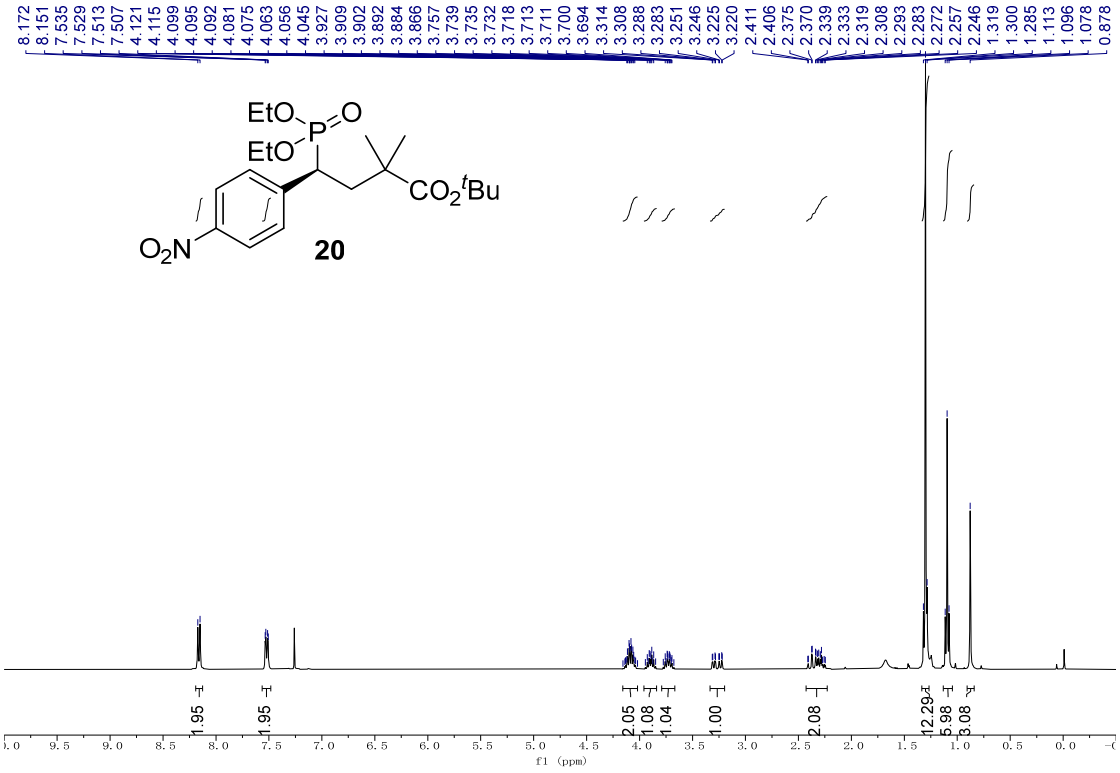
^{13}C NMR, 100 MHz, $CDCl_3$



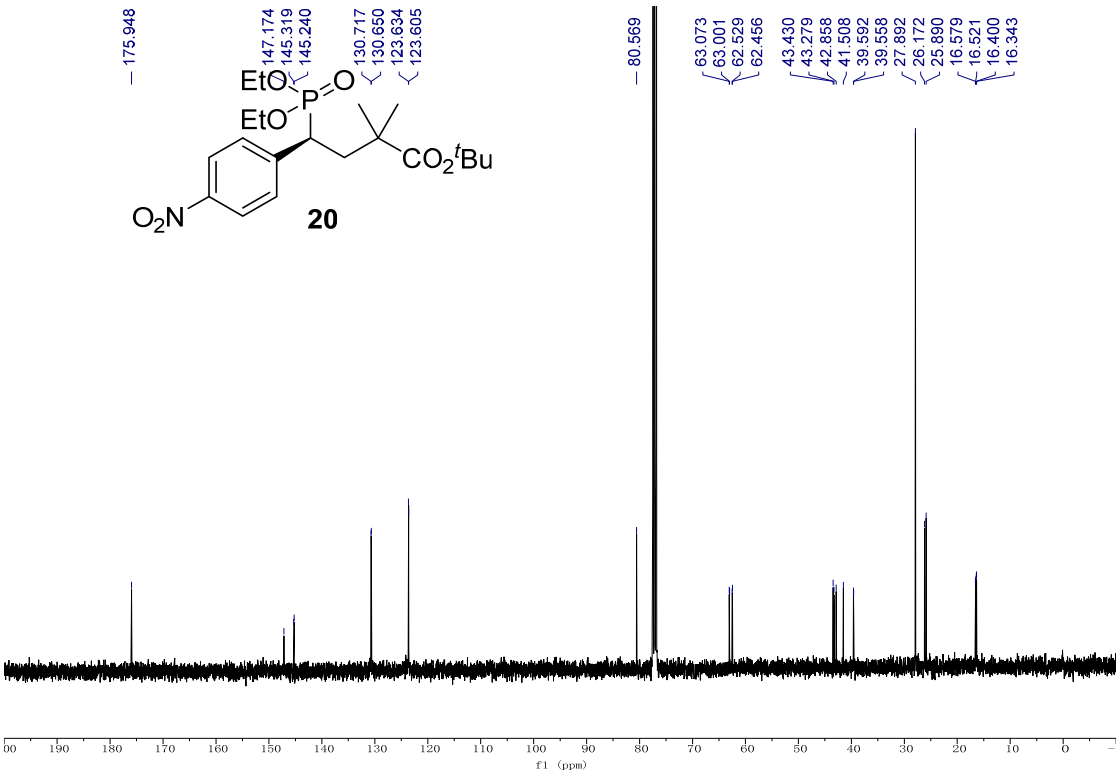
^{31}P NMR, 162 MHz, $CDCl_3$



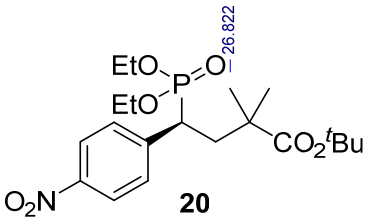
^{1}H NMR, 400 MHz, $CDCl_3$



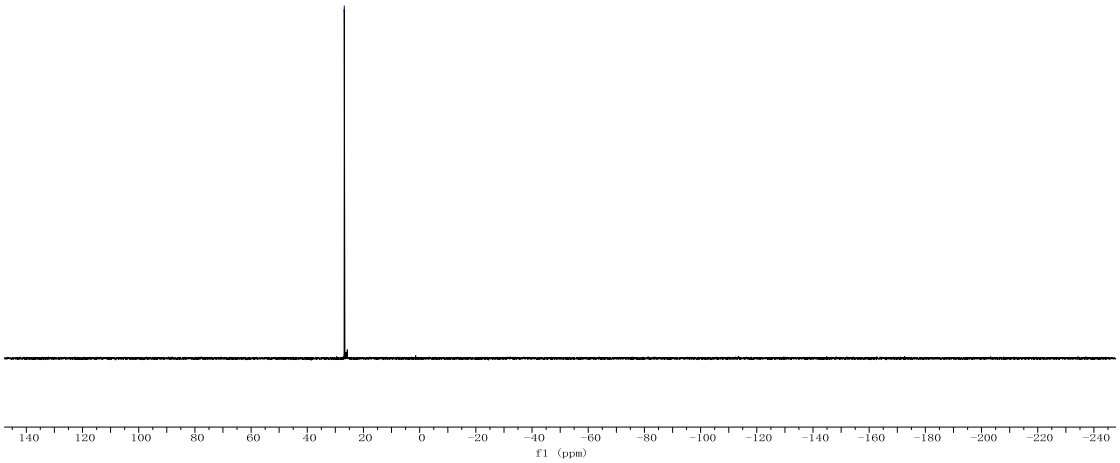
^{13}C NMR, 100 MHz, $CDCl_3$



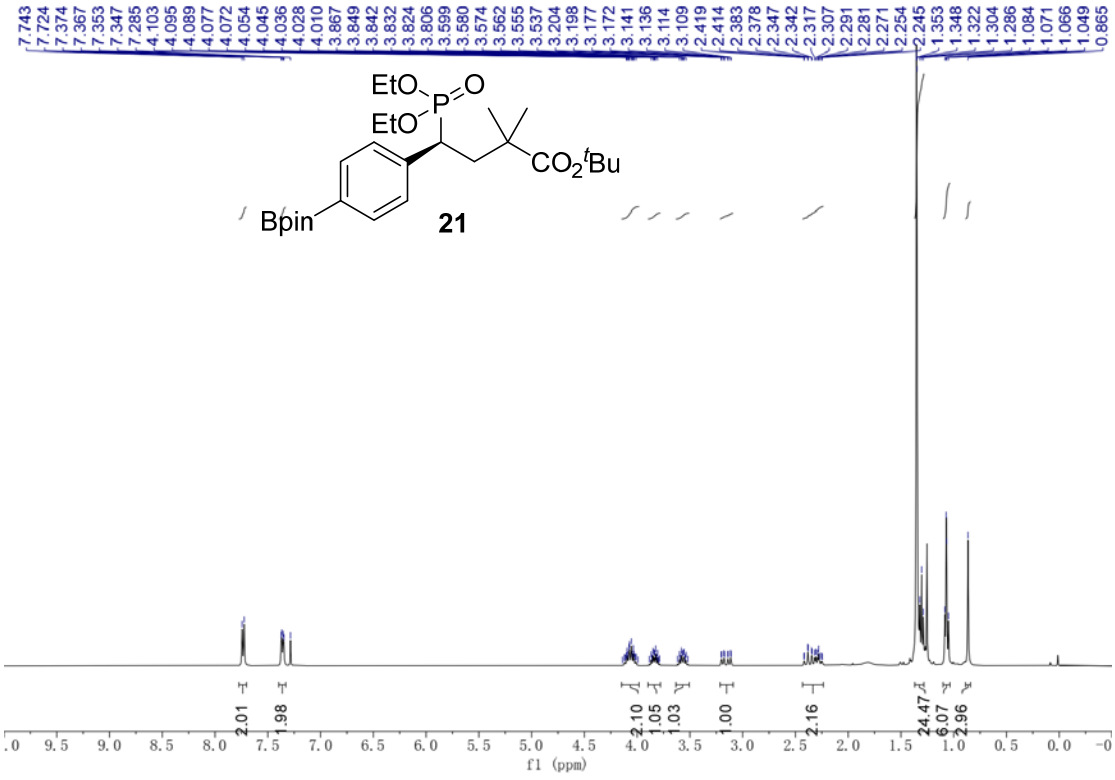
^{31}P NMR, 162 MHz, $CDCl_3$



20

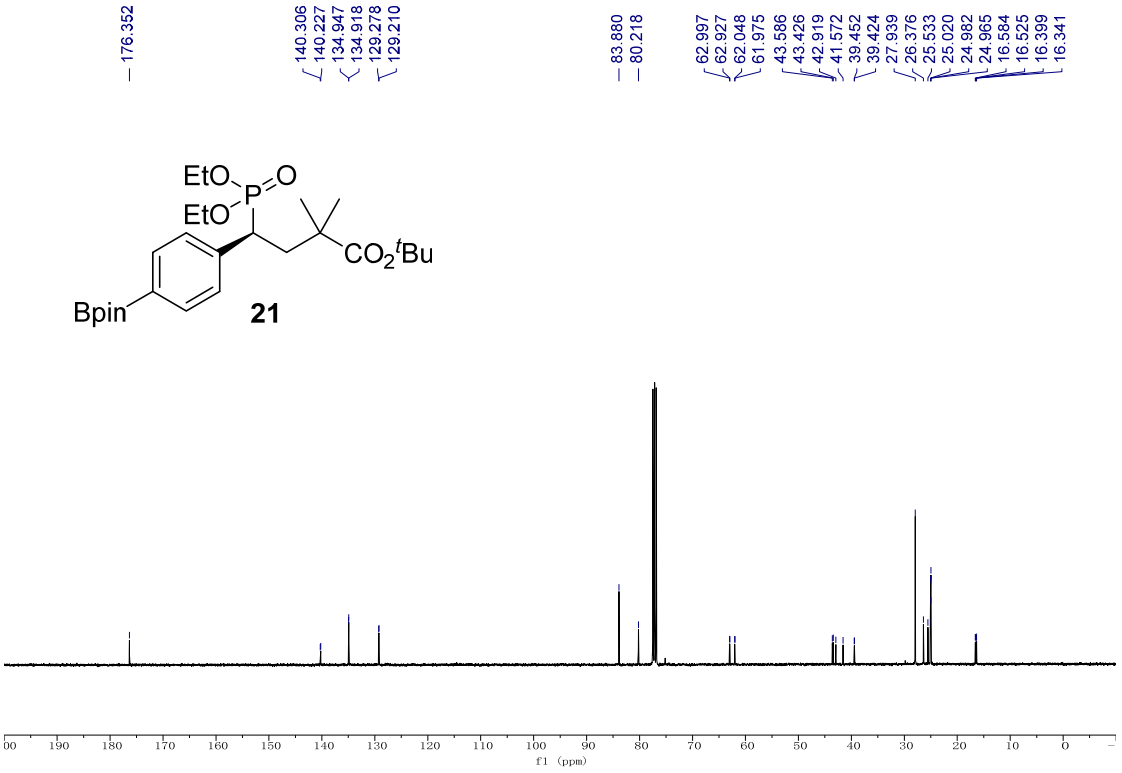


^{1}H NMR, 400 MHz, $CDCl_3$

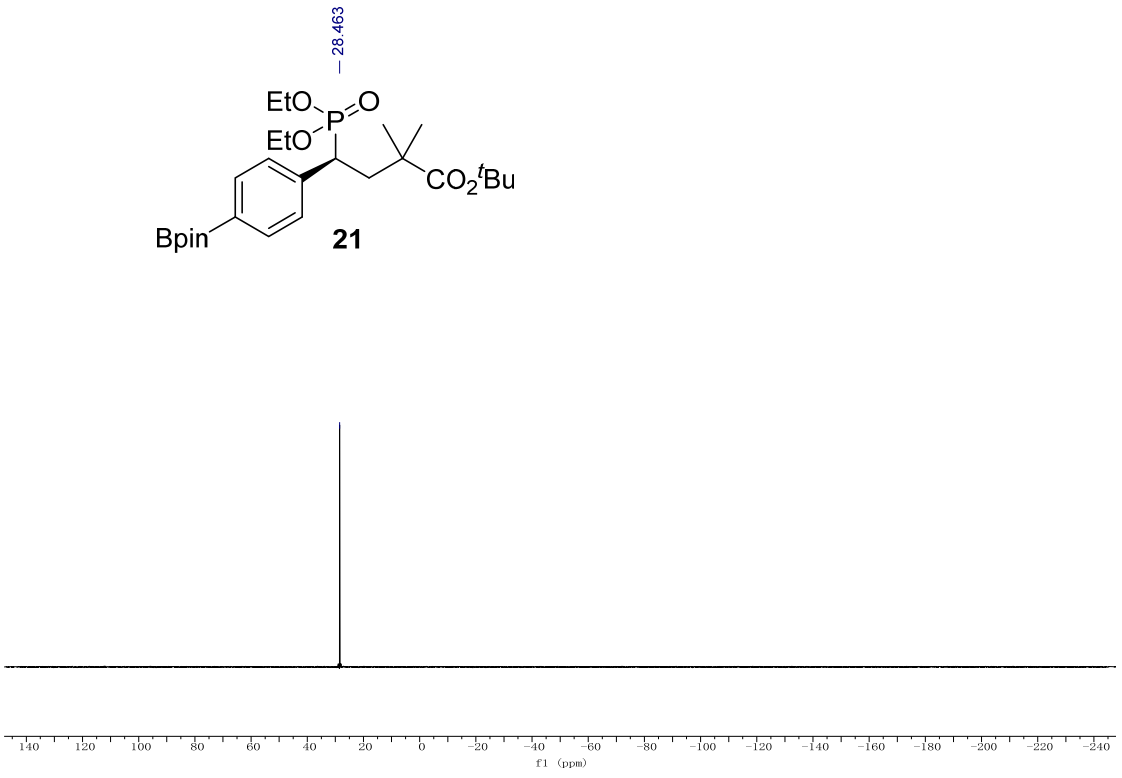


21

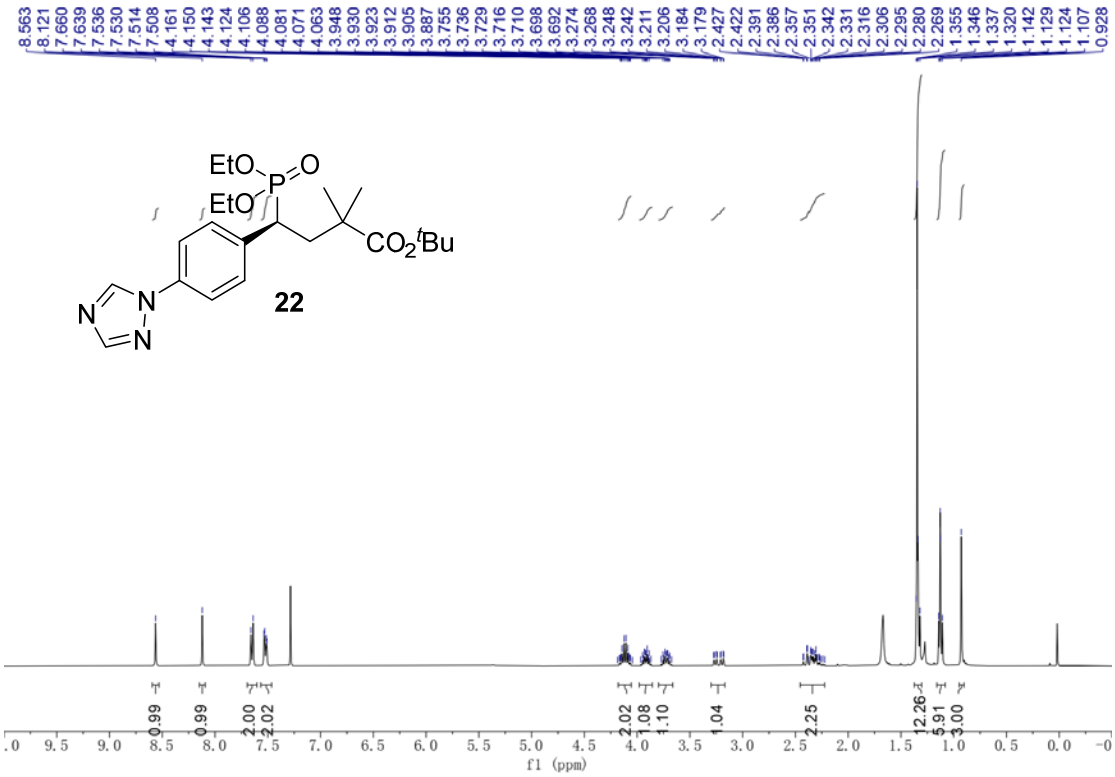
^{13}C NMR, 100 MHz, $CDCl_3$



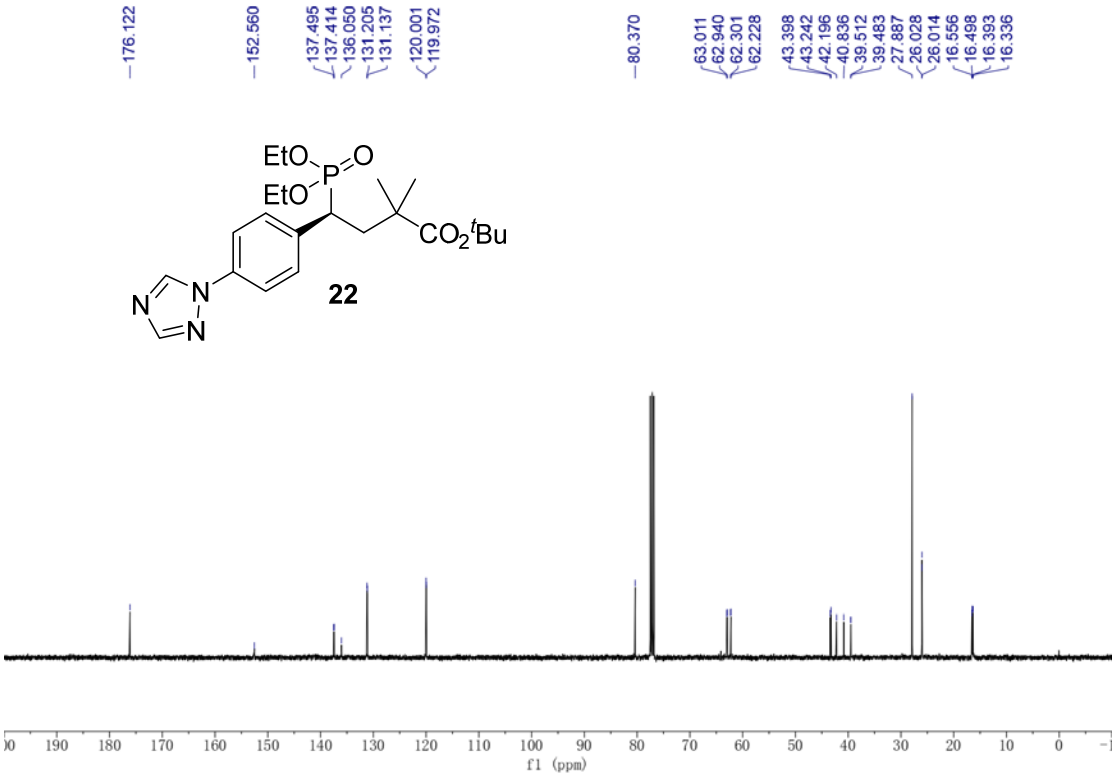
^{31}P NMR, 162 MHz, $CDCl_3$



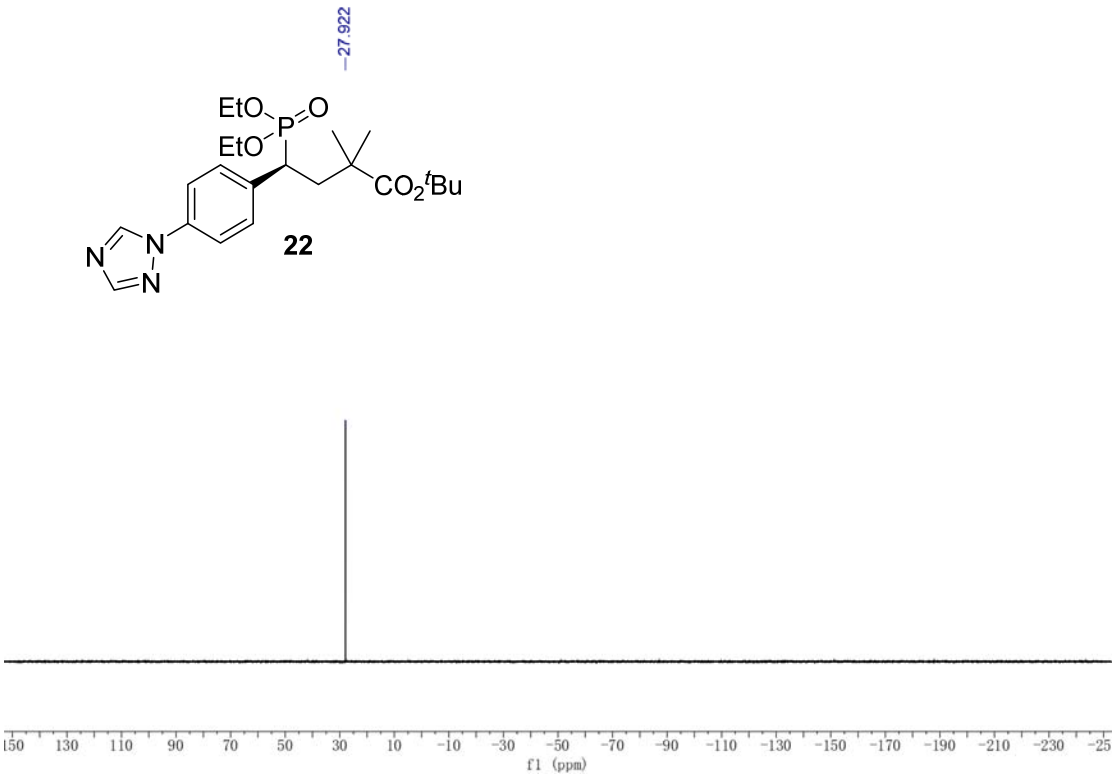
^{1}H NMR, 400 MHz, $CDCl_3$



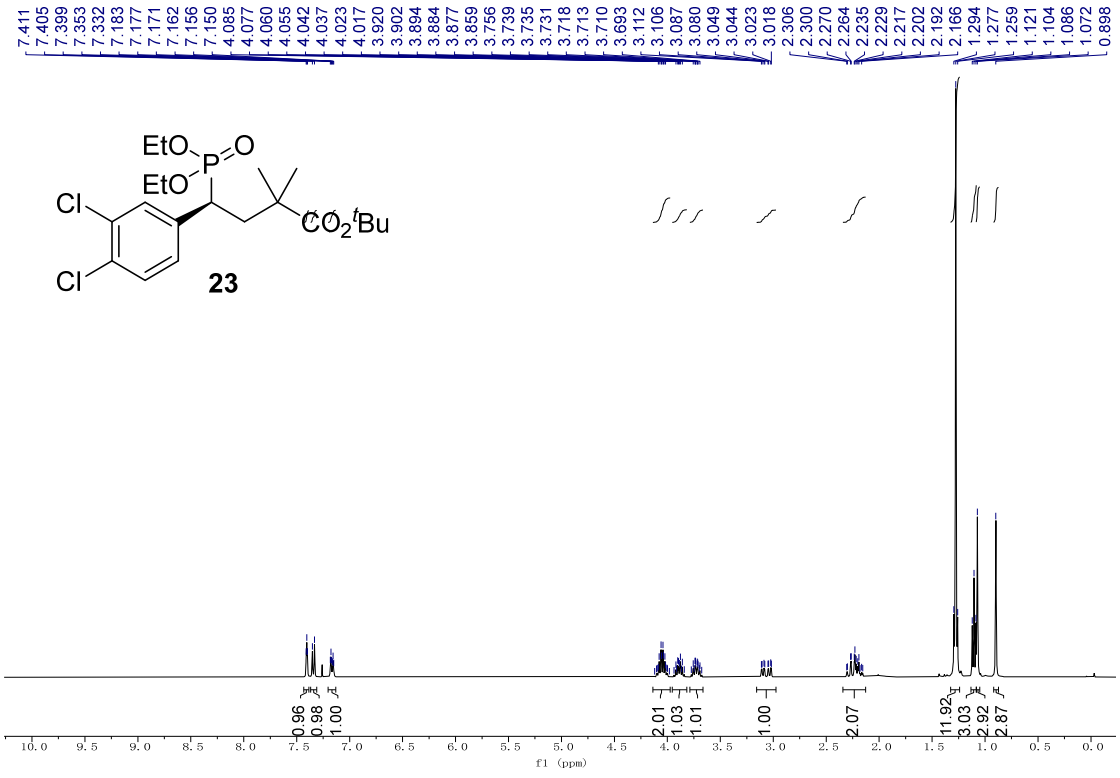
^{13}C NMR, 100 MHz, $CDCl_3$



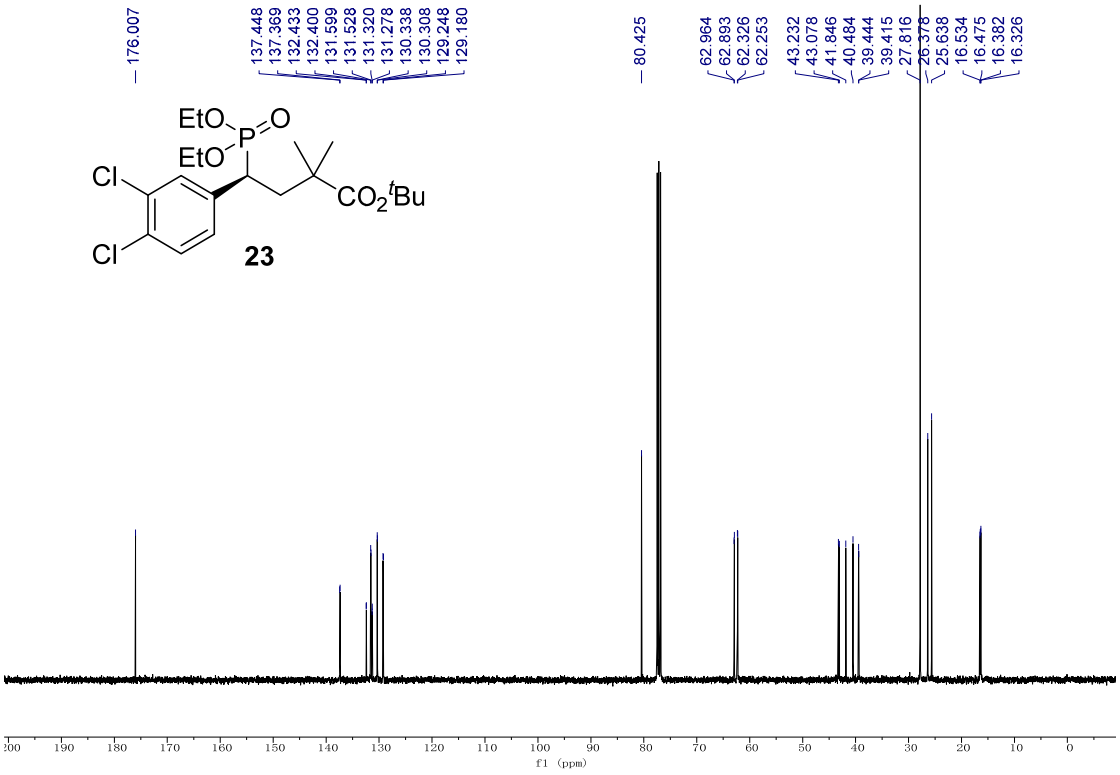
^{31}P NMR, 162 MHz, $CDCl_3$



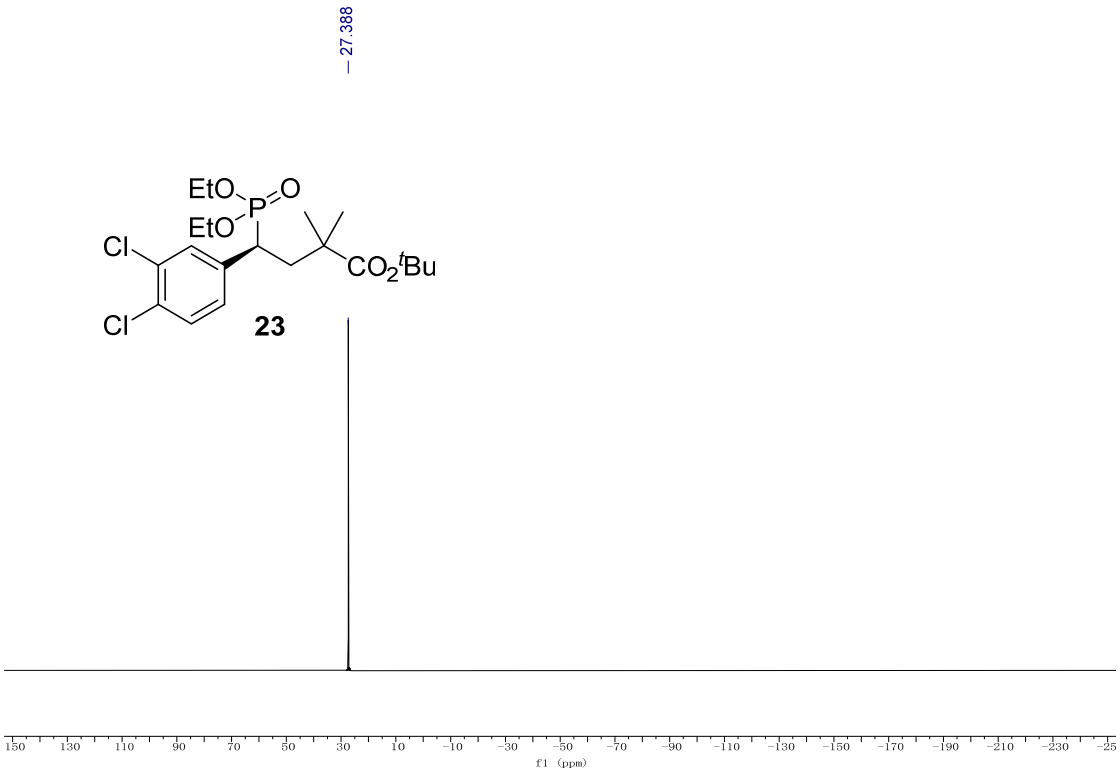
^{1}H NMR, 400 MHz, $CDCl_3$



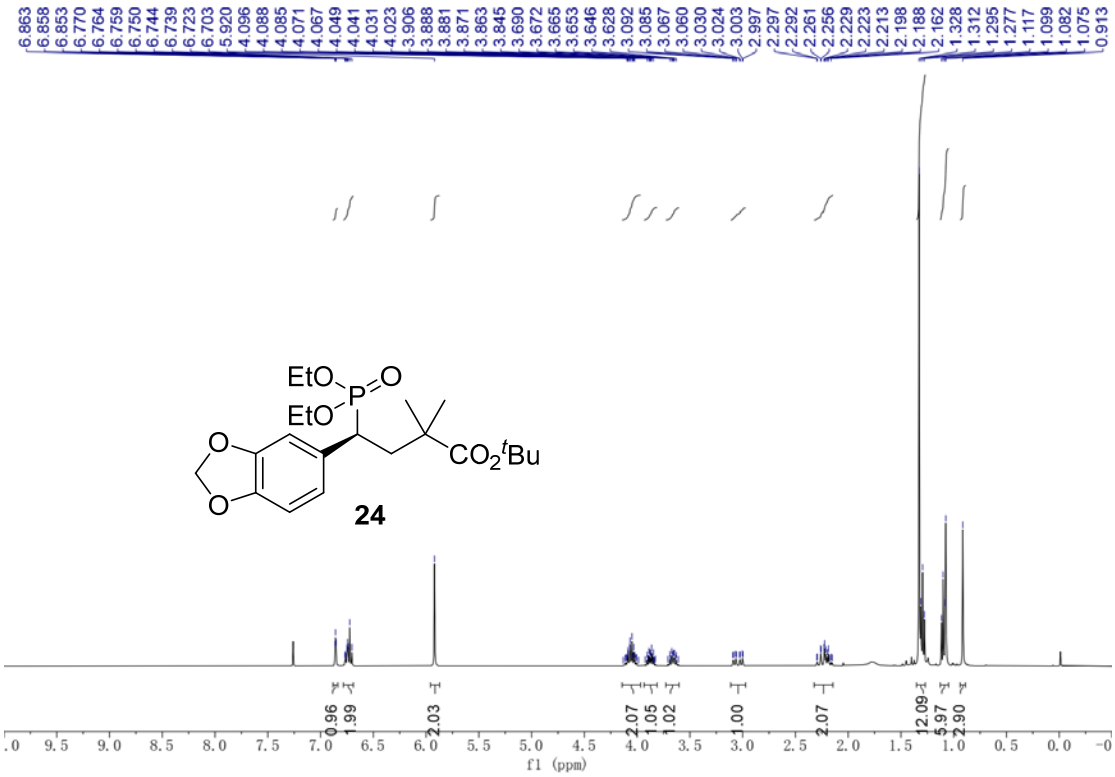
^{13}C NMR, 100 MHz, $CDCl_3$



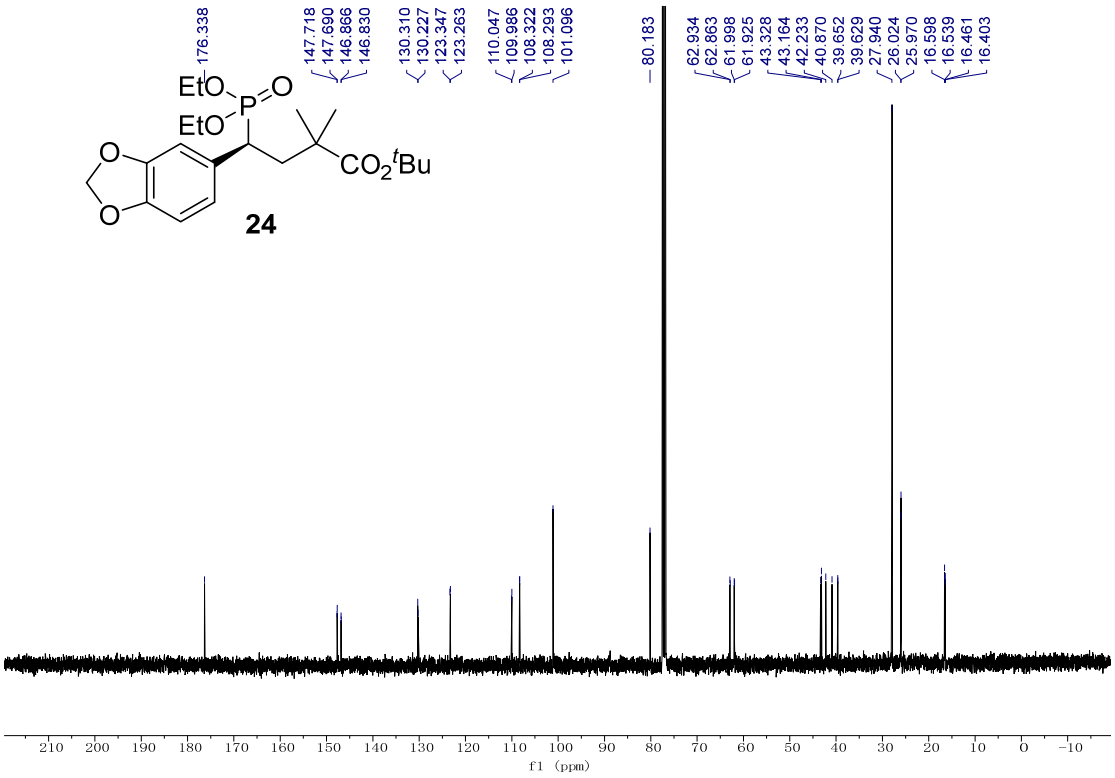
^{31}P NMR, 162 MHz, $CDCl_3$



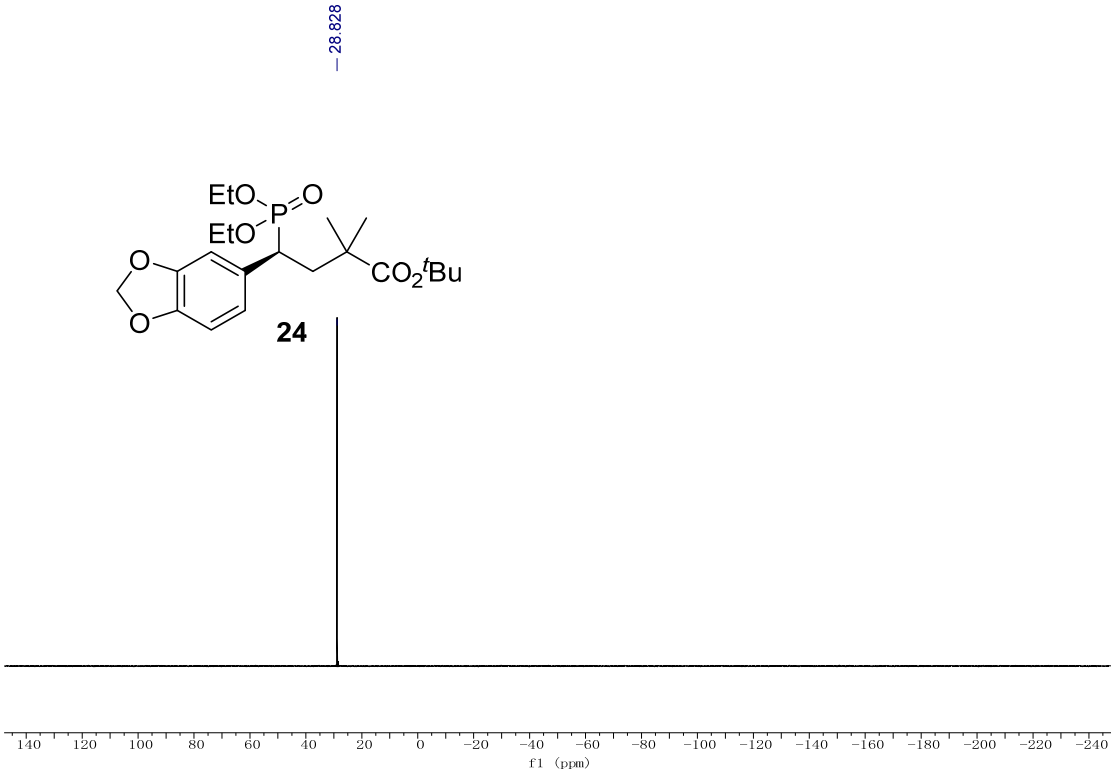
^{1}H NMR, 400 MHz, $CDCl_3$



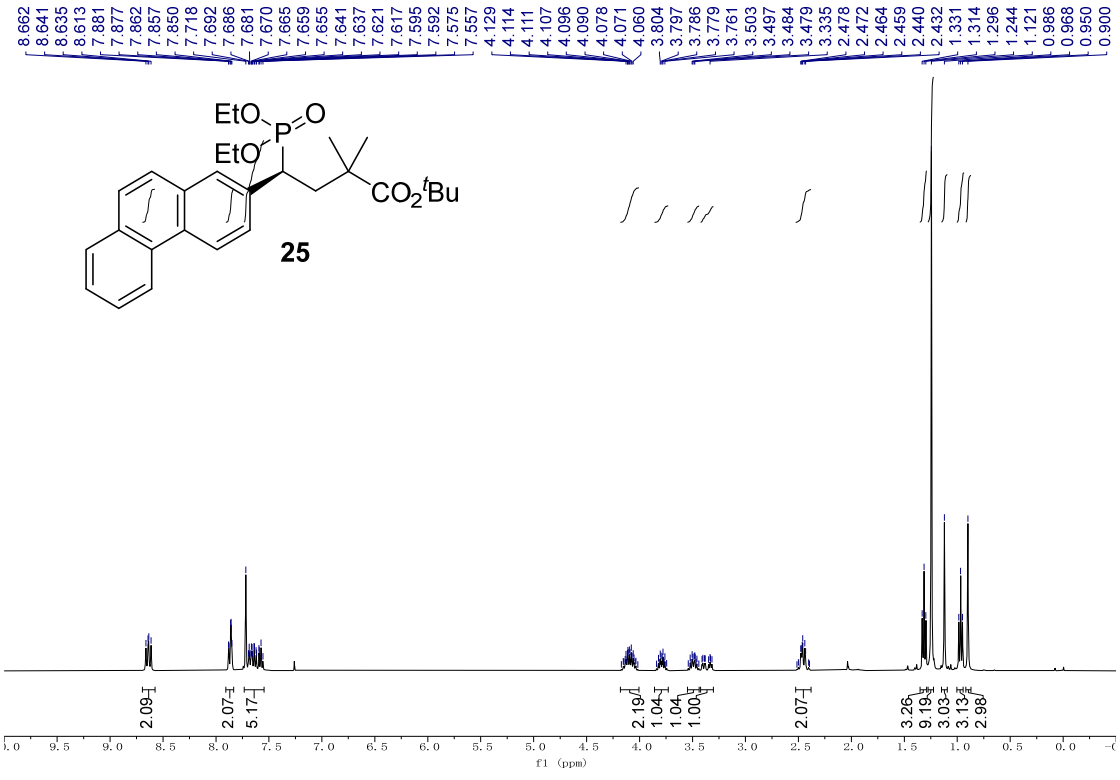
^{13}C NMR, 100 MHz, $CDCl_3$



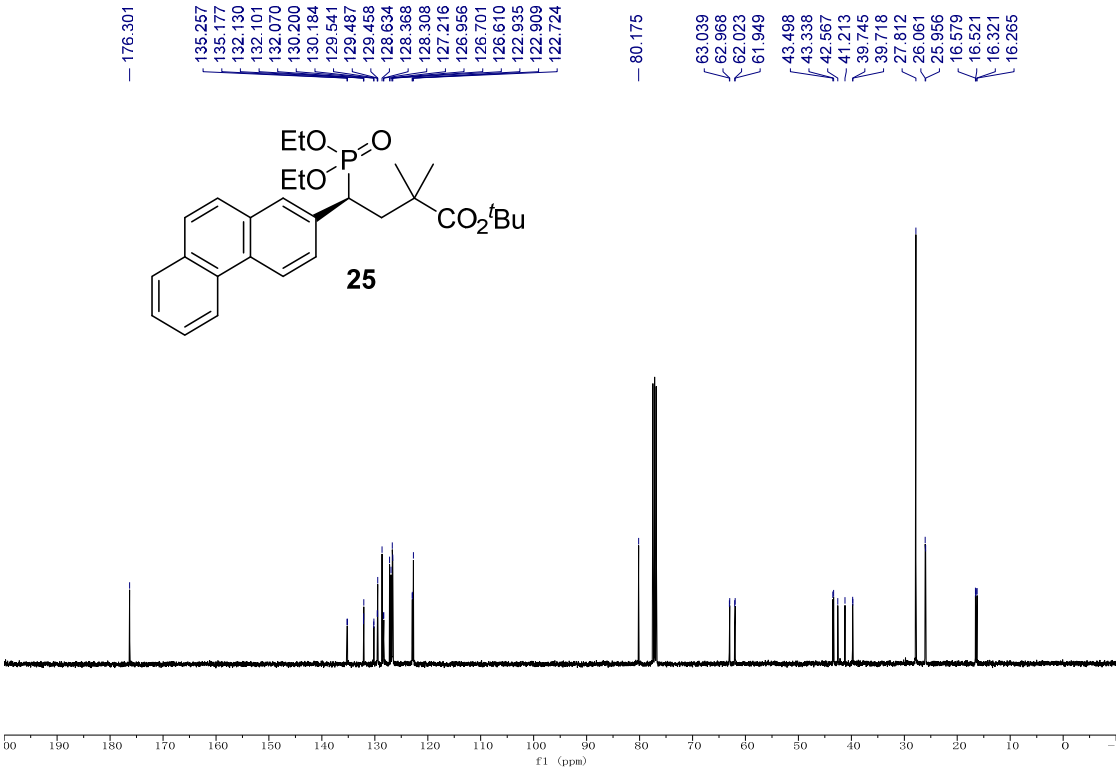
^{31}P NMR, 162 MHz, $CDCl_3$



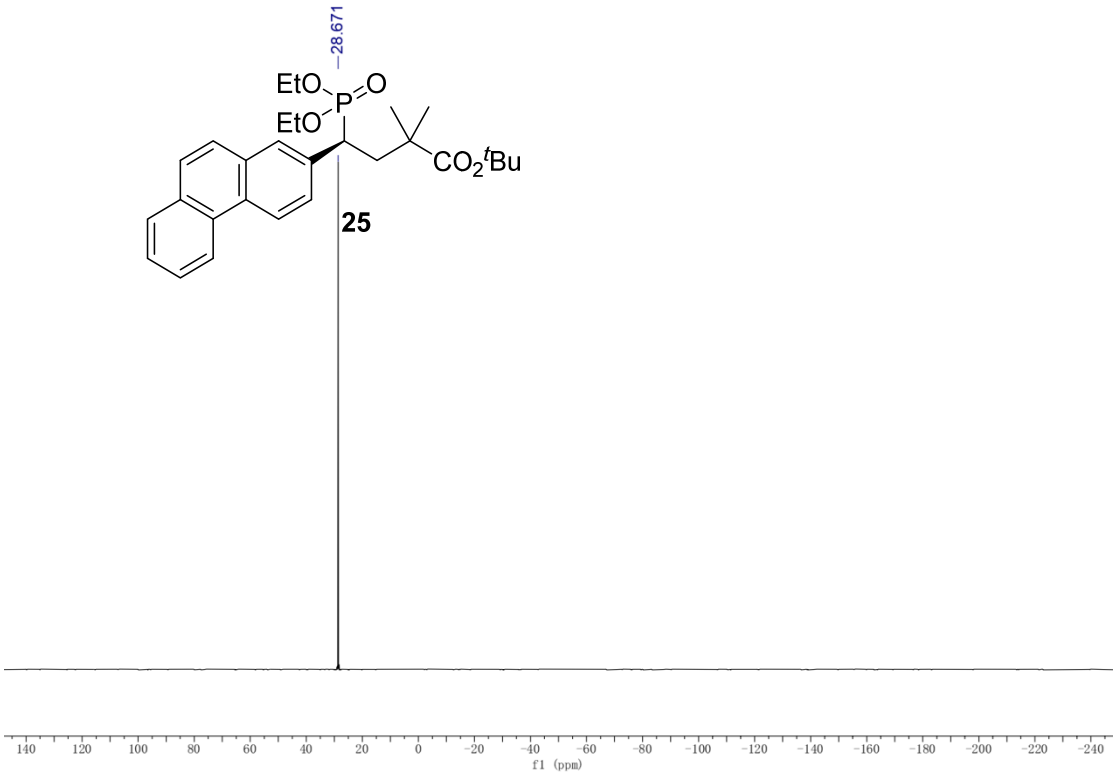
^{1}H NMR, 400 MHz, $CDCl_3$



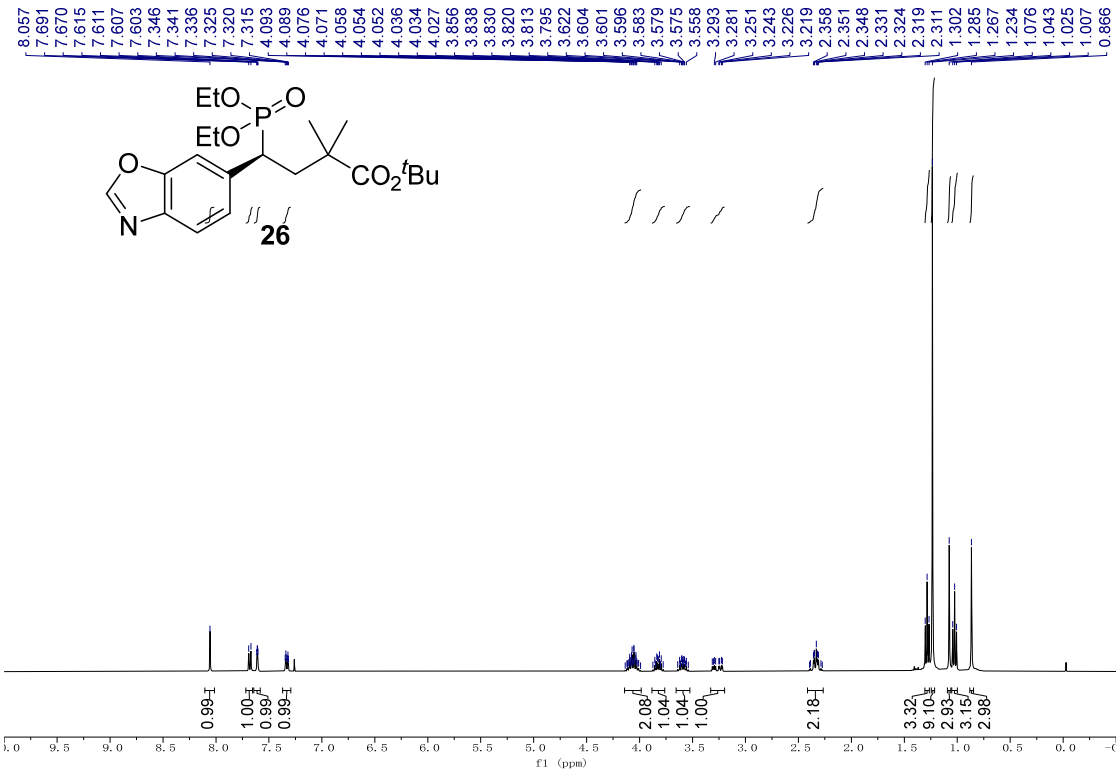
^{13}C NMR, 100 MHz, $CDCl_3$



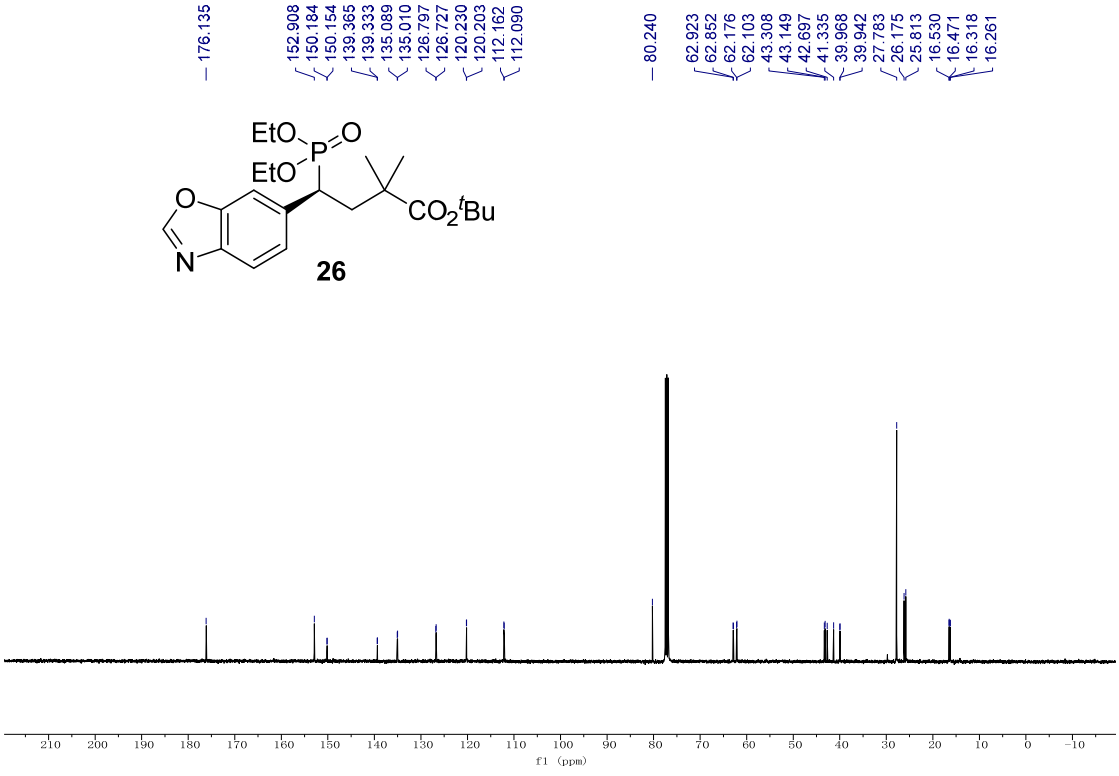
^{31}P NMR, 162 MHz, $CDCl_3$



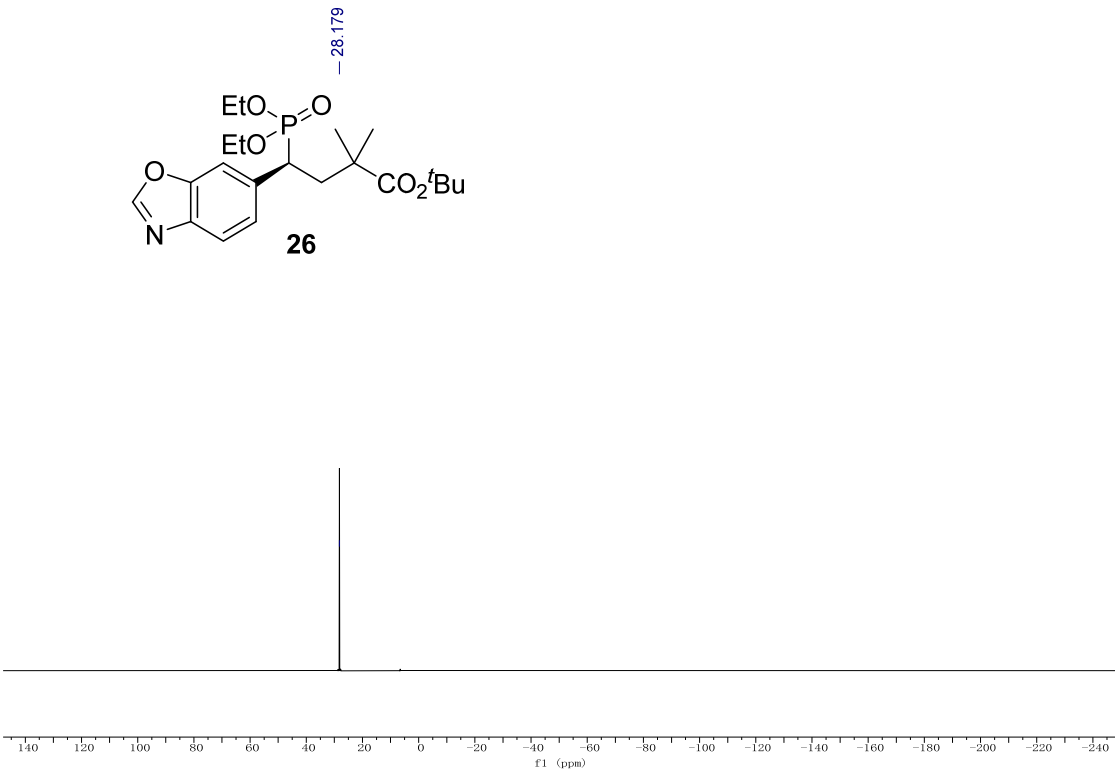
^{1}H NMR, 400 MHz, $CDCl_3$



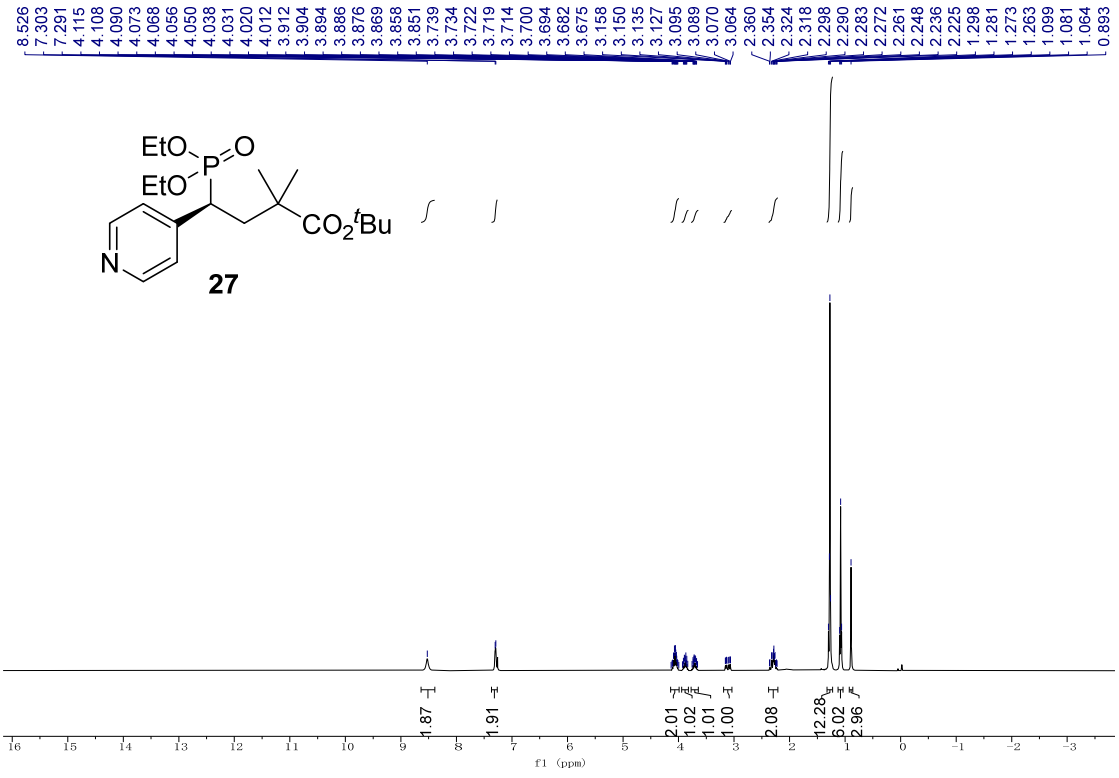
^{13}C NMR, 100 MHz, $CDCl_3$



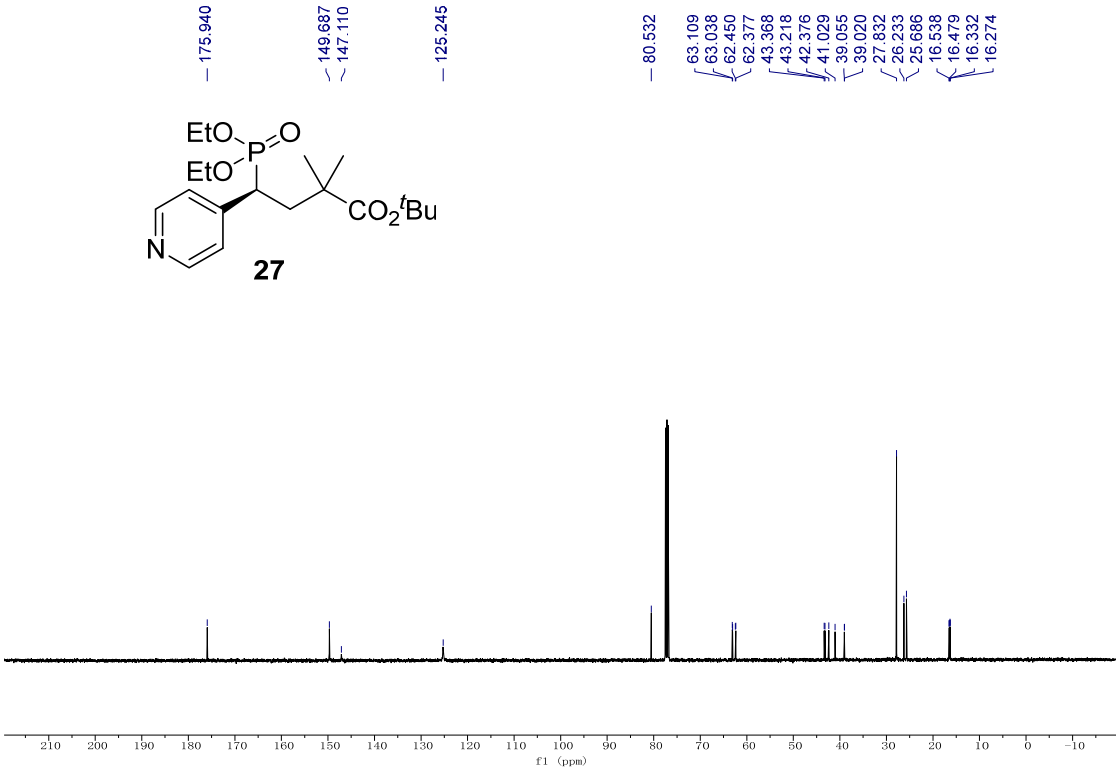
^{31}P NMR, 162 MHz, $CDCl_3$



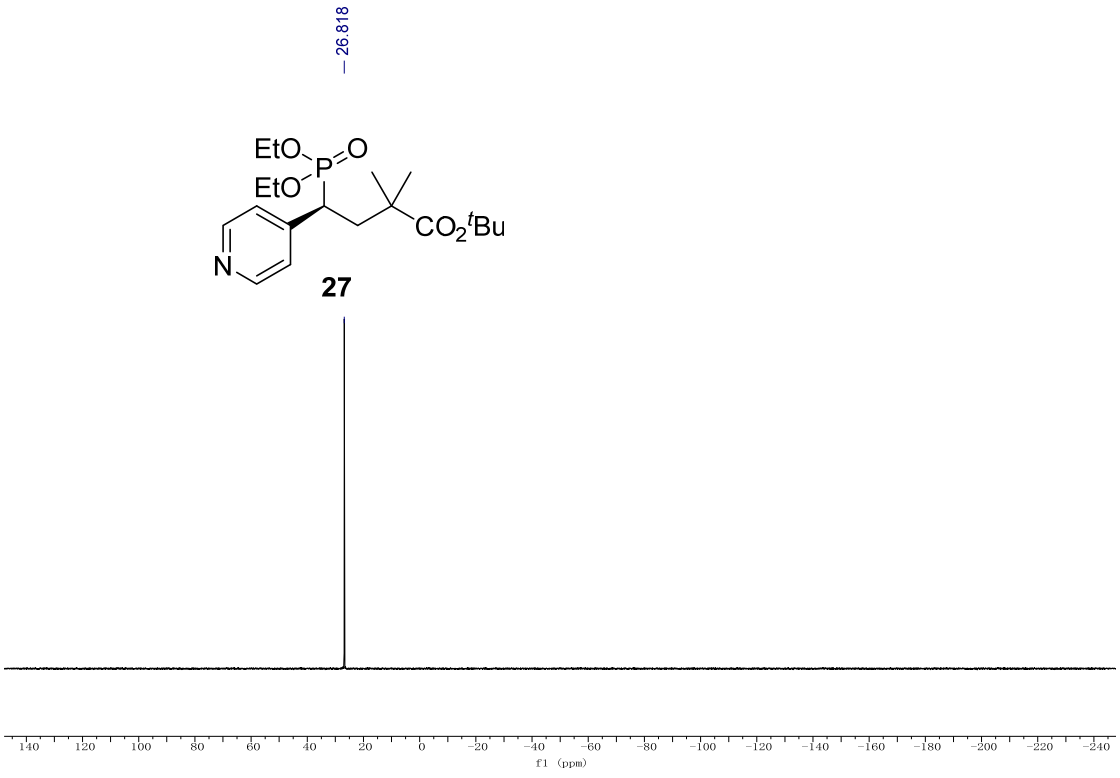
^{1}H NMR, 400 MHz, $CDCl_3$



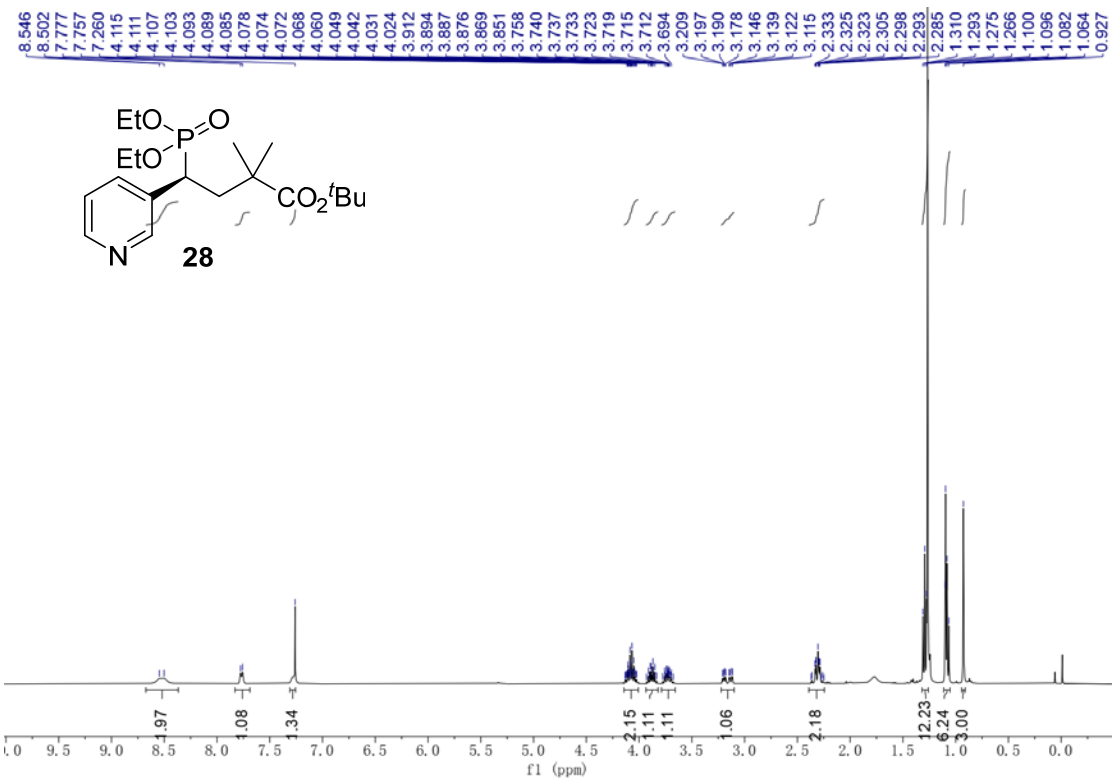
^{13}C NMR, 100 MHz, $CDCl_3$



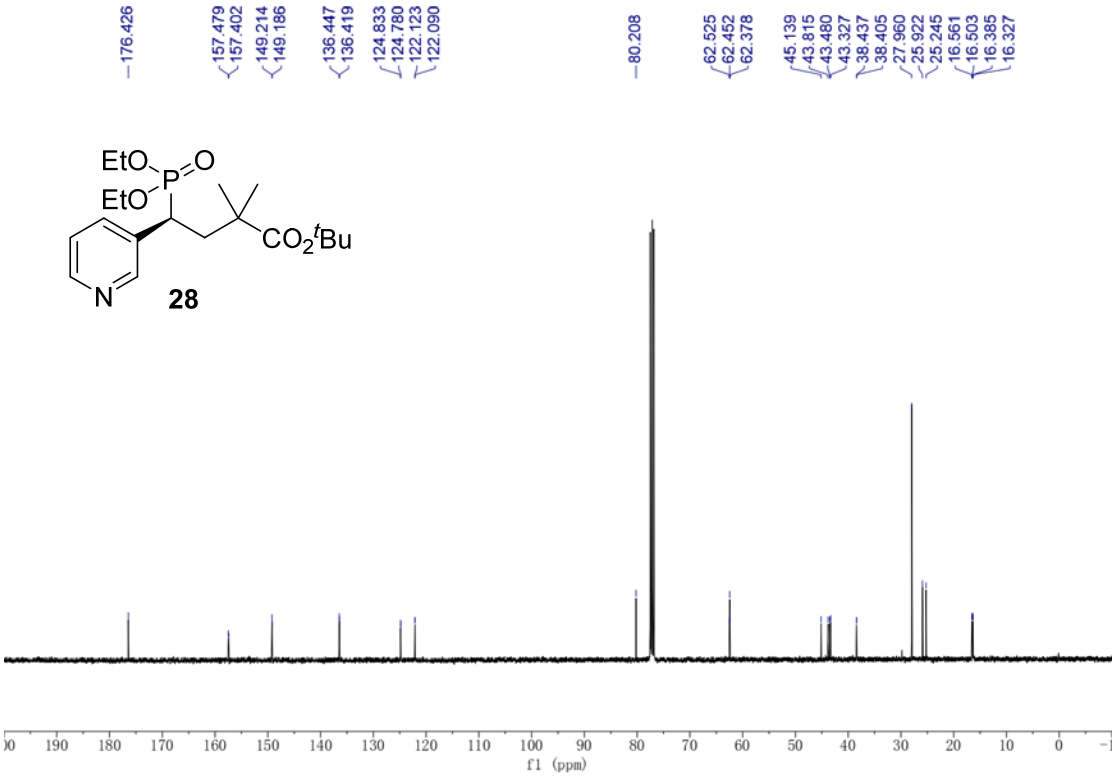
^{31}P NMR, 162 MHz, $CDCl_3$



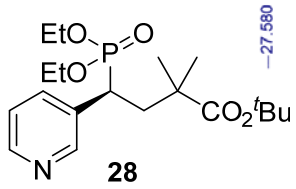
^{1}H NMR, 400 MHz, $CDCl_3$

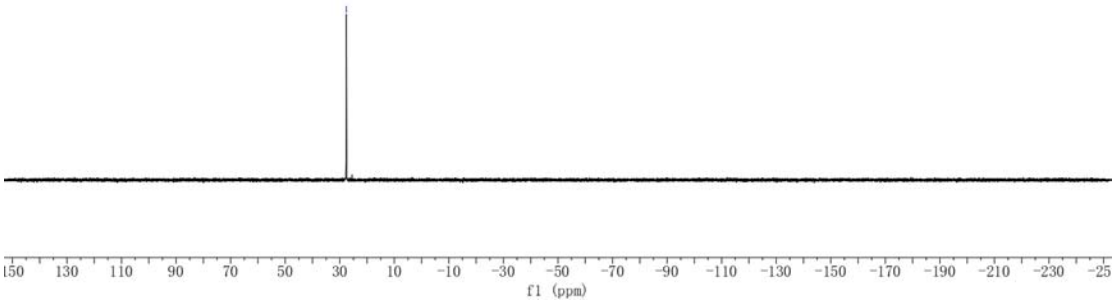


^{13}C NMR, 100 MHz, $CDCl_3$

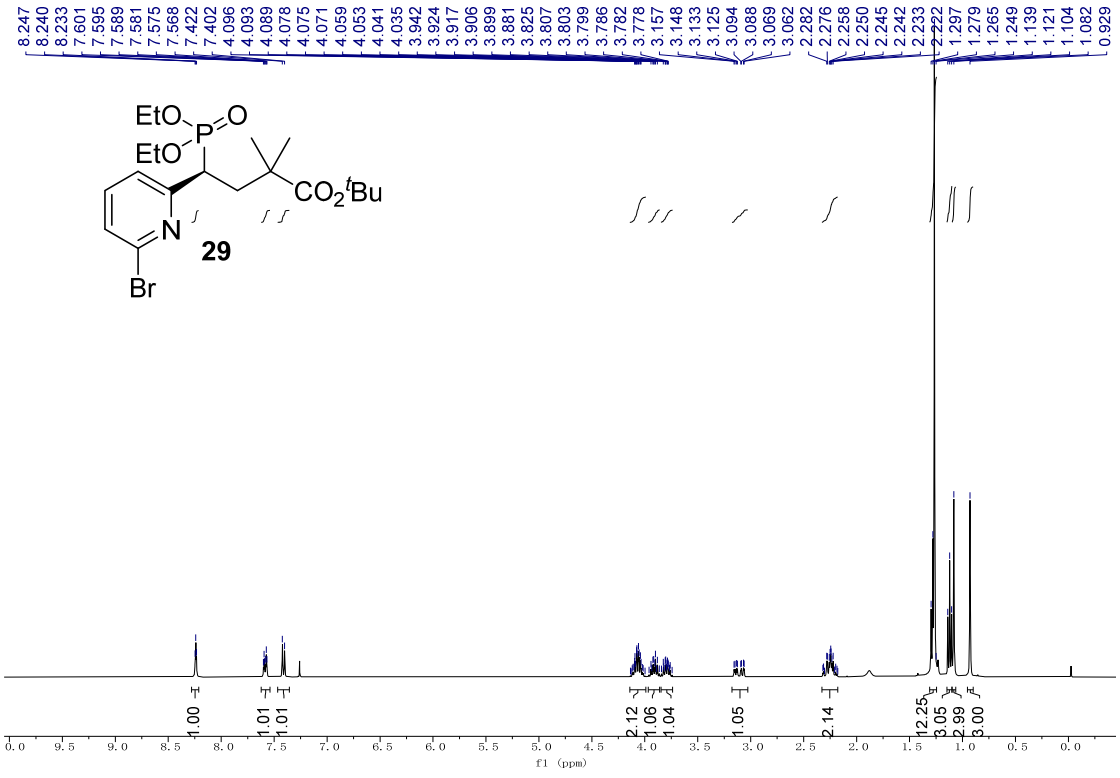


^{31}P NMR, 162 MHz, $CDCl_3$

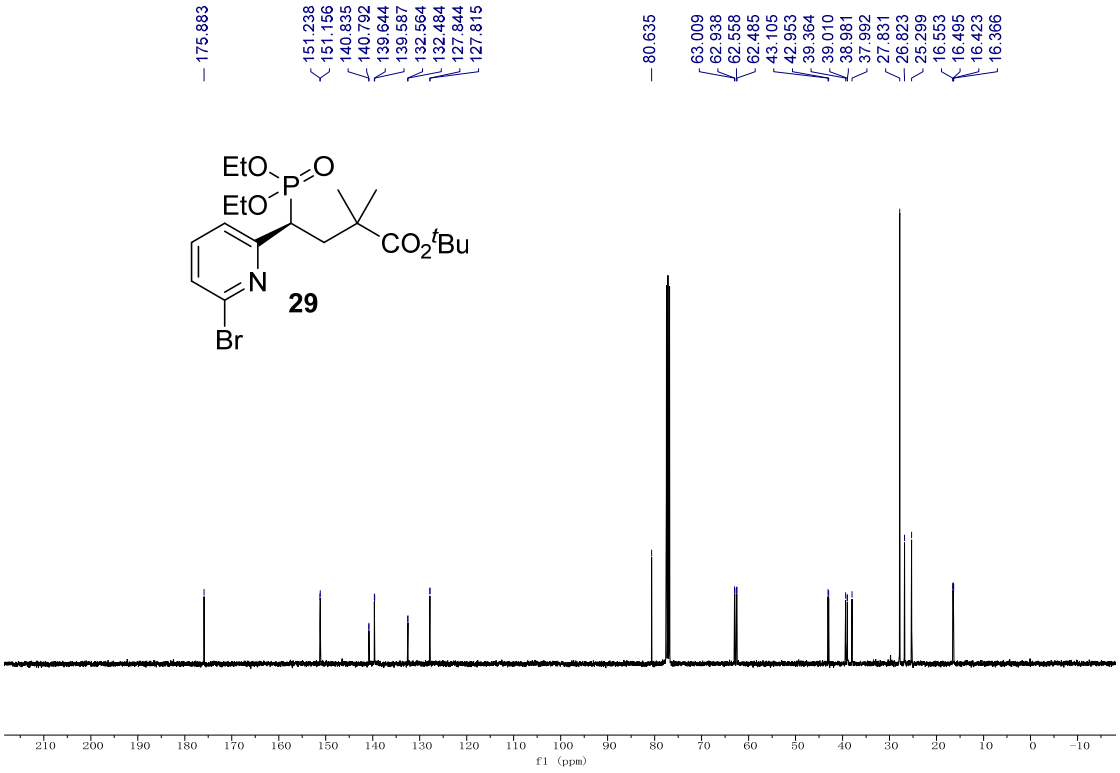




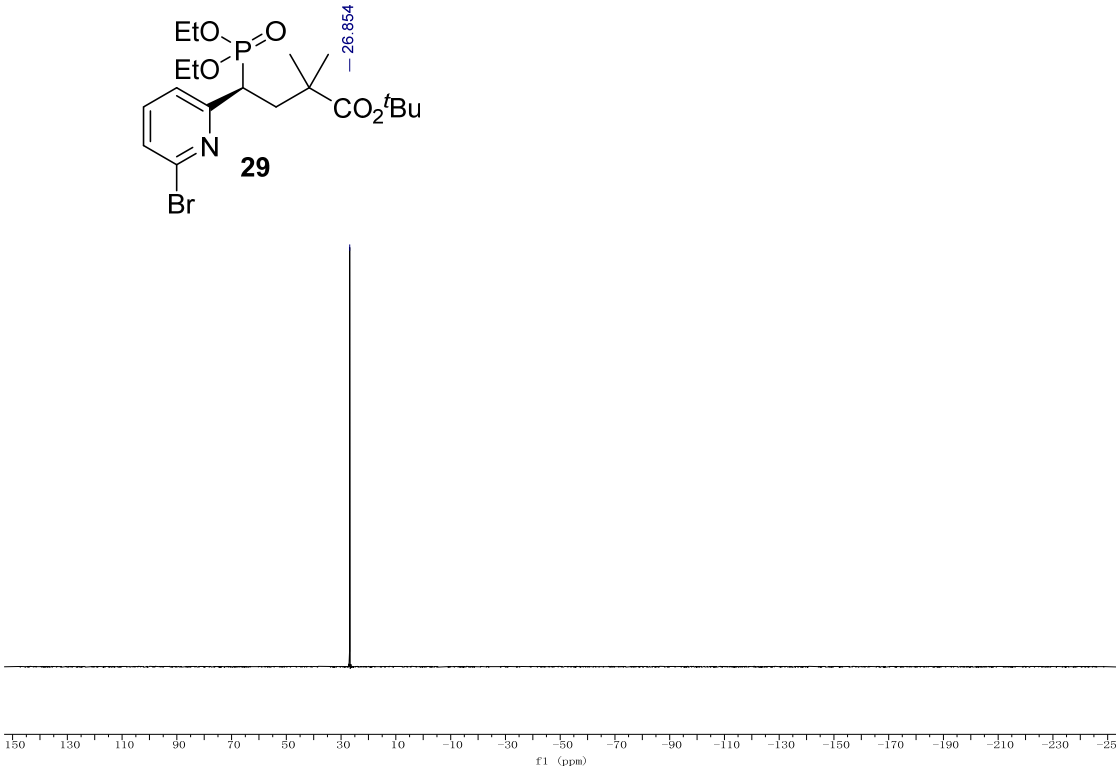
^{1}H NMR, 400 MHz, $CDCl_3$



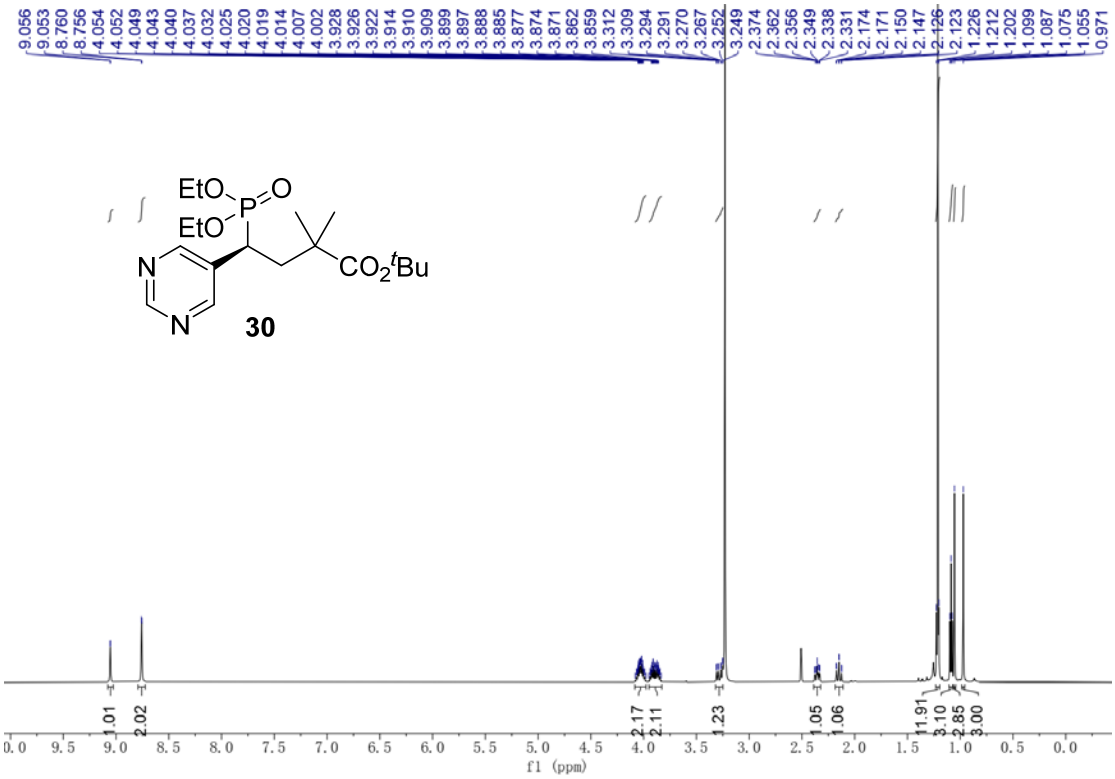
^{13}C NMR, 100 MHz, $CDCl_3$



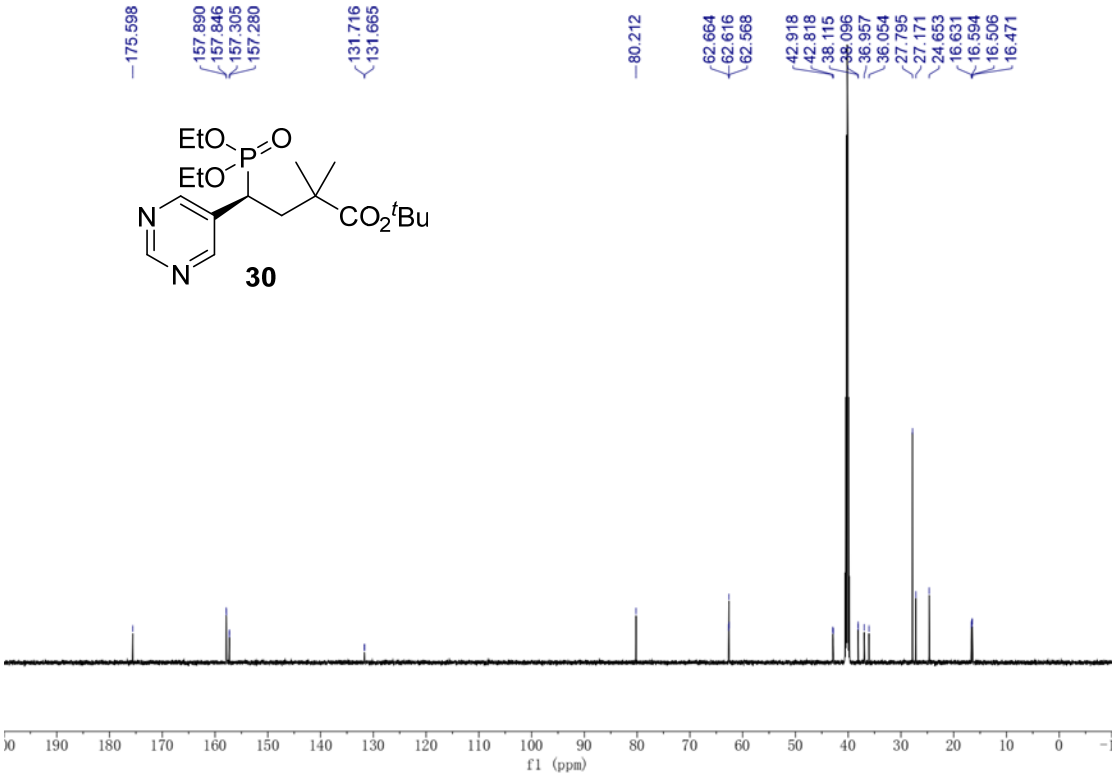
^{31}P NMR, 162 MHz, $CDCl_3$



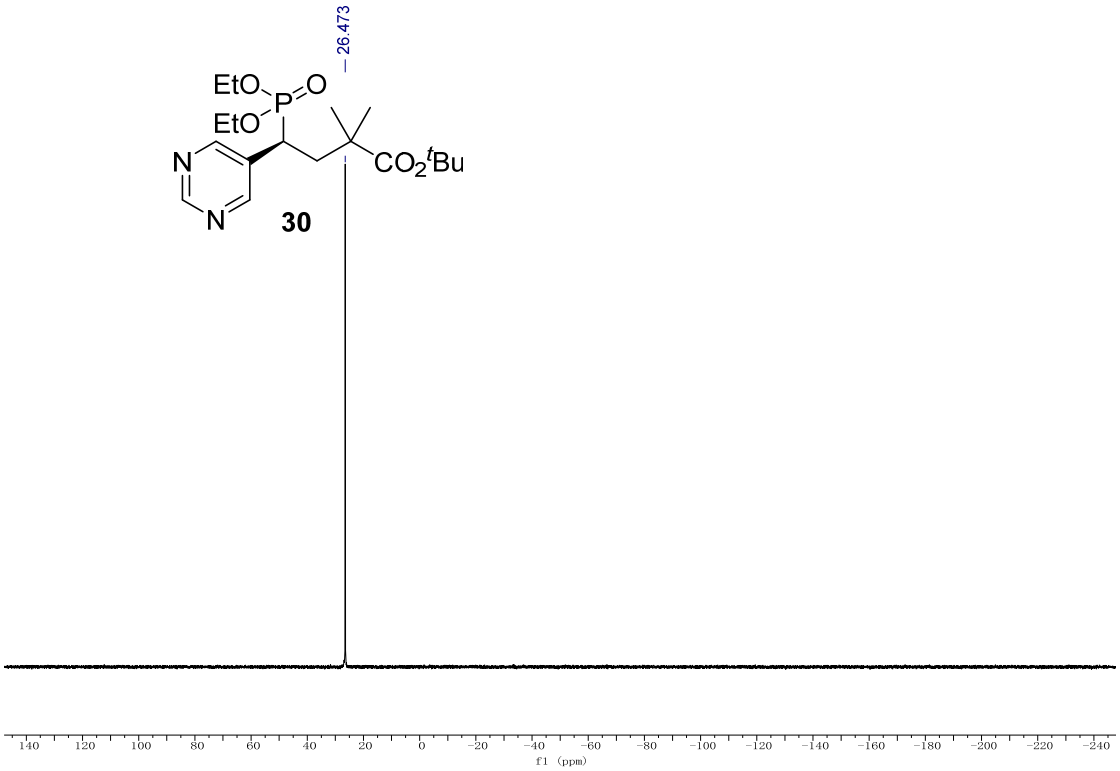
^{1}H NMR , 600 MHz, DMSO



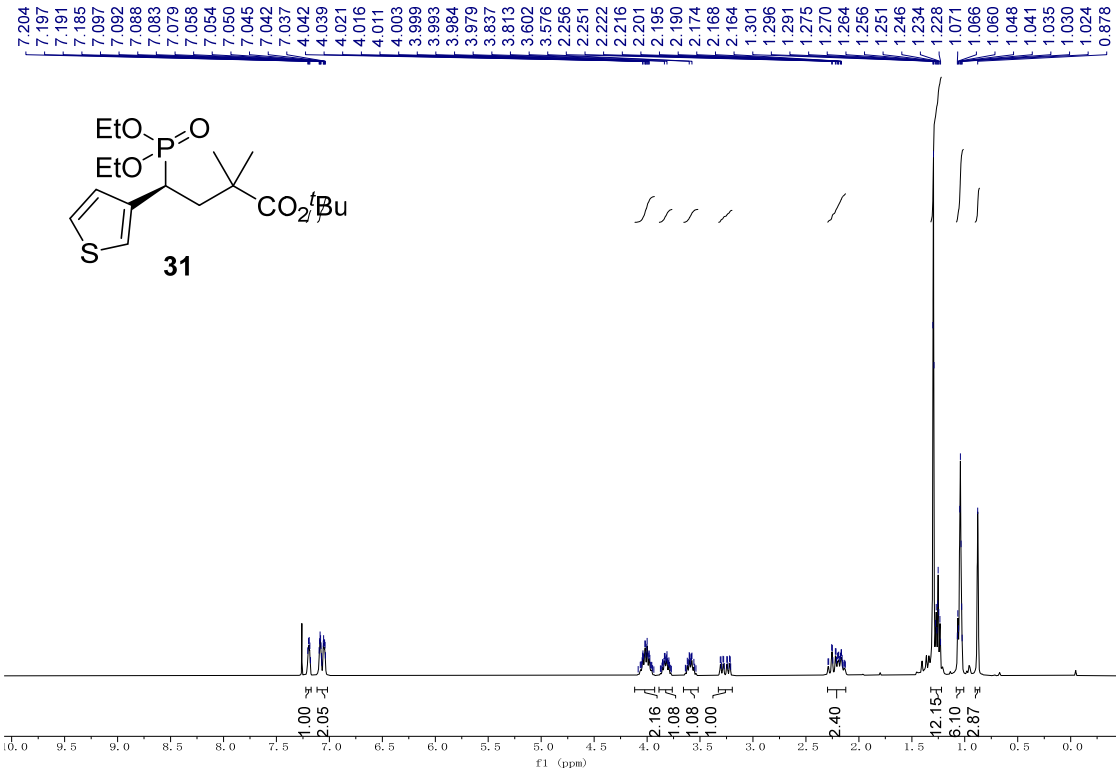
^{13}C NMR, 150 MHz, DMSO



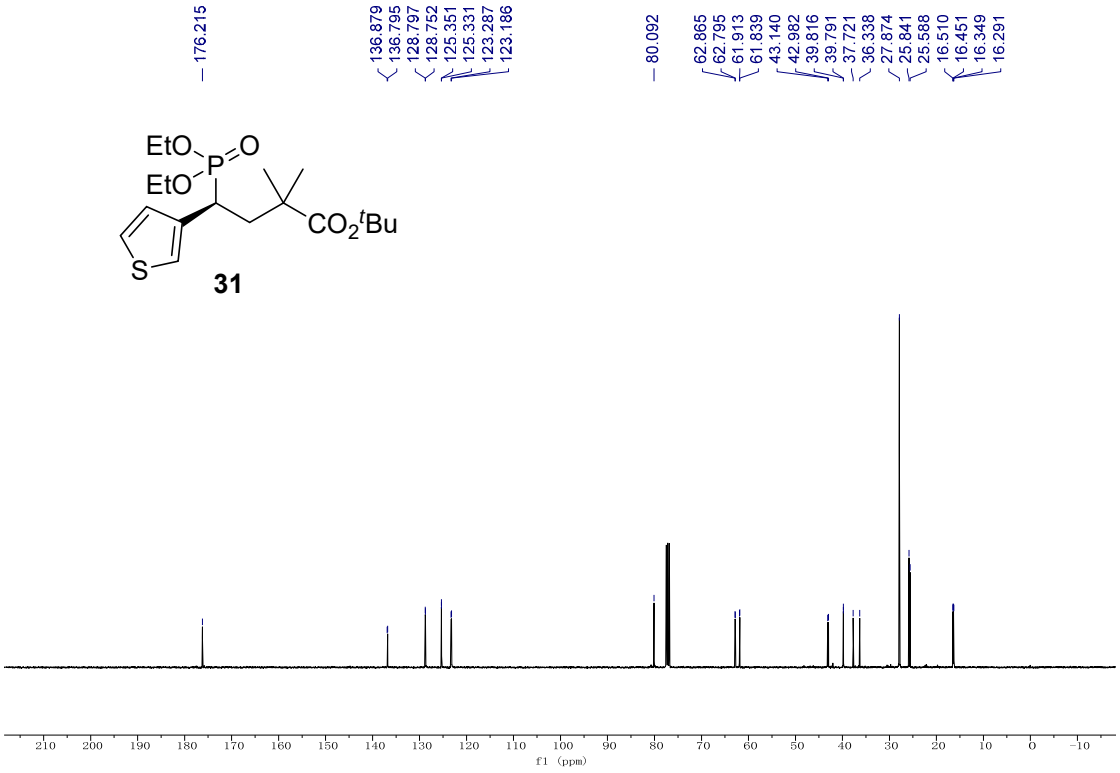
^{31}P NMR, 243 MHz, DMSO



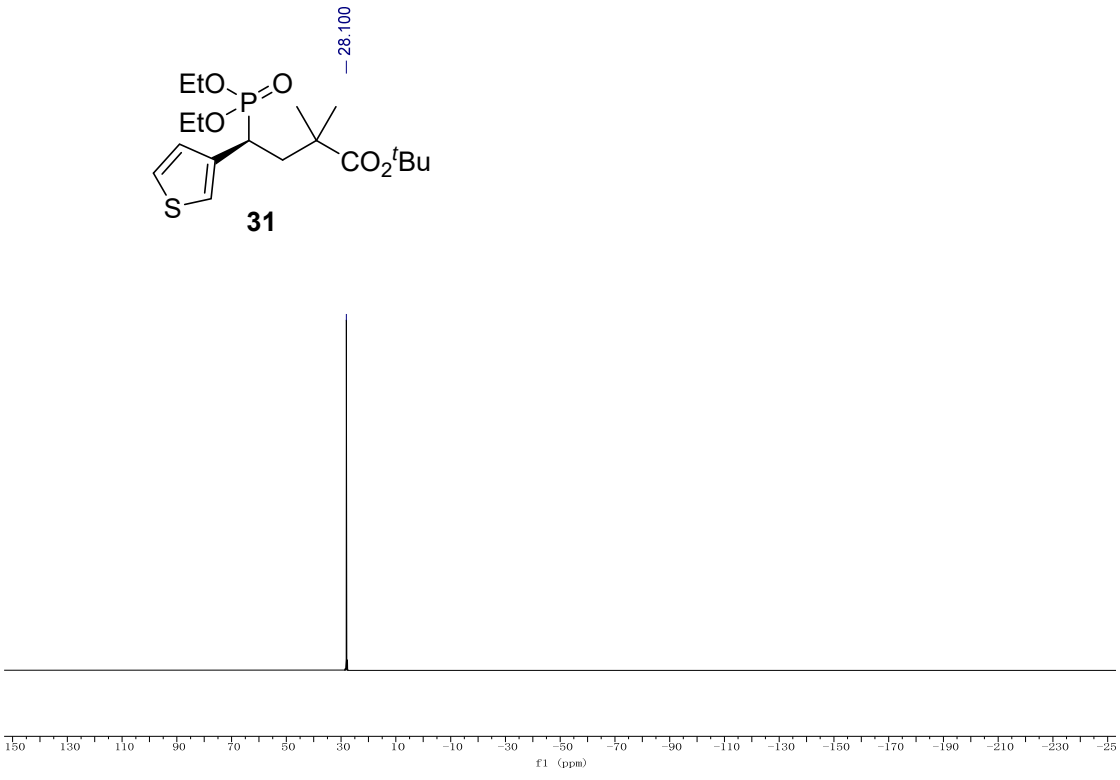
^{1}H NMR, 400 MHz, $CDCl_3$



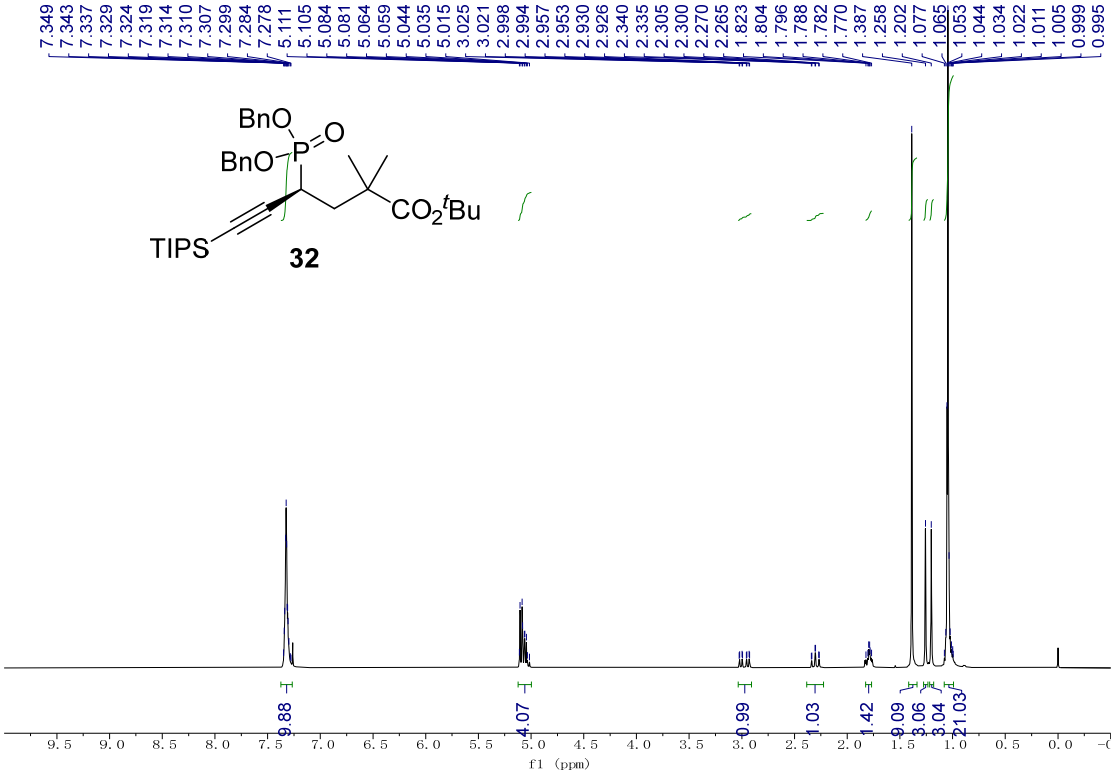
^{13}C NMR, 100 MHz, $CDCl_3$



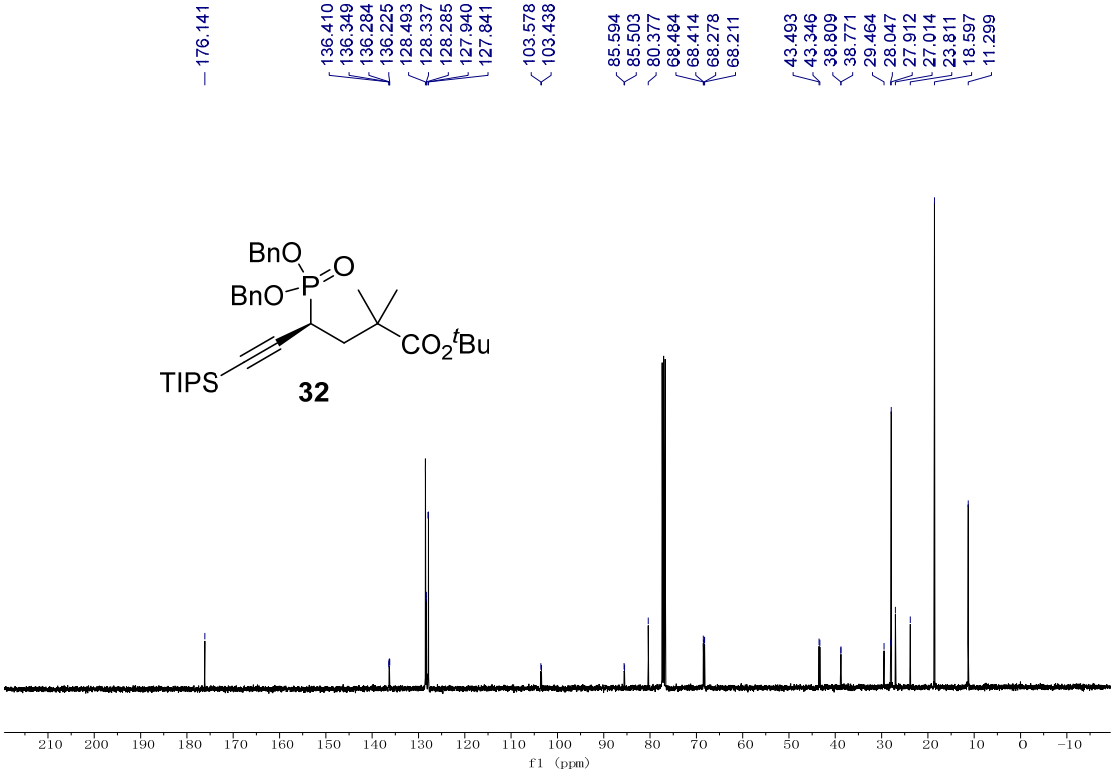
^{31}P NMR, 162 MHz, $CDCl_3$



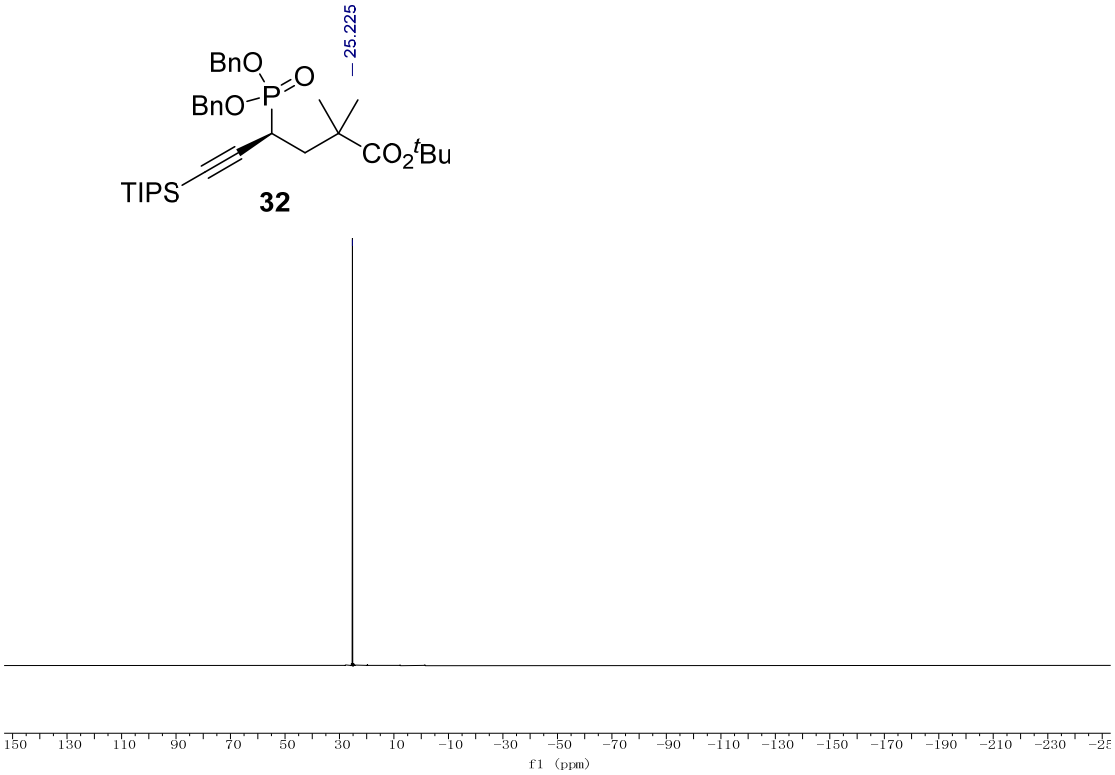
^{1}H NMR, 400 MHz, $CDCl_3$



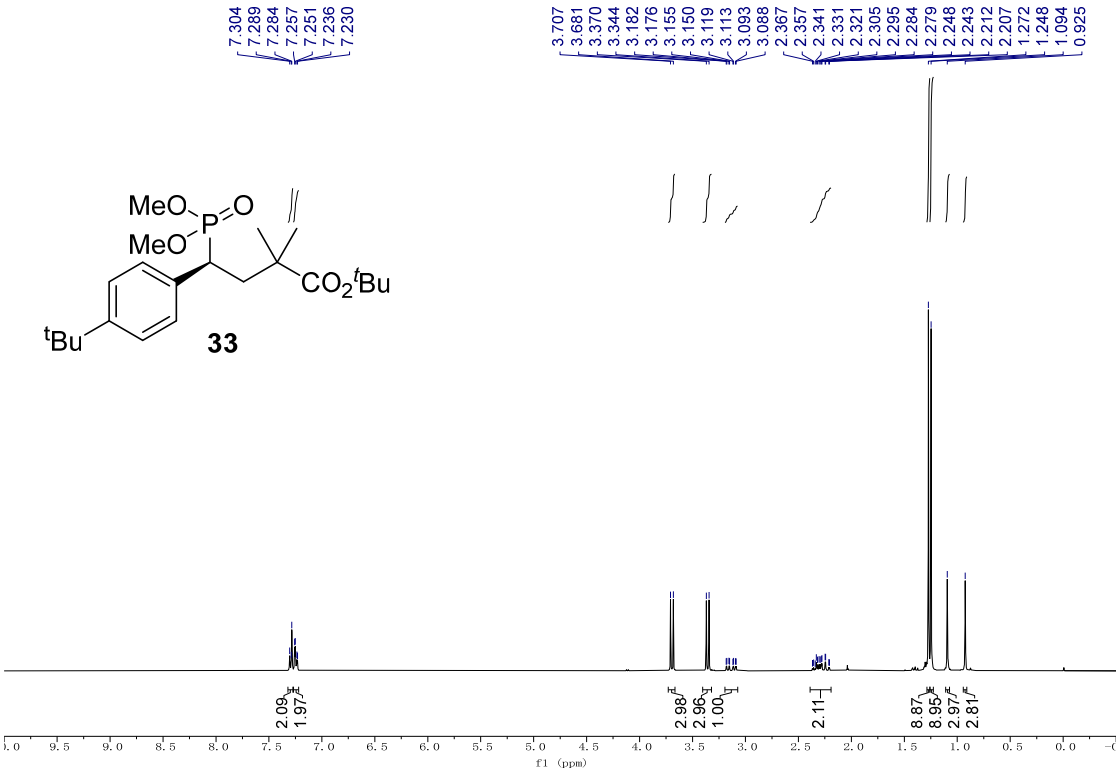
^{13}C NMR, 100 MHz, $CDCl_3$



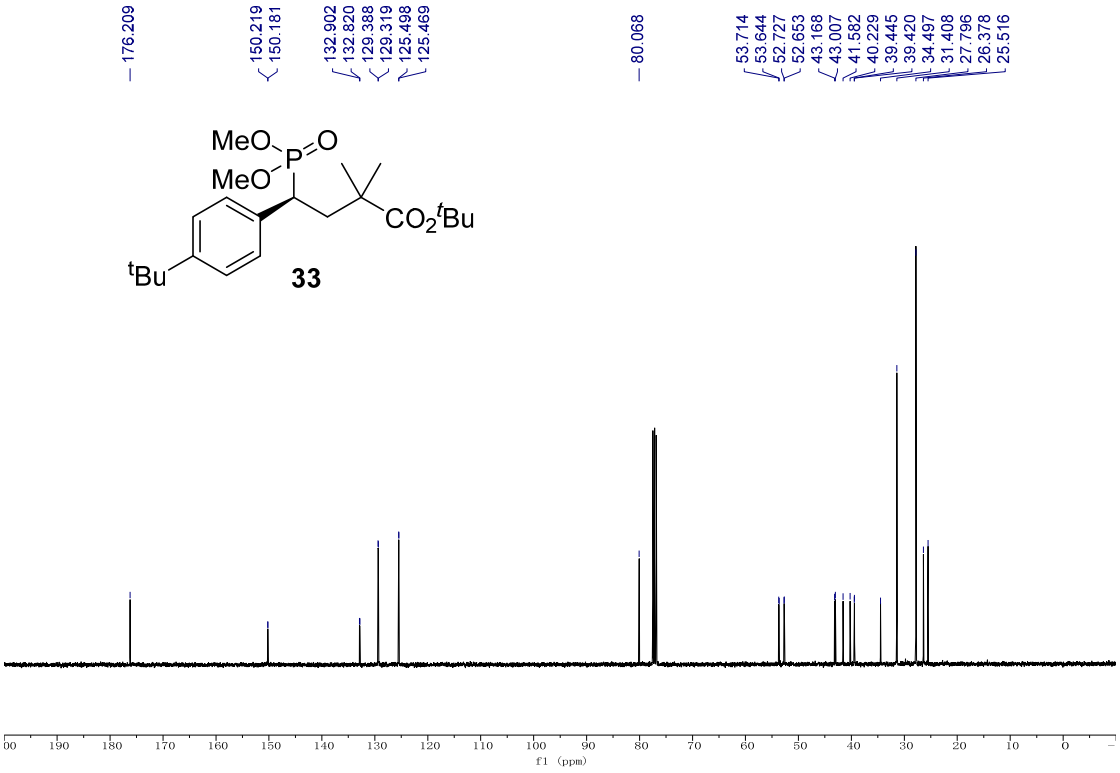
^{31}P NMR, 162 MHz, $CDCl_3$



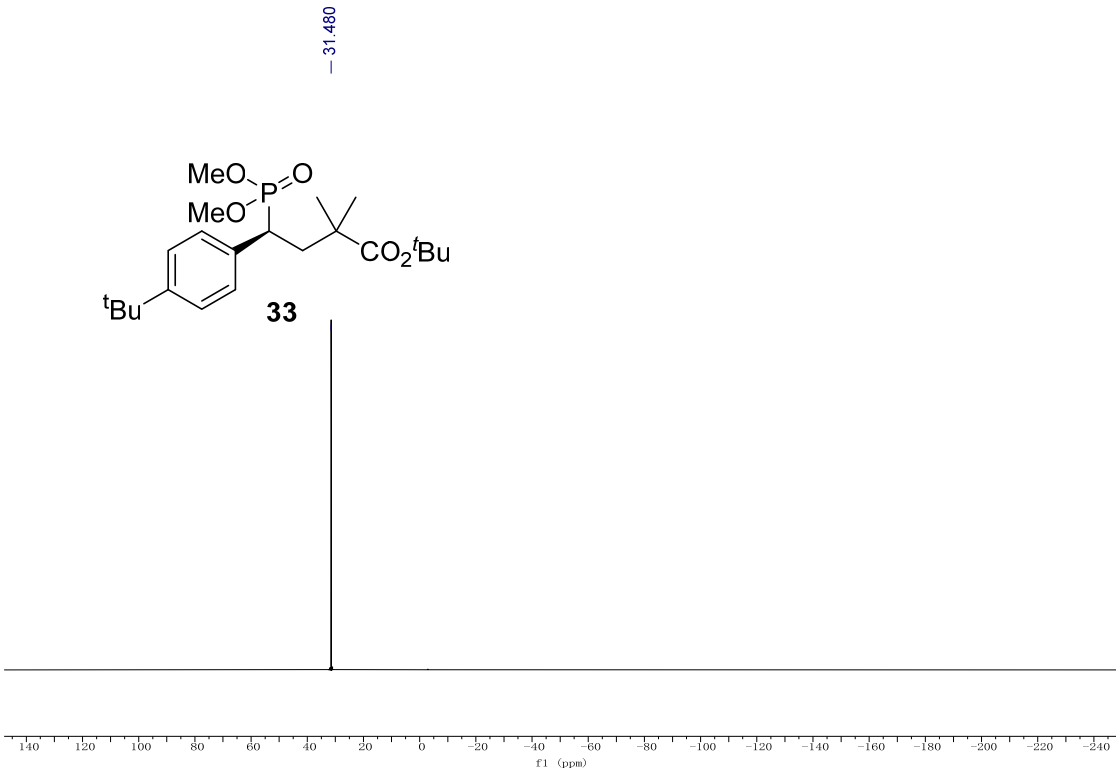
^{1}H NMR, 400 MHz, $CDCl_3$



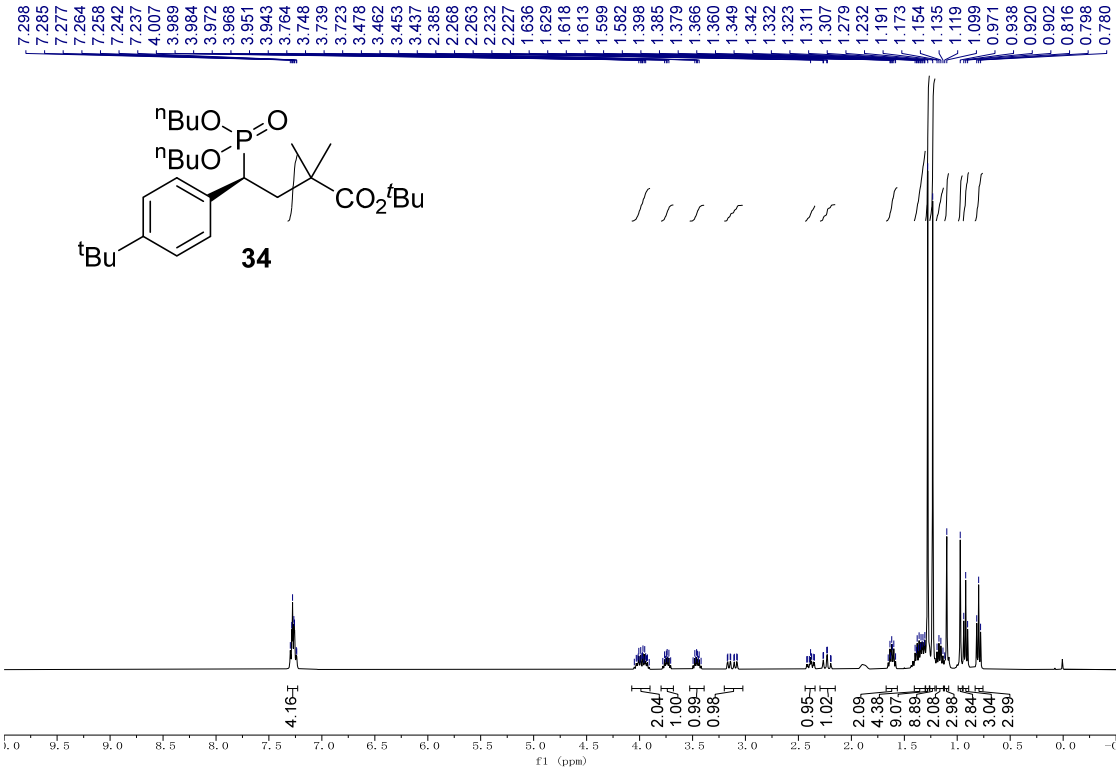
^{13}C NMR, 100 MHz, $CDCl_3$



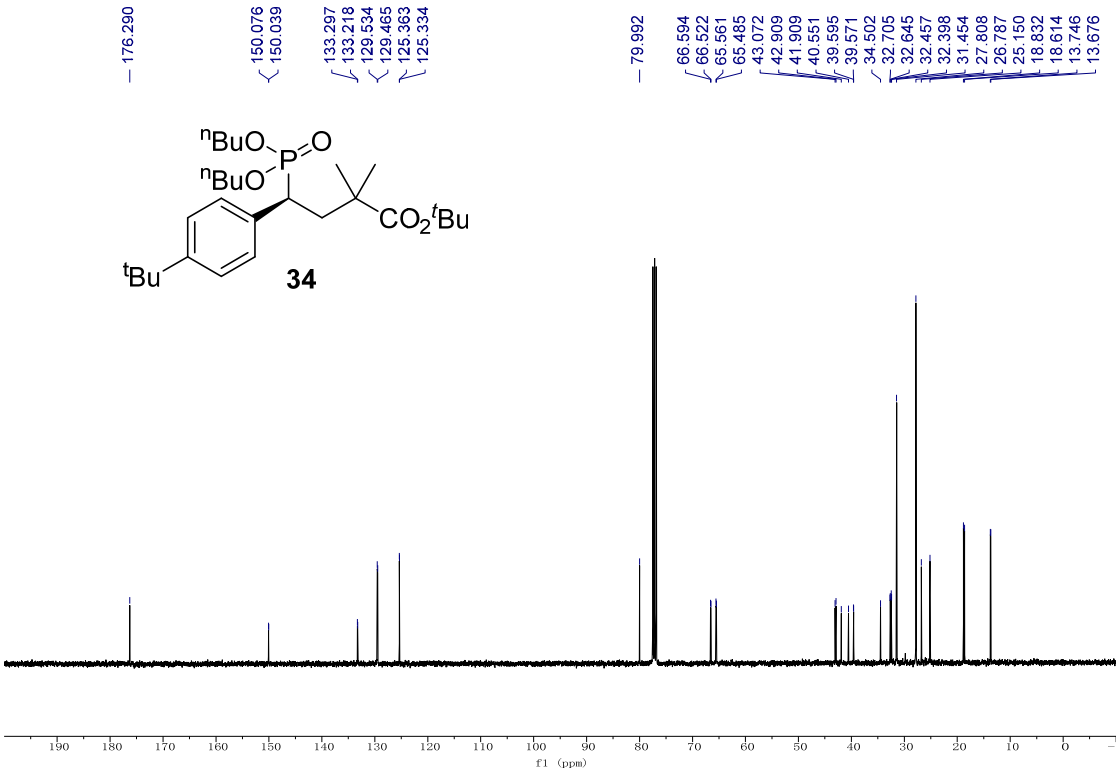
^{31}P NMR, 162 MHz, $CDCl_3$



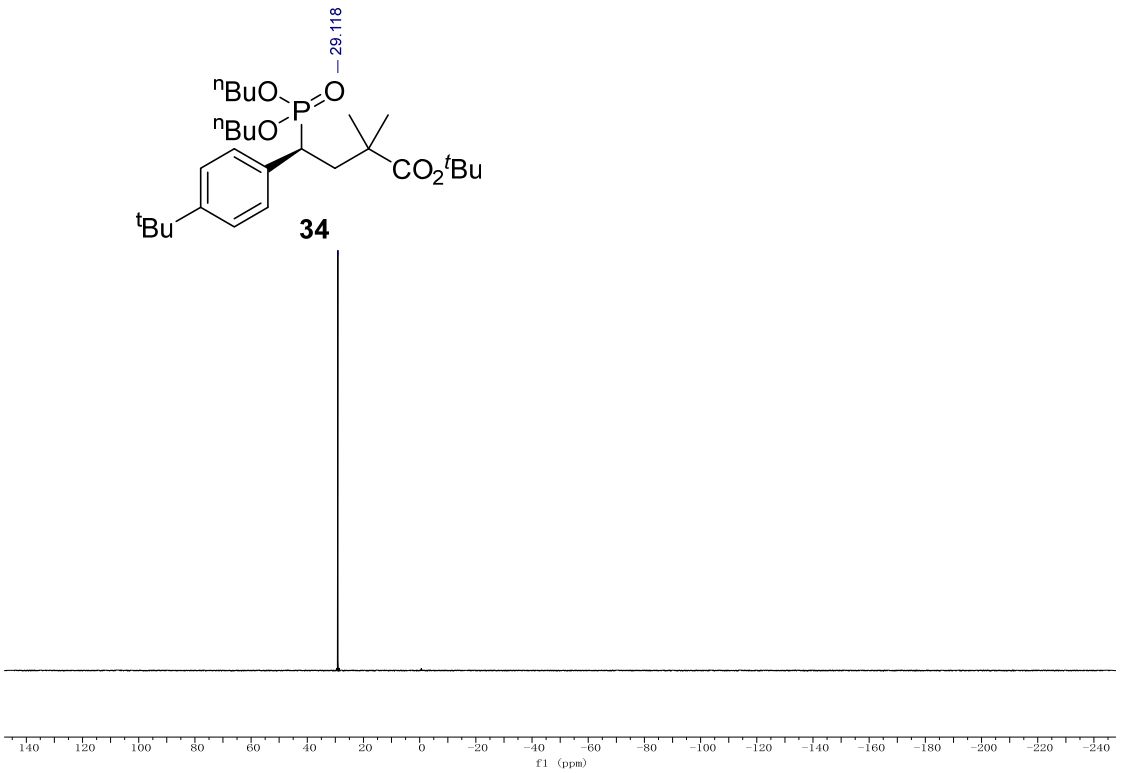
^{1}H NMR, 400 MHz, $CDCl_3$



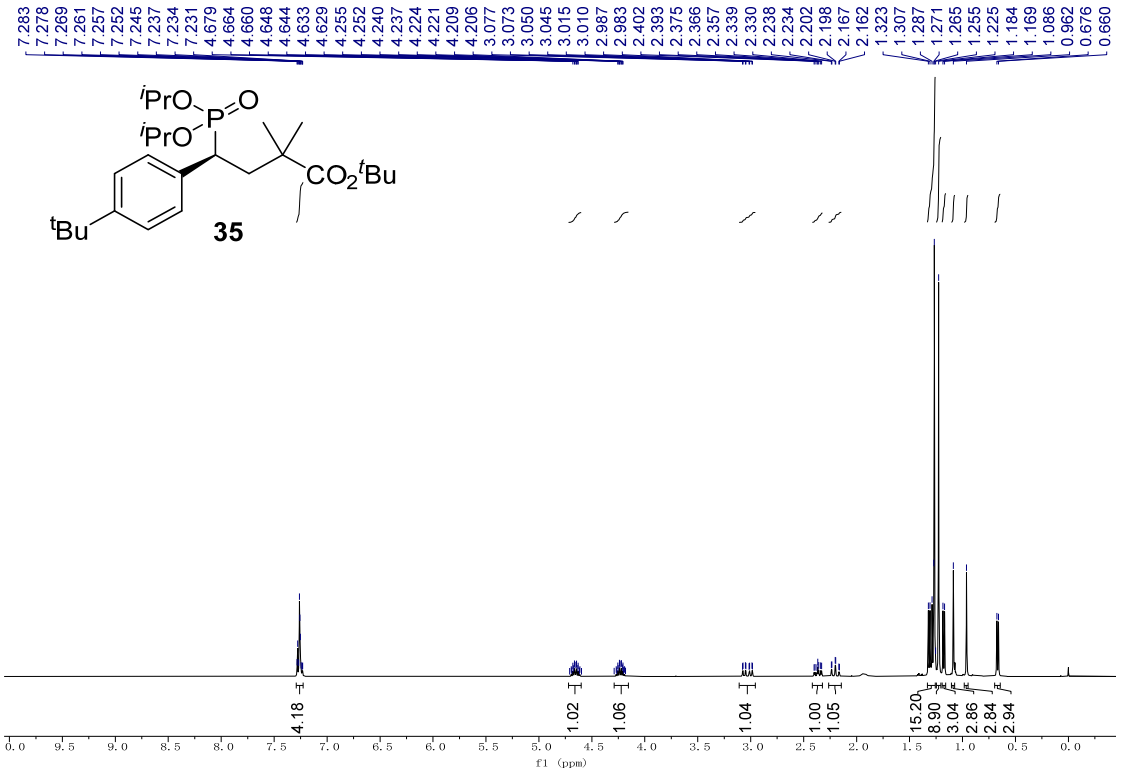
^{13}C NMR, 100 MHz, $CDCl_3$



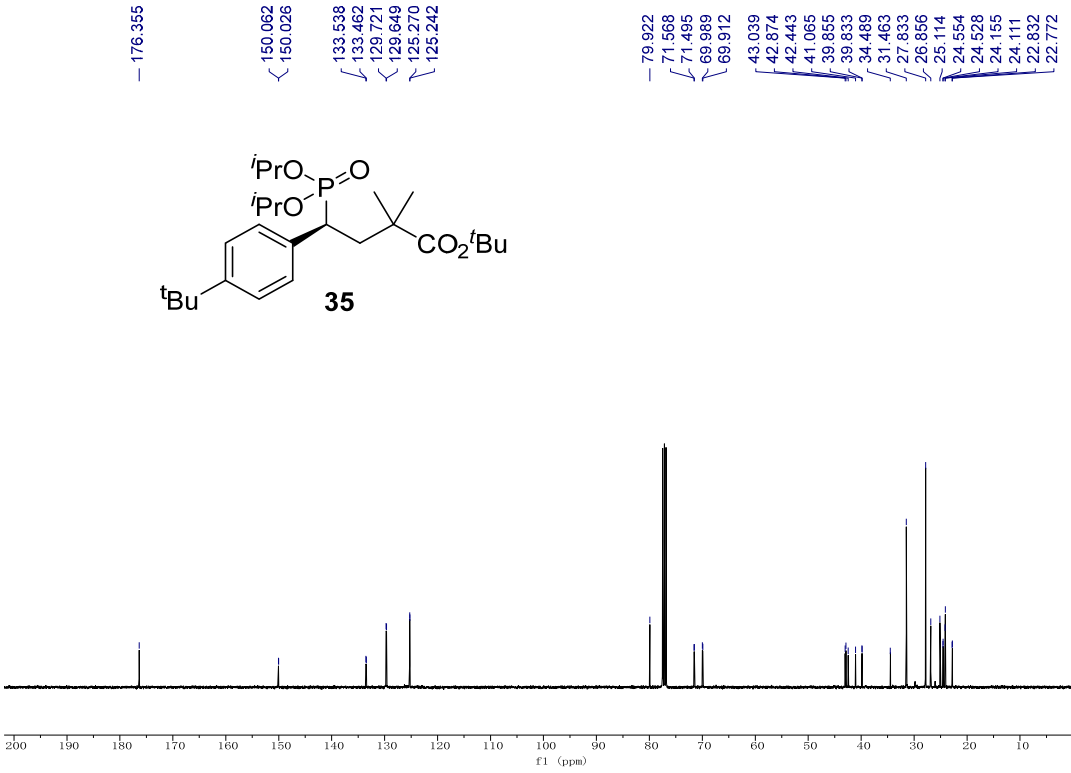
^{31}P NMR, 162 MHz, $CDCl_3$



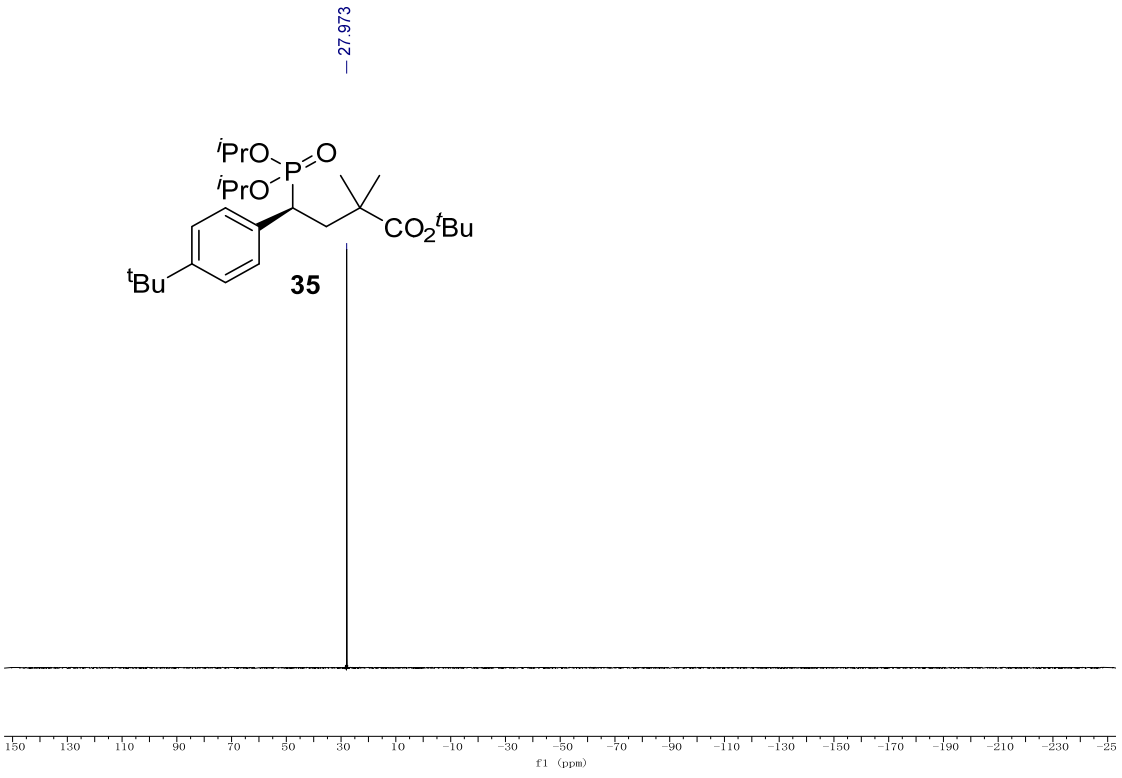
^{1}H NMR, 400 MHz, $CDCl_3$



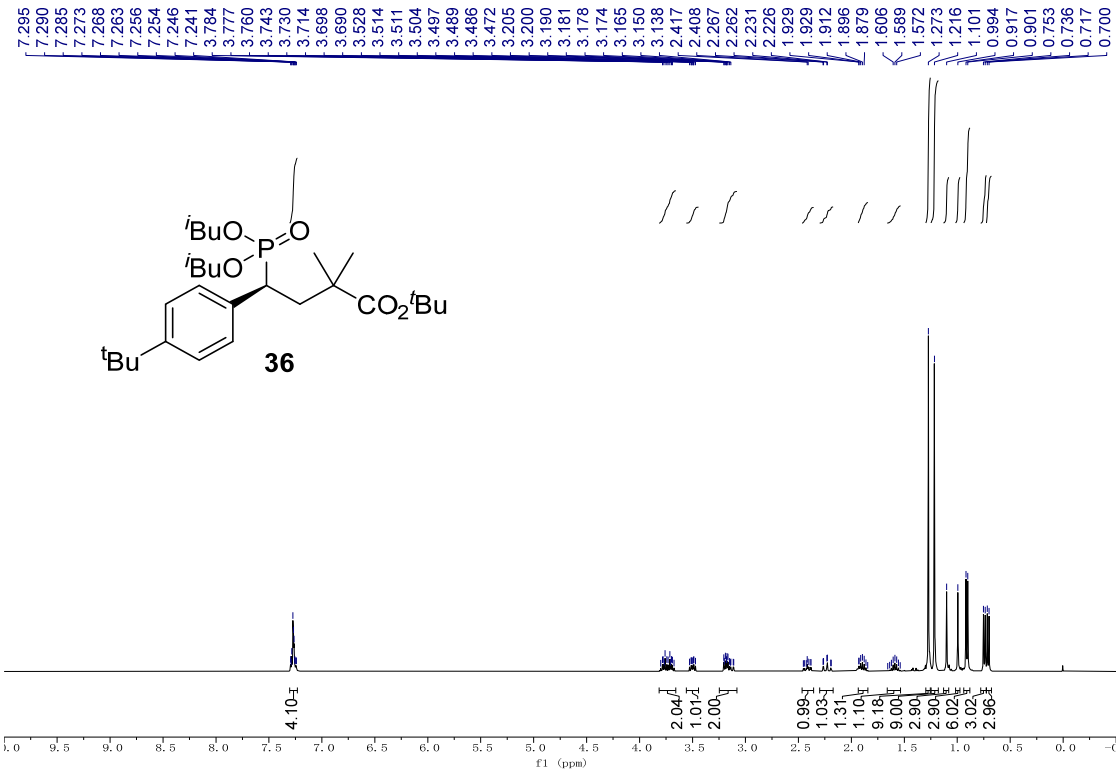
^{13}C NMR, 100 MHz, $CDCl_3$



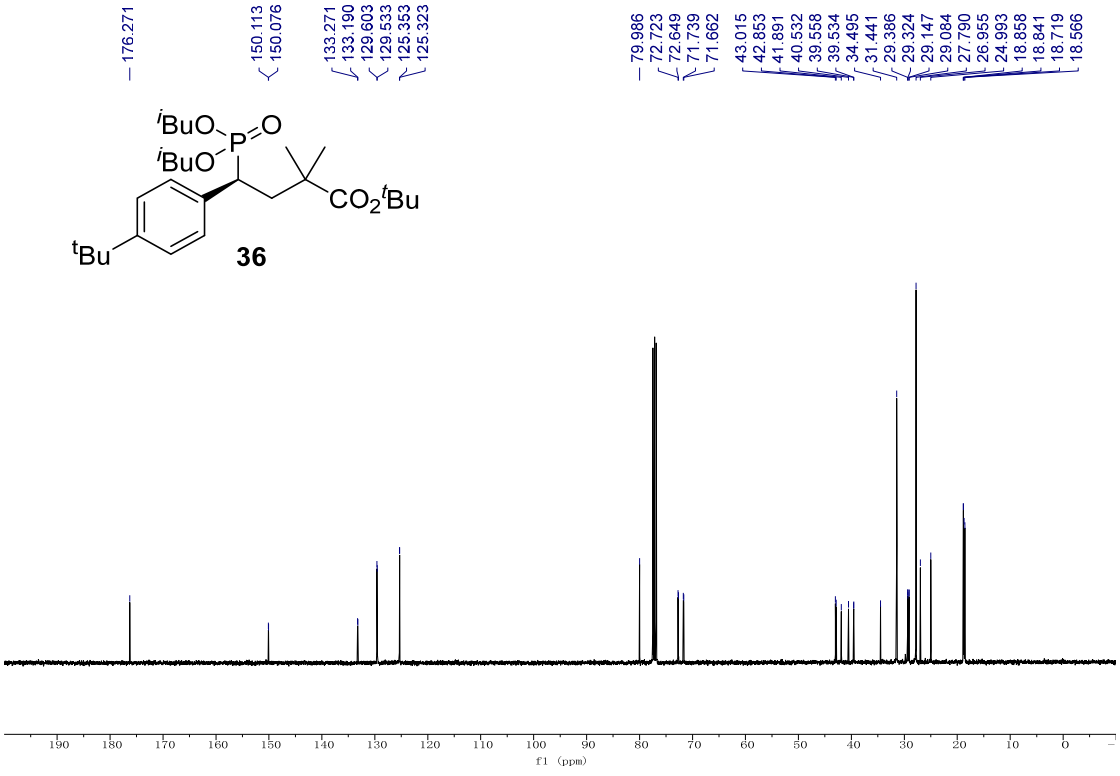
^{31}P NMR, 162 MHz, $CDCl_3$



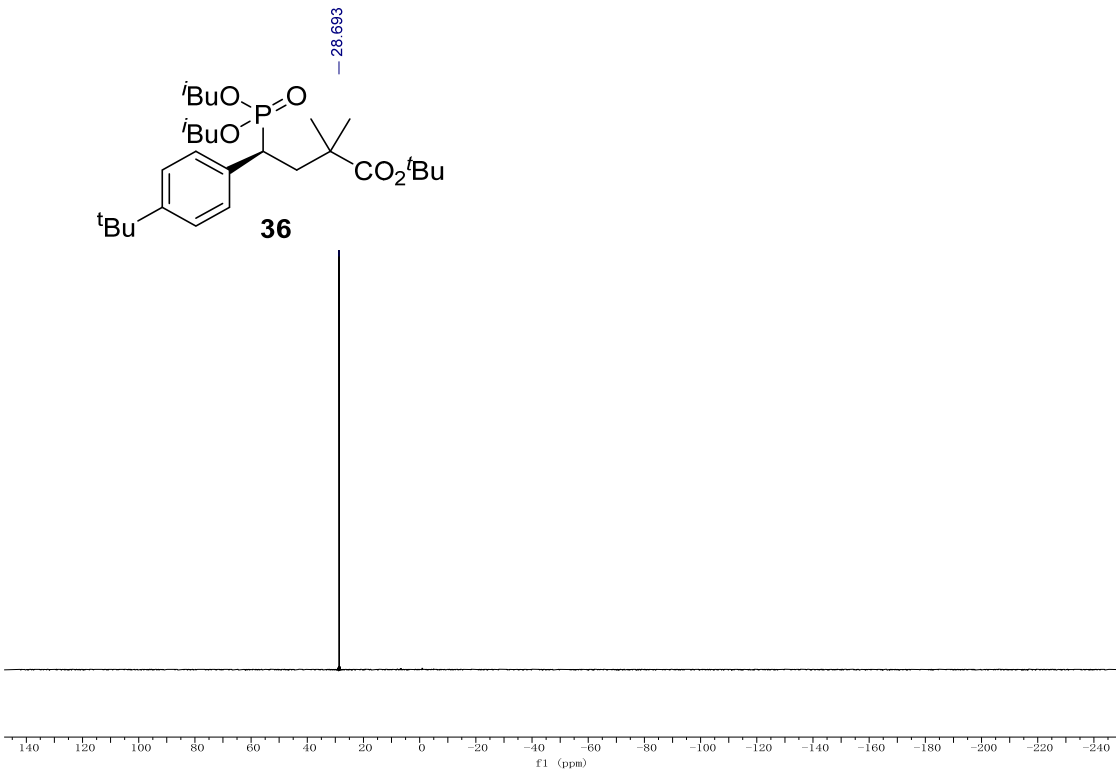
^{1}H NMR, 400 MHz, $CDCl_3$



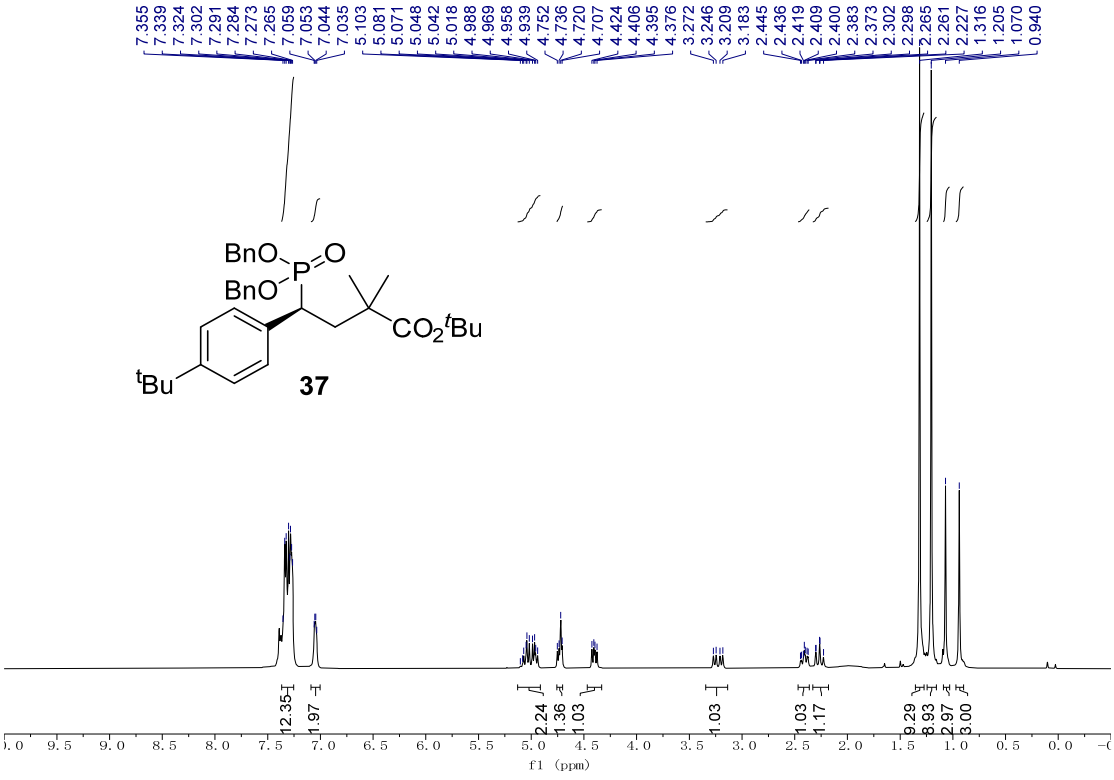
^{13}C NMR, 100 MHz, $CDCl_3$



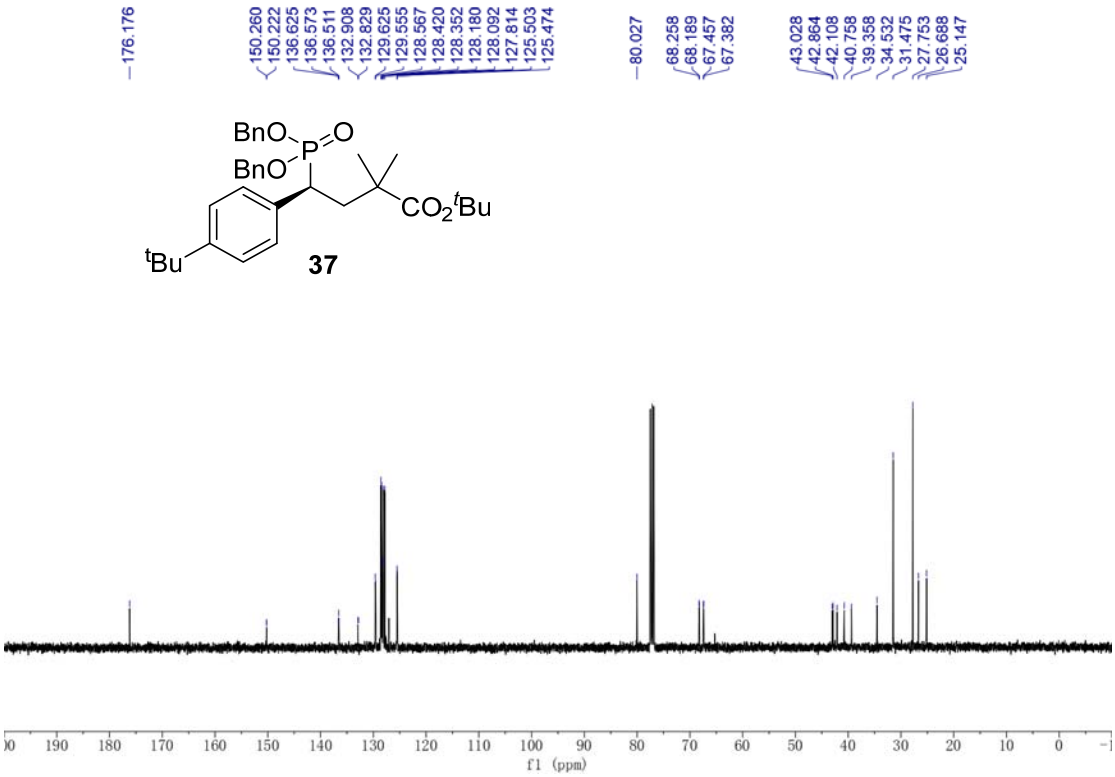
^{31}P NMR, 162 MHz, $CDCl_3$



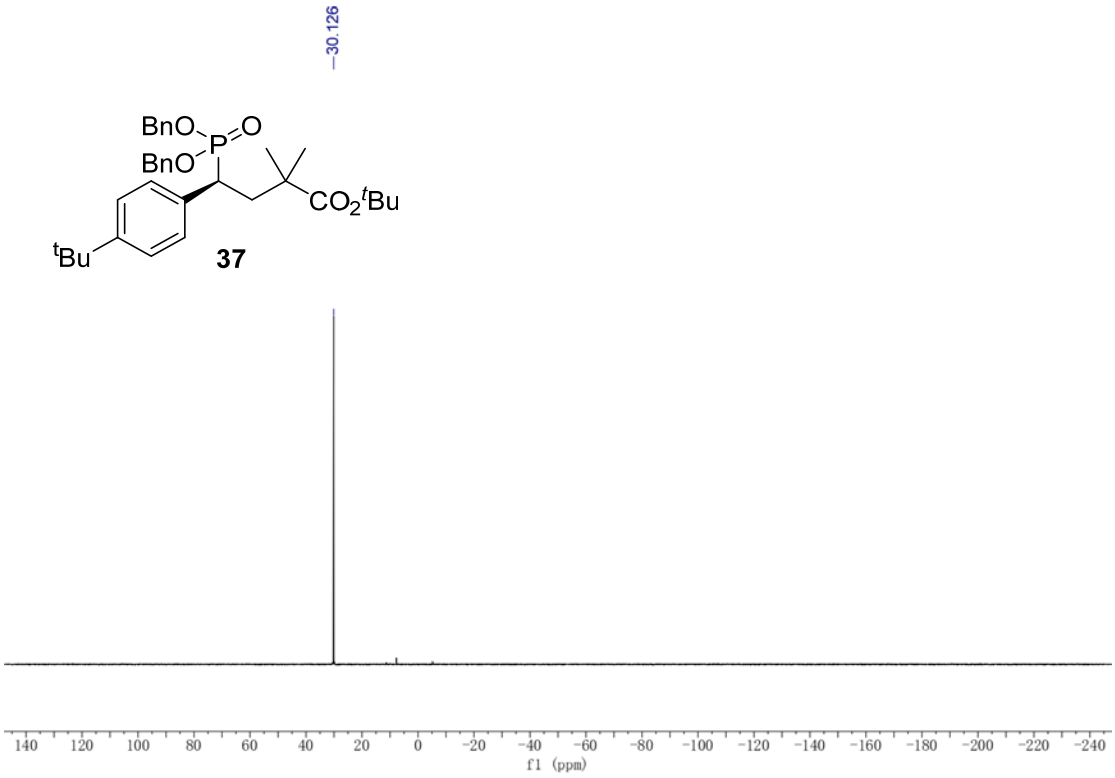
^{1}H NMR, 400 MHz, $CDCl_3$



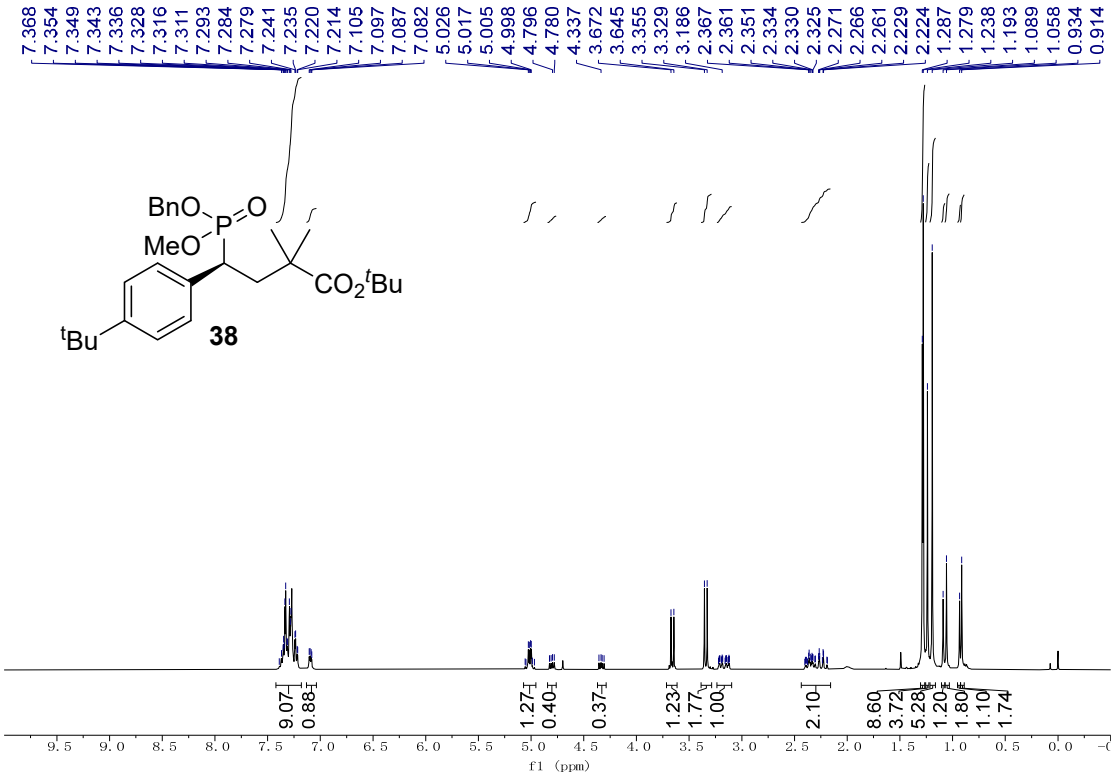
^{13}C NMR, 100 MHz, $CDCl_3$



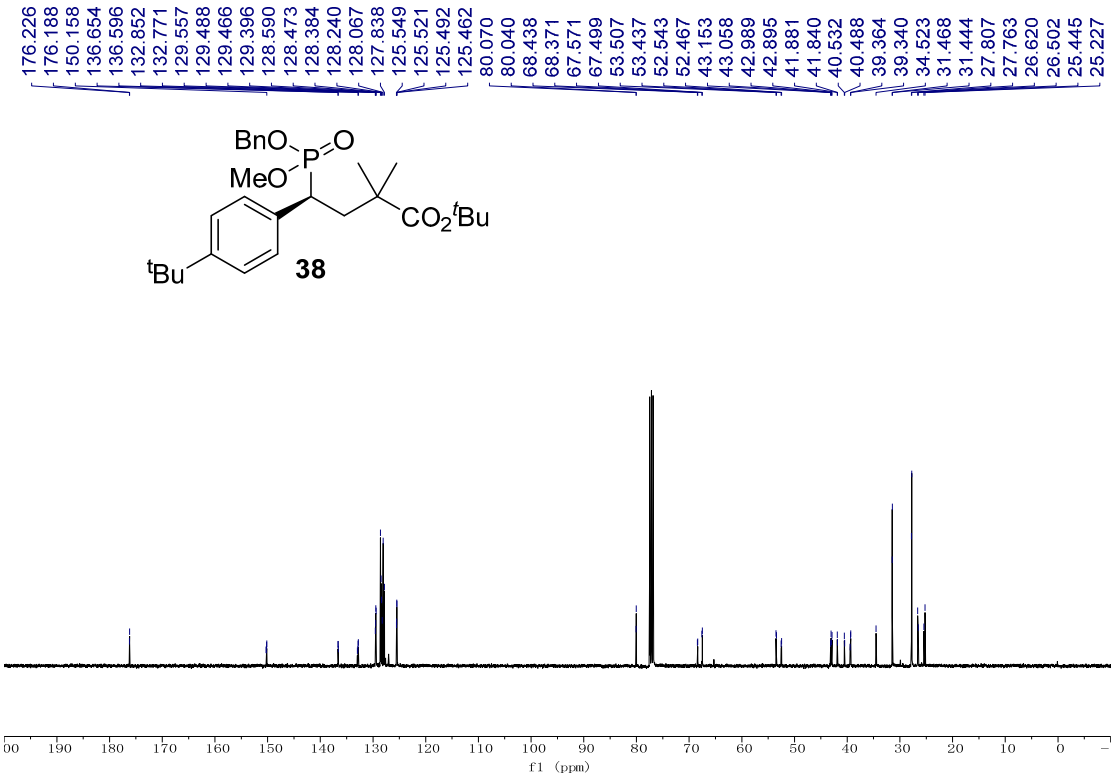
^{31}P NMR, 162 MHz, $CDCl_3$



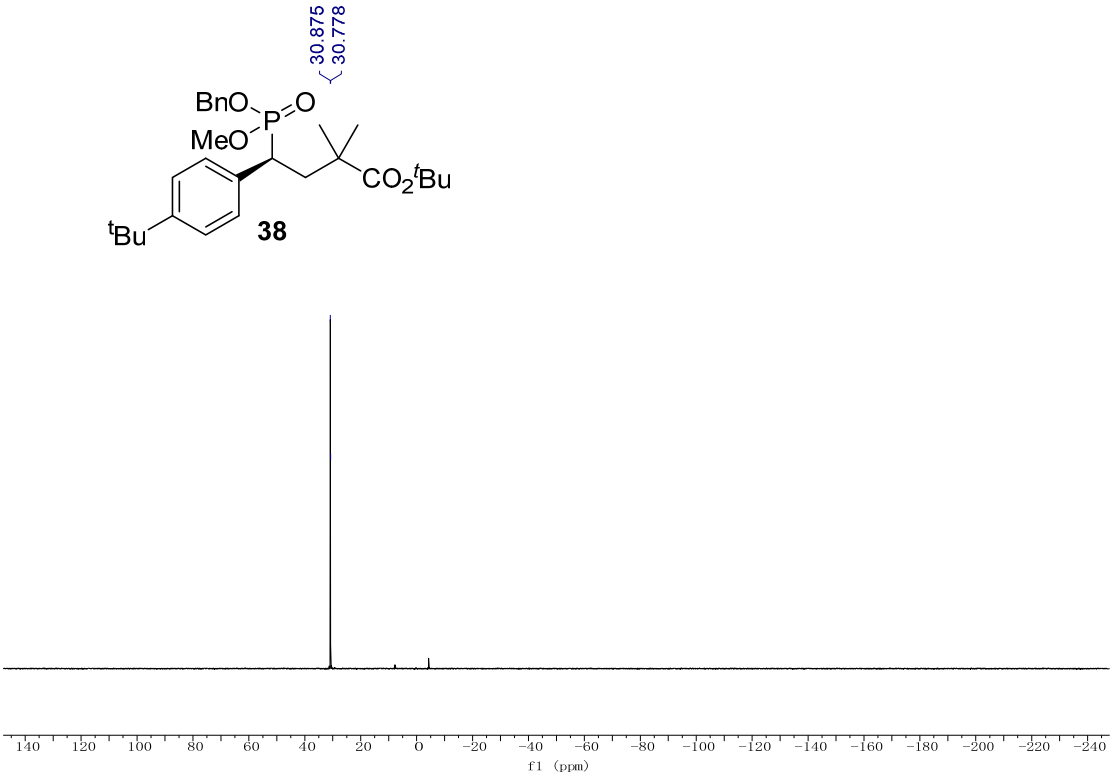
^{1}H NMR, 400 MHz, $CDCl_3$



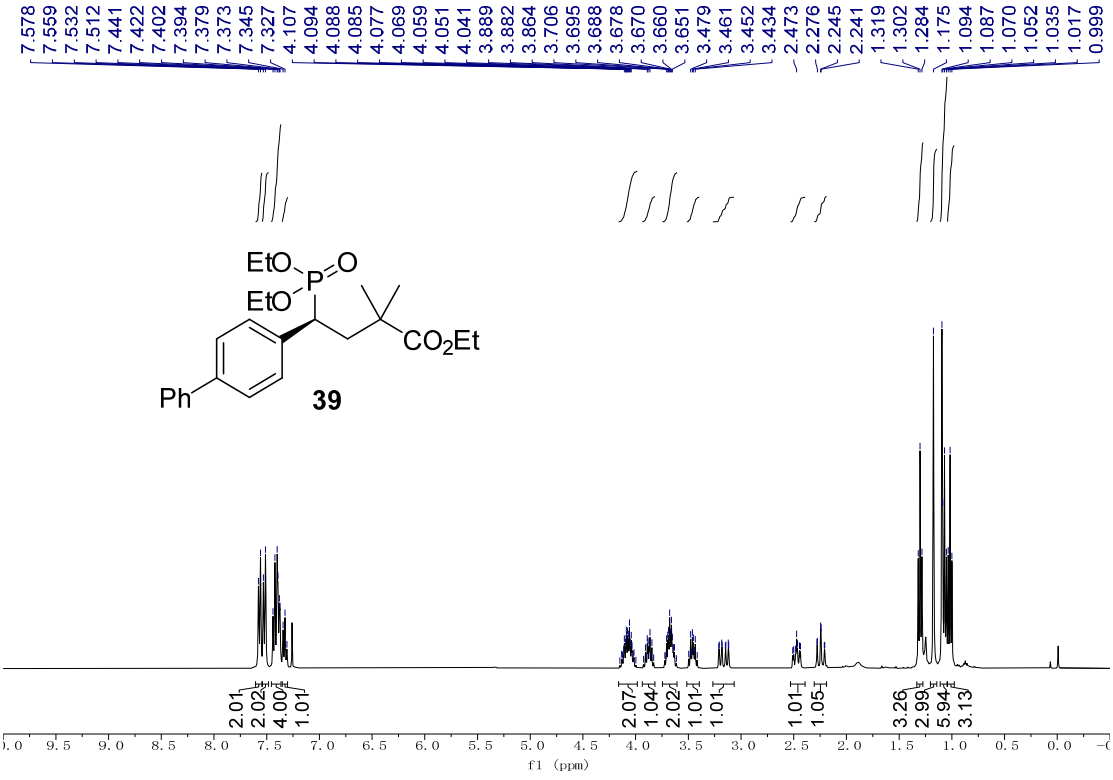
^{13}C NMR, 100 MHz, $CDCl_3$



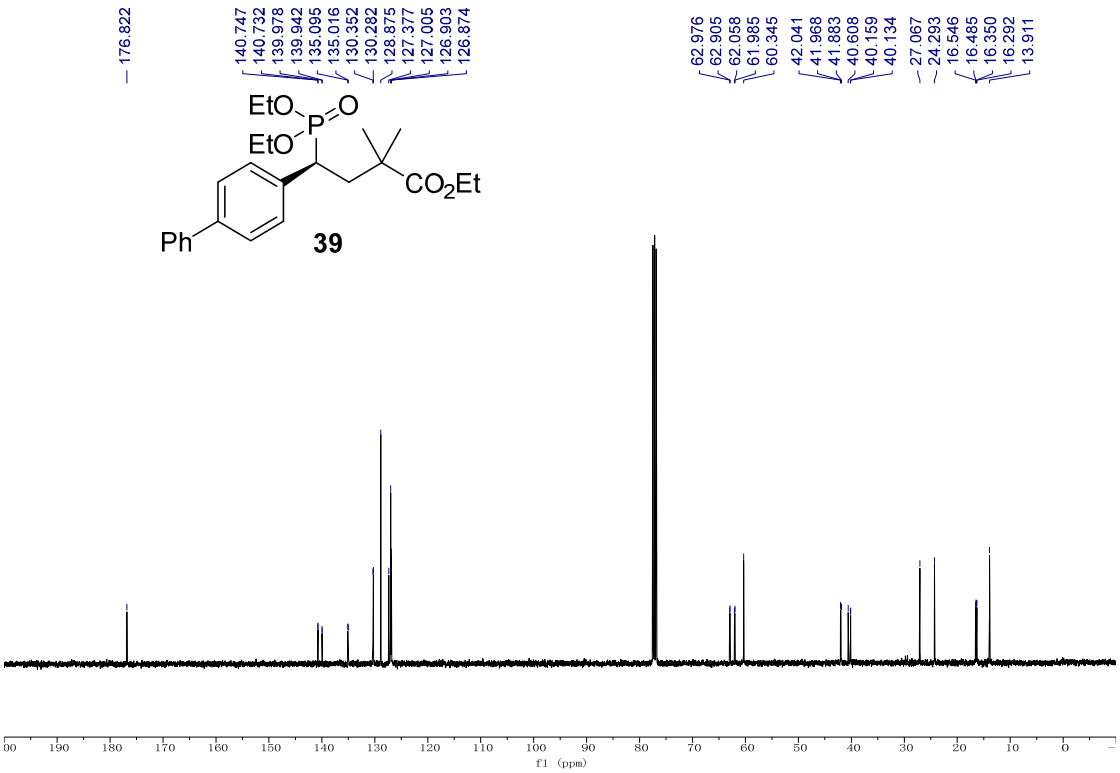
^{31}P NMR, 162 MHz, $CDCl_3$



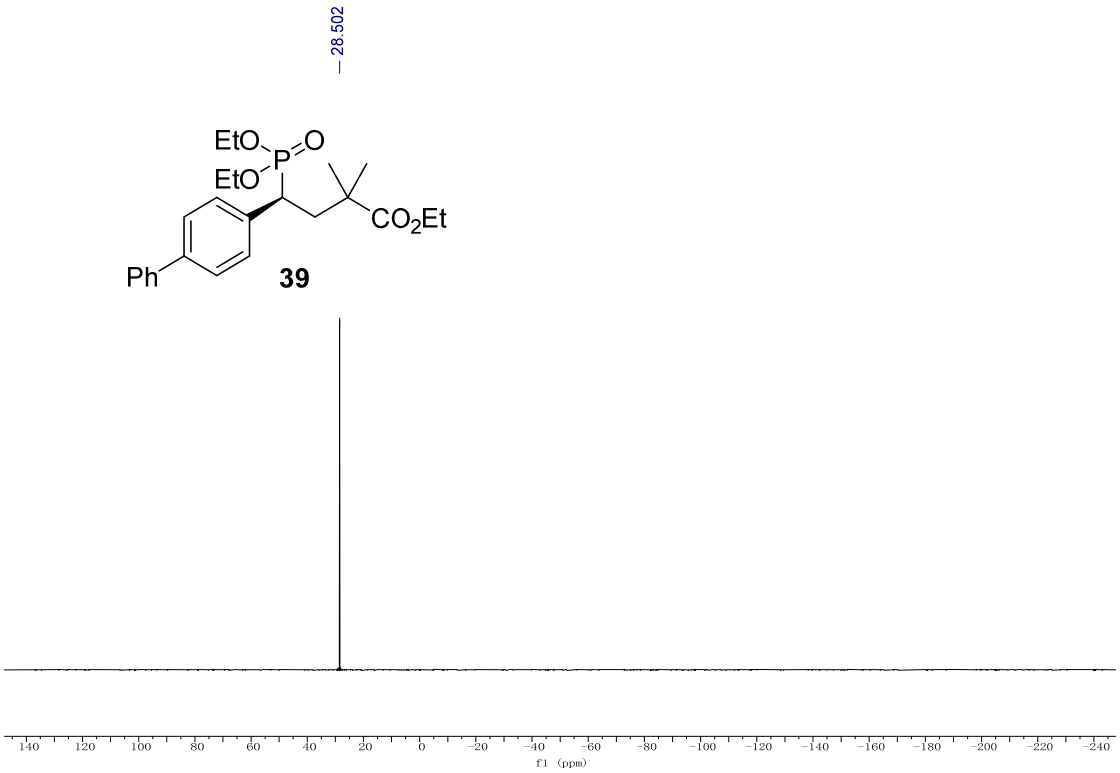
^{1}H NMR, 400 MHz, $CDCl_3$



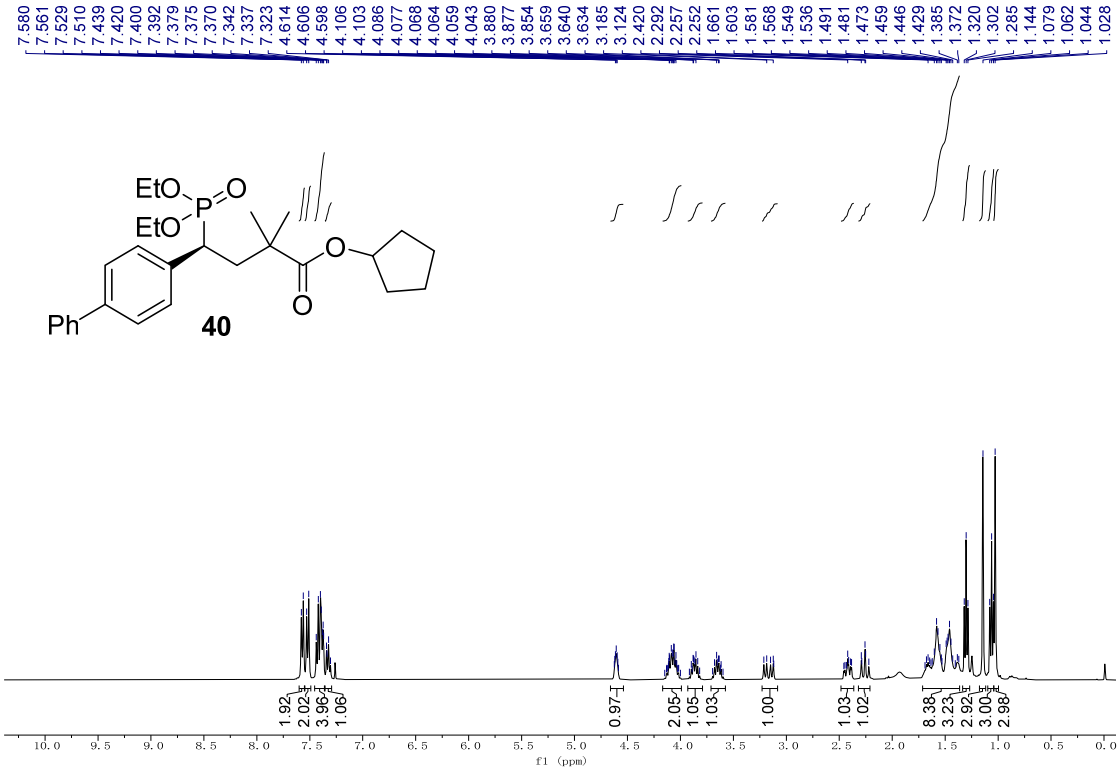
^{13}C NMR, 100 MHz, $CDCl_3$



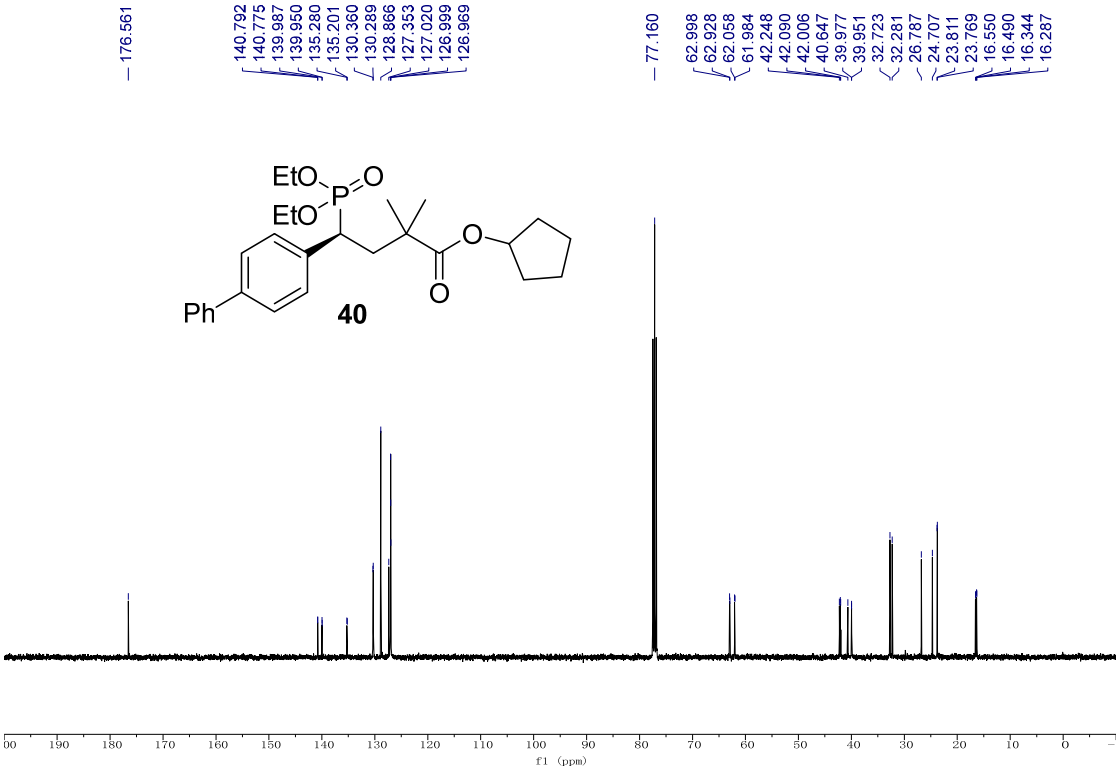
^{31}P NMR, 162 MHz, $CDCl_3$



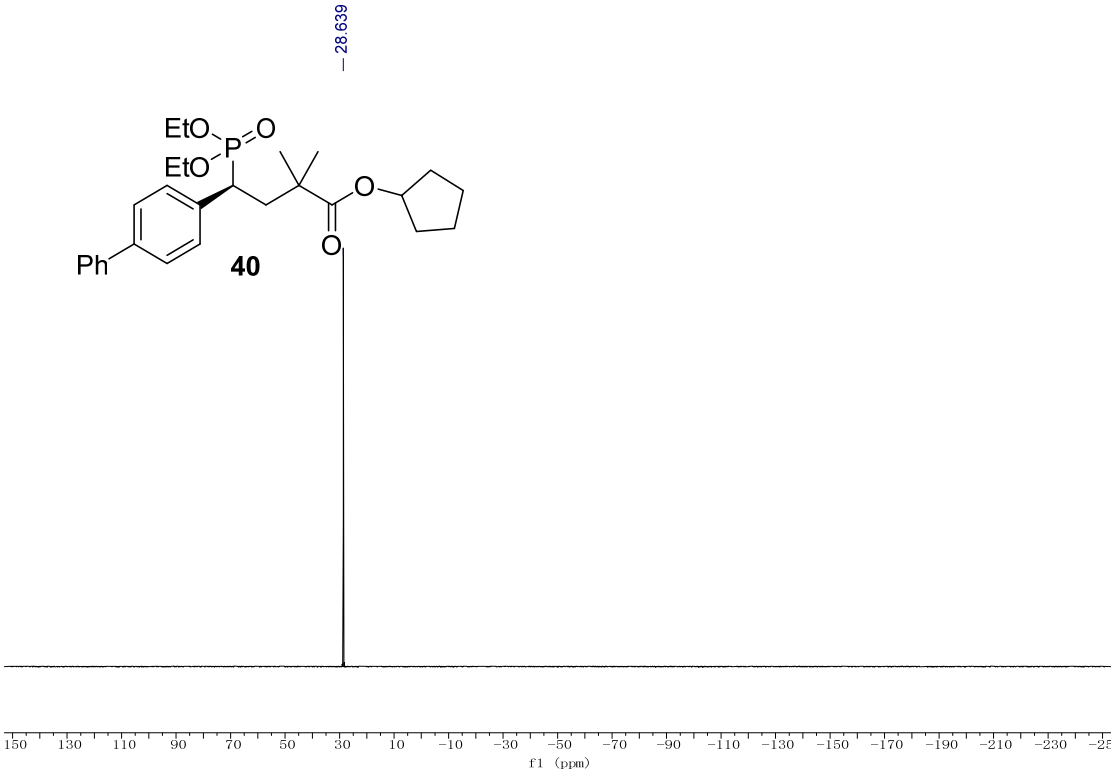
^{1}H NMR, 400 MHz, $CDCl_3$



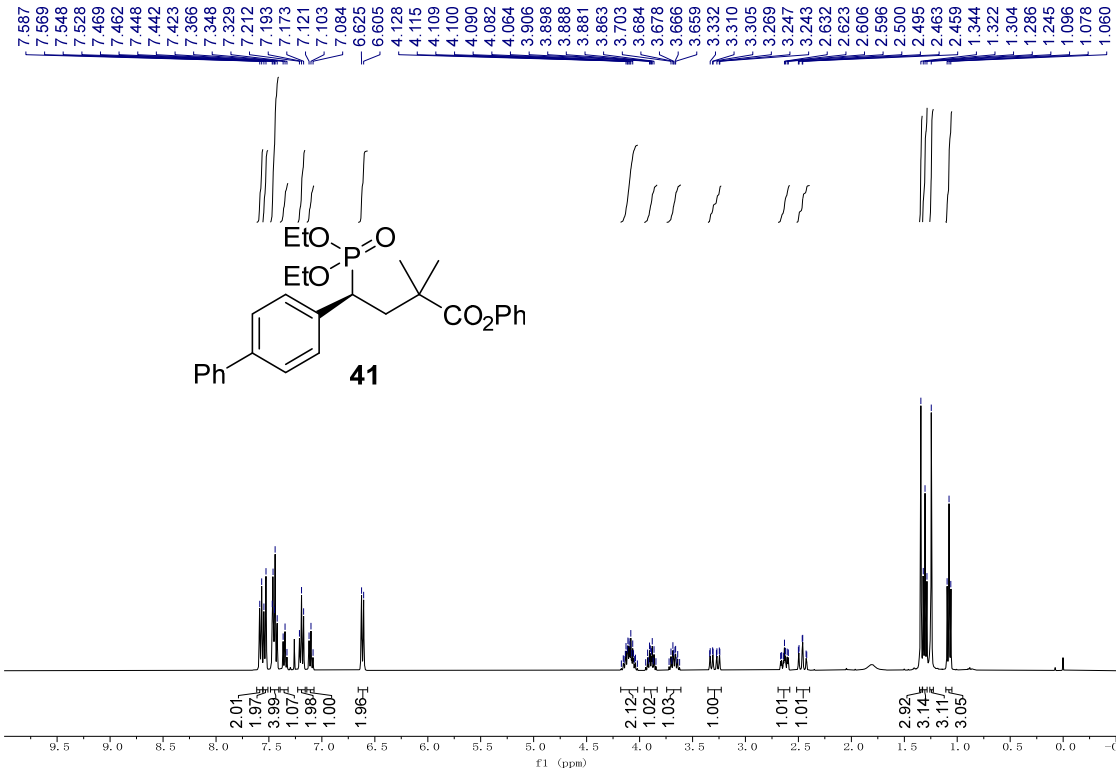
^{13}C NMR, 100 MHz, $CDCl_3$



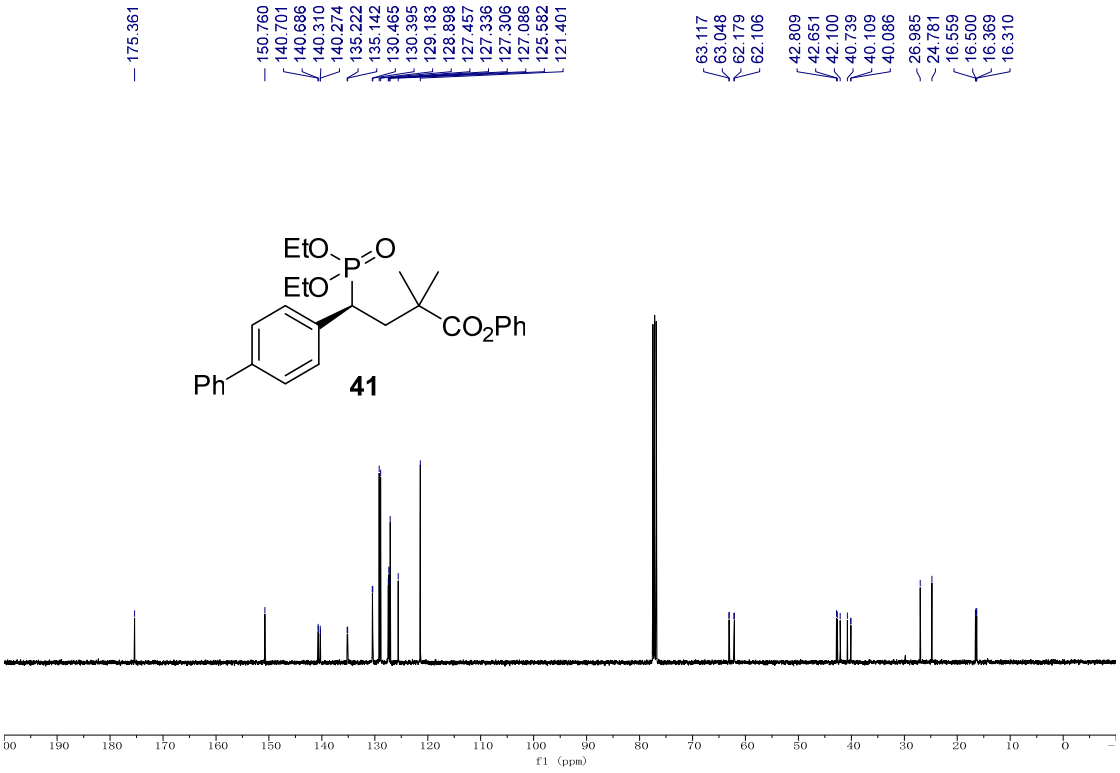
^{31}P NMR, 162 MHz, $CDCl_3$



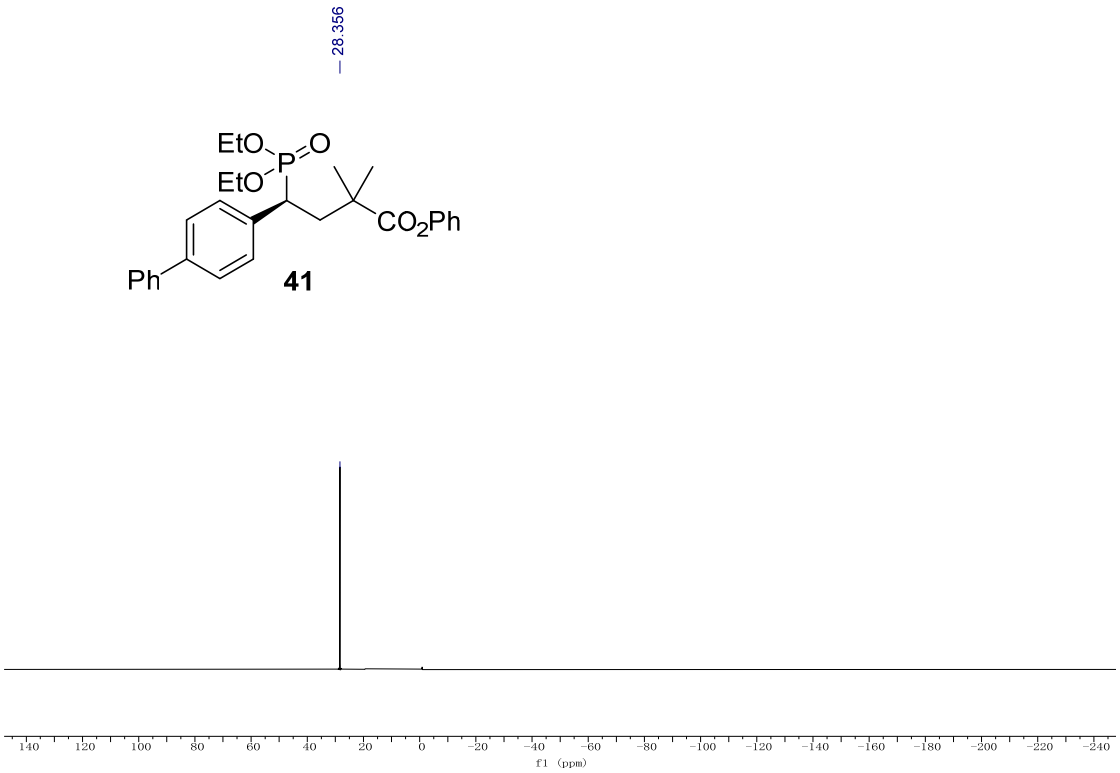
^{1}H NMR, 400 MHz, $CDCl_3$



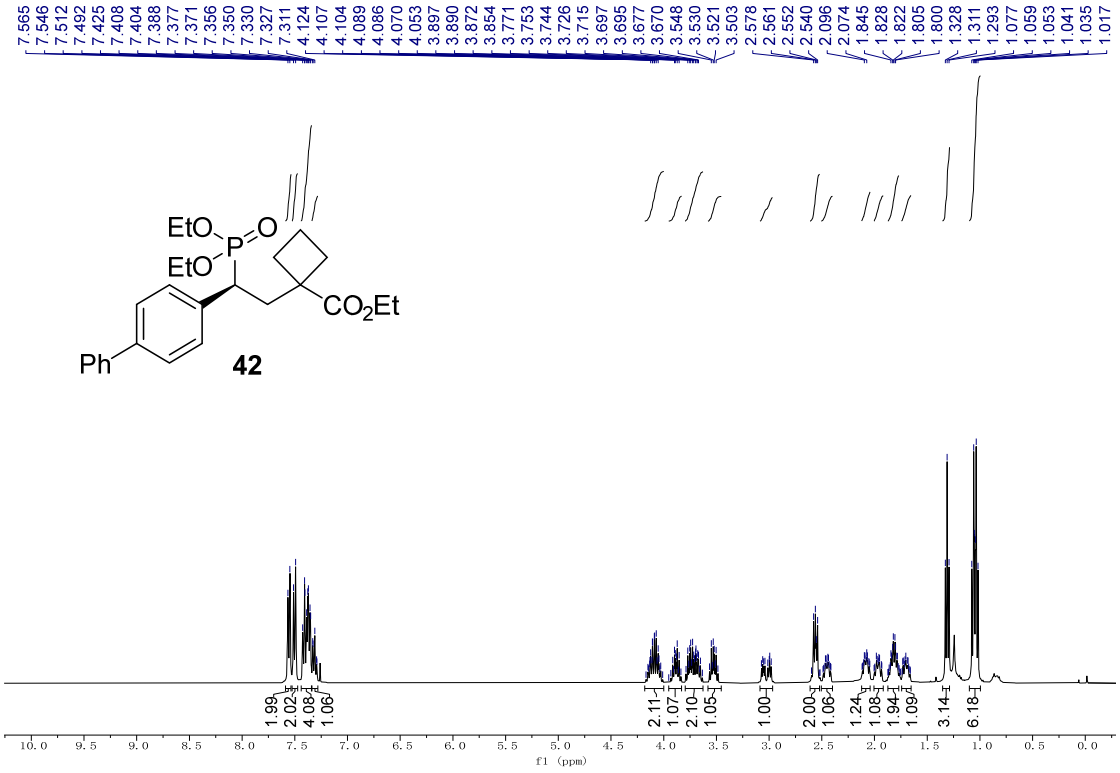
^{13}C NMR, 100 MHz, $CDCl_3$



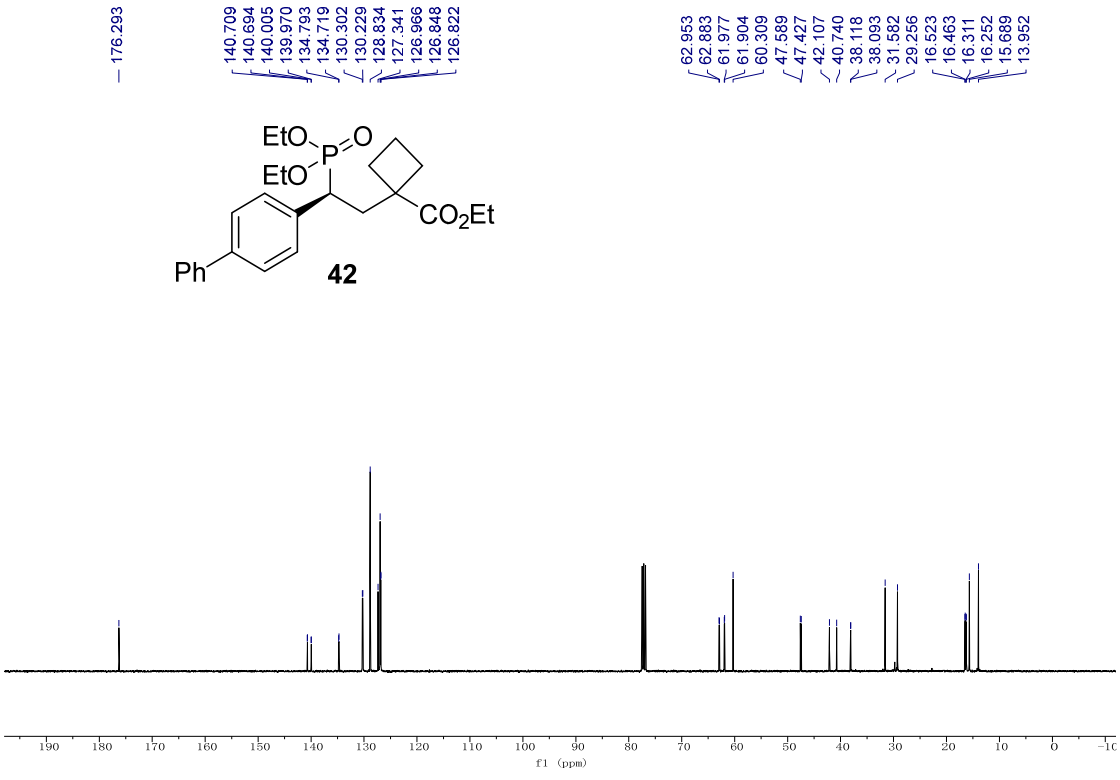
^{31}P NMR, 162 MHz, $CDCl_3$



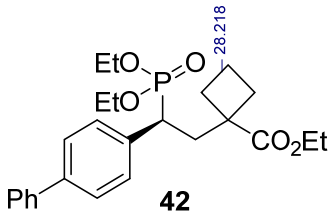
^{1}H NMR, 400 MHz, $CDCl_3$



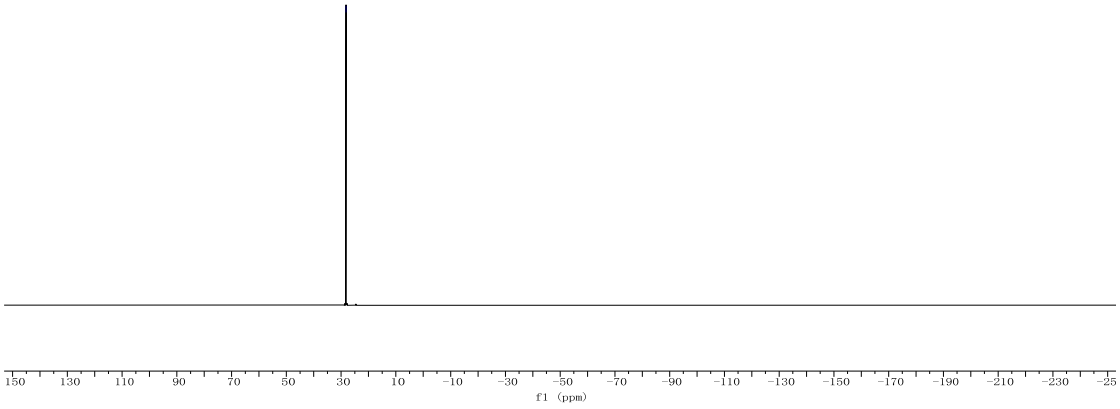
^{13}C NMR, 100 MHz, $CDCl_3$



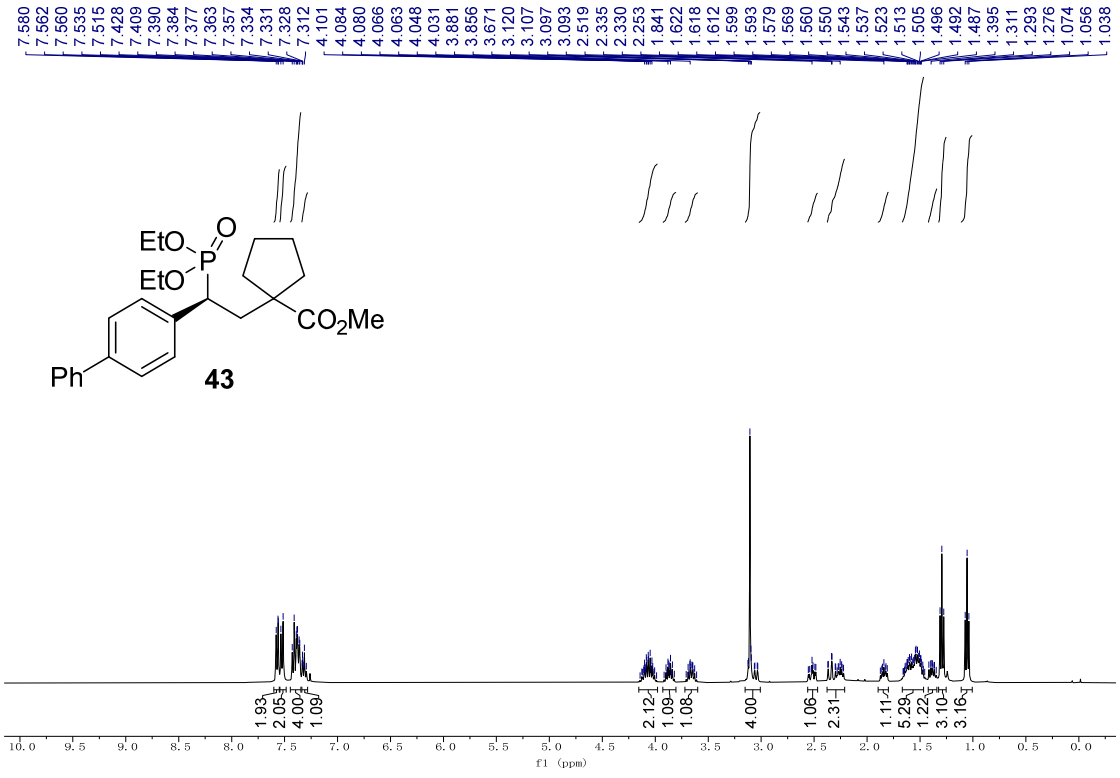
^{31}P NMR, 162 MHz, $CDCl_3$



42

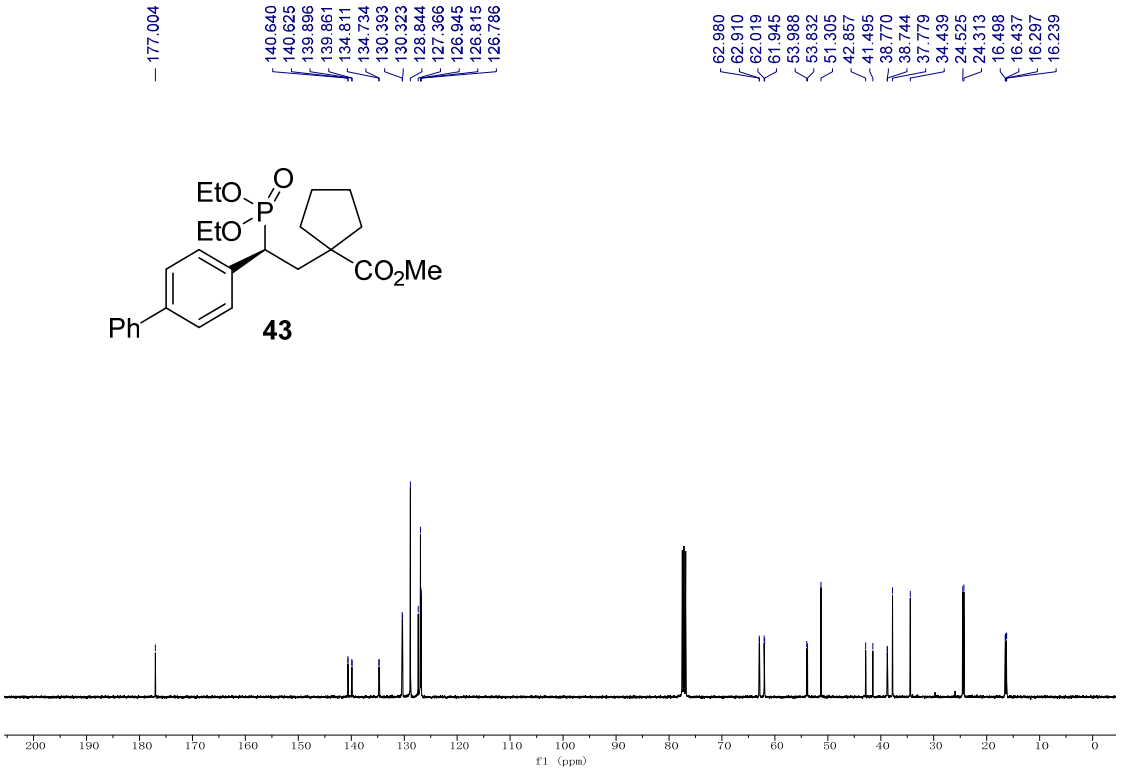


^{1}H NMR, 400 MHz, $CDCl_3$

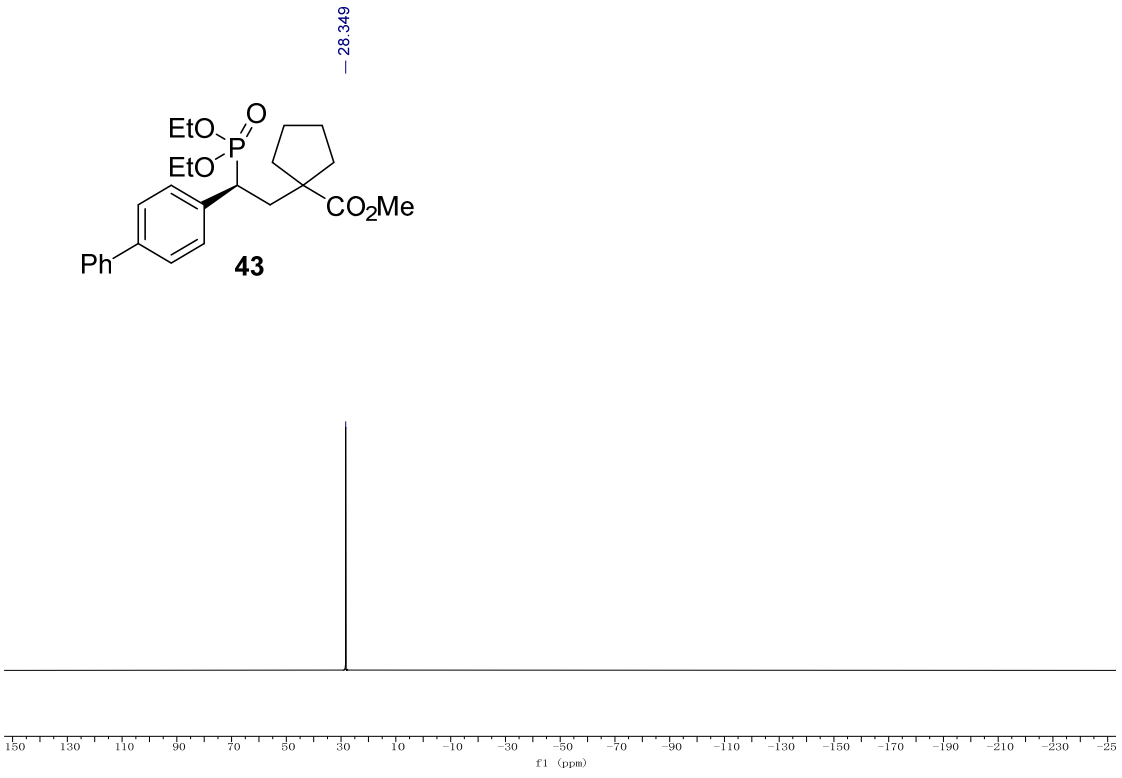


43

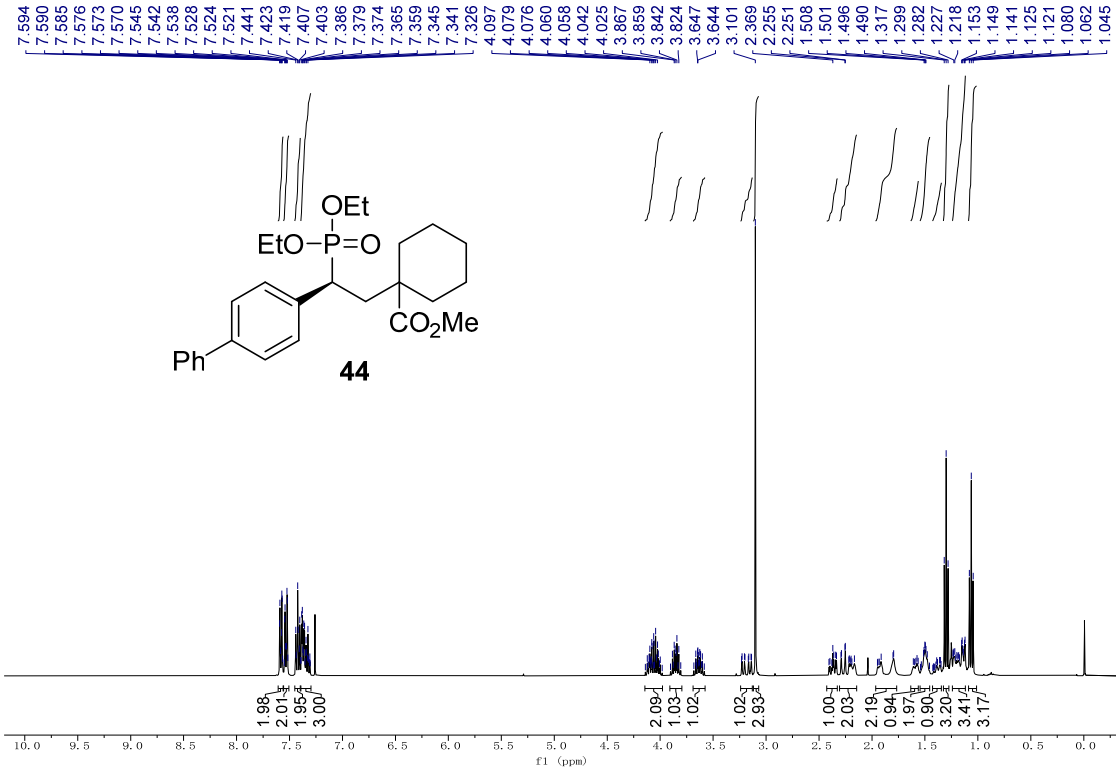
^{13}C NMR, 100 MHz, $CDCl_3$



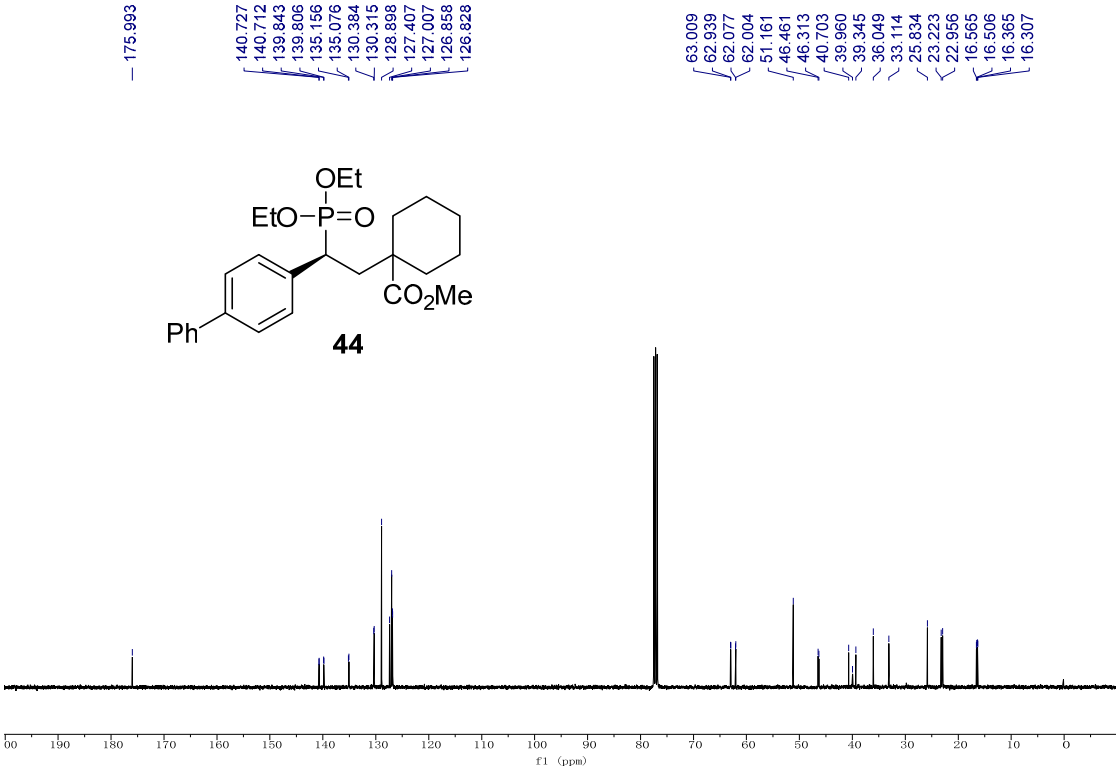
^{31}P NMR, 162 MHz, $CDCl_3$



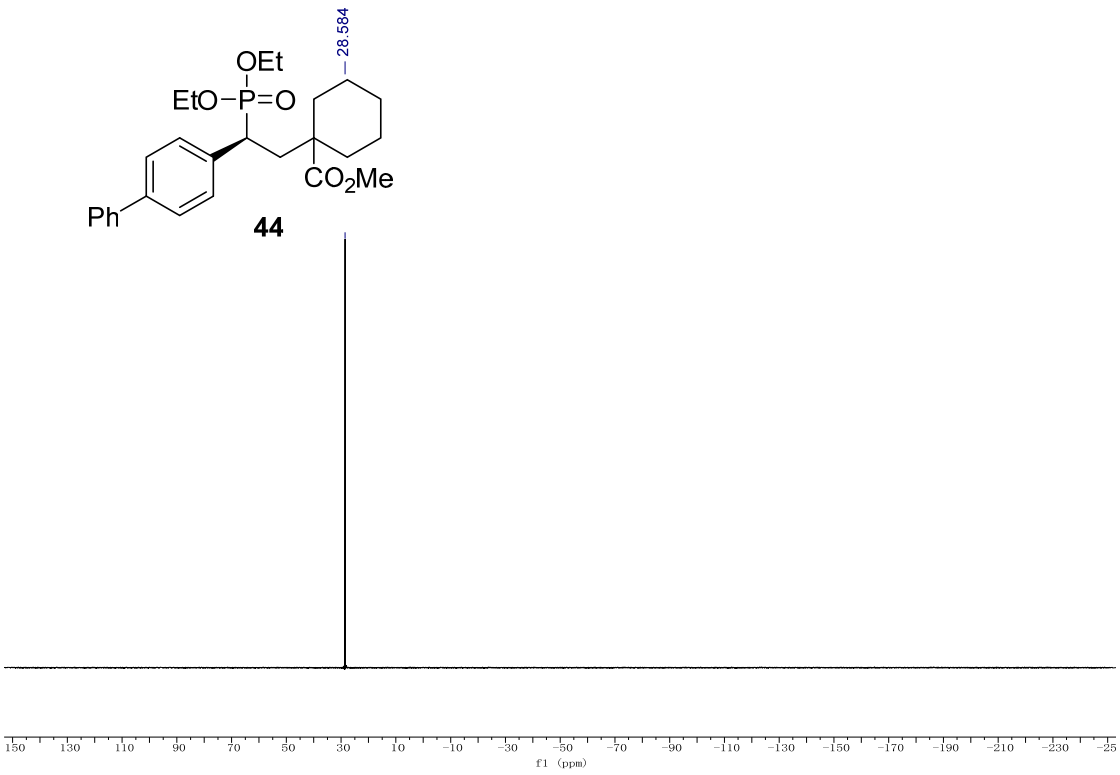
^{1}H NMR, 400 MHz, $CDCl_3$



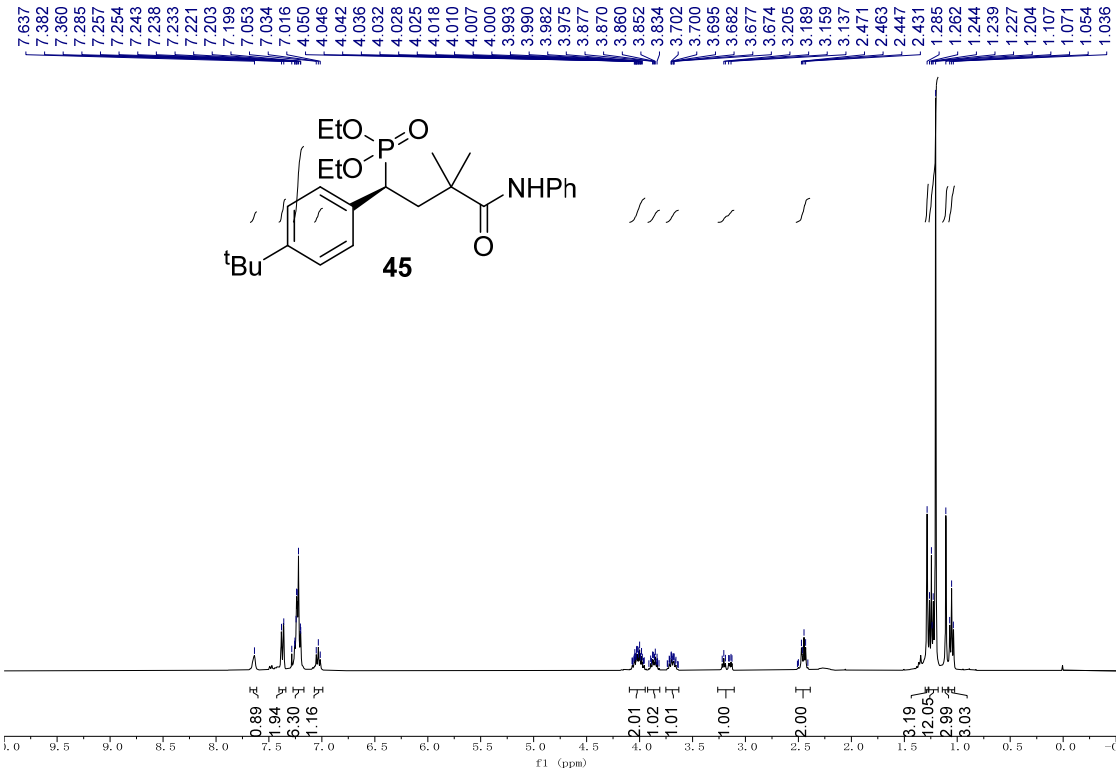
^{13}C NMR, 100 MHz, $CDCl_3$



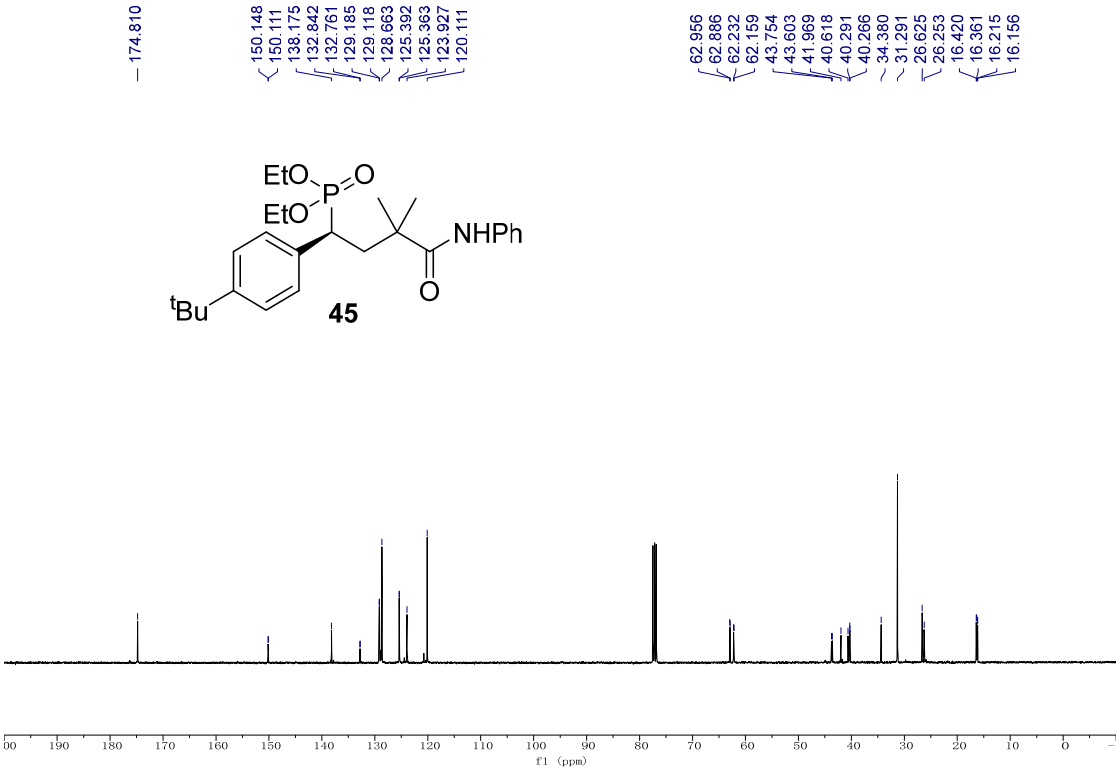
^{31}P NMR, 162 MHz, $CDCl_3$



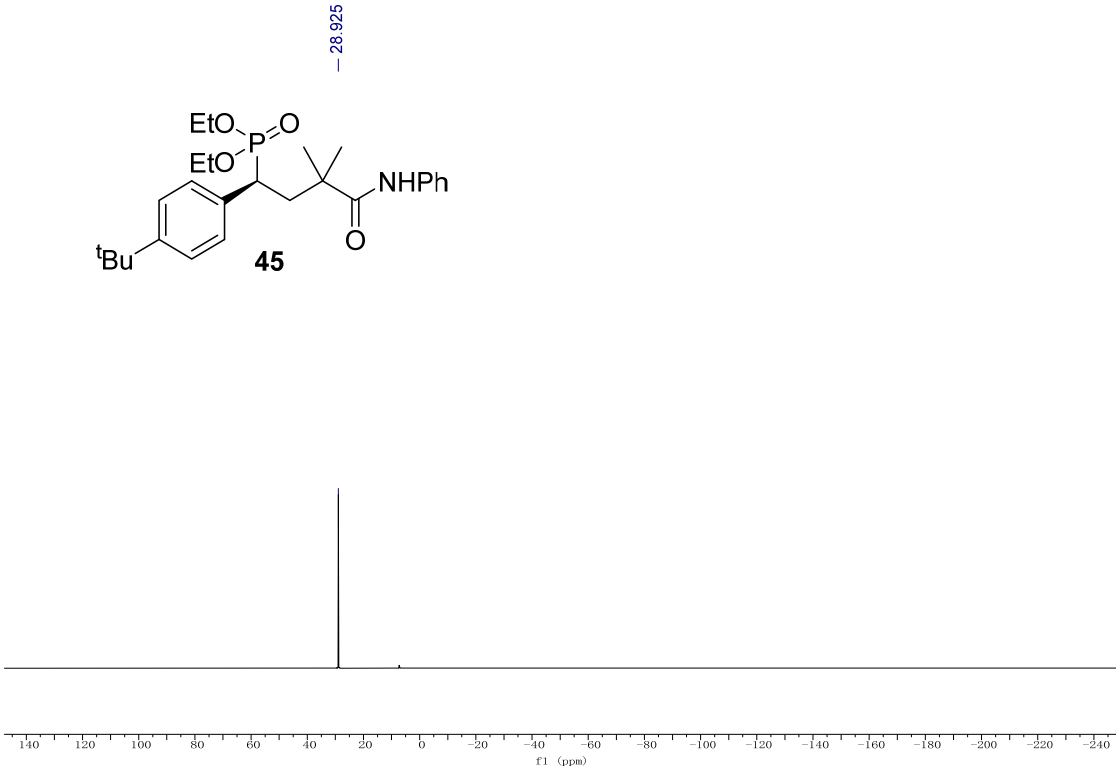
^{1}H NMR, 400 MHz, $CDCl_3$



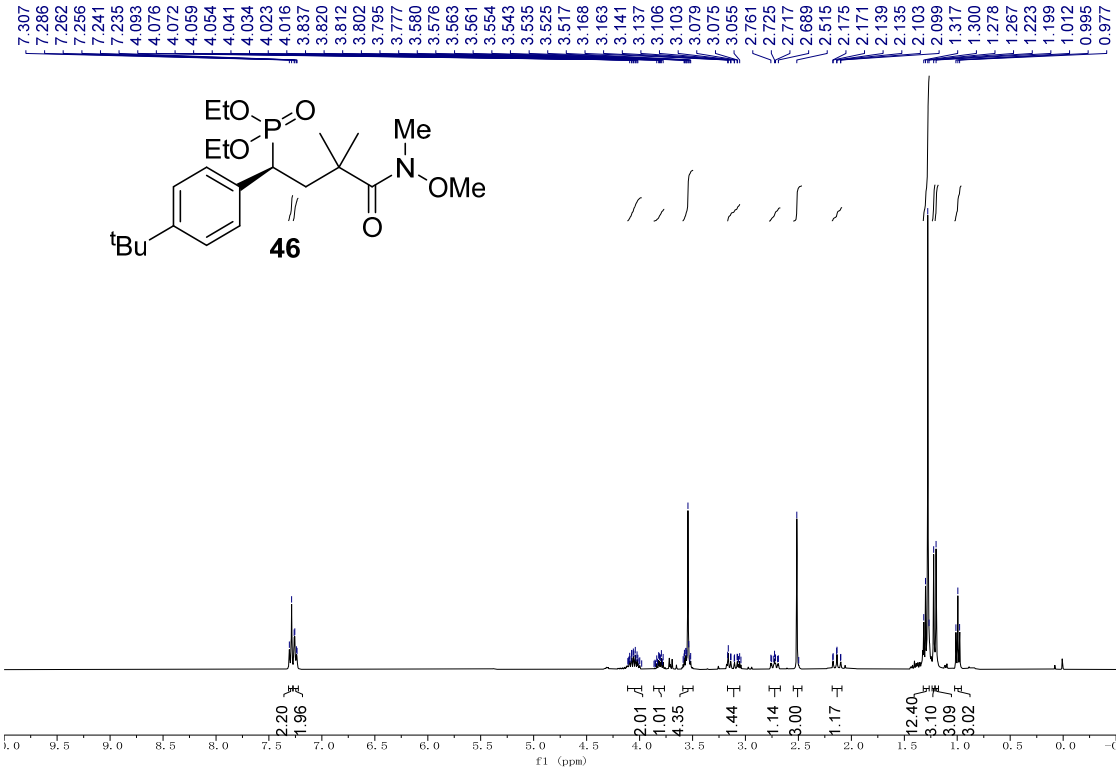
^{13}C NMR, 100 MHz, $CDCl_3$



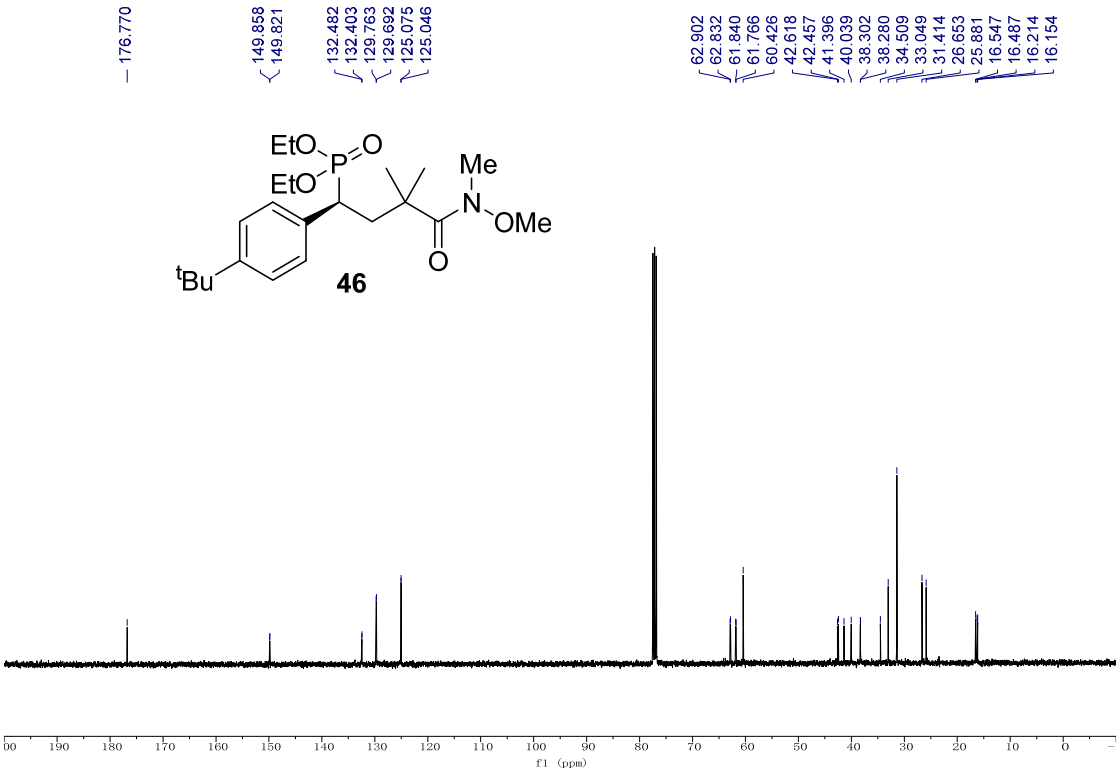
^{31}P NMR, 162 MHz, $CDCl_3$



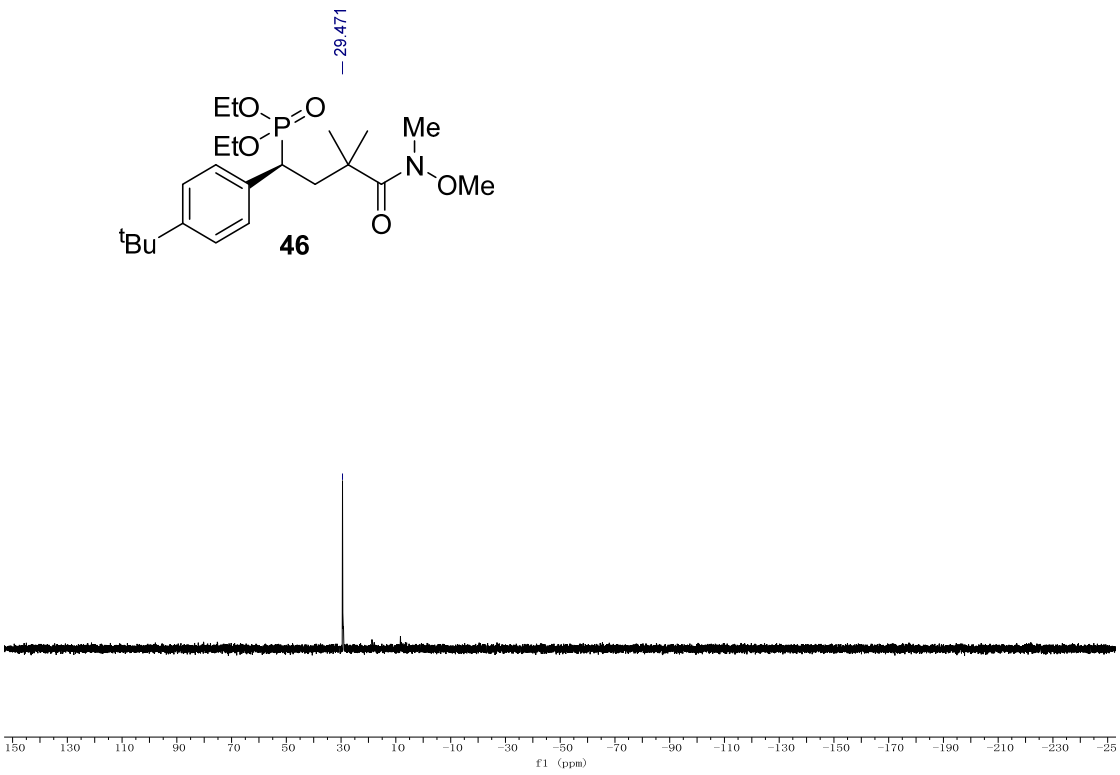
^{1}H NMR, 400 MHz, $CDCl_3$



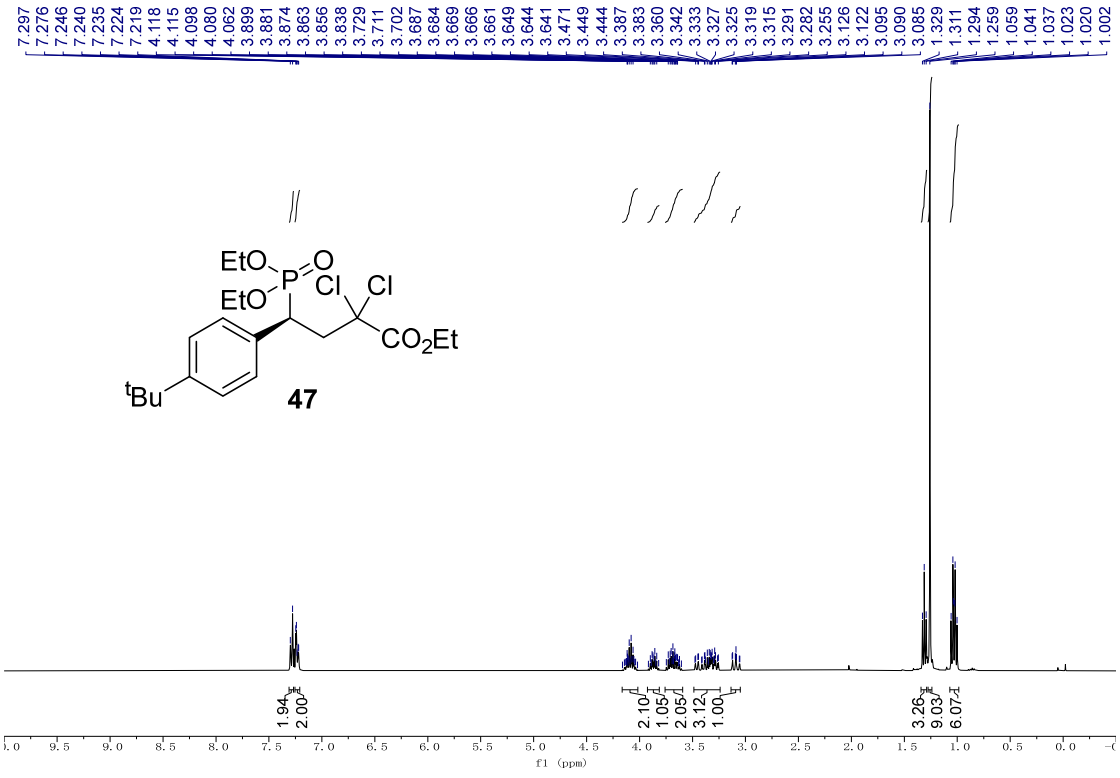
^{13}C NMR, 100 MHz, $CDCl_3$



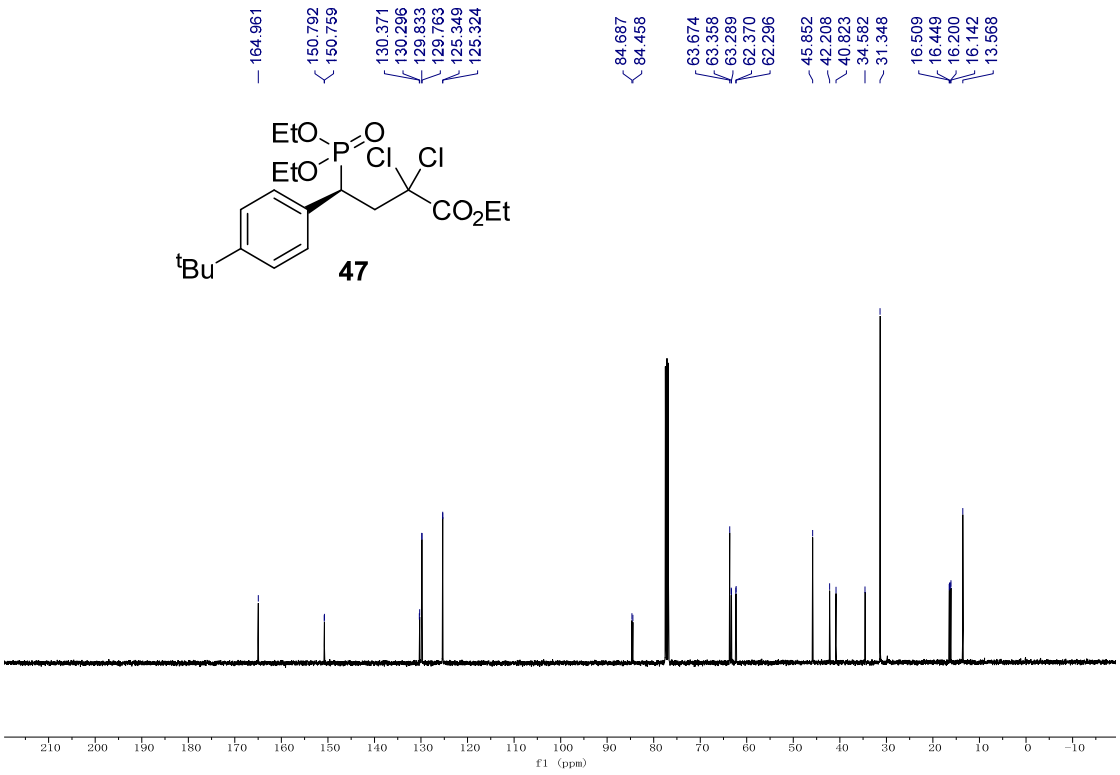
^{31}P NMR, 162 MHz, $CDCl_3$



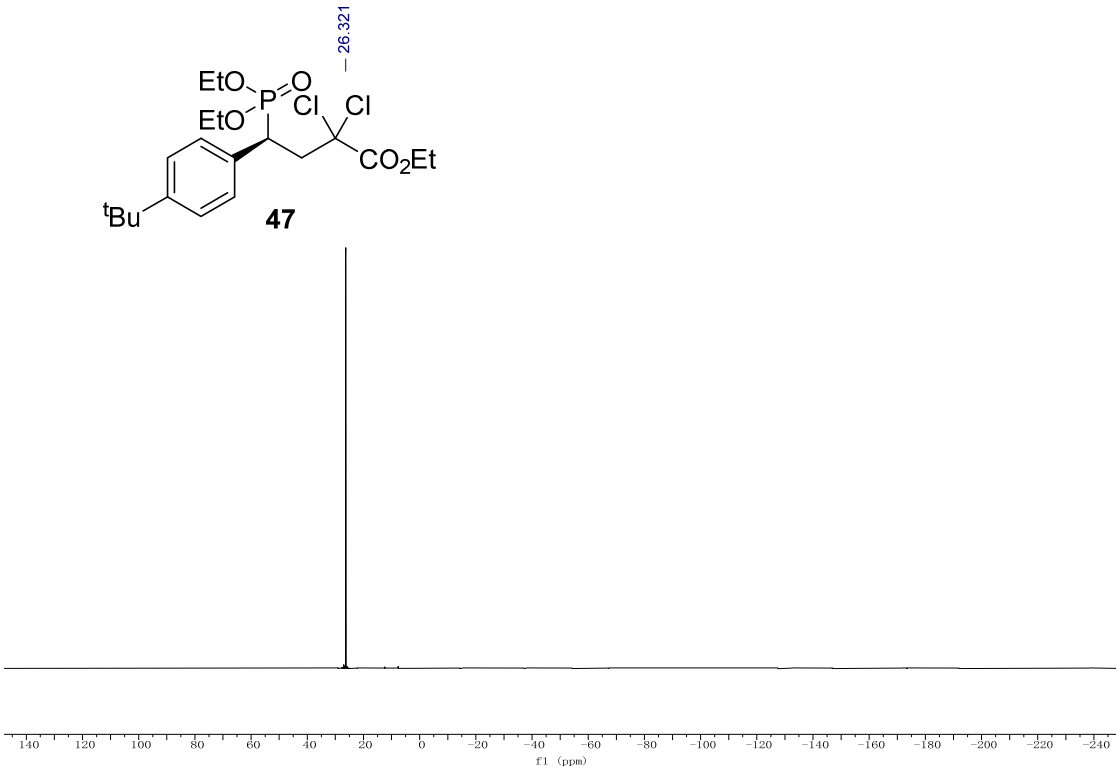
^{1}H NMR, 400 MHz, $CDCl_3$



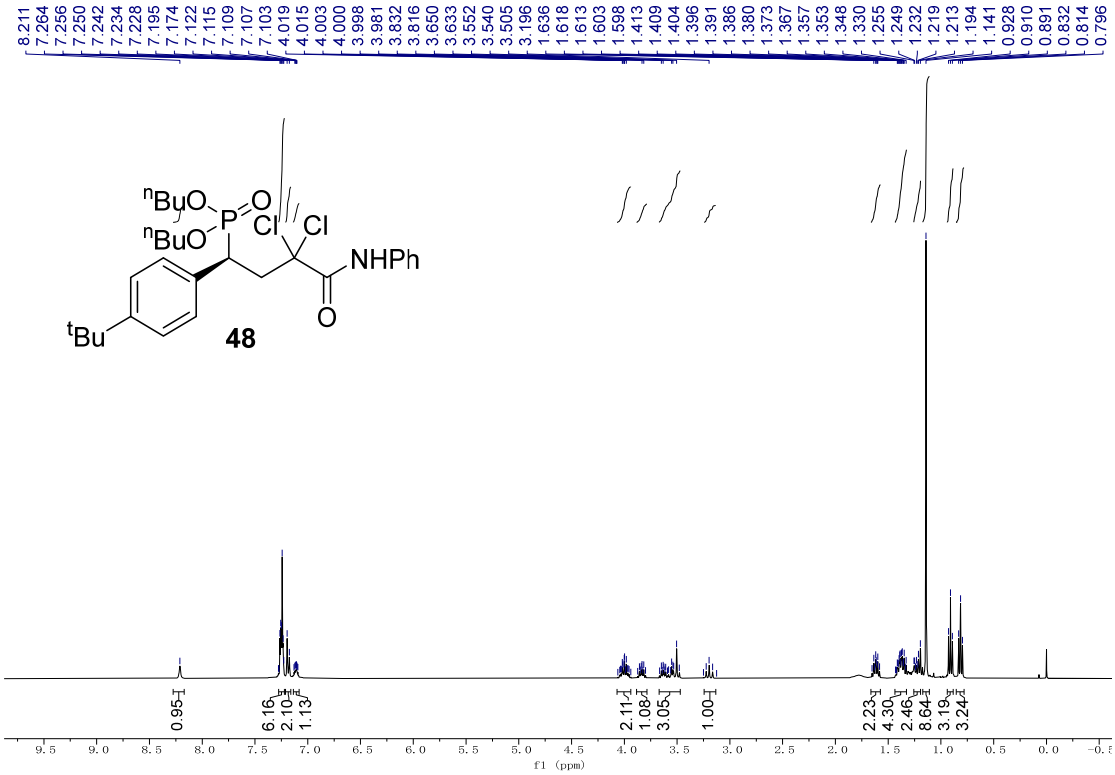
^{13}C NMR, 100 MHz, $CDCl_3$



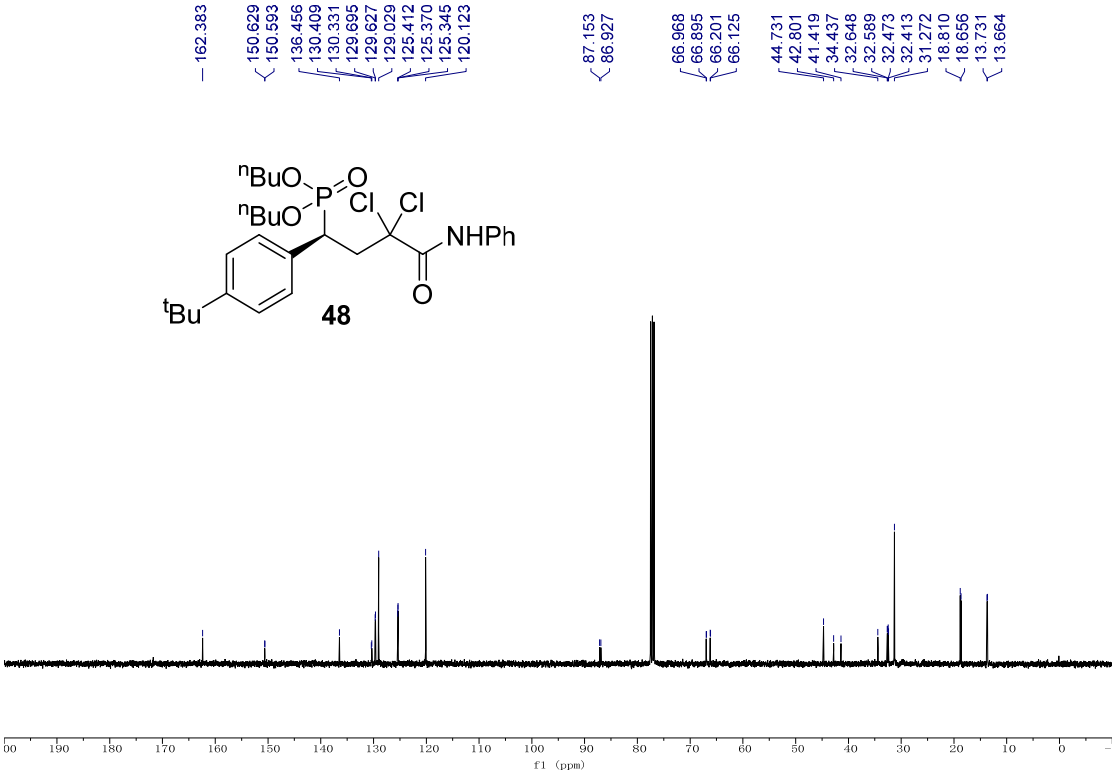
^{31}P NMR, 162 MHz, $CDCl_3$



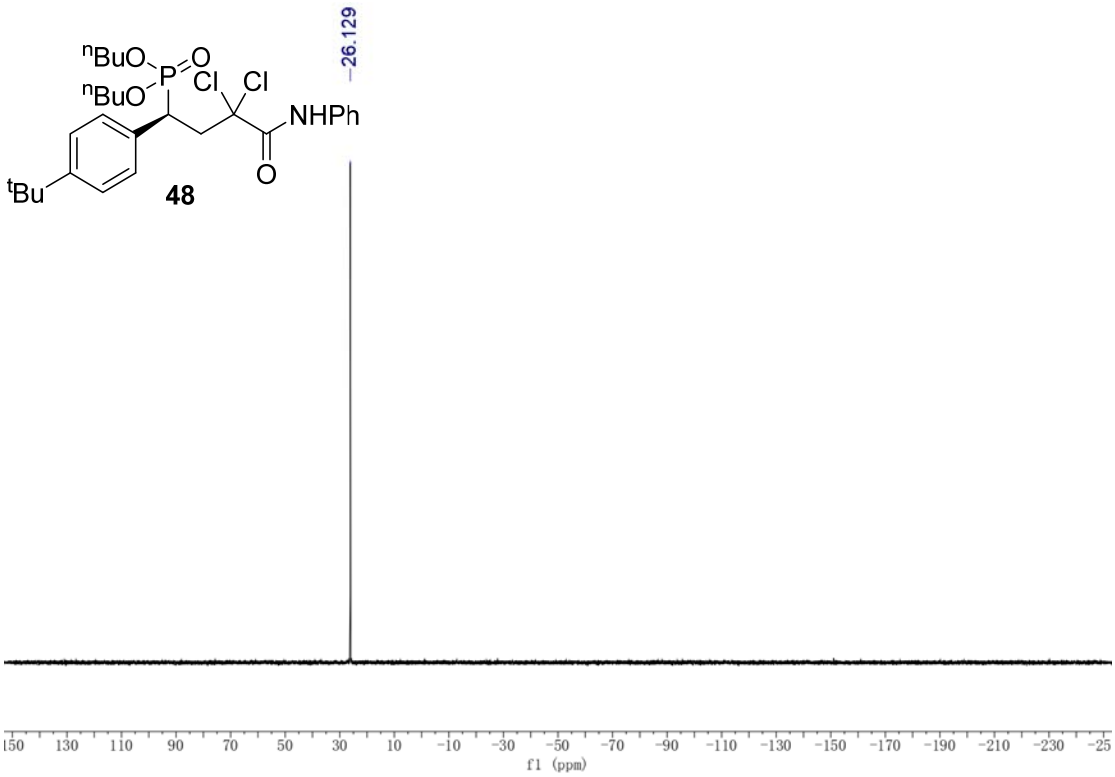
^{1}H NMR, 400 MHz, $CDCl_3$



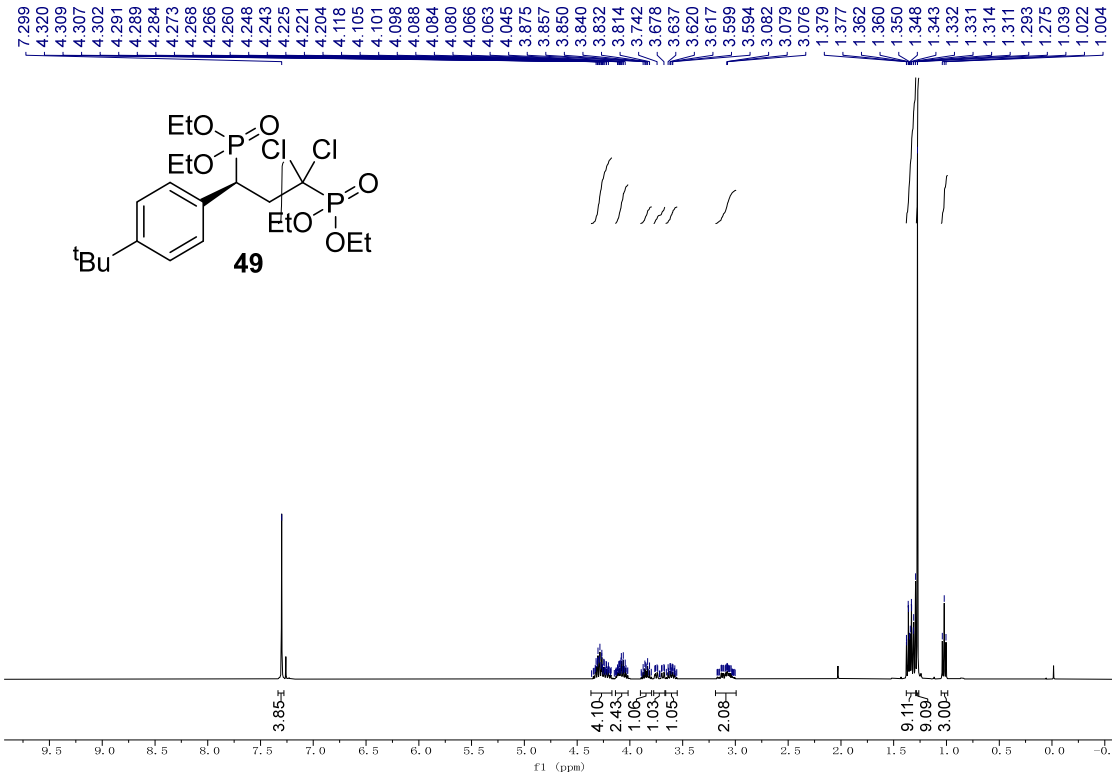
^{13}C NMR, 100 MHz, $CDCl_3$



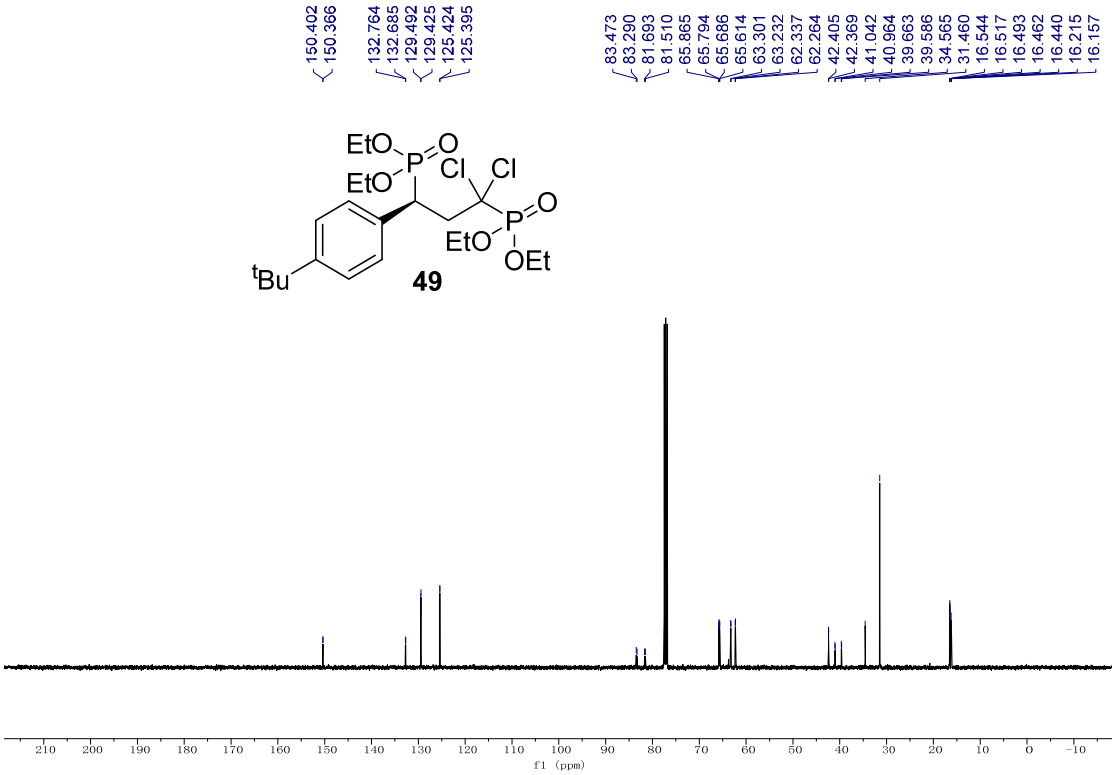
^{31}P NMR, 162 MHz, $CDCl_3$



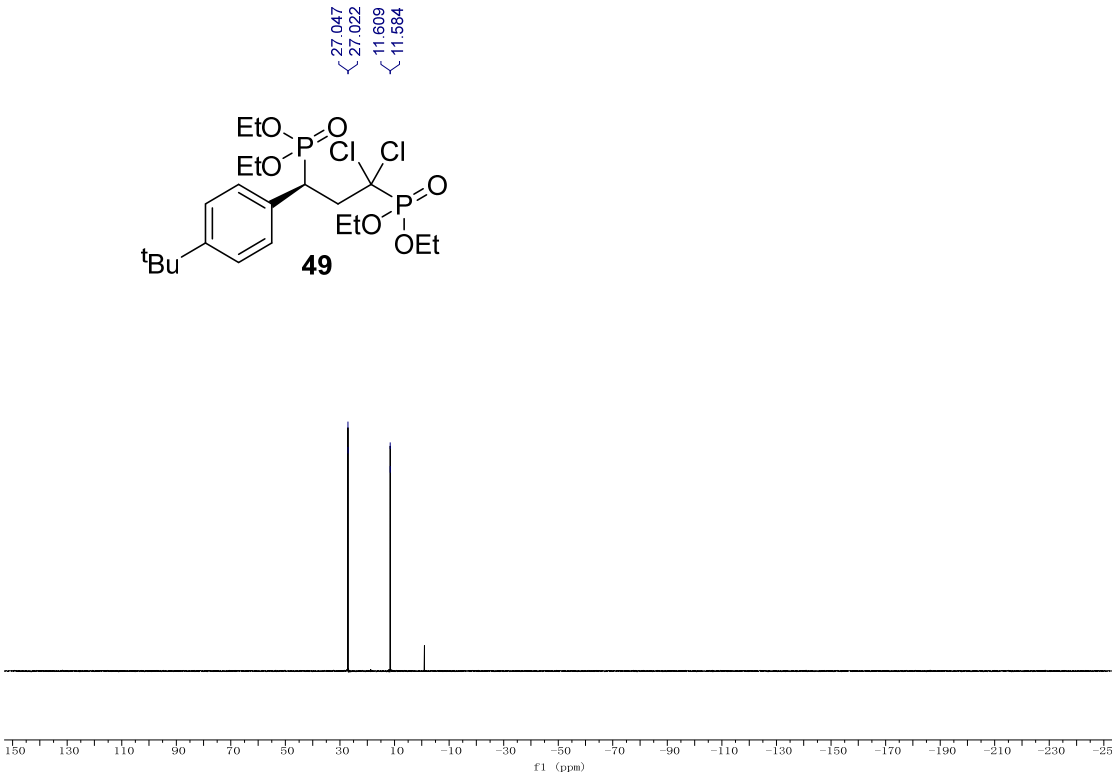
^{1}H NMR, 400 MHz, $CDCl_3$



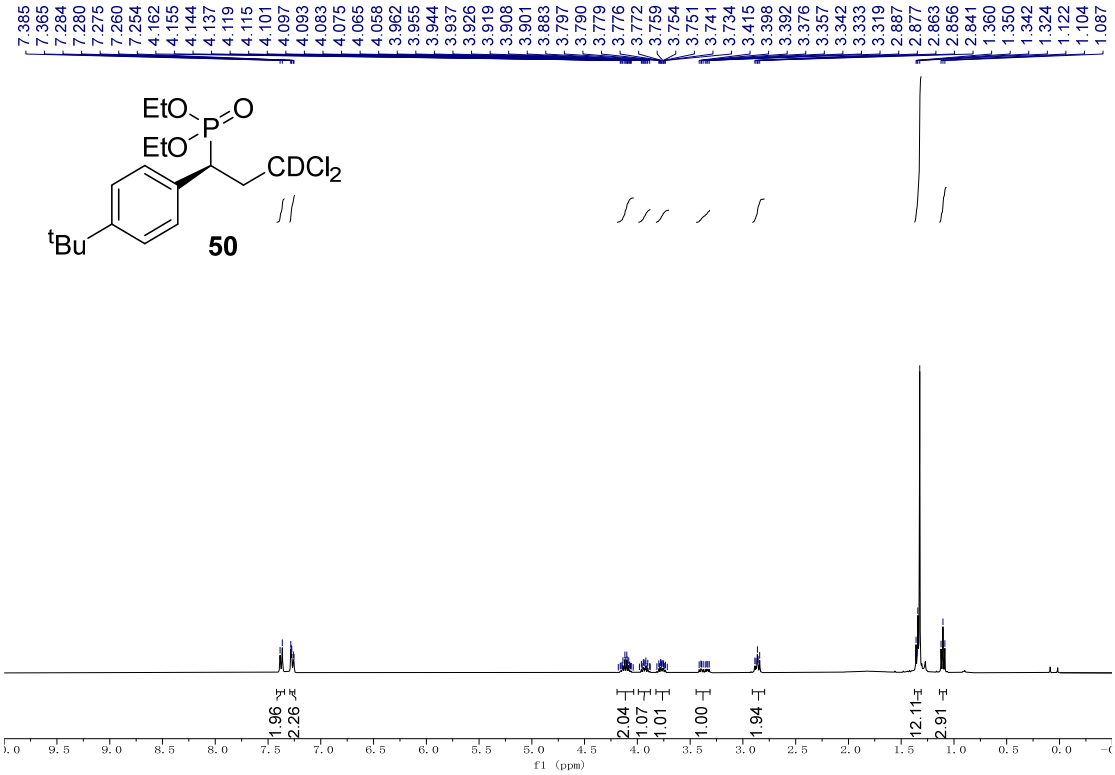
^{13}C NMR, 100 MHz, $CDCl_3$



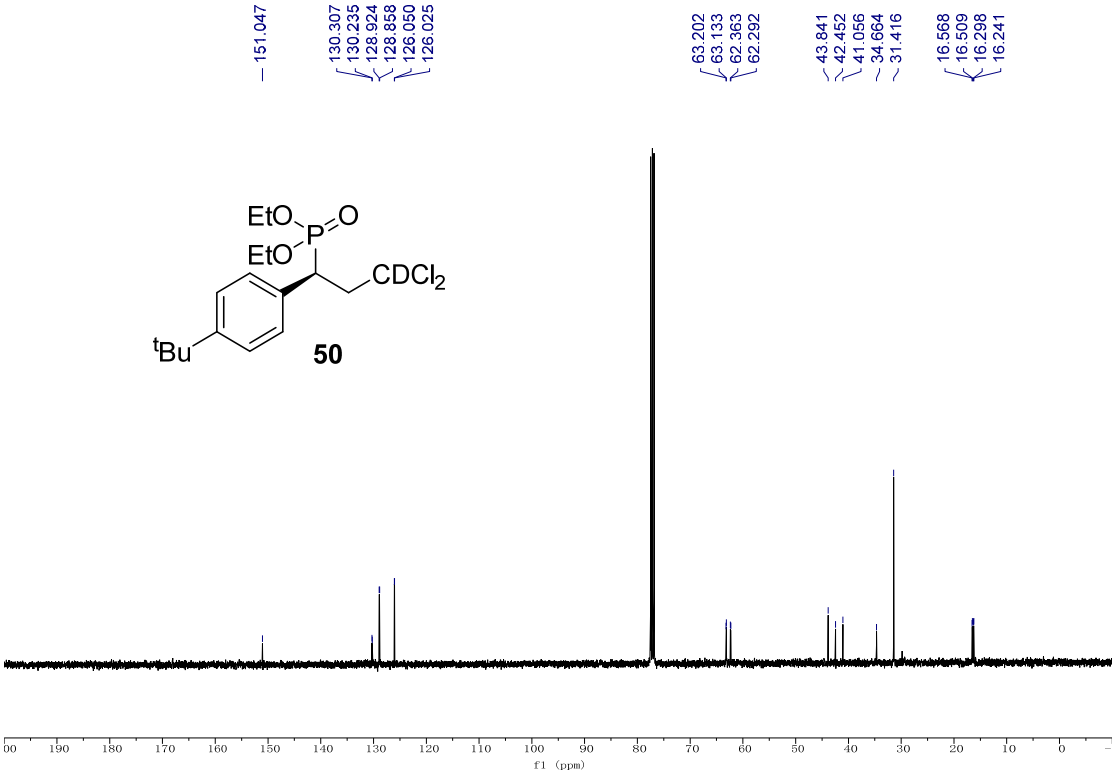
^{31}P NMR, 162 MHz, $CDCl_3$



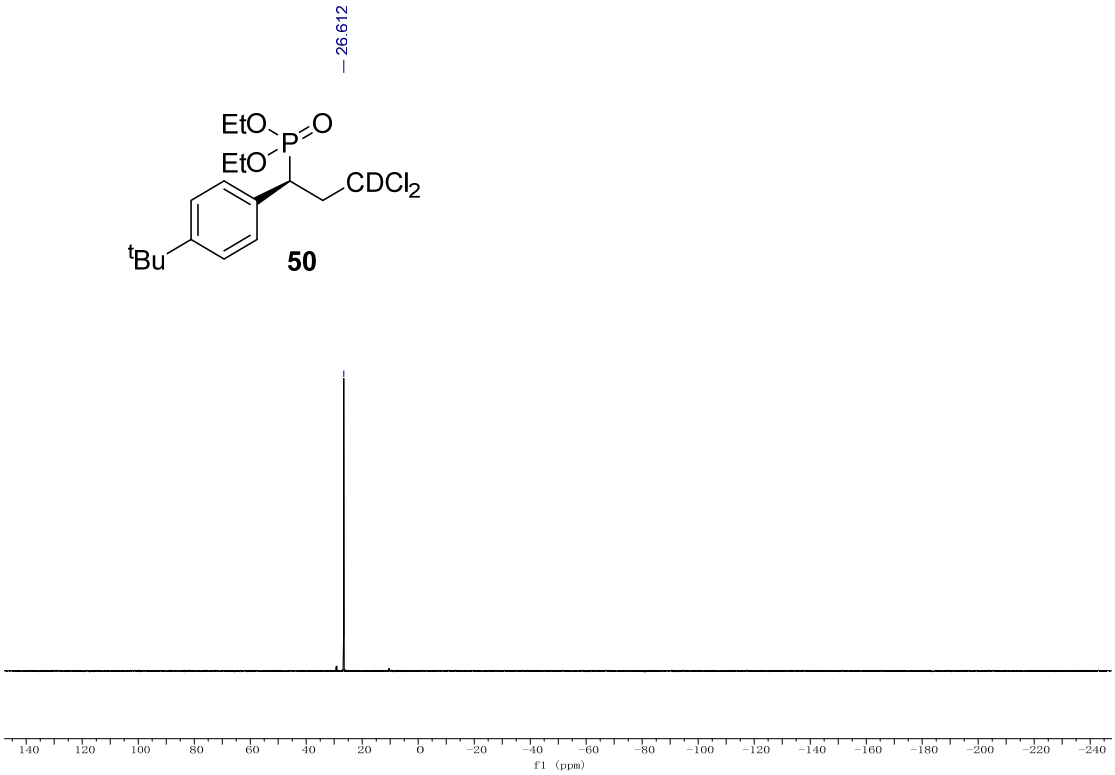
^{1}H NMR, 400 MHz, $CDCl_3$



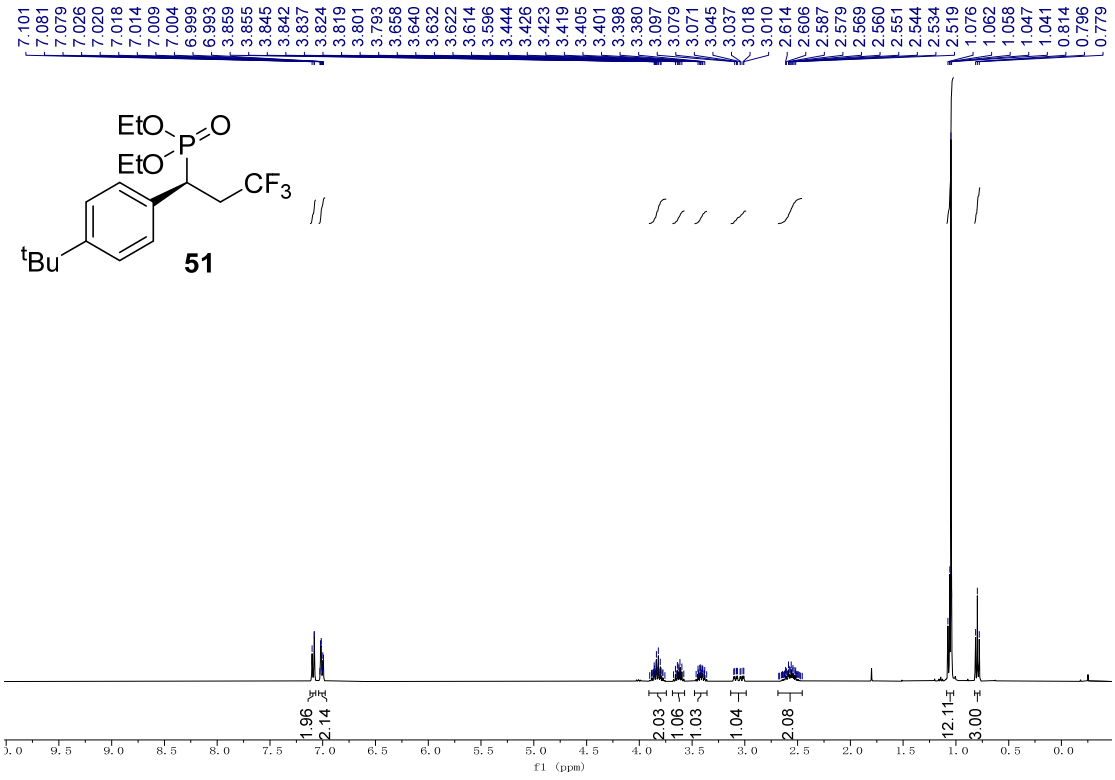
^{13}C NMR, 100 MHz, $CDCl_3$



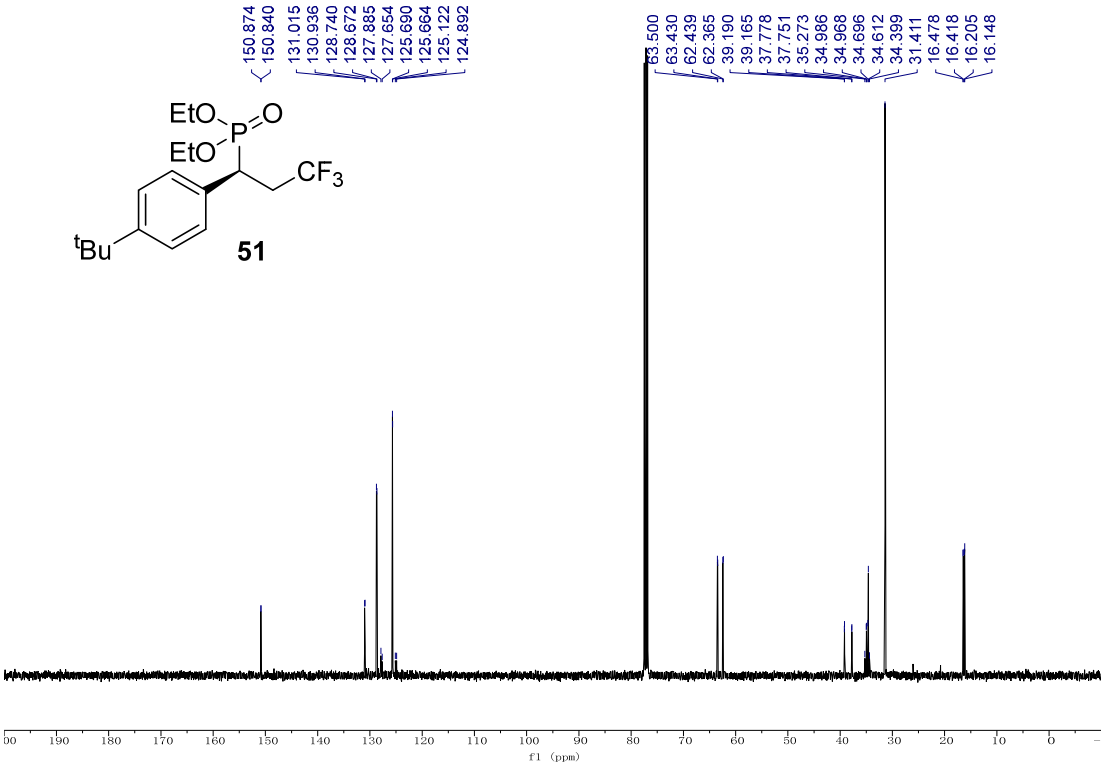
^{31}P NMR, 162 MHz, $CDCl_3$



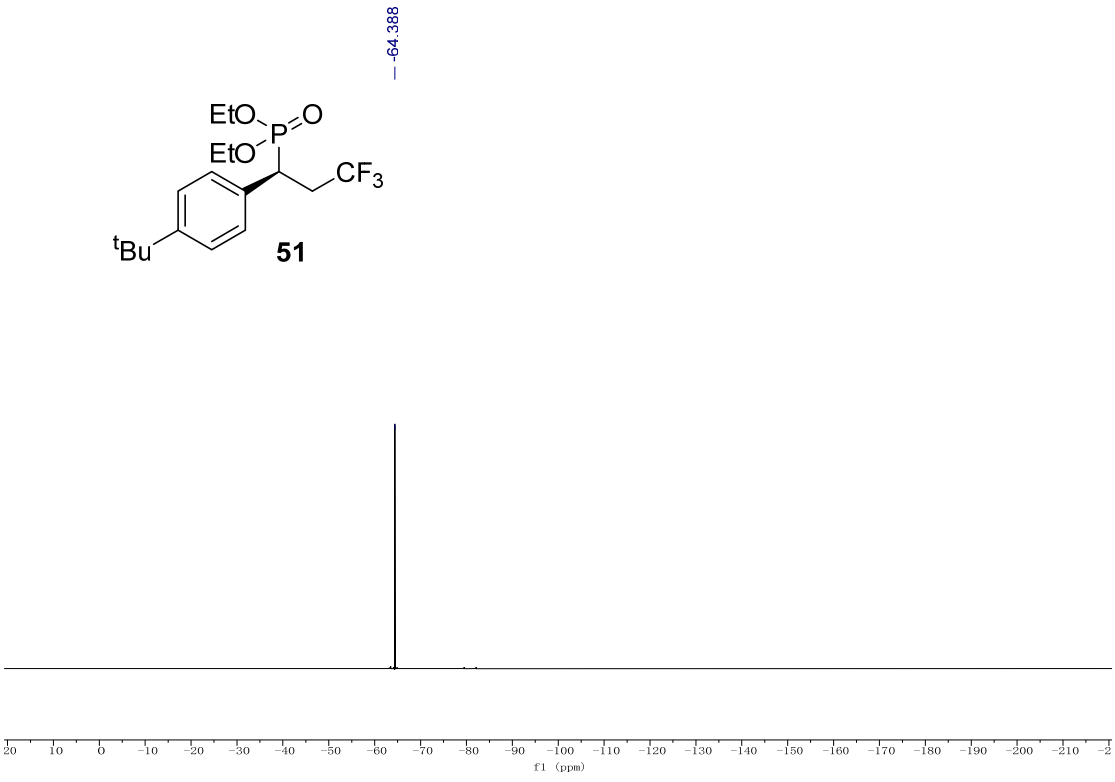
^{1}H NMR, 400 MHz, $CDCl_3$



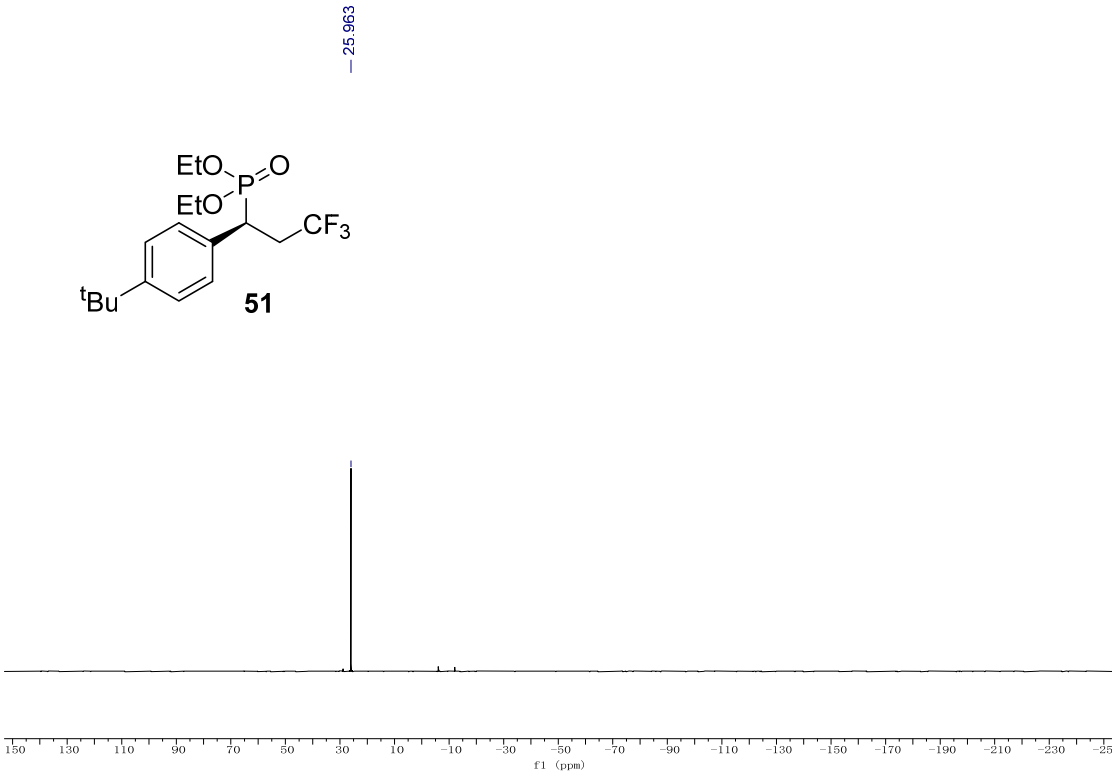
^{13}C NMR, 100 MHz, $CDCl_3$



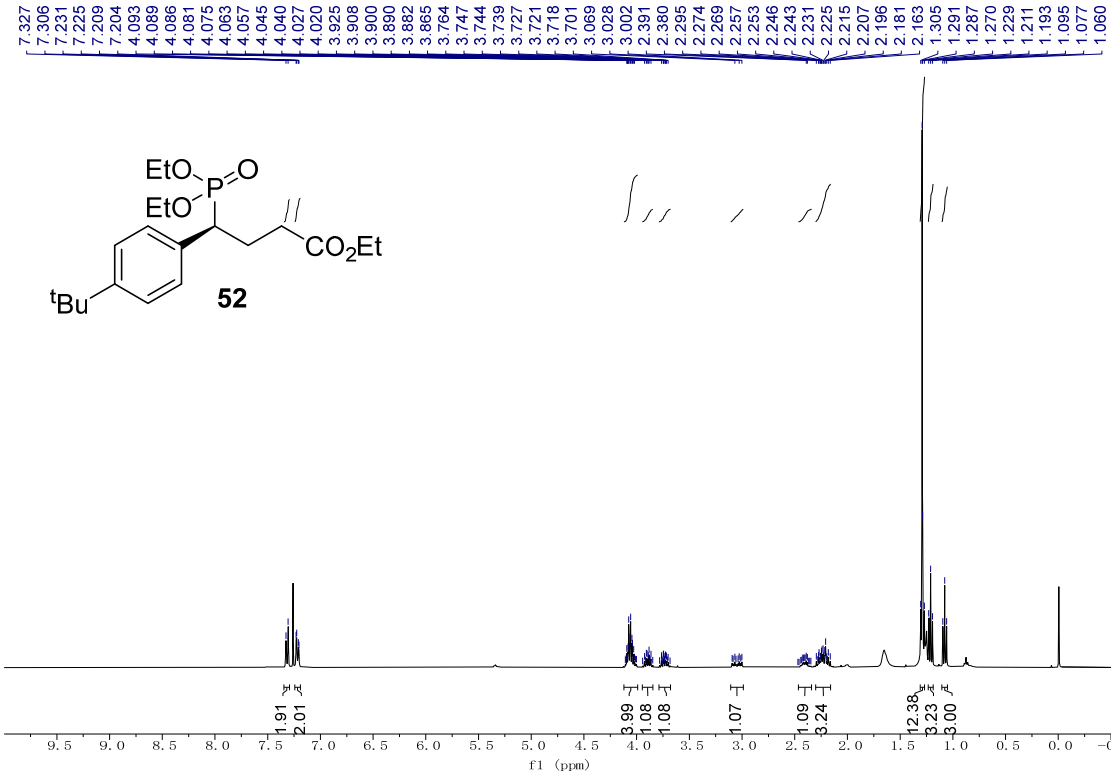
^{19}F NMR, 376 MHz, $CDCl_3$



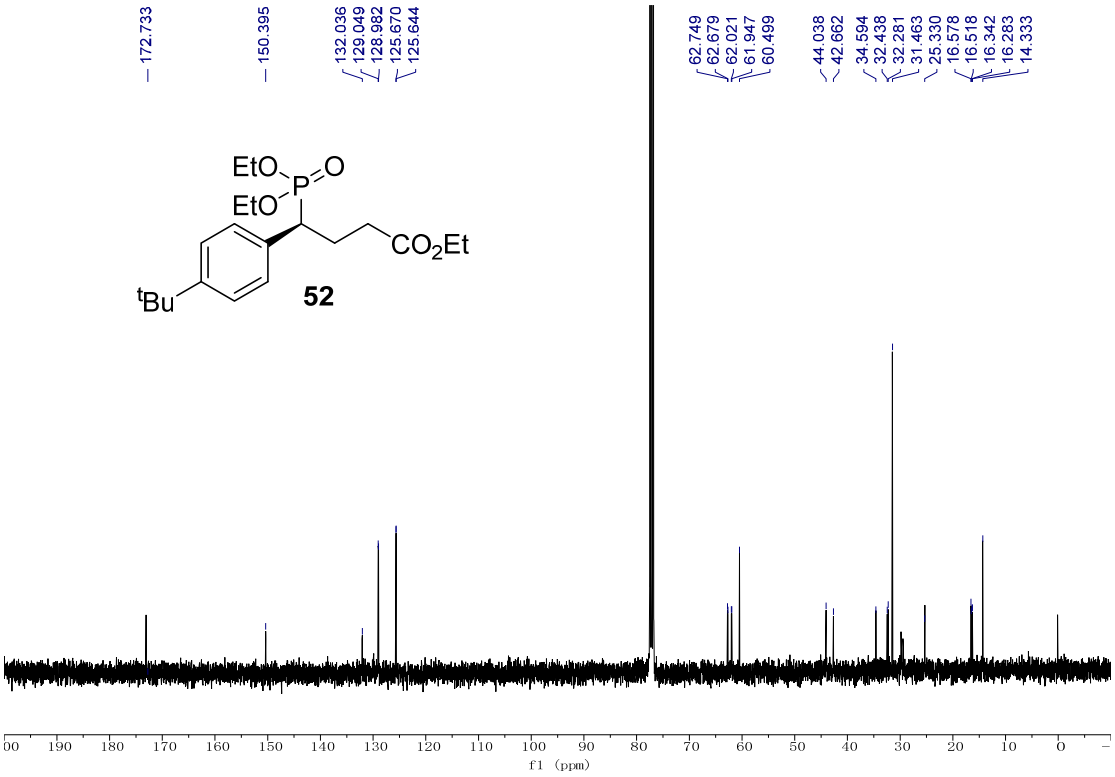
^{31}P NMR, 162 MHz, $CDCl_3$



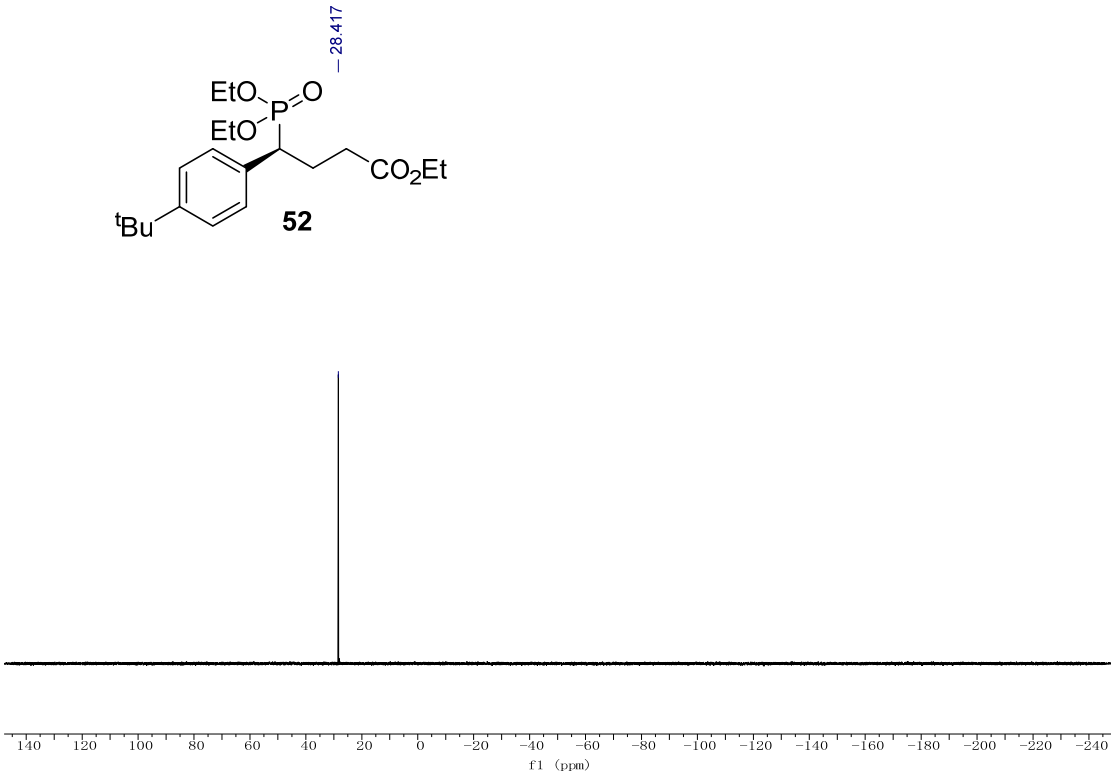
^{1}H NMR, 400 MHz, $CDCl_3$



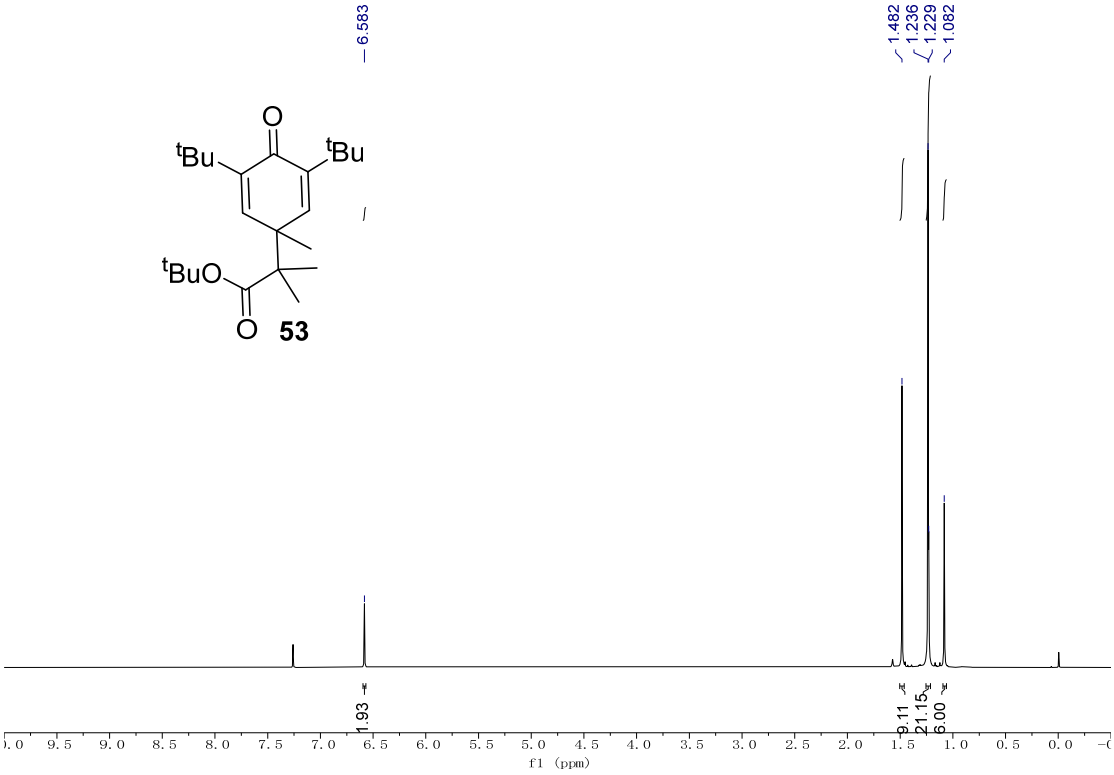
^{13}C NMR, 100 MHz, $CDCl_3$



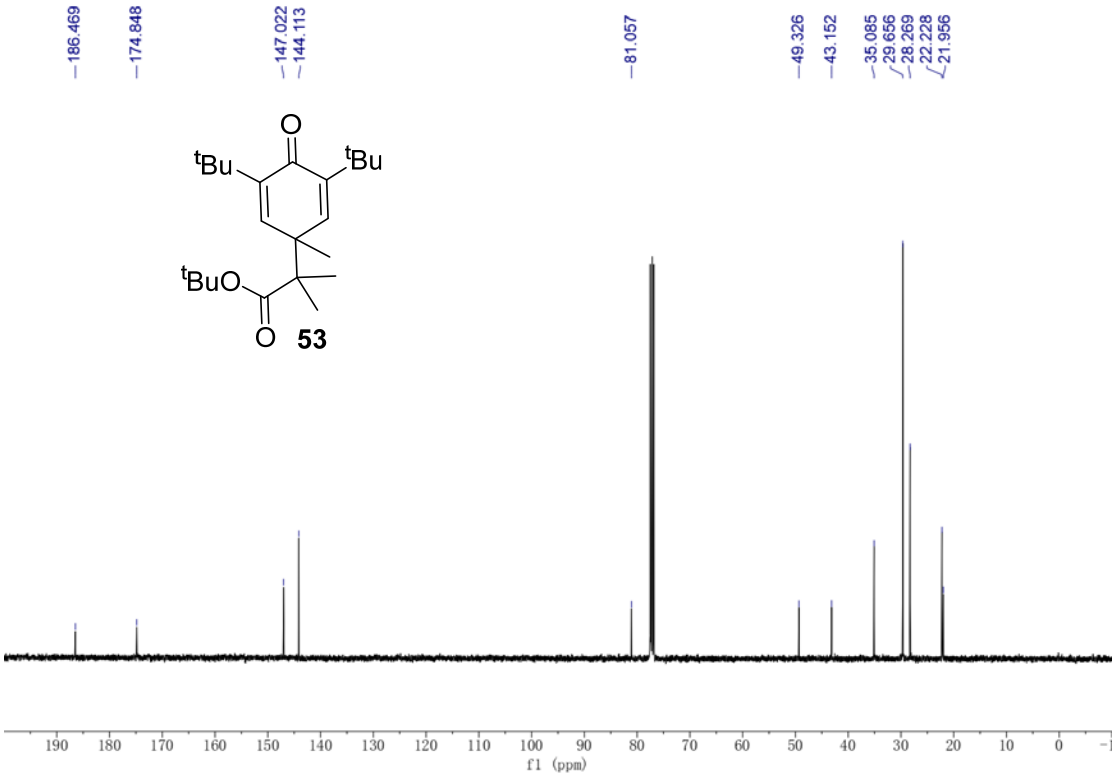
^{31}P NMR, 162 MHz, $CDCl_3$



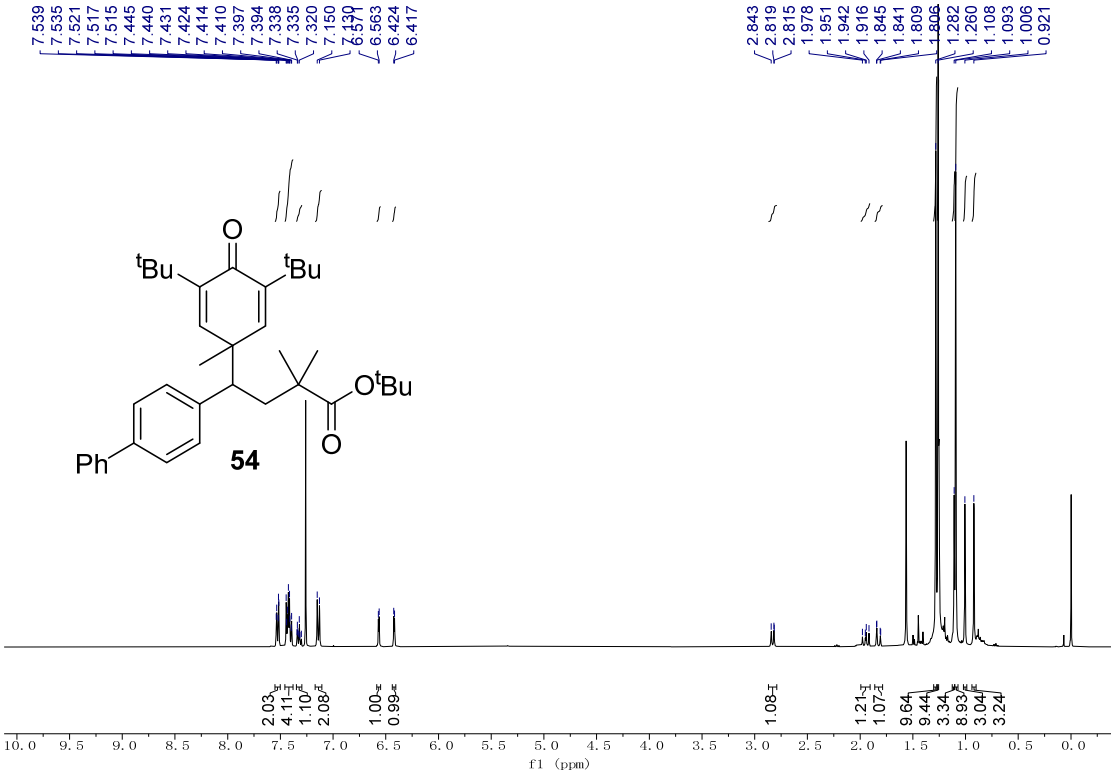
^{1}H NMR, 400 MHz, $CDCl_3$



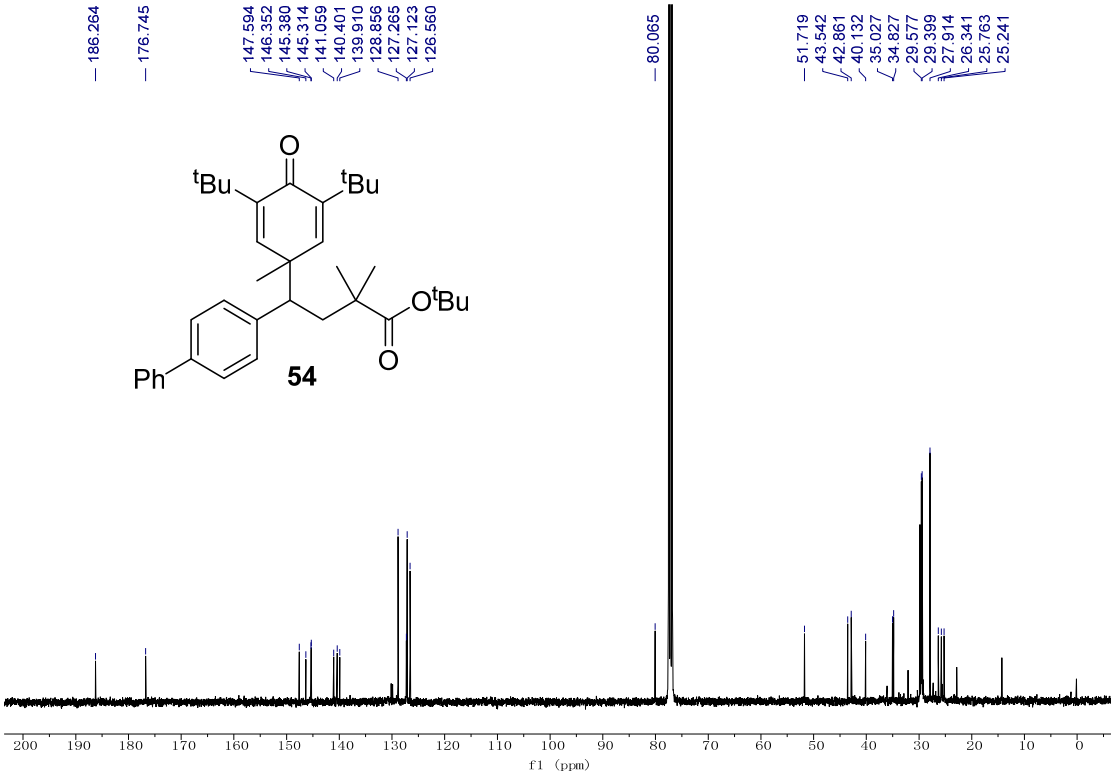
^{13}C NMR, 100 MHz, $CDCl_3$



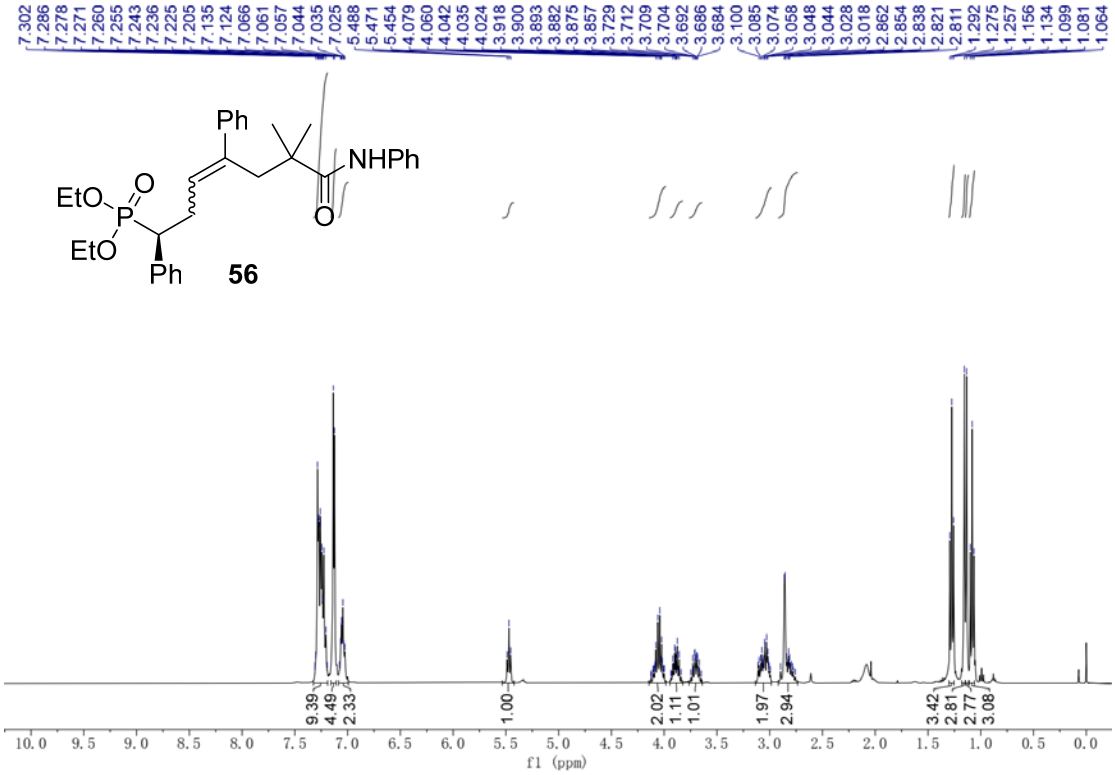
^{1}H NMR, 400 MHz, $CDCl_3$



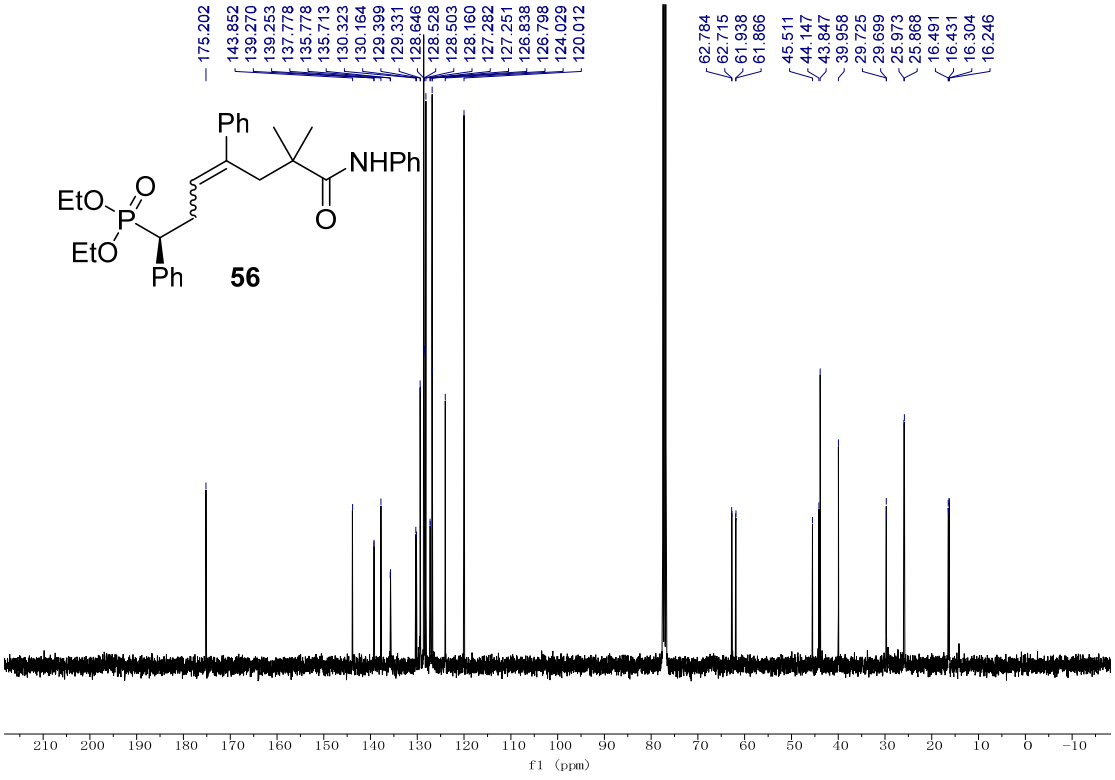
^{13}C NMR, 100 MHz, $CDCl_3$



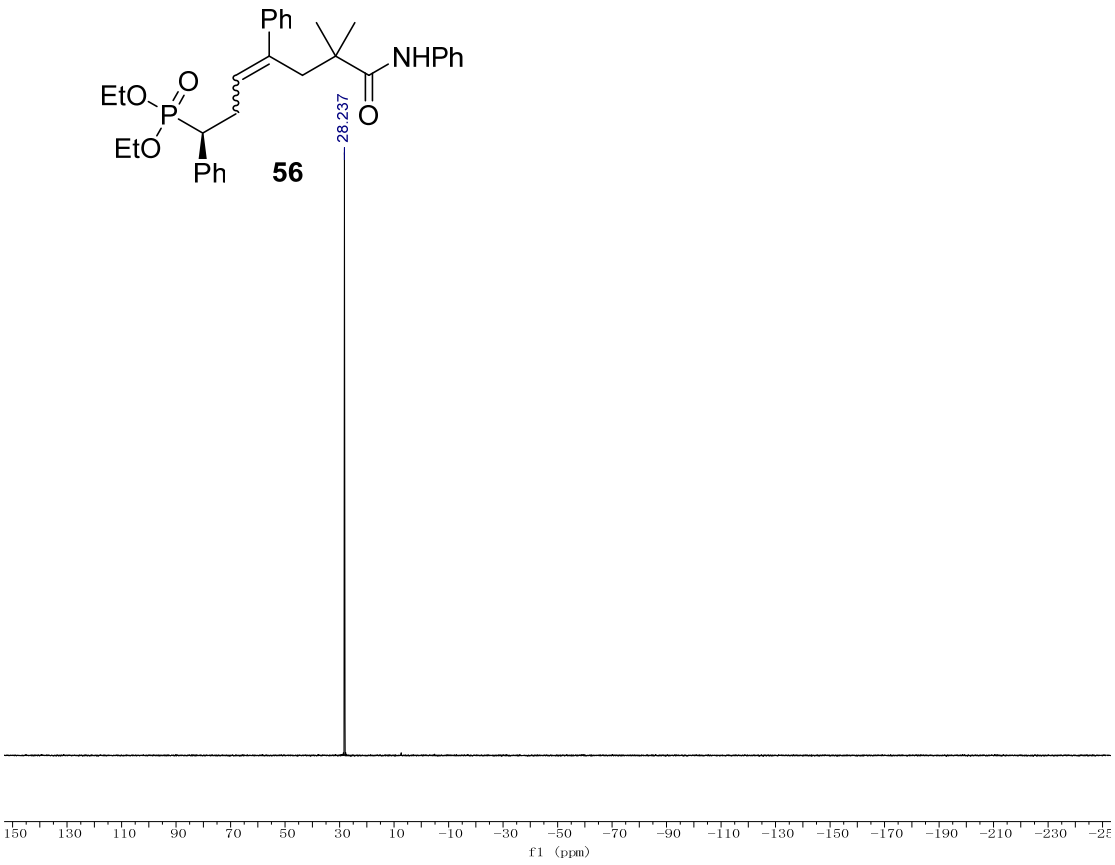
^{1}H NMR, 400 MHz, $CDCl_3$



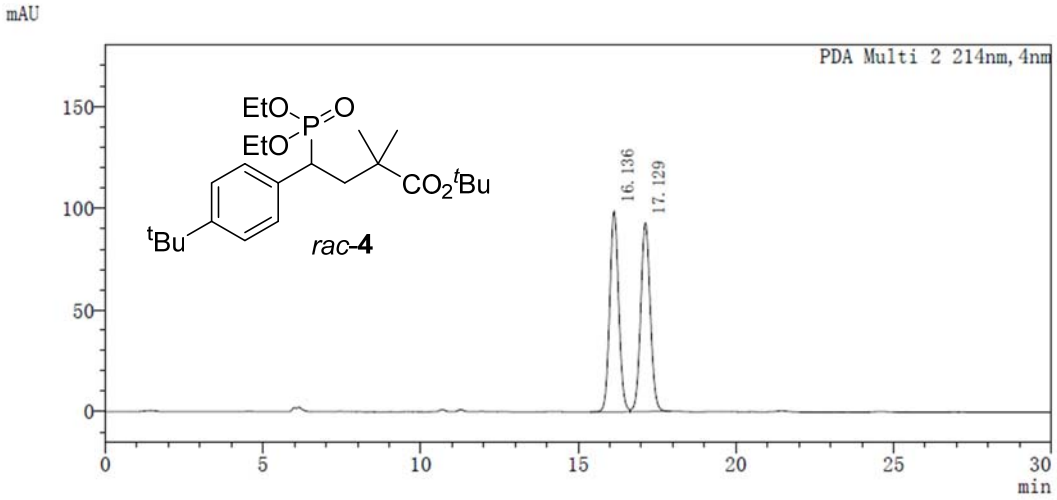
^{13}C NMR, 100 MHz, $CDCl_3$



^{31}P NMR, 162 MHz, $CDCl_3$



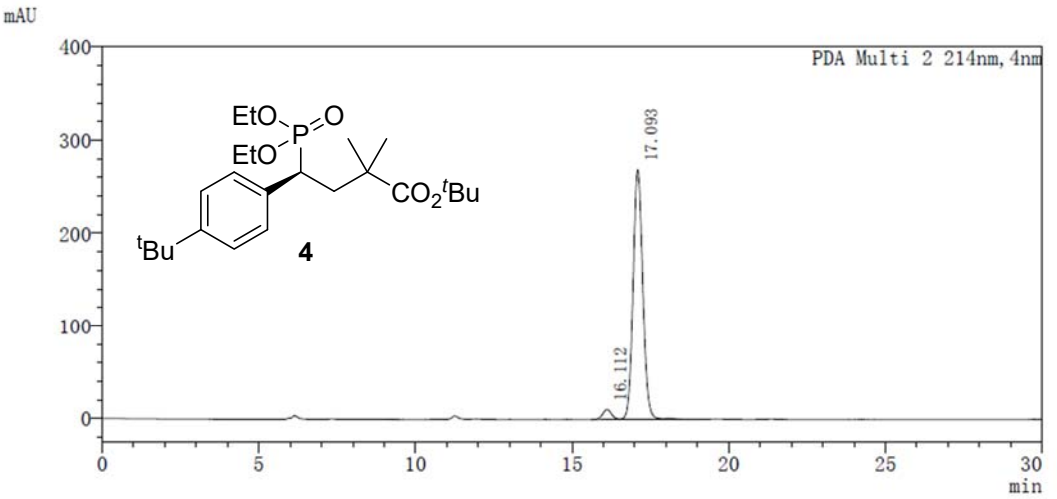
HPLC spectra



Peak Table

PDA Ch2 214nm

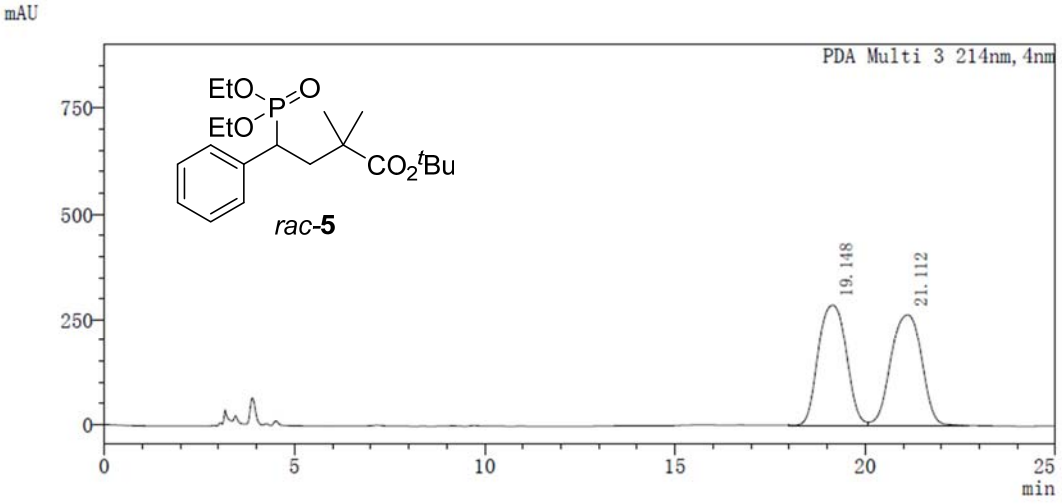
Peak#	Ret. Time	Area	Area%
1	16.136	1961208	50.053
2	17.129	1957058	49.947



Peak Table

PDA Ch2 214nm

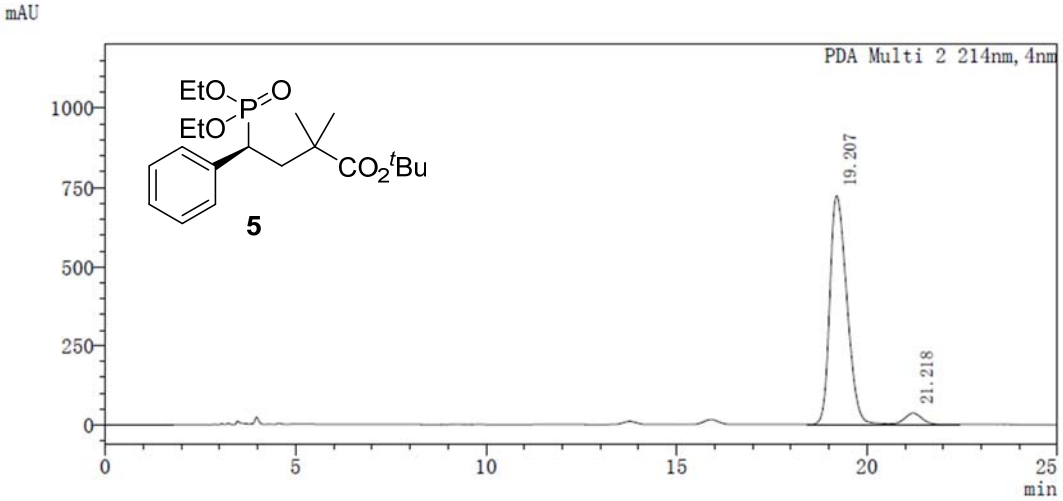
Peak#	Ret. Time	Area	Area%
1	16.112	212613	3.540
2	17.093	5793314	96.460



Peak Table

PDA Ch3 214nm

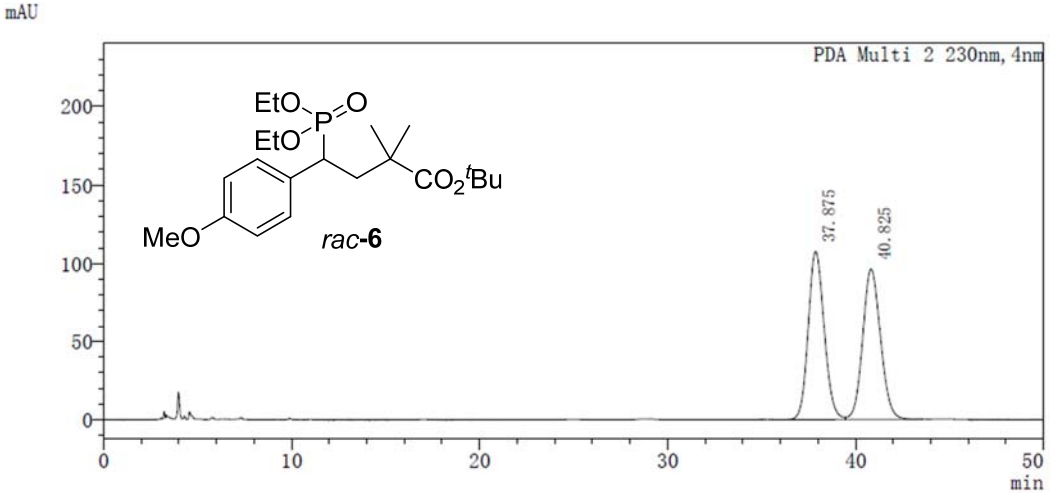
Peak#	Ret. Time	Area	Area%
1	19.148	14979977	49.790
2	21.112	15106343	50.210



Peak Table

PDA Ch2 214nm

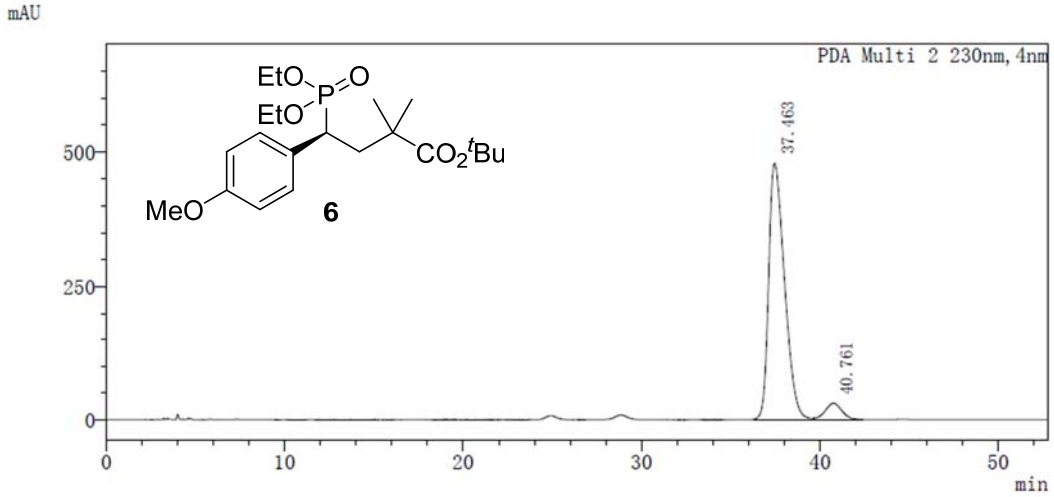
Peak#	Ret. Time	Area	Area%
1	19.207	22517587	95.166
2	21.218	1143671	4.834



Peak Table

PDA Ch2 230nm

Peak#	Ret. Time	Area	Area%
1	37.875	6366351	50.056
2	40.825	6351993	49.944

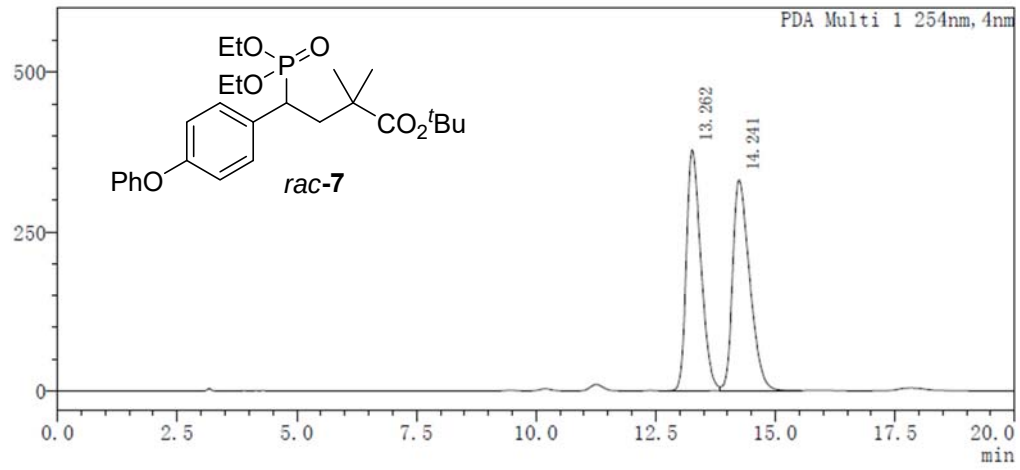


Peak Table

PDA Ch2 230nm

Peak#	Ret. Time	Area	Area%
1	37.463	29543933	93.832
2	40.761	1942088	6.168

mAU

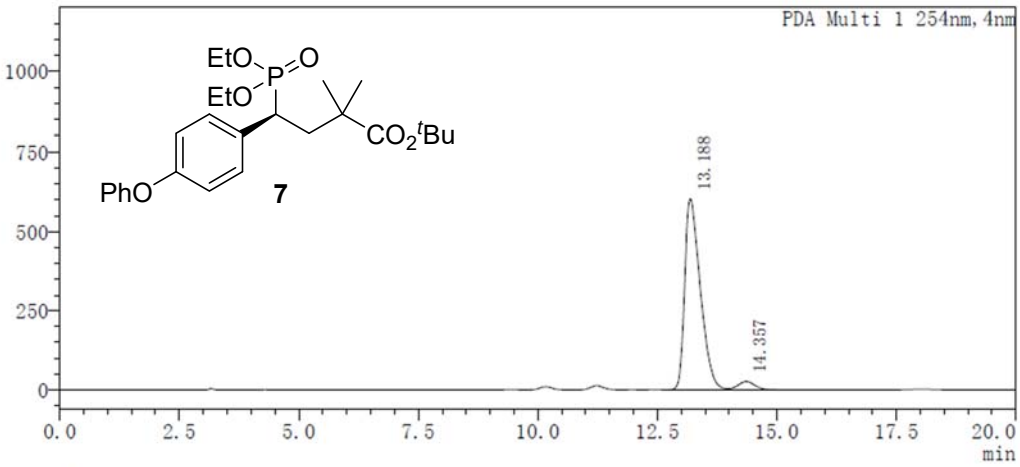


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.262	7999205	49.251
2	14.241	8242492	50.749

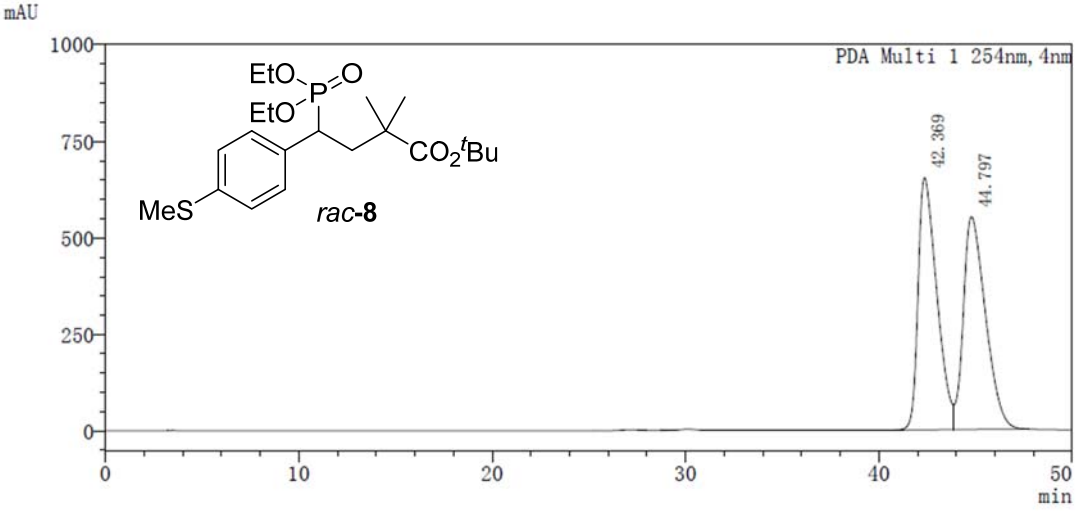
mAU



Peak Table

PDA Ch1 254nm

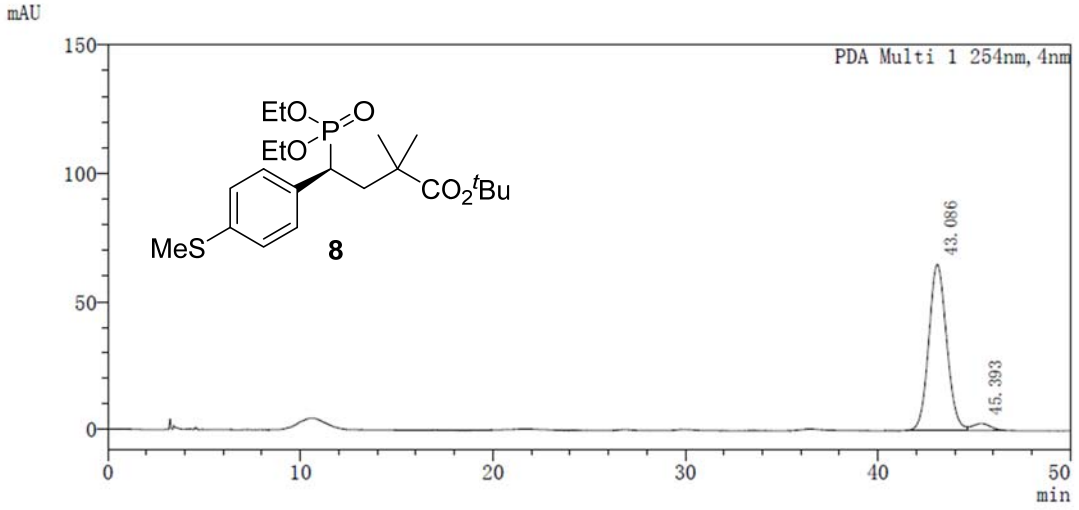
Peak#	Ret. Time	Area	Area%
1	13.188	13697952	95.475
2	14.357	649183	4.525



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	42.369	43994097	49.893
2	44.797	44182777	50.107

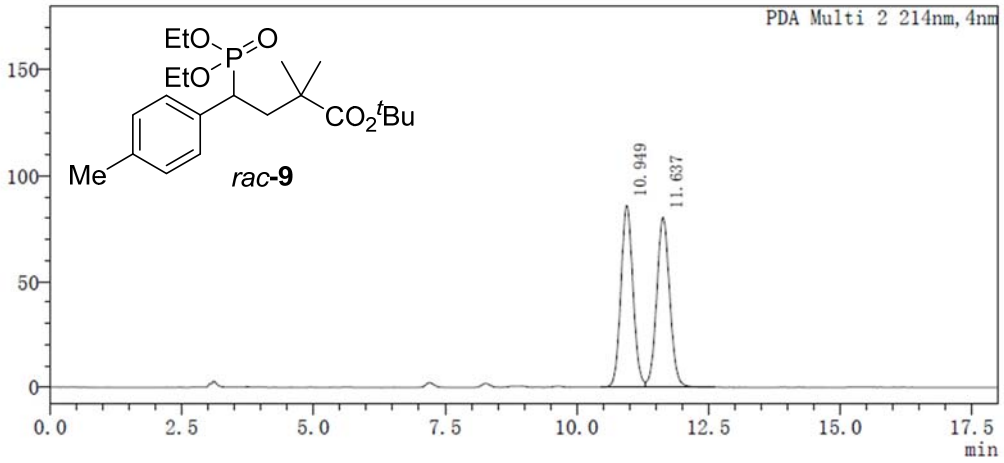


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	43.086	4205347	95.991
2	45.393	175625	4.009

mAU

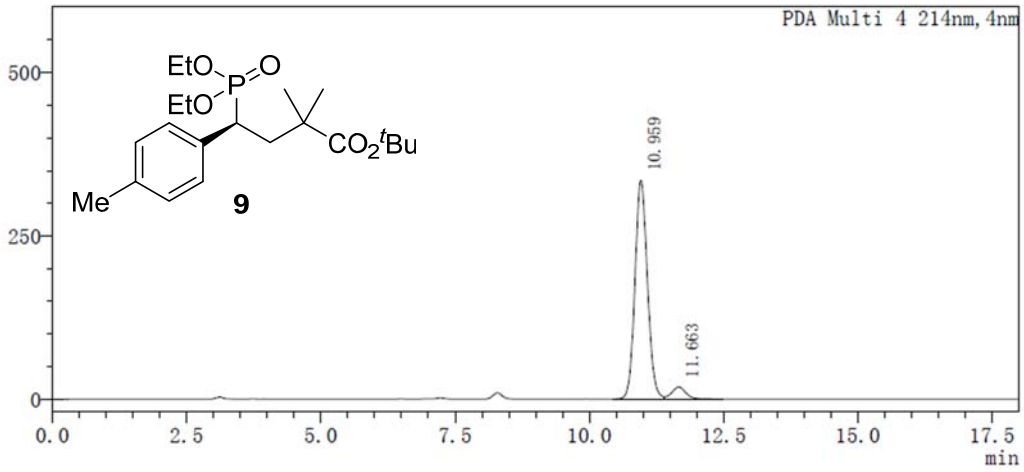


Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	10.949	1372713	49.774
2	11.637	1385151	50.226

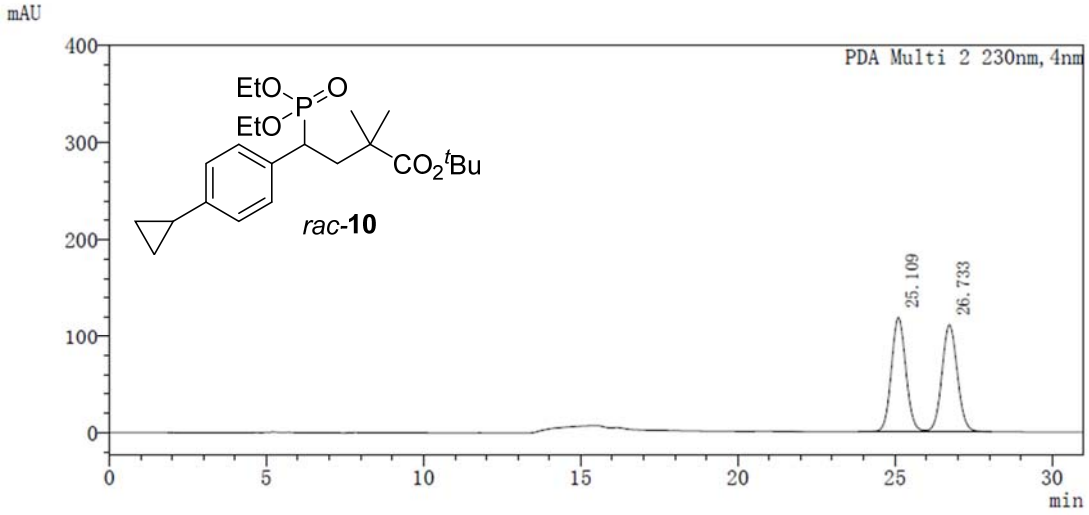
mAU



Peak Table

PDA Ch4 214nm

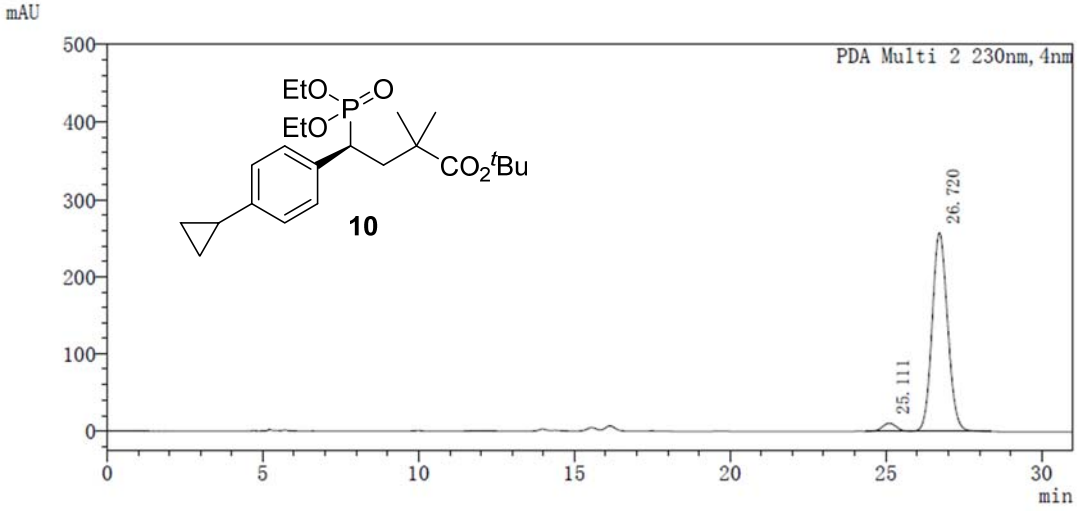
Peak#	Ret. Time	Area	Area%
1	10.959	5401661	94.260
2	11.663	328945	5.740



Peak Table

PDA Ch2 230nm

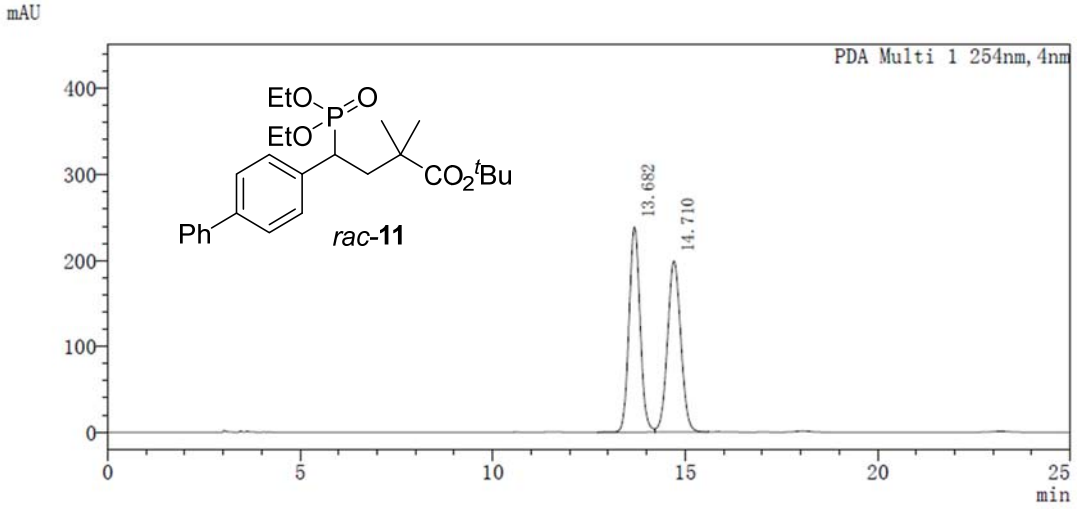
Peak#	Ret. Time	Area	Area%
1	25.109	3811435	50.084
2	26.733	3798654	49.916



Peak Table

PDA Ch2 230nm

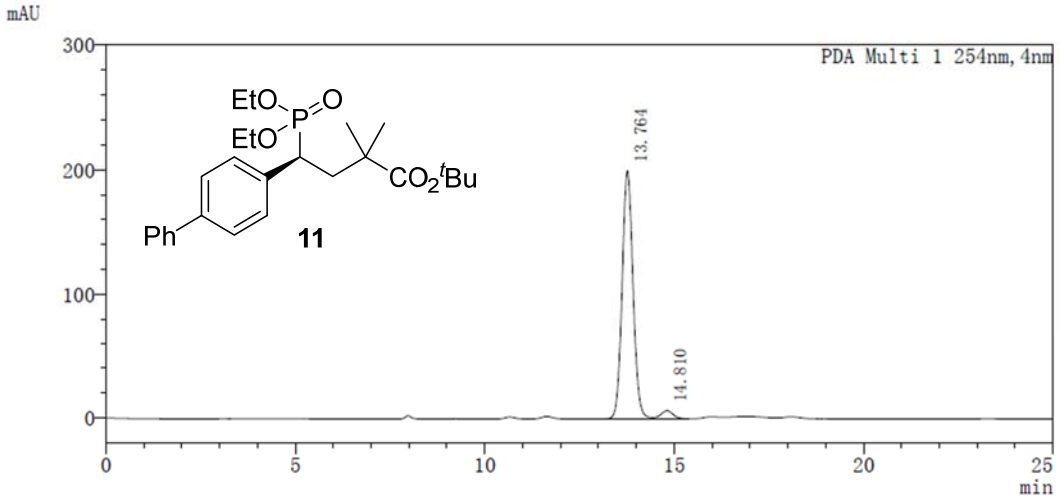
Peak#	Ret. Time	Area	Area%
1	25.111	343681	3.705
2	26.720	8932230	96.295



Peak Table

PDA Ch1 254nm

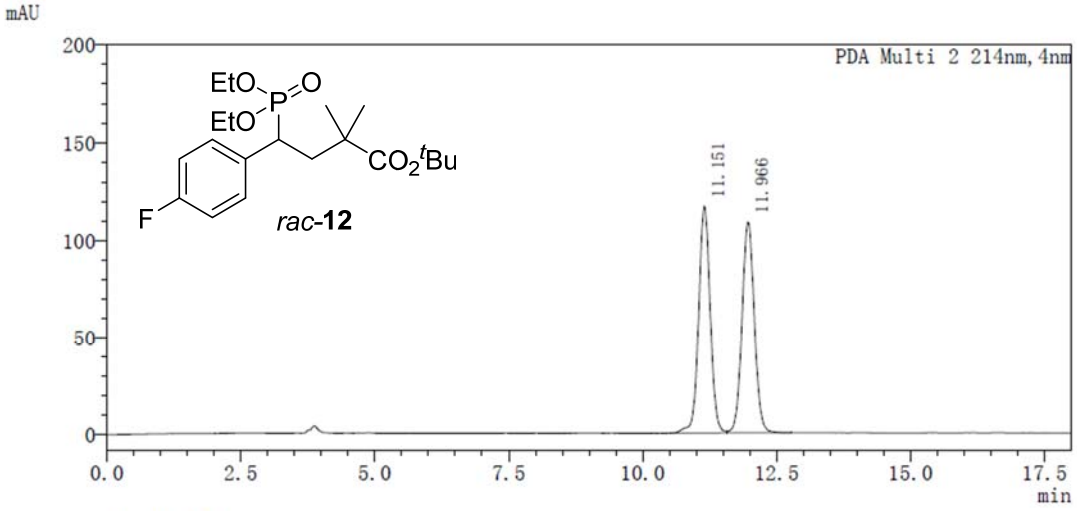
Peak#	Ret. Time	Area	Area%
1	13.682	4782777	50.045
2	14.710	4774226	49.955



Peak Table

PDA Ch1 254nm

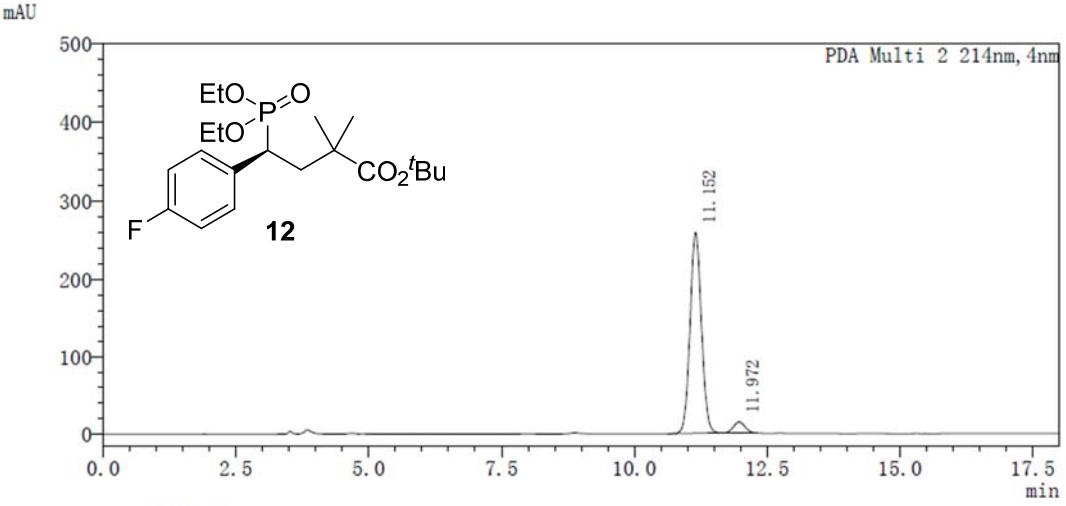
Peak#	Ret. Time	Area	Area%
1	13.764	3994890	96.512
2	14.810	144373	3.488



Peak Table

PDA Ch2 214nm

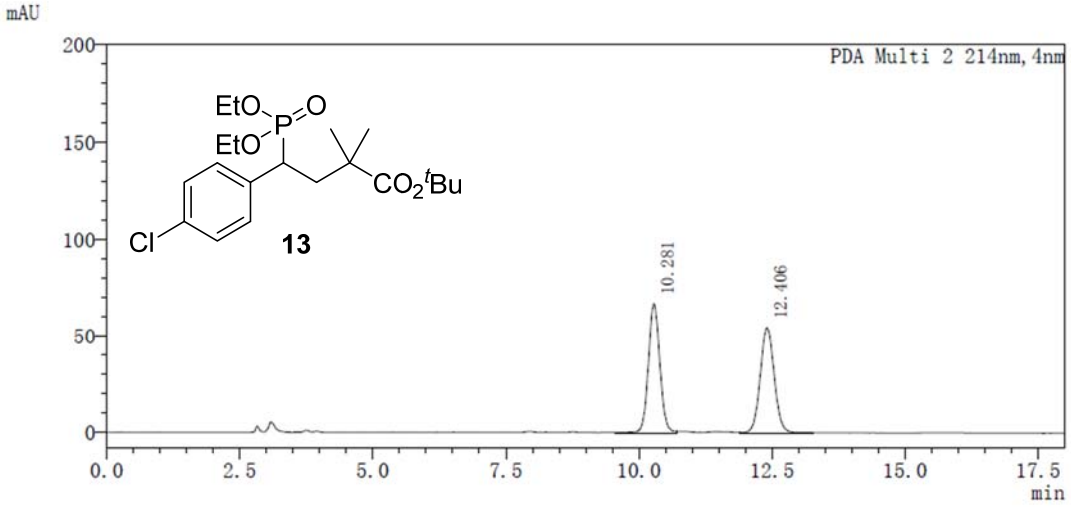
Peak#	Ret. Time	Area	Area%
1	11.151	1757520	50.327
2	11.966	1734647	49.673



Peak Table

PDA Ch2 214nm

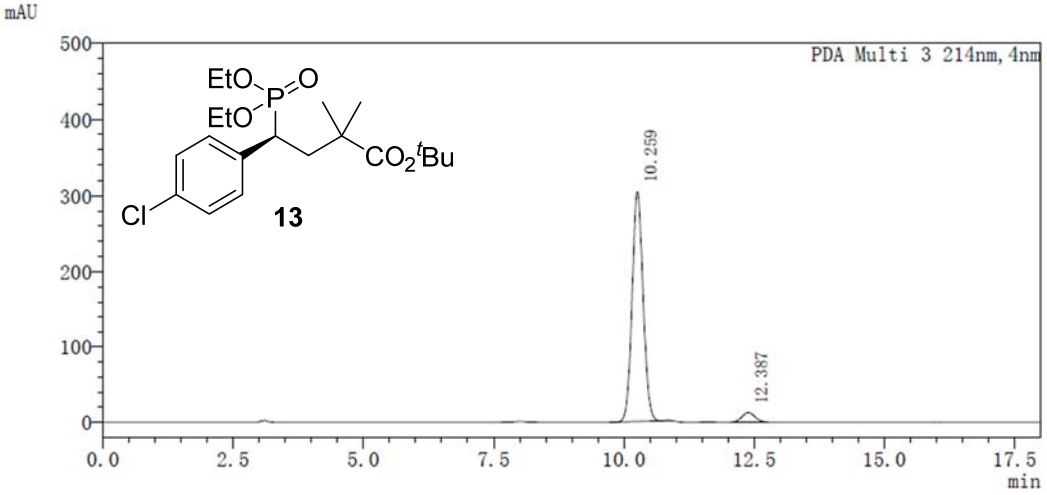
Peak#	Ret. Time	Area	Area%
1	11.152	3845999	94.737
2	11.972	213653	5.263



Peak Table

PDA Ch2 214nm

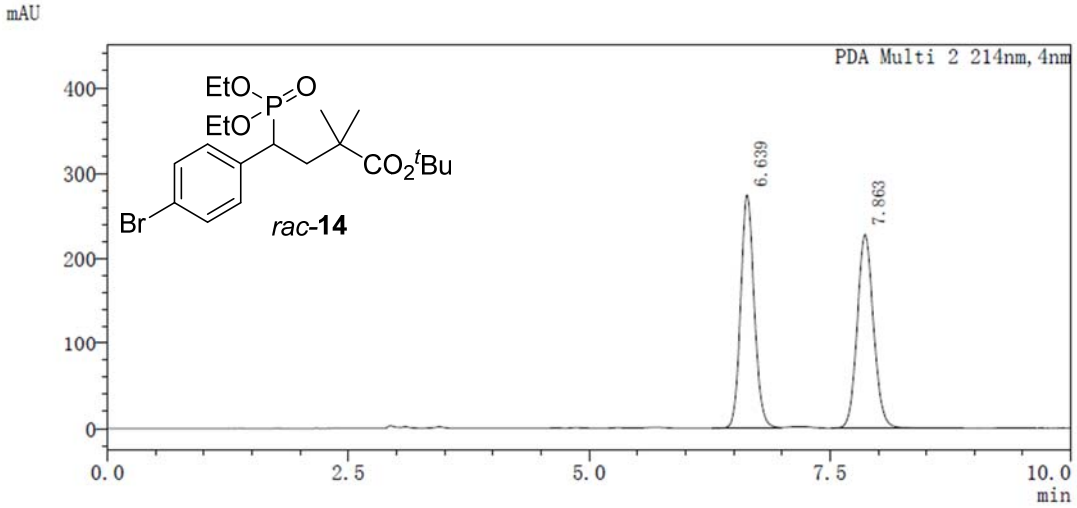
Peak#	Ret. Time	Area	Area%
1	10.281	999964	50.252
2	12.406	989918	49.748



Peak Table

PDA Ch3 214nm

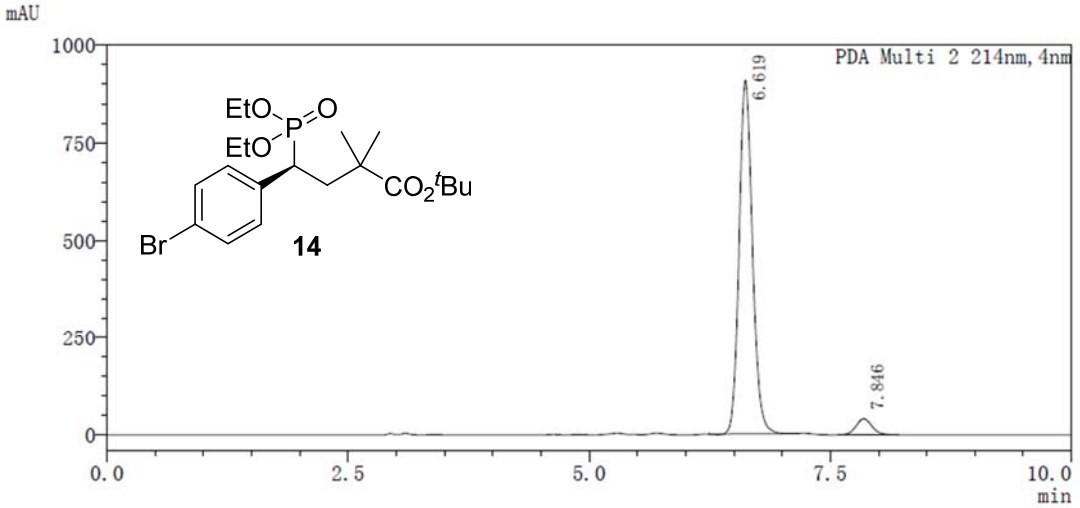
Peak#	Ret. Time	Area	Area%
1	10.259	4484300	95.431
2	12.387	214697	4.569



Peak Table

PDA Ch2 214nm

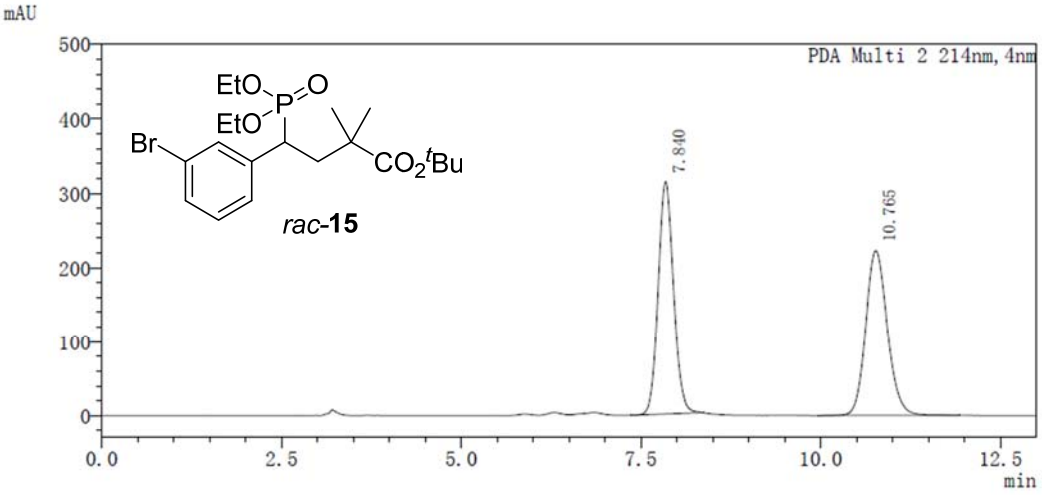
Peak#	Ret. Time	Area	Area%
1	6.639	2699385	50.051
2	7.863	2693909	49.949



Peak Table

PDA Ch2 214nm

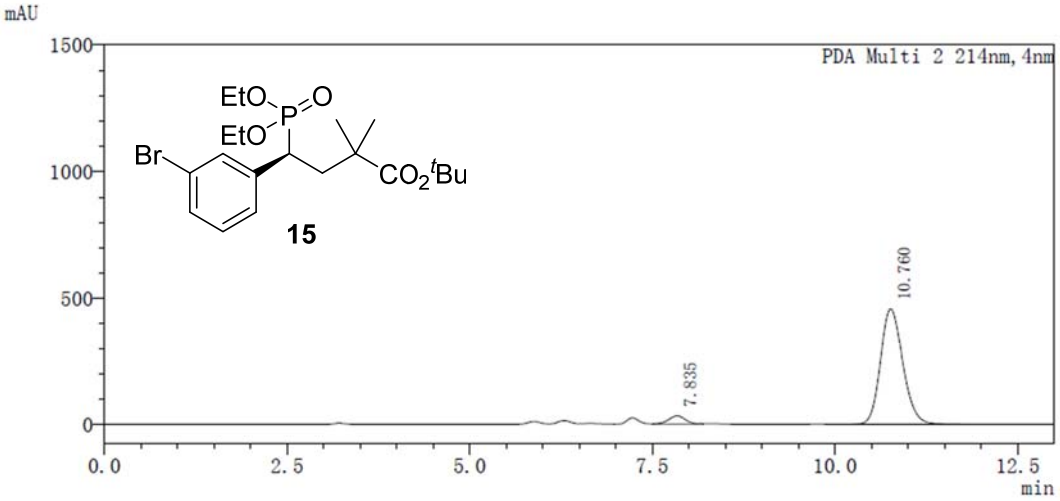
Peak#	Ret. Time	Area	Area%
1	6.619	8738436	94.904
2	7.846	469228	5.096



Peak Table

PDA Ch2 214nm

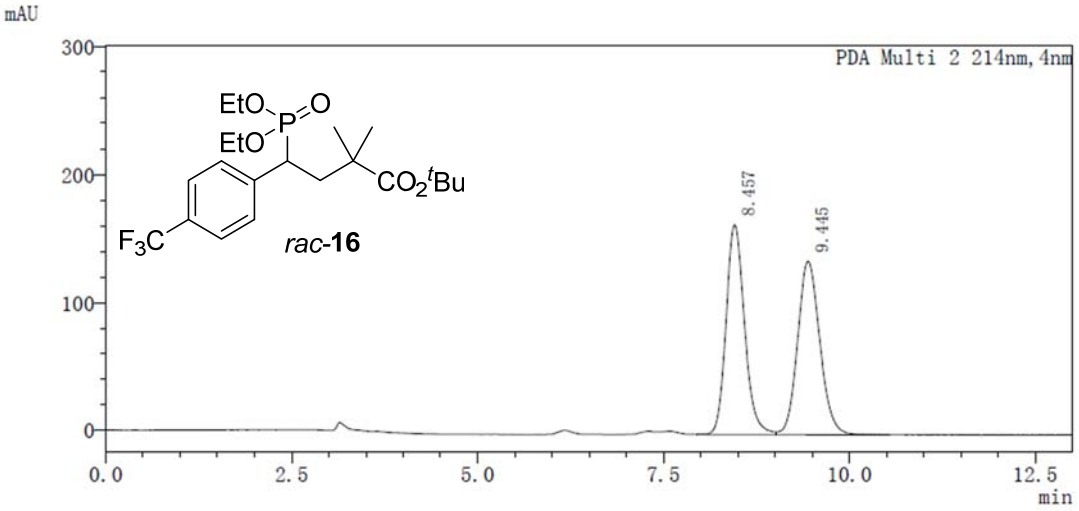
Peak#	Ret. Time	Area	Area%
1	7.840	4683781	50.103
2	10.765	4664588	49.897



Peak Table

PDA Ch2 214nm

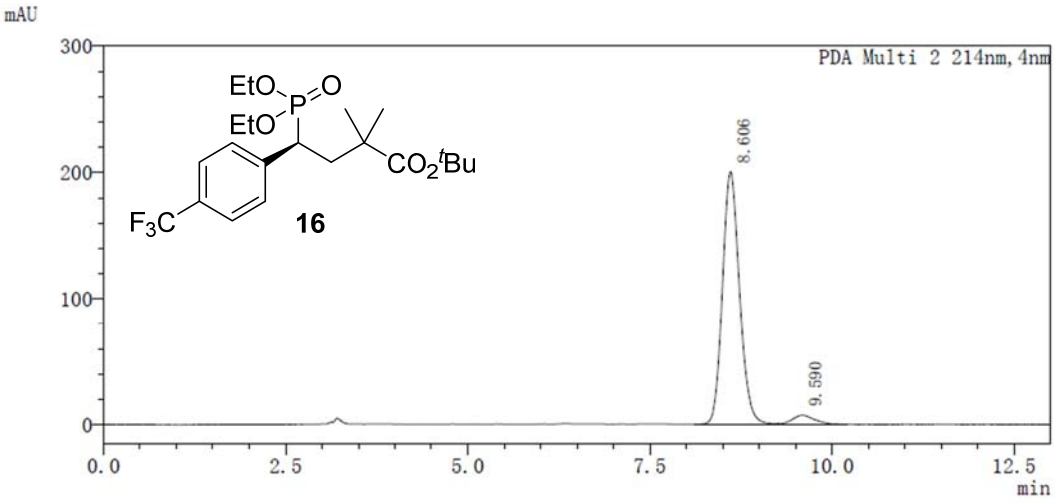
Peak#	Ret. Time	Area	Area%
1	7.835	498996	4.863
2	10.760	9762850	95.137



Peak Table

PDA Ch2 214nm

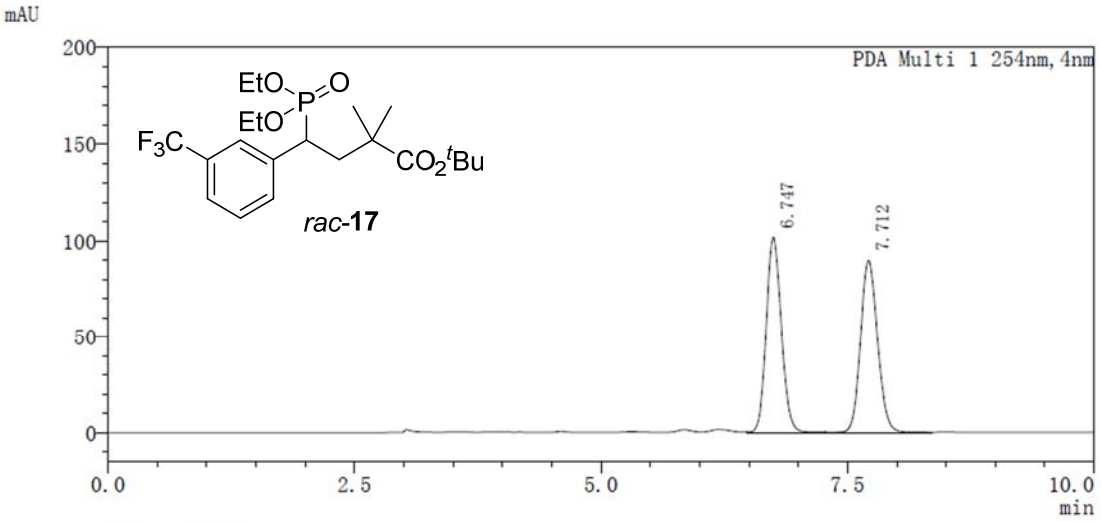
Peak#	Ret. Time	Area	Area%
1	8.457	2837031	50.066
2	9.445	2829573	49.934



Peak Table

PDA Ch2 214nm

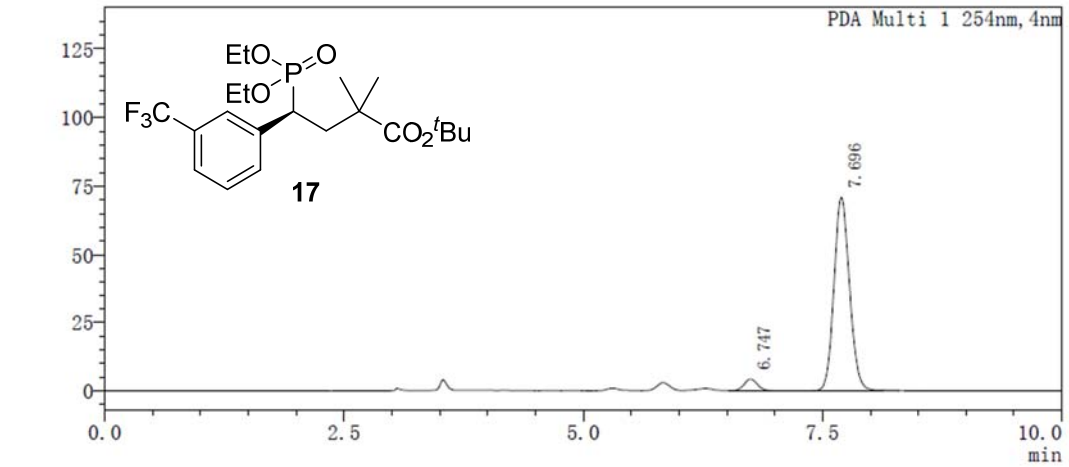
Peak#	Ret. Time	Area	Area%
1	8.606	3267133	95.499
2	9.590	153987	4.501



Peak Table

PDA Ch1 254nm

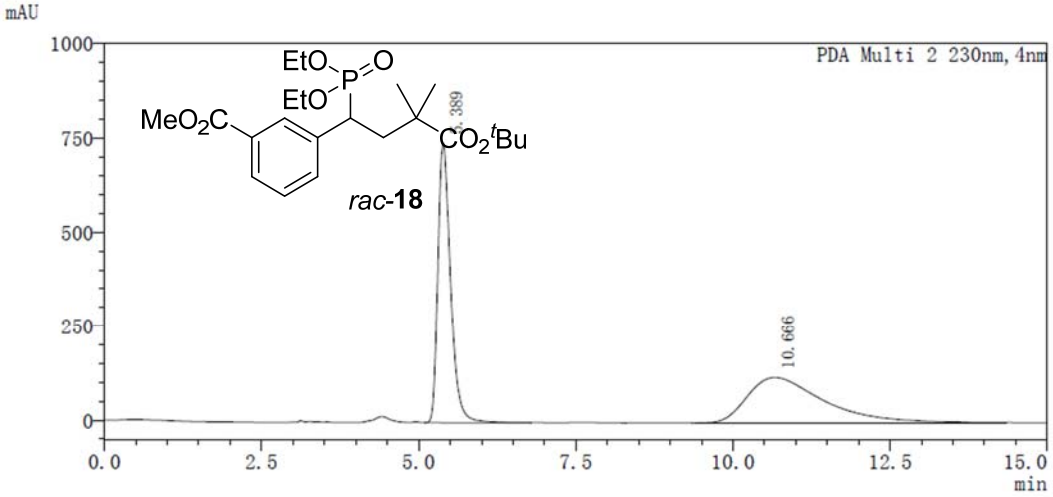
Peak#	Ret. Time	Area	Area%
1	6.747	1082278	50.227
2	7.712	1072487	49.773



Peak Table

PDA Ch1 254nm

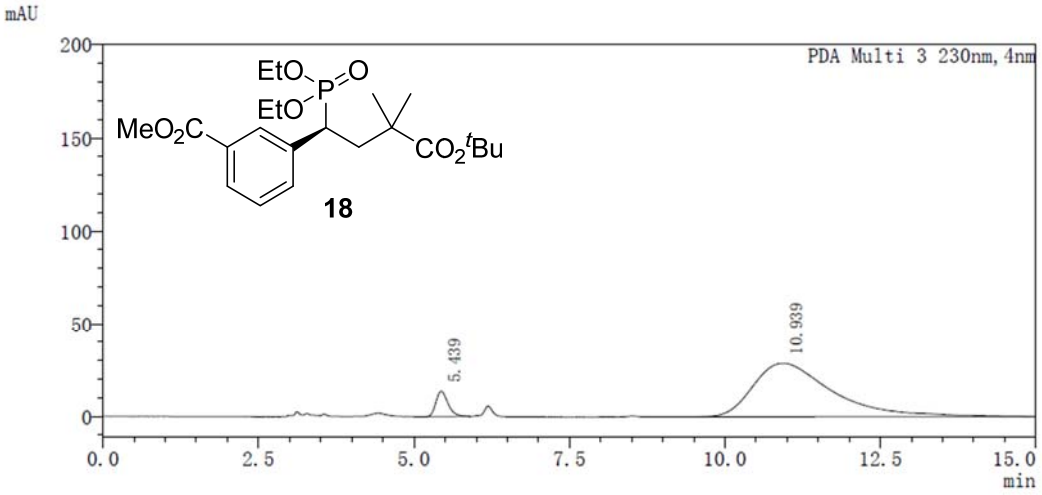
Peak#	Ret. Time	Area	Area%
1	6.747	42171	4.985
2	7.696	803739	95.015



Peak Table

PDA Ch2 230nm

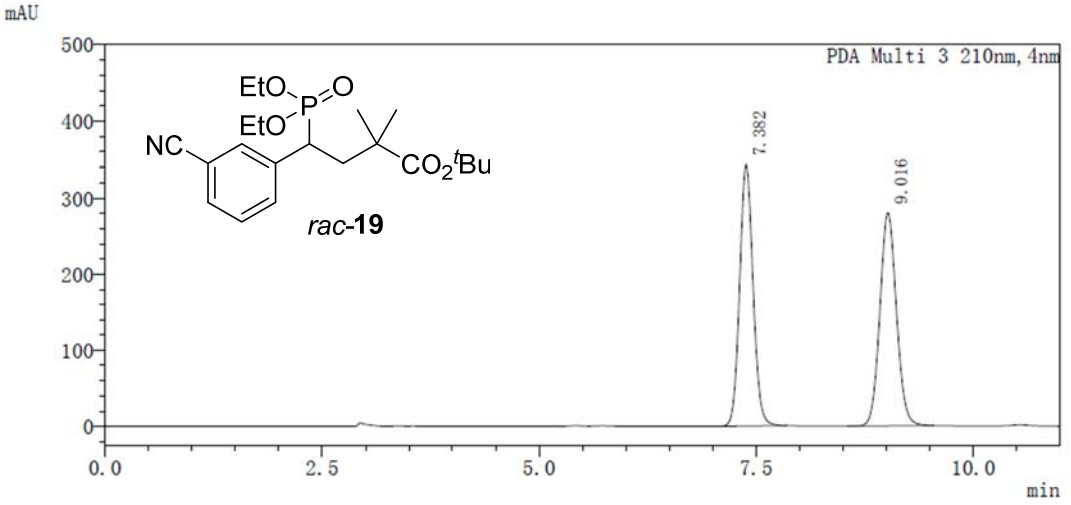
Peak#	Ret. Time	Area	Area%
1	5.389	10491761	50.422
2	10.666	10316145	49.578



Peak Table

PDA Ch3 230nm

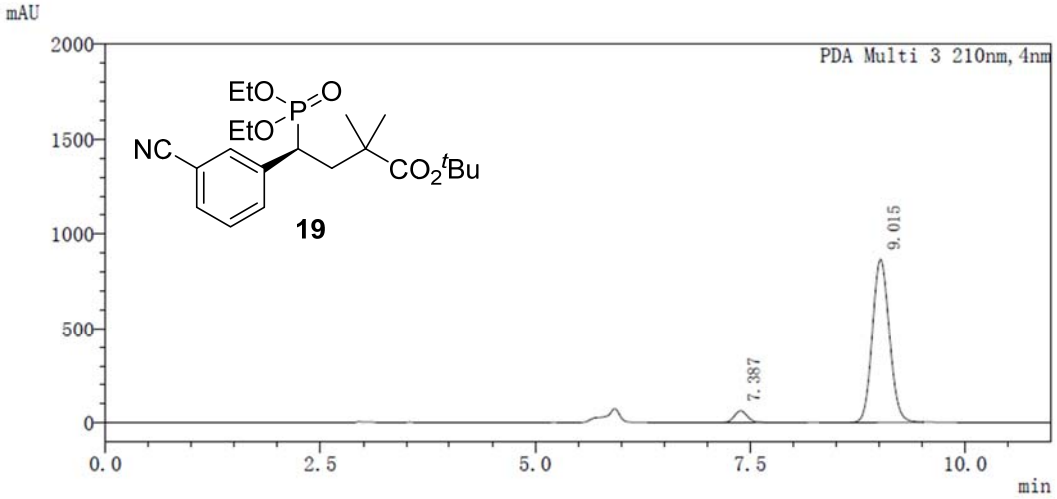
Peak#	Ret. Time	Area	Area%
1	5.439	182554	6.702
2	10.939	2541399	93.298



Peak Table

PDA Ch3 210nm

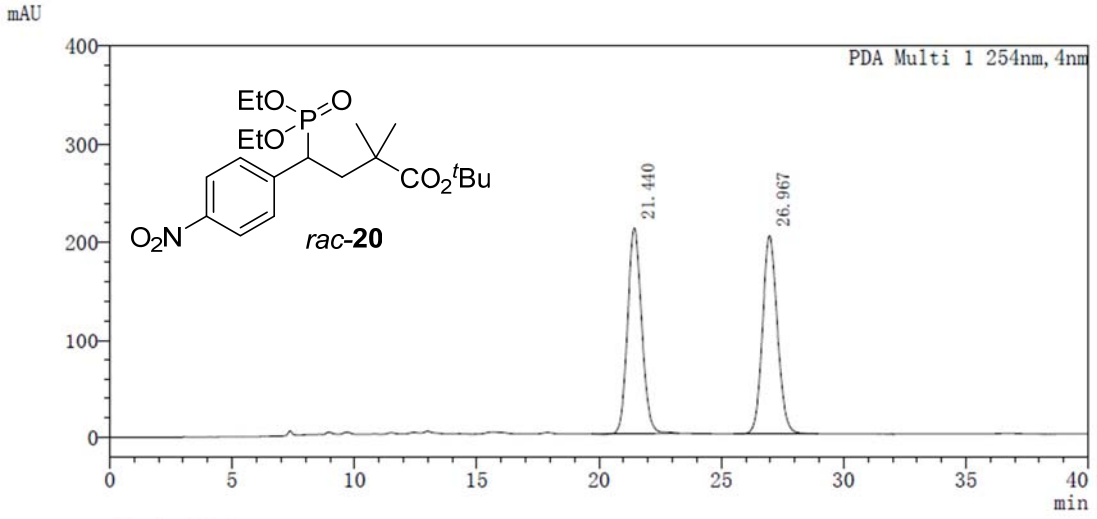
Peak#	Ret. Time	Area	Area%
1	7.382	3686971	49.861
2	9.016	3707593	50.139



Peak Table

PDA Ch3 210nm

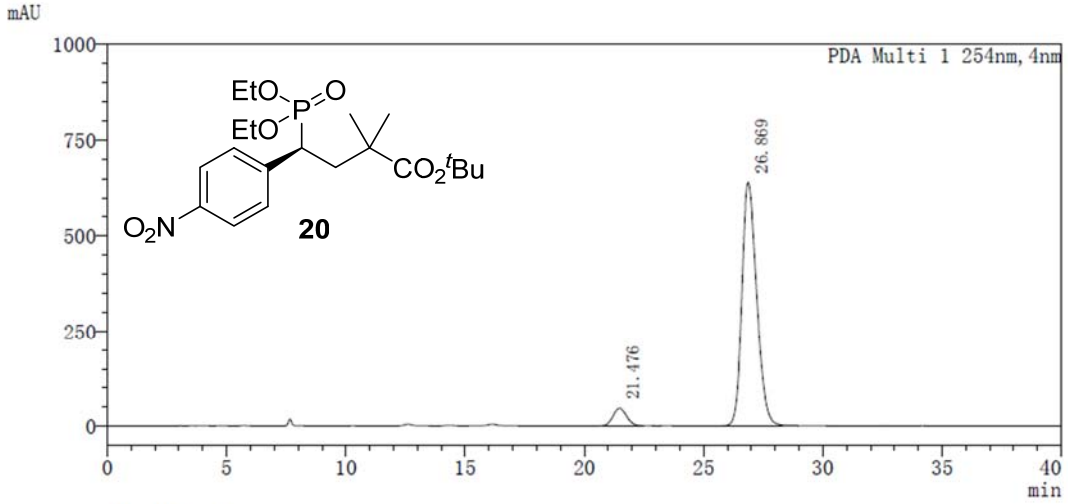
Peak#	Ret. Time	Area	Area%
1	7.387	644172	5.127
2	9.015	11920232	94.873



Peak Table

PDA Ch1 254nm

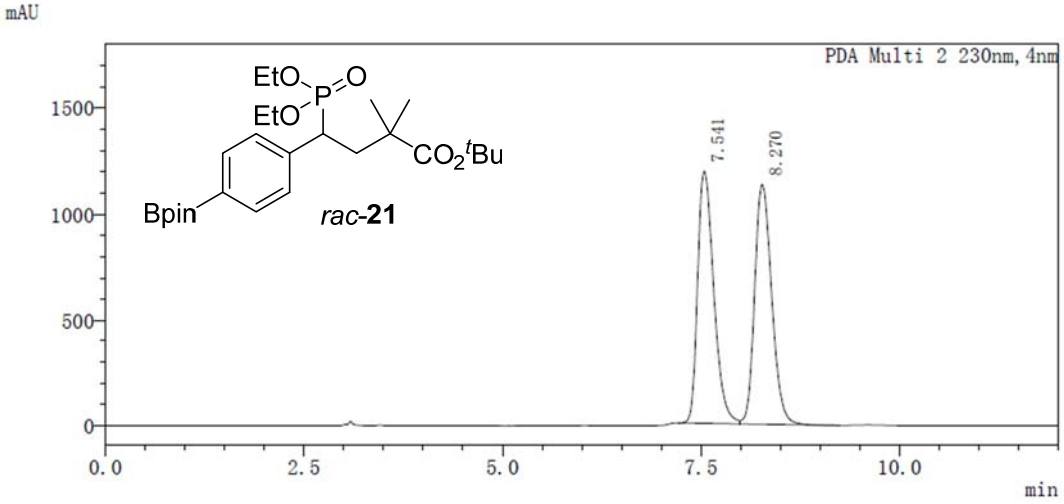
Peak#	Ret. Time	Area	Area%
1	21.440	8444228	49.522
2	26.967	8607124	50.478



Peak Table

PDA Ch1 254nm

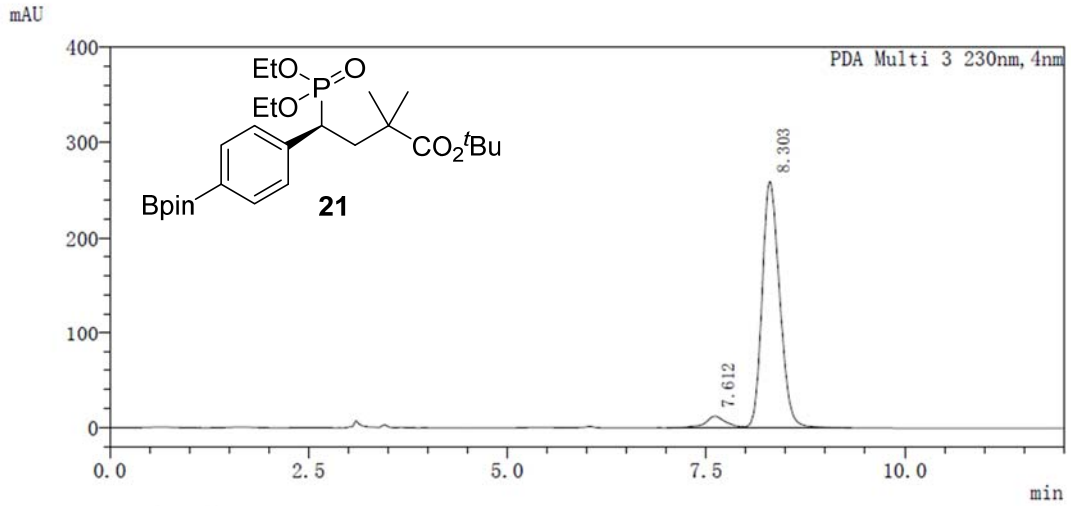
Peak#	Ret. Time	Area	Area%
1	21.476	1816597	6.195
2	26.869	27504749	93.805



Peak Table

PDA Ch2 230nm

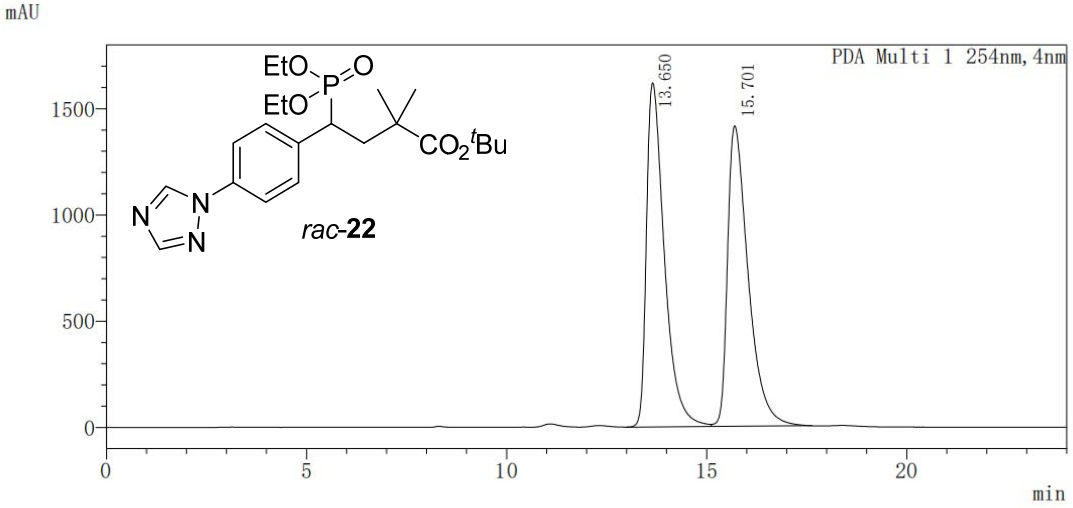
Peak#	Ret. Time	Area	Area%
1	7.541	16857717	49.876
2	8.270	16941544	50.124



Peak Table

PDA Ch3 230nm

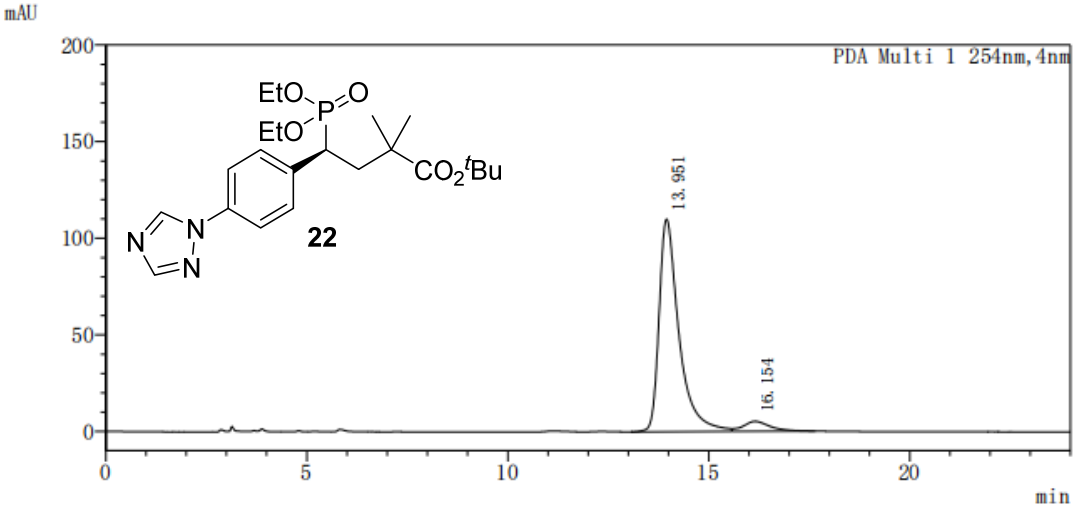
Peak#	Ret. Time	Area	Area%
1	7.612	226908	5.387
2	8.303	3985193	94.613



Peak Table

PDA Ch1 254nm

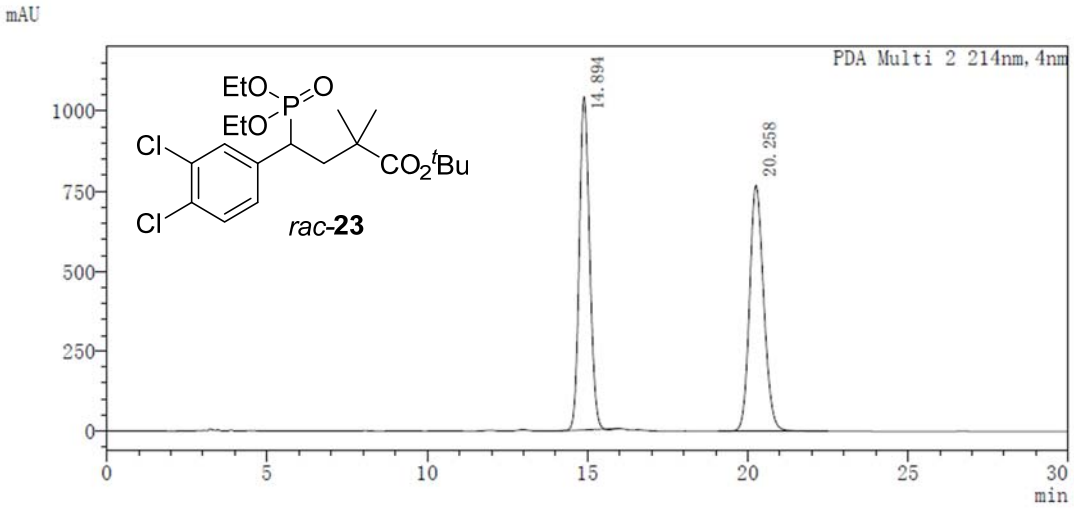
Peak#	Ret. Time	Area	Area%
1	13.650	50546071	49.869
2	15.701	50810756	50.131



Peak Table

PDA Ch1 254nm

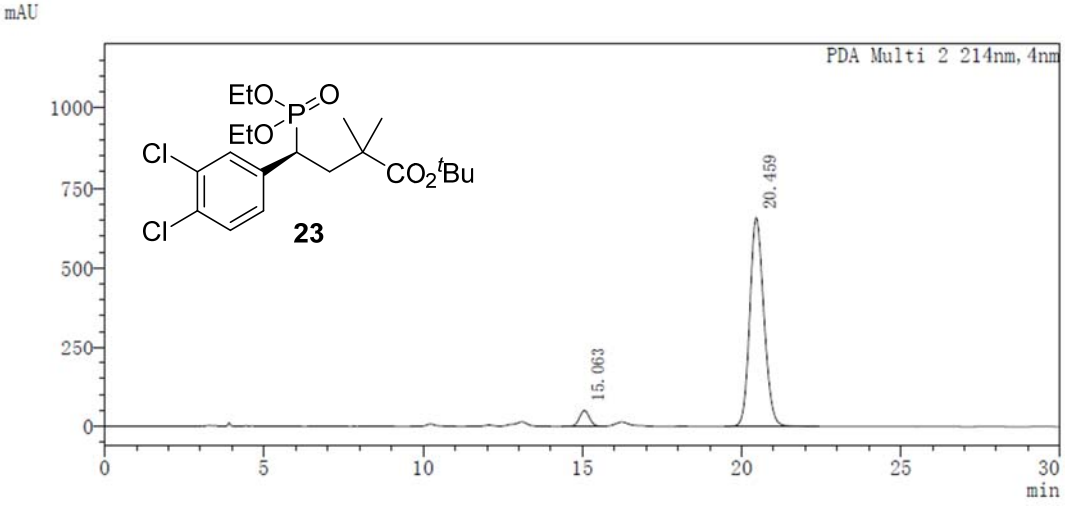
Peak#	Ret. Time	Area	Area%
1	13.951	3785027	93.942
2	16.154	244073	6.058



Peak Table

PDA Ch2 214nm

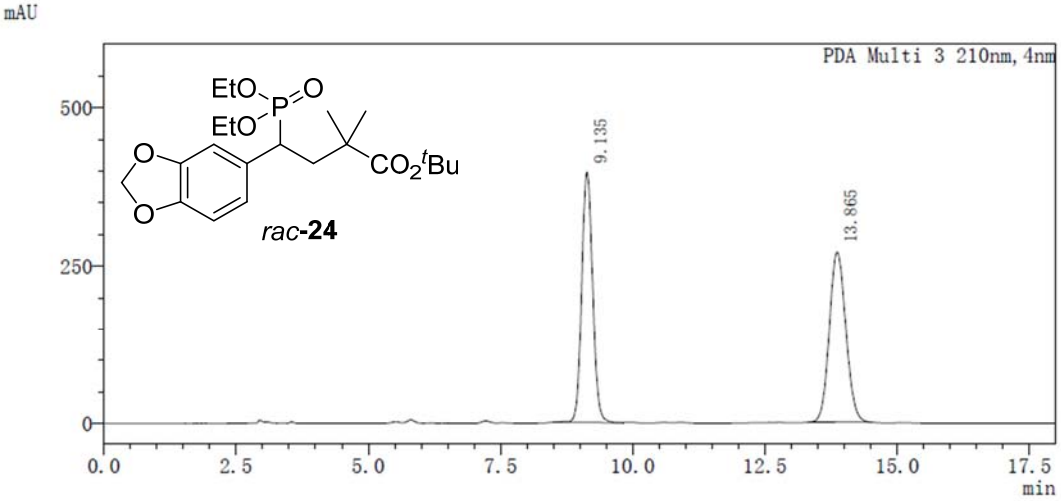
Peak#	Ret. Time	Area	Area%
1	14.894	23341188	49.630
2	20.258	23689389	50.370



Peak Table

PDA Ch2 214nm

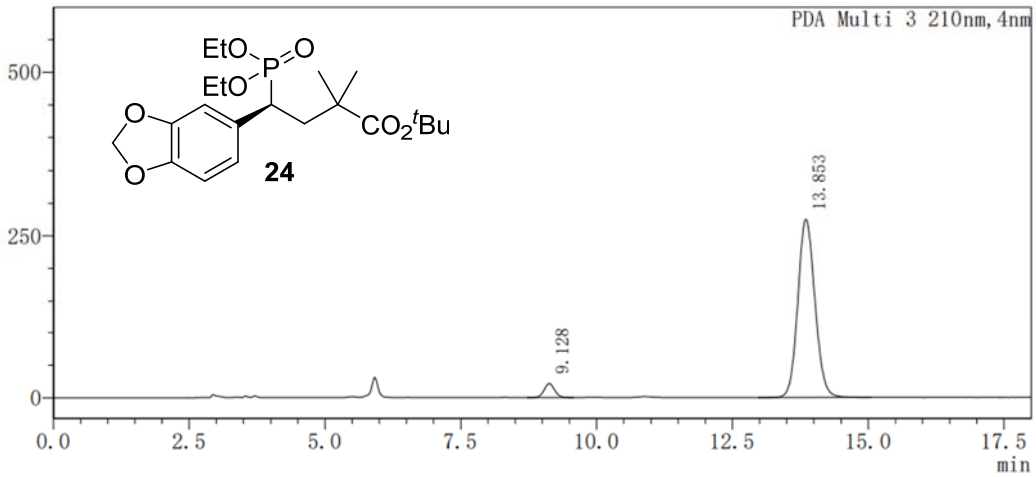
Peak#	Ret. Time	Area	Area%
1	15.063	1080700	5.038
2	20.459	20371563	94.962



Peak Table

PDA Ch3 210nm

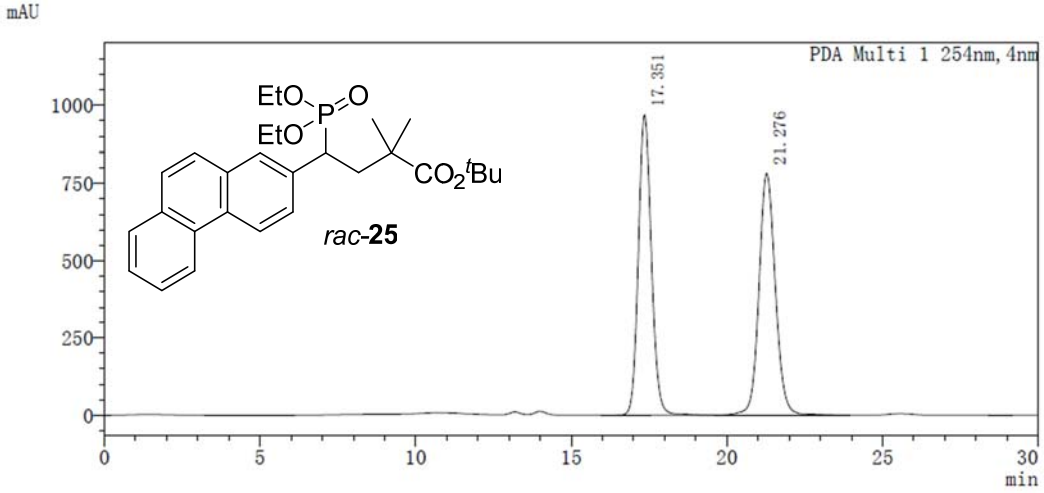
Peak#	Ret. Time	Area	Area%
1	9.135	5702615	49.323
2	13.865	5859121	50.677



Peak Table

PDA Ch3 210nm

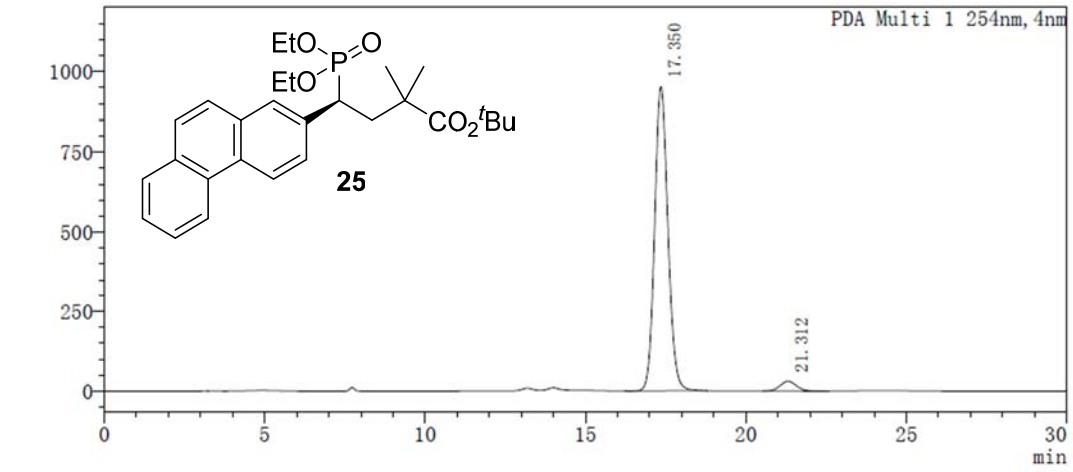
Peak#	Ret. Time	Area	Area%
1	9.128	286709	4.534
2	13.853	6036224	95.466



Peak Table

PDA Ch1 254nm

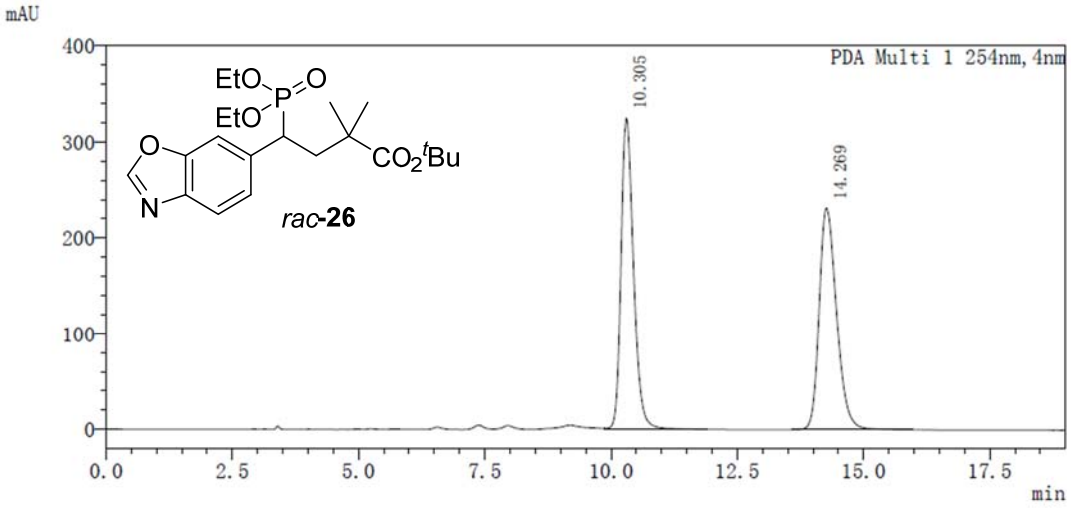
Peak#	Ret. Time	Area	Area%
1	17.351	28241783	49.671
2	21.276	28616467	50.329



Peak Table

PDA Ch1 254nm

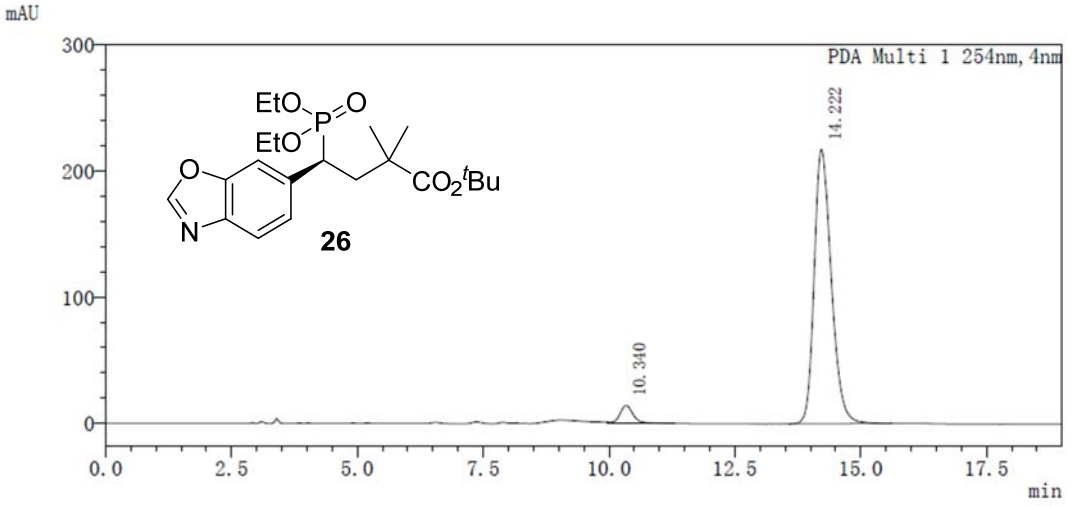
Peak#	Ret. Time	Area	Area%
1	17.350	27505856	96.257
2	21.312	1069682	3.743



Peak Table

PDA Ch1 254nm

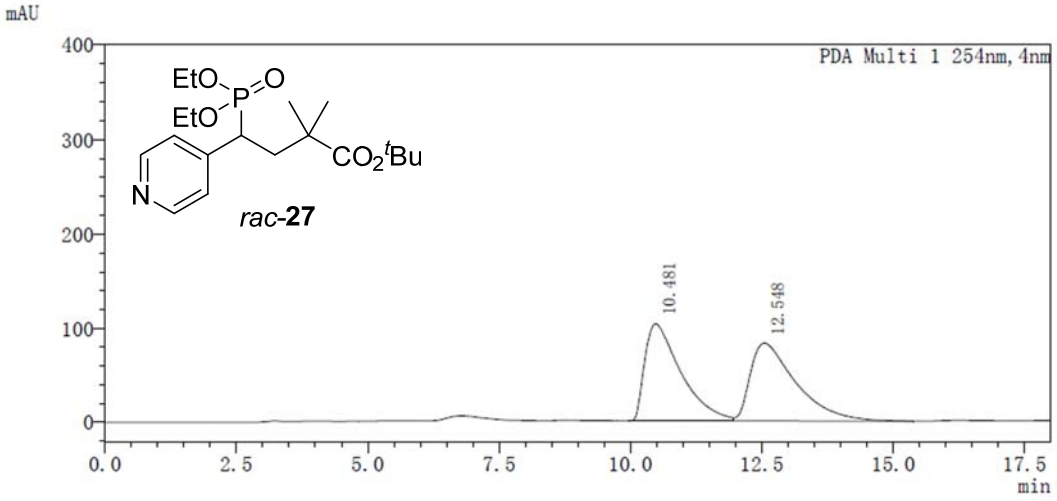
Peak#	Ret. Time	Area	Area%
1	10.305	5592506	50.201
2	14.269	5547612	49.799



Peak Table

PDA Ch1 254nm

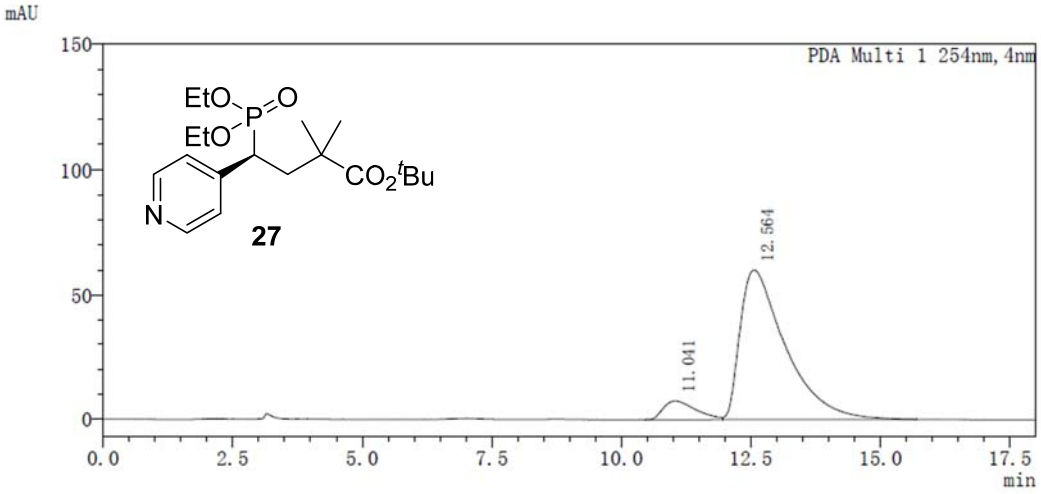
Peak#	Ret. Time	Area	Area%
1	10.340	263573	4.865
2	14.222	5154238	95.135



Peak Table

PDA Ch1 254nm

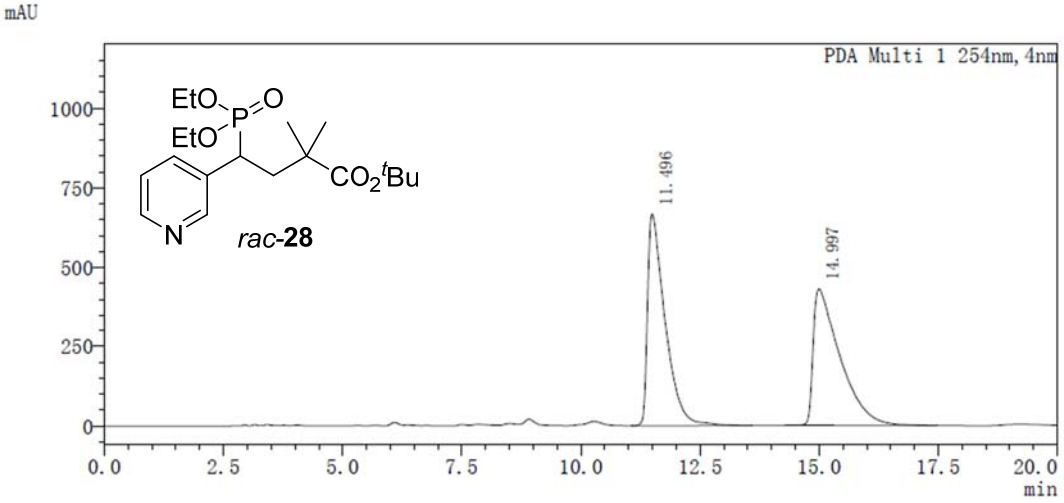
Peak#	Ret. Time	Area	Area%
1	10.481	4963289	49.672
2	12.548	5028851	50.328



Peak Table

PDA Ch1 254nm

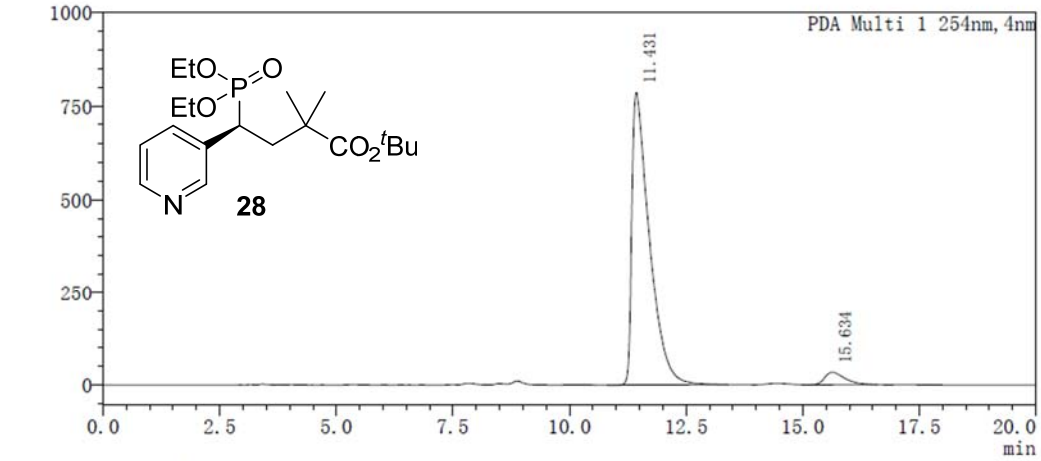
Peak#	Ret. Time	Area	Area%
1	11.041	327607	8.138
2	12.564	3698226	91.862



Peak Table

PDA Ch1 254nm

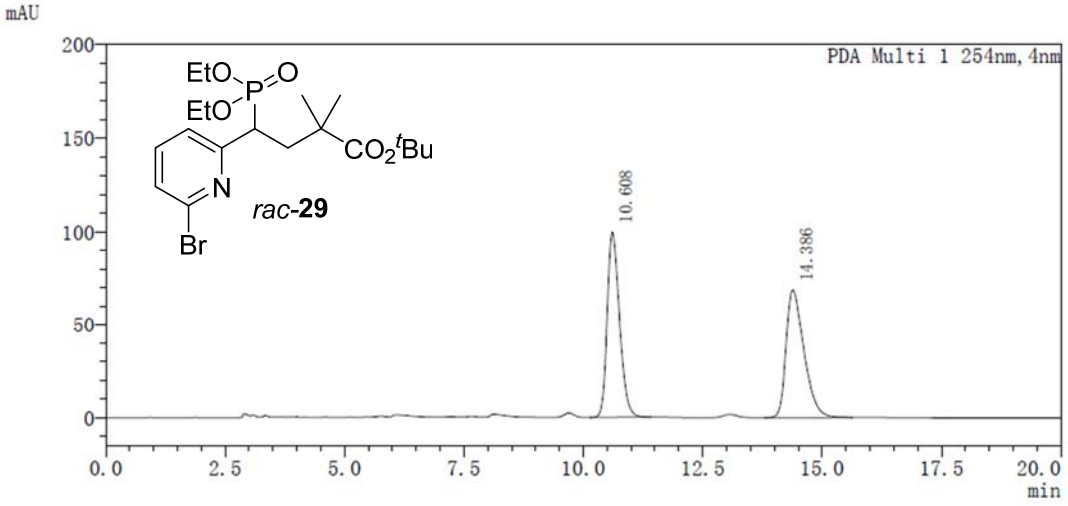
Peak#	Ret. Time	Area	Area%
1	11.496	17051111	50.326
2	14.997	16830140	49.674



Peak Table

PDA Ch1 254nm

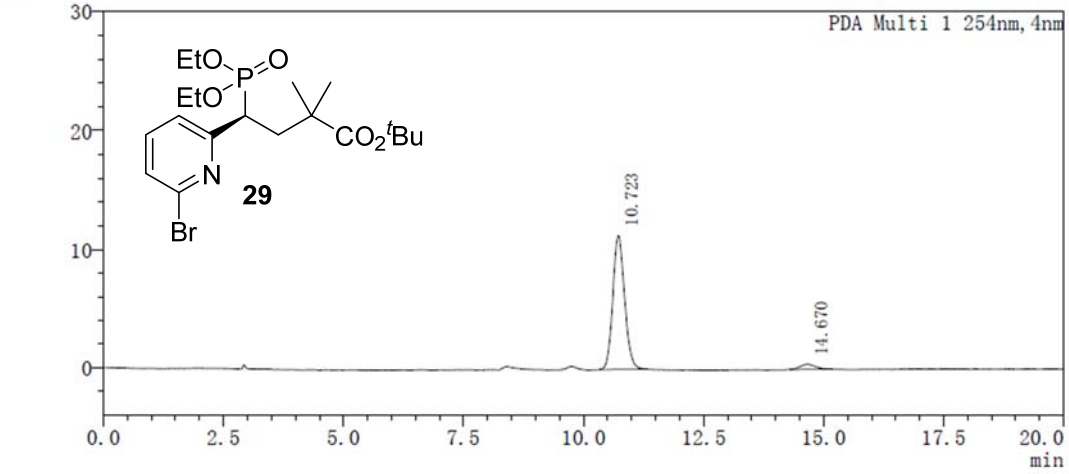
Peak#	Ret. Time	Area	Area%
1	11.431	20617948	95.354
2	15.634	1004531	4.646



Peak Table

PDA Ch1 254nm

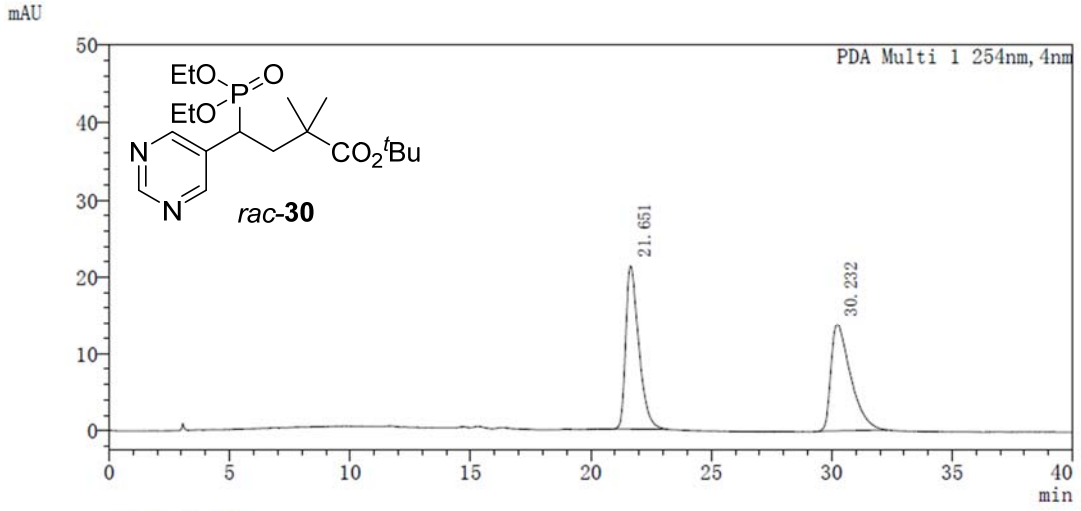
Peak#	Ret. Time	Area	Area%
1	10.608	1780810	49.906
2	14.386	1787520	50.094



Peak Table

PDA Ch1 254nm

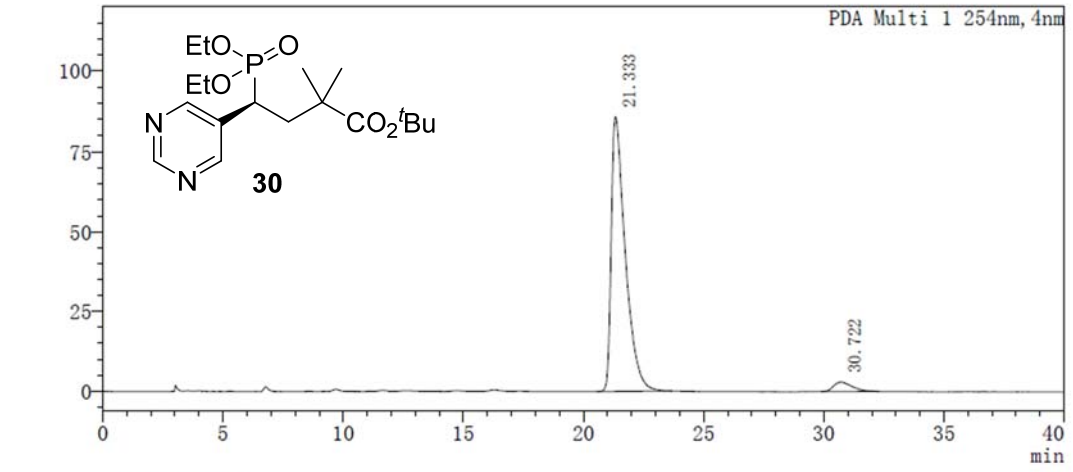
Peak#	Ret. Time	Area	Area%
1	10.723	192524	95.531
2	14.670	9005	4.469



Peak Table

PDA Ch1 254nm

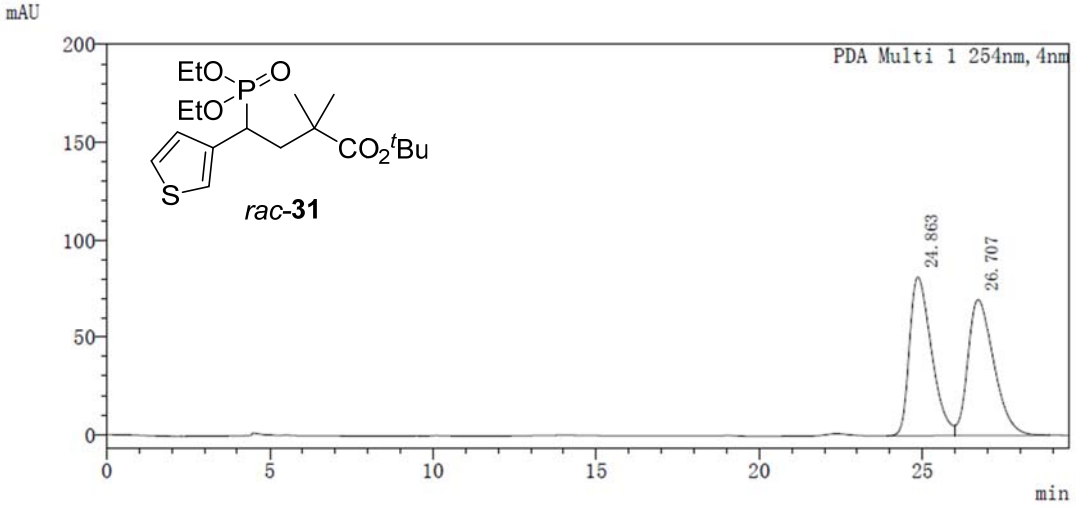
Peak#	Ret. Time	Area	Area%
1	21.651	802822	50.455
2	30.232	788351	49.545



Peak Table

PDA Ch1 254nm

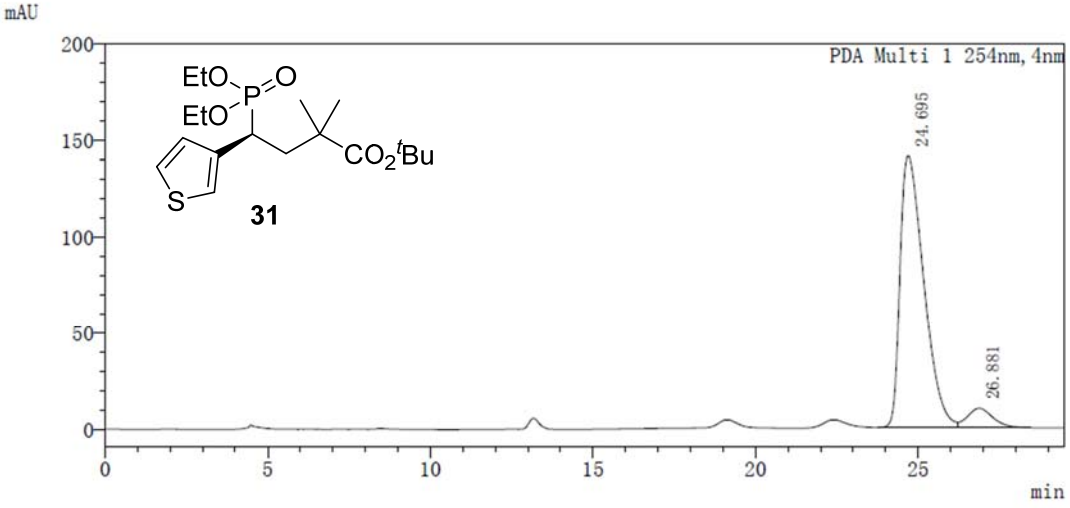
Peak#	Ret. Time	Area	Area%
1	21.333	3496725	95.706
2	30.722	156903	4.294



Peak Table

PDA Ch1 254nm

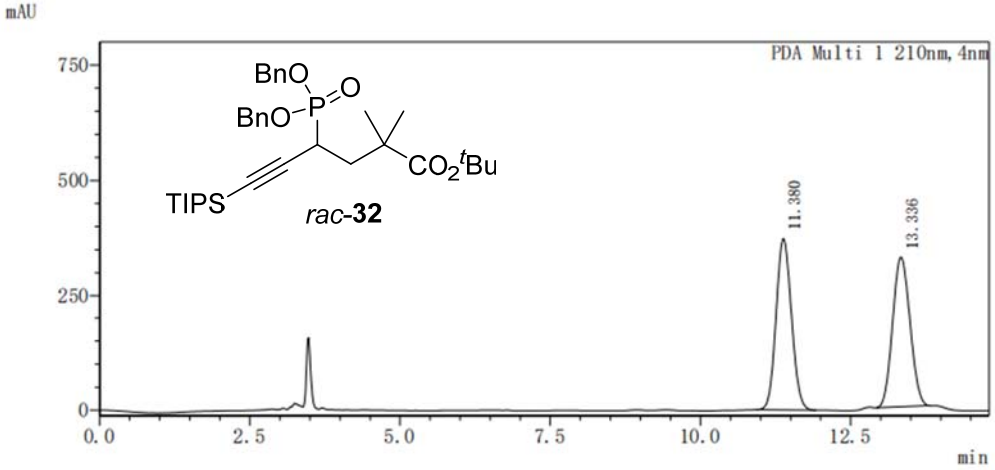
Peak#	Ret. Time	Area	Area%
1	24.863	3831469	49.749
2	26.707	3870067	50.251



Peak Table

PDA Ch1 254nm

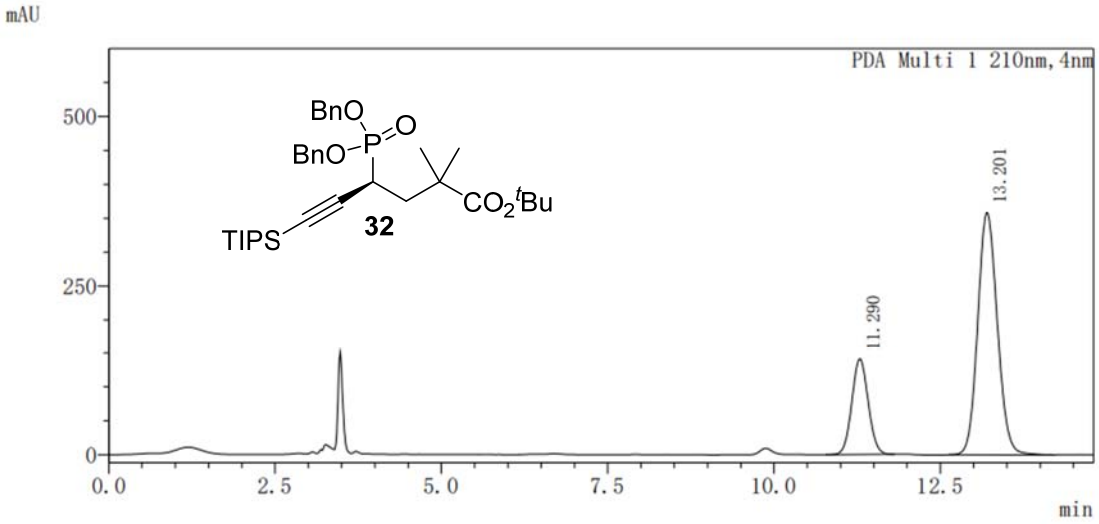
Peak#	Ret. Time	Area	Area%
1	24.695	7181687	92.914
2	26.881	547741	7.086



Peak Table

PDA Ch1 210nm

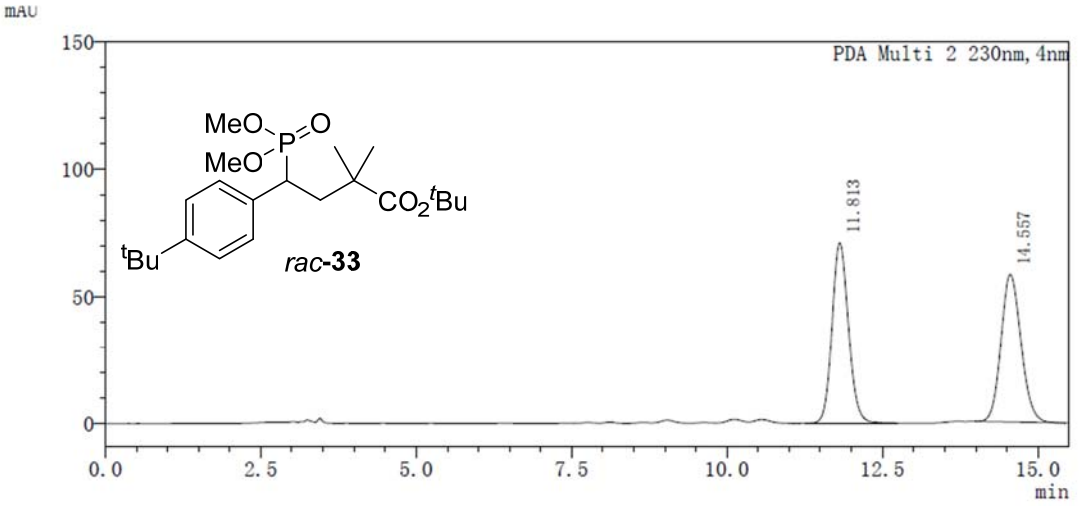
Peak#	Ret. Time	Area	Area%
1	11.380	6635800	50.291
2	13.336	6558984	49.709



Peak Table

PDA Ch1 210nm

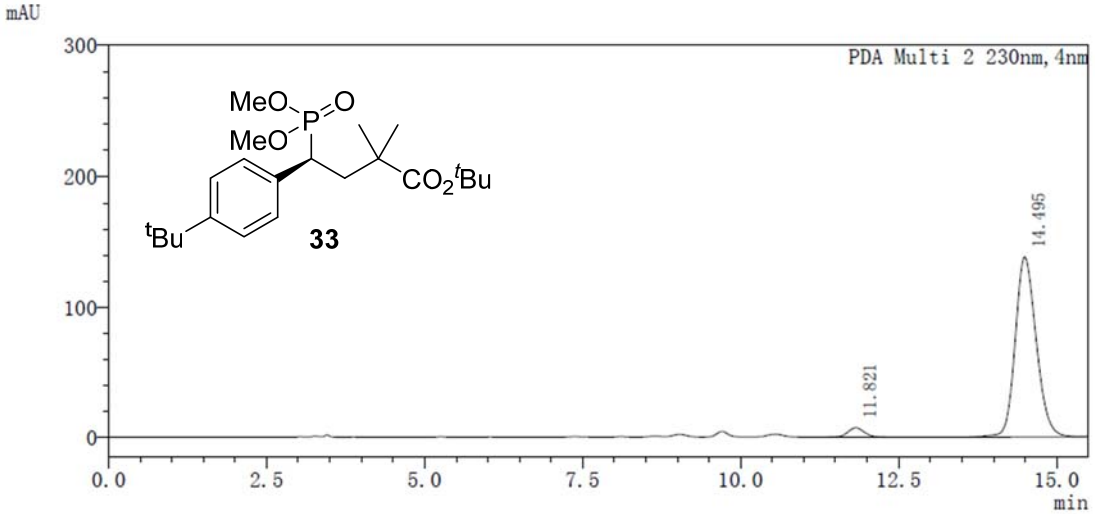
Peak#	Ret. Time	Area	Area%
1	11.290	2414308	24.690
2	13.201	7364073	75.310



Peak Table

PDA Ch2 230nm

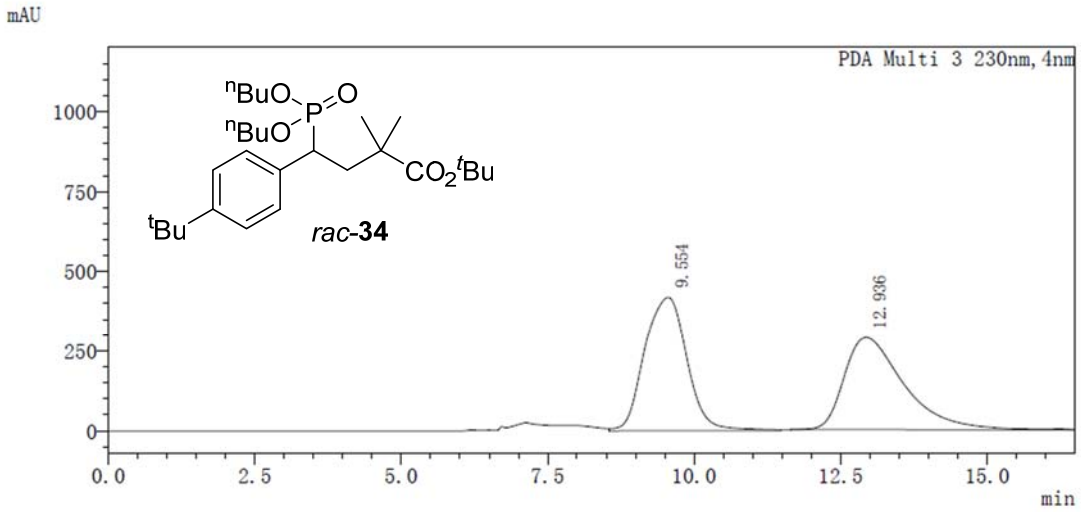
Peak#	Ret. Time	Area	Area%
1	11.813	1311032	50.095
2	14.557	1306081	49.905



Peak Table

PDA Ch2 230nm

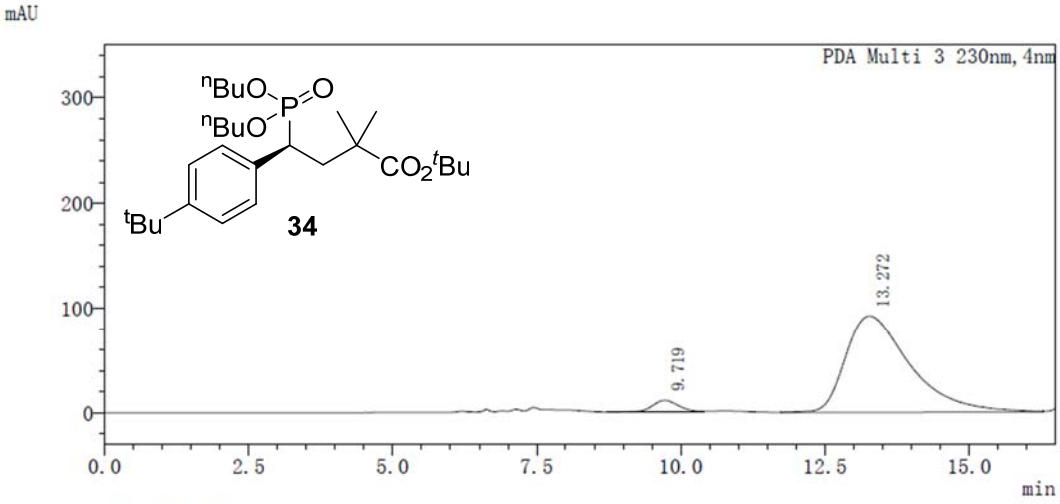
Peak#	Ret. Time	Area	Area%
1	11.821	130410	3.901
2	14.495	3212710	96.099



Peak Table

PDA Ch3 230nm

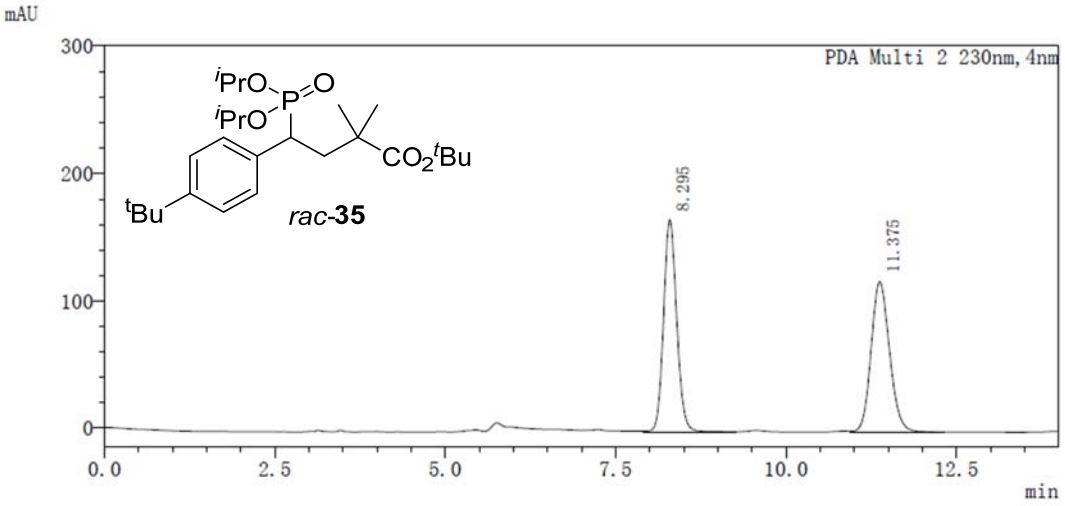
Peak#	Ret. Time	Area	Area%
1	9.554	21003388	50.641
2	12.936	20471392	49.359



Peak Table

PDA Ch3 230nm

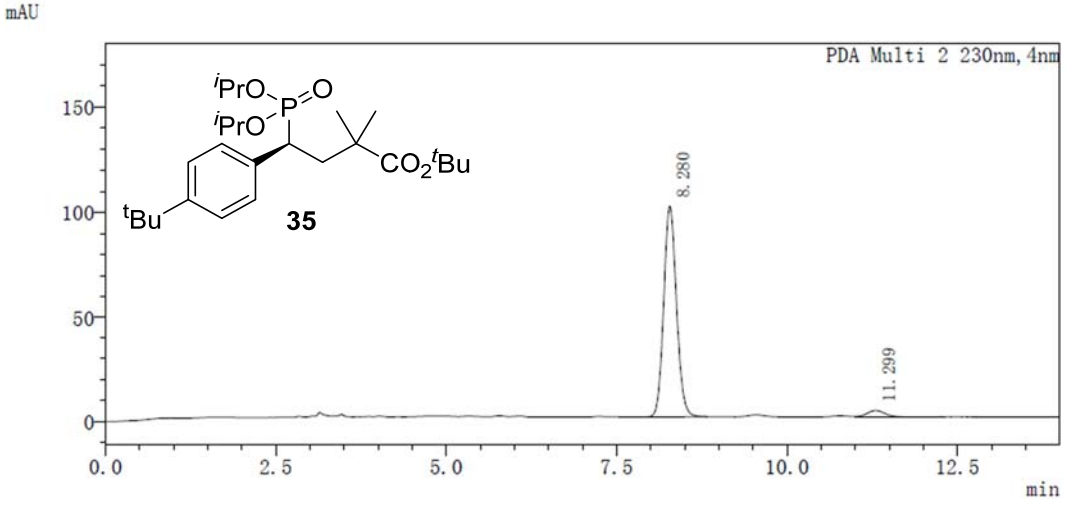
Peak#	Ret. Time	Area	Area%
1	9.719	385278	5.090
2	13.272	7184288	94.910



Peak Table

PDA Ch2 230nm

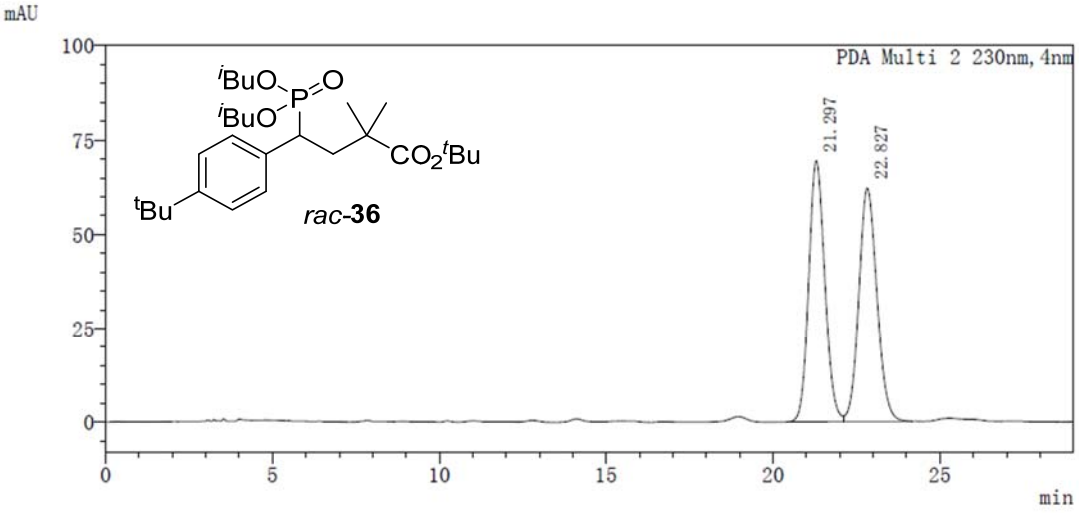
Peak#	Ret. Time	Area	Area%
1	8.295	2257063	50.226
2	11.375	2236749	49.774



Peak Table

PDA Ch2 230nm

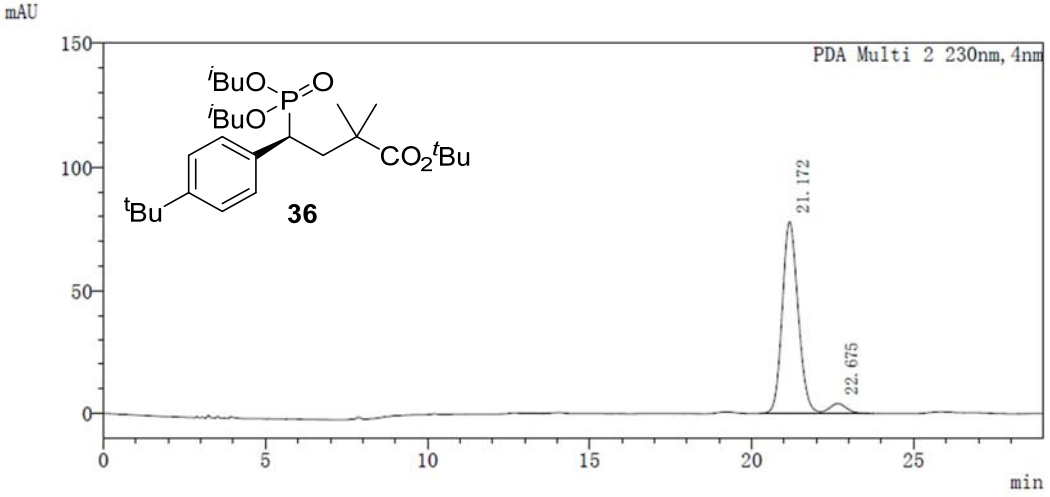
Peak#	Ret. Time	Area	Area%
1	8.280	1311261	95.931
2	11.299	55620	4.069



Peak Table

PDA Ch2 230nm

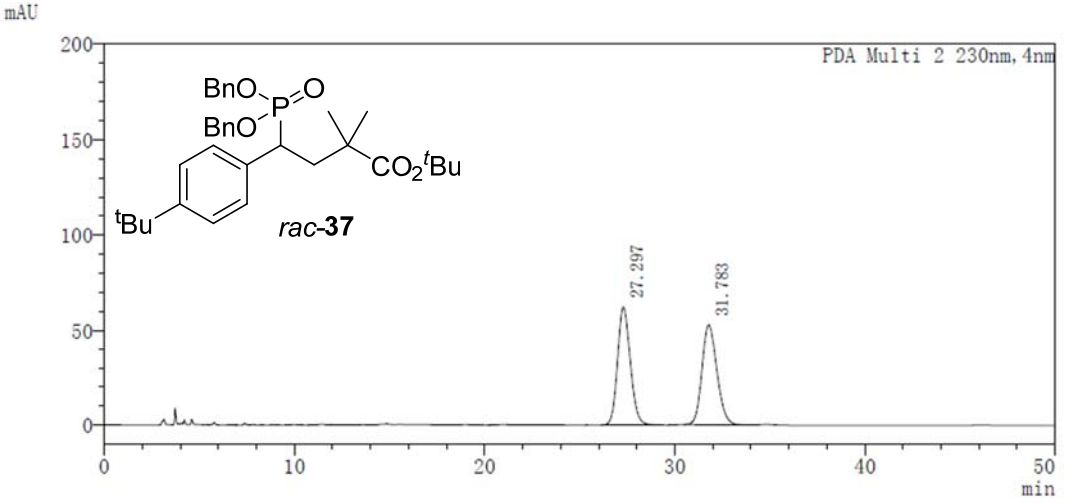
Peak#	Ret. Time	Area	Area%
1	21.297	2338950	49.895
2	22.827	2348810	50.105



Peak Table

PDA Ch2 230nm

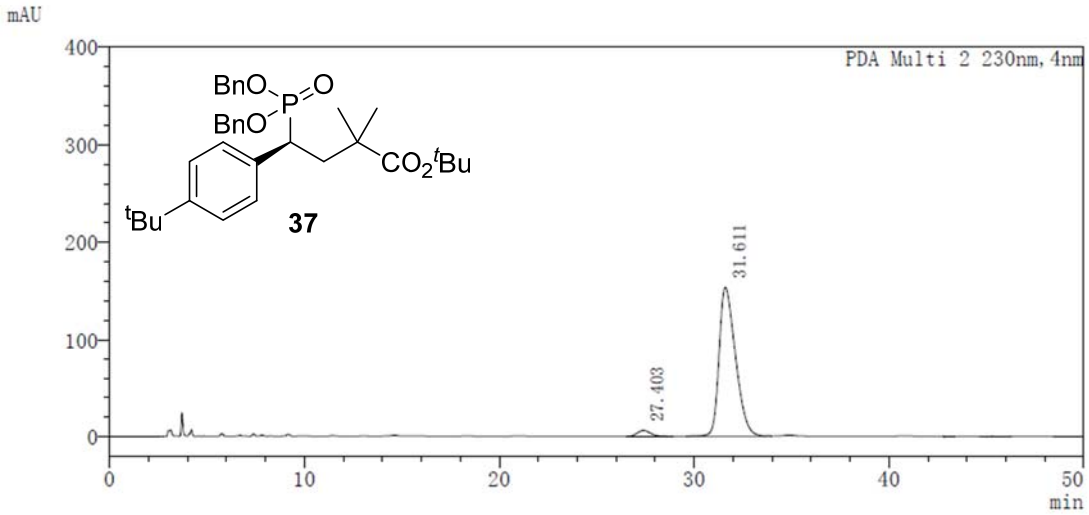
Peak#	Ret. Time	Area	Area%
1	21.172	2654237	94.724
2	22.675	147826	5.276



Peak Table

PDA Ch2 230nm

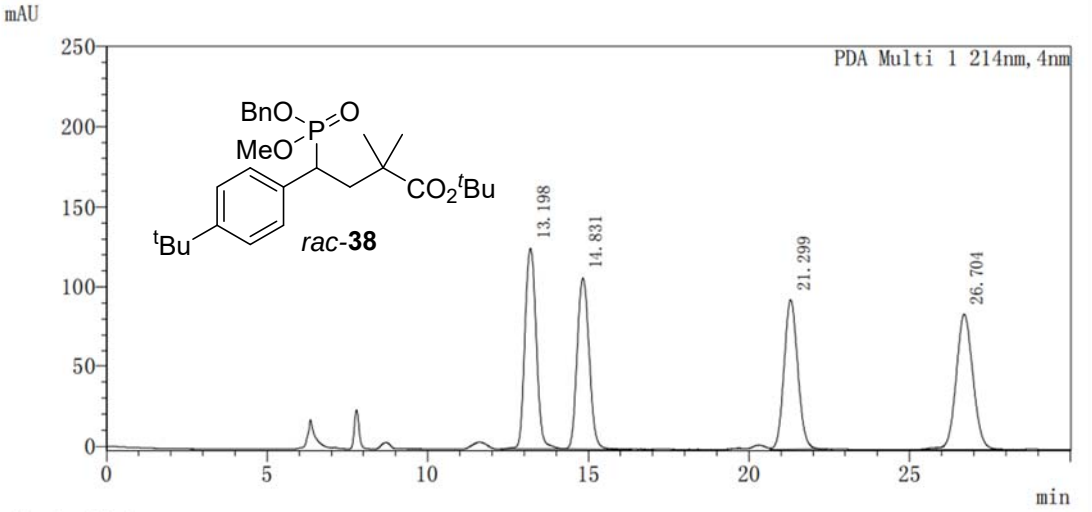
Peak#	Ret. Time	Area	Area%
1	27.297	2890514	50.153
2	31.783	2872838	49.847



Peak Table

PDA Ch2 230nm

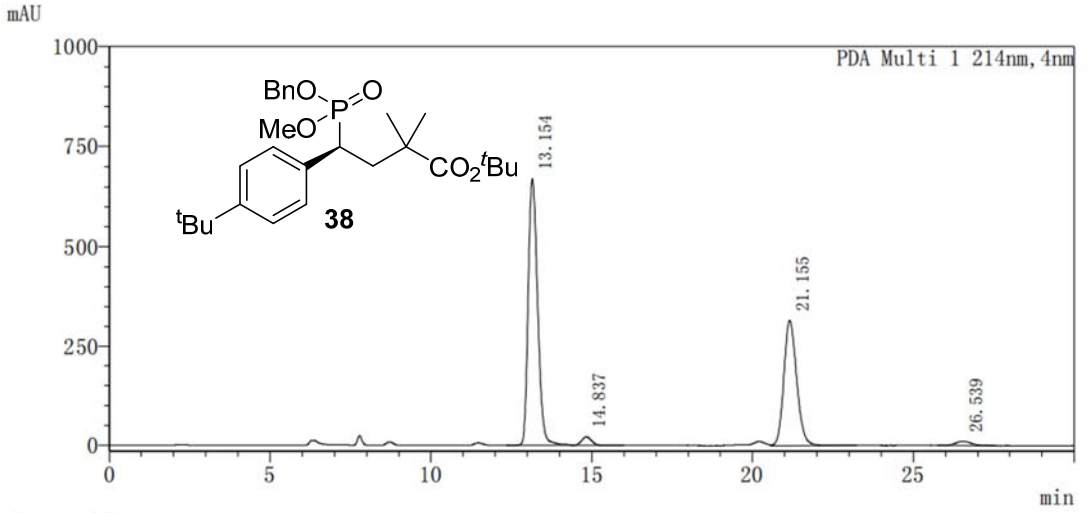
Peak#	Ret. Time	Area	Area%
1	27.403	295839	3.188
2	31.611	8982766	96.812



Peak Table

PDA Ch1 214nm

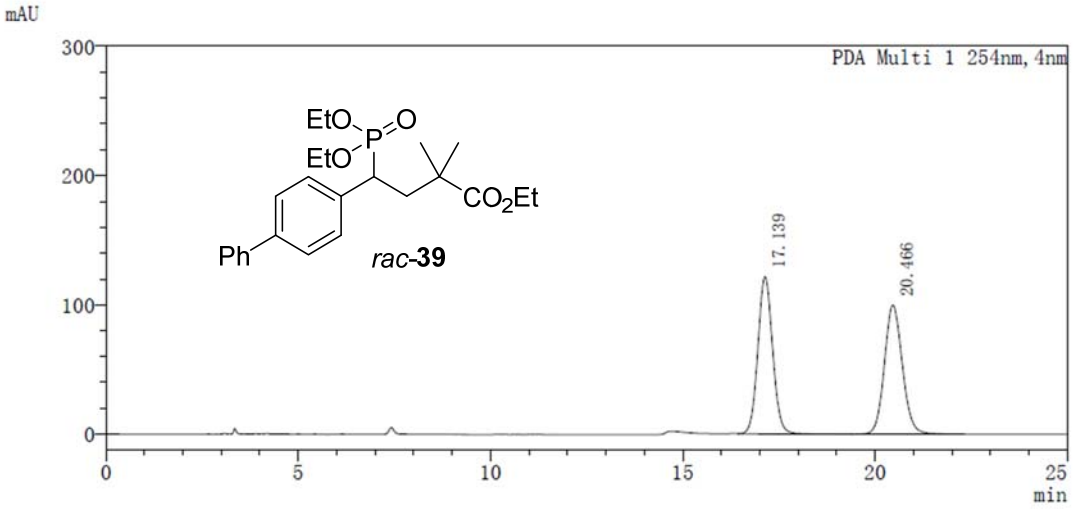
Peak#	Ret. Time	Area	Area%
1	13.198	3121624	26.403
2	14.831	2816971	23.827
3	21.299	2794991	23.641
4	26.704	3089190	26.129



Peak Table

PDA Ch1 214nm

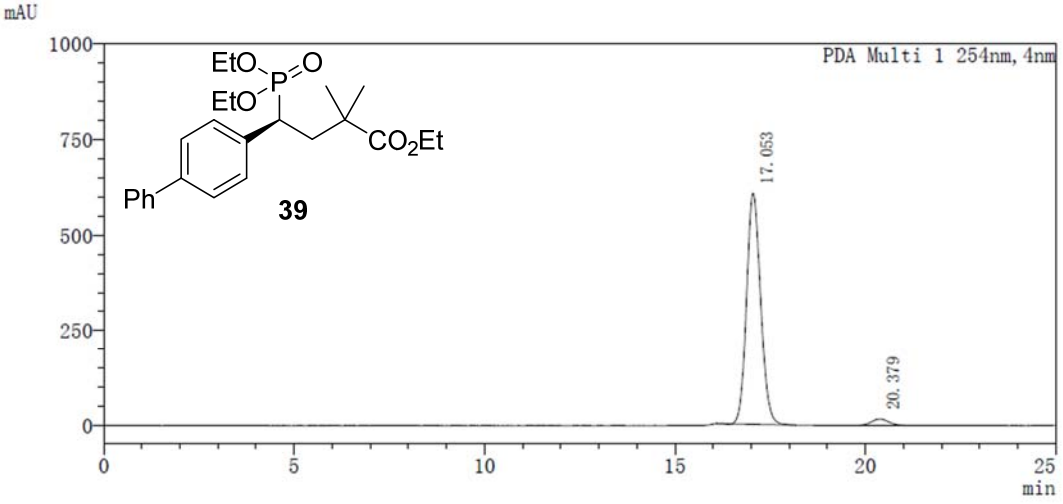
Peak#	Ret. Time	Area	Area%
1	13.154	13723853	58.725
2	14.837	489636	2.095
3	21.155	8800441	37.658
4	26.539	355572	1.522



Peak Table

PDA Ch1 254nm

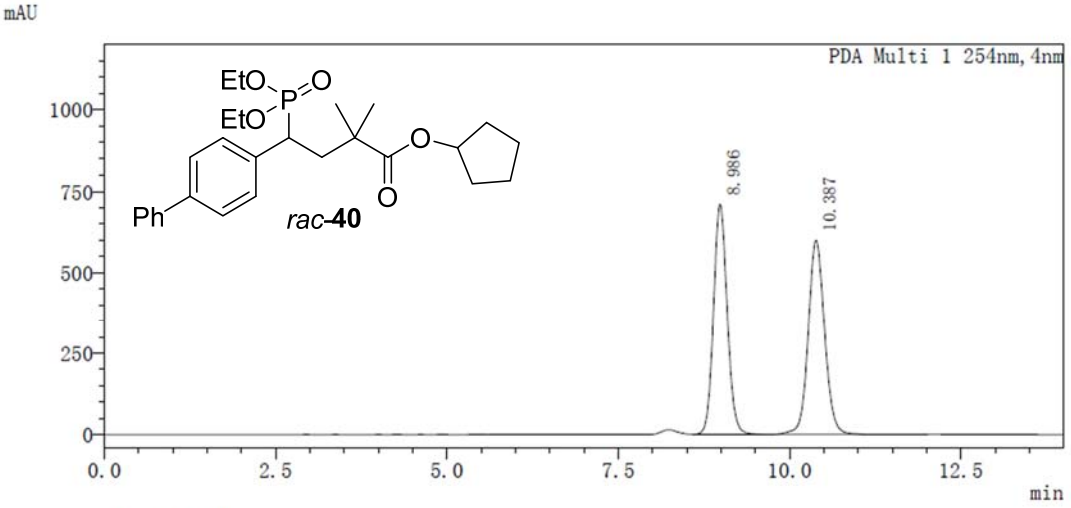
Peak#	Ret. Time	Area	Area%
1	17.139	3242283	49.980
2	20.466	3244888	50.020



Peak Table

PDA Ch1 254nm

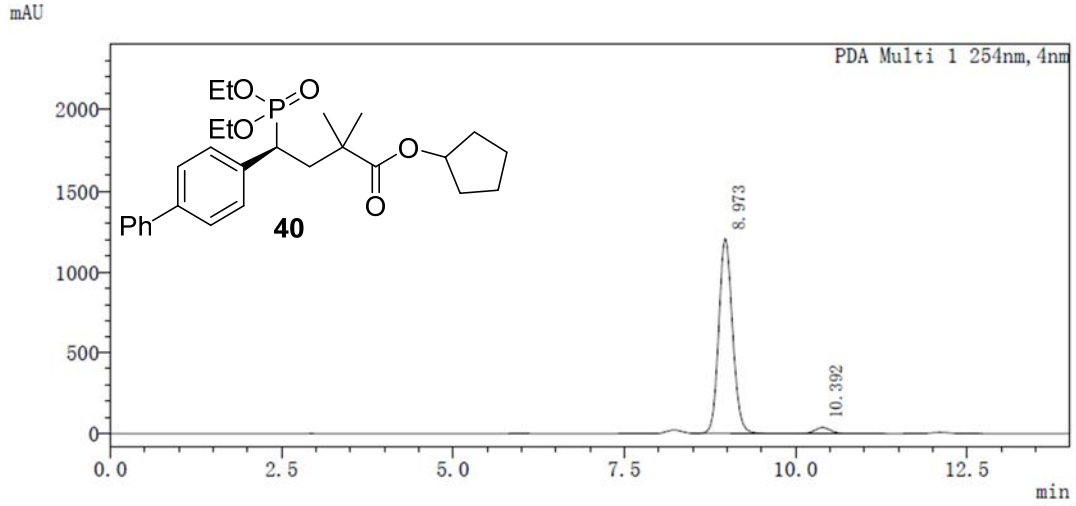
Peak#	Ret. Time	Area	Area%
1	17.053	15577547	96.757
2	20.379	522054	3.243



Peak Table

PDA Ch1 254nm

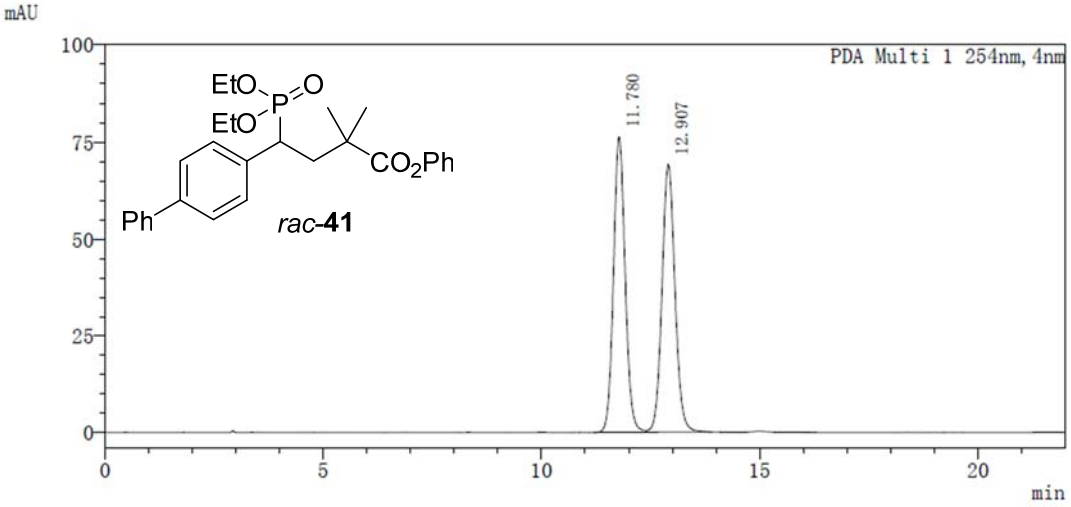
Peak#	Ret. Time	Area	Area%
1	8.986	9897772	49.956
2	10.387	9915312	50.044



Peak Table

PDA Ch1 254nm

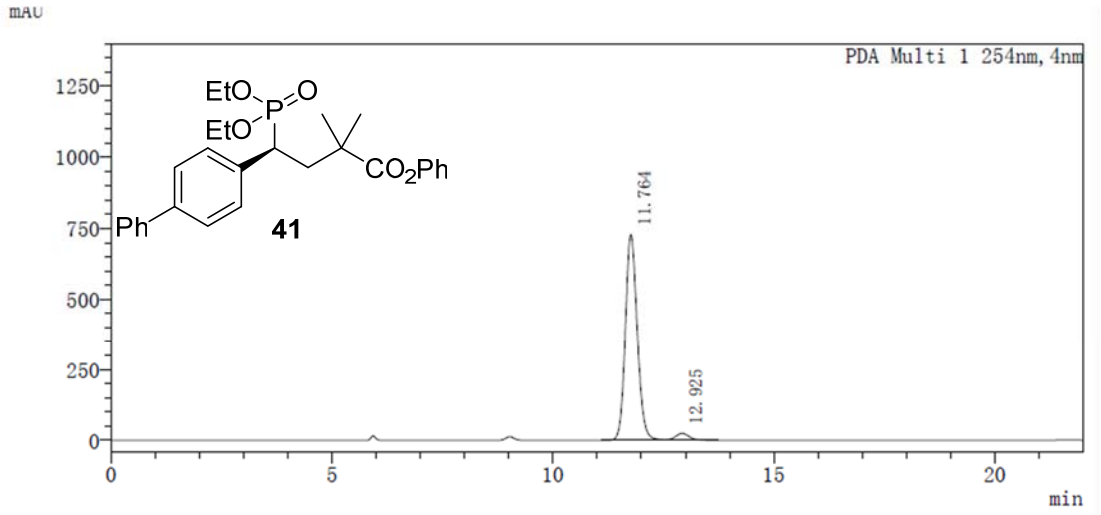
Peak#	Ret. Time	Area	Area%
1	8.973	16814363	96.541
2	10.392	602421	3.459



Peak Table

PDA Ch1 254nm

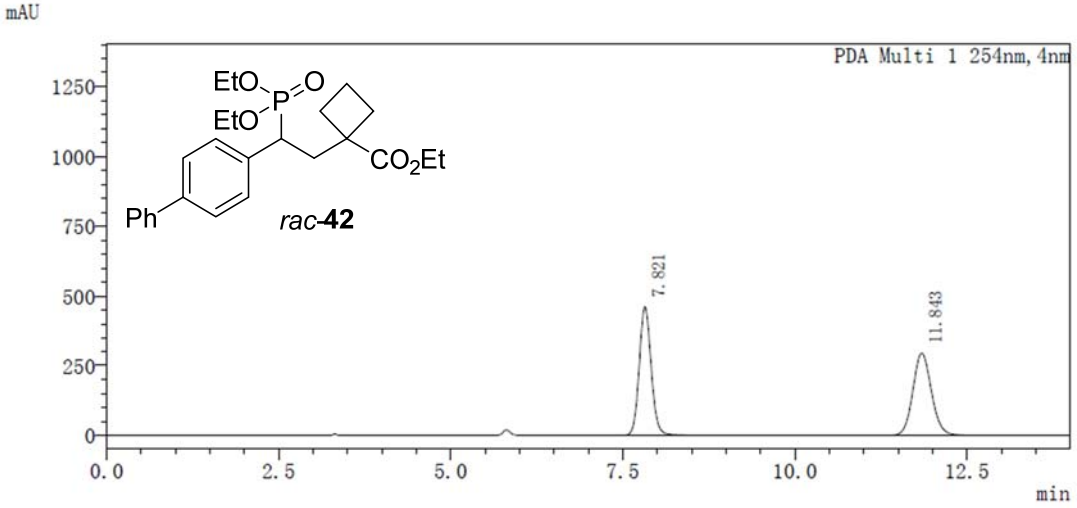
Peak#	Ret. Time	Area	Area%
1	11.780	1419330	49.839
2	12.907	1428494	50.161



Peak Table

PDA Ch1 254nm

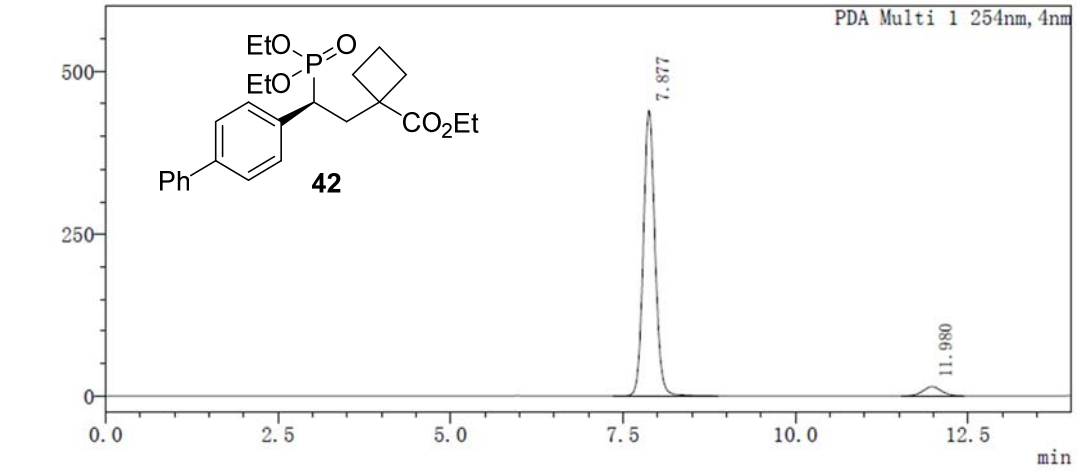
Peak#	Ret. Time	Area	Area%
1	11.764	13615596	96.141
2	12.925	546519	3.859



Peak Table

PDA Ch1 254nm

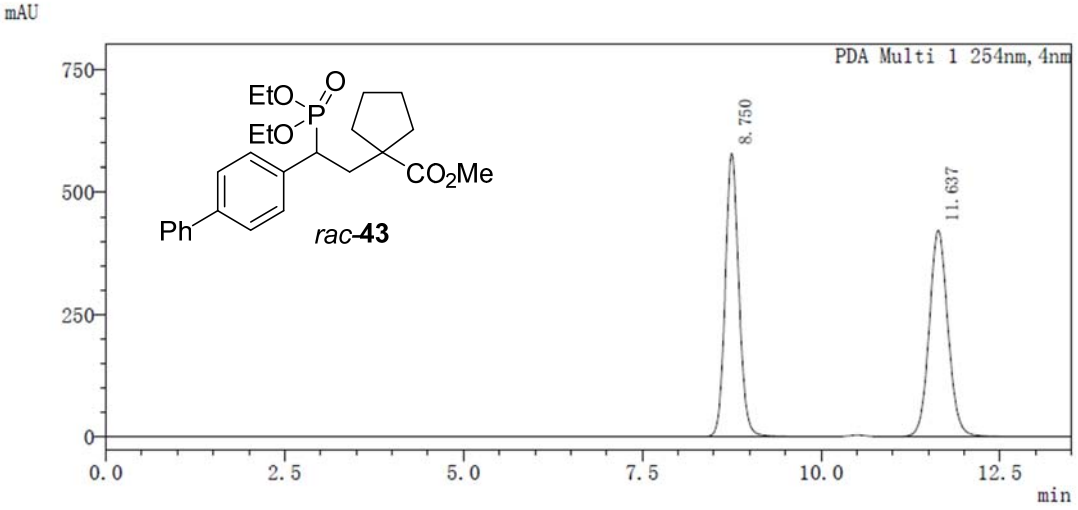
Peak#	Ret. Time	Area	Area%
1	7.821	5622967	50.353
2	11.843	5544171	49.647



Peak Table

PDA Ch1 254nm

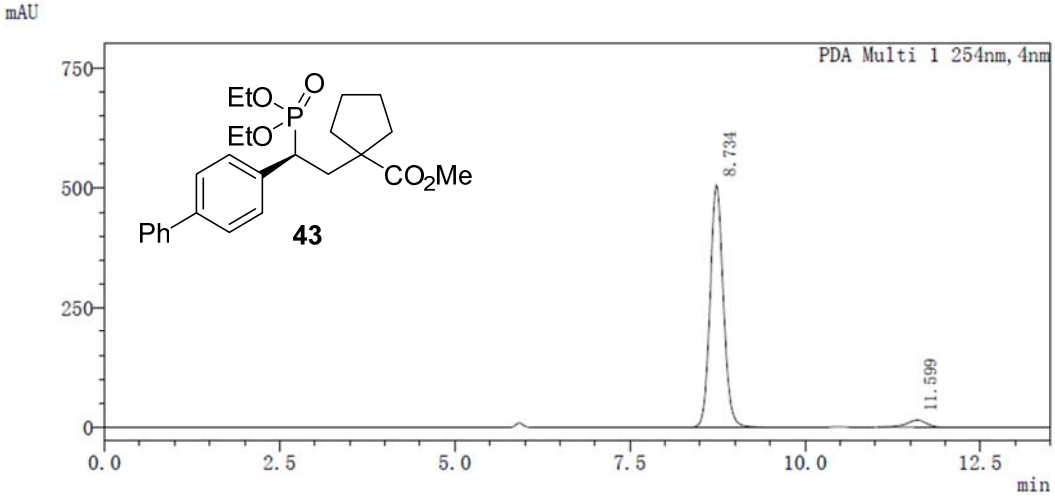
Peak#	Ret. Time	Area	Area%
1	7.877	5157299	95.273
2	11.980	255897	4.727



Peak Table

PDA Ch1 254nm

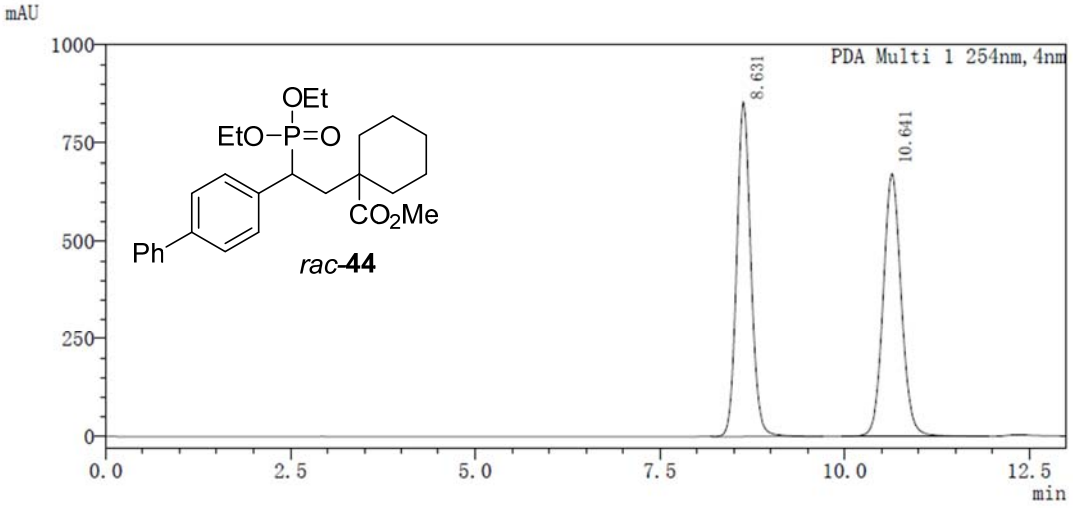
Peak#	Ret. Time	Area	Area%
1	8.750	7669595	49.958
2	11.637	7682566	50.042



Peak Table

PDA Ch1 254nm

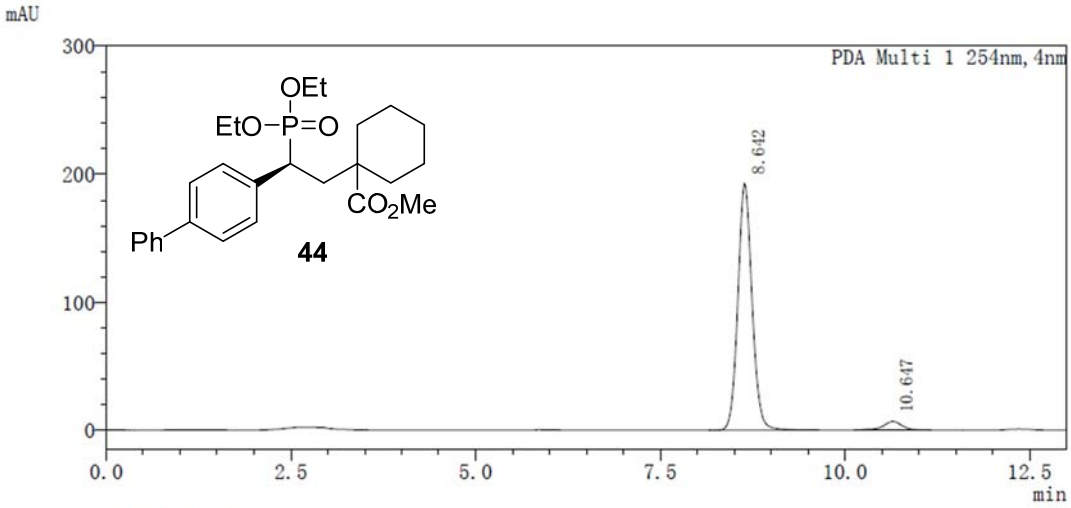
Peak#	Ret. Time	Area	Area%
1	8.734	6678442	95.836
2	11.599	290154	4.164



Peak Table

PDA Ch1 254nm

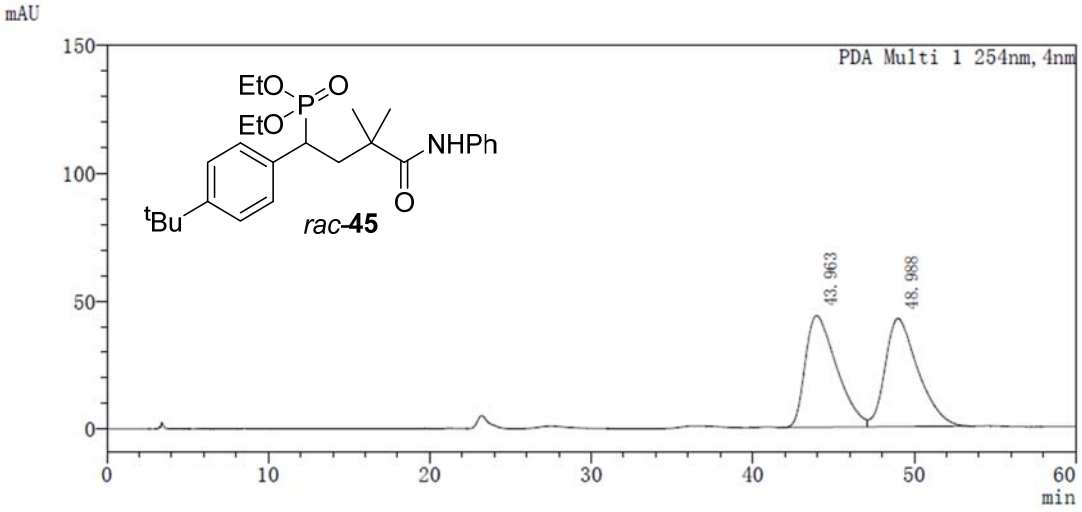
Peak#	Ret. Time	Area	Area%
1	8.631	11424669	49.894
2	10.641	11473120	50.106



Peak Table

PDA Ch1 254nm

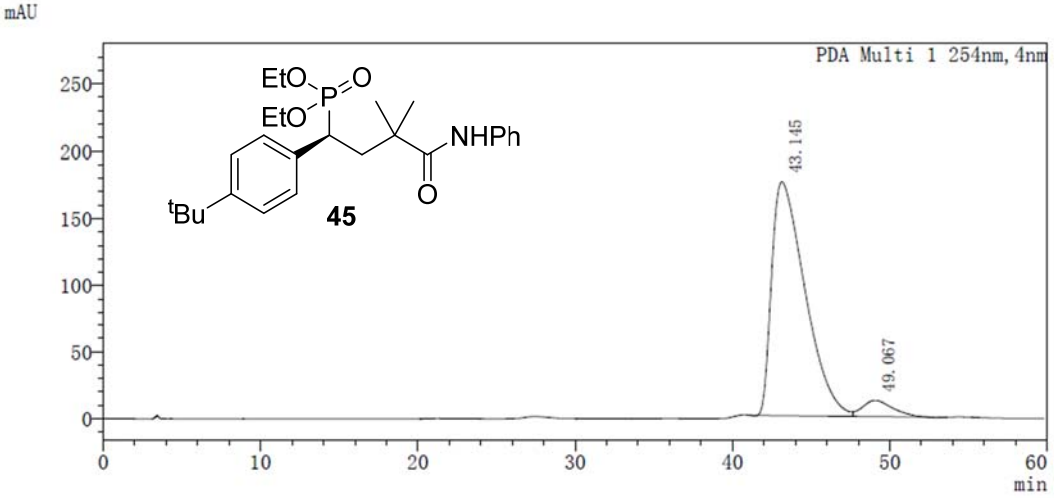
Peak#	Ret. Time	Area	Area%
1	8.642	2590416	95.531
2	10.647	121172	4.469



Peak Table

PDA Ch1 254nm

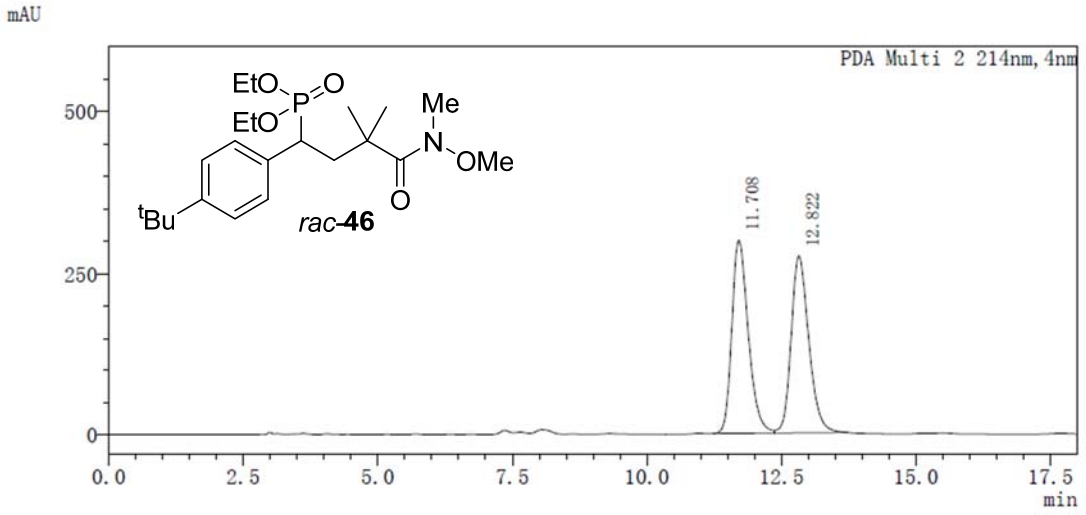
Peak#	Ret. Time	Area	Area%
1	43.963	5899796	49.587
2	48.988	5998144	50.413



Peak Table

PDA Ch1 254nm

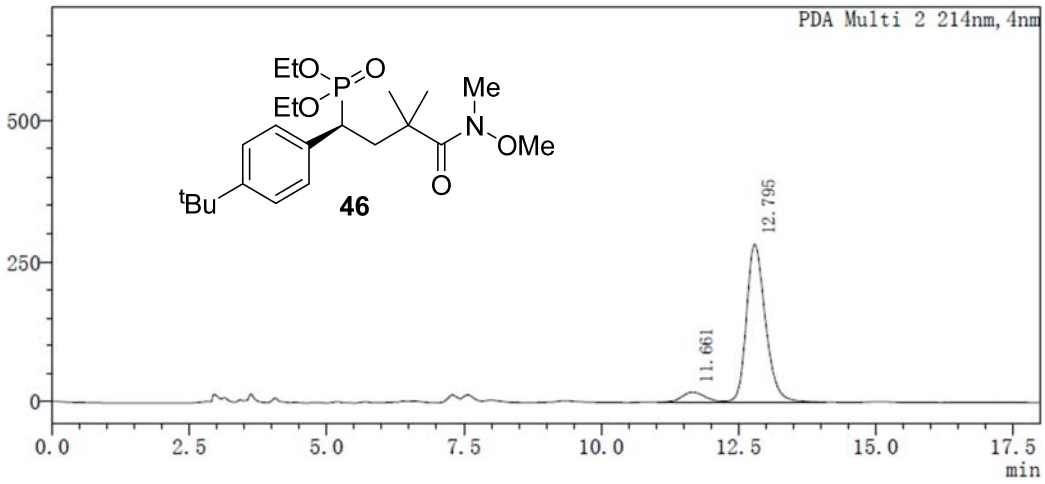
Peak#	Ret. Time	Area	Area%
1	43.145	25894091	94.152
2	49.067	1608373	5.848



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	11.708	6360049	50.360
2	12.822	6269142	49.640

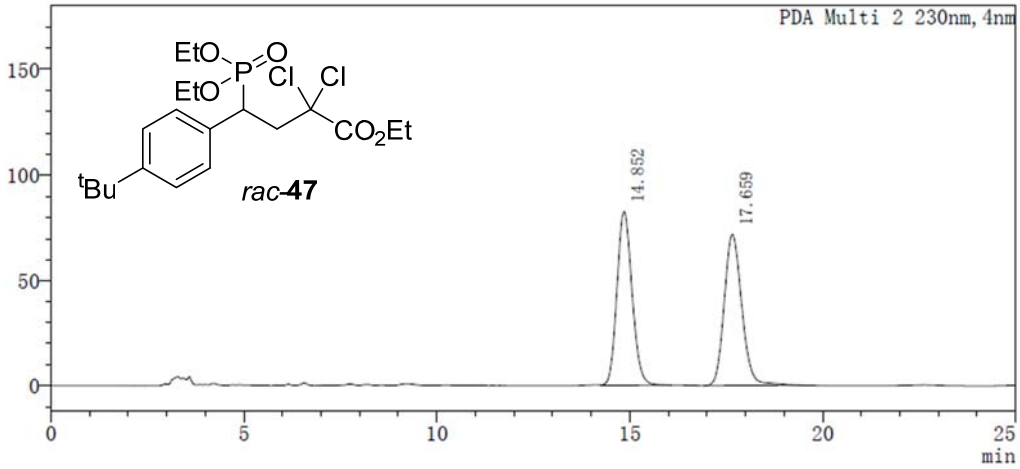


Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	11.661	518694	7.088
2	12.795	6798999	92.912

mAU

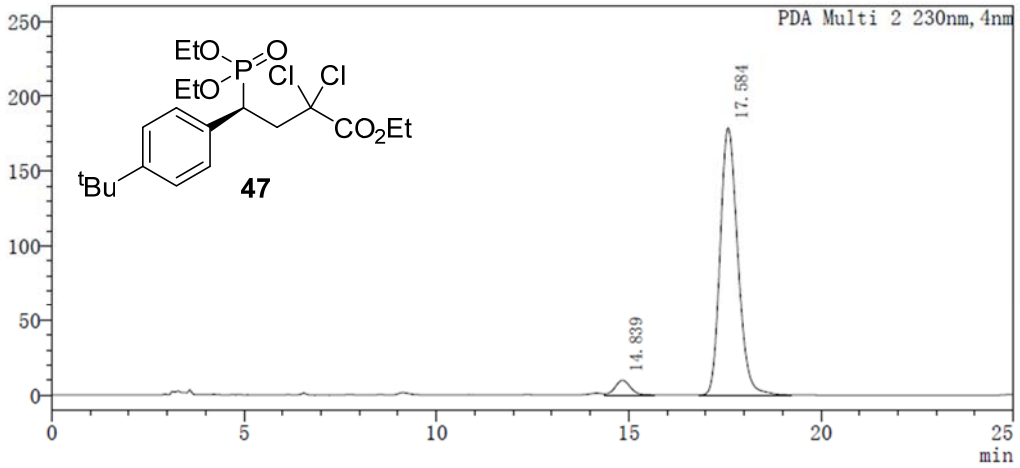


Peak Table

PDA Ch2 230nm

Peak#	Ret. Time	Area	Area%
1	14.852	2256385	49.734
2	17.659	2280477	50.266

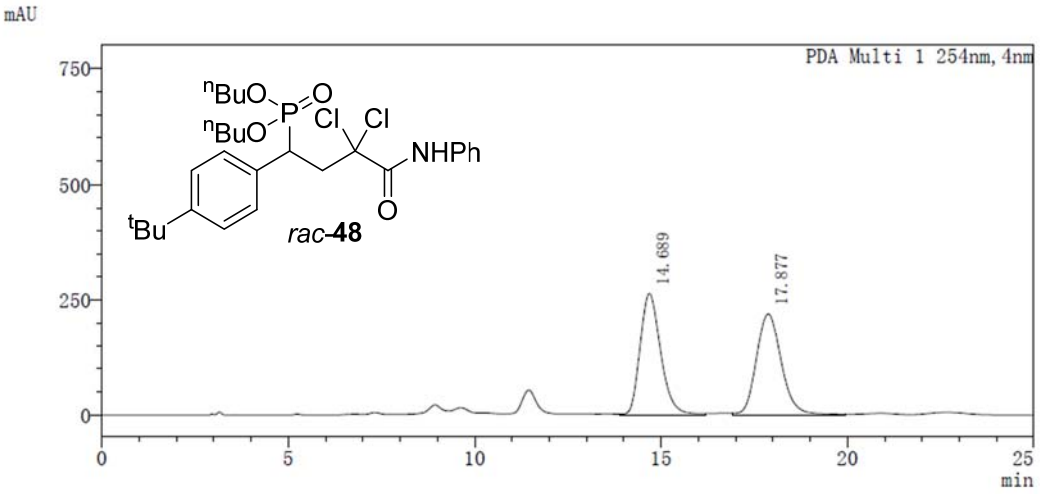
mAU



Peak Table

PDA Ch2 230nm

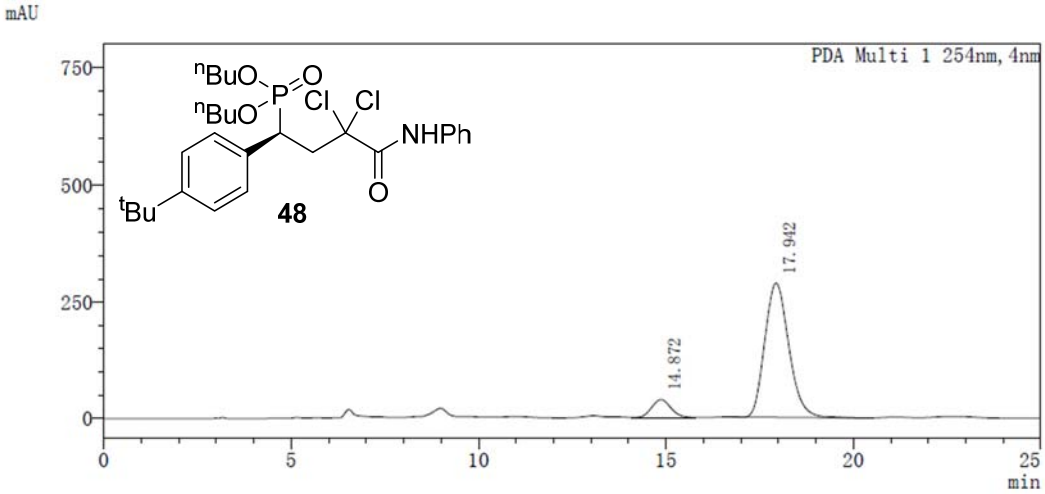
Peak#	Ret. Time	Area	Area%
1	14.839	267044	4.486
2	17.584	5685524	95.514



Peak Table

PDA Ch1 254nm

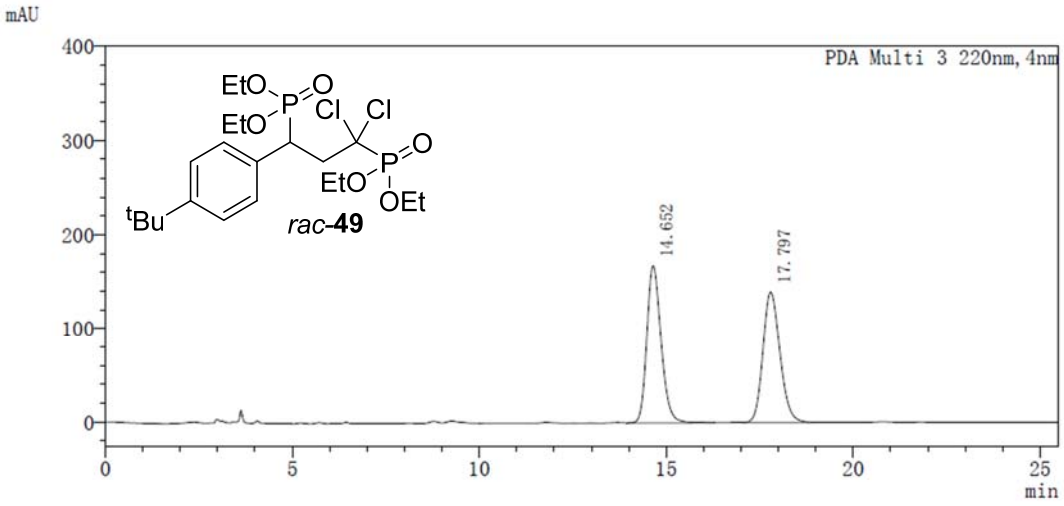
Peak#	Ret. Time	Area	Area%
1	14.689	10132798	49.834
2	17.877	10200315	50.166



Peak Table

PDA Ch1 254nm

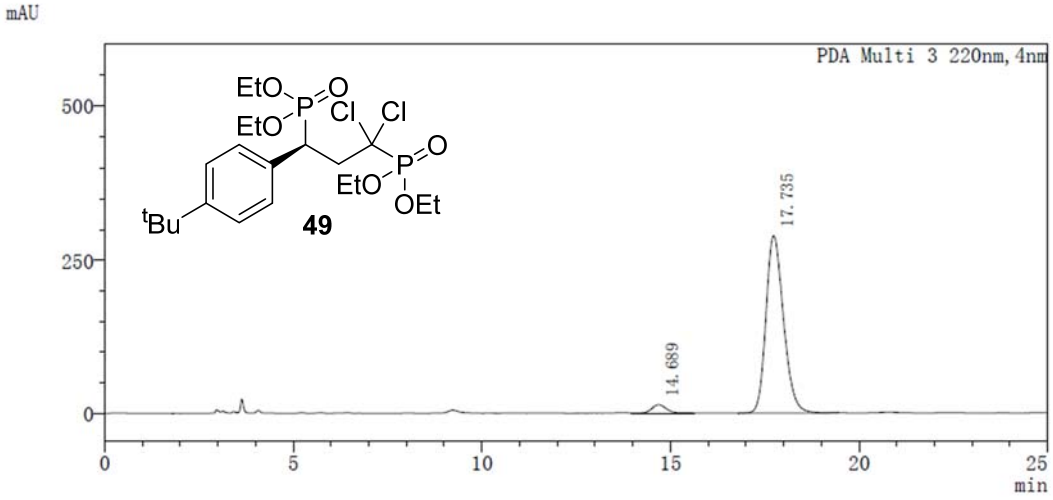
Peak#	Ret. Time	Area	Area%
1	14.872	1344672	9.440
2	17.942	12900154	90.560



Peak Table

PDA Ch3 220nm

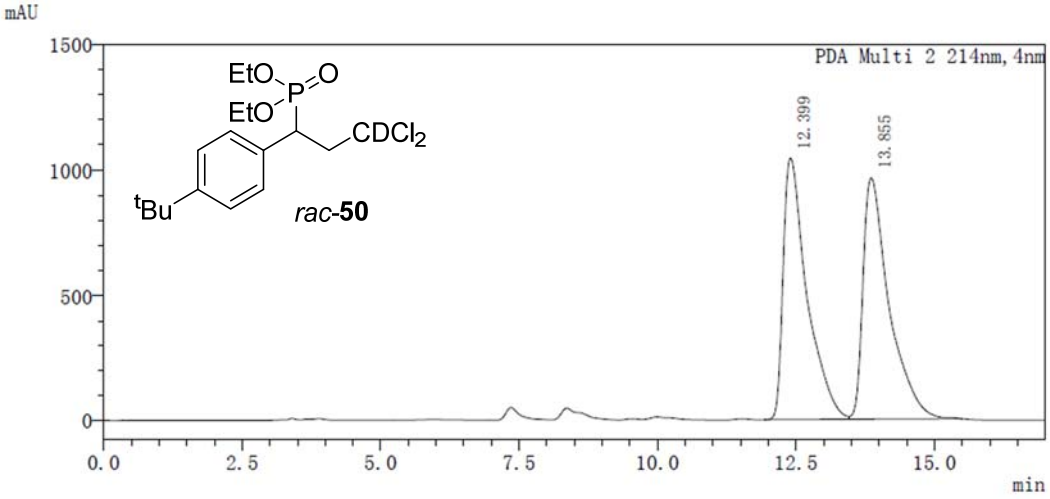
Peak#	Ret. Time	Area	Area%
1	14.652	4463904	50.153
2	17.797	4436749	49.847



Peak Table

PDA Ch3 220nm

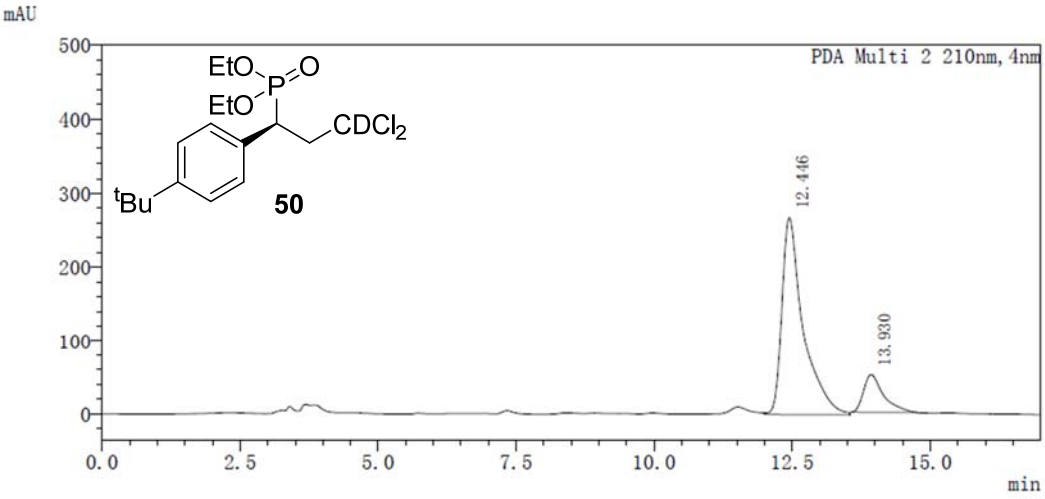
Peak#	Ret. Time	Area	Area%
1	14.689	360005	3.689
2	17.735	9399648	96.311



Peak Table

PDA Ch2 214nm

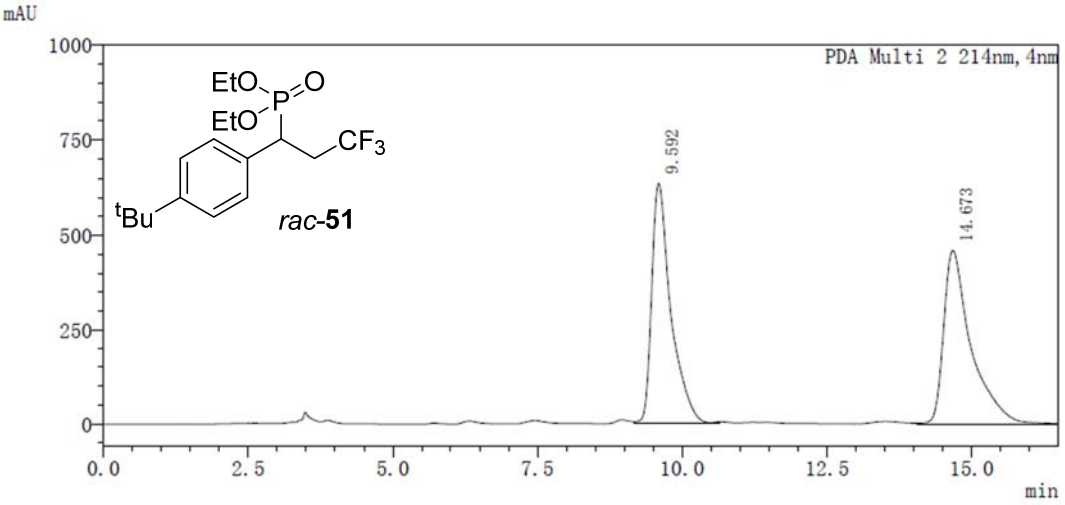
Peak#	Ret. Time	Area	Area%
1	12.399	31190284	49.631
2	13.855	31653877	50.369



Peak Table

PDA Ch2 210nm

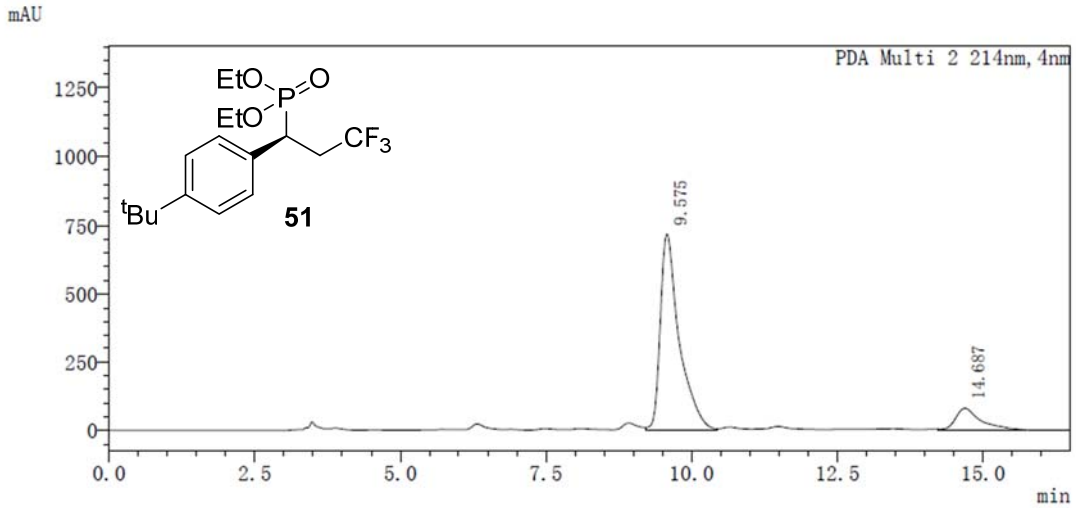
Peak#	Ret. Time	Area	Area%
1	12.446	7197815	84.843
2	13.930	1285863	15.157



Peak Table

PDA Ch2 214nm

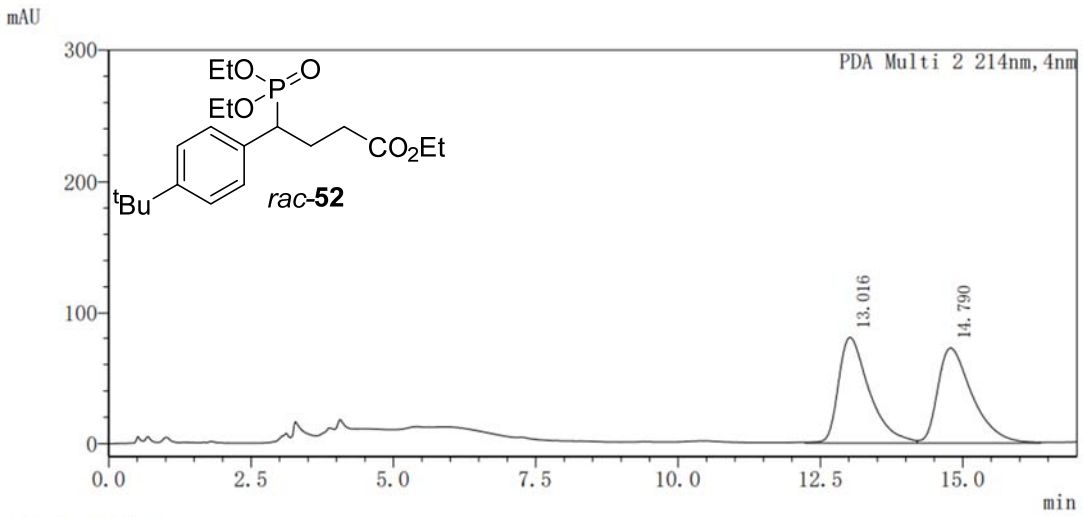
Peak#	Ret. Time	Area	Area%
1	9.592	14709147	49.349
2	14.673	15097400	50.651



Peak Table

PDA Ch2 214nm

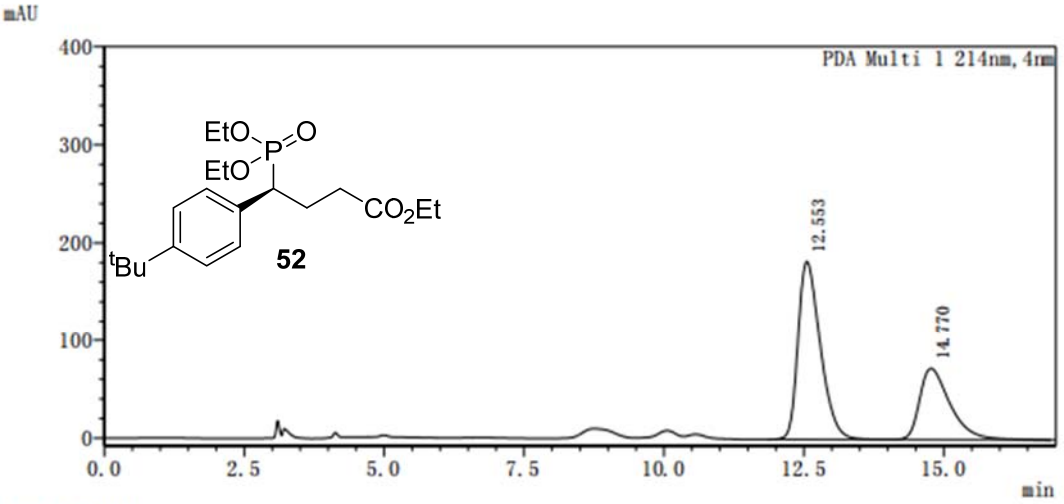
Peak#	Ret. Time	Area	Area%
1	9.575	16286921	86.763
2	14.687	2484749	13.237



Peak Table

PDA Ch2 214nm

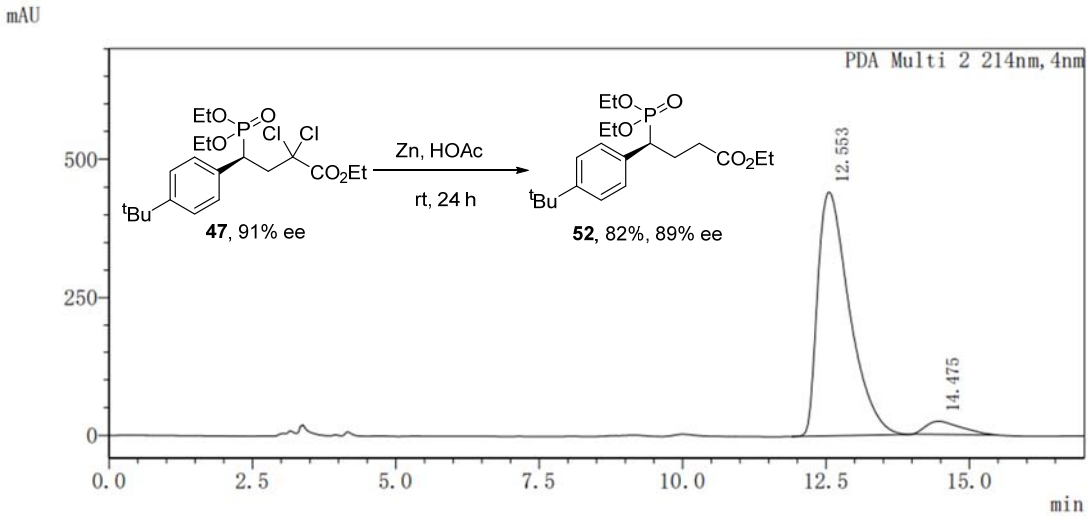
Peak#	Ret. Time	Area	Area%
1	13.016	3027529	49.776
2	14.790	3054721	50.224



Peak Table

PDA Ch1 214nm

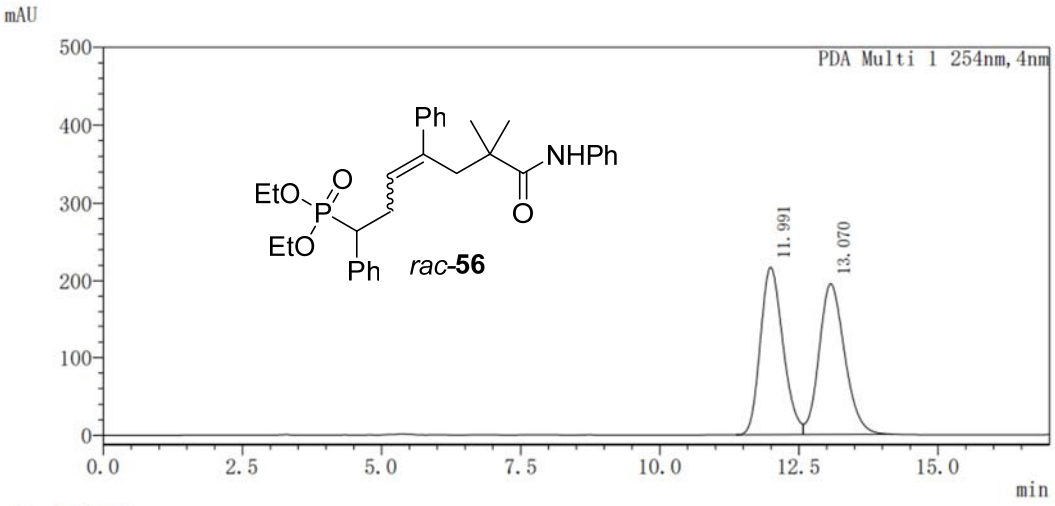
Peak#	Ret. Time	Area	Area%
1	12.553	5078885	64.621
2	14.770	2780638	35.379



Peak Table

PDA Ch2 214nm

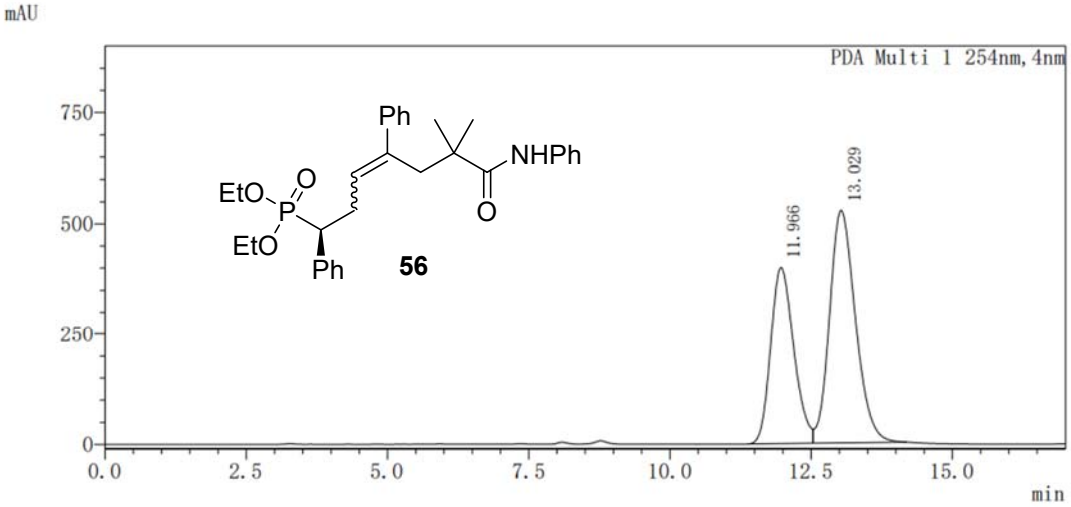
Peak#	Ret. Time	Area	Area%
1	12.553	17040142	94.395
2	14.475	1011867	5.605



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.991	6117624	49.586
2	13.070	6219817	50.414



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.966	11367981	40.334
2	13.029	16816637	59.666