Supporting Information

Pd(II)-Catalyzed Enantioselective C–H Olefination toward the Synthesis of *P*-stereogenic Phosphines

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Content

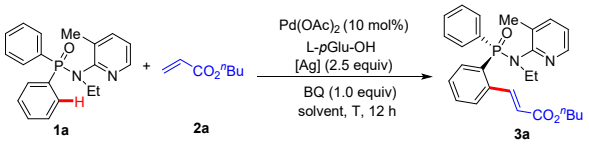
1. General Information

All the materials and solvent were purchased from commercial suppliers and used without additional purification. $Pd(OAc)_2$ was purchased from Laajoo (China). NMR spectra were recorded on a Bruke Avance operating for ^{1}H NMR at 400 MHz, ^{13}C NMR at 101 MHz, ^{19}F NMR at 376 MHz using TMS as internal standard. The peaks were internally referenced to residual undeuterated chloroform in $CDCl_3$ (δ H = 7.26 ppm, δ C = 77.16 ppm). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument. The *ee* value was determined on Shimadzu HPLC using CHIRALPAK column with hexane and 2-propanol as eluent, Wavelength = 254 nm.

2. Experiment Detail and Characterization Data

2.1 Optimization of Alkynylation

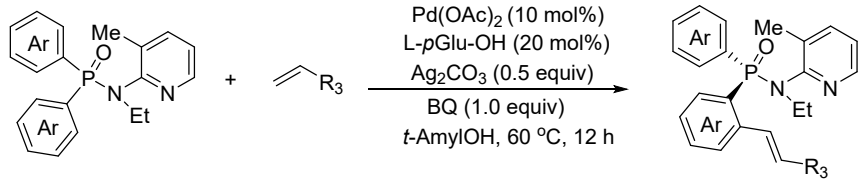
Table S1: Optimization of reaction conditions[a]



entry	Solvent	[Ag]	T (°C)	Yield of **3a** (%)[b]	*Ee* of **3a** (%)[c]	Conversion(%)
1	*t*-BuOH	Ag_2CO_3	60	50	93	55
2	PhCl	Ag_2CO_3	60	16	81	24
3	dioxane	Ag_2CO_3	60	60	89	66
4	*t*-AmylOH	Ag_2CO_3	60	65	95	69
5	*t*-AmylOH	Ag_2SO_4	60	25	92	30
6	*t*-AmylOH	AgOAc	60	38	92	48
7	*t*-AmylOH	Ag_3PO_4	60	44	95	50
8	*t*-AmylOH	Ag_2CO_3	50	39	94	42
9	*t*-AmylOH	Ag_2CO_3	70	50	94	53
10[d]	*t*-AmylOH	Ag_2CO_3	70	nr	--	--

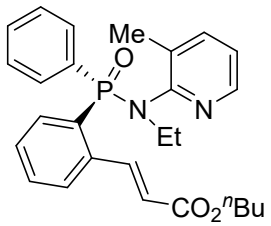
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), [Ag] (0.05 mmol), L-pGlu-OH (0.02 mmol), BQ (0.1 mmol), solvent (1.0 mL), air for 12 h. [b]Isolated yield. [c]The ee was determined by chiral HPLC. [d]Ar^F directing group was used.

2.2 General Procedure for Pd(II)-Catalyzed C−H Enantioselective Olefination and Characterization of Products



1 **2** **3**

To a 50 mL Schlenk tube was added substrate **1** (0.10 mmol), **2** (0.20 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), L-*p*Glu-OH (2.6 mg, 0.02 mmol), Ag_2CO_3 (13.8 mg, 0.05 mmol), BQ (10.8 mg, 0.10 mmol), *t*-AmylOH (1 mL). The mixture was stirred for 12 h at 60 °C under air. The resulting mixture was filtered through a celite pad and concentrated in vacuo. The residue was purified by preparative TLC using PE/EA as the eluent to afford the olefination product **3**.



butyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(phenyl)phosphoryl)phenyl) acrylate 3a

A purification by flash chromatography in petroleum ether : ethyl acetate= 2 : 1 gave **3a** as a yellow solid (30.7 mg, 66%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 85/15, flow = 0.8 mL/min) with t_r = 21.3 min (minor), 24.7 min (major): 95% *ee*.

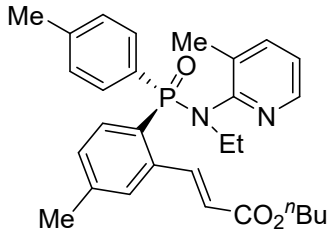
The absolute stereochemistry was assigned by X-ray diffraction analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 15.8 Hz, 1H), 8.47 – 8.37 (m, 1H), 8.27 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.75 – 7.63 (m, 2H), 7.58 – 7.41 (m, 3H), 7.35 (td, *J* = 7.4, 1.5 Hz, 1H), 7.31 – 7.20 (m, 3H), 6.94 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.10 (d, *J* = 15.8 Hz, 1H), 4.20 – 4.07 (m, 2H), 3.79 – 3.68 (m, 2H), 2.20 (s, 3H), 1.71 – 1.61 (m, 2H), 1.47 – 1.36 (m, 2H), 1.04 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 154.0 (d, $J_{c\text{-}p}$ = 3.9 Hz), 146.6, 143.6 (d, $J_{c\text{-}p}$ = 4.3 Hz), 139.5, 139.2 (d, $J_{c\text{-}p}$ = 10.9 Hz), 134.1 (d, $J_{c\text{-}p}$ = 10.1 Hz), 133.1 (d, $J_{c\text{-}p}$ = 2.9 Hz), 132.6 (d, $J_{c\text{-}p}$ = 10.9 Hz), 132.5 (d, $J_{c\text{-}p}$ = 121.5 Hz), 131.93 (d, $J_{c\text{-}p}$ = 125.3 Hz), 131.89 (d, $J_{c\text{-}p}$ = 3.1 Hz), 131.7 (d, $J_{c\text{-}p}$ = 2.9 Hz), 129.1 (d, $J_{c\text{-}p}$ = 12.8 Hz), 127.7 (d, $J_{c\text{-}p}$ = 11.0 Hz), 127.9 (d, $J_{c\text{-}p}$ = 12.8 Hz), 121.8, 120.7, 64.4, 44.5 (d, $J_{c\text{-}p}$ = 3.8 Hz), 30.8, 19.3, 18.6, 14.7 (d, $J_{c\text{-}p}$ = 2.8 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.83.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{31}N_2NaO_3P$: 485.1963; found: 485.1970.



butyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(p-tolyl)phosphoryl)-5-methylphenyl)acrylate 3b

A purification by flash chromatography in petroleum ether : ethyl acetate = 3 : 1 gave **3b** as a yellow foam (38.2 mg, 78%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with tr =7.4 min (minor), 12.7 min (major): 95% *ee*.

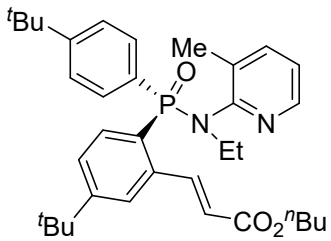
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 15.8 Hz, 1H), 8.30 – 8.22 (m, 2H), 7.59 – 7.51 (m, 2H), 7.34 (d, *J* = 4.4 Hz, 1H), 7.32 – 7.21 (m, 2H), 7.04 (dd, *J* = 8.1, 3.0 Hz, 2H), 6.94 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.09 (d, *J* = 15.8 Hz, 1H), 4.22 – 4.07 (m, 2H), 3.75 – 3.63 (m, 2H), 2.35 (s, 3H), 2.27 (s, 3H), 2.20 (s, 3H), 1.72 – 1.59 (m, 2H), 1.47 – 1.33 (m, 2H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 154.2 (d, $J_{c\text{-}p}$ = 3.6 Hz), 146.6, 143.8 (d, $J_{c\text{-}p}$ = 4.5 Hz), 142.1 (d, $J_{c\text{-}p}$ = 2.8 Hz), 141.9 (d, $J_{c\text{-}p}$ = 2.9 Hz), 139.5, 139.1 (d, $J_{c\text{-}p}$ = 10.1 Hz), 134.2 (d, $J_{c\text{-}p}$ = 10.7 Hz), 133.2 (d, $J_{c\text{-}p}$ = 2.8 Hz), 132.6 (d, $J_{c\text{-}p}$ = 10.4 Hz), 129.9 (d, $J_{c\text{-}p}$ = 13.2 Hz), 129.6 (d, $J_{c\text{-}p}$ = 124.2 Hz), 129.0 (d, $J_{c\text{-}p}$ = 128.3 Hz), 128.7 (d, $J_{c\text{-}p}$ = 13.5 Hz), 128.4 (d, $J_{c\text{-}p}$ = 11.3 Hz), 121.7, 120.3, 64.4, 44.5 (d, $J_{c\text{-}p}$ = 3.9 Hz), 30.9, 21.6, 21.5, 19.3, 18.7, 14.7 (d, $J_{c\text{-}p}$ = 2.9 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.18.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{35}N_2NaO_3P$: 513.2279; found: 513.2283.



butyl (*R, E*)-3-(5-(tert-butyl)-2-((4-(tert-butyl)phenyl)(ethyl(3-methylpyridin-2-yl) amino)phosphoryl)phenyl)acrylate 3c

A purification by flash chromatography in petroleum ether : ethyl acetate = 3 : 1 gave **3c** as a yellow foam (30.4 mg, 53%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with tr = 5.2 min (minor), 6.6 min (major): 88% *ee*.

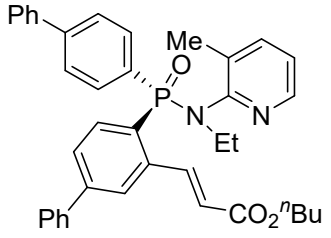
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 15.9 Hz, 1H), 8.32 – 8.20 (m, 2H), 7.64 – 7.57 (m, 2H), 7.54 (dd, *J* = 4.5, 1.9 Hz, 1H), 7.48 (dt, *J* = 8.2, 2.1 Hz, 1H), 7.30 – 7.22 (m, 3H), 6.92 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.11 (d, *J* = 15.8 Hz, 1H), 4.23 – 4.07 (m, 2H), 3.75 – 3.62 (m, 2H), 2.19 (s, 3H), 1.72 – 1.59 (m, 2H), 1.48 – 1.35 (m, 2H), 1.30 (s, 9H), 1.23 (s, 9H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 155.1 (d, $J_{c\text{-}p}$ = 2.9 Hz), 155.0 (d, $J_{c\text{-}p}$ = 2.8 Hz), 154.3 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.5, 144.4 (d, $J_{c\text{-}p}$ = 4.5 Hz), 139.3, 139.0 (d, $J_{c\text{-}p}$ = 9.5 Hz), 134.1 (d, $J_{c\text{-}p}$ = 10.6 Hz), 133.3 (d, $J_{c\text{-}p}$ = 3.1 Hz), 132.4 (d, $J_{c\text{-}p}$=10.5 Hz), 129.5 (d, $J_{c\text{-}p}$ = 124.4 Hz), 128.9 (d, $J_{c\text{-}p}$ = 128.9 Hz), 126.2 (d, $J_{c\text{-}p}$ = 13.2 Hz), 124.84 (d, $J_{c\text{-}p}$ = 12.9 Hz), 124.78 (d, $J_{c\text{-}p}$ = 11.1 Hz), 121.6, 120.2, 64.4, 44.4 (d, $J_{c\text{-}p}$ = 4.3 Hz), 35.0, 34.9, 31.2, 31.1, 30.9, 19.3, 18.7, 14.7 (d, $J_{c\text{-}p}$ = 3.3 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.13.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{35}H_{47}N_2NaO_3P$: 597.3219; found: 597.3222.



butyl (*R, E*)-3-(4-([1,1'-biphenyl]-4-yl(ethyl(3-methylpyridin-2-yl)amino) phosphoryl)-[1,1'-biphenyl]-3-yl)acrylate 3d

A purification by flash chromatography in petroleum ether : ethyl acetate = 3 : 1 gave **3d** as a yellow foam (35.6 mg, 58%). The *ee* value was determined by HPLC analysis

on a Chiralcel IA column (hexane/isopropanol = 70/30, flow = 0.7 mL/min) with tr = 12.7 min (minor), 20.5 min (major): 96% *ee*.

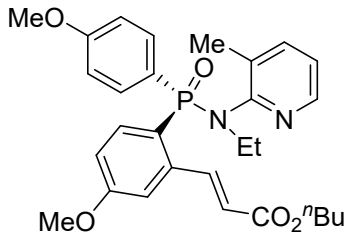
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 15.8 Hz, 1H), 8.52 (dd, *J* = 13.6, 8.0 Hz, 1H), 8.31 (dd, *J* = 4.7, 1.9 Hz, 1H), 7.89 – 7.75 (m, 3H), 7.72 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.56 – 7.28 (m, 11H), 6.96 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.22 (d, *J* = 15.8 Hz, 1H), 4.23 – 4.08 (m, 2H), 3.86 – 3.73 (m, 2H), 2.27 (s, 3H), 1.72 – 1.61 (m, 2H), 1.48 – 1.36 (m, 2H), 1.09 (t, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 154.0 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.7, 144.5 (d, $J_{c\text{-}p}$ = 2.9 Hz), 144.2 (d, $J_{c\text{-}p}$ = 2.9 Hz), 143.7 (d, $J_{c\text{-}p}$ = 4.4 Hz), 140.0, 139.7 (d, $J_{c\text{-}p}$ = 9.9 Hz), 139.6, 134.8 (d, $J_{c\text{-}p}$ = 10.7 Hz), 133.13 (d, $J_{c\text{-}p}$ = 10.2 Hz), 133.12 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.0 (d, $J_{c\text{-}p}$ = 124.3 Hz), 130.6 (d, $J_{c\text{-}p}$ = 127.0 Hz), 129.0 (d, $J_{c\text{-}p}$ = 12.0 Hz), 128.4, 128.2, 127.6 (d, $J_{c\text{-}p}$ = 13.3 Hz), 127.3, 126.6 (d, $J_{c\text{-}p}$ = 13.3 Hz), 126.4 (d, $J_{c\text{-}p}$ = 11.3 Hz), 121.9, 120.9, 64.5, 44.5 (d, $J_{c\text{-}p}$ = 3.9 Hz), 30.9, 19.3, 18.7, 14.8 (d, $J_{c\text{-}p}$ = 2.7 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.47.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{39}H_{39}N_2NaO_3P$: 637.2590; found: 637.2596.



butyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(4-methoxyphenyl) phosphoryl)-5-methoxyphenyl)acrylate 3e

A purification by flash chromatography in petroleum ether : ethyl acetate = 3 : 1 gave **3e** as a yellow foam (26.6 mg, 51%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with tr =9.5 min (minor), 15.6 min (major): 94% *ee*.

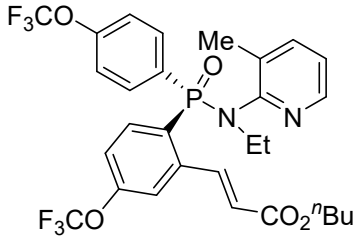
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 15.8 Hz, 1H), 8.32 (dd, *J* = 13.4, 8.5 Hz, 1H), 8.27 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.29 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.02 (dd, *J* = 3.8, 2.6 Hz, 1H), 6.98 (dt, *J* = 8.5, 2.2 Hz, 1H), 6.93 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.74 (dd, *J* = 8.8, 2.6 Hz, 2H), 6.09 (d, *J* = 15.8 Hz, 1H), 4.21 – 4.08 (m, 2H), 3.82 (s, 3H), 3.75 (s, 3H), 3.74 – 3.63 (m, 2H), 2.19 (s, 3H), 1.70 – 1.61 (m, 2H), 1.47 – 1.36 (m, 2H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 162.08 (d, $J_{c\text{-}p}$ = 3.0 Hz), 162.04 (d, $J_{c\text{-}p}$ = 2.8 Hz), 154.3 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.6, 143.7 (d, $J_{c\text{-}p}$ = 4.4 Hz), 141.1 (d, $J_{c\text{-}p}$ = 10.7 Hz), 139.5, 136.1 (d, $J_{c\text{-}p}$ = 3.9 Hz), 134.4 (d, $J_{c\text{-}p}$ = 11.2 Hz), 133.3 (d, $J_{c\text{-}p}$ = 2.7 Hz), 124.6 (d, $J_{c\text{-}p}$ = 129.4 Hz), 123.7 (d, $J_{c\text{-}p}$ = 132.8 Hz), 121.71, 120.70, 114.4 (d, $J_{c\text{-}p}$ = 13.8 Hz), 113.4 (d, $J_{c\text{-}p}$ = 13.9 Hz), 113.0 (d, $J_{c\text{-}p}$ = 12.0 Hz), 64.4, 55.5, 55.3, 44.5 (d, $J_{c\text{-}p}$ = 4.1 Hz), 30.9, 19.3, 18.7, 14.8 (d, $J_{c\text{-}p}$ = 2.7 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.67.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{35}N_2NaO_5P$: 545.2180; found: 545.2181.



butyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(4-(trifluoromethoxy) phenyl)phosphoryl)-5-(trifluoromethoxy)phenyl)acrylate 3f

A purification by flash chromatography in petroleum ether : ethyl acetate = 3 : 1 gave **3f** as a yellow foam (42.8 mg, 68%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 85/15, flow = 0.8 mL/min) with tr = 8.3 min (minor), 14.0 min (major): 95% *ee*.

The absolute stereochemistry was assigned by analogy to compound **3a**.

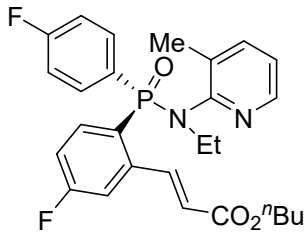
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.44 (m, 2H), 8.25 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.79 – 7.70 (m, 2H), 7.36 – 7.27 (m, 3H), 7.12 – 7.05 (m, 2H), 6.97 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.10 (d, *J* = 15.8 Hz, 1H), 4.22 – 4.09 (m, 2H), 3.77 – 3.66 (m, 2H), 2.18 (s, 3H), 1.70 – 1.60 (m, 2H), 1.47 – 1.35 (m, 2H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 153.5 (d, $J_{c\text{-}p}$ = 4.0 Hz), 151.9, 146.7, 141.9 (d, $J_{c\text{-}p}$ = 4.1 Hz), 141.8 (d, $J_{c\text{-}p}$ = 10.4 Hz), 139.8, 136.5 (d, $J_{c\text{-}p}$ = 11.7 Hz), 134.7 (d, $J_{c\text{-}p}$ = 11.1 Hz), 132.8 (d, $J_{c\text{-}p}$ = 3.0 Hz), 130.5 (d, $J_{c\text{-}p}$ = 125.2 Hz), 130.2 (d, $J_{c\text{-}p}$ = 128.3 Hz), 122.4, 122.2, 120.5 (d, $J_{c\text{-}p}$ = 13.7 Hz), 120.4 (q, $J_{C\text{-}F}$ = 260.3 Hz), 120.3 (q, $J_{C\text{-}F}$ = 259.9 Hz), 119.9 (d, $J_{c\text{-}p}$ = 13.8 Hz), 119.5 (d, $J_{c\text{-}p}$ = 12.0 Hz), 64.7, 44.3 (d, $J_{c\text{-}p}$ = 3.9 Hz), 30.8, 19.2, 18.4, 14.7 (d, $J_{c\text{-}p}$ = 2.2 Hz), 13.8.

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

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.56, -57.58.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{29}F_6N_2NaO_5P$: 653.1613; found: 653.1616.



butyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(4-fluorophenyl) phosphoryl)-5-fluorophenyl)acrylate 3g

A purification by flash chromatography in petroleum ether : acetone = 4 : 1 gave **3g** as a yellow foam (34.8 mg, 70%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 85/15, flow = 0.8 mL/min) with t_r = 16.9 min (minor), 22.2 min (major): 88% ee.

The absolute stereochemistry was assigned by analogy to compound **3a**.

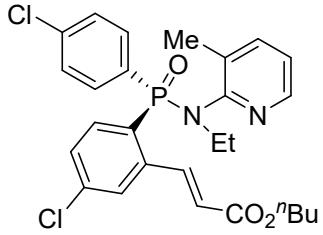
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.41 (m, 2H), 8.25 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.30 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.21 (dt, *J* = 9.9, 3.1 Hz, 1H), 7.15 (tt, *J* = 8.3, 2.1 Hz, 1H), 6.99 – 6.89 (m, 3H), 6.09 (d, *J* = 15.9 Hz, 1H), 4.21 – 4.09 (m, 2H), 3.76 – 3.65 (m, 2H), 2.17 (s, 3H), 1.69 – 1.61 (m, 2H), 1.46 – 1.35 (m, 2H), 1.03 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 164.9 (dd, $J_{C\text{-}F}$ = 254.4 Hz, $J_{C\text{-}P}$ = 3.2 Hz), 164.81 (dd, $J_{C\text{-}F}$ = 254.2 Hz, $J_{C\text{-}P}$ = 3.1 Hz), 153.7 (d, $J_{C\text{-}P}$ = 3.9 Hz), 146.7, 142.2 (dd, $J_{C\text{-}P}$ = 4.3 Hz, $J_{C\text{-}F}$ = 2.2 Hz), 142.1 (d, $J_{C\text{-}P}$ = 8.3 Hz), 139.8, 136.9 (dd, $J_{C\text{-}P}$ = 11.8 Hz, $J_{C\text{-}F}$ = 8.8 Hz), 135.2 (dd, $J_{C\text{-}P}$ = 11.3 Hz, $J_{C\text{-}F}$ = 8.9 Hz), 133.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 128.4 (dd, $J_{C\text{-}P}$ = 126.7 Hz, $J_{C\text{-}F}$ = 3.0 Hz), 127.8 (dd, $J_{C\text{-}P}$ = 129.8 Hz, $J_{C\text{-}F}$ = 3.4 Hz), 122.1, 121.9, 116.1 (dd, $J_{C\text{-}F}$ = 20.8 Hz, $J_{C\text{-}P}$ = 14.1 Hz), 115.4 (dd, $J_{C\text{-}F}$ = 21.4 Hz, $J_{C\text{-}P}$ = 14.0 Hz), 114.7 (dd, $J_{C\text{-}F}$ = 22.3 Hz, $J_{C\text{-}P}$ = 12.4 Hz), 64.6, 44.4 (d, $J_{C\text{-}P}$ = 3.9 Hz), 30.8, 19.2, 18.5, 14.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 13.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ 25.92.

^{19}F NMR (376 MHz, $CDCl_3$) δ -106.74, -107.29.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{29}F_2N_2NaO_3P$: 521.1779; found: 521.1782.



butyl (*R, E*)-3-(5-chloro-2-((4-chlorophenyl)(ethyl(3-methylpyridin-2-yl)amino) phosphoryl)phenyl)acrylate 3h

A purification by flash chromatography in petroleum ether : ethyl acetate = 3 : 1 gave **3h** as a yellow solid (29.7 mg, 56%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 70/30, flow = 0.7 mL/min) with t_r = 9.7 min (minor), 18.4 min (major): 94% *ee*.

The absolute stereochemistry was assigned by analogy to compound **3a**.

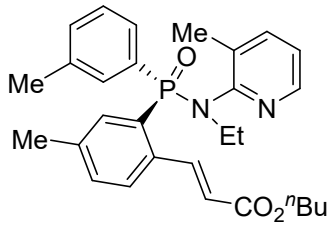
m.p. 103.0 – 104.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.34 (m, 2H), 8.25 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.50 (dd, *J* = 4.0, 2.0 Hz, 1H), 7.44 (dt, *J* = 8.3, 2.0 Hz, 1H), 7.32 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.23 (dd, *J* = 8.4, 2.6 Hz, 2H), 6.98 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.10 (d, *J*=15.8 Hz, 1H), 4.21 – 4.07 (m, 2H), 3.75 – 3.65 (m, 2H), 2.18 (s, 3H), 1.69 – 1.60 (m, 2H), 1.46 – 1.35 (m, 2H), 1.04 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 153.5 (d, $J_{c\text{-}p}$ = 4.3 Hz), 150.0, 146.7, 141.9 (d, $J_{c\text{-}p}$ = 4.3 Hz), 140.9 (d, $J_{c\text{-}p}$ = 10.3 Hz), 139.9, 138.5 (d, $J_{c\text{-}p}$ = 9.0 Hz), 135.7 (d, $J_{c\text{-}p}$ = 11.1 Hz), 134.0 (d, $J_{c\text{-}p}$ = 10.9 Hz), 132.9 (d, $J_{c\text{-}p}$ = 3.0 Hz), 130.4 (d, $J_{c\text{-}p}$ = 125.6 Hz), 130.0 (d, $J_{c\text{-}p}$ = 128.2 Hz), 129.1 (d, $J_{c\text{-}p}$ = 13.4 Hz), 128.5 (d, $J_{c\text{-}p}$ = 13.8 Hz), 127.8 (d, $J_{c\text{-}p}$ = 11.8 Hz), 122.3, 122.1, 64.7, 44.4 (d, $J_{c\text{-}p}$ = 4.3 Hz), 30.8, 19.3, 18.5, 14.7 (d, $J_{c\text{-}p}$ = 2.4 Hz), 13.9.

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

HRMS (ESI) m/z:$[M+Na]^+$ Calcd. for $C_{27}H_{29}Cl_2N_2NaO_3P$:553.1186; found:553.1191.



butyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(m-tolyl)phosphoryl) -4-methylphenyl)acrylate 3i

A purification by flash chromatography in petroleum ether : acetone = 4 : 1 gave **3i** as a yellow foam (38.2 mg, 78%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with t_r = 5.5 min (minor), 6.8 min (major): 96% *ee*.

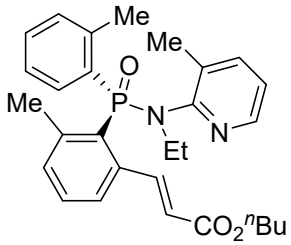
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J*=15.8 Hz, 1H), 8.27 – 8.18 (m, 2H), 7.57 – 7.50 (m, 2H), 7.40 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.29 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.18 – 7.12 (m, 2H), 6.92 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.04 (d, *J* = 15.8 Hz, 1H), 4.21 – 4.08 (m, 2H), 3.77 – 3.64 (m, 2H), 2.42 (s, 3H), 2.24 (s, 3H), 2.20 (s, 3H), 1.70 – 1.61 (m, 2H), 1.46 – 1.35 (m, 2H), 1.03 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 154.1 (d, $J_{c\text{-}p}$ = 3.1 Hz), 146.5, 143.6 (d, $J_{c\text{-}p}$ = 4.4 Hz), 139.4, 139.3 (d, $J_{c\text{-}p}$ = 12.6 Hz), 137.8 (d, $J_{c\text{-}p}$ = 12.6 Hz), 136.0 (d, $J_{c\text{-}p}$ = 9.1 Hz), 135.0 (d, $J_{c\text{-}p}$ = 9.7 Hz), 133.2 (d, $J_{c\text{-}p}$ = 9.9 Hz), 132.8 (d, $J_{c\text{-}p}$=3.2 Hz), 132.5 (d, $J_{c\text{-}p}$=2.8 Hz), 132.4 (d, $J_{c\text{-}p}$=3.1 Hz), 132.2 (d, $J_{c\text{-}p}$ = 120.7 Hz), 132.1 (d, $J_{c\text{-}p}$ = 125.6 Hz), 129.7 (d, $J_{c\text{-}p}$ = 10.1 Hz), 127.8 (d, $J_{c\text{-}p}$ = 13.4 Hz), 127.5 (d, $J_{c\text{-}p}$ = 11.7 Hz), 121.6, 119.7, 64.3, 44.4 (d, $J_{c\text{-}p}$=3.8 Hz), 30.9, 21.6, 21.4, 19.3, 18.6, 14.7 (d, $J_{c\text{-}p}$=3.0 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.91.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{35}N_2NaO_3P$: 513.2280; found: 513.2283.



butyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(o-tolyl)phosphoryl)-3-methylphenyl)acrylate 3j

A purification by flash chromatography in petroleum ether : acetone = 4 : 1 gave **3j** as a yellow foam (37.7 mg, 77%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 85/15, flow = 0.8 mL/min) with t_r = 9.7 min (major), 13.4 min (minor): 88% *ee*.

The absolute stereochemistry was assigned by analogy to compound **3a**.

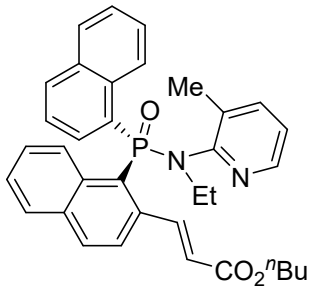
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.31 (m, 1H), 8.11 (dd, *J* = 4.7, 1.9 Hz, 1H), 7.97 (d, *J* = 15.6 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.18 (td, *J* = 7.7, 1.6 Hz, 1H), 7.10 – 7.04 (m, 2H), 6.96 (dd, *J* = 7.8, 4.2 Hz, 1H), 6.88 (dd, *J* = 7.5, 4.7 Hz, 1H), 5.60 (d, *J* = 15.6 Hz, 1H), 4.15 – 3.82 (m, 4H), 2.64 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H), 1.69 – 1.59 (m, 2H), 1.46 – 1.35 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 154.0 (d, $J_{c\text{-}p}$ = 2.5 Hz), 146.1 (d, $J_{c\text{-}p}$ = 5.1 Hz), 145.9, 145.2 (d, $J_{c\text{-}p}$ = 8.7 Hz), 142.3 (d, $J_{c\text{-}p}$ = 11.6 Hz), 139.8, 139.6 (d, $J_{c\text{-}p}$ = 10.7 Hz), 135.2 (d, $J_{c\text{-}p}$ = 125.9 Hz), 133.2 (d, $J_{c\text{-}p}$ = 11.5 Hz), 132.5 (d, $J_{c\text{-}p}$ = 10.3

Hz), 131.5 (d, $J_{c\text{-}p}$ = 12.4 Hz), 131.35 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.28 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.2 (d, $J_{c\text{-}p}$ = 3.7 Hz), 129.8 (d, $J_{c\text{-}p}$ = 115.3 Hz), 126.2 (d, $J_{c\text{-}p}$ = 10.9 Hz), 125.2 (d, $J_{c\text{-}p}$ = 13.1 Hz), 121.4, 119.2, 64.2, 43.8 (d, $J_{c\text{-}p}$ = 3.0 Hz), 30.8, 23.4 (d, $J_{c\text{-}p}$ = 3.7 Hz), 21.2 (d, $J_{c\text{-}p}$ = 4.3 Hz), 19.3, 18.5, 14.9 (d, $J_{c\text{-}p}$ = 2.5 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 31.59.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{35}N_2NaO_3P$: 513.2280; found: 513.2283.



butyl (*R, E*)-3-(1-((ethyl(3-methylpyridin-2-yl)amino)(naphthalen-1-yl) phosphoryl)naphthalen-2-yl)acrylate 3k

A purification by flash chromatography in petroleum ether : ethyl acetate = 2 : 1 gave **3k** as a yellow foam (23.0 mg, 41%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol = 90/10, flow = 0.8 mL/min) with t_r =14.0 min (major), 19.8 min (minor): 92% *ee*.

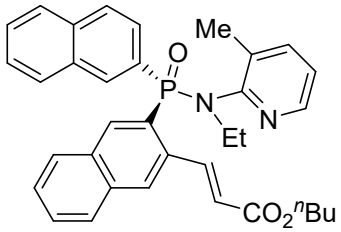
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (d, *J* = 8.8 Hz, 1H), 8.94 – 8.84 (m, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 8.08 (dd, *J* = 4.7, 1.9 Hz, 1H), 8.03 (d, *J* = 15.8 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.79 – 7.71 (m, 3H), 7.64 – 7.55 (m, 2H), 7.53 – 7.46 (m, 1H), 7.37 – 7.30 (m, 1H), 7.20 – 7.10 (m, 2H), 7.02 (dd, *J* = 8.5, 4.3 Hz, 1H), 6.81 (dd, *J* = 7.5, 4.7 Hz, 1H), 5.27 (d, *J* = 15.8 Hz, 1H), 4.22 – 4.12 (m, 2H), 4.06 (dt, *J* = 10.8, 6.7 Hz, 1H), 3.95 (dt, *J* = 10.8, 6.7 Hz, 1H), 2.10 (s, 3H), 1.67 – 1.57 (m, 2H), 1.47 – 1.35 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 153.8 (d, $J_{c\text{-}p}$ = 3.4 Hz), 146.2, 146.1, 145.9, 139.8, 139.2 (d, $J_{c\text{-}p}$ = 10.2 Hz), 134.8 (d, $J_{c\text{-}p}$ = 8.6 Hz), 134.0 (d, $J_{c\text{-}p}$ = 10.8 Hz), 133.8 (d, $J_{c\text{-}p}$ = 10.3 Hz), 133.2 (d, $J_{c\text{-}p}$ = 125.9 Hz), 133.1 (d, $J_{c\text{-}p}$ = 2.9 Hz), 132.7 (d, $J_{c\text{-}p}$ = 3.6 Hz), 132.6 (d, $J_{c\text{-}p}$ = 3.5 Hz), 131.5 (d, $J_{c\text{-}p}$ = 3.7 Hz), 129.0 (d, $J_{c\text{-}p}$ = 4.6 Hz), 128.5 (d, $J_{c\text{-}p}$ = 9.4 Hz), 127.9 (d, $J_{c\text{-}p}$ = 115.8 Hz), 127.3, 126.9, 126.7, 126.62, 126.57, 126.0, 125.6 (d, $J_{c\text{-}p}$ = 12.6 Hz), 124.7 (d, $J_{c\text{-}p}$ = 15.2 Hz), 121.5, 120.2, 64.1, 43.7 (d, $J_{c\text{-}p}$ = 3.6 Hz), 30.8, 19.3, 18.8, 15.0 (d, $J_{c\text{-}p}$ = 2.8 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.52.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{35}H_{35}N_2NaO_3P$: 585.2276; found: 585.2283.



butyl (*R, E*)-3-(3-((ethyl(3-methylpyridin-2-yl)amino)(naphthalen-2-yl) phosphoryl)naphthalen-2-yl)acrylate 3l

A purification by flash chromatography in petroleum ether : ethyl acetate = 2 : 1 gave **3l** as a yellow foam (36.5 mg, 64%). The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with tr = 12.6 min (major), 28.8 min (minor): 88% *ee*.

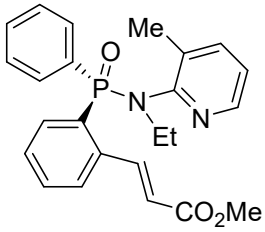
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 15.7 Hz, 1H), 8.59 (d, *J* = 15.7 Hz, 1H), 8.48 (d, *J* = 14.1 Hz, 1H), 8.35 – 8.25 (m, 1H), 8.09 – 8.02 (m, 1H), 7.98 (d, *J* = 4.5 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.43 (m, 6H), 7.24 (d, *J* = 12.4 Hz, 2H), 6.92 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.17 (d, *J* = 15.7 Hz, 1H), 4.18 – 4.05 (m, 2H), 3.95 – 3.81 (m, 2H), 2.24 (s, 3H), 1.67 – 1.57 (m, 2H), 1.44 – 1.33 (m, 2H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 154.1 (d, $J_{c\text{-}p}$ = 3.5 Hz), 146.7, 144.1 (d, $J_{c\text{-}p}$ = 3.3 Hz), 139.6, 136.3 (d, $J_{c\text{-}p}$ = 10.1 Hz), 134.9 (d, $J_{c\text{-}p}$ = 9.6 Hz), 134.6 (d, $J_{c\text{-}p}$ = 2.2 Hz), 134.5 (d, $J_{c\text{-}p}$ = 2.3 Hz), 133.0 (d, $J_{c\text{-}p}$ = 2.8 Hz), 132.7 (d, $J_{c\text{-}p}$ = 14.0 Hz), 132.3 (d, $J_{c\text{-}p}$ = 14.0 Hz), 129.59 (d, $J_{c\text{-}p}$ = 122.9 Hz), 129.29 (d, $J_{c\text{-}p}$ = 126.3 Hz), 129.25, 129.18, 128.6, 128.2 (d, $J_{c\text{-}p}$ = 3.1 Hz), 127.8, 127.5 (d, $J_{c\text{-}p}$ = 12.2 Hz), 127.4 (d, $J_{c\text{-}p}$ = 10.8 Hz), 126.6, 121.9, 120.5, 64.3, 44.7 (d, $J_{c\text{-}p}$ = 3.9 Hz), 30.9, 19.3, 18.7, 14.8 (d, $J_{c\text{-}p}$ = 2.5 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.03.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{35}H_{35}N_2NaO_3P$: 585.2281; found: 585.2283.



diethyl (*R, E*) - (2-((ethyl(3-methylpyridin-2-yl)amino)(phenyl)phosphoryl) styryl)phosphonate 3m

A purification by flash chromatography in petroleum ether : ethyl acetate = 4 : 1 gave **3m** as a yellow foam (25.3 mg, 60%). The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with tr = 8.0 min (minor), 9.5 min (major): 95% *ee*.

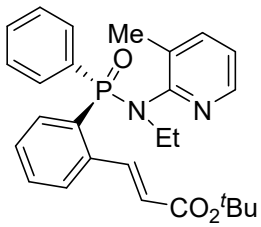
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 15.8 Hz, 1H), 8.42 – 8.32 (m, 1H), 8.26 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.75 – 7.65 (m, 2H), 7.57 – 7.49 (m, 1H), 7.48 – 7.42 (m, 2H), 7.38 – 7.31 (m, 1H), 7.29 – 7.22 (m, 3H), 6.93 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.10 (d, *J* = 15.9 Hz, 1H), 3.79 – 3.65 (m, 5H), 2.20 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 154.0 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.6, 143.9 (d, $J_{c\text{-}p}$ = 4.5 Hz), 139.5, 139.2 (d, $J_{c\text{-}p}$ = 9.4 Hz), 134.2 (d, $J_{c\text{-}p}$ = 10.3 Hz), 133.1 (d, $J_{c\text{-}p}$ = 3.2 Hz), 132.6 (d, $J_{c\text{-}p}$ = 9.7 Hz), 132.4 (d, $J_{c\text{-}p}$ = 122.6 Hz), 132.0 (d, $J_{c\text{-}p}$ = 125.4 Hz), 131.9 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.7 (d, $J_{c\text{-}p}$ = 2.8 Hz), 129.1 (d, $J_{c\text{-}p}$ = 13.1 Hz), 128.0 (d, $J_{c\text{-}p}$ = 12.6 Hz), 127.7 (d, $J_{c\text{-}p}$ = 11.0 Hz), 121.8, 120.2, 51.7, 44.5 (d, $J_{c\text{-}p}$ = 4.2 Hz), 18.6, 14.7 (d, $J_{c\text{-}p}$ = 2.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.74.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{32}N_2NaO_4P_2$: 443.1494; found: 443.1500.



***tert*-butyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(phenyl)phosphoryl) phenyl)acrylate 3n**

A purification by flash chromatography in petroleum ether : ethyl acetate = 1 : 1 gave **3n** as a yellow foam (33.1 mg, 72%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 70 / 30, flow = 1.0 mL/min) with t_r = 5.6 min (minor), 6.3 min (major): 93% *ee*.

The absolute stereochemistry was assigned by analogy to compound **3a**.

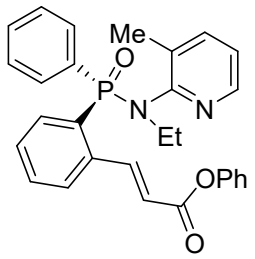
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.40 (m, 1H), 8.36 (d, *J* = 15.8 Hz, 1H), 8.26 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.74 – 7.60 (m, 2H), 7.54 – 7.40 (m, 3H), 7.37 – 7.31 (m, 1H), 7.30 – 7.19 (m, 3H), 6.93 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.00 (d, *J* = 15.8 Hz, 1H), 3.80 – 3.69 (m, 2H), 2.19 (s, 3H), 1.48 (s, 9H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 154.0 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.6, 142.5 (d, $J_{c\text{-}p}$ = 4.5 Hz), 139.5, 139.3 (d, $J_{c\text{-}p}$ = 9.2 Hz), 134.0 (d, $J_{c\text{-}p}$ = 10.3 Hz), 133.1 (d, $J_{c\text{-}p}$ = 2.9

Hz), 132.6 (d, $J_{c\text{-}p}$ = 9.7 Hz), 132.3 (d, $J_{c\text{-}p}$ = 122.9 Hz), 131.9 (d, $J_{c\text{-}p}$ = 124.5 Hz), 131.8 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.6 (d, $J_{c\text{-}p}$=2.8 Hz), 128.8 (d, $J_{c\text{-}p}$ = 12.7 Hz), 127.9 (d, $J_{c\text{-}p}$ = 12.8 Hz), 127.7 (d, $J_{c\text{-}p}$ = 11.1 Hz), 122.6, 121.8, 80.4, 44.4 (d, $J_{c\text{-}p}$ = 3.8 Hz), 28.2, 18.6, 14.7 (d, $J_{c\text{-}p}$ = 2.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.00.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{31}N_2NaO_3P$: 485.1964; found: 485.1970.



phenyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(phenyl)phosphoryl) phenyl)acrylate 3o

A purification by flash chromatography in petroleum ether : ethyl acetate : dichloromethane = 2 : 2 : 1 gave **3o** as a yellow foam (28.7 mg, 60%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 85/15, flow = 0.8 mL/min) with t_r =18.7 min (minor), 26.8 min (major): 93% *ee*.

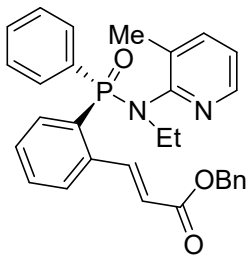
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 15.8 Hz, 1H), 8.52 – 8.42 (m, 1H), 8.27 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.64 – 7.57 (m, 1H), 7.55 – 7.45 (m, 2H), 7.43 – 7.32 (m, 3H), 7.31 – 7.19 (m, 4H), 7.17 – 7.08 (m, 2H), 6.94 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.27 (d, *J* = 15.8 Hz, 1H), 3.83 – 3.68 (m, 2H), 2.19 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 153.9 (d, $J_{c\text{-}p}$ = 4.0 Hz), 150.9, 146.7, 145.5 (d, $J_{c\text{-}p}$ = 4.5 Hz), 139.6, 138.7 (d, $J_{c\text{-}p}$ = 9.4 Hz), 134.2 (d, $J_{c\text{-}p}$ = 10.0 Hz), 133.1 (d, $J_{c\text{-}p}$ = 2.9 Hz), 132.8 (d, $J_{c\text{-}p}$ = 122.1 Hz), 132.6 (d, $J_{c\text{-}p}$ = 10.1 Hz), 132.0 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.9 (d, $J_{c\text{-}p}$ = 125.5 Hz), 131.7 (d, $J_{c\text{-}p}$ = 2.9 Hz), 129.6, 129.5, 128.0 (d, $J_{c\text{-}p}$ = 13.1 Hz), 127.8 (d, $J_{c\text{-}p}$ = 11.0 Hz), 125.8, 121.9, 121.8, 119.6, 44.6 (d, $J_{c\text{-}p}$ = 3.9 Hz), 18.6, 14.8 (d, $J_{c\text{-}p}$ = 2.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.62.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{27}N_2NaO_3P$: 505.1649; found: 505.1657.



benzyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(phenyl)phosphoryl) phenyl)acrylate 3p

A purification by flash chromatography in petroleum ether : ethyl acetate = 1 : 1 gave **3p** as a yellow foam (30.4 mg, 61%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 80/20, flow = 1.0 mL/min) with t_r = 34.1 min (minor), 49.7 min (major): 95% *ee*.

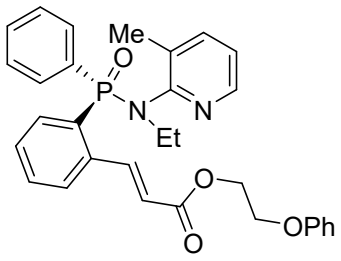
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 15.8 Hz, 1H), 8.47 – 8.36 (m, 1H), 8.25 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.55 – 7.24 (m, 10H), 7.20 – 7.13 (m, 2H), 6.92 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.14 (d, *J* = 15.8 Hz, 1H), 5.28 – 4.11 (m, 2H), 3.79 – 3.67 (m, 2H), 2.16 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 153.9 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.6, 144.2 (d, $J_{c\text{-}p}$ = 4.5 Hz), 139.5, 139.0 (d, $J_{c\text{-}p}$ = 9.3 Hz), 136.3, 134.2 (d, $J_{c\text{-}p}$ = 10.2 Hz), 133.1 (d, $J_{c\text{-}p}$ = 2.9 Hz), 132.56 (d, $J_{c\text{-}p}$ = 9.9 Hz), 132.55 (d, $J_{c\text{-}p}$ = 122.4 Hz), 131.9 (d, $J_{c\text{-}p}$ = 2.9 Hz), 131.8 (d, $J_{c\text{-}p}$ = 125.6 Hz), 131.6 (d, $J_{c\text{-}p}$ = 2.9 Hz), 129.2 (d, $J_{c\text{-}p}$ = 12.6 Hz), 128.6, 128.3, 128.2, 127.9 (d, $J_{c\text{-}p}$ = 12.8 Hz), 127.7 (d, $J_{c\text{-}p}$ = 11.0 Hz), 121.8, 120.2, 66.3, 44.5 (d, $J_{c\text{-}p}$ = 4.1 Hz), 18.6, 14.7 (d, $J_{c\text{-}p}$ = 2.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.70.

HRMS (ESI) m/z:$[M+Na]^+$ Calcd. for $C_{30}H_{29}N_2NaO_3P$: 519.1812; found: 519.1813.



2-phenoxyethyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(phenyl) phosphoryl)phenyl)acrylate 3q

A purification by flash chromatography in petroleum ether : ethyl acetate = 2 : 1 gave **3q** as a yellow foam (30.6 mg, 58%). The *ee* value was determined by HPLC analysis

on a Chiralcel IB N-5 column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with t_r =12.7 min (minor), 14.7 min (major): 95% *ee*.

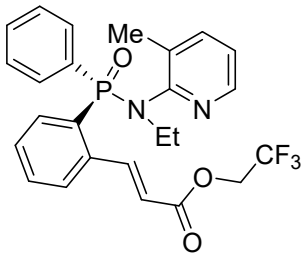
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 15.8 Hz, 1H), 8.44 – 8.36 (m, 1H), 8.26 (dd, *J* = 4.8, 1.8 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.54 – 7.41 (m, 3H), 7.33 – 7.24 (m, 4H), 7.23 – 7.16 (m, 2H), 6.99 – 6.89 (m, 4H), 6.14 (d, *J* = 15.8 Hz, 1H), 4.58 – 4.44 (m, 2H), 4.27 – 4.17 (m, 2H), 3.79 – 3.65 (m, 2H), 2.18 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 158.7, 154.0 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.6, 144.5 (d, $J_{c\text{-}p}$ = 4.4 Hz), 139.5, 139.0 (d, $J_{c\text{-}p}$ = 9.5 Hz), 134.2 (d, $J_{c\text{-}p}$ = 10.2 Hz), 133.0 (d, $J_{c\text{-}p}$ = 2.9 Hz), 132.63 (d, $J_{c\text{-}p}$ = 9.9 Hz), 132.61 (d, $J_{c\text{-}p}$ = 122.3 Hz), 132.0 (d, $J_{c\text{-}p}$ = 126.4 Hz), 131.9 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.7 (d, $J_{c\text{-}p}$ = 2.9 Hz), 129.6, 129.2 (d, $J_{c\text{-}p}$ = 13.0 Hz), 128.0 (d, $J_{c\text{-}p}$ = 13.0 Hz), 127.7 (d, $J_{c\text{-}p}$ = 11.0 Hz), 121.8, 121.2, 119.9, 114.8, 66.0, 62.9, 44.5 (d, $J_{c\text{-}p}$ = 3.8 Hz), 18.6, 14.7 (d, $J_{c\text{-}p}$ = 2.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.63.

HRMS (ESI) m/z:$[M+Na]^+$ Calcd. for $C_{31}H_{31}N_2NaO_4P$: 549.1918; found: 549.1919.



2,2,2-trifluoroethyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(phenyl) phosphoryl)phenyl)acrylate 3r

A purification by flash chromatography in petroleum ether : ethyl acetate = 1 : 1 gave **3r** as a yellow foam (29.3 mg, 60%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 90/10, flow = 0.8 mL/min) with t_r = 39.9 min (minor), 44.6 min (major): 95% *ee*.

The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 15.8 Hz, 1H), 8.51 – 8.42 (m, 1H), 8.28 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.71 – 7.61 (m, 2H), 7.58 – 7.43 (m, 3H), 7.38 – 7.31 (m, 1H), 7.30 – 7.19 (m, 3H), 6.95 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.15 (d, *J* = 15.8 Hz, 1H), 4.65 – 4.43 (m, 2H), 3.81 – 3.68 (m, 2H), 2.17 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).

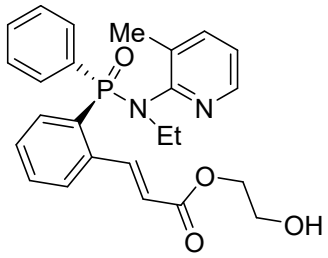
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 153.9 (d, $J_{C\text{-}P}$ = 3.9 Hz), 146.7, 146.3 (d, $J_{C\text{-}P}$ = 4.5 Hz), 139.6, 138.5 (d, $J_{C\text{-}P}$ = 9.1 Hz), 134.2 (d, $J_{C\text{-}P}$ = 10.1 Hz), 133.2 (d, $J_{C\text{-}P}$ =

2.7 Hz), 133.1 (d, $J_{C\text{-}P}$ = 121.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.8 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.7 (d, $J_{C\text{-}P}$ = 125.4 Hz), 129.7 (d, $J_{C\text{-}P}$ = 12.8 Hz), 128.0 (d, $J_{C\text{-}P}$ = 12.6 Hz), 127.9 (d, $J_{C\text{-}P}$ = 10.8 Hz), 123.2 (q, $J_{C\text{-}F}$ = 278.4 Hz), 121.9, 118.1, 60.3 (q, $J_{C\text{-}F}$ = 36.7 Hz), 44.6 (d, $J_{C\text{-}P}$ = 3.9 Hz), 18.5, 14.8 (d, $J_{C\text{-}P}$ = 2.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.40.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.60.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{24}F_3N_2NaO_3P$: 511.1370; found: 511.1374.



2-hydroxyethyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(phenyl) phosphoryl)phenyl)acrylate 3s

A purification by flash chromatography in methanol: ethyl acetate=1 : 20 gave **3s** as a yellow foam (26.5 mg, 59%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol = 94/6, flow = 0.6 mL/min) with t_r = 54.2 min (minor), 63.1 min (major): 94% *ee*.

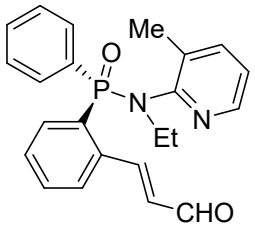
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 15.9 Hz, 1H), 8.35 – 8.23 (m, 2H), 7.84 – 7.76 (m, 2H), 7.49 – 7.38 (m, 4H), 7.37 – 7.30 (m, 2H), 7.28 – 7.26 (m, 1H), 6.96 (dd, *J*=7.6, 4.7 Hz, 1H), 6.01 (d, *J*=15.8 Hz, 1H), 4.36 – 4.24 (m, 2H), 3.97 – 3.90 (m, 2H), 3.83 – 3.67 (m, 2H), 2.63 (brs, 1H), 2.14 (s, 3H), 1.03 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 153.7 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.7, 144.0 (d, $J_{c\text{-}p}$ = 4.8 Hz), 139.8, 138.4 (d, $J_{c\text{-}p}$ = 8.8 Hz), 134.5 (d, $J_{c\text{-}p}$ = 10.3 Hz), 133.2 (d, $J_{c\text{-}p}$ = 2.4 Hz), 132.7 (d, $J_{c\text{-}p}$ = 10.1 Hz), 132.2 (d, $J_{c\text{-}p}$ = 2.7 Hz), 132.0 (d, $J_{c\text{-}p}$ = 2.6 Hz), 131.9 (d, $J_{c\text{-}p}$ = 129.0 Hz), 131.8 (d, $J_{c\text{-}p}$ = 121.5 Hz), 129.2 (d, $J_{c\text{-}p}$ = 13.0 Hz), 128.3 (d, $J_{c\text{-}p}$ = 12.8 Hz), 127.2 (d, $J_{c\text{-}p}$ = 10.5 Hz), 122.1, 119.7, 66.7, 61.1, 45.0 (d, $J_{c\text{-}p}$ = 4.1 Hz), 18.6, 14.6 (d, $J_{c\text{-}p}$ = 2.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.03.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{27}N_2NaO_4P$: 473.1600; found: 473.1606.



(*R, E*)-*N*-ethyl-*N*-(3-methylpyridin-2-yl)-*P*-(2-(3-oxoprop-1-en-1-yl)phenyl)-*P*-phenylphosphinic amide 3t

A purification by flash chromatography in petroleum ether : ethyl acetate = 2 : 1 gave **3t** as a yellow foam (22.2 mg, 57%). The *ee* value was determined by HPLC analysis on a Chiralcel AS-H column (hexane/isopropanol = 95/5, flow = 0.6 mL/min) with t_r = 43.7 min (major), 59.1 min (minor): 95% *ee*.

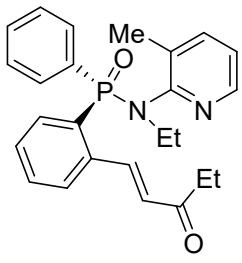
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 7.9 Hz, 1H), 8.80 (d, *J* = 15.8 Hz, 1H), 8.39 – 8.27 (m, 2H), 7.72 – 7.59 (m, 3H), 7.54 – 7.46 (m, 2H), 7.40 – 7.34 (m, 1H), 7.32 – 7.24 (m, 3H), 6.96 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.44 (dd, *J* = 15.8, 7.8 Hz, 1H), 3.75 – 3.65 (m, 2H), 2.19 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 153.8 (d, $J_{c\text{-}p}$ = 3.7 Hz), 152.0 (d, $J_{c\text{-}p}$ = 4.3 Hz), 146.8, 139.6, 138.8 (d, $J_{c\text{-}p}$ = 8.9 Hz), 134.4 (d, $J_{c\text{-}p}$ = 10.4 Hz), 133.3 (d, $J_{c\text{-}p}$ = 3.4 Hz), 132.5 (d, $J_{c\text{-}p}$ = 121.8 Hz), 132.4 (d, $J_{c\text{-}p}$ = 9.8 Hz), 132.1 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.9 (d, $J_{c\text{-}p}$ = 3.1 Hz), 131.7 (d, $J_{c\text{-}p}$ = 125.7 Hz), 130.4, 130.0 (d, $J_{c\text{-}p}$ = 13.1 Hz), 128.2 (d, $J_{c\text{-}p}$ = 12.8 Hz), 127.9 (d, $J_{c\text{-}p}$ = 10.9 Hz), 122.1, 44.7 (d, $J_{c\text{-}p}$=4.1 Hz), 18.6, 14.6 (d, $J_{c\text{-}p}$=3.3 Hz).

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

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{23}N_2NaO_2P$: 413.1392; found: 413.1395.



(*R, E*)-*N*-ethyl-*N*-(3-methylpyridin-2-yl)-*P*-(2-(3-oxopent-1-en-1-yl)phenyl)-*P*-phenylphosphinic amide 3u

A purification by flash chromatography in toluene : ethyl acetate = 1 : 1 gave **3u** as a yellow foam (24.2 mg, 58%). The *ee* value was determined by HPLC analysis on a

Chiralcel IA column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with tr = 5.5 min (minor), 6.7 min (major): 94% *ee*.

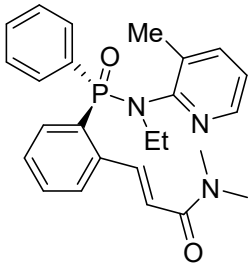
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 16.5 Hz, 1H), 8.47 – 8.37 (m, 1H), 8.30 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.67 – 7.56 (m, 3H), 7.52 – 7.45 (m, 2H), 7.38 – 7.31 (m, 1H), 7.30 – 7.20 (m, 3H), 6.95 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.31 (d, *J* = 16.5 Hz, 1H), 3.78 – 3.64 (m, 2H), 2.80 – 2.56 (m, 2H), 2.17 (s, 3H), 1.11 – 1.00 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) 202.5, 153.9 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.8, 142.3 (d, $J_{c\text{-}p}$ = 4.3 Hz), 139.7 (d, $J_{c\text{-}p}$ = 9.4 Hz), 139.5, 134.1 (d, $J_{c\text{-}p}$ = 10.3 Hz), 133.3 (d, $J_{c\text{-}p}$ = 2.8 Hz), 132.3 (d, $J_{c\text{-}p}$ = 9.7 Hz), 132.2 (d, $J_{c\text{-}p}$ = 122.3 Hz), 132.0 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.9 (d, $J_{c\text{-}p}$ = 125.2 Hz), 131.8 (d, $J_{c\text{-}p}$ = 2.8 Hz), 129.4, 129.2 (d, $J_{c\text{-}p}$ = 13.1 Hz), 128.0 (d, $J_{c\text{-}p}$ = 13.0 Hz), 127.6 (d, $J_{c\text{-}p}$ = 11.1 Hz), 122.0, 44.7 (d, $J_{c\text{-}p}$ = 3.9 Hz), 31.6, 18.6, 14.7 (d, $J_{c\text{-}p}$ = 3.0 Hz), 8.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.38.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{27}N_2NaO_2P$: 441.1704; found: 441.1708.



(*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(phenyl)phosphoryl)phenyl)-*N*,*N*-dimethylacrylamide 3v

A purification by flash chromatography in petroleum ether : ethyl acetate = 4 : 1 gave **3v** as a yellow foam (23.5 mg, 54%). The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with t_r = 8.0 min (minor), 11.0 min (major): 95% *ee*.

The absolute stereochemistry was assigned by analogy to compound **3a**.

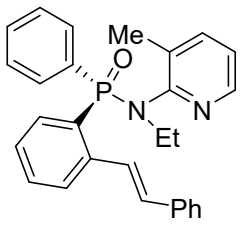
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.36 (m, 1H), 8.25 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.10 (d, *J* = 15.6 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.51 – 7.40 (m, 3H), 7.36 – 7.30 (m, 1H), 7.30 – 7.20 (m, 3H), 6.91 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 3.76 – 3.64 (m, 2H), 3.02 (s, 3H), 2.98 (s, 3H), 2.23 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 153.9 (d, $J_{c\text{-}p}$ = 3.5 Hz), 146.5, 140.4 (d, $J_{c\text{-}p}$ = 4.5 Hz), 140.3 (d, $J_{c\text{-}p}$ = 9.5 Hz), 139.5, 134.2 (d, $J_{c\text{-}p}$ = 10.2 Hz), 133.0 (d, $J_{c\text{-}p}$ = 3.0 Hz), 132.6 (d, $J_{c\text{-}p}$ = 10.1 Hz), 131.82 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.76 (d, $J_{c\text{-}p}$ = 125.9 Hz),

131.66 (d, $J_{c\text{-}p}$ = 123.2 Hz), 131.62 (d, $J_{c\text{-}p}$ = 2.9 Hz), 128.4 (d, $J_{c\text{-}p}$ = 13.1 Hz), 127.94 (d, $J_{c\text{-}p}$ = 13.0 Hz), 127.88 (d, $J_{c\text{-}p}$ = 11.1 Hz), 121.7, 121.1, 44.4 (d, $J_{c\text{-}p}$ = 3.8 Hz), 37.9, 35.9, 18.7, 14.6 (d, $J_{c\text{-}p}$ = 2.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.29.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{28}N_3NaO_2P$: 456.1815; found: 456.1817.



(*R, E*)-*N*-ethyl-*N*-(3-methylpyridin-2-yl)-*P*-phenyl-*P*-(2-styrylphenyl)phosphinic amide 3w

A purification by flash chromatography in petroleum ether : ethyl acetate = 1 : 1 gave **3w** as a yellow foam (24.9 mg, 57%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with t_r = 5.8 min (minor), 6.9 min (major): 93% *ee*.

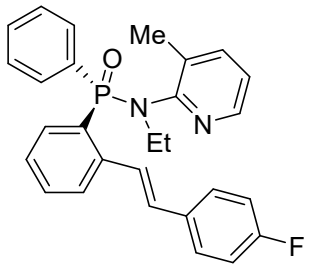
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.22 (m, 2H), 8.18 (d, *J* = 16.1 Hz, 1H), 7.77 – 7.63 (m, 3H), 7.48 – 7.42 (m, 3H), 7.39 – 7.18 (m, 8H), 6.92 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.80 (d, *J* = 16.1 Hz, 1H), 3.80 – 3.68 (m, 2H), 2.19 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.6, 142.2 (d, $J_{c\text{-}p}$ = 9.6 Hz), 139.4, 137.5, 134.1 (d, $J_{c\text{-}p}$ = 10.7 Hz), 133.4 (d, $J_{c\text{-}p}$ = 2.2 Hz), 132.50 (d, $J_{c\text{-}p}$ = 124.5 Hz), 132.46 (d, $J_{c\text{-}p}$ = 9.8 Hz), 131.9 (d, $J_{c\text{-}p}$ = 2.7 Hz), 131.5 (d, $J_{c\text{-}p}$ = 2.9 Hz), 130.8, 130.1 (d, $J_{c\text{-}p}$ = 123.7 Hz), 128.6, 127.9 (d, $J_{c\text{-}p}$ = 13.2 Hz), 127.8, 127.7, 127.1, 126.8 (d, $J_{c\text{-}p}$ = 13.0 Hz), 126.5 (d, $J_{c\text{-}p}$ = 11.5 Hz), 121.7, 44.7 (d, $J_{c\text{-}p}$ = 4.0 Hz), 18.8, 14.7 (d, $J_{c\text{-}p}$ = 3.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.01.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{28}N_2OP$: 439.1933; found: 439.1939.



(*R, E*)-*N*-ethyl-*P*-(2-(4-fluorostyryl)phenyl)-*N*-(3-methylpyridin-2-yl)-*P*-phenylphosphinic amide 3x

A purification by flash chromatography in petroleum ether : ethyl acetate = 4 : 1 gave **3x** as a yellow foam (21.7 mg, 48%). The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with t_r = 5.2 min (minor), 6.8 min (major): 92% *ee*.

The absolute stereochemistry was assigned by analogy to compound **3a**.

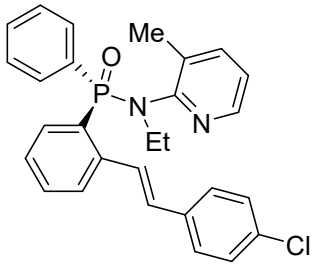
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.22 (m, 2H), 8.09 (d, *J* = 16.1 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.65 (dd, *J* = 7.8, 4.9 Hz, 1H), 7.51 – 7.19 (m, 8H), 6.99 (t, *J* = 8.5 Hz, 2H), 6.93 (dd, *J* = 7.5, 4.8 Hz, 1H), 6.75 (d, *J* = 16.2 Hz, 1H), 3.80 – 3.67 (m, 2H), 2.18 (s, 3H), 1.03 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, $J_{C\text{-}F}$ = 248.1 Hz), 154.2 (d, $J_{C\text{-}P}$ = 3.5 Hz), 146.6, 142.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 139.4, 134.2 (d, $J_{C\text{-}P}$ = 10.6 Hz), 133.8 (d, $J_{C\text{-}P}$ = 3.3 Hz), 133.4 (d, $J_{C\text{-}P}$ = 2.3 Hz), 132.5 (d, $J_{C\text{-}P}$ = 125.1 Hz), 132.4 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.4 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.1 (d, $J_{C\text{-}P}$ = 123.7 Hz), 129.5, 128.6 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.0 (d, $J_{C\text{-}P}$ = 12.7 Hz), 127.7 (d, $J_{C\text{-}F}$ = 4.8 Hz), 126.9 (d, $J_{C\text{-}P}$ = 13.1 Hz), 126.4 (d, $J_{C\text{-}P}$ = 11.4 Hz), 121.8, 115.5 (d, $J_{C\text{-}F}$ = 21.6 Hz), 44.7 (d, $J_{C\text{-}P}$ = 4.1 Hz), 18.8, 14.7 (d, $J_{C\text{-}P}$ = 3.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.46.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.21.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{27}FN_2OP$: 457.1839; found: 457.1845.



(*R, E*)-*P*-(2-(4-chlorostyryl)phenyl)-*N*-ethyl-*N*-(3-methylpyridin-2-yl)-*P*-phenylphosphinic amide 3y

A purification by flash chromatography in petroleum ether : ethyl acetate = 4 : 1 gave **3y** as a yellow foam (25.2 mg, 53%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with t_r = 6.3 min (minor), 8.7 min (major): 93% *ee*.

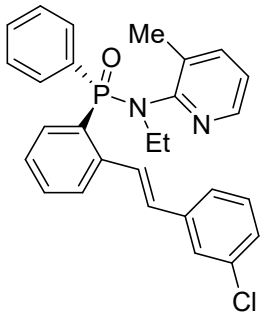
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.22 (m, 2H), 8.17 (d, *J* = 16.1 Hz, 1H), 7.76 – 7.61 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.20 (m, 9H), 6.93 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.74 (d, *J* = 16.1 Hz, 1H), 3.79 – 3.67 (m, 2H), 2.18 (s, 3H), 1.03 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.7, 141.9 (d, $J_{c\text{-}p}$ = 9.5 Hz), 139.5, 136.1, 134.2 (d, $J_{c\text{-}p}$ = 10.5 Hz), 133.4 (d, $J_{c\text{-}p}$ = 2.3 Hz), 133.3, 132.42 (d, $J_{c\text{-}p}$ = 9.9 Hz), 132.41 (d, $J_{c\text{-}p}$ = 125.0 Hz), 131.9 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.6 (d, $J_{c\text{-}p}$ = 3.1 Hz), 130.2 (d, $J_{c\text{-}p}$=123.7 Hz), 129.4, 128.8, 128.5 (d, $J_{c\text{-}p}$ = 4.6 Hz), 128.3, 128.0 (d, $J_{c\text{-}p}$ = 12.7 Hz), 127.1 (d, $J_{c\text{-}p}$ = 12.8 Hz), 126.5 (d, $J_{c\text{-}p}$ = 11.5 Hz), 121.8, 44.7 (d, $J_{c\text{-}p}$ = 4.0 Hz), 18.8, 14.7 (d, $J_{c\text{-}p}$ = 3.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.40.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{27}ClN_2OP$: 473.1549; found: 473.1550.



(*R, E*)-*P*-(2-(3-chlorostyryl)phenyl)-*N*-ethyl-*N*-(3-methylpyridin-2-yl)-*P*-phenylphosphinic amide 3z

A purification by flash chromatography in petroleum ether : ethyl acetate = 4 : 1 gave **3z** as a yellow foam (26.2 mg, 55%). The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with t_r = 4.8 min (minor), 5.6 min (major): 94% *ee*.

The absolute stereochemistry was assigned by analogy to compound **3a**.

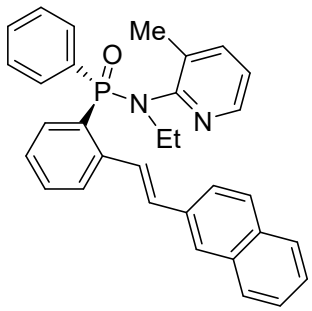
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.24 (m, 2H), 8.14 (d, *J* = 16.1 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.64 (dd, *J* = 7.8, 4.9 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.15 (m, 9H), 6.94 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.71 (d, *J* = 16.2 Hz, 1H), 3.80 – 3.68 (m, 2H), 2.18 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1 (d, $J_{c\text{-}p}$ = 3.8 Hz), 146.7, 141.7 (d, $J_{c\text{-}p}$ = 9.0 Hz), 139.5 (d, $J_{c\text{-}p}$ = 3.6 Hz), 134.5, 134.2 (d, $J_{c\text{-}p}$ = 10.6 Hz), 133.4 (d, $J_{c\text{-}p}$ = 2.5 Hz), 132.43 (d, $J_{c\text{-}p}$ = 125.2 Hz), 132.41 (d, $J_{c\text{-}p}$ = 10.2 Hz), 132.0 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.6 (d, $J_{c\text{-}p}$ = 2.9 Hz), 130.5 (d, $J_{c\text{-}p}$ = 123.7 Hz), 129.8, 129.41, 129.36 (d, $J_{c\text{-}p}$ = 4.9 Hz),

128.0 (d, $J_{c\text{-}p}$ = 12.6 Hz), 127.6, 127.3 (d, $J_{c\text{-}p}$ = 13.0 Hz), 127.0, 126.6 (d, $J_{c\text{-}p}$ = 11.5 Hz), 125.2, 121.8, 44.7 (d, $J_{c\text{-}p}$ = 4.3 Hz), 18.8, 14.7 (d, $J_{c\text{-}p}$ = 3.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.98.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{27}ClN_2OP$: 473.1549; found: 473.1550.



(*R, E*)-*N*-ethyl-*N*-(3-methylpyridin-2-yl)-*P*-(2-(2-(naphthalen-2-yl)vinyl) phenyl)-*P*-phenylphosphinic amide 3aa

A purification by flash chromatography in petroleum ether : ethyl acetate = 4 : 1 gave **3aa** as a yellow foam (25.2 mg, 52%). The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with t_r = 5.9 min (major), 8.5 min (minor): 94% *ee*.

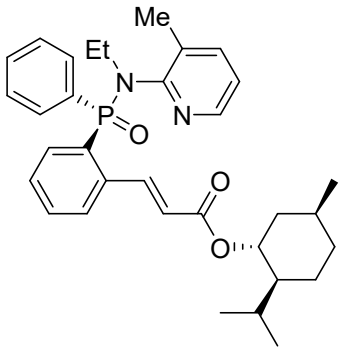
The absolute stereochemistry was assigned by analogy to compound **3a** .

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.21 (m, 3H), 7.83 – 7.69 (m, 8H), 7.51 – 7.21 (m, 8H), 7.00 – 6.89 (m, 2H), 3.82 – 2.71 (m, 2H), 2.19 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) 154.2 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.7, 142.2 (d, $J_{c\text{-}p}$=9.6Hz), 139.4, 135.2, 134.2 (d, $J_{c\text{-}p}$ = 10.4 Hz), 133.7, 133.4 (d, $J_{c\text{-}p}$ = 2.2 Hz), 133.2, 132.6 (d, $J_{c\text{-}p}$ = 125.9 Hz), 132.5 (d, $J_{c\text{-}p}$ = 9.8 Hz), 132.0 (d, $J_{c\text{-}p}$ = 2.4 Hz), 131.5 (d, $J_{c\text{-}p}$ = 2.5 Hz), 130.9, 130.2 (d, $J_{c\text{-}p}$ = 123.7 Hz), 128.3, 128.2, 128.0 (d, $J_{c\text{-}p}$ = 12.8 Hz), 127.8, 127.2, 126.9 (d, $J_{c\text{-}p}$ = 13.0 Hz), 126.5 (d, $J_{c\text{-}p}$ = 11.4 Hz), 126.3, 126.0, 124.3, 121.8, 44.7 (d, $J_{c\text{-}p}$ = 4.1 Hz), 18.8, 14.7 (d, $J_{c\text{-}p}$ = 3.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.17.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{32}H_{30}N_2OP$: 489.2094; found: 489.2096.



(*1R, 2S, 5S*)-2-isopropyl-5-methylcyclohexyl-(*E*)-3-(2-((*R*)-(ethyl (3-methylpyridin-2-yl)amino)(phenyl)phosphoryl)phenyl)acrylate 3ab

A purification by flash chromatography in petroleum ether : ethyl acetate = 4 : 1 gave **3ab** as a yellow foam (35.6 mg, 65%). The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol = 90/10, flow = 0.8 mL/min) with t_r = 10.2 min (minor), 17.1 min (major): 95% *ee*.

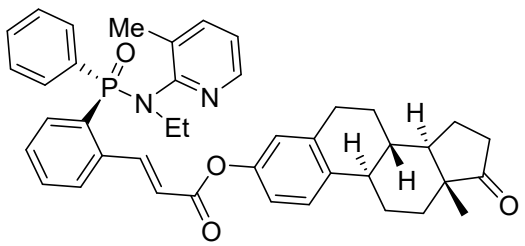
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.38 (m, 2H), 8.25 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.54 – 7.40 (m, 3H), 7.37 – 7.30 (m, 1H), 7.30 – 7.18 (m, 3H), 6.93 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.04 (d, *J* = 15.7 Hz, 1H), 4.74 (td, *J* = 10.9, 4.3 Hz, 1H), 3.80 – 3.69 (m, 2H), 2.18 (s, 3H), 2.04 – 1.82 (m, 2H), 1.73 – 1.63 (m, 2H), 1.57 – 1.35 (m, 2H), 1.09 – 0.96 (m, 5H), 0.94 – 0.85 (m, 7H), 0.75 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 154.0 (d, $J_{c\text{-}p}$ = 3.7 Hz), 146.6, 143.4 (d, $J_{c\text{-}p}$ = 4.8 Hz), 139.5, 139.3 (d, $J_{c\text{-}p}$ = 9.5 Hz), 134.1 (d, $J_{c\text{-}p}$ = 10.2 Hz), 133.1, 132.6 (d, $J_{c\text{-}p}$ = 10.2 Hz), 132.5 (d, $J_{c\text{-}p}$ = 125.0 Hz), 132.1 (d, $J_{c\text{-}p}$ = 125.2 Hz), 131.8 (d, $J_{c\text{-}p}$ = 2.7 Hz), 131.6 (d, $J_{c\text{-}p}$ = 3.2 Hz), 128.9 (d, $J_{c\text{-}p}$ = 13.0 Hz), 127.9 (d, $J_{c\text{-}p}$ = 13.1 Hz), 127.7 (d, $J_{c\text{-}p}$ = 11.0 Hz), 121.8, 121.2, 74.2, 47.1, 44.4 (d, $J_{c\text{-}p}$ = 4.0 Hz), 41.0, 34.4, 31.5, 26.2, 23.5, 22.2, 20.9, 18.6, 16.5, 14.7 (d, $J_{c\text{-}p}$ = 2.8 Hz).

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

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{41}N_2NaO_3P$: 567.2752; found: 567.2752.



(*8S, 9R, 13R, 14R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-

6H-cyclopenta[a]phenanthren-3-yl (*E*)-3-(2-((*R*)-(ethyl(3-methylpyridin-2-yl)amino)(phenyl)phosphoryl)phenyl)acrylate 3ac

A purification by flash chromatography in petroleum ether : ethyl acetate : dichloromethane = 2 : 2 : 1 gave **3ac** as a yellow foam (45.4 mg, 69%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 80/20, flow = 1.0 mL/min) with t_r = 34.1 min (minor), 49.7 min (major): 95% *ee*.

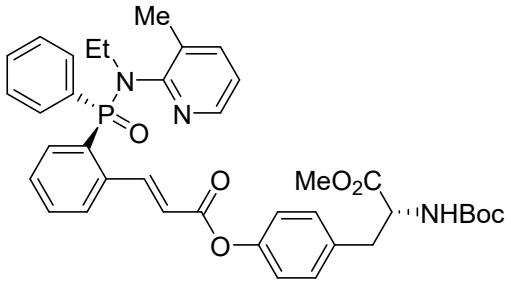
The absolute stereochemistry was assigned by analogy to compound **3a**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 15.8 Hz, 1H), 8.51 – 8.40 (m, 1H), 8.27 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.75 – 7.65 (m, 2H), 7.63 – 7.57 (m, 1H), 7.55 – 7.45 (m, 2H), 7.35 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 – 7.20 (m, 4H), 6.97 – 6.84 (m, 3H), 6.26 (d, *J* = 15.8 Hz, 1H), 3.82 – 3.68 (m, 2H), 2.97 – 2.87 (m, 2H), 2.51 (dd, *J* = 18.8, 8.5 Hz, 1H), 2.45 – 2.25 (m, 2H), 2.22 – 1.91 (m, 7H), 1.70 – 1.39 (m, 6H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 153.9 (d, $J_{c\text{-}p}$ = 3.7 Hz), 148.8, 146.6, 145.4 (d, $J_{c\text{-}p}$ = 4.5 Hz), 139.5, 138.8 (d, $J_{c\text{-}p}$ = 8.9 Hz), 138.0, 137.2, 134.2 (d, $J_{c\text{-}p}$ = 9.9 Hz), 133.1 (d, $J_{c\text{-}p}$ = 2.9 Hz), 132.8 (d, $J_{c\text{-}p}$ = 122.2 Hz), 132.6 (d, $J_{c\text{-}p}$ = 9.8 Hz), 132.0 (d, $J_{c\text{-}p}$ = 2.9 Hz), 131.8 (d, $J_{c\text{-}p}$ = 125.6 Hz), 131.7 (d, $J_{c\text{-}p}$ = 2.9 Hz), 129.4 (d, $J_{c\text{-}p}$ = 12.8 Hz), 128.0 (d, $J_{c\text{-}p}$ = 12.6 Hz), 127.8 (d, $J_{c\text{-}p}$ = 11.0 Hz), 126.4, 121.9, 121.8, 119.7, 118.9, 50.5, 48.1, 44.5 (d, $J_{c\text{-}p}$ = 4.2 Hz), 44.2, 38.1, 36.0, 31.6, 29.5, 26.4, 25.8, 21.7, 18.6, 14.7 (d, $J_{c\text{-}p}$ = 2.8 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.64.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{41}H_{43}N_2NaO_4P$: 681.2860; found: 681.2858.



4-((*R*)-2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl (*E*)-3-(2-((*R*)-(ethyl(3-methylpyridin-2-yl)amino)(phenyl)phosphoryl)phenyl)acrylate 3ad

A purification by flash chromatography in petroleum ether : ethyl acetate = 1 : 1 gave **3ad** as a yellow foam (36.8 mg, 54%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol = 70/30, flow = 1.0 mL/min) with t_r = 10.0 min (minor), 14.3 min (major): 95% *ee*.

The absolute stereochemistry was assigned by analogy to compound **3a**.

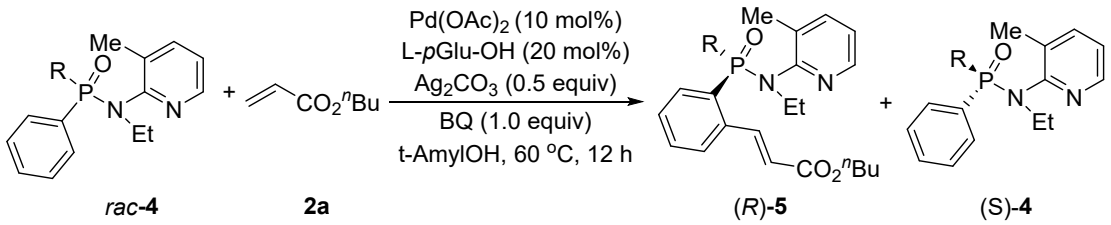
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 15.8 Hz, 1H), 8.50 – 8.41 (m, 1H), 8.27 (dd, *J* = 4.8, 1.9 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.62 – 7.58 (m, 1H), 7.55 – 7.46 (m, 2H), 7.35 (td, *J* = 7.4, 1.5 Hz, 1H), 7.31 – 7.21 (m, 3H), 7.17 – 7.11 (m, 2H), 7.09 – 7.03 (m, 2H), 6.94 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.25 (d, *J* = 15.8 Hz, 1H), 5.01 (d, *J* = 8.2 Hz, 1H), 4.63 – 4.53 (m, 1H), 3.81 – 3.68 (m, 5H), 3.17 – 3.01 (m, 2H), 2.18 (s, 3H), 1.43 (s, 9H), 1.05 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) 172.4, 164.8, 155.24, 153.9 (d, $J_{c\text{-}p}$ = 3.7 Hz), 150.0, 146.7, 145.6 (d, $J_{c\text{-}p}$ = 4.5 Hz), 139.5, 138.8 (d, $J_{c\text{-}p}$ = 9.3 Hz), 134.3 (d, $J_{c\text{-}p}$ = 9.9 Hz), 133.5, 133.1 (d, $J_{c\text{-}p}$ = 3.0 Hz), 132.9 (d, $J_{c\text{-}p}$ = 122.5 Hz), 132.6 (d, $J_{c\text{-}p}$ = 10.1 Hz), 132.0 (d, $J_{c\text{-}p}$ = 2.2 Hz), 131.9 (d, $J_{c\text{-}p}$ = 126.1 Hz), 131.7 (d, $J_{c\text{-}p}$ = 2.6 Hz), 130.3, 129.5 (d, $J_{c\text{-}p}$ = 12.7 Hz), 128.0 (d, $J_{c\text{-}p}$ = 12.8 Hz), 127.8 (d, $J_{c\text{-}p}$ = 11.0 Hz), 121.9, 121.8, 119.6, 80.1, 54.5, 53.5, 52.4, 44.6 (d, $J_{c\text{-}p}$ = 4.1 Hz), 37.8, 28.4, 18.6, 14.7 (d, $J_{c\text{-}p}$ = 2.8 Hz).

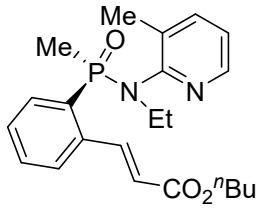
^{31}P NMR (162 MHz, $CDCl_3$) δ 27.60.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{38}H_{42}N_3NaO_7P$: 706.2655; found: 706.2658.

2.3 General Procedure for Pd(II)-Catalyzed C−H Olefination via Kinetic Resolution (KR)



To a 50 mL Schlenk tube was added substrate **1** (0.20 mmol), **2a** (0.40 mmol), $Pd(OAc)_2$ (4.4 mg, 0.01 mmol), L-*p*Glu-OH (5.2 mg, 0.04 mmol), Ag_2CO_3 (27.6 mg, 0.1 mmol), BQ (21.6 mg, 0.20 mmol), *t*-AmylOH (2 mL). The mixture was stirred for 12 h at 60 °C under air. The resulting mixture was filtered through a celite pad and concentrated in vacuo. The residue was purified by preparative TLC using PE/EA as the eluent to afford the alkynylation product **5** and unreacted **4**.



butyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(methyl)phosphoryl) phenyl)acrylate (*R*)**-5a**

A purification by preparative TLC in ethyl acetate : dichloromethane = 3 : 1 gave (*R*)**-5a** as a yellow foam (20.7 mg, 26%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol=70/30, flow=1.0 mL/min) with t_r =7.1 min (minor), 8.3 min (major): 71% *ee*.

The absolute stereochemistry was assigned by analogy to compound **3a**.

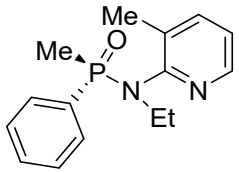
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, J = 15.8 Hz, 1H), 8.34 (dd, J = 4.7, 1.9 Hz, 1H), 8.25 – 8.15 (m, 1H), 7.64 – 7.61 (m, 1H), 7.56 – 7.44 (m, 3H), 7.07 (dd, J = 7.5, 4.7 Hz, 1H), 6.31 (d, J = 15.8 Hz, 1H), 4.24 – 4.14 (m, 2H), 3.50 – 3.40 (m, 2H), 2.44 (s, 3H), 1.70 – 1.58 (m, 5H), 1.44 – 1.36 (m, 2H), 0.99 – 0.92 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 154.2 (d, *J*c-p=2.6 Hz), 146.9, 143.6 (d, *J*c-p=4.4 Hz), 140.1, 138.3 (d, *J*c-p = 8.2 Hz), 134.3 (d, *J*c-p = 10.2 Hz), 132.4 (d, *Jc-p* =

119.9 Hz), 132.2 (d, *Jc-p* = 3.1 Hz), 132.0 (d, *Jc-p* = 2.8 Hz), 129.3 (d, *Jc-p* = 12.6 Hz), 127.7 (d, *Jc-p* = 12.6 Hz), 122.0, 121.6, 64.6, 43.3 (d, *Jc-p* = 4.0 Hz), 30.8, 19.2, 18.5, 16.8 (d, *Jc-p* = 92.2 Hz), 14.6 (d, *Jc-p* = 2.9 Hz), 13.9.

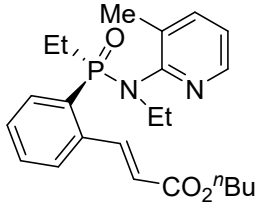
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.53.

HRMS (ESI) m/z:$[M+Na]^+$ Calcd. for $C_{22}H_{29}N_2NaO_3P$:423.1812; found:423.1813.



(*S*)-*N*-ethyl-P-methyl-*N*-(3-methylpyridin-2-yl)-P-phenylphosphinic amide (*S*)**-4a**

A purification by preparative TLC in ethyl acetate : dichloromethane = 3 : 1 gave (*S*)-**4a** as a yellow foam (23.8 mg, 43%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol=90/10, flow=0.8 mL/min) with t_r =13.0 min (minor), 14.8 min (major): 99% *ee*.



butyl (*R, E*)-3-(2-(ethyl(ethyl(3-methylpyridin-2-yl)amino)phosphoryl)phenyl) acrylate (*R*)**-5b**

A purification by preparative TLC in ethyl acetate : dichloromethane = 3 : 1 gave (*R*)-**5b** as a yellow foam (31.4 mg, 38%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol=90/10, flow=1.0 mL/min) with t_r =11.4 min (minor), 14.7 min (major): 90% *ee*.

The absolute stereochemistry was assigned by analogy to compound **3a**.

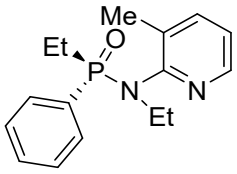
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 15.8 Hz, 1H), 8.36 (d, J = 4.6 Hz, 1H), 8.26 – 8.17 (m, 1H), 7.65 – 7.62 (m, 1H), 7.56 – 7.43 (m, 3H), 7.08 (dd, J = 7.5, 4.7 Hz, 1H), 6.30 (d, J = 15.8 Hz, 1H), 4.21– 4.17 (m, 2H), 3.53– 3.35 (m, 2H), 2.43 (s, 3H), 1.93 – 1.74 (m, 2H), 1.71 – 1.63 (m, 2H), 1.41 (q, J = 7.5 Hz, 2H), 0.98 – 0.87 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 154.0 (d, *Jc-p* = 3.0 Hz), 146.6, 143.5 (d, *Jc-p* = 3.7 Hz), 139.8, 138.8 (d, *Jc-p* = 8.3 Hz), 134.5 (d, *Jc-p* = 9.7 Hz), 132.2 (d, *Jc-p* = 3.4 Hz), 131.6 (d, *Jc-p* = 2.6 Hz), 130.6 (d, *Jc-p* = 115.0 Hz), 128.9 (d, *Jc-p* = 12.4

Hz), 127.3 (d, *Jc-p* = 10.4 Hz), 121.8, 121.1, 64.2, 43.3 (d, *Jc-p* = 3.3 Hz), 30.6, 22.8, 21.9, 19.0, 18.2, 14.2 (d, *Jc-p* = 2.8 Hz), 13.5.

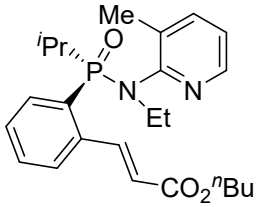
^{31}P NMR (162 MHz, $CDCl_3$) δ 37.57.

HRMS (ESI) m/z:$[M+Na]^+$ Calcd. for $C_{23}H_{31}N_2NaO_3P$:437.1964; found:437.1970.



(*S*)-*N*, P-diethyl-*N*-(3-methylpyridin-2-yl)-P-phenylphosphinic amide (*S*)**-4b**

A purification by preparative TLC in ethyl acetate : dichloromethane = 3 : 1 gave (*S*)-**4b** as a yellow foam (33.1 mg, 57%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol=95/5, flow=0.6 mL/min) with t_r =18.3 min (major), 20.5 min (minor): 79% *ee*.



butyl (*R, E*)-3-(2-((ethyl(3-methylpyridin-2-yl)amino)(isopropyl)phosphoryl) phenyl)acrylate (*R*)**-5c**

A purification by preparative TLC in ethyl acetate : dichloromethane = 4 : 1 gave (*R*)-**5c** as a yellow foam (32.1 mg, 38%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol=90/10, flow=0.8 mL/min) with t_r =12.5 min (minor), 15.6 min (major): 84% *ee*.

The absolute stereochemistry was assigned by analogy to compound **3a**.

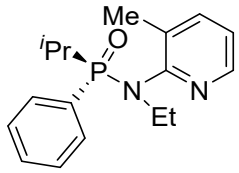
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 15.9 Hz, 1H), 8.31 (dd, *J* = 4.8, 1.9 Hz, 1H), 8.09 (ddd, *J* = 12.6, 7.6, 1.5 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.50 – 7.37 (m, 3H), 7.06 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.25 (d, *J* = 15.9 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 3.60 – 3.43 (m, 2H), 2.44 – 2.38 (m, 1H), 2.31 (s, 3H), 1.67 (dq, *J* = 8.8, 6.9 Hz, 2H), 1.48 – 1.36 (m, 2H), 1.06 (dd, *J* = 16.2, 7.0 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.80 (dd, *J* = 18.2, 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 153.7 (d, *Jc-p* = 2.9 Hz), 146.3, 144.1 (d, *Jc-p* = 3.2 Hz), 139.7 (d, *Jc-p* = 7.9 Hz), 139.6, 134.0 (d, *Jc-p* = 10.0 Hz), 132.4 (d, *Jc-p* = 3.1 Hz), 131.3 (d, *Jc-p* = 2.8 Hz), 130.2 (d, *Jc-p* = 110.2 Hz), 128.5 (d, *Jc-p* = 11.9

Hz), 127.3 (d, *Jc-p* = 10.3 Hz), 121.8, 120.5, 64.2, 42.9 (d, *Jc-p* = 2.9 Hz), 30.5, 26.8 (d, *Jc-p* = 89.1 Hz), 18.9, 18.0, 16.4, 15.0 (d, *Jc-p* = 3.7 Hz), 13.9 (d, *Jc-p* = 3.0 Hz), 13.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 43.22.

HRMS (ESI) m/z:$[M+Na]^+$ Calcd. for $C_{24}H_{33}N_2NaO_3P$:451.2125; found:451.2126.



(*S*)-*N*-ethyl-P-isopropyl-*N*-(3-methylpyridin-2-yl)-P-phenylphosphinic amide (*S*)-**4c**

A purification by preparative TLC in ethyl acetate : dichloromethane = 4 : 1 gave (*S*)-**4c** as a yellow foam (18.3 mg, 30%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol=92/8, flow=0.6 mL/min) with t_r =17.3 min (major), 20.9 min (minor): 84% *ee*.

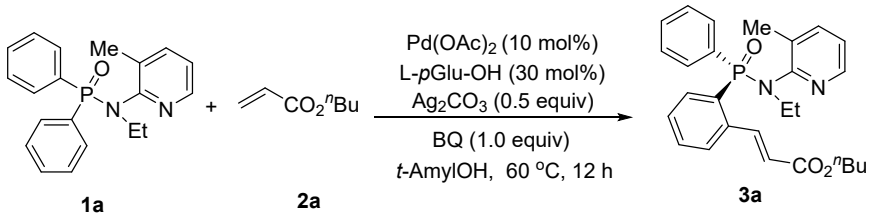
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J*=15.9 Hz, 1H), 8.25 (dd, *J*=4.8, 1.9 Hz, 1H), 8.21 – 8.10 (m, 1H), 7.67 – 7.57 (m, 1H), 7.52 – 7.39 (m, 3H), 7.02 (dd, *J*=7.6, 4.7 Hz, 1H), 6.25 (d, *J*=15.9 Hz, 1H), 5.13 – 4.83 (m, 1H), 4.23 – 4.08 (m, 2H), 3.59 – 3.47 (m, 2H), 2.37 (s, 3H), 1.62 (dt, *J*=8.5, 6.9 Hz, 2H), 1.39 (dt, *J*=10.5, 7.0 Hz, 8H), 0.95 (dt, *J*=13.1, 7.2 Hz, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 153.6 (d, *Jc-p* = 2.6 Hz), 146.5, 144.0 (d, *Jc-p* = 4.4 Hz), 139.6, 138.3 (d, *Jc-p* = 9.2 Hz), 133.8 (d, *Jc-p* = 9.5 Hz), 133.2 (d, *Jc-p* = 3.0 Hz), 131.9 (d, *Jc-p* = 2.9 Hz), 130.8 (d, *Jc-p* = 169.5 Hz), 129.0 (d, *Jc-p* = 14.0 Hz), 127.5 (d, *Jc-p* = 12.9 Hz), 121.8, 120.7, 71.0 (d, *Jc-p* = 6.4 Hz), 64.5, 43.6 (d, *Jc-p* = 4.4 Hz), 30.8, 24.3 (d, *Jc-p* = 3.2 Hz), 24.1 (d, *Jc-p* = 5.5 Hz), 19.2, 18.8, 14.1 (d, *Jc-p* = 5.1 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.31.

HRMS (ESI) m/z:$[M+Na]^+$ Calcd. for $C_{24}H_{33}N_2NaO_4P$:467.2074; found:467.2076.

2.4 Gram-Scale

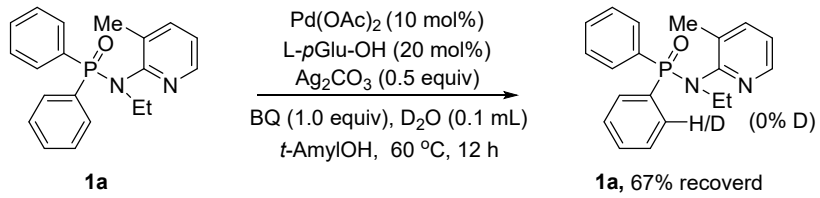


1a **2a** **3a**

To a 250 mL Schlenk tube was added substrate **1a** (1008.0 mg, 3.0 mmol), **2a** (0.9 mL, 6.0 mmol), $Pd(OAc)_2$ (66.0 mg, 0.3 mmol), L-*p*Glu-OH (116.2 mg, 0.9 mmol), Ag_2CO_3 (828.0 mg, 1.5 mmol), BQ (324.0 mg, 3.0 mmol), *t*-AmylOH (30 mL). The mixture was stirred for 12 h at 60 °C under Air. Then the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the resulting residue was purified by flash chromatography in petroleum ether: ethyl acetate = 2: 1 to give **3a** as yellow soild (920.8 mg, 66%, 90% *ee*).

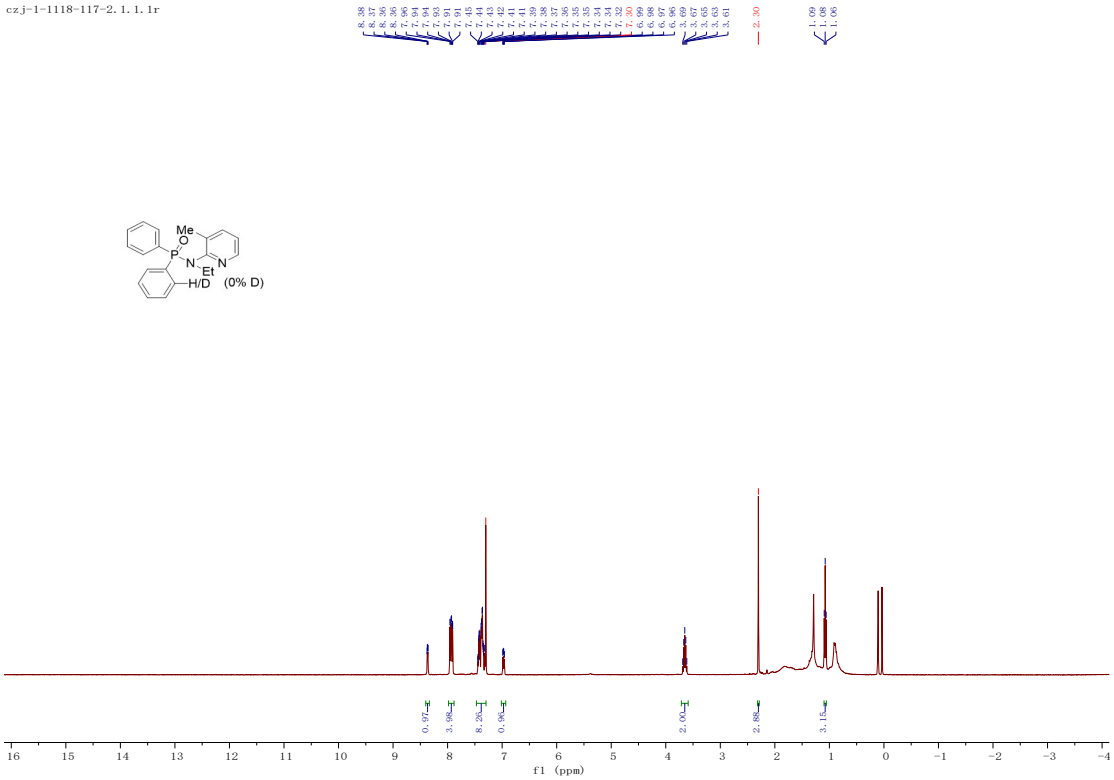
3. Mechanistic Studies

3.1 H/D exchange studies

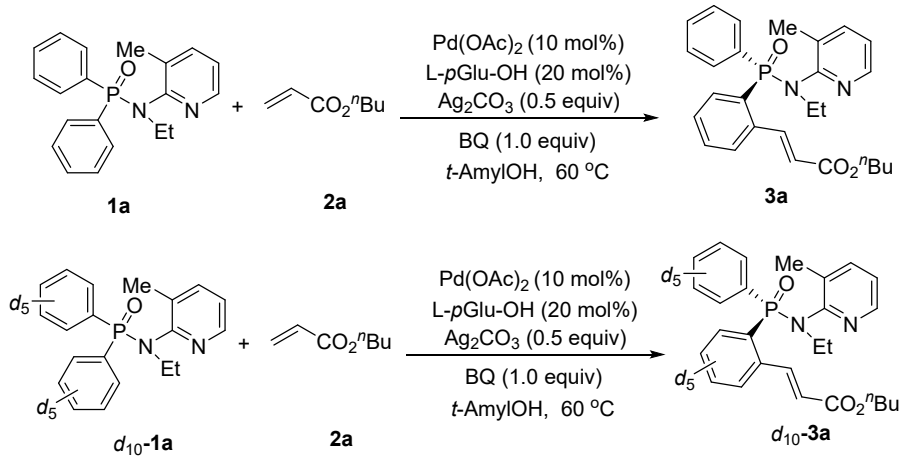


1a **1a,** 67% recoverd

To a 50 mL Schlenk tube was added **1a** (0.1 mmol), $Pd(OAc)_2$ (0.01 mmol), L-*p*Glu-OH (0.02 mmol), Ag_2CO_3 (0.05 mmol), BQ (0.10 mmol), *t*-AmylOH (1 mL). The mixture was stirred for 12 h at 60 °C under air. Then the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the resulting residue was purified by preparative TLC using hexane/EtOAc = 1:1 as the eluent, **1a** was recovered in 67% yield.



3.2 Kinetic isotopic effect experiment



To a 50 mL Schlenk tube was added **1a** (0.1 mmol), $Pd(OAc)_2$ (0.01 mmol), L-*p*Glu-OH (0.02 mmol), Ag_2CO_3 (0.05 mmol), BQ (0.10 mmol), *t*-AmylOH (1 mL). The mixture was stirred at 60 °C under air. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the yield was determined by ^{1}H NMR yield using 1,3,5-trimethoxybenzene as internal standard.

Table S2. Yield of 3a and d_{10}-3a reaction

experiment of **3a**		experiment of $\boldsymbol{d_{10}}$**-3a**	
time(s)	yield of **3a**(%)	time(s)	yield of $\boldsymbol{d_{10}}$**-3a**(%)
1800	3	1800	2.5
3600	5.5	3600	3.5
5400	9	7200	6.5
7200	12	9000	7
9000	13.5	10800	8

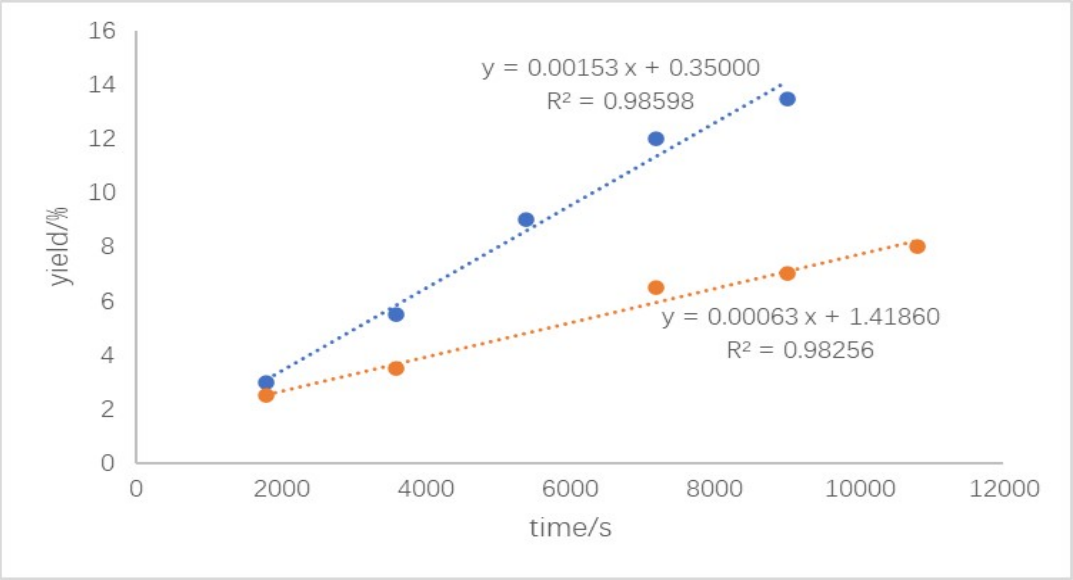


Figure S1. Kinetic profile of the reaction

4 Computational Details

All density functional theory (DFT) calculations were carried out using Gaussian16 software package[1]. All geometry optimizations were performed with B3LYP[2-3]-D3 (Becke−Johnson damping function)[4] functional using LANL2DZ[5] basis set for palladium and 6-31G(d) basis set for the other atoms. The vibrational frequencies were computed at the same level of theory as for the geometry optimizations, and to evaluate the zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. The single-point energies were computed based on the gas-phase optimized structures, using M06L[6] functional, and SDD[7-8] basis set for palladium and 6-311+G(d,p) basis set for the other atoms, with the inclusion of solvation energy corrections using a self-consistent reaction field (SCRF) based on SMD implicit solvent model[9] with 2-methyl-2-propanol as solvent. Multiwfn 3.8[10] was used to perform the independent gradient model based on Hirshfeld partition (IGMH) analyses[11] with the high-quality grid option. The calculated structures were visualized with VMD 1.9.3.[12] or CYLView[13].

4.1 DFT-calculated stereoselectivity for desymmetrization

The mechanistic experiments show that the irreversible activation of C−H bond is the decisive step of the reaction. Based on the experimental results, we then reveal the chiral induction model through DFT calculations. The C−H bond activation transition states of the two phenyl groups (colored by blue and black) of phosphonamide are located (Figure S2a). In **TS2-*R***, there is a significant steric repulsion between the methyl group on directing group and the phenyl group of phosphamide, so the favorable conformer for generating *R* enantiomer is **TS1-*R***. In the transition states that generates the *S* enantiomer, due to the favorable π-π stacking in **TS1-*S***, its energy is 1.6 kcal/mol lower than that of **TS2-*S***. Therefore, the enantioselectivity is determined by **TS1-*R*** and **TS1-*S***. The energy difference of 1.9 kcal/mol is consistent with the high ee value in the experiment. To elucidate the chiral induction model, the

C−H bond activation transition state of benzene catalyzed by Pd/L-pGlu-OH was optimized. The model transition state **TS1** suggested that the chiral amino acid intrinsically prefers to have the C−H bond activation occurring in the fourth quadrant (Figure S2b). The geometries of the benzene and pyridine fragments match well with the central chirality of the favored transition state **TS1-*R*** when the phosphamide tether links the two fragments in substrate **1g**. In contrast, chirality mismatch exists in the disfavored transition state **TS1-*S***. Thus, significant distortion of the amino acid ligand is required to have the C−H bond activation occurring in the fourth quadrant. The pyramidalization angle of the amino acid nitrogen in **TS1-*S*** is only 13.7°, indicating that the amino acid nitrogen is much more planar as compared to that in **TS1** or **TS1-*R*** (25.6°, 27.4°, respectively). In addition, there is an energy difference of 2.6 kcal/mol for Pd(L-pGlu-OH) fragments in **TS1-*R*** and **TS1-*S***, which further supports the chiral induction model in which the distortion of ligand determines the enantioselectivity.

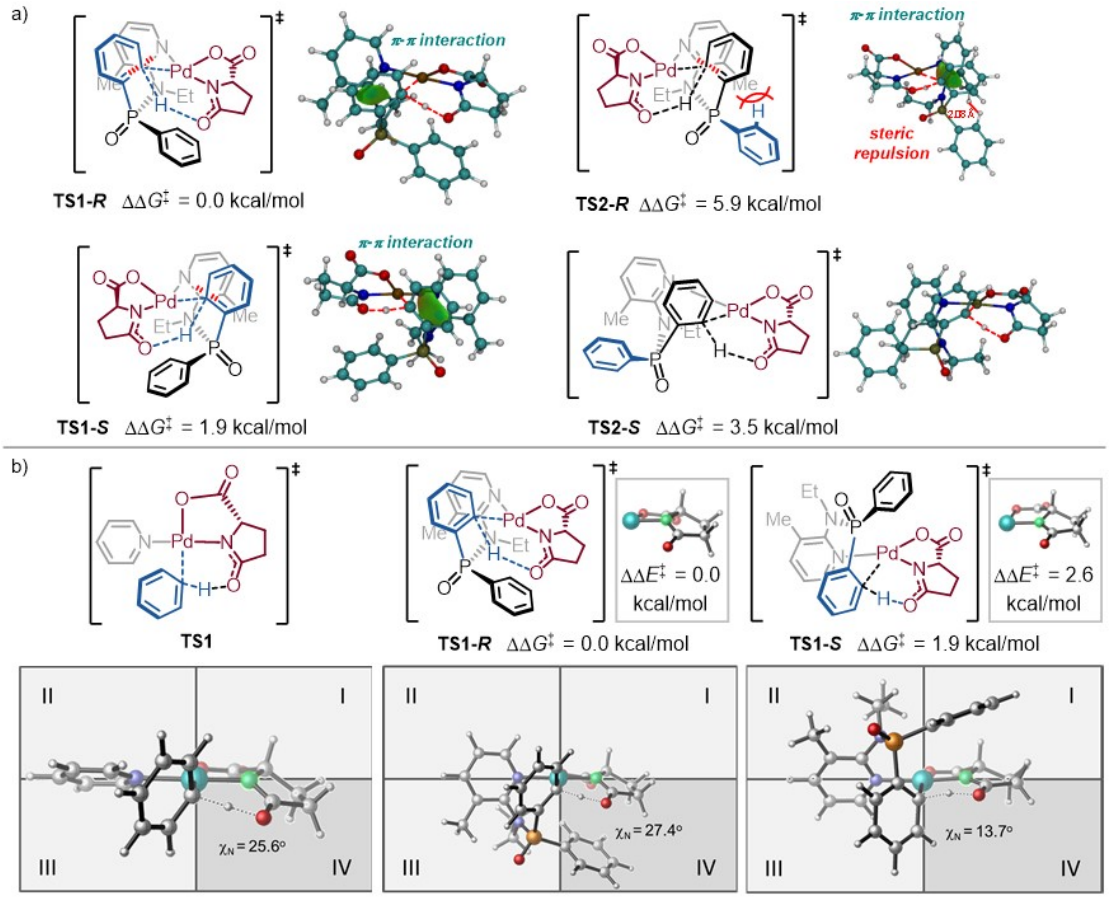


Figure S2. Origins of enantioselectivity in Pd/L-pGlu-OH-catalyzed asymmetric C−H

olefination of phosphinamide. a) The optimized transition states for giving R/S-enantiomer and their relative Gibbs free energies. b) Chiral induction through ligand distortion.

4.2 DFT-calculated stereoselectivity for kinetic resolution

We also calculated the stereoselective outcome for the kinetic resolution result when one the phenyl is replaced with methyl. The results show that in this case, the stereo-discrimination becomes worse. The energy span that determines the enantioselectivity is reduced to 0.9 kcal/mol (**TS1-*R*-(Me)** vs. **TS1-S-(Me)**), which is consistent with the experimental results (71 % ee).

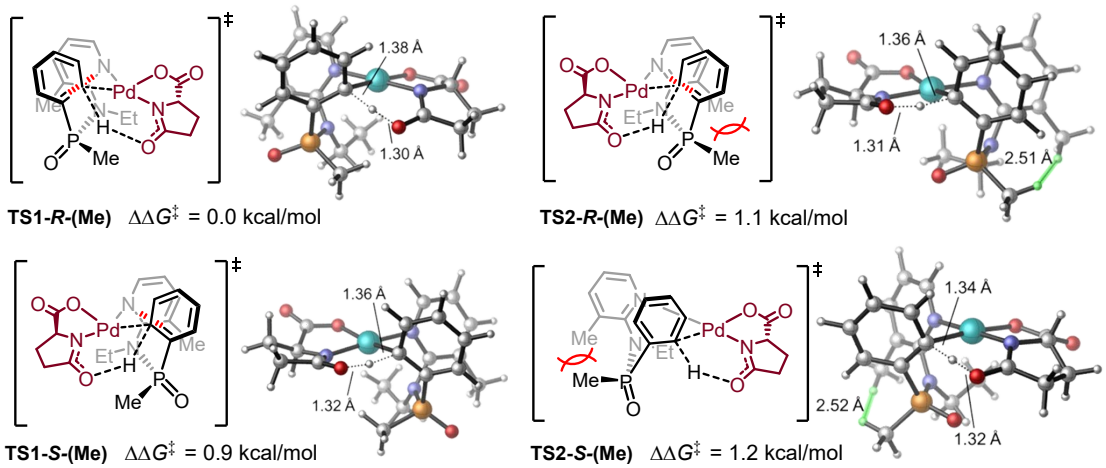


Figure S3. DFT-optimized structures of stereoselective C-H activation transition state and their relative energies.

4.3 Table of energies

Zero-point correction (*ZPE*), thermal correction to enthalpy (*TCH*), thermal correction to Gibbs free energy (*TCG*), energies (*E*), enthalpies (*H*), and Gibbs free energies (*G*) (in Hartree) of the structures calculated at the M06L/6-311+G(d,p)-SDD-SMD(2-methyl-2-propanol)//B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory.

Table S6. Energies for all calculated species

Structures	*ZPE*	*tcH*	*tcG*	*E*	*H*	*G*	Imaginary Frequency
TS1-*R*	0.471725	0.503407	0.410553	-1903.133045	-1902.629638	-1902.722492	1180.9*i*
TS2-*R*	0.470878	0.502965	0.408071	-1903.121212	-1902.618247	-1902.713141	1323.9*i*
TS1-*S*	0.471031	0.502995	0.409012	-1903.128437	-1902.625442	-1902.719425	1369.5*i*

TS2-*S*	0.471080	0.503082	0.408658	-1903.125515	-1902.622433	-1902.716857	1356.5*i*
TS1-*R*-(Me)	0.417490	0.446296	0.359866	-1711.371302	-1710.925006	-1711.011436	1480.4 *i*
TS2-*R*-(Me)	0.416610	0.445770	0.358069	-1711.367711	-1710.921941	-1711.009642	1377.1*i*
TS1-*S*-(Me)	0.416988	0.446033	0.358857	-1711.368833	-1710.922800	-1711.009976	1413.1*i*
TS2-*S*-(Me)	0.417061	0.445969	0.359219	-1711.368806	-1710.922837	-1711.009587	1238.8*i*

4.4 Cartesian coordinates of the structures

TS1

C	-1.55085400	1.87633400	1.22260400
C	-2.79583000	2.49256900	1.12161700
C	-0.69290100	1.75535500	0.10458200
C	-3.21918700	2.99813100	-0.11282000
C	-1.14057400	2.29694700	-1.12199300
H	0.57220700	2.10616200	0.42728100
C	-2.39189500	2.90310500	-1.23694400
H	-4.19173800	3.47625900	-0.19644100
H	-0.48858500	2.24248400	-1.99020000
H	-2.72230200	3.30728700	-2.19008800
C	2.52153200	1.58809400	0.31400600
C	3.11721000	-0.47478000	-0.56458900
C	4.32270200	0.01769200	0.26693800
C	4.03645100	1.52799000	0.44181200
H	3.34981900	-0.45706400	-1.64032400
H	4.31862600	-0.48894800	1.23714800
H	5.27976400	-0.19337500	-0.21360700
H	4.36171600	1.94332400	1.39886600
H	4.48914300	2.13371000	-0.35374800
N	2.07375300	0.50626600	-0.27854600
O	1.77419900	2.53271700	0.72824400
C	2.58489500	-1.88467900	-0.25327800
O	3.34917000	-2.81271500	-0.04837500
O	1.27063700	-1.99154300	-0.27705900
Pd	0.23792400	-0.20531500	-0.16196200
C	-2.79182600	-0.72065600	-0.32933900
C	-3.96601000	-1.45721200	-0.21861000
C	-1.51763500	-2.51790300	0.40778700
C	-3.89900700	-2.77349300	0.23526900
H	-4.91129800	-0.99762800	-0.48659500
C	-2.65174200	-3.31072100	0.54919300
H	-0.51620000	-2.88829800	0.59818600
H	-4.80039200	-3.37071900	0.33594000

H	-2.54670900	-4.33304300	0.89587200
N	-1.59140600	-1.23940700	-0.01395100
H	-1.22225800	1.48475300	2.18205600
H	-3.43864200	2.58095800	1.99333600
H	-2.79809700	0.30231800	-0.67984700

TS1-*R*

C	1.26928600	1.25819600	1.31464200
C	2.41315200	1.69648800	1.98246300
C	0.40345800	0.29615600	1.89702600
C	2.74455800	1.14815900	3.22629600
C	0.76099100	-0.22317300	3.15830000
H	-0.88760100	0.60169000	1.87942000
C	1.92479500	0.18204200	3.81267100
H	3.64214800	1.48294400	3.73921700
H	0.09421500	-0.93725600	3.63505700
H	2.18503900	-0.23755800	4.78065200
C	-2.77533700	-0.04888500	1.46494900
C	-3.05066100	-2.00720600	0.23969400
C	-4.41259000	-1.27424800	0.20105900
C	-4.27707100	-0.15764600	1.26492900
H	-3.12239800	-2.96539400	0.77468300
H	-4.56117300	-0.85695700	-0.79736100
H	-5.24835500	-1.94813800	0.40027700
H	-4.67849200	0.80859400	0.95030800
H	-4.75090100	-0.42054500	2.21841800
N	-2.16925100	-1.10525000	0.97265200
O	-2.17324400	0.92594700	2.01648600
C	-2.37967000	-2.30513000	-1.11961300
O	-3.04292600	-2.49107500	-2.12840100
O	-1.06404200	-2.35153100	-1.06971600
Pd	-0.26516300	-1.19661100	0.46814900
C	2.32126800	-0.40489100	-0.85416000
C	3.70717800	-0.39141900	-1.09977200
C	2.47971900	-2.40162600	0.34727900
C	4.45431200	-1.47105000	-0.62106100
C	3.84179800	-2.49524800	0.09689900
H	1.94488200	-3.14390500	0.92831600
H	5.52676700	-1.49186200	-0.79514700
H	4.40853000	-3.33794400	0.47696300
N	1.74496400	-1.38305000	-0.12446100
P	1.02424400	1.93034100	-0.36662100
H	3.03927800	2.45495100	1.52241400
N	1.45249100	0.59210100	-1.34818300

C	1.33050700	0.71862400	-2.82089300
H	2.22730800	1.17708300	-3.25224500
H	0.50886400	1.41457900	-3.00392400
C	4.37002000	0.76442700	-1.80239600
H	3.87138400	1.70845000	-1.56332000
H	5.42017100	0.83612300	-1.50385200
H	4.34753600	0.63963800	-2.89196200
C	-0.74271100	2.16146000	-0.69463500
C	-1.32696000	3.36210700	-0.26633600
C	-1.52795500	1.20691900	-1.35621700
C	-2.68464000	3.59241700	-0.47860900
H	-0.71321300	4.11213900	0.22283200
C	-2.88019700	1.45146300	-1.59042400
H	-1.09112100	0.27352400	-1.68606400
C	-3.46115000	2.63958600	-1.14319500
H	-3.13510500	4.51903500	-0.13542000
H	-3.46744700	0.70885500	-2.12157900
H	-4.51625500	2.82871300	-1.32158500
O	1.83778900	3.17206300	-0.58754500
C	1.03612700	-0.62945600	-3.47500800
H	0.83345800	-0.48481600	-4.54144000
H	1.89277600	-1.30718800	-3.38822500
H	0.17616000	-1.12403100	-3.01197400

TS2-*R*

C	1.02976800	-0.60858300	1.40462200
C	2.00950500	-0.25648700	2.33571300
C	-0.34181200	-0.64520600	1.75770200
C	1.63644100	0.09308400	3.63586600
C	-0.68072200	-0.28180700	3.07768600
H	-1.17083500	-1.66548500	1.45220700
C	0.28969800	0.08874700	4.00689000
H	2.39998600	0.36413400	4.35986600
H	-1.72497100	-0.32889000	3.37571900
H	0.00470500	0.36040300	5.01971700
C	1.03126700	1.87294700	-0.37018000
C	1.88786600	2.99441900	-0.40733900
C	1.47330600	4.15141200	0.25643700
C	-0.53083200	3.04920300	0.92287200
C	0.25833100	4.18949600	0.93363000
H	2.12142900	5.02389400	0.24897100
H	-1.49650000	3.00766800	1.41228700
H	-0.07460000	5.07971000	1.45517900
N	-0.15501900	1.93417200	0.27775000

C	-2.92081500	-2.21265300	0.57562500
C	-3.77462100	-0.89631200	-1.13369600
C	-4.94145000	-1.77569300	-0.64449100
C	-4.20399200	-2.90440700	0.12703000
H	-3.39133900	-1.27475700	-2.09585900
H	-5.57218800	-1.19464500	0.03645200
H	-5.56994700	-2.14304200	-1.45815500
H	-4.75504500	-3.30398700	0.98232300
H	-3.94434600	-3.74802000	-0.52566400
N	-2.76865200	-1.11058100	-0.10890600
O	-2.10640700	-2.60359900	1.47424500
C	-3.95311000	0.62026400	-1.31751400
O	-4.98539400	1.09436900	-1.76168000
O	-2.87392800	1.32218400	-1.01941100
Pd	-1.50187200	0.33267800	0.18070000
C	3.20870500	2.98009200	-1.13235400
H	3.11607400	3.43109900	-2.12840200
H	3.95469000	3.56290700	-0.58221800
H	3.58429700	1.96553700	-1.26749600
N	1.38630600	0.67946100	-1.03298300
C	1.35346400	0.70790800	-2.52046600
H	1.82566800	1.63737000	-2.85107000
H	1.98924200	-0.11094500	-2.87279100
P	1.39632900	-0.90508800	-0.34918700
H	3.05860800	-0.25357100	2.06068500
O	0.50161800	-1.88988100	-1.03457800
C	3.13482900	-1.42007300	-0.49983200
C	3.38029400	-2.73979400	-0.90175500
C	4.21604600	-0.57102200	-0.22379600
C	4.69108700	-3.20287400	-1.02198100
H	2.53543100	-3.38231900	-1.12674000
C	5.52478300	-1.03680700	-0.33939000
H	4.03484800	0.45388600	0.08086400
C	5.76270000	-2.35420500	-0.73958500
H	4.87548600	-4.22530200	-1.33878100
H	6.35744700	-0.37336100	-0.12348800
H	6.78259400	-2.71612900	-0.83395900
C	-0.05743000	0.58398800	-3.09187200
H	-0.48627500	-0.38120400	-2.81385300
H	-0.71709700	1.37062200	-2.71324800
H	-0.02160600	0.65778800	-4.18551800

TS1-*S*

C	-1.28315000	1.10861700	1.41805200

C	-2.38751500	1.31259500	2.24793000
C	-0.22156400	0.24921900	1.79628100
C	-2.47557600	0.63427500	3.46695600
C	-0.34504000	-0.41321500	3.03789300
H	1.06995300	0.64504900	1.75944200
C	-1.45691500	-0.23599300	3.86052600
H	-3.33828900	0.78905700	4.10920800
H	0.47143700	-1.05069800	3.36749500
H	-1.52485200	-0.76017600	4.80992300
C	-2.31039200	-0.57947600	-0.75678000
C	-3.70230700	-0.70214100	-0.90665100
C	-4.29095400	-1.88865300	-0.45425200
C	-2.15727200	-2.66415100	0.29087600
C	-3.52027200	-2.88556500	0.13651700
H	-5.36532000	-2.01699400	-0.55483700
H	-1.49813700	-3.38487900	0.76040000
H	-3.96457400	-3.80962500	0.48941400
N	-1.57905700	-1.53764600	-0.14682000
C	2.95100900	0.11288100	1.20266200
C	3.22709400	-1.36206300	-0.56056400
C	4.56533700	-1.35153100	0.19919100
C	4.45699500	-0.04152700	1.02649500
H	3.32018300	-0.76290100	-1.48384100
H	4.61349200	-2.22196900	0.86153900
H	5.43351000	-1.37941100	-0.46227600
H	4.96867800	-0.06779400	1.99188400
H	4.83422900	0.82836900	0.47233200
N	2.33718100	-0.67394100	0.35785600
O	2.34615900	0.87876600	2.02122000
C	2.54970300	-2.67572300	-0.98673000
O	3.19900500	-3.64335100	-1.34596100
O	1.23099300	-2.60533100	-0.99446800
Pd	0.44019700	-1.10312500	0.20760400
C	-4.53844500	0.40661800	-1.49159100
H	-4.59080800	0.33362600	-2.58504600
H	-5.56313800	0.34530200	-1.11283400
H	-4.12922700	1.38855200	-1.23704500
N	-1.58184900	0.54140300	-1.23818100
C	-1.53638800	0.72387400	-2.70679300
H	-2.52388800	0.99030100	-3.10123600
H	-0.88503600	1.58096800	-2.89410900
P	-1.35955200	1.90072500	-0.21813400
H	-3.17341000	1.98957000	1.92686000
O	-2.42592200	2.95542700	-0.29086500

C	0.28854100	2.53140600	-0.62987600
C	0.58722700	3.83188400	-0.19460800
C	1.26915200	1.78260300	-1.29267500
C	1.85958700	4.36216400	-0.39696400
H	-0.18339900	4.41982100	0.29407800
C	2.53771900	2.32135500	-1.50426800
H	1.04471500	0.77924200	-1.63156800
C	2.83707100	3.60584500	-1.04843100
H	2.08800300	5.36589300	-0.05110400
H	3.29048000	1.73581200	-2.02479900
H	3.82797800	4.02176600	-1.20776500
C	-0.99312700	-0.51819300	-3.40851600
H	-0.89264600	-0.32512700	-4.48189100
H	-0.01850200	-0.81138300	-3.00618700
H	-1.66612700	-1.37292900	-3.28330200

TS2-*S*

C	0.90330000	-1.83097900	-0.41009600
C	1.71988500	-2.65499400	-1.19164000
C	-0.49488400	-1.77365400	-0.64213400
C	1.17536200	-3.39897600	-2.24208200
C	-1.01269700	-2.55365900	-1.69829600
H	-1.31457600	-1.89909100	0.42942900
C	-0.19324200	-3.34467200	-2.50292800
H	1.82355200	-4.02564700	-2.84834100
H	-2.08565500	-2.54335700	-1.86855100
H	-0.61822600	-3.92568800	-3.31671300
C	-3.24795000	-1.49580000	0.95632000
C	-4.37808100	0.23809500	-0.09760700
C	-5.12407700	-0.04771900	1.23101700
C	-4.59614700	-1.43838900	1.65484500
H	-5.00450000	-0.01274800	-0.96538800
H	-4.84147900	0.70875600	1.96962900
H	-6.20892500	-0.00843000	1.11813100
H	-4.47761900	-1.56743100	2.73331800
H	-5.22937500	-2.25663900	1.28929100
N	-3.21842300	-0.64788200	-0.05100900
O	-2.26285400	-2.22523900	1.30090700
C	-3.91116200	1.69766100	-0.28890800
O	-4.69373900	2.61556300	-0.10463900
O	-2.66155700	1.85331800	-0.67503300
Pd	-1.50809500	0.14714100	-0.63524200
C	1.08342200	1.47562400	-0.01062100
C	2.07156600	2.47780300	-0.07932200

C	0.24343500	2.06313700	-2.11541500
C	2.10288500	3.27236100	-1.22913300
C	1.19148800	3.06705200	-2.26067900
H	-0.51700600	1.87025700	-2.86243900
H	2.85993100	4.04716000	-1.31574100
H	1.20511500	3.67572600	-3.15793100
N	0.19780700	1.29467300	-1.01622400
P	1.65187200	-0.97960700	1.01374100
H	2.78419500	-2.71941300	-0.99128600
N	0.98096400	0.59605900	1.08520100
C	0.53686200	1.12729200	2.39712200
H	1.05569900	0.55876200	3.17145000
H	0.86566700	2.16930600	2.46636500
C	3.07008800	2.69398700	1.02650300
H	4.03310100	3.00786700	0.61339900
H	2.73067500	3.47834500	1.71432500
H	3.22930100	1.78379100	1.60519300
C	3.39442500	-0.69691700	0.55917300
C	3.78640000	-0.19454700	-0.69110300
C	4.35364700	-0.87277600	1.56538700
C	5.11946400	0.14112700	-0.92376500
H	3.05502200	-0.07326700	-1.48431200
C	5.68714600	-0.53776700	1.32861500
H	4.03720400	-1.27136900	2.52440100
C	6.06949500	-0.02534500	0.08721300
H	5.41764900	0.52918400	-1.89367500
H	6.42751800	-0.67853800	2.11085800
H	7.10764600	0.23707700	-0.09597800
O	1.50736200	-1.66421900	2.33581500
C	-0.97274000	1.02852700	2.59720800
H	-1.51560000	1.59370000	1.83338500
H	-1.28748000	-0.01798900	2.55412200
H	-1.24101500	1.43112100	3.58184900

TS1-*R*-(Me)

C	-1.35673300	1.88096900	0.14299100
C	-2.39533000	2.65219600	-0.37887700
C	-0.08737600	1.82941900	-0.49240500
C	-2.20196700	3.37355300	-1.56252800
C	0.07656900	2.58764800	-1.66989200
H	1.01222100	1.99469400	0.31775900
C	-0.96658200	3.34304700	-2.20956400
H	-3.01688600	3.96417900	-1.97218600
H	1.04835600	2.58904100	-2.15720100

H	-0.81621500	3.90986200	-3.12439700
C	2.92796500	1.39080000	0.60423000
C	3.70684400	-0.52174400	-0.45054300
C	4.67003900	-0.23703300	0.72682200
C	4.35254800	1.22998200	1.10749000
H	4.20707000	-0.36783800	-1.41788900
H	4.43020500	-0.91056200	1.55544500
H	5.71615200	-0.40038400	0.46205400
H	4.41402700	1.44287100	2.17775500
H	5.00240100	1.94717700	0.59004400
N	2.65006800	0.47043600	-0.28459600
O	2.08840000	2.27383000	0.99672900
C	3.07295600	-1.92833400	-0.49366800
O	3.75316100	-2.91564700	-0.26695100
O	1.79666000	-1.95773600	-0.81843000
Pd	0.82206600	-0.13620600	-0.70019100
C	-1.89641300	-1.10625400	-0.02512500
C	-3.18101500	-1.65688700	-0.17087200
C	-1.43491100	-1.35824800	-2.30107300
C	-3.55299400	-2.07397000	-1.45302300
C	-2.67984400	-1.92998600	-2.52850000
H	-0.70628500	-1.21410700	-3.09002900
H	-4.53883400	-2.50491700	-1.60414100
H	-2.95673100	-2.24910300	-3.52720300
N	-1.06356600	-0.96229200	-1.07505100
P	-1.73400600	0.95163700	1.66668600
H	-3.34921100	2.67312600	0.13943400
N	-1.37508600	-0.66261900	1.21805900
C	-1.07028300	-1.68537100	2.24820800
H	-1.95355200	-1.90078700	2.86446200
H	-0.31417500	-1.24878800	2.90539100
C	-4.11441100	-1.78191400	1.00329100
H	-4.12372600	-0.85804700	1.59017300
H	-5.13063400	-1.99886000	0.66194800
H	-3.80566700	-2.60033700	1.66541100
C	-0.46004100	1.37135200	2.89488000
O	-3.13679300	1.20076200	2.14477900
C	-0.51474800	-2.96979200	1.63797200
H	-0.20760800	-3.64527900	2.44320900
H	-1.26876800	-3.49138900	1.03883500
H	0.34947100	-2.76971900	0.99695300
H	-0.55829000	2.44059200	3.10328800
H	-0.64550700	0.82536800	3.82336700
H	0.55026400	1.17920400	2.52925400

TS2-*R*-(Me)

C	1.25677300	1.85319700	0.14958500
C	2.39961000	2.42827100	-0.41275600
C	0.03357700	1.80469800	-0.56203000
C	2.34566400	2.96805900	-1.70007200
C	0.01657800	2.35757600	-1.85958900
H	-1.17492700	2.11490000	-0.02502000
C	1.15318400	2.93143300	-2.42672700
H	3.23489100	3.41689500	-2.13413000
H	-0.91968500	2.35469900	-2.41183700
H	1.11453500	3.35333100	-3.42738000
C	2.09813100	-1.00714800	-0.05378300
C	3.38056600	-1.48007200	-0.39684400
C	3.58540700	-1.91042700	-1.70991700
C	1.32338900	-1.35794500	-2.23413800
C	2.55246100	-1.85758900	-2.64163400
H	4.56687400	-2.27428000	-2.00209400
H	0.47504900	-1.28657100	-2.90435300
H	2.69393900	-2.18771300	-3.66464300
N	1.10846400	-0.95112500	-0.97372200
C	-3.07024400	1.47654900	0.29961000
C	-3.49469500	-0.80076800	0.42417000
C	-4.85600400	-0.12168900	0.17956300
C	-4.56561100	1.35315300	0.57006300
H	-3.41344700	-1.12224100	1.47567000
H	-5.11113000	-0.19410500	-0.88286900
H	-5.66733000	-0.57274100	0.75417700
H	-5.13079300	2.09354000	-0.00193600
H	-4.75157600	1.54216400	1.63528700
N	-2.55473400	0.28148200	0.18837200
O	-2.39552900	2.55182500	0.18201800
C	-3.05673600	-2.00770400	-0.42249000
O	-3.84774900	-2.87078600	-0.76400200
O	-1.75884900	-2.04208800	-0.66936100
Pd	-0.78456500	-0.22877900	-0.42876300
C	4.50054600	-1.50429100	0.60873600
H	4.49613100	-2.43133400	1.19530900
H	5.47116400	-1.43845500	0.10817800
H	4.40675800	-0.67657800	1.31623400
N	1.82233300	-0.60233200	1.26914500
C	1.63604200	-1.68466500	2.26944100
H	2.40634100	-2.44179300	2.08924800
H	1.83833700	-1.25906100	3.25778900

P	1.29835500	0.97224400	1.73592200
H	3.33846500	2.45047600	0.13217700
O	0.03803400	0.98241300	2.54036000
C	2.71329300	1.62640600	2.69132900
C	0.24261100	-2.30867000	2.23637300
H	-0.50580300	-1.55113100	2.48025200
H	0.00449000	-2.71769500	1.25019600
H	0.18211800	-3.11970800	2.97230900
H	3.65568500	1.57224600	2.13999900
H	2.51079500	2.66369900	2.97336300
H	2.80682100	1.03428600	3.60630500

TS1-*S*-(Me)

C	1.30074000	1.85553300	0.17718300
C	2.38526100	2.53189400	-0.38378100
C	0.05794800	1.75838800	-0.49879200
C	2.26458900	3.10900800	-1.65140500
C	-0.02540700	2.35772100	-1.77473500
H	-1.12923800	2.07970000	0.07868800
C	1.06018200	3.01671400	-2.35145600
H	3.11078600	3.63115300	-2.08952200
H	-0.97648800	2.32722300	-2.30033700
H	0.96688800	3.46656700	-3.33616900
C	1.99780100	-1.00063900	-0.07033500
C	3.32643000	-1.36801400	-0.33646500
C	3.63558000	-1.73042600	-1.65258300
C	1.37530000	-1.29794300	-2.30416700
C	2.65963300	-1.70554600	-2.64515700
H	4.65421600	-2.01978700	-1.89633600
H	0.56904600	-1.24157200	-3.02597900
H	2.88767600	-1.98377400	-3.66812900
N	1.06477300	-0.95927700	-1.04652000
C	-3.04369100	1.47761700	0.41833300
C	-3.54281500	-0.78578000	0.44072600
C	-4.86902600	-0.04965800	0.16723700
C	-4.55059800	1.39739100	0.62846100
H	-3.52585300	-1.16335500	1.47640300
H	-5.07895800	-0.07106000	-0.90721000
H	-5.71922000	-0.49657700	0.68583800
H	-5.06530800	2.17832100	0.06299900
H	-4.77829200	1.55308900	1.69121000
N	-2.55026500	0.27074700	0.30422400
O	-2.33453200	2.53618600	0.34898200
C	-3.12487300	-1.97138300	-0.44758100

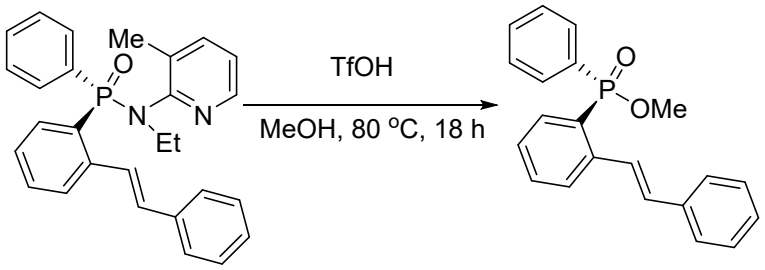
O	-3.94344300	-2.78934700	-0.83171000
O	-1.82615200	-2.04289400	-0.67325100
Pd	-0.81017100	-0.25226400	-0.42955100
C	4.37609800	-1.34795200	0.74343900
H	4.34313600	-2.26527800	1.34452300
H	5.37505700	-1.28176800	0.30241500
H	4.23016300	-0.49921800	1.41847300
N	1.53265900	-0.65720300	1.22556000
C	1.46800500	-1.73981700	2.23208800
H	2.46619000	-1.97655900	2.62229600
H	0.88603400	-1.35077900	3.07162200
P	1.61853300	0.98072500	1.73957800
H	3.31755200	2.58861400	0.17022000
O	2.91258200	1.37992600	2.38719600
C	0.15387700	1.20412900	2.80068500
C	0.79190300	-2.99284800	1.68050000
H	0.68614100	-3.73404700	2.47991800
H	-0.19651600	-2.76600800	1.26945900
H	1.38652600	-3.44908600	0.88185200
H	-0.74242500	0.77843800	2.34402800
H	0.33178500	0.74892000	3.77827800
H	0.01153800	2.27895600	2.94540100

TS2-*S*-(Me)

C	-1.12708600	1.84040000	0.52788300
C	-2.32285100	2.52156200	0.29954300
C	-0.02475100	1.97993700	-0.35414800
C	-2.44777300	3.34747400	-0.82287200
C	-0.18154200	2.82482200	-1.46879200
H	1.18319000	2.10337900	0.21004700
C	-1.38014300	3.49853700	-1.70932600
H	-3.38117600	3.87449000	-1.00088600
H	0.65919800	2.96053600	-2.14444400
H	-1.48439600	4.14249400	-2.57838700
C	3.05400600	1.34272000	0.39962900
C	3.58877900	-0.69364700	-0.58031500
C	4.55029900	-0.50561400	0.61384600
C	4.44985800	1.01016600	0.90639200
H	4.13072800	-0.60155200	-1.53444700
H	4.17710800	-1.08125300	1.46657000
H	5.56470600	-0.84562600	0.39653700
H	4.54356000	1.27375100	1.96241100
H	5.19181100	1.59345300	0.34592300
N	2.65094300	0.41571100	-0.44341100

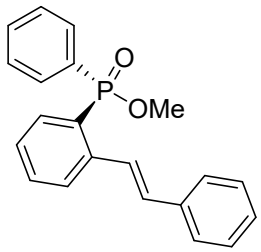
O	2.36200700	2.35073700	0.74154100
C	2.80907100	-2.01839900	-0.64738500
O	3.36107000	-3.08238700	-0.42163200
O	1.54381500	-1.90339700	-1.00812800
Pd	0.76515600	-0.00829700	-0.79689700
C	-2.00836200	-0.96005000	-0.06875800
C	-3.31850100	-1.43896700	-0.26820400
C	-1.67746100	-0.73886500	-2.37278300
C	-3.77013400	-1.57105200	-1.58217400
C	-2.94957500	-1.21753600	-2.65100700
H	-0.98634400	-0.44592300	-3.15435100
H	-4.77729300	-1.93665200	-1.76351000
H	-3.28597300	-1.30672200	-3.67783500
N	-1.21945300	-0.63241500	-1.11579700
P	-0.91785100	0.65618300	1.89452400
H	-3.16733600	2.41185600	0.97301700
N	-1.46970800	-0.82923900	1.22122700
C	-1.19013700	-2.05726500	2.01393400
H	-0.38794700	-1.78586900	2.70496400
H	-2.06914600	-2.33112800	2.61307100
C	-4.20175500	-1.78296200	0.89983800
H	-5.25241300	-1.81267600	0.59740800
H	-3.94748600	-2.76452200	1.31777000
H	-4.08655000	-1.05190500	1.70552300
C	-2.18077700	1.05766500	3.15410800
O	0.44992500	0.56432400	2.49015000
C	-0.73508000	-3.23089700	1.15087300
H	-1.53416700	-3.58072100	0.48716600
H	0.12813600	-2.96085700	0.53504900
H	-0.45615300	-4.06650900	1.80161600
H	-1.96077100	2.03260700	3.59852800
H	-3.19573400	1.05902600	2.74696600
H	-2.11849000	0.29846200	3.93944700

5. Derivatizations



3w, 94% *ee* **6w**, 72%, 92% *ee*

Compound **3w** (43.8 mg, 0.1 mmol) was dissolved in MeOH (1.0 mL), TfOH (0.3 mL) was added slowly into the solution at rt, and then the tube was sealed and heated to 80 °C for 18 h. After being cool to rt, the reaction mixture was diluted with DCM and neutralized with saturated aq. $NaHCO_3$ (30 mL). The organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. After concentration, the resulting residue was purified by preparative TLC in petroleum ether: ethyl acetate= 3: 1 to give **6w** as yellow foam (24.0 mg, 72%, 88% *ee*).



methyl (*S*, *E*)-phenyl(2-styrylphenyl)phosphinate 6w

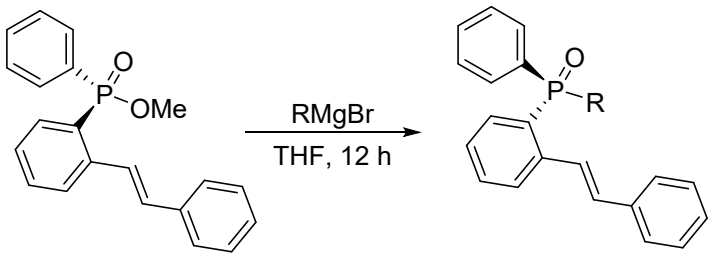
A purification by preparative TLC in petroleum ether: ethyl acetate = 3:1 gave **6w** as a yellow foam (24.0 mg, 72%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol=70/30, flow = 1.0 mL/min) with t_r = 7.7 min (minor), 8.4 min (major): 92% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–7.95(m, 1H), 7.87–7.70(m, 4H), 7.57(t, *J*=7.7 Hz, 1H), 7.52–7.46(m, 1H), 7.46–7.32(m, 7H), 7.30–7.26(m, 1H), 6.93(d, *J*=16.1 Hz, 1H), 3.81(d, *J*=11.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4(d, *Jc-p* = 10.5 Hz), 137.1, 133.8(d, *Jc-p* = 3.8 Hz), 132.8(d, *Jc-p* = 2,6 Hz), 132.3(d, J_{c-p} = 2.9 Hz), 131.8, 131.5(d, J_{c-p} = 10.4 Hz), 131.2(d, J_{c-p} = 5.9 Hz), 128.7(d, *Jc-p* = 4.6 Hz), 128.6, 128.2(d, J_{c-p} = 132.6 Hz), 128.1, 127.2(d, J_{c-p} = 12.4 Hz), 126.9, 126.7(d, J_{c-p} = 5.3 Hz), 126. 5(d, J_{c-p} = 11.8 Hz), 51.5(d, J_{c-p} = 5.9 Hz).

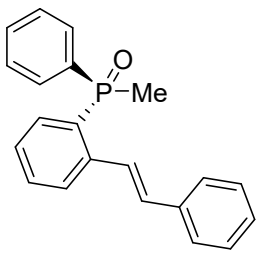
^{31}P NMR (162 MHz, $CDCl_3$) δ 33.79

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{20}O_2P$: 335.1195; found: 335.1201.



6w, 92% ee **7**

Under nitrogen atm compound **6w** (33.4 mg, 0.1 mmol) was dissolved in dry THF (1.0 mL), RMgBr (0.5 mmol, 5.0 equiv) was added slowly into the solution at rt, and then the tube was sttired at rt for 18 h. the reaction mixture was quenched with saturated aq. NH_4Cl and diluted with DCM. The organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by preparative TLC using PE/EA as the eluent to afford the alkynylation product **7**.



(*S*, *E*)-methyl(phenyl)(2-styrylphenyl)phosphine oxide 7a

A purification by preparative TLC in petroleum ether : ethyl acetate = 3 : 1 gave **7a** as a white foam (20.1 mg, 63%). The *ee* value was determined by HPLC analysis on a

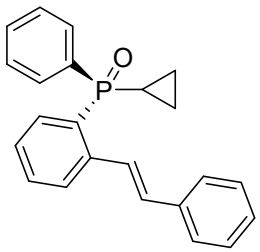
Chiralcel IA column (hexane/isopropanol=70/30, flow = 1.0 mL/min) with t_r = 8.0 min (minor), 9.2 min (major): 91% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.62 (m, 5H), 7.56 – 7.43 (m, 4H), 7.36 – 7.25 (m, 6H), 6.88 (d, J = 16.1 Hz, 1H), 2.05 (d, J = 13.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5 (d, $J_{c\text{-}p}$ = 7.8 Hz), 136.9, 134.6 (d, $J_{c\text{-}p}$ = 101.4 Hz), 132.4 (d, $J_{c\text{-}p}$ = 2.0 Hz), 132.0, 131.89, 131.88 (d, $J_{c\text{-}p}$ = 4.3 Hz), 131.1 (d, $J_{c\text{-}p}$ = 98.9 Hz), 130.57 (d, $J_{c\text{-}p}$ = 10.0 Hz), 128.8 (d, $J_{c\text{-}p}$ = 12.4 Hz), 128.7, 128.1, 127. 1 (d, $J_{c\text{-}p}$ = 10.5 Hz), 127.0 (d, $J_{c\text{-}p}$ = 8.3 Hz), 126.8 (d, $J_{c\text{-}p}$ = 6.0 Hz), 17.3 (d, $J_{c\text{-}p}$ = 74.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 31.84

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{20}OP$: 319.1246; found: 319.1246.



(*S*, *E*)-cyclopropyl(phenyl)(2-styrylphenyl)phosphine oxide 7b

A purification by preparative TLC in petroleum ether : ethyl acetate = 3 : 1 gave **7b** as a white foam (25.5 mg, 74%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol=70/30, flow = 1.0 mL/min) with t_r = 6.4 min (minor), 8.4 min (major): 89% *ee*.

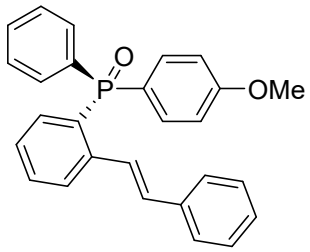
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.92 (m, 1H), 7.77 – 7.70 (m, 3H), 7.67 (d, J = 16.1 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.48 – 7.36 (m, 4H), 7.28 – 7.26 (m, 4H), 7.24 – 7.19 (m, 1H), 6.87 (d, J = 16.1 Hz, 1H), 1.37 – 1.28 (m, 1H), 1.20 – 1.09 (m, 2H), 1.03 – 0.93 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ141.6 (d, $J_{c\text{-}p}$ = 7.6 Hz), 137.1, 134.8 (d, $J_{c\text{-}p}$ = 103.3 Hz), 132.6 (d, $J_{c\text{-}p}$ = 10.2 Hz), 132.2 (d, $J_{c\text{-}p}$ = 2.3 Hz), 131.7 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.5, 131.93 (d, $J_{c\text{-}p}$ = 101.1 Hz), 130.8 (d, $J_{c\text{-}p}$ = 9.7 Hz), 128.7(d, $J_{c\text{-}p}$ = 11.9 Hz), 128.69,

128.0, 127.2 (d, $J_{c\text{-}p}$ = 5.8 Hz), 127.1 (d, $J_{c\text{-}p}$ = 12.1 Hz), 126.9, 126.7 (d, $J_{c\text{-}p}$ = 9.8 Hz), 7.5 (d, $J_{c\text{-}p}$ = 106.6 Hz), 3.6 (d, $J_{c\text{-}p}$ = 4.1 Hz) , 3.4 (d, $J_{c\text{-}p}$ = 4.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 33.28

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{21}NaOP$: 367.1222; found: 367.1223.



(*R*, *E*)-(4-methoxyphenyl)(phenyl)(2-styrylphenyl)phosphine oxide 7c

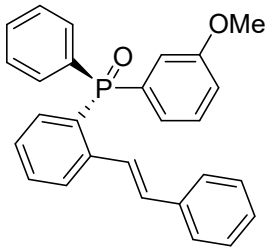
A purification by preparative TLC in petroleum ether: ethyl acetate = 3:1 gave **7c** as a yellow foam (29.1 mg, 71%). The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol=70/30, flow = 1.0 mL/min) with tr = 6.7 min (minor), 7.4 min (major): 88% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 2H), 7.68 (ddd, *J* = 12.0, 8.1, 1.5 Hz, 2H), 7.61 (dd, *J* = 11.5, 8.7 Hz, 2H), 7.53 – 7.41 (m, 4H), 7.26 – 7.18 (m, 7H), 6.95 (dd, *J* = 8.9, 2.3 Hz, 2H), 6.90 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 142.3 (d, $J_{c\text{-}p}$ = 7.3 Hz), 137.2, 133.9 (d, $J_{c\text{-}p}$ = 11.2 Hz), 133.8, 133.0, 132.3 (d, $J_{c\text{-}p}$ = 2.1 Hz), 132.0 (d, $J_{c\text{-}p}$ = 9.9 Hz), 131.8 (d, $J_{c\text{-}p}$ = 2.7 Hz), 131.4, 130.7 (d, $J_{c\text{-}p}$ = 102.1 Hz), 128.7, 128.6, 127.9, 127.5 (d, $J_{c\text{-}p}$ = 6.2 Hz), 127.0, 126.8 (d, $J_{c\text{-}p}$ = 4.4 Hz), 126.7, 124.50 (d, $J_{c\text{-}p}$ = 111.0 Hz), 114.3 (d, $J_{c\text{-}p}$ = 13.3 Hz), 55.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 31.04

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{24}O_2P$: 411.1508; found: 411.1509.



(*R*, *E*)- (3-methoxyphenyl)(phenyl)(2-styrylphenyl)phosphine oxide 7d

A purification by preparative TLC in petroleum ether: ethyl acetate = 3:1 gave **7d** as a yellow foam (27.9 mg, 68%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol=70/30, flow = 1.0 mL/min) with tr = 10.8 min (major), 12.6 min (minor): 90% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (ddd, *J* = 13.4, 7.6, 1.8 Hz, 1H), 7.83 – 7.71 (m, 4H), 7.51 – 7.37 (m, 5H), 7.32 (ddd, *J* = 14.8, 7.7, 1.4 Hz, 1H), 7.26 – 7.17 (m, 6H), 7.12 – 7.05 (m, 1H), 6.91 – 6.83 (m, 2H), 3.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 141.8 (d, $J_{c\text{-}p}$ = 7.5 Hz), 137.3, 134.7 (d, $J_{c\text{-}p}$ = 7.1 Hz), 134.4 (d, $J_{c\text{-}p}$ = 1.9 Hz), 133.5 (d, $J_{c\text{-}p}$ = 107.5 Hz), 133.3 (d, $J_{c\text{-}p}$ = 12.5 Hz), 132.2 (d, $J_{c\text{-}p}$ = 10.2 Hz), 131.8 (d, $J_{c\text{-}p}$ = 2.4 Hz), 131.6 (d, $J_{c\text{-}p}$ = 2.7 Hz), 131.0, 130.8 (d, $J_{c\text{-}p}$ = 105.9 Hz), 128.5, 128.3 (d, $J_{c\text{-}p}$ = 12.5 Hz), 127.8, 127.7 (d, $J_{c\text{-}p}$ = 6.5 Hz), 126.9, 126.7 (d, $J_{c\text{-}p}$ = 13.2 Hz), 126.3 (d, $J_{c\text{-}p}$ = 10.2 Hz), 121.2 (d, $J_{c\text{-}p}$ = 103.8 Hz), 121.4 (d, $J_{c\text{-}p}$ = 11.5 Hz), 111.6 (d, $J_{c\text{-}p}$ = 6.6 Hz), 55.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.19.04

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{24}O_2P$: 411.1508; found: 411.1508.

6. X-Ray Crystallographic Data

A single crystal of **3a** suitable for X-ray crystallography was obtained by crystallization via evaporation from its PE/DCM solution.

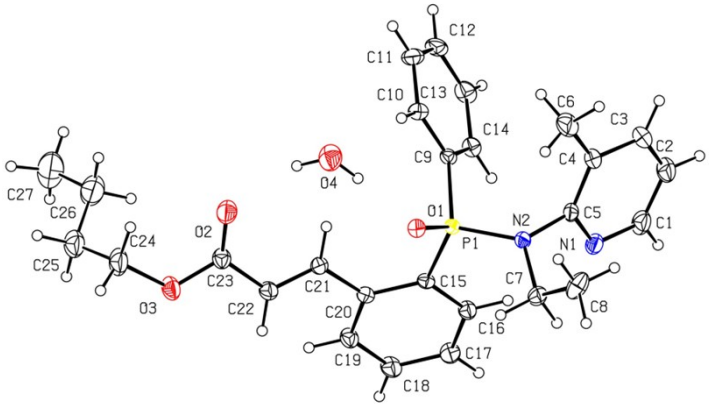


Figure S3. X-Ray crystallographic data of **3a**. Thermal ellipsoids are shown at the 30% level.

Table S4. Crystal data and structure refinement for **3a**

Bond precision	C-C=0.0030 A	Wavelength=0.71073	
Cell	a=11.2201(6)	b=8.4447(5)	c=13.8792(9)
	Alpha=90	beta=98.303(2)	gamma=90
Temperature	170 K		
	Calculated	Reported	
Volume	1301.28(13)	1301.28(13)	
Space group	P 21	P 1 21 1	
Hall group	P 2yb	P 2yb	
Moiety formula	C27 H31 N2 O3 P, H2 O	C27 H31 N2 O3 P, H2 O	
Sum formula	C27 H33 N2 O4 P	C27 H34 N3 O3 P	
Mr	480.52	479.54	
Dx, g cm^{-3}	1.226	1.224	
Z	2	2	
Mu (mm^{-1})	0.140	0.138	
F000	512.0	512.0	
F000’	512.42		

h, k, lmax	14, 10, 17	14, 10, 17
Nref	5751[3075]	5734
Tmin, Tmax	0.958, 0.969	0.715, 0.746
Tmin’	0.942	
Radiation type	MoK\a	
Flack	0.016(13)	

Correction method = # Reported T Limits: Tmin = 0.715 Tmax = 0.746
AbsCorr=MULTI-SCAN
Data completeness = 1.86/1.00 Theta(max) = 27.127
R (reflections) = 0.0309(5659) wR2(reflections) = 0.0803(5734)
S=1.076 Npar=345

7. References

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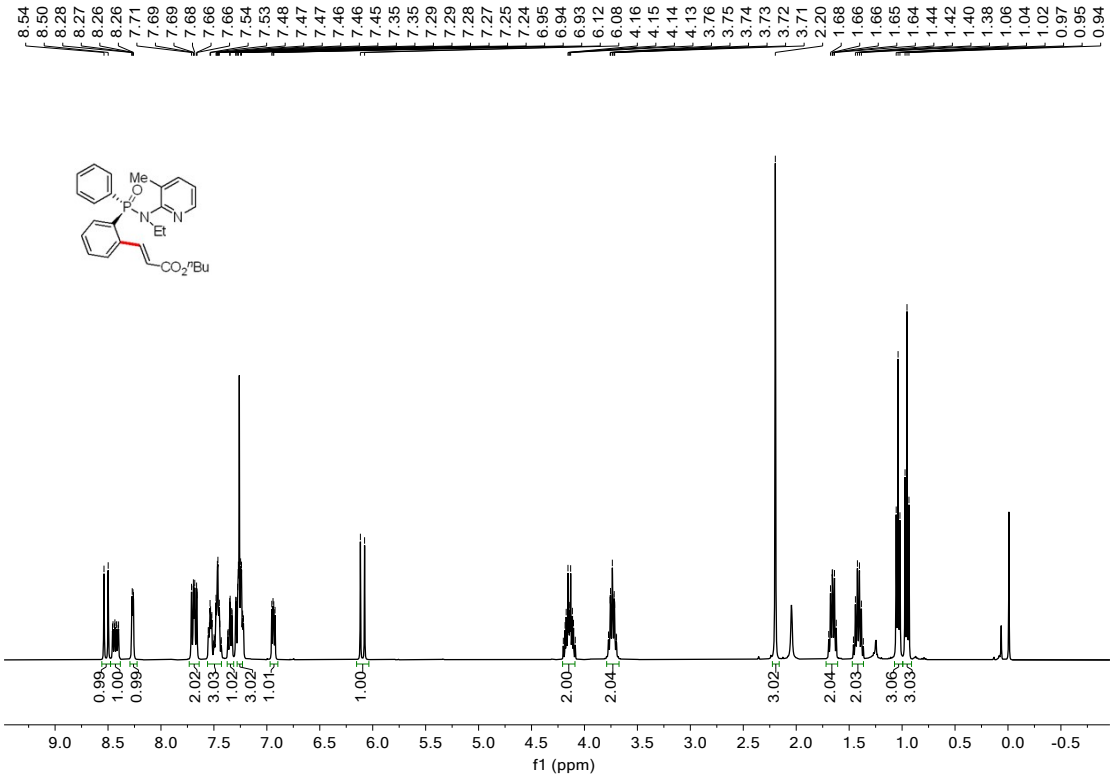
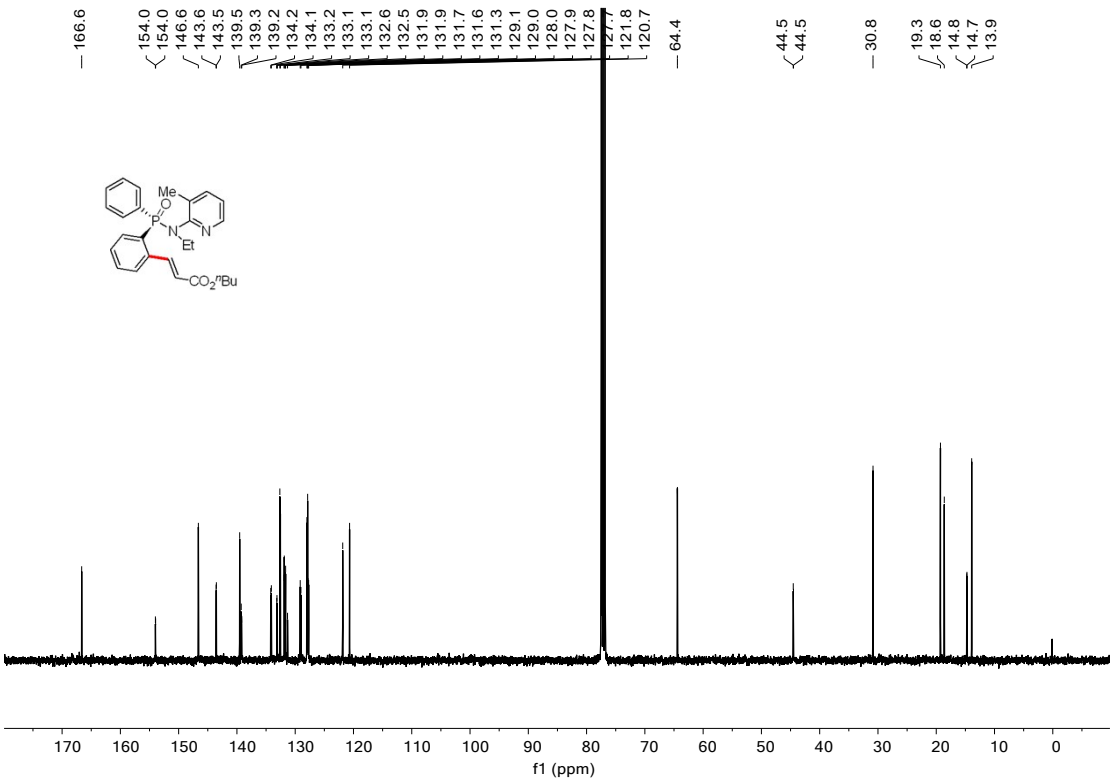
8. NMR Spectra

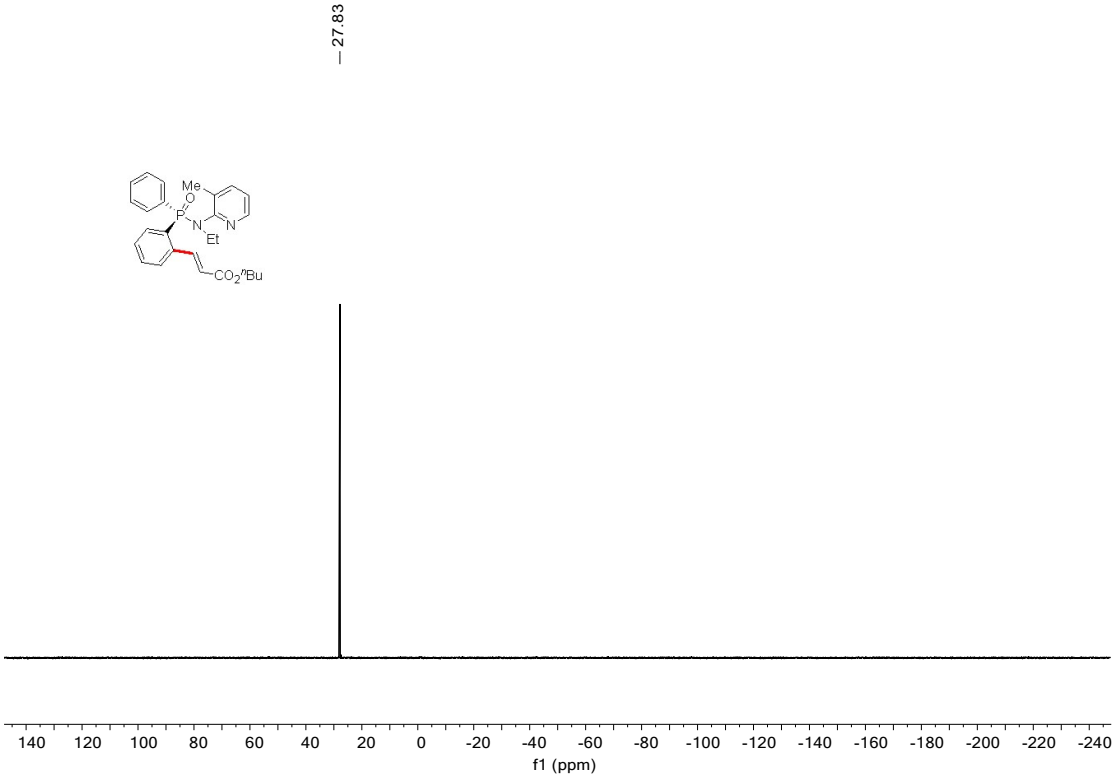
3a, ^{1}H NMR, 400 MHz, $CDCl_3$



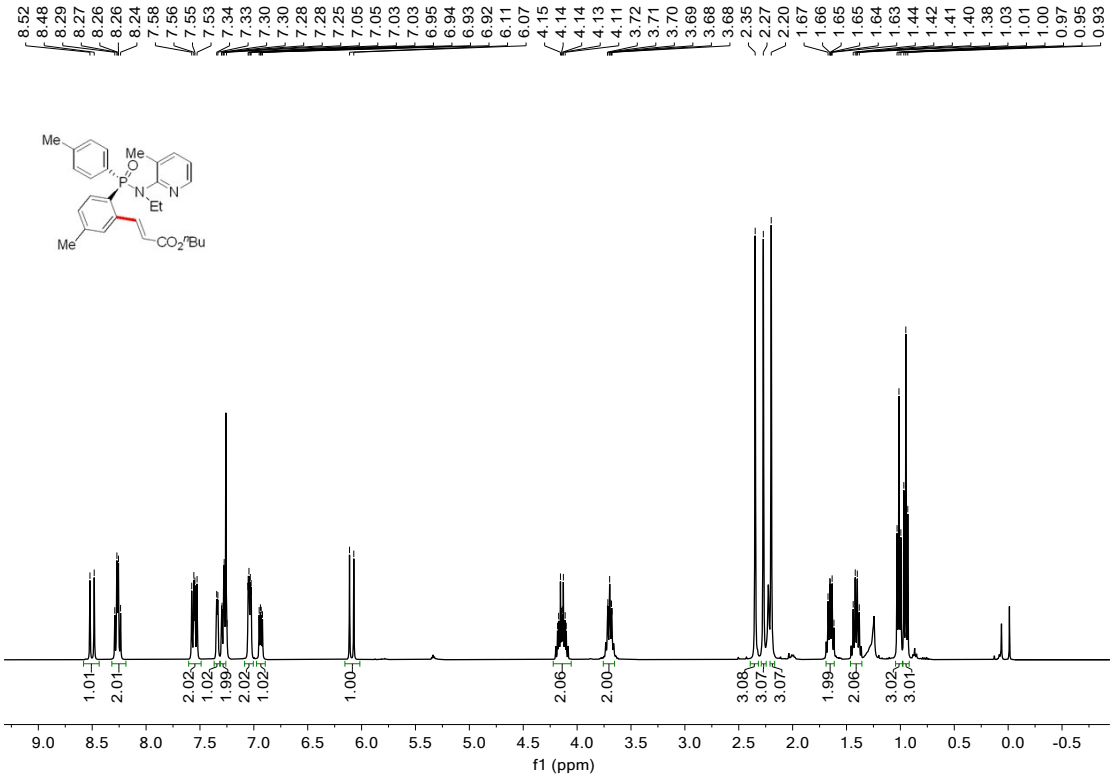
3a, ^{13}C NMR, 101 MHz, $CDCl_3$



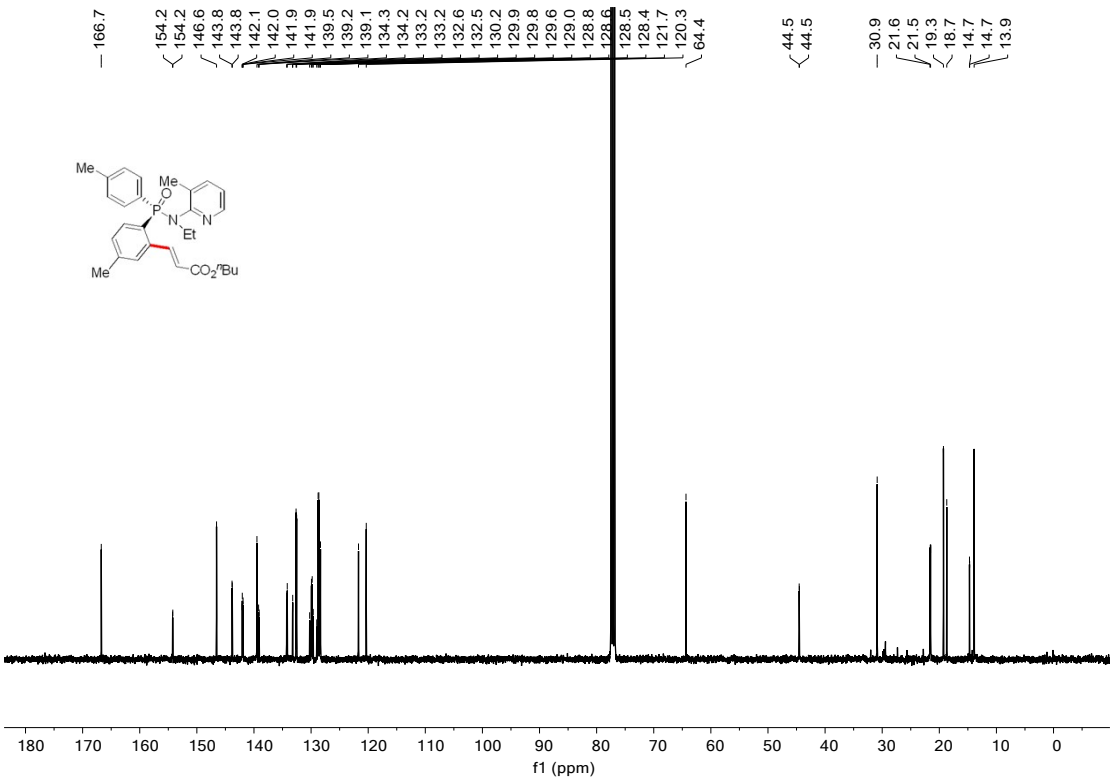
3a, ^{31}P NMR, 162 MHz, $CDCl_3$



3b, ^{1}H NMR, 400 MHz, $CDCl_3$



3b, ^{13}C NMR, 101 MHz, $CDCl_3$



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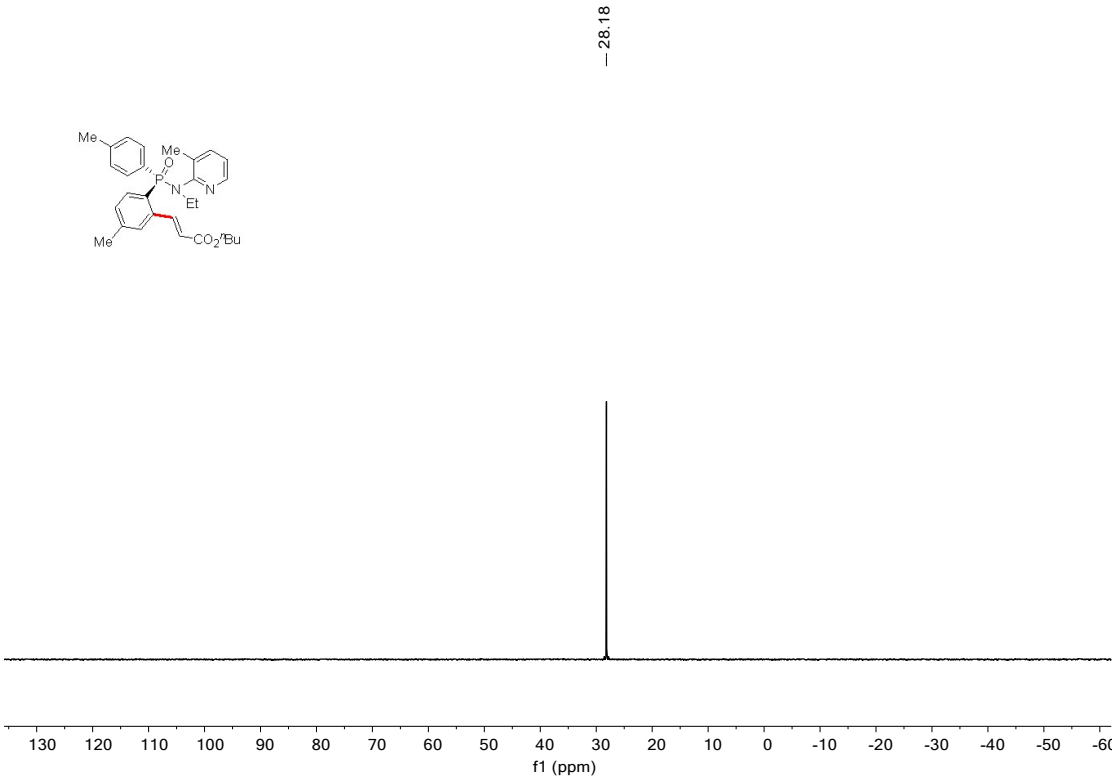

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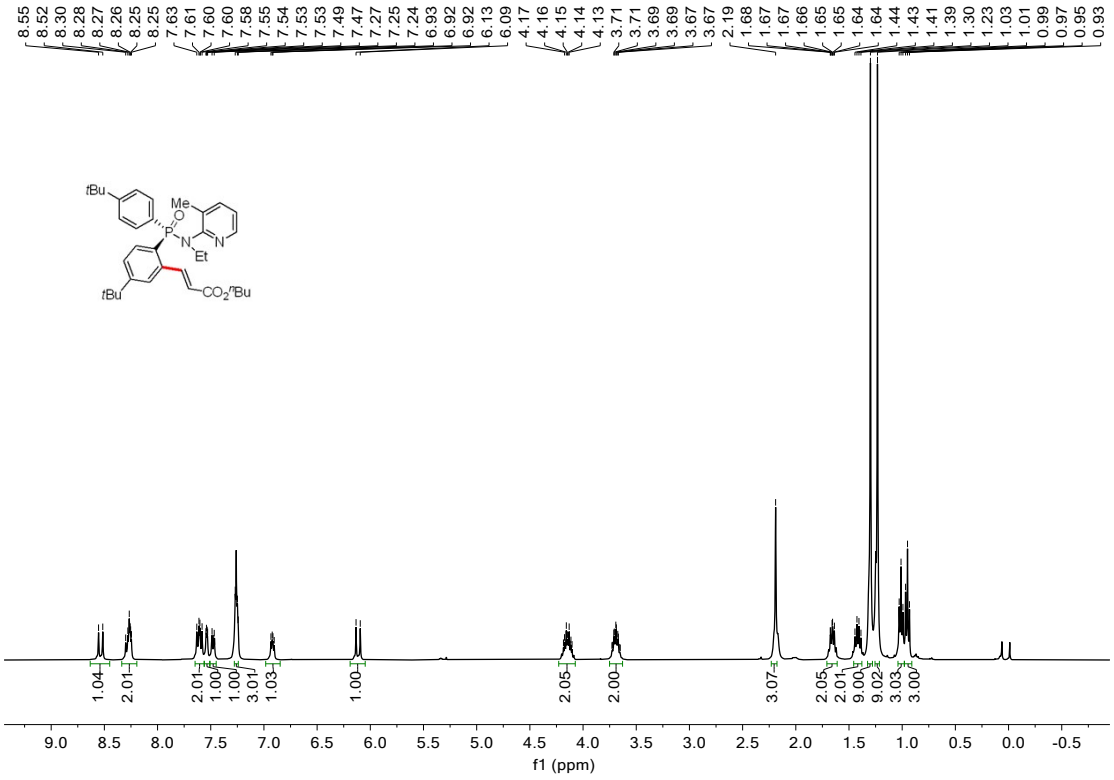

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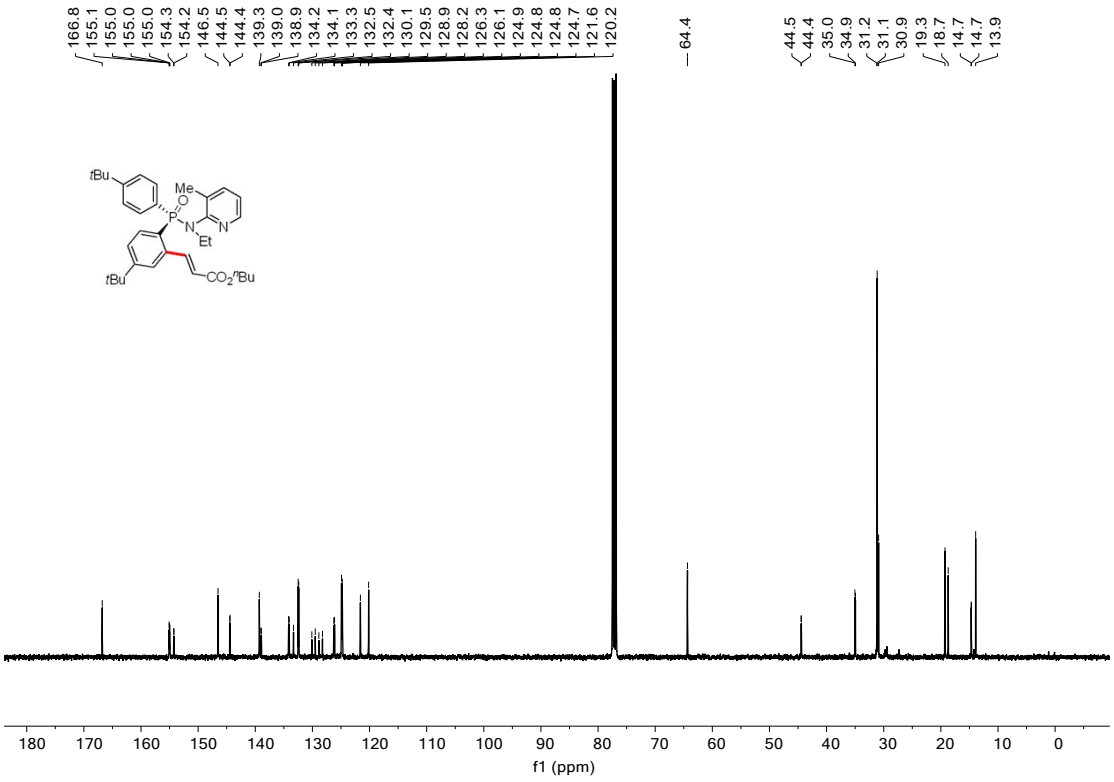

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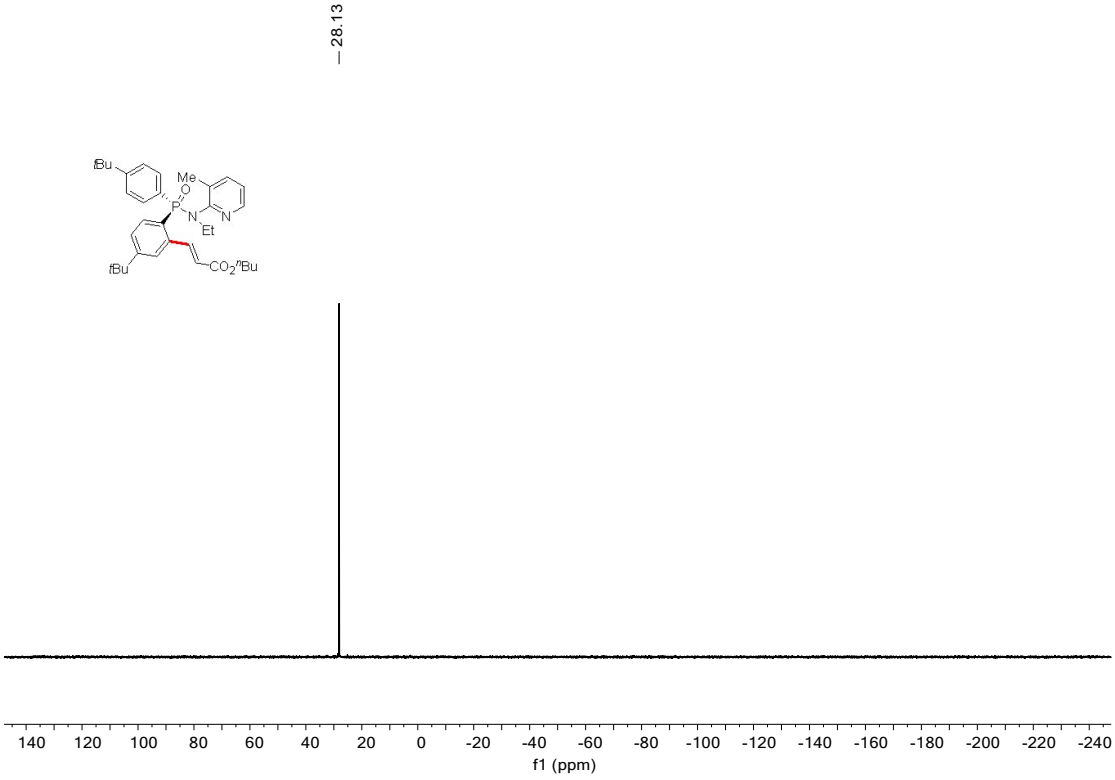

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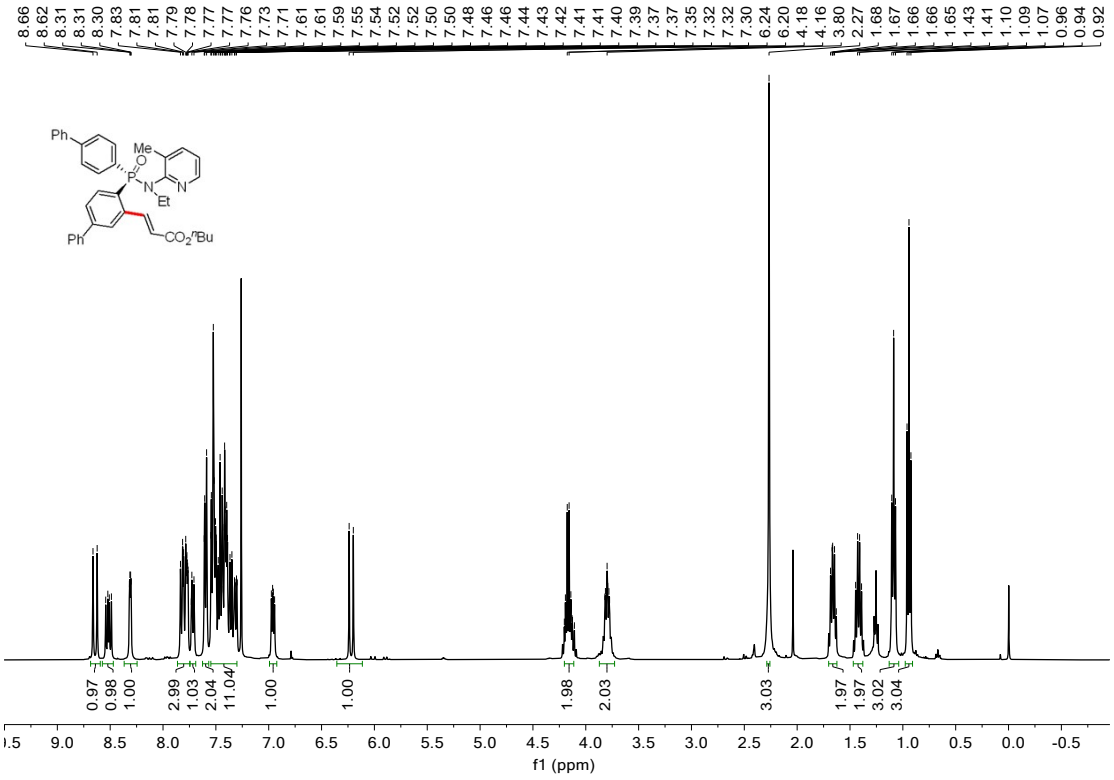

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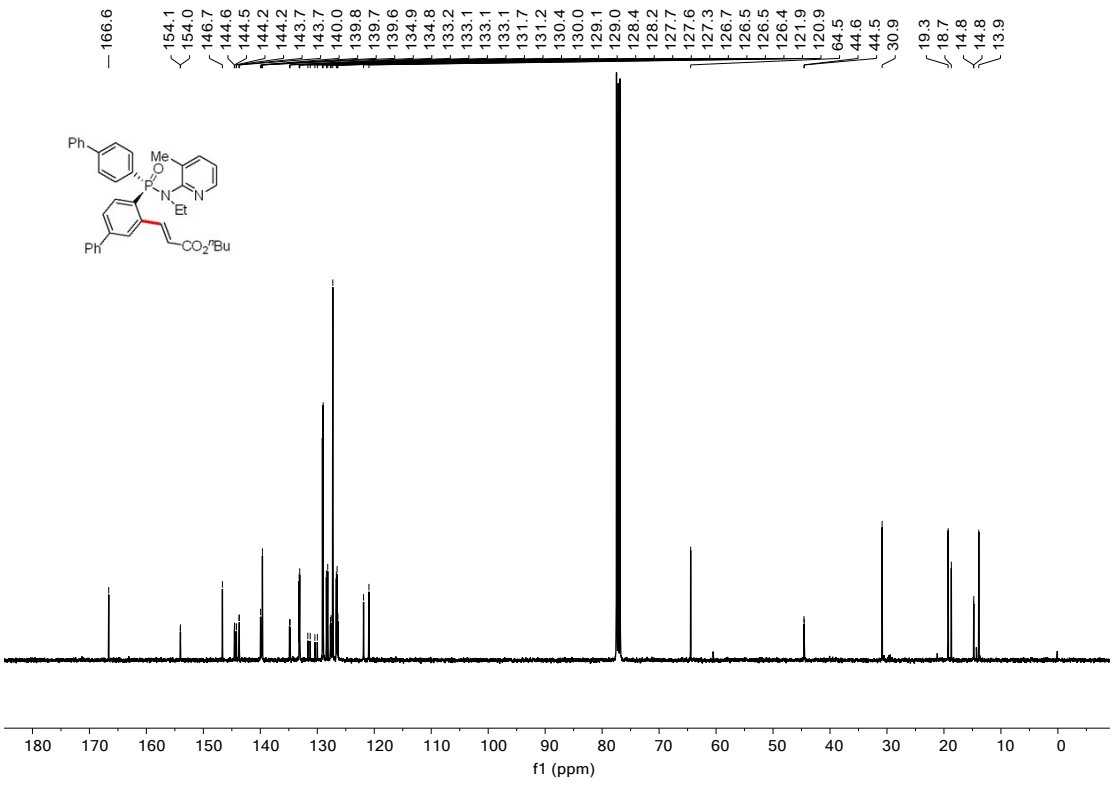

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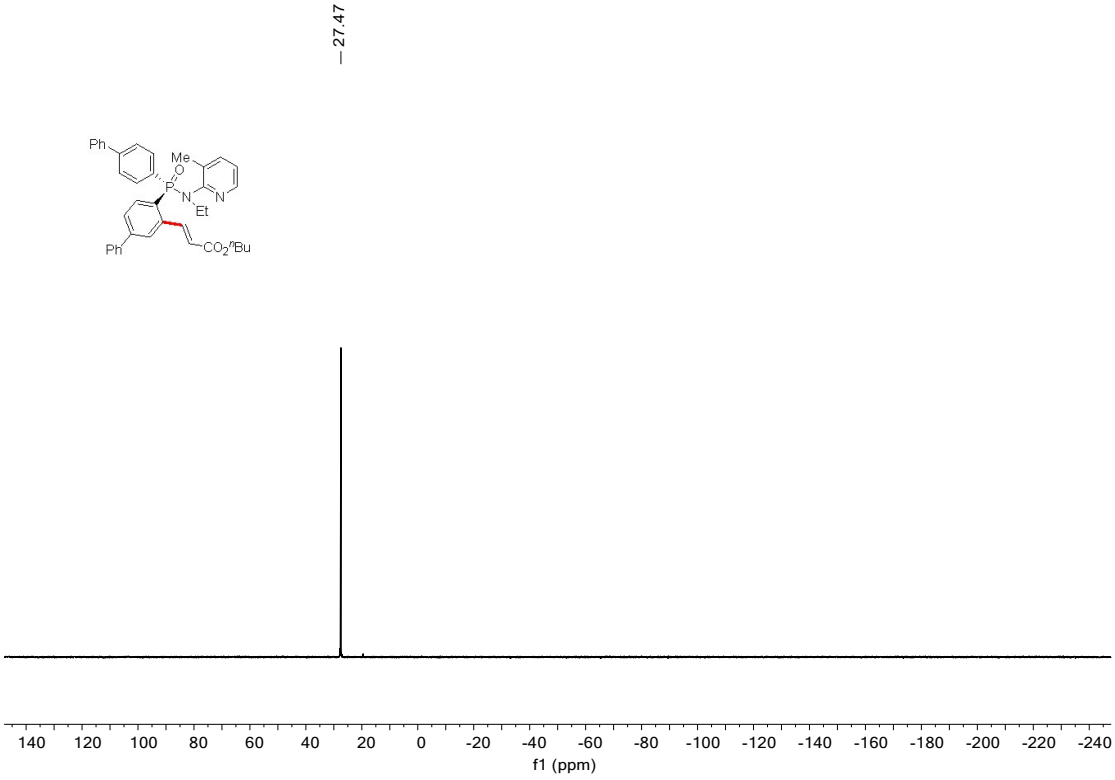
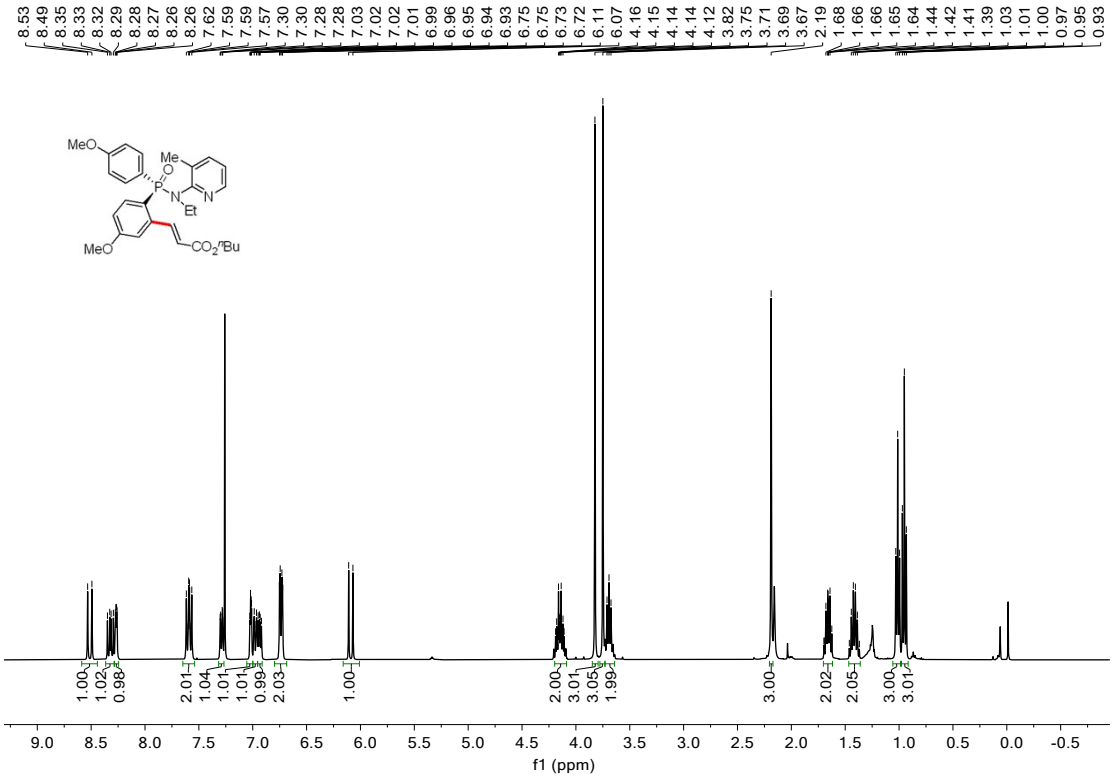


3e, ^{1}H NMR, 400 MHz, $CDCl_3$



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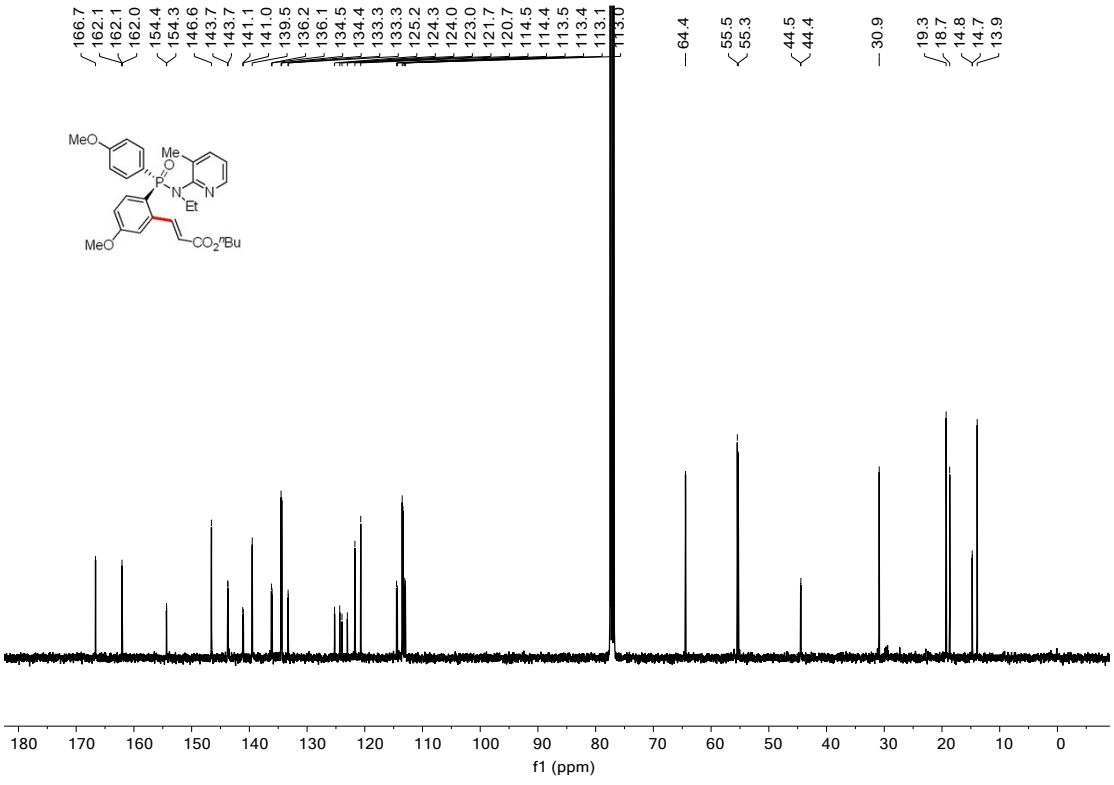

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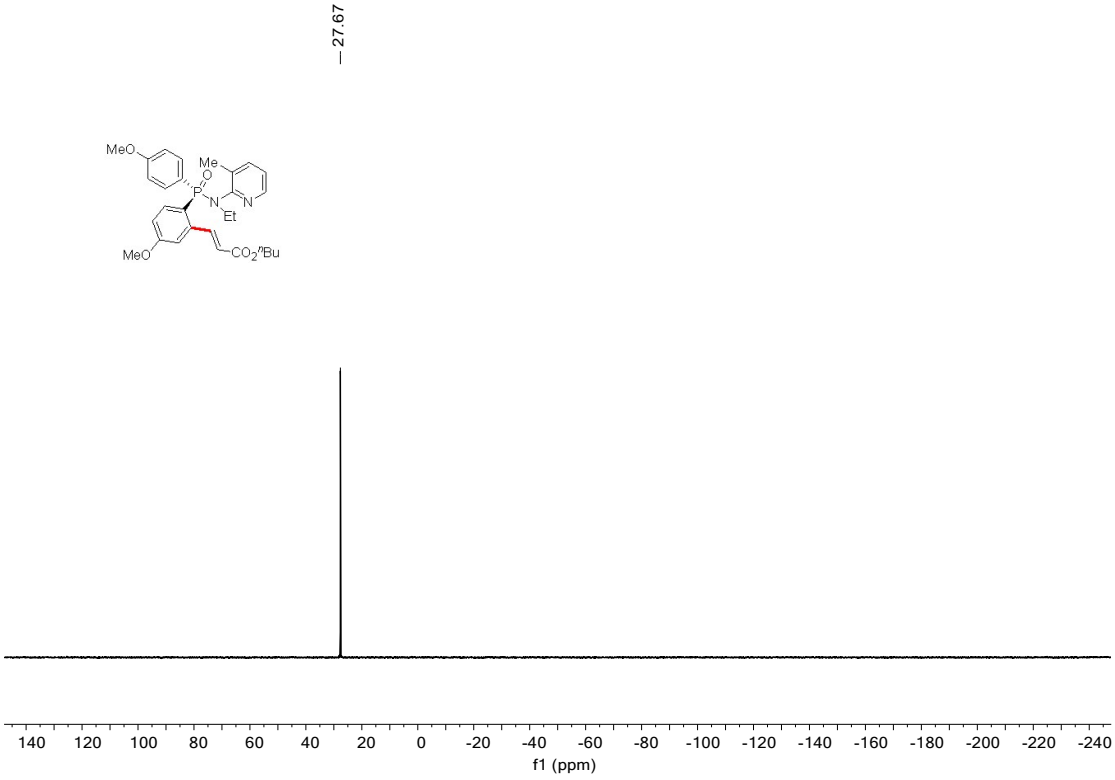
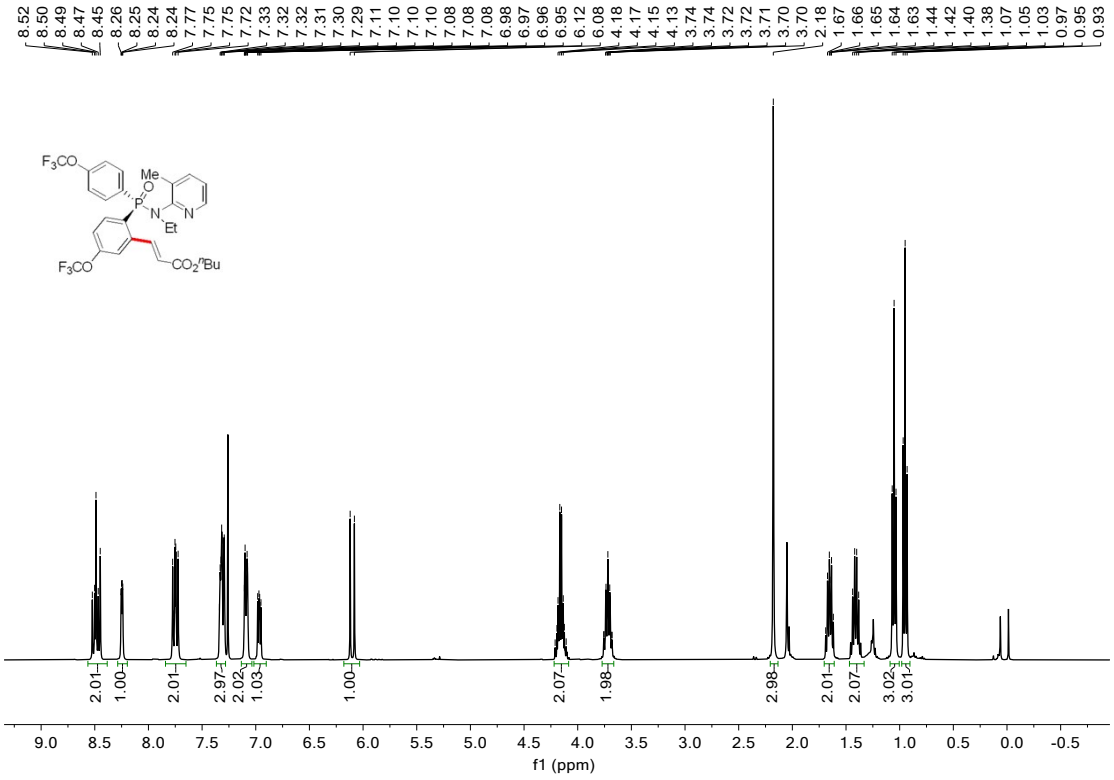


3f, ^{1}H NMR, 400 MHz, $CDCl_3$



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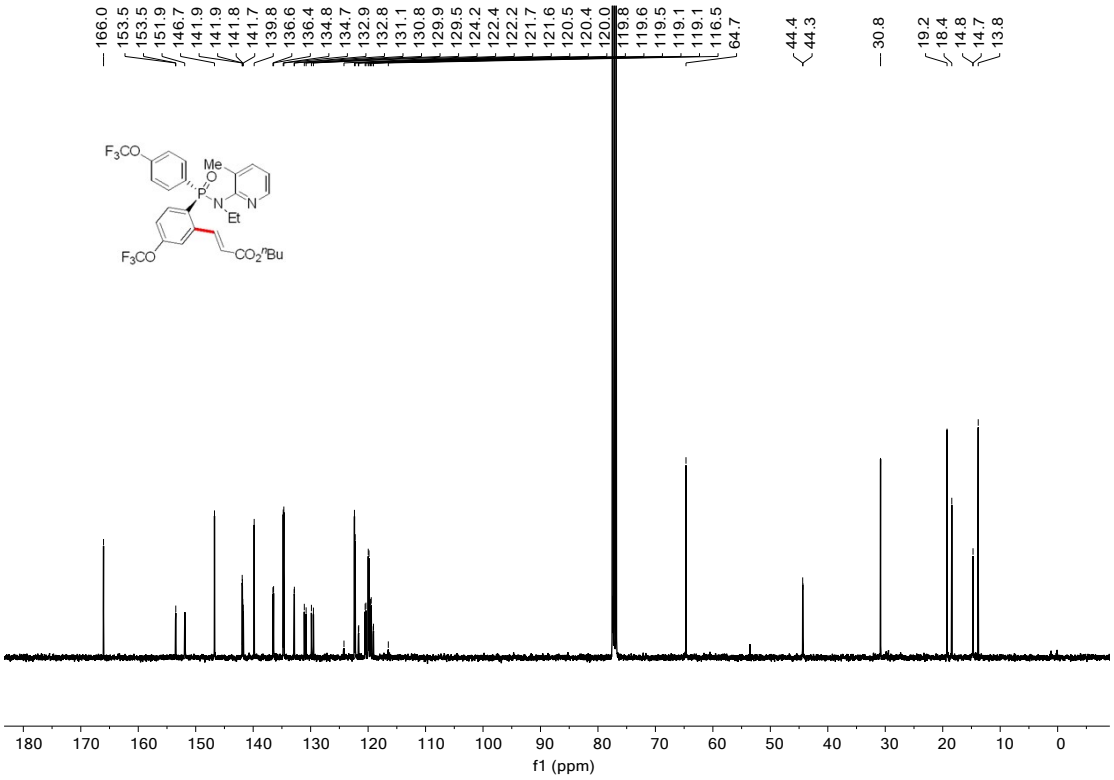
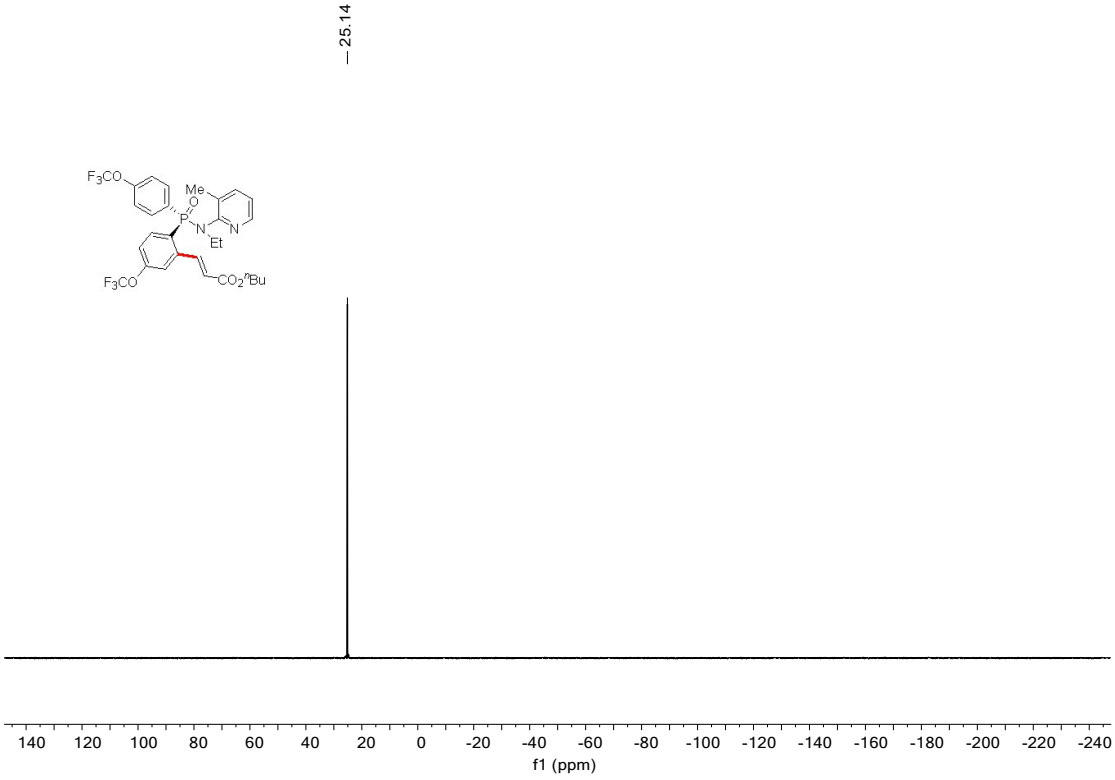
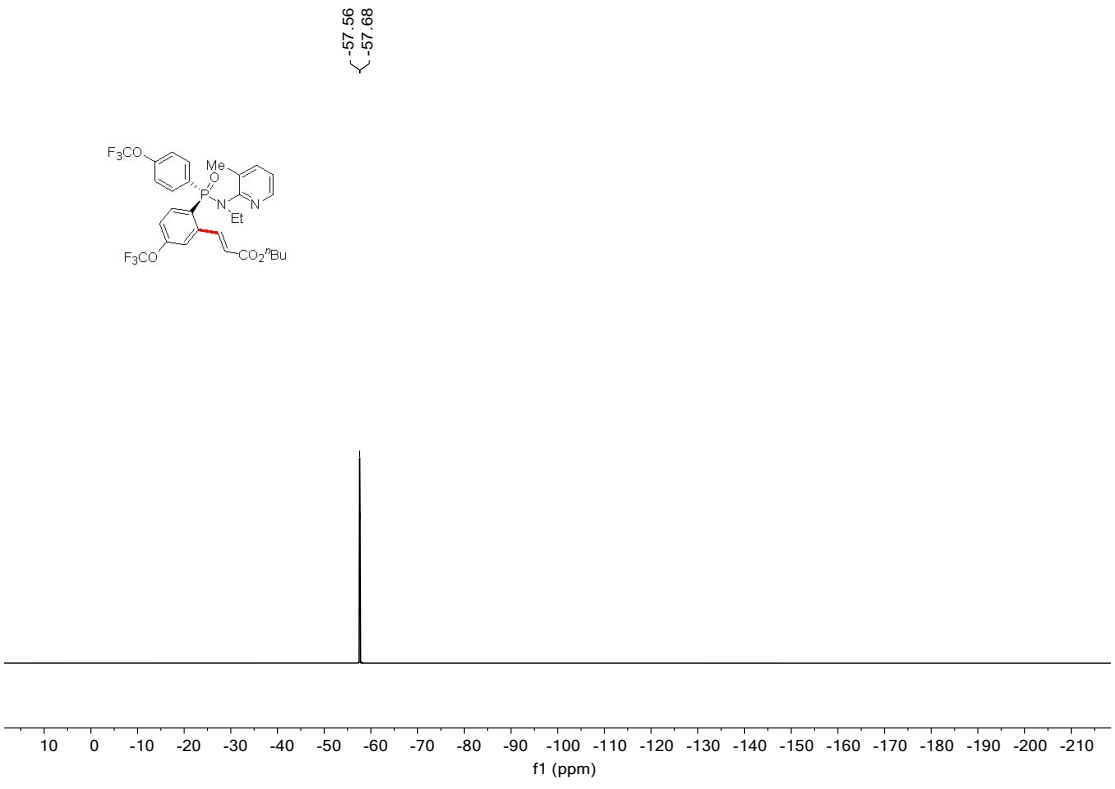


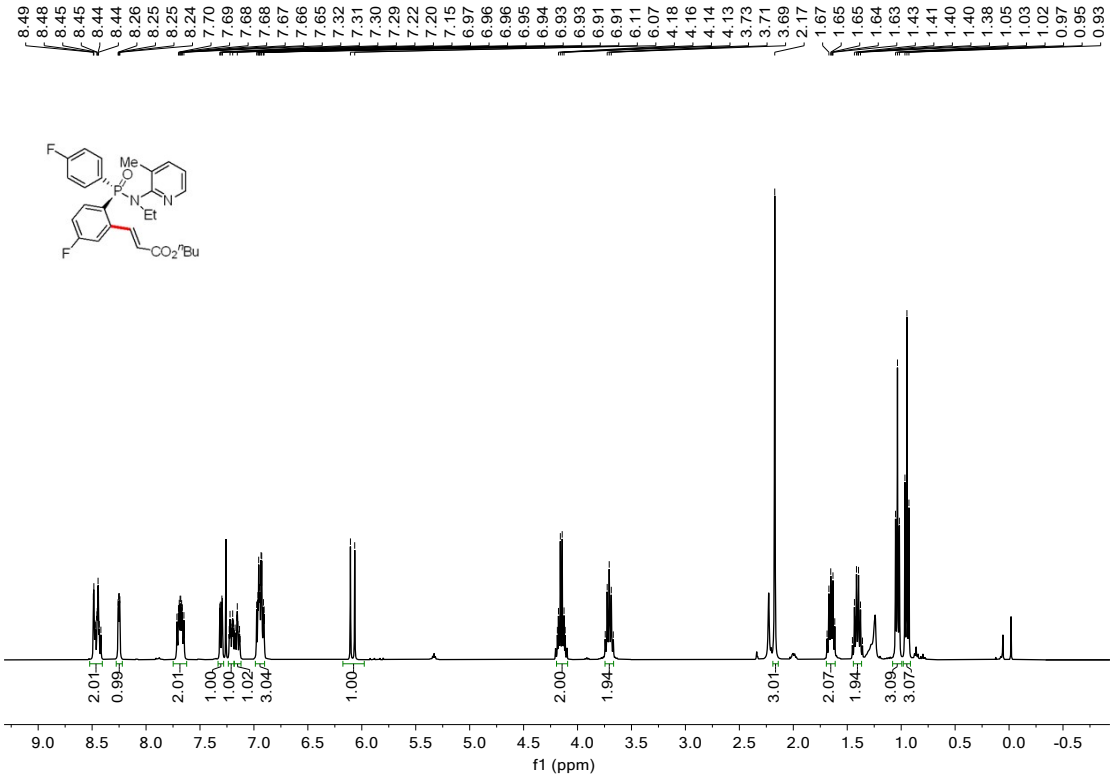
3f, ^{31}P NMR, 162 MHz, $CDCl_3$



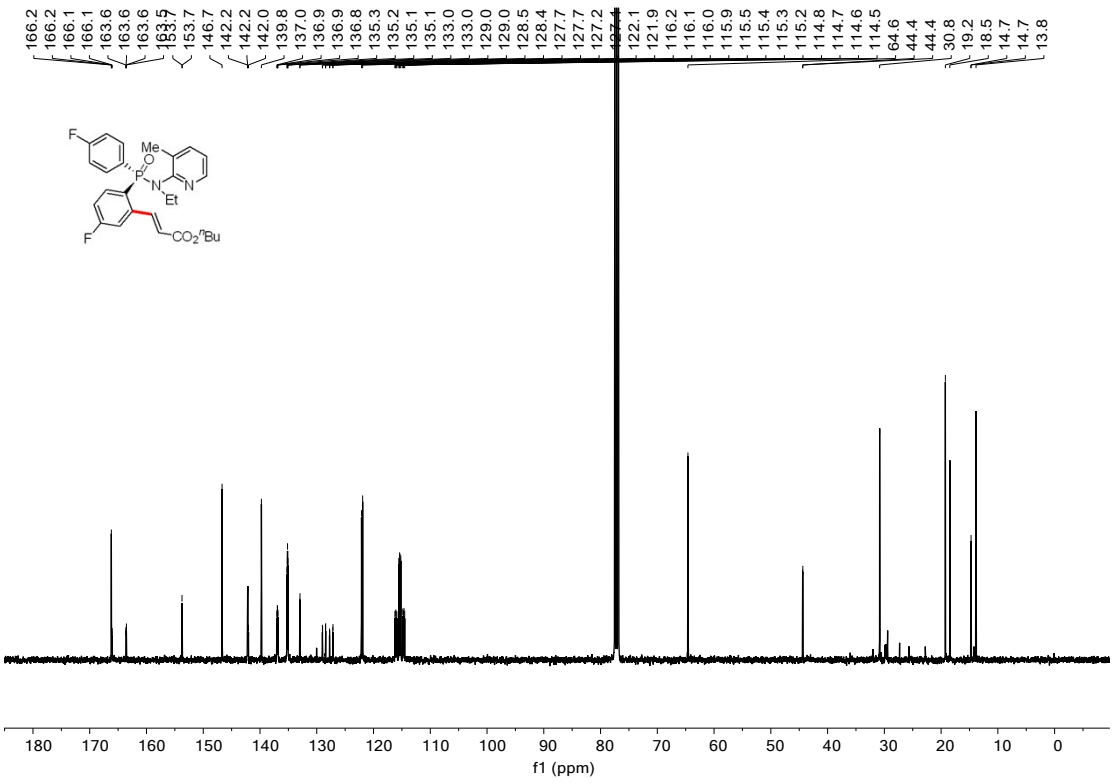
3f, ^{19}F NMR, 376 MHz, $CDCl_3$



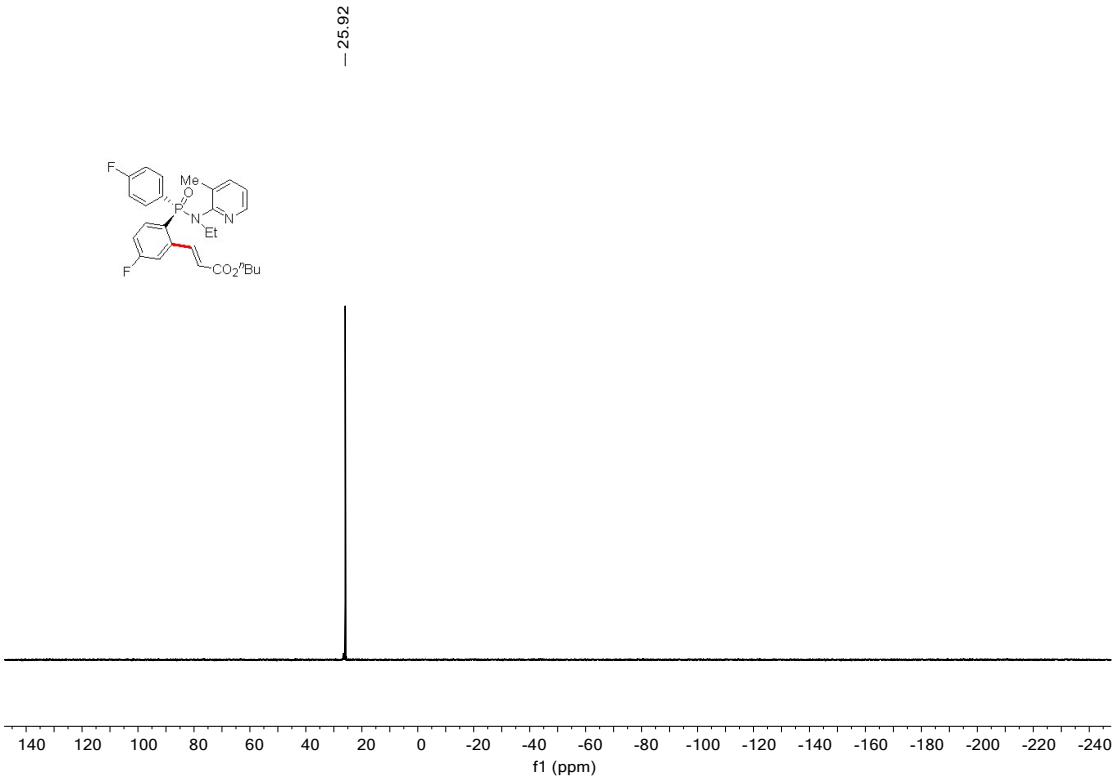
3g, ^{1}H NMR, 400 MHz, $CDCl_3$



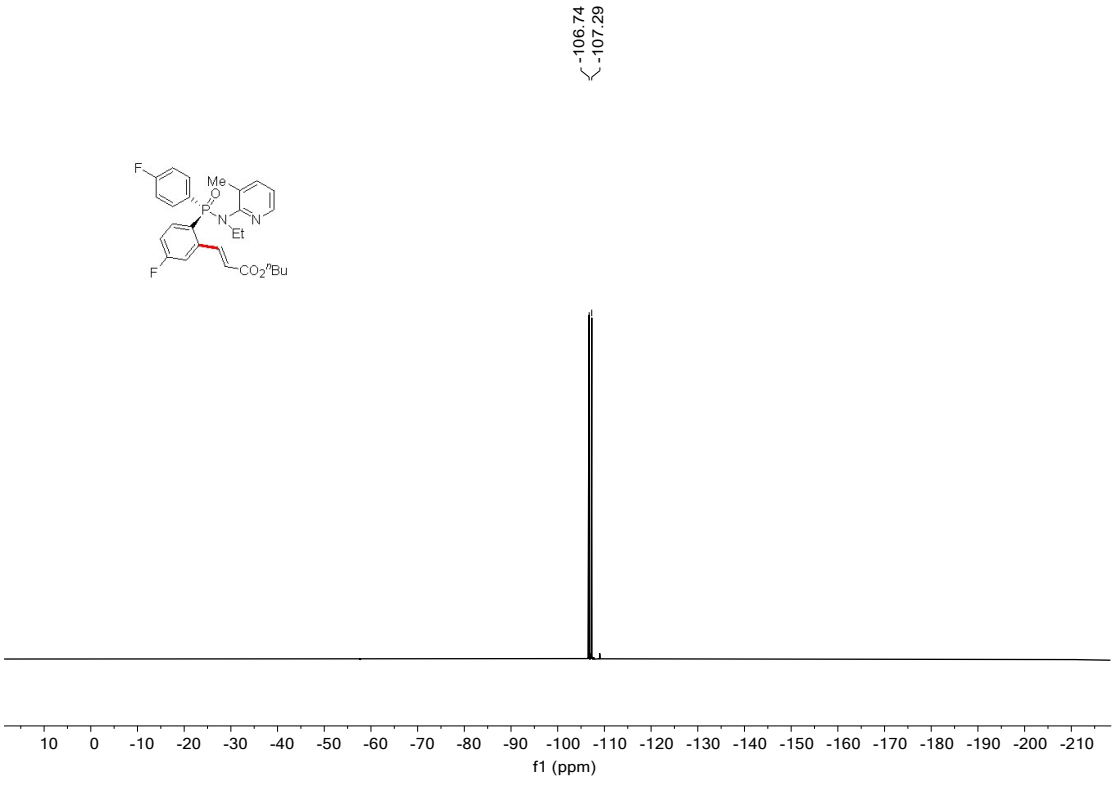
3g, ^{13}C NMR, 101 MHz, $CDCl_3$



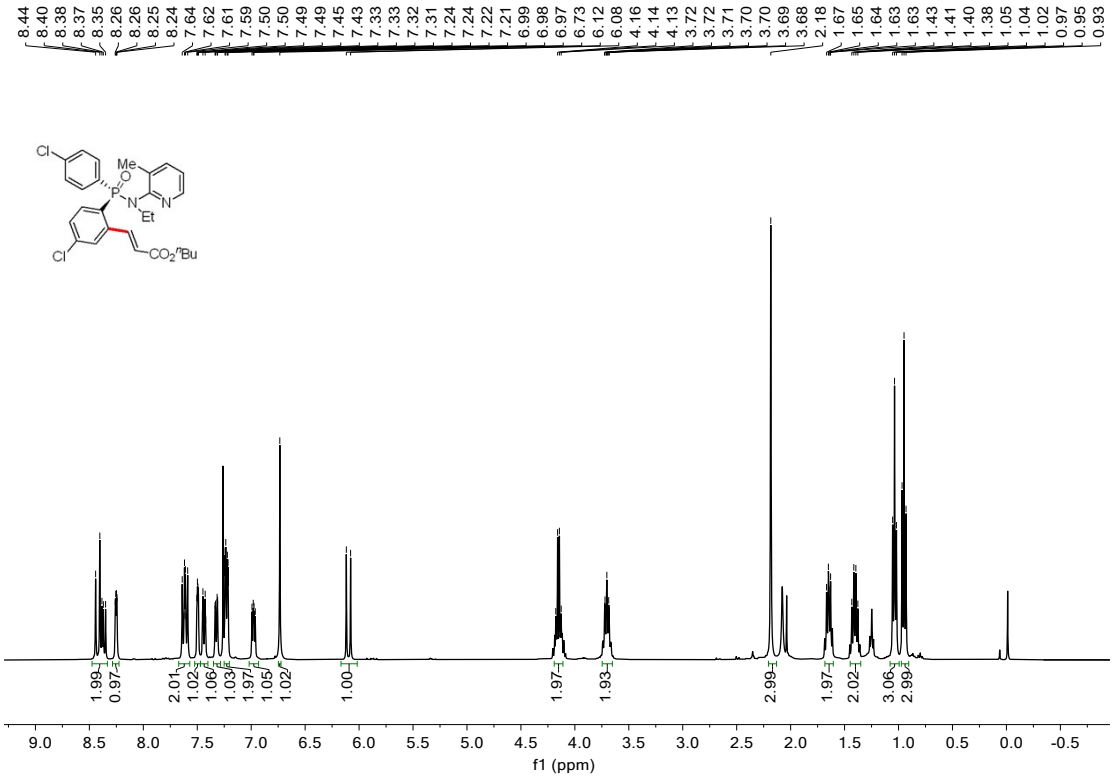
3g, ^{31}P NMR, 162 MHz, $CDCl_3$



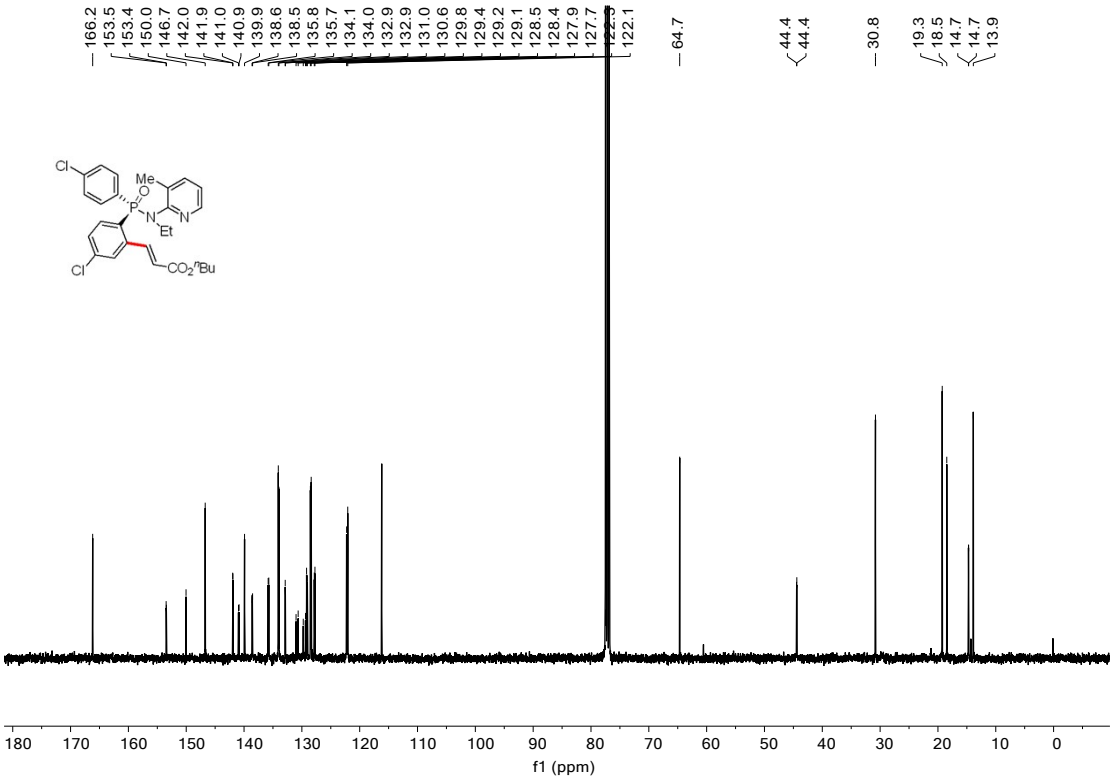
3g, ^{19}F NMR, 376 MHz, $CDCl_3$



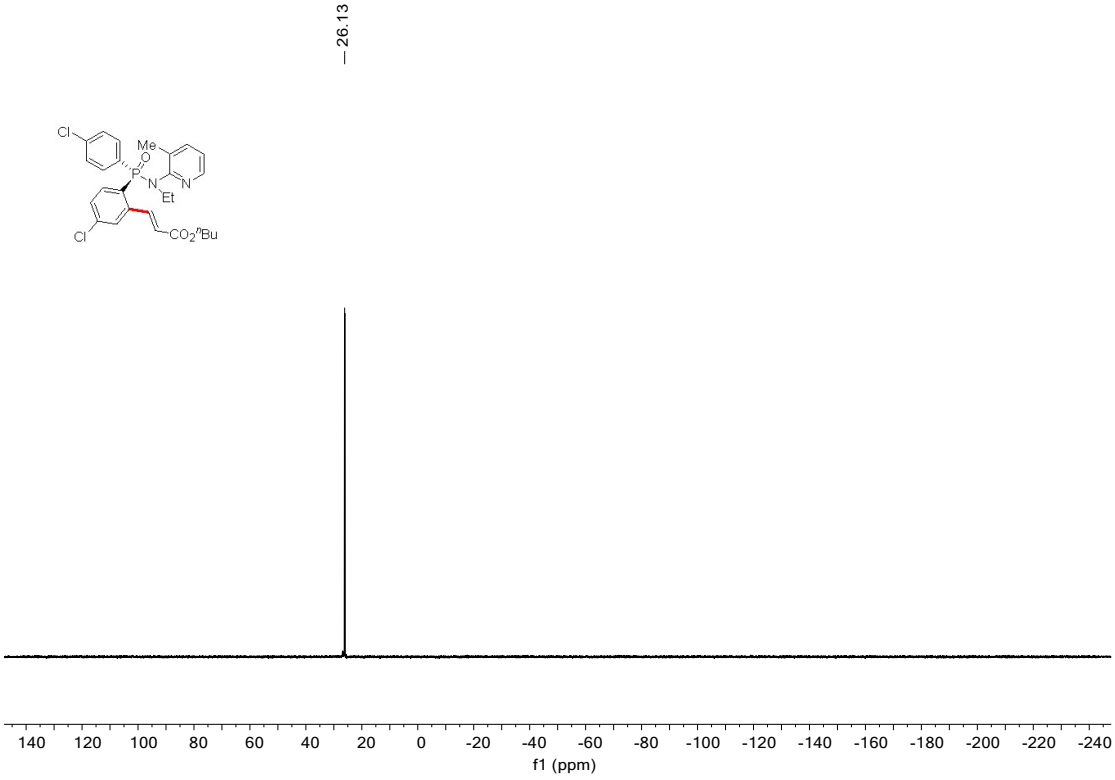
3h, ^{1}H NMR, 400 MHz, $CDCl_3$



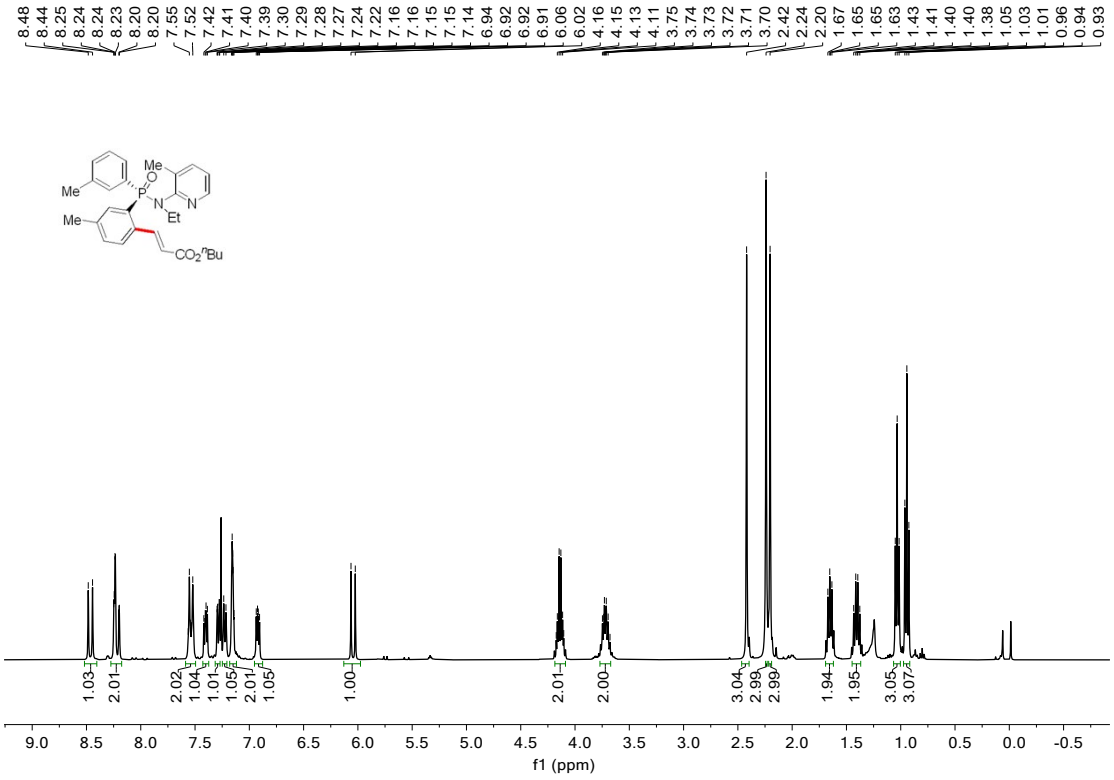
3h, ^{13}C NMR, 101 MHz, $CDCl_3$



3h, ^{31}P NMR, 162 MHz, $CDCl_3$



3i, ^{1}H NMR, 400 MHz, $CDCl_3$



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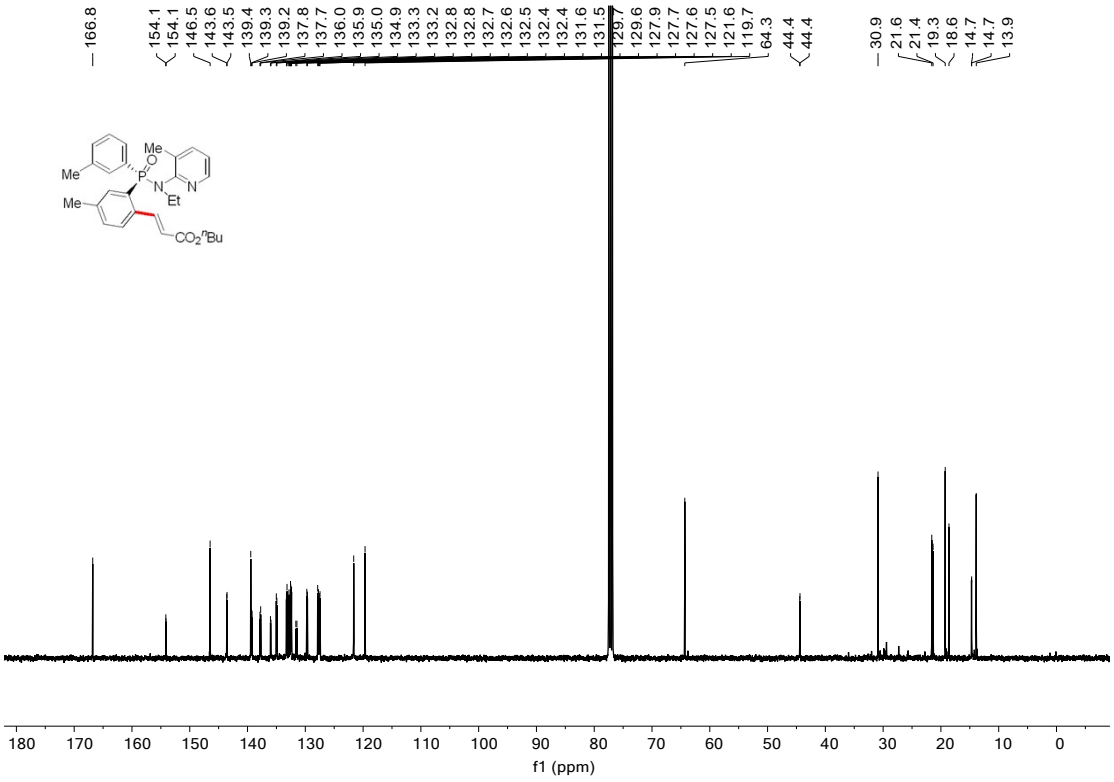

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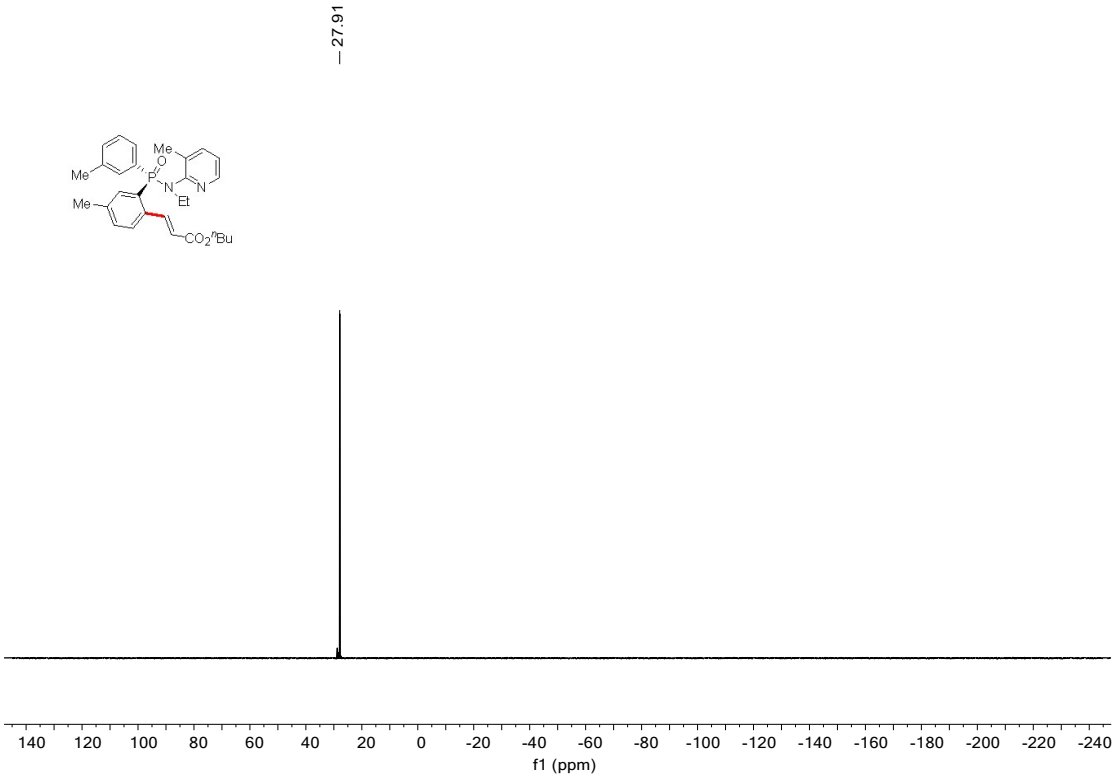
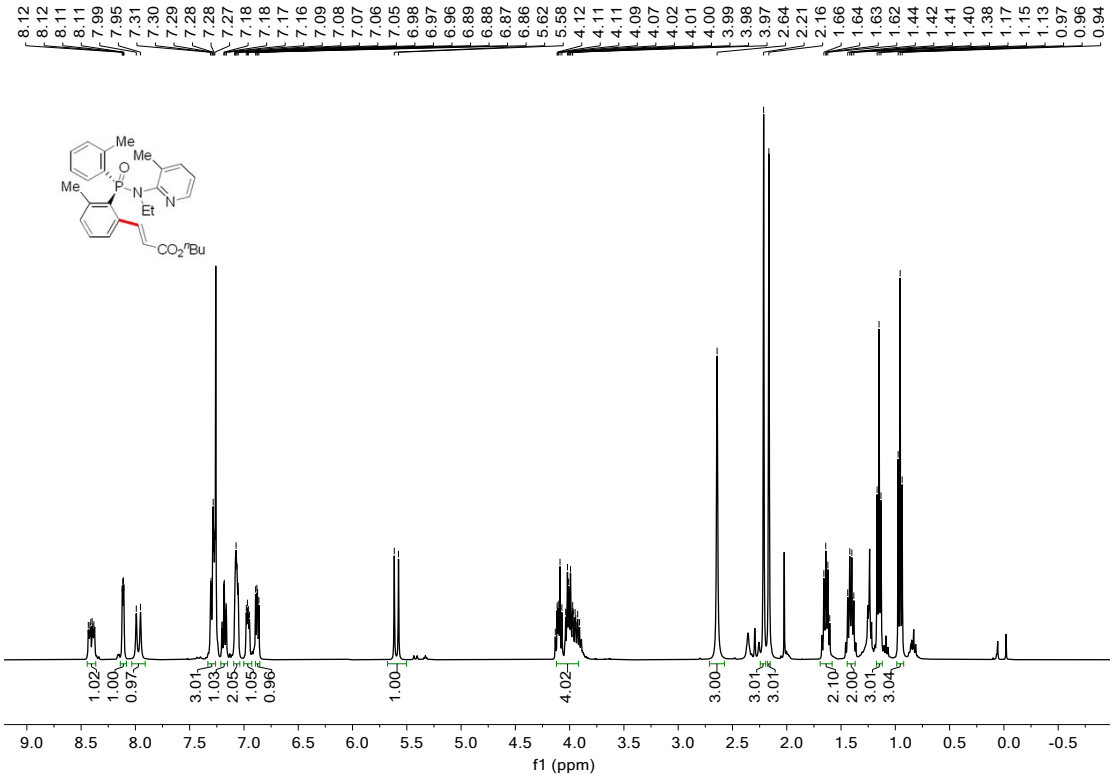
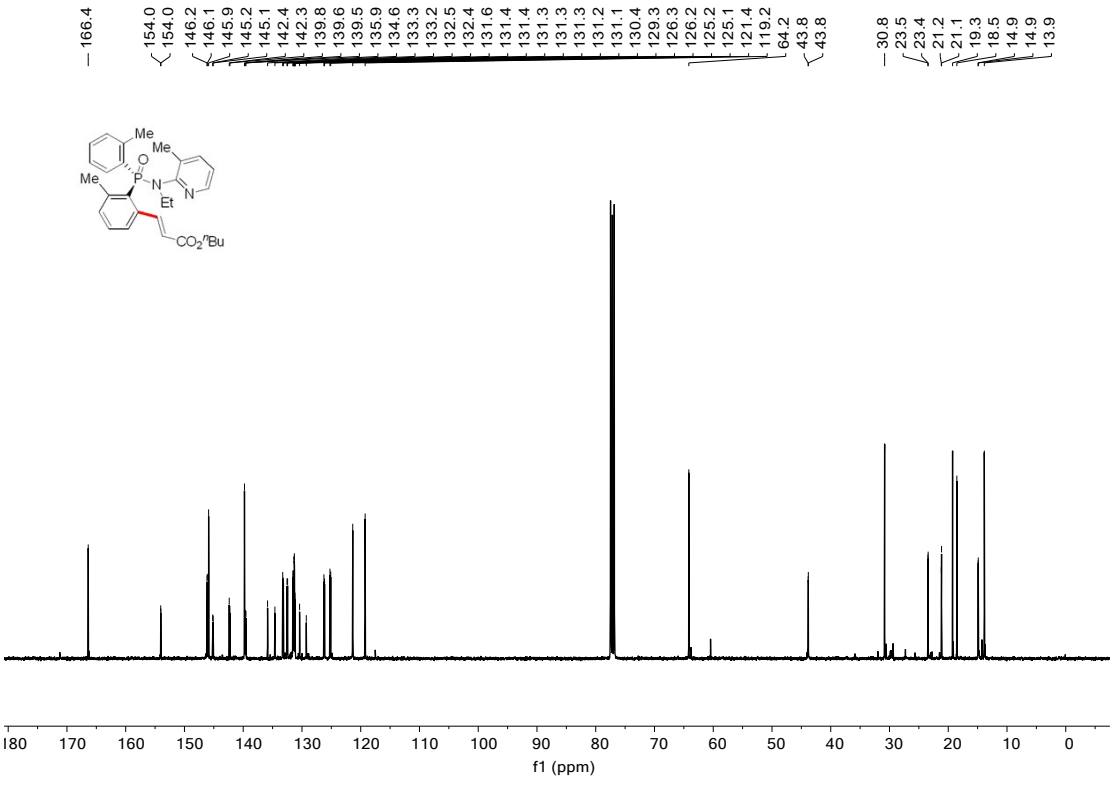


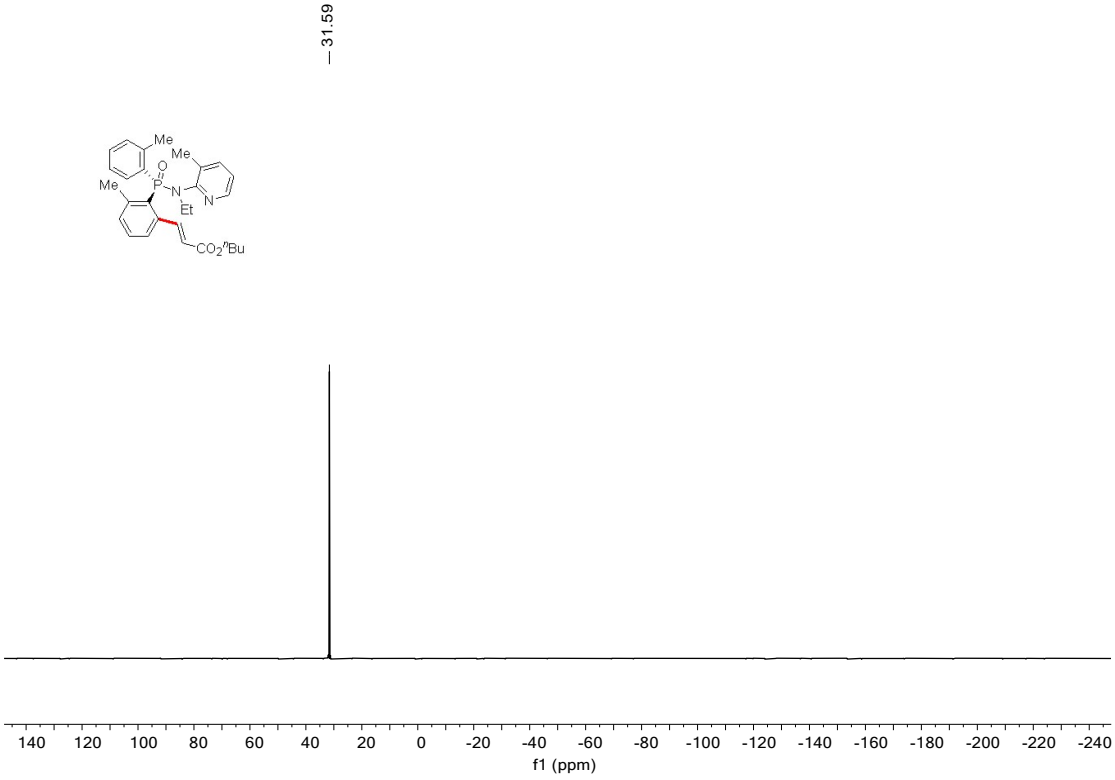
3j, ^{1}H NMR, 400 MHz, $CDCl_3$



3j, ^{13}C NMR, 101 MHz, $CDCl_3$



3j, ^{31}P NMR, 162 MHz, $CDCl_3$



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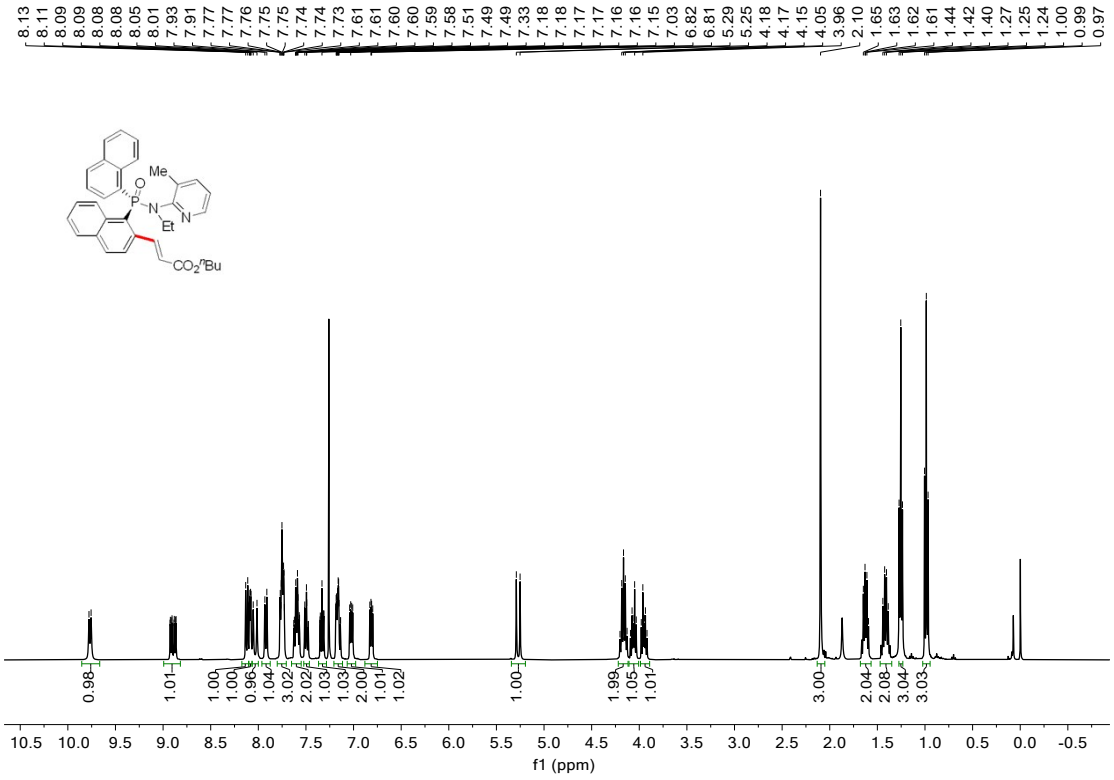
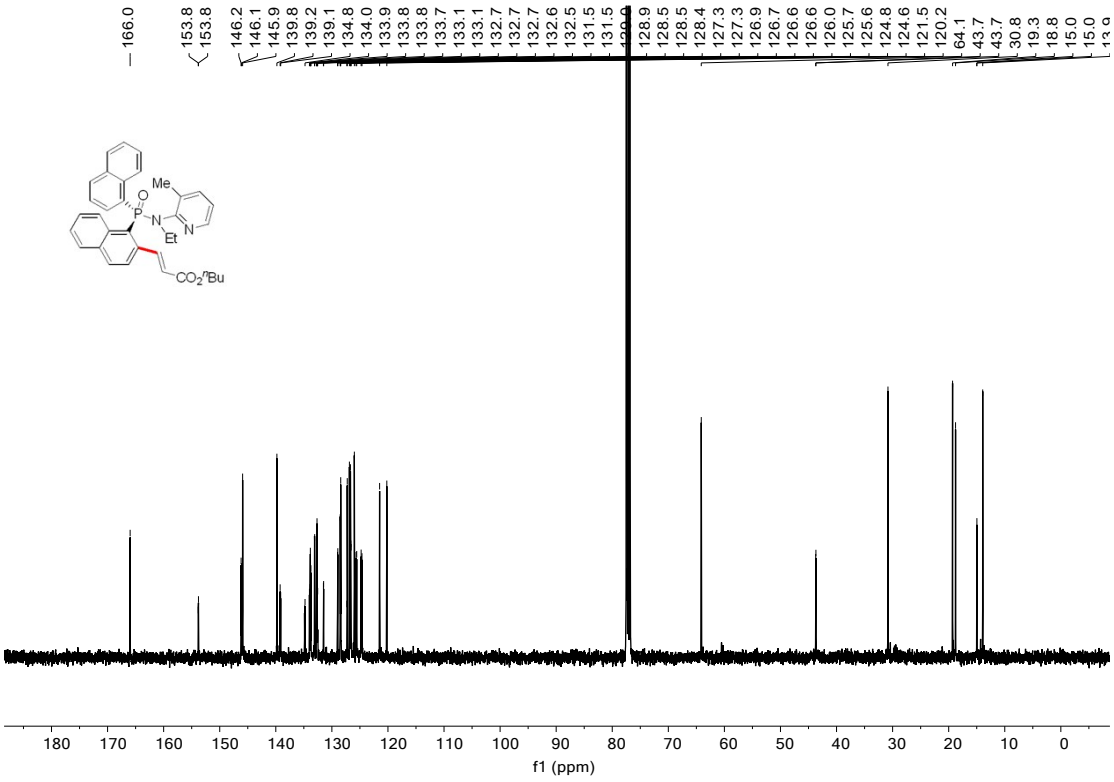
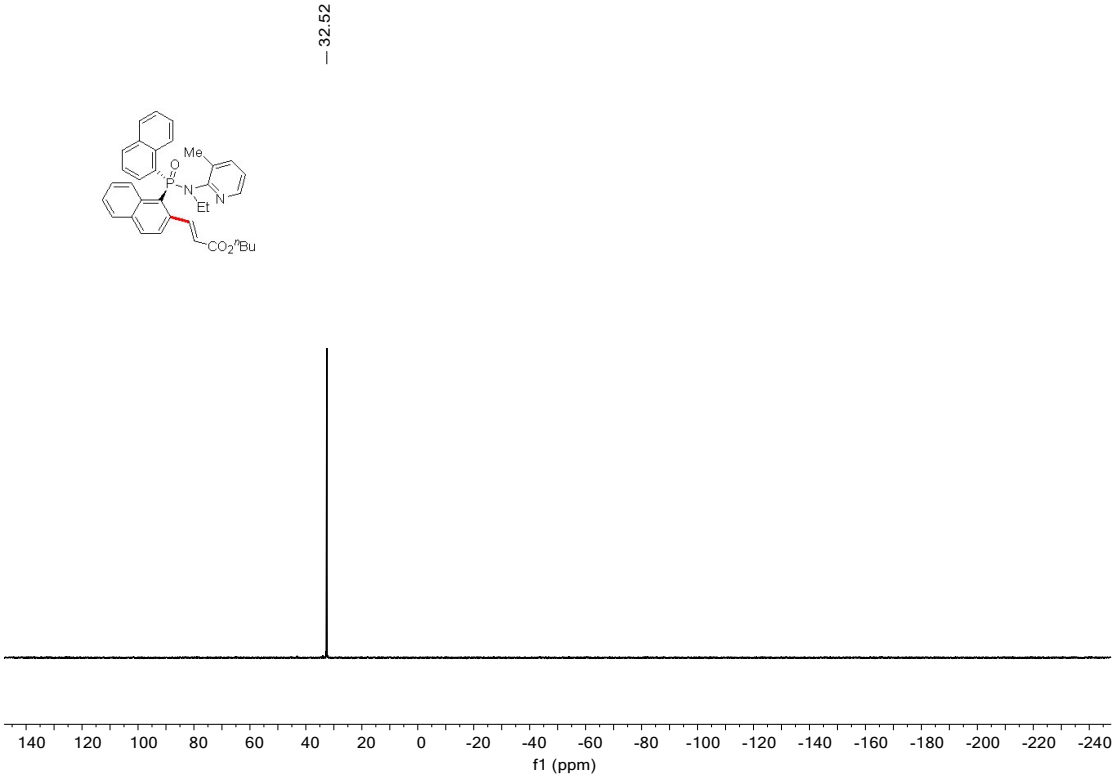


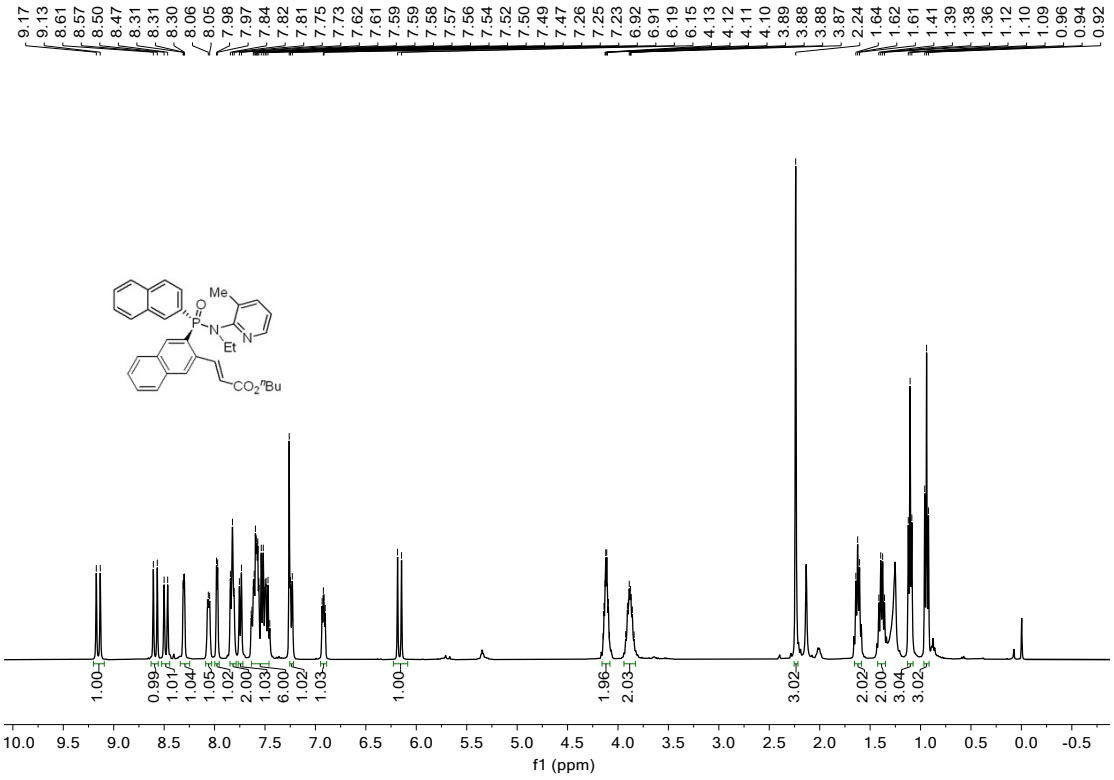
3k, ^{13}C NMR, 101 MHz, $CDCl_3$



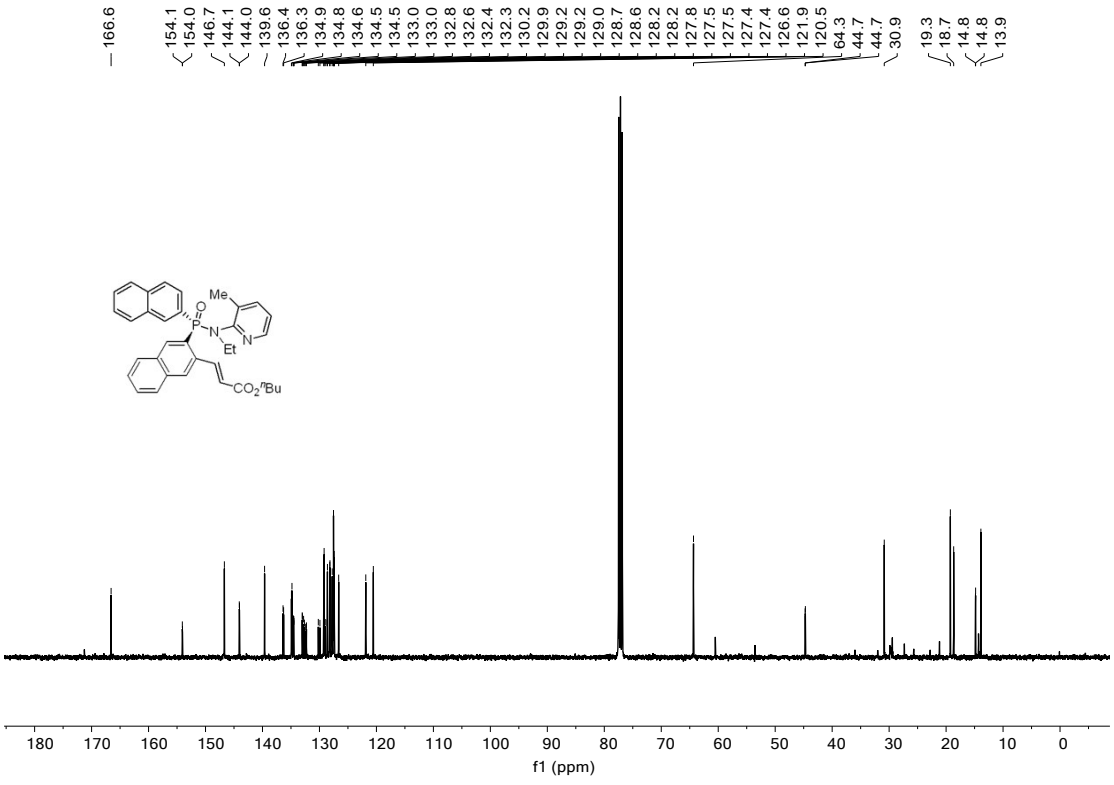
3k, ^{31}P NMR, 162 MHz, $CDCl_3$



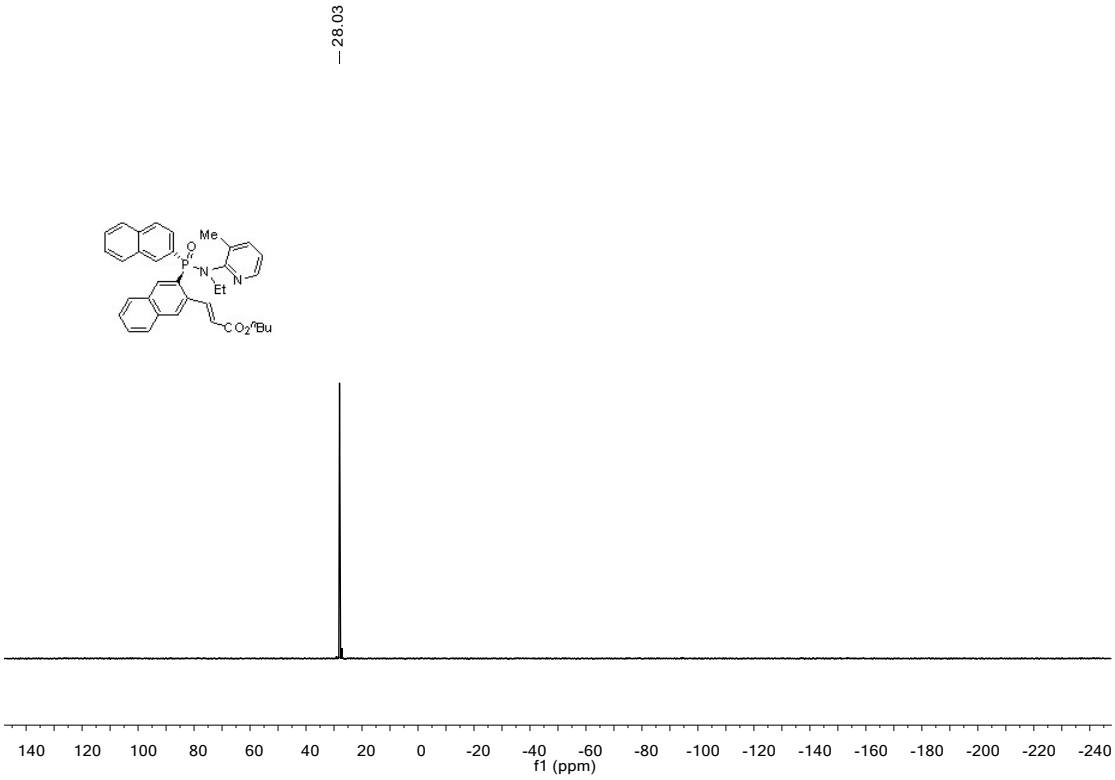
3l, ^{1}H NMR, 400 MHz, $CDCl_3$



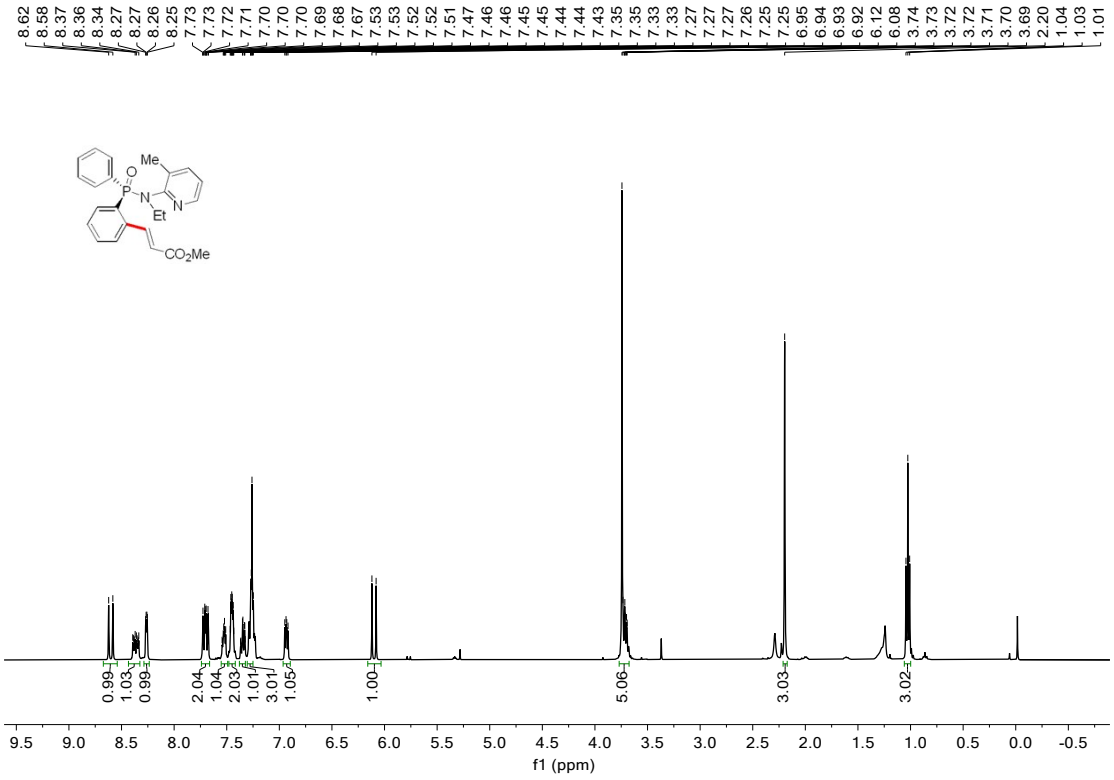
3l, ^{13}C NMR, 101 MHz, $CDCl_3$



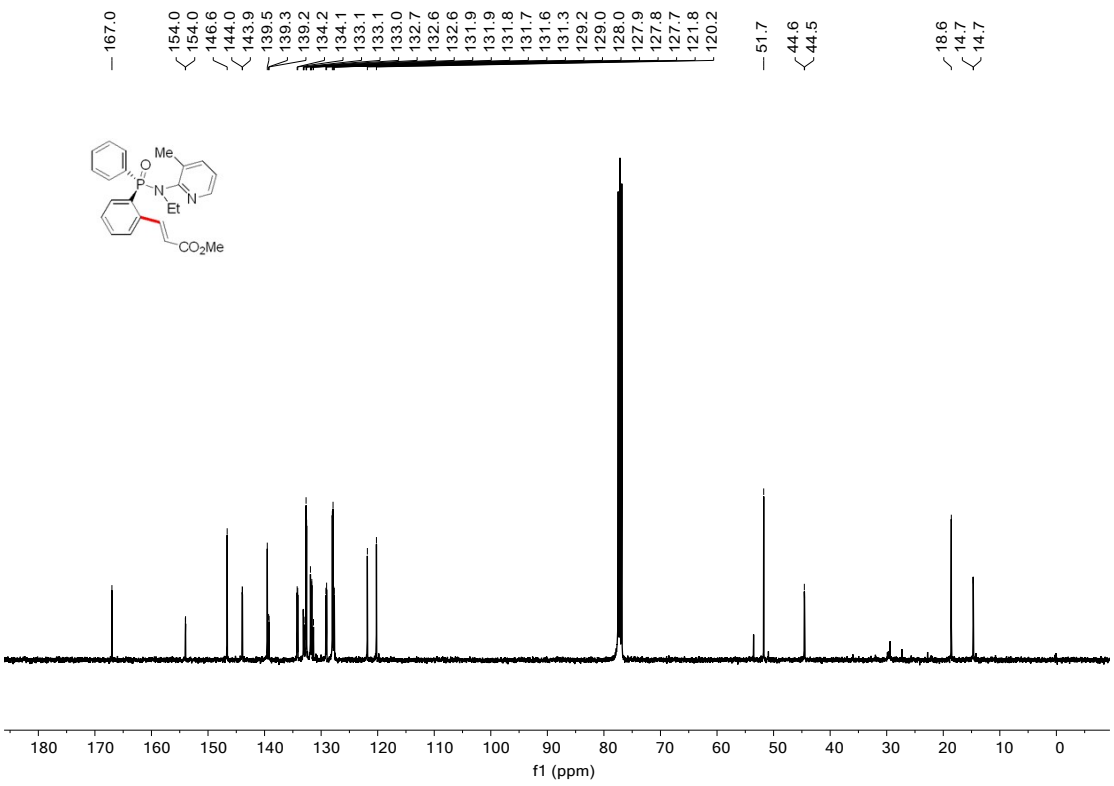
3l, ^{31}P NMR, 162 MHz, $CDCl_3$



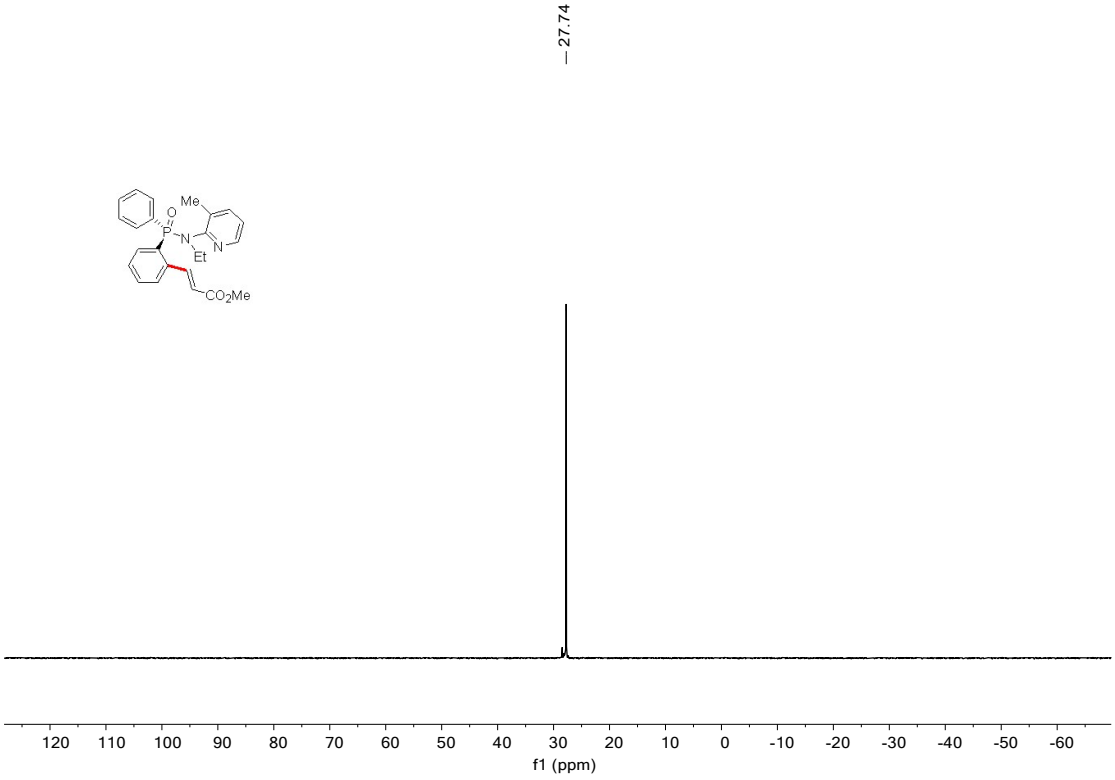
3m, ^{1}H NMR, 400 MHz, $CDCl_3$



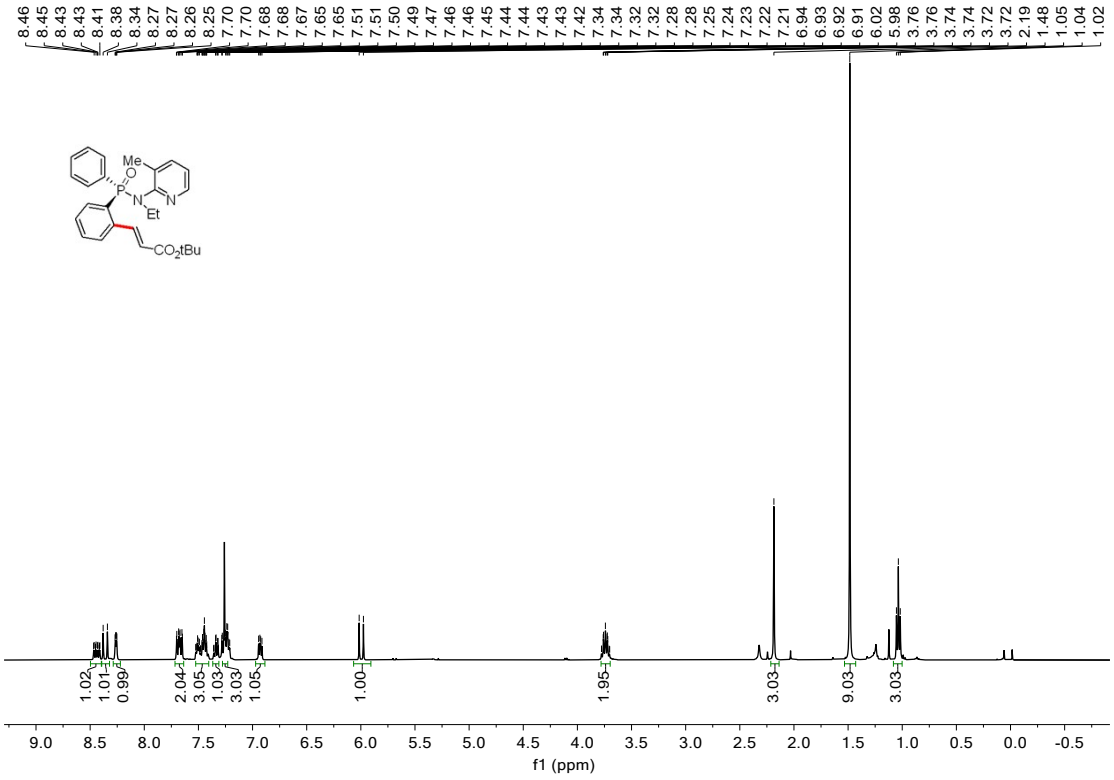
3m, ^{13}C NMR, 101 MHz, $CDCl_3$



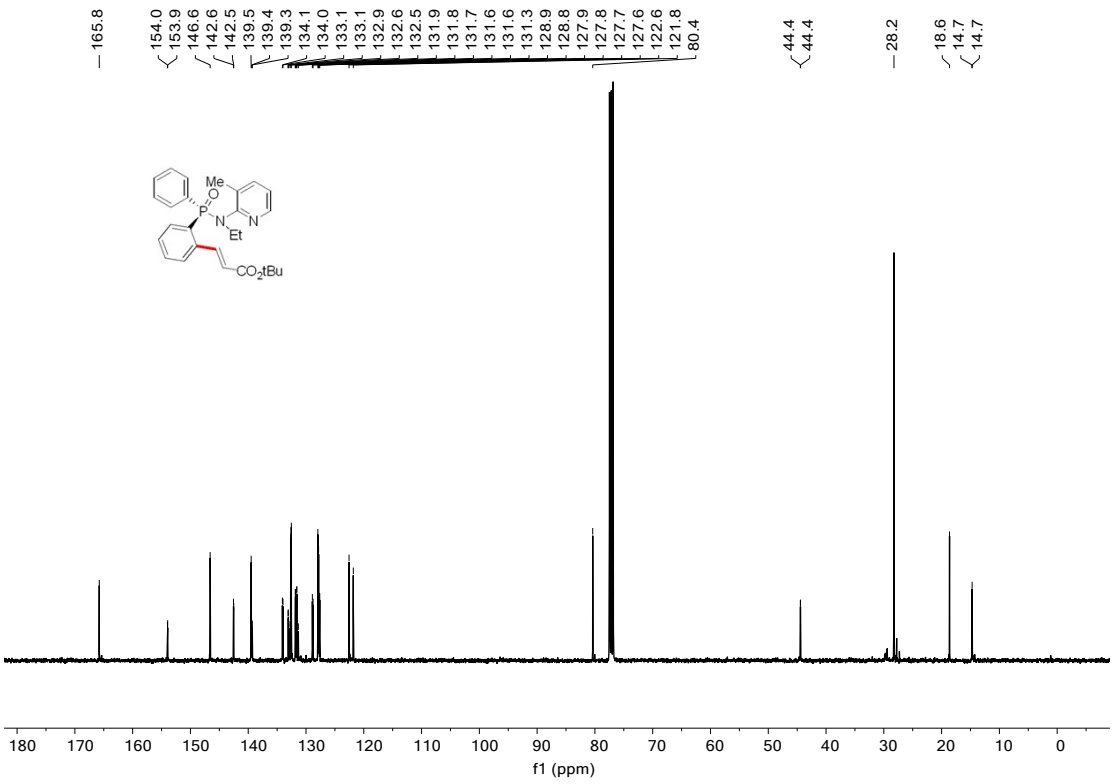
3m, ^{31}P NMR, 162 MHz, $CDCl_3$



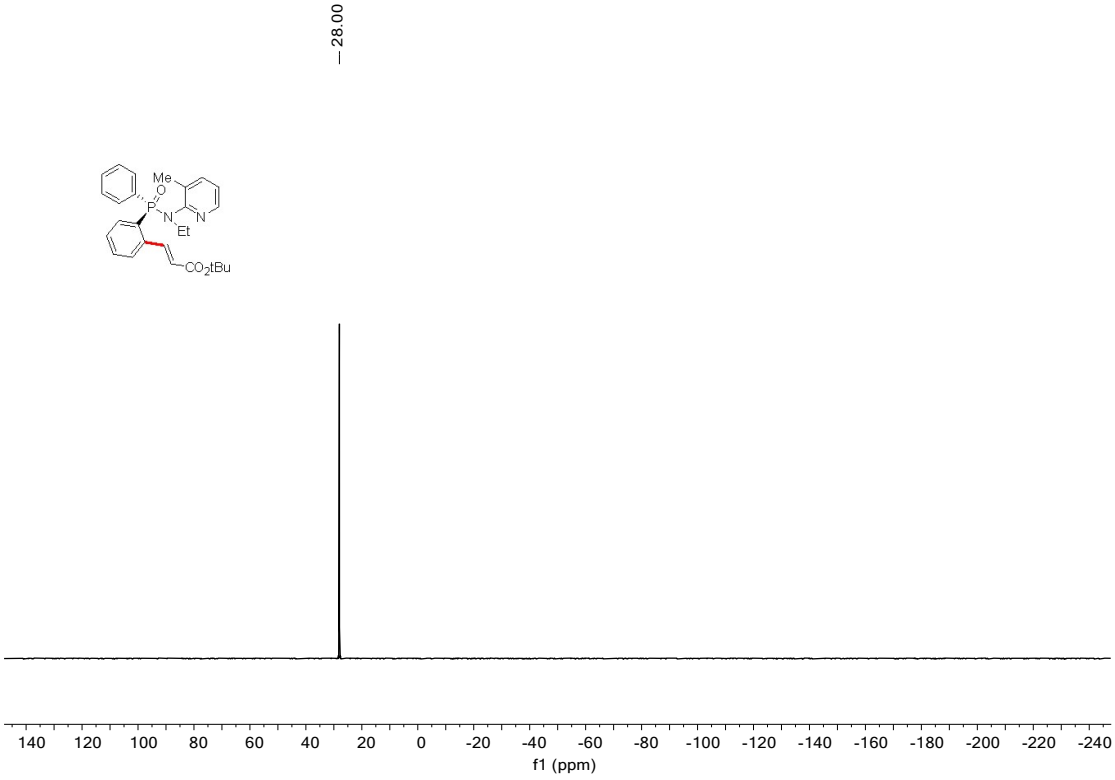
3n, ^{1}H NMR, 400 MHz, $CDCl_3$



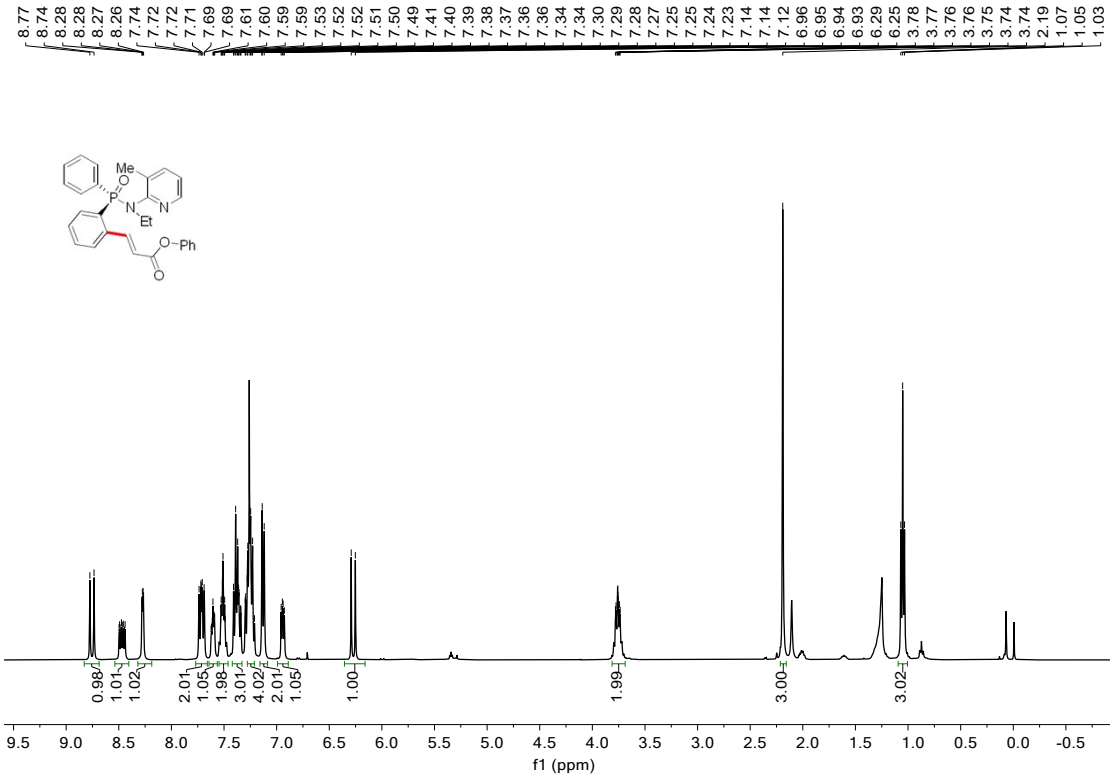
3n, ^{13}C NMR, 101 MHz, $CDCl_3$



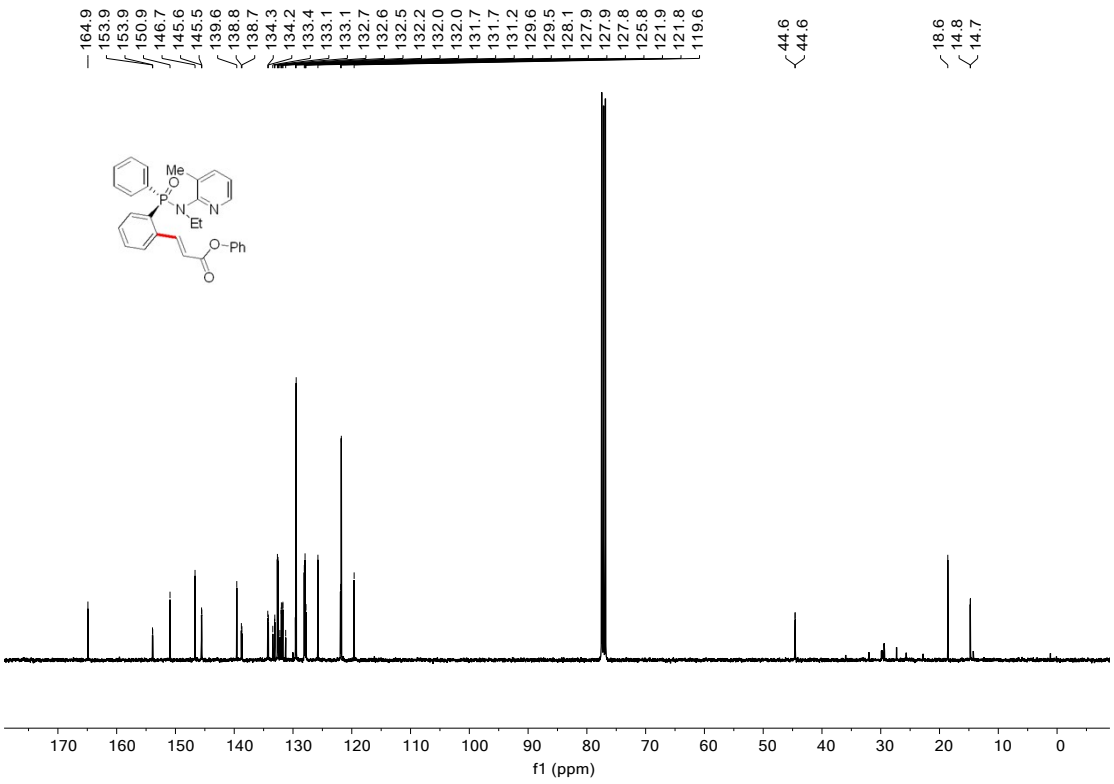
3n, ^{31}P NMR, 162 MHz, $CDCl_3$



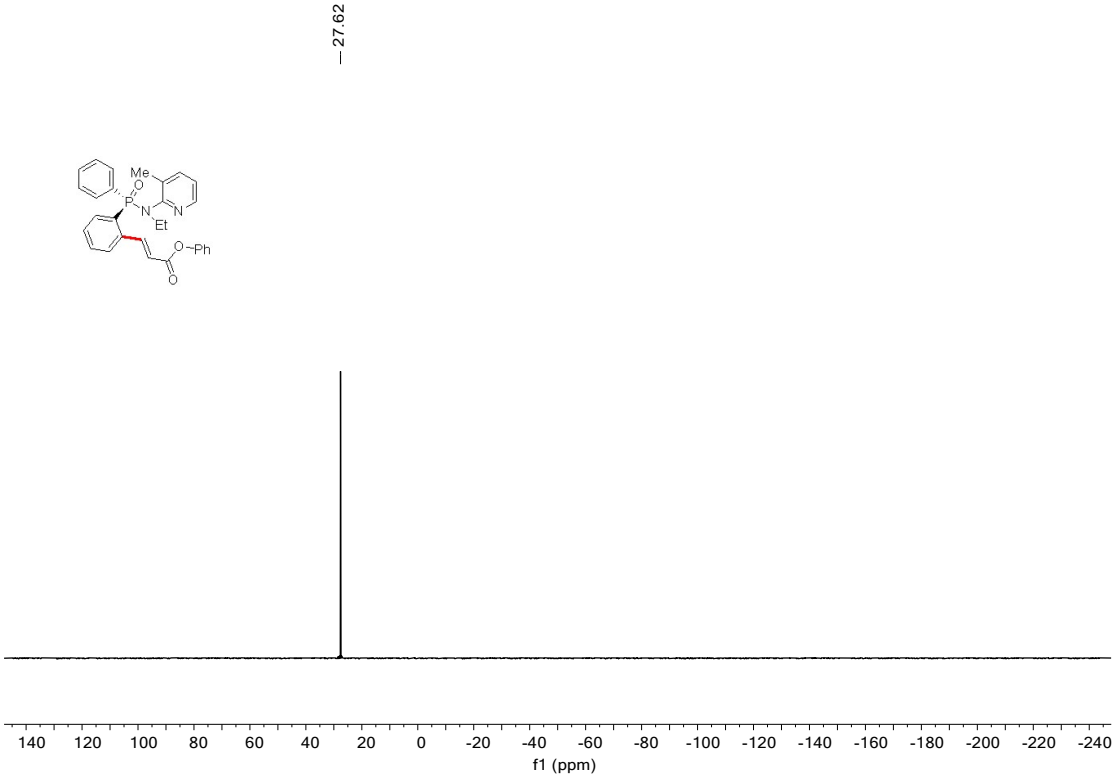
3o, ^{1}H NMR, 400 MHz, $CDCl_3$



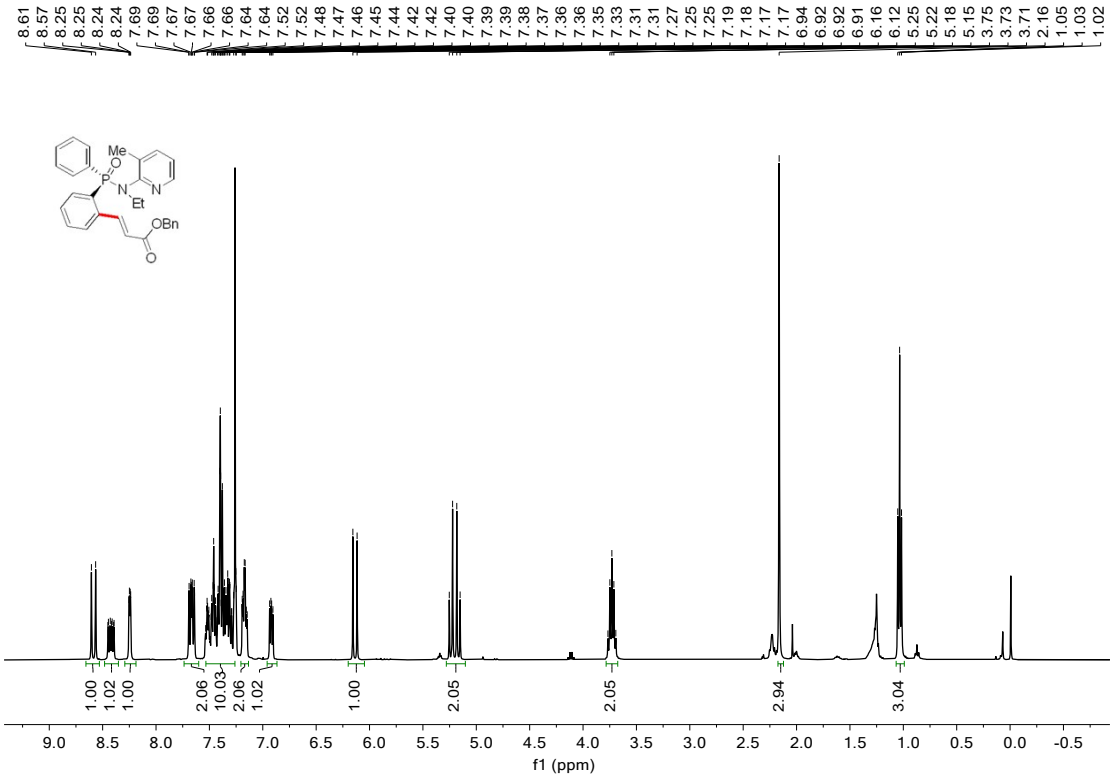
3o, ^{13}C NMR, 101 MHz, $CDCl_3$



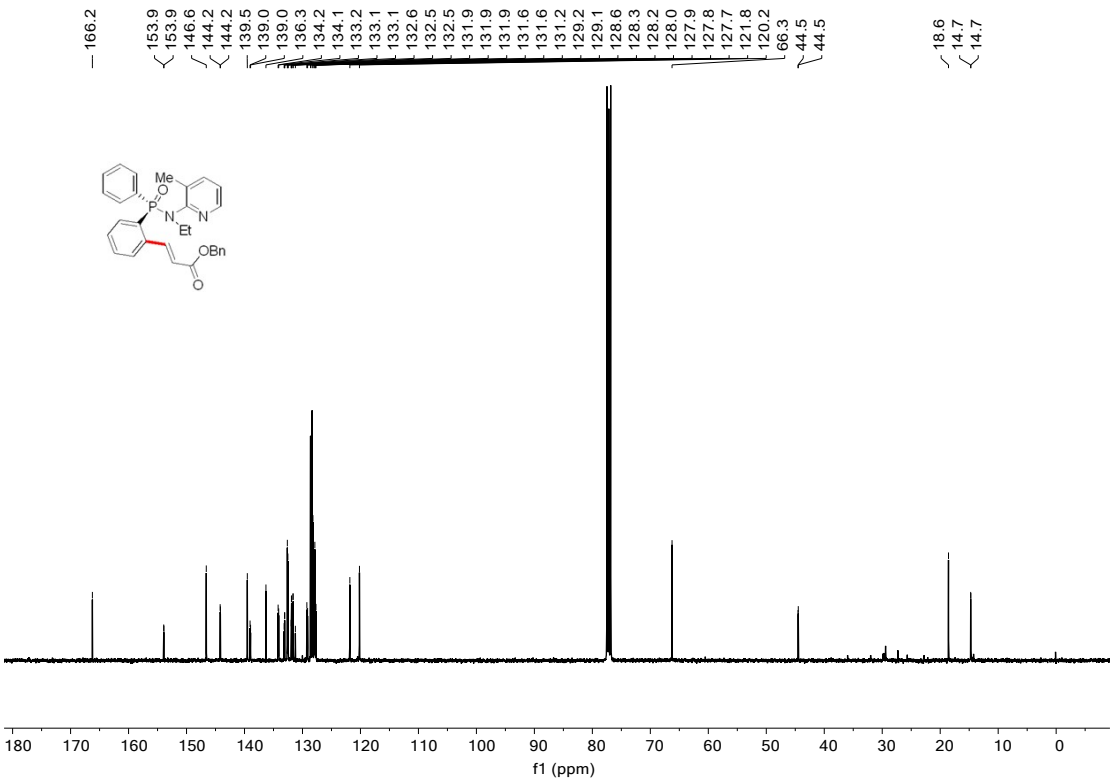
3o, ^{31}P NMR, 162 MHz, $CDCl_3$



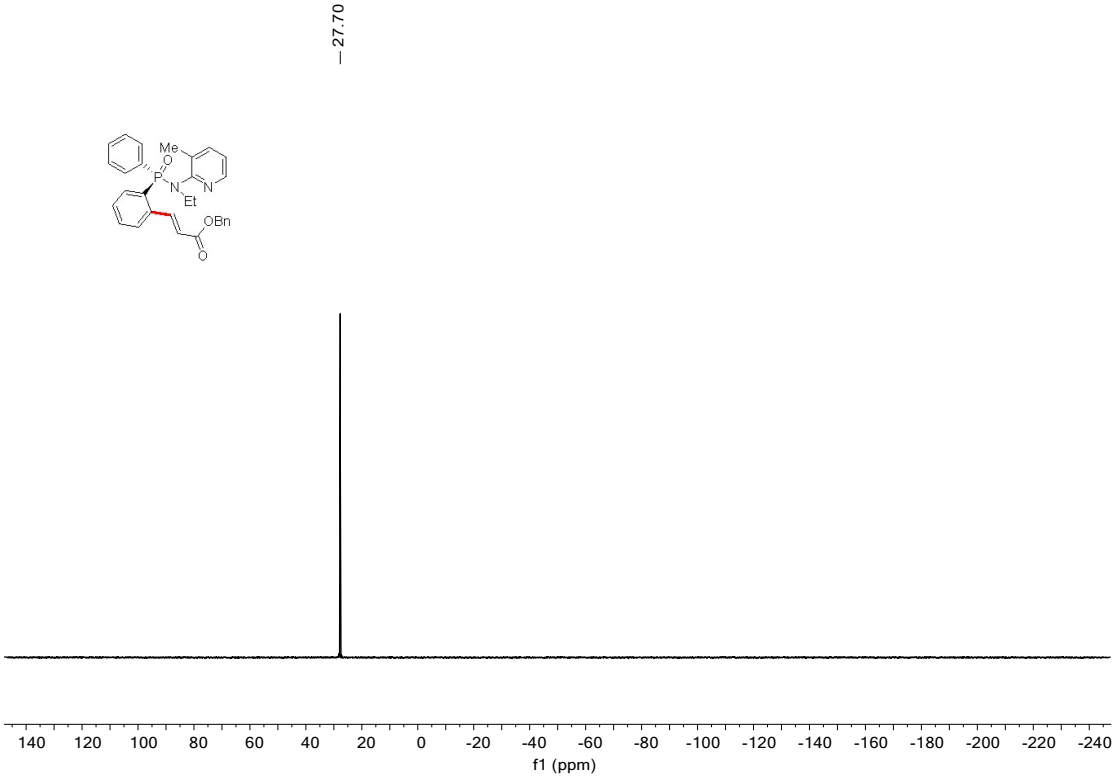
3p, ^{1}H NMR, 400 MHz, $CDCl_3$



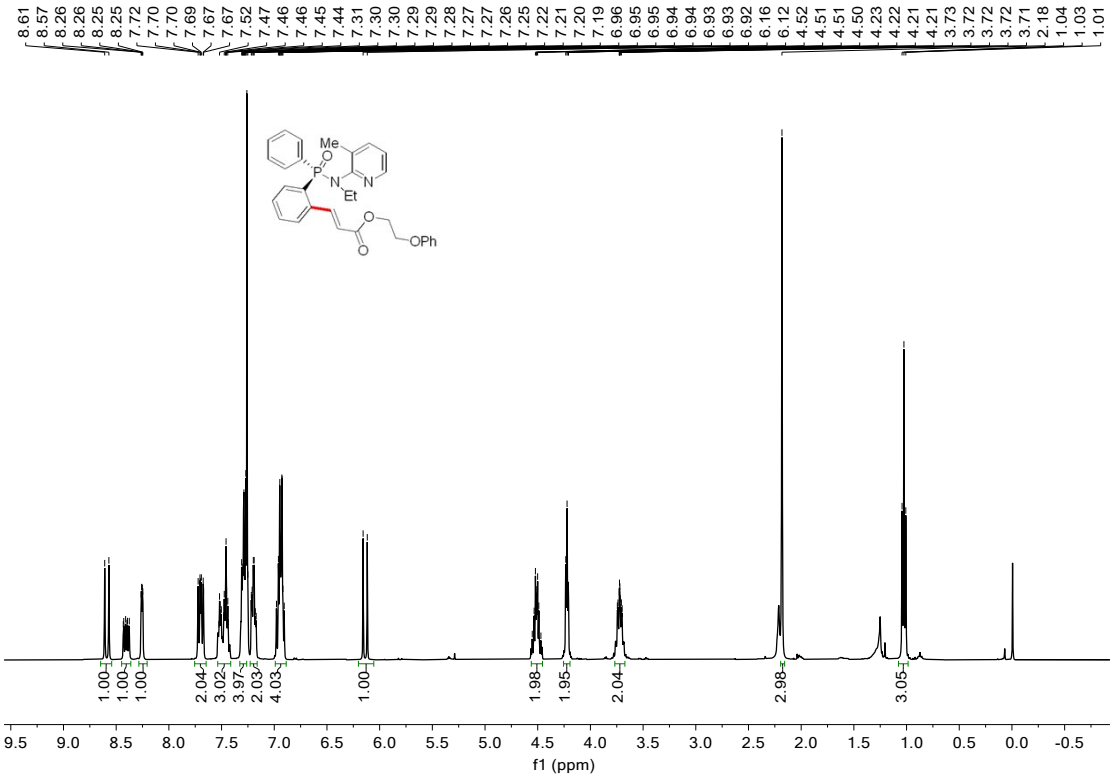
3p, ^{13}C NMR, 101 MHz, $CDCl_3$



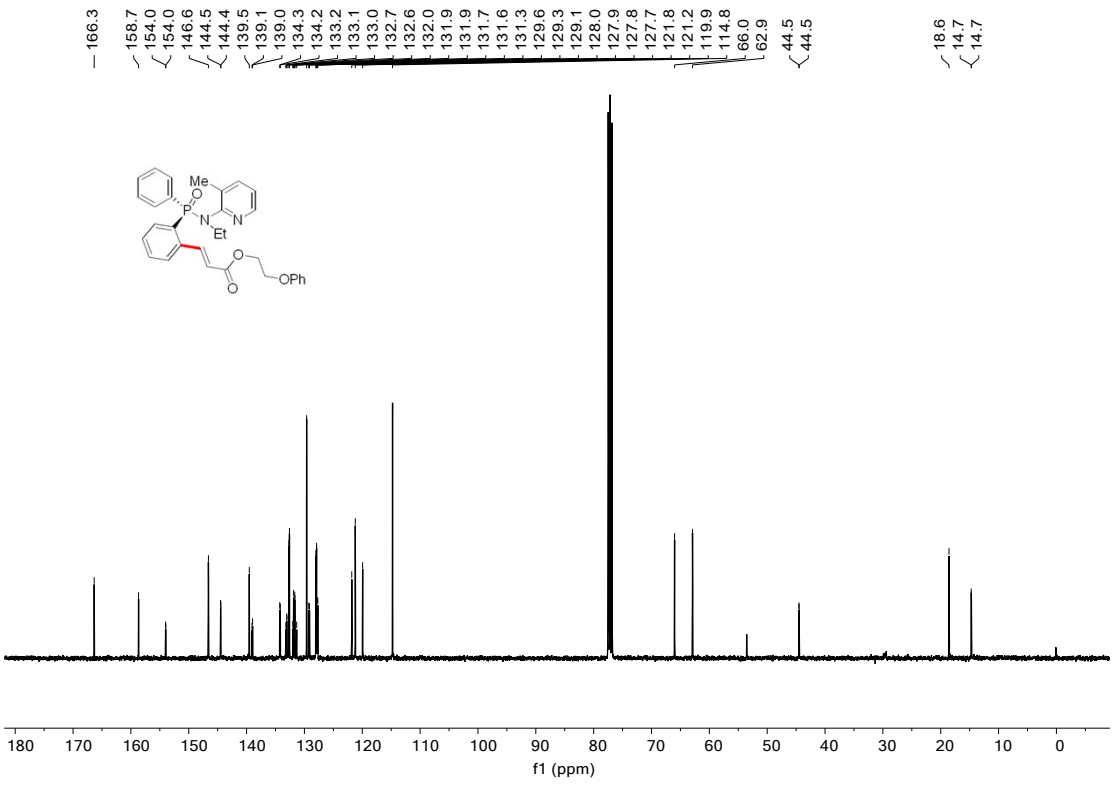
3p, ^{31}P NMR, 162 MHz, $CDCl_3$



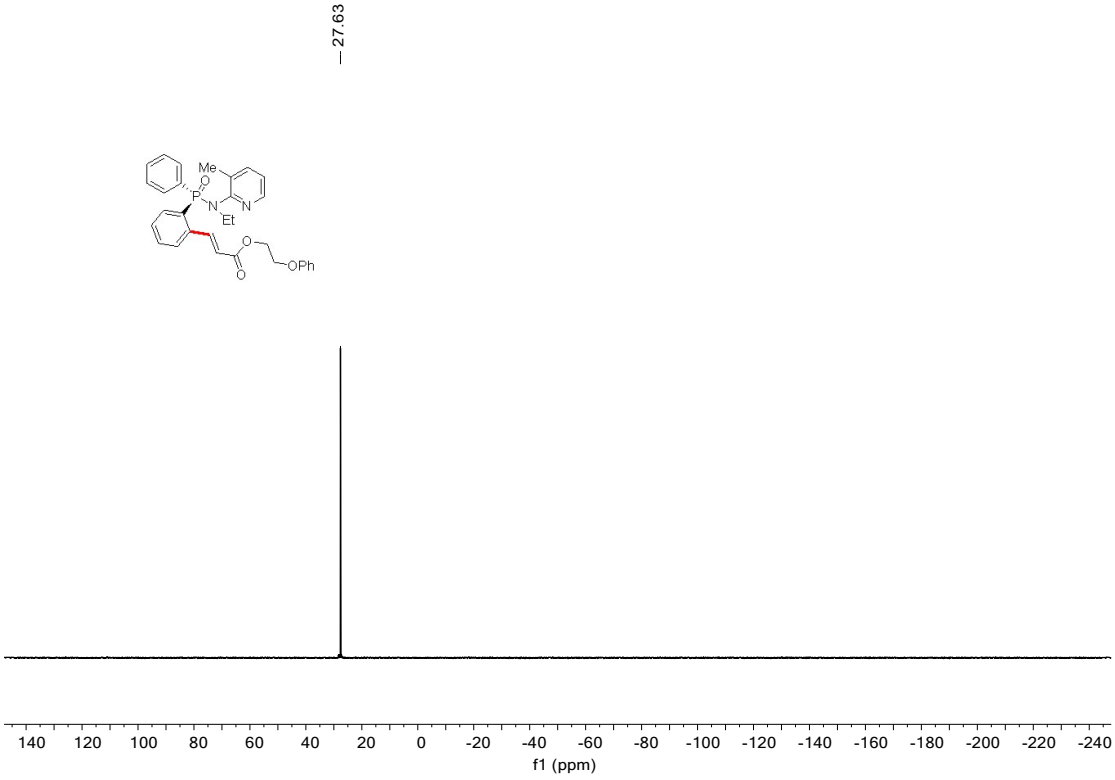
3q, ^{1}H NMR, 400 MHz, $CDCl_3$



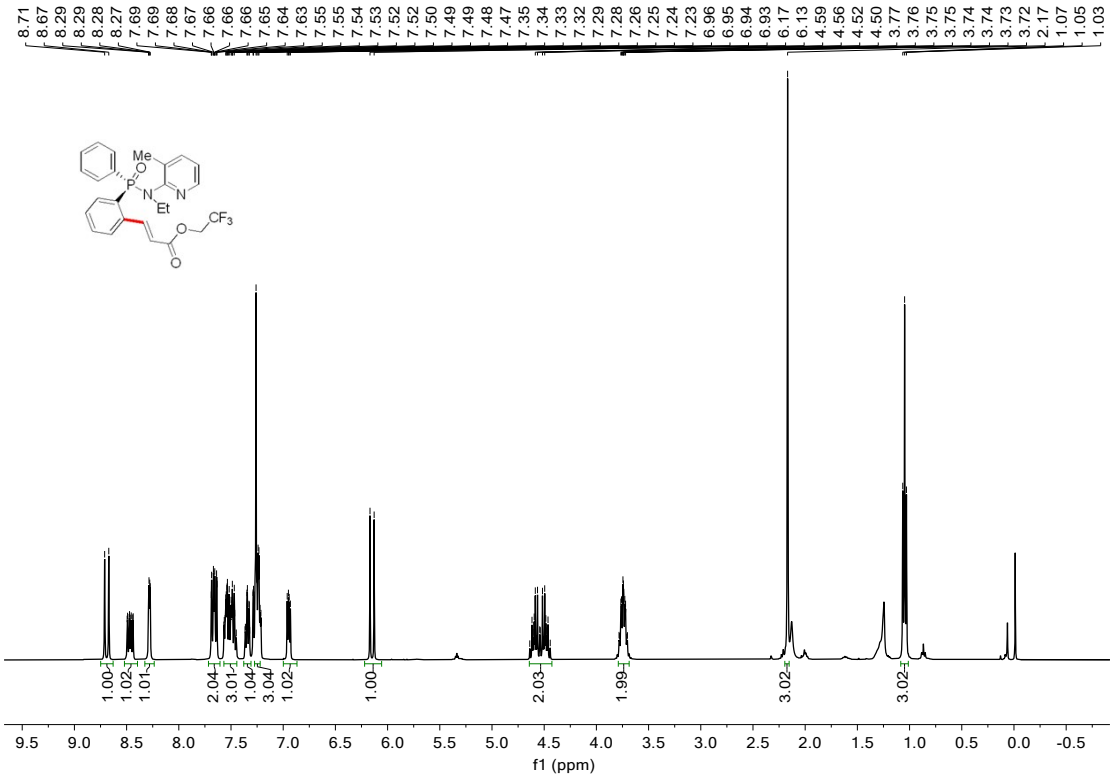
3q, ^{13}C NMR, 101 MHz, $CDCl_3$



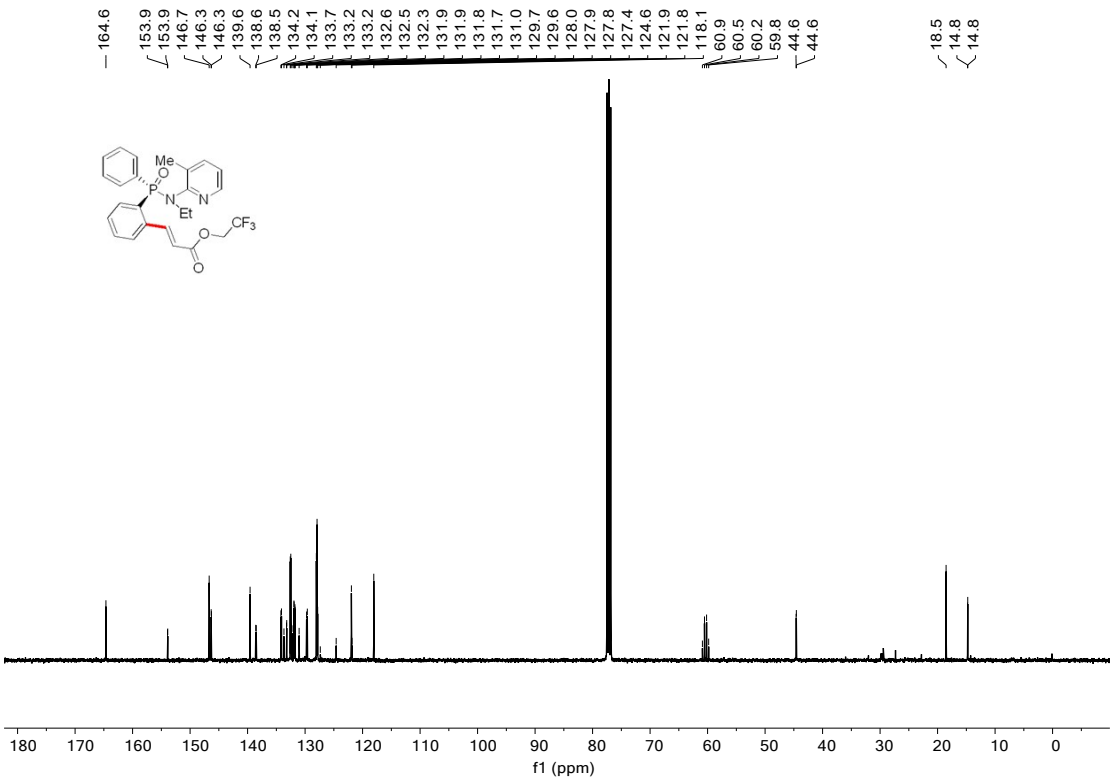
3q, ^{31}P NMR, 162 MHz, $CDCl_3$



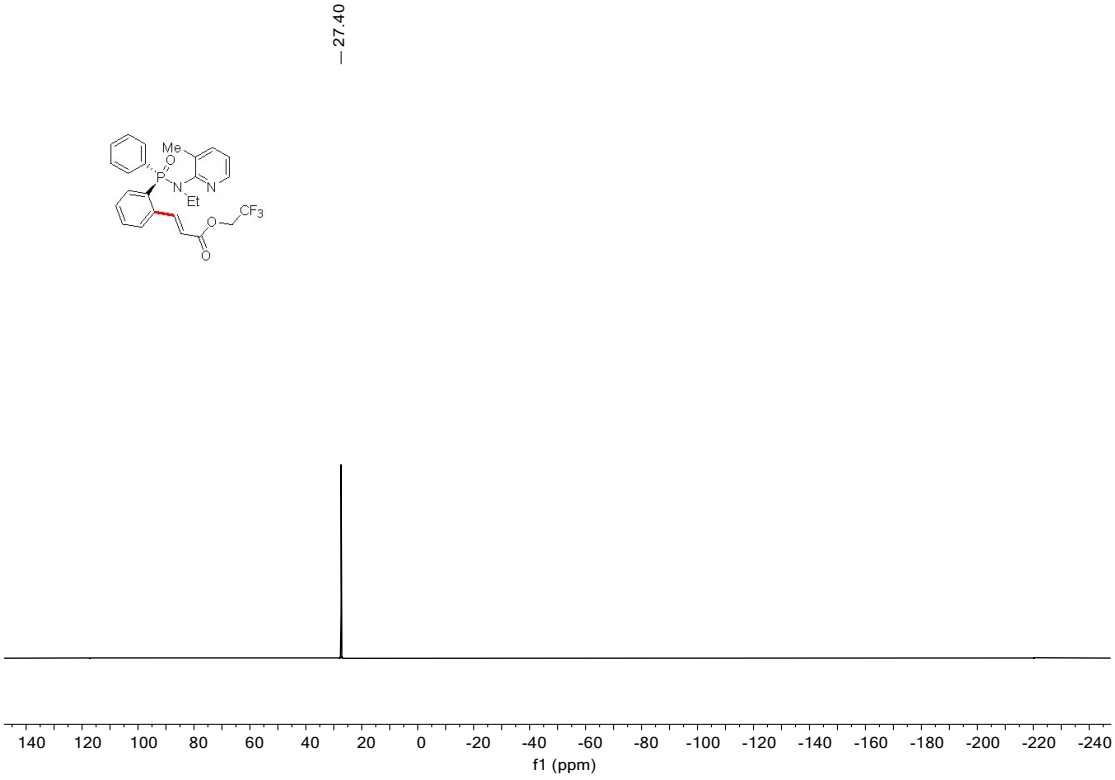
3r, ^{1}H NMR, 400 MHz, $CDCl_3$



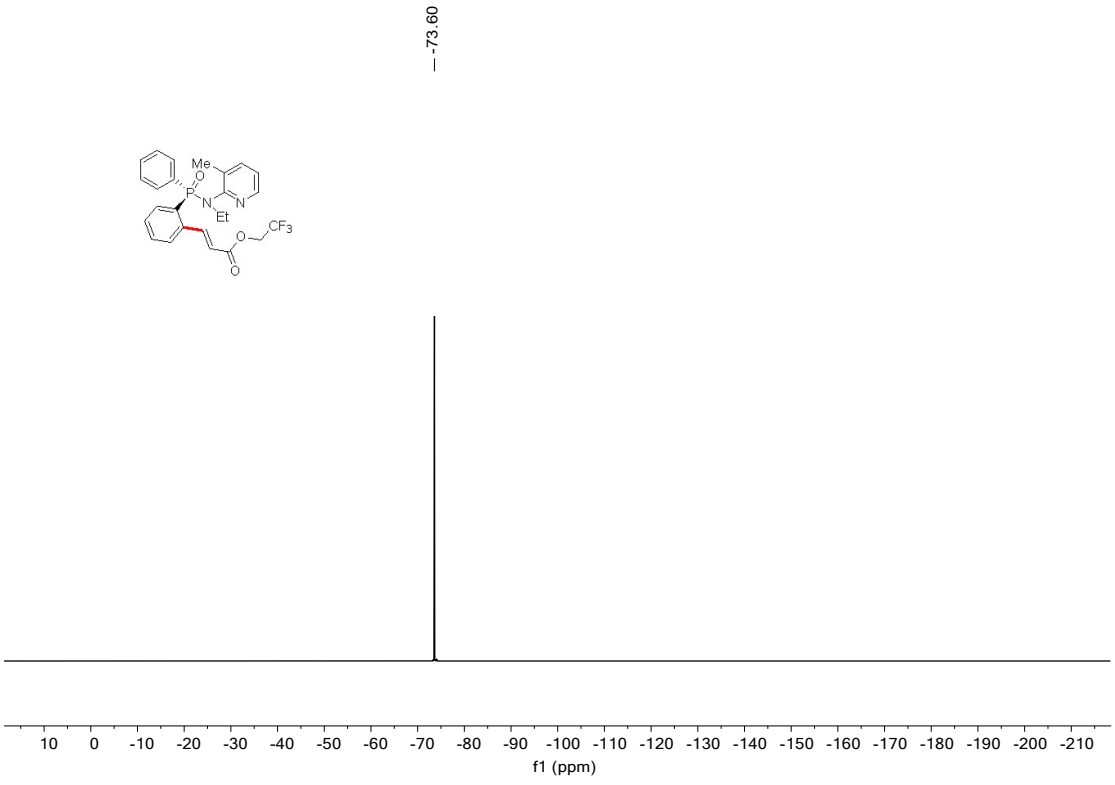
3r, ^{13}C NMR, 101 MHz, $CDCl_3$



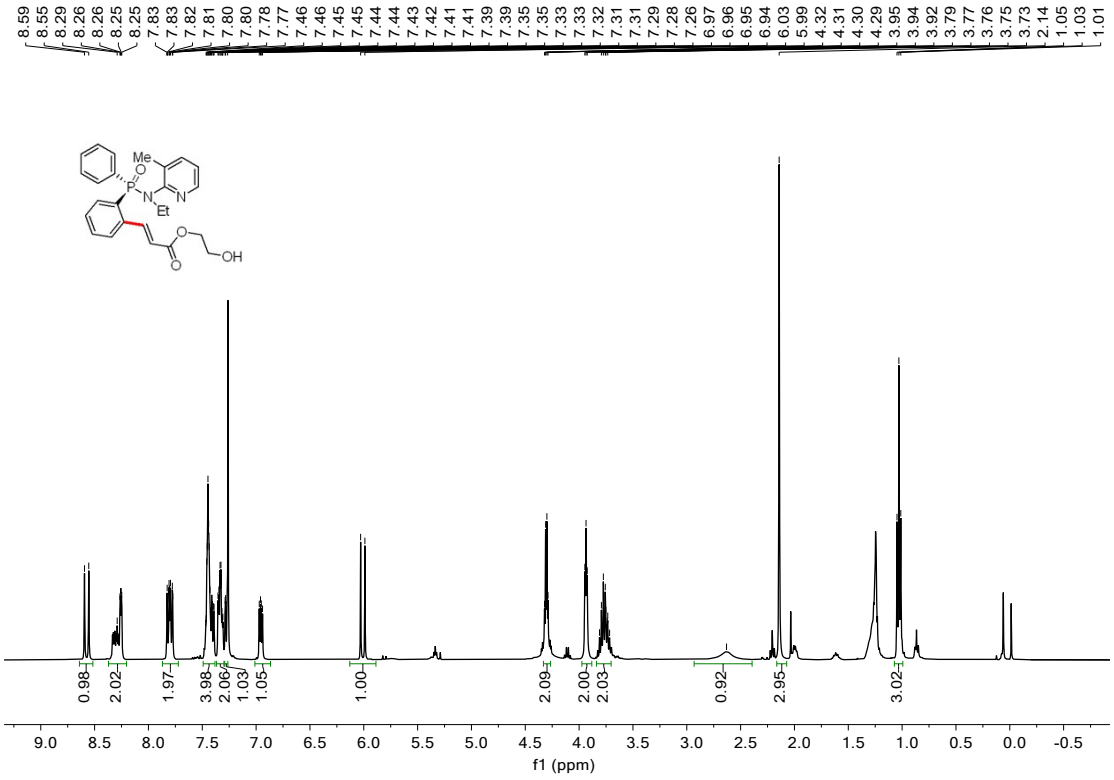
3r, ^{31}P NMR, 162 MHz, $CDCl_3$



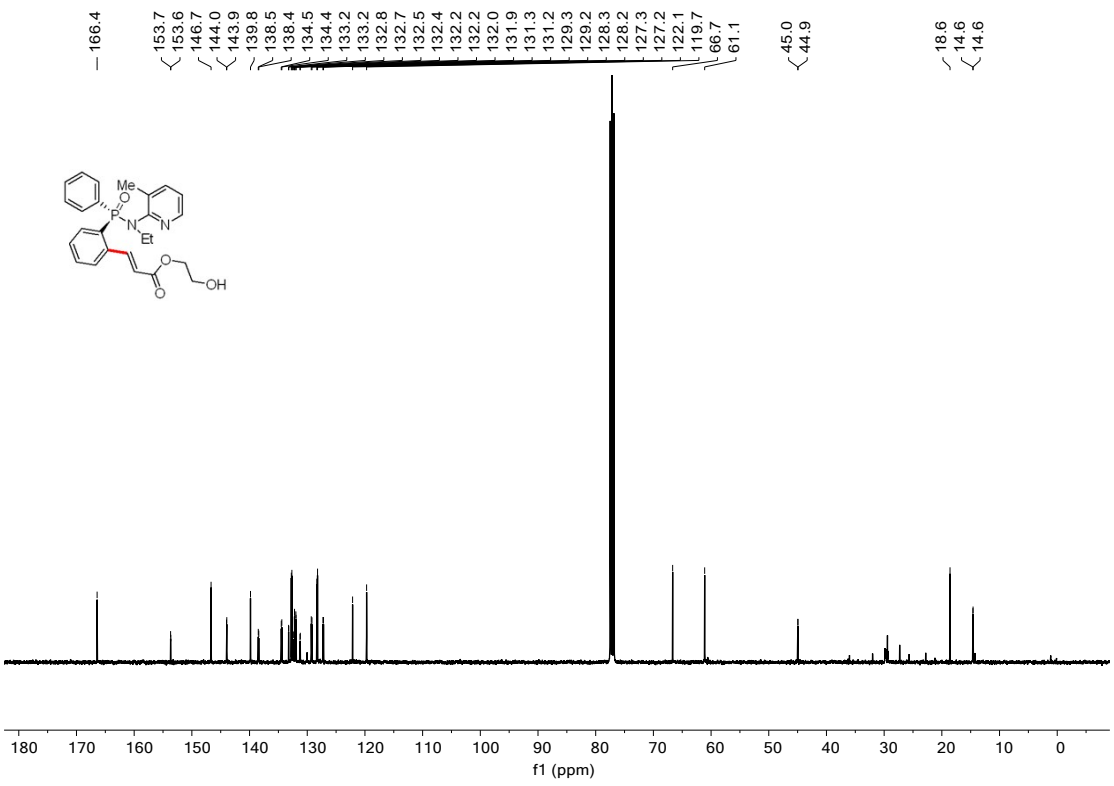
3r, ^{19}F NMR, 376 MHz, $CDCl_3$



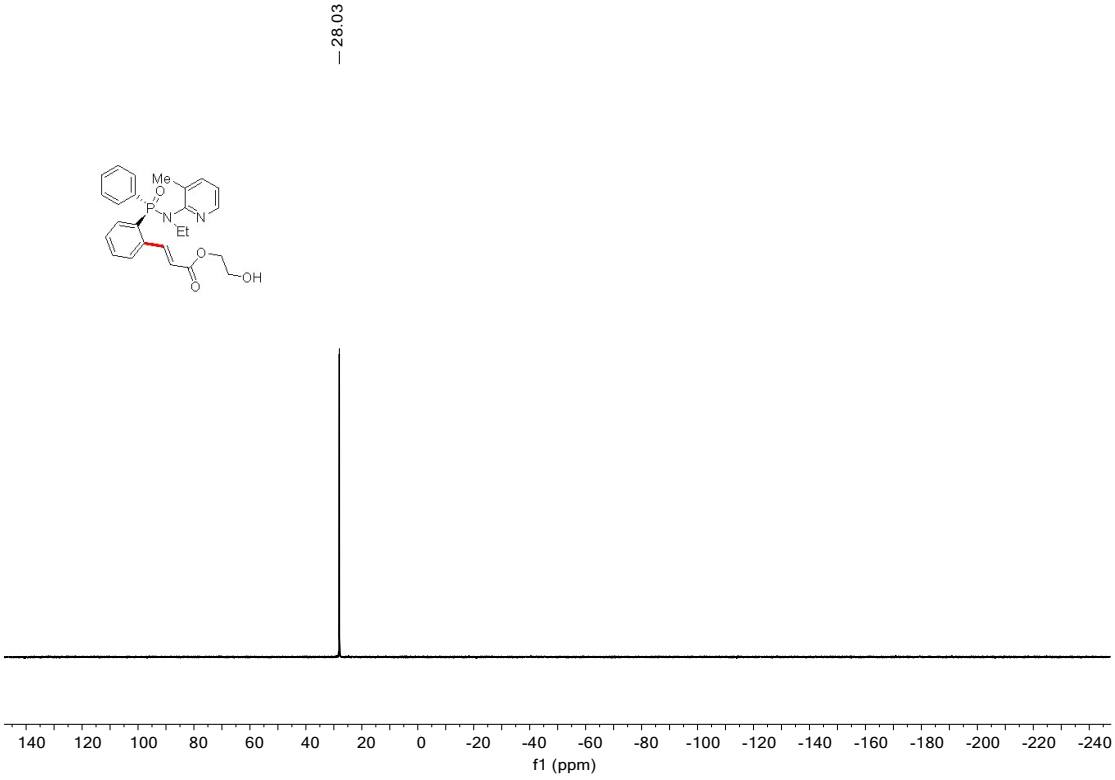
3s, ^{1}H NMR, 400 MHz, $CDCl_3$



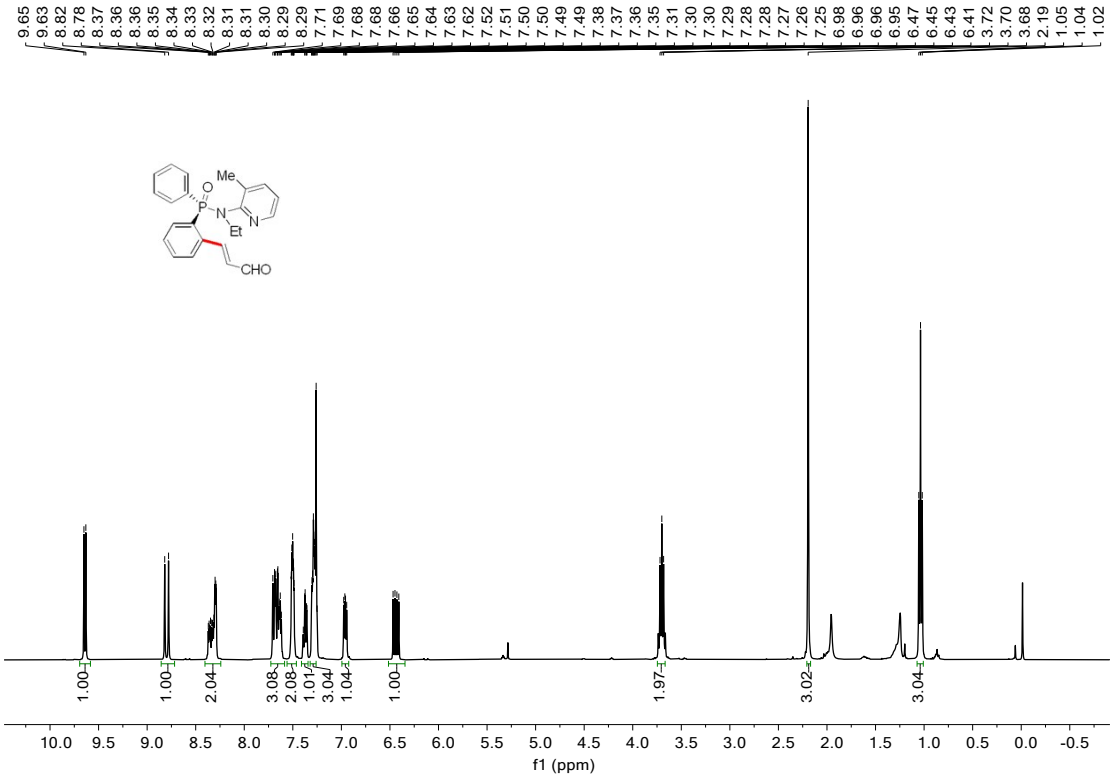
3s, ^{13}C NMR, 101 MHz, $CDCl_3$



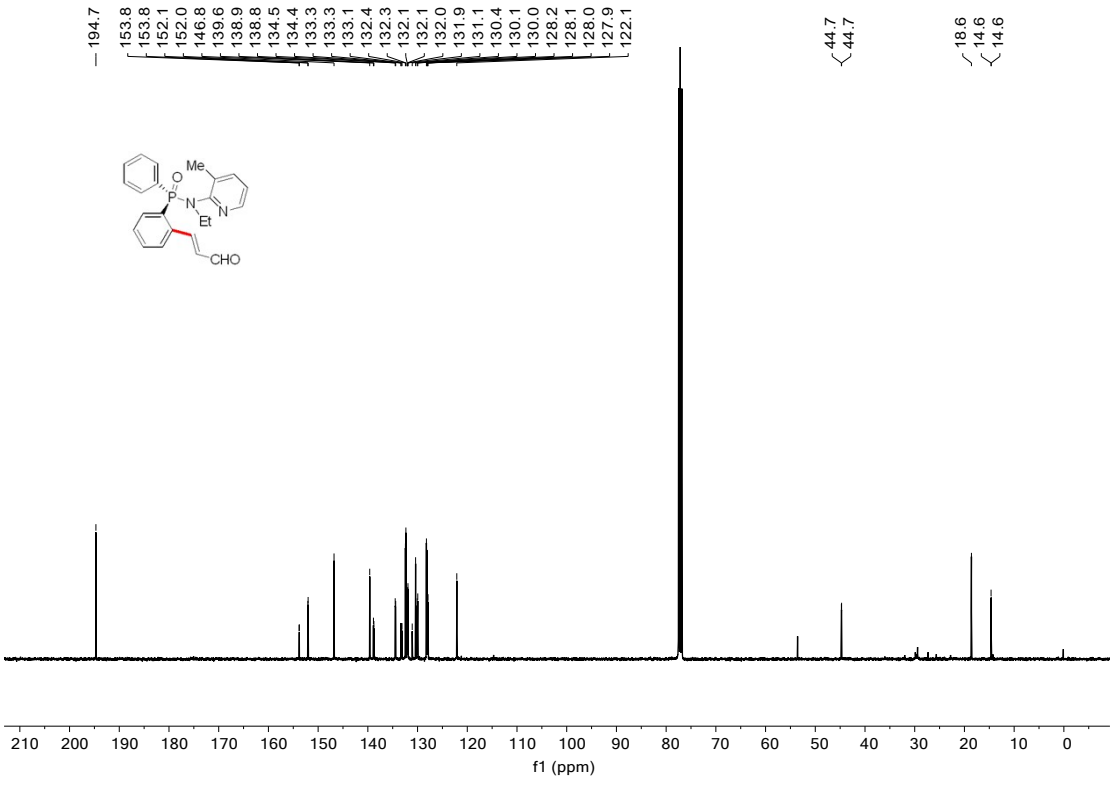
3s, ^{31}P NMR, 162 MHz, $CDCl_3$



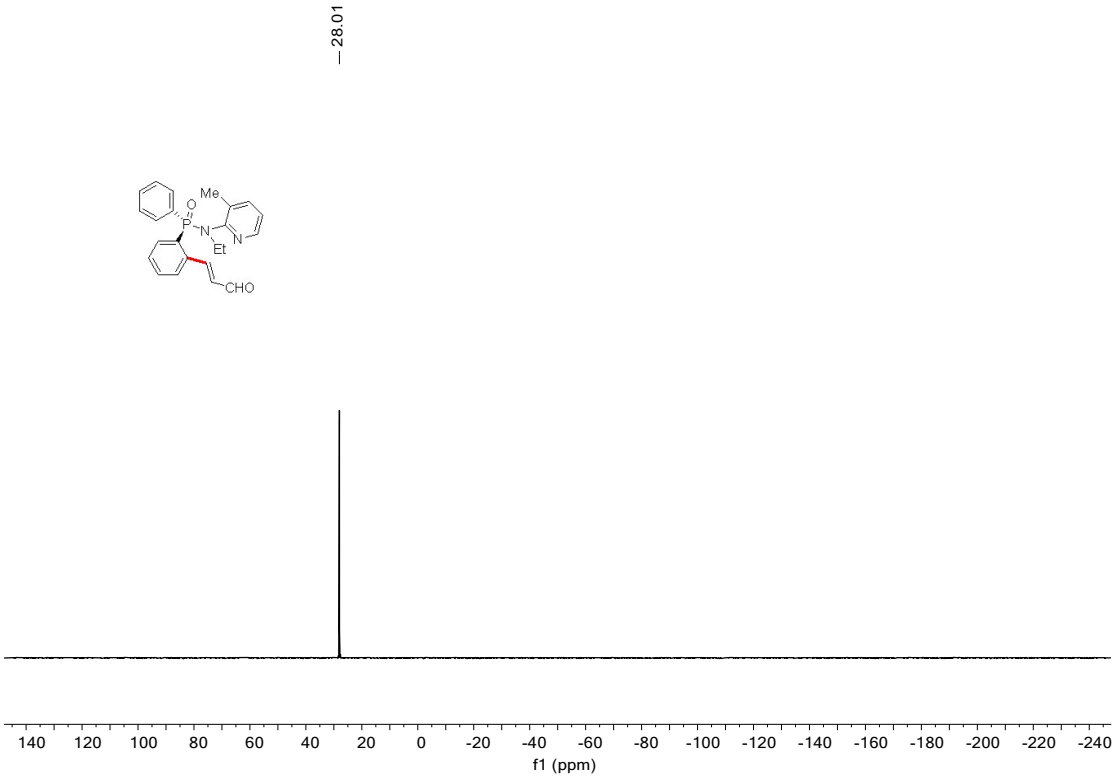
3t, ^{1}H NMR, 400 MHz, $CDCl_3$



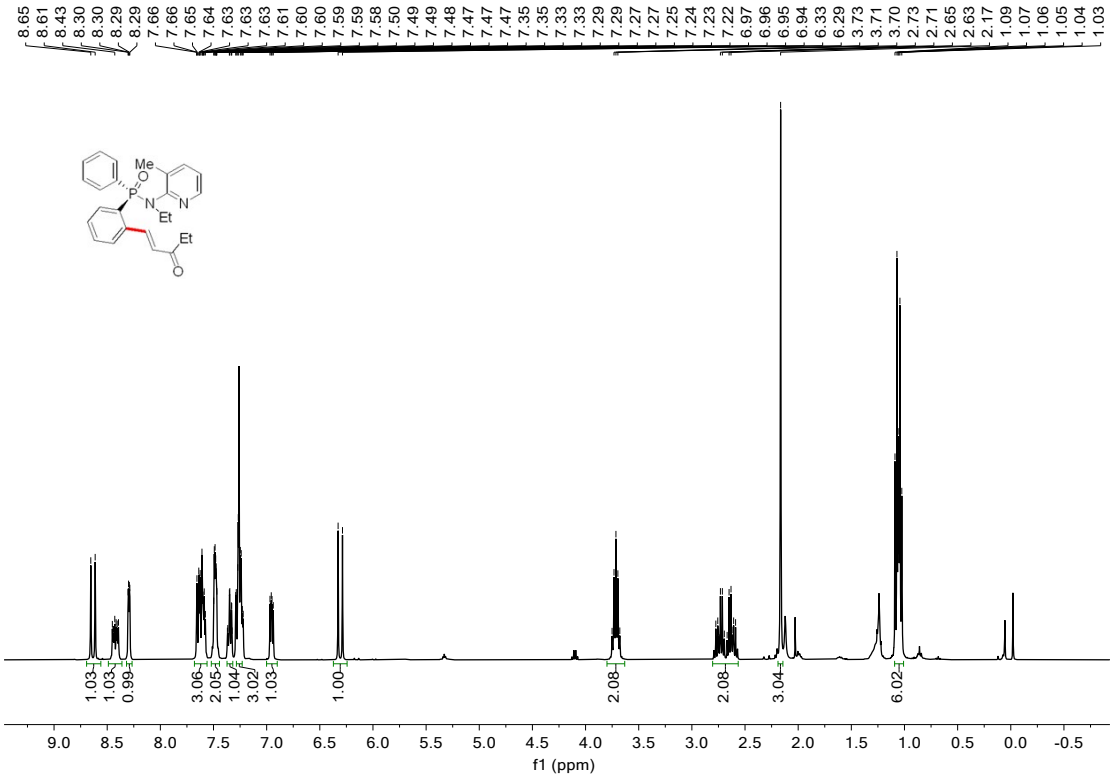
3t, ^{13}C NMR, 101 MHz, $CDCl_3$



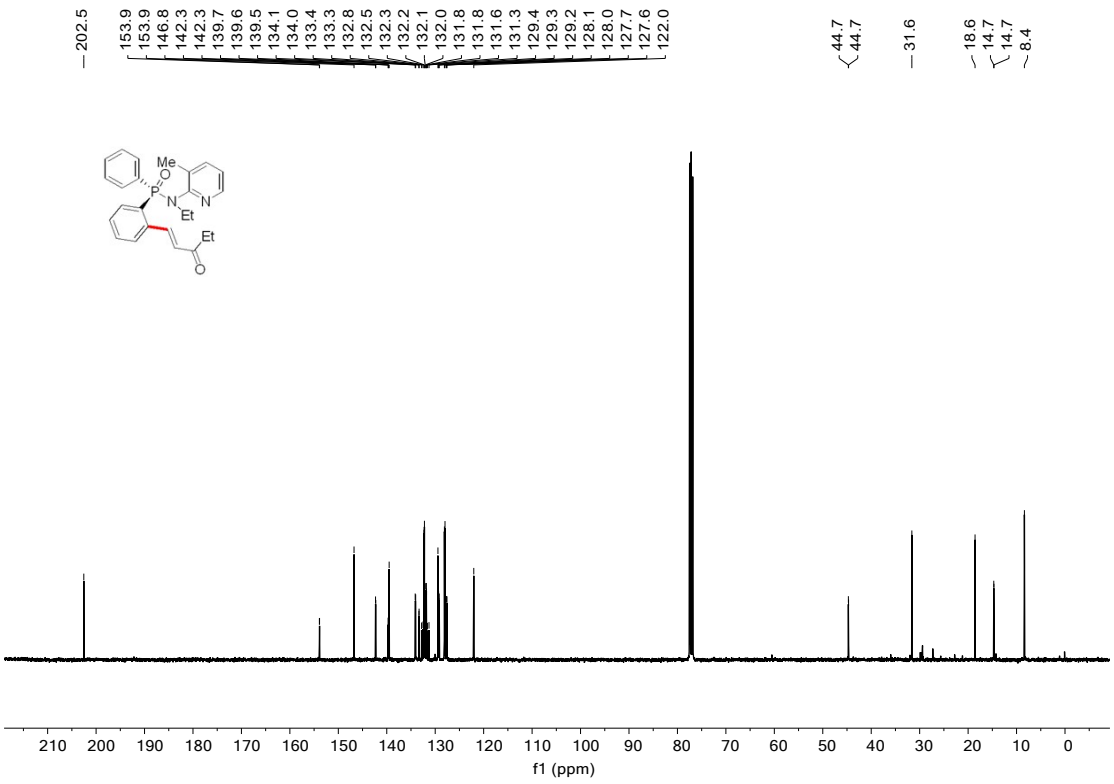
3t, ^{31}P NMR, 162 MHz, $CDCl_3$



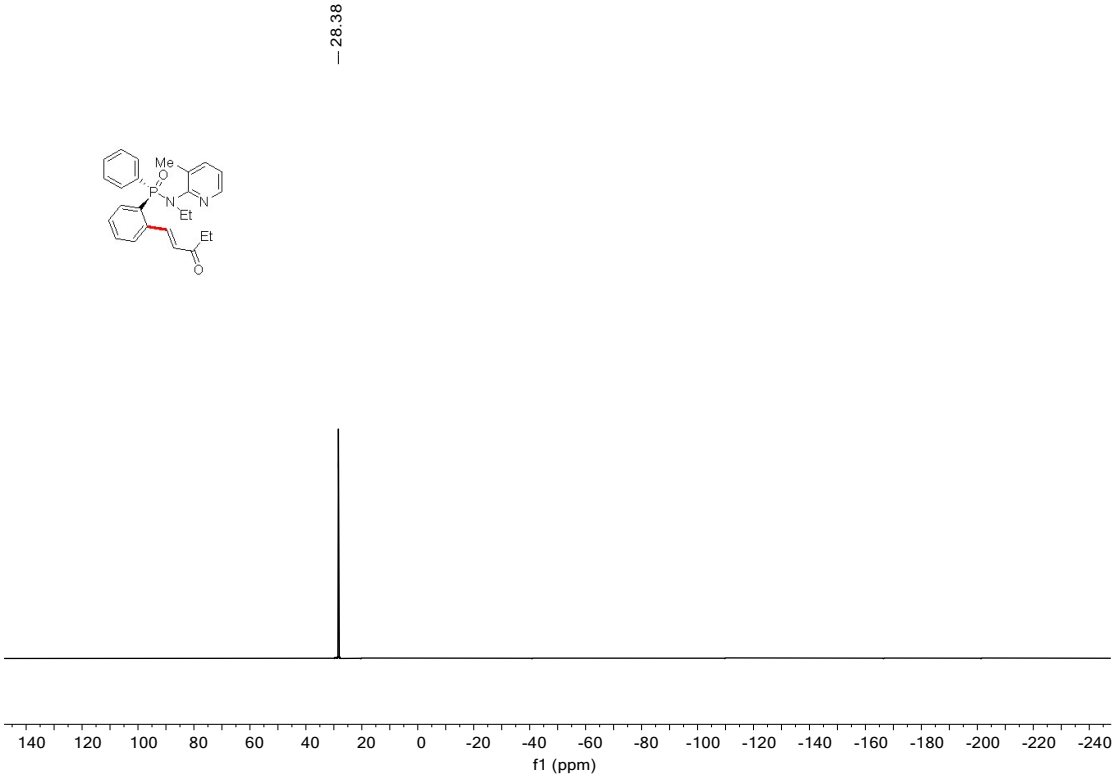
3u, ^{1}H NMR, 400 MHz, $CDCl_3$



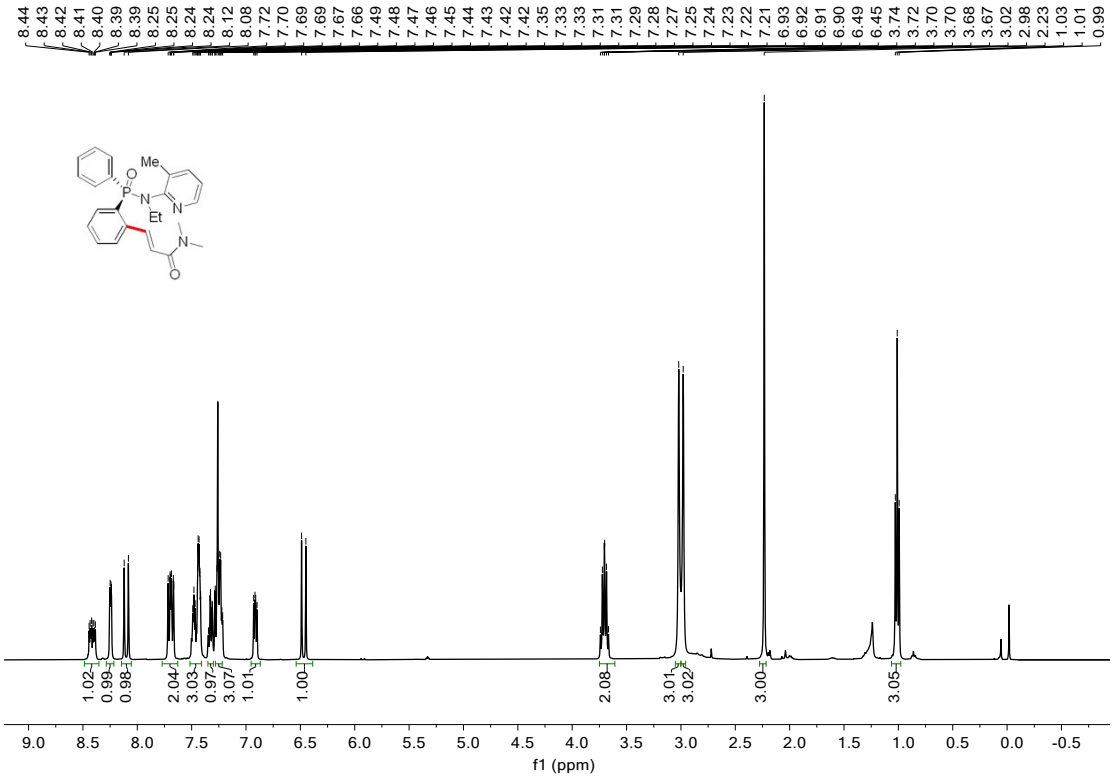
3u, ^{13}C NMR, 101 MHz, $CDCl_3$



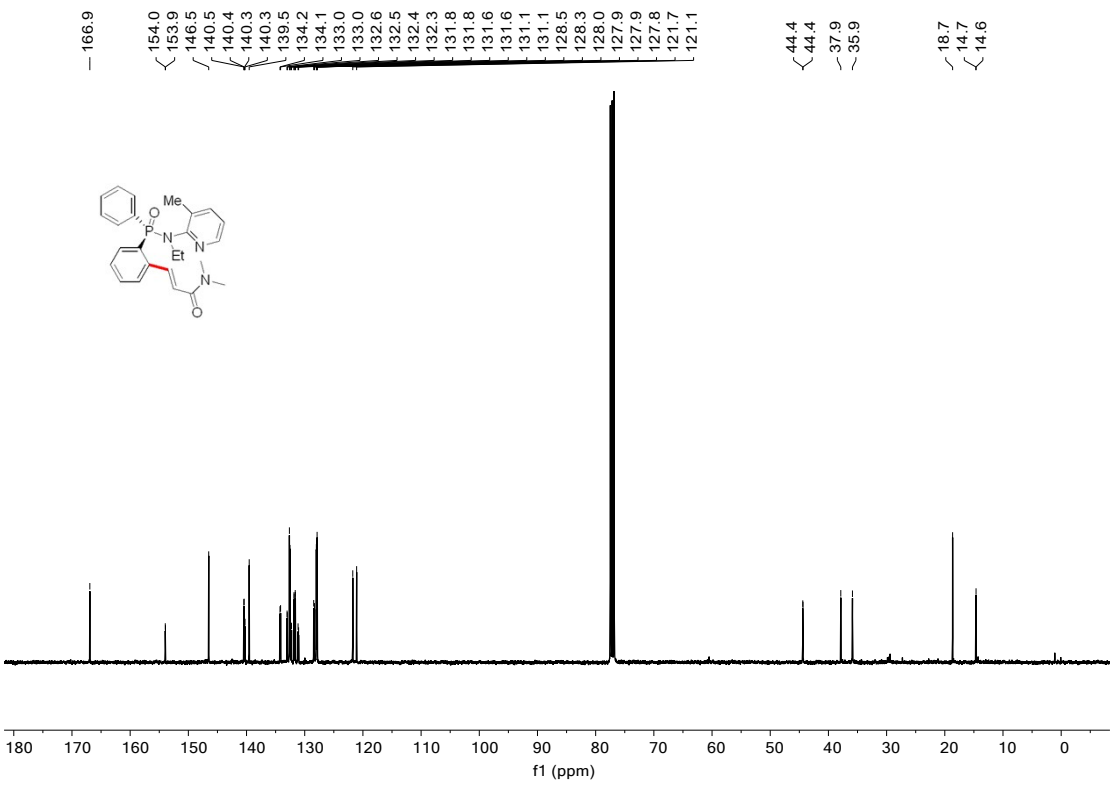
3u, ^{31}P NMR, 162 MHz, $CDCl_3$



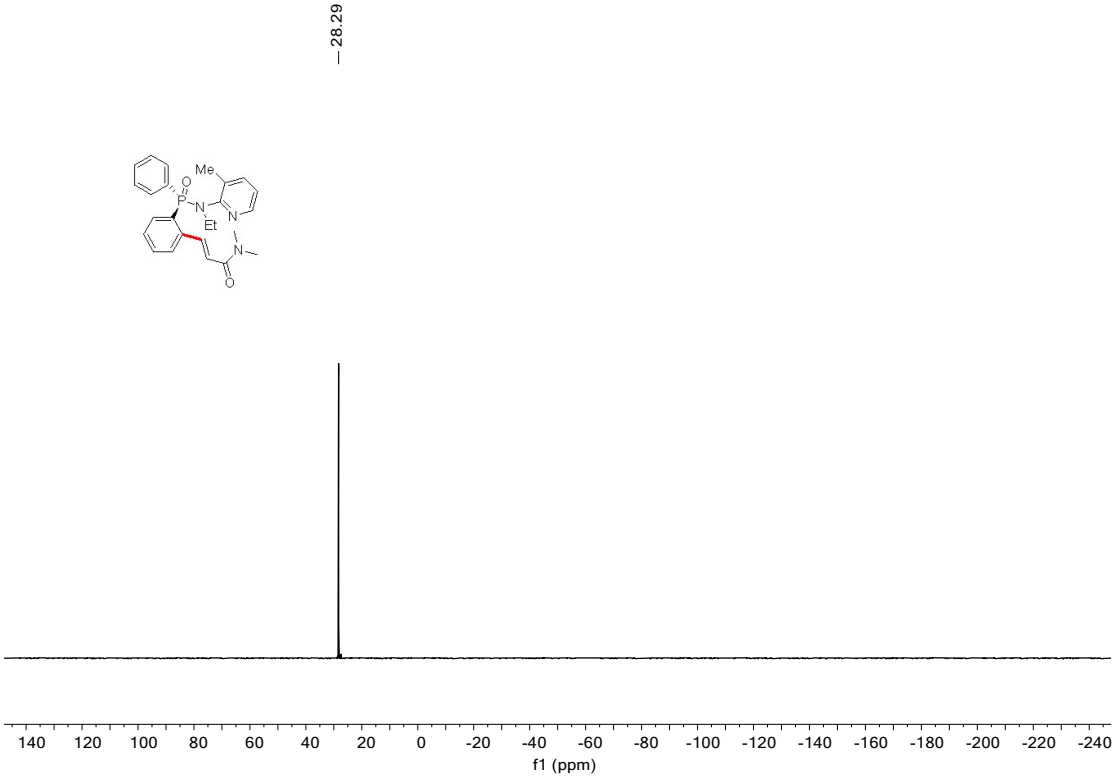
3v, ^{1}H NMR, 400 MHz, $CDCl_3$



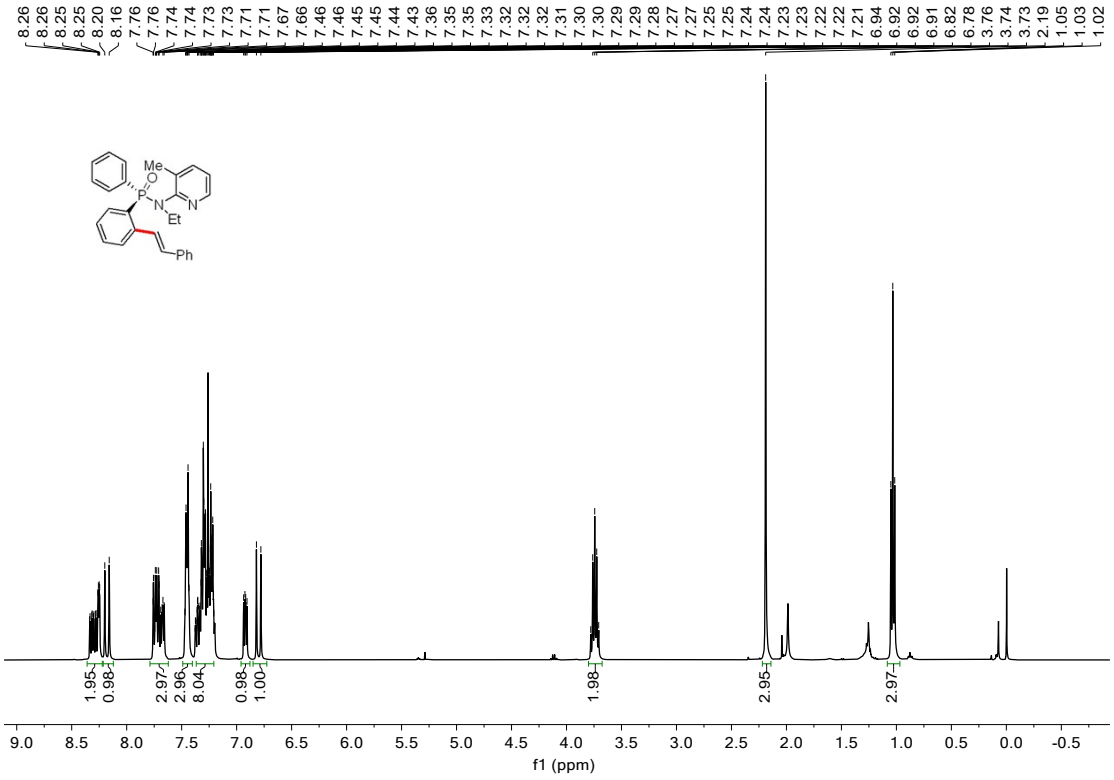
3v, ^{13}C NMR, 101 MHz, $CDCl_3$



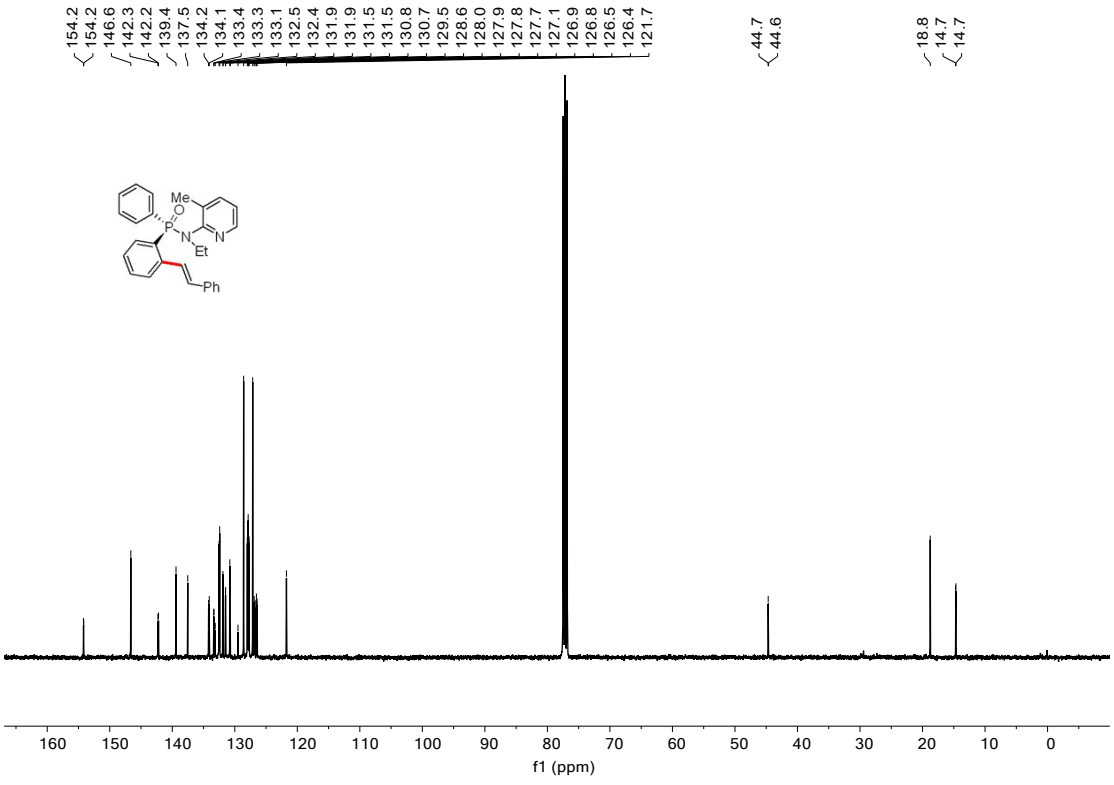
3v, ^{31}P NMR, 162 MHz, $CDCl_3$



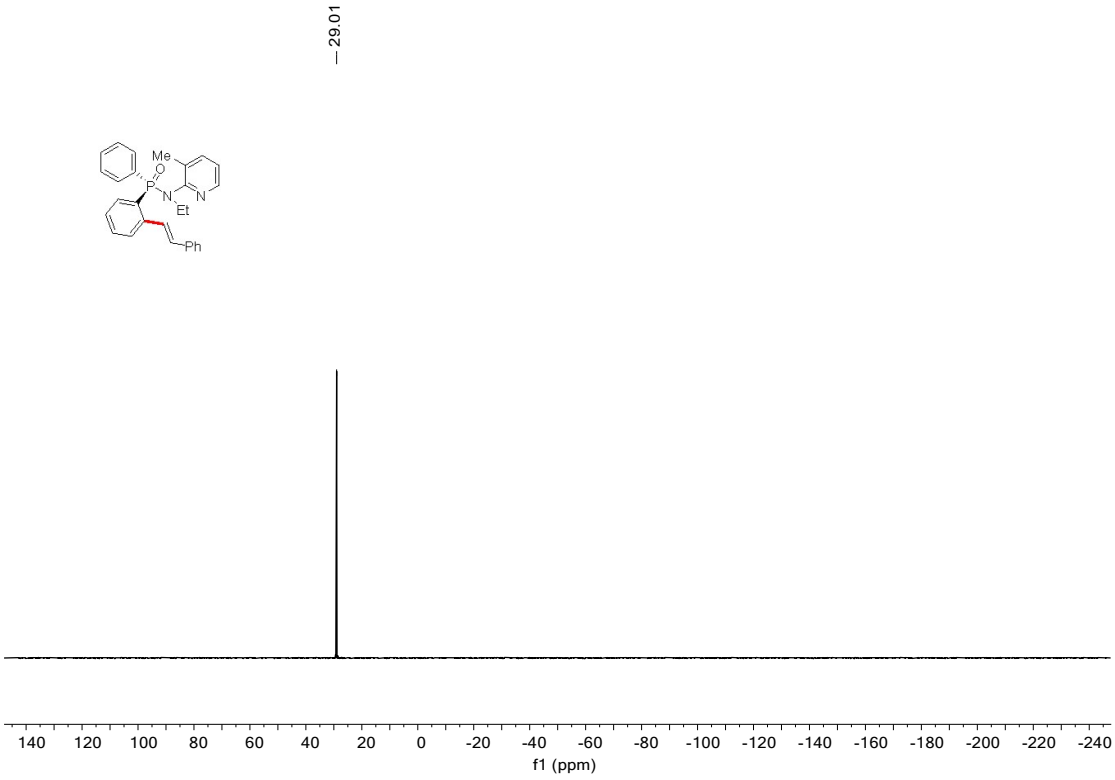
3w, ^{1}H NMR, 400 MHz, $CDCl_3$



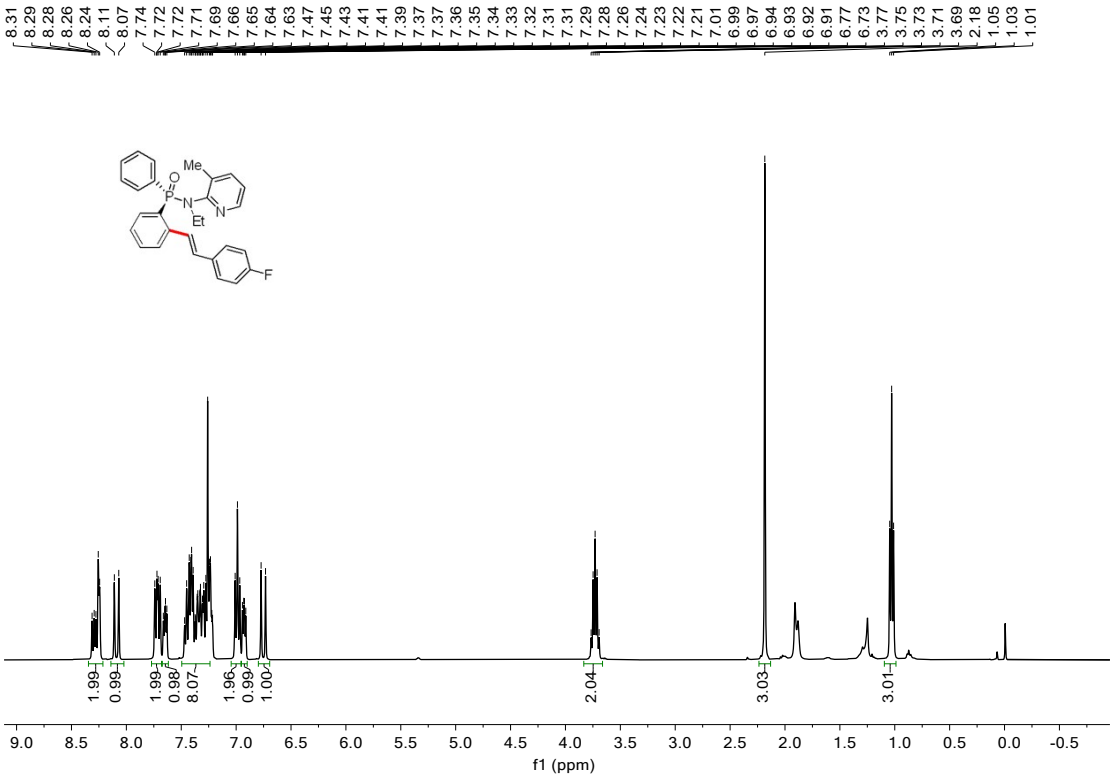
3w, ^{13}C NMR, 101 MHz, $CDCl_3$



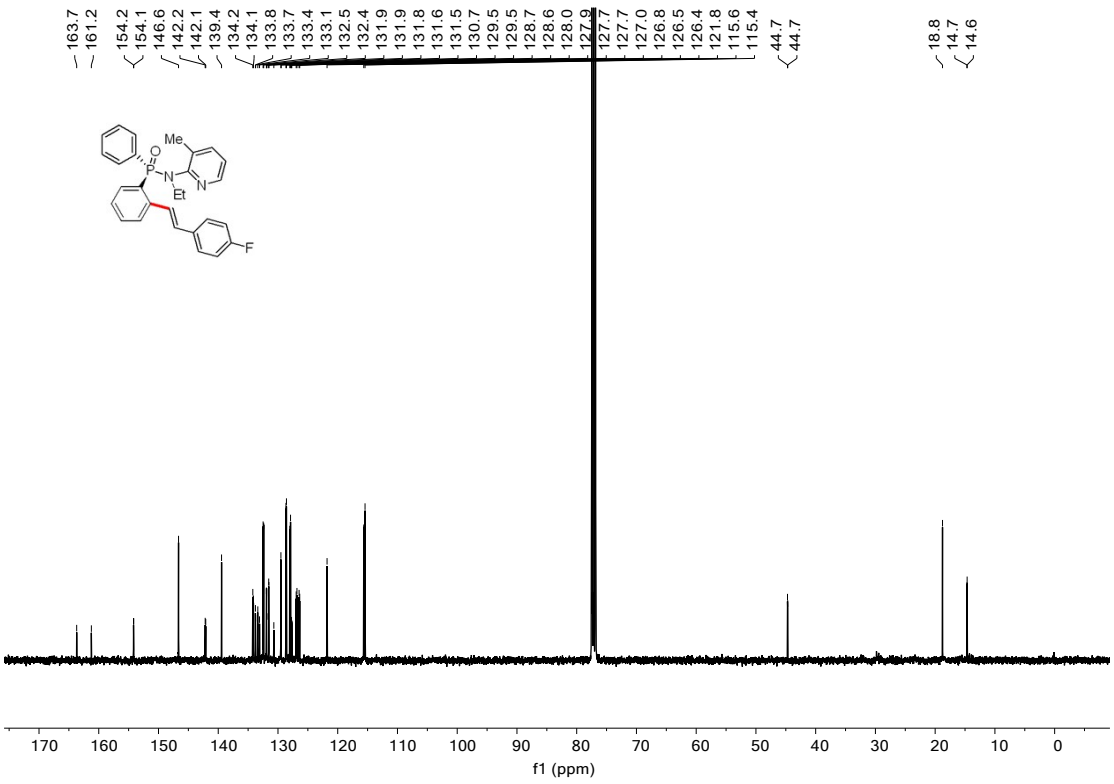
3w, ^{31}P NMR, 162 MHz, $CDCl_3$



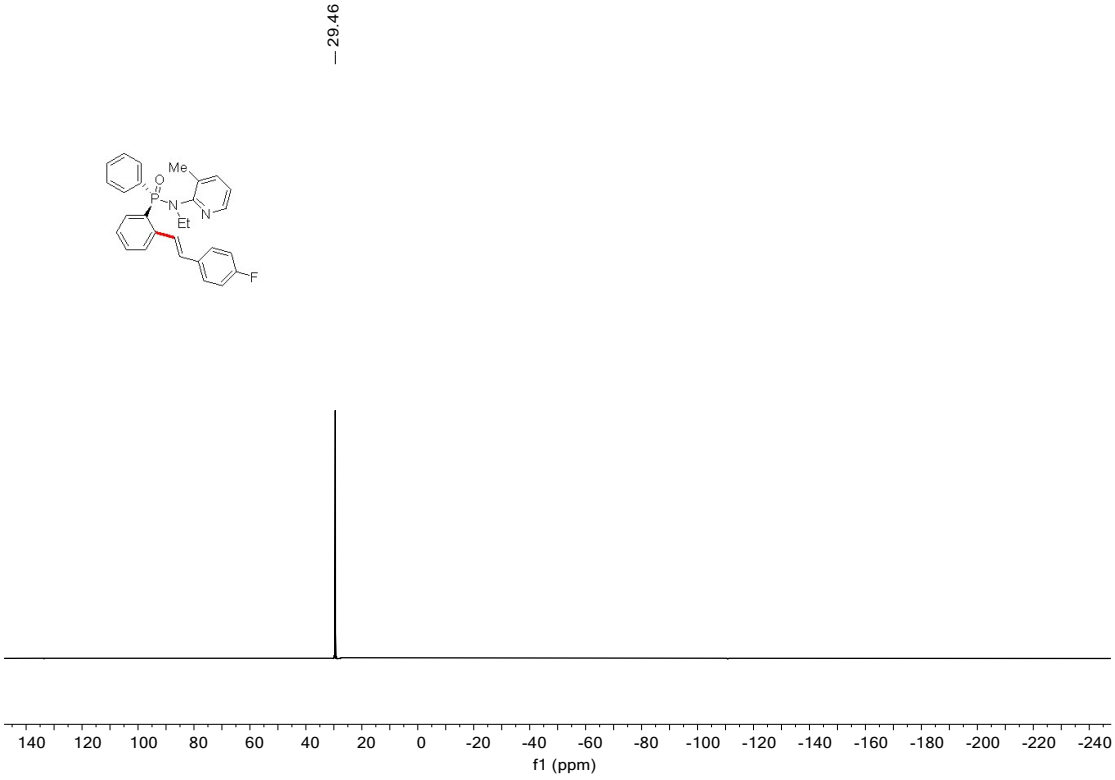
3x, ^{1}H NMR, 400 MHz, $CDCl_3$



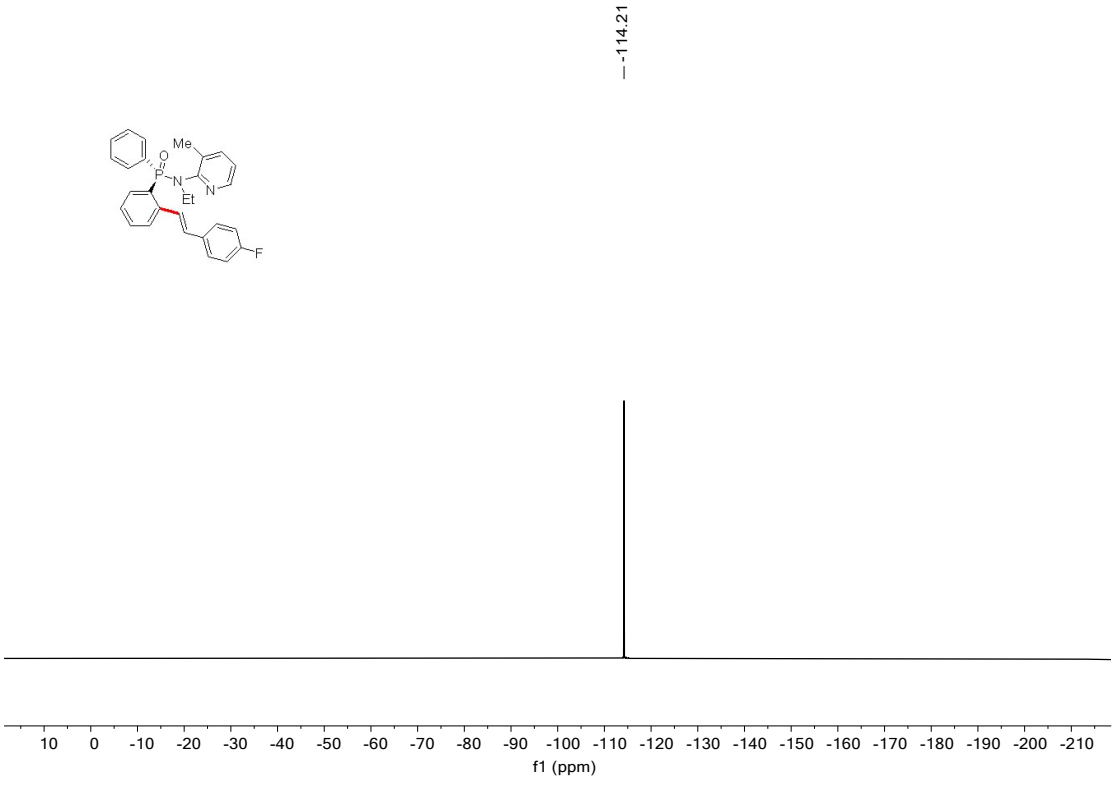
3x, ^{13}C NMR, 101 MHz, $CDCl_3$



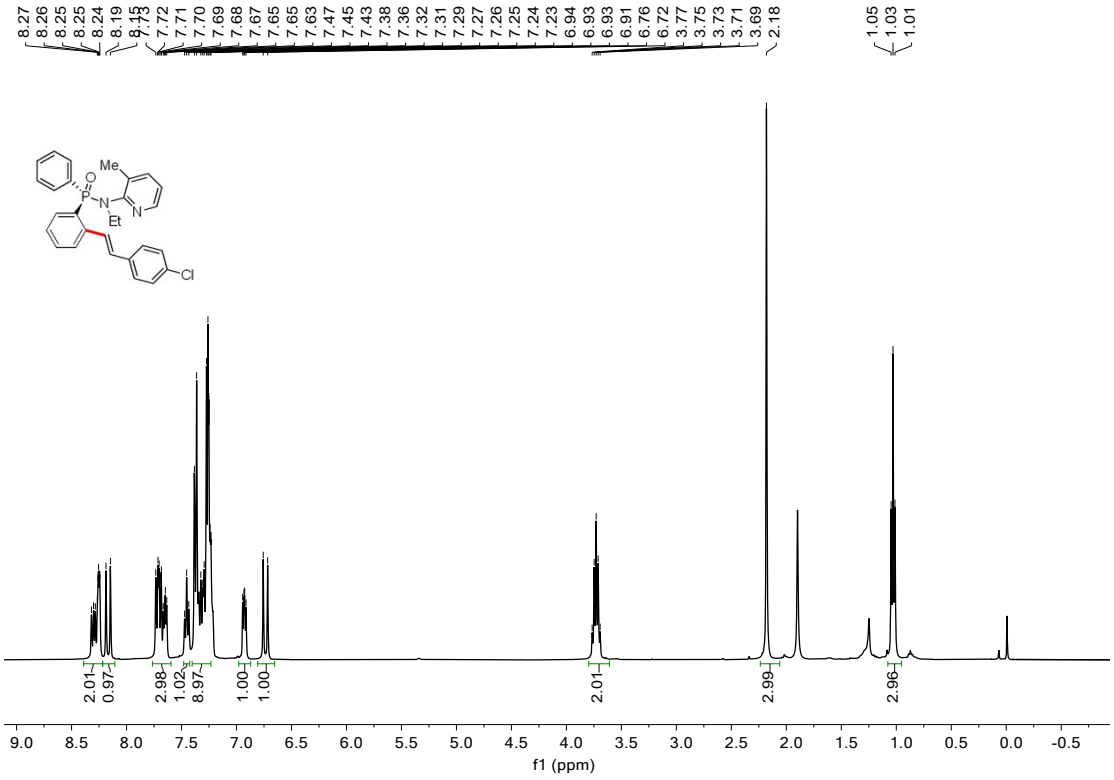
3x, ^{31}P NMR, 162 MHz, $CDCl_3$



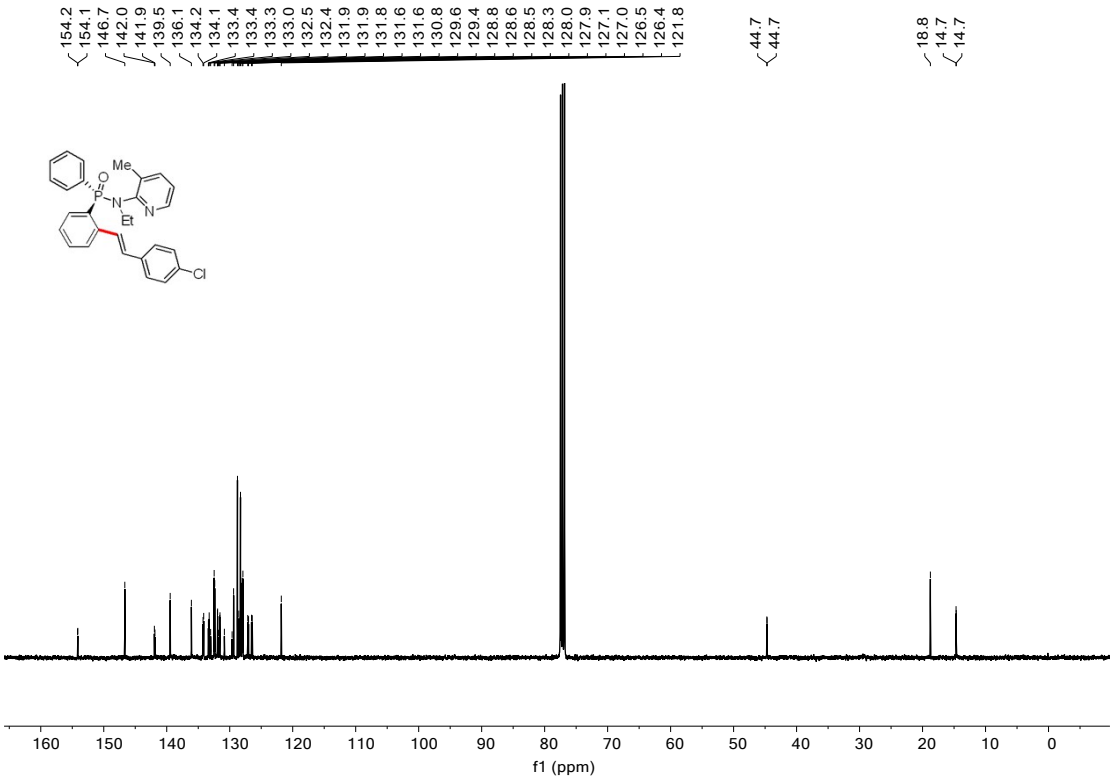
3x, ^{19}F NMR, 376 MHz, $CDCl_3$



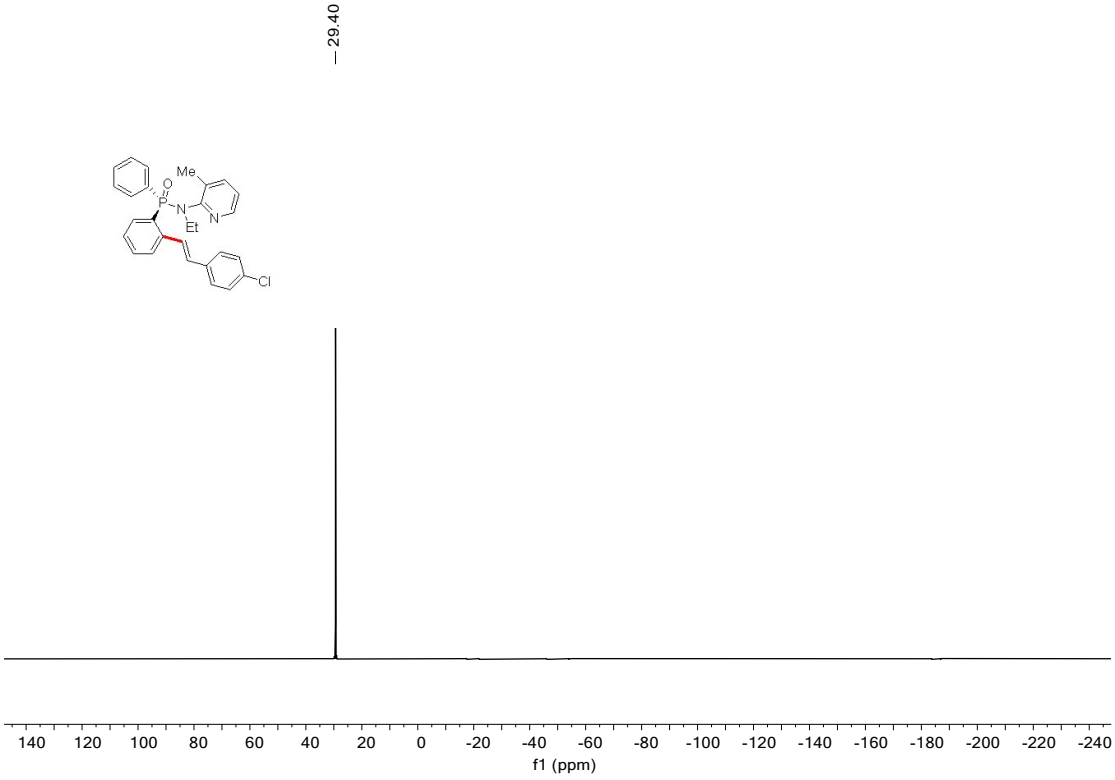
3y, ^{1}H NMR, 400 MHz, $CDCl_3$



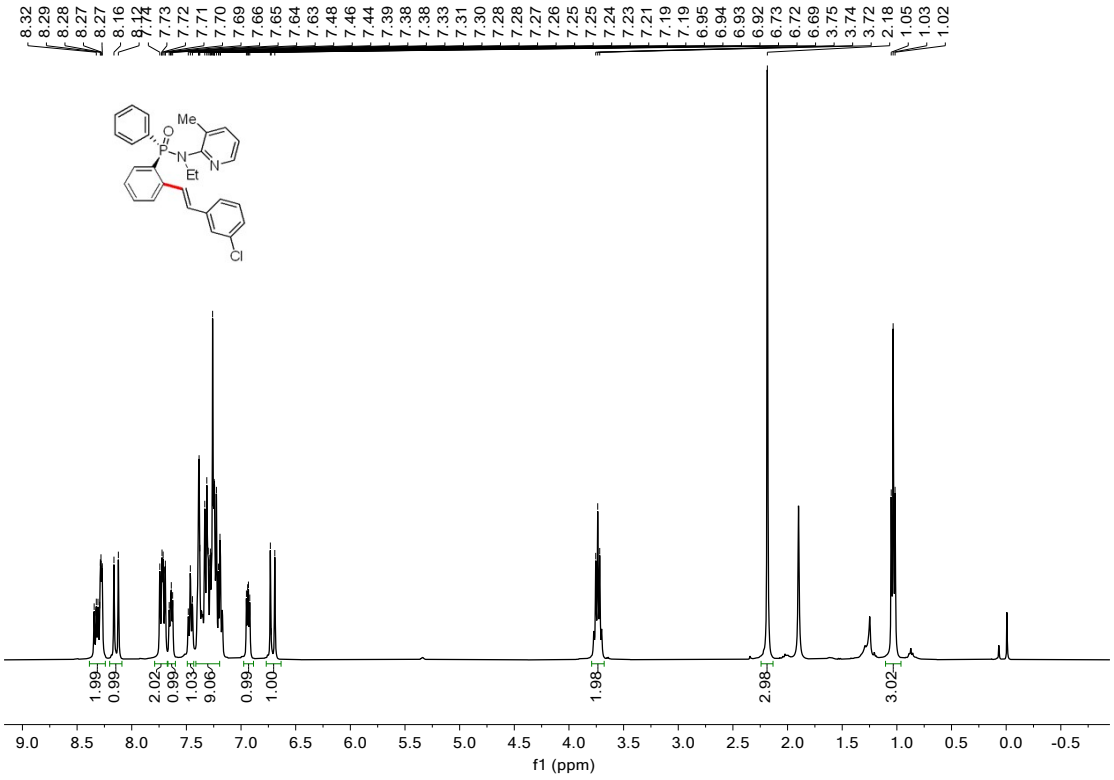
3y, ^{13}C NMR, 101 MHz, $CDCl_3$



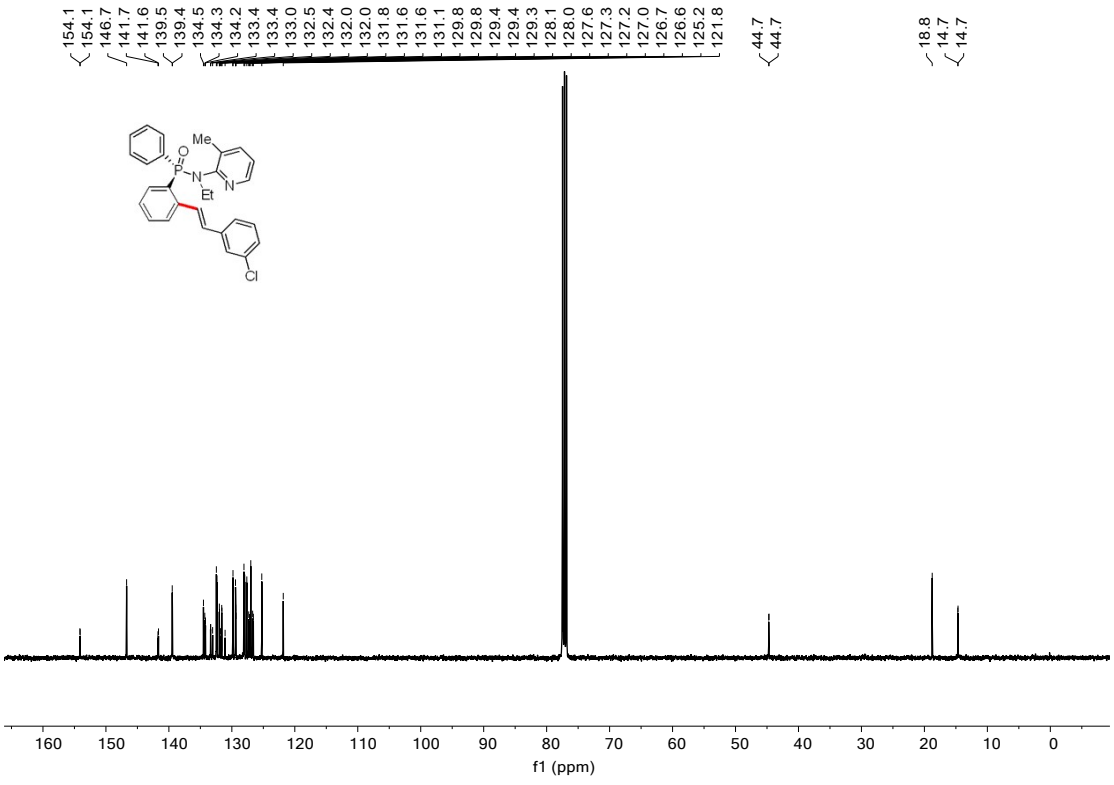
3y, ^{31}P NMR, 162 MHz, $CDCl_3$



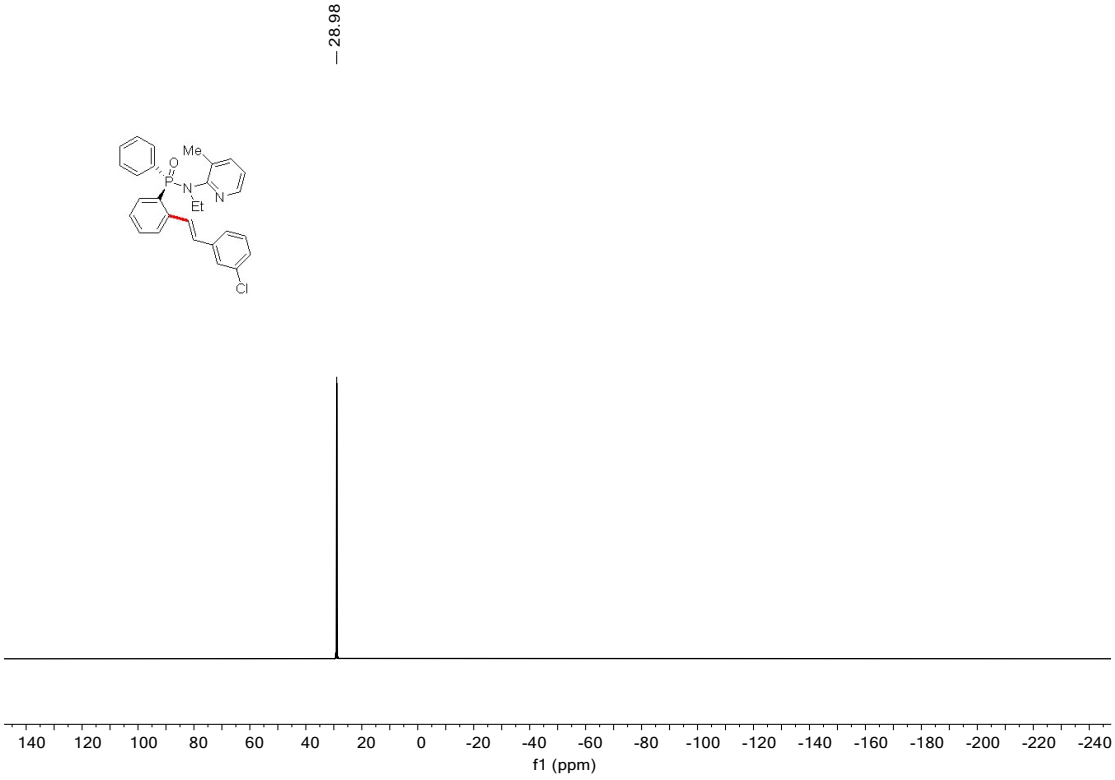
3z, ^{1}H NMR, 400 MHz, $CDCl_3$



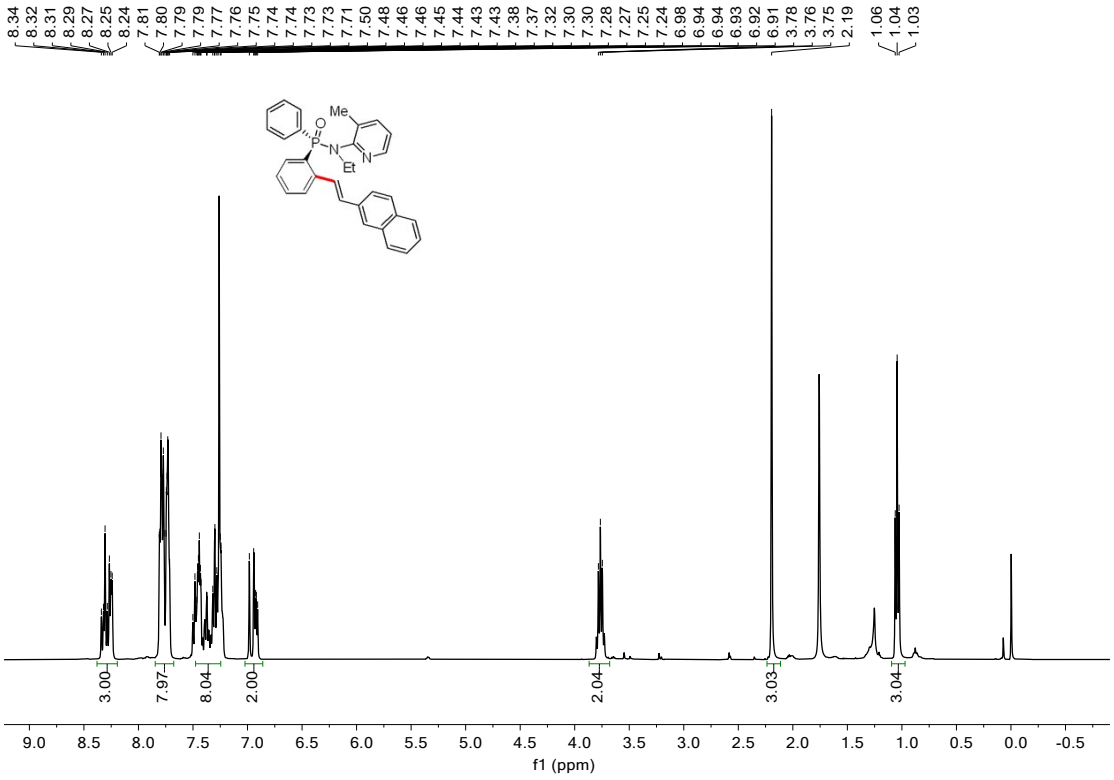
3z, ^{13}C NMR, 101 MHz, $CDCl_3$



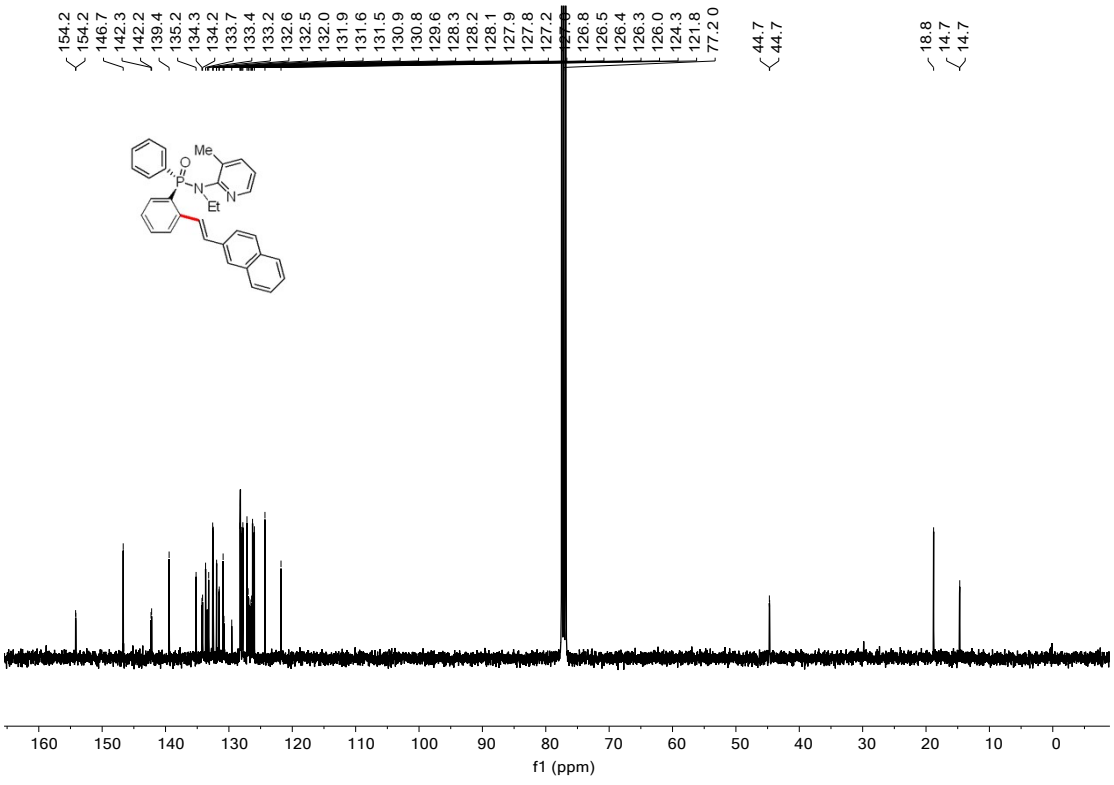
3z, ^{31}P NMR, 162 MHz, $CDCl_3$



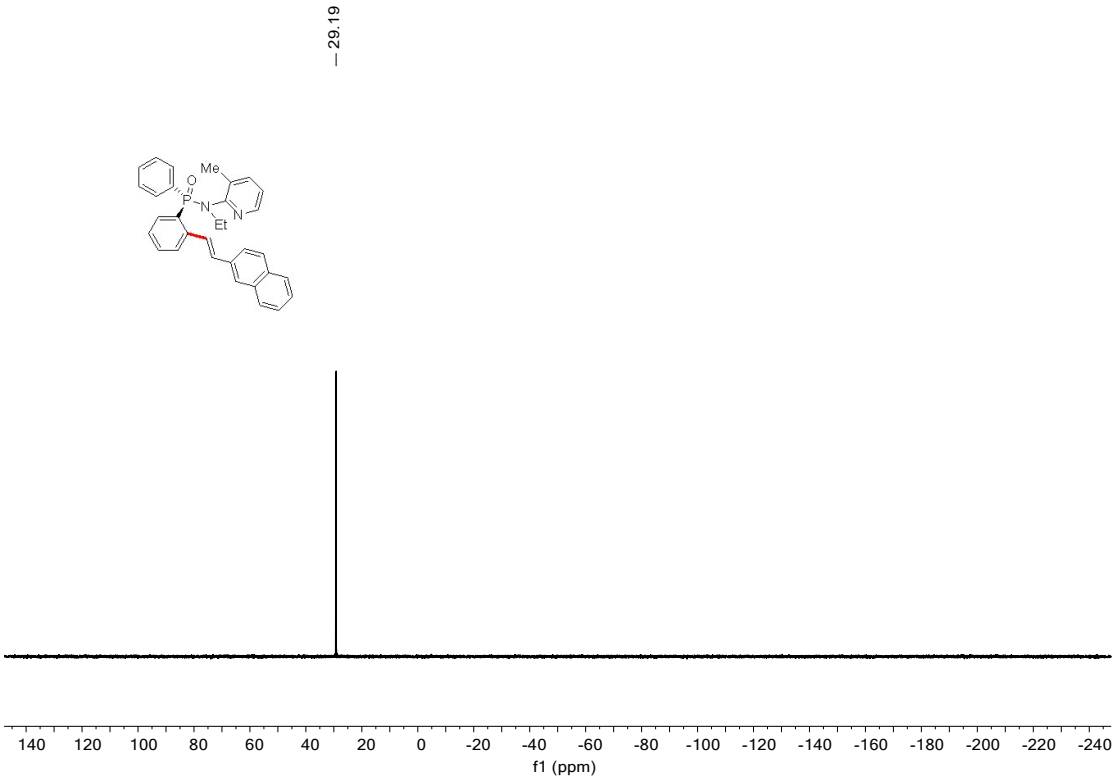
3aa, ^{1}H NMR, 400 MHz, $CDCl_3$



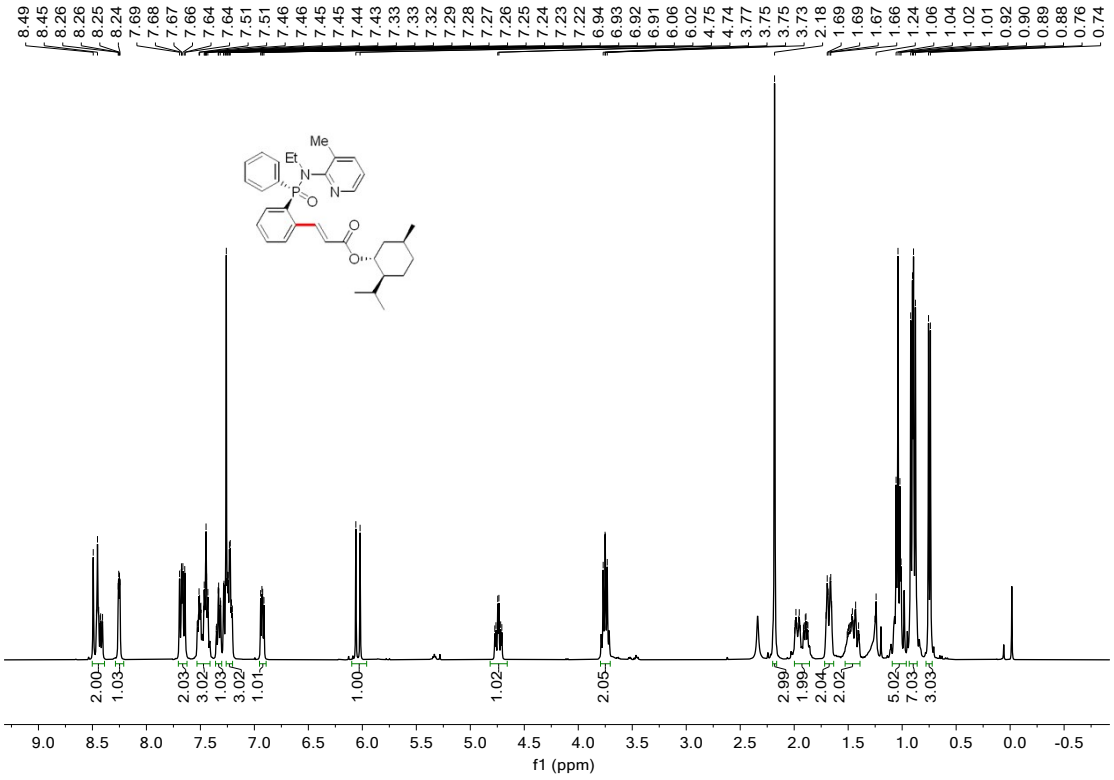
3aa, ^{13}C NMR, 101 MHz, $CDCl_3$



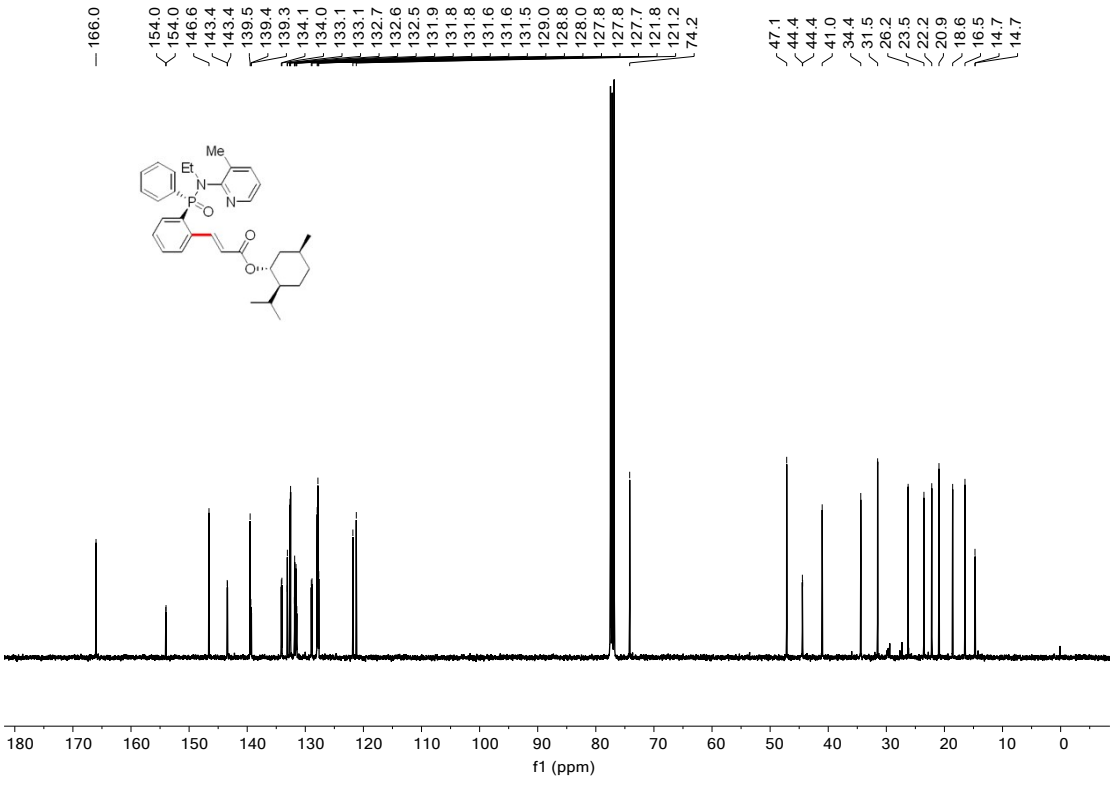
3aa, ^{31}P NMR, 162 MHz, $CDCl_3$



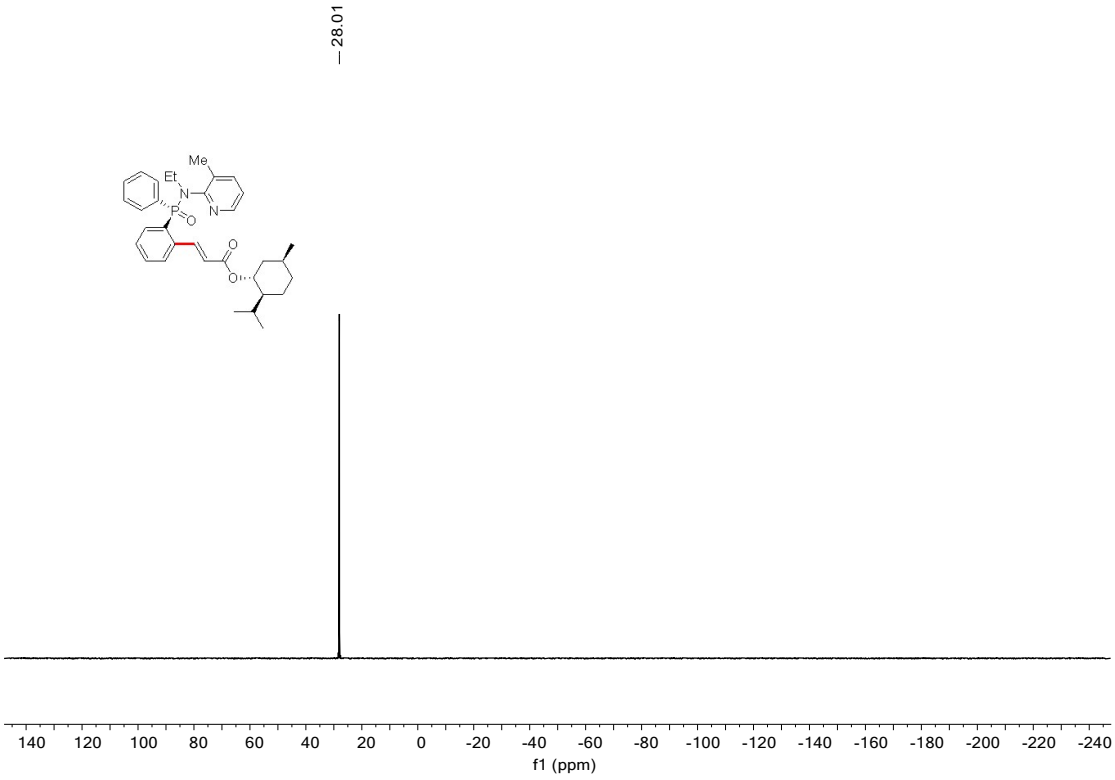
3ab, ^{1}H NMR, 400 MHz, $CDCl_3$



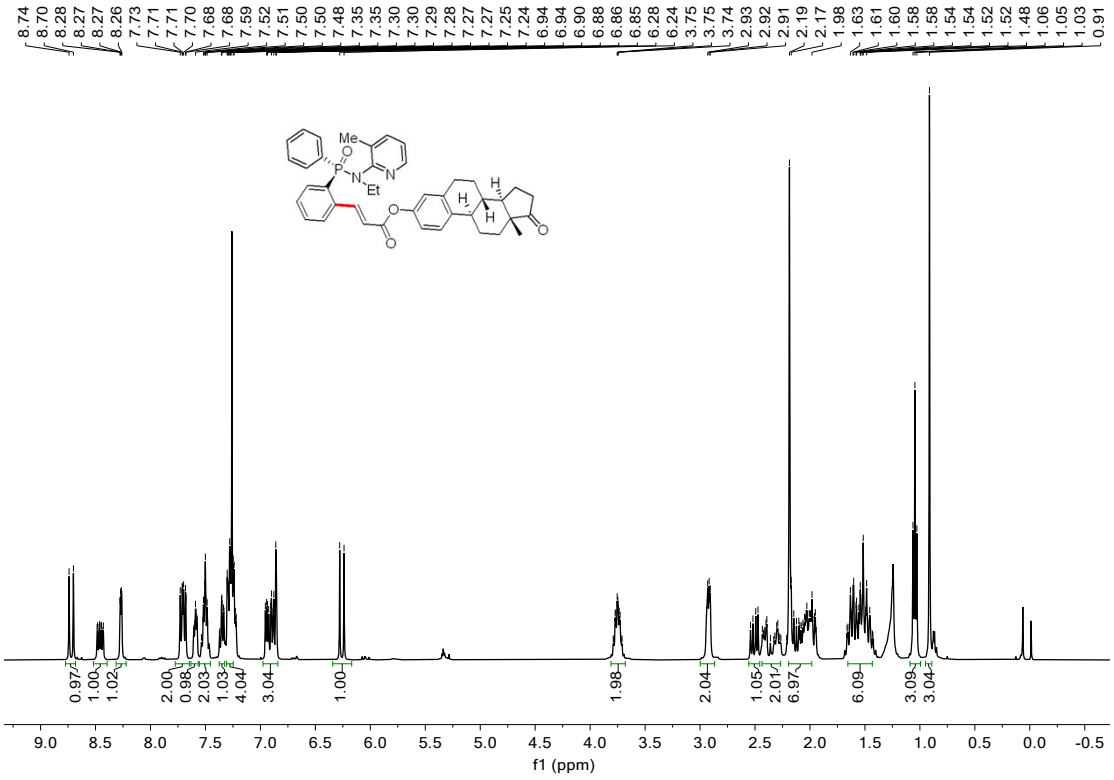
3ab, ^{13}C NMR, 101 MHz, $CDCl_3$



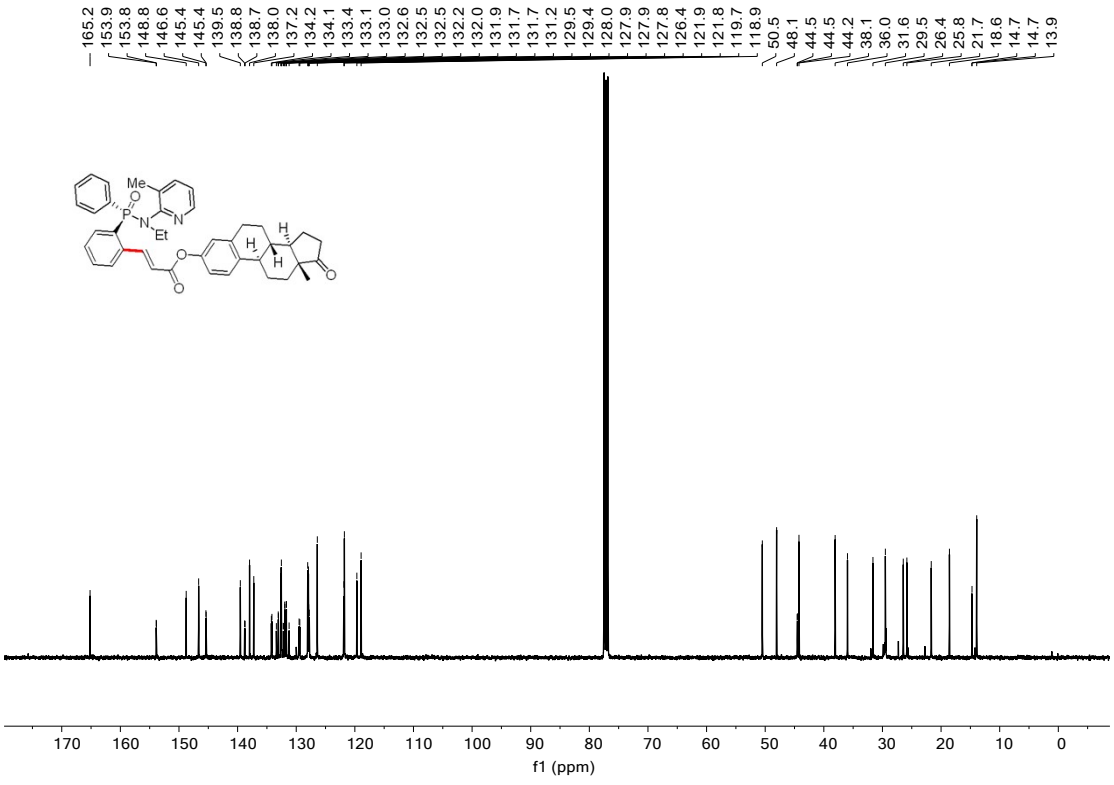
3ab, ^{31}P NMR, 162 MHz, $CDCl_3$



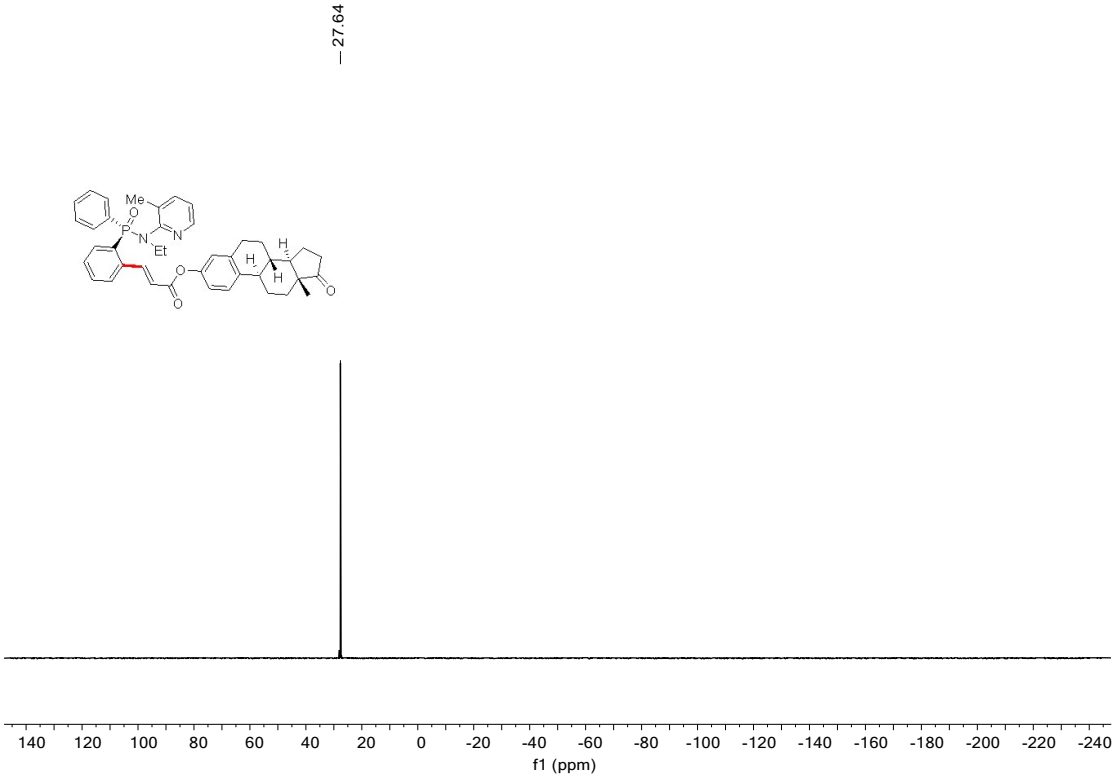
3ac, ^{1}H NMR, 400 MHz, $CDCl_3$



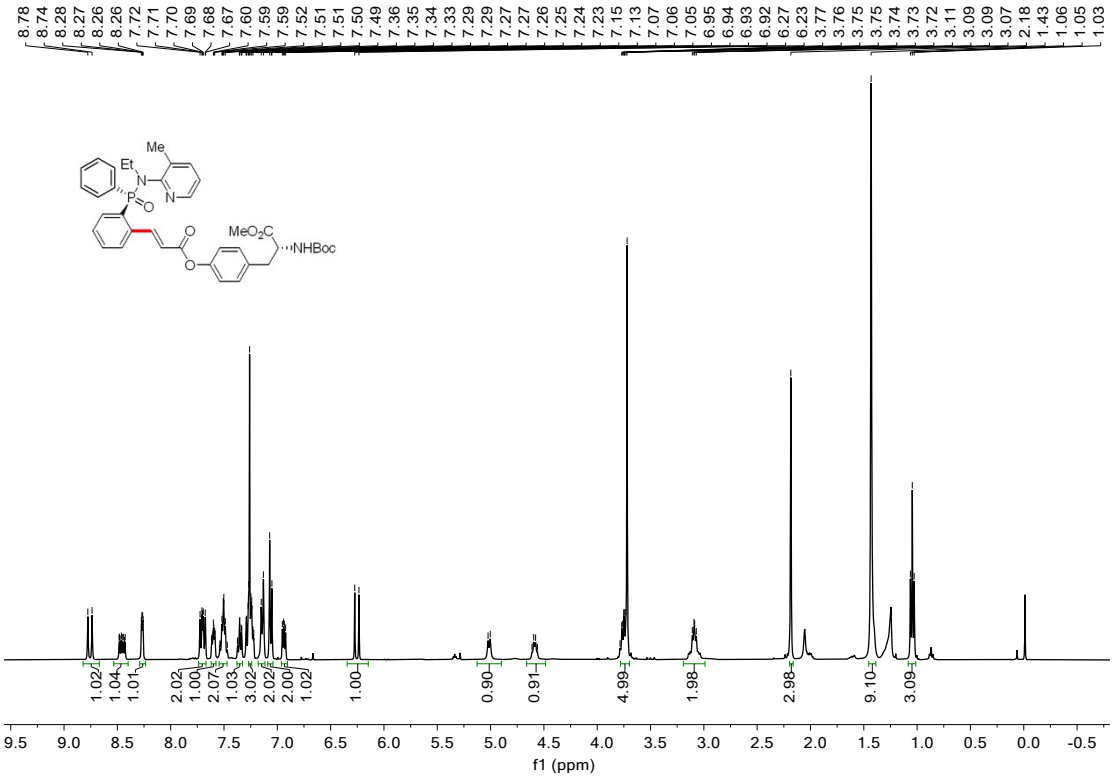
3ac, ^{13}C NMR, 101 MHz, $CDCl_3$



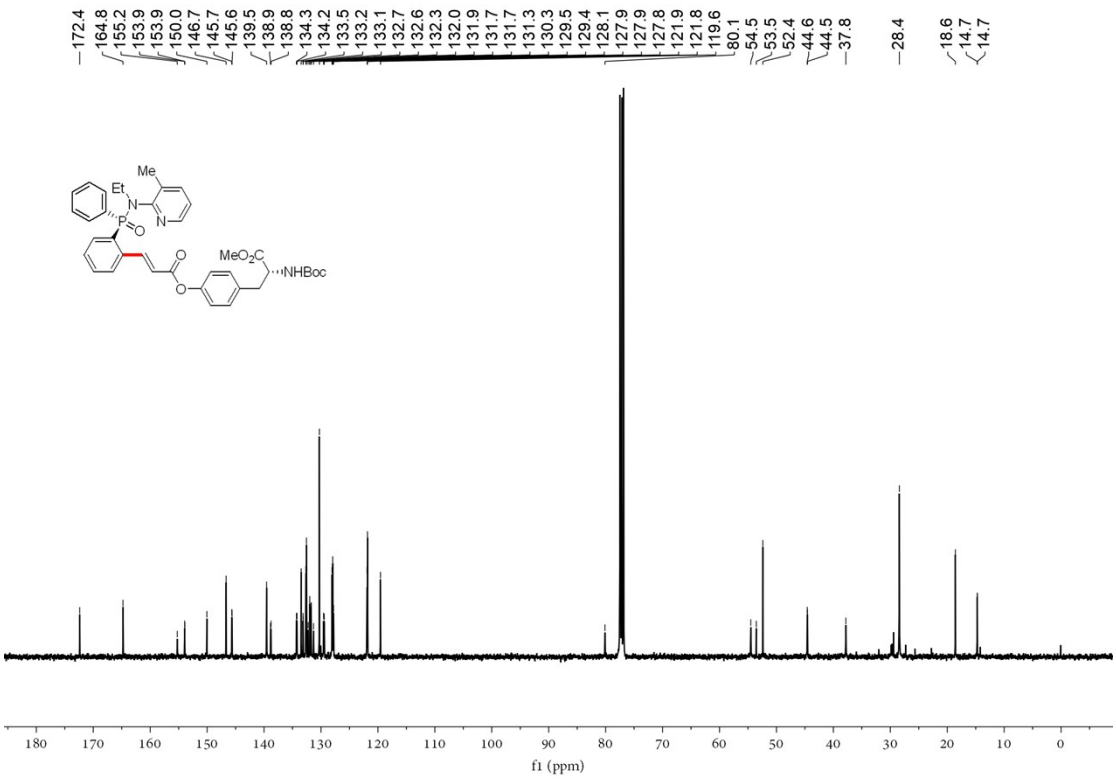
3ac, ^{31}P NMR, 162 MHz, $CDCl_3$



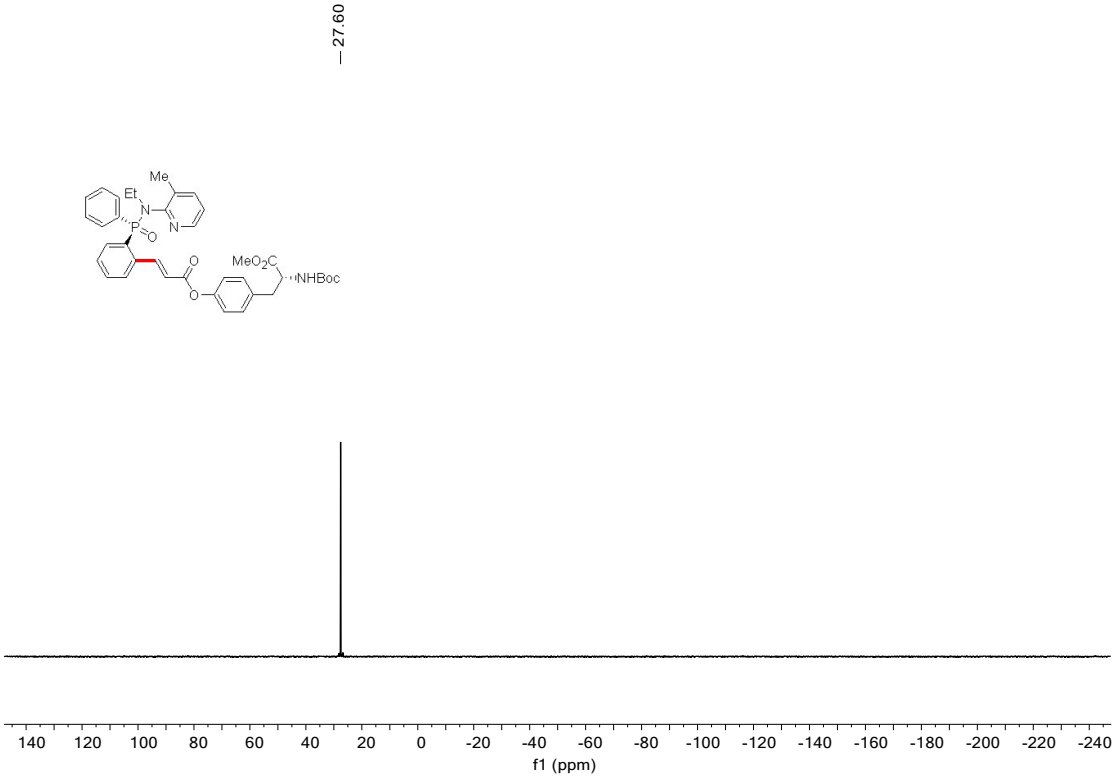
3ad, ^{1}H NMR, 400 MHz, $CDCl_3$



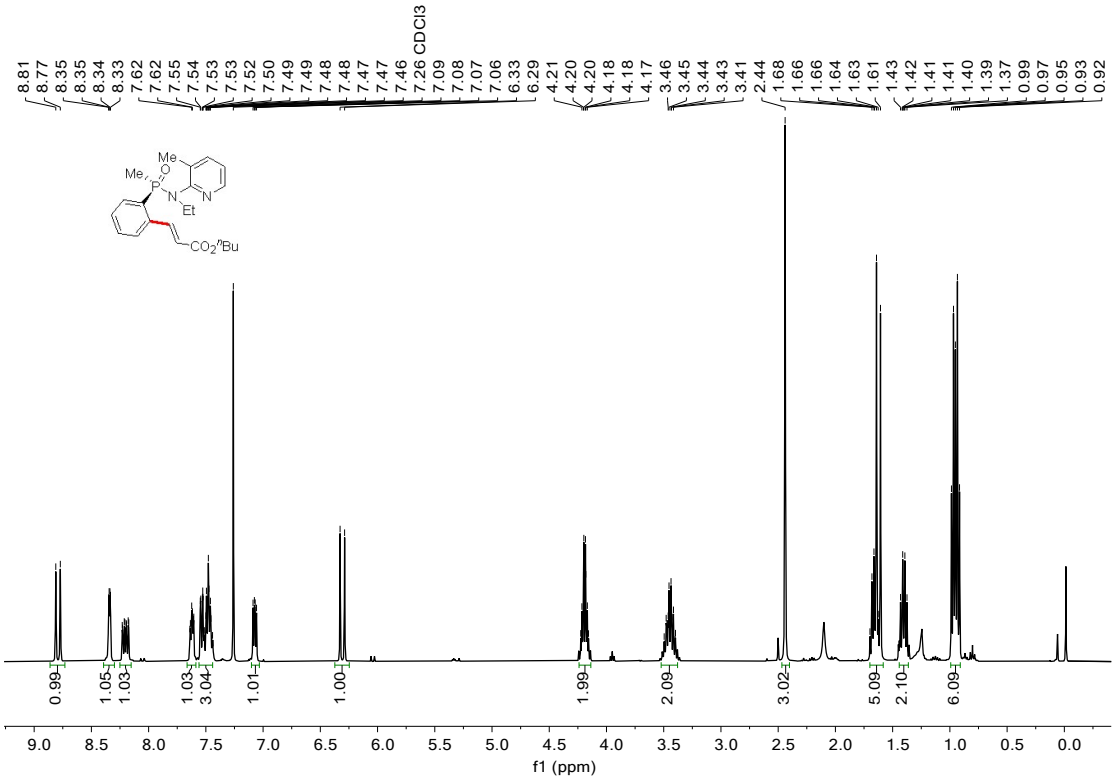
3ad, ^{13}C NMR, 101 MHz, $CDCl_3$



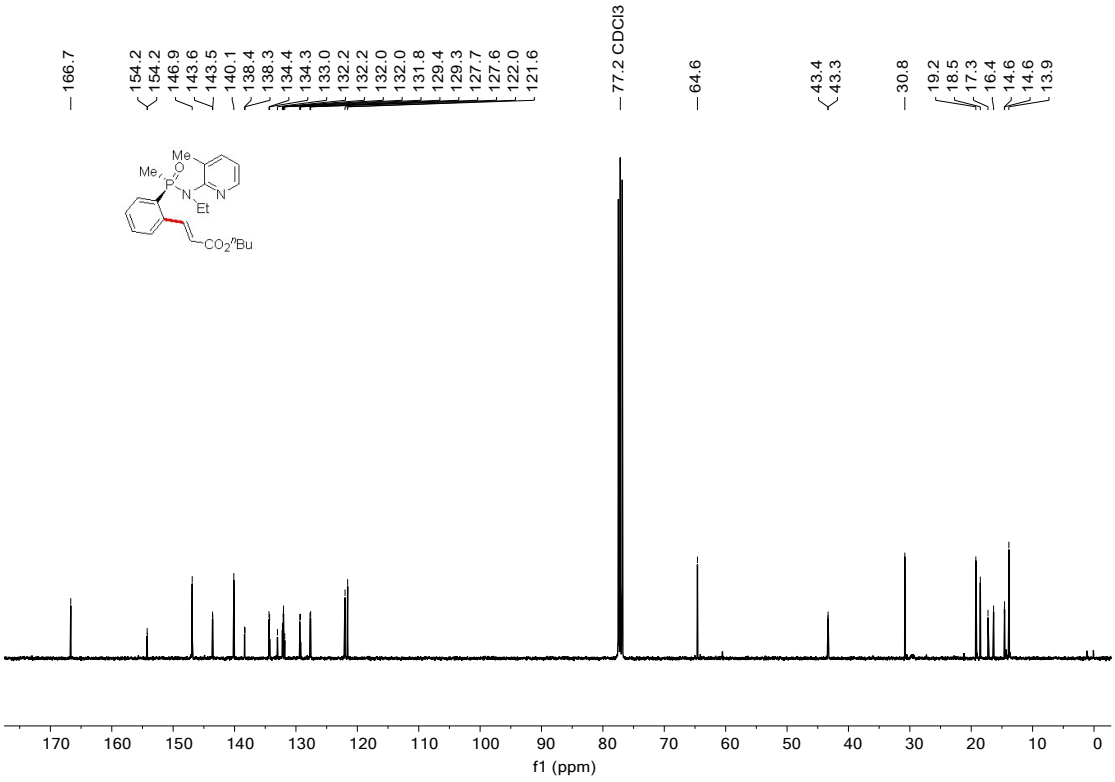
3ad, ^{31}P NMR, 162 MHz, $CDCl_3$



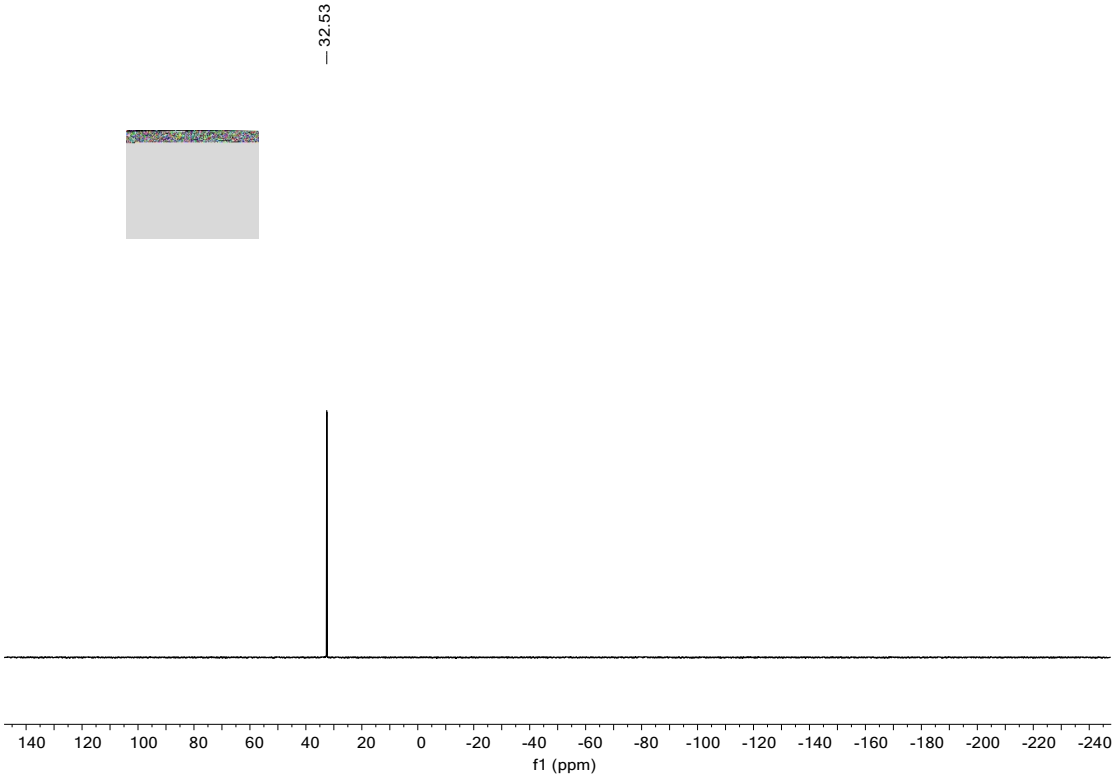
(*R*)-**7d, ^{1}H NMR, 400 MHz, $CDCl_3$**



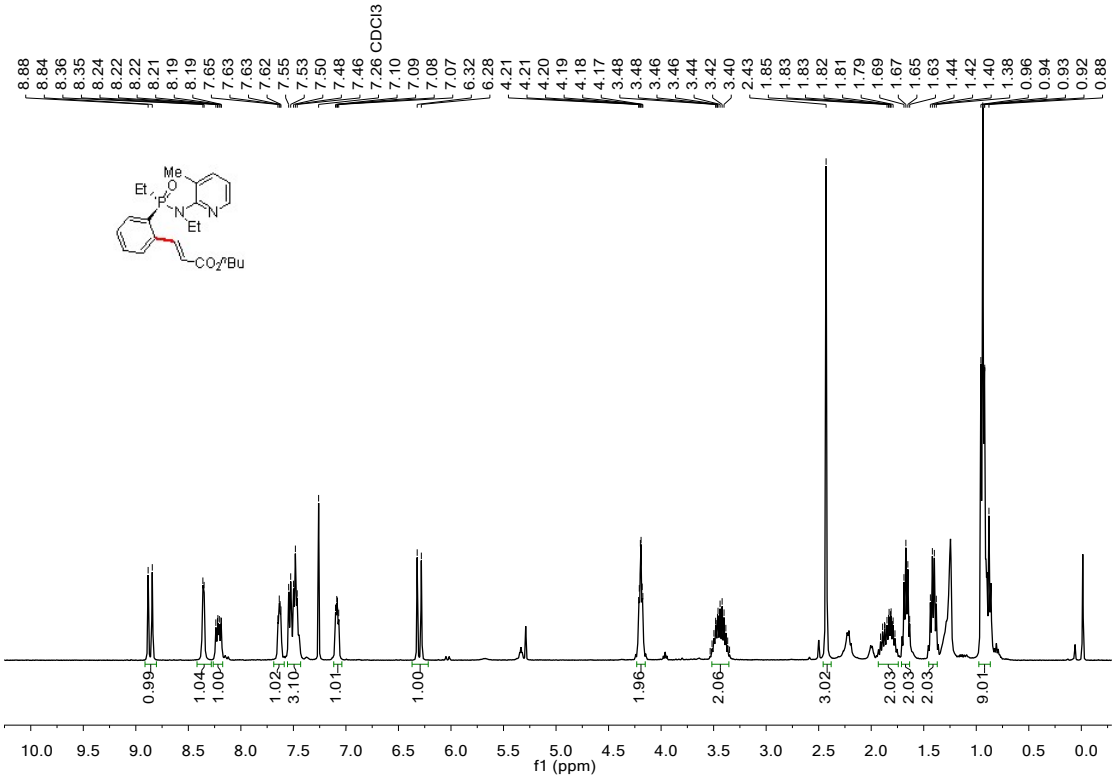
(*R*)-**7d, ^{13}C NMR, 101 MHz, $CDCl_3$**



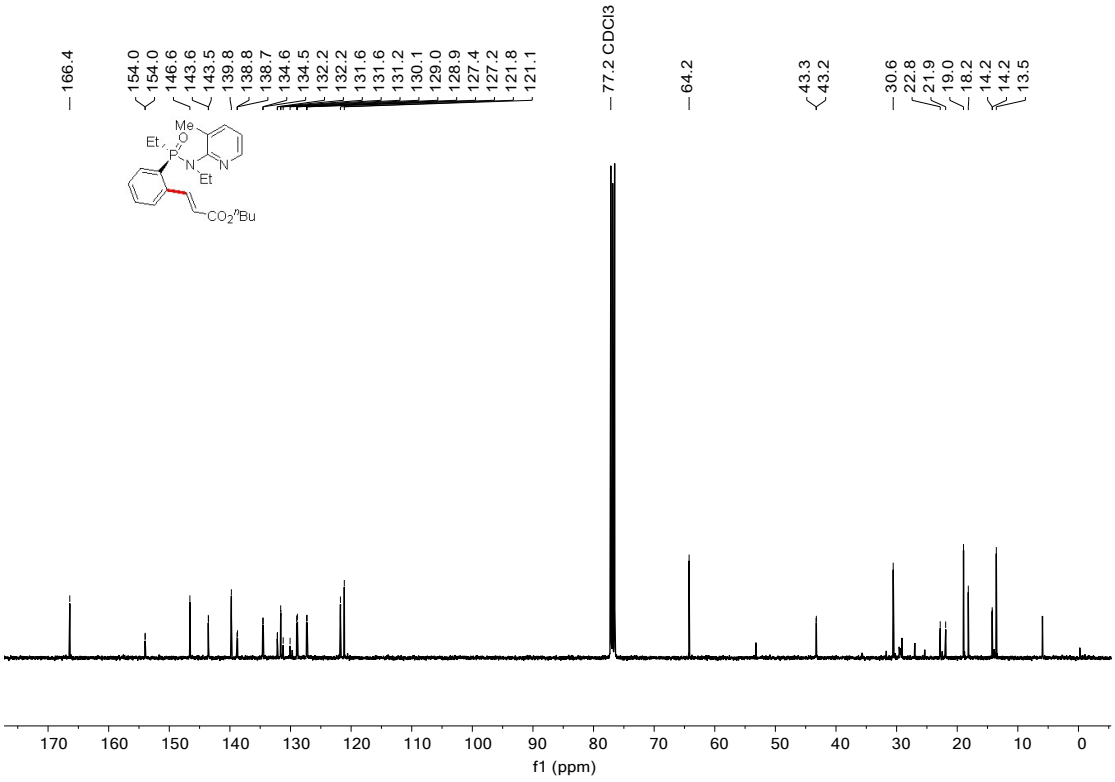
(*R*)-**7d, ^{31}P NMR, 162 MHz, $CDCl_3$**



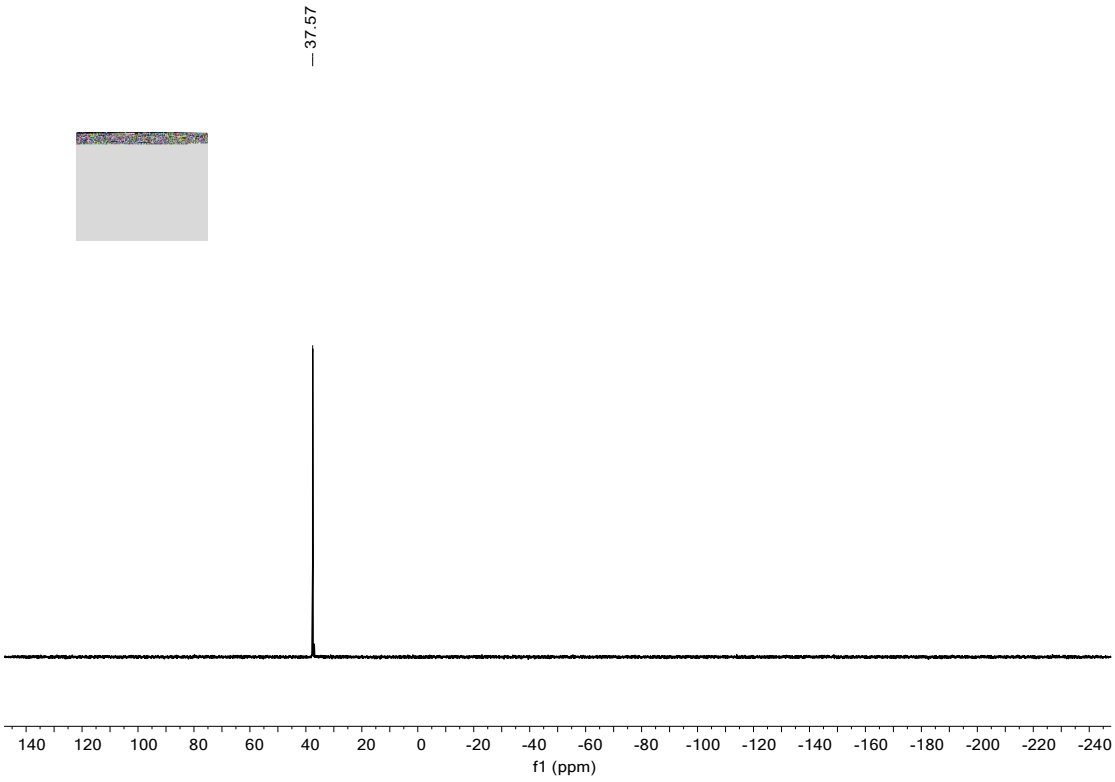
(*R*)-7e, ^{1}H NMR, 400 MHz, $CDCl_3$



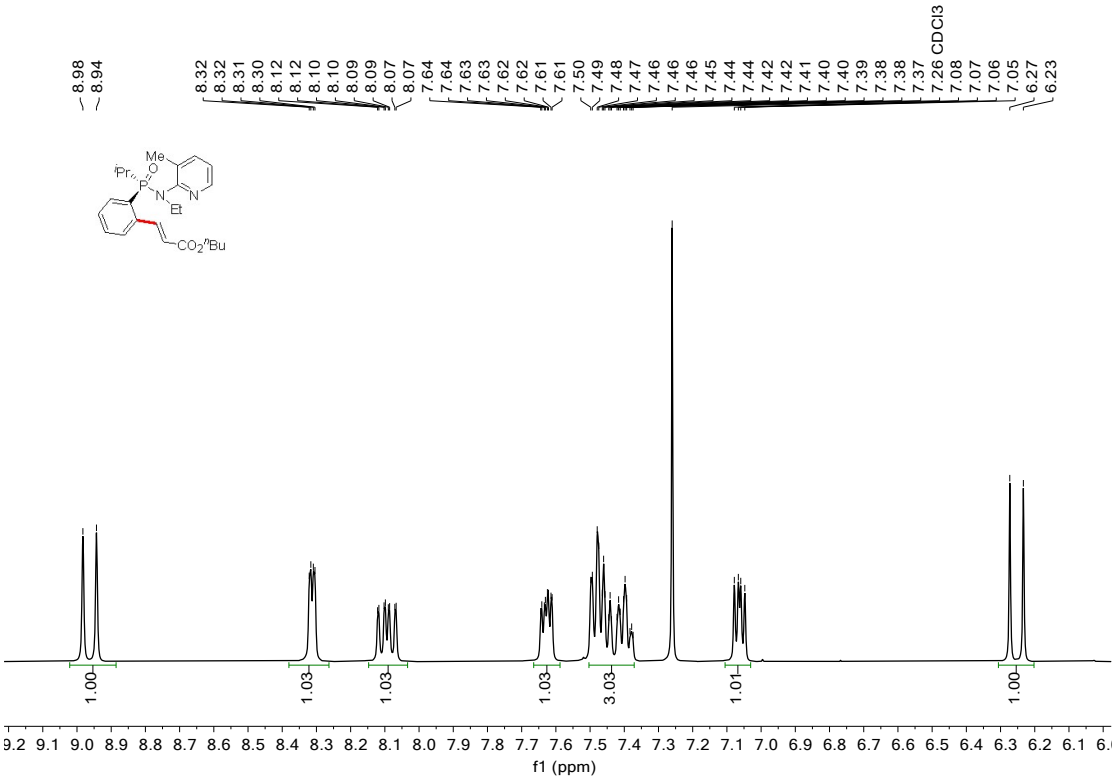
(*R*)-7e, ^{13}C NMR, 101 MHz, $CDCl_3$



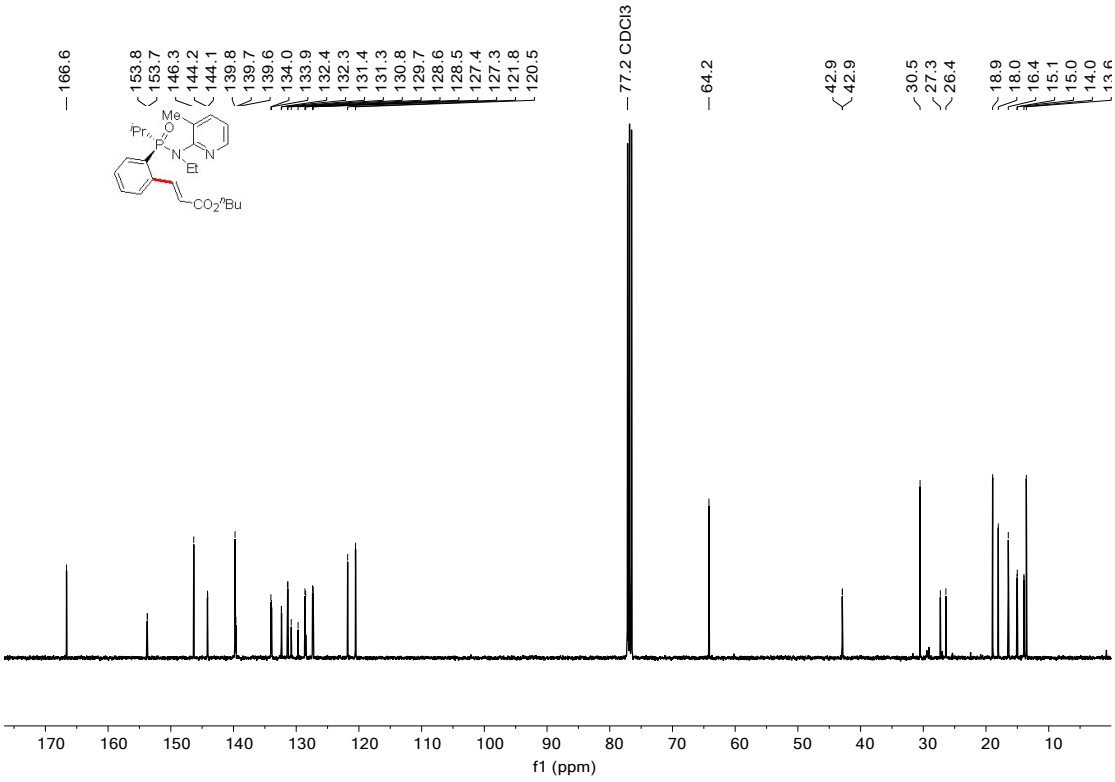
(*R*)-**7e, ^{31}P NMR, 162 MHz, $CDCl_3$**



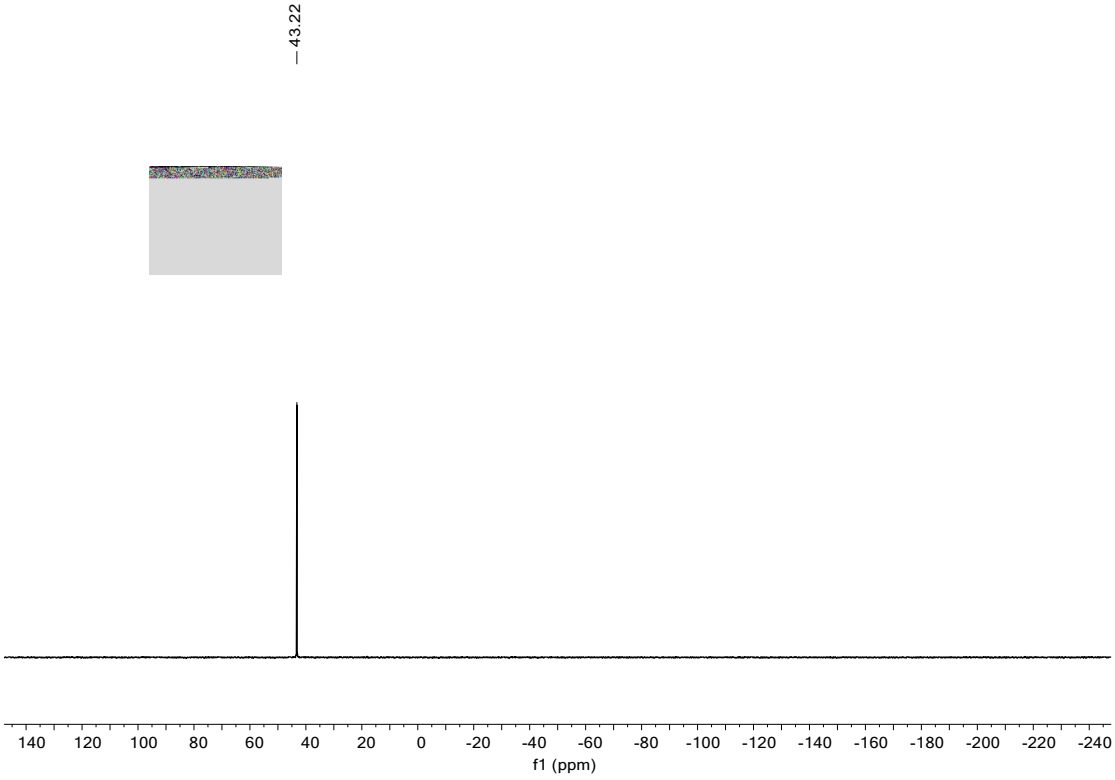
(*R*)-**7f**, **^{1}H NMR, 400 MHz, $CDCl_3$**



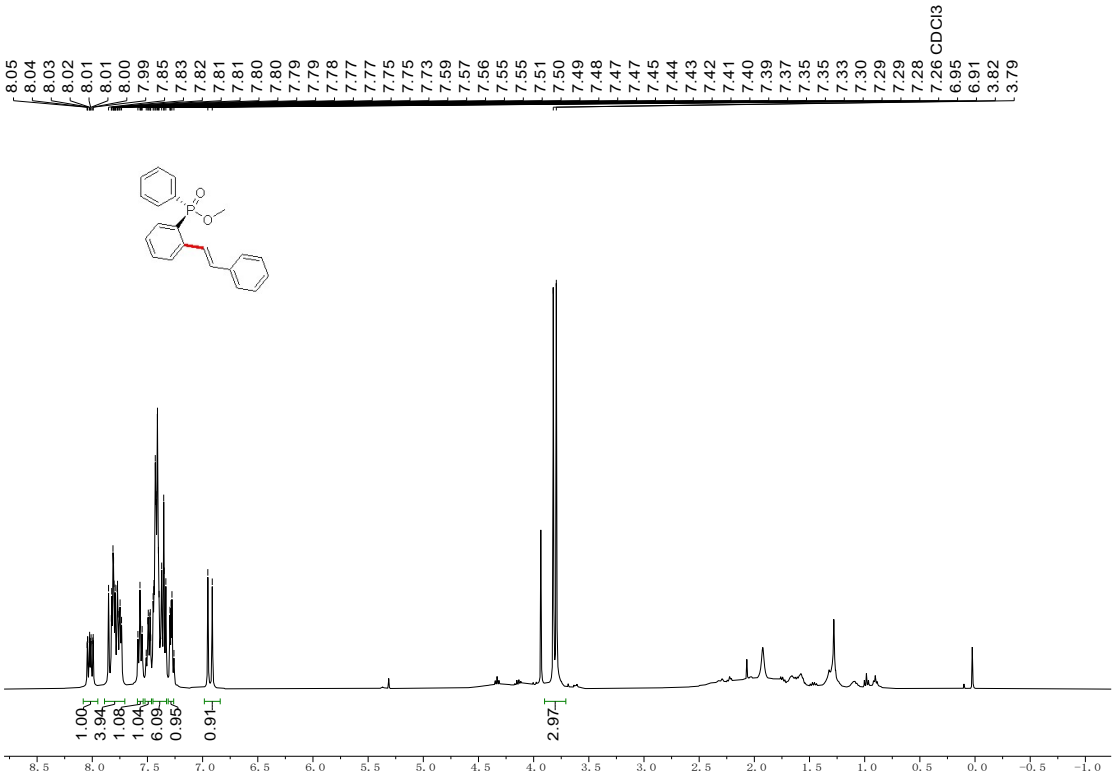
(*R*)-**7f**, **^{13}C NMR, 101 MHz, $CDCl_3$**



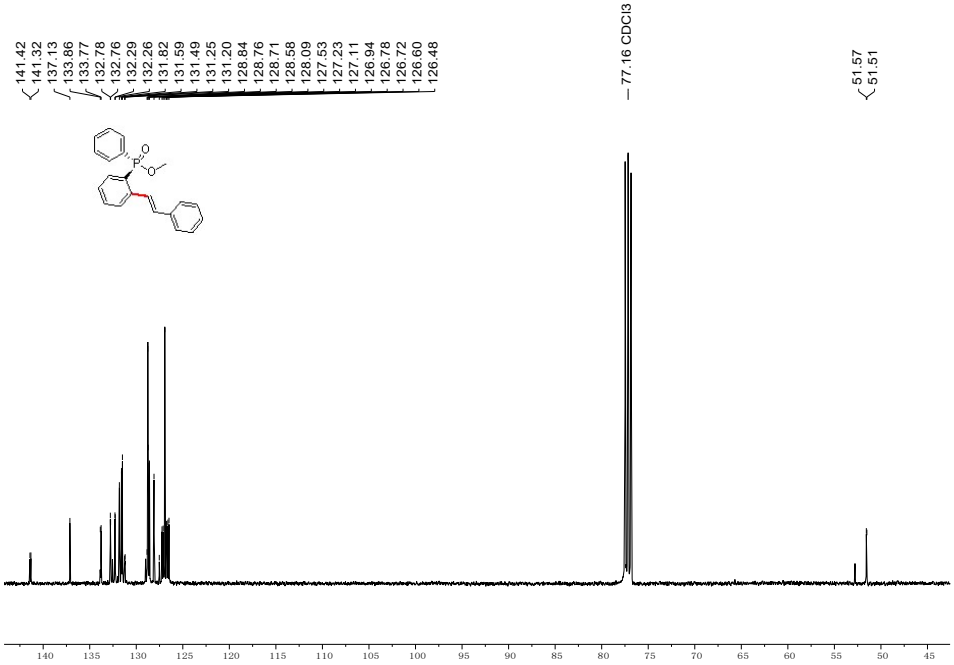
(*R*)-**7f, ^{31}P NMR, 162 MHz, $CDCl_3$**



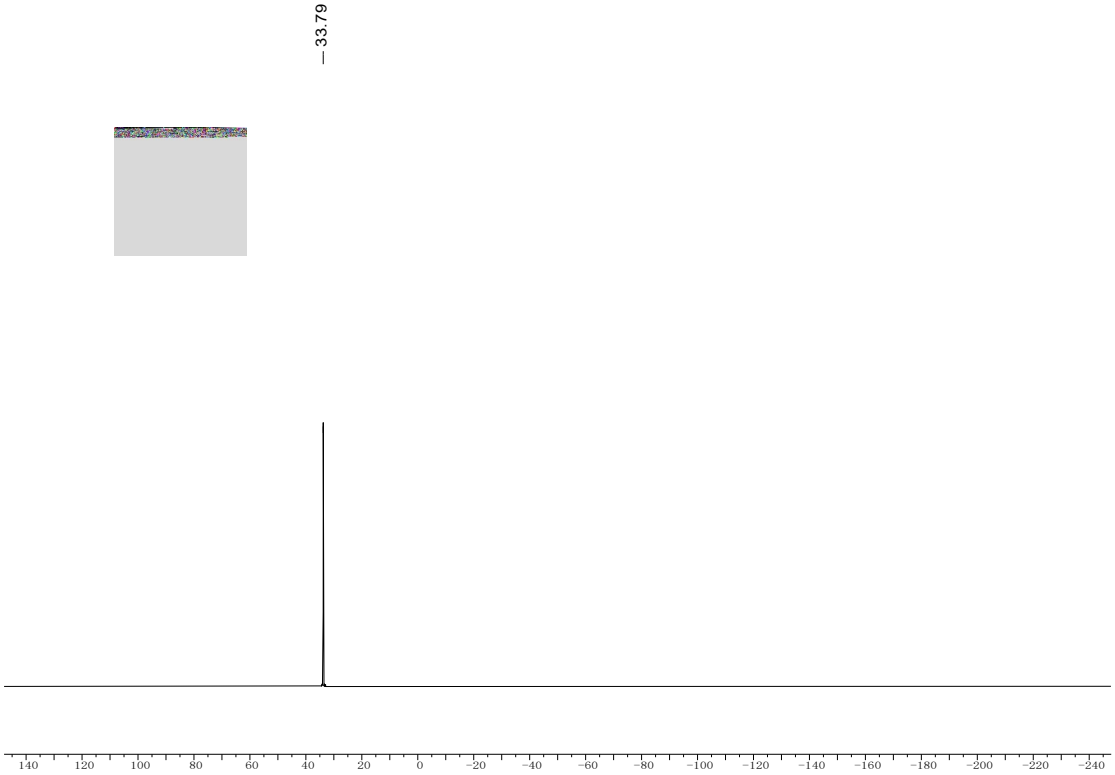
6w, ^{1}H NMR, 400 MHz, $CDCl_3$



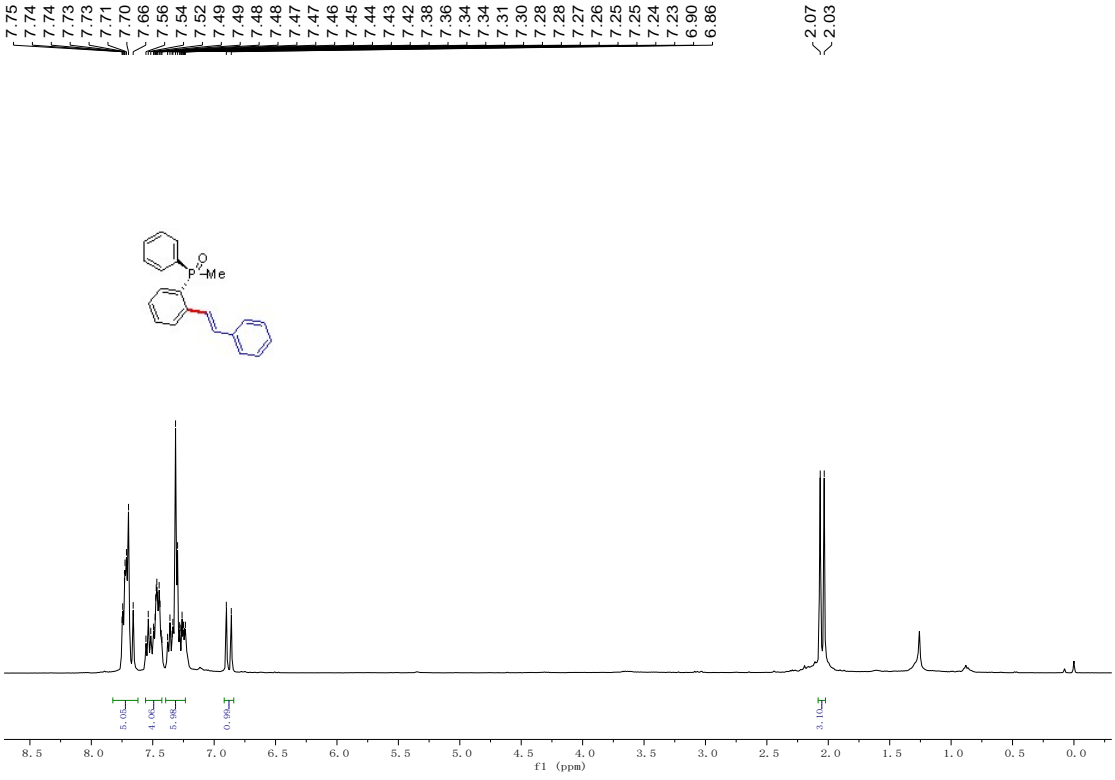
6w, ^{13}C NMR, 101 MHz, $CDCl_3$



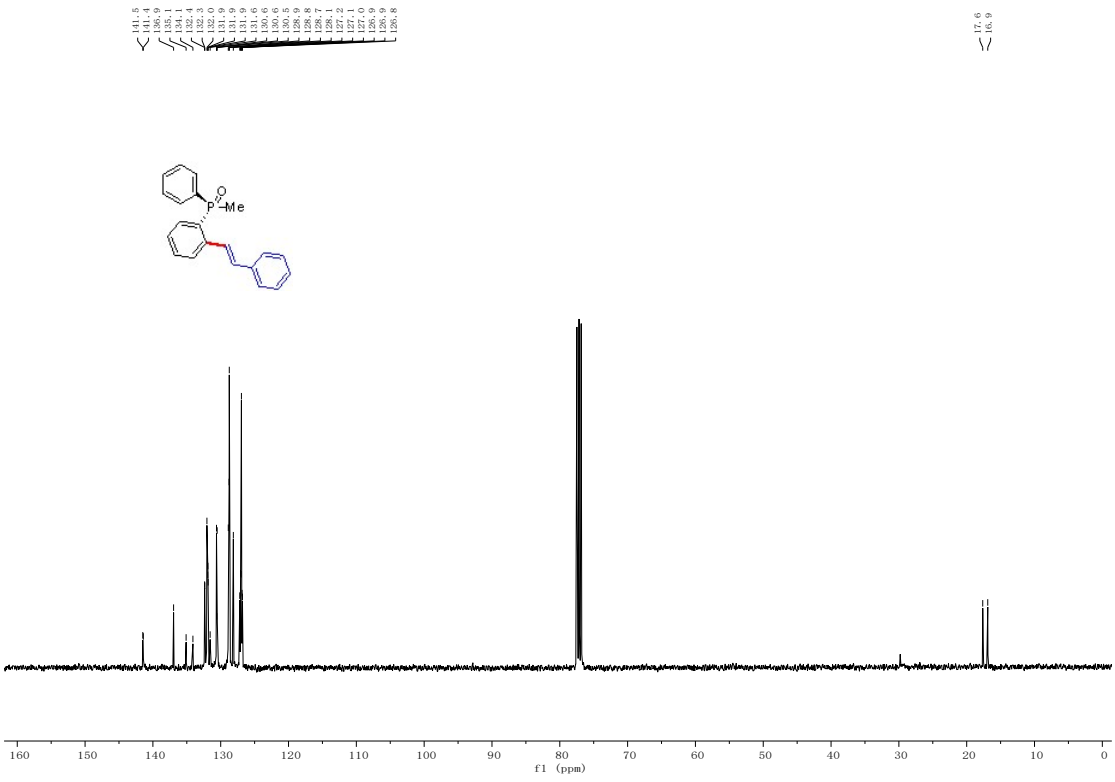
6w, ^{31}P NMR, 162 MHz, $CDCl_3$



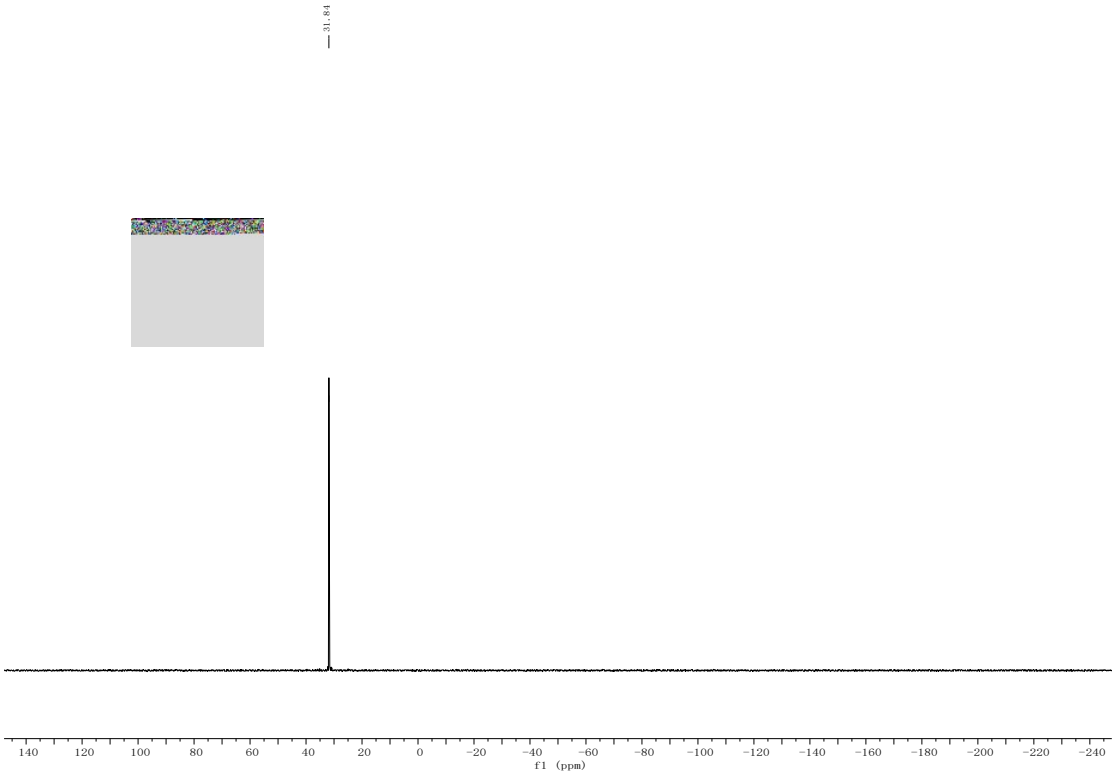
7a, ^{1}H NMR, 400 MHz, $CDCl_3$



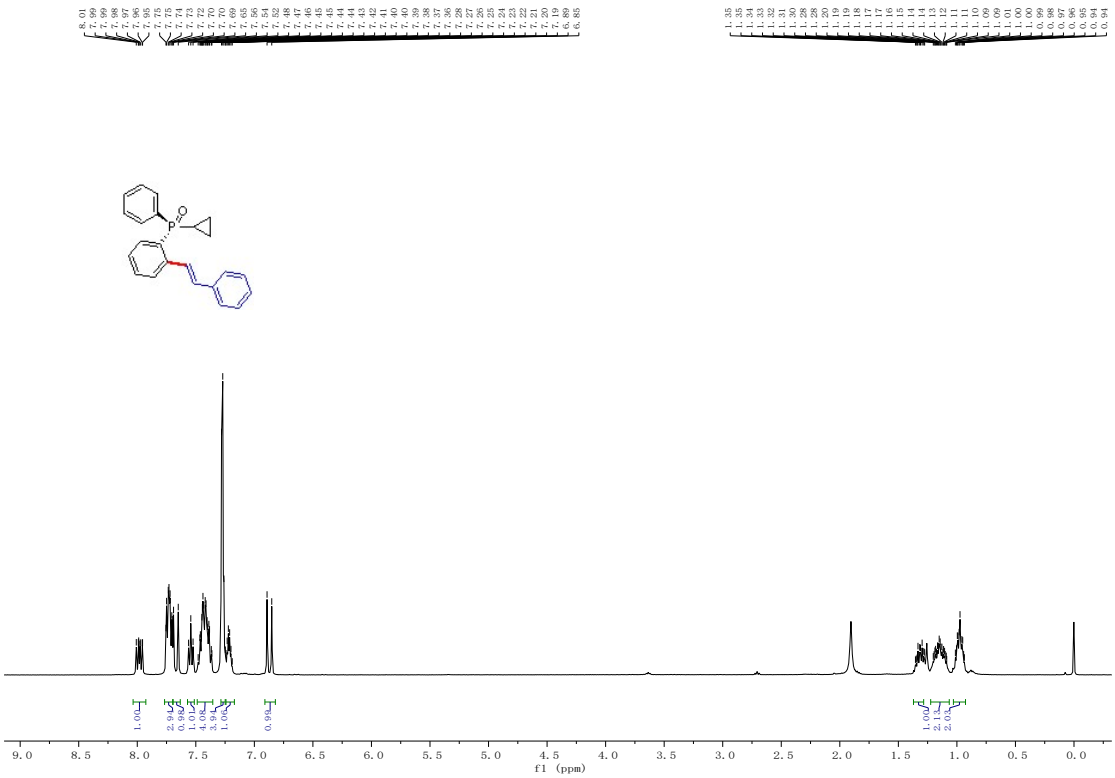
7a, ^{13}C NMR, 101 MHz, $CDCl_3$



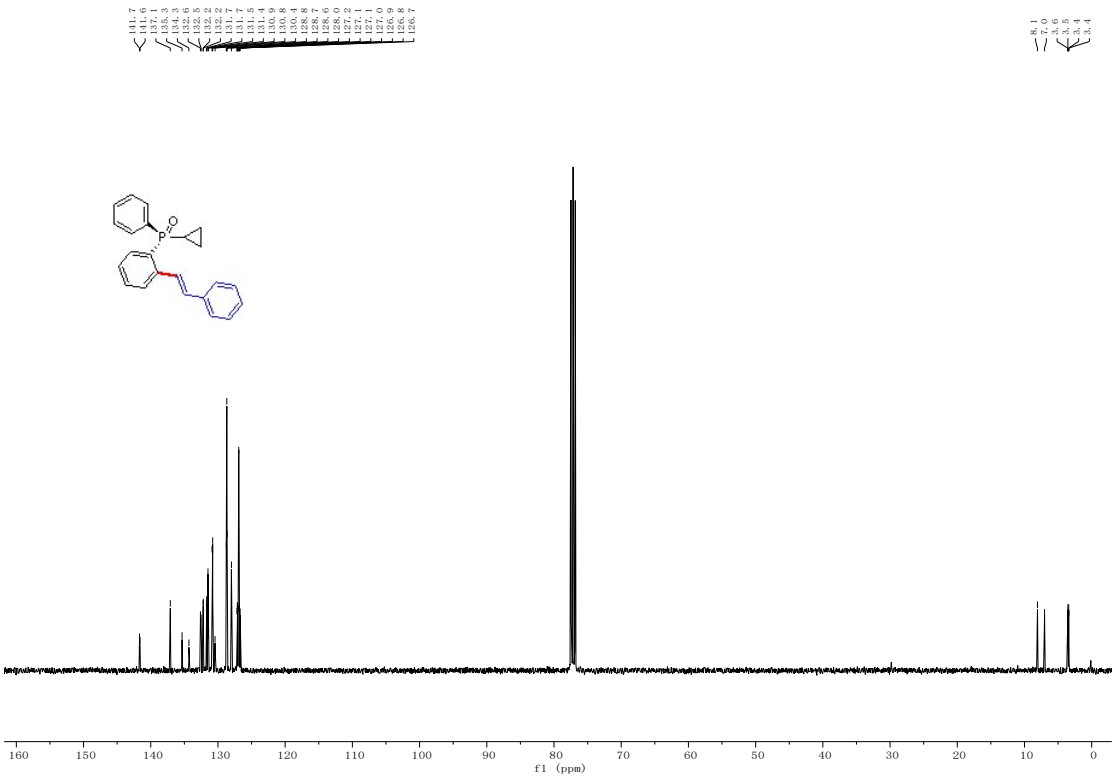
7a, ^{31}P NMR, 162 MHz, $CDCl_3$



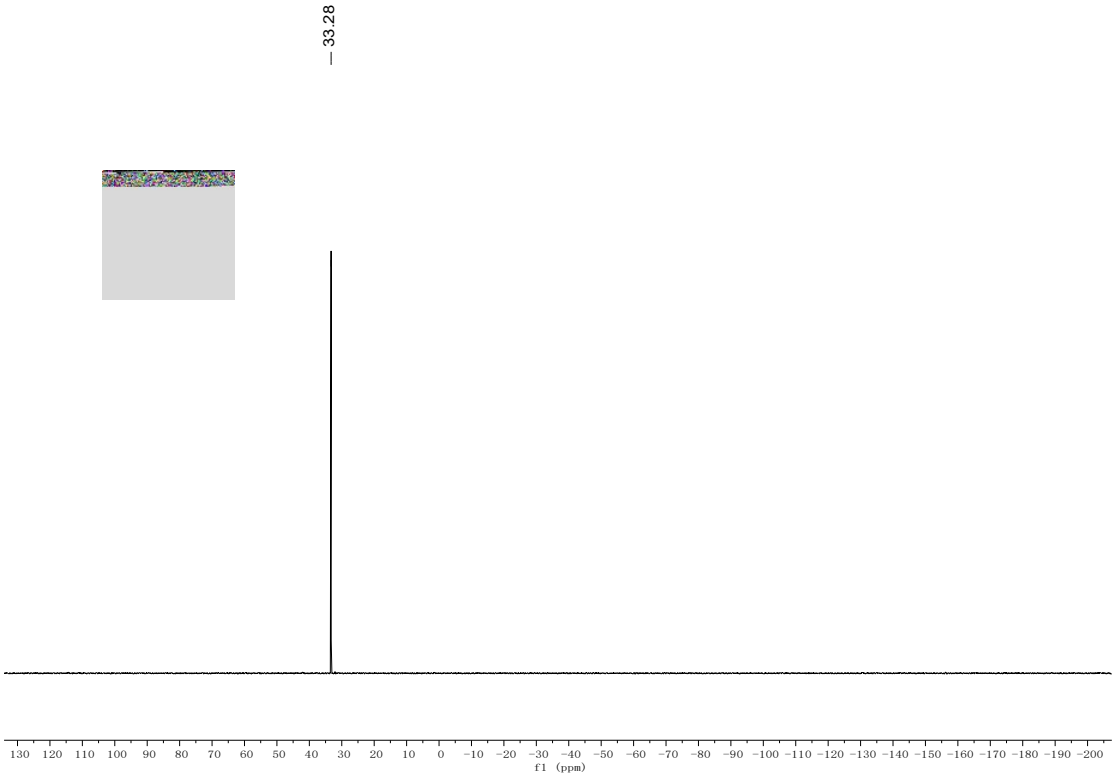
7b, ^{1}H NMR, 400 MHz, $CDCl_3$



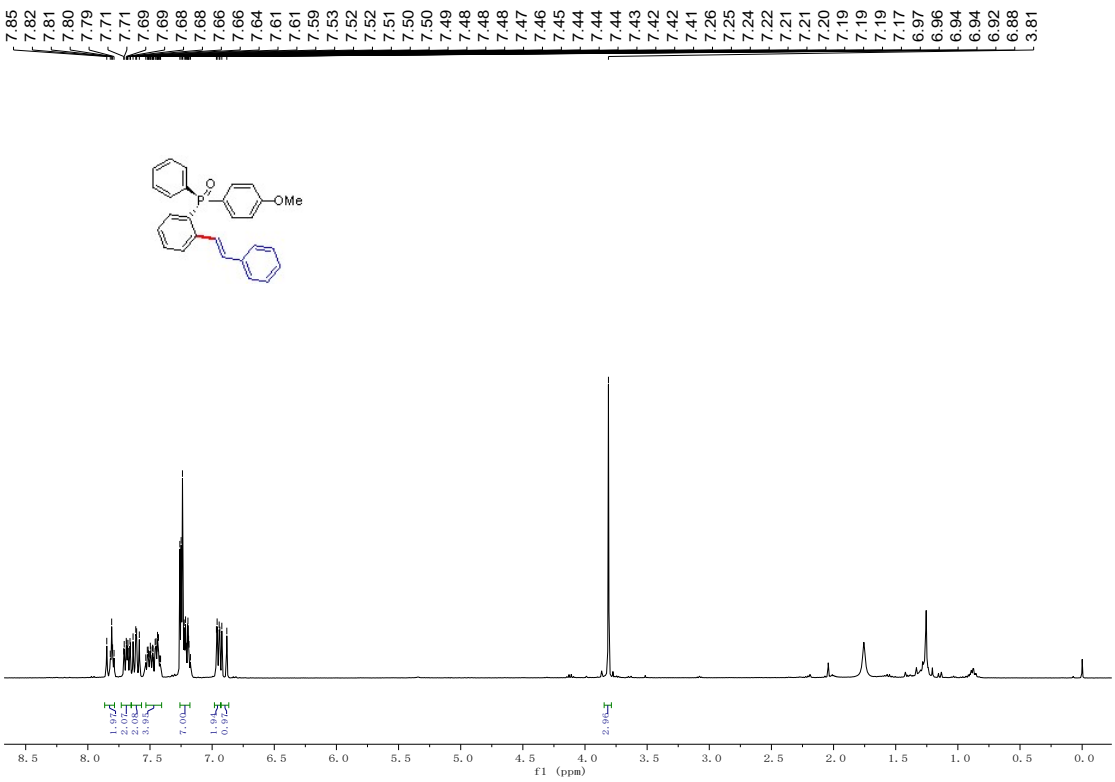
7b, ^{13}C NMR, 101 MHz, $CDCl_3$



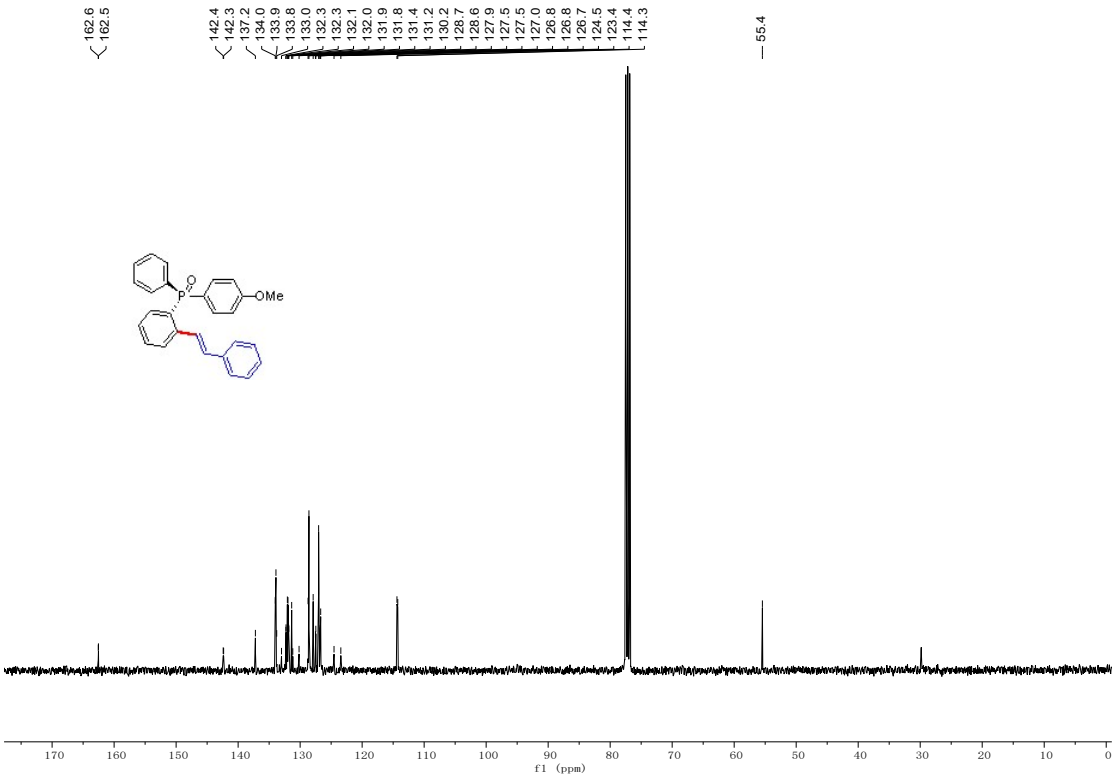
7b, ^{31}P NMR, 162 MHz, $CDCl_3$



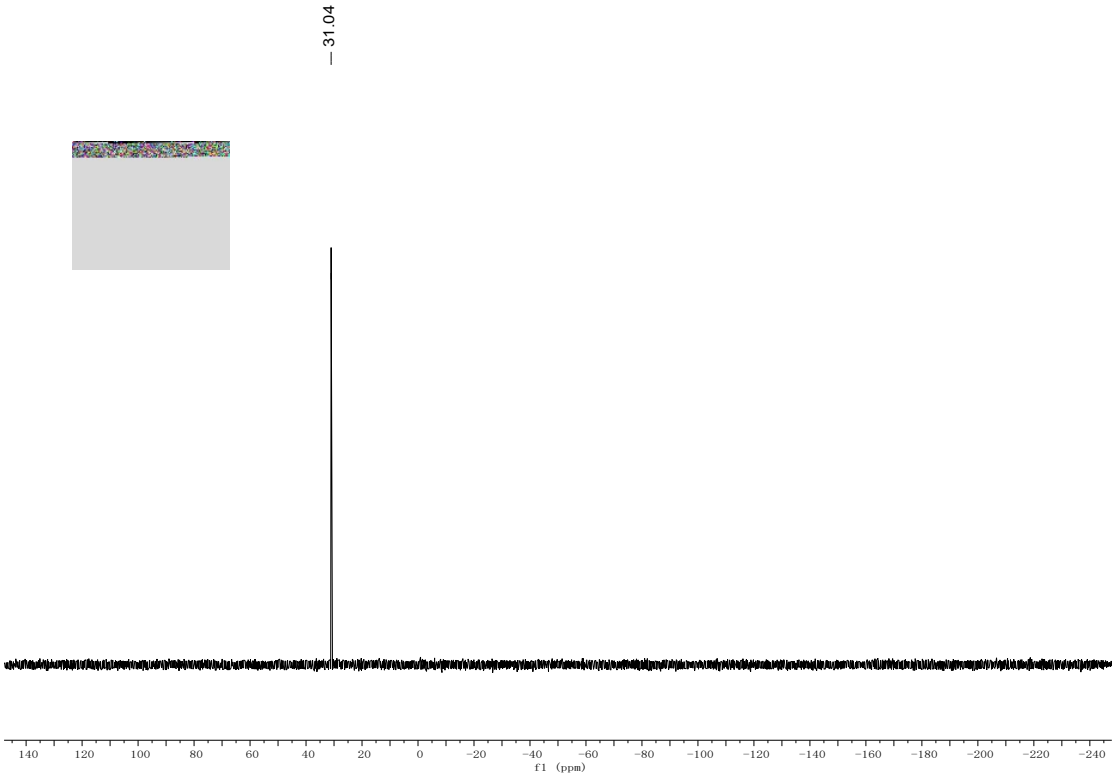
7c, ^{1}H NMR, 400 MHz, $CDCl_3$



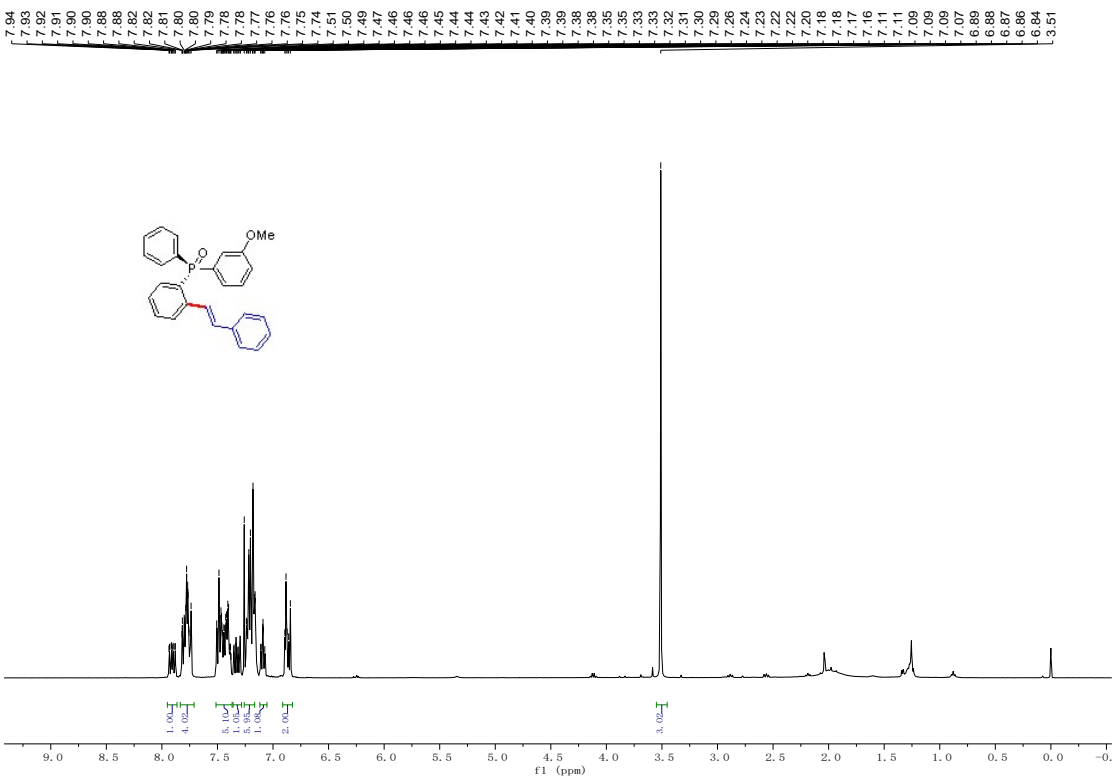
7c, ^{13}C NMR, 101 MHz, $CDCl_3$



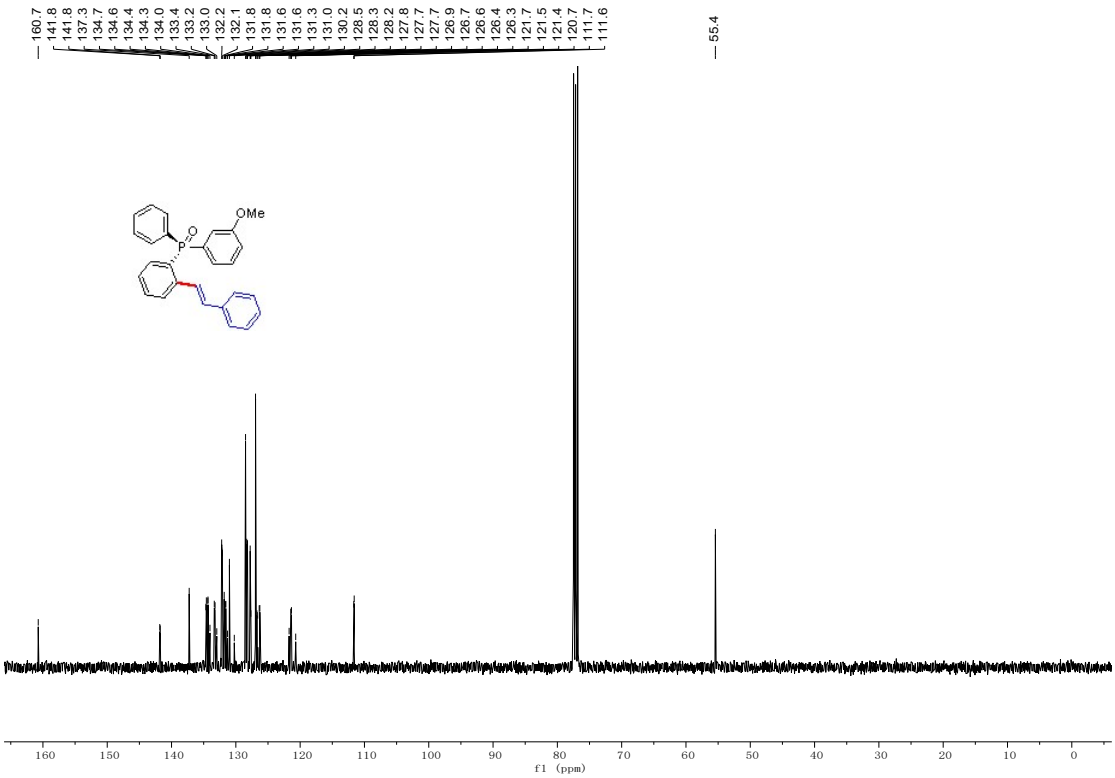
7c, ^{31}P NMR, 162 MHz, $CDCl_3$



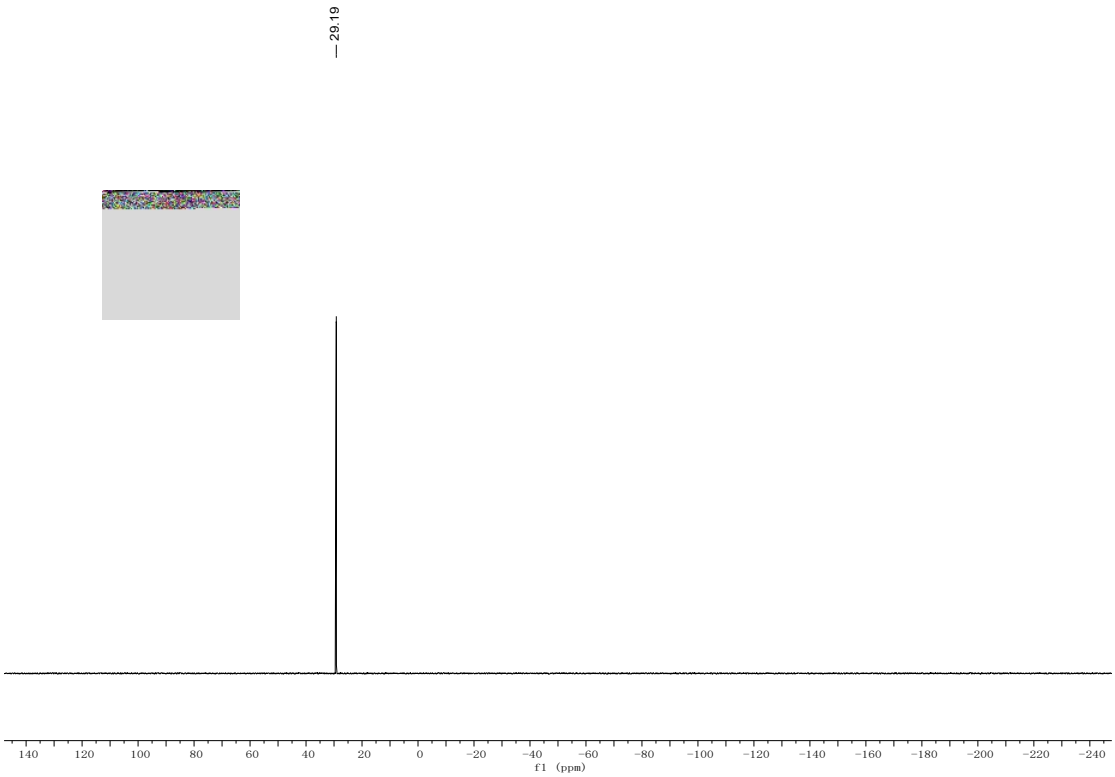
7d, ^{1}H NMR, 400 MHz, $CDCl_3$



7d, ^{13}C NMR, 101 MHz, $CDCl_3$



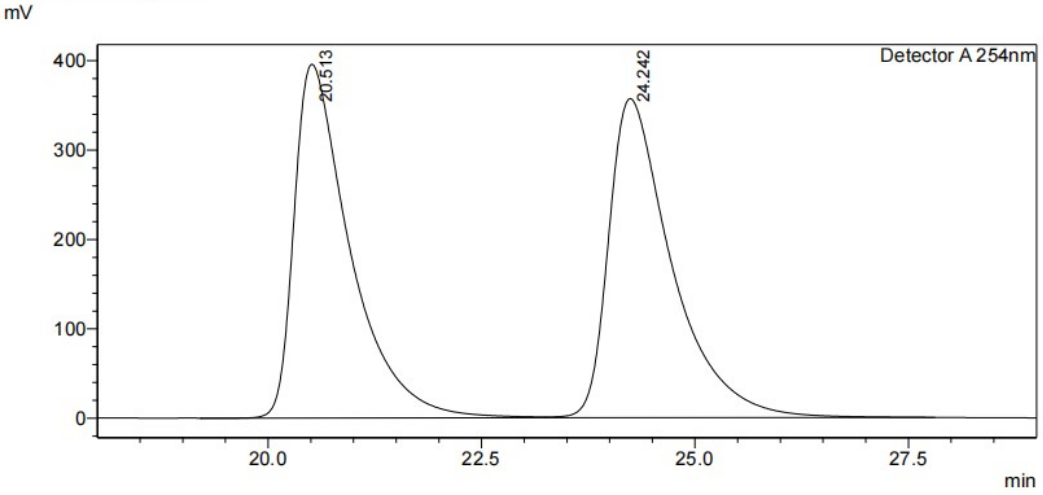
7d, ^{31}P NMR, 162 MHz, $CDCl_3$



9. HPLC Charts

3a: IA, Hexane/*i*PrOH = 85/15, rate = 0.8 mL/min, 254 nm

<Chromatogram>

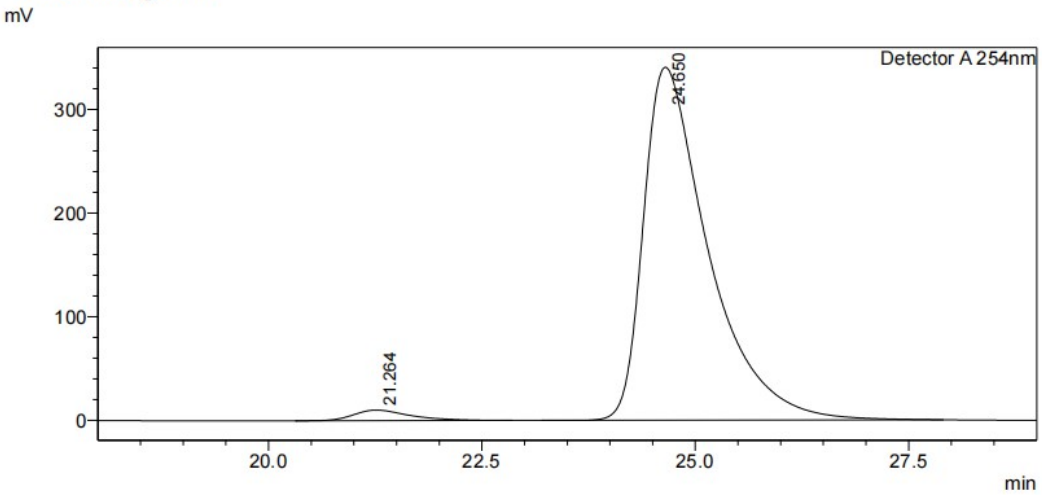


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.513	18021833	395566	49.461		M	
2	24.242	18414680	356883	50.539		V M	
Total		36436513	752449				

<Chromatogram>



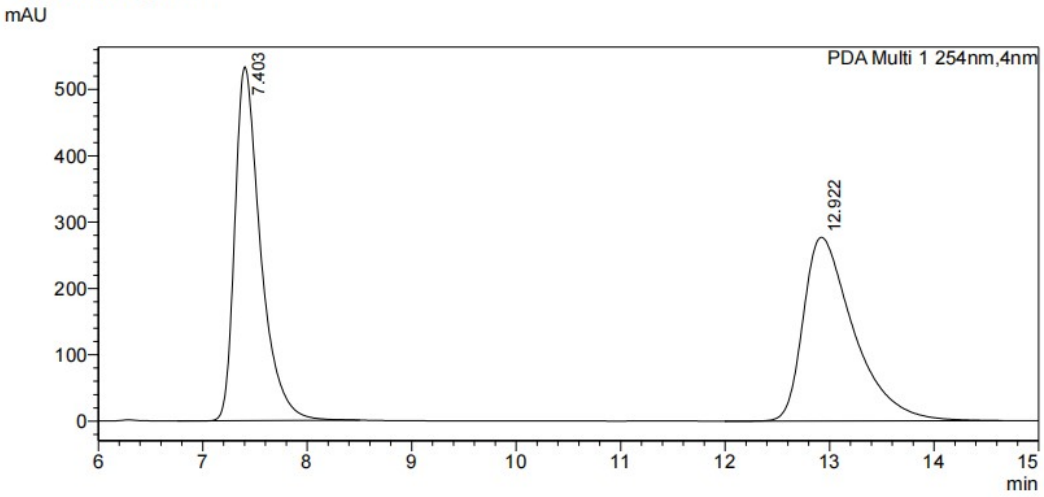
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.264	464334	10145	2.515		M	
2	24.650	17997694	340532	97.485		M	
Total		18462029	350677				

3b: IA, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

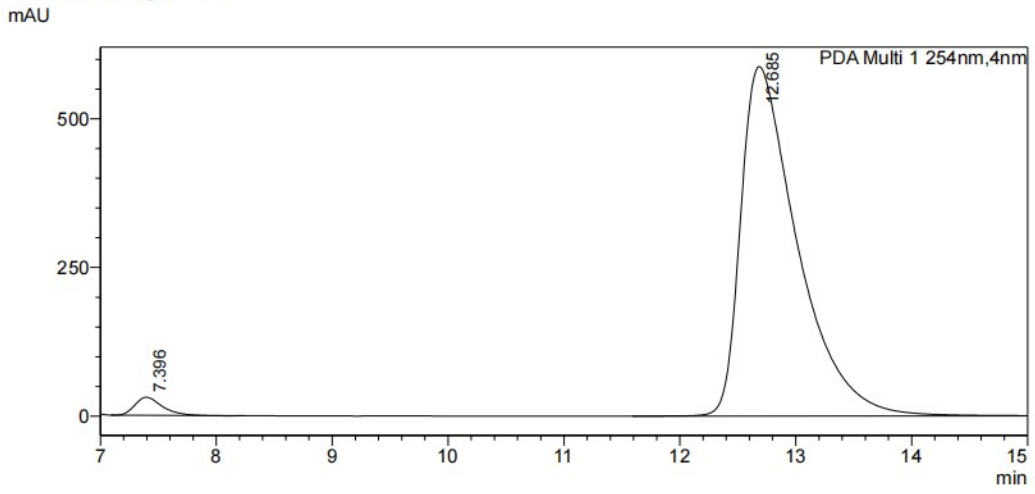


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	7.403	9126306	533248	49.570	0.000	
2	12.922	9284578	276810	50.430	0.000	
Total		18410884	810057	100.000		

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	7.396	493359	30391	2.406	0.000	
2	12.685	20013708	587648	97.594	0.000	
Total		20507066	618039	100.000		

3c: IA, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

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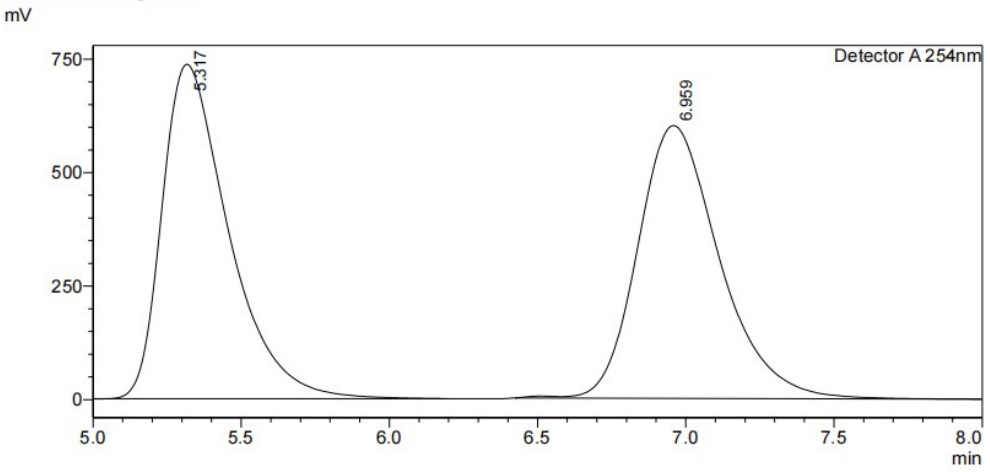
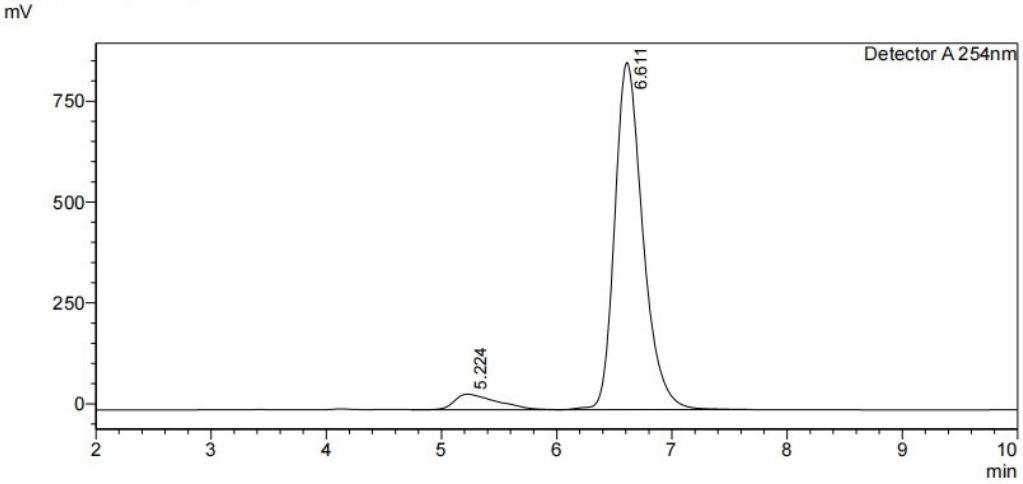


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.317	11512603	736915	49.950		M	
2	6.959	11535828	601005	50.050		M	
Total		23048431	1337920				

<Chromatogram>



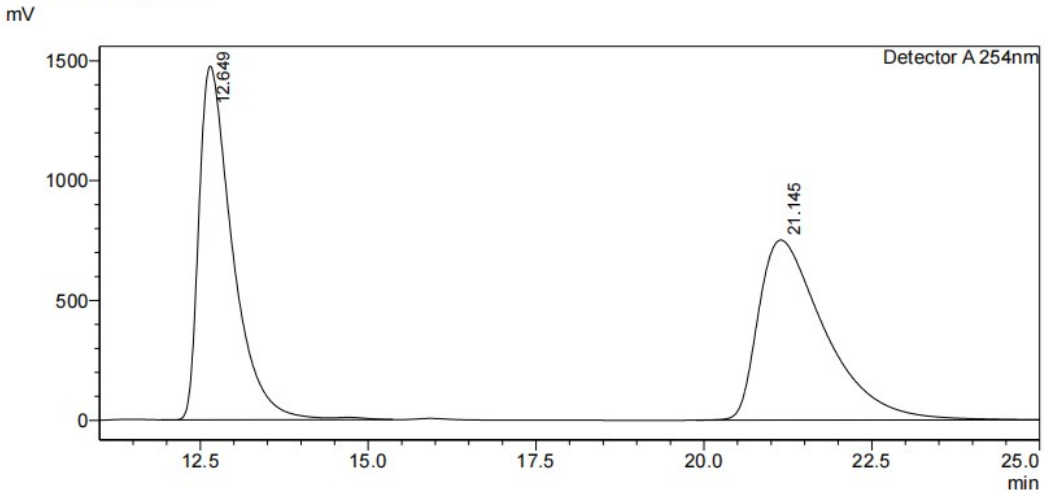
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.224	968158	38371	6.209		M	
2	6.611	14623791	859792	93.791		M	
Total		15591950	898163				

3d: IA, Hexane/*i*PrOH = 70/30, rate = 0.7 mL/min, 254 nm

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.649	51203290	1475885	49.622		M	
2	21.145	51983418	751423	50.378		M	
Total		103186708	2227308				

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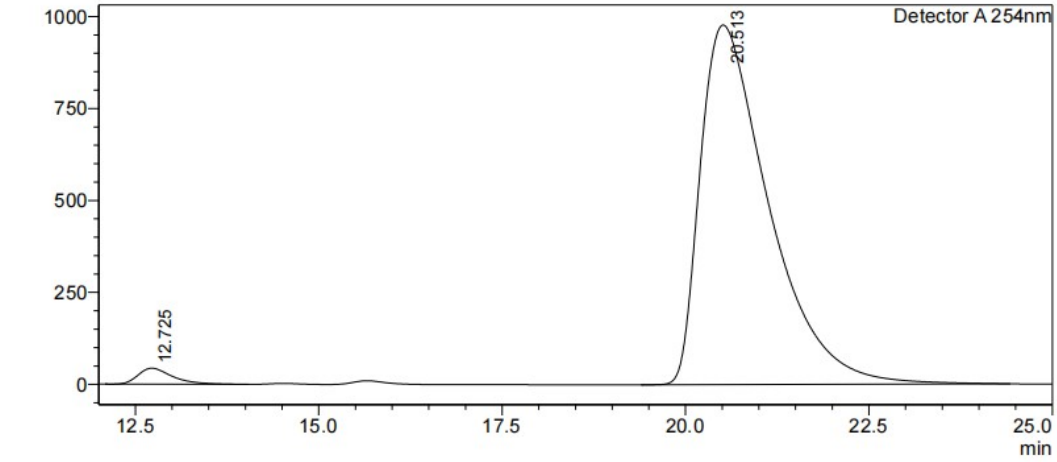


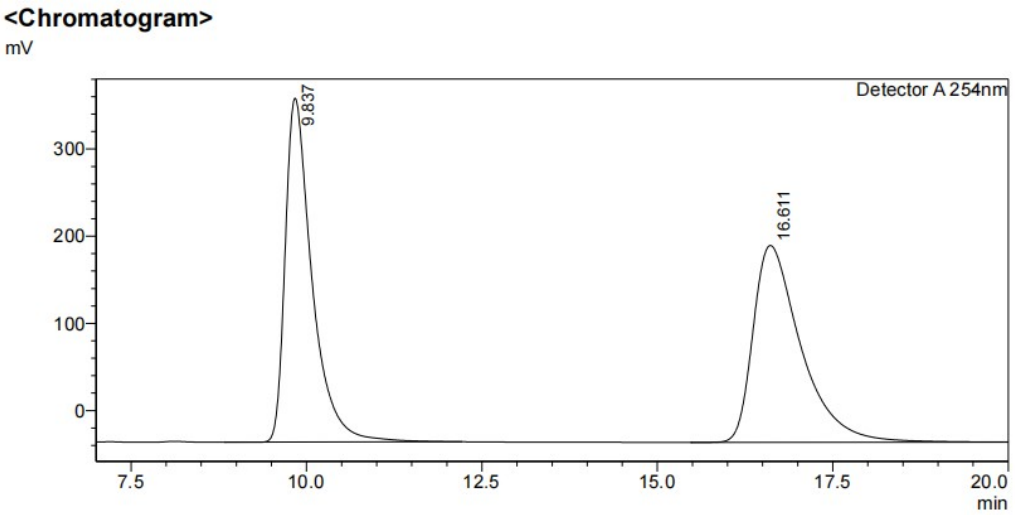
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.725	1417665	43510	2.178		M	
2	20.513	63671468	977221	97.822		M	
Total		65089133	1020732				

3e: IA, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

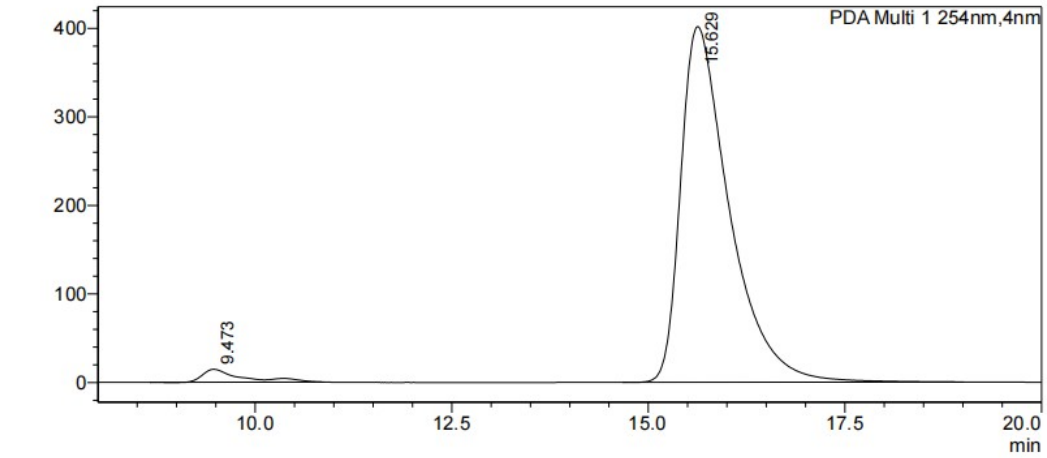


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.837	10495154	394293	49.424		M	
2	16.611	10739729	225816	50.576		M	
Total		21234883	620109				

<Chromatogram>



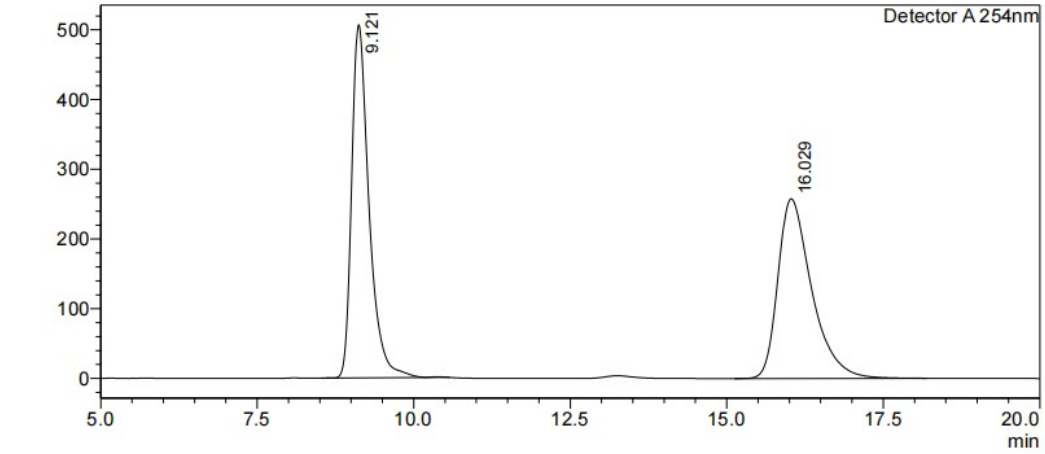
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	9.473	512813	14607	2.872	0.000	
2	15.629	17342430	401666	97.128	0.000	
Total		17855243	416274	100.000		

3f: IA Hexane/*i*PrOH = 85/15, rate = 0.8 mL/min, 254 nm

<Chromatogram>

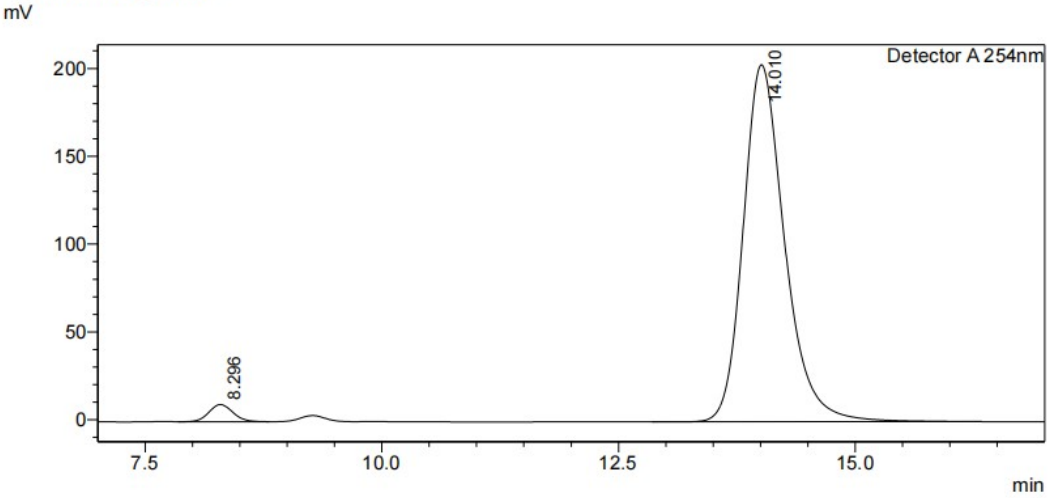


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.121	9742366	506350	50.209		M	
2	16.029	9661135	257617	49.791		M	
Total		19403501	763967				

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.296	171291	9745	2.689		M	
2	14.010	6199018	203297	97.311		M	
Total		6370309	213042				

3g: IA, Hexane/*i*PrOH = 85/15, rate = 0.8 mL/min, 254 nm

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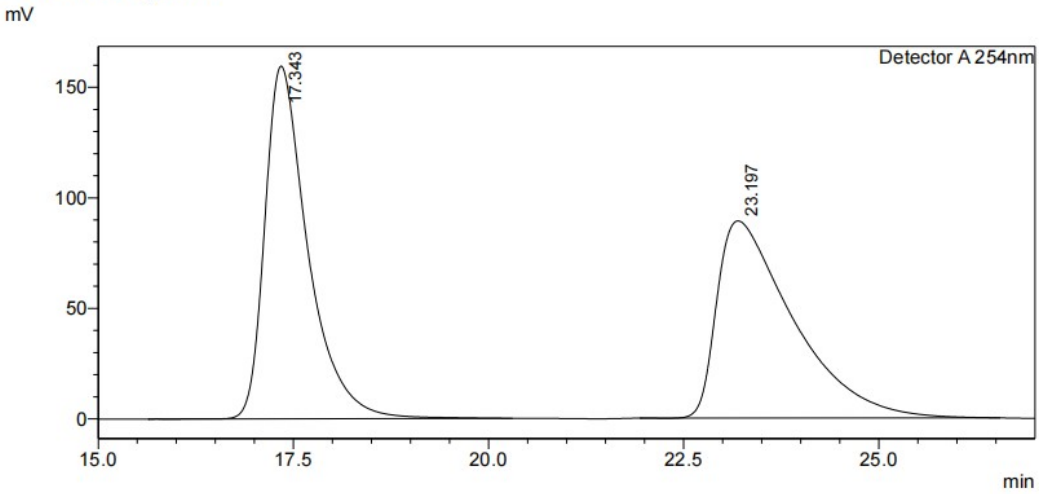
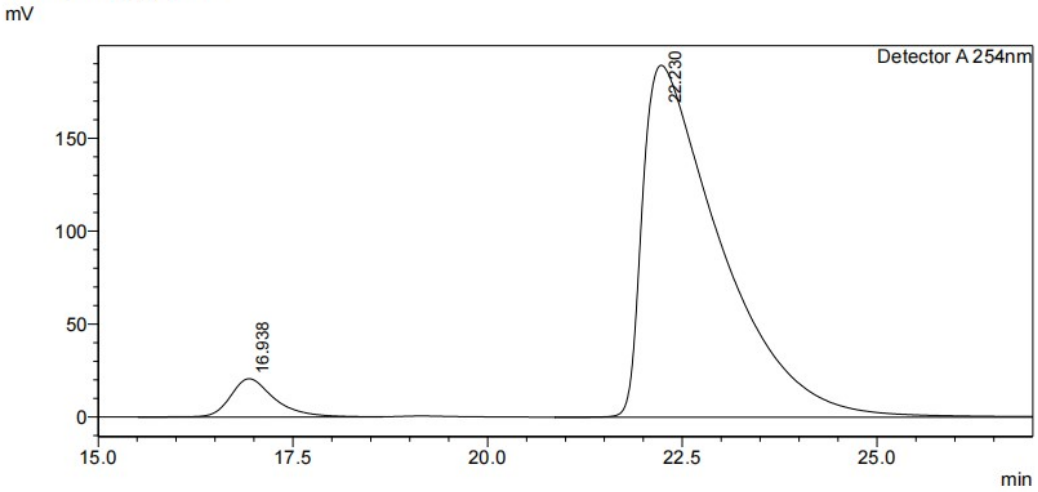


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.343	6125675	159542	50.225		M	
2	23.197	6070684	89202	49.775		M	
Total		12196359	248744				

<Chromatogram>



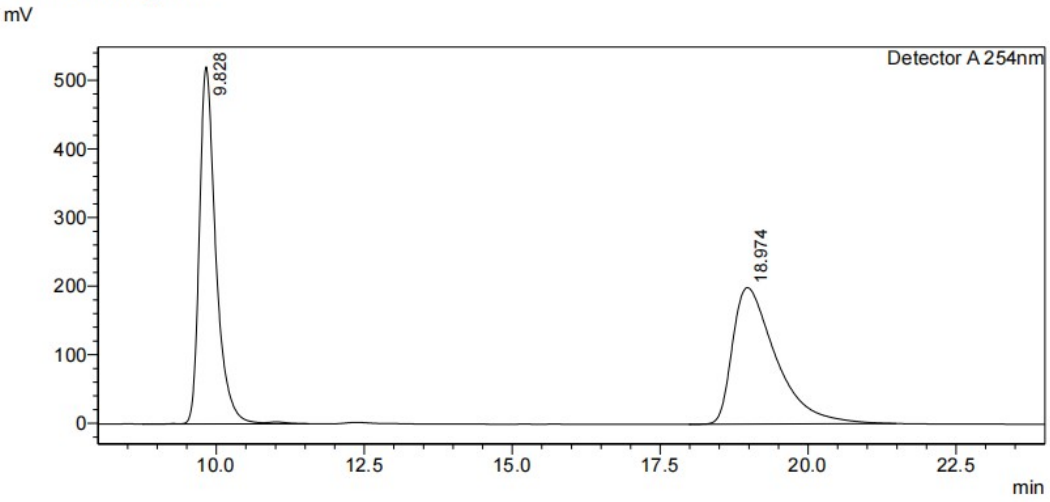
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.938	821603	20638	5.834		M	
2	22.230	13260520	189223	94.166		M	
Total		14082123	209862				

3h: IA, Hexane/*i*PrOH = 70/30, rate = 0.7 mL/min, 254 nm

<Chromatogram>

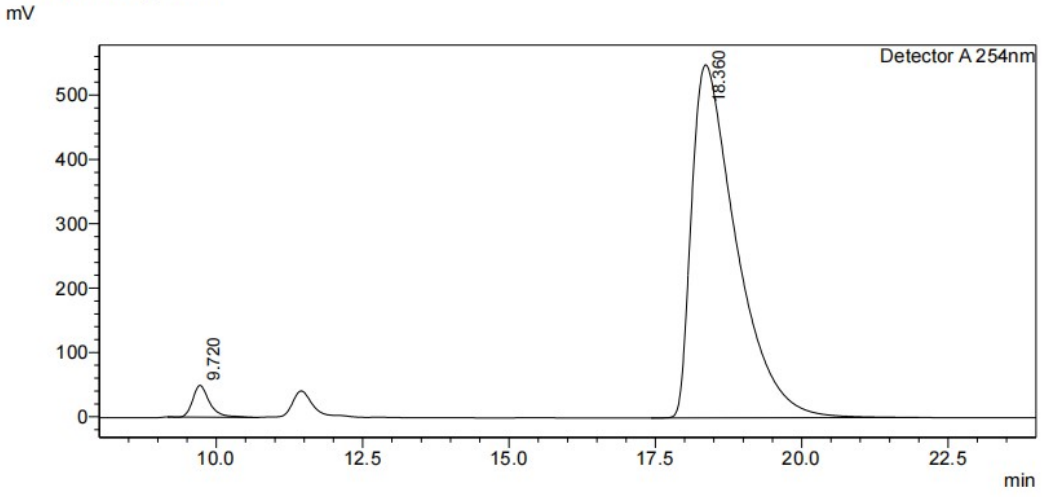


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.828	10056950	520217	49.716		M	
2	18.974	10171664	198909	50.284		M	
Total		20228614	719126				

<Chromatogram>



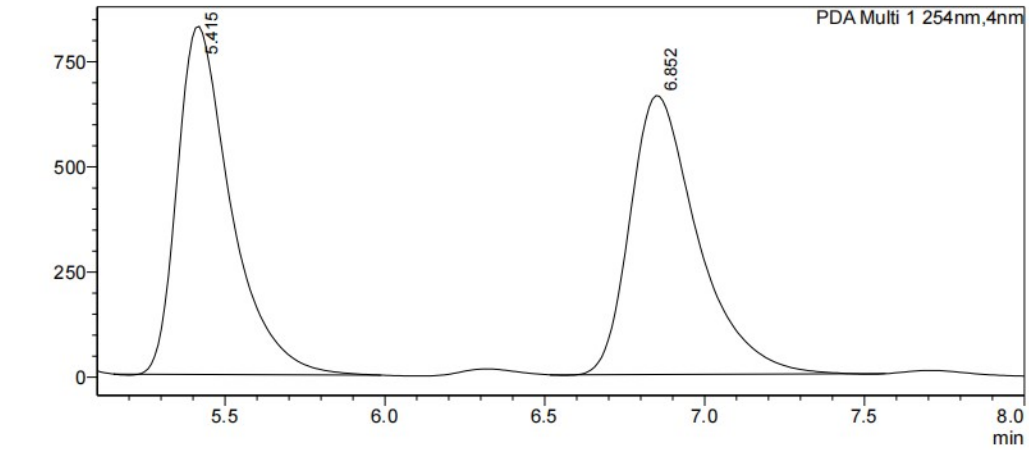
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.720	973349	49161	3.233		M	
2	18.360	29129745	548585	96.767		M	
Total		30103093	597746				

3i: IA, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

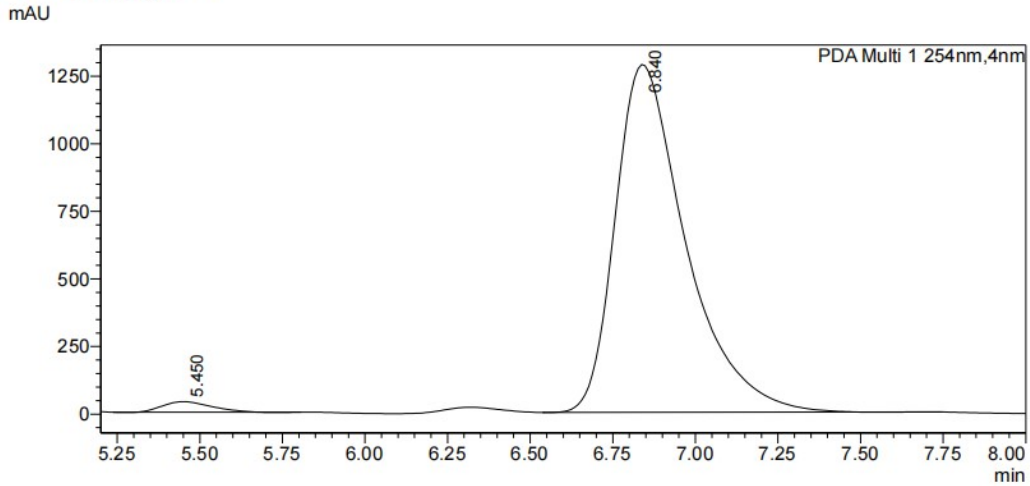


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	5.415	9675076	827030	49.723	0.000	
2	6.852	9782936	662962	50.277	0.000	
Total		19458012	1489992	100.000		

<Chromatogram>



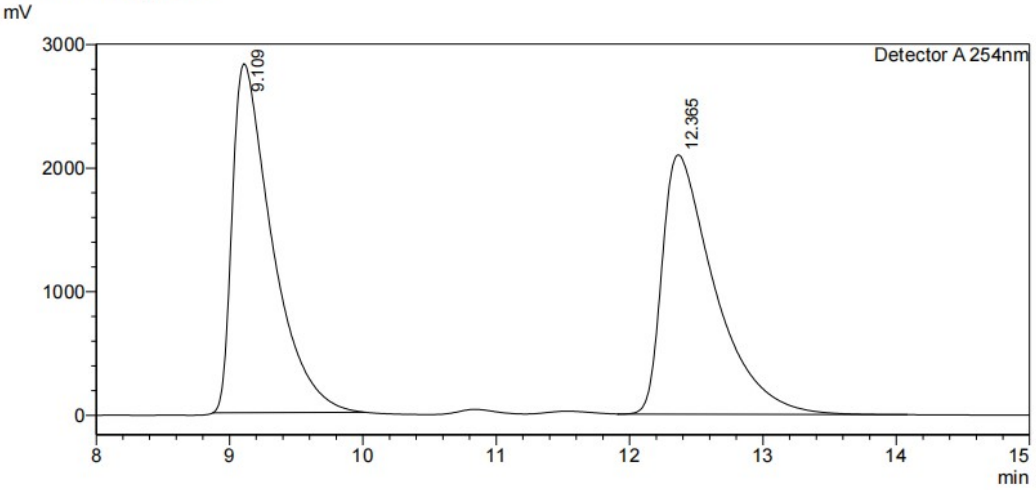
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	5.450	397216	39141	2.038	0.000	
2	6.840	19095539	1286700	97.962	0.000	
Total		19492755	1325841	100.000		

3j: IA, Hexane/*i*PrOH = 90/10, rate = 0.8 mL/min, 254 nm

<Chromatogram>

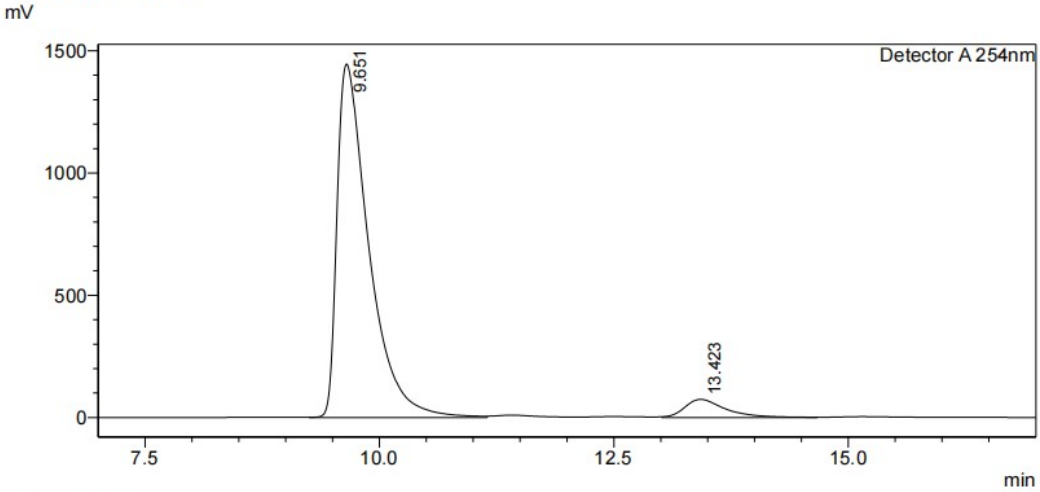


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.109	58421480	2823036	50.328		M	
2	12.365	57660971	2097505	49.672		M	
Total		116082451	4920541				

<Chromatogram>



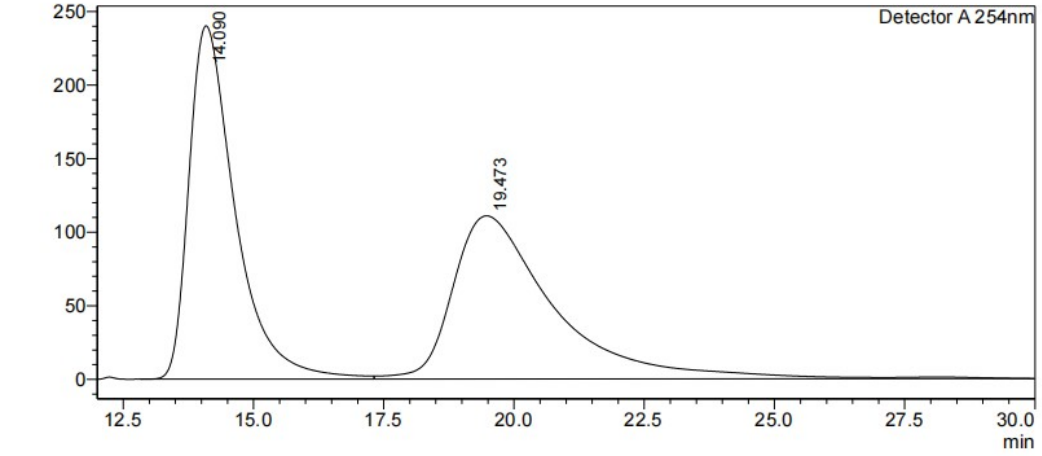
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.651	34078525	1445881	93.784		M	
2	13.423	2258634	74233	6.216		M	
Total		36337159	1520114				

3k: OD-H, Hexane/*i*PrOH = 90/10, rate = 0.8 mL/min, 254 nm

<Chromatogram>

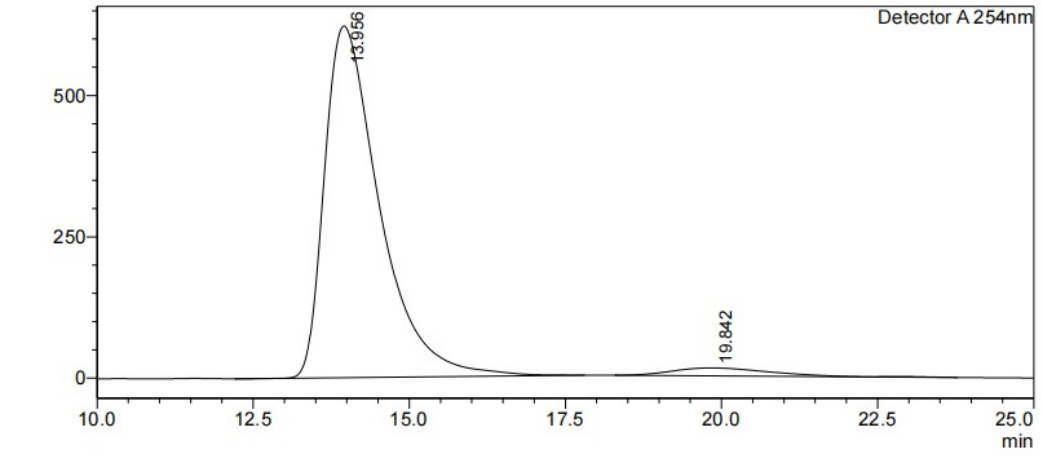


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.090	14837898	240021	49.688		M	
2	19.473	15024146	110793	50.312		V M	
Total		29862044	350814				

<Chromatogram>



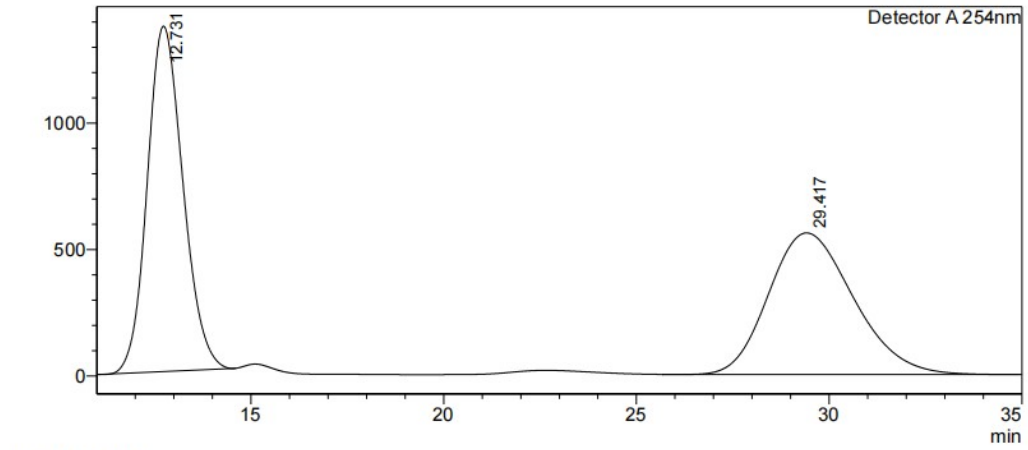
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.956	38145321	621816	96.086		M	
2	19.842	1553773	14039	3.914		M	
Total		39699094	635855				

3l: AD-H, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

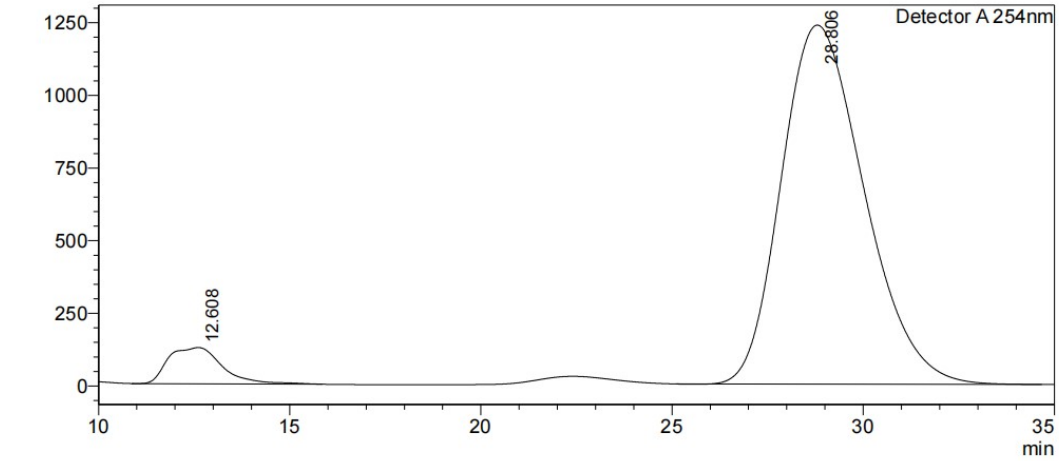


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.731	88170548	1366225	50.660		M	
2	29.417	85873866	559913	49.340		M	
Total		174044414	1926138				

<Chromatogram>



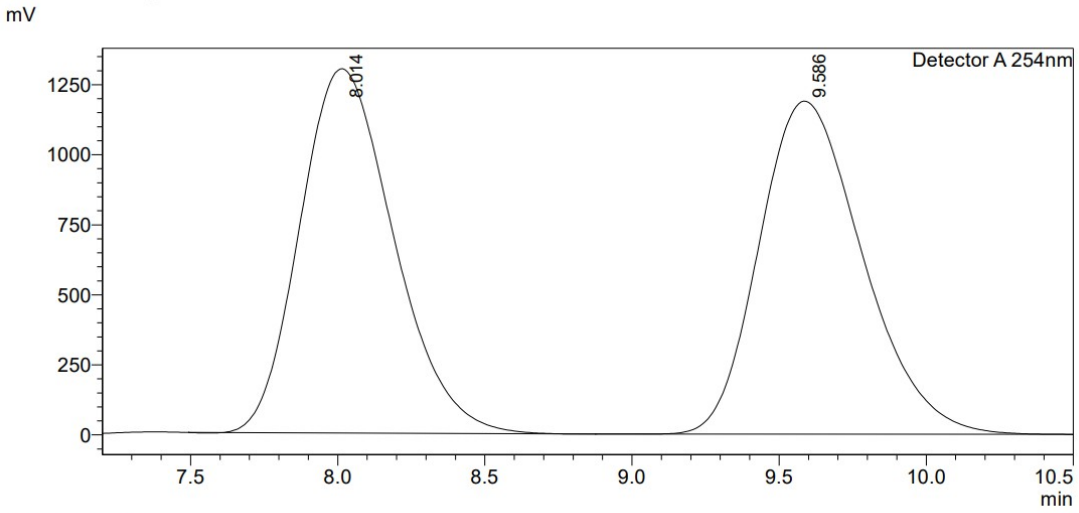
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.608	12228725	124709	6.162		M	
2	28.806	186237581	1235510	93.838		M	
Total		198466305	1360219				

3m: AD-H, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

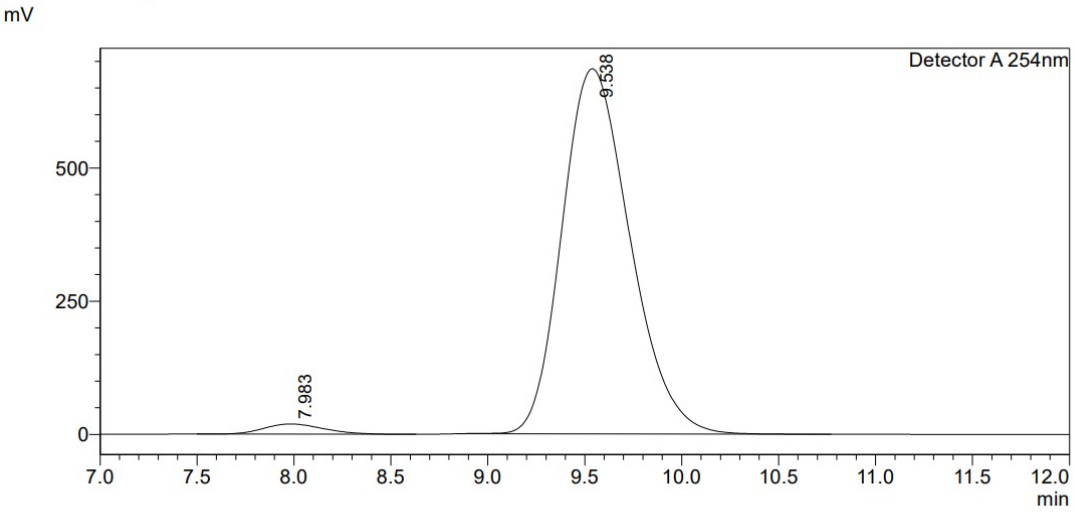


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.014	28883434	1300790	49.850		M	
2	9.586	29057279	1188804	50.150		M	
Total		57940712	2489593				

<Chromatogram>



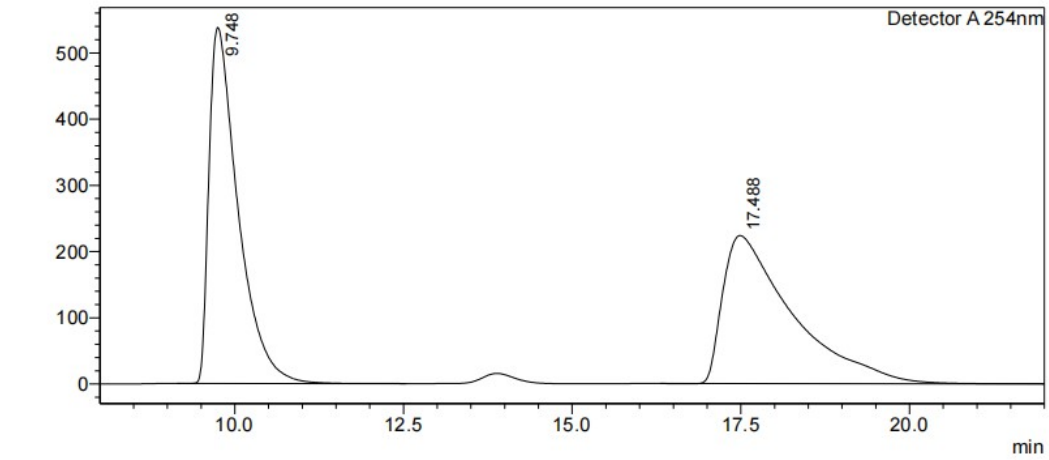
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.983	402683	18928	2.353		M	
2	9.538	16711307	685292	97.647		M	
Total		17113989	704220				

3n: IA, Hexane/*i*PrOH = 90/10, rate = 0.8 mL/min, 254 nm

<Chromatogram>

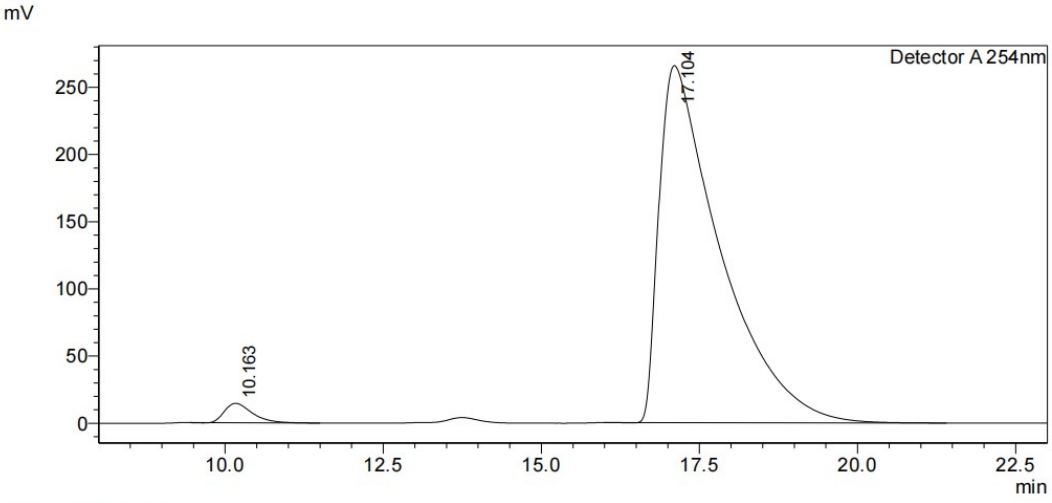


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.748	16174311	537669	50.198		M	
2	17.488	16046521	223459	49.802		M	
Total		32220832	761129				

<Chromatogram>



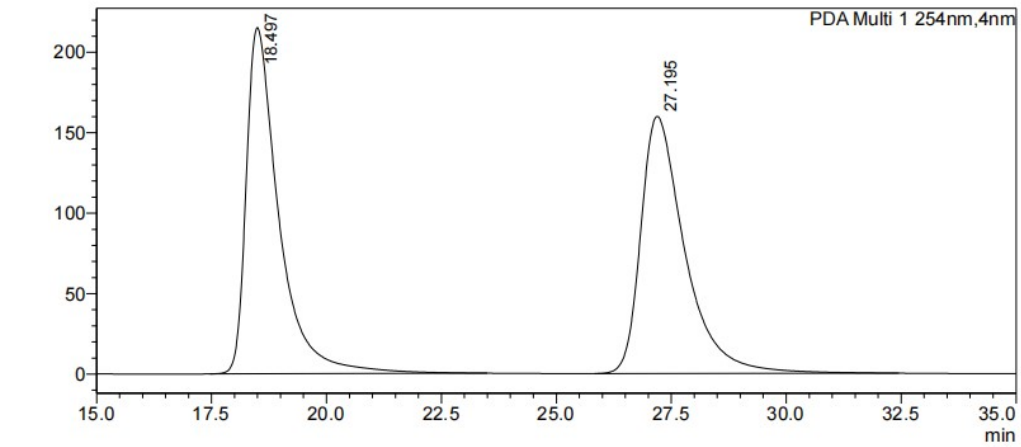
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.163	444737	14470	2.426		M	
2	17.104	17885238	265672	97.574		M	
Total		18329975	280142				

3o: IA, Hexane/*i*PrOH = 85/15, rate = 0.8 mL/min, 254 nm

<Chromatogram>

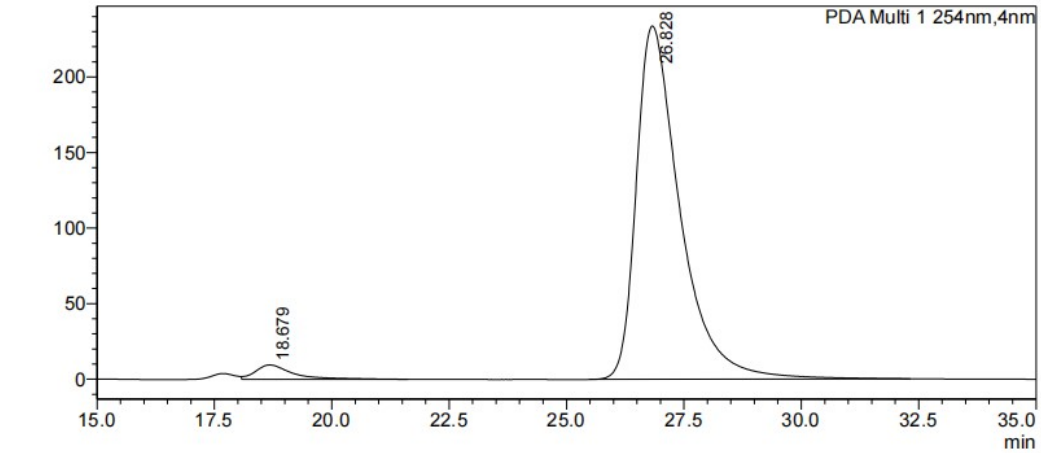


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	18.497	10635582	215092	49.899	0.000	
2	27.195	10678586	159753	50.101	0.000	
Total		21314169	374845	100.000		

<Chromatogram>



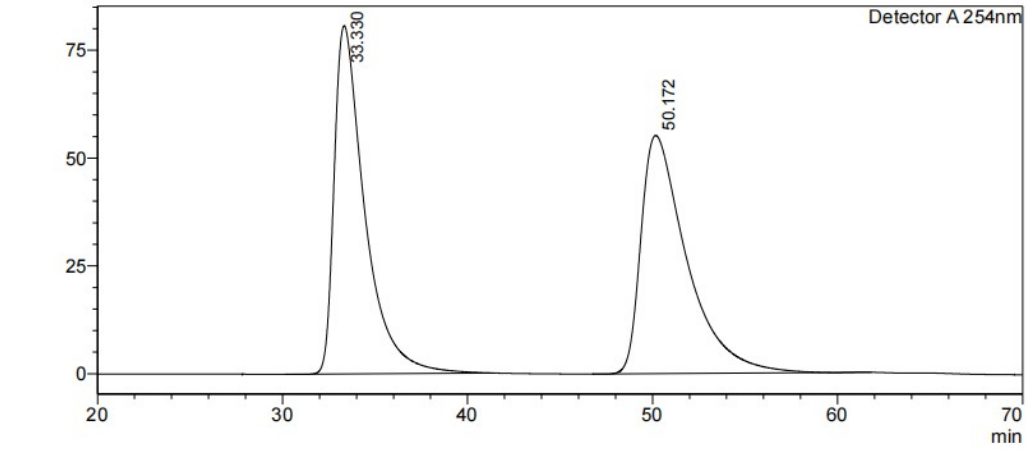
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	18.679	534709	9558	3.407	0.000	
2	26.828	15161589	233806	96.593	0.000	
Total		15696298	243364	100.000		

3p: IA, Hexane/*i*PrOH = 80/20, rate = 1.0 mL/min, 254 nm

<Chromatogram>

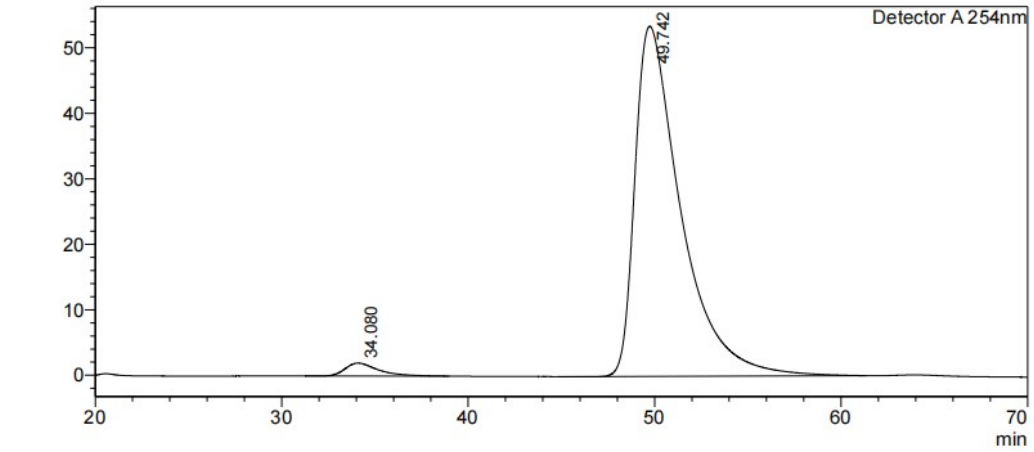


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	33.330	9271685	80746	49.335		M	
2	50.172	9521446	55251	50.665		M	
Total		18793131	135997				

<Chromatogram>



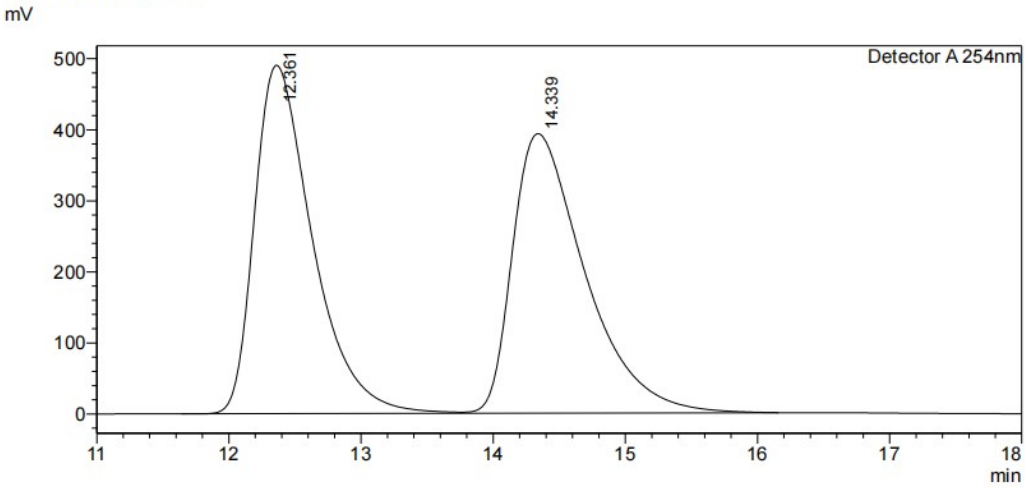
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.080	245072	1973	2.611		M	
2	49.742	9141682	53456	97.389		M	
Total		9386754	55429				

3q: IB *N*-5, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

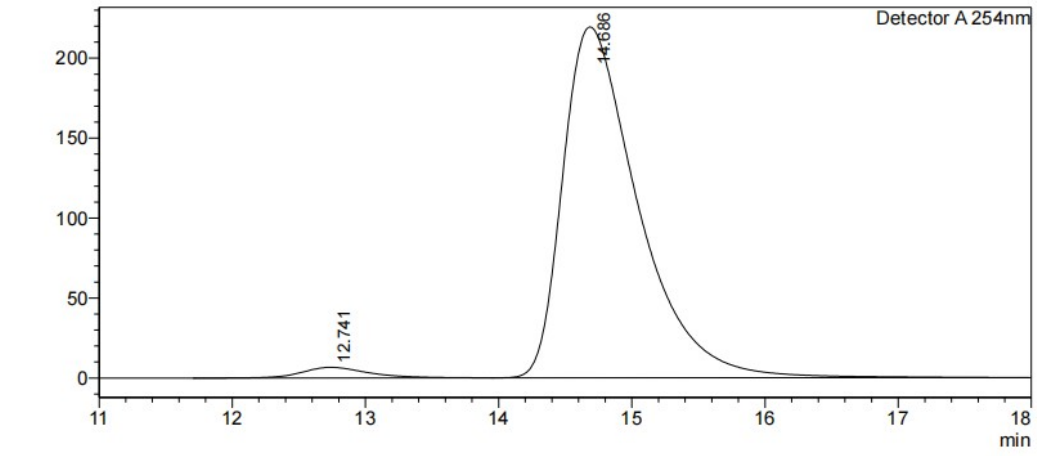


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.361	14937006	490299	49.908		M	
2	14.339	14992016	393370	50.092		V M	
Total		29929023	883670				

<Chromatogram>



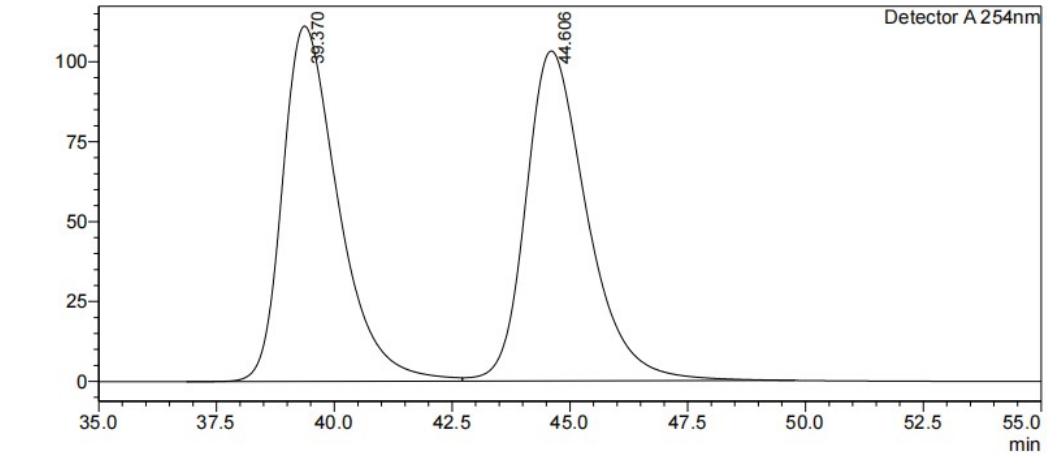
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.741	233180	6664	2.631		M	
2	14.686	8628251	219385	97.369		V M	
Total		8861431	226050				

3r: IA, Hexane/*i*PrOH = 90/10, rate = 0.8 mL/min, 254 nm

<Chromatogram>

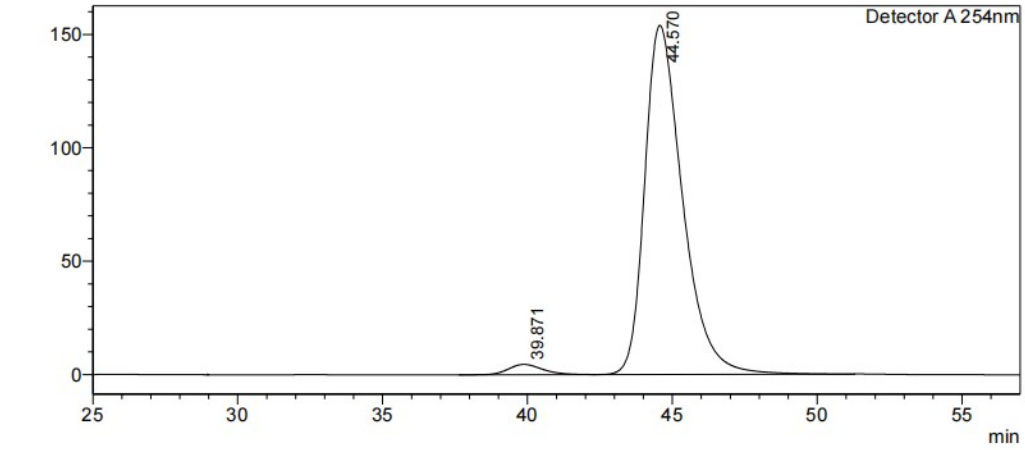


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	39.370	9164739	111125	49.489		M	
2	44.606	9354107	103213	50.511		V M	
Total		18518847	214338				

<Chromatogram>



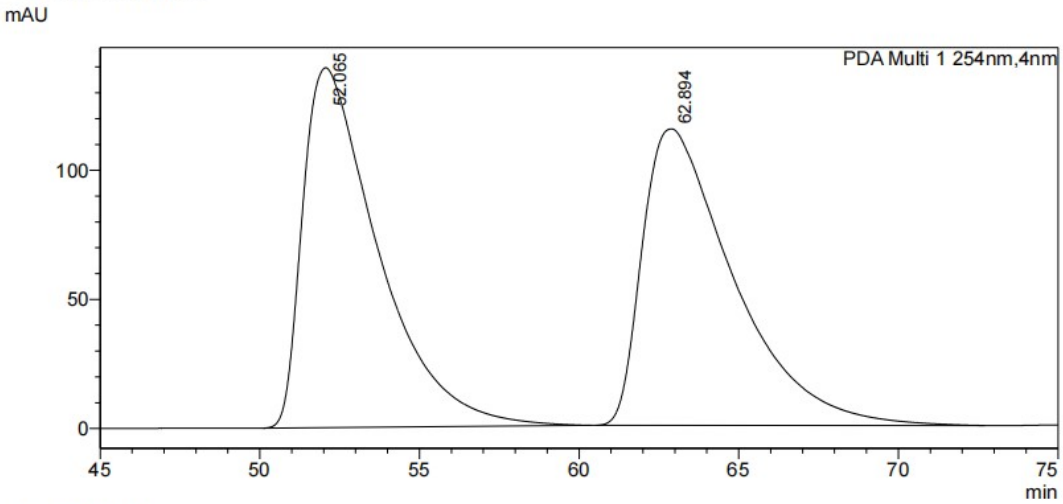
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	39.871	369866	4537	2.579		M	
2	44.570	13970836	153969	97.421		M	
Total		14340702	158506				

3s: OD-H, Hexane/*i*PrOH = 94/6, rate = 0.6 mL/min, 254 nm

<Chromatogram>

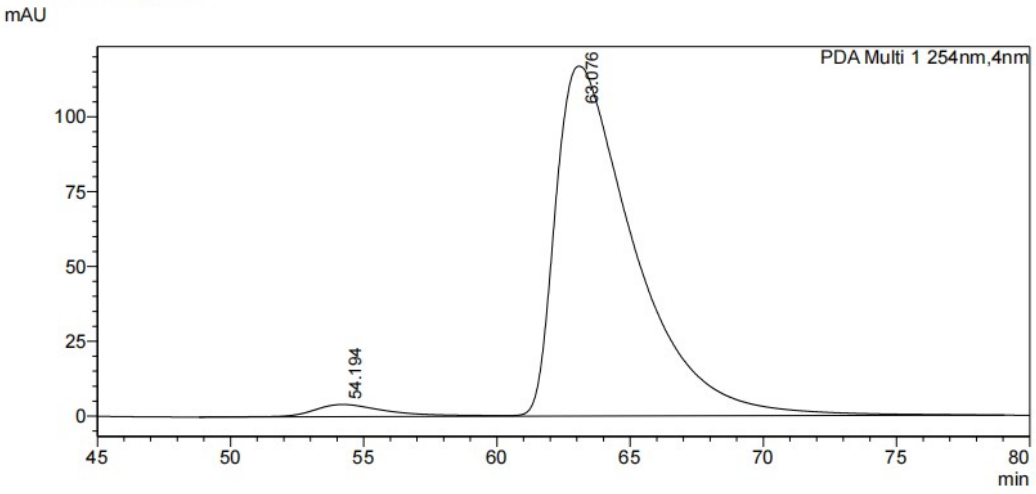


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	52.065	22932298	139350	50.061	0.000	
2	62.894	22876220	114817	49.939	0.000	
Total		45808518	254167	100.000		

<Chromatogram>



<Peak Table>

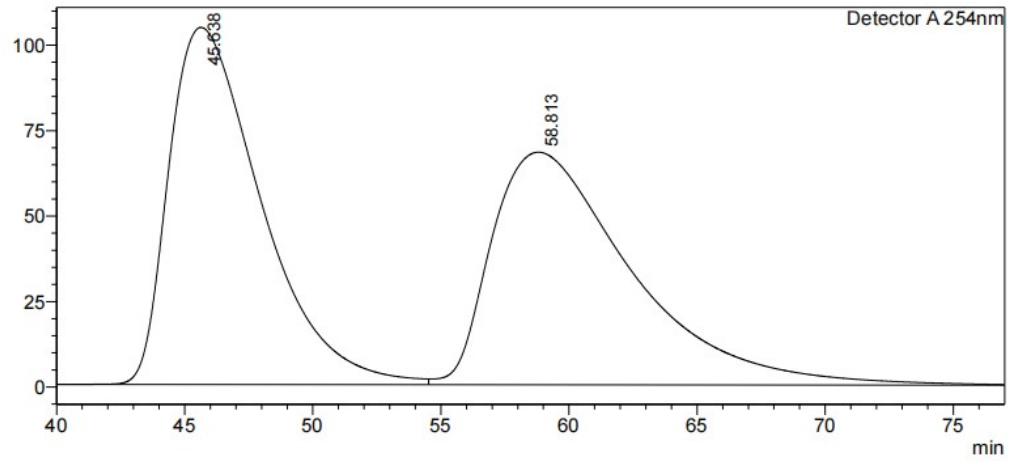
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	54.194	755574	4078	3.039	0.000	
2	63.076	24104505	116901	96.961	0.000	
Total		24860078	120979	100.000		

3t: AS-H, Hexane/*i*PrOH = 95/5, rate = 0.6 mL/min, 254 nm

<Chromatogram>

mV



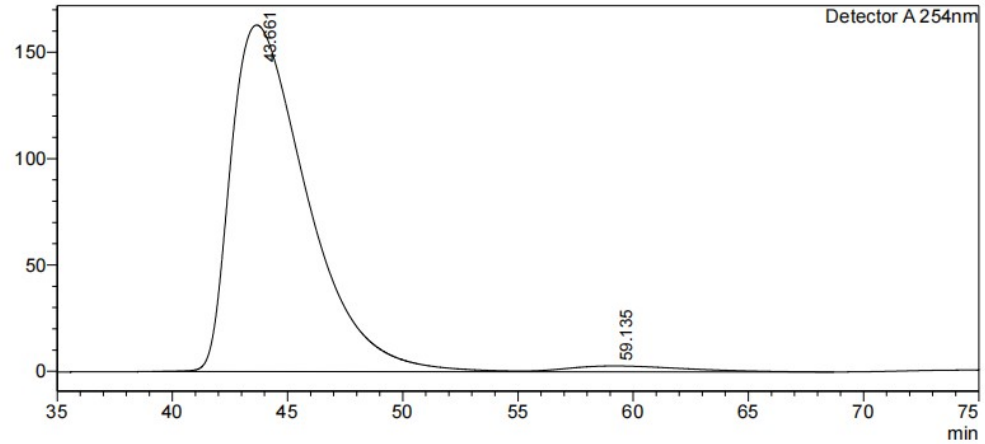
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	45.638	26246300	104497	50.229		M	
2	58.813	26006572	68067	49.771		V M	
Total		52252872	172564				

<Chromatogram>

mV



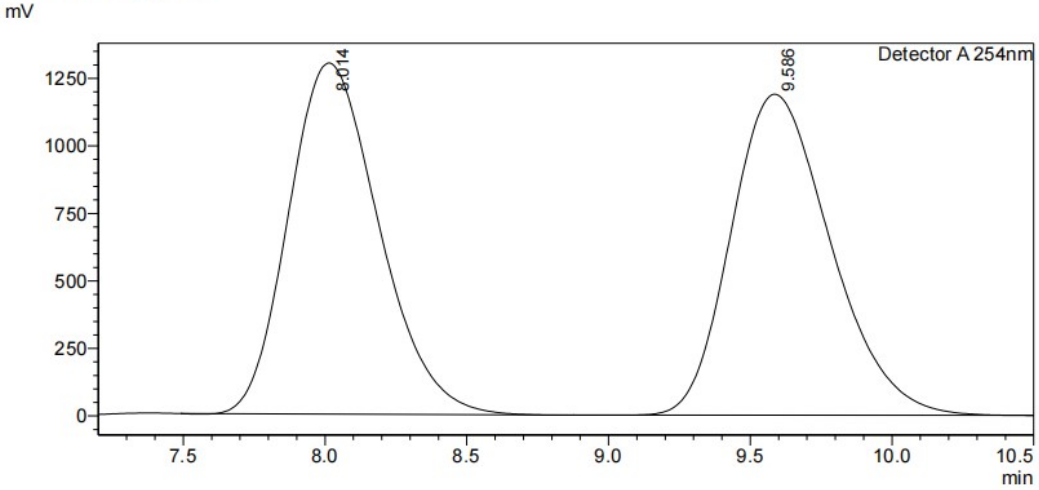
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	43.661	37451303	162892	97.467		M	
2	59.135	973190	2753	2.533		V M	
Total		38424493	165645				

3u: IA, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

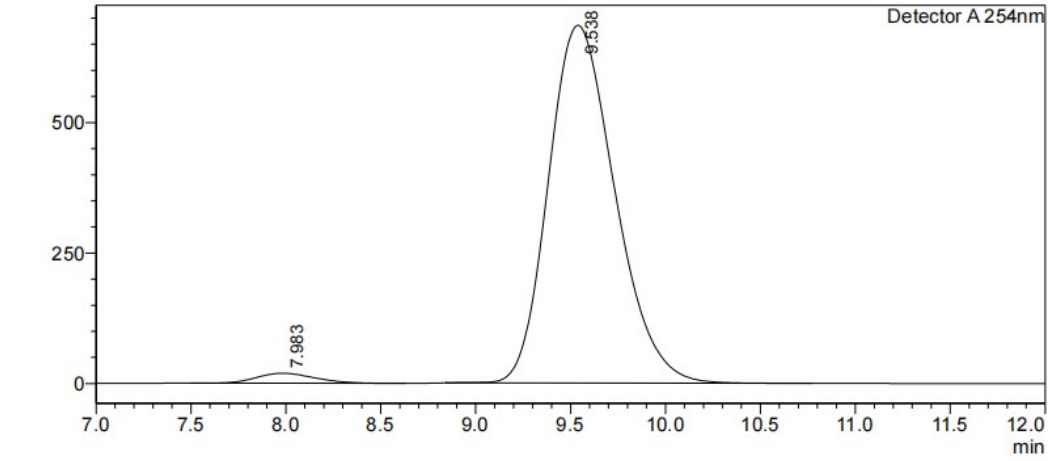


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.014	28883434	1300790	49.850		M	
2	9.586	29057279	1188804	50.150		M	
Total		57940712	2489593				

<Chromatogram>



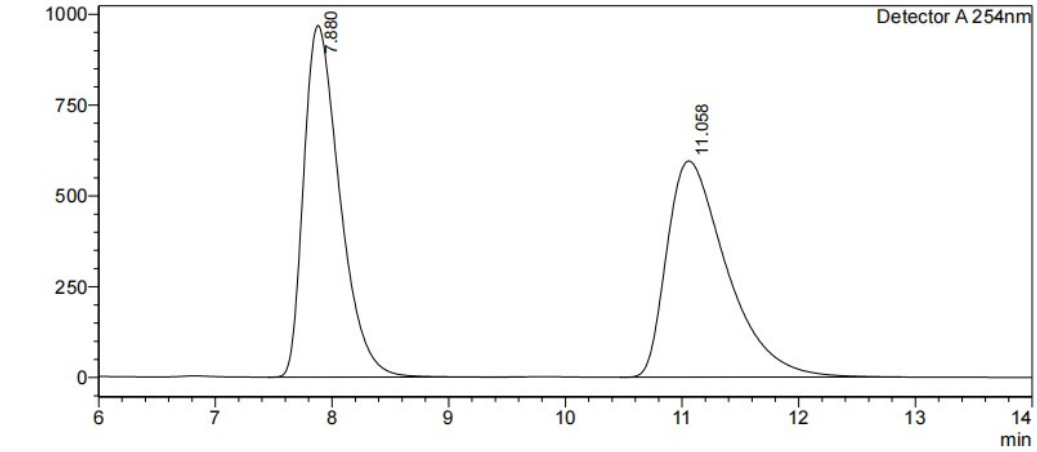
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.983	402683	18928	2.353		M	
2	9.538	16711307	685292	97.647		M	
Total		17113989	704220				

3v: AD-H, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

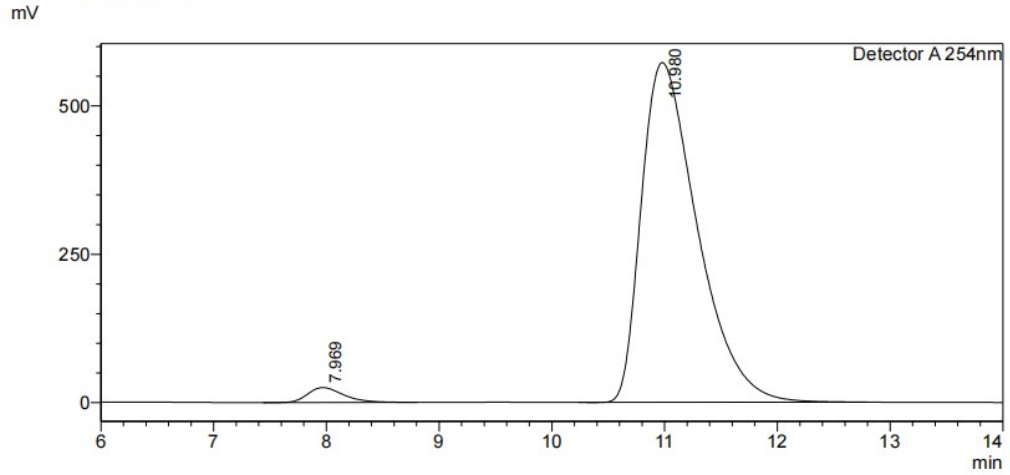


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.880	20762514	967623	49.415		M	
2	11.058	21254441	595290	50.585		M	
Total		42016955	1562912				

<Chromatogram>



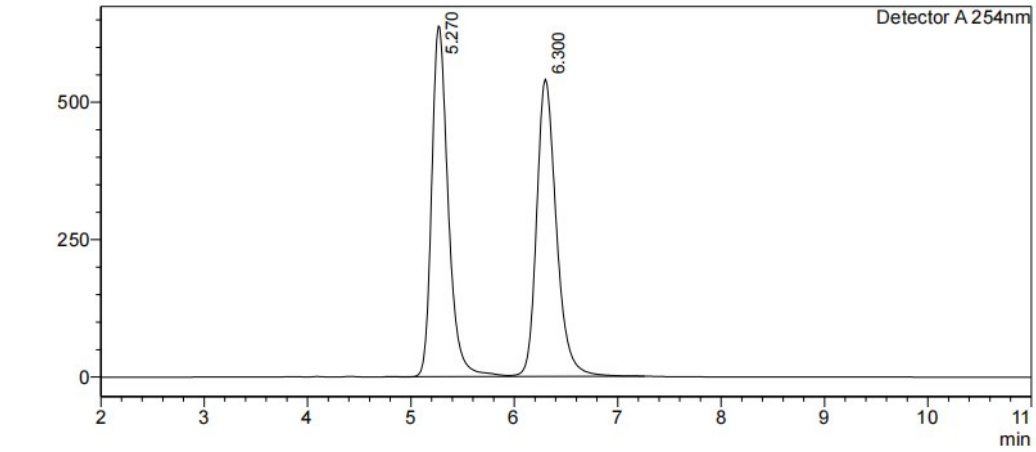
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.969	556323	25186	2.738		M	
2	10.980	19763477	572487	97.262		M	
Total		20319799	597673				

3w: IA, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

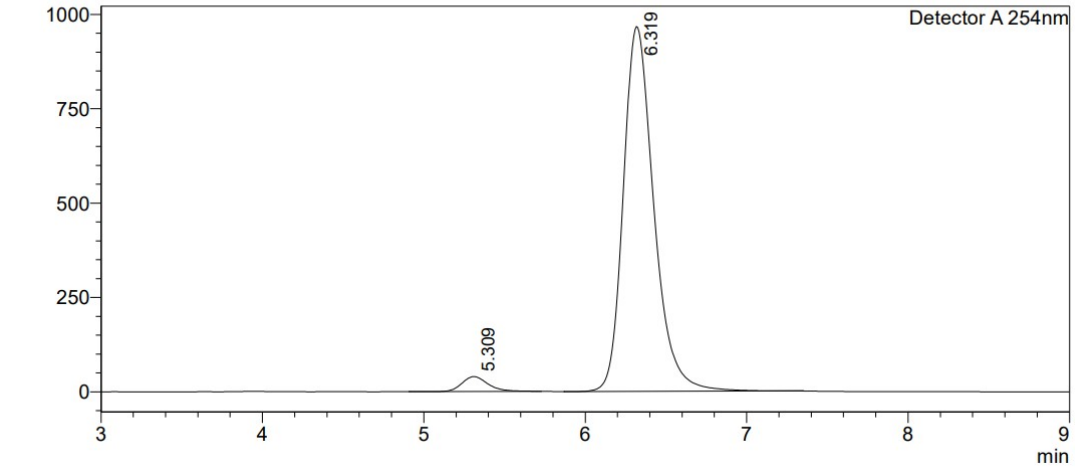


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.270	7090628	637884	49.732		M	
2	6.300	7167077	540466	50.268		V M	
Total		14257705	1178351				

<Chromatogram>



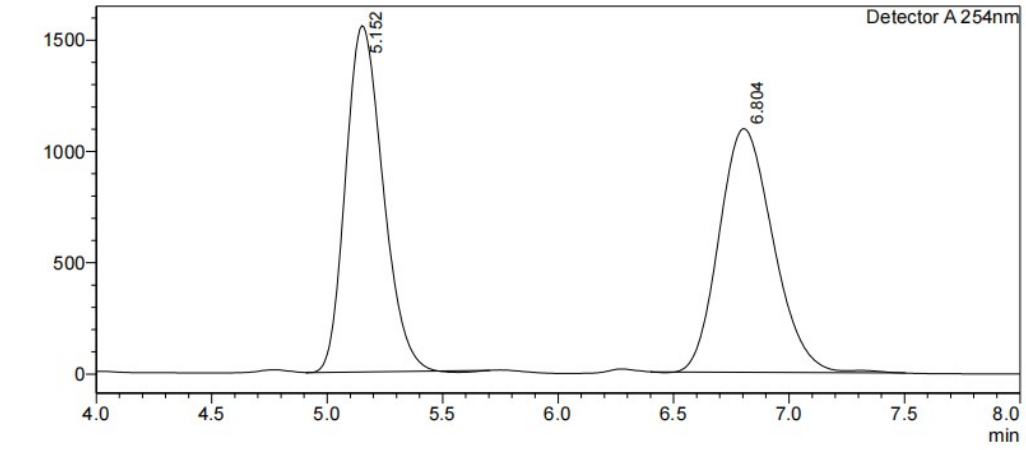
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.309	447386	39581	3.400		M	
2	6.319	12709938	966541	96.600		M	
Total		13157324	1006122				

3x: AD-H, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

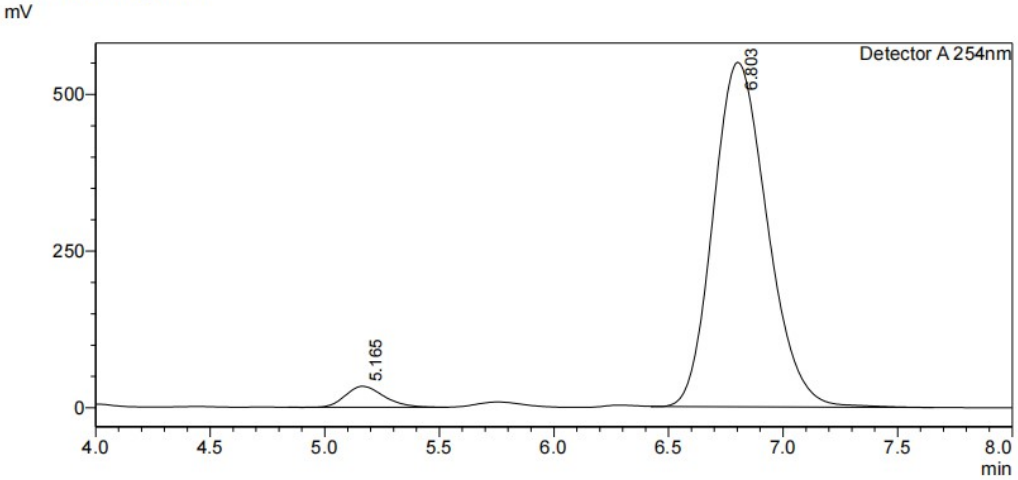


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.152	17482925	1554948	49.482		M	
2	6.804	17848807	1093742	50.518		M	
Total		35331732	2648690				

<Chromatogram>



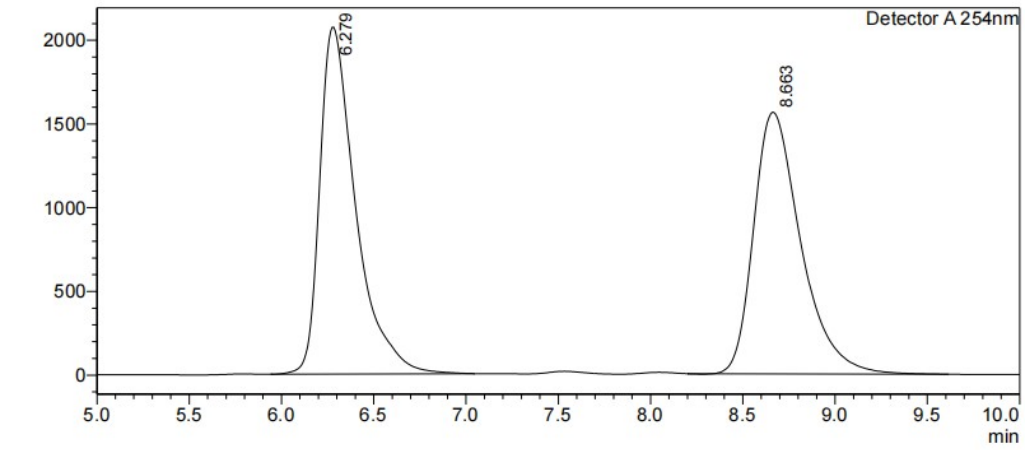
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.165	389666	33470	4.144		M	
2	6.803	9013588	549463	95.856		M	
Total		9403254	582932				

3y: IA, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

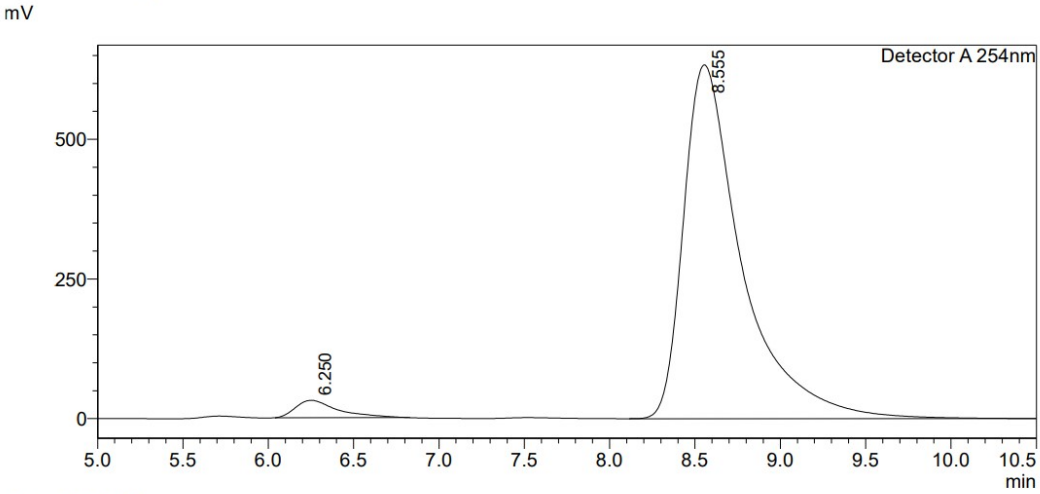


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.279	28086735	2071073	50.261		M	
2	8.663	27794973	1562857	49.739		M	
Total		55881708	3633930				

<Chromatogram>



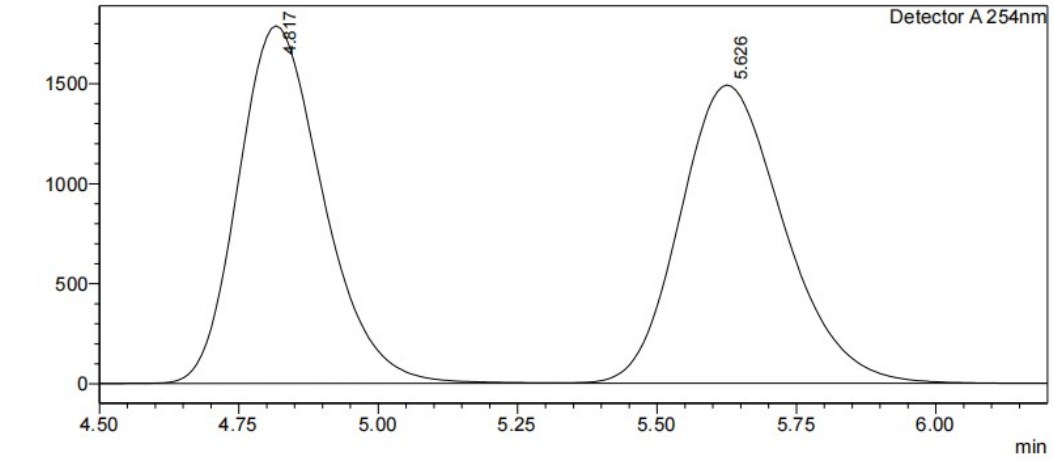
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.250	533678	31078	3.419		M	
2	8.555	15075850	633260	96.581		M	
Total		15609528	664338				

3z: AD-H, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

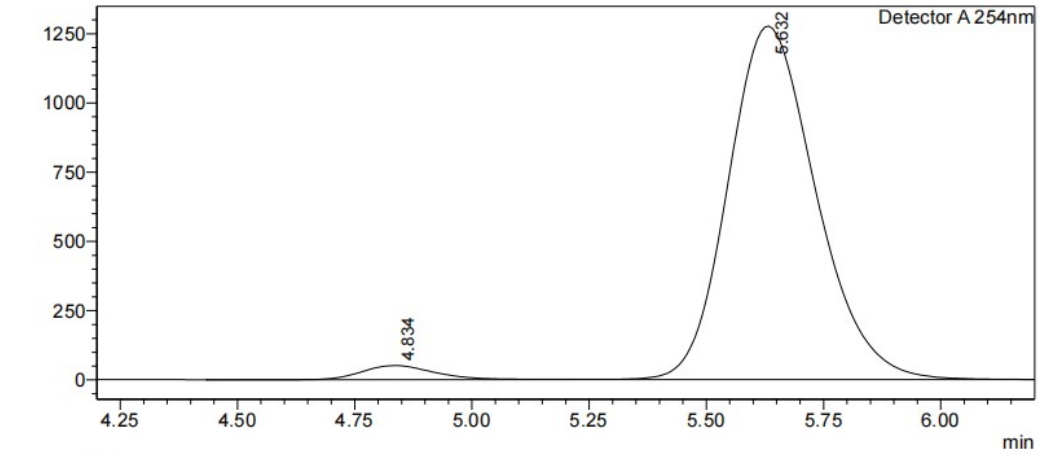


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.817	18908589	1786214	49.510		M	
2	5.626	19283207	1489662	50.490		V M	
Total		38191796	3275877				

<Chromatogram>



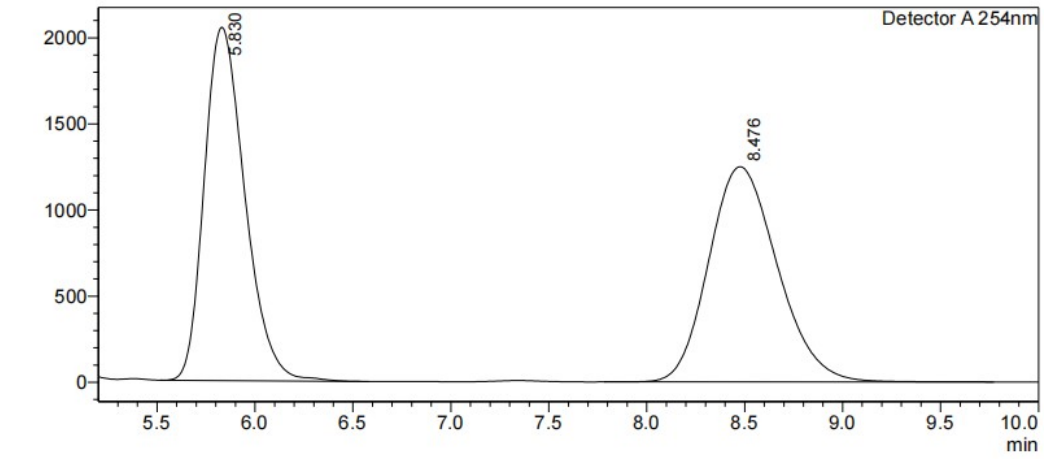
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.834	558077	50888	3.248		M	
2	5.632	16623452	1276331	96.752		V M	
Total		17181529	1327219				

3aa: AD-H, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

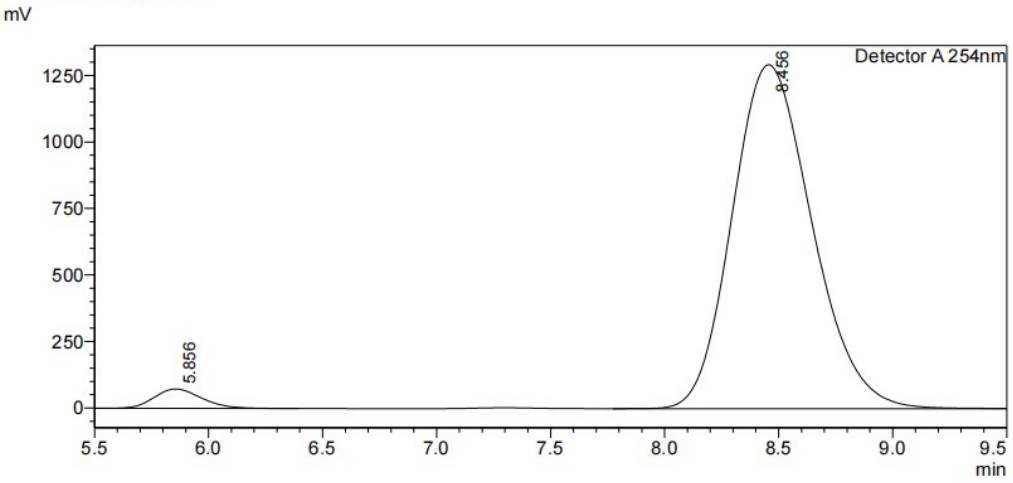


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.830	29629170	2051002	49.259		M	
2	8.476	30520234	1249179	50.741		M	
Total		60149404	3300180				

<Chromatogram>



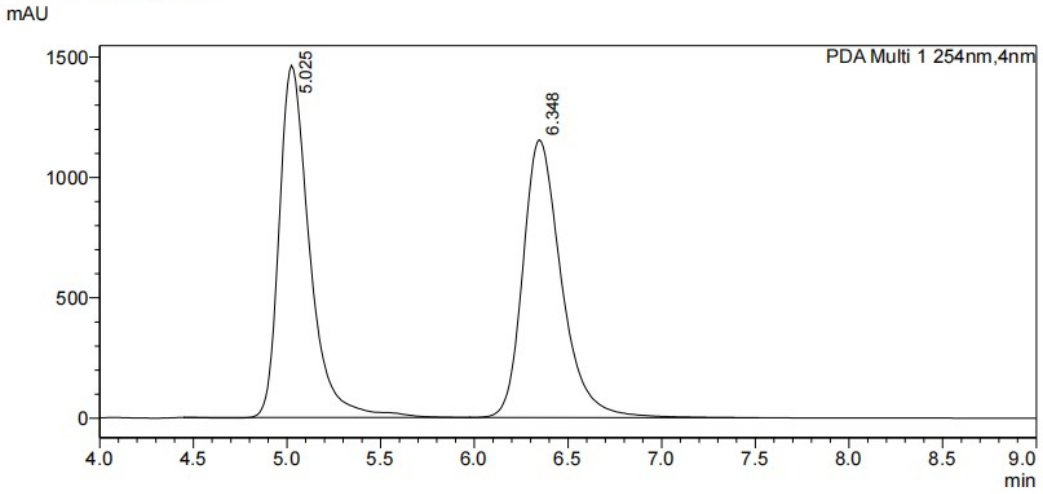
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.856	1056346	72954	3.246		M	
2	8.456	31483648	1292401	96.754		M	
Total		32539993	1365355				

3ab: AD-H, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

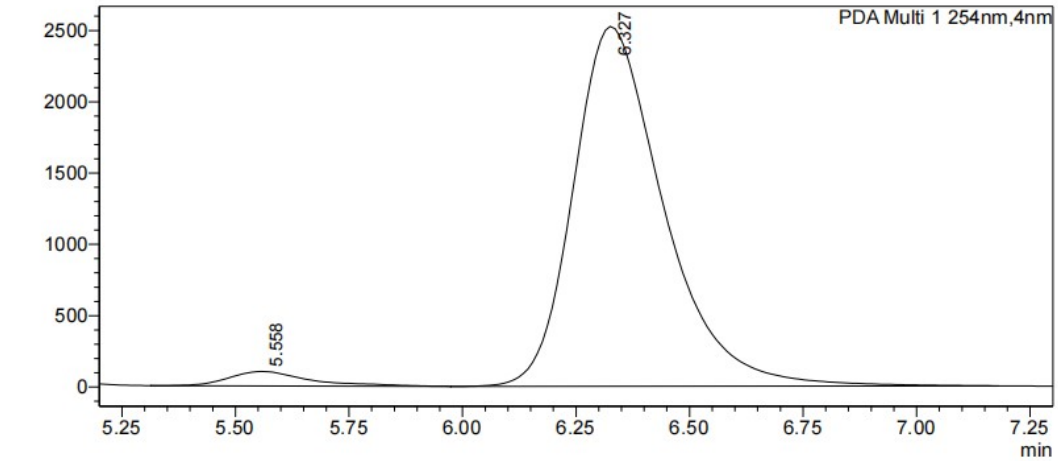


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	5.025	16492872	1461946	50.006	0.000	
2	6.348	16489096	1153951	49.994	0.000	
Total		32981967	2615898	100.000		

<Chromatogram>



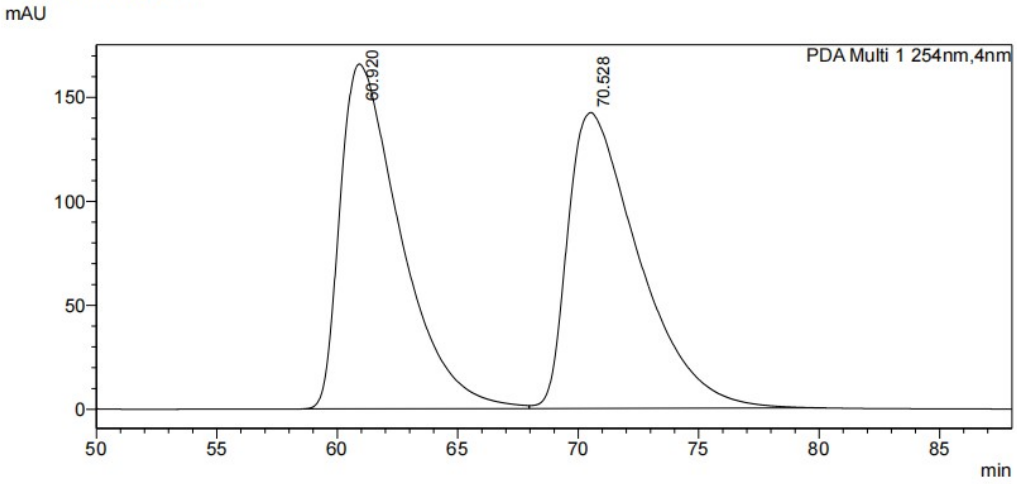
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	5.558	1227764	101181	3.387	0.000	
2	6.327	35016378	2522830	96.613	0.000	
Total		36244142	2624011	100.000		

3ac: OD-H, Hexane/*i*PrOH = 94/6, rate = 0.6 mL/min, 254 nm

<Chromatogram>

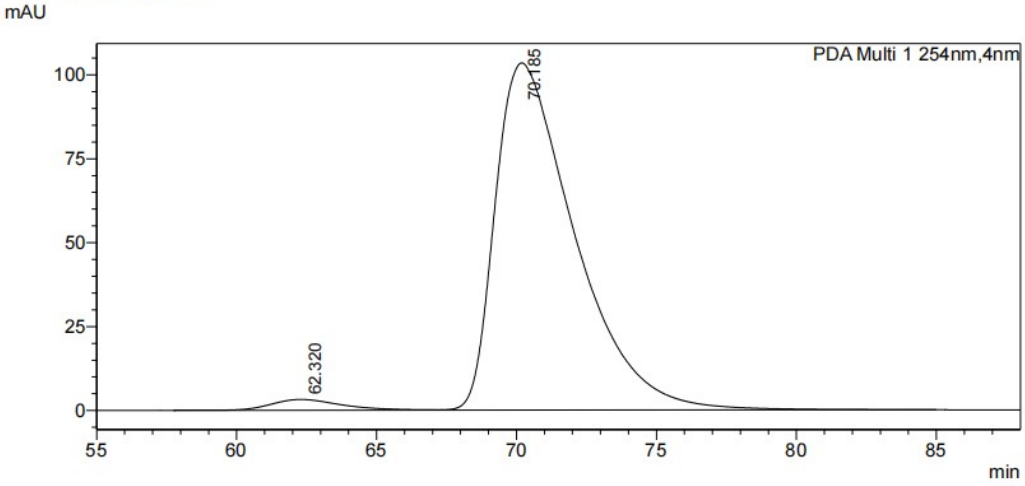


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	60.920	28988084	165763	49.777	0.000	
2	70.528	29248064	142266	50.223	0.000	
Total		58236148	308030	100.000		

<Chromatogram>



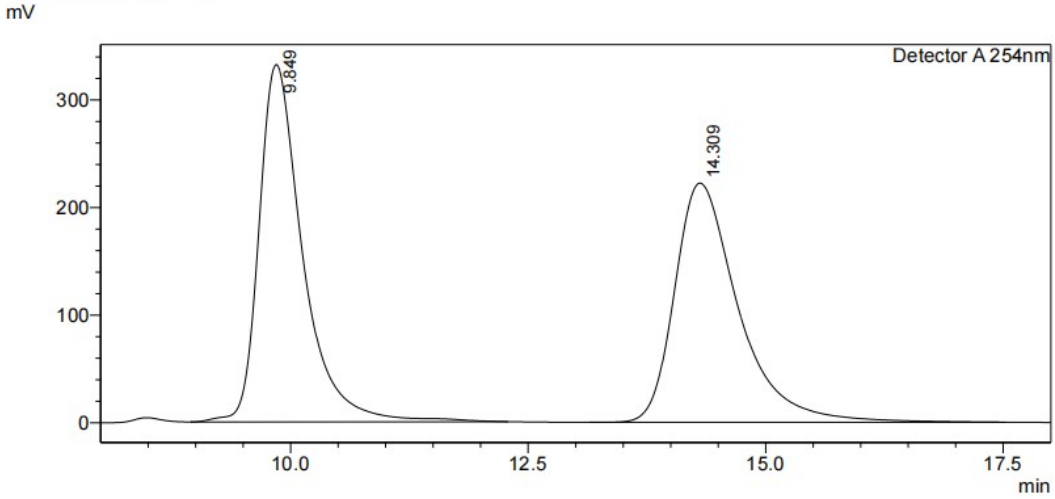
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	62.320	552768	3192	2.629	0.000	
2	70.185	20469840	103422	97.371	0.000	
Total		21022607	106614	100.000		

3ad: IA, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

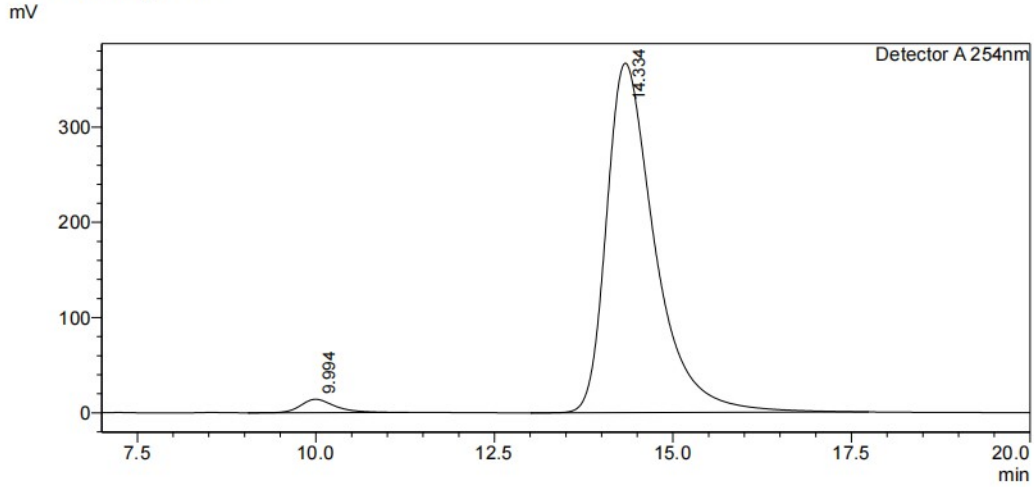


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.849	10630111	332129	50.584		M	
2	14.309	10384746	222432	49.416		M	
Total		21014857	554560				

<Chromatogram>



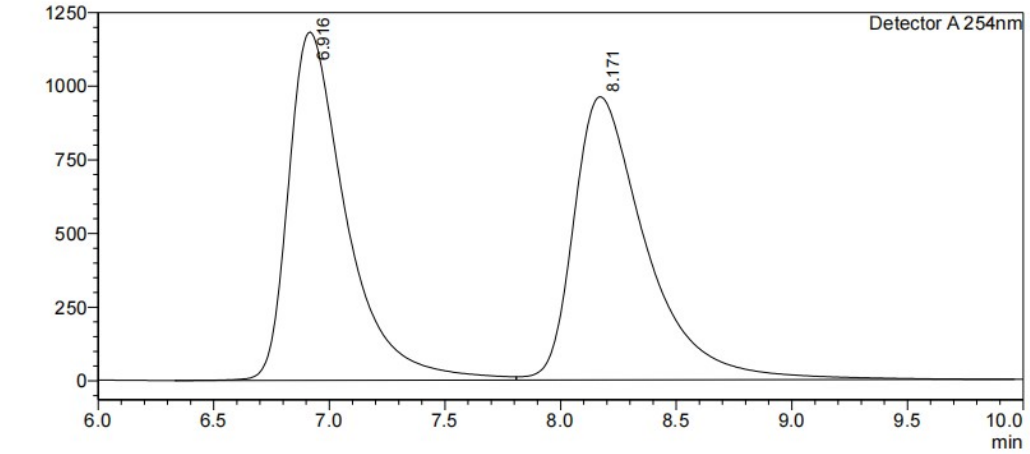
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.994	473620	14093	2.665		M	
2	14.334	17296143	366977	97.335		M	
Total		17769763	381070				

(*R*)-**7d**: IA, Hexane/*i*PrOH = 70/30, rate =1.0 mL/min, 254 nm

<Chromatogram>

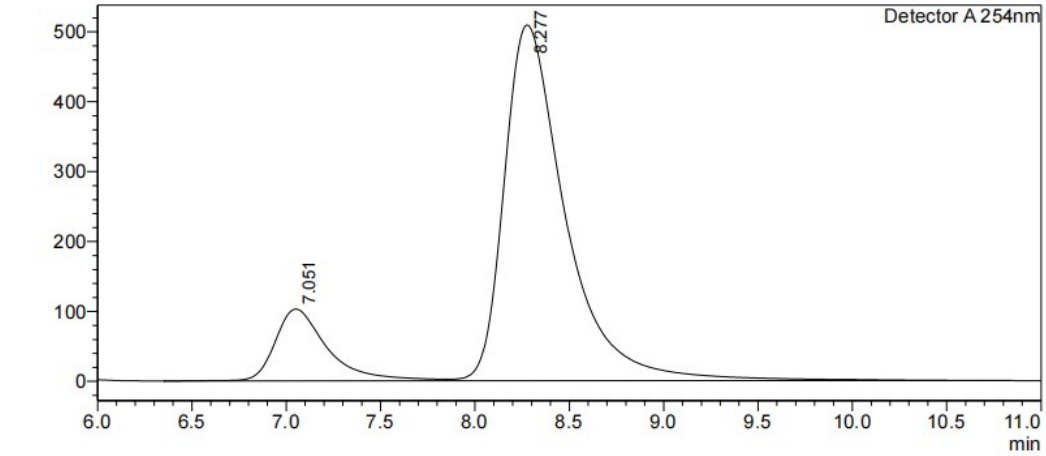


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.916	20571455	1182034	49.478		M	
2	8.171	21005165	960430	50.522		V M	
Total		41576621	2142464				

<Chromatogram>



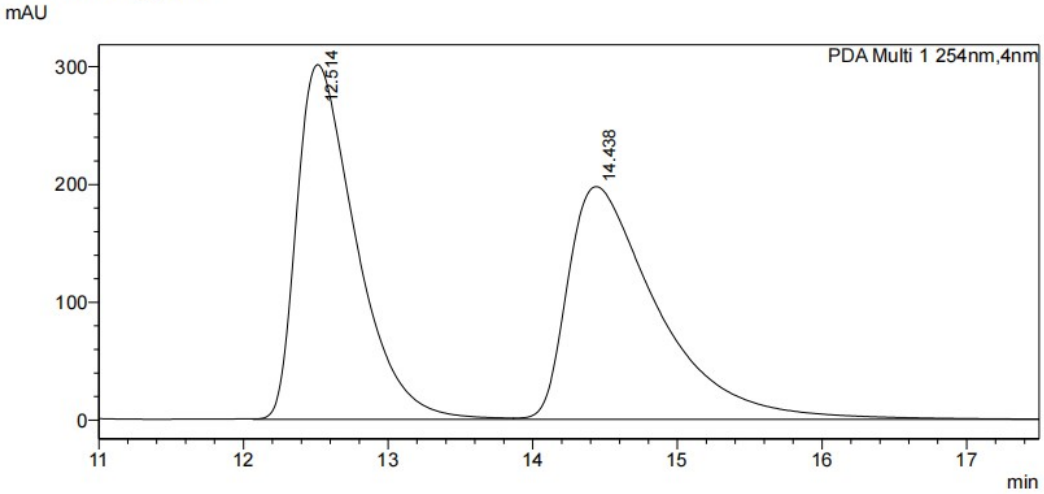
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.051	1982256	102765	14.650		M	
2	8.277	11548219	508888	85.350		V M	
Total		13530475	611653				

(*S*)-**6a**: OD-H, Hexane/*i*PrOH = 90/10, rate = 0.8 mL/min, 254 nm

<Chromatogram>

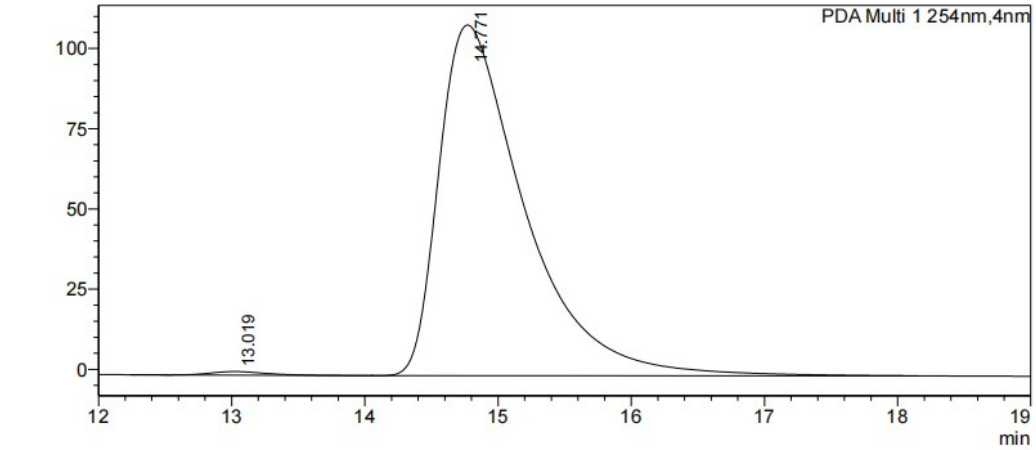


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	12.514	8554589	301188	49.877	0.000	
2	14.438	8596934	197601	50.123	0.000	
Total		17151523	498789	100.000		

<Chromatogram>



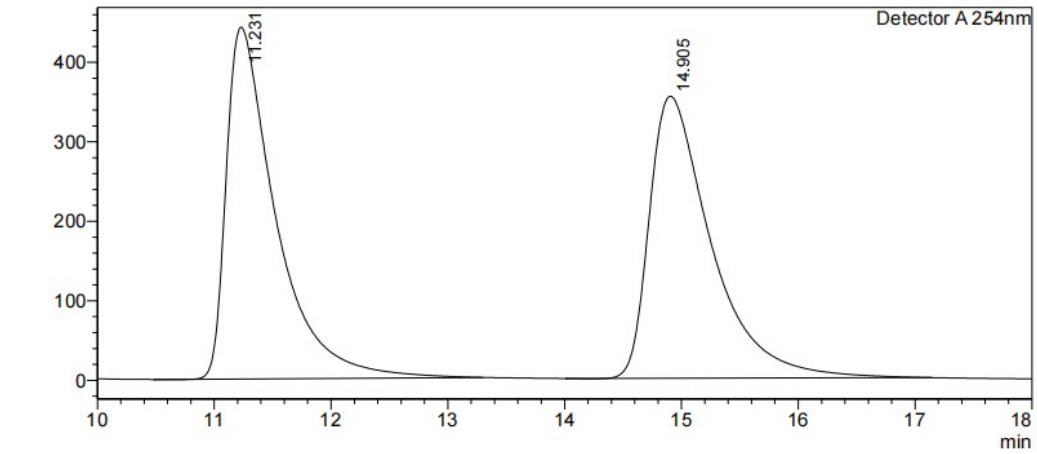
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	13.019	32664	1125	0.662	0.000	
2	14.771	4900132	109264	99.338	0.000	
Total		4932796	110389	100.000		

(*R*)-**7e**: IA, Hexane/*i*PrOH = 90/10, rate = 1.0 mL/min, 254 nm

<Chromatogram>

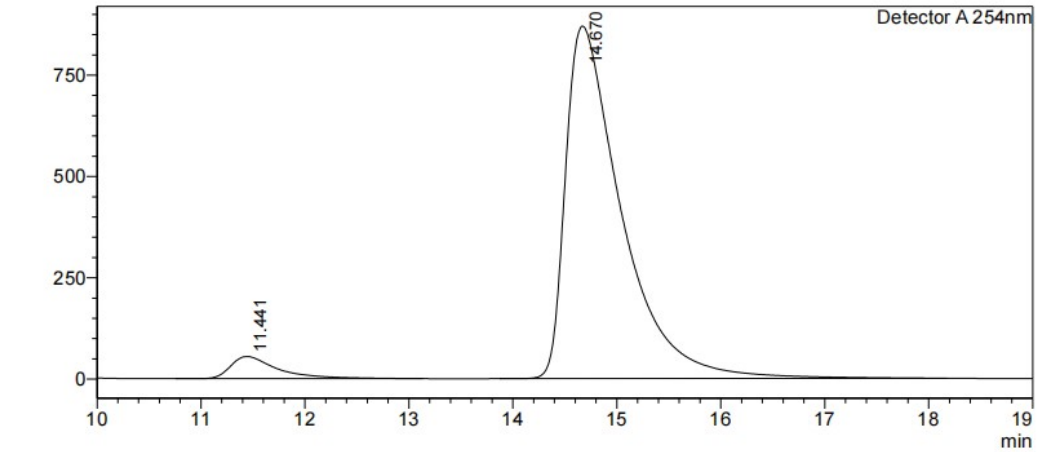


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.231	13026781	442491	49.854		M	
2	14.905	13103023	354824	50.146		M	
Total		26129805	797315				

<Chromatogram>



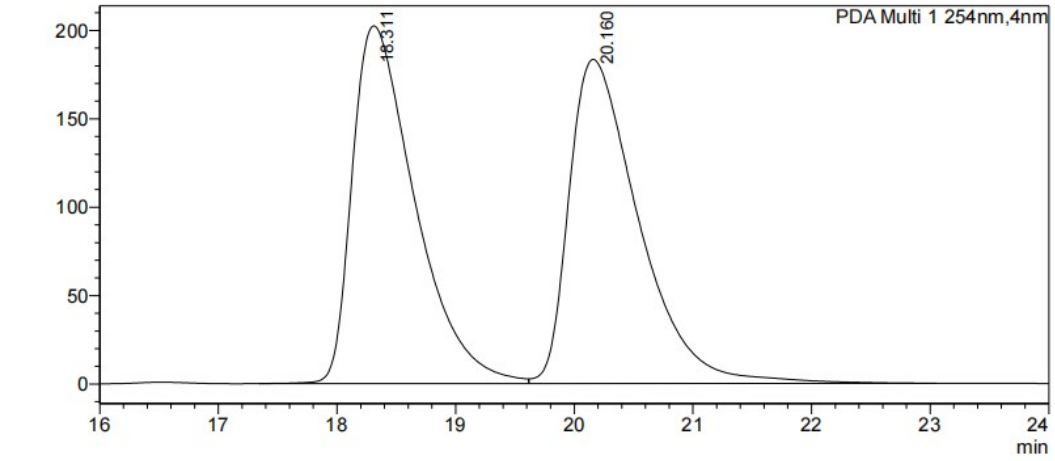
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.441	1693271	54421	4.951		M	
2	14.670	32505155	869609	95.049		M	
Total		34198426	924030				

(*S*)-**6b**: OD-H, Hexane/*i*PrOH = 95/5, rate = 0.6 mL/min, 254 nm

<Chromatogram>

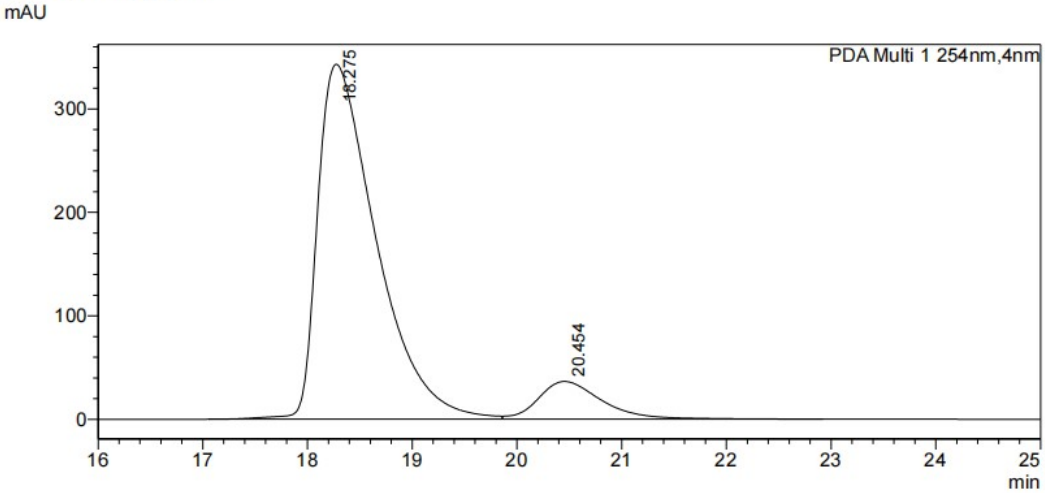


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	18.311	7448096	202308	49.791	0.000	
2	20.160	7510573	183277	50.209	0.000	
Total		14958669	385584	100.000		

<Chromatogram>



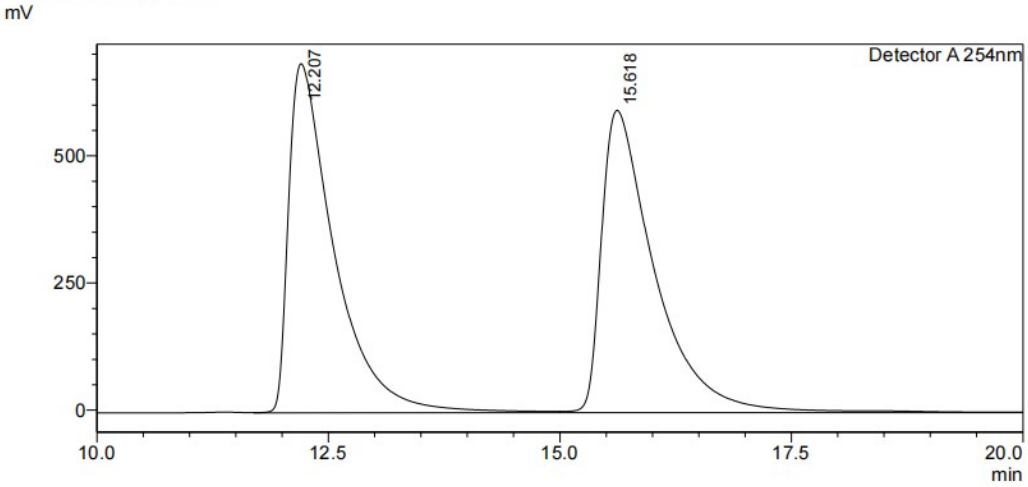
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	18.275	13334816	343012	89.636	0.000	
2	20.454	1541801	36478	10.364	0.000	
Total		14876617	379490	100.000		

(*R*)-**7f**: IA, Hexane/*i*PrOH = 90/10, rate = 0.8 mL/min, 254 nm

<Chromatogram>

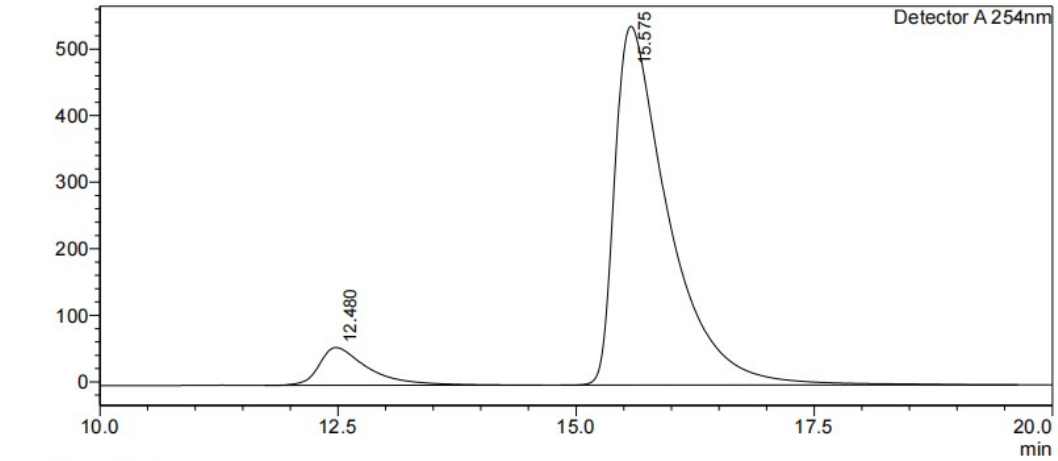


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.207	23509783	686344	49.508			
2	15.618	23976746	594572	50.492		V	
Total		47486529	1280917				

<Chromatogram>



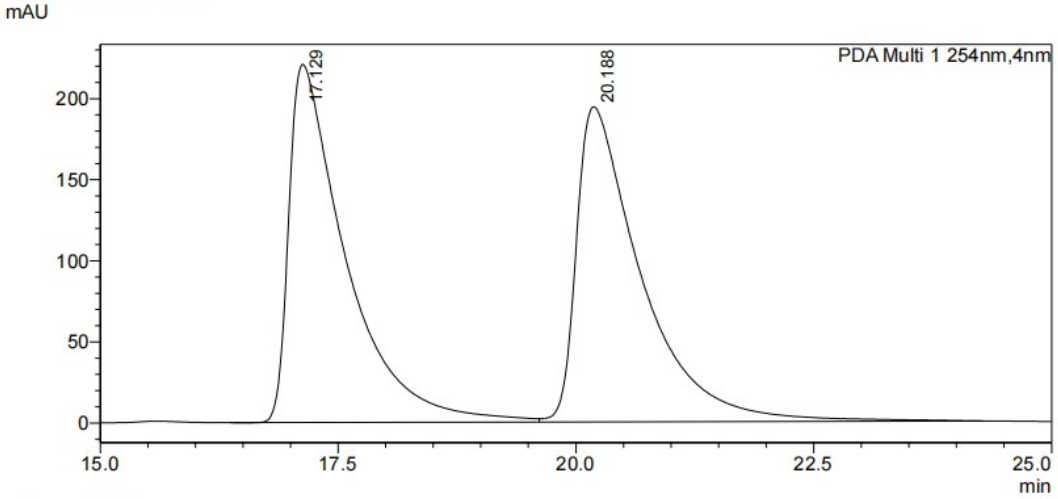
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.480	2043918	56871	8.795			
2	15.575	21196469	538965	91.205			
Total		23240387	595836				

(*S*)-**6c**: IA, Hexane/*i*PrOH = 92/8, rate = 0.6 mL/min, 254 nm

<Chromatogram>

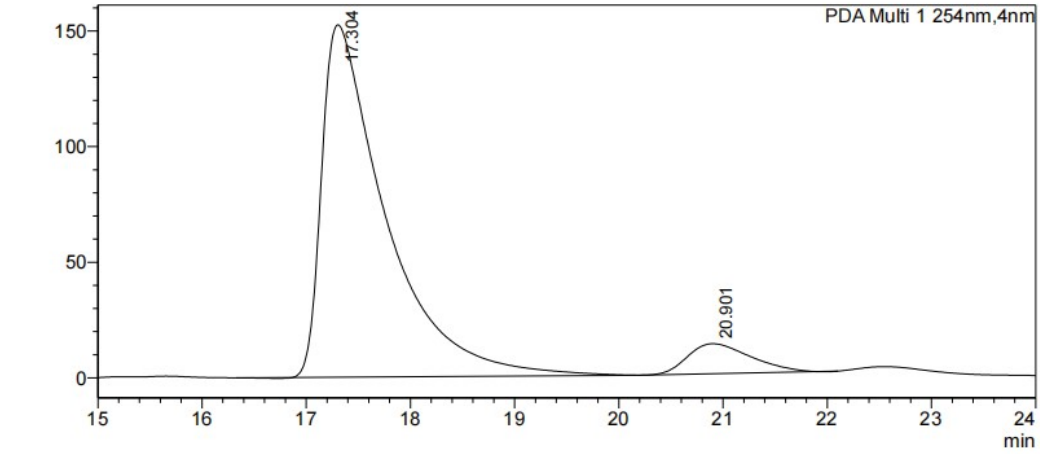


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	17.129	9210339	220823	49.957	0.000	
2	20.188	9226068	194217	50.043	0.000	
Total		18436407	415040	100.000		

<Chromatogram>



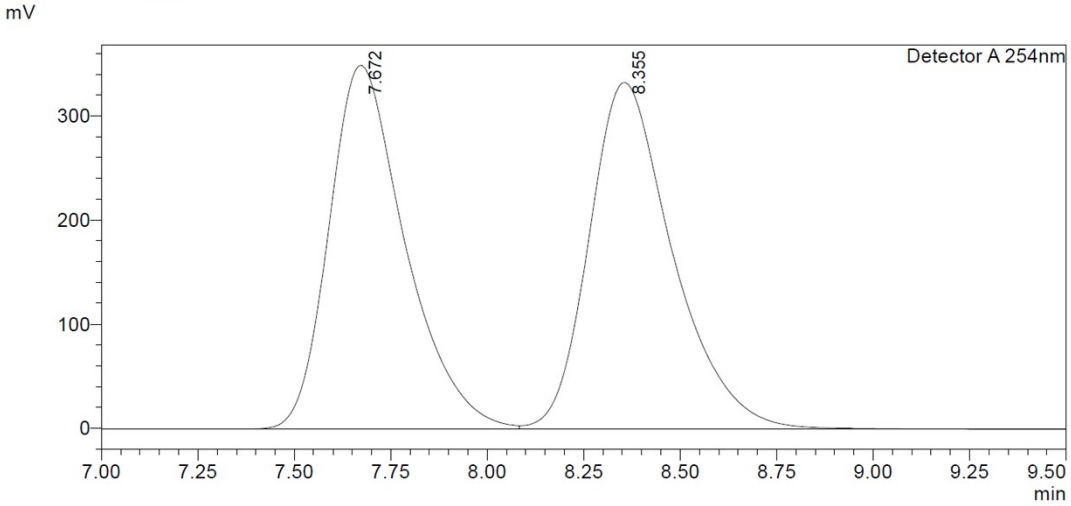
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	17.304	6491933	152381	92.245	0.000	
2	20.901	545777	12963	7.755	0.000	
Total		7037710	165344	100.000		

6w: OD-H, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

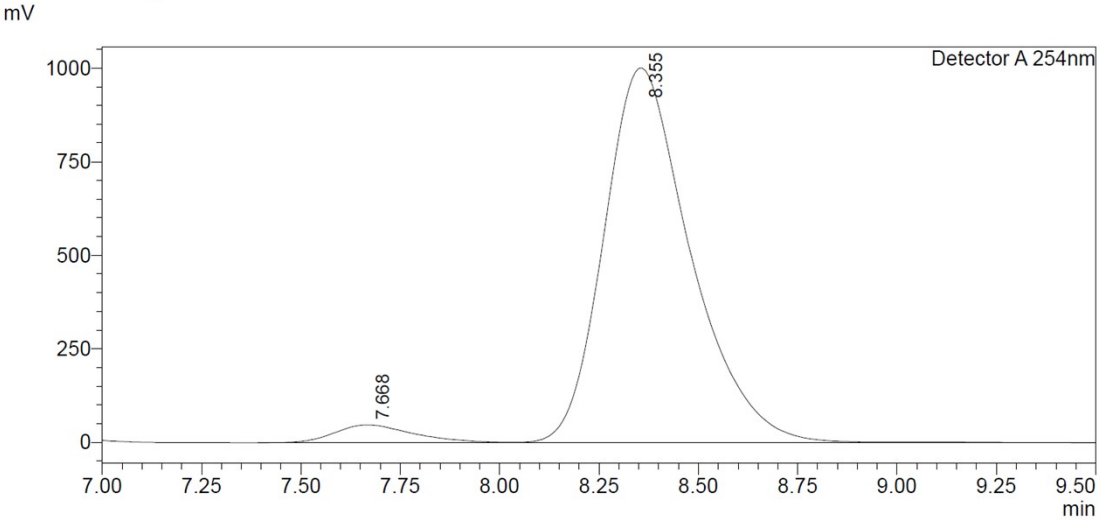


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.672	4812184	349769	48.858			
2	8.355	5037209	333174	51.142		SV	
Total		9849393	682943				

<Chromatogram>



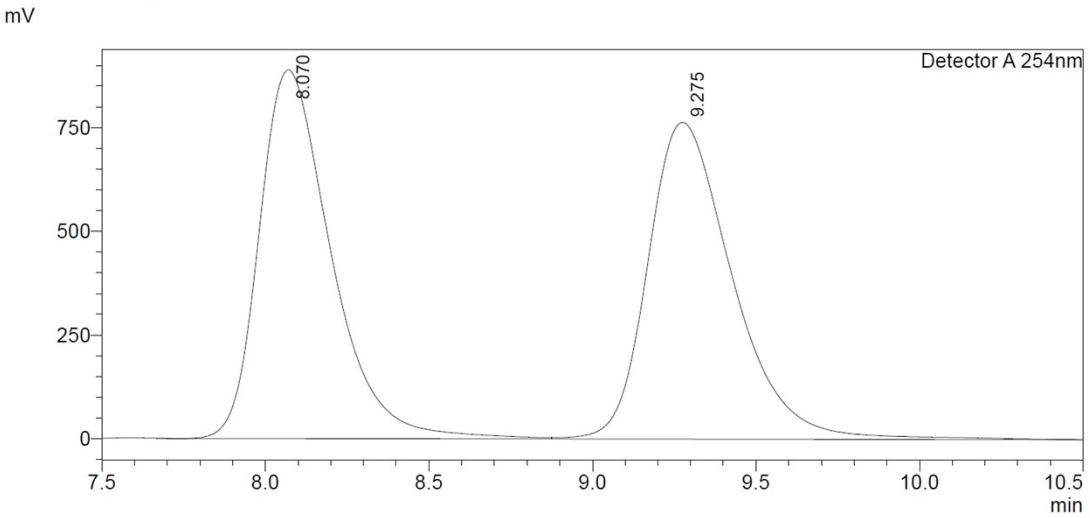
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.668	668244	47923	4.203			
2	8.355	15229833	1001753	95.797		V	
Total		15898076	1049676				

7a: IA, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

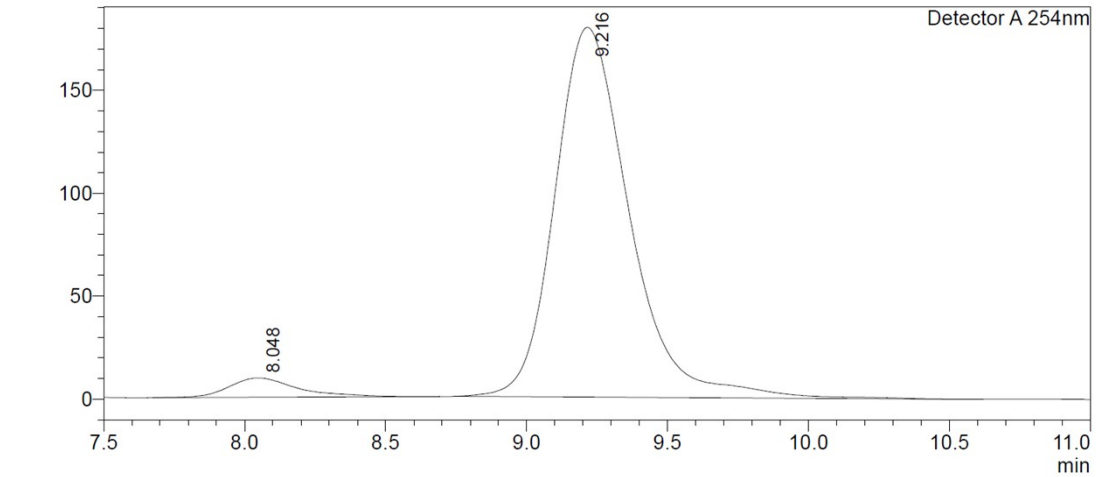


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.070	13576615	888641	49.603		M	
2	9.275	13793765	763567	50.397		V M	
Total		27370380	1652208				

<Chromatogram>



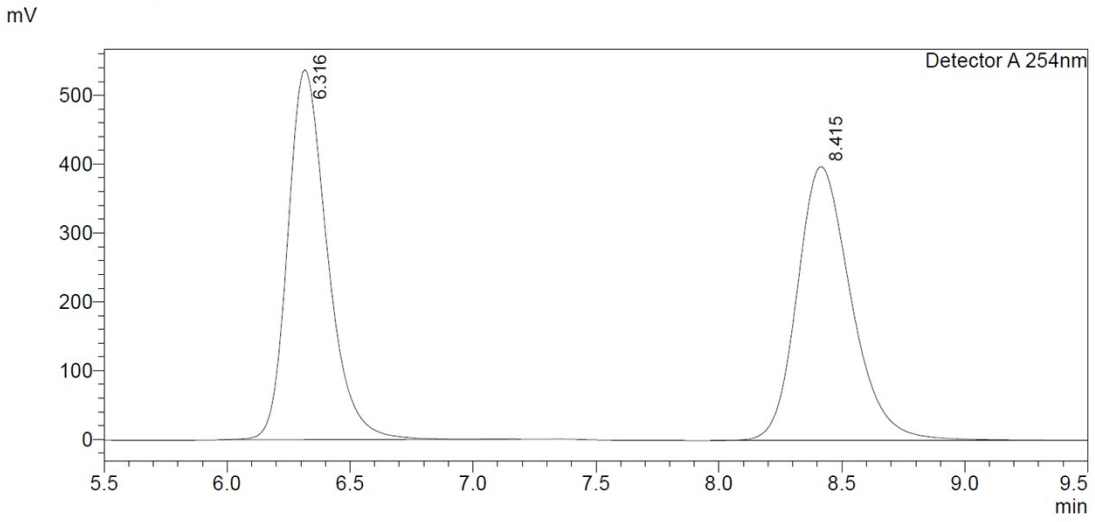
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.048	161376	9423	4.648		M	
2	9.216	3310370	179610	95.352		M	
Total		3471746	189033				

7b: IA, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

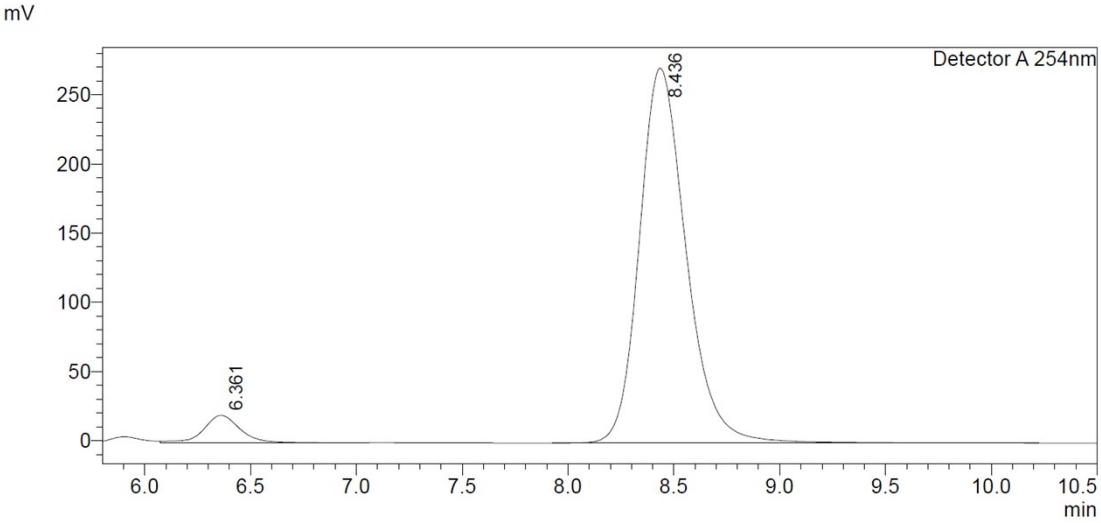


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.316	6018264	537511	49.664		M	
2	8.415	6099718	398037	50.336			
Total		12117982	935549				

<Chromatogram>



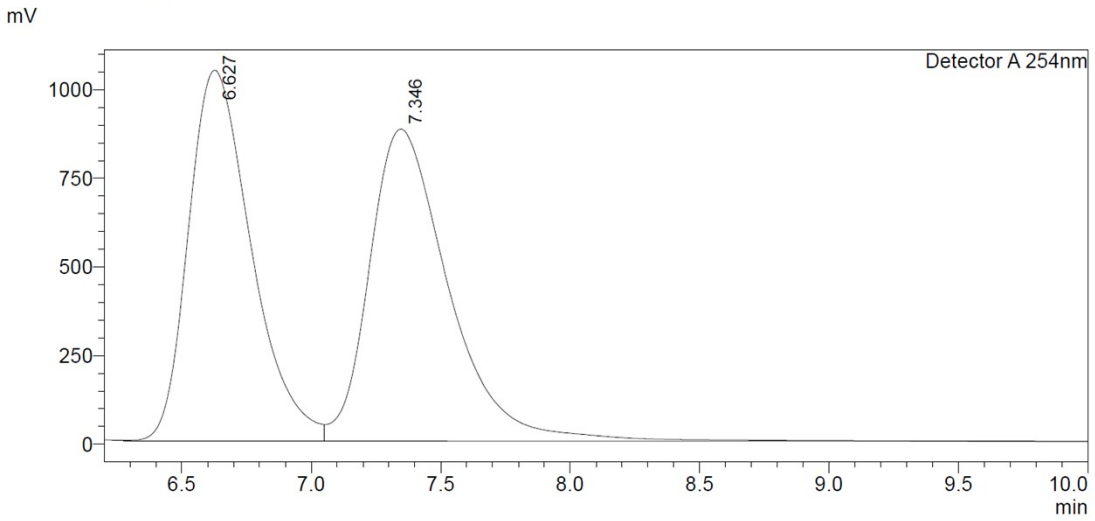
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.361	243124	19949	5.523			
2	8.436	4159063	270880	94.477			
Total		4402187	290829				

7c: AD-H, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

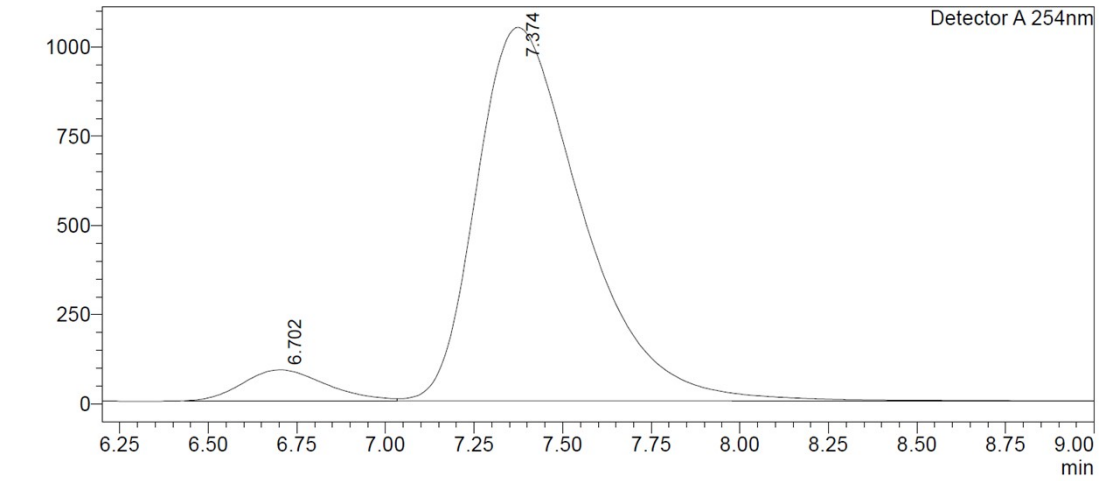


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.627	17679989	1045984	48.414			
2	7.346	18838540	879798	51.586		V	
Total		36518529	1925782				

<Chromatogram>



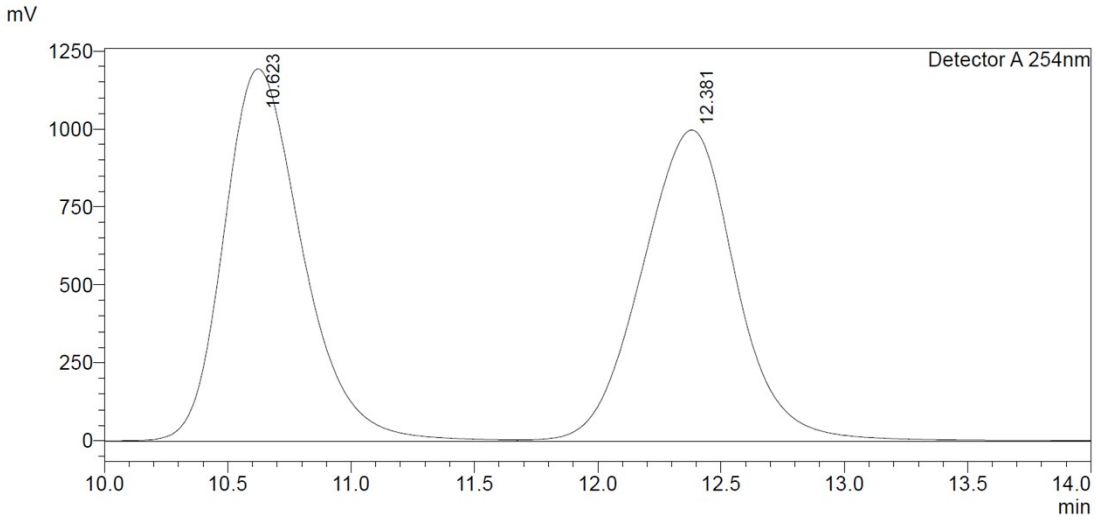
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.702	1413262	86679	6.084		M	
2	7.374	21816995	1046517	93.916		V M	
Total		23230256	1133196				

7d: IA, Hexane/*i*PrOH = 70/30, rate = 1.0 mL/min, 254 nm

<Chromatogram>

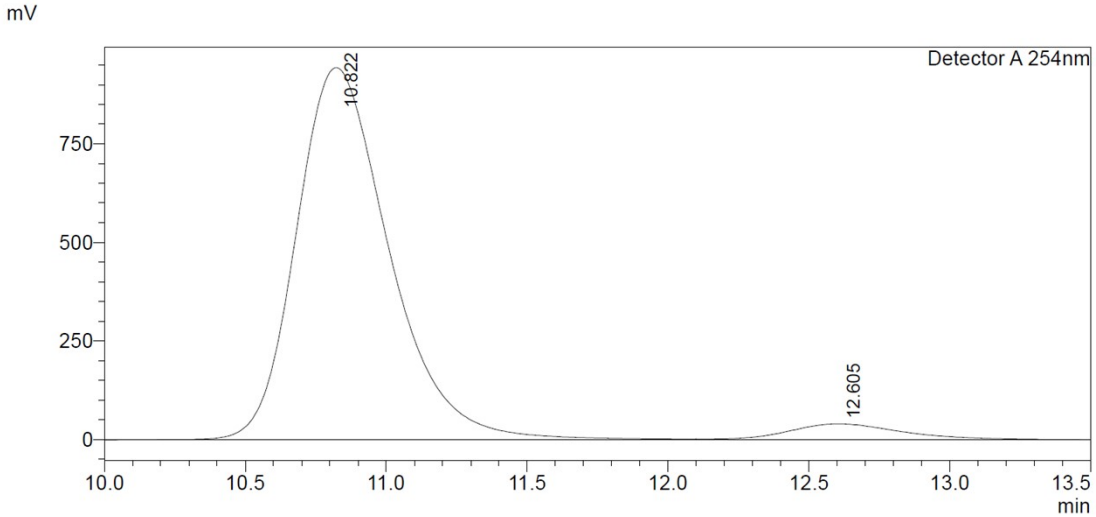


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.623	26585611	1193874	49.848			
2	12.381	26747870	997797	50.152		V	
Total		53333481	2191672				

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.822	21698355	944615	94.759			
2	12.605	1200123	40876	5.241		V	
Total		22898478	985491				