Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Stereoselective Preparation of *P,Axial*-Stereogenic Allenyl Bisphosphine oxides via Chirality-Transferrin

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General Chemistry:

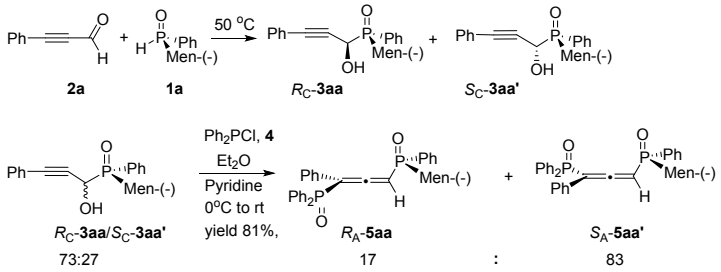
^{1}H NMR spectrum were recorded on a 400-MHz spectrometer. Chemical shift for ^{1}H NMR spectrum (in parts per million) relative to internal tetramethylsilane (Me_4Si, δ = 0.00 ppm) with $CDCl_3$. ^{13}C NMR spectrum were recorded at 101 MHz. Chemical shifts for ^{13}C NMR spectrum are reported (in parts per million) relative to $CDCl_3$ (δ = 77.0 ppm). ^{31}P NMR spectrum were recorded at 162 MHz, and chemical shifts reported (in parts per million) relative to external 85% phosphoric acid (δ = 0.0 ppm). TLC plates were visualized by UV. All products were further characterized by HRMS (high resolution mass spectrum) or Elemental Analysis. Copies of their ^{1}H, ^{31}P and ^{13}C NMR spectrum were provided. Melting points were determined on a Reichert Thermovar melting point apparatus and are uncorrected.

Reagent and solvents:

All the solvents used were dried and freshly distilled prior to use. Toluene, chloroform and dichloromethane distilled under calcium hydride. THF, ether and hexane were distilled under sodium and benzophenone. Unless otherwise stated, the commercially available reagents were used without further purification. Some of the Grignard reagent was prepared according standard procedure in ca. 0.8 M solution in ether or THF. All reactions were carried out under N_2 atmosphere in dry glassware using Schlenk-line techniques. Air and moisture sensitive liquids and solutions were transferred *via* syringe.

Part 1. Examination of the addition of 1a to 2a.

The addition of 1a to 2a to form 3aa/3aa' and their conversion to 5aa/5aa'.



Under the protection of N_2, the solution of **2a** (52 mg, 0.44 mmol 80 %) and **1a** (106 mg, 0.4 mmol) in toluene (0.5 mL) was stirred at 50 °C in an oil bath for 12 hours. The solvent was removed under vacuum. The residue was analyzed with NMR spectroscopy. The representative peaks on NMR spectrum were observed as: ^{31}P NMR (202 MHz, $CDCl_3$) δ = 42.78 (s, 73%), 40.67 (s, 27%).^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.32 (d, *J* = 10.9 Hz,1H), 5.03 (d, *J* = 9.8 Hz, 0.36H). The two stereoisomers were assigned as **3aa** and **3aa'**, respectively (Figure S1).

To the ice-water cooled solution of propargylic alcohol **3aa/3aa'** (79 mg, 0.2 mmol) in ether (1 mL), was added diphenylphosphonium chloride (0.036 mL, 0.2 mmol) and pyridine (0.017 mL, 0.2 mmol). The mixture was stirred overnight, until ice melted. After diluted hydrochloride solution (7%) added, the water layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous magnesium sulfate. Removing solvent afforded crude product, the residue was analyzed with NMR spectroscopy.

The representative peaks on NMR spectrum were observed as: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.81 (dd, *J* = 9.9, 3.3 Hz, 17%), 5.70 (dd, *J* = 9.9, 7.4 Hz, 83%). ^{31}P NMR (202 MHz, $CDCl_3$) δ = 33.55 (d, *J* = 12.9 Hz), 33.24 (d, *J* = 14.1 Hz), 28.12 (d, *J* = 14.5 Hz), 27.37 (d, *J* = 12.9 Hz). The two stereoisomers were assigned as **5aa** and **5aa'**, respectively (Figure S2).

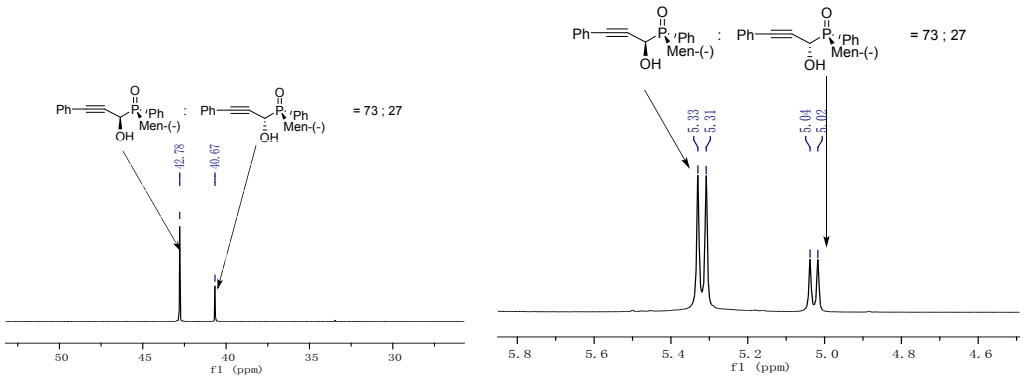


Figure S1. The NMR spectrum of 3aa / 3aa'.

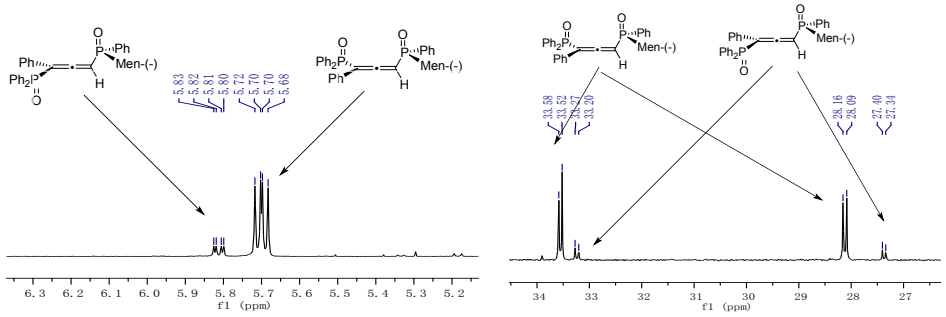


Figure S2. The NMR spectrum of the conversion of 3aa / 3aa' to 5aa / 5aa'.

Examination of the addition of 1a to 2a

General procedure:

Under the protection of N_2, the solution of **2a** (52 mg, 0.44 mmol 80 %) and **1a** (106 mg, 0.4 mmol), was added in a solvent (0.5 mL) and stirred for 12 hours. The solvent was removed in vacuo and the residue was dissolved in *d*-chloroform for the analysis with NMR spectrum.

When the reaction was carried out in the absence of solvent, the residue was dissolved and analyzed with NMR spectrum.

When catalyzed by a base, the reaction was quenched with diluted hydrochloric acid (7%). The mixture was extracted with dichloromethane (3 x 5 mL), washed with water. The solvent was removed in vacuo and the residue was analyzed with NMR spectrum.

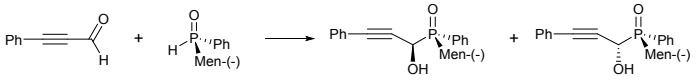
The yield and dr were estimated based on the above Figure S1 and S2, and the results were presented in Table S1.

Table S1. Examination of the addition of 1a to 2a.

entry	solvent	catalyst (%)	temp.	yield (%)[a]	dr [a]
1	Tol	no	120°C	99	50:50
2	Tol	no	80°C	99	62:38
3	Tol	no	50°C	99	73:27
4	Tol	no	rt	99	73:27
5	Tol	no	-20°C	99	70:30
6	no	no	50°C	99	66:34
7	no	no	120°C	99	17:83
8	$C_{10}H_{22}$	no	120°C (3min)	99	16:84
9	$C_{10}H_{22}$	no	120°C (4h)	99	7:93
10	$C_{10}H_{22}$	no	120°C (12h)	99	7:93
11	$C_{10}H_{22}$	no	150°C (3min)	99	8:92
12	$C_{10}H_{22}$	no	150°C (12h)	65	36:64
13	DMF	K_2CO_3 (25)	rt	99	55:45[b]
14	DMF	$Ca(OH)_2$ (25)	rt	99	60:40 [b]
15	DMSO	KOH (25)	rt	99	61:39 [b]
16	MeCN	KOH(25)	rt	99	72:28 [b]
17	MeCN	KOH(25)	-20°C/2 h	99	61:39 [b]

[a] The yield and dr were estimated by $^{31}P\{^1H\}$ -NMR spectrum, and dr was assigned as R_C-**3aa**/S_C-**3aa'**. [b] 25% moler of alkali catalyst was used.

Part 2. Preparation of alkynols 3/3':



2a **1a** R_C-**3aa** S_C-**3aa'**

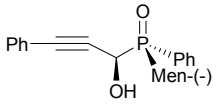
Typical procedure:

Under the protection of N_2, the solution of **1a** (106 mg, 0.4 mmol) and **2a** (52 mg, 0.44 mmol, 80 %) in toluene (0.5 mL) was stirred at 80 °C in an oil bath for 12 hours. Toluene was removed under reduced pressure to afford alkynol as an oily foam substance.

After recrystallization with ether at – 40 °C, ***R*$_P$,*S*$_C$-3aa'** was obtained in 99 : 1 dr, as a white solid, weighted 42 mg, yield 26 %.

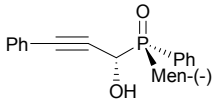
The mother liquid was purified with flash chromatography (silica gel, petroleum ether / ethyl acetate = 1 : 2 as eluent) afford ***R*$_P$,*R*$_C$-3aa** in 99 : 1 dr, as a yellow oil, weighted 60 mg, yield 37 %**.**

***R*$_P$,*R*$_C$-(*L*)-Menthyl (1-hydroxy-3-phenylprop-2-yn-1-yl) phenyl phosphine oxide (3aa)**



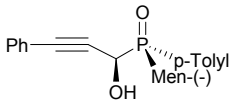
The optically pure **3aa** was obtained as a yellow oil (60 mg, 37%, <1:99 dr) from chromatography. ^{31}P NMR (162 MHz, cdcl$_3$) δ = 43.60 (s). ^{1}H NMR (400 MHz, cdcl$_3$) δ = 8.04 – 7.78 (m, 2H), 7.43 (ddd, *J*=30.0, 19.4, 9.2, 8H), 6.93 (s, 1H), 5.35 (dd, *J*=11.2, 4.5, 1H), 2.37 (dd, *J*=28.7, 14.2, 2H), 1.85 – 1.43 (m, 6H), 1.01 (t, *J*=8.0, 5H), 0.73 (d, *J*=6.6, 3H), 0.24 (d, *J*=6.6, 3H). ^{13}C NMR (101 MHz, cdcl$_3$) δ = 131.61 (dd, *J*=13.7, 5.2), 131.21 (s), 130.34 (s), 128.69 (s), 128.42 (s), 127.97 (d, *J*=11.2), 122.41 (d, *J*=3.0), 88.65 (d, *J*=8.5), 85.17 (s), 62.10 (s), 61.32 (s), 42.95 (d, *J*=4.0), 38.92 (s), 38.29 (s), 34.48 (s), 34.18 (s), 33.31 (d, *J*=12.8), 28.19 (s), 24.52 (d, *J*=11.4), 22.72 (s), 21.48 (s), 15.27 (s). **HRMS (ESI$^+$)** Calcd. for $C_{25}H_{31}O_2P$ [M+Na$^+$]:417.1959, Found:417.1960.

***R*$_P$,*S*$_C$-(*L*)-Menthyl (1-hydroxy-3-phenylprop-2-yn-1-yl) phenyl phosphine oxide (3aa')**



The optically pure **3aa'** was obtained as a white solid (42 mg, 26%, <1:99 dr) from recrystallization. m.p. 180.0 – 183.0°C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 40.46 (s, 1H). ^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.97 – 7.87 (m, 3H), 7.60 – 7.39 (m, 5H), 7.26 (d, *J*=13.0, 3H), 5.02 (d, *J*=10.4, 1H), 2.57 – 2.39 (m, 2H), 1.87 – 1.35 (m, 6H), 1.08 – 0.93 (m, 5H), 0.76 (d, *J*=6.6, 3H), 0.27 (d, *J*=6.6, 3H). ^{13}C NMR (101 MHz, cdcl$_3$) δ = 132.00 (dd, *J*=62.1, 47.7), 130.95 (d, *J*=8.1), 128.72 (s), 128.59 – 127.95 (m), 122.25 (s), 89.21 (d, *J*=7.7), 84.54 (s), 63.46 (s), 62.69 (s), 42.85 (d, *J*=3.5), 38.75 (s), 38.12 (s), 34.35 (d, *J*=16.4), 33.35 (d, *J*=13.1), 28.36 (d, *J*=3.2), 24.62 (d, *J*=12.4), 22.68 (s), 21.57 (s), 15.33 (s). **HRMS (ESI$^+$)** Calcd. for $C_{25}H_{31}O_2P$ [M+Na$^+$]:417.1959, Found:417.1958.

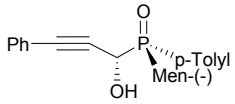
***R*$_P$,*R*$_C$-(*L*)-Menthyl (1-hydroxy-3-phenylprop-2-yn-1-yl) *p*-tolyl phosphine oxide (3ab)**



The optically pure **3ab** was obtained as an oil (64 mg, 40%, <1:99 dr) from chromatography.^{31}P

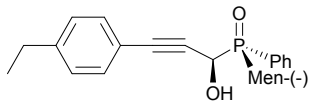
NMR (162 MHz, cdcl$_3$) δ = 42.76 (s).^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.77 (dd, *J*=10.0, 8.2, 2H), 7.44 – 7.38 (m, 2H), 7.35 (dd, *J*=5.2, 1.6, 3H), 7.18 (d, *J*=6.0, 2H), 6.42 (s, 1H), 5.29 (d, *J*=11.1, 1H), 2.39 – 2.24 (m, 5H), 1.87 – 1.33 (m, 6H), 1.02 (dd, *J*=21.3, 8.6, 5H), 0.75 (d, *J*=6.7, 3H), 0.28 (d, *J*=6.6, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 141.83 (d, *J*=2.8), 131.59 (dd, *J*=10.7, 5.4), 128.93 – 128.42 (m), 128.40 (s), 127.73 (s), 126.84 (s), 122.51 (d, *J*=3.0), 88.48 (d, *J*=8.5), 85.37 (s), 62.08 (s), 61.30 (s), 42.90 (d, *J*=4.0), 38.82 (s), 38.19 (s), 34.48 (s), 34.18 (s), 33.30 (d, *J*=12.7), 28.13 (d, *J*=3.2), 24.53 (d, *J*=11.7), 22.73 (s), 21.56 (d, *J*=13.1), 15.36 (s). **HRMS (ESI$^+$)**Calcd. For $C_{26}H_{33}O_2P$[M+Na$^+$]:431.2116, Found:431.2116.

***R*$_P$,*S*$_C$-(*L*)-Menthyl (1-hydroxy-3-phenylprop-2-yn-1-yl) *p*-tolyl phosphine oxide (3ab')**



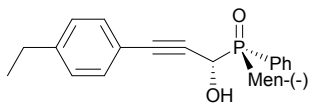
The optically pure **3ab'** was obtained as a white solid (82 mg, 50%, <1:99 dr) from recrystallization. m.p. 207.1 – 209.4 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 40.79 (s).^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.78 (t, *J*=8.9, 2H), 7.44 – 7.17 (m, 7H), 5.10 (d, *J*=5.4, 1H), 4.98 (dd, *J*=10.3, 4.5, 1H), 2.54 – 2.35 (m, 5H), 1.81 – 1.43 (m, 6H), 0.99 (dd, *J*=20.6, 8.0, 5H), 0.76 (d, *J*=6.5, 3H), 0.28 (d, *J*=6.5, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 141.92 (d, *J*=2.8), 131.69 (d, *J*=2.2), 130.99 (d, *J*=8.5), 129.29 (s), 128.90 (d, *J*=11.4), 128.75 – 128.16 (m), 122.42 (s), 88.92 (d, *J*=7.7), 84.88 (s), 63.62 (s), 62.84 (s), 42.83 (d, *J*=3.6), 38.74 (s), 38.11 (s), 34.66 – 34.14 (m), 33.36 (d, *J*=13.1), 28.27 (d, *J*=3.2), 24.65 (d, *J*=12.3), 22.68 (s), 21.58 (d, *J*=2.2), 15.41 (s). **HRMS (ESI$^+$)**Calcd. For $C_{26}H_{33}O_2P$[M+Na$^+$]:431.2116, Found:431.1987.

***R*$_P$,*R*$_C$-(*L*)-Menthyl (3-*p*-ethylphenyl-1-hydroxyprop-2-yn-1-yl) phenyl phosphine oxide (3ba)**



The optically pure **3ba** was obtained as a yellow oil (70 mg, 42%, <1:99 dr) from chromatography. ^{31}P NMR (162 MHz, cdcl$_3$) δ = 42.09 (s).^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.96 – 7.85 (m, 2H), 7.51 (t, *J*=7.1, 1H), 7.43 (d, *J*=5.1, 2H), 7.32 (d, *J*=7.6, 2H), 7.18 (d, *J*=7.8, 2H), 5.27 (d, *J*=10.4, 1H), 2.67 (q, *J*=7.4, 2H), 2.36 (dd, *J*=34.6, 23.3, 2H), 2.07 (s, 1H), 1.90 – 1.35 (m, 6H), 1.25 (t, *J*=7.5, 3H), 1.10 – 0.94 (m, 5H), 0.76 (d, *J*=6.5, 3H), 0.29 (dd, *J*=25.2, 6.7, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 145.19 (s), 132.14 – 130.98 (m), 130.38 (s), 127.94 (d, *J*=10.9), 119.57 (d, *J*=3.0), 88.86 (d, *J*=8.7), 84.37 (s), 62.12 (s), 61.34 (s), 42.92 (d, *J*=4.1), 38.87 (s), 38.24 (s), 34.47 (s), 34.18 (s), 33.30 (d, *J*=12.9), 29.70 (s), 28.84 (s), 28.20 (s), 24.51 (d, *J*=12.0), 22.72 (s), 21.48 (s), 15.30 (d, *J*=9.4). **HRMS (ESI$^+$)**Calcd. For$C_{27}H_{35}O_2P$[M+Na$^+$]: 445.2272, Found:445.2272.

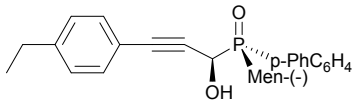
***R*$_P$,*S*$_C$-(*L*)-Menthyl (3-*p*-ethylphenyl-1-hydroxyprop-2-yn-1-yl) phenyl phosphine oxide (3ba')**



The optically pure **3ba'** was obtained as a white solid (76 mg, 45%, <1:99 dr) from recrystallization. m.p. 152.2 – 153.6 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 40.12 (s).^{1}H NMR (400 MHz, cdcl$_3$) δ = 8.00 – 7.84 (m, 2H), 7.50 (t, *J*=8.6, 1H), 7.43 (d, *J*=6.5, 2H), 7.30 – 7.19 (m, 2H), 7.12 (d, *J*=7.8, 2H), 4.97 (d, *J*=7.2, 1H), 4.73 (s, 1H), 2.63 (dd, *J*=15.0, 7.4, 2H), 2.50 (dd, *J*=37.4, 11.0, 2H), 1.92 – 1.35 (m, 6H), 1.22 (t, *J*=7.4, 3H), 1.00 (dd, *J*=26.2, 9.0, 5H), 0.76 (d, *J*=6.5, 3H), 0.25 (d, *J*=6.4, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 145.12 (s), 132.88 (s), 132.03 (s), 131.85 –

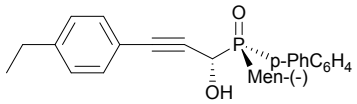
131.32 (m), 131.00 (d, *J*=8.1), 128.11 (d, *J*=11.3), 127.84 (s), 119.46 (s), 83.93 (s), 63.56 (s), 62.78 (s), 42.85 (d, *J*=3.6), 38.84 (s), 38.20 (s), 34.37 (d, *J*=13.4), 33.36 (d, *J*=13.1), 28.80 (s), 28.34 (s), 24.64 (d, *J*=12.1), 22.65 (s), 21.54 (s), 15.28 (d, *J*=4.7). **HRMS (ESI$^+$)**Calcd. For $C_{27}H_{35}O_2P$ [M+Na$^+$]: 445.2272, Found: 445.2272.

***R*$_P$,*R*$_C$-(*L*)-Menthyl (3-*p*-ethylphenyl-1-hydroxyprop-2-yn-1-yl)(1,1'-biphenyl)-4-yl phosphine oxide (3bc)**



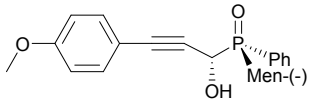
The optically pure **3bc** was obtained as a oil (67 mg, 34%, <1:99 dr) from chromatography. ^{31}P NMR (162 MHz, cdcl$_3$) δ = 43.24 (s).^{1}H NMR (400 MHz, cdcl$_3$) δ = 8.03 – 7.92 (m, 2H), 7.65 – 7.55 (m, 4H), 7.50 – 7.32 (m, 5H), 7.18 (d, *J*=7.8, 2H), 5.35 (d, *J*=10.7, 1H), 2.66 (dd, *J*=15.1, 7.5, 2H), 2.47 – 2.30 (m, 2H), 1.95 – 1.40 (m, 6H), 1.24 (t, *J*=7.3, 3H), 1.02 (t, *J*=9.7, 5H), 0.77 (d, *J*=6.6, 3H), 0.30 (d, *J*=6.6, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 145.27 (s), 140.14 (s), 132.20 (d, *J*=8.7), 131.55 (s), 128.84 (s), 127.96 (d, *J*=11.3), 127.23 (s), 126.67 (d, *J*=11.4), 42.97 (s), 34.19 (s), 33.27 (s), 28.82 (s), 28.32 (s), 22.69 (s), 21.49 (s), 15.33 (s). **HRMS (ESI$^+$)**Calcd. For $C_{33}H_{39}O_2P$ [M+Na$^+$]: 521.2585, Found: 521.2590.

***R*$_P$,*S*$_C$-(*L*)-Menthyl (3-*p*-ethylphenyl-1-hydroxyprop-2-yn-1-yl)(1,1'-biphenyl)-4-yl phosphine oxide (3bc')**



The optically pure **3bc'** was obtained as a white solid (75 mg, 38%, <1:99 dr) from recrystallization. m.p. 173.4 – 174.5 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 40.58 (s).^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.98 (t, *J*=8.8), 7.62 (dd, *J*=23.5, 7.9), 7.48 – 7.34 (m), 7.24 (d, *J*=7.5), 7.11 (d, *J*=7.6), 5.04 (d, *J*=9.9), 4.61 (s), 2.65 – 2.49 (m), 1.87 – 1.42 (m), 1.21 (t, *J*=7.6), 1.02 (dd, *J*=19.5, 7.7), 0.79 (d, *J*=6.4), 0.32 (d, *J*=6.4).^{13}C NMR (101 MHz, cdcl$_3$) δ = 145.09 (s), 144.13 (s), 139.99 (s), 132.17 (s), 131.91 – 131.18 (m), 131.06 (s), 130.55 (s), 129.97 (d, *J*=116.7), 129.97 (d, *J*=116.7), 129.28 (dd, *J*=139.6, 85.5), 130.84 – 127.50 (m), 130.84 – 126.45 (m), 126.63 – 126.45 (m), 119.50 (s), 89.41 (s), 84.11 (s), 42.78 (s), 34.44 (s), 33.37 (d, *J*=13.1), 28.78 (s), 28.49 (s), 24.63 (s), 22.67 (s), 21.56 (s), 15.42 (s), 15.21 (s). **HRMS (ESI$^+$)**Calcd. For $C_{33}H_{39}O_2P$ [M+Na$^+$]: 521.2585, Found: 521.2587.

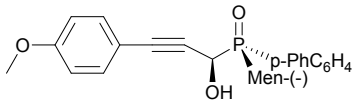
***R*$_P$,*S*$_C$-(*L*)-Menthyl (1-hydroxy-3-*p*-methoxyphenylprop-2-yn-1-yl) phenyl phosphine oxide (3ca')**



The optically pure **3ca'** was obtained as a white solid (114 mg, 67%, <1:99 dr) from recrystallization. m.p. 187.0 – 188.2 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 40.31 (s).^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.91 (t, *J*=8.8, 2H), 7.49 (dd, *J*=21.1, 6.7, 3H), 7.28 – 7.22 (m, 2H), 6.82 (d, *J*=8.1, 2H), 4.96 (d, *J*=9.7, 1H), 3.80 (d, *J*=0.7, 4H), 3.48 (d, *J*=0.8, 1H), 2.55 – 2.39 (m, 2H), 1.86 – 1.39 (m, 6H), 1.13 – 0.90 (m, 5H), 0.77 (d, *J*=6.4, 3H), 0.28 (d, *J*=6.4, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 159.93 (s), 133.28 (d, *J*=2.3), 132.76 (s), 131.91 (s), 131.61 (d, *J*=2.7), 130.94 (d, *J*=8.1), 128.15 (d, *J*=11.0), 114.23 (s), 113.93 (s), 89.46 (d, *J*=7.7), 82.91 (d, *J*=3.0, 2H), 63.42 (s), 62.65

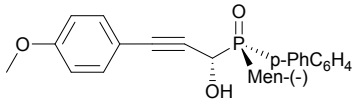
(s), 55.29 (s), 42.85 (d, *J*=3.6), 38.75 (s), 38.12 (s), 34.64 – 34.13 (m), 33.35 (d, *J*=13.1), 28.37 (d, *J*=3.2), 24.63 (d, *J*=12.3), 22.68 (s), 21.56 (s), 15.33 (s). **HRMS (ESI$^+$)**Calcd. For $C_{26}H_{33}O_3P$ [M+Na$^+$]: 447.2065, Found: 447.2065.

***R*$_P$,*R*$_C$-(*L*)-Menthyl (1-hydroxy-3-*p*-methoxyphenylprop-2-yn-1-yl)(1,1'-biphenyl)-4-yl phosphine oxide (3cc)**



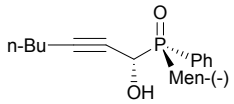
The optically pure **3cc** was obtained as an oil (64 mg, 32%, <1:99 dr) from chromatography. ^{31}P NMR (162 MHz, cdcl$_3$) δ = 42.96 (s).^{1}H NMR (400 MHz, cdcl$_3$) δ = 8.01 – 7.92 (m, 2H), 7.59 (dd, *J*=16.0, 7.7, 4H), 7.53 – 7.32 (m, 5H), 6.87 (d, *J*=8.5, 2H), 5.33 (d, *J*=10.3, 1H), 3.82 (s, 3H), 2.52 – 2.23 (m, 2H), 1.96 – 1.33 (m, 6H), 1.14 – 0.95 (m, 5H), 0.77 (d, *J*=6.5, 3H), 0.30 (d, *J*=6.4, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 159.94 (s), 140.12 (s), 133.06 (s), 132.21 (d, *J*=8.5), 128.86 (s), 127.92 (s), 127.24 (s), 126.66 (d, *J*=11.6), 114.08 (s), 83.39 (s), 62.16 (s), 61.38 (s), 55.32 (s), 42.99 (s), 34.45 (s), 34.17 (s), 33.32 (d, *J*=12.9), 28.32 (s), 22.72 (s), 21.51 (s), 15.36 (s). **HRMS (ESI$^+$)**Calcd. For $C_{32}H_{37}O_3P$ [M+Na$^+$]: 523.2378, Found: 523.2385.

***R*$_P$,*S*$_C$-(*L*)-Menthyl (1-hydroxy-3-*p*-methoxyphenylprop-2-yn-1-yl)(1,1'-biphenyl)-4-yl phosphine oxide (3cc')**



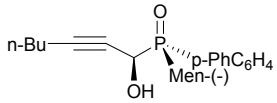
The optically pure **3cc'** was obtained as a white solid (80 mg, 40%, <1:99 dr) from recrystallization. m.p. 176.4 – 178.0 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 40.61 (s).^{1}H NMR (400 MHz, cdcl$_3$) δ = 8.03 – 7.92 (m, 2H), 7.67 (d, *J*=6.2, 2H), 7.61 (d, *J*=7.3, 2H), 7.45 (t, *J*=7.4, 2H), 7.38 (t, *J*=7.3, 1H), 7.25 (d, *J*=10.2, 2H), 6.80 (d, *J*=8.7, 2H), 5.01 (d, *J*=6.9, 1H), 3.88 (s, 1H), 3.79 (s, 3H), 2.49 (d, *J*=12.5, 2H), 1.85 (s, 1H), 1.75 (d, *J*=10.1, 2H), 1.63 – 1.42 (m, 2H), 1.13 – 0.95 (m, 5H), 0.80 (d, *J*=6.6, 3H), 0.34 (d, *J*=6.6, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 133.30 (s), 131.51 (d, *J*=8.3), 128.90 (s), 128.06 (s), 127.20 (s), 126.74 (d, *J*=11.2), 113.94 (s), 55.27 (s), 42.89 (s), 34.30 (s), 33.44 (s), 28.46 (s), 22.69 (s), 21.57 (s), 15.44 (s). **HRMS (ESI$^+$)**Calcd. For $C_{32}H_{37}O_3P$ [M+Na$^+$]: 523.2378, Found: 523.2382.

***R*$_P$,*S*$_C$-(*L*)-Menthyl (1-hydroxyhept-2-yn-1-yl) phenyl phosphine oxide (3da')**



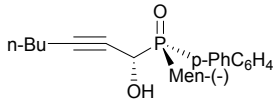
The optically pure **3da'** was obtained as a white solid (74 mg, 45%, <1:99 dr) from recrystallization. m.p. 137.8 – 140.7 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 39.38 (s).^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.94 – 7.82 (m, 2H), 7.49 (dd, *J*=20.0, 5.7, 3H), 4.74 (d, *J*=7.8, 1H), 3.32 (s, 1H), 2.39 (d, *J*=12.2, 2H), 2.20 (d, *J*=6.3, 2H), 1.73 (d, *J*=10.8, 4H), 1.54 – 1.29 (m, 6H), 1.12 – 0.93 (m, 5H), 0.89 (t, *J*=7.2, 3H), 0.78 (d, *J*=6.7, 3H), 0.28 (d, *J*=6.6, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 132.79 (s), 131.94 (s), 131.44 (d, *J*=2.6), 131.00 (d, *J*=8.1), 128.00 (d, *J*=11.0), 90.56 (d, *J*=7.7), 75.27 (d, *J*=2.3), 62.99 (s), 62.20 (s), 42.74 (d, *J*=3.6), 38.59 (s), 37.95 (s), 34.28 (s), 33.28 (d, *J*=13.0), 30.32 (d, *J*=2.1), 28.26 (d, *J*=3.2), 24.60 (d, *J*=12.2), 22.62 (s), 21.83 (s), 21.54 (s), 18.62 (d, *J*=2.1), 15.25 (s), 13.58 (s). **HRMS (ESI$^+$)**Calcd. For $C_{23}H_{35}O_2P$ [M+Na$^+$]: 397.2272, Found: 397.2271.

***R_P,R_C*-(*L*)-Menthyl (1-hydroxyhept-2-yn-1-yl)(1,1'-biphenyl)-4-yl phosphine oxide (3dc)**



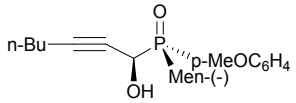
The optically pure **3dc** was obtained as a oil (68 mg, 38%, <1:99 dr) from chromatography. ^{31}P NMR (162 MHz, cdcl$_3$) δ = 42.58 (s). ^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.95 – 7.85 (m, 2H), 7.57 (dd, *J*=13.7, 5.1, 4H), 7.43 – 7.33 (m, 3H), 5.11 (d, *J*=10.3, 1H), 2.39 – 2.20 (m, 4H), 1.76 (s, 1H), 1.57 – 1.40 (m, 6H), 1.07 – 0.89 (m, 8H), 0.74 (d, *J*=6.7, 3H), 0.29 (d, *J*=6.6, 3H). ^{13}C NMR (101 MHz, cdcl$_3$) δ = 143.94 (s), 140.18 (s), 132.20 (d, *J*=8.4), 129.85 (s), 128.84 (s), 127.84 (s), 127.19 (s), 126.53 (d, *J*=11.5), 89.90 (d, *J*=8.6), 75.88 (s), 61.87 (s), 61.07 (s), 42.82 (d, *J*=3.9), 38.90 (s), 38.27 (s), 34.18 (s), 33.29 (d, *J*=12.9), 30.36 (d, *J*=2.0), 28.19 (s), 24.56 (d, *J*=11.5), 22.63 (s), 21.99 (s), 21.45 (s), 18.72 (s), 15.29 (s), 13.60 (s). **HRMS (ESI$^+$)**Calcd. For $C_{29}H_{39}O_2P$ [M+Na$^+$]: 473.2585, Found:473.2589.

***R_P,R_C*-(*L*)-Menthyl (1-hydroxyhept-2-yn-1-yl)(1,1'-biphenyl)-4-yl phosphine oxide (3dc')**



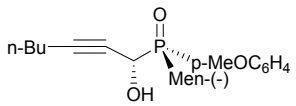
The optically pure **3dc'** was obtained as a white solid (61 mg, 34%, <1:99 dr) from recrystallization. m.p. 153.8 – 155.9 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 40.07 (s). ^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.92 (t, *J*=9.0, 2H), 7.76 – 7.64 (m, 2H), 7.61 (d, *J*=7.2, 2H), 7.45 (t, *J*=7.5, 2H), 7.38 (t, *J*=7.2, 1H), 4.81 (s, 1H), 3.90 (s, 1H), 2.43 (s, 2H), 2.20 (s, 2H), 1.82 – 1.71 (m, 3H), 1.54 – 1.29 (m, 6H), 1.13 – 0.95 (m, 5H), 0.86 (t, *J*=7.2, 3H), 0.79 (d, *J*=6.6, 3H), 0.32 (d, *J*=6.6, 3H). ^{13}C NMR (101 MHz, cdcl$_3$) δ = 144.10 (s), 139.97 (s), 131.47 (t, *J*=11.5), 130.49 (s), 128.89 (s), 128.02 (s), 127.17 (s), 126.63 (d, *J*=11.2), 90.71 (s), 75.25 (s), 63.03 (s), 62.24 (s), 42.77 (d, *J*=3.8), 38.70 (s), 38.06 (s), 34.29 (s), 33.30 (d, *J*=13.0), 30.33 (s), 28.34 (s), 24.64 (d, *J*=12.1), 22.63 (s), 21.84 (s), 21.56 (s), 18.63 (s), 15.37 (s), 13.57 (s). **HRMS (ESI$^+$)**Calcd. For $C_{29}H_{39}O_2P$ [M+Na$^+$]: 473.2585, Found: 473.2583.

***R_P,R_C*-(*L*)-Menthyl (1-hydroxyhept-2-yn-1-yl)(4-methoxyphenyl) phosphine oxide (3dd)**



The optically pure **3dd** was obtained as an oil (71 mg, 44%, <1:99 dr) from chromatography. ^{31}P NMR (162 MHz, cdcl$_3$) δ = 42.29 (s).^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.76 (t, *J*=9.0, 2H), 6.89 (d, *J*=7.2, 2H), 4.98 (s, 1H), 3.81 (s, 3H), 2.20 (d, *J*=41.5, 4H), 1.72 (s, 4H), 1.53 – 1.29 (m, 5H), 0.92 (dd, *J*=15.0, 7.3, 8H), 0.74 (d, *J*=6.5, 3H), 0.29 (d, *J*=6.5, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 162.16 (s), 133.42 (d, *J*=9.2), 113.54 (d, *J*=12.1), 75.99 (s), 61.66 (s), 60.86 (s), 55.18 (s), 42.77 (s), 38.70 (s), 38.07 (s), 34.13 (s), 33.25 (d, *J*=13.0), 30.36 (s), 28.08 (s), 24.54 (d, *J*=11.8), 22.60 (s), 21.95 (s), 21.47 (s), 18.68 (s), 15.30 (s), 13.57 (s). **HRMS (ESI$^+$)**Calcd. For $C_{24}H_{37}O_3P$ [M+Na$^+$]: 427.2378, Found: 427.2377.

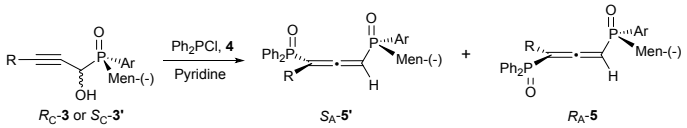
***R_P,S_C*-(*L*)-Menthyl (1-hydroxyhept-2-yn-1-yl)(4-methoxyphenyl) phosphine oxide (3dd')**



The optically pure **3dd'** was obtained as a white solid (61 mg, 38%, <1:99 dr) from

recrystallization. m.p. 105.4 – 107.8 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 42.29 (s).^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.77 (t, *J*=9.0, 2H), 6.93 (d, *J*=7.2, 2H), 4.71 (d, *J*=9.2, 1H), 3.83 (s, 3H), 2.27 (dd, *J*=69.7, 16.1, 4H), 1.77 – 1.69 (m, 3H), 1.42 – 1.31 (m, 5H), 0.95 (s, 5H), 0.87 (t, *J*=7.2, 3H), 0.76 (d, *J*=6.5, 3H), 0.30 (d, *J*=6.5, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 162.16 (s), 133.42 (d, *J*=9.2), 113.54 (d, *J*=12.1), 75.99 (s), 61.66 (s), 60.86 (s), 55.18 (s), 42.77 (s), 38.70 (s), 38.07 (s), 34.14 (s), 33.25 (d, *J*=13.0), 30.36 (s), 28.08 (s), 24.54 (d, *J*=11.8), 22.60 (s), 21.95 (s), 21.47 (s), 18.68 (s), 15.30 (s), 13.57 (s). **HRMS (ESI$^+$)**Calcd. For $C_{24}H_{37}O_3P$ [M+Na$^+$]: 427.2378, Found: 427.2377.

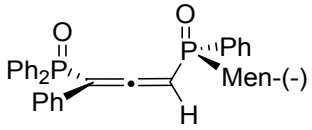
Part 3. The conversion of R_C-3 or S_C-3' to 5 or 5'.



General procedure:

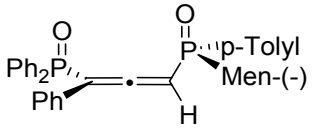
To the ice-water cooled solution of propargylic alcohol **3/3'** (0.2 mmol) in ether (1 mL), was added diphenylphosphonium chloride (0.036 mL, 0.2 mmol) and pyridine (0.017 mL, 0.2 mmol) in this order. The mixture was stirred overnight, until ice melted. After diluted hydrochloride solution (7%) added, the water layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous magnesium sulfate. Removing solvent afforded crude product, which was recrystallized with petroleum ether and dichloromethane (5 : 1).

***S_P,S_A*-(*L*)-Menthyl (3-diphenylphosphoryl-3-phenylpropa-1,2-dien-1-yl) phenylphosphine oxide (5aa')**



The optically pure **5aa'** was obtained as a white solid (25 mg, 20%, <1:99 dr) from recrystallization, m.p. 220.7 – 222.1 °C ^{31}P NMR (202 MHz, $CDCl_3$) δ = 40.35 (d, *J*=14.5), 34.66 (d, *J*=14.6).^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.94 (dd, *J*=11.8, 7.5, 2H), 7.59 – 7.52 (m, 5H), 7.46 (dd, *J*=12.9, 8.1, 5H), 7.39 (d, *J*=3.5, 2H), 7.29 – 7.19 (m, 4H), 7.13 (d, *J*=7.2, 2H), 5.88 (dd, *J*=9.6, 7.2, 1H), 2.02 – 1.83 (m, 2H), 1.77 – 1.58 (m, 4H), 1.31 (s, 1H), 1.05 (ddd, *J*=40.1, 18.5, 10.0, 2H), 0.89 (d, *J*=6.2, 4H), 0.77 (d, *J*=6.6, 3H), 0.36 (d, *J*=6.6, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ = 136.48 (s), 136.32 – 136.12 (m), 136.12 – 135.29 (m), 134.00 (s), 133.48 – 133.07 (m), 132.73 (s), 133.07 – 131.15 (m), 81.50 (s), 81.49 – 80.80 (m), 52.98 (d, *J*=21.2), 52.72 (s), 52.55 (s), 52.38 (s), 47.36 (s), 39.70 (s), 37.92 (s), 36.93 (s), 32.30 (s), 28.37 (s), 26.16 (s), 25.10 (s), 18.87 (s). **HRMS (ESI$^+$)**Calcd. For $C_{37}H_{40}O_2P_2$ [M+Na$^+$]: 601.2401, Found: 601.2417.

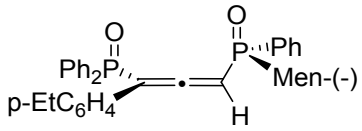
***S_P,S_A*-(*L*)-Menthyl (3-diphenylphosphoryl-3-phenylpropa-1,2-dien-1-yl)(p-tolyl)phosphine oxide (5ab')**



The optically pure **5ab'** was obtained as a white solid (42 mg, 43%, **5ab:5ab'** = 3:97 dr) from recrystallization, m.p. 200.4 – 202.7 °C. ^{31}P NMR (162 MHz, $cdcl_3$) δ = 34.19 (d, *J*=13.5), 28.18 (d, *J*=13.5).^{1}H NMR (400 MHz, $cdcl_3$) δ = 7.96 (dd, *J*=12.2, 7.8, 2H), 7.61 (dd, *J*=11.9, 7.7, 2H), 7.45 (d, *J*=5.9, 5H), 7.33 (dd, *J*=10.8, 8.0, 2H), 7.17 (d, *J*=6.5, 6H), 7.06 (dd, *J*=7.6, 4.9, 2H), 5.70 (dd, *J*=9.8, 7.1, 1H), 2.40 (d, *J*=10.5, 3H), 2.09 (d, *J*=4.7, 2H), 1.66 (t, *J*=14.5, 4H), 1.34 – 1.05 (m, 2H), 1.01 – 0.81 (m, 6H), 0.76 (d, *J*=6.8, 3H), 0.39 (d, *J*=6.7, 3H). ^{13}C NMR (101 MHz, $cdcl_3$) δ 213.46 – 210.92 (m), 141.72 (s), 132.81 – 132.40 (m), 132.17 (s), 131.46 (s), 130.48 – 130.29 (m), 129.68 (s), 129.12 (s), 128.50 (s), 127.97 (s), 127.58 – 127.08 (m), 104.27 – 101.28 (m), 88.28 – 85.29 (m), 43.63 – 42.94 (m), 42.33 – 40.71 (m), 35.95 – 35.50 (m), 34.39 – 33.41 (m), 33.66 –

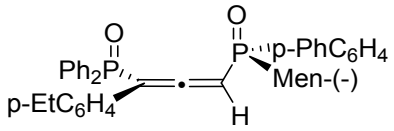
32.74 (m), 28.21 (s), 25.02 – 24.04 (m), 22.89 – 22.03 (m), 21.41 (s), 15.73 – 14.87 (m).**HRMS (ESI$^+$)**Calcd. For $C_{38}H_{42}O_2P_2$ [M+Na$^+$]: 615.2558, Found: 615.2587.

***S*$_P$,*S*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-*p*-ethylphenylpropa-1,2-dien-1-yl) phenylphosphine oxide (5ba')**



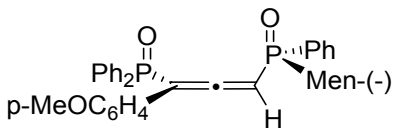
The optically pure **5ba'** was obtained as a white solid (46 mg, 38%, <1:99 dr) from recrystallization, m.p. 192.6 – 194.5 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 33.82 (d, *J*=14.5), 28.39 (d, *J*=14.5).^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.98 (s, 2H), 7.65 – 7.53 (m, 2H), 7.46 (s, 6H), 7.38 (d, *J*=7.2, 4H), 7.14 (d, *J*=6.5, 1H), 7.01 (d, *J*=7.8, 4H), 5.68 (t, *J*=8.6, 1H), 2.60 – 2.45 (m, 2H), 2.06 (s, 2H), 1.68 (s, 4H), 1.21 (dd, *J*=17.3, 10.3, 2H), 1.14 (t, *J*=7.4, 3H), 1.01 – 0.82 (m, 5H), 0.77 (d, *J*=6.5, 3H), 0.37 (d, *J*=6.5, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 212.62 (s), 144.24 (s), 134.31 (s), 133.34 (s), 132.96 – 132.46 (m), 132.24 (t, *J*=17.4), 131.88 (s), 131.49 (dd, *J*=23.4, 12.8), 130.23 (d, *J*=9.0), 129.03 – 128.01 (m), 127.81 (d, *J*=12.7), 86.41 (s), 65.79 (s), 43.27 (s), 41.91 (s), 41.20 (s), 35.79 (s), 34.10 (s), 33.03 (d, *J*=13.8), 28.48 (s), 28.24 (s), 24.49 (d, *J*=13.0), 22.40 (s), 21.43 (s), 15.20 (d, *J*=14.3). **HRMS (ESI$^+$)**Calcd. For $C_{39}H_{44}O_2P_2$ [M+Na$^+$]: 629.2714, Found: 629.2733.

***S*$_P$,*S*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-*p*-ethylphenylpropa-1,2-dien-1-yl) (1,1'-biphenyl)-4-ylphosphine oxide (5bc')**



The optically pure **5bc'** was obtained as a white solid (54 mg, 40%, <1:99 dr) from recrystallization. m.p. 185.3 – 186.2 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 33.64 (d, *J*=13.7), 28.29 (d, *J*=13.7).^{1}H NMR (400 MHz, cdcl$_3$) δ = 8.09 – 7.94 (m, 2H), 7.60 (dd, *J*=11.8, 7.1, 6H), 7.56 – 7.37 (m, 10H), 7.12 (t, *J*=7.1, 1H), 7.02 (dd, *J*=17.9, 6.4, 4H), 5.79 – 5.65 (m, 1H), 2.52 (q, *J*=7.4, 2H), 2.12 (dd, *J*=17.4, 11.0, 2H), 1.86 (s, 1H), 1.71 (d, *J*=8.8, 4H), 1.31 – 1.17 (m, 2H), 1.12 (t, *J*=7.6, 3H), 1.07 – 0.84 (m, 5H), 0.80 (d, *J*=6.7, 3H), 0.42 (d, *J*=6.6, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 144.25 (s), 144.03 (s), 139.86 (s), 132.34 – 131.78 (m), 131.78 – 131.14 (m), 130.74 (d, *J*=9.2), 128.98 (s), 128.51 (dd, *J*=11.8, 8.7), 128.00 (dd, *J*=27.8, 8.1), 127.26 – 126.65 (m), 43.30 (s), 41.87 (s), 41.16 (s), 35.72 (s), 34.11 (s), 33.04 (d, *J*=13.7), 28.41 (d, *J*=16.2), 24.50 (d, *J*=13.1), 22.45 (s), 21.49 (s), 15.29 (d, *J*=5.3). **HRMS (ESI$^+$)**Calcd. For $C_{45}H_{48}O_2P_2$ [M+Na$^+$]: 705.3027, Found: 705.3049.

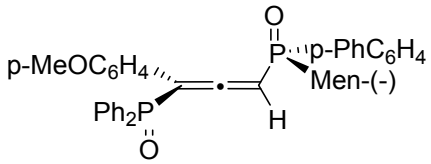
***S*$_P$,*S*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-*p*-methoxyphenylpropa-1,2-dien-1-yl) phenylphosphine oxide (5ca')**



The optically pure **5ca'** was obtained as a white solid (55 mg, 45%, <1:99 dr) from recrystallization. m.p. 236.2 – 237.7 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 33.32 (d, *J*=13.8), 28.27 (d, *J*=13.8).^{1}H NMR (400 MHz, cdcl$_3$) δ = 8.00 – 7.93 (m, 2H), 7.61 – 7.55 (m, 2H), 7.50 – 7.38 (m,

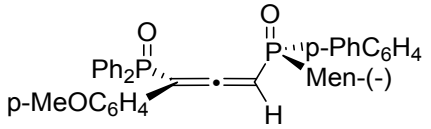
10H), 7.13 (d, *J*=6.1, 1H), 7.02 (td, *J*=7.5, 3.1, 2H), 6.71 (d, *J*=8.8, 2H), 5.68 (dd, *J*=9.8, 7.7, 1H), 3.71 (s, 3H), 2.10 – 1.98 (m, 1H), 1.71 (dd, *J*=24.9, 21.3, 5H), 1.29 – 1.07 (m, 2H), 1.00 – 0.84 (m, 5H), 0.77 (d, *J*=6.8, 3H), 0.35 (d, *J*=6.7, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 159.41 (s), 132.28 – 131.74 (m), 131.47 (dd, *J*=18.7, 13.9), 130.22 (d, *J*=9.0), 129.77 (s), 128.45 (dd, *J*=22.0, 12.1), 127.82 (d, *J*=12.6), 114.07 (s), 55.17 (s), 43.27 (d, *J*=3.2), 41.83 (s), 41.12 (s), 35.73 (s), 34.08 (s), 33.01 (d, *J*=13.7), 28.28 (s), 24.47 (d, *J*=13.2), 22.45 (s), 21.48 (s), 15.15 (s). **HRMS (ESI$^+$)**Calcd. For $C_{38}H_{42}O_3P_2$ [M+Na$^+$]: 631.2507, Found: 631.2526.

***S*$_P$,*R*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-*p*-methoxyphenylpropa-1,2-dien-1-yl) (1,1'-biphenyl)-4-yl phosphine oxide (5cc)**



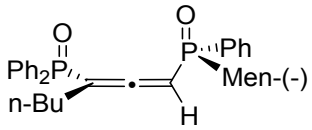
The optically pure **5cc** was obtained as a white solid (58 mg, 43%, <1:99 dr) from recrystallization. m.p. 175.6 – 177.5 °C ^{31}P NMR (202 MHz, $CDCl_3$) δ 33.03 (d, *J* = 13.3 Hz, 1H), 27.54 (d, *J* = 13.7 Hz, 1H). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 11.7, 7.7 Hz, 2H), 7.69 – 7.60 (m, 8H), 7.53 – 7.40 (m, 7H), 7.34 (dd, *J* = 16.0, 6.8 Hz, 4H), 6.71 (d, *J* = 8.5 Hz, 2H), 5.83 (dd, *J* = 9.7, 2.8 Hz, 1H), 3.70 (s, 3H), 2.09 – 1.88 (m, 3H), 1.79 (s, 1H), 1.69 (d, *J* = 11.5 Hz, 2H), 1.27 (d, *J* = 17.0 Hz, 2H), 1.07 (dt, *J* = 19.2, 12.6 Hz, 1H), 1.01 – 0.79 (m, 5H), 0.73 (d, *J* = 6.6 Hz, 3H), 0.36 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 211.91 (d, *J*=7.8), 159.44 (s), 144.22 (d, *J*=2.5), 139.79 (s), 132.96 (s), 132.18 (s), 132.09 (d, *J*=2.3), 132.00 (s), 131.90 (d, *J*=5.9), 131.80 (s), 131.50 (s), 131.32 (s), 131.21 (d, *J*=9.3), 130.65 (s), 129.78 (d, *J*=3.5), 129.04 (s), 128.60 (s), 128.48 (d, *J*=4.9), 128.36 (s), 128.26 (s), 127.25 (s), 127.05 (s), 126.96 (s), 122.74 (s), 114.27 (s), 103.35 – 101.21 (m), 88.10 (dd, *J*=88.7, 11.2), 55.21 (s), 43.26 (d, *J*=2.8), 42.08 (d, *J*=71.1), 35.21 (d, *J*=2.4), 34.22 (s), 33.36 (d, *J*=13.4), 28.38 (d, *J*=2.5), 24.58 (d, *J*=13.1), 22.56 (s), 21.39 (s), 15.24 (s). **HRMS (ESI$^+$)**Calcd. For $C_{44}H_{46}O_3P_2$ [M+Na$^+$]: 707.2820, Found:707.2836.

***S*$_P$,*S*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-*p* -methoxyphenylpropa-1,2-dien-1-yl) (1,1'-biphenyl)-4-ylphosphine oxide (5cc')**



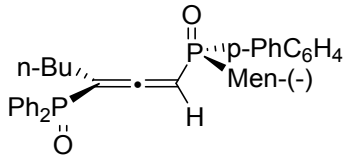
The optically pure **5cc'** was obtained as a white solid (74 mg, 54%, <1:99 dr) from recrystallization. m.p. 186.3 – 188.4 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 33.59 (d, *J*=13.8), 28.43 (d, *J*=13.8).^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.97 (d, *J*=5.9, 2H), 7.66 – 7.57 (m, 6H), 7.54 – 7.41 (m, 10H), 7.11 (d, *J*=6.9, 2H), 7.04 (s, 2H), 6.70 (d, *J*=8.3, 2H), 5.79 – 5.62 (m, 1H), 3.69 (s, 3H), 2.30 (s, 1H), 2.12 (s, 1H), 1.83 (s, 1H), 1.71 (d, *J*=8.0, 3H), 1.26 (s, 1H), 1.16 (dd, *J*=18.7, 12.1, 1H), 1.05 – 0.84 (m, 5H), 0.80 (d, *J*=6.5, 3H), 0.40 (t, *J*=12.3, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 159.41 (s), 132.89 – 131.90 (m), 131.57 (d, *J*=9.7), 130.75 (d, *J*=9.0), 129.82 (s), 128.99 (s), 128.57 (d, *J*=12.6), 128.17 (s), 127.87 (d, *J*=12.5), 127.35 – 126.75 (m), 114.08 (s), 55.16 (s), 43.31 (s), 41.14 (s), 35.69 (s), 34.10 (s), 33.03 (d, *J*=13.7), 28.31 (s), 22.45 (s), 21.50 (s), 15.26 (s). **HRMS (ESI$^+$)**Calcd. For $C_{44}H_{46}O_3P_2$ [M+Na$^+$]: 707.2820, Found: 707.2837.

***S*$_P$,*S*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-hepta-1,2-dien-1-yl) phenylphosphine oxide (5da')**



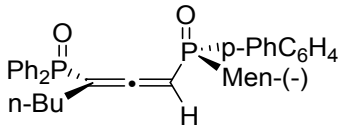
The optically pure **5da'** was obtained as a white solid (45 mg, 39%, <1:99 dr) from recrystallization, m.p. 169.5 – 171.7 °C ^{31}P NMR (162 MHz, cdcl$_3$) δ = 32.92 (d, *J*=14.5), 28.88 (d, *J*=15.1).^{1}H NMR (400 MHz, cdcl$_3$) δ = 8.01 (s, 2H), 7.49 (dt, *J*=20.3, 10.9, 10H), 7.19 (d, *J*=7.6, 1H), 7.05 (s, 2H), 5.47 (s, 1H), 2.25 (s, 1H), 1.99 (s, 2H), 1.68 (s, 5H), 1.34 – 1.10 (m, 6H), 0.90 (t, *J*=15.3, 5H), 0.80 (d, *J*=5.9, 6H), 0.31 (d, *J*=6.7, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 209.75 (d, *J*=7.6), 134.40 (s), 133.45 (s), 132.17 – 131.83 (m), 131.75 (s), 131.65 – 130.88 (m), 130.69 (s), 130.21 (d, *J*=8.9), 128.44 (dd, *J*=29.9, 12.0), 127.86 (d, *J*=12.5), 100.89 (d, *J*=11.0), 99.94 (d, *J*=11.0), 86.96 (d, *J*=12.2), 86.07 (d, *J*=12.2), 43.28 (d, *J*=3.1), 41.59 (s), 40.88 (s), 35.64 (s), 34.09 (s), 33.07 (d, *J*=13.8), 30.30 (d, *J*=5.7), 28.21 (d, *J*=2.9), 27.00 (t, *J*=4.6), 24.45 (d, *J*=13.0), 22.49 (s), 22.29 (s), 21.51 (s), 15.08 (s), 13.81 (s). **HRMS (ESI$^+$)**Calcd. For $C_{35}H_{44}O_2P_2$ [M+Na$^+$]: 581.2714, Found: 581.2734.

***S*$_P$,*R*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-hepta-1,2-dien-1-yl)(1,1'-biphenyl)-4-ylphosphine oxide (5dc)**



The optically pure **5dc** was obtained as a white solid (46 mg, 37%, **5dc:5dc'** = 97:3 dr) from recrystallization, m. p. 173.0 – 175.1 °C. ^{31}P NMR (202 MHz, CDCl$_3$) δ = 32.22 (d, *J*=13.2), 28.45 (d, *J*=14.1).^{1}H NMR (500 MHz, CDCl$_3$) δ 7.77 – 7.64 (m, 10H), 7.52 – 7.36 (m, 9H), 5.69 – 5.60 (m, 1H), 2.33 – 2.19 (m, 1H), 2.10 (ddd, *J* = 16.4, 10.9, 6.1 Hz, 1H), 1.99 (dd, *J* = 9.1, 4.2 Hz, 1H), 1.80 (dd, *J* = 6.2, 3.3 Hz, 1H), 1.68 (dd, *J* = 15.6, 6.4 Hz, 2H), 1.37 – 1.16 (m, 6H), 1.00 (dtd, *J* = 14.8, 12.6, 4.5 Hz, 2H), 0.91 – 0.79 (m, 5H), 0.77 (d, *J* = 6.8 Hz, 3H), 0.71 (t, *J* = 7.2 Hz, 3H), 0.35 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ = 209.73 (d, *J*=7.3), 144.09 (d, *J*=2.5), 139.79 (s), 133.50 (s), 132.73 (s), 132.03 (d, *J*=2.5), 131.99 – 131.72 (m), 131.68 (s), 131.24 – 131.01 (m), 130.83 (s), 130.30 (s), 129.04 (s), 128.61 (d, *J*=12.3), 128.38 (s), 128.26 (d, *J*=5.3), 127.22 (s), 126.93 (d, *J*=11.8), 99.96 (s), 87.35 (dd, *J*=91.1, 12.0), 43.27 (d, *J*=2.7), 41.83 (d, *J*=71.6), 35.17 (d, *J*=2.4), 34.27 (s), 33.36 (d, *J*=13.6), 30.41 (d, *J*=5.5), 28.34 (d, *J*=2.6), 27.23 (t, *J*=4.5), 24.56 (d, *J*=13.0), 22.62 (s), 22.22 (s), 21.46 (s), 15.22 (s), 13.75 (s). **HRMS (ESI$^+$)**Calcd. For $C_{41}H_{48}O_2P_2$ [M+Na$^+$]: 657.3027, Found: 657.3045.

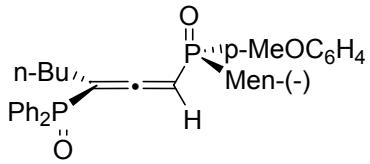
***S*$_P$,*S*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-hepta-1,2-dien-1-yl)(1,1'-biphenyl)-4-ylphosphine oxide (5dc')**



The optically pure **5dc'** was obtained as a white solid (32 mg, 25%, <1:99 dr) from recrystallization, m. p. 175.2 – 177.7 °C. ^{31}P NMR (202 MHz, CDCl$_3$) δ = 39.83 (d, *J*=4.5), 31.10 (d, *J*=4.8).^{1}H NMR (400 MHz, cdcl$_3$) δ = 7.98 (dd, *J*=11.8, 4.0, 2H), 7.47 (ddd, *J*=30.1, 16.0, 7.3, 10H), 7.16 (d, *J*=7.3, 1H), 7.04 (d, *J*=7.4, 2H), 5.45 (t, *J*=9.4, 1H), 2.23 (s, 1H), 2.11 – 1.86 (m,

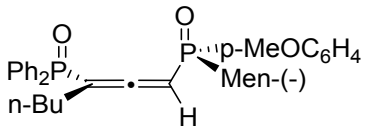
2H), 1.82 – 1.57 (m, 5H), 1.42 – 1.03 (m, 6H), 1.02 – 0.82 (m, 5H), 0.77 (t, *J*=5.9, 6H), 0.30 (d, *J*=6.6, 3H).^{13}C NMR (101 MHz, cdcl$_3$) δ = 209.87 (s), 134.46 (s), 133.51 (s), 132.67 – 131.22 (m), 132.82 – 131.22 (m), 133.24 – 129.15 (m), 129.63 (s), 129.63 (s), 128.32 (s), 127.78 (s), 43.27 (s), 35.71 (s), 34.12 (s), 33.15 (s), 30.35 (s), 28.24 (s), 27.04 (s), 24.54 (s), 22.44 (s), 21.86 (d, *J*=77.9), 15.08 (s), 13.73 (s). **HRMS (ESI$^+$)**Calcd. For $C_{41}H_{48}O_2P_2$ [M+Na$^+$]: 657.3027, Found: 657.3045.

***S*$_P$,*R*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-hepta-1,2-dien-1-yl)(4-methoxyphenyl)phosphine oxide (5dd)**



The optically pure **5dd** was obtained as a white solid (38 mg, 32%, <1:99 dr) from recrystallization, m. p. 168.6 – 170.1 °C. ^{31}P NMR (202 MHz, CDCl$_3$) δ = 32.41 (d, *J*=14.6), 28.58 (d, *J*=13.5). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.71 – 7.56 (m, 6H), 7.53 – 7.40 (m, 6H), 7.00 (dd, *J* = 8.7, 2.0 Hz, 2H), 5.61 (ddd, *J* = 10.0, 5.9, 3.7 Hz, 1H), 3.89 (s, 3H), 2.29 – 2.19 (m, 1H), 2.08 (ddd, *J* = 9.7, 7.6, 4.6 Hz, 1H), 2.02 – 1.92 (m, 1H), 1.83 – 1.76 (m, 1H), 1.73 – 1.63 (m, 2H), 1.37 – 1.19 (m, 6H), 1.06 – 0.91 (m, 2H), 0.91 – 0.78 (m, 5H), 0.78 – 0.72 (m, 6H), 0.36 (d, *J* = 8.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ = 209.51 (d, *J*=8.0), 162.10 (d, *J*=2.7), 132.49 (d, *J*=10.2), 131.99 (dt, *J*=8.9, 4.6), 131.82 (d, *J*=9.7), 131.54 (s), 131.20 (s), 130.68 (s), 130.37 (s), 128.70 – 128.40 (m), 128.28 (d, *J*=12.7), 125.59 (s), 124.79 (s), 113.92 (d, *J*=12.3), 99.94 (dd, *J*=96.0, 10.8), 87.58 (dd, *J*=91.0, 12.0), 55.36 (s), 43.22 (d, *J*=2.8), 42.14 (s), 41.56 (s), 35.18 (d, *J*=2.5), 34.24 (s), 33.29 (d, *J*=13.6), 30.40 (d, *J*=5.5), 29.70 (s), 28.22 (d, *J*=2.6), 27.14 (t, *J*=4.5), 24.51 (d, *J*=13.0), 22.60 (s), 22.22 (s), 21.46 (s), 15.20 (s), 13.74 (s). **HRMS (ESI$^+$)**Calcd. For $C_{36}H_{46}O_3P_2$ [M+Na$^+$]: 611.2820, Found: 611.2840.

***S*$_P$,*S*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-hepta-1,2-dien-1-yl)(4-methoxyphenyl)phosphine oxide (5dd')**

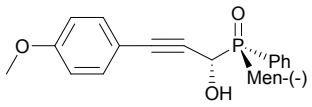


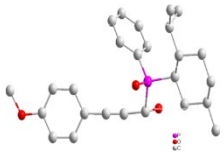
The optically pure **5dd'** was obtained as a white solid (35 mg, 39%, <1:99 dr) from recrystallization, m. p. 163.4 – 165.9 °C. ^{31}P NMR (202 MHz, CDCl$_3$) δ 33.22 (d, *J* = 14.1 Hz), 28.81 (d, *J* = 14.4 Hz).^{1}H NMR (500 MHz, CDCl$_3$) δ 7.97 (dd, *J* = 11.2, 7.2 Hz, 2H), 7.61 – 7.49 (m, 5H), 7.42 – 7.35 (m, 2H), 7.25 (s, 1H), 7.13 (t, *J* = 6.3 Hz, 2H), 6.91 (d, *J* = 7.3 Hz, 2H), 5.50 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.86 (s, 3H), 2.22 (d, *J* = 3.9 Hz, 1H), 2.07 – 1.97 (m, 2H), 1.66 (dd, *J* = 31.1, 11.9 Hz, 5H), 1.32 – 1.19 (m, 5H), 1.10 (td, *J* = 12.2, 6.9 Hz, 1H), 1.01 – 0.85 (m, 5H), 0.83 – 0.74 (m, 6H), 0.37 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 209.82 (s), 162.00 (s), 132.21 – 131.97 (m), 131.88 (s), 131.52 (d, *J* = 9.3 Hz), 131.35 – 131.29 (m), 131.03 (s), 130.67 – 130.35 (m), 128.58 (d, *J* = 12.2 Hz), 127.98 (d, *J* = 12.3 Hz), 125.31 (s), 124.63 – 124.43 (m), 113.86 (d, *J* = 12.7 Hz), 100.63 – 100.47 (m), 99.83 – 99.74 (m), 87.38 – 87.11 (m), 86.56 (s), 55.38 (s), 43.31 (s), 41.72 (s), 41.14 (s), 35.66 (s), 34.16 (s), 33.08 (d, *J* = 13.7 Hz), 30.39 (d, *J* = 5.4 Hz), 28.16 (s), 27.15 (s), 24.50 (d, *J* = 12.8 Hz), 22.50 (s), 22.30 (s), 21.55 (s), 15.23 (s), 13.78 (s).**HRMS (ESI$^+$)**Calcd. For $C_{36}H_{46}O_3P_2$ [M+Na$^+$]: 611.2820, Found: 611.2840.

Part 4. Crystallographic information 3ca', 5aa' and 5ab'.

Table S2. Crystallography data of R_P,S_C-(*L*)-Menthyl (1-hydroxy-3-*p*-methoxyphenylprop-2-yn-1-yl) phenyl phosphine oxide (3ca')

The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of **3ca'** in dichloromethane and petroleum ether (60-90℃).

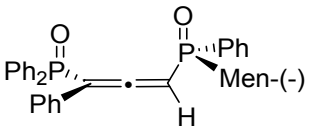


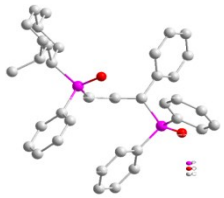


Empirical formula	C_{26} H_{33} O_3 P
Crystal system	Orthorhombic
space group	P2(1)2(1)2(1)
Formula weight	424.49
a,Å	8.8154(7)
b,Å	11.3911(9)
c,Å	24.121(2)
α,deg	90
β,deg	90
γ,deg	90
V,Å^3	2422.2(3)
Z	4
T,K	298(2)
λ,Å	0.71073
ρ,Mg /m^3	1.164
Rint	0.0468
R1 [I N 2σ(1)]	0.0443
R2 (all data)	0.0773
wR2 [I N 2σ(1)]	0.0967
wR2 (all data)	0.1118
Flack	0.15(12)
CCDC	1920863

Table S3. Crystallography data of S_P,S_A-(*L*)-Menthyl (3-diphenylphosphoryl-3-phenylpropa-1,2-dien-1-yl) phenylphosphine oxide (5aa')

The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of **5aa'** in dichloromethane and petroleum ether (60-90℃).



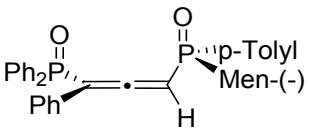


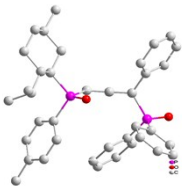
Empirical formula	C_{37} H_{40} O_2 P_2
Crystal system	Orthorhombic
space group	P2(1)2(1)2(1)
Formula weight	578.63
a,Å	12.9764(11)
b,Å	14.3781(12)
c,Å	17.5765(15)
α,deg	90
β,deg	90
γ,deg	90
V,Å^3	3279.4(5)
Z	4
T,K	298(2)
λ,Å	0.71073
ρ,Mg /m^3	1.172
Rint	0.0609
R1 [I N 2σ(1)]	0.0522
R2 (all data)	0.0836
wR2 [I N 2σ(1)]	0.1025
wR2 (all data)	0.1121
Flack	-0.08(7)
CCDC	1920864

Table S4. Crystallography data of S_P,S_A-(*L*)-Menthyl (3-diphenylphosphoryl-3-phenylpropa-

1,2-dien-1-yl)(p-tolyl)phosphine oxide (5ab')

The single crystal suited for the X-ray diffraction was obtained from the evaporation of the solution of **5ab'** in dichloromethane and petroleum ether (60-90℃).

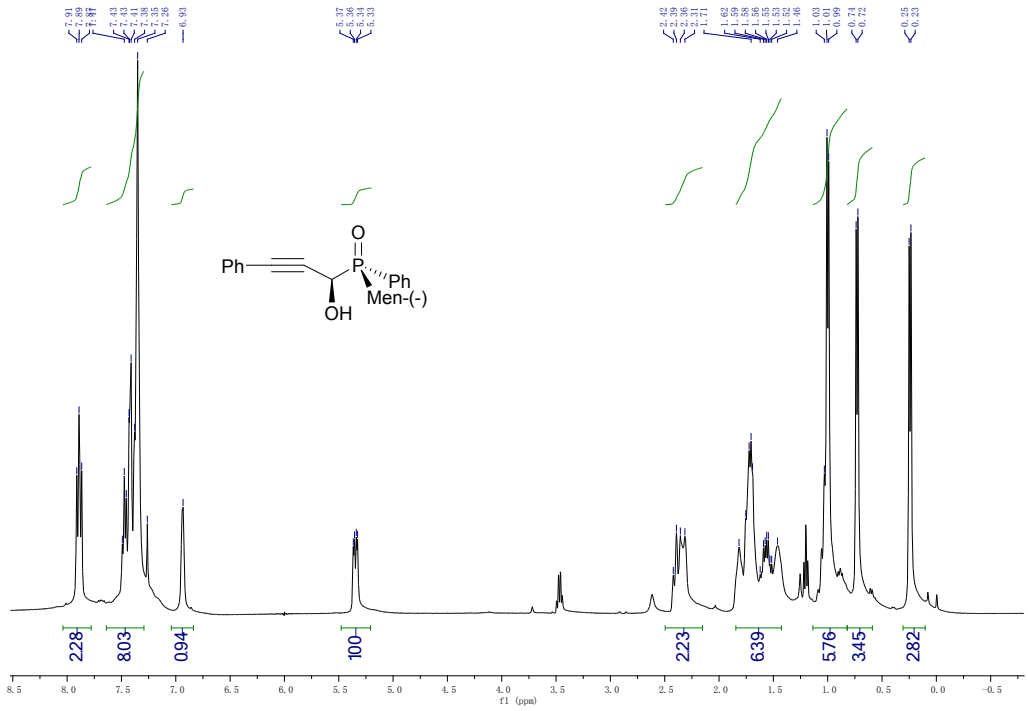


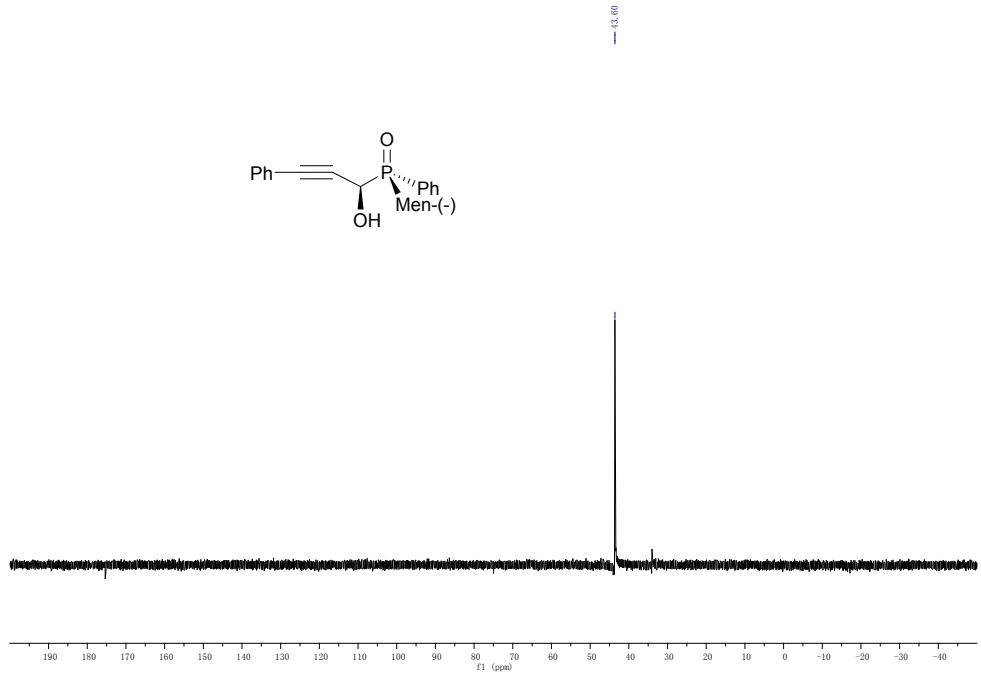


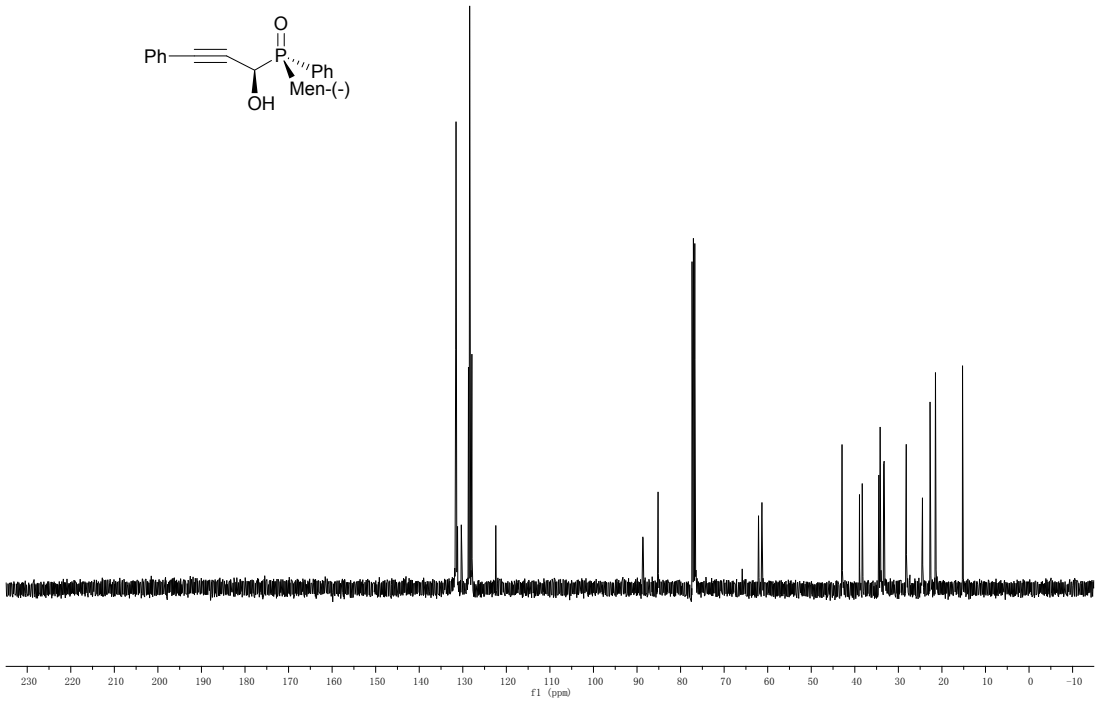
Empirical formula	C38 H42 O2 P2
Crystal system	orthorhombic
space group	P 2(1) 2(1) 2(1)
Formula weight	592.65
a,Å	13.2801(12)
b,Å	14.3298(13)
c,Å	17.9616(15)
α,deg	90
β,deg	90
γ,deg	90
V,Å^3	3418.1(5)
Z	4
T,K	298(2)
λ,Å	0.71073
ρ,Mg /m^3	1.152
Rint	0.0581
R1 [I N 2σ(1)]	0.0492
R2 (all data)	0.0952
wR2 [I N 2σ(1)]	0.0805
wR2 (all data)	0.0912
Flack	0.06(6)
CCDC	1920865

Part 5. Selected photocopies of ^{1}H, ^{31}P and ^{13}C NMR spectroscopy.

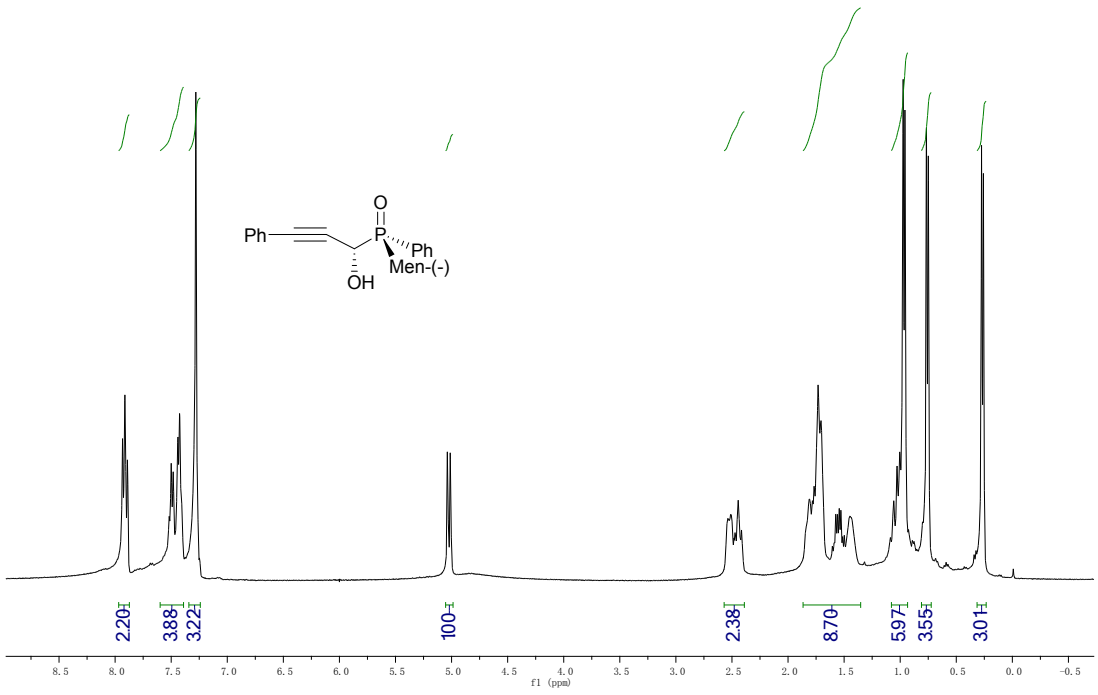
R_P,R_C-(*L*)-Menthyl (1-hydroxy-3-phenylprop-2-yn-1-yl) phenyl phosphine oxide (3aa)

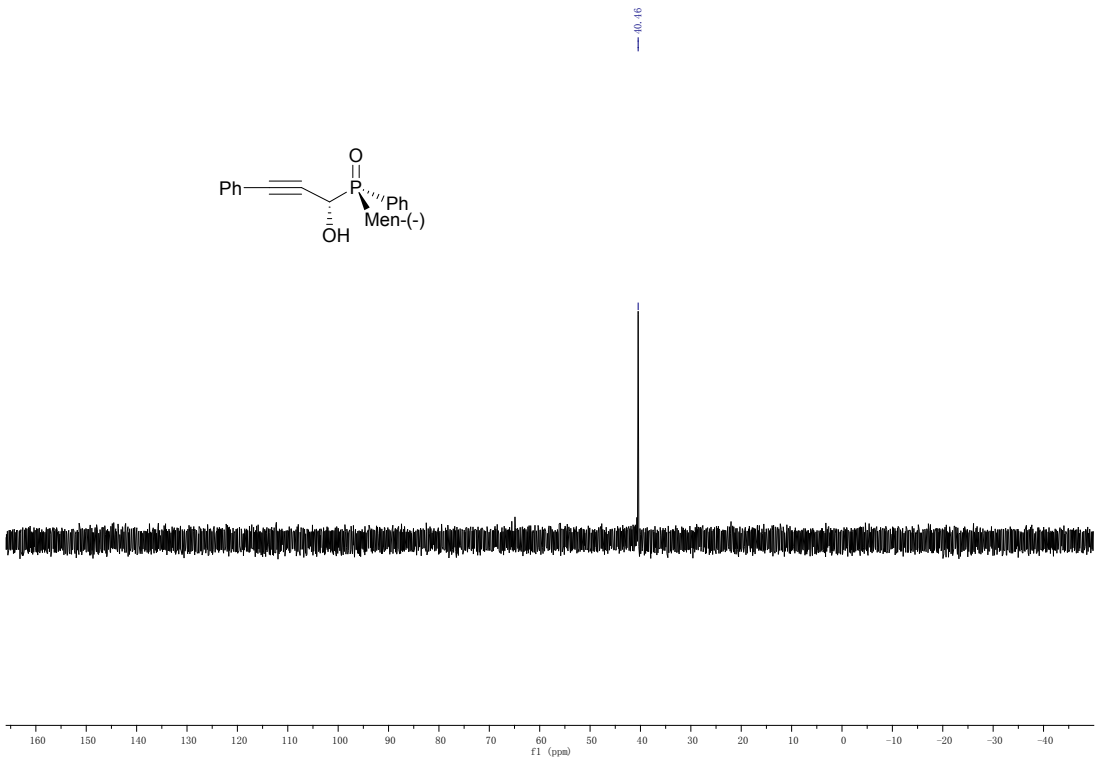


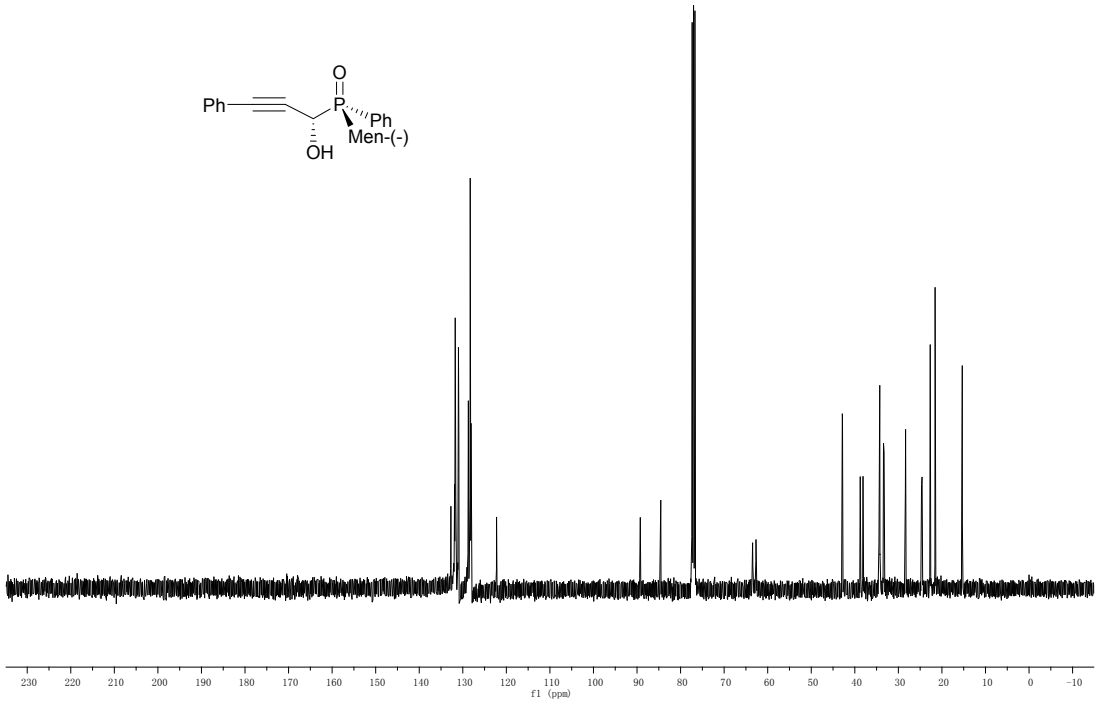




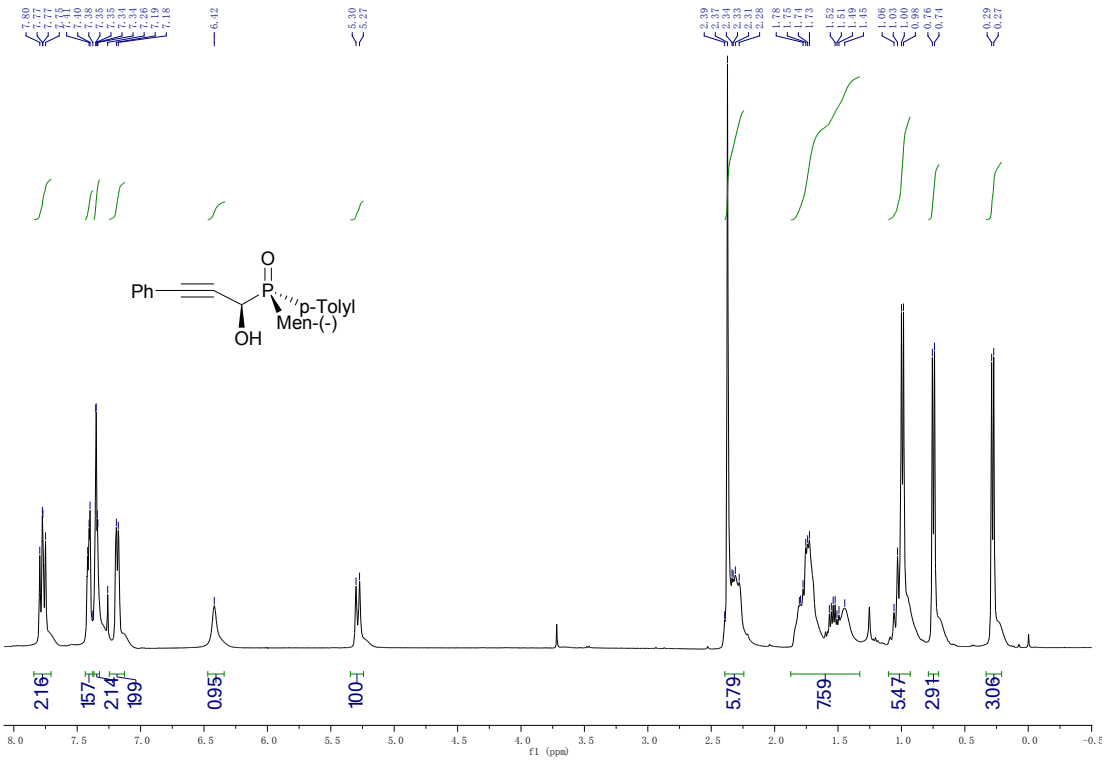
R_P,S_C-(*L*)-Menthyl (1-hydroxy-3-phenylprop-2-yn-1-yl) phenyl phosphine oxide (3aa')







R_P,R_C-(*L*)-Menthyl (1-hydroxy-3-phenylprop-2-yn-1-yl) p-tolyl phosphine oxide (3ab)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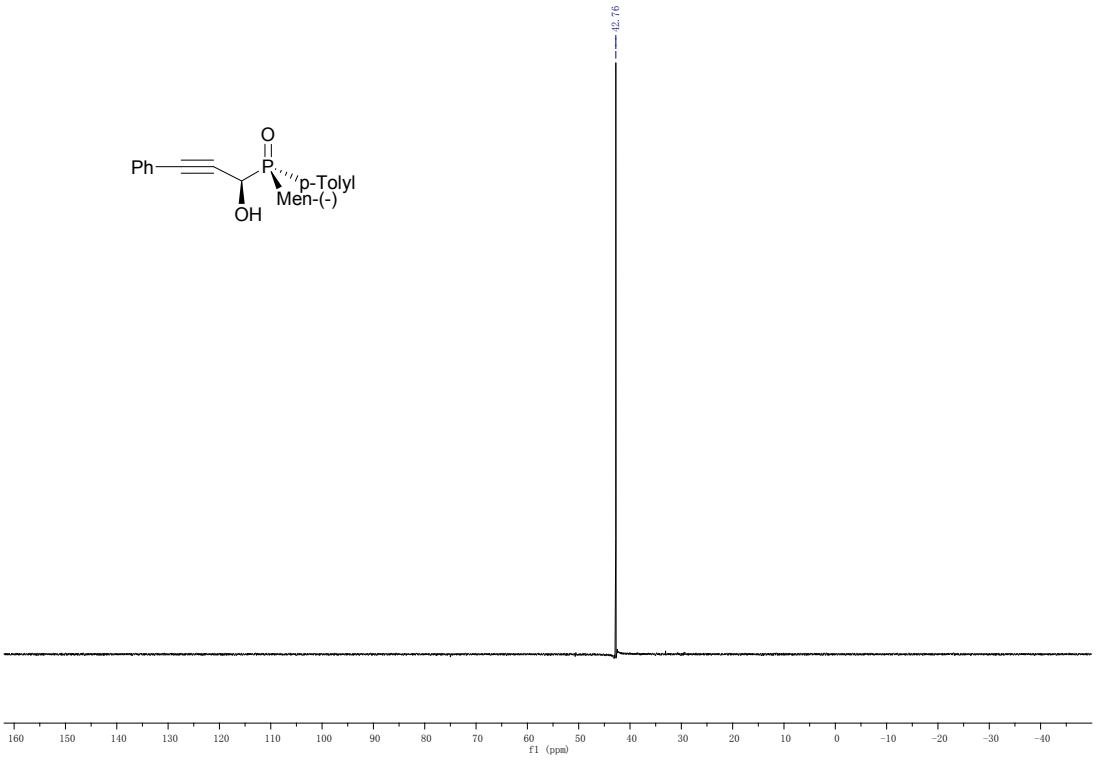
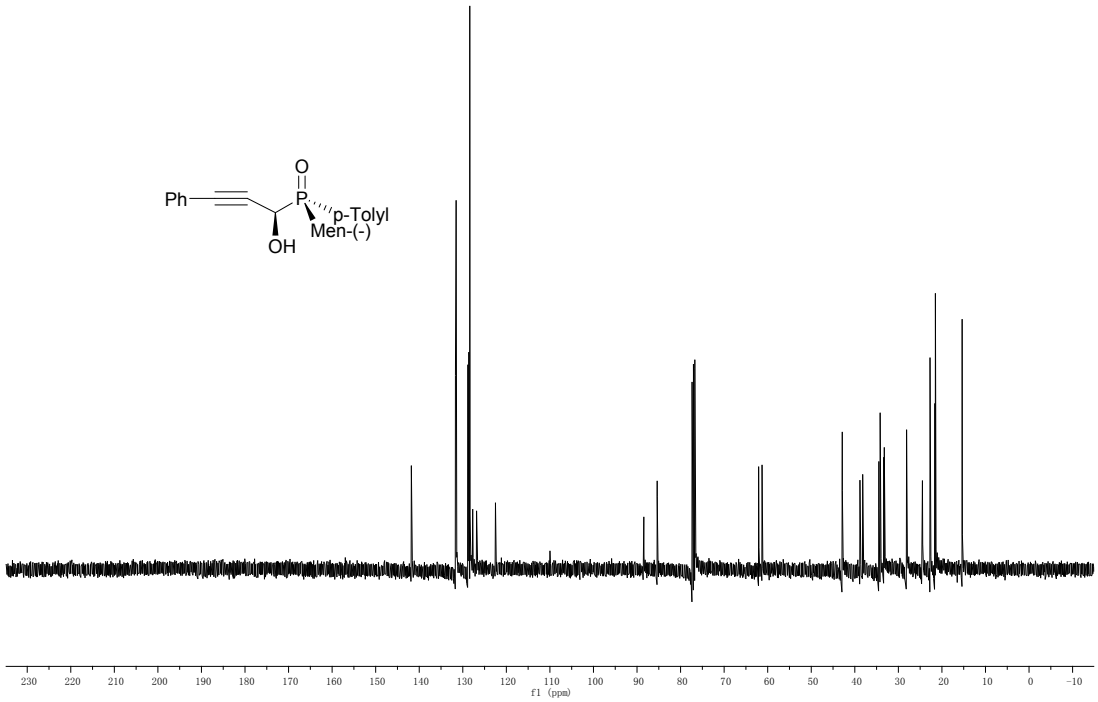
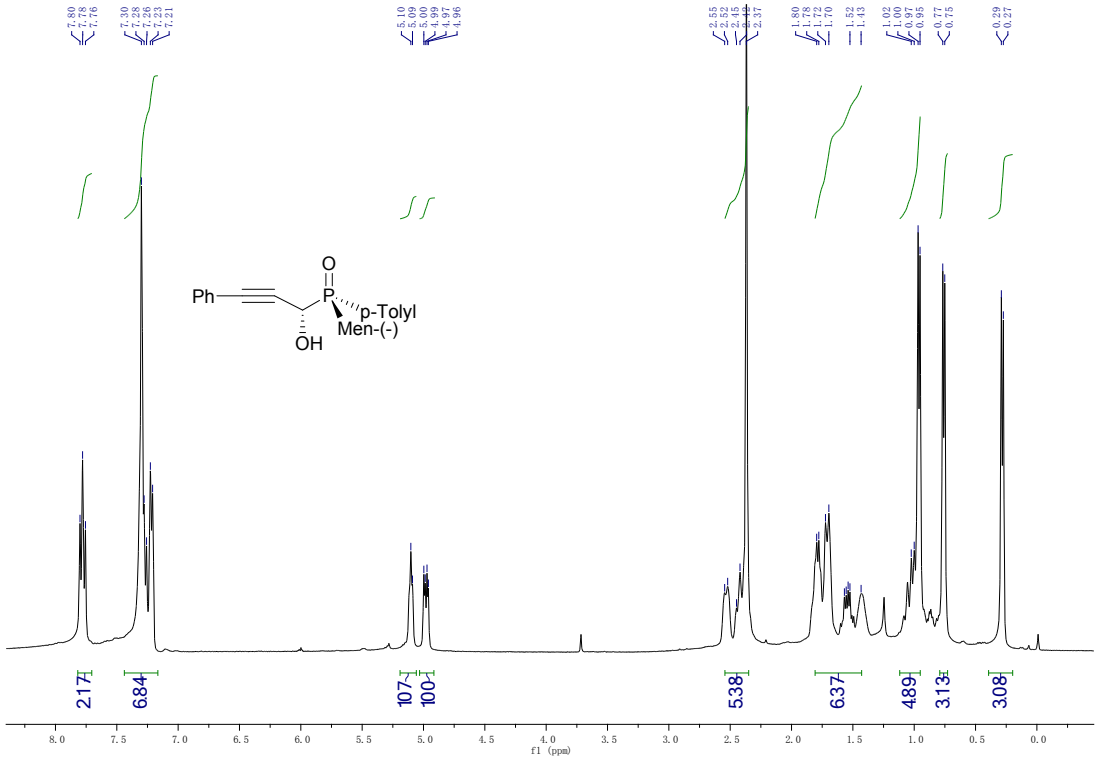
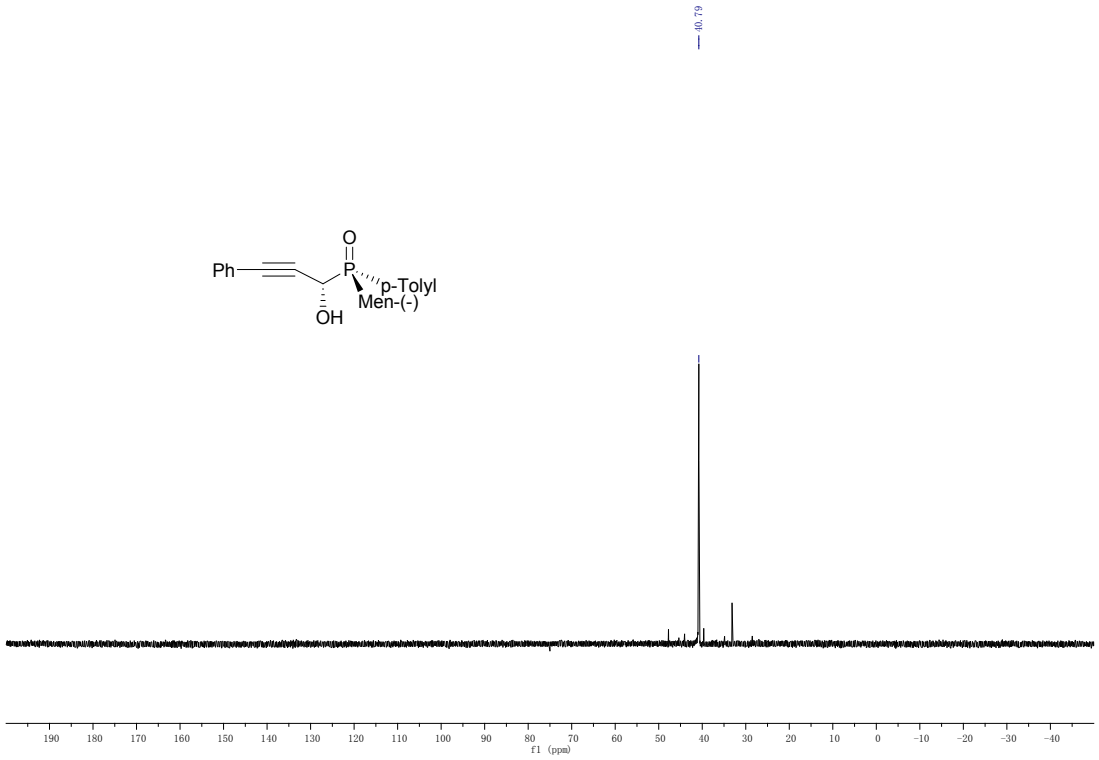
7.77
7.77
7.77
7.75
7.41
7.40
7.38
7.36
7.35
7.34
7.34
7.20
7.19
7.18
6.42
5.30
5.27
2.39
2.37
2.34
2.33
2.31
2.28
1.78
1.75
1.74
1.73
1.52
1.51
1.49
1.45
1.06
1.03
1.00
0.98
0.76
0.74
0.29
0.27
Ph
O
P
p-Tolyl
Men-(-)
OH
216
157
214
199
095
100
579
759
547
291
306
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

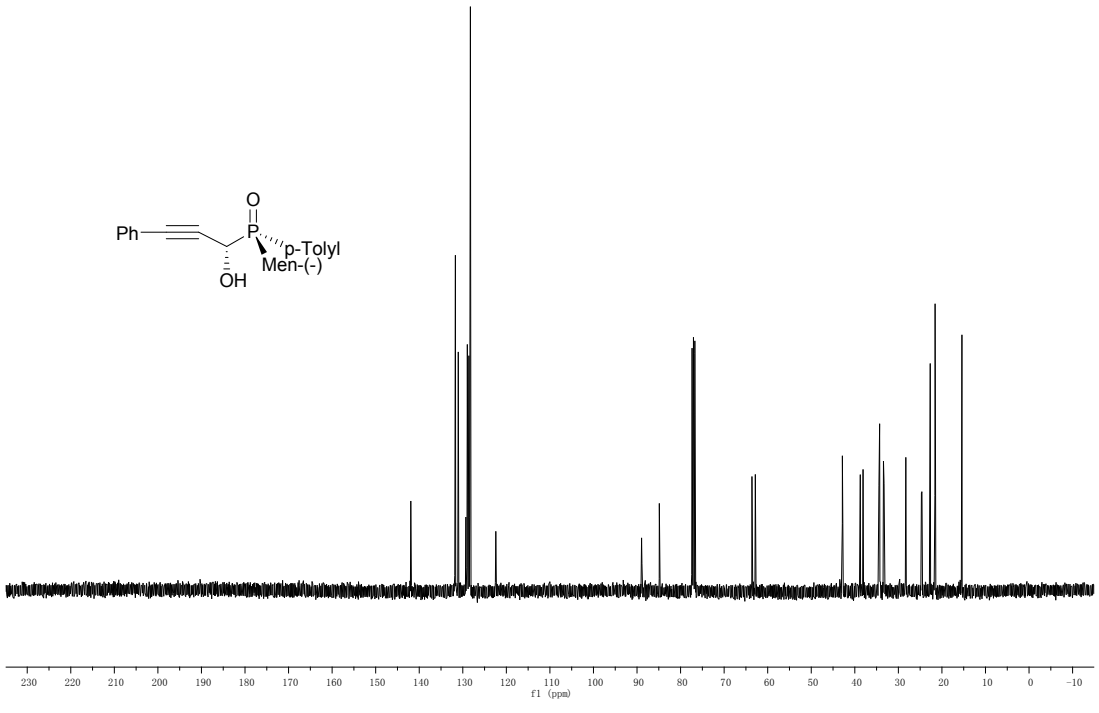

42.76
Ph
O
P
p-Tolyl
Men-(-)
OH
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)



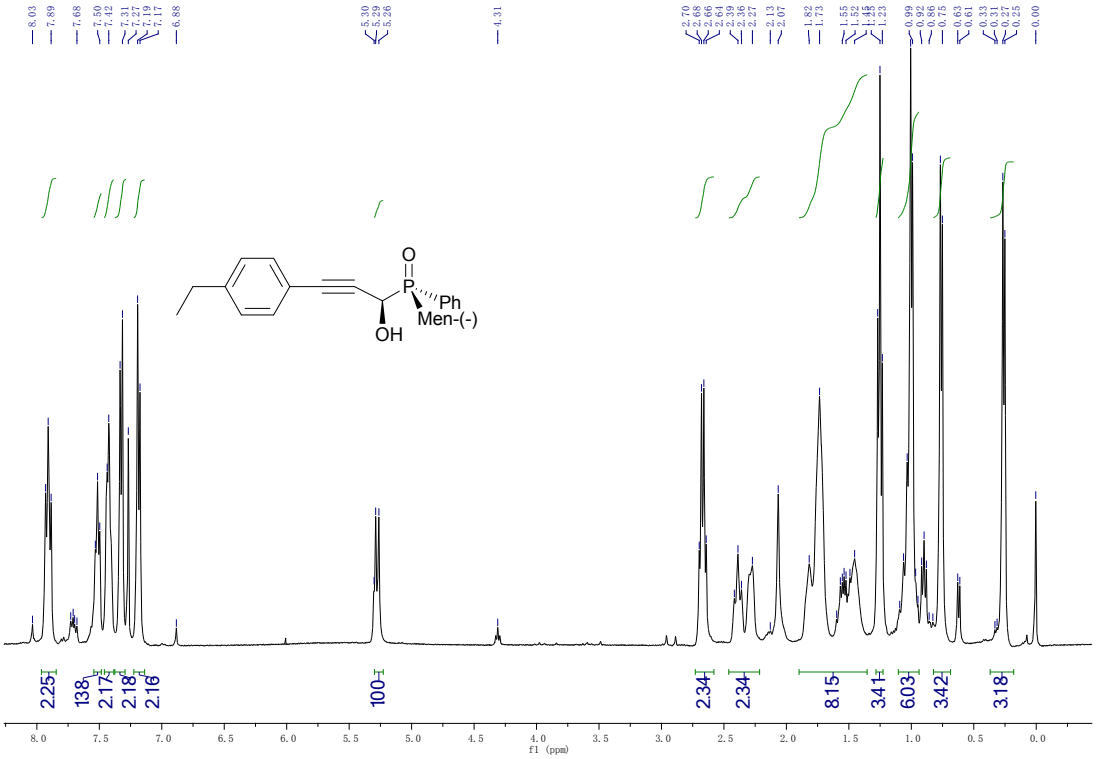
R_P,S_C-(*L*)-Menthyl (1-hydroxy-3-phenylprop-2-yn-1-yl) p-tolyl phosphine oxide (3ab')

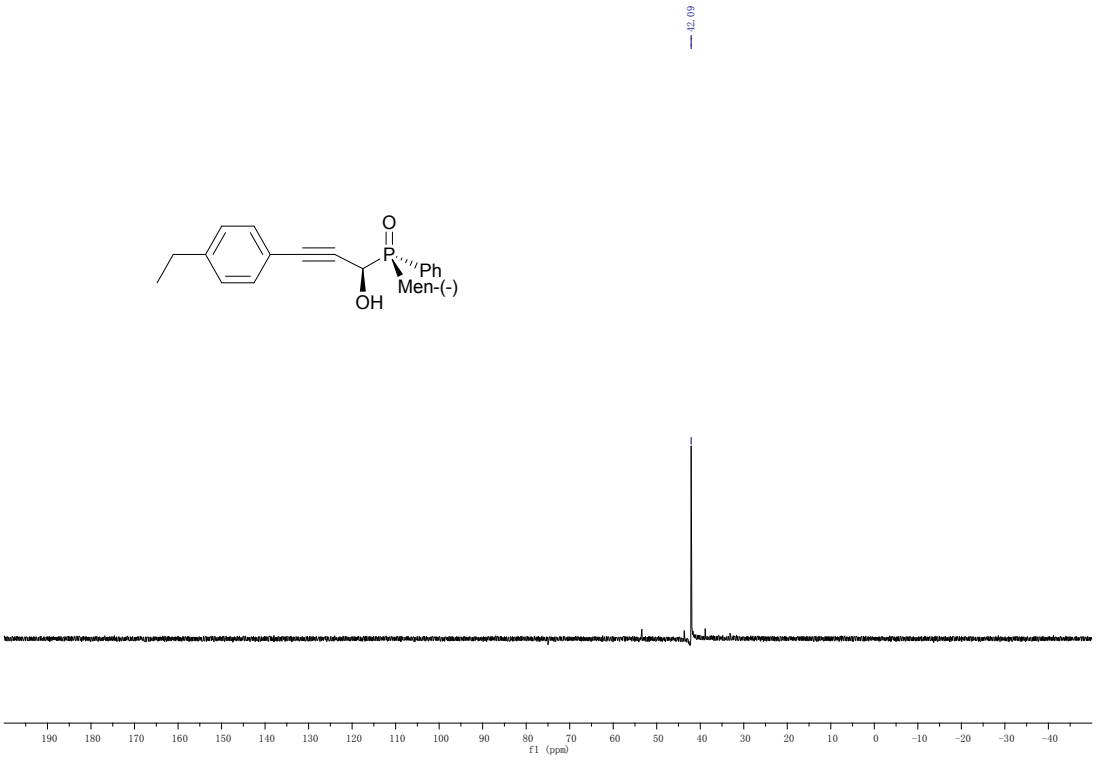


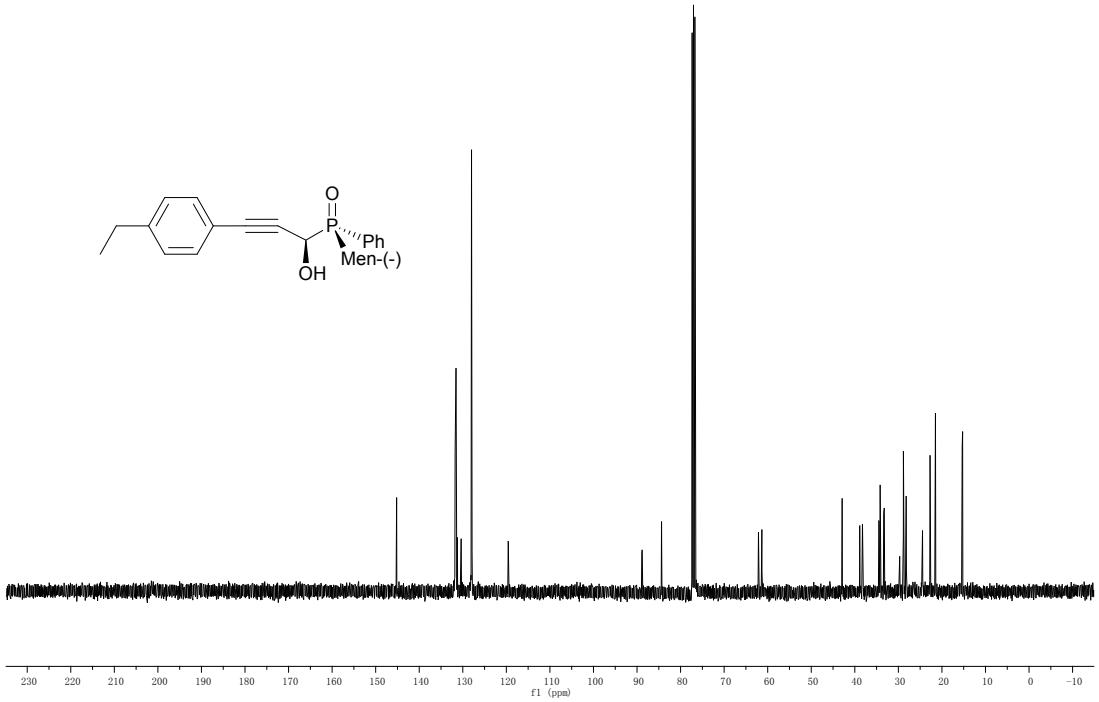




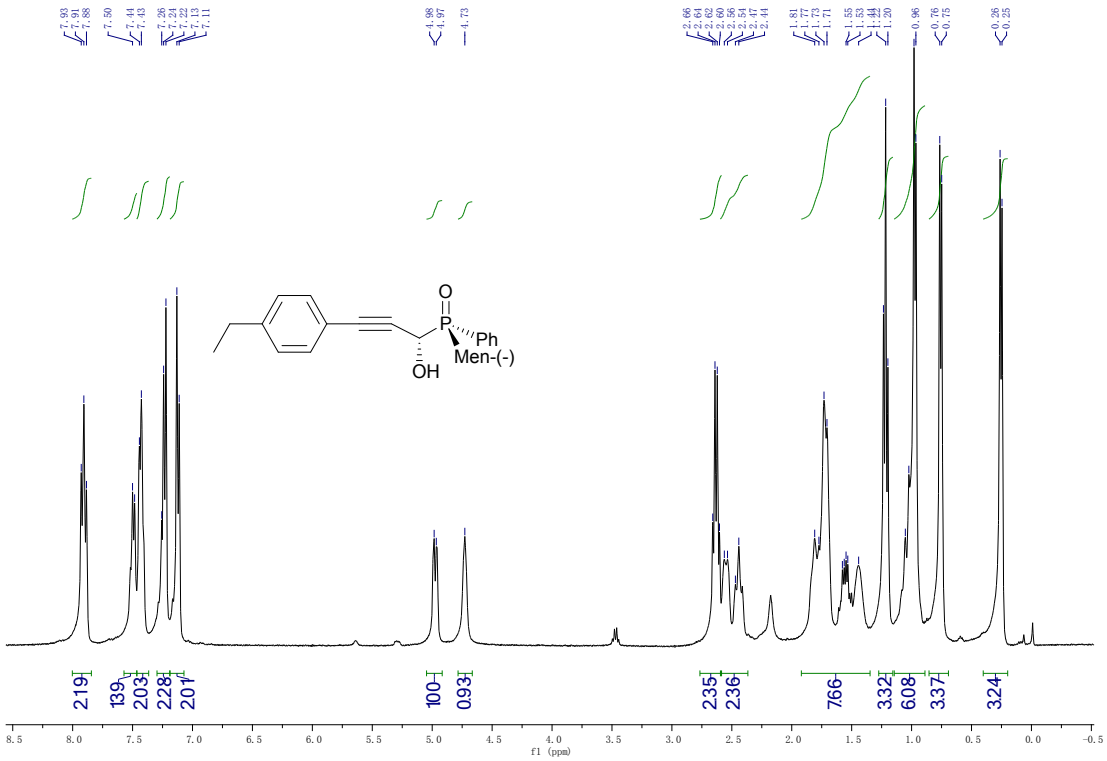
R_P,R_C-(*L*)-Menthyl (3-*p*-ethylphenyl-1-hydroxyprop-2-yn-1-yl) phenyl phosphine oxide (3ba)

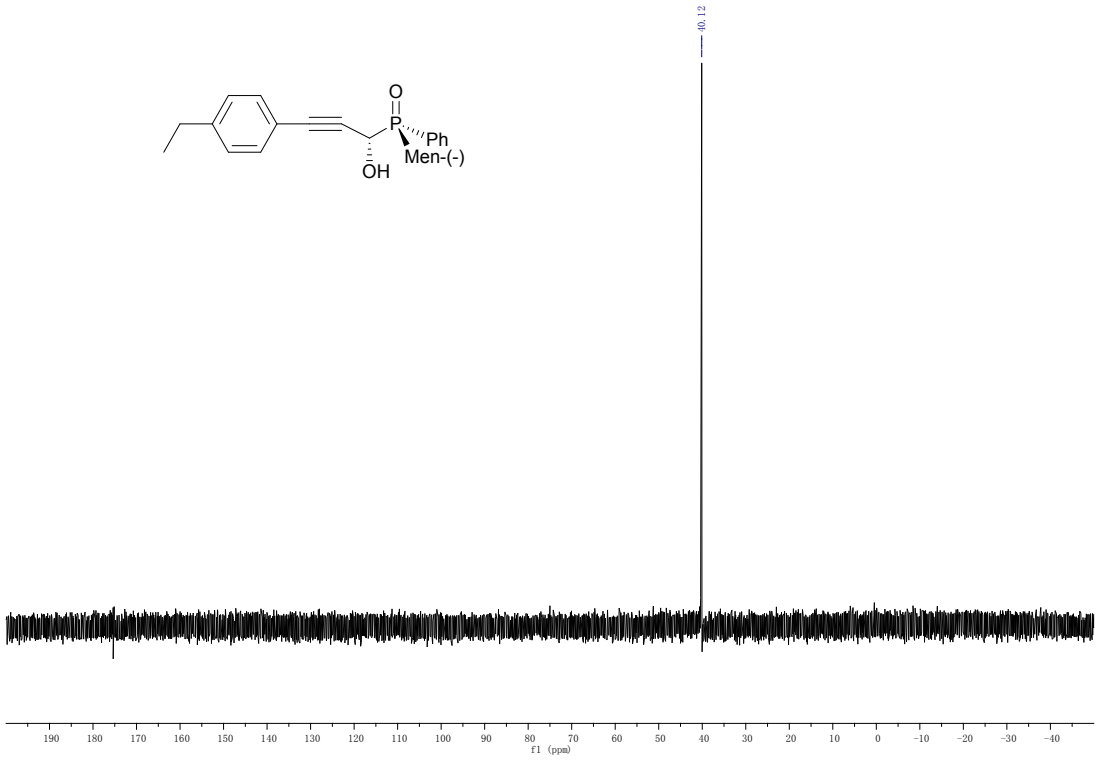

8.03
7.89
7.68
7.50
7.42
7.31
7.27
7.19
7.17
6.88
5.30
5.29
5.26
4.31
2.70
2.68
2.66
2.64
2.39
2.36
2.27
2.13
2.07
1.82
1.73
1.55
1.52
1.45
1.43
1.23
0.99
0.92
0.66
0.65
0.63
0.61
0.33
0.31
0.27
0.25
0.00
O
P
Ph
Men-(-)
OH
2.25
1.38
2.17
2.18
2.16
100
2.34
2.34
8.15
3.41
6.03
3.42
3.18
f1 (ppm)

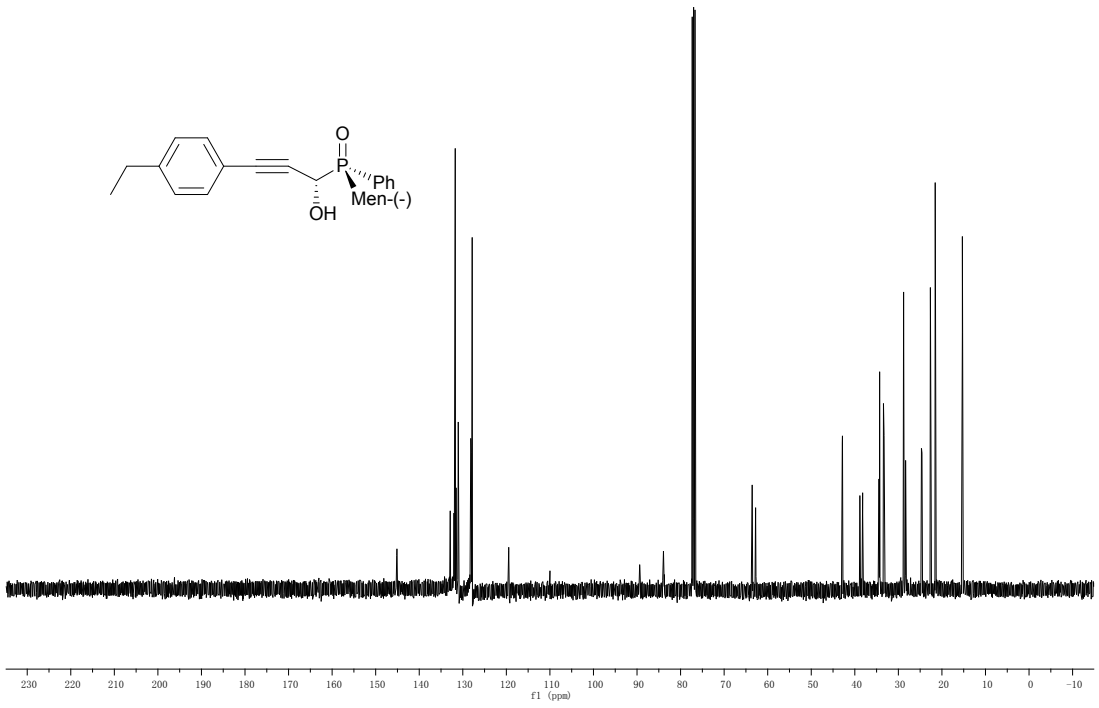

42.09
O
P
Ph
Men-(-)
OH
f1 (ppm)



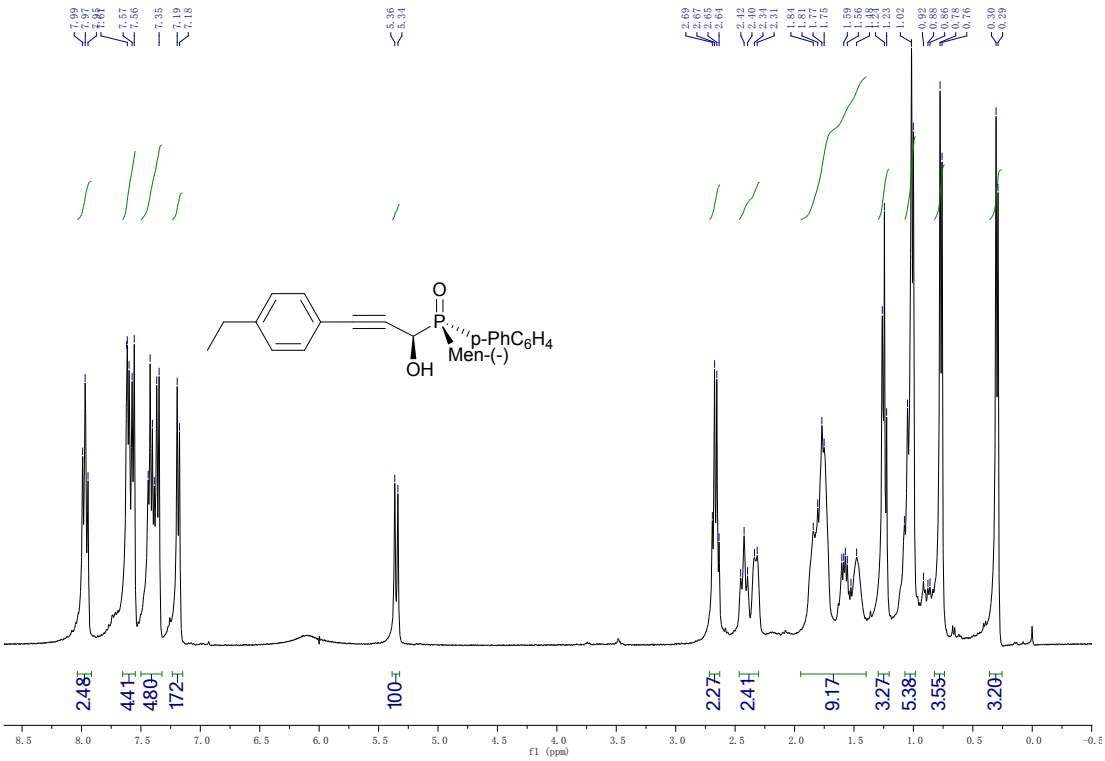
R_P,S_C-(*L*)-Menthyl (3-*p*-ethylphenyl-1-hydroxyprop-2-yn-1-yl) phenyl phosphine oxide (3ba')







R_P,R_C-(*L*)-Menthyl (3-*p*-ethylphenyl-1-hydroxyprop-2-yn-1-yl)(1,1'-biphenyl)-4-yl phosphine oxide (3bc)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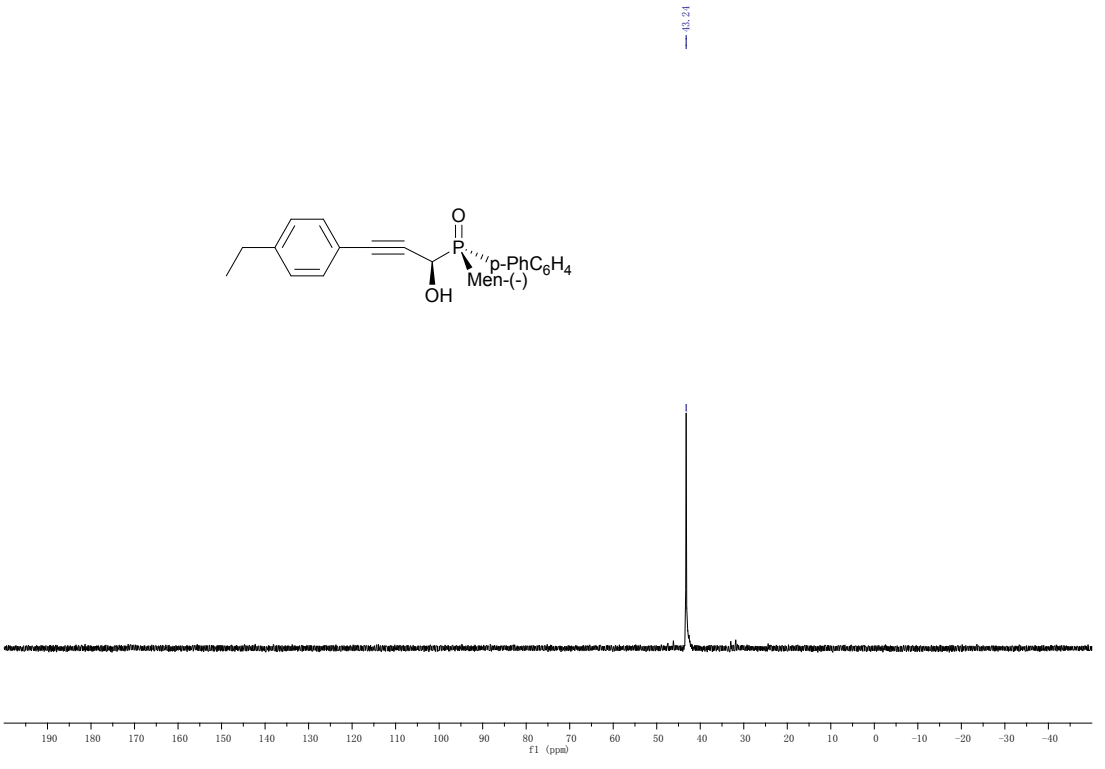
7.97
7.88
7.86
7.57
7.56
7.35
7.19
7.18
5.36
5.34
2.69
2.67
2.65
2.64
2.42
2.40
2.31
1.84
1.81
1.77
1.75
1.59
1.56
1.48
1.44
1.23
1.02
0.92
0.88
0.86
0.76
0.30
0.29
O
P
p-PhC6H4
Men-(-)
OH
2.48
4.41
4.80
1.72
1.00
2.27
2.41
9.17
3.27
5.38
3.55
3.20
f1 (ppm)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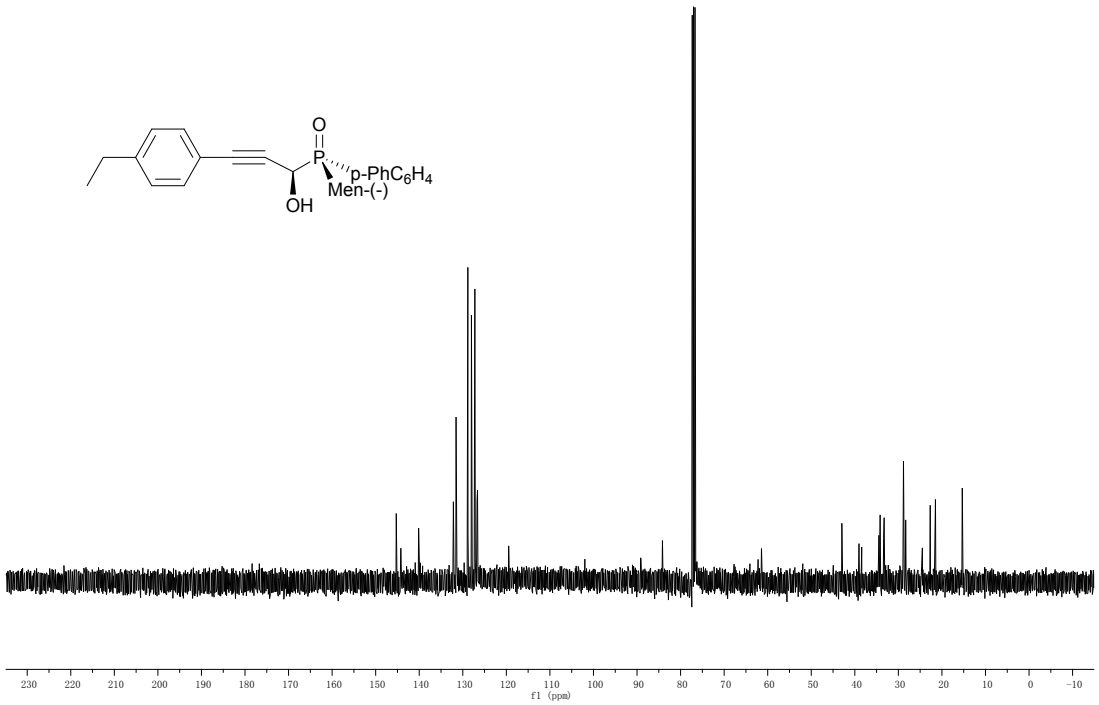
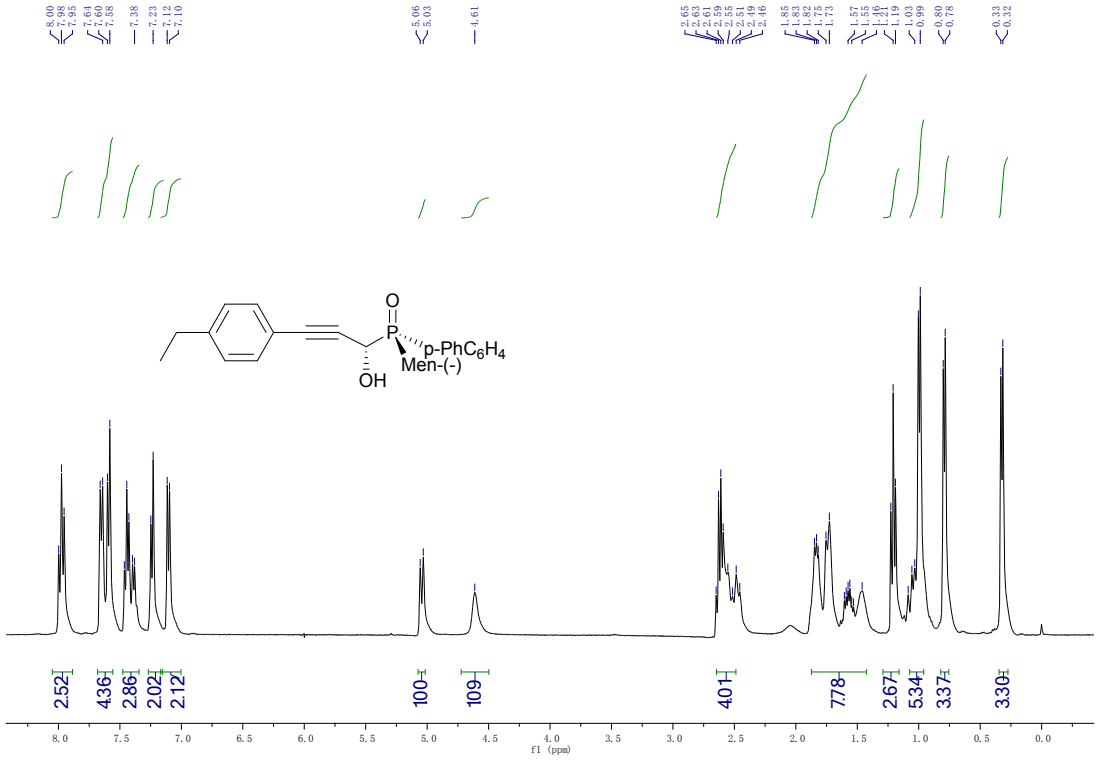
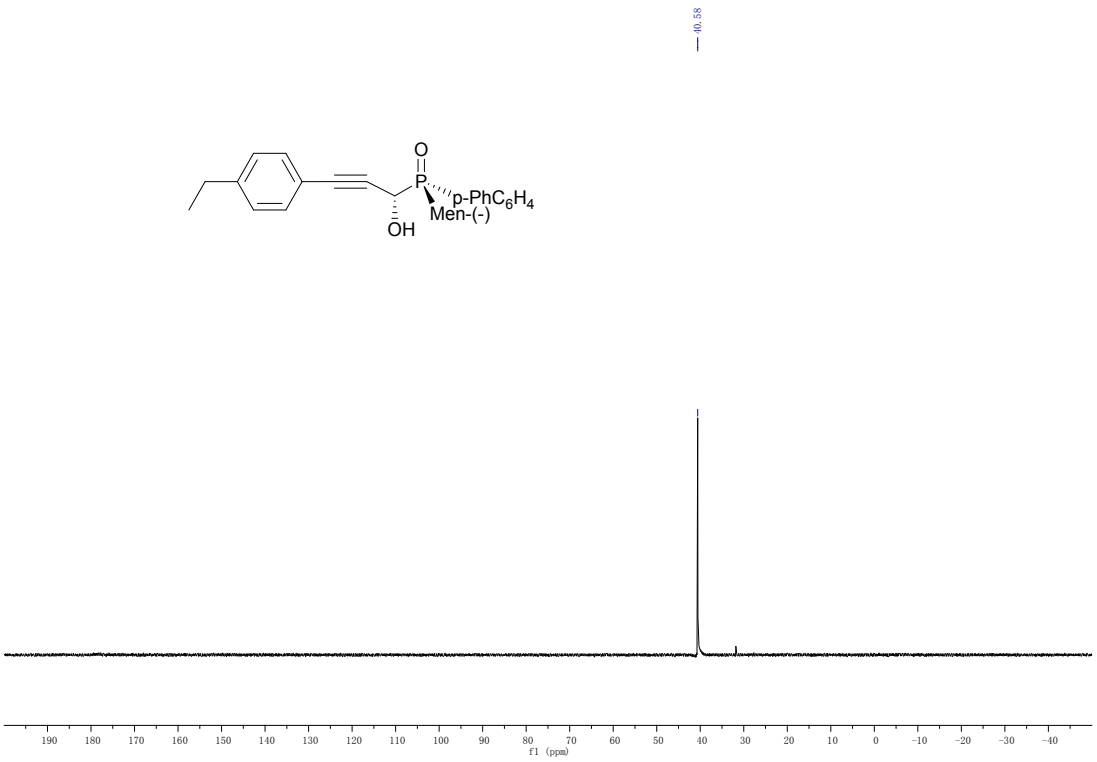
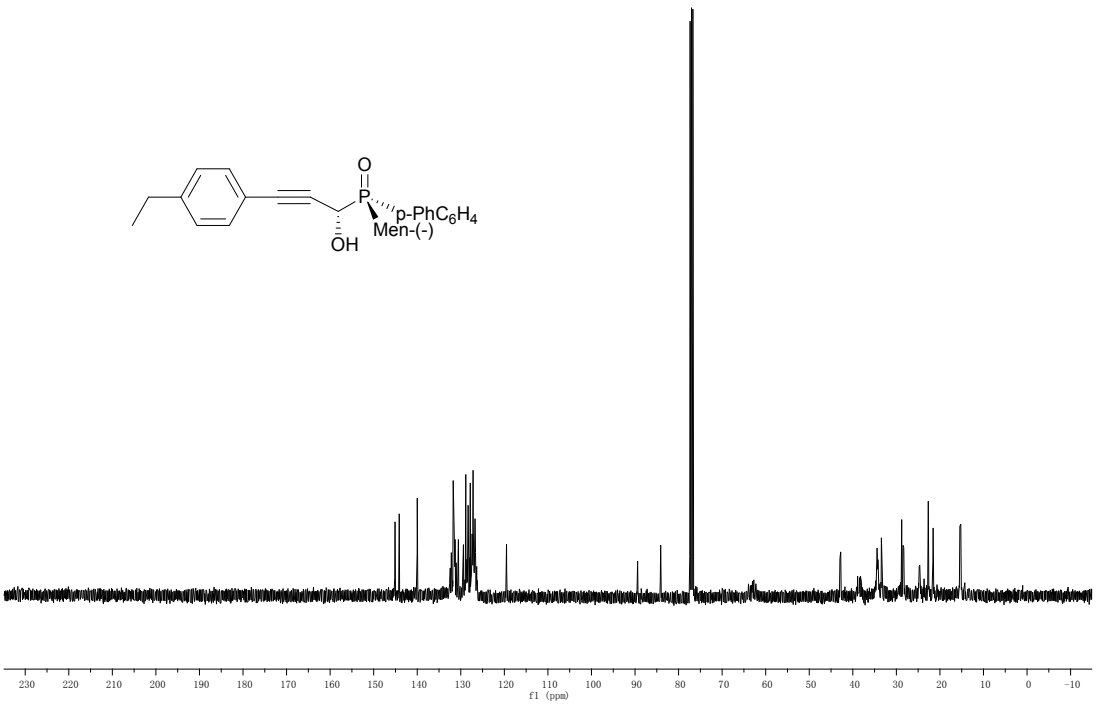
O
P
p-PhC6H4
Men-(-)
OH
f1 (ppm)



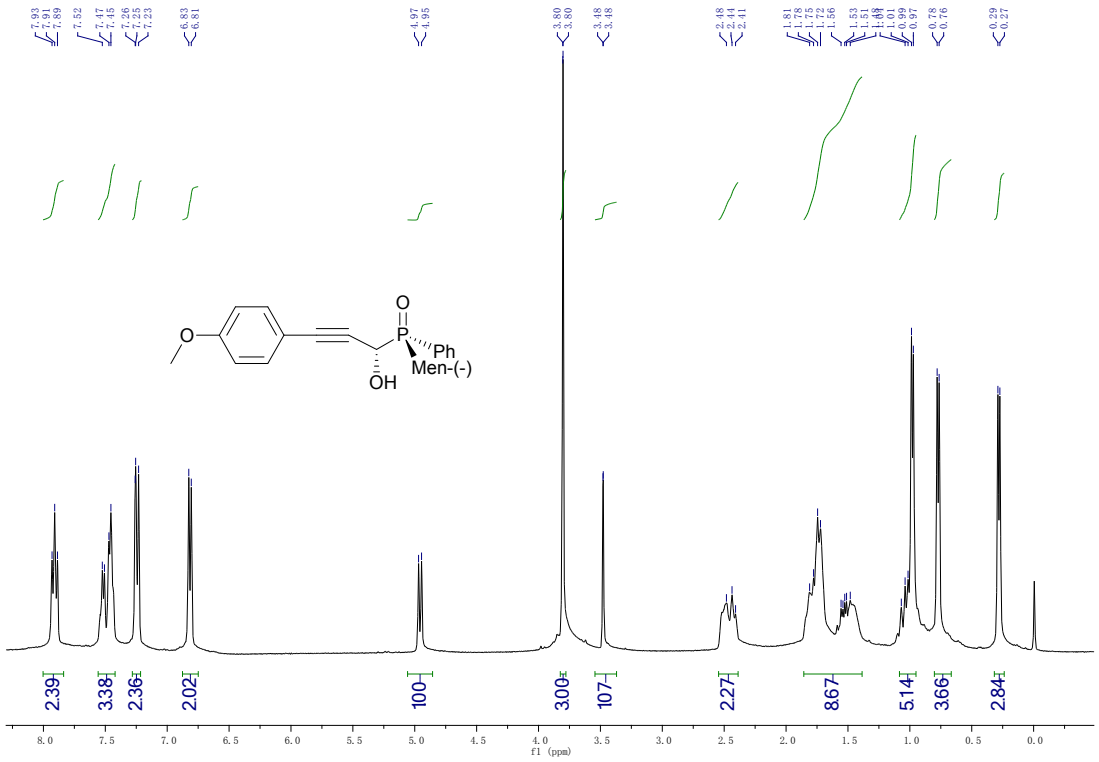
R_P,S_C-(*L*)-Menthyl (3-*p*-ethylphenyl-1-hydroxyprop-2-yn-1-yl)(1,1'-biphenyl)-4-yl phosphine oxide (3bc')

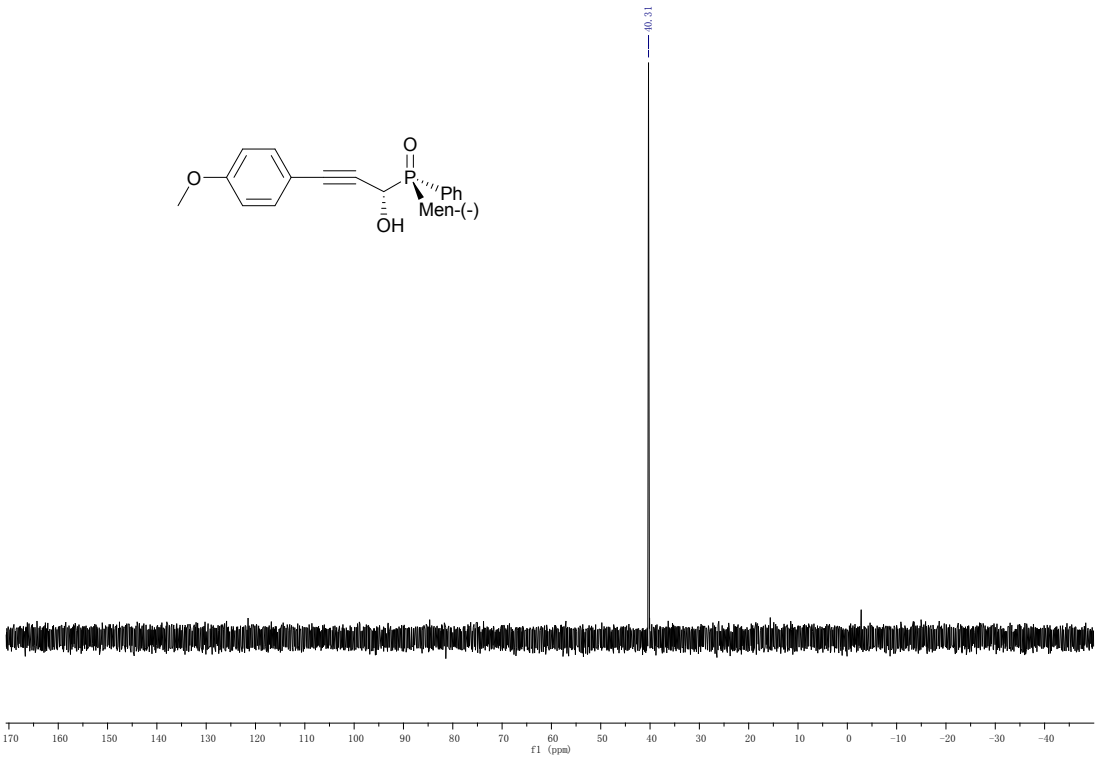


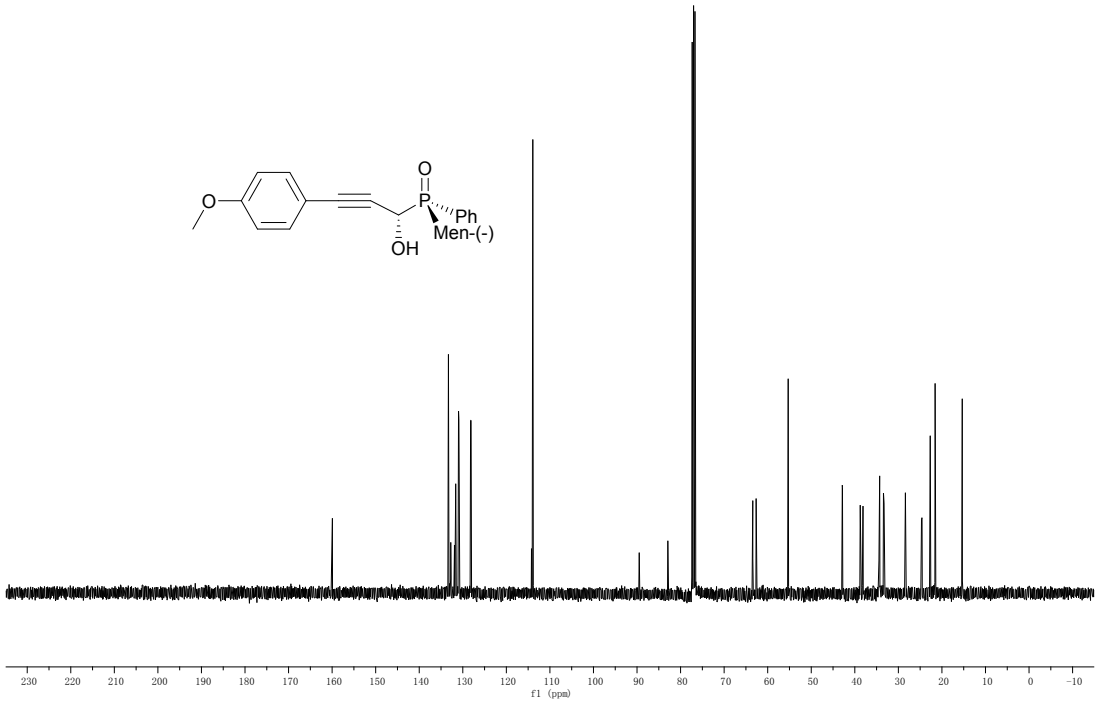




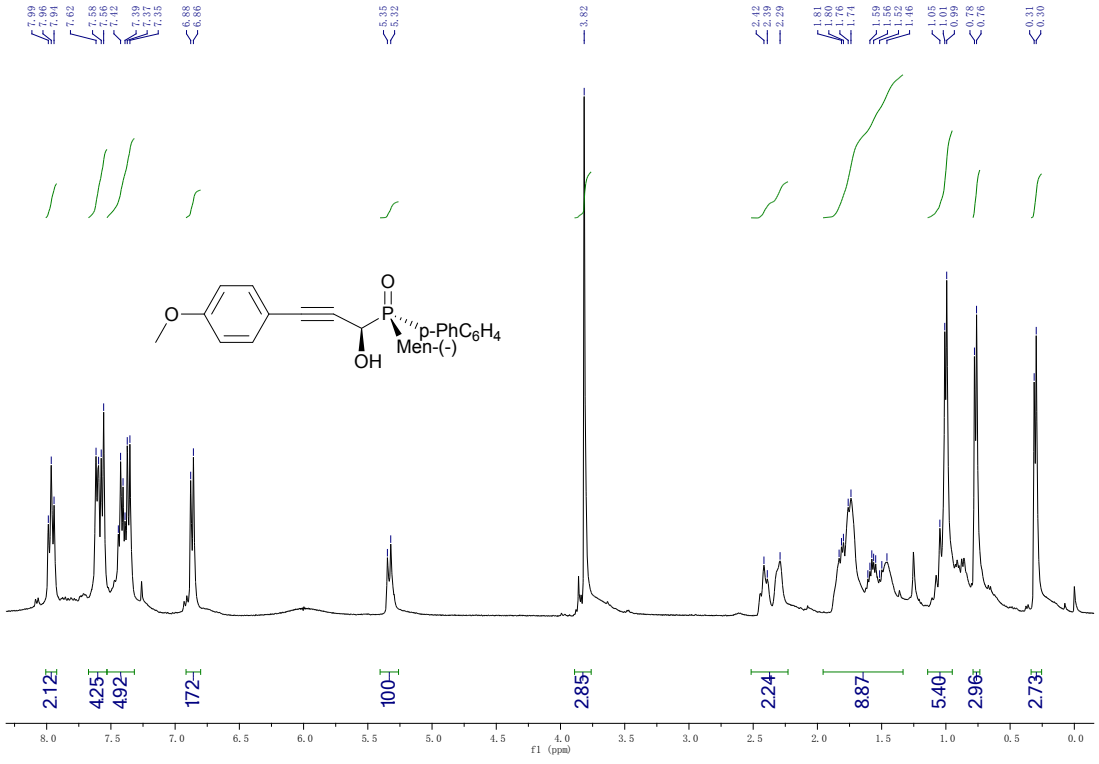
R_P,S_C-(*L*)-Menthyl (1-hydroxy-3-*p*-methoxyphenylprop-2-yn-1-yl) phenyl phosphine oxide (3ca')

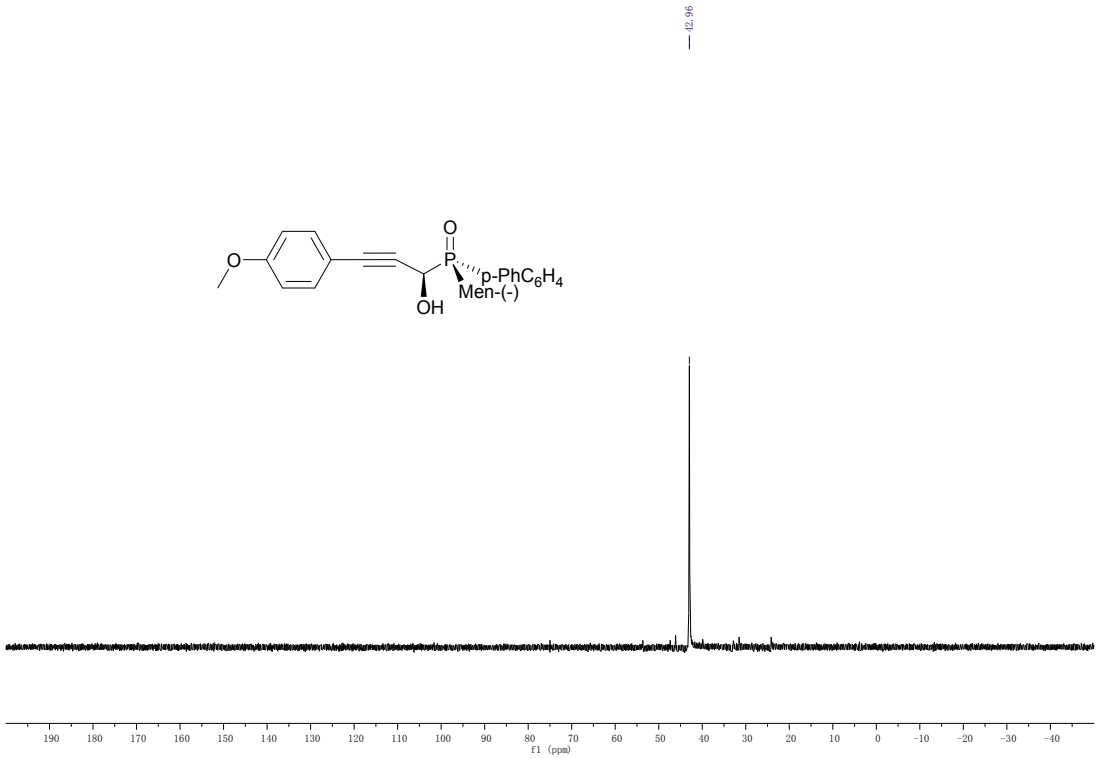

7.93
7.91
7.89
7.52
7.47
7.45
7.26
7.25
7.23
6.83
6.81
4.97
4.95
3.80
3.80
3.48
3.48
2.48
2.44
2.41
1.81
1.78
1.75
1.72
1.56
1.53
1.51
1.04
1.01
0.99
0.97
0.78
0.76
0.29
0.27
O
O
P
Ph
Men-(-)
OH
2.39
3.38
2.36
2.02
100
300
107
2.27
8.67
5.14
3.66
2.84
f1 (ppm)

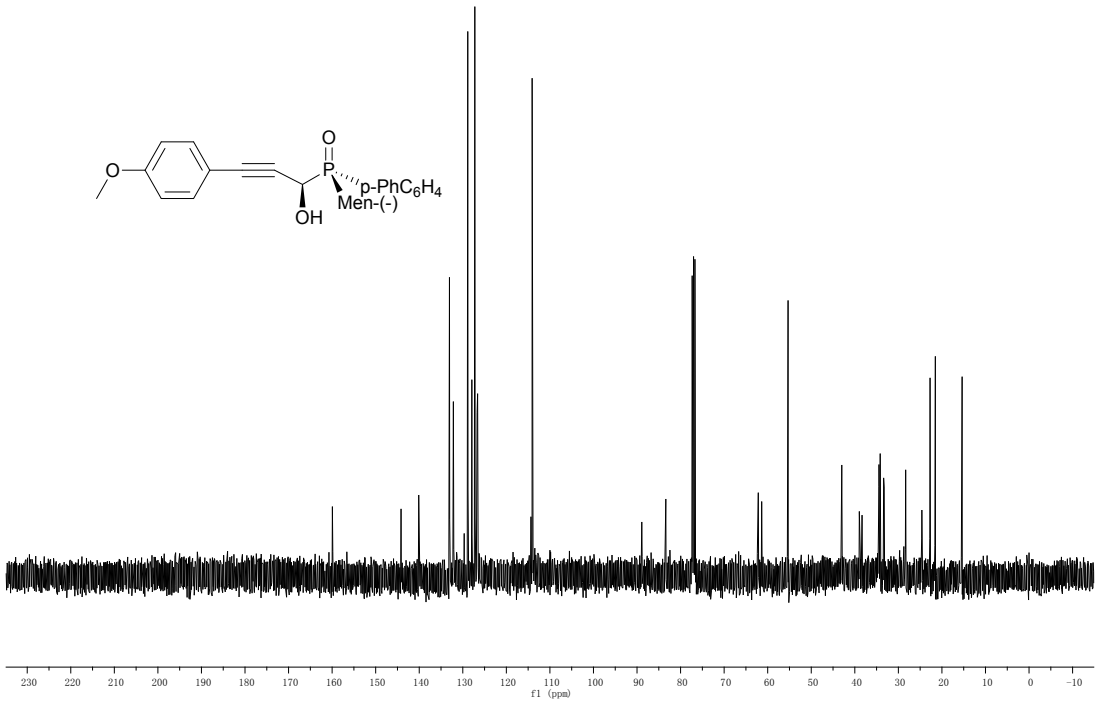

40.31
O
O
P
Ph
Men-(-)
OH
f1 (ppm)



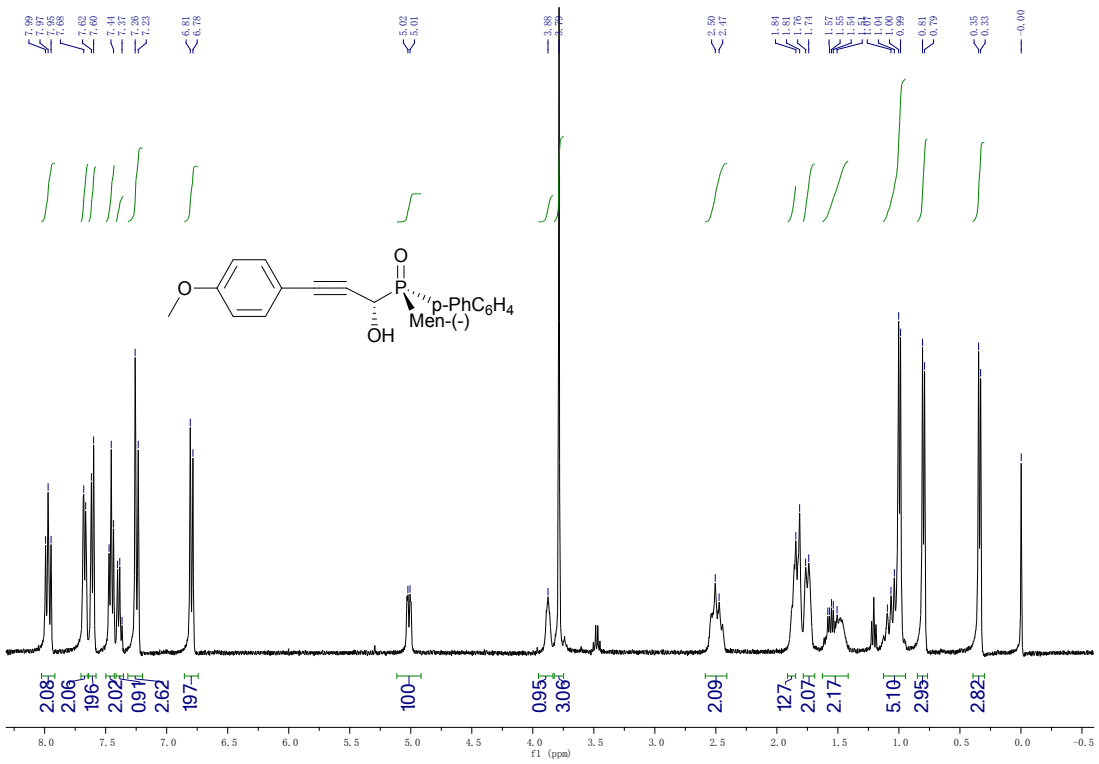
R_P,R_C-(*L*)-Menthyl (1-hydroxy-3-*p*-methoxyphenylprop-2-yn-1-yl)(1,1'-biphenyl)-4-yl phosphine oxide (3cc)

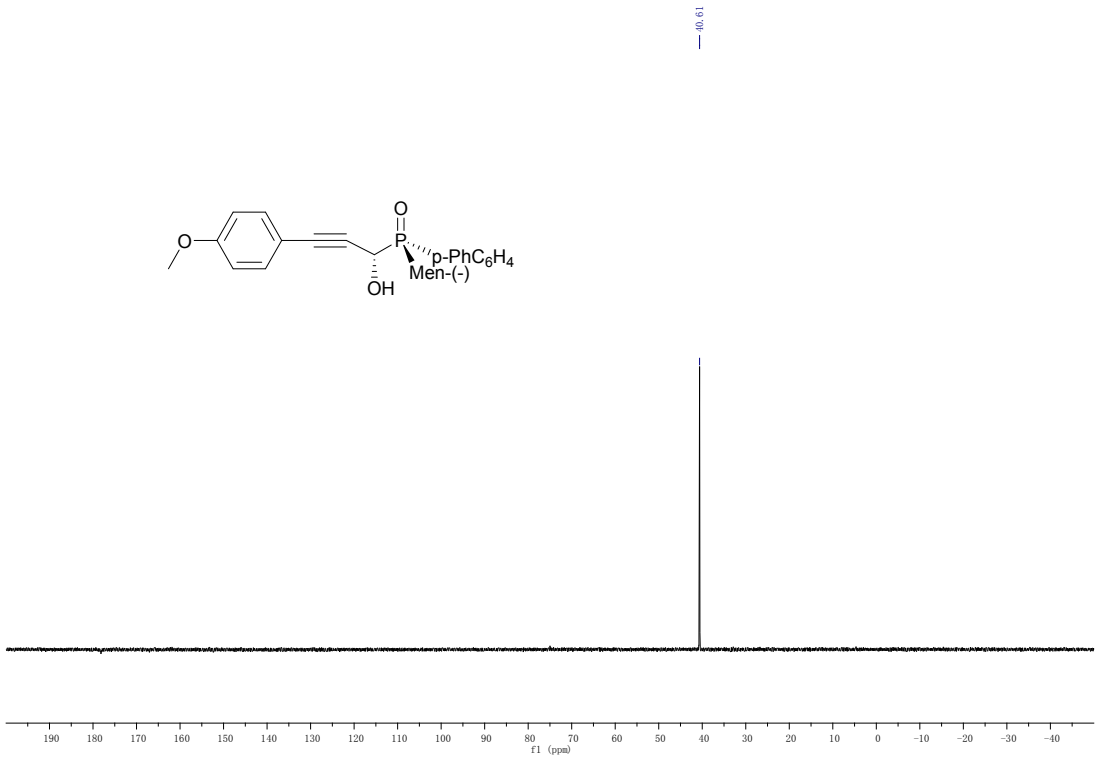


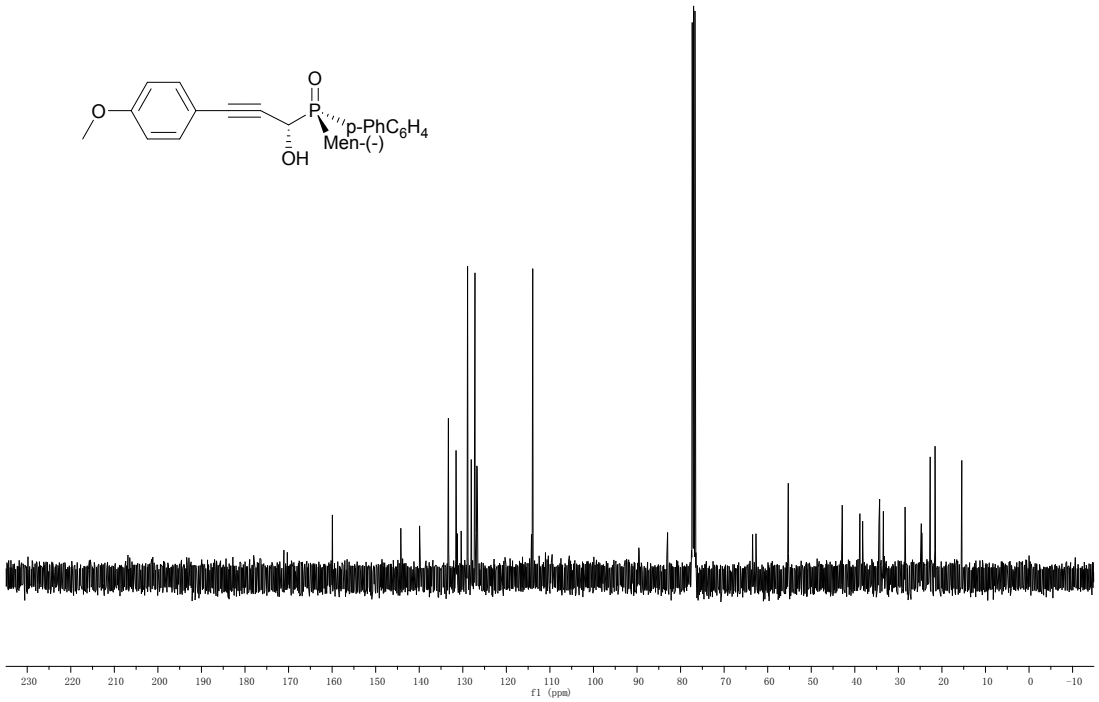




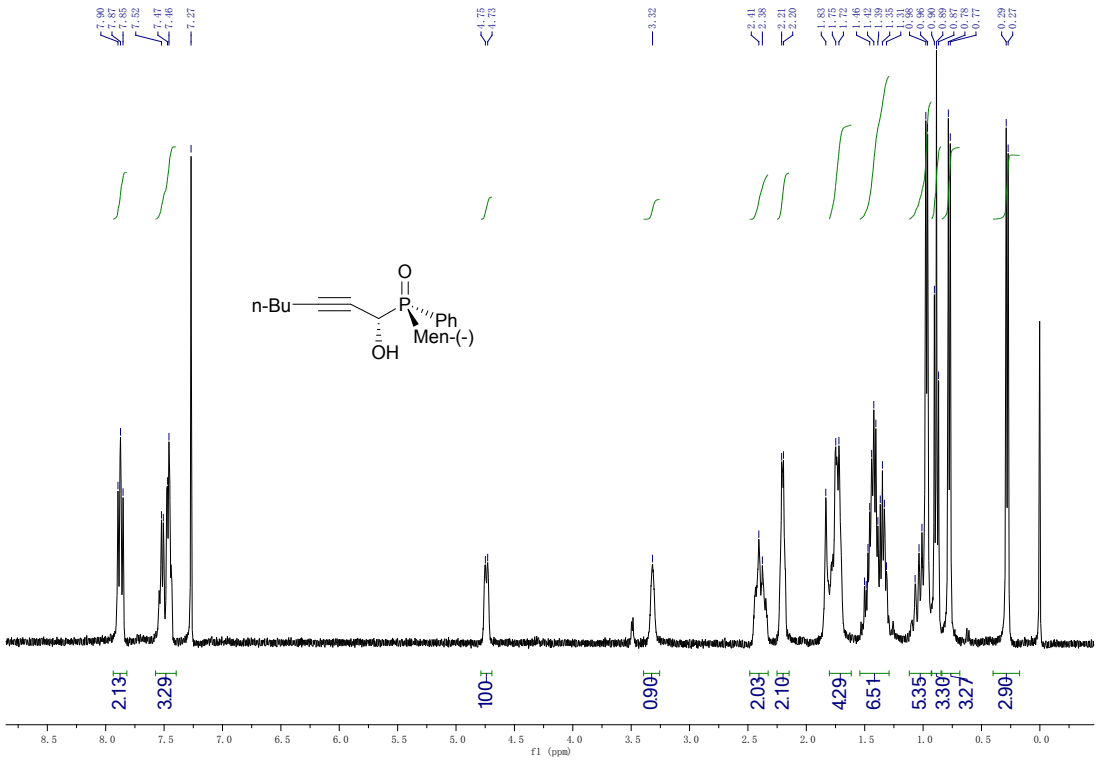
R_P,S_C-(*L*)-Menthyl (1-hydroxy-3-*p*-methoxyphenylprop-2-yn-1-yl)(1,1'-biphenyl)-4-yl phosphine oxide (3cc')

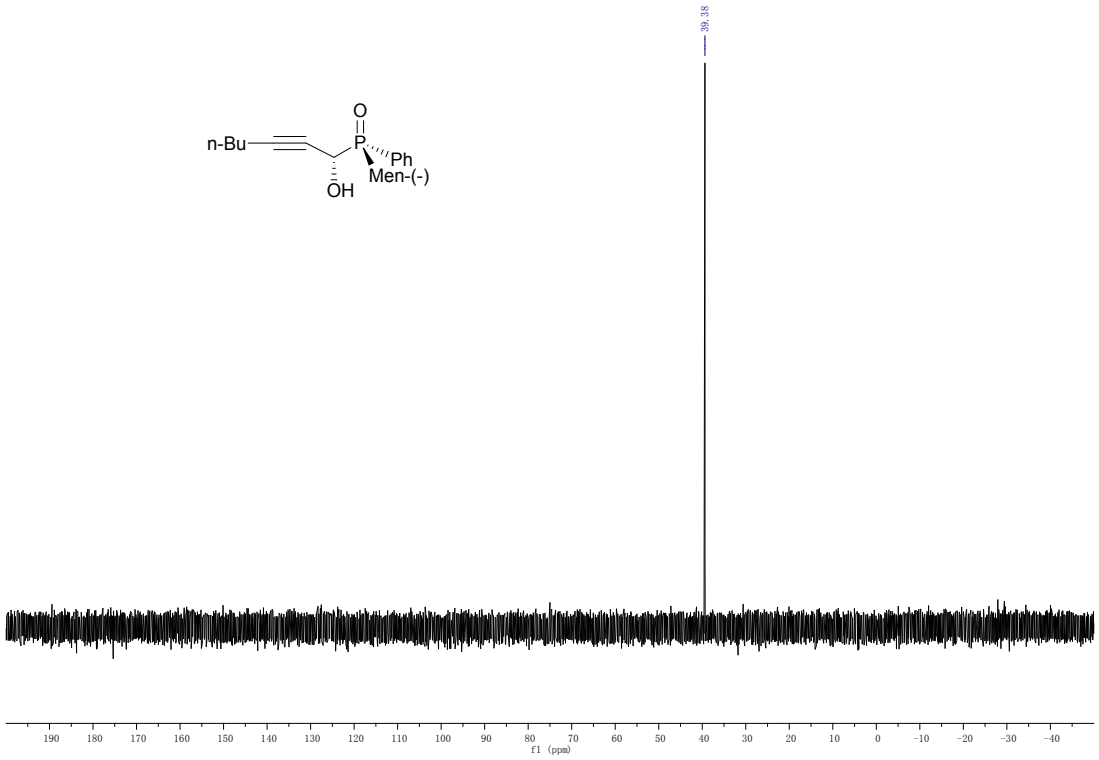

7.99
7.97
7.95
7.68
7.66
7.62
7.60
7.44
7.37
7.35
7.23
6.81
6.78
5.02
5.01
3.88
3.79
2.50
2.47
1.84
1.81
1.76
1.74
1.57
1.55
1.54
1.51
1.07
1.04
1.00
0.99
0.81
0.79
0.35
0.33
-0.00
O
O
P
p-PhC6H4
Men-(-)
OH
2.08
2.06
1.96
2.02
0.91
2.62
1.97
1.00
0.95
3.06
2.09
1.27
2.07
2.17
5.10
2.95
2.82
f1 (ppm)

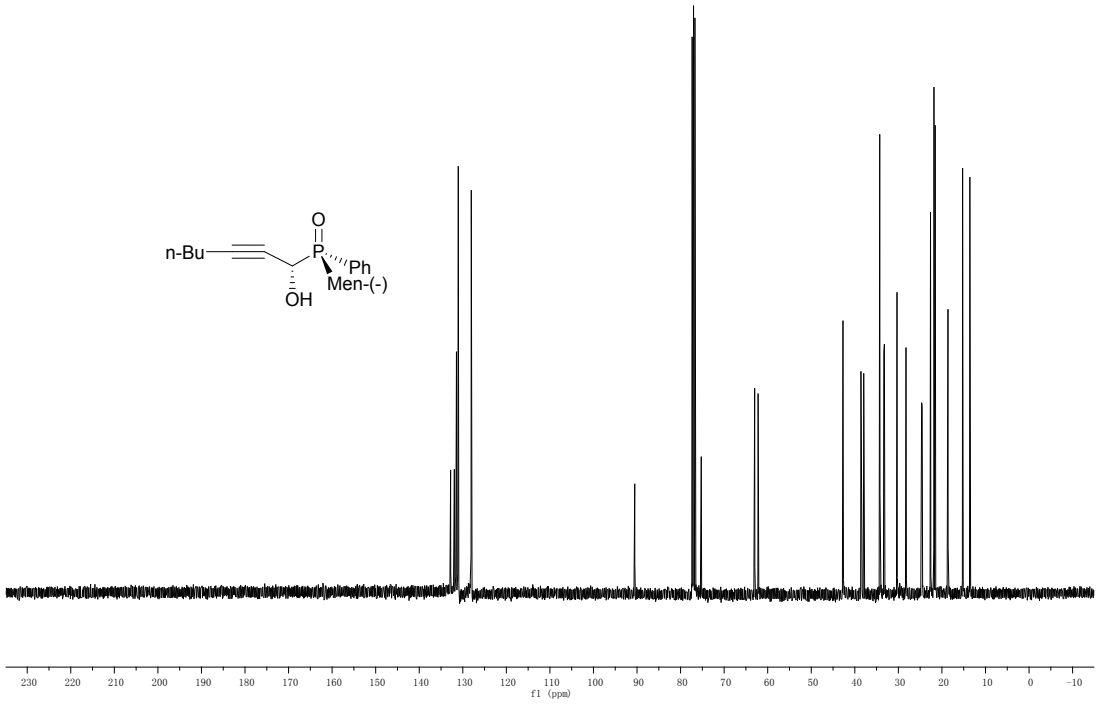

40.61
O
O
P
p-PhC6H4
Men-(-)
OH
f1 (ppm)



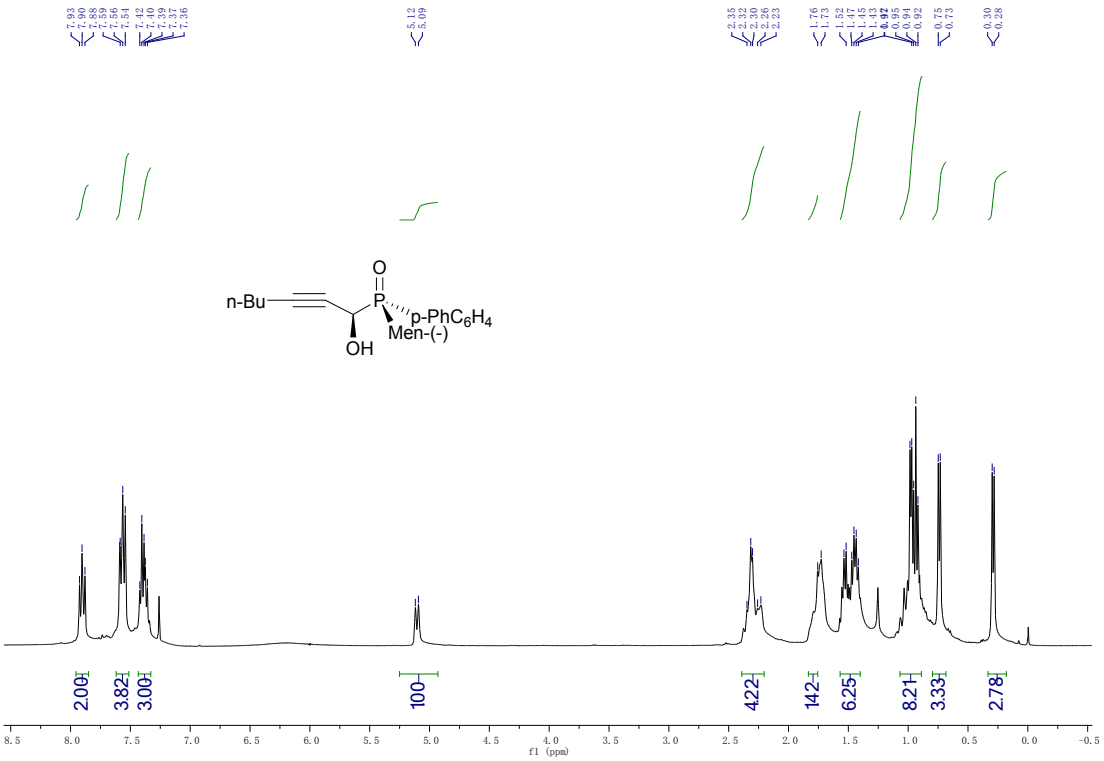
R_P,S_C-(*L*)-Menthyl (1-hydroxyhept-2-yn-1-yl) phenyl phosphine oxide (3da')

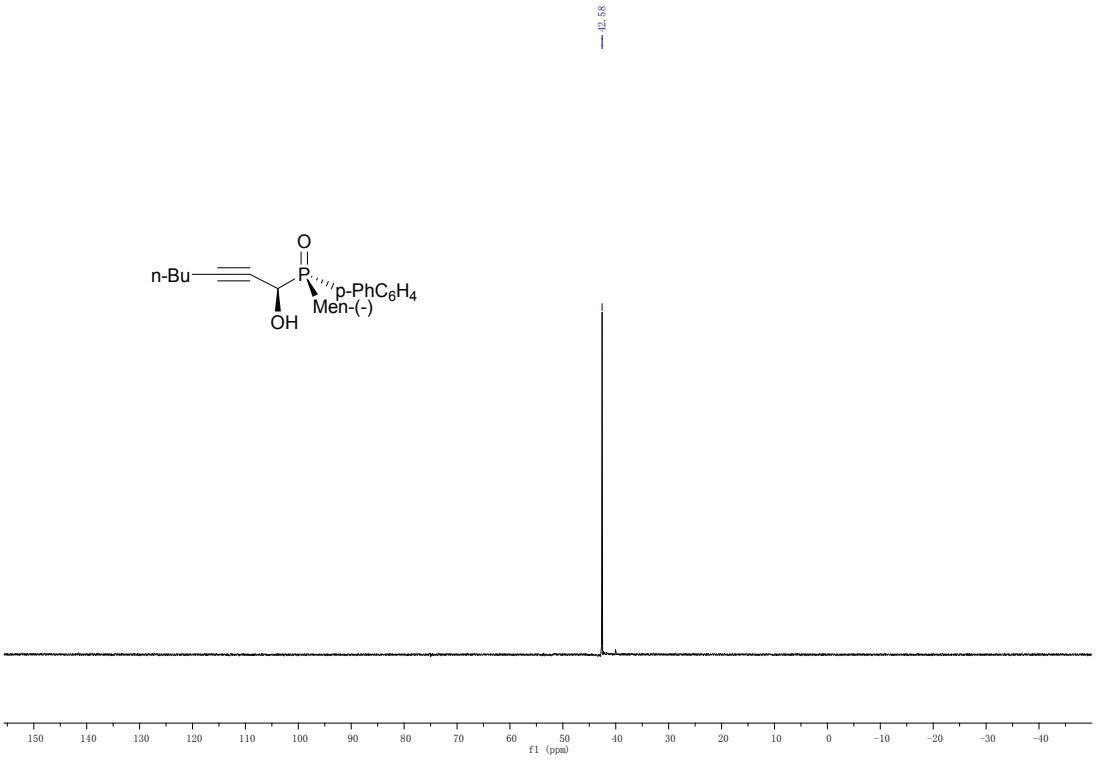


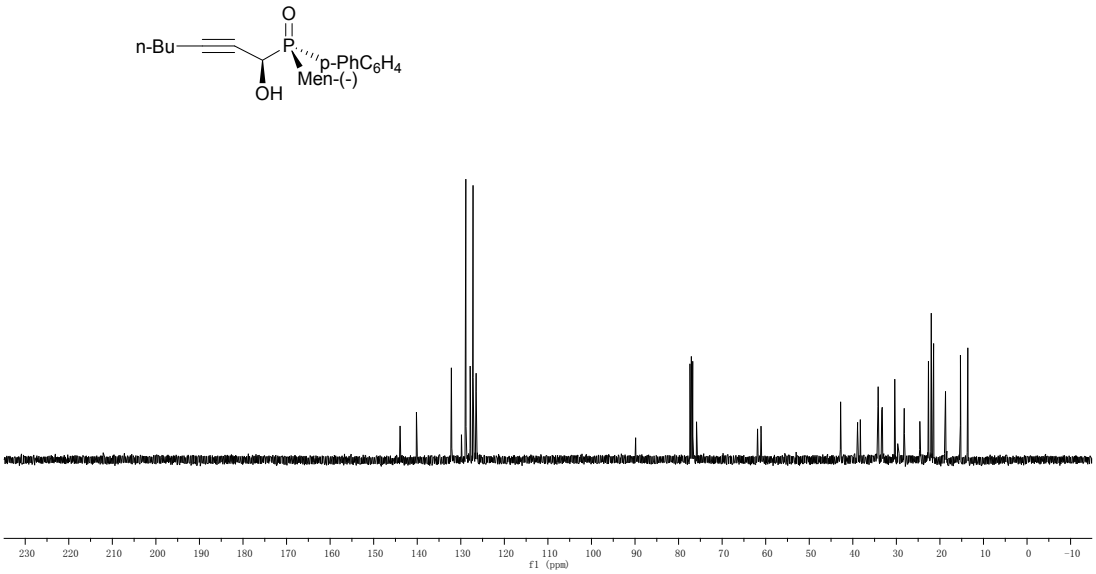




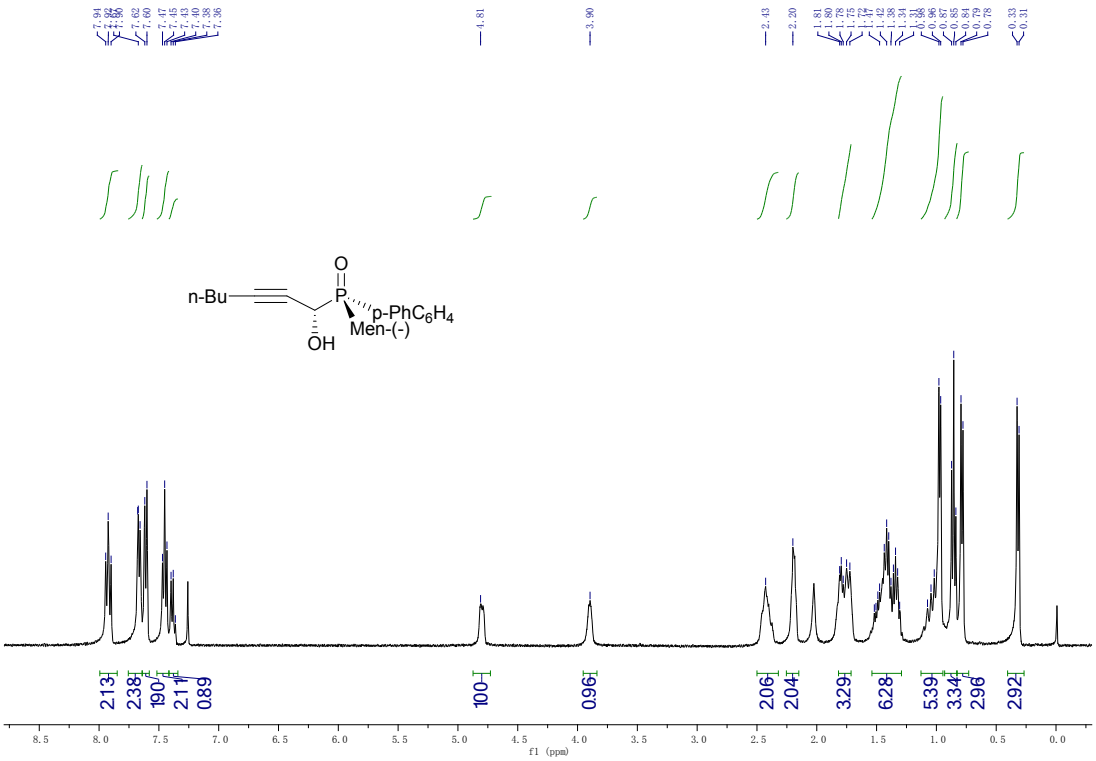
R_P,R_C-(*L*)-Menthyl (1-hydroxyhept-2-yn-1-yl)(1,1'-biphenyl)-4-yl phosphine oxide (3dc)

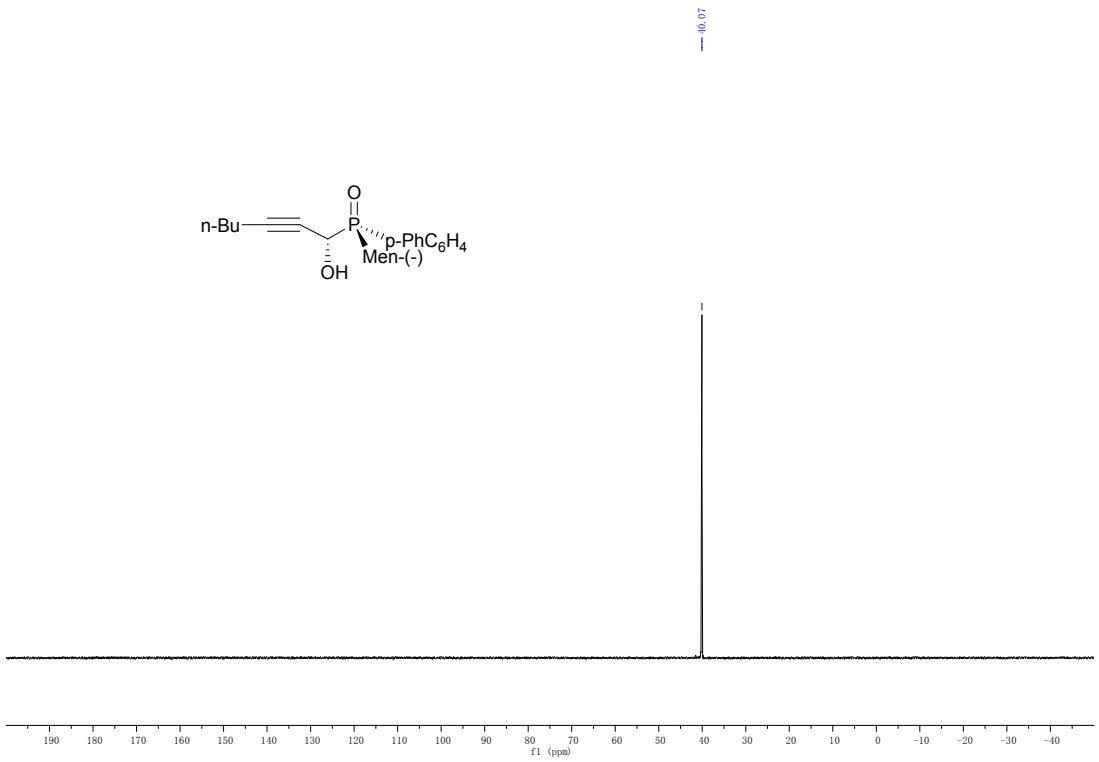

7.93
7.90
7.88
7.59
7.56
7.54
7.42
7.40
7.39
7.37
7.36
5.12
5.09
2.35
2.32
2.30
2.26
2.23
1.76
1.73
1.52
1.47
1.45
1.43
0.97
0.95
0.94
0.92
0.75
0.73
0.30
0.28
n-Bu
O
P
p-PhC6H4
Men-(-)
OH
2.00
3.82
3.00
100
4.22
1.42
6.25
8.21
3.33
2.78
f1 (ppm)

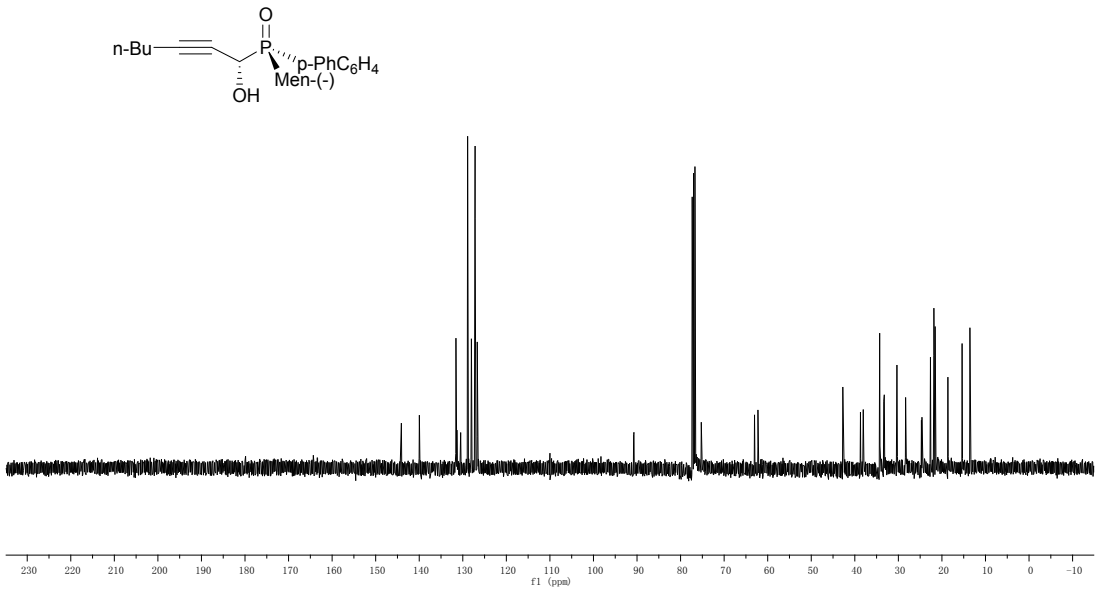

42.58
n-Bu
O
P
p-PhC6H4
Men-(-)
OH
f1 (ppm)



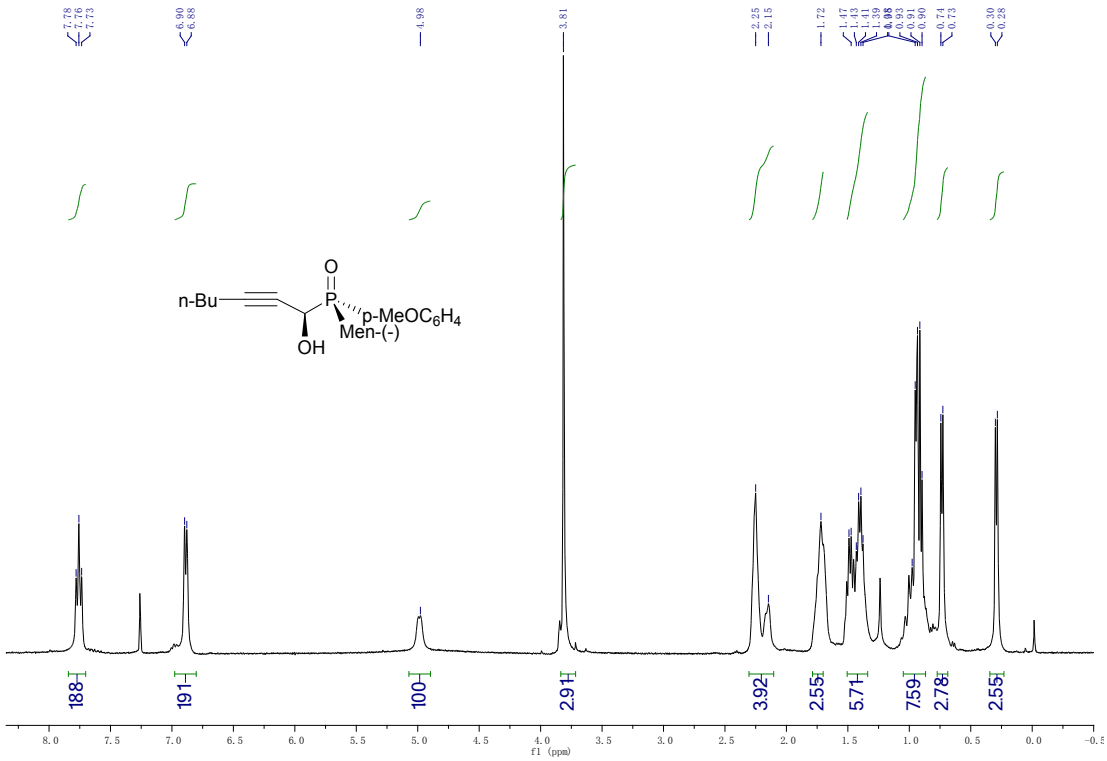
R_P,R_C-(*L*)-Menthyl (1-hydroxyhept-2-yn-1-yl)(1,1'-biphenyl)-4-yl phosphine oxide (3dc')

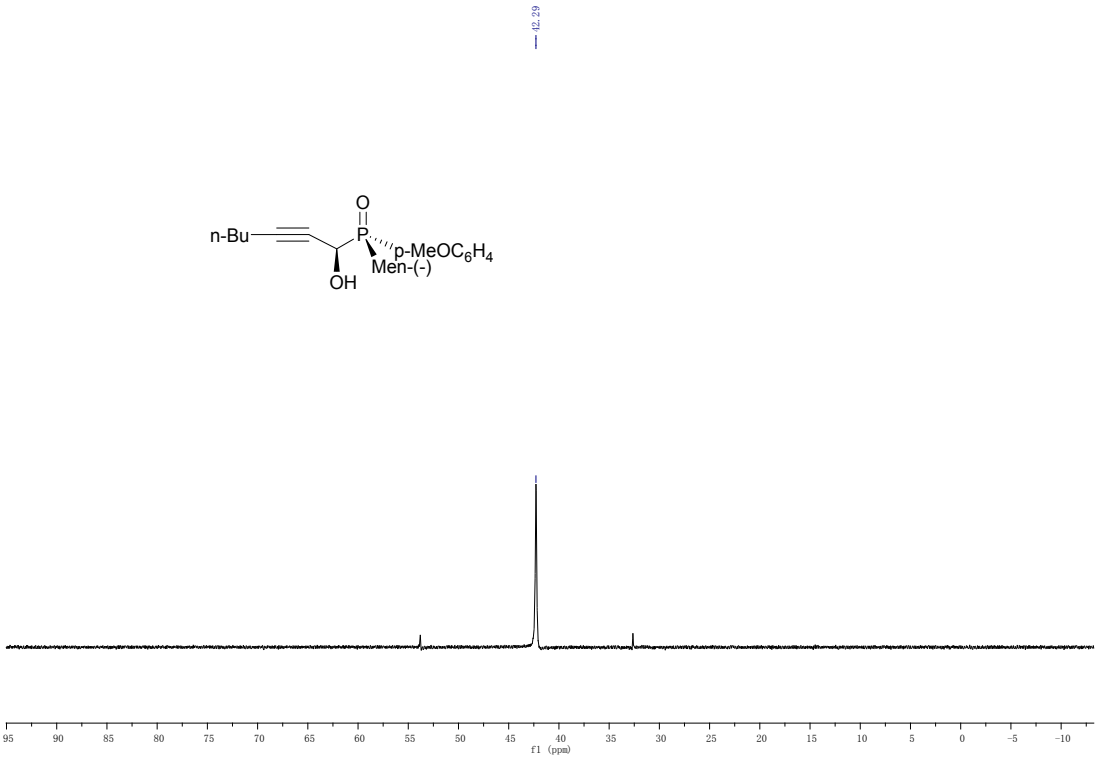


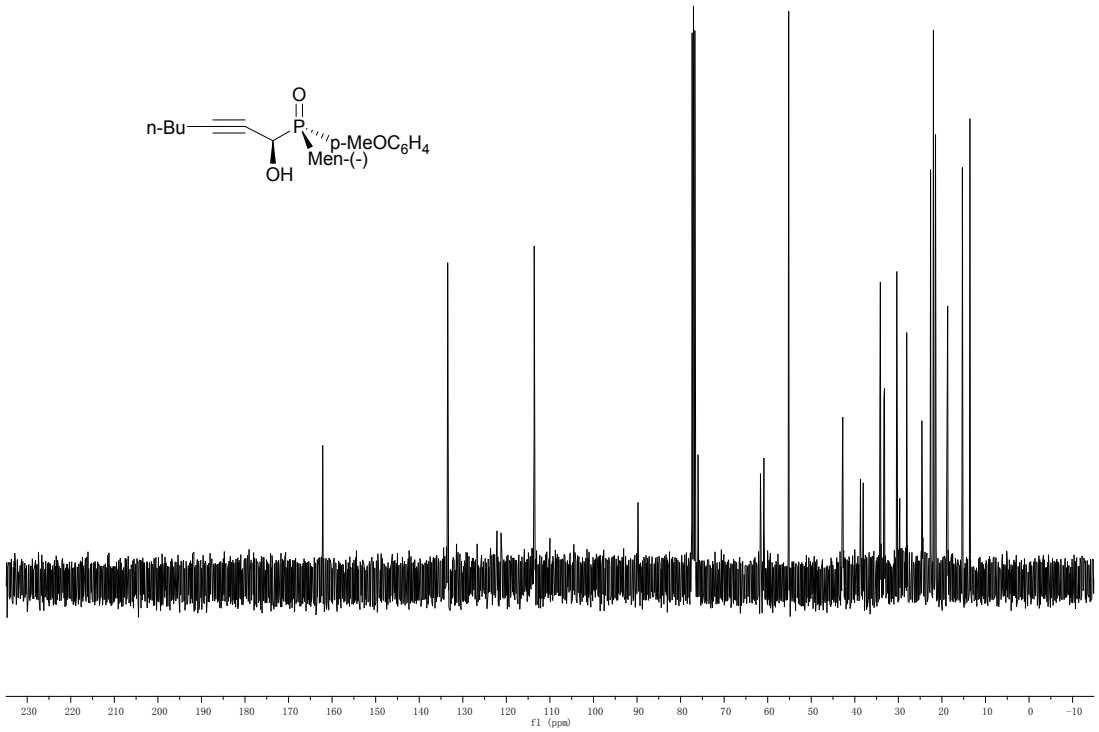




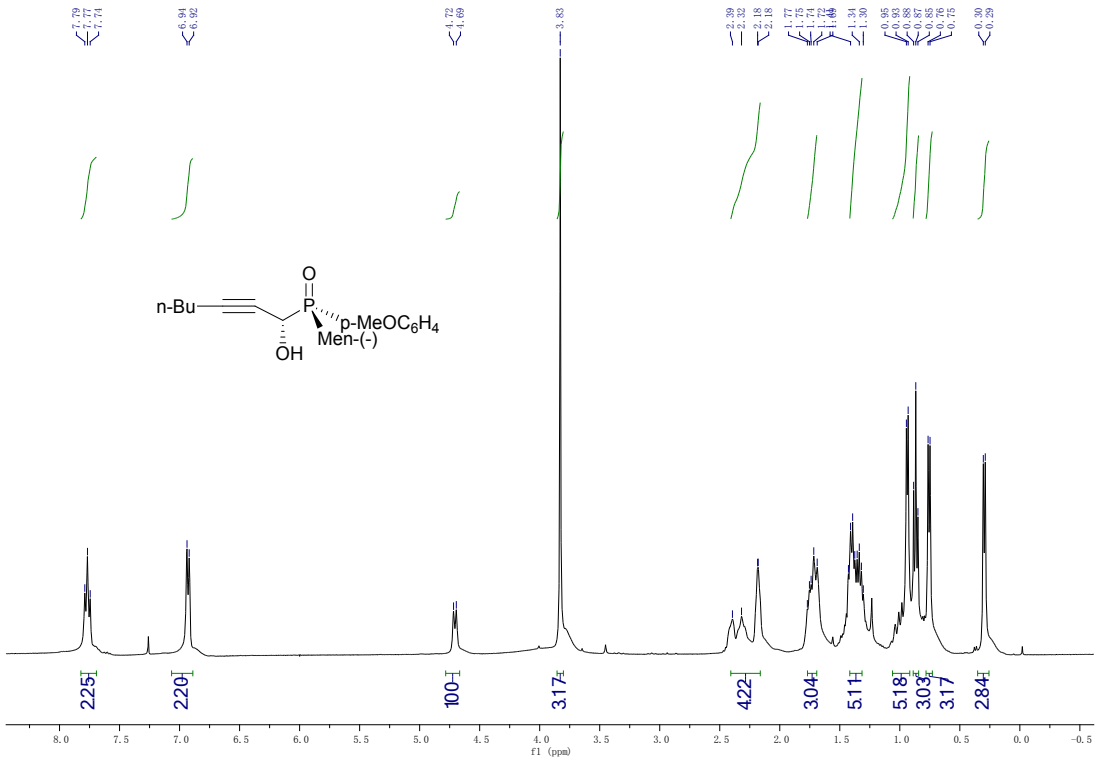
R_P,R_C-(*L*)-Menthyl (1-hydroxyhept-2-yn-1-yl)(4-methoxyphenyl) phosphine oxide (3dd)

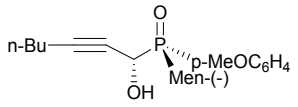

7.78
7.76
7.73
6.90
6.88
4.98
3.81
2.25
2.15
1.72
1.47
1.43
1.41
1.39
0.93
0.91
0.90
0.74
0.73
0.30
0.28
n-Bu
O
P
p-MeOC6H4
Men-(-)
OH
1.88
1.91
1.00
2.91
3.92
2.55
5.71
7.59
2.78
2.55
f1 (ppm)


42.29
n-Bu
O
P
p-MeOC6H4
Men-(-)
OH
f1 (ppm)

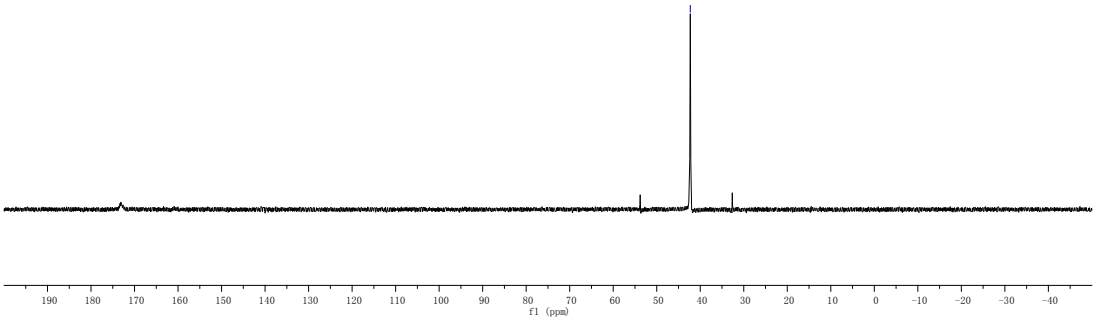


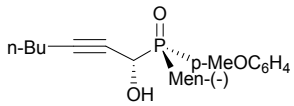
R_P,S_C-(*L*)-Menthyl (1-hydroxyhept-2-yn-1-yl)(4-methoxyphenyl) phosphine oxide (3dd')




n-Bu
O
P
p-MeOC6H4
Men-(-)
OH

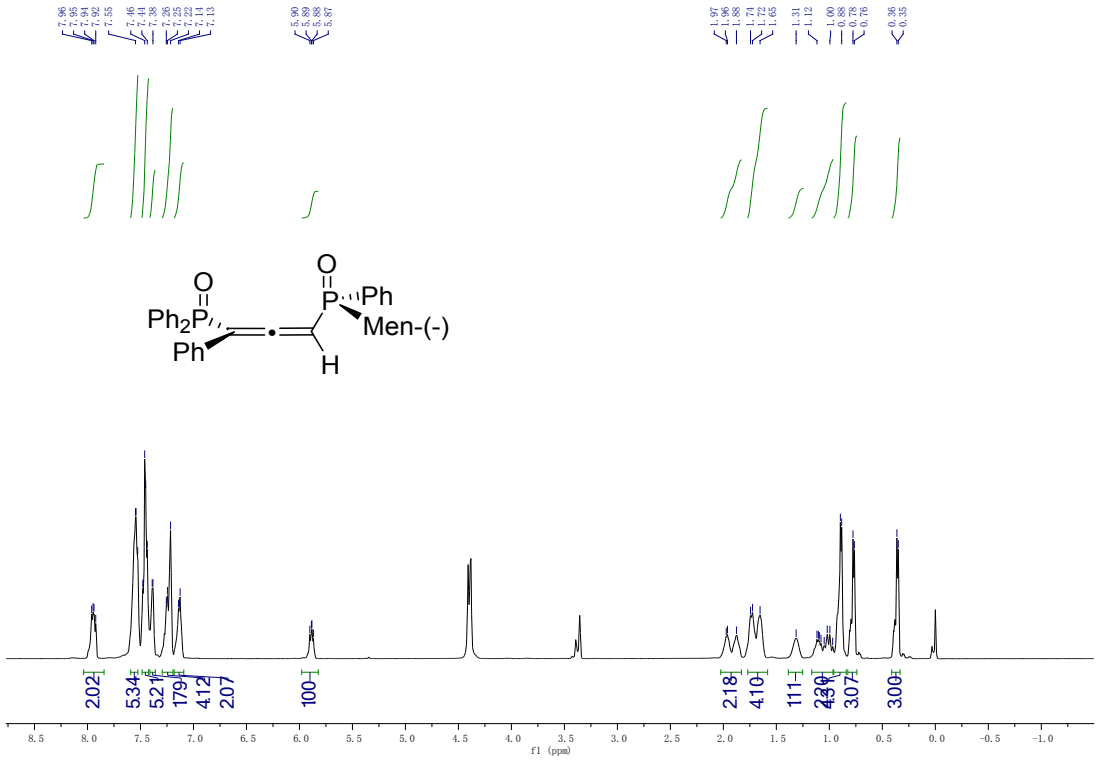
42.29

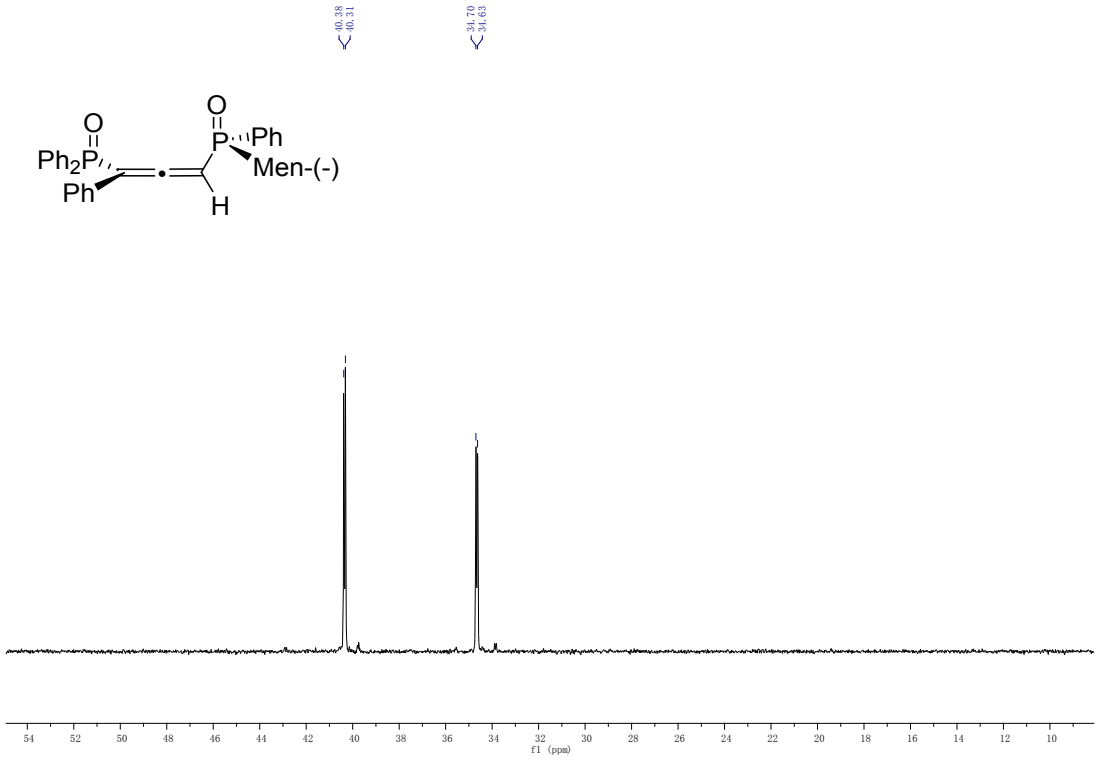

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

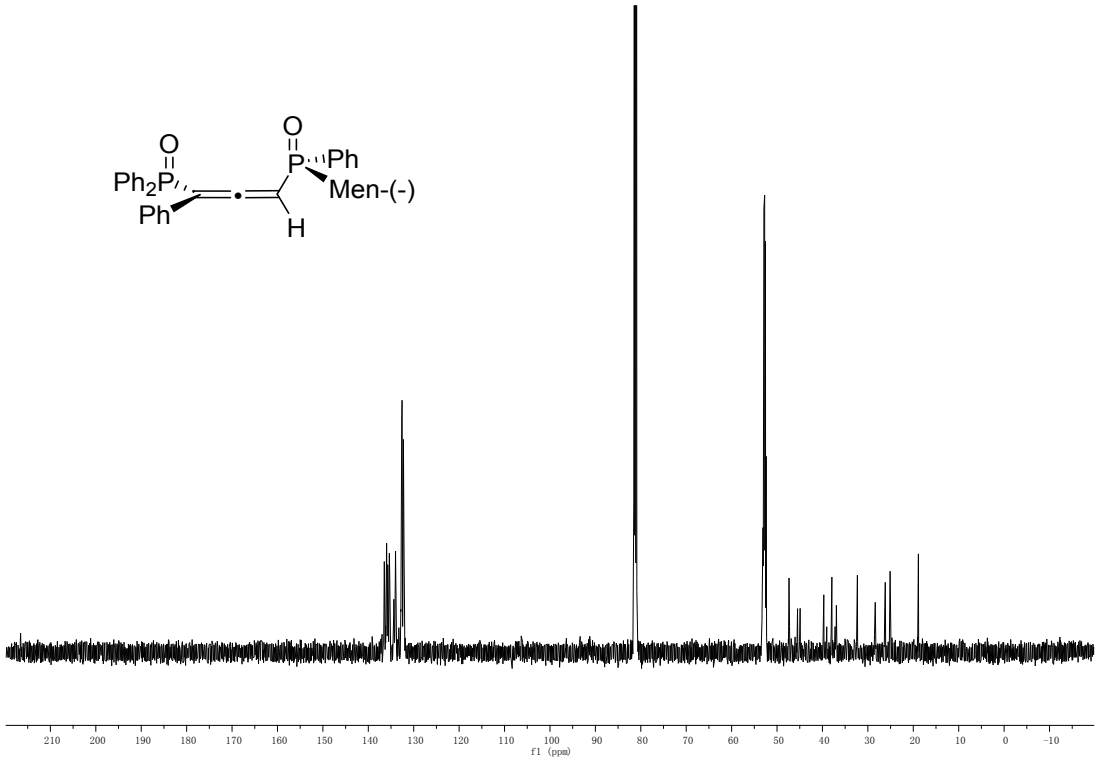

n-Bu
O
P
p-MeOC6H4
Men-(-)
OH

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

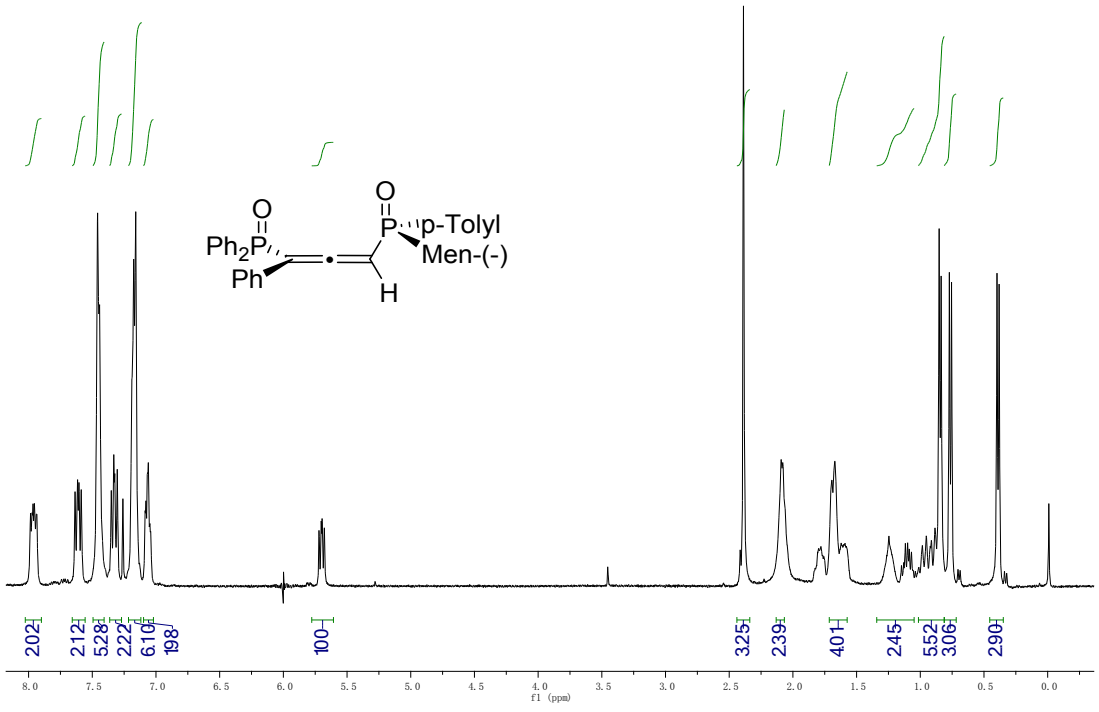
S_P,S_A-(*L*)-Menthyl (3-diphenylphosphoryl-3-phenylpropa-1,2-dien-1-yl) phenylphosphine oxide (5aa')

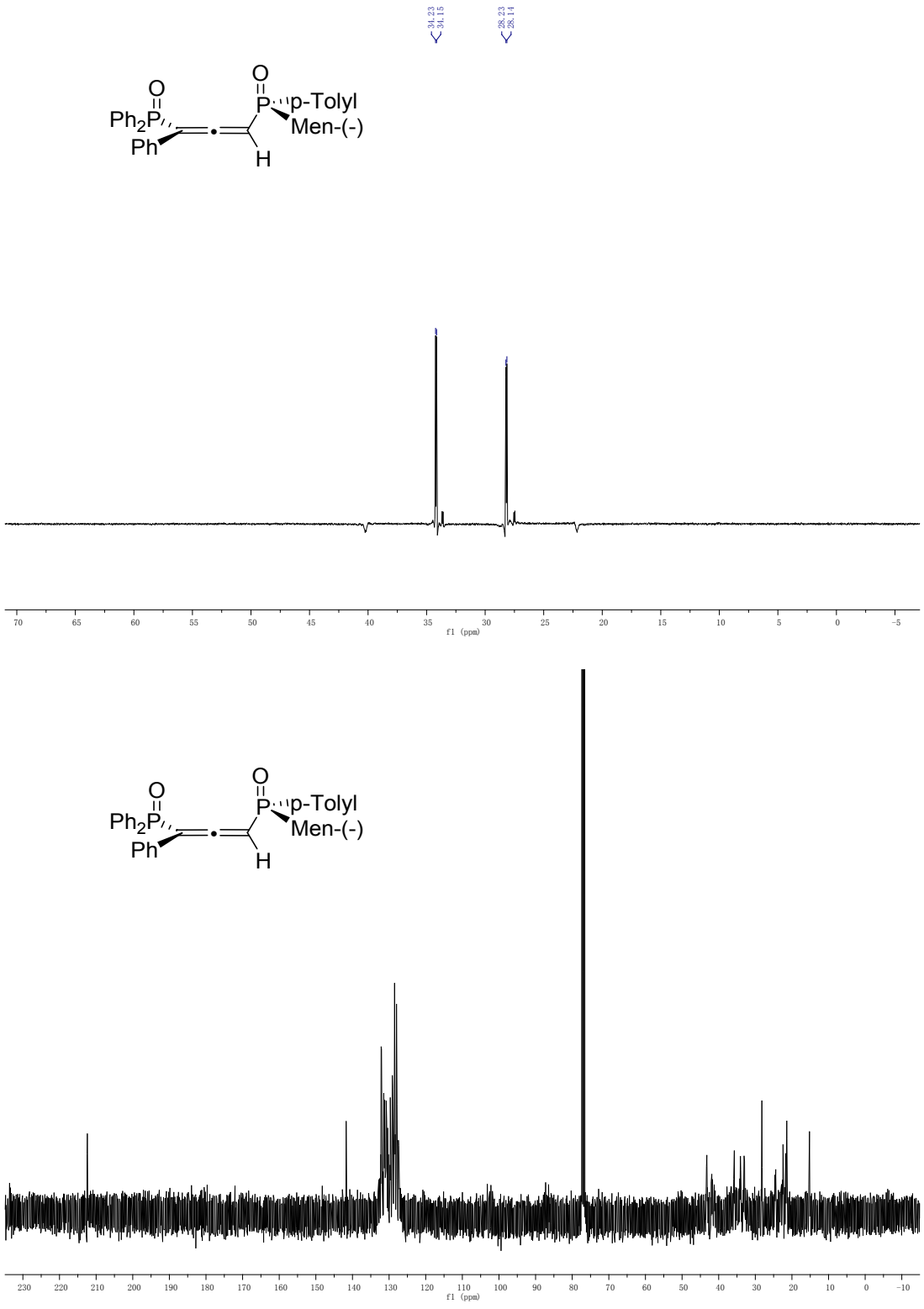




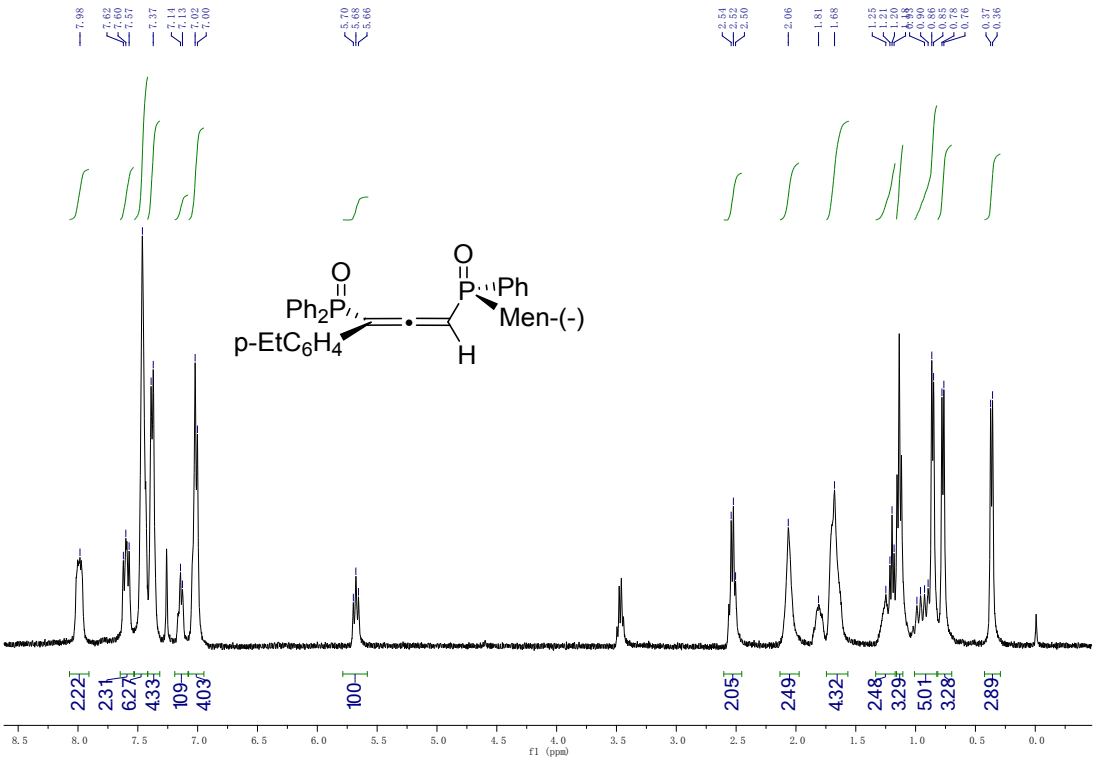


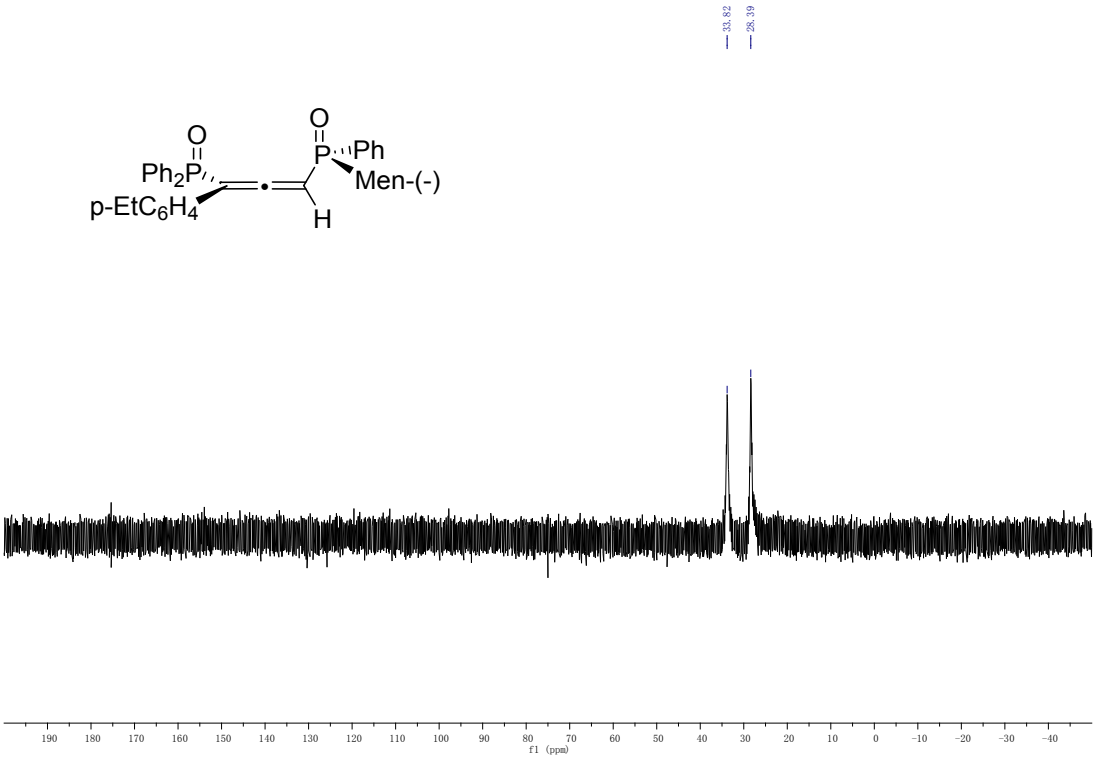
***S*$_P$,*S*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-phenylpropa-1,2-dien-1-yl)(p-tolyl)phosphine oxide (5ab')**

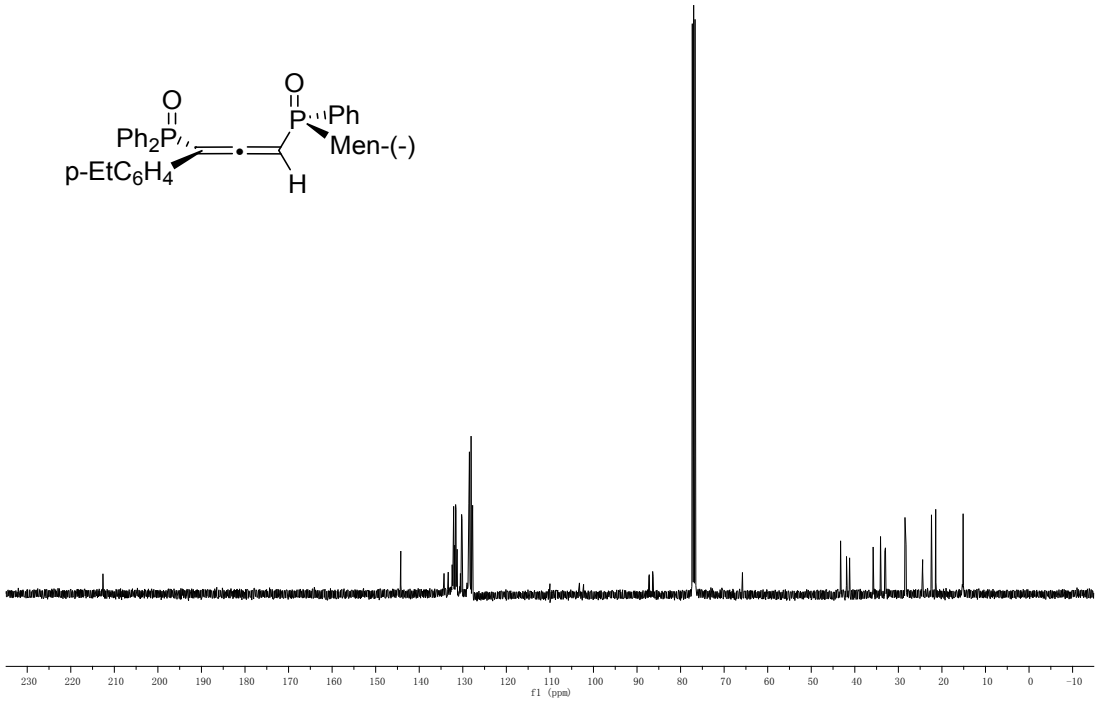




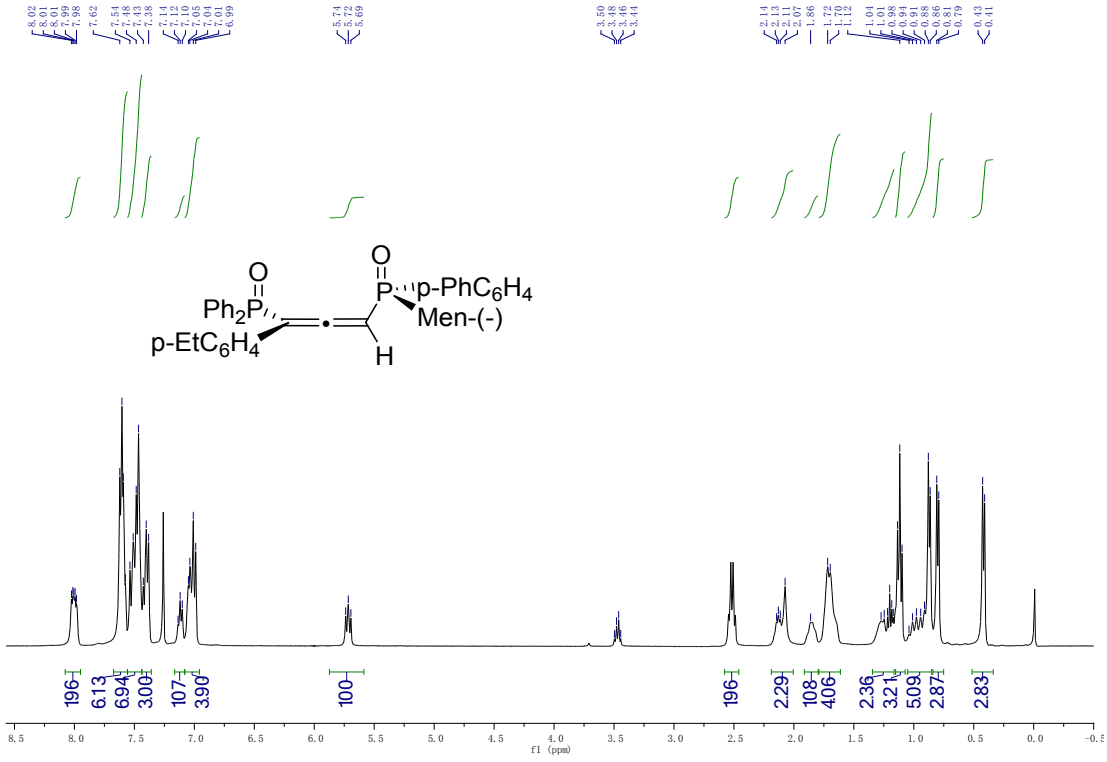
***S*$_P$,*S*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-*p*-ethylphenylpropa-1,2-dien-1-yl) phenylphosphine oxide (5ba')**

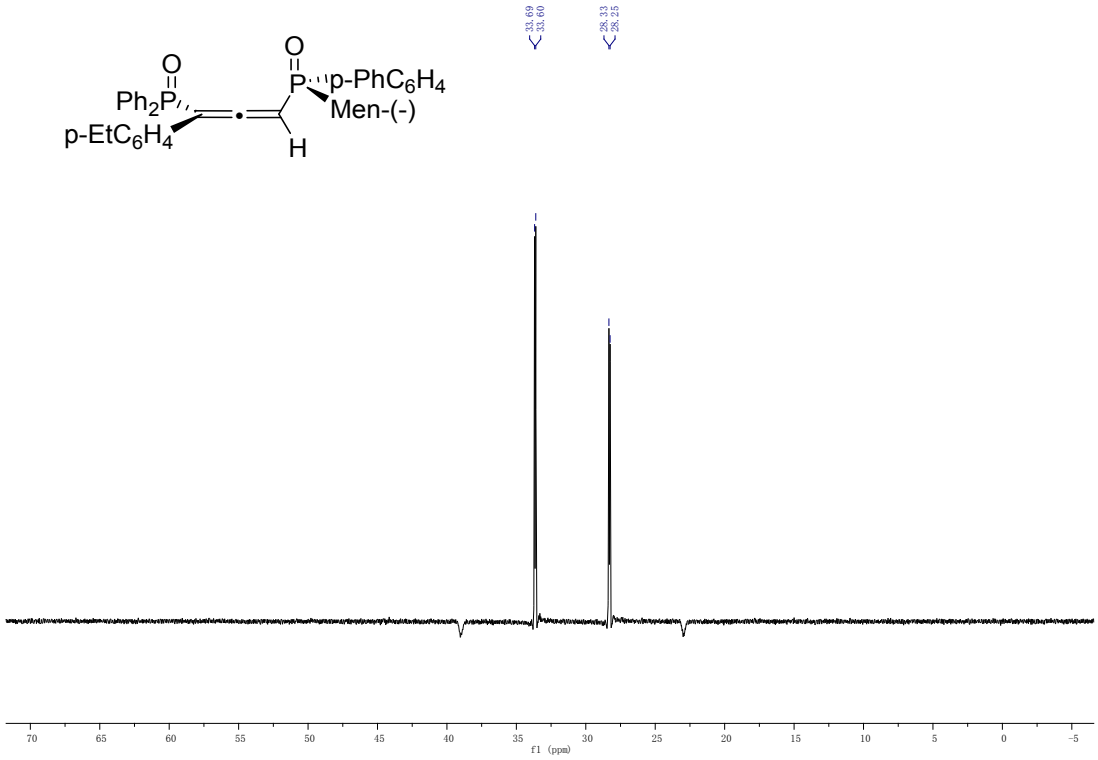

7.98
7.62
7.60
7.57
7.37
7.14
7.13
7.02
7.00
5.70
5.68
5.66
2.54
2.52
2.50
2.06
1.81
1.68
1.25
1.21
1.20
0.90
0.86
0.85
0.78
0.76
0.37
0.36
O
Ph2P
p-EtC6H4
P
Ph
Men-(-)
H
222
231
627
433
109
403
100
205
249
432
248
329
501
328
289
f1 (ppm)

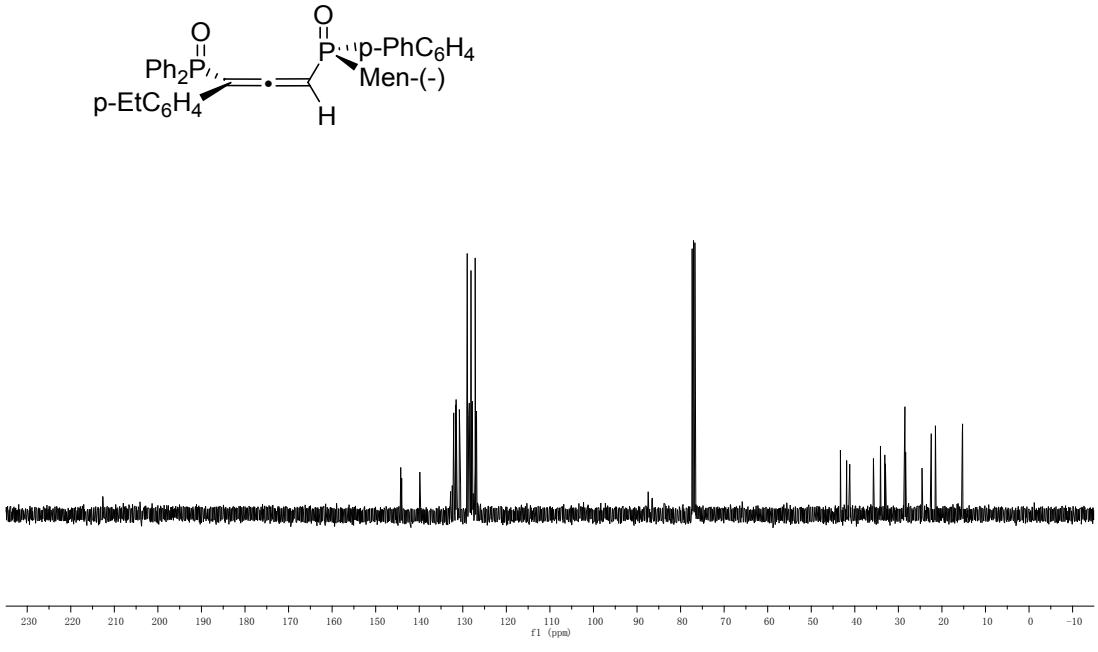

33.82
28.39
O
Ph2P
p-EtC6H4
P
Ph
Men-(-)
H
f1 (ppm)



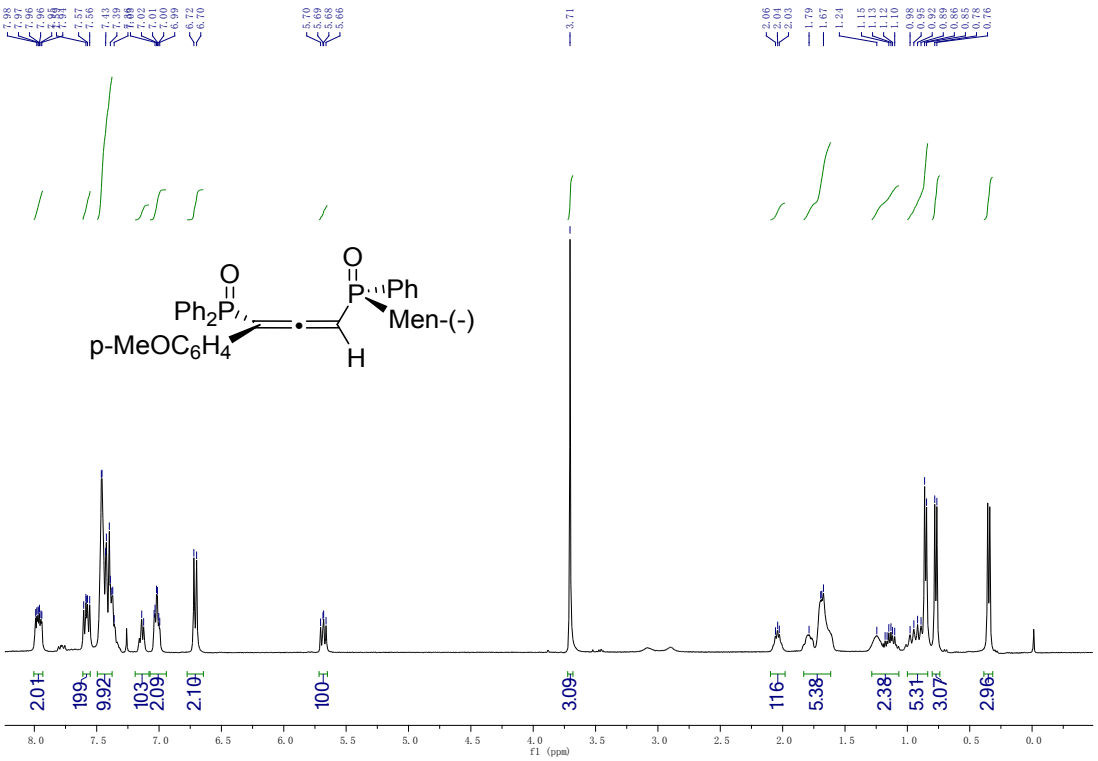
***S*$_P$,*S*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-*p*-ethylphenylpropa-1,2-dien-1-yl) (1,1'-biphenyl)-4-ylphosphine oxide (5bc')**

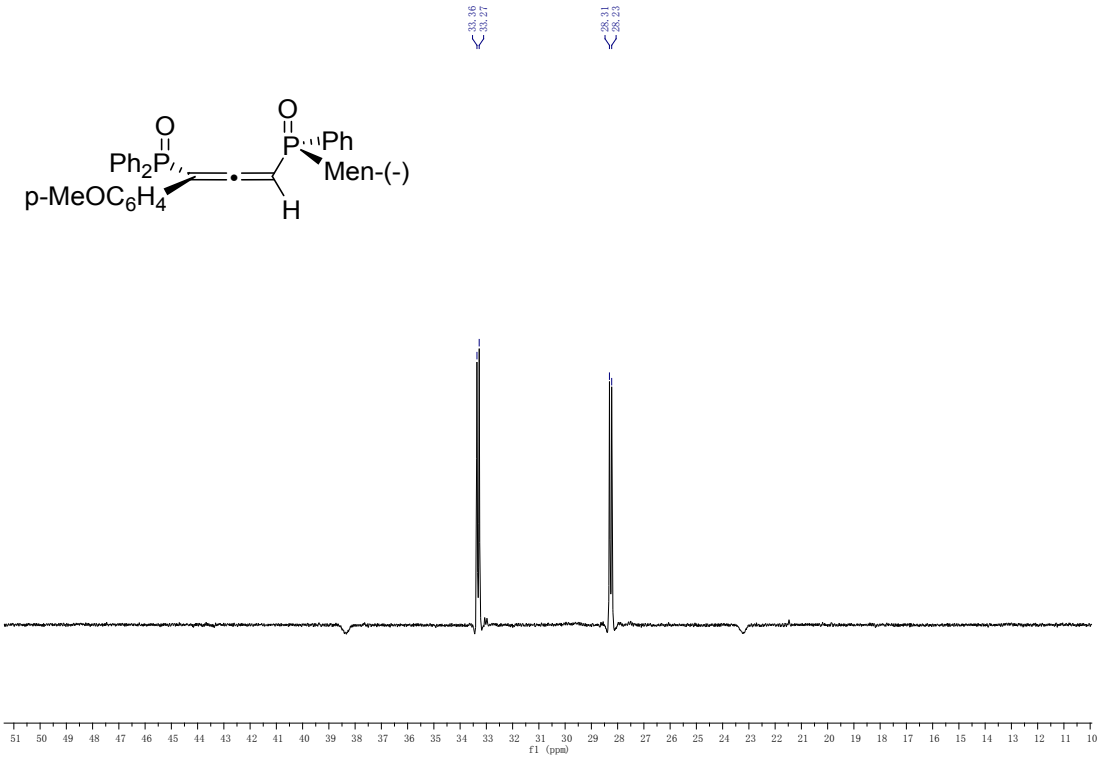


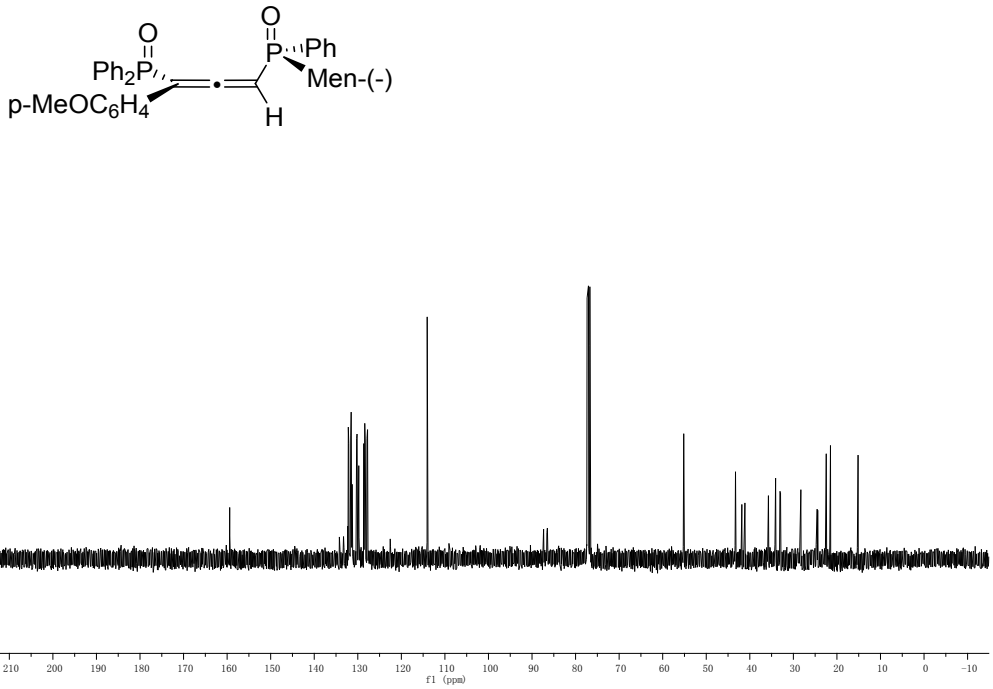




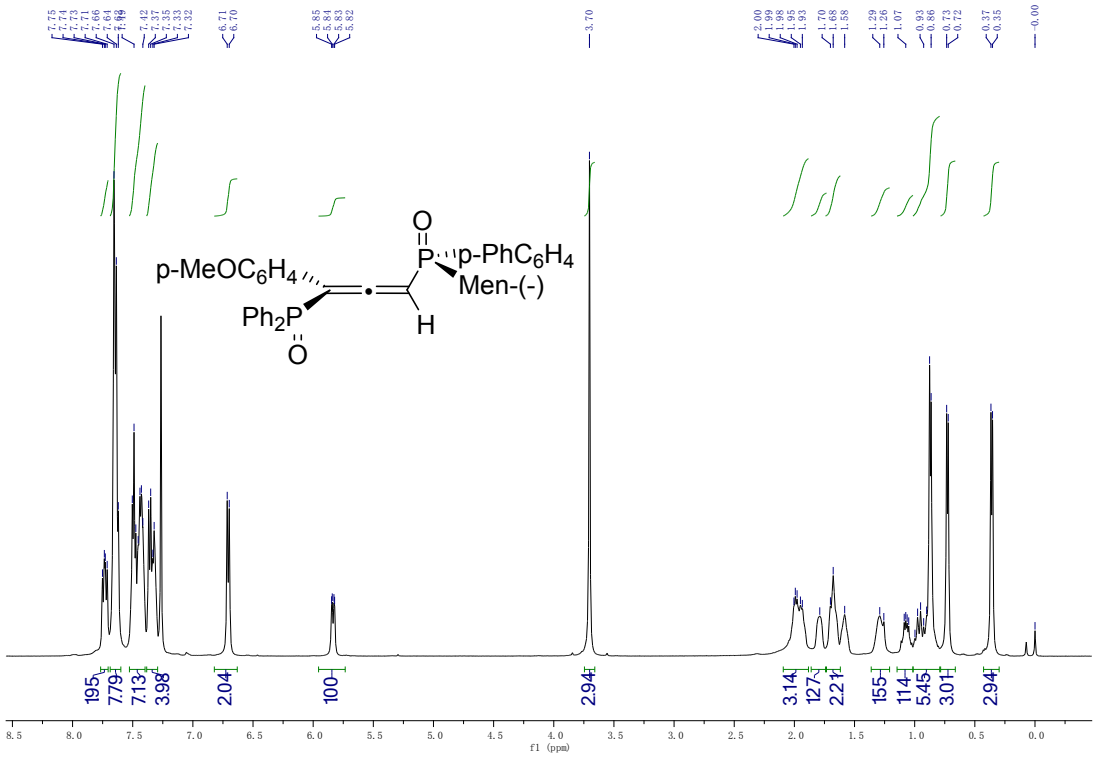
S_P,S_A-(*L*)-Menthyl (3-diphenylphosphoryl-3-*p*-methoxyphenylpropa-1,2-dien-1-yl) phenylphosphine oxide (5ca')

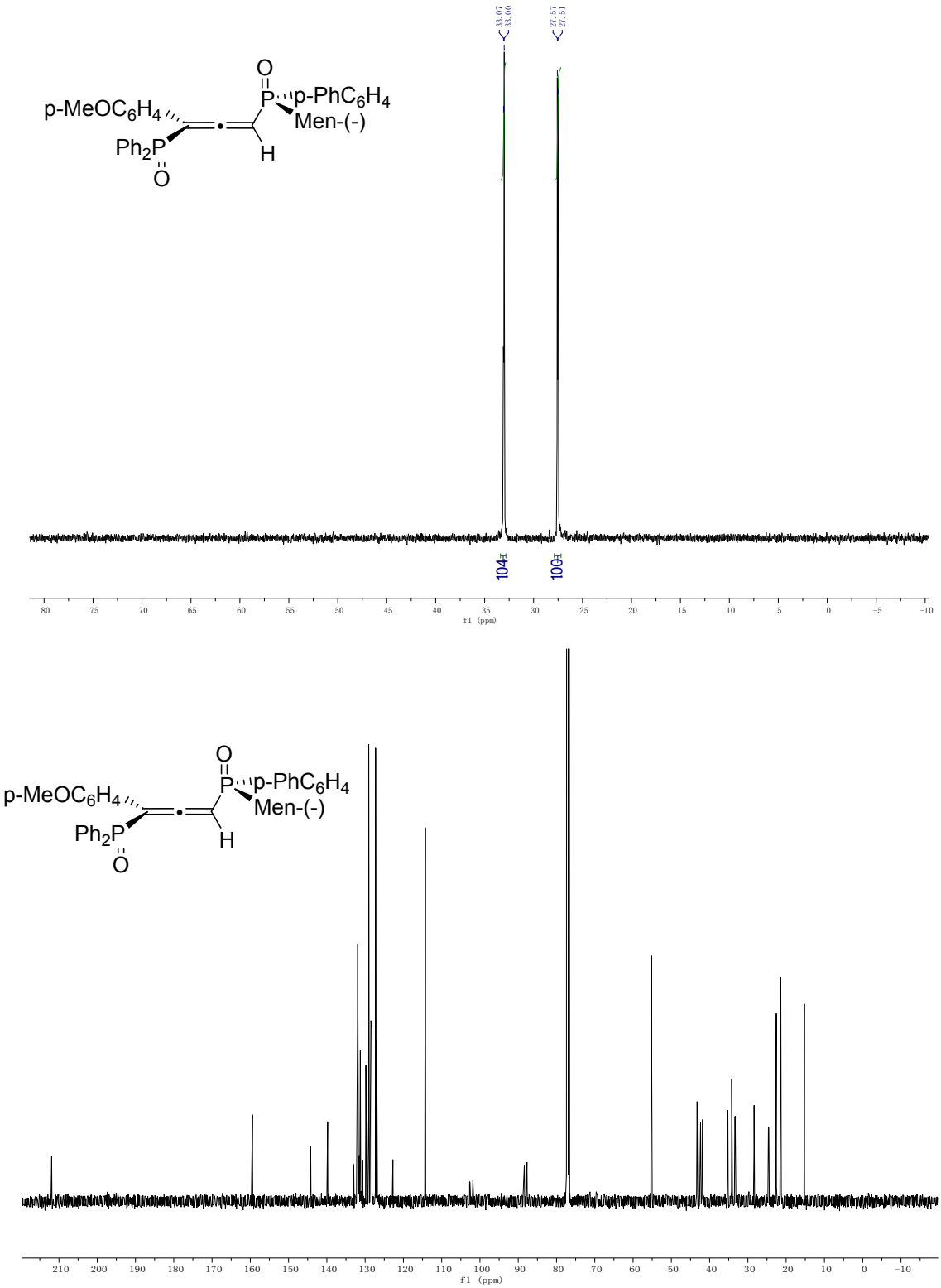

7.98
7.97
7.96
7.96
7.57
7.56
7.43
7.39
7.02
7.01
7.00
6.99
6.72
6.70
5.70
5.69
5.68
5.66
3.71
2.06
2.04
2.03
1.79
1.67
1.24
1.15
1.13
1.12
1.10
0.98
0.95
0.92
0.89
0.86
0.85
0.78
0.76
O
Ph2P
p-MeOC6H4
P
Ph
Men-(-)
H
2.01
1.99
9.92
1.03
2.09
2.10
1.00
3.09
1.16
5.38
2.38
5.31
3.07
2.96
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


33.36
33.27
28.31
28.23
O
Ph2P
p-MeOC6H4
P
Ph
Men-(-)
H
51
50
49
48
47
46
45
44
43
42
41
40
39
38
37
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
f1 (ppm)

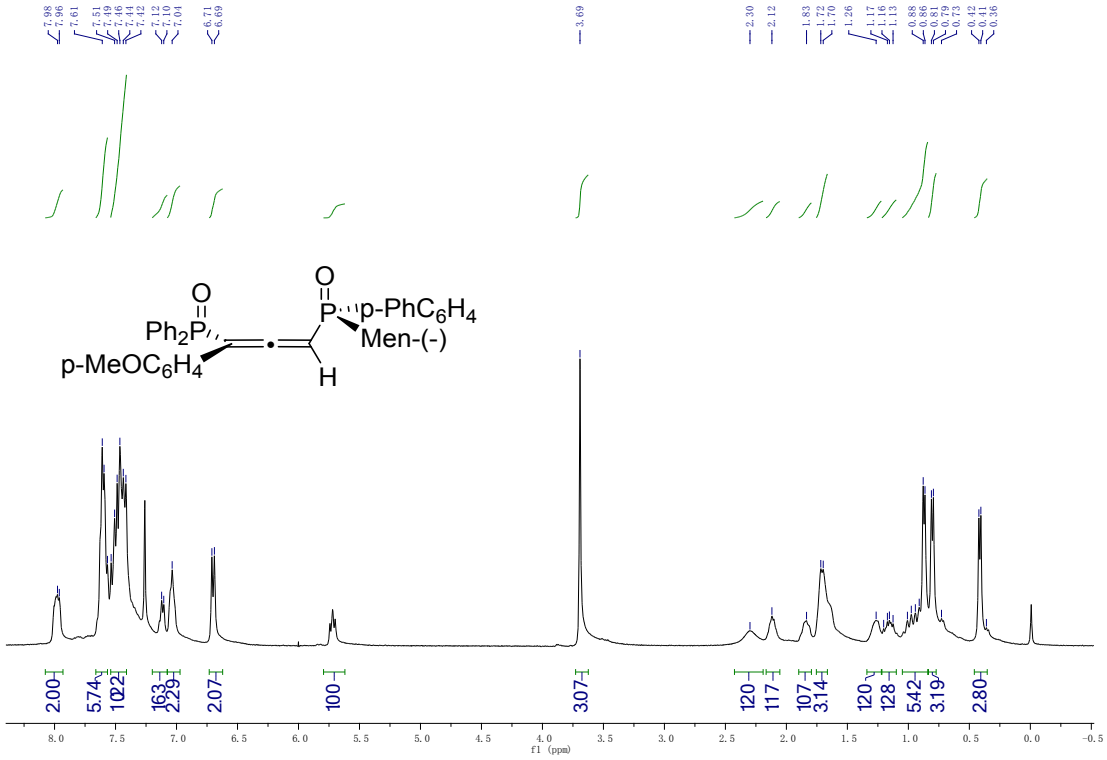


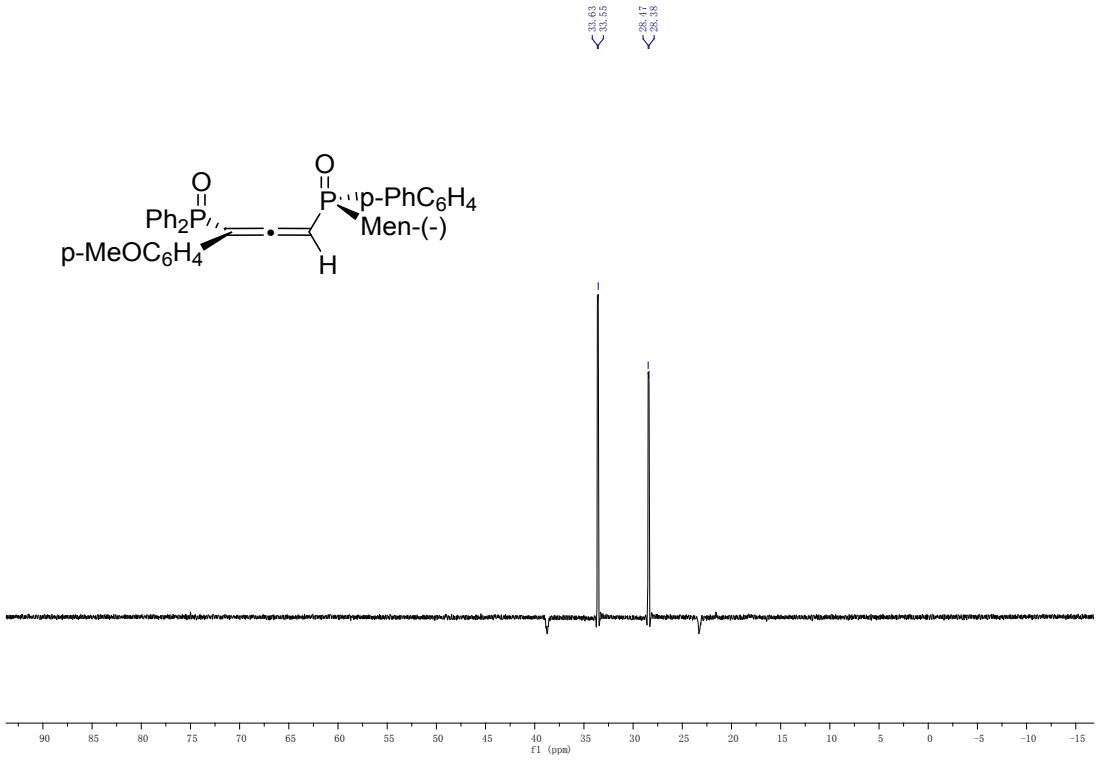
***S*$_P$,*R*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-*p*-methoxyphenylpropa-1,2-dien-1-yl) (1,1'-biphenyl)-4-ylphosphine oxide (5cc)**

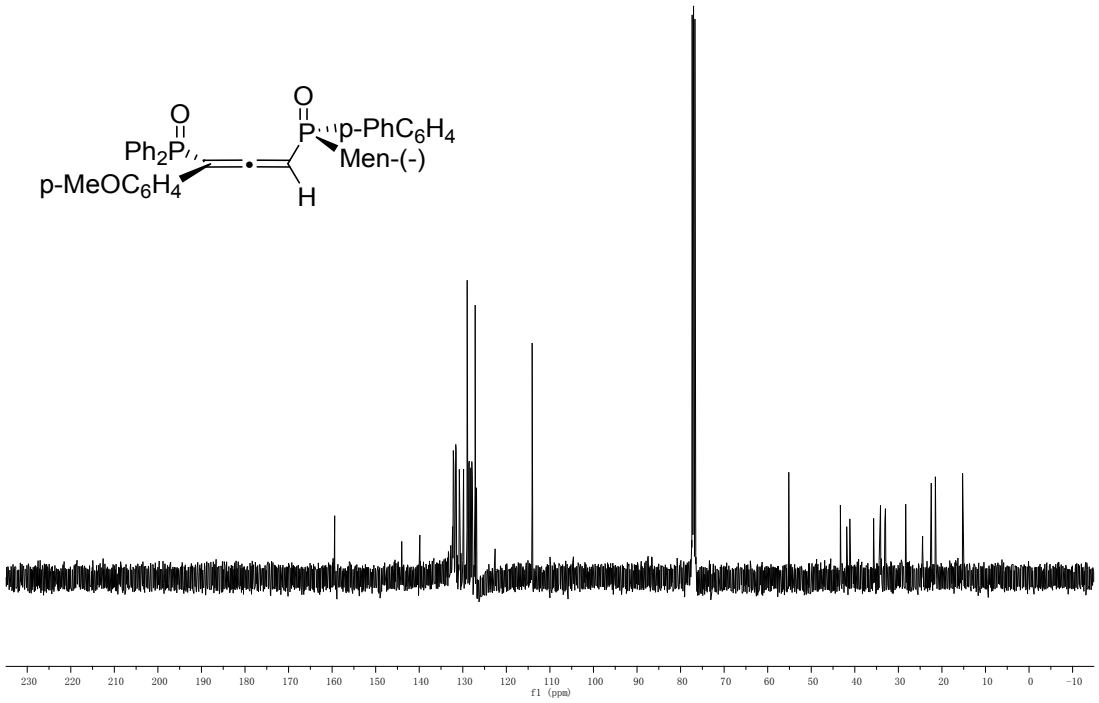




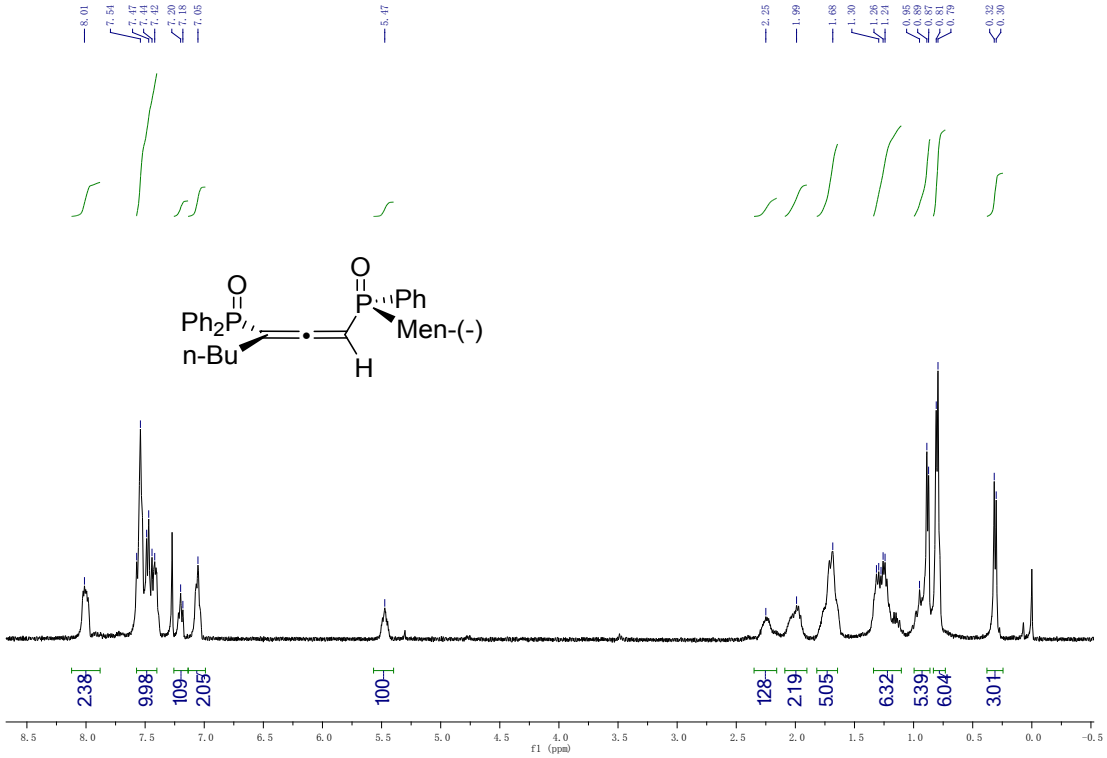
S_P,S_A-(*L*)-Menthyl (3-diphenylphosphoryl-3-*p*-methoxyphenylpropa-1,2-dien-1-yl) (1,1'-biphenyl)-4-ylphosphine oxide (5cc')

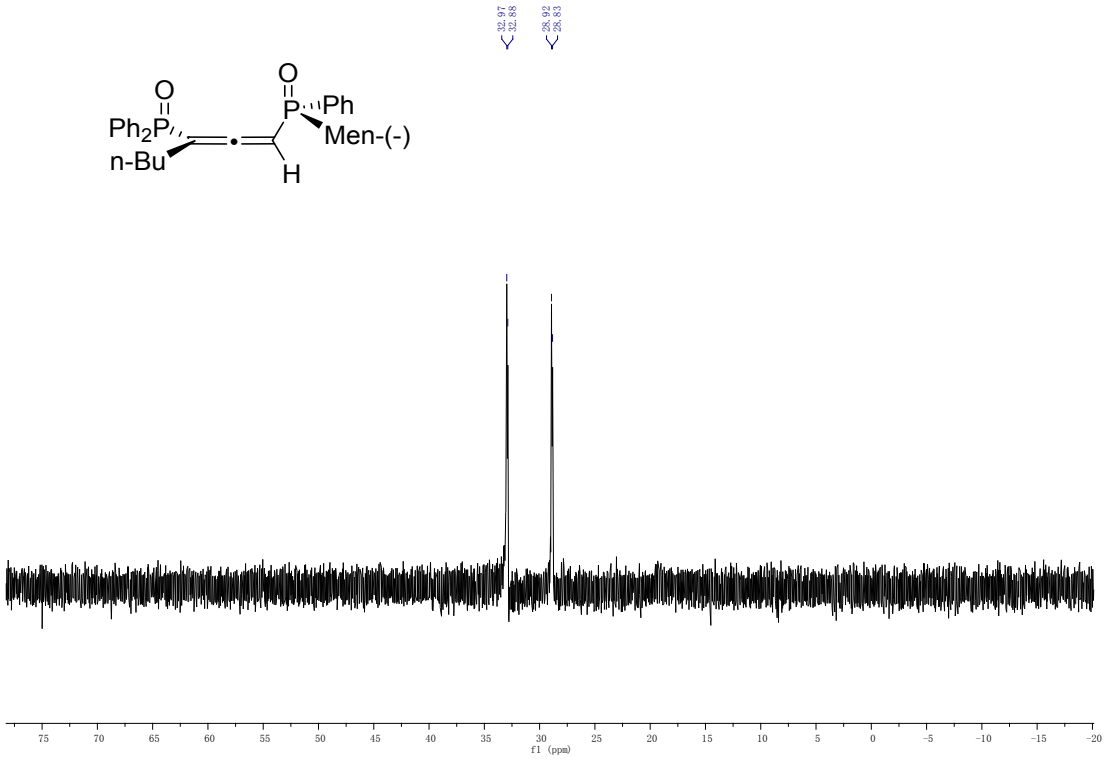

7.98
7.96
7.61
7.51
7.49
7.46
7.44
7.42
7.12
7.10
7.04
6.71
6.69
3.69
2.30
2.12
1.83
1.72
1.70
1.26
1.17
1.16
1.13
0.88
0.86
0.81
0.79
0.73
0.42
0.41
0.36
O
Ph2P
p-MeOC6H4
O
P
p-PhC6H4
Men-(-)
H
2.00
5.74
10.21
1.63
2.29
2.07
1.00
3.07
1.20
1.17
1.07
3.14
1.20
1.28
5.42
3.19
2.80
f1 (ppm)

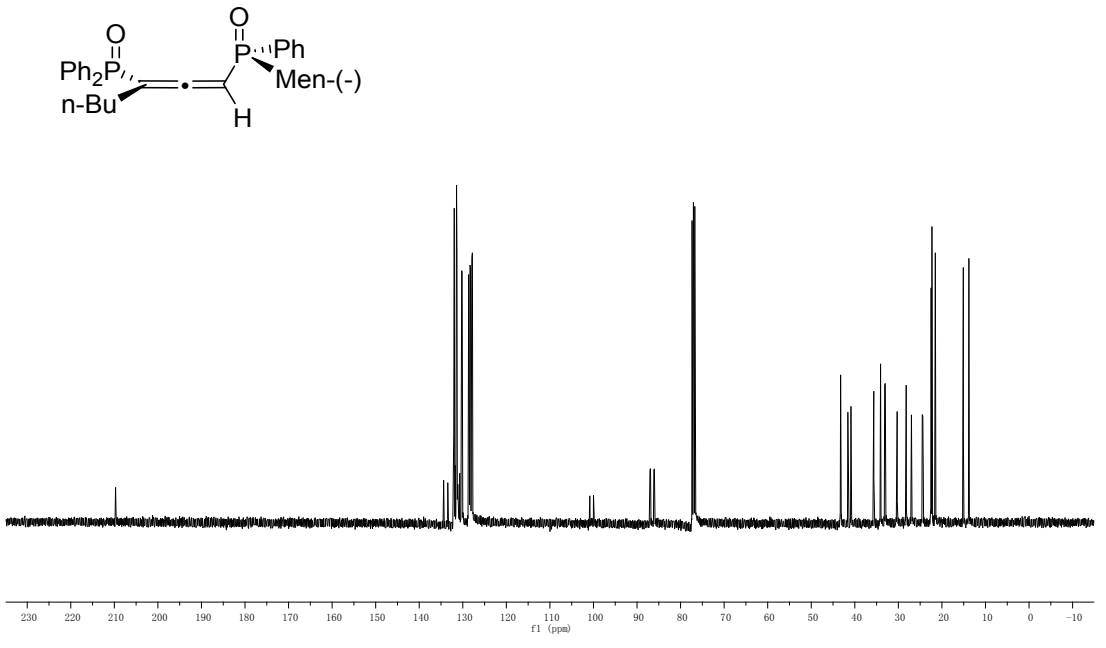

33.63
33.55
28.47
28.38
O
Ph2P
p-MeOC6H4
O
P
p-PhC6H4
Men-(-)
H
f1 (ppm)



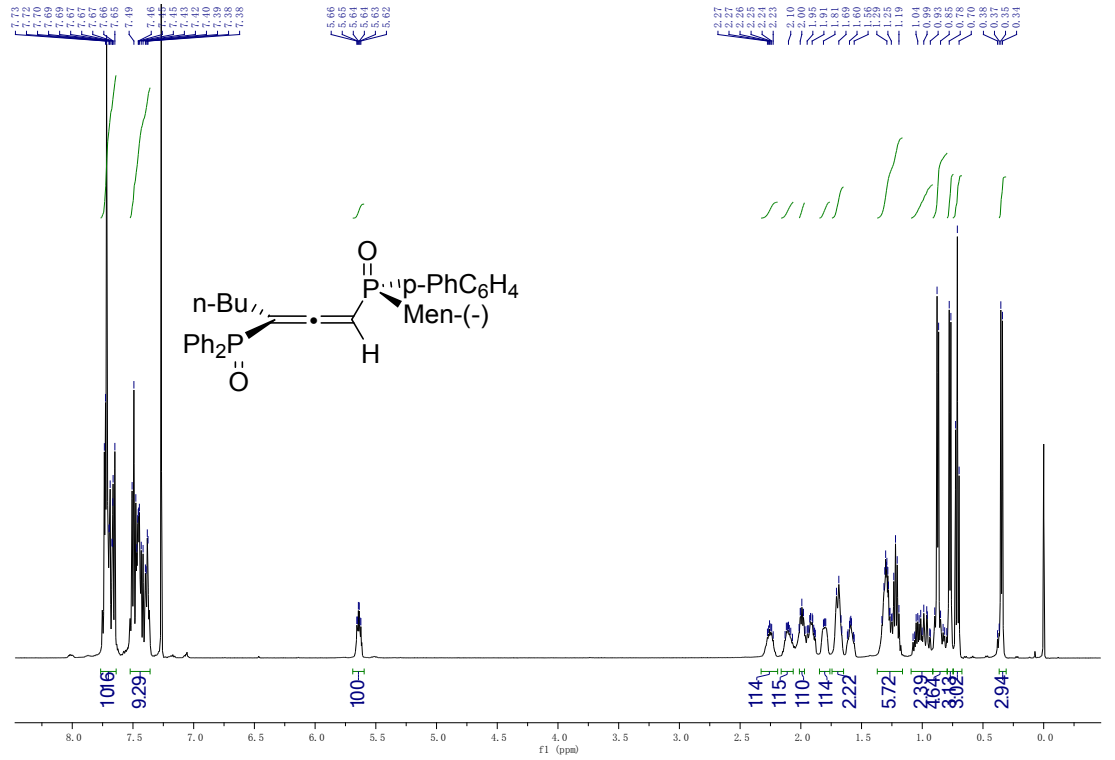
***S*$_P$,*S*$_A$-(*L*)-Menthyl (3-diphenylphosphoryl-3-hepta-1,2-dien-1-yl) phenylphosphine oxide (5da')**

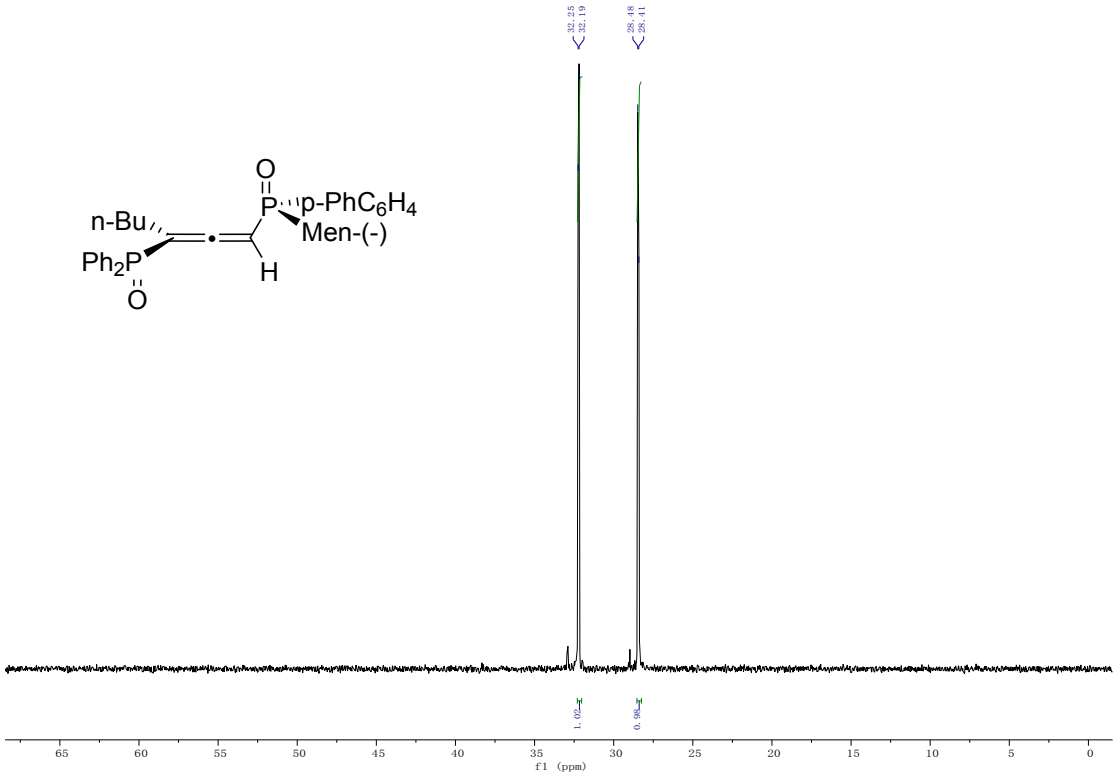


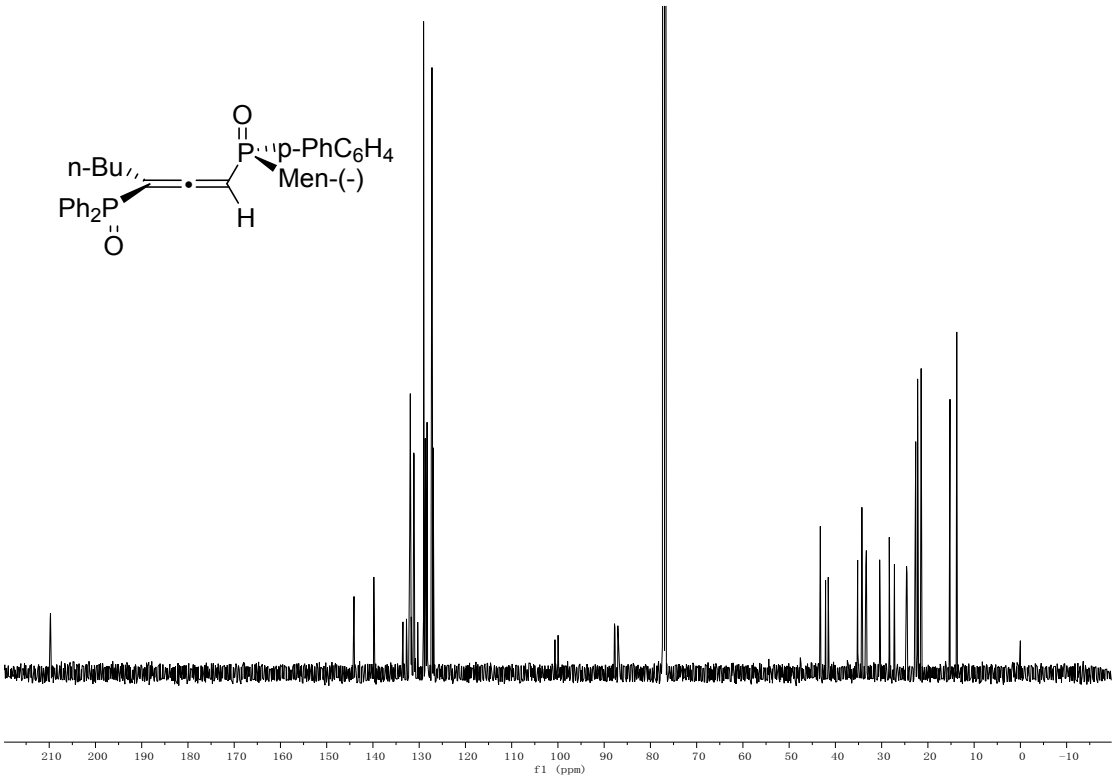




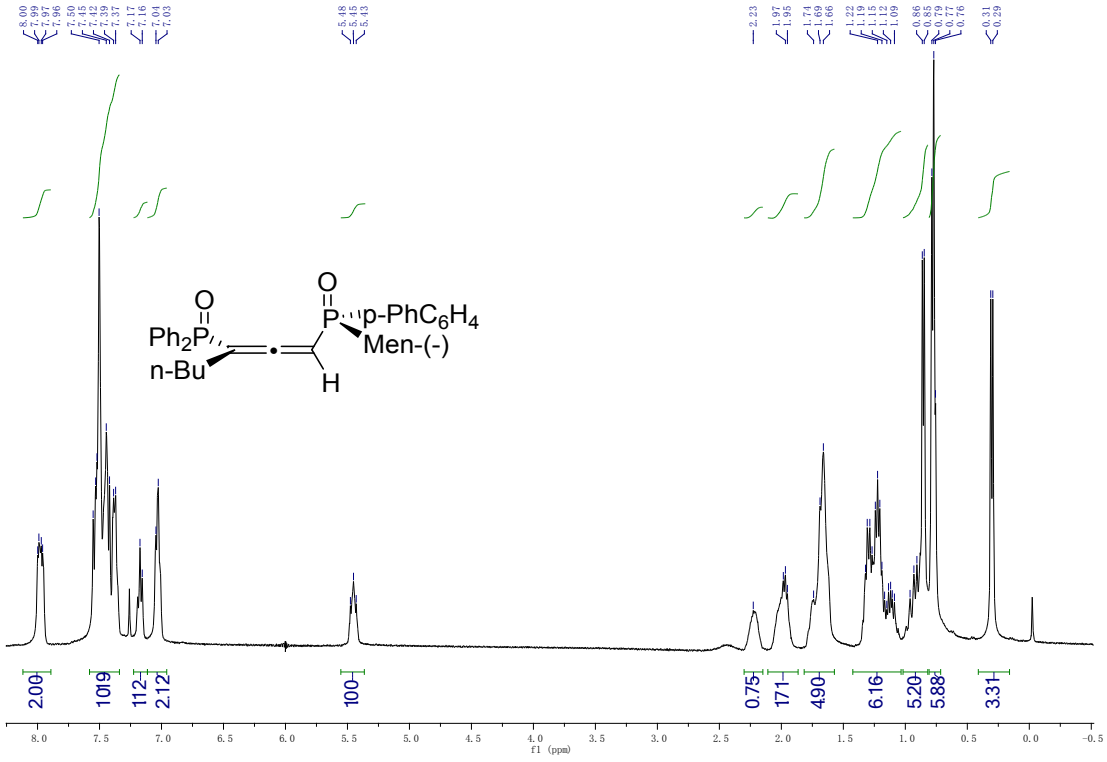
S_P,R_A-(*L*)-Menthyl (3-diphenylphosphoryl-3-hepta-1,2-dien-1-yl)(1,1'-biphenyl)-4-ylphosphine oxide (5dc)

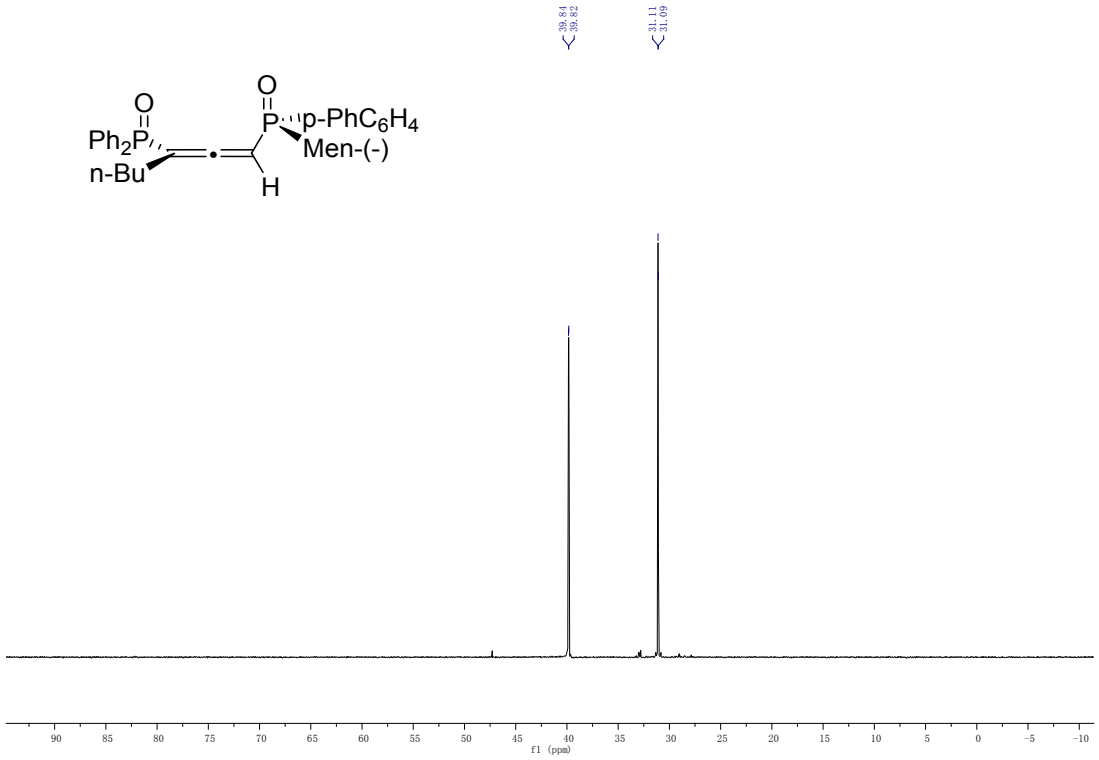

n-Bu
Ph2P
O
O
P
p-PhC6H4
Men-(-)
H
f1 (ppm)

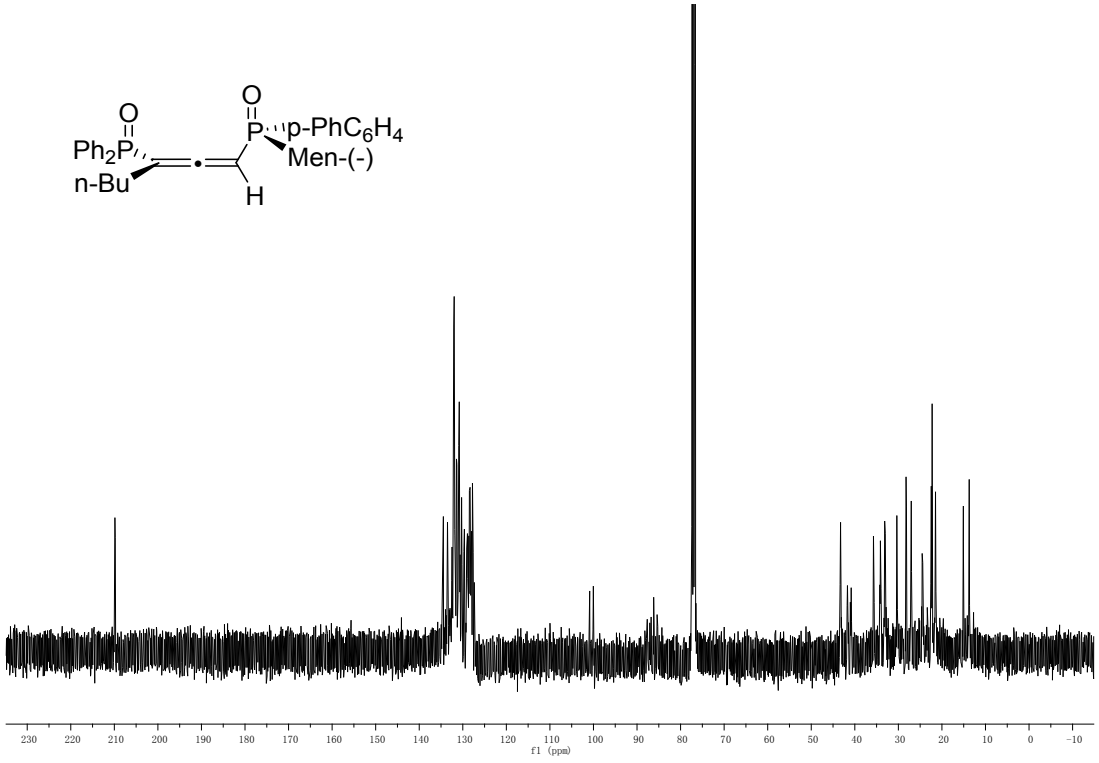

n-Bu
Ph2P
O
O
P
p-PhC6H4
Men-(-)
H
f1 (ppm)



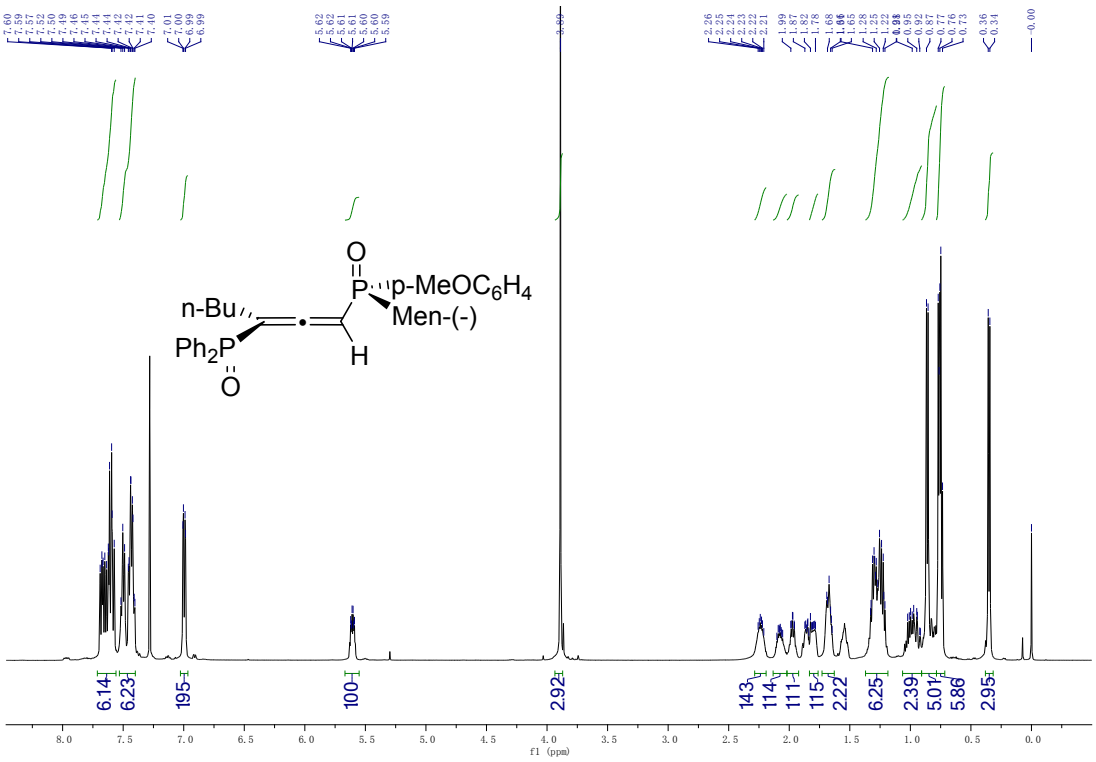
S_P,S_A-(*L*)-Menthyl (3-diphenylphosphoryl-3-hepta-1,2-dien-1-yl)(1,1'-biphenyl)-4-ylphosphine oxide (5dc')

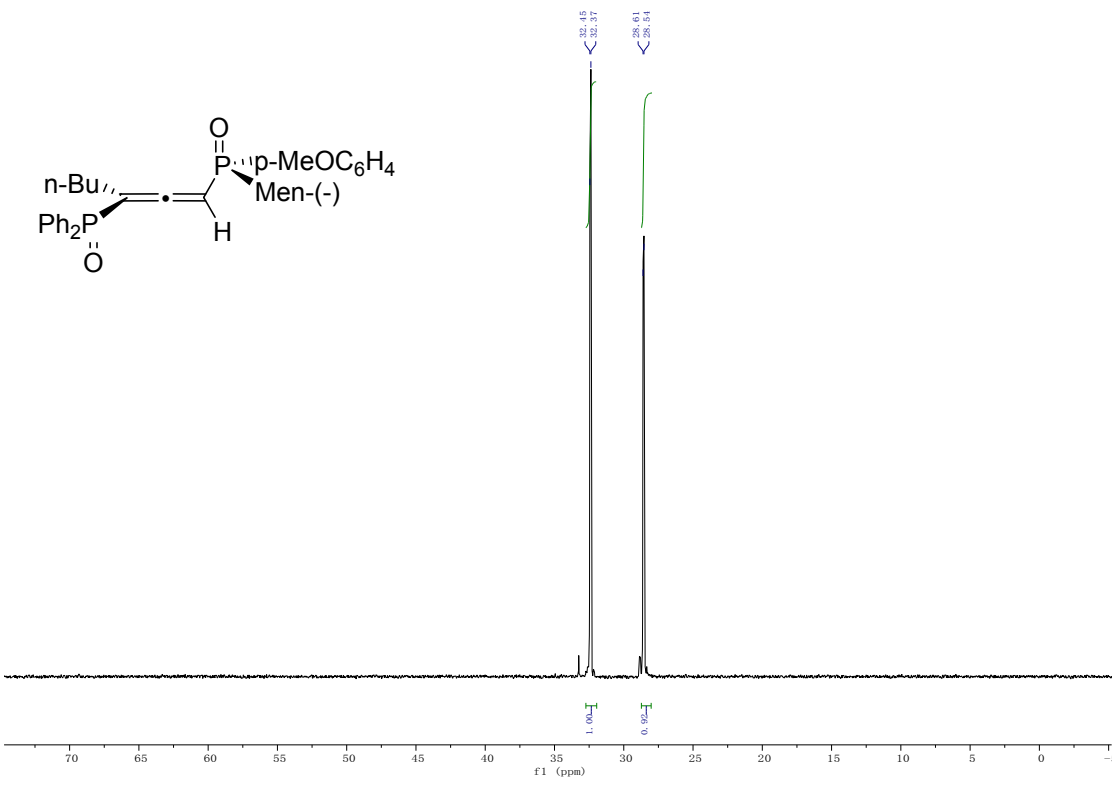


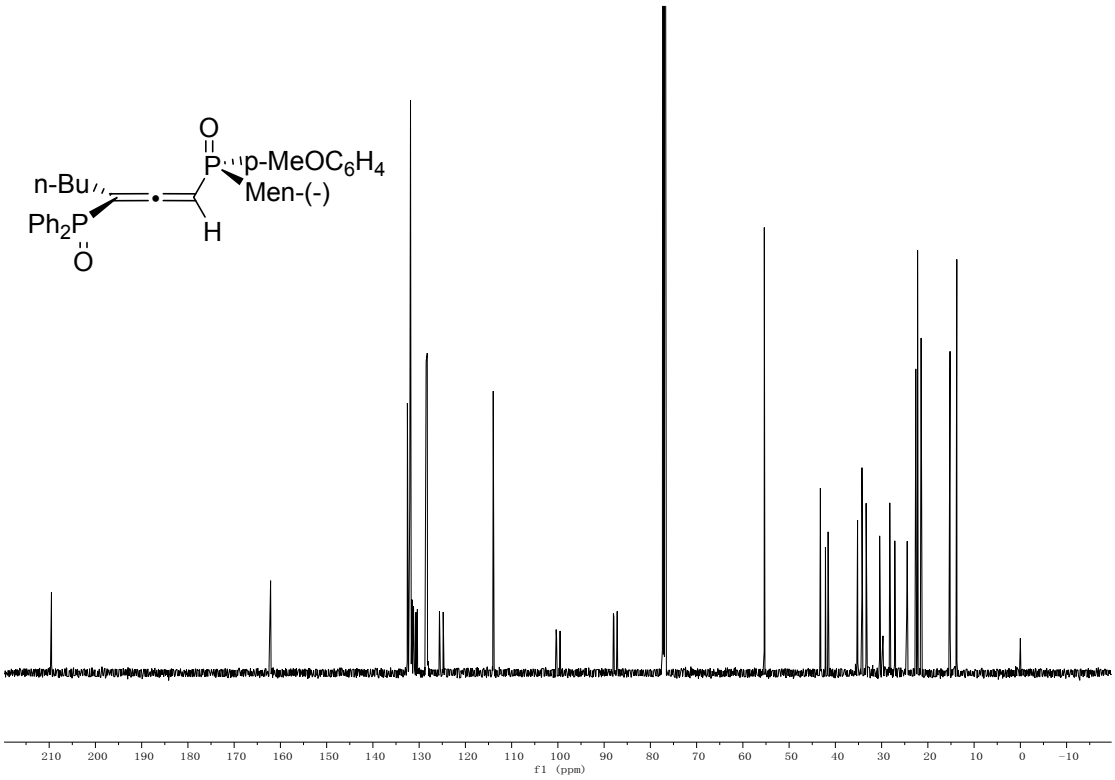




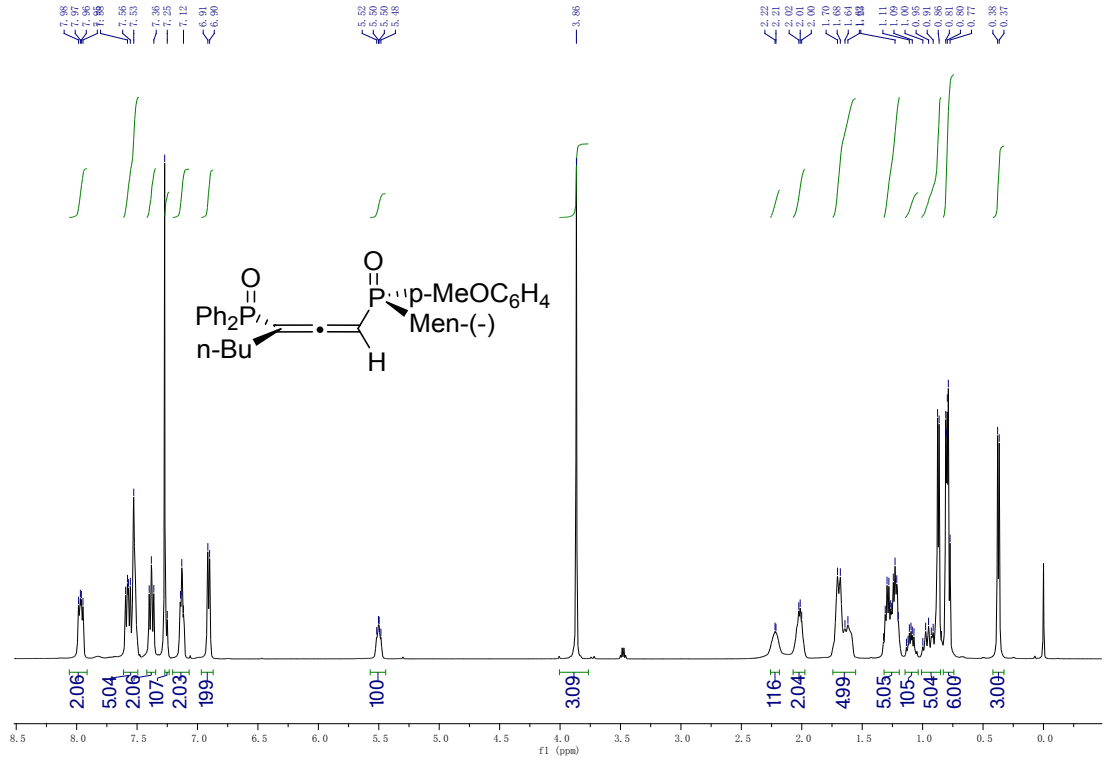
S_P,R_A-(*L*)-Menthyl (3-diphenylphosphoryl-3-hepta-1,2-dien-1-yl)(4-methoxyphenyl)phosphine oxide (5dd)

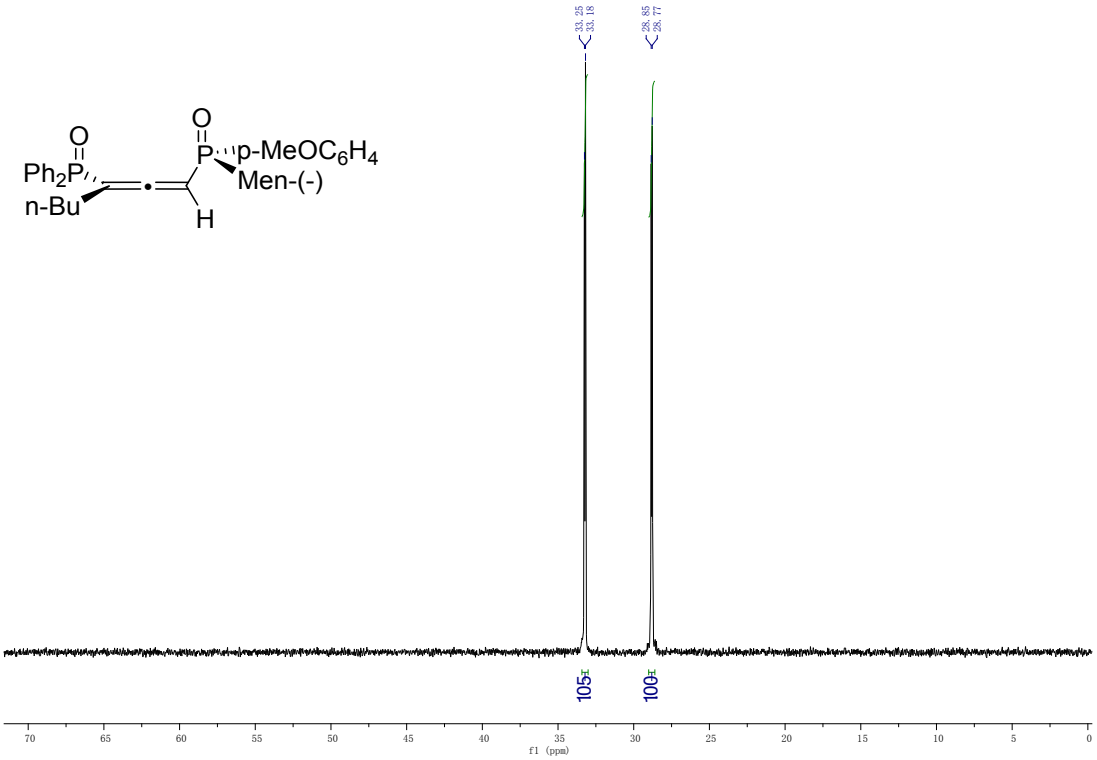

n-Bu
Ph2P
O
O
P
p-MeOC6H4
Men-(-)
H
f1 (ppm)

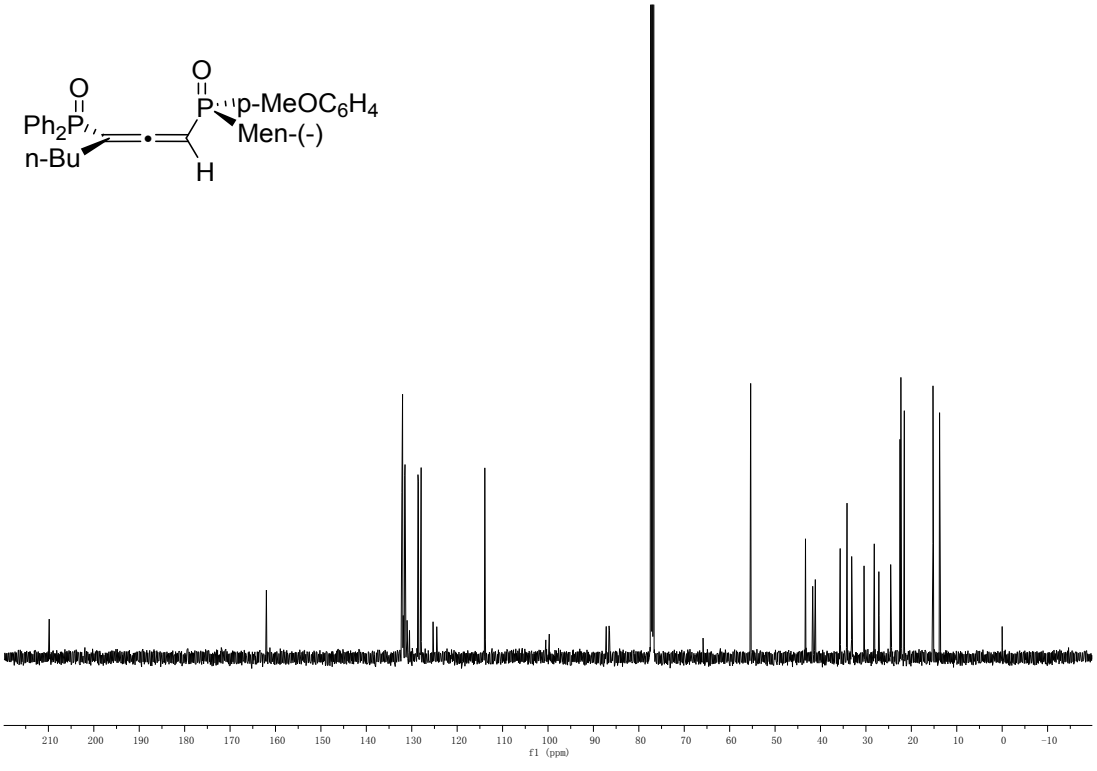

n-Bu
Ph2P
O
O
P
p-MeOC6H4
Men-(-)
H
f1 (ppm)



S_P,S_A-(*L*)-Menthyl (3-diphenylphosphoryl-3-hepta-1,2-dien-1-yl)(4-methoxyphenyl)phosphine oxide (5dd')




33.25
33.18
28.85
28.77
O
Ph2P
n-Bu
O
P
p-MeOC6H4
Men-(-)
H
105.00
100.00
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


O
Ph2P
n-Bu
O
P
p-MeOC6H4
Men-(-)
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)