Palladium-Catalyzed Asymmetric Hydrophosphorylation of Alkynes: Facile Access to P-Stereogenic Phosphinates

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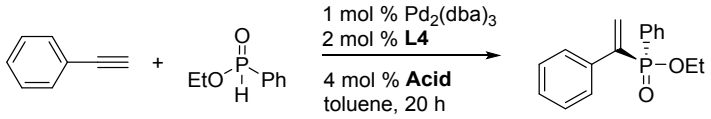
1. General information

NMR Spectra were recorded on a Bruker DPX-500 (400) spectrometer at 500 MHz or 400 MHz for ^{1}H NMR, 200MHz or 160MHz for ^{31}P NMR, 376 MHz for ^{19}F NMR and 100 MHz or 125 MHz for ^{13}C NMR in $CDCl_3$ with tetramethylsilane (TMS) or the residual deuterated solvent peaks as internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). Flash column chromatograph was carried out using 200-300 mesh silica gel at medium pressure. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer. ESI-HRMS data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source. Optical rotation was obtained on a Rudolph Research Analytical (Atopol I). HPLC analysis was performed on Agilent 1260 series. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon. Anhydrous toluene and THF (Tetrahydrofuran) were distilled from sodium benzophenone prior to use. Anhydrous DCE and 1, 4-dioxane was distilled from calcium hydride and stored under argon.

2. Screening of the reaction conditions

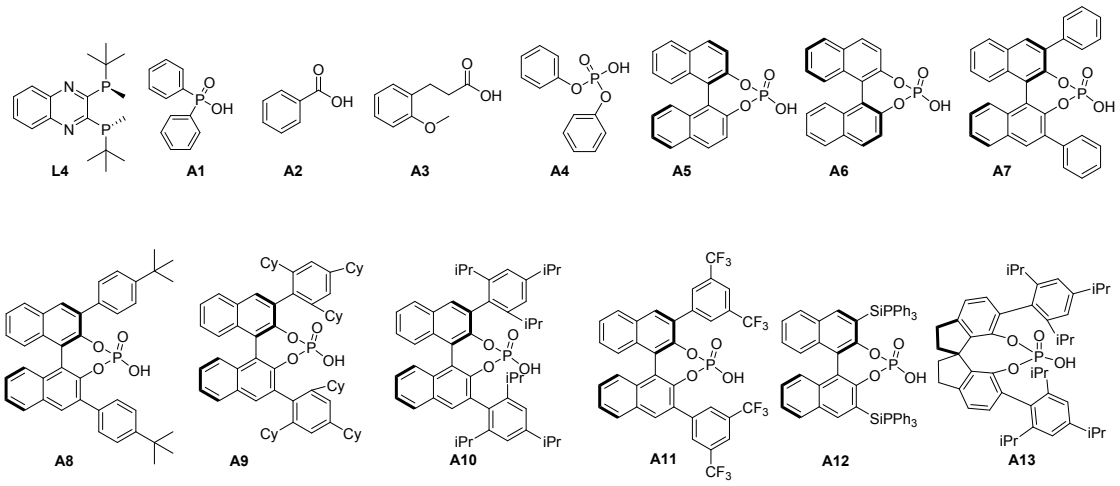
1) Table S1. Screening of acids



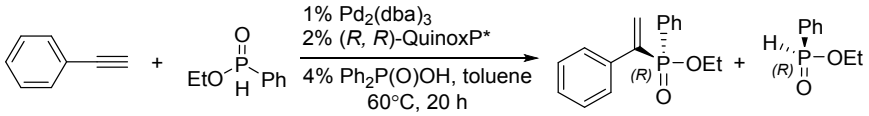
1a, 0.25 mmol **2a**,1.0 mmol **3aa**

entry	Acid	T/°C	**3aa** (yield %, ee %)
1	**A1**	60	70, 83
2	**A2**	60	44, 76
3	**A3**	60	44, 84
4	**A4**	60	65, 77
5[b]	**A5**	70	50, 57
6[b]	**A6**	70	56, 56
7[b]	**A7**	70	50, 64
8[b]	**A8**	70	55, 72
9[b]	**A9**	70	92, 77
10[b]	**A10**	70	76, 84
11[b]	**A10**	60	44, 83
12[b]	**A11**	70	57, 45
13[b]	**A12**	70	20, 81
14[b]	**A13**	70	54, 80

[a]Condition: 1 mol % $Pd_2(dba)_3$, 2 mol % **L4**, and 4 mol % **Acid** in toluene were stirred for 10 min in argon atmosphere. 0.25 mmol alkyne and 1 mmol ethyl phenylphosphinate were added. The mixture was stirred under argon atmosphere for 20 h. [b] 24 h.



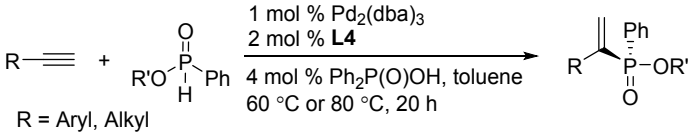
2) Table S2. Screening of the ratio of 1a/2a



entry	Alkyne/P-H	T/°C	***R*-2a** (yield %, ee%)	**3aa** (yield %, ee%)	***S***
1	1/1	60	40, 61	50, 55	6
2	3/1	60	16, 53	51, 59	6
3	1/1	50	72, 16	18, 74	8
4	1/1	40	63, 7	9, 80	10
5	1/3	60	-	59, 78	-
6	1/4	60	-	70, 83	-
7	1/6	60	-	34, 85	-

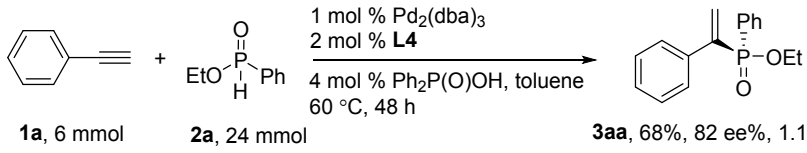
[a]Condition: 1 mol % $Pd_2(dba)_3$, 2 mol % (*R, R*)-QuinoxP, and 4 mol % diphenylphosphinic acid in 1mL toluene were stirred for 10 min in argon atmosphere. Alkynes and ethyl phenylphosphinates were added, and the mixture was stirred at 60 °C for 20h.

3. **Typical procedure for hydrophosphination of alkynes**



An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with 1 mol % $Pd_2(dba)_3$ (2.3 mg), 2 mol % (*R*, *R*)-QuinoxP* (1.7 mg), 4 mol % diphenylphosphinic acid (2.2 mg) in 1 mL toluene under argon atmosphere and stirred at room temperature for 10 min. Then, 0.25 mmol alkynes and 1 mmol H-phosphinate were added and the mixture was stirred at 60 °C or 80 °C for 20 h. After removal of the solvent, the residues were passed through a short silica chromatography (EA / PE = 1:3) to afford the desired product.

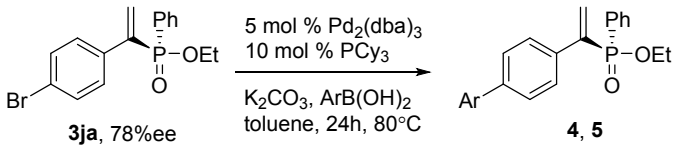
4. **Gram-scale alkenylphosphinate synthesis**



An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with 1 mol % $Pd_2(dba)_3$ (54.9 mg), 2 mol % (*R*, *R*)-QuinoxP*(40.0 mg), 4 mol % diphenylphosphinic acid (52.3 mg) in 24 mL toluene under argon atmosphere and stirred at room temperature for 10 min. Then, 6.0 mmol alkynes

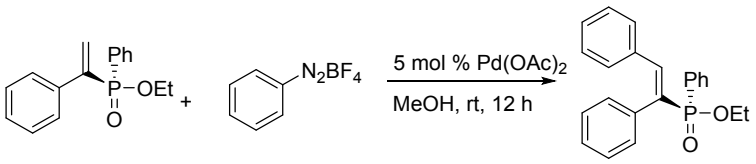
(616 mg) and 24 mmol ethyl phenylphosphinate (4.08 g) were added and the mixture was stirred at 60 ^{o}C for 48 h. After removal of the solvent, the residues were passed through a short silica chromatography (EA / PE = 1:3) to afford the desired product **3aa** (1.11 g, 68% yield). The enantioselective excess of the product was determined to be 82% ee by chiral HPLC.

5. Synthetic transformation of the products



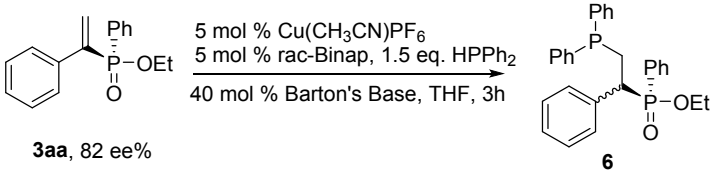
3ja, 78%ee **4**, **5**

An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with 5 mol % $Pd_2(dba)_3$ (4.6 mg), 10 mol % PCy_3 (2.8 mg), 2 eq K_2CO_3 (0.2 mmol) in 1 mL toluene under argon atmosphere and stirred at room temperature for 10 min. Then, 0.1 mmol **3ja** (35.0 mg) and 0.2 mmol $ArB(OH)_2$ were added and the mixture was stirred at 80 ^{o}C for 20 h. After removal of the solvent, the residues were passed through a short silica chromatography (EA / PE = 1:3) to afford the desired product **4** (98%, 77% ee) and **5** (75%, 77% ee).



3aa, 83 %ee **3qa**, 99%, 82 ee%

An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with 5 mol % $Pd(OAc)_2$ (1.1 mg) in 1 mL CH_3OH under argon atmosphere. Then, 0.1 mmol **3aa** (27.2 mg) and 0.12 mmol PhN_2BF_4 (23 mg) were added and the mixture was stirred at rt for 12 h. After removal of the solvent, the residues were passed through a short silica chromatography (EA / PE = 1:3) to afford the desired product **3qa** (34.7 mg, 99% yield, 82% ee).

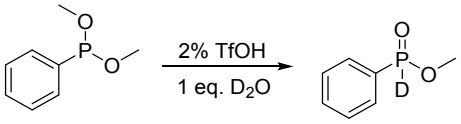


3aa, 82 ee% **6**

An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with $[Cu(CH_3CN)_4]PF_6$

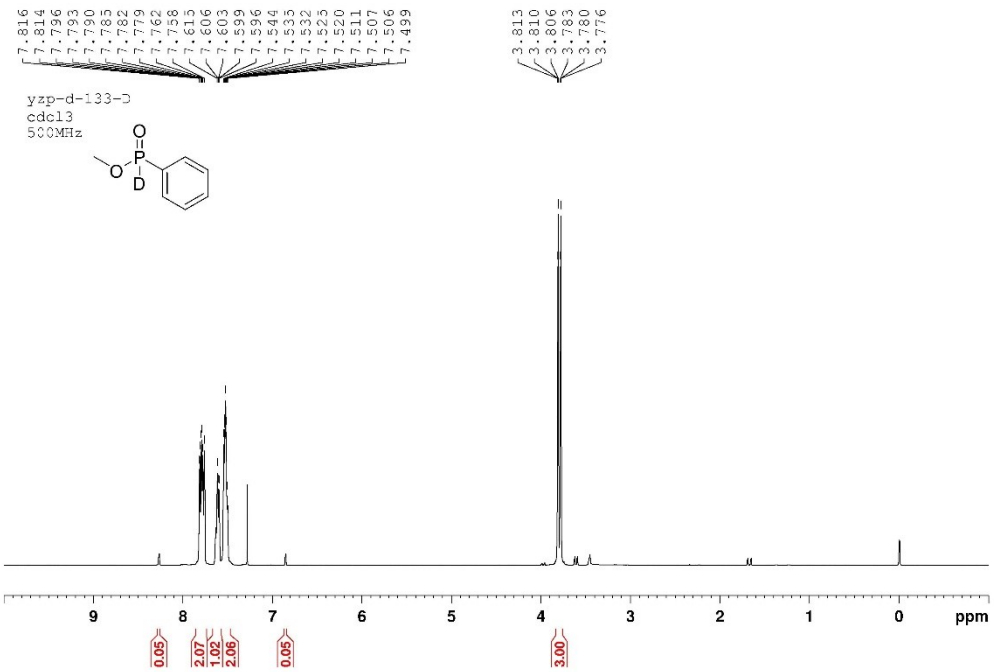
(1.8 mg) and rac-Binap (3.1 mg) in a glove box under argon atmosphere. Anhydrous THF (1.0 mL, 0.10 M) was added. The mixture was stirred at room temperature for 15 minutes. Then **3aa** (27.2 mg) and $HPPh_2$ (28.0 mg) were added sequentially. Then the Schlenk tube was taken out of the glove box. After the mixture was cooled to 0 °C, Barton's Base (8μL) was added. The resulting reaction mixture was stirred at 0 °C for 3 hours. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (EA / PE = 1:3) to give the desired product **6** (42.0 mg, 92% yield, major 79% ee, minor 79% ee).

6. Deuterium labelling experiment



column chromatography，56% D
solvent and TfOH extracted by pump， 90% D

To an oven-dried vial fitted with a stirrer bar was added dimethyl phenylphosphonite (1.70 g, 10 mmol), 1 equiv. H_2O (180 uL), trifluorormethanesulfonic acid (18 uL, 2 mol%) under argon atmosphere. The tube was then sealed, slightly shaken at room temperature, in 5 minutes. Solvent and trifluorormethanesulfonic acid were extracted by pump. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.71 (m, 2H), 7.63-7.55 (m, 2H), 7.55-7.46 (m, 2H), 3.82-3.73 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.2 (t, J = 2.8), 130.9 (t, J = 11.8), 128.7 (t, J = 13.9), 52.0 (d, J = 6.5 Hz). ^{31}P NMR (160 MHz, $CDCl_3$): δ 26.6 (t, J = 85.9).


7.816
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7.796
7.793
7.790
7.785
7.782
7.779
7.762
7.758
7.615
7.606
7.603
7.599
7.596
7.544
7.535
7.532
7.525
7.520
7.511
7.507
7.506
7.499
3.813
3.810
3.806
3.783
3.780
3.776
yzp-d-133-D
cdcl3
500MHz
O
P
O
D
9
8
7
6
5
4
3
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1
0
ppm
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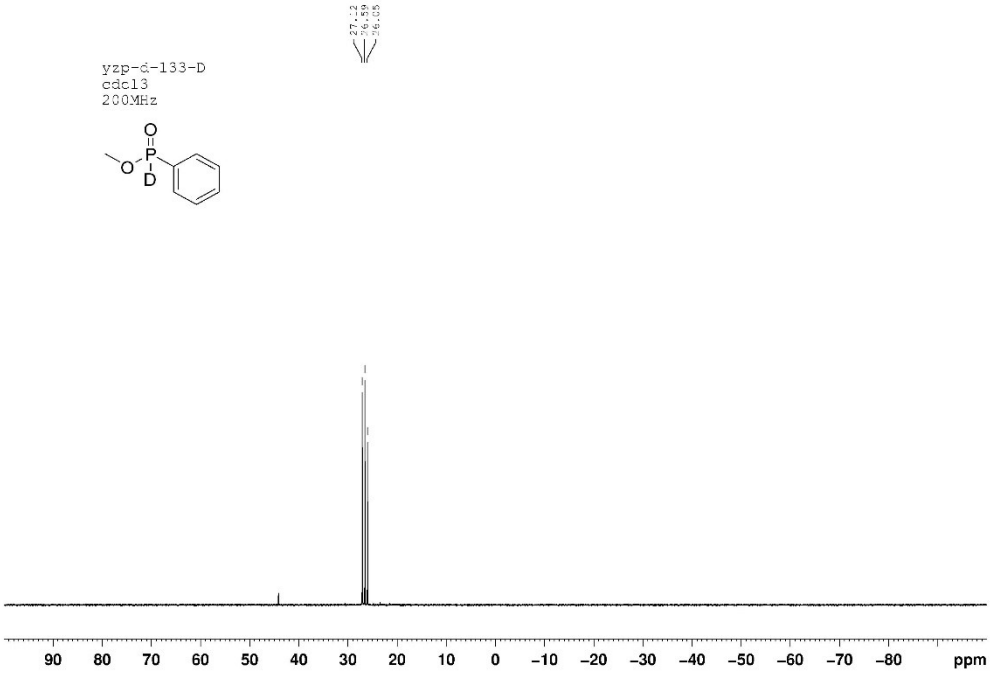
2.07
1.02
2.06
0.05
3.00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P
O
D
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80
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−70
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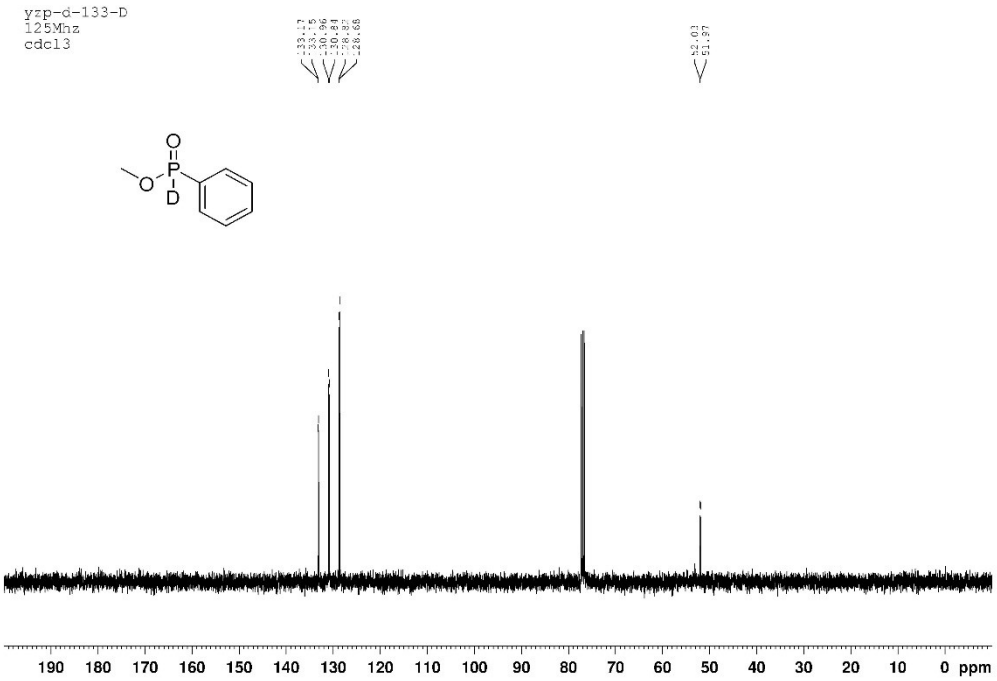
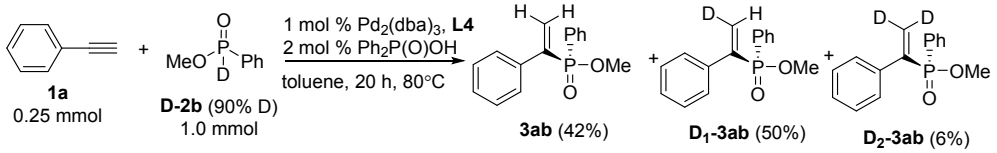
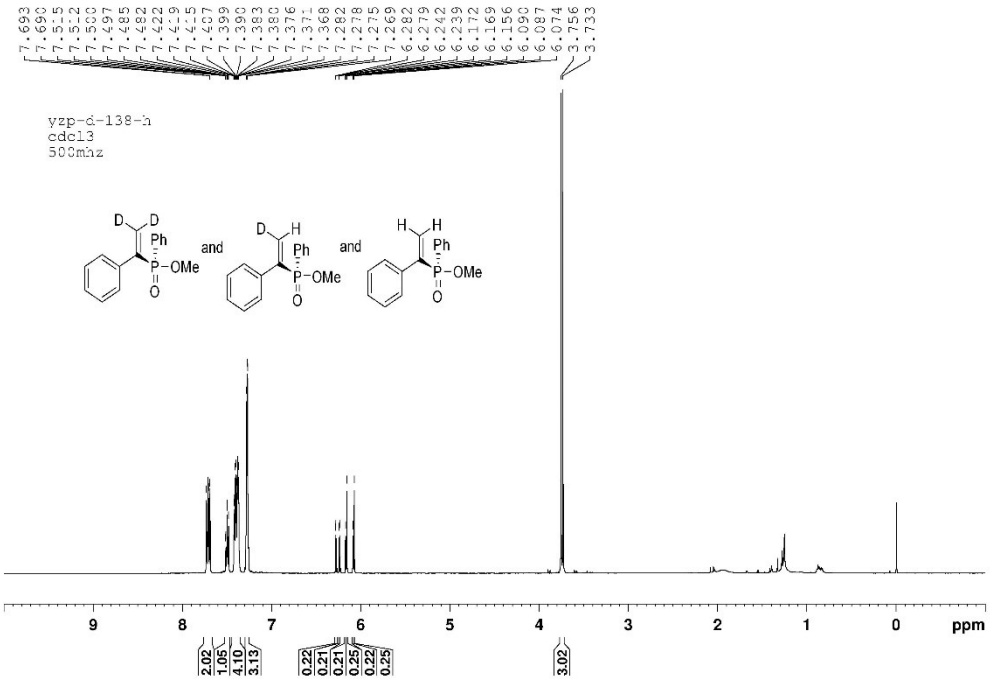
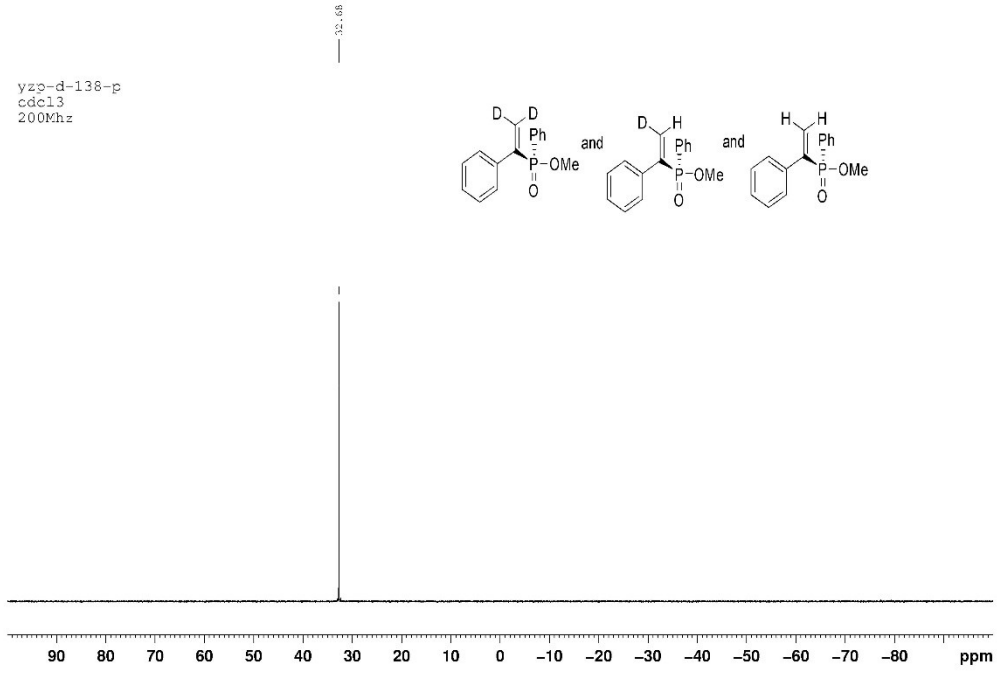
ppm





General procedure was used with phenylacetylene (25.5 mg, 0.25 mmol, 1 equiv) and D-P(O)(OMe)Ph (156 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford desired product **3ab** as colorless oil (44.0 mg, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.66 (m, 2H), 7.53 – 7.46 (m, 1H), 7.45 – 7.34 (m, 4H), 7.31 – 7.25 (m, 3H), 6.26 (dd, J = 20.1, 1.4 Hz, 0.43H), 6.13 (dd, J = 41.0, 1.4 Hz, 0.43H), 6.11 (d, J = 40.9 Hz, 0.5H), 3.74 (d, J = 11.1 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 32.7. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6 (dd, J = 125.1, 14.0 Hz), 137.0 (dd, J = 11.6, 4.0 Hz), 132.3 (d, J_{CP} = 2.8 Hz), 131.9 (d, J_{CP} = 10.1 Hz), 131.7 (d, J_{CP} = 8.6 Hz), 129.7 (d, J_{CP} = 135.3 Hz), 128.4 (d, J_{CP} = 13.2 Hz), 128.3, 128.1, 127.8 (d, J_{CP} = 4.7 Hz), 51.5 (d, J_{CP} = 6.2 Hz).


yzp-d-138-h
cdcl3
500mhz
and
and
ppm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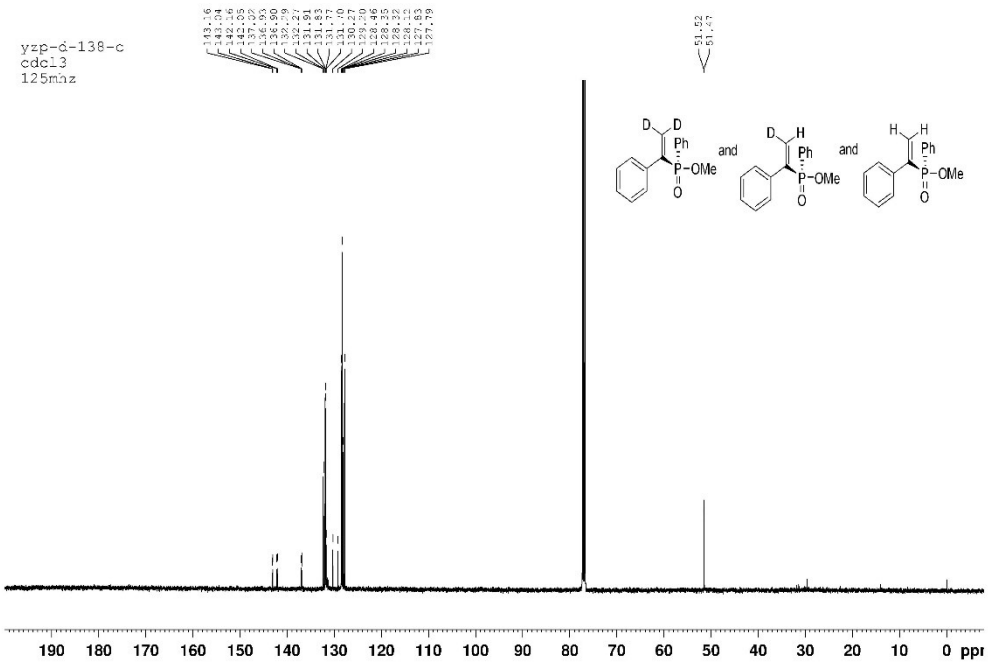
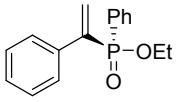
and
and
ppm



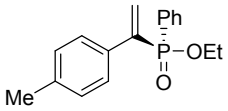
7. **Analytic data for the products**

Ethyl phenyl(1-phenylvinyl)phosphinate (3aa)



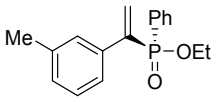
General procedure was used with phenylacetylene (25.5 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinates (170 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3aa** as colorless oil (47.6 mg, 70% yield, 83% ee). $[\alpha]^{20}_{D}$ = 3.4 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.67 (m, 2H), 7.54 – 7.46 (m, 1H), 7.44 – 7.36 (m, 4H), 7.31 – 7.26 (m, 3H), 6.27 (dd, J = 20.0, 1.5 Hz, 1H), 6.13 (dd, J = 40.7, 1.5 Hz, 1H), 4.20 – 4.04 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 30.8. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0 (d, J_{CP} = 124.7 Hz), 137.0 (d, J_{CP} = 11.8 Hz), 132.1 (d, J_{CP} = 2.7 Hz), 131.7 (d, J_{CP} = 10.0 Hz), 131.4 (d, J_{CP} = 8.3 Hz), 130.4 (d, J_{CP} = 135.3Hz), 128.3 (d, J_{CP} = 18.2 Hz), 128.2 (d, J_{CP} = 5.3 Hz), 128.0, 127.8 (d, J_{CP} = 5.1 Hz), 61.1 (d, J_{CP} = 6.0 Hz), 16.4 (d, J_{CP} = 6.5 Hz). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 17.0 min, t (minor) = 18.5 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{18}O_2P$, 273.1039; found 273.1036.

Ethyl phenyl(1-(*p*-tolyl)vinyl)phosphinate (3ba)



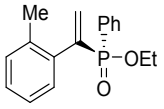
General procedure was used with 4-ethynyltoluene (29.0 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3ba** as colorless oil (50.0 mg, 70% yield, 82% ee). $[\alpha]^{20}_{D}$ = 1.9 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.66 (m, 2H), 7.53 – 7.44 (m, 1H), 7.43 – 7.34 (m, 2H), 7.32 – 7.26 (m, 2H), 7.12 – 7.04 (m, 2H), 6.23 (dd, *J* = 19.9, 1.5 Hz, 1H), 6.10 (dd, *J* = 40.9, 1.5 Hz, 1H), 4.18 – 4.01 (m, 2H), 2.30 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 31.0. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7 (d, J_{CP} = 124.5 Hz), 137.9, 134.1 (d, J_{CP} = 11.8 Hz), 132.1 (d, J_{CP} = 2.8 Hz), 131.8 (d, J_{CP} = 9.9 Hz), 130.8 (d, J_{CP} = 8.7 Hz), 130.6 (d, J_{CP} = 134.6 Hz), 129.0, 128.3 (d, J_{CP} = 12.8 Hz), 127.6 (d, J_{CP} = 4.9 Hz), 61.1 (d, J_{CP} = 5.8 Hz), 21.1, 16.4 (d, J_{CP} = 6.6 Hz). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 15.5 min, t (minor) = 17.1 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{20}OP$, 287.1195 ; found 287.1194.

Ethyl phenyl(1-(*m*-tolyl)vinyl)phosphinate (3ca)



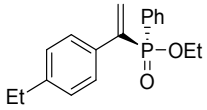
General procedure was used with 3-ethynyltoluene (29.0 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) 60 °C for 20 h to afford **3ca** as colorless oil (50.0 mg, 70% yield, 81% ee). $[\alpha]^{20}_{D}$ = 3.7 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 2H), 7.52 – 7.45 (m, 1H), 7.44 – 7.36 (m, 2H), 7.22 – 7.10 (m, 3H), 7.09 – 7.04 (m, 1H), 6.22 (dd, *J* = 20, 1.5 Hz, 1H), 6.09 (dd, *J* = 40.9, 1.5 Hz, 1H), 4.19 – 3.97 (m, 2H), 2.29 (s, 3H), 1.32 (t, *J* = 7.0 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 30.9. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1 (d, J_{CP} = 124.9 Hz), 137.8, 137.0 (d, J_{CP} = 11.7 Hz), 132.1 (d, J_{CP} = 2.7 Hz), 131.8 (d, J_{CP} = 9.7 Hz), 131.2 (d, J_{CP} = 8.4 Hz), 130.5 (d, J_{CP} = 134.3 Hz), 128.8, 128.5 (d, J_{CP} = 5.2 Hz), 128.3 (d, J_{CP} = 15.6 Hz), 128.1, 124.9 (d, J_{CP} = 4.6 Hz), 61.1 (d, J_{CP} = 5.9 Hz), 21.35, 16.4 (d, J_{CP} = 6.4 Hz). The enantiomeric excess was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (minor) = 19.3 min, t (major) = 23.5 min.HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{20}OP$, 287.1195; found 287.1194.

Ethyl phenyl(1-(*o*-tolyl)vinyl)phosphinate (3da)



General procedure was used with 2-ethynyltoluene (29.0 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3da** as colorless oil (65.0 mg, 91% yield, 30% ee). $[\alpha]^{20}_{D}$ = 5.0 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 2H), 7.53-7.47 (m, 1H), 7.40 – 7.29 (m, 2H), 7.2 – 7.14 (m, 1H), 7.14 – 7.05 (m, 2H), 7.04 – 6.95 (m, 1H), 6.41 (dd, *J* = 20.5, 1.9 Hz, 1H), 5.82 (dd, *J* = 42.2, 1.9 Hz, 1H), 4.18 – 4.07 (m, 1H), 4.04 – 3.91 (m, 1H), 1.97 (s, 3H), 1.32 (t, *J* = 7.01 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 29.6. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3 (d, J_{CP} = 125.4 Hz), 136.4 (d, J_{CP} = 9.4 Hz), 136.3 (d, J_{CP} = 4.6 Hz), 132.3 (d, J_{CP} = 8.6 Hz), 132.1, 132.0, 130.0, 129.8 (d, J_{CP} = 132.4 Hz), 129.3 (d, J_{CP} = 3.2 Hz), 128.1 (d, J_{CP} = 12.6 Hz), 127.7 (d, J_{CP} = 2.1 Hz), 125.0, 61.0 (d, J_{CP} = 6.0 Hz), 19.6, 16.3 (d, J_{CP} = 6.7 Hz). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 12.4 min, t (minor) = 13.2 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{20}OP$, 287.1195; found 287.1194.

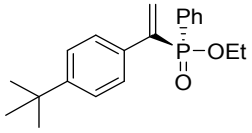
Ethyl (1-(4-ethylphenyl)vinyl)(phenyl)phosphinate (3ea)



General procedure was used with 4-ethylphenylacetylene (32.5 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3ea** as colorless oil (54.0 mg, 72% yield, 83% ee). $[\alpha]^{20}_{D}$ = 2.3 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.63 (m, 2H), 7.47 (td, *J* = 7.5, 1.3 Hz, 1H), 7.40 (td, *J* = 7.8, 3.5 Hz, 2H), 7.32 (m, 2H), 7.09 (m, 2H), 6.22 (dd, *J* = 19.9, 1.5 Hz, 1H), 6.10 (dd, *J* = 40.9, 1.5 Hz, 1H), 4.17 – 3.97 (m, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.6 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 31.1. ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 142.6 (d, J_{CP} = 124.7 Hz), 134.2 (d, J_{CP} = 11.8 Hz), 132.0 (d, J_{CP} = 2.8 Hz), 131.7 (d, J_{CP} = 10.2 Hz), 130.9 (d, J_{CP} = 8.6 Hz), 130.5 (d, J_{CP} = 135.2 Hz), 128.0 (d, J_{CP} = 80.0 Hz), 127.7, 127.6 (d, J_{CP} = 71.8 Hz), 61.0 (d, J_{CP} = 6.4 Hz), 28.4, 16.3 (d, J_{CP} = 6.4 Hz), 15.3. The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98

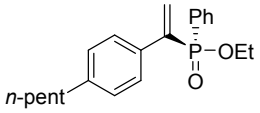
/ 2, 1.0 mL/min, λ = 254 nm, t (major) = 13.4 min, t (minor) = 14.2 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{22}O_2P$, 301.1352; found 301.1353.

Ethyl (1-(4-(*tert*-butyl)phenyl)vinyl)(phenyl)phosphinate (3fa)



General procedure was used with 4-(tert-butyl)phenylacetylene (39.5 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3fa** as colorless oil (68.9 mg, 84% yield, 81% ee). $[\alpha]^{20}_D$ = 0.9 (c 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.70 (m, 2H), 7.57 – 7.47 (m, 1H), 7.40 (td, *J* = 7.4, 3.4 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.26 (m, 2H), 6.22 (d, *J* = 20.0 Hz, 1H), 6.13 (d, *J* = 40.9 Hz, 1H), 4.16 – 4.03 (m, 2H), 1.32 (t, *J* = 7.0 Hz, 3H), 1.27 (d, *J* = 10.3 Hz, 9H). ^{31}P NMR (160 MHz, $CDCl_3$) δ 31.1. ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 142.8 (d, J_{CP} = 124.6 Hz), 134.0 (d, J_{CP} = 11.7 Hz), 132.0 (d, J_{CP} = 2.7 Hz), 131.8, 131.7, 130.9 (d, J_{CP} = 135.0 Hz), 130.8 (d, J_{CP} = 8.4 Hz), 128.3 (d, J_{CP} = 13.1 Hz), 127.5 (d, J_{CP} = 5.0 Hz), 125.2, 61.1 (d, J_{CP} = 6.2 Hz), 34.5, 31.2, 16.4 (d, J_{CP} = 6.4 Hz). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (minor) = 11.2 min, t (major) = 12.1 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{26}O_2P$, 329.1665; found 329.1665.

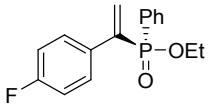
Ethyl (1-(4-pentylphenyl)vinyl)(phenyl)phosphinate (3ga)



General procedure was used with 1-ethynyl-4-pentylbenzene (43.0 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3ga** as colorless oil (46.1 mg, 54% yield, 82% ee). $[\alpha]^{20}_D$ = 1.8 (c 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.66 (m, 2H), 7.44 – 7.51 (m, 1H), 7.41 (td, *J* = 7.6, 3.5 Hz, 2H), 7.27– 7.33 (m, 2H), 7.04 – 7.12 (m, 2H), 6.25 (dd, *J* = 20.0, 1.4 Hz, 1H), 6.13 (dd, *J* = 40.9, 1.4 Hz, 1H), 4.21 – 4.00 (m, 2H), 2.65 – 2.49 (m, 2H), 1.59 (m, 2H), 1.32 (m, 7H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 31.1. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 142.7 (d, J_{CP} = 124.6 Hz), 134.2 (d, J_{CP} = 11.7 Hz), 132.0 (d, J_{CP} = 2.7 Hz),

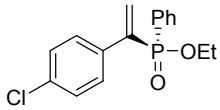
131.7 (d, J_{CP} = 10.1 Hz), 130.8 (d, J_{CP} = 8.3 Hz), 130.6 (d, J_{CP} = 134.8 Hz), 128.3, 128.2 (d, J_{CP} = 13.0 Hz), 127.6 (d, J_{CP} = 5.2 Hz), 61.1 (d, J_{CP} = 5.9 Hz), 35.5, 31.4 , 30.9, 22.4, 16.4 (d, J_{CP} = 6.7 Hz), 14.0. The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (major) = 8.3 min, t (minor) = 8.8 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{28}O_2P$, 343.1821; found 343.1822.

Ethyl (1-(4-fluorophenyl)vinyl)(phenyl)phosphinate (3ha)



General procedure was used with 4-fluorophenylacetylene (30.0 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford **3ha** as colorless oil (55.1 mg, 76% yield, 77% ee). $[\alpha]^{20}_D$ = -0.5 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.57 (m, 2H), 7.57 – 7.44 (m, 1H), 7.44 – 7.30 (m, 4H), 6.95 (t, *J* = 8.6 Hz, 2H), 6.21 (d, *J* = 19.8 Hz, 1H), 6.06 (d, *J* = 40.6 Hz, 1H), 4.19 – 3.94 (m, 2H), 1.37 – 1.24 (t, *J* = 7.0 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 30.6. ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6 (d, *J* = 248.1 Hz), 142.1 (d, *J* = 125.0 Hz), 133.0 (dd, *J* = 2.8, 11.8 Hz), 132.2 (d, *J* = 2.6 Hz), 131.8 (d, *J* = 10.2 Hz), 131.1 (d, *J* = 8.6 Hz), 130.9, 129.6 (dd, *J* = 5.3, 8.1 Hz), 128.4 (d, *J* = 12.9 Hz), 115.2 (d, *J* = 21.4 Hz), 61.2 (d, *J* = 6.0 Hz), 16.4 (d, *J* = 6.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.8. The enantiomeric excess was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 17.4 min, t (major) = 21.1 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{17}FO_2P$, 291.0945; found 291.0945.

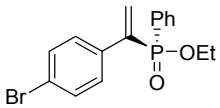
Ethyl (1-(4-chlorophenyl)vinyl)(phenyl)phosphinate (3ia)



General procedure was used with 4-chlorophenylacetylene (34.1 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford **3ia** as yellow oil (54.3 mg, 71% yield, 83% ee). $[\alpha]^{20}_D$ = -3.0 (c 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 2H), 7.52 – 7.47 (m, 1H), 7.44 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.26 – 7.21 (m, 2H), 6.23 (dd, *J* = 19.8, 1.3 Hz, 1H), 6.08 (dd, *J* = 40.4, 1.3 Hz, 1H), 4.22 – 3.96 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{31}P NMR

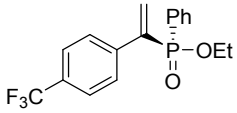
(200 MHz, $CDCl_3$) δ 30.4. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2 (d, J_{CP} = 126.0 Hz), 135.5 (d, J_{CP} = 12.0 Hz), 134.2, 132.3 (d, J_{CP} = 2.6 Hz), 131.8 (d, J_{CP} = 10.0 Hz), 131.5 (d, J_{CP} = 8.2 Hz), 130.1 (d, J_{CP} = 129.4 Hz), 128.8 (d, J_{CP} = 84.5 Hz), 128.7 (d, J_{CP} = 102.4 Hz), 128.5, 61.2 (d, J_{CP} = 5.9 Hz), 16.4 (d, J_{CP} = 6.5 Hz). The enantiomeric excess was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 19.7 min, t (major) = 25.9 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{17}ClO_2P$, 307.0649; found 307.0649.

Ethyl (1-(4-bromophenyl)vinyl)(phenyl)phosphinate (3ja)



General procedure was used with 4-bromophenylacetylene (45.2 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford **3ja** as yellow oil (69 mg, 79% yield, 79% ee). $[\alpha]^{20}_D$ = -3.7 (c 1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 12.1, 7.6 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.46 – 7.35 (m, 4H), 7.33 – 7.22 (m, 2H), 6.25 (d, *J* = 19.8 Hz, 1H), 6.10 (d, *J* = 40.3 Hz, 1H), 4.22 – 3.99 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 30.2. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2 (d, J_{CP} = 126.5 Hz), 136.0 (d, J_{CP} = 11.7 Hz), 132.3 (d, J_{CP} = 2.7 Hz), 131.8 (d, J_{CP} = 9.9 Hz), 131.5, 131.4, 130.1 (d, J_{CP} = 135.2 Hz), 129.5 (d, J_{CP} = 4.9 Hz), 128.4 (d, J_{CP} = 13.0 Hz), 122.4, 61.3 (d, J_{CP} = 6.0 Hz), 16.4 (d, J_{CP} = 6.4 Hz). The enantiomeric excess was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 22.0 min, t (major) = 30.0 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{17}BrO_2P$, 351.0144; found 351.0144.

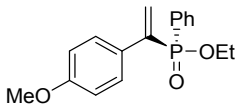
Ethyl phenyl(1-(4-(trifluoromethyl)phenyl)vinyl)phosphinate (3ka)



General procedure was used with 4-trifluoromethylphenylacetylene (42.5 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford **3ka** as yellow oil (35.8 mg, 42% yield, 82% ee). $[\alpha]^{20}_D$ = -1.2 (c 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.65

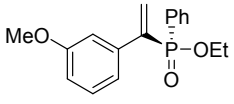
(m, 2H), 7.58 – 7.46 (m, 5H), 7.45 – 7.36 (m, 2H), 6.27 (dd, J = 19.9, 1.2 Hz, 1H), 6.13 (dd, J = 40.1, 1.2 Hz, 1H), 4.23 – 3.98 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) 30.1. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4 (d, J_{CP} = 126.3 Hz), 140.8 (d, J_{CP} = 11.7 Hz), 132.5 (d, J_{CP} = 2.2 Hz), 132.4,131.8 (d, J_{CP} = 10.4 Hz), 130.1 (q, $J_{C\text{-}F}$ = 32.8 Hz), 129.9 (d, J_{CP} = 135.5 Hz), 128.5 (d, J_{CP} = 13.4 Hz), 128.2 (d, J_{CP} = 4.4 Hz), 125.3 (q, $J_{C\text{-}F}$ =3.8 Hz), 124.0 (q, $J_{C\text{-}F}$ = 274.6 Hz), 61.4 (d, J_{CP} = 5.7 Hz), 16.4 (d, J_{CP} = 6.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7. The enantiomeric excess was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 16.7 min, t (major) = 20.2 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{17}F_3O_2P$, 341.0913; found 341.0912.

Ethyl (1-(4-methoxyphenyl)vinyl)(phenyl)phosphinate (3la)



General procedure was used with 4-ethynylanisole (33.0 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford **3la** as yellow oil (70.9 mg, 94% yield, 63% ee). $[\alpha]^{20}_D$ = 0.6 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.52 – 7.45 (m, 1H), 7.40 (td, J = 7.6, 3.5 Hz, 2H), 7.37 – 7.33 (m, 2H), 6.83 – 6.77 (m, 2H), 6.19 (dd, J = 19.9, 1.3 Hz, 1H), 6.07 (dd, J = 41.0, 1.3 Hz, 1H), 4.16 – 4.04 (m, 2H), 3.77 (s, 3H), 1.33 (t, J = 7.0 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 31.2. ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 142.7 (d, J_{CP} = 124.9 Hz), 132.1 (d, J_{CP} = 2.7 Hz), 131.8 (d, J_{CP} = 10.0 Hz), 131.2, 130.2 (d, J_{CP} = 8.6 Hz), 129.4 (d, J_{CP} = 12.1 Hz), 128.7 (d, J_{CP} = 98.1 Hz), 128.6 (d, J_{CP} = 80.2 Hz), 113.7, 61.1 (d, J_{CP} = 5.9 Hz), 55.2, 16.4 (d, J_{CP} = 6.8 Hz). The enantiomeric excess was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (minor) = 14.1 min, t (major) = 20.2 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{20}O_3P$, 303.1145; found 303.1144.

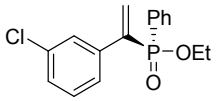
Ethyl (1-(3-methoxyphenyl)vinyl)(phenyl)phosphinate (3ma)



General procedure was used with 3-ethynylanisole (33.0 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford **3ma** as yellow oil (66.4 mg,

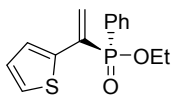
88% yield, 72% ee). $[\alpha]^{20}_D$ = 4.0 (c 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.65 (m, 2H), 7.52 – 7.45 (m, 1H), 7.39 (td, *J* = 7.5, 3.5 Hz, 2H), 7.17 (t, *J* = 7.9 Hz, 1H), 6.95 (m, 1H), 6.92 (m, 1H), 6.81 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.27 (dd, *J* = 19.8, 1.5 Hz, 1H), 6.12 (dd, *J* = 40.4, 1.5 Hz, 1H), 4.16 – 4.04 (m, 2H), 3.72 (s, 3H), 1.32 (t, *J* = 7.0 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 30.5. ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 143.0 (d, J_{CP} = 124.9 Hz), 138.6 (d, J_{CP} = 11.8 Hz), 132.2 (d, J_{CP} = 2.7 Hz), 131.8 (d, J_{CP} = 10.0 Hz), 131.6 (d, J_{CP} = 8.3 Hz) , 130.5 (d, J_{CP} = 135.0 Hz), 128.8 (d, J_{CP} = 122.7 Hz), 128.5, 120.4 (d, J_{CP} = 4.6 Hz), 114.0, 113.3(d, J_{CP} = 5.5 Hz), 61.2 (d, J_{CP} = 5.6 Hz), 55.2, 16.5 (d, J_{CP} = 6.4 Hz). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexaneds / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (major) = 10.7 min, t (minor) = 11.5 min.HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{20}O_3P$, 303.1145; found 303.1144.

Ethyl (1-(3-chlorophenyl)vinyl)(phenyl)phosphinate (3na)



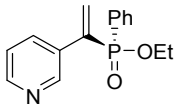
General procedure was used with 3-chlorophenylacetylene (34.1 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford **3na** as yellow oil (37.8 mg, 50% yield, 78% ee). $[\alpha]^{20}_D$ = -3.6 (c 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.74 (m, 2H), 7.53 – 7.47 (m, 1H), 7.44 – 7.38 (m, 2H), 7.38 – 7.33 (m, 1H), 7.31 – 7.27 (m, 1H), 7.25 – 7.22 (m, 1H), 7.22 – 7.17 (m, 1H), 6.25 (dd, *J* = 19.8, 1.2 Hz, 1H), 6.09 (dd, *J* = 40.2, 1.2 Hz, 1H), 4.18 – 4.00 (m, 2H), 1.33 (t, *J* = 7.03 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 30.2. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2 (d, J_{CP} = 126.5 Hz), 138.8 (d, J_{CP} = 12.0 Hz), 134.1, 132.4 (d, J_{CP} = 2.8 Hz), 132.0 (d, J_{CP} = 8.2 Hz), 131.8 (d, J_{CP} = 10.1 Hz), 130.0 (d, J_{CP} = 135.4 Hz), 129.5, 128.4 (d, J_{CP} = 12.6 Hz), 128.2, 127.9 (d, J_{CP} = 5.1 Hz), 126.1 (d, J_{CP} = 4.5 Hz), 61.3 (d, J_{CP} = 6.0 Hz), 16.4 (d, J_{CP} = 6.6 Hz). The enantiomeric excess was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 14.2 min, t (major) = 16.0 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{17}ClO_2P$, 307.0649; found 307.0649.

Ethyl phenyl(1-(thiophen-2-yl)vinyl)phosphinate (3oa)



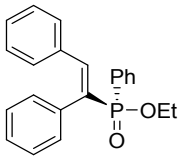
General procedure was used with 2-ethynylthiophene (27 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford **3oa** as yellow oil (50.7 mg, 73% yield, 84% ee). $[\alpha]^{20}_D$ = 5.4 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.68 (m, 2H), 7.54 – 7.46 (m, 2H), 7.44 – 7.39 (m, 2H), 7.25 – 7.21 (m, 1H), 7.21 – 7.16 (m, 1H), 6.25 (d, *J* = 22.4 Hz, 1H), 6.19 (s, 1H), 4.18 – 4.07 (m, 2H), 1.35 (t, *J* = 6.9 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 30.7. ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1 (d, J_{CP} = 81.1 Hz) , 136.6 (d, J_{CP} = 32.4 Hz), 132.2 (d, J_{CP} = 2.8 Hz), 131.6 (d, J_{CP} = 10.4 Hz), 130.6 (d, J_{CP} = 136.2 Hz), 129.4 (d, J_{CP} = 7.6 Hz), 128.4 (d, J_{CP} = 12.8 Hz), 126.5 (d, J_{CP} = 6.6 Hz), 125.6, 123.9 (d, J_{CP} = 4.6 Hz), 61.2 (d, J_{CP} = 5.6 Hz), 16.4 (d, J_{CP} = 6.4 Hz). The enantiomeric excess was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 23.8 min, t (major) = 28.4 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{16}O_2PS$, 279.0603; found 279.0602.

Ethyl phenyl(1-(pyridin-3-yl)vinyl)phosphinate (3pa)



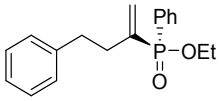
General procedure was used with 3-ethynylpyridine (25.7 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford **3pa** as yellow oil (30.0 mg, 44% yield, 86% ee). $[\alpha]^{20}_D$ = -2.3 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 21.0 Hz, 2H), 7.82 – 7.73 (m, 1H), 7.73 – 7.63 (m, 2H), 7.53 – 7.45 (m, 1H), 7.40 (td, *J* = 7.6, 3.6 Hz, 2H), 7.21 (dd, *J* = 7.7, 4.8 Hz, 1H), 6.29 (dd, *J* = 19.8, 1.1 Hz, 1H), 6.12 (dd, *J* = 40.1, 1.1 Hz, 1H), 4.20 – 3.95 (m, 2H), 1.35 (t, *J* = 7.6 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 29.9. ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 148.5 (d, J_{CP} = 5.6 Hz), 140.4 (d, J_{CP} = 126.7 Hz), 135.3 (d, J_{CP} = 3.8 Hz), 132.5 (d, J_{CP} = 2.7 Hz), 132.4 (d, J_{CP} = 7.5 Hz), 131.8 (d, J_{CP} = 10.0 Hz), 129.7 (d, J_{CP} = 135.4 Hz), 128.6 (d, J_{CP} = 12.8 Hz), 123.0, 61.4 (d, J_{CP} = 6.0 Hz), 16.4 (d, J_{CP} = 6.4 Hz). The enantiomeric excess was determined by Daicel Chiralcel AD (0.46 cm x 25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (minor) = 18.9 min, t (major) = 20.0 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{17}NO_2P$, 274.0991; found 274.0990.

Ethyl (*Z*)-(1,2-diphenylvinyl)(phenyl)phosphinate (3qa)



General procedure was used with diphenylacetylene (44.5 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford **3qa** as yellow oil (60.0 mg, 69% yield, 61% ee). $[\alpha]^{20}_{D}$ = 25.3 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 21.9 Hz, 1H), 7.53 – 7.64 (m, 2H), 7.46 (t, *J* = 7.1 Hz, 1H), 7.34 (td, *J* = 7.6, 3.3 Hz, 2H), 7.29 – 7.22 (m, 3H), 7.19 – 7.14 (m, 1H), 7.07 – 7.14 (m, 2H), 7.08 – 7.01 (m, 2H), 6.98 (m, 2H), 4.22 – 4.04 (m, 2H), 1.34 (t, *J* = 7.0 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 30.7. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6 (d, J_{CP} = 10.0 Hz), 135.5 (d, J_{CP} = 9.1 Hz), 134.7 (d, J_{CP} = 19.0 Hz), 134.3 (d, J_{CP} = 127.1 Hz), 132.0, 131.9, 131.8 (d, J_{CP} = 2.6 Hz), 130.2, 130.1 (d, J_{CP} = 136.6 Hz), 129.4 (d, J_{CP} = 4.5 Hz), 128.6, 128.4 (d, J_{CP} = 112.2 Hz), 128.1, 127.6 (d, J_{CP} = 2.7 Hz), 60.9 (d, J_{CP} = 6.8 Hz), 16.4 (d, J_{CP} = 7.0 Hz). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 12.5 min, t (minor) = 13.7 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{22}O_2P$, 349.1352; found 349.1352.

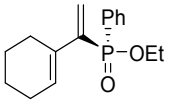
Ethyl phenyl(4-phenylbut-1-en-2-yl)phosphinate (3ra)



General procedure was used with 4-phenyl-1-butyne (32.5 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3ra** as yellow oil (45.0 mg, 60% yield, 84% ee). $[\alpha]^{20}_{D}$ = -3.6 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7. 70 (m, 2H), 7.57 – 7.51 (m, 1H), 7.47 (td, *J* = 7.5, 3.4 Hz, 2H), 7.24 (m, 2H), 7.16 (m, 1H), 7.09 (m, 2H), 6.02 (dd, *J* = 21.1, 0.8 Hz, 1H), 5.78 (dd, *J* = 43.5, 0.8 Hz, 1H), 4.16 – 3.94 (m, 2H), 2.82 – 2.64 (m, 2H), 2.60 – 2.40 (m, 2H), 1.33 (t, *J* = 7.0 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 32.8. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 141.3, 141.0, 132.2 (d, J_{CP} = 2.8 Hz), 131.8 (d, J_{CP} = 10.1 Hz), 130.3 (d, J_{CP} = 131.7 Hz), 128.7 (d, J_{CP} = 9.0 Hz), 128.5 (d, J_{CP} = 12.7 Hz), 128.3 (d, J_{CP} = 4.6 Hz), 125.9, 60.8 (d, J_{CP} = 5.5 Hz), 34.3 (d, J_{CP} = 5.5 Hz), 33.1 (d, J_{CP} = 11.8 Hz), 16.4 (d, J_{CP} = 6.3 Hz). The enantiomeric excess was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ =

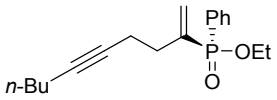
250 nm, t (minor) = 24.6 min, t (major) = 26.4 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{22}O_2P$, 301.1352; found 301.1354.

Ethyl (1-(cyclohex-1-en-1-yl)vinyl)(phenyl)phosphinate (3sa)



General procedure was used with 1-ethynylcyclohexene (26.5 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3sa** as colorless oil (38.0 mg, 55% yield, 51% ee). $[\alpha]^{20}_D$ = -4.8 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.70 (m, 2H), 7.54 – 7.47 (m, 1H), 7.47 – 7.36 (m, 2H), 6.22 (m, 1H), 5.92 (d, *J* = 8.2 Hz, 1H), 5.87 (d, *J* = 28.7 Hz, 1H), 4.16 – 3.95 (m, 2H), 2.12 – 2.08 (m, 2H), 2.08 – 2.01 (m, 2H), 1.67 – 1.55 (m, 2H), 1.55 – 1.45 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 31.0. ^{13}C NMR (125 MHz, CDCl3) δ 143.4 (d, J_{CP} = 122 Hz), 132.9 (d, J_{CP} = 10.8 Hz), 131.9 (d, J_{CP} = 2.7 Hz), 131.5 (d, J_{CP} = 133.9 Hz), 131.4 (d, J_{CP} = 10.2 Hz), 130.4 (d, J_{CP} = 5.4 Hz), 128.3 (d, J_{CP} = 12.7 Hz), 126.6 (d, J_{CP} = 8.4 Hz), 60.9 (d, J_{CP} = 5.9 Hz), 26.9 (d, J_{CP} = 6.2 Hz), 25.8, 22.6, 21.6, 16.4 (d, J_{CP} = 6.8 Hz). The enantiomeric excess was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 12.2 min, t (major) = 13.3 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{22}O_2P$, 277.1352; found 277.1352.

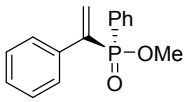
Ethyl dec-1-en-5-yn-2-yl(phenyl)phosphinate (3ta)



General procedure was used with 1,5-decadiyne (33.5 mg, 0.25 mmol, 1 equiv) and ethyl phenylphosphinatess (170 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford **3ta** as colorless oil (51.7 mg, 68% yield, 74% ee). $[\alpha]^{20}_D$ = 0.4 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.69 (m, 2H), 7.57 – 7.48 (m, 1H), 7.48 – 7.40 (m, 2H), 6.04 (d, *J* = 20.9 Hz, 1H), 5.86 (dd, *J* = 43.1, 1.2 Hz, 1H), 4.21 – 3.87 (m, 2H), 2.43 – 2.31 (m, 2H), 2.31 – 2.24 (m, 2H), 2.13 – 1.99 (m, 2H), 1.43 – 1.28 (m, 7H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 32.5. ^{13}C NMR (125 MHz, $CDCl_3$) δ

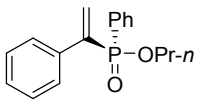
140.7 (d, J_{CP} = 125.5 Hz), 132.1 (d, J_{CP} = 2.6 Hz), 131.7 (d, J_{CP} = 10.0 Hz), 130.3 (d, J_{CP} = 132.2 Hz), 129.3 (d, J_{CP} = 8.5 Hz), 128.4 (d, J_{CP} = 12.8 Hz), 81.2, 78.5, 60.8 (d, J_{CP} = 6.1 Hz), 31.1, 31.0, 30.9, 21.8, 18.3, 17.0 (dd, J_{CP} = 163.0, 5.8 Hz), 13.5. The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 9.3, t (minor) = 10.4 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{26}O_2P$, 305.1665; found 305.1665.

Methyl phenyl(1-phenylvinyl)phosphinate (3ab)



General procedure was used with phenylacetylene (25.5 mg, 0.25 mmol, 1 equiv) and methyl phenylphosphinates (156 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3ab** as colorless oil (50.0 mg, 78% yield, 71% ee). $[\alpha]^{20}_D$ = 4.7 (c 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.66 (m, 2H), 7.53 – 7.46 (m, 1H), 7.45 – 7.34 (m, 4H), 7.31 – 7.25 (m, 3H), 6.26 (dd, *J* = 20.1, 1.4 Hz, 1H), 6.13 (dd, *J* = 41.0, 1.4 Hz, 1H), 3.74 (d, *J* = 11.1 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 32.7. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6 (d, J_{CP} = 123.2 Hz), 137.0 (d, J_{CP} = 11.6 Hz), 132.3 (d, J_{CP} = 2.7 Hz), 131.9 (d, J_{CP} = 10.1 Hz), 131.8 (d, J_{CP} = 8.7 Hz), 129.7 (d, J_{CP} = 135.1 Hz), 128.4 (d, J_{CP} = 13.4 Hz), 128.3, 128.1, 127.8 (d, J_{CP} = 4.7 Hz), 51.5 (d, J_{CP} = 6.1 Hz). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 13.3 min, t (minor) = 14.1 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{16}O_2P$, 259.0882; found 259.0883.

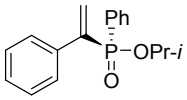
Propyl phenyl(1-phenylvinyl)phosphinate (3ac)



General procedure was used with phenylacetylene (25.5 mg, 0.25 mmol, 1 equiv) and propyl phenylphosphinates (184 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3ac** as colorless oil (50.8 mg, 71% yield, 80% ee). $[\alpha]^{20}_D$ = 3.8 (c 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.65 (m, 2H), 7.52 – 7.45 (m, 1H), 7.43 – 7.35 (m, 4H), 7.31 – 7.23 (m, 3H), 6.28 (dd, *J* = 20.0, 1.5 Hz, 1H), 6.12 (dd, *J* = 40.7, 1.5 Hz, 1H), 4.07 – 3.88 (m, 2H), 1.76 – 1.64 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{31}P NMR (200

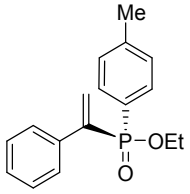
MHz, $CDCl_3$) δ 30.6. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1 (d, J_{CP} = 124.9 Hz), 137.1 (d, J_{CP} = 11.7 Hz), 132.1 (d, J_{CP} = 2.7 Hz), 131.8 (d, J_{CP} = 10.0 Hz), 131.4 (d, J_{CP} = 8.3 Hz), 130.4 (d, J_{CP} = 134.9 Hz), 128.3 (d, J_{CP} = 12.8 Hz), 128.2, 128.0, 127.8 (d, J_{CP} = 5.0 Hz), 66.5 (d, J_{CP} = 6.1 Hz), 23.8 (d, J_{CP} = 6.7 Hz), 10.1. The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 11.5 min, t (minor) = 14.5 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{20}O_2P$, 287.1195; found 287.1195.

Isopropyl phenyl(1-phenylvinyl)phosphinate (3ad)



General procedure was used with phenylacetylene (25.5 mg, 0.25 mmol, 1 equiv) and isopropyl phenylphosphinates (184 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3ad** as colorless oil (22.9 mg, 32% yield, 73% ee). $[\alpha]^{20}_D$ = 4.0 (c 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.51 – 7.45 (m, 1H), 7.43 – 7.35 (m, 4H), 7.31 – 7.17 (m, 3H), 6.24 (dd, *J* = 20.0, 1.5 Hz, 1H), 6.10 (dd, *J* = 40.7, 1.5 Hz, 1H), 4.78 – 4.57 (m, 1H), 1.32 (d, *J* = 6.2 Hz, 3H), 1.27 (d, *J* = 6.2 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 29.4. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7 (d, J_{CP} = 124.7 Hz), 137.2 (d, J_{CP} = 11.9 Hz), 132.0 (d, J_{CP} = 2.6 Hz), 131.8 (d, J_{CP} = 10.3 Hz), 131.0 (d, J_{CP} = 8.2 Hz), 130.8, 128.2, 128.1 (d, J_{CP} = 40.8 Hz), 127.9, 127.8, 70.4 (d, J_{CP} = 6.2 Hz), 24.2 (q, J_{CP} = 2.0 Hz). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 15.8 min, t (minor) = 22.7 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{20}O_2P$, 287.1195; found 287.1194.

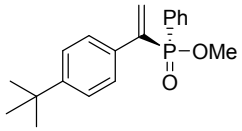
Ethyl (1-phenylvinyl)(*p*-tolyl)phosphinate (3ae)



General procedure was used with phenylacetylene (25.5 mg, 0.25 mmol, 1 equiv) and ethyl *p*-tolylphosphinate (184 mg, 1 mmol, 4 equiv) at 80 °C for 20 h to afford **3ae** as colorless oil (33.6 mg, 43% yield, 37% ee). $[\alpha]^{20}_D$ = 1.0 (c 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.43-7.37 (m, 2H), 7.30 – 7.25 (m, 3H), 7.24 – 7.18 (m, 2H), 6.24 (dd, *J* = 20.0, 1.6 Hz, 1H), 6.1 (dd, *J*

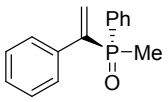
= 40.0, 1.6 Hz, 1H), 4.16 – 4.10 (m, 2H), 2.36 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 31.2. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3 (d, J_{CP} = 125.0 Hz), 142.7 (d, J_{CP} = 2.8 Hz), 137.2 (d, J_{CP} = 11.8 Hz), 131.8 (d, J_{CP} = 10.0 Hz), 131.1 (d, J_{CP} = 8.2 Hz), 129.1 (d, J_{CP} = 13.5 Hz), 128.2 128.0, 127.9, 127.8, 61.0 (d, J_{CP} = 6.0 Hz), 21.6, 16.4 (d, J_{CP} = 6.5Hz). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 13.7 min, t (minor) = 17.4 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{20}OP$, 287.1195; found 287.1194.

Methyl (1-(4-(*tert*-butyl)phenyl)vinyl)(phenyl)phosphinate (3fb)



General procedure was used with 4-(tert-butyl)phenylacetylene (39.5 mg, 0.25 mmol, 1 equiv) and methyl phenylphosphinates (156 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3fb** as colorless oil (40.0 mg, 51% yield, 71% ee). $[\alpha]^{20}_D$ = 2.9 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 2H), 7.55 – 7.46 (m, 1H), 7.45 – 7.38 (m, 2H), 7.36 – 7.27 (m, 4H), 6.22 (d, J = 1.2 Hz, 0.5H), 6.18 (d, J = 1.0 Hz, 1H), 6.10 (d, J = 1.3 Hz, 0.5H), 3.74 (d, J = 11.1, 3H), 1.28 (s, 9H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 33.2. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 142.2 (d, J_{CP} = 123.8 Hz), 133.9 (d, J_{CP} = 12.0 Hz), 132.2 (d, J_{CP} = 2.8 Hz), 131.8 (d, J_{CP} = 10.0 Hz), 131.2 (d, J_{CP} = 8.6 Hz), 130.0 (d, J_{CP} = 135.2 Hz), 128.4 (d, J_{CP} = 13.0 Hz), 127.4 (d, J_{CP} = 5.2 Hz), 125.3, 51.5 (d, J_{CP} = 6.3 Hz), 34.5, 31.2. The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 13.3 min, t (minor) = 14.1 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{24}O_2P$, 315.1508; found 315.1509.

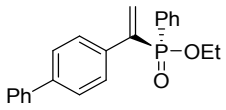
Methyl(phenyl)(1-phenylvinyl)phosphine oxide (3af)



General procedure was used with phenylacetylene (25.5 mg, 0.25 mmol, 1 equiv) and methyl(phenyl)phosphine oxide (140 mg, 1 mmol, 4 equiv) at 60 °C for 20 h to afford **3af** as colorless oil (17.0 mg, 28% yield, 54% ee). $[\alpha]^{20}_D$ = -4.1 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 –

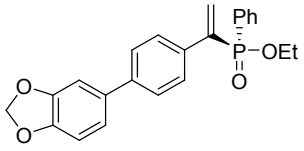
7.64 (m, 2H), 7.57 – 7.50 (m, 1H), 7.43-7.50 (m, 2H), 7.32 – 7.24 (m, 5H), 6.12 (dt, J = 8.3, 1.1 Hz, 1H), 6.07 (dd, J = 26.9, 1.1 Hz, 1H), 1.81 (d, J = 13.1 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 30.7. ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8 (d, J_{CP} = 89.1 Hz), 137.5 (d, J_{CP} = 11.0 Hz), 132.7 (d, J_{CP} = 100.8 Hz), 131.8 (d, J_{CP} = 2.7 Hz), 130.7 (d, J_{CP} = 9.4 Hz), 129.6 (d, J_{CP} = 8.2 Hz), 128.5 (d, J_{CP} = 11.6 Hz), 128.4, 128.1, 127.8 (d, J_{CP} = 4.5 Hz), 15.2 (d, J_{CP} = 74.4 Hz). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (major) = 23.4 min, t (minor) = 25.8 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{16}OP$, 243.0933; found 243.0933.

Ethyl (1-([1,1'-biphenyl]-4-yl)vinyl)(phenyl)phosphinate (4)



White solid (34.1 mg, 98% yield, 77% ee). Mp 86-87°C. $[\alpha]^{20}_D$ = -4.8 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 2H), 7.59 – 7.55 (m, 2H), 7.54 – 7.47 (m, 5H), 7.46 – 7.39 (m, 4H), 7.37 – 7.31 (m, 1H), 6.28 (d, J = 19.9 Hz, 1H), 6.19 (d, J = 40.7 Hz, 1H), 4.22 – 4.03 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 30.9. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6 (d, J = 125.2 Hz), 140.8, 140.4, 136.0 (d, J = 11.8 Hz), 132.2 (d, J = 2.8 Hz), 131.8 (d, J = 10.1 Hz), 131.2 (d, J = 7.8 Hz), 130.5 (d, J = 134.8 Hz), 128.8, 128.4 (d, J = 12.8 Hz), 128.3, 128.2, 127.4, 127.0, 61.2 (d, J = 5.9 Hz), 16.4 (d, J = 6.5 Hz). The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (minor) = 16.4min, t (major) = 17.8 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{22}O_2P$, 349.1352; found 349.1347.

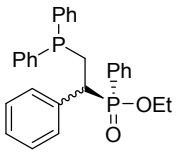
Ethyl (1-(4-(benzo[*d*][1,3]dioxol-5-yl)phenyl)vinyl)(phenyl)phosphinate (5)



Yellow oil (30.0 mg, 77% yield, 77% ee). $[\alpha]^{20}_D$ = 11.0 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.68(m, 2H), 7.51 – 7.38 (m, 7H), 7.07 – 6.99 (m, 2H), 6.89 – 6.81 (m, 1H), 6.26 (d, J = 20.0 Hz, 1H), 6.16 (d, J = 40.0 Hz, 1H), 5.97 (s, 2H), 4.23 – 3.97 (m, 2H), 1.34 (t, J = 7.0 Hz, 3H)). ^{31}P NMR (160 MHz, $CDCl_3$) δ 30.9. ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6 (d, J = 93.4 Hz) , 142.5 (d, J = 124.4

Hz), 140.5, 135.6 (d, *J* = 11.8 Hz), 134.7, 132.2 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 10.1 Hz), 131.1 (d, *J* = 8.4 Hz), 130.4 (d, *J* = 135.4 Hz), 128.4, 128.3**,** 128.2 (d, *J* = 5.1), 126.6, 120.5 , 108.5, 107.4, 101.1, 61.2 (d, *J* = 6.0 Hz), 16.4 (d, *J* = 6.5 Hz). The enantiomeric excess was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), Hexanes / IPA = 75 / 25, 1.0 mL/min, λ = 254 nm, t (minor) = 10.9min, t (major) = 14.1 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{22}O_4P$, 393.1250; found 393.1245.

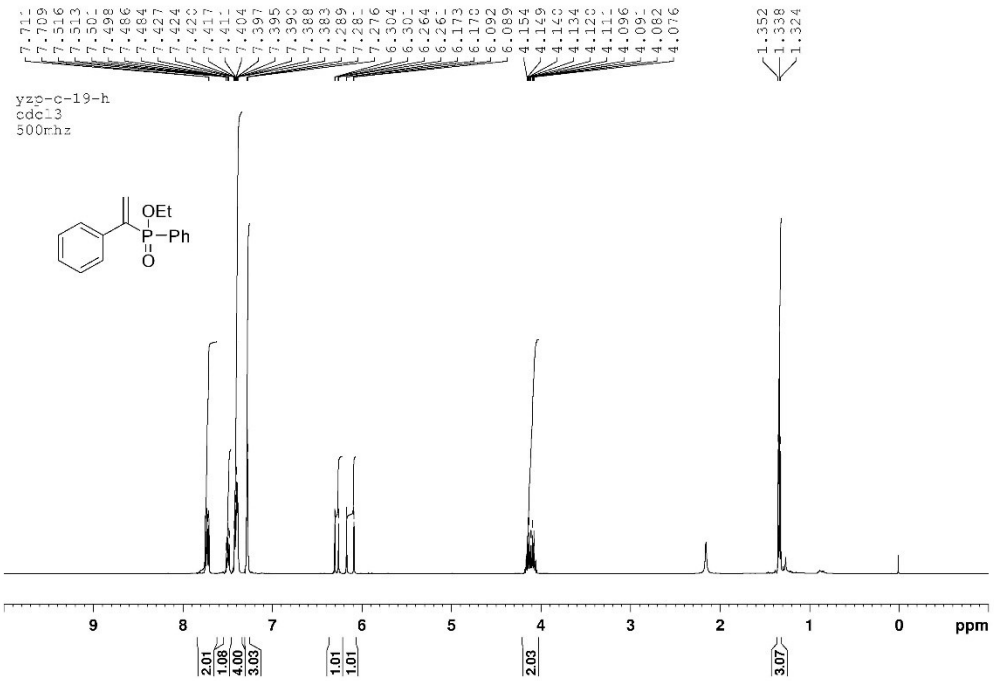
Ethyl (*S*)-(2-(diphenylphosphaneyl)-1-phenylethyl)(phenyl)phosphinate (6)

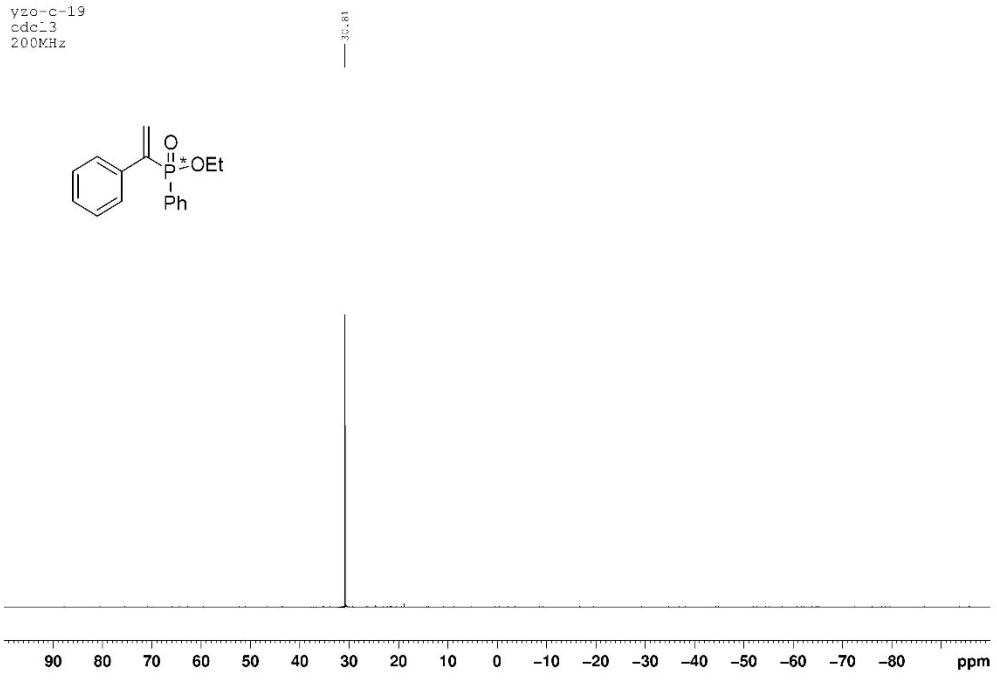


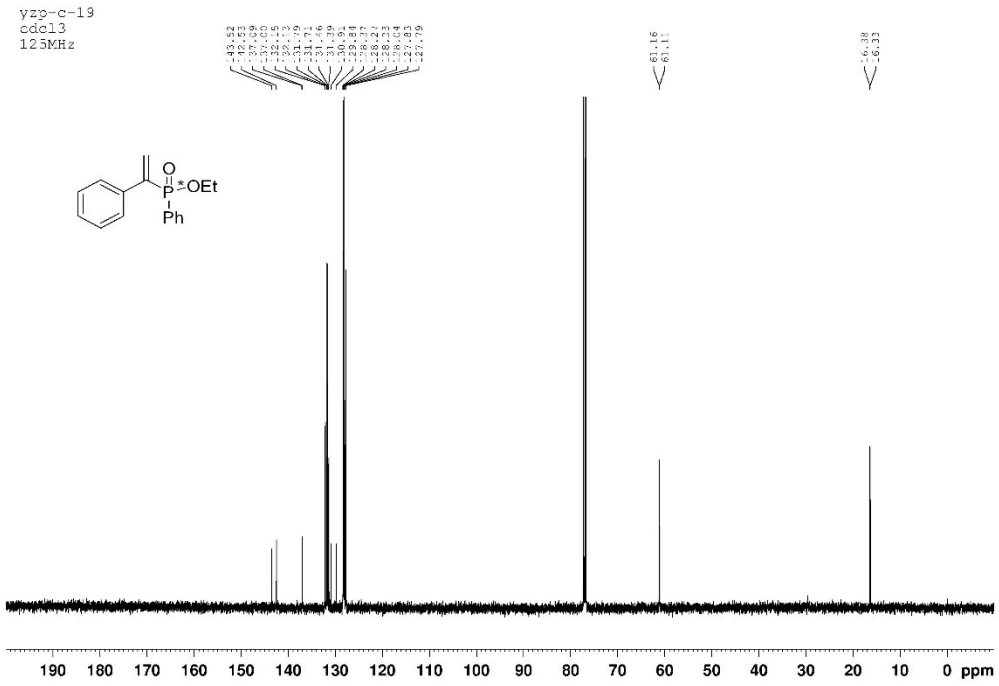
Colorless oil (42.0 mg, 92% yield, dr 3:2, major 79% ee, minor 79% ee). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 1.24H), 7.48 – 7.42 (m, 1.25H), 7.41 – 7.34 (m, 5H), 7.30 – 7.14 (m, 10.0H), 7.13 – 7.08 (m, 1.82H), 7.03 – 6.94 (m, 1.19H), 4.22 – 4.05 (m, 0.64H), 3.95 – 3.83 (m, 0.62H), 3.83 – 3.68 (m, 0.81H), 3.15 – 2.89 (m, 1.64H), 2.75 – 2.55 (m, 1.41H), 1.30 (t, *J* = 7.0 Hz, 1.88H), 1.07 (t, *J* = 7.0 Hz, 1.2H). ^{31}P NMR (200 MHz, $CDCl_3$) δ 43.1, 42.9, 41.6, 41.4, -20.2, -20.3, -20.7, -20.9. ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0 (d, *J* = 13.7 Hz), 136.8 (d, *J* = 15.0 Hz), 136.3 (d, *J* = 15.3 Hz), 135.2 (dd, *J* = 7.2, 3.1 Hz), 134.85 (t, *J* = 3.5 Hz), 133.8, 133.6, 133.4, 132.3 – 131.9 (m), 131.7 (d, *J* = 18.0 Hz), 130.1, 129.7 (d, *J* = 5.9 Hz), 129.6 (d, *J* = 6.0 Hz), 129.2, 129.1, 128.5 (d, *J* = 7.1Hz), 128.42 – 127.87 (m), 127.3 (d, *J* = 2.8 Hz), 127.1 (d, *J* = 3.2 Hz), 61.1 (t, *J* = 7.3 Hz), 44.8 (d, *J* = 15.0 Hz), 44.5 (d, *J* = 14.5 Hz), 44.1 (d, *J* = 15.0 Hz), 43.8 (d, *J* = 14.5 Hz), 27.9 (d, *J* = 15.6 Hz), 27.5 (dd, *J* = 15.6, 3.4 Hz), 16.4 (d, *J* = 6.4 Hz), 16.2 (d, *J* = 6.2 Hz). The enantiomeric excess was determined by Daicel Chiralcel IA (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 210 nm, t1 (major) = 22.1 min, t1 (minor) = 24.5 min，t2 (major) = 27.6 min, t2 (minor) = 29.6 min. HRMS (ESI-ion trap) *m/z*: $[M+H]^+$ calcd for $C_{28}H_{29}O_2P_2$, 459.1637; found 459.1630.

7. NMR spectrum

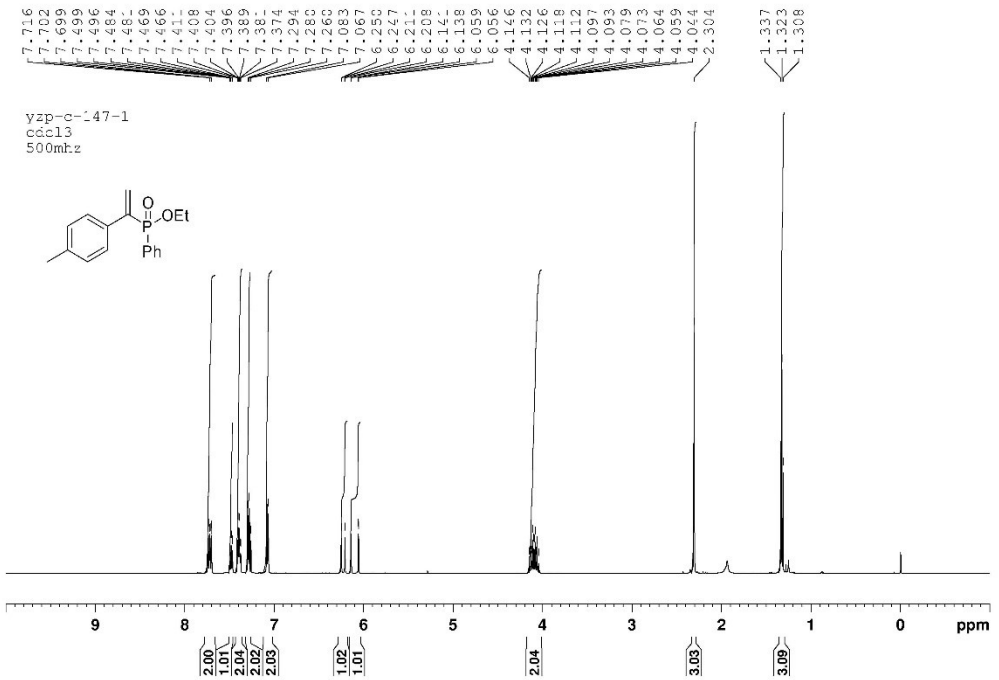
Ethyl phenyl(1-phenylvinyl)phosphinate (3aa)

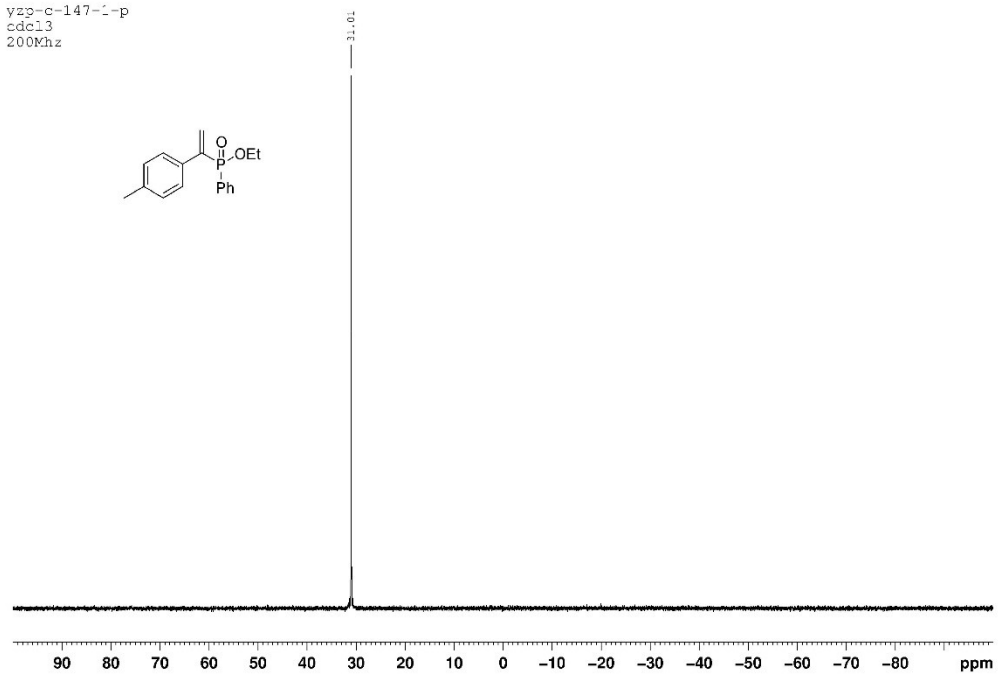

yzo-c-19-h
cdcl3
500mhz
OEt
P–Ph
O
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.08
4.00
3.03
1.01
1.01
2.03
3.07

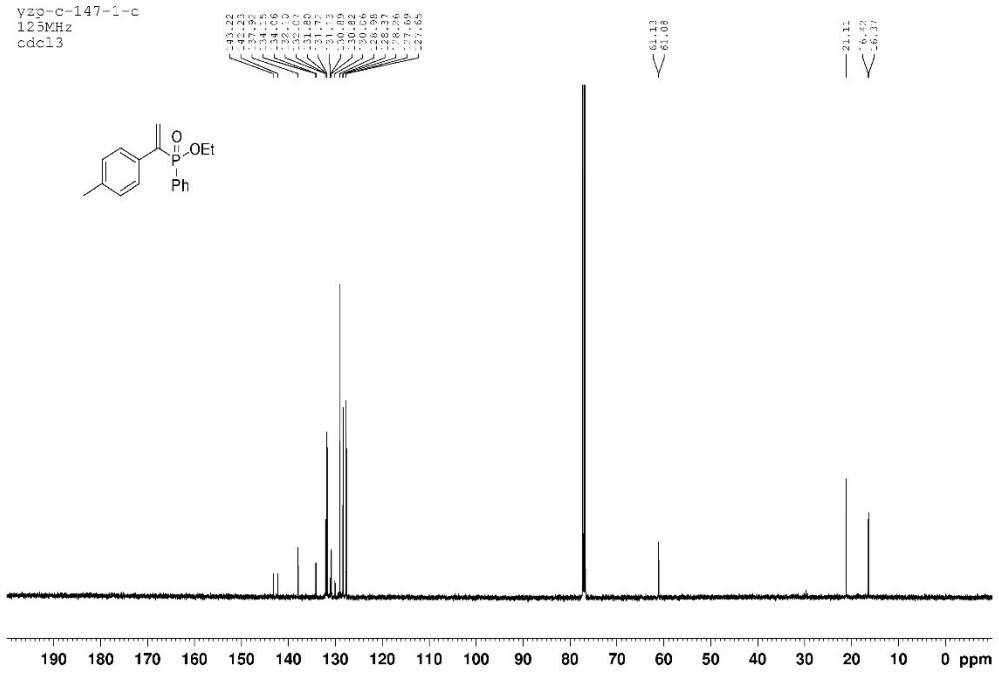

yzo-c-19
cdcl3
200MHz
O
P
OEt
Ph
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm



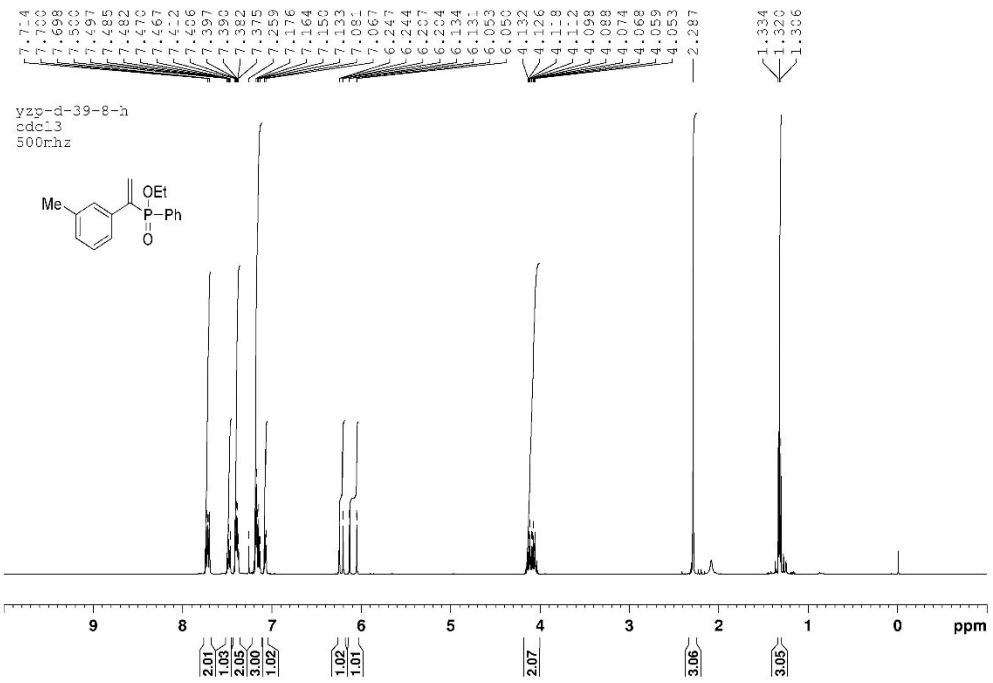
Ethyl phenyl(1-(*p*-tolyl)vinyl)phosphinate (3ba)

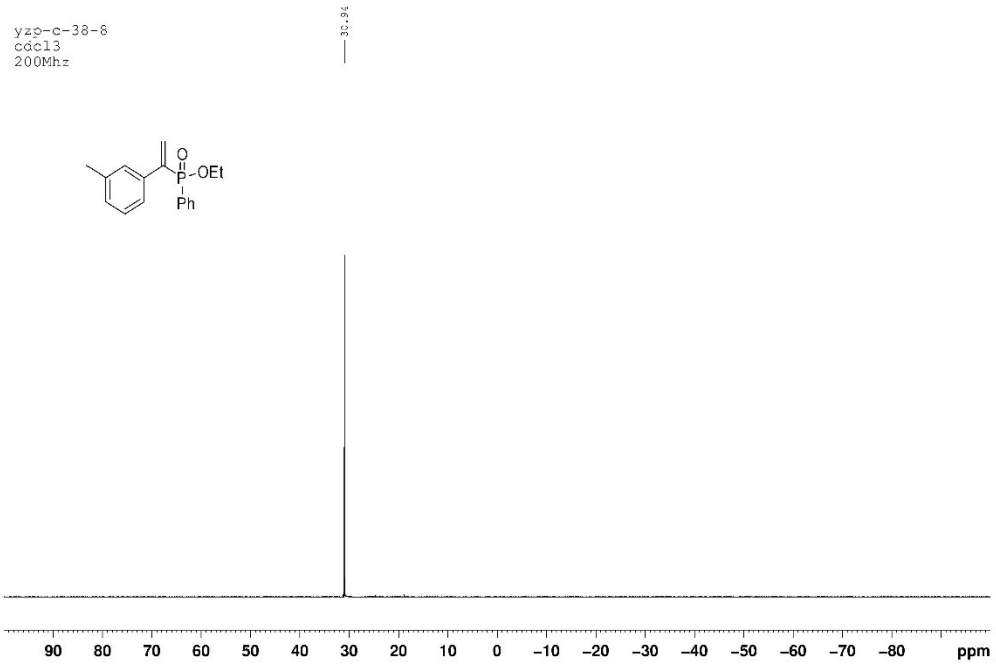


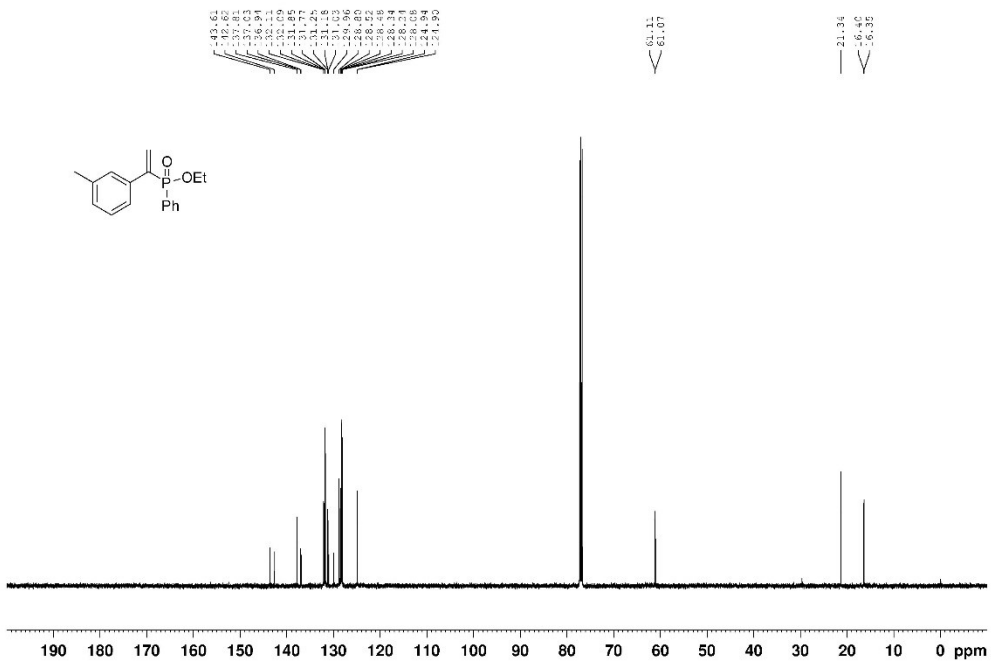




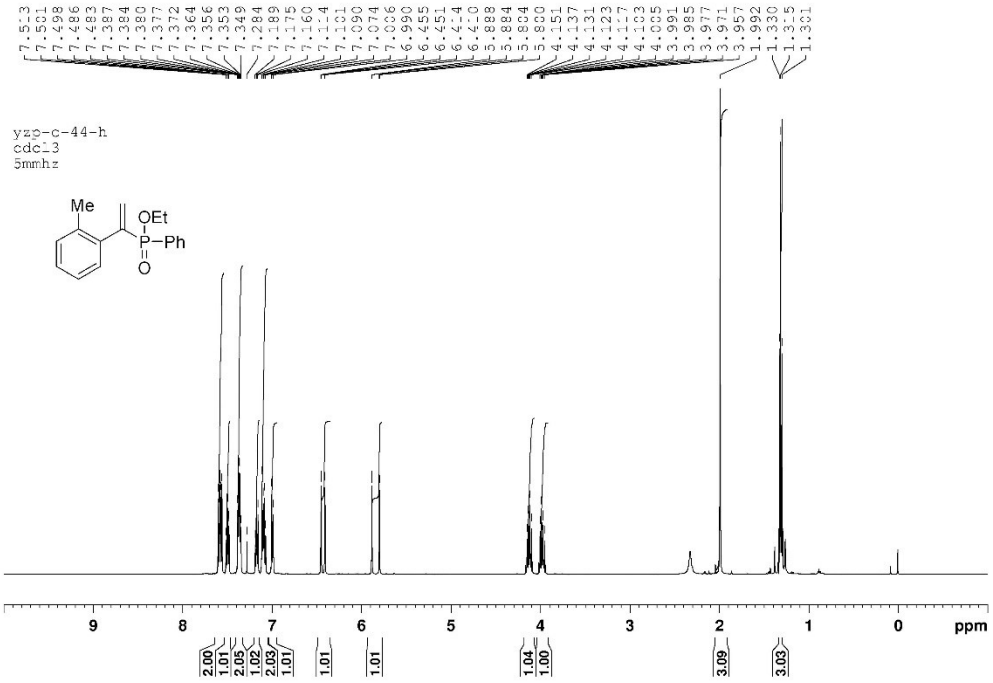
Ethyl phenyl(1-(*m*-tolyl)vinyl) phosphinate (3ca)

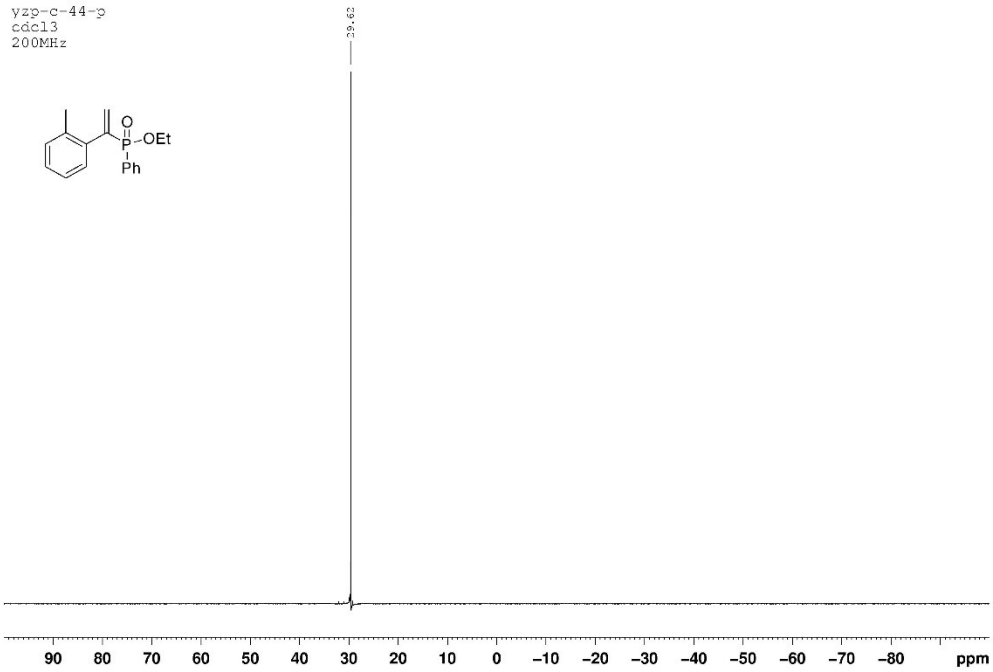

yzp-d-39-8-h
cdcl3
500mhz
Me
OEt
P–Ph
O
ppm

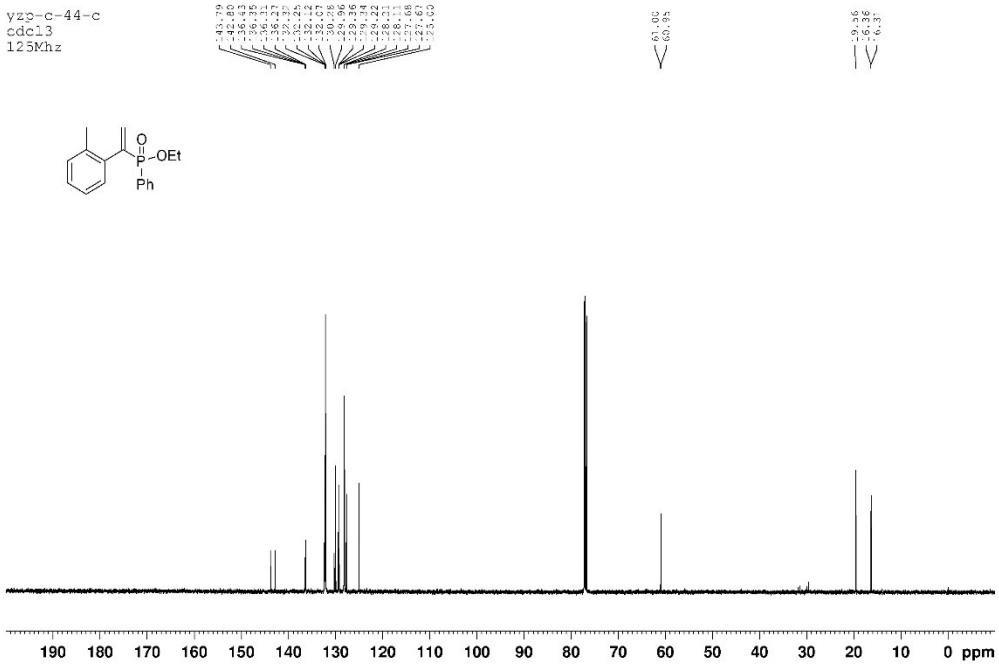

yzp-c-38-8
cdcl3
200Mhz
30.94
O
P
OEt
Ph
ppm



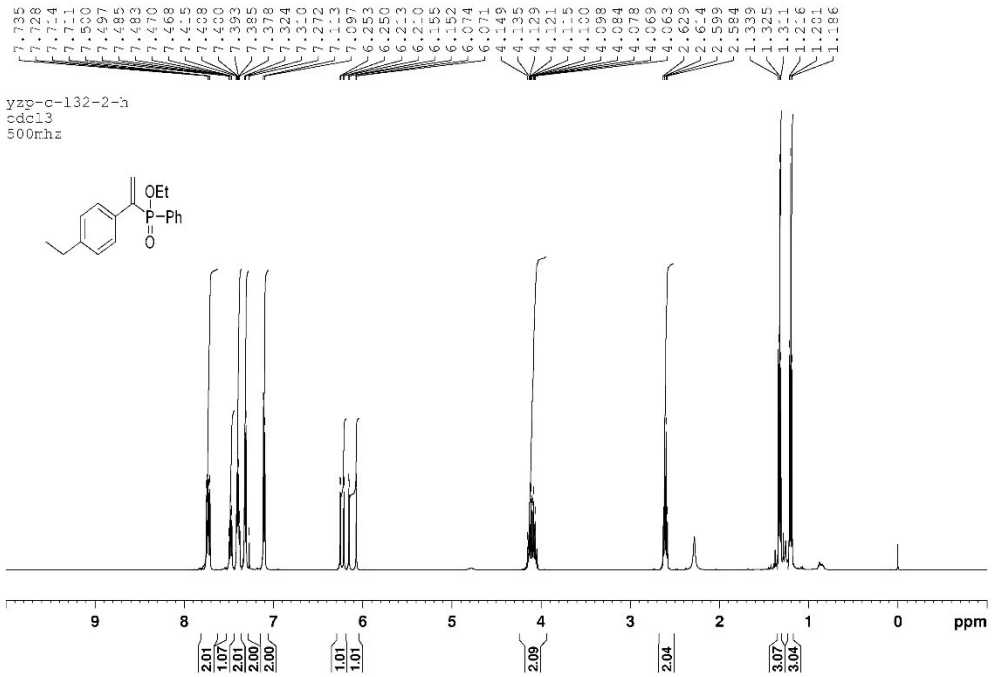
Ethyl phenyl(1-(*o*-tolyl)vinyl)phosphinate (3da)

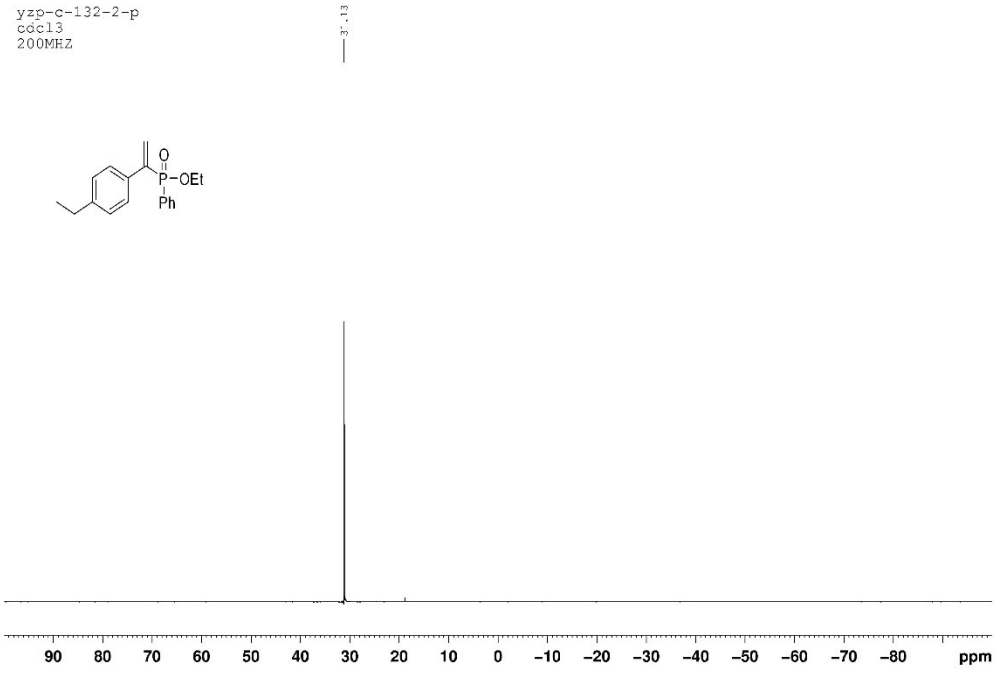

yzp-c-44-h
cdcl3
5mmhz
Me
OEt
P–Ph
O
ppm

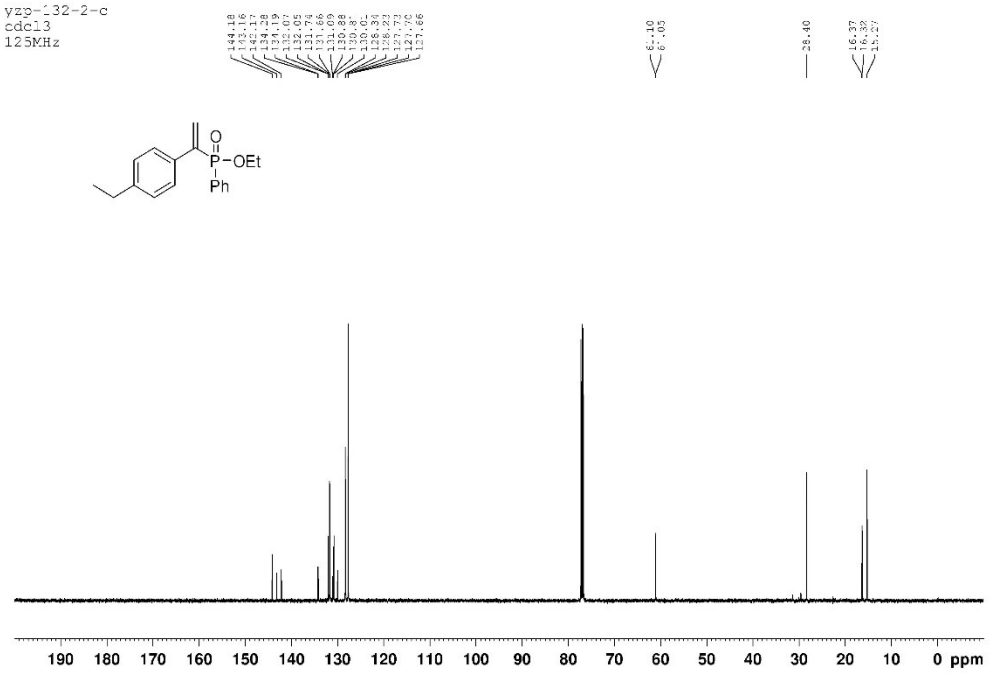

yzp-c-44-p
cdcl3
200MHz
39.62
O
P–OEt
Ph
ppm



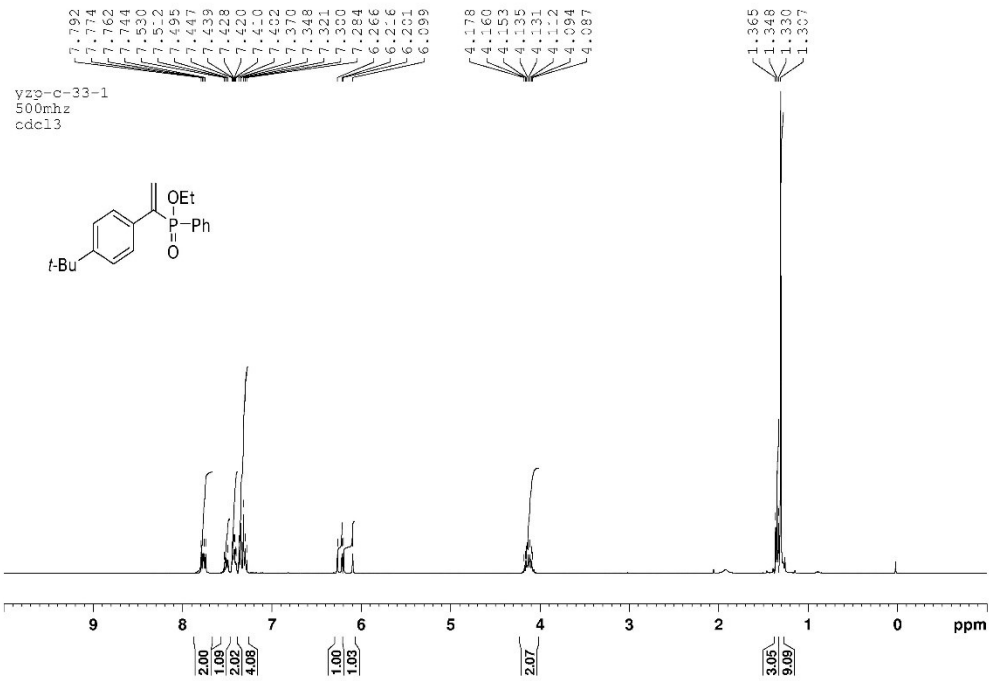
Ethyl (1-(4-ethylphenyl)vinyl)(phenyl)phosphinate (3ea)

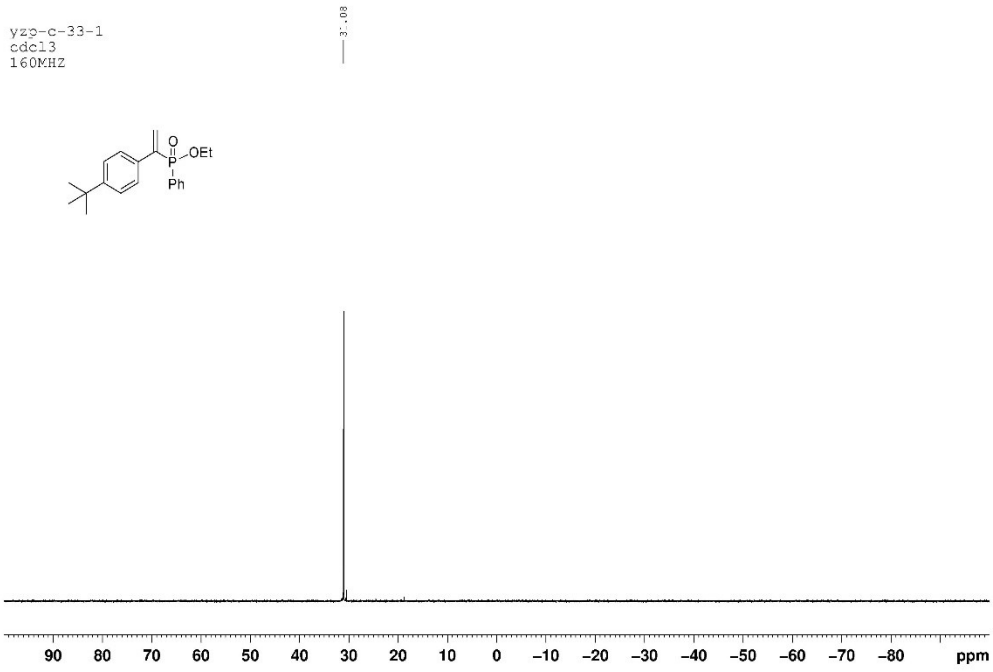


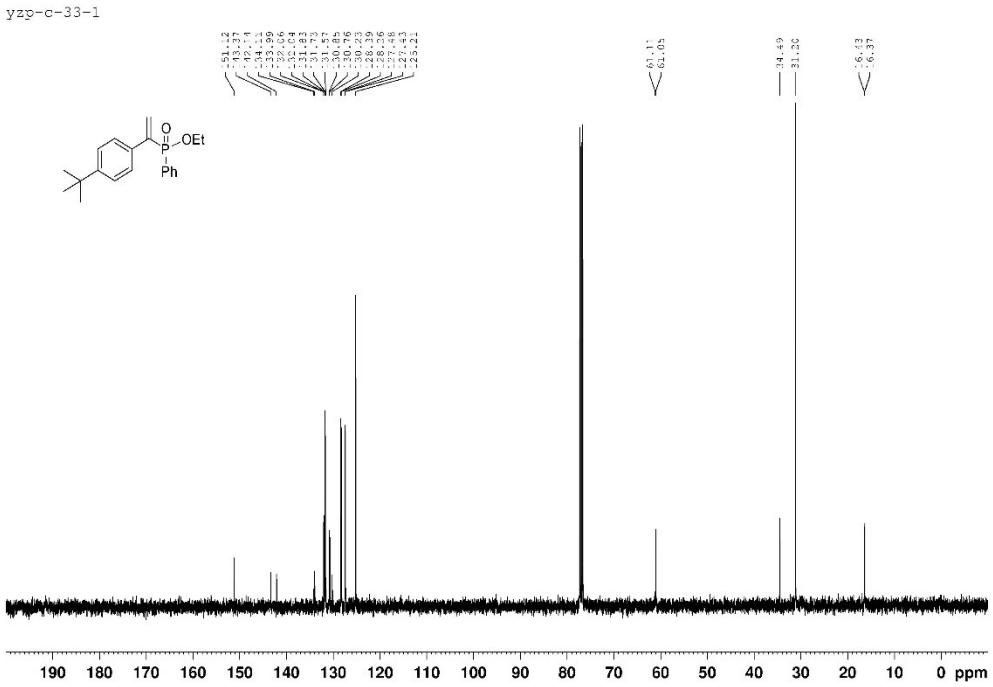

yzp-c-132-2-p
cdcl3
200MHz
31.13
O
P-OEt
Ph
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm


yzp-132-2-c
cdcl3
125MHz
144.18
143.16
140.17
134.28
134.19
132.07
132.05
131.78
131.66
131.09
130.88
130.81
130.74
128.34
128.23
127.73
127.72
127.66
127.66
61.10
61.05
28.40
16.37
16.32
15.27
O
P-OEt
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

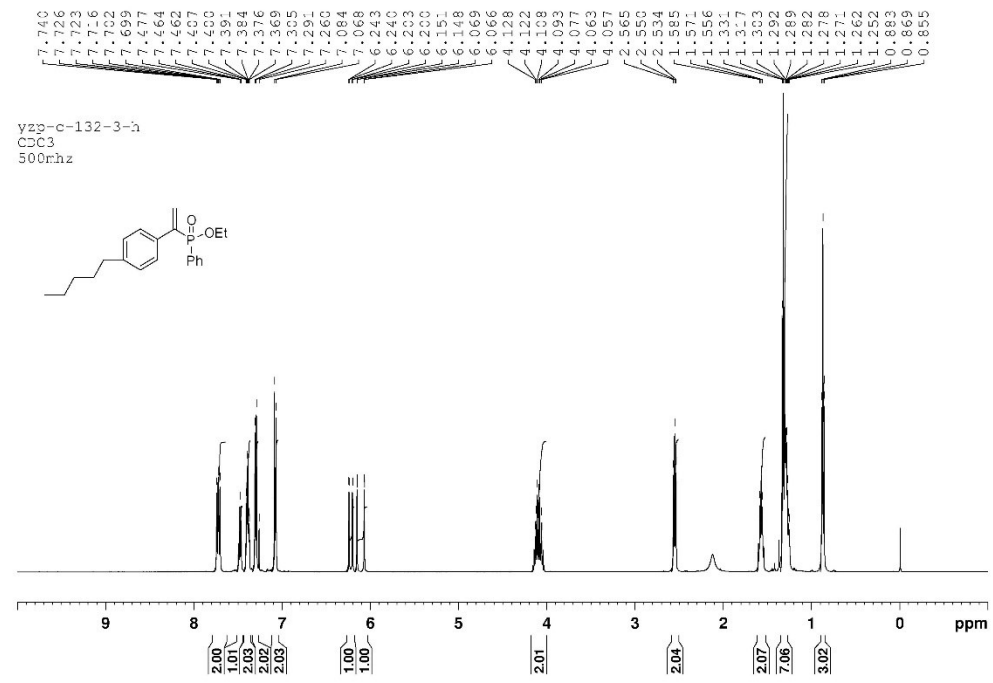
Ethyl (1-(4-(*tert*-butyl)phenyl)vinyl)(phenyl)phosphinate (3fa)

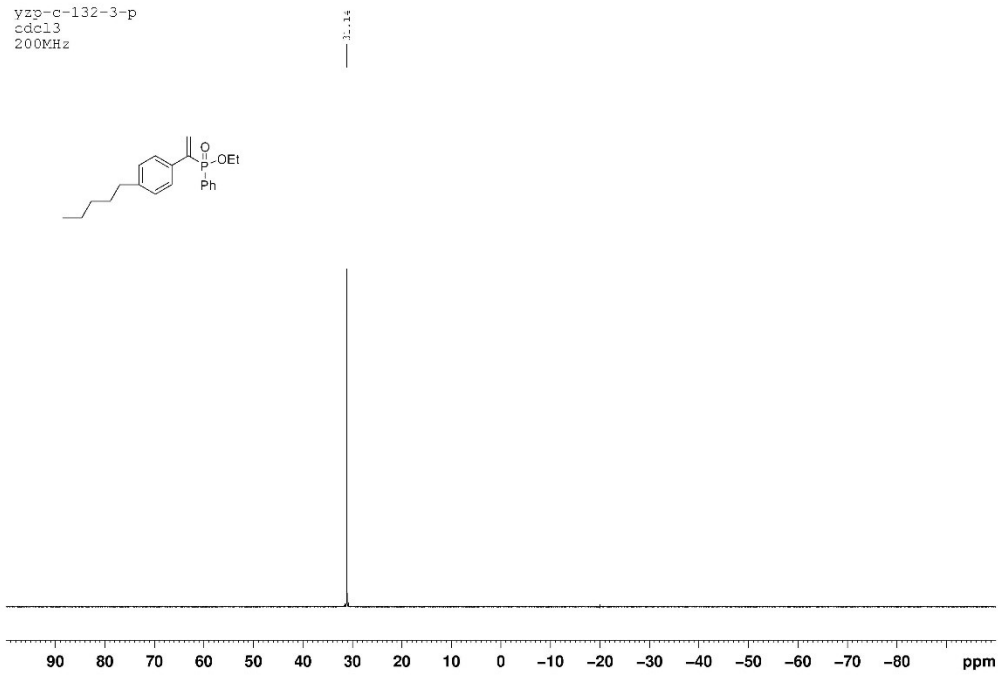


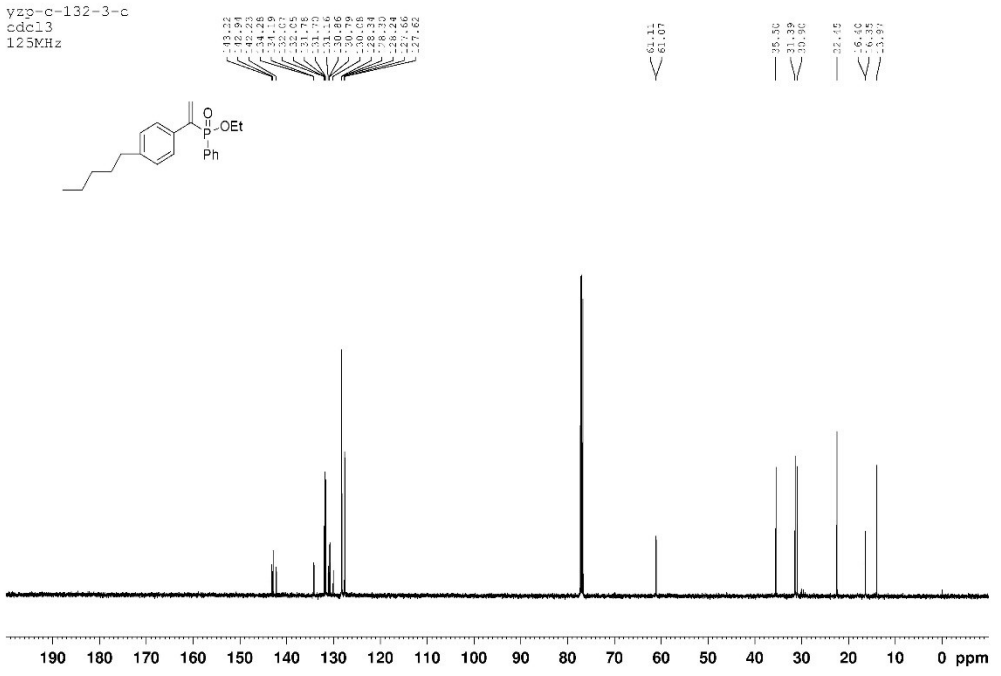




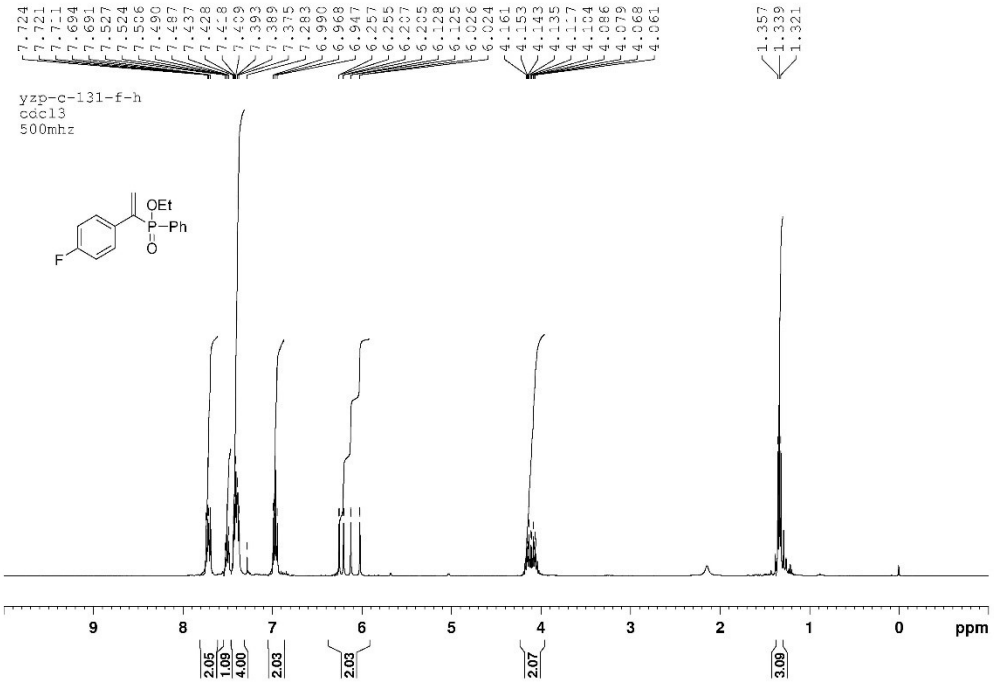
Ethyl (1-(4-pentylphenyl)vinyl)(phenyl)phosphinate (3ga)

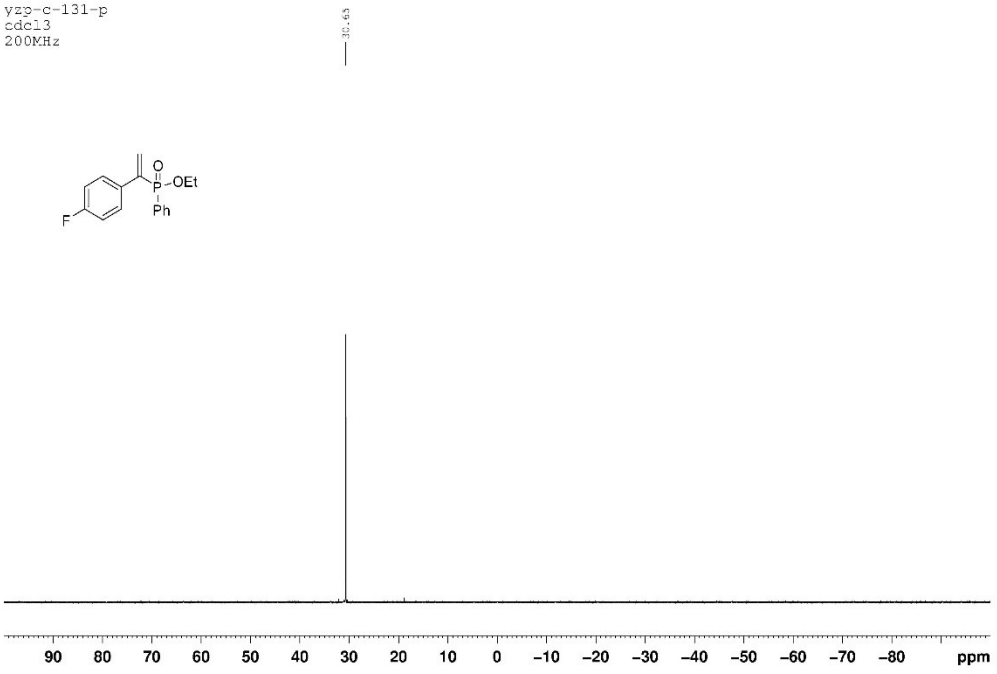


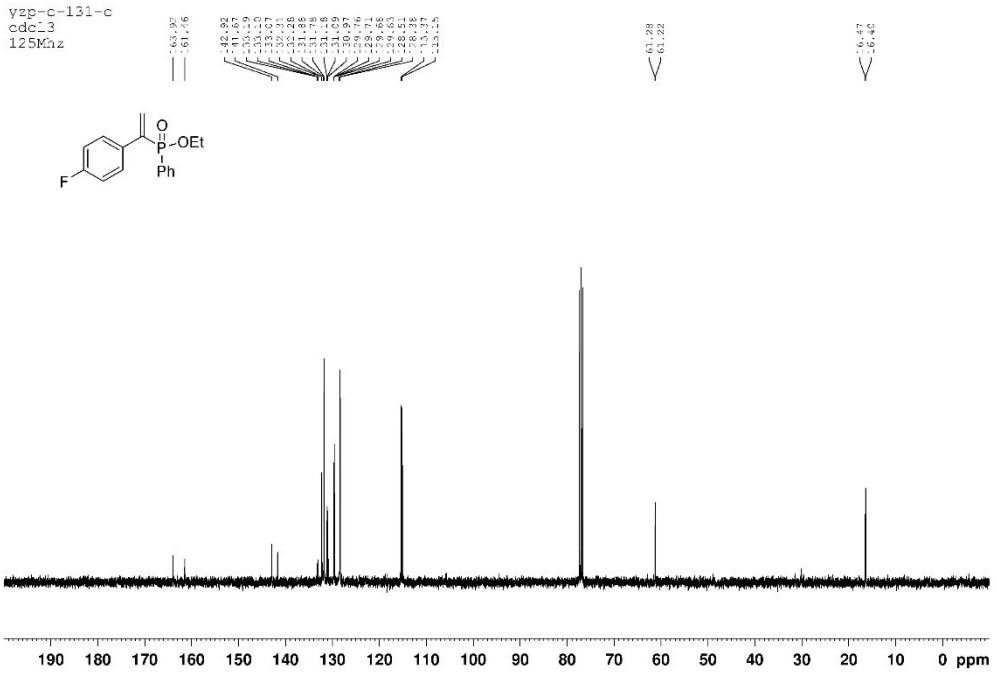

yzp-c-132-3-p
cdcl3
200MHz
30.14
O
P
OEt
Ph
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

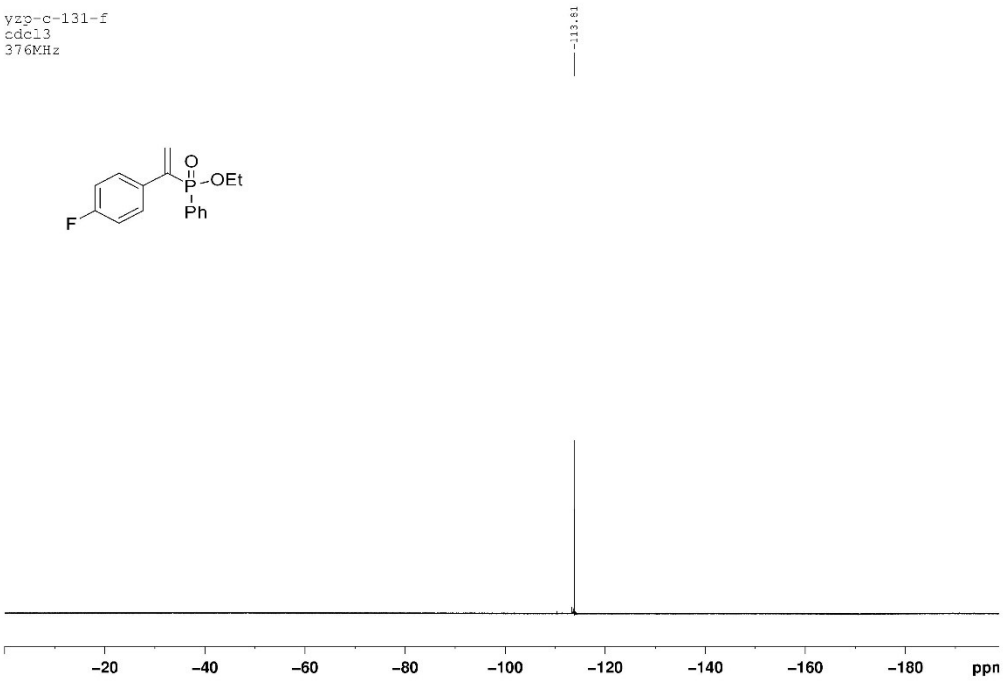

yzp-c-132-3-c
cdcl3
125MHz
143.22
142.91
142.23
134.28
133.79
133.72
132.05
131.78
131.70
131.66
130.86
130.79
130.06
128.34
128.23
128.04
127.66
127.62
61.11
61.07
35.58
31.39
30.98
22.45
14.05
13.97
O
P
OEt
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Ethyl (1-(4-fluorophenyl)vinyl)(phenyl)phosphinate (3ha)

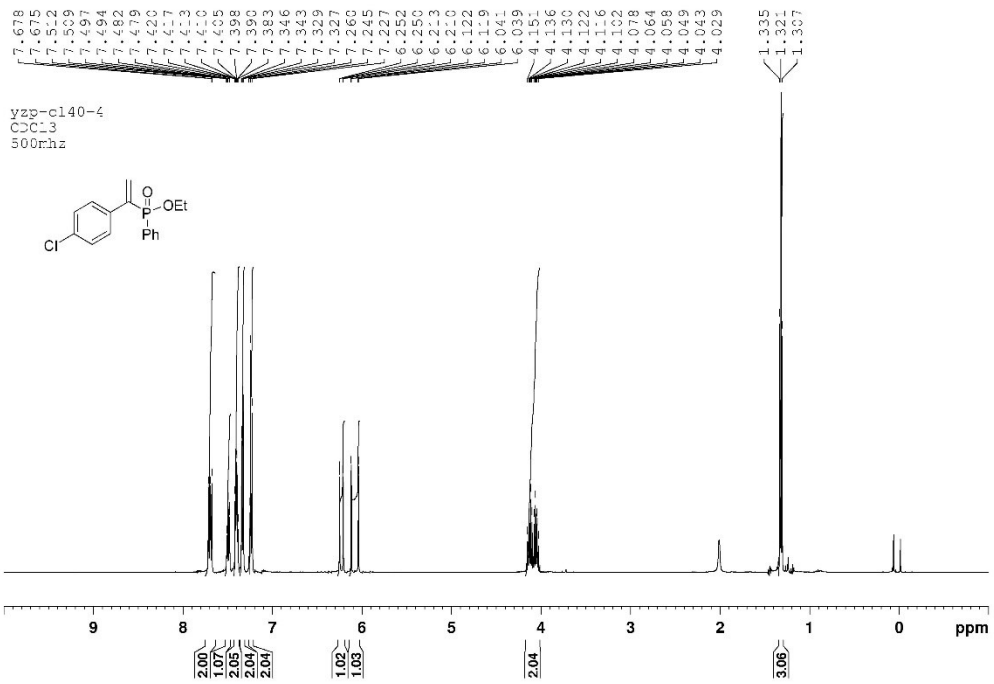


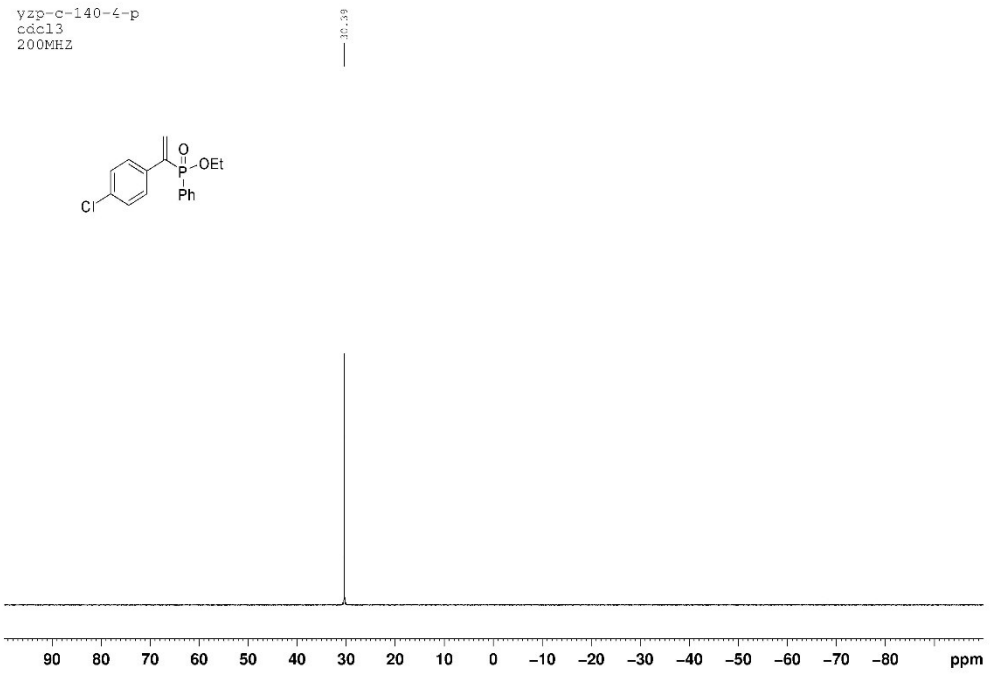


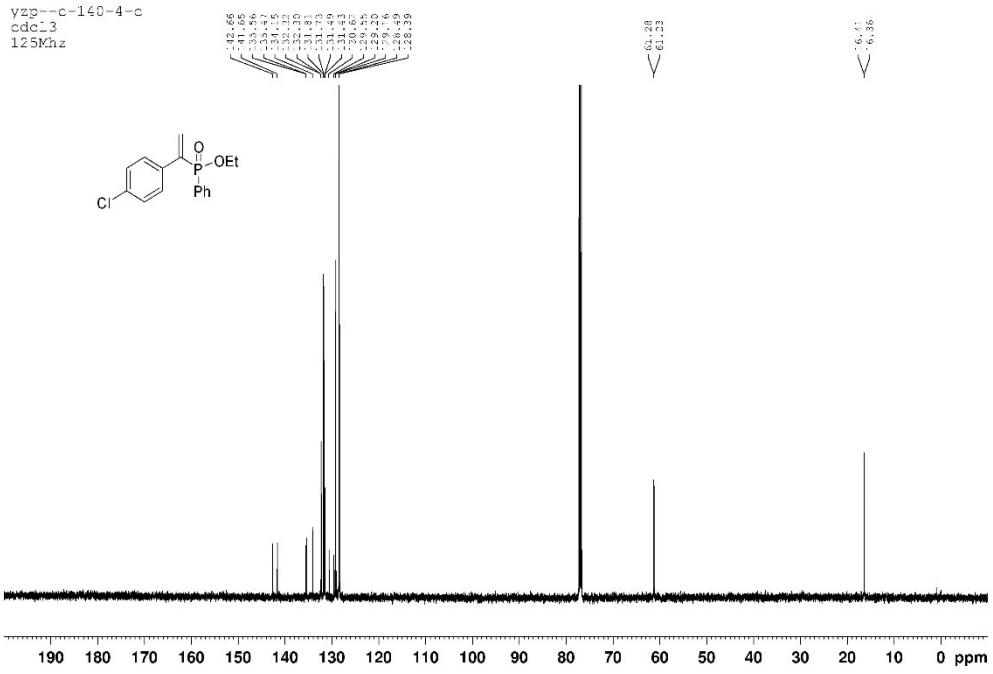

yzp-c-131-c
cdcl3
125Mhz
63.93
61.76
42.92
41.67
33.07
32.28
31.88
31.78
31.68
31.59
30.97
29.76
29.72
29.65
29.63
28.51
28.38
15.37
15.25
61.28
61.22
16.47
16.40
O
P
OEt
Ph
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


yzp-c-131-f
cdcl3
376MHz
-113.61
O
P
OEt
Ph
F
-20 -40 -60 -80 -100 -120 -140 -160 -180 ppm

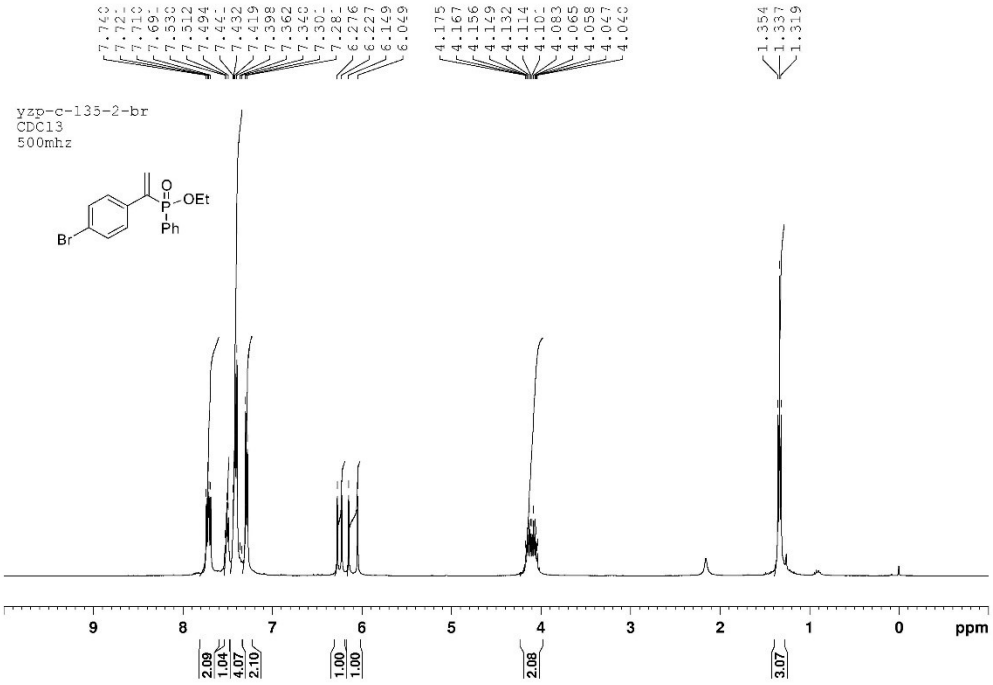
Ethyl (1-(4-chlorophenyl)vinyl)(phenyl)phosphinate (3ia)

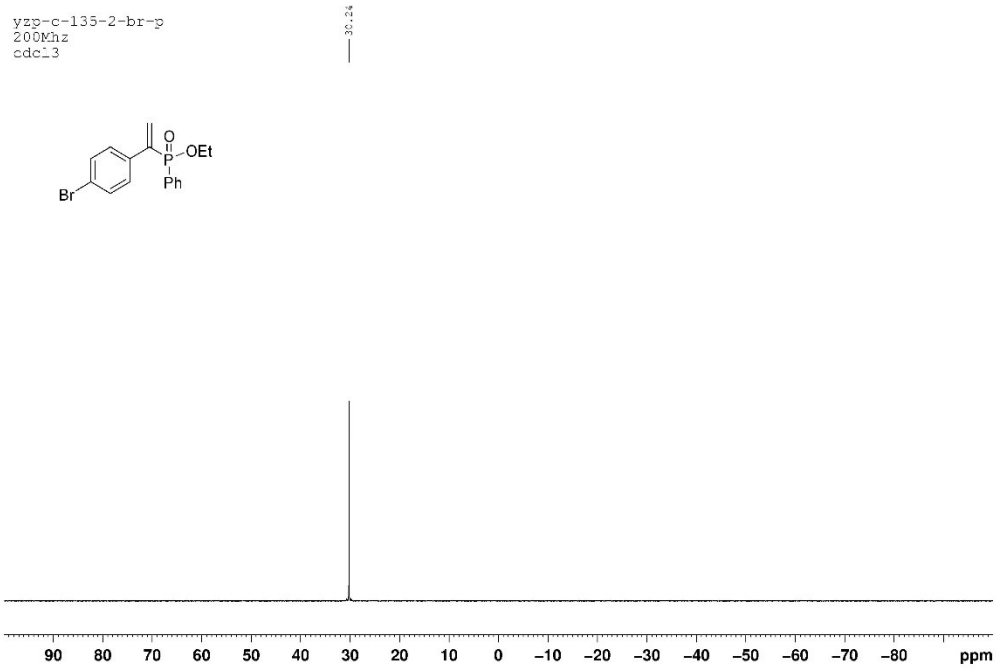


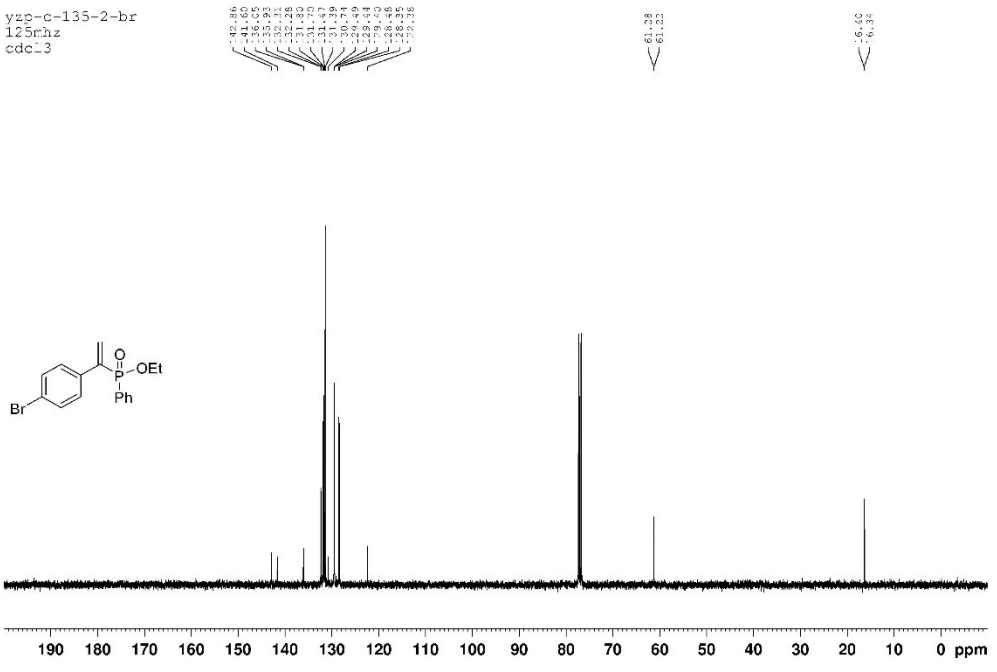




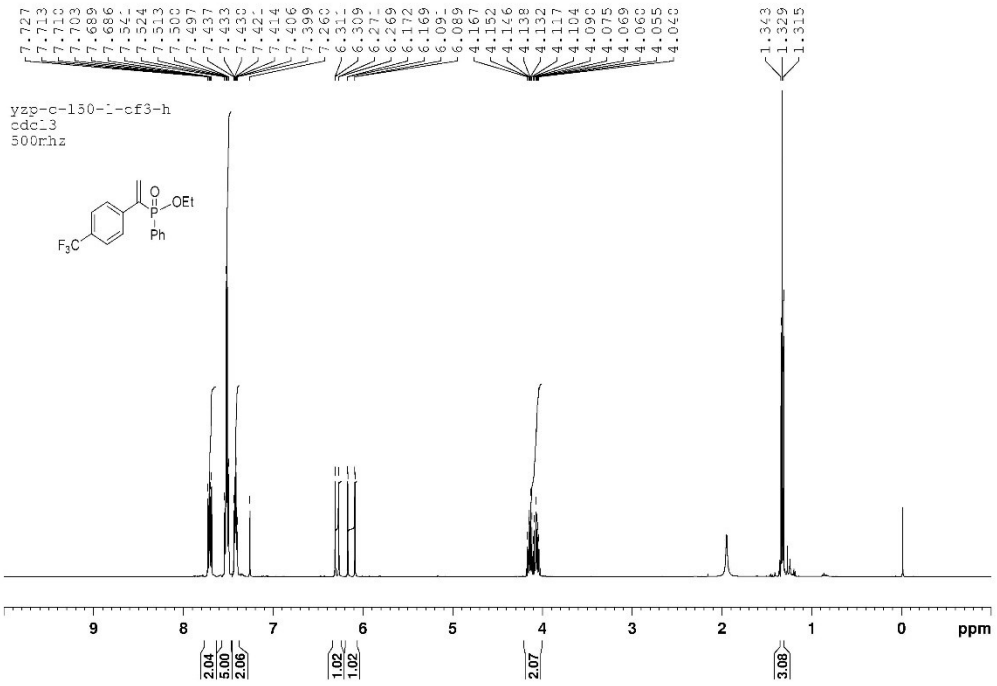
Ethyl (1-(4-bromophenyl)vinyl)(phenyl)phosphinate (3ja)

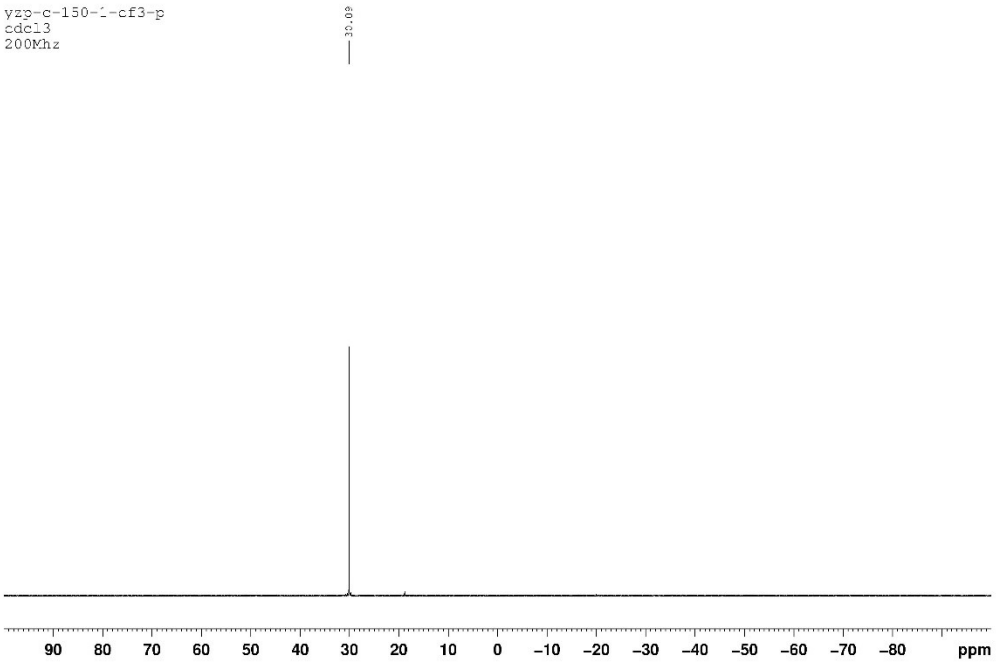


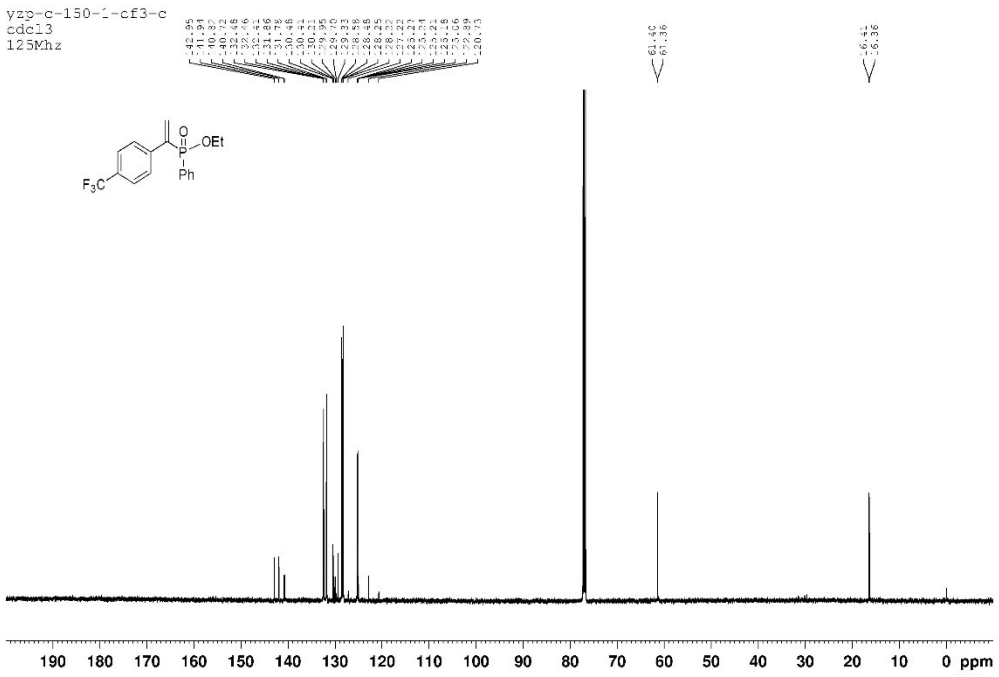

yzp-c-135-2-br-p
200Mhz
cdcl3
30.24
Br
O
P
OEt
Ph
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 ppm

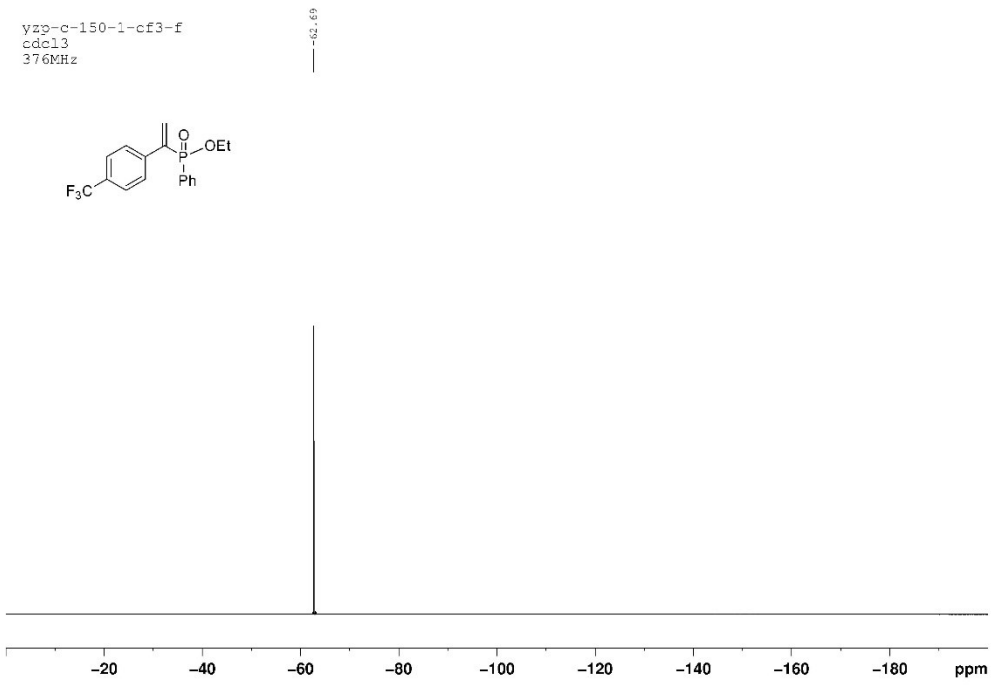

yzp-c-135-2-br
125mhz
cdcl3
142.86
141.60
136.95
135.83
132.73
132.28
131.80
131.70
131.47
131.39
130.74
129.49
129.19
128.50
128.46
128.35
122.38
61.38
61.22
16.40
16.34
Br
O
P
OEt
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Ethyl phenyl(1-(4-(trifluoromethyl)phenyl)vinyl)phosphinate (3ka)

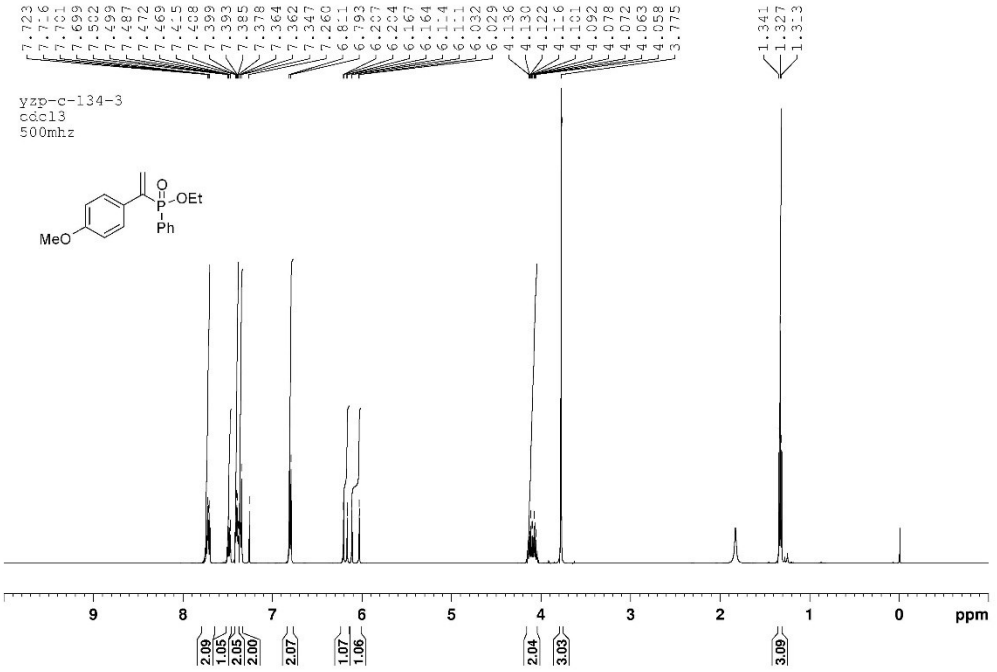


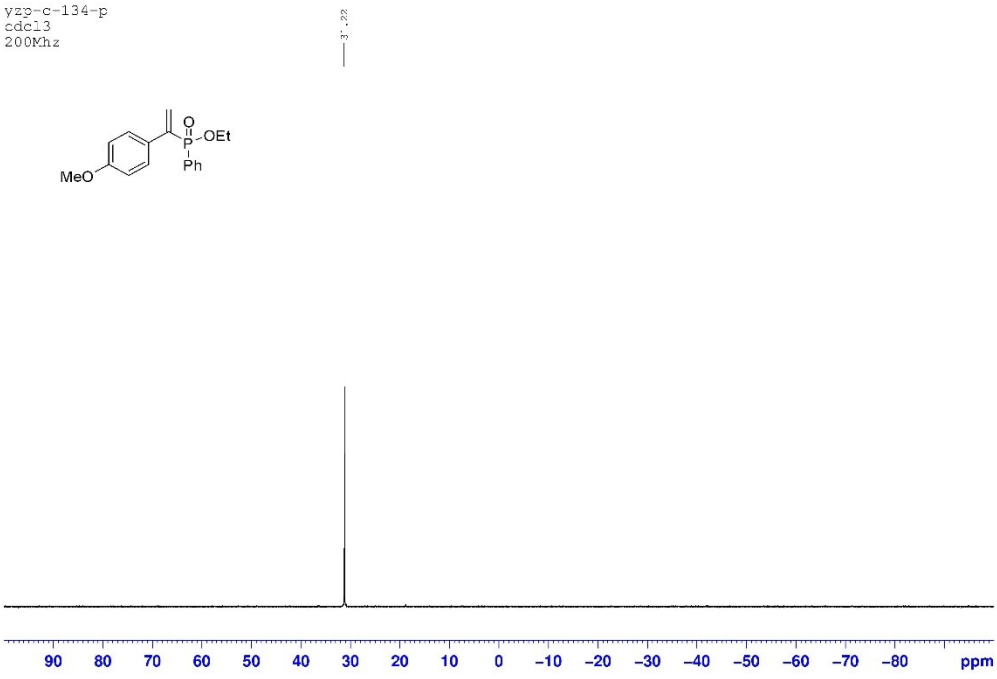


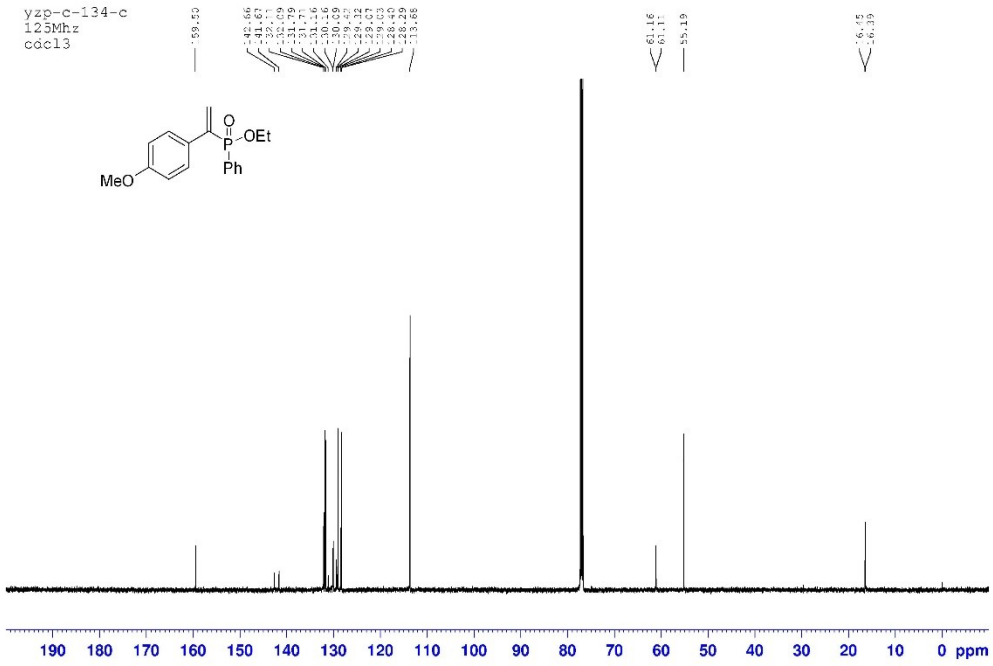

yzp-c-150-1-cf3-c
cdcl3
125Mhz
61.40
61.36
16.41
16.36
OEt
Ph
F3C
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


yzp-c-150-1-cf3-f
cdcl3
376MHz
-62.69
OEt
Ph
F3C
-20 -40 -60 -80 -100 -120 -140 -160 -180 ppm

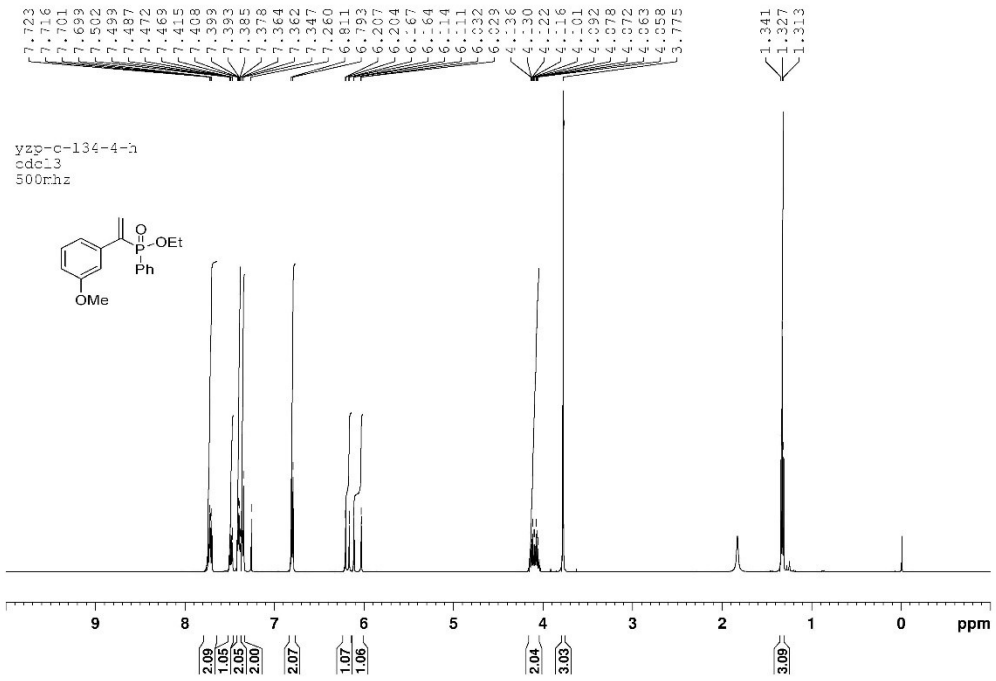
Ethyl (1-(4-methoxyphenyl)vinyl)(phenyl)phosphinate (3la)

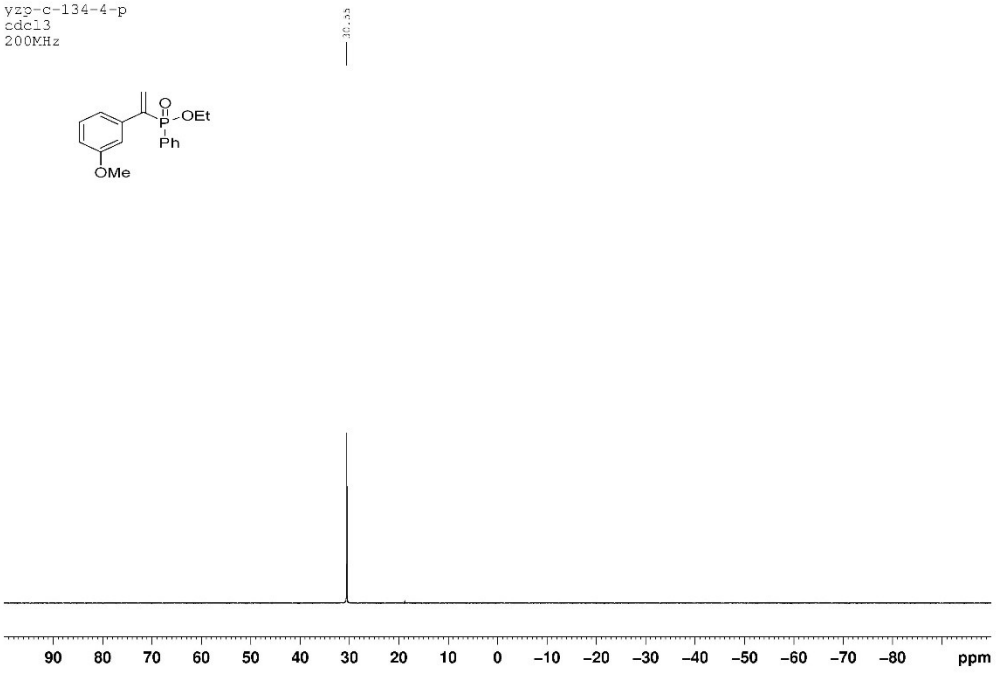


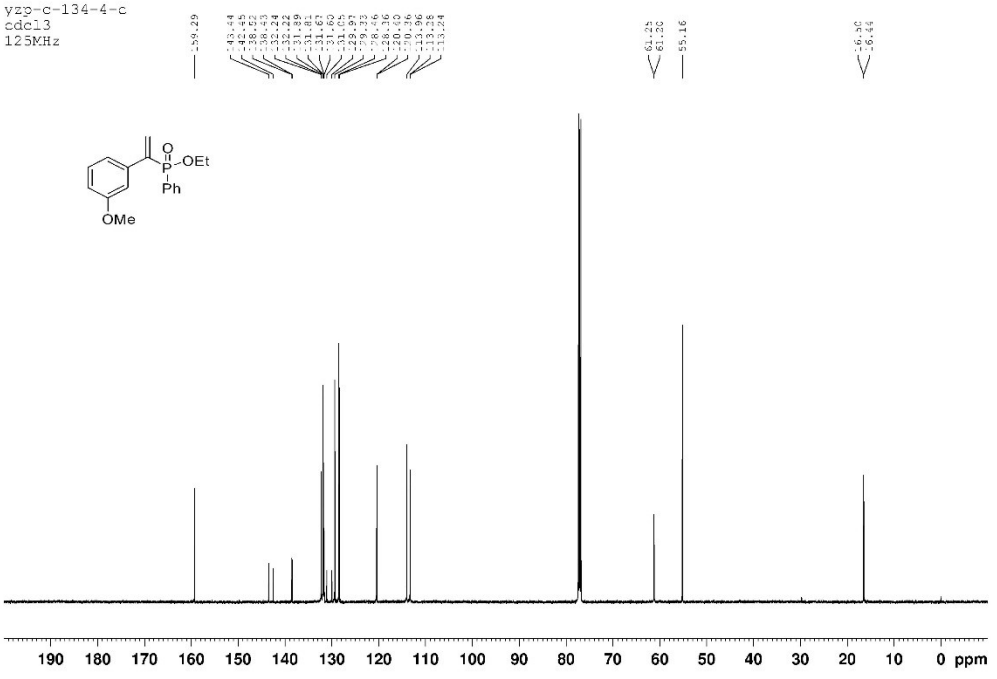




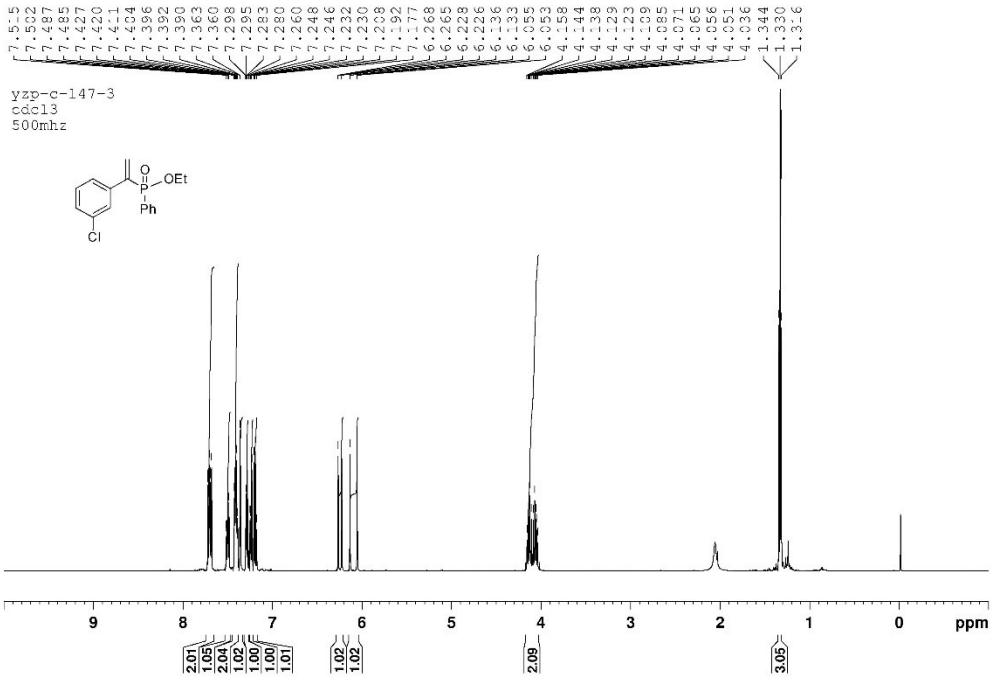
Ethyl (1-(3-methoxyphenyl)vinyl)(phenyl)phosphinate (3ma)

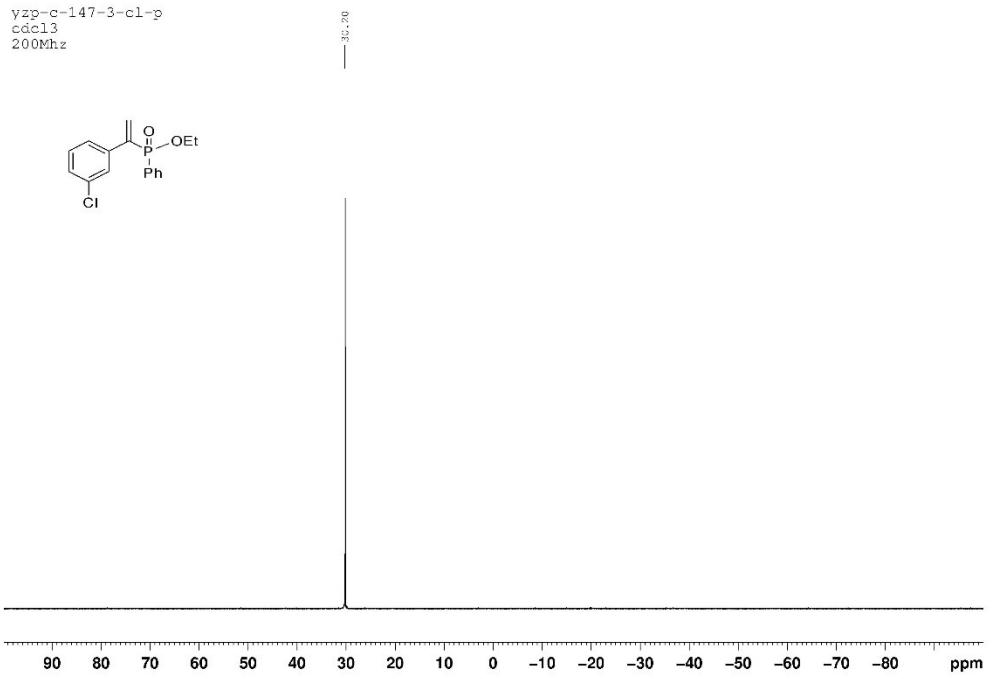


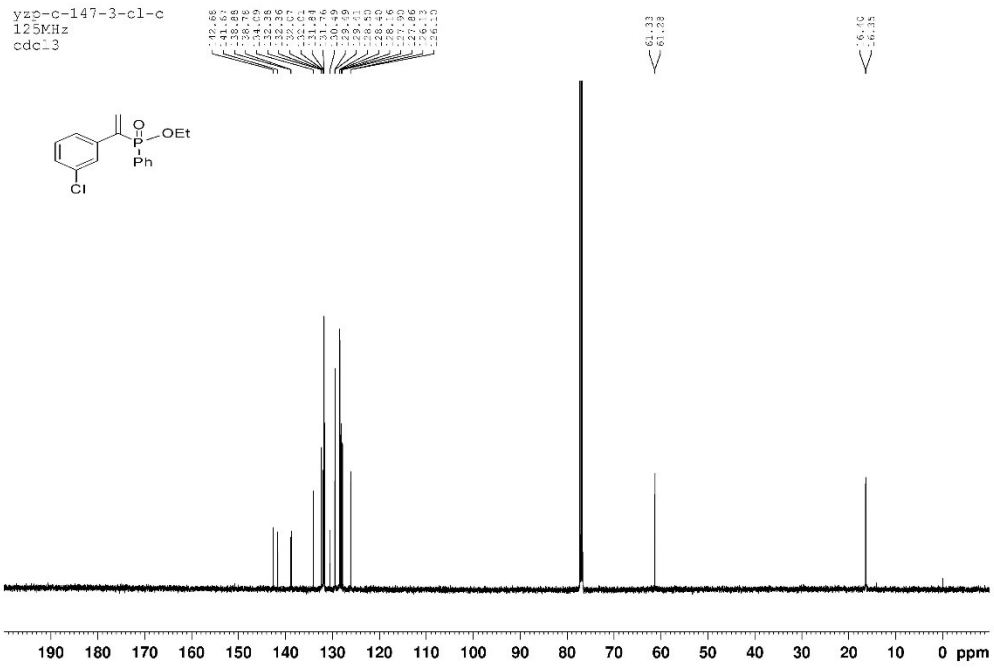

yzp-c-134-4-p
cdcl3
200MHz
O
OEt
P
Ph
OMe
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 ppm


yzp-c-134-4-c
cdcl3
125MHz
159.29
61.25
61.00
55.16
16.36
16.44
O
OEt
P
Ph
OMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

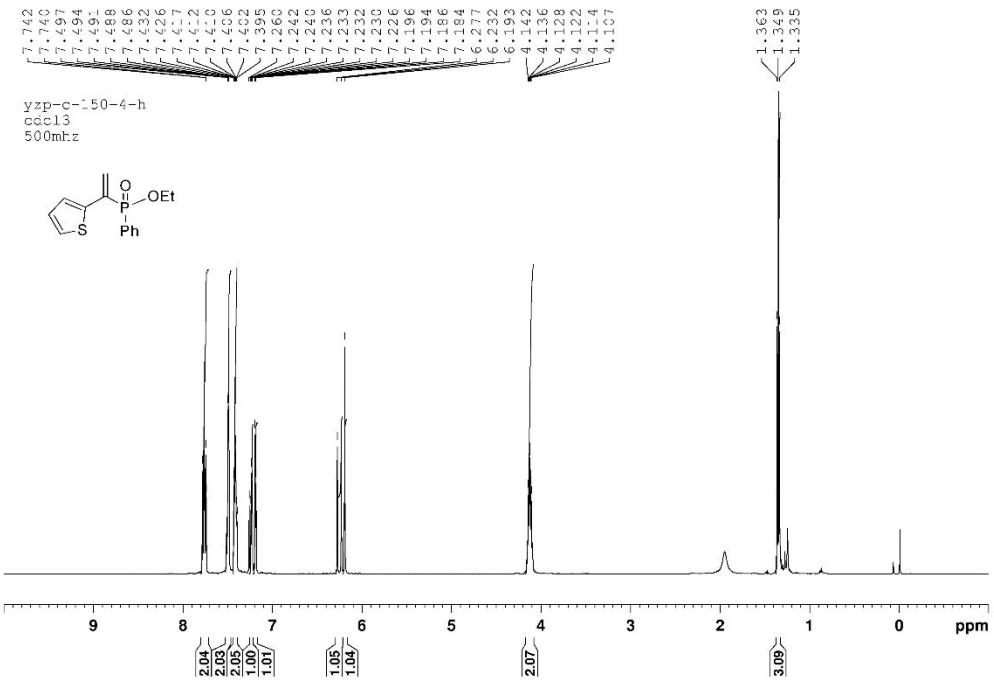
Ethyl (1-(3-chlorophenyl)vinyl)(phenyl)phosphinate (3na)

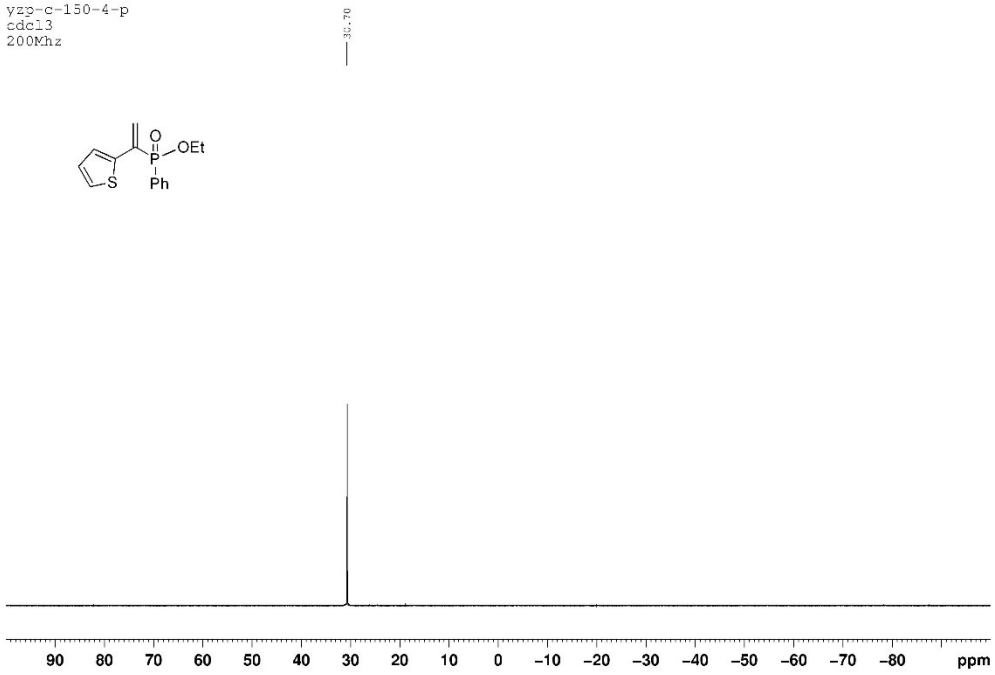


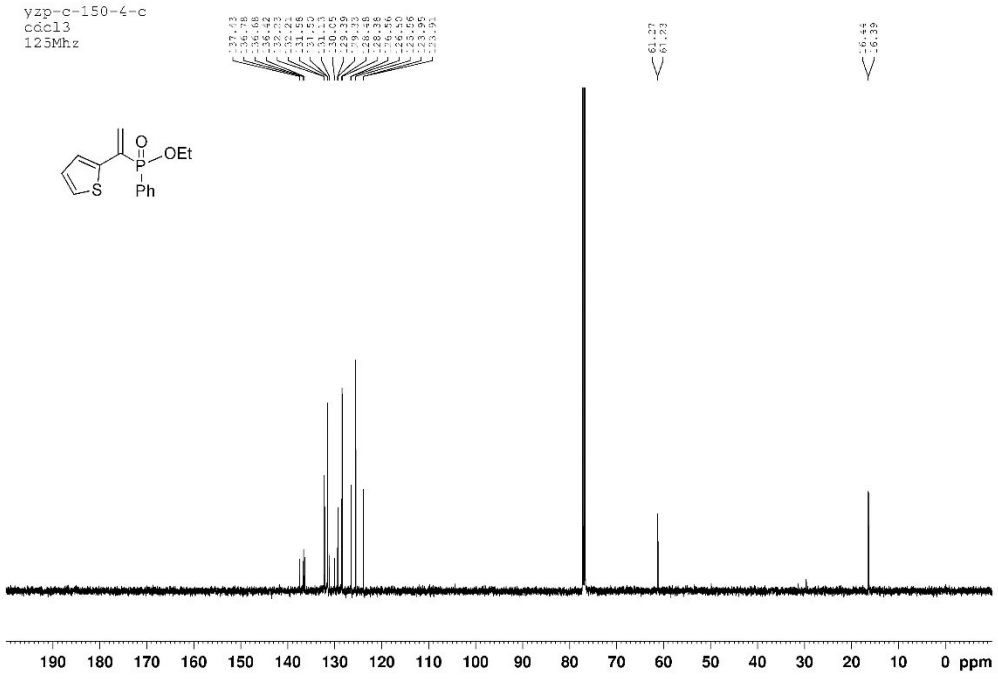




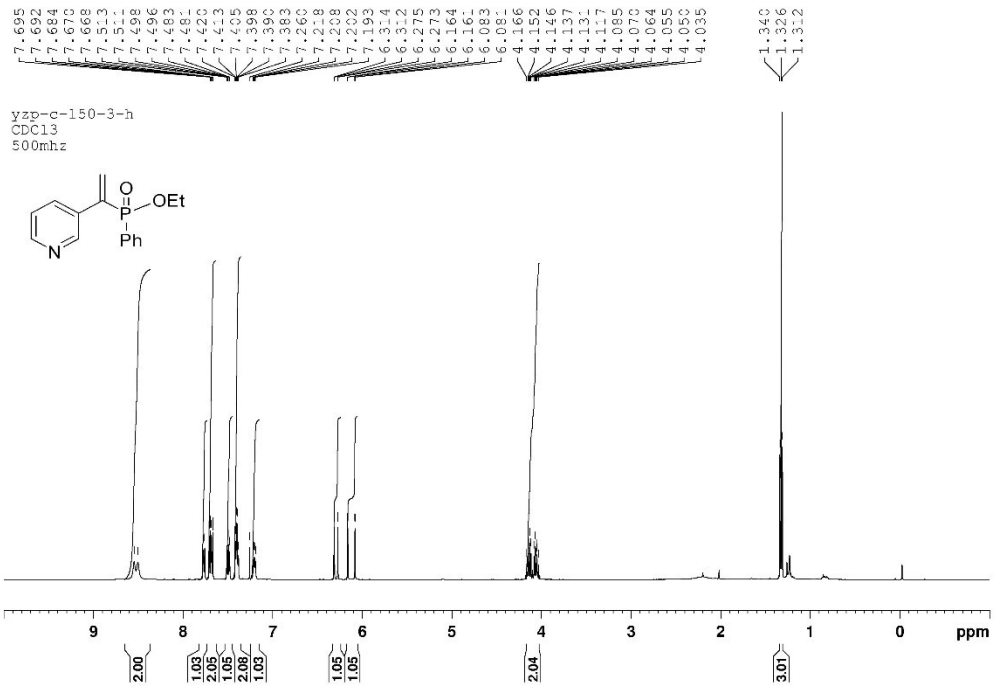
Ethyl phenyl(1-(thiophen-2-yl)vinyl)phosphinate (3oa)

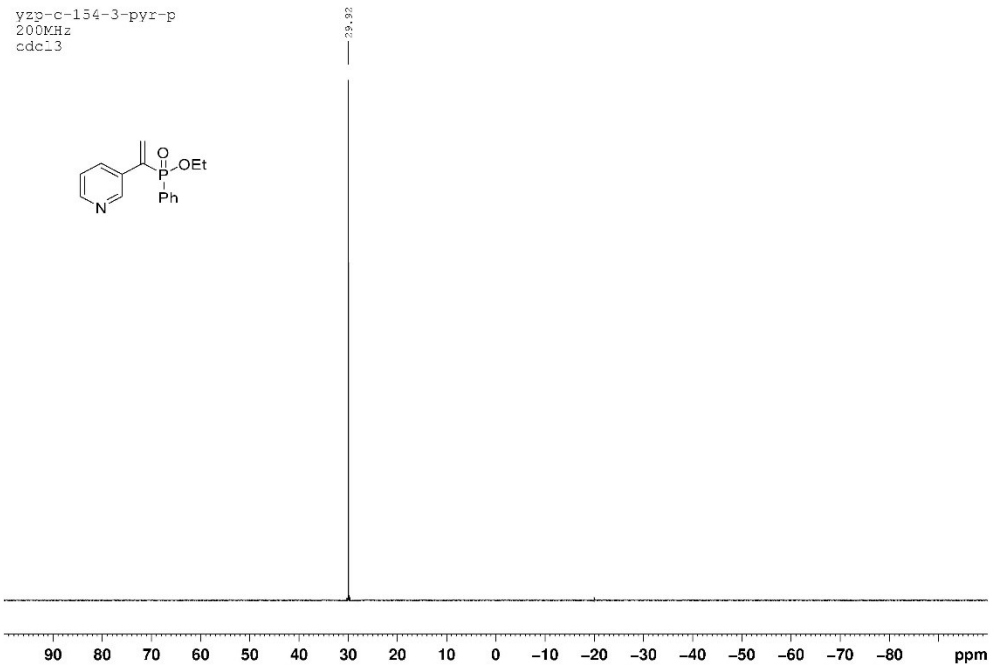


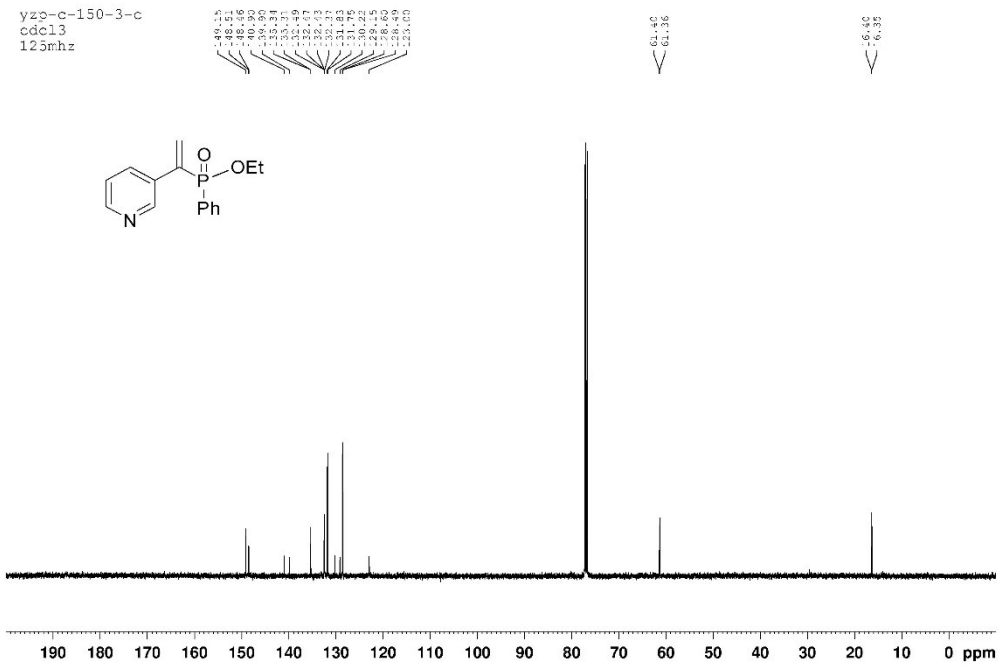

yzp-c-150-4-p
cdcl3
200Mhz
30.70
OEt
P
O
S
Ph
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm


yzp-c-150-4-c
cdcl3
125Mhz
137.13
136.78
136.46
136.42
132.33
132.21
131.58
131.50
131.13
130.05
129.39
129.33
129.18
128.98
128.38
126.56
126.50
123.96
123.95
123.91
61.27
61.23
16.44
16.39
OEt
P
O
S
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

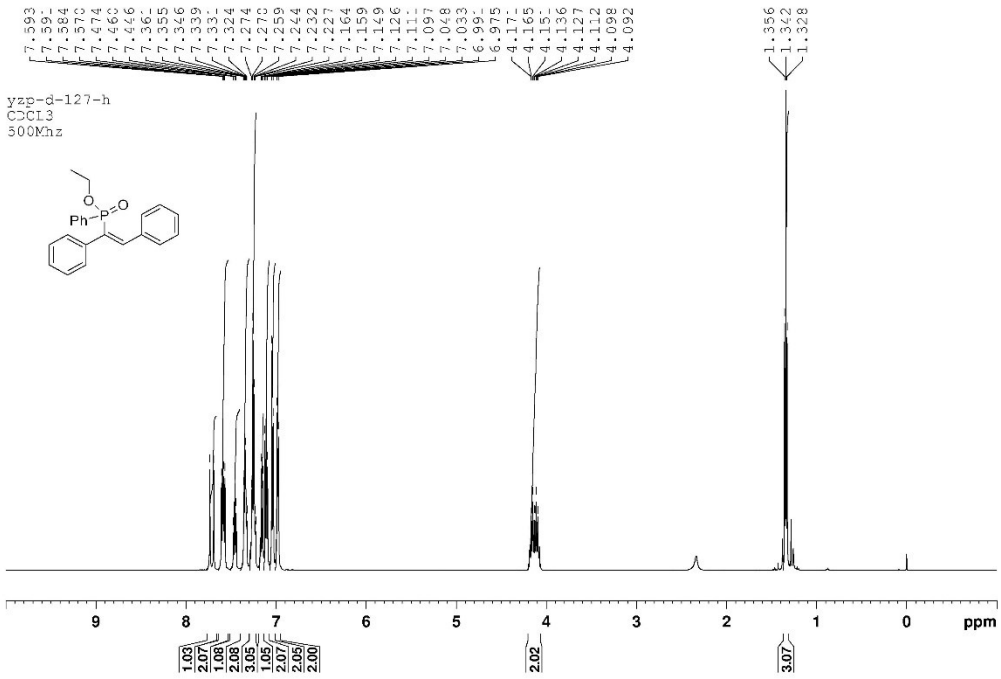
Ethyl phenyl(1-(pyridin-3-yl)vinyl)phosphinate (3pa)

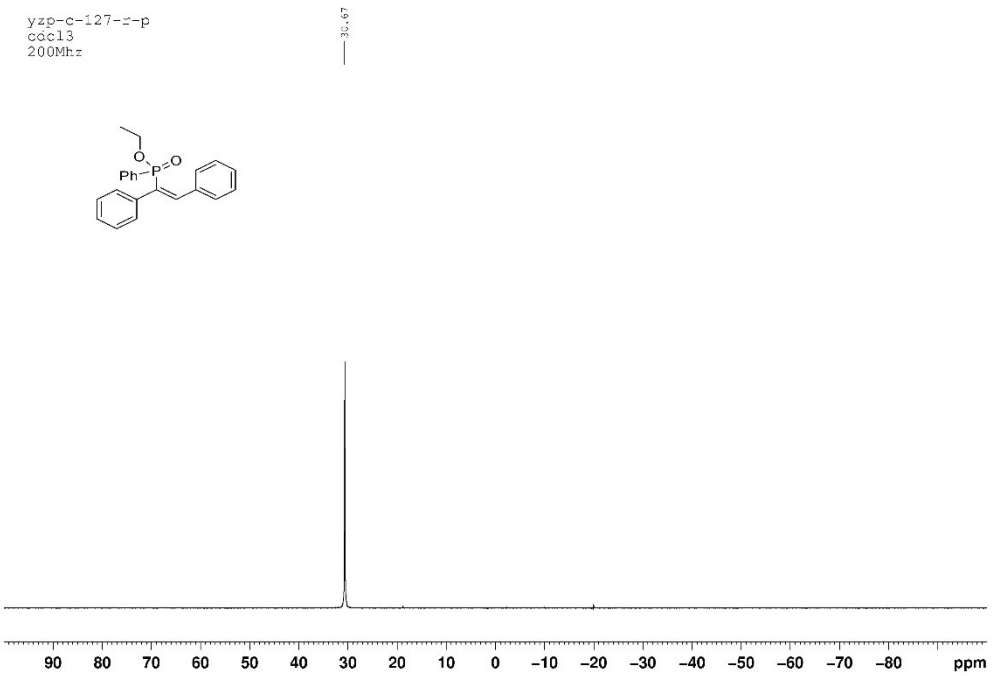


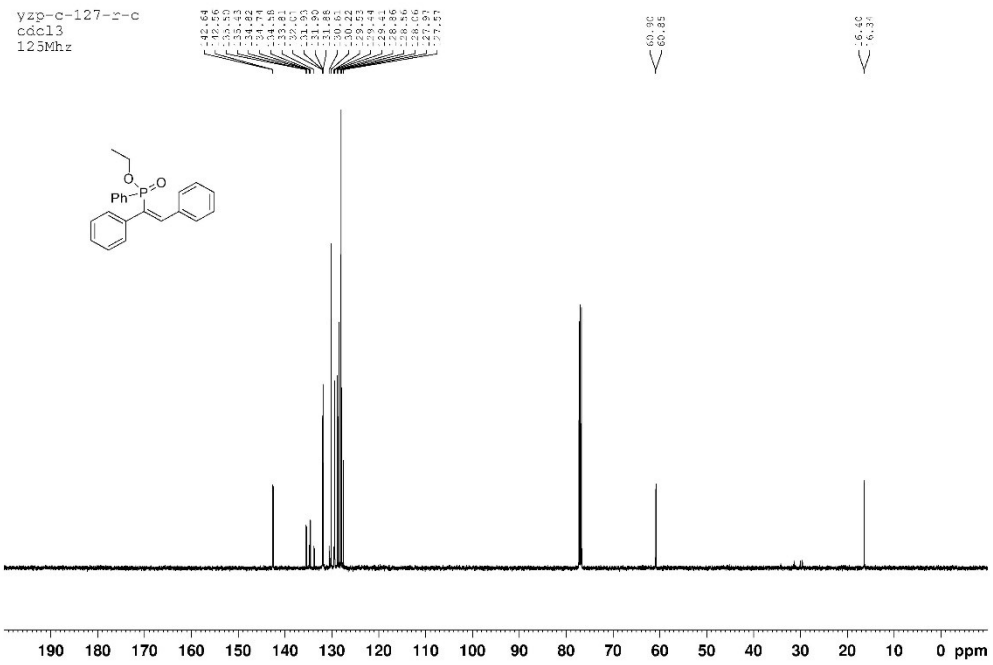




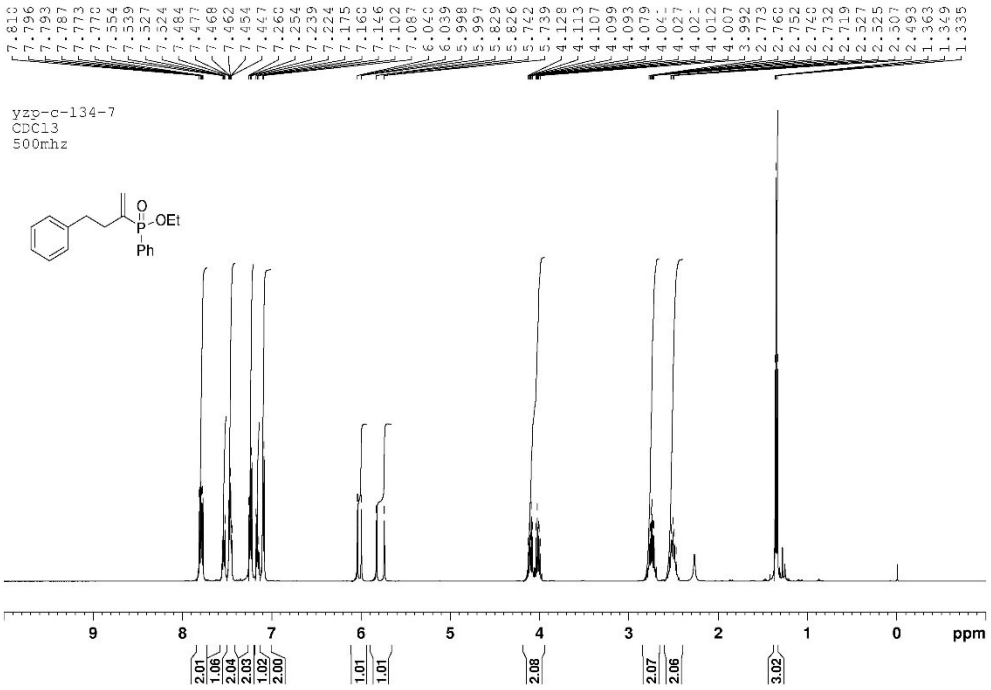
Ethyl (*Z*)-(1,2-diphenylvinyl)(phenyl)phosphinate (3qa)

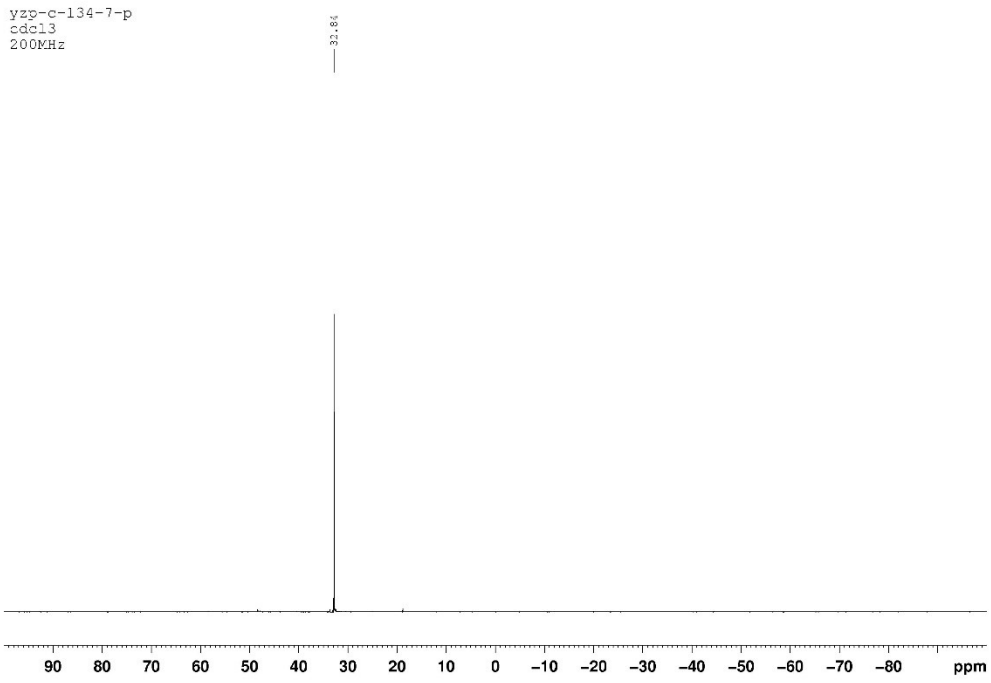


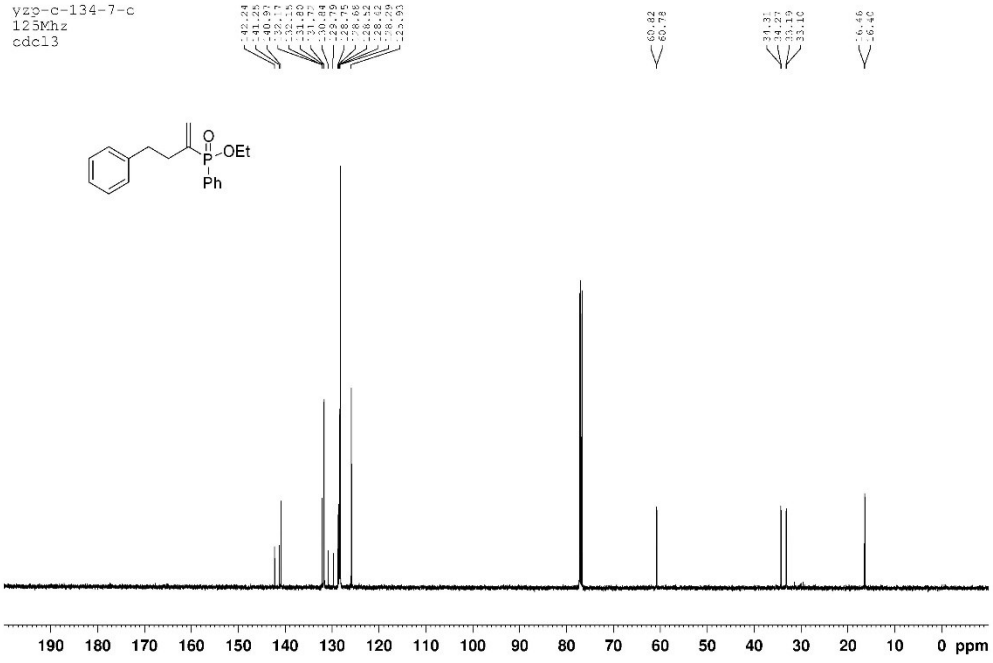

yzp-c-127-z-p
cdcl3
200Mhz
30.67
Ph
P
O
O
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm


yzp-c-127-z-c
cdcl3
125Mhz
60.90
60.85
16.46
16.36
Ph
P
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

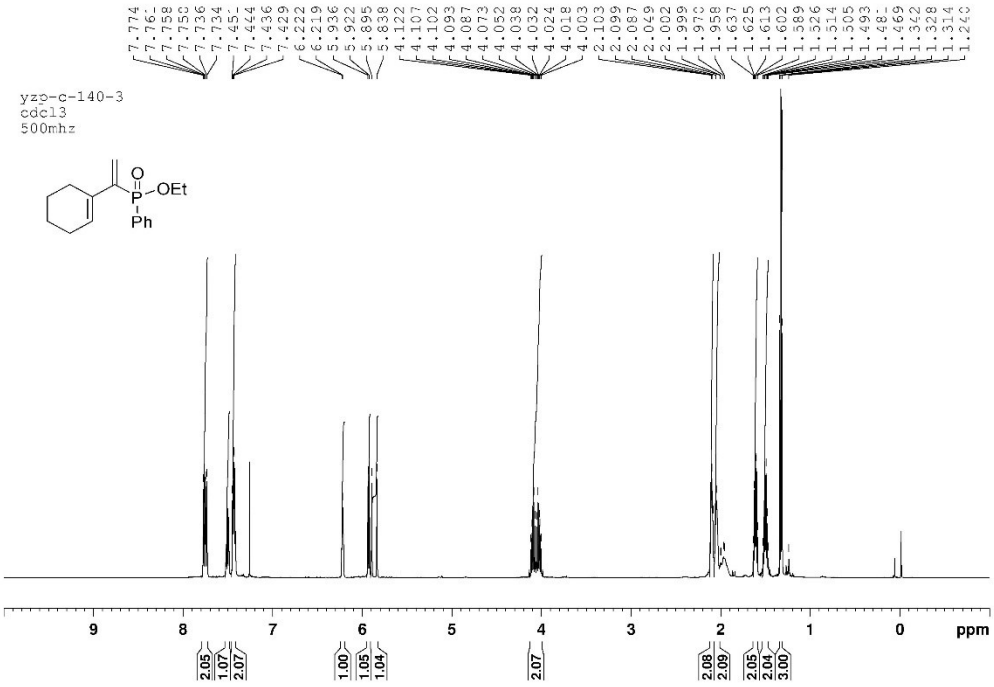
Ethyl phenyl(4-phenylbut-1-en-2-yl)phosphinate (3ra)

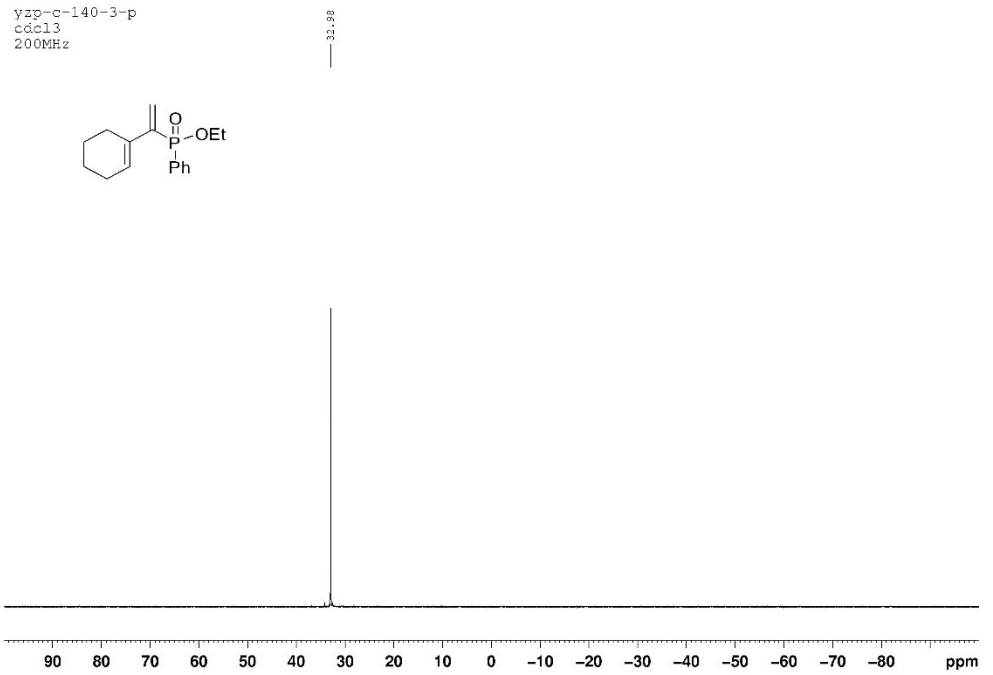


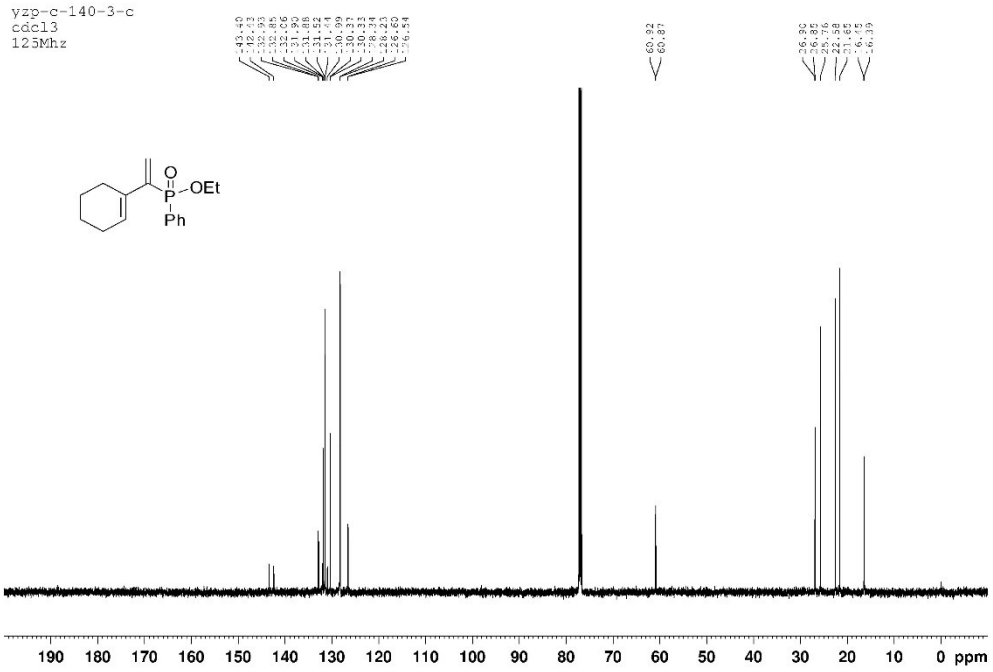




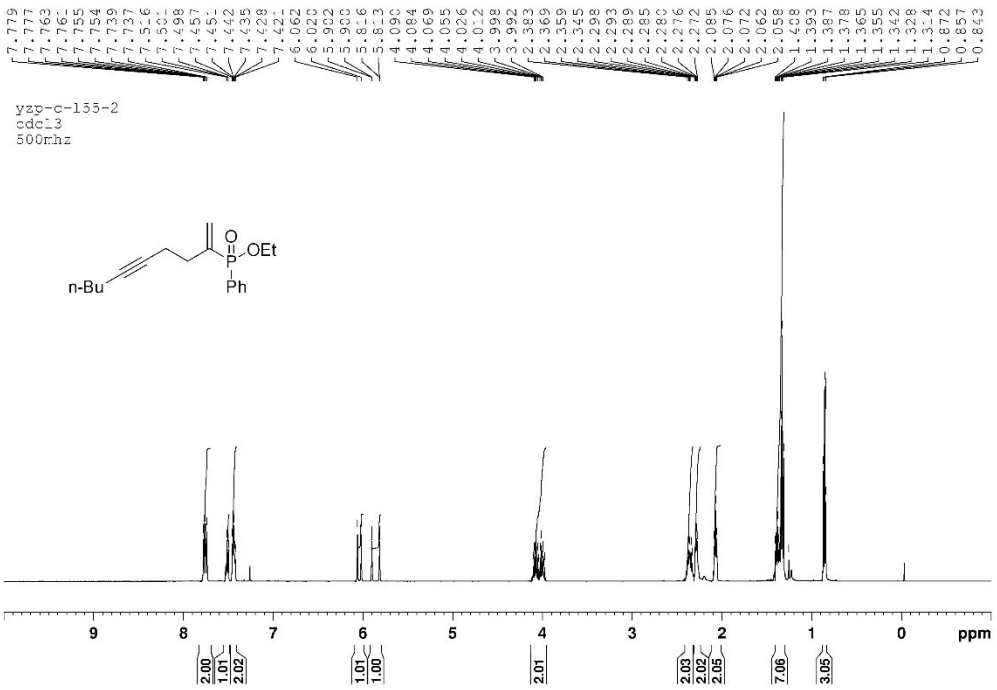
Ethyl (1-(cyclohex-1-en-1-yl)vinyl)(phenyl)phosphinate (3sa)

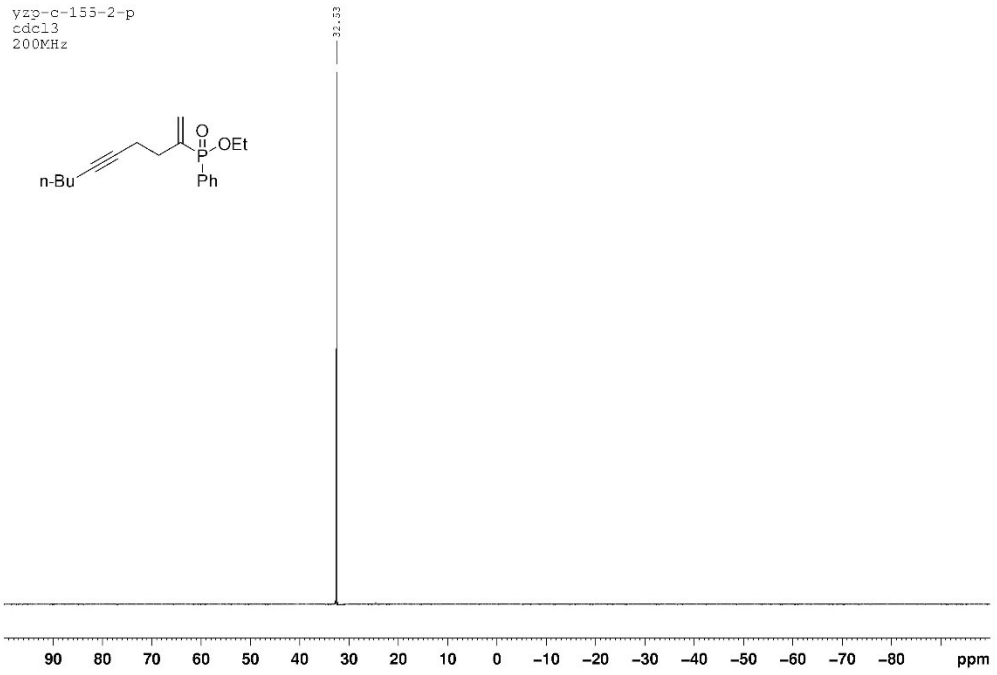


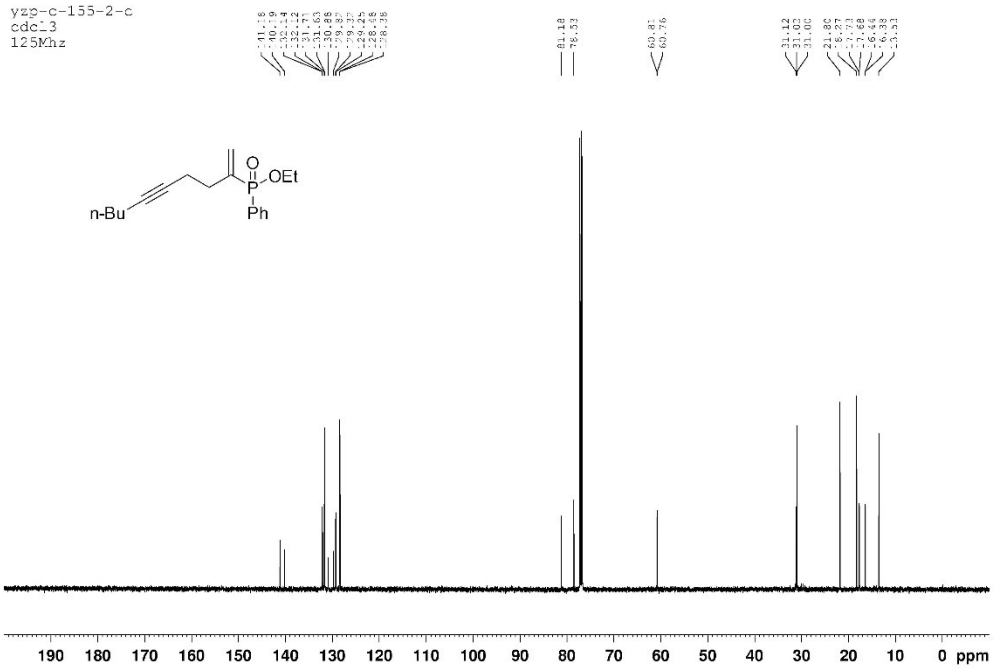

yzp-c-140-3-p
cdcl3
200MHz
32.98
O
P
OEt
Ph
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm


yzp-c-140-3-c
cdcl3
125Mhz
143.40
142.13
132.93
132.85
131.66
131.59
131.88
131.52
131.44
130.99
130.37
130.33
128.34
128.23
126.63
126.54
60.92
60.87
26.96
26.85
26.76
22.98
21.65
16.15
16.39
O
P
OEt
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

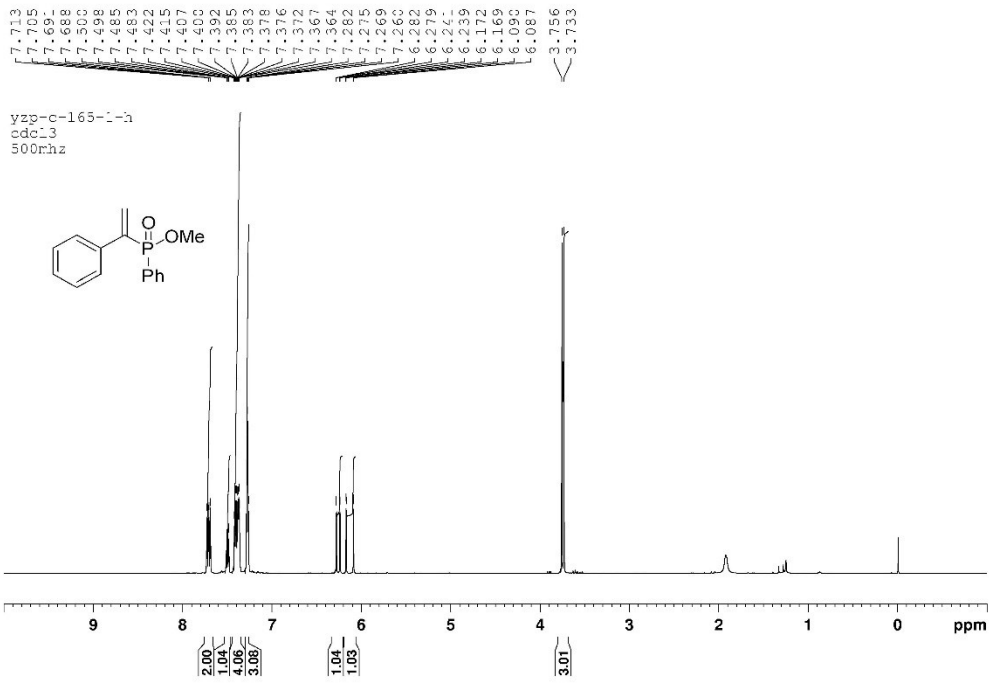
Ethyl dec-1-en-5-yn-2-yl(phenyl)phosphinate (3ta)

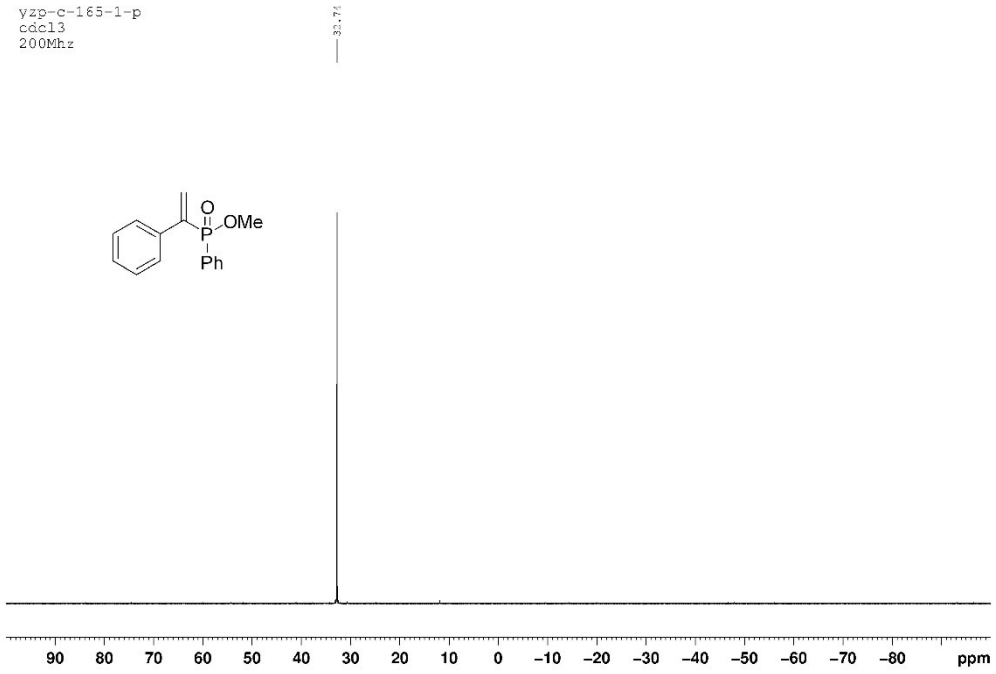


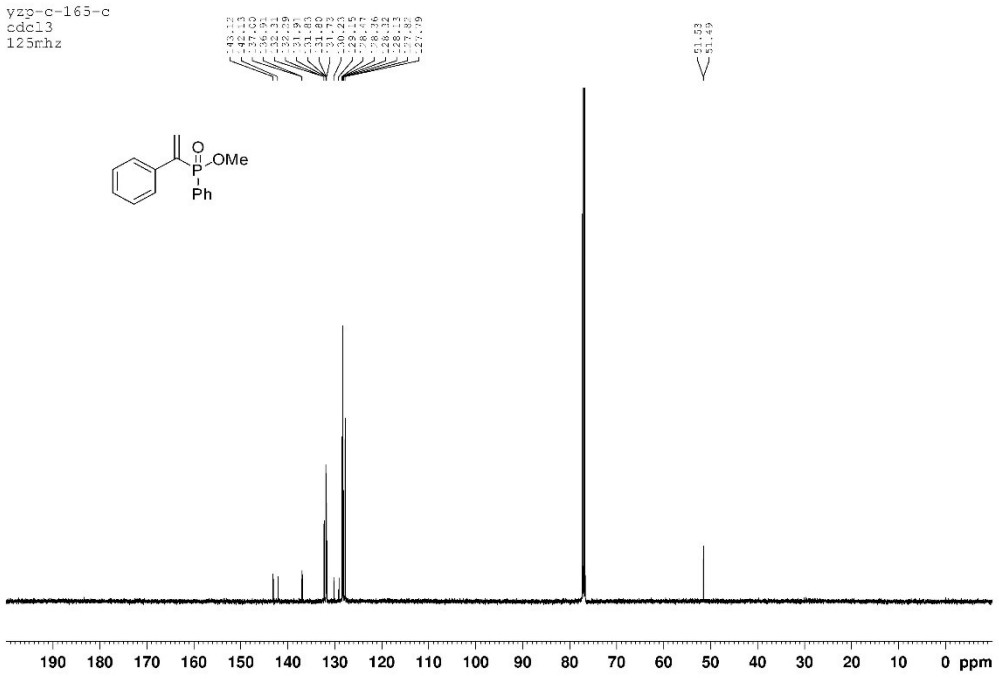




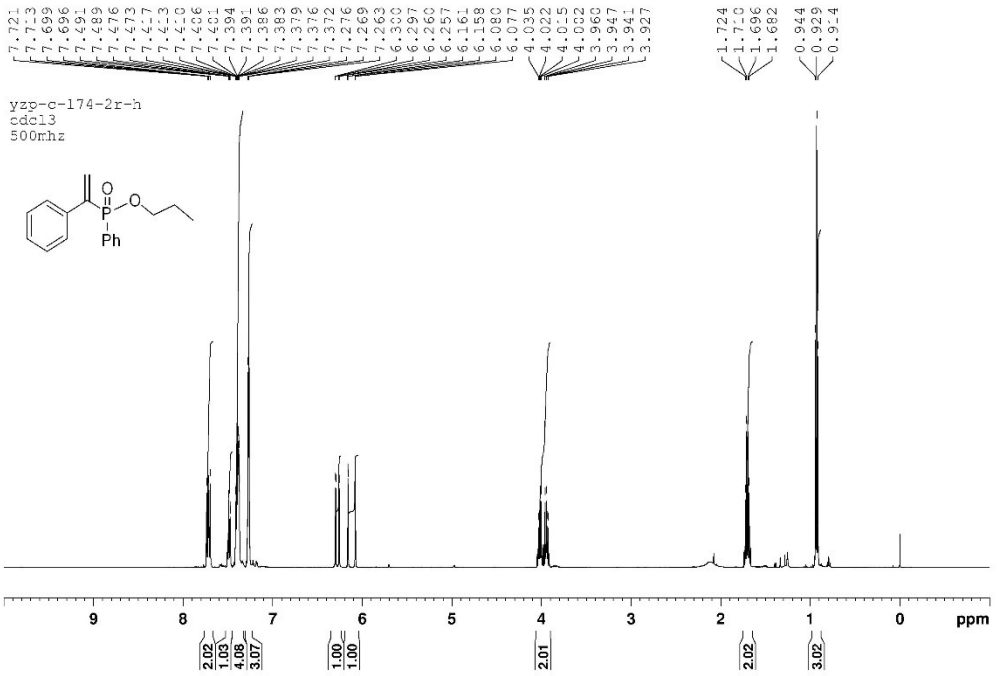
Methyl phenyl(1-phenylvinyl)phosphinate (3ab)

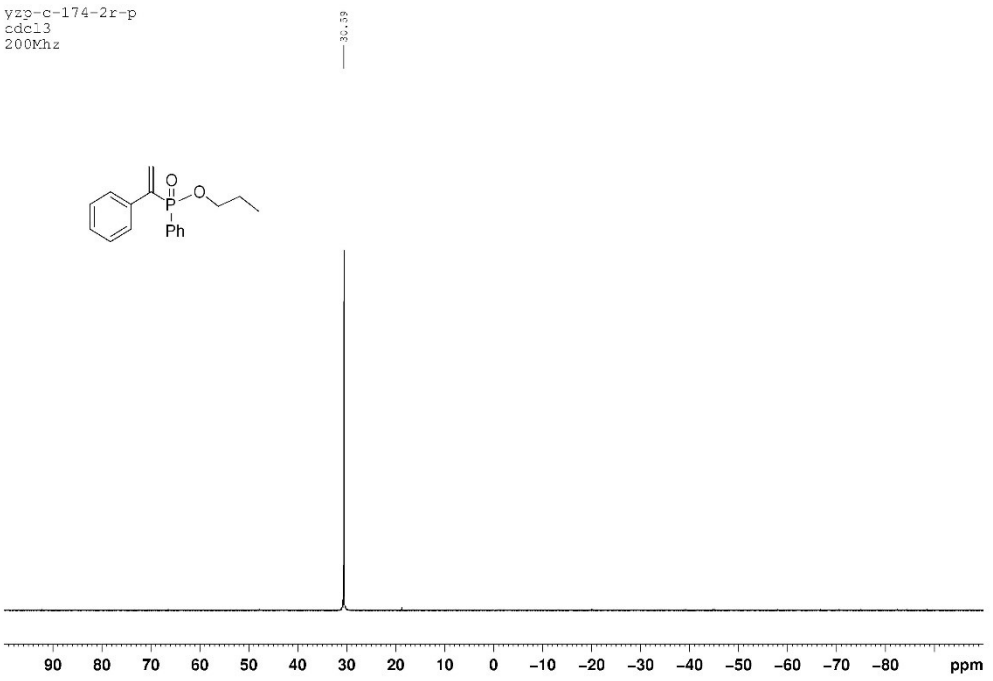


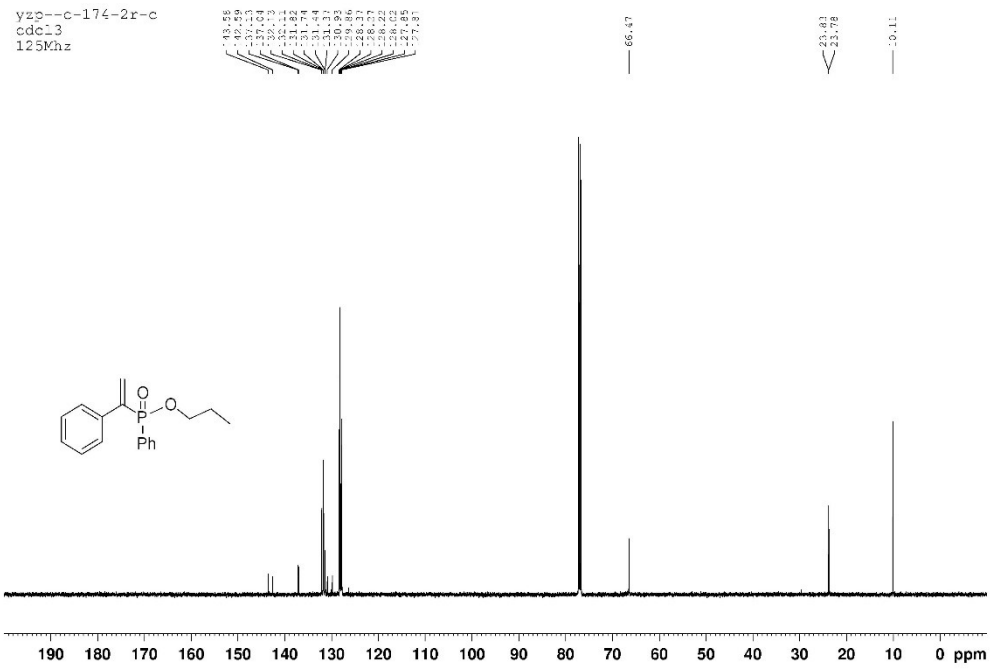

yzp-c-165-1-p
cdcl3
200Mhz
33.71
O
OMe
P
Ph
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 ppm


yzp-c-165-c
cdcl3
125mhz
143.12
137.60
136.91
133.31
131.83
131.80
131.73
130.23
128.45
128.17
128.36
128.12
127.83
127.32
127.19
51.53
51.49
O
OMe
P
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

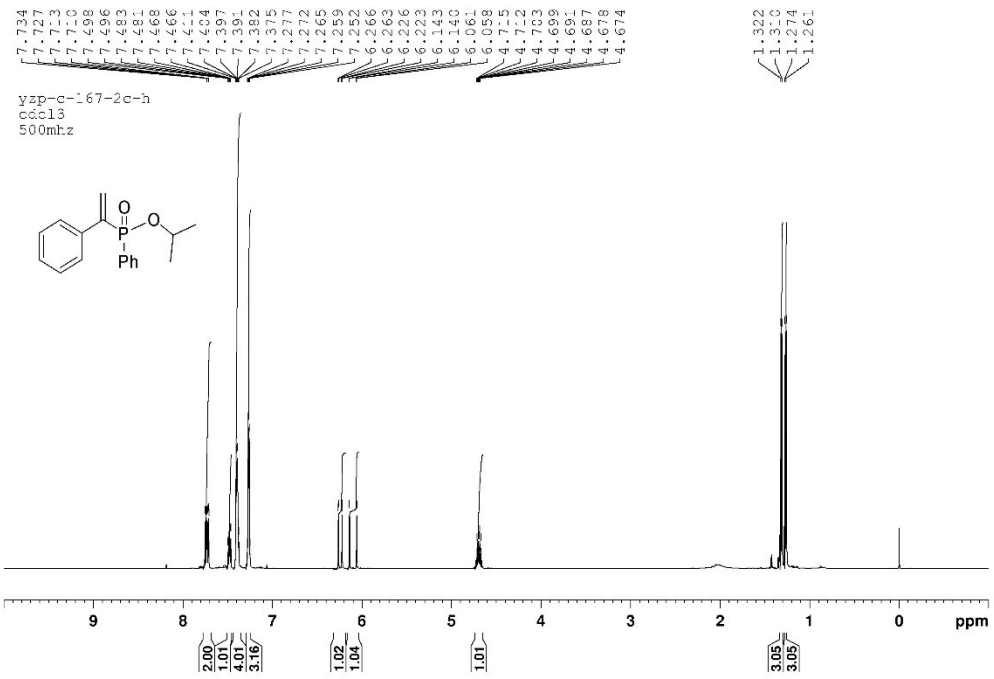
Propyl phenyl(1-phenylvinyl) phosphinate (3ac)

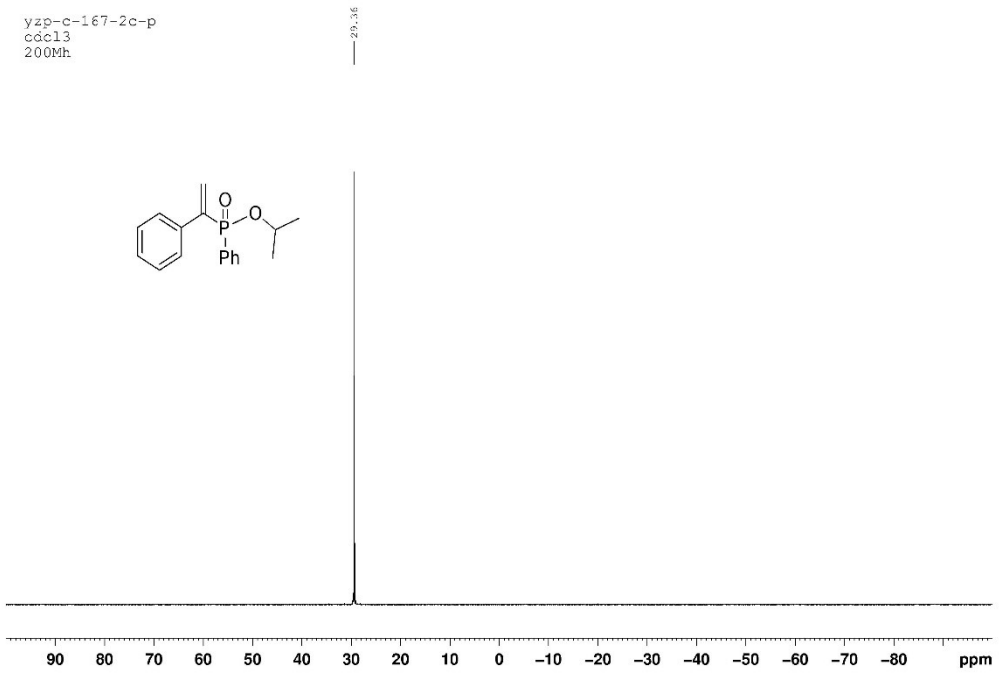


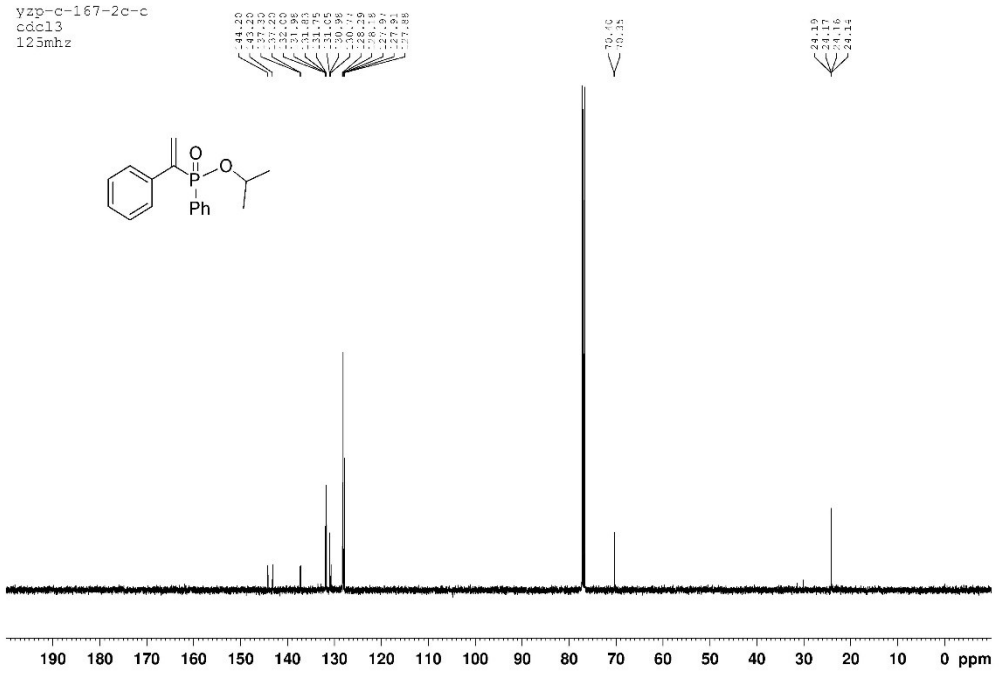




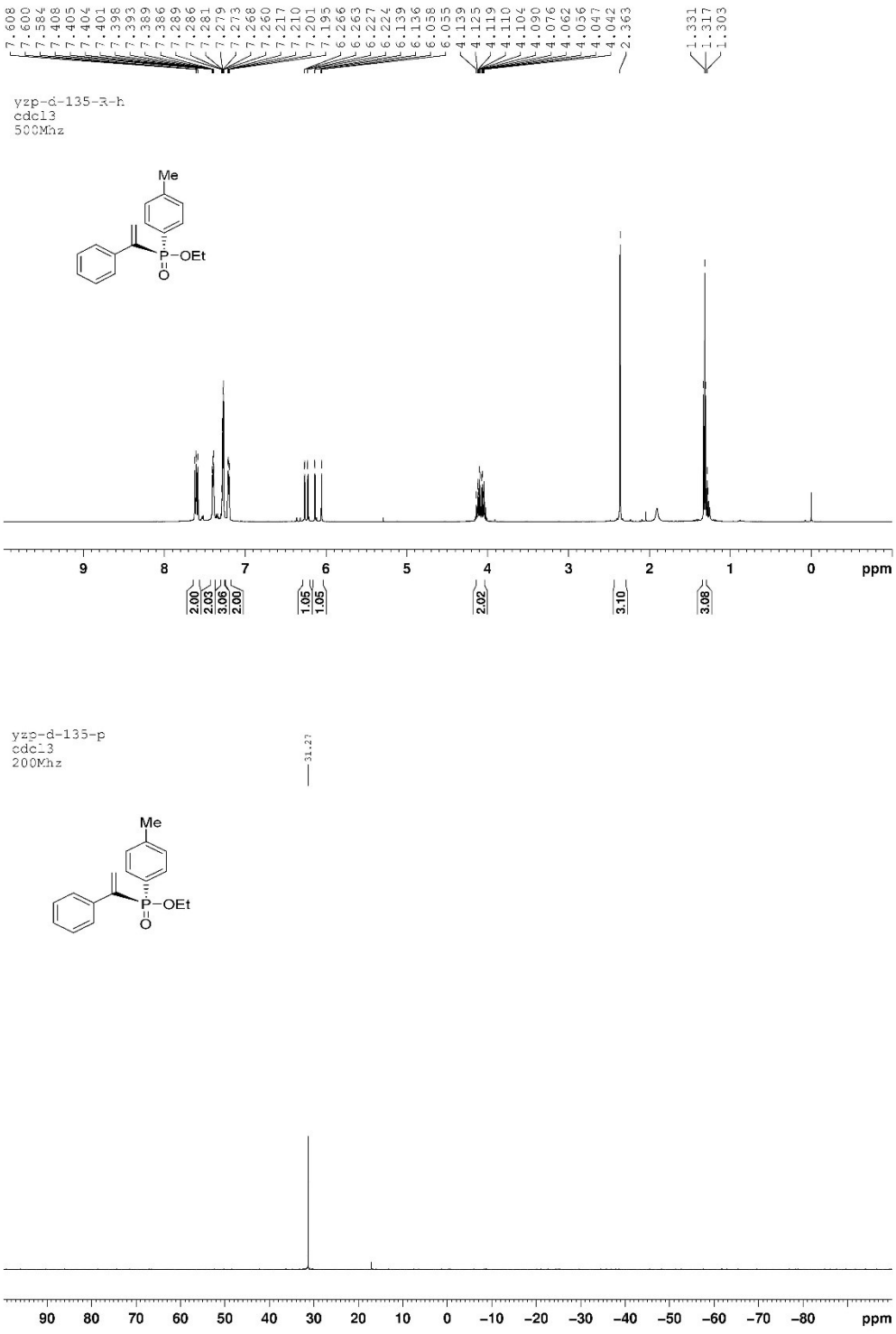
Isopropyl phenyl(1-phenylvinyl)phosphinate (3ad)

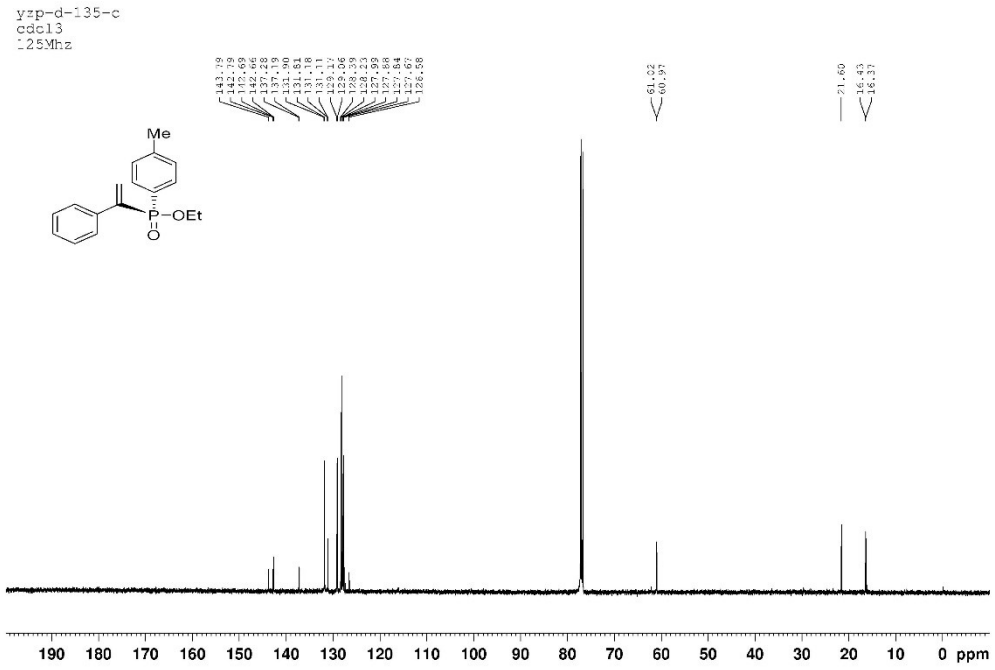



yzp-c-167-2c-p
cdcl3
200Mh
29.36
O
O
P
Ph
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 ppm

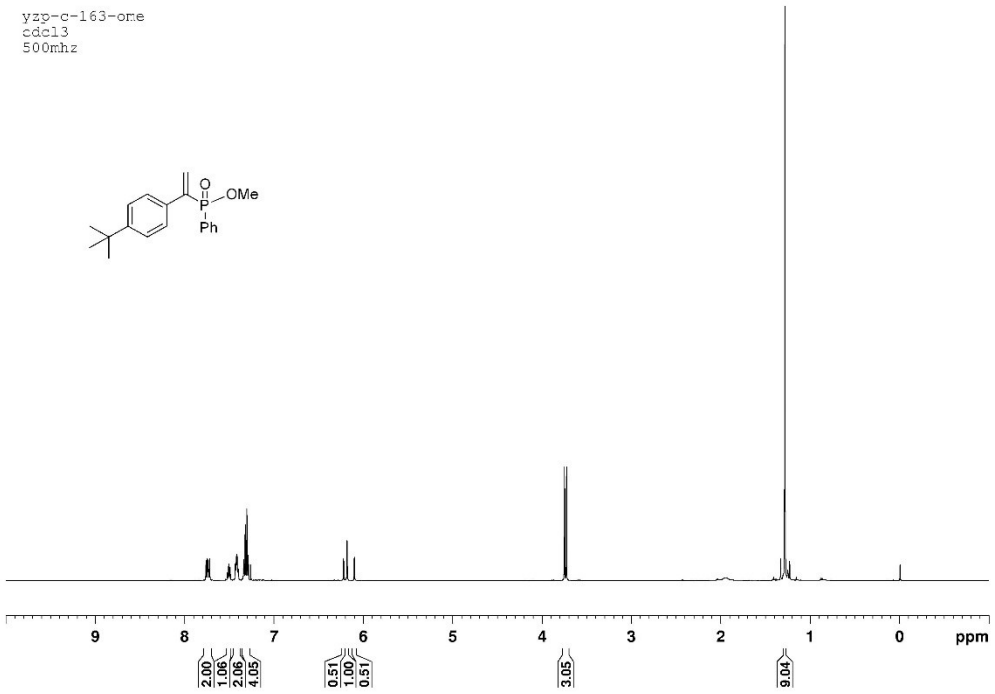

yzp-c-167-2c-c
cdcl3
125mhz
144.20
143.20
137.30
132.20
132.00
131.98
131.83
131.75
131.65
131.58
130.77
128.59
128.39
127.91
127.81
127.68
70.06
69.85
24.19
24.17
24.16
24.14
O
O
P
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

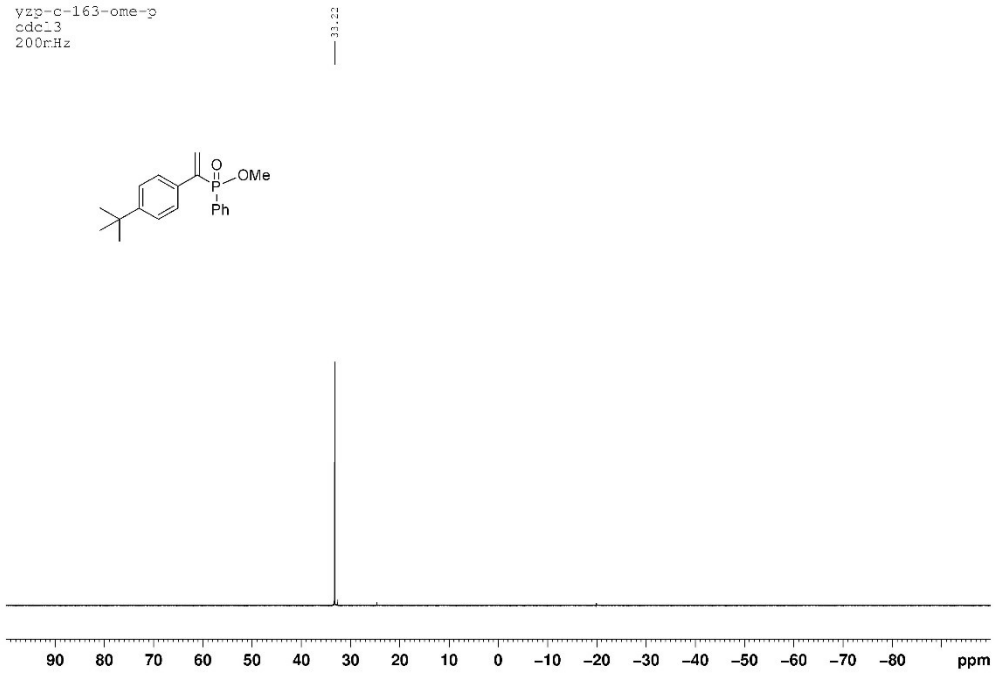
Ethyl (1-phenylvinyl)(*p*-tolyl)phosphinate (3ae)

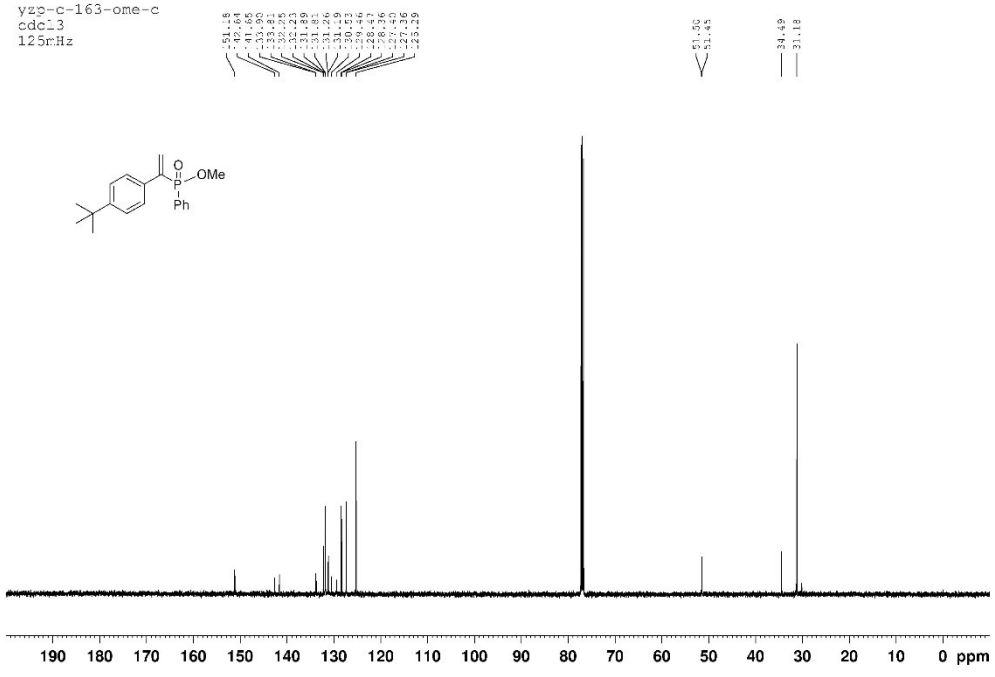




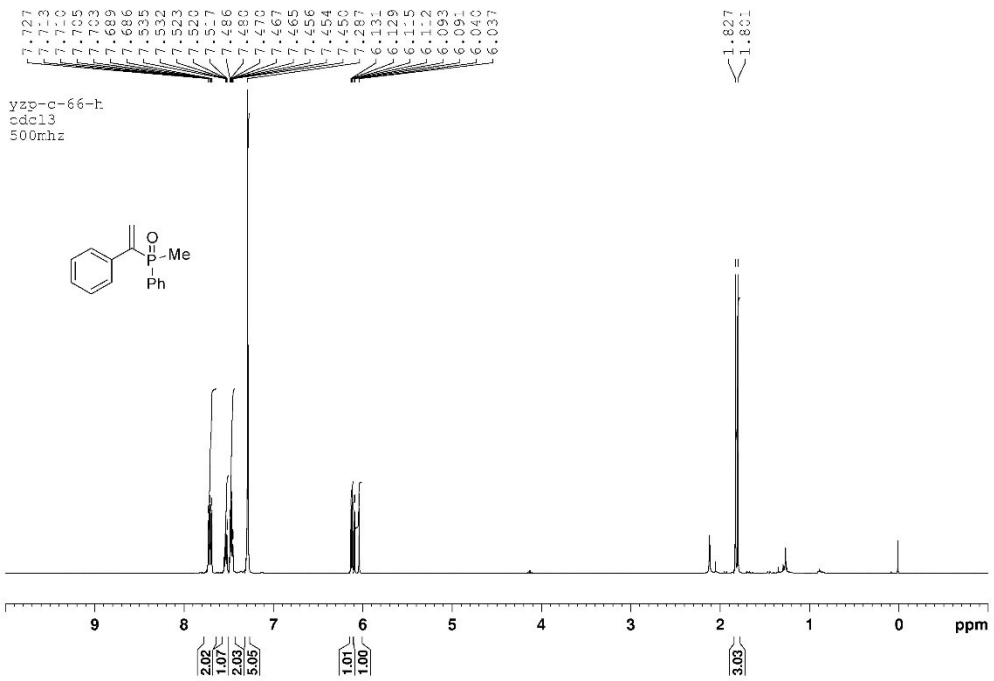
Methyl (1-(4-(*tert*-butyl)phenyl)vinyl)(phenyl)phosphinate (3fb)

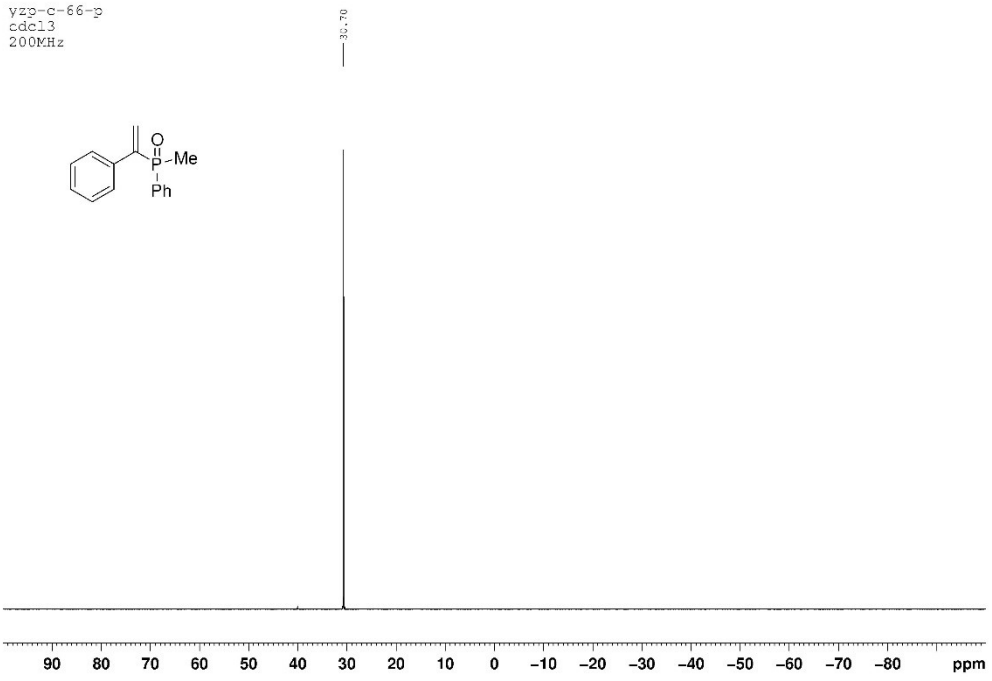


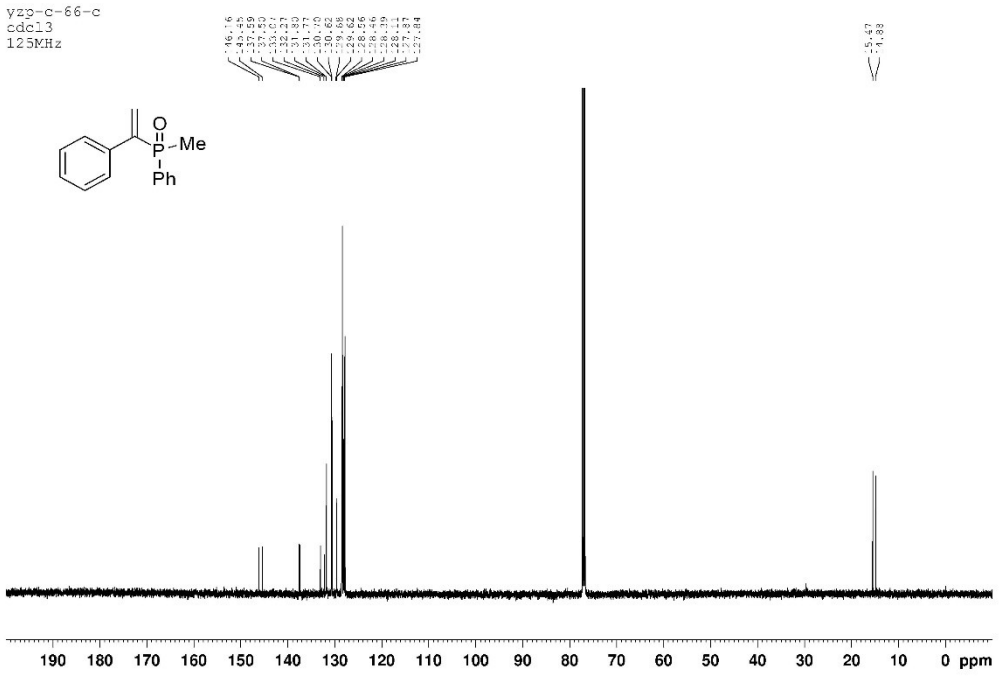

yzp-c-163-ome-p
cdcl3
200mHz
33.22
O
P
OMe
Ph
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm


yzp-c-163-ome-c
cdcl3
125mHz
151.18
142.64
141.65
133.90
133.81
132.26
132.23
131.89
131.81
131.26
131.19
130.53
129.46
128.97
128.56
127.45
127.36
125.29
61.50
61.45
34.49
31.18
O
P
OMe
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

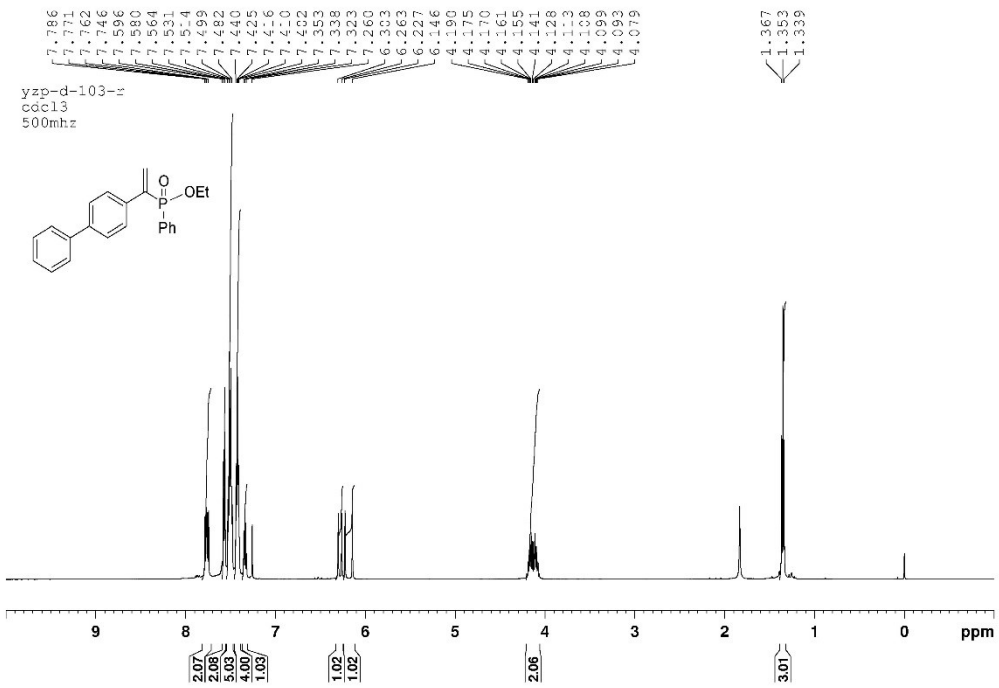
Methyl(phenyl)(1-phenylvinyl)phosphine oxide (3af)

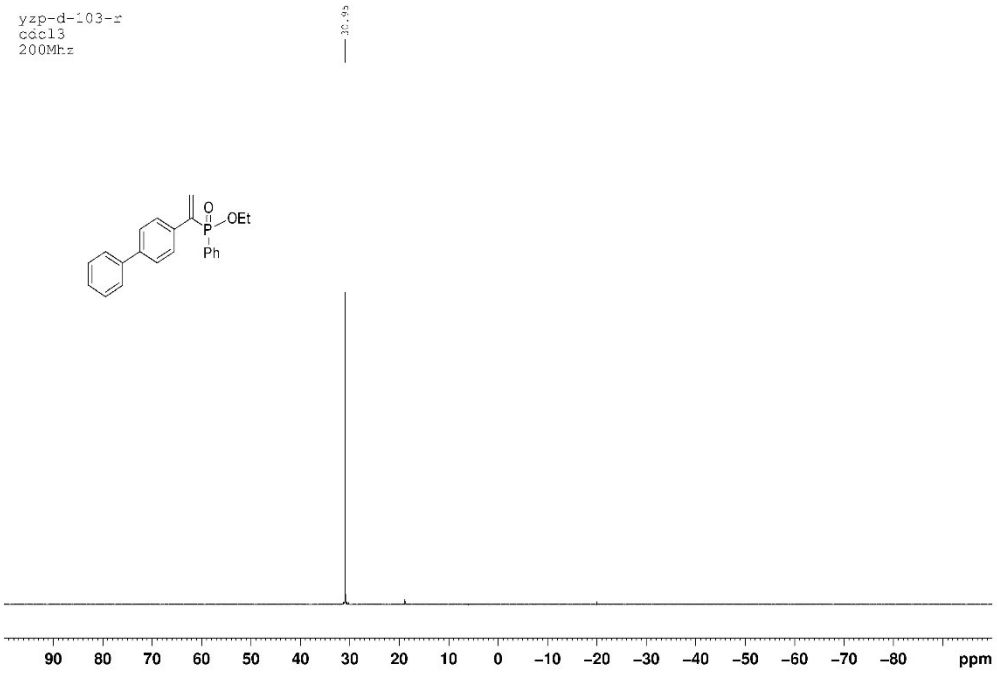


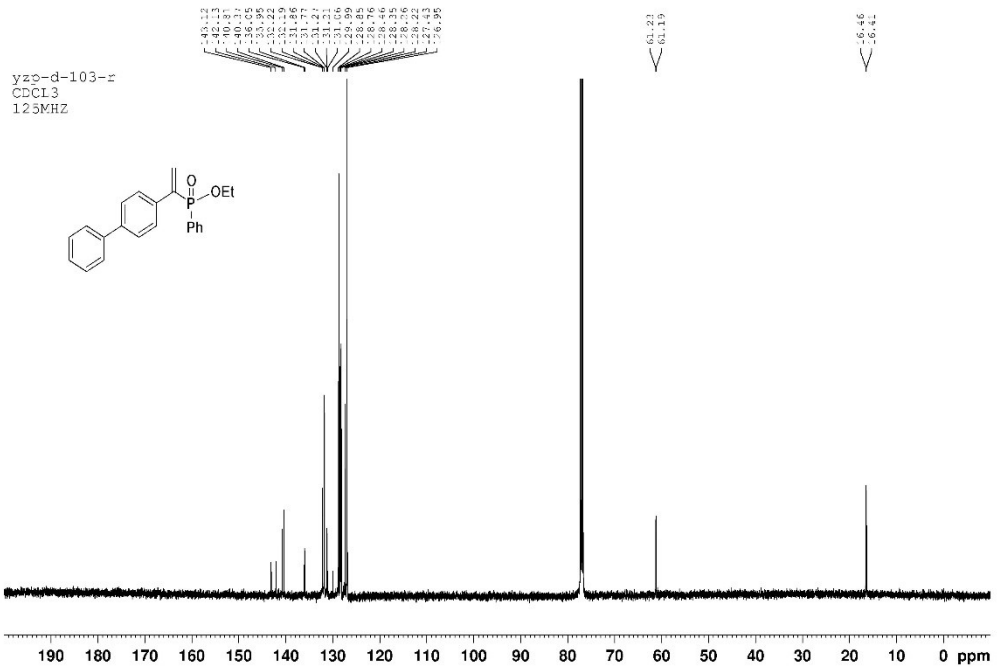




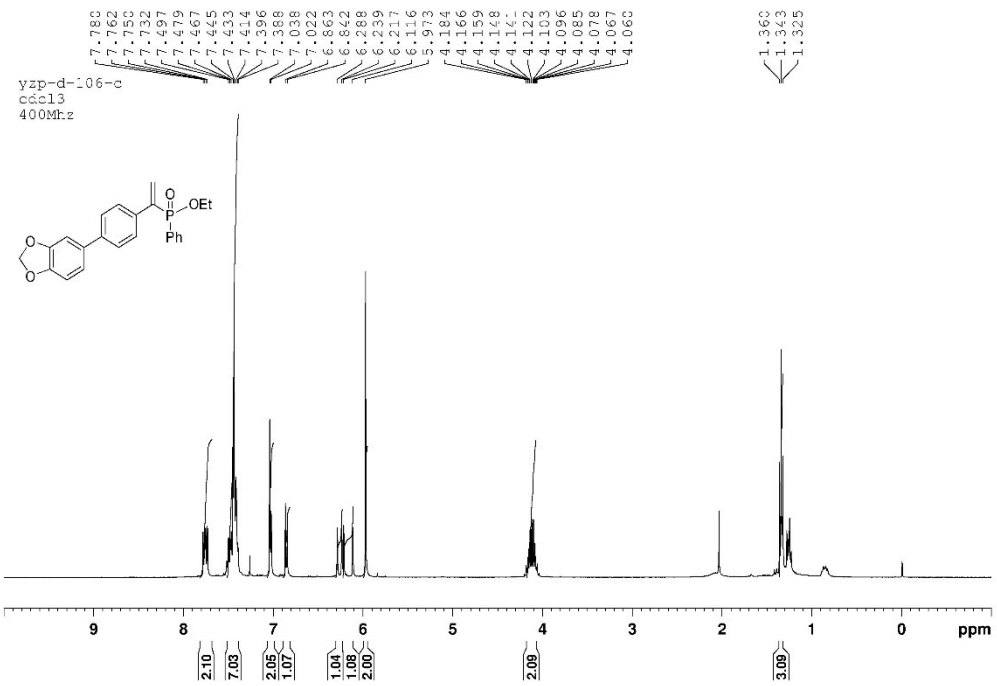
Ethyl (1-([1,1'-biphenyl]-4-yl)vinyl)(phenyl)phosphinate (4)

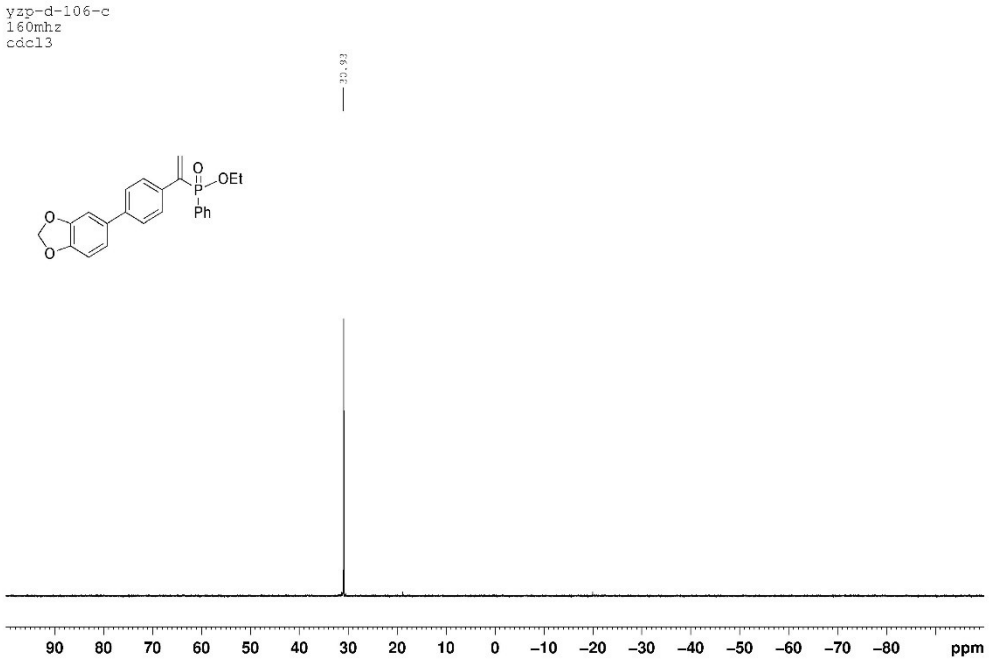


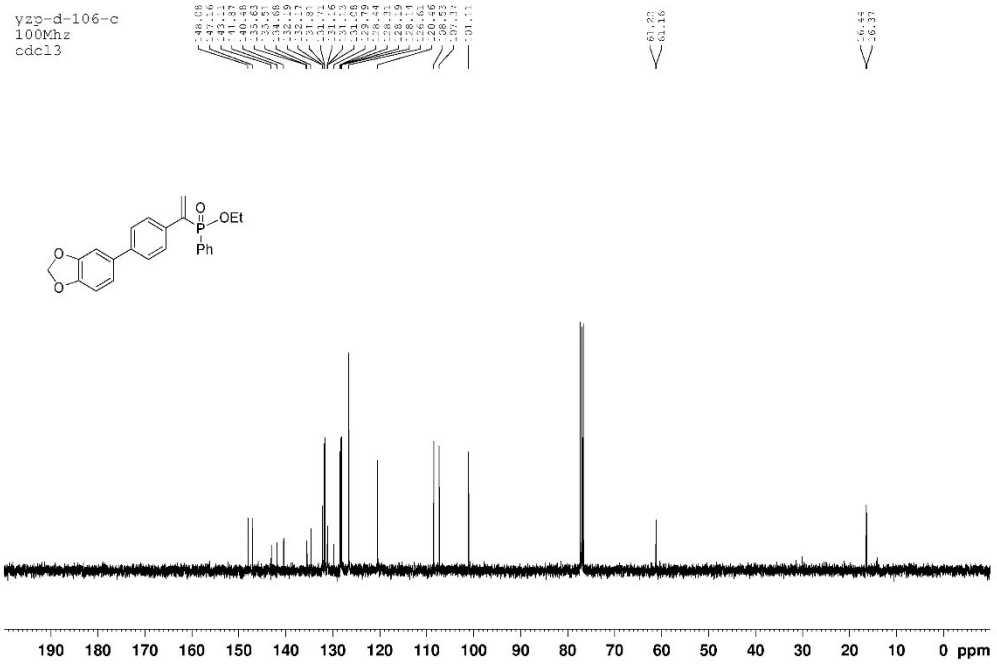

yzp-d-103-z
cdcl3
200Mhz
30.99
O
OEt
P
Ph
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 ppm


yzp-d-103-z
CDCL3
125MHZ
61.23
61.19
16.46
16.42
O
OEt
P
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

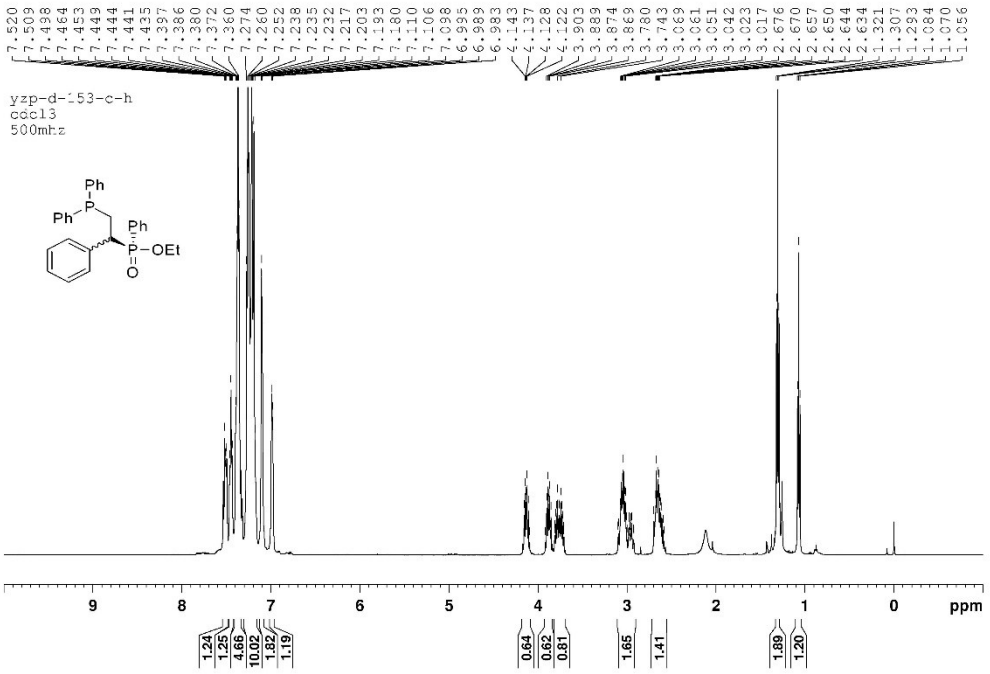
Ethyl (1-(4-(benzo[d][1,3]dioxol-5-yl)phenyl)vinyl)(phenyl)phosphinate (5)

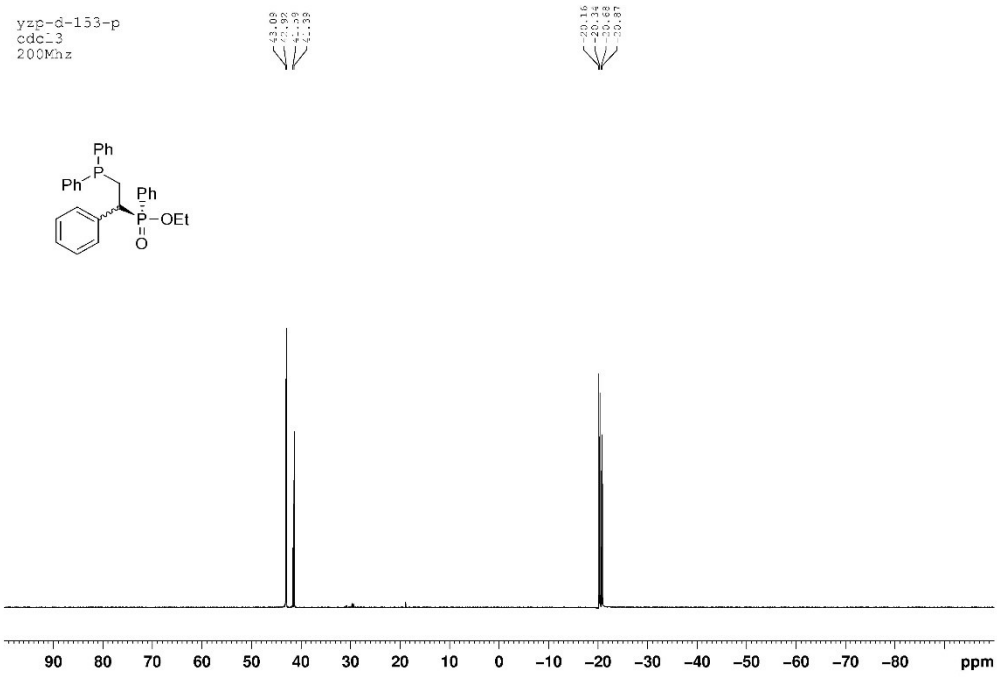


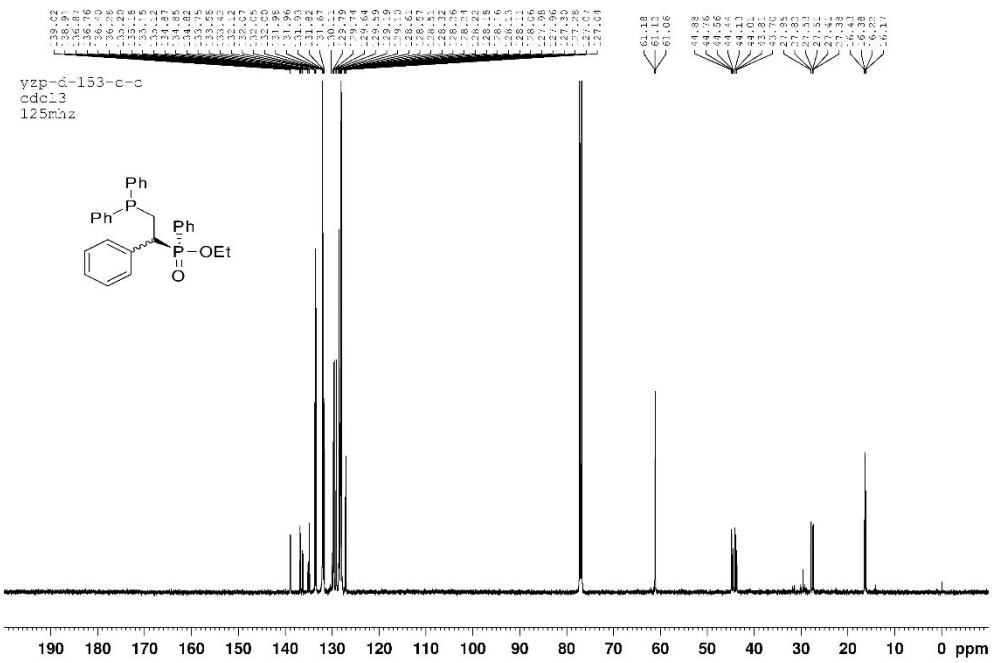




Ethyl (2-(diphenylphosphaneyl)-1-phenylethyl)(phenyl)phosphinate (6)

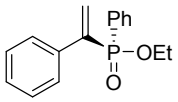


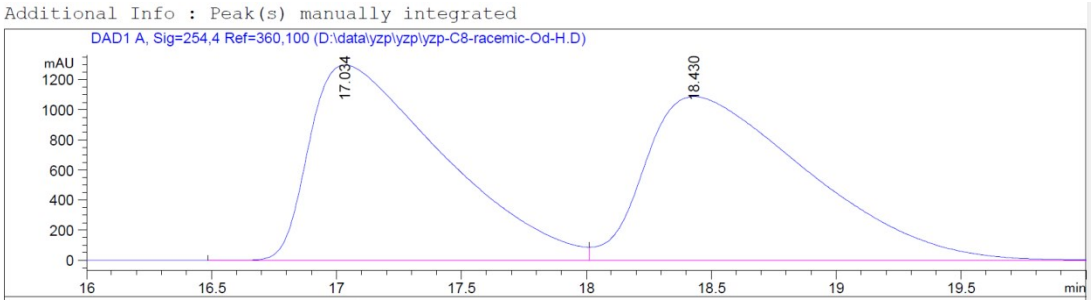

yzp-d-153-p
cdcl3
200Mhz
Ph
Ph
P
Ph
P–OEt
O
90 80 70 60 50 40 30 20 10 0 –10 –20 –30 –40 –50 –60 –70 –80 ppm


yzp-d-153-c-c
cdcl3
125mhz
Ph
Ph
P
Ph
P–OEt
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

8. HPLC spectrum

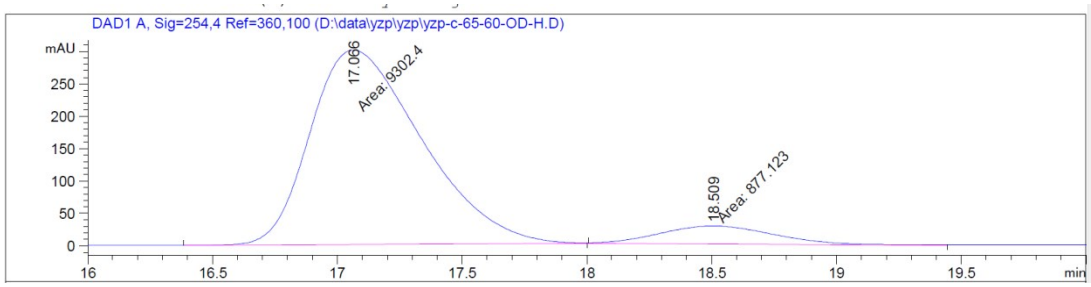
Ethyl phenyl(1-phenylvinyl)phosphinate (3aa)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

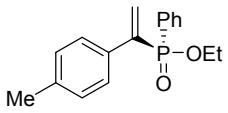
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.034	BV	0.5613	4.83012e4	1300.63135	49.5106
2	18.430	VB	0.6996	4.92561e4	1089.20264	50.4894
Totals :				9.75574e4	2389.83398	

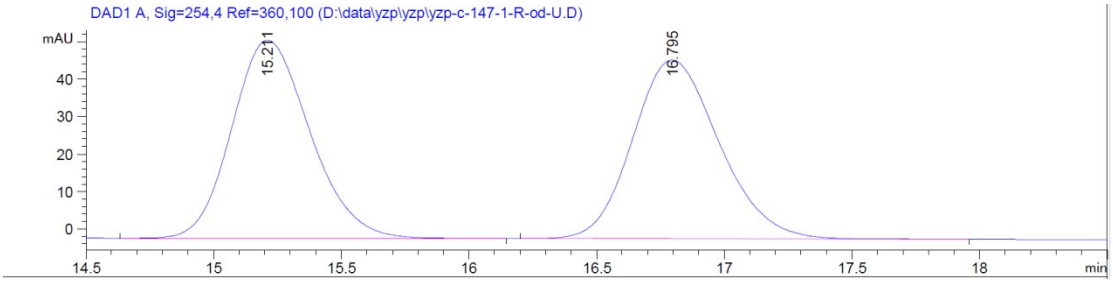


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.066	MM	0.5170	9302.40039	299.89902	91.3835
2	18.509	MM	0.5262	877.12329	27.78295	8.6165
Totals :				1.01795e4	327.68197	

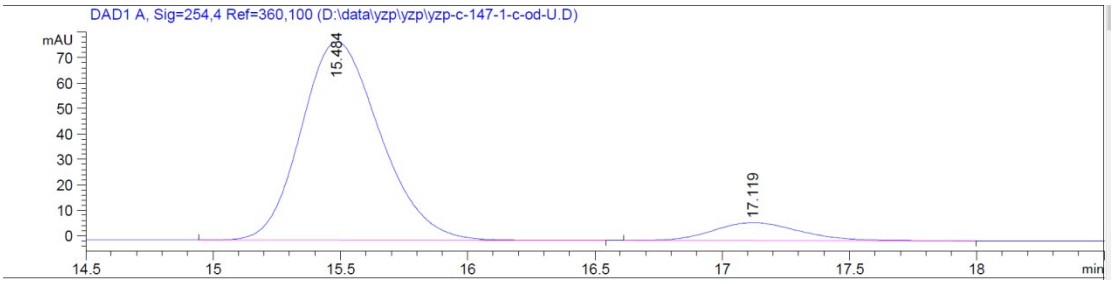
Ethyl phenyl(1-(*p*-tolyl)vinyl)phosphinate (3ba)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

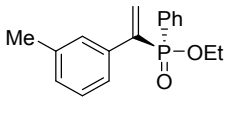
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.211	BB	0.3308	1127.07507	52.85910	49.9613
2	16.795	BB	0.3659	1128.82263	47.73948	50.0387
Totals :				2255.89771	100.59859	

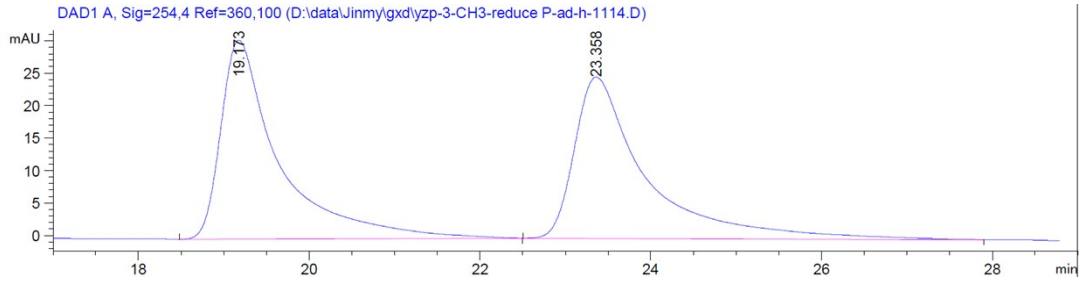


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.484	BB	0.3341	1685.26575	78.00603	90.9952
2	17.119	BB	0.3671	166.77249	7.07304	9.0048
Totals :				1852.03824	85.07908	

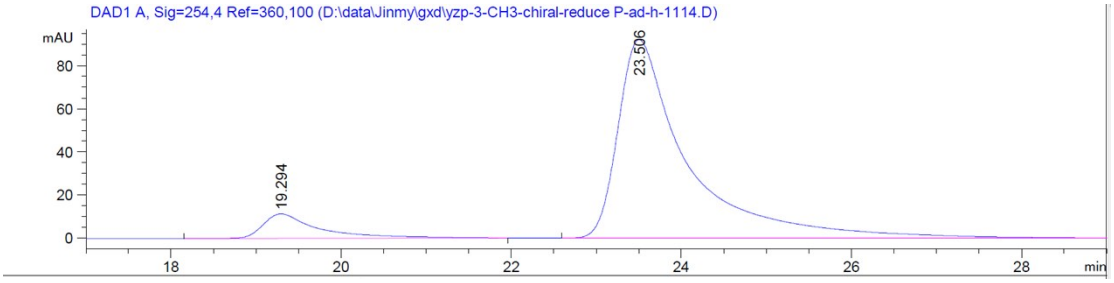
Ethyl phenyl(1-(*m*-tolyl)vinyl)phosphinate (3ca)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

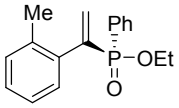
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.173	BB	0.6725	1455.57947	30.62736	50.1816
2	23.358	BB	0.8205	1445.04675	24.84810	49.8184
Totals :				2900.62622	55.47547	

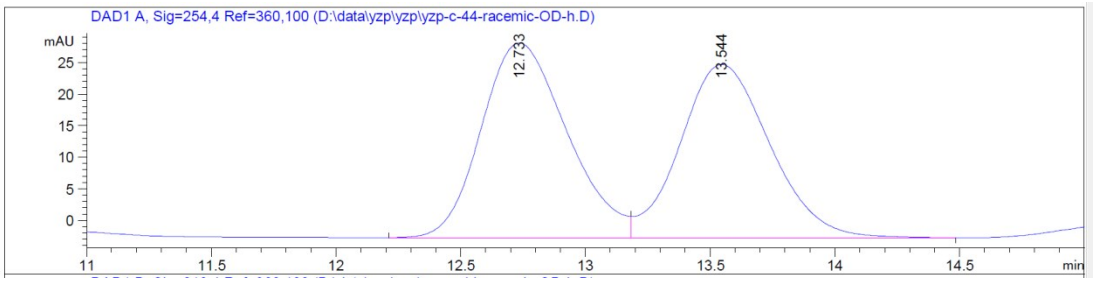


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.294	BB	0.6499	524.17285	11.41032	9.0270
2	23.506	BB	0.8016	5282.54395	92.31250	90.9730
Totals :				5806.71680	103.72282	

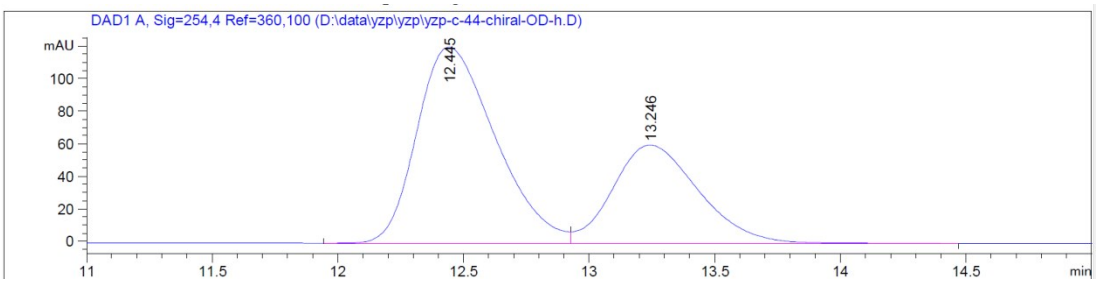
Ethyl phenyl(1-(*o*-tolyl)vinyl)phosphinate (3da)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

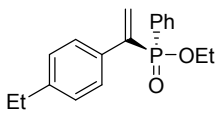
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.733	BV	0.3705	736.65143	30.85783	51.7973
2	13.544	VB	0.3871	685.52838	27.47429	48.2027
Totals :				1422.17981	58.33212	

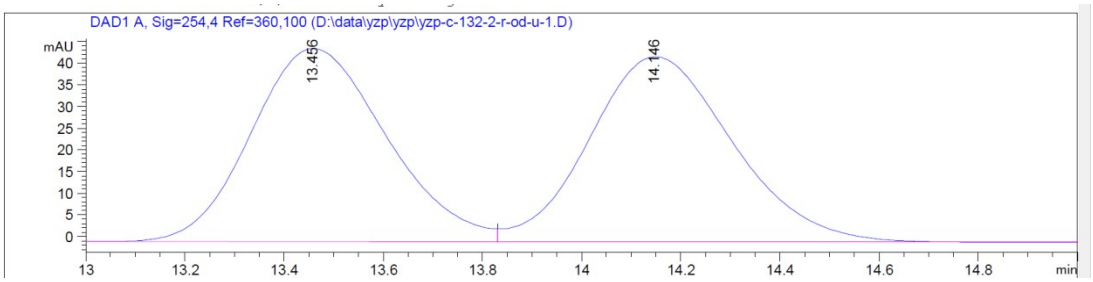


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.445	BV	0.3372	2618.21777	120.62339	64.5660
2	13.246	VB	0.3650	1436.88525	60.52047	35.4340
Totals :				4055.10303	181.14386	

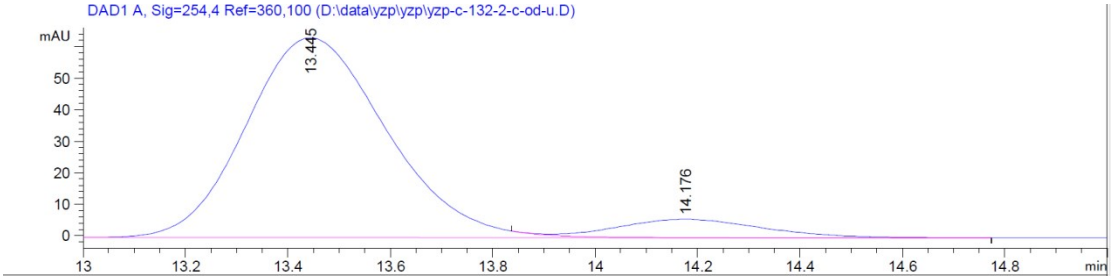
Ethyl (1-(4-ethylphenyl)vinyl)(phenyl)phosphinate (3ea)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

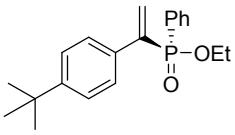
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.456	BV	0.2957	848.08154	44.63076	49.6177
2	14.146	VB	0.3108	861.14893	42.79587	50.3823
Totals :				1709.23047	87.42663	

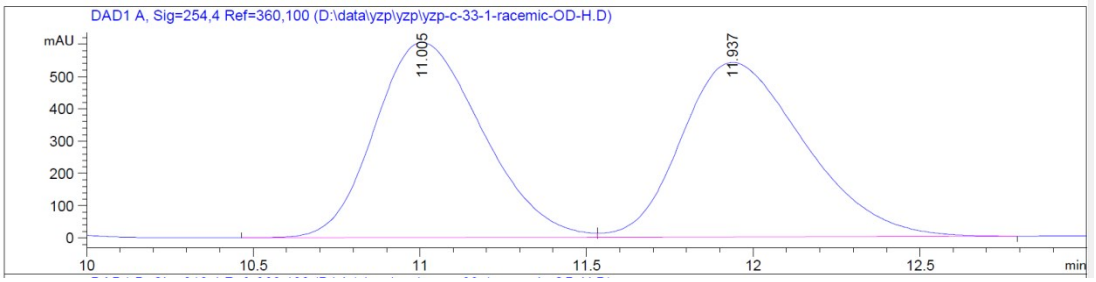


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

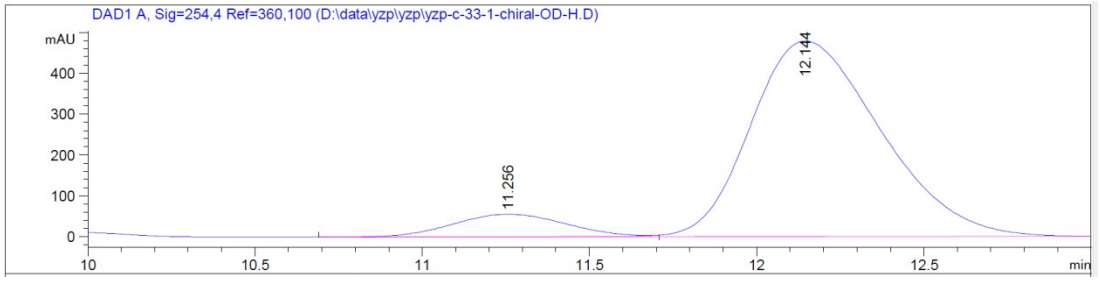
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.445	BV R	0.2952	1213.60986	63.44499	91.3723
2	14.176	VB E	0.2987	114.59372	5.84656	8.6277
Totals :				1328.20358	69.29155	

Ethyl (1-(4-(*tert*-butyl)phenyl)vinyl)(phenyl)phosphinate (3fa)





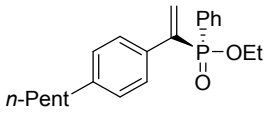
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.005	BV	0.3510	1.35163e4	604.23236	49.4166
2	11.937	VB	0.3967	1.38354e4	540.29620	50.5834
Totals :				2.73517e4	1144.52856	

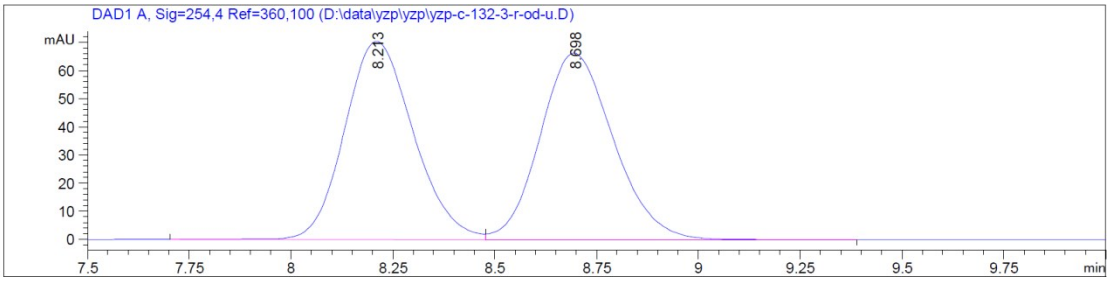


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.256	BV E	0.3731	1313.57458	55.69807	9.2287
2	12.144	VB R	0.4210	1.29200e4	478.50732	90.7713
Totals :				1.42336e4	534.20539	

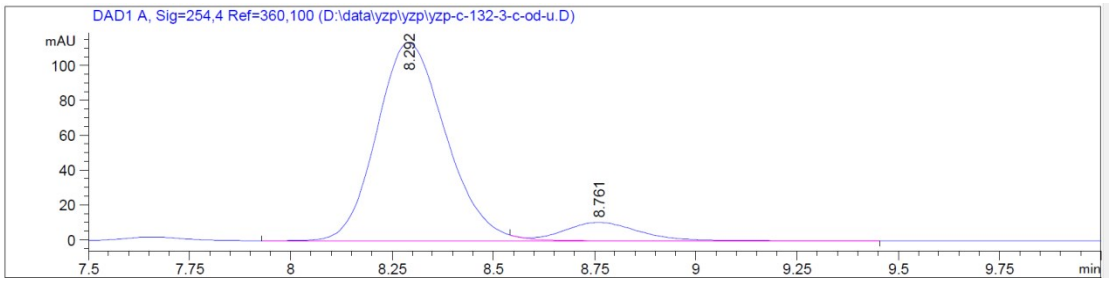
Ethyl (1-(4-pentylphenyl)vinyl)(phenyl)phosphinate (3ga)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

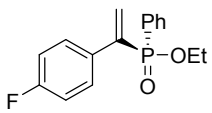
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.213	BV	0.1809	827.99847	70.53882	49.8606
2	8.698	VB	0.1944	832.62897	66.32990	50.1394
Totals :				1660.62744	136.86871	

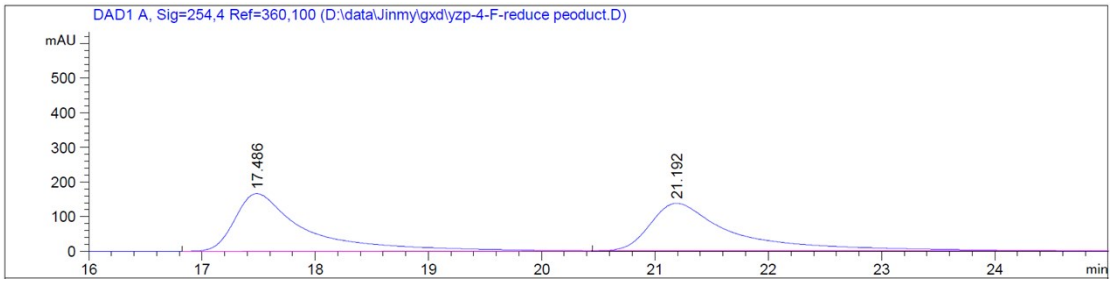


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.292	BV R	0.1823	1349.61511	113.81870	90.9758
2	8.761	VB E	0.1961	133.87355	10.54477	9.0242
Totals :				1483.48866	124.36347	

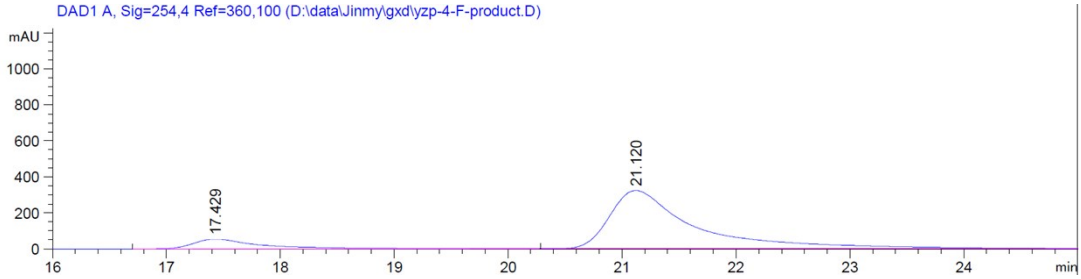
Ethyl (1-(4-fluorophenyl)vinyl)(phenyl)phosphinate (3ha)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

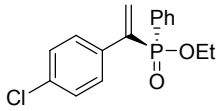
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.486	BB	0.6041	7085.03564	165.96121	50.0418
2	21.192	BBA	0.7303	7073.19629	137.01465	49.9582
Totals :				1.41582e4	302.97586	

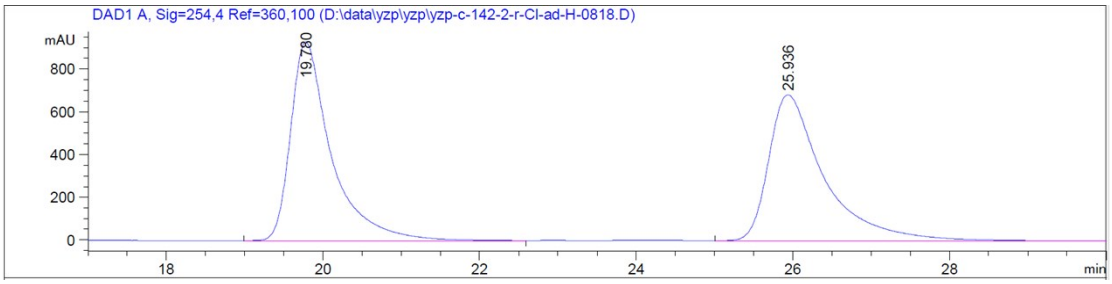


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.429	BB	0.5972	2296.09277	54.53732	11.8369
2	21.120	BBA	0.7435	1.71017e4	324.16965	88.1631
Totals :				1.93978e4	378.70697	

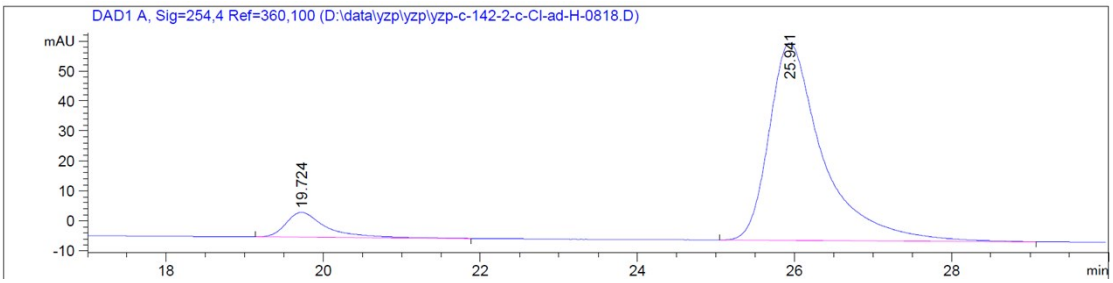
Ethyl (1-(4-chlorophenyl)vinyl)(phenyl)phosphinate (3ia)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

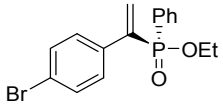
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.780	BB	0.5283	3.35288e4	930.75446	49.9538
2	25.936	BBA	0.7156	3.35908e4	683.27417	50.0462
Totals :				6.71197e4	1614.02863	

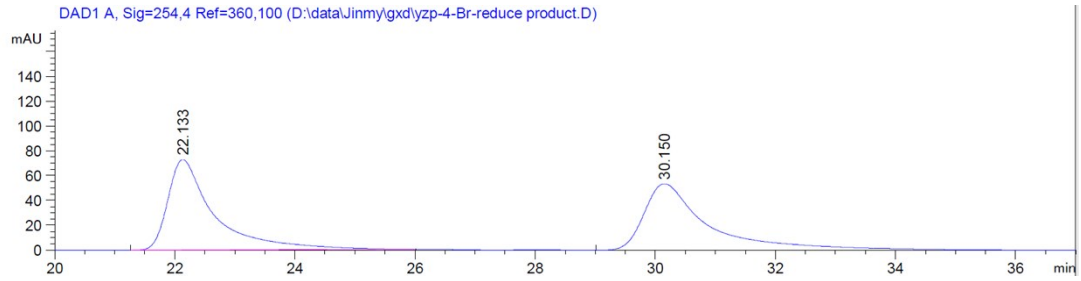


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.724	BB	0.5084	294.05746	8.27934	8.5991
2	25.941	BB	0.6977	3125.58203	65.86158	91.4009
Totals :				3419.63950	74.14091	

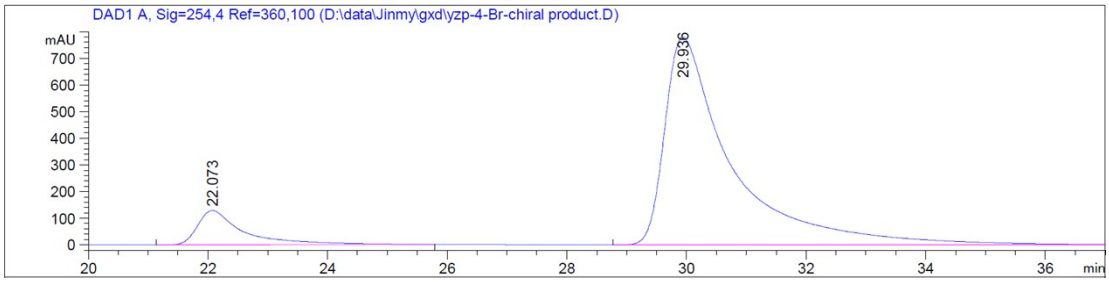
Ethyl (1-(4-bromophenyl)vinyl)(phenyl)phosphinate (3ja)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

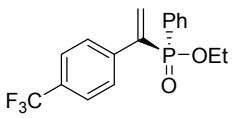
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.133	BB	0.7671	3936.78735	73.00545	49.5685
2	30.150	BB	1.0514	4005.33057	53.62398	50.4315
Totals :				7942.11792	126.62943	

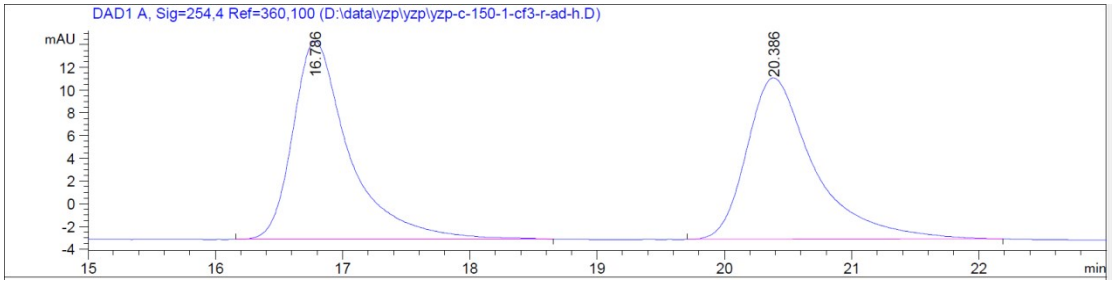


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.073	BB	0.7676	6949.57031	128.77031	10.2714
2	29.936	BB	1.0923	6.07102e4	779.75720	89.7286
Totals :				6.76598e4	908.52751	

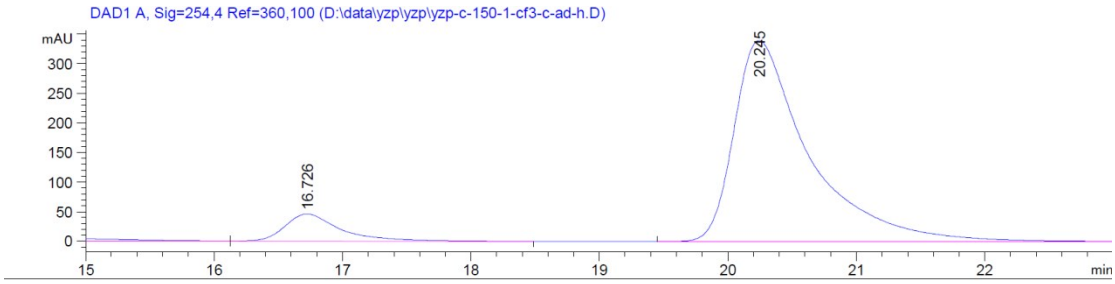
Ethyl phenyl(1-(4-(trifluoromethyl)phenyl)vinyl)phosphinate (3ka)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

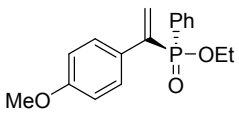
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.786	BB	0.4495	539.09833	17.49617	50.6946
2	20.386	BB	0.5484	524.32599	14.21295	49.3054
Totals :				1063.42432	31.70912	

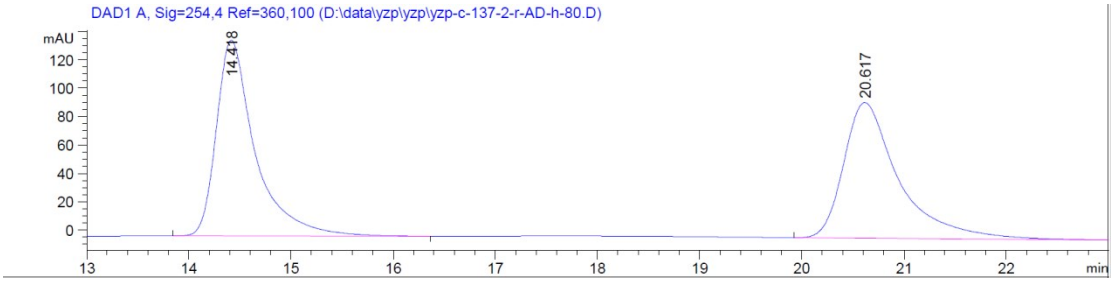


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.726	BB	0.4421	1374.91882	45.82354	9.1003
2	20.245	BB	0.5856	1.37336e4	339.73163	90.8997
Totals :				1.51086e4	385.55517	

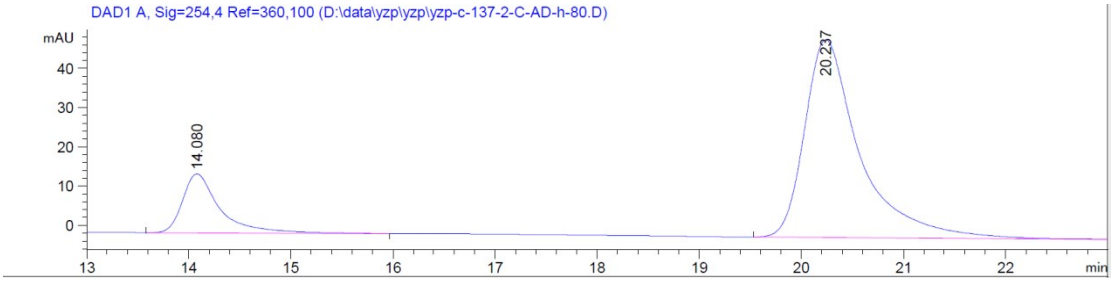
Ethyl (1-(4-methoxyphenyl)vinyl)(phenyl)phosphinate (3la)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

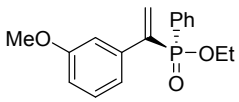
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.418	BB	0.3871	3628.31055	137.82220	50.2696
2	20.617	BBA	0.5522	3589.38574	95.55950	49.7304
Totals :				7217.69629	233.38171	

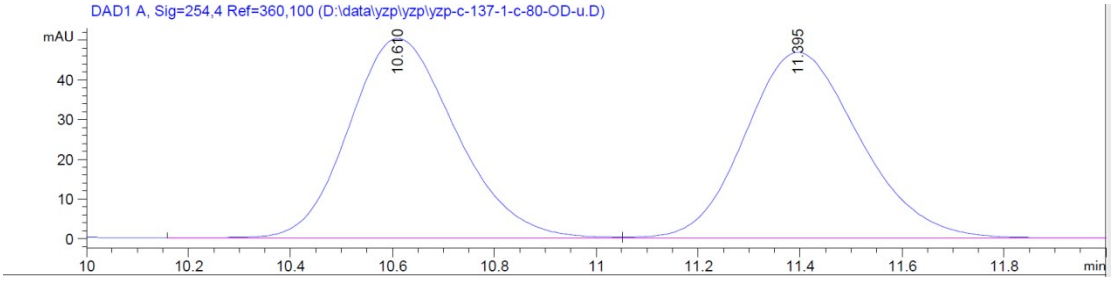


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.080	BB	0.3740	384.34708	15.04927	16.8566
2	20.237	BB	0.5545	1895.75647	50.43964	83.1434
Totals :				2280.10355	65.48891	

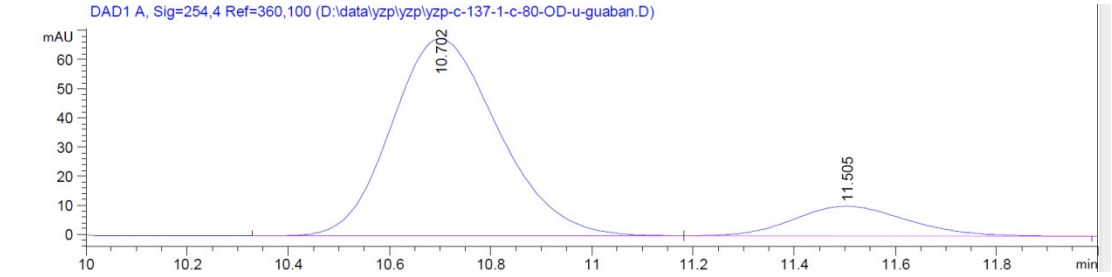
Ethyl (1-(3-methoxyphenyl)vinyl)(phenyl)phosphinate (3ma)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

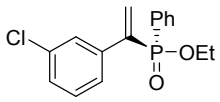
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.610	BV	0.2257	730.76105	50.23415	50.0569
2	11.395	VB	0.2421	729.09918	46.70588	49.9431
Totals :				1459.86023	96.94004	

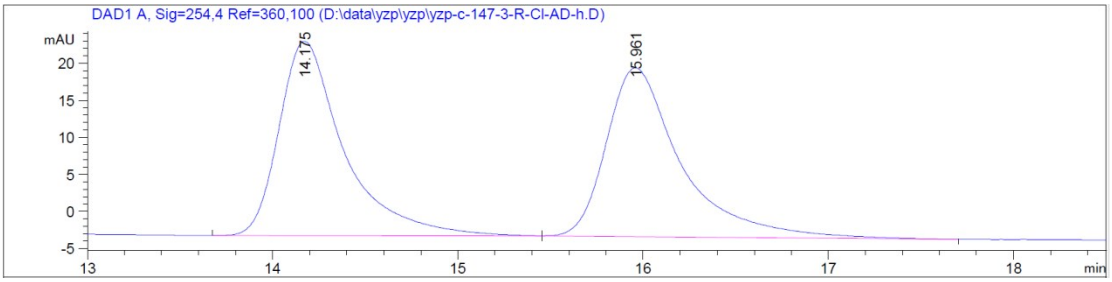


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.702	BB	0.2294	994.26141	67.68888	86.2171
2	11.505	BB	0.2406	158.94597	10.15432	13.7829
Totals :				1153.20738	77.84320	

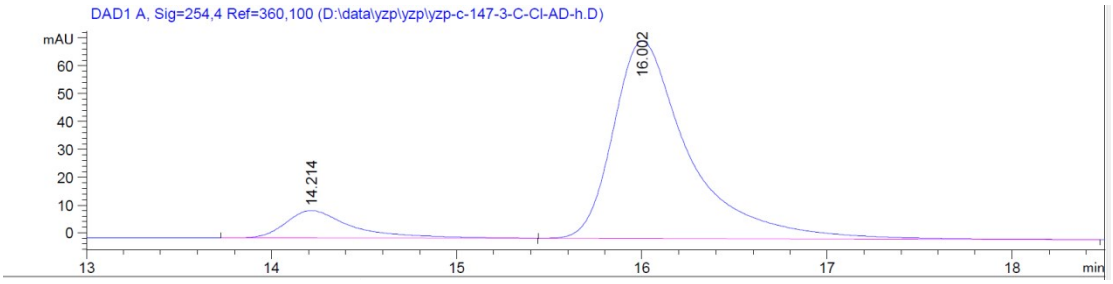
Ethyl (1-(3-chlorophenyl)vinyl)(phenyl)phosphinate (3na)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

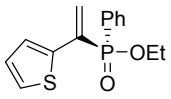
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.175	BB	0.3578	637.51459	26.20414	49.9793
2	15.961	BB	0.4132	638.04175	22.74858	50.0207
Totals :				1275.55634	48.95271	

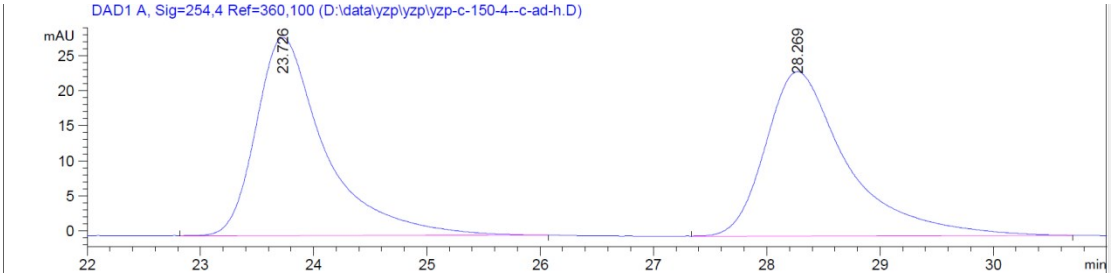


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.214	BB	0.3644	244.77248	9.83293	10.8374
2	16.002	BB	0.4179	2013.81152	70.79815	89.1626
Totals :				2258.58400	80.63108	

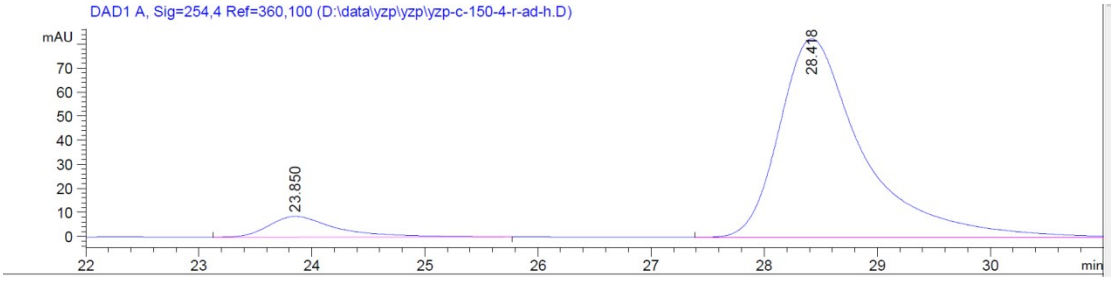
Ethyl phenyl(1-(thiophen-2-yl)vinyl)phosphinate (3oa)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

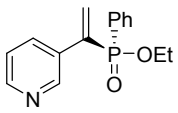
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.726	BB	0.6240	1199.77063	28.33216	50.4731
2	28.269	BB	0.7346	1177.27844	23.49385	49.5269
Totals :				2377.04907	51.82601	

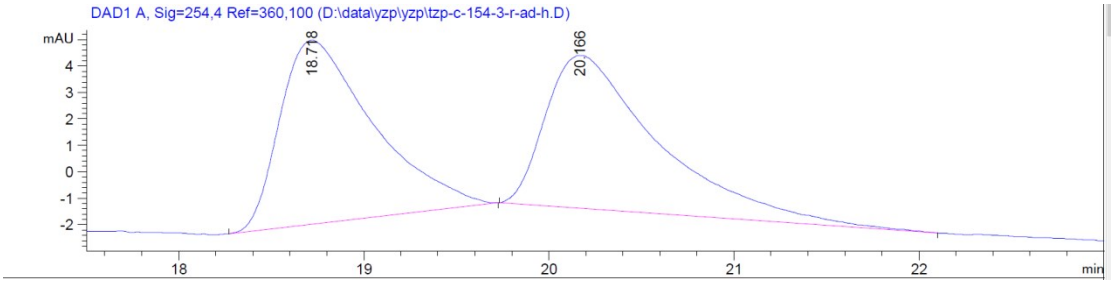


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.850	BB	0.6010	362.60214	8.61544	7.8429
2	28.418	BB	0.7536	4260.73926	82.62840	92.1571
Totals :				4623.34140	91.24384	

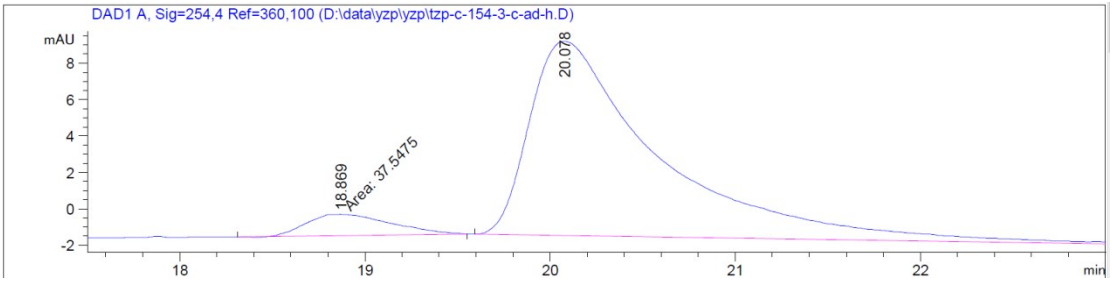
Ethyl phenyl(1-(pyridin-3-yl)vinyl)phosphinate (3pa)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

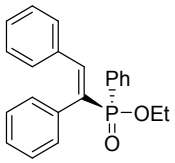
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.718	BB	0.4868	242.45108	6.95281	49.7336
2	20.166	BB	0.5886	245.04849	5.77976	50.2664
Totals :				487.49957	12.73257	

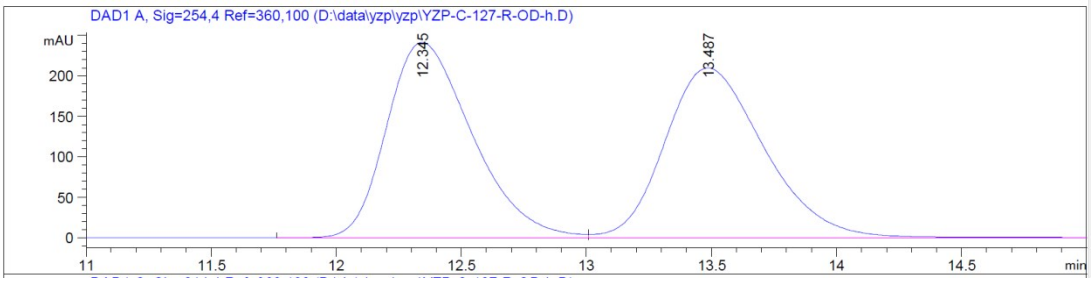


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.869	MM	0.5303	37.54748	1.18003	6.7609
2	20.078	BB	0.6762	517.81714	10.67050	93.2391
Totals :				555.36462	11.85053	

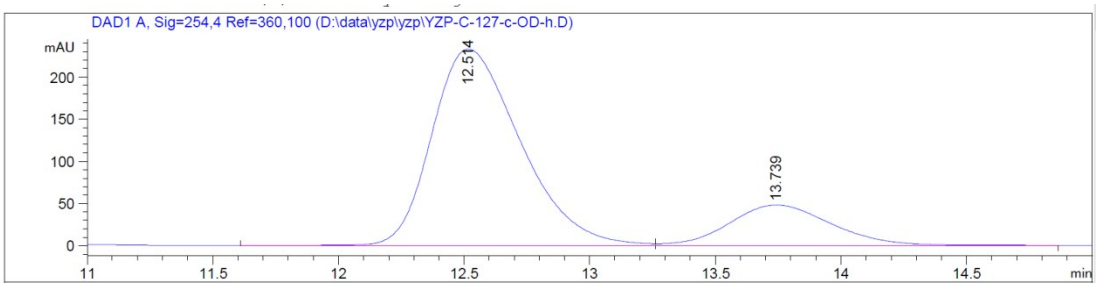
Ethyl (*Z*)-(1,2-diphenylvinyl)(phenyl)phosphinate (3qa)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

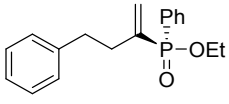
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.345	BV	0.3669	5725.15137	241.20590	49.6995
2	13.487	VB	0.4265	5794.37842	209.63976	50.3005
Totals :				1.15195e4	450.84566	

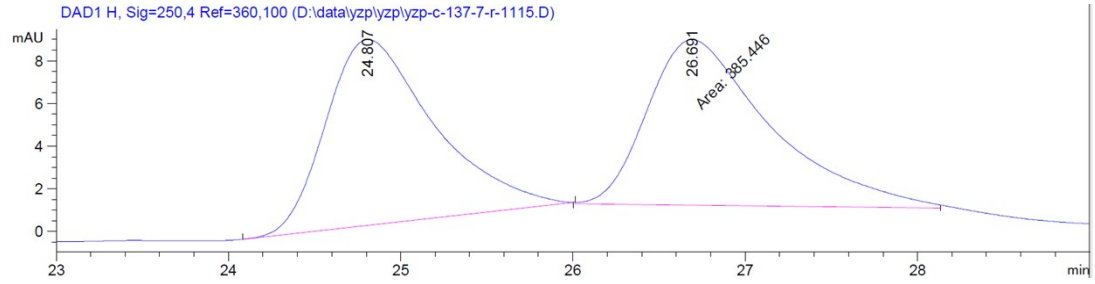


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.514	BV	0.3776	5703.88672	232.99278	80.8349
2	13.739	VB	0.4371	1352.33093	47.93449	19.1651
Totals :				7056.21765	280.92727	

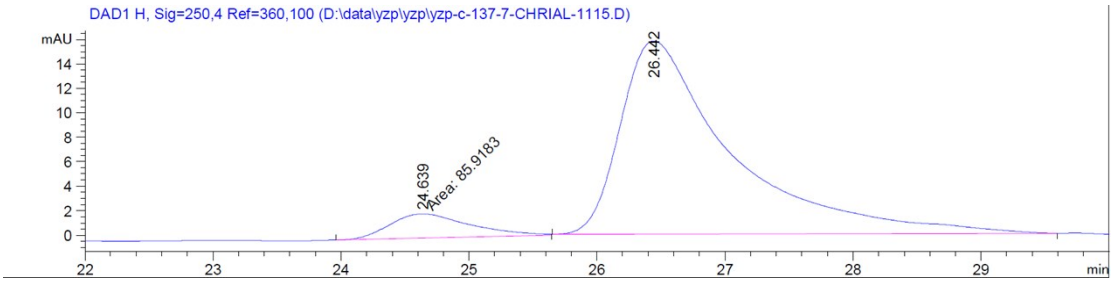
Ethyl phenyl(4-phenylbut-1-en-2-yl)phosphinate (3ra)





Signal 8: DAD1 H, Sig=250,4 Ref=360,100

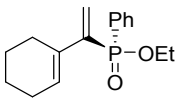
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.807	BB	0.6532	379.97043	8.70611	49.6423
2	26.691	MM	0.8276	385.44553	7.76210	50.3577

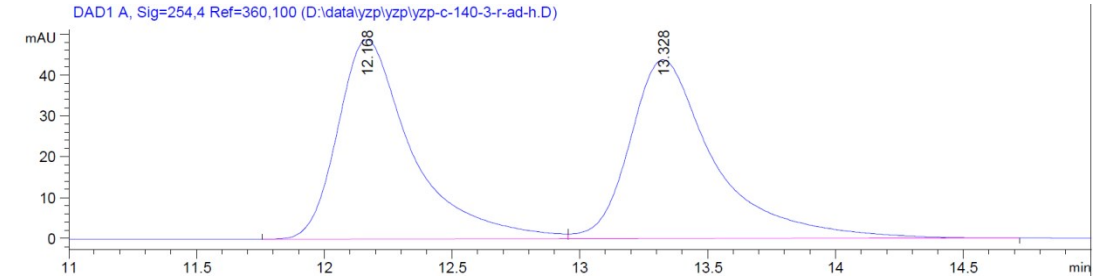


Signal 8: DAD1 H, Sig=250,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.639	MM	0.7256	85.91833	1.97359	8.2975
2	26.442	BB	0.8468	949.55420	15.80893	91.7025
Totals :				1035.47253	17.78252	

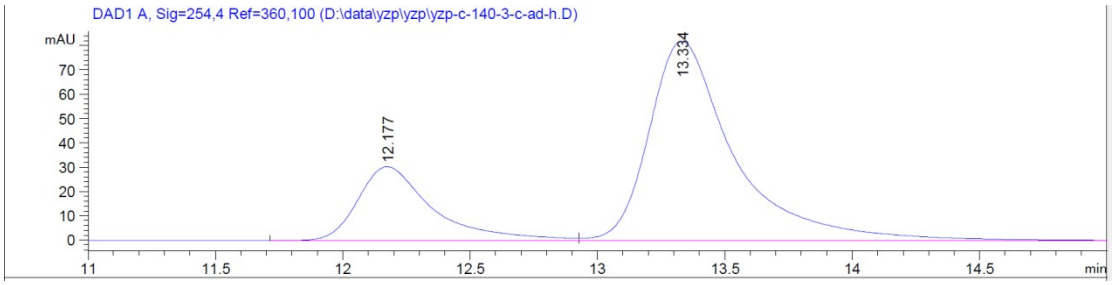
Ethyl (1-(cyclohex-1-en-1-yl)vinyl)(phenyl)phosphinate (3sa)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

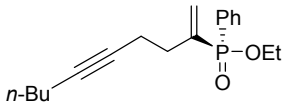
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.168	BV	0.2981	987.60193	48.80626	49.4378
2	13.328	VB	0.3393	1010.06213	43.75435	50.5622
Totals :				1997.66406	92.56062	

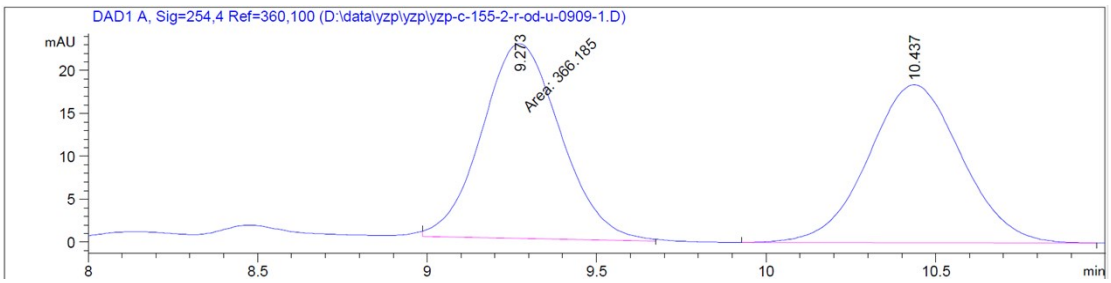


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.177	BV	0.3024	620.33344	30.36318	24.4034
2	13.334	VB	0.3431	1921.66394	82.09179	75.5966
Totals :				2541.99738	112.45497	

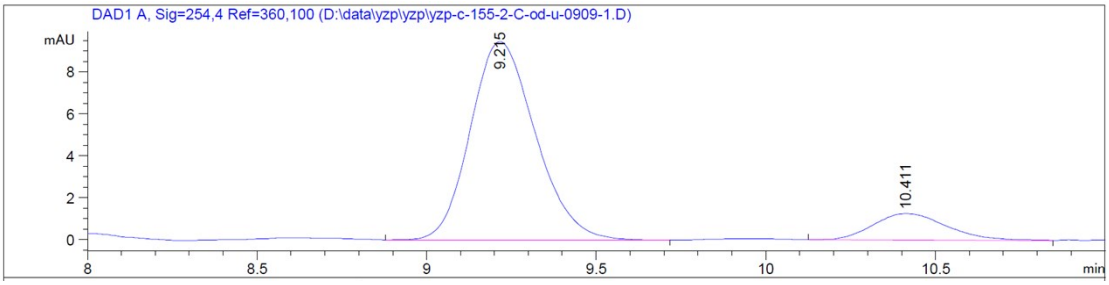
Ethyl dec-1-en-5-yn-2-yl(phenyl)phosphinate (3ta)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

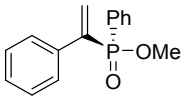
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.273	FM	0.2693	366.18530	22.66425	50.9785
2	10.437	BB	0.2954	352.12766	18.38955	49.0215
Totals :				718.31296	41.05380	

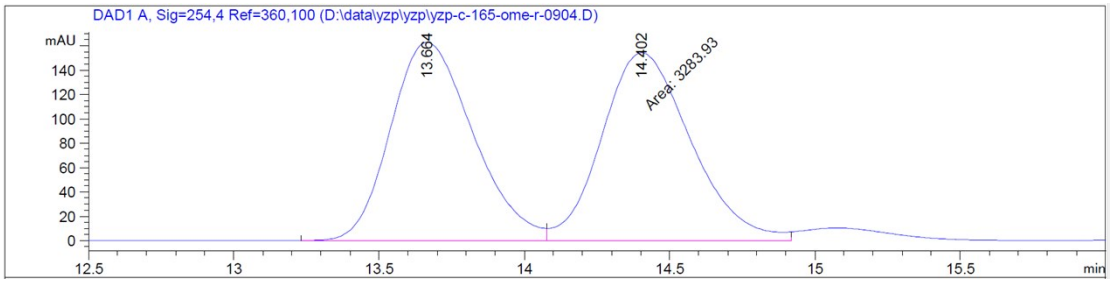


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.215	BB	0.2056	126.38673	9.47484	86.9516
2	10.411	BB	0.2295	18.96622	1.26053	13.0484
Totals :				145.35295	10.73537	

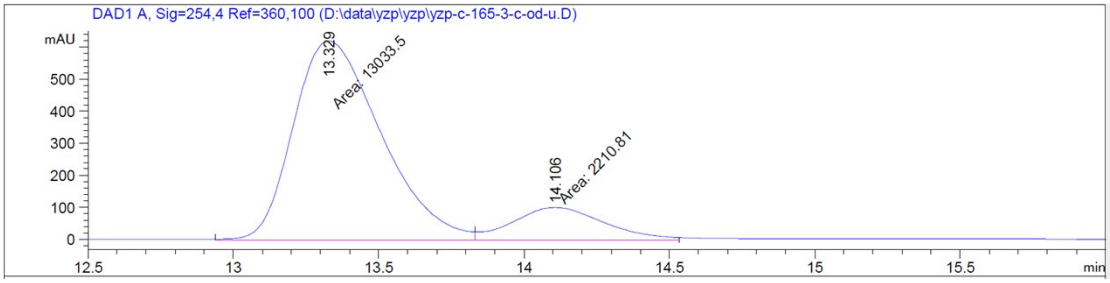
Methyl phenyl(1-phenylvinyl)phosphinate (3ab)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

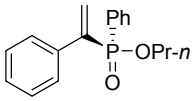
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.664	BV	0.3039	3208.71436	162.84334	49.4208
2	14.402	MF	0.3550	3283.92749	154.18130	50.5792
Totals :				6492.64185	317.02464	

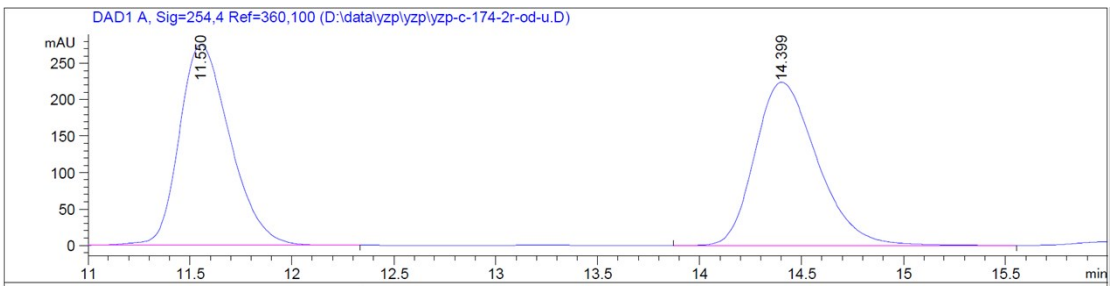


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.329	MF	0.3494	1.30335e4	621.63159	85.4974
2	14.106	FM	0.3633	2210.81201	101.41106	14.5026
Totals :				1.52443e4	723.04265	

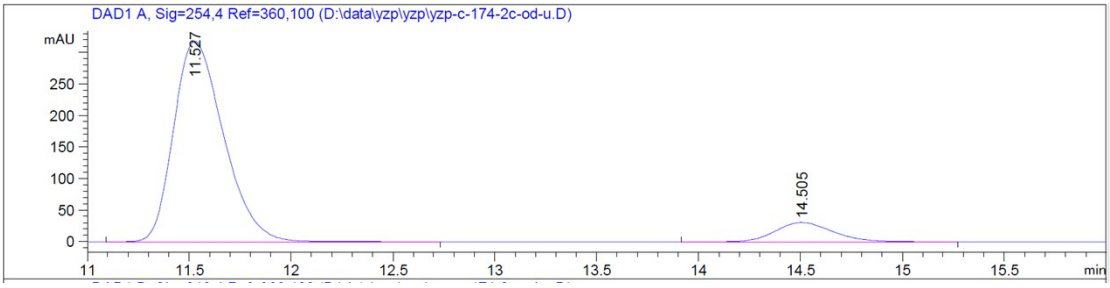
Propyl phenyl(1-phenylvinyl)phosphinate (3ac)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

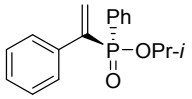
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.550	BB	0.2652	4757.17090	275.84192	49.9634
2	14.399	BB	0.3277	4764.14355	224.41707	50.0366
Totals :				9521.31445	500.25899	

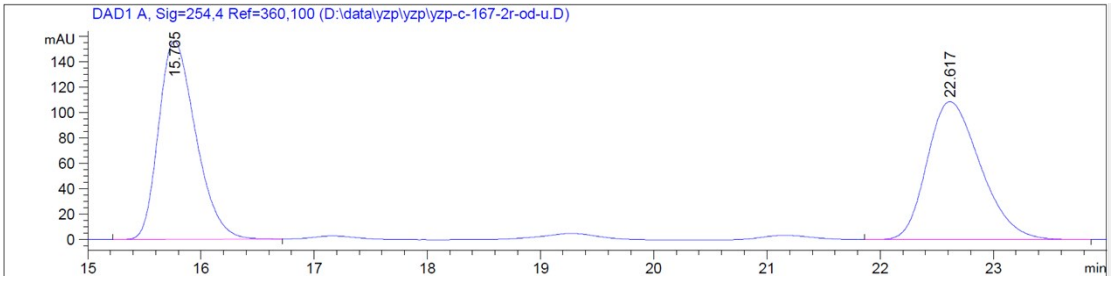


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.527	BB	0.2624	5408.20215	318.08746	89.9798
2	14.505	BB	0.3037	602.26172	30.58710	10.0202
Totals :				6010.46387	348.67456	

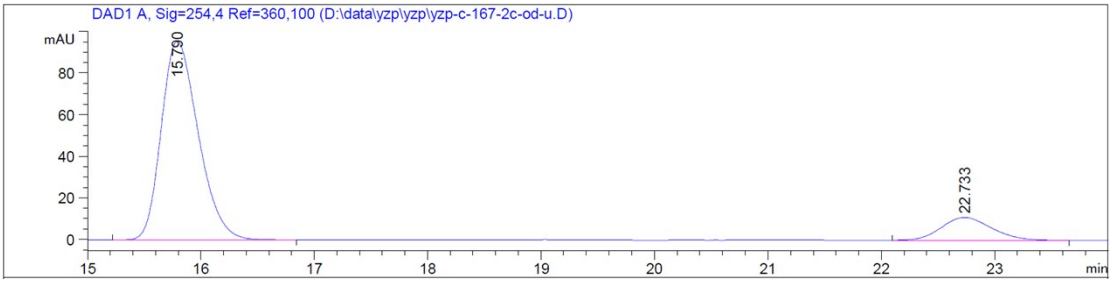
Isopropyl phenyl(1-phenylvinyl)phosphinate (3ad)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

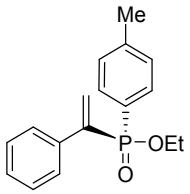
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.765	BB	0.3517	3556.52637	156.15768	49.9463
2	22.617	BB	0.5104	3564.17554	108.75292	50.0537
Totals :				7120.70190	264.91061	

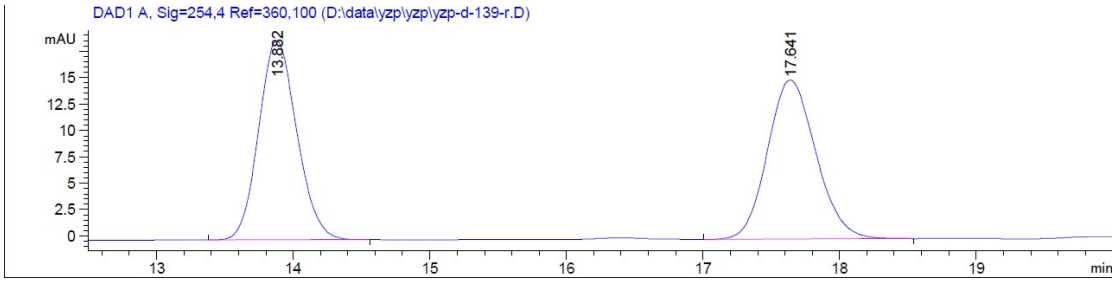


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.790	BB	0.3524	2167.35767	95.61871	86.4514
2	22.733	BB	0.4723	339.66675	10.99948	13.5486
Totals :				2507.02441	106.61819	

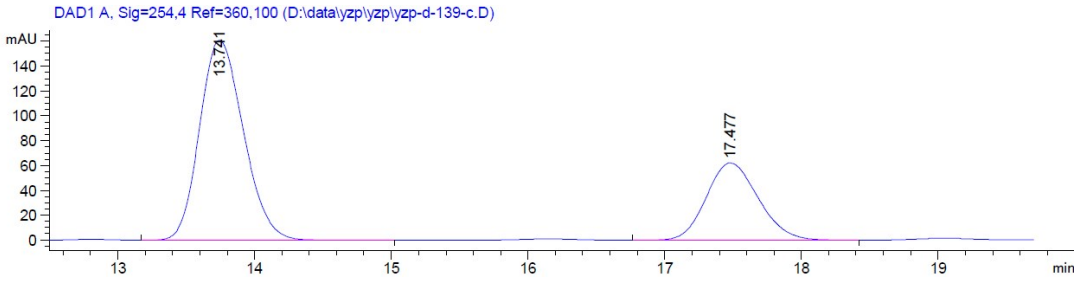
Ethyl (1-phenylvinyl)(*p*-tolyl)phosphinate (3ae)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

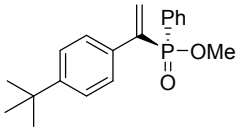
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.882	BB	0.2997	365.34946	18.88466	49.6452
2	17.641	BB	0.3792	370.57196	15.05156	50.3548
Totals :				735.92142	33.93622	

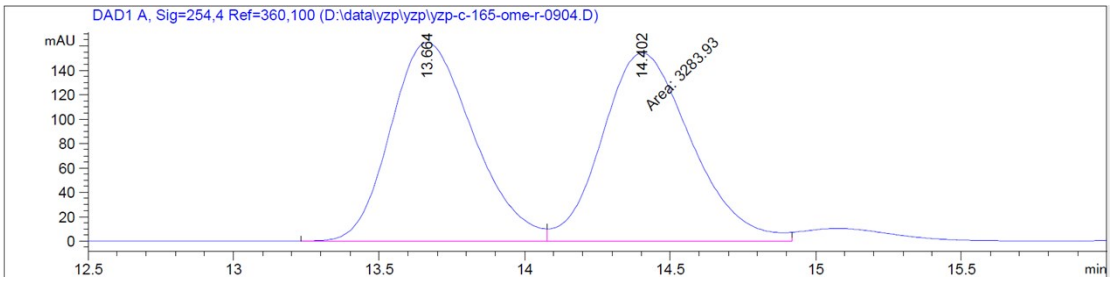


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.741	BB	0.3495	3580.47192	160.94972	68.5631
2	17.477	BB	0.4102	1641.68225	62.15380	31.4369
Totals :				5222.15417	223.10352	

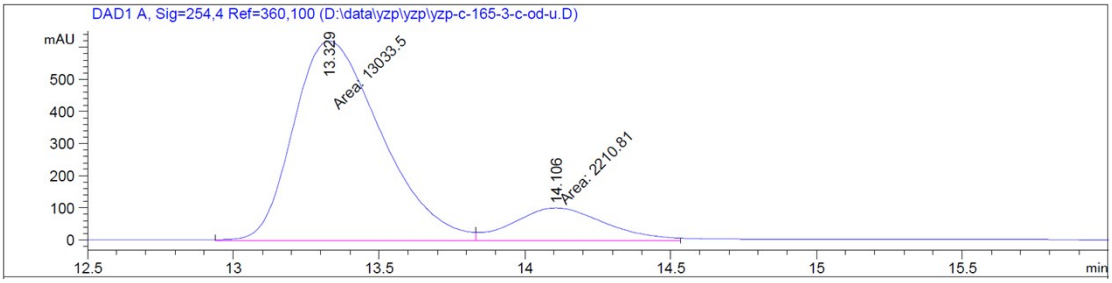
Methyl (1-(4-(tert-butyl)phenyl)vinyl)(phenyl)phosphinate (3fb)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

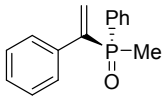
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.664	BV	0.3039	3208.71436	162.84334	49.4208
2	14.402	MF	0.3550	3283.92749	154.18130	50.5792
Totals :				6492.64185	317.02464	

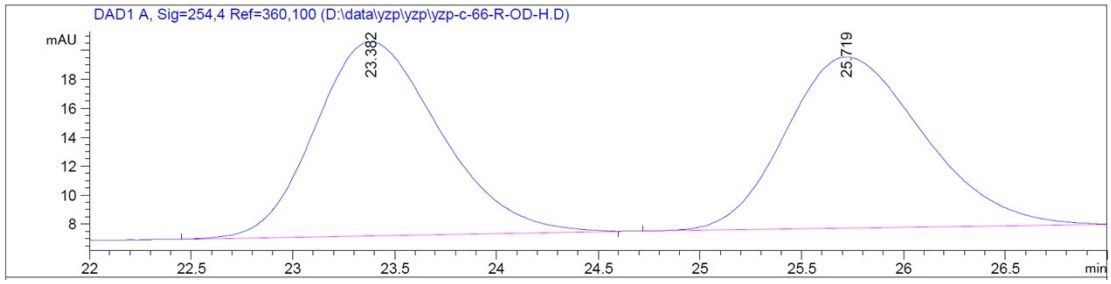


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.329	MF	0.3494	1.30335e4	621.63159	85.4974
2	14.106	FM	0.3633	2210.81201	101.41106	14.5026
Totals :				1.52443e4	723.04265	

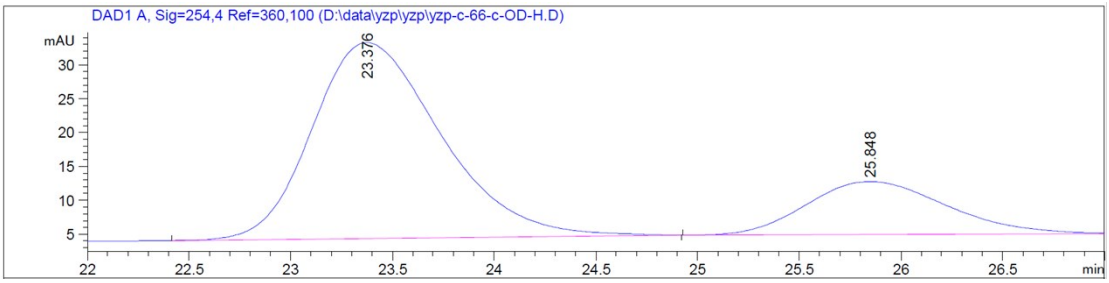
Methyl(phenyl)(1-phenylvinyl)phosphine oxide (3af)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

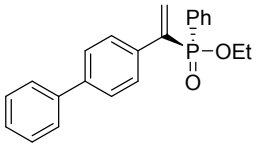
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.382	BB	0.6469	572.43549	13.44032	50.6044
2	25.719	BB	0.7180	558.76111	11.85214	49.3956
Totals :				1131.19659	25.29246	

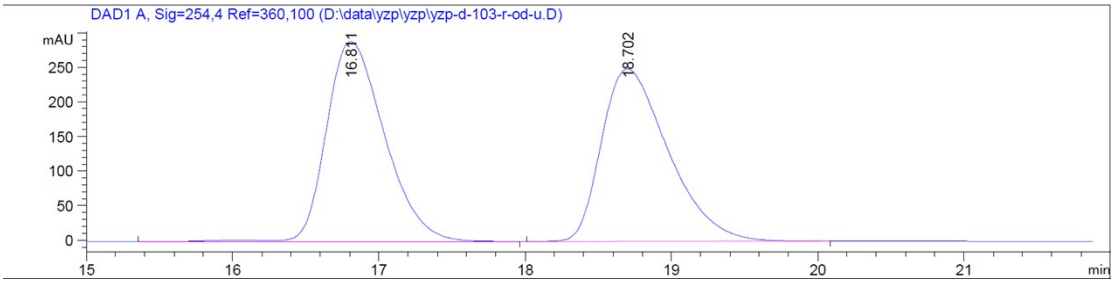


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.376	BB	0.6754	1274.11572	28.95158	77.2414
2	25.848	BB	0.6960	375.40952	7.82153	22.7586
Totals :				1649.52524	36.77311	

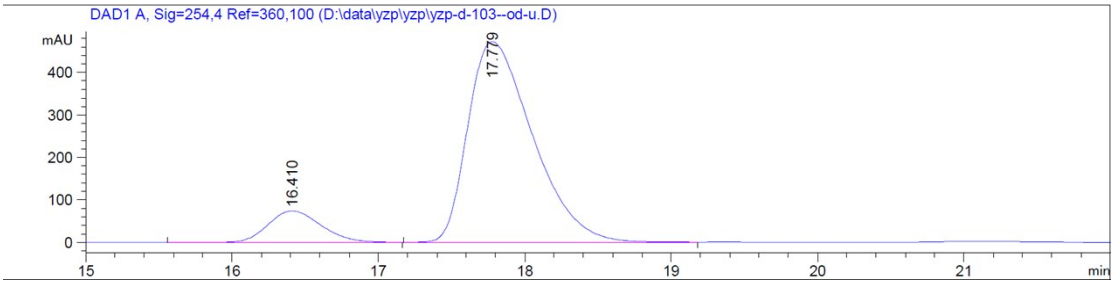
Ethyl (1-([1,1'-biphenyl]-4-yl)vinyl)(phenyl)phosphinate (4)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

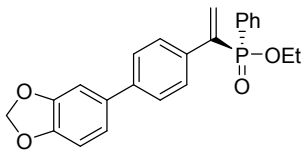
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.811	BB	0.4277	7969.07227	289.00461	50.2286
2	18.702	BB	0.4877	7896.53174	249.20995	49.7714
Totals :				1.58656e4	538.21455	

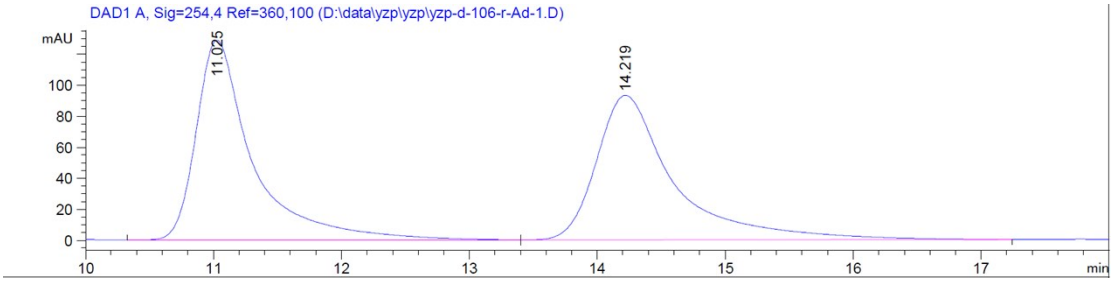


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.410	BB	0.3914	1863.21716	74.09490	11.3717
2	17.779	BB	0.4746	1.45215e4	472.37955	88.6283
Totals :				1.63847e4	546.47445	

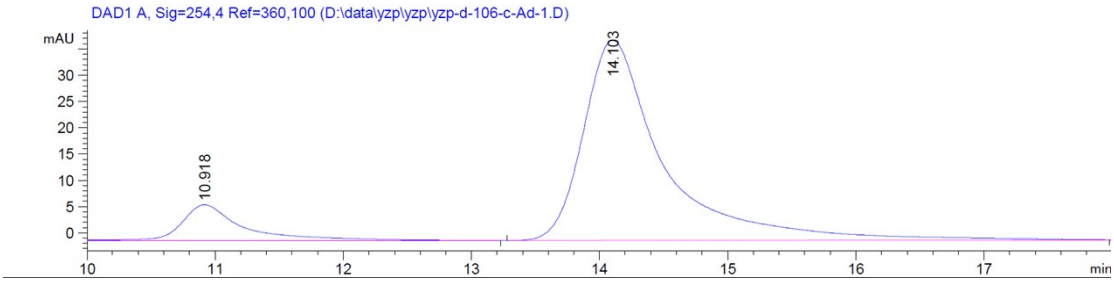
Ethyl (1-(4-(benzo[*d*][1,3]dioxol-5-yl)phenyl)vinyl)(phenyl)phosphinate (5)





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.025	BB	0.4453	3969.77563	128.89926	50.1733
2	14.219	BB	0.6134	3942.35986	93.22731	49.8267
Totals :				7912.13550	222.12657	

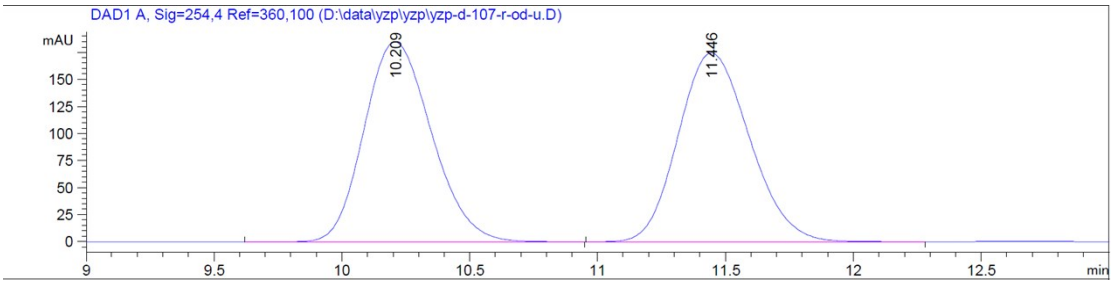


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.918	BB	0.4691	223.26852	6.76452	11.8293
2	14.103	BB	0.6301	1664.15625	38.06036	88.1707
Totals :				1887.42477	44.82488	

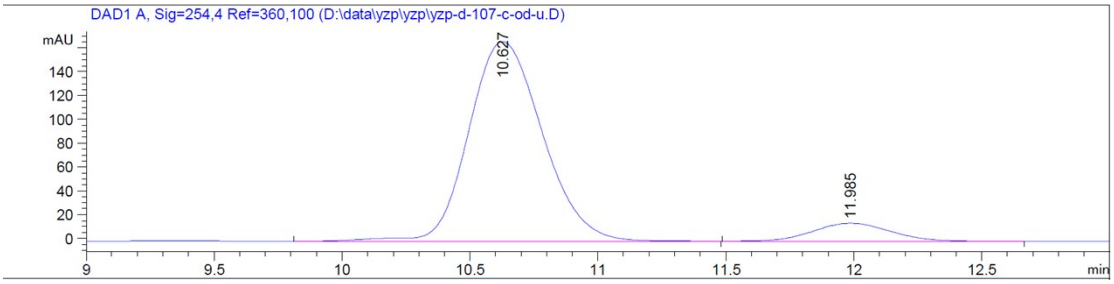
Ethyl (*Z*)-(1,2-diphenylvinyl)(phenyl)phosphinate (3qa)

Synthesized by Heck Reaction from **3aa**



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

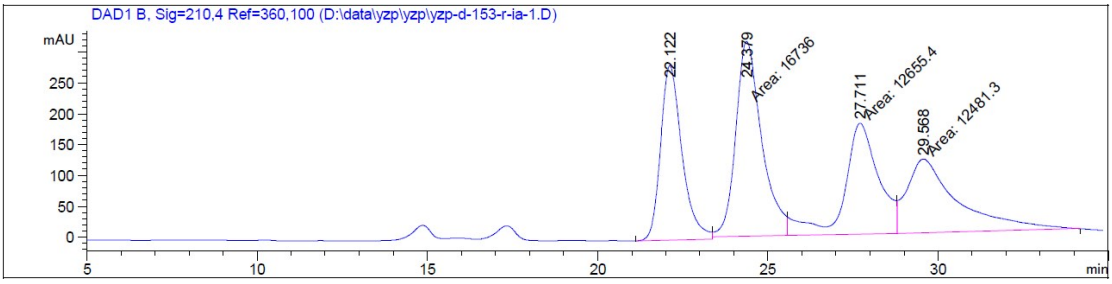
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.209	BB	0.2879	3391.75781	185.00055	50.0071
2	11.446	BB	0.3043	3390.79492	174.78204	49.9929
Totals :				6782.55273	359.78259	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

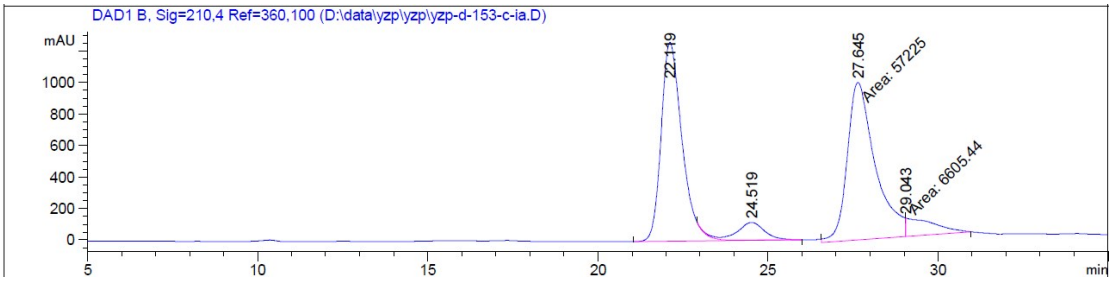
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.627	BB	0.3133	3352.64258	167.64192	91.3298
2	11.985	BB	0.3279	318.27710	15.10228	8.6702
Totals :				3670.91968	182.74420	

Ethyl (2-(diphenylphosphaneyl)-1-phenylethyl)(phenyl)phosphinate (6)



Signal 2: DAD1 B, Sig=210,4 Ref=360,100

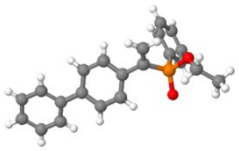
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.122	BV	0.6636	1.24106e4	283.02176	22.8626
2	24.379	MF	0.8836	1.67360e4	315.67279	30.8309
3	27.711	FM	1.1735	1.26554e4	179.73544	23.3137
4	29.568	MM	1.7431	1.24813e4	119.34130	22.9928
Totals :				5.42833e4	897.77129	

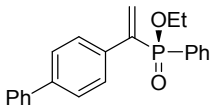


Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.119	BV R	0.6486	5.40321e4	1264.40503	43.4386
2	24.519	VB E	0.8350	6524.84131	114.46527	5.2456
3	27.645	MF	0.9533	5.72250e4	1000.44855	46.0054
4	29.043	FM	0.9372	6605.43604	117.47057	5.3104
Totals :				1.24387e5	2496.78942	

9. X-ray crystal structure of 4





4

Table S3

Identification code	cxy1119_0m
Empirical formula	$C_{22}H_{21}O_2P$
Formula weight	348.36
Temperature/K	100
Crystal system	monoclinic

Space group	$P2_1$
a/Å	6.0977(4)
b/Å	8.3134(6)
c/Å	18.1062(12)
α/°	90
β/°	97.792(2)
γ/°	90
Volume/Å^3	909.38(11)