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Supporting Information

Ruthenium-Catalyzed C–H Bond Alkylation of Arylphosphine Oxides with Alkenes: A Straightforward Access to Bifunctional Phosphorous Ligands with a Pendent Carboxylate

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1. General information

All reactions were carried out under argon atmosphere with standard Schlenk techniques. All reagents were obtained from commercial sources and used as supplied. 1,2-Dichloroethane was distilled over CaH₂ and stored under molecular sieves and argon atmosphere. prior used. [Ru(*p*-cymene)Cl₂]₂ was prepared from RuCl₃.*n*H₂O according the literature.^[1] Technical grade petroleum ether (40-60) and ethyl acetate were used for column chromatography.

¹H NMR spectra were recorded on Bruker GPX (300, 400 or 500 MHz) spectrometer. Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.28 ppm for ¹H; 77.23 ppm for ¹³C), constants were reported in Hertz. ¹H NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). ¹³C NMR spectra were recorded at 100 MHz on the same spectrometer and reported in ppm.

GC-MS analyses were performed with a GCMS-QP2010S (Shimadzu) instrument with a GC-2010 equipped with a 30 m capillary column (Supelco, SLBTM- 5ms, fused silica capillary column, 30 m x 0.25 mm x 0.25 mm film thickness), which was used with helium as the vector gas. The following GC conditions were used: initial temperature 80 °C for 5 minutes, then rate 20 °C/min until 280 °C and 280 °C for 28 minutes.

HRMS were recorded on a Waters Q-ToF 2 mass spectrometer at the corresponding facilities of the CRMPO, Centre Régional de Mesures Physiques de l'Ouest, Université de Rennes 1.

Melting points were performed on a LEICA VMHB Kofler system.

2. General method for the preparation of starting materials: aryl phosphine oxides

In a dried 50 mL Schlenk tube with a magnetic stirrer, to a solution of phosphine derivative (10 mmol) in THF (20 mL), H₂O₂ (30% aqueous solution, 12 mmol) was slowly added drop by drop over 10 minutes. Then, the mixture was stirred at room temperature during 30 minutes. After complete consumption of the phosphine derivative, which was evaluated by TLC, the THF was removed by evaporation to dryness. Then, the crude solid was dissolved in CH₂Cl₂ and the solution was dried over anhydrous Mg₂SO₄. CH₂Cl₂ was removed in vacuo to afford the desired phosphine oxide without further purification.

Triphenylphosphine oxide (**1a**),^[2] tri-*p*-tolylphosphine oxide (**1b**),^[3] tris(4-methoxyphenyl)phosphine oxide (**1c**),^[4] tris(4-fluorophenyl)phosphine oxide (**1d**),^[5] benzylidiphenylphosphine oxide (**1e**),^[6] butyldiphenylphosphine oxide (**1f**),^[7] and methyl diphenylphosphinate (**1g**)^[8] were prepared according this procedure and NMR spectrum are identical to those reported in literature.

3. General procedures for ruthenium-catalyzed C–H bond functionalization of aryl phosphine oxides

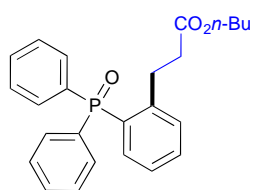
General Procedure A: Ruthenium-Catalyzed direct alkylation

In a dried 15 mL Schlenk tube with a magnetic stirrer, aryl-phosphine oxide (0.6 mmol), [RuCl₂(*p*-cymene)]₂ (0.015 mmol, 9 mg), AgSbF₆ (0.06 mmol, 20 mg), solvent DCE (3.0 mL) were successively introduced into the Schlenk tube. Michal acceptor (0.3 mmol) and AcOH (1.2 mmol, 72 mg) were added dropwise into the Schlenk tube, then the reaction mixture was stirred at 120 °C over 12 h. After cooling, the solvent was removed by evaporation to dryness, and the crude product was purified using flash column chromatography to afford the desired *ortho*-alkylated arylphosphine oxide. The yields are calculated based on the limiting reagent (i.e. Michal acceptor).

General Procedure B: Ruthenium-Catalyzed direct alkenylation

In a dried 15 mL Schlenk tube with a magnetic stirrer, aryl-phosphine oxide (0.6 mmol), [RuCl₂(*p*-cymene)]₂ (0.015 mmol, 9 mg), AgSbF₆ (0.06 mmol, 20 mg), Cu(OAc)₂·H₂O (0.3 mmol, 60 mg), NaHCO₃ (0.3 mmol, 25 mg), solvent DCE (3.0 mL) were successively introduced. Michal acceptor (0.3 mmol, 38 mg) was added dropwise into the Schlenk tube, then the reaction mixture was stirred at 120 °C over 12 h. After that the solvent was removed by evaporation to dryness, and the crude product was purified using flash column chromatography to afford the desired *ortho*-alkenylated arylphosphine oxide. The yields are calculated based on the limiting reagent (i.e. Michal acceptor).

4. Product characterizations



n-Butyl 3-(2-(diphenylphosphoryl) phenyl) propanoate (**3aa**):

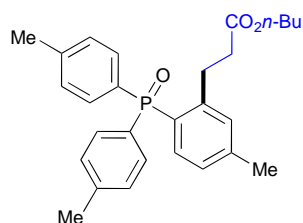
Following the general procedure A using tri-phenylphosphine oxide (0.6 mmol, 166 mg) and *n*-butyl acrylate (0.3 mmol, 38 mg), **3aa** was isolated in 72 % yield (88 mg) as a colorless oil, after purified using flash column chromatography with pentane-ethyl acetate (1:2).

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.60 (dd, *J* = 7.4 and 11.6 Hz, 4H), 7.49 (t, *J* = 7.1 Hz, 2H), 7.41 (m, 5H), 7.31 (dd, *J* = 3.6 and 7.4 Hz, 1H), 7.res11 (t, *J* = 7.1 Hz, 1H), 7.02 (dd, *J* = 7.6 and 13.8 Hz, 1H), 3.95 (t, *J* = 6.6 Hz, 2H), 3.15 (t, *J* = 7.7 Hz, 2H), 2.49 (t, *J* = 7.8 Hz, 2H), 1.54–1.44 (m, 2H), 1.25 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 173.0, 146.2 (d, *J*_{C,P} = 6.6 Hz), 133.7 (d, *J*_{C,P} = 12.4 Hz), 132.9 (d, *J*_{C,P} = 101.3 Hz), 132.3, 132.0 (d, *J*_{C,P} = 8.9 Hz), 131.9, 131.1 (d, *J*_{C,P} = 105.2 Hz), 131.0 (d, *J*_{C,P} = 9.0 Hz), 128.6 (d, *J*_{C,P} = 11.3 Hz), 125.8 (d, *J*_{C,P} = 12.0 Hz), 64.2, 35.7, 30.6, 29.7 (d, *J*_{C,P} = 1.9 Hz), 19.1 (s), 13.7 (s).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ (ppm) = 31.4(s).

MS (EI) m/z (%) = 406 ($[\text{M}]^+$, 36), 333 (23), 305 (100), 290 (23), 201 (26).



***n*-Butyl 3-(2-(di-*p*-tolylphosphoryl)-5-methylphenyl)propanoate (3ba):** Following the general procedure A using tri-*p*-tolylphosphine oxide (0.6 mmol, 192 mg) and *n*-butyl acrylate (0.3 mmol, 38 mg), **3ba** was isolated in 58 % yield (78 mg) as a colorless oil, after purified using flash column chromatography with pentane-

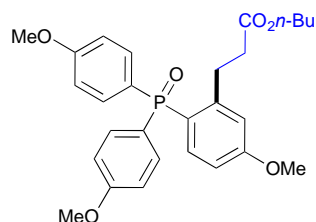
ethyl acetate (1:2).

^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.50 (dd, J = 8.0 and 11.7 Hz, 4H), 7.29–7.21 (m, 4H), 7.14 (d, J = 3.2 Hz, 1H), 6.97–6.92 (m, 2H), 4.00 (t, J = 6.7 Hz, 2H), 3.13 (t, J = 7.8 Hz, 2H), 2.51 (t, J = 7.8 Hz, 2H), 2.42 (s, 6H), 2.36 (s, 3H), 1.61–1.50 (m, 2H), 1.38–1.25 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm) = 173.2, 146.0, 142.5, 142.0, 133.9 (d, $J_{\text{C,P}}$ = 13.7 Hz), 131.9 (m), 131.2 (d, $J_{\text{C,P}}$ = 107.2 Hz), 129.3 (m), 128.1 (d, $J_{\text{C,P}}$ = 106.1 Hz), 126.4 (d, $J_{\text{C,P}}$ = 12.0 Hz), 120.8, 64.1, 35.8, 30.7, 29.7 (d, $J_{\text{C,P}}$ = 1.9 Hz), 21.6, 21.4, 19.1, 13.7.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ (ppm) = 31.4(s).

MS (EI) m/z (%) = 448 ($[\text{M}]^+$, 44), 375 (16), 347 (100), 332 (14), 229 (24), 163 (10), 91 (10).



***n*-Butyl 3-(2-(bis(4-methoxyphenyl)phosphoryl)-5-methoxyphenyl)propanoate (3ca):** Following the general procedure A using tris-(4-methoxyphenyl) phosphine oxide (0.6 mmol, 220 mg) and *n*-butyl acrylate (0.3 mmol, 38 mg), **3ca** was isolated in 64 % yield (95 mg) as a colorless oil, after purified

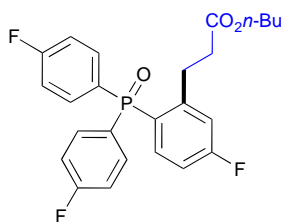
using flash column chromatography with pentane-ethyl acetate (1:2).

^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.52 (t, J = 9.5 Hz, 4H), 7.04–6.90 (m, 5H), 6.86 (m, 1H), 6.65 (d, J = 8.1 Hz, 1H), 3.99 (t, J = 6.6 Hz, 2H), 3.84 (s, 6H), 3.80 (s, 3H), 3.14 (t, J = 7.0 Hz, 2H), 2.52 (t, J = 7.1 Hz, 2H), 1.57–1.49 (m, 2H), 1.34–1.28 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm) = 173.1, 162.4, 162.3, 148.2 (d, $J_{\text{C,P}}$ = 8.4 Hz), 135.7 (d, $J_{\text{C,P}}$ = 14.1 Hz), 133.7 (d, $J_{\text{C,P}}$ = 10.6 Hz), 124.8 (d, $J_{\text{C,P}}$ = 112.3 Hz), 123.8 (d, $J_{\text{C,P}}$ = 110.1 Hz), 116.6 (d, $J_{\text{C,P}}$ = 10.9 Hz), 114.1 (d, $J_{\text{C,P}}$ = 12.9 Hz), 110.8 (d, $J_{\text{C,P}}$ = 14.0 Hz), 64.2, 55.3, 55.2, 35.6, 30.6, 29.7 (d, $J_{\text{C,P}}$ = 1.9 Hz), 19.1, 13.7.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ (ppm) = 30.7(s).

HRMS (ESI) Calcd for: $\text{C}_{28}\text{H}_{33}\text{O}_6\text{PNa}^+$: 519.1912; found: 519.19125 $[\text{M}+\text{Na}]^+$.



***n*-Butyl 3-(2-(bis(4-fluorophenyl)phosphoryl)-5-fluorophenyl)**

propanoate (3da): Following the general procedure **A** using tris-(4-fluorophenyl) phosphine oxide (0.6 mmol, 199 mg) and *n*-butyl acrylate (0.3 mmol, 38 mg), **3da** was isolated in 68 % yield (94 mg) as colorless oil, after purified using flash column chromatography with pentane-ethyl acetate (1:2).

with pentane-ethyl acetate (1:2).

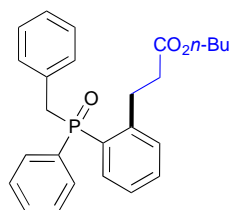
¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.60 (ddd, *J* = 5.5, 8.7 and 11.5 Hz, 4H), 7.16 (td, *J* = 2.0 and 8.7 Hz, 4H), 7.08 (dt, *J* = 2.8 and 9.9 Hz, 1H), 7.05 – 6.96 (m, 1H), 6.85 (ddd, *J* = 2.0, 4.1 and 10.4 Hz, 1H), 4.00 (t, *J* = 6.7 Hz, 2H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 7.7 Hz, 2H), 1.57 – 1.47 (m, 2H), 1.30 – 1.26 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 172.5, 165.2 (dd, *J*_{C,F} = 254.4 Hz), 165.1 (dd, *J*_{C,F} = 254.4 Hz), 149.6 (dd, *J*_{C,F} = 9.5 and *J*_{C,P} = 8.3, Hz), 134.3 (dd, *J*_{C,F} = 8.8 and *J*_{C,P} = 11.2 Hz), 135.94 (dd, *J*_{C,P} = 8.9 and *J*_{C,F} = 14.6 Hz), 128.7 (dd, *J*_{C,P} = 107.2 and *J*_{C,F} = 3.9 Hz), 126.6 (dd, *J*_{C,P} = 107.2 and *J*_{C,F} = 3.9 Hz), 118.3 (dd, *J*_{C,P} = 11.4 and *J*_{C,F} = 21.3 Hz), 116.2 (dd, *J*_{C,P} = 13.3 and *J*_{C,F} = 21.4 Hz), 113.0 (dd, *J*_{C,P} = 14.1 and *J*_{C,F} = 20.8 Hz), 64.4, 35.2, 30.6, 29.6 (d, *J*_{C,P} = 3.6 Hz), 19.1, 13.7.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) = -106.1(s), -106.3(s).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ (ppm) = 29.0(s).

MS (EI) *m/z* (%) = 460 ([M]⁺, 36), 387 (25), 359 (100), 344 (19), 245 (20), 237 (39), 167 (11), 77 (9).



***n*-Butyl 3-(2-(benzyl(phenyl)phosphoryl)phenyl)propanoate (3ea):**

Following the general procedure **A** using benzyl(diphenyl)phosphine oxide (0.6 mmol, 175 mg) and *n*-butyl acrylate (0.3 mmol, 38 mg), **3ea** was isolated in 63 % yield (79 mg) as a white solid, after purified using flash column chromatography with pentane-ethyl acetate (1:2).

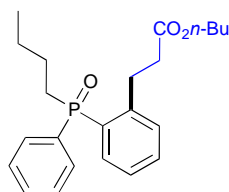
mp 118-120 °C.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.68 (dd, *J* = 7.9 and 12.2 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.40 – 7.27 (m, 4H), 7.20 – 7.15 (m, 3H), 7.06 (d, *J* = 3.4 Hz, 2H), 3.98 (t, *J* = 6.7 Hz, 2H), 3.79 (t, *J* = 14.7 Hz, 1H), 3.68 – 3.58 (m, 1H), 3.06 (t, *J* = 7.8 Hz, 2H), 2.55 (dt, *J* = 7.8 and 15.9, Hz, 1H), 2.39 – 2.28 (m, 1H), 1.55 – 1.48 (m, 2H), 1.33 – 1.27 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 173.0, 146.3(d, *J*_{C,P} = 5.4 Hz), 133.5 (d, *J*_{C,P} = 99.5 Hz), 132.2, 131.6, 131.4 (d, *J*_{C,P} = 10.0 Hz), 131.0 (d, *J*_{C,P} = 9.3 Hz), 130.3 (d, *J*_{C,P} = 4.2 Hz), 128.5, 128.4, 128.3, 126.8, 126.0 (d, *J*_{C,P} = 11.6 Hz), 64.1, 38.0 (d, *J*_{C,P} = 67.0 Hz), 35.9, 30.6, 29.4 (d, *J*_{C,P} = 3.6 Hz), 19.1, 13.7.

³¹P{¹H} NMR (162 MHz, CDCl₃) δ (ppm) = 30.5(s).

MS (EI) *m/z* (%) = 420 ([M]⁺, 19), 347 (15), 319 (36), 273 (68), 227 (20), 133 (100), 91 (69).



***n*-Butyl 3-(2-(*n*-butyl(phenyl)phosphoryl)phenyl) propanoate (3fa):**

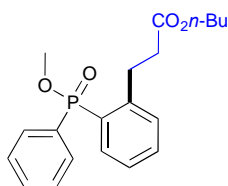
Following the general procedure **A** using *n*-butyldiphenylphosphine oxide (0.6 mmol, 155 mg) and *n*-butyl acrylate (0.3 mmol, 38 mg), **3fa** was isolated in 47 % yield (54 mg) as a colorless oil, after purified using flash column chromatography with pentane-ethyl acetate (1:2).

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.65 (t, *J* = 8.0 Hz, 3H), 7.54 – 7.41 (m, 4H), 7.37 – 7.28 (m, 2H), 4.02 (t, *J* = 6.7 Hz, 2H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.60 – 2.48 (m, 1H), 2.40 – 2.29 (m, 1H), 2.04 (m, 1H), 1.70 (m, 1H), 1.60 – 1.51 (m, 3H), 1.45 (m, 2H), 1.38 – 1.25 (m, 3H), 0.95 – 0.88 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 172.9, 145.6 (d, *J*_{C,P} = 5.4 Hz), 134.2 (d, *J*_{C,P} = 93.8 Hz), 132.0, 131.5, 131.4, 131.2 (d, *J*_{C,P} = 8.7 Hz), 130.7 (d, *J*_{C,P} = 8.5 Hz), 128.6 (d, *J*_{C,P} = 10.7 Hz), 126.0 (d, *J*_{C,P} = 11.1 Hz), 64.2, 35.8, 30.1, 29.7 (d, *J*_{C,P} = 3.6 Hz), 29.4, 24.1 (d, *J*_{C,P} = 14.5 Hz), 23.4, 19.1, 13.7, 13.6.

³¹P{¹H} NMR (162 MHz, CDCl₃) δ (ppm) = 33.9(s).

MS (EI) *m/z* (%) = 386([M]⁺,7), 357 (15), 313 (31), 285 (80), 273 (100), 257 (20), 133 (68), 125(23), 91(11).



***n*-Butyl 3-(2-(methoxy(phenyl)phosphoryl)phenyl) propanoate (3ga):**

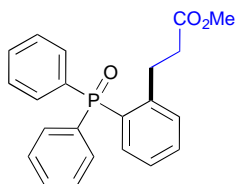
Following the general procedure **A** using methyl diphenylphosphinate (0.6 mmol, 139 mg) and butyl acrylate (0.3 mmol, 38 mg), **3ga** was isolated in 53% yield (57 mg) as a colorless oil, after purified using flash column chromatography with pentane-ethyl acetate (1:2).

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.86 (dd, *J* = 7.7 and 12.9, 1H), 7.79 (dd, *J* = 7.6 and 12.2, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 5.7 Hz, 3H), 7.36 – 7.29 (m, 2H), 4.06 (t, *J* = 6.7 Hz, 2H), 3.79 (d, *J* = 11.1 Hz, 3H), 3.23 – 3.14 (m, 2H), 2.60 – 2.49 (m, 2H), 2.49 – 2.36 (m, 2H), 1.64 – 1.54 (m, 2H), 1.35 (dt, *J* = 7.2 and 14.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 172.9, 144.9 (d, *J*_{C,P} = 11.2 Hz), 133.3 (d, *J*_{C,P} = 9.4 Hz), 132.6, 132.2, 131.8 (d, *J*_{C,P} = 10.5 Hz), 130.6 (d, *J*_{C,P} = 12.5 Hz), 131.4 (d, *J*_{C,P} = 88.9 Hz), 128.6 (d, *J*_{C,P} = 13.1 Hz), 126.1 (d, *J*_{C,P} = 12.6 Hz), 64.3, 51.4 (d, *J*_{C,P} = 5.9 Hz), 35.8, 30.6, 29.5 (d, *J*_{C,P} = 4.3 Hz), 19.1, 13.7.

³¹P{¹H} NMR (162 MHz, CDCl₃) δ (ppm) = 33.7(s).

MS (EI) *m/z* (%) = 360 ([M]⁺,36), 287 (32), 259 (100), 227 (31), 155 (52), 149 (35), 77 (32).



***n*-Methyl 3-(2-(diphenylphosphoryl)phenyl)propanoate (3ab):**

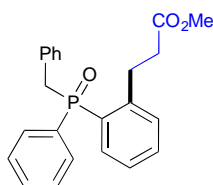
Following the general procedure **A** using methyl triphenylphosphine oxide (0.6 mmol, 166 mg) and methyl acrylate (0.3 mmol, 26 mg), **3ab** was isolated in 62 % yield (68 mg) as a colorless oil, after purified using flash column chromatography with pentane-ethyl acetate (1:2).

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.67 – 7.60 (m, 4H), 7.58 – 7.51 (m, 2H), 7.50 – 7.42 (m, 5H), 7.35 (dd, *J* = 4.1 and 7.5 Hz, 1H), 7.16 (t, *J* = 6.9 Hz, 1H), 7.05 (ddd, *J* = 1.4, 7.8 and 14.0 Hz, 1H), 3.59 (s, 3H), 3.18 (t, *J* = 7.7 Hz, 2H), 2.54 (t, *J* = 7.8 Hz, 2H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm) = 173.3, 146.1 (d, *J*_{C,P} = 8.0 Hz), 133.7 (d, *J*_{C,P} = 12.8 Hz), 133.5, 132.5, 132.5 (d, *J*_{C,P} = 98.1 Hz), 132.0 (d, *J*_{C,P} = 9.7 Hz), 131.9 (d, *J*_{C,P} = 2.8 Hz), 131.0 (d, *J*_{C,P} = 103.5 Hz), 128.6 (d, *J*_{C,P} = 12.1 Hz), 125.8 (d, *J*_{C,P} = 12.8 Hz), 51.5, 35.5, 29.7 (d, *J*_{C,P} = 5.3 Hz).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ (ppm) = 31.4 (s).

MS (EI) *m/z* (%) = 364 ([M]⁺, 51), 333 (20), 305 (100), 290 (29), 201 (21), 149 (15), 77 (18).



Methyl 3-(2-(benzyl(phenyl)phosphoryl)phenyl)propanoate (3eb):

Following the general procedure **A** using methyl benzyldiphenylphosphine oxide (0.6 mmol, 175 mg) and methyl acrylate (0.3 mmol, 26 mg), **3eb** was isolated in 65 % yield (73 mg) as a white solid, after purified using flash column chromatography with pentane-ethyl

acetate (1 : 2).

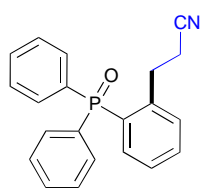
mp 168-170 °C.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.73 – 7.66 (m, 1H), 7.55 – 7.45 (m, 4H), 7.42 – 7.35 (m, 2H), 7.35 – 7.29 (m, 2H), 7.22 – 7.17 (m, 3H), 7.10 – 7.04 (m, 2H), 3.81 (t, *J* = 14.7 Hz, 1H), 3.70 – 3.61 (m, 1H), 3.60 (s, 3H), 3.09 (t, *J* = 7.8 Hz, 2H), 2.60 (dt, *J* = 15.9, 7.8 Hz, 1H), 2.44 – 2.33 (m, 1H).

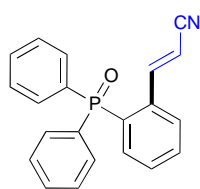
¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm) = 173.3, 146.2 (d, *J*_{C,P} = 7.6 Hz), 133.3 (d, *J*_{C,P} = 98.4 Hz), 132.2 (d, *J*_{C,P} = 2.7 Hz), 131.6 (d, *J*_{C,P} = 2.9 Hz), 131.5 (d, *J*_{C,P} = 4.6 Hz), 131.3 (d, *J*_{C,P} = 6.2 Hz), 131.0 (d, *J*_{C,P} = 9.5 Hz), 130.9 (d, *J*_{C,P} = 7.5 Hz), 130.7 (d, *J*_{C,P} = 95.3 Hz), 130.3 (d, *J*_{C,P} = 4.5 Hz), 128.4 (d, *J*_{C,P} = 11.8 Hz), 128.3 (d, *J*_{C,P} = 2.2 Hz), 126.8 (d, *J*_{C,P} = 4.0 Hz), 126.0 (d, *J*_{C,P} = 11.2 Hz), 51.4, 38.0 (d, *J*_{C,P} = 66.3 Hz), 35.6, 29.5 (d, *J*_{C,P} = 4.5 Hz).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ (ppm) = 30.7(s).

MS (EI) *m/z* (%) = 378 ([M]⁺, 21), 347 (11), 319 (38), 287 (88), 227 (27), 155 (100), 149 (32), 91 (84), 77 (20).



3-(2-(Diphenylphosphoryl)phenyl)acrylonitrile (3ac) and 3-(2-(diphenylphosphoryl)phenyl) acrylonitrile (4ac): Following the general procedure **A** using methyl triphenylphosphine oxide (0.6 mmol, 166 mg) and acrylonitrile (0.3 mmol, 16 mg), **3ac/4ac** were isolated in 24 % yield (24 mg) in 1:4 ratio as a colorless oil, after purified using flash column chromatography with pentane-ethyl acetate (2:1).

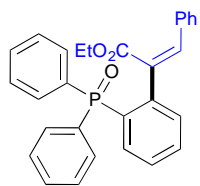


¹H NMR (400 MHz, CDCl₃) of **4ac** δ (ppm) = 8.27 (d, *J* = 16.4 Hz, 1H), 7.67 – 7.53 (m, 8H), 7.48 (m, 4H), 7.40 – 7.32 (m, 1H), 7.15 (dd, *J* = 7.7 and 13.9 Hz, 1H), 5.70 (d, *J* = 16.4 Hz, 1H).

¹³C{¹H} NMR (101 MHz, CDCl₃) of **4ac** δ (ppm) = 148.8 (d, *J*_{C,P} = 5.7 Hz), 138.5 (d, *J*_{C,P} = 6.7 Hz), 133.87 (d, *J*_{C,P} = 11.5 Hz), 132.5 (d, *J*_{C,P} = 2.5 Hz), 132.4 (d, *J*_{C,P} = 2.8 Hz), 132.1 (d, *J*_{C,P} = 98.7 Hz), 132.0 (d, *J*_{C,P} = 10.0 Hz), 131.8 (d, *J*_{C,P} = 105.2 Hz), 129.8 (d, *J*_{C,P} = 12.3 Hz), 128.8 (d, *J*_{C,P} = 12.3 Hz), 127.41 (d, *J*_{C,P} = 9.2 Hz), 117.4, 99.3.

³¹P{¹H} NMR (162 MHz, CDCl₃) of **4ac** δ (ppm) = 31.38 (s).

MS(EI) of **4ac** *m/z* (%) = 329 ([M]⁺, 100), 301 (13), 250 (21), 213 (13), 77 (25), 51 (18).



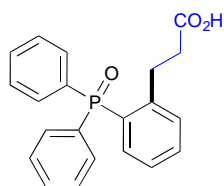
(E)-ethyl 2-(2-(diphenylphosphoryl)phenyl)-3-phenylacrylate (3ad): Following the general procedure **A** using methyl triphenylphosphine oxide (0.6 mmol, 166 mg) and methyl 3-phenylpropiolate (0.3 mmol, 48 mg), **3ad** was isolated in 67% yield (91 mg) as a colorless oil, after purified using flash column chromatography with pentane-ethyl acetate (1:2).

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.80 – 7.70 (m, 4H), 7.60 – 7.53 (m, 1H), 7.50 (m, 3H), 7.46 – 7.37 (m, 5H), 7.36 – 7.28 (m, 2H), 7.23 (m, 3H), 7.06 (m, 2H), 3.89 (q, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm) = 167.2, 144.0 (d, *J*_{C,P} = 7.7 Hz), 143.6, 135.9, 134.3 (d, *J*_{C,P} = 12.5 Hz), 133.0 (d, *J*_{C,P} = 105.2 Hz), 132.0 (d, *J*_{C,P} = 97.8 Hz), 131.8 (d, *J*_{C,P} = 9.5 Hz), 131.6 (d, *J*_{C,P} = 2.4 Hz), 131.5, 131.4 (d, *J*_{C,P} = 2.9 Hz), 128.8, 128.4 (d, *J*_{C,P} = 12.2 Hz), 128.0, 127.5, 127.1 (d, *J*_{C,P} = 12.5 Hz), 105.0, 60.6, 13.5.

³¹P{¹H} NMR (162 MHz, CDCl₃) δ (ppm) = 29.3(s).

MS (EI) *m/z* (%) = 452 ([M]⁺, 22), 405(7), 379 (100), 253 (6), 189 (6), 77 (7).



3-(2-(Diphenylphosphoryl)phenyl)propanoic acid (5aa): *n*-Butyl 3-(2-(diphenylphosphoryl)phenyl)propanoate (**3aa**) (0.6 mmol, 250 mg) and KOH 6.0 mmol, 336 mg) were dissolved in THF/H₂O/MeOH (3:3:1) solvent mixture (6 mL) and stirred for 12 h at 60°C. The mixture was concentrated under reduced pressure and the residue was acidified with HCl (2N). The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic

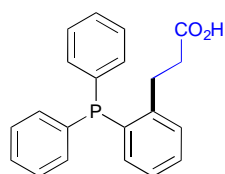
layers were dried (Na₂SO₄), filtered and concentrated to offer the desired product **5aa** in 75% yield (185 mg) without further purification as a white solid.

mp 223-226 °C.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.65 – 7.54 (m, 6H), 7.54 – 7.44 (m, 5H), 7.35 (dd, *J* = 4.1 and 7.4 Hz, 1H), 7.25 – 7.16 (m, 1H), 7.00 (dd, *J* = 7.6 and 14.2 Hz, 1H), 3.09 (dd, *J* = 6.7 and 9.3 Hz, 2H), 2.71 (dd, *J* = 6.5 and 9.5 Hz, 2H).

¹³C{¹H} NMR (75 MHz, CDCl₃) δ (ppm) = 174.1, 146.6 (d, *J*_{C,P} = 7.7 Hz), 134.1 (d, *J*_{C,P} = 13.6 Hz), 132.9 (d, *J*_{C,P} = 2.6 Hz), 132.5 (d, *J*_{C,P} = 2.8 Hz), 132.5 (d, *J*_{C,P} = 2.8 Hz), 131.2 (d, *J*_{C,P} = 10.1 Hz), 130.5, 129.1 (d, *J*_{C,P} = 103.1 Hz), 128.8 (d, *J*_{C,P} = 12.4 Hz), 126.2 (d, *J*_{C,P} = 13.2 Hz), 38.3, 31.1 (d, *J*_{C,P} = 5.4 Hz).

³¹P NMR (162 MHz, CDCl₃) δ (ppm) = 35.5(s).



3-(2-(Diphenylphosphino)phenyl)propanoic acid (6aa): In a dried 15 mL Schlenk tube flushed with argon 3-(2-(diphenylphosphoryl)phenyl)propanoic acid (**5aa**) (0.25 mmol, 93 mg) was added to a solution of CF₃SO₃H (5 mol%, 2 mg) in toluene (1.5 mL).

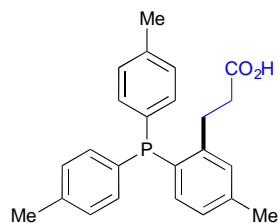
The reaction mixture was stirred for 5 min at 25°C. Subsequently, PhSiH₃ (1.0 mmol, 108 mg) was added, the Schlenk tube was flushed with argon, sealed and the reaction mixture was stirred for 24 h at 100°. After that the solvent was removed by evaporation to dryness, and the crude product was purified using flash column chromatography with pentane-ethyl acetate (1:1) to afford **6aa** in 67% yield. (50 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.40 – 7.34 (m, 6H), 7.34 – 7.26 (m, 6H), 7.16 (td, *J* = 7.4, 1.6 Hz, 1H), 6.92 (dd, *J* = 7.1, 4.2 Hz, 1H), 3.22 (t, *J* = 7.9 Hz, 2H), 2.68 – 2.58 (m, 2H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm) = 178.5, 144.8 (d, *J*_{C,P} = 25.3 Hz), 136.6 (d, *J*_{C,P} = 10.2 Hz), 135.8 (d, *J*_{C,P} = 13.1 Hz), 133.9 (d, *J*_{C,P} = 19.7 Hz), 133.9, 129.3, 129.1 (d, *J* = 5.0 Hz), 129.8, 128.6 (d, *J*_{C,P} = 6.9 Hz), 126.8, 35.16 (d, *J*_{C,P} = 3.8 Hz), 29.3 (d, *J*_{C,P} = 21.7 Hz).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ (ppm) = -15.7(s).

HRMS (ESI) Calcd for: C₂₁H₂₀O₂P⁺: 335.1201, found: 335.12009 [M+H]⁺.



3-(2-(Di-p-tolylphosphoryl)-5-methylphenyl)propanoic acid

(6ba): Butyl 3-(2-(di-p-tolylphosphoryl)-5-methylphenyl)propanoate (**3ba**) (0.3 mmol, 134 mg) and KOH (3.0 mmol, 336 mg) were dissolved in THF/H₂O/MeOH (3:3:1) solvent mixture (6 mL) and stirred for 12 h at 60°C. The mixture was

concentrated under reduced pressure and the residue was acidified with HCl (2N). The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried (Na₂SO₄), filtered and concentrated. Then, in a 15 mL Schlenk tube the crude mixture was

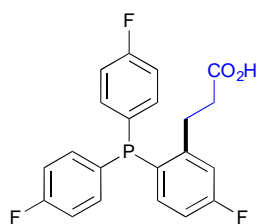
added to a solution of $\text{CF}_3\text{SO}_3\text{H}$ (5 mol%, 2.25 mg) in toluene (1.5 mL). The reaction mixture was stirred for 5 min at 25°C. Subsequently, PhSiH_3 (1.0 mmol, 108 mg) was added, the Schlenk tube was flushed with argon, sealed and the reaction mixture was stirred for 24 h at 100°C. After that the solvent was removed by evaporation to dryness, and the crude product was purified using flash column chromatography with pentane-ethyl acetate (1:1) to afford **6ba** in 42% yield (47 mg) over two steps as a colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.18 – 7.11 (m, 8H), 7.07 (m, 1H), 6.94 (m, 1H), 6.79 (m, 1H), 3.14 (t, $J = 7.9$ Hz, 2H), 2.64 – 2.56 (m, 2H), 2.34 (s, 6H), 2.31 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ (ppm) = 176.8, 144.6 (d, $J_{\text{C,P}} = 25.3$ Hz), 139.1, 138.6, 133.8 (d, $J_{\text{C,P}} = 19.4$ Hz), 133.7 (md, $J_{\text{C,P}} = 100.1$ Hz), 131.9 (d, $J_{\text{C,P}} = 10.5$ Hz), 130.0 (d, $J_{\text{C,P}} = 5.2$ Hz), 129.58 (d, $J_{\text{C,P}} = 12.6$ Hz), 129.4 (d, $J_{\text{C,P}} = 7.2$ Hz), 127.6, 35.0 (d, $J_{\text{C,P}} = 3.8$ Hz), 29.4 (d, $J_{\text{C,P}} = 21.0$ Hz), 21.3, 21.2.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ (ppm) = -18.32 (s).

HRMS (ESI) Calcd for: $\text{C}_{24}\text{H}_{26}\text{O}_2\text{P}^+$: 377.1592; found: 377.16704 $[\text{M}+\text{H}]^+$.



3-(2-(Bis(4-fluorophenyl)phosphino)-5-fluorophenyl)propanoic acid (6ca):

Butyl 3-(2-(bis(4-fluorophenyl)phosphoryl)-5-fluorophenyl) propanoate (**3ca**) (0.3 mmol, 138 mg) and KOH (3.0 mmol, 336 mg) were dissolved in THF/ H_2O /MeOH (3:3:1) solvent mixture (6 mL) and stirred for 12 h at 60°C. The mixture was concentrated under reduced pressure and the residue was acidified with HCl (2N). The aqueous layer was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried (Na_2SO_4), filtered and concentrated. Then, in a 15 mL Schlenk tube the crude mixture was added to a solution of $\text{CF}_3\text{SO}_3\text{H}$ (5 mol%, 2.25 mg) in toluene (1.5 mL). The reaction mixture was stirred for 5 min at 25°C. Subsequently, PhSiH_3 (1.0 mmol, 108 mg) was added, the Schlenk tube was flushed with argon, sealed and the reaction mixture was stirred for 24 h at 100°C. After that the solvent was removed by evaporation to dryness, and the crude product was purified using flash column chromatography with pentane-ethyl acetate (1:1) to afford **6ca** in 63% yield (73 mg) over two steps as a colorless oil.

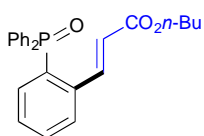
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.25 – 7.17 (m, 4H), 7.10 – 6.97 (m, 5H), 6.84 (m, 2H), 3.16 (t, $J = 7.6$ Hz, 2H), 2.65 – 2.56 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ (ppm) = 178.2, 163.6 (d, $J_{\text{C,F}} = 249.6$ Hz), 163.5 (d, $J_{\text{C,F}} = 249.6$ Hz), 147.2 (dd, $J_{\text{C,P}} = 7.4$ and $J_{\text{C,F}} = 27.4$ Hz), 135.6 (dd, $J_{\text{C,P}} = 8.1$ and $J_{\text{C,F}} = 21.4$ Hz), 135.6 (d, $J_{\text{C,P}} = 8.4$ Hz), 133.7 (md, $J_{\text{C,P}} = 98.7$ Hz), 131.7 (dd, $J_{\text{C,P}} = 3.5$ and $J_{\text{C,F}} = 10.2$ Hz), 131.0 (dd, $J_{\text{C,P}} = 3.1$ and $J_{\text{C,F}} = 9.6$ Hz), 116.1 (dd, $J_{\text{C,P}} = 7.7$ and $J_{\text{C,F}} = 21.1$ Hz), 114.1 (d, $J_{\text{C,F}} = 20.4$ Hz), 34.74 (d, $J_{\text{C,P}} = 3.9$ Hz), 29.12 (dd, $J_{\text{C,F}} = 1.6$ and $J_{\text{C,P}} = 22.0$ Hz).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ (ppm) = -19.44 (s).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ (ppm) = -111.73 (s), -111.74 (s).

HRMS (ESI) Calcd for: C₂₁H₁₇F₃O₂P⁺: 389.3195; found: 389.09183 [M+H]⁺.



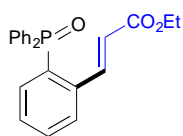
(E)-n-Butyl 3-(2-(diphenylphosphoryl)phenyl)acrylate (4aa): Following the general procedure **B** using tri-phenylphosphine oxide (0.6 mmol, 166 mg) and *n*-butyl acrylate (0.3 mmol, 38 mg), **4aa** was isolated in 48 % yield (58 mg) as a white solid, after purified using flash column chromatography with pentane-ethyl acetate (1 : 2).

¹H NMR (300 MHz, CDCl₃) δ (ppm) = 8.24 (d, *J* = 15.8 Hz, 1H), 7.73 – 7.60 (m, 5H), 7.58 – 7.49 (m, 3H), 7.45 (ddd, *J* = 2.1, 5.2 and 7.0 Hz, 4H), 7.38 – 7.25 (m, 2H), 6.16 (d, *J* = 15.8 Hz, 1H), 4.06 (t, *J* = 6.6 Hz, 2H), 1.57 (m, 2H), 1.44 – 1.21 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

¹³C{¹H} NMR (75 MHz, CDCl₃) δ (ppm) = 166.0, 142.5 (d, *J*_{C,P} = 6.0 Hz), 139.2 (d, *J*_{C,P} = 7.1 Hz), 133.8 (d, *J*_{C,P} = 11.3 Hz), 132.4 (d, *J*_{C,P} = 2.3 Hz), 132.2 (d, *J*_{C,P} = 104.3 Hz), 132.0, 132.0 (d, *J*_{C,P} = 7.7 Hz), 128.9 (d, *J*_{C,P} = 12.3 Hz), 128.6 (d, *J*_{C,P} = 12.3 Hz), 127.9 (d, *J*_{C,P} = 9.4 Hz), 121.3, 64.3, 30.6, 19.1, 13.7.

³¹P{¹H} NMR (121 MHz, CDCl₃) δ (ppm) = 30.3 (s).

MS (EI) *m/z* (%) = 404 ([M]⁺, 24), 331(12), 303 (100), 289(29), 271 (19), 213(16), 165(14).



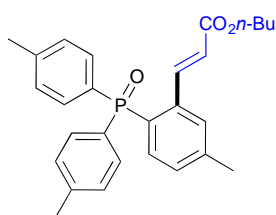
(E)-Ethyl 3-(2-(diphenylphosphoryl)phenyl)acrylate (4ae): Following the general procedure **B** using tri-phenylphosphine oxide (0.6 mmol, 166 mg) and ethyl acrylate (0.3 mmol, 30 mg), **4ae** in 42 % yield (47 mg) as a colorless oil, after purified using flash column chromatography with pentane-ethyl acetate (1:2).

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.24 (d, *J* = 15.8 Hz, 1H), 7.73 – 7.64 (m, 5H), 7.58 – 7.50 (m, 3H), 7.50 – 7.42 (m, 4H), 7.37 – 7.33 (m, 1H), 7.29 (d, *J* = 6.5 Hz, 1H), 6.16 (d, *J* = 15.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm) = 166.0, 142.6 (d, *J*_{C,P} = 5.9 Hz), 139.2 (d, *J*_{C,P} = 7.1 Hz), 133.8 (d, *J*_{C,P} = 11.2 Hz), 132.4 (d, *J*_{C,P} = 2.3 Hz), 132.2 (d, *J*_{C,P} = 104.1 Hz), 132.0, 131.9, 128.9 (d, *J*_{C,P} = 12.3 Hz), 128.6 (d, *J*_{C,P} = 12.1 Hz), 127.9 (d, *J*_{C,P} = 9.3 Hz), 121.3, 60.4, 14.2.

³¹P{¹H} NMR (121 MHz, CDCl₃) δ (ppm) = 29.9 (s).

MS (EI) *m/z* (%) = 376 ([M]⁺, 7), 331 (4), 303 (100), 225 (11), 201 (10), 77 (32), 51 (19).



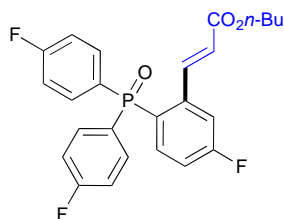
(E)-Butyl 3-(2-(di-*p*-tolylphosphoryl)-5-methylphenyl)acrylate (4ba): Following the general procedure **B** using tri-*p*-tolylphosphine oxide (0.6 mmol, 192 mg) and *n*-butyl acrylate (0.3 mmol, 38 mg), **4ba** was isolated in 38 % yield (51 mg) as a colorless oil, after purified using flash column chromatography with pentane-ethyl acetate (1:2).

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.25 (d, *J* = 15.8 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 3.2 Hz, 1H), 7.30 – 7.25 (m, 4H), 7.24 – 7.20 (m, 1H), 7.18 – 7.12 (m, 1H), 6.19 (d, *J* = 15.8 Hz, 1H), 4.09 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 9H), 1.66 – 1.54 (m, 2H), 1.43 – 1.33 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm) = 166.2, 142.8 (d, *J*_{C,P} = 5.8 Hz), 142.6 (d, *J*_{C,P} = 2.3 Hz), 142.3 (d, *J*_{C,P} = 2.6 Hz), 139.0 (d, *J*_{C,P} = 7.3 Hz), 133.9 (d, *J*_{C,P} = 11.6 Hz), 132.0 (d, *J*_{C,P} = 10.0 Hz), 129.6 (d, *J*_{C,P} = 12.7 Hz), 129.5 (d, *J*_{C,P} = 101.5 Hz), 129.3 (d, *J*_{C,P} = 12.5 Hz), 128.4 (d, *J*_{C,P} = 103.5 Hz), , 128.5 (d, *J*_{C,P} = 9.8 Hz), 120.9, 64.2, 30.7, 21.6, 21.6, 19.1, 13.8.

³¹P{¹H} NMR (121 MHz, CDCl₃) δ (ppm) = 30.3 (s).

HRMS (ESI) Calcd for: C₂₈H₃₁O₃PNa⁺: 469.1909; found: 469.1913 [M+Na]⁺.



(E)-Butyl 3-(2-(bis(4-fluorophenyl)phosphoryl)-5-fluorophenyl)acrylate (4da): Following the general procedure **B** using tris(4-fluorophenyl)phosphine oxide (0.6 mmol, 199 mg) and *n*-butyl acrylate (0.3 mmol, 38 mg), **4da** was isolated in 47 % yield (64 mg) as a colorless oil, after purified using flash column chromatography with pentane-ethyl acetate (1:2).

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.16 (d, *J* = 15.7 Hz, 1H), 7.68 – 7.56 (m, 4H), 7.38 (d, *J* = 9.6 Hz, 1H), 7.32 – 7.21 (m, 1H), 7.17 (t, *J* = 8.2 Hz, 4H), 7.10 – 6.98 (m, 1H), 6.18 (d, *J* = 15.7 Hz, 1H), 4.08 (t, *J* = 6.6 Hz, 2H), 1.64 – 1.52 (m, 2H), 1.43 – 1.29 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ (ppm) = 165.5, 165.2 (d *J*_{C,F} = 255.8 Hz), 165.1 (d *J*_{C,F} = 255.8 Hz), 142.2 (t, *J*_{C,F} and *J*_{C,P} = 8.1 Hz), 140.9 (m), 136.2 (t, *J*_{C,F} and *J*_{C,P} = 10.6 Hz), 134.4 (dd, *J*_{C,F} = 8.7 and *J*_{C,P} = 11.0 Hz), 128.0 (md, *J*_{C,P} = 107.9 Hz), 122.8, 116.3 (dd, *J*_{C,P} = 13.1, and *J*_{C,F} = 21.4 Hz), 115.9 (d, *J*_{C,F} = 13.2 Hz), 115.2 (dd, *J*_{C,P} = 10.2, and *J*_{C,F} = 22.4 Hz), 64.6, 30.6, 19.1, 13.7.

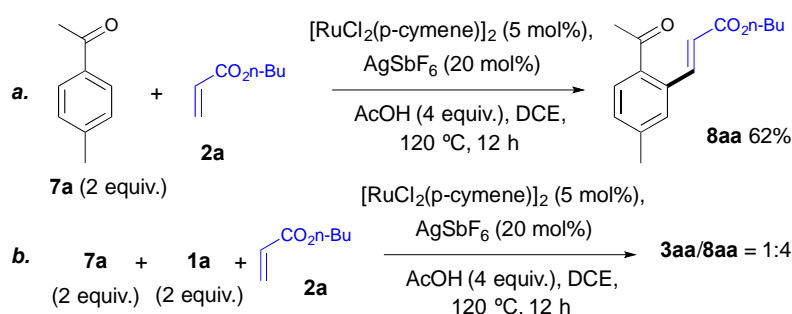
¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) = -105.62 (s), -105.67 (s).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ (ppm) = 27.7 (s).

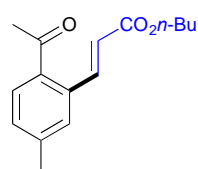
MS (EI) *m/z* (%) = 458 ([M]⁺, 7), 357 (100), 261 (11), 237 (15), 214 (12), 95 (9), 77 (6).

5. Reactivity of arylphosphine oxide versus aryl ketone

To gain more insight into the key factors which drive the chemoselectivity of the reaction between *ortho*-alkylation and *ortho*-alkenylation, we performed some additional experiments (Scheme S1). Under our conditions, the reaction between the aromatic ketone **7a** and **2a** gave only the *ortho*-alkenylated product **8aa** in 62% yield, even in the presence of a large excess of acid (Scheme S1a). From an equimolar ratio of 1-(*p*-tolyl)ethan-1-one (**7a**) (2 equiv) and triphenylphosphine oxide (**1a**) (2 equiv) in the presence of *n*-butyl acrylate (**1a**) (1 equiv) as the coupling partner, we observed the formation of a mixture of **3aa** and **8aa** in a 1:4 ratio (Scheme S1b). These results suggest that the alkylation chemoselectivity did not only depend of the acid/basic media but it is also altering by the nature of the directing group.



Scheme S1. Control experiments



***n*-Butyl 3-(2-acetyl-5-methylphenyl)acrylate (**8aa**):** Following the general procedure **A** using methyl 1-(*p*-tolyl)ethanone (1.0 mmol, 134 mg) and *n*-butyl acrylate (0.5 mmol, 64 mg), **8aa** was isolated in 62 % yield (80 mg) as a colorless oil, after purified using flash column chromatography with pentane-ethyl acetate (10:1).

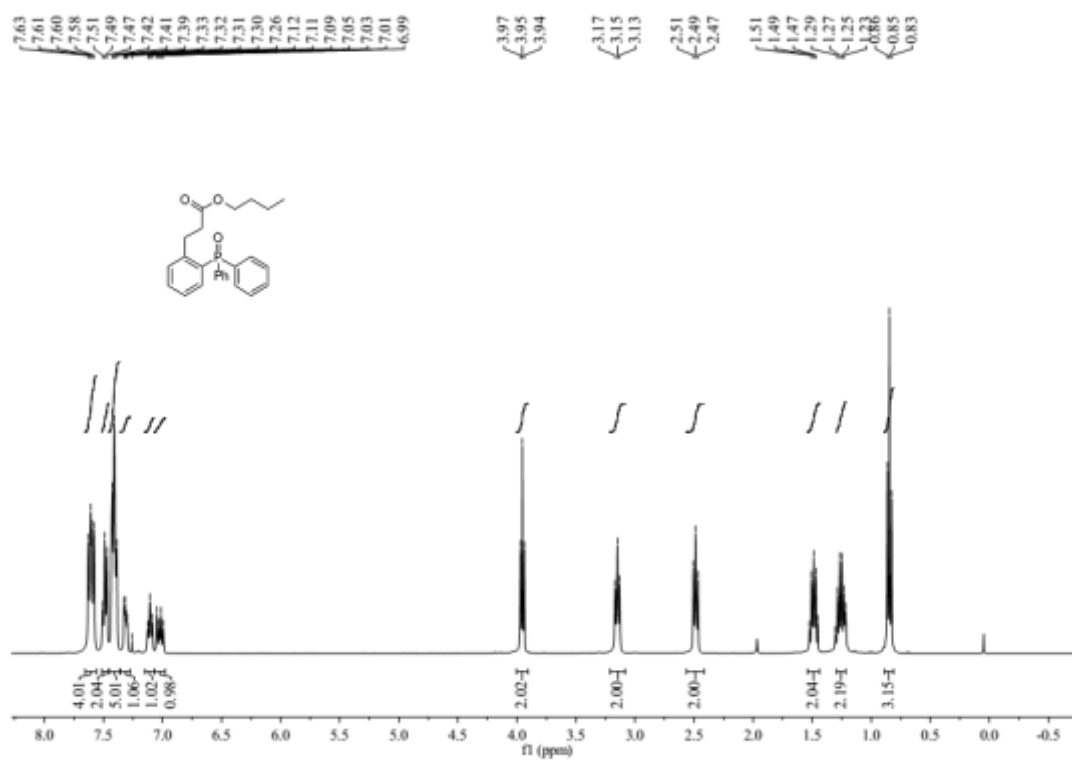
¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.11 (d, J = 15.9 Hz, 1H), 7.59 (d, J = 7.9 Hz, 1H), 7.30 (s, 1H), 7.17 (d, J = 7.9 Hz, 1H), 6.18 (d, J = 15.9 Hz, 1H), 4.13 (t, J = 6.7 Hz, 2H), 2.51 (s, 3H), 2.33 (s, 3H), 1.66 – 1.56 (m, 2H), 1.38–1.33 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H).

¹³C{¹H} NMR (75 MHz, CDCl₃) δ (ppm) = 200.2, 166.7, 144.4, 142.7, 135.3, 130.2, 129.8, 128.8, 120.7, 64.4, 30.8, 29.0, 21.4, 19.2, 13.7.

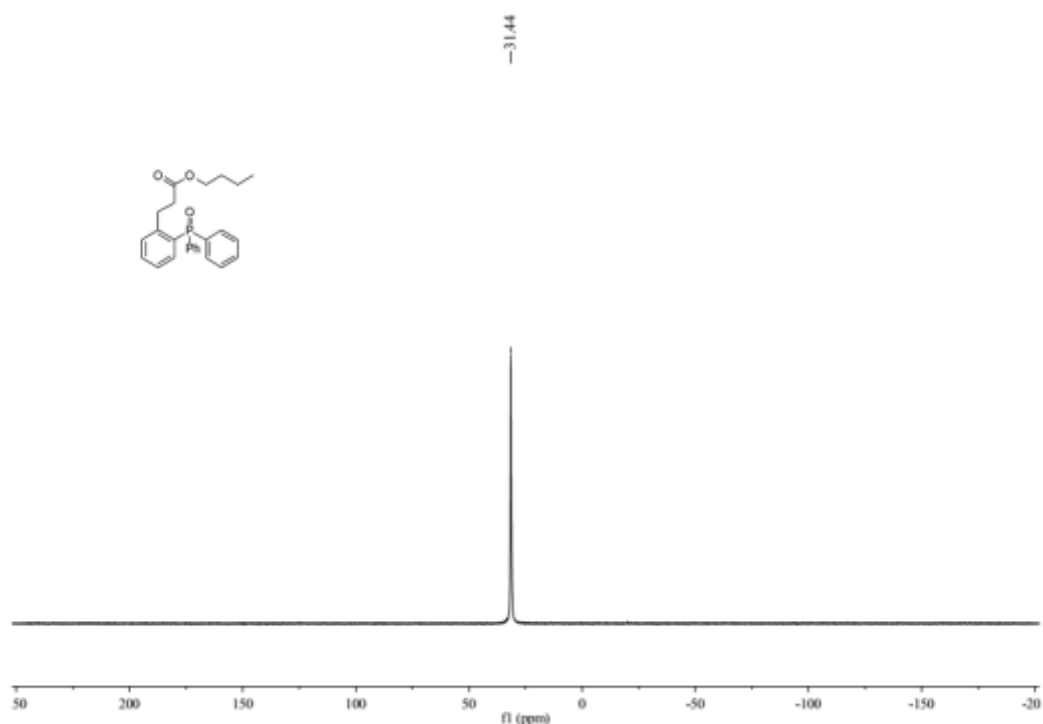
This compound is known and NMR spectrum are identical to those reported in literature.^[9]

6. NMR Charts

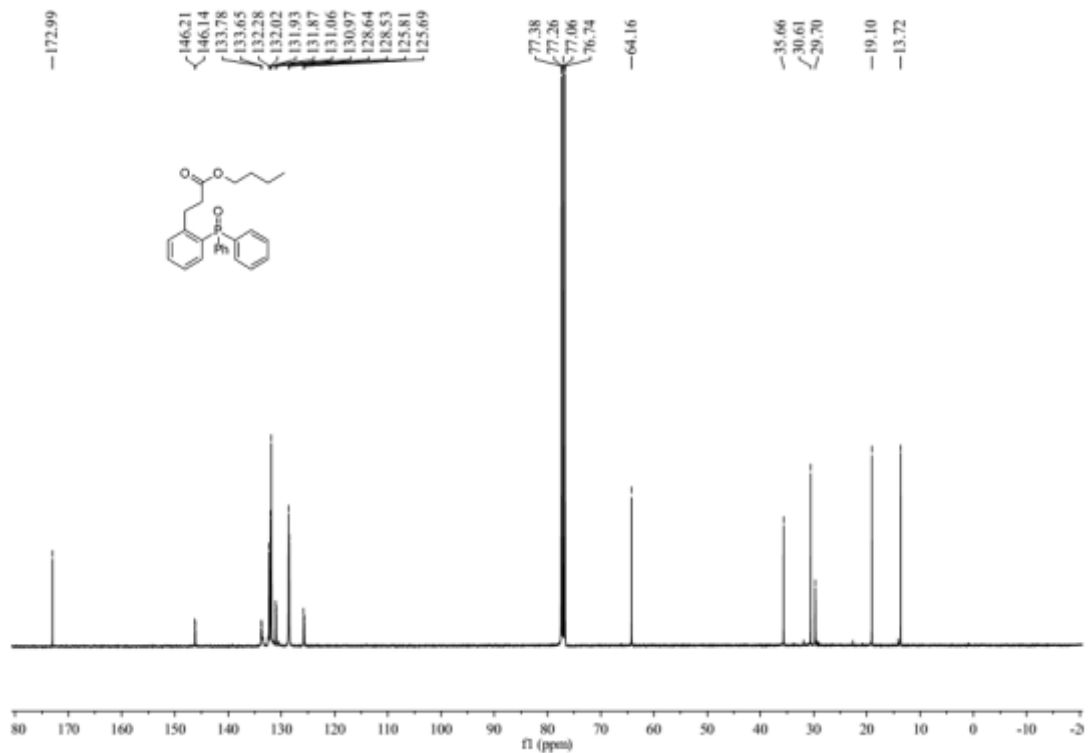
¹H NMR of Butyl 3-(2-(diphenylphosphoryl)phenyl)propanoate (3aa)



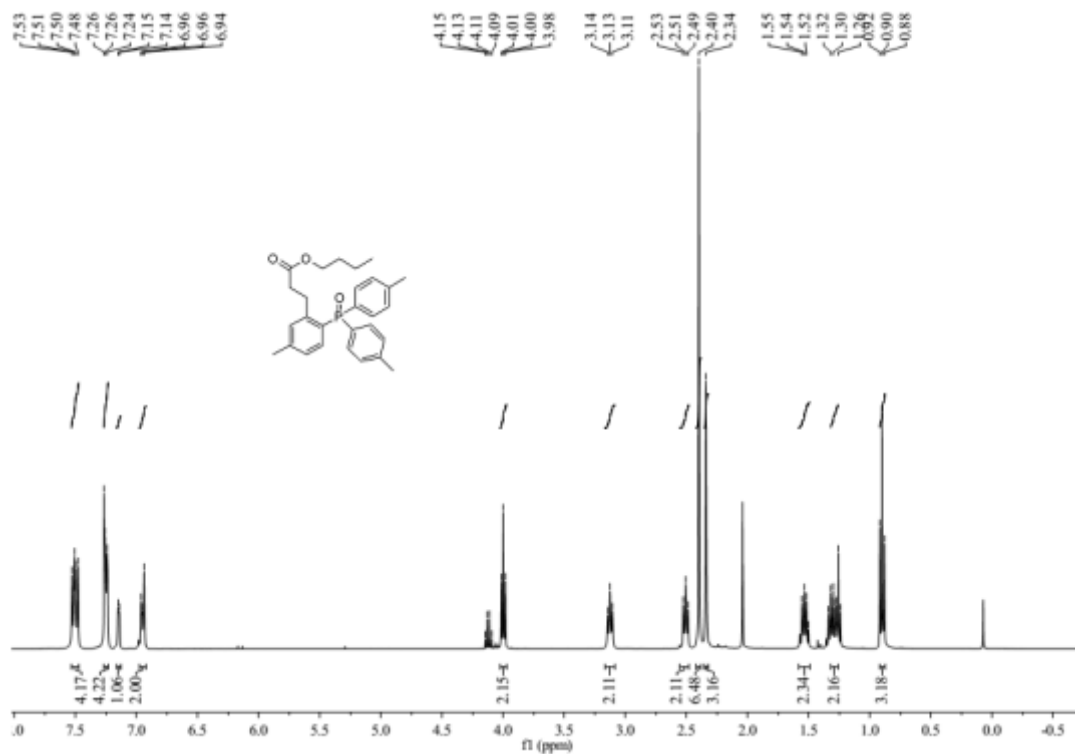
³¹P NMR of Butyl 3-(2-(diphenylphosphoryl)phenyl)propanoate (3aa)



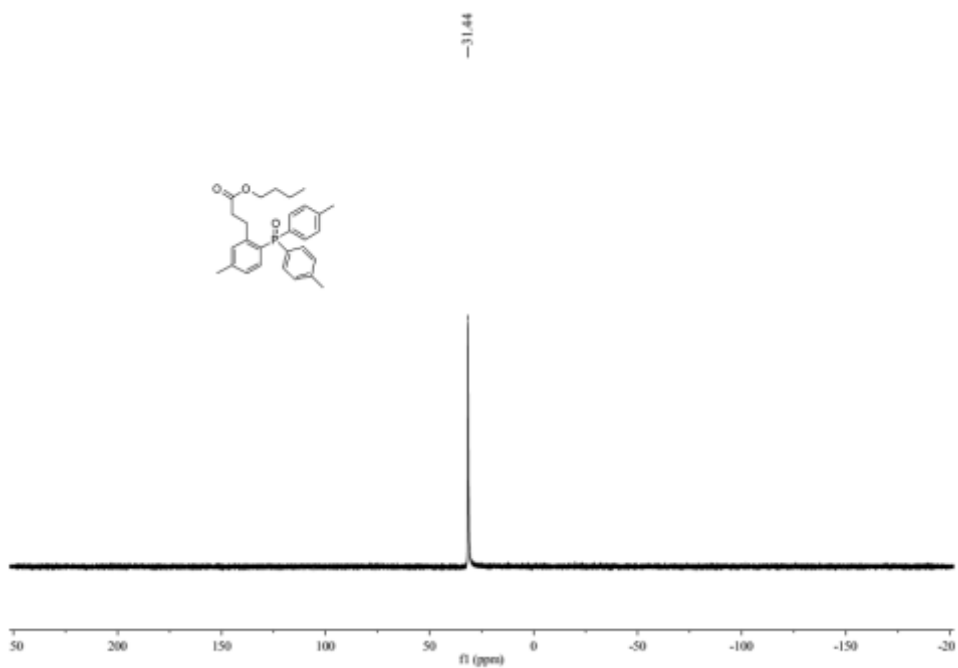
¹³C NMR of Butyl 3-(2-(diphenylphosphoryl)phenyl)propanoate(3aa)



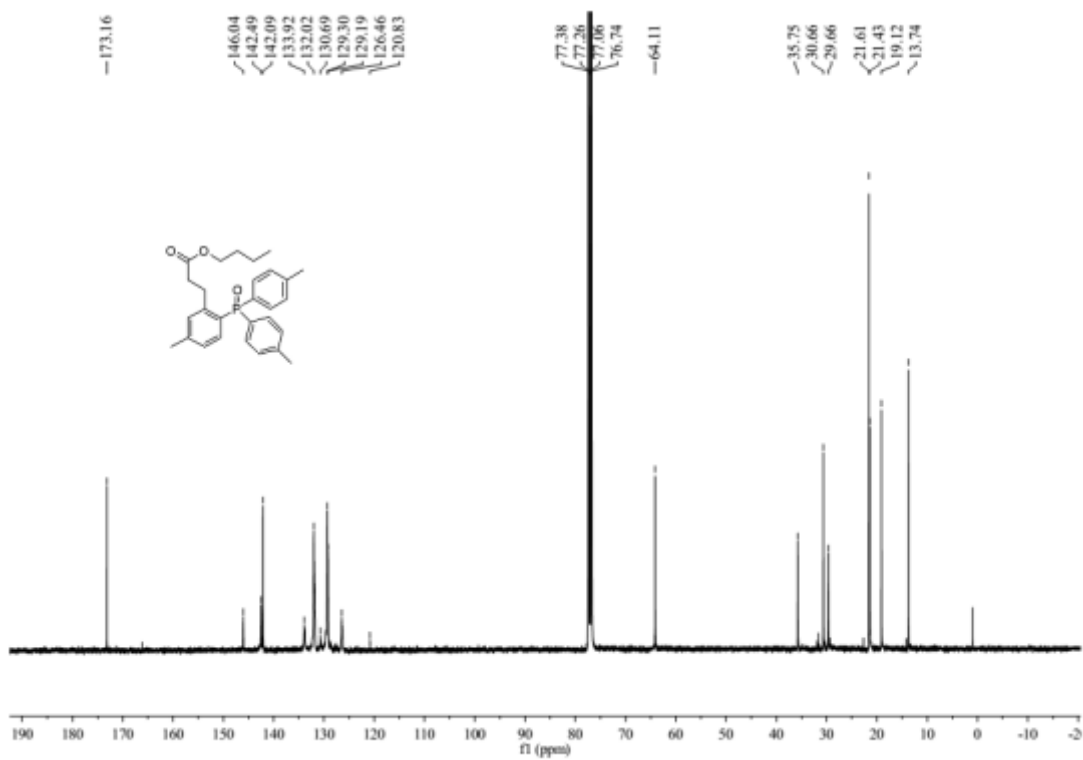
¹H NMR Butyl 3-(2-(di-*p*-tolylphosphoryl)-5-methylphenyl) propanoate(3ba).



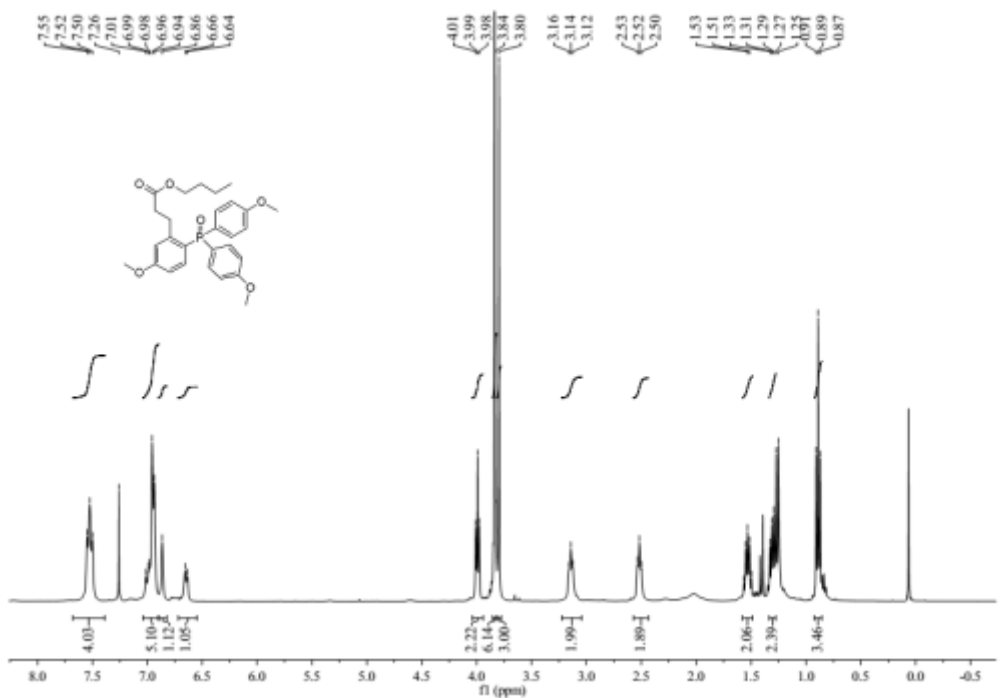
³¹P NMR Butyl 3-(2-(di-*p*-tolylphosphoryl)-5-methylphenyl) propanoate(3ba)..



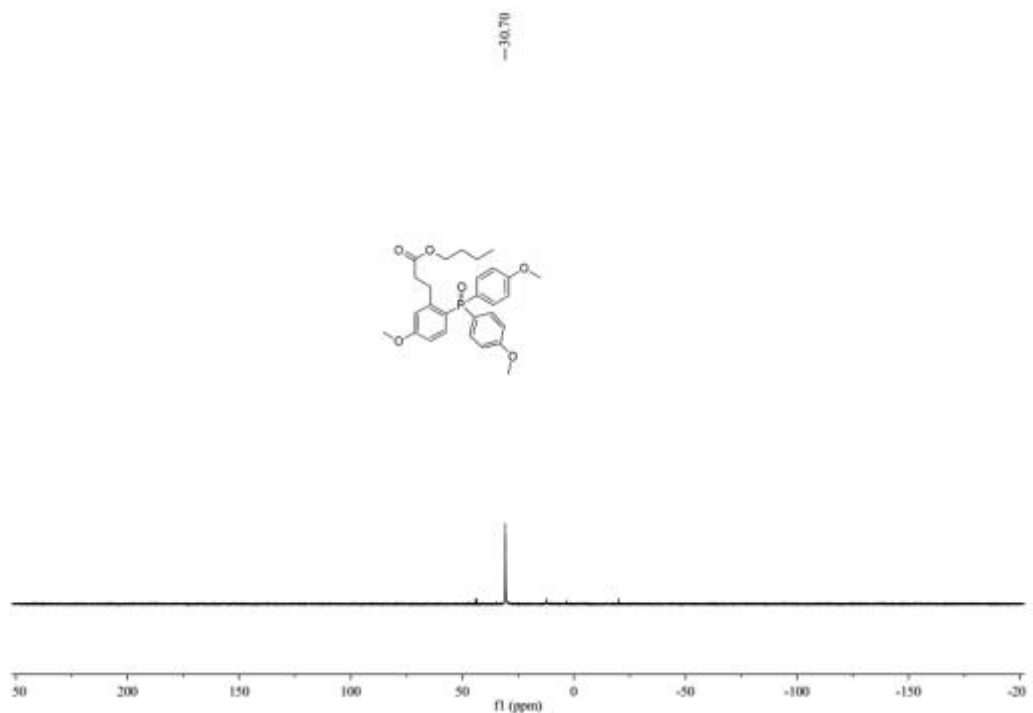
¹³C NMR Butyl 3-(2-(di-*p*-tolylphosphoryl)-5-methylphenyl) propanoate(3ba)..



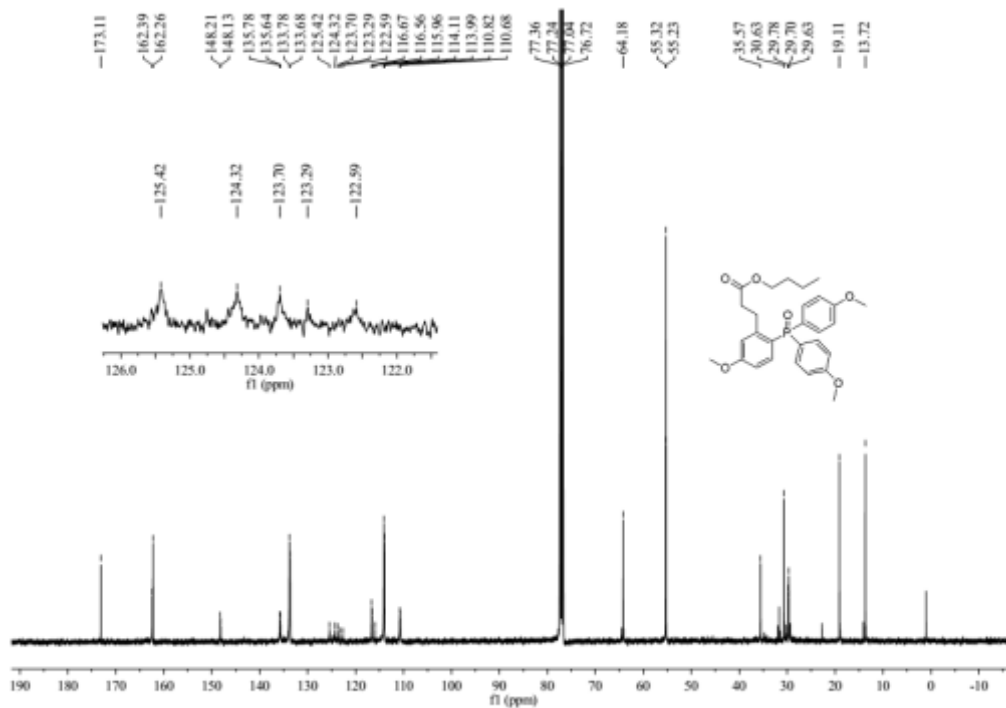
¹³C NMR Butyl 3-(2-(bis(4-methoxyphenyl) phosphoryl) -5-methoxy phenyl) propanoate (3ca).



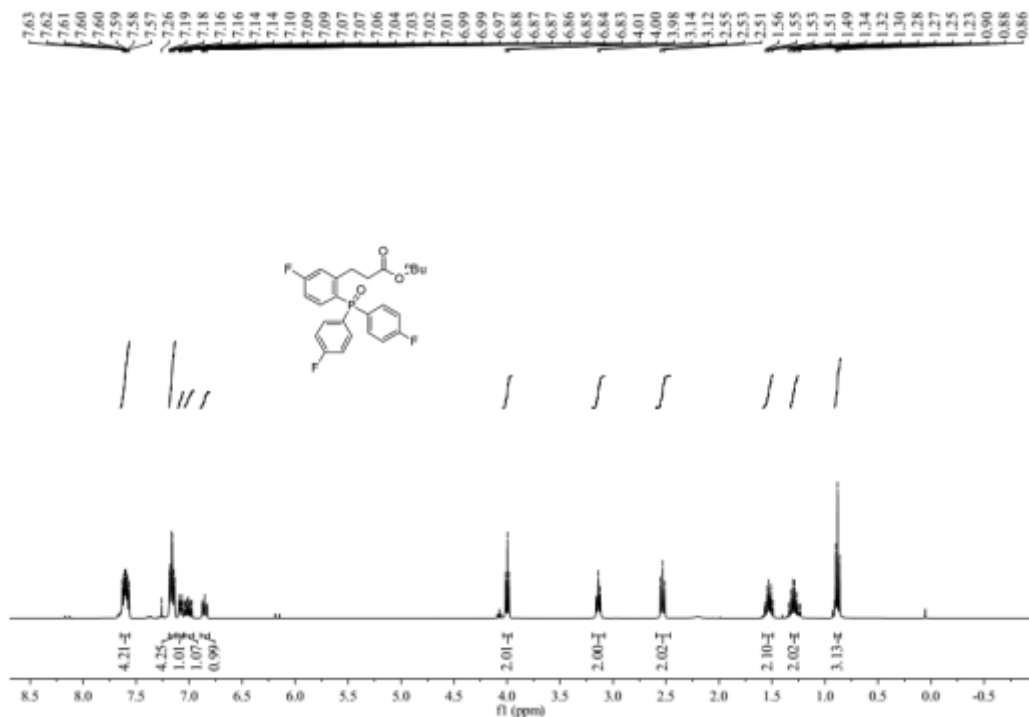
³¹P NMR Butyl 3-(2-(bis(4-methoxyphenyl) phosphoryl) -5-methoxy phenyl) propanoate (3ca)



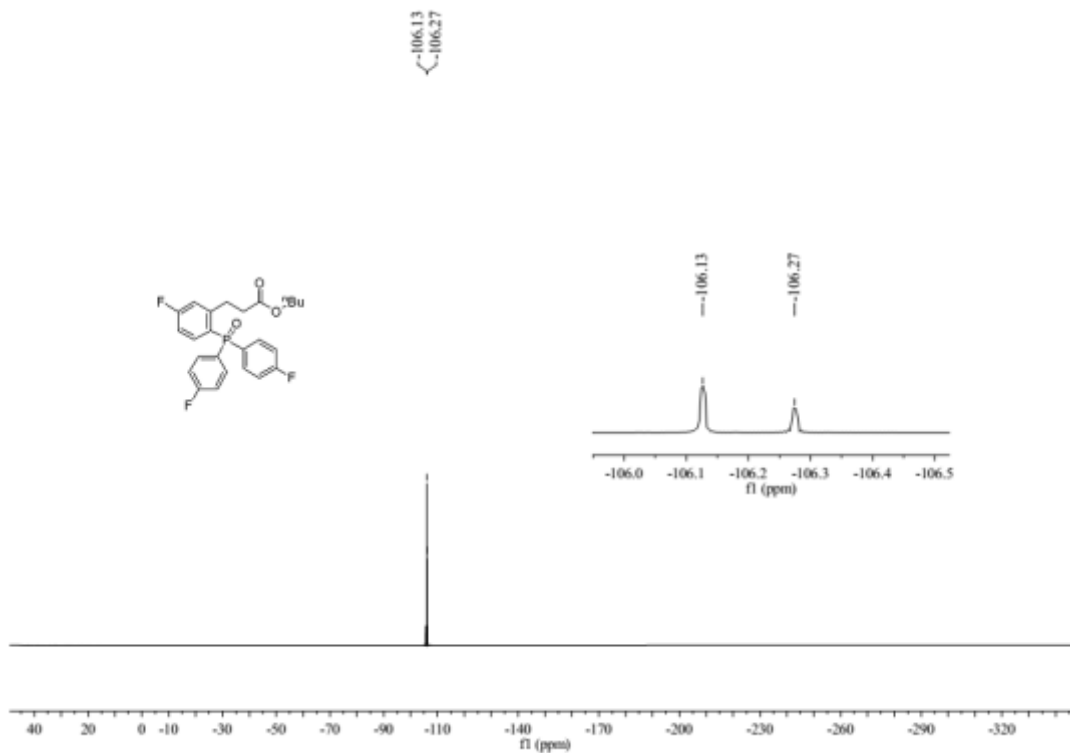
¹³C NMR Butyl 3-(2-(bis(4-methoxyphenyl) phosphoryl) -5-methoxy phenyl) propanoate (3ca)



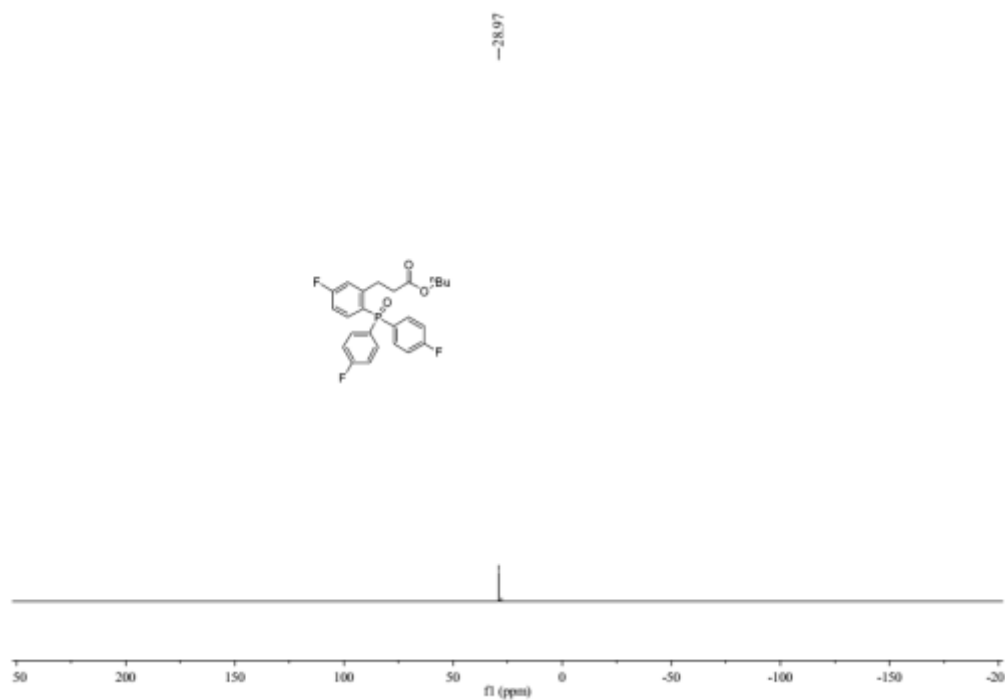
¹H NMR of Butyl 3-(2-(bis(4-fluorophenyl) phosphoryl)-5-fluorophenyl) propanoate (3da)



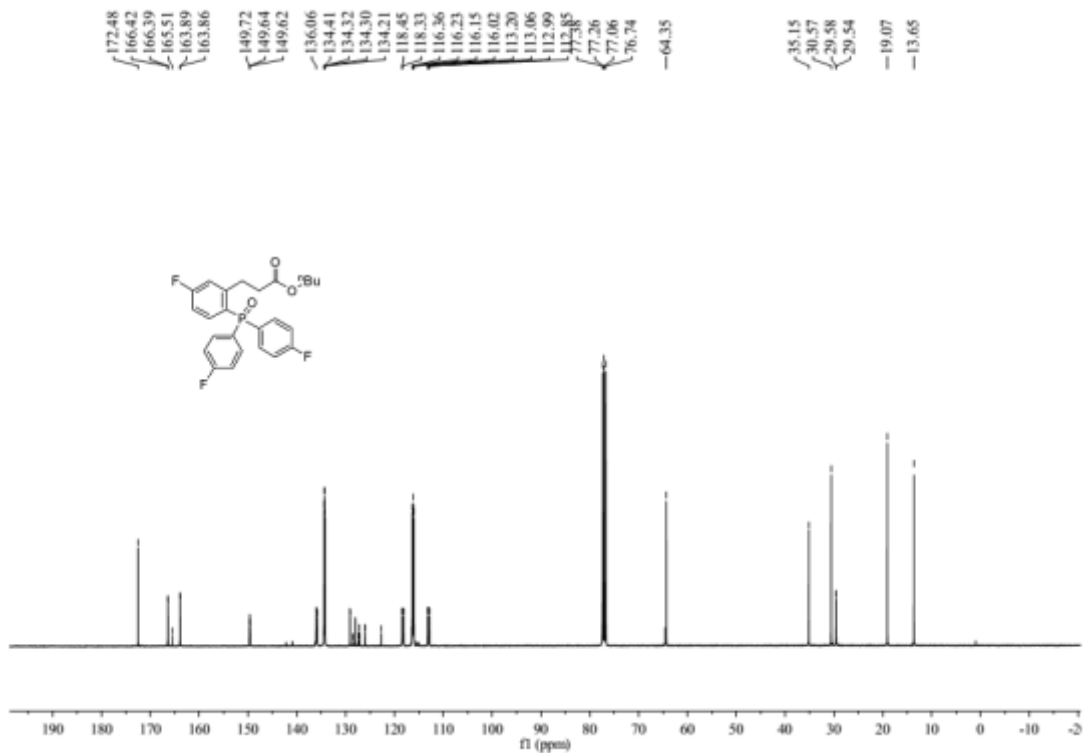
¹⁹F NMR of Butyl 3-(2-(bis(4-fluorophenyl) phosphoryl)-5-fluorophenyl) propanoate (3da)



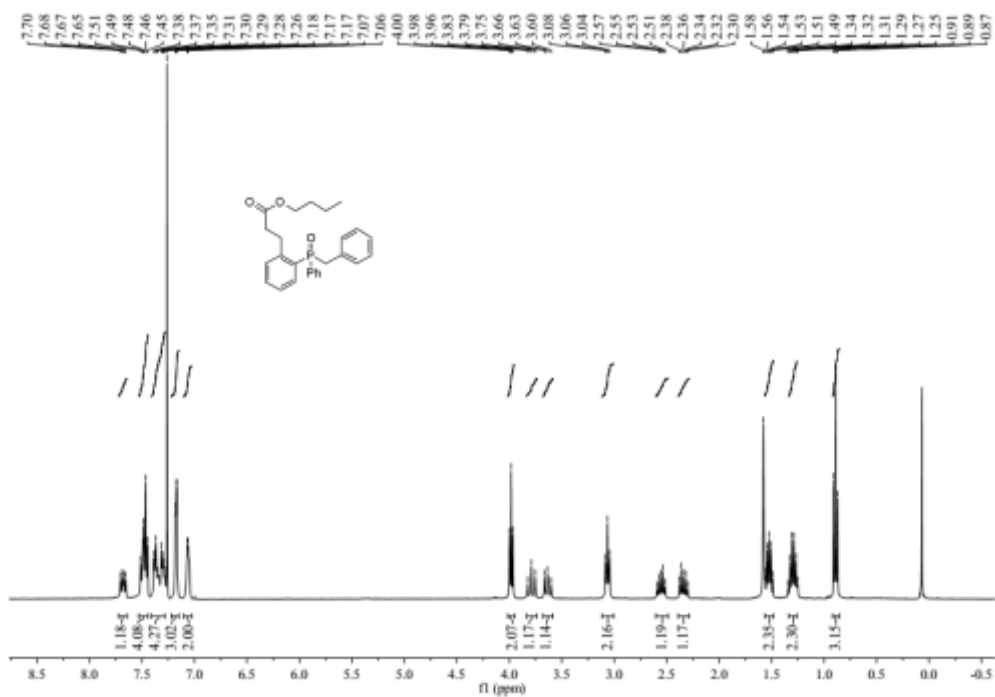
³¹P NMR of Butyl 3-(2-(bis(4-fluorophenyl) phosphoryl)-5-fluorophenyl) propanoate (3da)



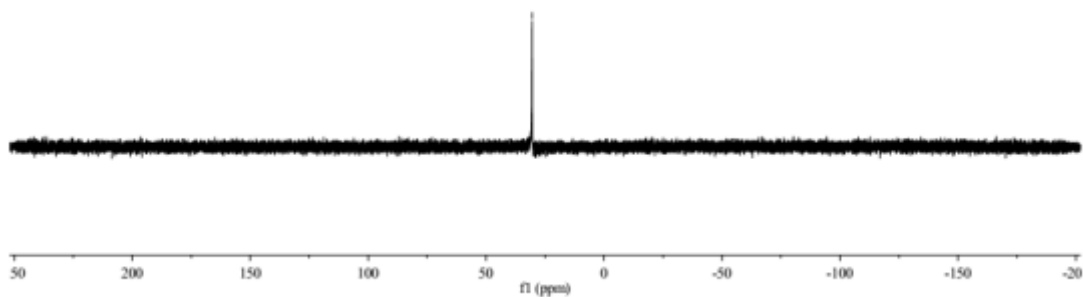
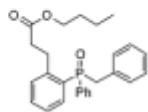
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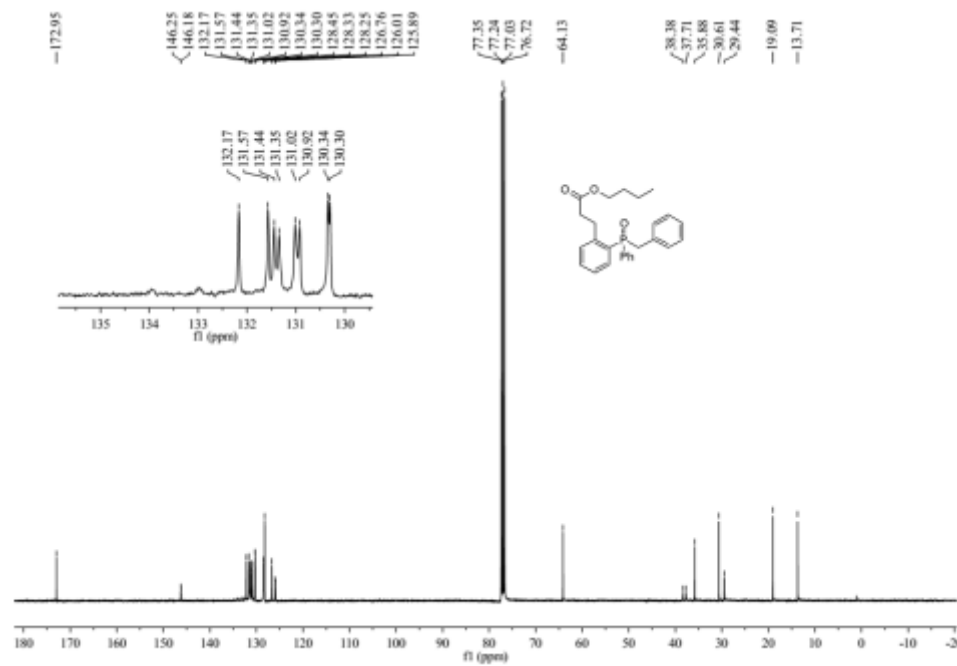
¹H NMR of Butyl 3-(2-(benzyl(phenyl)phosphoryl) phenyl) propanoate (3ea)



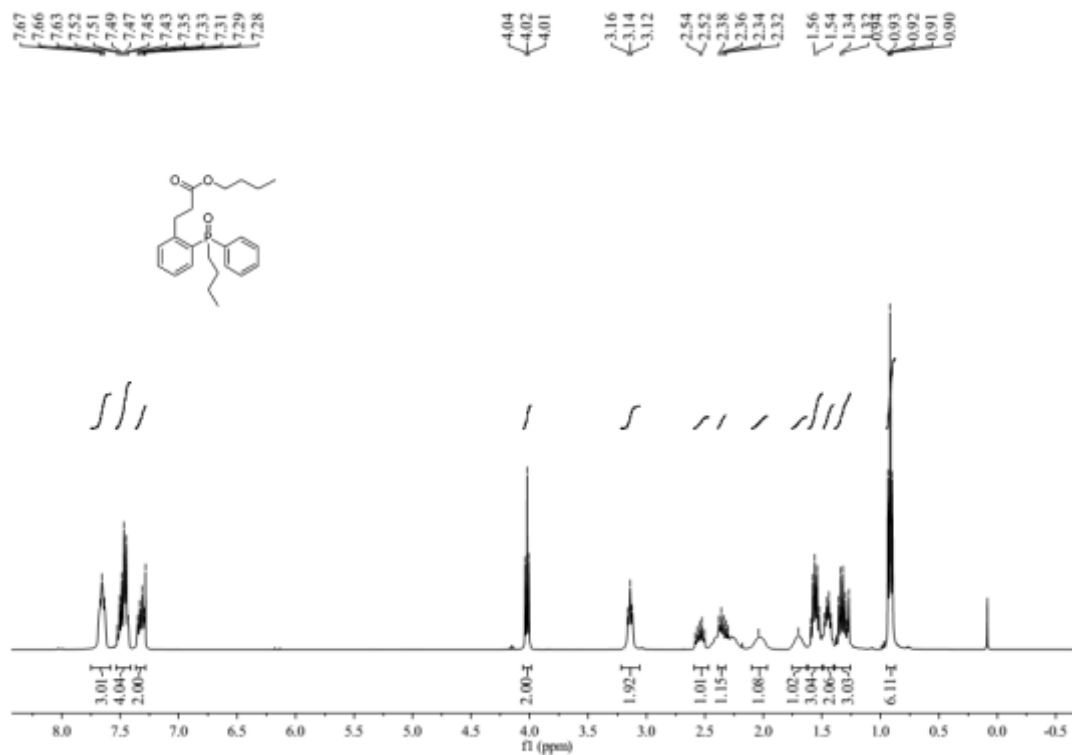
³¹P NMR of Butyl 3-(2-(benzyl(phenyl)phosphoryl) phenyl) propanoate (3ea)



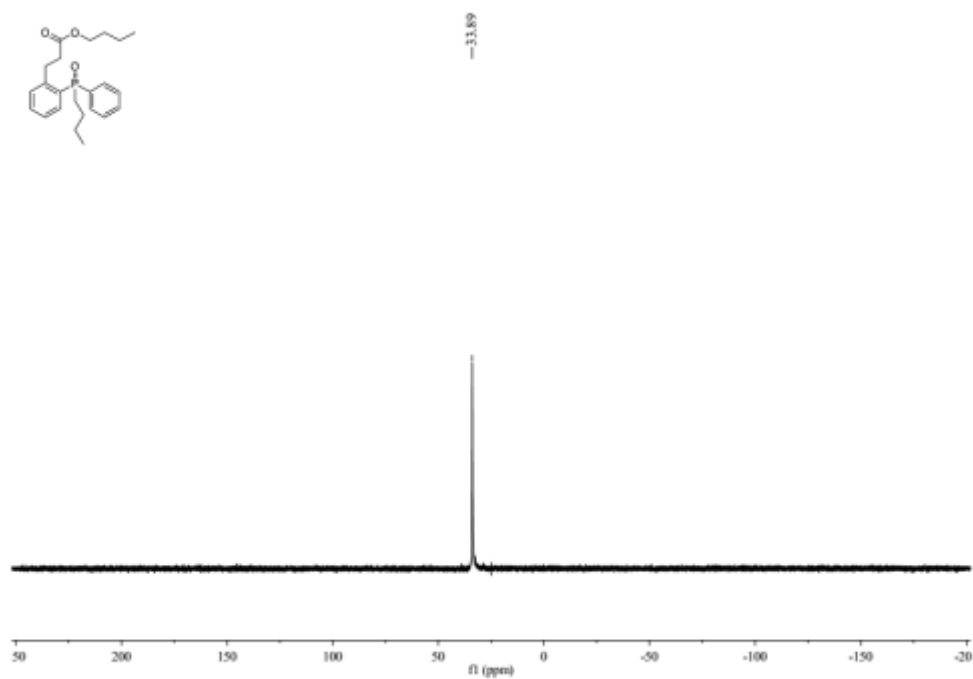
¹³CNMR of Butyl 3-(2-(benzyl(phenyl)phosphoryl)phenyl) propanoate (3ea)



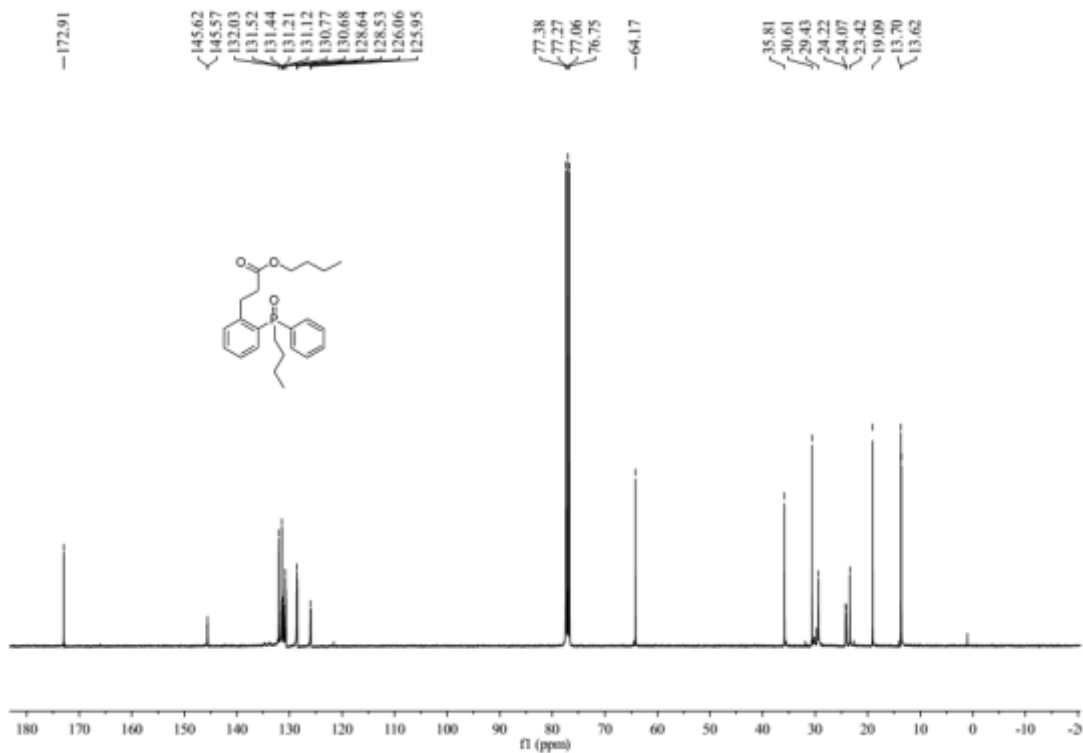
¹H NMR of Butyl 3-(2-(butyl(phenyl)phosphoryl)phenyl) propanoate (3fa)



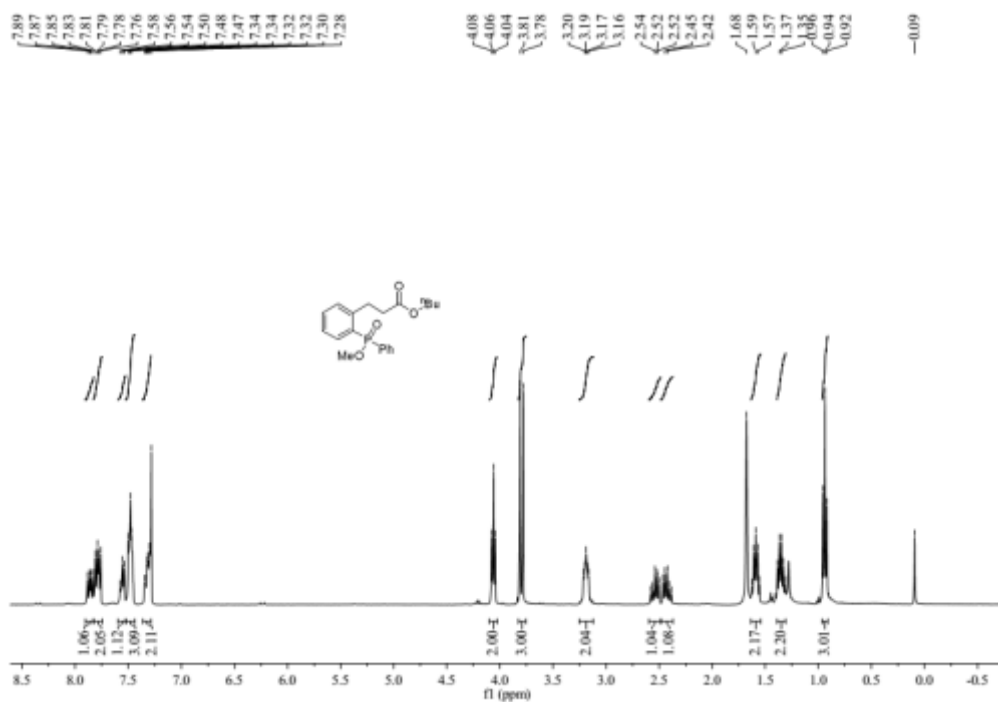
³¹P NMR of Butyl 3-(2-(butyl(phenyl)phosphoryl)phenyl) propanoate (3fa)



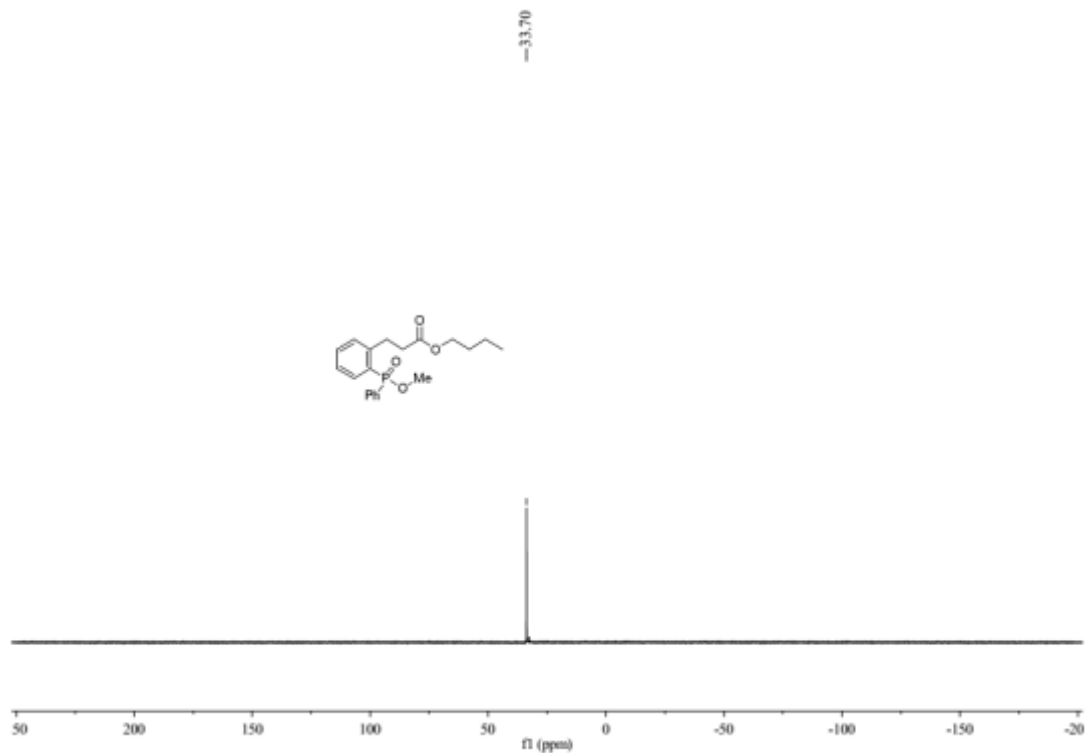
¹³C NMR of Butyl 3-(2-(butyl (phenyl) phosphoryl) phenyl) propanoate (3fa)



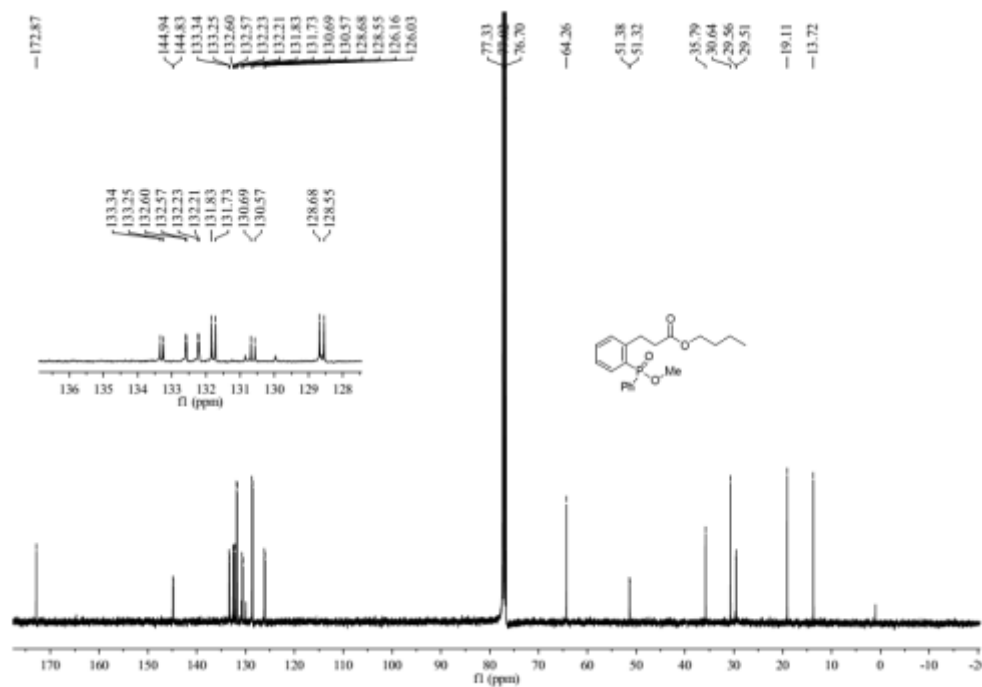
¹H NMR of Butyl 3-(2-(methoxy(phenyl) phosphoryl) phenyl) propanoate (3ga)



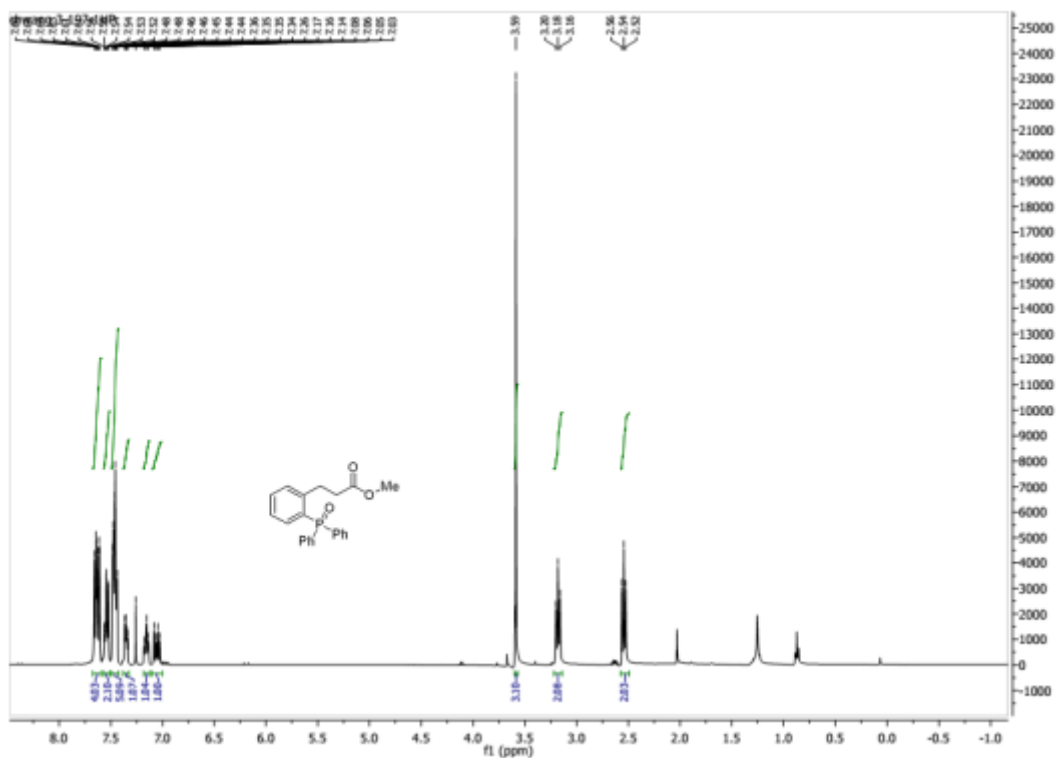
³¹P NMR of Butyl 3-(2-(methoxy(phenyl) phosphoryl) phenyl) propanoate (3ga)



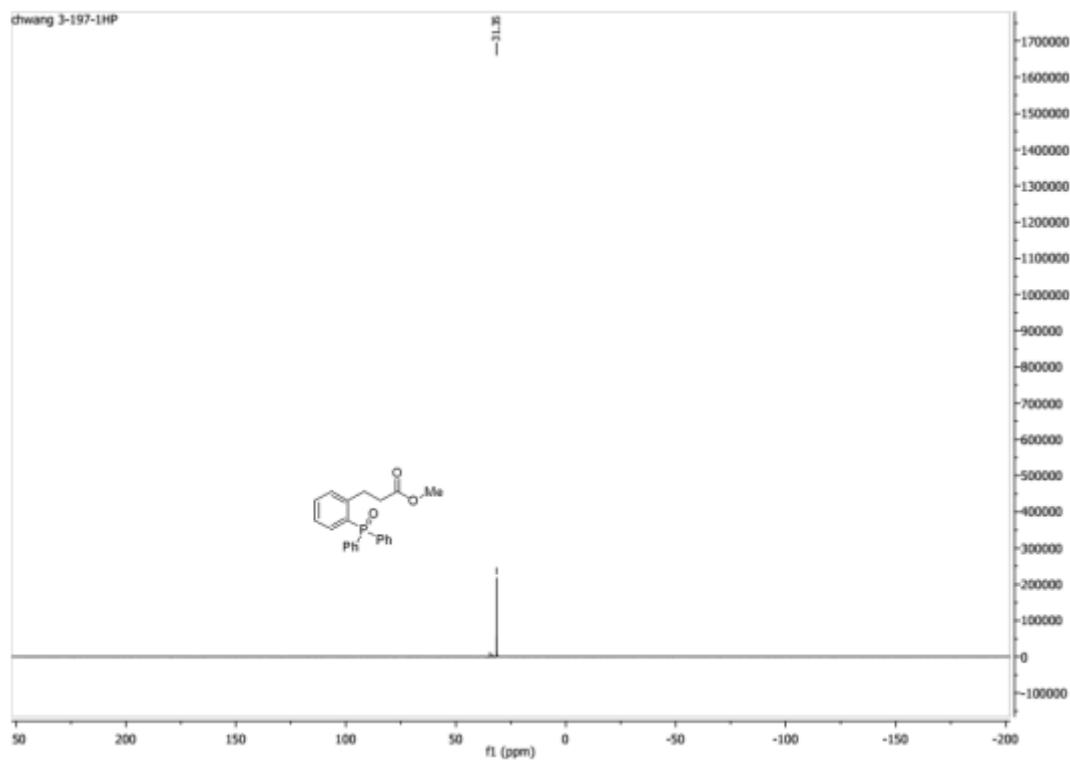
^{13}C NMR of Butyl 3-(2-(methoxy(phenyl) phosphoryl) phenyl) propanoate (3ga)



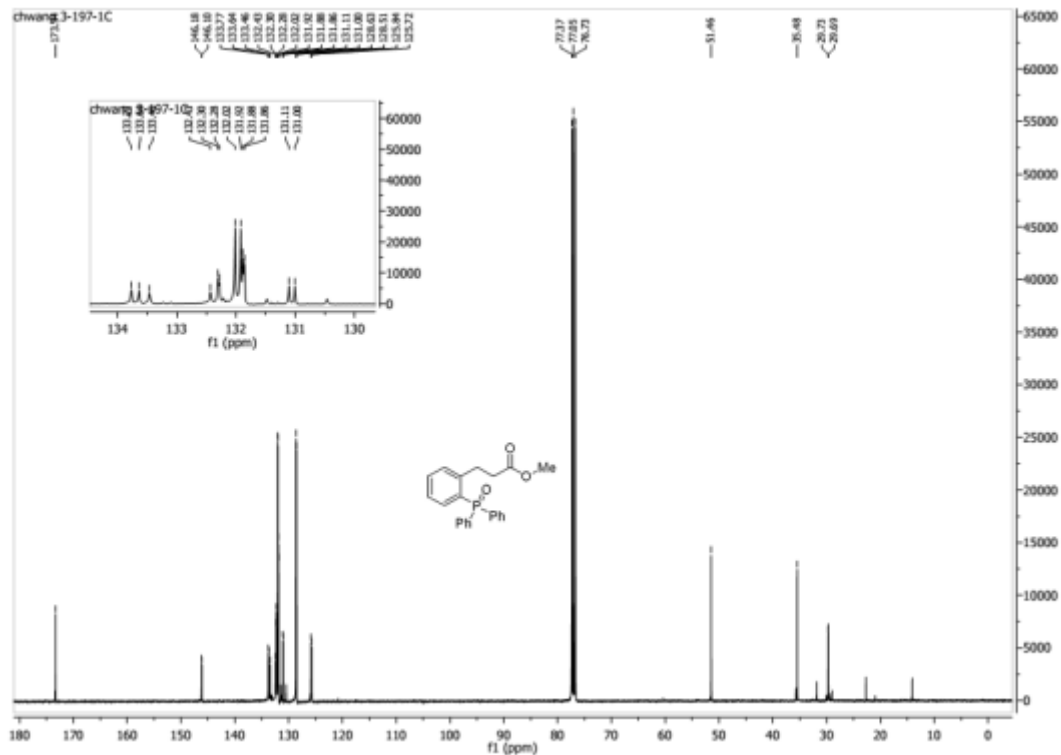
^1H NMR of methyl 3-(2-(diphenylphosphoryl)phenyl)propanoate. (3ab)



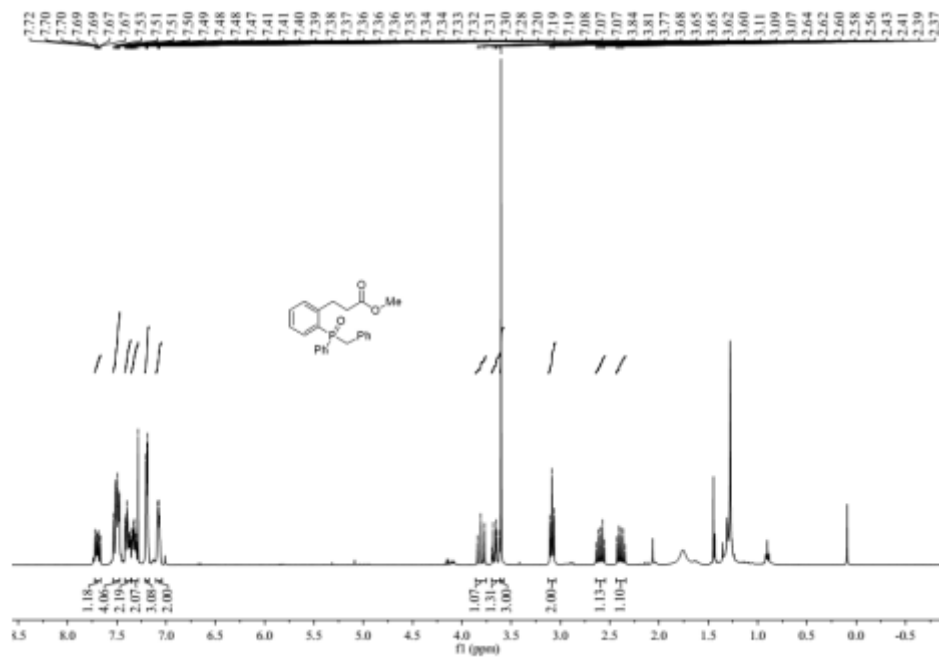
^{31}P NMR of methyl 3-(2-(diphenylphosphoryl)phenyl)propanoate. (3ab)



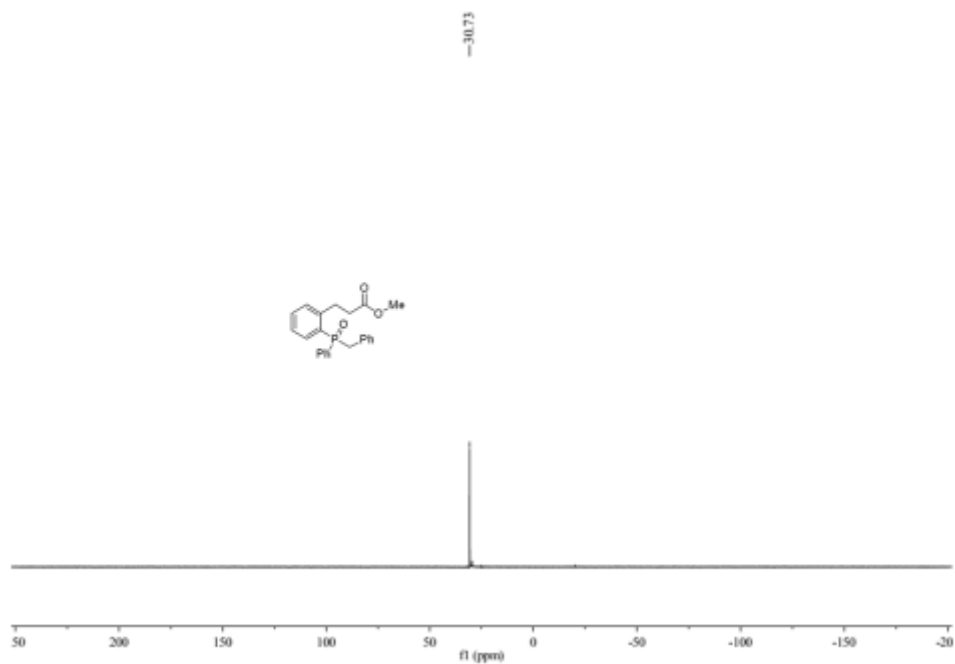
^{13}C NMR of methyl 3-(2-(diphenylphosphoryl)phenyl)propanoate. (3ab)



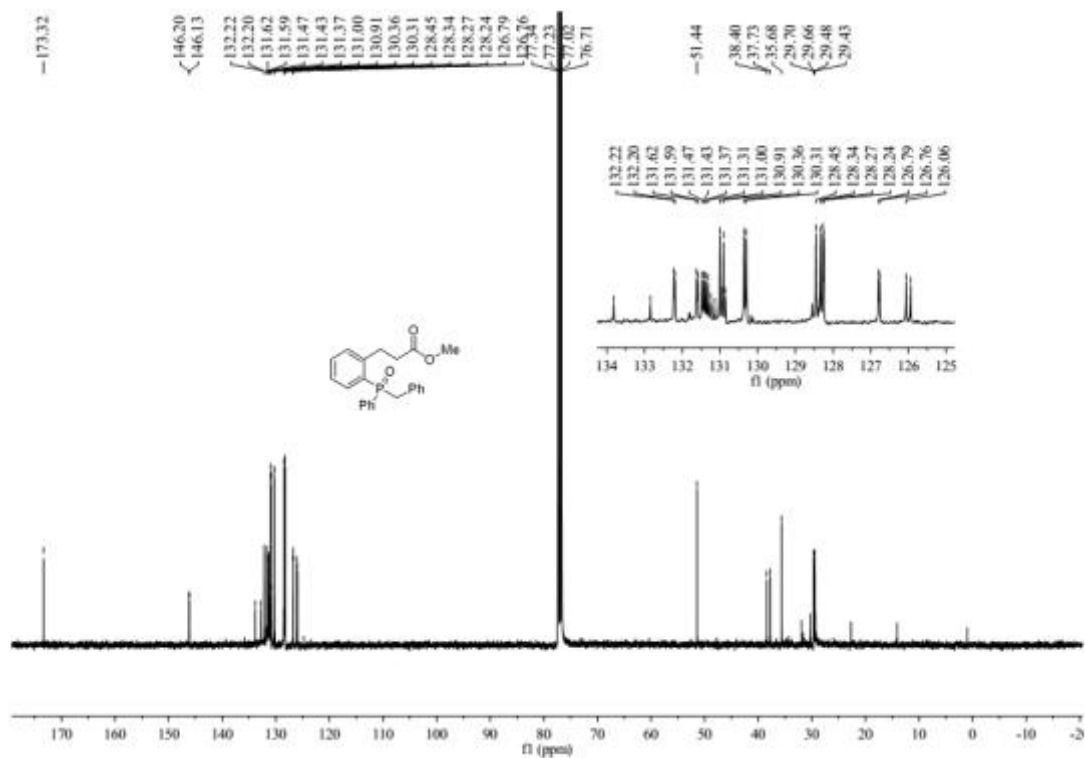
¹H NMR of Methyl-3-(2-(benzyl(phenyl) phosphoryl) phenyl) propanoate (3eb).



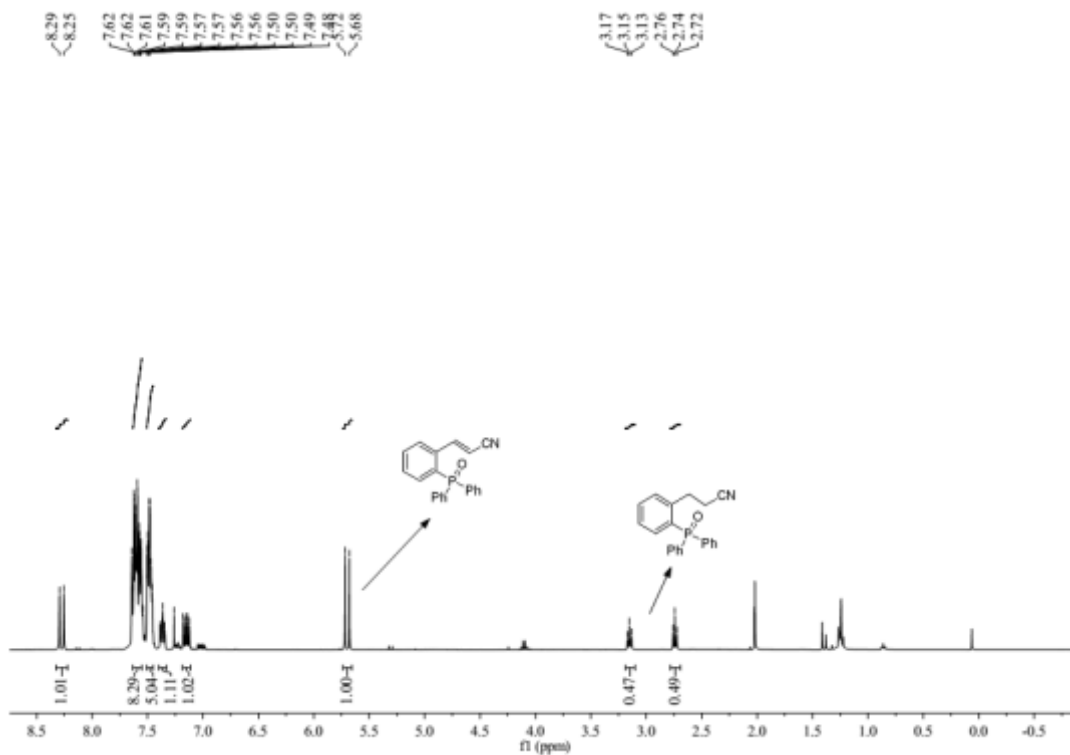
³¹P NMR of Methyl-3-(2-(benzyl(phenyl) phosphoryl) phenyl) propanoate (3eb).



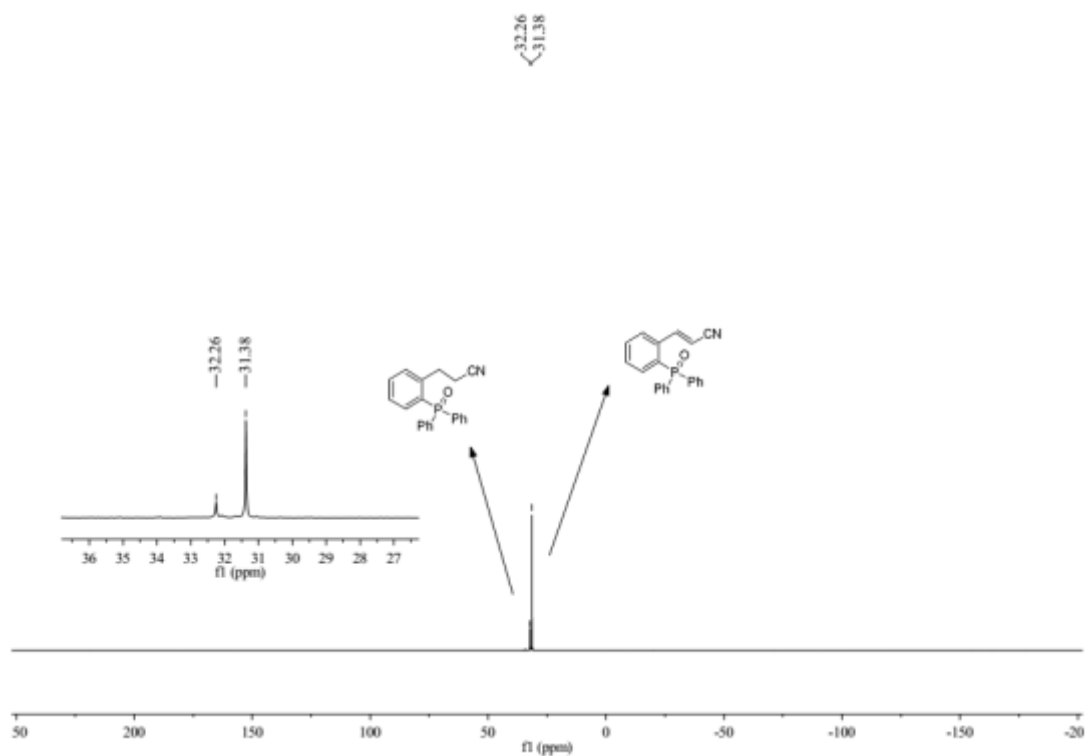
¹³C NMR of Methyl-3-(2-(benzyl(phenyl)phosphoryl) phenyl) propanoate (3eb).



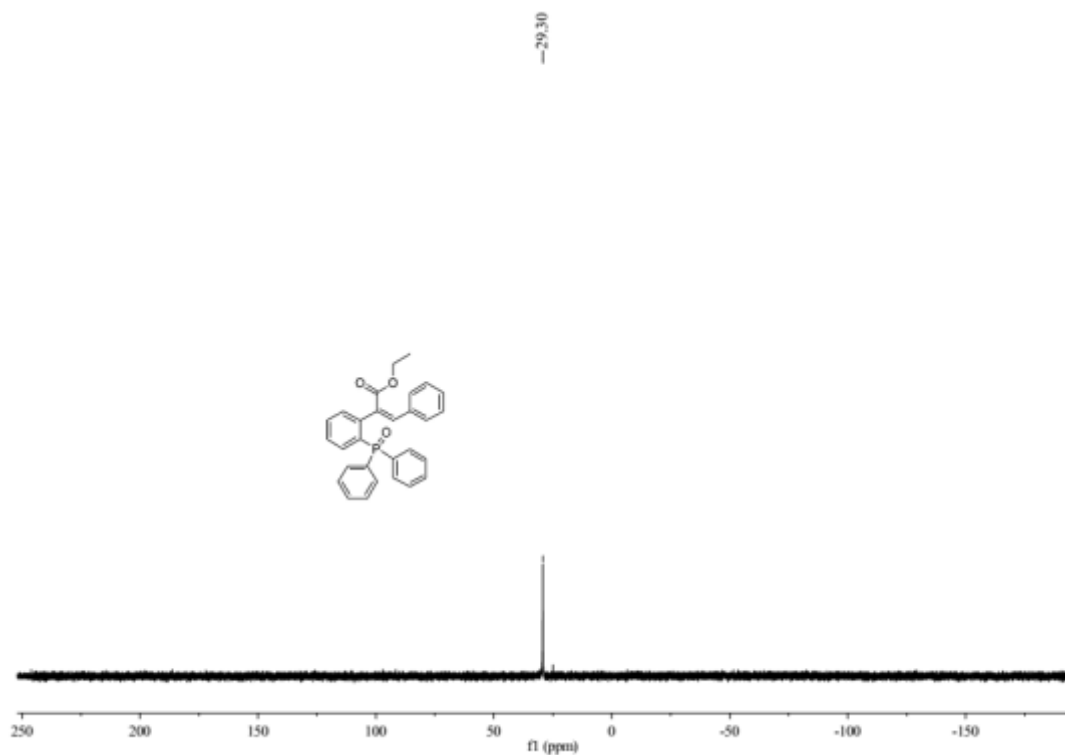
¹H NMR of 3-(2-(diphenylphosphoryl)phenyl)acrylonitrile (3ac/4ac).



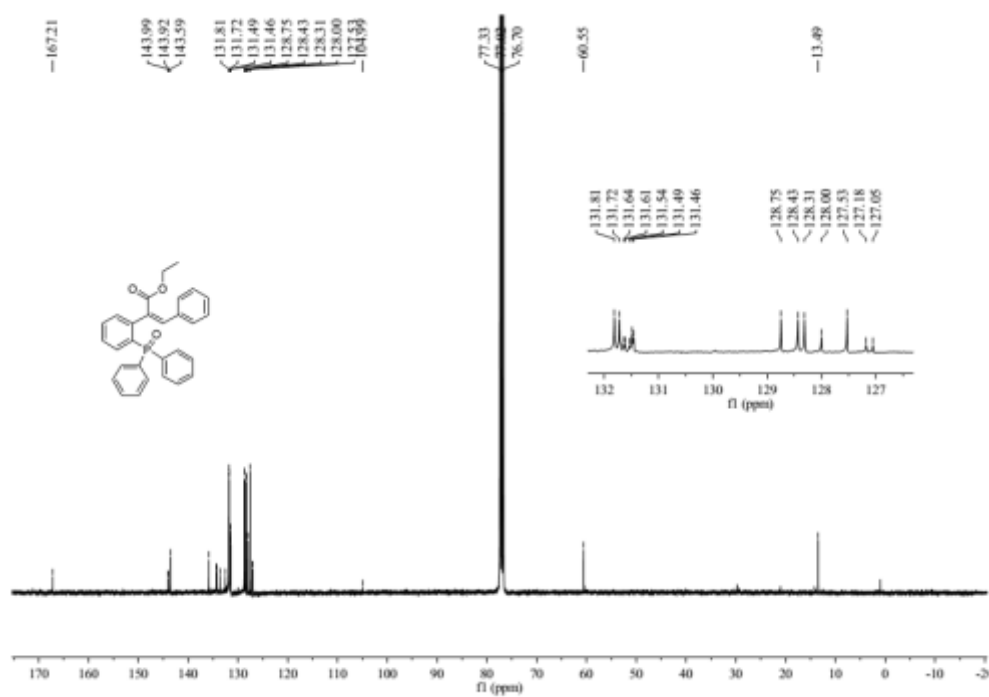
³¹P NMR of 3-(2-(diphenylphosphoryl)phenyl)acrylonitrile (3ac/4ac).



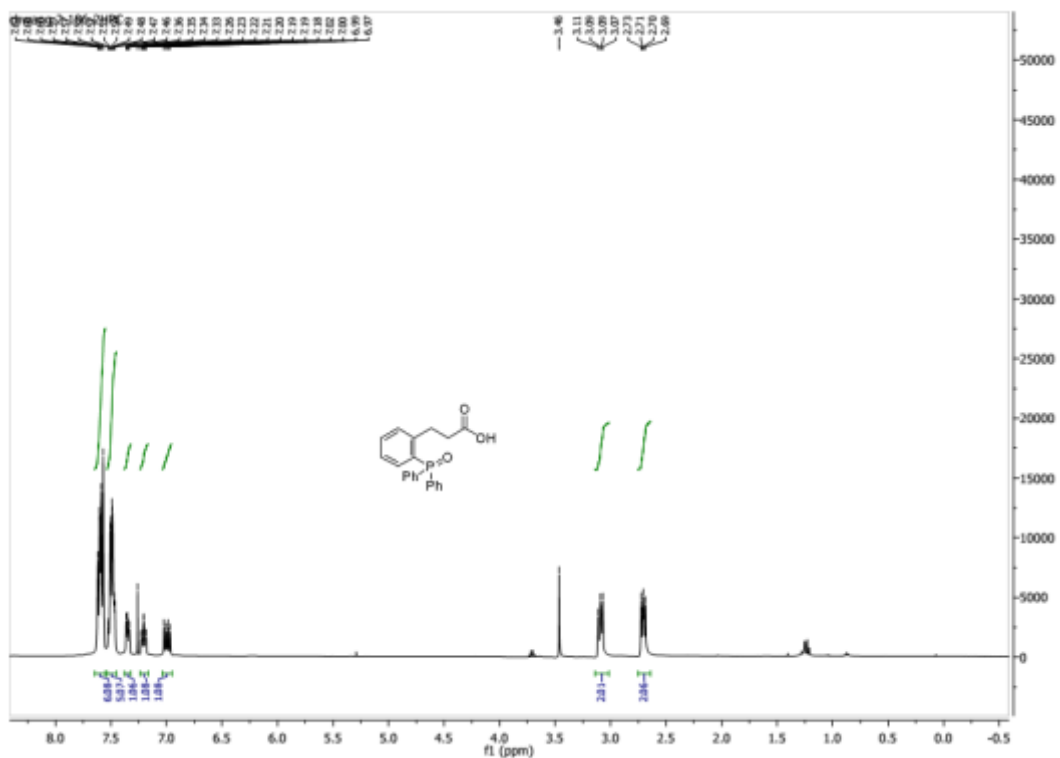
¹³C NMR of 3-(2-(diphenylphosphoryl)phenyl)acrylonitrile (3ac/4ac).



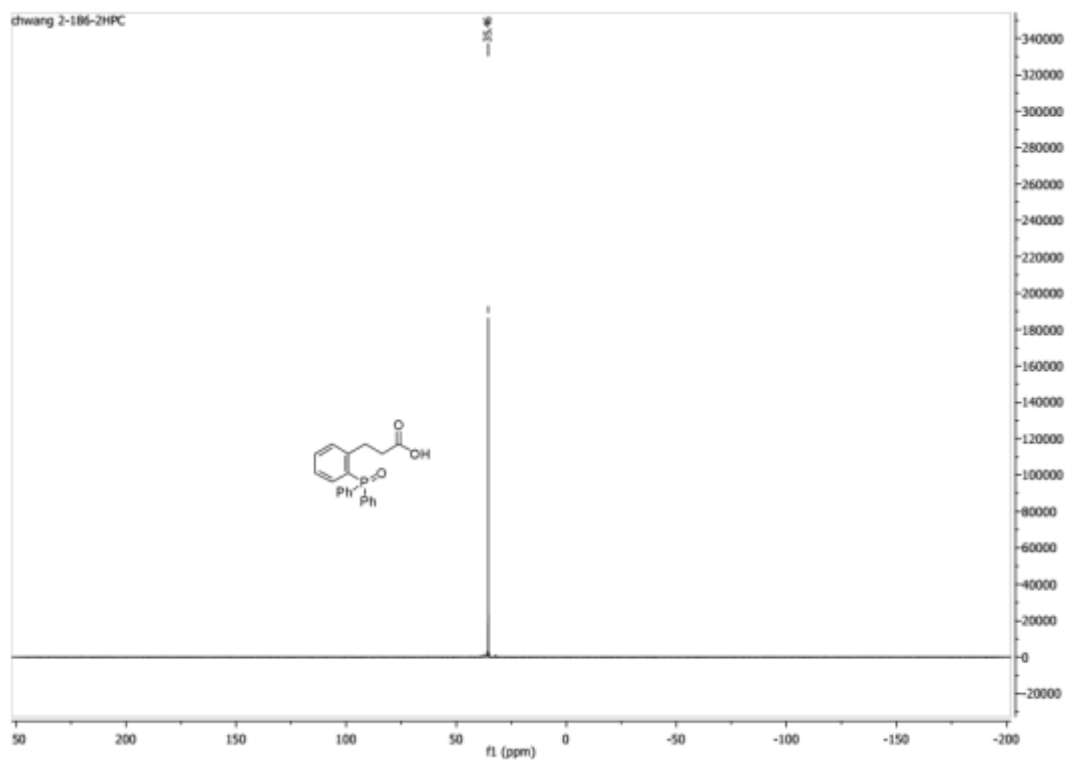
^{13}C NMR of (E)-ethyl 2-(2-(diphenylphosphoryl)phenyl)-3-phenylacrylate (3ad)



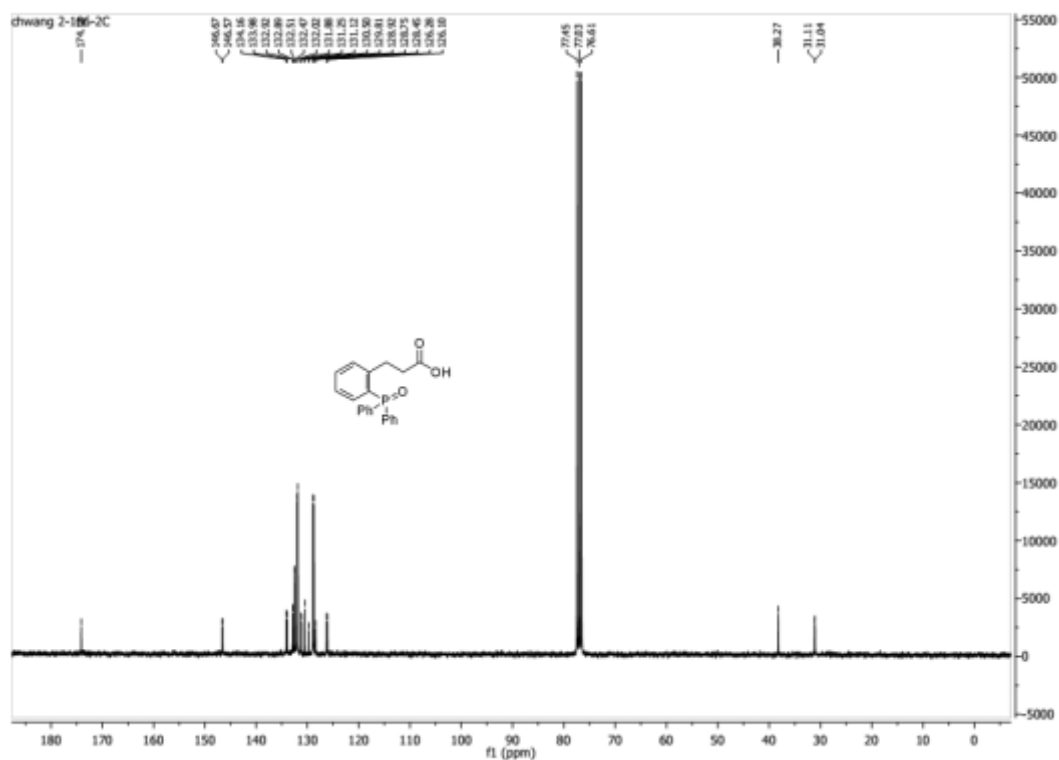
^1H NMR of 3-(2-(diphenylphosphoryl) phenyl)propanoic acid (5aa)



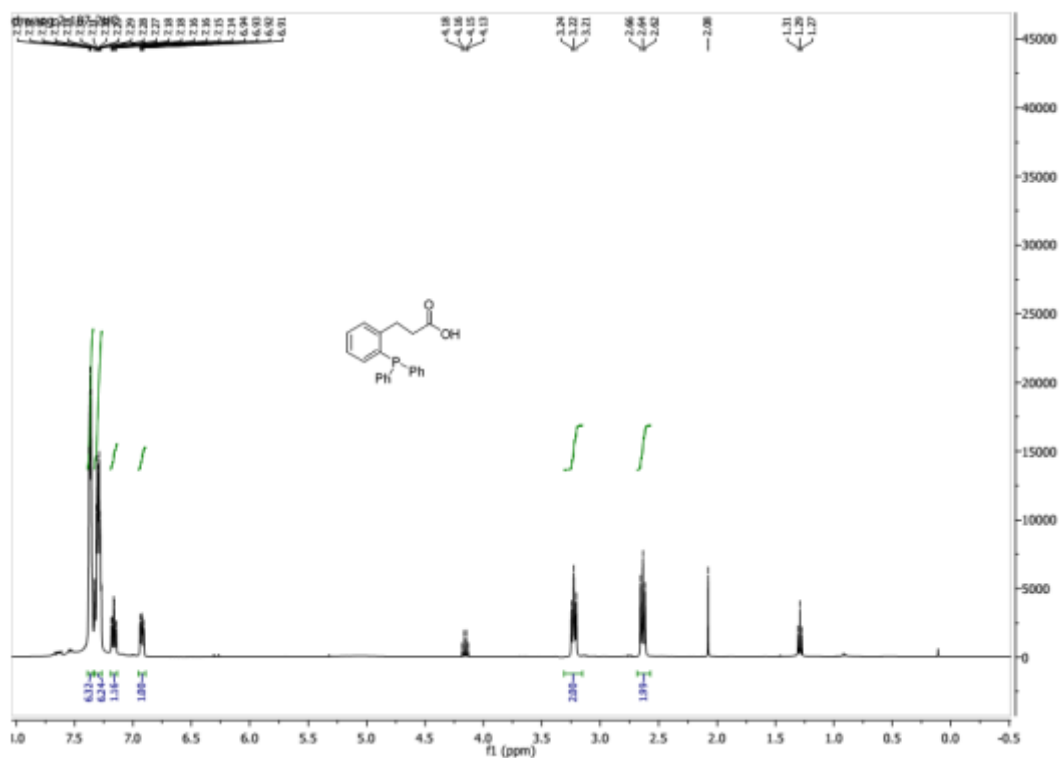
³¹P NMR of 3-(2-(diphenylphosphoryl) phenyl) propanoic acid (5aa)



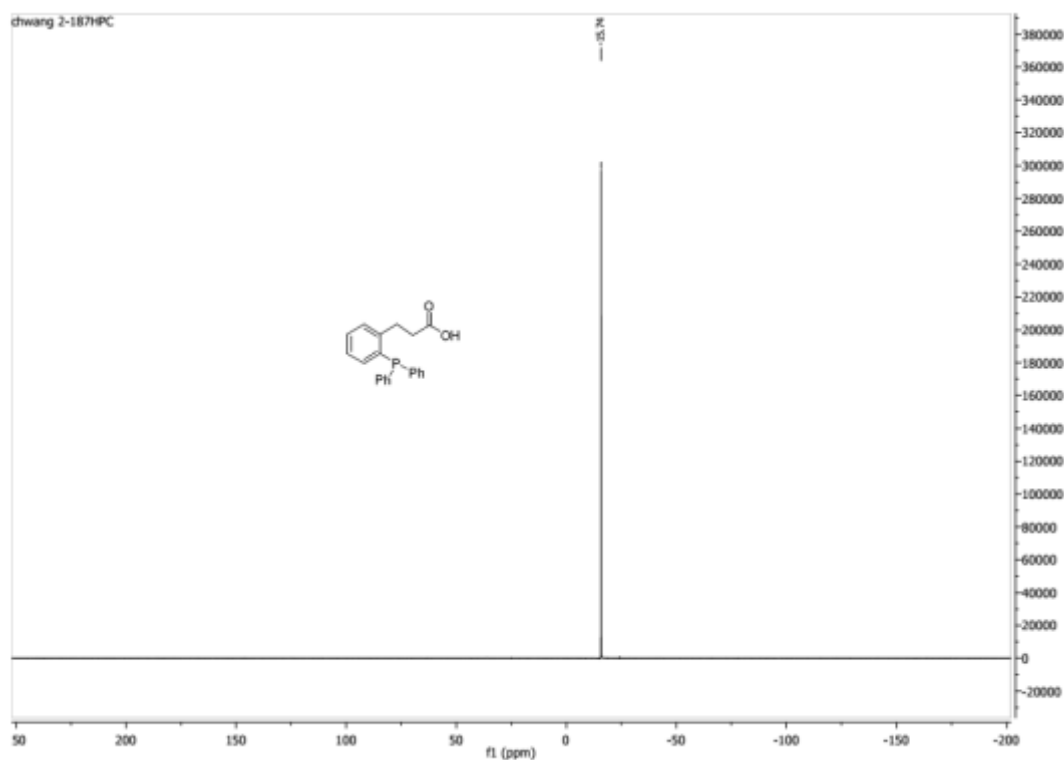
¹³C NMR of 3-(2-(diphenylphosphoryl)phenyl)propanoic acid (5aa)



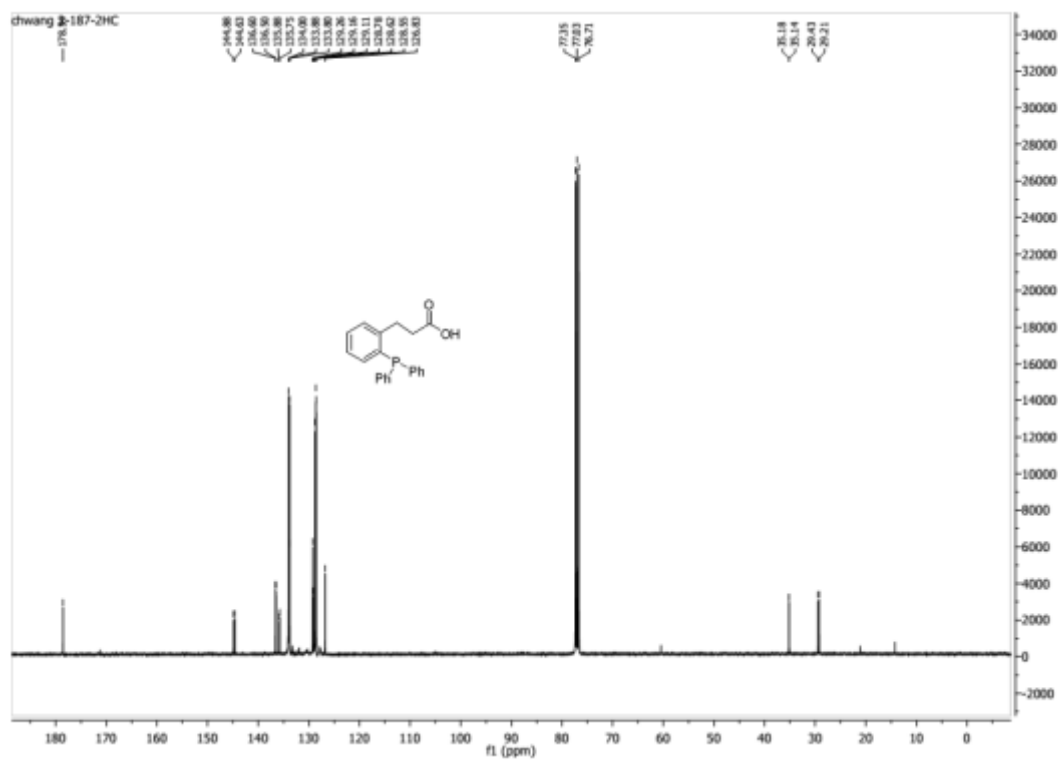
¹H NMR of 3-(2-(diphenylphosphino) phenyl) propanoic acid (6aa)



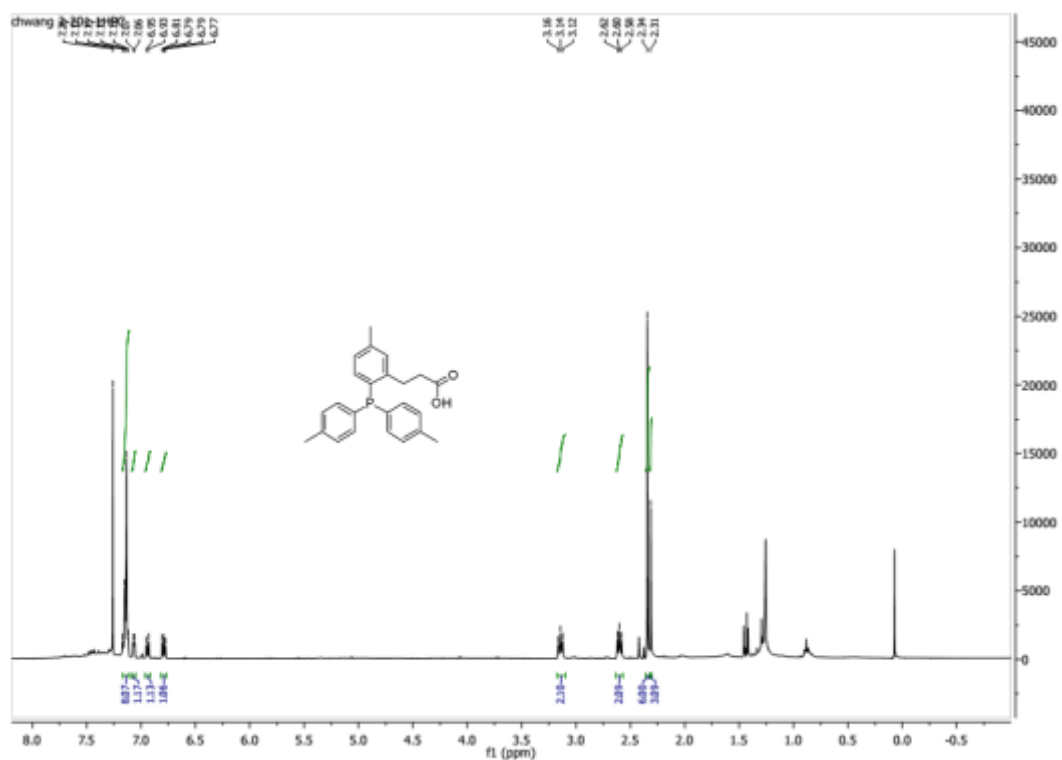
³¹P NMR of 3-(2-(diphenylphosphino)phenyl)propanoic acid (6aa)



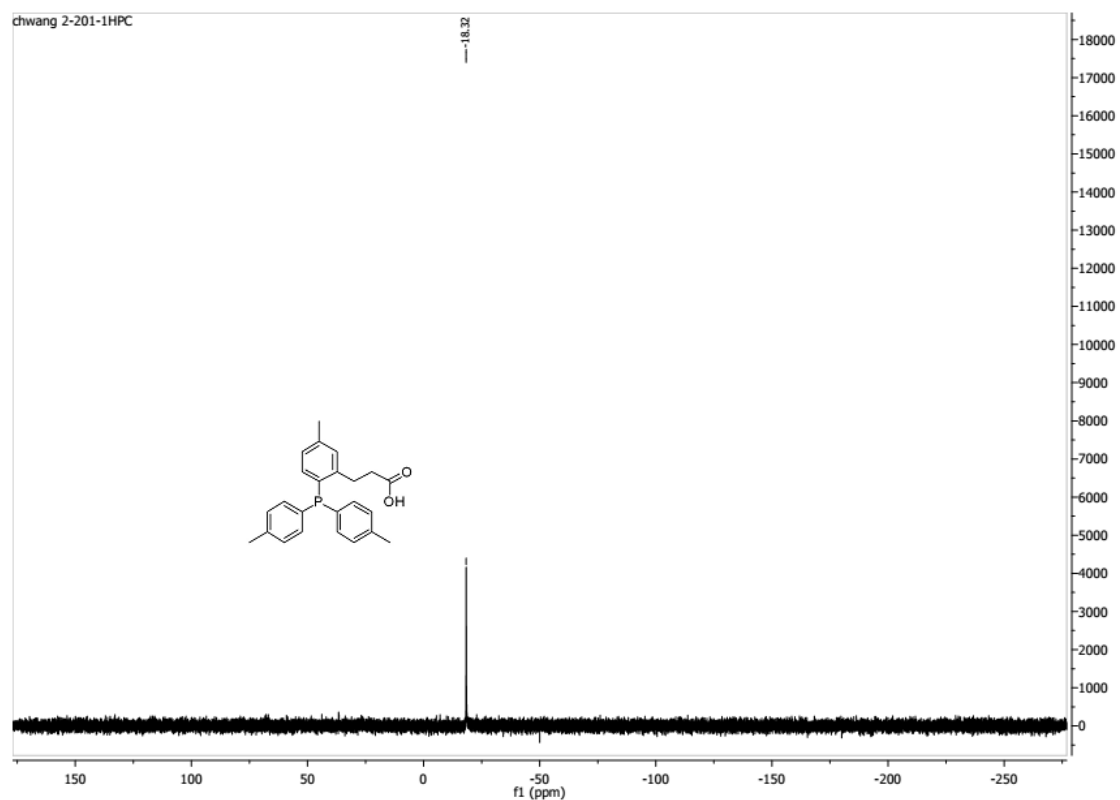
¹³C NMR of 3-(2-(diphenylphosphino) phenyl) propanoic acid (6aa)



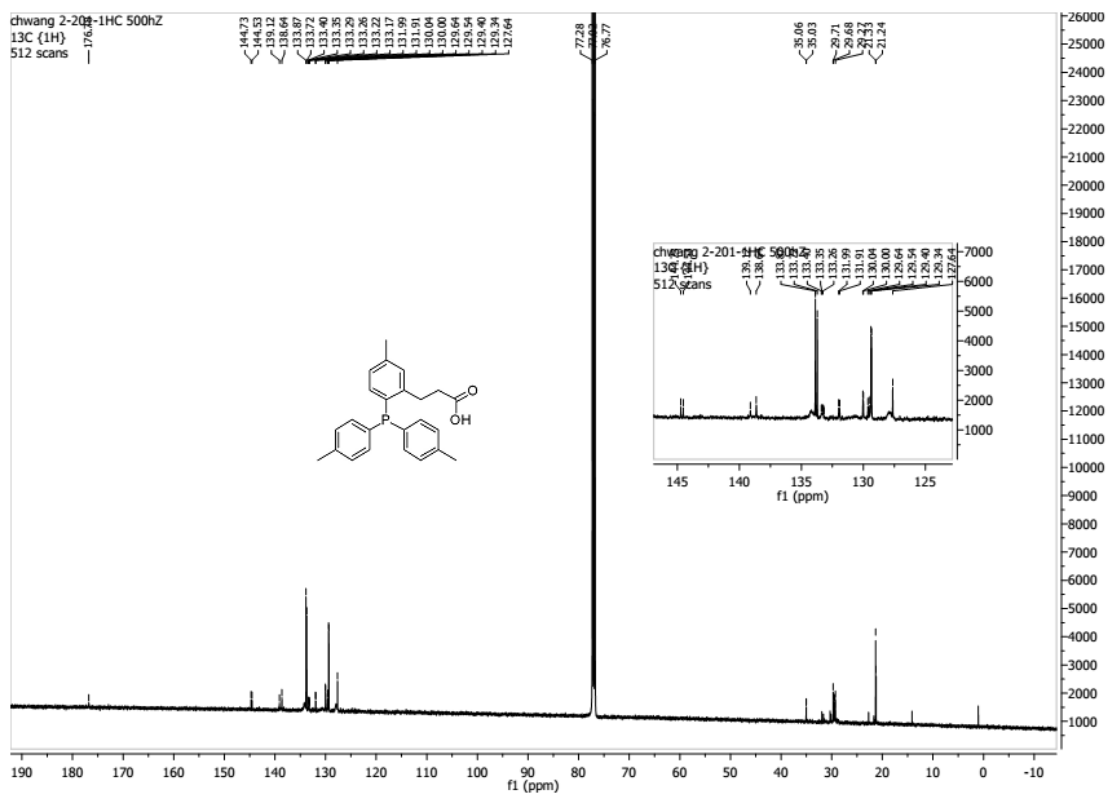
¹H NMR of 3-(2-(di-p-tolylphosphino)-5-methylphenyl)propanoic acid (6ba)



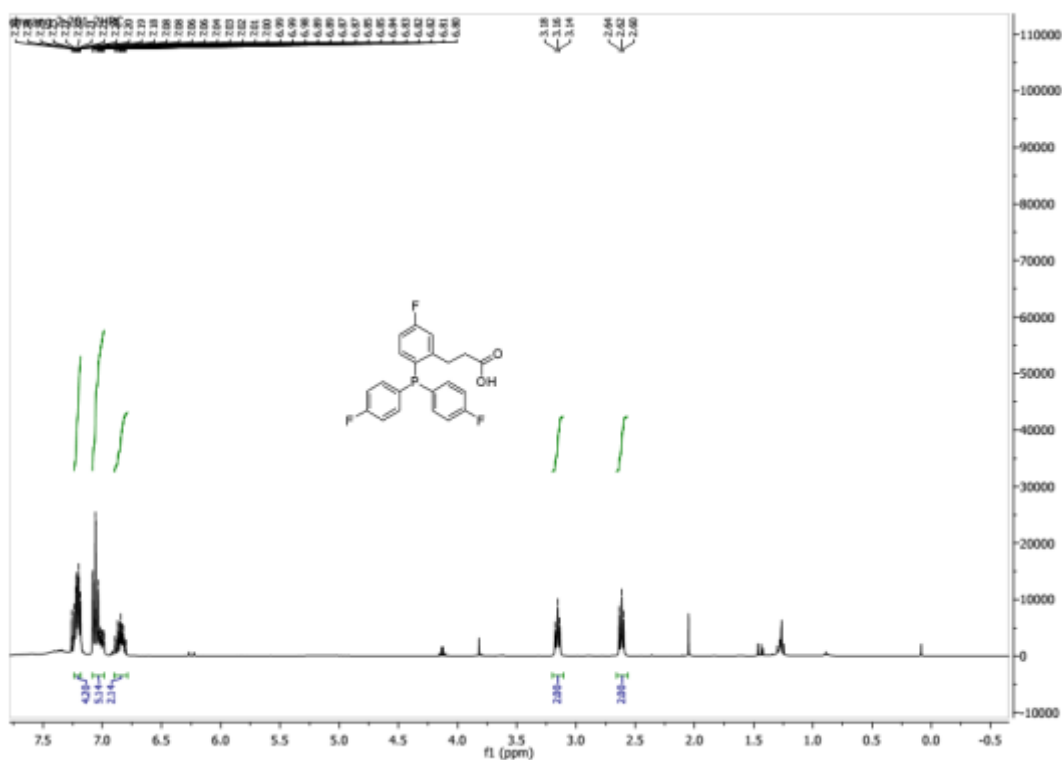
³¹P NMR of 3-(2-(di-p-tolylphosphino)-5-methylphenyl)propanoic acid (6ba)



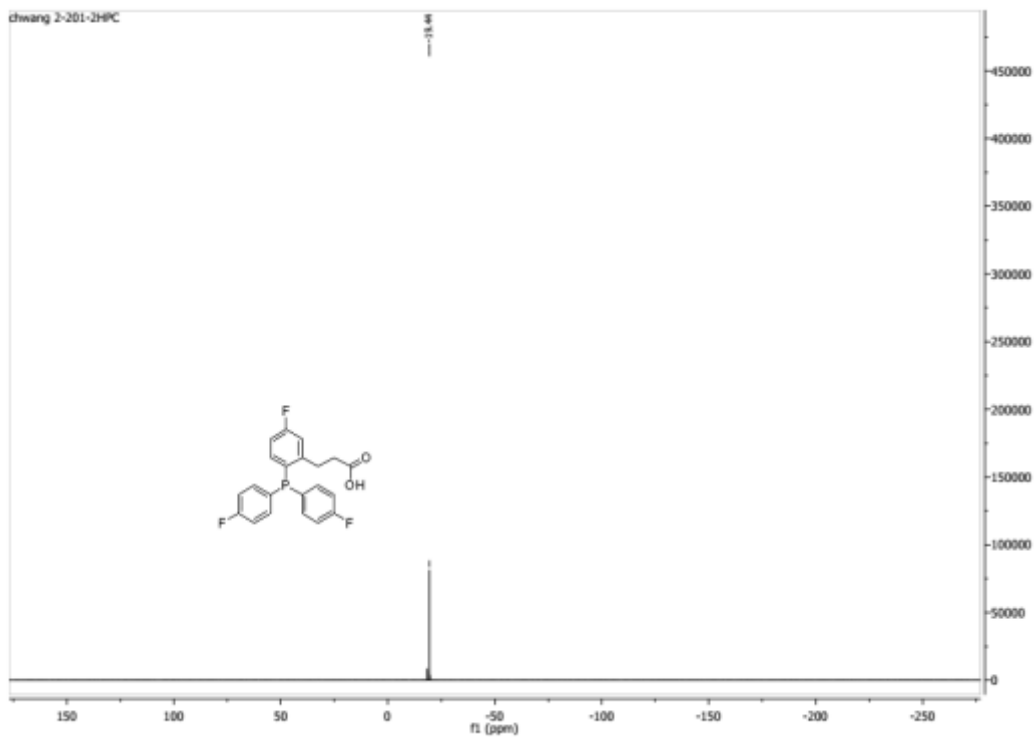
¹³C NMR of 3-(2-(di-p-tolylphosphino)-5-methylphenyl)propanoic acid (6ba)



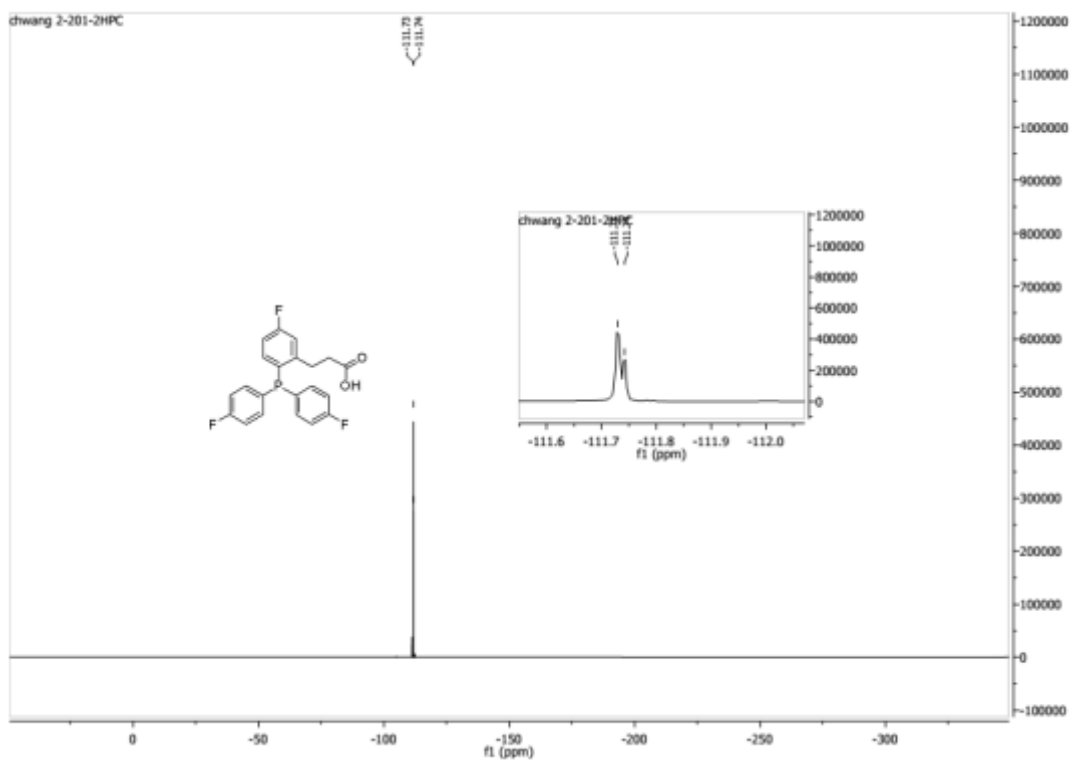
^1H NMR of 3-(2-(bis(4-fluorophenyl)phosphino)-5-fluorophenyl)propanoic acid (6ca)



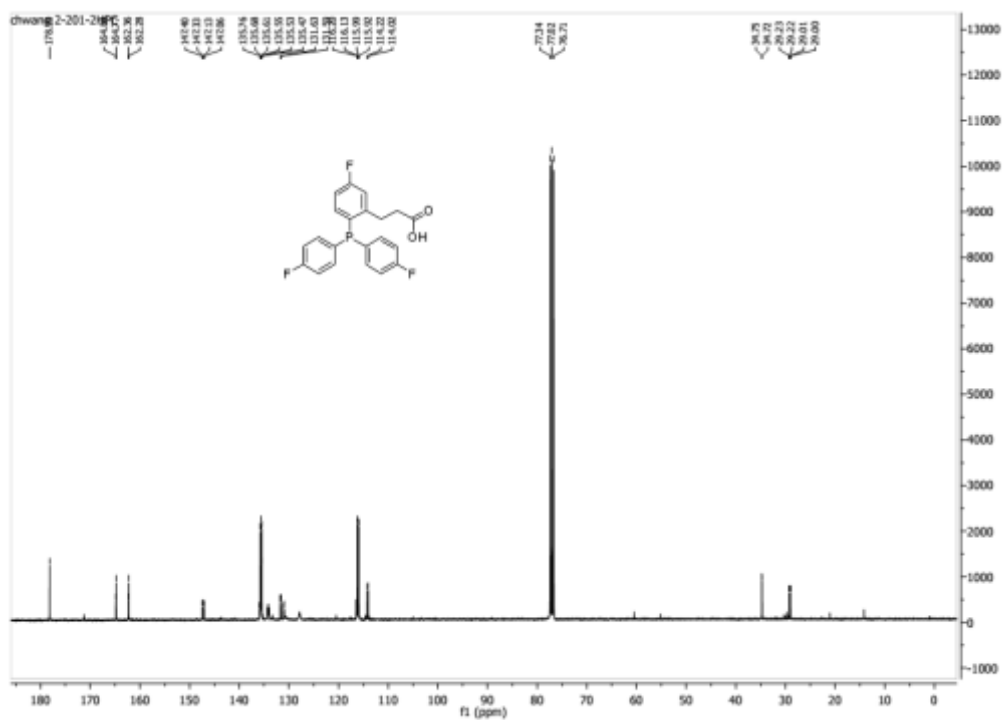
^{31}P NMR of
3-(2-(bis(4-fluorophenyl)phosphino)-5-fluorophenyl)propanoic acid (6ca)



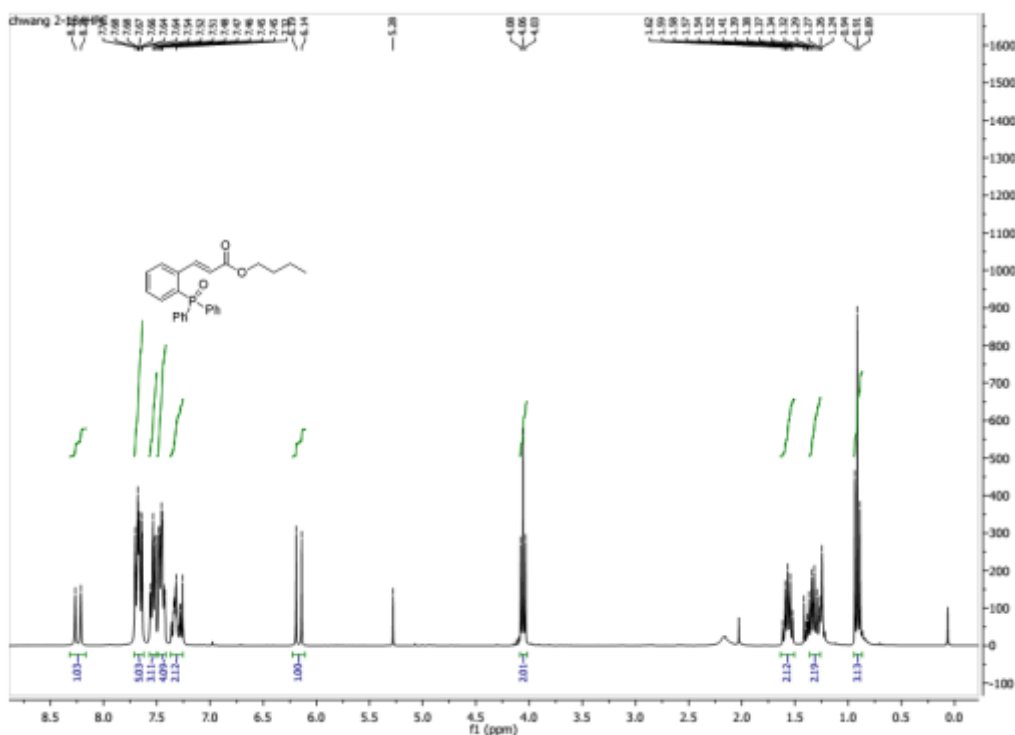
**^{19}F NMR of
3-(2-(bis(4-fluorophenyl)phosphino)-5-fluorophenyl)propanoic acid (6ca)**



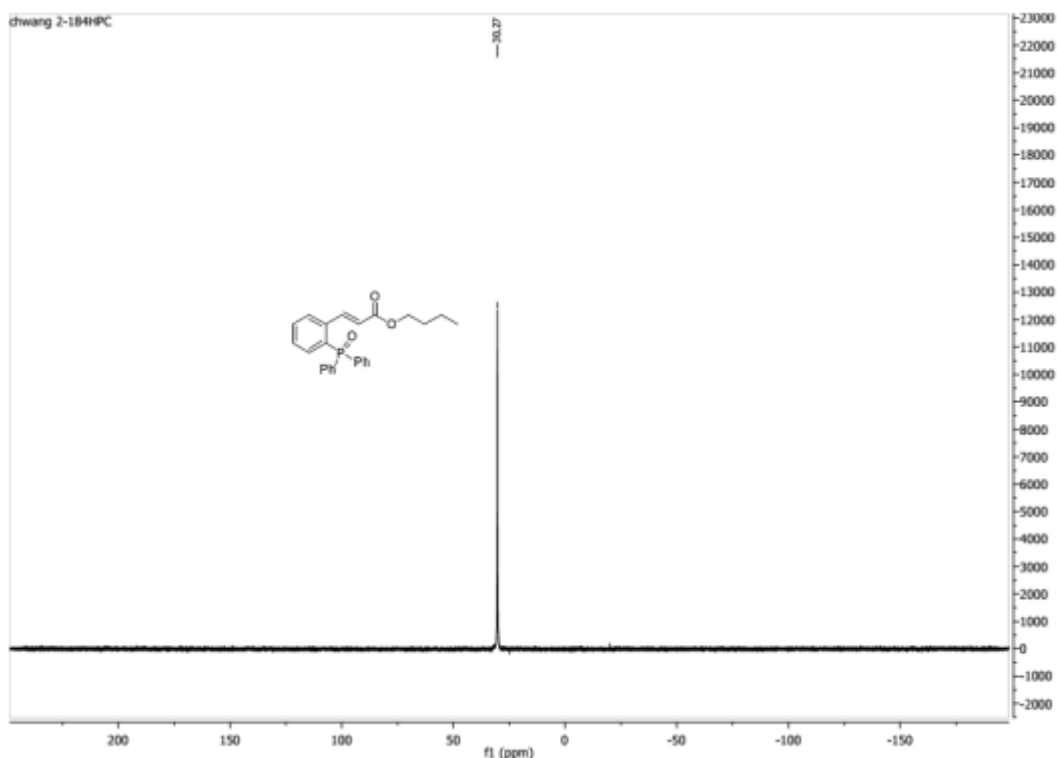
**^{13}C NMR of
3-(2-(bis(4-fluorophenyl)phosphino)-5-fluorophenyl)propanoic acid (6ca)**



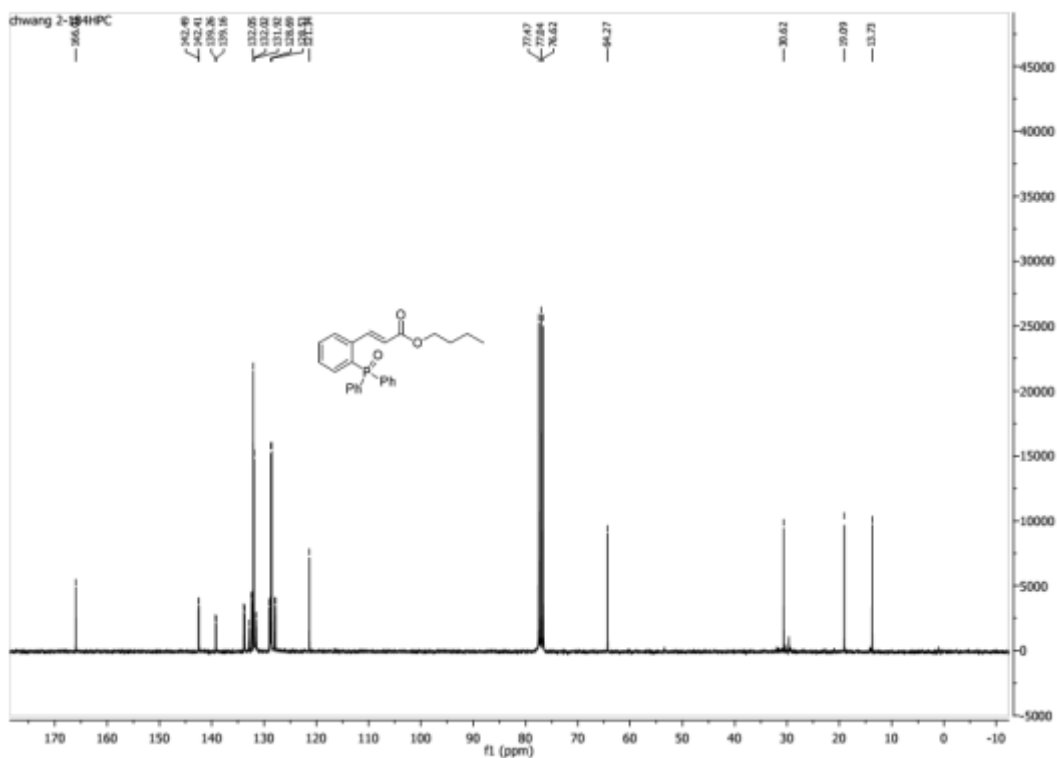
¹H NMR of Butyl 3-(2-(diphenylphosphoryl) phenyl) acrylate (4aa).



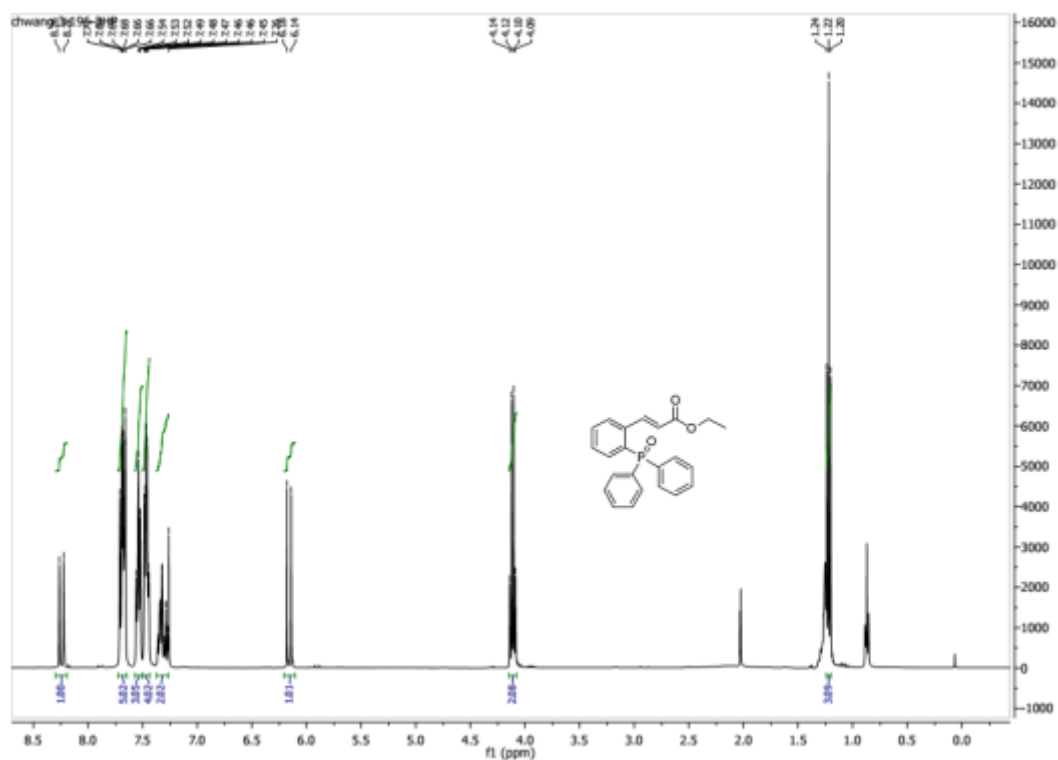
³¹P NMR of Butyl 3-(2-(diphenylphosphoryl)phenyl) acrylate (4aa).



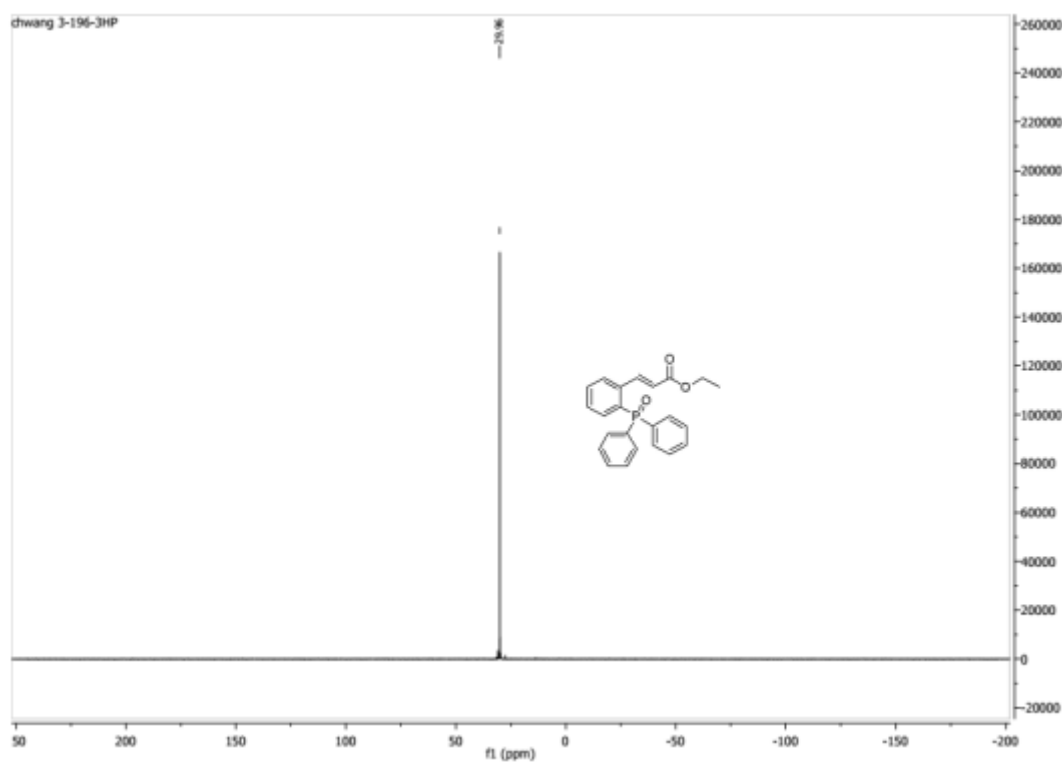
¹³C NMR of Butyl 3-(2-(diphenylphosphoryl) phenyl) acrylate (4aa).



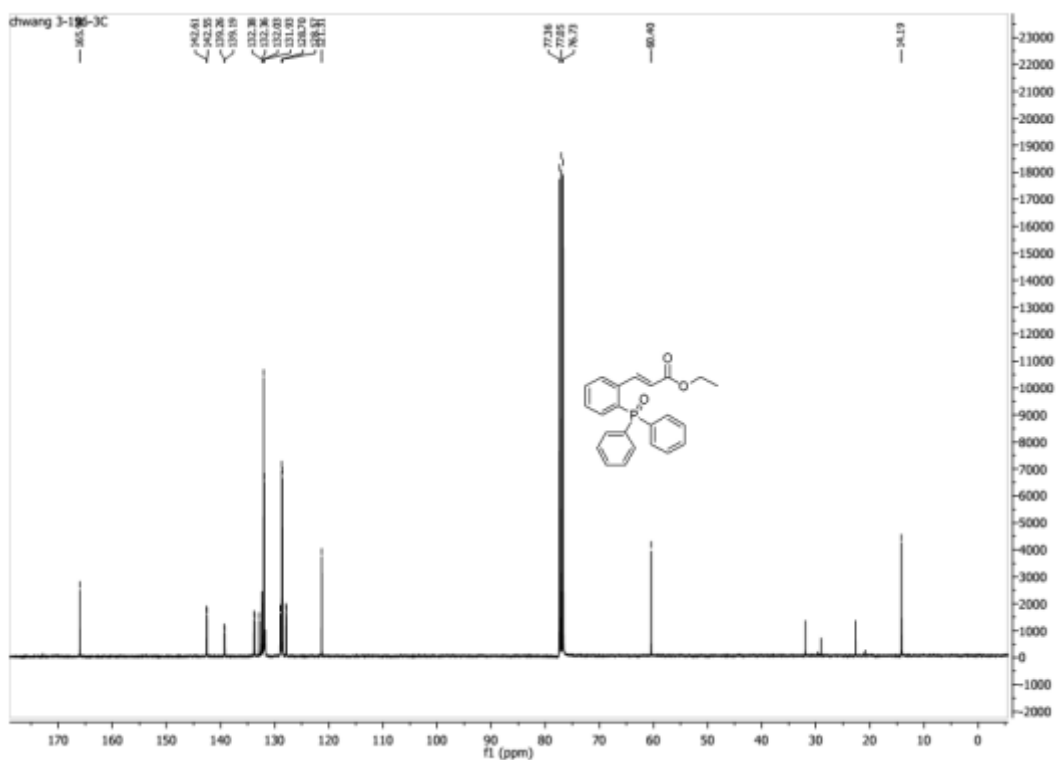
¹H NMR of (E)-Ethyl 3-(2-(diphenylphosphoryl)phenyl)acrylate (4ae)



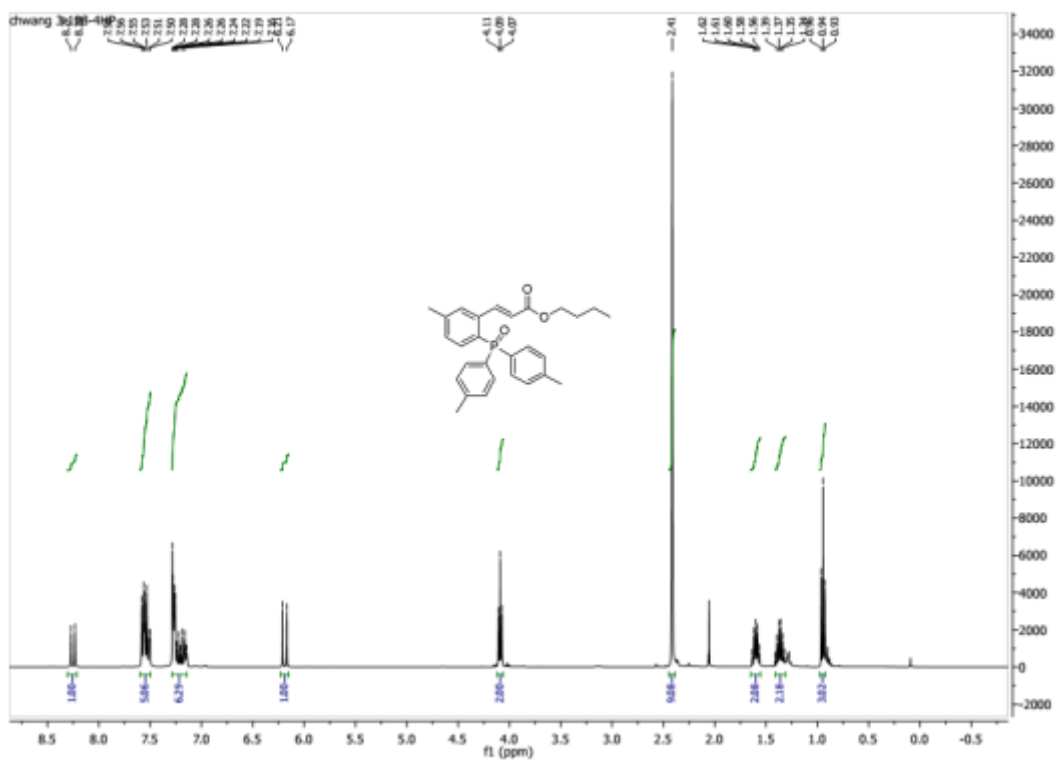
³¹P NMR of (E)-Ethyl 3-(2-(diphenylphosphoryl)phenyl)acrylate (4ae)



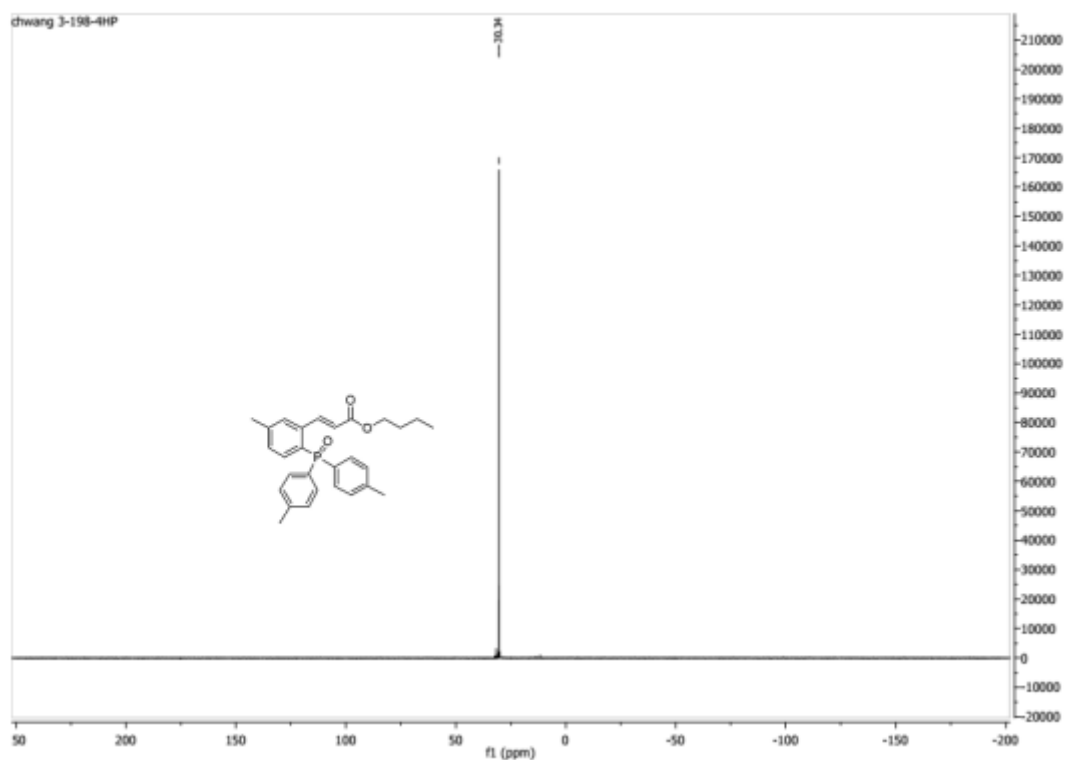
¹³C NMR of (E)-Ethyl 3-(2-(diphenylphosphoryl)phenyl)acrylate (4ae)



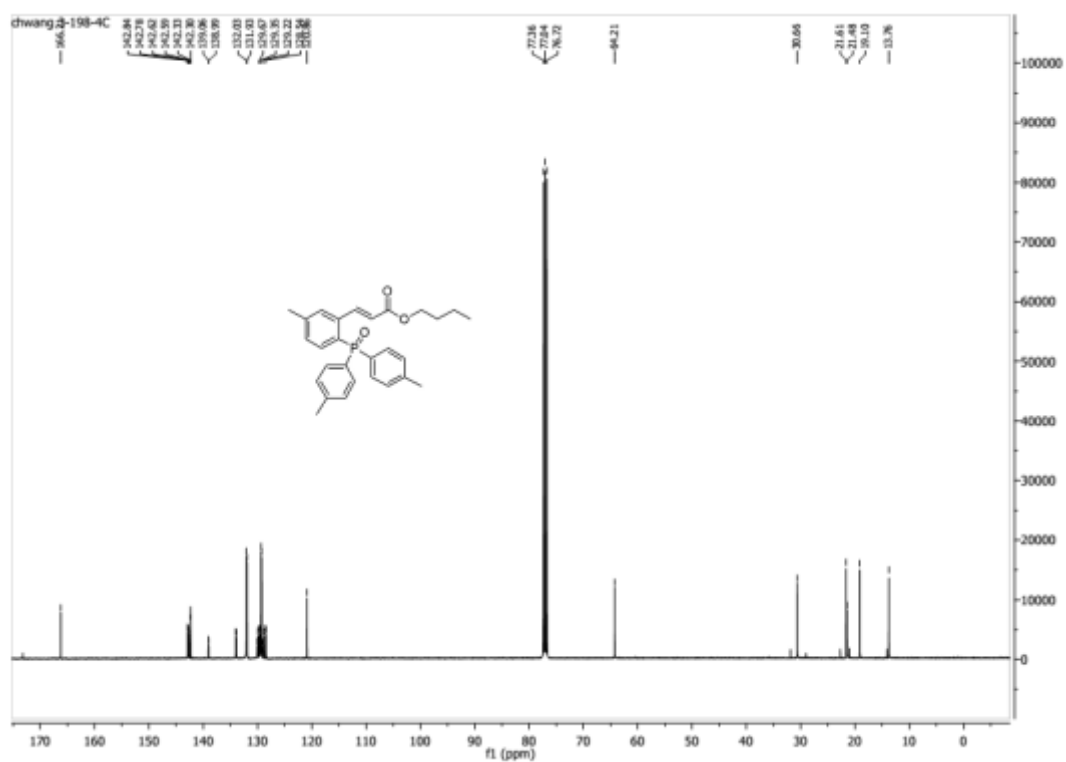
¹H NMR of (E)-Butyl 3-(2-(di-p-tolylphosphoryl)-5-methylphenyl)acrylate (4ba)



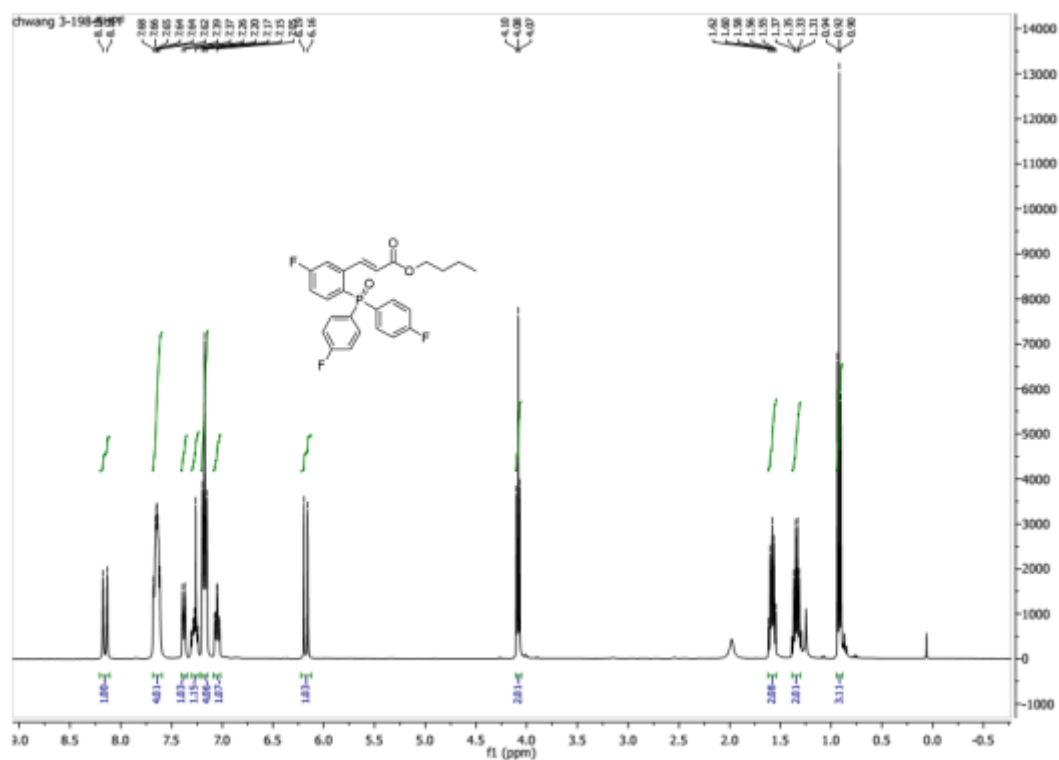
³¹P NMR of (E)-Butyl 3-(2-(di-p-tolylphosphoryl)-5-methylphenyl)acrylate (4ba)



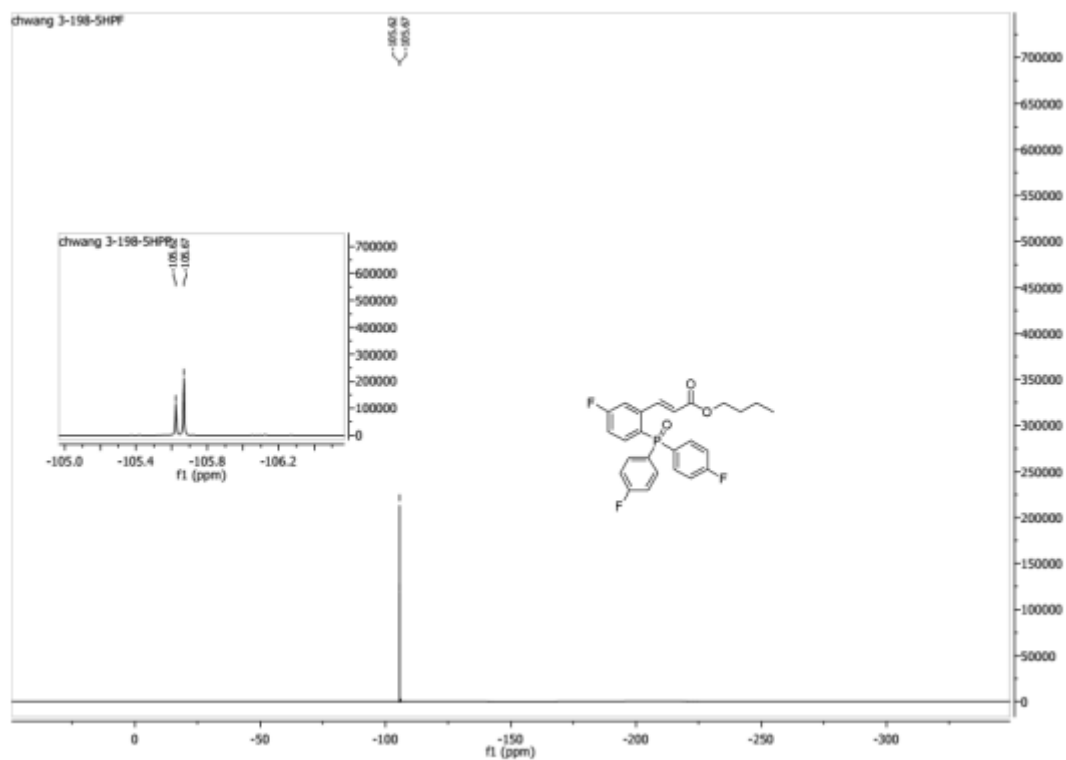
¹³C NMR of (E)-Butyl 3-(2-(di-p-tolylphosphoryl)-5-methylphenyl)acrylate (4ba)



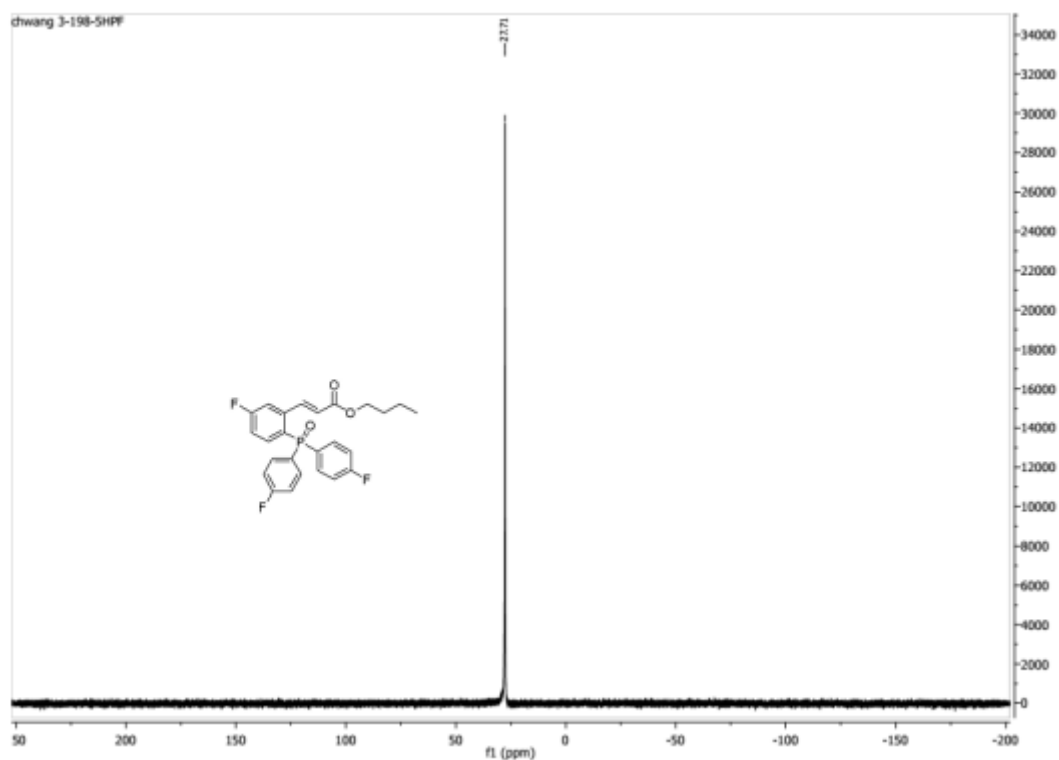
¹H NMR of (E)-butyl 3-(2-(bis(4-fluorophenyl)phosphoryl)-5-fluorophenyl)acrylate (4da)



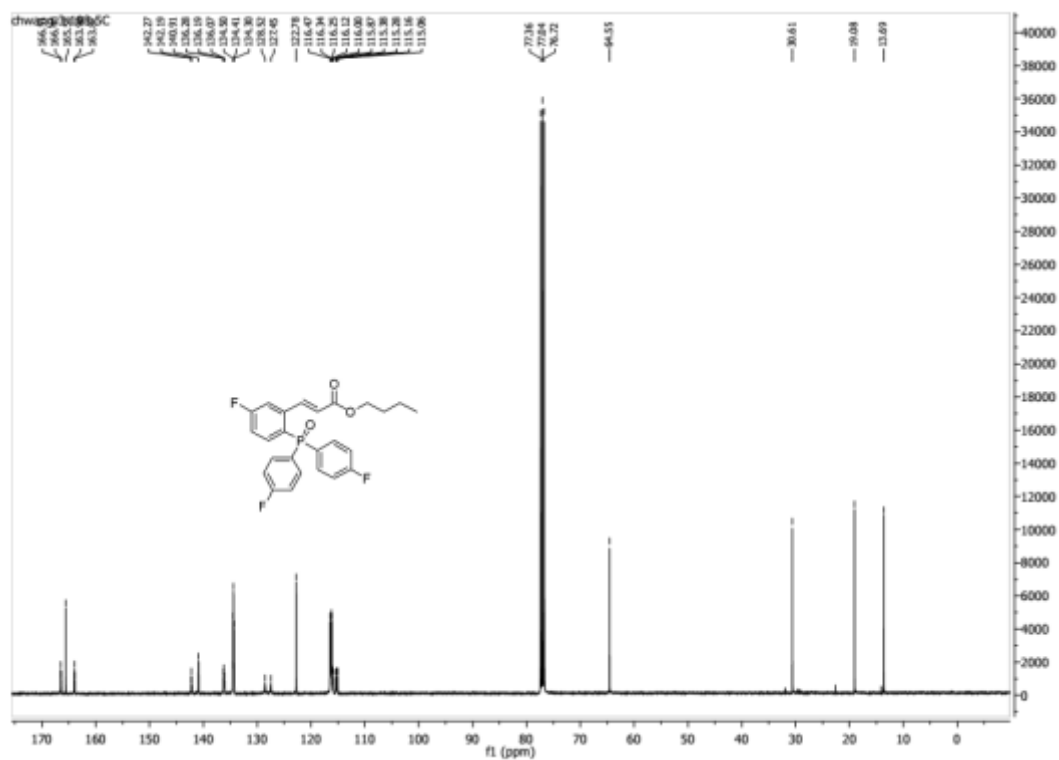
¹H NMR of (E)-butyl 3-(2-(bis(4-fluorophenyl)phosphoryl)-5-fluorophenyl)acrylate (4da)



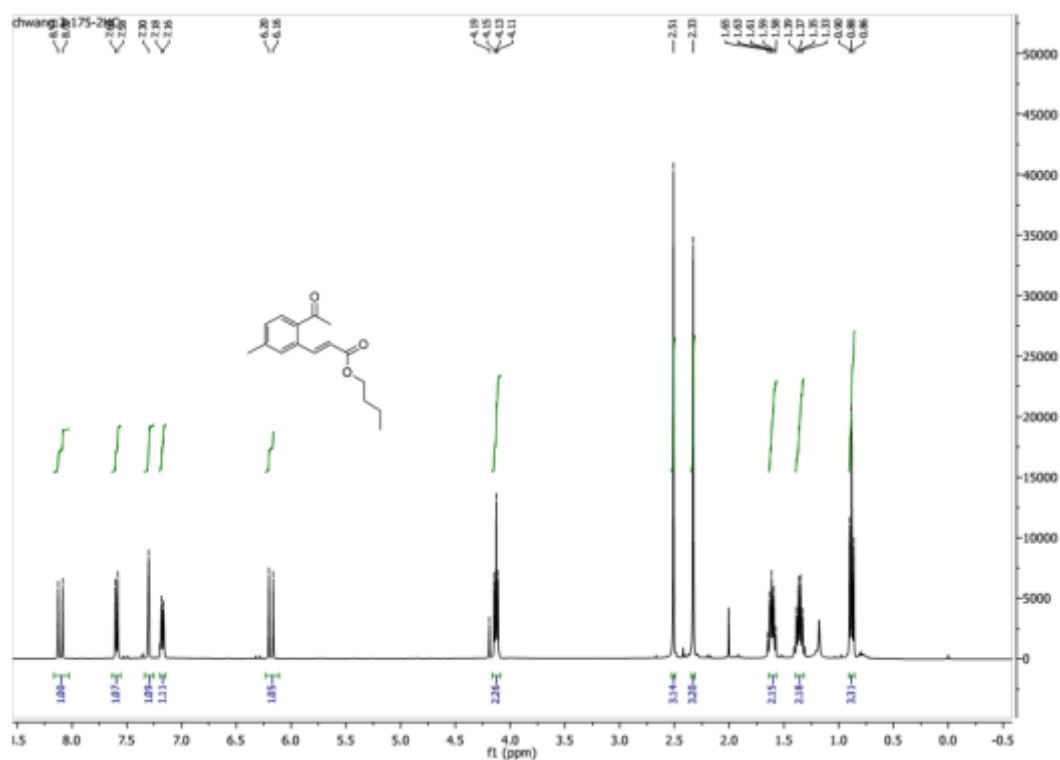
³¹P NMR of (E)-butyl 3-(2-(bis(4-fluorophenyl)phosphoryl)-5-fluorophenyl)acrylate (4da)



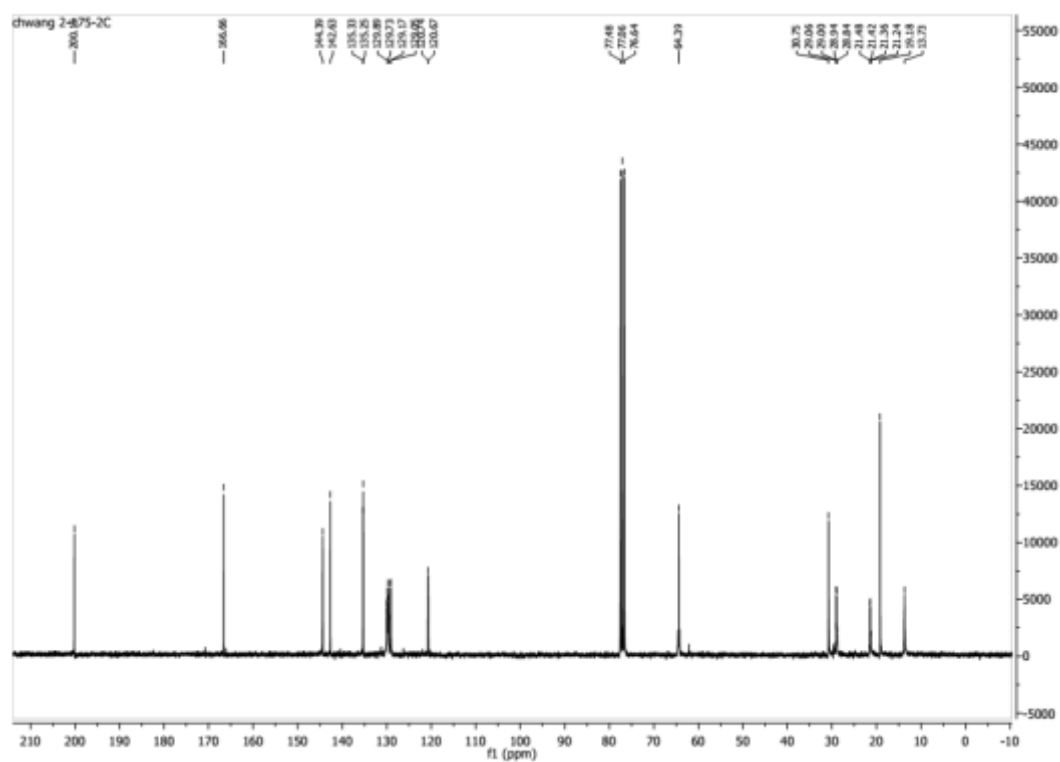
^{13}C NMR of (E)-butyl 3-(2-(bis(4-fluorophenyl)phosphoryl)-5-fluorophenyl)acrylate (4da)



¹H NMR of Butyl 3-(2-acetyl-5-methylphenyl)acrylate (8aa)



¹³C NMR of Butyl 3-(2-acetyl-5-methylphenyl)acrylate (8aa)



7. References

- [1] M. A. Bennett, T. N. Huang, T. W. Matheson, A. K. Smith, S. Ittel, W. Nickerson, in *Inorg. Synth.*, John Wiley & Sons, Inc., **2007**, pp. 74-78.
- [2] R. Berrino, S. Cacchi, G. Fabrizi, A. Goggiamani, P. Stabile, *Org. Biomol. Chem.* **2010**, *8*, 4518-4520.
- [3] F. Däbritz, A. Jäger, I. Bauer, *Eur. J. Org. Chem.* **2008**, *2008*, 5571-5576.
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