Supporting Information

Manganese(III)-mediated Selective Phosphorylation of Direct Synthesis of *β*-Phosphoryl Enamides

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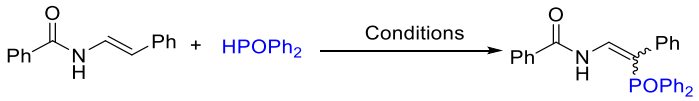
1. General Methods

^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (101 or 75 MHz) spectra were determined with $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard or 85% H_3PO_4 as external standard for ^{31}P NMR (162 MHz). Chemical shifts were reported in ppm from internal TMS (δ), all coupling constants (J values) were reported in Hertz (Hz). High resolution mass spectra were recorded on a TOF machine (ESI). Column chromatography was performed with 300-400 mesh silica gel using flash column techniques. All of the reagents were used directly as obtained commercially unless otherwise noted.

2. Optimization of the reaction conditions

Table S1. Phosphorus-centered radical initiating system screening results[a]

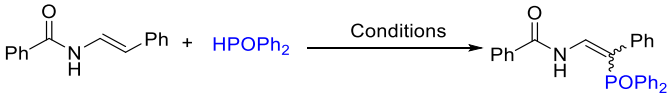


1a **2a** **3a**

Entry	Additive (equiv)	Solvent	T (°C)	Time (h)	Yield (%)[b] (*E*:*Z*)[c]
1	$Mn(OAc)_3{\cdot}2H_2O$ (2.5)	CH_3CN	80	6	40 (55:45)
2	$Mn(OAc)_3{\cdot}2H_2O$ (3)	CH_3CN	80	6	39 (53:47)
3	$Cu(OAc)_2$ (0.25), $K_2S_2O_8$ (3)	CH_3CN	80	6	30 (34:66)
4	$AgNO_3$ (0.05), $K_2S_2O_8$ (3)	CH_3CN	80	6	23 (22:78)
5	$CuBr_2$ (0.1), TBHP (3)	CH_3CN	80	6	15 (45:55)
6	$CuBr_2$ (0.1), TBHP (5)	CH_3CN	80	6	20 (45:55)
7	$CuBr_2$ (0.1), TBHP (5)	CH_3CN	80	12	24 (46:54)
8	$Mn(OAc)_2{\cdot}2H_2O$ (0.1), MnO_2 (3)	CH_3CN	80	6	20 (28:72)
9	$Mn(OAc)_2{\cdot}2H_2O$ (0.1), MnO_2 (3)	HOAc	70	6	25 (32:68)

[a] *Reaction conditions:* **1a** (1.0 mmol), **2a** (2.0 mmol), additive in solvent (10 mL), in air. [b] Yield of isolated products. [c] Ratio of *E*:*Z* determined by isolated yield.

Table S2. Optimization of reaction conditions[a]

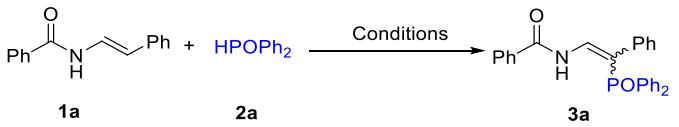


1a **2a** **3a**

Entry	Solvent	Temp (°C)	Time (h)	Yield (%)[b] (*E*:*Z*)[c]
1	CH_3CN	80	6	40 (55:45)
2	CH_3CN	60	6	41 (55:45)
3	CH_3CN	60	0.5	45 (56:44)
4	CH_3OH	80	6	35 (60:40)
5	CH_3OH	60	6	39 (60:40)
6	CH_3OH	60	0.5	53 (66:34)
7	HAc	80	6	13 (0:100)
8	HAc	60	6	25 (0:100)
9	HAc	60	0.5	21 (0:100)
10	NMP	80	6	25 (65:35)
11	NMP	60	12	35 (60:40)
12	NMP	60	0.5	45 (62:38)

[a] *Reaction conditions:* **1a** (1.0 mmol), **2a** (2.0 mmol), $Mn(OAc)_3.2H_2O$ (2.5 equiv), solvent (10 mL), in air. [b] Yield of isolated products. [c] Ratio of *E:Z* determined by isolated yield.

Table S3. Base screening results[a]

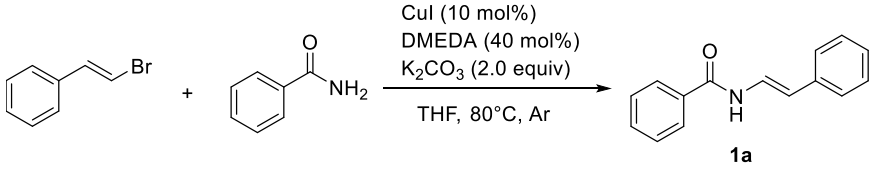


1a **2a** **3a**

Entry	Additive (equiv)	Temp (°C)	Yield (%)[b] (*E:Z*)[c]
1	$Mn(OAc)_3{\cdot}2H_2O$ (2.5)	60	53 (66:34)
2	$Mn(OAc)_3{\cdot}2H_2O$ (2.5), K_2CO_3 (2)	60	62 (64:36)
3	$Mn(OAc)_3{\cdot}2H_2O$ (2.5), K_2HPO_3 (2)	60	54 (63:37)
4	$Mn(OAc)_3{\cdot}2H_2O$ (2.5), DMEDA (2)	60	35 (66:34)
5	$Mn(OAc)_3{\cdot}2H_2O$ (2.5), *t*-BuOK (2)	60	50 (70:30)
6	$Mn(OAc)_3{\cdot}2H_2O$ (2.5), K_2CO_3 (2)	40	68 (67:33)
7	$Mn(OAc)_3{\cdot}2H_2O$ (2.5), K_2CO_3 (2)	rt	77 (71:29)
8	$Mn(OAc)_3{\cdot}2H_2O$ (1.5), K_2CO_3 (2)	rt	15 (67:33)
9	$Mn(OAc)_3{\cdot}2H_2O$ (3.5), K_2CO_3 (2)	rt	73 (73:27)
10	$Mn(OAc)_3{\cdot}2H_2O$ (2.5), K_2CO_3 (2)	rt	20[d] (69:31)
11	$Mn(OAc)_3{\cdot}2H_2O$ (2.5), K_2CO_3 (2)	rt	71[e](70:30)
12	$Mn(OAc)_3{\cdot}2H_2O$ (2.5), K_2CO_3 (3)	rt	70 (73:27)

[a] *Reaction conditions:* **1a** (1.0 mmol), **2a** (2.0 mmol), $Mn(OAc)_3.2H_2O$, MeOH (10 mL) stirring for 0.5 h under air. [b] Yield of isolated products. [c] Ratio of *E:Z* determined by isolated yield. [d] 1.0 equiv of **2a** was used. [e] 3.0 equiv of **2a** was used.

3. Typical procedure for the synthesis of (*E*)-N-styrylbenzamide (1a)



1a

An oven-dried 25 mL resealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with (*E*)-(2-bromovinyl)benzene (900 mg, 4.92 mmol, 1.0 equiv), benzamide (714 mg, 5.90 mmol, 1.2 equiv), CuI (93.7 mg, 0.492 mmol, 10 mol %), and K_2CO_3 (1.36 g, 9.84 mmol, 2.0 equiv). The tube was then evacuated and backfilled with argon (this sequence was repeated a total of three times). N,N′-dimethylethylenediamine (DMEDA) (212 μL, 1.97 mmol, 40 mol %) were added into the tube followed by anhydrous THF (10.0 mL) via syringe. The sealed tube was placed in a preheated oil bath (80 ℃). After stirring at the same temperature for 18 h, the reaction mixture was allowed to cool to room temperature. The reaction mixture was then extracted with ethyl acetate (EtOAc) (20 mL) and deionized water (100 mL) in a separation funnel. The aqueous fraction was further extracted with EtOAc (10 mL × 2). The combined organic fractions were then dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on

silica gel (EtOAc/*n*-Hexane = 1:7, then 1:4) to afford the desired product **1a**. Other enamides **1** were prepared according to the reported procedures.[1]

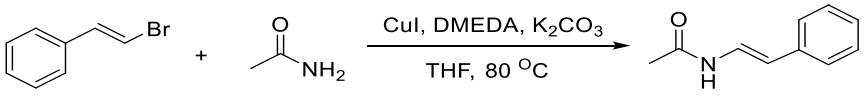
4. Typical procedure for the preparation of N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide (3a-*Z*) and (3a-*E*)

To a solution of CH_3OH (10 mL), (*E*)-N-styrylbenzamide (**1a**) (0.2231 g, 1.0 mmol), K_2CO_3 (0.2758 g, 2.0 mmol) and diphenylphosphine oxide (**2a**) (0.4041 g, 2.0 mmol) was added $Mn(OAc)_3.2H_2O$ (0.6700 g, 2.5 mmol) for three times in 10 minutes in air at room temperature, then the mixture was stirred for 20 minutes under same conditions. After completion of the reaction, the solvent was removed under vacuum. To the residue was added water (20 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic fractions were dried over anhydrous Na_2SO_4, and concentrated under vacuum to yield the crude product, which was purified by column chromatography (silica gel, ethyl acetate/petroleum ether (1:8) and CH_3OH/CH_2Cl_2 (1:100) to give pure (*Z*)-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide (**3a**-*Z*) in 22% yield first, then (*E*)-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide (**3a**-*E*) in 55% yield.

5. Scope of substrates: Preparation and reaction of alkyl enamide and N-alkenyl benzamide such as (*E*)-N-styrylacetamide (I), (*E*)-N-(prop-1-en-1-yl)benzamide (II) and (*Z*)-N- (prop-1-en-1-yl)acetamide (III)

*5.1 Procedure for the synthesis of (E)-N-styrylacetamide (**I**), (E)-N-(prop-1-en-1-yl)benzamide (**II**) and (Z)-N- (prop- 1-en-1-yl)acetamide (**III**)*

*Synthesis of (E)-N-styrylacetamide (**I**)*[1]

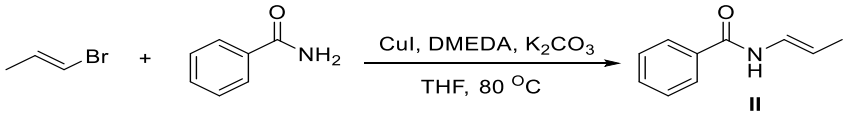


I

An oven-dried 25 mL resealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with (*E*)-(2-bromovinyl)benzene (900 mg, 4.92 mmol, 1.0 equiv), acetamide (348 mg, 5.90 mmol, 1.2 equiv), CuI (93.7 mg, 0.492 mmol, 10 mol %), and K_2CO_3 (1.36 g, 9.84 mmol, 2.0 equiv). The tube was then evacuated and backfilled with argon (this sequence was repeated a total of three times). N,N′-dimethylethylenediamine (DMEDA) (212 μL, 1.97 mmol, 40 mol %) were added into the tube followed by anhydrous THF (10.0 mL) via syringe. The sealed tube was placed in a

preheated oil bath (80 ℃). After stirring at the same temperature for 18 h, the reaction mixture was allowed to cool to room temperature. The reaction mixture was then extracted with ethyl acetate (EtOAc) (20 mL) and deionized water (100 mL) in a separation funnel. The aqueous fraction was further extracted with EtOAc (10 mL × 2). The combined organic fractions were then dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/*n*-Hexane = 1:7, then 1:4) to afford the desired product **I**. White solid, 55% yield (400 mg), m.p 116–119 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56–7.48 (m, 1H), 7.35–7.23 (m, 5H), 7.19–7.14 (m, 1H), 6.11 (d, J = 14.6 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.14, 136.10, 128.70, 126.68, 125.58, 122.76, 112.93, 23.28.

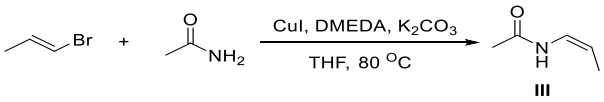
*Synthesis of (E)-N-(prop-1-en-1-yl)benzamide (**II**)*[1]



II

(*E*)-N-(prop-1-en-1-yl)benzamide (**II**) was prepared as the synthetic procedure of compound **I.** Compound **II**, white solid, 58% yield (460 mg), m.p 111–113 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88–7.73 (m, 2H), 7.64 (s, 1H), 7.54–7.49 (m, 1H), 7.47–7.41 (m, 2H), 7.01–6.93 (m, 1H), 5.36–5.27 (m, 1H), 1.77–1.71 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.35, 133.87, 131.75, 128.63, 127.05, 123.65, 108.96, 14.99.

*Synthesis of (Z)-N-(prop-1-en-1-yl)acetamide (**III**)*[1]

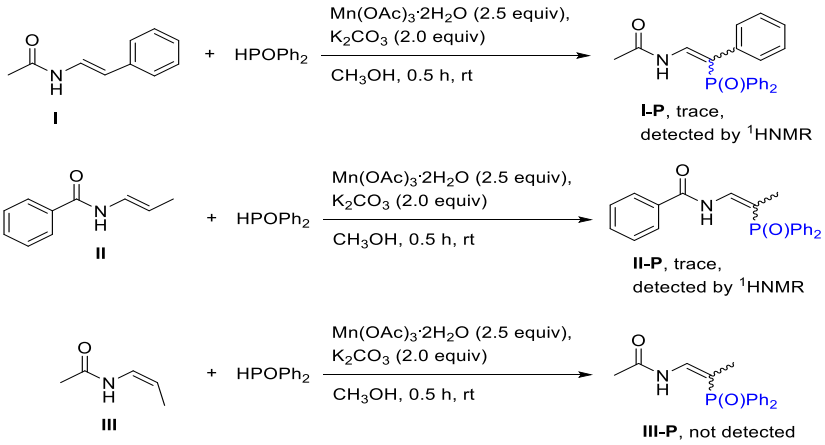


III

(Z)-N-(prop-1-en-1-yl)acetamide (**III**) was prepared as the synthetic procedure of compound **I.** Compound **III**, white solid, 41% yield (200 mg), m.p 68–70^0C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.09 (s, 1H), 6.73–6.65 (m, 1H), 4.82–4.72 (m, 1H), 2.07 (s, 3H), 1.62–1.58 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.90, 121.91, 105.48, 23.10, 10.90.

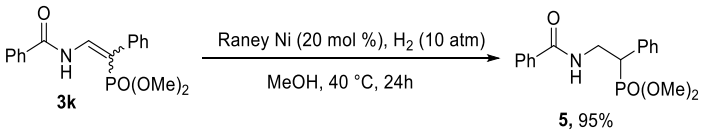
*5.2 Reaction of (E)-N-styrylacetamide (**I**), (E)-N-(prop-1-en-1-yl)benzamide (**II**) and (Z)-N-(prop-1-en-1-yl)acetamide (**III**) with diphenyl phosphine oxide (**2a**)*

The reactions of **I** and **II** with diphenyl phosphine oxide (**2a**) under the standard reaction conditions gave the trace of amount of the desired products **I-P** and **II-P**, respectively, which could be detected with ^1H NMR. No desired product **III-P** was detected for the reaction of **III** with diphenyl phosphine oxide (Scheme S1)



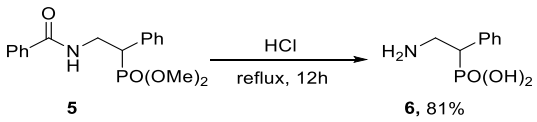
Scheme S1. The reaction of (E)-N-styrylacetamide (**I**), (E)-N-(prop-1-en-1-yl)benzamide (**II**) and (Z)-N-(prop-1-en-1-yl)acetamide (**III**) with diphenyl phosphine oxide (**2a**)

6. Typical procedure for the synthesis of dimethyl (2-benzamido-1-phenylethyl)phosphonate (5)



A solution of dimethyl (2-benzamido-1-phenylvinyl)phosphonate (**3k**, 3.3 g, 10 mmol) in 200 mL of MeOH was hydrogenated over Raney-Ni (660 mg, 20 mol %) at 40 °C at a pressure of 10 atm for 24 h. After removal of the catalyst by filtration, the solvent was evaporated to give dimethyl (2-benzamido-1-phenylethyl)phosphonate (**5**) (3.1g, 95% yield).

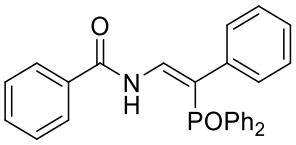
7. Typical procedure for the synthesis of *β*-amino-1-phenylethyl phosphonic acid (6)



A mixture of the dimethyl (2-benzamido-1-phenylethyl)phosphonate (**5**) (0.133 g, 0.4 mmol) and 8 M hydrochloric acid (20 mL) was refluxed for 12 h. The reaction mixture was then cooled to room temperature, washed with dichloromethane (20 mL × 3) and concentrated under vacuo. To the residue was added MeOH (10 mL), then the mixture was stirred for a few minutes, filtered to remove the undissolved solid. To the filtrate was added propylene oxide (100 μL), then stirred at 0 ℃ for 30 minutes, filtered to collect formed solid, dried to give *β*-amino-1-phenylethyl phosphonic acid (**6**) (65 mg, 81% yield).

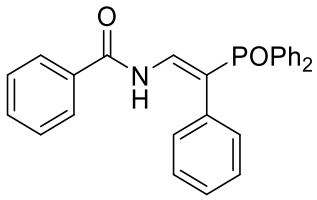
8. Structure characterization of compounds 3-8

***(Z)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)benzamide* (3a-*Z*)**



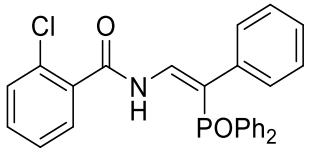
White solid, mp 210–211 °C, 22% yield (93 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.77 (d, J = 10.4 Hz, 1H), 8.14–8.01 (m, 3H), 7.64 (dd, J = 12.1, 7.5 Hz, 4H), 7.55 (t, J = 7.3 Hz, 3H), 7.49 (t, J = 7.4 Hz, 2H), 7.43 (td, J = 7.6, 2.7 Hz, 4H), 7.22–7.16 (m, 1H), 7.13 (t, J = 7.4 Hz, 2H), 6.87 (d, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.96, 141.15 (d, J = 1.0 Hz), 136.10 (d, J = 9.7 Hz), 132.03, 131.86 (d, J = 2.7 Hz), 131.82 (d, J = 66.2 Hz), 131.62 (d, J = 10.1 Hz), 130.45, 129.63 (d, J = 3.9 Hz), 128.34, 128.05 (d, J = 12.3 Hz), 127.81, 127.36, 126.99 (d, J = 1.3 Hz), 109.08 (d, J = 96.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.44. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{27}H_{23}NO_2P$ 424.1466, found 424.1467.

***(E)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)benzamide* (3a-*E*)**



White solid, mp 229–230 °C, 55% yield (232.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 11.2 Hz, 1H), 7.77 (dd, J = 11.0, 7.9 Hz, 4H), 7.70–7.62 (m, 1H), 7.56 (d, J = 7.6 Hz, 2H), 7.53–7.41 (m, 7H), 7.41–7.28 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.46, 133.89 (d, J = 21.9 Hz), 132.41 (d, J = 6.8 Hz), 132.26, 131.86, 131.65 (d, J = 9.6 Hz), 131.47 (d, J = 2.7 Hz), 130.91 (d, J = 105.9 Hz), 129.41 (d, J = 4.1 Hz), 129.01, 128.44, 128.07, 127.94, 126.67, 115.64 (d, J = 106.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.44. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{22}NO_2PNa$ 446.1286, found 446.1272.

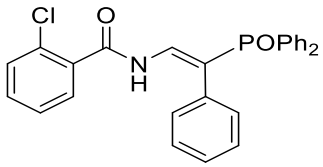
***(Z)-2-Chloro-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide* (3b-*Z*)**



White solid, mp 185–186 °C, 16% yield (73.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.19 (d, J = 10.5 Hz, 1H), 8.00 (dd, J = 30.5, 10.7 Hz, 1H), 7.71 (dd, J = 7.3, 1.2 Hz, 1H), 7.64–7.59 (m, 3H), 7.55 (dd, J = 14.4, 6.9 Hz, 3H), 7.47–7.32 (m, 7H), 7.22–7.17 (m, 1H), 7.13 (t, J = 7.4 Hz, 2H), 6.86 (d, J = 7.9

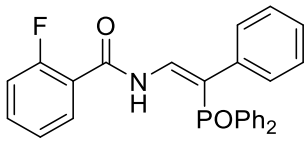
Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.03, 140.08, 135.99 (d, J = 9.5 Hz), 133.63, 131.83 (d, J = 2.8 Hz), 131.60 (d, J = 10.0 Hz), 131.45, 131.40, 130.36, 130.31, 129.60 (d, J = 3.9 Hz), 129.43, 128.01 (d, J = 12.3 Hz), 127.78 (d, J = 0.5 Hz), 127.06 (d, J = 1.4 Hz), 126.63, 110.56 (d, J = 95.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.09. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{21}ClNO_2PNa$ 480.0896, found 480.0908.

(E)-2-Chloro-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide **(3b-*E*)**



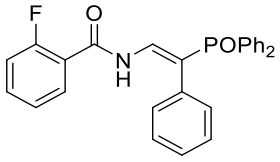
White solid, mp 213–214 °C, 58% yield (265 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, J = 11.4 Hz, 1H), 7.80–7.73 (m, 5H), 7.69 (dd, J = 14.1, 11.5 Hz, 1H), 7.55–7.50 (m, 2H), 7.48–7.43 (m, 4H), 7.38–7.26 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.55, 133.52 (d, J = 22.0 Hz), 132.26, 132.18, 131.72, 131.62, 131.56, 131.48 (d, J = 2.7 Hz), 131.32, 130.24 (d, J = 7.7 Hz), 130.12, 129.72 (d, J = 4.0 Hz), 128.74, 127.99 (d, J = 12.2 Hz), 127.90, 126.97, 116.63 (d, J = 106.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.16. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{27}H_{22}ClNO_2P$ 458.1077, found 458.1075.

(Z)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)-2-fluorobenzamide **(3c-*Z*)**



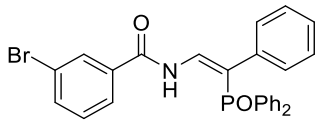
White solid, mp 158–159 °C, 17% yield (74.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.54–12.42 (m, 1H), 8.16–8.01 (m, 2H), 7.63 (dd, J = 12.0, 7.3 Hz, 4H), 7.56–7.49 (m, 3H), 7.41 (td, J = 7.6, 2.7 Hz, 4H), 7.26 (d, J = 14.9 Hz, 1H), 7.22–7.16 (m, 2H), 7.15–7.10 (m, 2H), 6.87 (d, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.18 (d, J = 2.1 Hz), 160.56 (d, J = 253.1 Hz), 140.29, 136.27 (d, J = 9.5 Hz), 133.63 (d, J = 9.0 Hz), 131.74, 131.65 (d, J = 10.1 Hz), 131.33 (d, J = 1.6 Hz), 130.55, 129.65 (d, J = 3.9 Hz), 127.95 (d, J = 12.3 Hz), 127.76, 126.99 (d, J = 1.3 Hz), 124.13 (d, J = 3.5 Hz), 120.33 (d, J = 11.3 Hz), 116.16 (d, J = 23.3 Hz), 110.72 (d, J = 95.8 H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.95. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{27}H_{22}FNO_2P$ 442.1372, found 442.1374.

(E)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)-2-fluorobenzamide **(3c-*E*)**



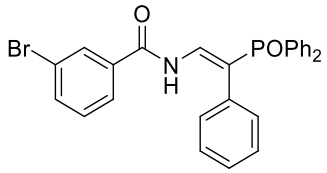
White solid, mp 232–233 °C, 67% yield (295.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81–8.67 (m, 1H), 8.05 (t, J = 7.4 Hz, 1H), 7.77 (dd, J = 11.5, 7.6 Hz, 4H), 7.73–7.64 (m, 1H), 7.55–7.42 (m, 7H), 7.38–7.32 (m, 2H), 7.32–7.26 (m, 3H), 7.21 (dd, J = 17.7, 7.3 Hz, 1H), 7.01 (dd, J = 12.1, 8.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.23 (d, J = 248.6 Hz), 160.07 (d, J = 3.3 Hz), 134.21 (d, J = 9.5 Hz), 133.76 (d, J = 22.1 Hz), 132.36 (d, J = 6.7 Hz), 131.90, 131.67 (d, J = 9.7 Hz), 131.45 (d, J = 2.8 Hz), 130.43, 129.40 (d, J = 4.1 Hz), 128.80, 127.98 (d, J = 12.2 Hz), 127.86, 124.70 (d, J = 3.1 Hz), 118.73 (d, J = 10.7 Hz), 116.36 (d, J = 106.4 Hz), 115.73 (d, J = 24.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.36. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{21}FNO_2PNa$ 464.1192, found 464.1192.

(Z)-3-Bromo-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide **(3d-*Z*)**



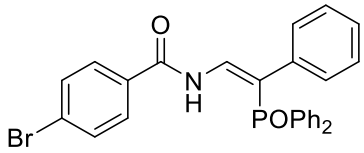
White solid, mp 230–231 °C, 12% yield (60.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.82 (d, J = 10.4 Hz, 1H), 8.23 (s, 1H), 8.03 (dd, J = 30.5, 10.5 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.68 (dd, J = 8.1, 0.9 Hz, 1H), 7.63 (dd, J = 12.2, 7.2 Hz, 4H).7.56 (t, J = 6.9 Hz, 2H), 7.44 (td, J = 7.6, 2.9 Hz, 4H), 7.36 (t, J = 7.9 Hz, 1H), 7.23–7.17 (m, 1H), 7.13 (t, J = 7.5 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.55, 140.78, 135.89 (d, J = 9.6 Hz), 134.96, 134.19, 131.94 (d, J = 2.7 Hz), 131.62 (d, J = 10.1 Hz), 131.28, 130.97, 130.24, 129.84, 129.58 (d, J = 3.9 Hz), 128.08 (d, J = 12.3 Hz), 127.83, 127.10 (d, J = 1.3 Hz), 125.34, 122.67, 109.99 (d, J = 95.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.59. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{21}BrNO_2PNa$ 524.0391, found 524.0395.

(E)-3-Bromo-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide **(3d-*E*)**



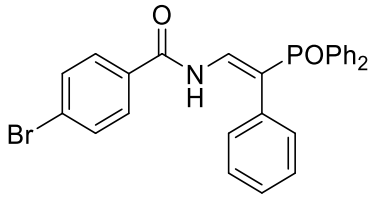
White solid, mp 192–193 °C, 55% yield (275.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 11.3 Hz, 1H), 7.85–7.72 (m, 5H), 7.65 (t, J = 11.5 Hz, 2H), 7.57–7.51 (m, 2H), 7.50–7.44 (m, 4H), 7.39 (dd, J = 13.8, 7.5 Hz, 3H), 7.29 (dt, J = 18.0, 12.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.14, 135.16, 133.87, 133.53 (d, J = 23.2 Hz), 132.22 (d, J = 6.4 Hz), 131.64 (d, J = 9.6 Hz), 131.55 (d, J = 2.0 Hz), 131.27, 130.26, 129.90, 129.37 (d, J = 3.5 Hz), 129.05, 128.09, 127.97, 124.82, 122.70, 116.46 (d, J = 105.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.44. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{21}BrNO_2PNa$ 524.0391, found 524.0378.

***(Z)-4-Bromo-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide* (3e-*Z*)**



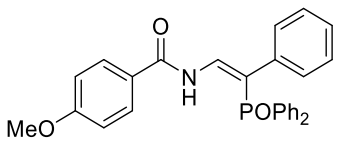
White solid, mp 219–220 °C, 9% yield (45.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.83 (d, J = 10.4 Hz, 1H), 8.03 (dd, J = 30.6, 10.5 Hz, 1H), 7.93 (d, J = 8.5 Hz, 2H), 7.69–7.59 (m, 6H), 7.56 (t, J = 7.0 Hz, 2H), 7.44 (td, J = 7.6, 2.8 Hz, 4H), 7.20 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.5 Hz, 2H), 6.86 (d, J = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.99, 140.89, 135.92 (d, J = 9.6 Hz), 131.94 (d, J = 2.7 Hz), 131.65, 131.57 (d, J = 4.2 Hz), 131.18 (d, J = 26.5 Hz), 130.26, 129.58 (d, J = 3.9 Hz), 128.92, 128.08 (d, J = 12.3 Hz), 127.84, 127.08 (d, J = 1.2 Hz,), 126.98, 109.62 (d, J = 95.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.74. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{21}BrNO_2PNa$ 524.0391, found 524.0389.

***(E)-4-Bromo-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide* (3e-*E*)**



White solid, mp 222–223 °C, 68% yield (340.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 11.4 Hz, 1H), 7.80 (dd, J = 11.9, 7.2 Hz, 4H), 7.68 (dd, J = 13.6, 11.9 Hz, 1H), 7.62–7.54 (m, 4H), 7.54–7.44 (m, 6H), 7.44–7.39 (m, 2H), 7.35 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.58, 137.71, 133.59 (d, J = 21.9 Hz), 132.29 (d, J = 6.8 Hz), 131.74, 131.69, 131.59, 131.53, 131.51, 131.31, 130.71, 130.25, 129.37 (d, J = 4.1 Hz), 129.04, 128.18, 128.08, 127.96, 127.21, 116.23 (d, J = 106.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.31. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{21}BrNO_2PNa$ 524.0391, found 524.0382.

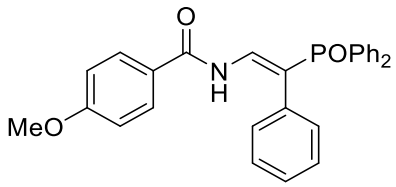
***(Z)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)-4-methoxybenzamide* (3f-*Z*)**



White solid, mp 213–214 °C, 18% yield (81.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.66 (d, J = 10.2 Hz, 1H), 8.13–7.99 (m, 3H), 7.64 (dd, J = 11.7, 7.7 Hz, 4H), 7.54 (t, J = 6.9 Hz, 2H), 7.44 (d, J = 5.1 Hz, 4H), 7.17 (d, J = 7.0 Hz, 1H), 7.12 (t, J = 7.2 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 7.3 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.95, 163.03, 141.91, 136.70 (d, J = 9.8 Hz),

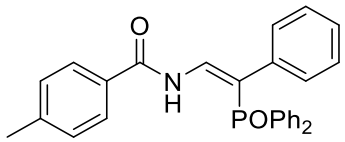
132.28 (d, *J* = 2.7 Hz), 132.09 (d, *J* = 10.1 Hz), 131.59 (d, *J* = 104.9 Hz), 130.12 (d, *J* = 4.0 Hz), 129.86, 128.49 (d, *J* = 12.3 Hz), 128.25, 127.36 (d, *J* = 1.3 Hz), 124.99, 114.02, 108.65 (d, *J* = 96.6 Hz), 55.46. ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.50. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{28}H_{24}NO_3PNa$ 476.1391, found 476.1397.

***(E)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)-4-methoxybenzamide* (3f-*E*)**



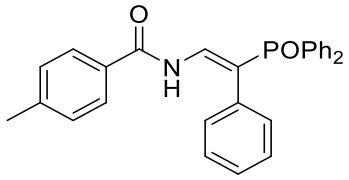
White solid, mp 220–221 °C, 56% yield (253.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 10.6 Hz, 1H), 7.87–7.70 (m, 4H), 7.63 (dd, *J* = 14.3, 11.7 Hz, 1H), 7.51 (dd, *J* = 9.1, 5.0 Hz, 4H), 7.48–7.42 (m, 4H), 7.41–7.27 (m, 5H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.79 (d, *J* = 18.2 Hz), 134.18 (d, *J* = 22.4 Hz), 132.57 (d, *J* = 6.8 Hz), 131.66 (d, *J* = 9.6 Hz), 131.54, 131.42 (d, *J* = 2.7 Hz), 130.49, 129.46 (d, *J* = 4.1 Hz,), 128.98, 128.69, 127.99 (d, *J* = 12.1 Hz), 127.86 (d, *J* = 1.2 Hz), 123.95, 114.83 (d, *J* = 107.7 Hz), 113.68, 55.01. ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.73. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{28}H_{24}NO_3PNa$ 476.1391, found 476.1393.

***(Z)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)-4-methylbenzamide* (3g-*Z*)**



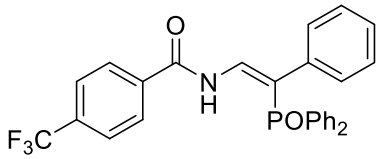
White solid, mp 190–191 °C, 13% yield (56.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.74 (d, *J* = 10.4 Hz, 1H), 8.12 (dd, *J* = 30.7, 10.6 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.69 (dd, *J* = 12.1, 7.5 Hz, 4H), 7.60 (t, *J* = 7.1 Hz, 2H), 7.48 (td, *J* = 7.6, 2.6 Hz, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.27–7.21 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 2H), 6.92 (d, *J* = 7.7 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.93, 141.99 (d, *J* = 139.8 Hz), 136.19 (d, *J* = 9.7 Hz), 131.81 (d, *J* = 2.7 Hz), 131.62 (d, *J* = 10.1 Hz), 131.59, 130.55, 129.64 (d, *J* = 4.0 Hz), 129.35, 129.01, 128.02 (d, *J* = 12.3 Hz,), 127.78, 127.40, 126.92 (d, *J* = 1.1 Hz), 108.63 (d, *J* = 96.4 Hz), 21.14. ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.37. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{28}H_{25}NO_2P$ 438.1623, found 438.1614.

***(E)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)-4-methylbenzamide* (3g-*E*)**



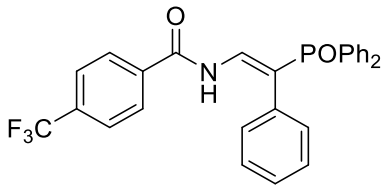
White solid, mp 202–203 °C, 60% yield (262.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 11.5 Hz, 1H), 7.83–7.75 (m, 4H), 7.66 (dd, J = 14.3, 11.6 Hz, 1H), 7.56–7.51 (m, 2H), 7.50–7.43 (m, 6H), 7.41–7.30 (m, 5H), 7.20 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.86, 143.54, 134.51 (d, J = 22.3 Hz), 132.97 (d, J = 6.7 Hz), 132.13 (d, J = 9.6 Hz), 131.92 (d, J = 2.7 Hz), 131.45 (d, J = 105.7 Hz), 129.92 (d, J = 4.1 Hz), 129.59, 129.49, 129.46, 128.47 (d, J = 12.1 Hz), 128.36 (d, J = 1.3 Hz), 127.18, 115.69 (d, J = 107.3 Hz), 21.54. ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.56. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{28}H_{24}NO_2PNa$ 460.1442, found 460.1436.

***(Z)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)-4-(trifluoromethyl)benzamide* (3h-*Z*)**



White solid, mp 175–176 °C, 10% yield (49.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.97 (d, J = 8.9 Hz, 1H), 8.18 (d, J = 7.1 Hz, 2H), 8.04 (dd, J = 30.4, 10.1 Hz, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.68–7.59 (m, 4H), 7.56 (d, J = 6.4 Hz, 2H), 7.45 (s, 4H), 7.20 (d, J = 6.6 Hz, 1H), 7.15 (d, J = 6.8 Hz, 2H), 6.87 (d, J = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.10, 141.11, 136.26 (d, J = 9.5 Hz,), 135.96, 133.95 (q, J = 32.3 Hz), 132.48 (d, J = 2.4 Hz), 132.08 (d, J = 10.1 Hz), 131.65, 130.61, 130.04 (d, J = 3.8 Hz), 128.58 (d, J = 12.3 Hz), 128.31 (d, J = 8.0 Hz), 127.66, 125.83 (q, J = 3.0 Hz), 123.67 (q, J = 278.4 Hz,), 110.85 (d, J = 95.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.79. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{28}H_{22}F_3NO_2P$ 492.1340, found 492.1345.

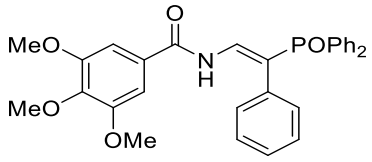
***(E)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)-4-(trifluoromethyl)benzamide* (3h-*E*)**



White solid, mp 199–200 °C, 38% yield (186.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 11.0 Hz, 1H), 7.81–7.73 (m, 4H), 7.72–7.62 (m, 5H), 7.53 (d, J = 7.1 Hz, 2H), 7.50–7.43 (m, 4H), 7.41–7.35 (m, 2H), 7.31 (d, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.28, 135.19, 133.74 (d, J = 33.0 Hz), 133.35 (d, J = 21.7 Hz), 132.18 (d, J = 6.6 Hz,), 131.68, 131.58, 131.55, 130.69 (d, J = 105.9

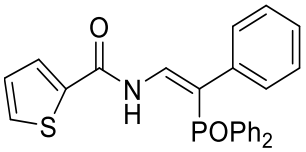
Hz), 129.34 (d, *J* = 4.1 Hz), 129.07, 128.13 (d, *J* = 1.4 Hz), 128.03 (d, *J* = 12.2 Hz), 127.16, 125.50 (q, *J* = 3.6 Hz), 122.87 (q, *J* = 274.7 Hz), 116.93 (d, *J* = 105.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.09. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{28}H_{21}F_3NO_2PNa$ 514.1160, found 514.1164.

***(E)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)-3,4,5-trimethoxybenzamide* (3i)**



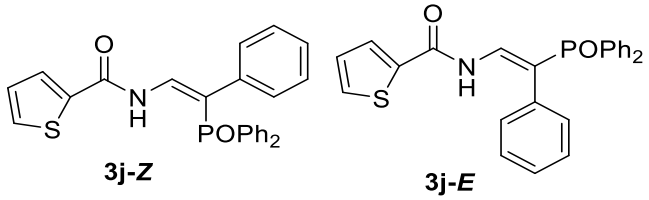
White solid, mp 232–233 °C, 20% yield (102.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 11.5 Hz, 1H), 7.77 (dd, *J* = 11.9, 7.1 Hz, 4H), 7.62 (dd, *J* = 13.9, 11.7 Hz, 1H), 7.52 (dd, *J* = 10.4, 4.2 Hz, 2H), 7.49–7.42 (m, 4H), 7.39–7.29 (m, 5H), 6.76 (s, 2H), 3.85 (s, 3H), 3.77 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.88, 152.79, 141.46, 134.00 (d, *J* = 21.8 Hz), 132.63 (d, *J* =6.8 Hz), 131.63 (d, *J* = 9.7 Hz), 131.50 (d, *J* = 2.7 Hz), 130.85(d, *J* = 105.9 Hz), 129.53 (d, *J* = 4.0 Hz), 128.90, 128.01 (d, *J*= 12.2 Hz,), 127.91 (d, *J* = 1.0 Hz,), 127.00, 115.56 (d, *J* =107.3 Hz), 103.95, 60.44, 55.64. ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.23. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{30}H_{29}NO_5P$ 514.1783, found 514.1769.

***(Z)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)thiophene-2-carboxamide* (3j-*Z*)**



White solid, mp 185–186 °C, 16% yield (68.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.70 (d, *J* = 10.6 Hz, 1H), 7.98 (dd, *J* = 30.5, 10.6 Hz, 1H), 7.82 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.67–7.60 (m, 4H), 7.59–7.52 (m, 3H), 7.47–7.40 (m, 4H), 7.21–7.16 (m, 1H), 7.15–7.09 (m, 3H), 6.86 (dd, *J* = 7.0, 1.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.80, 140.62 (d, *J* = 1.2 Hz), 137.76, 136.02 (d, *J* = 9.6 Hz), 131.86 (d, *J* = 2.7 Hz), 131.65, 131.55, 130.97 (d, *J* = 105.1 Hz), 129.61 (d, *J* = 3.9 Hz), 129.37, 128.04 (d, *J* = 12.3 Hz), 127.81, 127.57, 127.00 (d, *J* = 1.3 Hz), 108.81 (d, *J* = 95.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.40. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{25}H_{20}SNO_2PNa$ 452.0850, found 452.0844.

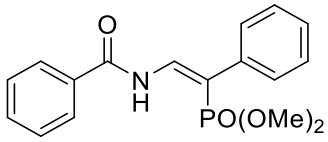
***Mixture of (Z)-N-(2-(diphenylphosphoryl)-2-phenylvinyl)thiophene-2-carboxamide* (3j-*Z*) *and (E)-N-(2-(diphenylphosphoryl)-2-phenylvinyl)thiophene-2-carboxamide* (3j-*E*)**



3j-*Z* **3j-*E***

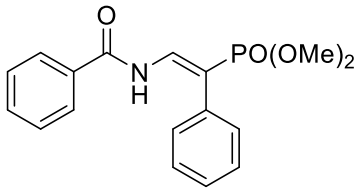
White solid, 65% yield (278.9 mg), **3j-*E* : 3j-*Z*** = 22 : 3, analyzed by ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 11.4 Hz, 1H), 7.81–7.71 (m, 4H), 7.62–7.49 (m, 5H), 7.45 (t, J = 7.0 Hz, 4H), 7.39–7.30 (m, 4H), 7.25–7.21 (m, 1H), 7.07–6.98 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.44, 136.89, 133.96 (d, J = 22.3 Hz), 132.80 (d, J = 6.7 Hz), 132.30, 132.12 (d, J = 9.7 Hz), 131.98 (d, J = 2.6 Hz), 131.82, 130.77, 129.91 (d, J = 4.1 Hz), 129.48, 129.34, 128.50 (d, J =12.1 Hz), 128.04, 115.87 (d, J = 106.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.41, 28.54. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{25}H_{20}SNO_2PNa$ 452.0850, found 452.0844.

***Dimethyl (Z)-(2-benzamido-1-phenylvinyl)phosphonate* (3k-*Z*)**



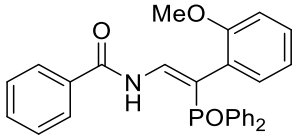
White solid, mp 100–101 °C, 17% yield (56.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.85 (d, J = 11.0 Hz, 1H), 8.17 (dd, J = 43.5, 11.1 Hz, 1H), 8.05–8.00 (m, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.44–7.40 (m, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.32–7.27 (m, 1H), 3.76 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.84, 135.34 (d, J = 7.9 Hz), 132.27, 131.84, 128.42, 128.22, 127.34 (d, J = 5.2 Hz), 127.23, 127.00 (d, J = 0.9 Hz), 105.11, 103.35, 52.09, 52.04. ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.89. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{17}H_{19}NO_4$ 332.1052, found 332.1063.

***Dimethyl (E)-(2-benzamido-1-phenylvinyl)phosphonate* (3k-*E*)**



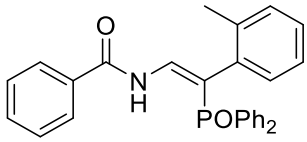
White solid, mp 116–117 °C, 54% yield (178.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20–8.05 (m, 2H),, 7.64–7.60 (m, 2H), 7.52 (dd, J = 15.0, 7.5 Hz, 3H), 7.45–7.37 (m, 5H), 3.78 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.49, 134.76 (d, J = 22.3 Hz), 132.33, 131.89 (d, J = 8.8 Hz), 129.16 (d, J = 1.1 Hz), 128.70 (d, J = 5.1 Hz), 128.46, 128.11 (d, J = 1.9 Hz), 128.01, 126.74, 108.98 (d, J = 197.5 Hz), 52.30, 52.24. ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.01. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{17}H_{18}NO_4PNa$ 354.0871, found 354.0869.

***(Z)-N-(2-(Diphenylphosphoryl)-2-(2-methoxyphenyl)vinyl)benzamide* (4a)**



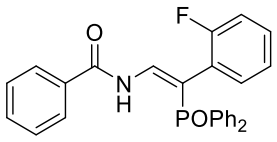
White solid, mp 190–191 °C, 18% yield (81.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.42 (d, J = 10.0 Hz, 1H), 8.05 (d, J = 7.7 Hz, 2H), 7.96 (dd, J = 31.2, 10.6 Hz, 1H), 7.60 (dd, J = 11.6, 8.0 Hz, 4H), 7.48 (dd, J = 15.8, 8.5 Hz, 5H), 7.39 (d, J = 7.0 Hz, 4H), 7.18 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 6.8 Hz, 1H), 6.75 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 8.1 Hz, 1H), 3.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.32, 157.89 (d, J = 3.3 Hz), 141.38, 132.69, 132.38, 132.27 (d, J = 15.8 Hz), 131.95, 131.87, 131.85, 131.15, 129.44 (d, J = 1.8 Hz), 128.44 (d, J = 63.9 Hz), 127.90 (d, J = 20.2 Hz), 124.45 (d, J = 8.5 Hz), 119.99 (d, J = 1.1 Hz), 110.28 (d, J = 1.0 Hz), 106.52 (d, J = 98.2 Hz), 54.43. ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.00. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{28}H_{24}NO_3PNa$ 476.1391, found 476.1385.

(Z)-N-(2-(Diphenylphosphoryl)-2-(o-tolyl)vinyl)benzamide **(4b)**



White solid, mp 146–147 °C, 11% yield (48.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.65 (d, J = 10.5 Hz, 1H), 8.09 (dd, J = 5.3, 3.3 Hz, 2H), 7.90 (dd, J = 31.7, 10.5 Hz, 1H), 7.57–7.47 (m, 9H), 7.42–7.36 (m, 4H), 7.13 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 7.7 Hz, 1H), 1.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.89, 140.57, 138.80 (d, J = 4.2 Hz), 133.97 (d, J = 8.5 Hz), 132.18, 132.00, 131.76 (d, J = 2.7 Hz), 131.48, 131.38, 130.75 (d, J = 2.9 Hz), 129.89, 128.34, 127.89 (d, J = 12.1 Hz), 127.56 (d, J = 1.9 Hz), 127.35, 124.83 (d, J = 1.5 Hz), 108.04 (d, J = 95.0 Hz), 19.21. ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.23. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{28}H_{24}NO_2PNa$ 460.1442, found 460.1435.

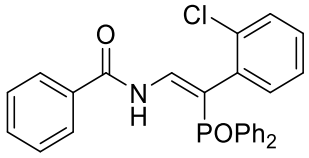
(Z)-N-(2-(Diphenylphosphoryl)-2-(2-fluorophenyl)vinyl)benzamide **(4c)**



White solid, mp 174–175 °C, 17% yield (74.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.68 (d, J = 10.4 Hz, 1H), 8.18–8.02 (m, 3H), 7.69 (dd, J = 12.1, 7.5 Hz, 4H), 7.60 (dd, J = 8.8, 4.5 Hz, 3H), 7.54 (t, J = 7.4 Hz, 2H), 7.51–7.44 (m, 4H), 7.23 (dd, J = 13.2, 7.0 Hz, 1H), 6.93 (dd, J = 15.3, 7.8 Hz, 2H), 6.78 (t, J = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.9, 160.25 (dd, J = 247.0, 4.3 Hz), 142.39, 132.40 (t, J = 2.0 Hz), 132.12, 131.99, 131.88 (d, J = 2.7 Hz), 131.50 (d, J = 10.1 Hz), 130.44 (d, J = 105.5 Hz), 129.25 (dd, J = 8.1, 1.6 Hz), 128.18 (d, J = 33.6 Hz), 127.64 (d, J = 50.9 Hz), 123.22 (d, J = 9.6

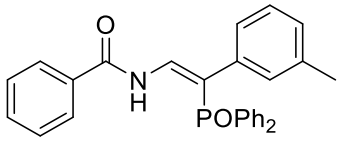
Hz), 123.08 (dd, *J* = 3.9, 1.2 Hz), 123.02, 115.31 (d, *J* = 22.8 Hz), 102.21 (d, *J* = 98.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.56. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{27}H_{22}FNO_2P$ 442.1372, found 442.1374.

(Z)-N-(2-(2-Chlorophenyl)-2-(diphenylphosphoryl)vinyl)benzamide **(4d)**



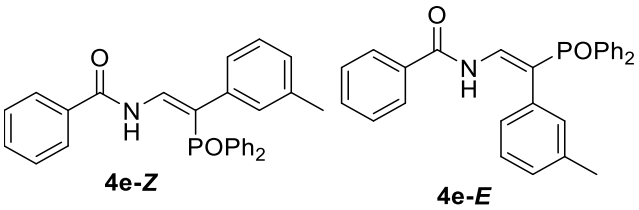
White solid, mp 180–181 °C, 15% yield (75.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.63 (d, *J* = 10.5 Hz, 1H), 8.13–8.06 (m, 2H), 7.99 (dd, *J* = 30.7, 10.6 Hz, 1H), 7.59 (dd, *J* = 6.6, 5.6 Hz, 3H), 7.53 (dd, *J* = 11.0, 4.2 Hz, 4H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.40 (td, *J* = 7.7, 3.0 Hz, 4H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.40, 142.70, 136.56 (d, *J* = 4.5 Hz), 134.10 (d, *J* = 9.1 Hz), 132.66 (d, *J* = 2.9 Hz), 132.61, 132.47, 132.37 (d, *J* = 2.7 Hz), 131.95 (d, *J* = 10.0 Hz), 130.59 (d, *J* = 105.3 Hz), 129.85, 129.26(d, *J* = 1.7 Hz), 128.84, 128.44 (d, *J* = 12.3 Hz), 127.88, 126.21(d, *J* = 1.3 Hz), 106.51 (d, *J* = 98.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.70. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{21}ClNO_2PNa$ 480.0896, found 480.0893.

(Z)-N-(2-(Diphenylphosphoryl)-2-(m-tolyl)vinyl)benzamide **(4e-*Z*)**



White solid, mp 226–227 °C, 25% yield (109.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.76 (d, *J* = 10.5 Hz, 1H), 8.12–8.00 (m, 3H), 7.64 (dd, *J* = 12.1, 7.2 Hz, 4H), 7.55 (t, *J* = 7.3 Hz, 3H), 7.50 (d, *J* = 7.7 Hz, 2H), 7.44 (td, *J* = 7.7, 2.9 Hz, 4H), 7.05–6.95 (m, 2H), 6.67 (d, *J* = 6.2 Hz, 1H), 6.64 (s, 1H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.95, 140.96 (d, *J* = 1.2 Hz), 137.41, 135.92 (d, *J* = 9.6 Hz), 132.18, 131.99, 131.81 (d, *J* = 2.7 Hz), 131.65 (d, *J* = 10.1 Hz), 131.12 (d, *J* = 104.9 Hz), 130.51 (d, *J* = 4.2 Hz), 128.32, 127.98 (d, *J* = 12.3 Hz), 127.66 (d, *J* = 1.5 Hz), 127.57, 127.34, 126.56 (d, *J* = 3.8 Hz), 109.18 (d, *J* = 96.0 Hz), 20.77. ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.37. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{28}H_{24}NO_2PNa$ 460.1442, found 460.1429.

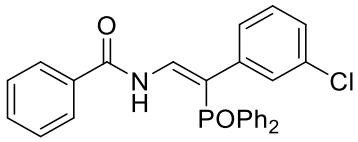
Mixture of (E)-N-(2-(diphenylphosphoryl)-2-(m-tolyl)vinyl) benzamide **(4e-*E*)** ***and (Z)-N-(2-(diphenylphosphoryl)-2-(m-tolyl)vinyl) benzamide*** **(4e-*Z*)**



4e-*Z* **4e-*E***

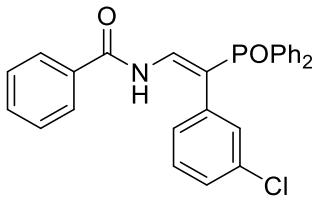
White solid, 60% yield (262.2 mg), **4e-*E* : 4e-*Z*** = 19 : 1, analyzed by ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.3 Hz, 1H), 7.78 (s, 4H), 7.58–7.48 (m, 6H), 7.45 (s, 4H), 7.41–7.36 (m, 2H), 7.24 (s, 1H), 7.12 (d, J = 17.2 Hz, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.43, 138.83, 132.26, 131.99, 131.79 (d, J = 19.3 Hz), 131.79, 131.60, 131.52, 130.25, 128.79, 128.44, 128.06, 127.95 (d, J = 3.2 Hz), 127.88 (d, J = 62.2 Hz), 127.83 (d, J = 98.9 Hz), 126.70, 126.28, 21.00. ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.40, 28.68. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{28}H_{25}NO_2P$ 438.1623, found 438.1608.

***(Z)-N-(2-(3-Chlorophenyl)-2-(diphenylphosphoryl)vinyl)benzamide* (4f-*Z*)**



White solid, mp 245–246 ^{o}C, 20% yield (91.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.77 (d, J = 10.6 Hz, 1H), 8.14–8.04 (m, 3H), 7.68–7.61 (m, 4H), 7.59–7.53 (m, 3H), 7.51–7.43 (m, 6H), 7.16 (dd, J = 8.0, 0.9 Hz, 1H), 7.06 (t, J = 7.9 Hz, 1H), 6.83 (d, J = 1.3 Hz, 1H), 6.78 (d, J = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.44, 142.16, 138.55 (d, J = 9.9 Hz), 134.05, 132.66, 132.59 (d, J= 2.7 Hz), 132.43, 132.05 (d, J = 10.1 Hz), 131.11 (d, J = 105.4Hz), 130.07 (d, J = 4.0 Hz), 129.48, 128.85, 128.68 (d, J = 12.3Hz), 128.15 (d, J = 3.8 Hz), 127.86, 127.57 (d, J = 1.1 Hz), 108.31 (d, J = 96.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.32. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{21}ClNO_2PNa$ 480.0896, found 480.0888.

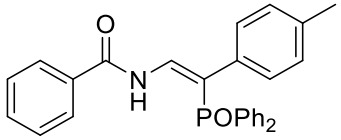
***(E)-N-(2-(3-Chlorophenyl)-2-(diphenylphosphoryl)vinyl)benzamide* (4f-*E*)**



White solid, mp 233–234 ^{o}C, 64% yield (292.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 11.6 Hz, 1H), 7.77 (dd, J = 11.6, 7.5 Hz, 4H), 7.65–7.51 (m, 6H), 7.48 (dd, J = 9.7, 4.4 Hz, 4H), 7.42 (t, J = 7.6 Hz, 2H), 7.37–7.27 (m, 3H), 7.24 (d, J = 6.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.97, 135.29, 134.88 (d, J = 13.7 Hz), 134.74, 132.91, 132.14, 132.05, 131.50, 130.70, 130.44, 129.93 (d, J =

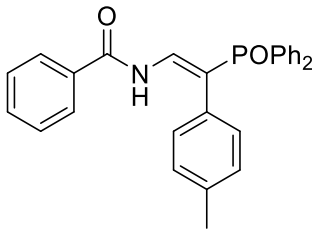
4.0 Hz), 129.00, 128.67, 128.55, 128.12 (d, *J* = 4.1 Hz), 127.18, 114.81 (d, *J* = 106.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.50. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{21}ClNO_2PNa$ 480.0896, found 480.0882.

(Z)-N-(2-(Diphenylphosphoryl)-2-(p-tolyl)vinyl)benzamide **(4g-*Z*)**



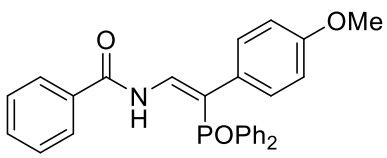
White solid, mp 157–158 °C, 19% yield (83.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.77 (d, *J* = 10.5 Hz, 1H), 8.11–7.98 (m, 3H), 7.68–7.60 (m, 4H), 7.55 (dd, *J* = 10.5, 4.2 Hz, 3H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.43 (td, *J* = 7.6, 2.9 Hz, 4H), 6.94 (d, *J* = 7.9 Hz, 2H), 6.75 (d, *J* = 7.2 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.92, 140.95, 136.78 (d, *J* = 1.5 Hz), 133.04 (d, *J* = 9.7 Hz), 132.21, 131.97, 131.81 (d, *J* = 2.6 Hz), 131.69, 131.59, 130.56, 129.49 (d, *J* = 3.9 Hz), 128.51, 128.32, 128.07, 127.95, 127.34, 108.95 (d, *J* = 96.1 Hz), 20.59. ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.38. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{28}H_{25}NO_2P$ 438.1623, found 438.1634.

(E)-N-(2-(Diphenylphosphoryl)-2-(p-tolyl)vinyl)benzamide **(4g-*E*)**



White solid, mp 223–224 °C, 60% yield (262.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 11.3 Hz, 1H), 7.76 (dd, *J* = 11.5, 7.7 Hz, 4H), 7.67–7.62 (m, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.52–7.48 (m, 3H), 7.47–7.41 (m, 4H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.18 (dd, *J* = 20.4, 7.8 Hz, 4H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.97, 138.28, 134.28 (d, *J* = 22.6 Hz), 132.69, 132.41, 132.13 (d, *J* = 9.6 Hz), 131.91 (d, *J* = 2.3 Hz), 130.90, 130.21, 129.70 (d, *J* = 4.1 Hz), 129.61, 128.90, 128.46 (d, *J* = 12.1 Hz), 127.16, 115.99 (d, *J* = 107.1 Hz), 21.26. ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.67. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{28}H_{24}NO_2PNa$ 460.1442, found 460.1433.

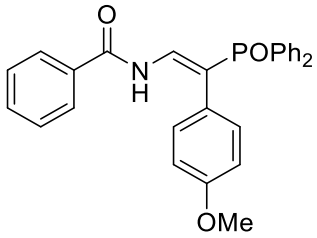
(Z)-N-(2-(Diphenylphosphoryl)-2-(4-methoxyphenyl)vinyl)benzamide **(4h-*Z*)**



White solid, mp 166–167 °C, 17% yield (77.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.75 (d, *J* = 10.5

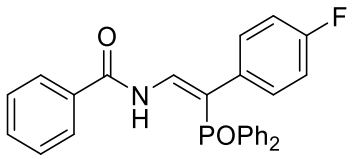
Hz, 1H), 8.09–7.97 (m, 3H), 7.68–7.60 (m, 4H), 7.55 (dd, *J* = 11.1, 4.0 Hz, 3H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.43 (td, *J* = 7.6, 3.0 Hz, 4H), 6.77 (dd, *J* = 8.7, 1.2 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.38, 159.00 (d, *J* = 1.4 Hz), 141.29 (d, *J* = 1.9 Hz), 132.68, 132.45, 132.30 (d, *J* = 2.7 Hz), 132.10 (d, *J* = 10.0 Hz), 131.98, 131.34 (d, *J* = 3.9 Hz), 130.94, 128.80, 128.51 (d, *J* = 12.2 Hz), 127.81, 113.69, 109.13 (d, *J* = 96.4 Hz), 55.19. ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.30. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{28}H_{24}NO_3PNa$ 476.1391, found 476.1383.

***(E)-N-(2-(Diphenylphosphoryl)-2-(4-methoxyphenyl)vinyl)benzamide* (4h-*E*)**



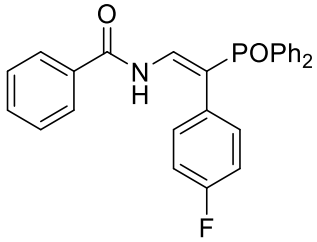
White solid, mp 234–235 °C, 52% yield (235.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 11.3 Hz, 1H), 7.76 (dd, *J* = 11.6, 7.4 Hz, 4H), 7.66–7.60 (m, 1H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 6.0 Hz, 3H), 7.46 (dd, *J* = 9.8, 4.5 Hz, 4H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.93, 159.48, 134.27 (d, *J* = 23.7 Hz), 132.71, 132.40, 132.13 (d, *J* = 9.6 Hz), 131.90, 131.17 (d, *J* = 3.9 Hz), 130.93, 128.93, 128.48 (d, *J* = 12.1 Hz), 127.16, 124.57 (d, *J* = 6.1 Hz), 115.75 (d, *J* = 107.5Hz), 114.96, 55.27. ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.66. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{28}H_{25}NO_3P$ 454.1572, found 454.1564.

***(Z)-N-(2-(Diphenylphosphoryl)-2-(4-fluorophenyl)vinyl)benzamide* (4i-*Z*)**



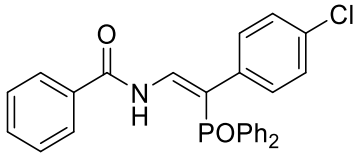
White solid, mp 136–137 °C, 17% yield (75.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.73 (d, *J* = 10.6 Hz, 1H), 8.09–7.97 (m, 3H), 7.63 (dd, *J* = 6.7, 5.5 Hz, 3H), 7.60 (d, *J* = 1.2 Hz, 1H), 7.59–7.53 (m, 3H), 7.52–7.42 (m, 6H), 6.82 (d, *J* = 7.1 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.44, 163.41 (d, *J* = 1.6 Hz), 160.95 (d, *J* = 1.7 Hz), 141.78, 132.58, 132.51, 132.46 (d, *J* = 2.7 Hz), 132.11, 132.01, 131.91 (d, *J* = 3.8 Hz), 131.83 (d, *J* = 3.8 Hz), 131.65, 130.61, 128.83, 128.67,128.55, 127.83, 115.26 (d, *J* = 21.3 Hz), 108.53 (d, *J* = 96.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.30. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{27}H_{22}FNO_2P$ 442.1372, found 442.1370.

***(E)-N-(2-(Diphenylphosphoryl)-2-(4-fluorophenyl)vinyl)benzamide* (4i-*E*)**



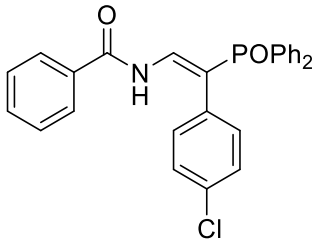
White solid, mp 211–212 °C, 54% yield (238.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 11.3 Hz, 1H), 7.76 (dd, J = 11.9, 7.2 Hz, 4H), 7.65–7.60 (m, 1H), 7.57 (d, J = 7.6 Hz, 3H), 7.53 (dd, J = 5.3, 1.8 Hz, 2H), 7.47 (td, J = 7.4, 2.7 Hz, 4H), 7.41 (t, J = 7.7 Hz, 2H), 7.32 (dd, J = 7.3, 5.5 Hz, 2H), 7.07 (t, J = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.50, 163.30 (d, J = 1.4 Hz), 160.83 (d, J = 1.6 Hz), 134.14 (d, J = 22.7 Hz), 132.39, 131.73 (d, J = 0.6 Hz), 131.66, 131.61 (d, J = 2.8 Hz), 131.57, 131.38 (d, J = 4.1 Hz), 131.29 (d, J = 4.1 Hz), 131.09, 130.04, 128.51, 128.16, 128.04, 126.66, 116.16 (d, J = 21.7 Hz), 114.66 (d, J = 107.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.73. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{21}FNO_2PNa$ 464.1192, found 464.1191.

(Z)-N-(2-(4-Chlorophenyl)-2-(diphenylphosphoryl)vinyl)benzamide **(4j-*Z*)**



White solid, mp 228–229 °C, 14% yield (64.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.76 (d, J = 10.5 Hz, 1H), 8.11–7.98 (m, 3H), 7.64 (dd, J = 6.7, 5.5 Hz, 3H), 7.61 (d, J = 1.2 Hz, 1H), 7.59–7.53 (m, 3H), 7.52–7.42 (m, 6H), 7.11 (d, J = 8.3 Hz, 2H), 6.79 (dd, J = 8.3, 1.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.44, 141.90 (d, J = 0.8 Hz), 135.18 (d, J = 9.9 Hz), 133.57 (d, J = 1.8 Hz), 132.61, 132.52 (d, J = 2.7 Hz), 132.46, 132.05 (d, J = 10.1 Hz), 131.34 (d, J = 3.9 Hz), 131.15 (d, J =105.2 Hz), 128.84, 128.65 (d, J = 12.3 Hz), 128.50, 127.84, 108.37 (d, J = 96.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.23. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{27}H_{22}ClNO_2P$ 458.1077, found 458.1073.

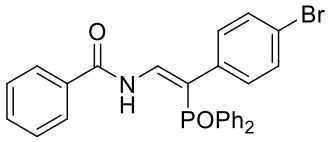
(E)-N-(2-(4-Chlorophenyl)-2-(diphenylphosphoryl)vinyl)benzamide **(4j-*E*)**



White solid, mp 221–222 °C, 52% yield (237.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 11.5 Hz, 1H), 7.81–7.71 (m, 4H), 7.63–7.51 (m, 6H), 7.50–7.44 (m, 4H), 7.42 (t, J = 7.7 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 7.32–7.28 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.52, 134.11 (d, J = 22.0 Hz),

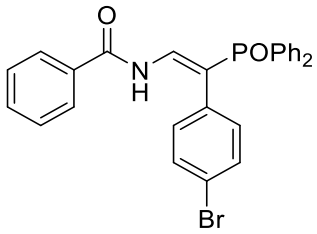
134.04 (d, *J* = 1.7 Hz), 132.43, 131.66, 131.62, 131.56, 131.09, 130.92, 130.85, 130.83, 130.79, 130.04, 129.28, 128.53, 128.18, 128.06, 126.69, 114.52 (d, *J* = 107.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 28.61. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{21}ClNO_2PNa$ 480.0896, found 480.0878.

(Z)-N-(2-(4-Bromophenyl)-2-(diphenylphosphoryl)vinyl)benzamide **(4k-*Z*)**



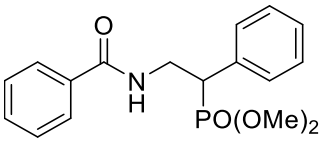
White solid, mp 175–176 °C, 19% yield (95.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 12.77 (d, *J* = 10.3 Hz, 1H), 8.11–7.99 (m, 3H), 7.63 (dd, *J* = 12.1, 7.7 Hz, 3H), 7.56 (dd, *J* = 6.3, 4.4 Hz, 3H), 7.47 (dt, *J* = 7.0, 6.2 Hz, 7H), 7.26 (d, *J* = 7.8 Hz, 2H), 6.73 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 163.96, 141.39, 135.21 (d, *J* = 9.8 Hz), 132.14, 132.04 (d, *J* = 2.7 Hz), 131.97, 131.57 (d, *J* = 10.1 Hz), 131.15 (d, *J* = 3.9 Hz), 130.97, 130.15, 128.36, 128.18 (d, *J* = 12.3 Hz), 127.36, 121.25 (d, *J* = 2.0 Hz), 107.89 (d, *J* = 96.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 35.08. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{27}H_{22}BrNO_2P$ 502.0572, found 502.0559.

(E)-N-(2-(4-Bromophenyl)-2-(diphenylphosphoryl)vinyl)benzamide **(4k-*E*)**



White solid, mp 224–225 °C, 51% yield (255.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.05 (d, *J* = 11.0 Hz, 1H), 7.76 (dd, *J* = 11.5, 7.7 Hz, 4H), 7.60 (t, *J* = 11.6 Hz, 3H), 7.55–7.44 (m, 9H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 164.02, 138.60, 134.57 (d, *J* = 22.2 Hz), 132.91, 132.69, 132.13, 132.03, 131.86 (d, *J* = 6.7 Hz), 131.56 (d, *J* = 4.2 Hz), 131.00 (d, *J* = 106.3 Hz), 129.00, 128.61 (d, *J* = 12.2 Hz), 127.19, 122.77 (d, *J* = 1.8 Hz), 114.96 (d, *J* = 106.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 28.62. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{27}H_{21}BrNO_2PNa$ 524.0391, found 524.0389.

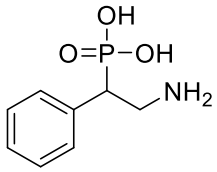
Dimethyl (2-benzamido-1-phenylethyl)phosphonate **(5)**



White solid, mp 82–83 °C, 95% yield (3.1 g). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.72 (t, *J* = 5.6 Hz, 1H),

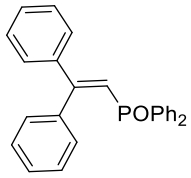
7.70–7.65 (m, 2H), 7.40–7.31 (m, 3H), 7.27 (t, *J* = 7.4 Hz, 4H), 7.24 – 7.20 (m, 1H), 4.10–3.98 (m, 1H), 3.97–3.83 (m, 1H), 3.74–3.63 (m, 4H), 3.46 (d, *J* = 10.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 167.54, 134.16, 134.00 (d, *J* = 6.7 Hz), 131.22, 129.14 (d, *J* = 6.7 Hz), 128.60 (d, *J* = 1.9 Hz), 128.23, 127.54 (d, *J* = 2.7 Hz), 126.92, 53.29 (d, *J* = 7.0 Hz), 52.70 (d, *J* = 7.2 Hz), 42.91 (d, *J* = 135.5 Hz), 40.45. ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 28.75. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{17}H_{20}NO_4PNa$ 356.1028, found 356.1028.

β-Amino-1-phenylethyl phosphonic acid **(6)**



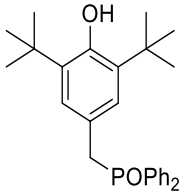
White solid, mp 295–296 °C, 81% yield (65 mg). ^{1}H NMR (400 MHz, D_2O): *δ* 7.40–7.24 (m, 5H), 3.62–3.36 (m, 2H), 3.30–3.11 (m, 1H). ^{13}C NMR (101 MHz, D_2O): *δ* 134.66 (d, *J* = 6.4 Hz), 129.01, 128.85 (d, *J* = 4.0 Hz), 127.75, 44.73 (d, *J* = 127.0 Hz), 40.60. ^{31}P NMR (162 MHz, D_2O): *δ* 16.73.

(2,2-Diphenylvinyl)diphenylphosphine oxide **(7)**



^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.73–7.63 (m, 4H), 7.39–7.28 (m, 11H), 7.24–7.20 (m, 2H), 7.14–7.05 (m, 3H), 6.79 (d, *J* = 18.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 161.67 (d, *J* = 2.2 Hz), 141.36 (d, *J* = 16.2 Hz), 137.50 (d, *J* = 6.7 Hz), 133.71 (d, *J* = 106.2 Hz), 130.64 (d, *J* = 2.6 Hz), 130.40 (d, *J* = 9.5 Hz), 129.82, 129.08, 128.17, 127.89 (d, *J* = 3.2 Hz), 127.82, 127.75, 127.12, 119.86 (d, *J* = 103.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 19.21. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{26}H_{22}OP$ 381.1408, found 381.1395.

(3,5-Di-tert-butyl-4-hydroxybenzyl)diphenylphosphine oxide (BHT-POPh$_2$) **(8)**



^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.71–7.62 (m, 4H), 7.53–7.48 (m, 2H), 7.47–7.40 (m, 4H), 6.73 (d, *J* = 2.1 Hz, 2H), 5.06 (s, 1H), 3.57 (d, *J* = 13.8 Hz, 2H), 1.28 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): *δ* 152.30 (d, *J* = 3.4 Hz), 135.30 (d, *J* = 2.6 Hz), 132.02, 131.27 (d, *J* = 2.6 Hz), 131.00, 130.91, 127.97,

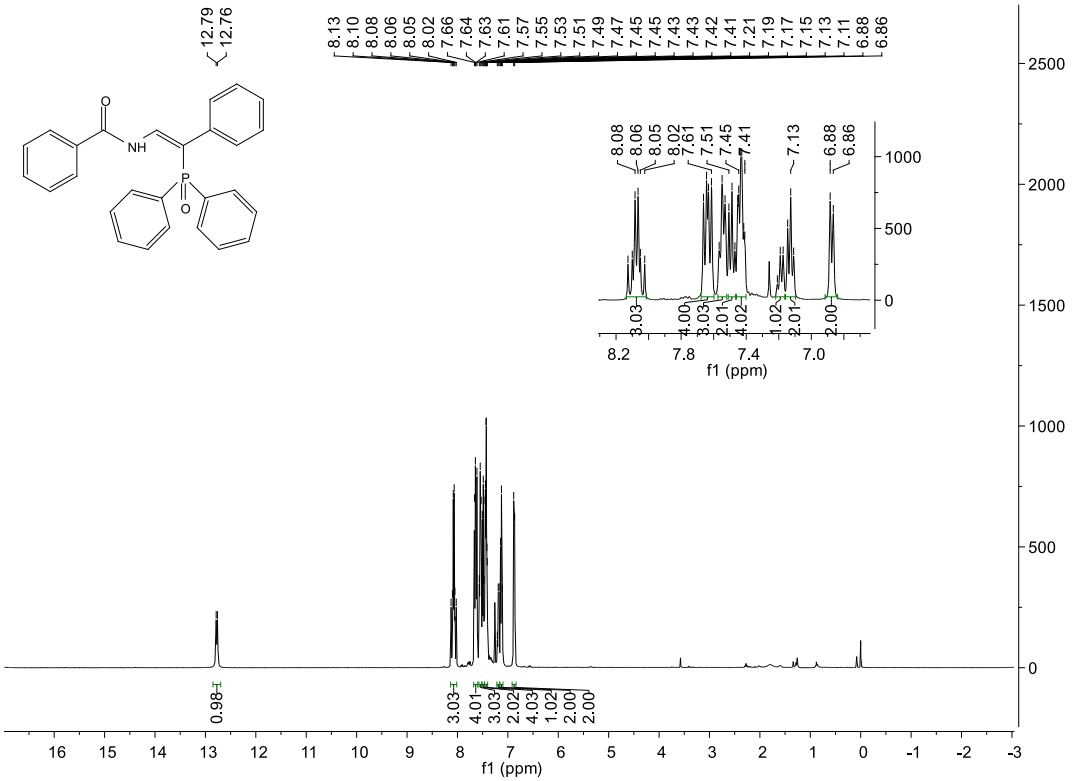
127.86, 126.50 (d, J = 5.0 Hz), 120.56 (d, J = 8.0 Hz), 37.48 (d, J = 67.2 Hz), 33.65, 29.64. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.91. HRMS (ESI-TOF) m/z: $(M+Na)^+$ Calcd for $C_{27}H_{33}O_2PNa$ 443.2116, found 443.2124.

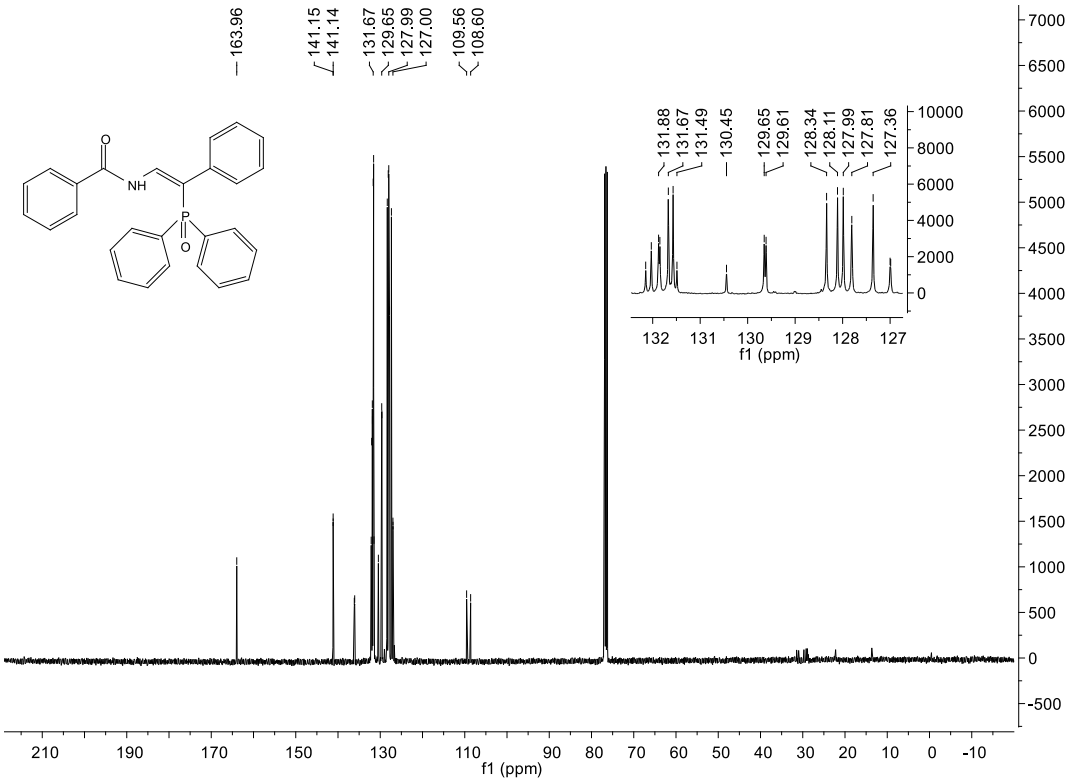
Reference:

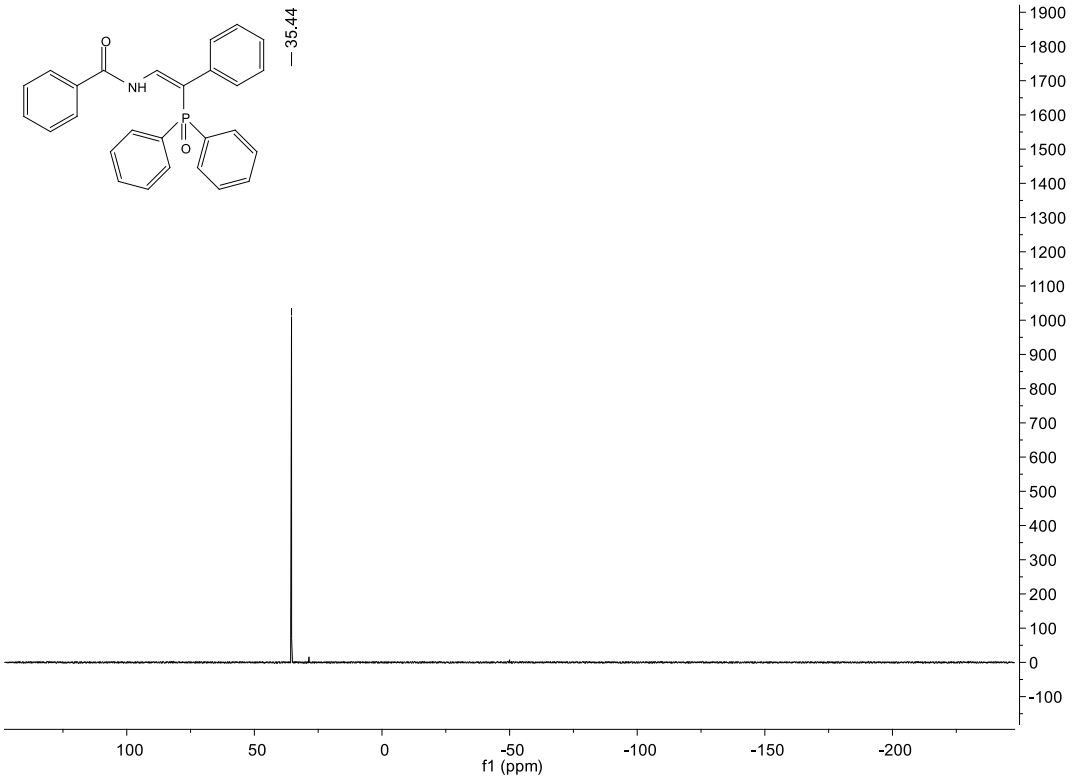
1. Cheung, C. W.; Buchwald, S. L. *J. Org. Chem.* **2012**, *77*, 7526.

9. ^{1}H, ^{13}C and ^{31}P NMR spectra of compounds 3-8

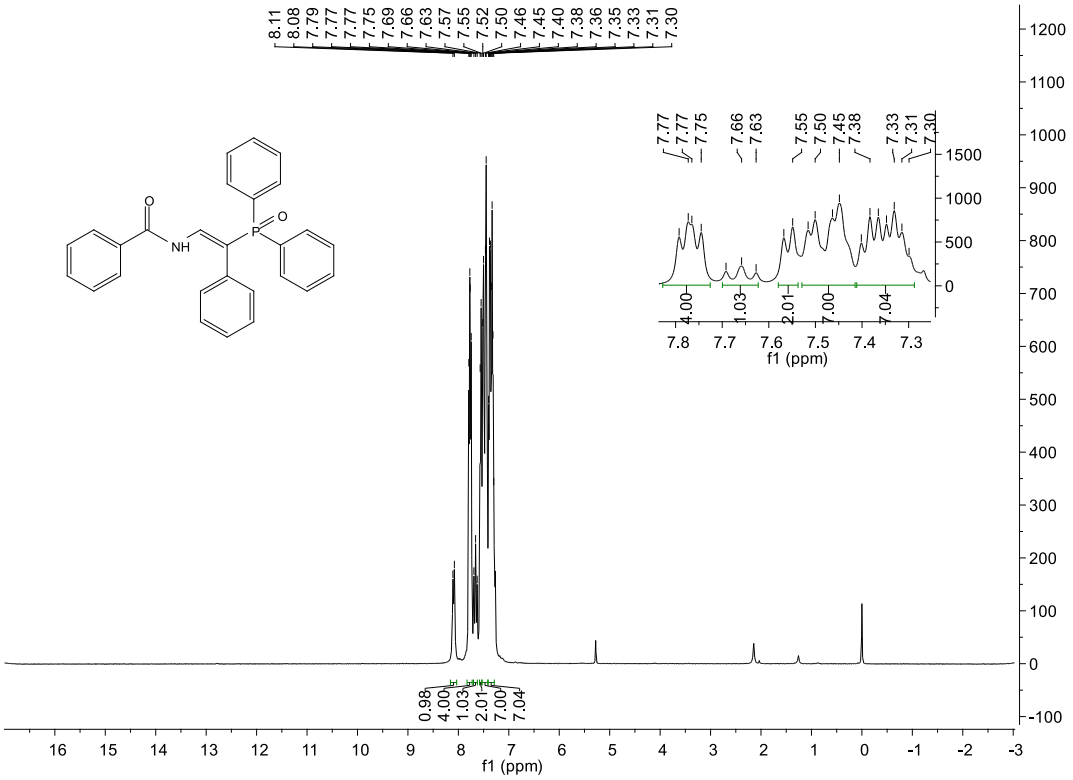
Compound 3a-*Z*

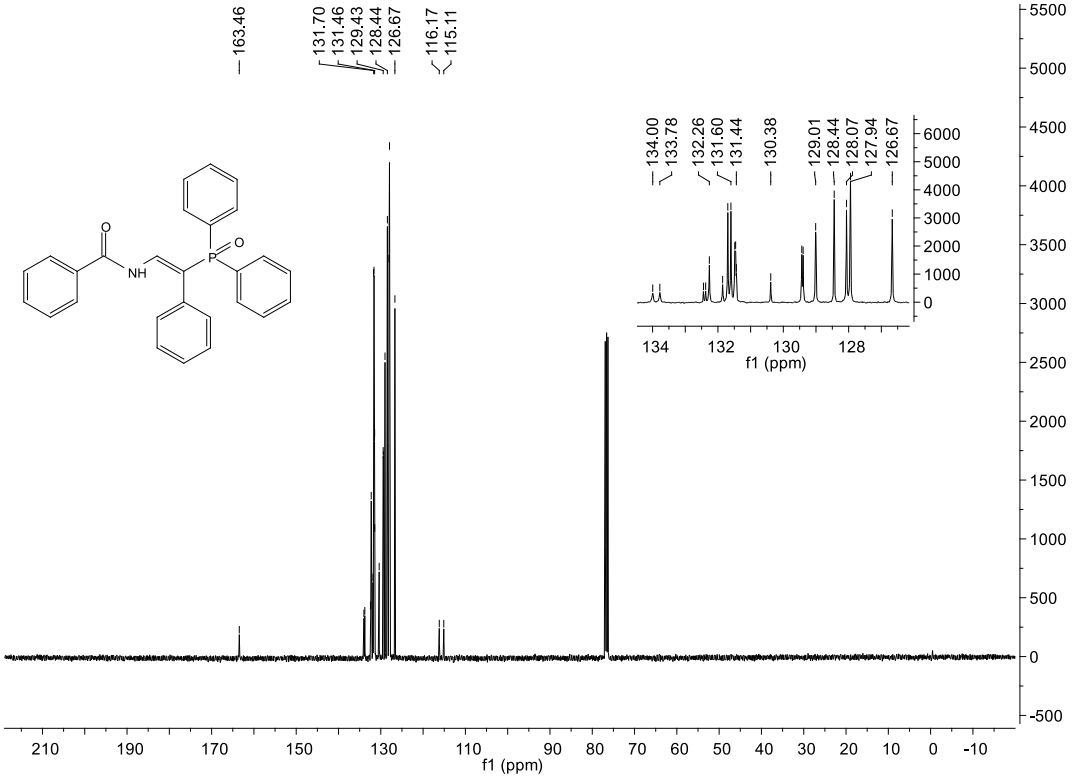


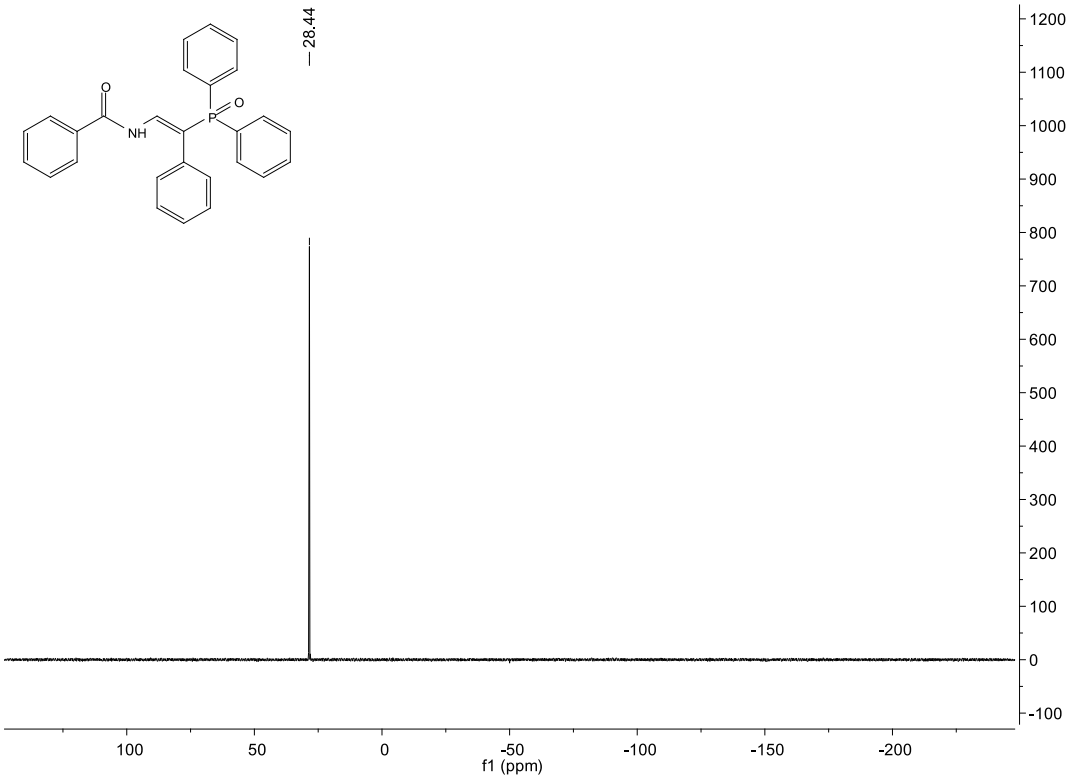




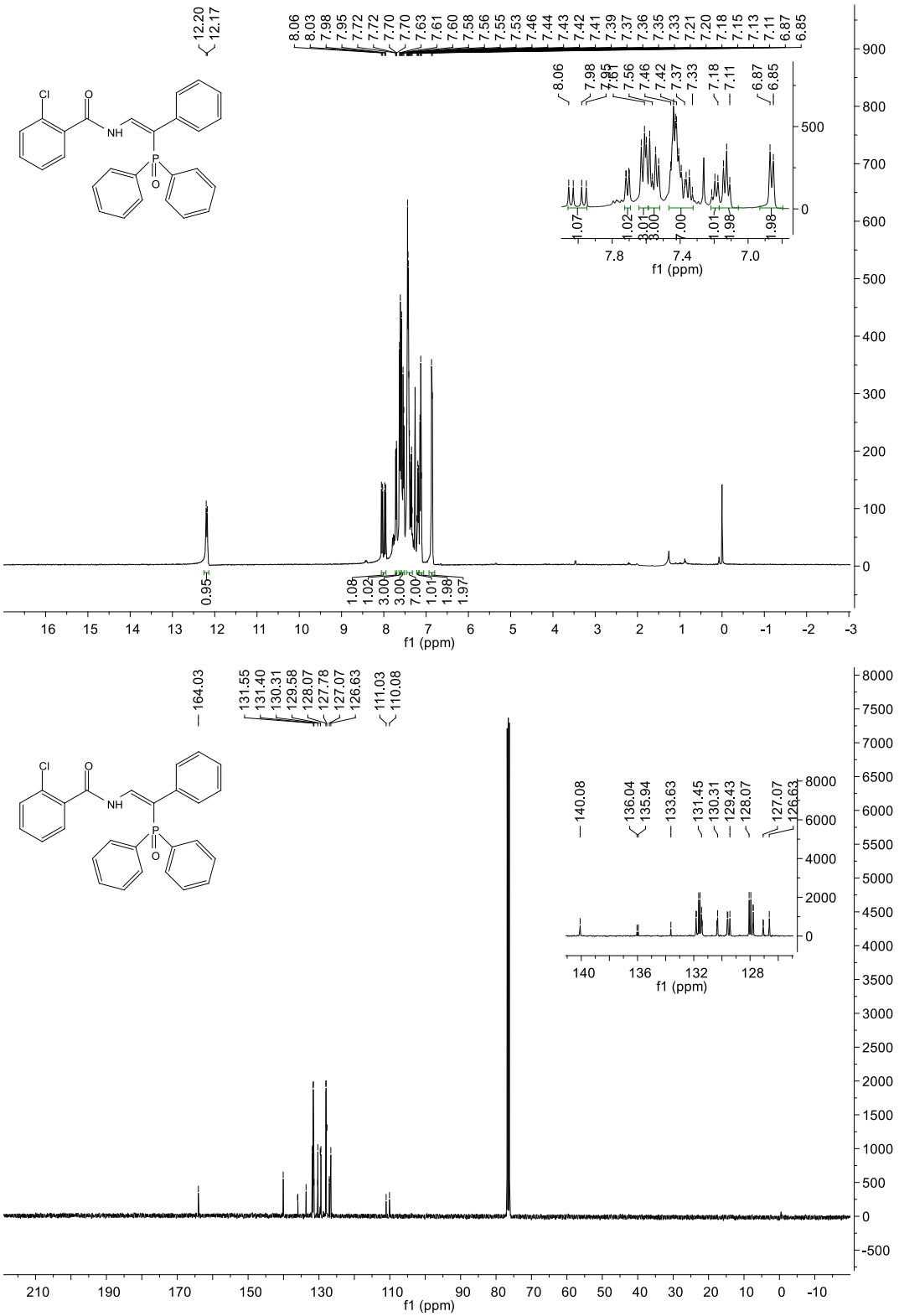
Compound 3a-*E*

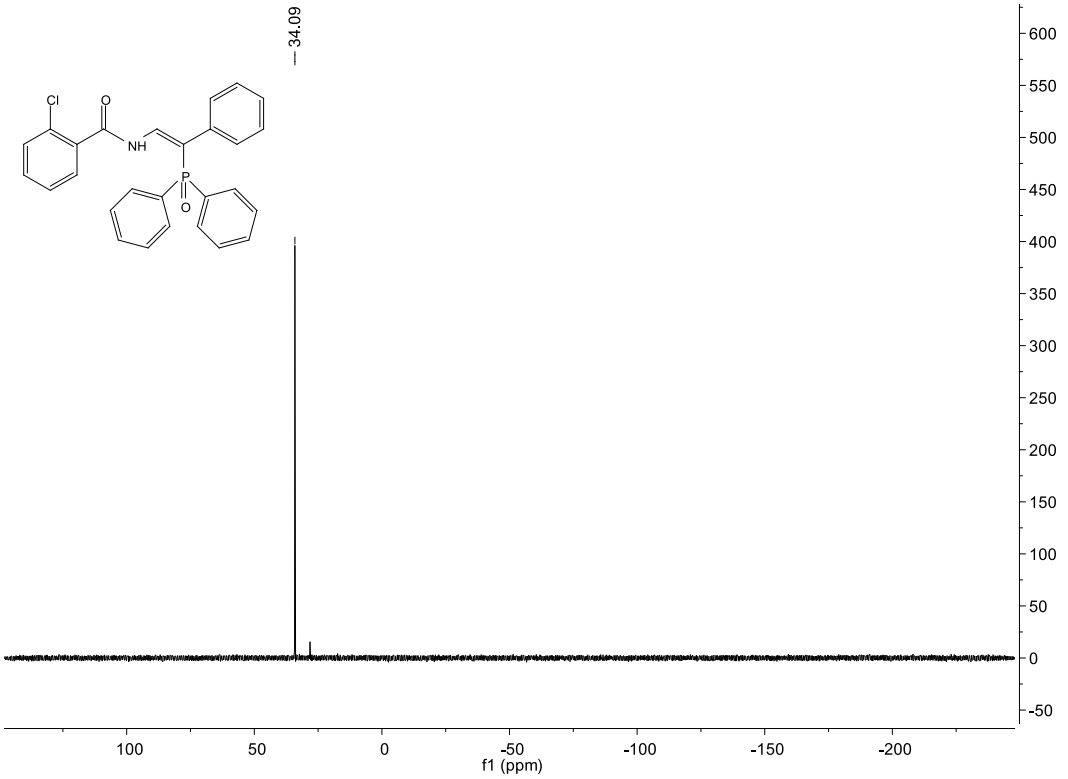



163.46
131.70
131.46
129.43
128.44
126.67
116.17
115.11
134.00
133.78
132.26
131.60
131.44
130.38
129.01
128.44
128.07
127.94
126.67
f1 (ppm)
f1 (ppm)

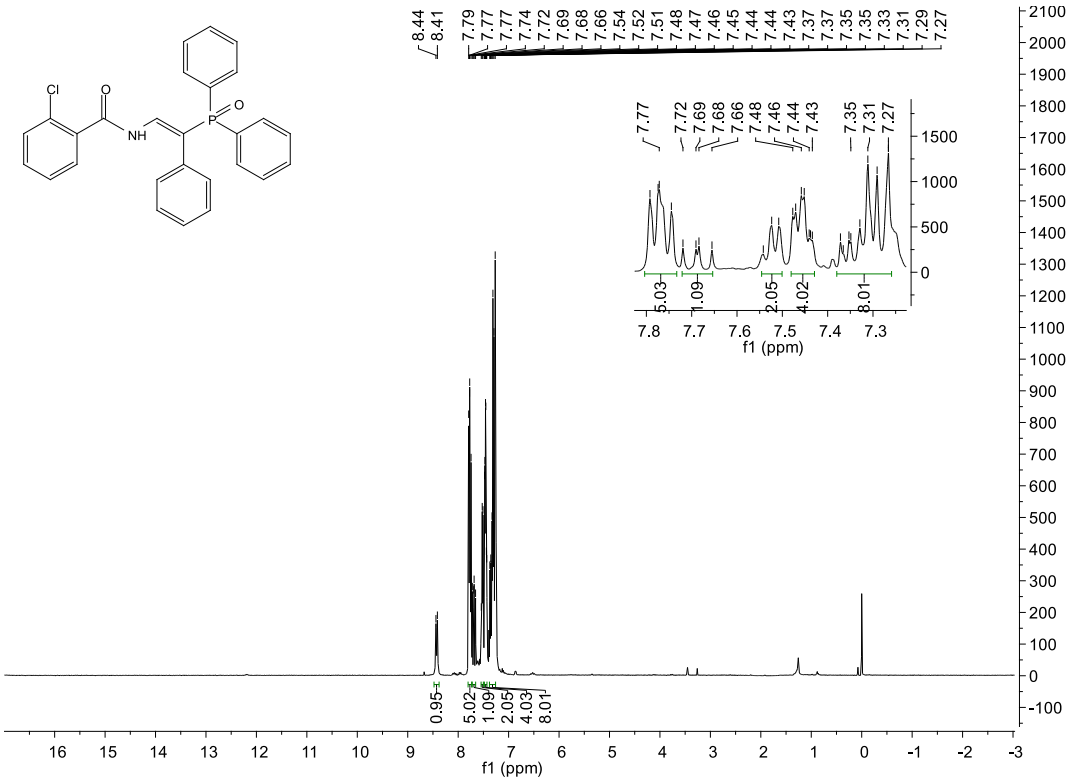

28.44
f1 (ppm)

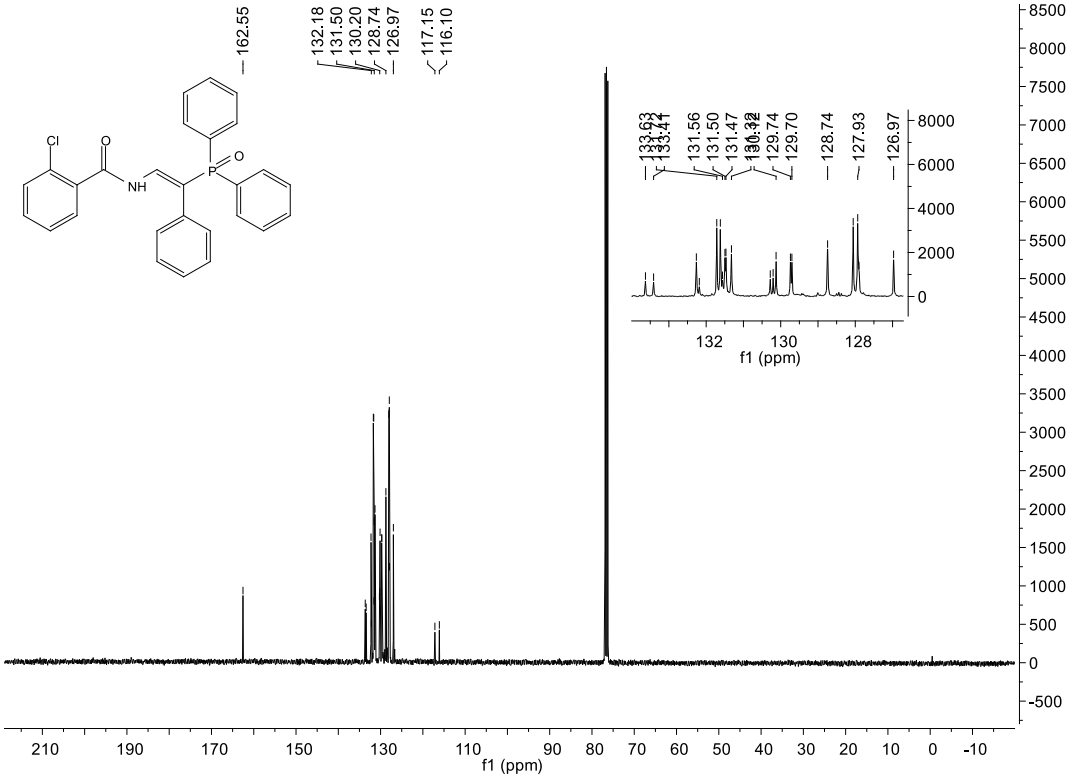
Compound 3b-*Z*

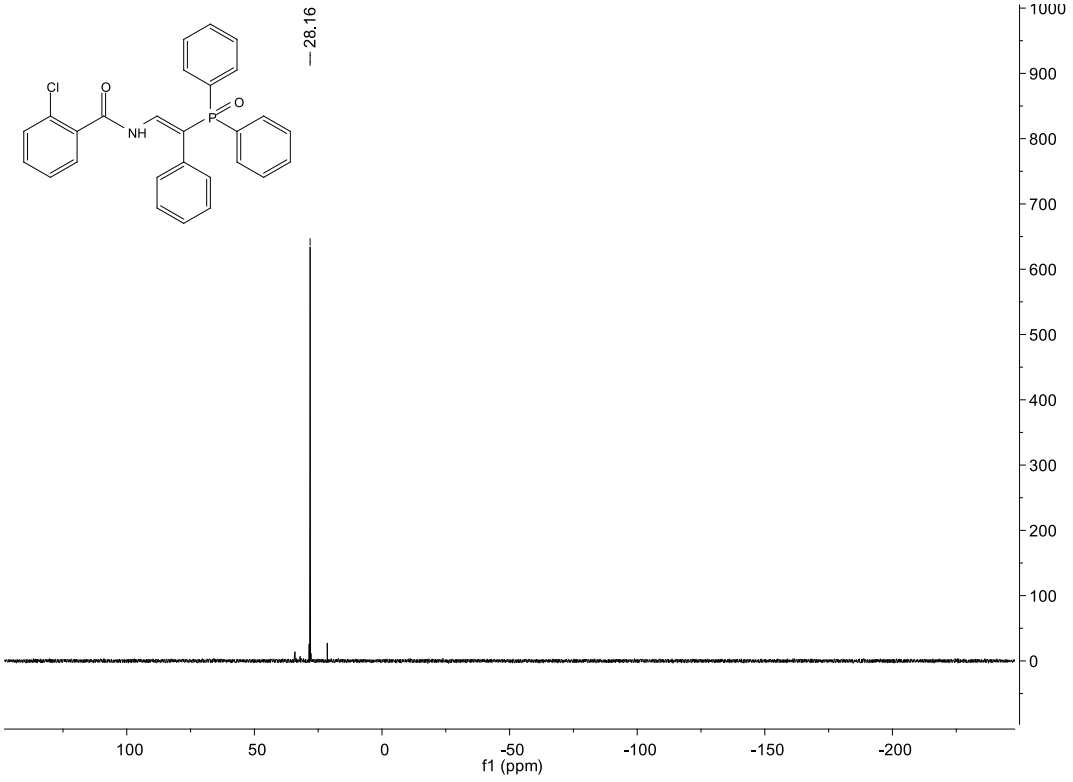


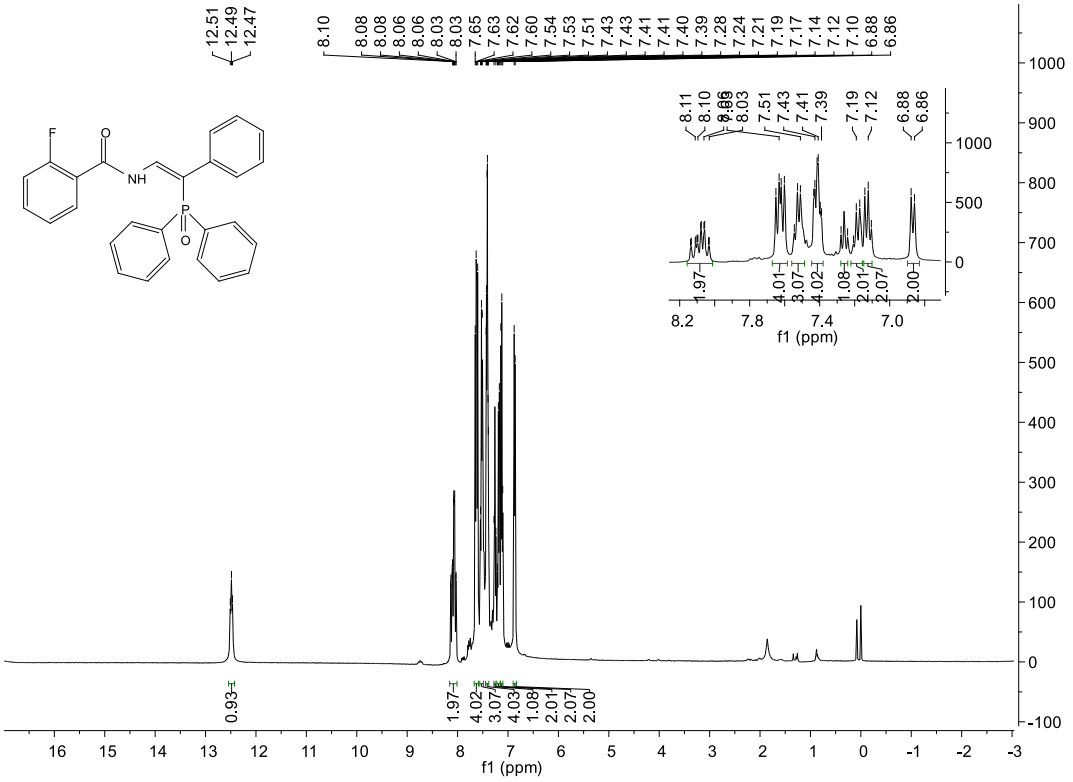


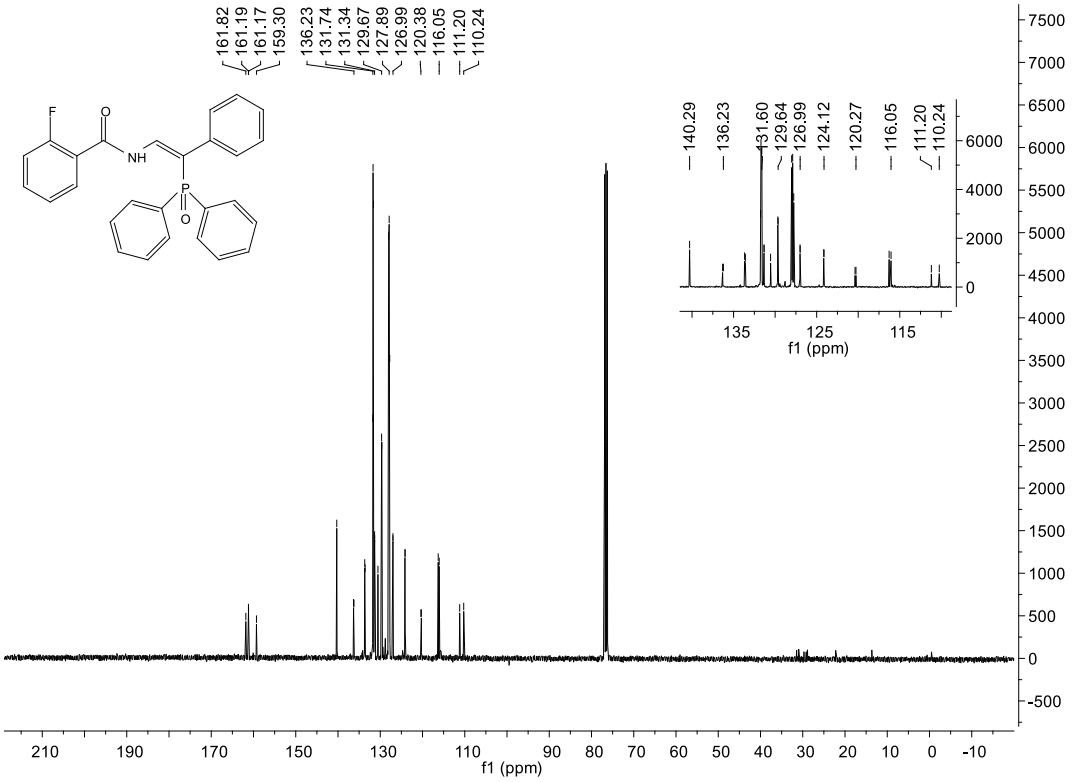
Compound 3b-*E*

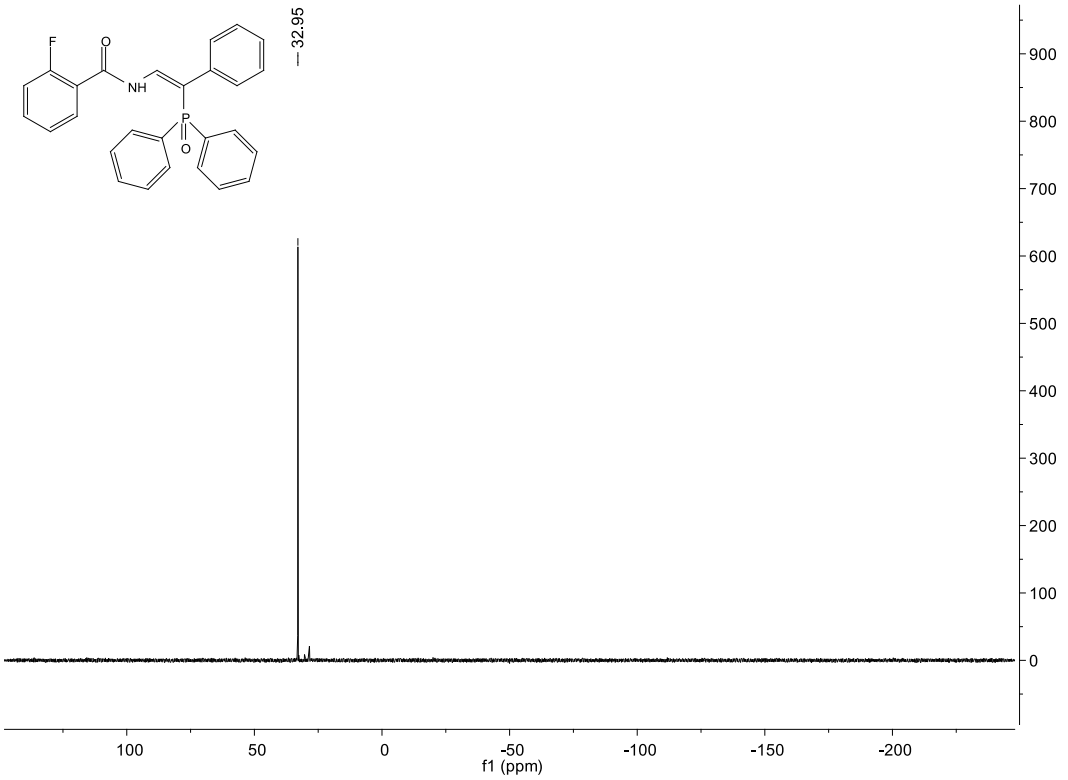



Cl
O
NH
P
O
162.55
132.18
131.50
130.20
128.74
126.97
117.15
116.10
133.63
133.41
131.56
131.50
131.47
129.74
129.70
128.74
127.93
126.97
f1 (ppm)
f1 (ppm)

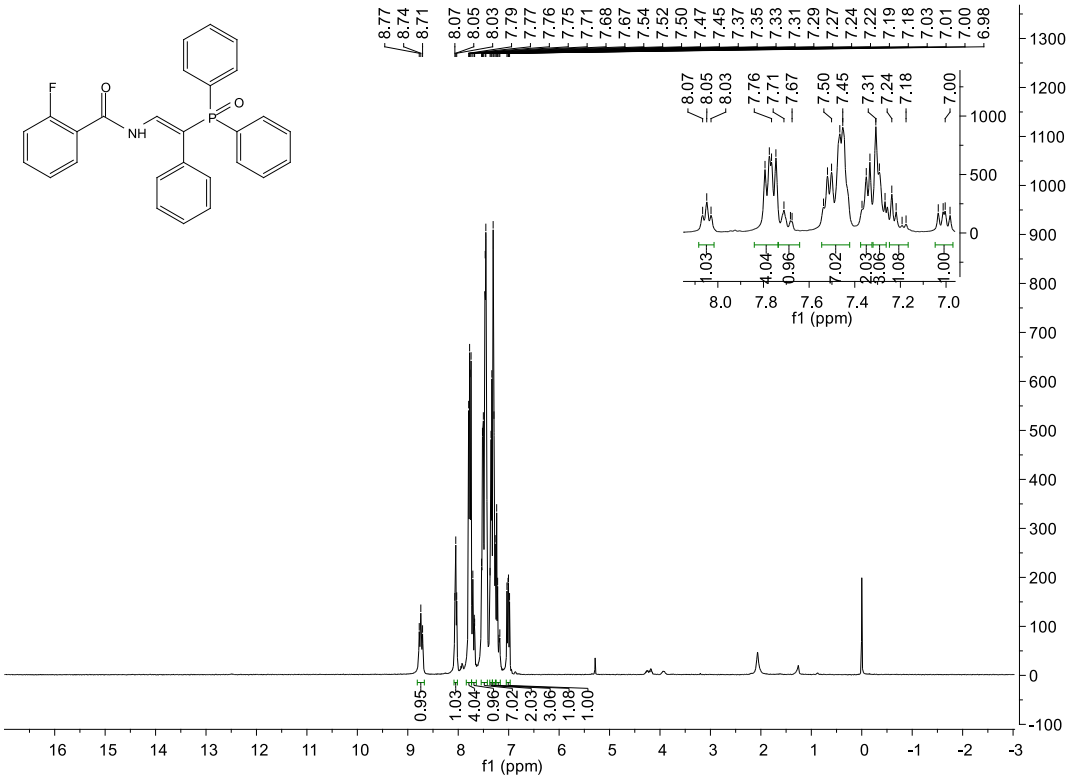

Cl
O
NH
P
O
28.16
f1 (ppm)

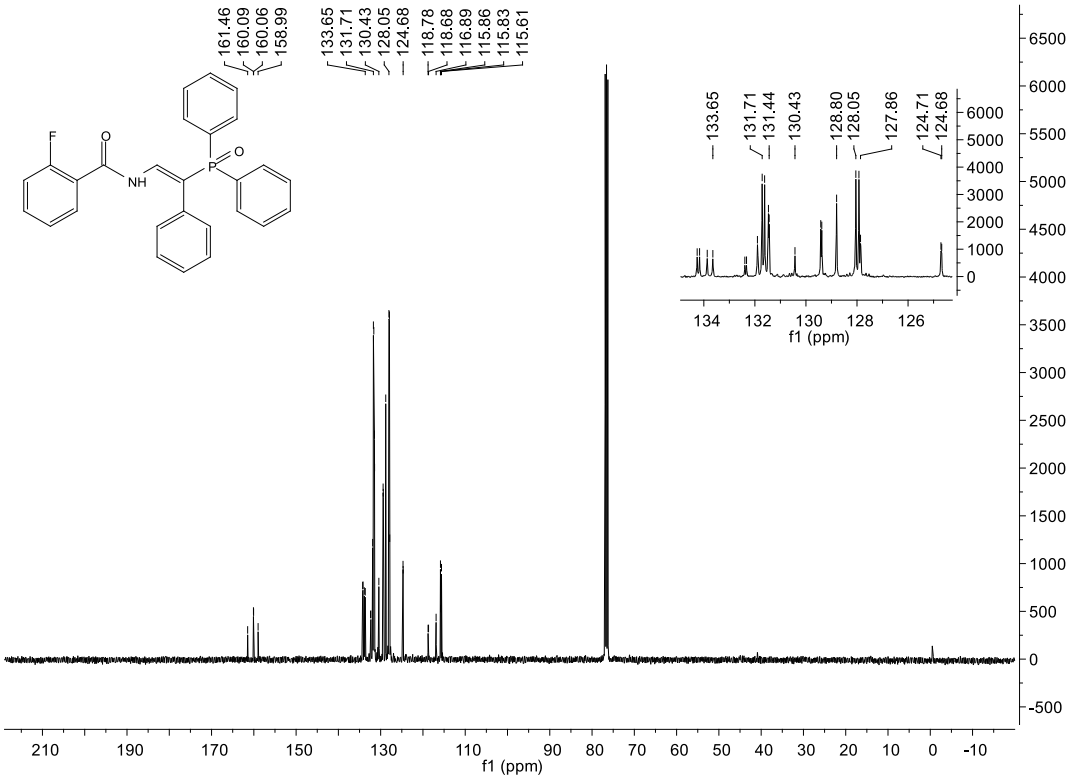

12.51
12.49
12.47
8.10
8.08
8.08
8.06
8.06
8.03
8.03
7.65
7.63
7.62
7.60
7.54
7.53
7.51
7.43
7.43
7.41
7.41
7.40
7.39
7.28
7.24
7.21
7.19
7.17
7.14
7.12
7.10
6.88
6.86
F
O
NH
P
O
0.93
1.97
4.02
3.07
4.03
1.08
2.01
2.07
2.00
f1 (ppm)
8.11
8.10
8.03
7.51
7.43
7.41
7.39
7.19
7.12
6.88
6.86
1.97
4.01
3.07
4.02
1.08
2.01
2.07
2.00
8.2
7.8
7.4
7.0
f1 (ppm)

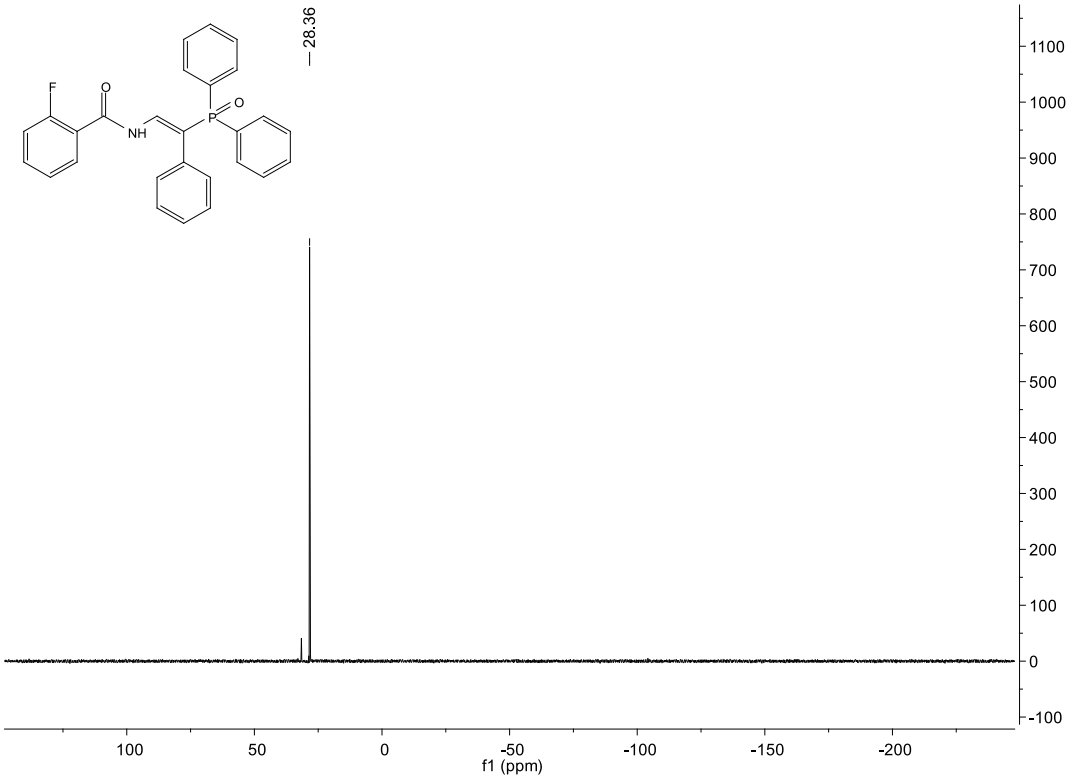

161.82
161.19
161.17
159.30
136.23
131.74
131.34
129.67
127.89
126.99
120.38
116.05
111.20
110.24
F
O
NH
P
O
f1 (ppm)
140.29
136.23
131.60
129.64
126.99
124.12
120.27
116.05
111.20
110.24
135
125
115
f1 (ppm)



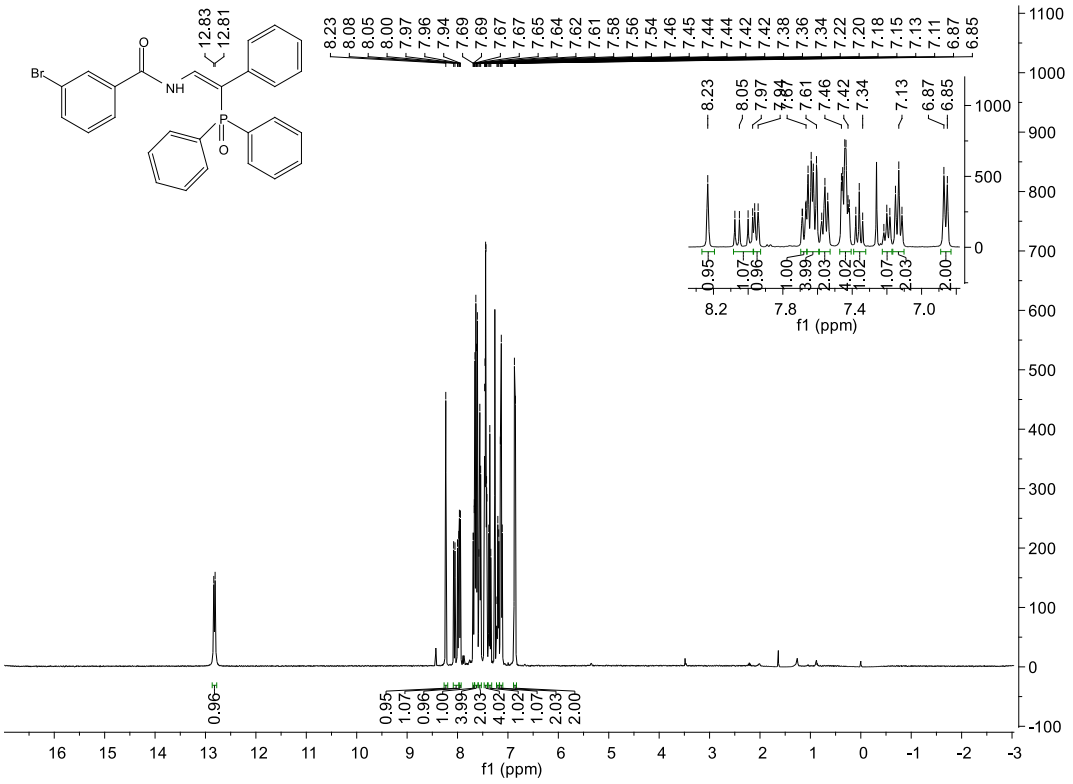
Compound 3c-*E*

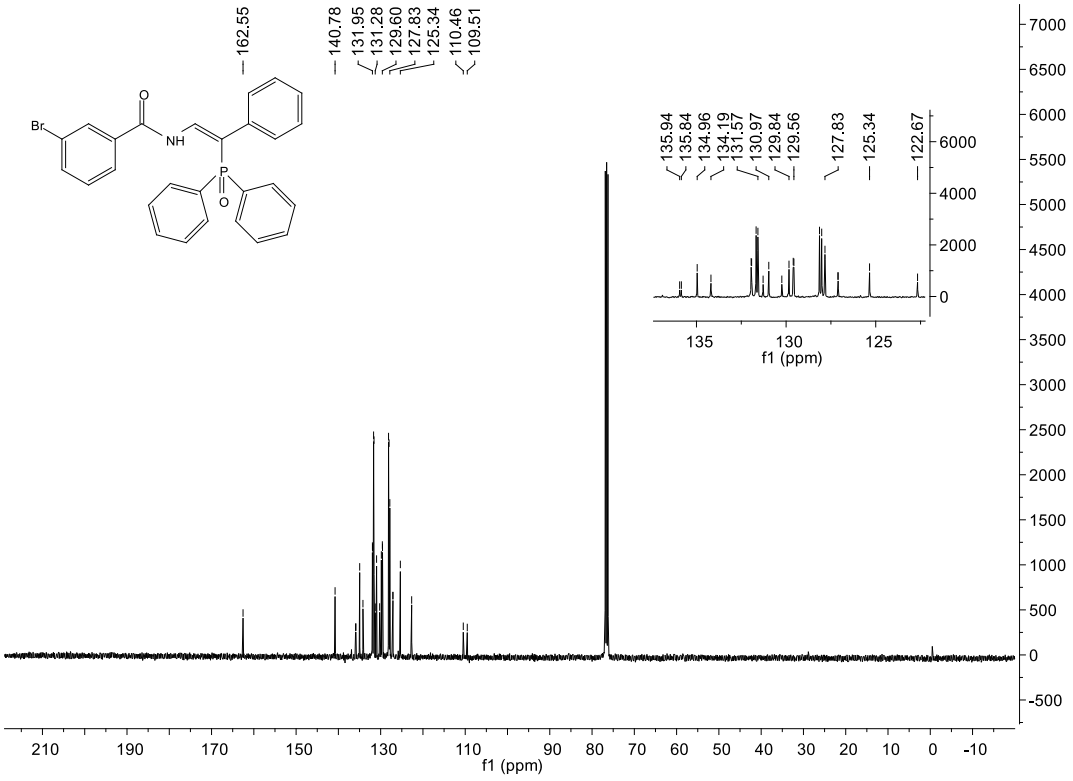


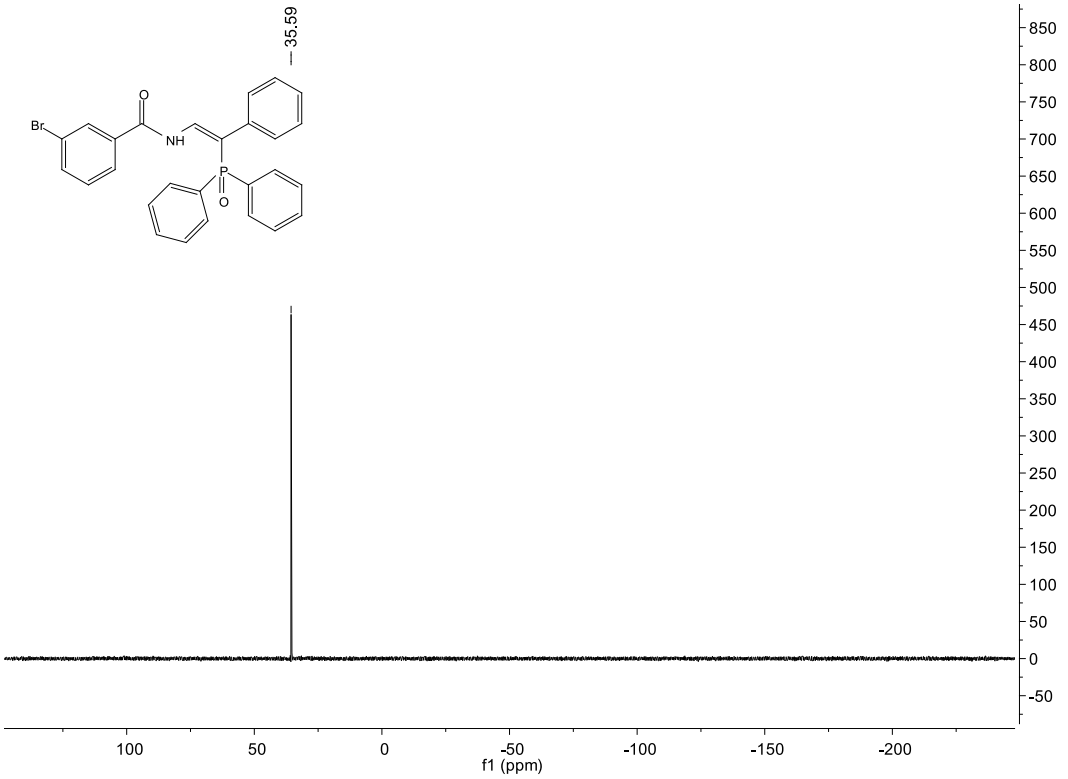

161.46
160.09
160.06
158.99
133.65
131.71
130.43
128.05
124.68
118.78
118.68
116.89
115.86
115.83
115.61
F
O
NH
P
O
133.65
131.71
131.44
130.43
128.80
128.05
127.86
124.71
124.68
f1 (ppm)
f1 (ppm)


28.36
F
O
NH
P
O
f1 (ppm)

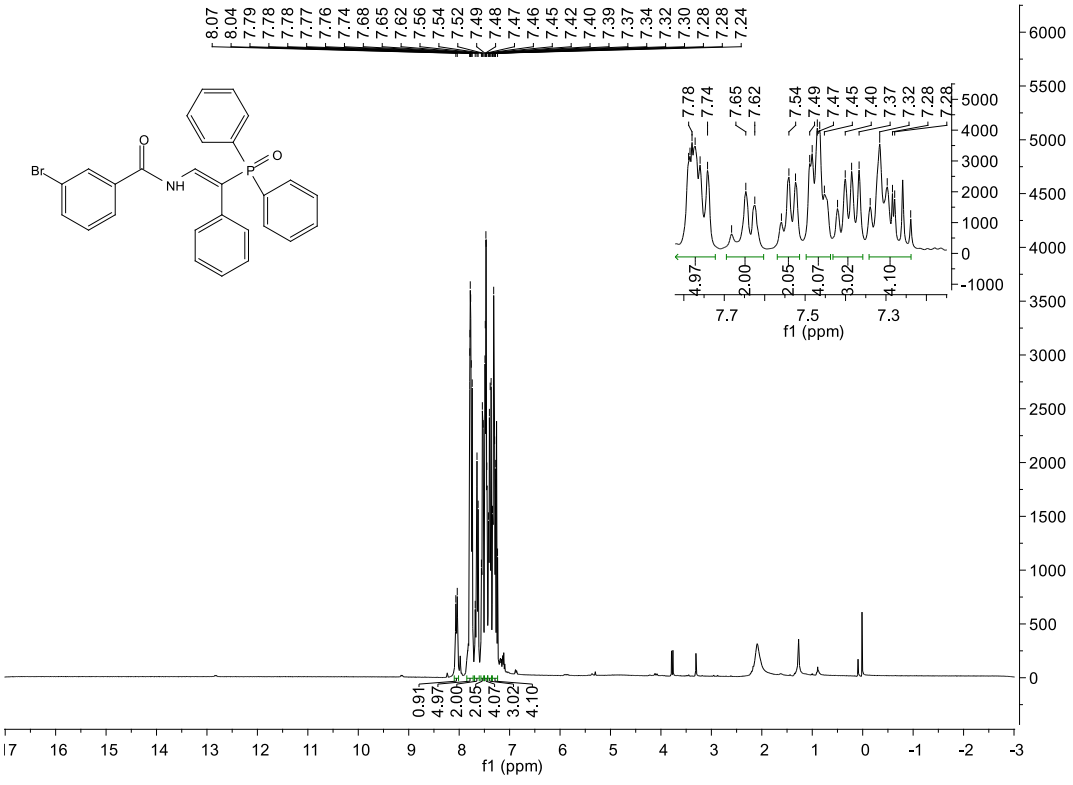
Compound 3d-*Z*

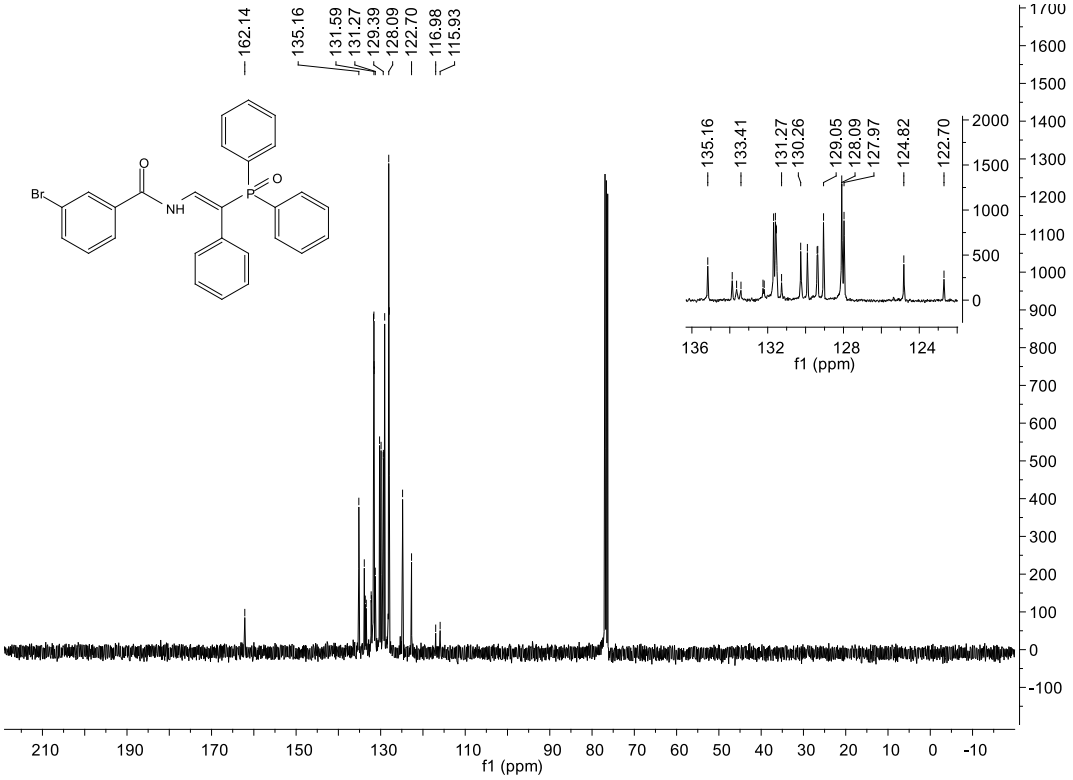


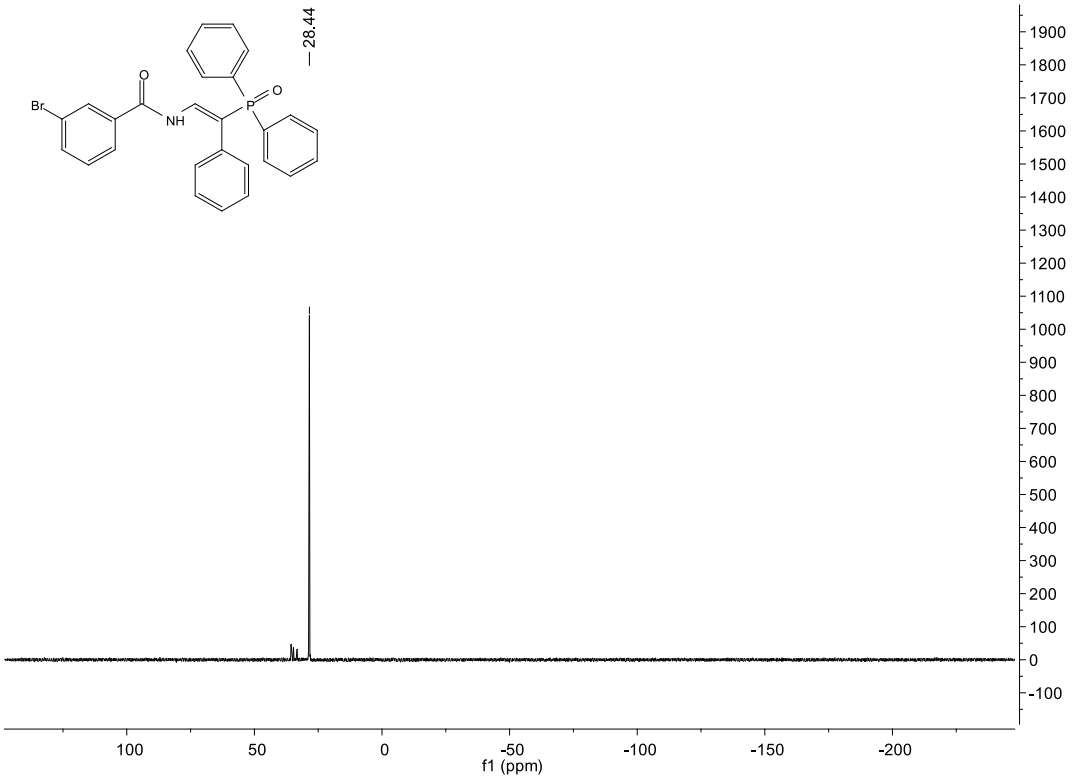




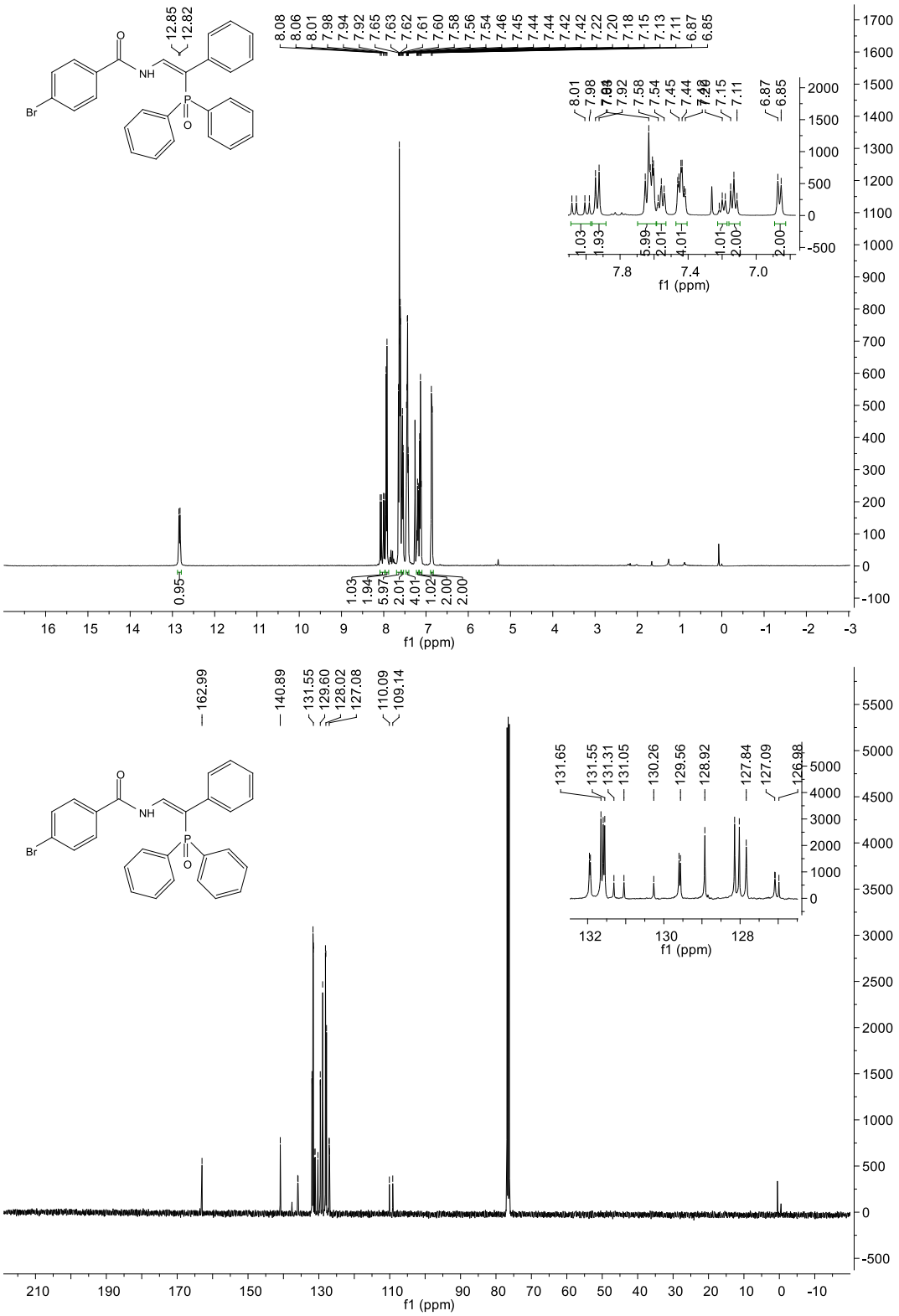
Compound 3d-*E*

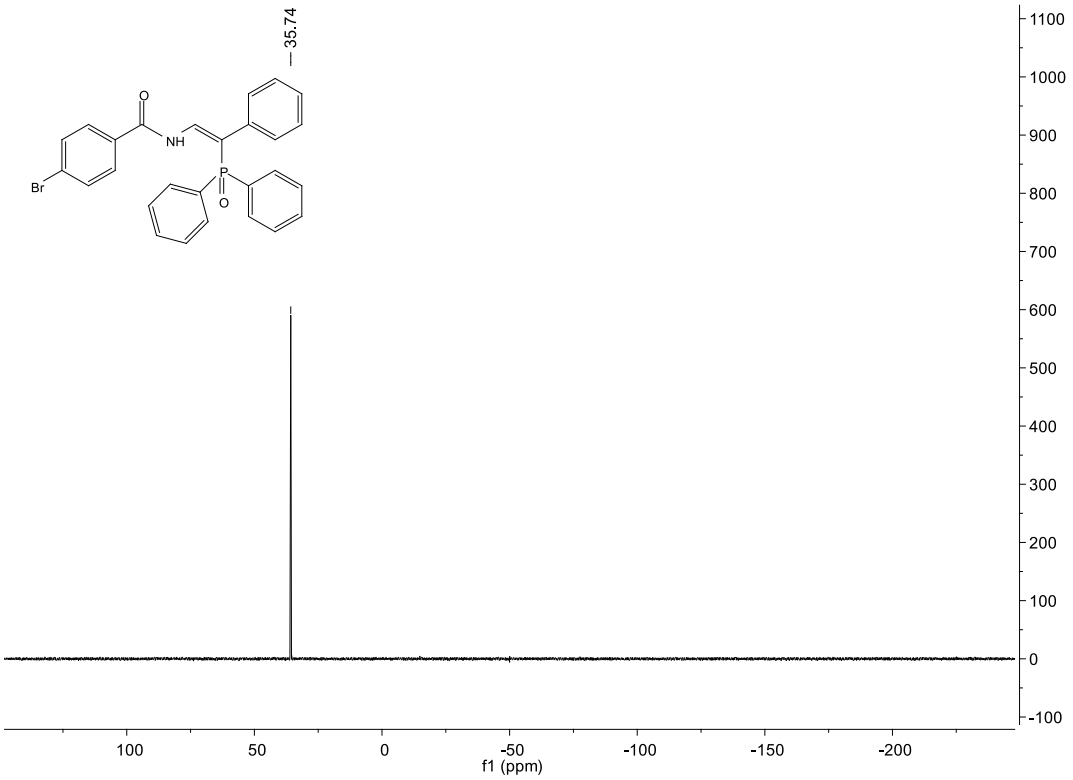



162.14
135.16
131.59
131.27
129.39
128.09
122.70
116.98
115.93
Br
O
NH
P
O
135.16
133.41
131.27
130.26
129.05
128.09
127.97
124.82
122.70
f1 (ppm)
f1 (ppm)

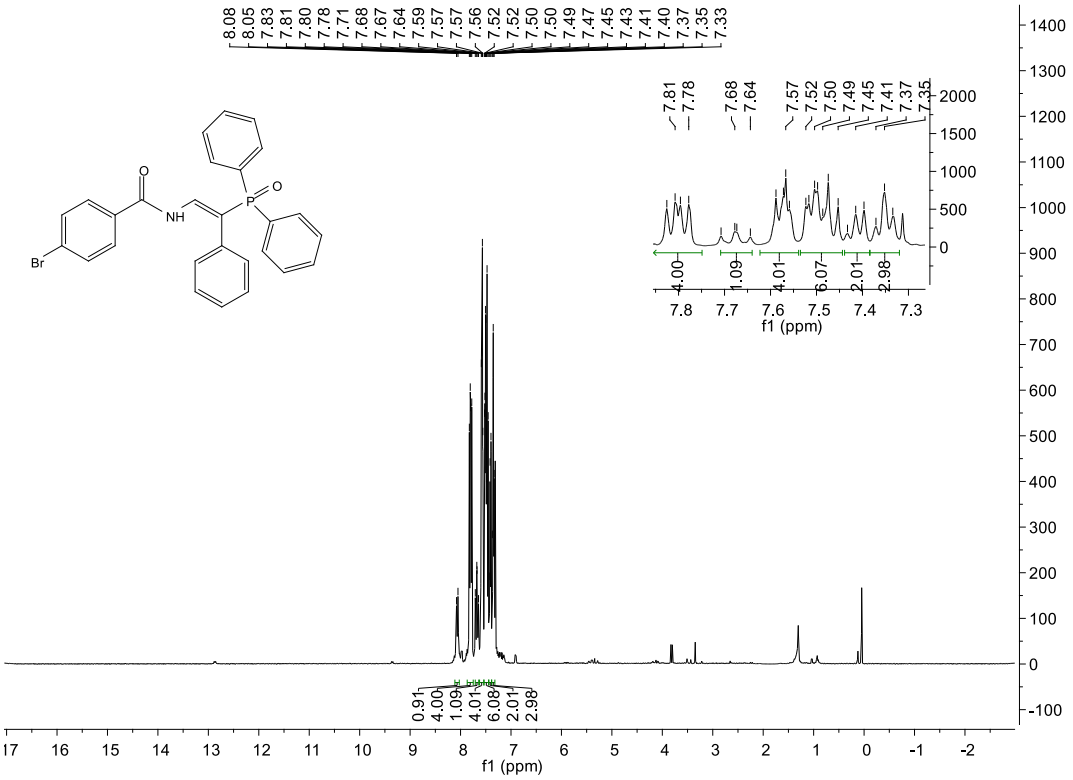

28.44
Br
O
NH
P
O
f1 (ppm)

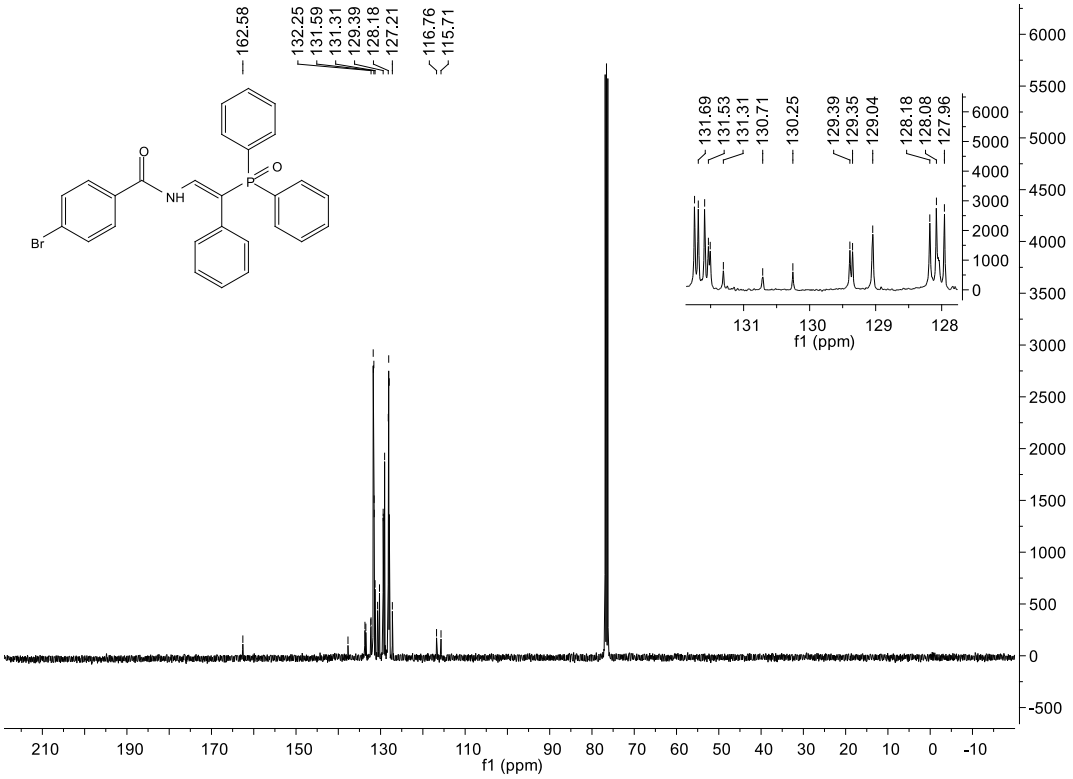
Compound 3e-*Z*

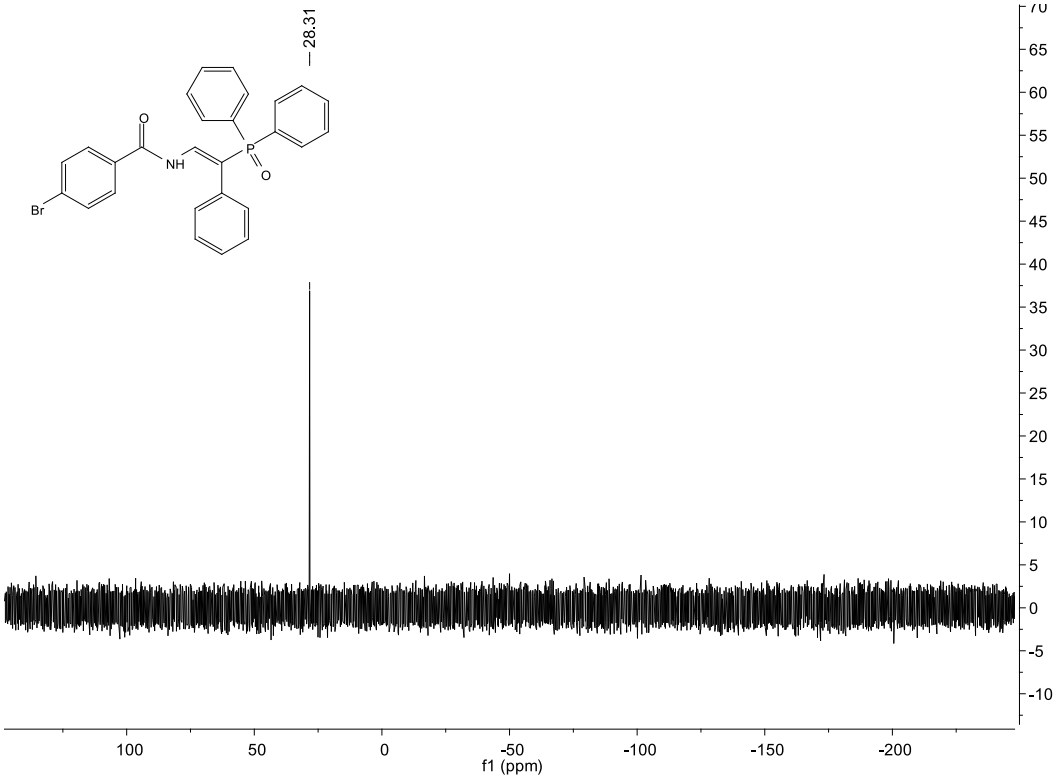




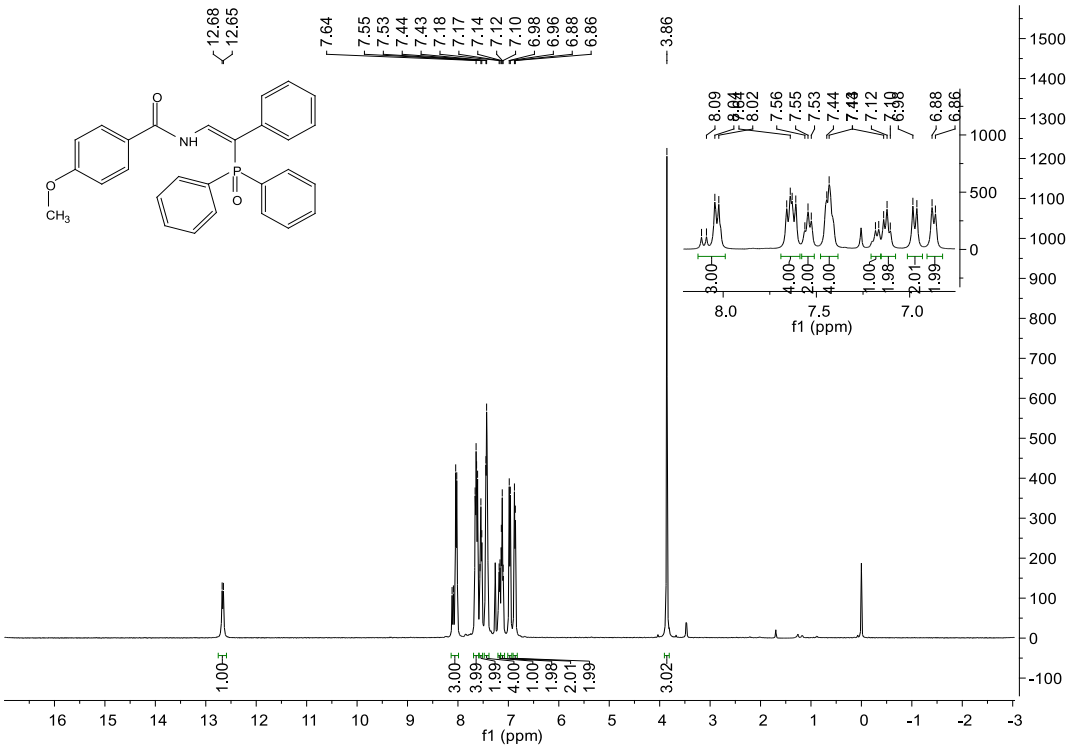
Compound 3e-*E*

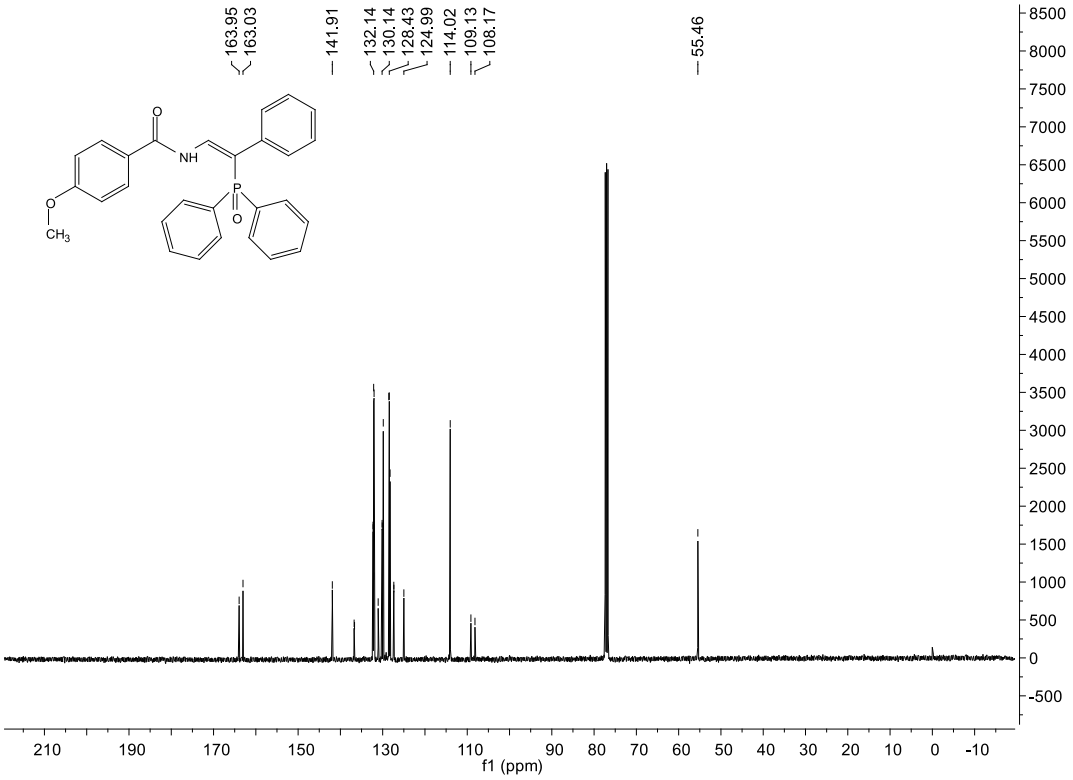


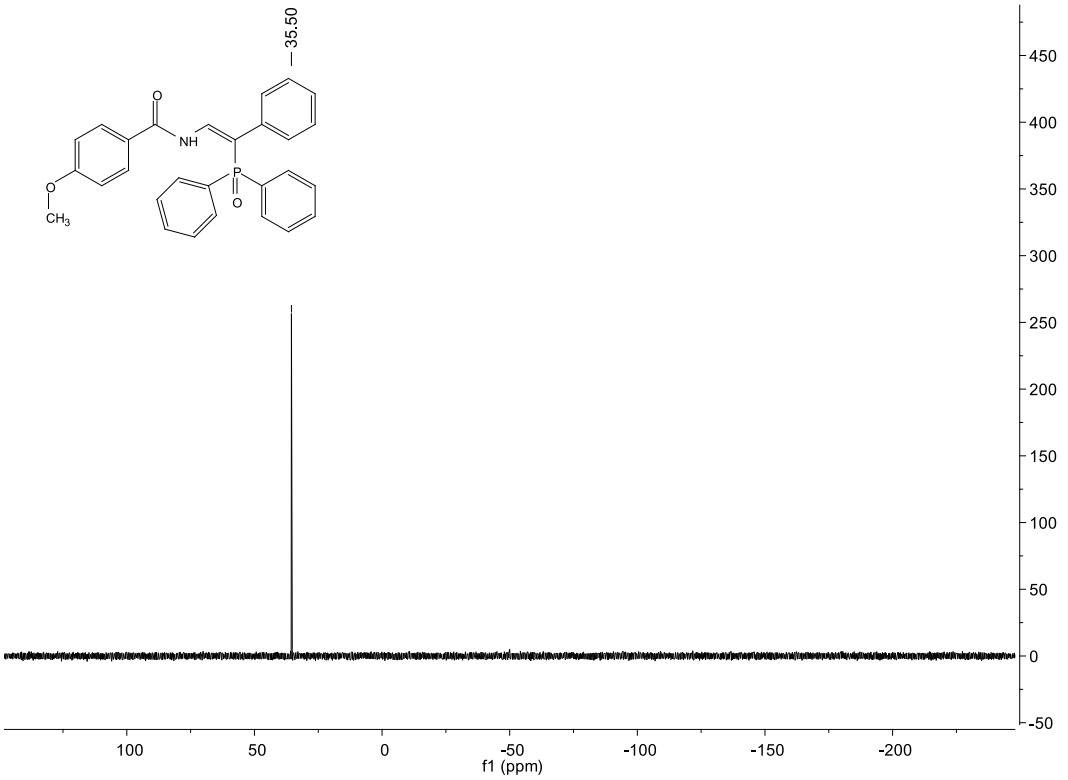

162.58
132.25
131.59
131.31
129.39
128.18
127.21
116.76
115.71
131.69
131.53
131.31
130.71
130.25
129.39
129.35
129.04
128.18
128.08
127.96
O
NH
P
O
Br
f1 (ppm)


28.31
O
NH
P
O
Br
f1 (ppm)

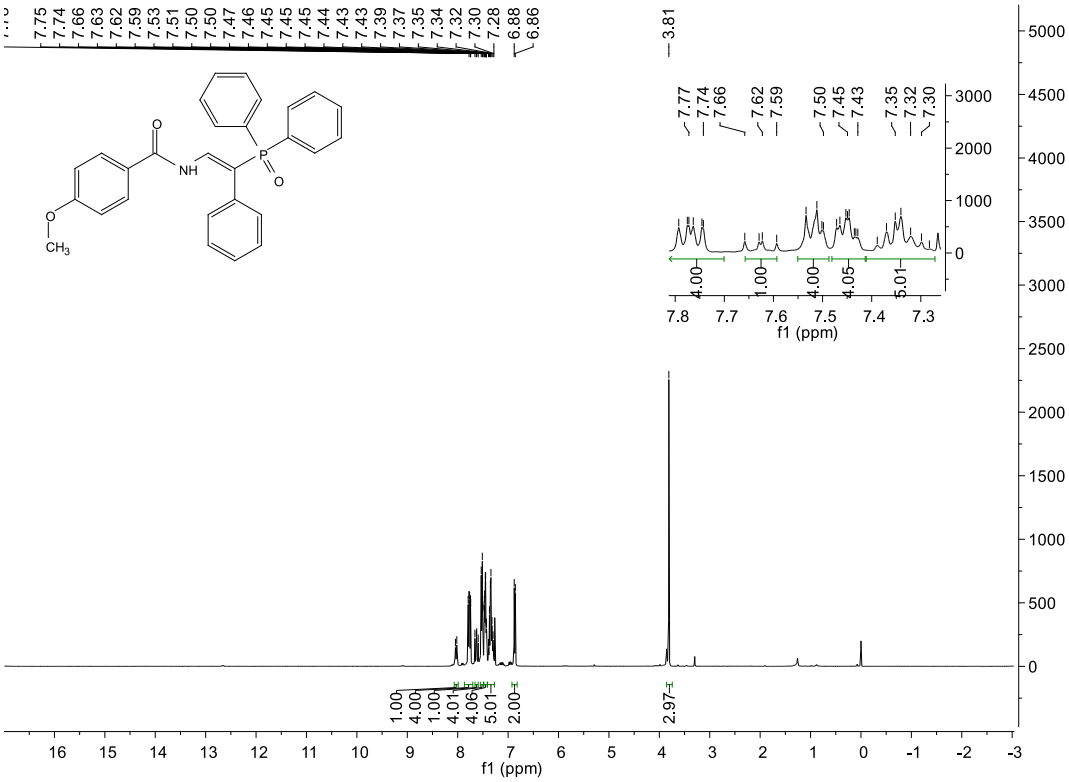
Compound 3f-*Z*

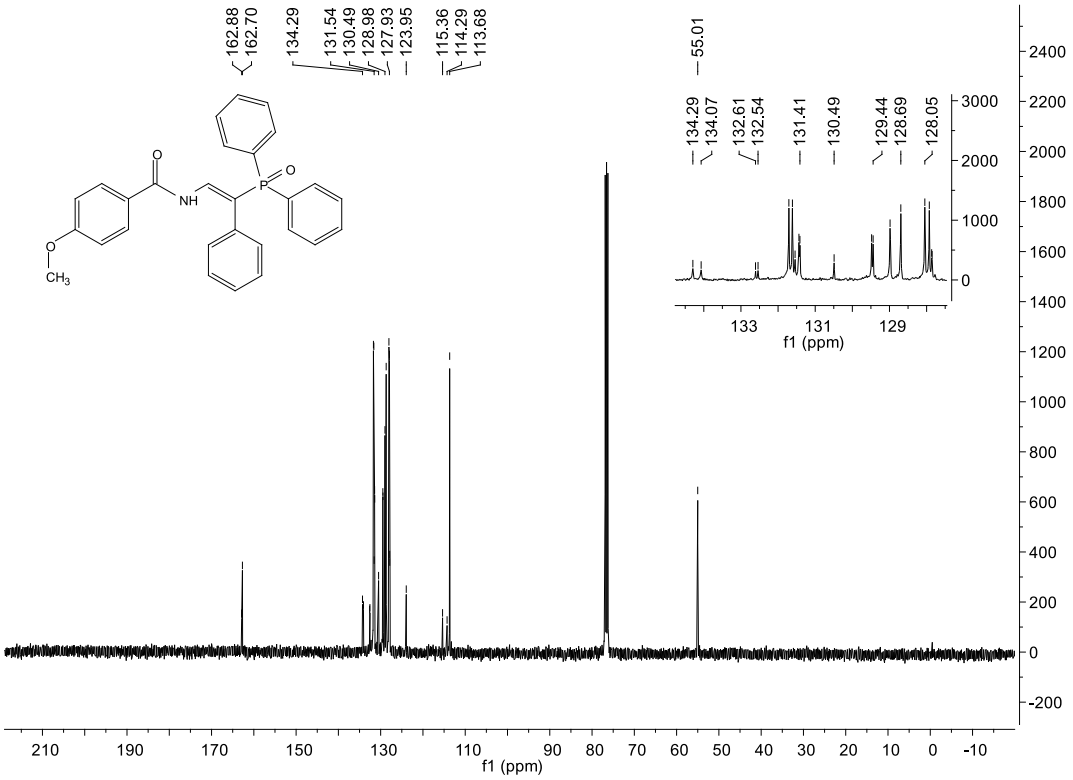


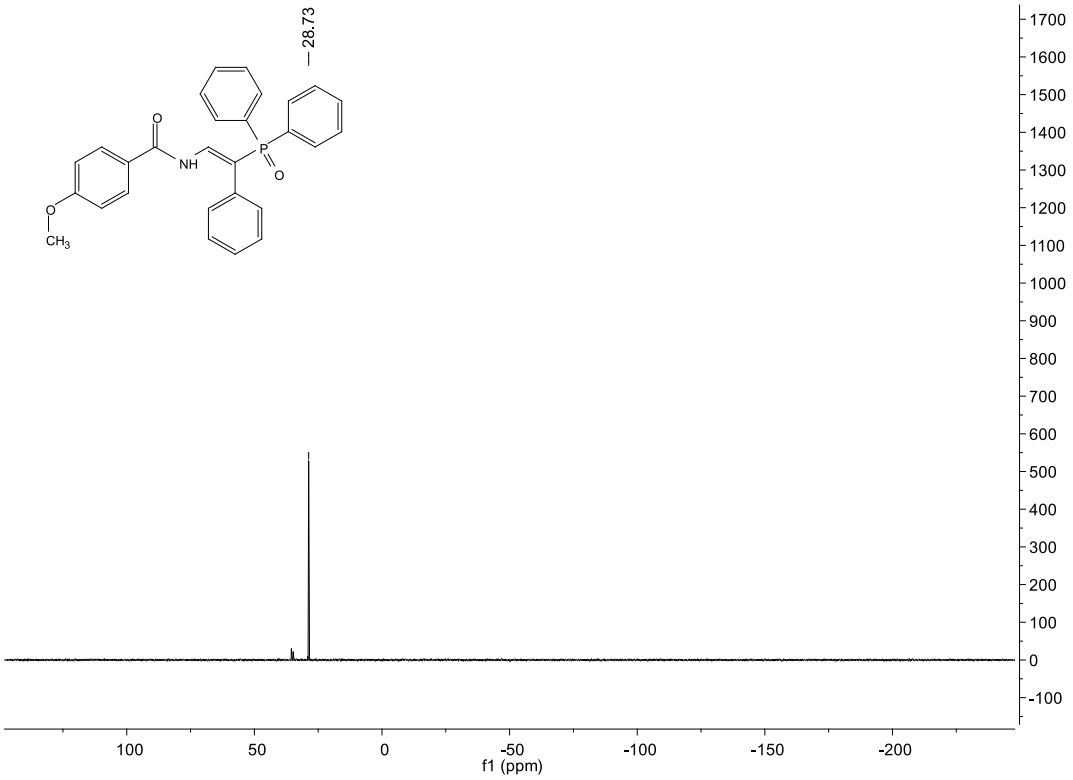




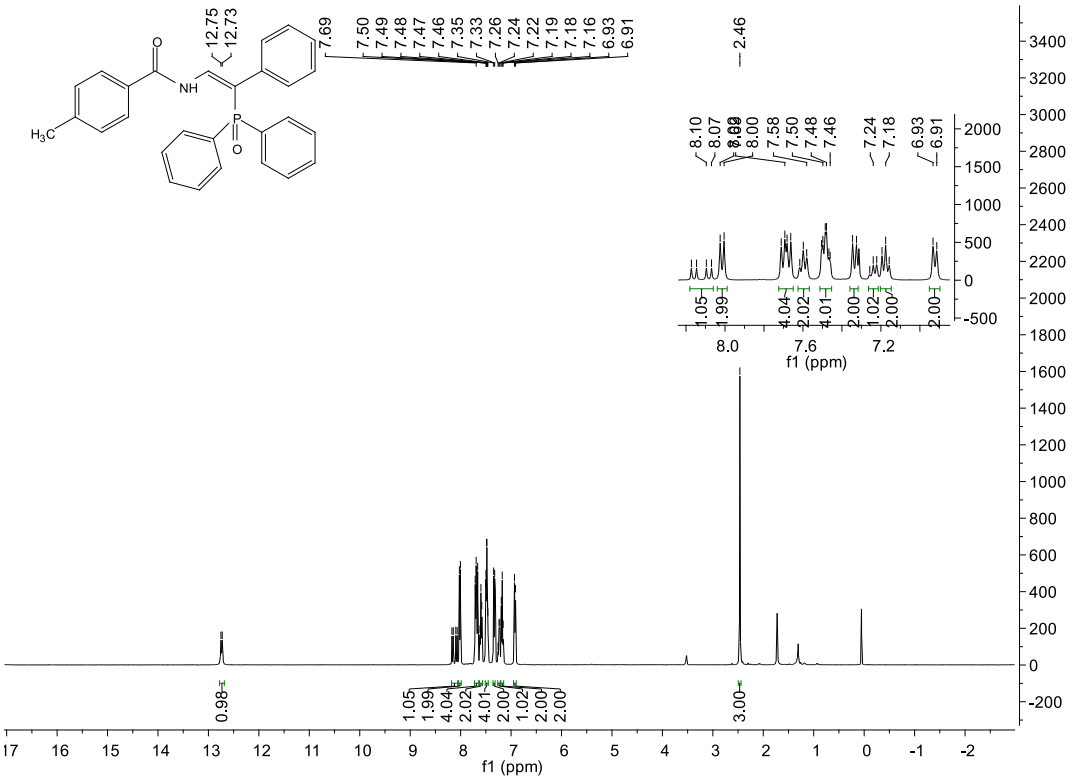
Compound 3f-*E*

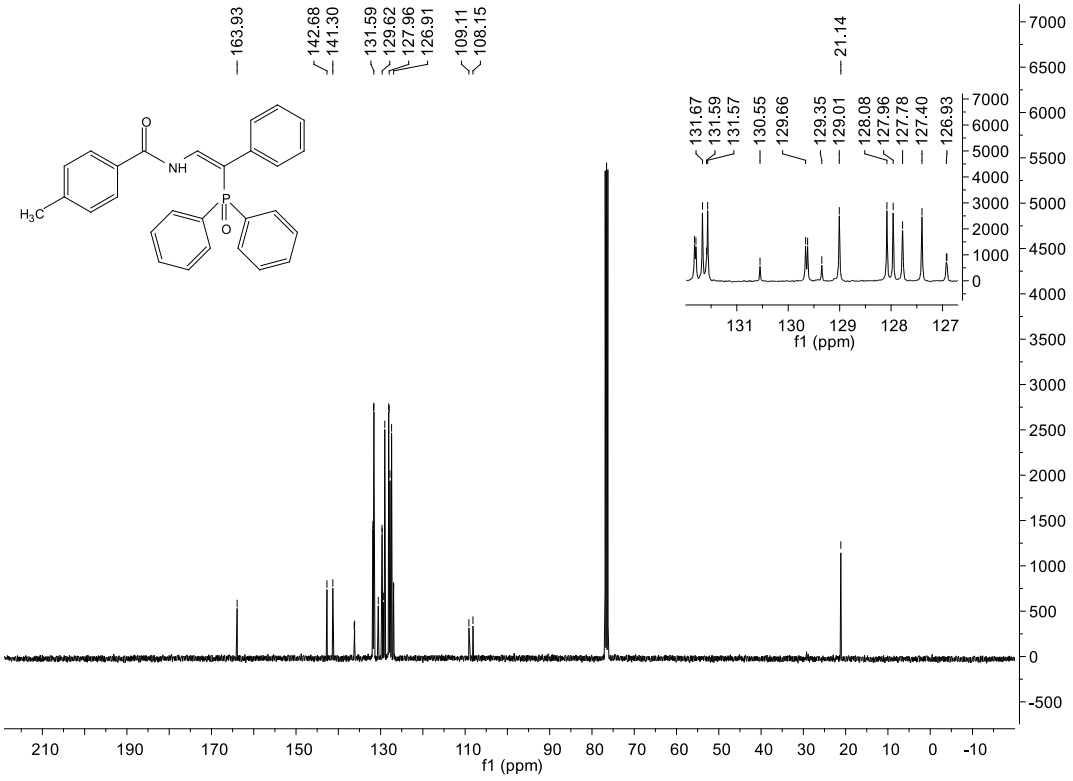



162.88
162.70
134.29
131.54
130.49
128.98
127.93
123.95
115.36
114.29
113.68
55.01
134.29
134.07
132.61
132.54
131.41
130.49
129.44
128.69
128.05
f1 (ppm)
f1 (ppm)

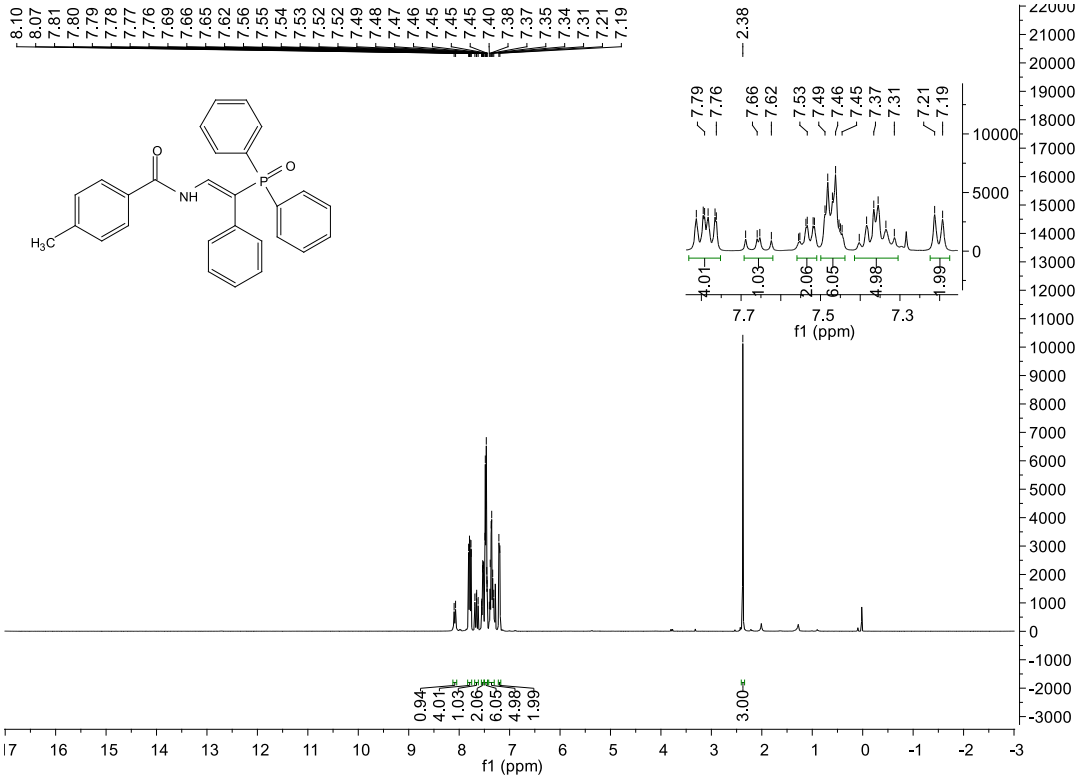

28.73
f1 (ppm)

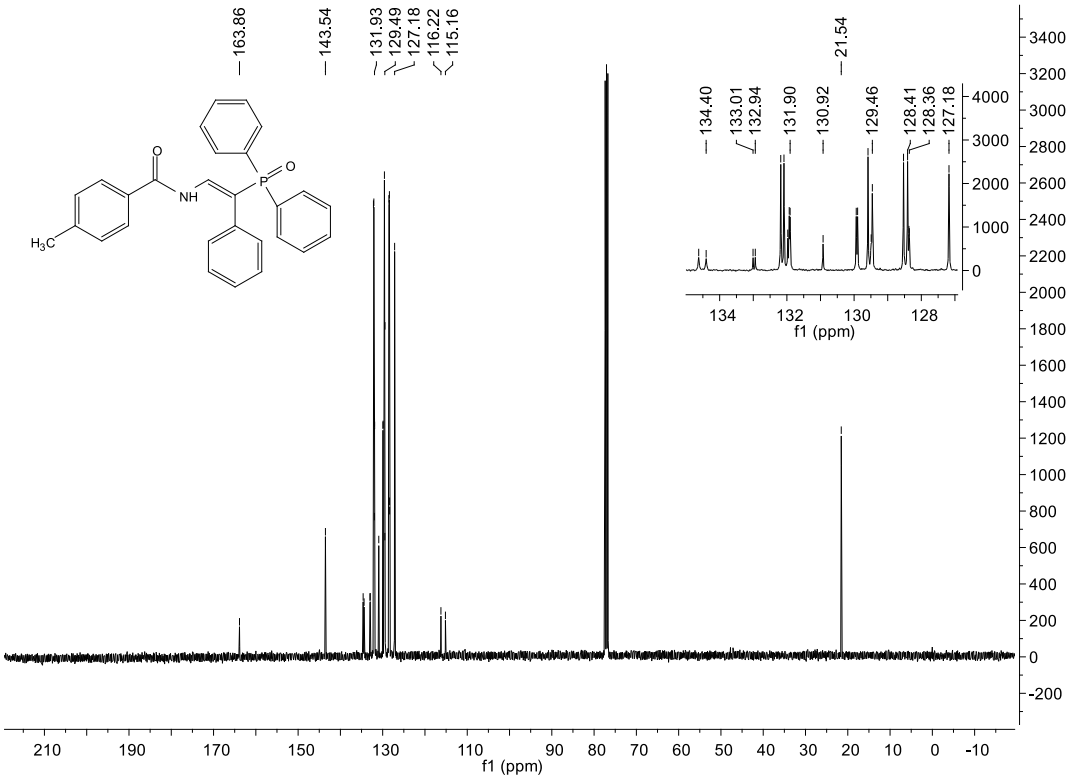
Compound 3g-*Z*

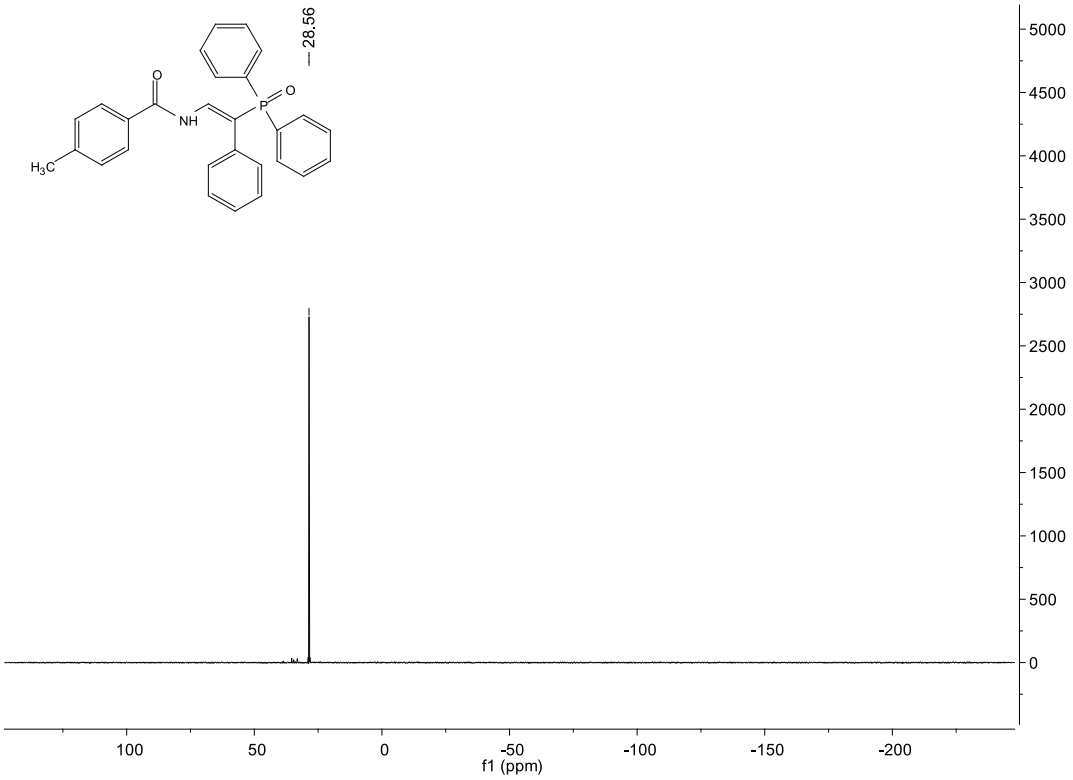




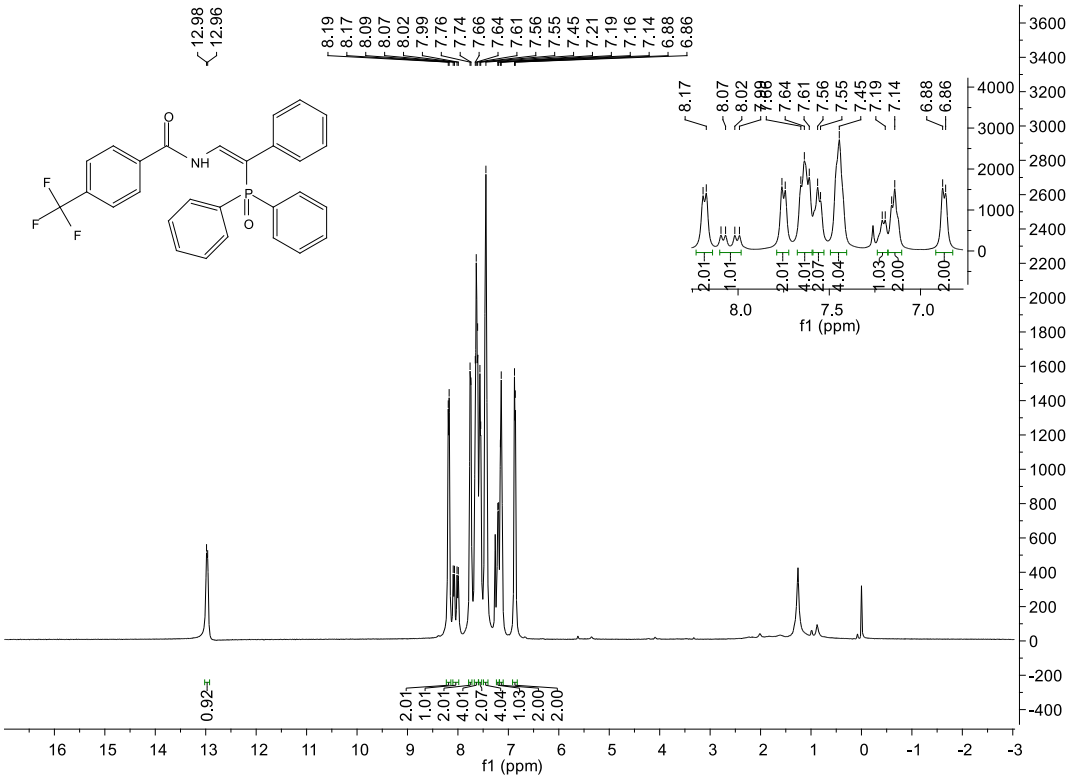
Compound 3g-*E*

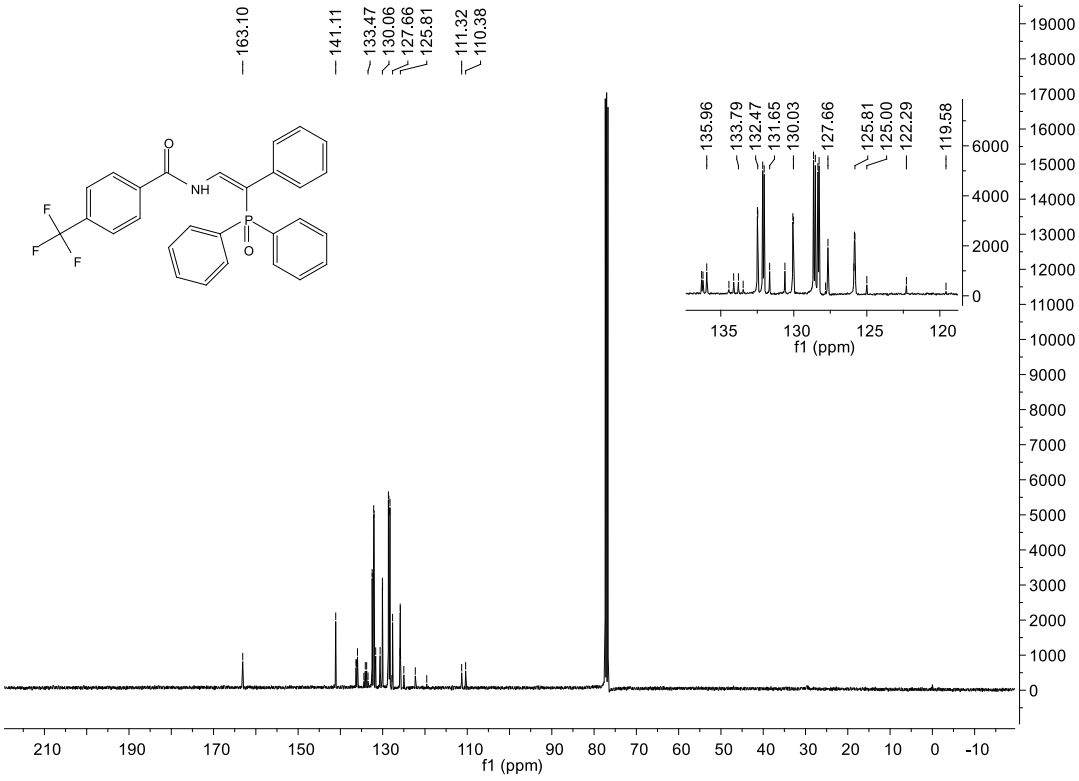


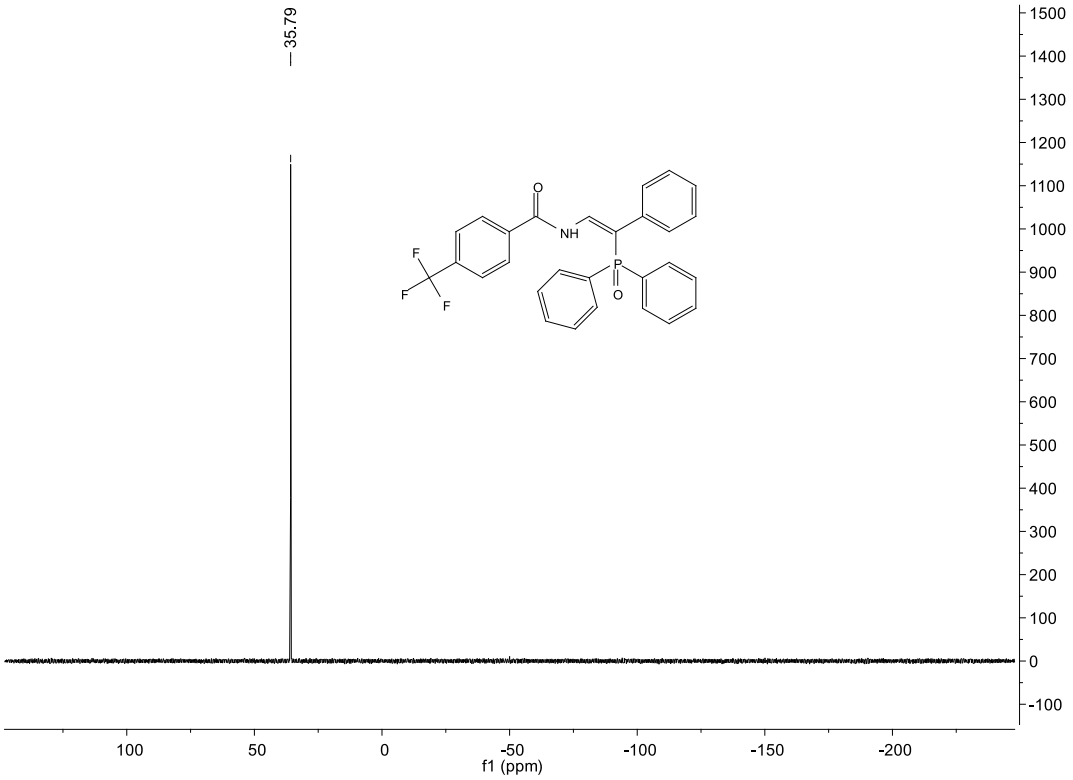

163.86
143.54
131.93
129.49
127.18
116.22
115.16
21.54
134.40
133.01
132.94
131.90
130.92
129.46
128.41
128.36
127.18
f1 (ppm)
f1 (ppm)


28.56
f1 (ppm)

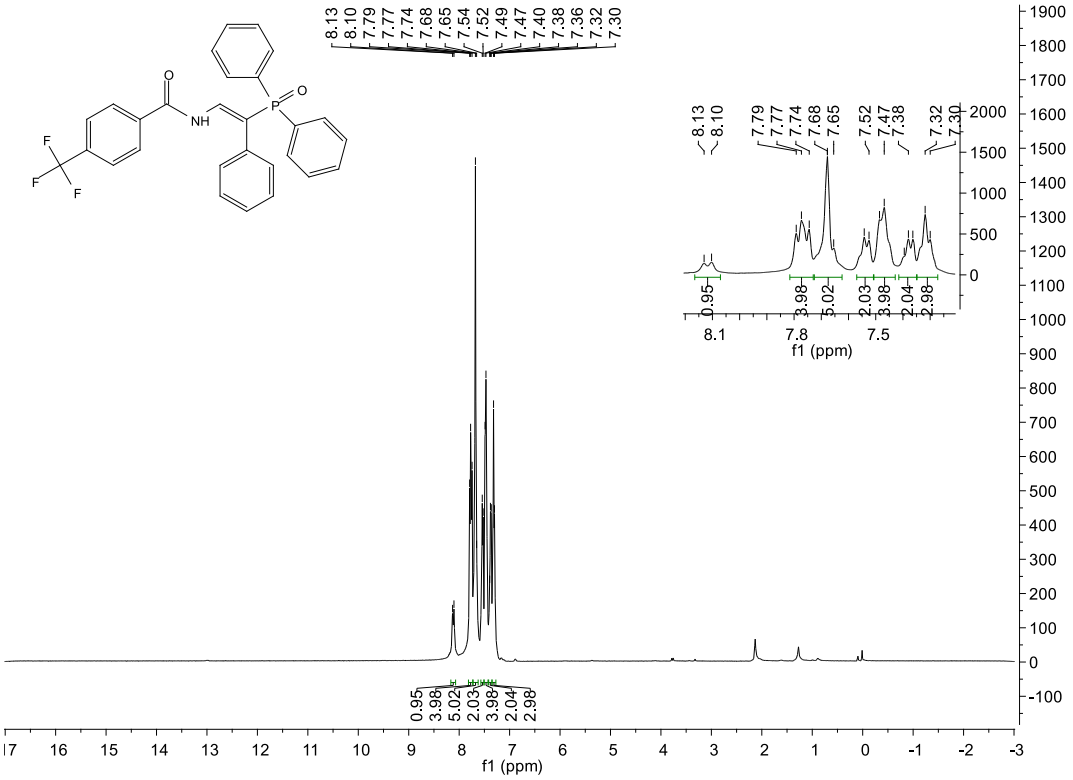
Compound 3h-*Z*

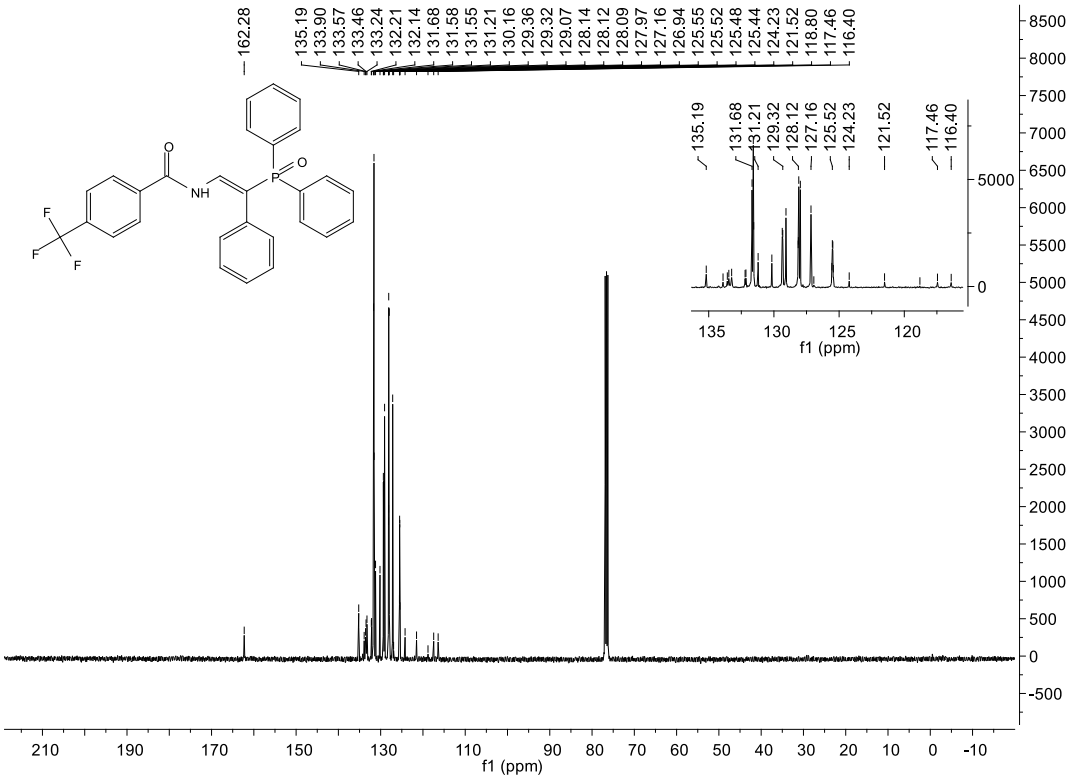


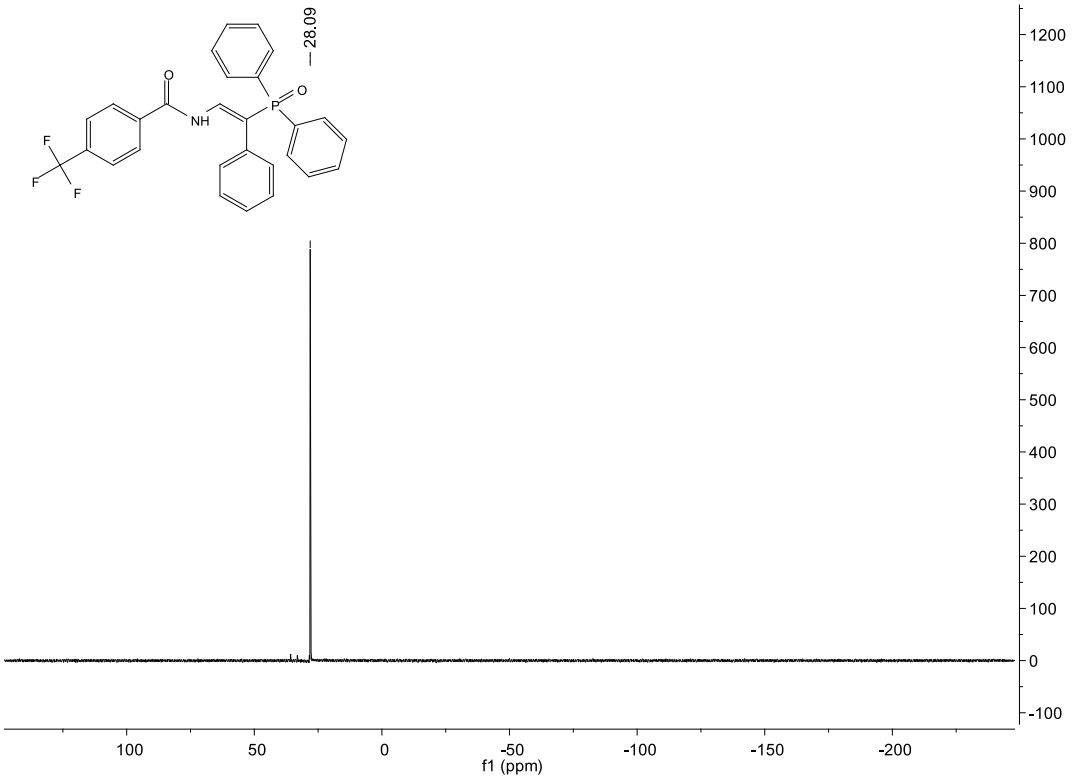




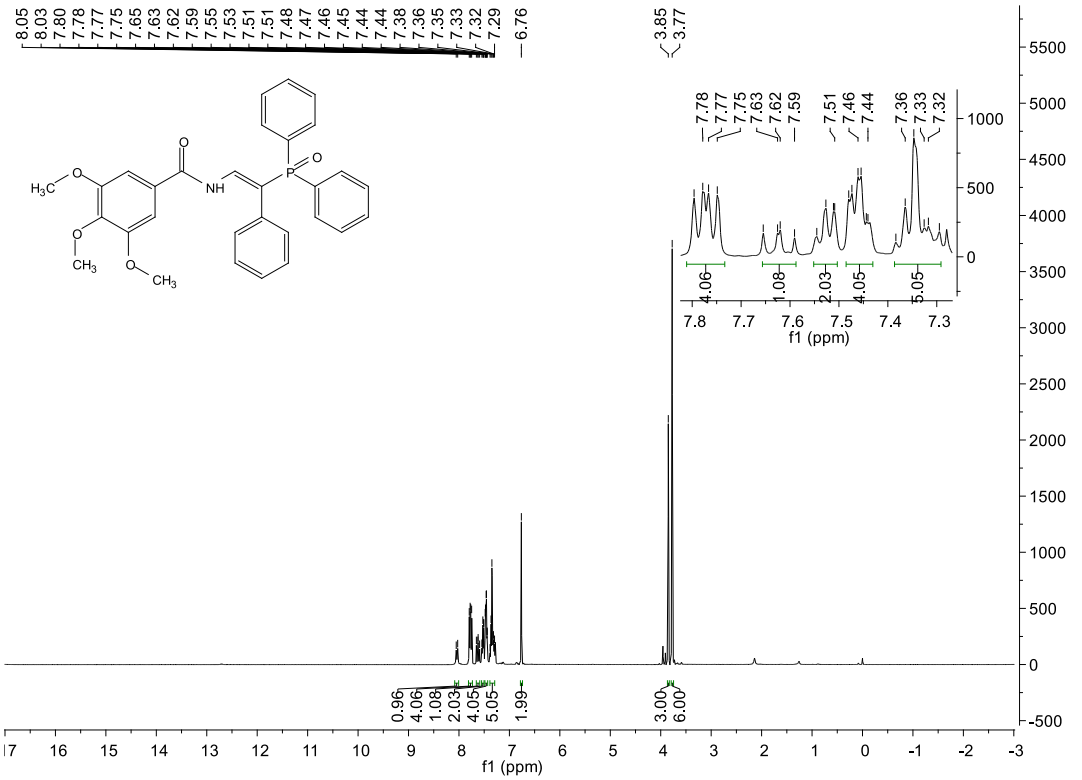
Compound 3h-*E*

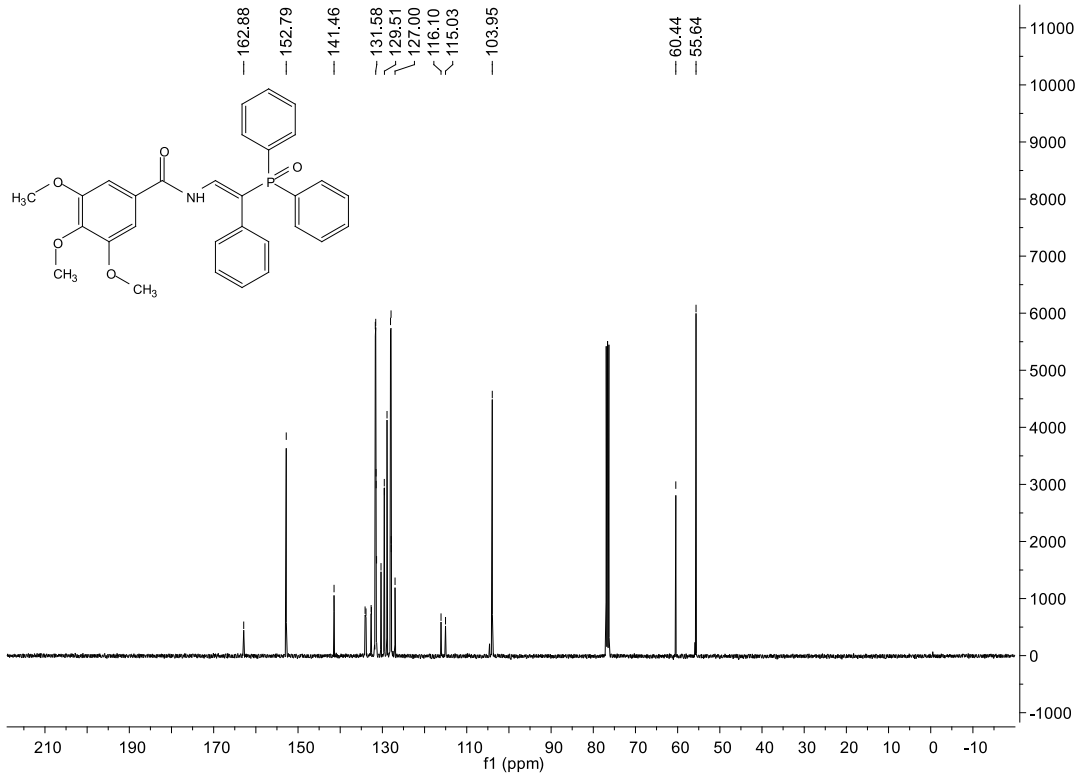


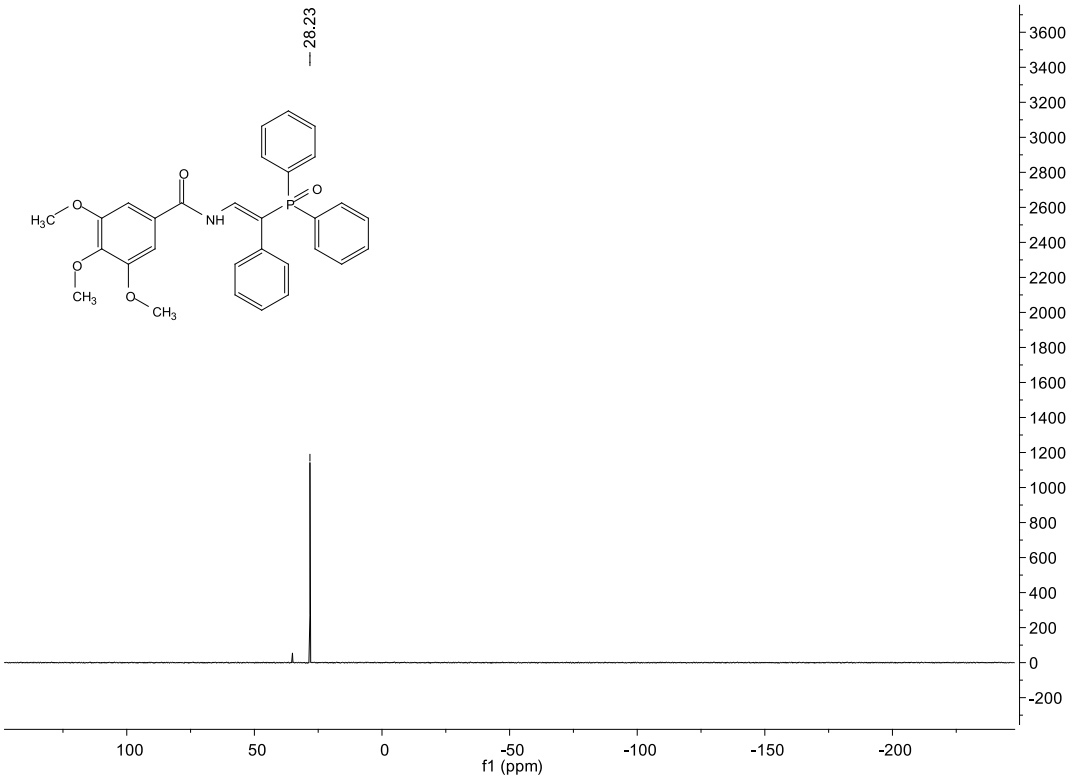

162.28
135.19
133.90
133.57
133.46
133.24
132.21
132.14
131.68
131.58
131.55
131.21
130.16
129.36
129.32
129.07
128.14
128.12
128.09
127.97
127.16
126.94
125.55
125.52
125.48
125.44
124.23
121.52
118.80
117.46
116.40
O
NH
P
O
F
F
F
135.19
131.68
131.21
129.32
128.12
127.16
125.52
124.23
121.52
117.46
116.40
5000
0
135
130
125
120
f1 (ppm)
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


28.09
O
NH
P
O
F
F
F
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
100
50
0
-50
-100
-150
-200
f1 (ppm)

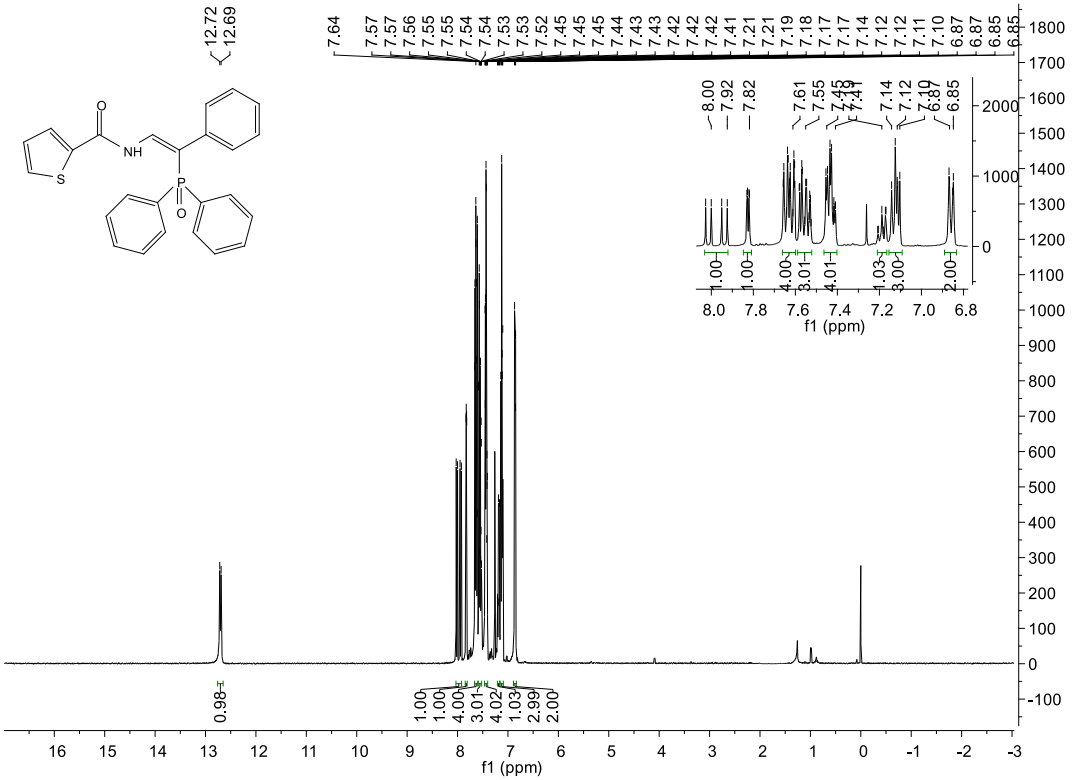
Compound 3i

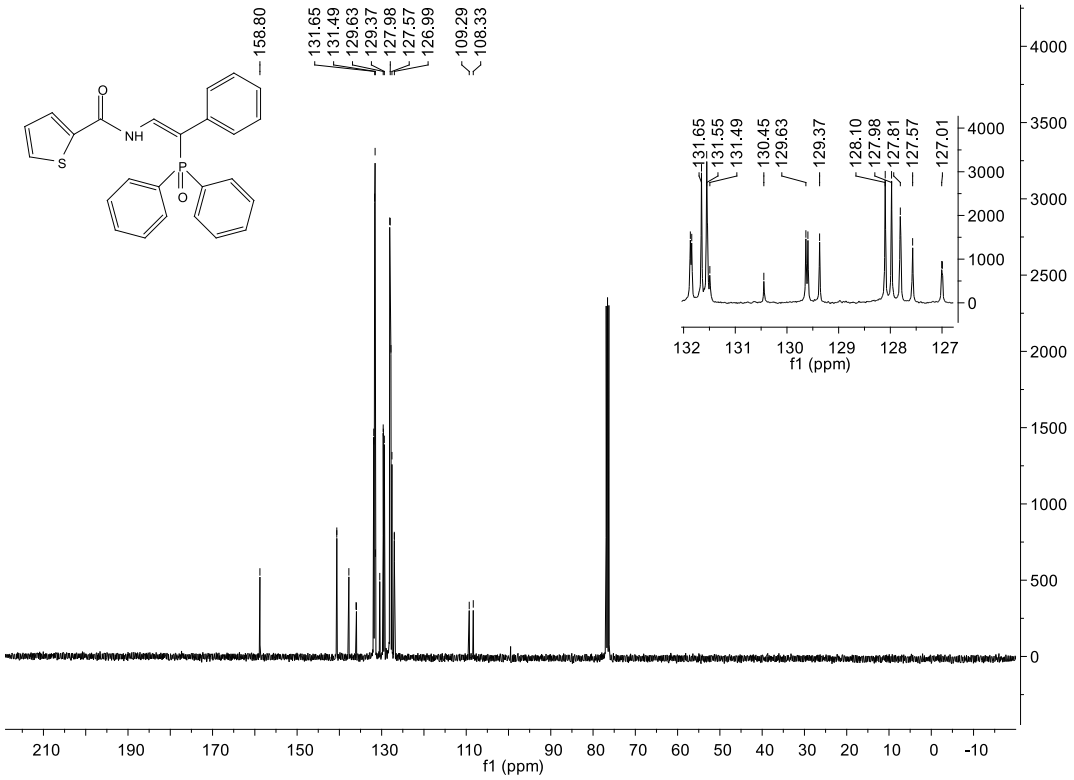

8.05
8.03
7.80
7.78
7.77
7.75
7.65
7.63
7.62
7.59
7.55
7.53
7.51
7.51
7.48
7.47
7.46
7.45
7.44
7.44
7.38
7.36
7.35
7.33
7.32
7.29
6.76
3.85
3.77
O
NH
P
O
H3C
O
O
CH3
O
CH3
7.78
7.77
7.75
7.63
7.62
7.59
7.51
7.46
7.44
7.36
7.33
7.32
4.06
1.08
2.03
4.05
5.05
7.8
7.7
7.6
7.5
7.4
7.3
f1 (ppm)
0.96
4.06
1.08
2.03
4.05
5.05
1.99
3.00
6.00
f1 (ppm)

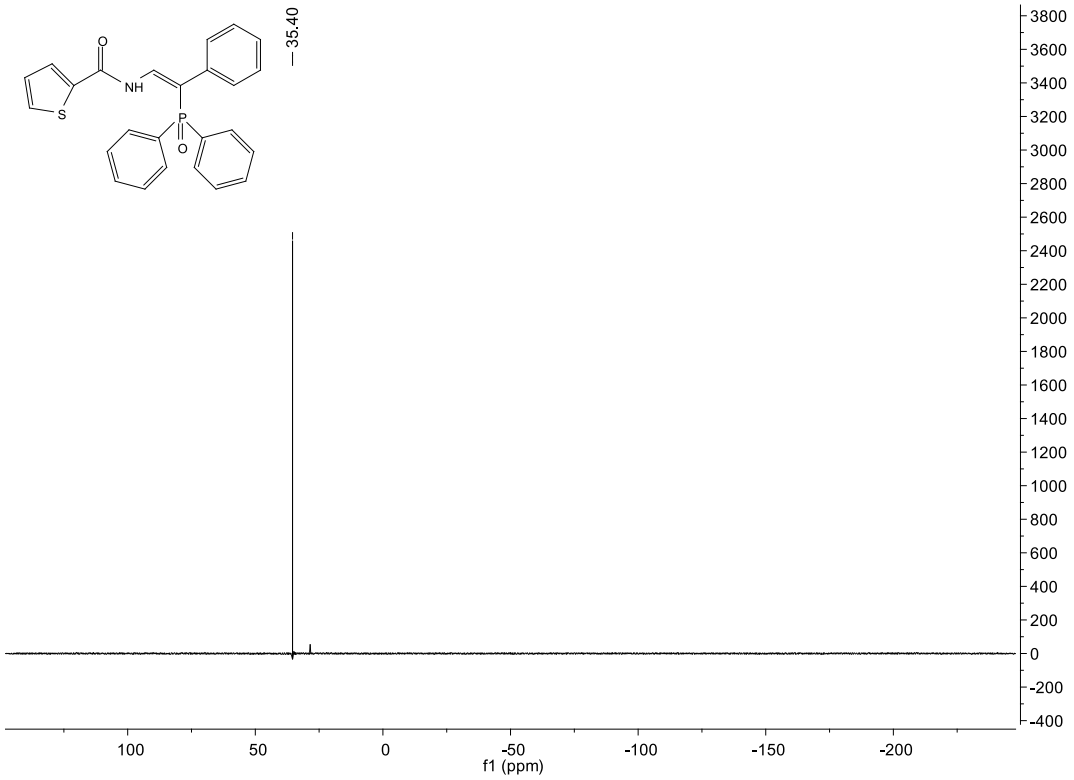

162.88
152.79
141.46
131.58
129.51
127.00
116.10
115.03
103.95
60.44
55.64
O
NH
P
O
H3C
O
O
CH3
O
CH3
f1 (ppm)



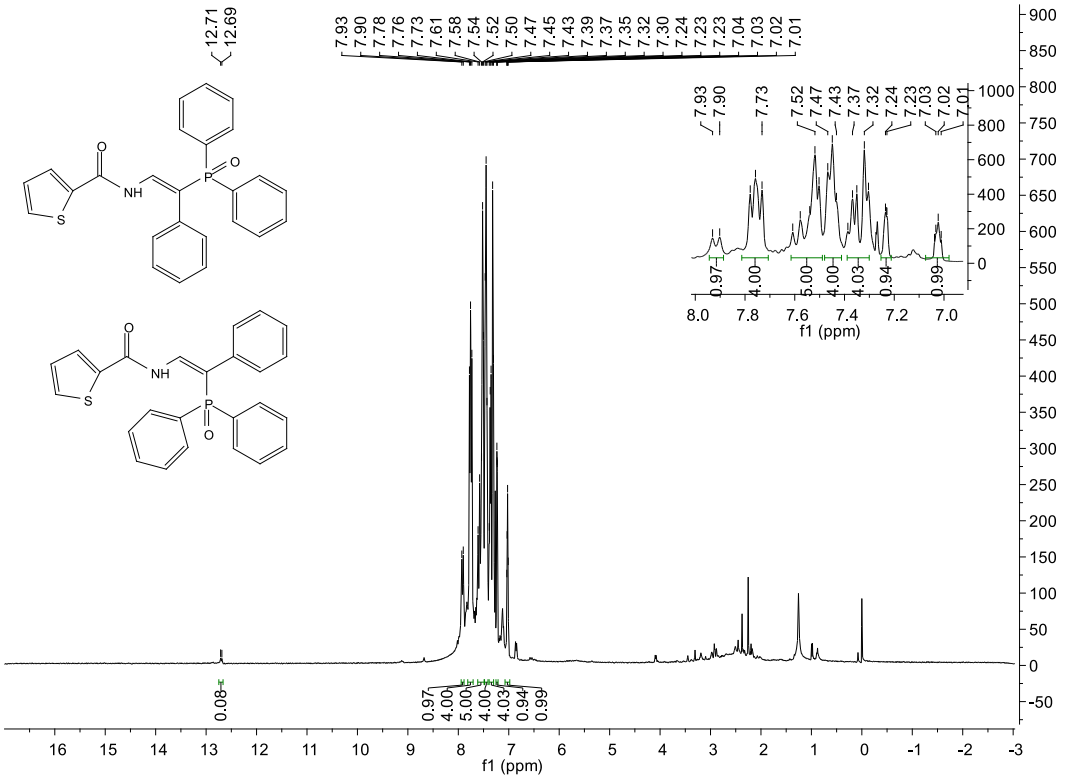
Compound 3j-*Z*

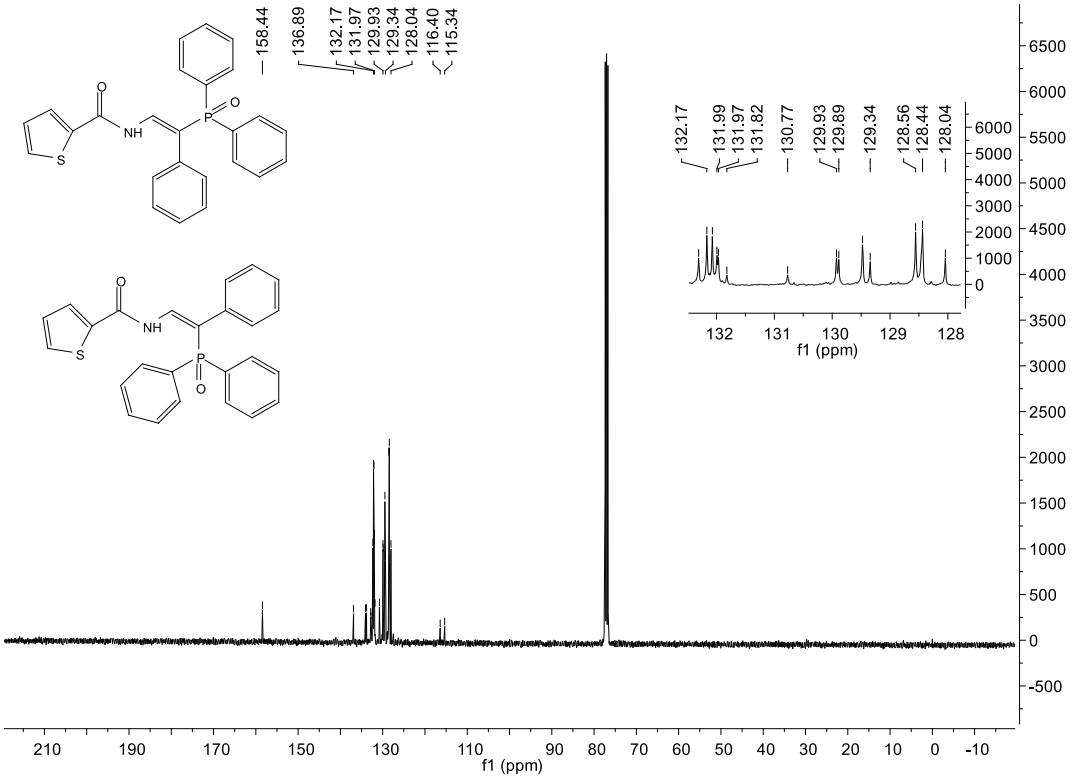


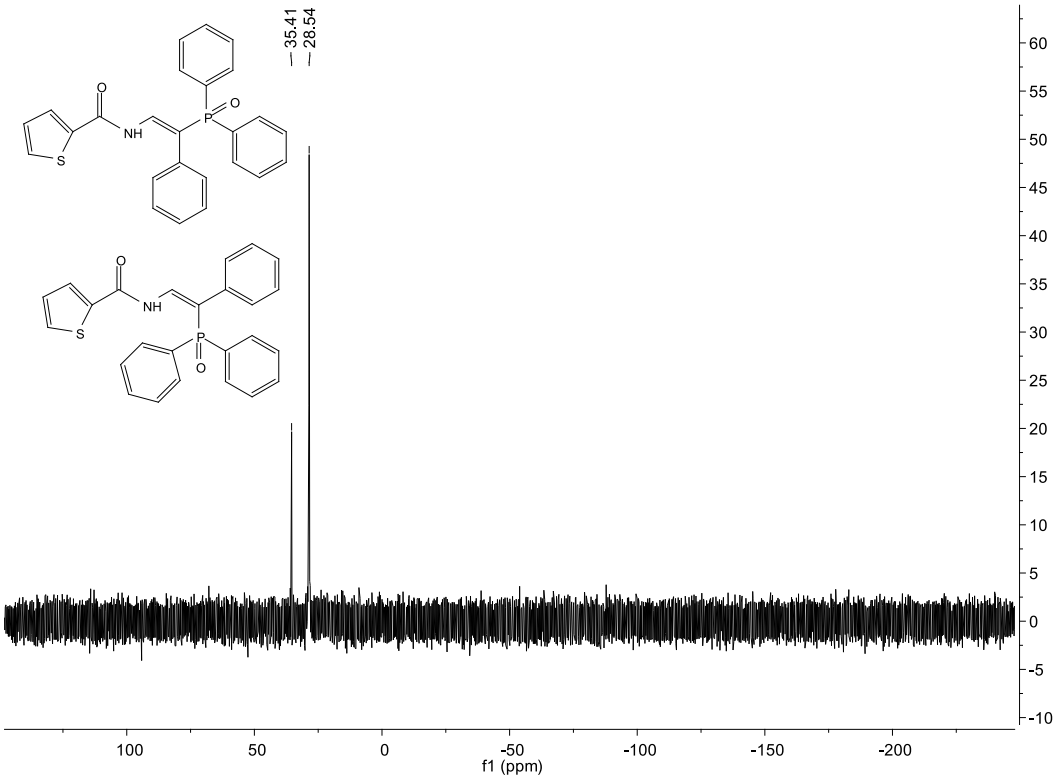

158.80
131.65
131.49
129.63
129.37
127.98
127.57
126.99
109.29
108.33
O
NH
S
P
O
131.65
131.55
131.49
130.45
129.63
129.37
128.10
127.98
127.81
127.57
127.01
132
131
130
129
128
127
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


35.40
O
NH
S
P
O
100
50
0
-50
-100
-150
-200
f1 (ppm)

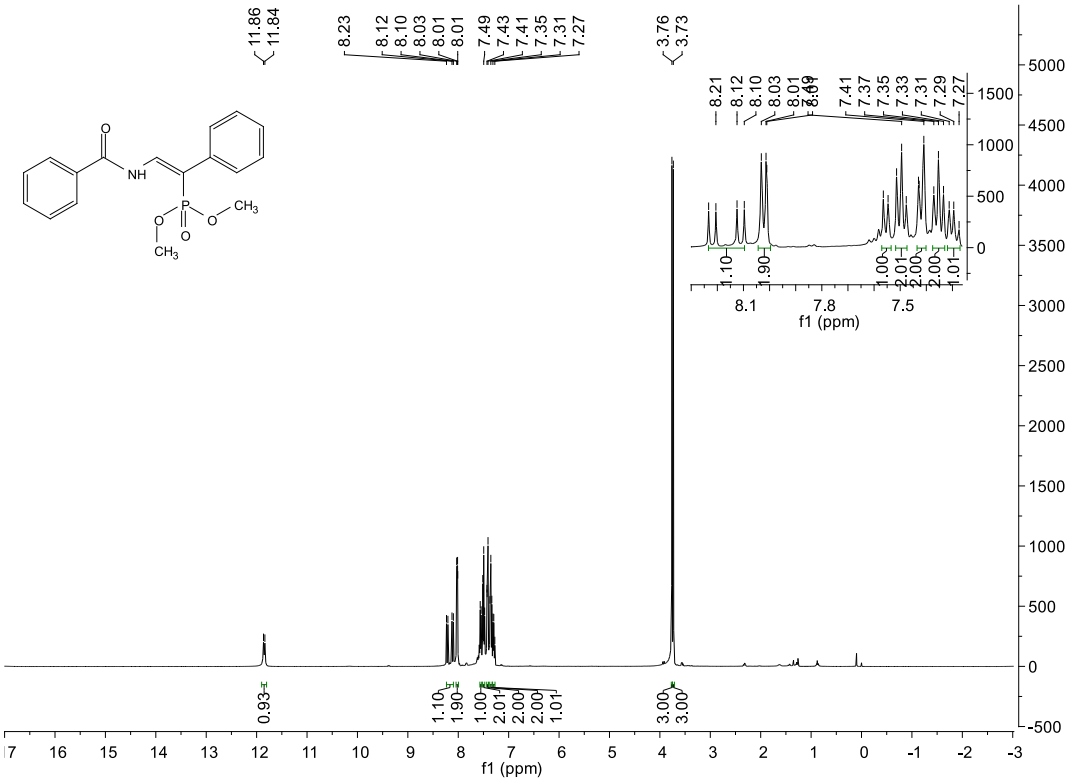
Mixture of 3j-*E* and 3j-*Z*

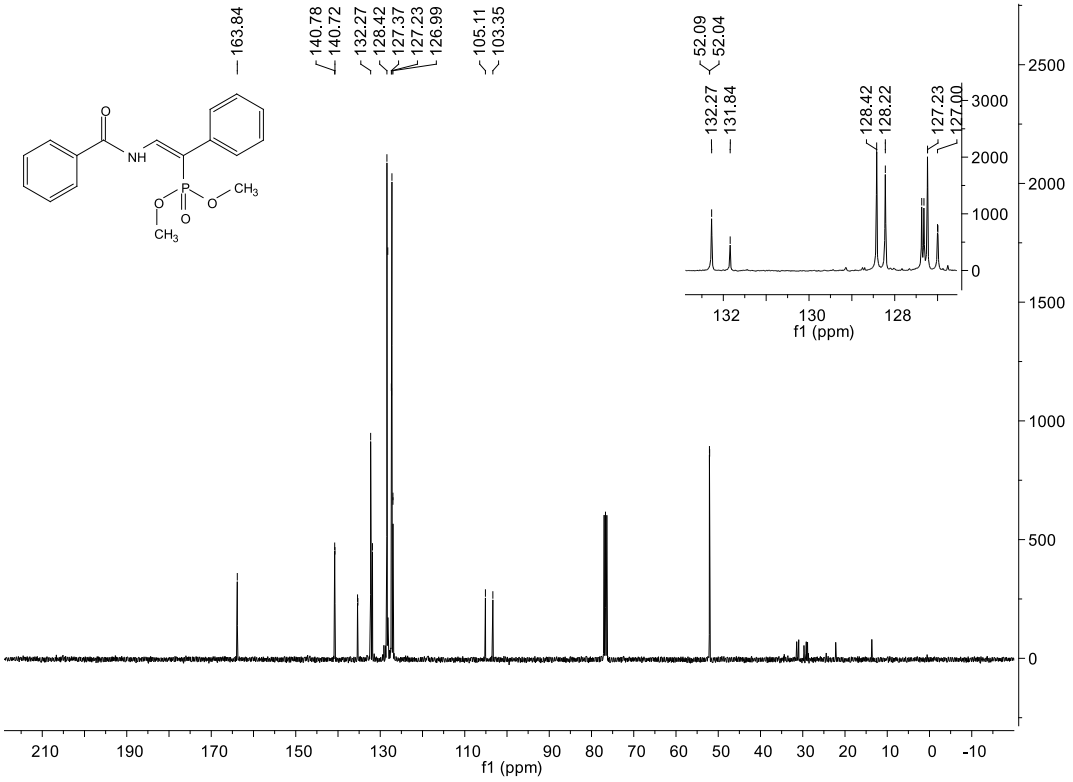


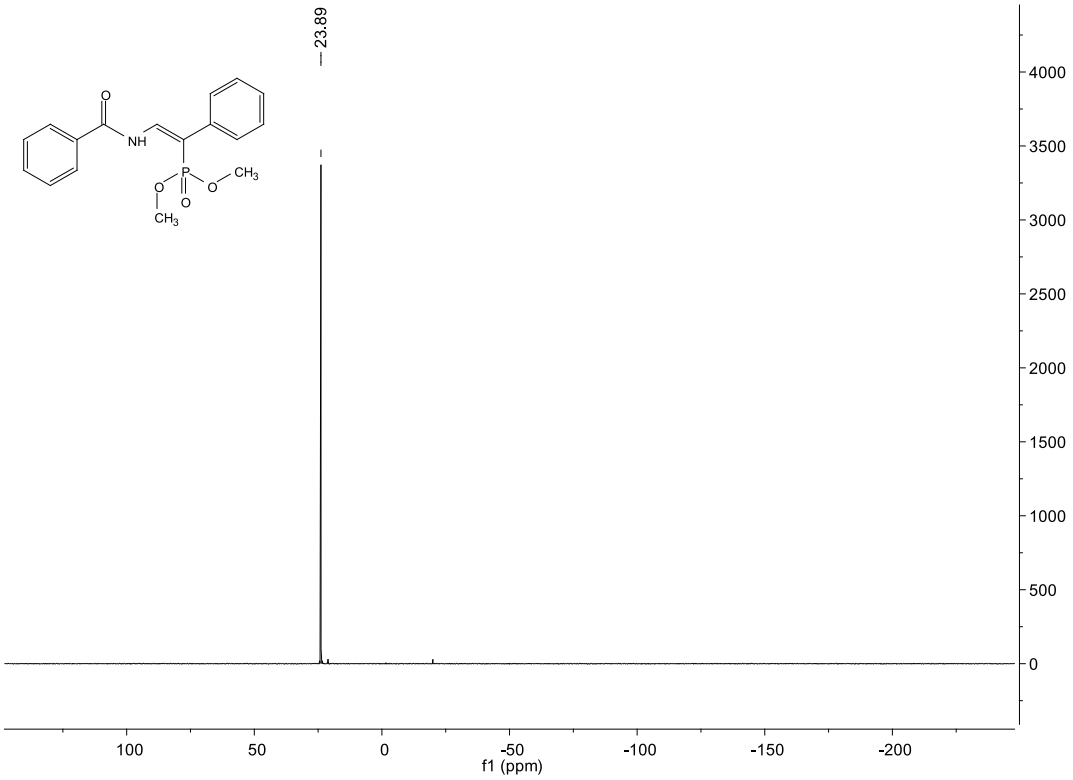




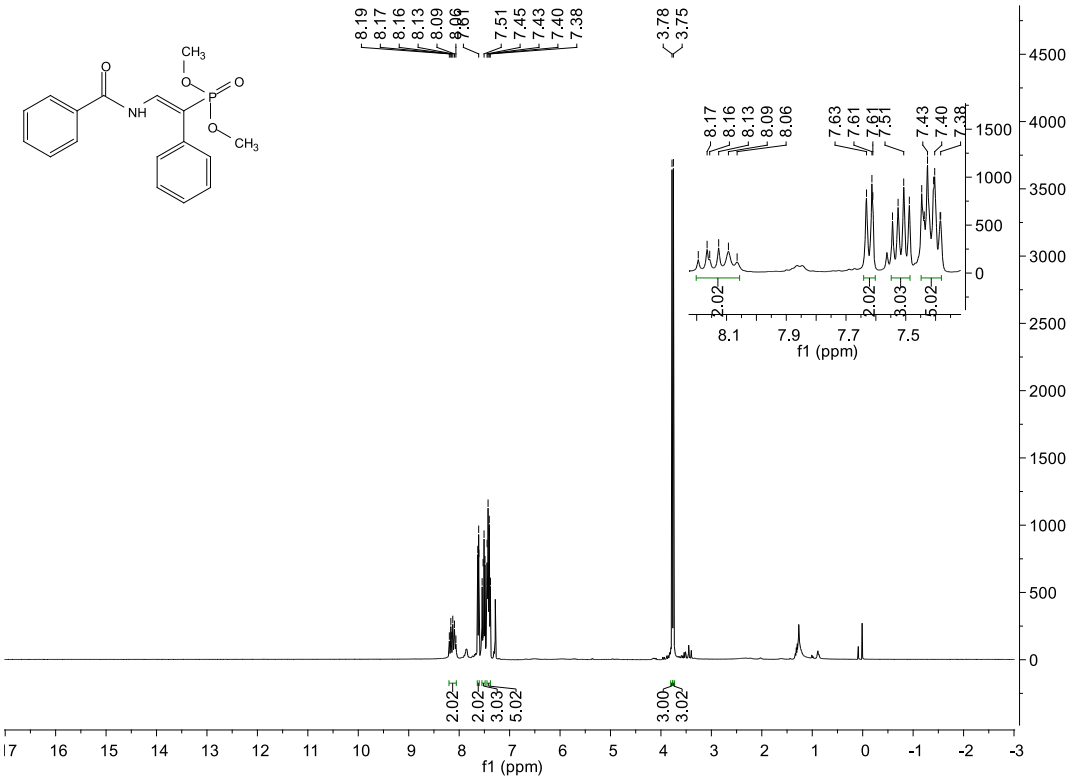
Compound 3k-*Z*

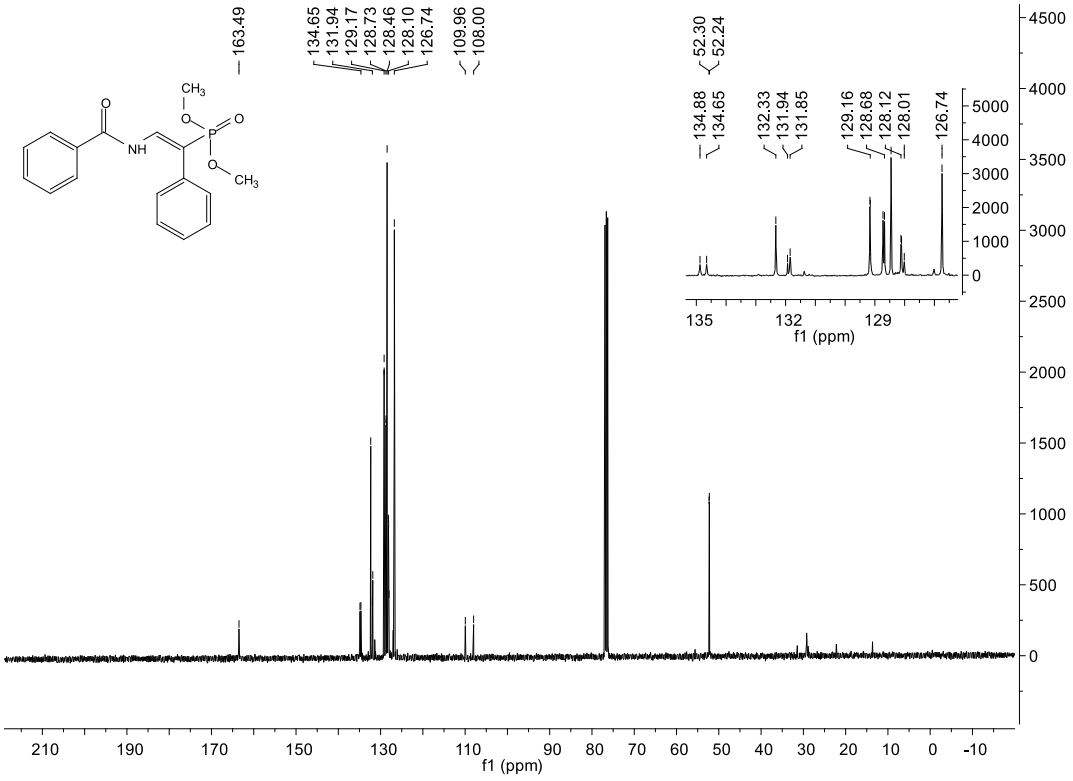


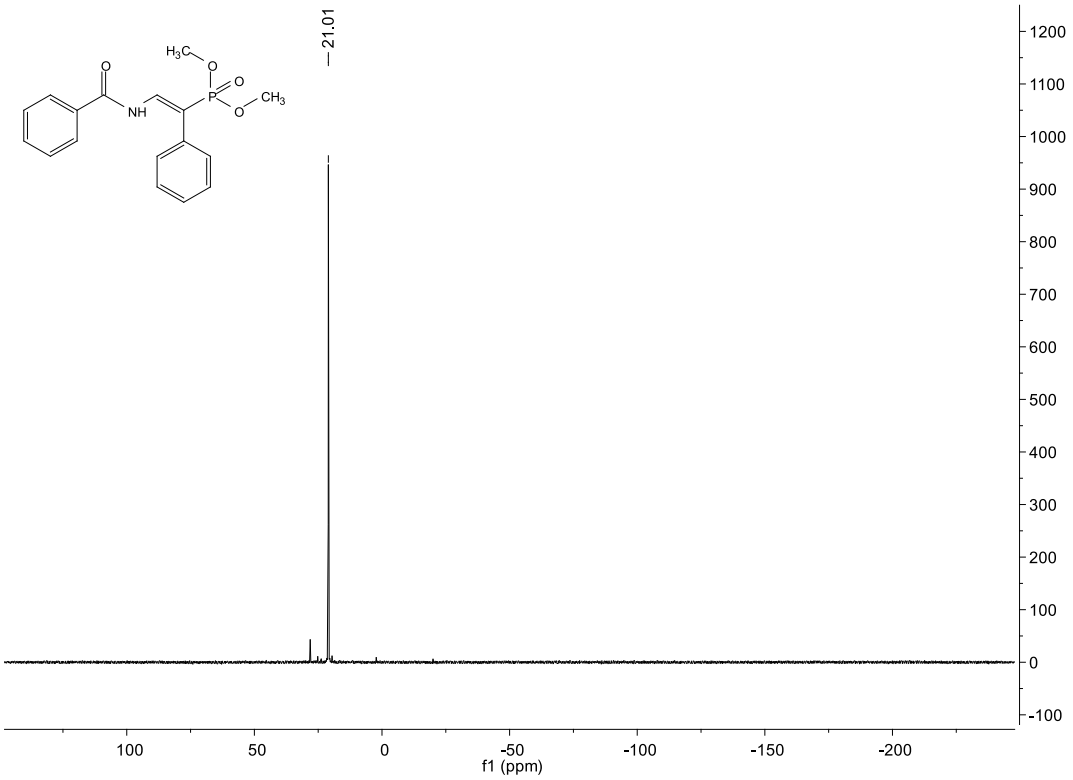

163.84
140.78
140.72
132.27
128.42
127.37
127.23
126.99
105.11
103.35
52.09
52.04
132.27
131.84
128.42
128.22
127.23
127.00
NH
O
O
P
O
CH3
O
CH3
f1 (ppm)


23.89
NH
O
O
P
O
CH3
O
CH3
f1 (ppm)

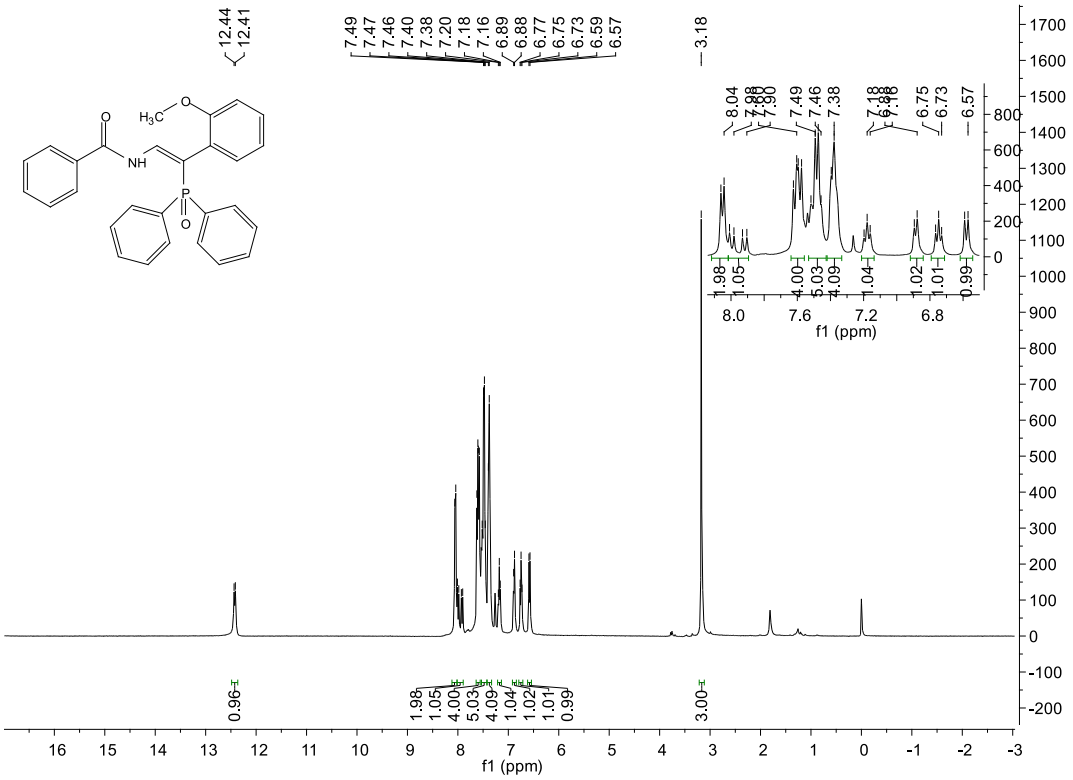
Compound **3k-*E***

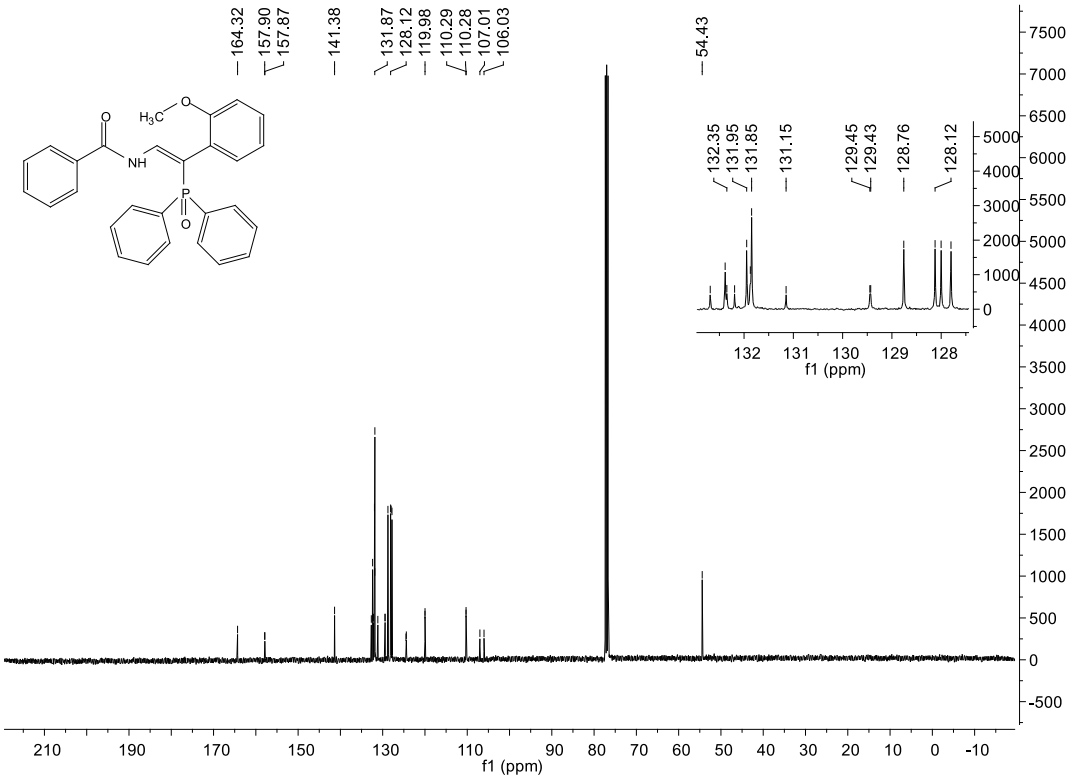


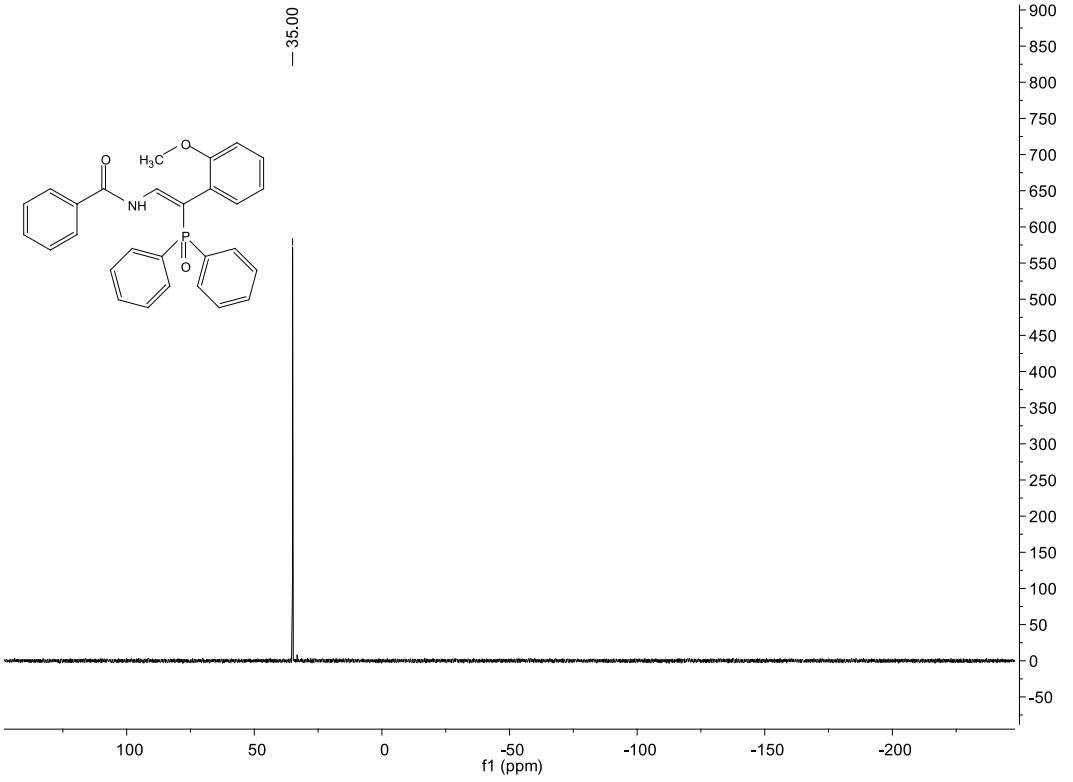



21.01
f1 (ppm)

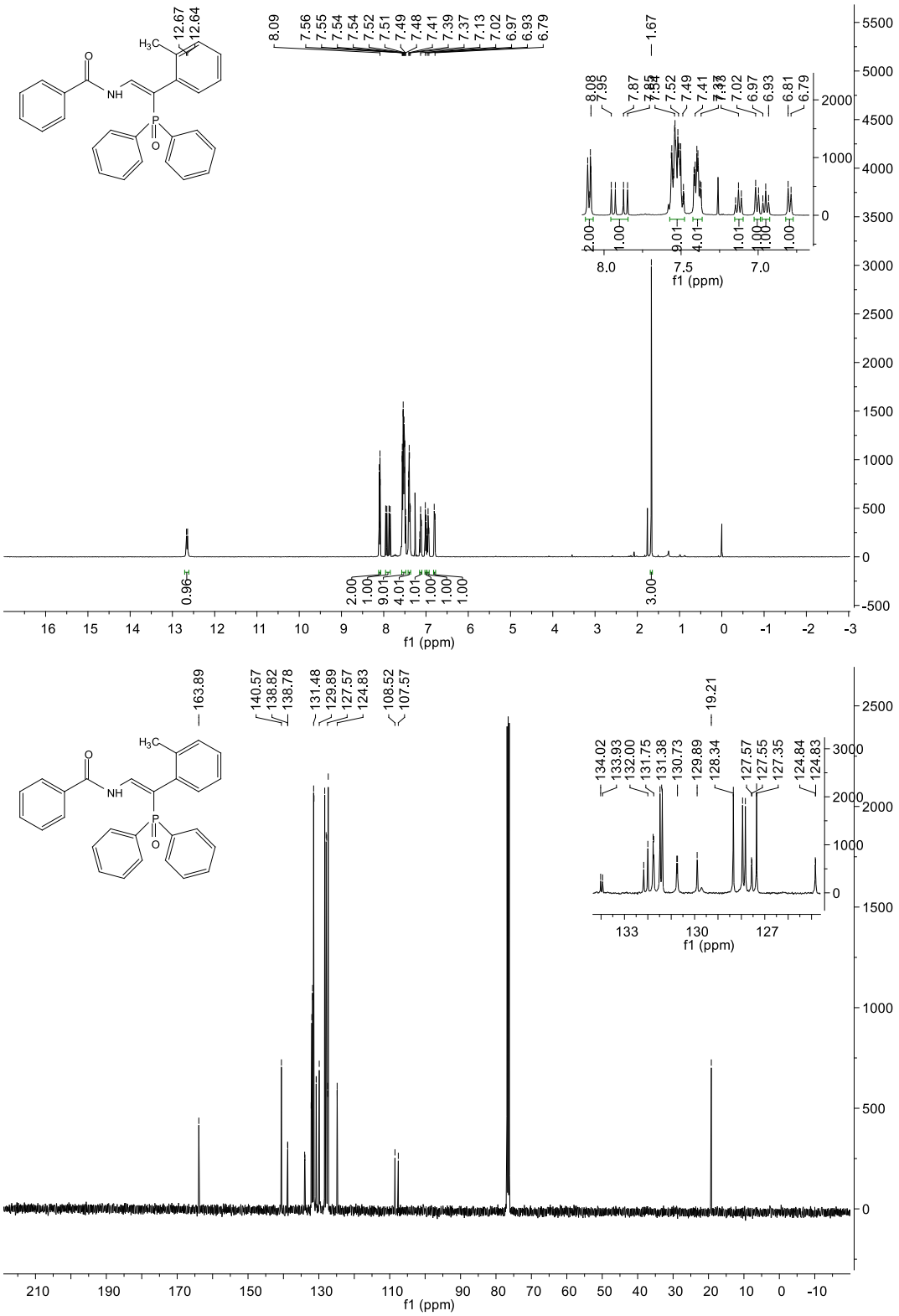
Compound 4a

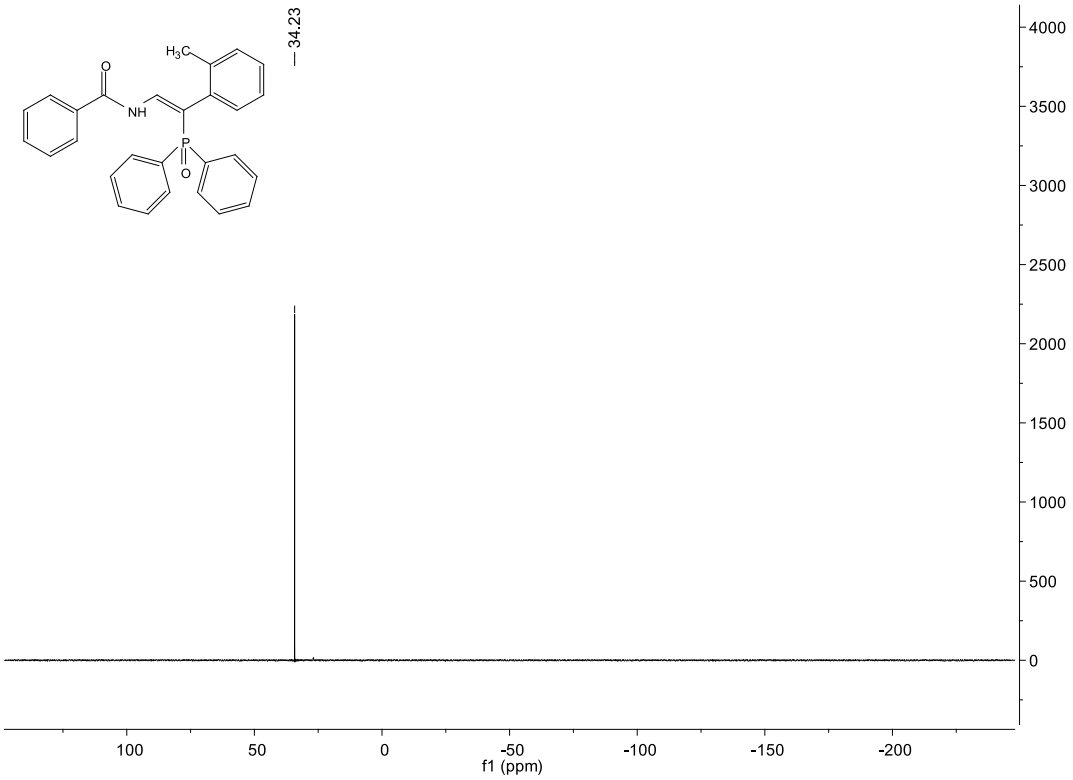

12.44
12.41
7.49
7.47
7.46
7.40
7.38
7.20
7.18
7.16
6.89
6.88
6.77
6.75
6.73
6.59
6.57
3.18
8.04
7.90
7.49
7.46
7.38
6.75
6.73
6.57
1.98
1.05
4.00
5.03
4.09
1.04
1.02
1.01
0.99
0.96
3.00
f1 (ppm)


164.32
157.90
157.87
141.38
131.87
128.12
119.98
110.29
110.28
107.01
106.03
54.43
132.35
131.95
131.85
131.15
129.45
129.43
128.76
128.12
f1 (ppm)

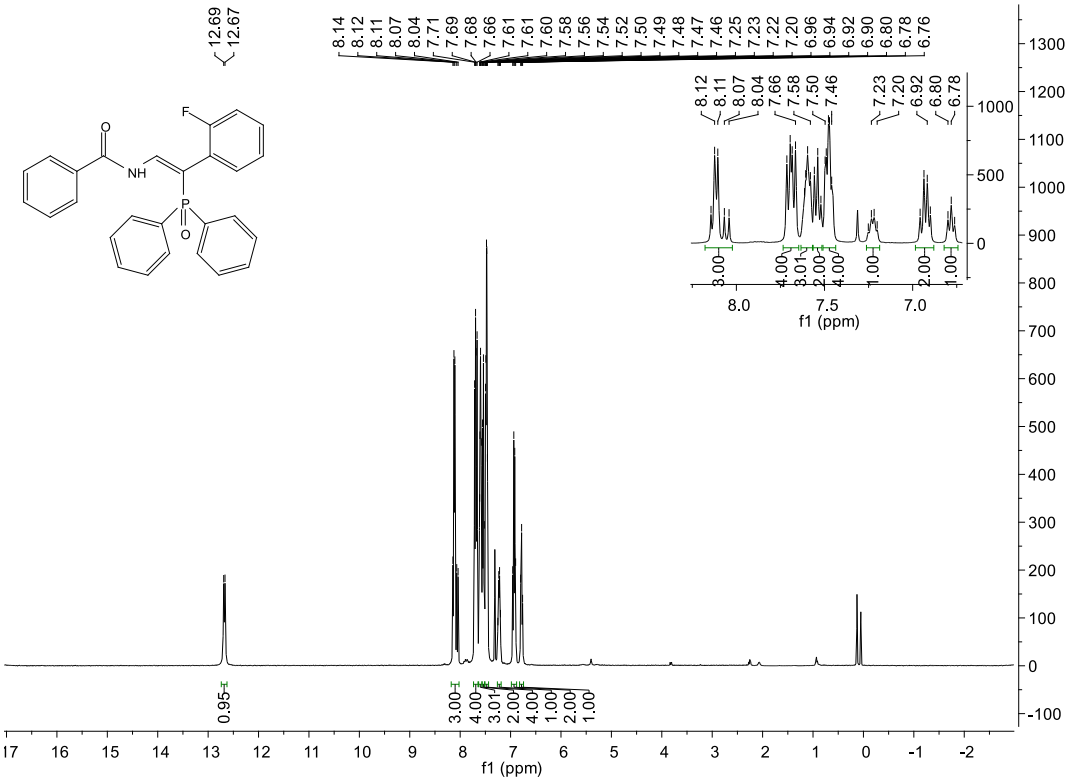

35.00
f1 (ppm)

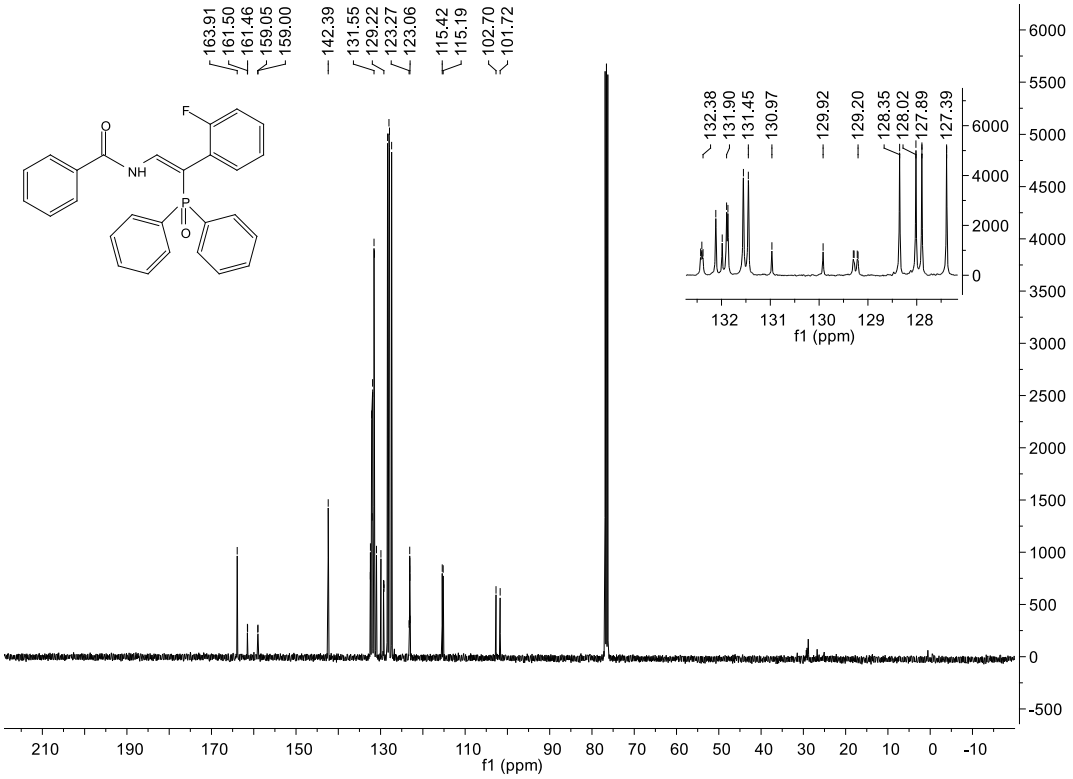
Compound 4b

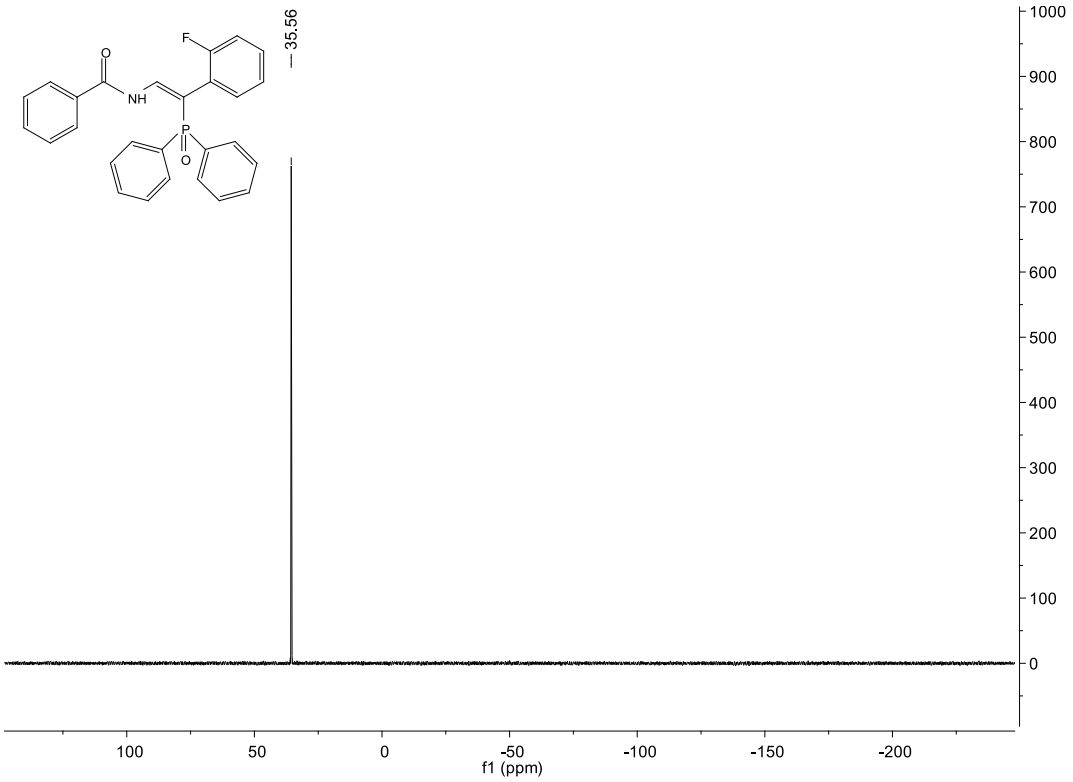

12.67
12.64
8.09
7.56
7.55
7.54
7.54
7.52
7.51
7.49
7.48
7.41
7.39
7.37
7.13
7.02
6.97
6.93
6.79
1.67
8.08
7.95
7.87
7.52
7.49
7.41
7.02
6.97
6.93
6.81
6.79
f1 (ppm)
0.96
2.00
1.00
9.01
4.01
1.01
1.00
1.00
3.00
f1 (ppm)
163.89
140.57
138.82
138.78
131.48
129.89
127.57
124.83
108.52
107.57
19.21
134.02
133.93
132.00
131.75
131.38
130.73
129.89
128.34
127.57
127.55
127.35
124.84
124.83
f1 (ppm)


34.23
H3C
O
NH
P
O
4000
3500
3000
2500
2000
1500
1000
500
0
100
50
0
-50
-100
-150
-200
f1 (ppm)

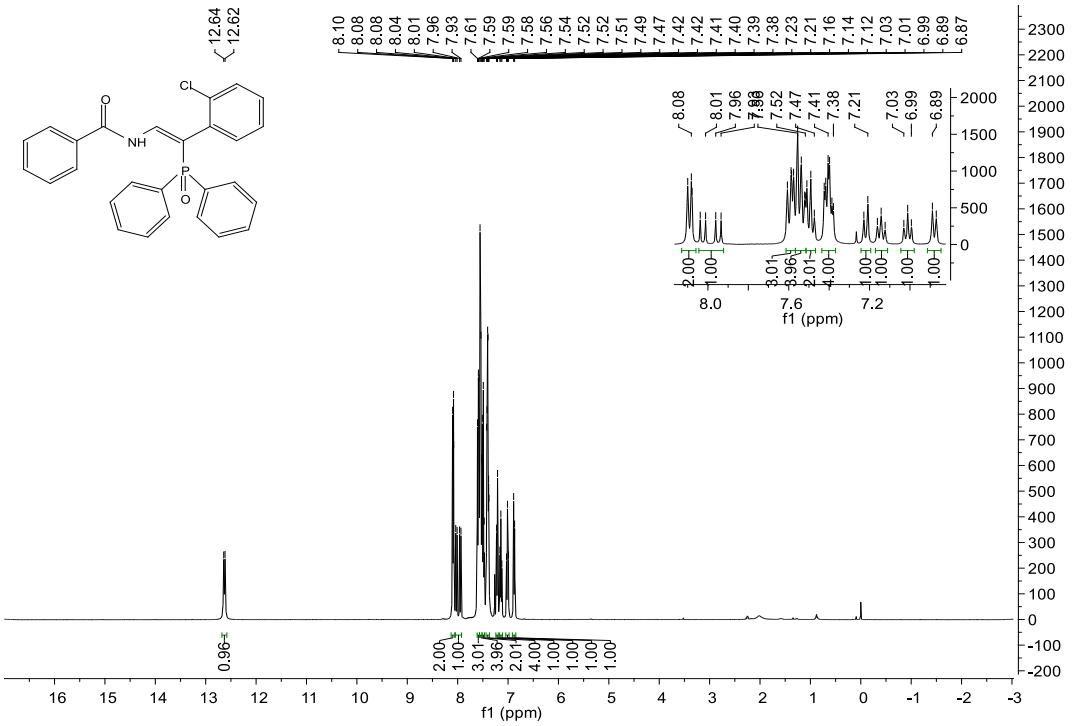
Compound 4c

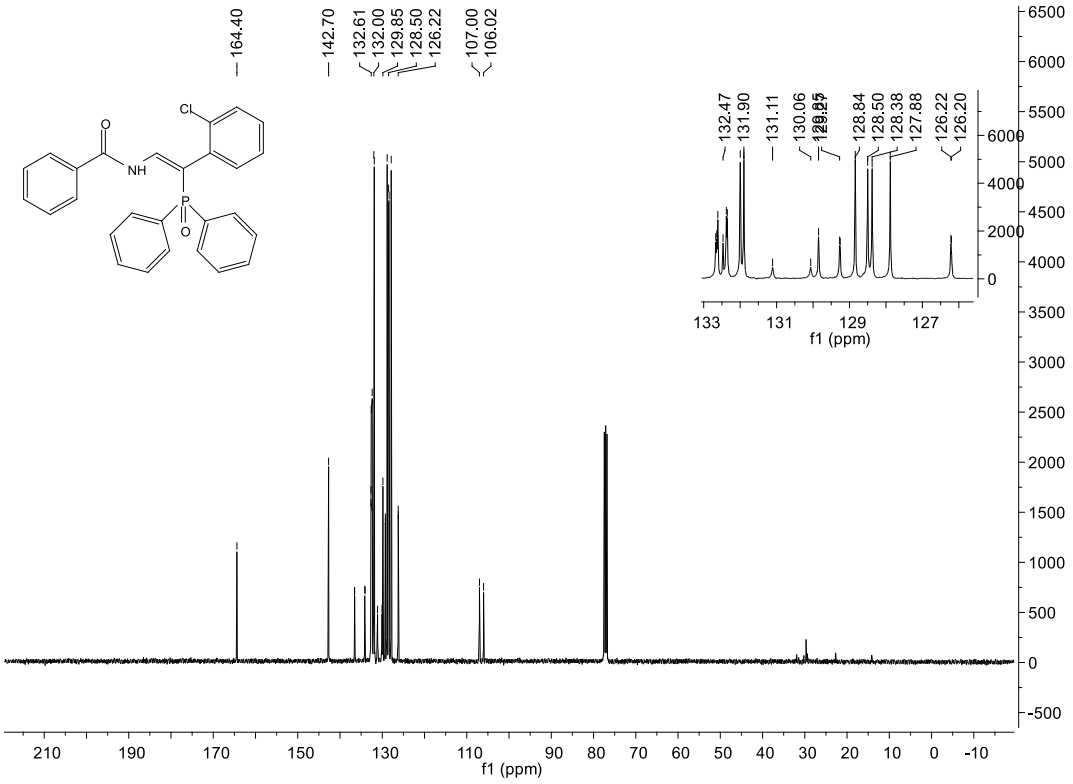

12.69
12.67
8.14
8.12
8.11
8.07
8.04
7.71
7.69
7.68
7.66
7.61
7.61
7.60
7.58
7.56
7.54
7.52
7.50
7.49
7.48
7.47
7.46
7.25
7.23
7.22
7.20
6.96
6.94
6.92
6.90
6.80
6.78
6.76
F
O
NH
P
O
0.95
3.00
4.00
3.01
2.00
4.00
1.00
2.00
1.00
f1 (ppm)

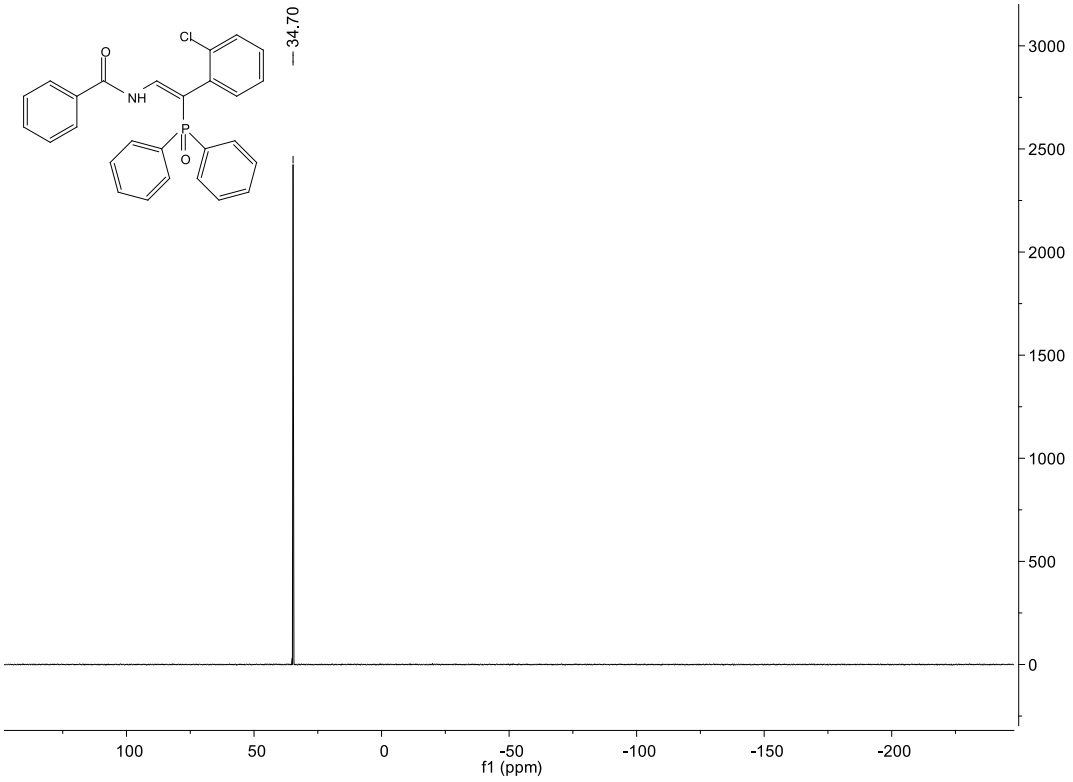

163.91
161.50
161.46
159.05
159.00
142.39
131.55
129.22
123.27
123.06
115.42
115.19
102.70
101.72
132.38
131.90
131.45
130.97
129.92
129.20
128.35
128.02
127.89
127.39
f1 (ppm)
f1 (ppm)


35.56
f1 (ppm)

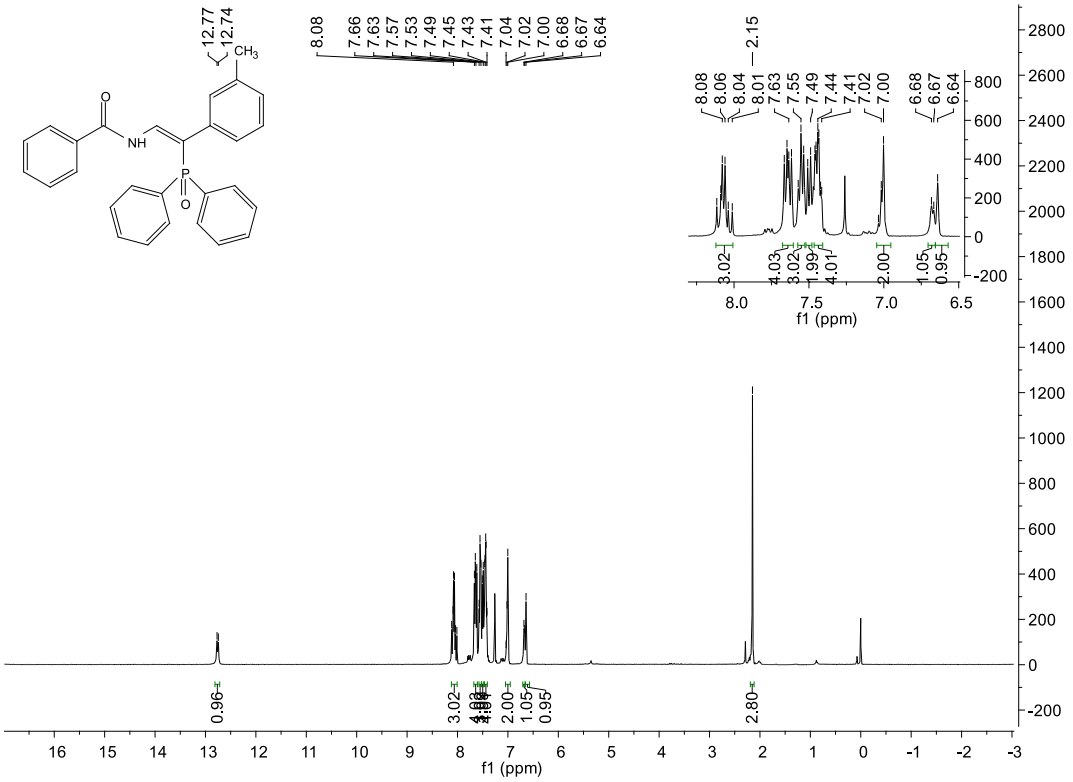
Compound 4d

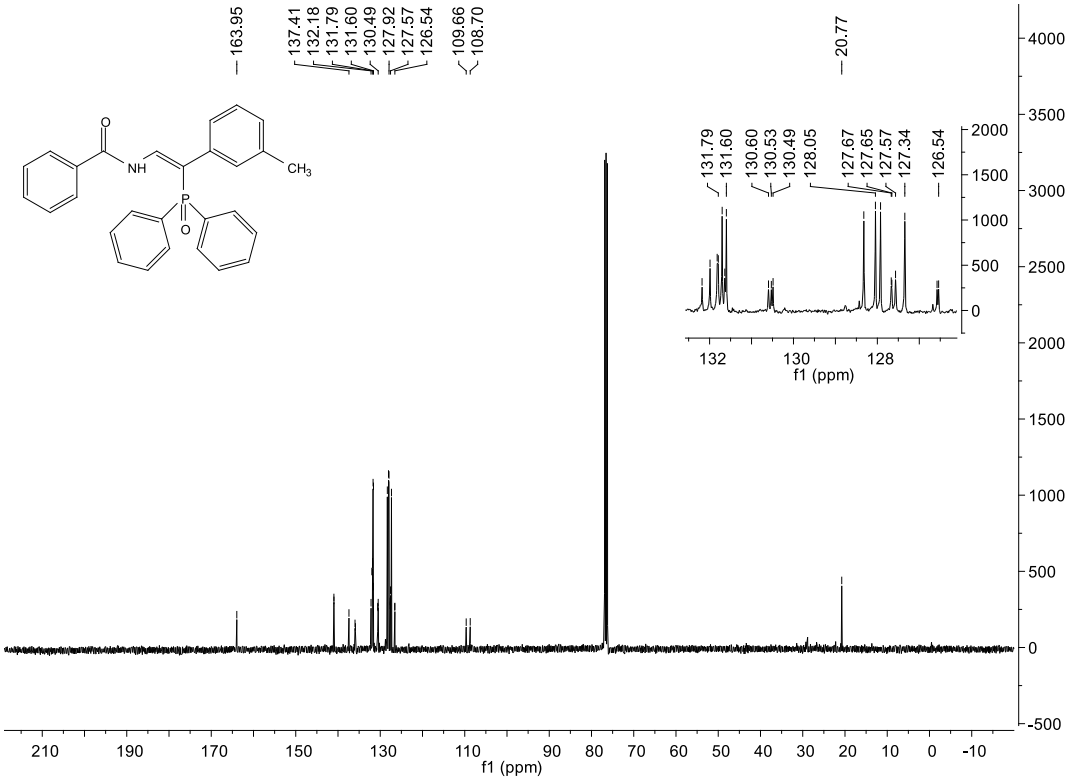

12.64
12.62
8.10
8.08
8.08
8.04
8.01
7.96
7.93
7.61
7.59
7.59
7.58
7.56
7.54
7.52
7.52
7.51
7.49
7.47
7.42
7.42
7.41
7.40
7.39
7.38
7.23
7.21
7.16
7.14
7.12
7.03
7.01
6.99
6.89
6.87
Cl
O
NH
P
O
8.08
8.01
7.96
7.52
7.47
7.41
7.38
7.21
7.03
6.99
6.89
2.00
1.00
3.01
3.96
2.01
4.00
1.00
1.00
1.00
1.00
8.0
7.6
7.2
f1 (ppm)
0.96
2.00
1.00
3.01
3.96
2.01
4.00
1.00
1.00
1.00
1.00
f1 (ppm)

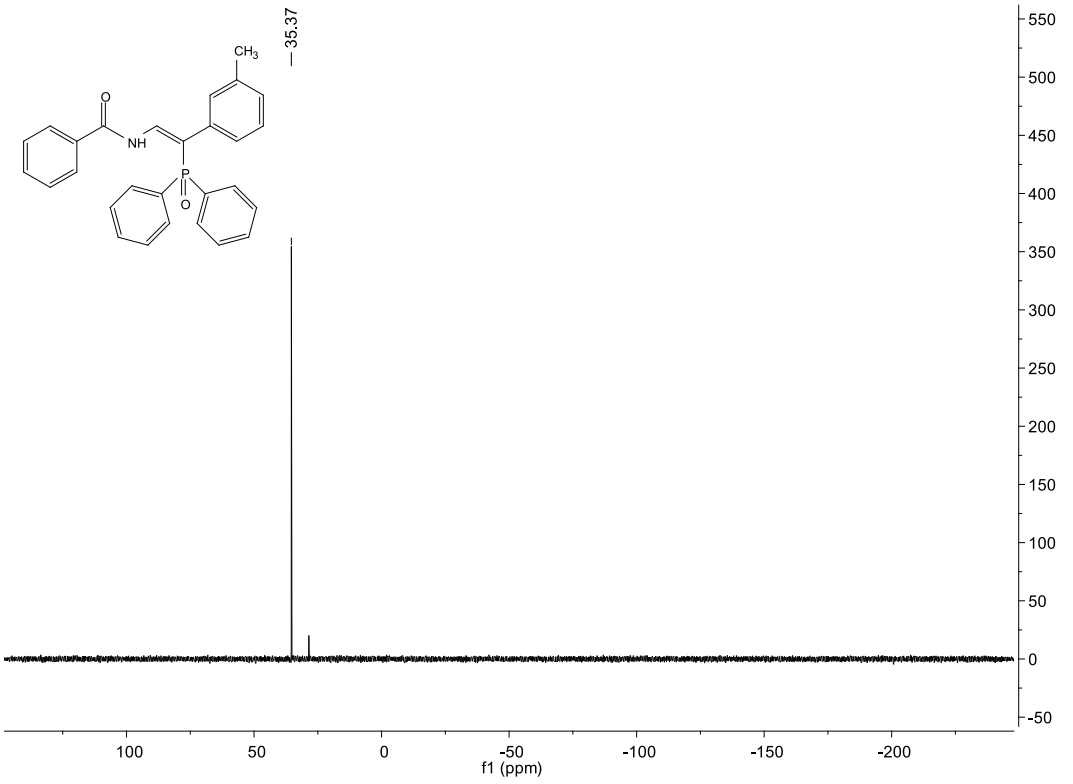

164.40
142.70
132.61
132.00
129.85
128.50
126.22
107.00
106.02
Cl
O
NH
P
O
132.47
131.90
131.11
130.06
128.84
128.50
128.38
127.88
126.22
126.20
133
131
129
127
f1 (ppm)
f1 (ppm)



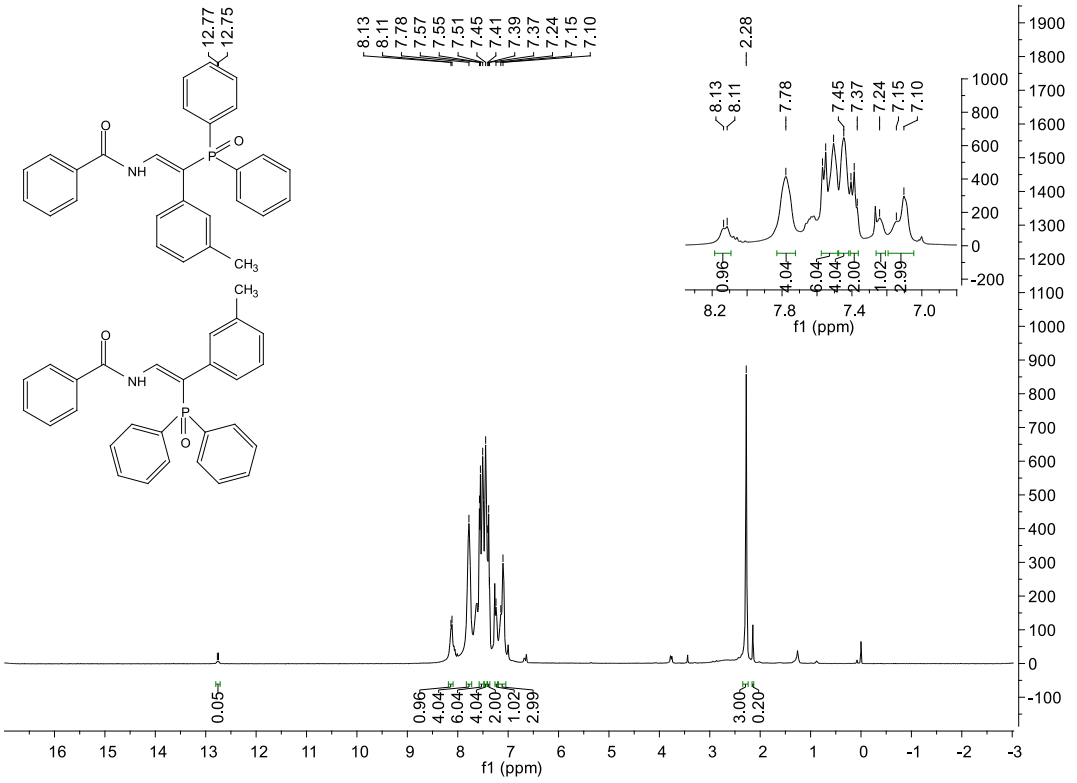
Compound 4e-*Z*

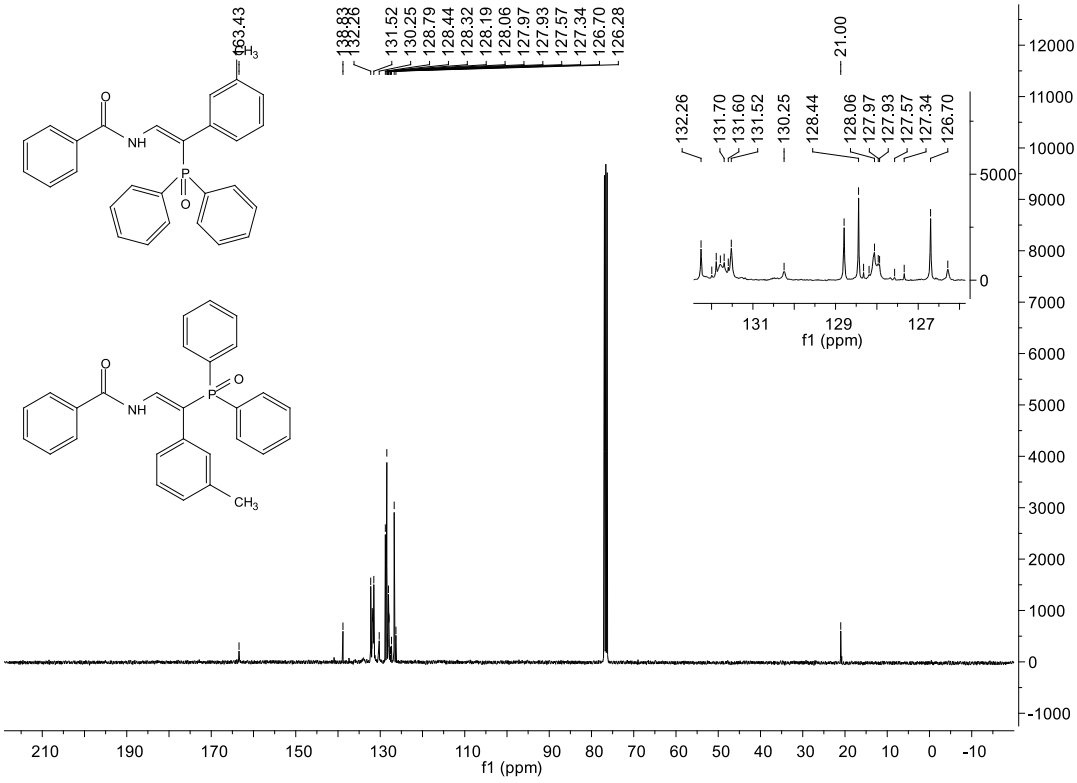


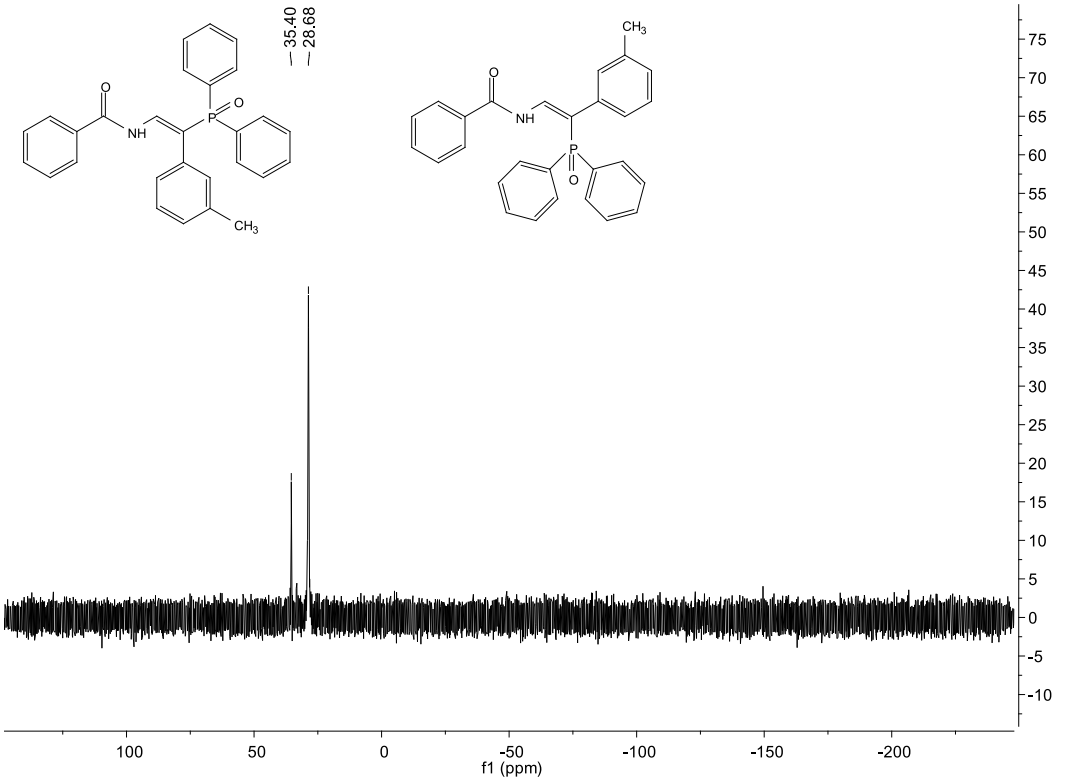

163.95
137.41
132.18
131.79
131.60
130.49
127.92
127.57
126.54
109.66
108.70
20.77
131.79
131.60
130.60
130.53
130.49
128.05
127.67
127.65
127.57
127.34
126.54
NH
O
P
O
CH3
f1 (ppm)


35.37
NH
O
P
O
CH3
f1 (ppm)

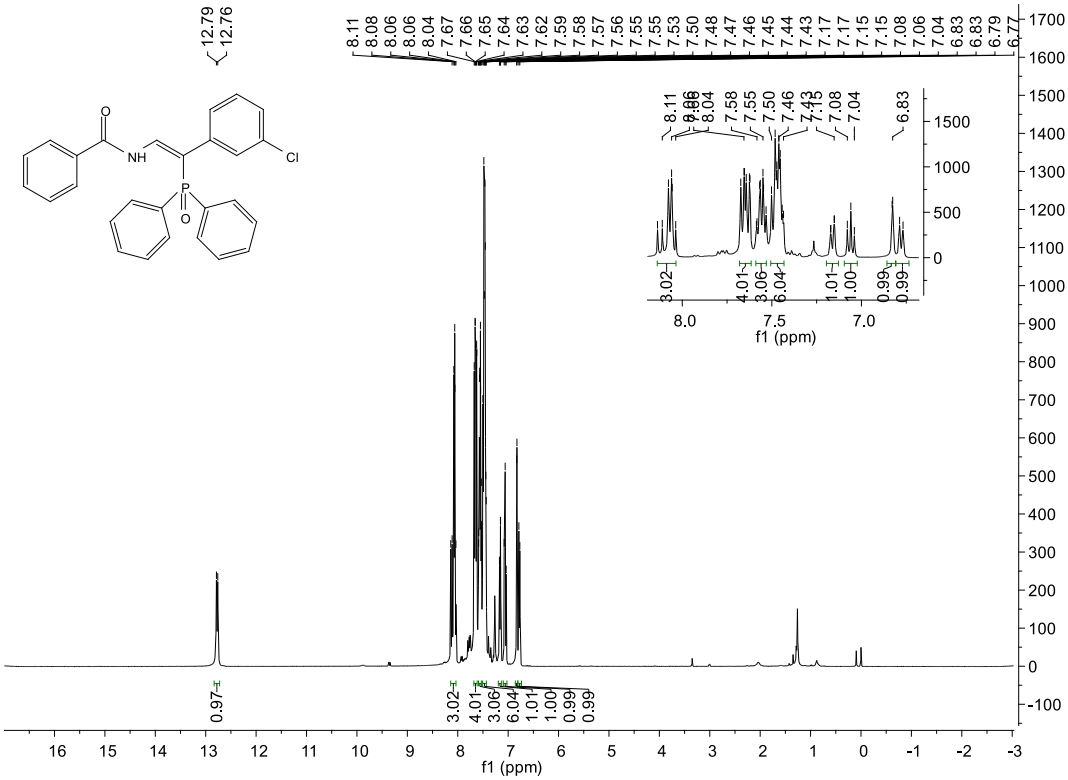
Mixture of 4e-*E* and 4e-*Z*

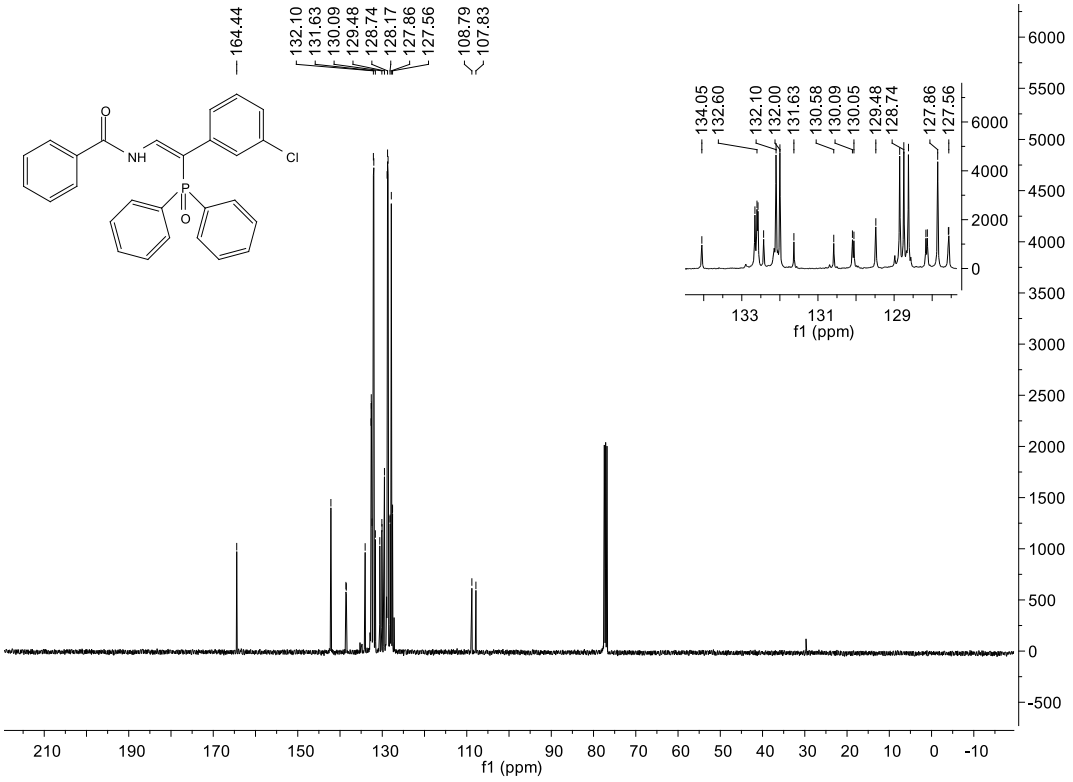


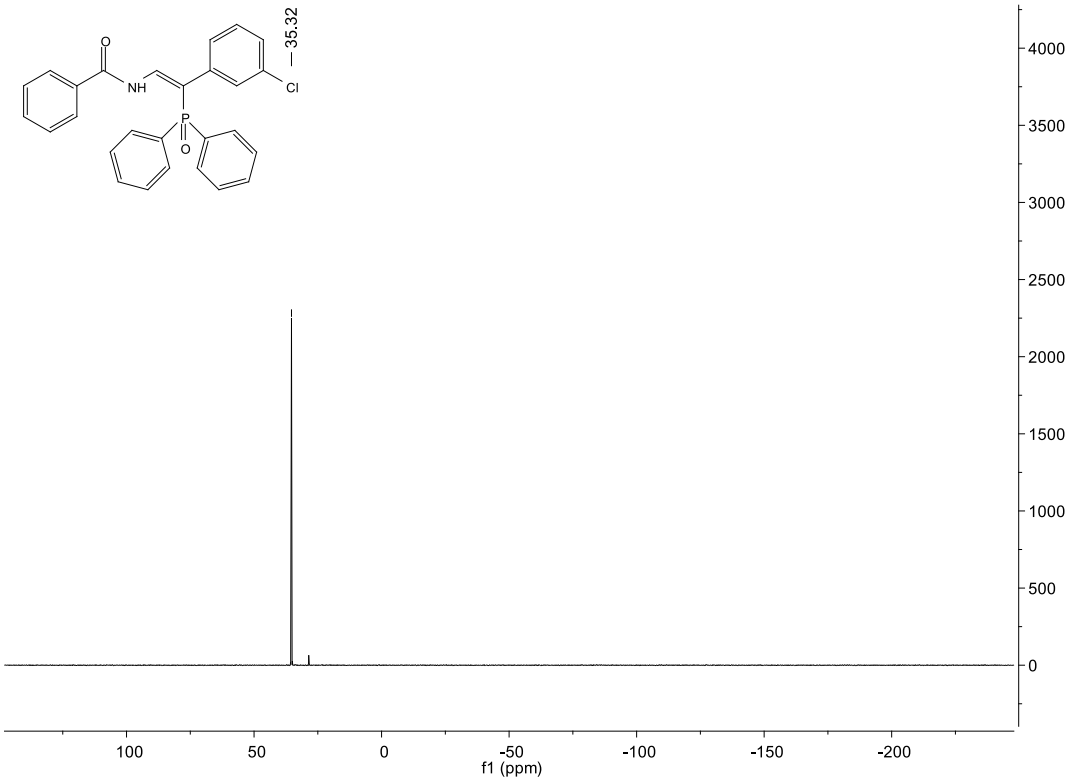




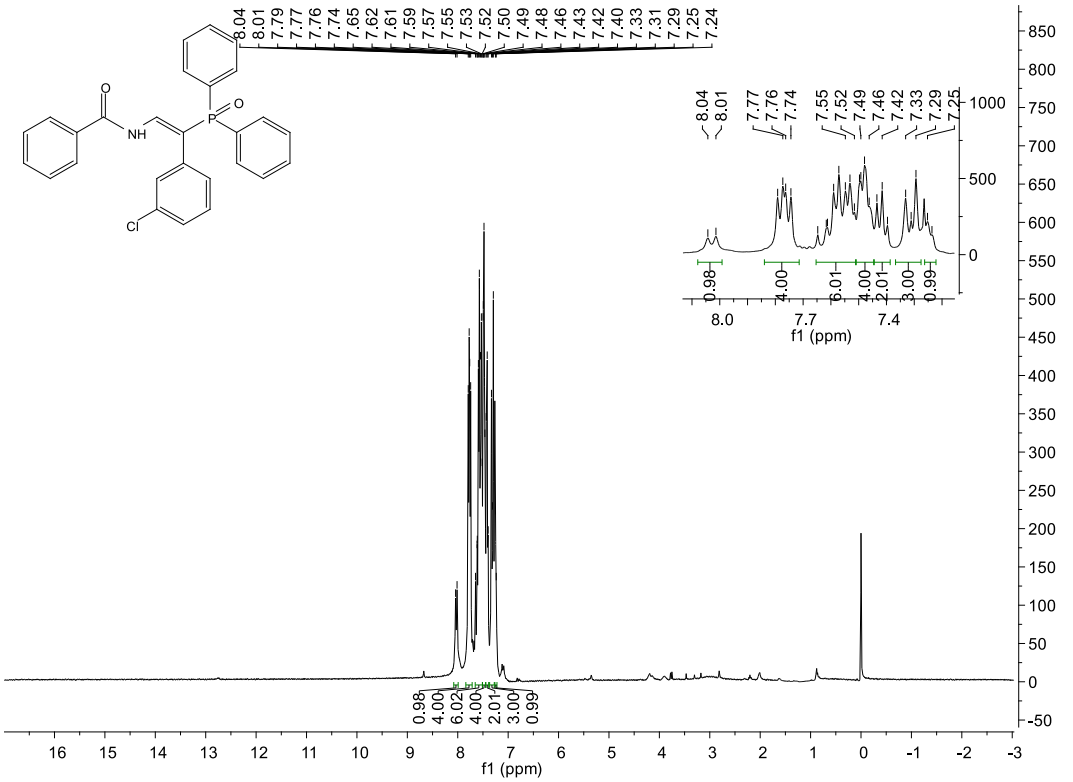
Compound 4f-*Z*

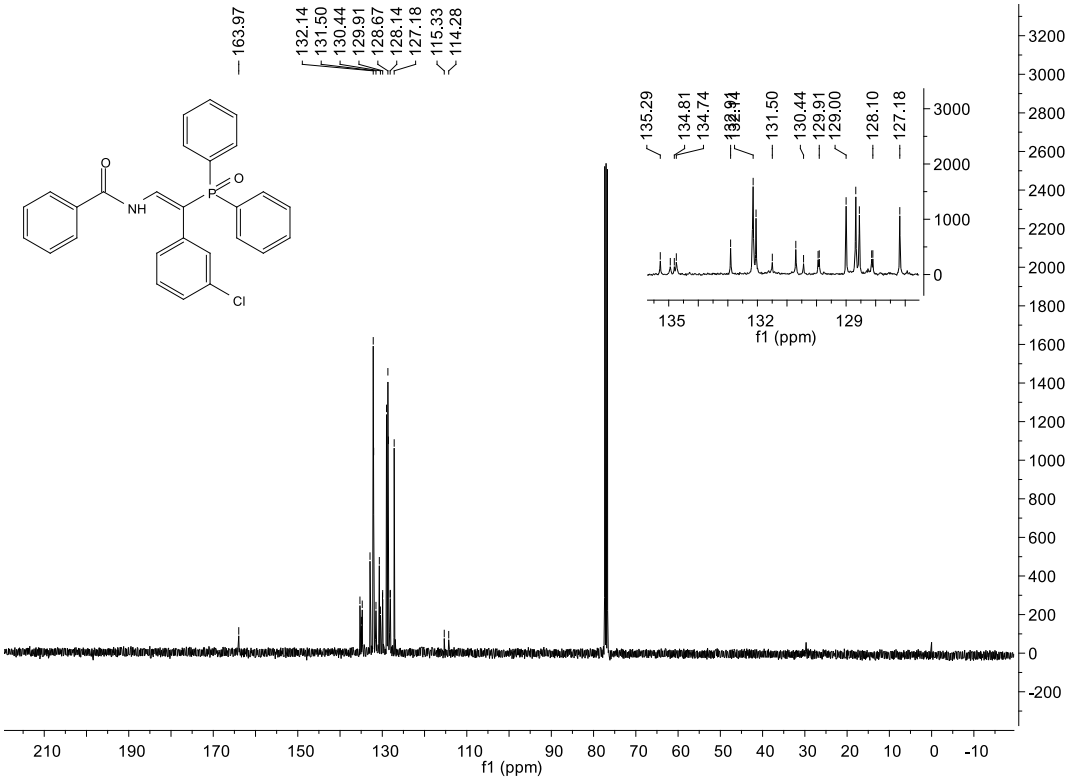


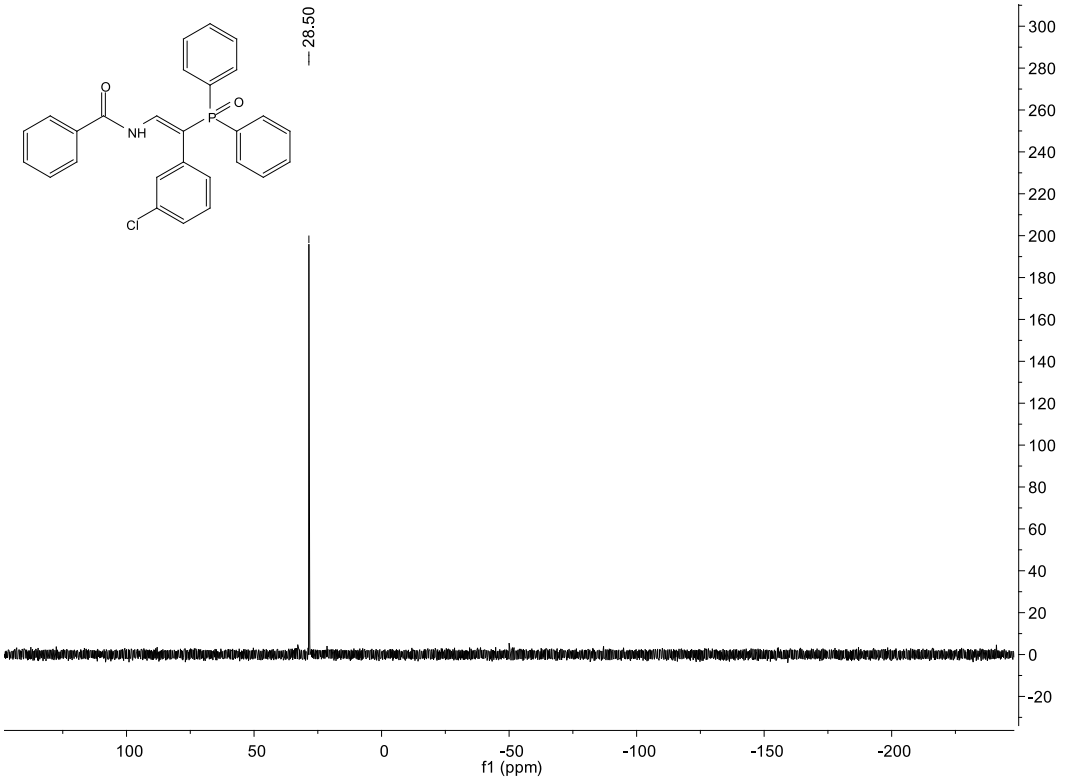

164.44
132.10
131.63
130.09
129.48
128.74
128.17
127.86
127.56
108.79
107.83
O
NH
Cl
P
O
134.05
132.60
132.10
132.00
131.63
130.58
130.09
130.05
129.48
128.74
127.86
127.56
133
131
129
f1 (ppm)
f1 (ppm)


35.32
O
NH
Cl
P
O
f1 (ppm)

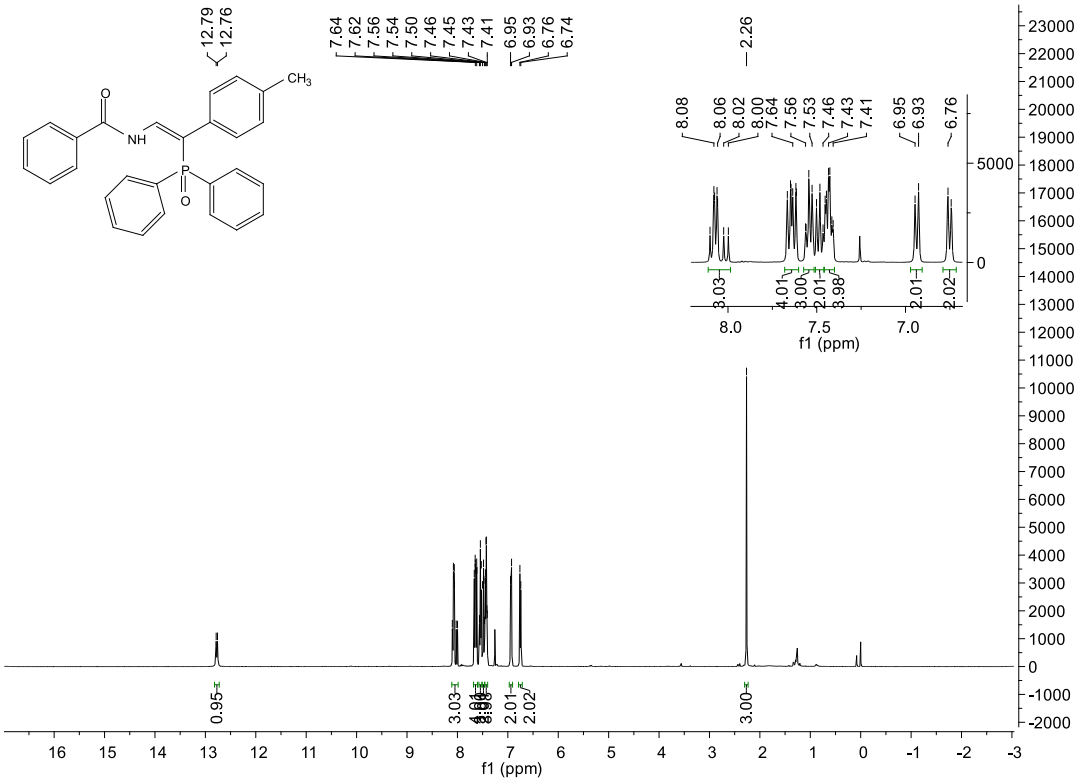
Compound 4f-*E*

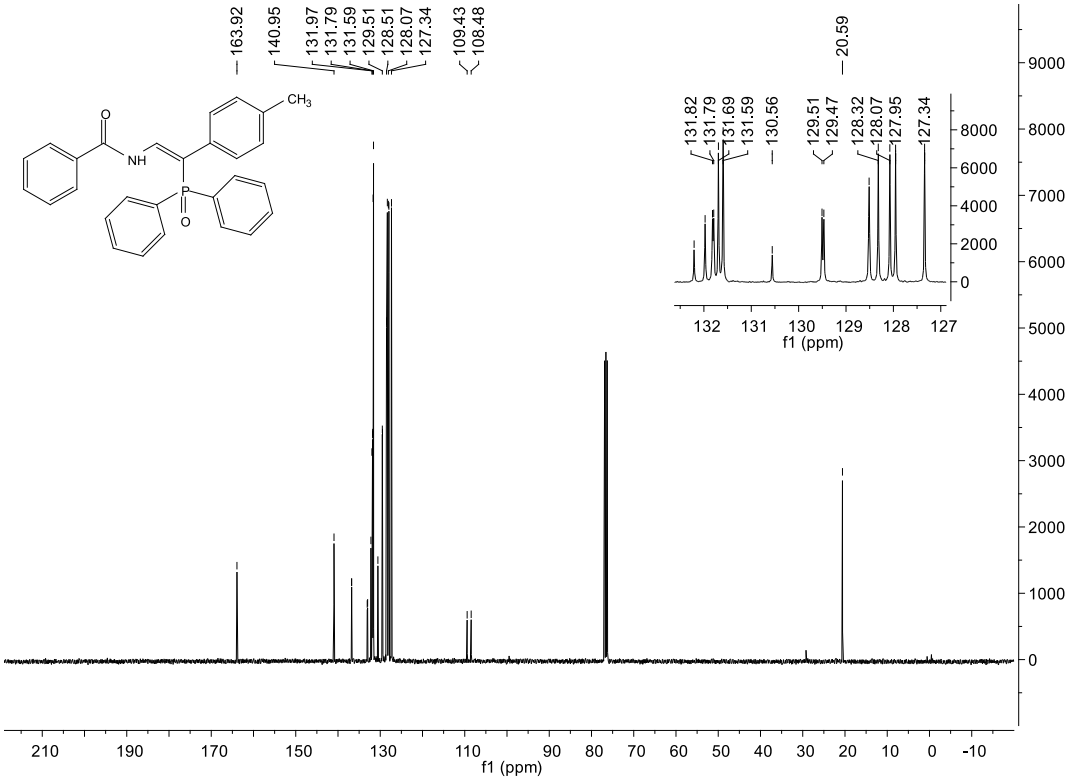


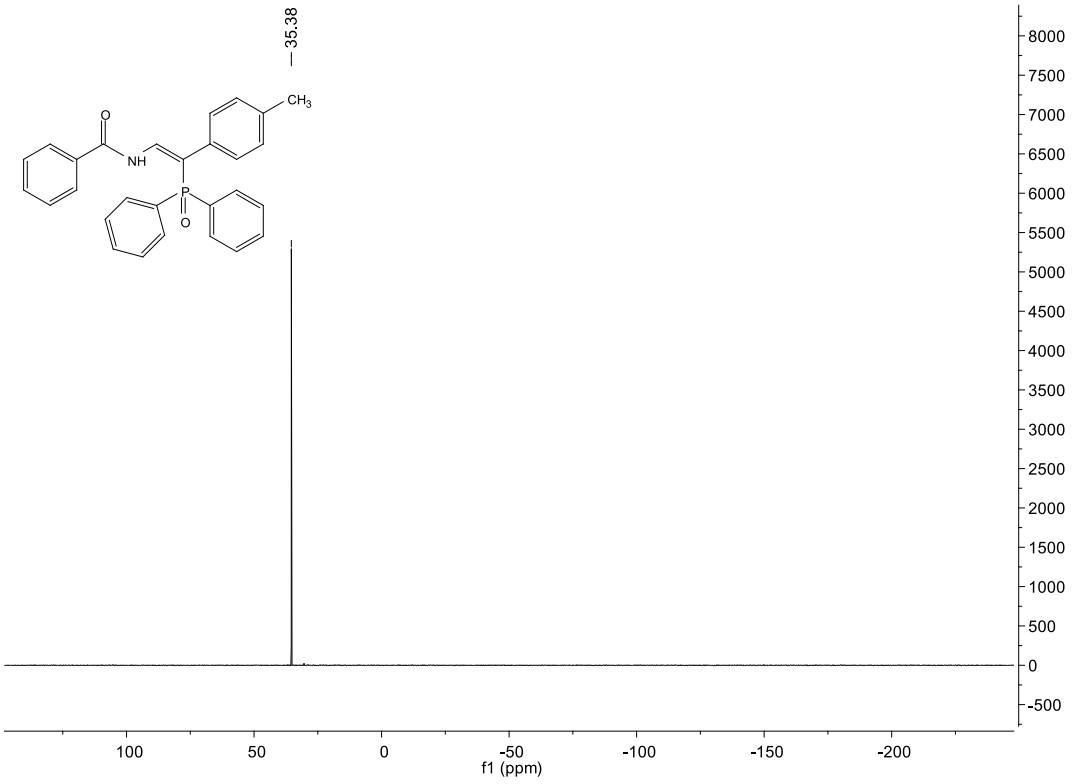




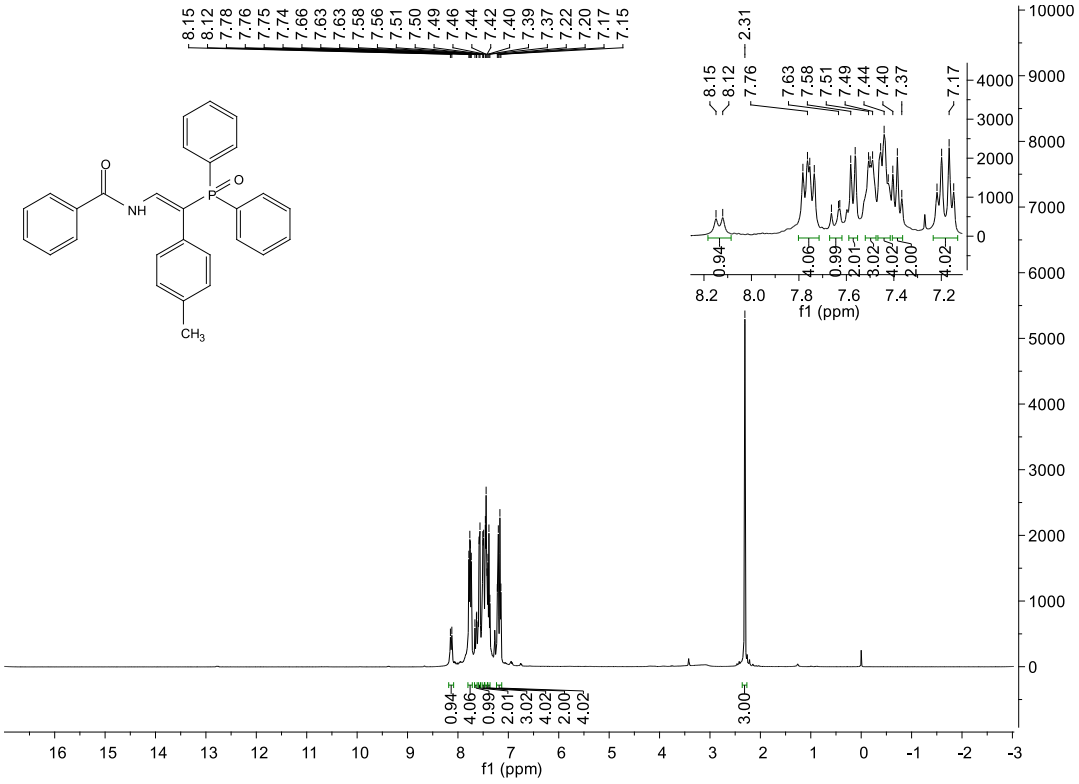
Compound 4g-*Z*

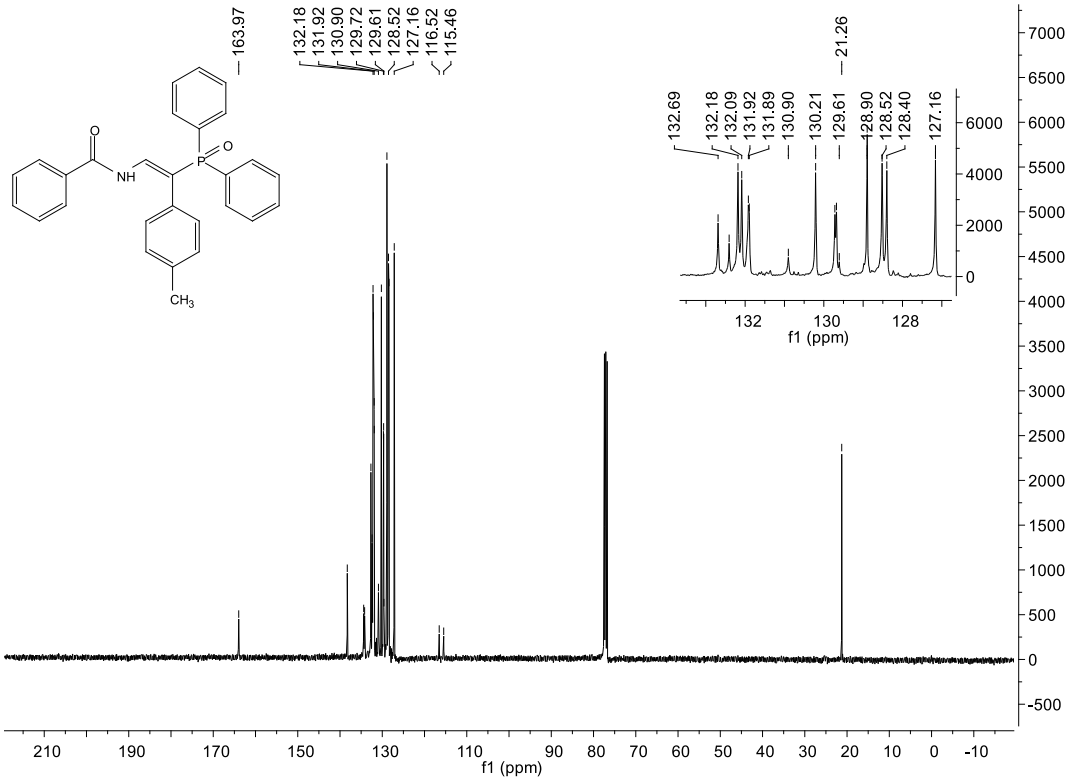


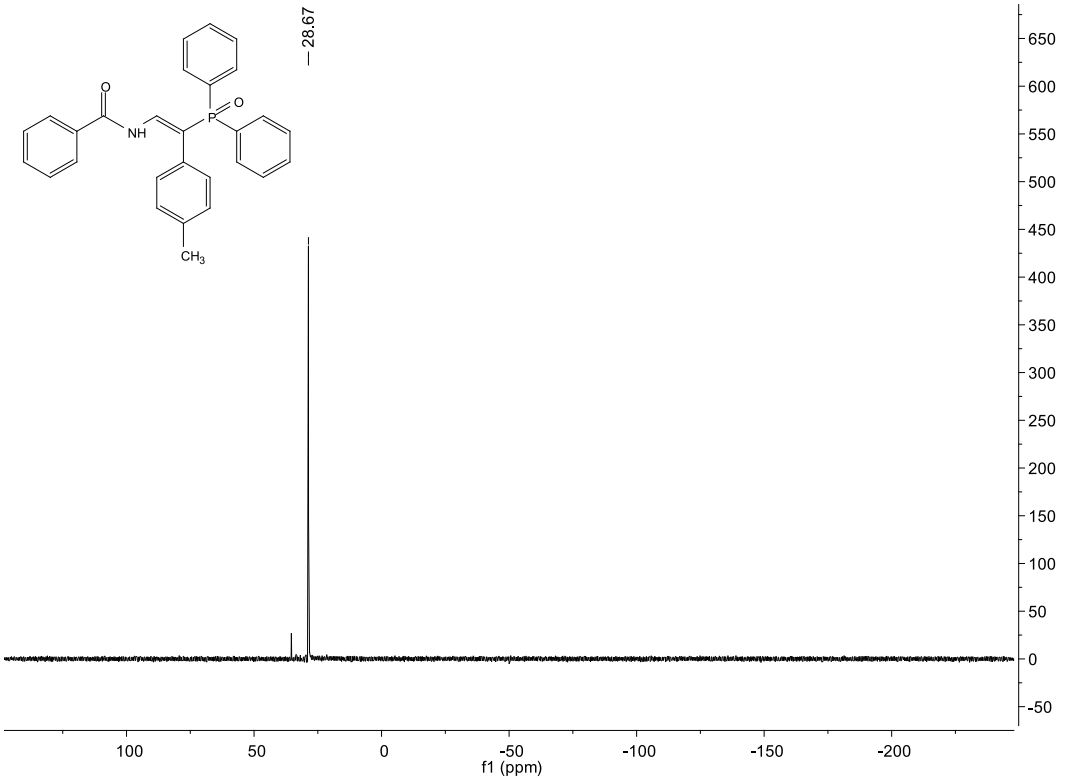

163.92
140.95
131.97
131.79
131.59
129.51
128.51
128.07
127.34
109.43
108.48
20.59
131.82
131.79
131.69
131.59
130.56
129.51
129.47
128.32
128.07
127.95
127.34
CH3
NH
O
P
f1 (ppm)


35.38
CH3
NH
O
P
f1 (ppm)

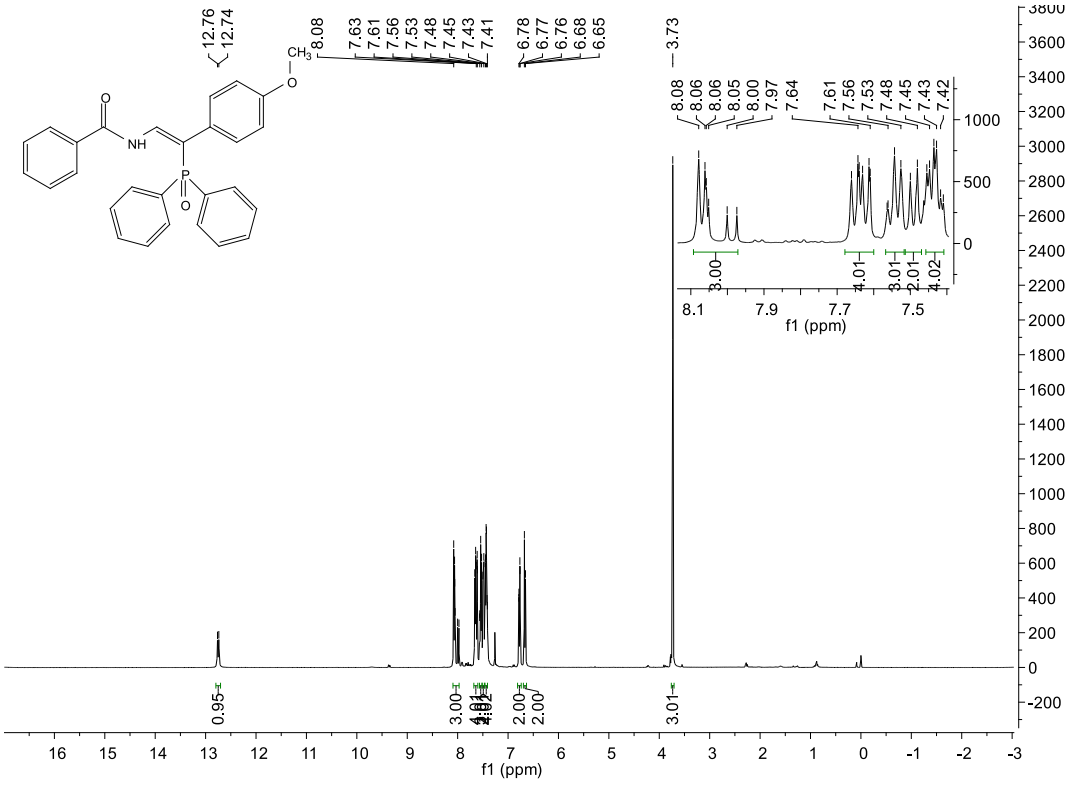
Compound 4g-*E*

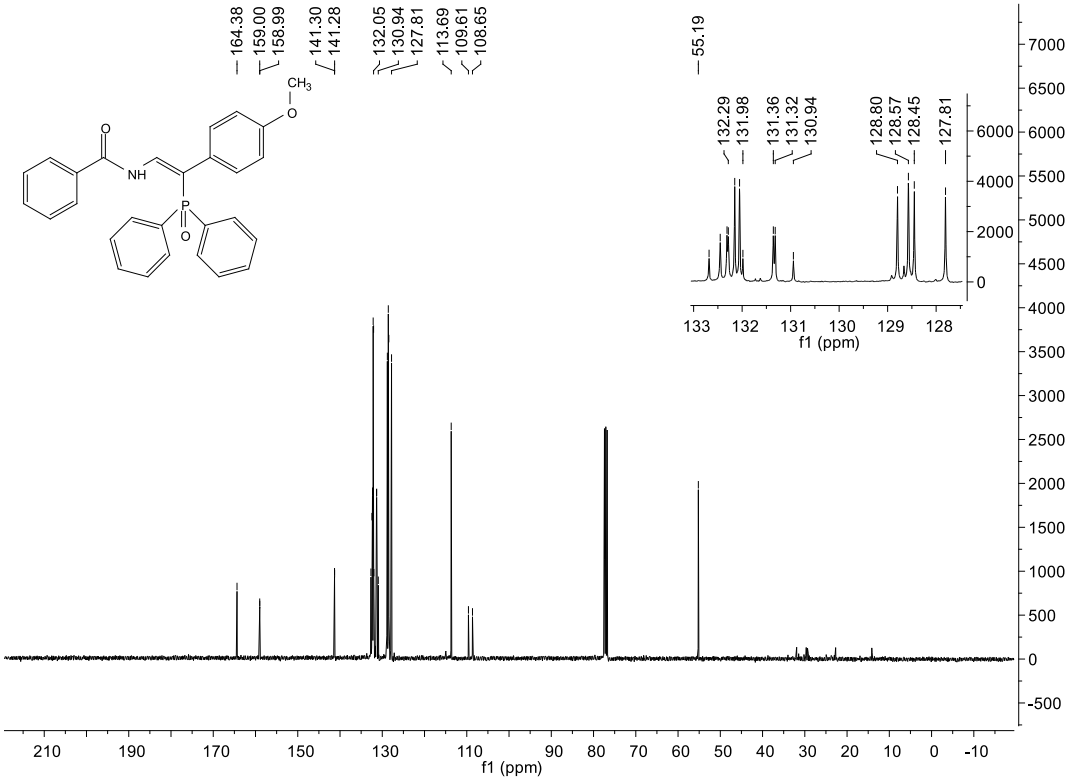


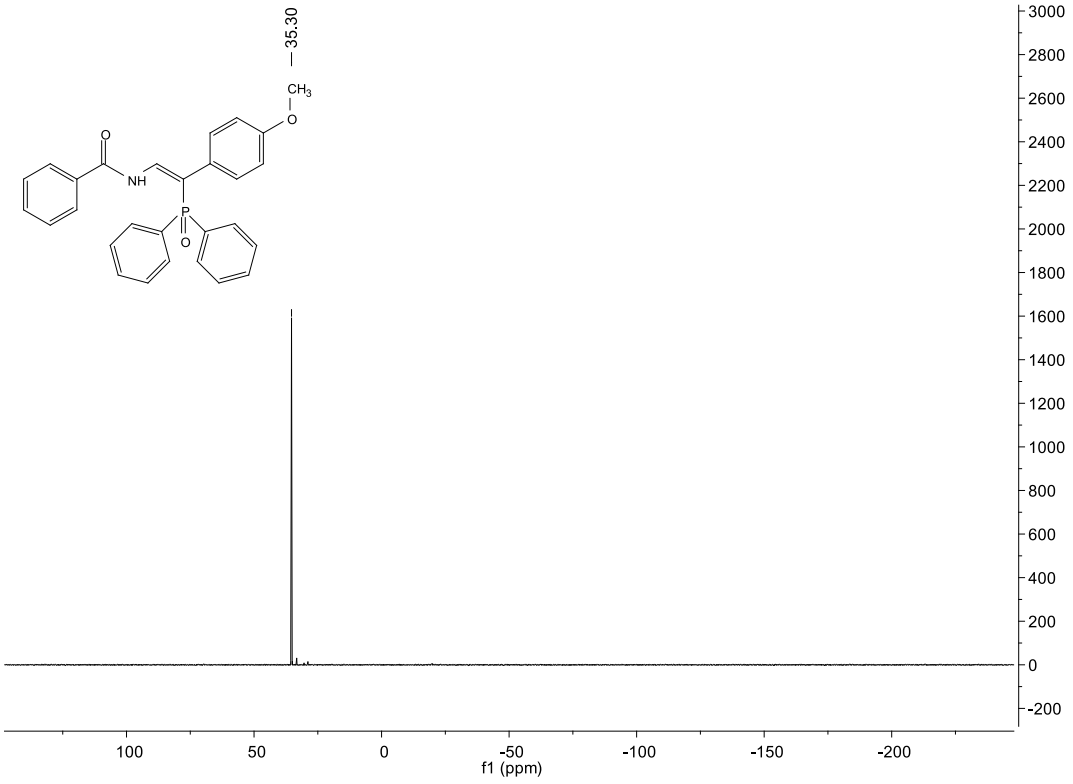




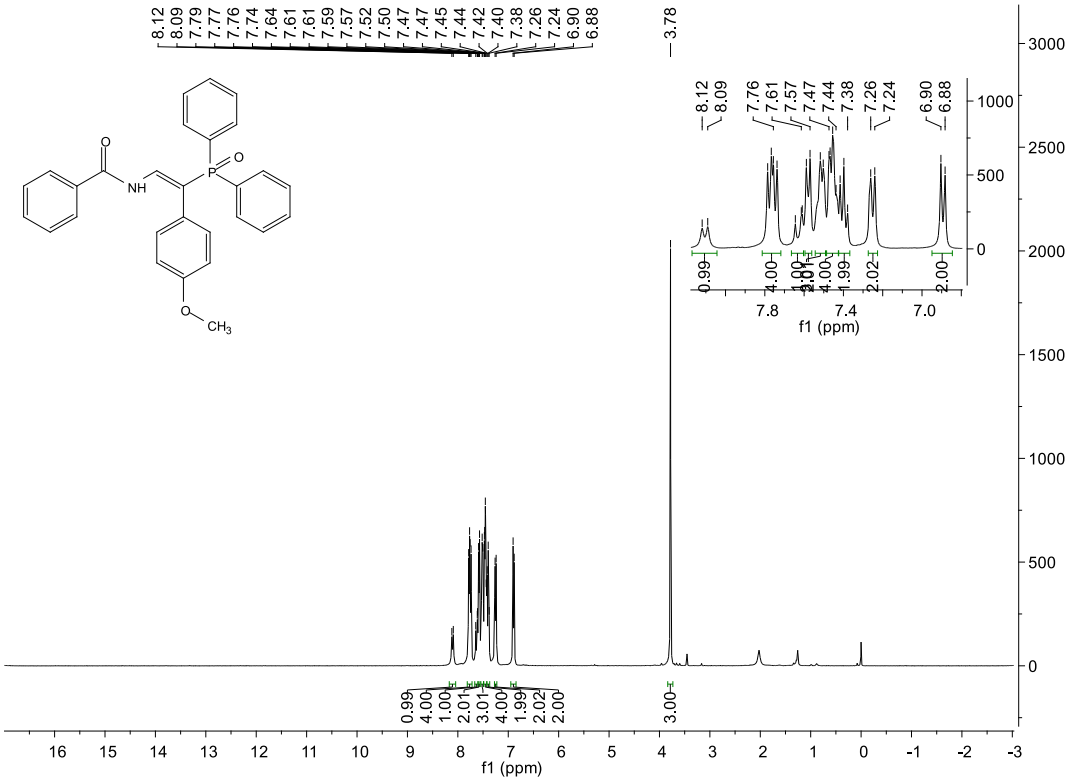
Compound 4h-*Z*

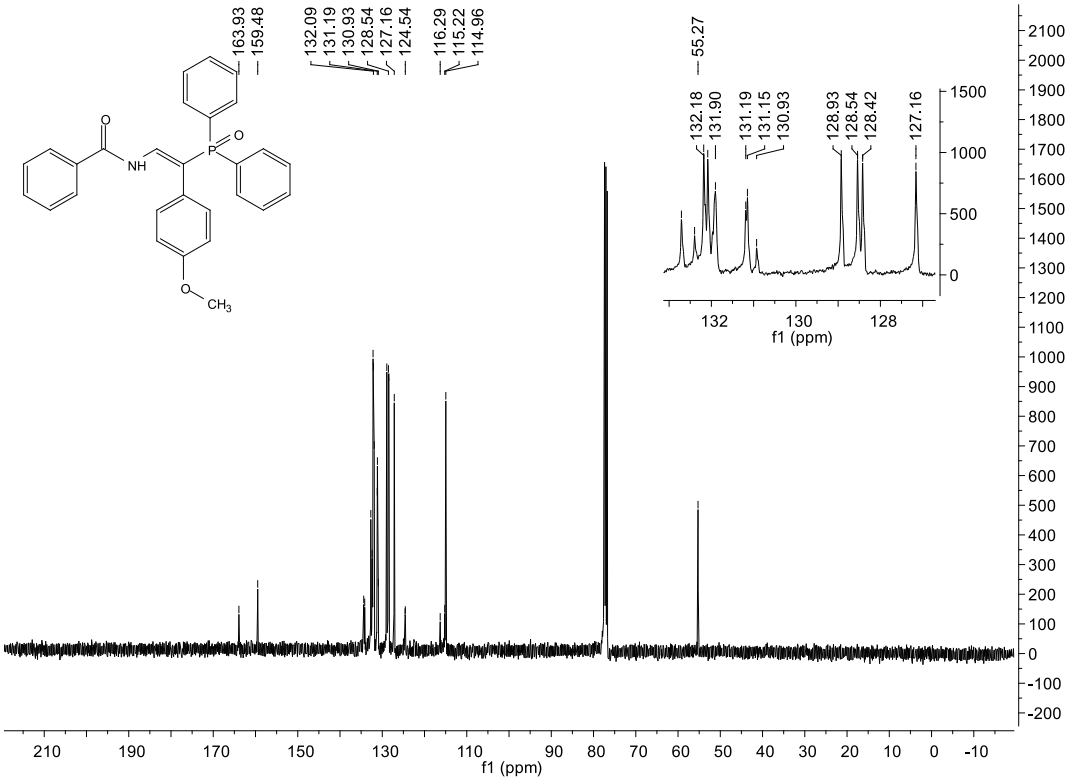


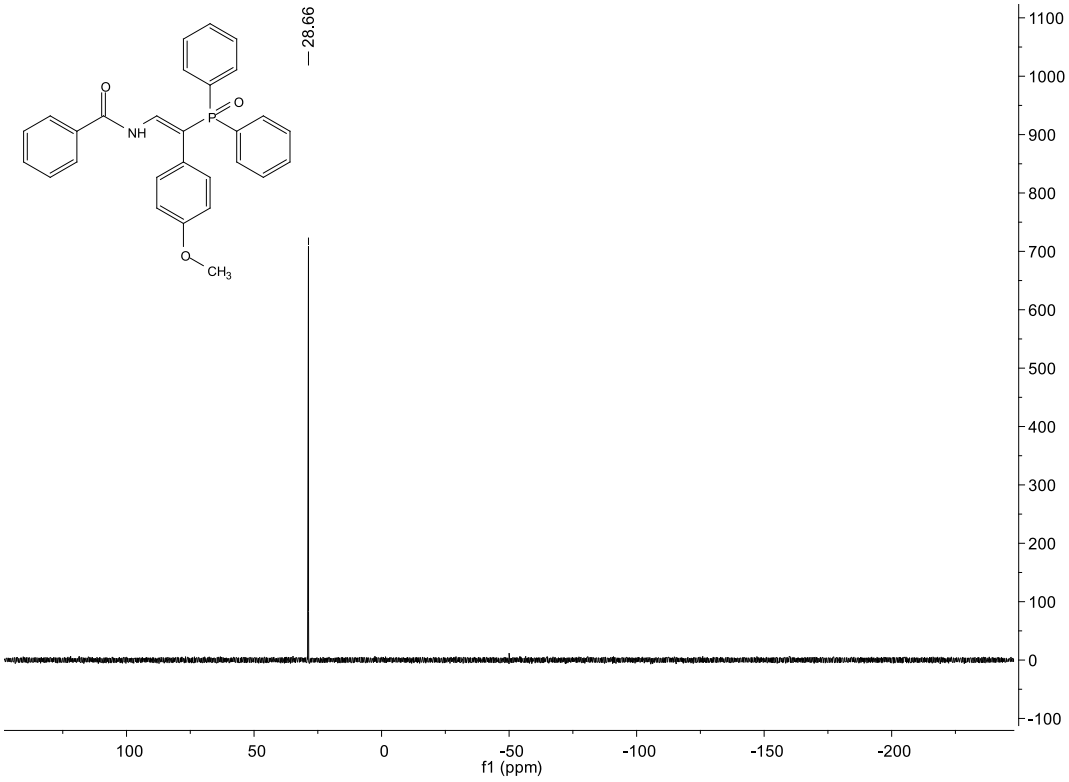

164.38
159.00
158.99
141.30
141.28
132.05
130.94
127.81
113.69
109.61
108.65
55.19
132.29
131.98
131.36
131.32
130.94
128.80
128.57
128.45
127.81
CH3
O
NH
P
O
f1 (ppm)


35.30
CH3
O
NH
P
O
f1 (ppm)

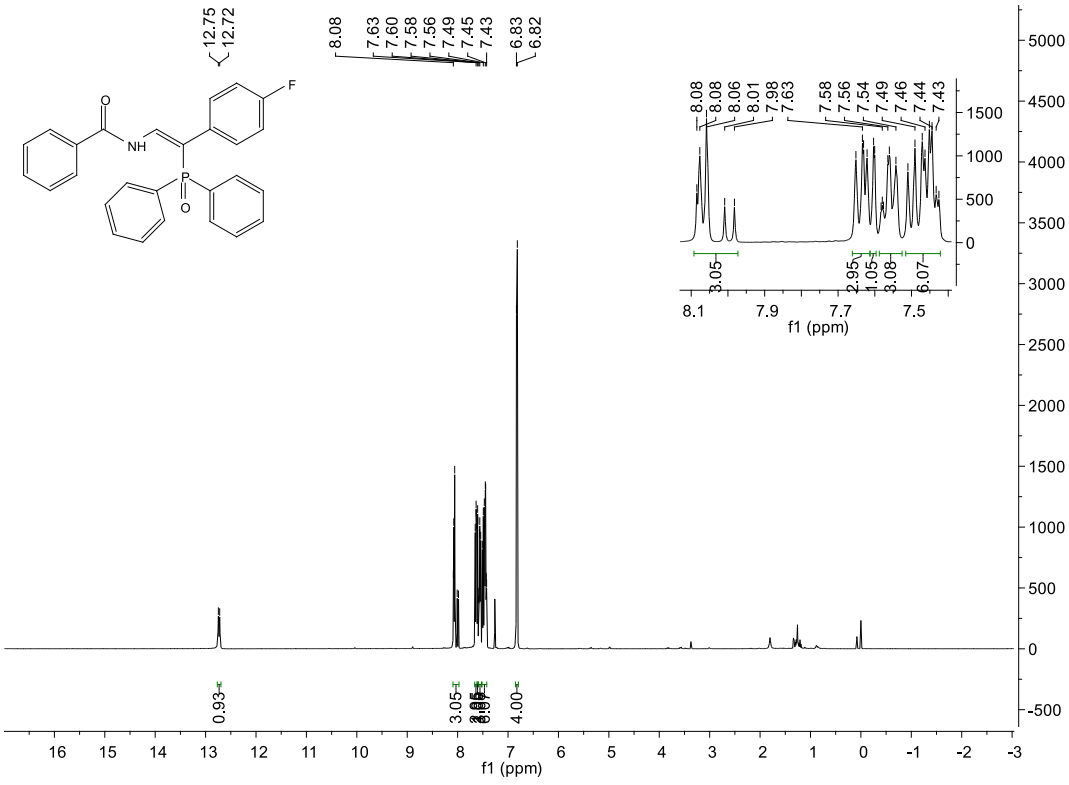
Compound 4h-*E*

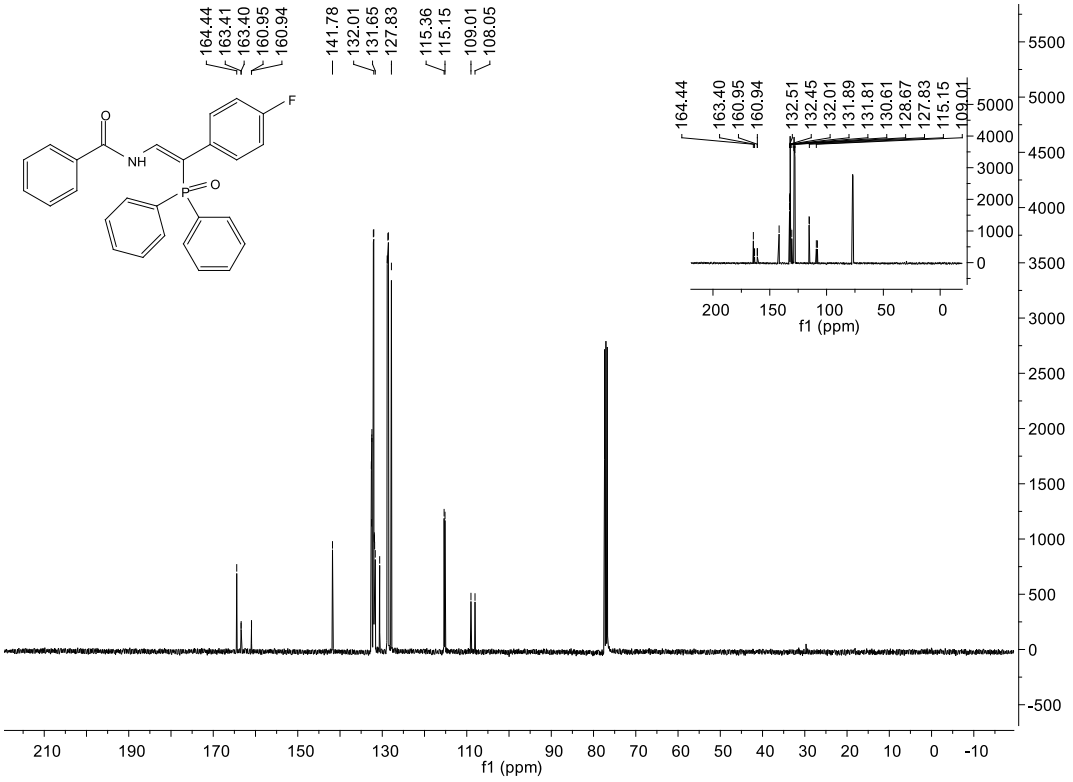






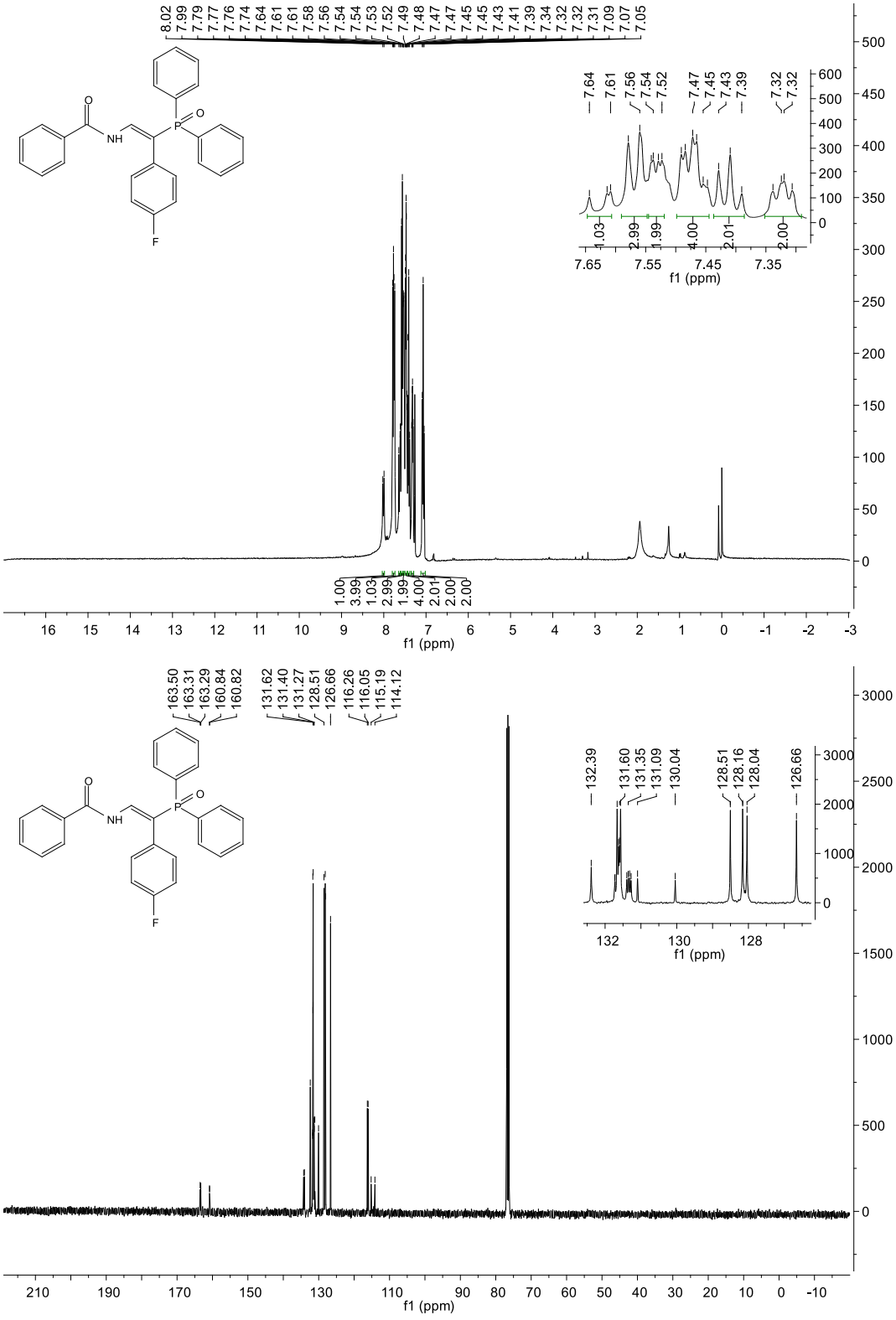
Compound 4i-*Z*

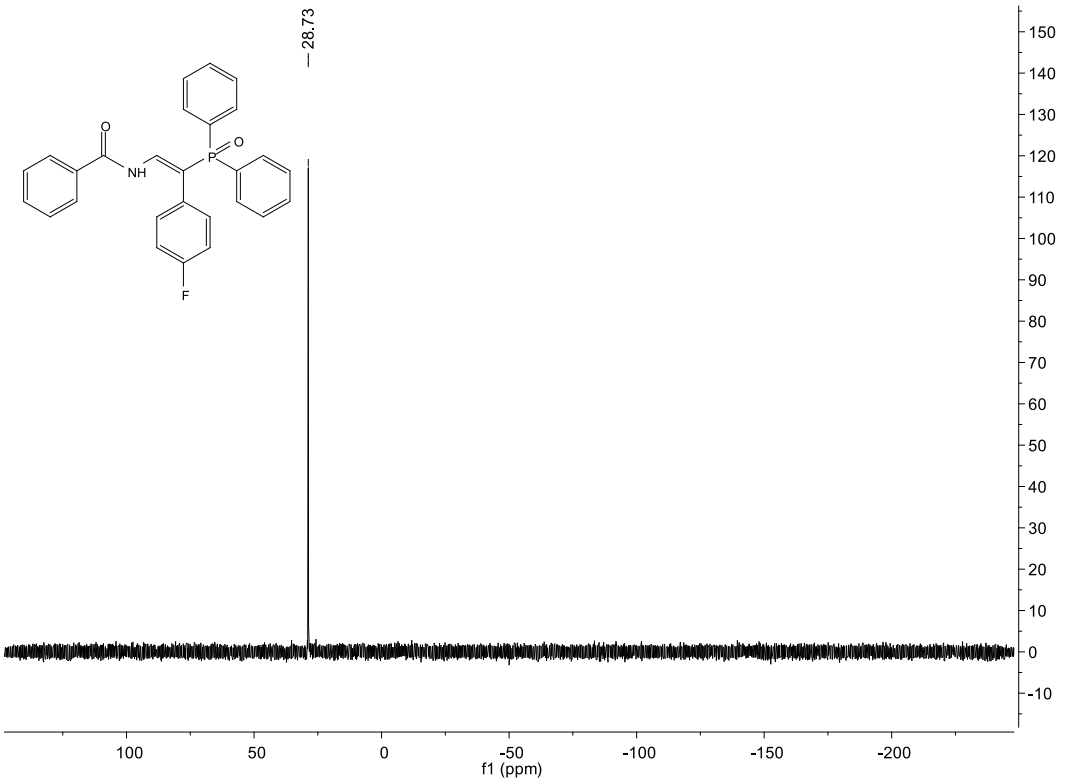



164.44
163.41
163.40
160.95
160.94
141.78
132.01
131.65
127.83
115.36
115.15
109.01
108.05
O
NH
P
O
F
164.44
163.40
160.95
160.94
132.51
132.45
132.01
131.89
131.81
130.61
128.67
127.83
115.15
109.01
f1 (ppm)
f1 (ppm)

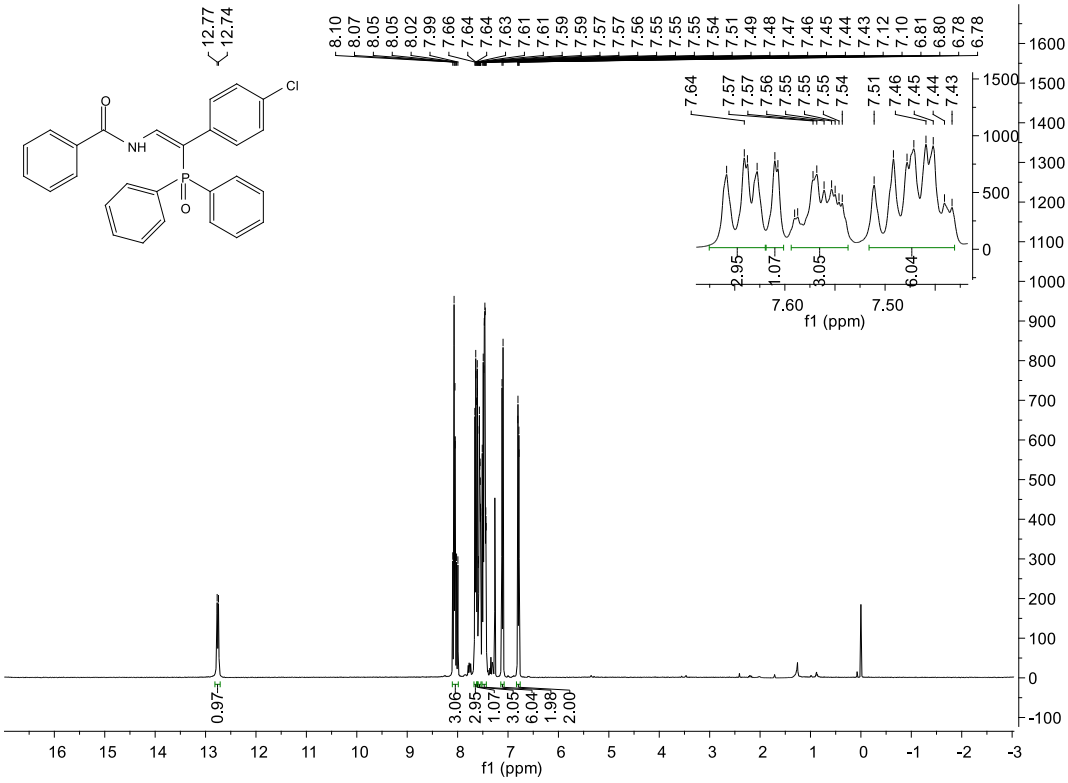

35.30
O
NH
P
O
F
f1 (ppm)

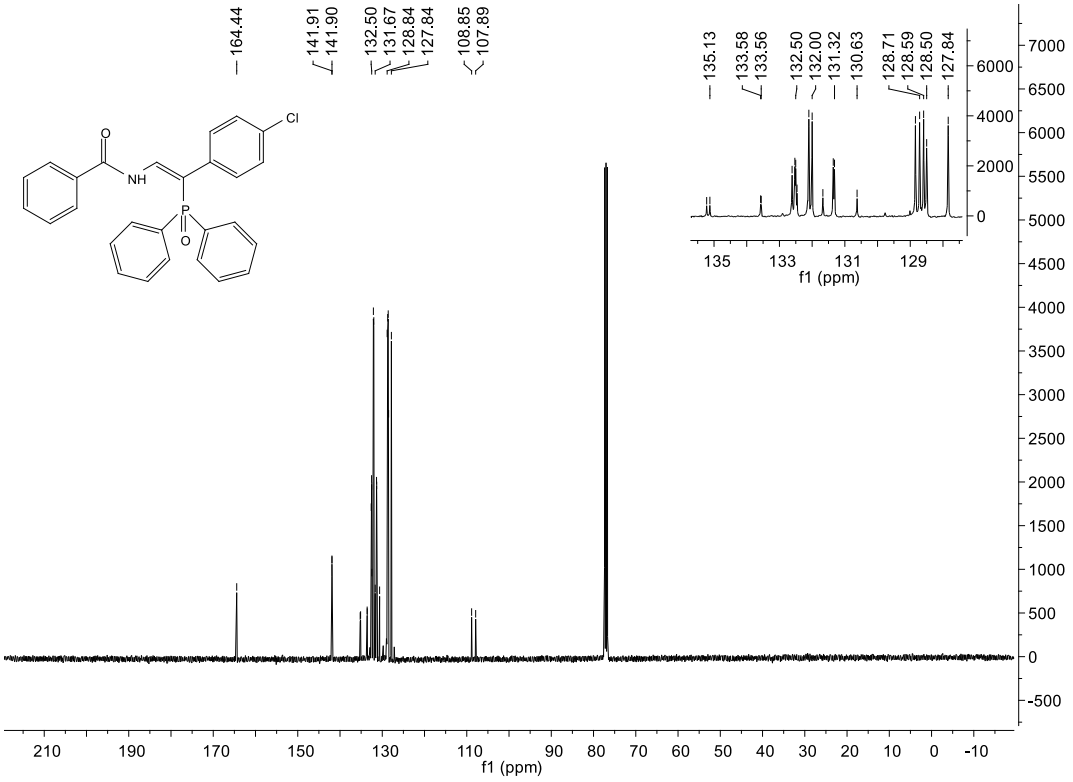
Compound 4i-*E*





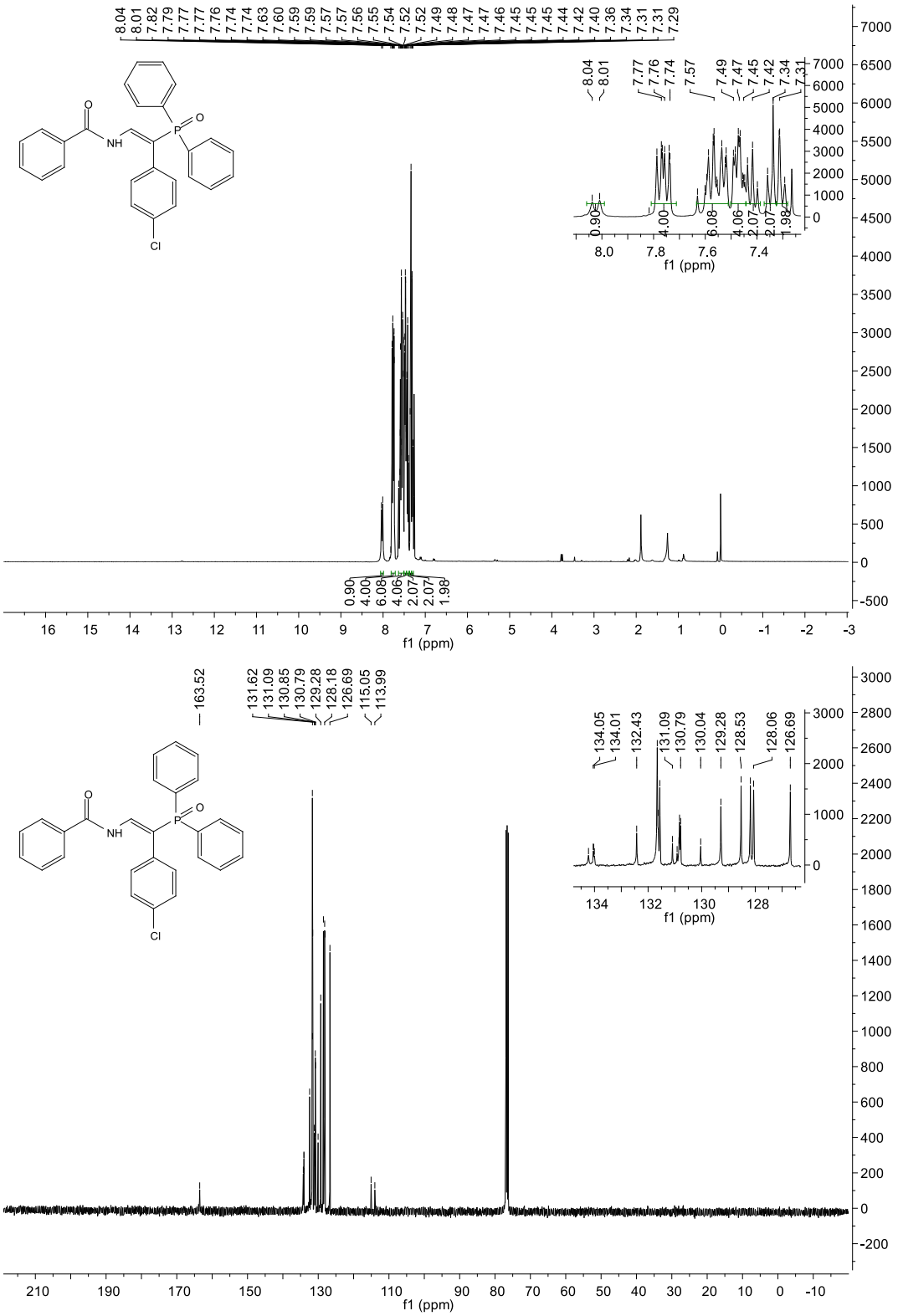
Compound 4j-*Z*

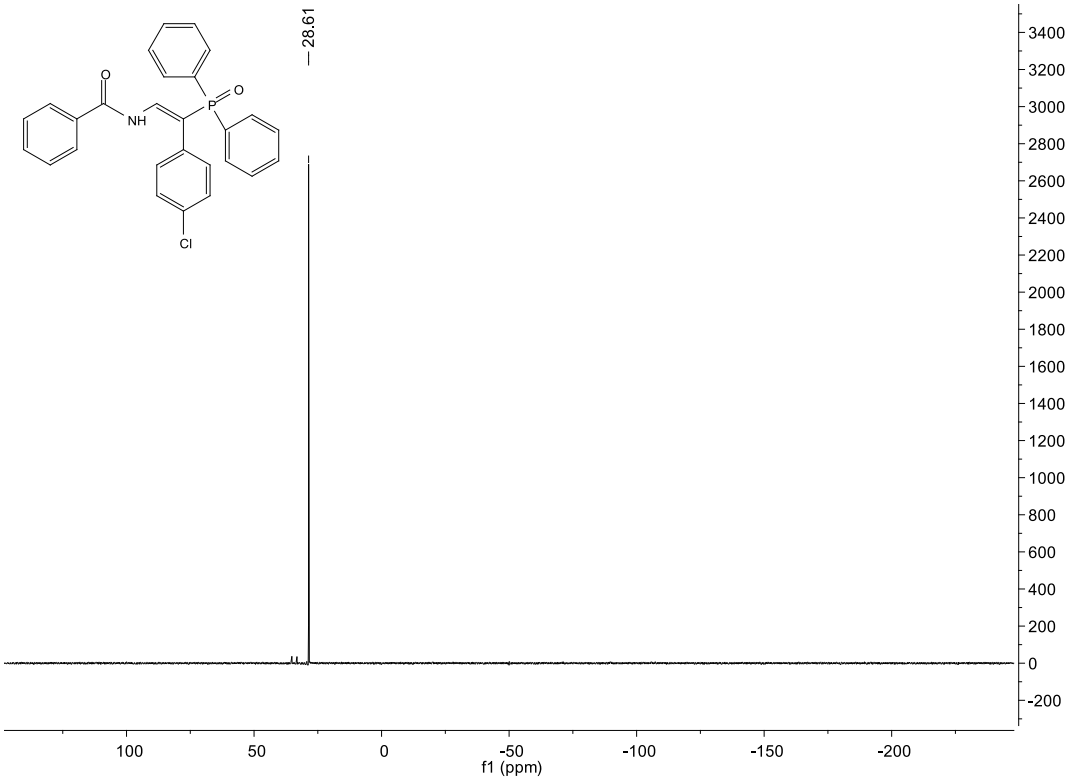



164.44
141.91
141.90
132.50
131.67
128.84
127.84
108.85
107.89
135.13
133.58
133.56
132.50
132.00
131.32
130.63
128.71
128.59
128.50
127.84
f1 (ppm)
f1 (ppm)

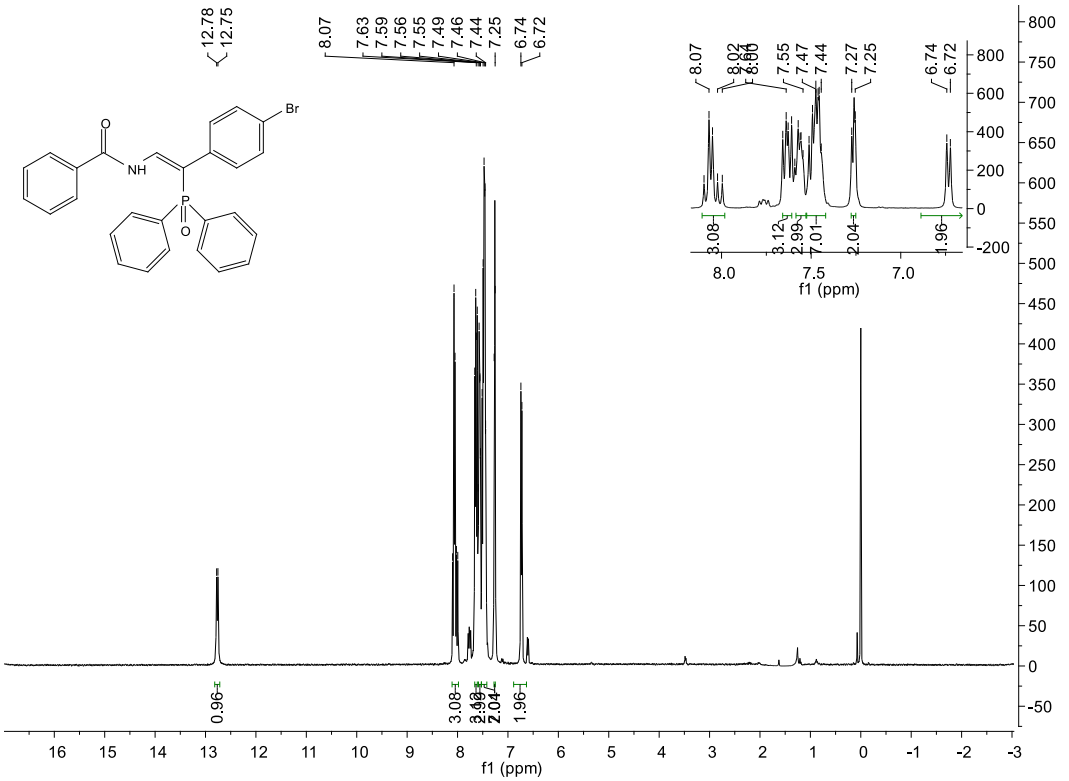

35.23
f1 (ppm)

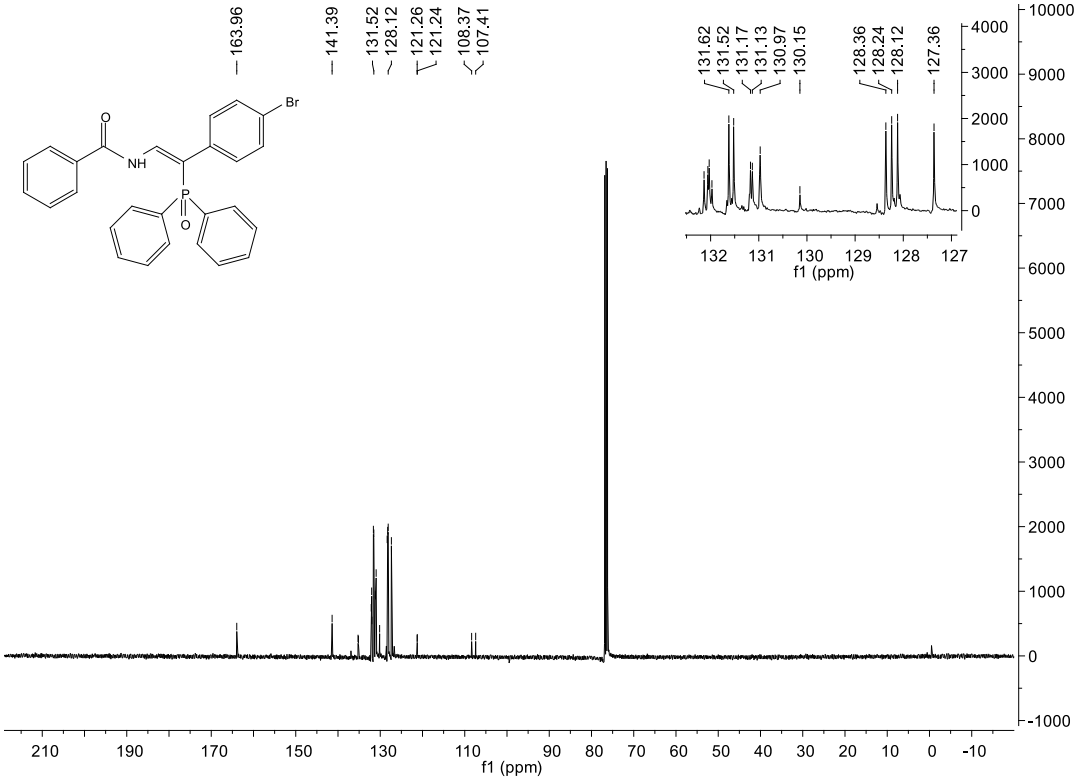
Compound 4j-*E*

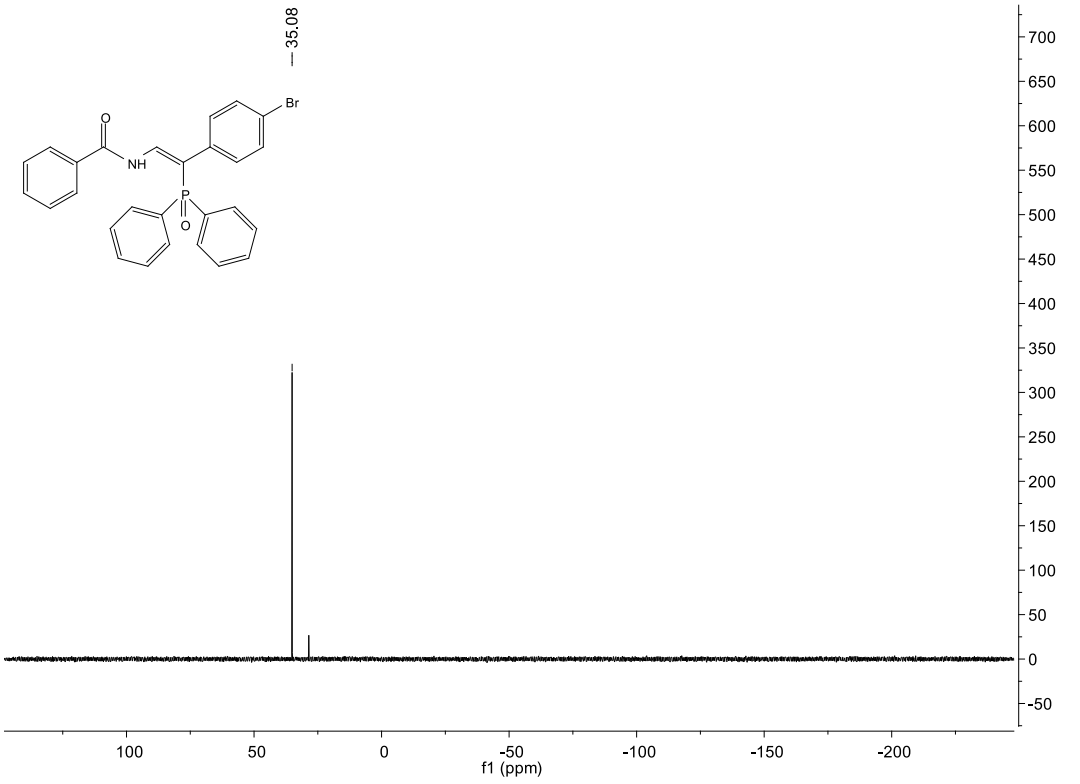




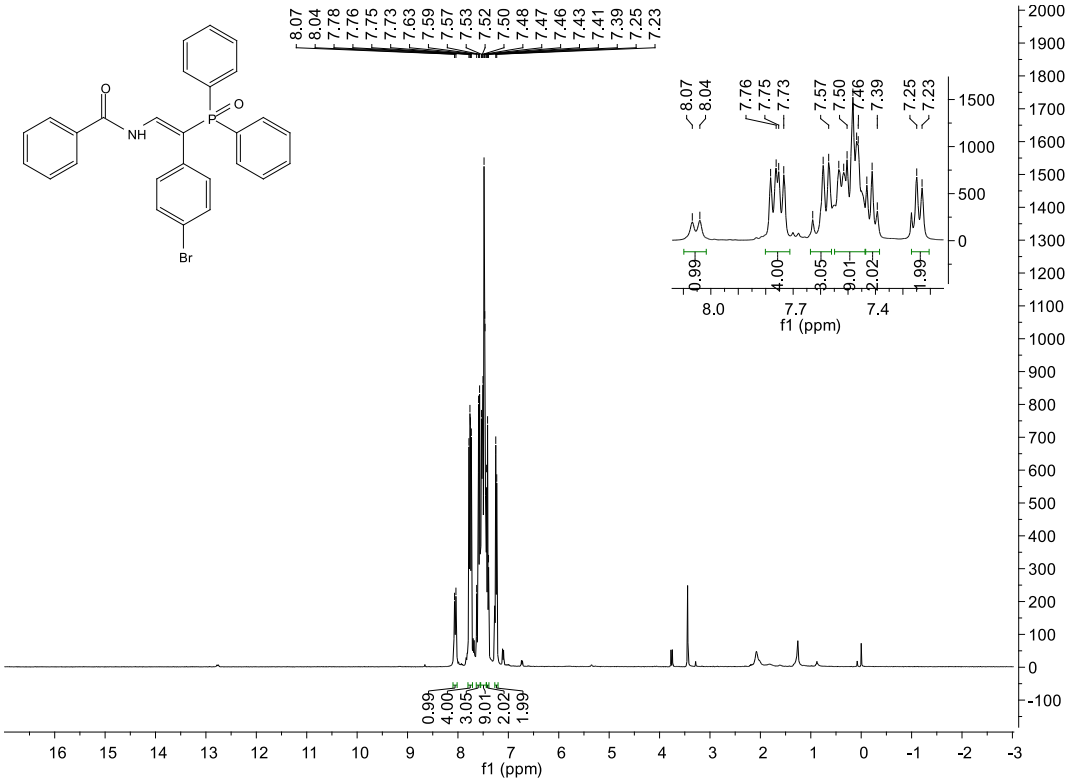
Compound 4k-*Z*

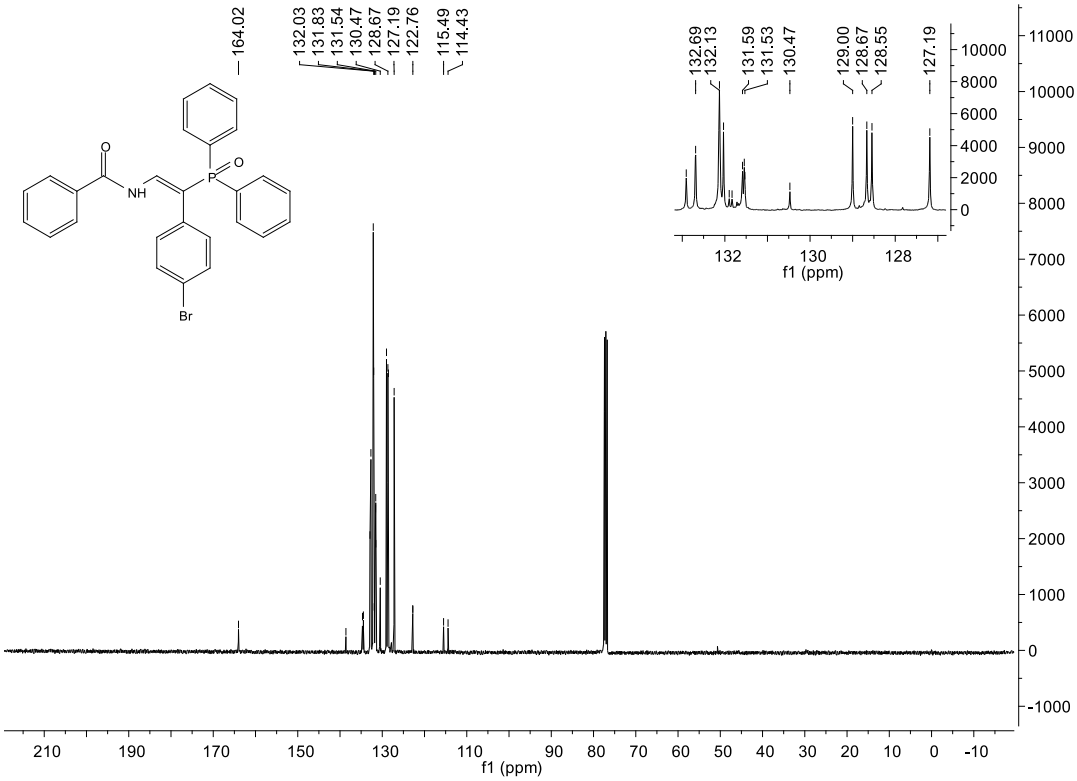


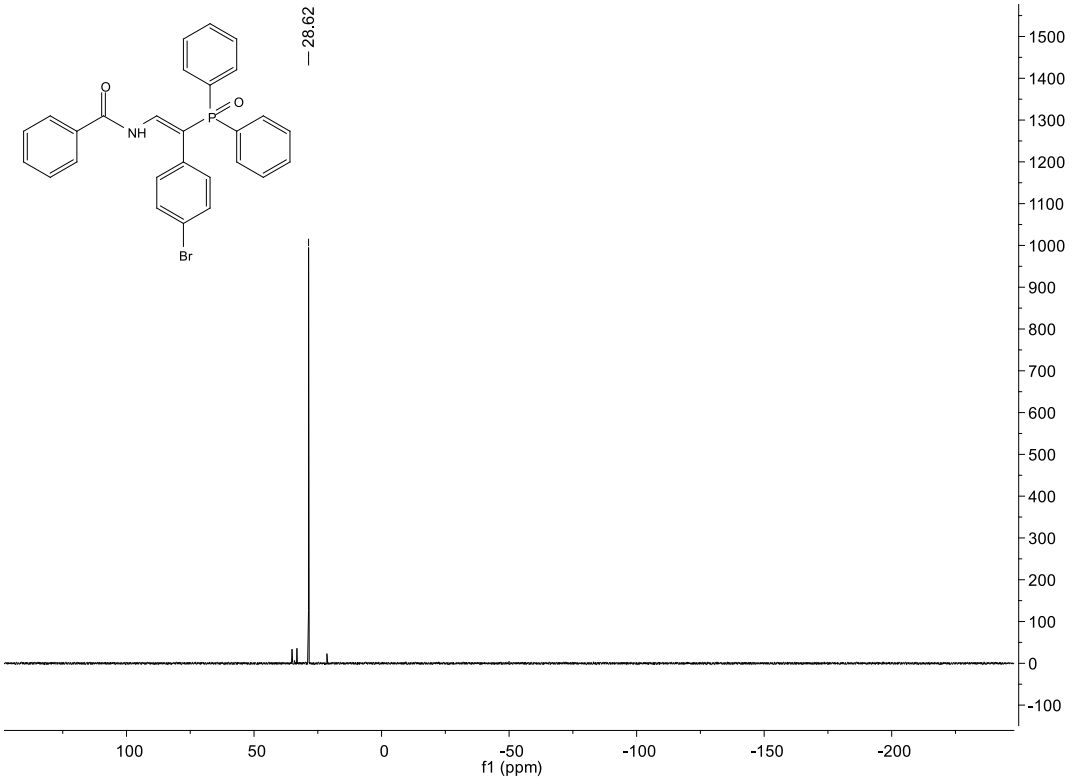

163.96
141.39
131.52
128.12
121.26
121.24
108.37
107.41
131.62
131.52
131.17
131.13
130.97
130.15
128.36
128.24
128.12
127.36
Br
O
NH
P
O
f1 (ppm)


35.08
Br
O
NH
P
O
f1 (ppm)

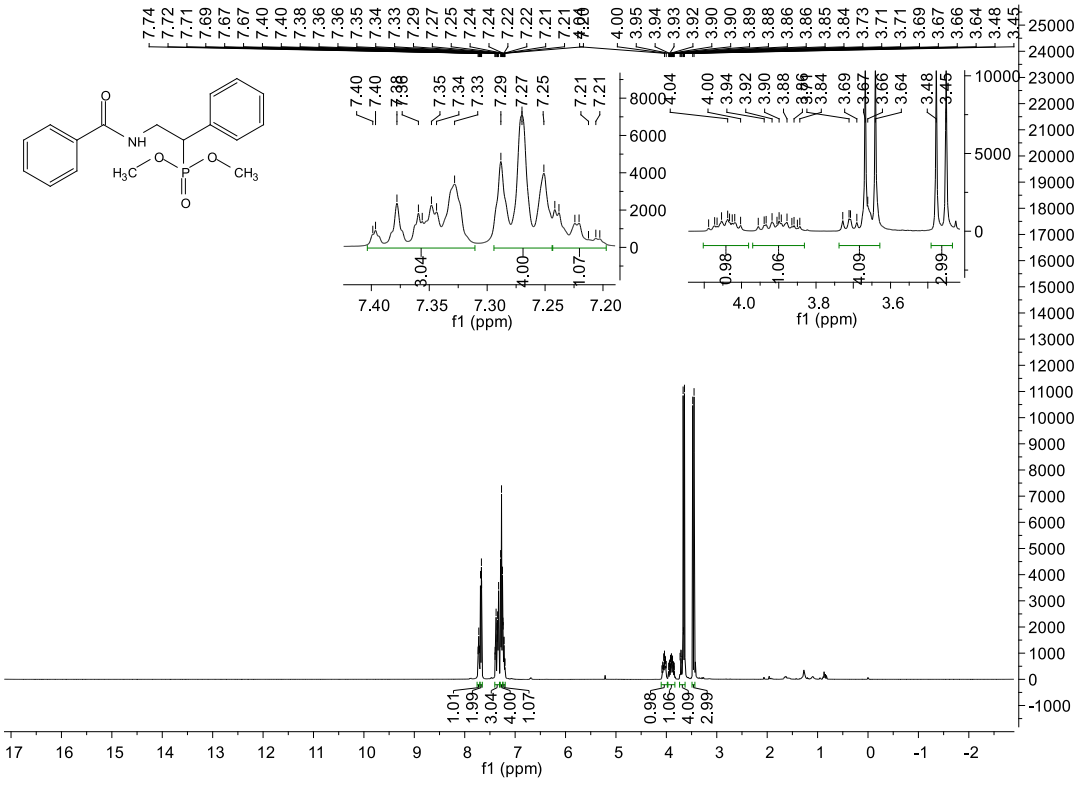
Compound 4k-*E*

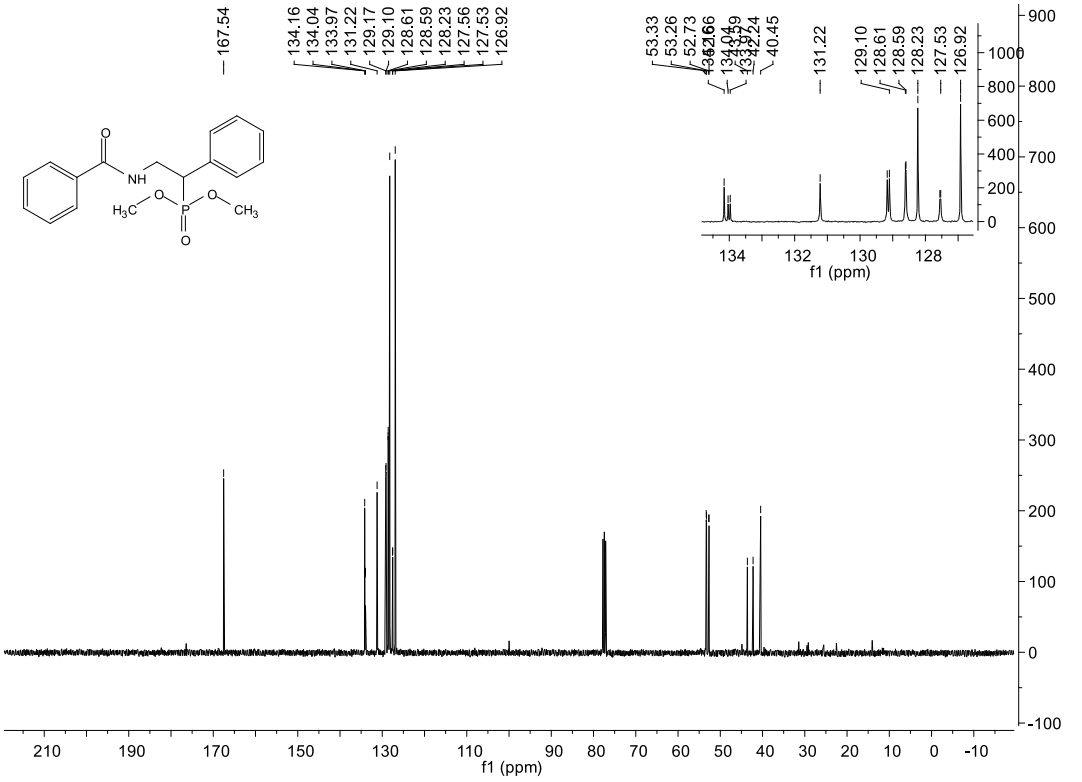






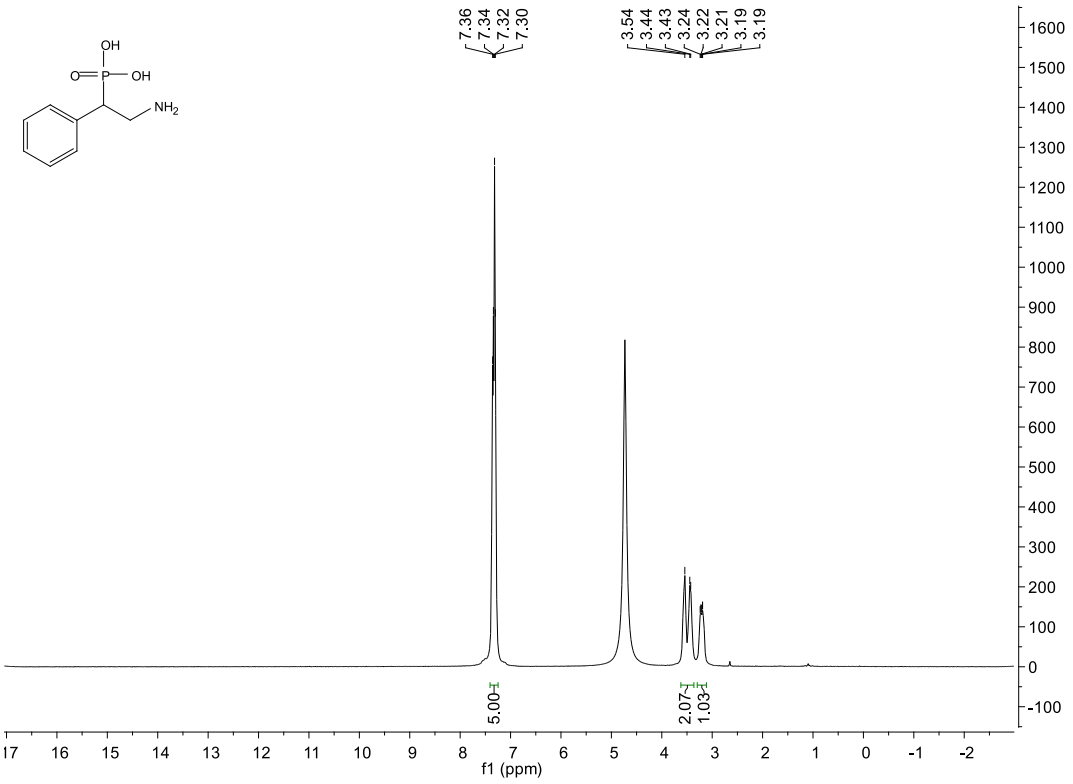
Compound 5

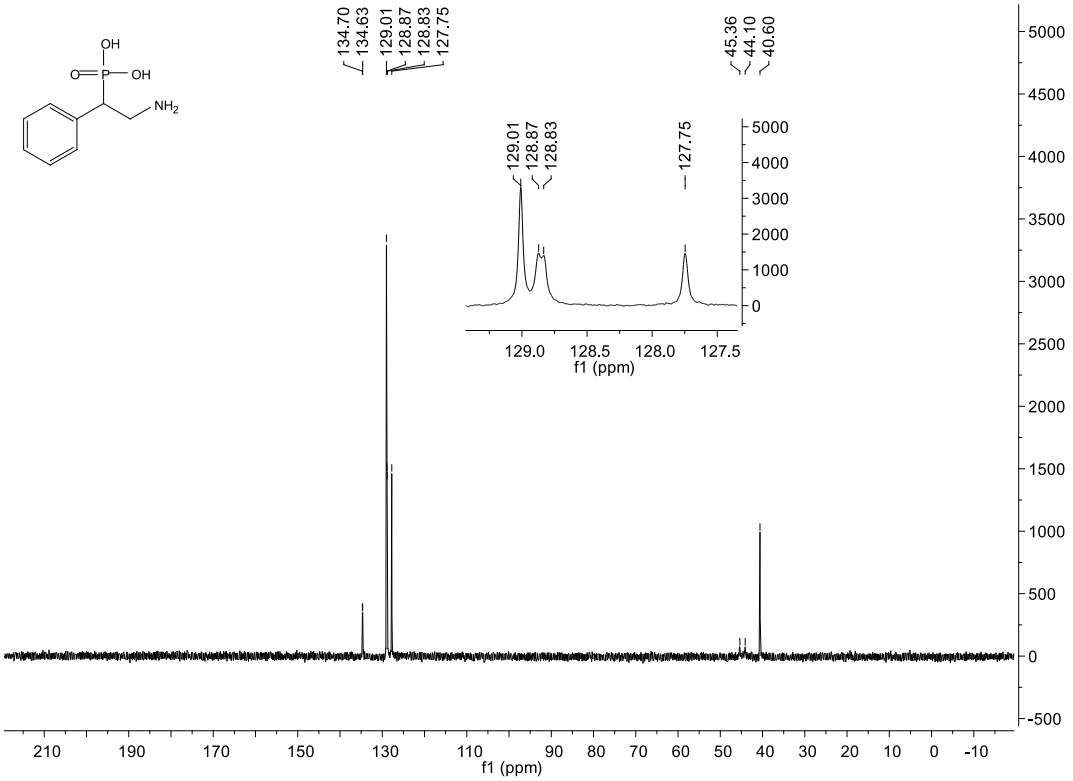


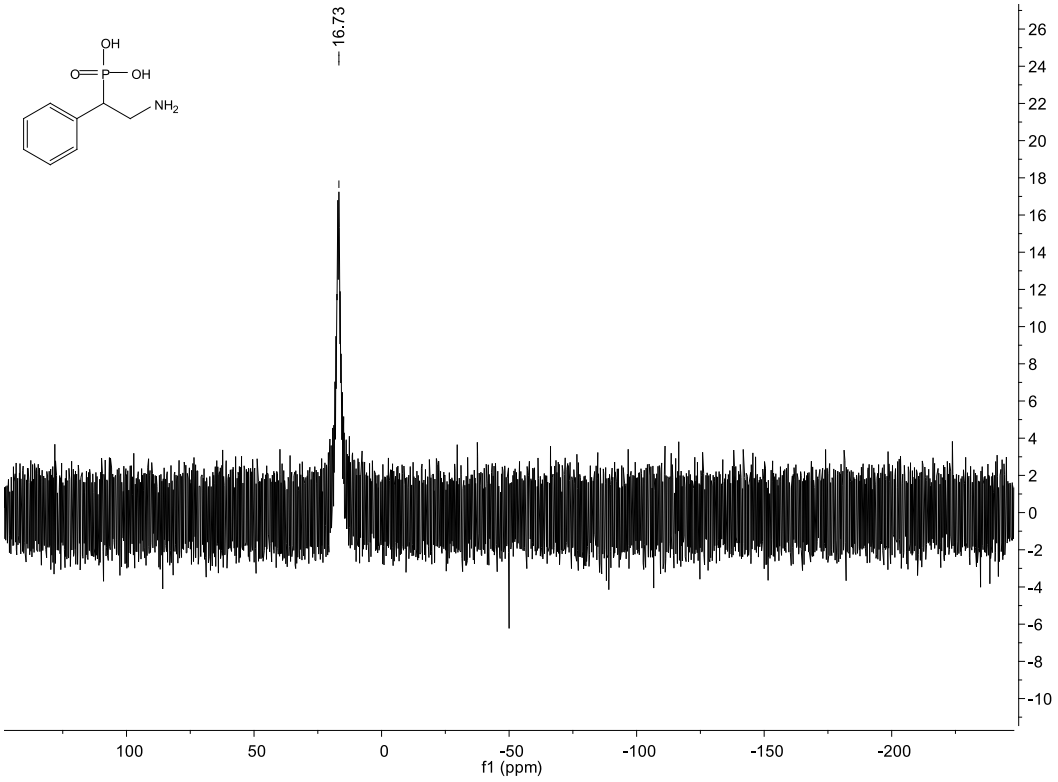

167.54
134.16
134.04
133.97
131.22
129.17
129.10
128.61
128.59
128.23
127.56
127.53
126.92
53.33
53.26
52.73
40.45
131.22
129.10
128.61
128.59
128.23
127.53
126.92
f1 (ppm)
f1 (ppm)


28.75
f1 (ppm)

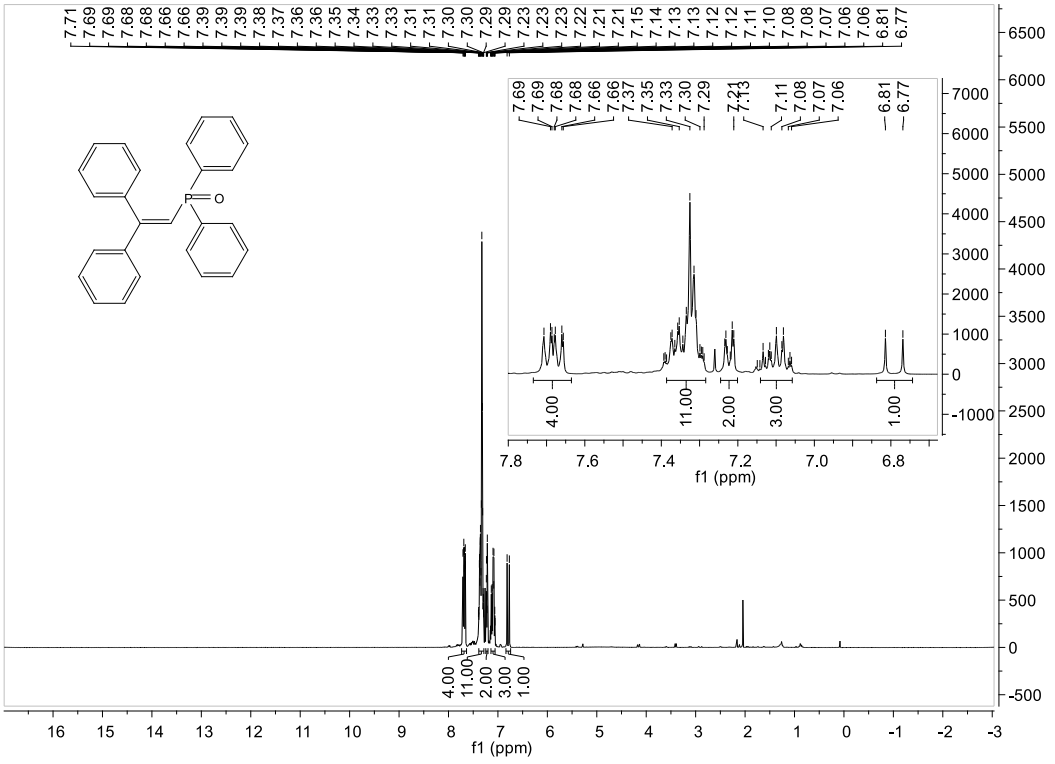
Compound 6

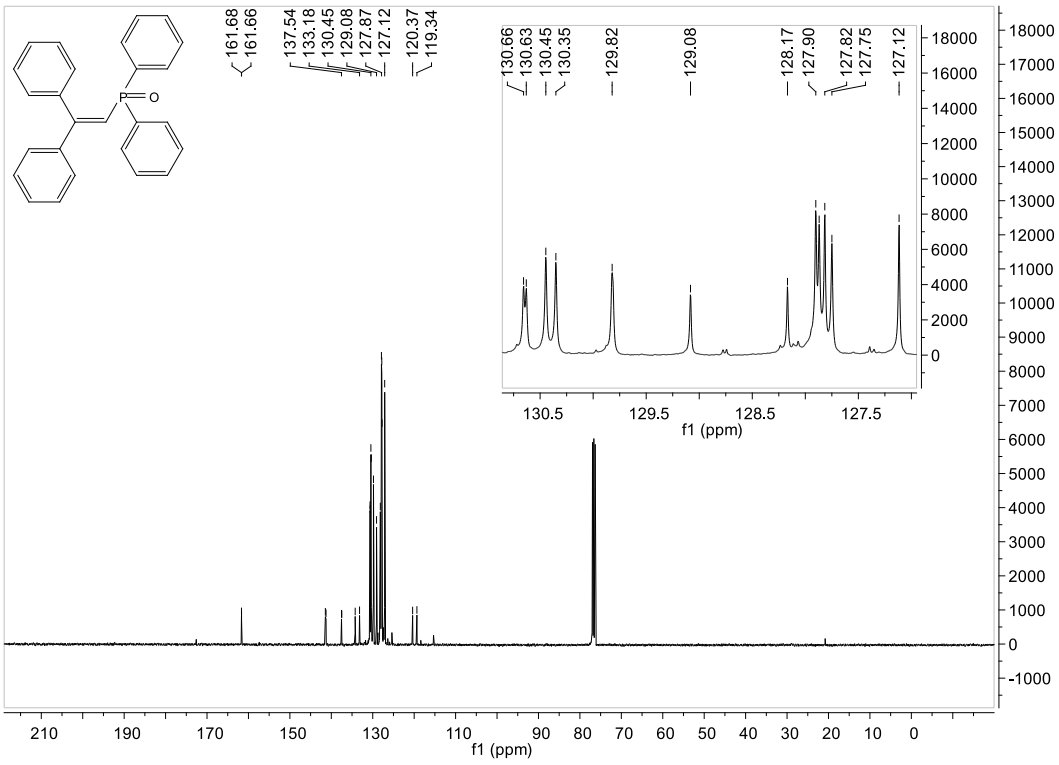

7.36
7.34
7.32
7.30
3.54
3.44
3.43
3.24
3.22
3.21
3.19
3.19
OH
O=P—OH
NH2
5.00
2.07
1.03
f1 (ppm)

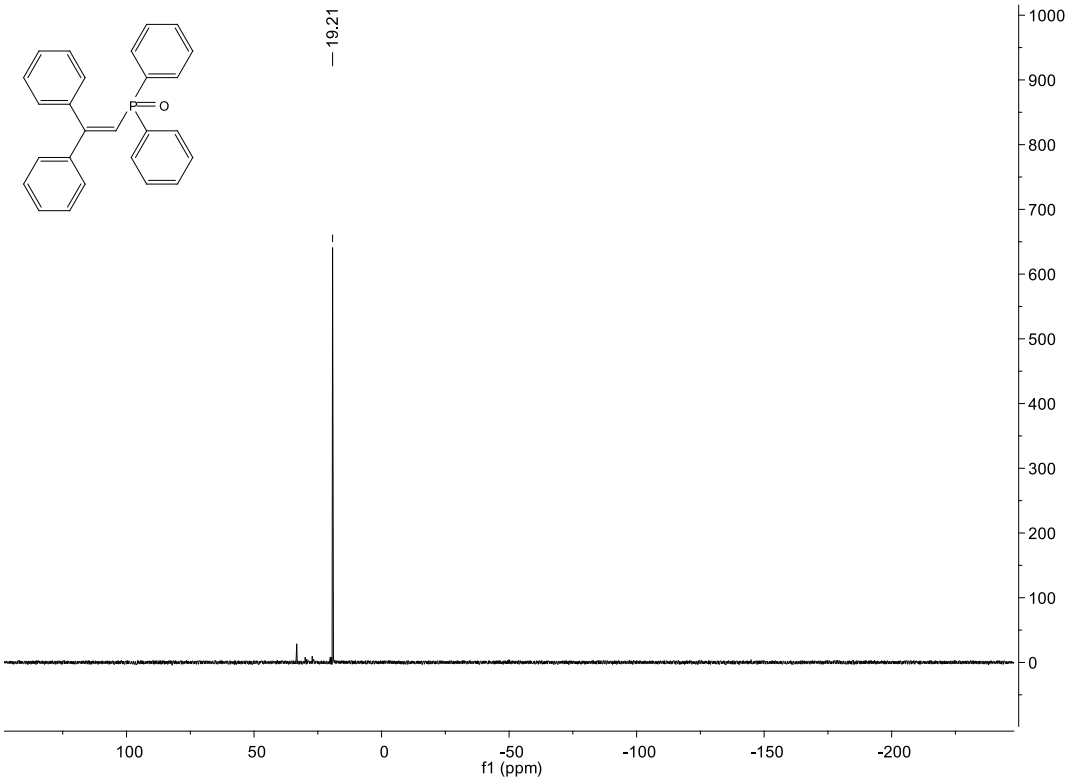

134.70
134.63
129.01
128.87
128.83
127.75
45.36
44.10
40.60
129.01
128.87
128.83
127.75
OH
O=P—OH
NH2
f1 (ppm)



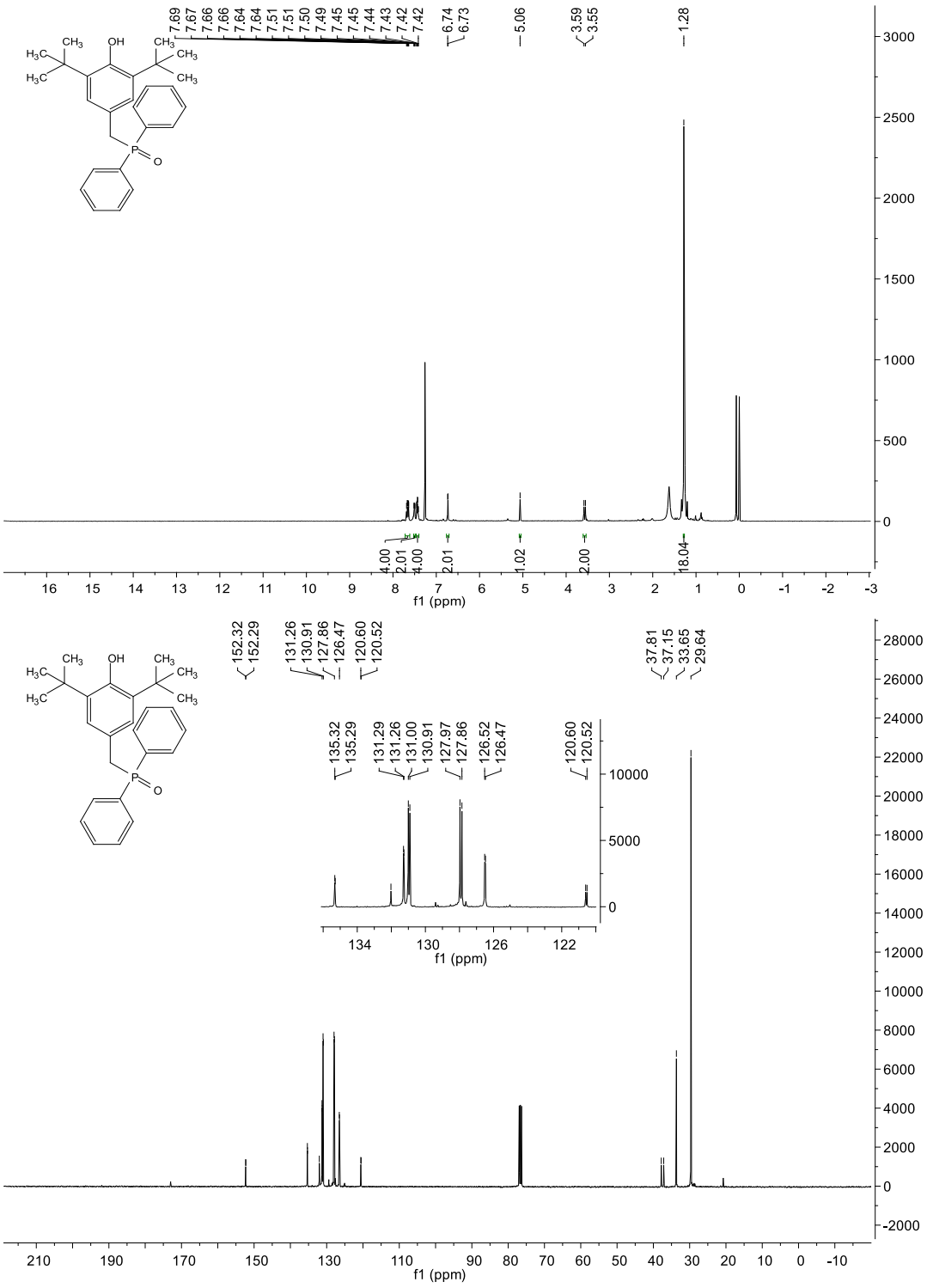
Compound 7

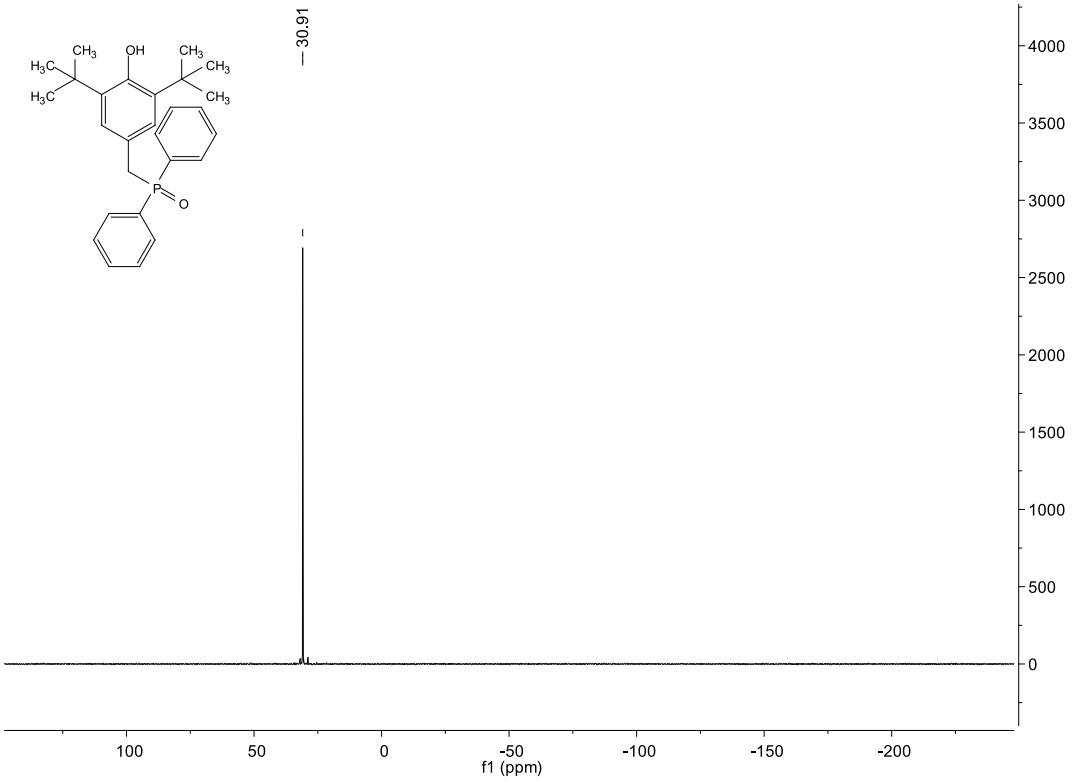



161.68
161.66
137.54
133.18
130.45
129.08
127.87
127.12
120.37
119.34
130.66
130.63
130.45
130.35
129.82
129.08
128.17
127.90
127.82
127.75
127.12
f1 (ppm)
f1 (ppm)


19.21
f1 (ppm)

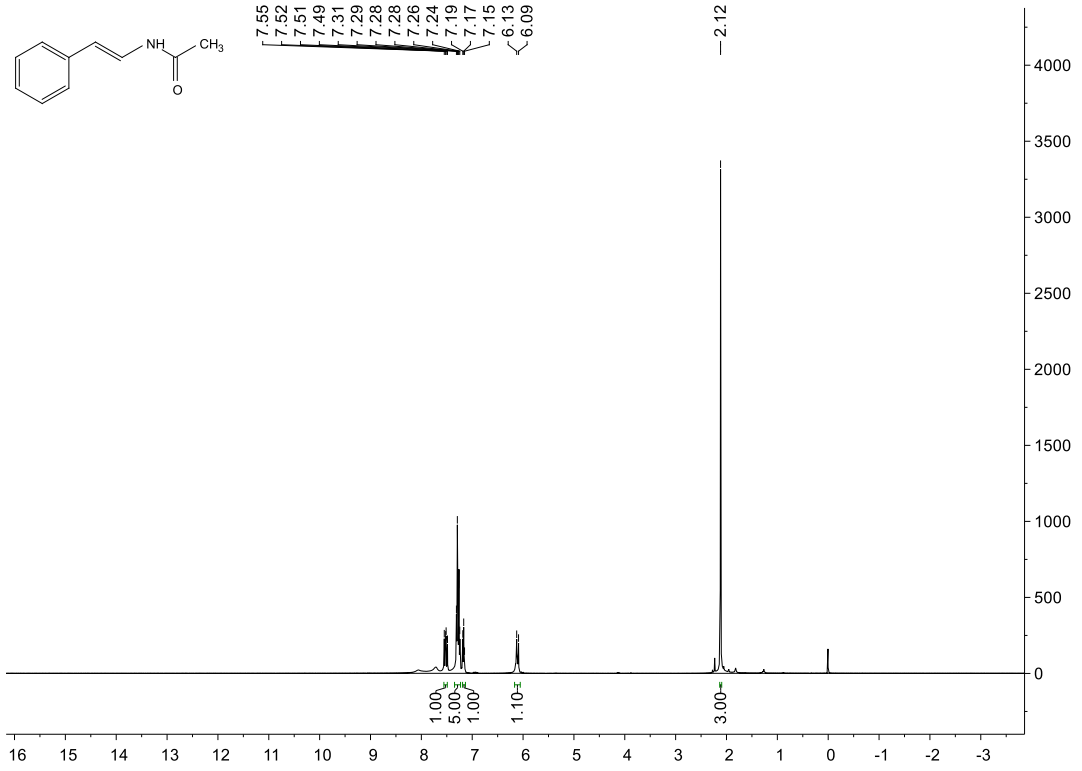
Compound 8

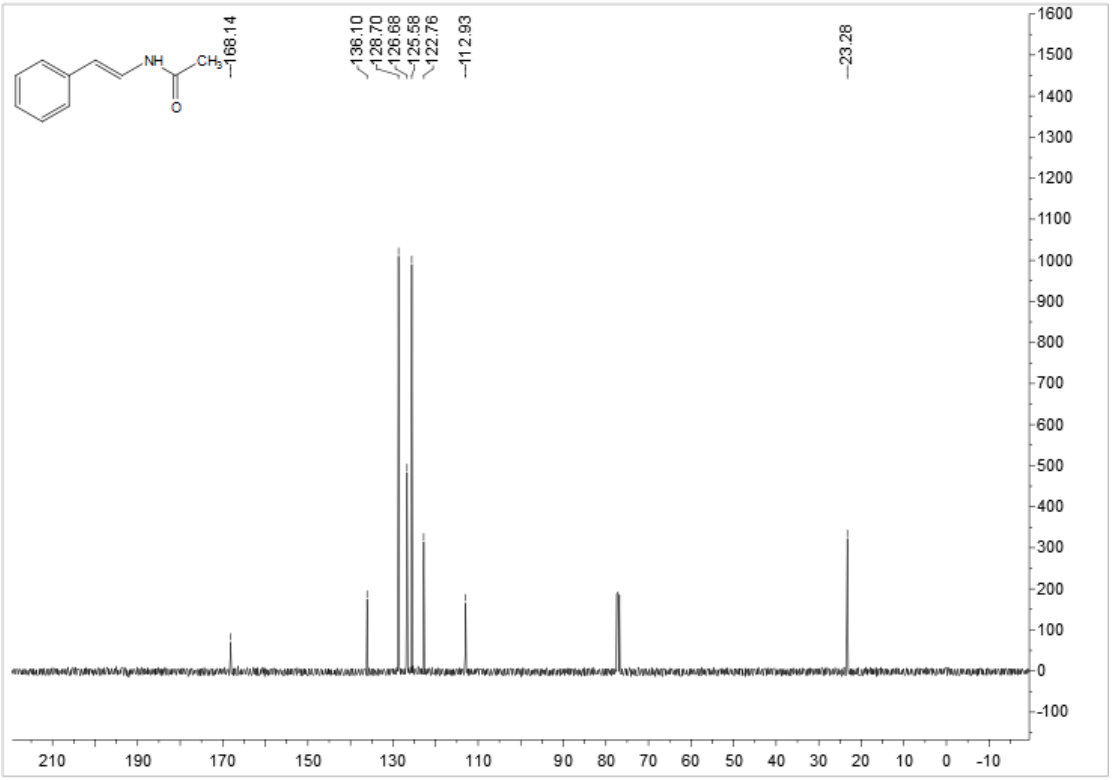

7.69
7.67
7.66
7.66
7.64
7.64
7.51
7.51
7.50
7.49
7.45
7.45
7.44
7.43
7.42
7.42
6.74
6.73
5.06
3.59
3.55
1.28
4.00
2.01
4.00
2.01
1.02
2.00
18.04
f1 (ppm)
152.32
152.29
131.26
130.91
127.86
126.47
120.60
120.52
37.81
37.15
33.65
29.64
135.32
135.29
131.29
131.26
131.00
130.91
127.97
127.86
126.52
126.47
120.60
120.52
f1 (ppm)
f1 (ppm)


30.91
4000
3500
3000
2500
2000
1500
1000
500
0
100
50
0
-50
-100
-150
-200
f1 (ppm)

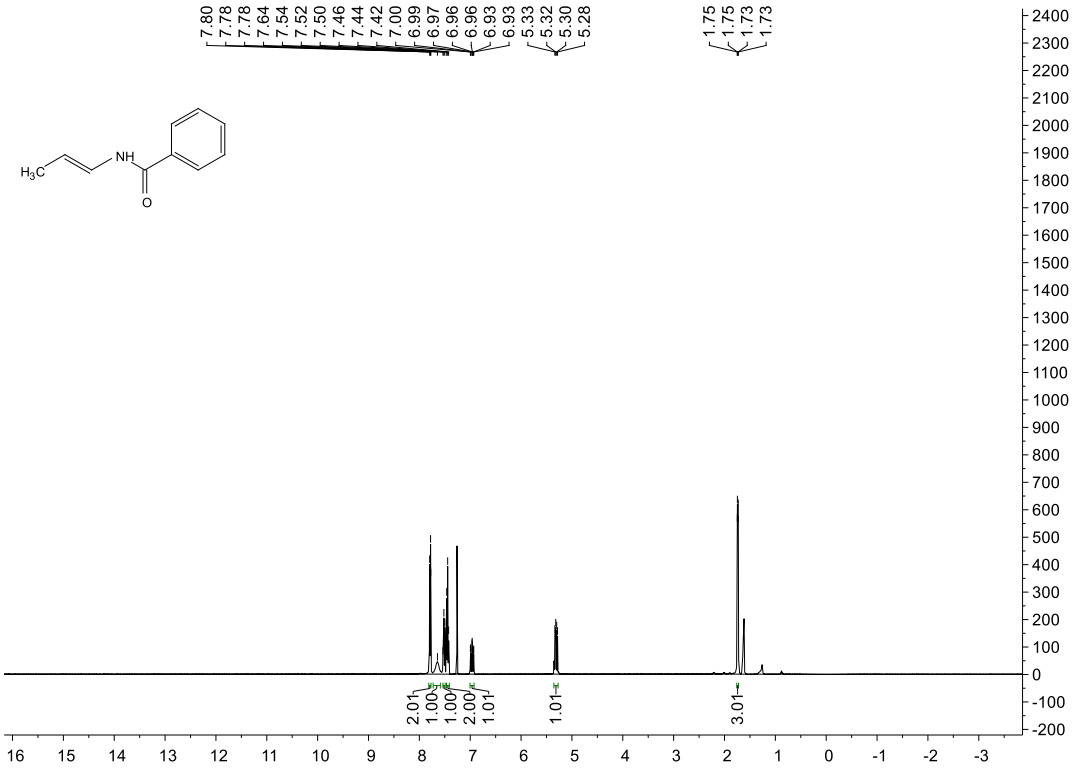
10. ^{1}H and ^{13}C NMR spectra of compounds I-III, and ^{1}H NMR spectra of trace amount of I-P and II-P

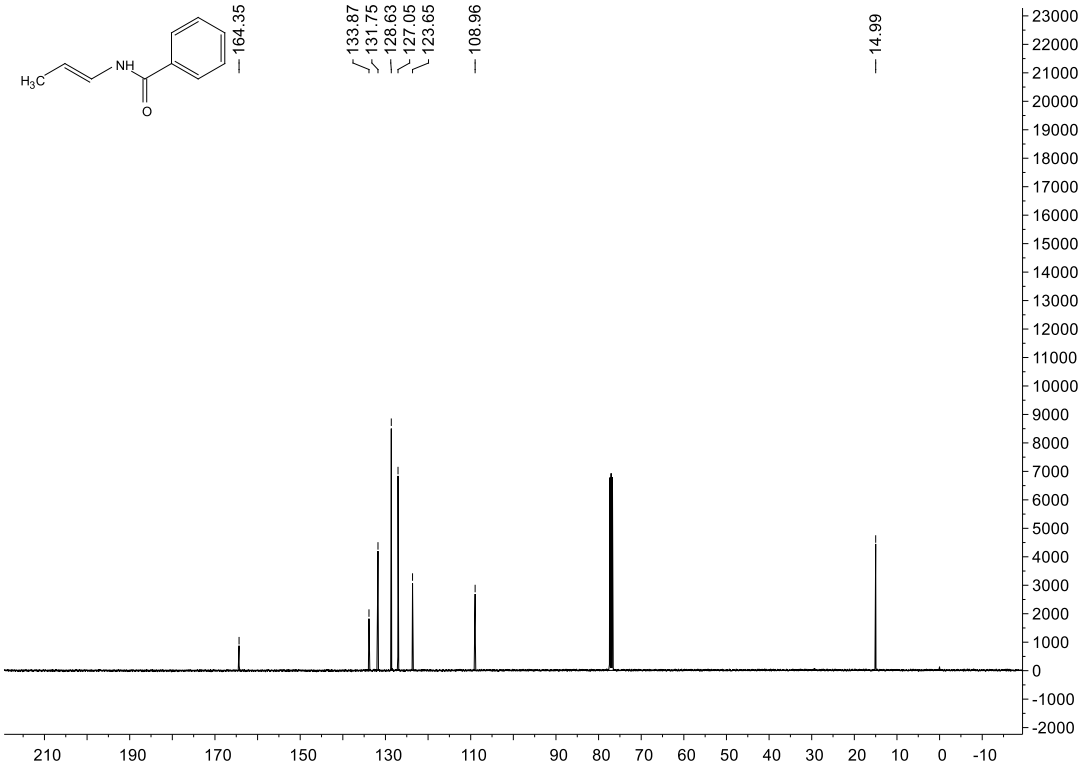
Compound **I**



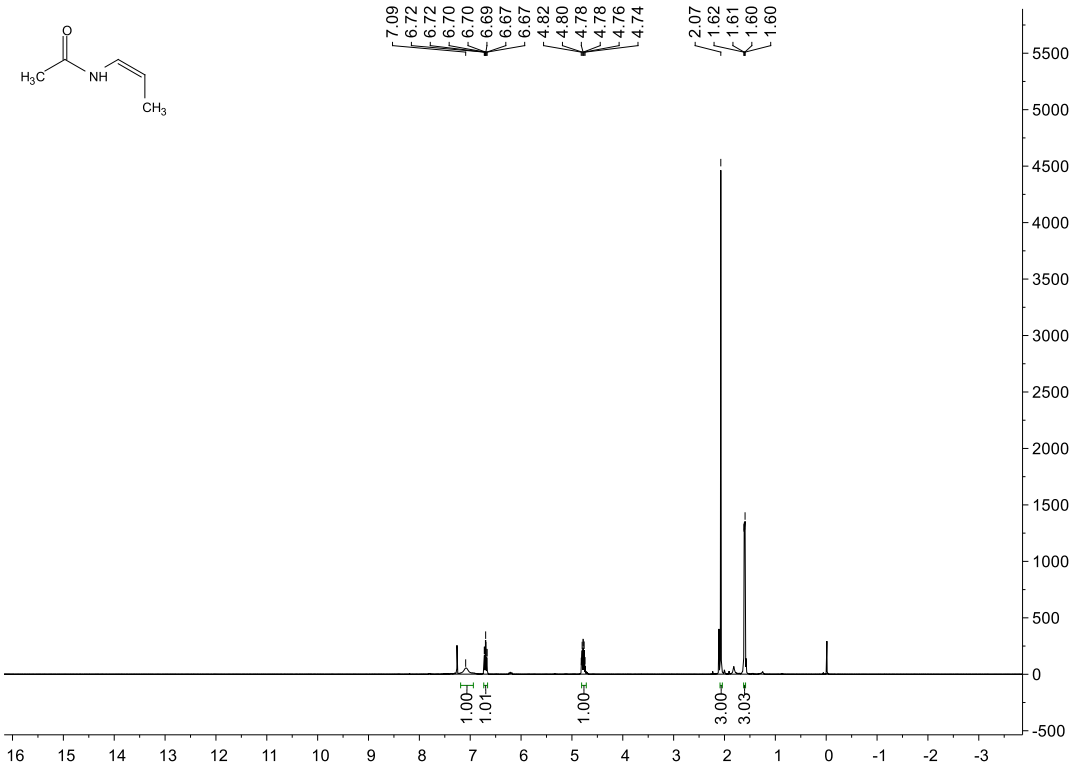


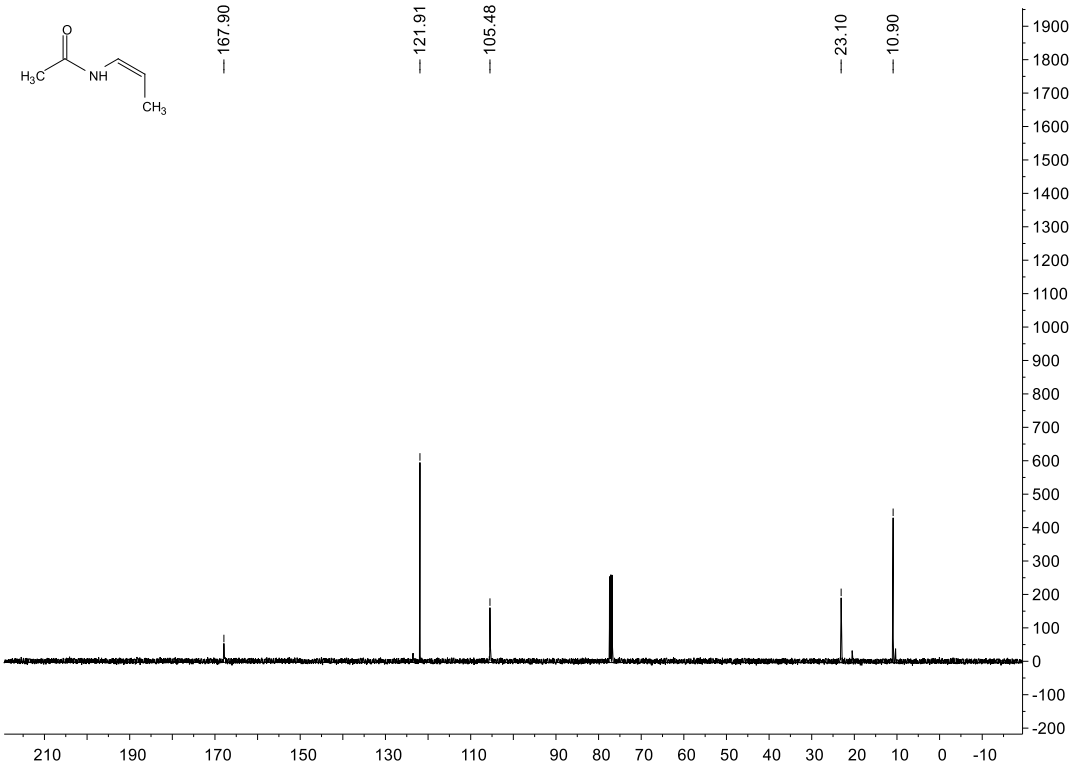
Compound **II**


7.80
7.78
7.78
7.64
7.54
7.52
7.50
7.46
7.44
7.42
7.00
6.99
6.97
6.96
6.96
6.93
6.93
5.33
5.32
5.30
5.28
1.75
1.75
1.73
1.73
NH
O
H3C
2.01
1.00
1.00
2.00
1.01
1.01
3.01

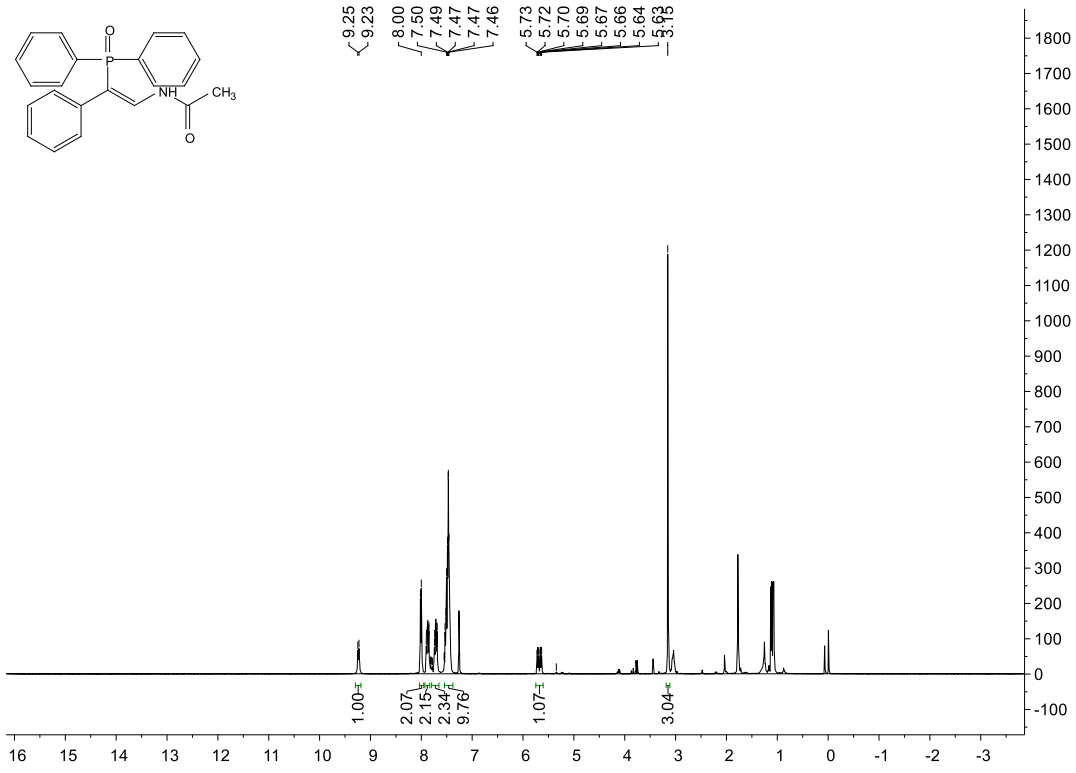

164.35
133.87
131.75
128.63
127.05
123.65
108.96
14.99
NH
O
H3C

Compound **III**

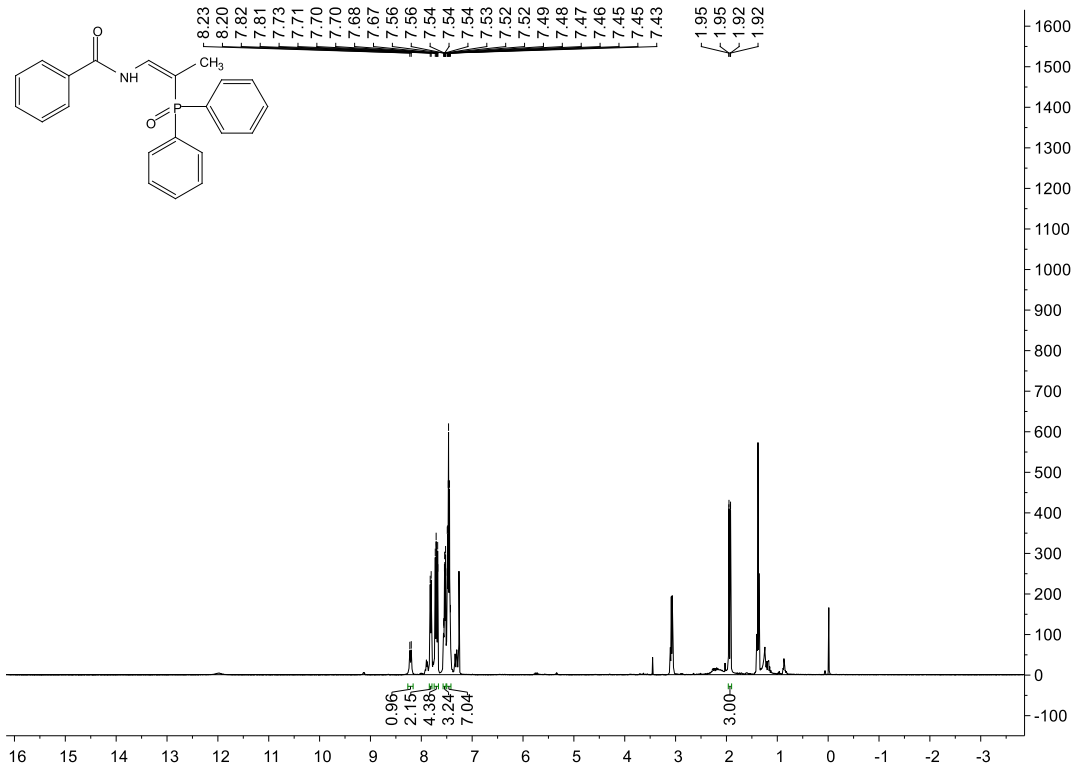




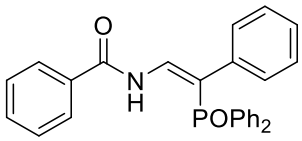
^{1}H NMR of trace amount of **I-P**



^{1}H NMR of trace amount of **II-P**

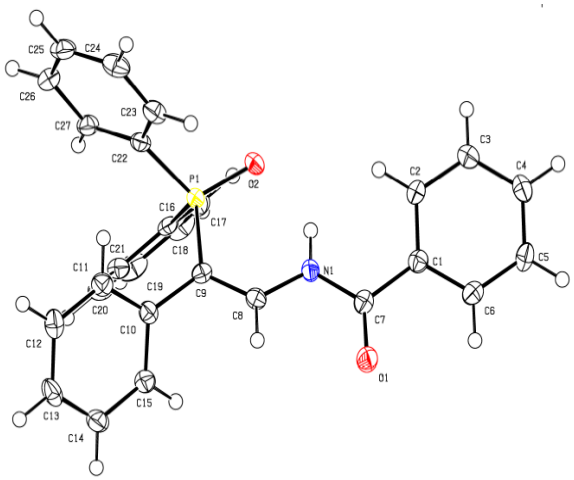


11. X-ray crystallographic data for compounds 3a-*Z* and 3a-*E*

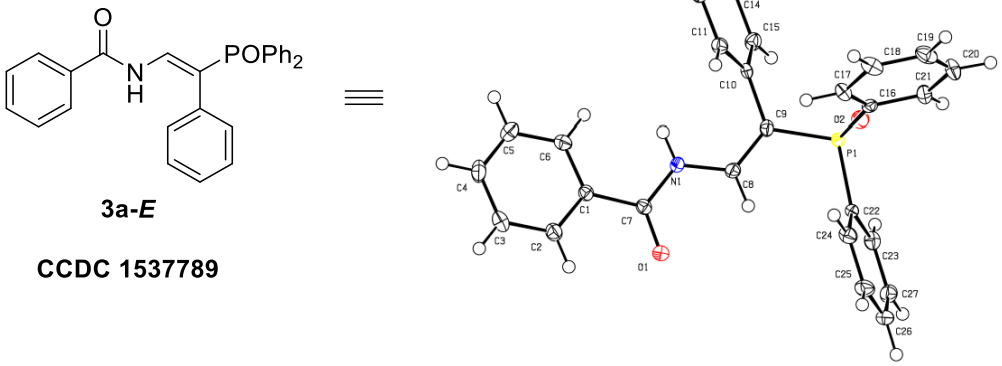


3a-*Z*

CCDC 1871954



Compound	**3a-*Z***
formula	$C_{27}H_{22}NO_2P$
fw	423.42
crystal system	monoclinic
T/K	120(2)
a/Å	7.8836(5)
b/Å	12.2399(8)
c/Å	11.1988(8)
α/°	90.00
β/°	90.174(2)
γ/°	90.00
V/Å^3	1080.62(13)
Z	2
D_C/g cm^{-3}	1.301
F(000)	444
collected	4503
GOF	1.026
Final R indices [I>2 sigma (I)]	R1 = 0.0269 wR2 = 0.0732
R indices (all data)	R1 = 0.0275 wR2 = 0.0738
Largest diff. peak, hole/e.Å^{-3}	0.210, -0.251



3a-*E*

CCDC 1537789

Compound	**3a-*E***
formula	$C_{27}H_{22}NO_2P$
fw	423.43
crystal system	triclinic
T/K	120(2)
a/Å	6.0253(6)
b/Å	9.0011(9)
c/Å	10.3679(11)
α/°	75.005(3)
β/°	76.437(3)
γ/°	89.090(3)
V/Å^3	527.40(9)
Z	1
D_C/g cm^{-3}	1.333
F(000)	222
collected	8754
GOF	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0427 wR2 = 0.0850
R indices (all data)	R1 = 0.0488 wR2 = 0.0879
Largest diff. peak, hole/e.Å^{-3}	0.264, -0.277