Catalytic Asymmetric Stetter Reaction Onto Vinylphosphine Oxides and Vinylphosphonates

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Supporting Information

1 General Methods……..2
2 Aldehyde Synthesis……..……4
3 Stetter Substrate Synthesis……...…..10
4 X-ray crystallographic data…….……...18
5 ^{1}H, ^{13}C and ^{31}P NMR for new aldehydes……...34
6 ^{1}H, ^{13}C and ^{31}P NMR for new Stetter substrates...…….52
7 ^{1}H, ^{13}C and ^{31}P NMR for global reduction products……..70

General Methods. All reactions were carried out under an atmosphere of argon in flame dried glassware with magnetic stirring. Reactions were monitored using thin layer chromatography using Silicycle .25mm silica gel 60-F plates. Visualization was accomplished with UV light, $KMnO_4$, and aqueous ceric ammonium molybdate dips followed by heating. Flash column chromatography was performed using Silicycle silicagel 40-63 μm, 60 Å. Data for NMR are reported as follows: chemical shift in parts per million (δ ppm) from an internal standard [tetramethylsilane (TMS) or chloroform ($CHCl_3$)], multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). ^{13}C NMR chemical shifts are reported in ppm from $CDCl_3$ (taken as 77.0 ppm). Enantiomeric excesses were determined by analytical high performance liquid chromatography (HPLC) using a gradient of isoproponal and are reported as follows; % isopropanol, flow rate, retention time (in minutes) for major and minor enantiomers. HPLC was performed using a Chiralcel OD-H, AD-H (0.46 cm X 25 cm) chiral columns. Toluene was degassed with argon and passed through one column of neutral alumina and one column of Q5 reactant. All racemic products were prepared analogously to the asymmetric reaction utilizing achiral catalyst.

General procedure for oxidation of alkynes to vinylphosphine oxides.
A flame dried round bottom flask was charged with the bromide salt of Wilkinson's catalyst (0.04 eq). To this flask was added diphenylphosphine oxide (1.0 eq), the corresponding alkyne of type **3** (1.0 eq) and toluene (for a final concentration of 1M). The resulting solution was heated to 60 °C and allowed to stir for 12 hours. The reaction mixture was placed directly onto a silica gel column and eluted with a suitable solution of ethyl acetate and MeOH (20:1). Evaporation of solvent afforded analytically pure vinylphosphine oxide.

General procedure for preparation of vinylphosphonates.
A flame dried round bottom flask was charged with diisopropylamine (DIA) (2.0 eq) in THF (2M) and cooled to 0 °C. To the flask with stirring was added *n*-BuLi (2.0 eq) and the reaction was allowed to stir for 10 min. The reaction mixture was then cooled to -78 °C and a solution of diethyl methylphosphonate (1.0 eq) in THF (2M) was added dropwise via syringe. The reaction was allowed to stir for 10 min at -78 °C and a solution of diethyl chlorophosphate (1.0 eq) in THF (2M) was added dropwise via syringe and allowed to stir for an additional 20 min at the same temperature. A solution of aldehyde (1.0 eq) in THF (1M) was added dropwise via syringe and the reaction warmed to -20 °C (by placing in the appropriate bath) and allowed to stir for an additional 1 hour. The reaction mixture was extracted with Et_2O and washed with H_2O (2x), $NaHCO_3$ (1x), and brine (2x). Rotary evaporation afforded the crude vinylphosphonate which was purified by silica gel column chromatography using a solution of ethyl acetate and MeOH (20:1). Evaporation of solvent afforded analytically pure vinylphosphonate.

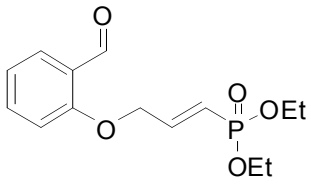
General procedure for deprotection of dimethyl acetals.
The dimethyl acetal was deprotected by stirring the vinylphosphonate in a mixture of 4:1 AcOH:H_2O for 12 hours followed by extraction with EtOAc and rotary evaporation.

Silica gel column chromatography using ethyl acetate and MeOH (20:1) followed by rotary evaporation afforded analytically pure aldehyde.

General procedure for deprotection of 1,3 dithianes.
A flame dried round bottom flask was charged with vinylphosphine oxide (1.0 eq), chloroform (0.25 M) and MeOH (3-5 drops) and to it was added $Hg(O_2CCF_3)_2$ (1.5 eq). The reaction mixture was stirred at ambient temperature and monitored by TLC. The reaction mixture was then filtered through a pad of celite and evaporated. The crude reaction mixture was then placed on a silica gel column and eluted with a suitable solution of ethyl acetate and MeOH (20:1). Evaporation of solvent afforded analytically pure aldehyde.

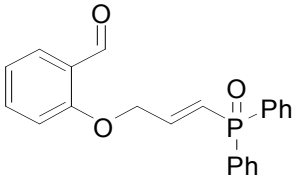
General procedure for the asymmetric intramolecular Stetter reaction.
A flame dried round bottom flask was charged with triazolium salt (0.2 eq) and 1.0 mL of toluene. To this solution was added KHMDS (0.5 M in toluene prepared prior to use from 0.05 g of KHMDS in 0.5 mL of toluene) (0.2 eq) via syringe and the solution was allowed to stir at ambient temperature for 15 minutes. A solution of the substrate (1.0 eq) in 2.0 mL of toluene was added. The resulting solution was allowed to stir at ambient temperature and monitored by TLC. The reaction mixture was placed directly onto a silica gel column and eluted with a suitable solution of ethyl acetate and MeOH (20:1). Evaporation of solvent afforded analytically pure product.

(E)-diethyl 3-(2-formylphenoxy)prop-1-enylphosphonate (8)



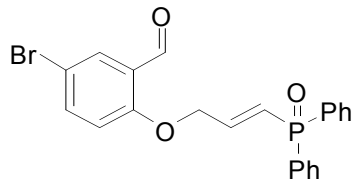
According to the general procedure, DIA (80.0 μL, 0.566 mmol, 2.0 eq) treated with *n*BuLi (354.0 µL, 0.566 mmol, 2.0 eq). The mixture was cooled and treated with diethyl methyl phosphonate (43.0 mg, 0.283 mmol, 1.0 eq), diethyl chlorophosphate (41.0 µL, 0.283 mmol, 1.0 eq) and aldehyde (72.0 mg, 0.283 mmol, 1.0 eq). Upon workup and column chromatography, the vinylphosphonate 97.0 mg (0.25 mmol, 88% yield). According to the general procedure, the vinylphosphonate 1,3 dithiane (95.0 mg, 0.245 mmol, 1.0 eq) was treated with $Hg(O_2CCF_3)_2$ (157.0 mg, 0.367 mmol, 1.5 eq) and stirred for 4 hours and filtered through celite. Column chromatography (ethyl acetate:MeOH, 20:1) afforded 52.0 mg (0.17 mmol, 71% yield) of **8** as a yellow oil in 63% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (1H, s), 7.82 (1H, dd, J = 7.7, 1.7 Hz), 7.51 (1H, ddd, J = 8.6, 7.5, 2.0 Hz), 7.04 (1H, dd, J = 7.7, 7.7 Hz), 6.92 (1H, dddd, J = 23.0 (H-P), 17.0, 3.7, 3.7 Hz), 6.90 (1H, d, J = 8.6 Hz), 6.10 (1H, dddd, J = 19.0 (H-P), 17.0, 2.0, 2.0 Hz), 4.78 (2H, ddd, J = 3.7, 3.7, 2.0 Hz), 4.07 (4H, dq, J = 8.6, 1.3 Hz), 1.29 (6H, dd, J = 7.0, 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 160.2, 145.7 (d, $J_{C\text{-}P}$ = 8.0 Hz), 136.1, 129.1, 125.2, 121.7, 118 (d, $J_{C\text{-}P}$ = 189 Hz), 112.7, 67.7 (d, $J_{C\text{-}P}$ = 24.0 Hz), 62.2 (d, $J_{C\text{-}P}$ = 5.6 Hz), 16.5 (d, $J_{C\text{-}P}$ = 5.6 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 18.28; IR (NaCl dep from $CHCl_3$) 1689, 1599, 1482, 1209. HRMS (ES+) calcd for $C_{14}H_{20}O_5P$, 299.1043 $[M+H]^+$, Found 299.1043.

(E)-2-(3-(diphenylphosphoryl)allyloxy)benzaldehyde (4a)



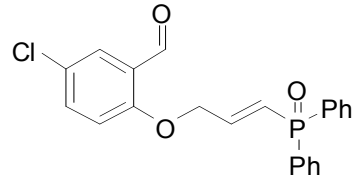
According to the general procedure, the corresponding alkyne (500.0 mg, 2.0 mmol, 1.0 eq) was treated with diphenylphosphine oxide (404.0 mg, 2.0 mmol, 1.0 eq) and catalyst (77.5 mg, 0.08 mmol, 0.04 eq) in toluene (1M) for 12 hours at 60 °C. The reaction was placed directly on a silica gel column and eluted with ethyl acetate:MeOH (20:1). Evaporation gave analytically pure vinylphosphine oxide 436.0 mg (0.9 mmol, 48% yield) as a yellow oil. According to the general procedure, the vinylphosphine oxide (250.0 mg, 0.55 mol, 1.0 eq) was treated with $Hg(O_2CCF_3)_2$ (352.0 mg, 0.825 mmol, 1.5 eq) and stirred for 4 hours and filtered through celite. Column chromatography (ethyl acetate:MeOH, 20:1) afforded 180 mg (0.49 mmol, 91% yield) of **4a** as a yellow oil in 45% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.5 (1H, s), 7.83 (1H, dd, J = 10.5, 1.7 Hz), 7.70-7.62 (4H, m), 7.54-7.41 (7H, m), 7.08-6.91 (3H, m), 6.71 (ddd, J = 24.0 (H-P), 17.0, 2.0 Hz), 4.92-4.86 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 160.2, 144.7, 136.2, 132.2, 132.1 (d, $J_{C\text{-}P}$ = 108.0 Hz), 131.4 (d, $J_{C\text{-}P}$ = 11.0 Hz), 129.4, 128.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 125.2, 121.3 (d, $J_{C\text{-}P}$ = 100.0 Hz), 121.7, 112.9, 68.1 (d, $J_{C\text{-}P}$ = 18.5 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 24.2. IR (NaCl dep from $CHCl_3$) 1687, 1438, 1189, 695 cm^{-1}. HRMS (ES+) calcd for $C_{22}H_{20}O_3P$, 363.1144 $[M+H]^+$, Found 363.1136.

(E)-5-bromo-2-(3-(diphenylphosphoryl)allyloxy)benzaldehyde (4b)



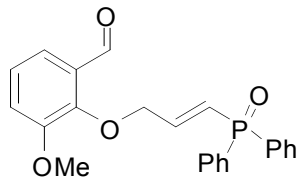
According to the general procedure, the corresponding alkyne (1.5 g, 4.6 mmol, 1.0 eq) was treated with diphenylphosphine oxide (929.0 mg, 4.6 mmol, 1.0 eq) and catalyst (175.0 mg, 0.184 mmol, 0.04 eq) in toluene (1M) for 12 hours at 60 °C. The reaction was placed directly on a silica gel column and eluted with ethyl acetate:MeOH (20:1). Evaporation gave analytically pure vinylphosphine oxide 1.0 g (2.3 mmol, 50%) as a yellow solid. The vinylphosphine oxide (231.0 mg, 0.46mmol, 1.0 eq) was treated with $Hg(O_2CCF_3)_2$ (395.0 mg, 0.93 mmol, 2.0 eq) according to the general procedure and stirred for 4 hours and filtered through celite. Column chromatography (ethyl acetate:MeOH, 20:1) afforded 195.0 mg (0.44 mmol, 95%) of **4b** as a yellow oil in 48% for the two steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.42 (1H, s), 7.93 (1H, d, J = 2.6 Hz), 7.74-7.35 (1H, m), 7.14-6.96 (1H, m), 6.82 (1H, d, J = 8.8 Hz), 6.65 (1H, dd, J = 24.5 (H-P), 17.2 Hz), 4.81 (2H, s); ^{13}C NMR (100 MHz $CDCl_3$) δ 188, 159.1, 144.5, 138.5, 132.8, 132.3, 131.7, 131.4 (d, J_{C-P} = 9.8 Hz), 129 (d, J_{C-P} = 12.2 Hz), 126.4, 123.1 (d, J_{C-P} = 103.8 Hz), 115, 114.4, 68.5 (d, J_{C-P} = 17.1 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 24.21; IR (NaCl dep from $CHCl_3$) 1685, 1590, 1479, 1271 cm^{-1}. HRMS (ES+) calcd for $C_{22}H_{18}BrO_3P$, 441.0249 $[M+H]^{+,}$ Found 441.0251.

(E)-5-chloro-2-(3-(diphenylphosphoryl)allyloxy) Benzaldehyde (4c)



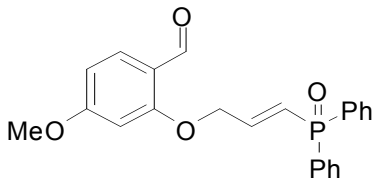
According to the general procedure, the corresponding alkyne (284.0 mg, 1.0 mmol, 1.0 eq) was treated with diphenylphosphine oxide (202.0 mg, 1.0 mmol, 1.0 eq) and catalyst (39.0 mg, 0.04 mmol, 0.04 eq) in toluene (1M) for 12 hours at 60 °C. The reaction was placed directly on a silica gel column and eluted with ethyl acetate:MeOH (20:1). Evaporation gave analytically pure vinylphosphine oxide 285.0 mg (0.6 mmol, 60%) as a yellow oil. The vinylphosphine oxide (140.0 mg, 0.288 mmol, 1.0 eq) was treated with $Hg(O_2CCF_3)_2$ (184.0 mg, 0.43 mmol, 1.5 eq) according to the general procedure and stirred for 4 hours and filtered through celite. Column chromatography (ethyl acetate:MeOH, 20:1) afforded 98.0 mg (0.25 mmol, 86%) of **4c** as a yellow oil in 52% for the two steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (1H, s), 7.78 (1H, d, J = 3.0 Hz), 7.7-7.62 (4H, m), 7.55-7.49 (2H, m), 7.48-7.42 (5H, m), 6.98 (1H, dddd, J = 21.0 (H-P), 17.0, 3.4, 3.4 Hz), 6.88 (1H, d, J = 9.0 Hz), 6.68 (1H, dddd, J = 24.0 (H-P), 17.0, 2.0, 2.0 Hz), 4.85 (2H, ddd, J = 3.4, 3.4, 2.0 Hz); ^{13}C NMR (100 MHz $CDCl_3$) δ 188.1, 158.6, 144.1, 135.6, 132.4 (d, J_{C-P} = 106.3 Hz), 132.3 (d, J_{C-P} = 2.0 Hz), 131.4 (d, J_{C-P} = 11.0 Hz), 128.9 (d, J_{C-P} = 13.0 Hz), 128.8, 127.4, 126.1, 124.0 (d, J_{C-P} = 101.0 Hz), 114.6, 68.6 (d, J_{C-P} = 16.5 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 24.08; IR (NaCl dep from $CHCl_3$) 1683, 1480, 1182 cm^{-1}. HRMS (ES+) calcd for $C_{22}H_{19}O_3PCl$, 397.0755 $[M+H]^+$, Found 397.0747.

(E)-2-(3-(diphenylphosphoryl)allyloxy)-3-methoxybenzaldehyde (4d)



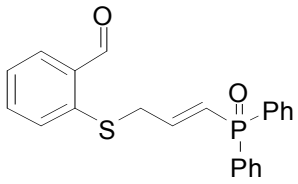
According to the general procedure, the corresponding alkyne (175.0 mg, 0.625 mmol, 1.0 eq) was treated with diphenylphosphine oxide (126.0 mg, 0.625 mmol, 1.0 eq) and catalyst (24.2 mg, 0.025 mmol, 0.04 eq) in toluene (1M) for 12 hours at 60 °C. The reaction was placed directly on a silica gel column and eluted with ethyl acetate:MeOH (20:1). Evaporation gave analytically pure vinylphosphine oxide 221.0 mg (0.444 mmol, 71%) as a yellow oil. The vinylphosphine oxide (78.0 mg, 0.13 mmol, 1.0 eq) was treated with $Hg(O_2CCF_3)_2$ (83.0 mg, 0.195 mmol, 1.5 eq) according to the general procedure and stirred for 4 hours and filtered through celite. Column chromatography (ethyl acetate:MeOH, 20:1) afforded 45.0 mg (0.115 mmol, 88%) of **4d** as a yellow oil in 62% for the two steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.31 (1H, s), 7.85-7.5 (1H, m), 7.17-7.05 (10H, m), 6.87-6.82 (1H, m), 6.62-6.59 (1H, m), 6.43-6.4 (1H, m), 4.92-4.86 (2H, m), 3.85 (3H, s); ^{13}C NMR (100 MHz $CDCl_3$) δ 189.0, 166.9, 162.2 (d, J_{C-P} = 15.0 Hz), 146.4, 133.0 132.1, 131.5 (d, J_{C-P} = 11.0 Hz), 129.2 (d, J_{C-P} = 13.0 Hz), 121.5, 120.6, 118.8, 107.2, 99.1, 68.0 (d, J_{C-P} = 17.0 Hz), 56.0; ^{31}P NMR (121.5 MHz $CDCl_3$) δ 29.6; IR (NaCl dep from $CHCl_3$) 1679, 1475, 1177 cm^{-1}. HRMS (ES+) calcd for $C_{23}H_{22}O_4P$, 393.1250 $[M+H]^+$, Found 393.1244.

(E)-2-(3-(diphenylphosphoryl)allyloxy)-4-methoxybenzaldehyde (4e)



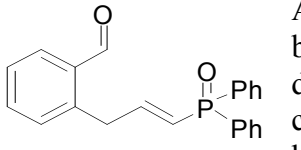
According to the general procedure, the corresponding alkyne (175.0 mg, 0.625 mmol, 1.0 eq) was treated with diphenylphosphine oxide (126.0 mg, 0.625 mmol, 1.0 eq) and catalyst (24.2 mg, 0.025 mmol, 0.04 eq) in toluene (1M) for 12 hours at 60 °C. The reaction was placed directly on a silica gel column and eluted with ethyl acetate:MeOH (20:1). Evaporation gave analytically pure vinylphosphine oxide 160.0 mg (0.338 mmol, 54%) as a yellow oil. The vinylphosphine oxide (124.0 mg, 0.25 mmol, 1.0 eq) was treated with $Hg(O_2CCF_3)_2$ (160.0 mg, 0.37 mmol, 1.5 eq) according to the general procedure and allowed to stir for 4 hours and filtered through celite. Column chromatography (ethyl acetate:MeOH, 20:1) afforded 100.0 mg (0.25 mmol, 99%) of **4e** as a yellow oil in 53% for the two steps.^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (1H, s), 7.81 (1H, d, J = 8.8 Hz), 7.72-7.64 (4H, m), 7.57-7.4 (6H, m), 7.02 (1H, dddd, J = 20.1 (H-P), 17.1, 3.3, 3.3 Hz), 6.81-6.64 (1H, m), 6.58 (1H, dd, J = 8.8, 1.8 Hz), 6.38 (1H, d, J = 2.2 Hz), 4.84 (2H, d, J = 2.2 Hz), 3.81 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.07, 166.26, 161.86, 144.66, 132.5 (d, J_{C-P} = 109.1 Hz), 132.3, 131.4 (d, J_{C-P} = 10.0 Hz), 128.9 (d, J_{C-P} = 12.6 Hz), 123.9, 122.6, 119.3, 106.8, 99.2, 66.1 (d, J_{C-P} = 16.8 Hz), 55.9; ^{31}P NMR (121.5 MHz $CDCl_3$) δ 29.85; IR (NaCl dep from $CHCl_3$) 16.76.7, 1600.97, 1437, 1260 cm^{-1}. HRMS (ES+) calcd for $C_{23}H_{21}O_4P$, 393.1250 $[M+H]^+$, Found 393.1262

(E)-2-(3-(diphenylphosphoryl)allylthio)benzaldehyde (4f)



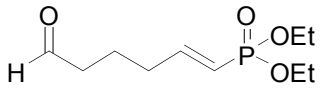
According to the general procedure, the corresponding alkyne (500.0 mg, 2.8 mmol, 1.0 eq) was treated with diphenylphosphine oxide (567.0 mg, 2.8 mmol, 1.0 eq) and catalyst (136.0 mg, 0.05 mmol, 0.05 eq) in toluene (1M) for 12 hours at 60 °C. The reaction was placed directly on a silica gel column and eluted with ethyl acetate:MeOH (20:1). Evaporation gave analytically pure vinylphosphine oxide 636.0 mg (1.68 mmol, 60%) as a yellow oil. The vinylphosphine oxide (50.0 mg, 0.13 mmol, 1.0 eq) was oxidized using Dess-Martin periodinane (84.0 mg, 0.2 mmol, 1.5 eq) to afford 30.0 mg (0.6 mmol, 60%) of **4f** in 24% over two steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (1H, s), 7.81 (1H, dd, J = 7.5, 1.3 Hz), 7.52-7.44 (6H, m), 7.43-7.28 (7H, m), 6.74 (1H, dddd, J = 18.1 (H-P), 16.6, 6.1, 6.1 Hz), 6.33 (1H, dddd, J = 22.8 (H-P), 16.6, 1.5, 1.5 Hz), 3.75 (2H, ddd, J = 6.1, 1.5, 1.5 Hz); ^{13}C NMR (100 MHz $CDCl_3$) δ 191.7, 145.0 (d, $J_{C\text{-}P}$ = 3.4 Hz), 139.4, 134.9, 134.2, 132.5, 132.4 (d, $J_{C\text{-}P}$ = 106 Hz), 132.2, 131.4 (d, $J_{C\text{-}P}$ = 9.1 Hz), 129.9, 128.8 (d, $J_{C\text{-}P}$ = 11 Hz), 126.6, 125.9 (d, $J_{C\text{-}P}$ = 99 Hz), 36.8 (d, $J_{C\text{-}P}$ = 18.3 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 24.02; IR (NaCl dep from $CHCl_3$) 1690, 1437, 1190 cm^{-1}. HRMS (ES+) calcd for $C_{22}H_{20}O_2PS$, 379.0916 $[M+H]^+$, Found 379.0905.

(E)-2-(3-(diphenylphosphoryl)allyl)benzaldehyde (4g)



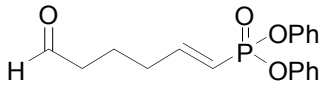
According to the general procedure, the corresponding alkynyl benzyl alcohol (400.0 mg, 2.74 mmol, 1.0 eq) was treated with diphenylphosphine oxide (728.0 mg, 2.74 mmol, 1.0 eq) and catalyst (190.0 mg, 0.05 mmol, 0.05 eq) in toluene (1M) for 12 hours at 60 °C. The reaction was placed directly on a silica gel column and eluted with ethyl acetate:MeOH (20:1). Evaporation gave analytically pure vinylphosphine oxide 760.0 mg (2.2 mmol, 82%) as a colorless solid. The vinylphosphine oxide (587.0 mg, 1.7 mmol, 1.0 eq) was oxidized using Dess-Martin periodinane (787.0mg, 1.85 mmol, 1.1 eq) to afford 480.0 mg (1.4 mmol, 65%) of **4g** in 54% over two steps as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (1H, s), 7.82 (1H, d, J = 7.7 Hz), 7.63 (4H, dd, J = 12.0, 7.7 Hz), 7.58-7.39 (8H, m), 7.27 (1H, d, J = 8.4 Hz), 6.87 (1H, dddd, J = 19.2 (H-P), 17.2, 5.9, 5.9 Hz), 6.12 (1H, dd, J = 22.3 (H-P), 17.2 Hz), 4.06 (2H, dd, J = 5.9, 2.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 150.2, 139.5, 134.3, 134.3, 132.0, 131.9, 131.6, 131.4, 128.8, 128.7, 127.8, 123.7 (d, $J_{C\text{-}P}$ = 102.2 Hz), 37.7 (d, $J_{C\text{-}P}$ = 18.2 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 24.88; IR (NaCl dep from $CHCl_3$) 1693, 1437, 1190, 1120 cm^{-1}. HRMS (ES+) calcd for $C_{22}H_{19}O_2P$, 347.1200 $[M+H]^+$, Found 347.1203.

(E)-diethyl 6-oxohex-1-enylphosphonate (6)



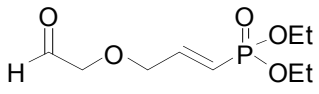
According to the general procedure, DIA (1.39 mL, 9.95 mmol, 2.0 eq) treated with *n*BuLi (6.2 mL, 9.95 mmol, 2.0 eq). The mixture was cooled and treated with diethyl methyl phosphonate (720.0 mg, 4.73 mmol, 1.0 eq), diethyl chlorophosphate (684.0 μL, 4.73 mmol, 1.0 eq) and aldehyde (690.0 mg, 0.283 mmol, 1.0 eq). Upon workup and column chromatography, the vinylphosphonate 866.0 mg (3.1 mmol, 66% yield). According to the general procedure, dimethyl acetal (100.0 mg, 0.357, 1eq) was stirred overnight in AcOH:H_2O (80:20, 2.0 mL). Workup followed by column chromatography (ethyl acetate:MeOH, 20:1) afforded 75.0 mg (0.293 mmol, 82% yield) of **6** as a yellow oil in 54% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (1H, s), 6.69 (1H, dddd, J = 22.7 (H-P), 17.2, 6.6, 6.6 Hz), 5.63 (1H, ddd, J = 20.1 (H-P), 17.2, 1.1 Hz), 4.02 (4H, qt, J = 14.6, 7.7 Hz), 2.45 (2H, t, J = 7.3, 7.3 Hz), 2.22 (2H, q, J = 13.9, 7.0 Hz), 1.75 (2H, qt, J = 14.6, 7.3, 7.3 Hz), 1.27 (6H, t, J = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 152.3 (d, J_{C-P} = 4.2 Hz), 118.0 (d, J_{C-P} = 187.6 Hz), 61.8 (d, J_{C-P} = 5.6 Hz), 43.1, 33.3 (d, J_{C-P} = 22.4 Hz), 20.2, 16.6 (d, J_{C-P} = 7.0 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 19.26; IR (NaCl dep from $CHCl_3$) 2984, 1721, 1633, 1234, 1026 cm^{-1}. HRMS (ES+) calcd for $C_{10}H_{20}O_4P$, 235.1094 $[M+H]^+$, Found 235.1088.

(E)-diphenyl 6-oxohex-1-enylphosphonate (10b)



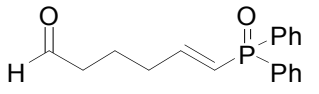
A solution of 5,5-dimethoxypentanal (250.0 mg, 1.5 mmol, 1.0 eq), *O,O*-Diphenyl (triphenylphosphanylidene)methyl-phosphonate (1.12 g, 2.25 mmol, 1.5 eq) and toluene (5.0 mL) heated to reflux overnight. Toluene was removed under reduced pressure and the residue was placed on a silica gel column and eluted with a solution of ethyl acetate and MeOH (20:1) afforded 310.0 mg (0.824 mmol, 48% yield) of the corresponding dimethyl acetal as a yellow oil. According to the general procedure, dimethyl acetal (310.0 mg, 0.824 mmol) was allowed to stir overnight in AcOH:H_2O (80:20, 5.0 mL). Workup followed by column chromatography (ethyl acetate:MeOH, 20:1) afforded 214.0 mg (0.693 mmol, 84%) of **10b** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (1H, s), 7.37-7.29 (4H, m), 7.24-7.13 (6H, m), 6.93 (1H, dddd, J = 23.7 (H-P), 17.5, 6.8, 6.8 Hz), 5.89 (1H, dddd, J = 22.1 (H-P), 17.5, 1.5, 1.5 Hz), 2.38 (2H, t, J = 7.2, 7.2 Hz), 2.3 (2H, q, J = 14.5, 7.2 Hz), 1.77 (2H, qt, J = 14.5, 7.2, 7.2 Hz). ^{13}C NMR (100 MHz $CDCl_3$) δ 201.7, 155.6, 150.4 (d, J_{C-P} = 7.2 Hz), 130.0, 125.4, 120.9 (d, J_{C-P} = 5.6), 116.9 (d, J_{C-P} = 190.4), 42.9, 33.4 (d, J_{C-P} = 24), 20.1; ^{31}P NMR (121.5 MHz $CDCl_3$) δ 12.40; IR (NaCl dep from $CHCl_3$) 1723, 1210, 1163 cm^{-1}. HRMS (ES+) calcd for $C_{18}H_{19}O_4P$, 331.1093 $[M+H]^+$, Found 331.1095.

(E)-diethyl 3-(2-oxoethoxy)prop-1-enylphosphonate (10c)



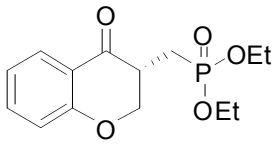
According to the general procedure, DIA (1.7 mL, 12.2 mmol, 2.0 eq) treated with *n*BuLi (7.5 mL, 12.2 mmol, 2.0 eq). The mixture was cooled and treated with diethyl methyl phosphonate (932.0 mg, 6.1 mmol, 1.0 eq), diethyl chlorophosphate (881.0 μL, 6.1 mmol, 1.0 eq) and aldehyde (1.35g, 6.1 mmol, 1.0 eq). Upon workup and column chromatography, the vinylphosphonate 1.16 g (3.3 mmol, 54% yield). The resulting vinylphosphonate (1.16 g, 2.9 mmol, 1.0 eq) was treated with HF-pyr (412.0 μL, 4.4 mmol 1.5 eq) in THF overnight. Workup followed by column chromatography afforded the alcohol (425.0 mg, 1.78 mmol, 62% yield). The resulting alcohol (280.0 mg, 1.18 mmol, 1.0 eq) was oxidized under Swern conditions to afford 180.0 mg (0.89 mmol, 76% yield) of **10c** as a yellow oil in 25% yield over 3 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.7 (1H, s), 6.74 (1H, ddddd, J = 22.7 (H-P), 17.4, 4.0, 4.0, 4.0 Hz), 5.98 (1H, ddddd, J = 19.0 (H-P), 17.4, 13.0, 2.0, 2.0 Hz), 4.24-4.17 (2H, m), 4.12-3.95 (4H, m), 3.42 (2H, s), 1.5-1.2 (6H, m); ^{13}C NMR (100 MHz $CDCl_3$) δ 199.4, 148.8, 116.7 (d, J_{C-P} = 201.0 Hz), 73.4, 62.0 (d, J_{C-P} = 5.4 Hz), 55.2, 16.5 (d, J_{C-P} = 7.5 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 19.3; IR (NaCl dep from $CHCl_3$) 1740, 1239, 1017 cm^{-1}. HRMS (ES+) calcd for $C_9H_{18}O_5P$, 235.1094 $[M+H]^+$, Found 235.1092.

(E)-6-(diphenylphosphoryl)hex-5-enal (10d)



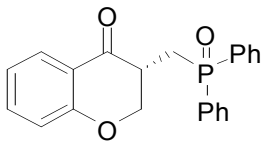
According to the general procedure, the corresponding alkynyl alcohol (50.0 mg, 0.5 mmol, 1.0eq) was treated with diphenylphosphine oxide (101.0 mg, 0.5 mmol, 1.0 eq) and catalyst (20.0 mg, 0.02 mmol, 0.04 eq) in toluene (1M) for 12 hours at 60 °C. The reaction was placed directly on a silica gel column and eluted with ethyl acetate:MeOH (20:1). Evaporation gave analytically pure vinylphosphine oxide 112.0 mg (0.37 mmol, 75%) as a yellow oil. The vinylphosphine oxide (88.0 mg, 0.13 mmol, 1eq) was oxidized using Swern conditions to afford 65.0 mg (0.22 mmol, 75%) of **10d** in 56% over two steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (1H, d, J = 1.5 Hz), 7.74-7.64 (4H, m), 7.57-7.42 (6H, m), 6.72 (1H, dddd, J = 19.4 (H-P), 16.8, 6.6, 6.6 Hz), 6.28 (1H, dddd, J = 24.2 (H-P), 16.8, 1.5, 1.5 Hz), 2.5 (2H, dt, J = 7.0, 7.0, 1.0 Hz), 2.4-2.3 (2H, m), 1.83 (2H, qt, J = 7.0, 7.0, 14.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 151.3, 133.0 (d, J_{C-P} = 105.0 Hz), 132.0 (d, J_{C-P} = 2.8 Hz), 131.4 (d, J_{C-P} = 98 Hz), 128. 8 (d, J_{C-P} = 12.6 Hz), 123.0 (d, J_{C-P} = 102.2 Hz), 43.2, 33.7 (d, J_{C-P} = 16.8 Hz), 20.4; ^{31}P NMR (121.5 MHz $CDCl_3$) δ 24.41; IR (NaCl dep from $CHCl_3$) 2987, 1720, 1629, 1437, 1182 cm^{-1}. HRMS (ES+) calcd for $C_{18}H_{20}O_2P$, 299.1193 $[M+H]^+$, Found 299.1195.

(R)-diethyl (4-oxochroman-3-yl)methylphosphonate (9)



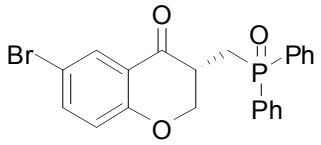
According to the general procedure, **1c** (3.0 mg, 0.0067 mmol, 0.2 eq) in toluene (1.0 mL) was treated with KHMDS (0.0067 mmol, 0.2 eq). To it was added **8** (10.0 mg, 0.033 mmol, 1.0 eq) in toluene (2.0 mL) via syringe and stirred. Column chromatography afforded 6.5 mg (0.0215 mmol, 65% yield.) of **9** as a yellow oil. $[\alpha]_D^{23}$ = - 12° ($CHCl_3$); HPLC analysis – Chiracel AD-H column, 80:20 hexanes to isopropanol 1mL/min. Major 8.70 minutes, minor 8.05 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (1H, dd, *J* = 7.9, 1.7 Hz), 7.46 (1H, ddd, *J* = 8.5, 7.2, 1.9 Hz), 6.99 (1H, ddd, *J* = 7.9, 0.5, 0.5 Hz), 6.95 (1H, d, *J* = 8.5 Hz), 4.81 (1H, dd, *J* = 11.5, 5.1 Hz), 4.22 (1H, dd, *J* = 11.5, 11.5 Hz), 4.17-4.05 (4H, m), 3.2-3.08 (1H, m), 2.63 (1H, ddd, *J* = 19.0 (H-P), 16.0, 3.0 Hz), 1.63 (1H, ddd, *J* = 17.0 (H-P), 16.0, 10.2 Hz), 1.32 (3H, ddd, *J* = 7.0, 7.0, 1.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0 (d, J_{C-P} = 14.7 Hz), 161.9, 136.3, 127.7, 121.8, 120.3, 118.1, 70.6, 62.2 (dd, J_{C-P} = 14.7, 7.3 Hz), 41.1 (d, J_{C-P} = 3.6 Hz), 21.4 (d, J_{C-P} = 143.6 Hz), 16.6 (d, J_{C-P} = 5.5 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 30.51; IR (NaCl dep from $CHCl_3$) 1682, 1590, 1480. HRMS (ES+) calcd for $C_{14}H_{20}O_5P$, 299.1043 $[M+H]^+$, Found 299.1049.

(R)-3-((diphenylphosphoryl)methyl)chroman-4-one (7a)



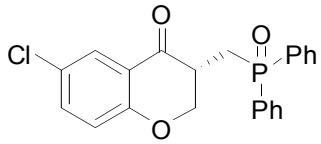
According to the general procedure, **1c** (2.6 mg, 0.0055 mmol, 0.2 eq) in toluene (1.0 mL) was treated with KHMDS (0.0055 mmol, 0.2 eq). To it was added **4a** (10.0 mg, 0.027 mmol, 1.0 eq) in toluene (2.0 mL) via syringe and stirred. Column chromatography afforded 9.0 mg (0.0221 mmol, 90% yield.) of **7a** as a yellow oil. $[\alpha]_D^{23}$ = - 9° ($CHCl_3$); HPLC analysis – Chiracel AD-H column, 70:30 hexanes to isopropanol 1mL/min. Major 20.57 minutes, minor 37.24 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.72 (5H, m), 7.55-7.41 (6H, m), 6.97 (1H, ddd, *J* = 14.9, 7.9, 1.1 Hz), 6.92 (1H, d *J* = 8.5 Hz), 4.97 (1H, dd, *J* = 11.3, 5.3 Hz), 4.24 (1H, dd, *J* = 11.9, 11.9 Hz), 3.28 (1H, ddd, *J* = 15.6, 7.5, 2 Hz), 3.17-3.03 (1H, m), 2.04 (1H, ddd, *J* = 15.6, 13.4, 10.9 Hz); ^{13}C NMR (100 MHz $CDCl_3$) δ 192.7 (d, J_{C-P} = 1.0 Hz), 162.26, 136.4, 132.3 (d, J_{C-P} = 7.3 Hz), 131.2 (d, J_{C-P} = 9.2 Hz), 130.7 (d, J_{C-P} = 9.2 Hz), 129.2 (d, J_{C-P} = 12.8 Hz), 127.7, 121.6, 118.2, 70.8, 41, 29.9, 25.1 (d, J_{C-P} = 73 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 33.03. IR (NaCl dep from $CHCl_3$) 1686, 1605, 1479, 1292 cm^{-1}. HRMS (ES+) calcd for $C_{22}H_{20}O_3P$, 363.1144 $[M+H]^+$, Found 363.1146.

(R)-6-bromo-3-((diphenylphosphoryl)methyl)chroman-4-one (7b)



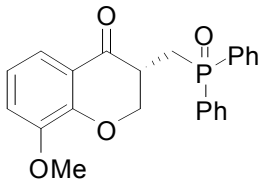
According to the general procedure, **1c** (2.1 mg, 0.0045 mmol, 0.2 eq) in toluene (1.0 mL) was treated with KHMDS (0.0045 mmol, 0.2 eq). To it was added **4b** (10.0 mg, 0.0227 mmol, 1.0 eq) in toluene (2.0 mL) via syringe and stirred. Column chromatography afforded 8.8 mg (0.02 mmol, 88% yield.) of **7b** as a yellow oil. $[\alpha]_D^{23}$ = - 35° ($CHCl_3$); HPLC analysis – Chiracel AD-H column, 55:45 hexanes to isopropanol 1mL/min. Major 14.67 minutes, minor 16.47 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (1H, d, *J* = 2.4 Hz), 7.84-7.71 (4H, m), 7.55-7.42 (7H, m), 6.82 (1H, d, *J* = 8.7 Hz), 4.98 (1H, dd, *J* = 11.5, 5.3 Hz), 4.22 (1H, dd, *J* = 12.1, 12.1 Hz), 3.25 (1H, ddd, *J* = 15.8, 7.7, 2.1 Hz), 3.08 (1H, ddddd, *J* = 12.1, 10.6, 7.7, 5.3, 2.1 Hz), 2.02 (1H, ddd, *J* = 15.8, 13.9, 10.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4 (d, J_{C-P} = 12.0 Hz), 160.9, 139.0, 133.5 (d, J_{C-P} = 101.0 Hz), 132.4 (d, J_{C-P} = 9.9 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 130.6 (d, J_{C-P} = 9.2 Hz), 129.1 (dd, J_{C-P} = 16.5, 11.0 Hz), 121.4, 120.3, 114.3, 70.9, 40.8, 24.9 (d, J_{C-P} = 73.0 Hz)' ^{31}P NMR (121.5 MHz $CDCl_3$) δ 32.89; IR (NaCl dep from $CHCl_3$) 1693, 1475, 1271, 1191 cm^{-1}. HRMS (ES+) calcd for $C_{22}H_{18}BrO_3P$ $[M+H]^+$, 441.0255. Found 441.0242

(R)-6-chloro-3-((diphenylphosphoryl)methyl)chroman-4-one (7c)



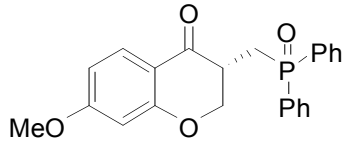
According to the general procedure, **1c** (1.8 mg, 0.005 mmol, 0.2 eq) in toluene (1.0 mL) was treated with KHMDS (0.005 mmol, 0.2 eq). To it was added **4c** (10.0 mg, 0.025 mmol, 1.0 eq) in toluene (2.0 mL) via syringe and stirred. Column chromatography afforded 9.0 mg (0.0227 mmol, 90% yield.) of **7c** as a yellow oil. $[\alpha]_D^{23}$ = - 33° ($CHCl_3$); HPLC analysis – Chiracel OD-H column, 90:10 hexanes to isopropanol 1mL/min. Major 21.99 minutes, minor 19.68 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.7 (5H, m), 7.56-7.43 (6H, m), 7.37 (1H, dd, *J* = 9.0, 3.0 Hz), 6.9 (1H, d, *J* = 9.0 Hz), 4.99 (1H, dd, *J* = 12.0, 5.5 Hz), 4.23 (1H, dd, *J* = 12.0, 12.0 Hz), 3.25 (1H, ddd, *J* = 16.0, 8.0, 2.0 Hz), 3.08 (1H, ddddd, *J* = 13.0, 11.0, 8.0, 5.5, 2.0 Hz), 2.03 (1H, ddd, *J* = 15.0, 14.0, 11.0 Hz); ^{13}C NMR (100 MHz $CDCl_3$) δ 192.2, 160.4, 136.3, 134.1, 132.4 (d, J_{C-P} = 125 Hz), 132.3 (d, J_{C-P} = 11.0 Hz), 131.2 (d, J_{C-P} = 9.2 Hz), 130.6 (d, J_{C-P} = 9.2 Hz), 129.2 (dd, J_{C-P} = 16.5, 11.0 Hz), 127.2, 126.9, 70.9, 40.8, 25.0 (d, J_{C-P} = 73.0 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 32.93; IR (NaCl dep from $CHCl_3$) 1693, 1476, 1271, 1191 cm^{-1}.HRMS (ES+) calcd for $C_{22}H_{19}O_3PCl$, 397.0760 $[M+H]^+$, Found 397.0754.

(R)-3-((diphenylphosphoryl)methyl)-8-methoxychroman-4-one (7d)



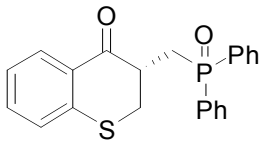
According to the general procedure, catalyst **1c** (2.4 mg, 0.0051 mmol, 0.2 eq) in toluene (1.0 mL) was treated with KHMDS (0.0051 mmol, 0.2 eq). To it was added **4d** (10.0 mg, 0.0255 mmol, 1.0 eq) in toluene (2.0 mL) via syringe and stirred. Column chromatography afforded 7.5 mg (0.018 mmol, 75% yield.) of **7d** as a yellow oil. $[\alpha]_D^{23}$ = - 15^o ($CHCl_3$); HPLC analysis – Chiracel AD-H column, 80:20 hexanes to isopropanol 1mL/min. Major 52.52 minutes, minor 36.72 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (4H, dddd, *J* = 15.1, 11.5, 6.8, 1.5 Hz), 7.54-7.4 (7H, m), 7.0 (1H, dd, *J* = 7.7, 1.0 Hz), 6.91 (1H, dd, *J* = 8.0, 8.0 Hz), 5.06 (1H, dd, *J* = 11.4, 5.4 Hz), 4.26 (1H, dd, *J* = 11.9, 11.9 Hz), 3.27 (1H, ddd, *J* = 14.8, 8.0, 2.0 Hz), 3.13 (1H, m), 2.05 (1H, ddd, *J* = 10.6, 13.4, 15.0, 8.0 Hz); ^{13}C NMR (100 MHz $CDCl_3$) δ 192.4 (d, $J_{C\text{-}P}$ = 5.0 Hz), 152 (d, $J_{C\text{-}P}$ = 300.0 Hz), 148.9, 132.3 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.9 (d, $J_{C\text{-}P}$ = 11.0 Hz), 131.1, 130.7, 129.0 (d, $J_{C\text{-}P}$ = 11.0 Hz), 121.1, 118.7, 117, 71.3, 56.5, 40.8, 25.1 (d, $J_{C\text{-}P}$ = 73.3 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 32.57; IR (NaCl dep from $CHCl_3$) 1688, 1491, 1283 cm^{-1}. HRMS (ES+) calcd for $C_{23}H_{22}O_4P$, 393.1250 $[M+H]^+$, Found 393.1248.

(R)-3-((diphenylphosphoryl)methyl)-7-methoxychroman-4-one (7e)



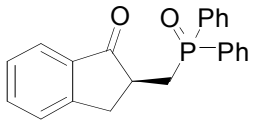
According to the general procedure, **1c** (2.4 mg, 0.0051 mmol, 0.2 eq) in toluene (1.0 mL) was treated with KHMDS (0.0051 mmol, 0.2 eq). To it was added **4e** (10.0 mg, 0.0255 mmol, 1.0 eq) in toluene (2.0 mL) via syringe and stirred. Column chromatography afforded 8.6 mg (0.022 mmol, 86% yield.) of **7e** as a yellow oil. $[\alpha]_D^{23}$ = - 19^o ($CHCl_3$); HPLC analysis – Chiracel AD-H column, 80:20 hexanes to isopropanol 1mL/min. Major 18.77 minutes, minor 24.58 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.8 (2H, m), 7.70-7.7 (3H, m), 7.54-7.41 (5H, m), 6.53 (1H, dd, *J* = 8.7, 2.3 Hz), 6.35 (1H, d, *J* = 2.3 Hz), 4.96 (1H, dd, *J* = 11.3, 5.3 Hz), 4.24 (1H, dd, *J* = 11.3, 11.3 Hz), 3.79 (3H, s), 3.29 (1H, ddd, *J* = 15.5, 7.5, 2.0 Hz), 3.03 (1H, m), 2.01 (1H, ddd, *J* = 24.5, 14.0, 11.0 Hz); ^{13}C NMR (100 MHz $CDCl_3$) δ 191.1 (d, $J_{C\text{-}P}$ = 13 Hz), 165.0 (d, $J_{C\text{-}P}$ = 227.0 Hz), 133.8 (d, $J_{C\text{-}P}$ = 103.0 Hz), 132.3 (d, $J_{C\text{-}P}$ = 11.0 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 129.3 (d, $J_{C\text{-}P}$ = 15.0 Hz), 129.1 (d, $J_{C\text{-}P}$ = 5.0 Hz), 114.9, 110.5, 100.7, 71.2, 55.9, 40.6, 25.2 (d, $J_{C\text{-}P}$ = 73.0 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 33.23; IR (NaCl dep from $CHCl_3$) 1678, 1436, 1246 cm^{-1}. HRMS (ES+) calcd for $C_{23}H_{22}O_4P$, 393.1250 $[M+H]^+$, Found 393.1243.

(R)-3-((diphenylphosphoryl)methyl)thiochroman-4-one (7f)



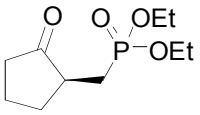
According to the general procedure, **1c** (2.5 mg, 0.0053 mmol, 0.2 eq) in toluene (1.0 mL) was treated with KHMDS (0.0053 mmol, 0.2 eq). To it was added **4f** (10.0 mg, 0.0265 mmol, 1.0 eq) in toluene (2.0 mL) via syringe and stirred. Column chromatography afforded 7.0 mg (0.0185 mmol, 70% yield.) of **7f** as a yellow oil. $[\alpha]_D^{23}$ = - 9^o ($CHCl_3$); HPLC analysis – Chiracel AD-H column, 55:45 hexanes to isopropanol 1mL/min. Major 15.86 minutes, minor 9.53 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.0, 1.0 Hz), 7.86-7.74 (4H, m), 7.56-7.45 (6H, m), 7.36 (1H, ddd, *J* = 8.0, 7.2. 2.0 Hz), 7.22 (1H, dd, *J* = 7.2, 1.3 Hz), 7.15 (1H, ddd, *J* = 8.3, 7.2, 1.3 Hz), 3.73 (1H, dd, *J* = 13.2, 3.7 Hz), 3.36-3.27 (2H, m), 3.22-3.09 (1H, m), 2.33 (1H, dddd, *J* = 15.8, 13.2, 10.6, 0.0 Hz); ^{13}C NMR (100 MHz $CDCl_3$) δ 194.5 (d, J_{C-P} = 13.0 Hz), 142.5, 133.8 (d, J_{C-P} = 99.0 Hz), 133.6, 132.3 (d, J_{C-P} = 7.0 Hz), 131.3 (d, J_{C-P} = 9.0 Hz), 130.7 (d, J_{C-P} = 9.0 Hz), 130.4, 129.1 (dd, J_{C-P} = 16.0, 11.0 Hz), 127.7, 125.1, 43.0, 31.8, 28.1 (d, J_{C-P} = 71.5 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 33.32; IR (NaCl dep from $CHCl_3$) 1677, 1437, 1191, 743 cm^{-1}. HRMS (ES+) calcd for $C_{22}H_{20}O_2PS$, 379.0916 $[M+H]^+$, Found 379.0909.

(S)-2-((diphenylphosphoryl)methyl)-2,3-dihydro-1H-inden-1-one (7g)



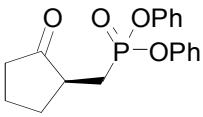
According to the general procedure, **1c** (6.7 mg, 0.0144 mmol, 0.2 eq) in toluene (1.0 mL) was treated with KHMDS (0.0144 mmol, 0.2 eq). To it was added **4g** (25.0 mg, 0.072 mmol, 1.0 eq) in toluene (2.0 mL) via syringe and stirred. Column chromatography afforded 25.0 mg (0.072 mmol, 99% yield.) of **7g** as a white solid. $[\alpha]_D^{23}$ = - 7^o ($CHCl_3$); HPLC analysis – Chiracel AD-H column, 70:30 hexanes to isopropanol 1mL/min. Major 10.85 minutes, minor 14.90 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.66 (5H, m), 7.57-7.27 (9H, m), 3.41 (1H, dd, *J* = 17.3, 7.2 Hz), 3.16 (1H, dddd, *J* = 15.1, 8.3, 2.5, 2.5 Hz), 3.06 (1H, dd, *J* = 17.3, 4.7 Hz), 2.82 (1H, ddddd, *J* = 7.2, 7.2, 4.7, 4.7, 4.7, 2.5 Hz), 2.18 (1H, dddd, *J* = 24.8, 15.1, 12.6, 2.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4 (d, J_{C-P} = 14.6 Hz), 153.9, 135.4, 132.0 (d, J_{C-P} = 11.0 Hz), 131.3 (d, J_{C-P} = 9.0 Hz), 130.8 (d, J_{C-P} = 9.0 Hz), 129.1 (d, J_{C-P} = 11.0 Hz), 128.9 (d, J_{C-P} = 11.0 Hz), 127.68, 126.8, 124.2, 42.1 (d, J_{C-P} = 4.0 Hz), 34.0, 31.4 (d, J_{C-P} = 73.0 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 33.02; IR (NaCl dep from $CHCl_3$) 1711, 1437, 1191 cm^{-1}. HRMS (ES+) calcd for $C_{22}H_{19}O_2P$, 347.1201 $[M+H]^+$, Found 347.1211

(S)-diethyl (2-oxocyclopentyl)methylphosphonate (11a)



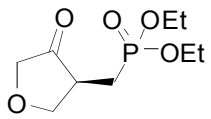
According to the general procedure, **1c** (7.4 mg, 0.0159 mmol, 0.2 eq) in toluene (1.0 mL) was treated with KHMDS (0.0159 mmol, 0.2 eq). To it was added **6** (7.5 mg, 00318 mmol, 1.0 eq) in toluene (2.0 mL) via syringe and stirred. Column chromatography afforded 5.0 mg (0.0211 mmol, 66% yield.) of **11a** as a yellow oil. $[\alpha]_D^{23}$ = - .9° ($CHCl_3$); HPLC analysis – Chiracel AD-H column, 80:20 hexanes to isopropanol 1mL/min. Major 15.79 minutes, minor 12.49 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19-3.97 (4H, m), 2.56-2.28 (4H, m), 2.18-1.99 (2H, m), 1.89-1.71 (1H, m), 1.66-1.47 (2H, m), 1.35-1.28 (6H, m); ^{13}C NMR (100 MHz $CDCl_3$) δ 218.9, 61.8 (dd, J_{C-P} = 20.0, 7.0 Hz), 44.4 (d, J_{C-P} = 3.5 Hz), 37.1, 30.7, 27.1 (d, J_{C-P} = 144.0 Hz), 20.7, 16.6 (d, J_{C-P} = 5.5 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 31.87; IR (NaCl dep from $CHCl_3$) 1741, 1248, 1053, 1027 cm^{-1}; HRMS (FES+) calcd for $C_{10}H_{20}O_4P$, 235.1034 $[M+H]_+$, Found 235.1093

(S)-diphenyl (2-oxocyclopentyl)methylphosphonate (11b)



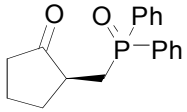
According to the general procedure, **1c** (7.0 mg, 0.0152 mmol, 0.2 eq) in toluene (1.0 mL) was treated with KHMDS (0.0152 mmol, 0.2 eq). To it was added **10b** (25.0 mg, 0.0758 mmol, 1.0 eq) in toluene (2.0 mL) via syringe and stirred. Column chromatography afforded 20.0 mg (0.061 mmol, 80% yield.) of **11b** as a yellow oil. $[\alpha]_D^{23}$ = - 9° ($CHCl_3$); HPLC analysis – Chiracel AD-H column, 80:20 hexanes to isopropanol 1mL/min. Major 16.49 minutes, minor 15.11 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.29 (4H, m), 7.2-7.15 (6H, m), 2.76 (1H, ddd, J = 18.5, 15.8, 3.0 Hz), 2.68-2.49 (2H, m), 2.45-2.35 (1H, m), 2.2-2.05 (2H, m), 1.96-1.77 (2H, m), 1.76-1.63 (1H, m); ^{13}C NMR (100 MHz $CDCl_3$) δ 218.4, 150.2, 130.1, 125.4, 120.6, 44.3, 36.9, 30.7, 26.2 (d, J_{C-P} = 147 Hz), 20.7; ^{31}P NMR (121.5 MHz $CDCl_3$) δ 25.35.IR (NaCl dep from $CHCl_3$) 1740, 1489, 1187 cm^{-1}. HRMS (ES+) calcd for $C_{18}H_{20}O_4P$, 331.1094 $[M+H]^+$, Found 331.1079

(S)-diethyl (4-oxotetrahydrofuran-3-yl)methylphosphonate (11c)



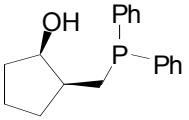
According to the general procedure, **1c** (5.9 mg, 0.0126 mmol, 0.2 eq) in toluene (1.0 mL) was treated with KHMDS (0.0126 mmol, 0.2 eq). To it was added **10c** (15.0 mg, 0.0632 mmol, 1.0 eq) in toluene (2.0 mL) via syringe and stirred. Column chromatography afforded 14.0 mg (0.0588 mmol, 94% yield.) of **11c** as a yellow oil. $[\alpha]_D^{23}$ = - 2° ($CHCl_3$); HPLC analysis – Chiracel AD-H column, 80:20 hexanes to isopropanol 1mL/min. Major 8.092 minutes, minor 3.64 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (1H, dd, *J* = 9.0, 9.0 Hz), 4.18-4.03 (4H, m), 3.86-3.77 (2H, m), 2.8-2.7 (1H, m), 2.33 (1H, ddd, *J* = 18.7, 15.7, 3.0 Hz), 1.64 (1H, ddd, *J* = 16.8, 15.7, 11.0 Hz), 1.33 (1H, dd, *J* = 7.7 Hz), 1.35-1.25 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.6 (d, J_{C-P} = 17.0 Hz), 72.4, 70.6, 62.3 (dd, J_{C-P} = 11.2, 5.6 Hz), 42.4 (d, J_{C-P} = 4.2 Hz), 23.5 (d, J_{C-P} = 147 Hz), 16.6 (d, J_{C-P} = 5.6 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ 29.9; IR (NaCl dep from $CHCl_3$) 1689, 1209, 1024 cm^{-1}. HRMS (ES+) calcd for $C_9H_{18}O_5P$, 235.1094 $[M+H]^+$, Found 235.1088.

(S)-2-((diphenylphosphoryl)methyl)cyclopentanone (11d)



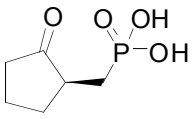
According to the general procedure, **1c** (7.5 mg, 0.016 mmol, 0.2 eq) in toluene (1.0 mL) was treated with KHMDS (0.016 mmol, 0.2 eq). To it was added **10d** (10.0 mg, 0.033 mmol, 1.0 eq) in toluene (2.0 mL) via syringe and stirred. Column chromatography afforded 9.6 mg (0.032 mmol, 96% yield.) of **11d** as a yellow oil. $[\alpha]_D^{23}$ = - 2° ($CHCl_3$); HPLC analysis – Chiracel AD-H column, 80:20 hexanes to isopropanol 1mL/min. Major 12.44 minutes, minor 15.77 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.69 (4H, m), 7.53-7.4 (6H, m), 3.01 (1H, ddd, *J* = 15.3, 9.6, 1.7 Hz), 2.4-2.25 (3H, m), 2.08-1.9 (3H, m), 1.75-1.6 (1H, m), 1.52-1.38 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 219. 5 (d, J_{C-P} = 13.8 Hz), 133.8 (d, J_{C-P} = 12.4 Hz), 132 (dd, J_{C-P} = 8.0, 2.5 Hz), 130.9 (dd, J_{C-P} = 19.2, 9.2 Hz), 128.9 (dd, J_{C-P} = 13.2, 12.0 Hz), 44.2 (d, J_{C-P} = 3.5 Hz), 36.8, 31.2, 29.9 (d, J_{C-P} = 74.0 Hz), 20.75; ^{31}P NMR (121.5 MHz $CDCl_3$) δ 32.47; IR (NaCl dep from $CHCl_3$) 1737, 1437, 1182 cm^{-1}; HRMS (ES+) calcd for $C_{18}H_{19}O_2P$, 299.1195 $[M+H]^+$, Found 299.1202.

(S)-2-((diphenylphosphino)methyl)cyclopentanol (12)



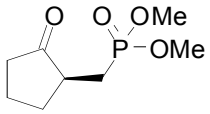
Cerium chloride (90.0 mg, 0.366 mmol, 2.2 eq) (previously dried for 4 hours at 150 °C under high vacuum) was added to THF (1.0 mL) and stirred for 30 minutes. The suspension was cooled to 0 °C and $LiAlH_4$ (42.0 mg, 1.09 mmol, 6.6 eq) was added to the suspension and stirred for 90 minutes at room temperature. The suspension was then cooled to 0 °C and a solution of **11d** in THF (1.0 mL) was added dropwise over a 5 minute period. The reaction was allowed to stir for 30 minutes at 0 °C and to it was added H_2O (5.0 mL) dropwise and diluted with EtOAc (2.0 mL). The reaction mixture was extracted with EtOAc (2 x 2.0 mL) and washed with water (2 x 2.0 mL) and brine (2 x 2.0 mL) and dried over $MgSO_4$. Concentration under reduced pressure followed by flash column chromatography afforded 28.0 mg (0.098 mmol, 58%) of **12** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.4 (4H, m), 7.35-7.28 (6H, m), 3.96 (1H, dd, J = 6.4, 6.4 Hz), 2.21 (1H, dd, J = 13.5, 7.5 Hz), 2.08 (1H, dd, J = 13.5, 7.5 Hz), 1.98-1.90 (2H, m), 1.80-1.69 (1H, m), 1.68-1.45 (3H, m), 1.38-1.28 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1 (d, $J_{C\text{-}P}$ = 14.5 Hz), 132.9 (d, $J_{C\text{-}P}$ = 13.0 Hz), 129.0, 128.8 (d, $J_{C\text{-}P}$ = 4.0 Hz), 128.7 (d, $J_{C\text{-}P}$ = 4.5 Hz), 80.43 (d, $J_{C\text{-}P}$ = 7.0 Hz), 45.3 (d, $J_{C\text{-}P}$ = 11.0 Hz), 34.1, 32.9 (d, $J_{C\text{-}P}$ = 11.0 Hz), 31.7 (d, $J_{C\text{-}P}$ = 9.0 Hz); ^{31}P NMR (121.5 MHz $CDCl_3$) δ -19.5; IR (NaCl dep from $CHCl_3$) 3432, 1218, 1020 cm^{-1}. HRMS (ES+) calcd for $C_{18}H_{21}OP$, 284.133 $[M+H]^+$, Found 284.1332.

(S)-(2-oxocyclopentyl)methylphosphonic acid (13)



To a solution of **11a** (50.0 mg, 0.214 mmol, 1.0 eq) in dichloromethane (0.5 mL) was added TMSBr (56.0 µL, 0.43 mmol, 2.0 eq) and the reaction stirred overnight. Solvent was removed under reduced pressure and MeOH (1.0 mL) and H_2O (0.1 mL) were added and stirred for 1 hour. Evaporation of the solvent afforded 38.0 mg (0.213 mmol, 99%) of **13** as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31-2.13 (3H, m), 2.08-1.94 (2H, m), 1.9-1.82 (1H, m), 1.68-1.56 (1H, m), 1.53-1.39 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.8, 47.2, 39.8, 32.6, 29.1 (d, $J_{C\text{-}P}$ = 140.0 Hz), 22.7; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 29.8; HRMS (ES-) calcd for $C_6H_{11}O_4P$, 177.0495 $[M-H]^-$, Found 177.0521.

(S)-dimethyl (2-oxocyclopentyl)methylphosphonate (14)



To a solution of **13** (20.0 mg, 0.112 mmol, 1.0 eq) in MeOH (1.1 mL) and DCM (.2 mL) was added (trimethylsilyl)diazomethane (2.0 M in ether, 337.0 μL, 0.674 mmol, 6.0 eq) at room temperature. The solution was stirred for 30 minutes and concentrated directly under reduced pressure. Column chromatography afforded 19.5 mg (0.095 mmol, 85%) of **14** as a yellow oil. HPLC analysis – Chiracel AD-H column, 80:20 hexanes to isopropanol 1mL/min. Major 15.79 minutes, minor 12.49 minutes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.1 (6H, d, J = 10.9, 1.3 Hz), 2.39-2.27 (3H, m), 2.13-1.95 (2H, m), 1.87-1.68 (2H, m), 1.62-1.45 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.6 (d, $J_{C\text{-}P}$ = 16.0 Hz), 52.7 (d, $J_{C\text{-}P}$ = 8.0 Hz), 52.5 (d, $J_{C\text{-}P}$ = 8.0 Hz), 44.3, 37.0, 30.7, 24.4 (d, $J_{C\text{-}P}$ = 145.0 Hz), 20.6; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 34.6; HRMS (ES-) calcd for $C_8H_{15}O_4P$, 206.0708 $[M\text{-}H]^-$, Found 206.0706.

X-ray structure of **7g**

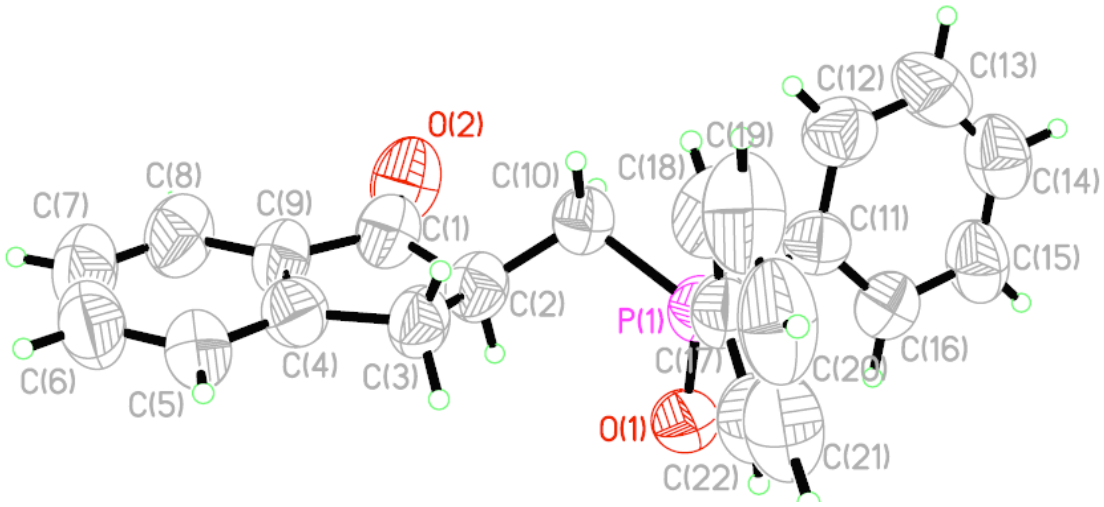


Table 1. Crystal data and structure refinement for r01.

Identification code	r01
Empirical formula	$C_{22}0H_{19}0_2P$
Formula weight	346.34
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	
	a: = 9.3998(13) Å α = 65.820º
	b: = 9.9414(13) Å β = 74.446º
	c: = 11.4269(15) Å γ = 71.540º
Volume	912.1(2) $Å^2$
Density (calculated)	1.261 Mg/m^{30}
Absorption coefficient	0.162 mm^{-1}
F(000)	364
Crystal size	0.57 x 0.14 x 0.09 mm^3
Theta range for data collection	1.98 to 28.34∞
Limiting indices	-12≤h≤12, -13≤k≤13, -14≤ l ≤15
Reflections collected	8846
Independent reflections	7708 ([Rint) = 0.0319)]
Completeness to theta = 28.34º	96.0 %
Absorption correction	Analytical
Max. and min. transmission	0.9851 and 0.9138
Refinement method	Full-matrix least-squares on F^20
Data / restraints / parameters	7708 / 3 / 452
Goodness-of-fit on F^2	0.882
Final R indices [I>2Sigma(I)]	R1 = 0.0694, wR2 = 0.1980
R indices (all data)	R1 = 0.1168, wR2 = 0.2486
Absolute structure parameter	-0.04(13)
Largest diff. peak and hole	0.480 and -0.385 e.≈$^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for r01. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
P(1)	4197(1)	-320(1)	2088(1)	65(1)
P(2)	1952(1)	6449(1)	-394(1)	66(1)
O(1)	4047(4)	-1655(4)	1888(4)	77(1)
O(2)	4192(5)	2737(5)	-2215(4)	96(1)
C(1)	2985(6)	2504(6)	-1502(5)	72(1)
C(2)	2879(6)	1393(6)	-104(5)	71(1)
C(3)	1168(6)	1773(6)	461(5)	70(1)
C(4)	391(6)	2697(6)	-712(5)	71(1)
C(5)	-1135(7)	3144(7)	-805(6)	85(2)
C(6)	-1575(9)	4069(9)	-2006(8)	101(2)
C(7)	-555(10)	4514(9)	-3097(7)	102(2)
C(8)	982(9)	4065(8)	-3031(5)	92(2)
C(9)	1439(6)	3145(6)	-1831(5)	71(1)
C(10)	4000(6)	1390(6)	658(5)	65(1)
C(11)	6024(6)	-630(6)	2488(5)	67(1)
C(12)	6538(7)	517(7)	2531(6)	85(2)
C(13)	7973(8)	176(10)	2874(7)	96(2)
C(14)	8838(7)	-1288(9)	3195(6)	90(2)
C(15)	8362(7)	-2423(9)	3158(6)	88(2)
C(16)	6940(6)	-2090(7)	2801(5)	73(1)
C(17)	2832(6)	62(6)	3420(5)	67(1)
C(18)	2504(8)	1389(8)	3664(6)	93(2)
C(19)	1521(9)	1574(11)	4765(7)	111(3)
C(20)	818(8)	466(14)	5611(7)	113(3)
C(21)	1127(8)	-875(14)	5385(7)	115(3)
C(22)	2132(7)	-1099(9)	4289(6)	92(2)

Table 3. Bond lengths [Å] and angles [°] for r01.

P(1)-O(1)	1.490(4)
P(1)-C(11)	1.795(5)
P(1)-C(17)	1.796(6)
P(1)-C(10)	1.812(5)
P(2)-O(3)	1.485(4)
P(2)-C(39)	1.796(5)
P(2)-C(33)	1.797(6)
P(2)-C(32)	1.812(6)
O(2)-C(1)	1.233(7)
C(3)-C(4)	1.505(7)
C(3)-C(2)	1.551(8)
C(11)-C(16)	1.388(8)
C(11)-C(12)	1.394(8)
C(10)-C(2)	1.535(7)
C(9)-C(4)	1.392(8)
C(9)-C(8)	1.393(7)
C(9)-C(1)	1.473(7)
C(1)-C(2)	1.524(8)
C(17)-C(18)	1.383(9)
C(17)-C(22)	1.394(8)
C(16)-C(15)	1.402(8)
C(4)-C(5)	1.381(8)
C(14)-C(15)	1.359(10)
C(14)-C(13)	1.374(11)
C(8)-C(7)	1.384(10)
C(20)-C(19)	1.353(13)
C(20)-C(21)	1.387(13)
C(12)-C(13)	1.404(9)
C(7)-C(6)	1.358(11)
C(22)-C(21)	1.404(11)
C(5)-C(6)	1.389(10)
C(18)-C(19)	1.389(9)
O(4)-C(23)	1.193(7)
C(25)-C(26)	1.498(7)
C(25)-C(24)	1.534(8)
C(39)-C(44)	1.379(7)
C(39)-C(40)	1.399(8)
C(23)-C(31)	1.505(8)
C(23)-C(24)	1.528(7)
C(24)-C(32)	1.538(7)
C(31)-C(30)	1.371(8)
C(31)-C(26)	1.383(8)

C(43)-C(44)	1.380(9)
C(43)-C(42)	1.386(10)
C(40)-C(41)	1.402(9)
C(42)-C(41)	1.365(10)
C(33)-C(34)	1.370(8)
C(33)-C(38)	1.402(8)
C(26)-C(27)	1.378(9)
C(38)-C(37)	1.394(9)
C(30)-C(29)	1.395(11)
C(27)-C(28)	1.397(10)
C(34)-C(35)	1.379(11)
C(35)-C(36)	1.359(12)
C(29)-C(28)	1.375(12)
C(37)-C(36)	1.400(13)
O(1)-P(1)-C(11)	111.7(2)
O(1)-P(1)-C(17)	111.8(2)
C(11)-P(1)-C(17)	105.7(2)
O(1)-P(1)-C(10)	112.9(2)
C(11)-P(1)-C(10)	106.0(2)
C(17)-P(1)-C(10)	108.4(2)
O(3)-P(2)-C(39)	111.5(2)
O(3)-P(2)-C(33)	111.4(3)
C(39)-P(2)-C(33)	105.9(2)
O(3)-P(2)-C(32)	112.6(3)
C(39)-P(2)-C(32)	107.5(2)
C(33)-P(2)-C(32)	107.5(2)
C(4)-C(3)-C(2)	104.6(4)
C(16)-C(11)-C(12)	119.0(5)
C(16)-C(11)-P(1)	118.0(4)
C(12)-C(11)-P(1)	123.0(4)
C(2)-C(10)-P(1)	110.0(4)
C(4)-C(9)-C(8)	121.7(6)
C(4)-C(9)-C(1)	109.3(4)
C(8)-C(9)-C(1)	129.1(6)
O(2)-C(1)-C(9)	128.0(5)
O(2)-C(1)-C(2)	123.8(5)
C(9)-C(1)-C(2)	108.1(5)
C(18)-C(17)-C(22)	118.9(6)
C(18)-C(17)-P(1)	124.1(4)
C(22)-C(17)-P(1)	116.9(5)
C(11)-C(16)-C(15)	121.0(6)
C(5)-C(4)-C(9)	119.0(5)
C(5)-C(4)-C(3)	129.8(5)
C(9)-C(4)-C(3)	111.2(5)
C(15)-C(14)-C(13)	121.7(6)
C(14)-C(15)-C(16)	118.9(7)

C(7)-C(8)-C(9)	118.3(6)
C(19)-C(20)-C(21)	119.2(7)
C(1)-C(2)-C(10)	114.0(5)
C(1)-C(2)-C(3)	104.0(4)
C(10)-C(2)-C(3)	116.6(4)
C(11)-C(12)-C(13)	119.5(6)
C(6)-C(7)-C(8)	119.9(6)
C(17)-C(22)-C(21)	118.5(8)
C(4)-C(5)-C(6)	118.7(6)
C(17)-C(18)-C(19)	121.5(7)
C(20)-C(19)-C(18)	120.4(9)
C(14)-C(13)-C(12)	119.8(6)
C(20)-C(21)-C(22)	121.6(8)
C(7)-C(6)-C(5)	122.4(7)
C(26)-C(25)-C(24)	104.3(4)
C(44)-C(39)-C(40)	118.8(5)
C(44)-C(39)-P(2)	118.0(5)
C(40)-C(39)-P(2)	123.1(4)
O(4)-C(23)-C(31)	127.5(5)
O(4)-C(23)-C(24)	126.9(6)
C(31)-C(23)-C(24)	105.5(5)
C(23)-C(24)-C(25)	104.8(4)
C(23)-C(24)-C(32)	113.0(5)
C(25)-C(24)-C(32)	117.6(4)
C(24)-C(32)-P(2)	110.0(4)
C(30)-C(31)-C(26)	122.5(6)
C(30)-C(31)-C(23)	128.1(6)
C(26)-C(31)-C(23)	109.4(5)
C(44)-C(43)-C(42)	120.7(6)
C(39)-C(44)-C(43)	120.9(6)
C(39)-C(40)-C(41)	119.6(5)
C(41)-C(42)-C(43)	119.1(6)
C(34)-C(33)-C(38)	118.0(6)
C(34)-C(33)-P(2)	120.7(5)
C(38)-C(33)-P(2)	121.3(4)
C(27)-C(26)-C(31)	119.6(5)
C(27)-C(26)-C(25)	129.0(6)
C(31)-C(26)-C(25)	111.3(5)
C(37)-C(38)-C(33)	120.8(7)
C(31)-C(30)-C(29)	118.3(7)
C(26)-C(27)-C(28)	118.1(7)
C(33)-C(34)-C(35)	122.1(7)
C(36)-C(35)-C(34)	119.8(8)
C(28)-C(29)-C(30)	119.5(6)
C(42)-C(41)-C(40)	120.9(6)
C(38)-C(37)-C(36)	118.5(7)

C(35)-C(36)-C(37)	120.8(7)
C(29)-C(28)-C(27)	122.0(7)

Symmetry transformations used to generate equivalent atoms

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for r01. The anisotropic displacement factor exponent takes the form: -2π [(h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b*U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	63(1)	63(1)	63(1)	-17(1)	-14(1)	-12(1)
P(2)	66(1)	68(1)	62(1)	-21(1)	-15(1)	-15(1)
O(1)	80(2)	62(2)	92(3)	-25(2)	-27(2)	-14(2)
O(2)	93(3)	108(3)	61(2)	-21(2)	-3(2)	-9(2)
C(3)	74(3)	72(3)	53(3)	-9(2)	-16(2)	-17(2)
C(11)	64(3)	69(3)	66(3)	-23(2)	-4(2)	-20(2)
C(10)	60(3)	68(3)	62(3)	-19(2)	-11(2)	-11(2)
C(9)	79(3)	70(3)	55(3)	-20(2)	-21(2)	0(2)
C(1)	76(3)	75(3)	57(3)	-25(2)	-8(3)	-7(3)
C(17)	56(3)	73(3)	60(3)	-11(2)	-16(2)	-12(2)
C(16)	72(3)	69(3)	71(3)	-21(2)	-13(2)	-12(2)
C(4)	78(3)	74(3)	62(3)	-25(2)	-15(2)	-18(2)
C(14)	58(3)	129(6)	78(4)	-29(4)	-10(3)	-26(4)
C(15)	57(3)	118(5)	81(4)	-26(3)	-18(3)	-16(3)
C(8)	123(5)	95(4)	53(3)	-23(3)	-26(3)	-15(4)
C(20)	75(4)	179(9)	62(4)	-35(5)	-5(3)	-15(5)
C(2)	79(3)	69(3)	60(3)	-21(2)	-16(2)	-12(2)
C(12)	83(4)	81(4)	85(4)	-19(3)	-9(3)	-28(3)
C(7)	119(6)	101(5)	83(5)	-29(4)	-48(4)	0(4)
C(22)	71(3)	119(5)	70(4)	-13(3)	-7(3)	-31(3)
C(5)	80(4)	88(4)	85(4)	-24(3)	-30(3)	-14(3)
C(18)	89(4)	92(4)	75(4)	-27(3)	1(3)	-8(3)
C(19)	92(5)	148(7)	78(4)	-55(5)	-13(4)	12(5)
C(13)	79(4)	127(6)	105(5)	-49(4)	-10(3)	-46(4)
C(21)	73(4)	181(9)	69(4)	-13(5)	-5(3)	-48(5)
C(6)	95(5)	108(5)	109(6)	-41(4)	-47(4)	-8(4)
O(3)	87(2)	60(2)	87(2)	-24(2)	-24(2)	-12(2)
O(4)	106(4)	134(4)	63(3)	-17(2)	-7(2)	-40(3)
C(25)	69(3)	84(3)	58(3)	-26(2)	-16(2)	-7(2)
C(39)	56(3)	77(3)	59(3)	-23(2)	-7(2)	-18(2)
C(23)	88(4)	89(4)	49(3)	-14(2)	-10(3)	-31(3)
C(24)	87(3)	71(3)	55(3)	-14(2)	-21(2)	-20(3)
C(32)	60(3)	83(3)	69(3)	-28(3)	-9(2)	-13(2)

C(31)	86(3)	77(3)	64(3)	-20(2)	-26(3)	-14(3)
C(43)	74(4)	104(5)	90(4)	-37(3)	-23(3)	-19(3)
C(44)	69(3)	82(4)	80(3)	-29(3)	-12(3)	-20(3)
C(40)	72(3)	81(4)	85(3)	-38(3)	-17(3)	-14(3)
C(42)	63(3)	103(5)	94(4)	-36(4)	-16(3)	-5(3)
C(33)	66(3)	78(3)	65(3)	-21(2)	-22(2)	-14(2)
C(26)	85(4)	67(3)	73(3)	-27(3)	-28(3)	-2(3)
C(38)	83(4)	102(4)	64(3)	-25(3)	-14(3)	-29(3)
C(30)	122(5)	84(4)	71(3)	-17(3)	-36(4)	-11(4)
C(27)	84(4)	97(4)	89(4)	-41(3)	-29(3)	6(3)
C(34)	70(3)	107(5)	71(4)	-39(3)	-13(3)	-3(3)
C(35)	85(4)	130(6)	66(4)	-28(4)	-10(3)	-5(4)
C(29)	130(6)	110(6)	90(5)	-22(4)	-60(5)	-8(5)
C(41)	71(3)	87(4)	100(4)	-45(3)	-11(3)	-2(3)
C(37)	95(5)	118(5)	77(4)	-9(4)	-19(4)	-53(4)
C(36)	95(5)	146(7)	65(4)	-7(4)	-14(3)	-44(5)
C(28)	100(5)	111(5)	128(7)	-56(5)	-57(5)	15(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for r01.

	x	y	z	U(eq)
H(3A)	807	853	961	83
H(3B)	986	2351	1016	83
H(10A)	3635	2273	916	78
H(10B)	4982	1443	109	78
H(16)	6605	-2861	2773	87
H(14)	9774	-1507	3444	108
H(15)	8969	-3405	3367	106
H(8)	1692	4370	-3768	110
H(20)	135	602	6334	136
H(2)	3123	373	-137	85
H(12)	5935	1501	2334	102
H(7)	-890	5119	-3888	122
H(22)	2326	-2001	4146	111
H(5)	-1854	2831	-78	102
H(18)	2952	2175	3079	112
H(19)	1345	2465	4922	133
H(13)	8336	939	2883	116

H(21)	657	-1644	5974	138
H(6)	-2604	4397	-2064	121
H(25A)	5618	5137	320	86
H(25B)	5231	6693	535	86
H(24)	3504	4513	1550	86
H(32A)	2503	7696	703	86
H(32B)	1351	6705	1627	86
H(43)	-2636	7588	-1959	104
H(44)	-305	6162	1384	92
H(40)	25	9366	-262	91
H(42)	-3632	9945	-1750	107
H(38)	2822	9313	-1645	99
H(30)	4993	3875	5192	114
H(27)	8303	4639	1250	109
H(34)	4104	5421	-2300	101
H(35)	5776	6407	4106	122
H(29)	7623	3199	5160	133
H(41)	-2318	10809	886	104
H(37)	4531	10323	3460	117
H(36)	6002	8829	-4687	130
H(28)	9230	378	208	132

X-ray structure of **7g**

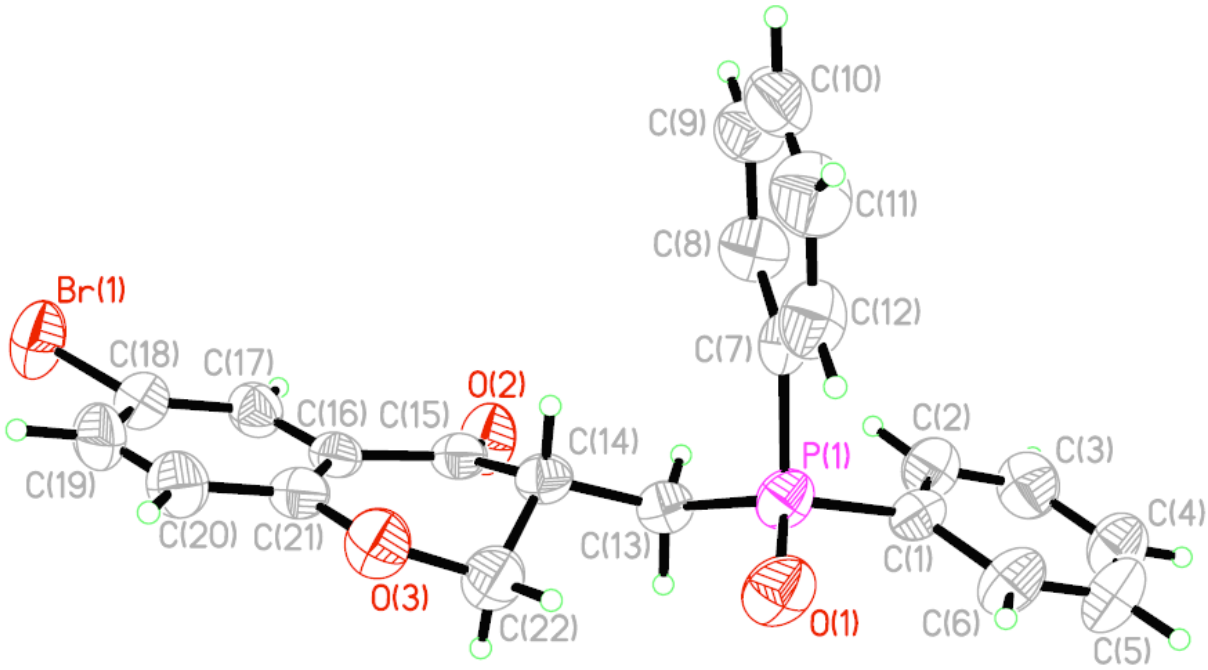


Table 1. Crystal data and structure refinement for rovis32.

Identification code	rovis32	
Empirical formula	C22 H18 Br O3 P	
Formula weight	441.24	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.9407(12) Å	α= 90°.
	b = 6.2424(6) Å	β= 101.211°.
	c = 26.774(3) Å	γ = 90°.
Volume	1957.6(3) $Å^3$	
Z	4	
Density (calculated)	1.497 Mg/m^3	
Absorption coefficient	2.201 mm^{-1}	
F(000)	896	
Crystal size	0.069 x 0.084 x 1.05 mm^3	
Theta range for data collection	1.76 to 24.73°.	
Index ranges	-14<=h<=12, -7<=k<=7, -31<=l<=31	
Reflections collected	27374	
Independent reflections	3346 [R(int) = 0.0473]	
Completeness to theta = 24.73°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3346 / 0 / 244	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0810	
R indices (all data)	R1 = 0.0735, wR2 = 0.0931	
Largest diff. peak and hole	0.432 and -0.423 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for rovis32. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7183(3)	1879(5)	3928(1)	41(1)
C(2)	6788(3)	-187(6)	3858(1)	50(1)
C(3)	5827(3)	-841(7)	4035(1)	60(1)
C(4)	5278(3)	584(8)	4295(2)	67(1)
C(5)	5665(3)	2638(8)	4376(2)	72(1)
C(6)	6610(3)	3312(6)	4190(2)	60(1)
C(7)	9663(3)	1810(6)	4132(1)	41(1)
C(8)	10043(3)	-268(6)	4097(2)	57(1)
C(9)	11026(4)	-972(7)	4417(2)	64(1)
C(10)	11615(4)	398(9)	4778(2)	70(1)
C(11)	11239(4)	2421(9)	4817(2)	76(1)
C(12)	10271(3)	3151(7)	4496(1)	57(1)
C(13)	8418(3)	1772(5)	3096(1)	40(1)
C(14)	9500(3)	2252(5)	2891(1)	39(1)
C(15)	9634(3)	839(6)	2450(1)	40(1)
C(16)	10518(3)	1592(5)	2172(1)	37(1)
C(17)	10934(3)	221(6)	1836(1)	44(1)
C(18)	11812(3)	897(6)	1613(1)	50(1)
C(19)	12286(3)	2914(6)	1712(1)	55(1)
C(20)	11879(3)	4273(6)	2036(1)	53(1)
C(21)	10998(3)	3616(5)	2267(1)	41(1)
C(22)	9554(3)	4566(5)	2721(2)	53(1)
O(1)	8440(2)	5299(4)	3718(1)	59(1)
O(2)	9095(2)	-790(4)	2341(1)	56(1)
O(3)	10636(2)	5048(4)	2586(1)	54(1)
P(1)	8421(1)	2930(1)	3714(1)	43(1)
Br(1)	12420(1)	-950(1)	1166(1)	72(1)

Table 3. Bond lengths [Å] and angles [°] for rovis32.

C(1)-C(2)	1.374(5)
C(1)-C(6)	1.395(5)
C(1)-P(1)	1.809(3)
C(2)-C(3)	1.384(5)
C(3)-C(4)	1.373(5)
C(4)-C(5)	1.366(6)
C(5)-C(6)	1.384(5)
C(7)-C(12)	1.380(5)
C(7)-C(8)	1.383(5)
C(7)-P(1)	1.815(3)
C(8)-C(9)	1.383(5)
C(9)-C(10)	1.377(6)
C(10)-C(11)	1.351(6)
C(11)-C(12)	1.378(5)
C(13)-C(14)	1.529(4)
C(13)-P(1)	1.804(3)
C(14)-C(15)	1.507(4)
C(14)-C(22)	1.520(5)
C(15)-O(2)	1.209(4)
C(15)-C(16)	1.482(4)
C(16)-C(21)	1.390(4)
C(16)-C(17)	1.399(5)
C(17)-C(18)	1.371(5)
C(18)-C(19)	1.385(5)
C(18)-Br(1)	1.903(3)
C(19)-C(20)	1.369(5)
C(20)-C(21)	1.382(5)
C(21)-O(3)	1.364(4)
C(22)-O(3)	1.439(4)
O(1)-P(1)	1.479(2)
C(2)-C(1)-C(6)	118.8(3)
C(2)-C(1)-P(1)	125.3(3)
C(6)-C(1)-P(1)	115.9(3)
C(1)-C(2)-C(3)	121.0(4)

C(4)-C(3)-C(2)	119.5(4)
C(5)-C(4)-C(3)	120.5(4)
C(4)-C(5)-C(6)	120.2(4)
C(5)-C(6)-C(1)	119.9(4)
C(12)-C(7)-C(8)	118.8(3)
C(12)-C(7)-P(1)	117.2(3)
C(8)-C(7)-P(1)	124.0(3)
C(9)-C(8)-C(7)	120.5(4)
C(10)-C(9)-C(8)	119.5(4)
C(11)-C(10)-C(9)	120.3(4)
C(10)-C(11)-C(12)	120.8(4)
C(11)-C(12)-C(7)	120.2(4)
C(14)-C(13)-P(1)	113.6(2)
C(15)-C(14)-C(22)	107.7(3)
C(15)-C(14)-C(13)	113.1(3)
C(22)-C(14)-C(13)	112.5(3)
O(2)-C(15)-C(16)	122.9(3)
O(2)-C(15)-C(14)	123.2(3)
C(16)-C(15)-C(14)	113.8(3)
C(21)-C(16)-C(17)	119.2(3)
C(21)-C(16)-C(15)	120.2(3)
C(17)-C(16)-C(15)	120.4(3)
C(18)-C(17)-C(16)	119.3(3)
C(17)-C(18)-C(19)	120.9(3)
C(17)-C(18)-Br(1)	120.4(3)
C(19)-C(18)-Br(1)	118.7(3)
C(20)-C(19)-C(18)	120.2(3)
C(19)-C(20)-C(21)	119.7(3)
O(3)-C(21)-C(20)	116.6(3)
O(3)-C(21)-C(16)	122.8(3)
C(20)-C(21)-C(16)	120.6(3)
O(3)-C(22)-C(14)	111.5(3)
C(21)-O(3)-C(22)	115.4(3)
O(1)-P(1)-C(13)	113.88(16)
O(1)-P(1)-C(1)	111.87(15)
C(13)-P(1)-C(1)	106.79(15)

O(1)-P(1)-C(7)	111.79(16)
C(13)-P(1)-C(7)	105.48(15)
C(1)-P(1)-C(7)	106.52(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for rovis32. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

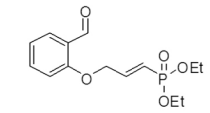
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	36(2)	40(2)	44(2)	-4(2)	6(2)	6(2)
C(2)	48(2)	51(2)	53(2)	-7(2)	11(2)	-2(2)
C(3)	53(2)	64(3)	61(2)	0(2)	11(2)	-10(2)
C(4)	43(2)	88(4)	72(3)	7(3)	19(2)	3(2)
C(5)	58(3)	80(3)	86(3)	-12(3)	32(2)	14(3)
C(6)	56(2)	51(2)	74(3)	-14(2)	18(2)	6(2)
C(7)	40(2)	44(2)	41(2)	-4(2)	16(2)	-6(2)
C(8)	61(3)	49(3)	59(2)	-3(2)	7(2)	-3(2)
C(9)	64(3)	57(3)	72(3)	16(2)	17(2)	7(2)
C(10)	56(3)	102(4)	51(3)	19(3)	8(2)	1(3)
C(11)	65(3)	105(4)	49(3)	-18(3)	-7(2)	-13(3)
C(12)	59(2)	61(3)	52(2)	-18(2)	12(2)	-7(2)
C(13)	39(2)	36(2)	44(2)	-2(2)	6(2)	-1(2)
C(14)	35(2)	38(2)	43(2)	1(2)	2(2)	1(2)
C(15)	37(2)	35(2)	45(2)	5(2)	4(2)	4(2)
C(16)	33(2)	36(2)	39(2)	8(2)	2(2)	1(2)
C(17)	45(2)	41(2)	46(2)	5(2)	9(2)	-4(2)
C(18)	45(2)	54(2)	51(2)	4(2)	14(2)	5(2)
C(19)	45(2)	60(3)	62(2)	12(2)	19(2)	-10(2)
C(20)	49(2)	47(2)	64(2)	5(2)	12(2)	-10(2)
C(21)	38(2)	37(2)	46(2)	4(2)	3(2)	0(2)
C(22)	53(2)	42(2)	68(3)	0(2)	20(2)	-1(2)
O(1)	65(2)	36(2)	79(2)	-10(1)	21(1)	0(1)
O(2)	61(2)	42(2)	72(2)	-12(1)	28(1)	-15(1)
O(3)	57(2)	36(1)	71(2)	-4(1)	20(1)	-10(1)

P(1)	43(1)	37(1)	49(1)	-9(1)	11(1)	-1(1)
Br(1)	69(1)	79(1)	79(1)	-10(1)	40(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)
for rovis32.

	x	y	z	U(eq)
H(2)	7171	-1162	3688	61
H(3)	5557	-2234	3978	72
H(4)	4636	148	4417	80
H(5)	5293	3586	4556	87
H(6)	6864	4718	4240	71
H(8)	9635	-1198	3858	68
H(9)	11288	-2361	4388	77
H(10)	12273	-71	4995	84
H(11)	11639	3331	5064	91
H(12)	10026	4552	4525	69
H(13A)	8331	232	3118	48
H(13B)	7763	2315	2857	48
H(14)	10156	1998	3167	47
H(17)	10618	-1133	1766	53
H(19)	12882	3347	1557	66
H(20)	12195	5631	2101	64
H(22A)	8947	4826	2430	64
H(22B)	9436	5511	2994	64

Table 6. Torsion angles [°] for rovis32.



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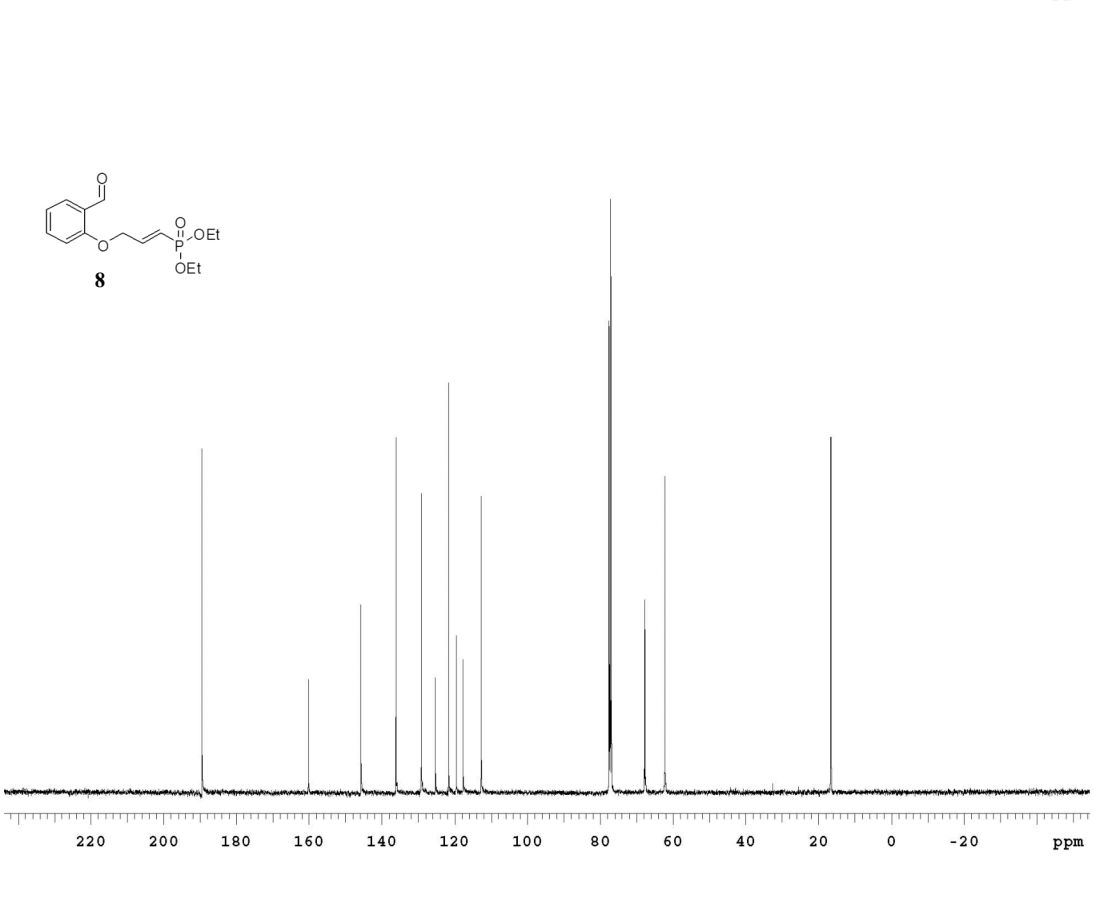
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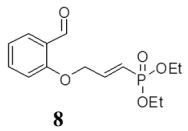

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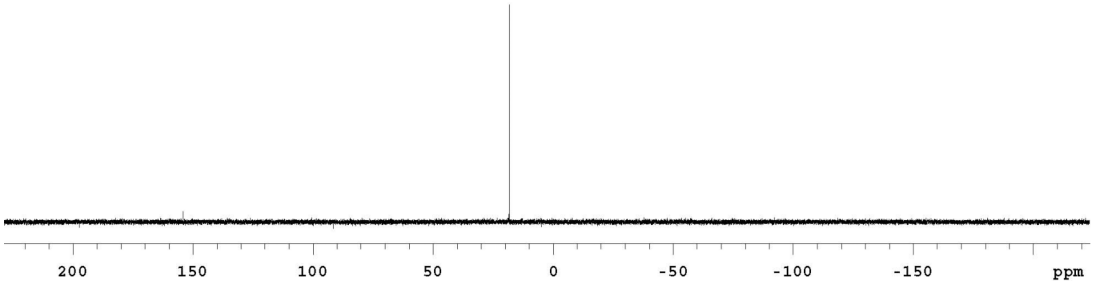

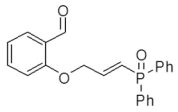

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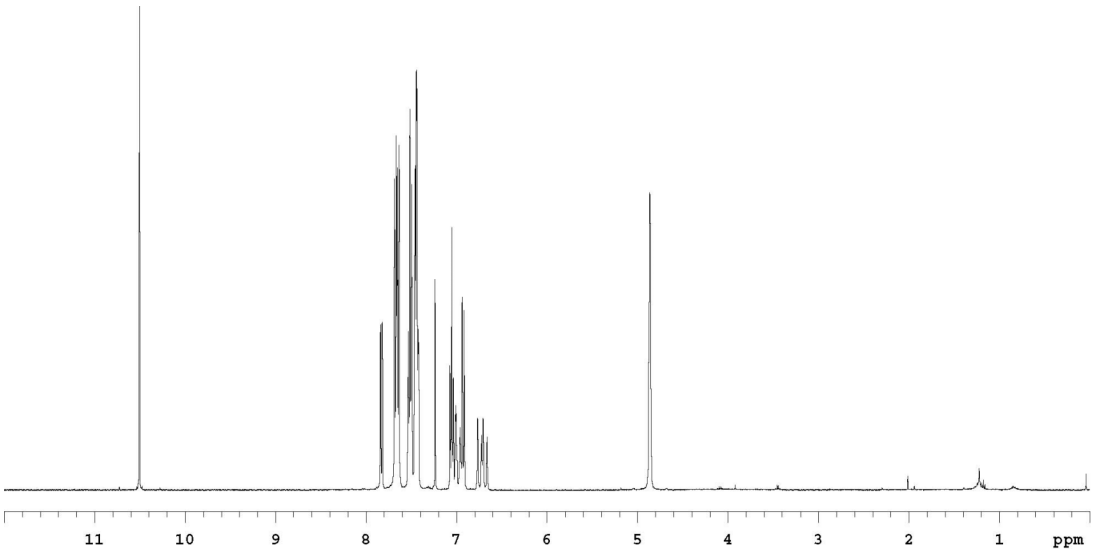

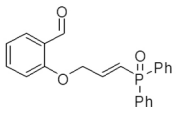

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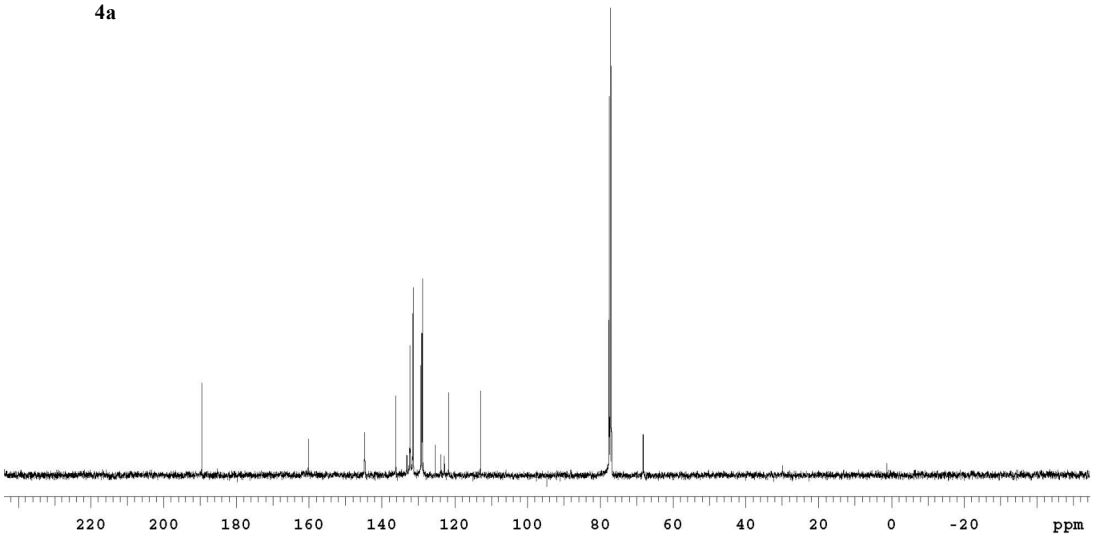
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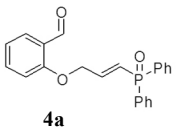

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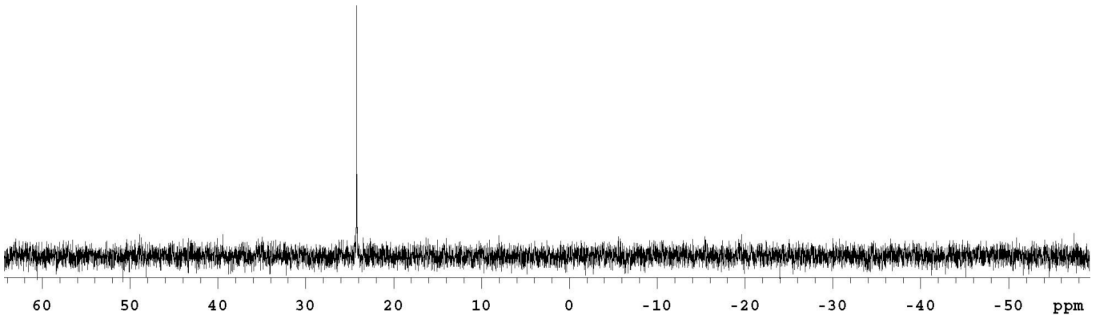
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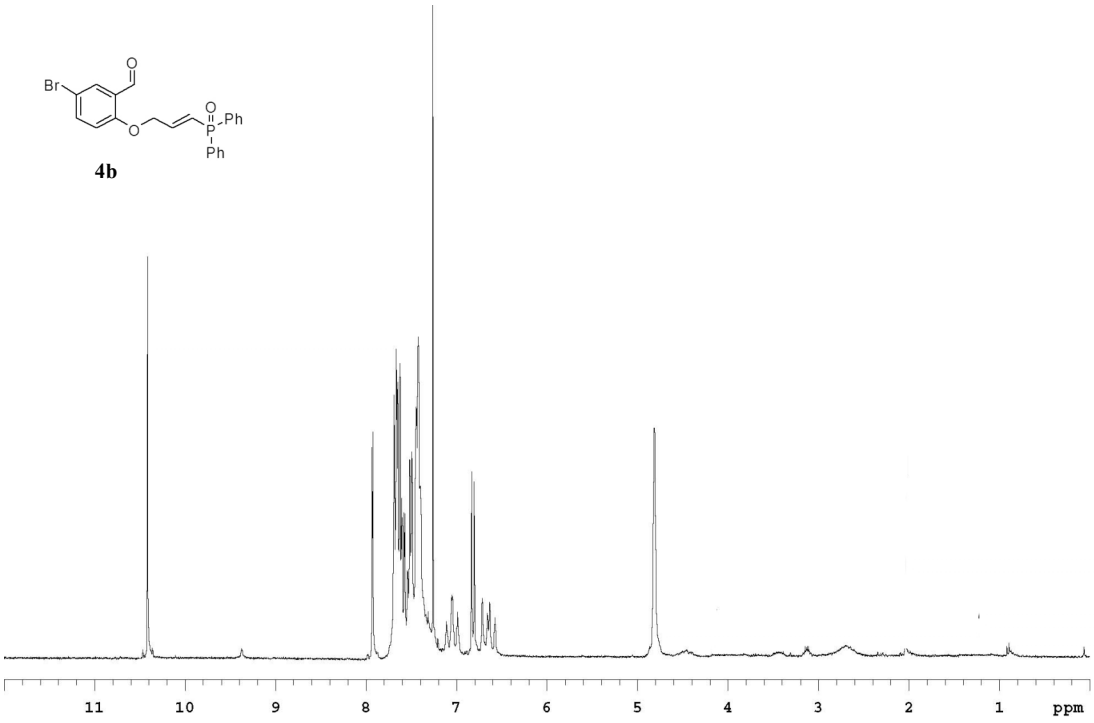
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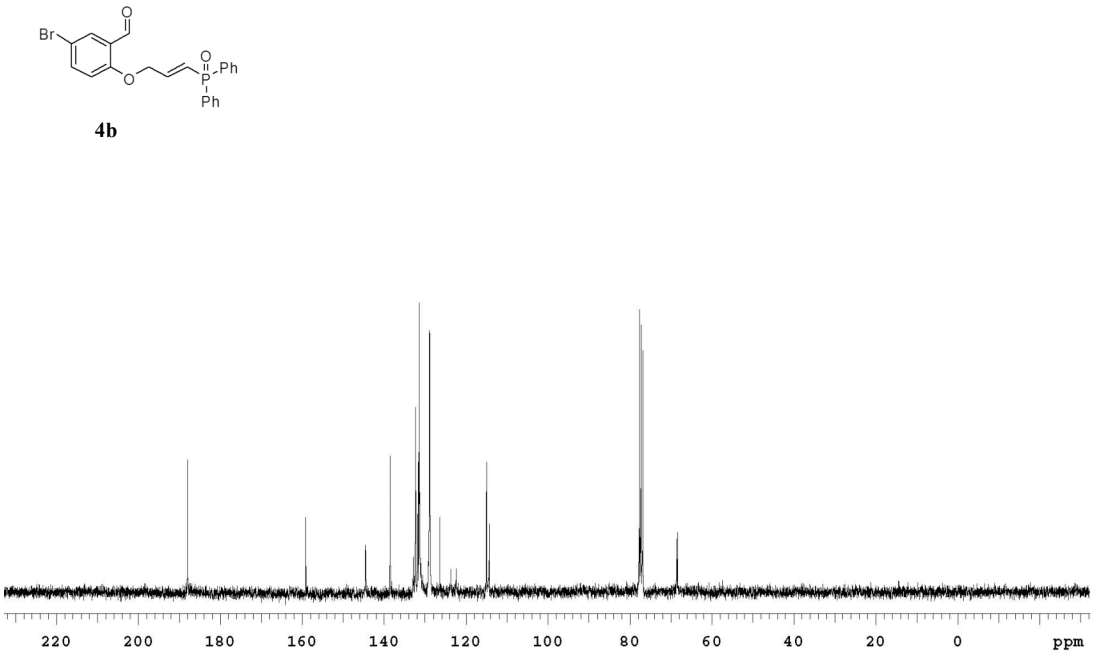
ppm

4b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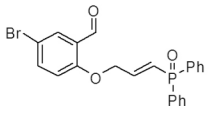
ppm

4b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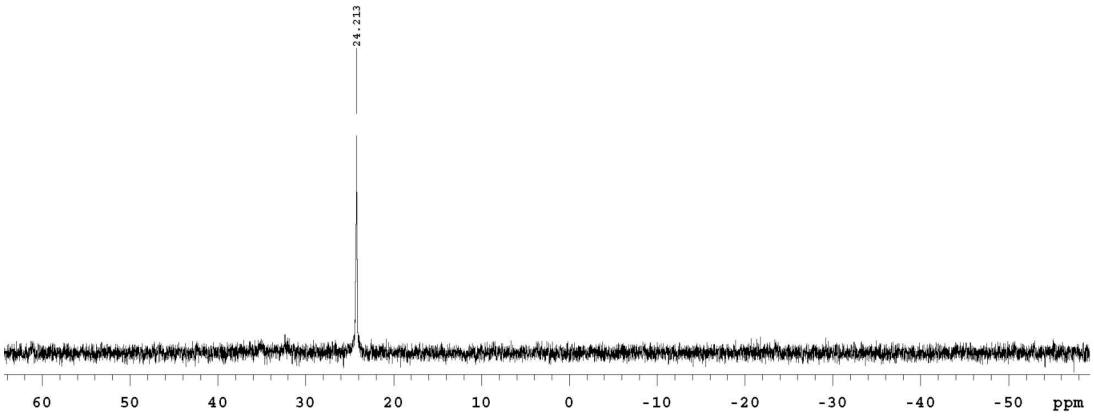
Ph

4b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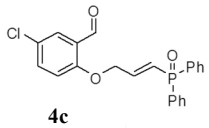
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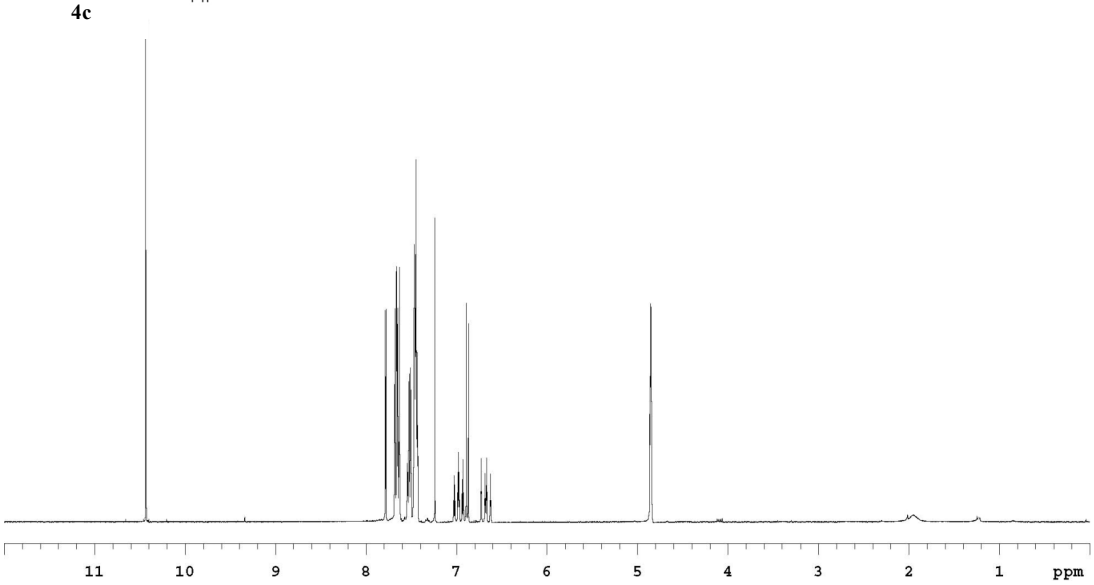
Ph

4c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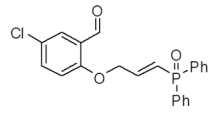

4c

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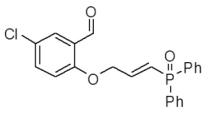

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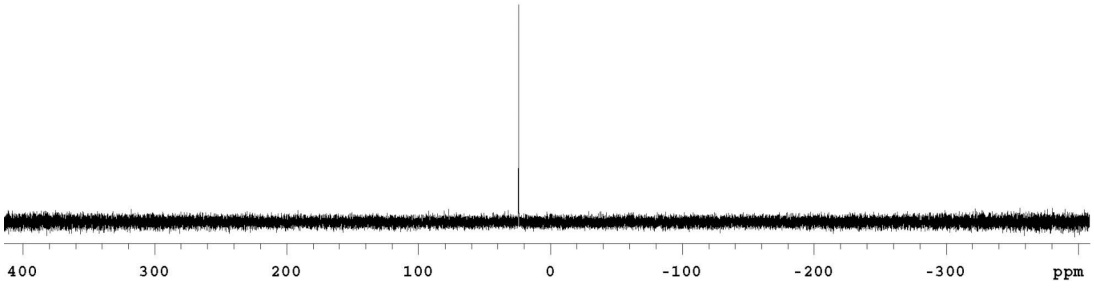
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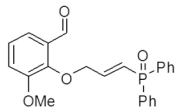
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P
Ph
OMe

4d

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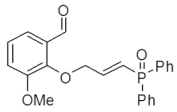
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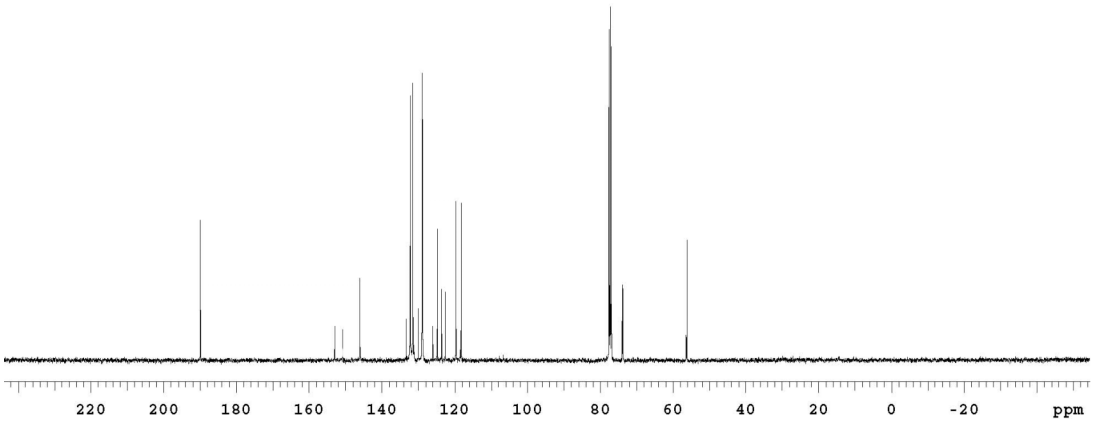
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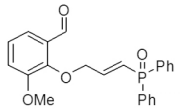
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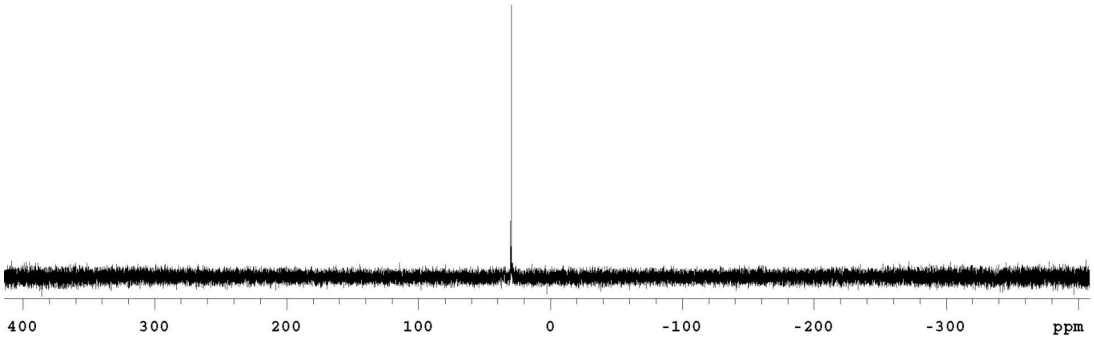
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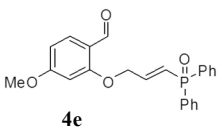
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Ph

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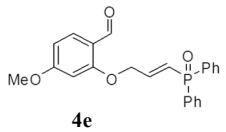
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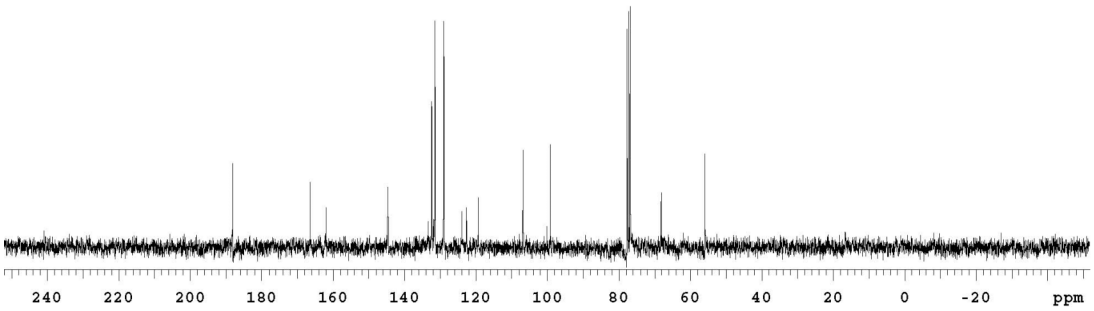
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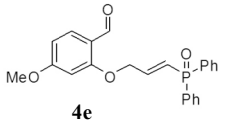
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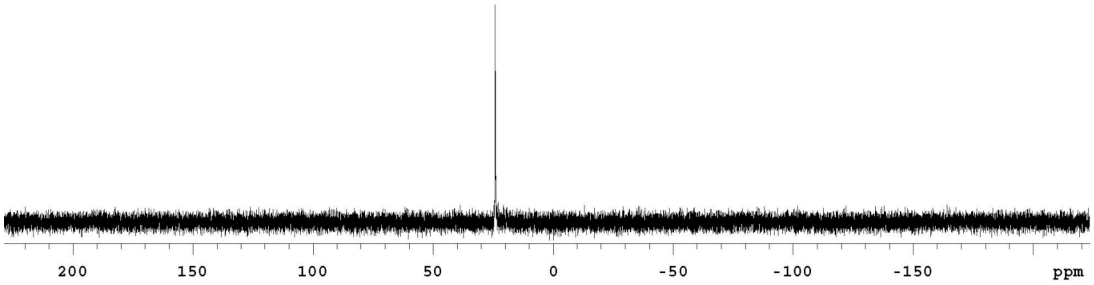
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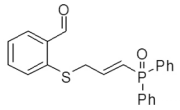

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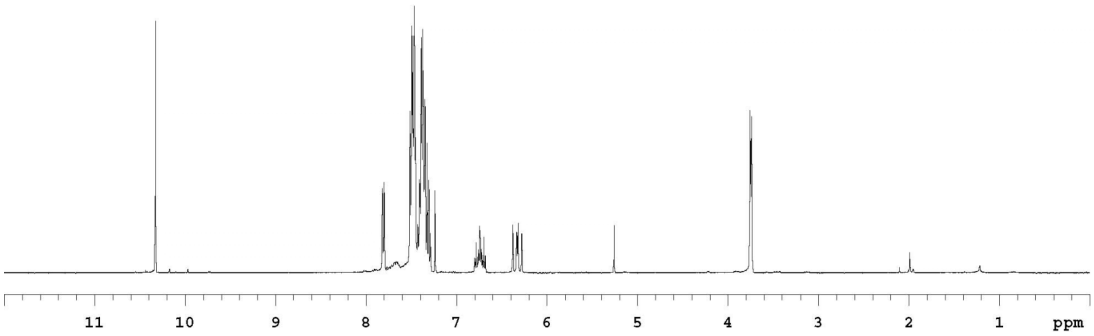
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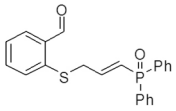

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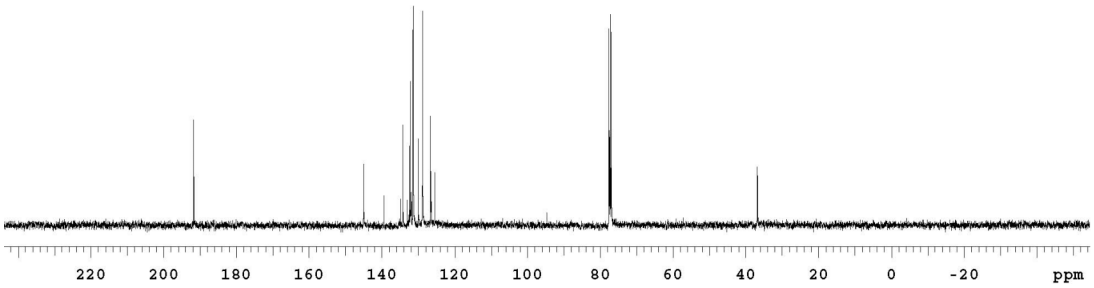
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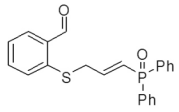

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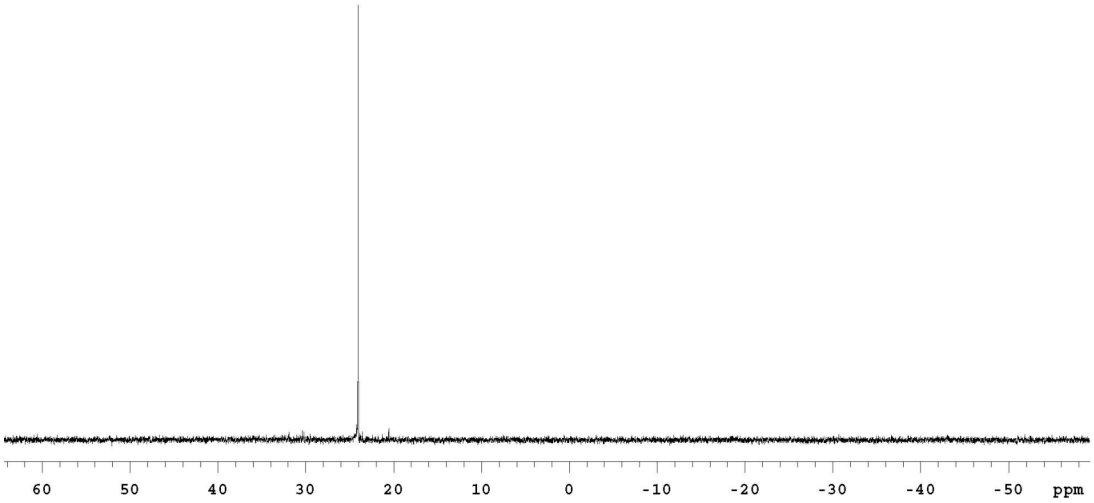

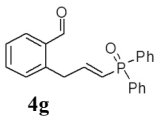

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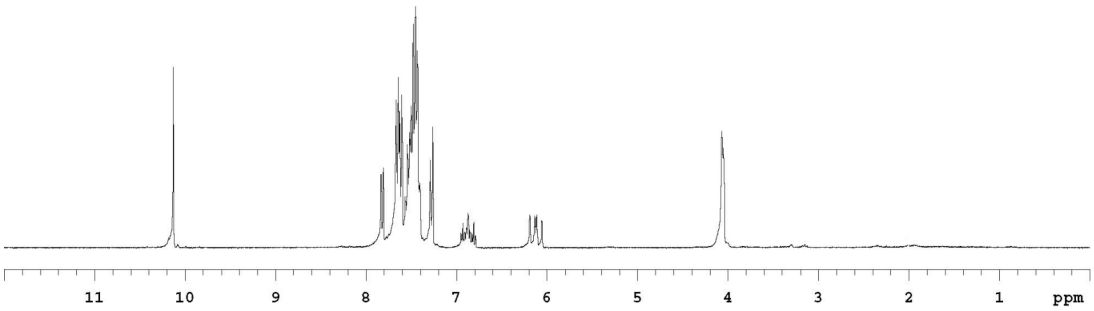

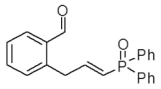

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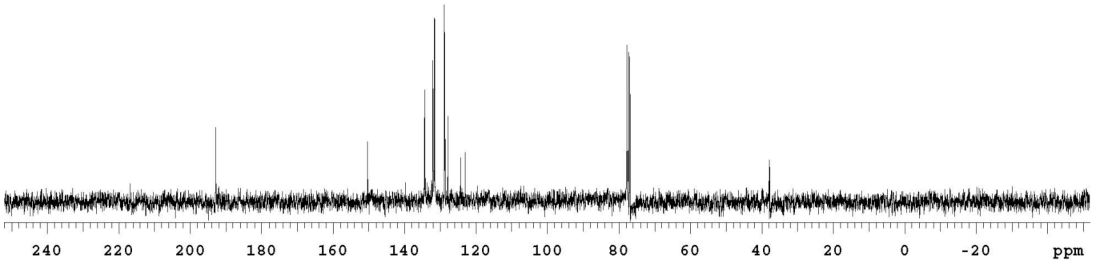
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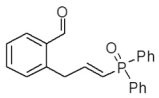

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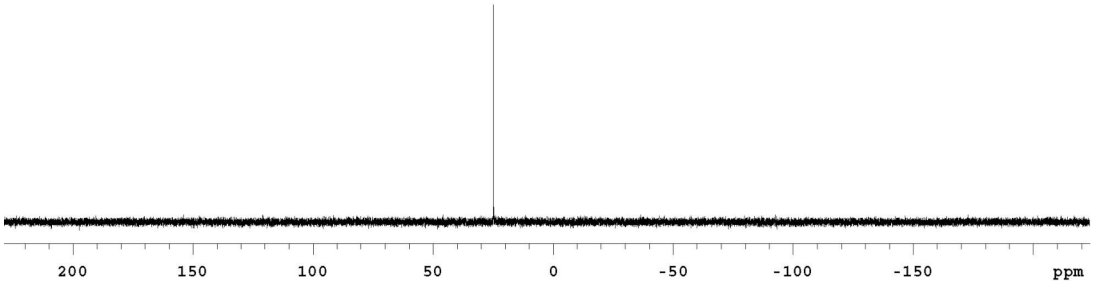
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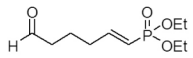

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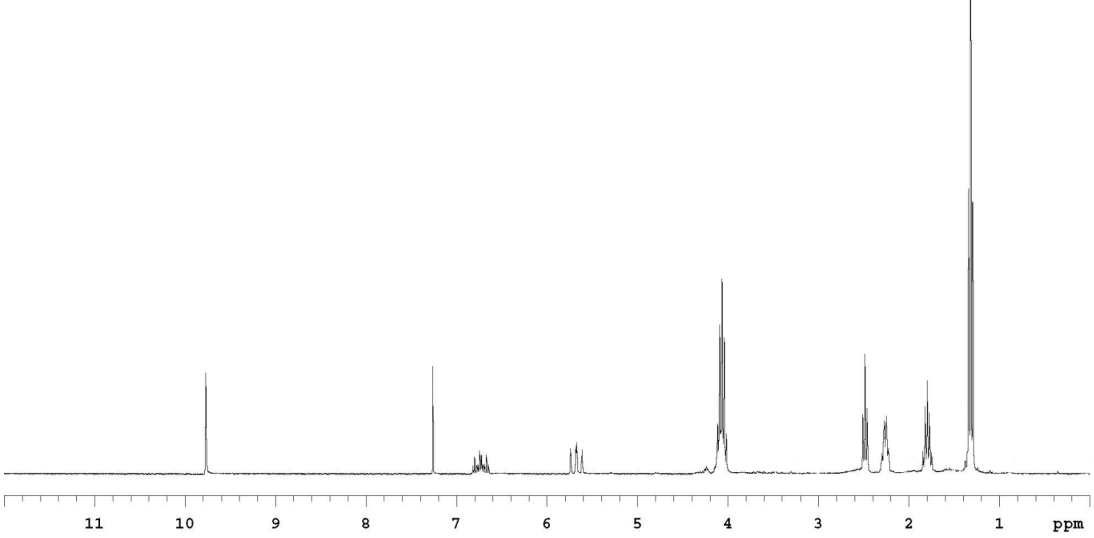
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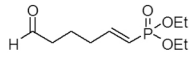

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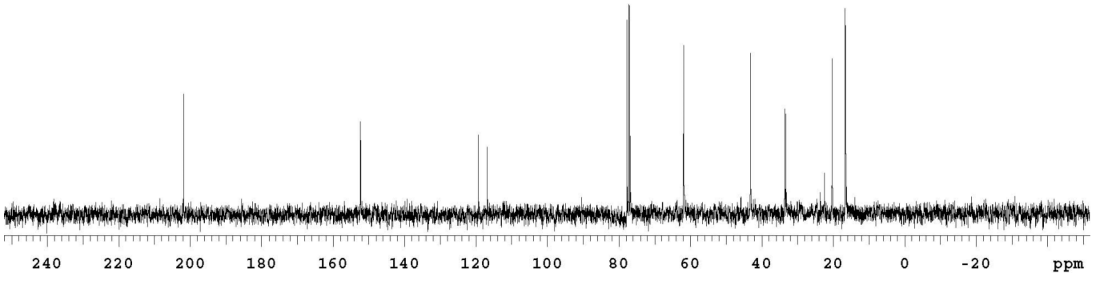
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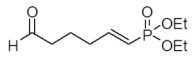
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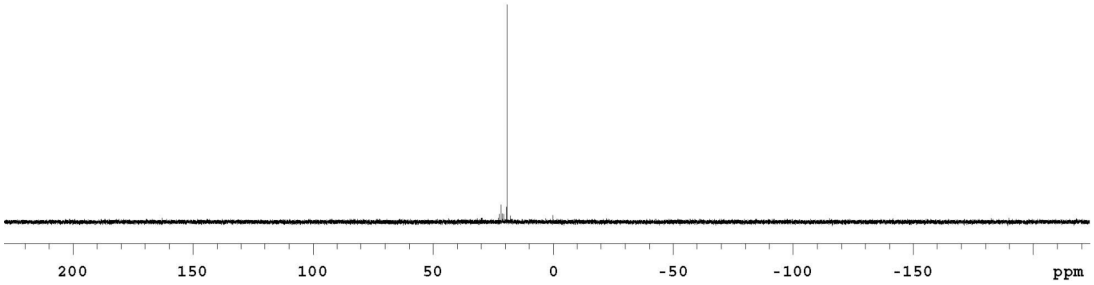
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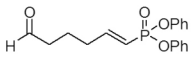
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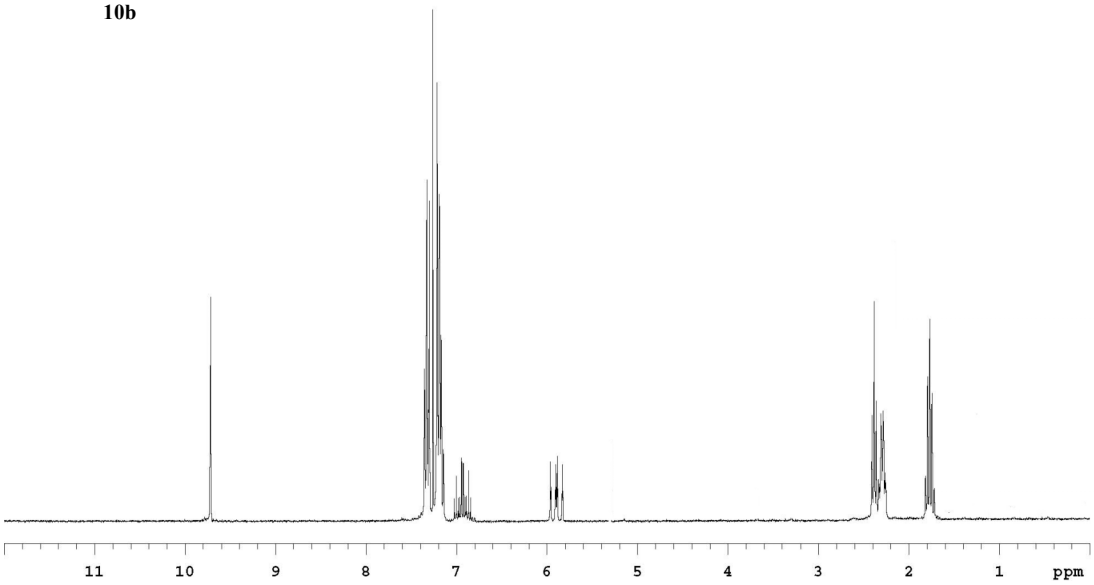
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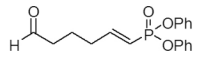

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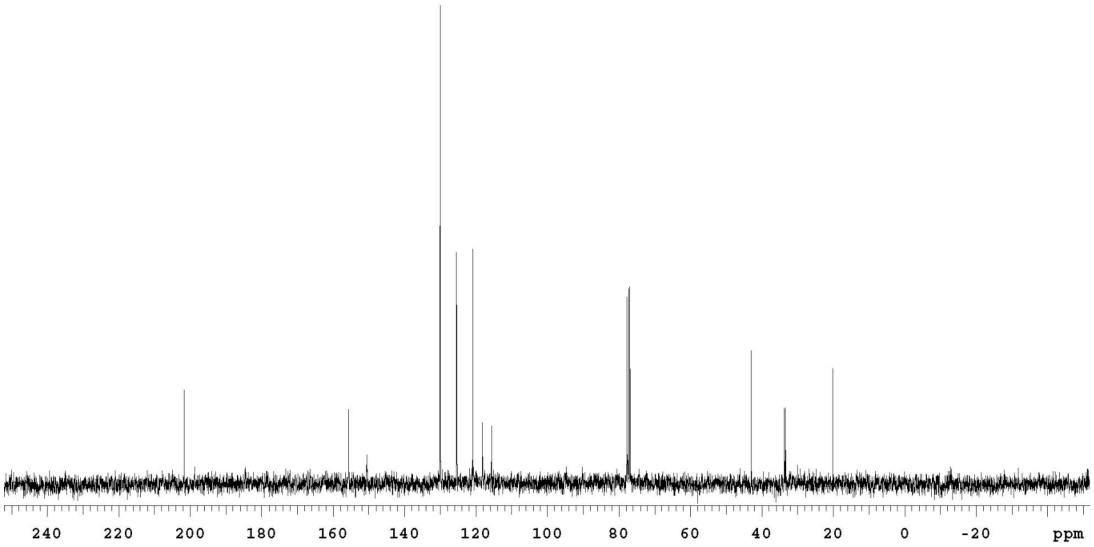
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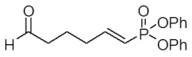

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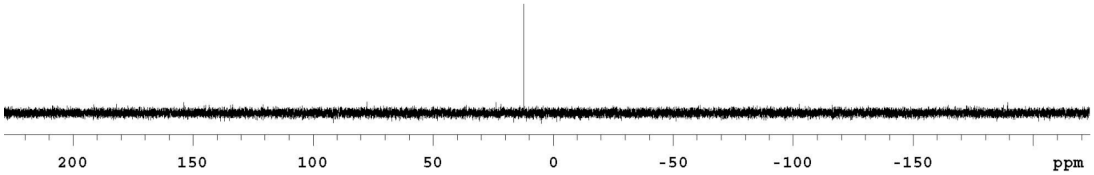
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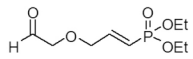

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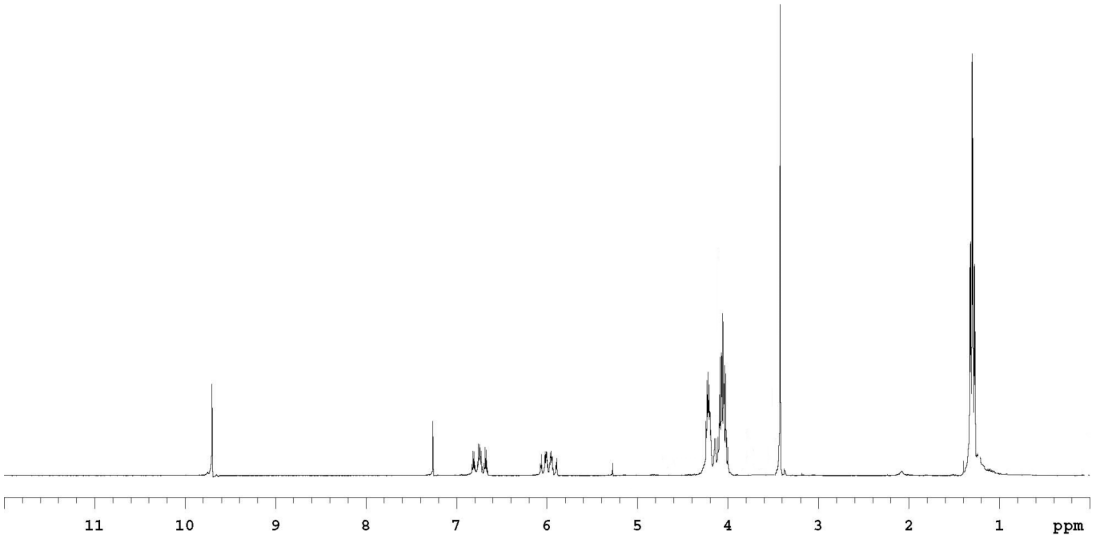
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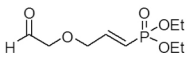

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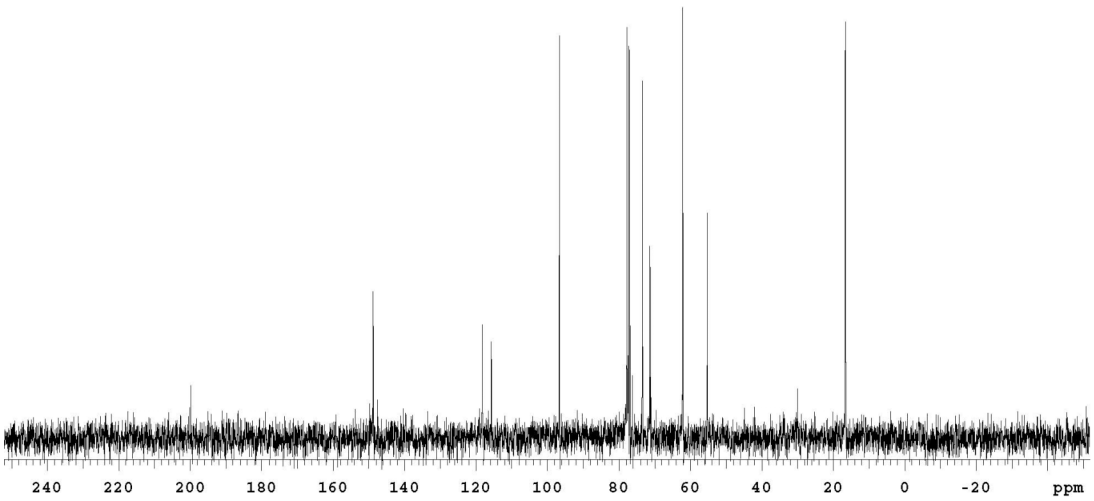
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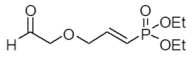

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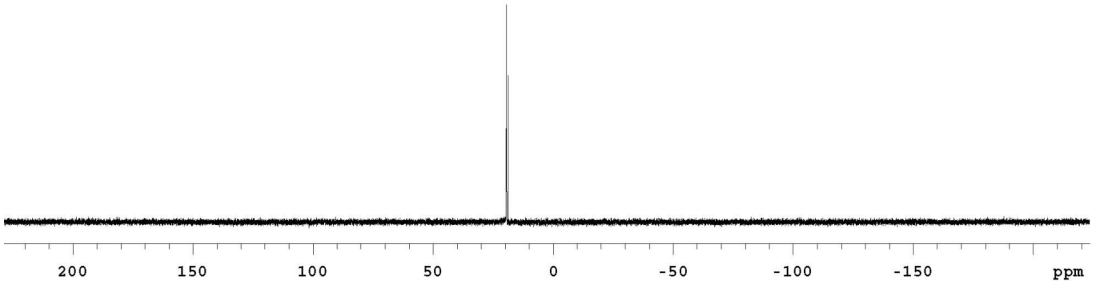

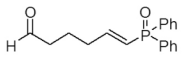

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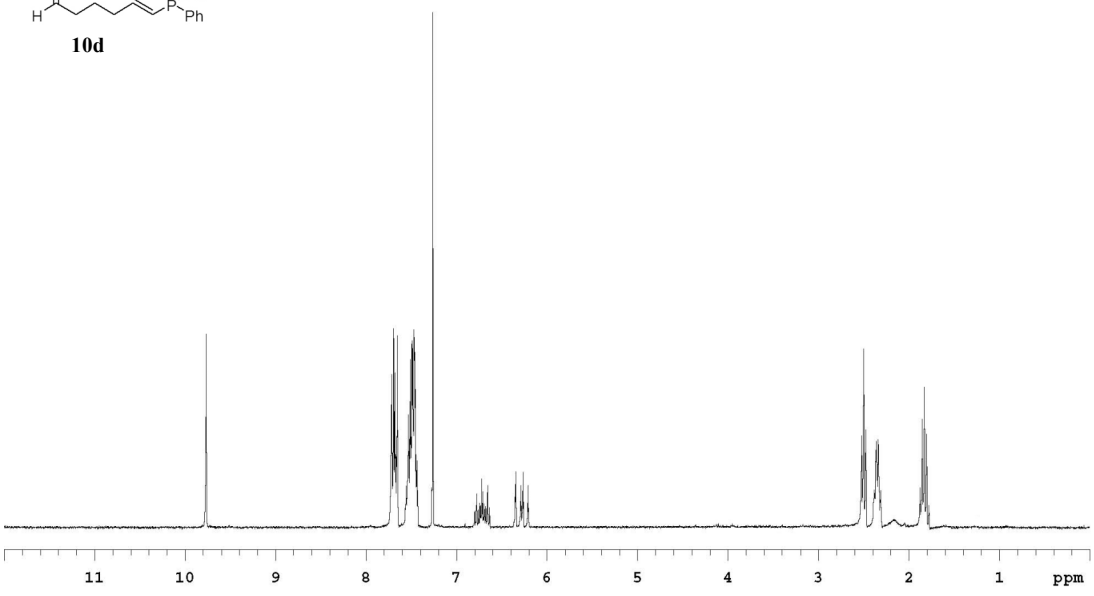

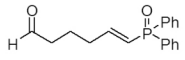

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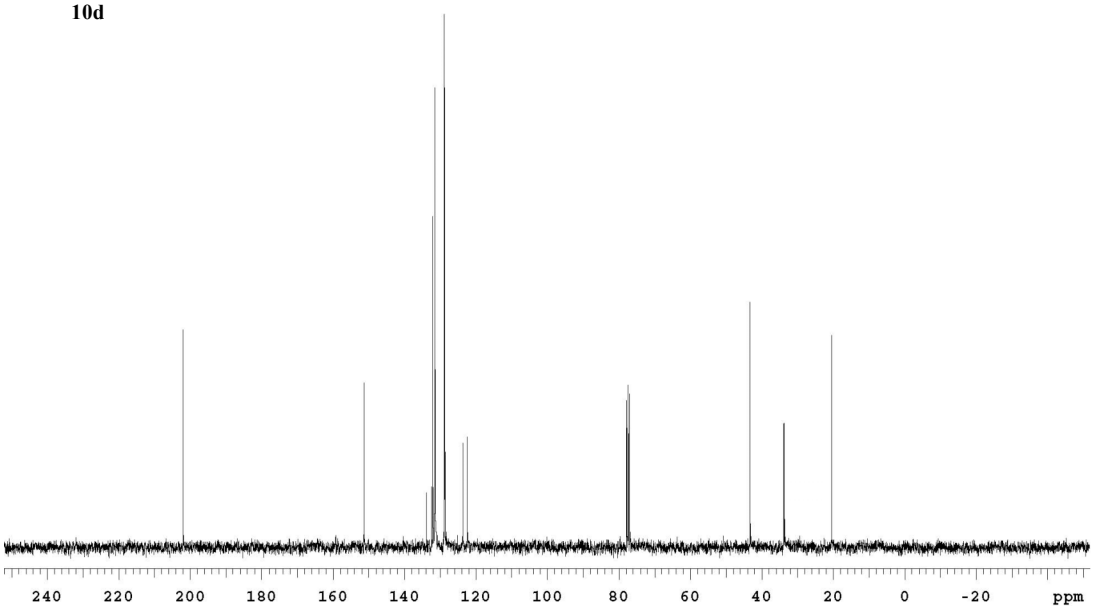
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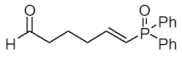

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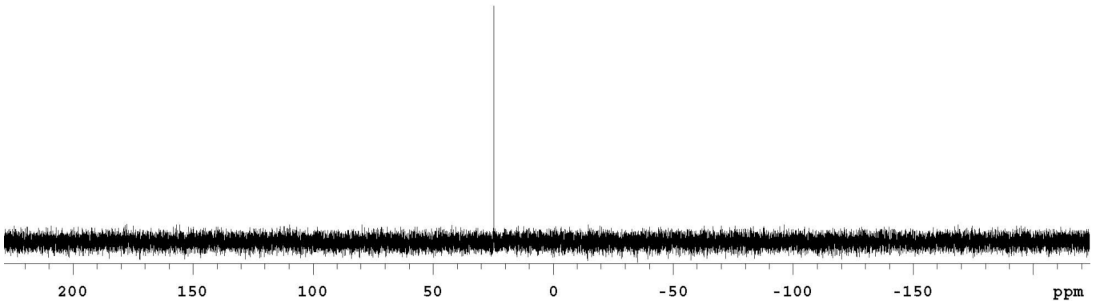
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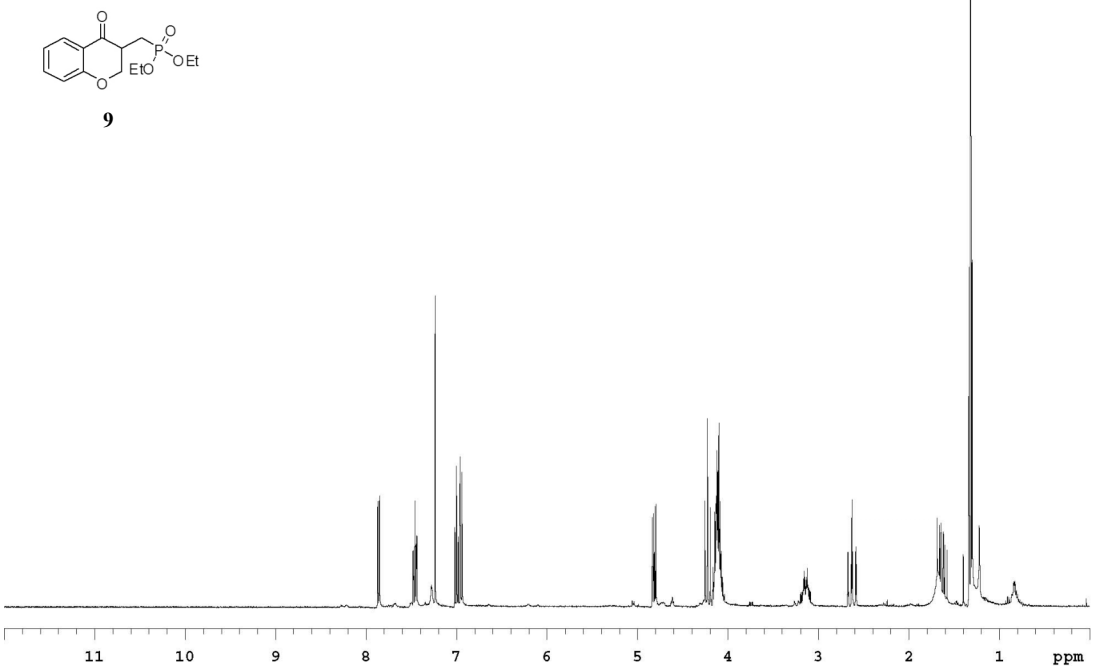
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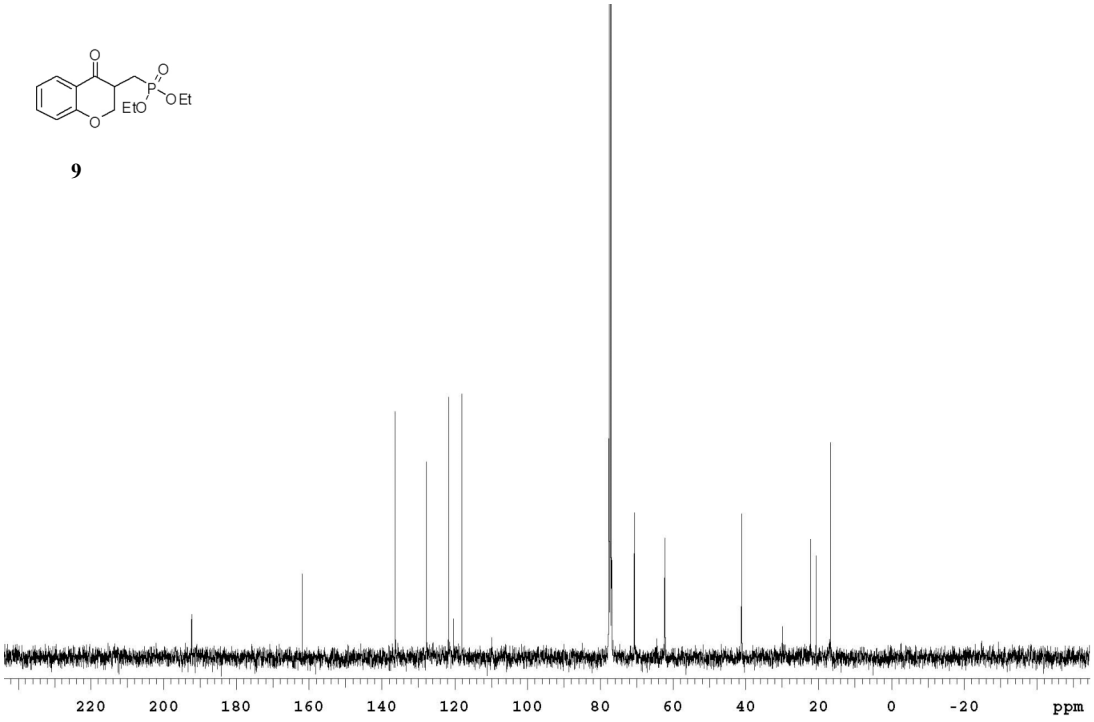
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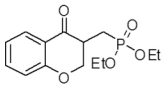

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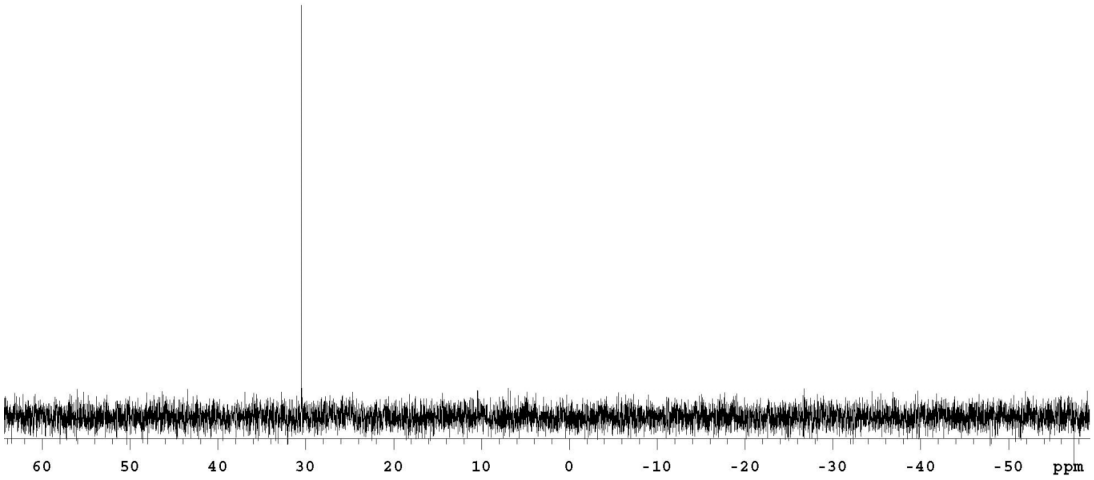

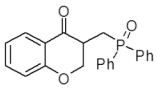

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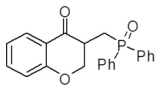

7a

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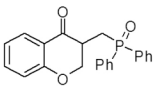

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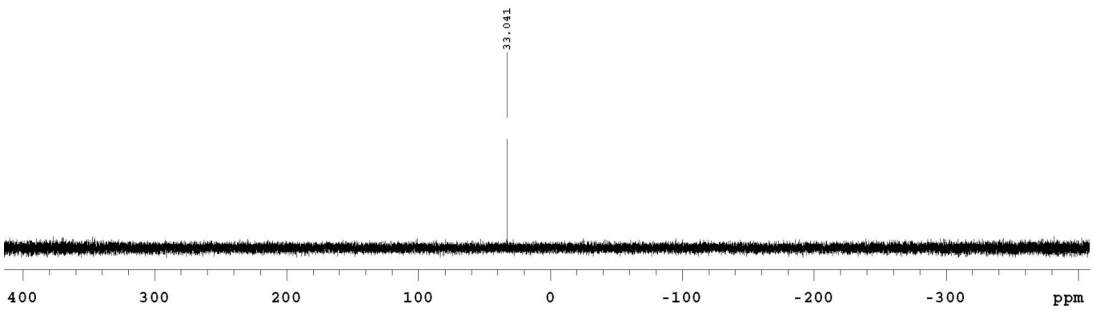
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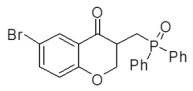
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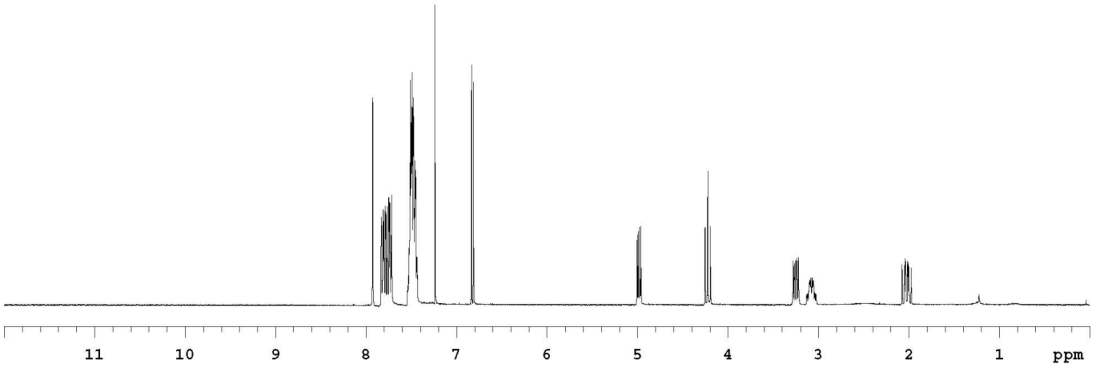
O
P
Ph
Ph
O

7b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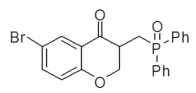
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O
O
Ph
P
Ph
O

7b

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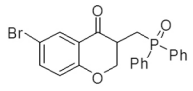
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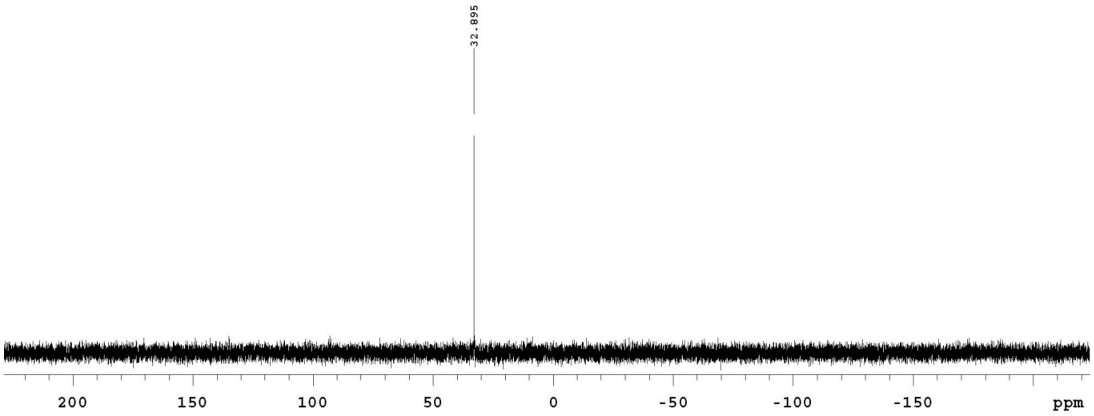
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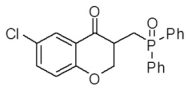
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P
Ph
Ph
O

7c

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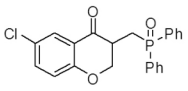
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7c

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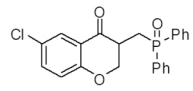
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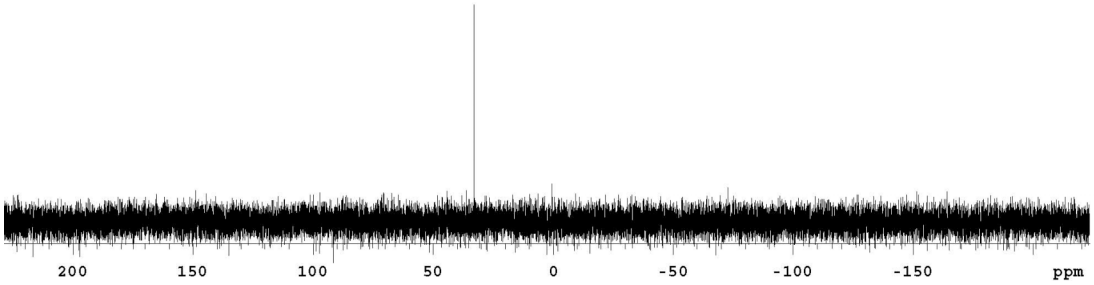
7c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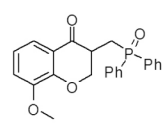

7d

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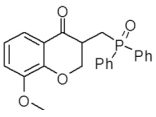

7d

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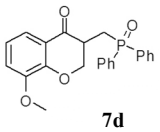

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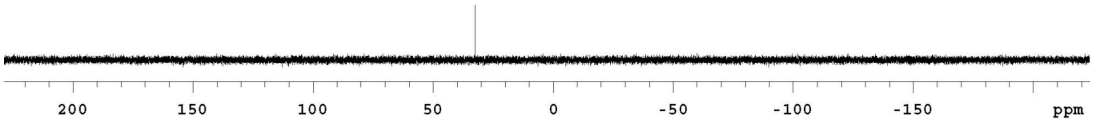

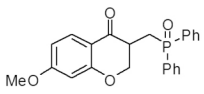

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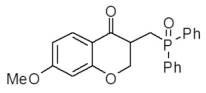
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Ph
MeO
O

7e

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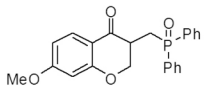
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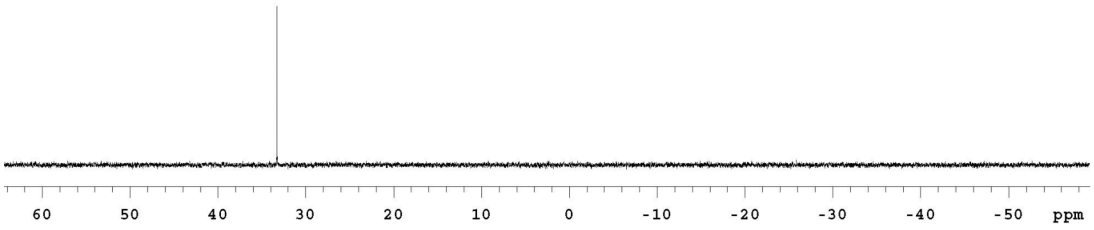
MeO
O

7e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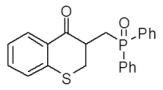

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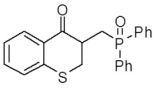

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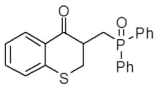

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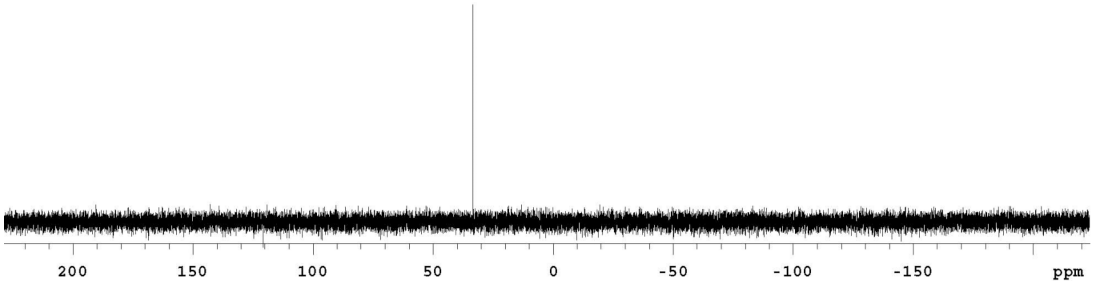
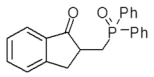
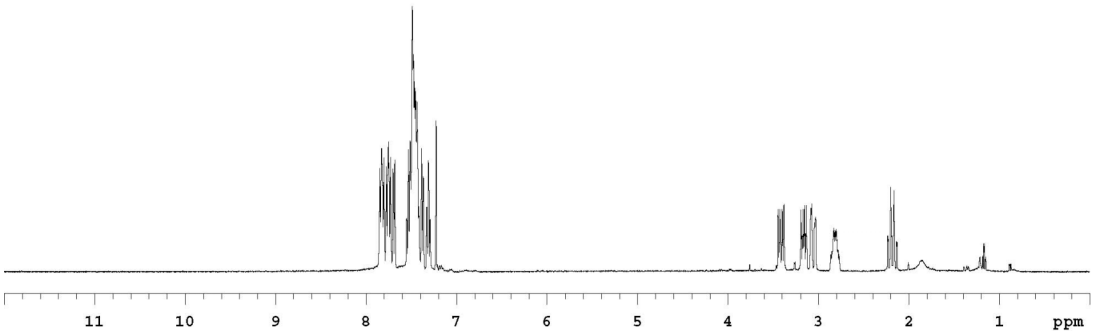
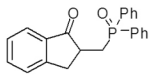




7g





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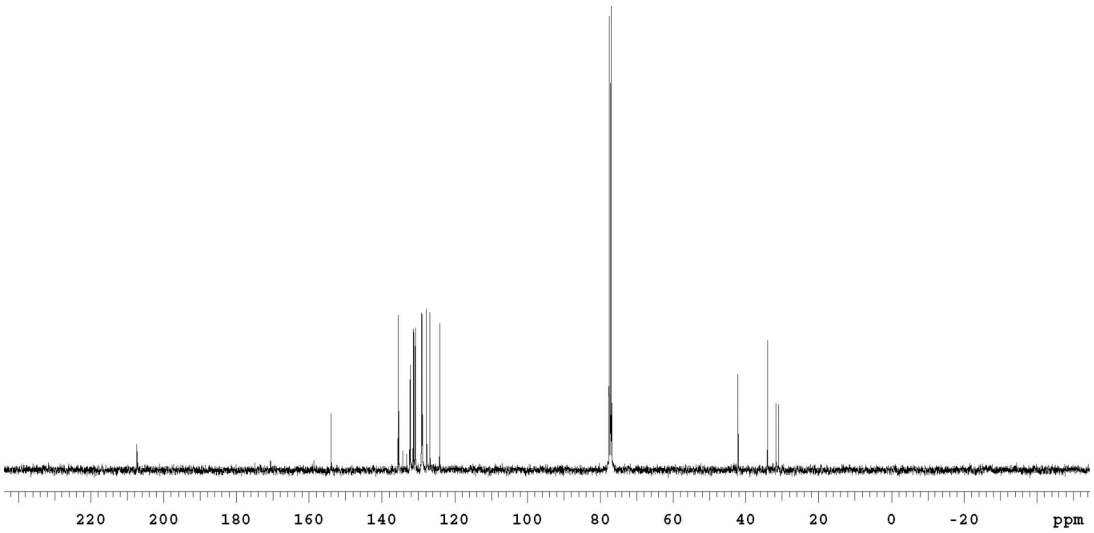
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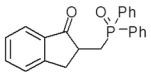

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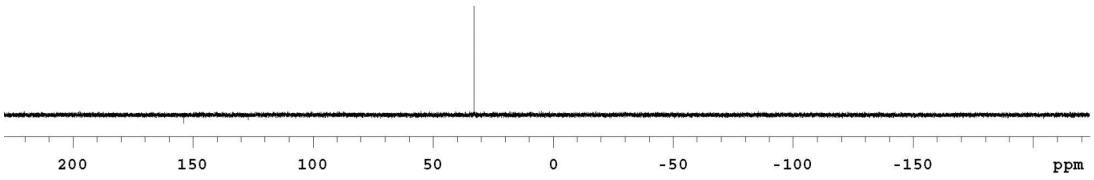
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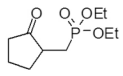

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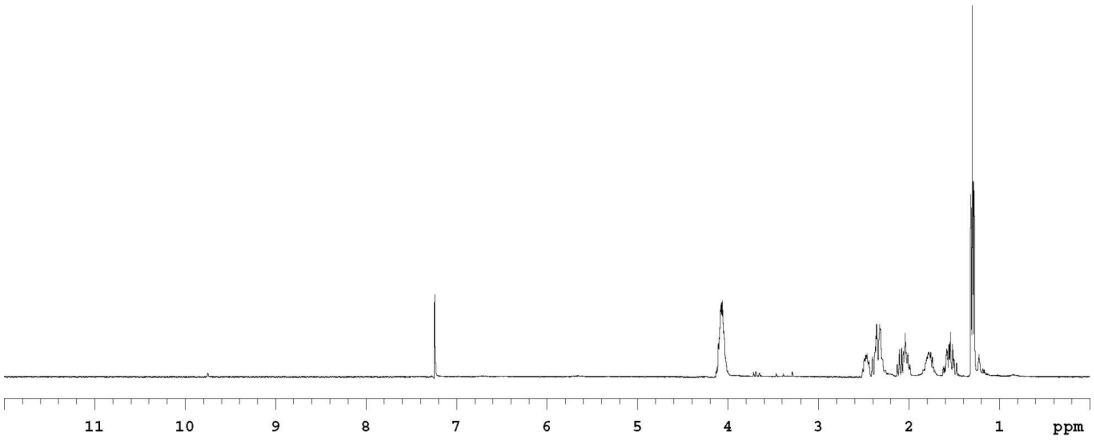
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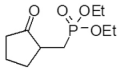

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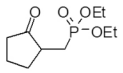

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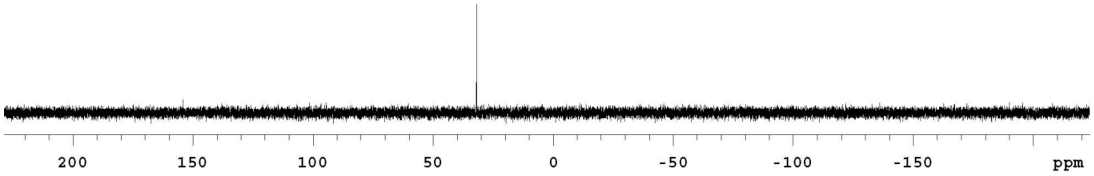

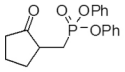

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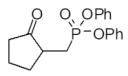

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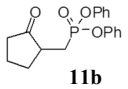

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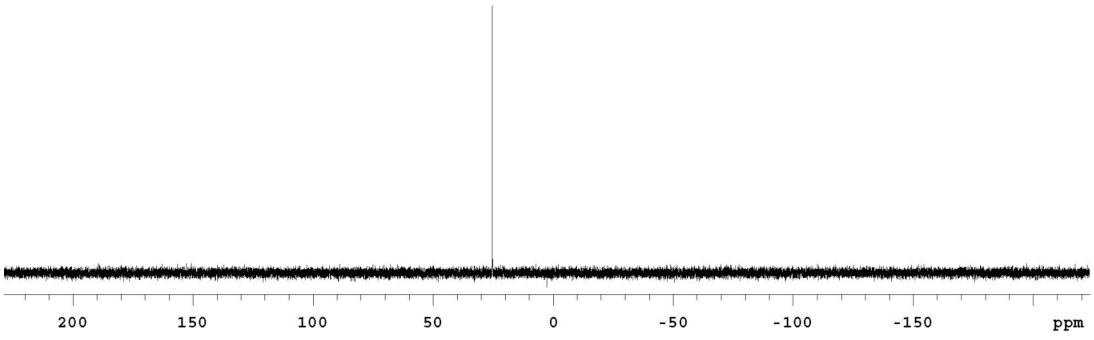
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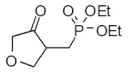

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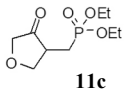

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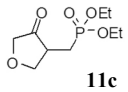

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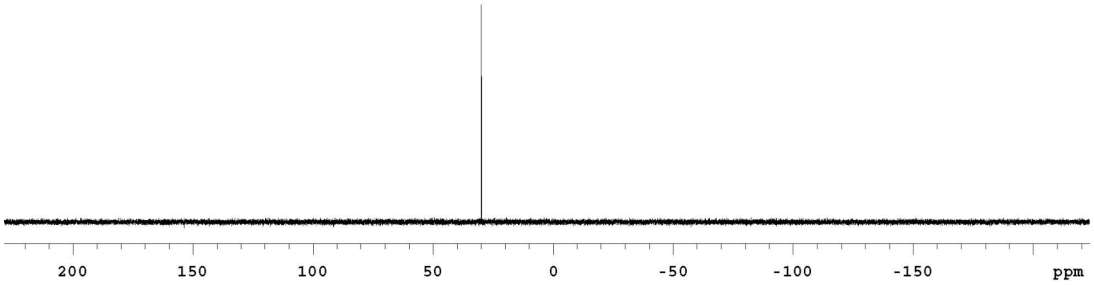

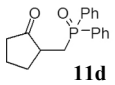

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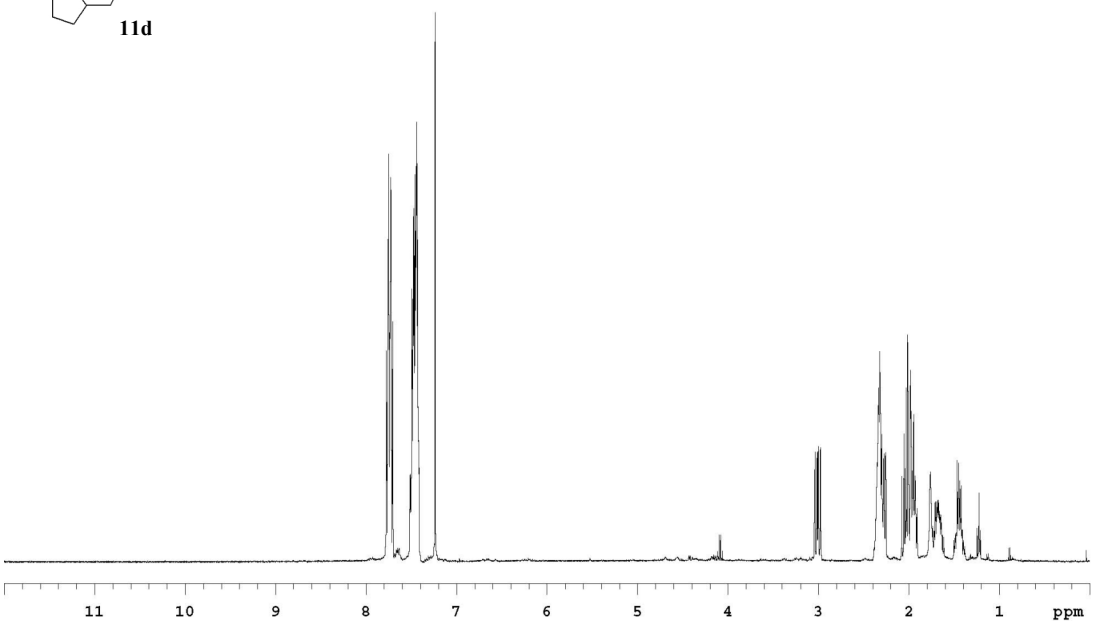

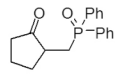

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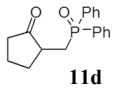

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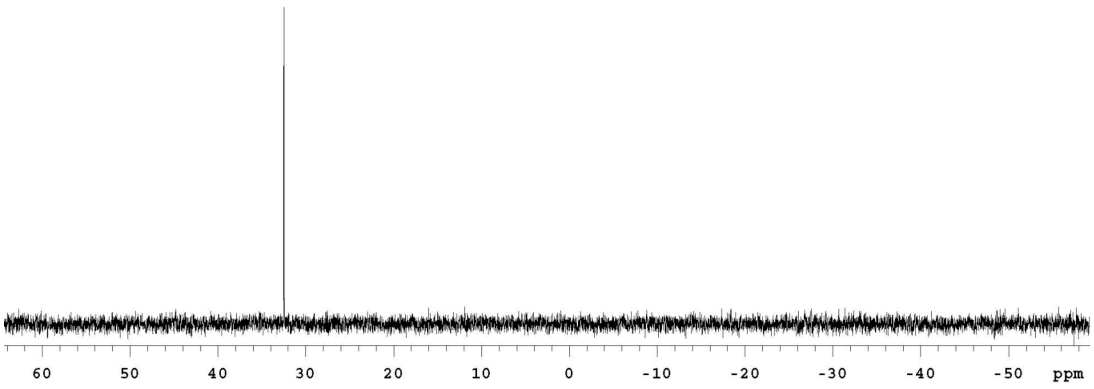
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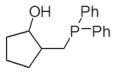
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Ph

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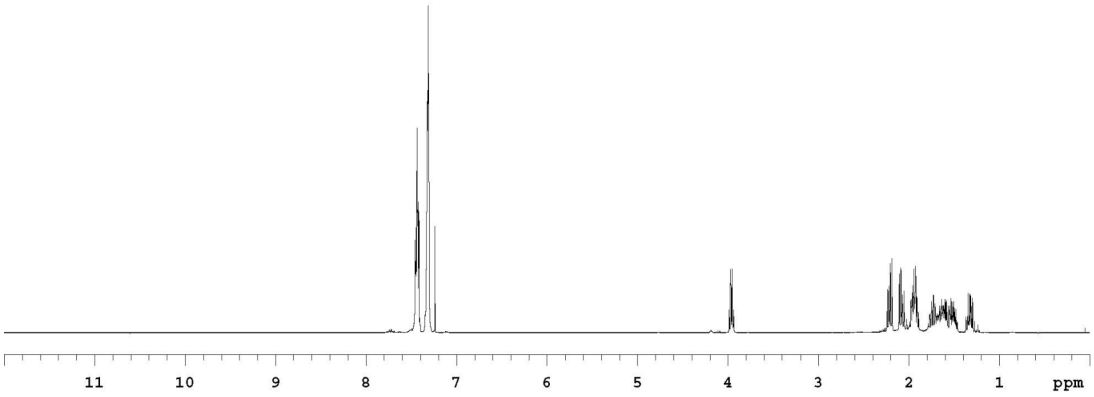
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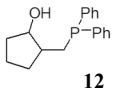
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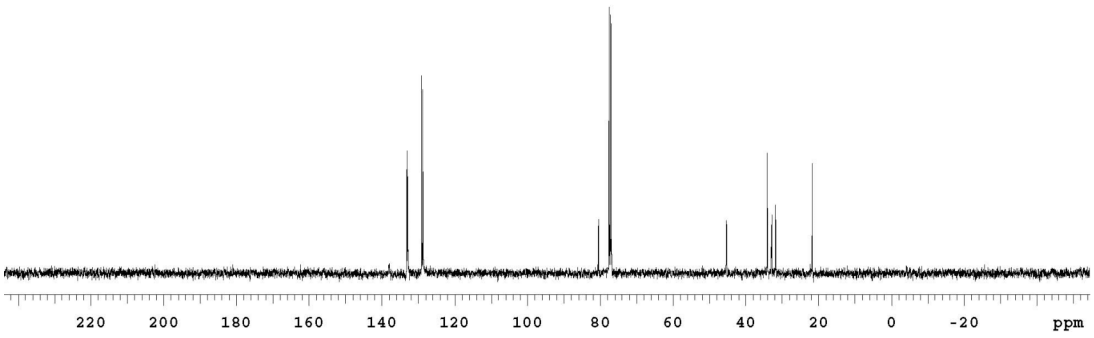
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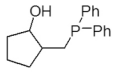
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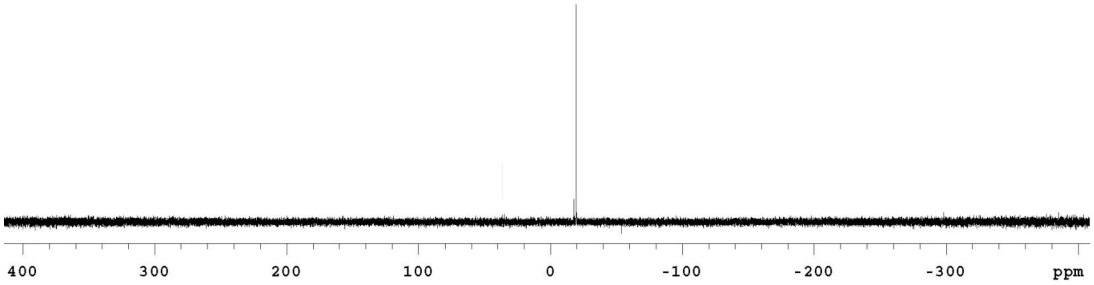
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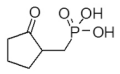
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OH
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OH

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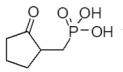

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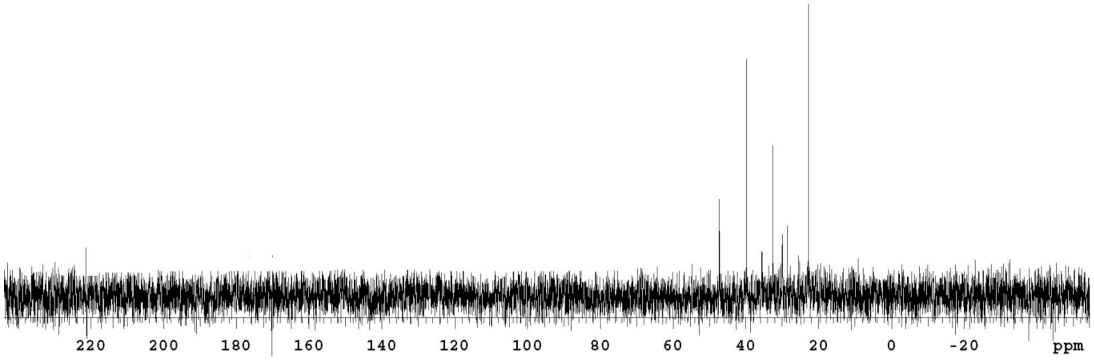
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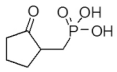

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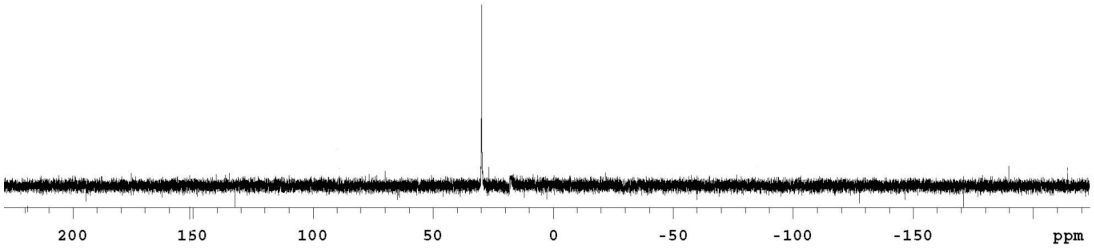
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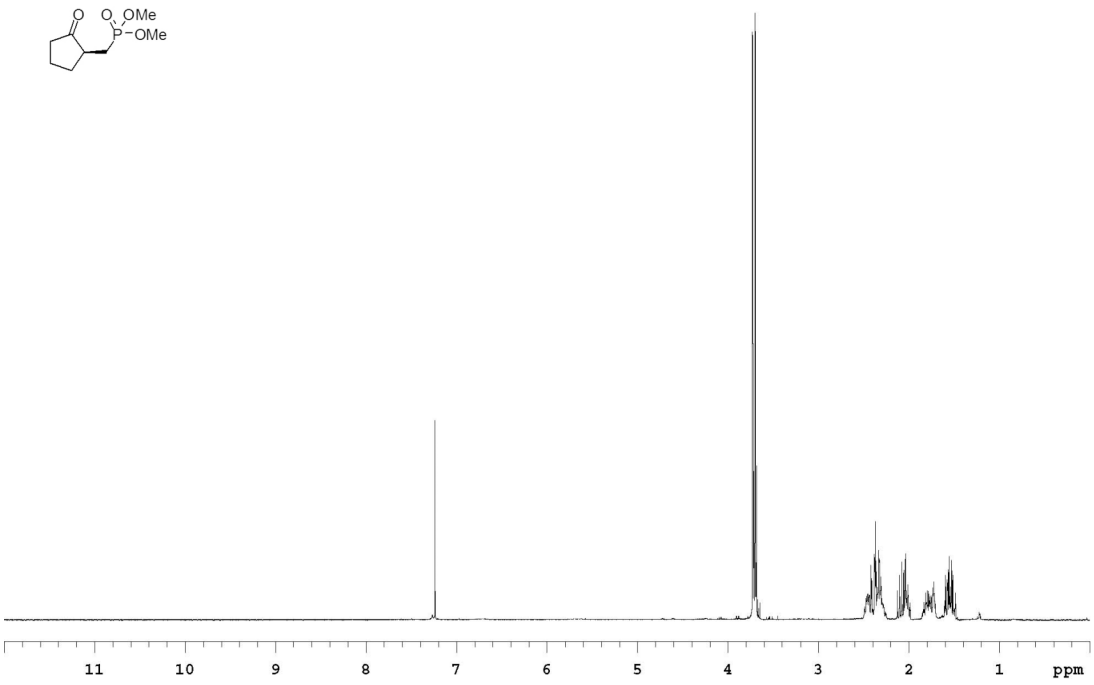
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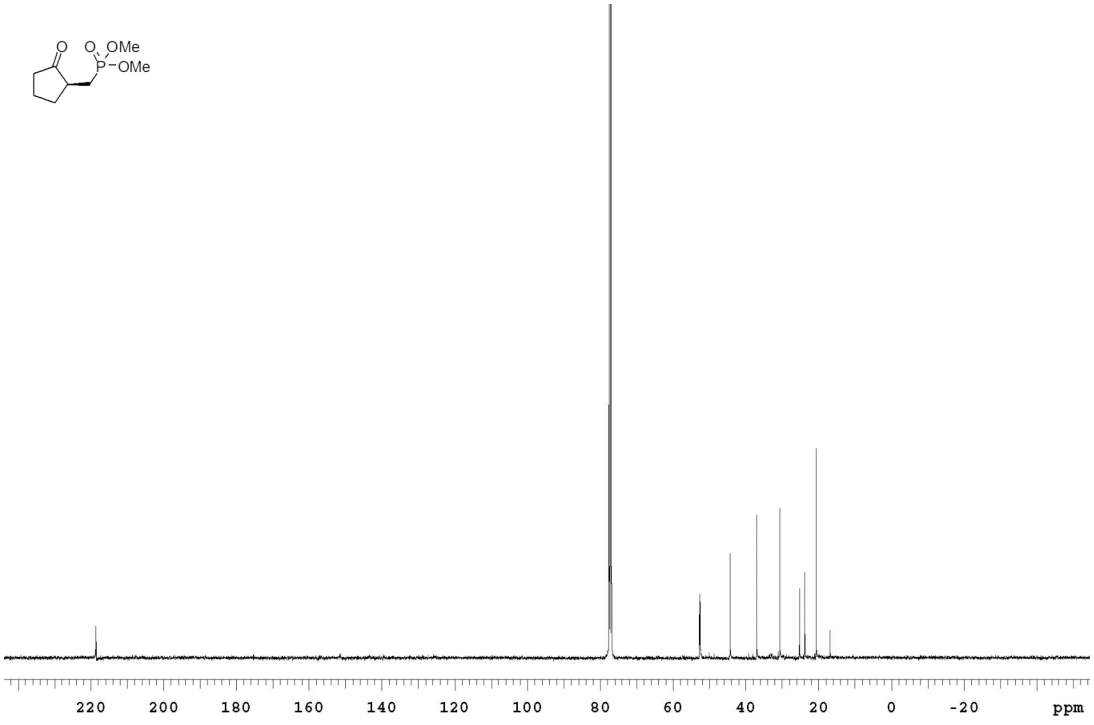
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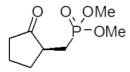
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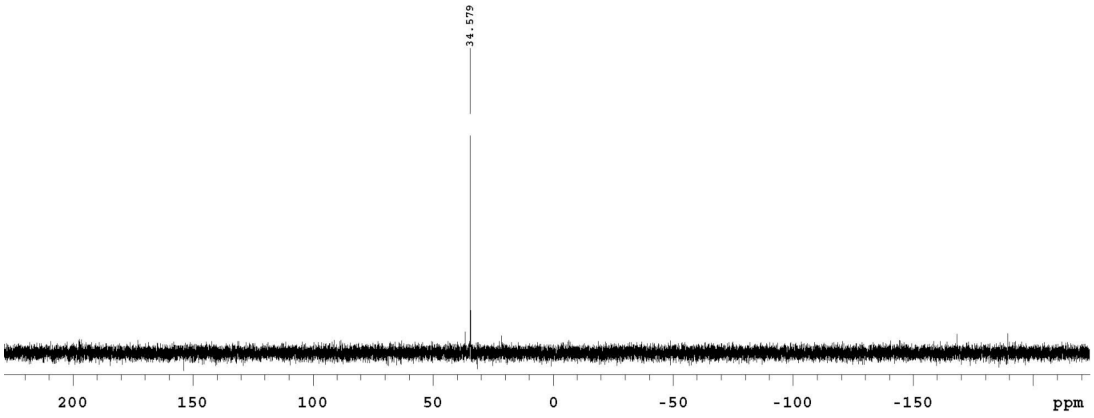
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