Metal-free hydrodifunctionalization of enaminones for the synthesis of ketomethylene functionalized phosphoryl alcohols

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General experimental information

All enaminones **1** were synthesized following literature process.[1] All other chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. The NMR spectra were recorded in 400 MHz apparatus in DMSO-d_6 or $CDCl_3$. The frequencies for ^1H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR test are 400 MHz, 100 MHz, 162 MHz and 376 MHz, respectively. The chemical shifts were reported in ppm with TMS as internal standard. Melting points were tested in X-4A instrument without correcting temperature and the HRMS data for all new products were obtained under ESI model with TOF analyzer.

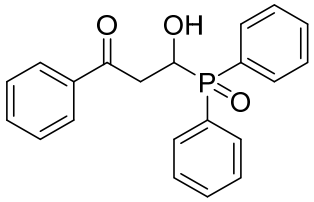
General procedure for the synthesis of 3

In a 25 mL sealed tube were added enaminone **1** (0.3 mmol, 1.0 equiv), dialkyl phosphonate **2** (0.39 mmol, 1.3 equiv), $H_2C_2O_4 \cdot 2H_2O$ (0.6 mmol, 2.0 equiv) and H_2O/CH_2Cl_2=1:1. After sealing the tube with Teflon cap, the mixture was stirred at 60 °C with oil bath heating for 12 h. After being cooled down to room temperature, 5 mL of water was added, and the resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL). Dried with anhydrous Na_2SO_4 and filtered. the mixture was transferred into the round bottom flask, after removing the solvent under reduced pressure, the resulting residue was recrystallized with ethyl acetate/CH_2Cl_2 to afford **3**.

Procedure of the 1 mmol scale reaction for 3a synthesis

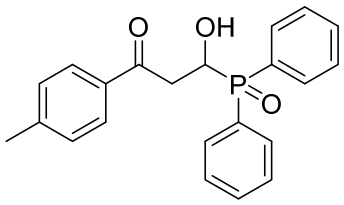
In a 50 mL sealed tube were added enaminone **1a** (1.0 mmol, 1.0 equiv), dialkyl phosphonate **2a** (1.3 mmol, 1.3 equiv), $H_2C_2O_4 \cdot 2H_2O$ (2.0 mmol, 2.0 equiv) and H_2O/CH_2Cl_2=3:3. After sealing the tube with Teflon cap, the mixture was stirred at 60 °C with oil bath heating for 12 h. After being cooled down to room temperature, 10 mL of water was added, and the resulting mixture was extracted with CH_2Cl_2 (3 × 20 mL). Dried with anhydrous Na_2SO_4 and filtered. the mixture was transferred into the round bottom flask, after removing the solvent under reduced pressure, the resulting residue was recrystallized with ethyl acetate/CH_2Cl_2 to afford **3a** (288.1 mg, 82% yield).

Characterization data of products 3

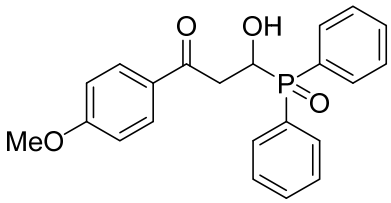


3-(Diphenylphosphoryl)-3-hydroxy-1-phenylpropan-1-one (**3a**). White solid (90.1 mg, 86% yield); mp 182-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 8.9 Hz, 2H), 7.93-7.80 (m, 4H), 7.61-7.41 (m, 7H), 7.38 (t, *J* = 7.7 Hz, 2H), 5.23 (d, *J* = 9.0 Hz, 1H), 4.02 (s, 1H), 3.58 (d, *J* = 17.2 Hz, 1H), 3.36-3.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0 (d, *J* = 13.5 Hz), 136.3, 133.6, 132.3, 132.23, 132.18, 132.1, 131.5 (d, *J* = 8.2 Hz), 128.7, 128.6, 128.5, 128.4, 128.3, 67.2 (d, *J* = 90.6 Hz), 38.9 (d, *J* = 2.8 Hz); ^{31}P

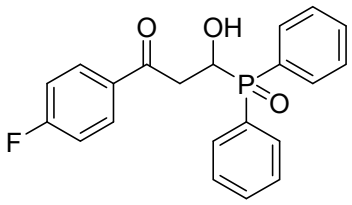
NMR (162 MHz, $CDCl_3$) δ 30.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{20}O_3P$ 351.1145; Found 351.11462.



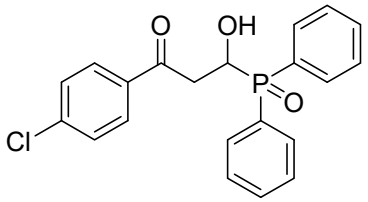
3-(Diphenylphosphoryl)-3-hydroxy-1-(p-tolyl)propan-1-one (**3b**). White solid (84.8 mg, 78% yield); mp 176-178 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00-7.92 (m, 2H), 7.91-7.83 (m, 2H), 7.78 (d, J = 8.1 Hz, 2H), 7.64-7.49 (m, 6H), 7.28 (d, J = 8.0 Hz, 2H), 5.13 (d, J = 9.6 Hz, 1H), 3.72 (s, 1H), 3.36-3.26 (m, 1H), 3.24-3.16 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.1 (d, J = 13.8 Hz), 144.2, 134.7, 132.3, 132.3, 132.24, 132.21, 131.6, 131.5, 129.7, 129.1 (d, J = 11.0 Hz), 128.9 (d, J = 11.1 Hz), 128.6, 66.6 (d, J = 90.6 Hz), 40.1, 21.6; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}O_3P$ 365.1301; Found 365.13062.



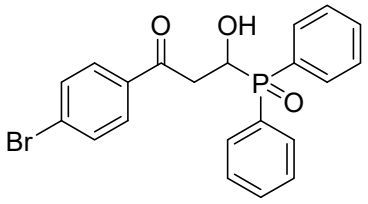
3-(Diphenylphosphoryl)-3-hydroxy-1-(4-methoxyphenyl)propan-1-one (**3c**). White solid (99.5 mg, 87% yield); mp 178-180 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02-7.91 (m, 2H), 7.86 (d, J = 7.6 Hz, 4H), 7.65-7.45 (m, 6H), 7.01 (d, J = 8.3 Hz, 2H), 6.06 (s, 1H), 5.13 (s, 1H), 3.81 (s, 3H), 3.34-3.23 (m, 1H), 3.22-3.11 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 195.9 (d, J = 13.8 Hz), 163.7, 132.3, 132.2, 131.6, 131.5, 130.9, 130.1, 129.1, 129.0, 128.9, 128.8, 114.4, 66.6 (d, J = 91.0 Hz), 56.0, 39.7; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}O_4P$ 381.1250; Found 381.12509.



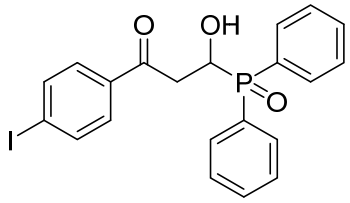
3-(Diphenylphosphoryl)-1-(4-fluorophenyl)-3-hydroxypropan-1-one (**3d**). White solid (94.3 mg, 85% yield); mp 186-188 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03-7.94 (m, 3H), 7.94-7.78 (m, 3H), 7.63-7.48 (m, 6H), 7.31 (t, J = 8.8 Hz, 2H), 5.12 (d, J = 9.4 Hz, 1H), 3.39-3.27 (m, 1H), 3.27-3.20 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.3 (d, J = 13.9 Hz), 165.5 (d, J = 252.1 Hz), 132.3, 132.2, 131.61, 131.57, 131.53, 131.48, 129.1, 129.0, 128.9, 128.8, 116.2 (d, J = 21.9 Hz), 66.6 (d, J = 90.7 Hz), 40.2; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.6; ^{19}F NMR (376 MHz, DMSO-d_6) δ -105.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}FO_3P$ 369.1050; Found 369.10522.



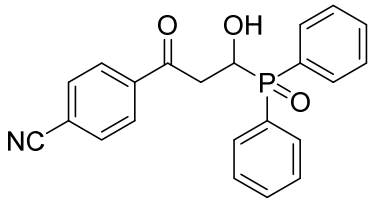
1-(4-Chlorophenyl)-3-(diphenylphosphoryl)-3-hydroxypropan-1-one (**3e**). White solid (96.1 mg, 83% yield); mp 188-190 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99-7.90 (m, 2H), 7.90-7.81 (m, 4H), 7.65-7.46 (m, 8H), 5.10 (d, J = 8.9 Hz, 1H), 3.36-3.28 (m, 1H), 3.27-3.20 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.7 (d, J = 13.9 Hz), 138.7, 135.8, 132.3, 132.2, 131.6, 131.5, 130.4, 129.3, 129.1, 129.0, 128.9, 128.8, 66.6 (d, J = 90.6 Hz), 40.3; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}ClO_3P$ 385.0755; Found 385.07547.



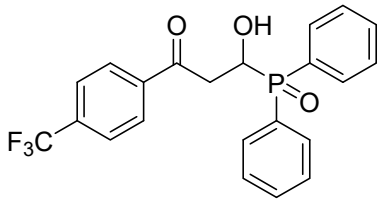
1-(4-Bromophenyl)-3-(diphenylphosphoryl)-3-hydroxypropan-1-one (**3f**). White solid (105.0 mg, 82% yield); mp 177-179 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02-7.90 (m, 2H), 7.90-7.82 (m, 2H), 7.80 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.65-7.46 (m, 6H), 6.09 (s, 1H), 5.10 (d, J = 8.8 Hz, 1H), 3.35-3.26 (m, 1H), 3.26-3.18 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.9 (d, J = 13.8 Hz), 136.1, 132.3, 132.23, 132.19, 131.6, 131.5, 130.5, 129.1, 129.0, 128.9, 128.8, 127.9, 66.5 (d, J = 90.7 Hz), 40.3; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}BrO_3P$ 429.0250; Found 429.02520.



3-(Diphenylphosphoryl)-3-hydroxy-1-(4-iodophenyl)propan-1-one (**3g**). White solid (118.1 mg, 83% yield); mp 190-192 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98-7.90 (m, 2H), 7.90-7.80 (m, 4H), 7.66-7.58 (m, 3H), 7.58-7.47 (m, 5H), 5.10 (d, J = 8.8 Hz, 1H), 3.30-3.19 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.2 (d, J = 13.9 Hz), 138.1, 136.4, 132.31, 132.27, 132.2, 132.1, 131.6, 131.5, 130.2, 129.1 (d, J = 11.0 Hz), 128.9 (d, J = 11.1 Hz), 102.3, 66.5 (d, J = 90.8 Hz), 40.1; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}IO_3PNa$ 498.9930; Found 498.99265.

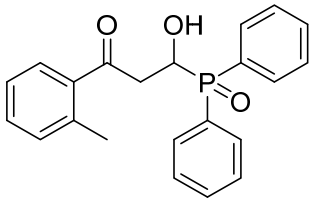


4-(3-(Diphenylphosphoryl)-3-hydroxypropanoyl)benzonitrile (**3h**). White solid (90.5 mg, 80% yield); mp 175-177 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08-7.89 (m, 6H), 7.89-7.81 (m, 2H), 7.65-7.48 (m, 6H), 6.11 (s, 1H), 5.15-5.01 (m, 1H), 3.38-3.27 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.3 (d, J = 13.9 Hz), 140.3, 133.2, 132.3, 132.21, 132.15, 131.6, 131.5, 129.2, 129.0, 128.9, 128.8, 118.6, 115.7, 66.5 (d, J = 90.6 Hz), 40.7; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}NO_3P$ 376.1097; Found 376.10977.

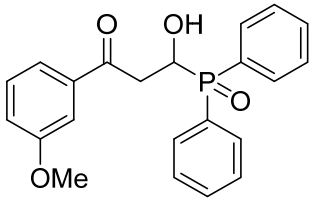


3-(Diphenylphosphoryl)-3-hydroxy-1-(4-(trifluoromethyl)phenyl)propan-1-one (**3i**). White solid (107.1 mg, 85% yield); mp 167-169 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (d, J = 8.1 Hz, 2H), 7.99-7.90 (m, 2H), 7.90-7.81 (m, 4H), 7.64-7.50 (m, 6H), 5.11 (d, J = 8.9 Hz, 1H), 3.41-3.27 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.3

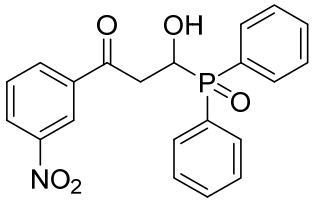
(d, J = 13.9 Hz), 140.3, 133.1, 133.0 (d, J = 32.0 Hz), 132.3, 132.2, 131.7, 131.6 (d, J = 8.7 Hz), 130.7, 129.3, 129.1 (d, J = 11.0 Hz), 128.9 (d, J = 11.1 Hz), 126.1 (q, J = 3.8 Hz), 124.2 (d, J = 272.8 Hz), 66.5 (d, J = 90.8 Hz), 40.7; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.4; ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}F_3O_3P$ 419.1018; Found 419.10220.



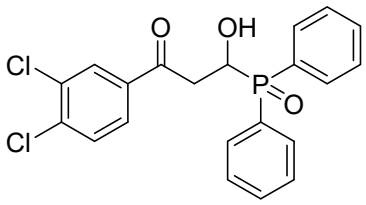
3-(Diphenylphosphoryl)-3-hydroxy-1-(o-tolyl)propan-1-one (**3j**). White solid (91.4 mg, 84% yield); mp 170-172 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02-7.76 (m, 4H), 7.67-7.45 (m, 7H), 7.41 (t, *J* = 7.1 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 6.09 (s, 1H), 5.02 (d, *J* = 7.0 Hz, 1H), 3.19-3.14 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 201.6 (d, *J* = 13.7 Hz), 138.4, 137.5, 132.24, 132.16, 132.0, 131.74, 131.71, 131.6, 131.5, 129.1, 129.0, 128.9, 128.8, 126.3, 66.8 (d, *J* = 90.4 Hz), 43.3 (d, *J* = 6.0 Hz), 20.9; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}O_3P$ 365.1301; Found 365.13016.



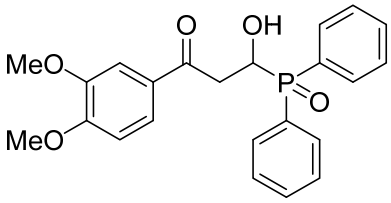
3-(Diphenylphosphoryl)-3-hydroxy-1-(3-methoxyphenyl)propan-1-one (**3k**). White solid (98.5 mg, 86% yield); mp 173-175 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06-7.78 (m, 4H), 7.56 (s, 6H), 7.47-7.34 (m, 3H), 7.24-7.15 (m, 1H), 5.09 (d, *J* = 7.8 Hz, 1H), 3.61 (s, 3H), 3.32-3.18 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.5 (d, *J* = 13.9 Hz), 159.8, 138.6, 132.3, 132.2, 131.6, 131.5, 130.4, 129.1, 129.0, 128.9, 128.8, 121.1, 119.7, 113.0, 66.6 (d, *J* = 90.8 Hz), 55.8, 40.4; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}O_4P$ 381.1250; Found 381.12515.



3-(Diphenylphosphoryl)-3-hydroxy-1-(3-nitrophenyl)propan-1-one (**3l**). Eluent: V_{PET}/V_{EA} = 1:2; White solid (94.4 mg, 80% yield); mp 147-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.37 (d, *J* = 8.2 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.03-7.93 (m, 2H), 7.90-7.80 (m, 2H), 7.63-7.54 (m, 2H), 7.53-7.41 (m, 5H), 5.31-5.20 (m, 1H), 4.58 (s, 1H), 3.59-3.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6 (d, *J* = 13.9 Hz), 148.5, 137.7, 133.8, 132.33, 132.30, 132.27, 132.1 (d, *J* = 8.9 Hz), 131.4 (d, *J* = 9.2 Hz), 129.9, 128.8, 128.7, 128.5, 127.7, 123.1, 67.0 (d, *J* = 89.2 Hz), 39.5 (d, *J* = 5.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}NO_5PNa$ 418.0815; Found 418.08148.

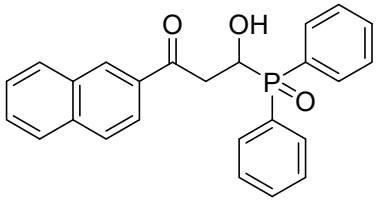


1-(3,4-Dichlorophenyl)-3-(diphenylphosphoryl)-3-hydroxypropan-1-one (**3m**). White solid (100.9 mg, 80% yield); mp 160-162 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (d, *J* = 1.8 Hz, 1H), 7.97-7.89 (m, 2H), 7.88-7.78 (m, 3H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.66-7.42 (m, 6H), 6.07 (s, 1H), 5.06 (d, *J* = 9.0 Hz, 1H), 3.35-3.29 (m, 1H), 3.28-3.22 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.1 (d, *J* = 13.9 Hz), 137.4, 136.5, 132.3, 132.23, 132.19, 131.6, 131.5, 130.4, 129.1, 129.0, 128.9, 128.8, 128.6, 66.6 (d, *J* = 90.1 Hz), 40.5; ^{31}P NMR (162 MHz, DMSO-d_6) δ 34.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{17}Cl_2O_3PNa$ 441.0185; Found 441.01874.

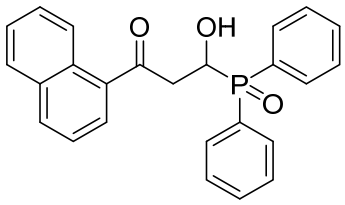


1-(3,4-Dimethoxyphenyl)-3-(diphenylphosphoryl)-3-hydroxypropan-1-one (**3n**). White solid (91.5 mg, 74% yield); mp 171-173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-

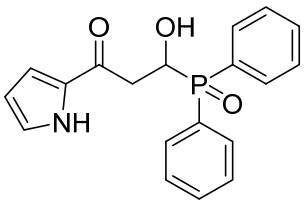
7.92 (m, 2H), 7.92-7.80 (m, 2H), 7.60-7.34 (m, 8H), 6.76 (d, J = 8.4 Hz, 1H), 5.23 (d, J = 11.5 Hz, 1H), 3.85 (d, J = 21.3 Hz, 6H), 3.54-3.44 (m, 1H), 3.34-3.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4 (d, J = 14.0 Hz), 153.7, 149.0, 132.3, 132.2, 132.1, 131.5, 131.4, 129.6, 128.6, 128.50, 128.45, 128.3, 123.4, 110.1, 67.3 (d, J = 90.7 Hz), 56.0, 55.9, 38.4 (d, J = 4.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{23}O_5PNa$ 433.1175; Found 433.11761.



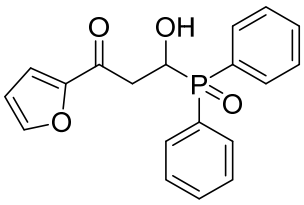
3-(Diphenylphosphoryl)-3-hydroxy-1-(naphthalen-2-yl)propan-1-one (**3o**). Yellow solid (93.4 mg, 78% yield); mp 188-190 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.54 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.04-7.84 (m, 7H), 7.69-7.47 (m, 8H), 5.23 (d, J = 9.2 Hz, 1H), 3.57-3.50 (m, 1H), 3.40-3.33 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.6 (d, J = 13.8 Hz), 135.5, 134.5, 132.5, 132.3, 132.2, 131.6 (d, J = 8.6 Hz), 130.5, 130.1, 129.2, 129.0 (d, J = 9.2 Hz), 128.8 (d, J = 10.1 Hz), 128.1, 127.4, 124.0, 66.7 (d, J = 90.8 Hz), 40.2; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}O_3P$ 401.1301; Found 401.13034.



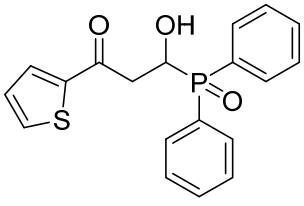
3-(Diphenylphosphoryl)-3-hydroxy-1-(naphthalen-1-yl)propan-1-one (**3p**). White solid (96.5 mg, 80% yield); mp 185-187 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.43 (d, J = 6.7 Hz, 1H), 8.12 (d, J = 7.9 Hz, 1H), 7.98 (s, 1H), 7.96-7.90 (m, 2H), 7.89-7.82 (m, 2H), 7.70-7.37 (m, 9H), 6.19 (s, 1H), 5.13 (s, 1H), 3.39 (s, 1H), 3.18 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 201.7 (d, J = 13.9 Hz), 136.1, 133.9, 132.9, 132.29, 132.26, 132.2, 131.6 (d, J = 8.7 Hz), 129.8, 129.2, 129.0, 128.93, 128.87, 128.8, 128.5, 128.1, 126.9, 125.9, 125.3, 67.0 (d, J = 90.1 Hz), 43.8 (d, J = 6.1 Hz); ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}O_3P$ 401.1301; Found 401.13049.



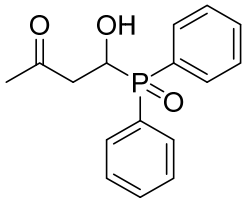
3-(Diphenylphosphoryl)-3-hydroxy-1-(1H-pyrrol-2-yl)propan-1-one (**3q**). White solid (77.7 mg, 76% yield); mp 171-173 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.88 (s, 1H), 8.03-7.90 (m, 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.66-7.44 (m, 6H), 7.10 (s, 1H), 6.83 (s, 1H), 6.24-6.11 (m, 1H), 5.10 (d, J = 10.0 Hz, 1H), 3.21-3.07 (m, 1H), 2.99-2.86 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 186.7 (d, J = 14.3 Hz), 133.2, 132.3, 132.24, 132.16, 131.9, 131.6 (d, J = 8.6 Hz), 131.0, 129.1 (d, J = 10.9 Hz), 128.9 (d, J = 11.0 Hz), 126.3, 117.5, 110.4, 66.9 (d, J = 90.7 Hz), 39.6; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.8; HRMS (ESI-TOF) m/z: [M + Na]$^{+}$ Calcd for $C_{19}H_{18}NO_3PNa$ 362.0917; Found 362.09177.



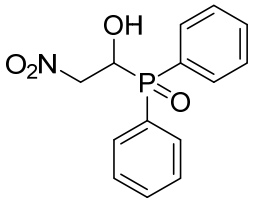
3-(Diphenylphosphoryl)-1-(furan-2-yl)-3-hydroxypropan-1-one (**3r**). Eluent: V_{PET}/V_{EA} = 1:2; White solid (69.1 mg, 68% yield); mp 169-171 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02-7.95 (m, 1H), 7.95-7.88 (m, 2H), 7.88-7.80 (m, 2H), 7.63-7.59 (m, 1H), 7.58-7.52 (m, 4H), 7.36 (d, J = 3.5 Hz, 1H), 6.79-6.58 (m, 1H), 6.19-5.98 (m, 1H), 5.06 (t, J = 8.5 Hz, 1H), 3.22-3.10 (m, 1H), 3.04-2.92 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 185.9 (d, J = 14.4 Hz), 152.5 (d, J = 2.1 Hz), 148.3, 132.3 (d, J = 2.6 Hz), 132.2, 132.1, 131.5 (d, J = 8.6 Hz), 129.1, 129.0, 128.9, 128.8, 119.2, 113.1, 66.4 (d, J = 90.8 Hz), 40.1; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.4; HRMS (ESI-TOF) m/z: [M + Na]$^{+}$ Calcd for $C_{19}H_{17}O_4PNa$ 363.0757; Found 363.07520.



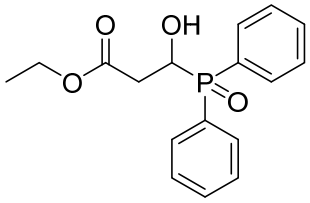
3-(Diphenylphosphoryl)-3-hydroxy-1-(thiophen-2-yl)propan-1-one (**3s**). White solid (84.8 mg, 79% yield); mp 176-178 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00-7.92 (m, 3H), 7.92-7.84 (m, 2H), 7.80 (d, J = 3.4 Hz, 1H), 7.68-7.49 (m, 6H), 7.26-7.16 (m, 1H), 5.11 (d, J = 9.7 Hz, 1H), 3.35-3.20 (m, 1H), 3.17-3.09 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 190.5 (d, J = 14.3 Hz), 144.2 (d, J = 2.1 Hz), 135.6, 134.1, 132.3, 132.2, 131.6, 131.5, 129.22, 129.15, 129.04, 128.95, 128.8, 66.8 (d, J = 90.6 Hz), 40.9 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.5; HRMS (ESI-TOF) m/z: [M + H]$^{+}$ Calcd for $C_{19}H_{18}O_3PS$ 357.0709; Found 357.07104.



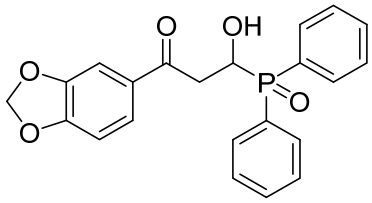
4-(Diphenylphosphoryl)-4-hydroxybutan-2-one (**3t**). Eluent: V_{CH2Cl2}/V_{MeOH} =50:1; White solid (52.2 mg, 60% yield); mp 137-139 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.88 (m, 2H), 7.88-7.79 (m, 2H), 7.59-7.41 (m, 6H), 5.02 (d, J = 10.2 Hz, 1H), 3.64 (s, 1H), 2.97 (d, J = 17.5 Hz, 1H), 2.85-2.71 (m, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7 (d, J = 13.8 Hz), 132.2, 132.1, 131.5, 131.4, 128.7, 128.6, 128.5, 128.4, 66.8 (d, J = 89.7 Hz), 43.6, 30.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.8; HRMS (ESI-TOF) m/z: [M + H]$^{+}$ Calcd for $C_{16}H_{18}O_3P$ 289.0988; Found 289.09897.



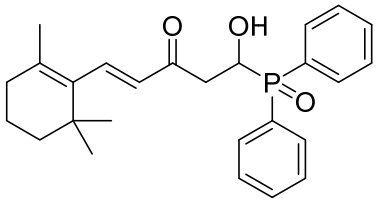
(1-Hydroxy-2-nitroethyl)diphenylphosphine oxide (3u). Eluent: V_{PET}/V_{EA} = 1:2; White solid (61.0 mg, 70% yield); mp 128-130 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.84 (m, 2H), 7.83-7.76 (m, 2H), 7.65-7.53 (m, 2H), 7.53-7.42 (m, 4H), 5.32-5.20 (m, 1H), 4.71-4.62 (m, 1H), 4.60-4.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.81, 132.79, 132.7, 132.0 (d, J = 9.1 Hz), 131.4 (d, J = 9.4 Hz), 129.0, 128.9, 128.8, 76.5 (d, J = 13.1 Hz), 68.5 (d, J = 84.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.1; HRMS (ESI-TOF) m/z: [M + H]$^{+}$ Calcd for $C_{14}H_{15}NO_4P$ 292.0733; Found 292.07349.



Ethyl 3-(diphenylphosphoryl)-3-hydroxypropanoate (**3v**). Eluent: V_{CH2Cl2}/V_{MeOH} =100:1; White solid (62.4 mg, 65% yield); mp 134-136 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.89 (m, 2H), 7.89-7.81 (m, 2H), 7.59-7.50 (m, 2H), 7.50-7.41 (m, 4H), 5.09-4.79 (m, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.94-2.79 (m, 1H), 2.70-2.54 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (d, *J* = 18.7 Hz), 132.2, 132.1, 131.6, 131.5, 131.3, 128.6, 128.5, 128.4, 67.3 (d, *J* = 88.8 Hz), 61.1, 35.7 (d, *J* = 5.4 Hz), 14.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{20}O_4P$ 319.1094; Found 319.10974.

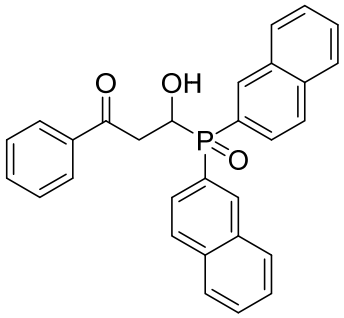


1-(Benzo[d][1,3]dioxol-5-yl)-3-(diphenylphosphoryl)-3-hydroxypropan-1-one (**3w**). White solid (92.6 mg, 78% yield); mp 168-170 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03-7.92 (m, 2H), 7.92-7.81 (m, 2H), 7.70-7.41 (m, 7H), 7.36 (d, *J* = 1.4 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.11 (s, 2H), 5.13 (d, *J* = 9.7 Hz, 1H), 3.65 (s, 1H), 3.36-3.23 (m, 1H), 3.22-3.12 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 195.6 (d, *J* = 13.9 Hz), 152.0, 148.3, 132.29, 132.26, 132.2, 131.9, 131.6 (d, *J* = 8.5 Hz), 129.1, 129.0, 128.9, 128.8, 125.1, 108.4, 107.8, 102.5, 66.7 (d, *J* = 90.7 Hz), 39.9; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}O_5P$ 395.1043; Found 395.10461.

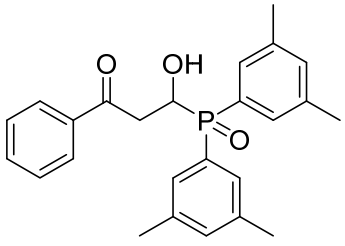


(E)-5-(Diphenylphosphoryl)-5-hydroxy-1-(2,6,6-trimethylcyclohex-1-en-1-yl)pent-1-en-3-one (**3x**). Eluent: V_{PET}/V_{EA} = 1:1; Yellow liquid (86.5 mg, 68% yield);

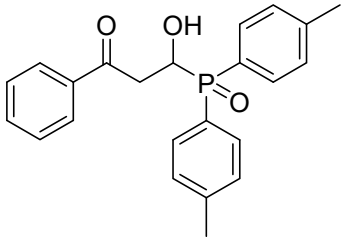
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.93 (m, 2H), 7.92-7.84 (m, 2H), 7.58-7.47 (m, 4H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.34 (d, *J* = 16.3 Hz, 1H), 6.12 (d, *J* = 16.3 Hz, 1H), 5.18-5.05 (m, 1H), 4.71 (s, 1H), 3.31-3.10 (m, 1H), 2.94-2.82 (m, 1H), 2.05 (t, *J* = 6.2 Hz, 2H), 1.72 (s, 3H), 1.64-1.54 (m, 2H), 1.49-1.39 (m, 2H), 1.03 (d, *J* = 2.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2 (d, *J* = 13.7 Hz), 143.9, 138.0, 136.0, 132.3, 132.21, 132.16, 131.5 (d, *J* = 9.2 Hz), 129.7, 128.6, 128.53, 128.49, 128.4, 67.4 (d, *J* = 90.8 Hz), 40.2 (d, *J* = 3.3 Hz), 39.8, 34.0, 33.8, 28.8, 28.7, 21.8, 18.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{32}O_3P$ 423.2084; Found 423.20865.



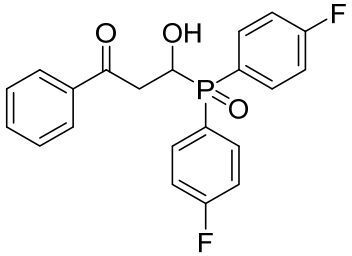
3-(Di(naphthalen-2-yl)phosphoryl)-3-hydroxy-1-phenylpropan-1-one (**3aa**). White solid (91.5 mg, 68% yield); mp 151-153 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.78-8.50 (m, 2H), 8.18-8.01 (m, 5H), 8.00-7.90 (m, 3H), 7.87 (d, *J* = 7.4 Hz, 2H), 7.70-7.50 (m, 5H), 7.45 (t, *J* = 7.5 Hz, 2H), 6.22 (s, 1H), 5.37 (d, *J* = 8.4 Hz, 1H), 3.41-3.25 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.7 (d, *J* = 13.9 Hz), 137.1, 134.8 (d, *J* = 2.2 Hz), 134.7 (d, *J* = 2.2 Hz), 134.0 (d, *J* = 7.9 Hz), 133.7, 133.2 (d, *J* = 8.2 Hz), 132.6, 132.5, 130.6, 129.7, 129.3 (d, *J* = 4.3 Hz), 129.1, 128.8, 128.69, 128.66, 128.50, 128.47, 128.40, 128.36, 128.2 (d, *J* = 2.7 Hz), 127.5, 127.44, 127.37, 126.8 (d, *J* = 9.5 Hz), 66.6 (d, *J* = 91.0 Hz), 40.3; ^{31}P NMR (162 MHz, DMSO-d_6) δ 30.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{24}O_3P$ 451.1458; Found 451.14581.



3-(Bis(3,5-dimethylphenyl)phosphoryl)-3-hydroxy-1-phenylpropan-1-one (**3ab**). White solid (107.6 mg, 88% yield); mp 145-147 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (d, J = 7.5 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.58-7.38 (m, 6H), 7.18 (d, J = 16.0 Hz, 2H), 5.99 (s, 1H), 5.08 (d, J = 9.3 Hz, 1H), 3.36-3.25 (m, 1H), 3.24-3.15 (m, 1H), 2.30 (d, J = 15.9 Hz, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.8 (d, J = 13.6 Hz), 138.3, 138.2, 138.0, 137.9, 137.2, 133.7, 133.6, 129.7, 129.6, 129.2, 129.0, 128.9, 128.5, 66.5 (d, J = 90.2 Hz), 21.4, 21.3; ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{27}O_3PNa$ 429.1590; Found 429.15872.

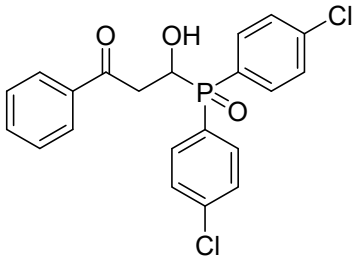


3-(Di-p-tolylphosphoryl)-3-hydroxy-1-phenylpropan-1-one (**3ac**). White solid (94.5 mg, 83% yield); mp 143-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.78 (m, 4H), 7.78-7.68 (m, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.34 (t, J = 7.6 Hz, 2H), 7.27-7.14 (m, 4H), 5.20 (d, J = 11.1 Hz, 1H), 4.26 (s, 1H), 3.57-3.43 (m, 1H), 3.39-3.26 (m, 1H), 2.35 (d, J = 11.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8 (d, J = 14.0 Hz), 142.5, 142.43, 142.40, 136.5, 133.4, 132.2 (d, J = 9.1 Hz), 131.5 (d, J = 9.3 Hz), 129.4, 129.2, 129.1, 128.5, 128.3, 67.0 (d, J = 90.8 Hz), 39.1 (d, J = 4.5 Hz), 21.6, 21.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}O_3P$ 379.1458; Found 379.14575.

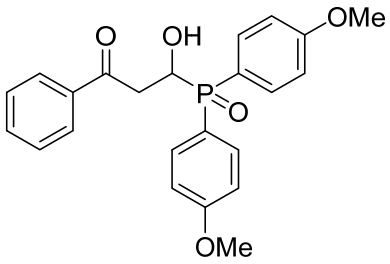


3-(Bis(4-fluorophenyl)phosphoryl)-3-hydroxy-1-phenylpropan-1-one (**3ad**). Eluent: V_{PET}/V_{EA} = 1:1; Yellow solid (80.6 mg, 70% yield); mp 141-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.95-7.80 (m, 4H), 7.56 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.25-7.08 (m, 4H), 5.16 (d, J = 9.4 Hz, 1H), 3.65 (d, J = 17.5 Hz, 1H),

3.28-3.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0 (d, *J* = 12.7 Hz), 166.6 (d, *J* = 15.3 Hz), 164.0 (d, *J* = 15.5 Hz), 136.2, 134.8 (t, *J* = 6.7 Hz), 134.0 (t, *J* = 6.6 Hz), 133.8, 128.7, 128.2, 116.3-115.7 (m), 67.4 (d, *J* = 90.7 Hz), 38.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}F_2O_3P$ 387.0956; Found 387.09595.



3-(Bis(4-chlorophenyl)phosphoryl)-3-hydroxy-1-phenylpropan-1-one (**3ae**). Eluent: V_{PET}/V_{EA} = 3:2; White solid (88.8 mg, 71% yield); mp 154-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-7.69 (m, 6H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.50-7.33 (m, 6H), 5.19 (d, *J* = 7.7 Hz, 1H), 3.59 (d, *J* = 15.6 Hz, 1H), 3.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6 (d, *J* = 6.0 Hz), 139.0 (d, *J* = 15.6 Hz), 136.2, 133.8, 133.7, 132.9, 129.0, 128.7, 128.2, 67.2 (d, *J* = 89.5 Hz), 38.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}Cl_2O_3P$ 419.0365; Found 419.03687.

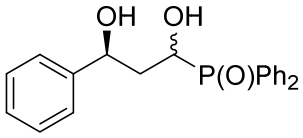


3-(Bis(4-methoxyphenyl)phosphoryl)-3-hydroxy-1-phenylpropan-1-one (**3af**). Eluent: V_{PET}/V_{EA} = 1:2; White solid (84.1 mg, 68% yield); mp 114-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.81 (m, 4H), 7.81-7.73 (m, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.03-6.86 (m, 4H), 5.22-5.07 (m, 1H), 4.05 (s, 1H), 3.84-3.77 (m, 6H), 3.62-3.48 (m, 1H), 3.38-3.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1 (d, *J* = 15.3 Hz), 162.6 (d, *J* = 2.8 Hz), 162.5 (d, *J* = 2.6 Hz), 136.5, 134.1, 134.0, 133.5, 133.4, 133.3, 128.5, 128.3, 114.2, 114.1, 114.0, 67.3 (d, *J* = 90.9 Hz), 55.3, 39.1 (d, *J*

= 4.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}O_5P$ 411.1356; Found 411.13586.

Procedure for the synthesis of 4

Compound **3a** (0.2 mmol) was dissolved in MeOH (2 mL) in a 25 mL round-bottom flask. To this solution was slowly added $NaBH_4$ (0.6 mmol) in 3 mins. The mixture was stirred at room temperature for 12 h. The pH was then adjusted to 3 with 10% (m/m) aqueous HCl solution. The mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic phase was successively washed with saturated sodium bicarbonate solution and brine for three times and dried with anhydrous Na_2SO_4. the mixture was transferred into the round bottom flask, after removing the solvent under reduced pressure, the resulting residue was recrystallized with ethyl acetate/CH_2Cl_2 to afford **4**.

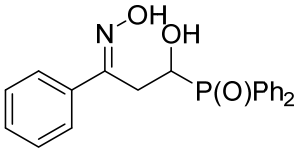


(1,3-Dihydroxy-3-phenylpropyl)diphenylphosphine oxide (**4**). White solid (64.7 mg, 92% yield); mp 152-154 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91-7.79 (m, 3H), 7.73-7.66 (m, 1H), 7.58-7.45 (m, 6H), 7.35-7.26 (m, 4H), 7.25-7.15 (m, 1H), 5.97 (s, 1H), 5.48 (s, 1H), 4.86-4.79 (m, 1H), 4.19 (s, 1H), 2.00-1.92 (m, 1H), 1.88-1.64 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.9, 145.3, 132.2, 132.13, 132.10, 132.0, 131.5, 131.4, 129.1, 128.99, 128.95, 128.9, 128.8, 128.7, 128.5 (d, J = 2.9 Hz), 127.5, 127.1, 126.6, 125.9, 70.6 (d, J = 12.7 Hz), 68.0 (d, J = 12.1 Hz), 67.1 (d, J = 12.6 Hz), 66.1, 41.4 (d, J = 4.2 Hz), 41.3 (d, J = 3.8 Hz); ^{31}P NMR (162 MHz, DMSO-d_6) δ 29.8, 29.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}O_3P$ 353.1301; Found 353.13043.

Procedure for the synthesis of 5

In a 15 mL reaction tube was equipped with **3a** (0.2 mmol), $NH_2OH{\cdot}HCl$ (0.6 mmol) and MeOH (2 mL). The mixture was then stirred at room temperature for 12 h. Upon completion (TLC), the reaction mixture was diluted with ethyl acetate, and transferred into a round bottom flask. After removing the solvent atreduced temperature,

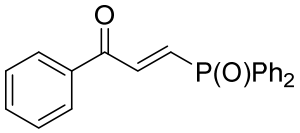
the resulting mixture was purified by silica gel column chromatography with the election of mixed CH_2Cl_2 and MeOH (v: v=50:1).



(E)-(1-Hydroxy-3-(hydroxyimino)-3-phenylpropyl)diphenylphosphine oxide (**5**). Eluent: V_{CH2Cl2}/V_{MeOH}=50:1; White solid (60.9 mg, 83% yield); mp 142-144 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.37 (s, 1H), 7.95-7.86 (m, 2H), 7.85-7.77 (m, 2H), 7.61-7.55 (m, 5H), 7.54-7.49 (m, 3H), 7.36-7.30 (m, 3H), 5.98 (t, *J* = 8.1 Hz, 1H), 4.90 (t, *J* = 9.3 Hz, 1H), 3.16-3.07 (m, 1H), 2.93-2.81 (m, 1H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 154.7 (d, *J* = 12.8 Hz), 137.3, 133.4, 132.2, 132.1, 131.6, 131.5, 129.0, 128.9, 128.9, 128.8, 128.6, 126.8, 67.1 (d, *J* = 88.2 Hz), 28.6 (d, *J* = 6.4 Hz); ^{31}P NMR (162 MHz, DMSO-*d*$_6$) δ 29.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}NO_3PNa$ 388.1073; Found 388.10754.

Procedure for the synthesis of 6

In a 15 mL reaction tube was equipped with **3a** (0.2 mmol), Et_3N (0.6 mmol), $(CF_3CO)_2O$ (0.4 mmol) and CH_2Cl_2 (2 mL). The mixture was then stirred at room temperature for 12 h. Upon completion (TLC), the mixture was poured into cold water (10 mL), extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was dried over $NaSO_4$, filtered. The solvent was removed under vacuo and the residue was purified by flash chromatography (petroleum/ethyl acetate = 2/1), affording **6**.



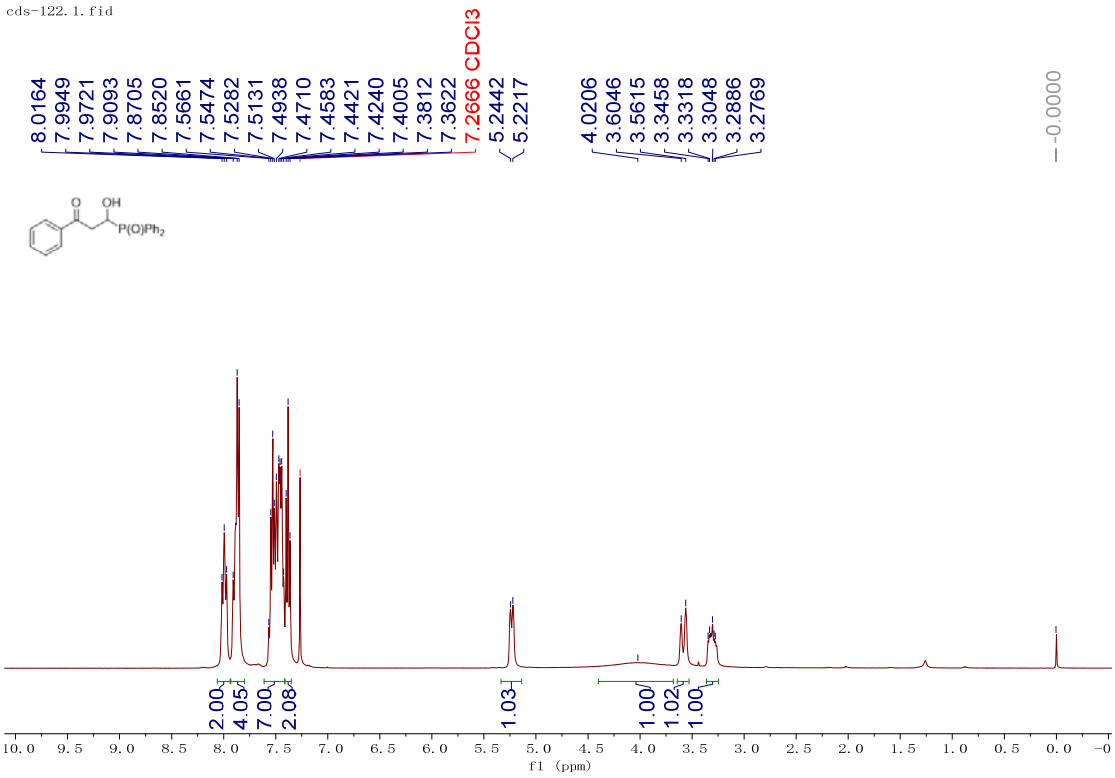
(E)-3-(Diphenylphosphoryl)-1-phenylprop-2-en-1-one (**6**). Eluent: V_{EA}/V_{PE}=1:2; White solid (56.7 mg, 85% yield); mp 109-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.02 (m, 3H), 7.82-7.72 (m, 4H), 7.71-7.63 (m, 1H), 7.63-7.55 (m, 3H), 7.55-7.45 (m,

6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2 (d, J = 16.6 Hz), 139.4, 136.4, 133.9, 132.4, 131.4, 131.3, 129.1, 129.0, 128.9, 128.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.5.

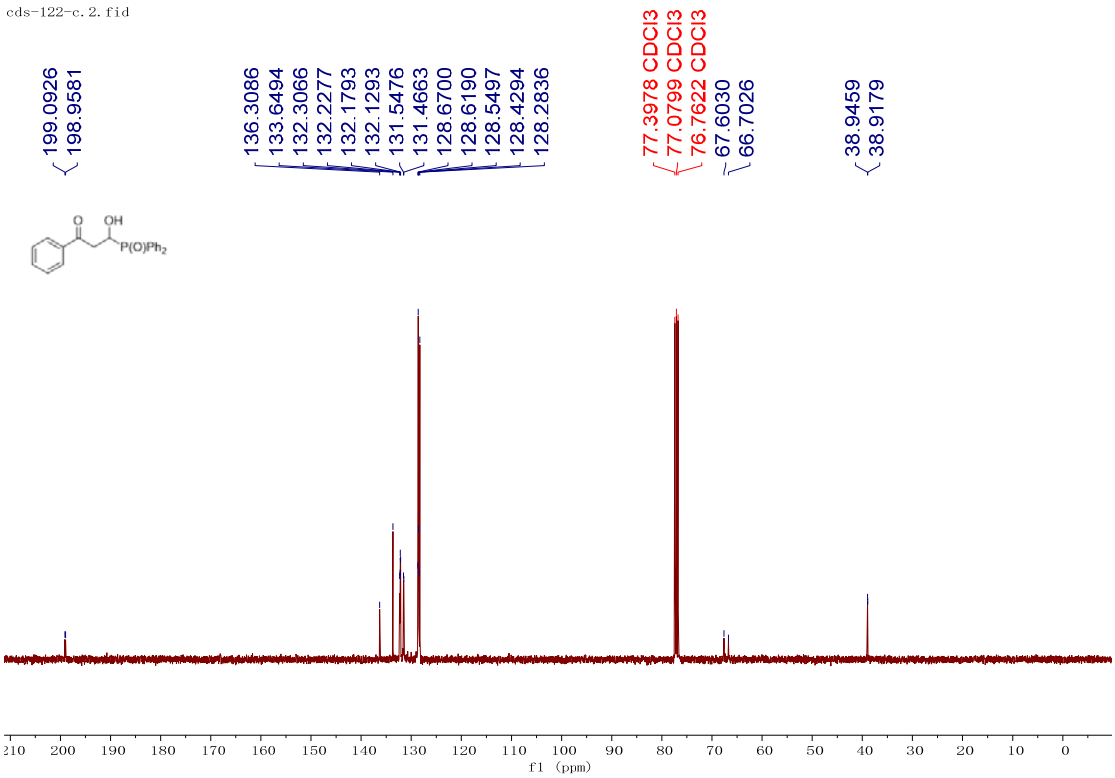
Refernces

1. (a) H. Guo, T. Luo and J.-P. Wan, *Org. Lett*., 2022, **24**, 228-233. (b) J. Ying, T. Liu, Y. Liu and J.-P. Wan, *Org. Lett.,* 2022, **24**, 2404-2408.

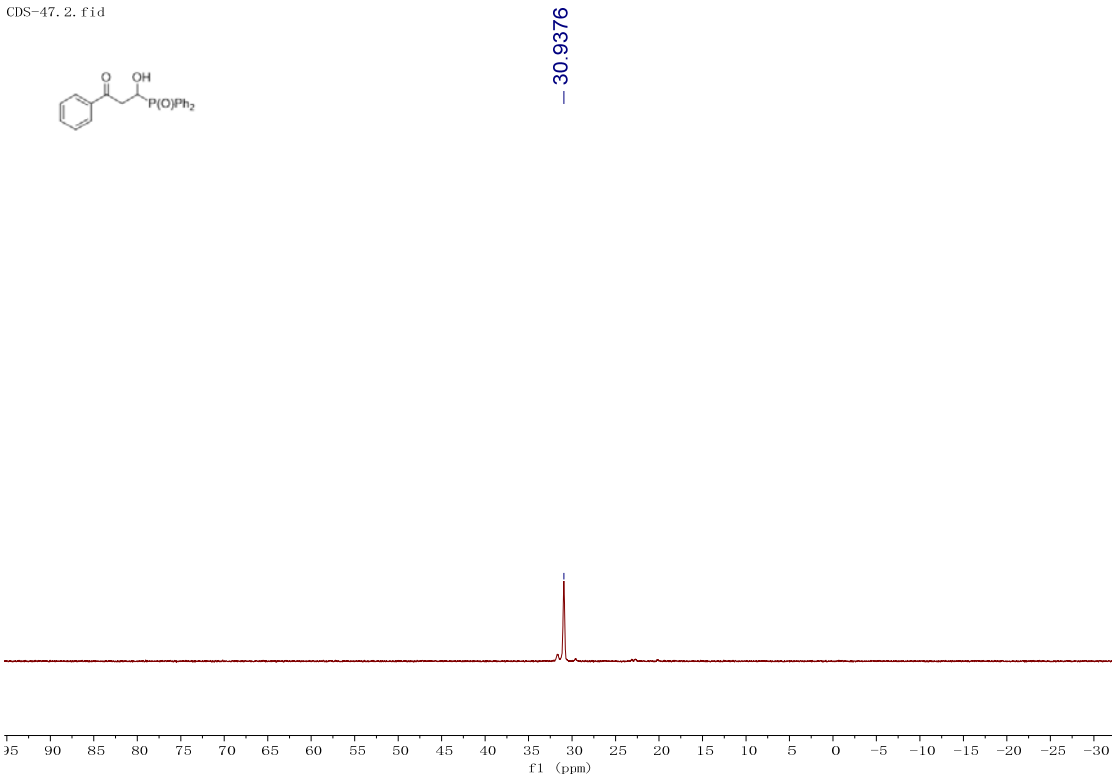
NMR spectra of all products



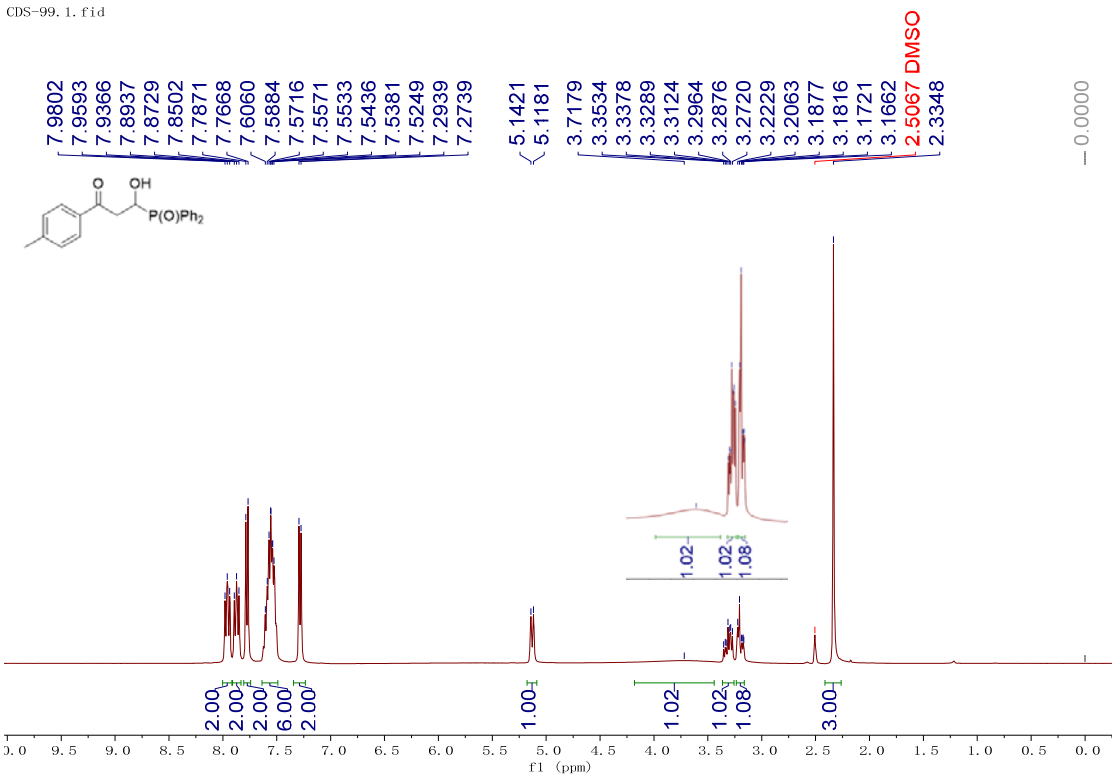
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



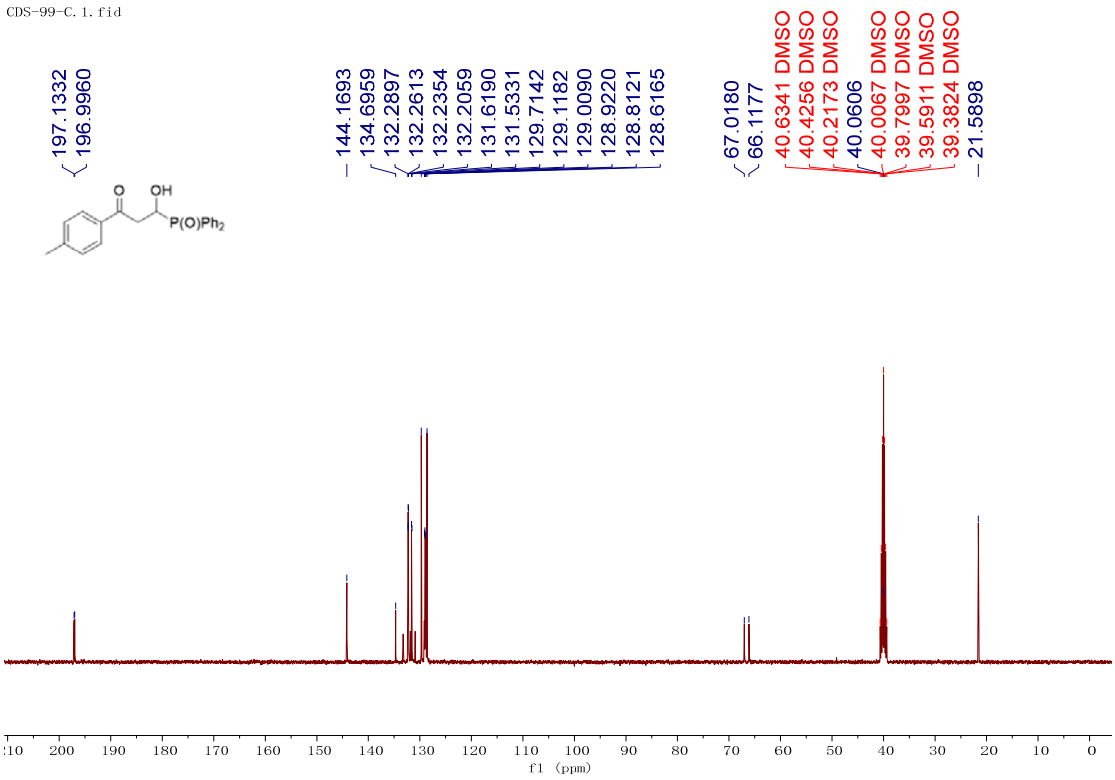
^{13}C NMR spectrum of **3a** (100 MHz, $CDCl_3$)



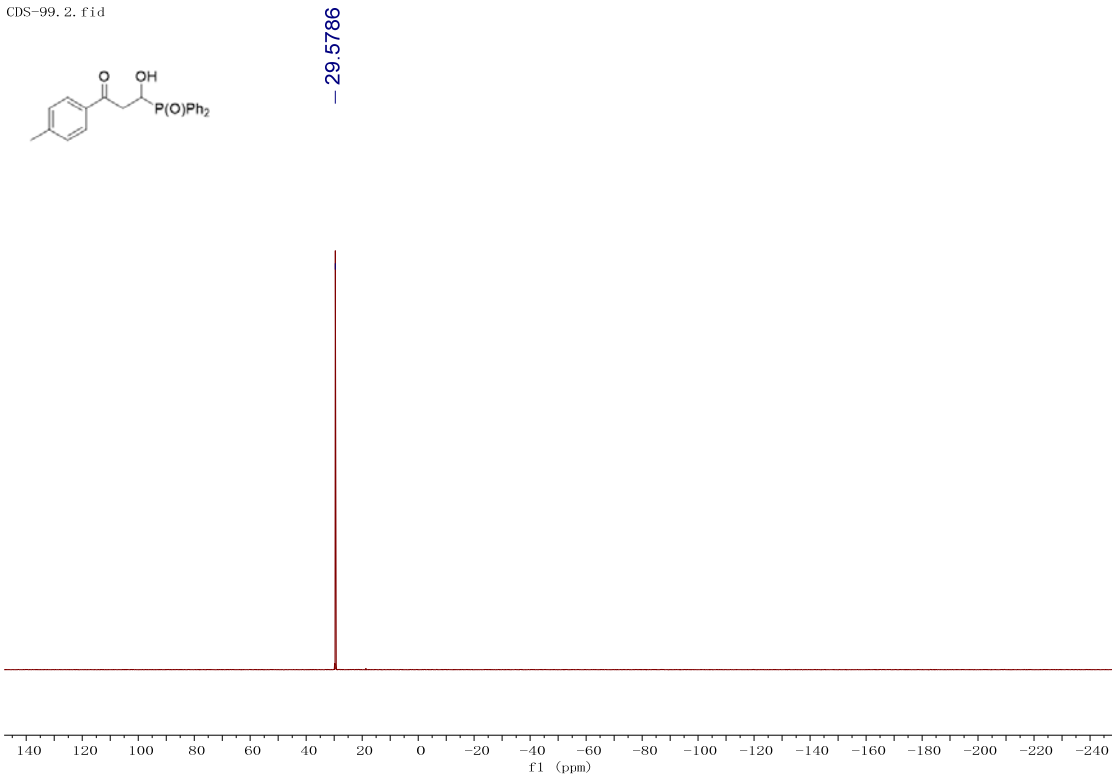
^{31}P NMR spectrum of **3a** (162 MHz, $CDCl_3$)



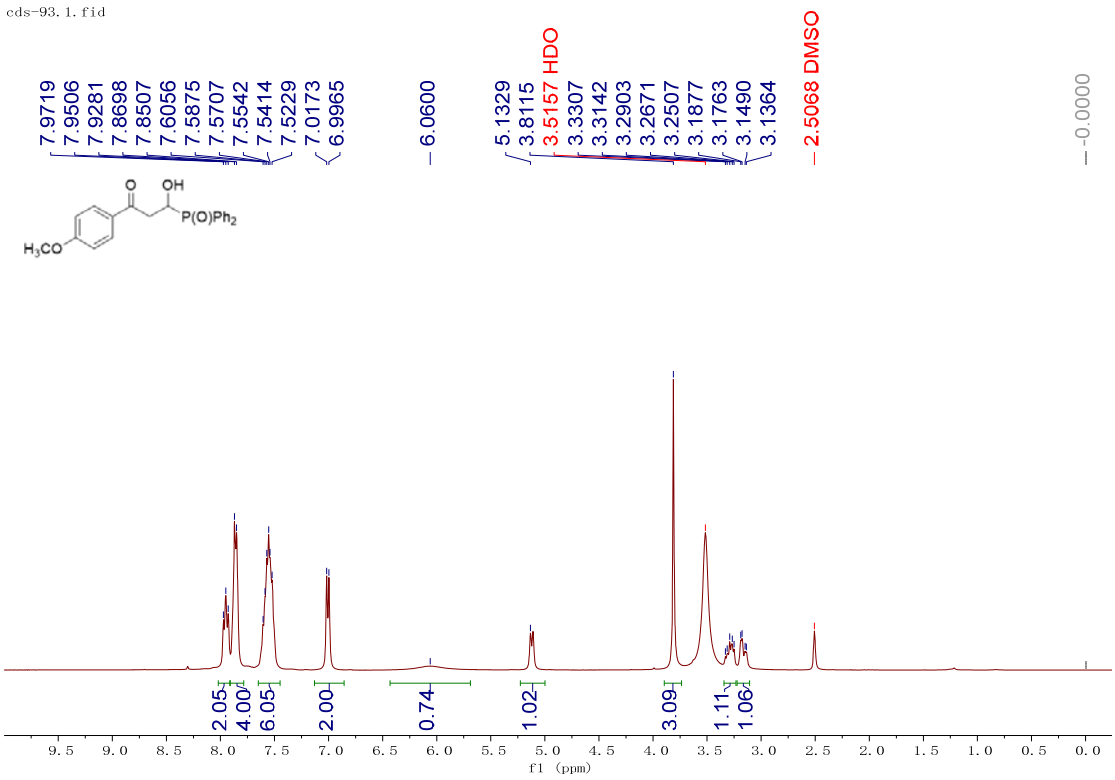
^{1}H NMR spectrum of **3b** (400 MHz, DMSO-d_6)



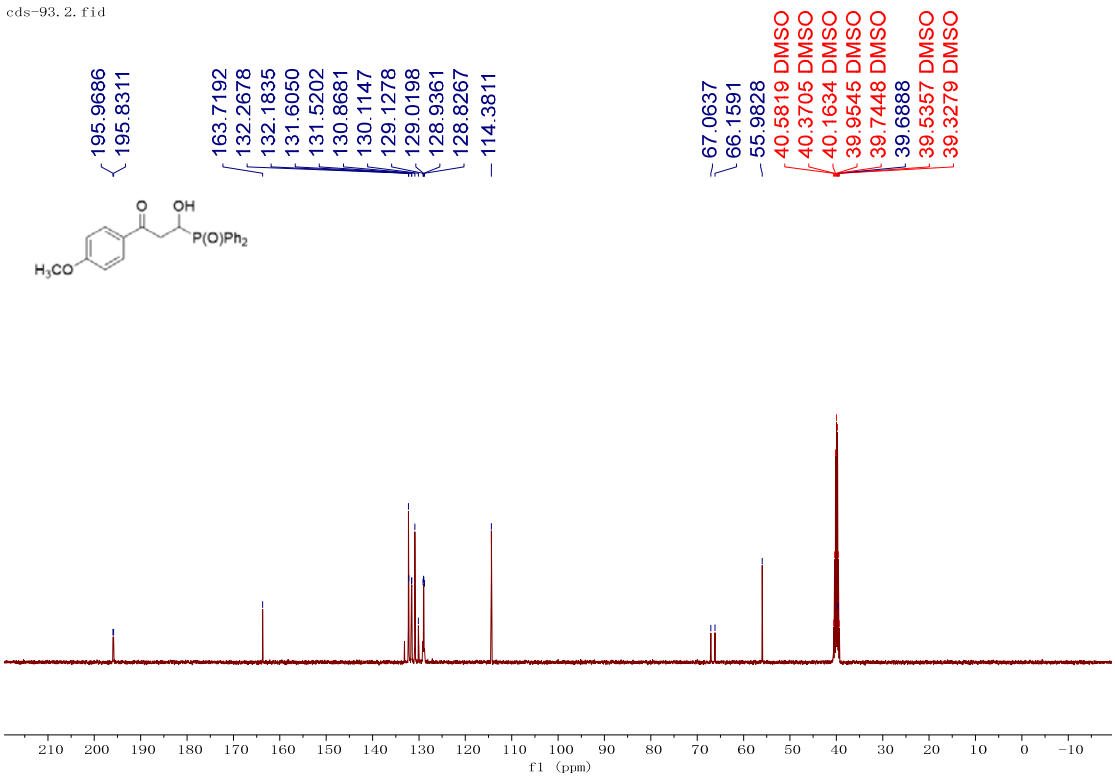
^{13}C NMR spectrum of **3b** (100 MHz, DMSO-d_6)



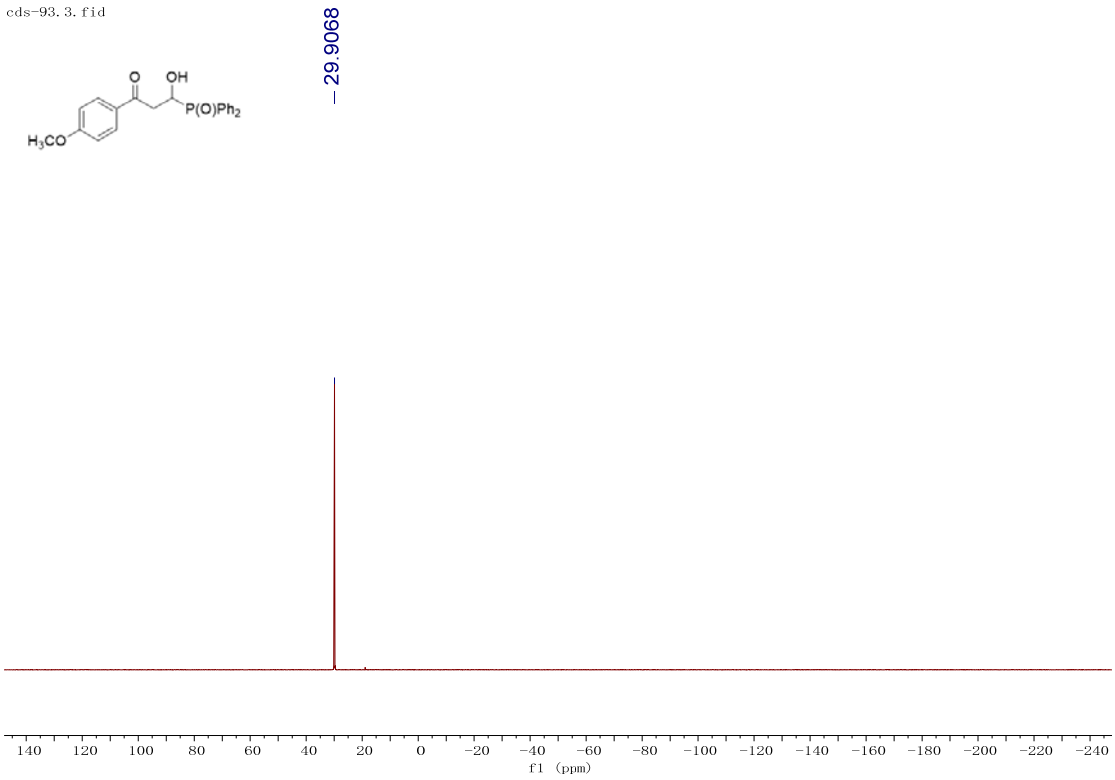
^{31}P NMR spectrum of **3b** (162 MHz, DMSO-d_6)



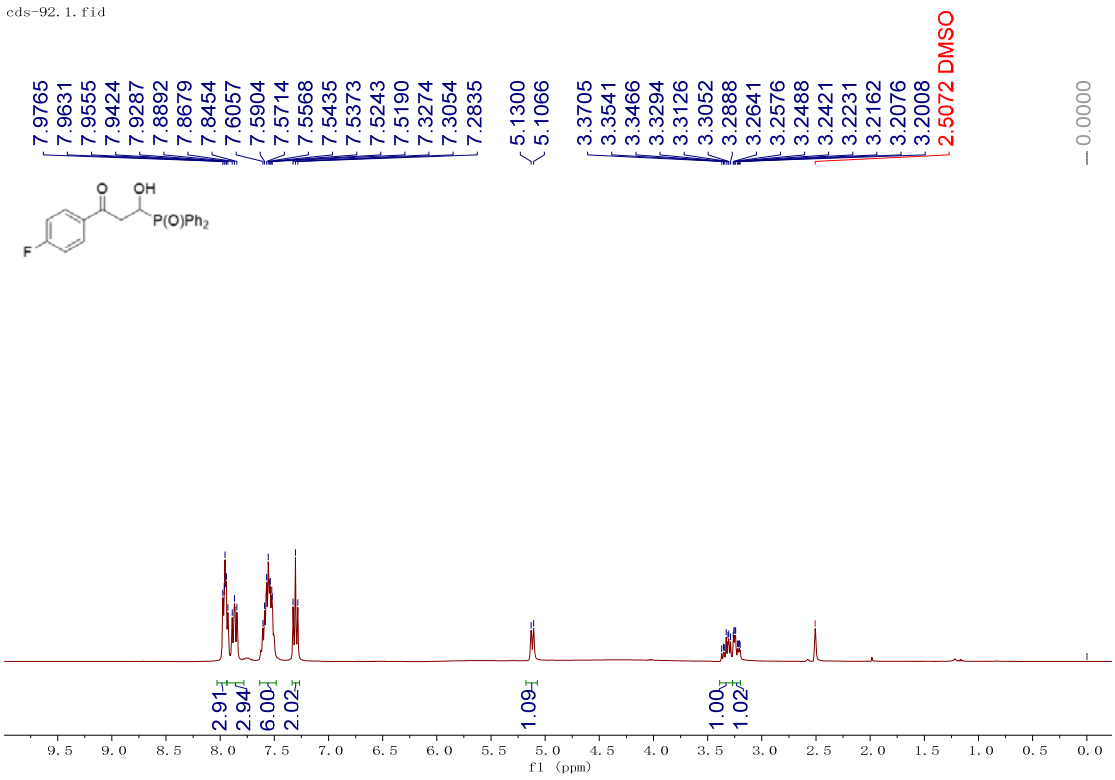
^{1}H NMR spectrum of **3c** (400 MHz, DMSO-d_6)



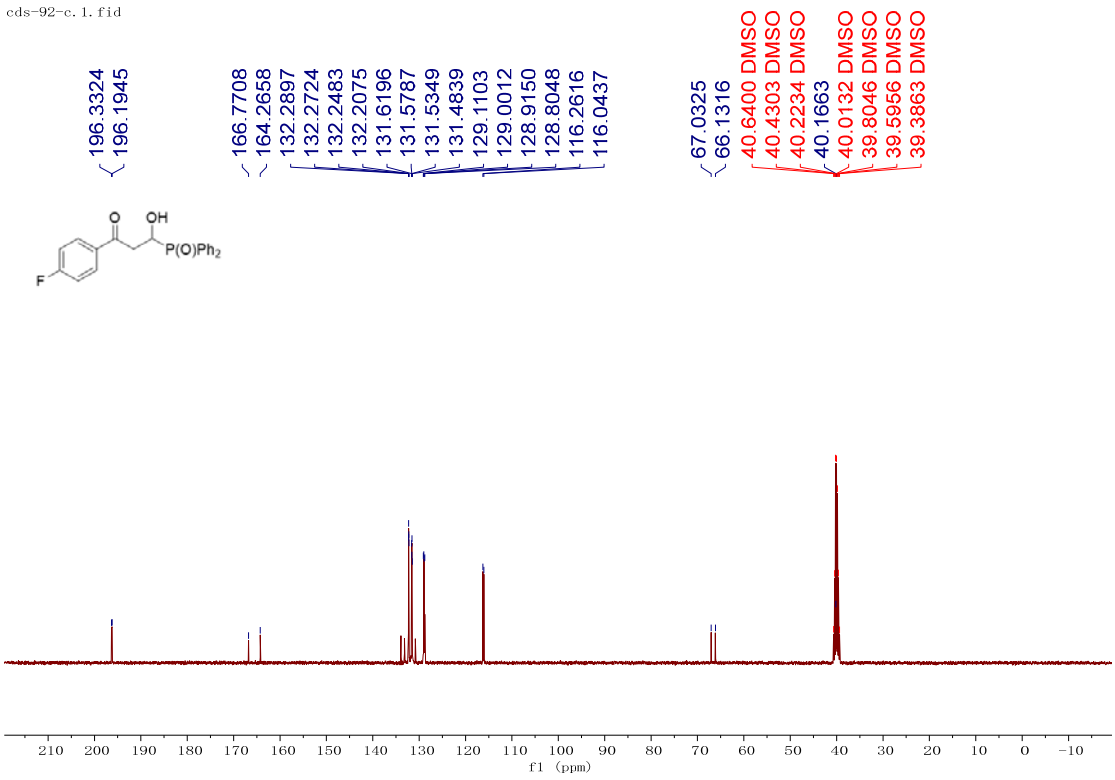
^{13}C NMR spectrum of **3c** (100 MHz, DMSO-d_6)



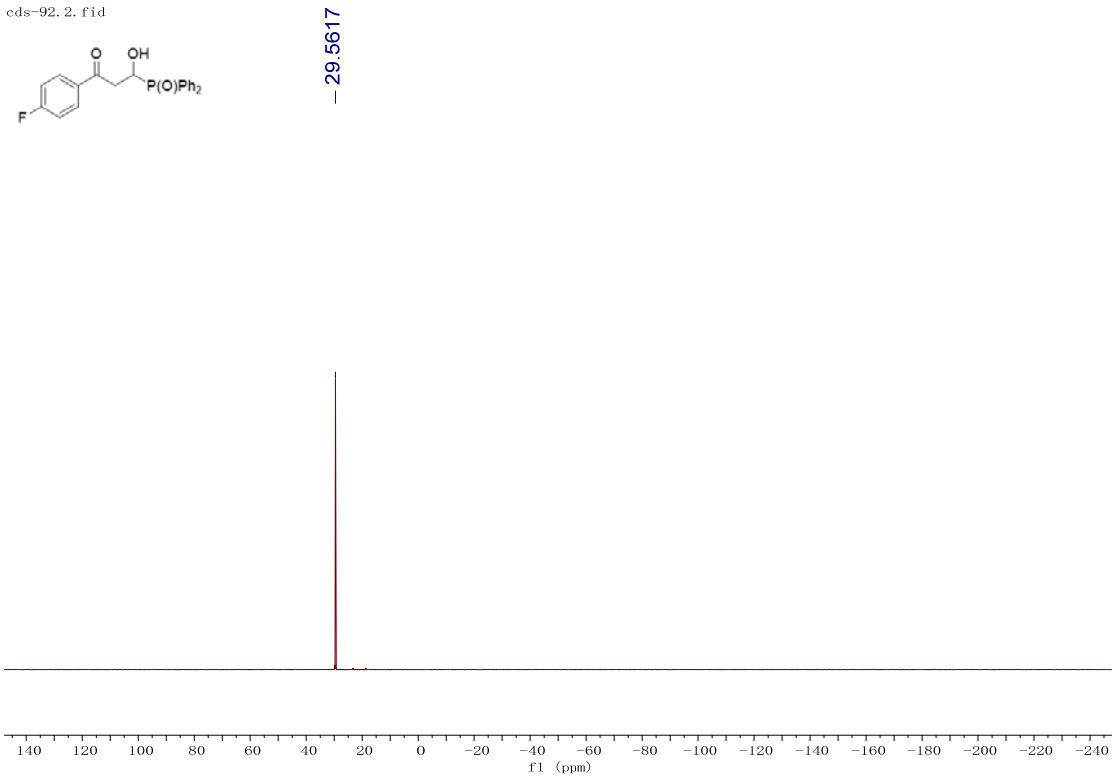
^{31}P NMR spectrum of **3c** (162 MHz, DMSO-d_6)



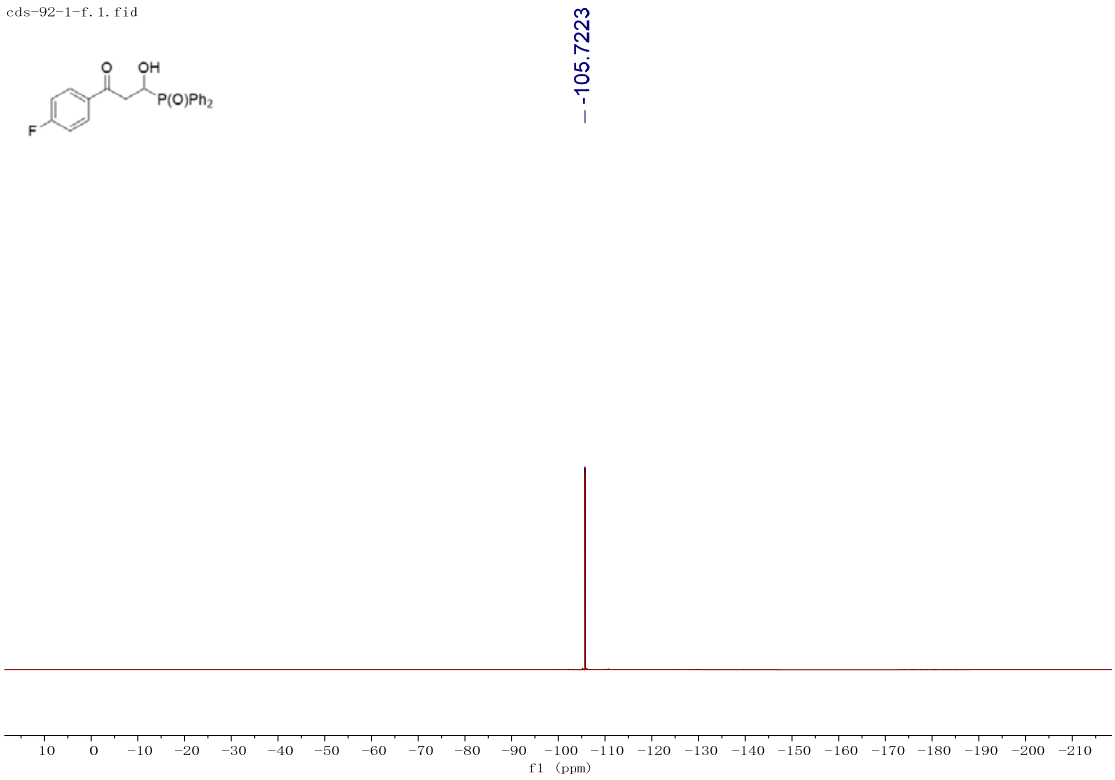
^{1}H NMR spectrum of **3d** (400 MHz, DMSO-d_6)



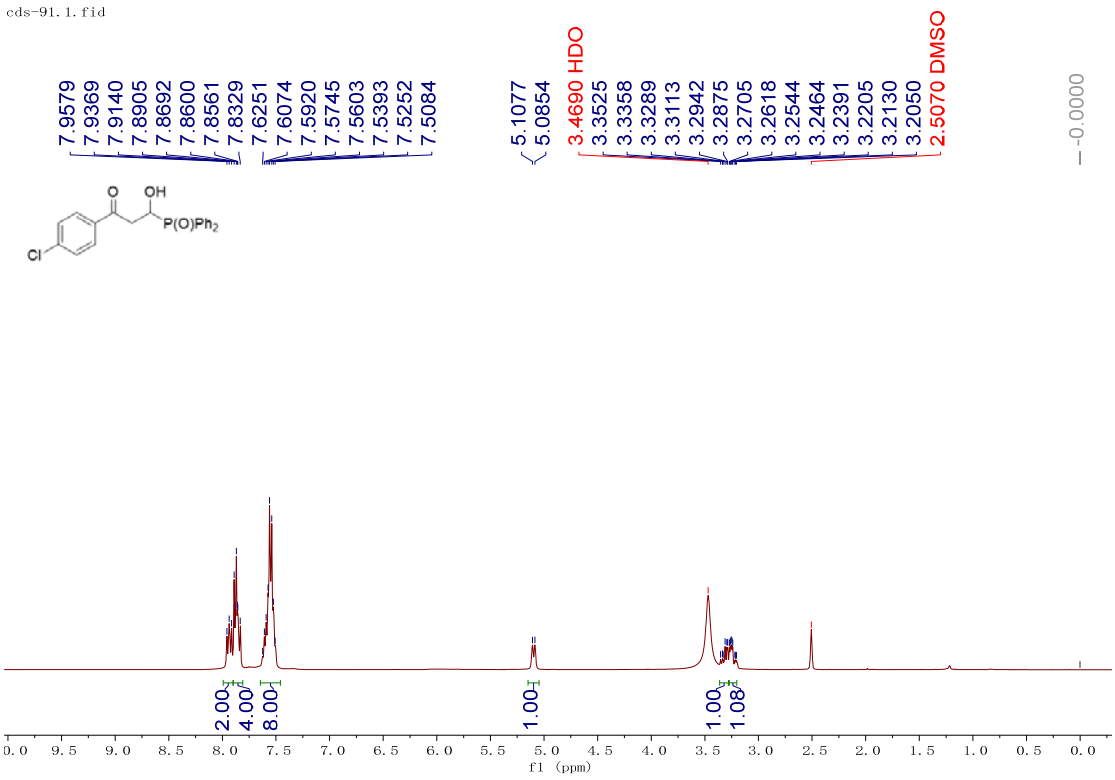
^{13}C NMR spectrum of **3d** (100 MHz, DMSO-d_6)



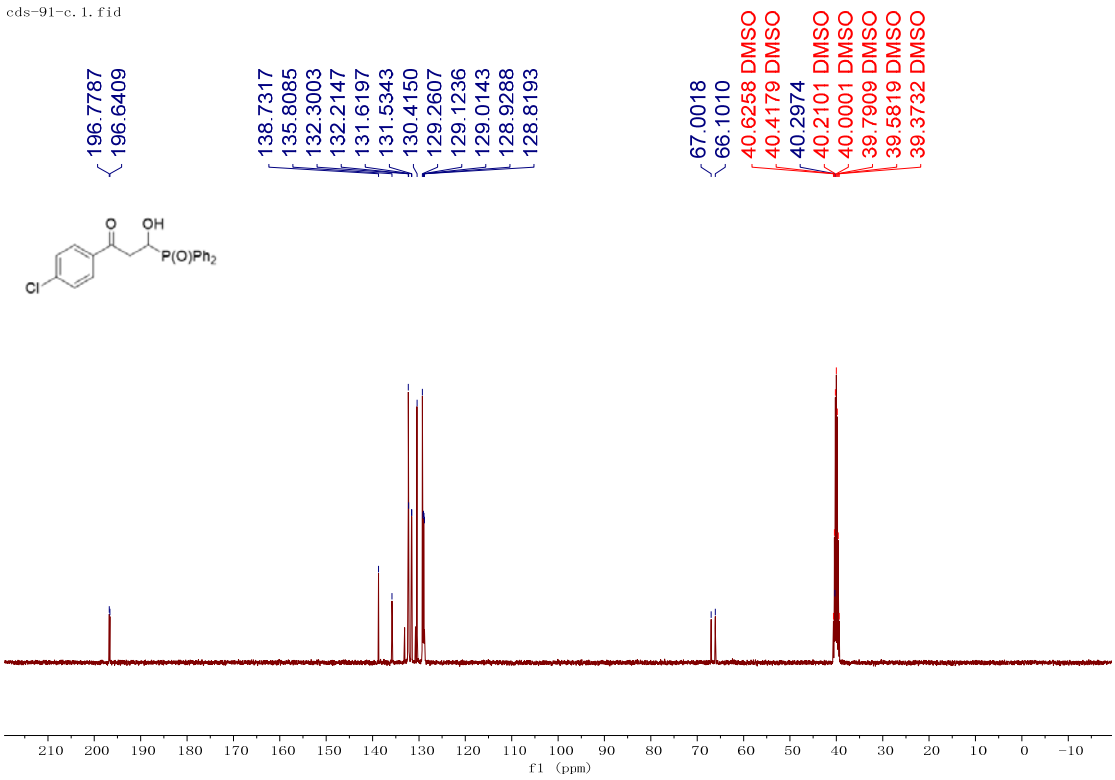
^{31}P NMR spectrum of **3d** (162 MHz, DMSO-d_6)



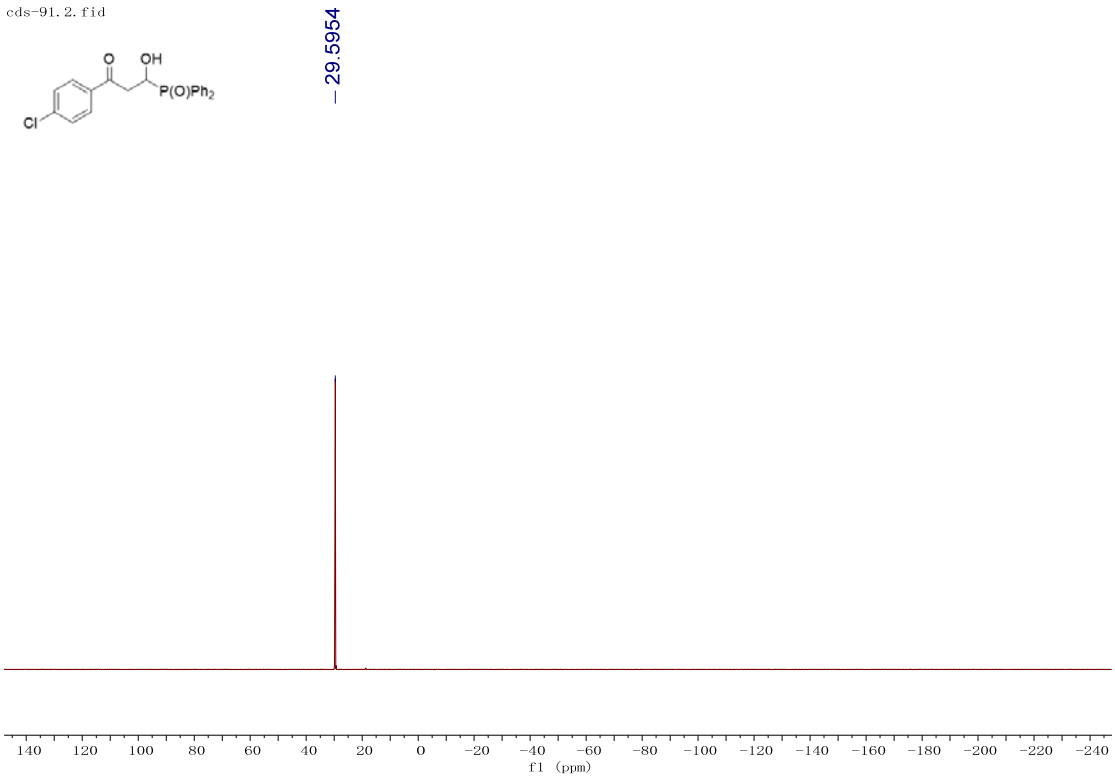
^{19}F NMR spectrum of **3d** (376 MHz, DMSO-d_6)



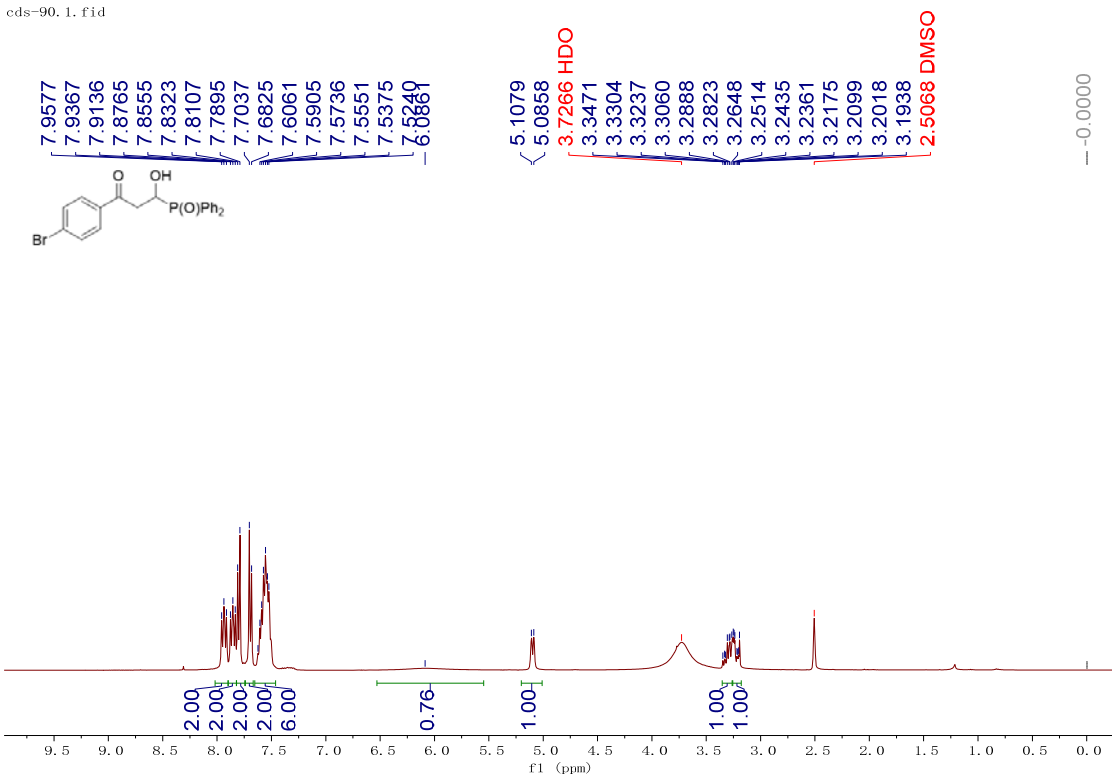
^{1}H NMR spectrum of **3e** (400 MHz, DMSO-d_6)



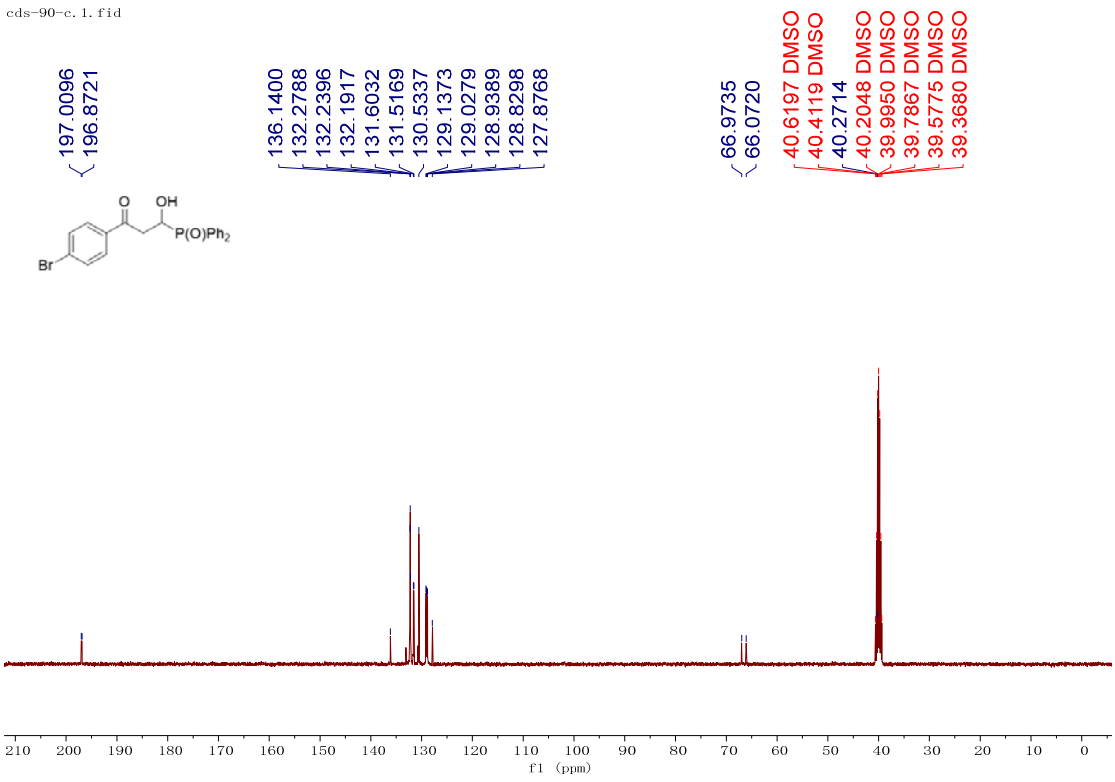
^{13}C NMR spectrum of **3e** (100 MHz, DMSO-d_6)



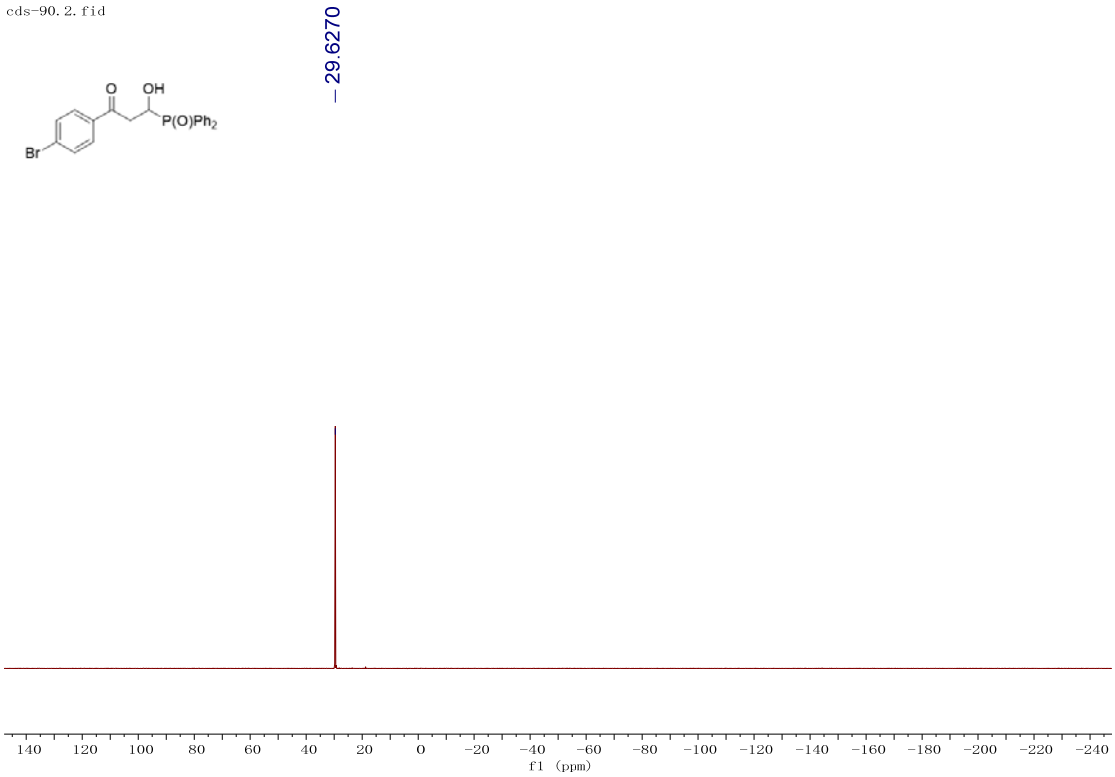
^{31}P NMR spectrum of **3e** (162 MHz, DMSO-d_6)



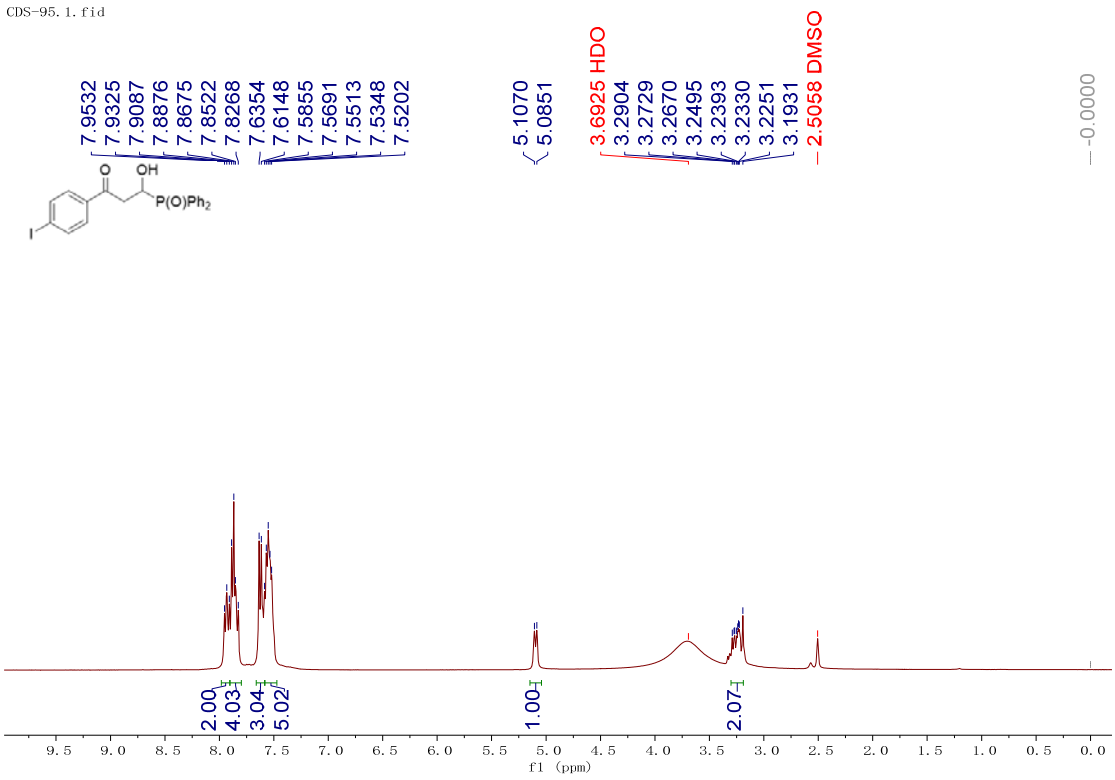
^{1}H NMR spectrum of **3f** (400 MHz, DMSO-d_6)



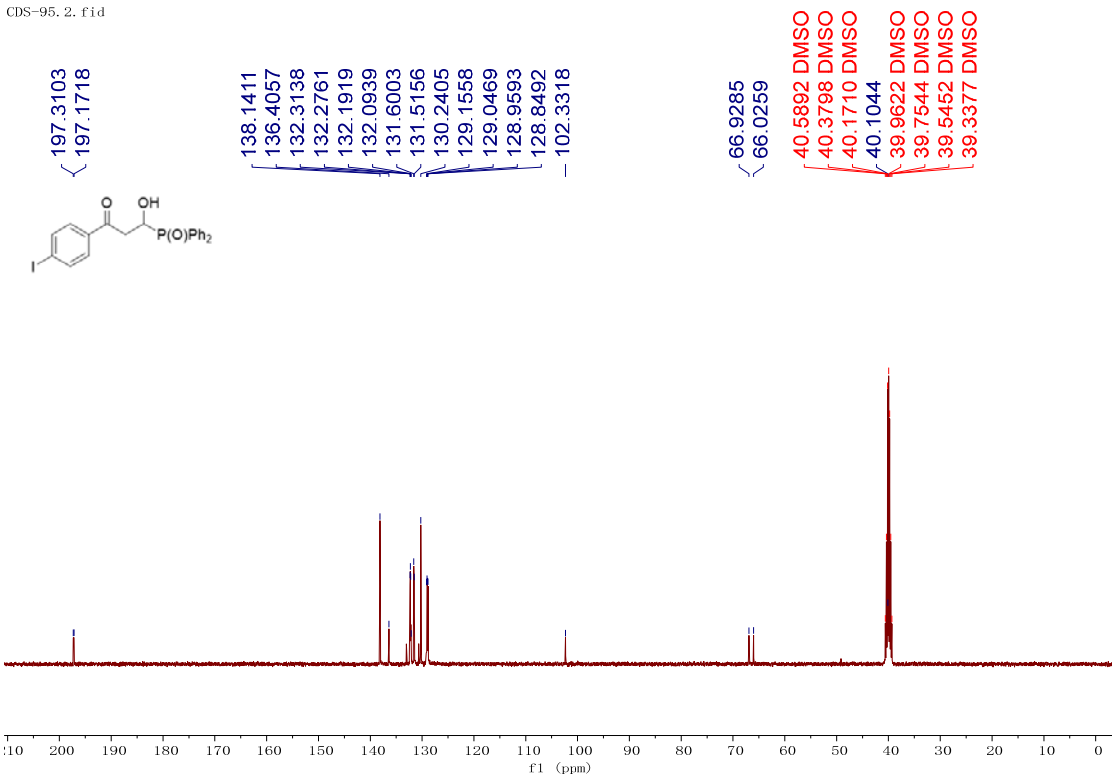
^{13}C NMR spectrum of **3f** (100 MHz, DMSO-d_6)



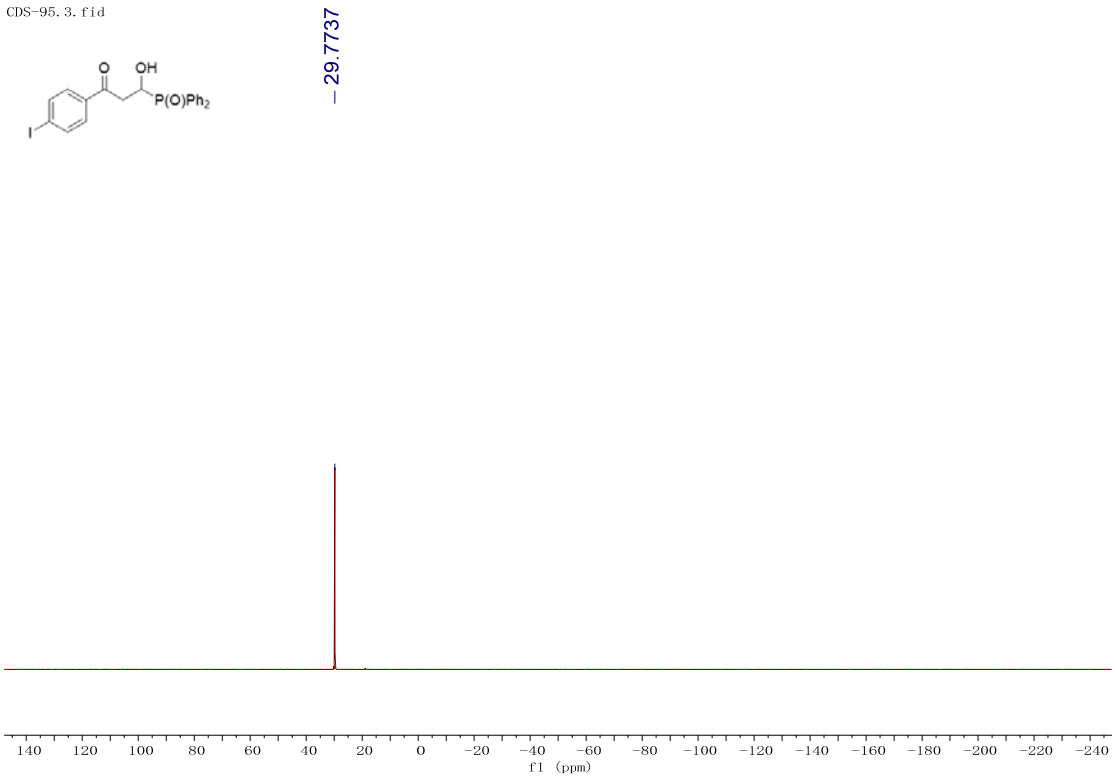
^{31}P NMR spectrum of **3f** (162 MHz, DMSO-d_6)



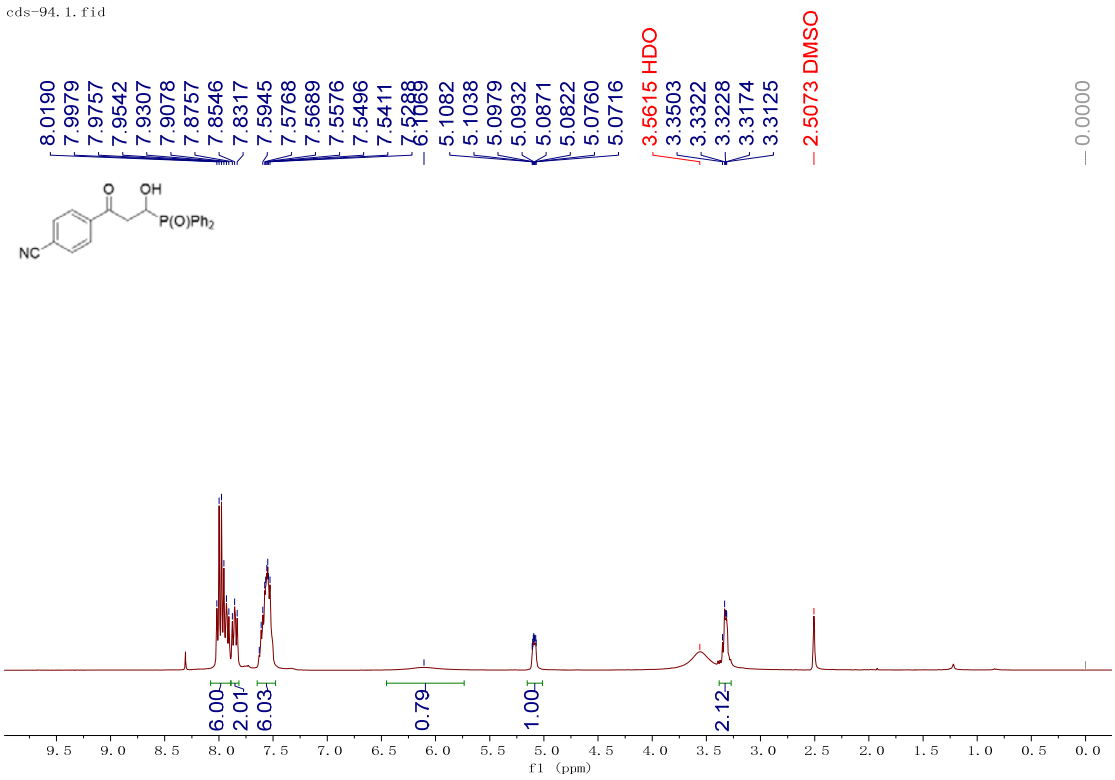
^{1}H NMR spectrum of **3g** (400 MHz, DMSO-d_6)



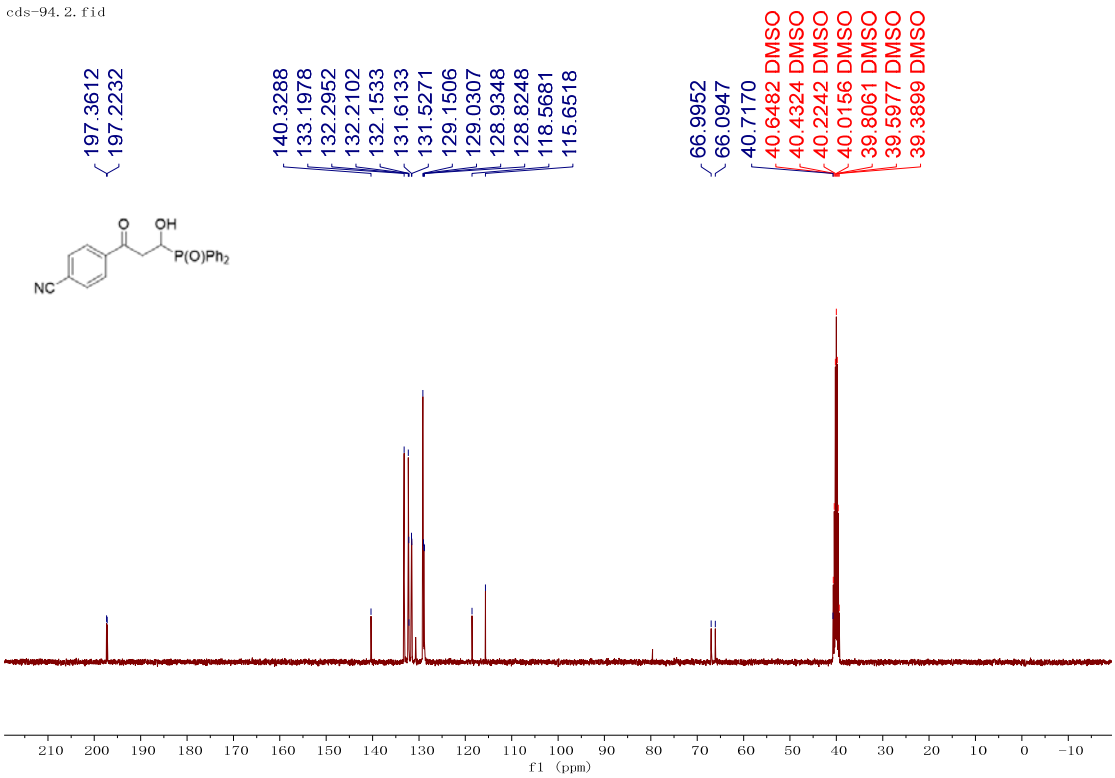
^{13}C NMR spectrum of **3g** (100 MHz, DMSO-d_6)



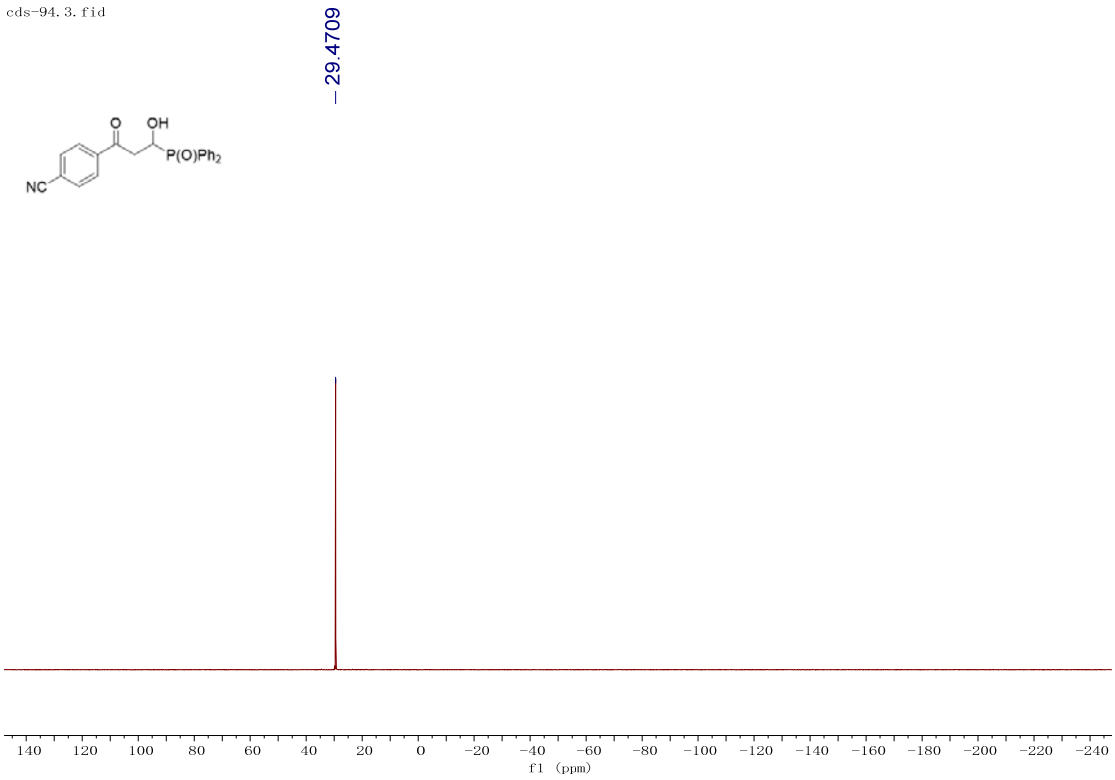
^{31}P NMR spectrum of **3g** (162 MHz, DMSO-d_6)



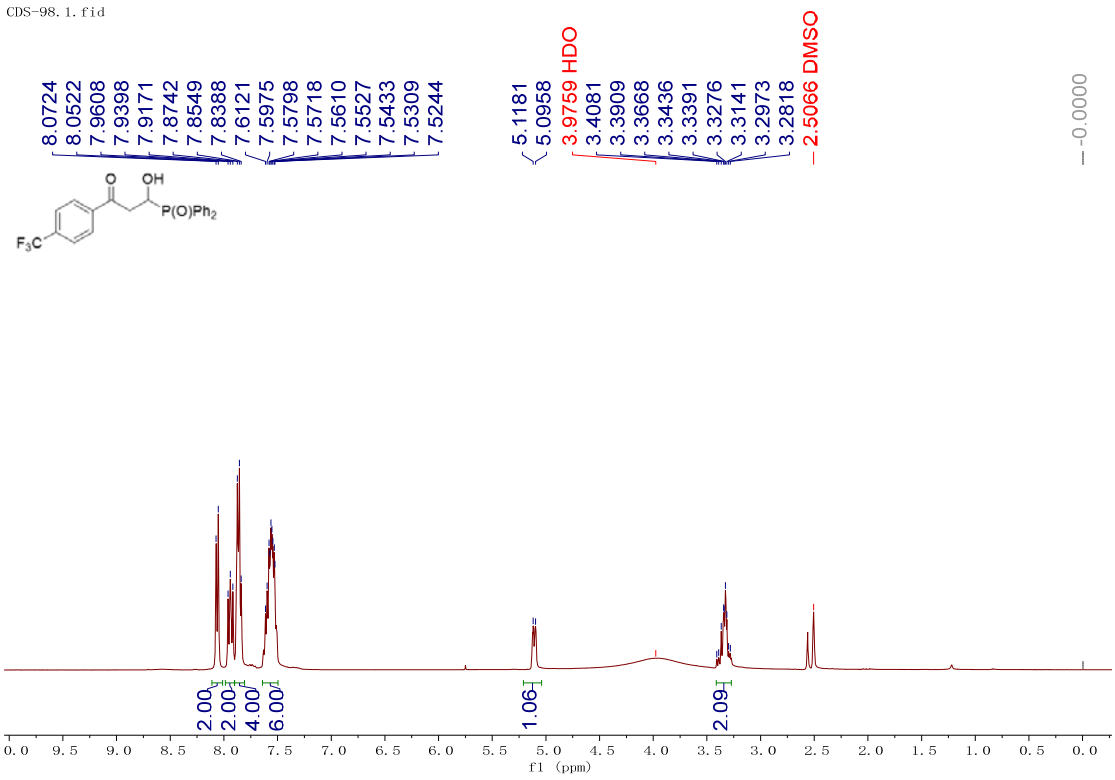
^{1}H NMR spectrum of **3h** (400 MHz, DMSO-d_6)



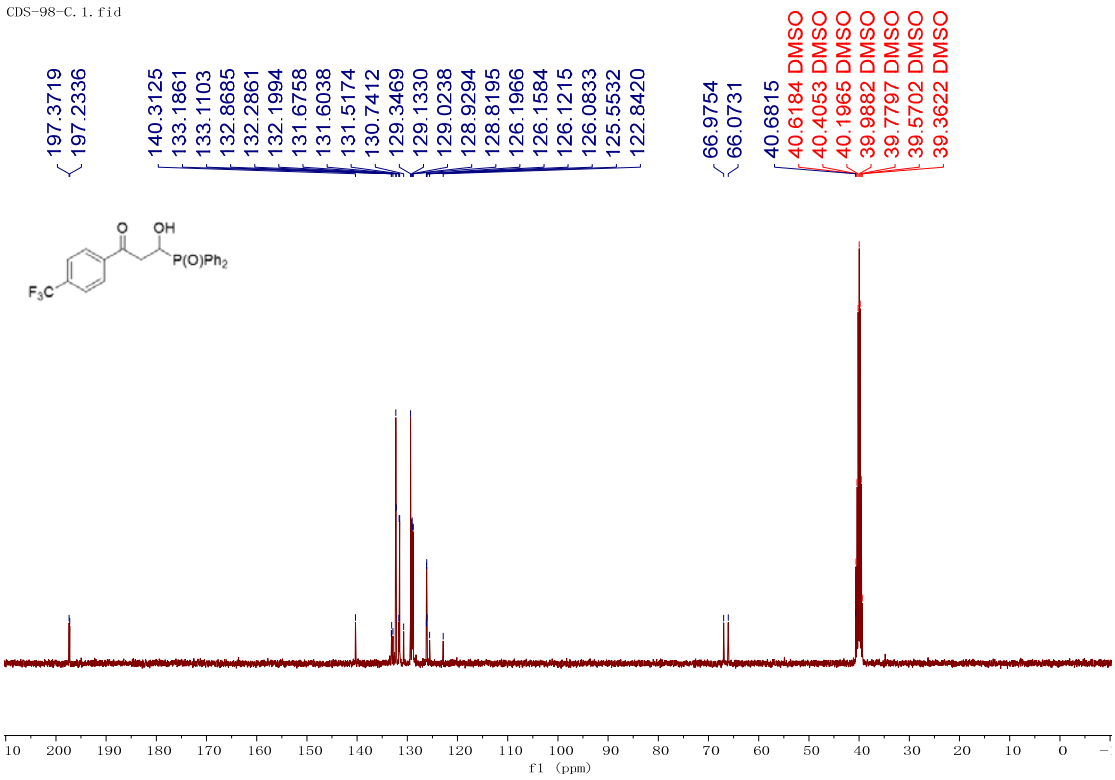
^{13}C NMR spectrum of **3h** (100 MHz, DMSO-d_6)



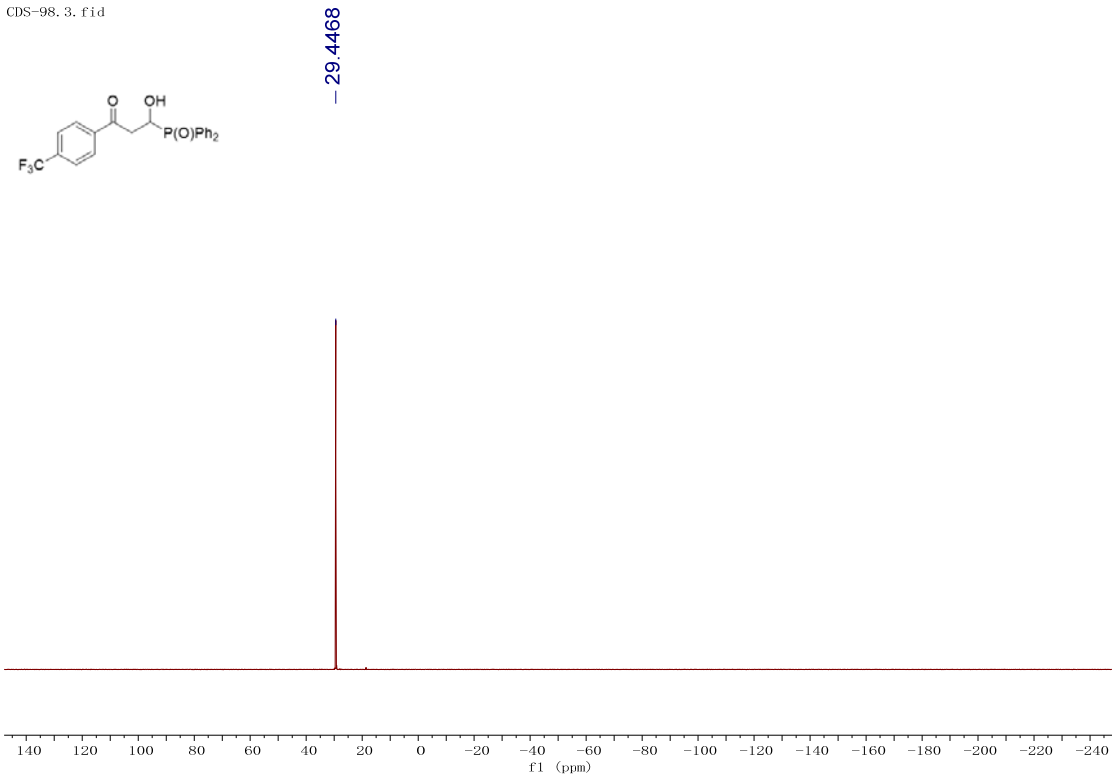
^{31}P NMR spectrum of **3h** (162 MHz, DMSO-d_6)



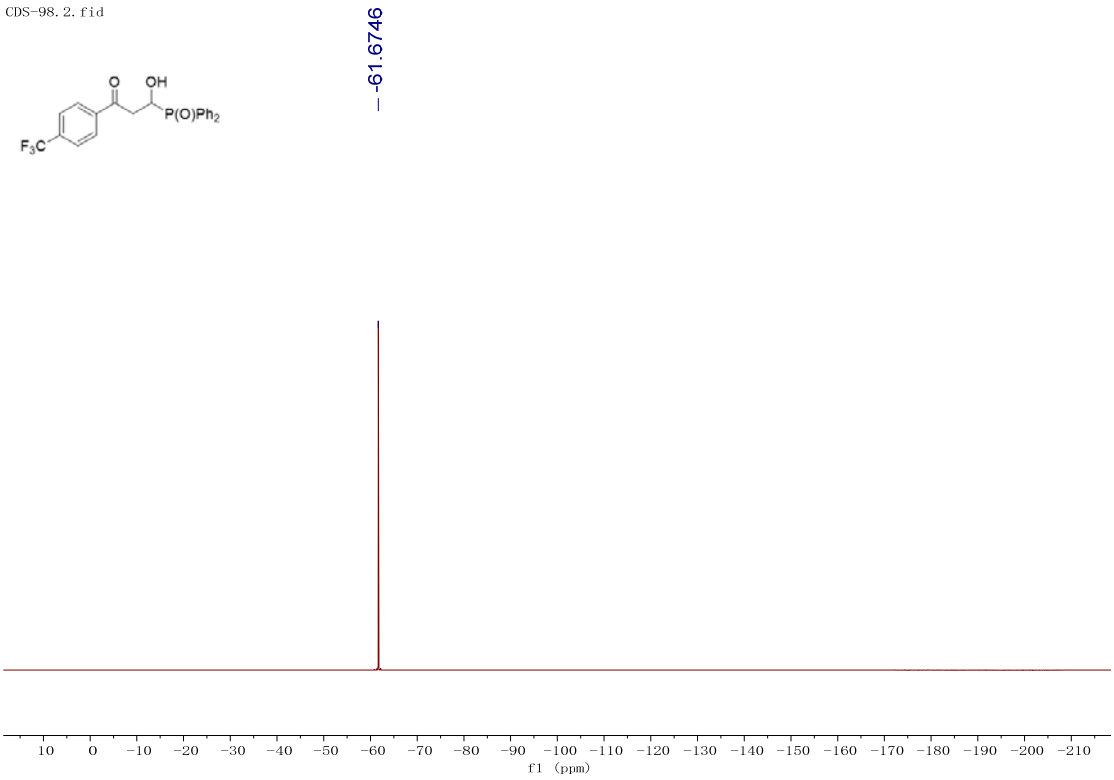
^{1}H NMR spectrum of **3i** (400 MHz, DMSO-d_6)



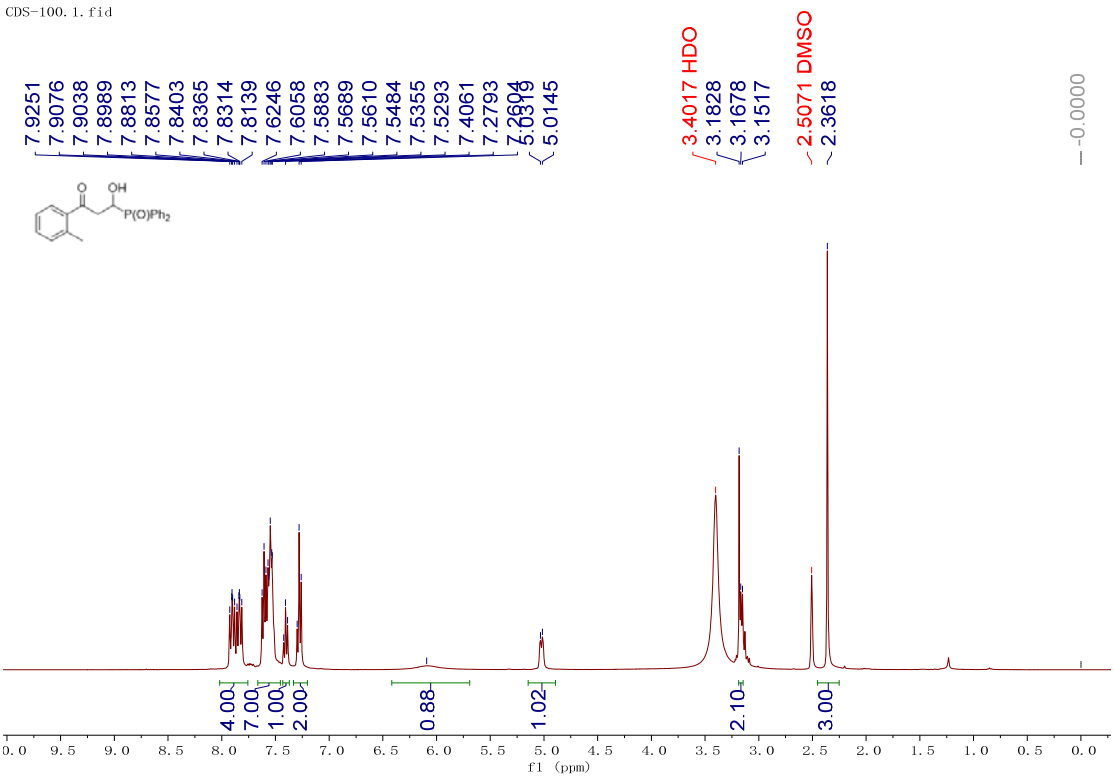
^{13}C NMR spectrum of **3i** (100 MHz, DMSO-d_6)



^{31}P NMR spectrum of **3i** (162 MHz, DMSO-d_6)



^{19}F NMR spectrum of **3i** (376 MHz, DMSO-d_6)



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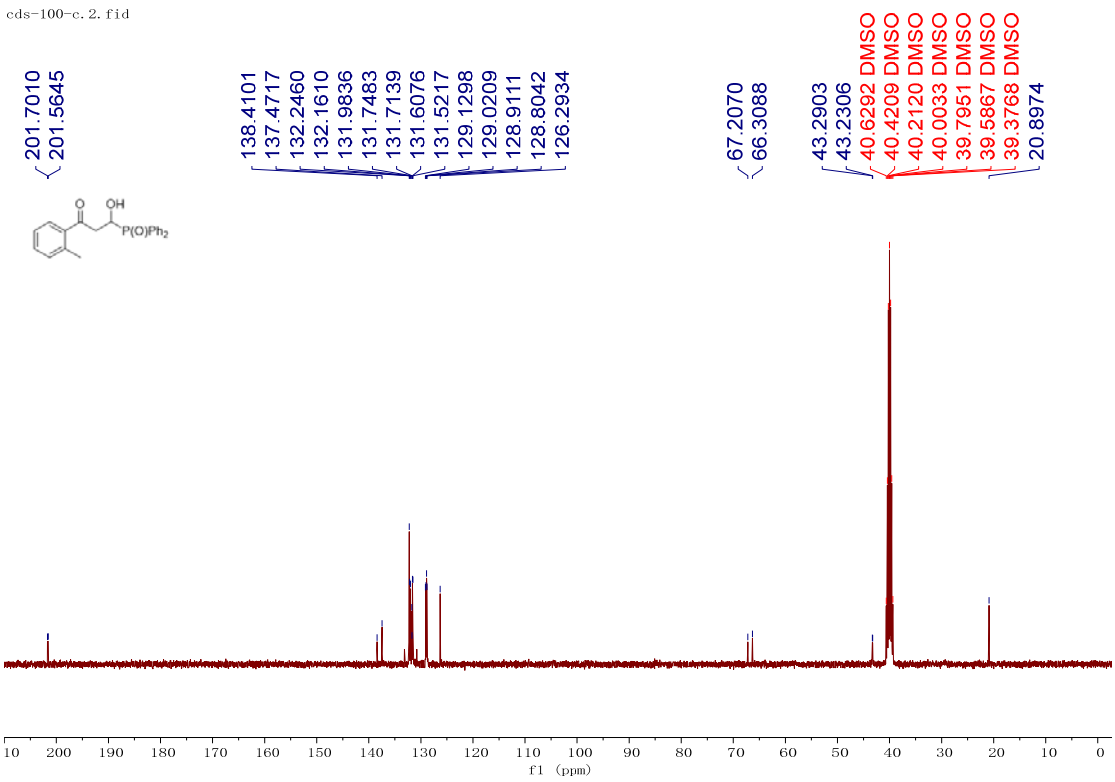
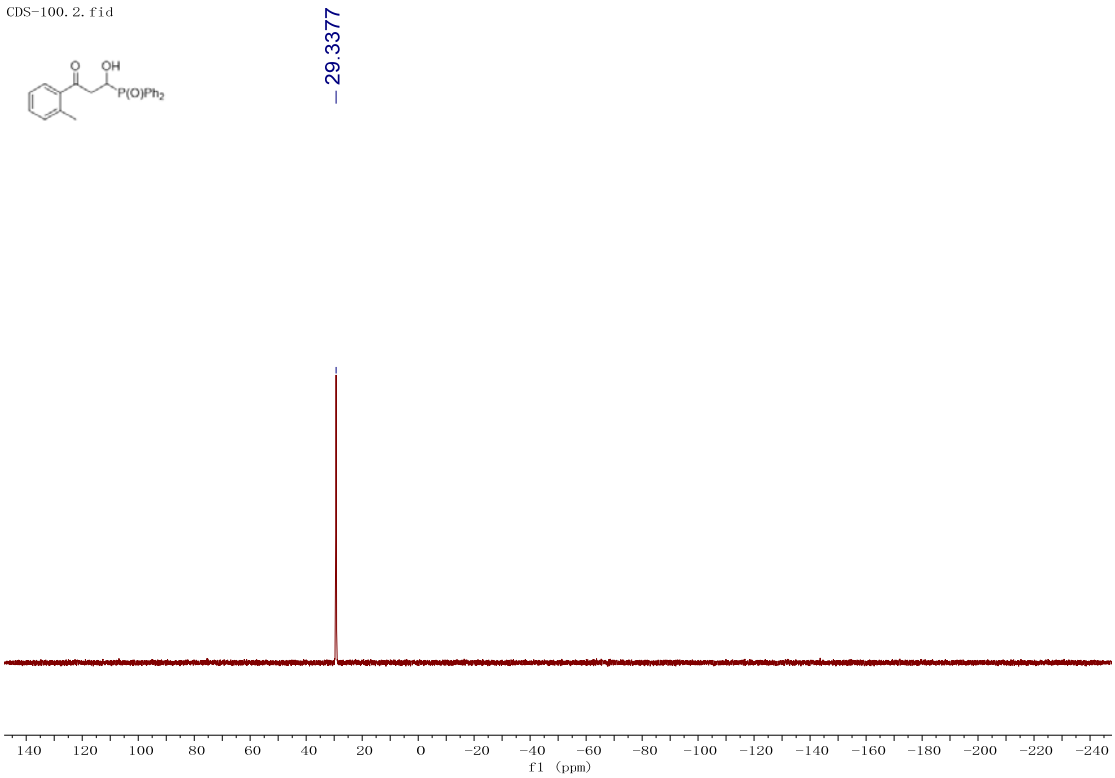
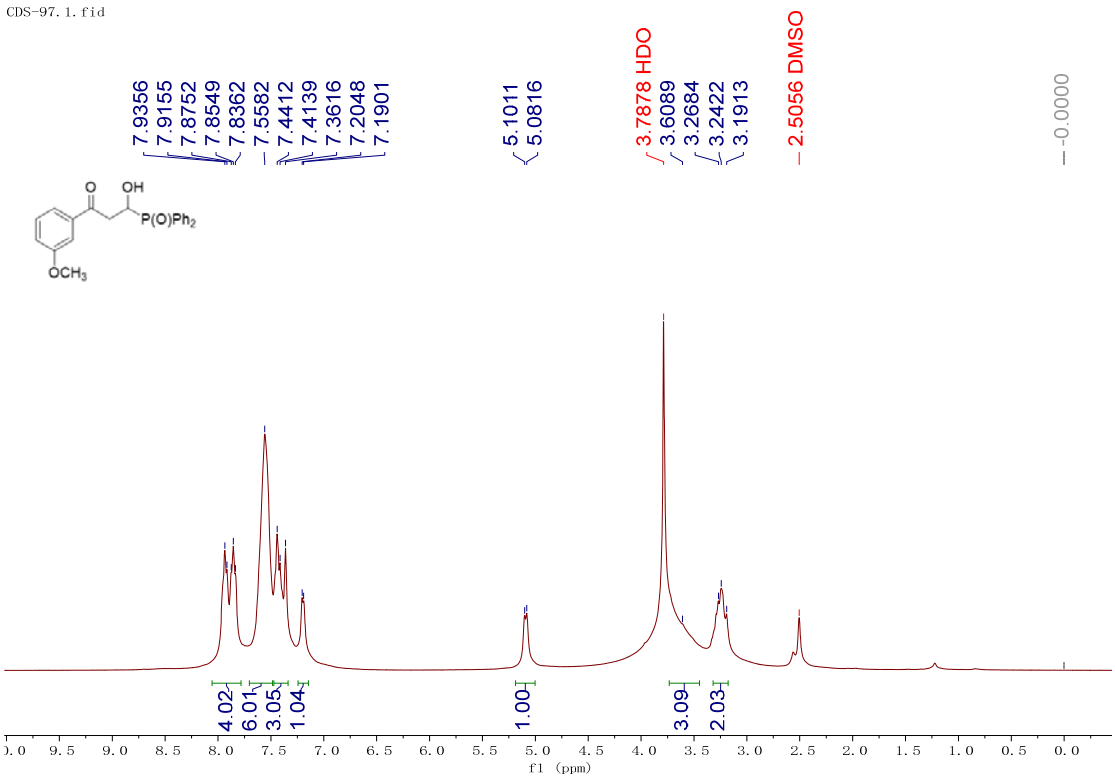


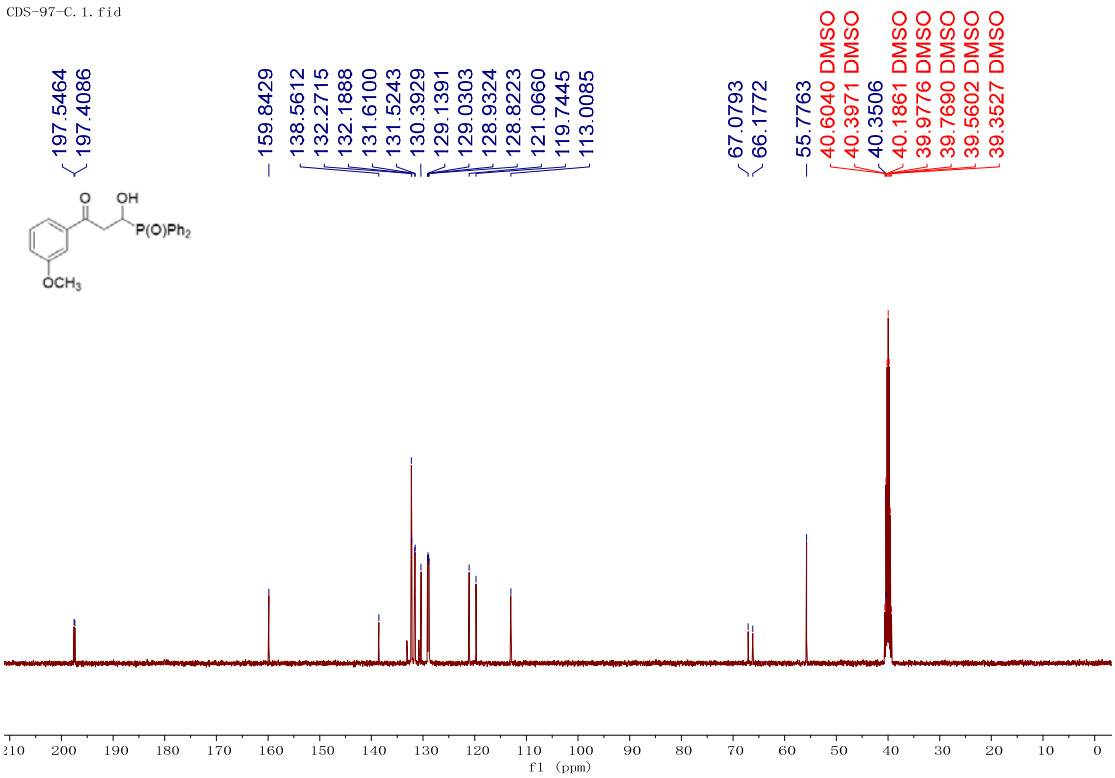
^{13}C NMR spectrum of **3j** (100 MHz, DMSO-d_6)



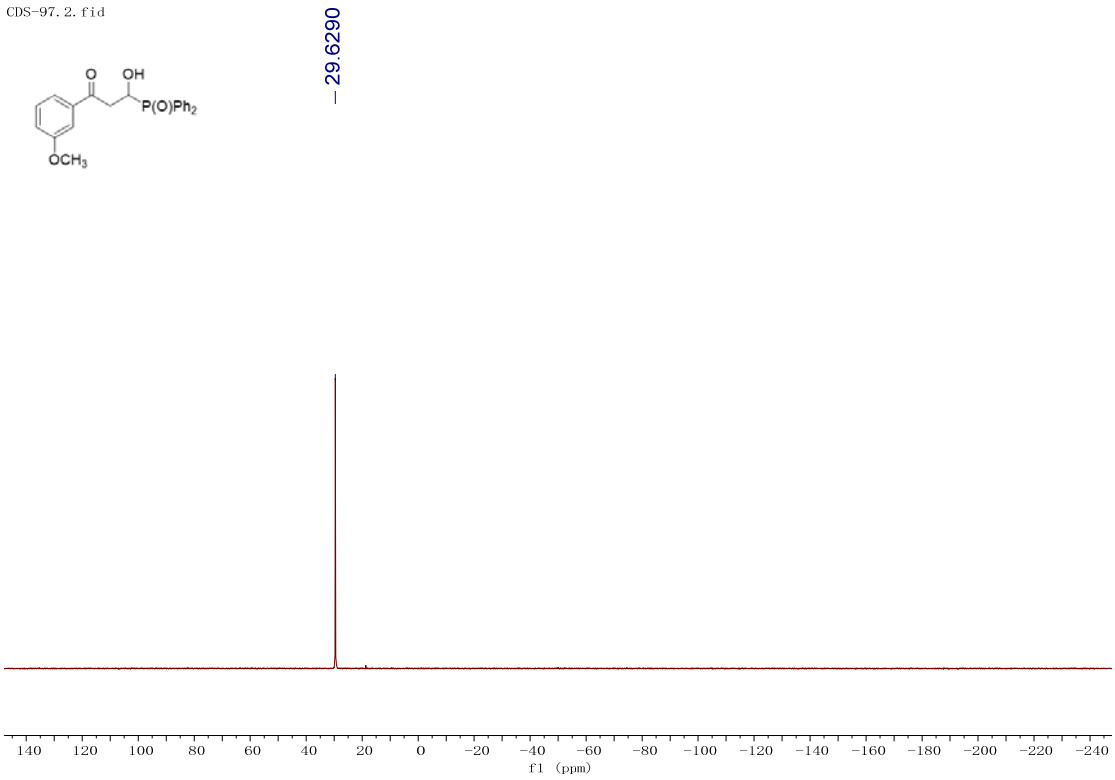
^{31}P NMR spectrum of **3j** (162 MHz, DMSO-d_6)



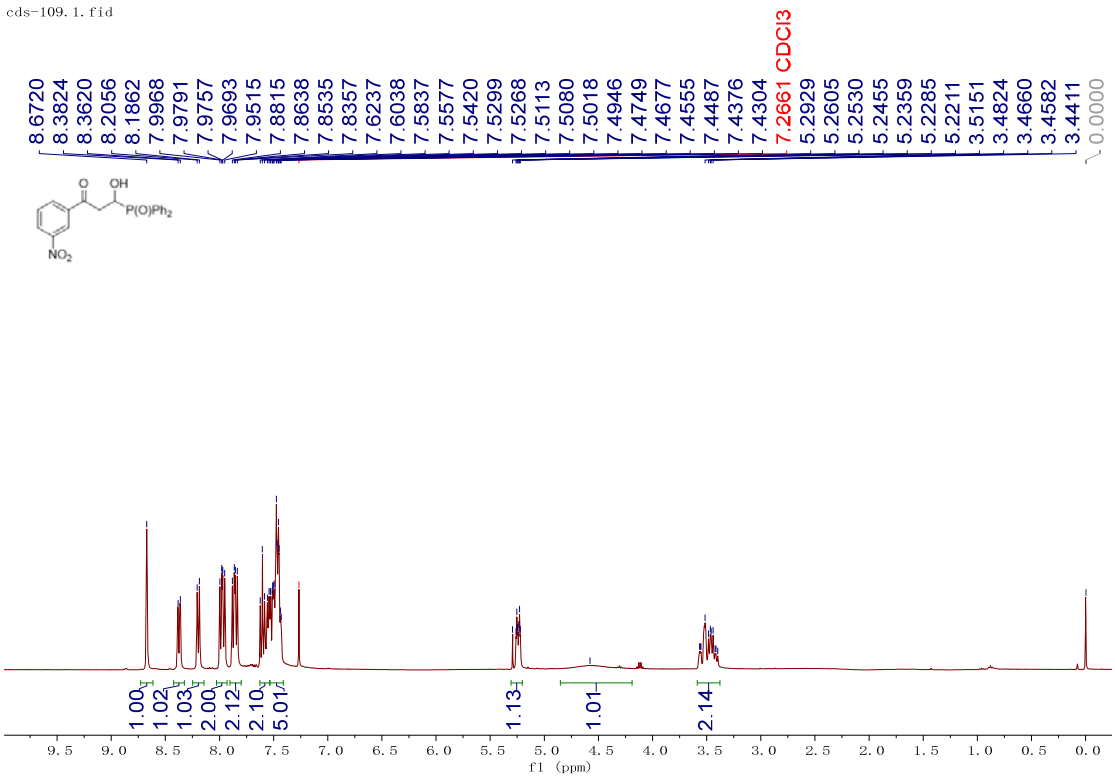
^{1}H NMR spectrum of **3k** (400 MHz, DMSO-d_6)



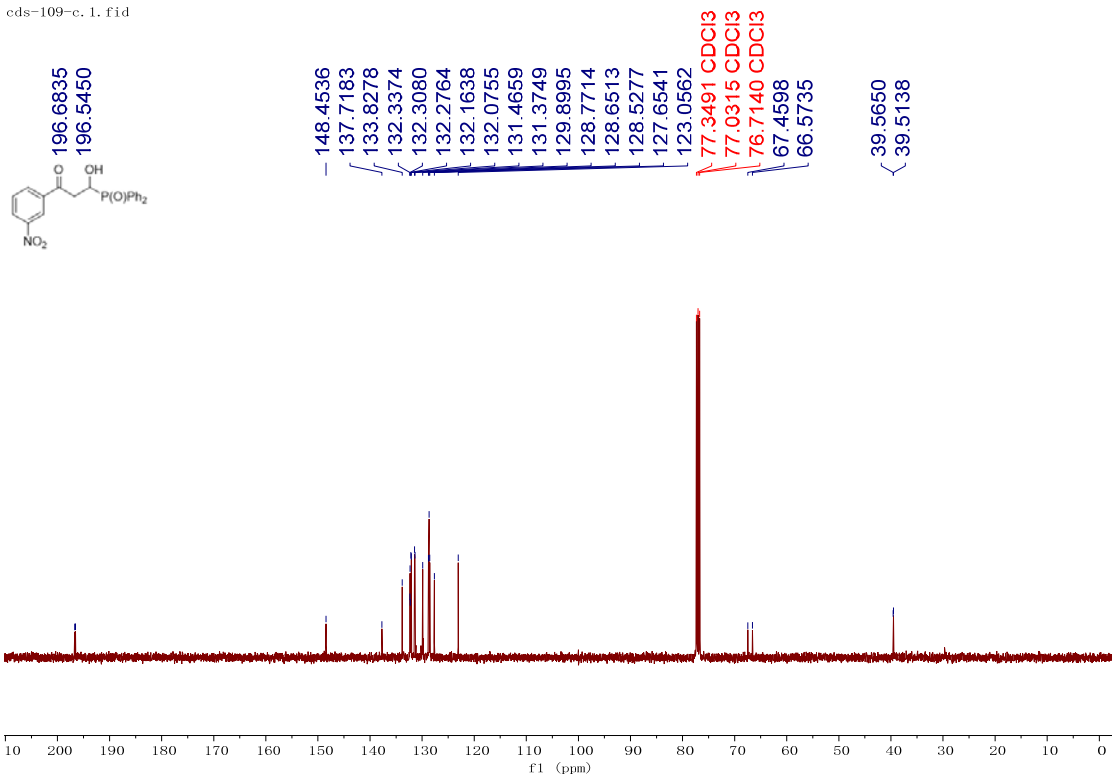
^{13}C NMR spectrum of **3k** (100 MHz, DMSO-d_6)



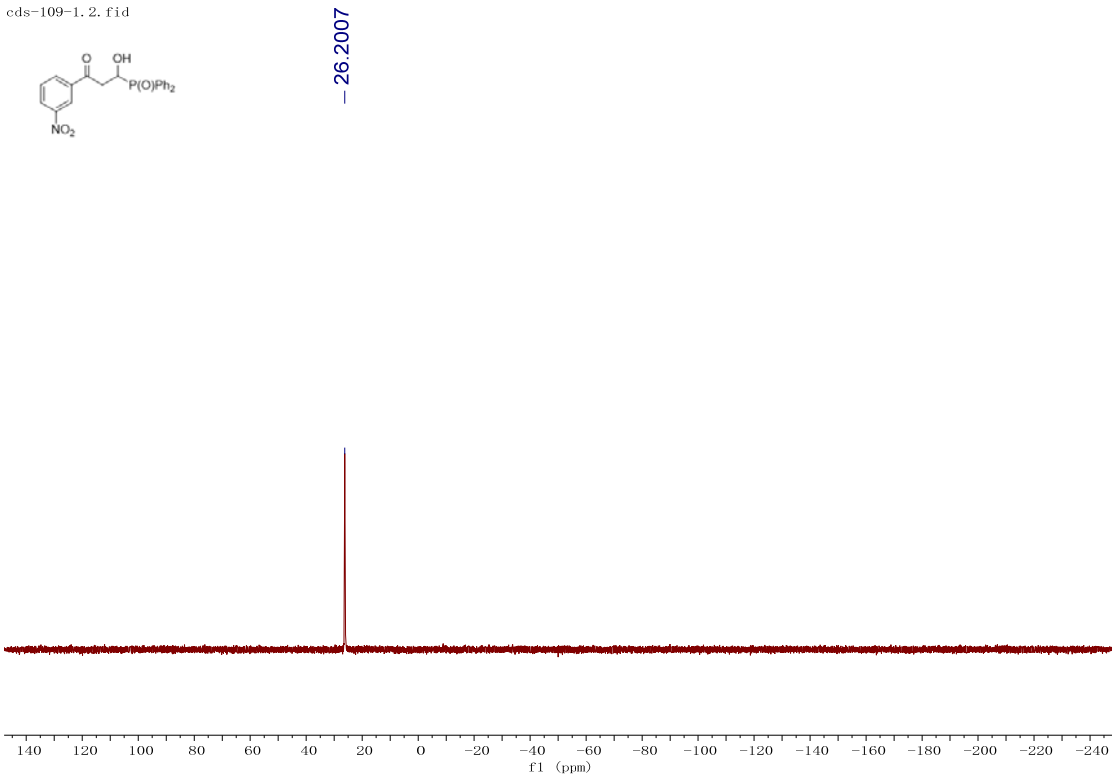
^{31}P NMR spectrum of **3k** (162 MHz, DMSO-d_6)



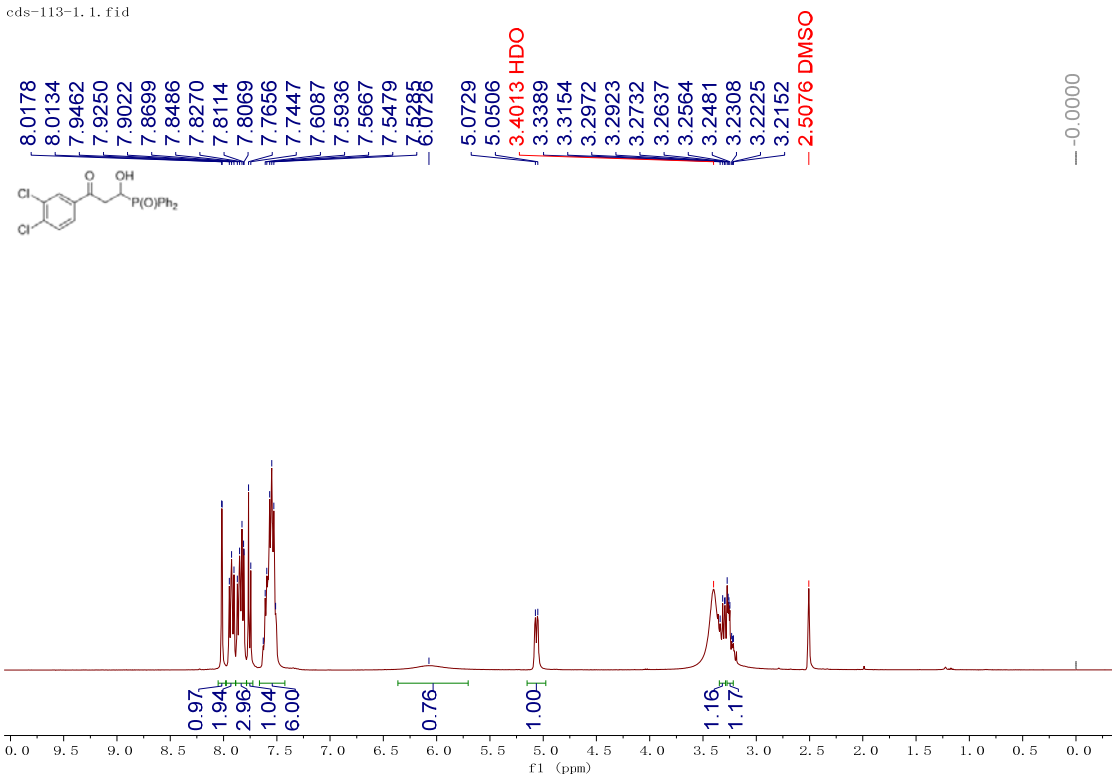
^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)



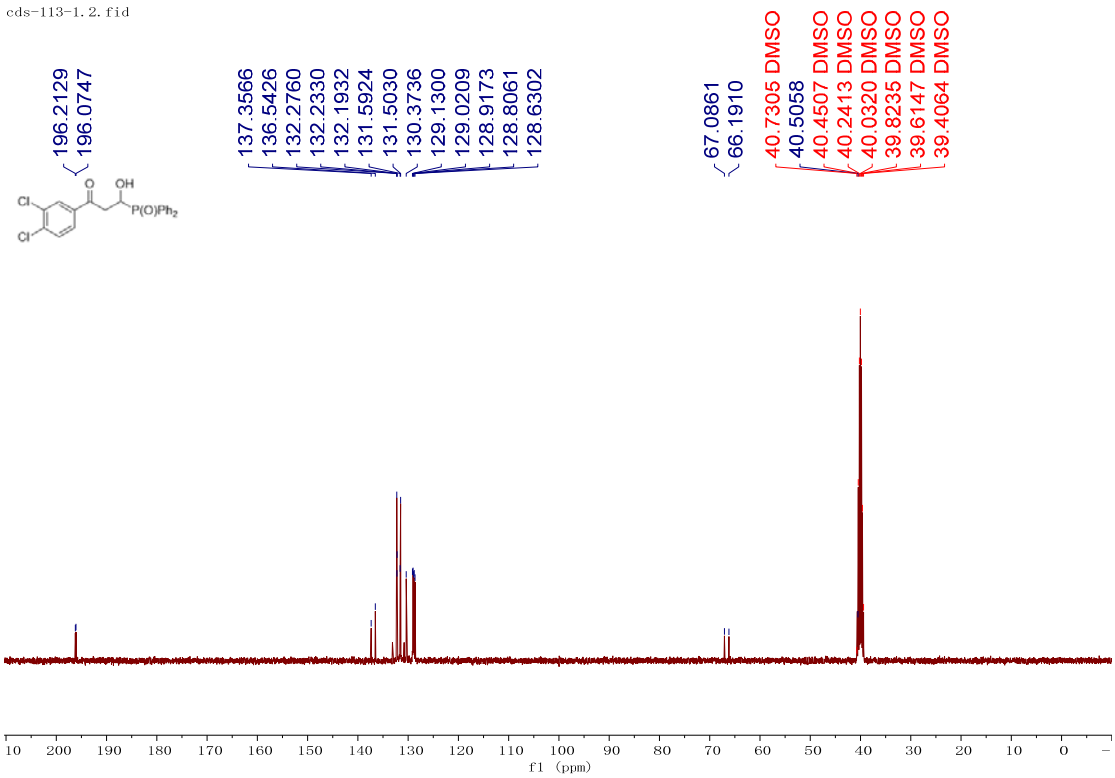
^{13}C NMR spectrum of **3l** (100 MHz, $CDCl_3$)



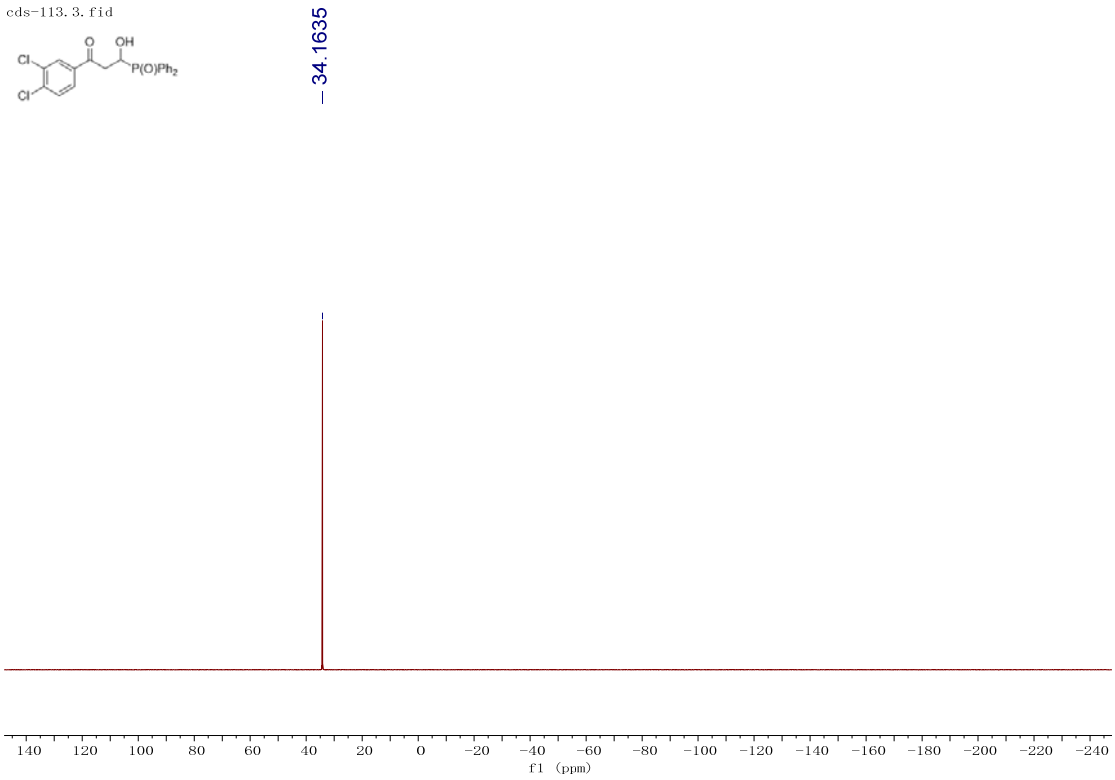
^{31}P NMR spectrum of **3l** (162 MHz, $CDCl_3$)\



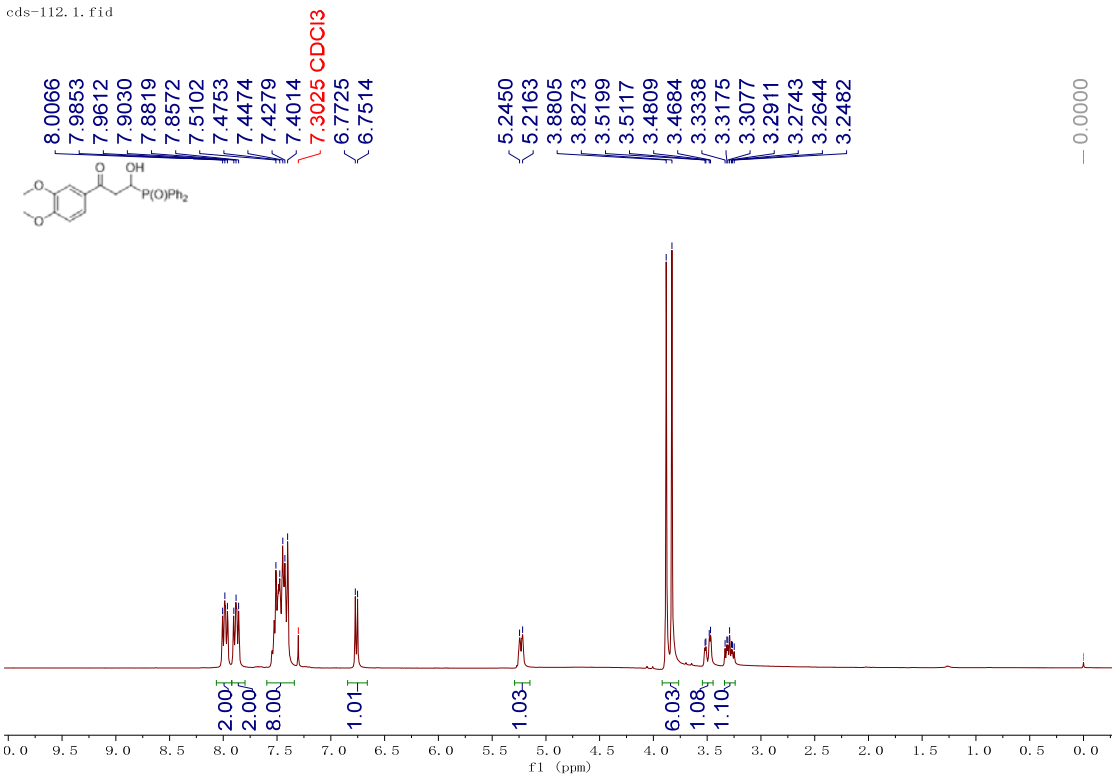
^{1}H NMR spectrum of **3m** (400 MHz, DMSO-d_6)



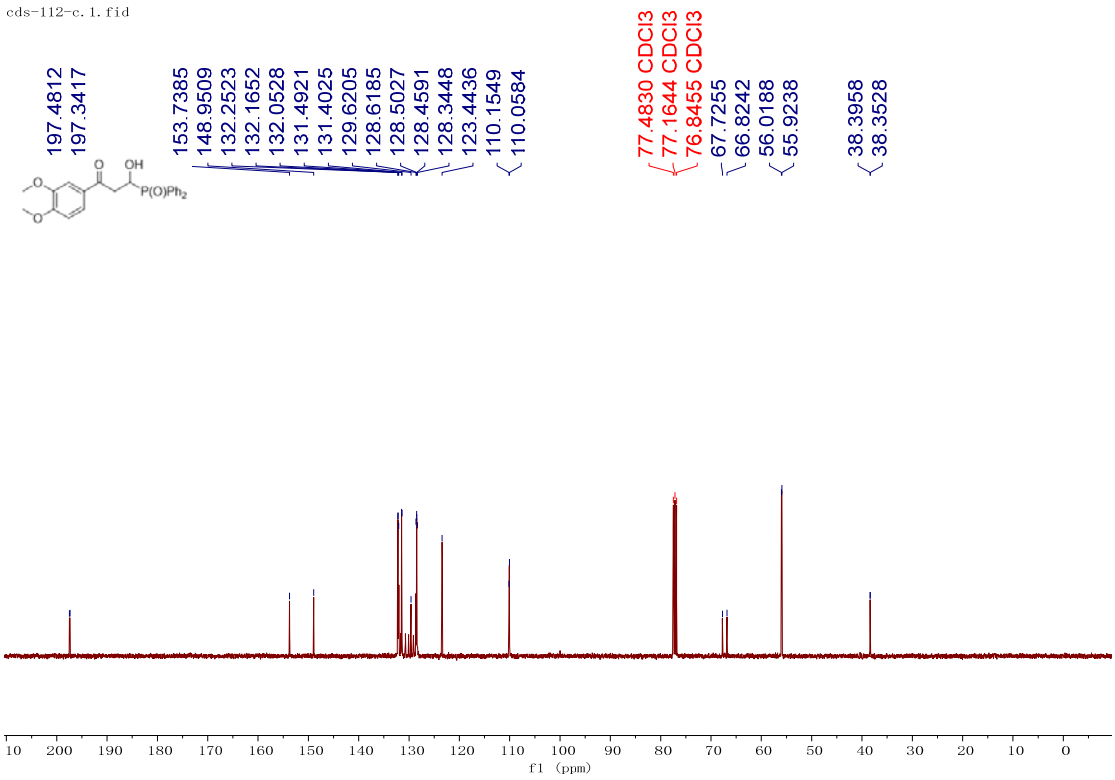
^{13}C NMR spectrum of **3m** (100 MHz, DMSO-d_6)



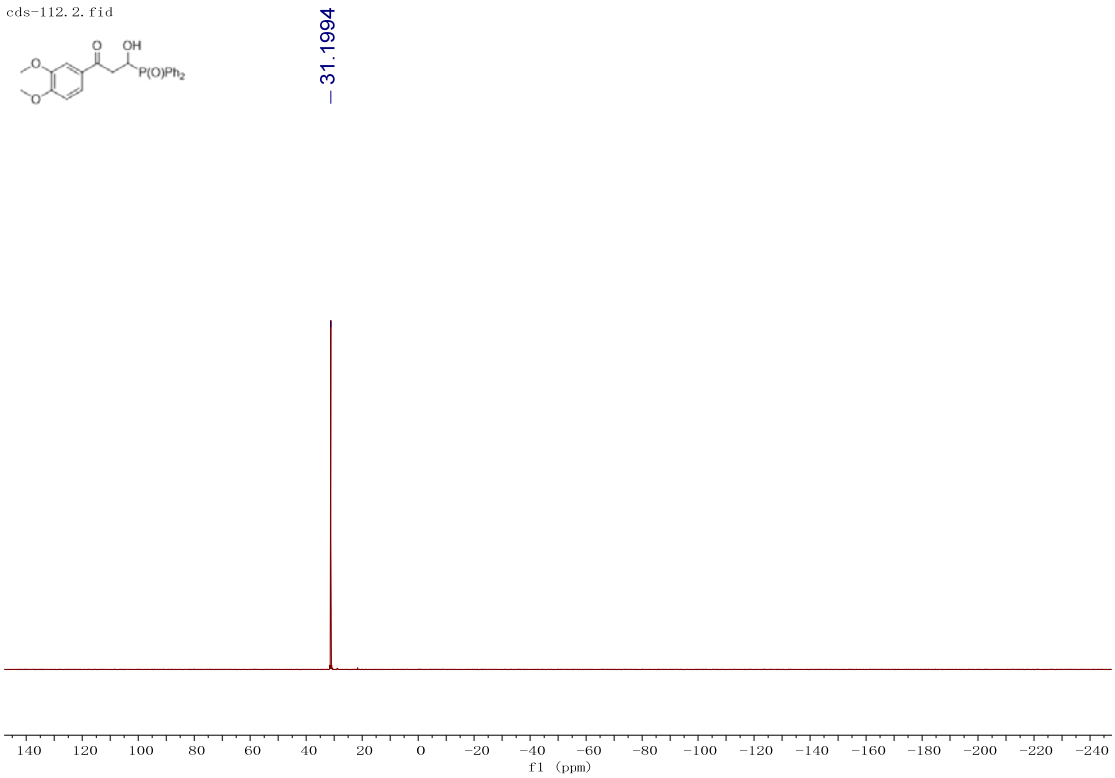
^{31}P NMR spectrum of **3m** (162 MHz, DMSO-d_6)



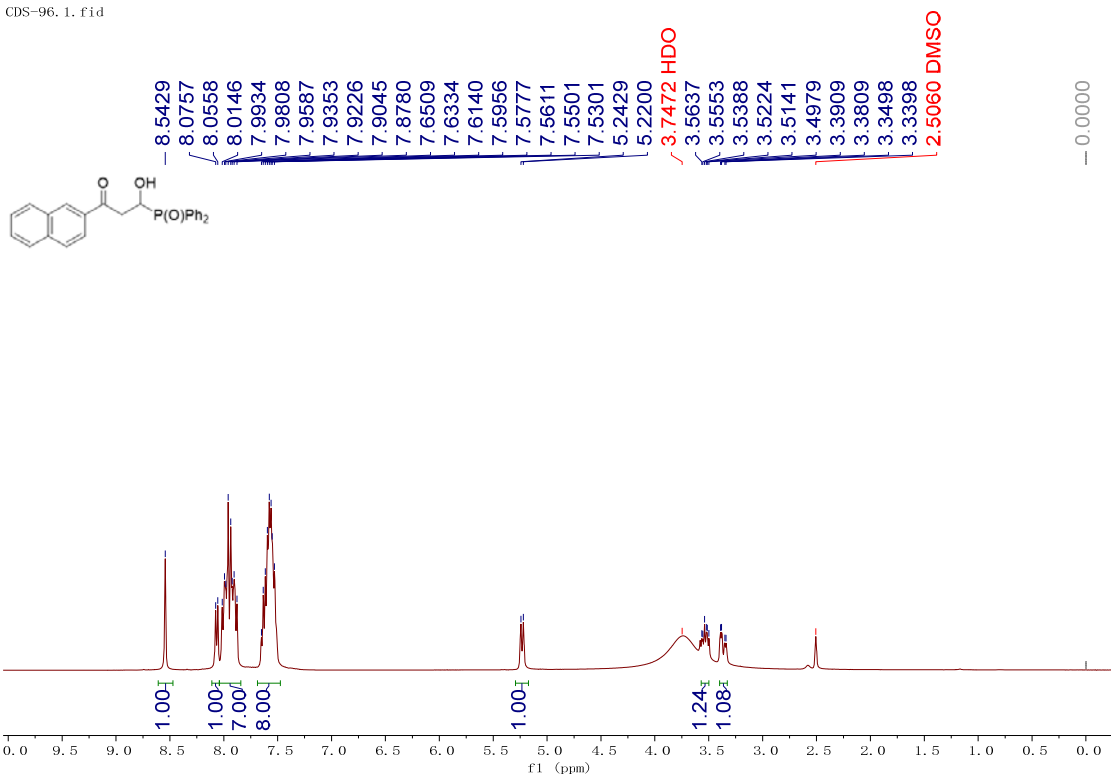
^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$)



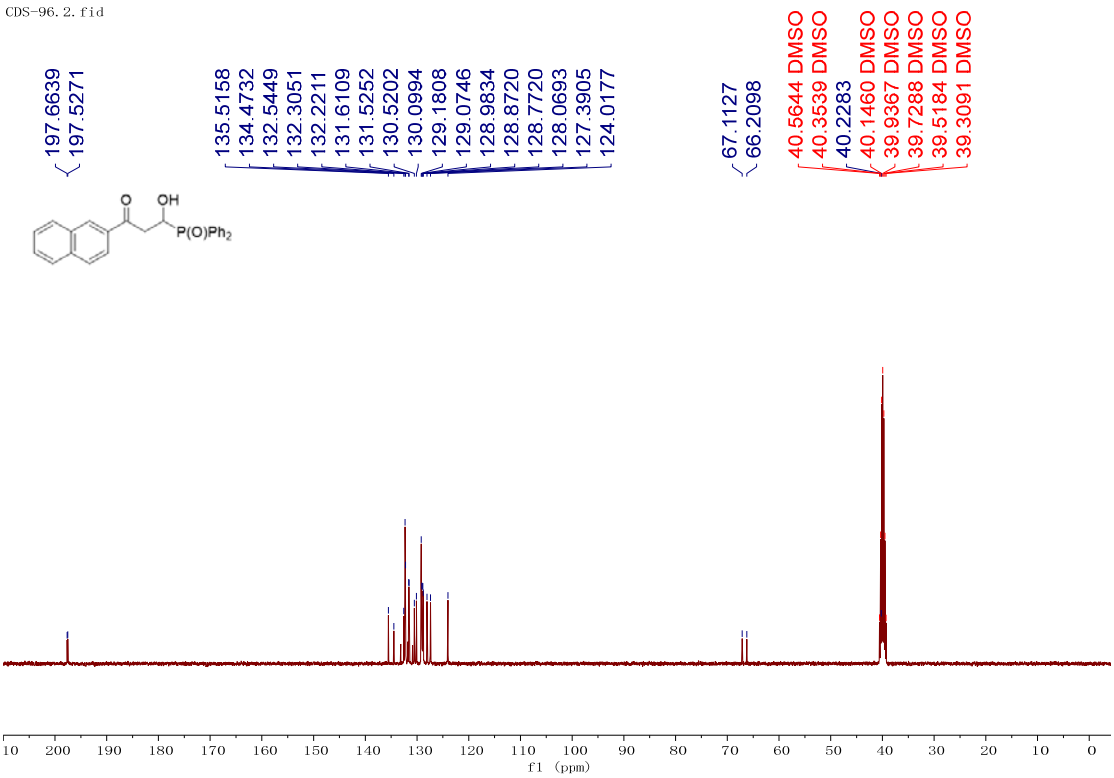
^{13}C NMR spectrum of **3n** (100 MHz, $CDCl_3$)



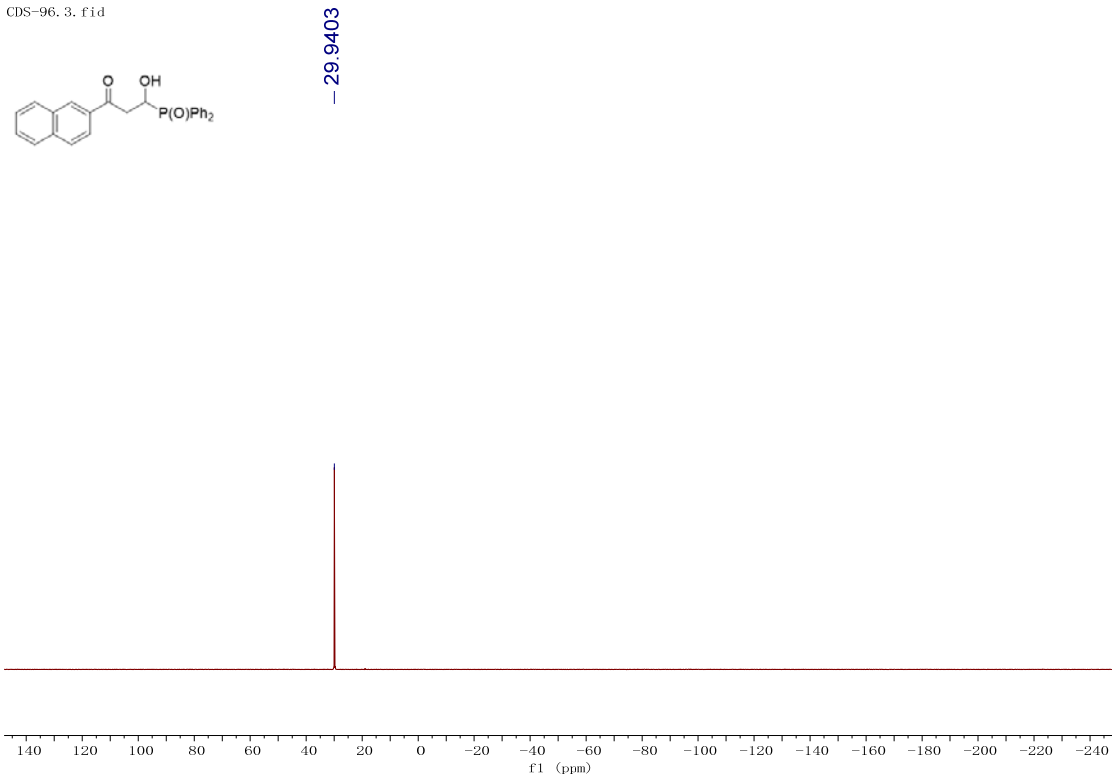
^{31}P NMR spectrum of **3n** (162 MHz, $CDCl_3$)



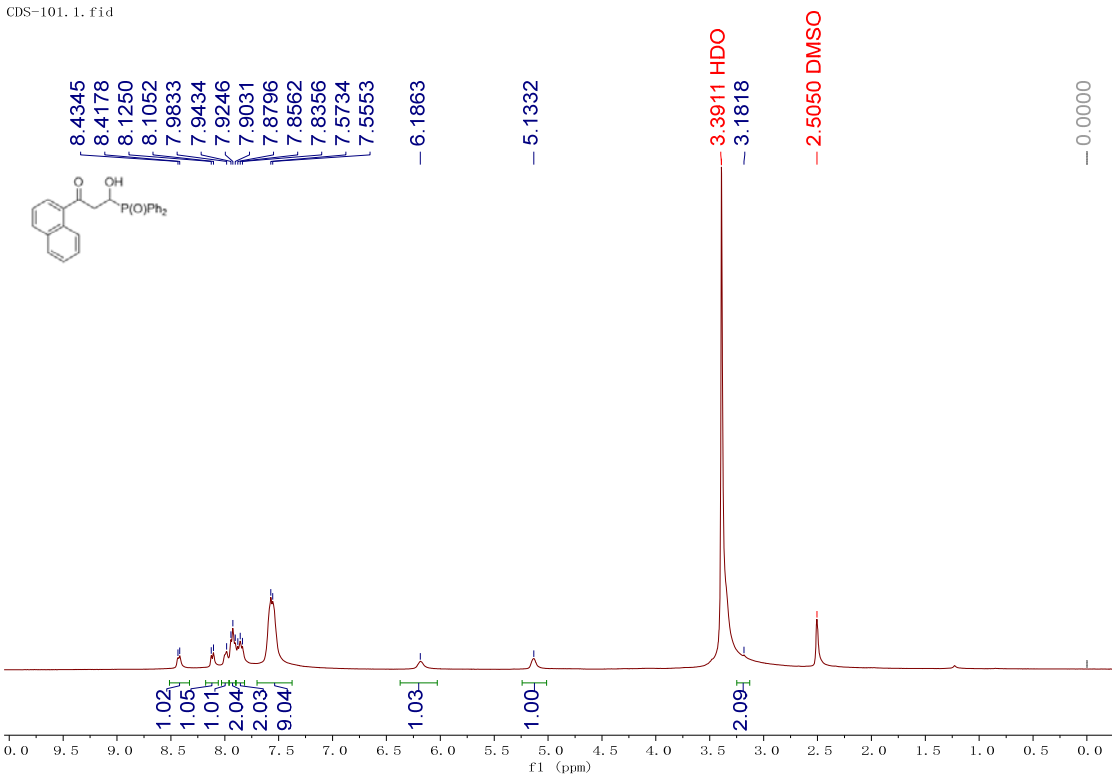
^{1}H NMR spectrum of **3o** (400 MHz, DMSO-d_6)



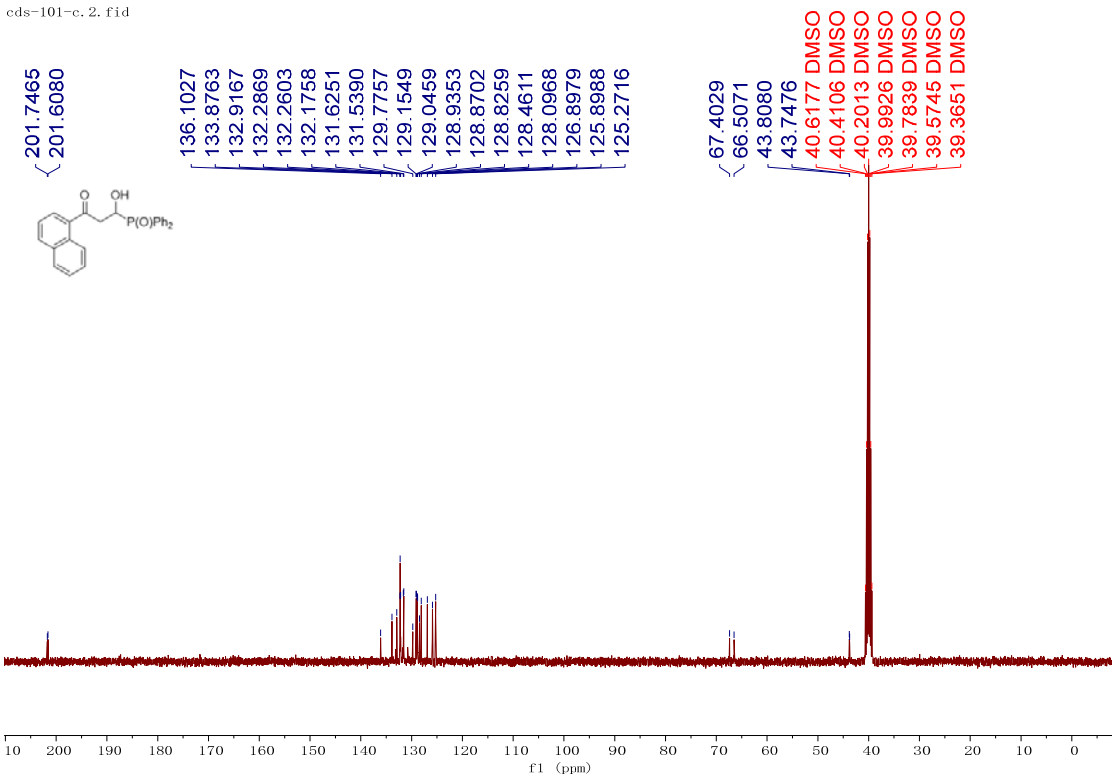
^{13}C NMR spectrum of **3o** (100 MHz, DMSO-d_6)



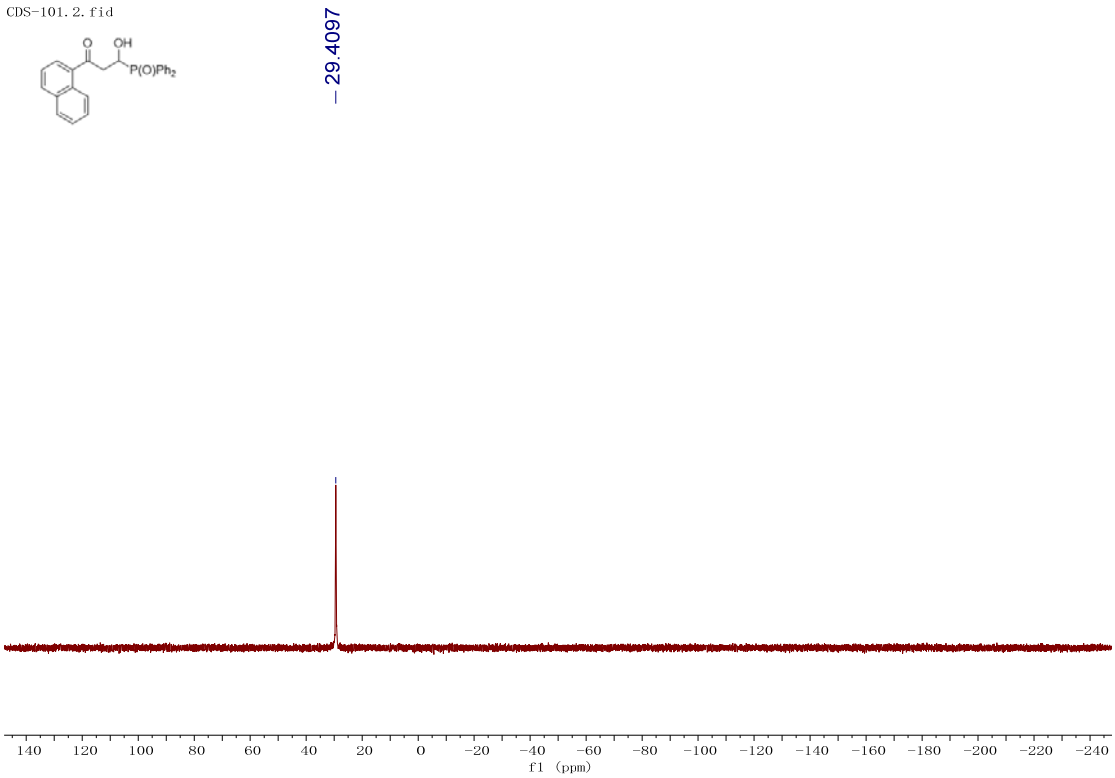
^{31}P NMR spectrum of **3o** (162 MHz, DMSO-d_6)



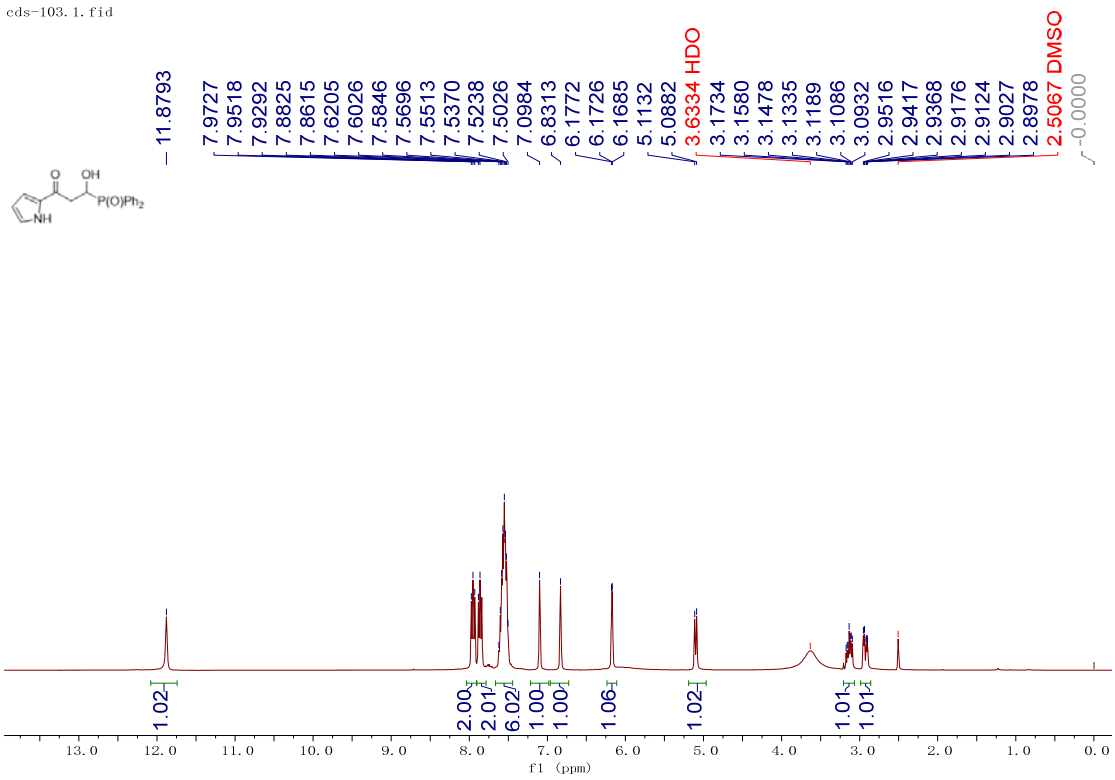
^{1}H NMR spectrum of **3p** (400 MHz, DMSO-d_6)



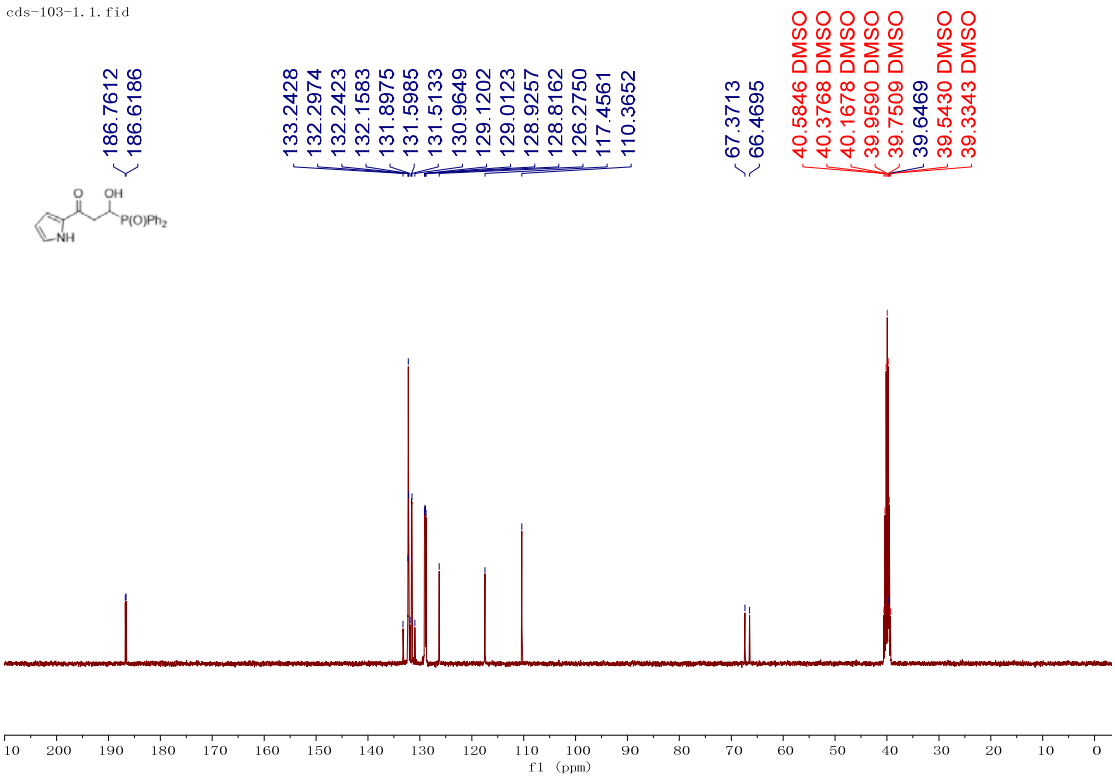
^{13}C NMR spectrum of **3p** (100 MHz, DMSO-d_6)



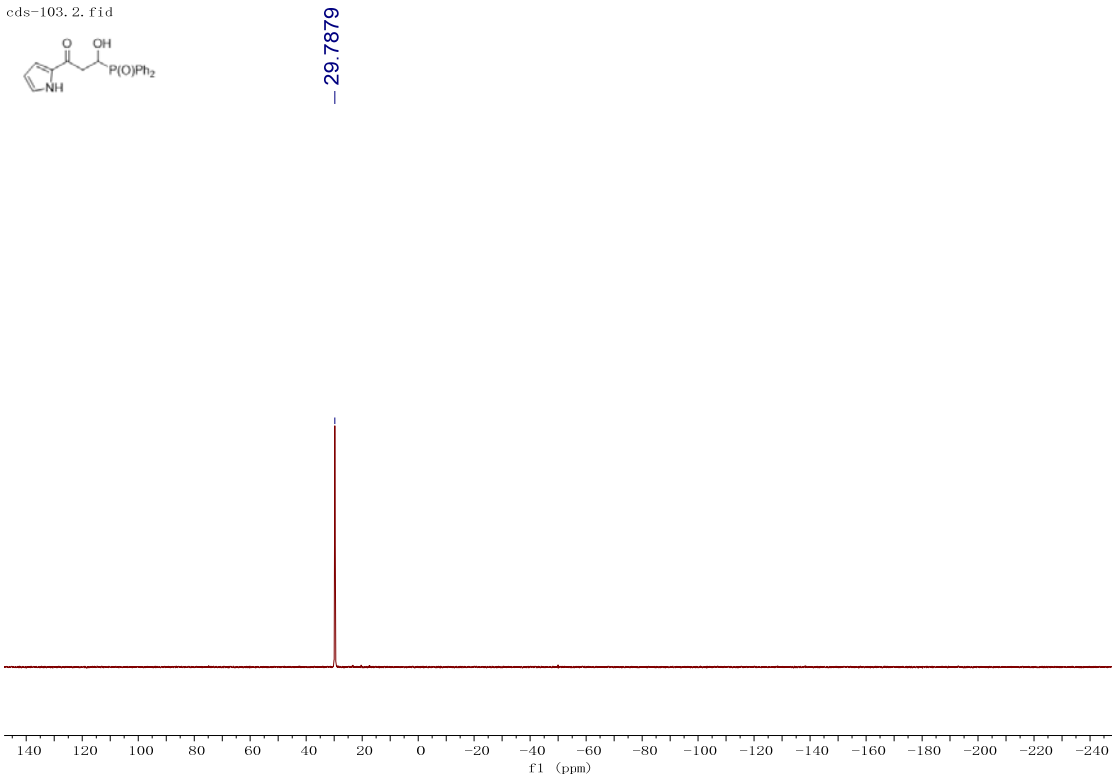
^{31}P NMR spectrum of **3p** (162 MHz, DMSO-d_6)



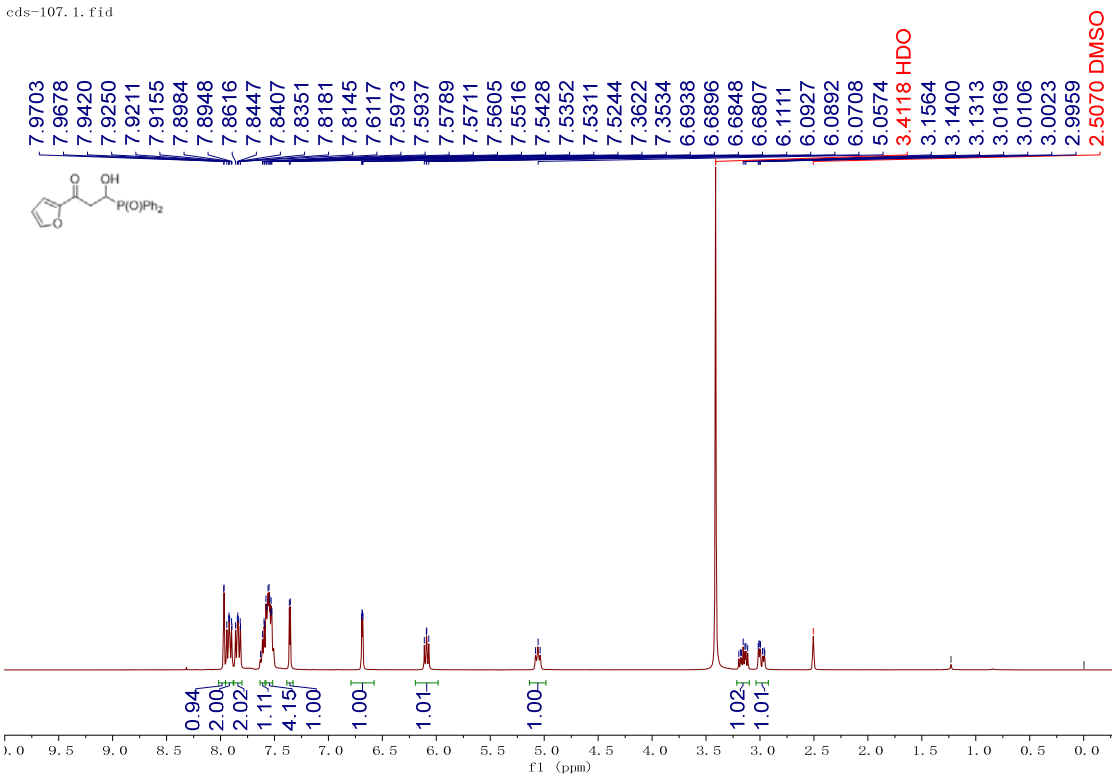
^{1}H NMR spectrum of **3q** (400 MHz, DMSO-d_6)



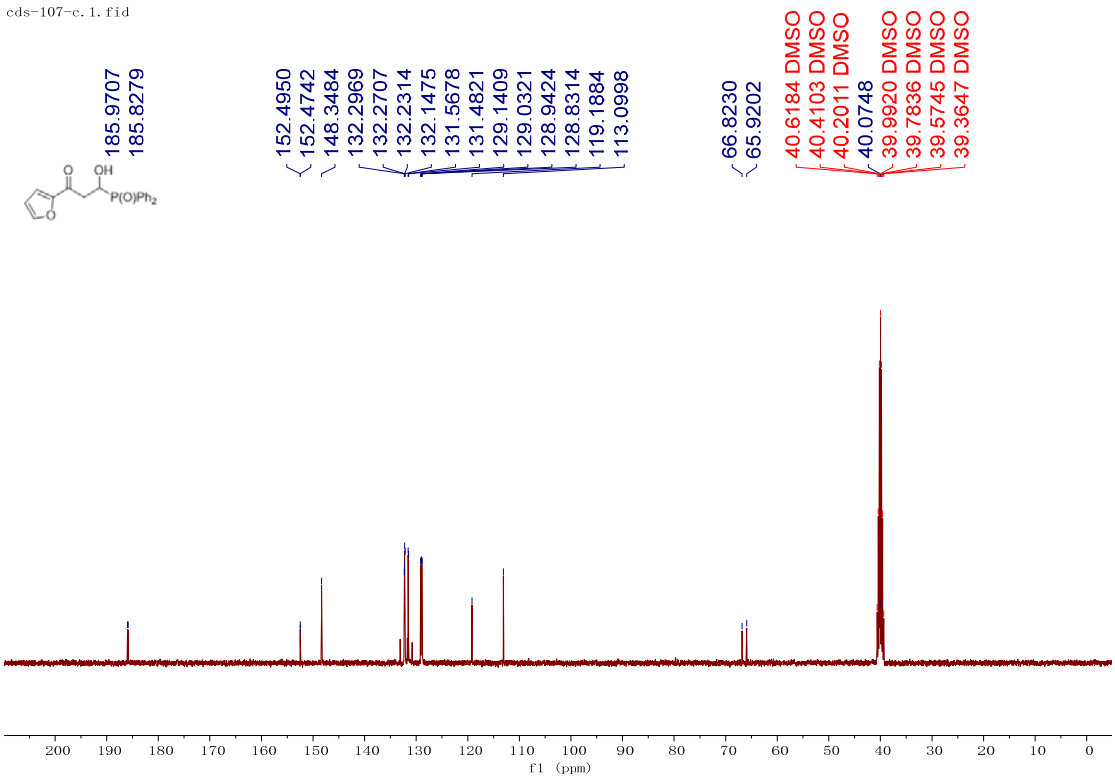
^{13}C NMR spectrum of **3q** (100 MHz, DMSO-d_6)



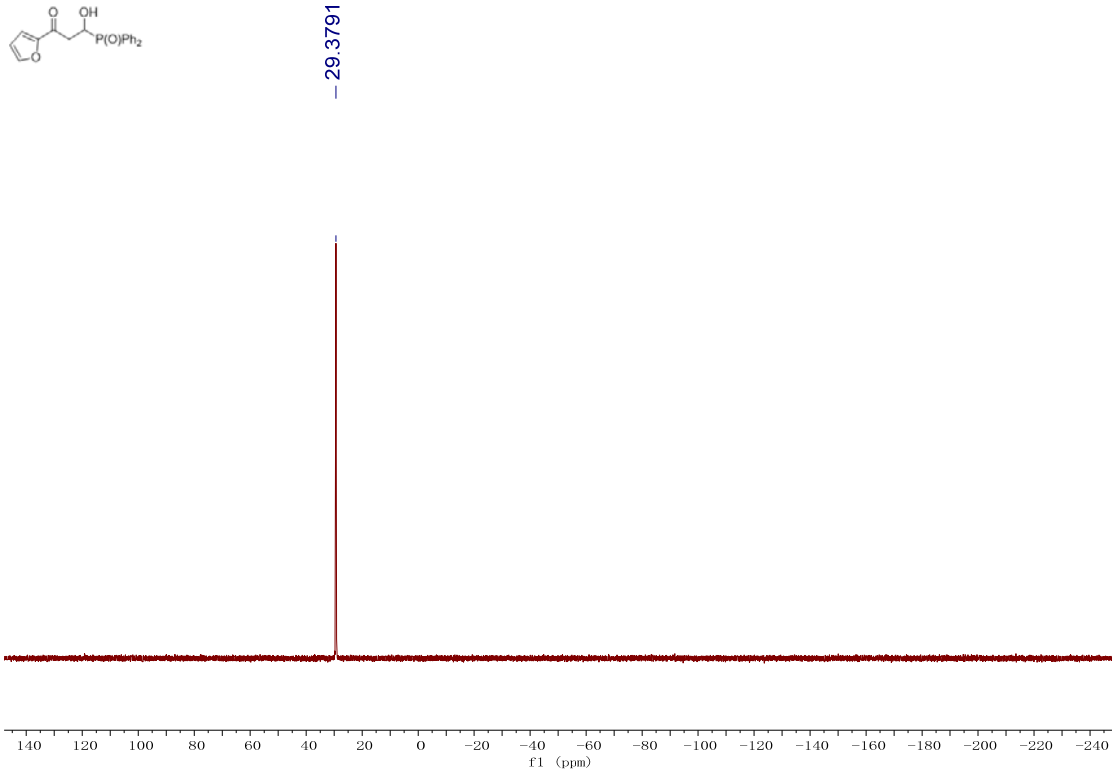
^{31}P NMR spectrum of **3q** (162 MHz, DMSO-d_6)



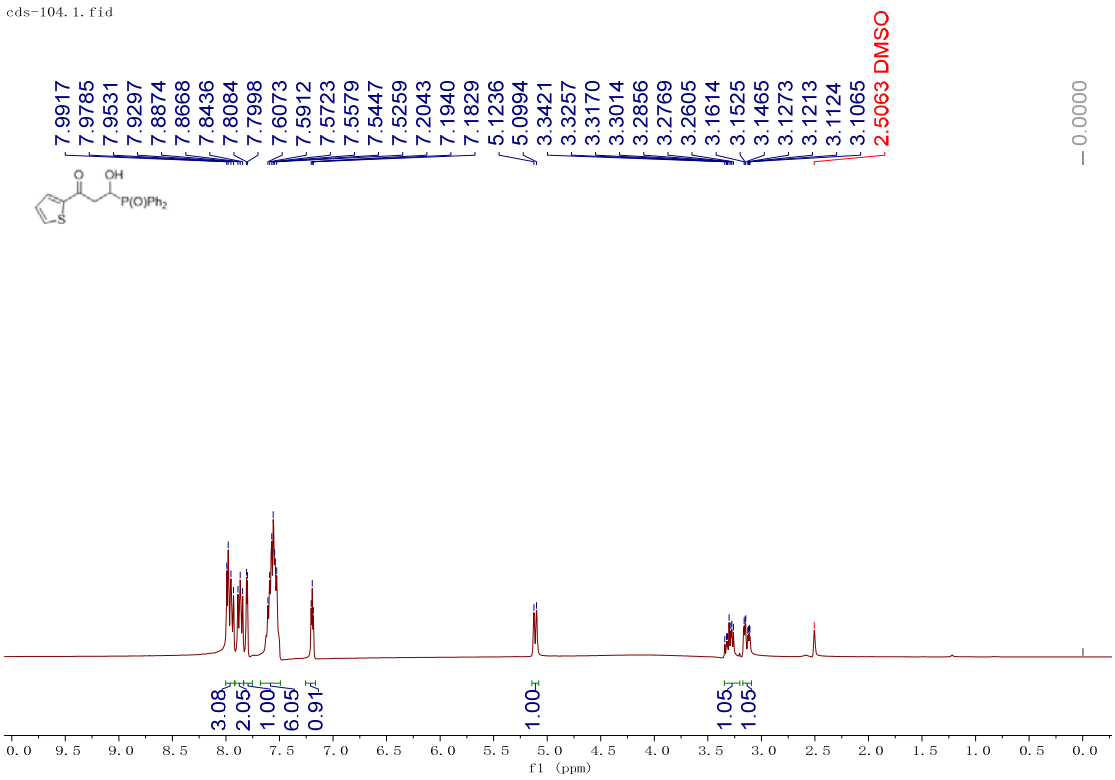
^{1}H NMR spectrum of **3r** (400 MHz, DMSO-d_6)



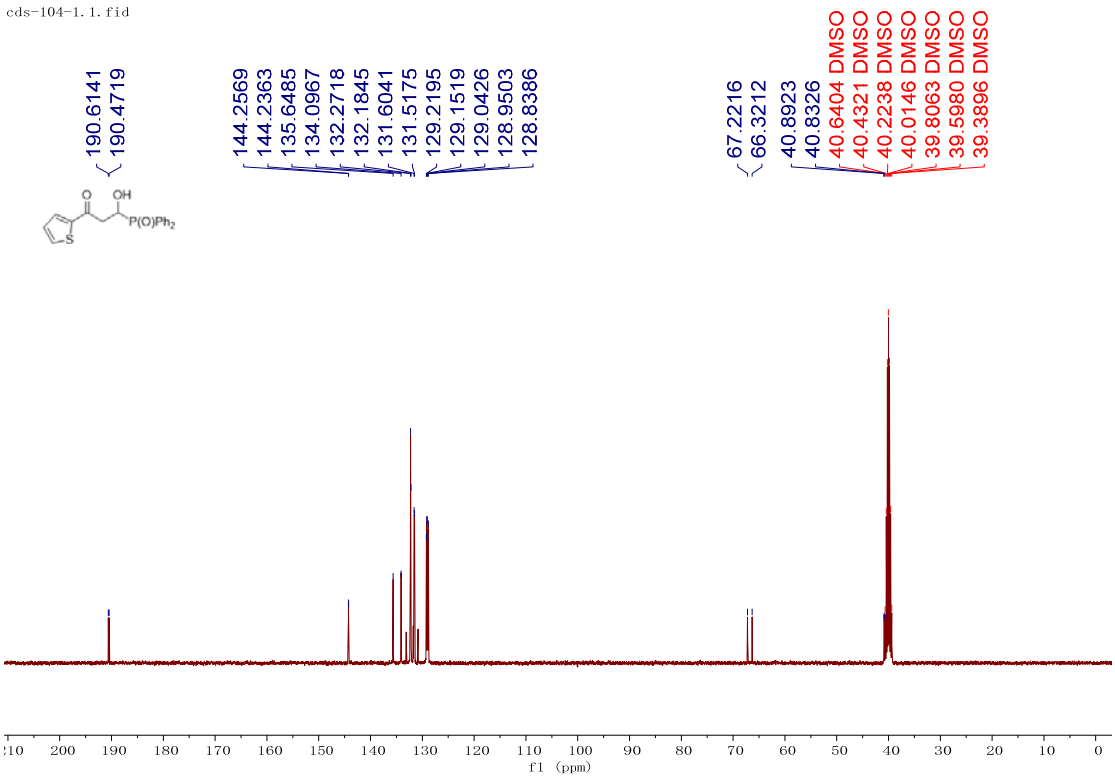
^{13}C NMR spectrum of **3r** (100 MHz, DMSO-d_6)



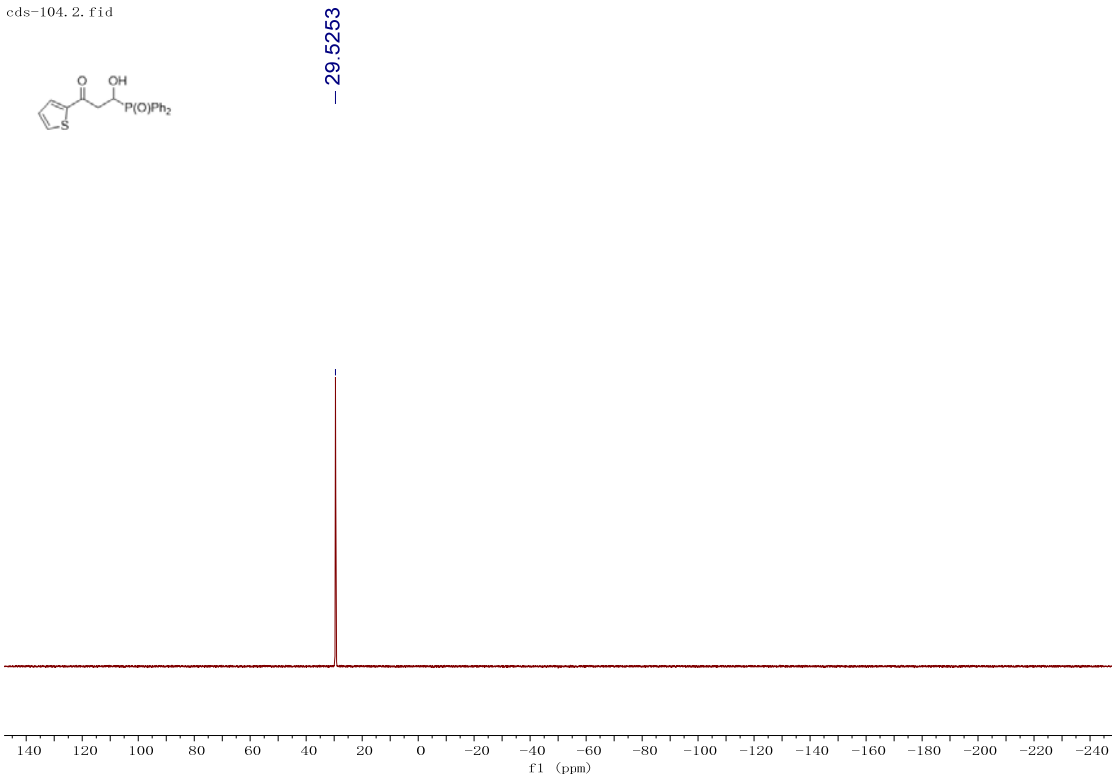
^{31}P NMR spectrum of **3r** (162 MHz, DMSO-d_6)



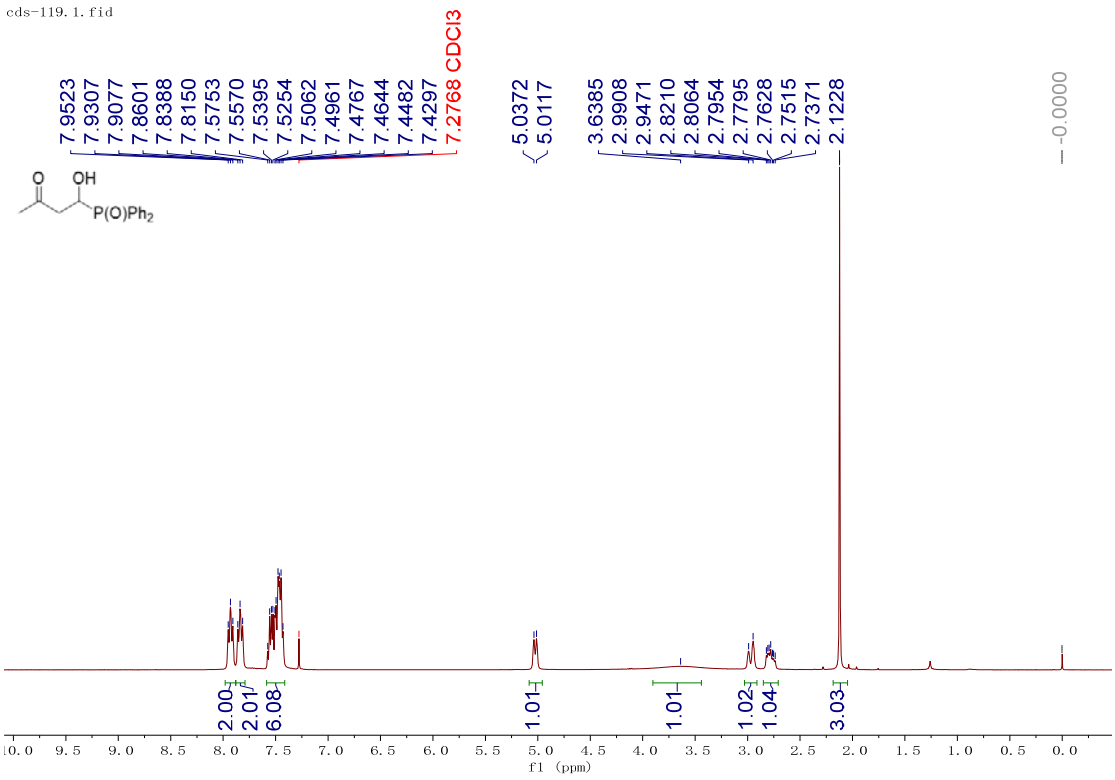
^{1}H NMR spectrum of **3s** (400 MHz, DMSO-d_6)



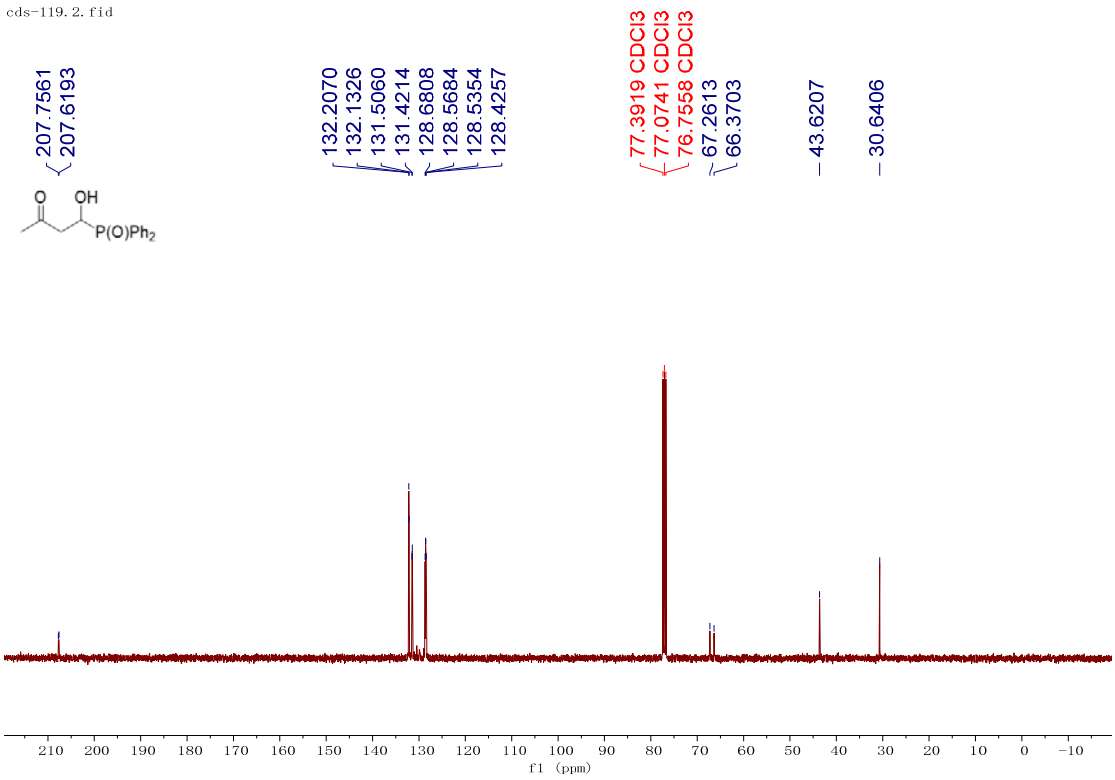
^{13}C NMR spectrum of **3s** (100 MHz, DMSO-d_6)



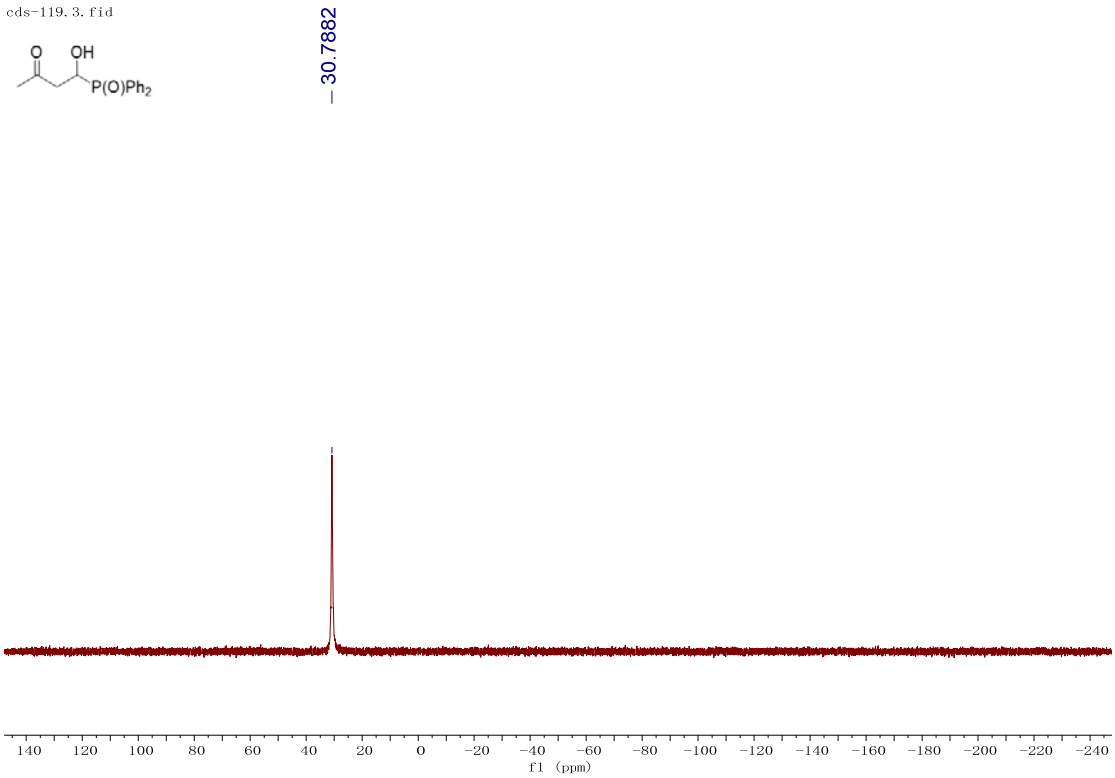
^{31}P NMR spectrum of **3s** (162 MHz, DMSO-d_6)



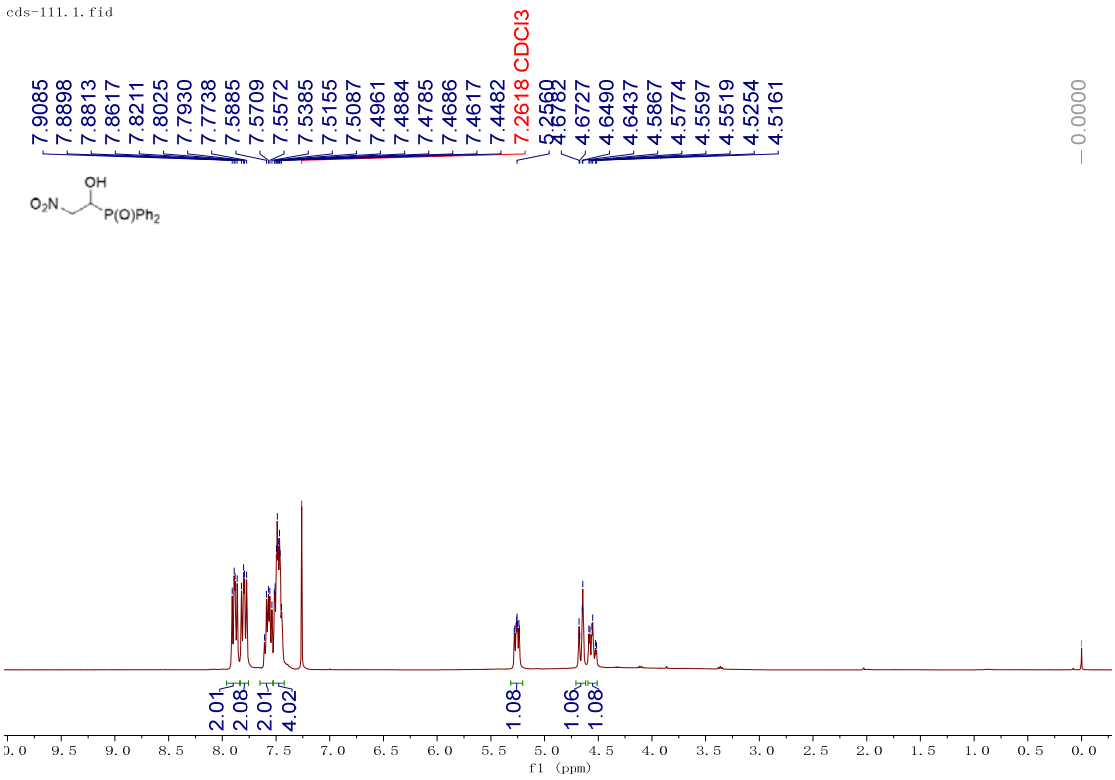
^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$)



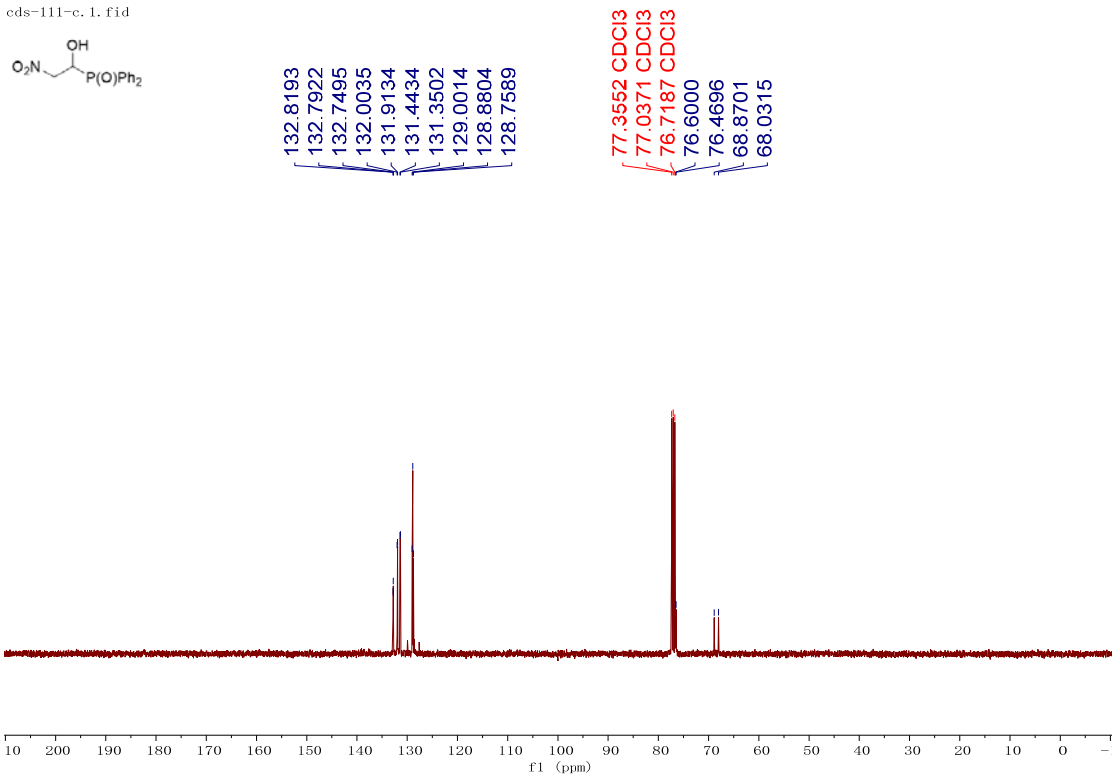
^{13}C NMR spectrum of **3t** (100 MHz, $CDCl_3$)



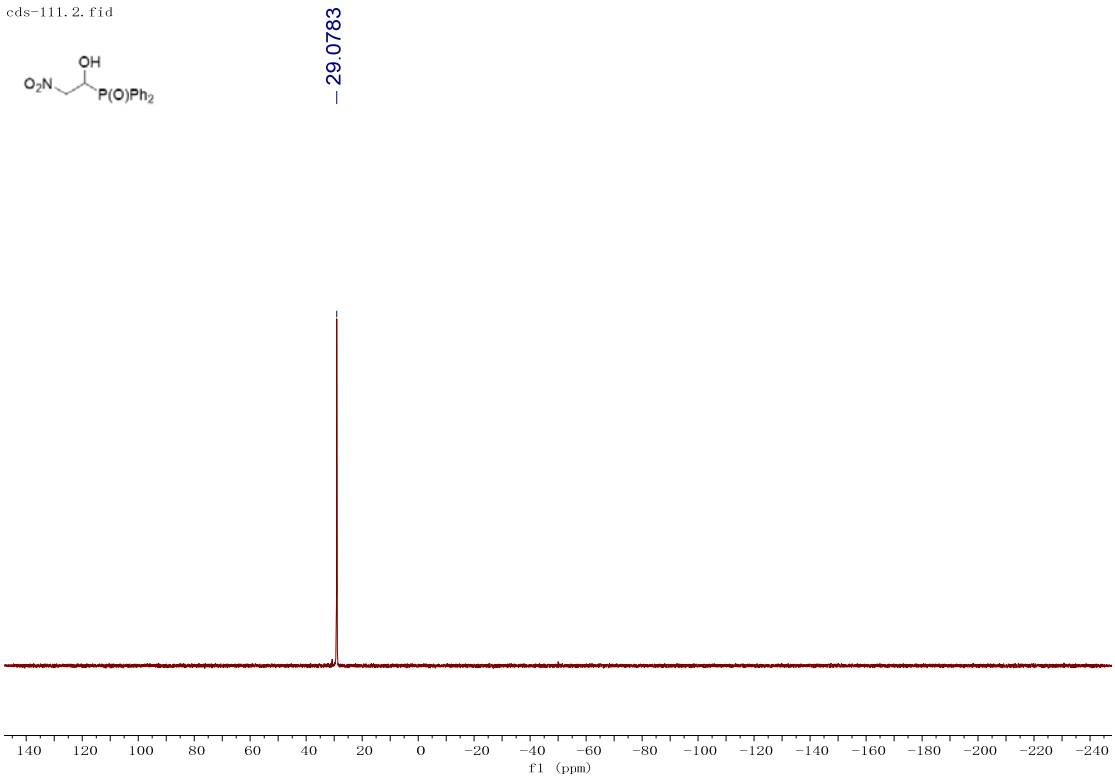
^{31}P NMR spectrum of **3t** (162 MHz, $CDCl_3$)



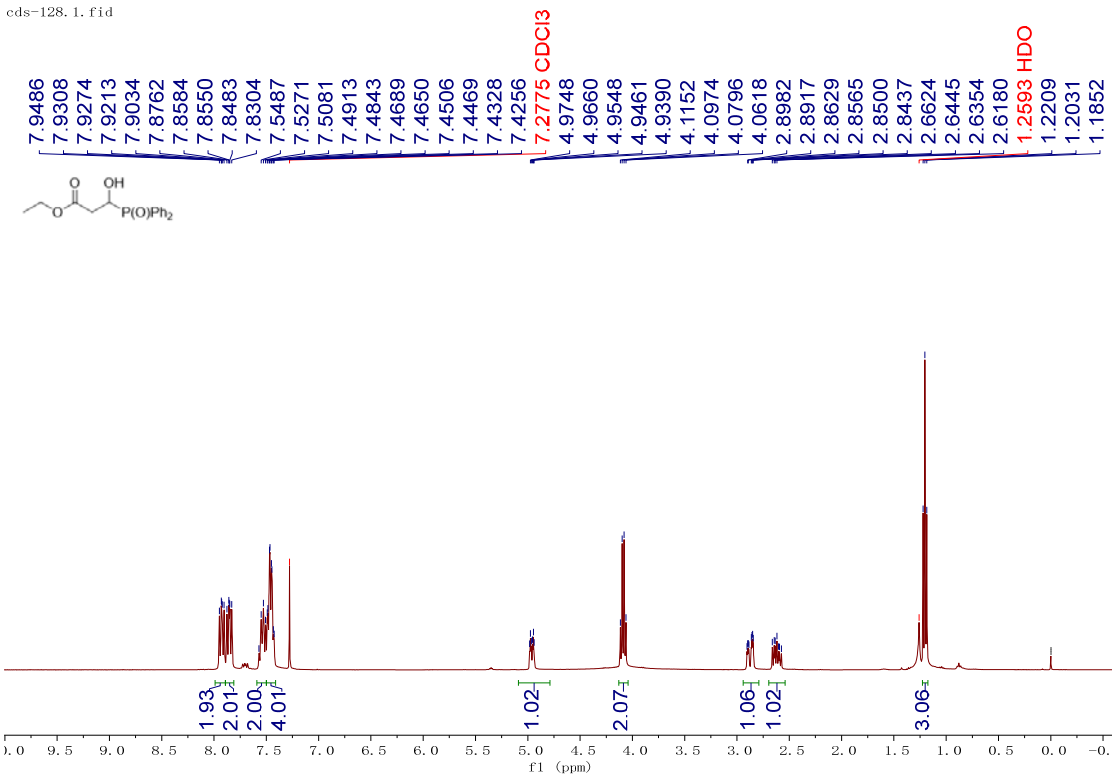
^{1}H NMR spectrum of **3u** (400 MHz, $CDCl_3$)



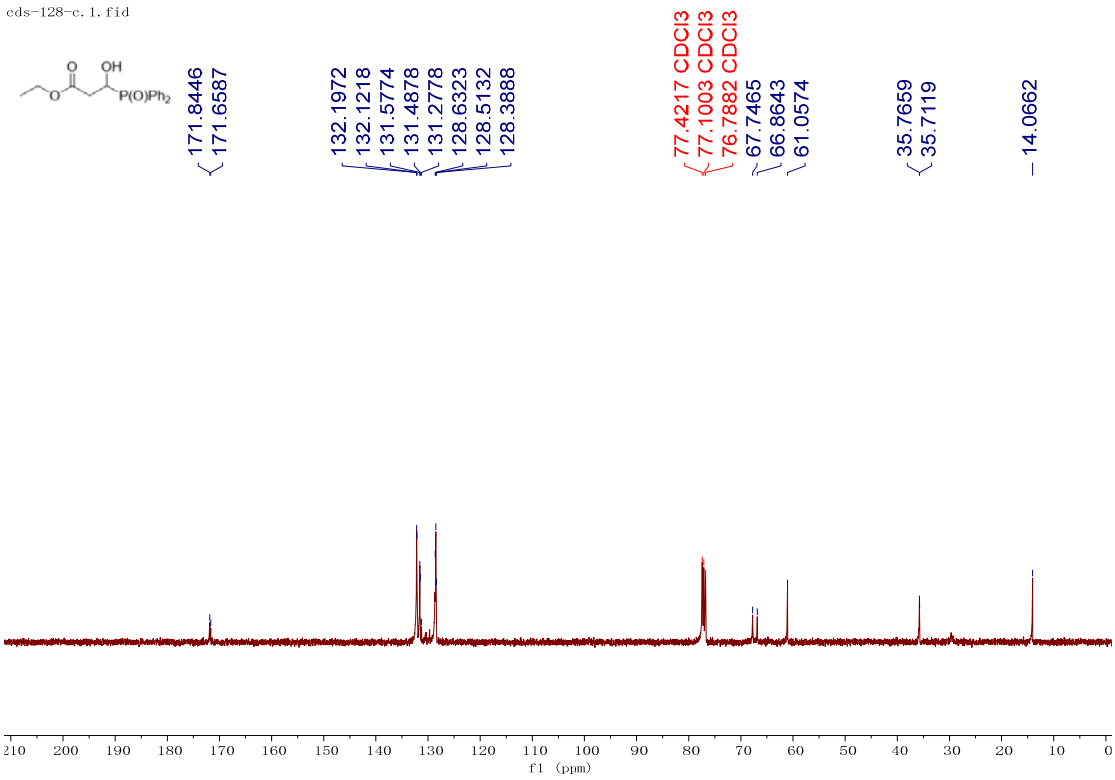
^{13}C NMR spectrum of **3u** (100 MHz, $CDCl_3$)



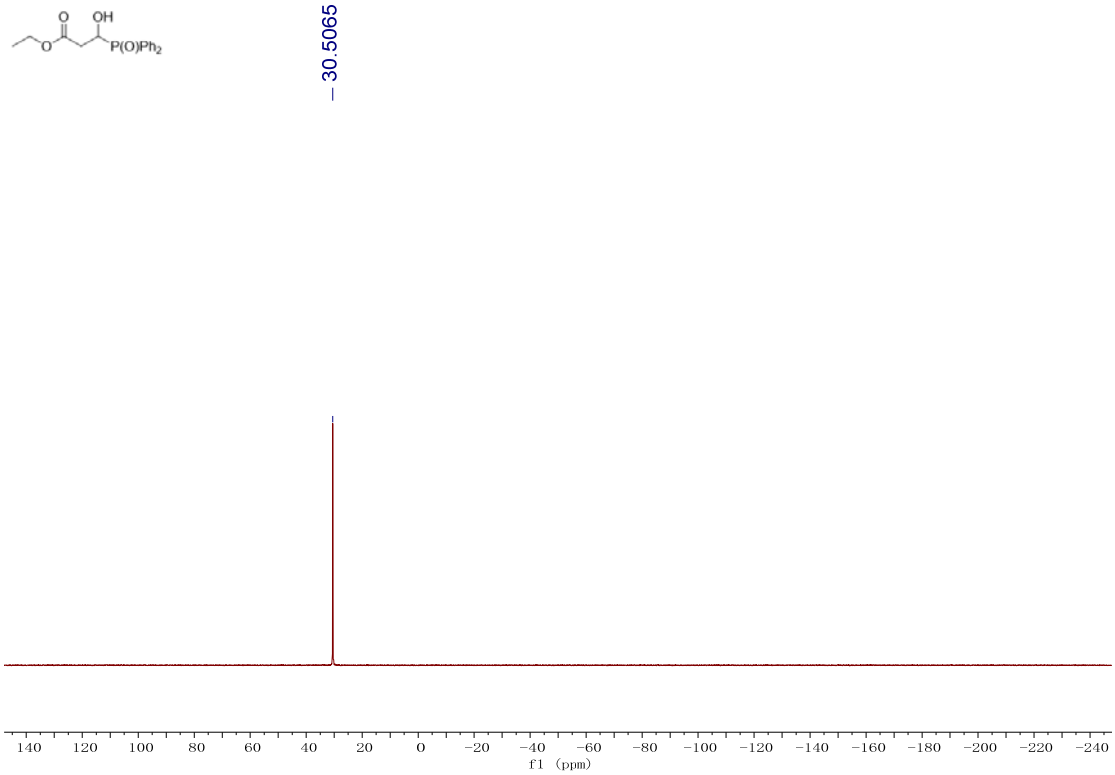
^{31}P NMR spectrum of **3u** (162 MHz, $CDCl_3$)



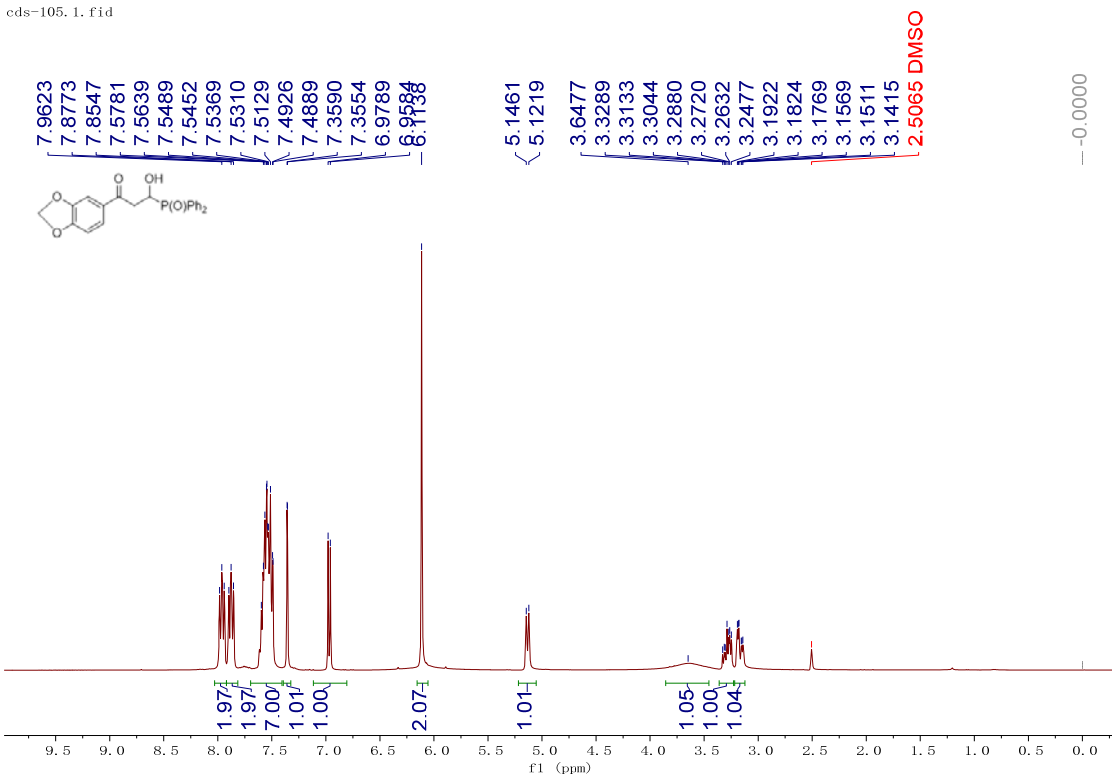
^{1}H NMR spectrum of **3v** (400 MHz, $CDCl_3$)



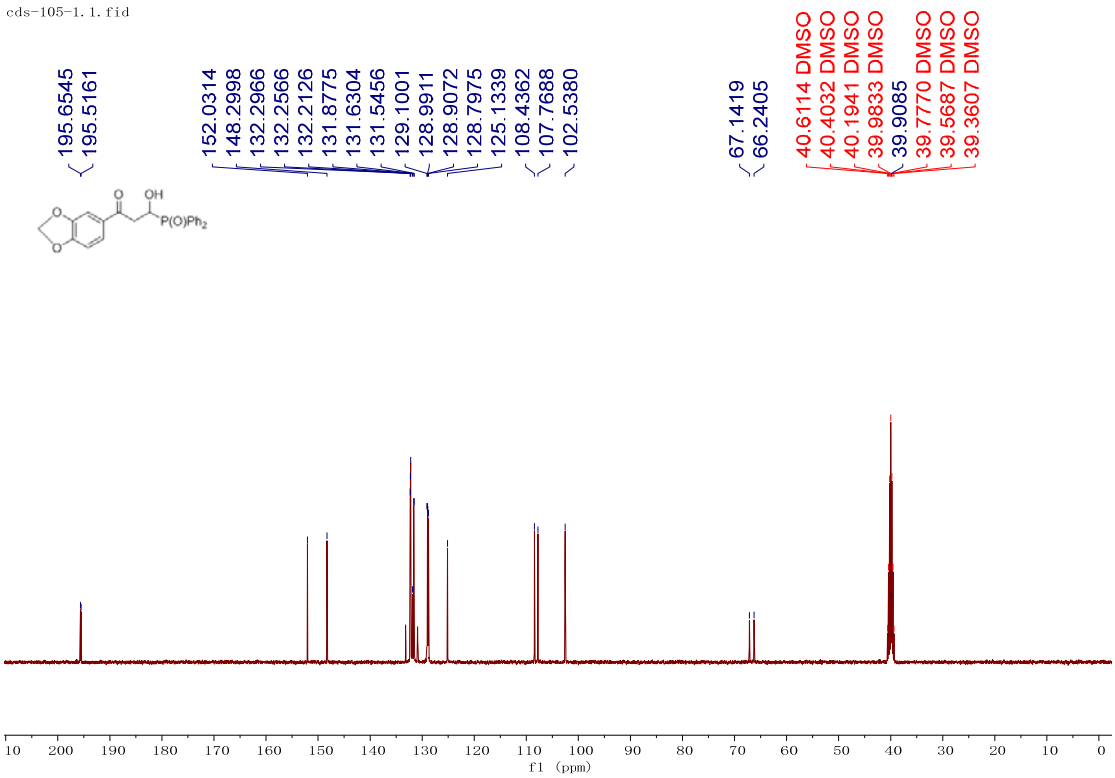
^{13}C NMR spectrum of **3v** (100 MHz, $CDCl_3$)



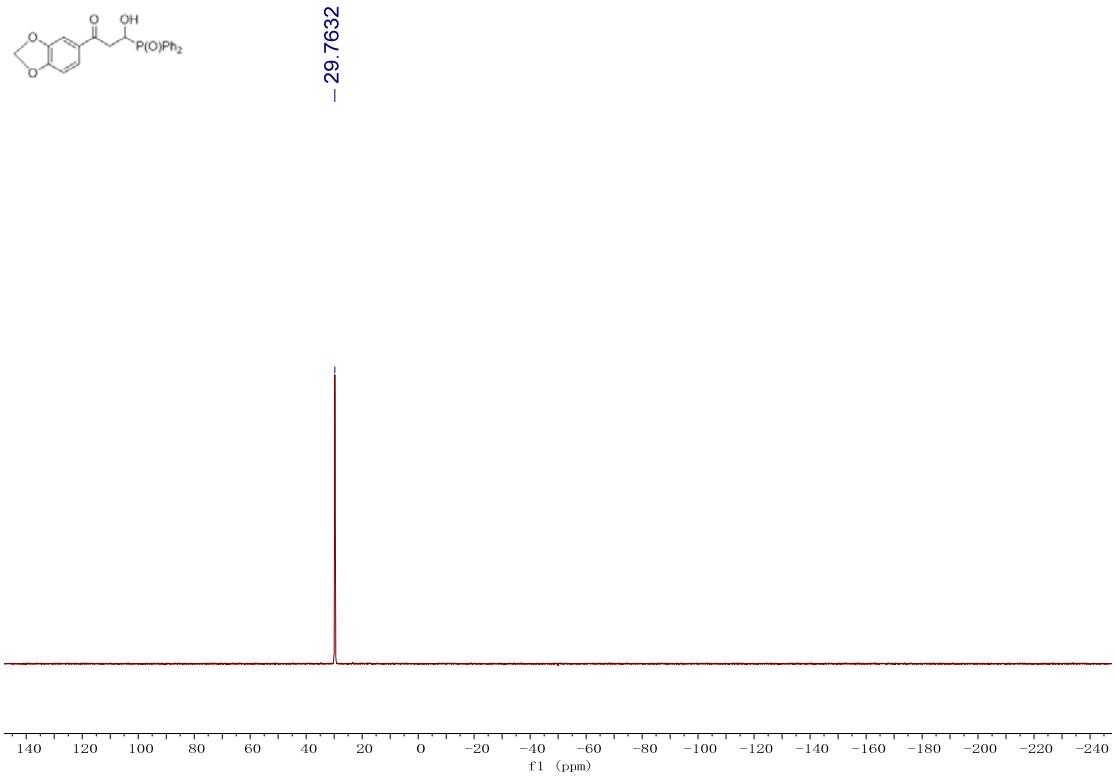
^{31}P NMR spectrum of **3v** (162 MHz, $CDCl_3$)



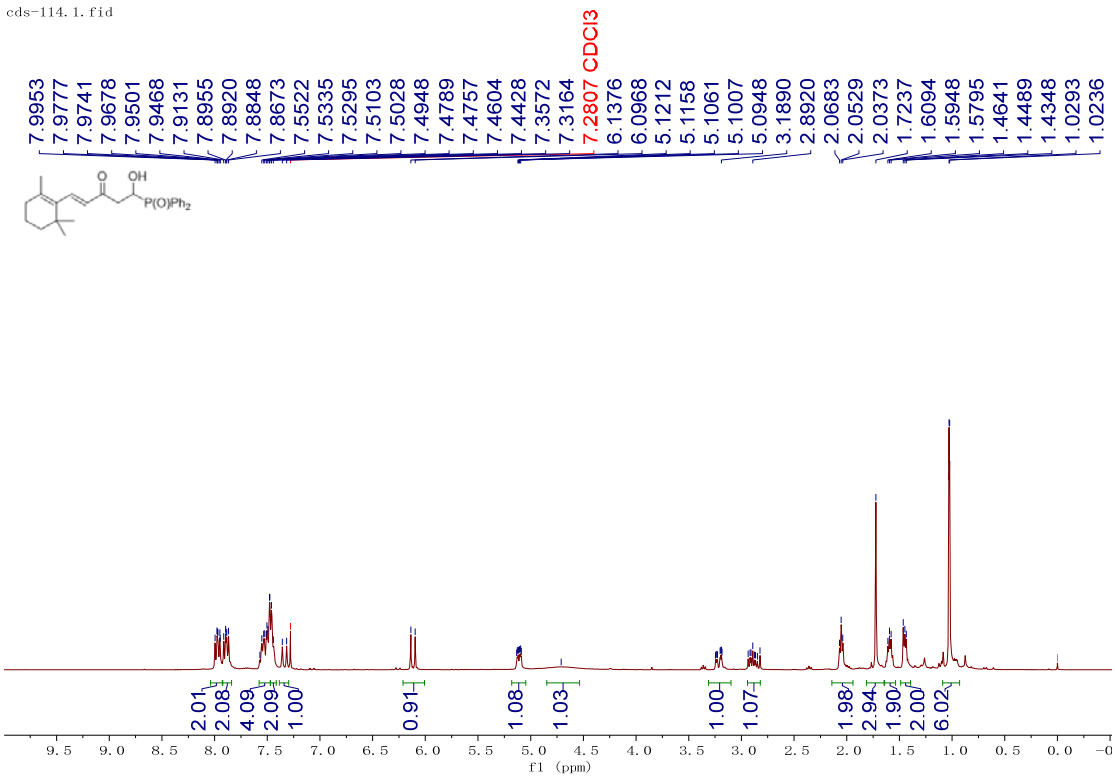
^{1}H NMR spectrum of **3w** (400 MHz, DMSO-d_6)



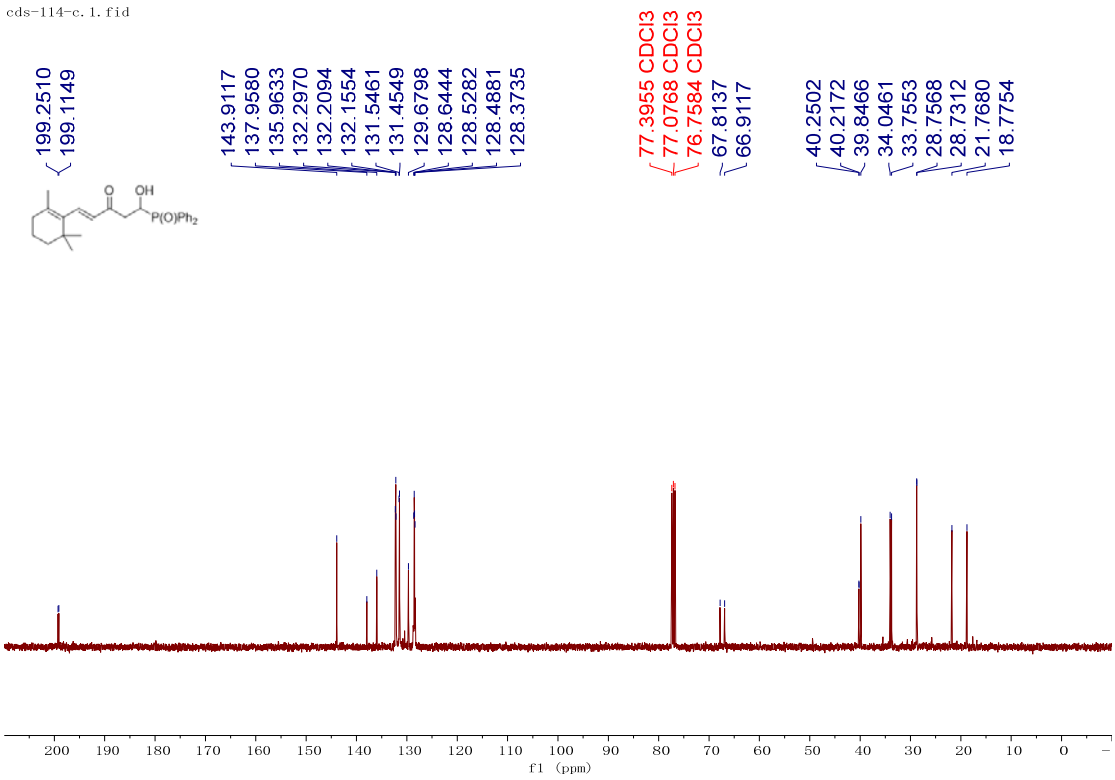
^{13}C NMR spectrum of **3w** (100 MHz, DMSO-d_6)



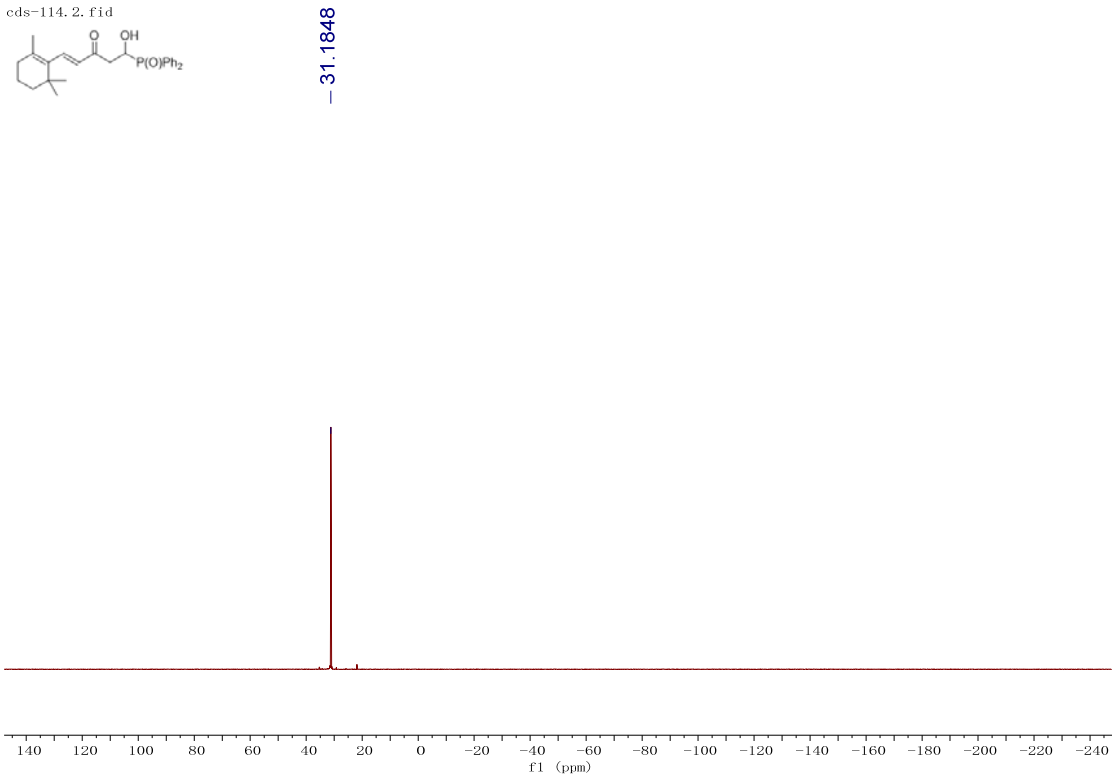
^{31}P NMR spectrum of **3w** (162 MHz, DMSO-d_6)



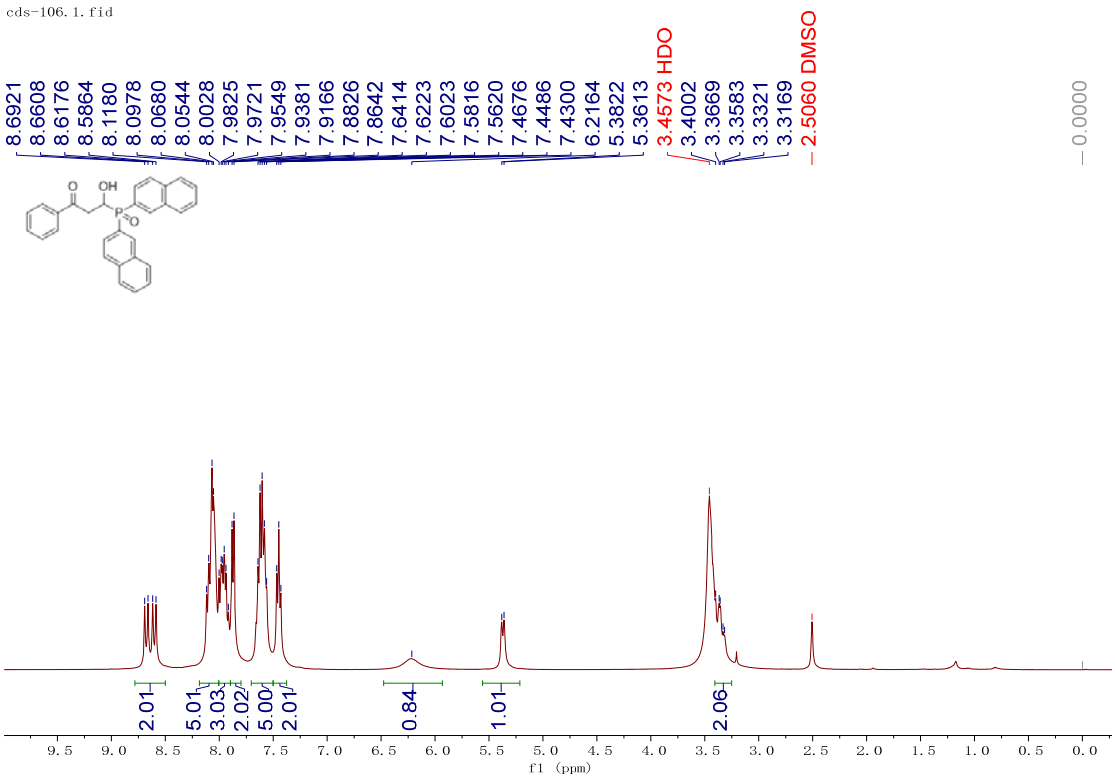
^{1}H NMR spectrum of **3x** (400 MHz, $CDCl_3$)



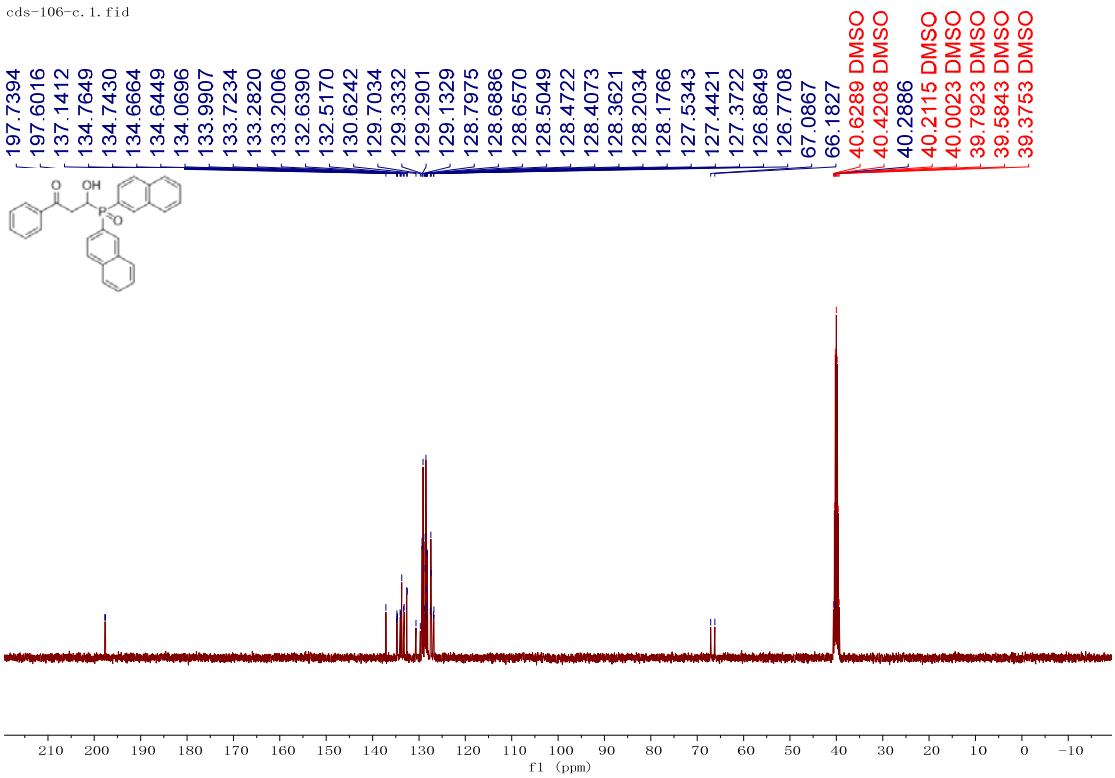
^{13}C NMR spectrum of **3x** (100 MHz, $CDCl_3$)



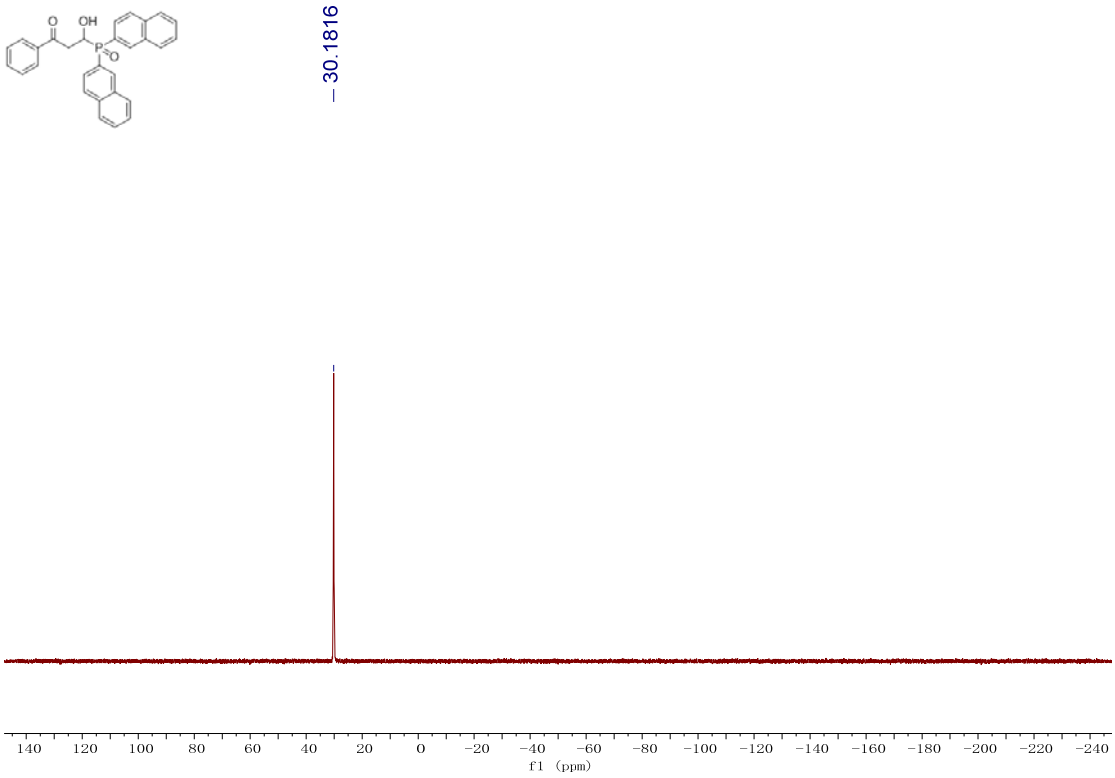
^{31}P NMR spectrum of **3x** (162 MHz, $CDCl_3$)



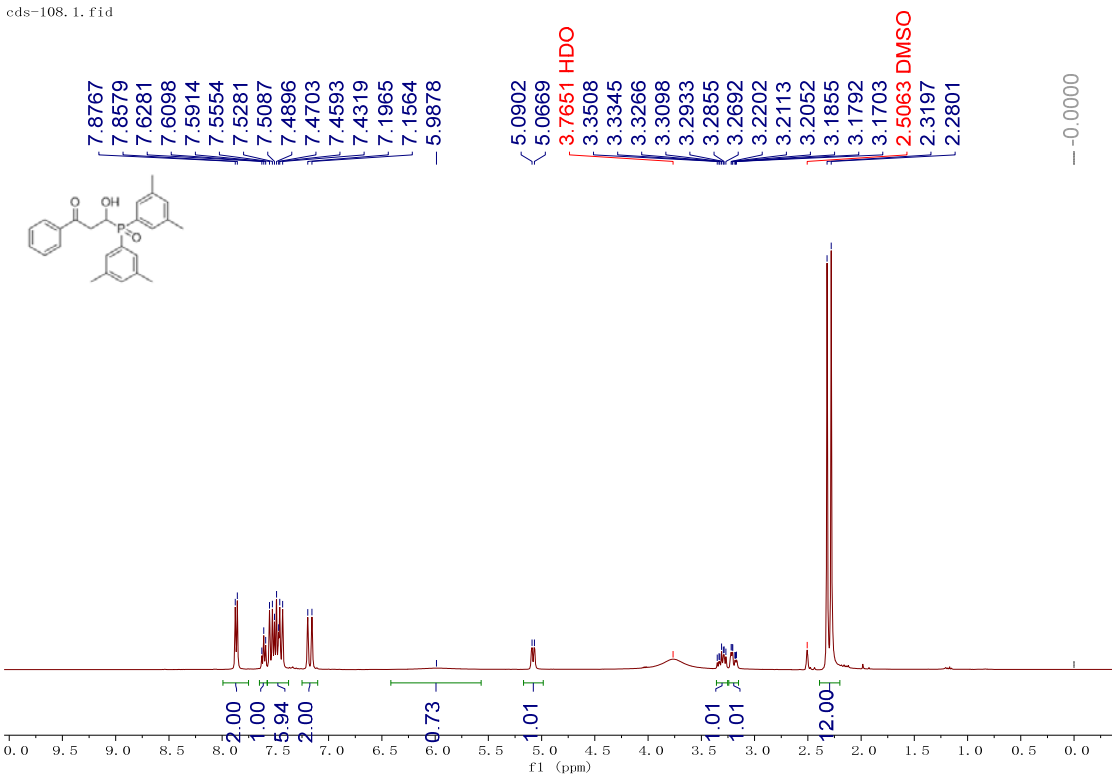
^{1}H NMR spectrum of **3aa** (400 MHz, DMSO-d_6)



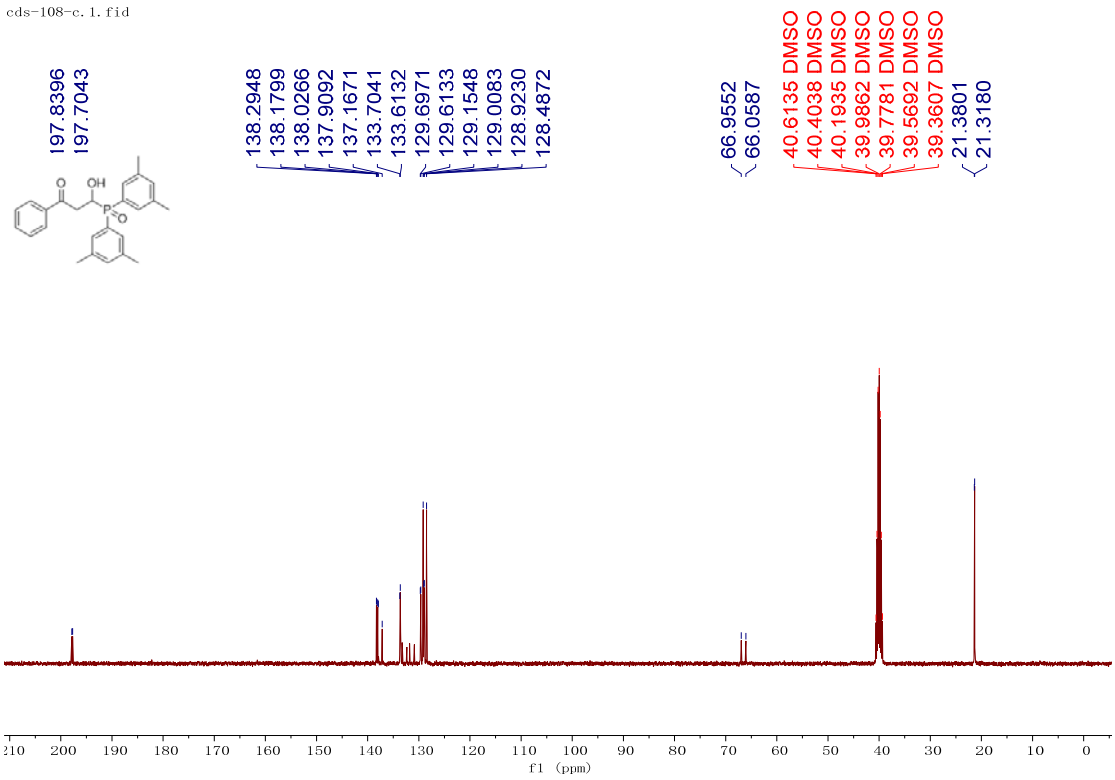
^{13}C NMR spectrum of **3aa** (100 MHz, DMSO-d_6)



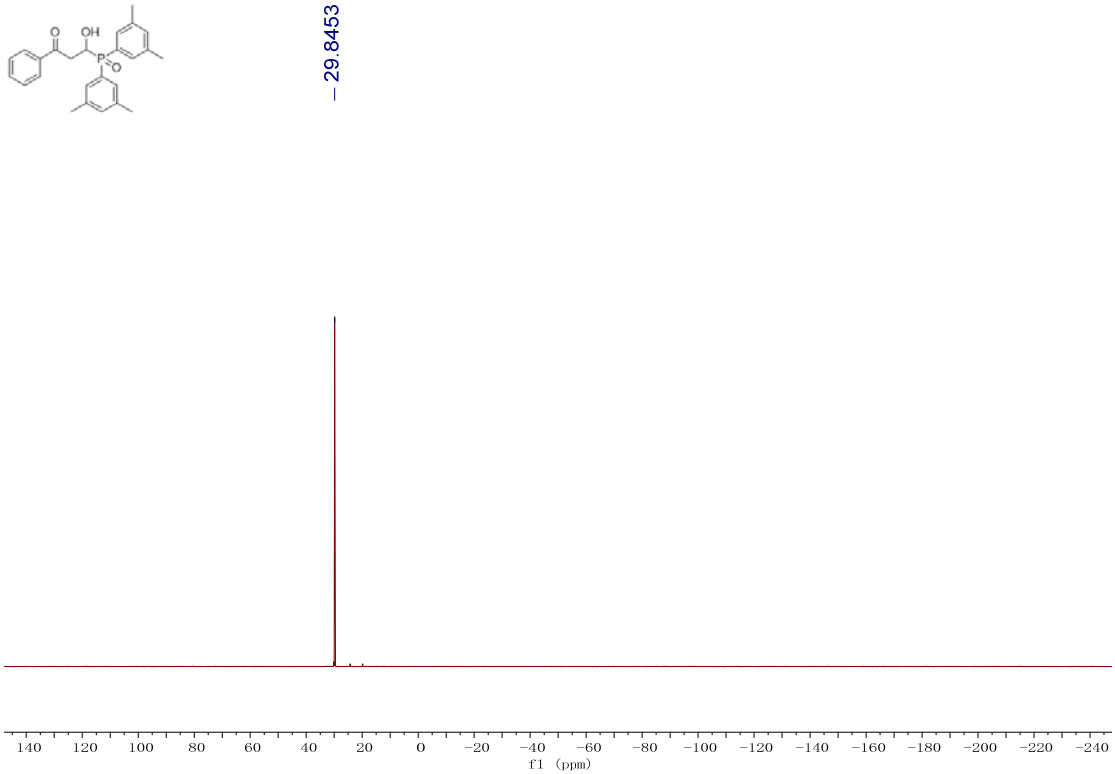
^{31}P NMR spectrum of **3aa** (162 MHz, DMSO-d_6)



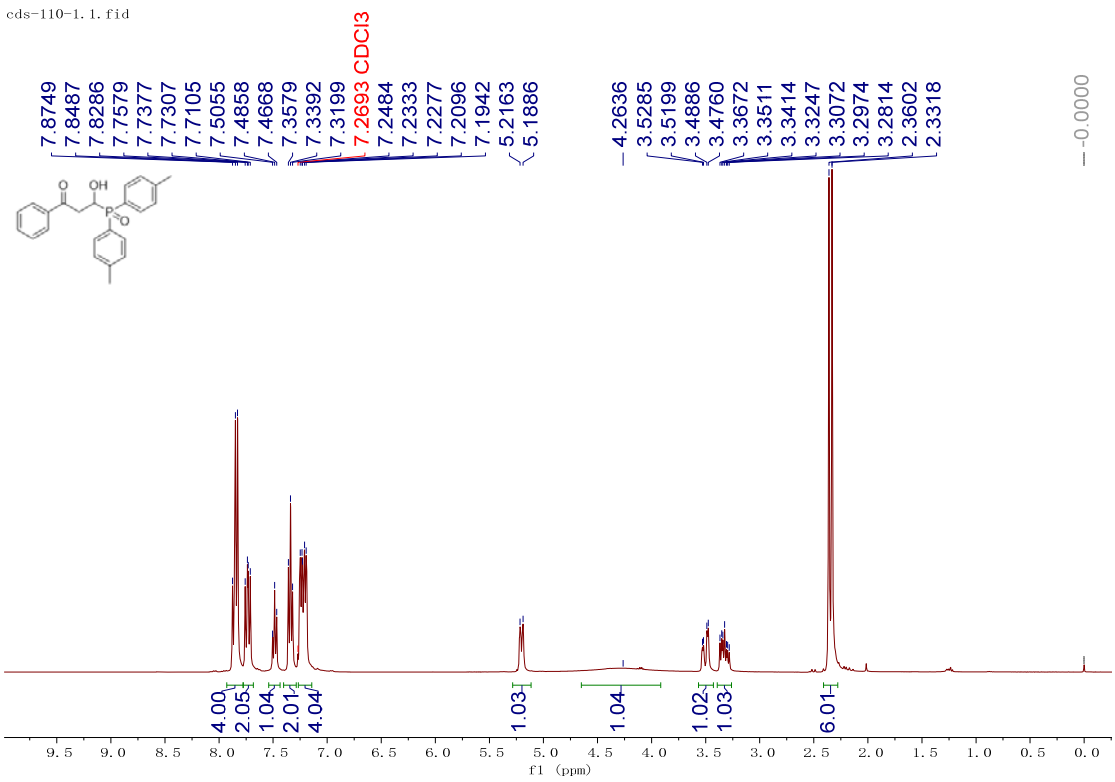
^{1}H NMR spectrum of **3ab** (400 MHz, DMSO-d_6)



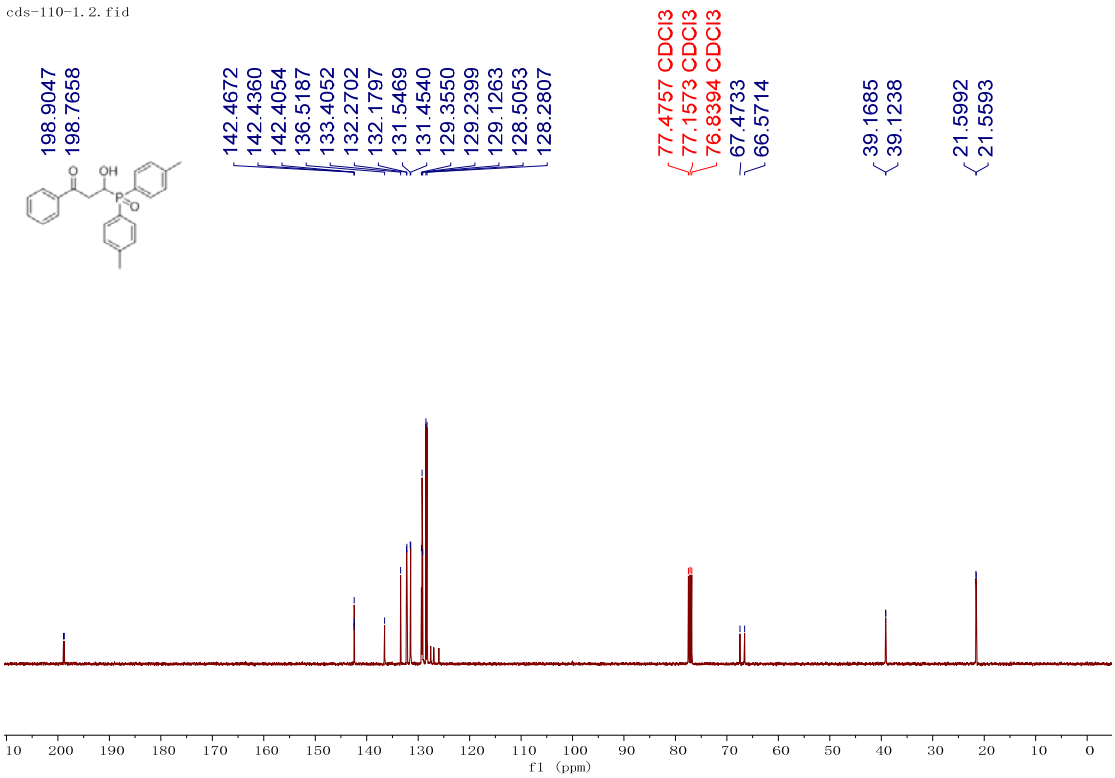
^{13}C NMR spectrum of **3ab** (100 MHz, DMSO-d_6)



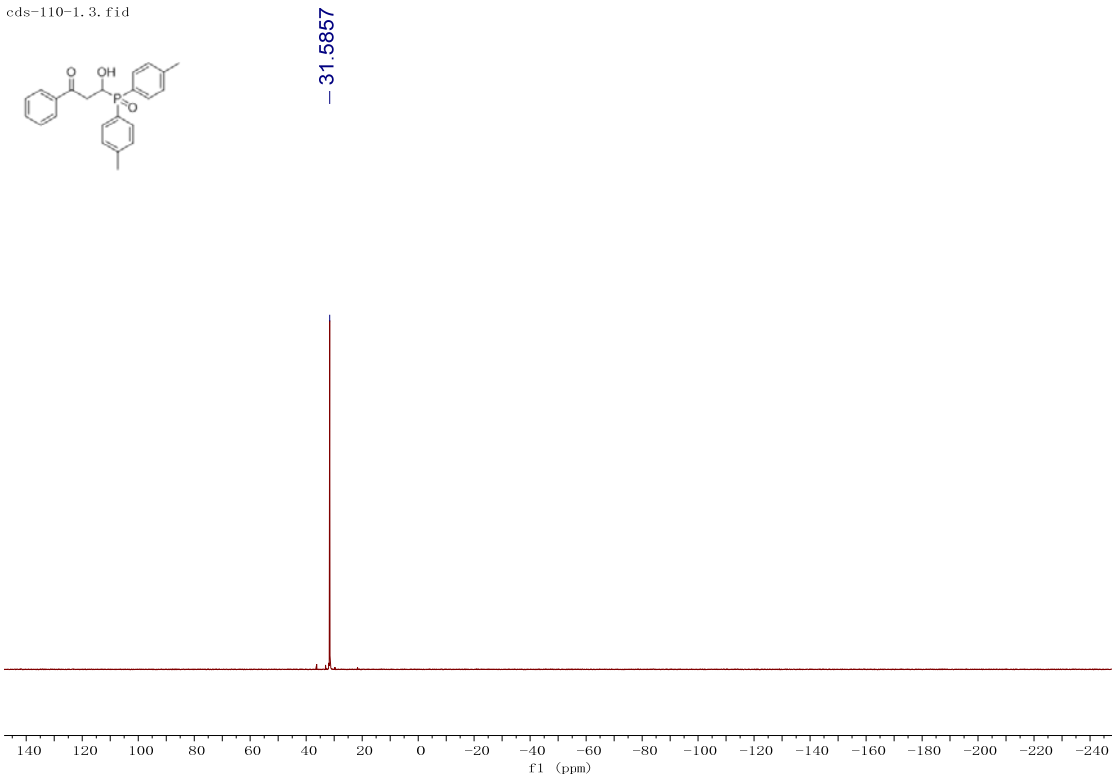
^{31}P NMR spectrum of **3ab** (162 MHz, DMSO-d_6)



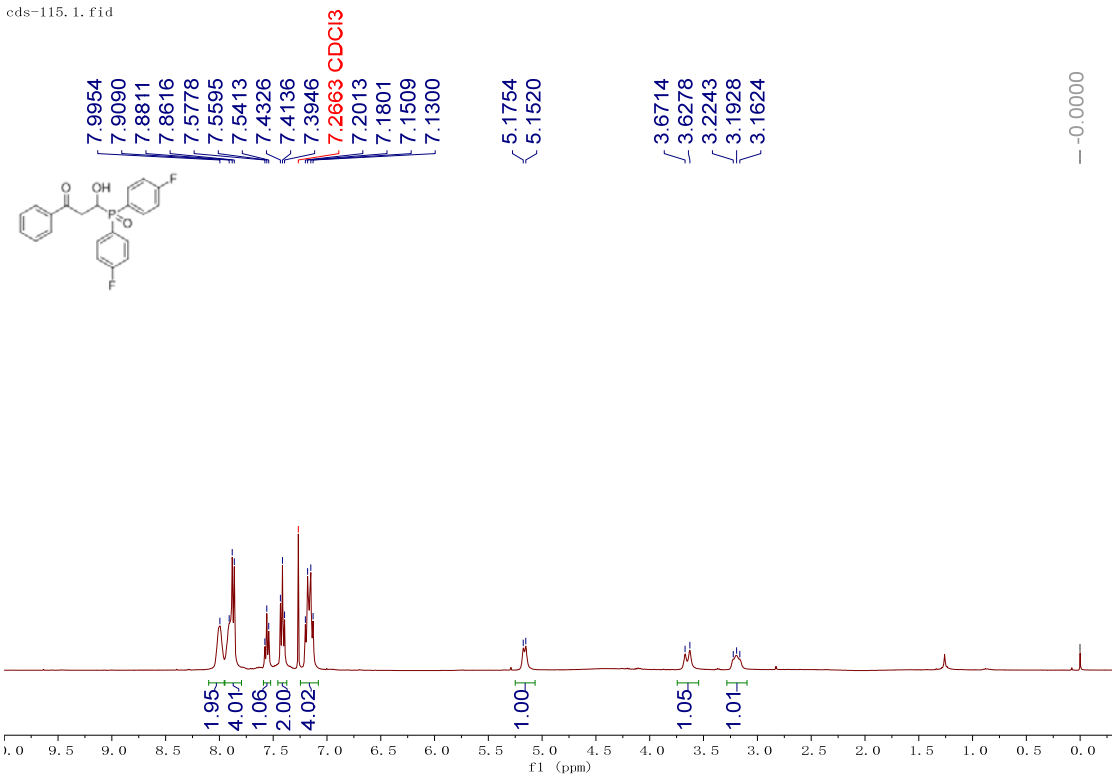
^{1}H NMR spectrum of **3ac** (400 MHz, $CDCl_3$)



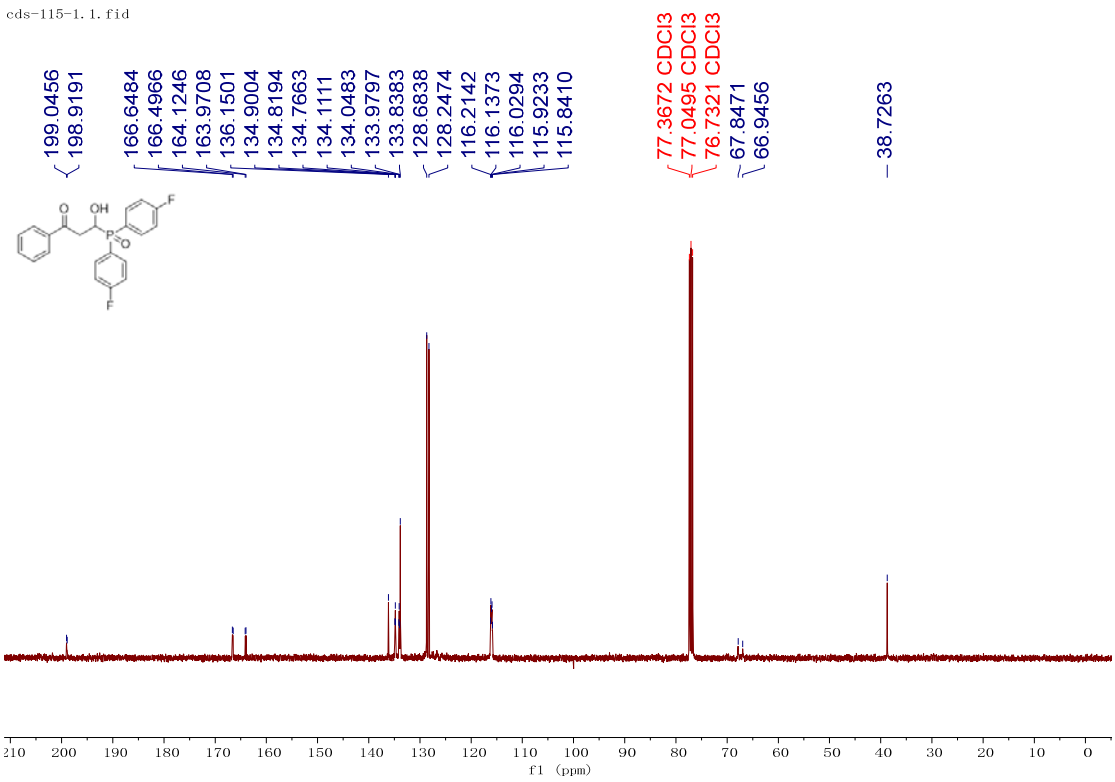
^{13}C NMR spectrum of **3ac** (100 MHz, $CDCl_3$)



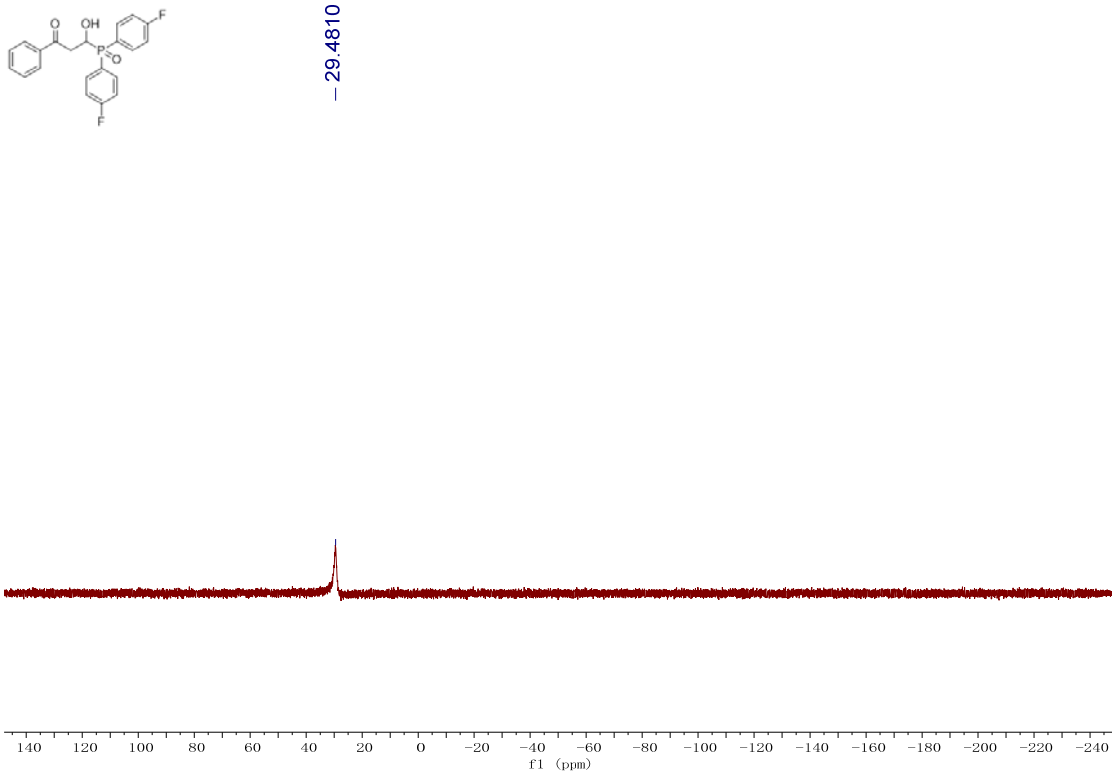
^{31}P NMR spectrum of **3ac** (162 MHz, $CDCl_3$)



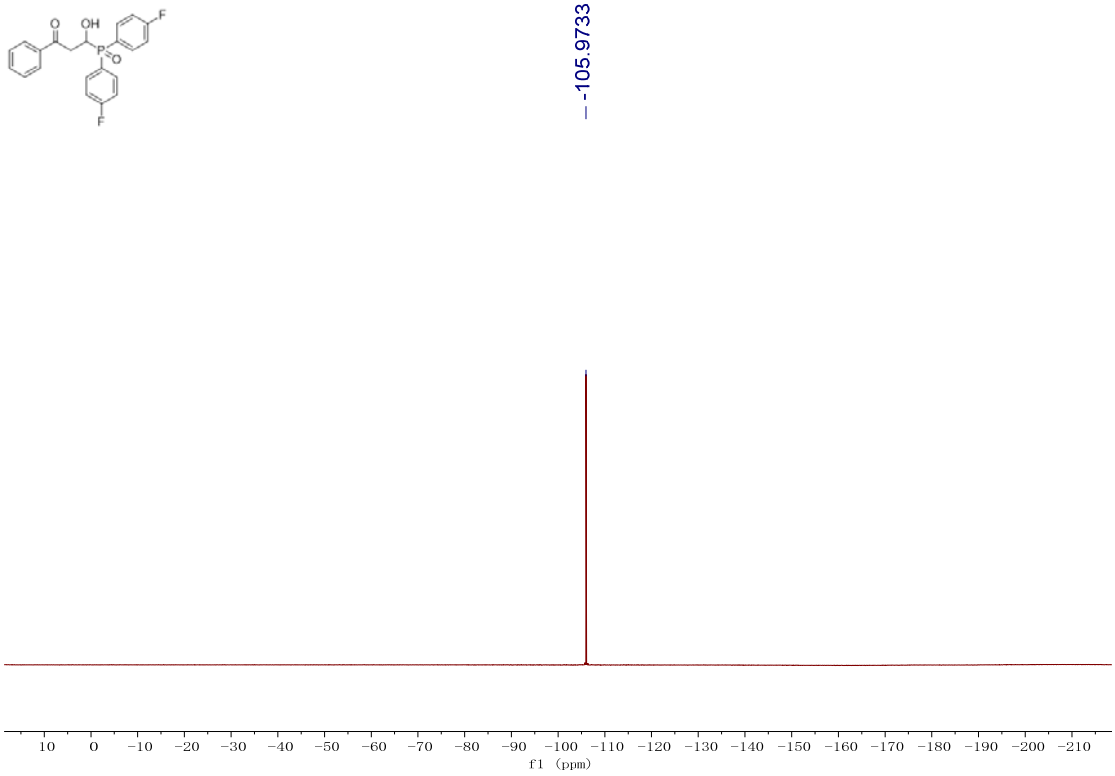
^{1}H NMR spectrum of **3ad** (400 MHz, $CDCl_3$)



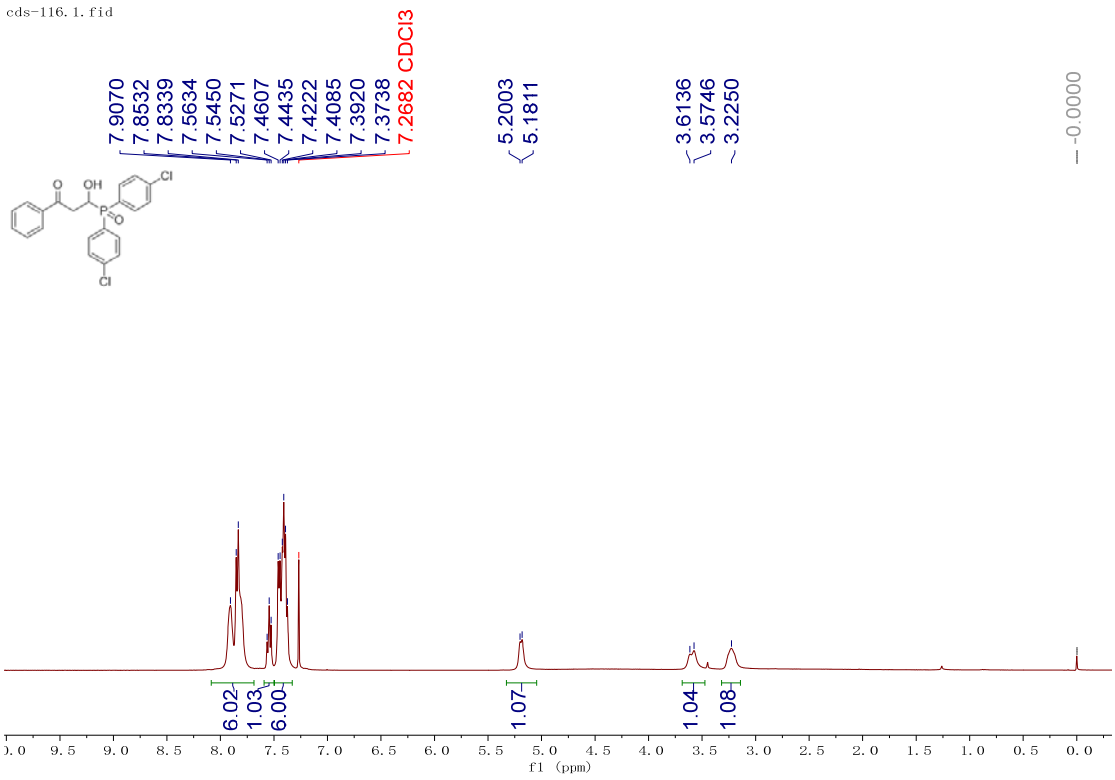
^{13}C NMR spectrum of **3ad** (100 MHz, $CDCl_3$)



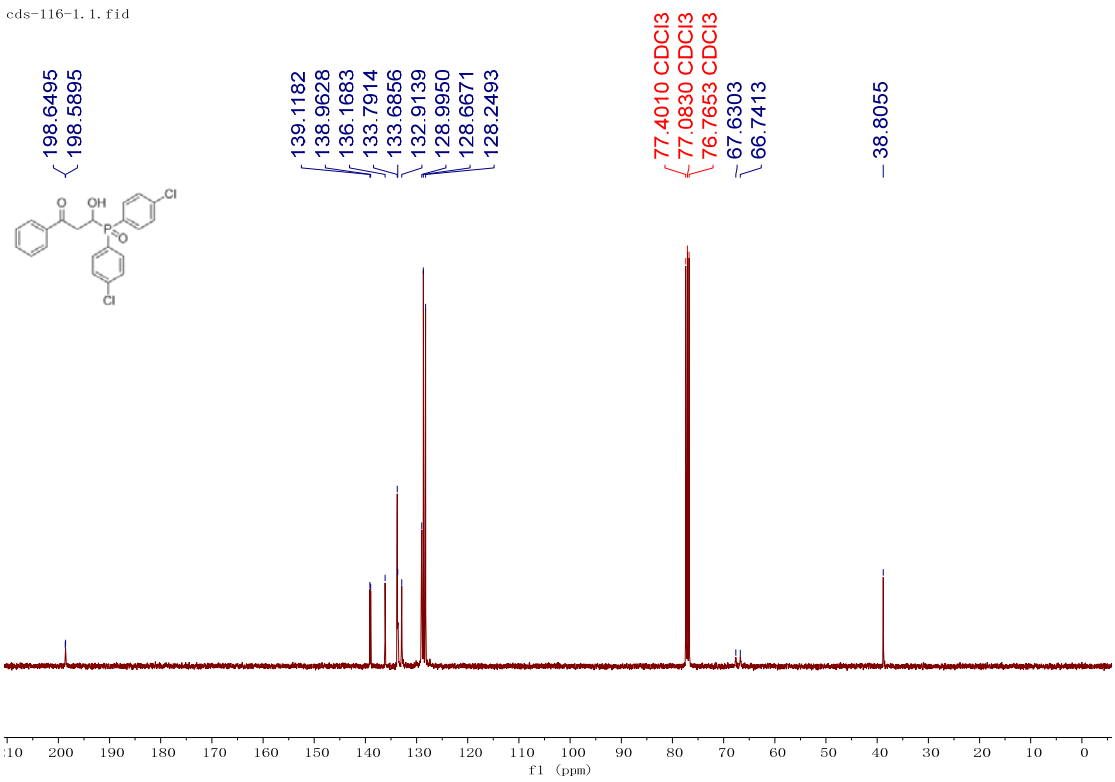
^{31}P NMR spectrum of **3ad** (162 MHz, $CDCl_3$)



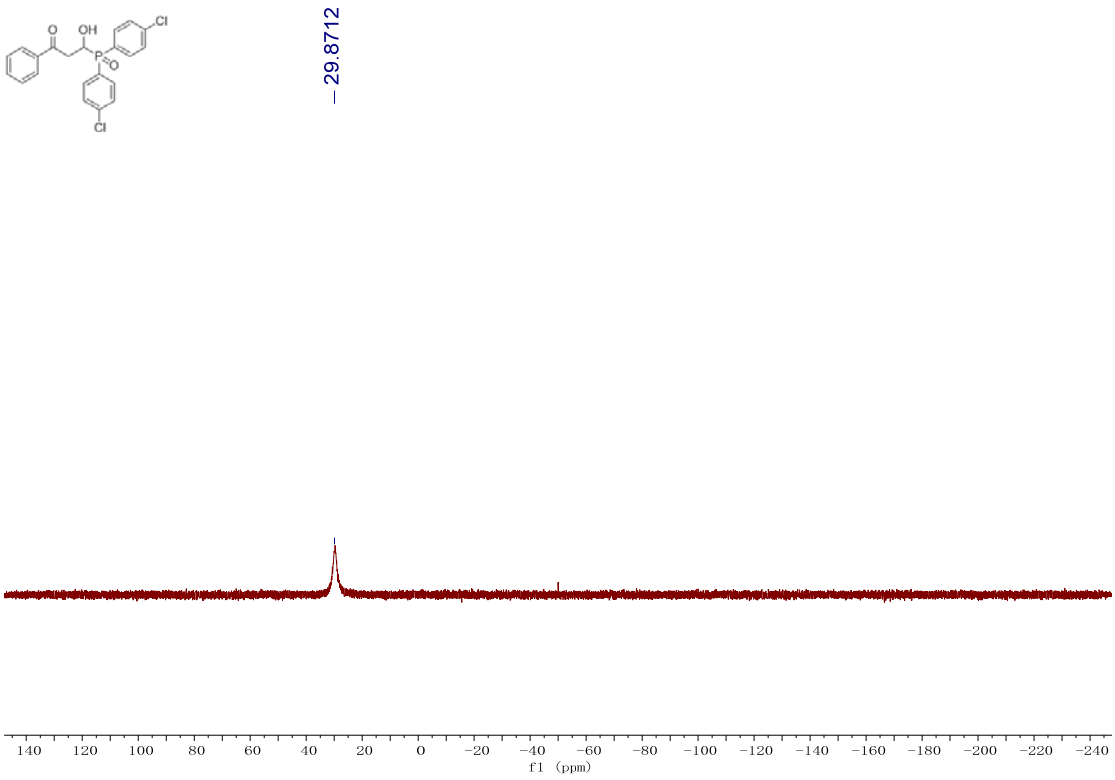
^{19}F NMR spectrum of **3ad** (376 MHz, $CDCl_3$)



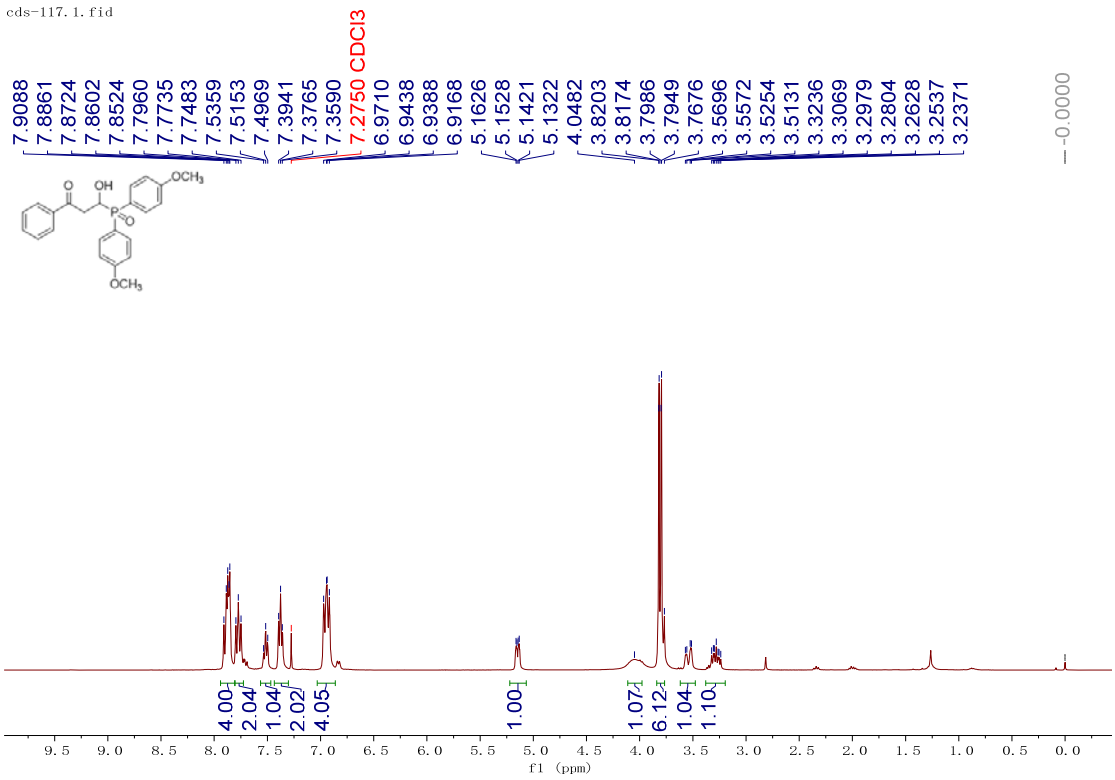
^{1}H NMR spectrum of **3ae** (400 MHz, $CDCl_3$)



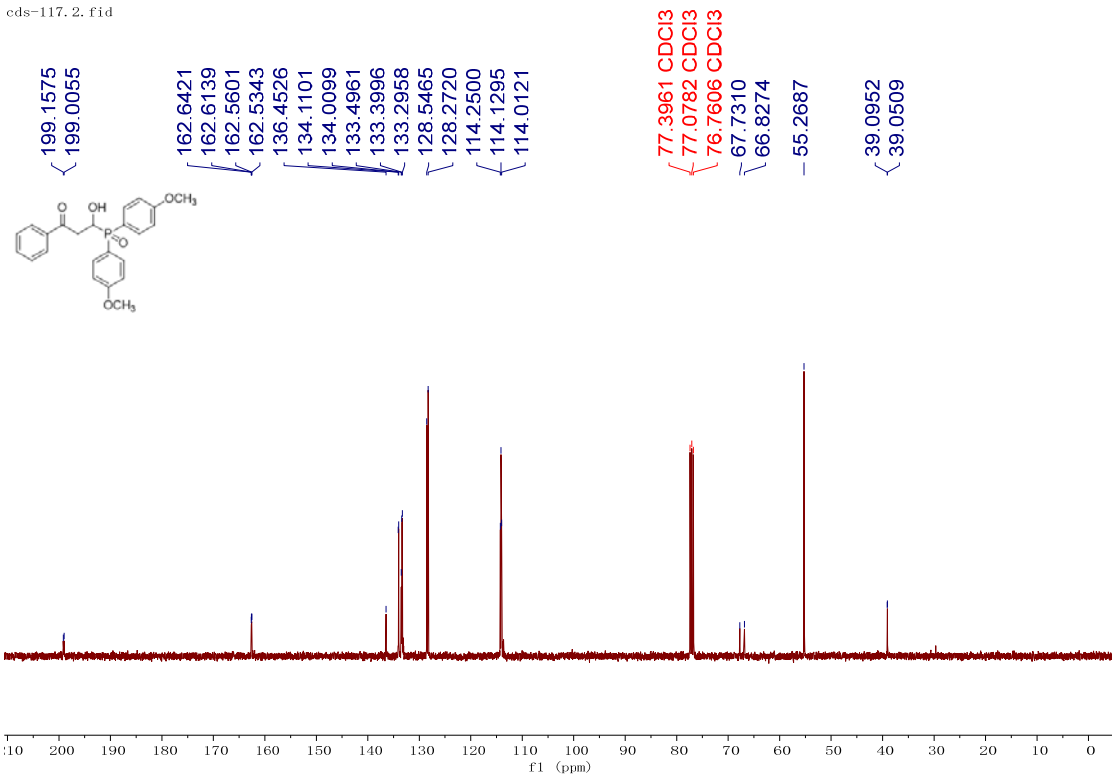
^{13}C NMR spectrum of **3ae** (100 MHz, $CDCl_3$)



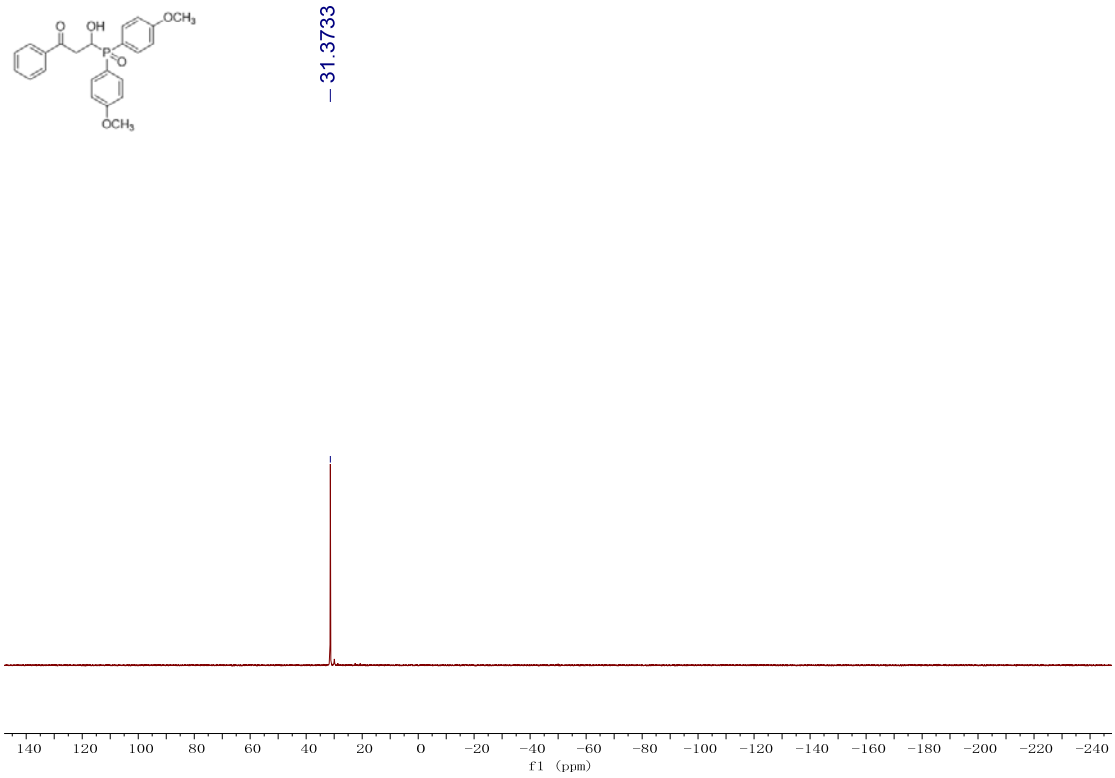
^{31}P NMR spectrum of **3ae** (162 MHz, $CDCl_3$)



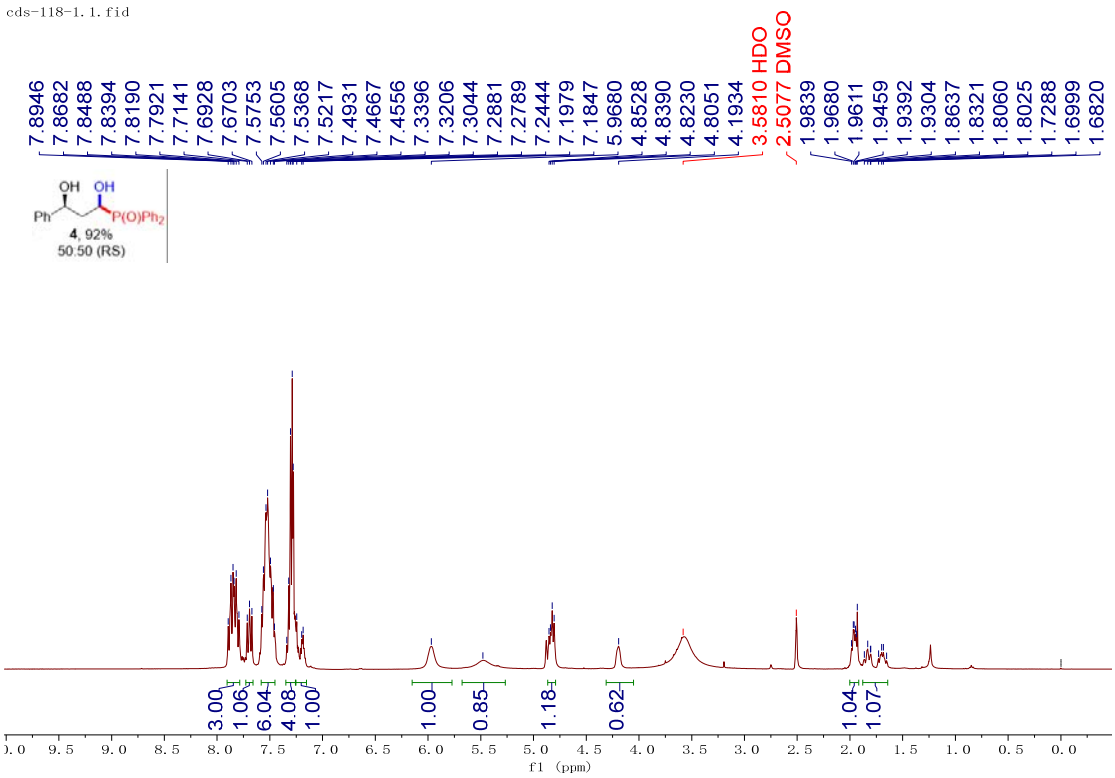
^{1}H NMR spectrum of **3af** (400 MHz, $CDCl_3$)



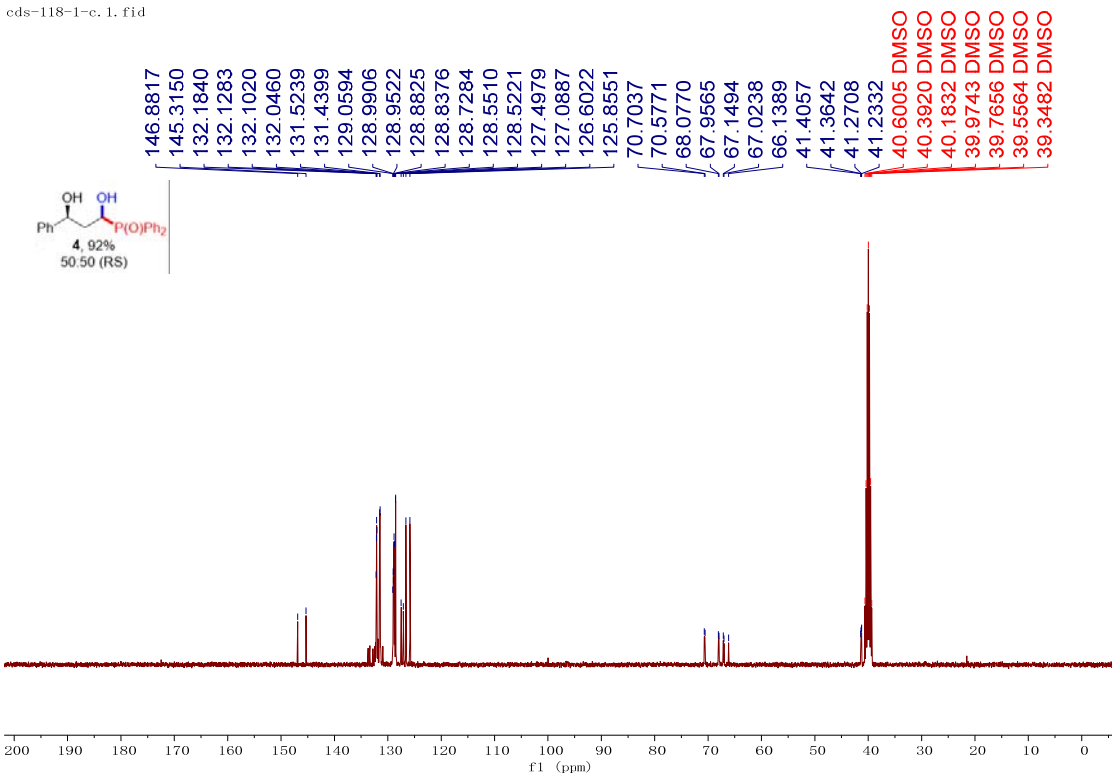
^{13}C NMR spectrum of **3af** (100 MHz, $CDCl_3$)



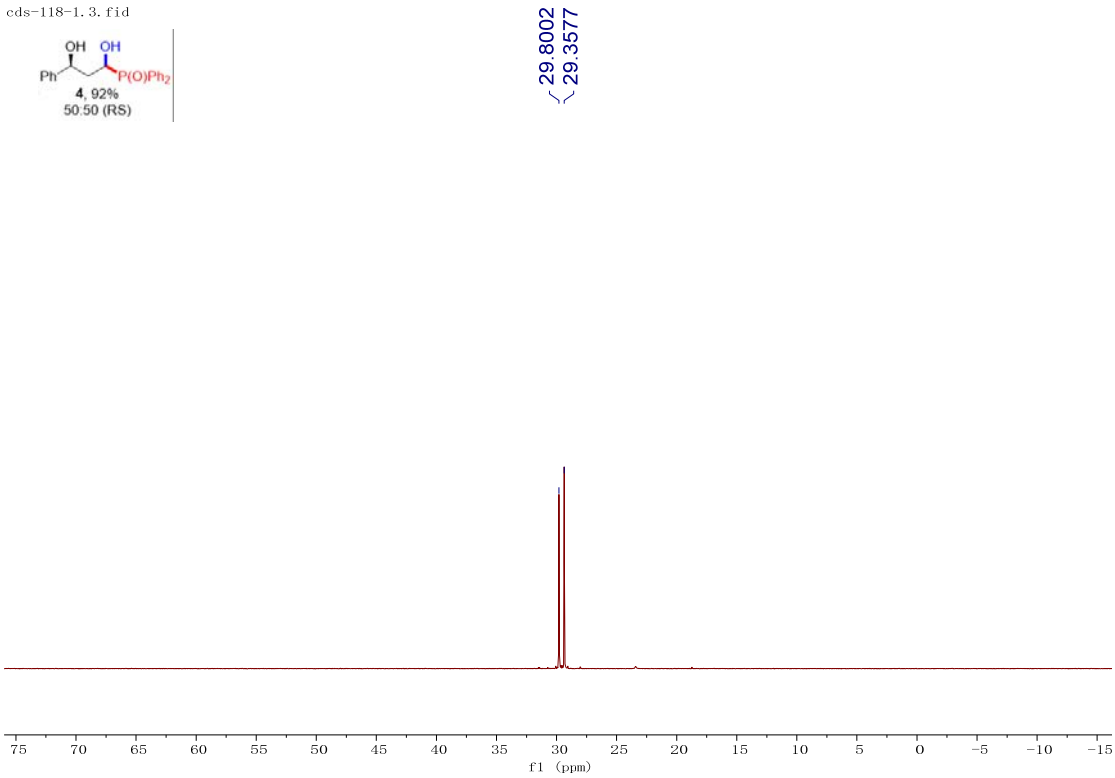
^{31}P NMR spectrum of **3af** (162 MHz, $CDCl_3$)



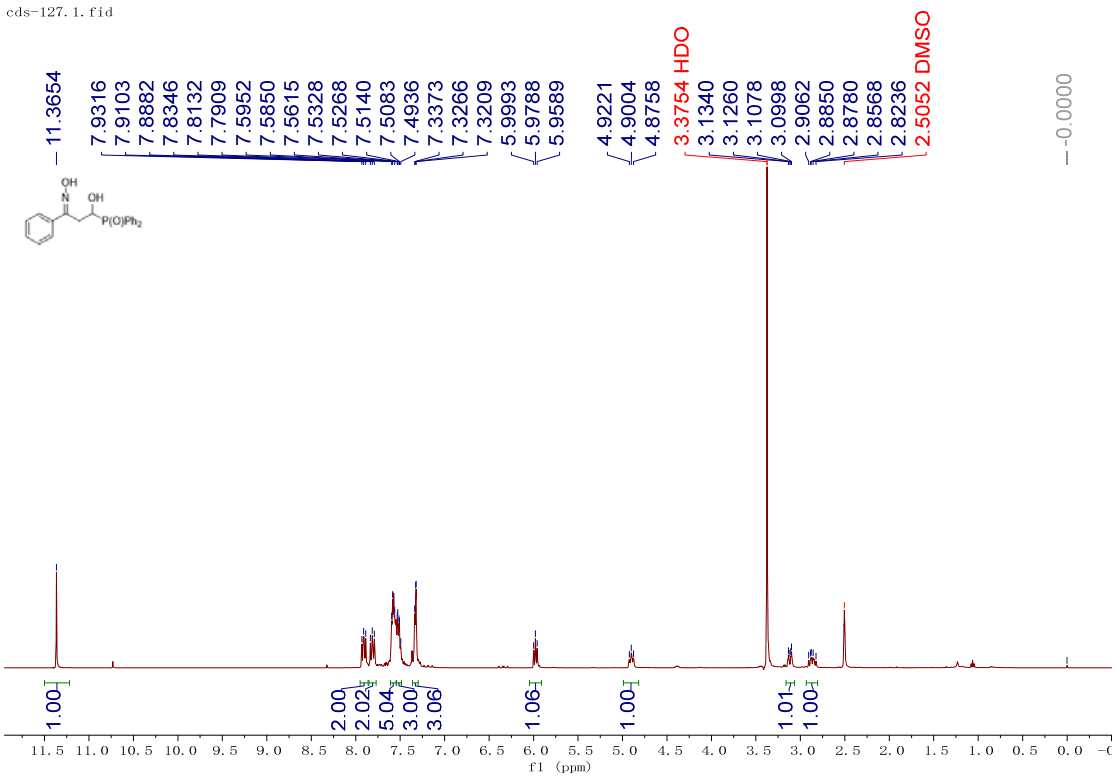
^{1}H NMR spectrum of **4** (400 MHz, DMSO-d_6)



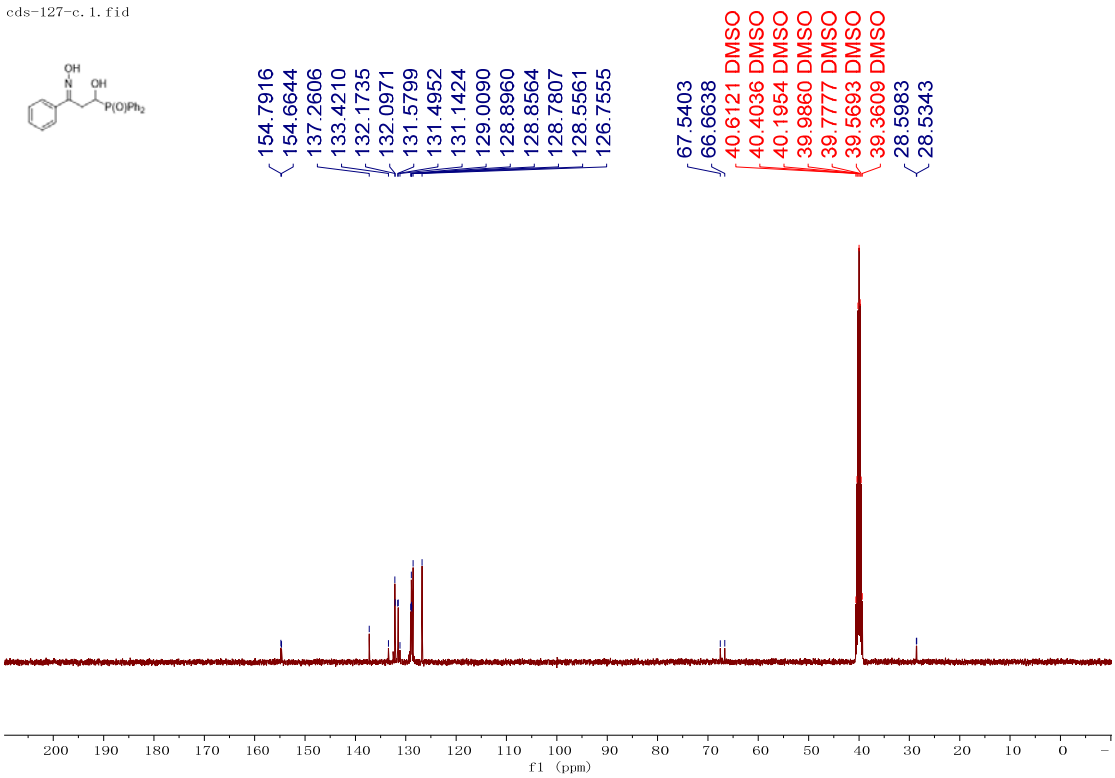
^{13}C NMR spectrum of **4** (100 MHz, DMSO-d_6)



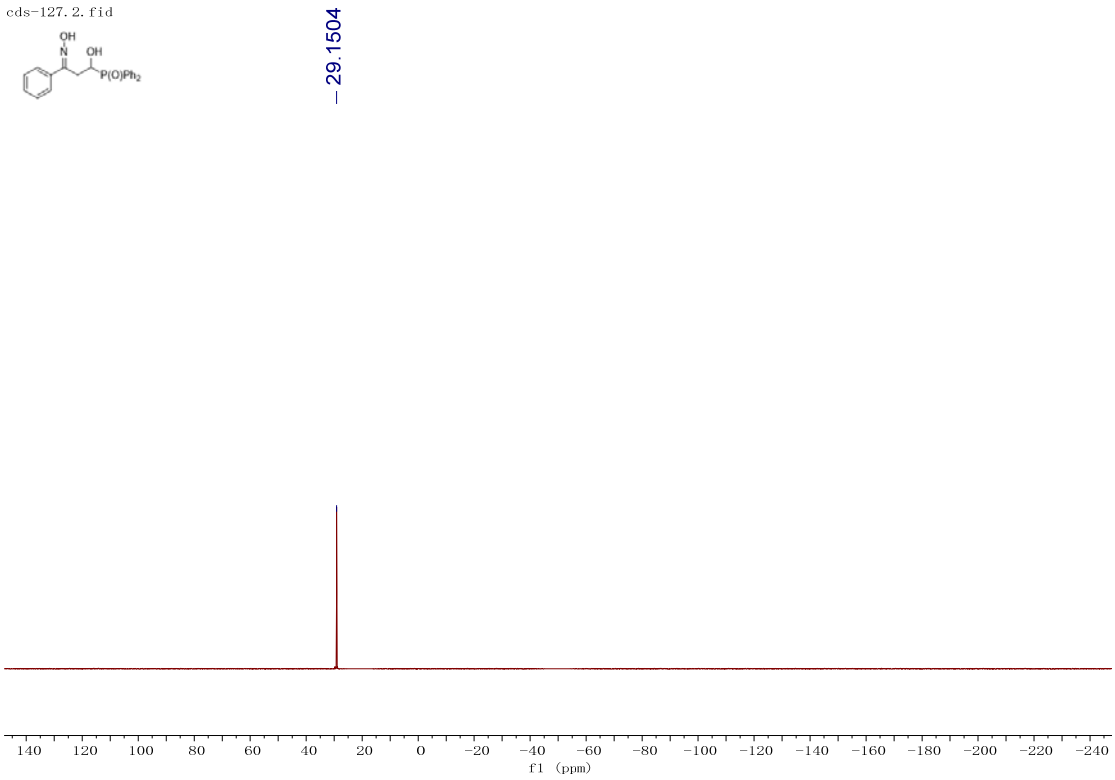
^{31}P NMR spectrum of **4** (162 MHz, DMSO-d_6)



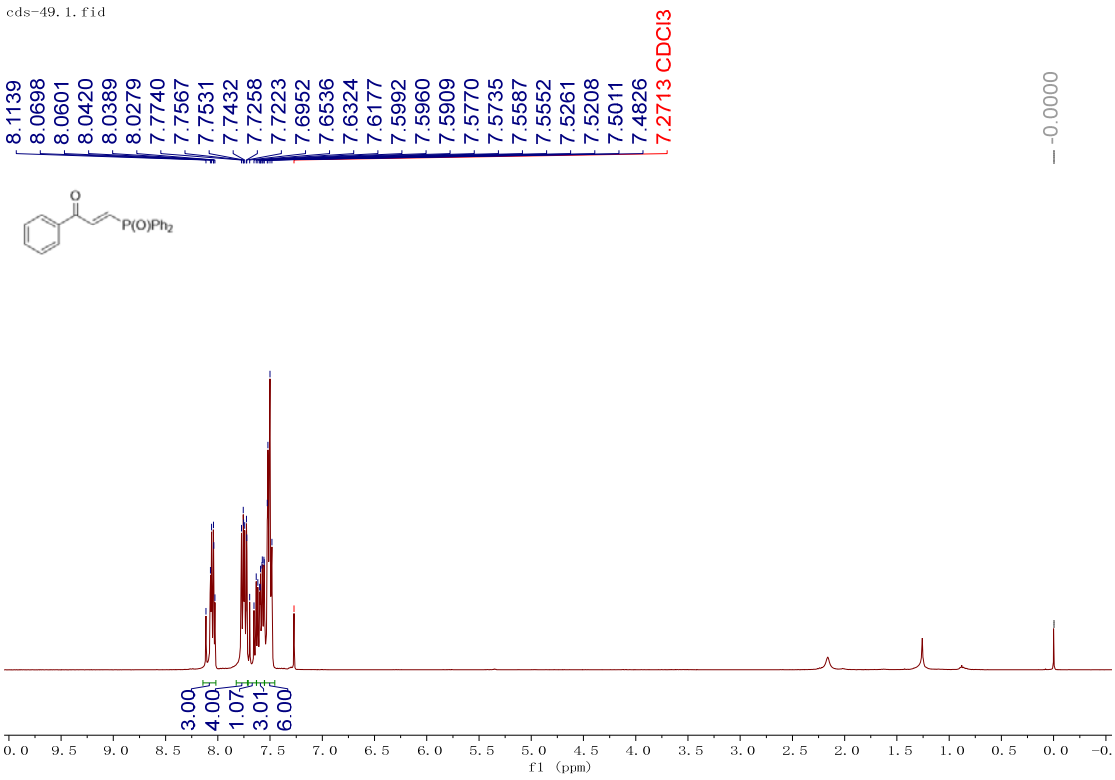
^{1}H NMR spectrum of **5** (400 MHz, DMSO-d_6)



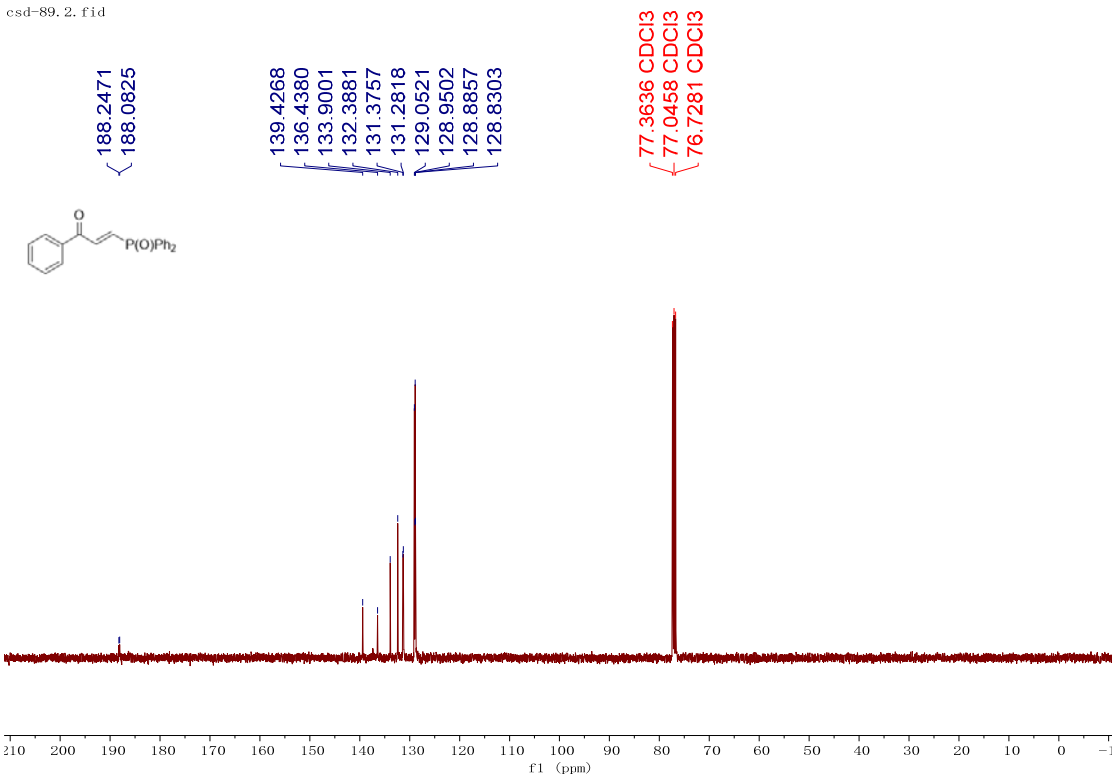
^{13}C NMR spectrum of **5** (100 MHz, DMSO-d_6)



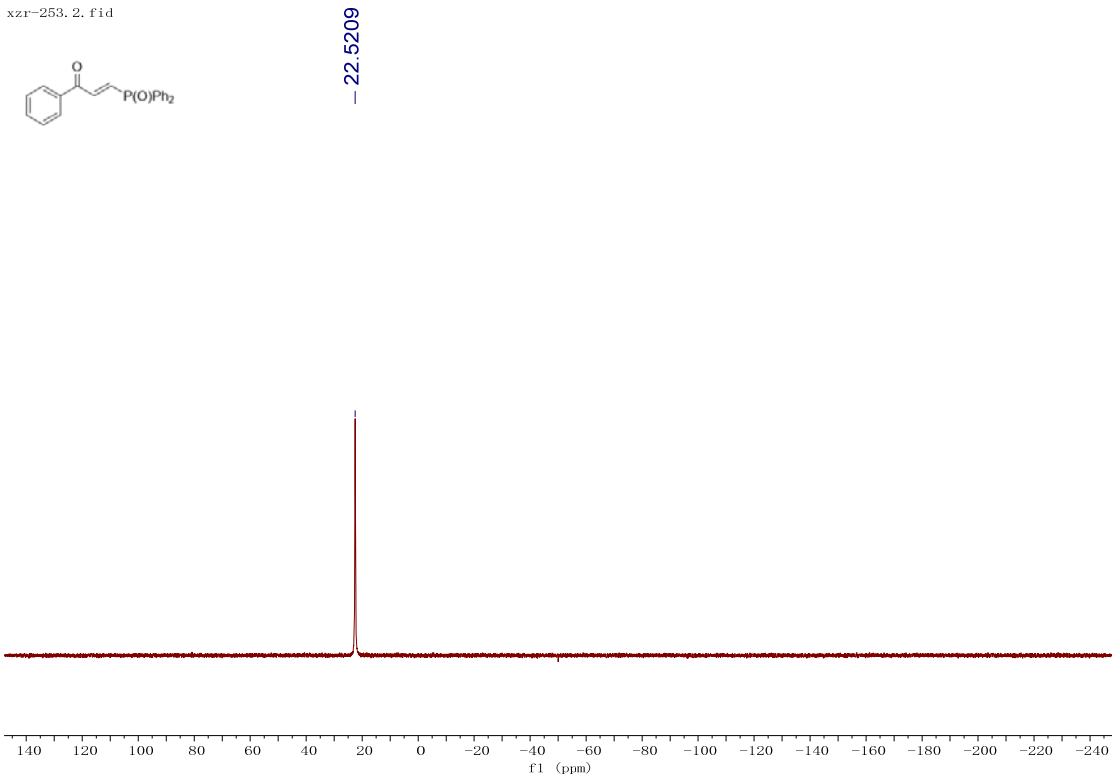
^{31}P NMR spectrum of **5** (162 MHz, DMSO-d_6)



^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$)



^{31}P NMR spectrum of **6** (162 MHz, $CDCl_3$)