Supporting Information

Manganese(III)-Promoted Highly Stereoselective Phosphorylation of Acyclic Tertiary Enamides to Synthesize *E*-Selective β-Phosphoryl Enamides

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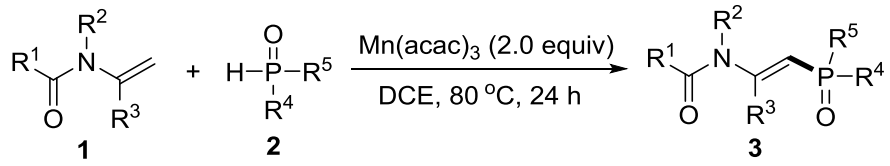
1. General information

All chemicals were dried or purified according to standard procedures prior to use. Flash column chromatography was performed on silica gel (100-200). Reactions were monitored using pre-coated, glass-backed silica gel plates and visualized by means of UV irridation (254 nm) or $KMnO_4$, phosphomolybdic acid, ninhydrine, pancaldi, and *p*-anisaldehyde vanillin. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded using 500 MHz spectrometers at ambient temperature. Chemical shifts are reported in ppm with either tetramethylsilane or the residual solvent resonance used as an internal standard. Abbreviations are used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (*J*, Hz). Mass spectra was measured on Bruker APEX-2 (HRMS) using GCT-MS spectrometer. All yields reported were isolated yields. All acyclic tertiary enamides are known compounds and prepared according to the reported literature procedures.[1]

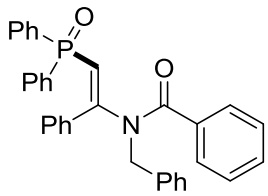
2. Scope of the β-Phosphorylation Reactions

2.1 General Procedure for the Synthesis of 3



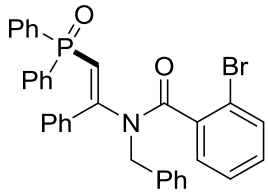
To a Schlenk tube (10 mL) equipped with a magnetic stirrer were added **1** (0.5 mmol), **2** (1.0 mmol), $Mn(acac)_3$ (1.0 mmol) and dry DCE (5 mL). The reaction mixture was stirred at 80 °C for 24 h and then $NaHCO_3$ aqueous (10%) solution (20 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate (3 × 20 mL), and combined organic layer was washed with brine (50 mL) and dried over anhydrous Na_2SO_4. The solvents were removed in *vacuo* and the residue was purified by flash column chromatography (PE : EA = 1 : 1) to afford products **3**.

2.2. Characterization of 3



(*E*)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)benzamide (3aa)

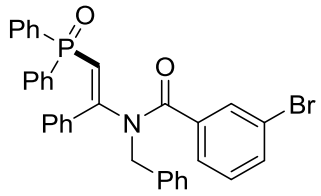
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3aa** was obtained as a white solid (200.2 mg, 78% yield). m.p. 172-174 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.59 (d, J = 7.2 Hz, 2H), 7.50-7.41 (m, 3H), 7.37-7.28 (m, 7H), 7.27-7.19 (m, 6H), 7.18-7.13 (m, 1H), 7.10-6.99 (m, 6H), 5.99 (dd, J = 13.8, 2.5 Hz, 1H), 4.82 (s, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.68; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.28, 156.73 (d, J_{C-P} = 8.8 Hz), 136.60 (d, J_{C-P} = 55.4 Hz), 134.42 (d, J_{C-P} = 3.8 Hz), 134.07 (d, J_{C-P} = 105.8 Hz), 130.98 (d, J_{C-P} = 1.3 Hz), 130.46, 130.06, 129.99, 129.51, 128.45, 128.42, 128.19, 128.10, 128.01, 127.90, 127.75, 127.37, 118.59 (d, J_{C-P} = 102.1 Hz), 50.90; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{34}H_{29}NO_2P$ 514.1930; Found 514.1924.



(*E*)-*N*-benzyl-2-bromo-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)benzamide (3ba)

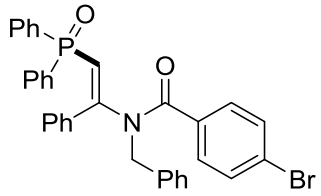
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ba** was obtained as a white solid (183.2 mg, 62% yield). m.p. 184-185 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.52-7.48 (m, 2H), 7.43-7.32 (m, 8H), 7.32-7.23 (m, 7H), 7.19 (t, J = 7.4 Hz, 1H), 7.08 (t, J = 7.6 Hz, 6H), 6.15 (d, J = 14.4 Hz, 1H), 4.82 (br, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 16.04; ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.31, 154.96 (d, J_{C-P} = 6.3 Hz), 137.94, 136.39, 133.92 (d, J_{C-P} = 3.8 Hz), 133.16, 131.24, 130.94, 130.19, 130.05, 129.97, 129.38, 128.62, 128.24, 127.83, 127.73 (d, J_{C-P} =

12.6 Hz), 127.64, 120.40, 119.34 (d, J_{C-P} = 102.1 Hz), 49.89; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{34}H_{28}BrNO_2P$ 592.1036, 594.1015; Found 592.1029, 594.1009.



(*E*)-*N*-benzyl-3-bromo-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)benzamide (3ca)

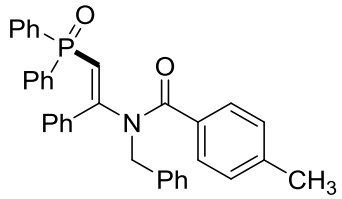
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ca** was obtained as a white solid (198.0 mg, 67% yield). m.p. 93-95 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.78 (t, J = 1.8 Hz, 1H), 7.67-7.62 (m, 1H), 7.57 (dt, J = 7.7, 1.3 Hz, 1H), 7.39-7.30 (m, 8H), 7.28-7.21 (m, 6H), 7.21-7.17 (m, 1H), 7.12-7.04 (m, 6H), 6.10 (d, J = 13.8 Hz, 1H), 4.78 (s, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.83; ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.59, 156.00 (d, J_{C-P} = 8.8 Hz), 138.61, 136.50, 134.10 (d, J_{C-P} = 3.8 Hz), 133.99 (d, J_{C-P} = 104.6 Hz), 133.04, 131.07 (d, J_{C-P} = 1.3 Hz), 130.56 (d, J_{C-P} = 8.8 Hz), 130.11, 130.03, 129.96, 129.59, 128.43, 128.26, 128.19 (d, J_{C-P} = 11.3 Hz), 127.82, 127.02 (d, J_{C-P} = 94.5 Hz), 121.73, 119.11 (d, J_{C-P} = 102.1 Hz), 50.72; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{34}H_{28}BrNO_2P$ 592.1036, 594.1015; Found 592.1031, 594.1010.



(*E*)-*N*-benzyl-4-bromo-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)benzamide (3da)

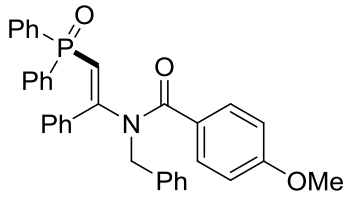
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3da** was obtained as a white solid (195.1 mg, 66% yield). m.p. 181-182 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.57 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.39-7.32 (m, 7H), 7.29-7.23 (m, 6H), 7.20 (t, J = 7.4 Hz, 1H), 7.12-7.06 (m, 6H), 6.03 (d, J = 14.0

Hz, 1H), 4.81 (s, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 16.00; ^{13}C NMR (126 MHz, DMSO-d_6) δ 170.32, 156.00 (d, J_{C-P} = 7.6 Hz), 136.04 (d, J_{C-P} = 149.9 Hz), 134.18 (d, J_{C-P} = 3.8 Hz), 134.00 (d, J_{C-P} = 107.1 Hz), 131.31, 131.12 (d, J_{C-P} = 1.3 Hz), 130.11, 130.08, 130.00, 129.86, 129.61, 128.46, 128.30, 128.14 (d, J_{C-P} = 11.3 Hz), 127.77, 127.42, 123.94, 118.98 (d, J_{C-P} = 102.1 Hz), 50.74; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{34}H_{28}BrNO_2P$ 592.1036, 594.1015; Found 592.1029, 594.1007.



(*E*)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)-4-methylbenzamide (3ea)

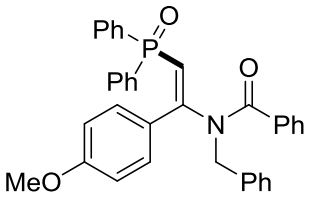
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ea** was obtained as a white solid (187.2 mg, 71% yield). m.p. 175-177 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.50 (d, J = 7.8 Hz, 2H), 7.40-7.28 (m, 8H), 7.25-7.19 (m, 8H), 7.12-7.02 (m, 6H), 5.92 (d, J = 13.9 Hz, 1H), 4.78 (s, 2H), 2.33 (s, 3H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.70; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.29, 156.71 (d, J_{C-P} = 8.8 Hz), 140.51, 136.88, 134.30 (d, J_{C-P} = 5.0 Hz), 134.13 (d, J_{C-P} = 105.8 Hz), 133.35, 130.99 (d, J_{C-P} = 1.3 Hz), 130.08, 130.04, 130.01, 129.53, 128.86, 128.42, 128.16, 128.06, 127.87 (d, J_{C-P} = 27.7 Hz), 127.32, 118.62 (d, J_{C-P} = 102.1 Hz), 50.76, 21.03; HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{35}H_{30}NO_2PNa$ 550.1906; Found 550.1911.



(*E*)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)-4-methoxybenzamide (3fa)

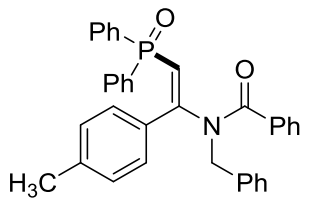
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3fa** was

obtained as a light yellow oil (184.6 mg, 68% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.55 (d, J = 8.8 Hz, 2H), 7.37–7.30 (m, 7H), 7.23 (ddd, J = 15.4, 8.4, 2.3 Hz, 6H), 7.17 (t, J = 7.3 Hz, 1H), 7.09 (td, J = 7.6, 3.4 Hz, 6H), 6.94 (d, J = 8.7 Hz, 2H), 5.92 (d, J = 13.9 Hz, 1H), 4.81 (s, 2H), 3.78 (s, 3H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.86; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.09, 161.12, 157.05 (d, $J_{C\text{-}P}$ = 7.6 Hz), 137.02, 134.54 (d, $J_{C\text{-}P}$ = 3.8 Hz), 134.22 (d, $J_{C\text{-}P}$ = 105.8 Hz), 130.99 (d, $J_{C\text{-}P}$ = 1.3 Hz), 130.12, 130.07, 130.04, 129.97, 129.48, 128.43, 128.22, 128.05 (d, $J_{C\text{-}P}$ = 11.3 Hz), 127.73, 127.33, 117.69 (d, $J_{C\text{-}P}$ = 103.3 Hz), 113.60, 55.38, 51.02; HRMS (ESI) m/z [M+Na]$^{+}$ Calcd. for $C_{35}H_{30}NO_3PNa$ 566.1856; Found 566.1862.



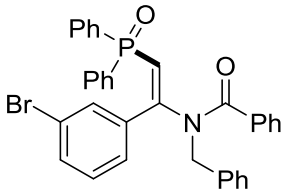
(*E*)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-methoxyphenyl)vinyl)benzamide (3ha)

The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ha** was obtained as a white solid (195.6 mg, 72% yield). m.p. 170-172 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.61 (d, J = 6.3 Hz, 2H), 7.51-7.43 (m, 3H), 7.39-7.29 (m, 7H), 7.28-7.20 (m, 6H), 7.04 (dd, J = 11.8, 7.6 Hz, 4H), 6.65 (d, J = 8.7 Hz, 2H), 5.81 (d, J = 13.9 Hz, 1H), 4.80 (s, 2H), 3.67 (s, 3H); ^{31}P NMR (202 MHz, Chloroform-d) δ 15.81; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.23, 160.67, 156.46 (d, $J_{C\text{-}P}$ = 8.8 Hz), 136.65 (d, $J_{C\text{-}P}$ = 55.4 Hz), 134.19 (d, $J_{C\text{-}P}$ = 107.1 Hz), 131.24, 130.94, 130.44, 130.10, 130.03, 128.42, 128.20, 128.08, 127.98, 127.83, 127.33, 126.55 (d, $J_{C\text{-}P}$ = 2.5 Hz), 117.49 (d, $J_{C\text{-}P}$ = 103.3 Hz), 113.31, 55.22, 50.86; HRMS (ESI) m/z [M+Na]$^{+}$ Calcd. for $C_{35}H_{30}NO_3PNa$ 566.1856; Found 566.1859.



(*E*)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(p-tolyl)vinyl)benzamide (3ia)

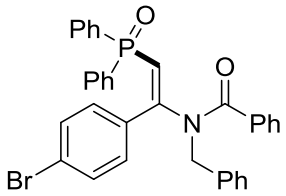
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ia** was obtained as a white solid (203.0 mg, 77% yield). m.p. 166-168 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63-7.58 (m, 2H), 7.39-7.35 (m, 2H), 7.34-7.24 (m, 10H), 7.14 (td, *J* = 7.7, 3.1 Hz, 4H), 7.11-7.05 (m, 4H), 6.95 (d, *J* = 7.9 Hz, 2H), 5.58 (d, *J* = 14.3 Hz, 1H), 4.82 (s, 2H), 2.25 (s, 3H); ^{31}P NMR (202 MHz, Chloroform-*d*) δ 17.60; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.83, 157.25 (d, $J_{C\text{-}P}$ = 7.6 Hz), 140.93, 136.59 (d, $J_{C\text{-}P}$ = 103.3 Hz), 133.75 (d, $J_{C\text{-}P}$ = 108.4 Hz), 131.34 (d, $J_{C\text{-}P}$ = 3.8 Hz), 131.04 (d, $J_{C\text{-}P}$ = 2.5 Hz), 130.84, 130.76, 130.60, 130.11, 129.05, 128.98, 128.68, 128.42 (d, $J_{C\text{-}P}$ = 16.4 Hz), 128.11, 128.01, 127.74, 118.98 (d, $J_{C\text{-}P}$ = 103.3 Hz), 51.48, 21.45; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{31}NO_2P$ 528.2087; Found 528.2080.



(*E*)-*N*-benzyl-*N*-(1-(3-bromophenyl)-2-(diphenylphosphoryl)vinyl)benzamide (3ja)

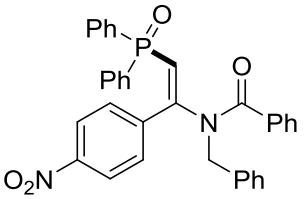
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ja** was obtained as a white solid (195.1 mg, 66% yield). m.p. 163-164 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.53 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.40-7.32 (m, 6H), 7.31-7.22 (m, 7H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 11.9, 7.7 Hz, 4H), 6.97 (t, *J* = 7.9 Hz, 1H), 6.19 (d, *J* = 13.3 Hz, 1H), 4.91 (s, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.64; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.30, 155.15 (d, $J_{C\text{-}P}$ = 7.6 Hz), 137.00 (d, $J_{C\text{-}P}$ = 3.8 Hz), 136.54 (d, $J_{C\text{-}P}$ = 58.0 Hz), 133.78 (d, $J_{C\text{-}P}$ = 107.1 Hz), 132.50 (d, $J_{C\text{-}P}$ = 21.4 Hz), 131.11 (d, $J_{C\text{-}P}$ = 2.5 Hz), 130.09 (d, $J_{C\text{-}P}$ = 113.4 Hz), 130.03, 129.95, 128.53, 128.43, 128.22, 128.16, 128.06, 127.86, 127.51 (d, $J_{C\text{-}P}$ = 7.6 Hz), 121.07, 118.89 (d, $J_{C\text{-}P}$ = 102.1 Hz), 51.15; HRMS

(ESI) m/z $[M+Na]^+$ Calcd. for $C_{34}H_{27}BrNO_2PNa$ 614.0855, 616.0835; Found 614.0851, 616.0830.



(*E*)-*N*-benzyl-*N*-(1-(4-bromophenyl)-2-(diphenylphosphoryl)vinyl)benzamide (3ka)

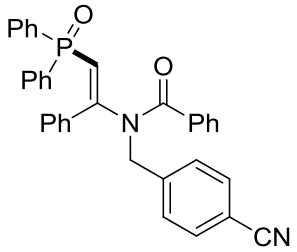
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ka** was obtained as a white solid (206.8 mg, 70% yield). m.p. 147-149 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.58-7.54 (m, 2H), 7.48-7.44 (m, 1H), 7.41 (dd, J = 8.0, 6.4 Hz, 2H), 7.40-7.31 (m, 5H), 7.29-7.18 (m, 8H), 7.20 (d, J = 8.6 Hz, 2H), 7.06 (dd, J = 11.9, 7.6 Hz, 4H), 6.09 (d, J = 13.8 Hz, 1H), 4.86 (s, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.76; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.26, 155.41 (d, $J_{C\text{-}P}$ = 7.6 Hz), 136.50 (d, $J_{C\text{-}P}$ = 50.4 Hz), 133.87 (d, $J_{C\text{-}P}$ = 105.8 Hz), 133.84 (d, $J_{C\text{-}P}$ = 3.8 Hz), 131.39, 131.10 (d, $J_{C\text{-}P}$ = 1.3 Hz), 130.63, 130.55, 130.13, 130.05, 128.51, 128.40, 128.23, 128.12 (d, $J_{C\text{-}P}$ = 11.3 Hz), 127.85, 127.44, 123.58, 118.84 (d, $J_{C\text{-}P}$ = 102.1 Hz), 50.88; HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{34}H_{27}BrNO_2PNa$ 614.0855, 616.0835; Found 614.0849, 616.0828.



(*E*)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-nitrophenyl)vinyl)benzamide (3la)

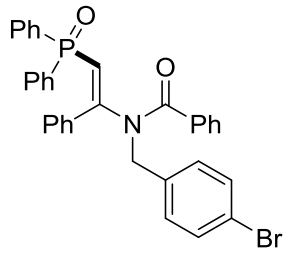
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3la** was obtained as a white solid (125.6 mg, 45% yield). m.p. 119-121 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.87-7.82 (m, 2H), 7.55-7.52 (m, 2H), 7.46-7.41 (m, 3H), 7.40-7.34 (m, 7H), 7.33-7.30 (m, 2H), 7.25 (td, J = 7.7, 2.8 Hz, 4H), 7.13-7.07 (m,

4H), 6.36 (d, J = 13.5 Hz, 1H), 4.94 (s, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.76; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.28, 154.09 (d, J_{C-P} = 8.8 Hz), 147.49, 141.36 (d, J_{C-P} = 3.8 Hz), 136.35 (d, J_{C-P} = 49.1 Hz), 133.59 (d, J_{C-P} = 107.1 Hz), 131.27 (d, J_{C-P} = 2.5 Hz), 130.84, 130.68, 130.19, 130.11, 128.61, 128.46, 128.32, 128.22 (d, J_{C-P} = 11.3 Hz), 127.87, 127.58, 122.47, 120.11 (d, J_{C-P} = 100.8 Hz), 50.97; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{34}H_{28}N_2O_4P$ 559.1781; Found 559.1786.



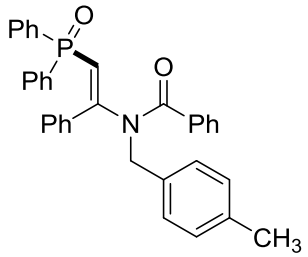
(*E*)-*N*-(4-cyanobenzyl)-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)benzamide (3na)

The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3na** was obtained as a white solid (188.4 mg, 70% yield). m.p. 107-108 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.78 (dd, J = 8.2, 3.8 Hz, 2H), 7.72-7.65 (m, 2H), 7.57-7.49 (m, 3H), 7.41 (td, J = 8.4, 3.8 Hz, 4H), 7.34 (dd, J = 7.7, 3.6 Hz, 2H), 7.26-7.18 (m, 5H), 7.15-7.09 (m, 2H), 7.05-7.00 (m, 4H), 6.09 (dd, J = 13.5, 3.9 Hz, 1H), 4.80 (s, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.49; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.24, 156.33 (d, J_{C-P} = 8.8 Hz), 142.58, 135.93, 134.00 (d, J_{C-P} = 107.1 Hz), 133.79 (d, J_{C-P} = 2.5 Hz), 132.33, 131.04, 130.47 (d, J_{C-P} = 47.9 Hz), 130.04, 129.96, 129.51, 128.89, 128.52, 128.14, 128.06 (d, J_{C-P} = 12.6 Hz), 127.96, 119.77 (d, J_{C-P} = 100.8 Hz), 118.75, 110.03, 50.49; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{28}N_2O_2P$ 539.1883; Found 539.1876.



(*E*)-*N*-(4-bromobenzyl)-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)benzamide (3oa)

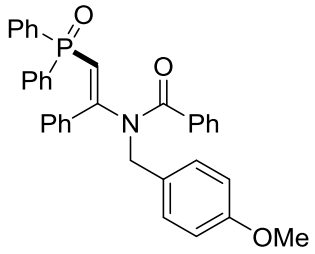
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3oa** was obtained as a white solid (192.1 mg, 65% yield). m.p. 95-97 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.66-7.60 (m, 2H), 7.57-7.42 (m, 5H), 7.40-7.31 (m, 4H), 7.27-7.15 (m, 7H), 7.11 (t, J = 7.6 Hz, 2H), 7.06-6.98 (m, 4H), 5.99 (d, J = 13.7 Hz, 1H), 4.74 (s, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.63; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.23, 156.37 (d, J_{C-P} = 7.6 Hz), 136.19, 136.13, 134.05 (d, J_{C-P} = 3.8 Hz), 134.03 (d, J_{C-P} = 105.8 Hz), 131.32, 131.03 (d, J_{C-P} = 1.3 Hz), 130.47, 130.36 (d, J_{C-P} = 49.1 Hz), 130.06, 129.98, 129.53, 128.46, 128.11, 128.01, 127.87, 120.50, 119.31 (d, J_{C-P} = 102.1 Hz), 50.08; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{34}H_{28}BrNO_2P$ 592.1036, 594.1015; Found 592.1040, 594.1019.



(*E*)-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)-*N*-(4-methylbenzyl)benzamide (3pa)

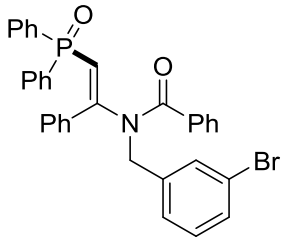
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3pa** was obtained as a white solid (187.2 mg, 71% yield). m.p. 116-118 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.60-7.56 (m, 2H), 7.50-7.41 (m, 3H), 7.37-7.32 (m, 4H), 7.22 (td, J = 7.8, 2.8 Hz, 4H), 7.18-7.11 (m, 5H), 7.09-7.00 (m, 6H), 5.94 (d, J = 13.8 Hz,

1H), 4.76 (s, 2H), 2.30 (s, 3H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.70; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.24, 156.69 (d, J_{C-P} = 7.6 Hz), 136.49 (d, J_{C-P} = 10.1 Hz), 134.45 (d, J_{C-P} = 3.8 Hz), 134.07 (d, J_{C-P} = 105.8 Hz), 133.74, 130.99 (d, J_{C-P} = 1.3 Hz), 130.43, 130.07, 130.00, 129.52, 129.00, 128.41, 128.29, 128.08, 127.99, 127.88, 127.74, 118.58 (d, J_{C-P} = 102.1 Hz), 50.59, 20.74; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{31}NO_2P$ 528.2087; Found 528.2082.



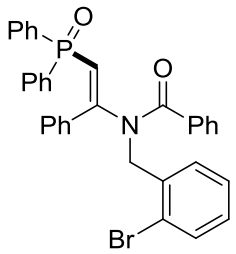
(*E*)-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)-*N*-(4-methoxybenzyl)benzamide (3qa)

The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3qa** was obtained as a white solid (214.6 mg, 79% yield). m.p. 173-174 ºC; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.60-7.55 (m, 2H), 7.47-7.40 (m, 3H), 7.38-7.31 (m, 4H), 7.22 (td, J = 7.7, 2.7 Hz, 4H), 7.19-7.14 (m, 3H), 7.10-7.01 (m, 6H), 6.92-6.87 (m, 2H), 5.92 (d, J = 13.9 Hz, 1H), 4.74 (s, 2H), 3.74 (s, 3H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.84; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.26, 158.61, 156.73 (d, J_{C-P} = 8.8 Hz), 136.48, 134.47, 133.63, 131.06 (d, J_{C-P} = 2.5 Hz), 130.47, 130.12, 130.04, 129.76, 129.56, 128.70, 128.46, 128.14, 128.05, 127.86 (d, J_{C-P} = 11.3 Hz), 118.71 (d, J_{C-P} = 103.3 Hz), 113.83, 55.09, 50.30; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{31}NO_3P$ 544.2036; Found 544.2043.



(*E*)-*N*-(3-bromobenzyl)-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)benzamide (3ra)

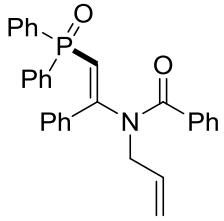
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ra** was obtained as a white solid (206.9 mg, 70% yield). m.p. 188-189 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.62-7.57 (m, 2H), 7.51 (d, J = 7.9 Hz, 1H), 7.48-7.41 (m, 4H), 7.37-7.31 (m, 5H), 7.28 (d, J = 7.8 Hz, 1H), 7.23 (td, J = 7.8, 2.8 Hz, 4H), 7.17 (t, J = 7.4 Hz, 1H), 7.09-7.02 (m, 6H), 6.07 (d, J = 13.7 Hz, 1H), 4.81 (s, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.70; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.39, 156.54 (d, J_{C-P} = 8.8 Hz), 139.61, 136.16, 134.29 (d, J_{C-P} = 3.8 Hz), 134.10 (d, J_{C-P} = 107.1 Hz), 131.07, 131.00 (d, J_{C-P} = 1.3 Hz), 130.69, 130.44 (d, J_{C-P} = 32.8 Hz), 130.01 (d, J_{C-P} = 10.1 Hz), 129.51, 128.41, 128.10 (d, J_{C-P} = 11.3 Hz), 128.01, 127.78, 127.25, 121.66, 118.48 (d, J_{C-P} = 102.1 Hz), 50.25; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{34}H_{28}BrNO_2P$ 592.1036, 594.1015; Found 592.1042, 594.1020.



(*E*)-*N*-(2-bromobenzyl)-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)benzamide (3sa)

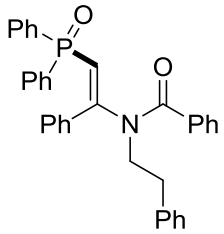
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3sa** was obtained as a white solid (198.0 mg, 67% yield). m.p. 145-147 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.73 (dd, J = 7.2, 2.1 Hz, 2H), 7.57-7.50 (m, 4H), 7.48 (d, J = 7.7 Hz, 1H), 7.39 (d, J = 7.4 Hz, 3H), 7.34 (t, J = 7.5 Hz, 2H), 7.27-7.16 (m, 6H), 7.10 (t, J = 7.6 Hz, 2H), 7.03 (dd, J = 11.9, 7.6 Hz, 4H), 6.16 (d, J = 13.6 Hz, 1H), 4.81 (s, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.48; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.17, 156.36 (d, J_{C-P} = 7.6 Hz), 136.04, 135.23, 134.07 (d, J_{C-P} = 107.1 Hz), 133.70 (d, J_{C-P} = 3.8 Hz), 132.46, 131.00 (d, J_{C-P} = 1.3 Hz), 130.38 (d, J_{C-P} = 45.4 Hz), 130.00 (d, J_{C-P} = 10.1 Hz), 129.45, 129.23 (d, J_{C-P} = 35.3 Hz), 128.54, 128.13, 128.06 (d, J_{C-P} = 11.3 Hz), 127.94, 127.91, 122.14, 119.71 (d, J_{C-P} = 102.1 Hz),

50.73; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{34}H_{28}BrNO_2P$ 592.1036, 594.1015; Found 592.1029, 594.1009.



(*E*)-*N*-allyl-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)benzamide (3ta)

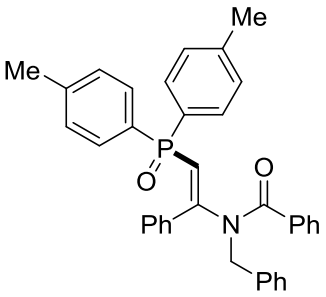
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ta** was obtained as a white solid (173.7 mg, 75% yield), m.p. 136-137 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.59 (d, J = 7.2 Hz, 2H), 7.53-7.44 (m, 5H), 7.34 (t, J = 7.4 Hz, 2H), 7.27-7.21 (m, 4H), 7.20-7.08 (m, 7H), 6.10 (d, J = 13.4 Hz, 1H), 5.95-5.85 (m, 1H), 5.17 (d, J = 10.3 Hz, 1H), 5.06 (d, J = 17.2 Hz, 1H), 4.14 (d, J = 5.9 Hz, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.48; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.13, 157.60 (d, J_{C-P} = 8.8 Hz), 136.88, 134.97 (d, J_{C-P} = 3.8 Hz), 134.63 (d, J_{C-P} = 105.8 Hz), 133.55, 131.48, 130.76 (d, J_{C-P} = 45.4 Hz), 130.55, 130.47, 129.92, 128.97, 128.56 (d, J_{C-P} = 12.6 Hz), 128.36, 128.32, 119.27 (d, J_{C-P} = 102.1 Hz), 118.54, 50.92; HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{30}H_{26}NO_2PNa$ 486.1593; Found 486.1598.



(*E*)-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)-*N*-phenethylbenzamide (3ua)

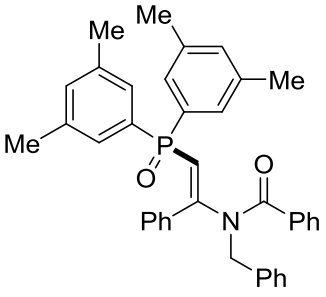
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ua** was obtained as a white solid (210.9 mg, 80% yield). m.p. 167-169 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.60-7.56 (m, 2H), 7.53-7.45 (m, 5H), 7.36 (t, J = 7.4 Hz, 2H), 7.26 (td, J = 7.7, 2.7 Hz, 4H), 7.23-7.19 (m, 3H), 7.18-7.08 (m, 7H), 7.06-7.01 (m, 2H), 5.96 (d, J = 13.5 Hz, 1H), 3.67 (t, J = 7.8 Hz, 2H), 2.90 (t, J = 7.8 Hz, 2H); ^{31}P

NMR (202 MHz, DMSO-d_6) δ 15.38; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.20, 157.68 (d, $J_{C\text{-}P}$ = 8.8 Hz), 138.99, 137.03, 134.88 (d, $J_{C\text{-}P}$ = 3.8 Hz), 134.60 (d, $J_{C\text{-}P}$ = 107.1 Hz), 131.50 (d, $J_{C\text{-}P}$ = 2.5 Hz), 130.77 (d, $J_{C\text{-}P}$ = 30.2 Hz), 130.54, 130.47, 129.92, 129.02, 128.99, 128.62, 128.53, 128.40, 128.31, 126.86, 119.44 (d, $J_{C\text{-}P}$ = 100.8 Hz), 50.37, 33.85; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{31}NO_2P$ 528.2087; Found 528.2091.



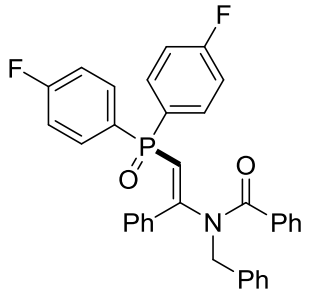
(*E*)-*N*-benzyl-*N*-(2-(di-*p*-tolylphosphoryl)-1-phenylvinyl)benzamide (3ab)

The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ab** was obtained as a light yellow solid (221.9 mg, 82% yield). m.p. 160-162 ºC; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.58 (d, J = 7.3 Hz, 2H), 7.44 (dt, J = 14.6, 7.1 Hz, 3H), 7.34 (ddd, J = 20.1, 13.3, 7.3 Hz, 5H), 7.23 (d, J = 7.1 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.10 (t, J = 7.6 Hz, 2H), 7.03 (dd, J = 8.0, 2.5 Hz, 4H), 6.89 (dd, J = 11.7, 7.8 Hz, 4H), 5.90 (d, J = 13.7 Hz, 1H), 4.79 (s, 2H), 2.22 (s, 6H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 15.96; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.19, 156.17 (d, $J_{C\text{-}P}$ = 8.8 Hz), 140.83, 136.57 (d, $J_{C\text{-}P}$ = 61.7 Hz), 134.34 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.51, 130.64, 130.41, 130.04 (d, $J_{C\text{-}P}$ = 10.1 Hz), 129.96, 129.56, 128.63 (d, $J_{C\text{-}P}$ = 12.6 Hz), 128.45, 128.39, 128.21, 127.87, 127.74, 127.37, 119.41 (d, $J_{C\text{-}P}$ = 100.8 Hz), 50.80, 20.91; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{36}H_{33}NO_2P$ 542.2243; Found 542.2236.



(*E*)-*N*-benzyl-*N*-(2-(bis(3,5-dimethylphenyl)phosphoryl)-1-phenylvinyl)benzamide (3ac)

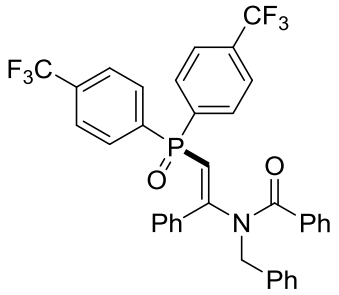
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ac** was obtained as a white solid (199.2 mg, 70% yield). m.p. 177-178 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.53 (d, J = 7.5 Hz, 2H), 7.39-7.34 (m, 3H), 7.33-7.27 (m, 7H), 7.15 (t, J = 7.3 Hz, 1H), 7.06 (t, J = 7.6 Hz, 2H), 6.95 (s, 2H), 6.73 (d, J = 12.0 Hz, 4H), 5.98 (d, J = 13.7 Hz, 1H), 4.84 (s, 2H), 2.15 (s, 12H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 16.16; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.23, 156.08 (d, J_{C-P} = 7.6 Hz), 137.18 (d, J_{C-P} = 13.9 Hz), 136.90, 136.22, 134.77 (d, J_{C-P} = 3.8 Hz), 133.86 (d, J_{C-P} = 104.6 Hz), 132.40 (d, J_{C-P} = 1.3 Hz), 130.00 (d, J_{C-P} = 78.1 Hz), 129.45, 128.43, 128.25, 128.16, 127.77, 127.69, 127.62, 127.51, 127.42, 118.11 (d, J_{C-P} = 102.1 Hz), 50.92, 20.75; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{38}H_{37}NO_2P$ 570.2556; Found 570.2551.



(*E*)-*N*-benzyl-*N*-(2-(bis(4-fluorophenyl)phosphoryl)-1-phenylvinyl)benzamide (3ad)

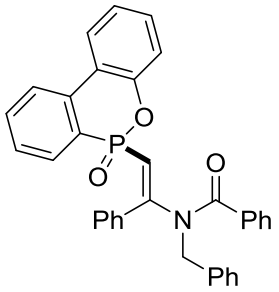
The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ad** was obtained as a light yellow oil (197.7 mg, 72% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.61-7.55 (m, 2H), 7.50-7.43 (m, 3H), 7.36 (dd, J = 8.0, 6.3 Hz, 2H), 7.33-7.28 (m, 3H), 7.28-7.23 (m, 2H), 7.21-7.17 (m, 1H), 7.12-7.00 (m, 10H), 6.02 (d, J = 14.1 Hz, 1H), 4.83 (s, 2H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 14.69; ^{19}F NMR (471 MHz, DMSO-d_6) δ -108.56; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.38, 163.66 (d, J_{C-F} = 252.0 Hz), 157.10 (d, J_{C-P} = 8.8 Hz), 136.79, 136.41, 134.39 (d, J_{C-P}

= 5.0 Hz), 132.86 (d, J_{C-P} = 10.1 Hz), 132.78 (d, J_{C-F} = 8.8 Hz), 130.52, 130.14, 129.66 (d, J_{C-P} = 2.5 Hz), 129.53, 128.48, 128.19, 127.86 (d, J_{C-P} = 15.1 Hz), 127.41, 117.80 (d, J_{C-P} = 104.6 Hz), 115.39 (d, J_{C-F} = 21.4 Hz), 115.29 (d, J_{C-P} = 21.4 Hz), 50.87; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{34}H_{27}F_2NO_2P$ 550.1742; Found 550.1737.



(*E*)-*N*-benzyl-*N*-(2-(bis(4-(trifluoromethyl)phenyl)phosphoryl)-1-phenylvinyl)benzamide (3ae)

The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3ae** was obtained as a white solid (230.5 mg, 71% yield). m.p. 144-146 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.60 (d, J = 7.5 Hz, 6H), 7.48-7.43 (m, 3H), 7.39 (t, J = 7.4 Hz, 2H), 7.33 (d, J = 7.1 Hz, 1H), 7.31-7.22 (m, 8H), 7.14 (t, J = 7.4 Hz, 1H), 7.03 (t, J = 7.6 Hz, 2H), 6.17 (d, J = 14.6 Hz, 1H), 4.88 (s, 2H); ^{31}P NMR (202 MHz, Chloroform-d) δ 19.21; ^{19}F NMR (471 MHz, Chloroform-d) δ -57.00; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.57, 158.24 (d, J_{C-P} = 8.8 Hz), 138.16 (d, J_{C-P} = 103.3 Hz), 136.56 (d, J_{C-P} = 49.1 Hz), 134.47 (d, J_{C-P} = 3.8 Hz), 131.35 (d, J_{C-P} = 2.5 Hz), 131.08, 131.00, 130.42 (d, J_{C-P} = 47.9 Hz), 129.51, 128.51, 128.48, 128.21, 128.01, 127.84, 127.44, 125.01 (q, J_{C-F} = 2.5 Hz), 124.9 (q, J_{C-F} = 3.8 Hz), 123.61 (q, J_{C-F} = 273.4 Hz), 115.57 (d, J_{C-P} = 107.1 Hz), 50.96; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{36}H_{27}F_6NO_2P$ 650.1678; Found 650.1683.

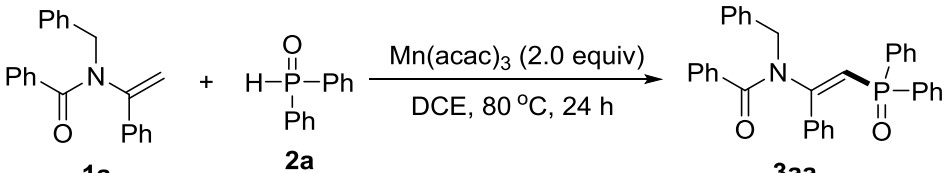


(*E*)-*N*-benzyl-*N*-(2-(6-oxidodibenzo[*c*,*e*][1,2]oxaphosphinin-6-yl)-1-phenylvinyl)benzamide (3af)

The title compound was synthesized following the general procedure and the residue was purified by flash chromatography on silica gel (PE : EA = 1 : 1). **3af** was obtained as a colorless oil (58.0 mg, 22% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.03 (dd, J = 8.0, 1.7 Hz, 1H), 8.00-7.95 (m, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.30-7.21 (m, 9H), 7.15-7.08 (m, 6H), 7.05 (dd, J = 8.0, 1.4 Hz, 2H), 6.95 (ddd, J = 13.4, 7.6, 1.4 Hz, 1H), 6.65 (dd, J = 8.1, 1.3 Hz, 1H), 5.80 (d, J = 13.5 Hz, 1H), 4.85 (d, J = 15.2 Hz, 1H), 4.70 (d, J = 15.1 Hz, 1H); ^{31}P NMR (202 MHz, DMSO-d_6) δ 20.76; ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.39, 157.44 (d, $J_{C\text{-}P}$ = 11.3 Hz), 147.94 (d, $J_{C\text{-}P}$ = 7.6 Hz), 136.85, 136.24, 135.41 (d, $J_{C\text{-}P}$ = 3.8 Hz), 134.38 (d, $J_{C\text{-}P}$ = 6.3 Hz), 132.91, 130.48, 130.25, 129.98, 129.54 (d, $J_{C\text{-}P}$ = 11.3 Hz), 129.30, 128.51, 128.16, 128.03, 127.99, 127.75, 127.43, 127.23, 125.62, 125.20 (d, $J_{C\text{-}P}$ = 131.0 Hz), 124.64, 123.88 (d, $J_{C\text{-}P}$ = 10.1 Hz), 121.91 (d, $J_{C\text{-}P}$ = 11.3 Hz), 119.74 (d, $J_{C\text{-}P}$ = 6.3 Hz), 112.61 (d, $J_{C\text{-}P}$ = 141.1 Hz), 52.19; HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{34}H_{27}NO_3P$ 528.1723; Found 528.1717.

3. Applications of the β-Phosphorylation Reaction

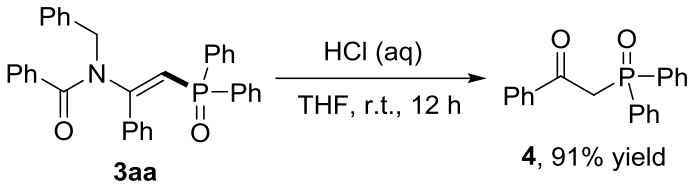
3.1. Gram-Scale Synthesis of Compound 3aa



To a Schlenk tube (50 mL) equipped with a magnetic stirrer were added enamide **1a** (3.0 mmol), **2** (6.0 mmol), $Mn(acac)_3$ (6.0 equiv) and dry DCE (30 mL). The

reaction mixture was stirred at 80 °C for 24 h and then $NaHCO_3$ aqueous (10%) solution (100 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate (3 × 80 mL), and combined organic layer was washed with brine (100 mL) and dried over anhydrous Na_2SO_4. The solvents were removed in *vacuo* and the residue was purified by flash column chromatography (PE : EA = 1 : 1) to afford products **3aa** in 72% yield.

3.2. Chemical Transformation of Compound 3aa



3aa **4**, 91% yield

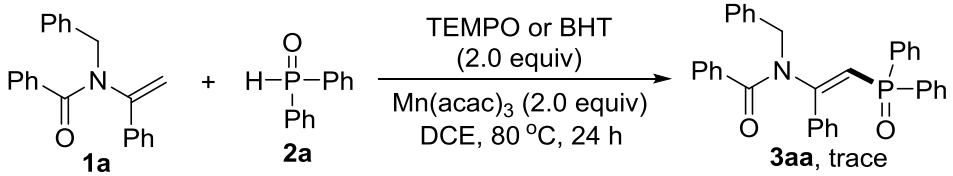
According to the reported literature procedures,[2] product **3aa** (0.3 mmol) was added into a reaction tube with a magnetic stirrer. THF (1 mL) and concentrated hydrochloric acid (1 mL) were then added sequentially by syringe. The resulting mixture was stirred at room temperature for about 12 h. Upon completion of the reaction as monitored by TLC, the solvent was then removed under vacuum. The residue was purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:3 v/v) to give compound **4**.

2-(Diphenylphosphoryl)-1-phenylethan-1-one (**4**)

Product **4** is a known compound and obtained as a white solid (87.4 mg, 91% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.81 (dd, *J* = 12.0, 7.5 Hz, 4H), 7.56-7.49 (m, 3H), 7.49-7.39 (m, 6H), 4.15 (d, *J* = 15.2 Hz, 2H). This is consistent with previous literatures.[3]

4. Control Experiments

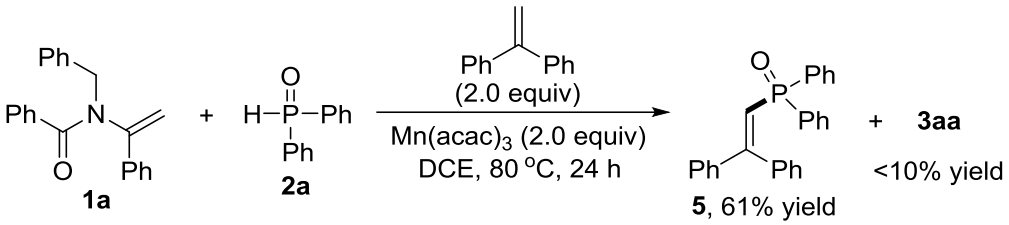
4.1. Reaction with Radical Trapping Agents TEMPO or BHT



1a **2a** **3aa**, trace

To a Schlenk tube (10 mL) equipped with a magnetic stirrer were added **1a** (0.5 mmol), **2a** (1.0 mmol), $Mn(acac)_3$ (1.0 mmol), TEMPO or BHT (1.0 mmol) and dry DCE (5 mL). The reaction mixture was stirred at 80 °C for 24 h and then $NaHCO_3$ aqueous (10%) solution (20 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate (3 × 20 mL), and combined organic layer was washed with brine (50 mL) and dried over anhydrous Na_2SO_4. TLC indicated that product **3aa** was not observed in the reaction system.

4.2. Reaction with 1,1-Diphenylethylene



To a Schlenk tube (10 mL) equipped with a magnetic stirrer were added **1a** (0.5 mmol), **2a** (1.0 mmol), $Mn(acac)_3$ (1.0 mmol), 1,1-Diphenylethylene (1.0 mmol) and dry DCE (5 mL). The reaction mixture was stirred at 80 °C for 24 h and then $NaHCO_3$ aqueous (10%) solution (20 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate (3 × 20 mL), and combined organic layer was washed with brine (50 mL) and dried over anhydrous Na_2SO_4. The solvents were removed in *vacuo* and the residue was purified by flash column chromatography (PE : EA = 1 : 1) to afford product **5** in 61% yield and trace amount of target product **3aa**.

(2,2-Diphenylvinyl)diphenylphosphine oxide (**5**)

Product **5** is a known compound and obtained as a white solid (116.0 mg, 61% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74-7.62 (m, 4H), 7.41-7.28 (m, 11H), 7,25-7.19 (m, 2H), 7.16-7.04 (m, 3H), 6.80 (d, *J* = 18.4 Hz, 1H). This is consistent with previous literatures.[4]

5. References

[1] (a) S. S. Kinderman, J. H. V. Maarseveen, H. E. Schoemaker, H. Hiemstra, F. P. J. T. Rutjes, *Org. Lett.* **2001**, *3*, 2045. (b) C.-H. Lei, D.-X. Wang, L. Zhao, J. Zhu, M.-X.

Wang, *J. Am. Chem. Soc*. **2013**, *135*, 4708.

[2] K. Zhao, Z.-Y. Zhang, X.-L. Cui, Y.-X. Wang, X.-D. Wu, W.-M. Li, J.-X. Wu, L.-L. Zhao, J.-Y. Guo, T.-P. Loh, *Org. Lett.* **2020**, *22*, 9029.

[3] (a) D. J. Fox, D. S. Pedersen, S. Warren, *Chem. Commun.* **2004**, 2598. (b) E. G. Leach, J. R. Shady, A. C. Boyden, A. Emig, A. T. Henry, E. K. Connor, R. J. Staples, S. Schaertel, E. J. Werner, S. M. Biros, *Dalton Trans.* **2017**, *46*, 15458.

[4] D.-L. Zhang, C.-K. Li, R.-S. Zeng, A. Shoberu, J.-P. Zou, *Org. Chem. Front.* **2019**, *6*, 236.

6. Crystallographic Data

High quality single crystals of **3aa** were cultivated from the evaporation of a solution of **3aa** in the mixture of EtOAc and *n*-hexane. As depicted below, the molecular structures were determined by X-ray diffraction analysis.

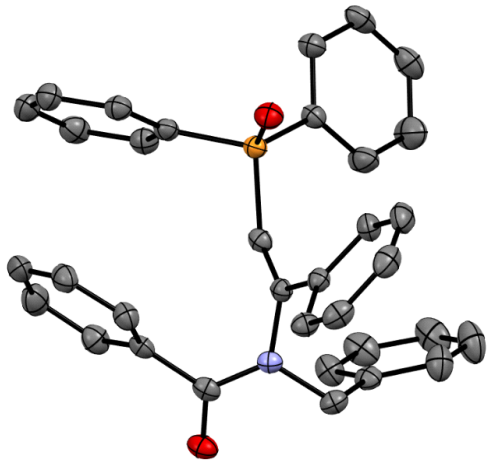


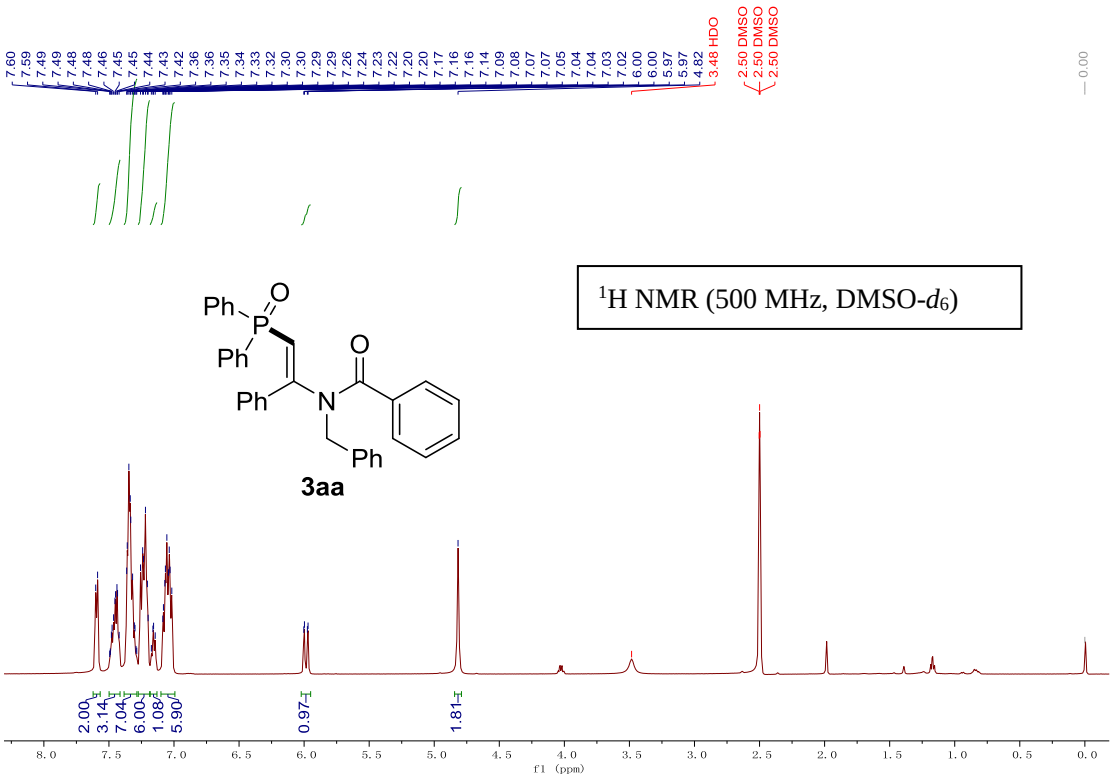
Figure S1. X-ray molecular structure of **3aa**. The molecular structure is depicted in an ellipsoid style at 50% probability level.

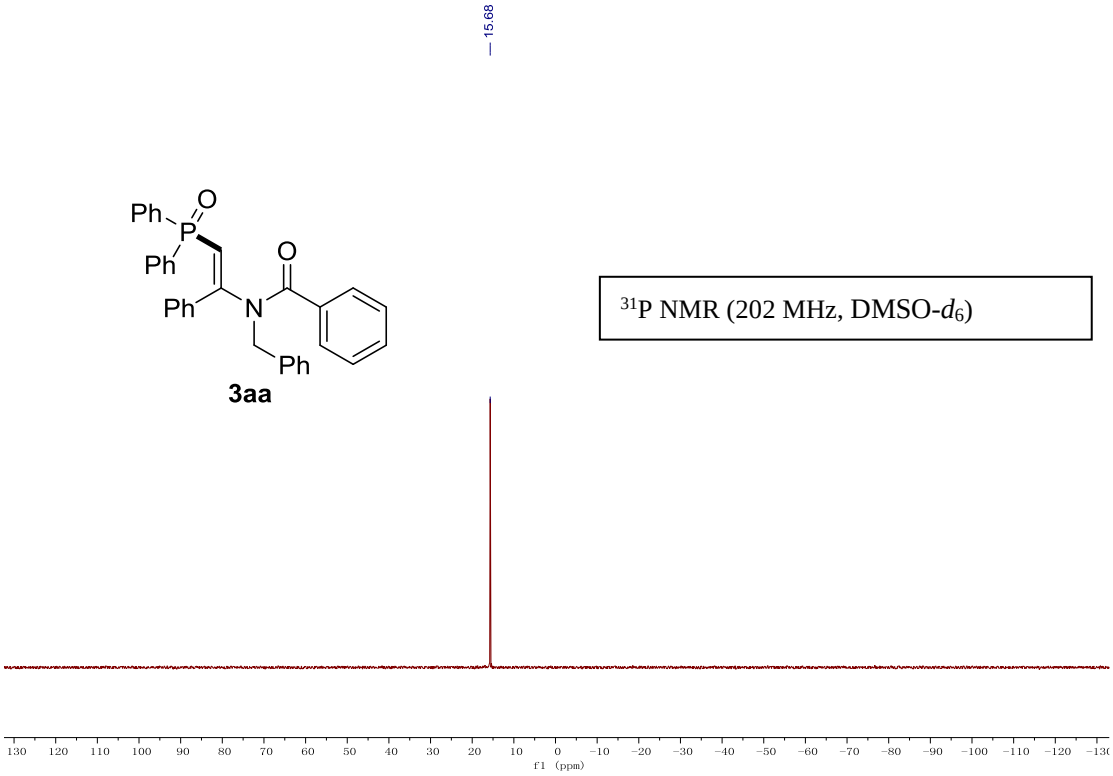
Crystallographic data and structure refinement of 3aa

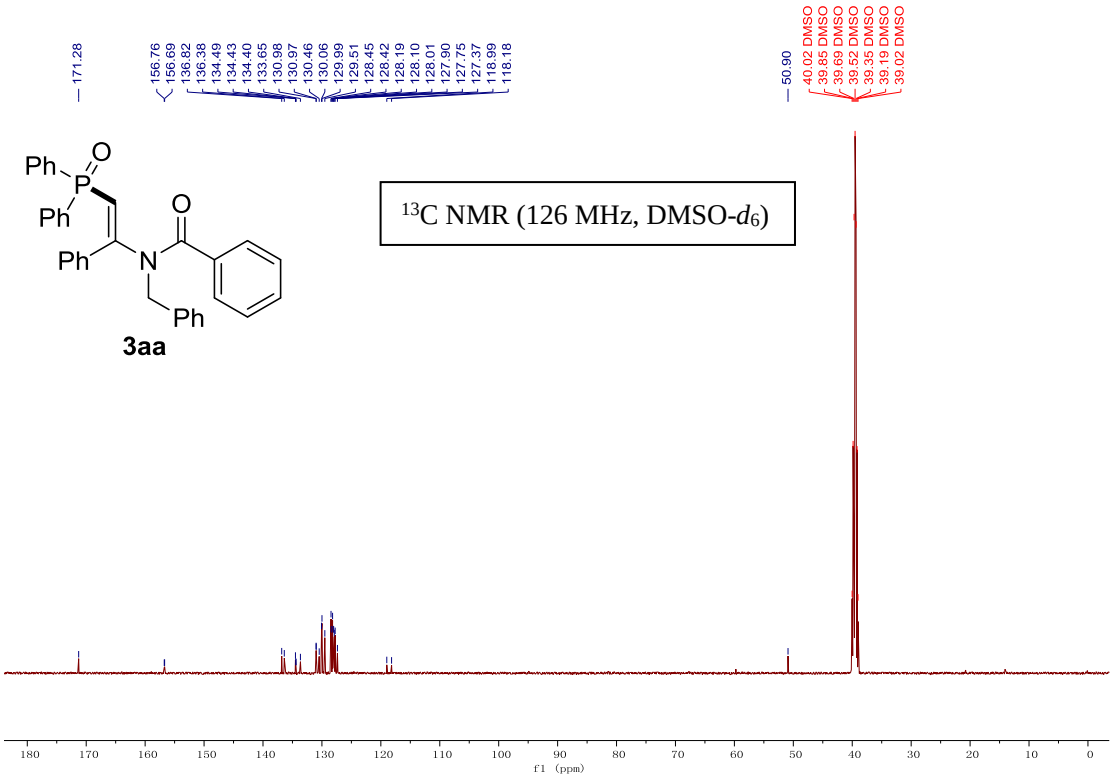
CCDC Number	2141502
Empirical formula	$C_{34}H_{28}NO_2P$
Formula weight	513.1858
Temperature	170.00 K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	P -1
a	9.2756 (1) Å
b	10.2061 (1) Å

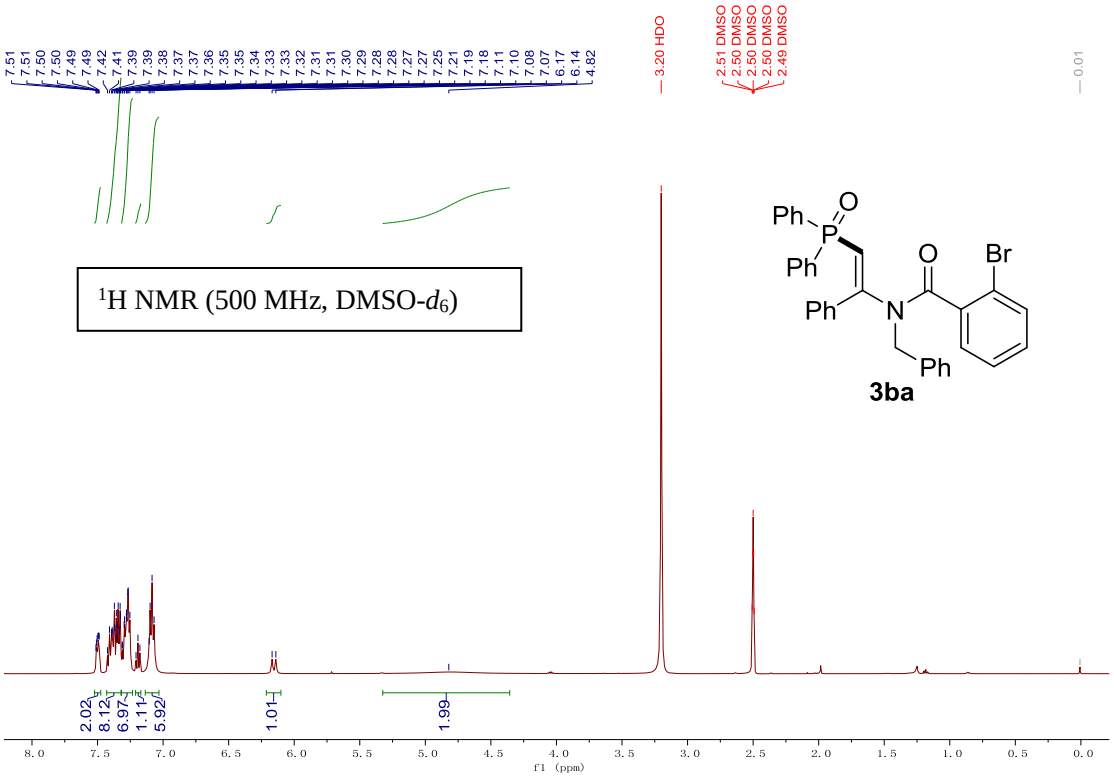
c	17.1546 (2) Å
α	79.024 (1) º
β	75.112 (1) °
γ	74.328 (1) º
Volumn	1498.29 (3) $Å^3$
Z	2
Density (calculated)	1.234
F(000)	590.0
Radiation type	Cu K\a
Goodness-of-fit on F^2	1.052
Completeness to theta = 66.97 °	99.42%
R (reflections)	0.0545 (5736)
wR2 (reflections)	0.1537 (5906)

7. Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR Spectra of Products



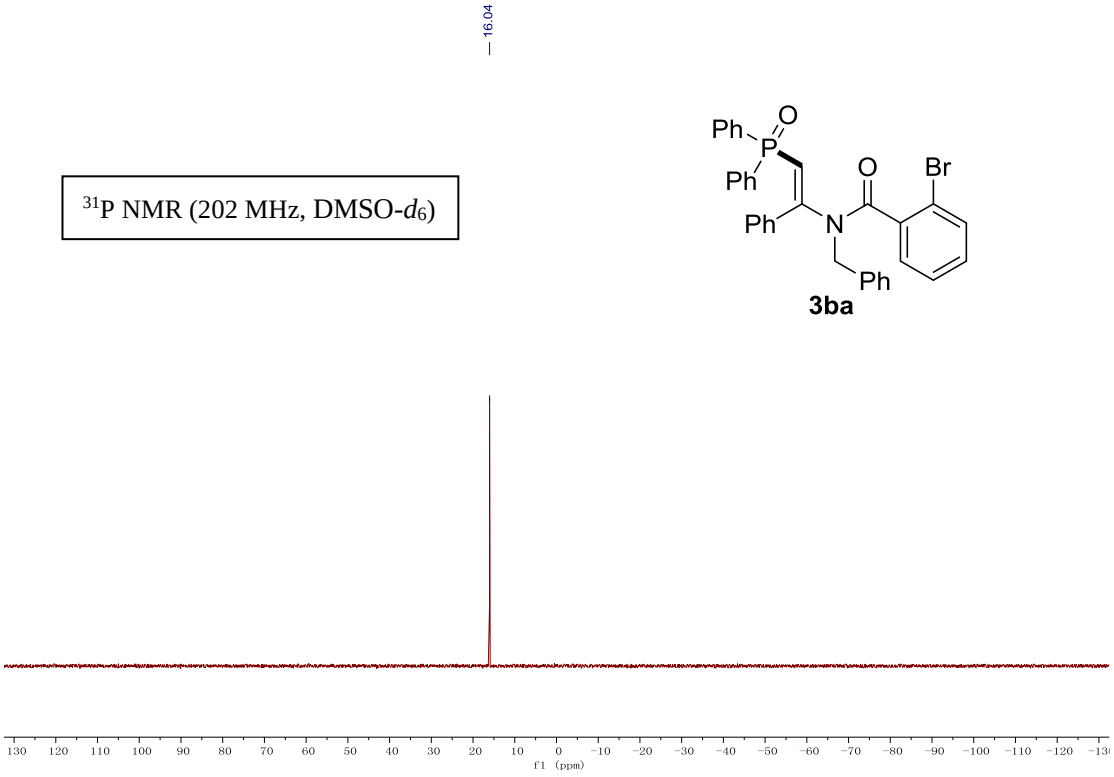

15.68
Ph
O
P
Ph
Ph
N
O
Ph
3aa
31P NMR (202 MHz, DMSO-d6)
f1 (ppm)


171.28
156.76
156.69
136.82
136.38
134.49
134.43
134.40
133.65
130.98
130.97
130.46
130.06
129.99
129.51
128.45
128.42
128.19
128.10
128.01
127.90
127.75
127.37
118.99
118.18
50.90
40.02 DMSO
39.85 DMSO
39.69 DMSO
39.52 DMSO
39.35 DMSO
39.19 DMSO
39.02 DMSO
Ph
O
P
Ph
Ph
N
O
Ph
3aa
13C NMR (126 MHz, DMSO-d6)
f1 (ppm)



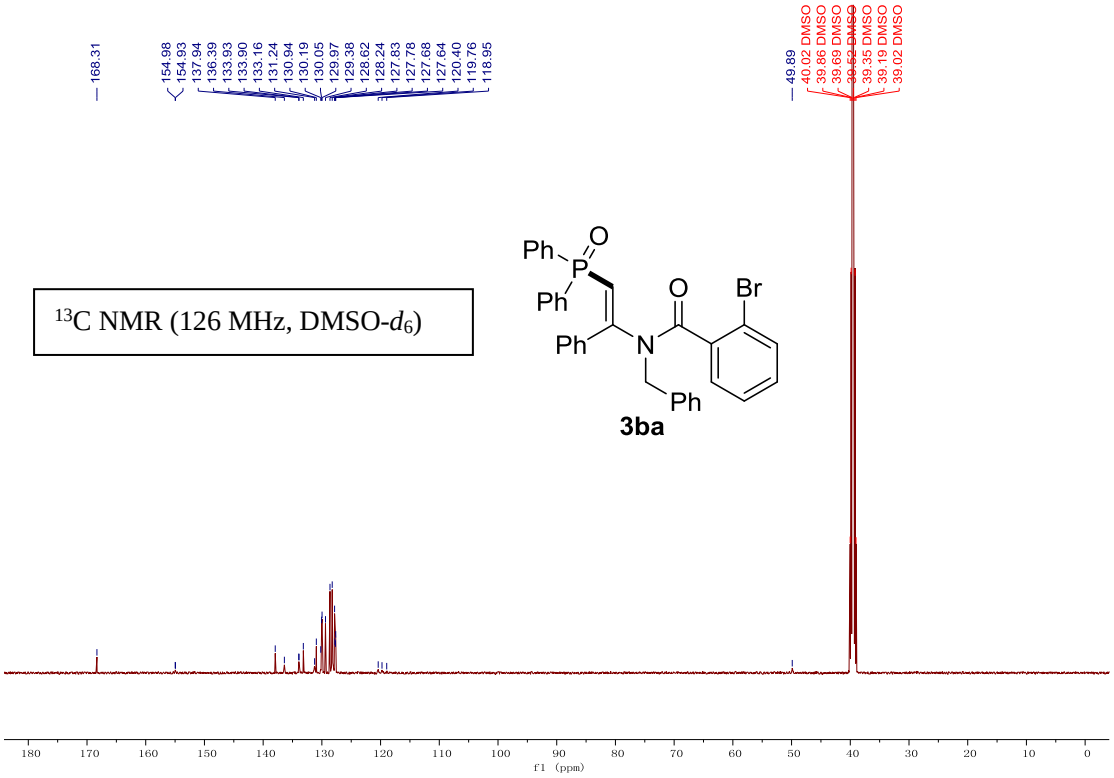
^{1}H NMR (500 MHz, DMSO-d_6)

3ba



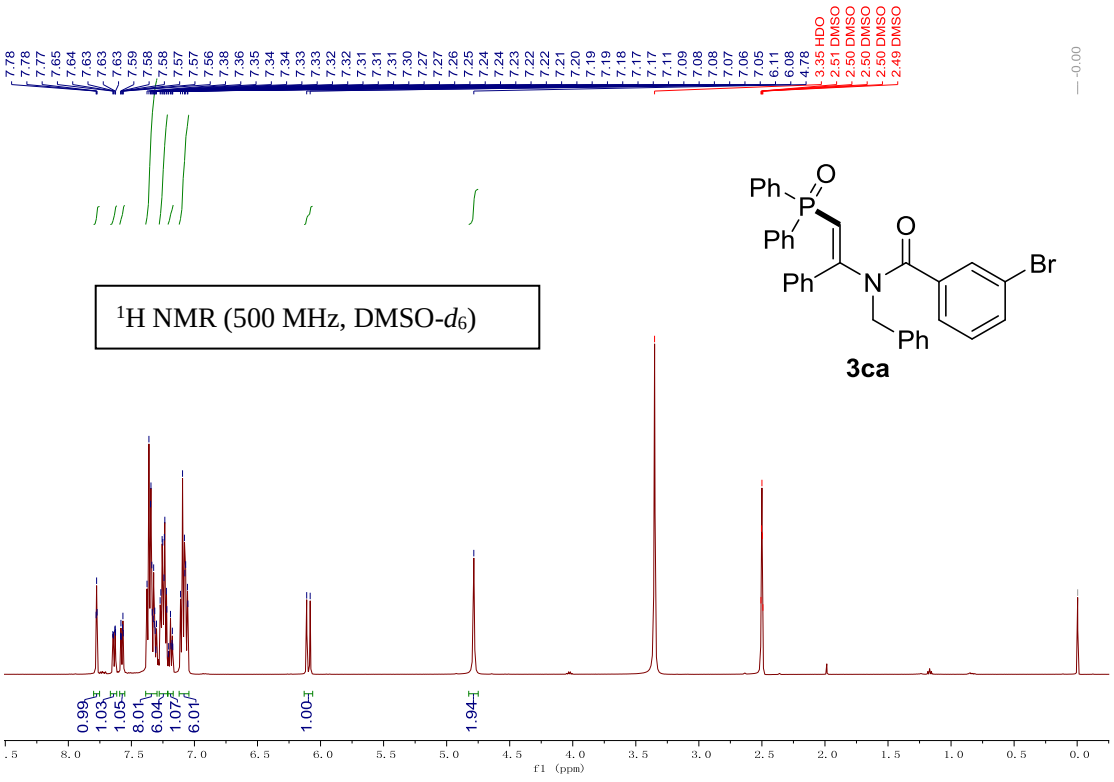
^{31}P NMR (202 MHz, DMSO-d_6)

3ba



^{13}C NMR (126 MHz, DMSO-d_6)

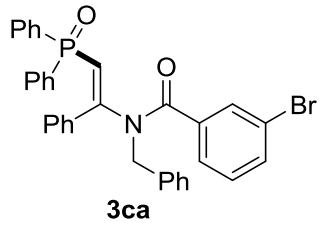
3ba



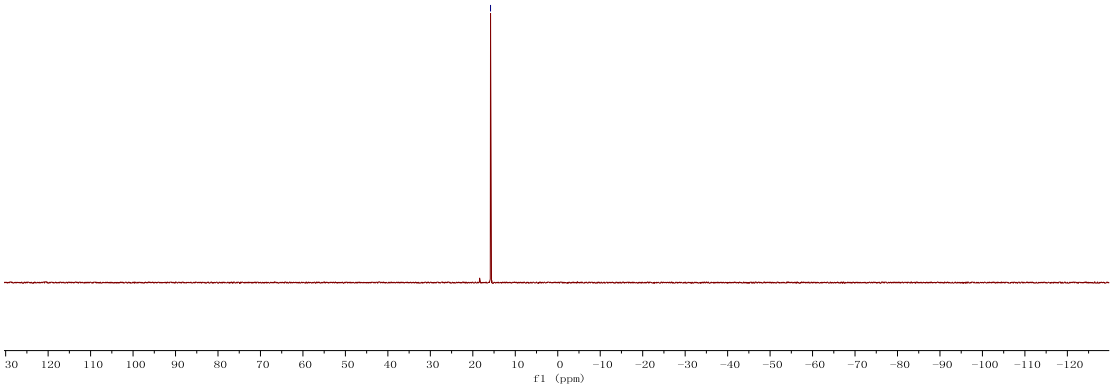
^{1}H NMR (500 MHz, DMSO-d_6)

3ca

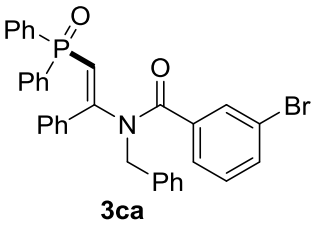
^{31}P NMR (202 MHz, DMSO-d_6)



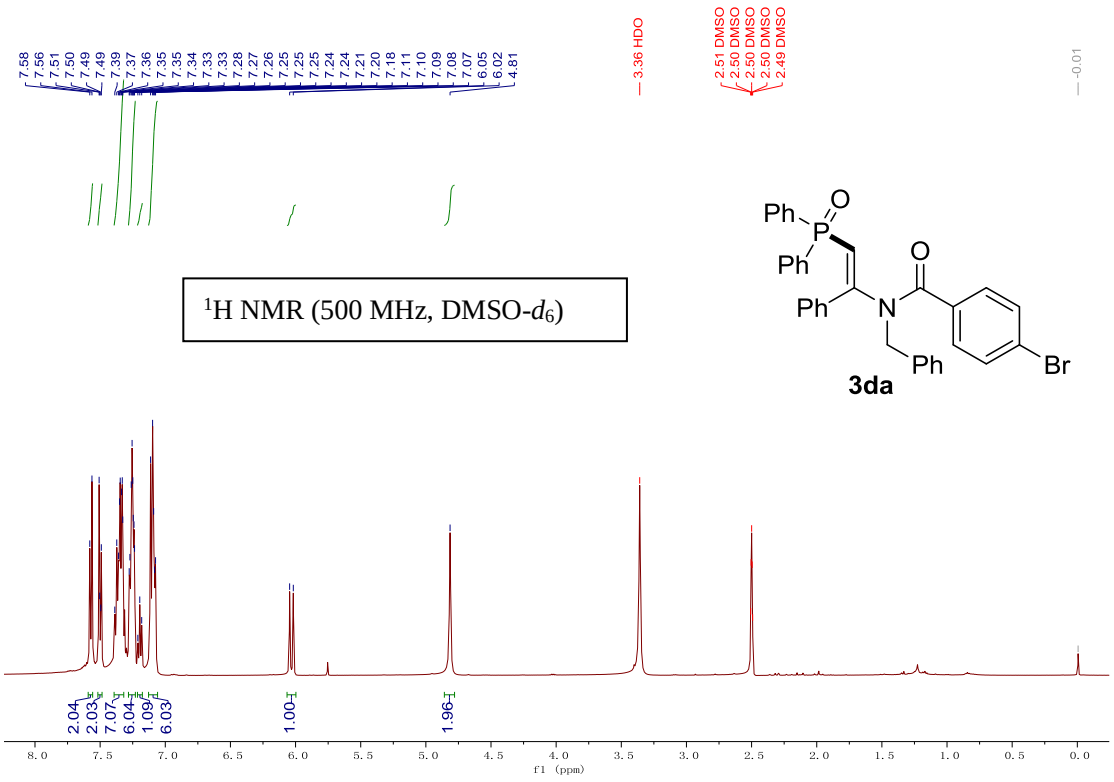
3ca



^{13}C NMR (126 MHz, DMSO-d_6)

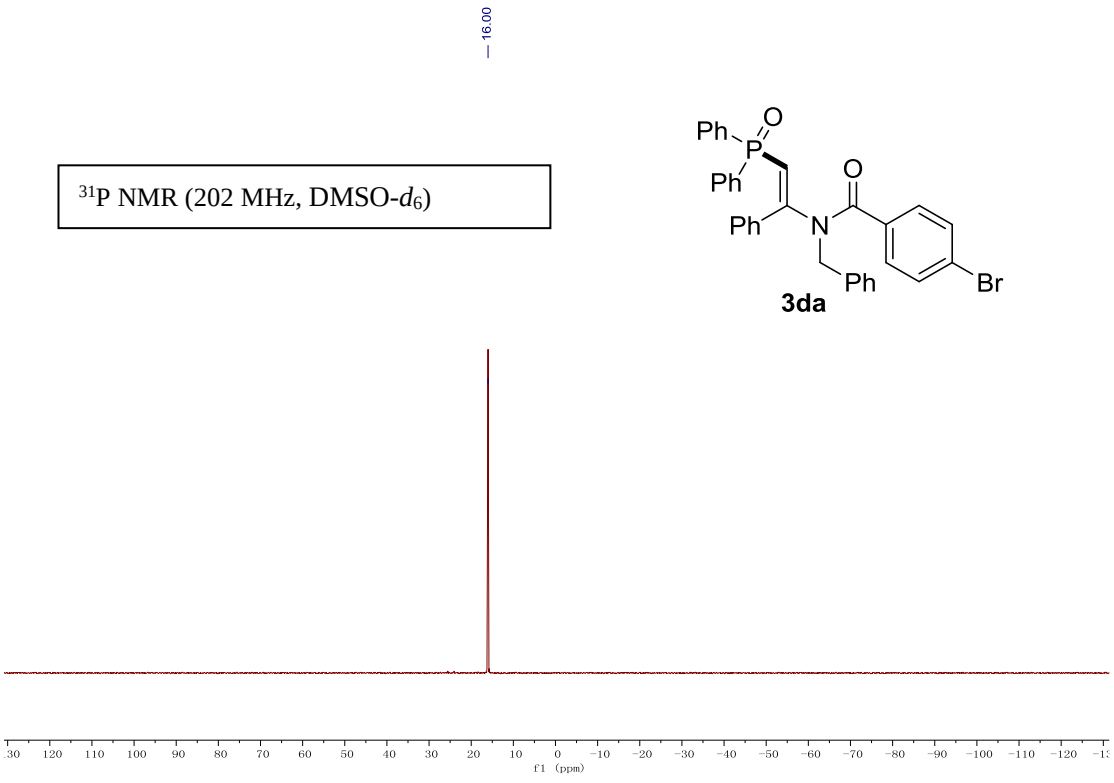


3ca



^{1}H NMR (500 MHz, DMSO-d_6)

3da



^{31}P NMR (202 MHz, DMSO-d_6)

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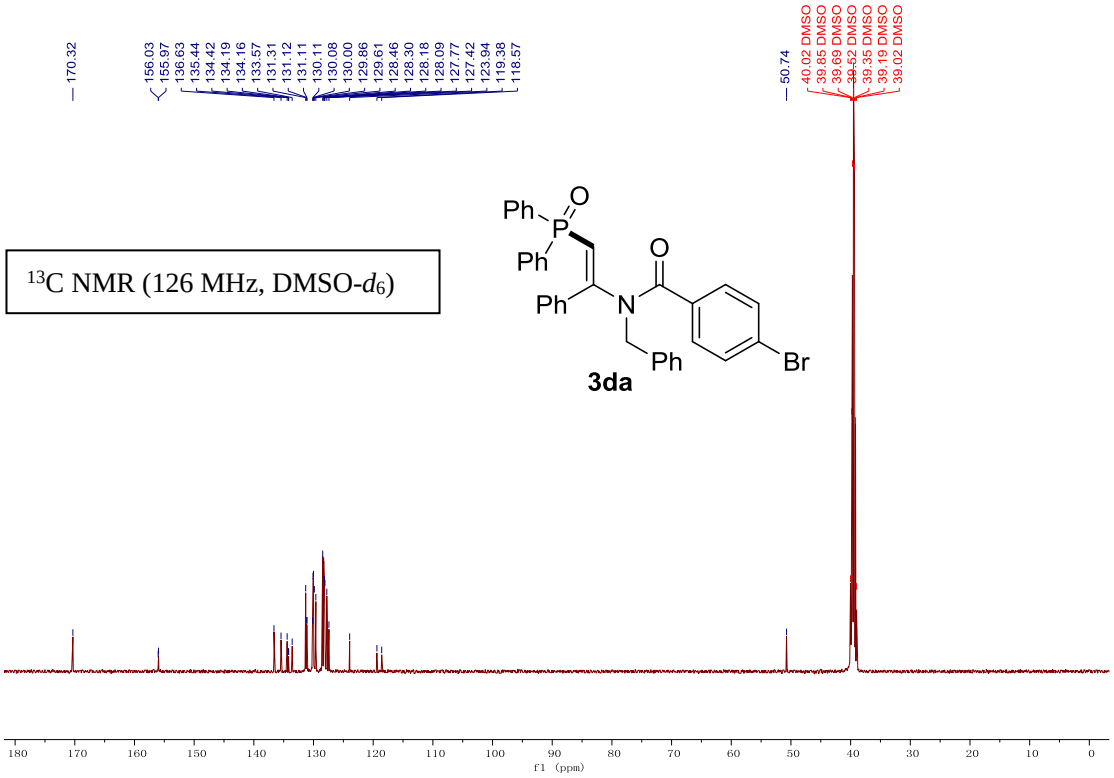
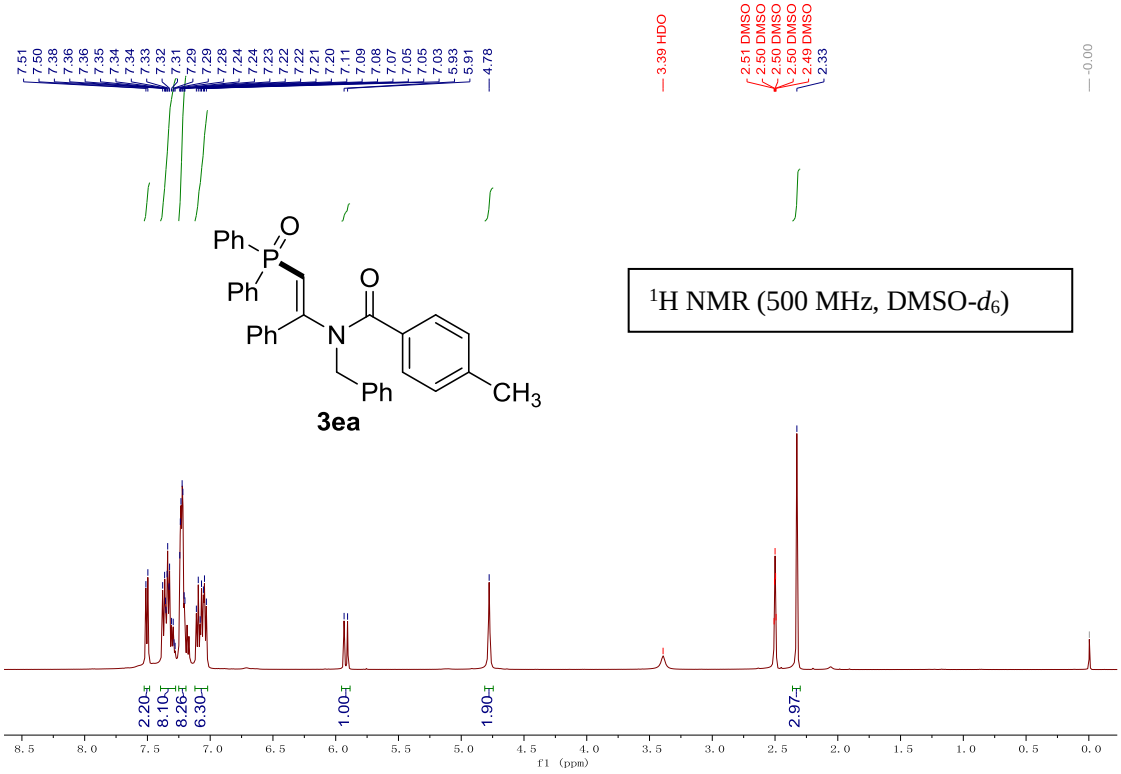


^{13}C NMR (126 MHz, DMSO-d_6)

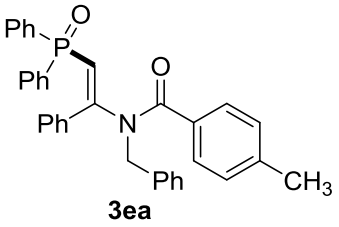
3da



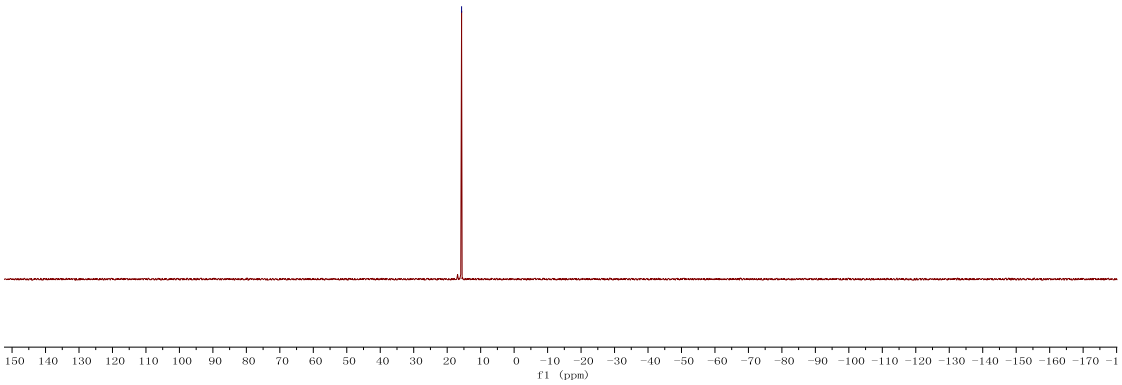
^{1}H NMR (500 MHz, DMSO-d_6)

3ea

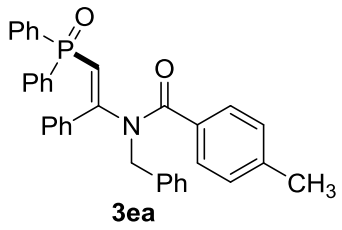
^{31}P NMR (202 MHz, DMSO-d_6)



3ea



^{13}C NMR (126 MHz, DMSO-d_6)



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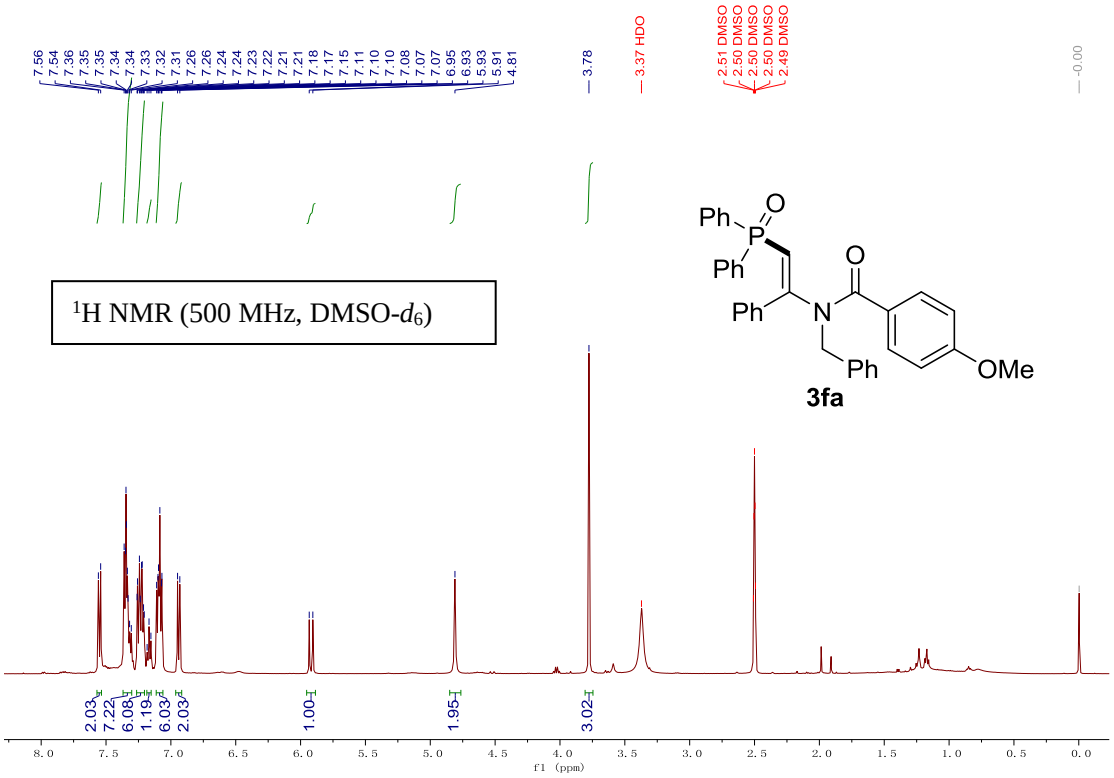
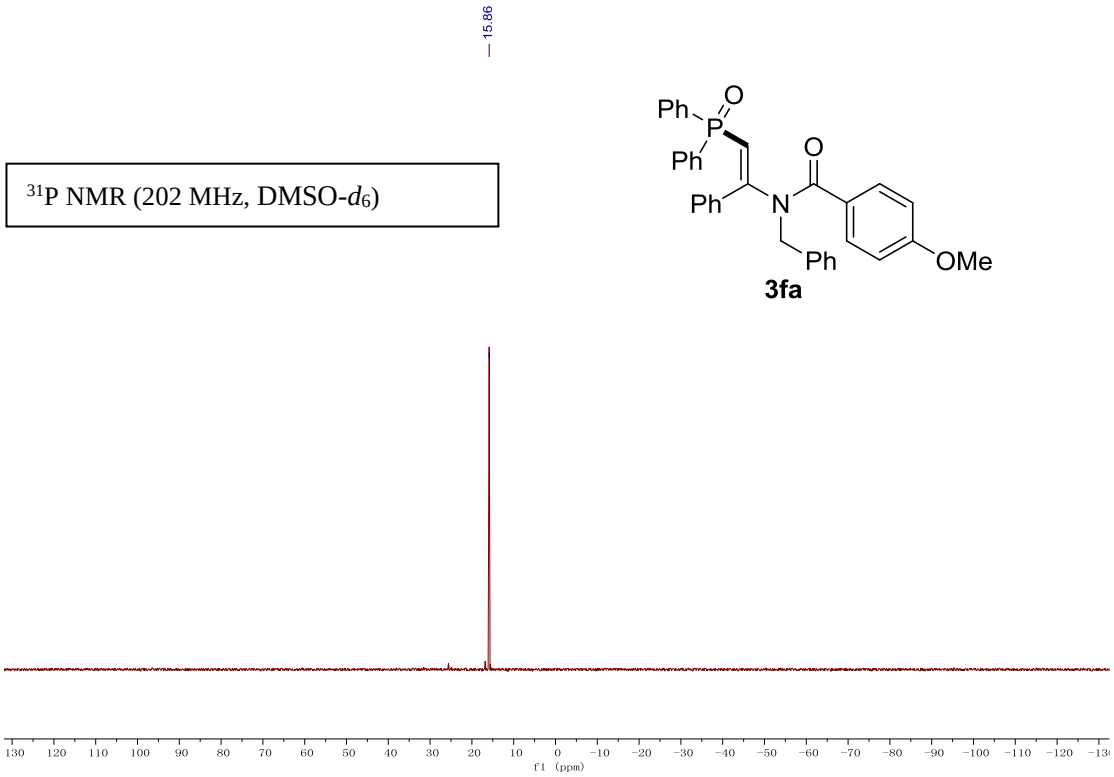


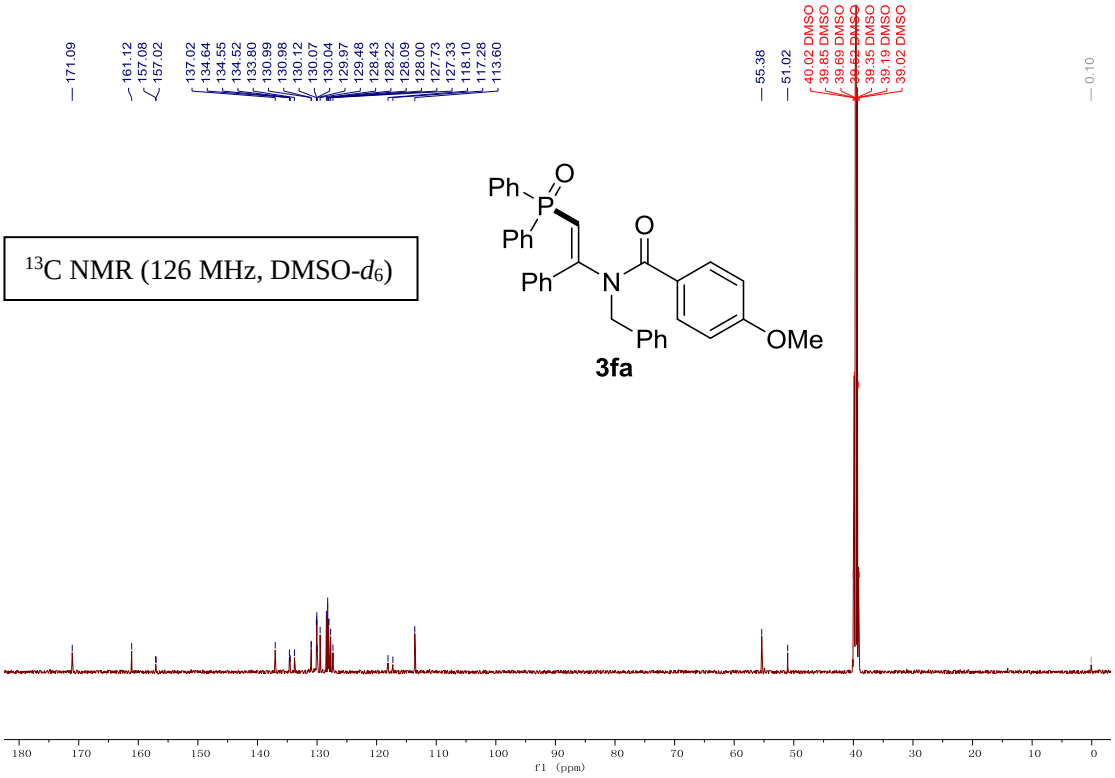
^{1}H NMR (500 MHz, DMSO-d_6)

3fa



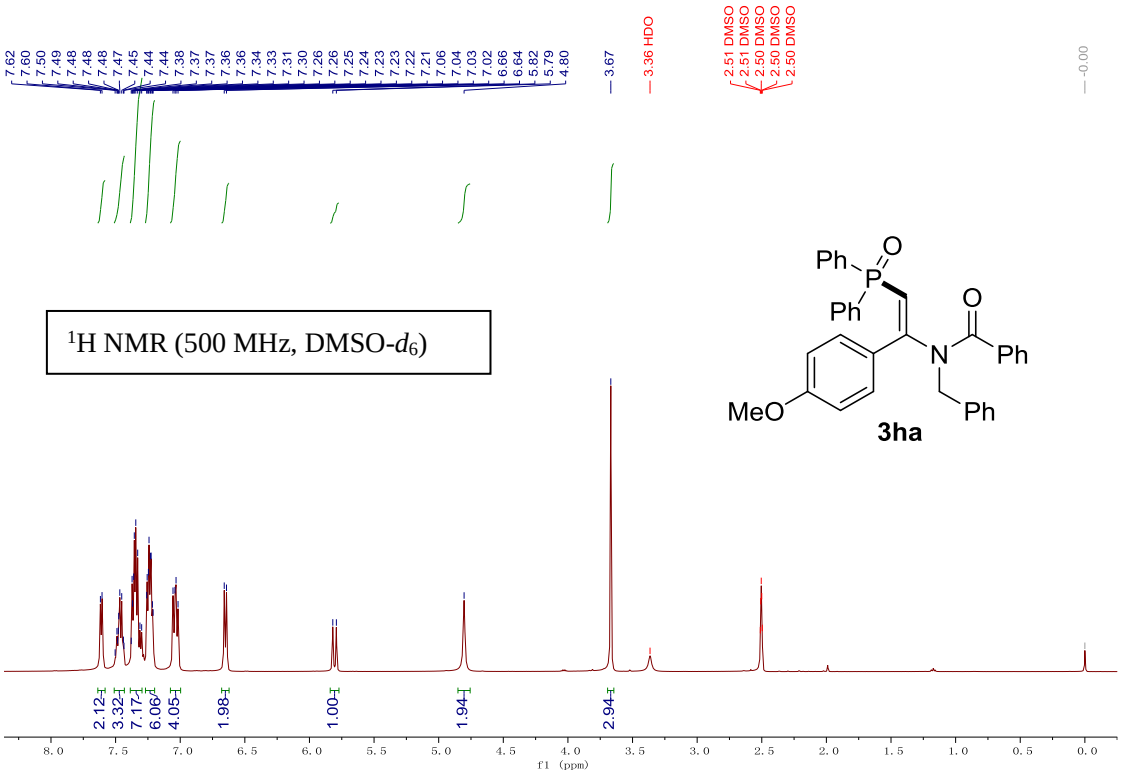
^{31}P NMR (202 MHz, DMSO-d_6)

3fa



^{13}C NMR (126 MHz, DMSO-d_6)

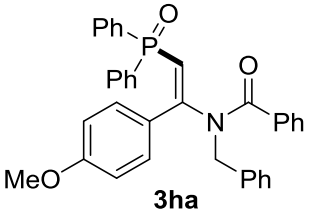
3fa



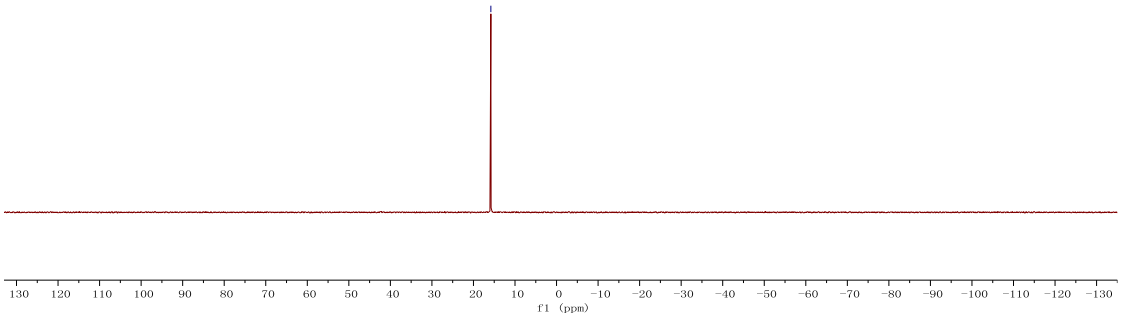
^{1}H NMR (500 MHz, DMSO-d_6)

3ha

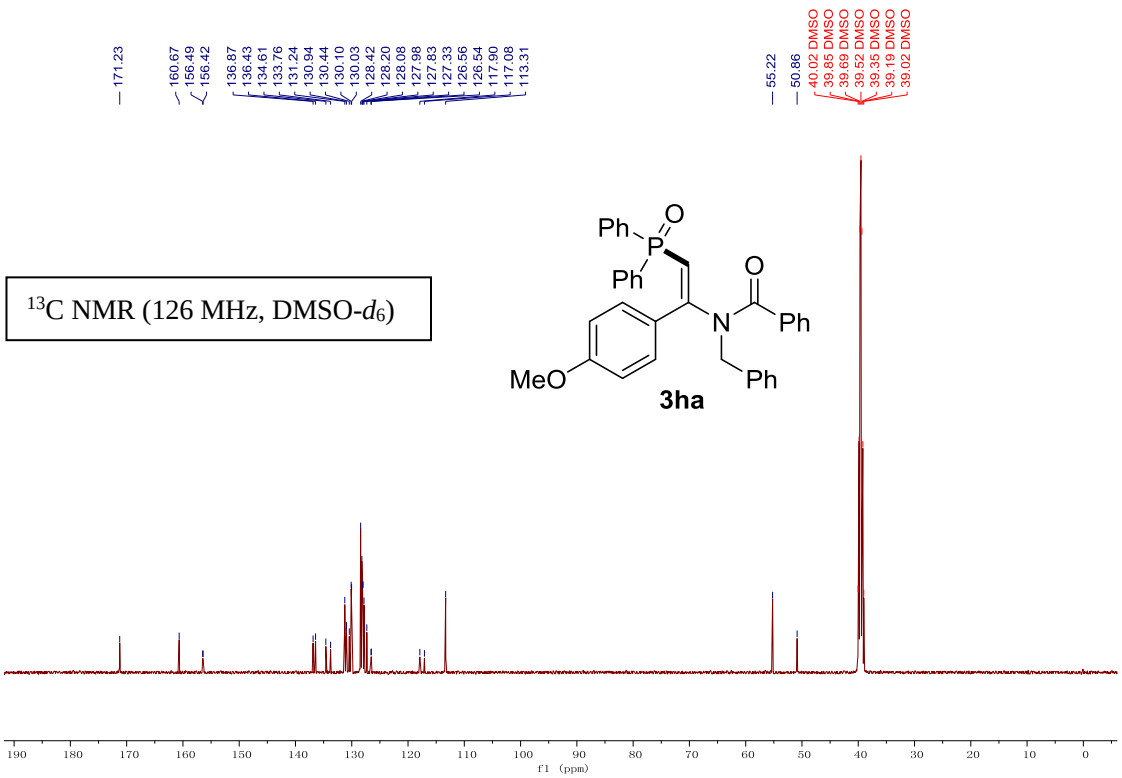
^{31}P NMR (202 MHz, Chloroform-*d*)



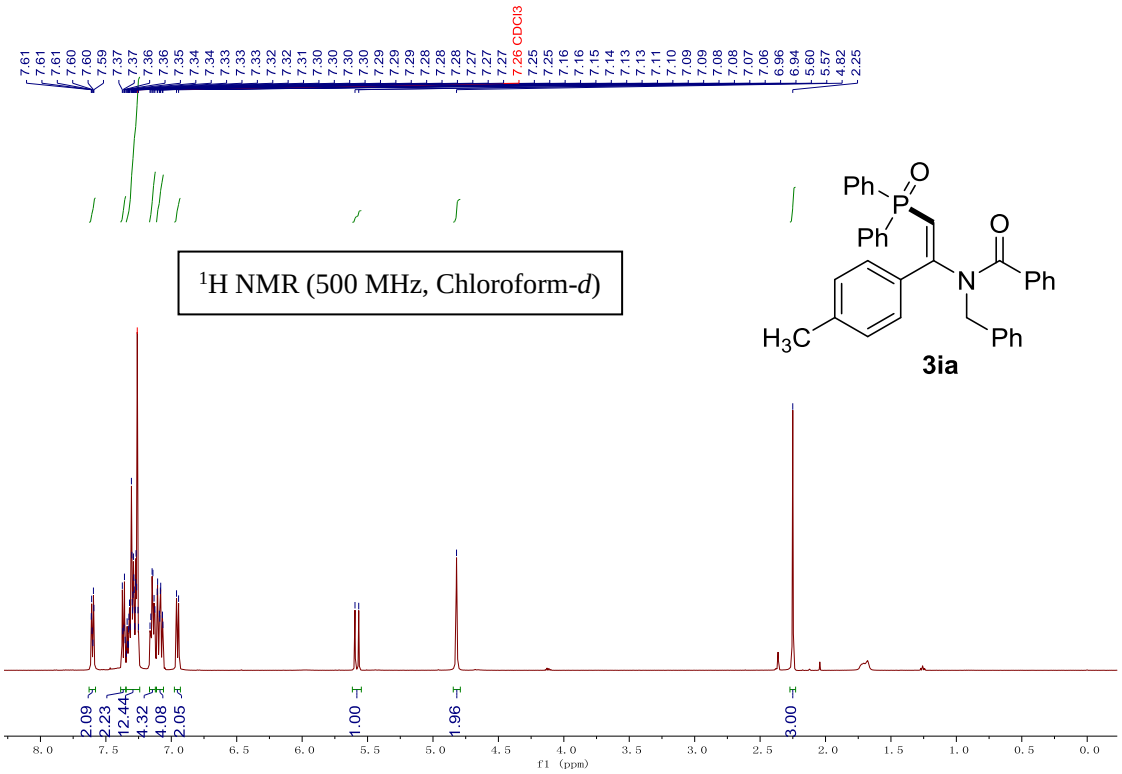
3ha



^{13}C NMR (126 MHz, DMSO-d_6)

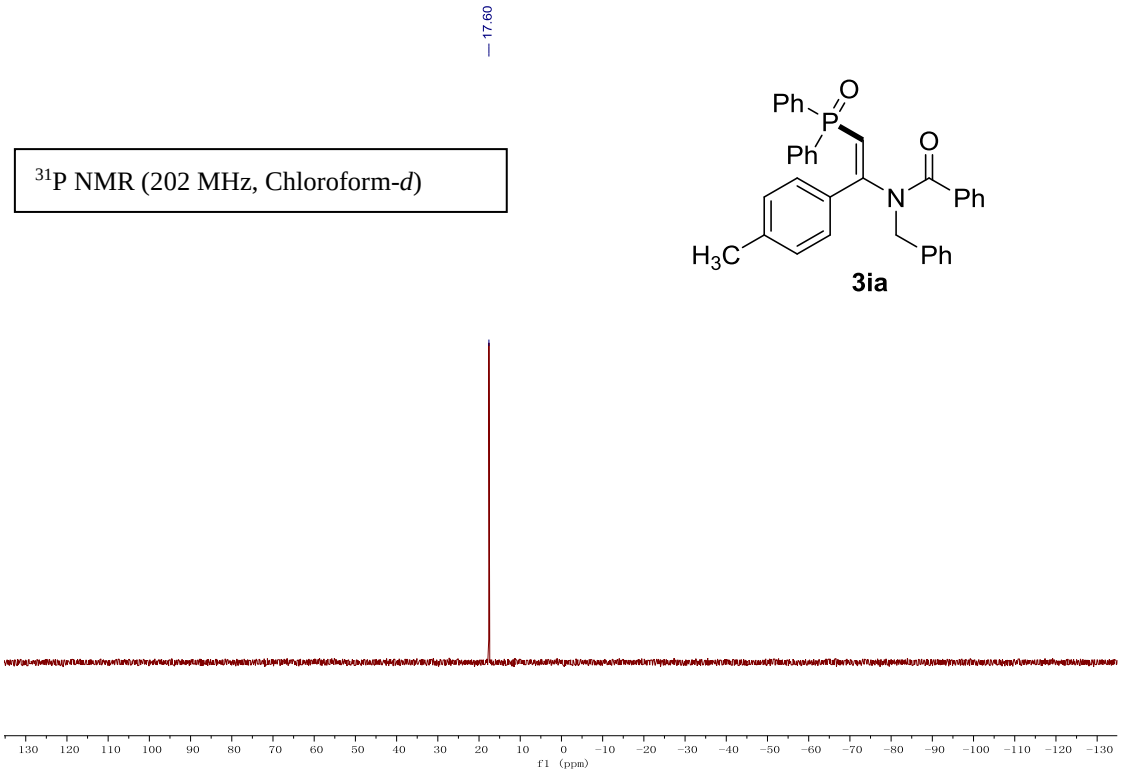


3ha



^{1}H NMR (500 MHz, Chloroform-*d*)

3ia



^{31}P NMR (202 MHz, Chloroform-*d*)

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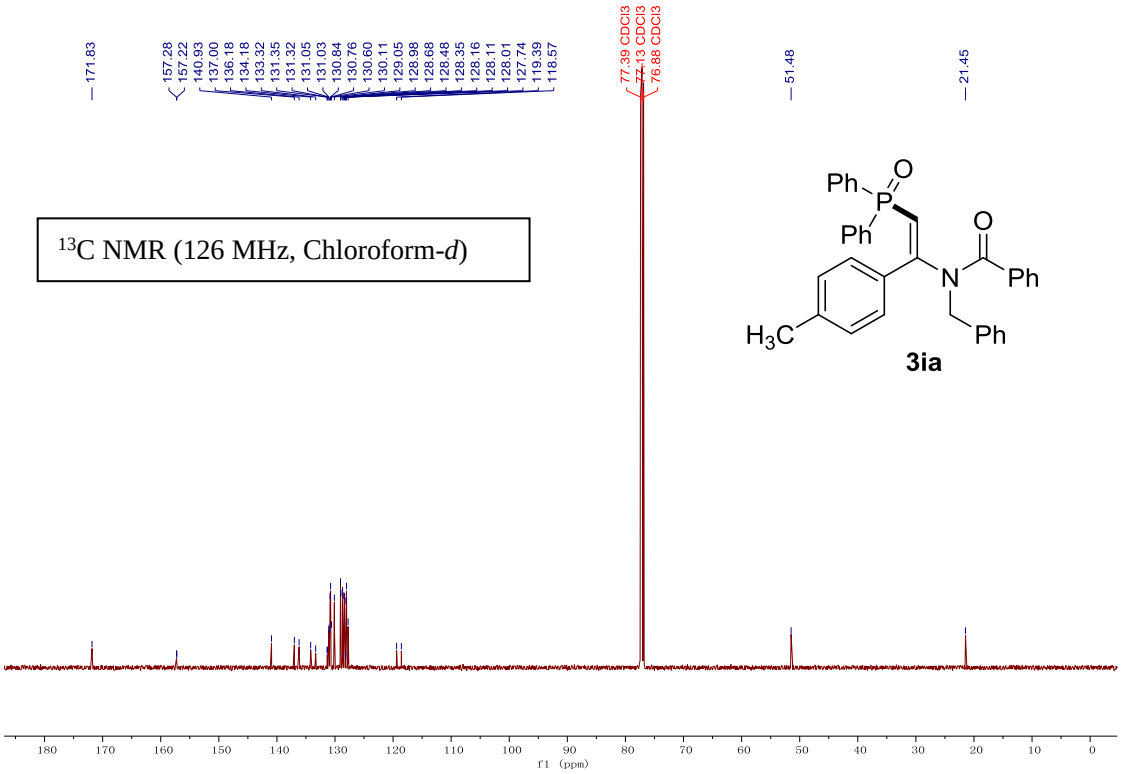
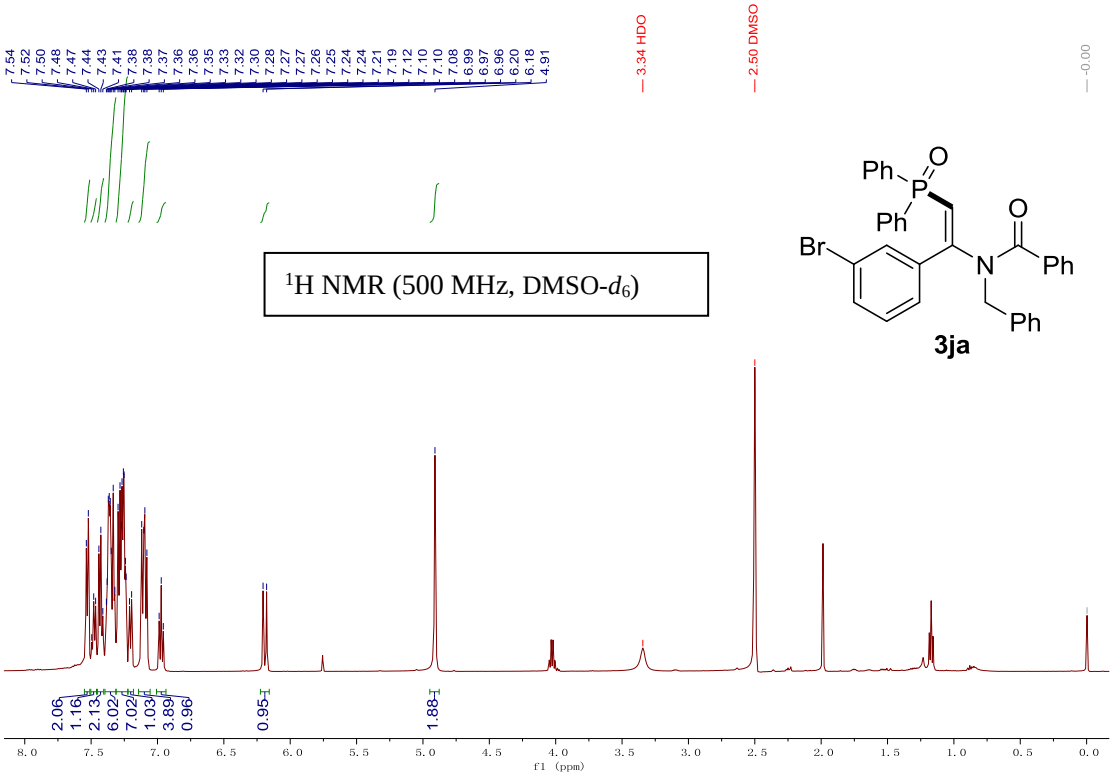


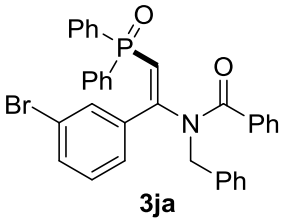
^{13}C NMR (126 MHz, Chloroform-*d*)

3ia



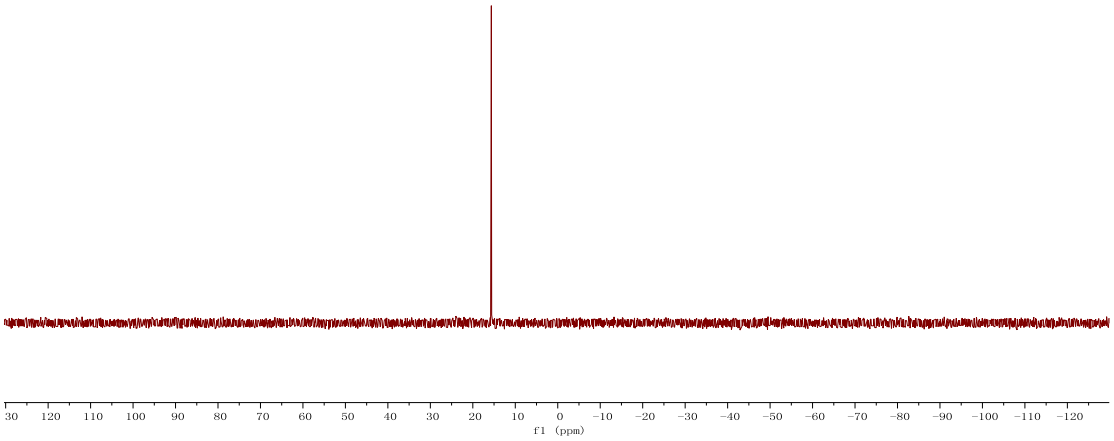
^{1}H NMR (500 MHz, DMSO-d_6)

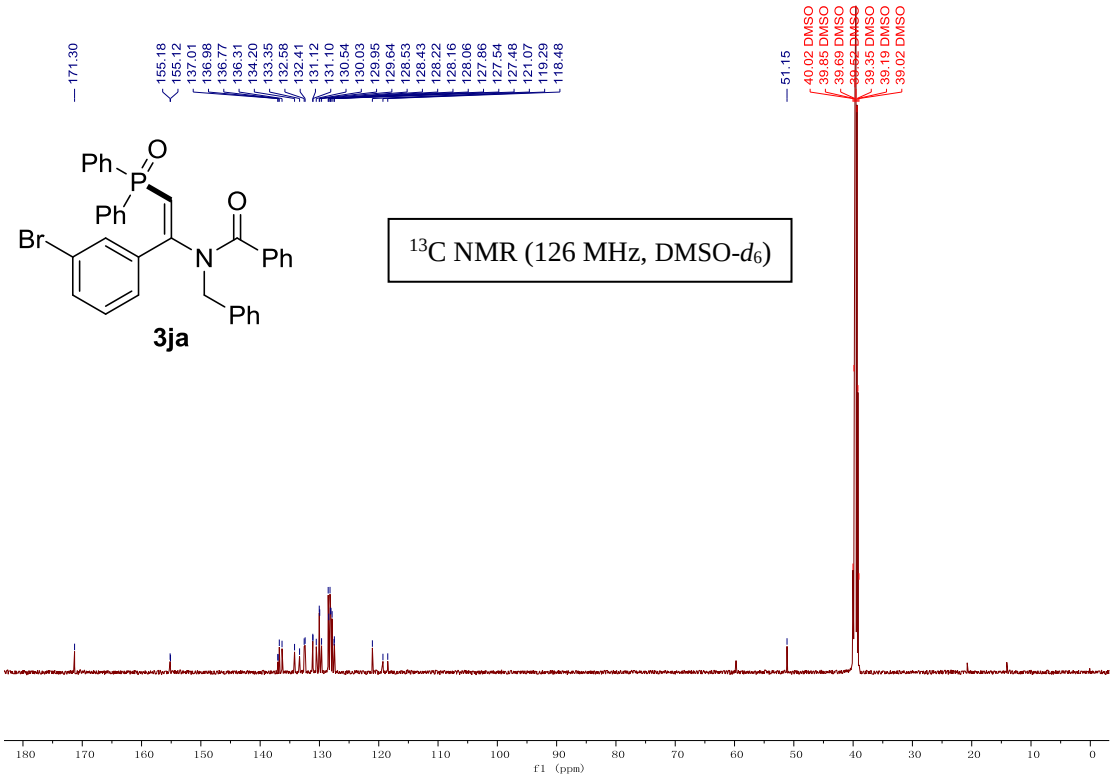
3ja



3ja

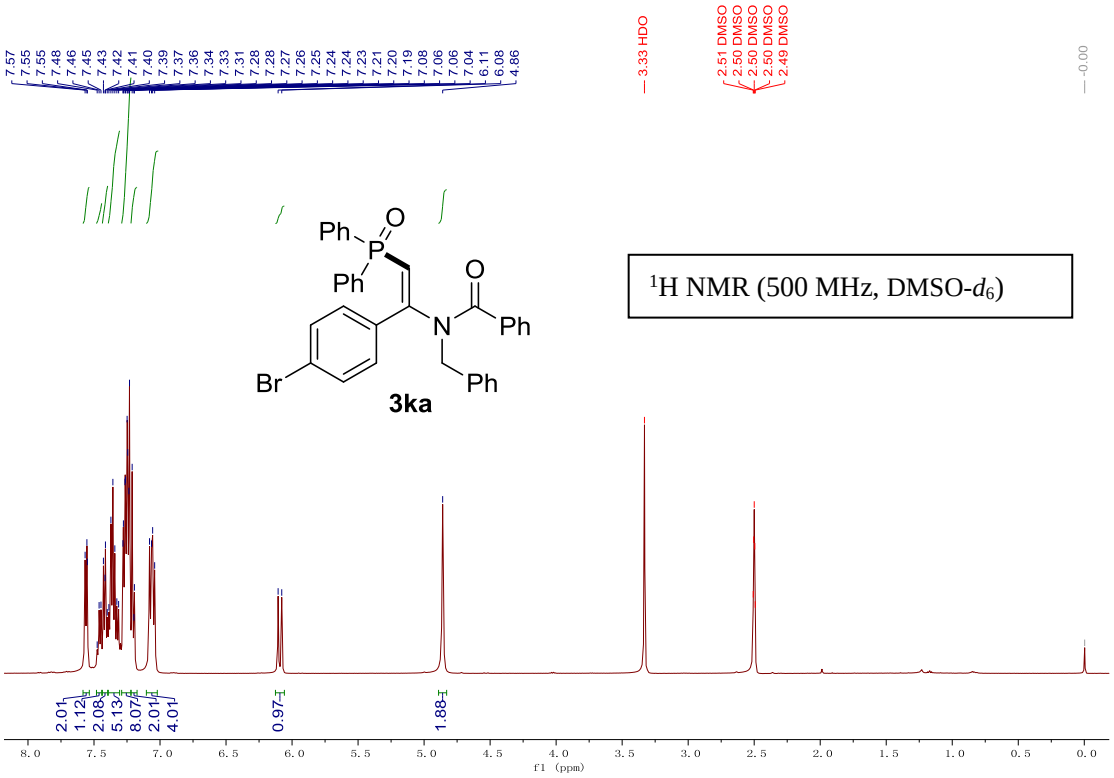
^{31}P NMR (202 MHz, DMSO-d_6)



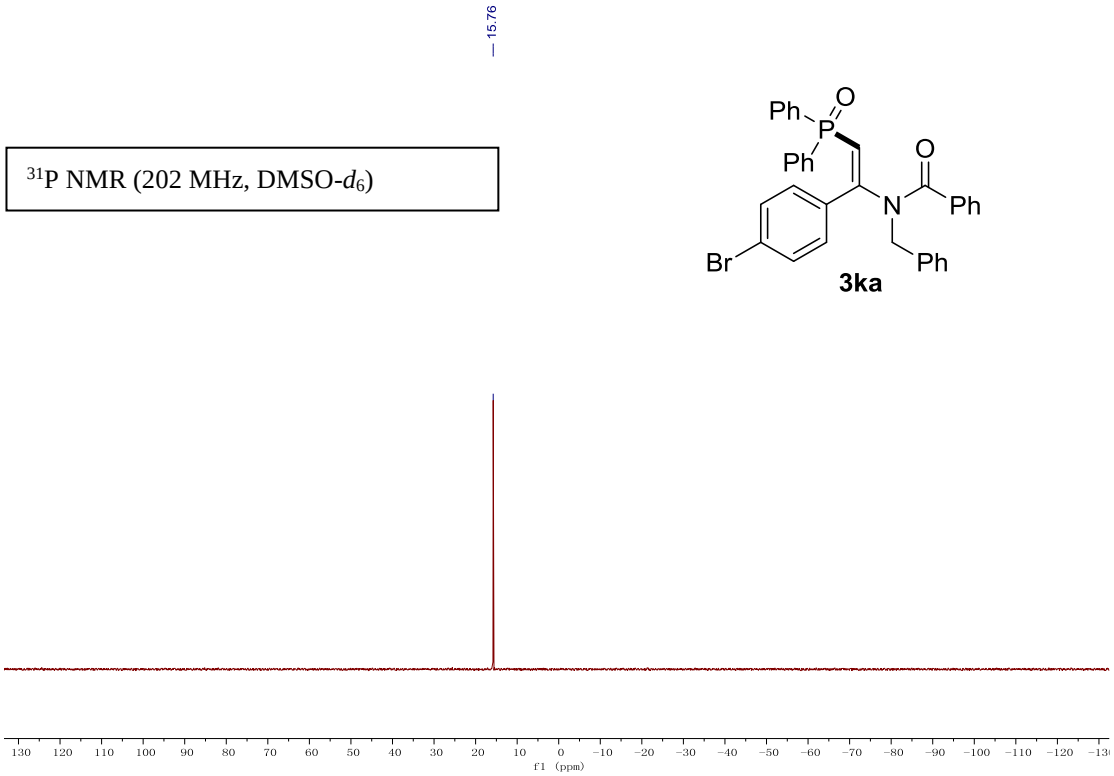


3ja

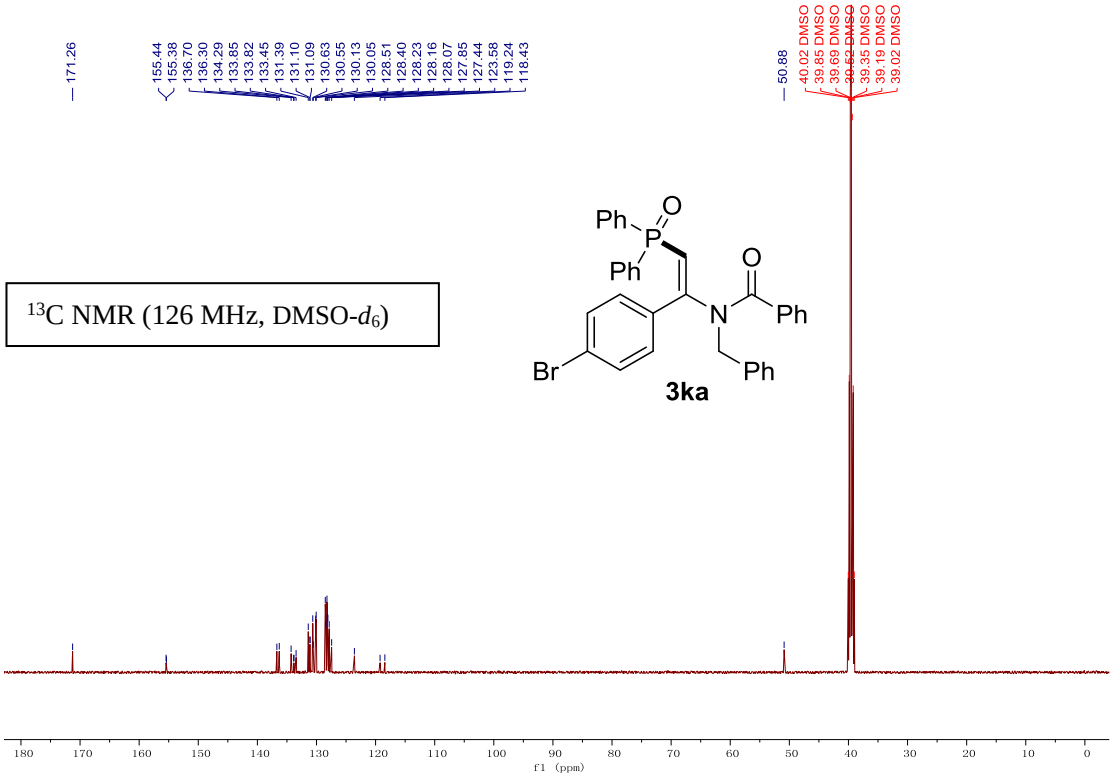
^{13}C NMR (126 MHz, DMSO-d_6)



^{1}H NMR (500 MHz, DMSO-d_6)

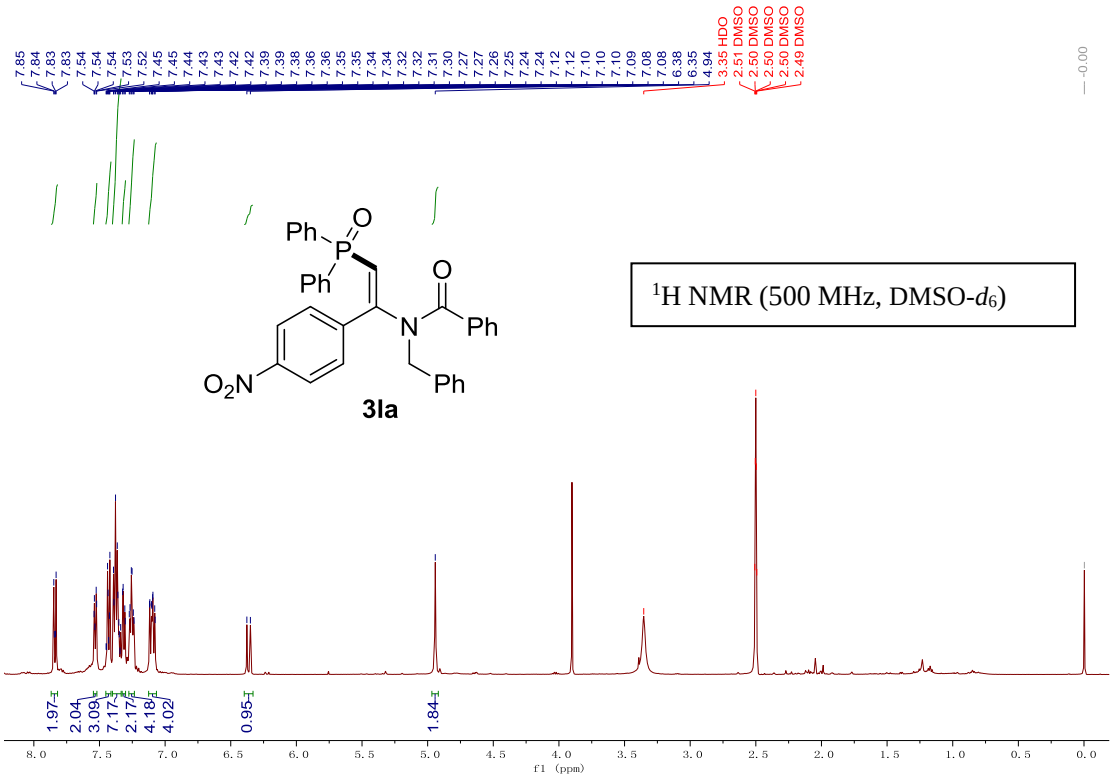


^{31}P NMR (202 MHz, DMSO-d_6)



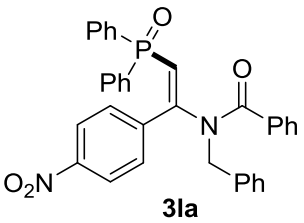
^{13}C NMR (126 MHz, DMSO-d_6)

3ka



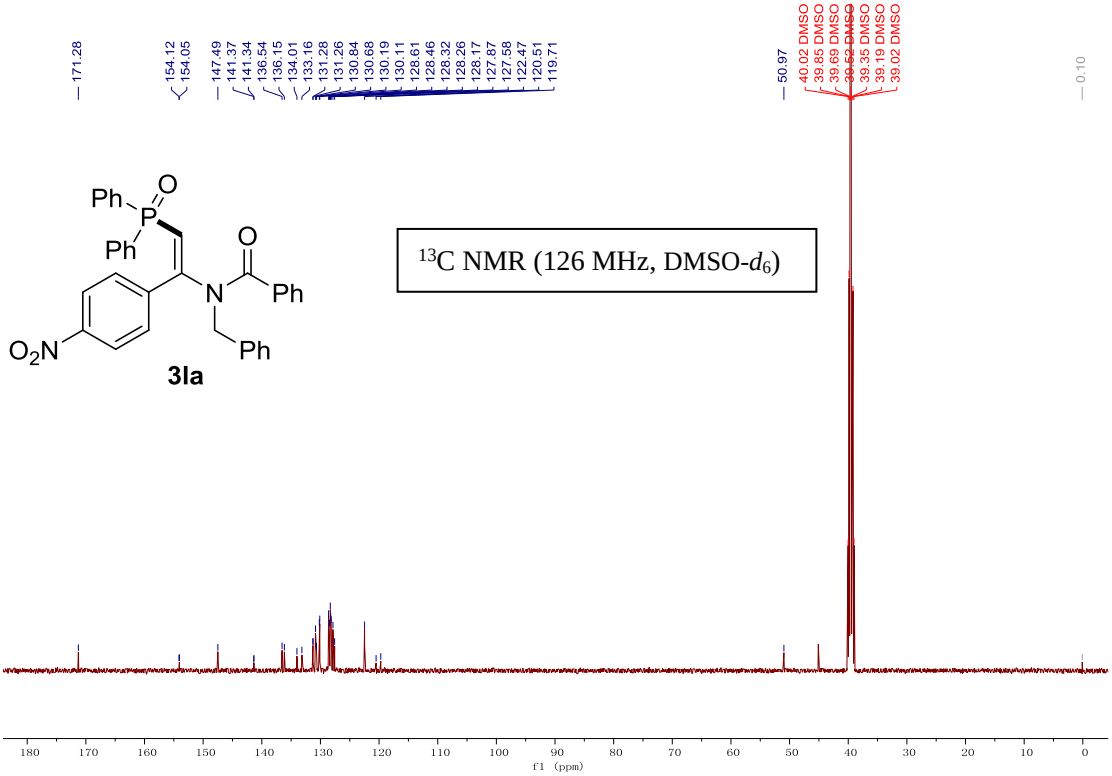
^{1}H NMR (500 MHz, DMSO-d_6)

3la



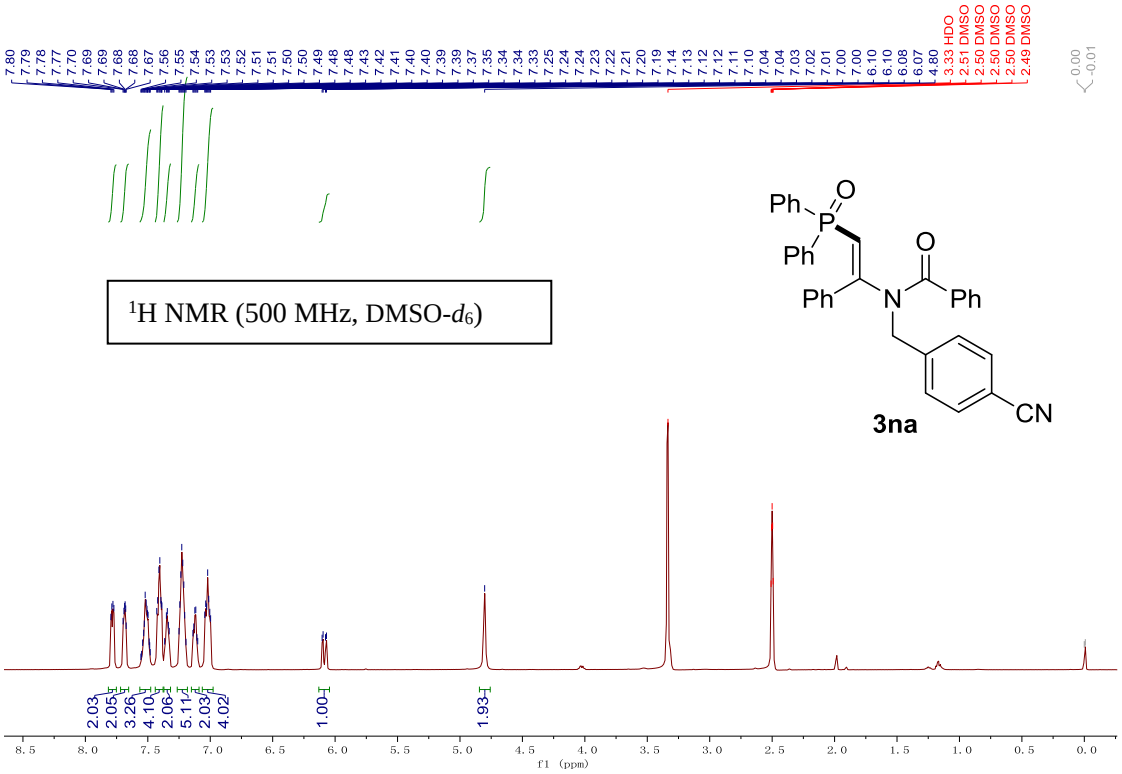
3la

^{31}P NMR (202 MHz, DMSO-d_6)



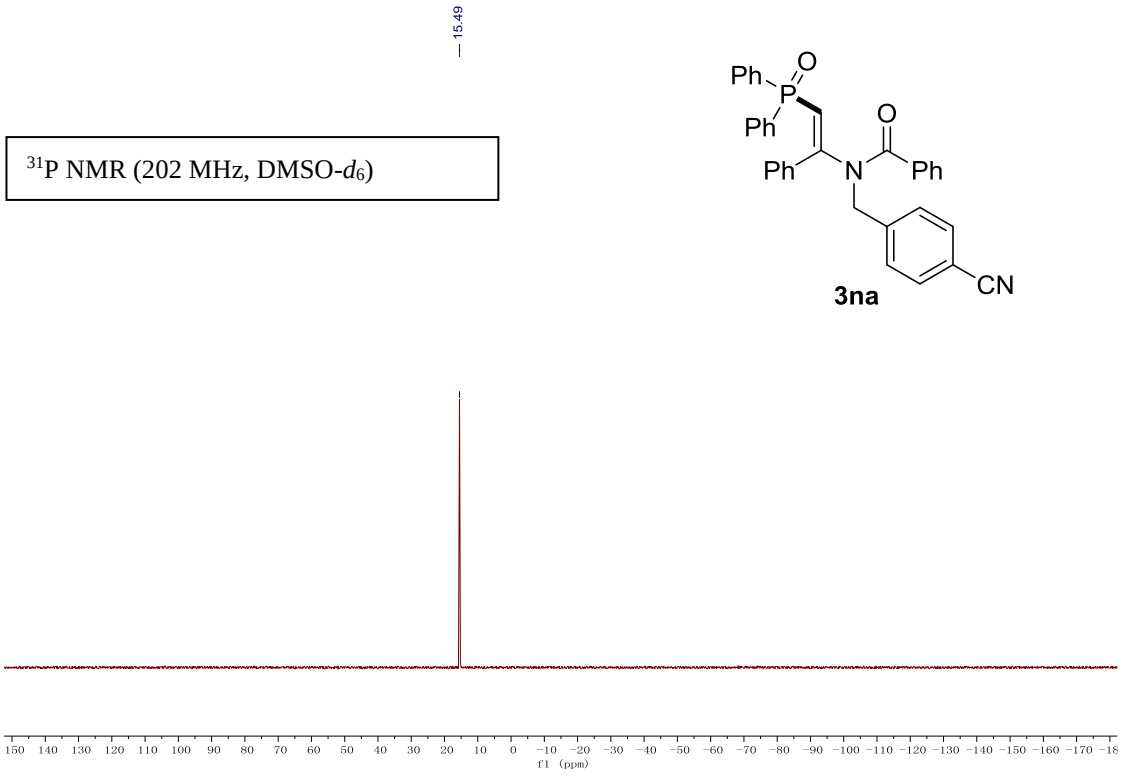
3la

^{13}C NMR (126 MHz, DMSO-d_6)



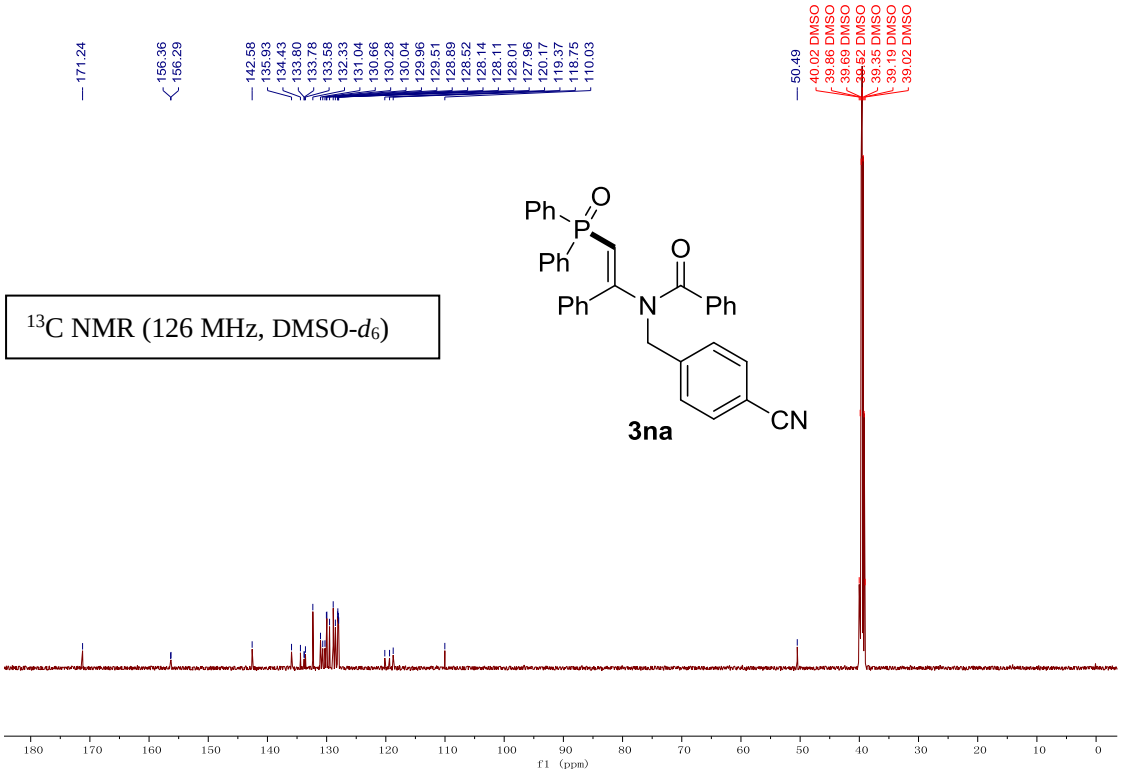
^{1}H NMR (500 MHz, DMSO-d_6)

3na

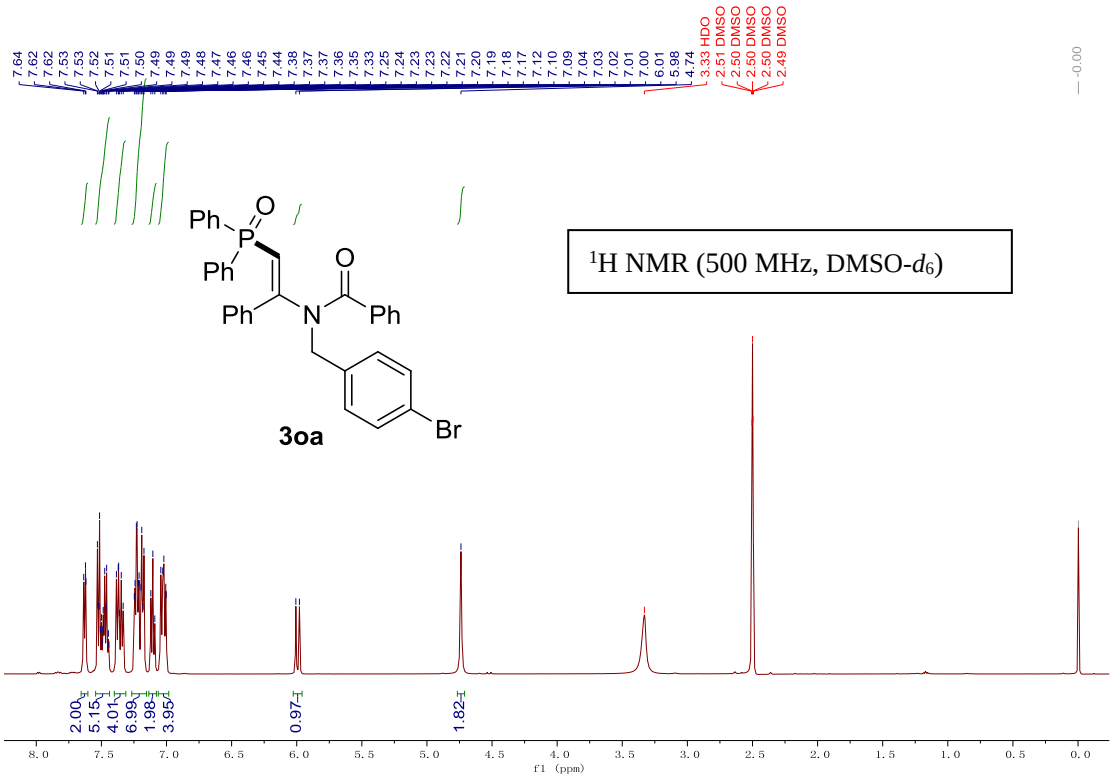


^{31}P NMR (202 MHz, DMSO-d_6)

3na

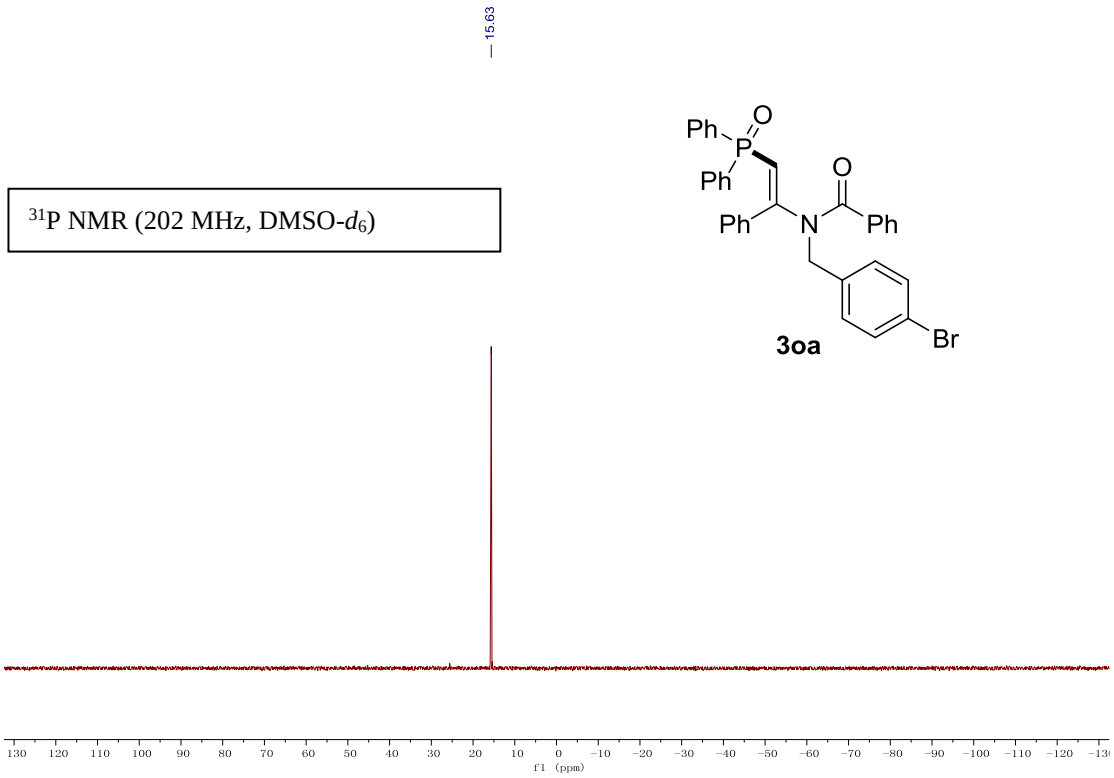


^{13}C NMR (126 MHz, DMSO-d_6)

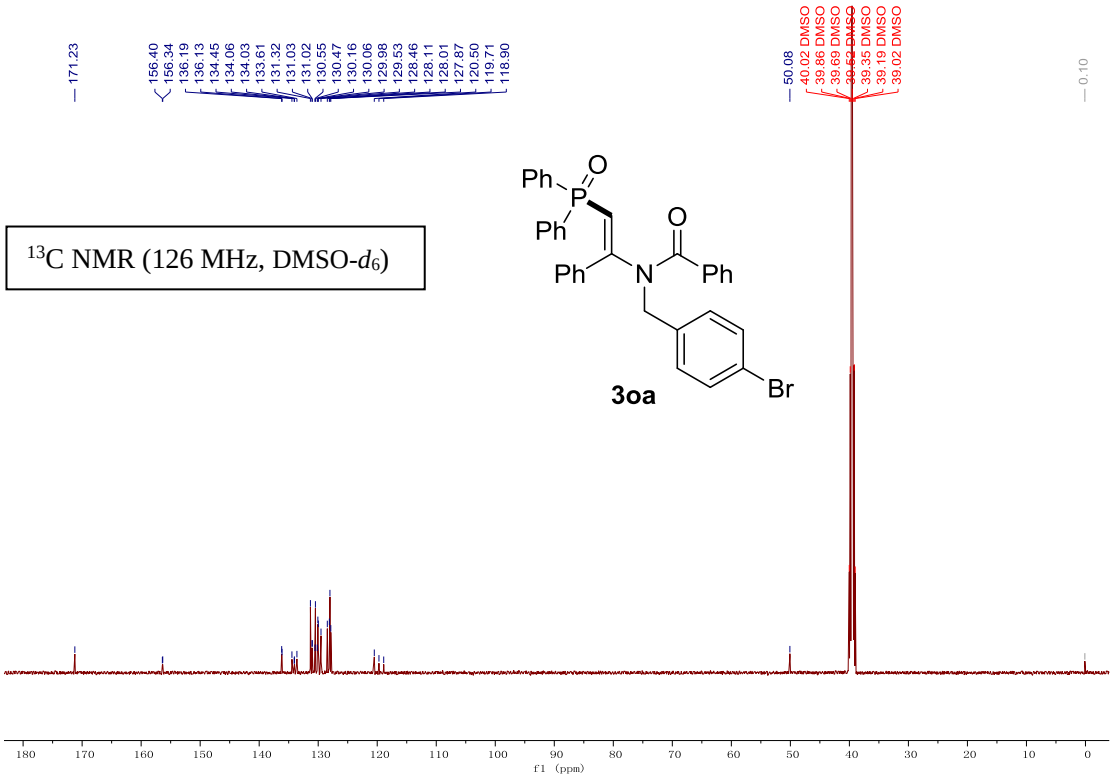


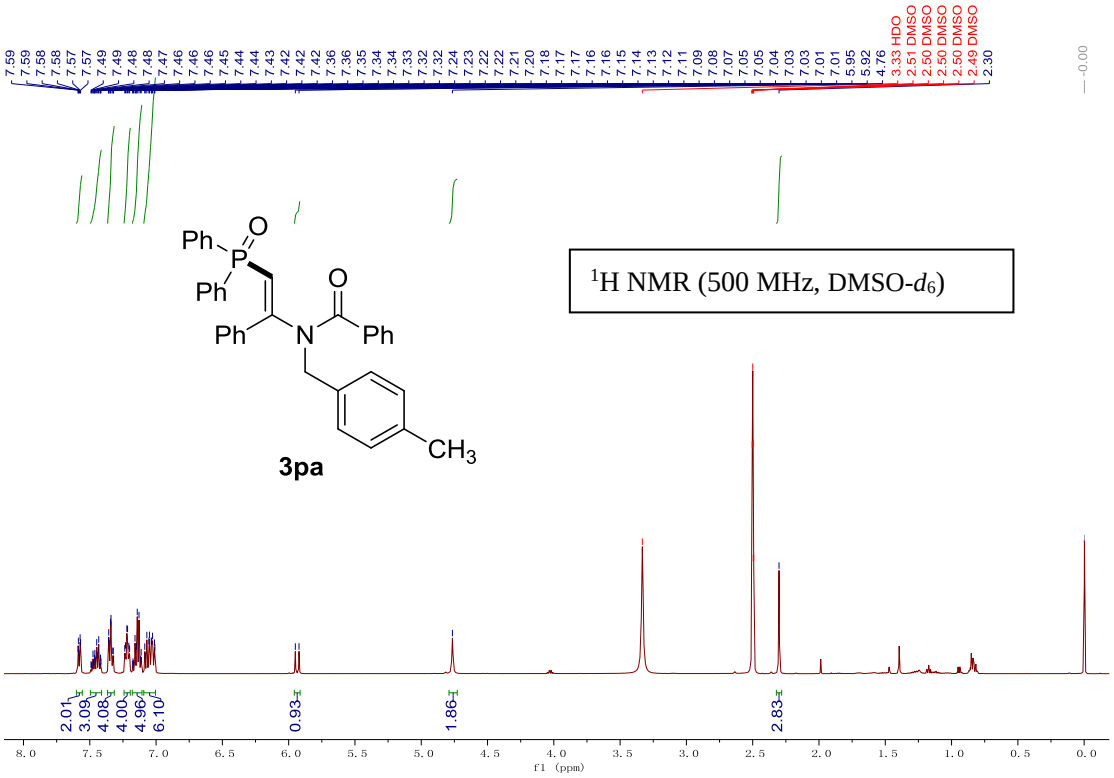
^{1}H NMR (500 MHz, DMSO-d_6)

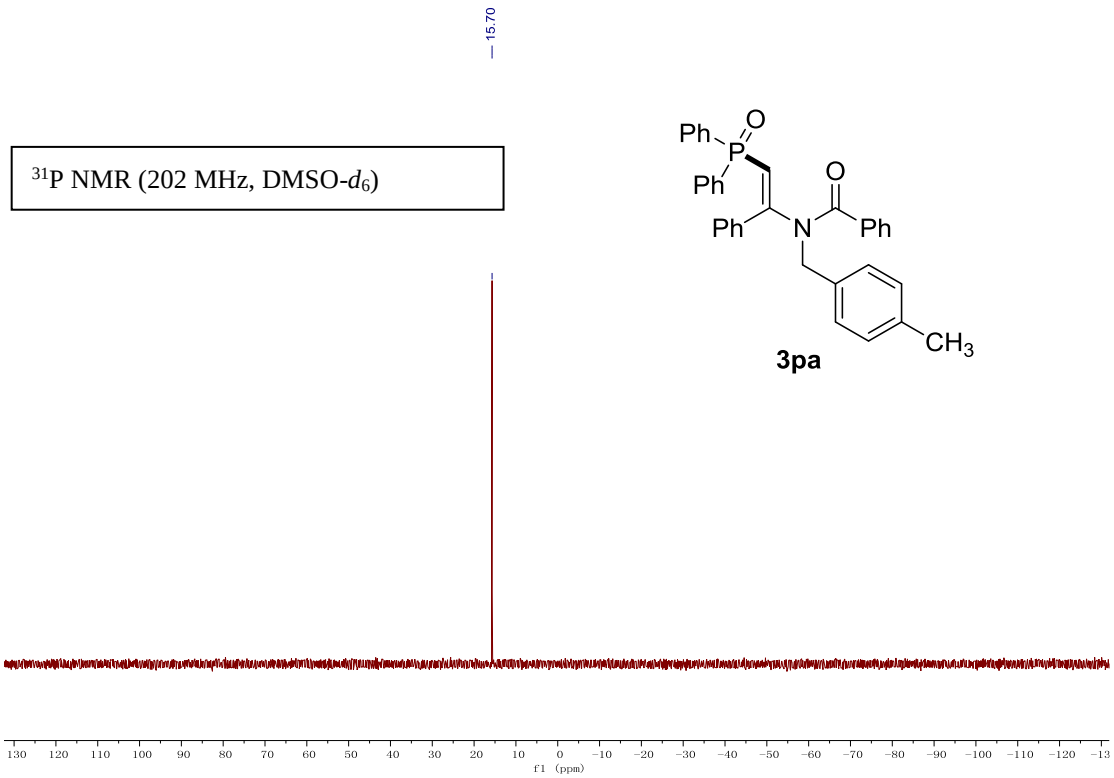
^{31}P NMR (202 MHz, DMSO-d_6)

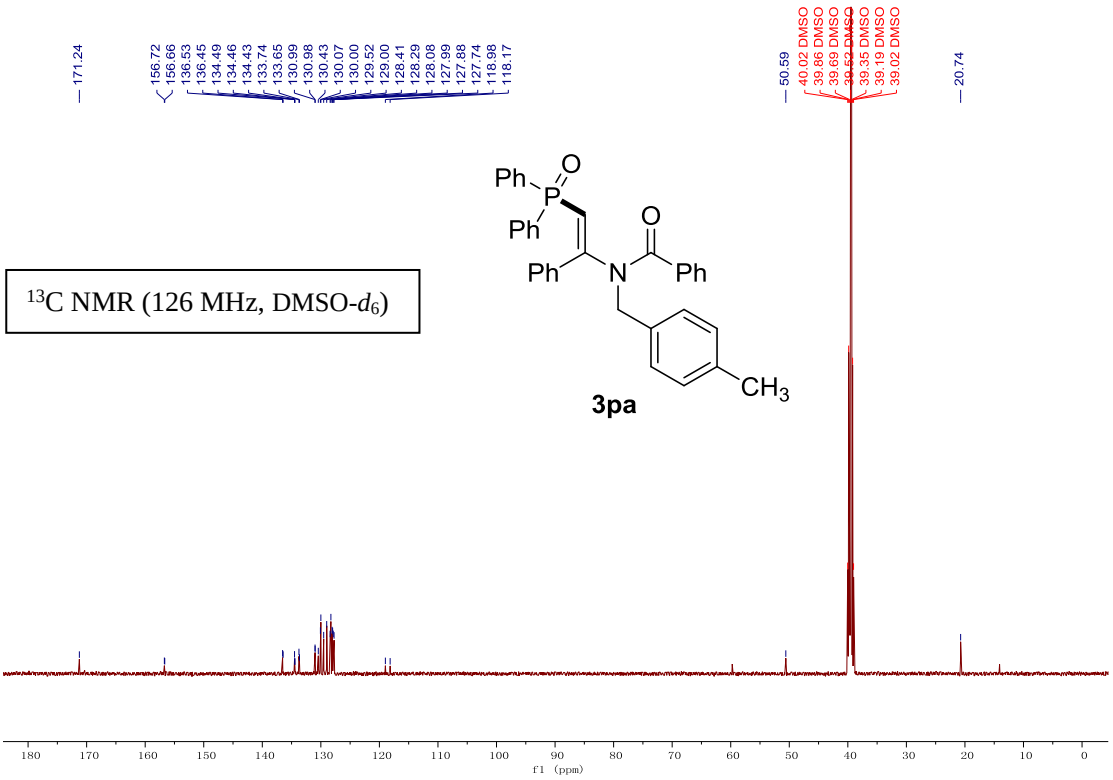


^{13}C NMR (126 MHz, DMSO-d_6)



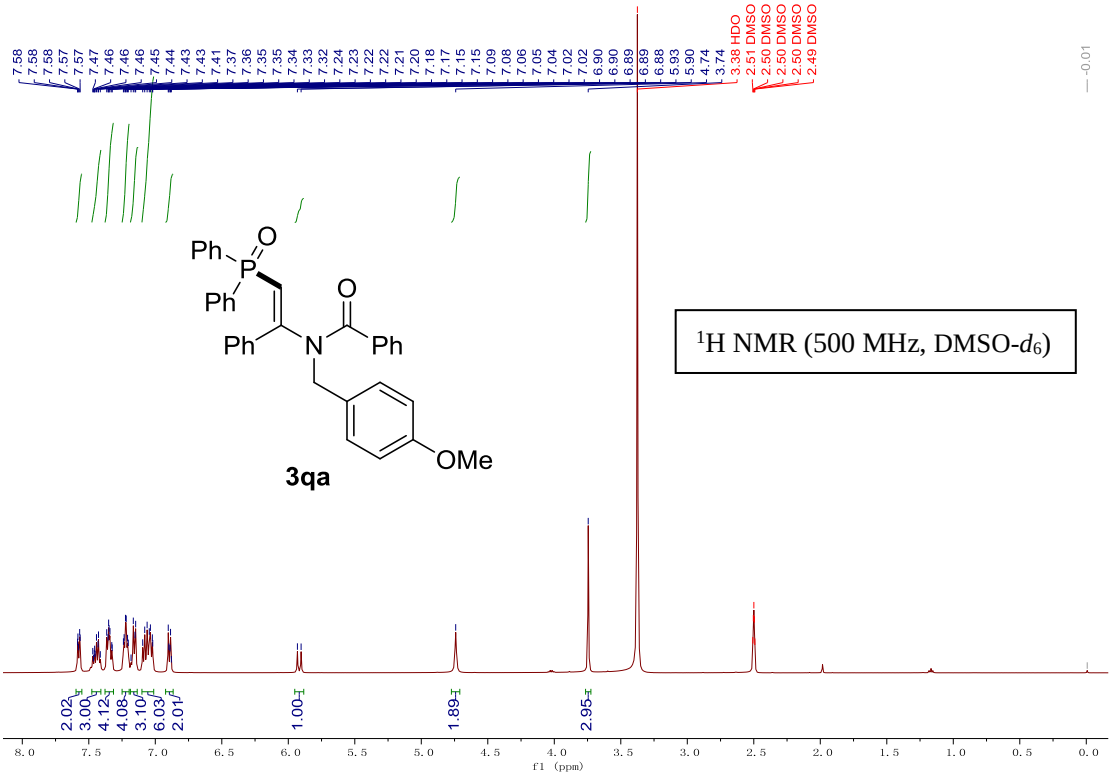

7.59 7.59 7.58 7.58 7.57 7.57 7.49 7.49 7.48 7.48 7.47 7.46 7.46 7.45 7.44 7.44 7.43 7.42 7.42 7.36 7.35 7.34 7.34 7.33 7.32 7.24 7.23 7.22 7.22 7.21 7.20 7.18 7.17 7.17 7.16 7.16 7.15 7.14 7.13 7.12 7.11 7.09 7.08 7.07 7.05 7.05 7.04 7.03 7.03 7.01 7.01 5.95 5.92 4.76 3.33 HDO 2.51 DMSO 2.50 DMSO 2.50 DMSO 2.50 DMSO 2.49 DMSO 2.30
-0.00
Ph
O
P
Ph
O
Ph
N
Ph
CH3
3pa
1H NMR (500 MHz, DMSO-d6)
2.01 3.09 4.08 4.00 4.96 6.10 0.93 1.86 2.83
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


15.70
31P NMR (202 MHz, DMSO-d6)
Ph
O
P
Ph
O
Ph
N
Ph
CH3
3pa
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -13
f1 (ppm)



^{13}C NMR (126 MHz, DMSO-d_6)

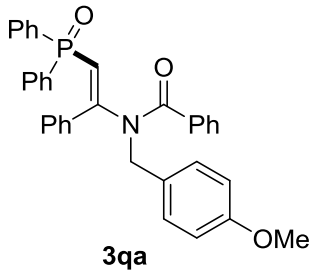
3pa



3qa

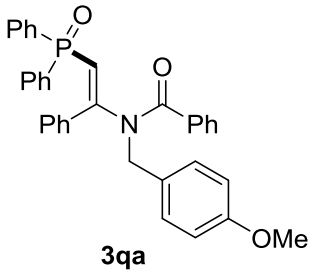
^{1}H NMR (500 MHz, DMSO-d_6)

^{31}P NMR (202 MHz, DMSO-d_6)

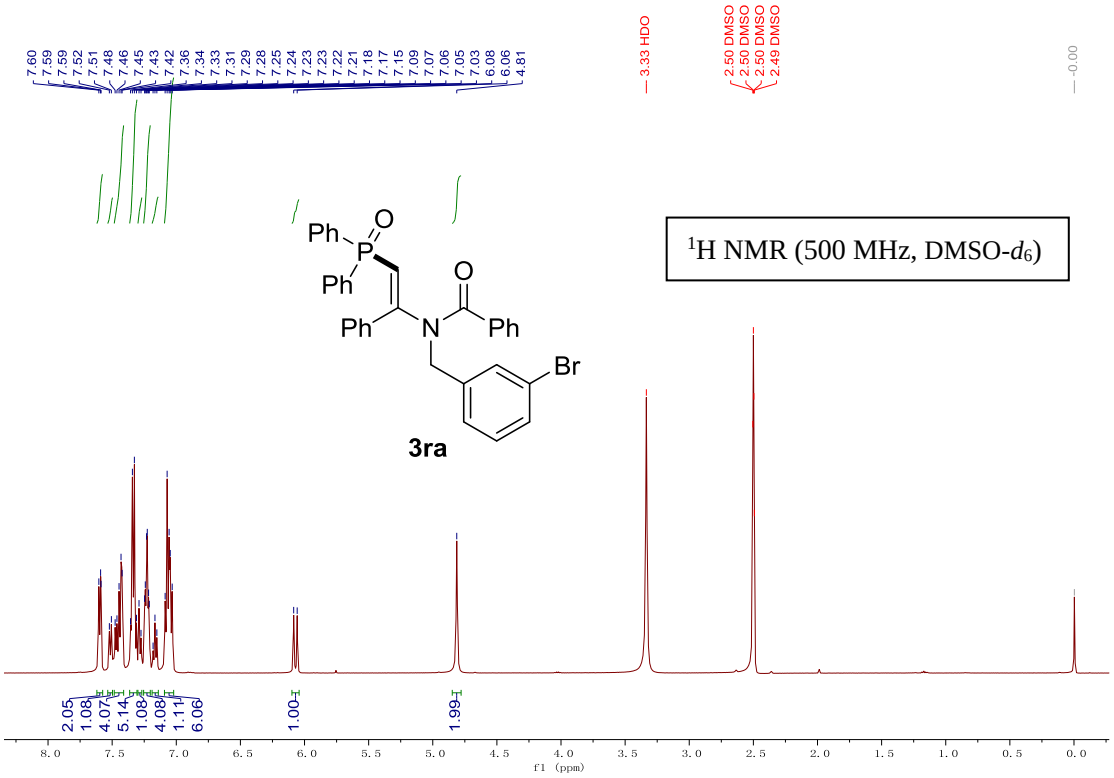


3qa

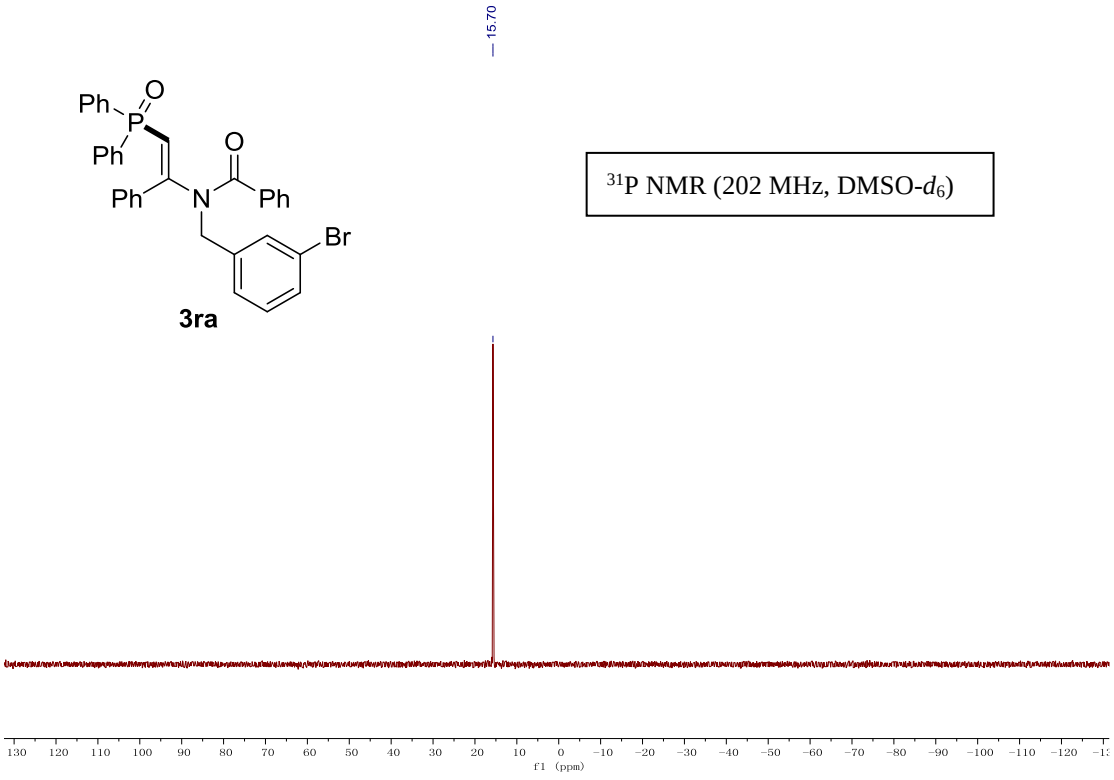
^{13}C NMR (126 MHz, DMSO-d_6)



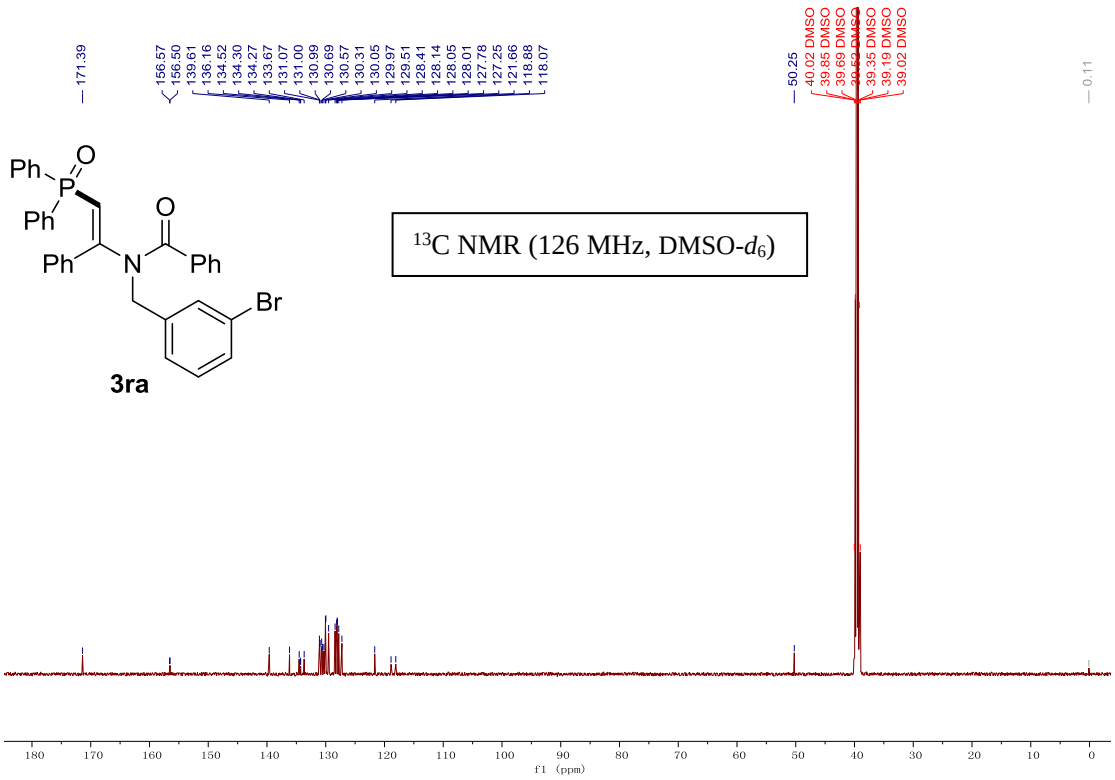
3qa

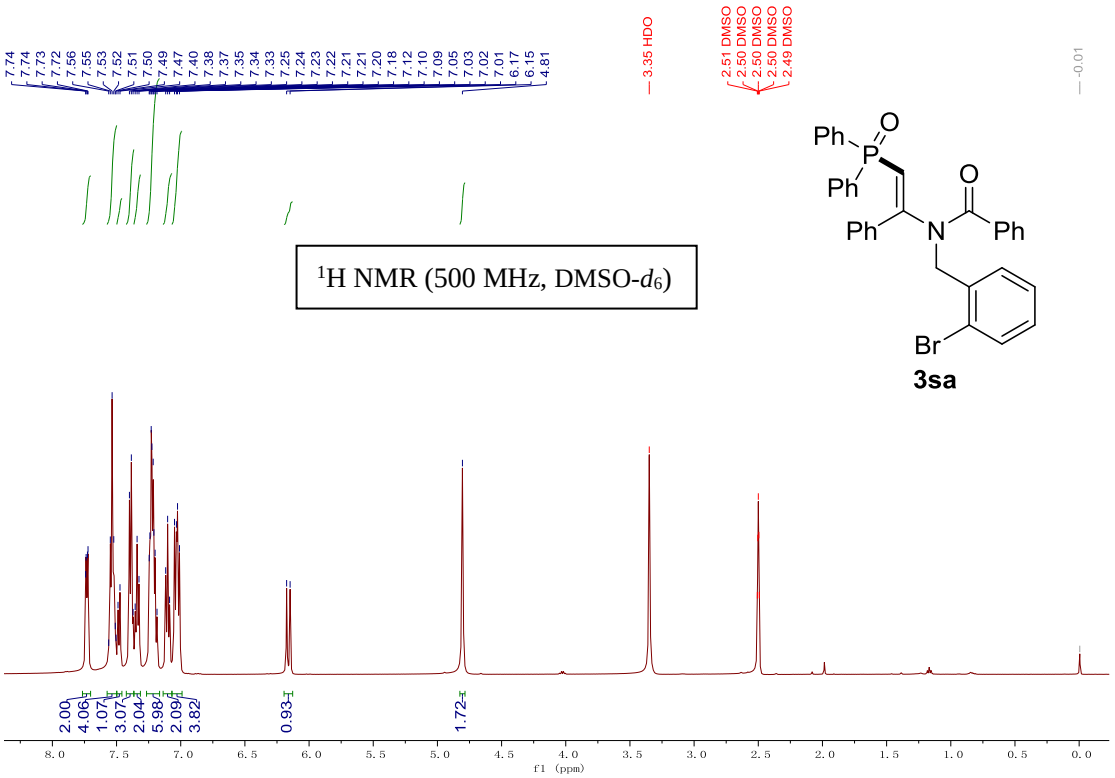


^{1}H NMR (500 MHz, DMSO-d_6)

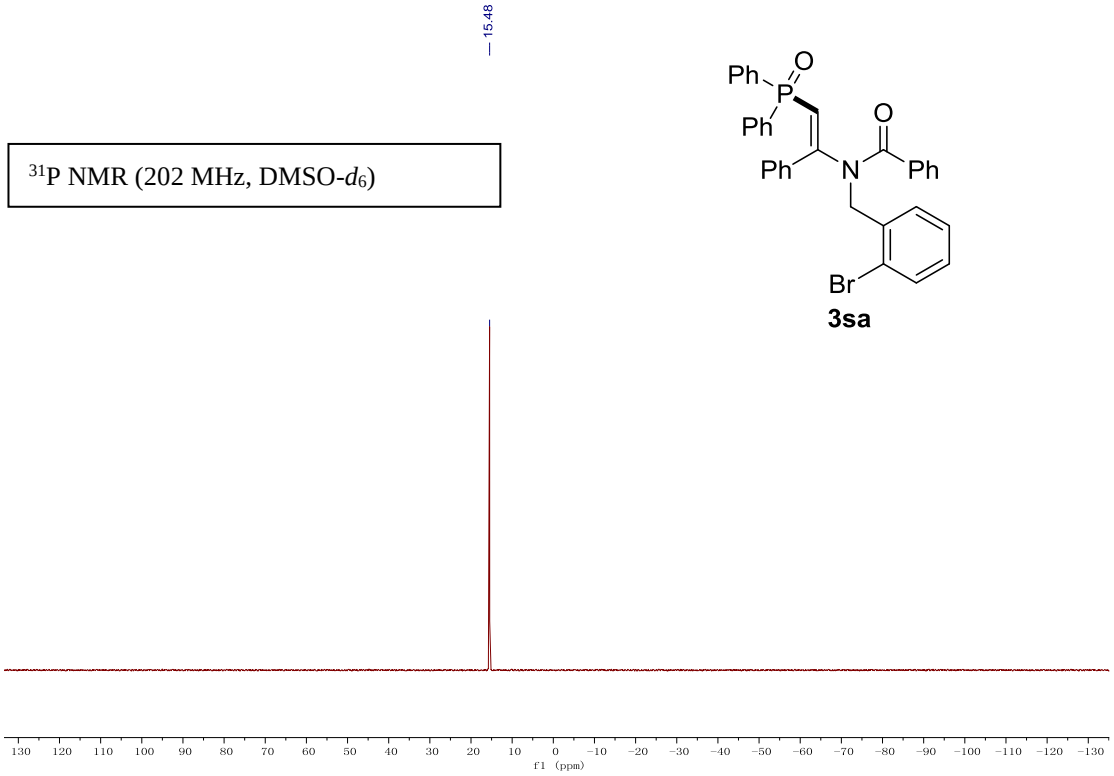


^{31}P NMR (202 MHz, DMSO-d_6)

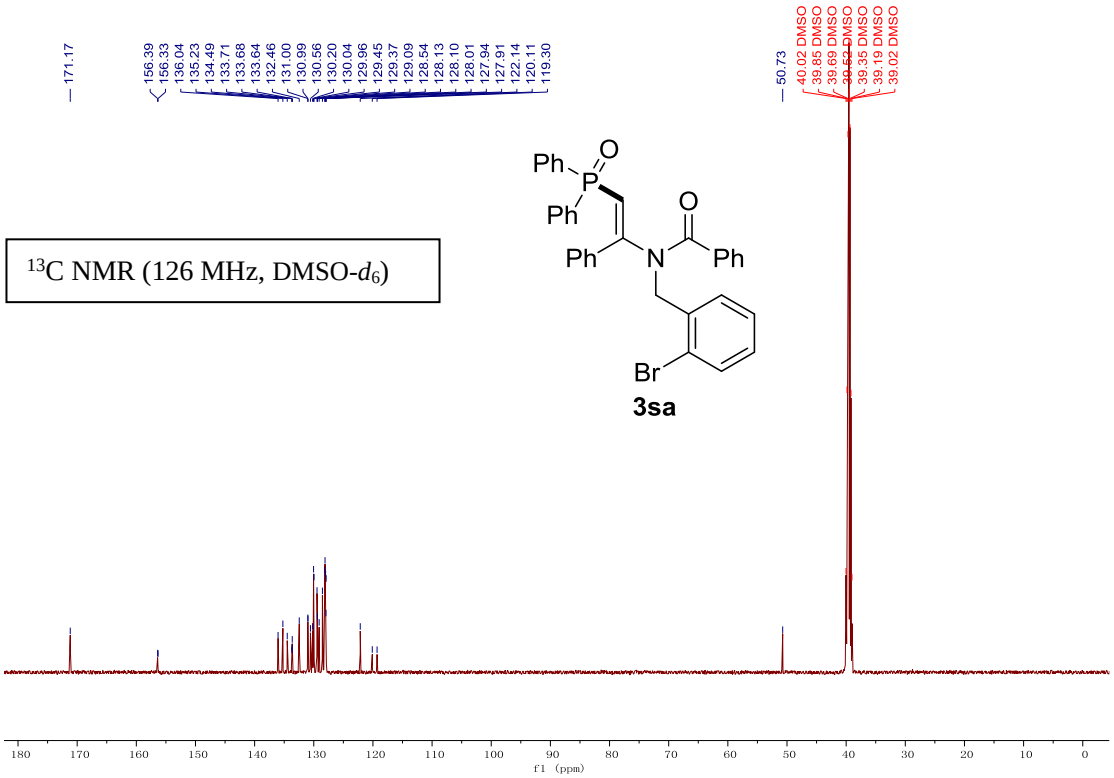

171.39
156.57
156.50
139.61
136.16
134.52
134.30
134.27
133.67
131.07
131.00
130.99
130.69
130.57
130.31
130.05
129.97
129.51
128.41
128.14
128.05
128.01
127.78
127.25
121.66
118.88
118.07
50.25
40.02 DMSO
39.85 DMSO
39.69 DMSO
39.52 DMSO
39.35 DMSO
39.19 DMSO
39.02 DMSO
0.11
Ph
O
P
Ph
Ph
N
O
Ph
Br
3ra
^{13}C NMR (126 MHz, DMSO-d_6)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

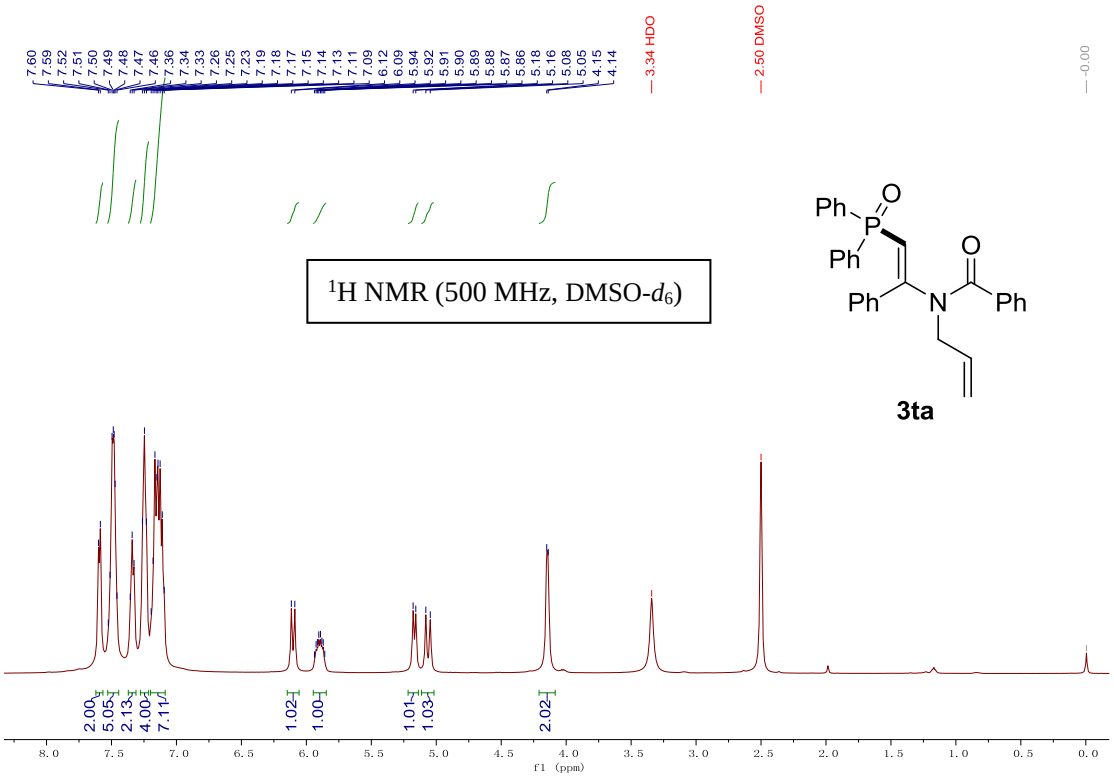

7.74
7.74
7.73
7.72
7.56
7.55
7.53
7.52
7.51
7.50
7.49
7.47
7.40
7.38
7.37
7.35
7.34
7.33
7.25
7.24
7.23
7.22
7.21
7.21
7.20
7.18
7.12
7.10
7.09
7.05
7.03
7.02
7.01
6.17
6.15
4.81
3.35 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
-0.01
Ph
O
P
Ph
Ph
N
O
Ph
Br
3sa
^{1}H NMR (500 MHz, DMSO-d_6)
2.00
4.06
1.07
3.07
2.04
5.98
2.09
3.82
0.93
1.72
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

^{31}P NMR (202 MHz, DMSO-d_6)



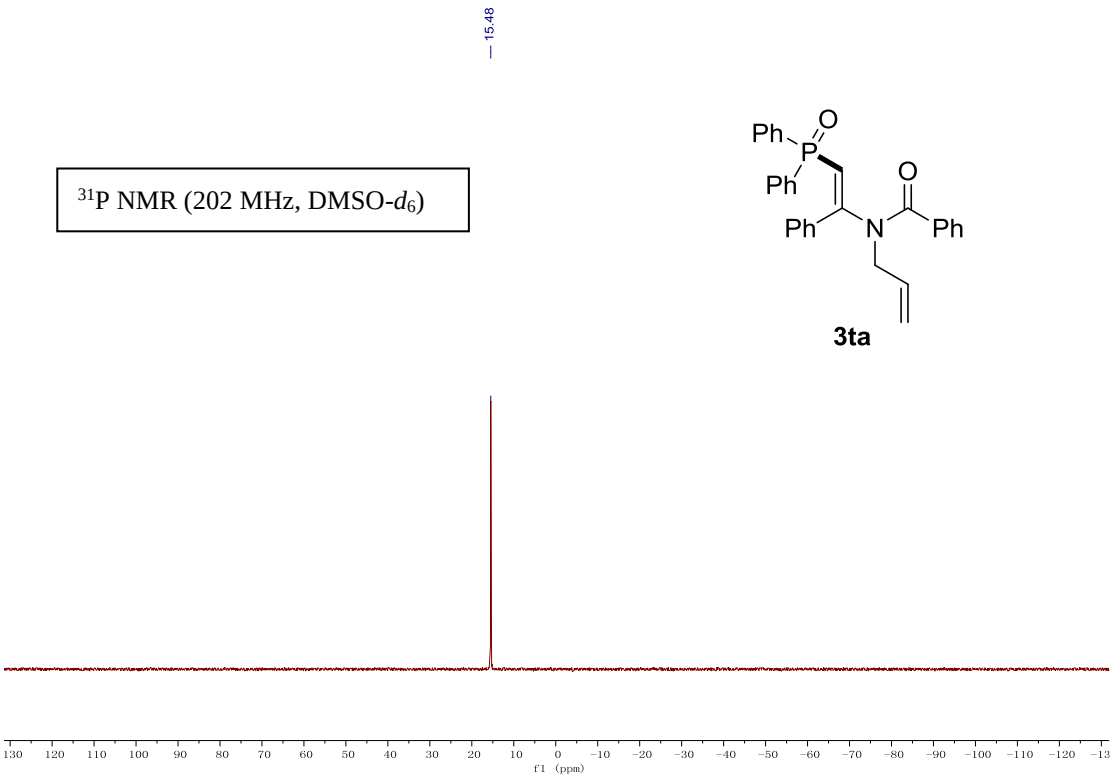
^{13}C NMR (126 MHz, DMSO-d_6)





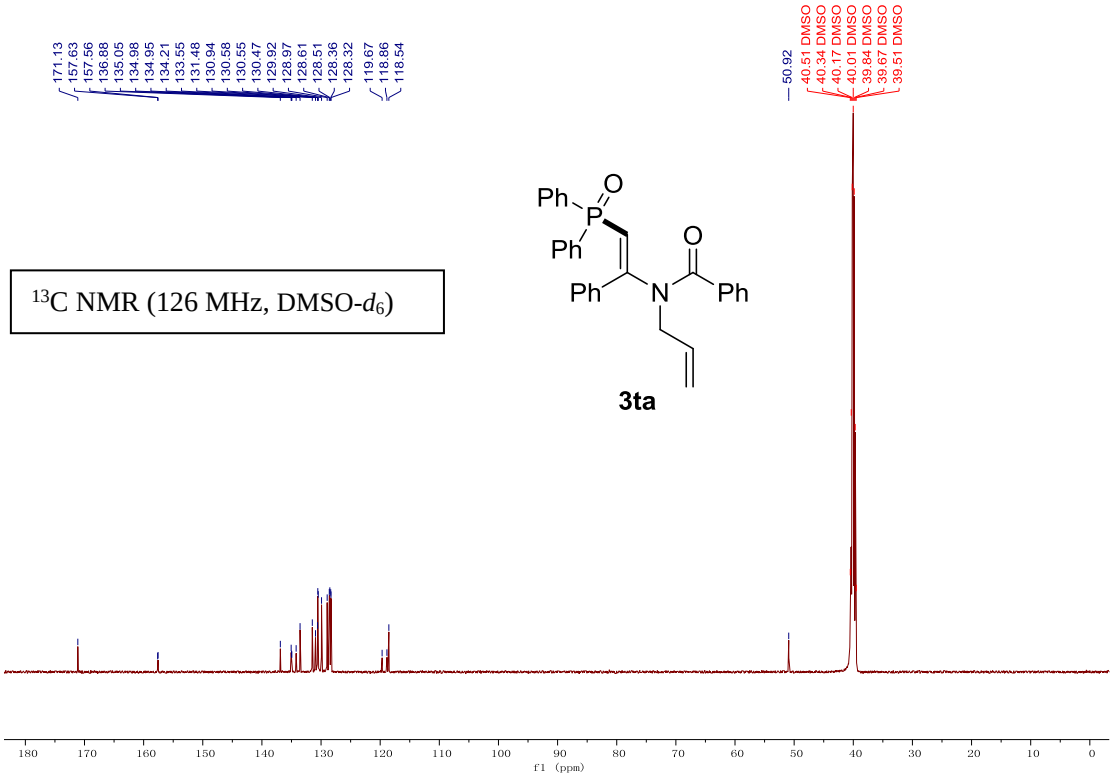
^{1}H NMR (500 MHz, DMSO-d_6)

3ta



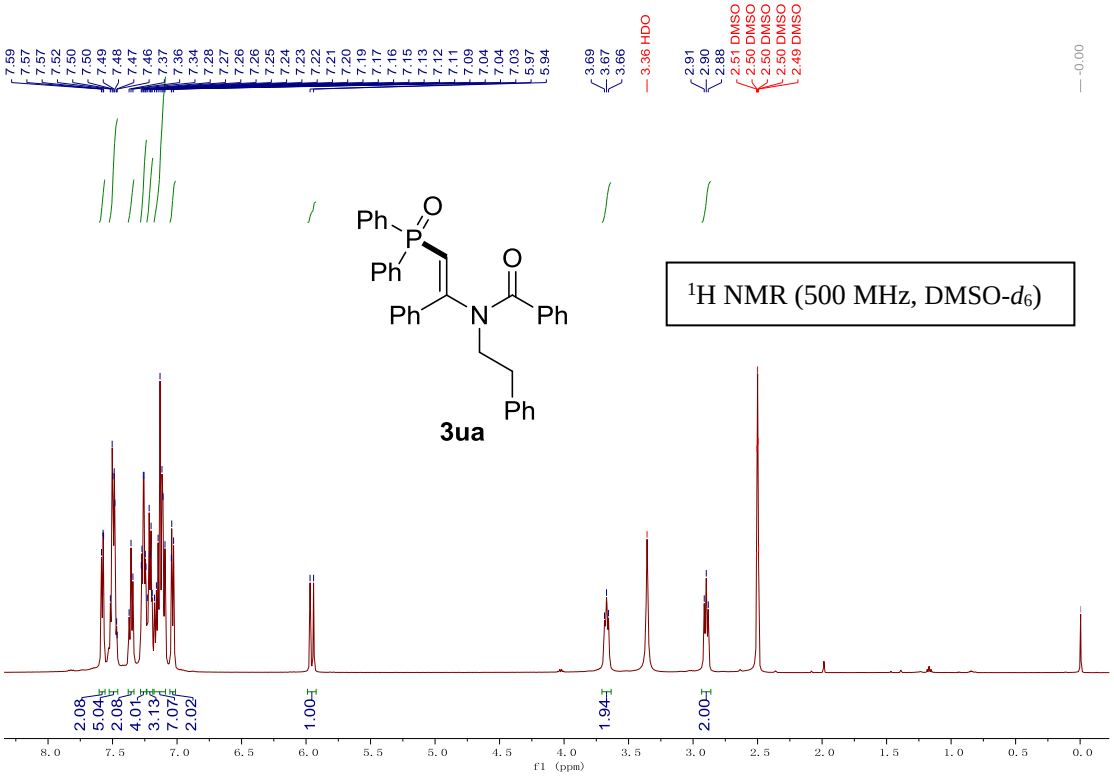
^{31}P NMR (202 MHz, DMSO-d_6)

3ta



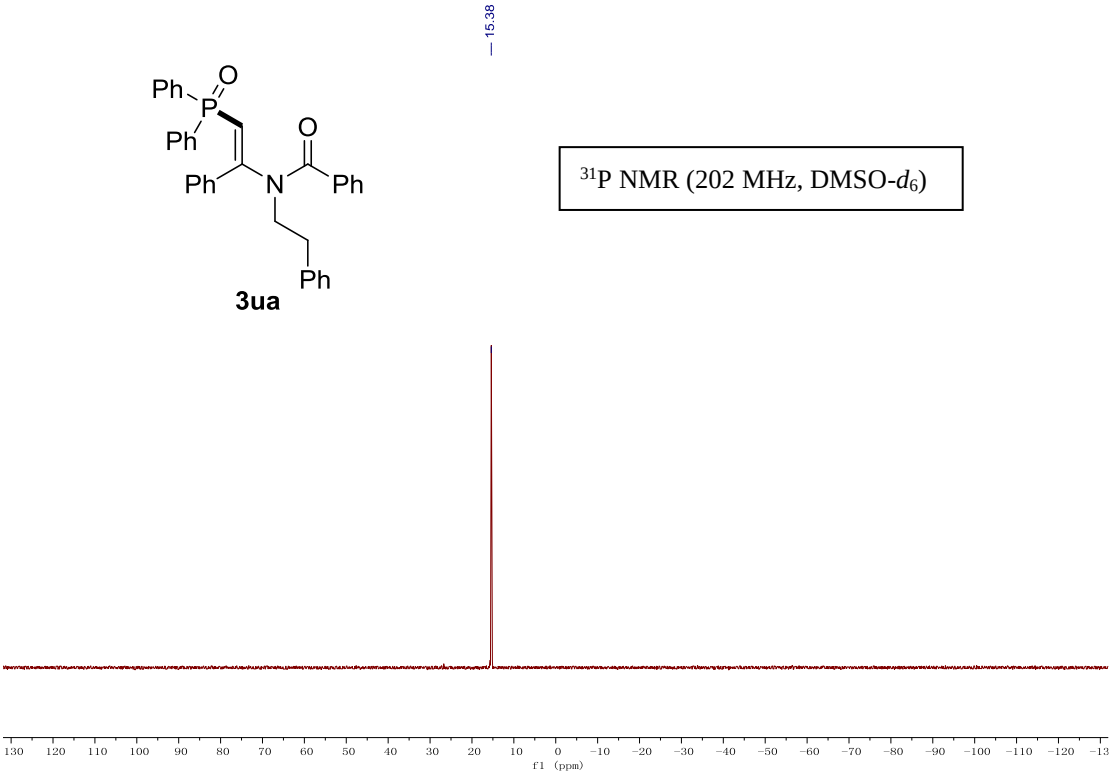
^{13}C NMR (126 MHz, DMSO-d_6)

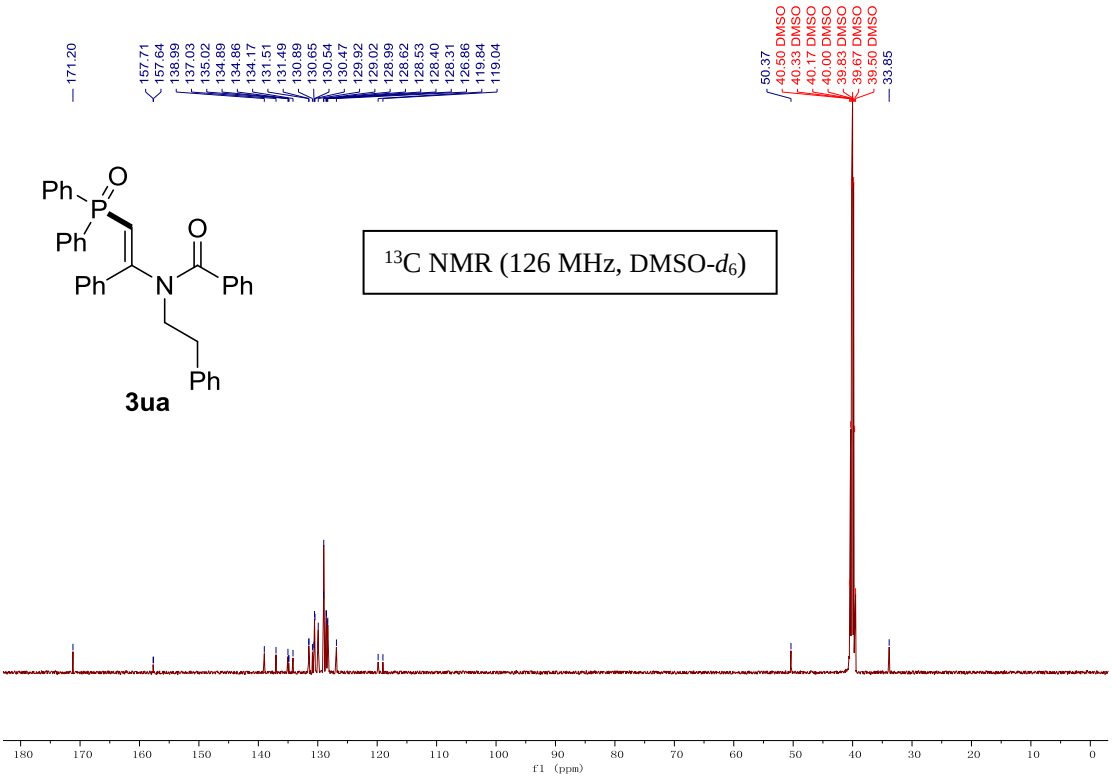
3ta

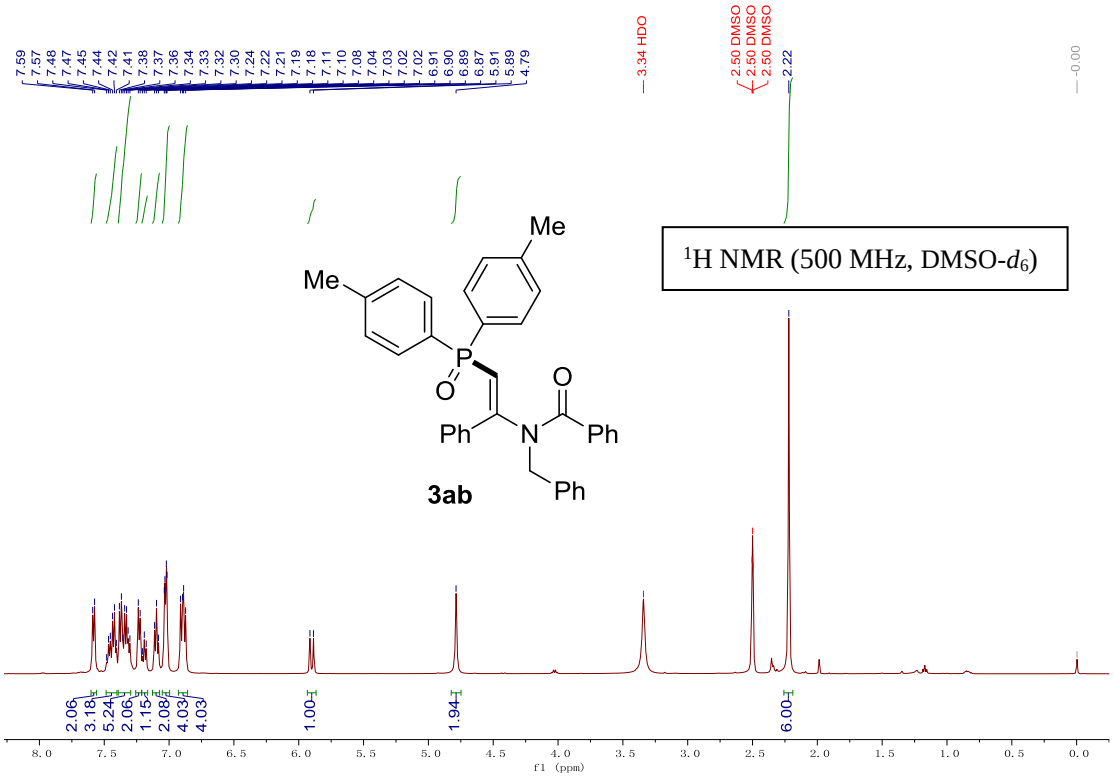


^{1}H NMR (500 MHz, DMSO-d_6)

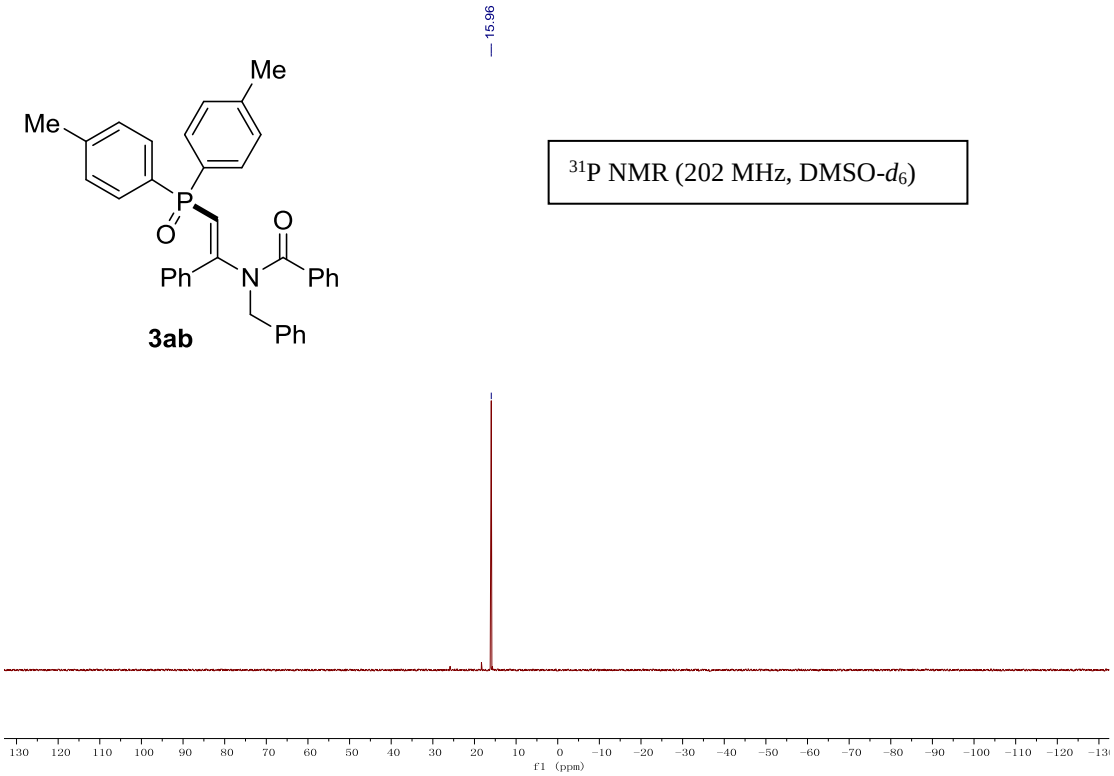
3ua


15.38
Ph
O
P
Ph
Ph
N
O
Ph
Ph
3ua
31P NMR (202 MHz, DMSO-d6)
f1 (ppm)

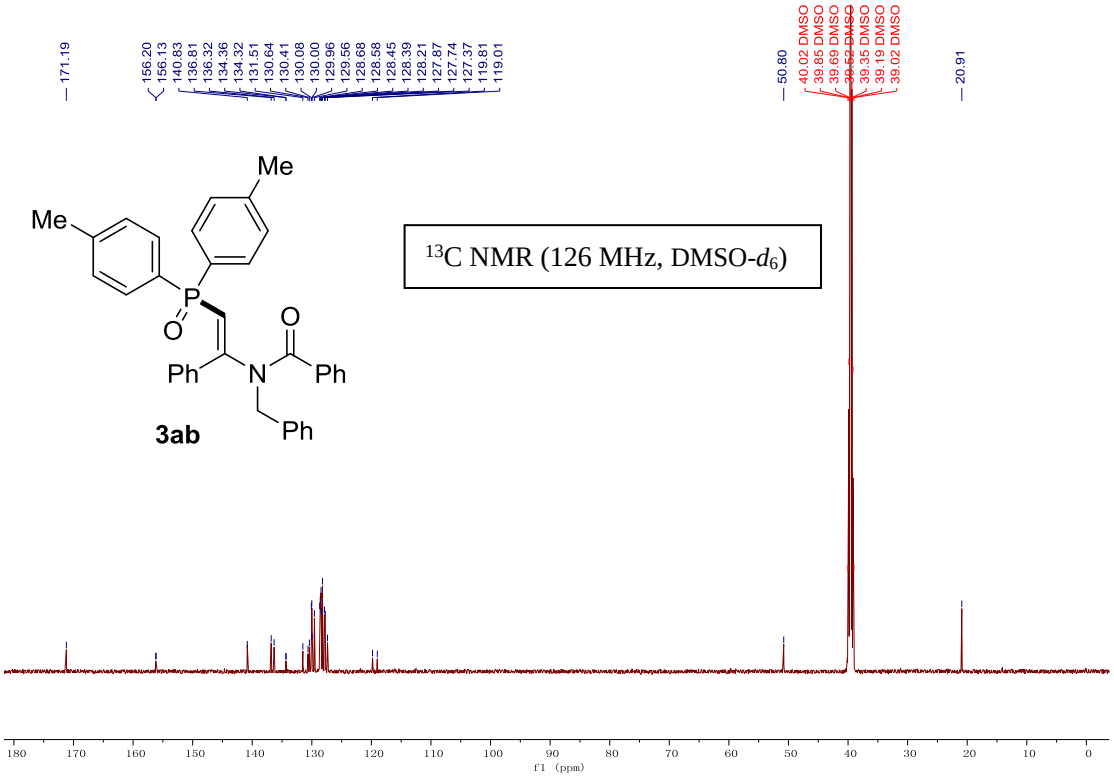

171.20
157.71
157.64
138.99
137.03
135.02
134.89
134.86
134.17
131.51
131.49
130.89
130.65
130.54
130.47
129.92
129.02
128.99
128.62
128.53
128.40
128.31
126.86
119.84
119.04
50.37
40.50 DMSO
40.33 DMSO
40.17 DMSO
40.00 DMSO
39.83 DMSO
39.67 DMSO
39.50 DMSO
33.85
Ph
O
P
Ph
Ph
N
O
Ph
Ph
3ua
13C NMR (126 MHz, DMSO-d6)
f1 (ppm)

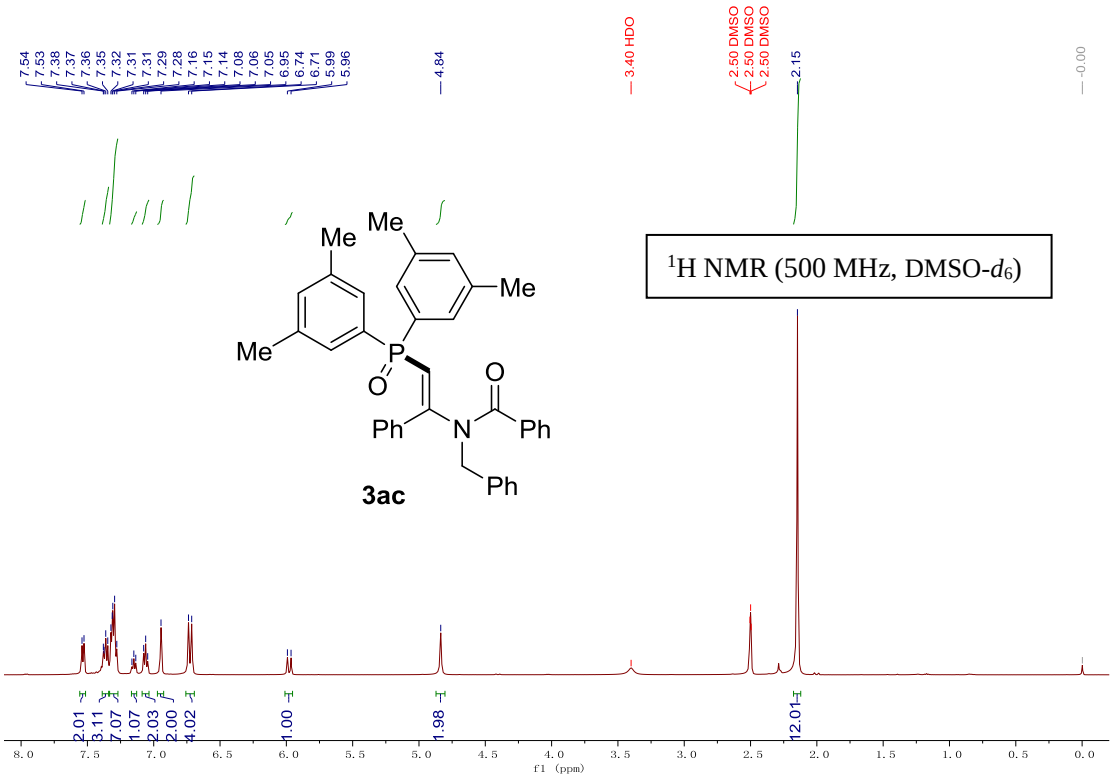


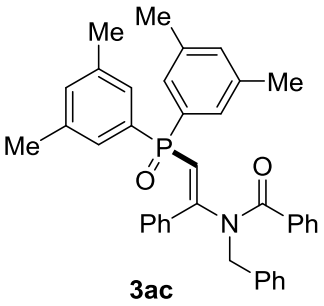
^{1}H NMR (500 MHz, DMSO-d_6)



^{31}P NMR (202 MHz, DMSO-d_6)

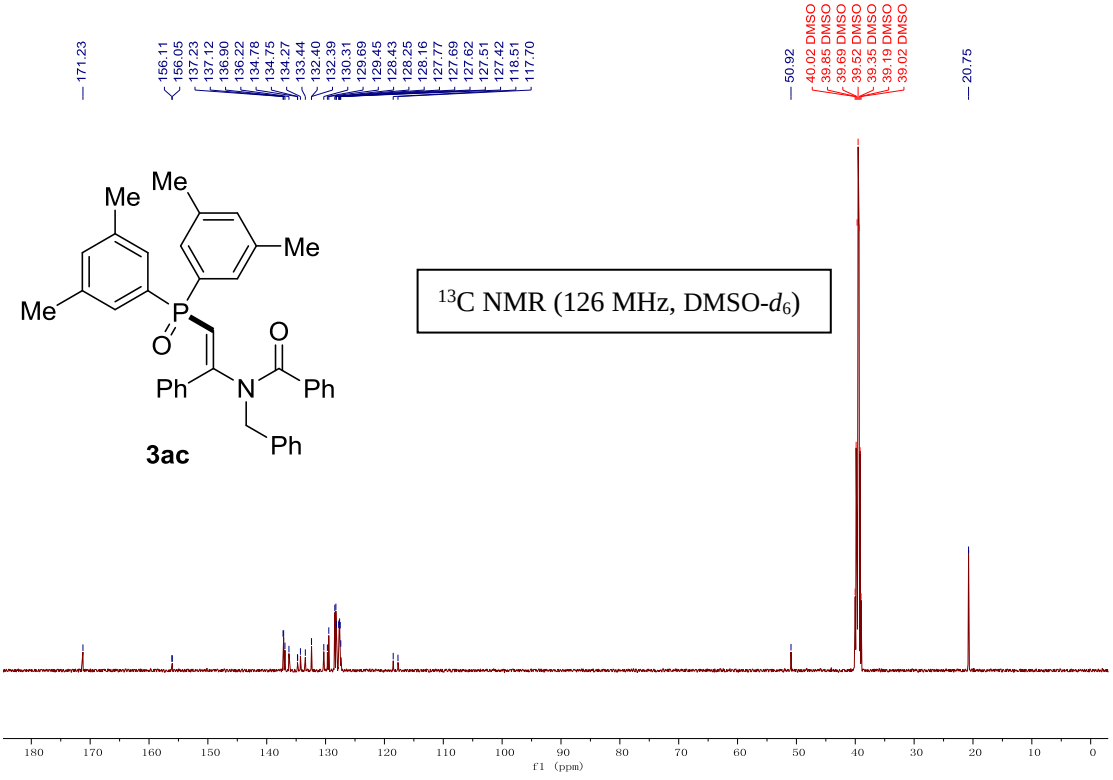

171.19
156.20
156.13
140.83
136.81
136.32
134.36
134.32
131.51
130.64
130.41
130.08
130.00
129.96
129.56
128.68
128.58
128.45
128.39
128.21
127.87
127.74
127.37
119.81
119.01
50.80
40.02 DMSO
39.85 DMSO
39.69 DMSO
39.52 DMSO
39.35 DMSO
39.19 DMSO
39.02 DMSO
20.91
Me
Me
P
O
O
Ph
N
Ph
Ph
3ab
^{13}C NMR (126 MHz, DMSO-d_6)
f1 (ppm)


7.54
7.53
7.38
7.37
7.36
7.35
7.32
7.31
7.31
7.29
7.28
7.16
7.15
7.14
7.08
7.06
7.05
6.95
6.74
6.71
5.99
5.96
4.84
3.40 HDO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.15
-0.00
Me
Me
Me
Me
P
O
O
Ph
N
Ph
Ph
3ac
^{1}H NMR (500 MHz, DMSO-d_6)
2.01
3.11
7.07
1.07
2.03
2.00
4.02
1.00
1.98
12.01
f1 (ppm)



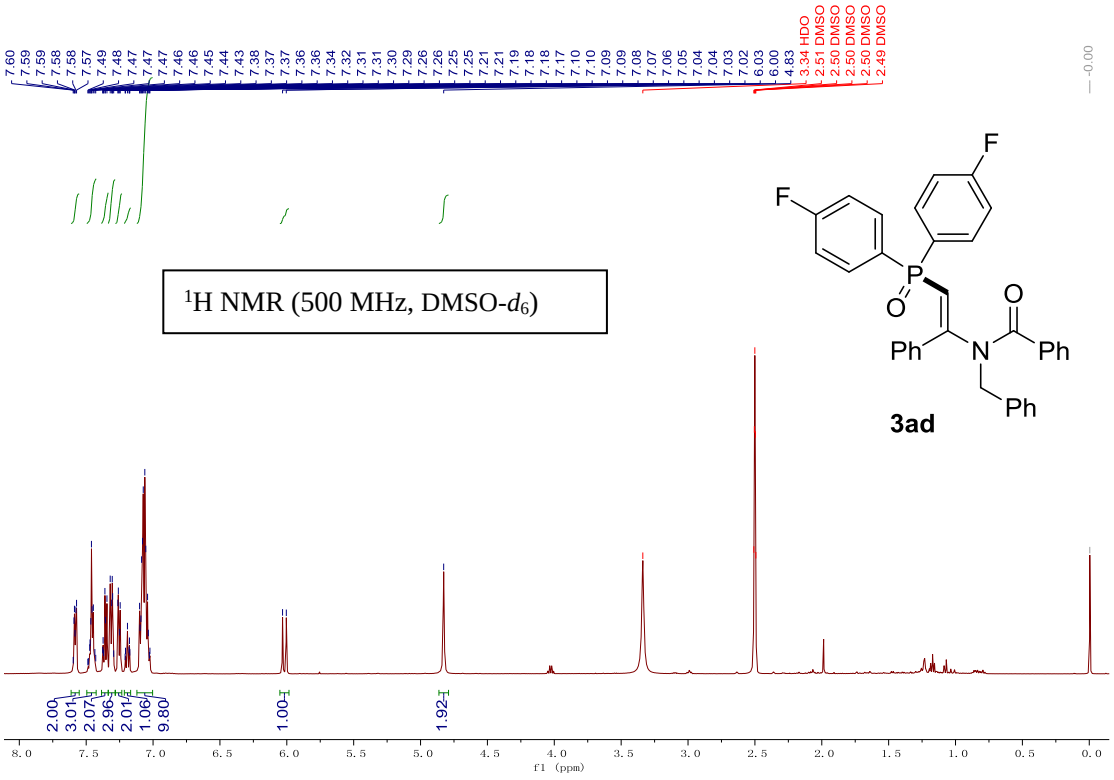
3ac

^{31}P NMR (202 MHz, DMSO-d_6)



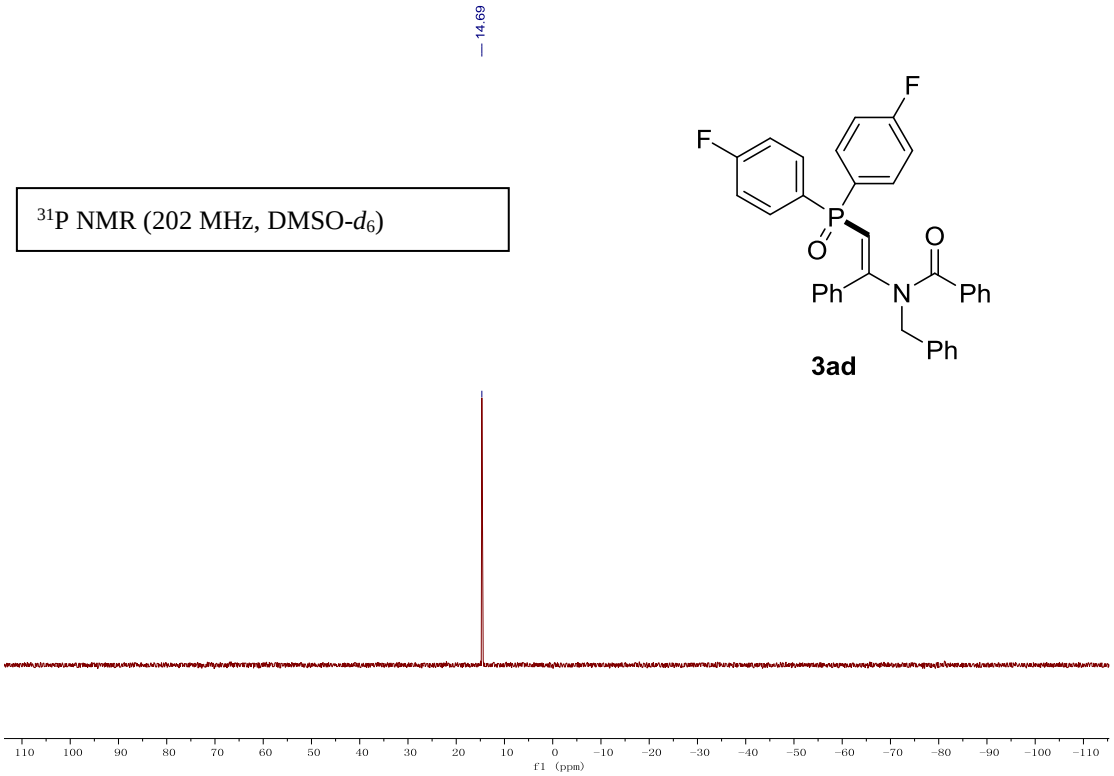
3ac

^{13}C NMR (126 MHz, DMSO-d_6)



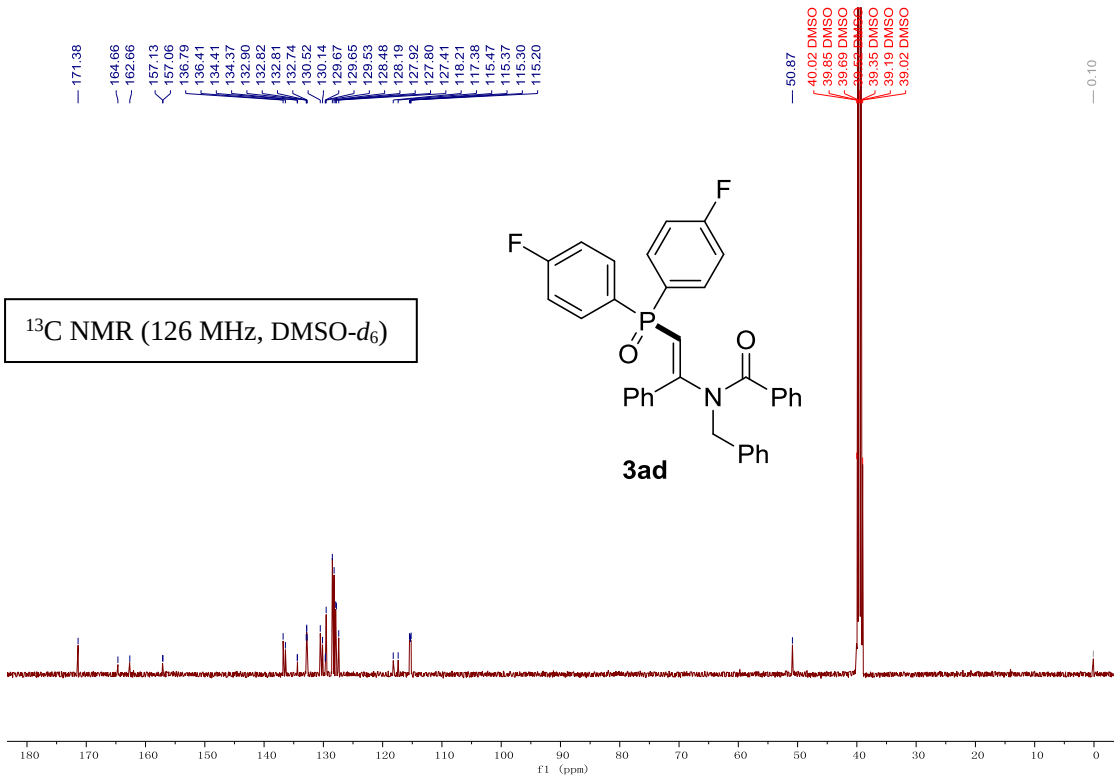
^{1}H NMR (500 MHz, DMSO-d_6)

3ad

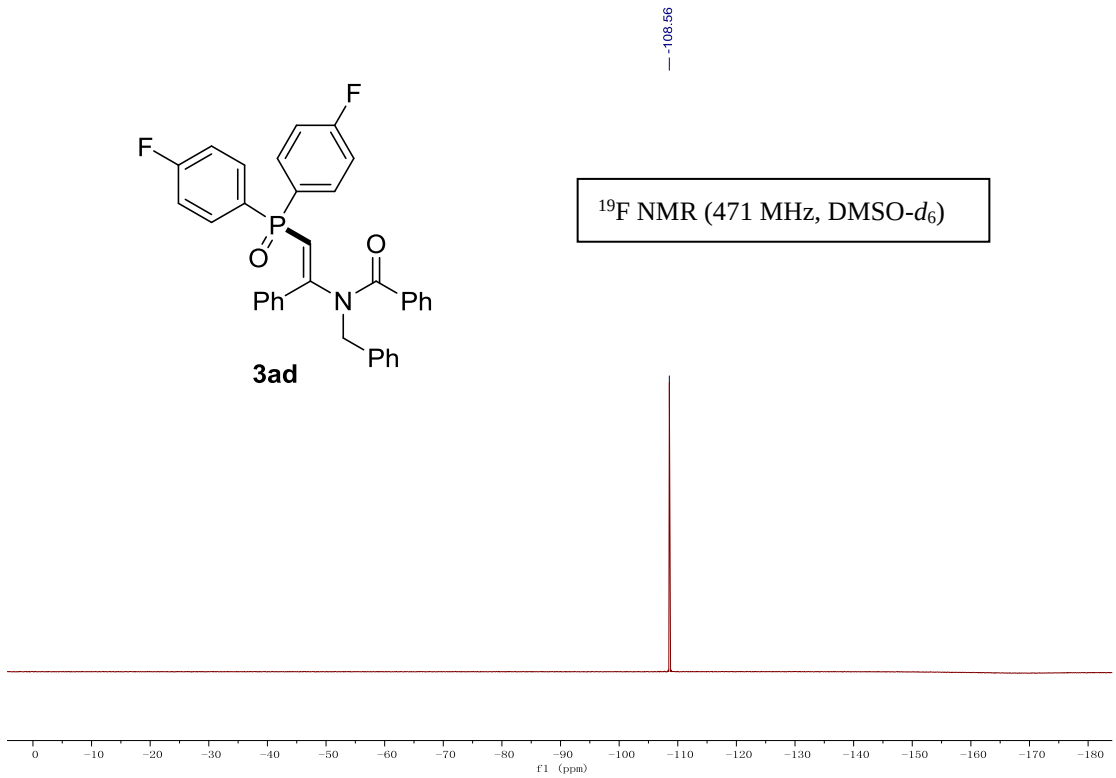


^{31}P NMR (202 MHz, DMSO-d_6)

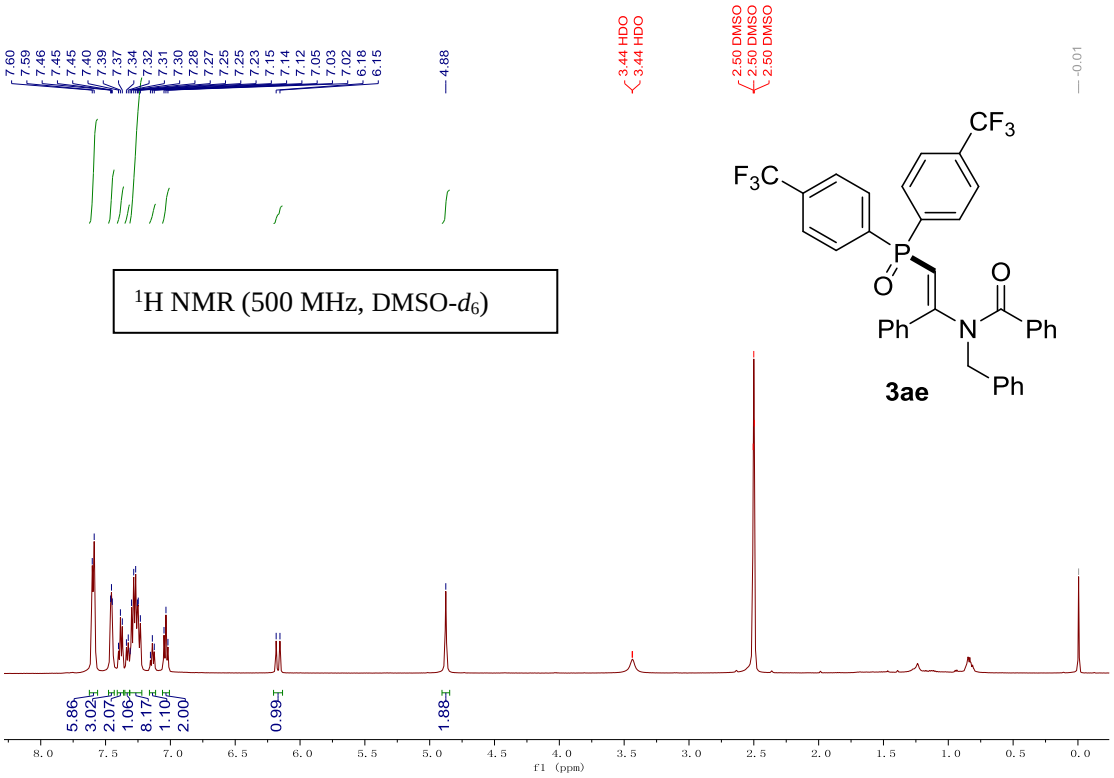
3ad



^{13}C NMR (126 MHz, DMSO-d_6)

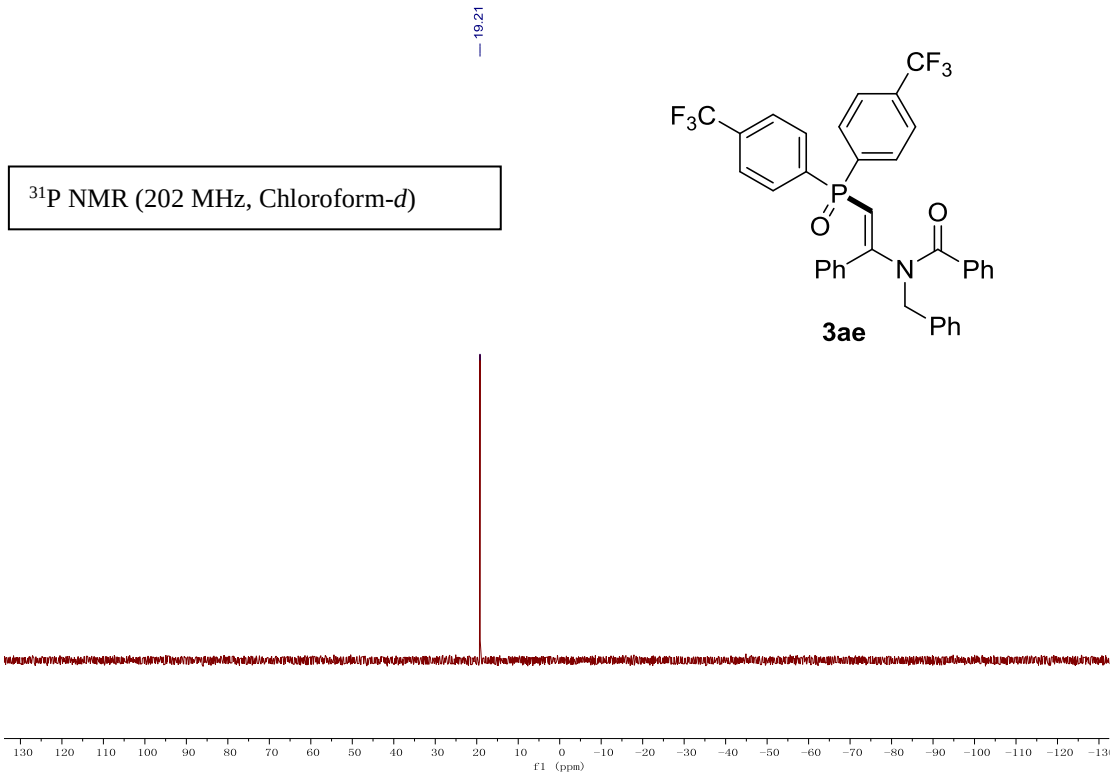


^{19}F NMR (471 MHz, DMSO-d_6)



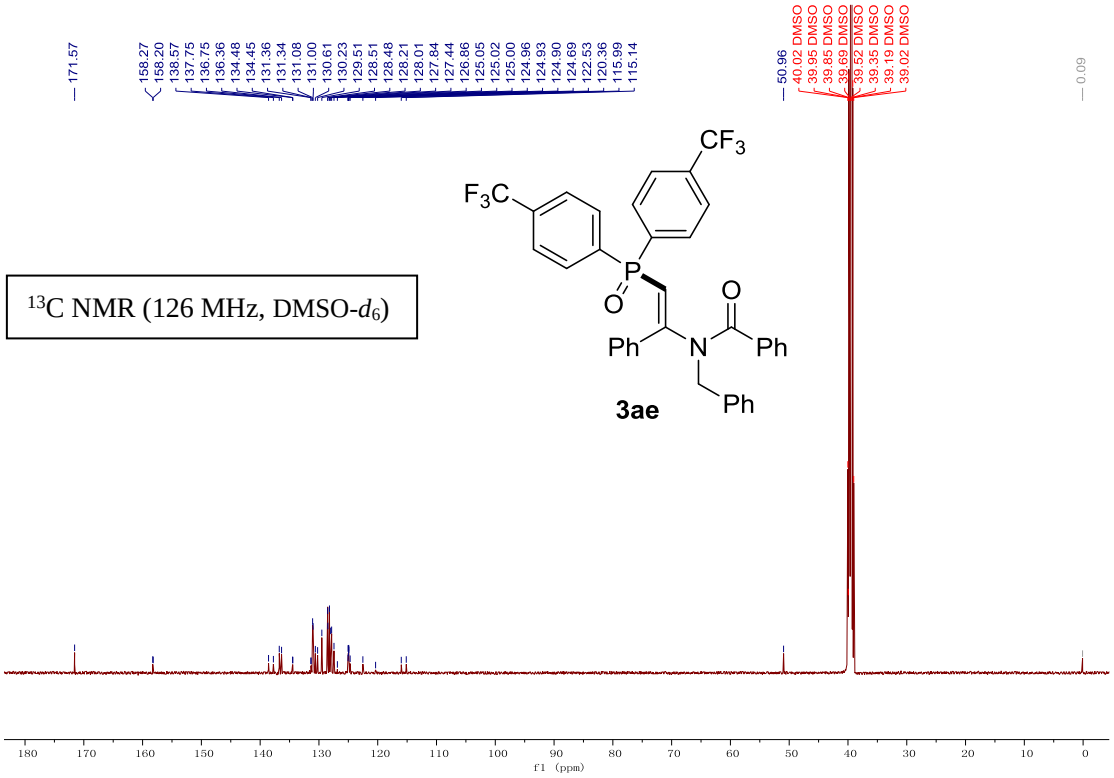
^{1}H NMR (500 MHz, DMSO-d_6)

3ae



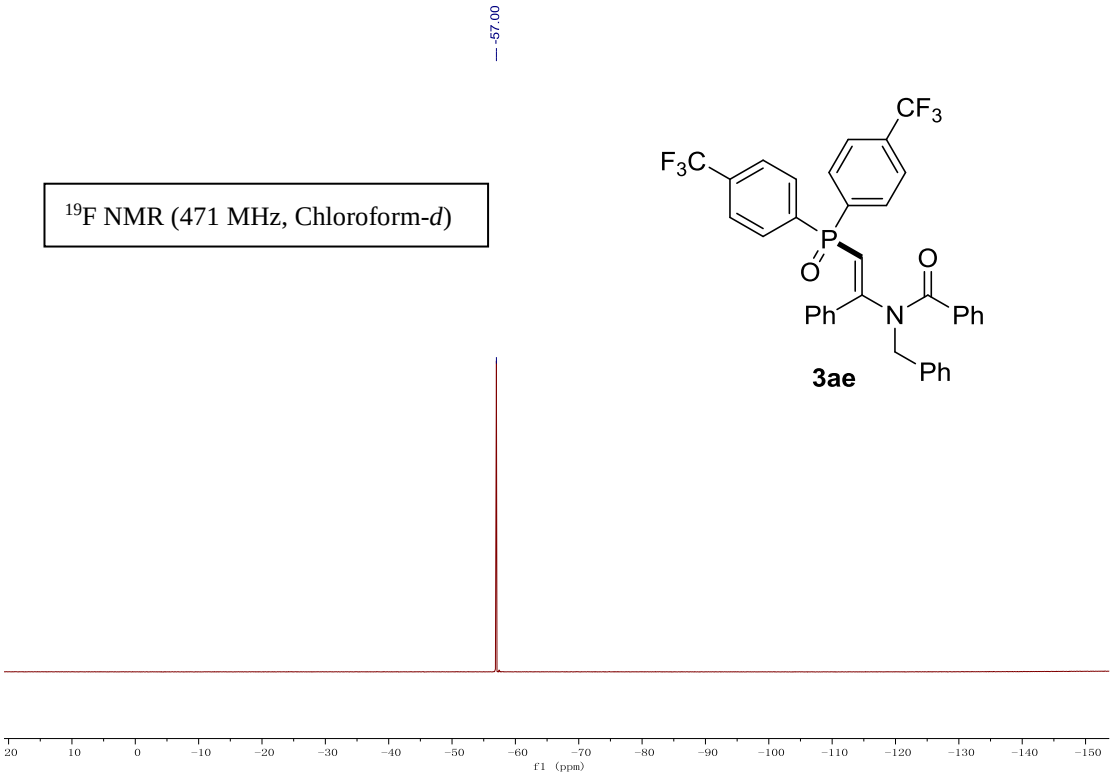
^{31}P NMR (202 MHz, Chloroform-*d*)

3ae



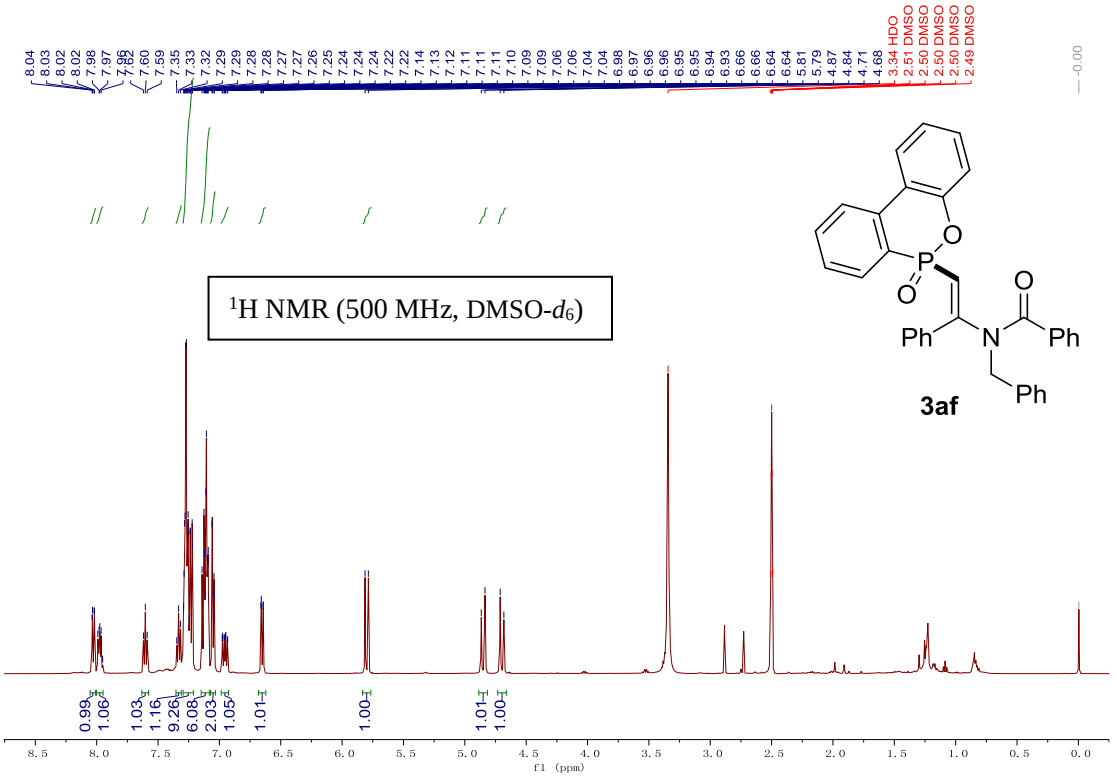
^{13}C NMR (126 MHz, DMSO-d_6)

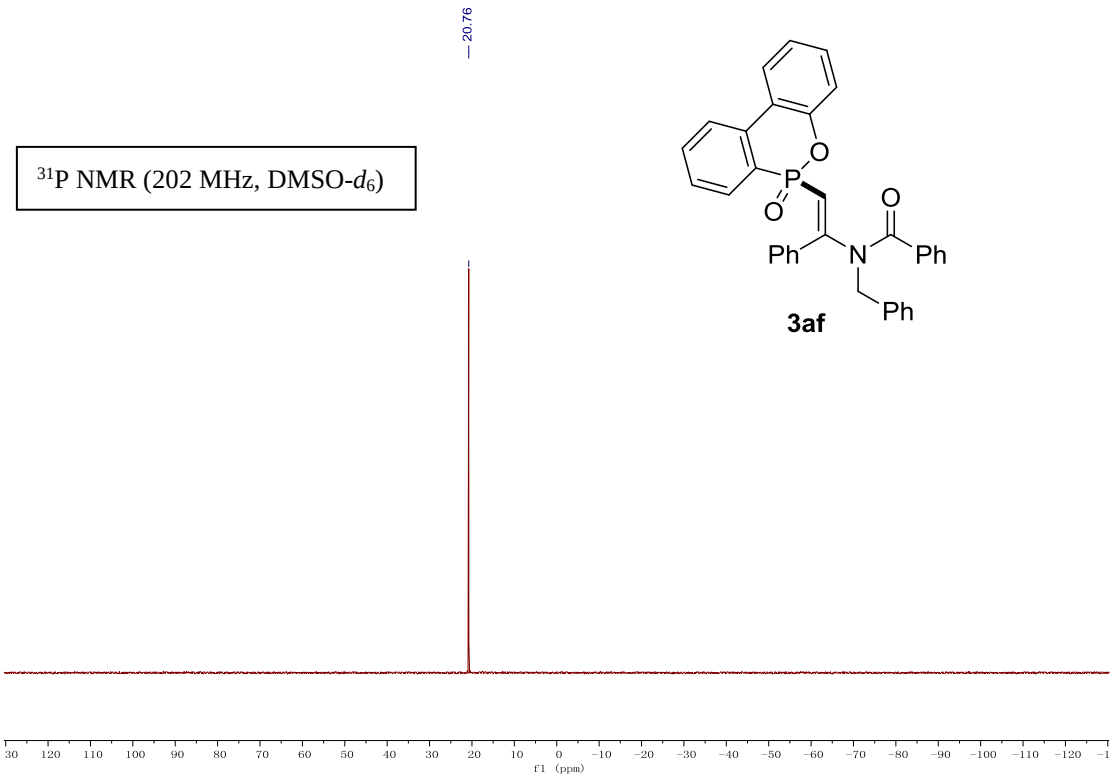
3ae

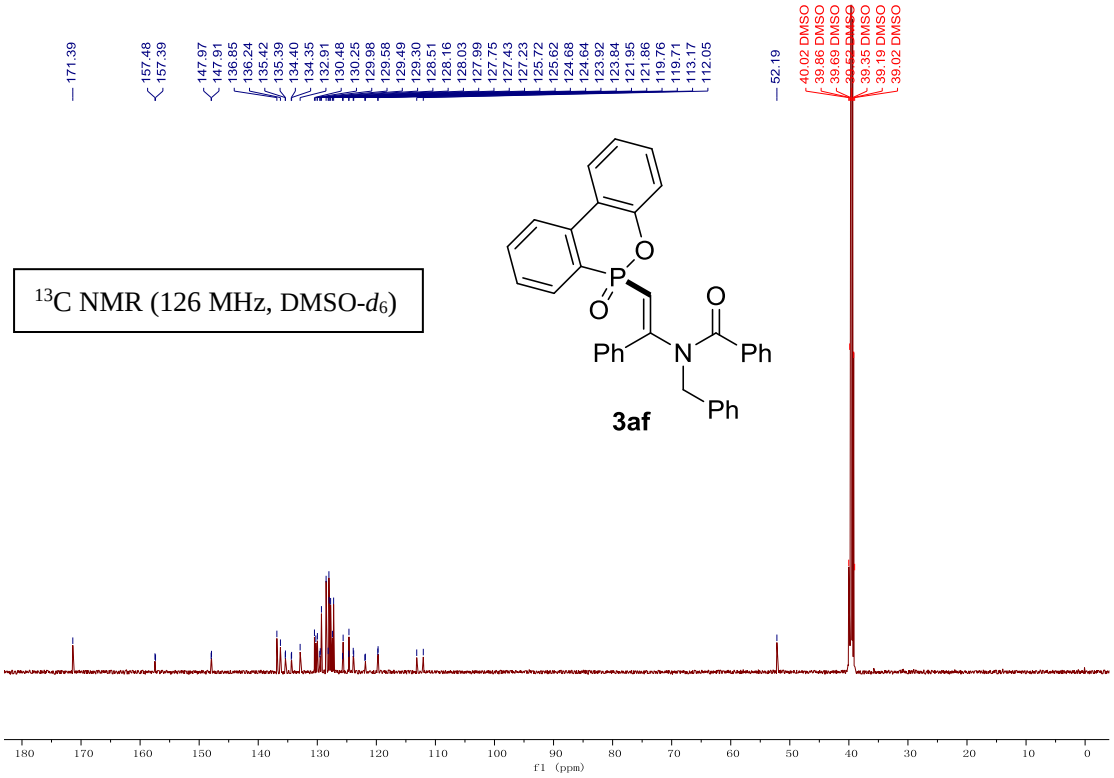


^{19}F NMR (471 MHz, Chloroform-d)

3ae


8.04 8.03 8.02 8.02 7.98 7.97 7.96 7.82 7.60 7.59 7.35 7.33 7.32 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.25 7.24 7.24 7.24 7.22 7.22 7.14 7.13 7.12 7.11 7.11 7.11 7.10 7.09 7.09 7.06 7.06 7.04 7.04 6.98 6.97 6.96 6.96 6.95 6.95 6.94 6.93 6.66 6.66 6.64 6.64 5.81 5.79 4.87 4.84 4.71 4.68 3.34 HDO 2.51 DMSO 2.50 DMSO 2.50 DMSO 2.50 DMSO 2.49 DMSO
0.00
1H NMR (500 MHz, DMSO-d6)
O
P
O
O
Ph
N
Ph
Ph
3af
0.99 1.06 1.03 1.16 9.26 6.08 2.03 1.05 1.01 1.00 1.01 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


20.76
31P NMR (202 MHz, DMSO-d6)
O
P
O
O
Ph
N
Ph
Ph
3af
30 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −1
f1 (ppm)


171.39
157.48
157.39
147.97
147.91
136.85
136.24
135.42
135.39
134.40
134.35
132.91
130.48
130.25
129.98
129.58
129.49
129.30
128.51
128.16
128.03
127.99
127.75
127.43
127.23
125.72
125.62
124.68
124.64
123.92
123.84
121.95
121.86
119.76
119.71
113.17
112.05
52.19
40.02 DMSO
39.86 DMSO
39.69 DMSO
39.35 DMSO
39.19 DMSO
39.02 DMSO
^{13}C NMR (126 MHz, DMSO-d_6)
O
P
O
Ph
N
O
Ph
Ph
3af
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)