Supporting Information

Visible-Light-Driven Metal-Free Aerobic Synthesis of Highly Diastereoselective Phosphinoylpyrroloindoles

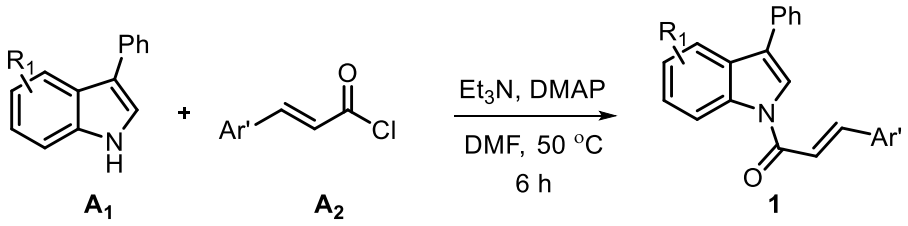
Ramesh Gorre, [+,a,b] Damodar Enagandhula, [+,a] Sridhar Balasubramanian [b,c] and Srirama Murthy Akondi [*a,b]

[a] Department of Organic Synthesis and Process Chemistry, CSIR-Indian Institute of Chemical Technology (CSIR-IICT), Hyderabad 500007, India
[b] Academy of scientific and innovative research (AcSIR), Ghaziabad 201002, India
[c] Department of Analytical Chemistry, CSIR-IICT, Hyderabad 500007, India
[+] These authors contributed equally

Table of Contents:

General information: Unless otherwise noted, reagents obtained from commercial suppliers were used without further purification. Reactions were monitored by silica gel thin-layer chromatography (TLC). Silica gel (100-200 mesh) packed in glass column was used for the column chromatography. NMR spectra were recorded at 300, 400, 500, 700 MHz (H) and at 75, 100, 125, 175 MHz (C), respectively. ^{31}P and ^{19}F NMR spectra were recorded at 162 and 376 MHz respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.0 ppm) as internal standard, and coupling constants (*J*) are measured in hertz (Hz). IR spectra were recorded on a BRUKER FT-IR spectrometer and the absorption peaks were reported in cm^{-1}. High-resolution mass spectra (HRMS) were recorded using ESI-TOF techniques. Melting points of solids were recorded using Electrothermal (IA9100) melting point apparatus. Fluorescent quenching studies were performed on a Jasco Spectrofluorometer (FP-8300).

General procedure for the synthesis of cinnamides 1:



To a stirred solution of 3-phenyl indole **A_1** (1.0 mmol), Et_3N (2.5 mmol) and DMAP (0.1 mmol) in DMF (5.0 mL) was added the corresponding cinnamoyl chloride **A_2** (2.0 mmol) in DMF (5.0 mL) at room temperature and the resulting solution was heated to 50 °C for 6 h. The reaction mixture was partitioned between water (30 mL) and EtOAc (50 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated to get the crude compound. The crude reaction mixture was purified by silica gel column chromatography to get the pure corresponding product. Cinnamides **1a-1e**, **1i** and **1m-1p** are known in the literature.[1]

(*E*)-3-(3,4-dichlorophenyl)-1-(3-phenyl-1*H*-indol-1-yl)prop-2-en-1-one (1f): Yellow solid (265.9 mg, 68%); mp = 143-145 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 15.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.71 (s, 1H), 7.70 – 7.66 (m, 2H), 7.54 – 7.35 (m, 7H), 7.28 (d, *J* = 15.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 143.9, 136.7, 134.8, 134.4, 133.5, 133.3, 131.1, 129.7, 129.3, 129.0, 128.1, 127.7, 127.6, 125.6, 124.5, 124.4, 121.2, 120.1, 119.0, 117.2; HRMS (ESI) calcd for $C_{23}H_{16}NOCl_2$ $[M+H]^+$: 392.0609; found: 392.0609.

(*E*)-3-(3,4-difluorophenyl)-1-(3-phenyl-1*H*-indol-1-yl)prop-2-en-1-one (1g): Brick red solid (254.9 mg, 71%); mp = 130-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 15.4 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.71 (s, 1H), 7.70 – 7.66 (m, 2H), 7.54 – 7.35 (m, 7H), 7.28 – 7.18 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 153.2, 153.0, 152.0, 151.9, 150.6, 150.5, 149.5, 149.4, 144.3, 136.7, 133.3, 131.7, 129.3, 129.0, 128.1, 127.7, 125.6, 125.4, 124.4, 124.3, 121.2, 120.1, 118.3, 118.2, 118.0, 117.2, 116.7, 116.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -133.1, -133.1, -136.1, -136.2; HRMS (ESI) calcd for $C_{23}H_{16}NOF_2$ $[M+H]^+$: 360.1200; found: 360.1205.

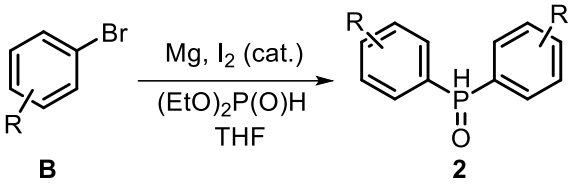
(*E*)-3-(3,4-dimethoxyphenyl)-1-(3-phenyl-1*H*-indol-1-yl)prop-2-en-1-one (1h): Brown solid (298.7 mg, 78%); mp = 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 15.3 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.76 (s, 1H), 7.71 – 7.65 (m, 2H), 7.53 – 7.47 (m, 2H), 7.47 – 7.33 (m, 3H), 7.29 – 7.26 (m, 1H), 7.16 (d, *J* = 1.9 Hz, 1H), 7.15 (d, *J* = 15.3 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 151.7, 149.4, 146.9, 136.7, 133.6, 129.2, 128.9, 128.1, 127.5, 127.5, 125.4, 124.0, 123.9, 123.2, 121.6, 119.9, 117.1, 114.8, 111.2, 110.2, 56.1; HRMS (ESI) calcd for $C_{25}H_{22}NO_3$ $[M+H]^+$: 384.1600; found: 384.1602.

(*E*)-1-(3-phenyl-1*H*-indol-1-yl)-3-(3-(trifluoromethoxy)phenyl)prop-2-en-1-one (1j): Yellow solid (248.3 mg, 61%); mp = 154-156 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 15.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.72 (s, 1H), 7.69 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.43 (m, 5H), 7.43 – 7.36 (m, 2H), 7.33 – 7.29 (m, 1H), 7.32 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 149.8, 144.8, 136.7, 136.5, 133.3, 130.5, 129.4, 129.0, 128.1, 127.7, 126.9, 125.6, 124.5, 124.3, 123.0, 121.2, 120.4, 120.1, 119.1, 117.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.7; HRMS (ESI) calcd for $C_{24}H_{17}NO_2F_3$ $[M+H]^+$: 408.1211; found: 408.1213.

(*E*)-3-(3,5-difluorophenyl)-1-(3-phenyl-1*H*-indol-1-yl)prop-2-en-1-one (1k): White solid (258.5 mg, 72%); mp = 174-176 °C;^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 15.4 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.70 (s, 1H), 7.69 – 7.66 (m, 2H), 7.53 – 7.48 (m, 2H), 7.48 – 7.36 (m, 3H), 7.29 (d, *J* = 15.4 Hz, 1H), 7.20 – 7.13 (m, 2H), 6.90 (tt, *J* = 8.7, 2.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 163.2, 162.3, 161.3, 161.2, 142.9, 136.6, 135.6, 132.2, 128.3, 128.0, 127.0, 126.7, 124.7, 123.6, 123.4, 120.1, 119.1, 118.9, 116.1, 110.1, 110.0, 109.9, 109.9, 105.1, 104.9, 104.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.6; HRMS (ESI) calcd for $C_{23}H_{16}NOF_2$ $[M+H]^+$: 360.1200; found: 360.1201.

(*E*)-1-(3-phenyl-1*H*-indol-1-yl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (1l): White solid (239.5 mg, 58%); mp = 77-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 15.3 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 6.6 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.54 – 7.48 (m, 2H), 7.47 – 7.34 (m, 3H), 7.17 (d, *J* = 15.3 Hz, 1H), 6.88 (s, 2H), 3.95 (s, 6H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 153.6, 146.9, 140.7, 136.7, 133.5, 129.9, 129.3, 129.0, 128.1, 127.6, 125.5, 124.1, 124.0, 121.5, 120.0, 117.1, 116.4, 105.8, 61.1, 56.4; HRMS (ESI) calcd for $C_{26}H_{24}NO_4$ $[M+H]^+$: 414.1705; found: 414.1706.

General procedure for the synthesis of phosphine oxides 2:



B **2**

To a stirred solution of magnesium turnings (10.0 mmol) and I_2 (cat.) in THF (50 mL) was added aryl bromide **B** (10.0 mmol) in THF (30 mL) slowly and heated under reflux for 1 hour. Then diethyl phosphate (3.33 mmol) in THF (20 mL) was added slowly under the cooling of an ice-water bath. The mixture thus obtained was heated under reflux for 1 hour. The resulting reaction mixture was cooled to 0 ^oC, and hydrochloric acid (15 mL, 6 N) was added slowly upon stirring. The residue was extracted with EtOAc (150 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo to give crude product.

Phoshine oxides **2a-2i** and **2l** are known in the literature.[2]

Bis(3,5-dimethoxyphenyl)phosphine oxide (2j): White solid ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J_{HP} = 485.8 Hz, 1H), 6.83 (dd, J = 15.2, 2.3 Hz, 4H), 6.61 (t, J = 2.1 Hz, 2H), 3.81 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 161.2, 133.4, 132.6, 108.1, 108.0, 104.9, 55.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.7; HRMS (ESI) calcd for $C_{16}H_{20}O_5P[M+H]^+$: 323.1048; found: 323.1039.

Bis(2,5-dimethoxyphenyl)phosphine oxide (2k): White solid ; ^1H NMR (400 MHz, DMSO) δ 8.06 (d, J_{HP} = 512.7 Hz, 1H), 7.16 (dd, J = 9.0, 3.1 Hz, 2H), 7.09 – 7.01 (m, 4H), 3.74 (s, 6H), 3.66 (s, 6H); ^{13}C NMR (101 MHz, DMSO) δ 154.9, 153.7, 153.5, 121.5, 120.5, 119.7, 117.8, 117.7, 113.7, 113.6, 56.8, 56.4; ^{31}P NMR (162 MHz, DMSO) δ 5.1; HRMS (ESI) calcd for $C_{16}H_{20}O_5P[M+H]^+$: 323.1048; found: 323.1049.

Description of the visible light reaction setup:

Reaction setup with 14 W white LED: (entry 1 in Table 1 of manuscript)

Cinnamide **1a** (0.1 mmol, 1.0 equiv), phosphine oxide **2a** (0.25 mmol, 2.5 equiv), and rose bengal (0.004 mmol, 0.04 equiv) were placed in a 5.0 mL oven dried vial. Then DMSO (1 mL) was added. The reaction mixture was irradiated by 14 W white LED at a distance of 2 cm from the vial and stirred at room temperature under ambient air for 12 h. Then, H_2O (3 mL) was added, and the mixture was extracted into EtOAc (3x10.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by column chromatography on silica gel to afford the corresponding product.

Reaction setup with Sigma-Aldrich® SynLED parallel photoreactor: (entry 2 in Table 1 of manuscript)

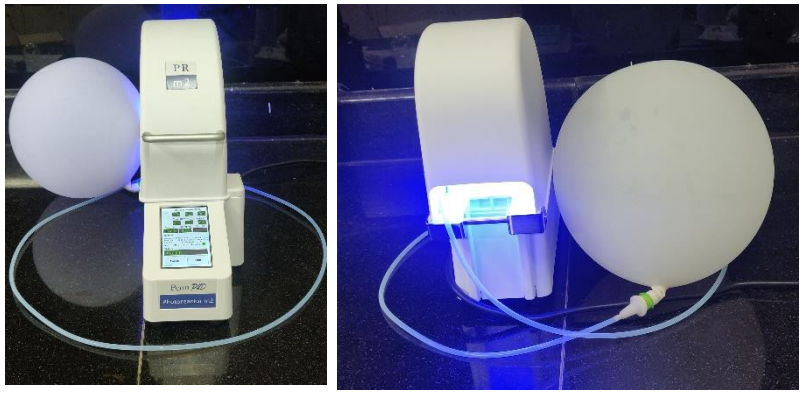
Cinnamide **1a** (0.1 mmol, 1.0 equiv), phosphine oxide **2a** (0.25 mmol, 2.5 equiv), and rose bengal (0.004 mmol, 0.04 equiv) were placed in a 2.5 mL oven dried vial. Then DMSO (1 mL) was added. The reaction mixture was introduced into synLED parallel photoreactor (blue LED, 465-470 nm) and stirred at room temperature under ambient air for 12 h. Then, H_2O (3 mL) was added, and the mixture was extracted into EtOAc (3x10.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by column chromatography on silica gel to afford the corresponding product.

Note: We separated the bottom fan part of the device to reduce its height in order to have proper stirring of the reaction mixture. We used an external cooler to cool the reaction.

Reaction setup with Penn *PhD* Photoreactor m2:

Under ambient air: (entries 3-14 of Table 1 in the manuscript)

Under N_2/O_2: (entries 16 and 17 of Table 1 in the manuscript)



Settings:

LED exposure: 100%

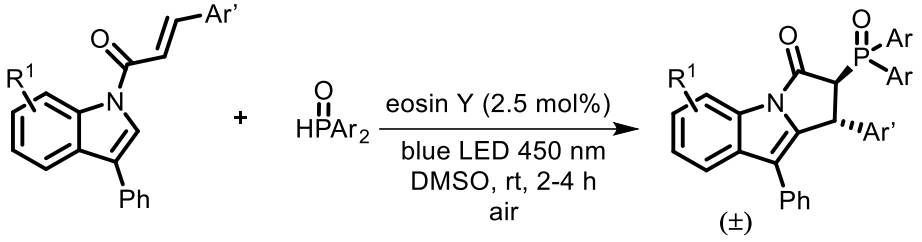
Fan (rpm): 6780

Stir (rpm): 1045

Cinnamide **1a** (0.1 mmol, 1.0 equiv), phosphine oxide **2a** (0.25 mmol, 2.5 equiv), and photocatalyst were placed in a 2.5 mL oven dried vial. Then solvent (1 mL) was added. The reaction mixture was introduced into Penn *PhD* photoreactor m2 (blue LED 450 nm) and stirred at room temperature under ambient air or 1atm N_2 or O_2 for 2 h. After 2 hours, H_2O (3 mL) was added, and the mixture was extracted into EtOAc (3x10.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude

reaction mixture was purified by column chromatography on silica gel to afford the corresponding product.

General procedure for the visible light driven synthesis of 2-phosphinoyl-3*H*-pyrrolo[1,2-*a*]indoles 3:



Cinnamide **1** (0.1 mmol, 1.0 equiv), phosphine oxide **2** (0.25 mmol, 2.5 equiv), and eosin Y (0.0025 mmol, 0.025 equiv) were placed in a 5.0 mL oven dried vial. Then DMSO (1 mL) was added. The reaction mixture was introduced into Penn *PhD* photoreactor m2 (blue LED 450 nm) and stirred at room temperature under ambient air for 2-4 h. After the completion of the reaction (monitored by TLC), H_2O (3 mL) was added, and the mixture was extracted into EtOAc (3x10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by column chromatography on silica gel to afford the corresponding product.

2-(Bis(4-chlorophenyl)phosphoryl)-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3aa): White solid (42.5 mg, 72%); mp = 218-220 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 – 7.95 (m, 1H), 7.92 – 7.81 (m, 2H), 7.68 – 7.62 (m, 1H), 7.63 – 7.53 (m, 2H), 7.51 – 7.46 (m, 2H), 7.39 – 7.29 (m, 2H), 7.29 – 7.12 (m, 10H), 7.03 – 6.95 (m, 2H), 5.20 (dd, *J* = 15.5, 2.7 Hz, 1H), 4.17 (dd, *J* = 13.9, 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 165.7, 141.2, 141.2, 139.7, 139.6, 139.4, 139.4, 139.0, 139.0, 134.0, 133.2, 133.1, 132.7, 132.6, 131.9, 130.7, 129.4, 129.2, 129.2, 128.9, 128.7, 128.6, 128.2, 127.8, 127.3, 127.2, 126.8, 125.0, 124.6, 120.3, 117.1, 113.9, 59.8 (d,

J = 58.8 Hz), 40.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.8; IR (neat, cm^{-1}): 1730, 1455, 1196, 753; HRMS (ESI) calcd for $C_{35}H_{25}NO_2PCl_2$ $[M+H]^+$: 592.1000; found: 592.1006.

2-(Bis(4-chlorophenyl)phosphoryl)-1-(4-bromophenyl)-9-phenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ba): Pale yellow solid (45.5 mg, 68%); mp = 254-256 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.00 – 7.94 (m, 1H), 7.92 – 7.84 (m, 2H), 7.68 – 7.63 (m, 1H), 7.61 – 7.54 (m, 2H), 7.54 – 7.50 (m, 2H), 7.38 – 7.31 (m, 4H), 7.31 – 7.28 (m, 2H), 7.26 – 7.23 (m, 1H), 7.21 – 7.16 (m, 4H), 6.93 – 6.89 (m, 2H), 5.22 (dd, *J* = 15.3, 2.7 Hz, 1H), 4.11 (dd, *J* = 14.4, 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.4, 140.0, 140.0, 139.9, 139.8, 139.6, 138.1, 133.9, 133.2, 133.1, 132.7, 132.6, 132.3, 131.7, 130.7, 129.4, 129.3, 129.0, 128.9, 128.8, 128.7, 128.1, 127.4, 126.4, 125.2, 124.8, 121.8, 120.4, 117.4, 113.9, 59.7 (d, *J* = 58.5 Hz), 40.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.8; IR (neat, cm^{-1}): 1731, 1466, 826, 756; HRMS (ESI) calcd for $C_{35}H_{24}NO_2PCl_2Br$ $[M+H]^+$: 670.0105; found: 670.0106.

2-(Bis(4-chlorophenyl)phosphoryl)-1-(4-methoxyphenyl)-9-phenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ca): White solid (37.8 mg, 61%); mp = 122-124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 – 7.92 (m, 1H), 7.85 (dd, *J* = 11.8, 8.4 Hz, 2H), 7.68 – 7.45 (m, 5H), 7.40 – 7.13 (m, 9H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 5.15 (dd, *J* = 15.4, 2.5 Hz, 1H), 4.14 (dd, *J* = 13.9, 2.7 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 165.7, 159.0, 139.6, 139.4, 139.3, 134.0, 133.2, 133.1, 132.9, 132.8, 132.7, 132.6, 132.0, 130.7, 129.3, 129.2, 128.9, 128.7, 128.6, 128.4, 128.2, 127.8, 127.2, 126.8, 125.0, 124.5, 120.3, 116.9, 114.5, 113.9, 59.9 (d, *J* = 58.8 Hz), 55.3, 39.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.2; IR (neat, cm^{-1}): 1729, 1460, 1189, 755; HRMS (ESI) calcd for $C_{36}H_{27}NO_3PCl_2$ $[M+H]^+$: 622.1107; found: 622.1106.

2-(Bis(4-chlorophenyl)phosphoryl)-1-(4-fluorophenyl)-9-phenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3da): White solid (45.0 mg, 74%); mp = 242-244 °C; ^{1}H NMR

($CDCl_3$, 500 MHz) δ 8.03 – 7.93 (m, 1H), 7.93 – 7.80 (m, 2H), 7.67 – 7.62 (m, 1H), 7.62 – 7.54 (m, 2H), 7.54 – 7.48 (m, 2H), 7.41 – 7.31 (m, 2H), 7.31 – 7.22 (m, 3H), 7.22 – 7.15 (m, 4H), 7.02 – 6.95 (m, 2H), 6.93 – 6.85 (m, 2H), 5.23 (dd, *J* = 15.4, 2.8 Hz, 1H), 4.12 (dd, *J* = 14.2, 2.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 165.5, 163.3, 160.9, 139.7, 139.6, 138.6, 136.7, 134.0, 133.2, 133.1, 132.7, 132.6, 131.8, 130.7, 129.4, 129.3, 129.0, 129.0, 128.9, 128.8, 128.6, 128.1, 127.6, 127.3, 126.6, 125.1, 124.7, 120.4, 117.3, 116.2, 115.9, 113.9, 59.8 (d, *J* = 58.9 Hz), 39.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.0; IR (neat, cm^{-1}): 1733, 1458, 1202, 758; HRMS (ESI) calcd for $C_{35}H_{24}NO_2PCl_2F$ $[M+H]^+$: 610.0906; found: 610.0911.

2-(Bis(4-chlorophenyl)phosphoryl)-1-(4-nitrophenyl)-9-phenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ea): Sticky mass (33.1 mg, 52%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.02 (m, 2H), 8.01 – 7.97 (m, 1H), 7.96 – 7.88 (m, 2H), 7.69 – 7.62 (m, 1H), 7.63 – 7.56 (m, 2H), 7.56 – 7.51 (m, 2H), 7.42 – 7.34 (m, 2H), 7.33 – 7.16 (m, 9H), 5.43 (dd, *J* = 15.3, 2.9 Hz, 1H), 4.13 (dd, *J* = 15.0, 3.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 147.6, 147.4, 140.1, 139.8, 137.0, 133.7, 133.2, 133.1, 132.7, 132.6, 131.4, 130.8, 129.5, 129.4, 129.1, 129.0, 128.9, 128.4, 127.9, 127.7, 127.1, 126.1, 125.4, 125.1, 124.4, 120.5, 118.0, 113.9, 59.6 (d, *J* = 58.2 Hz), 40.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.8; IR (neat, cm^{-1}): 1734, 1676, 1207, 758; HRMS (ESI) calcd for $C_{35}H_{24}N_2O_4PCl_2$ $[M+H]^+$: 637.0853; found: 637.0851.

2-(Bis(4-chlorophenyl)phosphoryl)-1-(3,4-dichlorophenyl)-9-phenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3fa): White solid (38.2 mg, 58%); mp = 110-112 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 1H), 7.93 – 7.85 (m, 2H), 7.67 – 7.64 (m, 1H), 7.62 – 7.56 (m, 2H), 7.56 – 7.52 (m, 2H), 7.39 – 7.33 (m, 3H), 7.32 – 7.27 (m, 3H), 7.23 – 7.17 (m, 4H), 7.01 (d, *J* = 2.2 Hz, 1H), 6.89 (dd, *J* = 8.4, 2.2 Hz, 1H), 5.22 (dd, *J* = 15.3, 2.9 Hz, 1H), 4.09 (dd, *J* =

14.2, 2.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.0, 139.8, 139.0, 138.7, 136.4, 132.8, 132.2, 132.2, 132.1, 131.7, 131.6, 131.0, 130.5, 130.0, 129.7, 128.5, 128.4, 128.3, 127.9, 127.8, 127.8, 127.0, 126.5, 126.2, 125.6, 125.4, 124.2, 123.9, 119.4, 116.7, 112.9, 58.5 (d, *J* = 58.8 Hz) , 38.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.7; IR (neat, cm^{-1}): 1732, 1456, 1203, 756; HRMS (ESI) calcd for $C_{35}H_{23}NO_2PCl_4$ $[M+H]^+$: 660.0221; found: 660.0215.

2-(Bis(4-chlorophenyl)phosphoryl)-1-(3,4-difluorophenyl)-9-phenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ga): Pale yellow syrup (43.3 mg, 69%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 1H), 7.94 – 7.87 (m, 2H), 7.69 – 7.63 (m, 1H), 7.61 – 7.50 (m, 4H), 7.40 – 7.32 (m, 2H), 7.32 – 7.29 (m, 2H), 7.28 – 7.23 (m, 1H), 7.22 – 7.17 (m, 4H), 7.02 – 6.95 (m, 1H), 6.89 – 6.82 (m, 1H), 6.81 – 6.75 (m, 1H), 5.25 (dd, *J* = 15.3, 2.9 Hz, 1H), 4.11 (dd, *J* = 14.7, 2.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 152.2, 152.0, 151.3, 148.9, 148.7, 148.2, 139.9, 139.7, 137.7, 133.8, 133.2, 133.1, 132.7, 132.6, 131.6, 130.7, 129.5, 129.3, 129.2, 129.0, 128.8, 128.8, 128.0, 127.8, 127.5, 126.2, 125.2, 124.9, 123.5, 120.4, 118.0, 117.8, 117.6, 116.6, 116.3, 113.9, 59.7 (d, *J* = 58.8 Hz), 39.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.65, -135.70, -138.19, -138.25; IR (neat, cm^{-1}): 1688, 1521, 1379, 1209, 756; HRMS (ESI) calcd for $C_{35}H_{23}NO_2PCl_2F_2$ $[M+H]^+$: 628.0812; found: 628.0810.

2-(Bis(4-chlorophenyl)phosphoryl)-1-(3,4-dimethoxyphenyl)-9-phenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ha): Pale yellow syrup (35.1 mg, 54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 1H), 7.92 – 7.81 (m, 2H), 7.69 – 7.63 (m, 1H), 7.62 – 7.55 (m, 2H), 7.50 (dd, *J* = 8.5, 2.4 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.29 – 7.26 (m, 1H), 7.26 – 7.18 (m, 5H), 6.68 (d, *J* = 8.3 Hz, 1H), 6.56 – 6.46 (m, 2H), 5.16 (dd, *J* = 15.5, 2.7 Hz, 1H), 4.18 (dd, *J* = 13.9, 2.8 Hz, 1H), 3.82 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 149.3, 148.5, 139.7, 139.5, 139.1, 134.0, 133.5, 133.4, 133.3, 133.2, 132.7, 132.6, 132.0, 130.7, 129.4, 129.2,

129.0, 128.9, 128.8, 128.6, 128.3, 127.7, 127.3, 126.7, 125.0, 124.6, 120.3, 119.3, 117.0, 113.9, 111.5, 110.5, 59.6 (d, J = 58.9 Hz), 55.9, 40.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.1; IR (neat, cm^{-1}): 1731, 1517, 756; HRMS (ESI) calcd for $C_{37}H_{29}NO_4PCl_2$ $[M+H]^+$: 652.1211; found: 652.1210.

1-(Benzo[d][1,3]dioxol-5-yl)-2-(bis(4-chlorophenyl)phosphoryl)-9-phenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ia): White solid (39.4 mg, 62%); mp = 179-181 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 – 7.94 (m, 1H), 7.92 – 7.83 (m, 2H), 7.70 – 7.62 (m, 1H), 7.60 – 7.48 (m, 4H), 7.39 – 7.28 (m, 4H), 7.27 – 7.24 (m, 1H), 7.24 – 7.16 (m, 4H), 6.62 (d, J = 8.0 Hz, 1H), 6.50 (d, J = 1.8 Hz, 1H), 6.43 (dd, J = 8.0, 1.8 Hz, 1H), 5.92 (dd, J = 5.7, 1.3 Hz, 2H), 5.13 (dd, J = 15.3, 2.6 Hz, 1H), 4.12 (dd, J = 14.1, 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 165.6, 148.4, 147.1, 139.7, 138.9, 134.9, 133.9, 133.2, 133.1, 132.7, 132.6, 131.9, 130.7, 129.4, 129.2, 128.9, 128.7, 128.6, 128.2, 127.2, 125.0, 124.6, 120.7, 120.3, 117.1, 113.9, 108.6, 107.5, 101.3, 59.9 (d, J = 58.4 Hz), 40.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.7; IR (neat, cm^{-1}): 1731, 1501, 1195, 756; HRMS (ESI) calcd for $C_{36}H_{25}NO_4PCl_2$ $[M+H]^+$: 636.0898; found: 636.0904.

2-(Bis(4-chlorophenyl)phosphoryl)-9-phenyl-1-(3-(trifluoromethoxy)phenyl)-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ja): Pale yellow solid (43.9 mg, 65%); mp = 126-128 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.03 – 7.96 (m, 1H), 7.92 – 7.83 (m, 2H), 7.69 – 7.58 (m, 3H), 7.54 – 7.48 (m, 2H), 7.40 – 7.32 (m, 2H), 7.30 – 7.20 (m, 6H), 7.18 – 7.14 (m, 2H), 7.08 – 7.03 (m, 1H), 7.01 – 6.97 (m, 1H), 6.79 (s, 1H), 5.25 (dd, J = 15.4, 3.0 Hz, 1H), 4.15 (dd, J = 13.9, 3.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 165.2, 149.5, 143.0, 142.9, 139.9, 139.6, 137.9, 133.9, 133.2, 133.1, 132.8, 132.6, 131.5, 130.7, 130.6, 129.5, 129.4, 129.0, 128.9, 128.67, 128.1, 127.9, 127.4, 126.4, 125.8, 125.2, 124.9, 121.5, 120.4, 120.2, 119.0, 117.6, 114.0, 59.3 (d, J = 59.4 Hz), 40.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.8; IR (neat, cm^{-1}): 1734, 1255, 758; HRMS (ESI) calcd for $C_{36}H_{24}NO_3PCl_2F_3$ $[M+H]^+$: 676.0823; found: 676.0823.

2-(Bis(4-chlorophenyl)phosphoryl)-1-(3,5-difluorophenyl)-9-phenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ka): Pale yellow solid (44.5 mg, 71%); mp = 222-224 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 – 7.95 (m, 1H), 7.95 – 7.87 (m, 2H), 7.69 – 7.63 (m, 1H), 7.61 – 7.51 (m, 4H), 7.41 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 7.23 – 7.17 (m, 4H), 6.64 (tt, *J* = 8.7, 2.3 Hz, 1H), 6.61 – 6.53 (m, 2H), 5.26 (dd, *J* = 15.2, 2.8 Hz, 1H), 4.12 (dd, *J* = 14.6, 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101MHz) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 164.6, 162.1, 144.4, 140.0, 139.7, 137.2, 133.7, 133.2, 133.1, 132.7, 132.6, 131.5, 130.8, 129.5, 129.4, 129.0, 128.8, 128.0, 127.9, 127.6, 127.3, 126.3, 125.3, 125.0, 120.5, 117.9, 113.9, 110.6, 110.3, 103.7, 103.5, 103.2, 59.6 (d, *J* = 58.5 Hz), 39.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.8; IR (neat, cm^{-1}): 1730, 1199, 757; HRMS (ESI) calcd for $C_{35}H_{23}NO_2PCl_2F_2$ $[M+H]^+$: 628.0812; found: 628.0815.

2-(Bis(4-chlorophenyl)phosphoryl)-9-phenyl-1-(3,4,5-trimethoxyphenyl)-1,2-dihydro-3*H*pyrrolo[1,2-*a*]indol-3-one (3la): White solid (34.8 mg, 51%); mp = 205-207 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 1H), 7.88 (dd, *J* = 11.8, 8.5 Hz, 2H), 7.70 – 7.64 (m, 1H), 7.61 (dd, *J* = 11.4, 8.5 Hz, 2H), 7.51 (dd, *J* = 8.5, 2.4 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.19 (m, 5H), 6.20 (s, 2H), 5.16 (dd, *J* = 15.6, 2.9 Hz, 1H), 4.21 (dd, *J* = 13.8, 3.0 Hz, 1H), 3.79 (s, 3H), 3.64 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 153.6, 139.7, 139.5, 138.6, 137.4, 136.3, 134.0, 133.3, 133.2, 132.7, 132.6, 131.9, 130.7, 129.3, 129.2, 128.9, 128.8, 128.6, 128.3, 127.6, 127.3, 126.8, 125.1, 124.7, 120.4, 117.3, 113.9, 104.4, 60.9, 59.5, 59.1, 56.2, 40.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9; IR (neat, cm^{-1}): 1735, 1527, 1210, 837; HRMS (ESI) calcd for $C_{38}H_{31}NO_5PCl_2$ $[M+H]^+$: 682.1317; found: 682.1316.

2-(Bis(4-chlorophenyl)phosphoryl)-7-chloro-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ma): White solid (41.25 mg, 66%); mp = 176-178 °C; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 1H), 7.82 (dd, *J* = 11.8, 8.5 Hz, 2H), 7.65 – 7.55 (m, 3H), 7.48 (dd, *J* = 8.5, 2.5 Hz, 2H), 7.31 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.29 – 7.17 (m, 8H), 7.13 – 7.08 (m, 2H), 7.00 – 6.89 (m, 2H), 5.17 (dd, *J* = 15.4, 2.7 Hz, 1H), 4.16 (dd, *J* = 13.4, 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 140.8, 140.8, 140.4, 140.4, 139.8, 139.8, 139.6, 139.6, 135.3, 133.2, 133.1, 132.7, 132.6, 131.2, 130.8, 129.4, 129.3, 129.2, 129.0, 128.9, 128.8, 128.7, 128.2, 127.9, 127.8, 127.5, 127.2, 126.7, 124.9, 120.1, 116.6, 114.7, 59.5 (d, *J* = 58.9 Hz), 40.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.0; HRMS (ESI) calcd for $C_{35}H_{24}NO_2PCl_3$ $[M+H]^+$: 626.0610; found: 626.0610.

2-(Bis(4-chlorophenyl)phosphoryl)-7-methoxy-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3na): White solid (39.1 mg, 63%); mp = 134-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.78 (m, 3H), 7.64 – 7.53 (m, 2H), 7.51 – 7.44 (m, 2H), 7.30 – 7.22 (m, 4H), 7.22 – 7.17 (m, 4H), 7.16 – 7.11 (m, 2H), 7.08 (d, *J* = 2.4 Hz, 1H), 7.01 – 6.96 (m, 2H), 6.94 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.16 (dd, *J* = 15.4, 2.7 Hz, 1H), 4.14 (dd, *J* = 13.8, 2.7 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 157.7, 141.2, 139.9, 139.6, 139.4, 135.2, 133.2, 133.1, 132.7, 132.6, 131.9, 129.3, 129.2, 129.1, 128.9, 128.8, 128.6, 128.1, 127.8, 127.3, 127.2, 126.7, 125.3, 117.1, 114.5, 112.9, 103.5, 59.5 (d, *J* = 59.3 Hz), 55.9, 40.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.1; IR (neat, cm^{-1}): 1733, 1460, 1195, 759; HRMS (ESI) calcd for $C_{36}H_{27}NO_3PCl_2$ $[M+H]^+$: 622.1107; found: 622.1108.

2-(Diphenylphosphoryl)-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ab): White solid (36.1 mg, 69%); mp = 197-199 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.02 – 7.98 (m, 1H), 7.97 – 7.91 (m, 2H), 7.76 – 7.68 (m, 2H), 7.63 – 7.57 (m, 2H), 7.54 – 7.49 (m, 2H), 7.38 – 7.32 (m, 1H), 7.32 – 7.29 (m, 2H), 7.28 – 7.22 (m, 5H), 7.22 – 7.14 (m, 5H), 6.98 – 6.92 (m, 2H), 5.26 (dd, *J* = 15.3, 2.6 Hz, 1H), 4.20 (dd, *J* = 13.6, 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101

MHz): δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 141.4, 139.4, 134.1, 132.6, 132.4, 132.1, 131.9, 131.8, 131.4, 131.3, 130.7, 130.1, 129.7, 129.0, 128.9, 128.8, 128.5, 128.4, 128.3, 127.5, 127.3, 127.0, 124.7, 124.3, 120.1, 116.7, 113.9, 59.7 (d, *J* = 57.5 Hz), 40.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.2; IR (neat, cm^{-1}): 1728, 1526, 1199, 758; HRMS (ESI) calcd for $C_{35}H_{27}NO_2P$ $[M+H]^+$: 524.1779; found: 524.1782.

2-(Di-*p*-tolylphosphoryl)-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ac): Pale yellow solid (33.7 mg, 61%); mp = 226-228 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 1H), 7.80 (dd, *J* = 12.1, 8.1 Hz, 2H), 7.62 (dt, *J* = 7.8, 3.4 Hz, 1H), 7.55 (dd, *J* = 11.7, 8.1 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.28 – 7.23 (m, 2H), 7.22 – 7.15 (m, 6H), 7.02 (dd, *J* = 7.9, 2.8 Hz, 2H), 6.99 – 6.94 (m, 2H), 5.23 (dd, *J* = 15.1, 2.5 Hz, 1H), 4.16 (dd, *J* = 13.8, 2.5 Hz, 1H), 2.42 (s, 3H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 166.3, 143.2, 143.0, 141.6, 141.5, 139.6, 134.0, 132.3, 131.8, 131.7, 131.4, 131.3, 130.7, 129.6, 129.4, 129.1, 129.0, 128.5, 128.2, 128.0, 127.5, 127.4, 127.0, 126.4, 125.3, 124.6, 124.2, 120.0, 116.5, 113.9, 59.9 (d, *J* = 57.1 Hz), 40.5, 21.7, 21.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.7; IR (neat, cm^{-1}): 1730, 1526, 1196, 762; HRMS (ESI) calcd for $C_{37}H_{31}NO_2P$ $[M+H]^+$: 552.2092; found: 552.2096.

2-(Bis(4-methoxyphenyl)phosphoryl)-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ad): White solid (36.1 mg, 62%); mp = 215-217 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 – 7.93 (m, 1H), 7.90 – 7.79 (m, 2H), 7.64 – 7.60 (m, 1H), 7.59 – 7.51 (m, 2H), 7.35 – 7.23 (m, 4H), 7.23 – 7.14 (m, 6H), 7.07 – 6.96 (m, 4H), 6.68 – 6.62 (m, 2H), 5.24 (dd, *J* = 15.0, 2.3 Hz, 1H), 4.14 (dd, *J* = 14.3, 2.3 Hz, 1H), 3.86 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 163.1, 162.8, 141.5, 141.4, 139.5, 134.0, 133.9, 133.8, 133.4, 133.3, 132.2, 130.8, 129.0, 128.5, 128.2, 127.5, 127.4, 127.0, 124.6, 124.3, 121.8, 120.9, 120.1, 120.0, 119.1, 116.5, 114.4, 114.3, 114.0, 113.9, 60.0 (d, *J* = 57.9 Hz), 55.5, 55.2, 40.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.6;

IR (neat, cm^{-1}): 1730, 1517, 825, 761; HRMS (ESI) calcd for $C_{37}H_{31}NO_4P$ $[M+H]^+$: 584.1991; found: 584.1992.

2-(Bis(4-fluorophenyl)phosphoryl)-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ae): White solid (40.2 mg, 72%); mp = 228-230 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.90 (m, 3H), 7.73 – 7.59 (m, 3H), 7.37 – 7.29 (m, 2H), 7.29 – 7.13 (m, 10H), 7.00 (dd, *J* = 6.7, 2.9 Hz, 2H), 6.91 (td, *J* = 8.7, 2.3 Hz, 2H), 5.24 (dd, *J* = 15.4, 2.6 Hz, 1H), 4.17 (dd, *J* = 14.1, 2.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 166.6, 165.9, 164.3, 164.1, 141.3, 141.2, 139.0, 134.5, 134.4, 134.3, 134.0, 133.9, 133.8, 132.0, 130.7, 129.2, 128.6, 128.2, 127.7, 127.3, 127.2, 126.9, 125.9, 125.4, 125.0, 124.5, 124.4, 120.3, 117.0, 116.5, 116.4, 116.3, 116.2, 116.0, 115.9, 115.8, 115.7, 113.8, 60.0 (d, *J* = 58.8 Hz), 40.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -104.85, -105.23; IR (neat, cm^{-1}): 1730, 1594, 1199, 830, 754; HRMS (ESI) calcd for $C_{35}H_{25}NO_2F_2P$ $[M+H]^+$: 560.1591; found: 560.1594.

2-(Bis(4-(dimethylamino)phenyl)phosphoryl)-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3af): Pale yellow syrup (23.1 mg, 38%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 1H), 7.72 (dd, *J* = 11.7, 8.9 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.43 – 7.36 (m, 2H), 7.30 – 7.23 (m, 4H), 7.22 – 7.15 (m, 6H), 7.09 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.72 (dd, *J* = 9.0, 2.4 Hz, 2H), 6.29 (dd, *J* = 9.0, 2.5 Hz, 2H), 5.22 (dd, *J* = 14.6, 1.9 Hz, 1H), 4.12 (dd, *J* = 14.9, 2.0 Hz, 1H), 3.02 (s, 6H), 2.79 (s, 6H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 167.1, 152.7, 152.4, 141.9, 140.0, 133.9, 133.3, 133.2, 132.7, 132.7, 132.6, 131.0, 128.9, 128.4, 128.2, 127.4, 127.2, 126.8, 124.1, 123.8, 119.8, 116.0, 113.9, 111.3, 111.2, 110.9, 110.8, 60.8 (d, *J* = 56.2 Hz), 40.7, 40.0, 39.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.8; IR (neat, cm^{-1}): 1728, 1598, 1363, 1115, 755; HRMS (ESI) calcd for $C_{39}H_{37}N_3O_2P$ $[M+H]^+$: 610.2623; found: 610.2627.

2-(Di-*m*-tolylphosphoryl)-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ag): Pale yellow syrup (37.5 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 1H), 7.76 – 7.67 (m, 2H), 7.64 – 7.58 (m, 1H), 7.50 – 7.35 (m, 4H), 7.34 – 7.28 (m, 2H), 7.28 – 7.24 (m, 1H), 7.24 – 7.08 (m, 9H), 7.03 – 6.96 (m, 2H), 5.23 (dd, *J* = 15.1, 2.4 Hz, 1H), 4.20 (dd, *J* = 14.3, 2.4 Hz, 1H), 2.37 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 141.5, 139.4, 138.8, 138.7, 138.5, 138.4, 134.0, 133.5, 133.2, 132.2, 132.2, 131.5, 131.5, 130.8, 129.8, 129.0, 128.9, 128.9, 128.7, 128.7, 128.6, 128.5, 128.3, 128.1, 127.5, 127.3, 127.0, 124.7, 124.3, 120.1, 116.6, 113.9, 59.8 (d, *J* = 56.8 Hz), 40.6, 21.5, 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.0; IR (neat, cm^{-1}): 1700, 1522, 1203, 767; HRMS (ESI) calcd for $C_{37}H_{31}NO_2P$ $[M+H]^+$: 552.2092; found: 552.2097.

2-(Bis(3-methoxyphenyl)phosphoryl)-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ah): Pale yellow syrup (41.2 mg, 71%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 1H), 7.80 (dd, *J* = 12.1, 8.1 Hz, 2H), 7.62 (dt, *J* = 7.8, 3.4 Hz, 1H), 7.55 (dd, *J* = 11.7, 8.1 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.28 – 7.23 (m, 2H), 7.22 – 7.15 (m, 6H), 7.02 (dd, *J* = 7.9, 2.8 Hz, 2H), 6.99 – 6.94 (m, 2H), 5.23 (dd, *J* = 15.1, 2.5 Hz, 1H), 4.16 (dd, *J* = 13.8, 2.5 Hz, 1H), 2.42 (s, 3H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 166.0, 159.8, 159.6, 159.5, 159.4, 141.6, 139.5, 134.1, 132.3, 132.1, 131.2, 131.0, 130.7, 130.1, 130.0, 129.6, 129.4, 129.0, 128.5, 128.3, 127.6, 127.3, 127.0, 124.7, 124.3, 124.1, 124.0, 123.6, 123.5, 120.1, 119.2, 119.0, 116.6, 116.3, 116.2, 115.7, 115.6, 113.9, 59.9 (d, *J* = 57.4 Hz), 55.5, 55.3, 40.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.4; IR (neat, cm^{-1}): 1731, 1467, 1251, 768; HRMS (ESI) calcd for $C_{37}H_{31}NO_4P$ $[M+H]^+$: 584.1991; found: 584.1995.

2-(Di-*o*-tolylphosphoryl)-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ai): Pale yellow syrup (26.4 mg, 48%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 1H), 8.00 (dd, *J* =

13.3, 7.7 Hz, 1H), 7.82 (dd, *J* = 13.9, 7.7 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.49 – 7.43 (m, 1H), 7.36 – 7.27 (m, 4H), 7.24 – 7.12 (m, 10H), 7.07 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.83 (dd, *J* = 7.6, 1.8 Hz, 2H), 5.18 (dd, *J* = 15.4, 3.0 Hz, 1H), 4.43 (dd, *J* = 11.2, 3.0 Hz, 1H), 2.33 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 142.6, 142.5, 142.1, 142.0, 141.4, 139.9, 134.3, 133.0, 132.9, 132.6, 132.2, 132.1, 131.9, 131.8, 130.7, 130.5, 129.5, 129.0, 128.4, 128.4, 128.0, 127.6, 127.5, 126.9, 125.9, 125.7, 125.4, 125.2, 124.7, 124.3, 120.1, 116.4, 114.0, 58.3 (d, *J* = 58.5 Hz), 41.3, 21.3, 21.2, 21.1, 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.2; IR (neat, cm^{-1}): 1732, 1455, 1185, 753; HRMS (ESI) calcd for $C_{37}H_{31}NO_2P$ $[M+H]^+$: 552.2092; found: 552.2098.

2-(Bis(3,5-dimethoxyphenyl)phosphoryl)-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3aj): Pale yellow syrup (41.8 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.95 (m, 1H), 7.71 – 7.58 (m, 1H), 7.36 – 7.29 (m, 2H), 7.29 – 7.23 (m, 2H), 7.23 – 7.16 (m, 6H), 7.08 (dd, *J* = 13.6, 2.3 Hz, 2H), 7.05 – 7.01 (m, 2H), 6.76 (dd, *J* = 13.2, 2.3 Hz, 2H), 6.64 (t, *J* = 2.2 Hz, 1H), 6.36 (t, *J* = 2.2 Hz, 1H), 5.27 (dd, *J* = 15.2, 2.5 Hz, 1H), 4.17 (dd, *J* = 14.4, 2.5 Hz, 1H), 3.77 (s, 6H), 3.54 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 161.1, 161.0, 160.8, 160.7, 141.6, 141.6, 139.5, 134.0, 132.4, 132.1, 131.6, 131.3, 130.8, 130.5, 129.4, 129.1, 128.5, 128.3, 127.6, 127.4, 127.0, 124.8, 124.3, 120.2, 120.0, 116.6, 114.0, 109.3, 109.2, 108.7, 108.7, 105.4, 105.0, 59.9 (d, *J* = 57.4 Hz), 55.7, 55.4, 40.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.1; IR (neat, cm^{-1}): 1730, 1591, 1452, 1163, 754; HRMS (ESI) calcd for $C_{39}H_{35}NO_6P$ $[M+H]^+$: 644.2202; found: 644.2202.

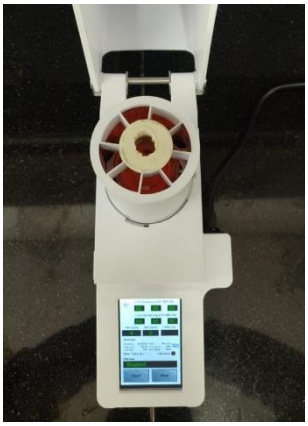
2-(Bis(2,5-dimethoxyphenyl)phosphoryl)-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3ak): White solid (38.6 mg, 60%); mp = 110-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 1H), 7.66 – 7.61 (m, 1H), 7.53 (dd, *J* = 11.1, 8.0 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.21 – 7.09 (m, 7H), 7.09 – 7.02 (m, 3H), 7.01 – 6.95 (m, 3H), 6.78 (dd, *J* = 9.0, 6.5 Hz, 1H), 6.59 (dd,

J = 9.0, 6.5 Hz, 1H), 5.06 (dd, *J* = 17.1, 3.2 Hz, 1H), 4.72 (dd, *J* = 19.2, 3.3 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.51 (s, 3H), 3.19 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 155.2, 154.7, 153.8, 153.7, 153.5, 153.4, 141.7, 141.6, 140.5, 134.1, 132.4, 130.8, 128.7, 128.4, 127.6, 127.2, 126.8, 124.3, 123.9, 120.2, 120.0, 119.8, 119.7, 119.1, 118.9, 118.7, 118.6, 117.9, 115.8, 114.0, 112.4, 112.3, 111.8, 111.7, 58.8 (d, *J* = 65.0 Hz), 56.1, 56.0, 55.8, 55.6, 41.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.8; IR (neat, cm^{-1}): 1732, 1510, 737; HRMS (ESI) calcd for $C_{39}H_{35}NO_6P$ $[M+H]^+$: 644.2202; found: 644.2211.

2-(Di(naphthalen-1-yl)phosphoryl)-1,9-diphenyl-1,2-dihydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (3al): White sticky solid (31.8 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.6 Hz, 1H), 8.55 (d, *J* = 8.6 Hz, 1H), 8.35 (dd, *J* = 15.3, 6.7 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.74 (dd, *J* = 16.1, 7.2 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.58 – 7.51 (m, 2H), 7.47 – 7.42 (m, 1H), 7.38 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 7.28 (ddd, *J* = 8.5, 6.8, 1.3 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.18 – 7.10 (m, 7H), 7.08 – 7.03 (m, 3H), 7.01 – 6.97 (m, 2H), 6.90 – 6.84 (m, 2H), 5.52 (dd, *J* = 15.4, 2.2 Hz, 1H), 4.56 (dd, *J* = 14.2, 2.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 141.5, 139.1, 133.9, 133.7, 133.5, 133.0, 132.1, 130.5, 129.1, 129.0, 128.6, 128.3, 128.2, 127.7, 127.5, 127.4, 127.2, 126.9, 126.5, 126.3, 125.9, 124.6, 124.5, 124.0, 119.9, 116.4, 113.7, 60.7 (d, *J* = 57.0 Hz), 41.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.8; IR (neat, cm^{-1}): 1724, 1524, 1198, 770; HRMS (ESI) calcd for $C_{43}H_{31}NO_2P$ $[M+H]^+$: 624.2092; found: 624.2094.

One mmol scale reaction to synthesize 3aa:

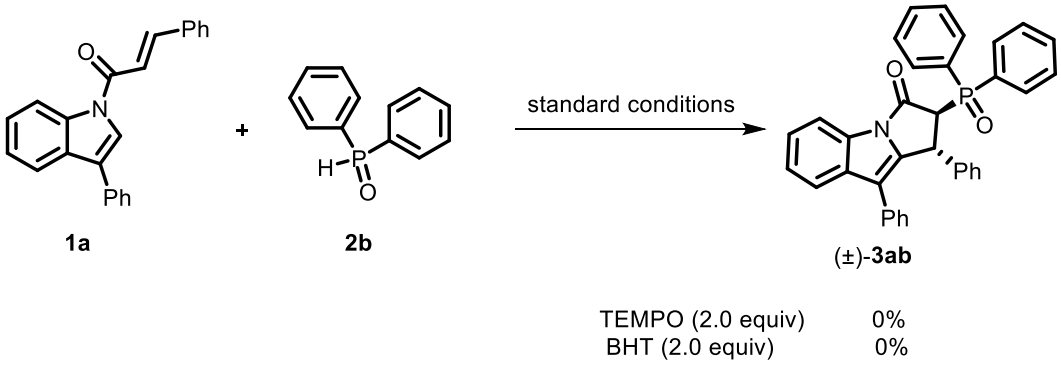
Cinnamide **1a** (323 mg, 1.0 mmol), phosphine oxide **2a** (2.5 mmol), and eosin Y (0.025 mmol) were placed in a 25 mL round bottom flask. Then DMSO (10 mL) was added. The reaction mixture was introduced into Penn *PhD* photoreactor m2 (blue LED 450 nm) with the help of an open septum. After the completion of the reaction (monitored by TLC), H_2O (30 mL) was added,



and the mixture was extracted into EtOAc (3x50.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the crude reaction mixture was purified by column chromatography on silica gel to afford the corresponding product in 65% yield.

Control experiments for mechanistic studies:

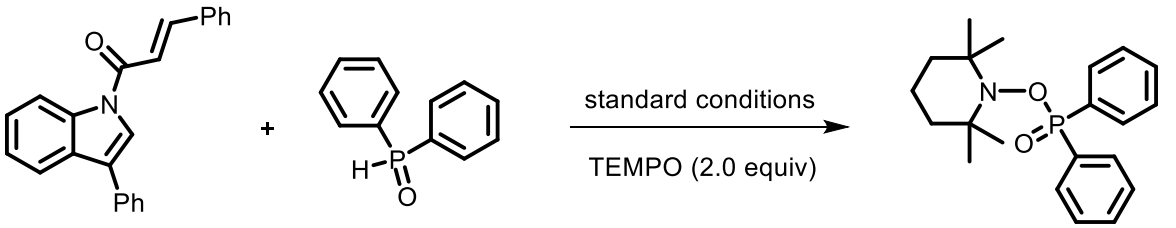
Radical inhibition experiments:



i) Cinnamide **1a** (32.3 mg, 0.1 mmol, 1.0 equiv), phosphine oxide **2b** (50.5 mg, 0.25 mmol, 2.5 equiv), eosin Y (1.6 mg, 0.0025 mmol, 0.025 equiv) and 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) (39.0 mg, 0.25 mmol, 2.5 equiv) were placed in a 5.0 mL oven dried vial. Then DMSO (1 mL) was added. The reaction mixture was introduced into Penn *PhD* photoreactor m2 (blue LED 450 nm). In this reaction the formation of product **3ab** was completely suppressed.

ii) Cinnamide **1a** (32.3 mg, 0.1 mmol, 1.0 equiv), phosphine oxide **2b** (50.5 mg, 0.25 mmol, 2.5 equiv), eosin Y (1.6 mg, 0.0025 mmol, 0.025 equiv) and butylated hydroxytoluene (BHT) (55 mg, 0.25 mmol, 2.5 equiv) were placed in a 5.0 mL oven dried vial. Then DMSO (1 mL) was added. The reaction mixture was introduced into Penn *PhD* photoreactor m2 (blue LED 450 nm). In this case also the formation of product **3ab** was completely suppressed.

Radical trapping experiment:



1a **2b** **4**

detected by HRMS and ^{31}P nmr

Cinnamide **1a** (32.3 mg, 0.1 mmol, 1.0 equiv), phosphine oxide **2b** (50.5 mg, 0.25 mmol, 2.5 equiv), eosin Y (1.6 mg, 0.0025 mmol, 0.025 equiv) and 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) (39.0 mg, 0.25 mmol, 2.5 equiv) were placed in a 5.0 mL oven dried vial. Then DMSO (1 mL) was added. The reaction mixture was introduced into Penn *PhD* photoreactor m2

(blue LED 450 nm). In this reaction the formation of product **3ab** was completely suppressed. The adduct of **2b** and TEMPO was detected by HRMS and ^{31}P nmr spectroscopy.

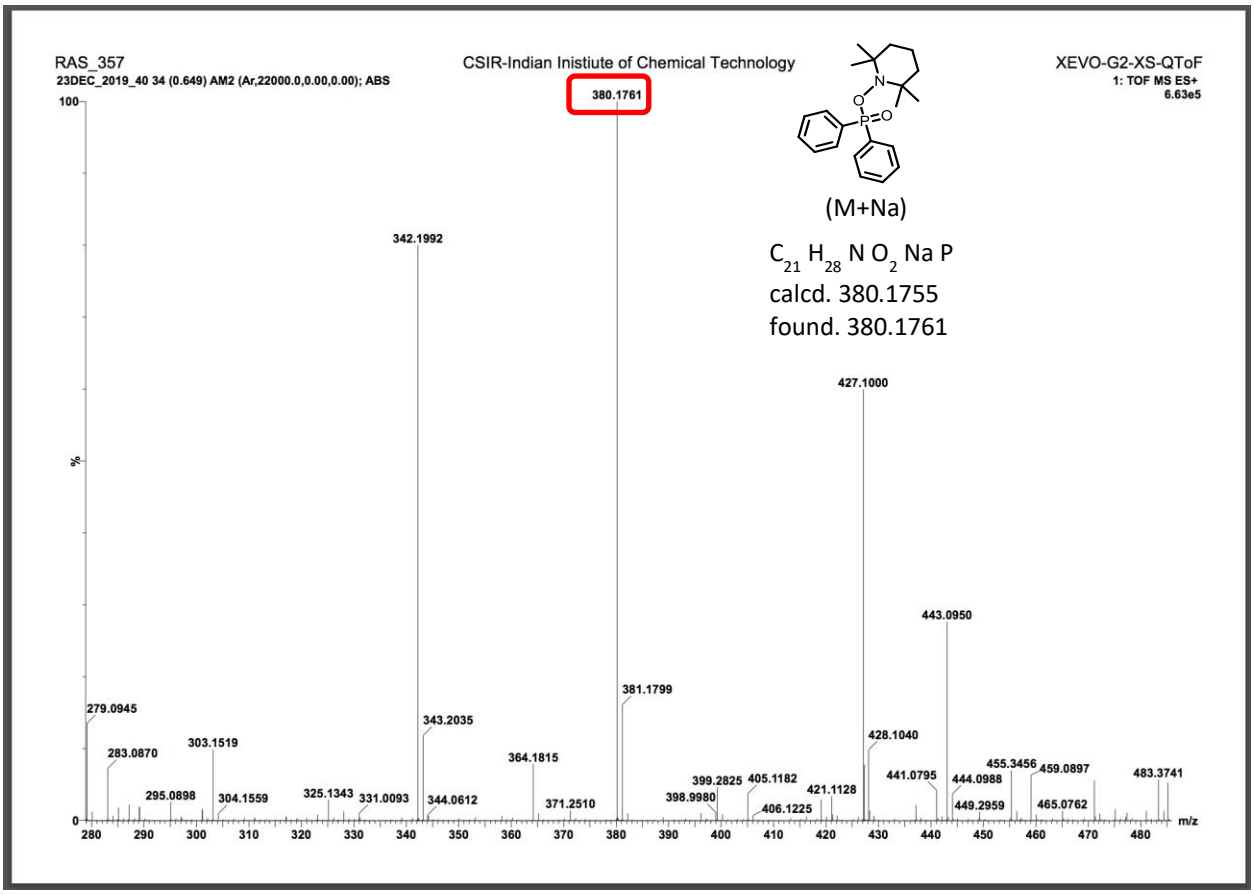


Figure S1. HRMS spectrum of compound **4**.

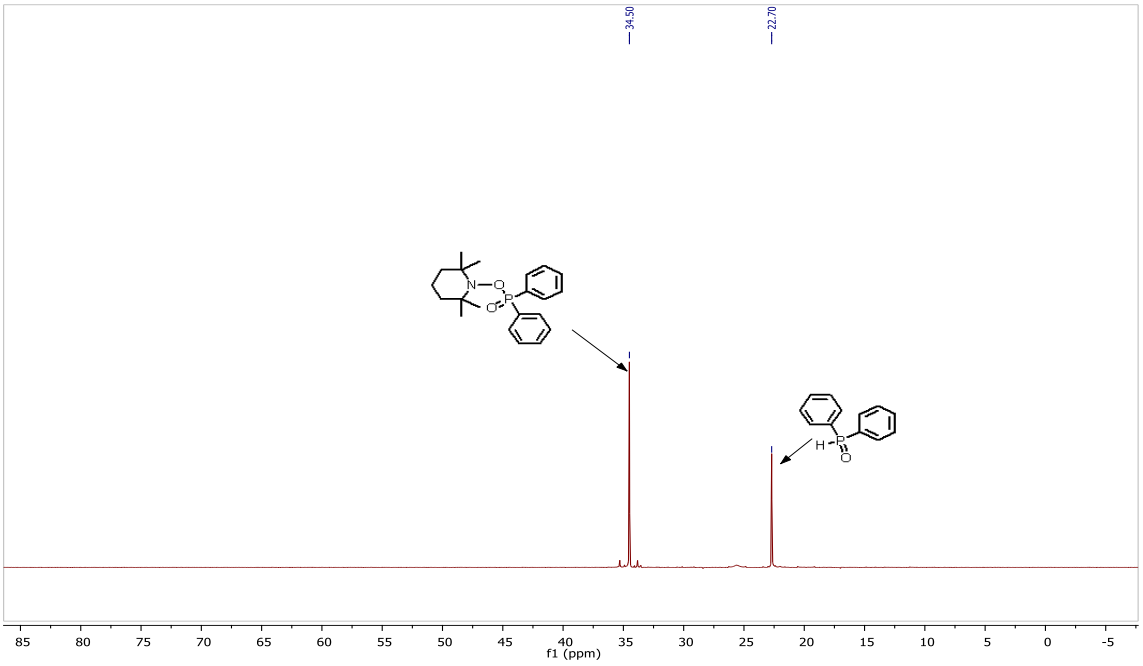


Figure S2. ^{31}P nmr spectrum of compound **4**.

Fluorescence quenching:

To a nitrogen degassed 2 ml solution of 3.3 μm eosin Y in DMSO placed in a quartz cuvett, was added 1.0 μl, 2.0 μl and 3.0 μl of 1.0 M phosphine oxide **2a** in DMSO consecutively at room temperature. These solutions were irradiated at 390 nm and fluorescence was measured from 530 nm to 700 nm.

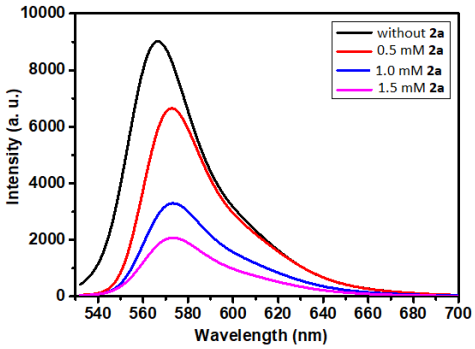


Figure S3. Fluorescence spectra of a 3.3 μm solution of eosin Y in DMSO containing 0 (black), 0.5 mM (red), 1.0 mM (blue), 1.5 mM (pink) of phosphine oxide **2a**.

X-ray Crystallography of 3aa:

X-ray data for the compound **3aa** (KA819) was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(C)$ for other H atoms].

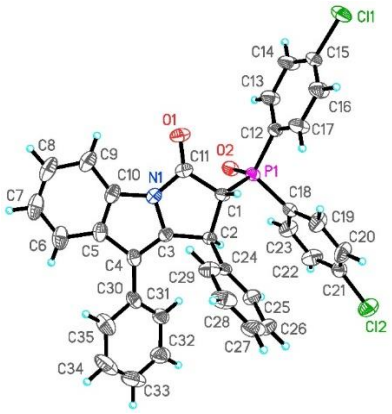


Figure Captions:

A view of **3aa** (KA819), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

Crystal structure determination of 3aa:

Crystal Data for $C_{35}H_{24}Cl_2NO_2P$ (M =592.42 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 12.8119(3) Å, b = 20.5439(4) Å, c = 11.4704(2) Å, β = 101.0819(9)°, V = 2962.79(10) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 0.306 mm^{-1}, *Dcalc* = 1.328 g/cm^3, 35746 reflections measured (4.798° ≤ 2Θ ≤ 52.498°), 5976 unique (R_{int} = 0.0879, R_{sigma} = 0.0646) which were used in all

calculations. The final R_1 was 0.0596 ($I > 2\sigma(I)$) and wR_2 was 0.1540 (all data). CCDC 1960675 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

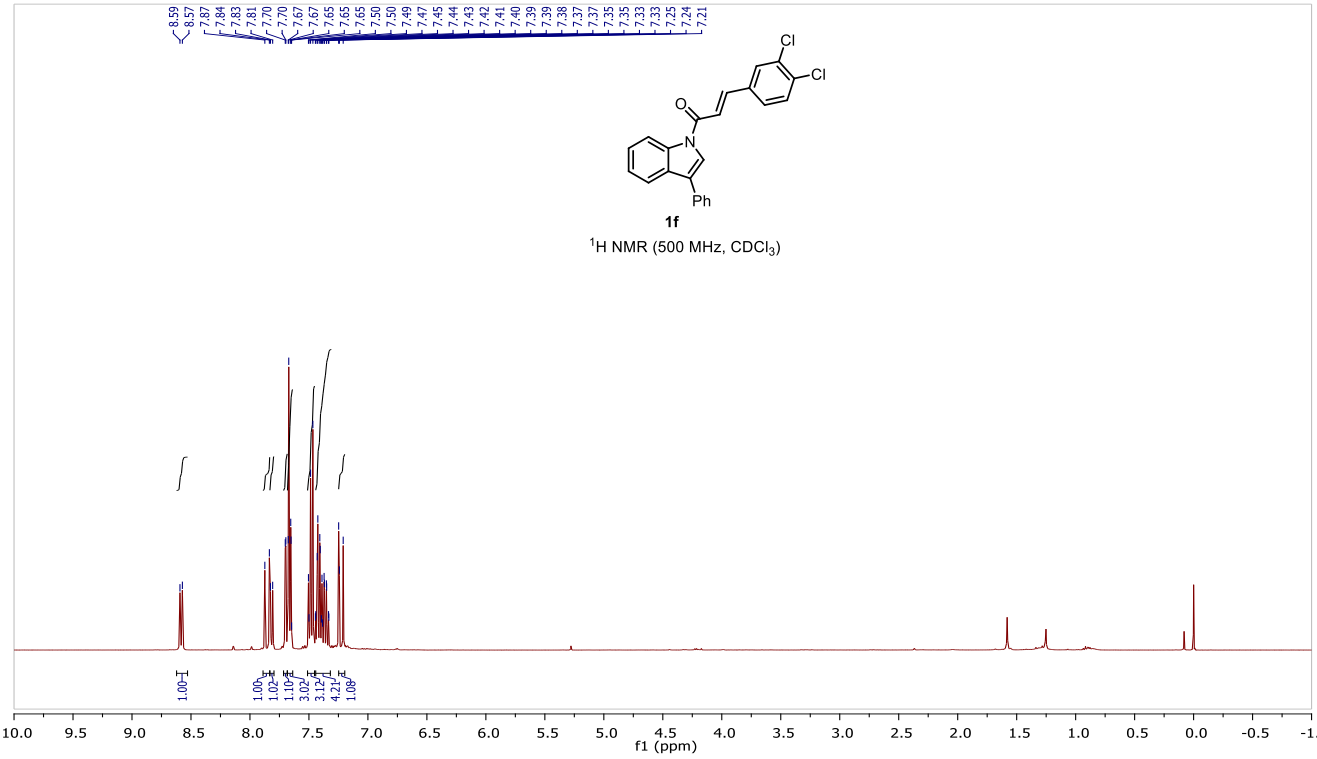
1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015) Acta Crystallogr C71: 3-8.

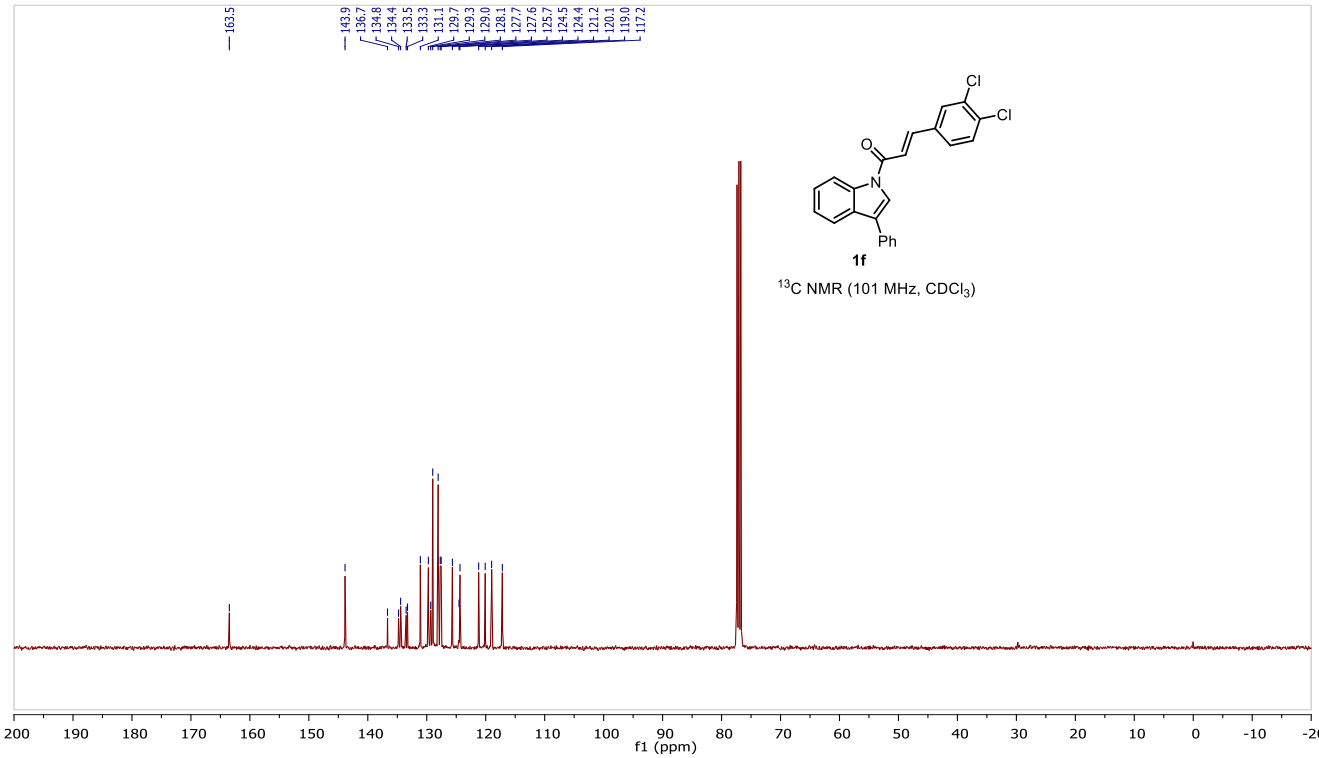
References

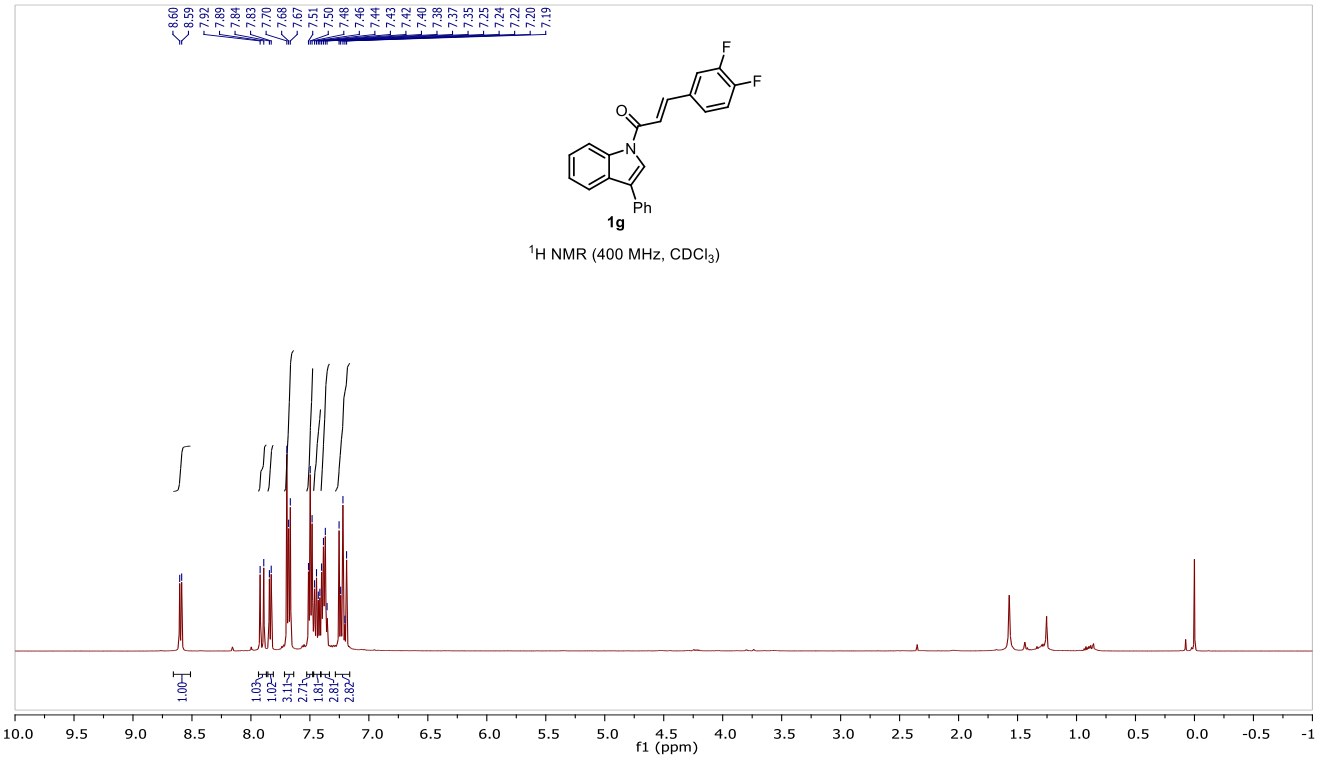
1. a) J. Xu, X. Yu and Q. Song, *Org. Lett.*, 2017, **19**, 980–983; b) J. Liu, S. Zhao, W. Song, R. Li, X. Guo, K. Zhuo and Y. Yue, *Adv. Synth. Catal.*, 2017, **359**, 609–615.

2. a) C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei and C. H. Senanayake, *Org. Lett.*, 2005, **7**, 4277–4280; b) Y. Unoh, K. Hirano and M. Miura, *J. Am. Chem. Soc.*, 2017, **139**, 6106–6109; c) Y. Sato, S. I. Kawaguchi and A. Ogawa, *Chem. Commun.*, 2015, **51**, 10385–10388; d) P. Peng, L. Peng, G. Wang, F. Wang, Y. Luo and A. Lei, *Org. Chem. Front.*, 2016, **3**, 749–752.

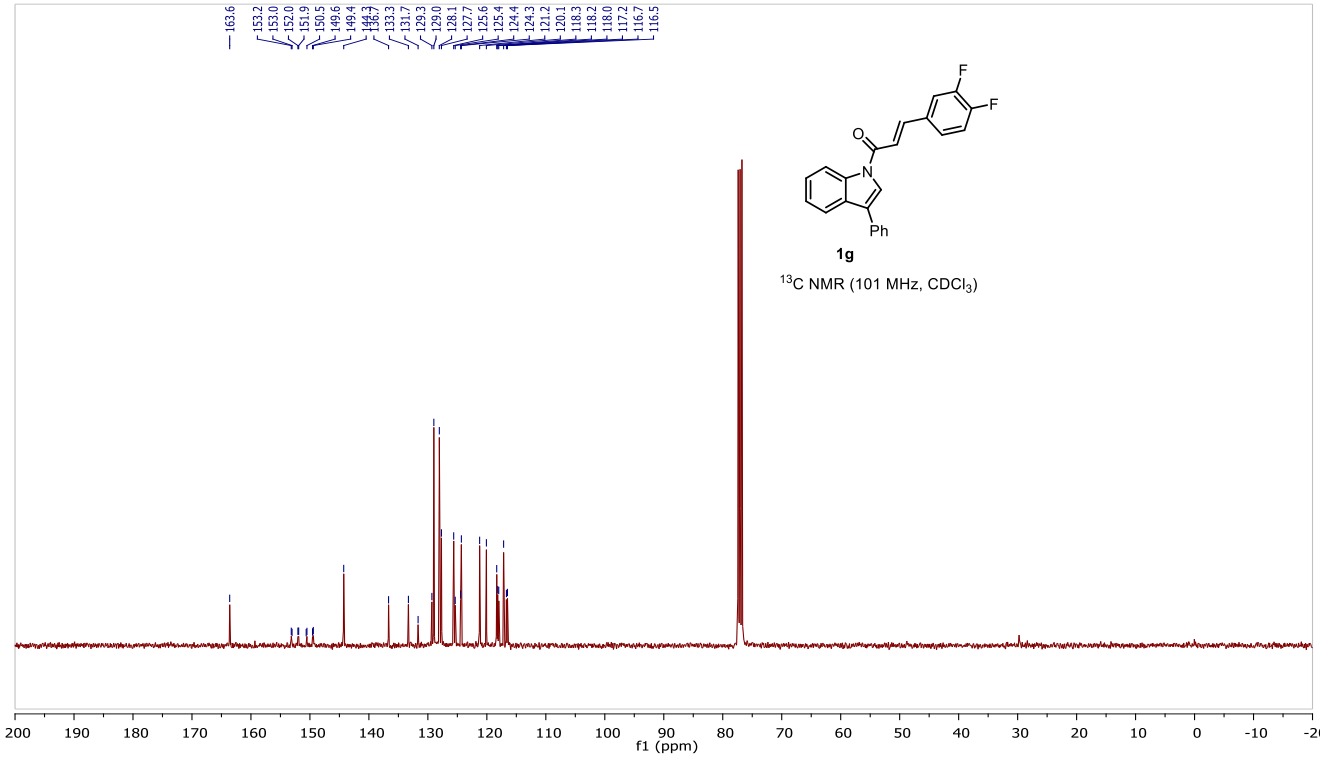
NMR spectra


8.59
8.57
7.87
7.84
7.83
7.81
7.70
7.70
7.67
7.67
7.65
7.65
7.65
7.50
7.50
7.49
7.47
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.35
7.35
7.33
7.33
7.25
7.24
7.21
Cl
Cl
O
N
Ph
1f
1H NMR (500 MHz, CDCl3)
1.00
1.00
1.02
1.10
3.02
3.12
4.21
1.06
f1 (ppm)

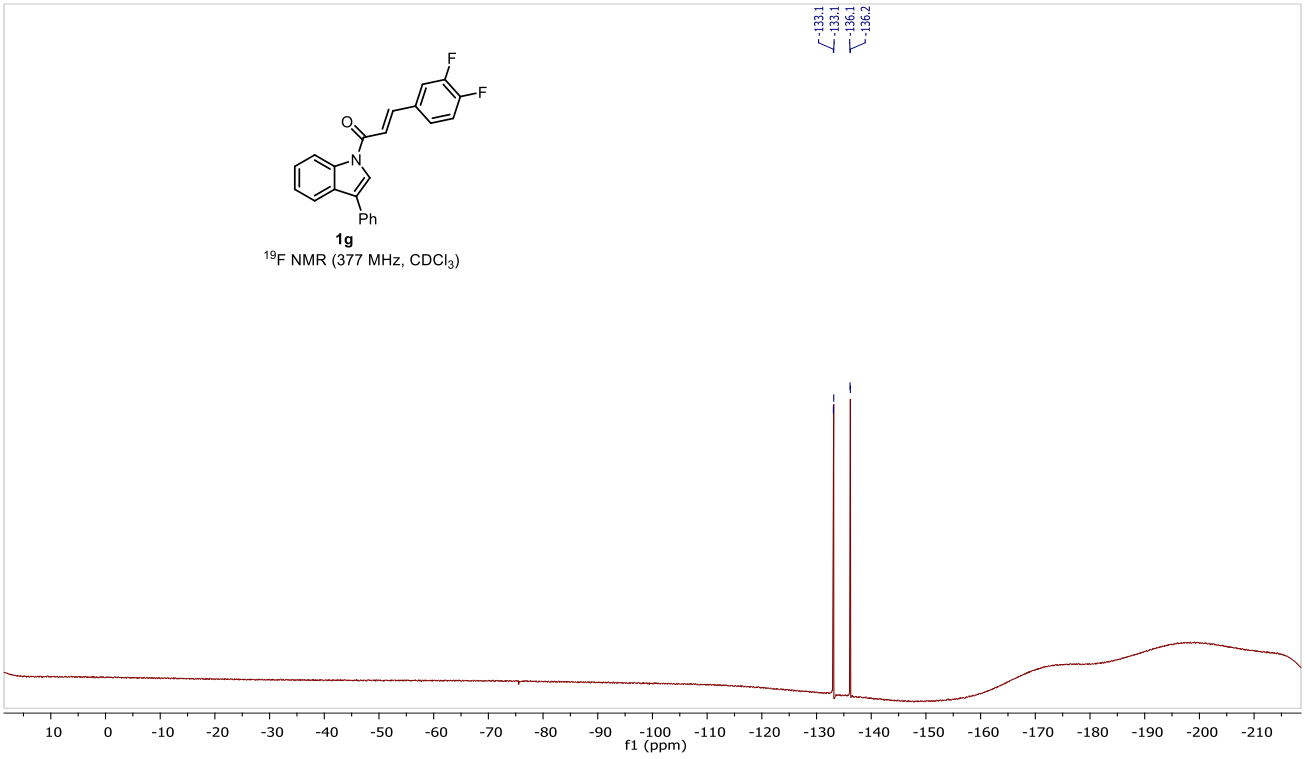

163.5
143.9
136.7
134.8
134.4
133.5
133.3
131.1
129.7
129.3
129.0
128.1
127.7
127.6
125.7
124.5
124.4
121.2
120.1
119.0
117.2
Cl
Cl
O
N
Ph
1f
13C NMR (101 MHz, CDCl3)
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)

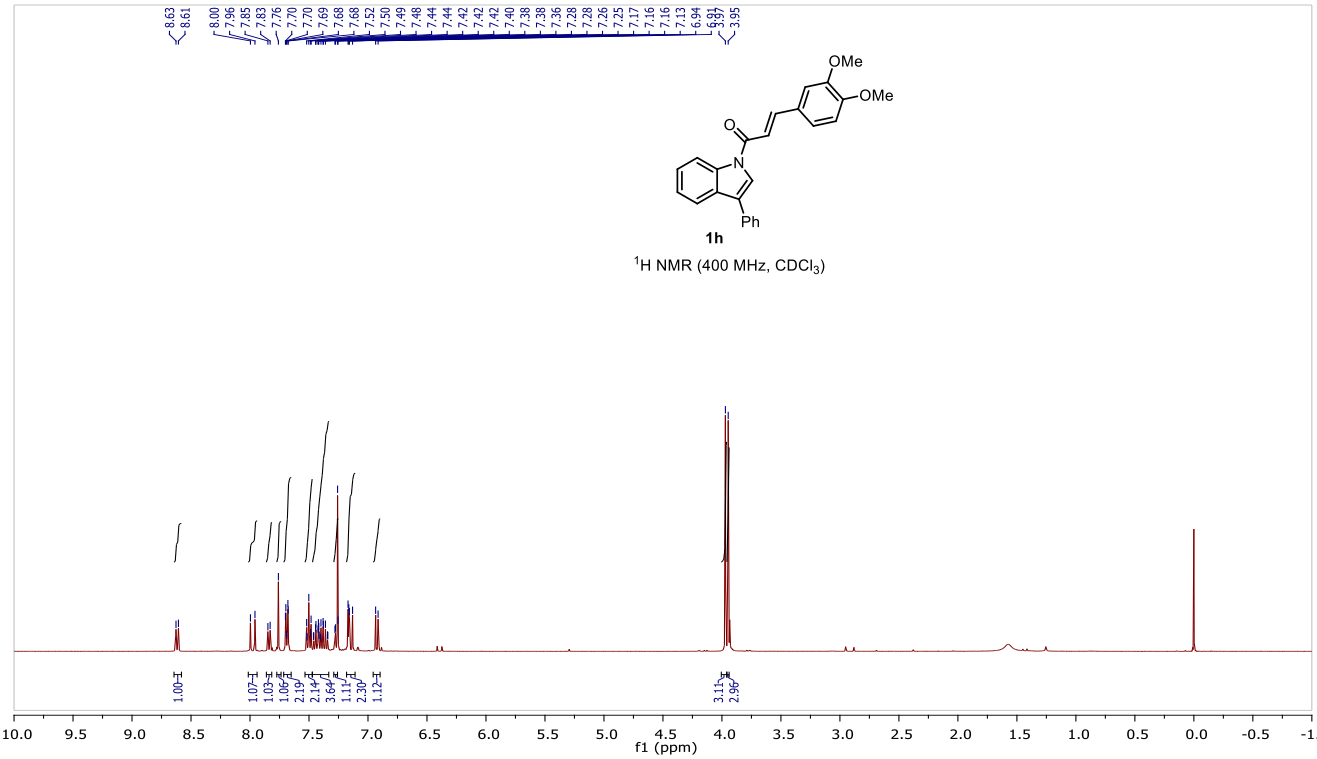


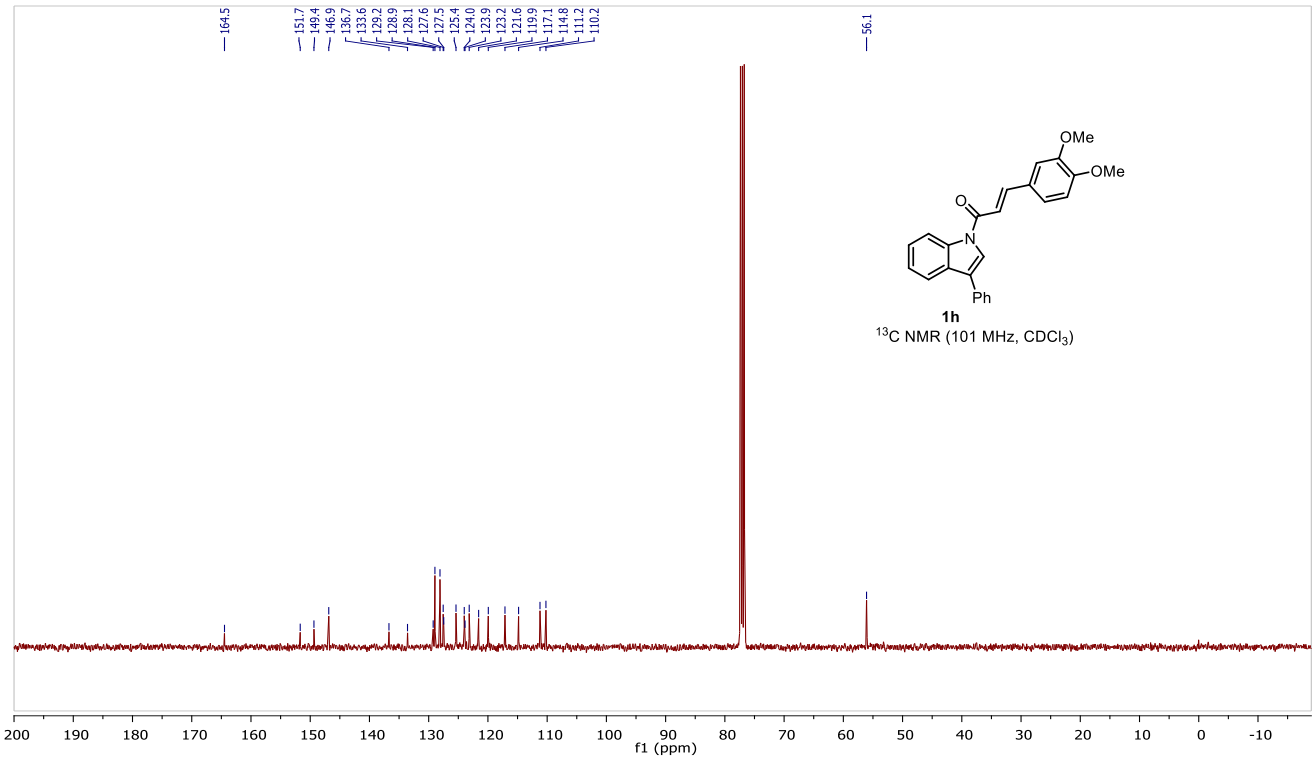
^{13}C NMR (101 MHz, $CDCl_3$)

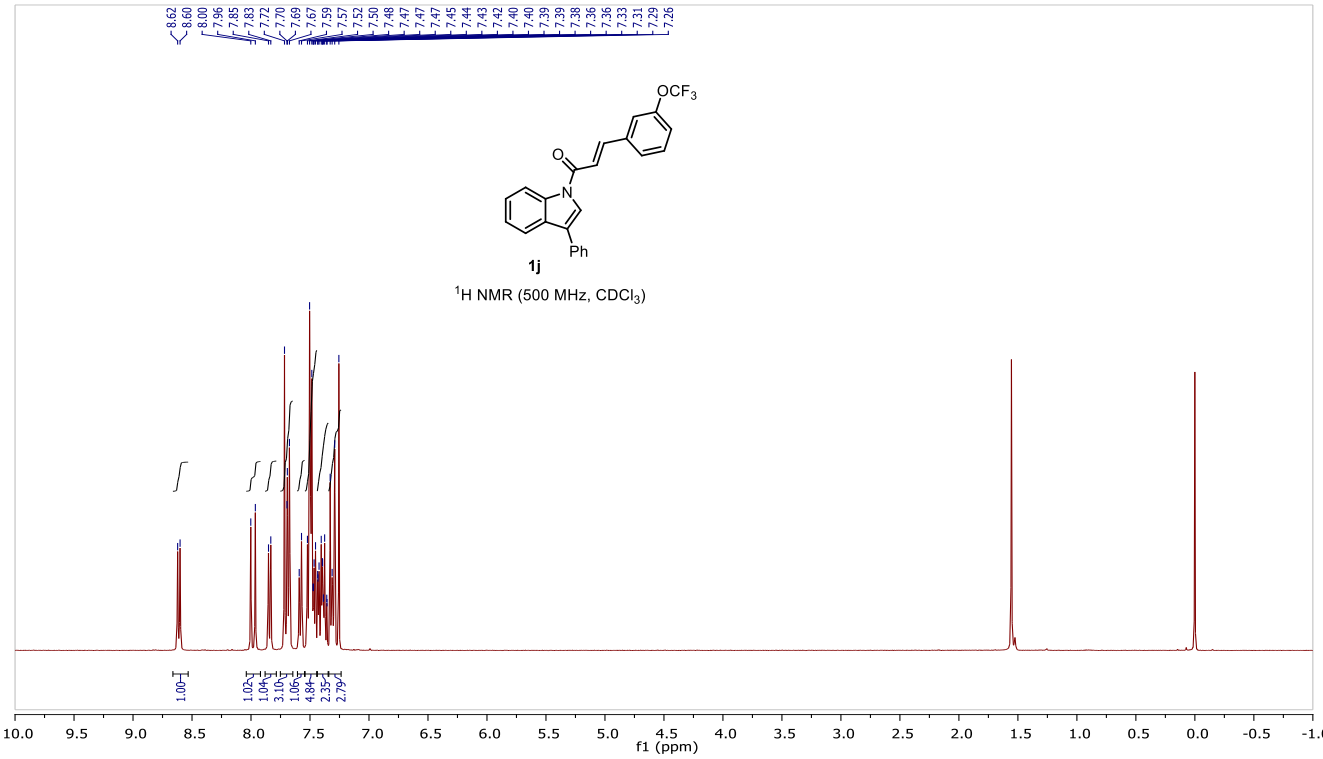


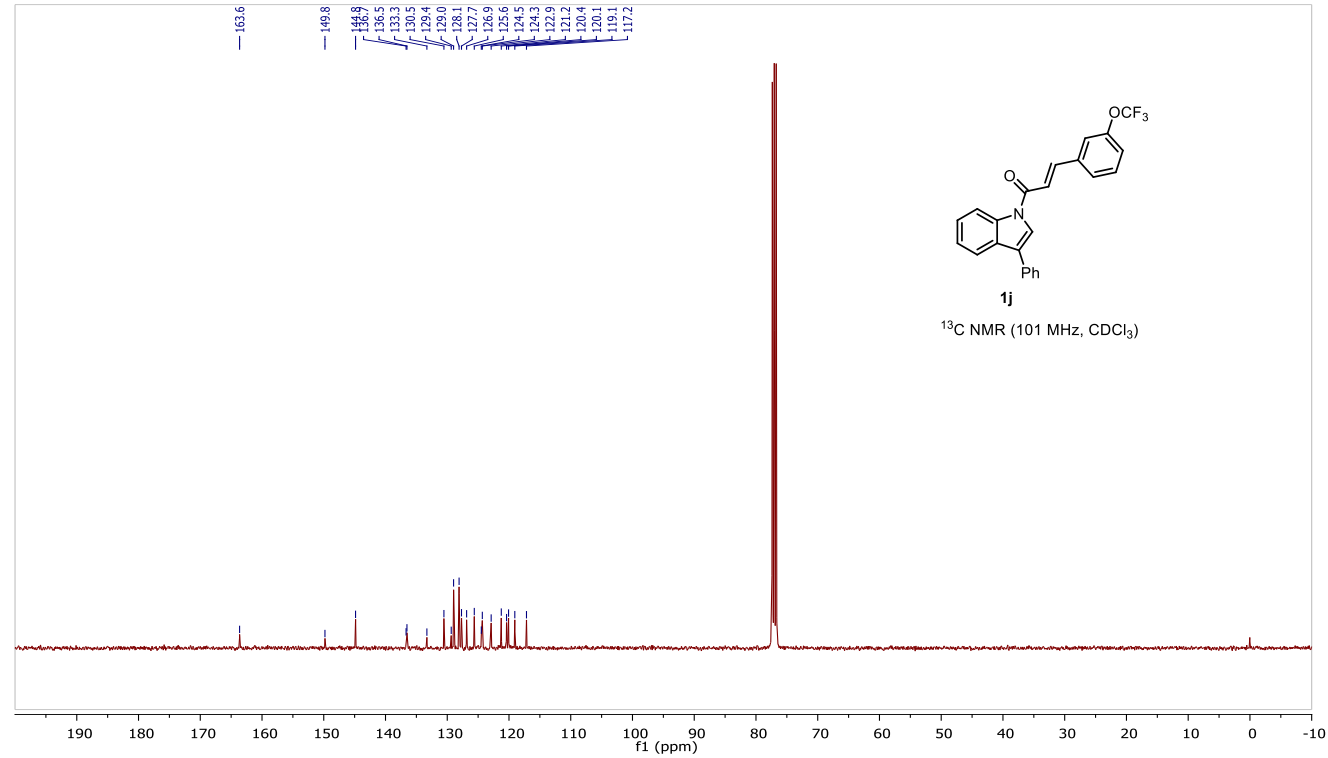
1g

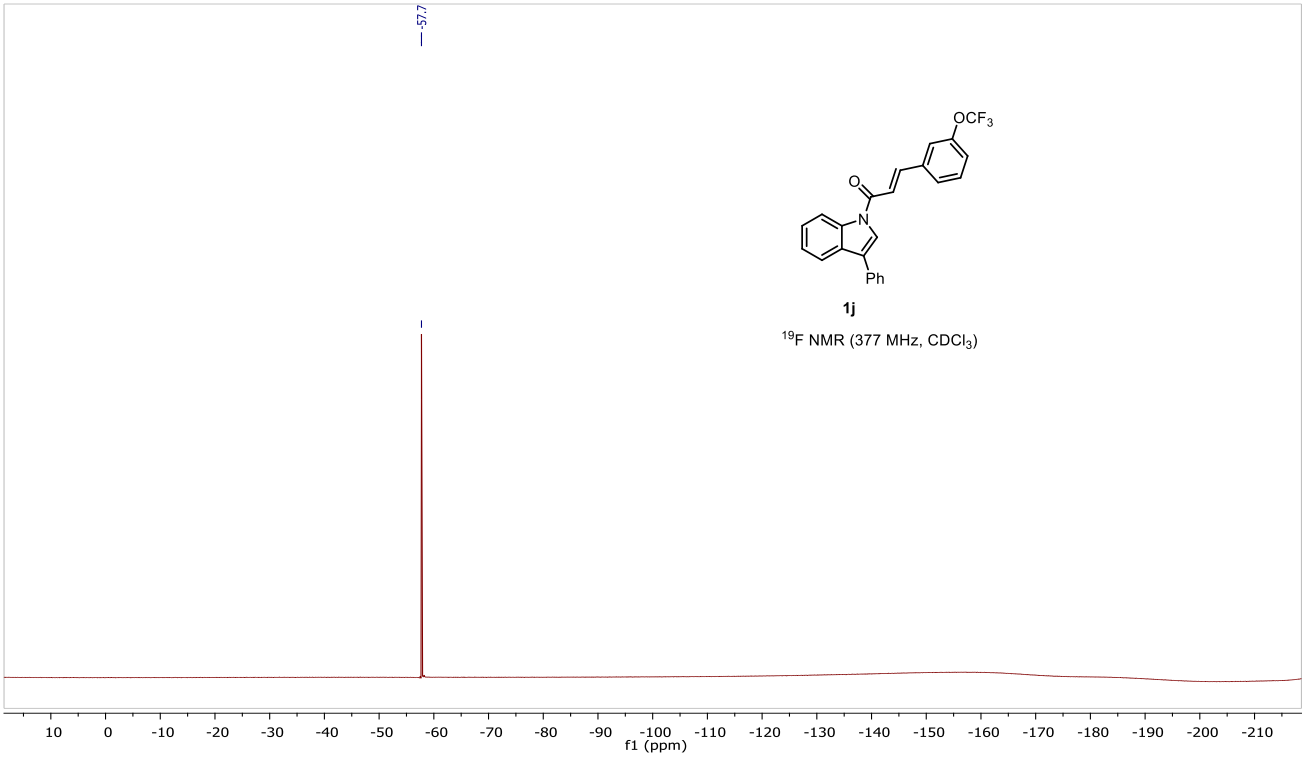
^{19}F NMR (377 MHz, $CDCl_3$)


8.63
8.61
8.00
7.96
7.85
7.83
7.76
7.70
7.70
7.69
7.68
7.68
7.52
7.50
7.49
7.48
7.44
7.44
7.42
7.42
7.40
7.38
7.38
7.36
7.28
7.28
7.26
7.25
7.17
7.16
7.16
7.13
6.94
6.91
3.97
3.95
OMe
OMe
O
N
Ph
1h
1H NMR (400 MHz, CDCl3)
1.00
1.07
1.03
1.06
2.19
2.14
3.64
1.17
2.30
1.12
3.11
2.96
10.0
9.5
9.0
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
-0.5
-1.0
f1 (ppm)


164.5
151.7
149.4
146.9
136.7
133.6
129.2
128.9
128.1
127.6
127.5
125.4
124.0
123.9
123.2
121.6
119.9
117.1
114.8
111.2
110.2
56.1
OMe
OMe
O
N
Ph
1h
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

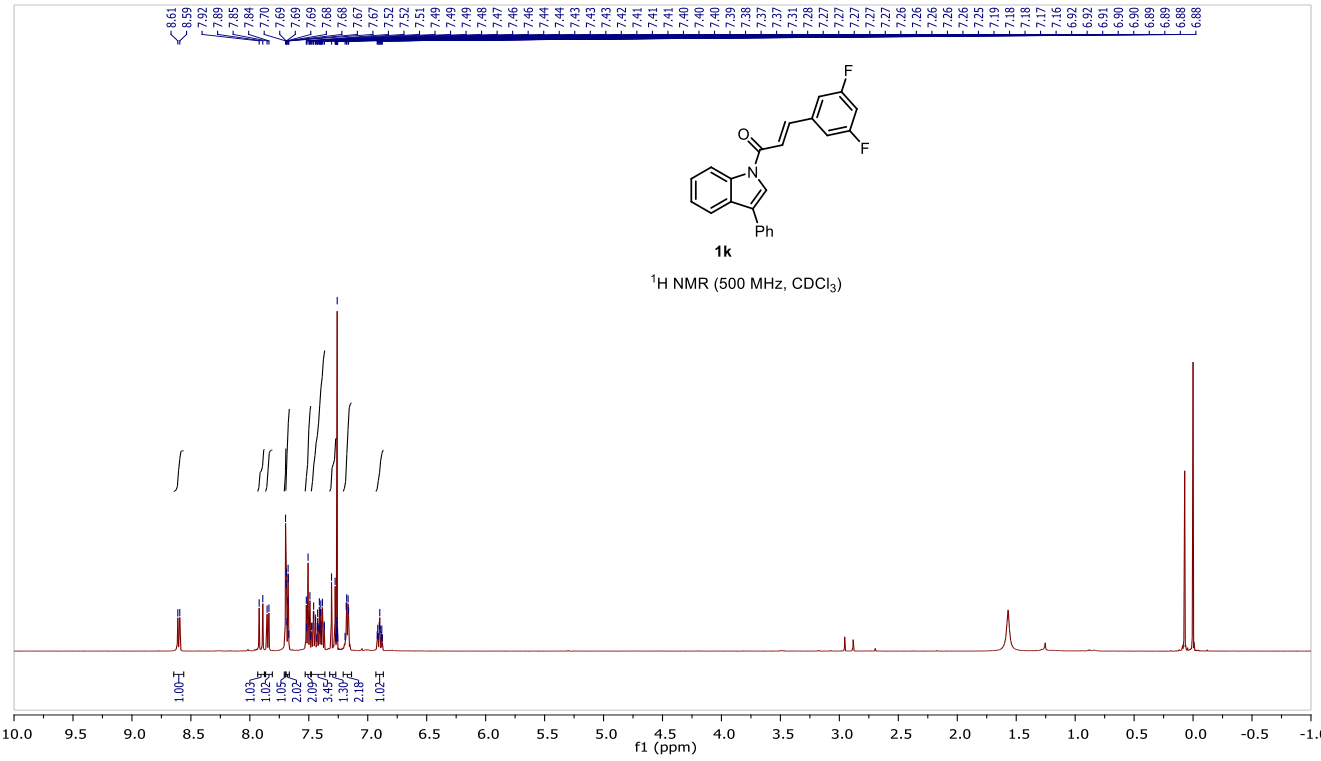

8.62
8.60
8.00
7.96
7.85
7.83
7.72
7.70
7.69
7.67
7.59
7.57
7.52
7.50
7.48
7.47
7.47
7.47
7.45
7.44
7.43
7.42
7.40
7.40
7.39
7.39
7.38
7.36
7.36
7.33
7.31
7.29
7.26
OCF3
O
N
Ph
1j
1H NMR (500 MHz, CDCl3)
1.00
1.02
1.04
3.10
1.06
4.84
2.35
2.79
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

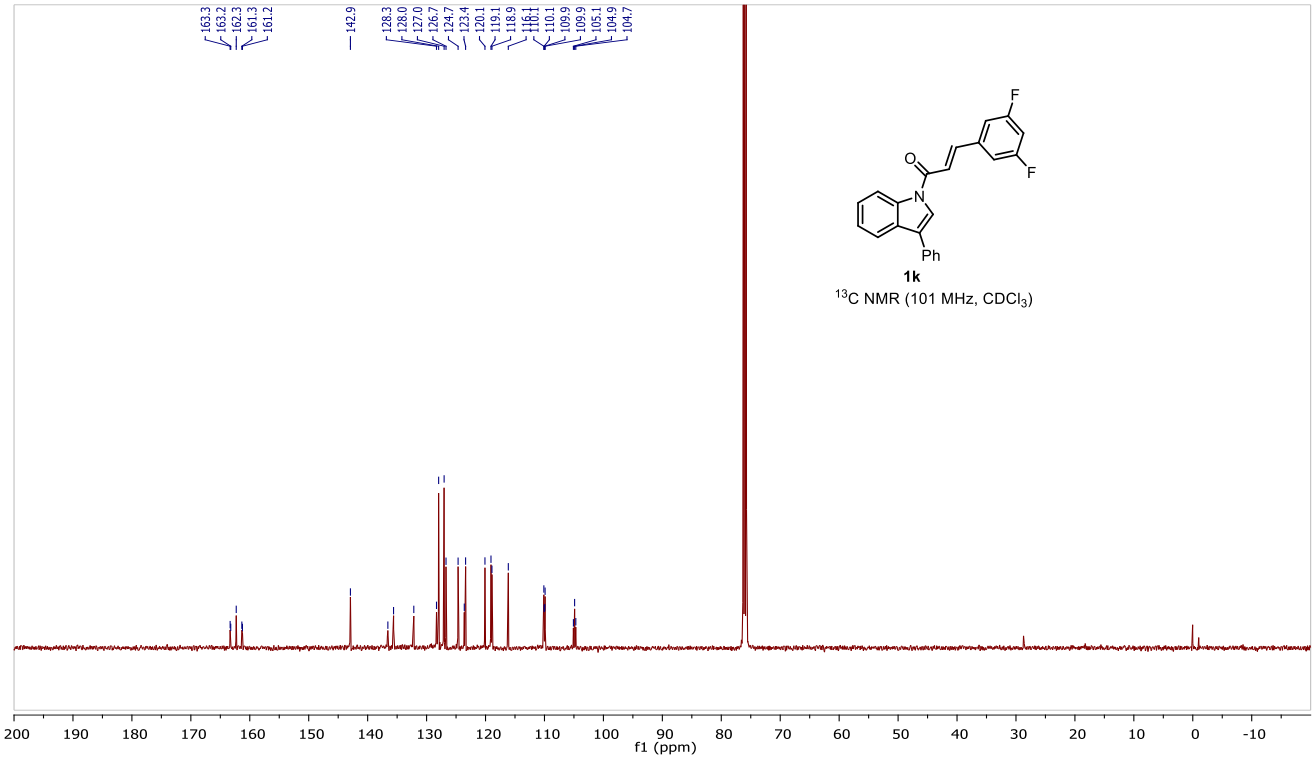

163.6
149.8
144.8
136.7
136.5
133.3
130.5
129.4
129.0
128.1
127.7
126.9
125.6
124.5
124.3
122.9
121.2
120.4
120.1
119.1
117.2
OCF3
O
N
Ph
1j
13C NMR (101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

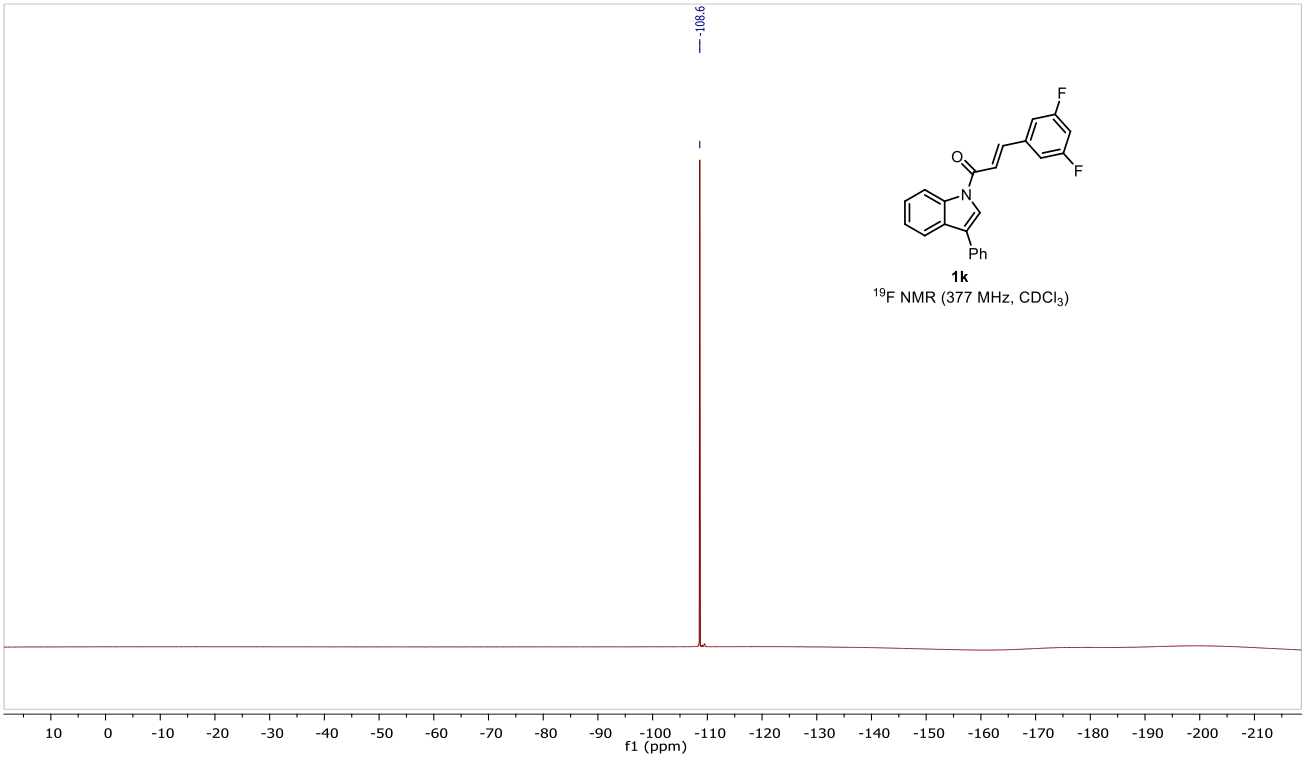


1j

^{19}F NMR (377 MHz, $CDCl_3$)

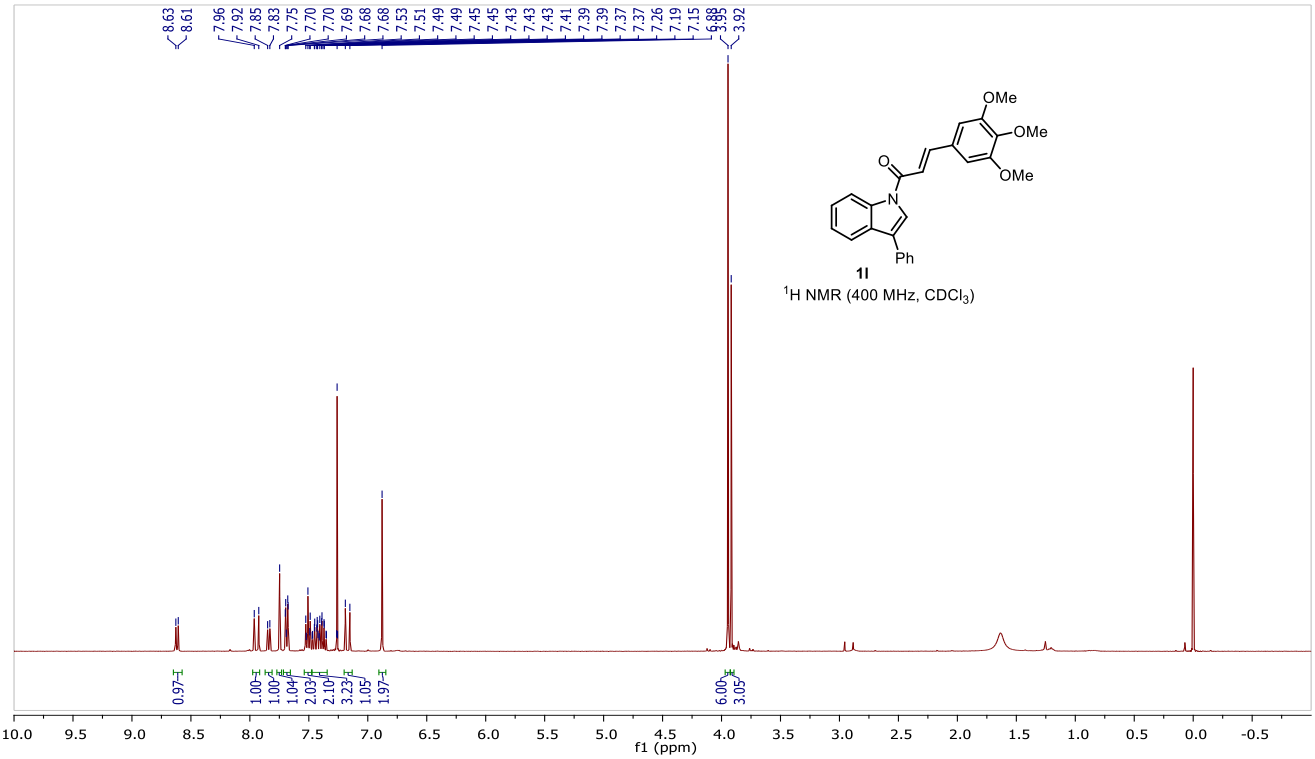

F
O
N
F
Ph
1k
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

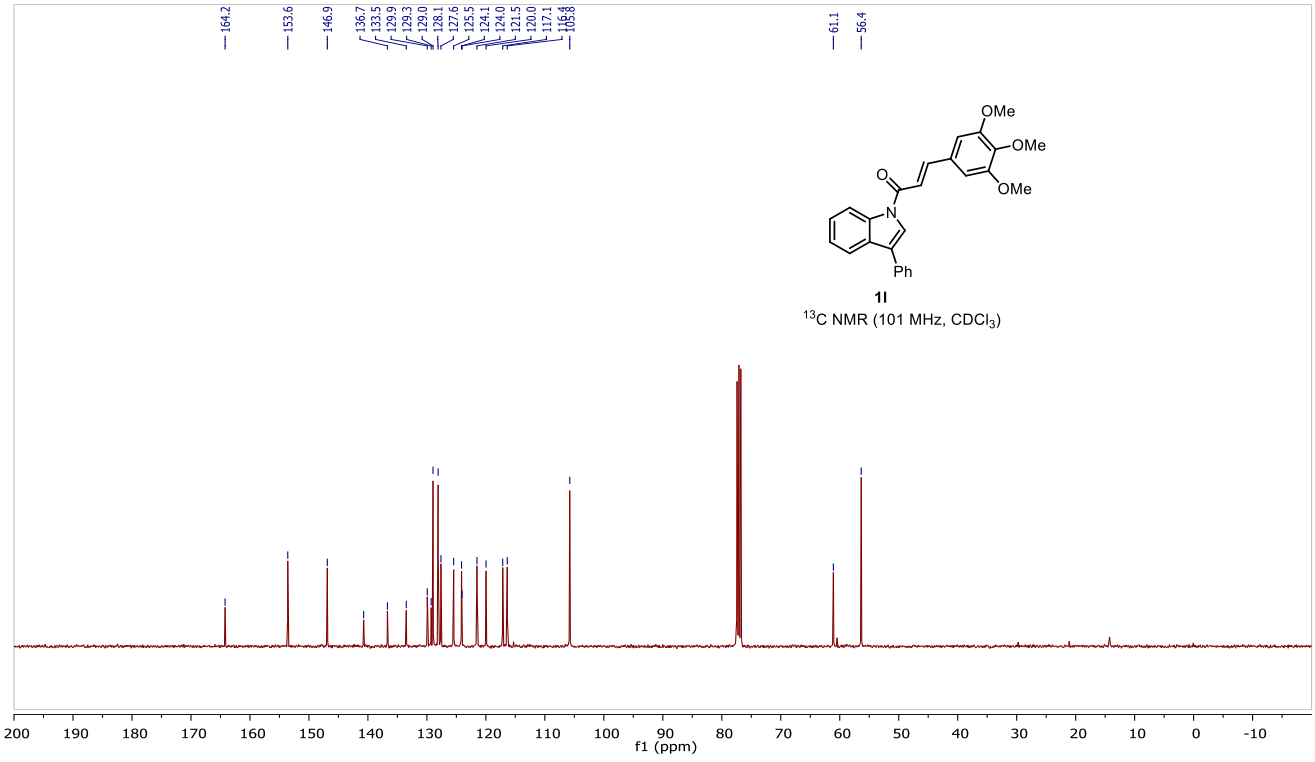

F
O
N
F
Ph
1k
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

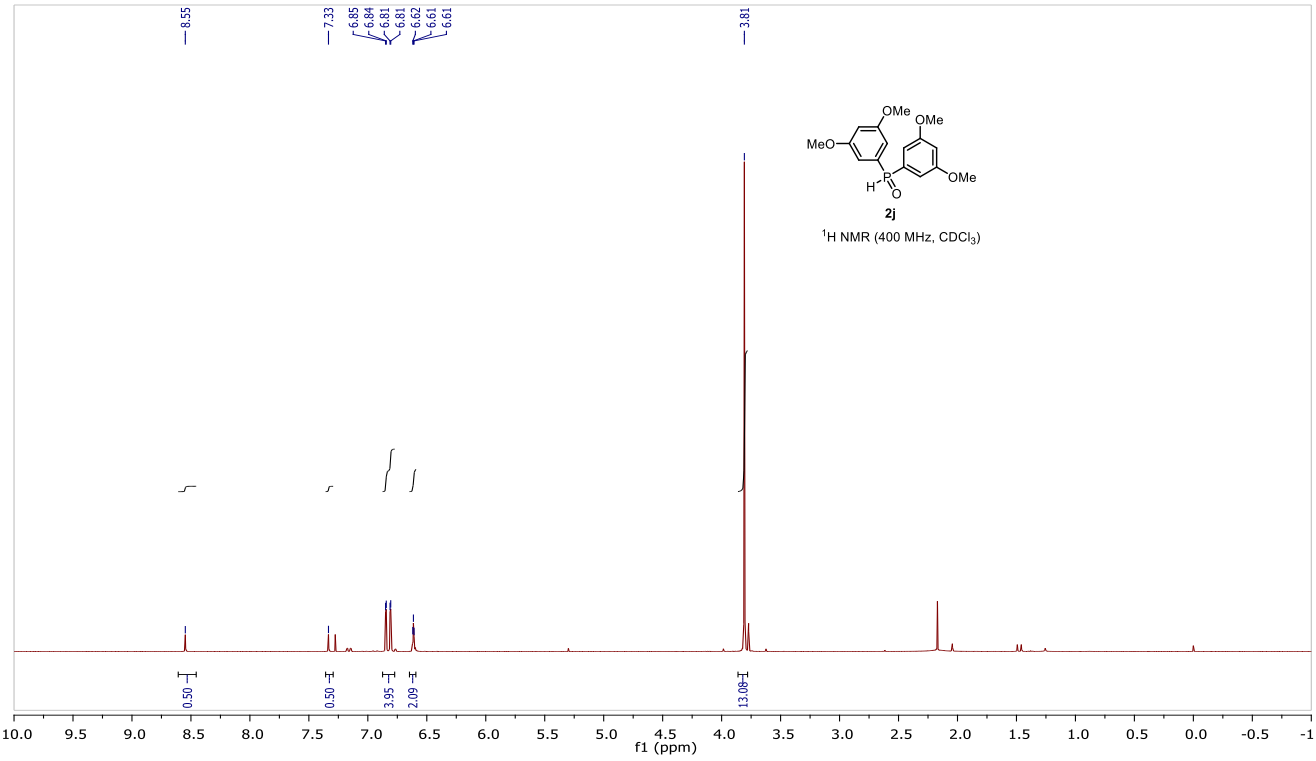


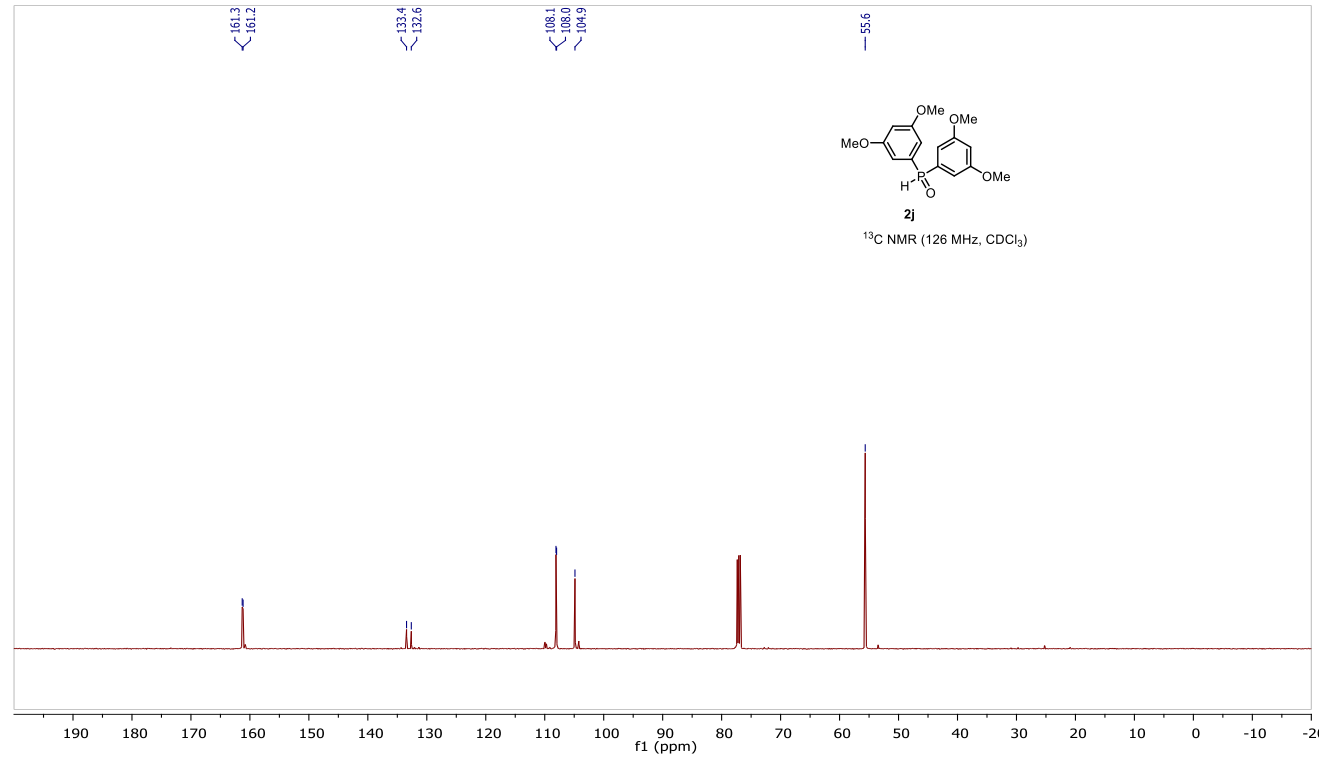
1k

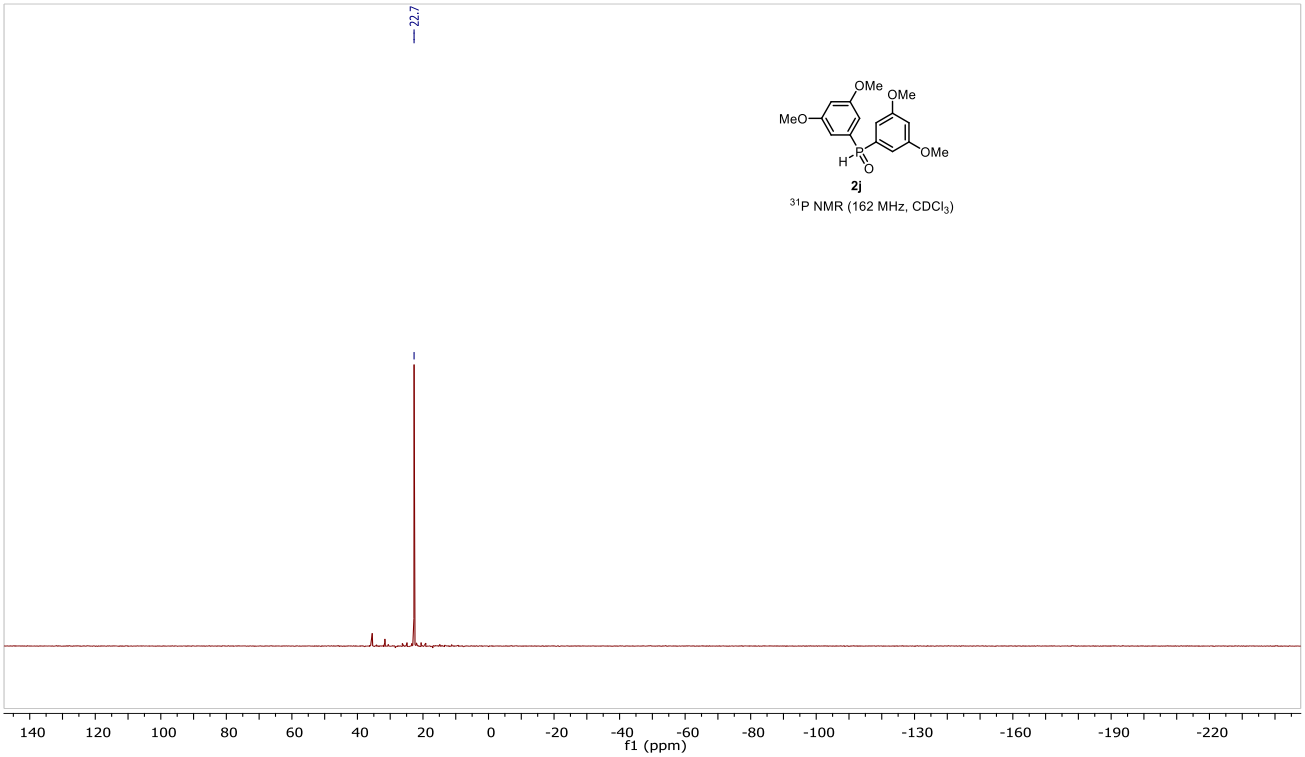
^{19}F NMR (377 MHz, $CDCl_3$)

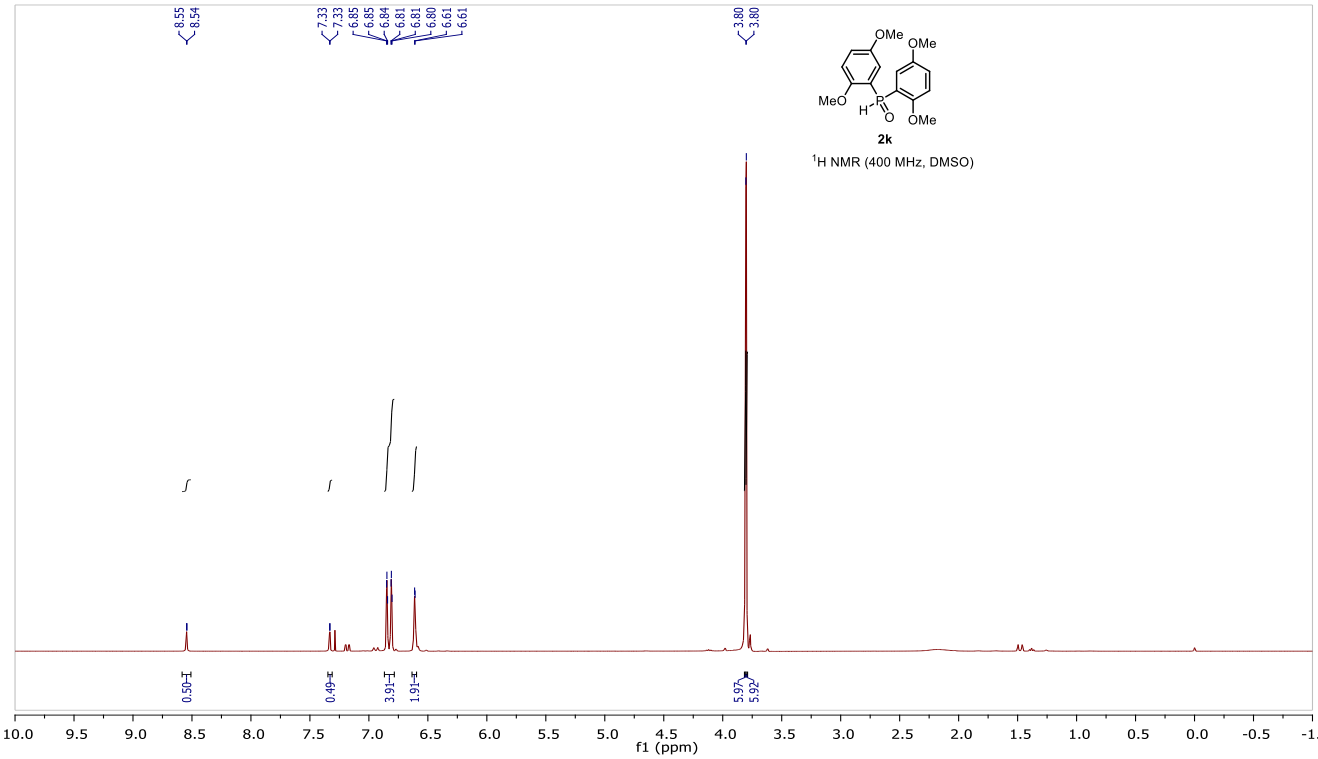

8.63
8.61
7.96
7.92
7.85
7.83
7.75
7.70
7.70
7.69
7.68
7.68
7.53
7.51
7.49
7.49
7.45
7.45
7.43
7.43
7.41
7.39
7.39
7.37
7.37
7.26
7.19
7.15
6.88
3.95
3.92
OMe
OMe
OMe
O
N
Ph
1l
^{1}H NMR (400 MHz, CDCl$_3$)
0.97
1.00
1.00
1.04
2.03
2.10
3.23
1.05
1.97
6.00
3.05
f1 (ppm)

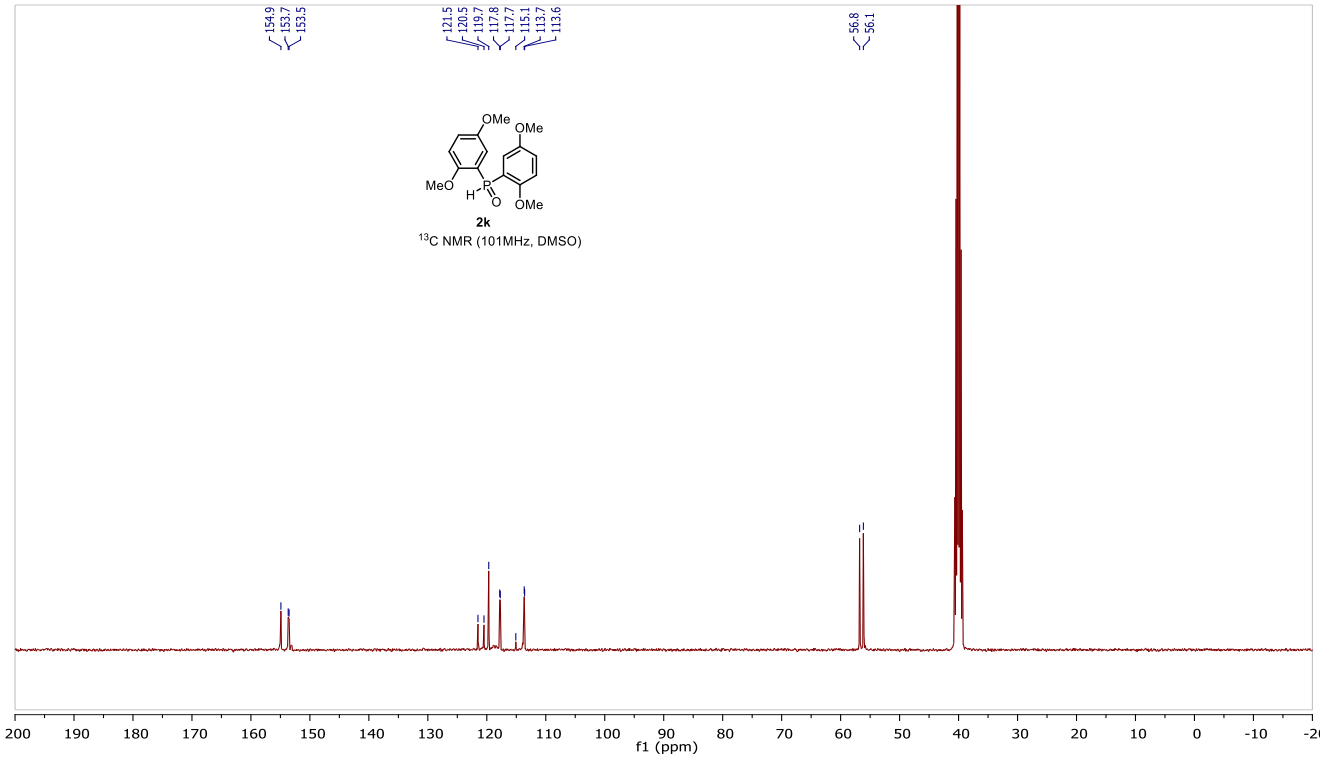

164.2
153.6
146.9
136.7
133.5
129.9
129.3
129.0
128.1
127.6
125.5
124.1
124.0
121.5
120.0
117.1
116.4
105.8
61.1
56.4
OMe
OMe
OMe
O
N
Ph
1l
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

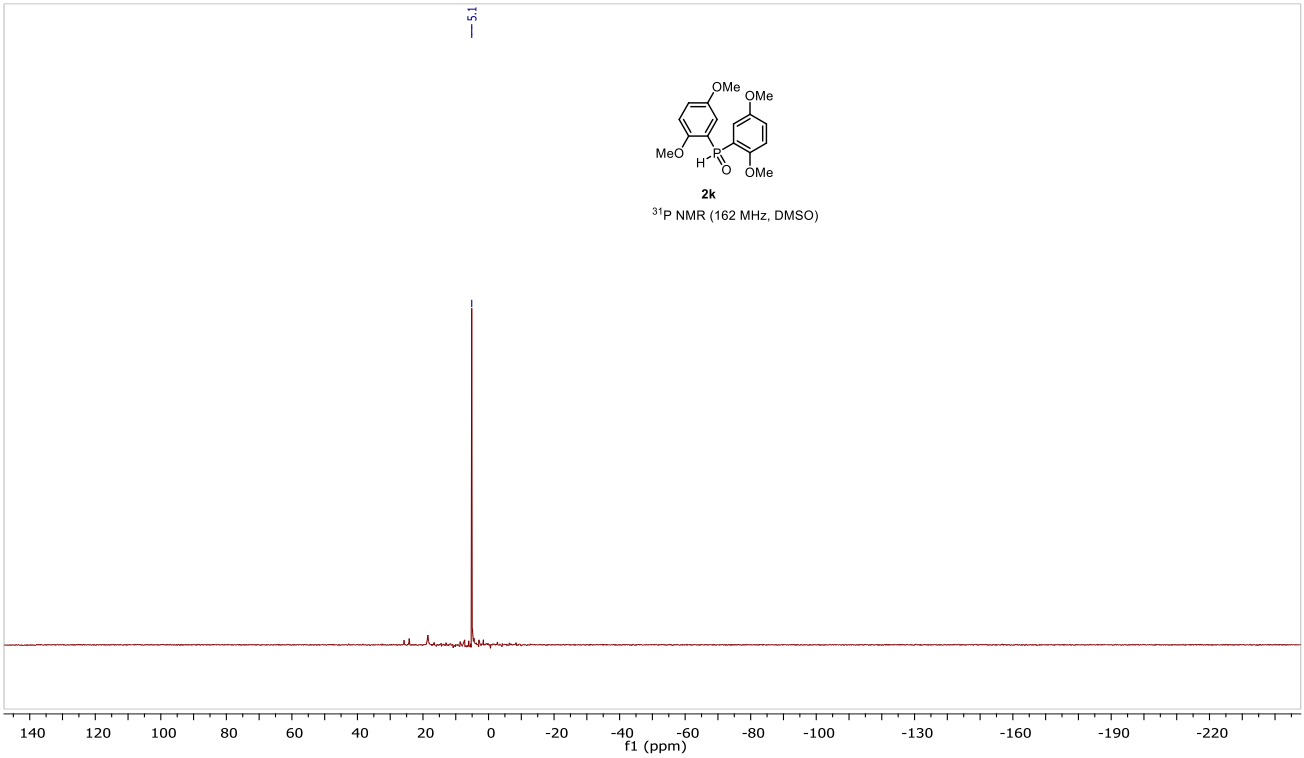

8.55
7.33
6.85
6.84
6.81
6.81
6.62
6.61
6.61
3.81
OMe
OMe
MeO
OMe
P
H
O
2j
^{1}H NMR (400 MHz, CDCl$_3$)
0.50
0.50
3.95
2.09
13.08
f1 (ppm)

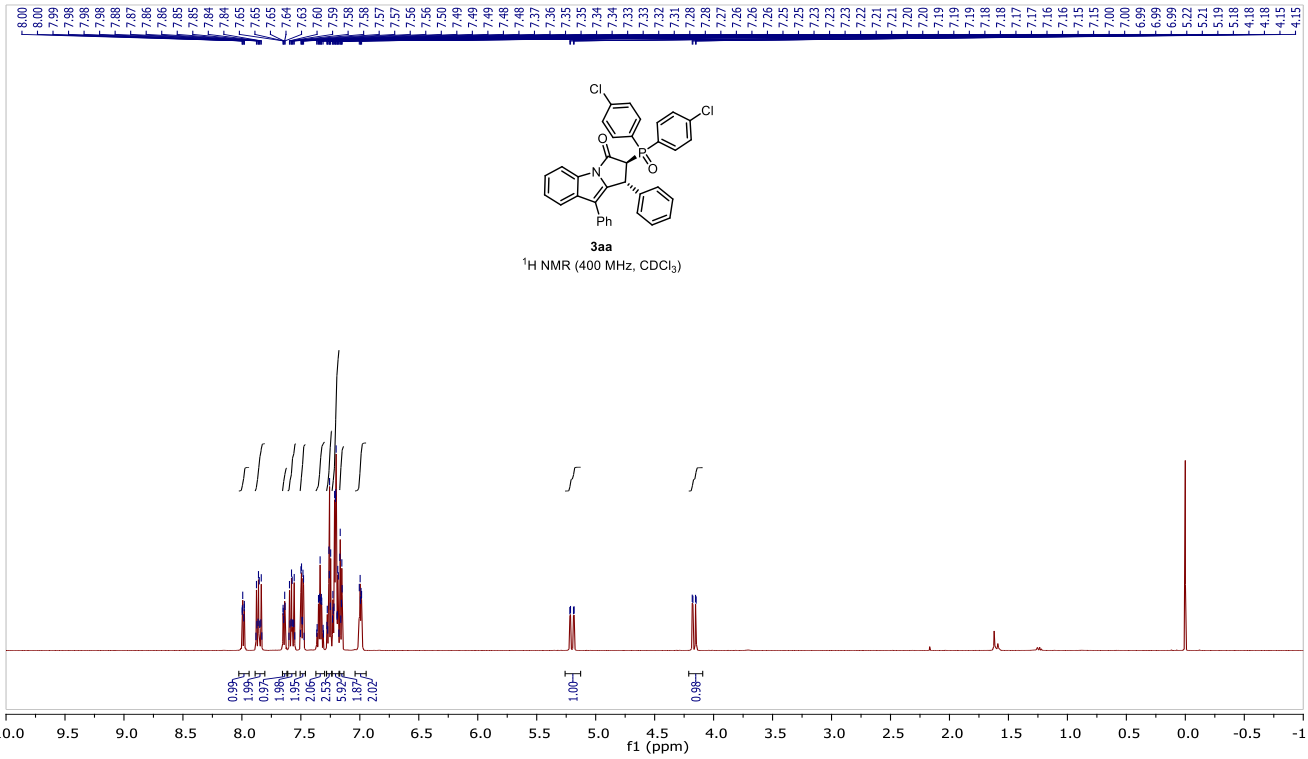

161.3
161.2
133.4
132.6
108.1
108.0
104.9
55.6
OMe
OMe
MeO
OMe
P
H
O
2j
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

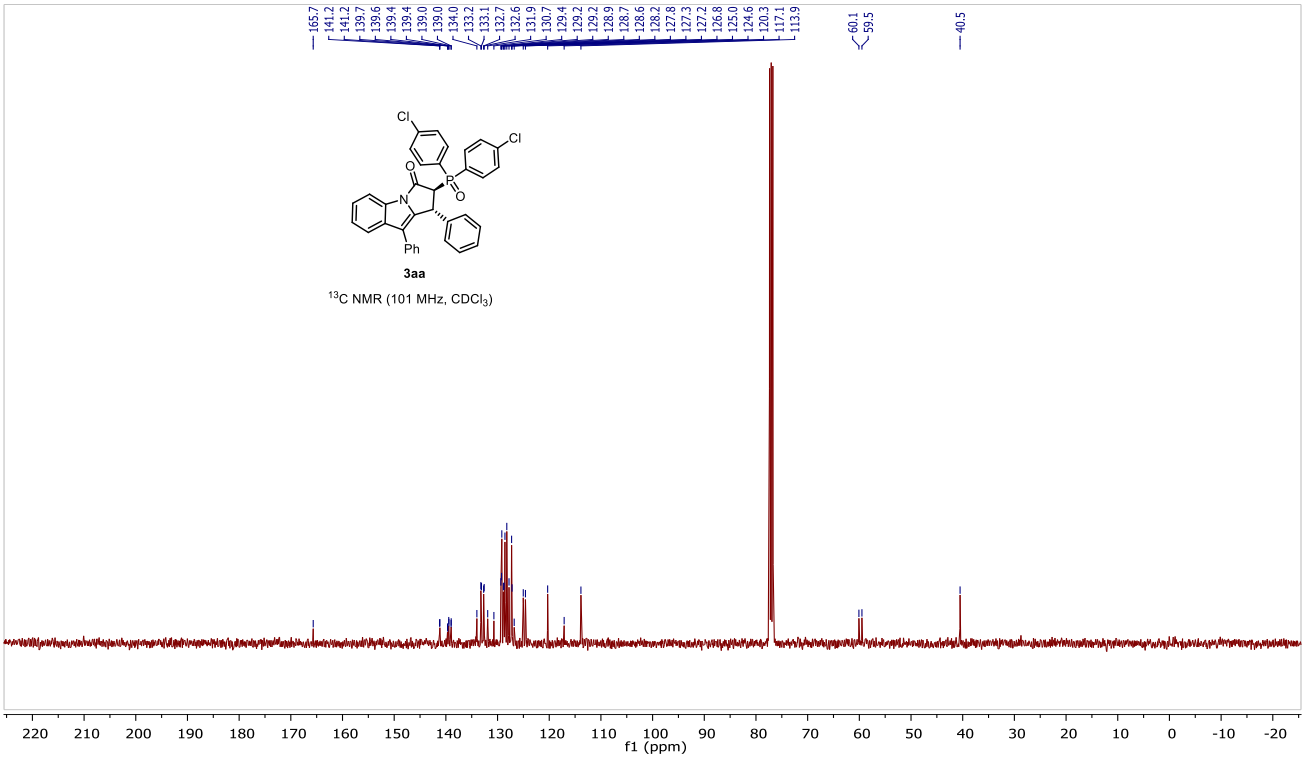

22.7
OMe
OMe
MeO
OMe
H
P
O
2j
31P NMR (162 MHz, CDCl3)
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
f1 (ppm)

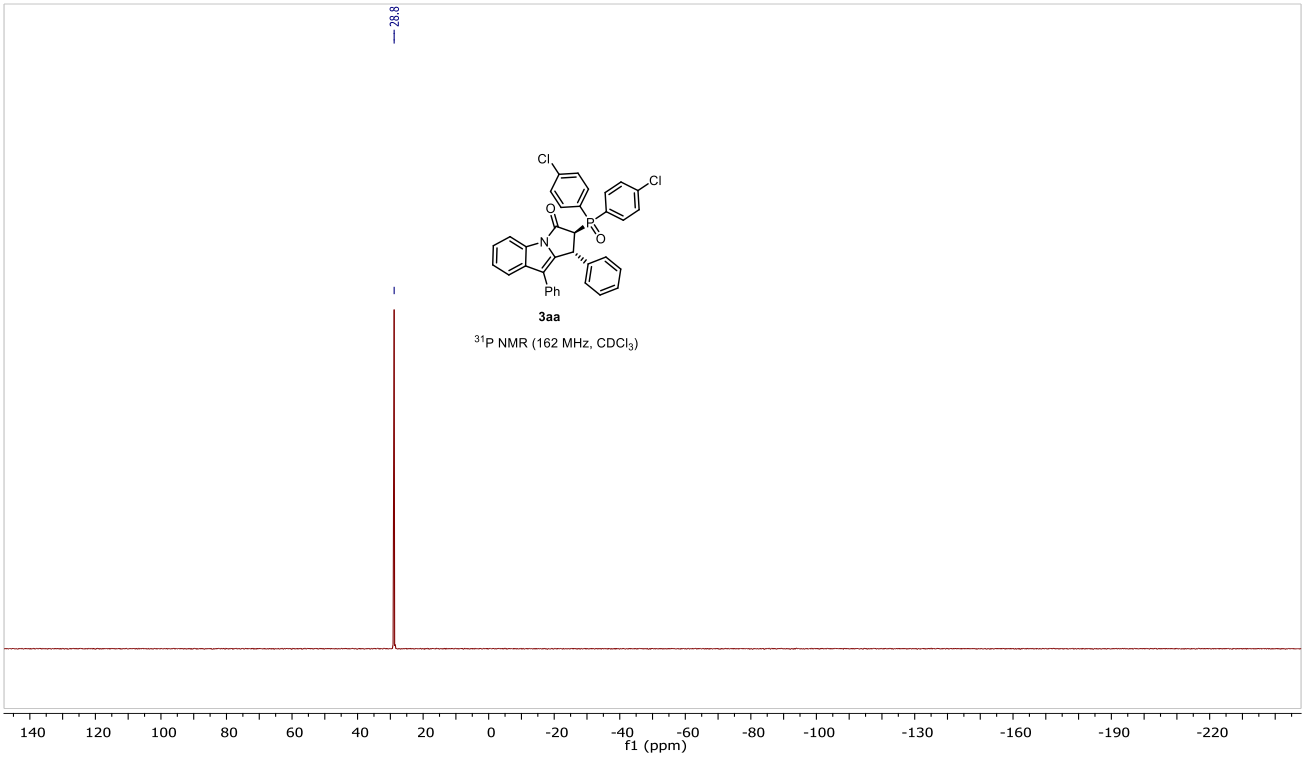

8.55
8.54
7.33
7.33
6.85
6.85
6.84
6.81
6.81
6.80
6.61
6.61
3.80
3.80
OMe
OMe
MeO
H
P
O
OMe
2k
1H NMR (400 MHz, DMSO)
0.50
0.49
3.91
1.91
5.97
5.92
f1 (ppm)


154.9
153.7
153.5
121.5
120.5
119.7
117.8
117.7
115.1
113.7
113.6
56.8
56.1
OMe
OMe
MeO
H
P
O
OMe
2k
13C NMR (101MHz, DMSO)
f1 (ppm)


5.1
OMe
OMe
MeO
P
H
O
OMe
2k
31P NMR (162 MHz, DMSO)
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
f1 (ppm)

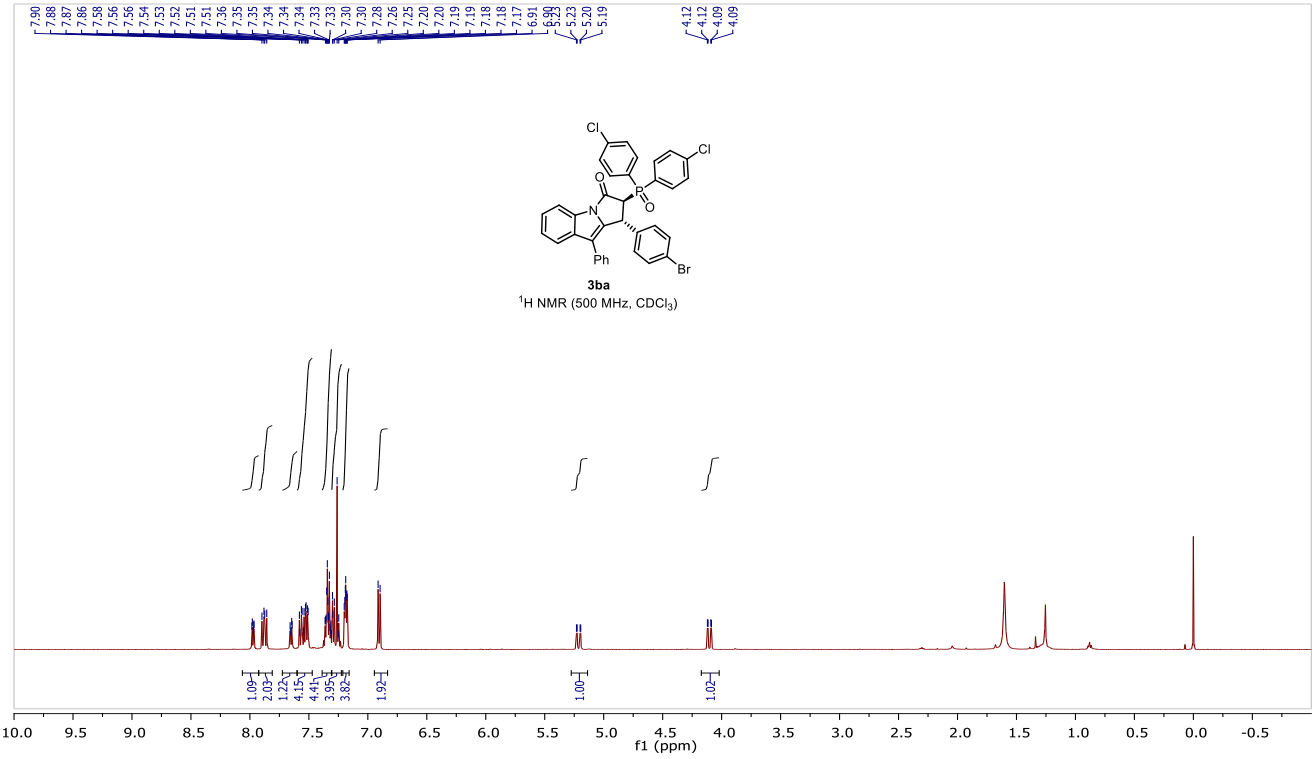

Cl
Cl
O
P
O
N
Ph
3aa
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

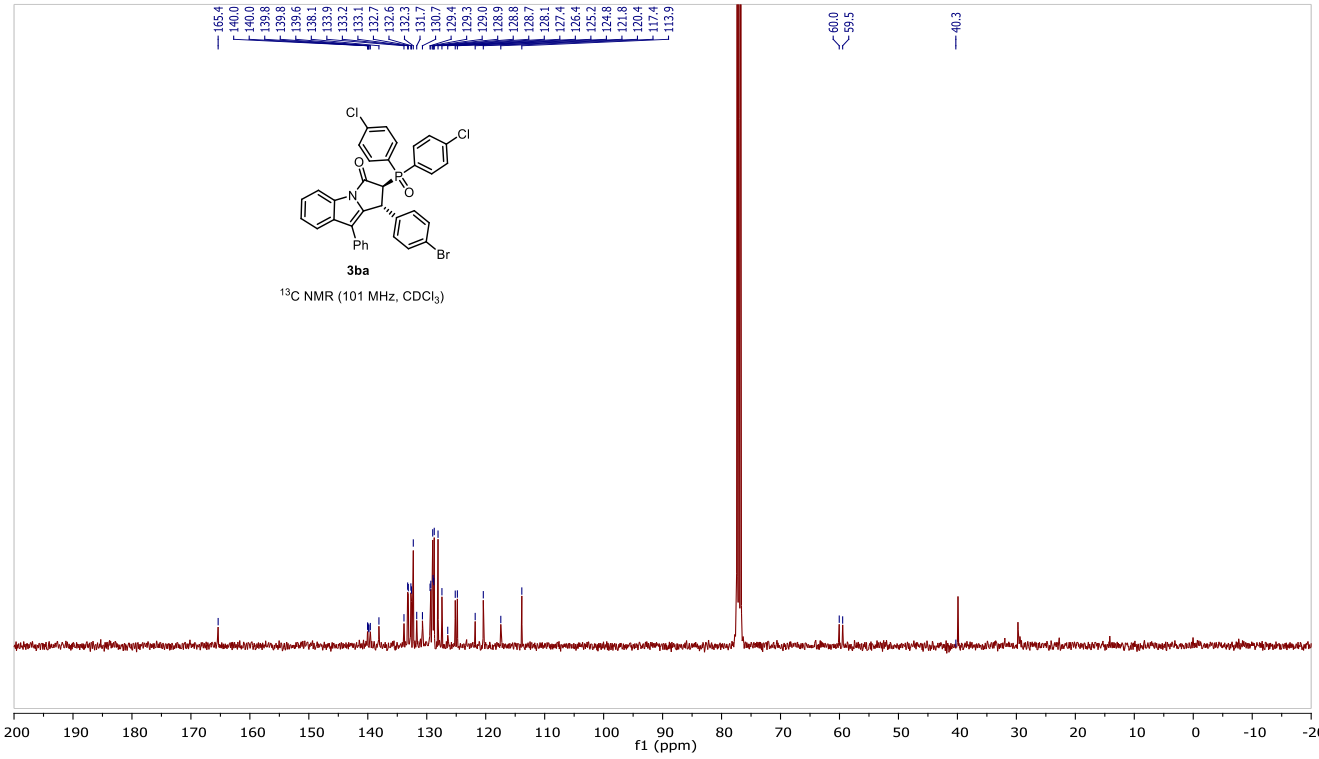

Cl
Cl
O
P
O
N
Ph
3aa
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

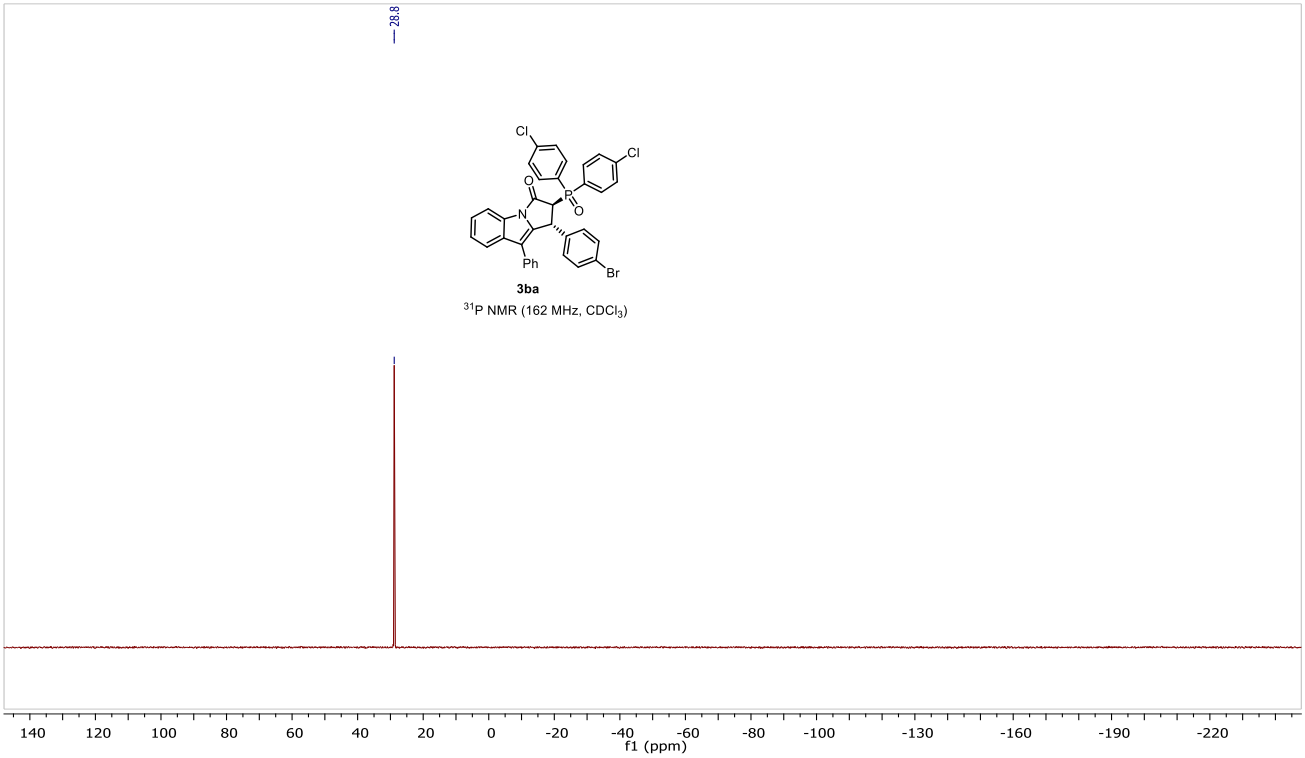


3aa

^{31}P NMR (162 MHz, $CDCl_3$)

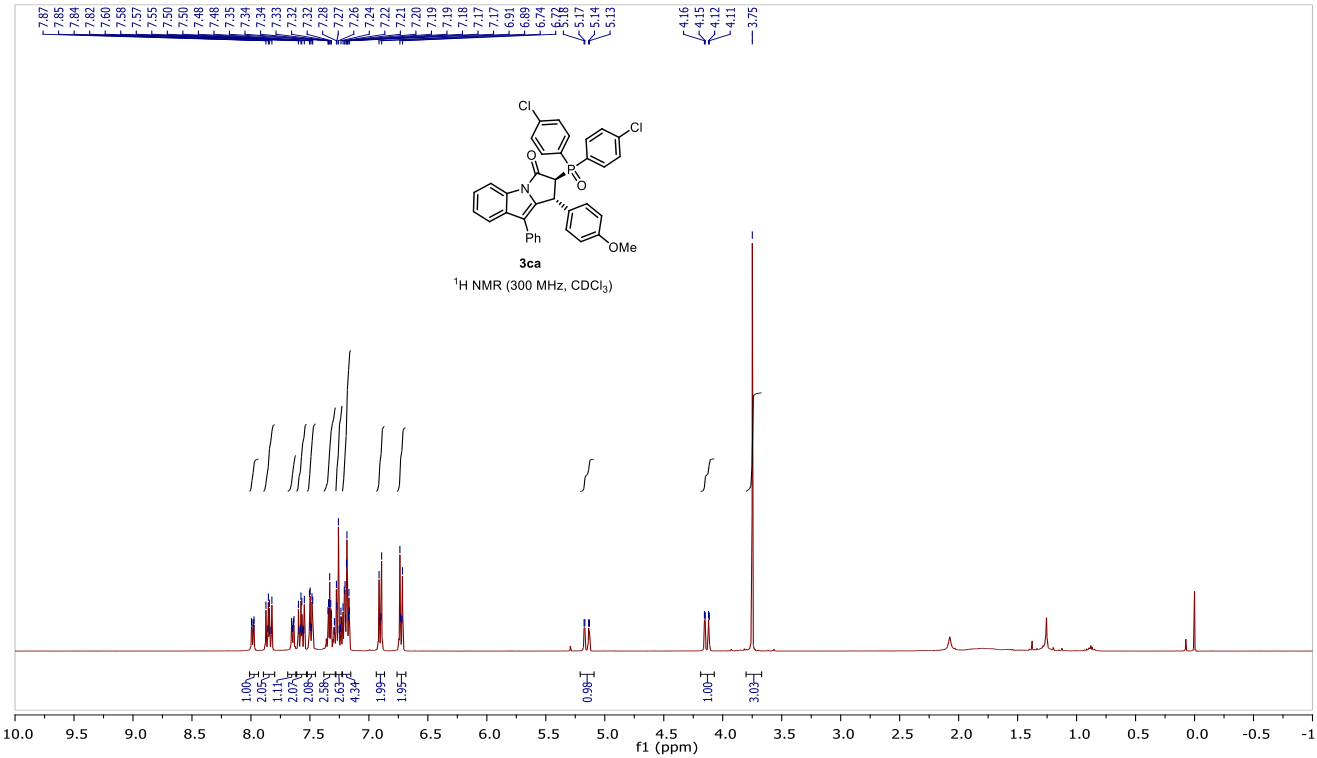

7.90 7.88 7.87 7.86 7.58 7.56 7.56 7.54 7.53 7.52 7.51 7.51 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.30 7.30 7.28 7.26 7.25 7.20 7.20 7.19 7.19 7.18 7.18 7.17 6.91 6.90 5.23 5.23 5.20 5.19 4.12 4.12 4.09 4.09
Cl
Cl
O
P
O
N
Ph
Br
3ba
1H NMR (500 MHz, CDCl3)
1.09 2.03 1.22 4.15 4.41 3.95 3.82 1.92 1.00 1.02
10.0 9.5 9.0 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 -0.5
f1 (ppm)

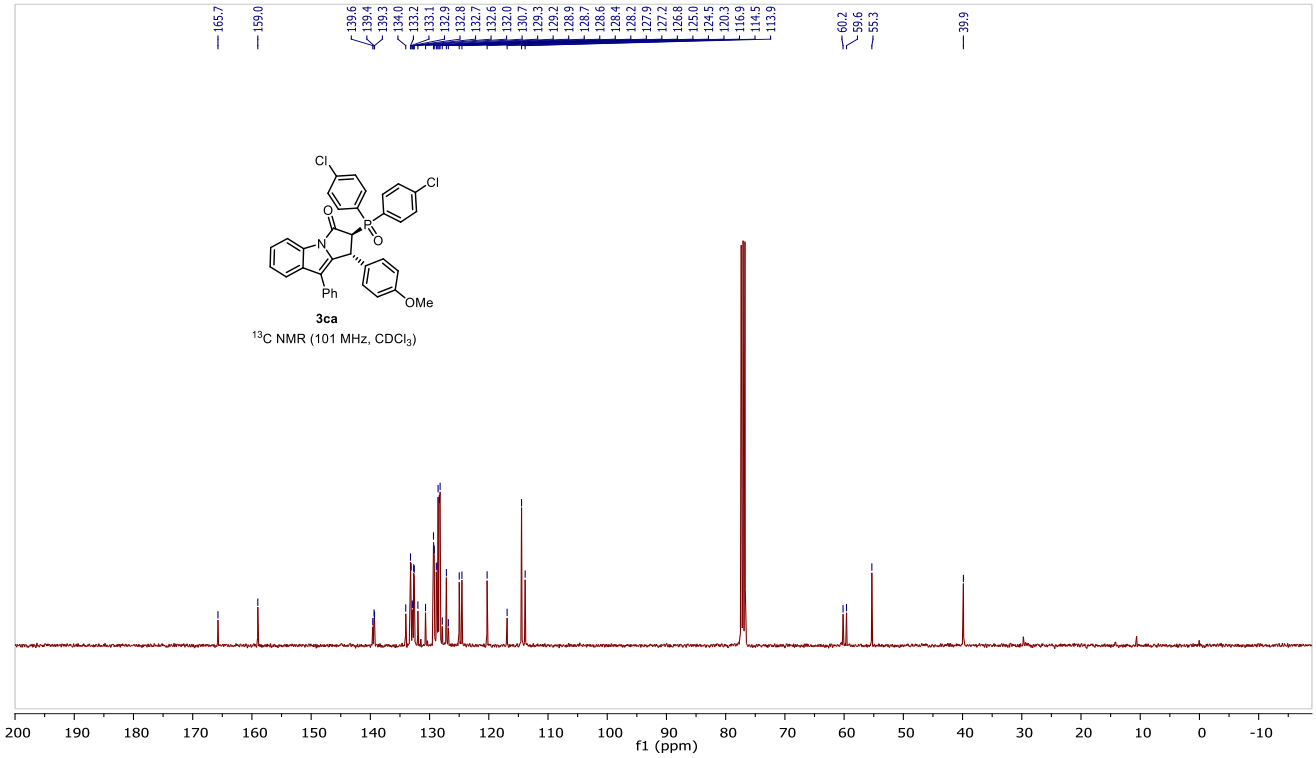

165.4 140.0 140.0 139.8 139.8 139.6 138.1 133.9 133.2 133.1 132.7 132.6 132.3 131.7 130.7 129.4 129.3 129.0 128.9 128.8 128.7 128.1 127.4 126.4 125.2 124.8 121.8 120.4 117.4 113.9 60.0 59.5 40.3
Cl
Cl
O
P
O
N
Ph
Br
3ba
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

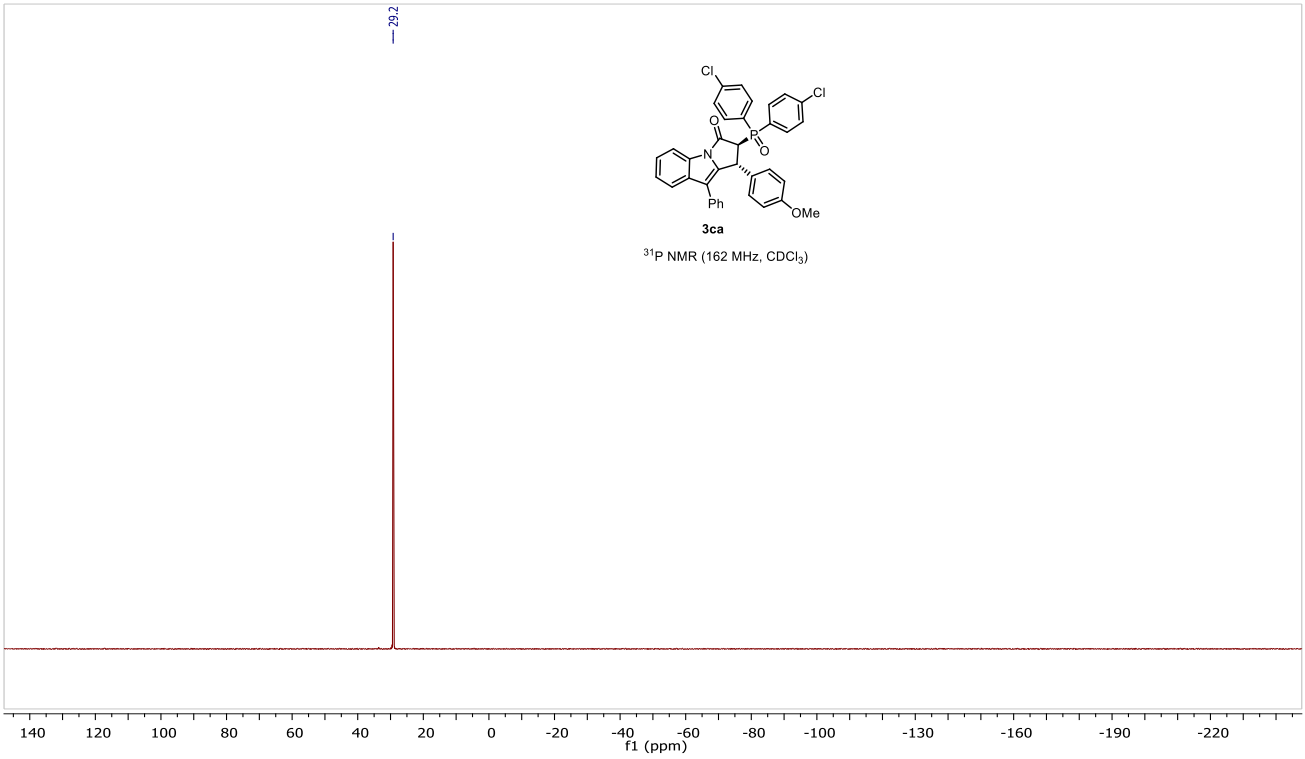


3ba

^{31}P NMR (162 MHz, $CDCl_3$)

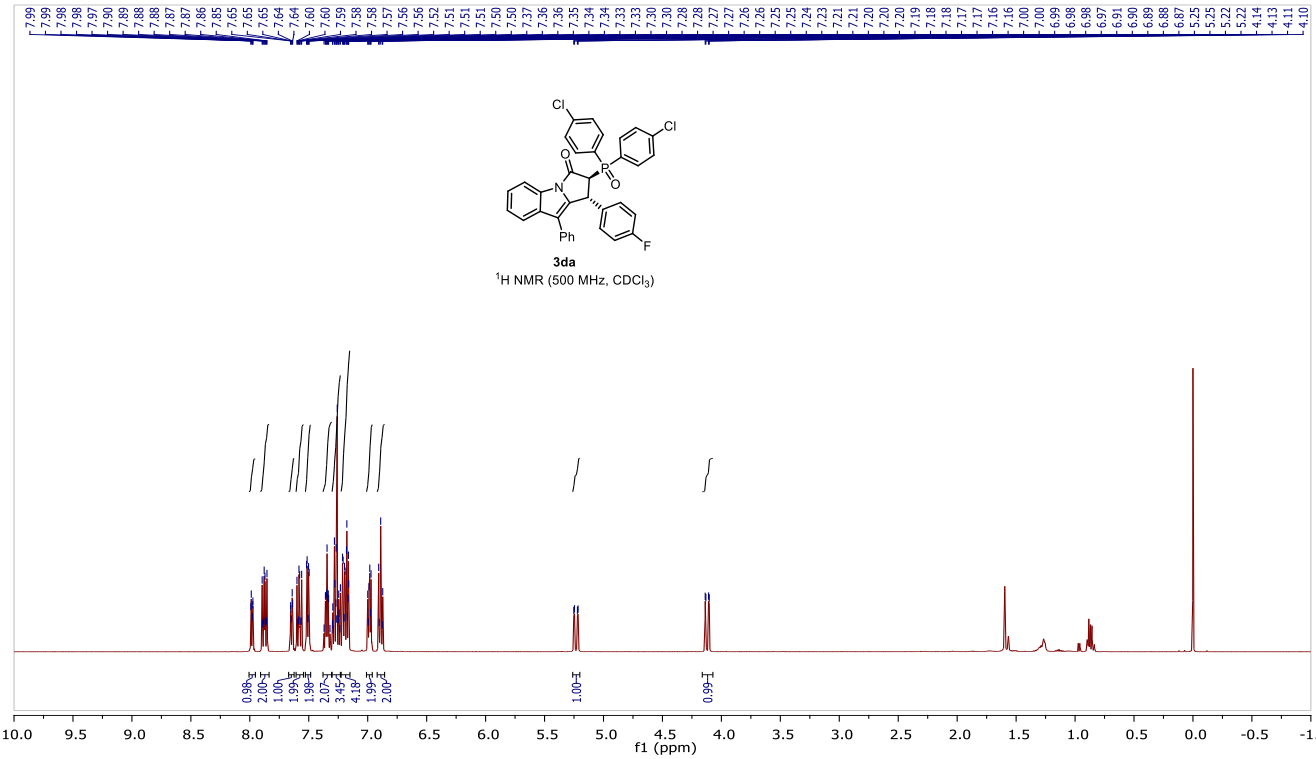

Cl
Cl
O
P
O
N
Ph
OMe
3ca
^{1}H NMR (300 MHz, $CDCl_3$)
f1 (ppm)

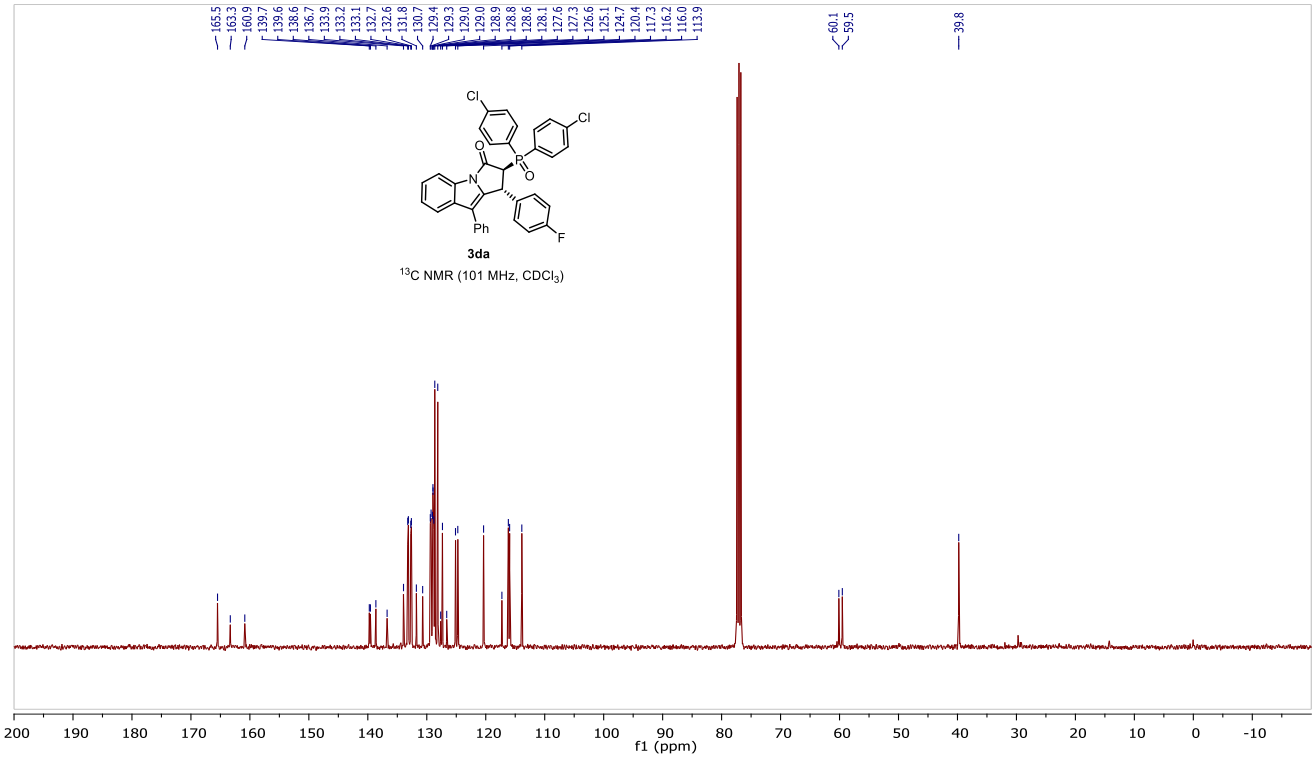

Cl
Cl
O
P
O
N
Ph
OMe
3ca
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

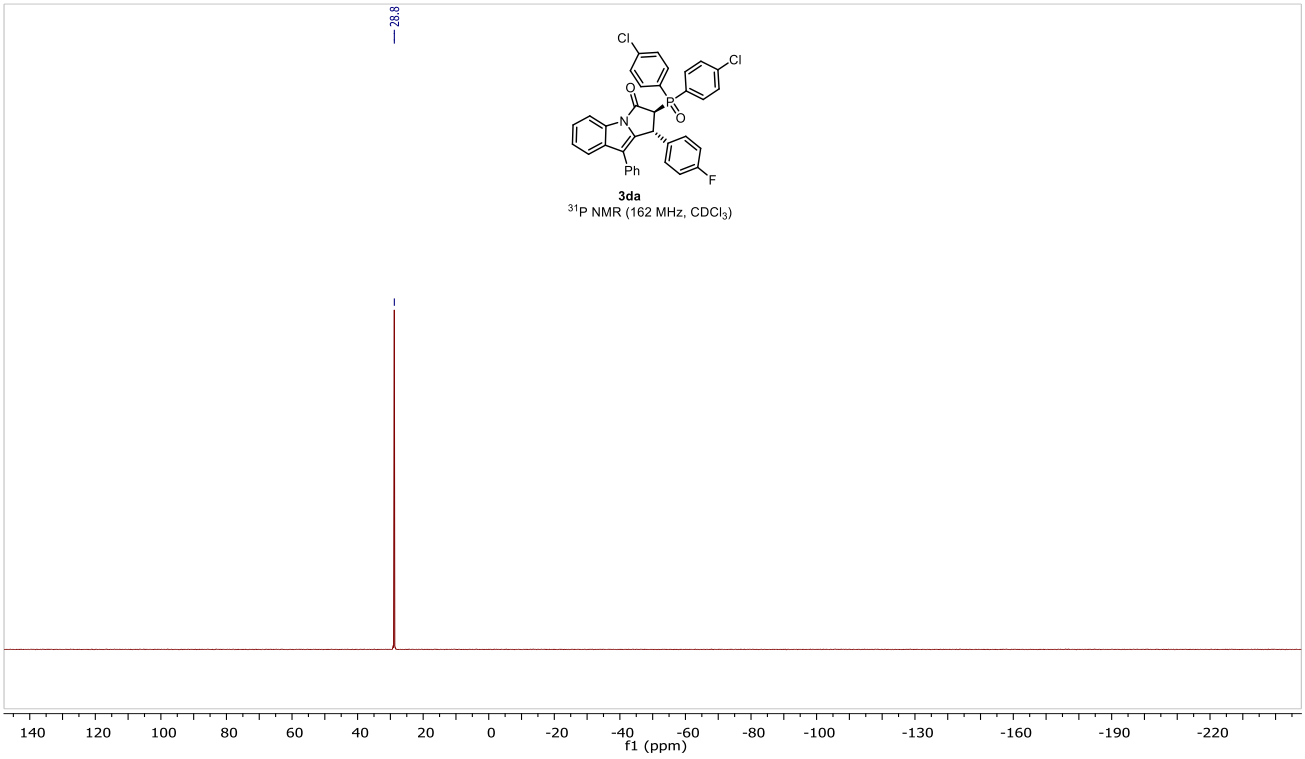


3ca

^{31}P NMR (162 MHz, $CDCl_3$)

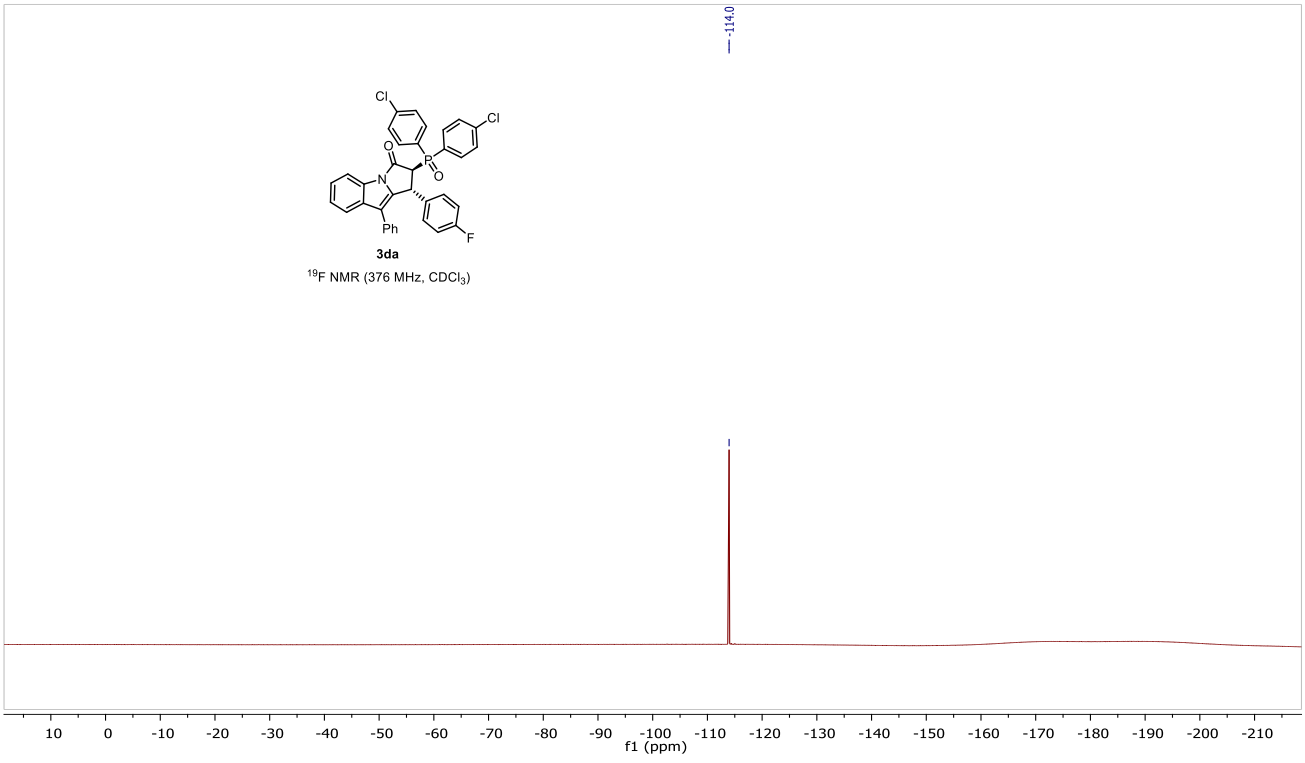

3da
1H NMR (500 MHz, CDCl3)
f1 (ppm)


3da
13C NMR (101 MHz, CDCl3)
f1 (ppm)



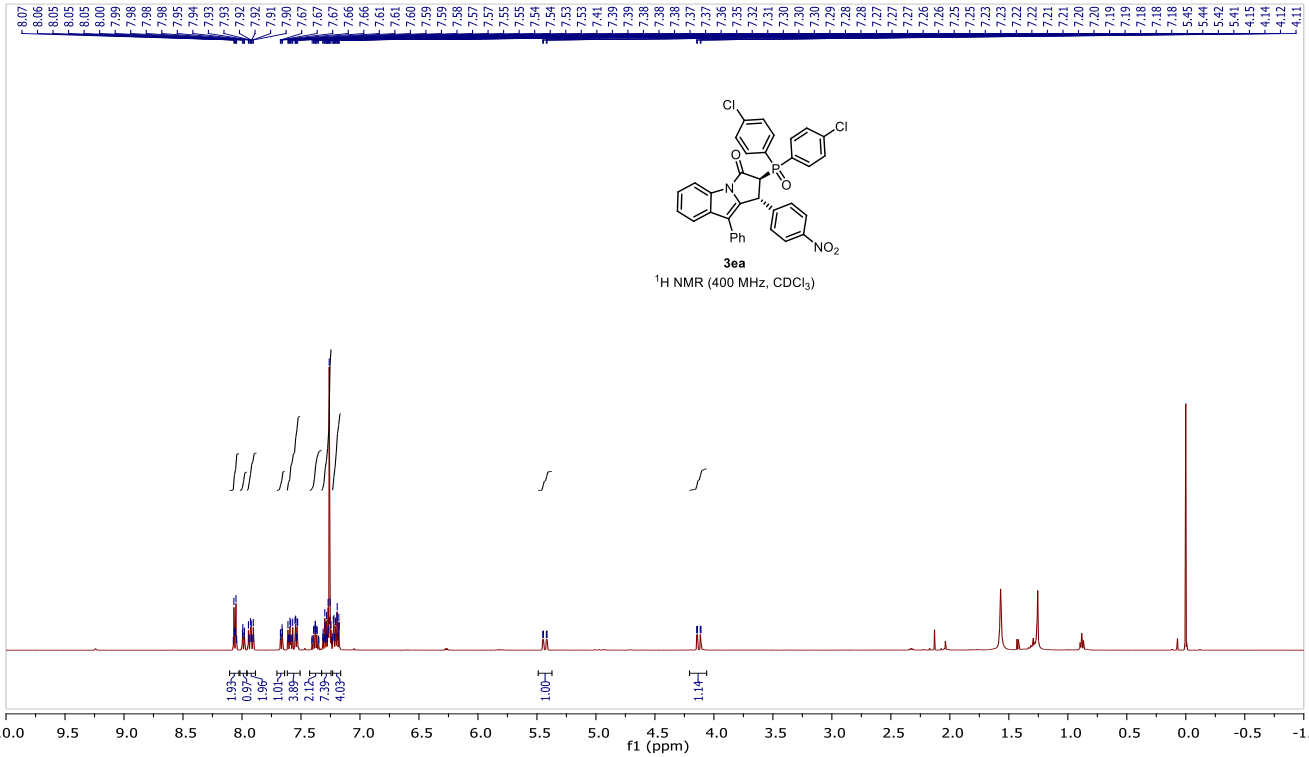
3da

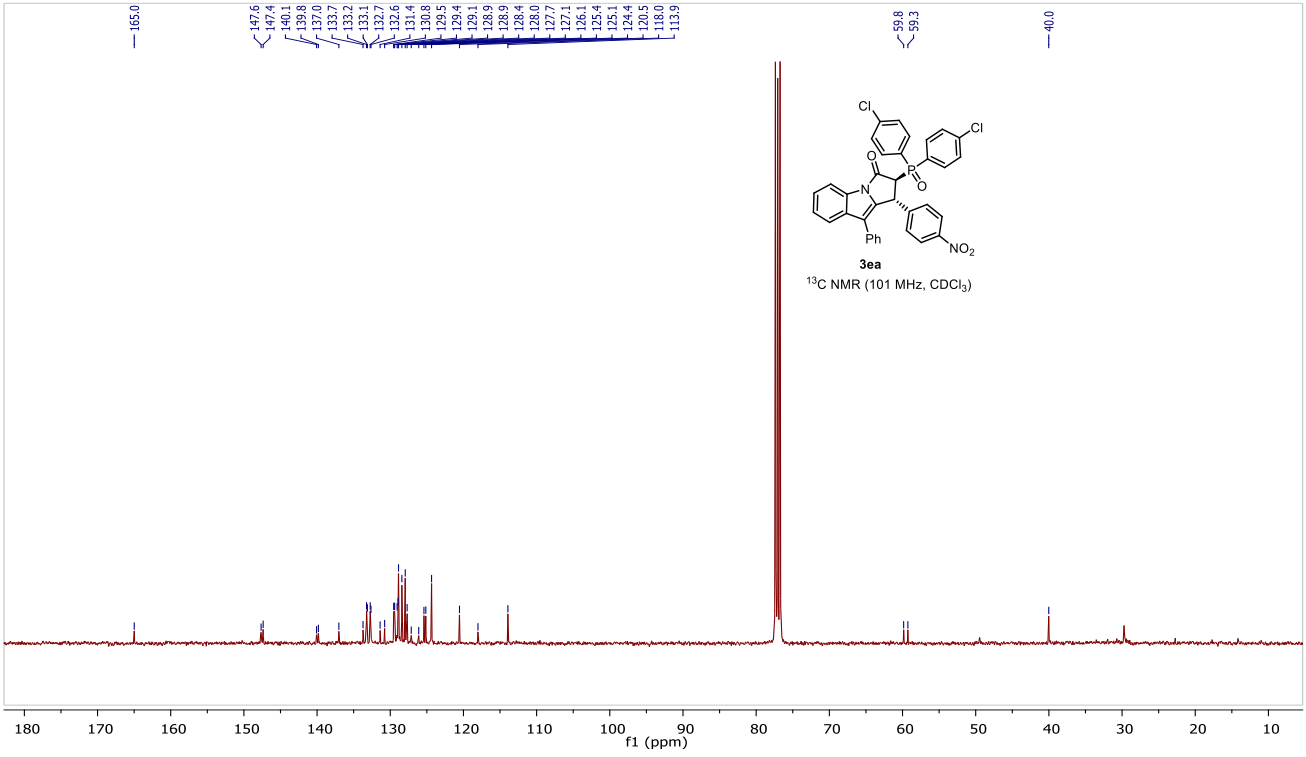
^{31}P NMR (162 MHz, $CDCl_3$)

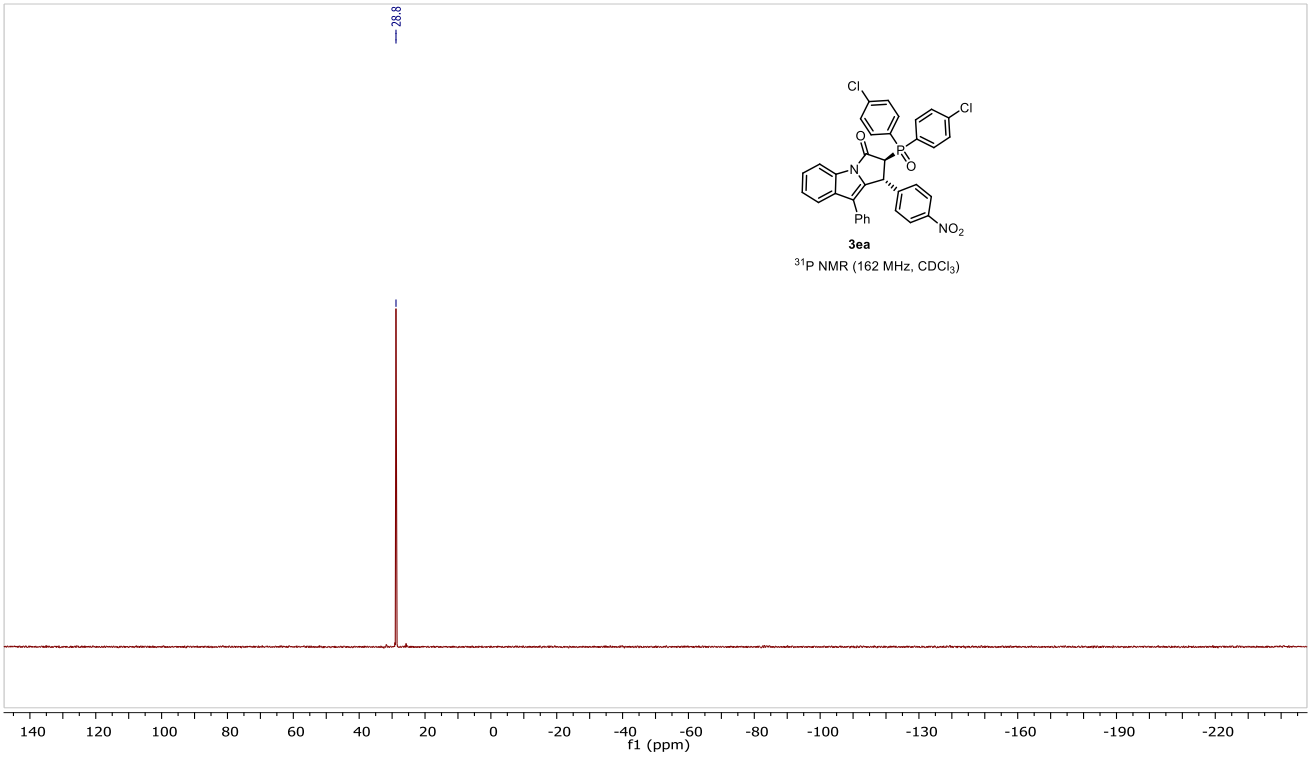


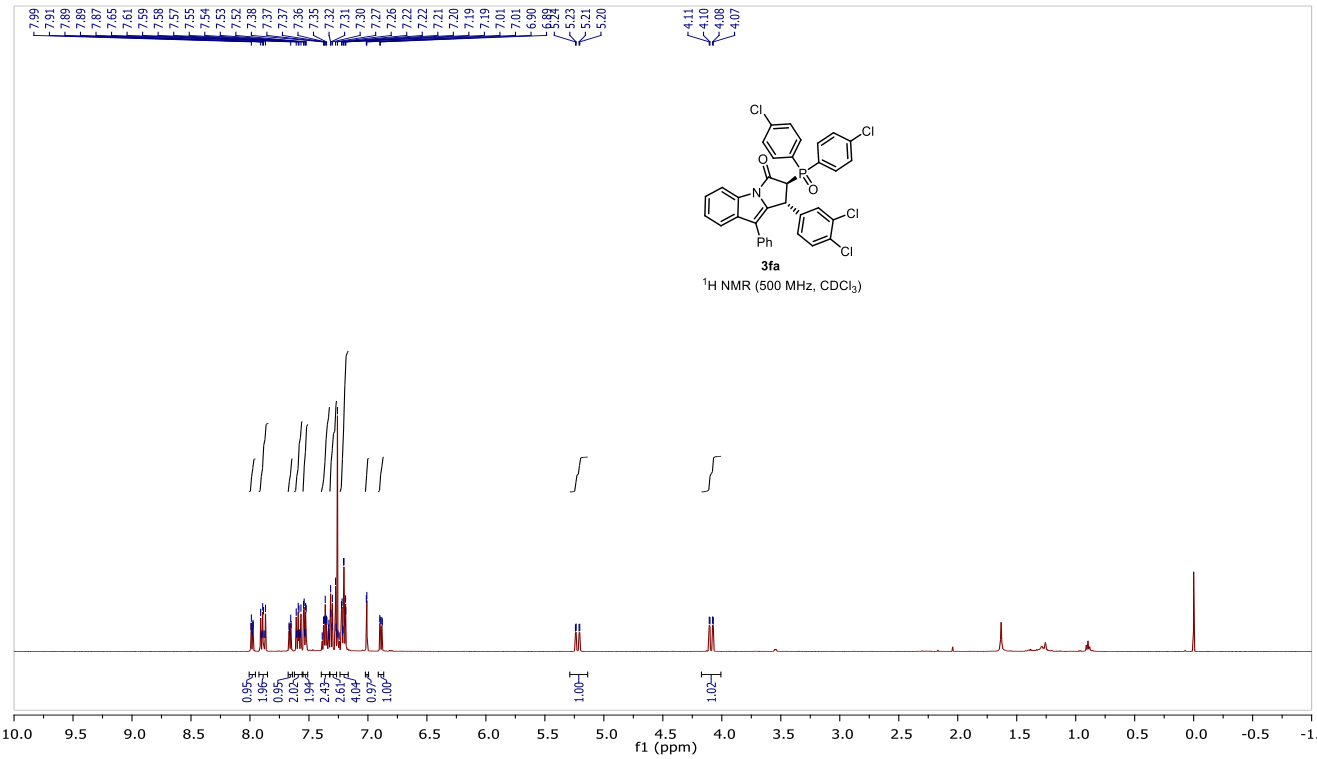
3da

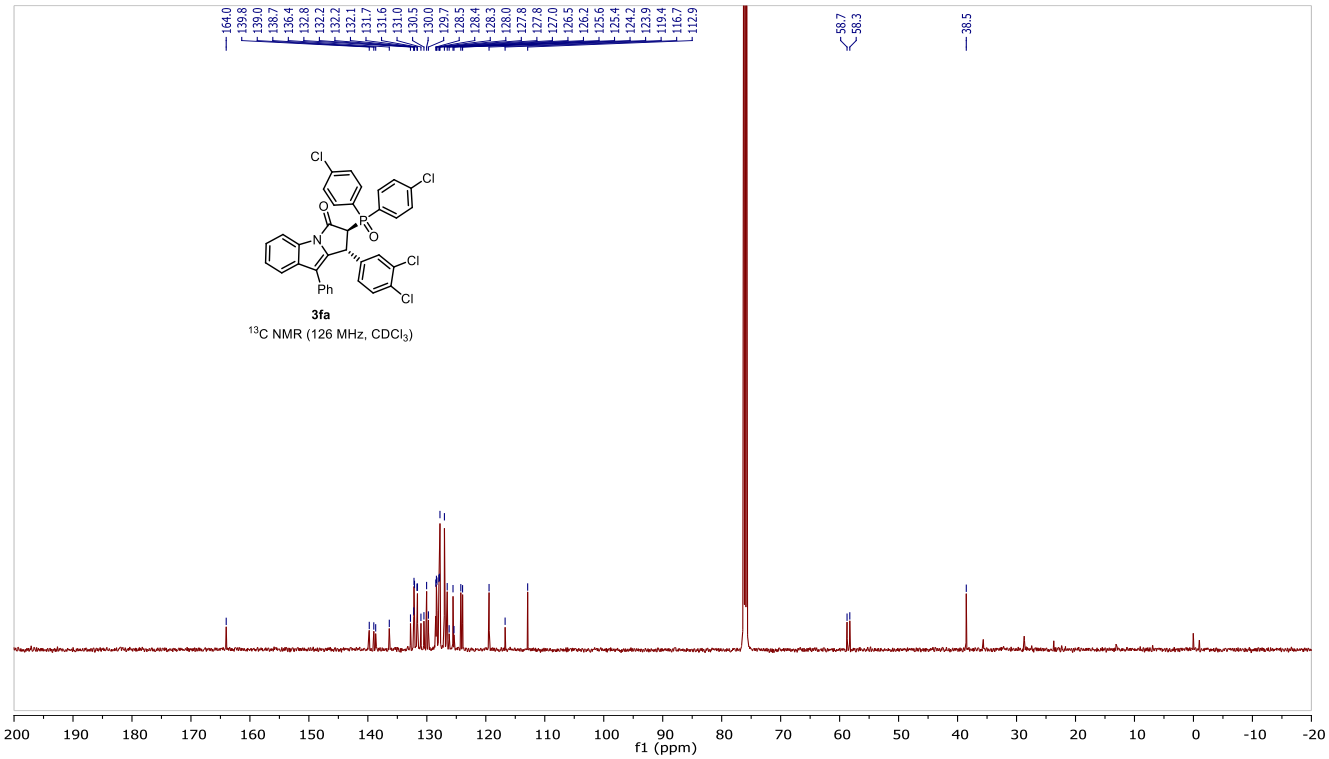
^{19}F NMR (376 MHz, $CDCl_3$)

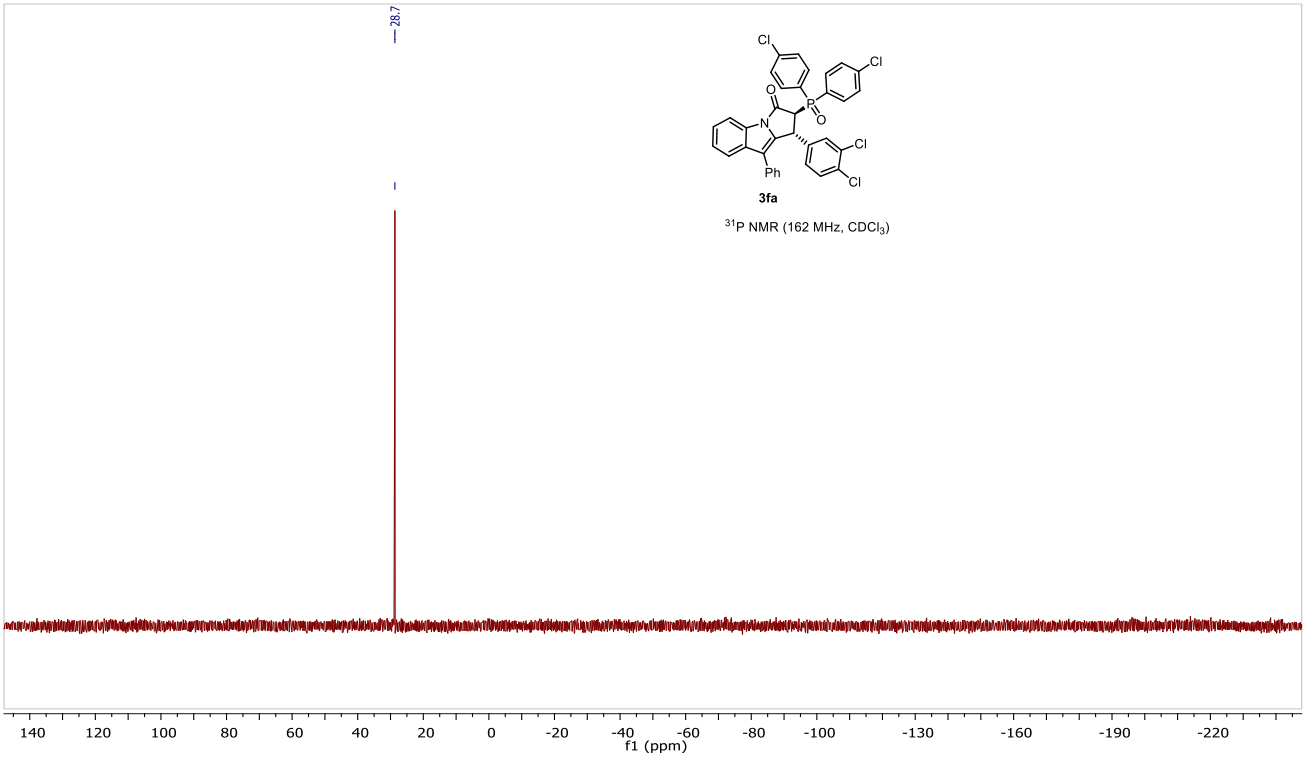

Cl
Cl
O
P
O
N
Ph
NO2
3ea
1H NMR (400 MHz, CDCl3)
1.93
0.97
1.96
1.01
3.89
2.12
7.39
4.03
1.00
1.14
f1 (ppm)

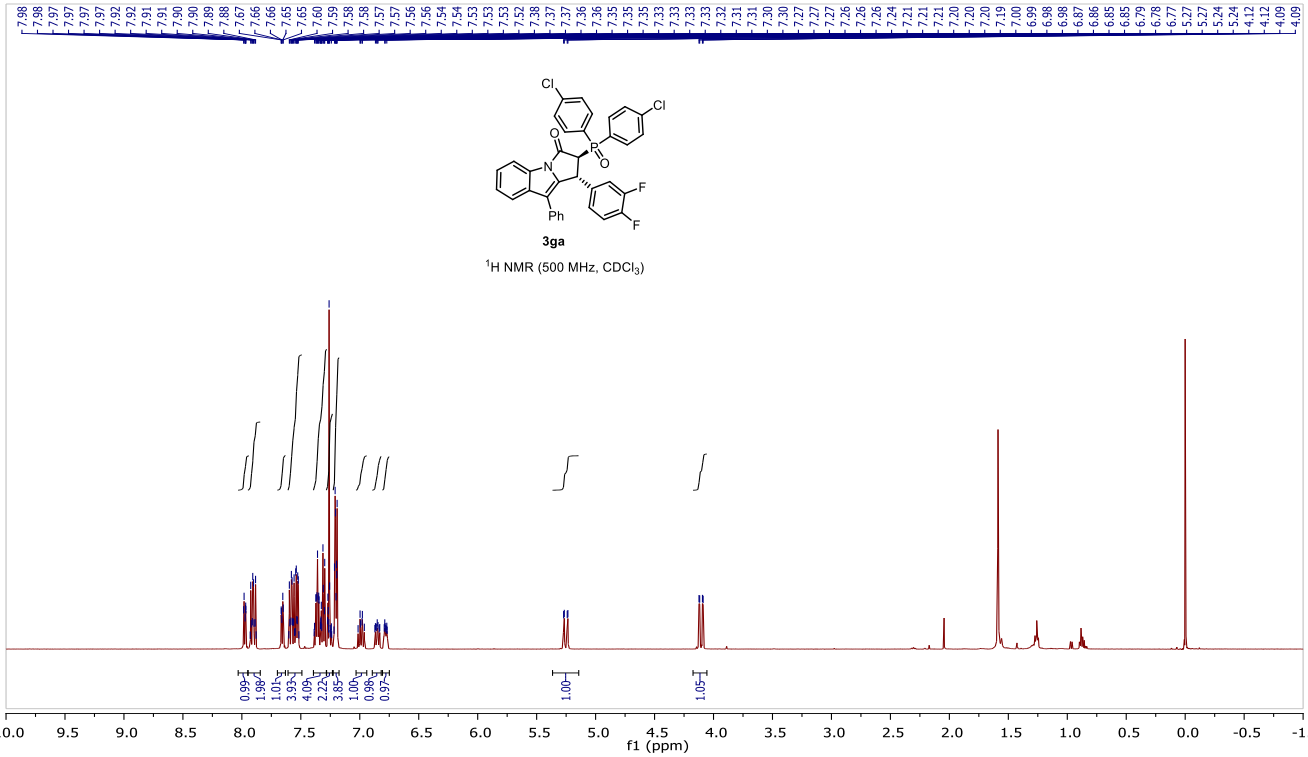

165.0
147.6
147.4
140.1
139.8
137.0
133.7
133.2
133.1
132.7
132.6
131.4
130.8
129.5
129.4
129.1
128.9
128.9
128.4
128.0
127.7
127.1
126.1
125.4
125.1
124.4
120.5
118.0
113.9
59.8
59.3
40.0
Cl
Cl
O
P
O
N
Ph
NO2
3ea
13C NMR (101 MHz, CDCl3)
f1 (ppm)

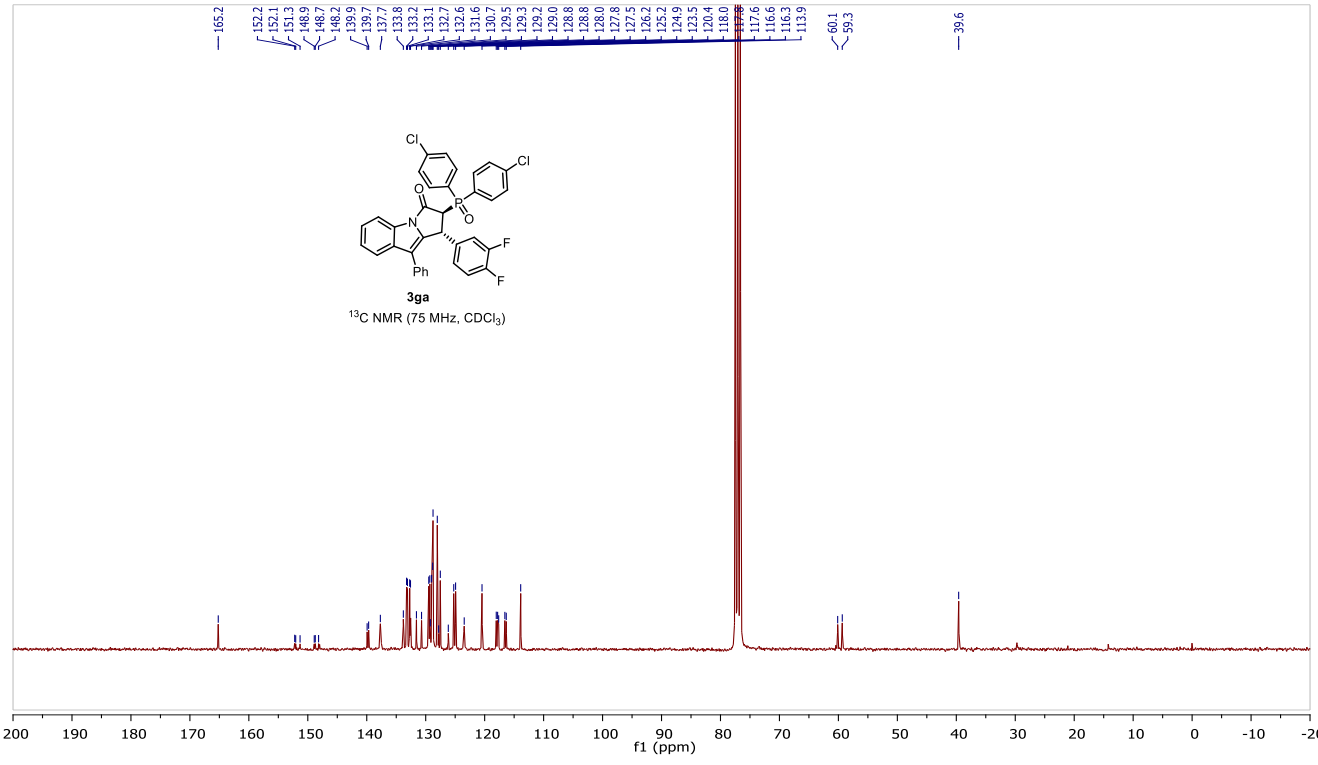

28.8
Cl
Cl
O
P
O
N
Ph
NO2
3ea
31P NMR (162 MHz, CDCl3)
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
f1 (ppm)

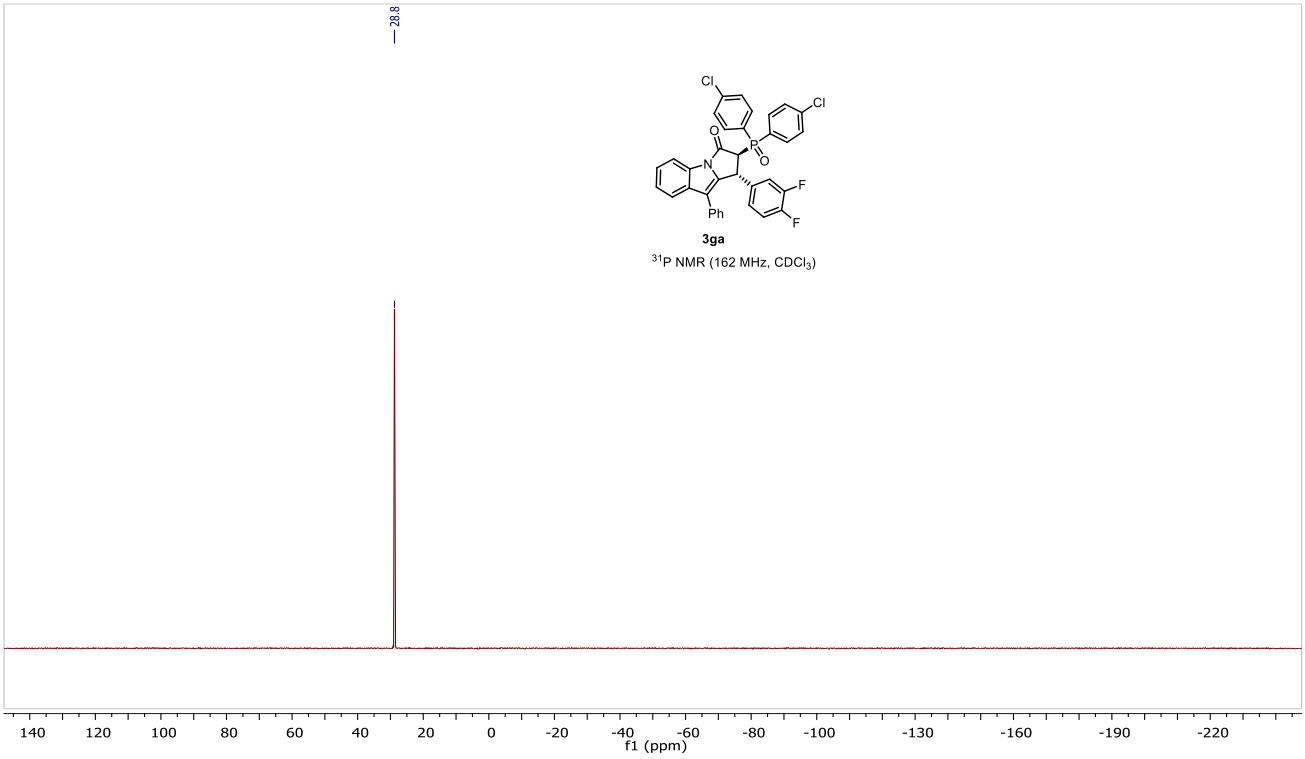

7.99 7.91 7.89 7.89 7.87 7.65 7.61 7.59 7.58 7.57 7.55 7.54 7.53 7.52 7.38 7.37 7.37 7.36 7.35 7.32 7.31 7.30 7.27 7.26 7.22 7.22 7.21 7.20 7.19 7.19 7.01 7.01 6.90 6.89 5.24 5.23 5.21 5.20
4.11 4.10 4.08 4.07
Cl
Cl
O
P
O
N
Cl
Ph
Cl
3fa
^{1}H NMR (500 MHz, $CDCl_3$)
0.95 1.96 0.95 2.02 1.94 2.43 2.61 4.04 0.97 1.00 1.00 1.02
10.0 9.5 9.0 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 -0.5 -1.0
f1 (ppm)

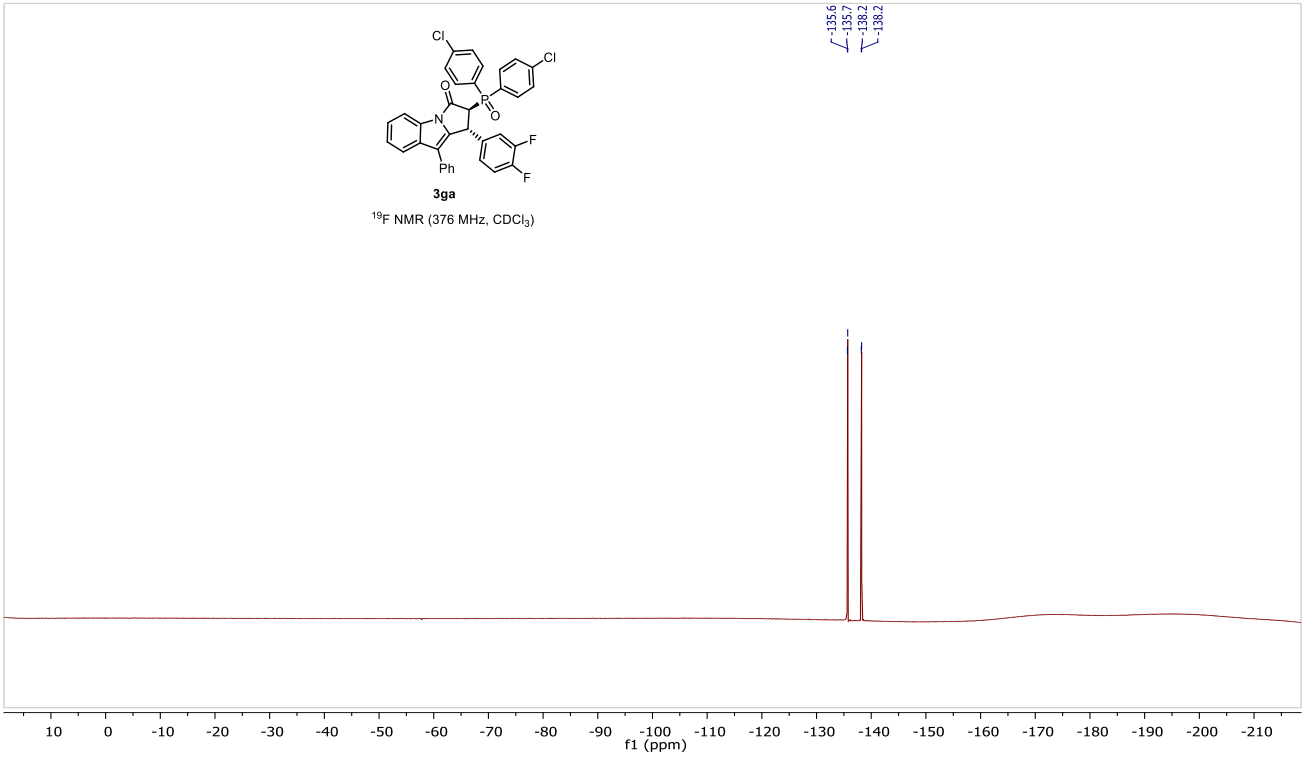

164.0 139.8 139.0 138.7 136.4 132.8 132.2 132.2 132.1 131.7 131.6 131.0 130.5 130.0 129.7 128.5 128.4 128.3 128.0 127.8 127.8 127.0 126.5 126.2 125.6 125.4 124.2 123.9 119.4 116.7 112.9
58.7 58.3
38.5
Cl
Cl
O
P
O
N
Cl
Ph
Cl
3fa
^{13}C NMR (126 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

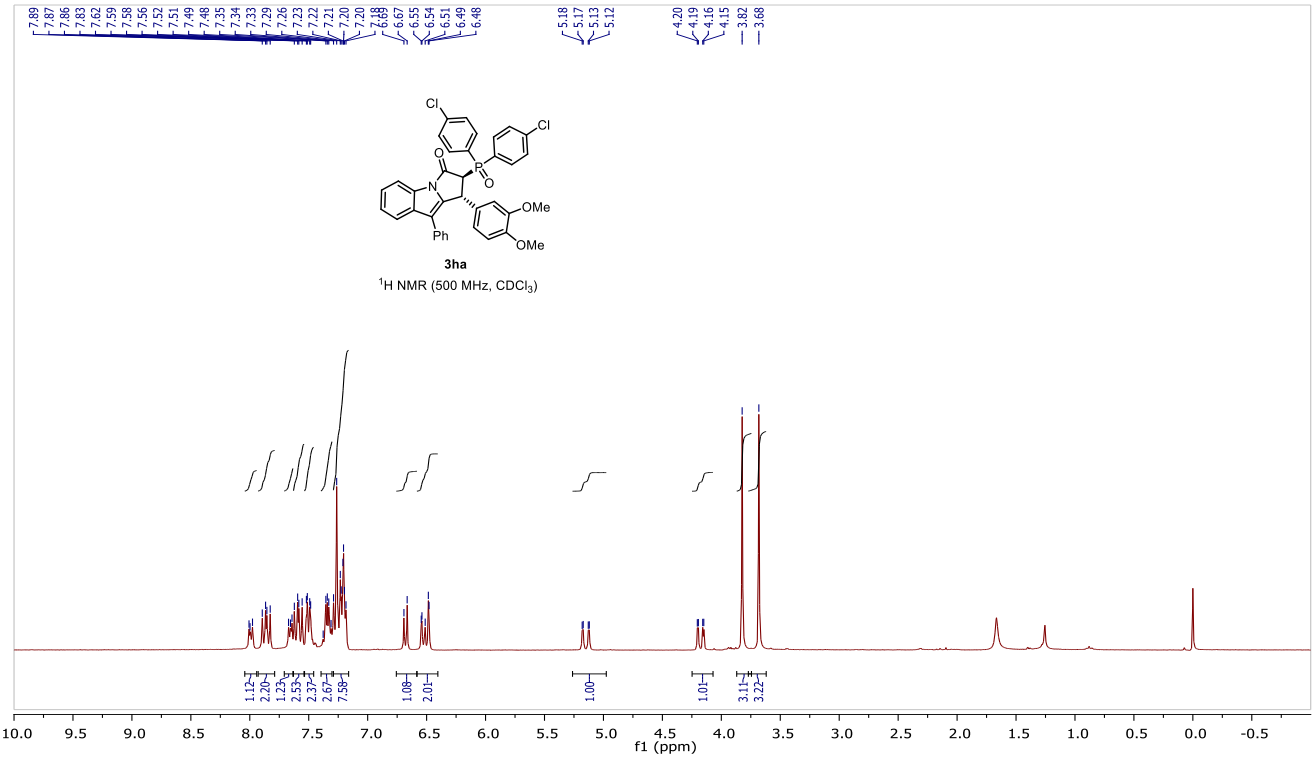

28.7
Cl
Cl
O
P
O
N
Cl
Cl
Ph
3fa
31P NMR (162 MHz, CDCl3)
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
f1 (ppm)

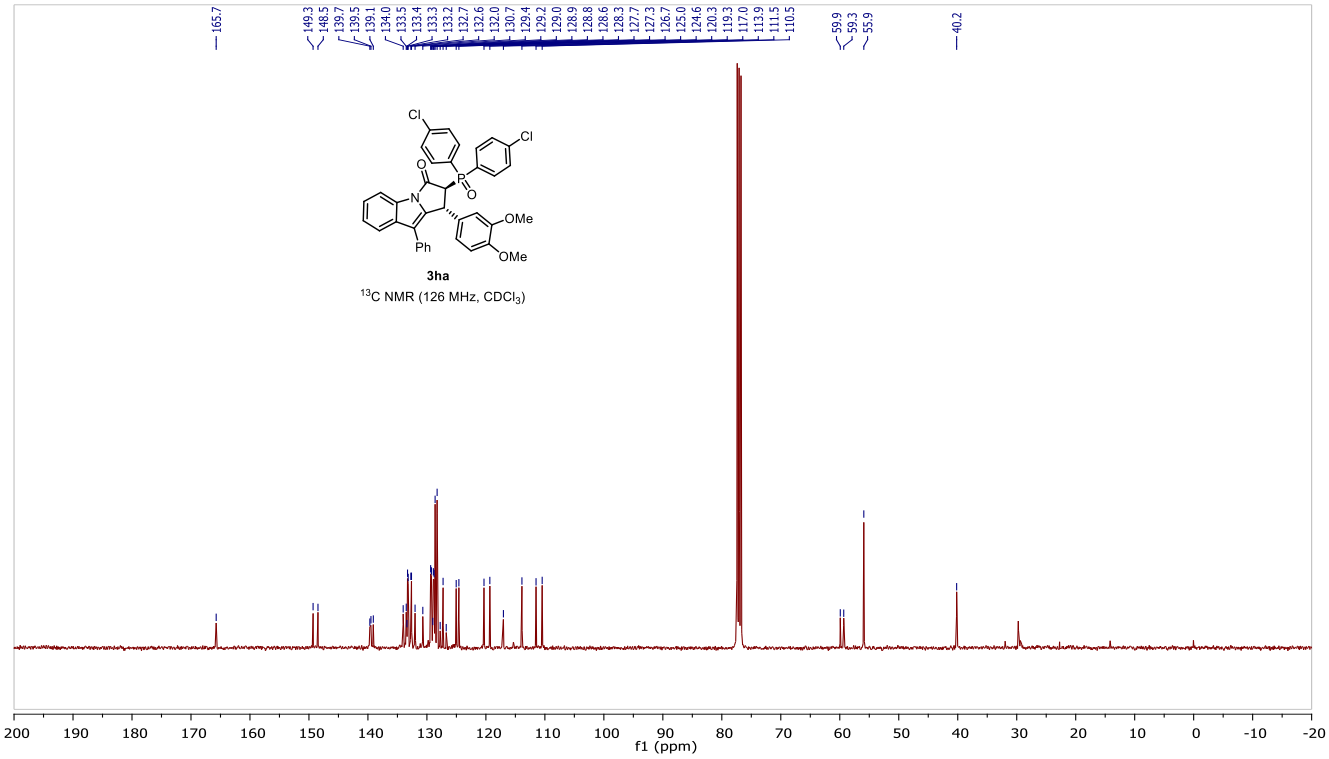

3ga
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)

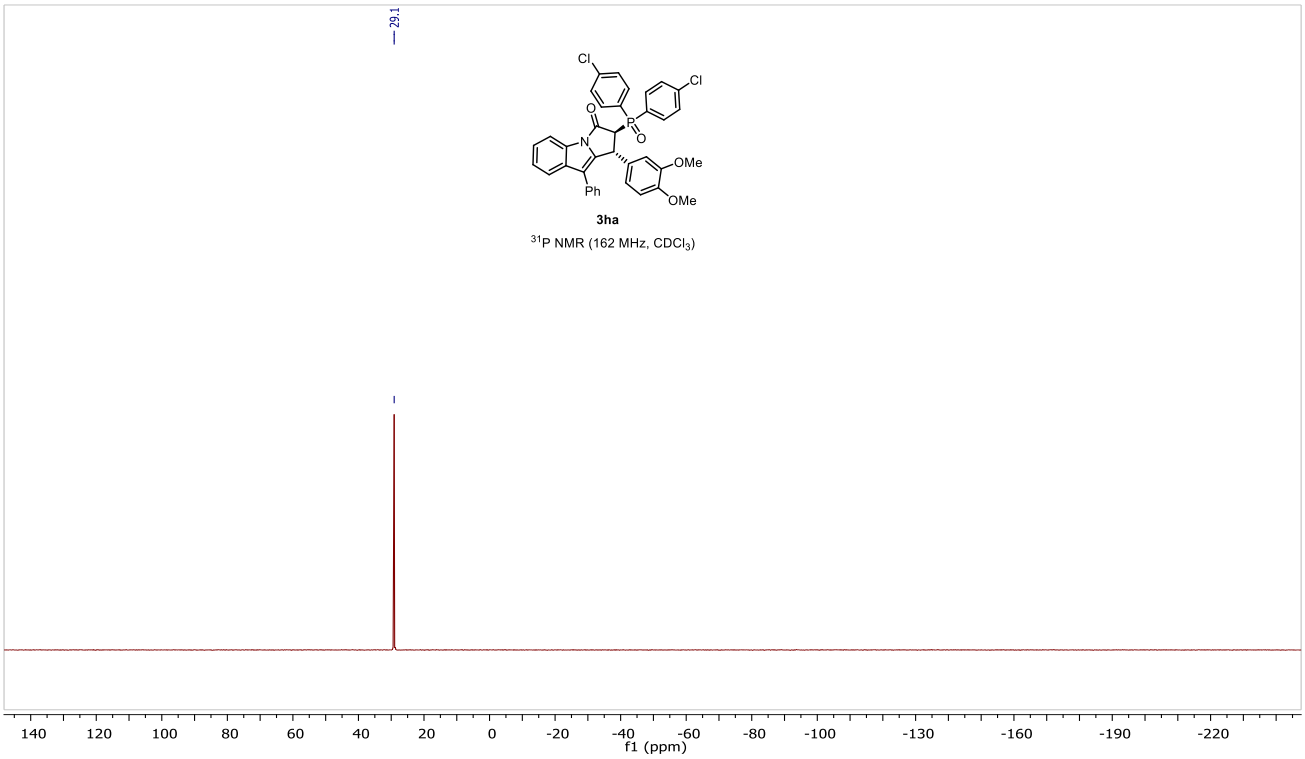

3ga
^{13}C NMR (75 MHz, CDCl$_3$)
f1 (ppm)


28.8
Cl
Cl
O
P
O
N
F
F
Ph
3ga
31P NMR (162 MHz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220
f1 (ppm)


-135.6
-135.7
-138.2
-138.2
Cl
Cl
O
P
O
N
F
F
Ph
3ga
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

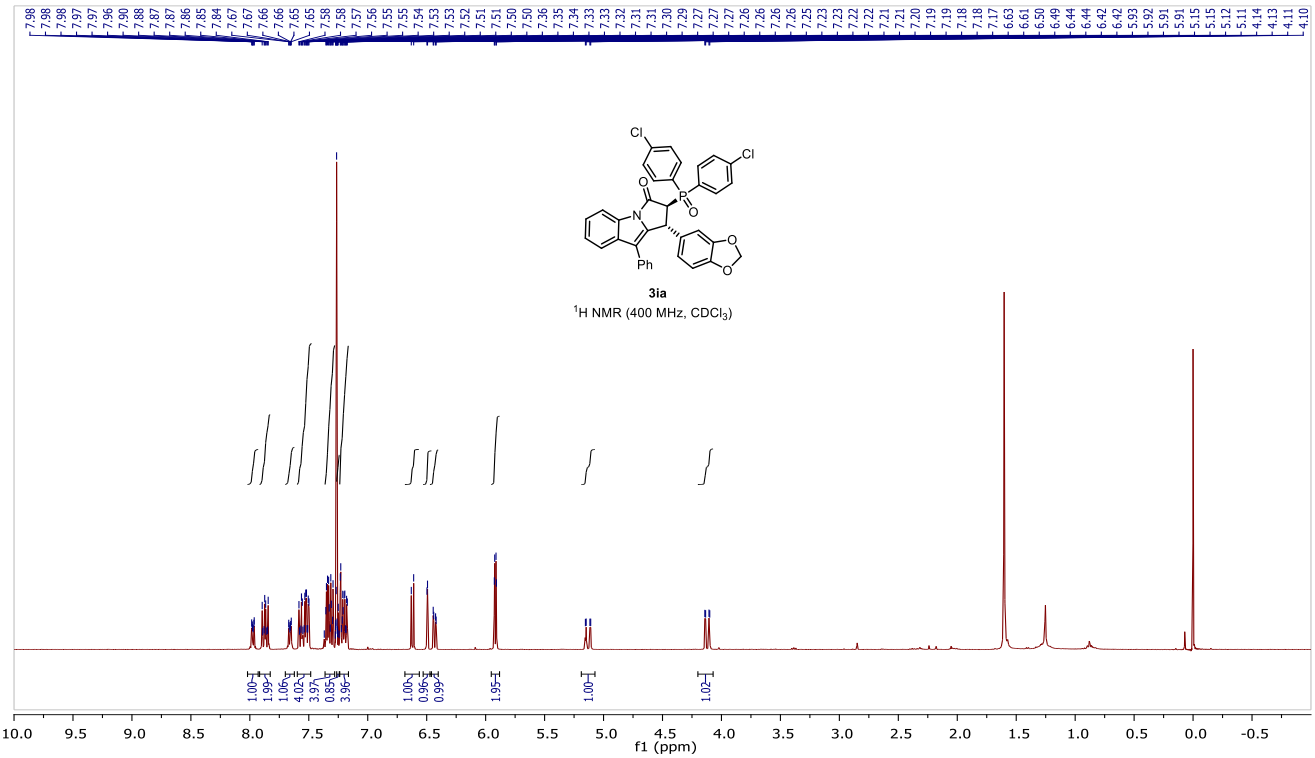

7.89
7.87
7.86
7.83
7.62
7.59
7.58
7.56
7.52
7.51
7.49
7.48
7.35
7.34
7.33
7.29
7.26
7.23
7.22
7.21
7.20
7.20
6.67
6.55
6.54
6.51
6.49
6.48
5.18
5.17
5.13
5.12
4.20
4.19
4.16
4.15
3.82
3.68
Cl
Cl
O
P
O
N
OMe
OMe
Ph
3ha
1H NMR (500 MHz, CDCl3)
1.12
2.20
1.23
2.53
2.37
2.67
7.58
1.08
2.01
1.00
1.01
3.11
3.22
10.0
9.5
9.0
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
-0.5
f1 (ppm)

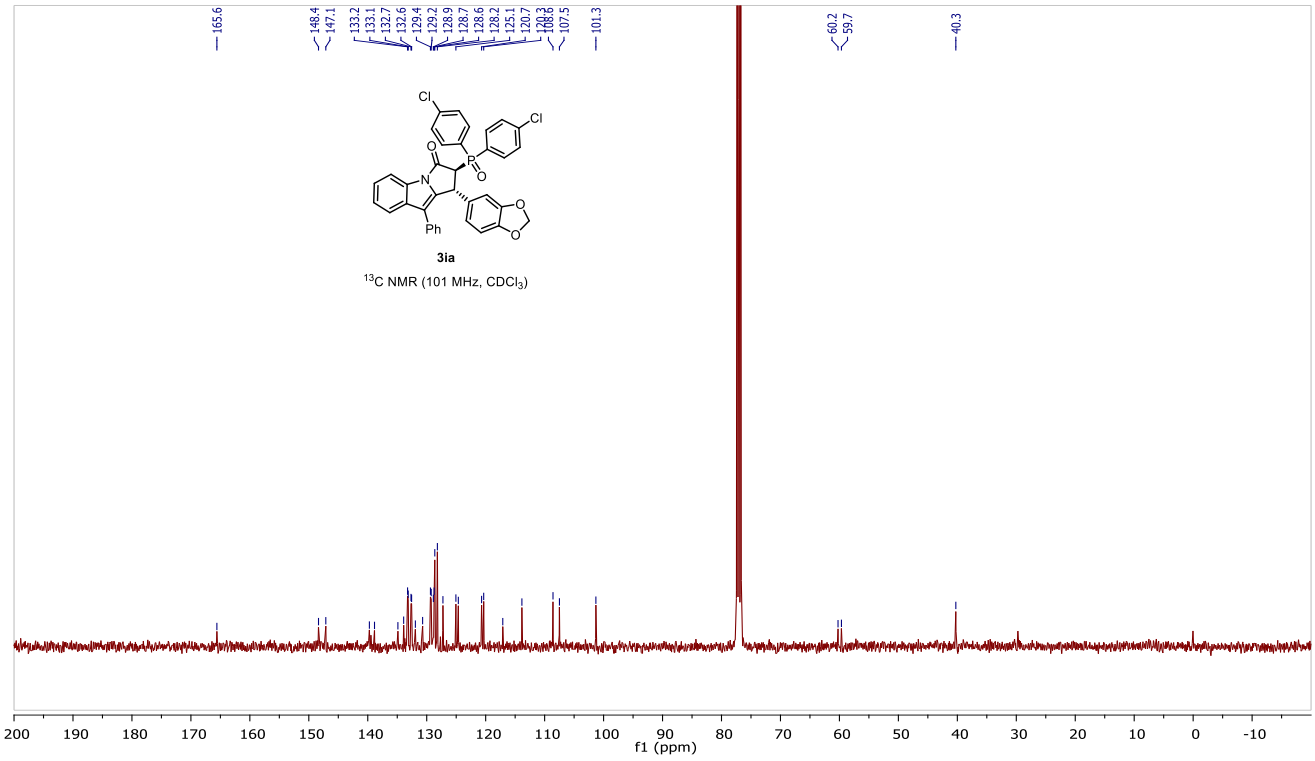

165.7
149.3
148.5
139.7
139.5
139.1
134.0
133.5
133.4
133.3
133.2
132.7
132.6
132.0
130.7
129.4
129.2
129.0
128.9
128.8
128.6
128.3
127.7
127.3
126.7
125.0
124.6
120.3
119.3
117.0
113.9
111.5
110.5
59.9
59.3
55.9
40.2
Cl
Cl
O
P
O
N
OMe
OMe
Ph
3ha
13C NMR (126 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

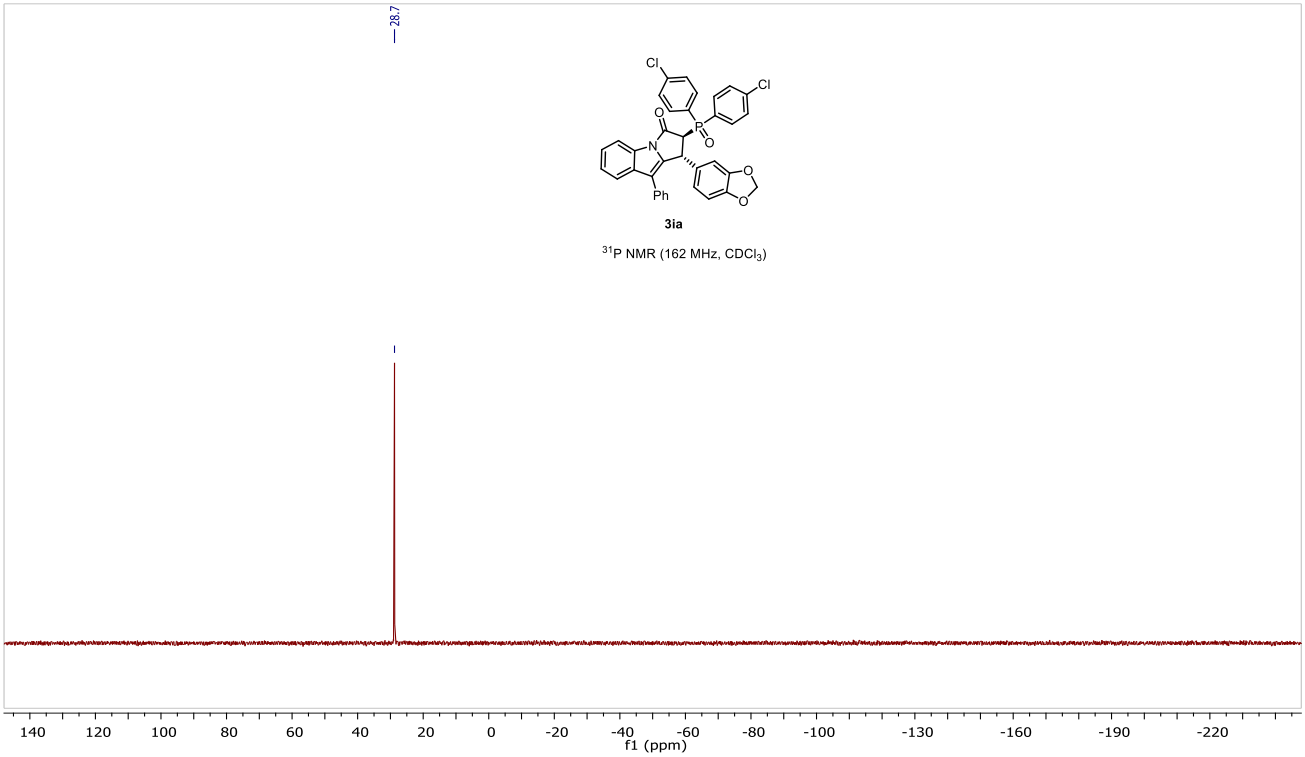


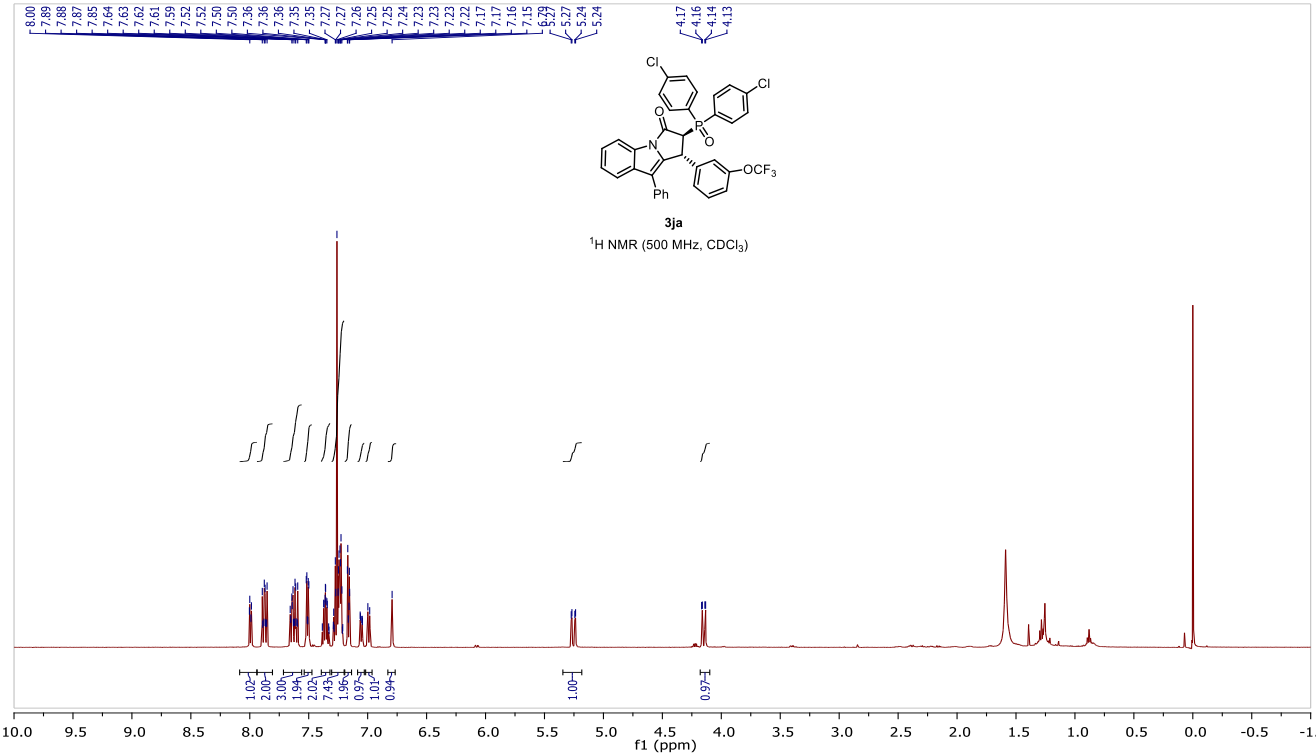
3ha

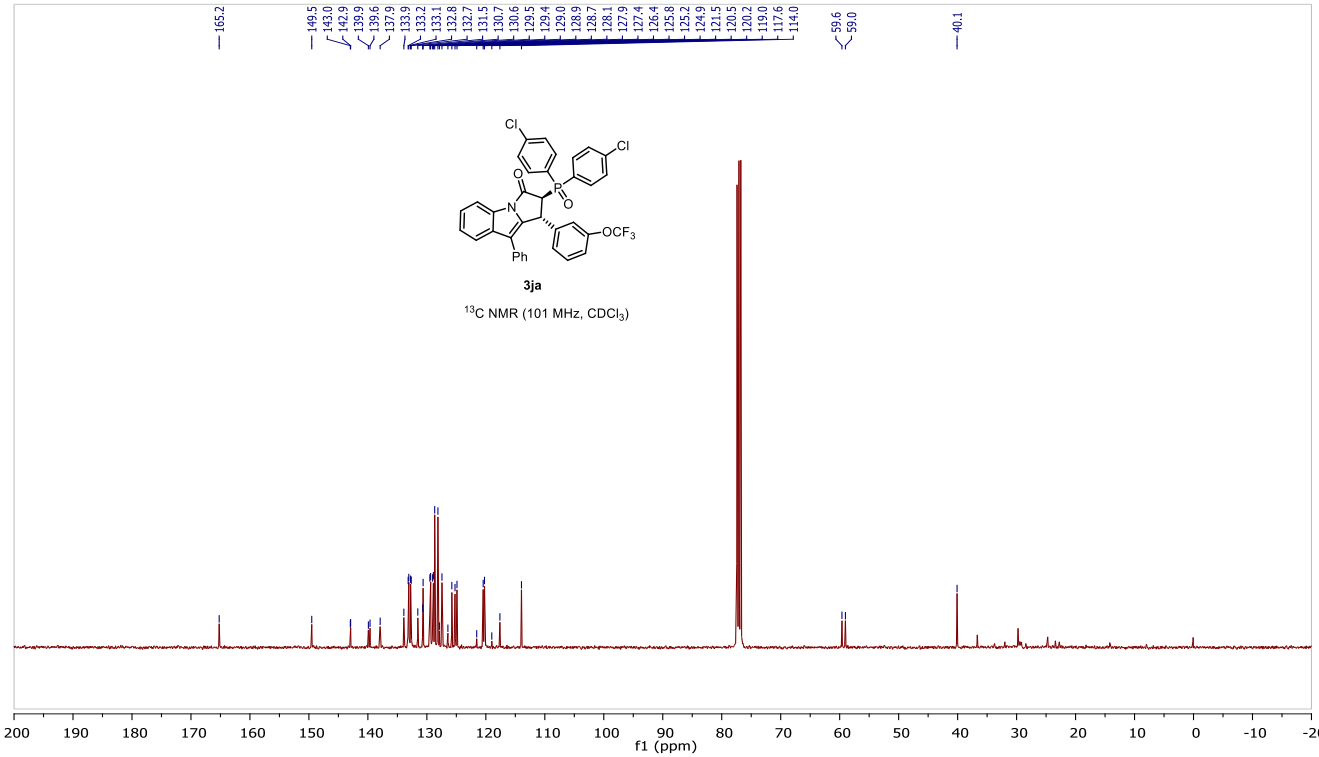
^{31}P NMR (162 MHz, $CDCl_3$)

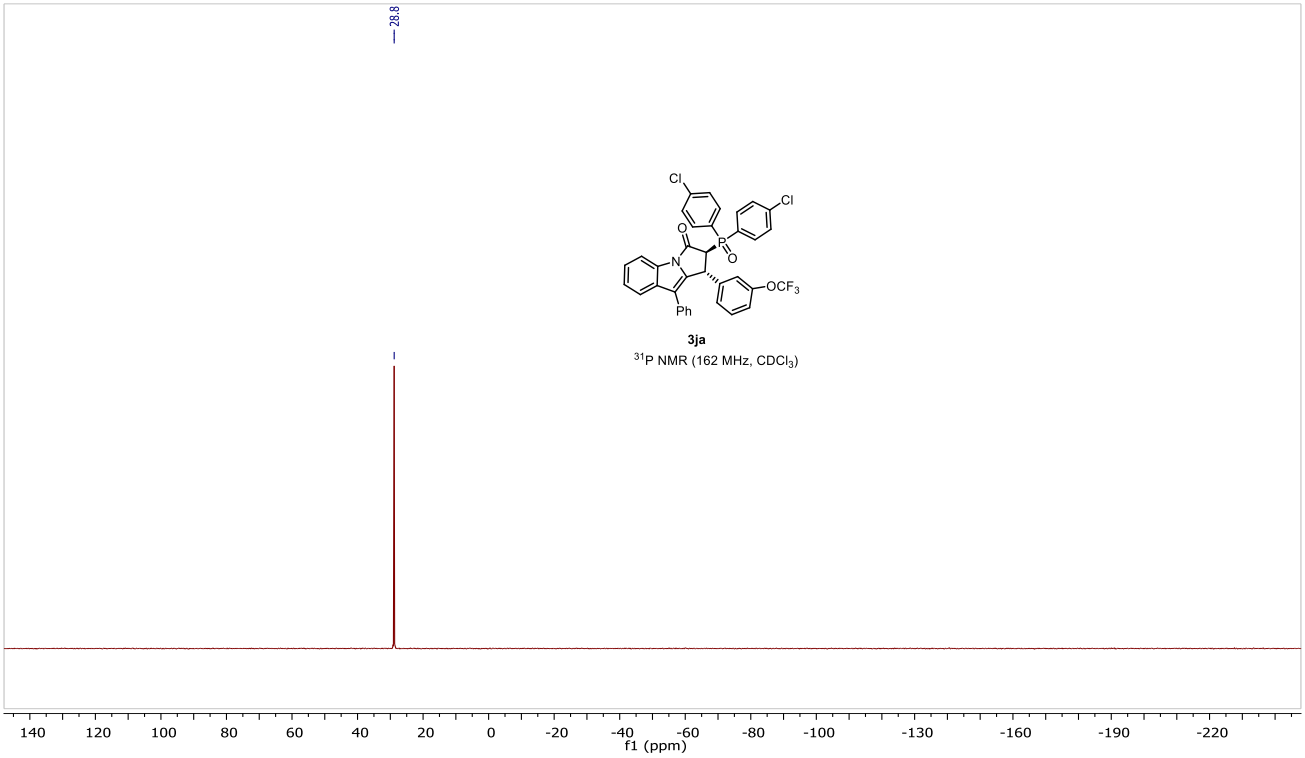

Cl
Cl
O
P
O
N
Ph
O
O
3ia
1H NMR (400 MHz, CDCl3)
1.00
1.99
1.06
4.02
3.97
0.85
3.96
1.00
0.96
0.99
1.95
1.00
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


165.6
148.4
147.1
133.2
133.1
132.7
132.6
129.4
129.2
128.9
128.7
128.6
128.2
125.1
120.7
108.3
108.0
107.5
101.3
60.2
59.7
40.3
Cl
Cl
O
P
O
N
Ph
O
O
3ia
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


28.7
Cl
Cl
O
P
O
N
Ph
O
O
3ia
31P NMR (162 MHz, CDCl3)
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
f1 (ppm)

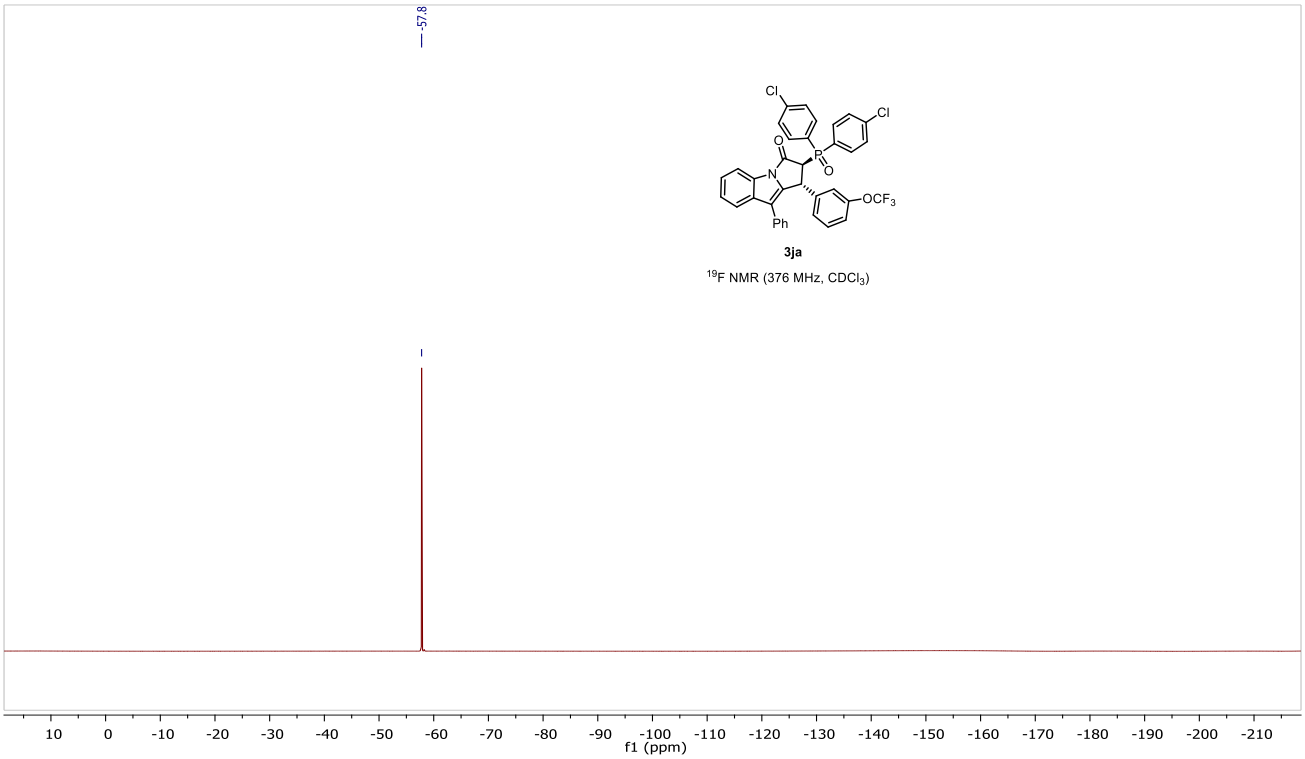

8.00 7.89 7.88 7.87 7.85 7.64 7.63 7.62 7.61 7.59 7.52 7.52 7.50 7.50 7.36 7.36 7.36 7.35 7.35 7.27 7.27 7.26 7.25 7.25 7.24 7.23 7.23 7.23 7.22 7.17 7.17 7.16 7.15 5.27 5.27 5.24 5.24
4.17 4.16 4.14 4.13
Cl
Cl
O
P
O
N
OCF3
Ph
3ja
1H NMR (500 MHz, CDCl3)
1.02 2.00 3.00 1.94 2.03 7.45 1.96 0.97 1.01 0.94 1.00 0.97
10.0 9.5 9.0 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 -0.5 -1.0
f1 (ppm)


165.2
149.5 143.0 142.9 139.9 139.6 137.9 133.9 133.2 133.1 132.8 132.7 131.5 130.7 130.6 129.5 129.4 129.0 128.9 128.7 128.1 127.9 127.4 126.4 125.8 125.2 124.9 121.5 120.5 120.2 119.0 117.6 114.0
59.6 59.0
40.1
Cl
Cl
O
P
O
N
OCF3
Ph
3ja
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



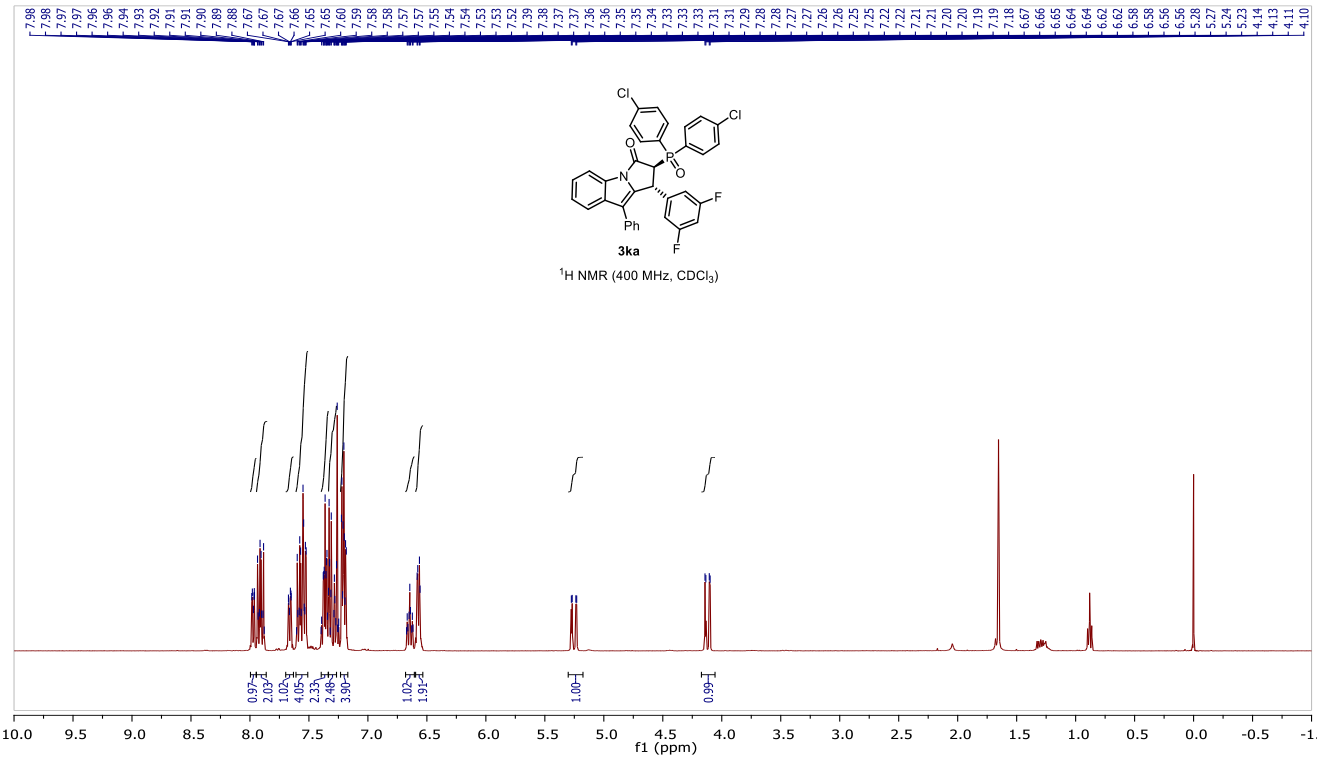
3ja

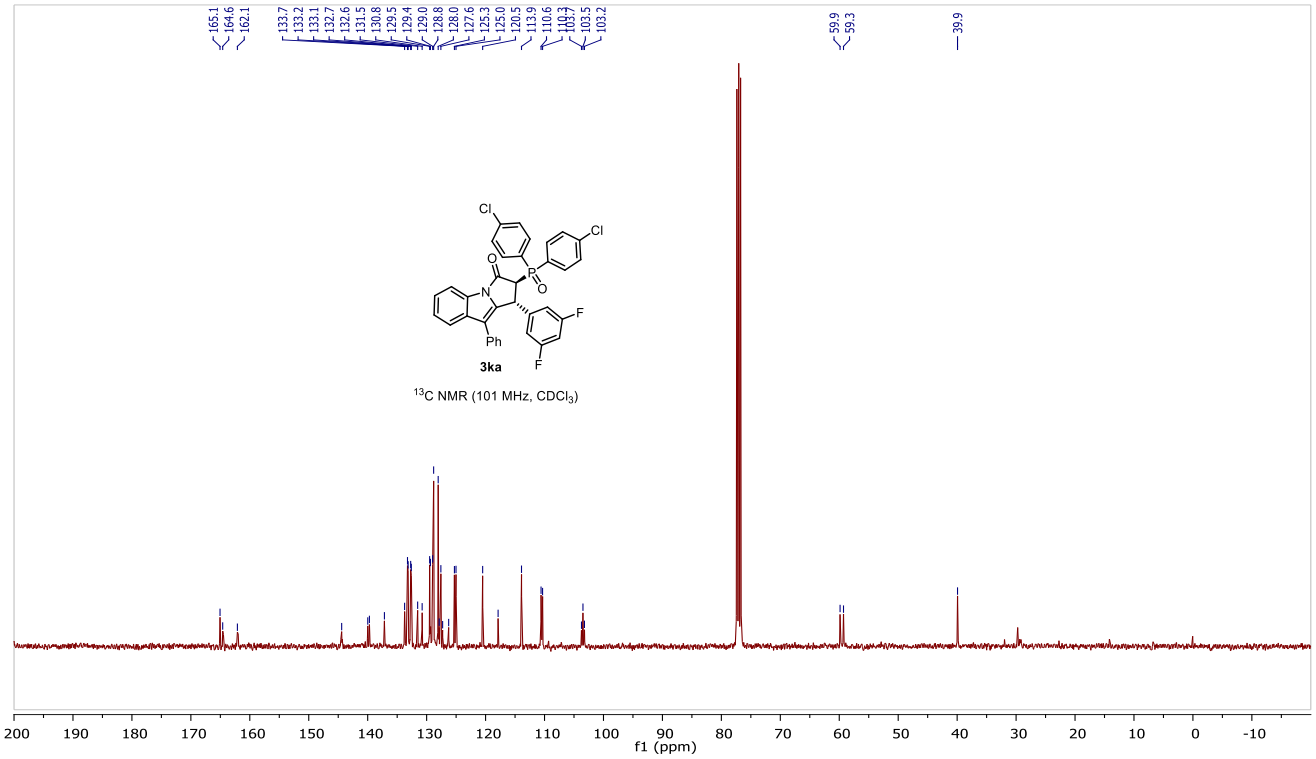
^{31}P NMR (162 MHz, $CDCl_3$)

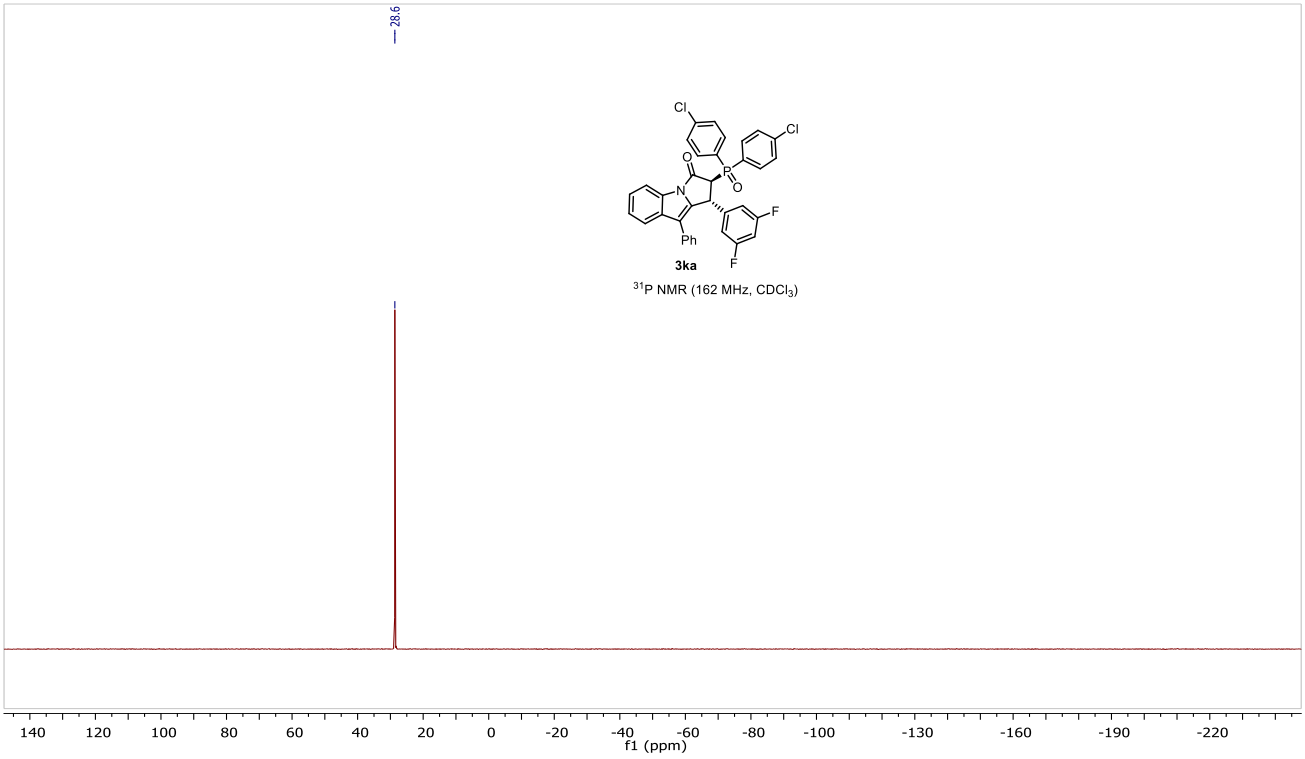


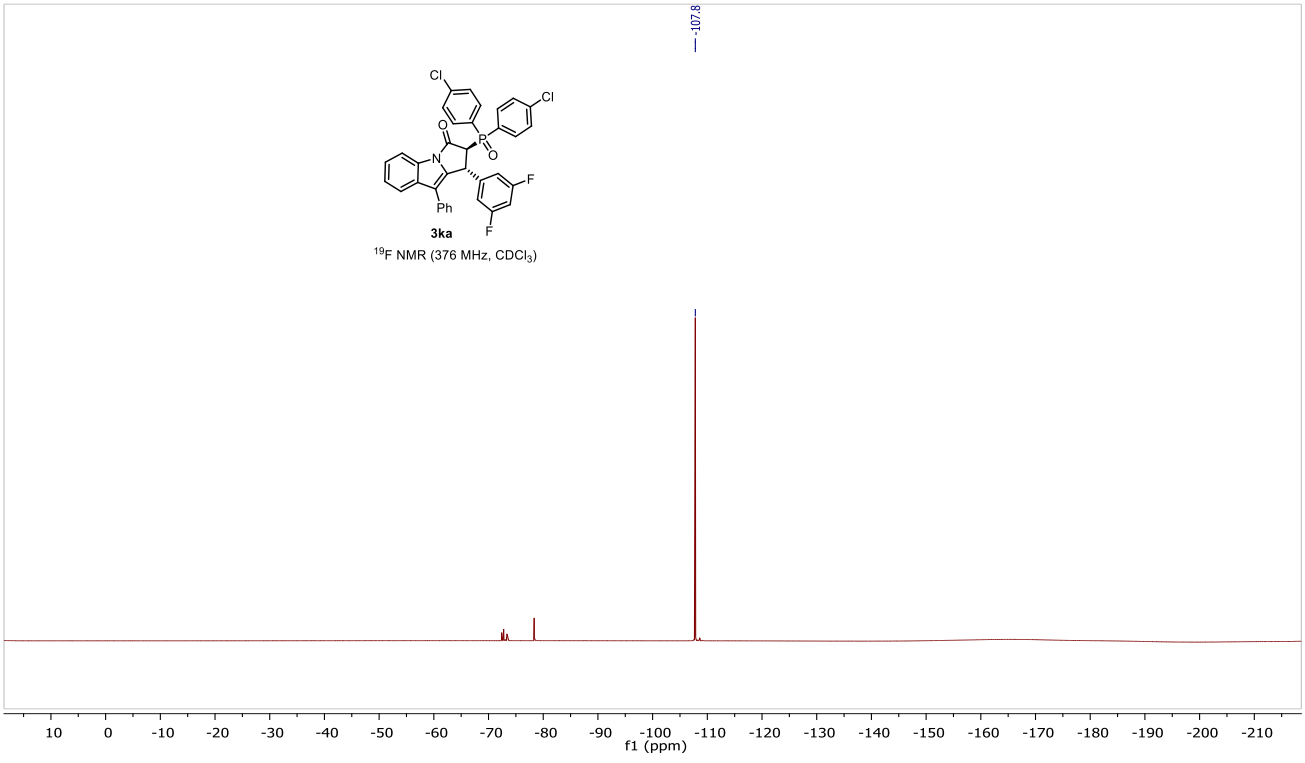
3ja

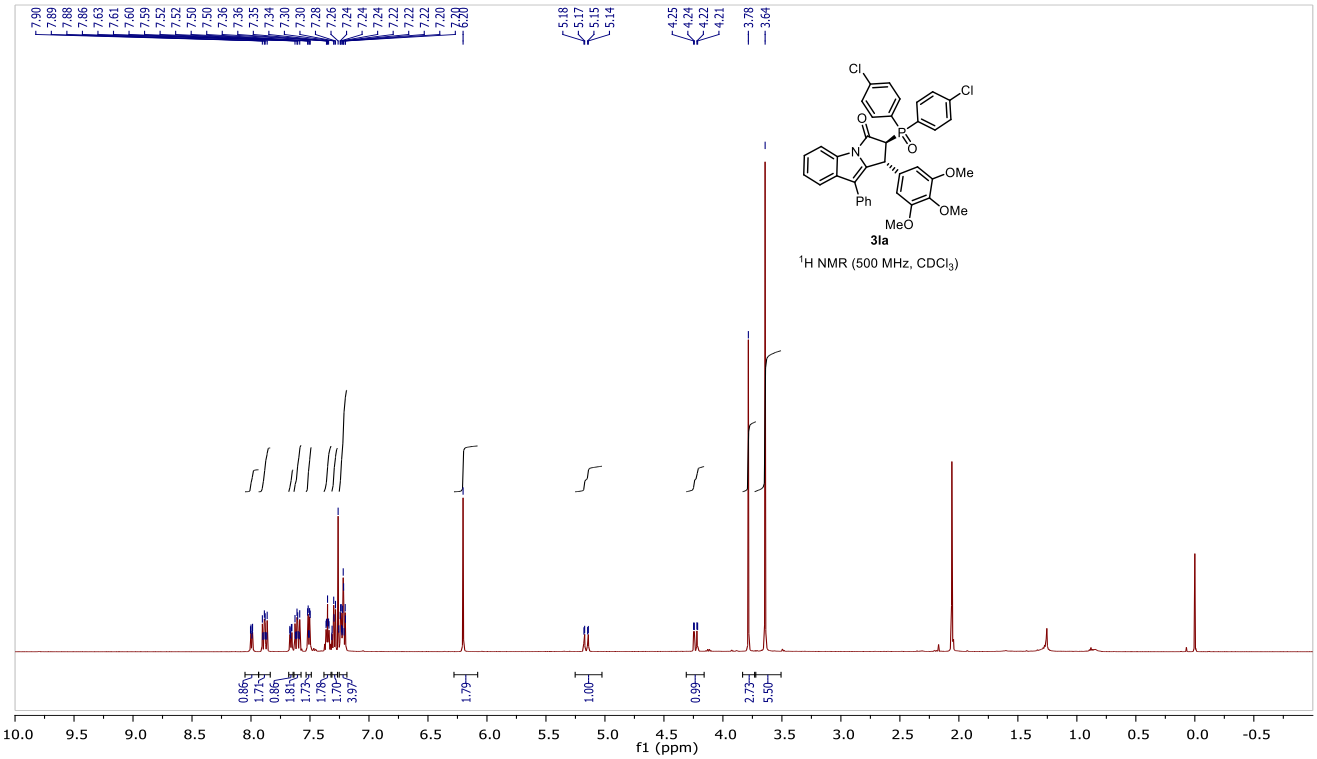
^{19}F NMR (376 MHz, $CDCl_3$)

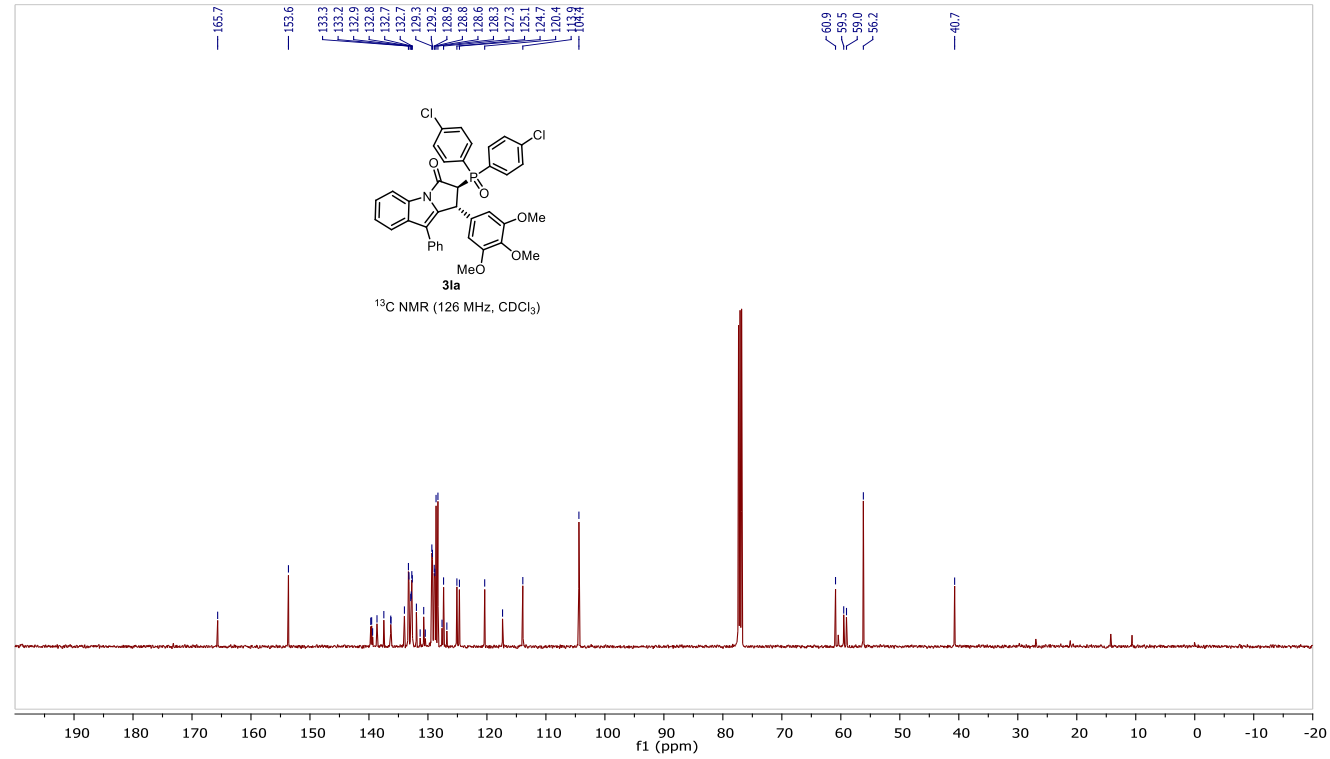

3ka
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

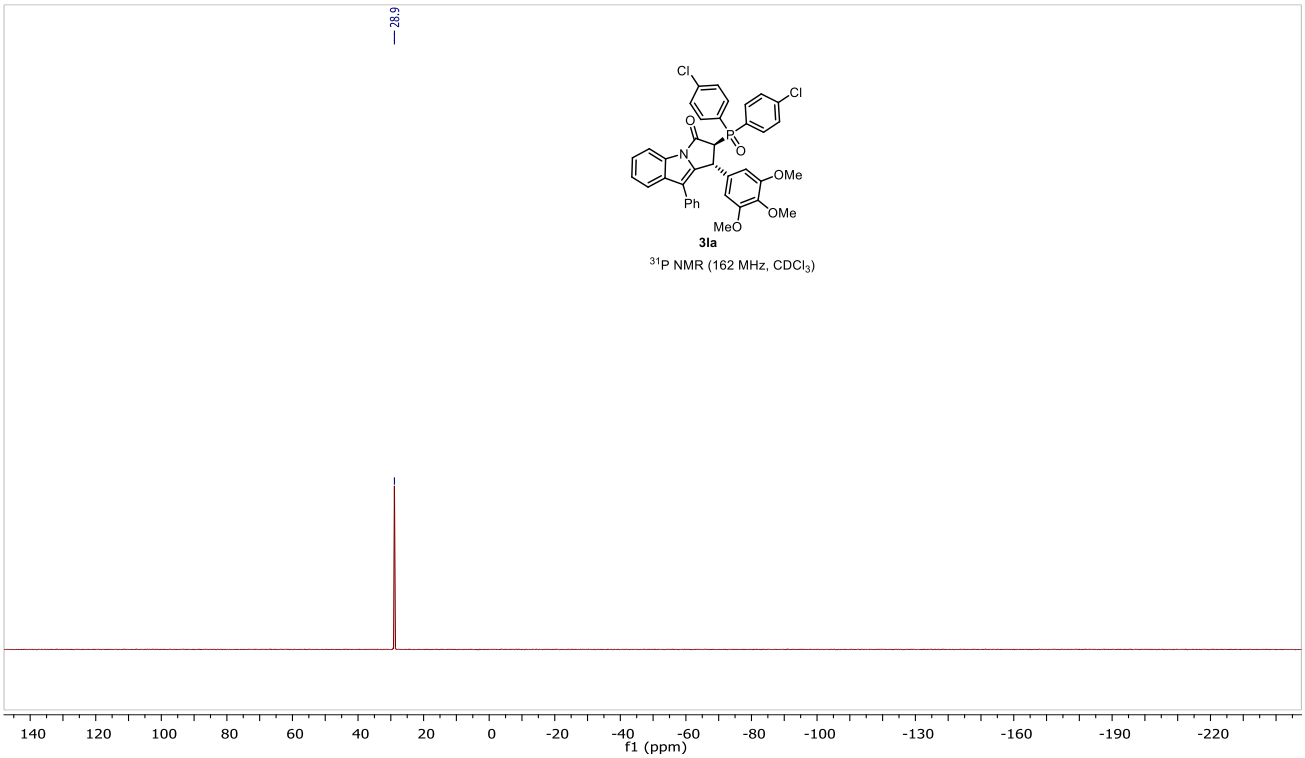

3ka
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

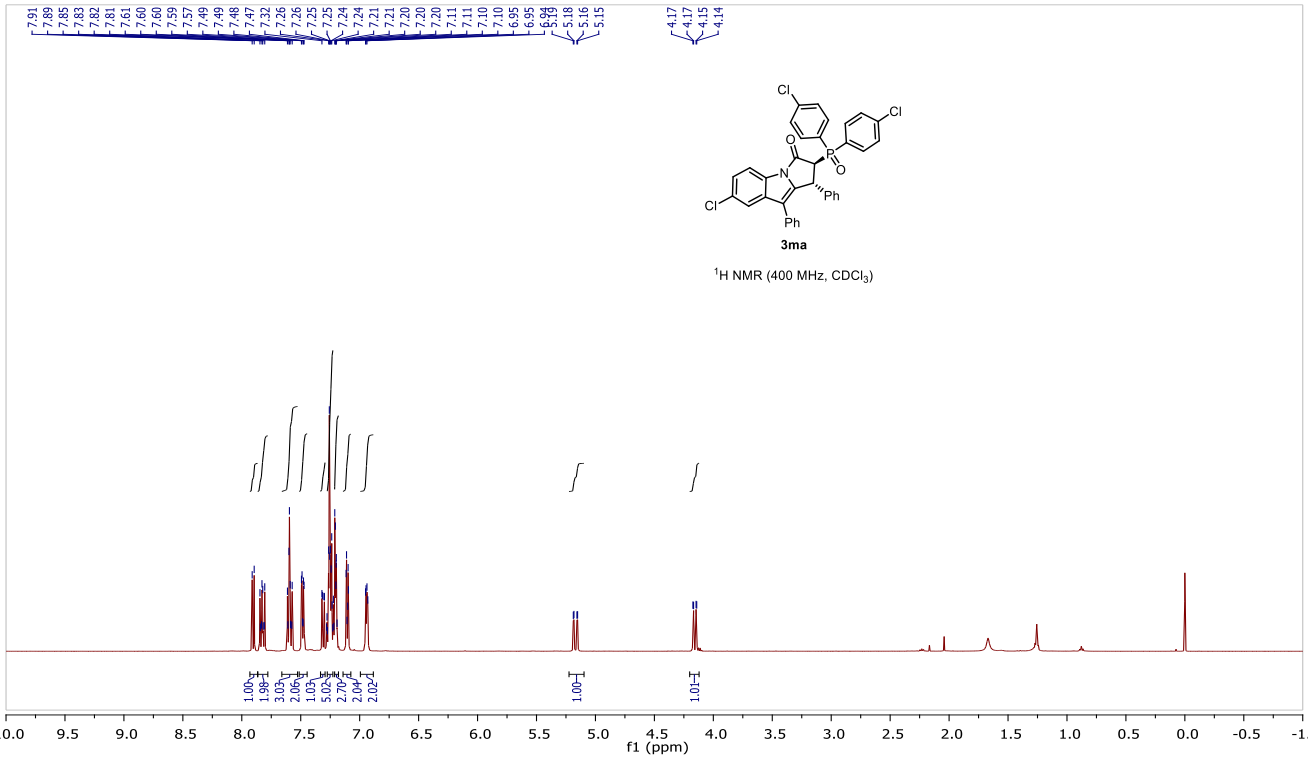

28.6
Cl
Cl
O
P
O
N
F
Ph
F
3ka
31P NMR (162 MHz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220
f1 (ppm)

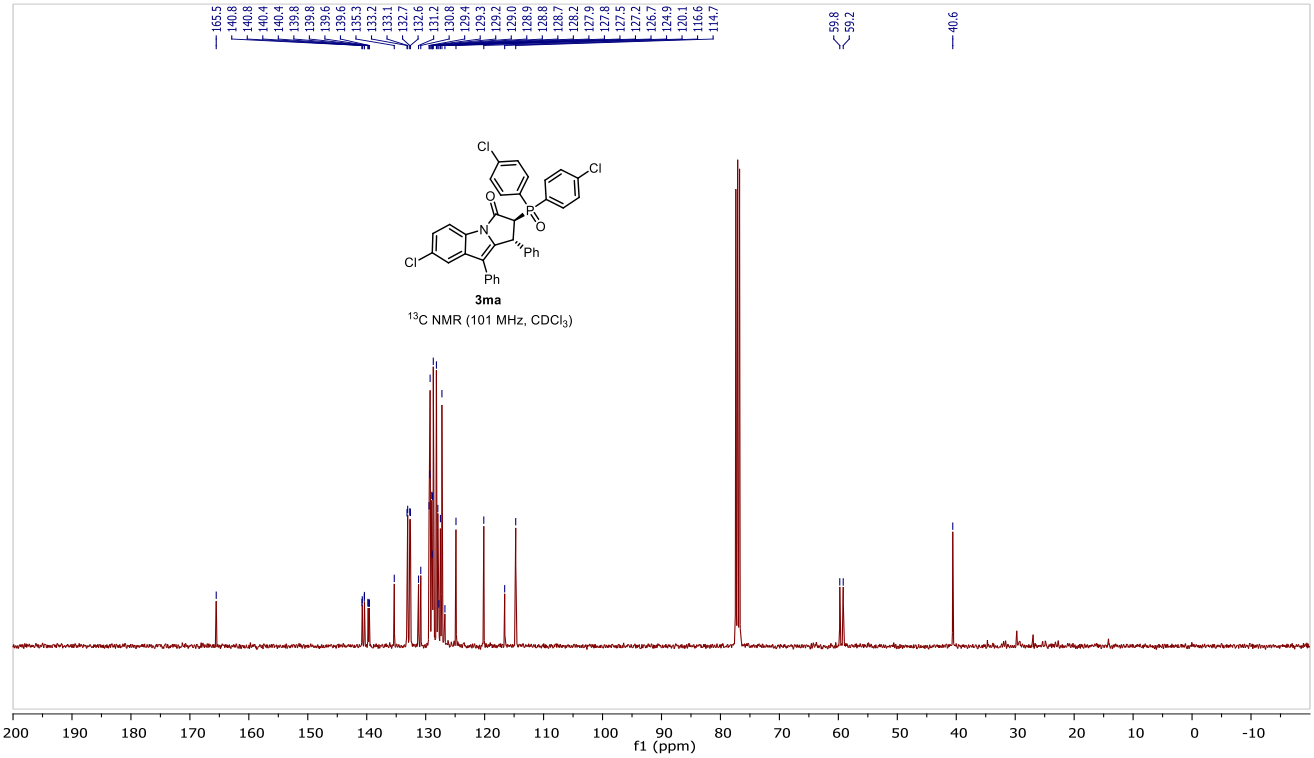

-107.8
Cl
Cl
O
P
O
N
F
Ph
F
3ka
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

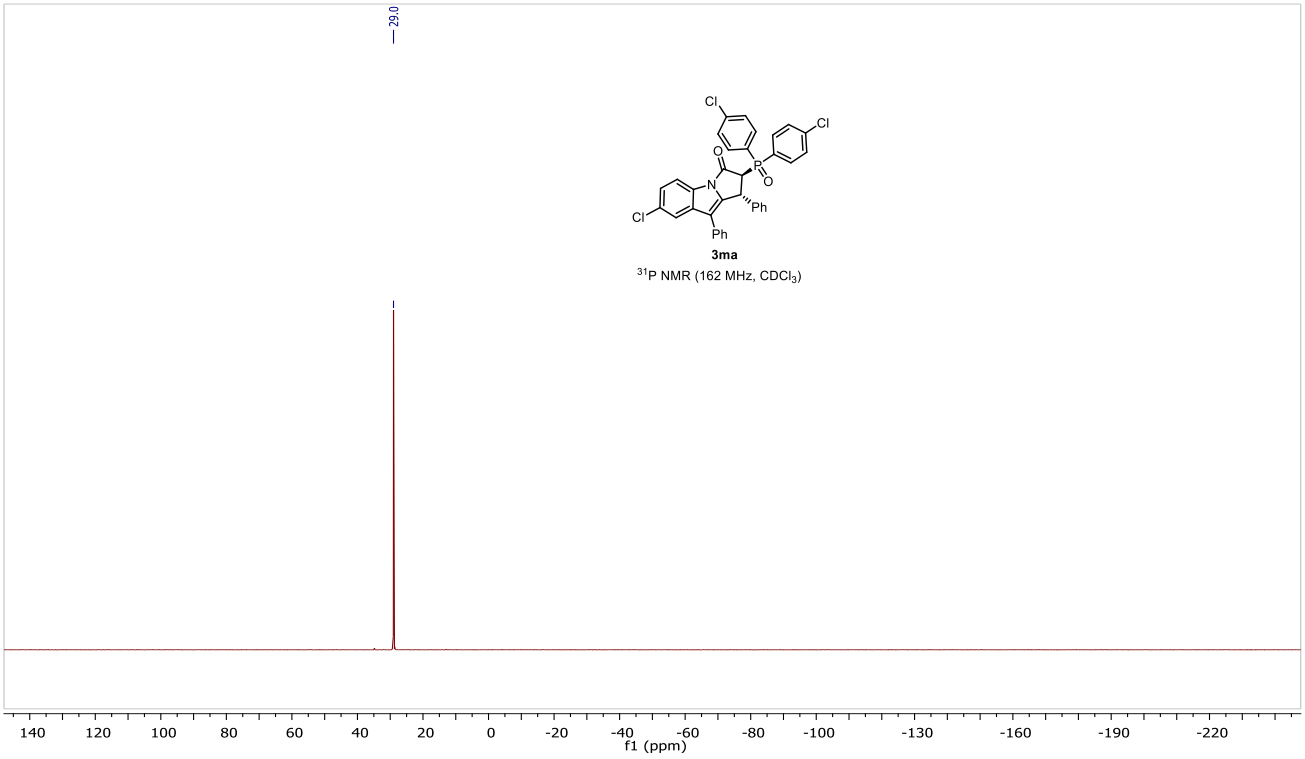

7.90
7.89
7.88
7.86
7.63
7.61
7.60
7.59
7.52
7.50
7.50
7.36
7.36
7.35
7.34
7.30
7.30
7.28
7.26
7.24
7.24
7.24
7.22
7.22
7.22
7.20
7.20
6.20
5.18
5.17
5.15
5.14
4.25
4.24
4.22
4.21
3.78
3.64
Cl
Cl
O
P
O
N
OMe
Ph
OMe
MeO
3la
^{1}H NMR (500 MHz, $CDCl_3$)
0.86
1.71
0.86
1.81
1.73
1.78
1.70
3.97
1.79
1.00
0.99
2.73
5.50
10.0
9.5
9.0
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
-0.5
f1 (ppm)


165.7
153.6
133.3
133.2
132.9
132.8
132.7
132.7
129.3
129.2
128.9
128.8
128.6
128.3
127.3
125.1
124.7
120.4
113.9
104.4
60.9
59.5
59.0
56.2
40.7
Cl
Cl
O
P
O
N
OMe
Ph
OMe
MeO
3la
^{13}C NMR (126 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


28.9
Cl
Cl
O
P
O
N
OMe
Ph
OMe
MeO
3la
^{31}P NMR (162 MHz, $CDCl_3$)
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
f1 (ppm)

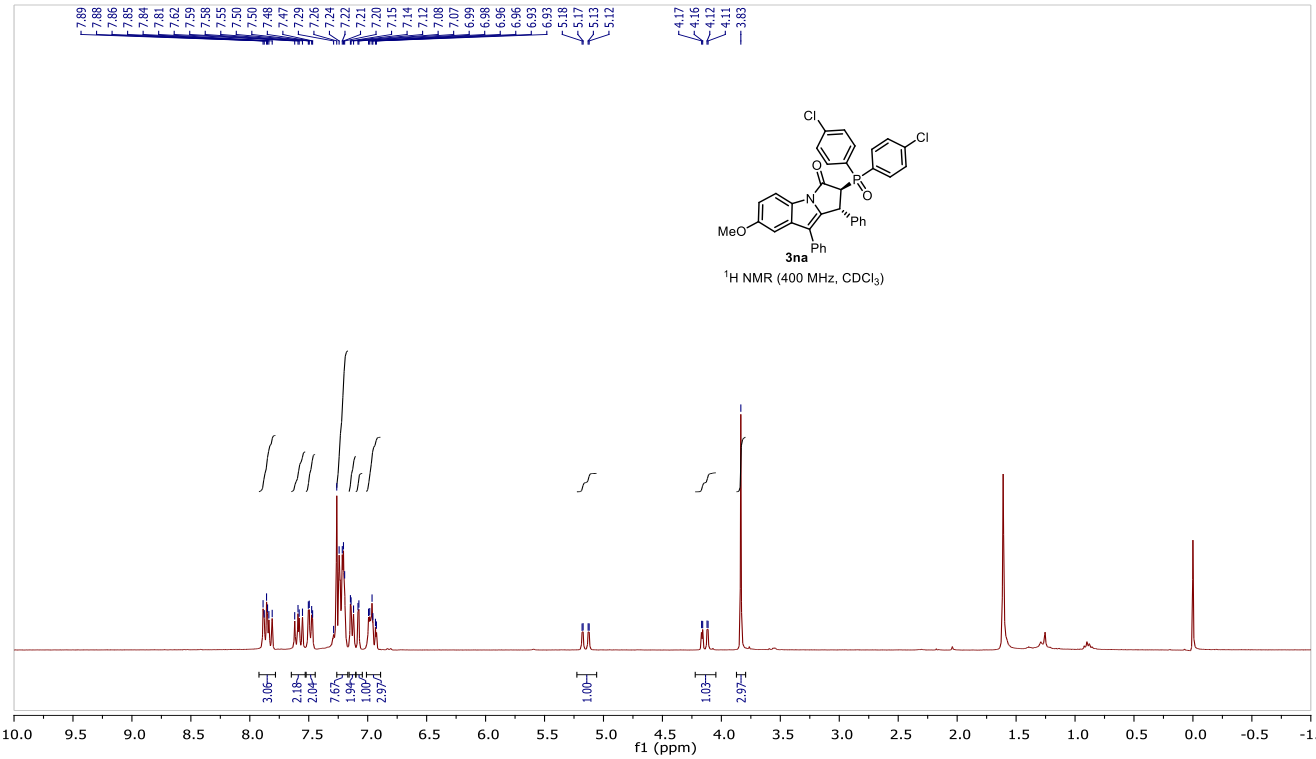

3ma
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

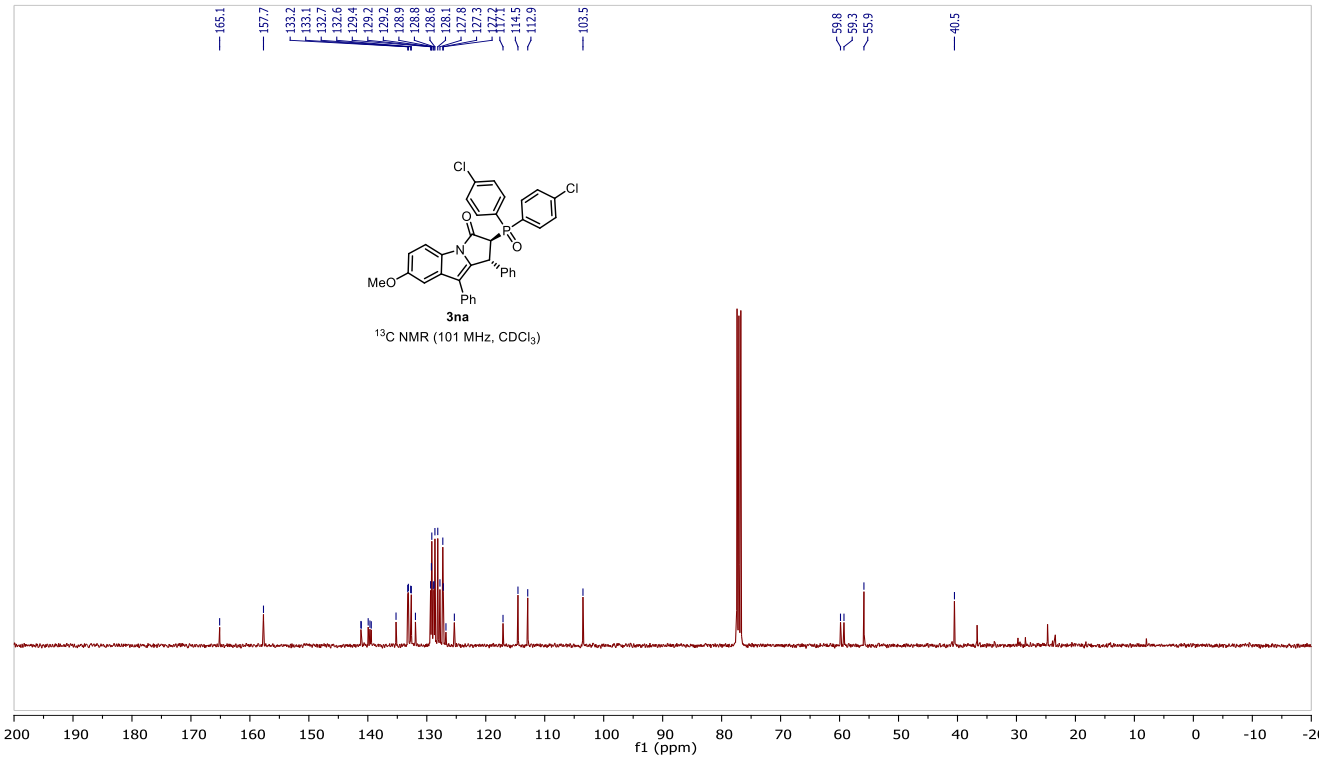

3ma
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

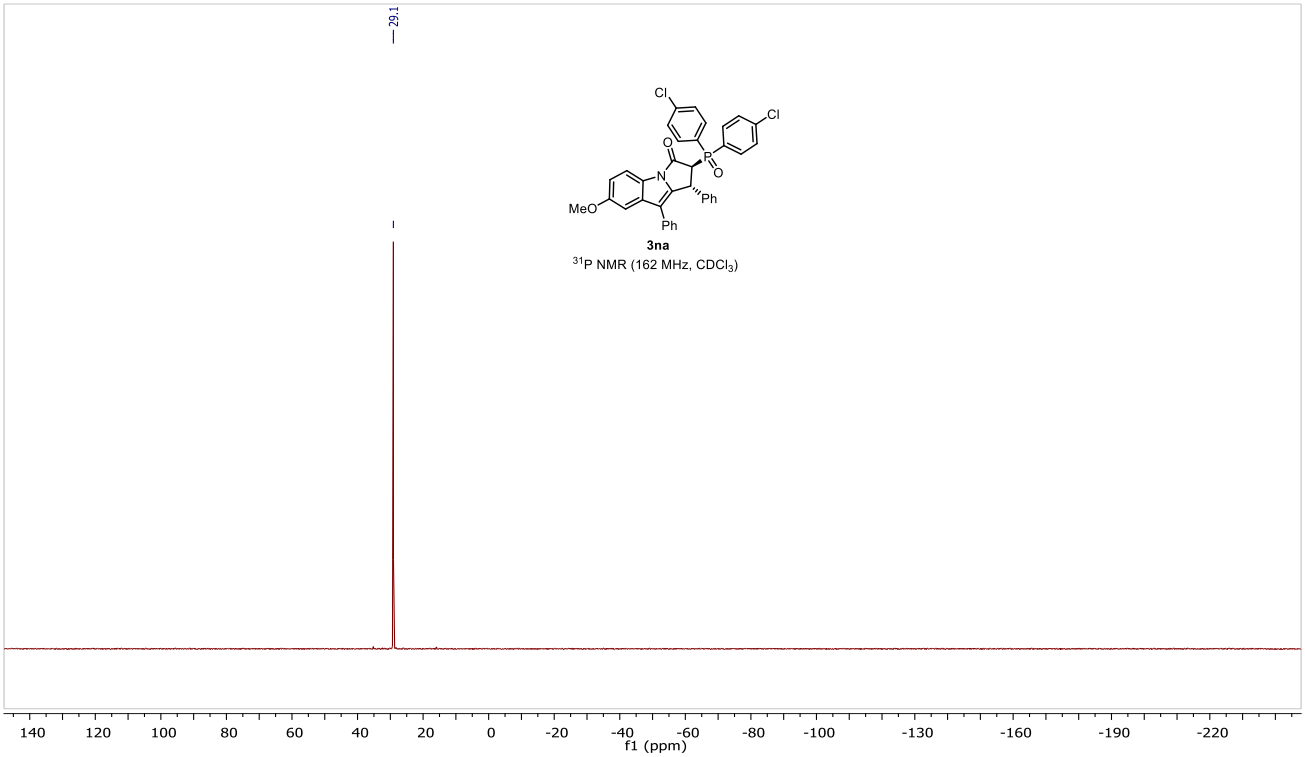


3ma

^{31}P NMR (162 MHz, $CDCl_3$)

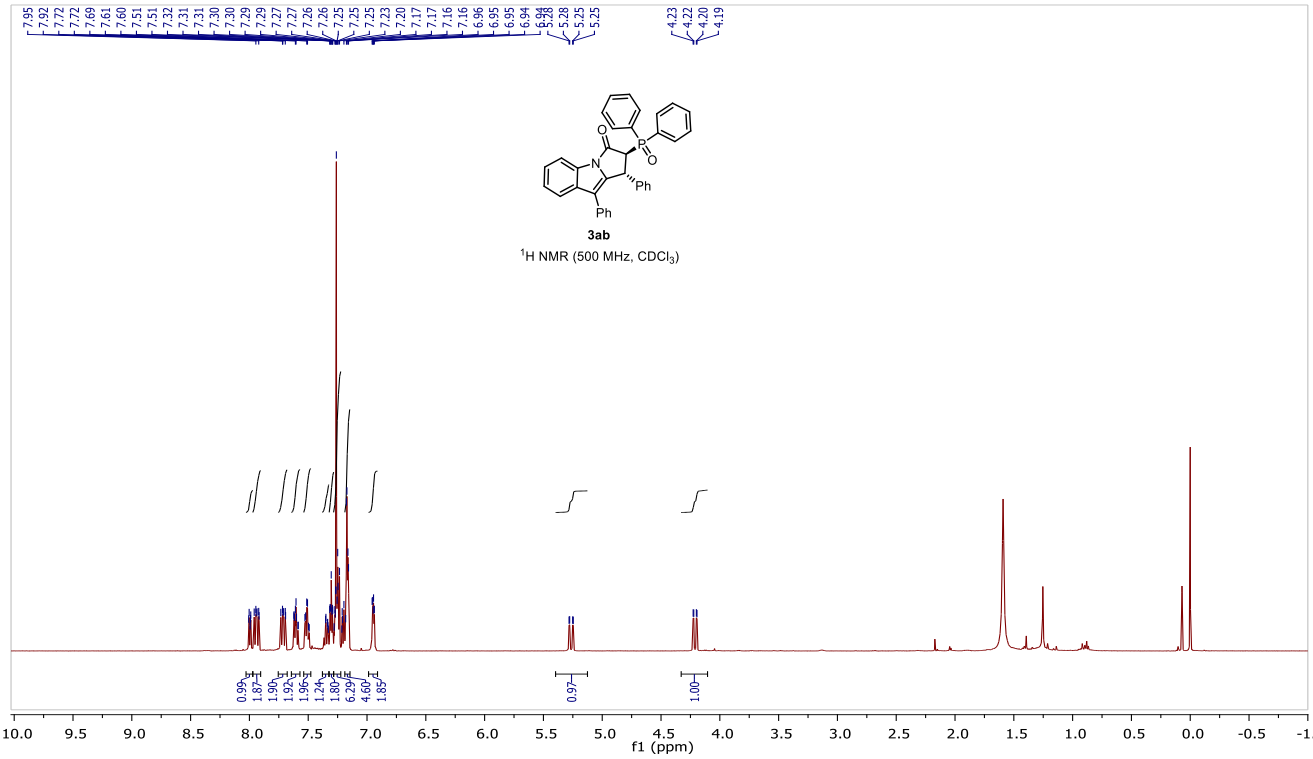

7.89 7.88 7.86 7.85 7.84 7.81 7.62 7.59 7.58 7.55 7.50 7.50 7.48 7.47 7.29 7.26 7.24 7.22 7.21 7.20 7.15 7.14 7.12 7.08 7.07 6.99 6.98 6.96 6.96 6.93 6.93 5.18 5.17 5.13 5.12
4.17 4.16 4.12 4.11 3.83
Cl
Cl
O
P
O
N
MeO
Ph
Ph
3na
1H NMR (400 MHz, CDCl3)
3.06 2.18 2.04 7.67 1.94 1.00 2.97 1.00 1.03 2.97
10.0 9.5 9.0 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 -0.5 -1.0
f1 (ppm)

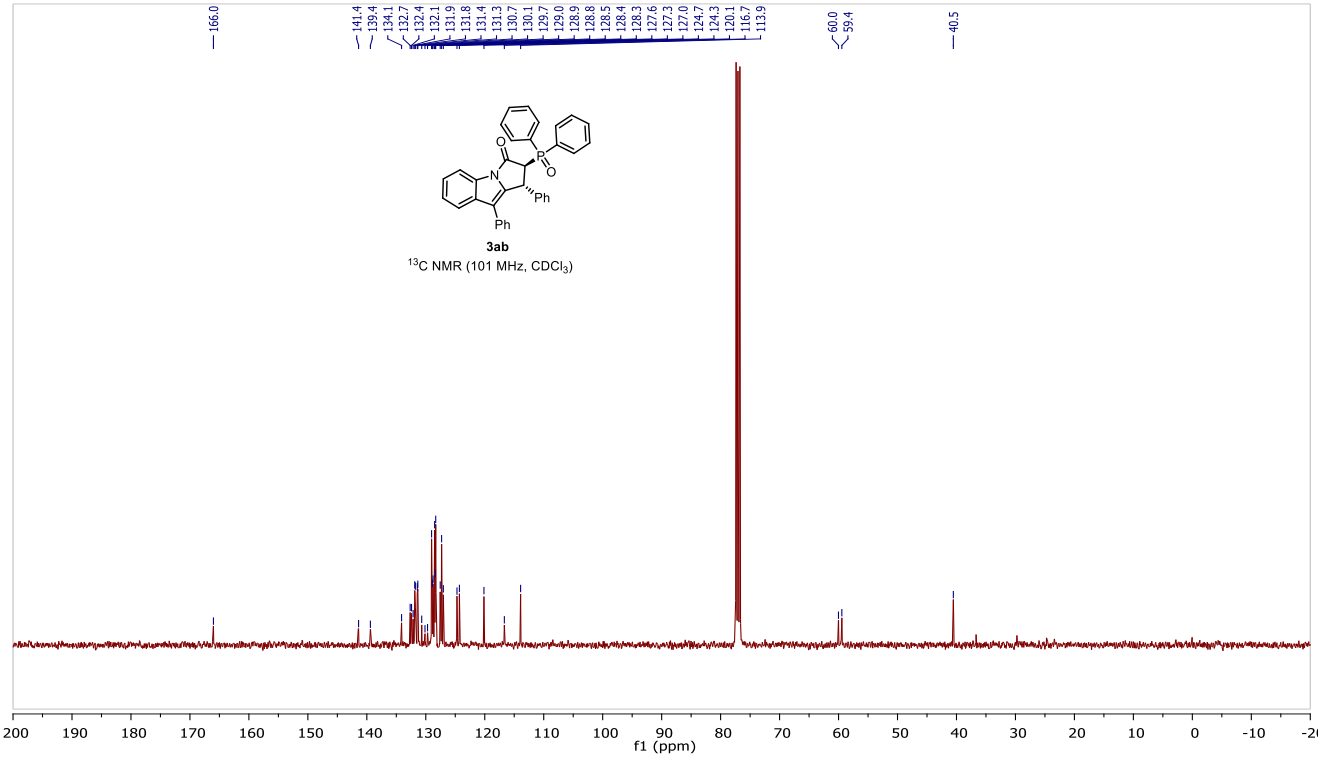

165.1 157.7 133.2 133.1 132.7 132.6 129.4 129.2 129.2 128.9 128.8 128.6 128.1 127.8 127.3 127.2 117.1 114.5 112.9 103.5
59.8 59.3 55.9 40.5
Cl
Cl
O
P
O
N
MeO
Ph
Ph
3na
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

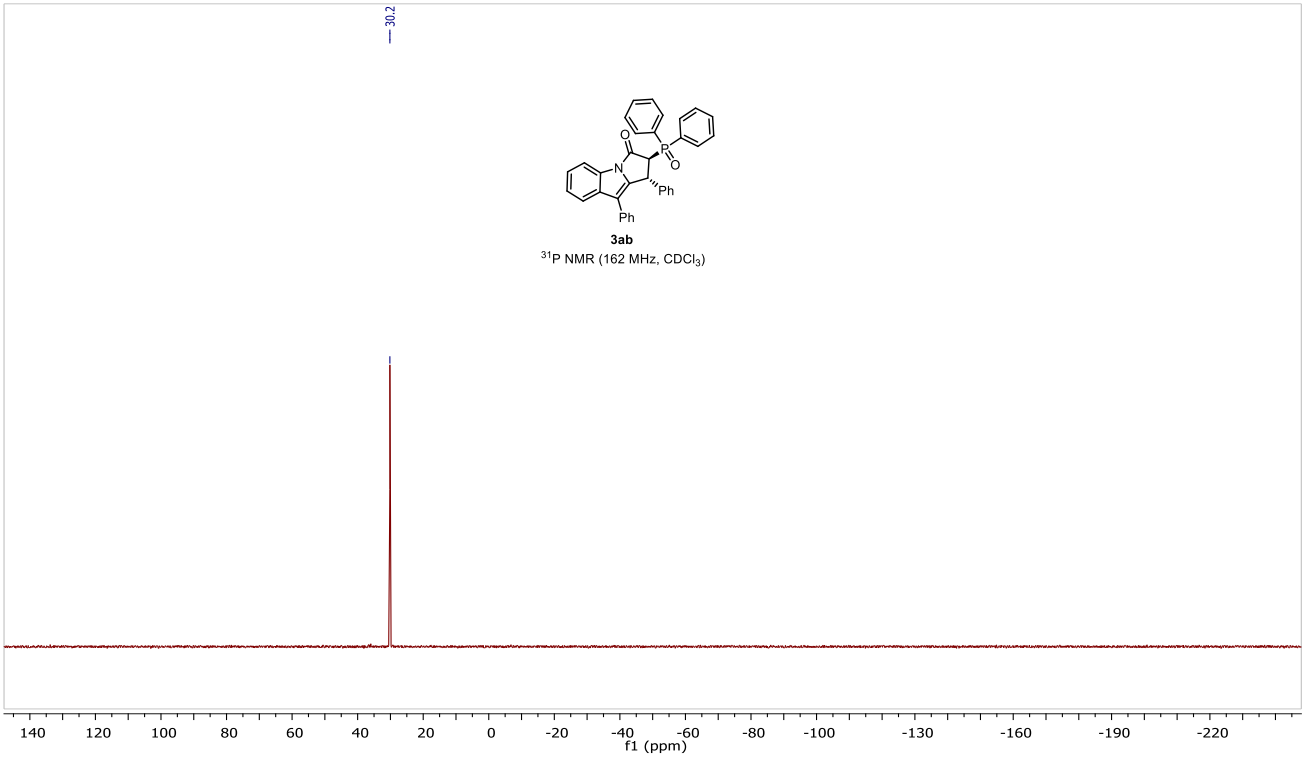


3na

^{31}P NMR (162 MHz, $CDCl_3$)

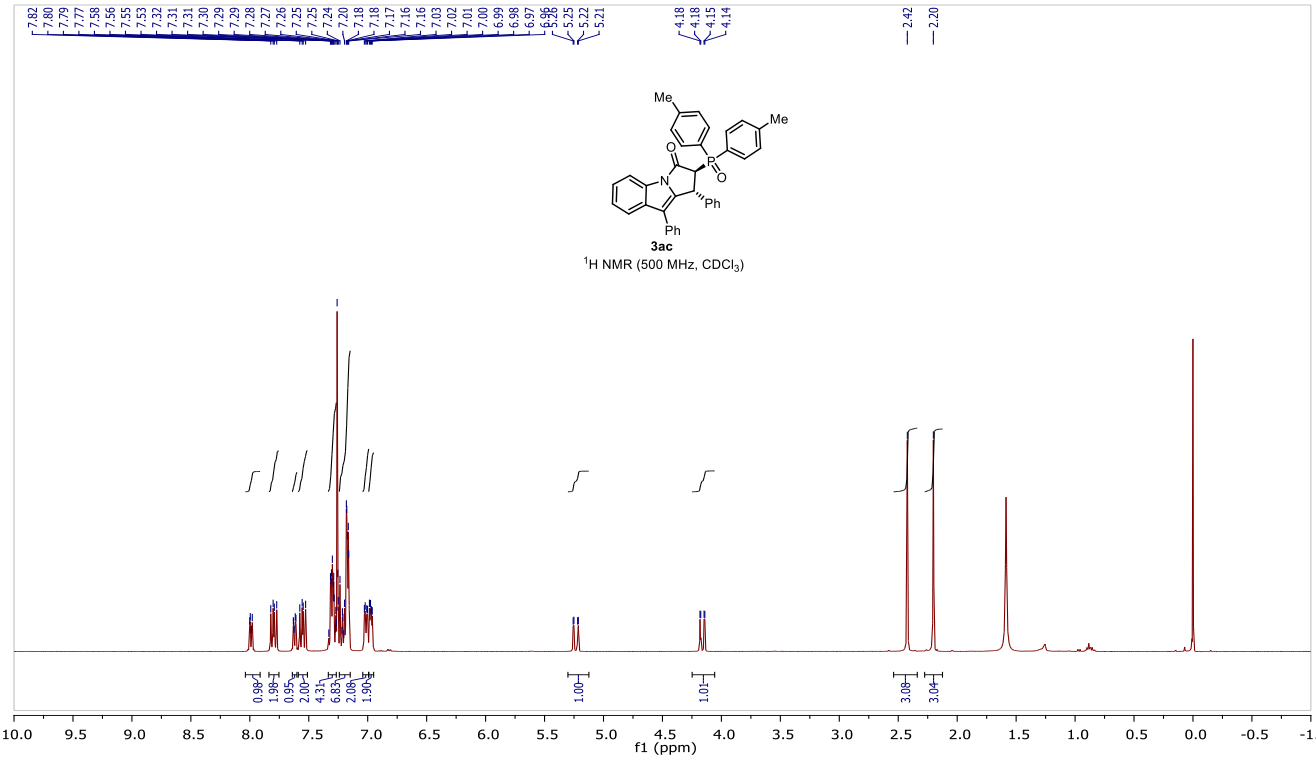

7.95 7.92 7.72 7.72 7.69 7.61 7.60 7.51 7.51 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.27 7.27 7.26 7.26 7.25 7.25 7.25 7.23 7.20 7.17 7.17 7.16 7.16 6.96 6.95 6.94 6.94 5.28 5.25 5.25
4.23 4.22 4.20 4.19
O
P
O
N
Ph
Ph
3ab
1H NMR (500 MHz, CDCl3)
0.99 1.87 1.90 1.92 1.96 1.24 1.80 6.29 4.66 1.89 0.97 1.00
10.0 9.5 9.0 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 -0.5 -1.0
f1 (ppm)

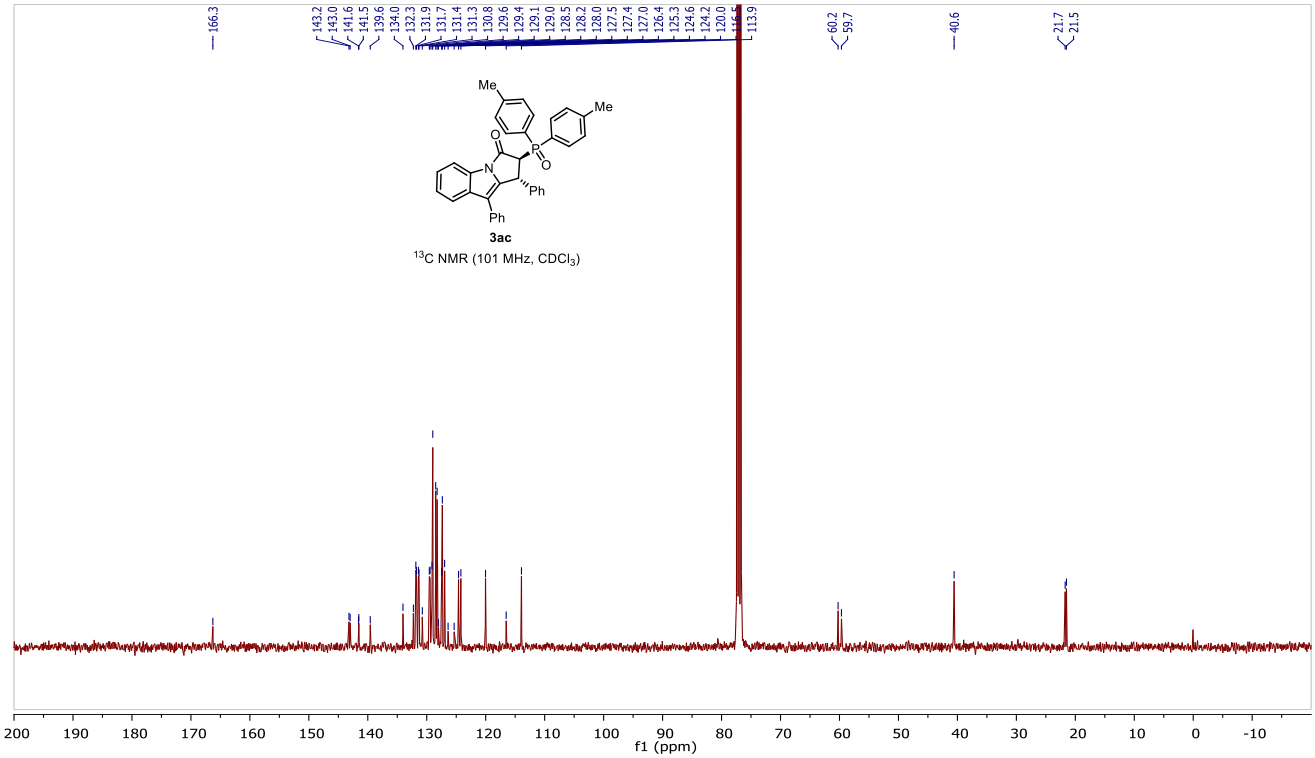

166.0
141.4 139.4 134.1 132.7 132.4 132.1 131.9 131.8 131.4 131.3 130.7 130.1 129.7 129.0 128.9 128.8 128.5 128.4 128.3 127.6 127.3 127.0 124.7 124.3 120.1 116.7 113.9
60.0 59.4
40.5
O
P
O
N
Ph
Ph
3ab
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

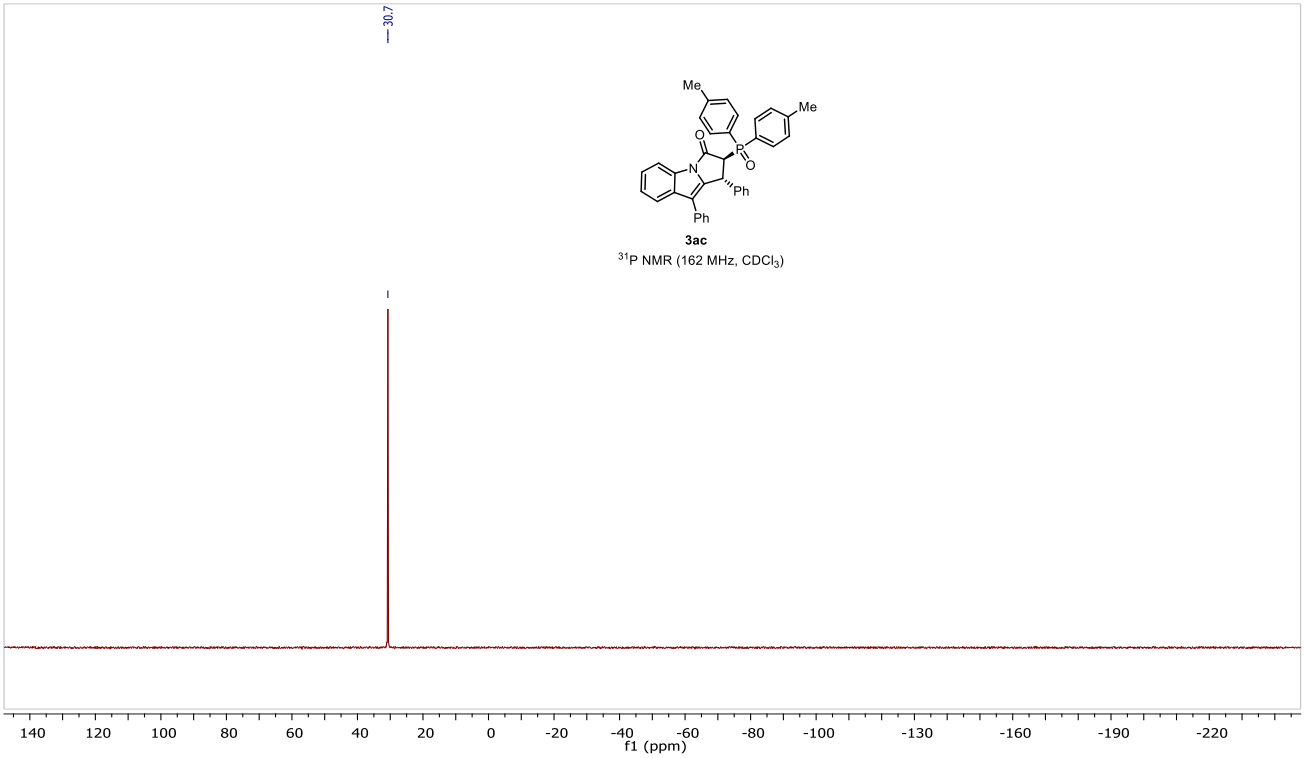


3ab

^{31}P NMR (162 MHz, $CDCl_3$)

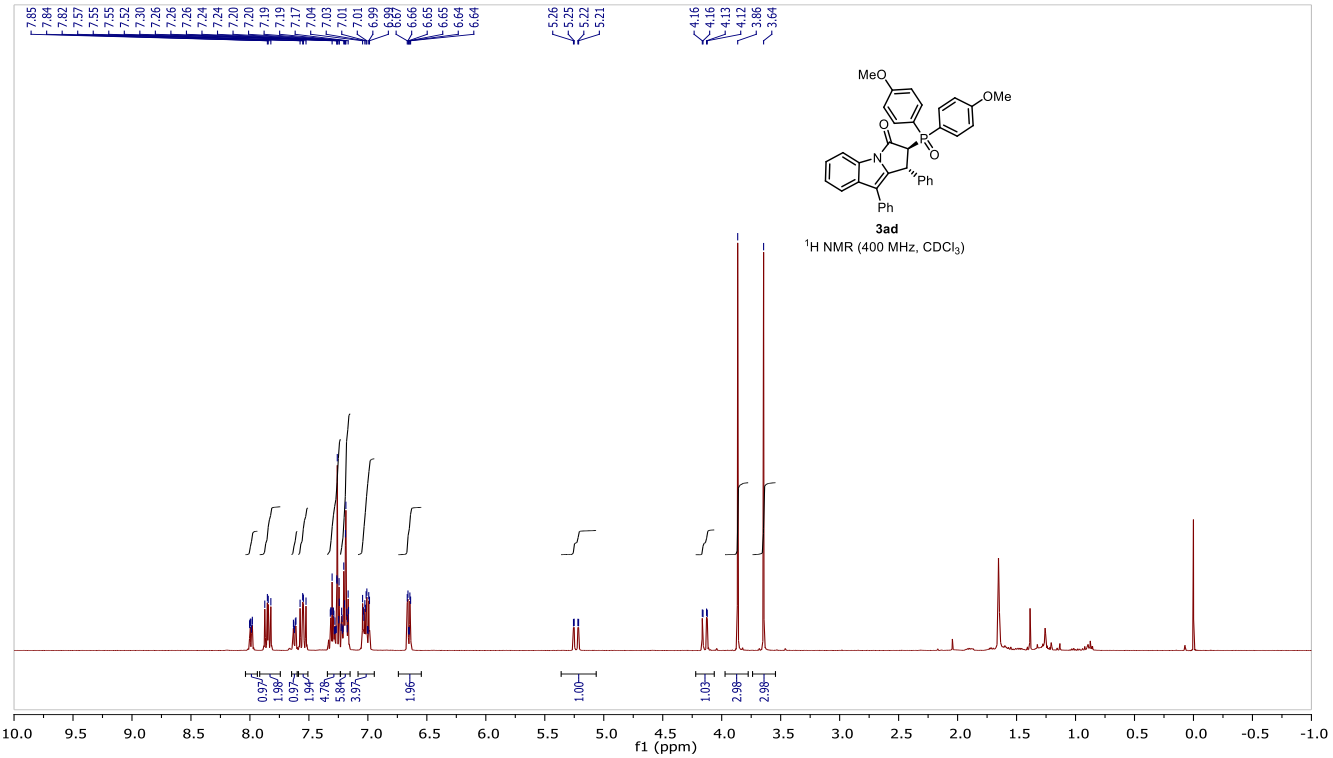

Me
Me
O
P
O
N
Ph
Ph
3ac
1H NMR (500 MHz, CDCl3)
f1 (ppm)

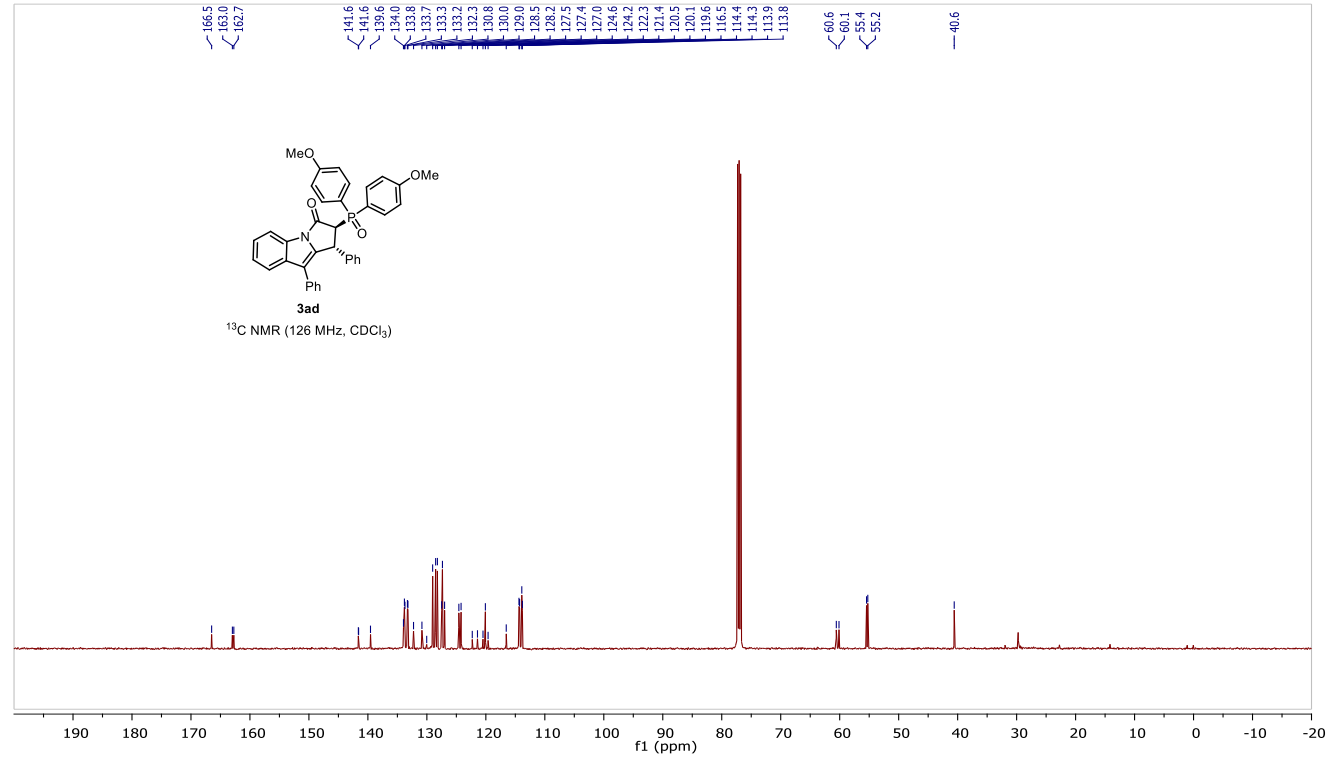

Me
Me
O
P
O
N
Ph
Ph
3ac
13C NMR (101 MHz, CDCl3)
f1 (ppm)

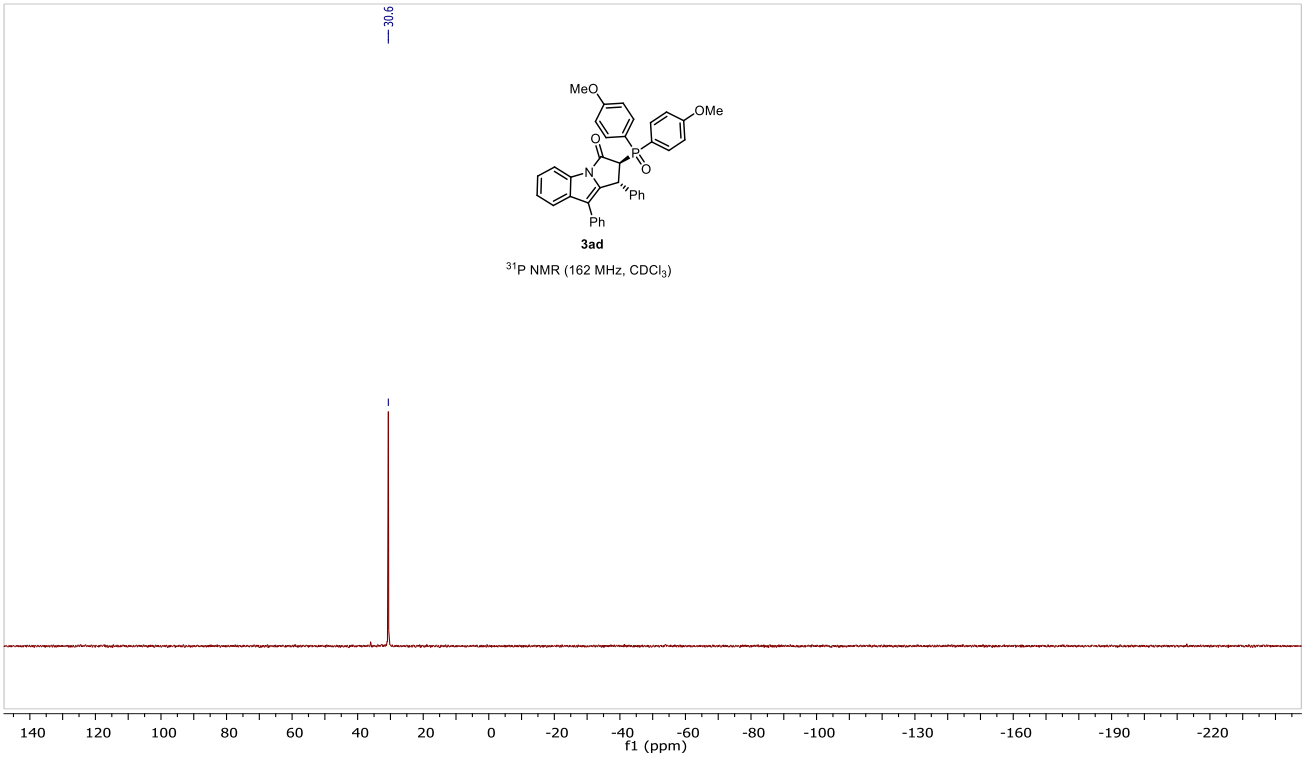


3ac

^{31}P NMR (162 MHz, $CDCl_3$)

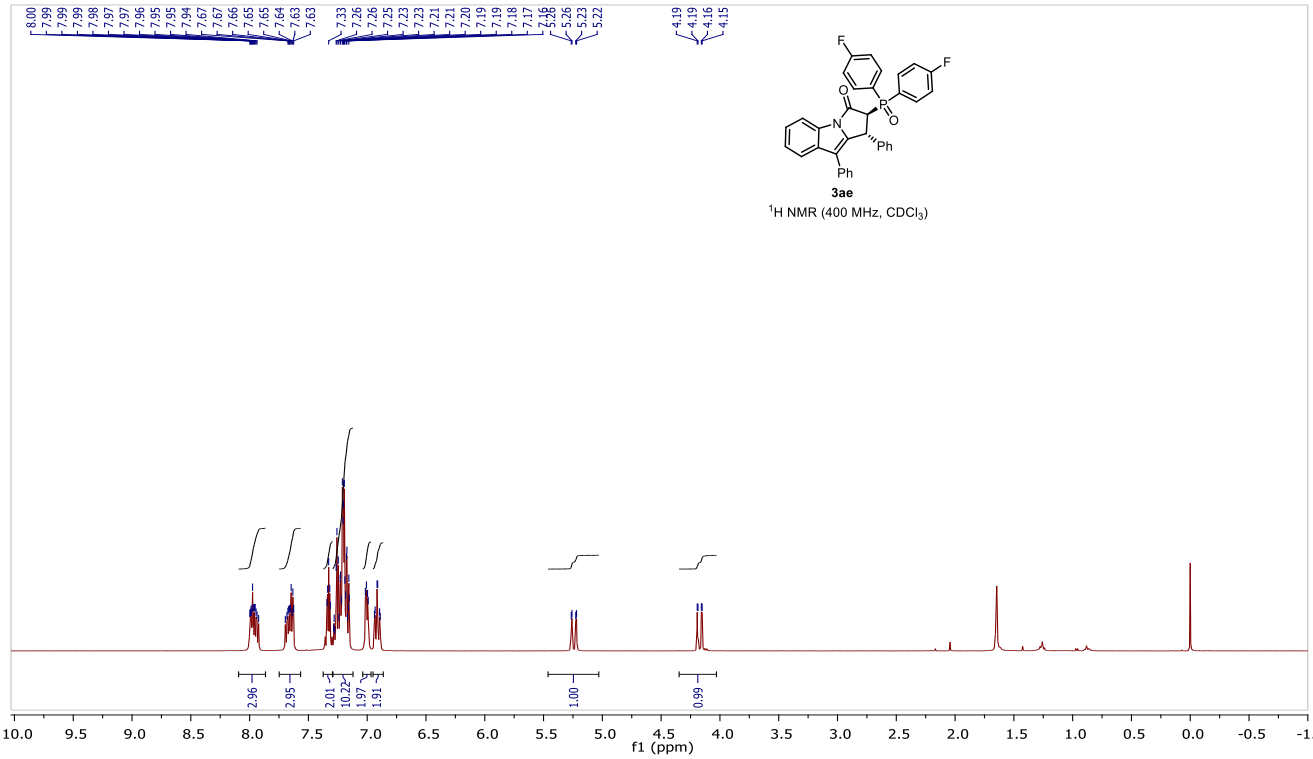

MeO
OMe
O
P
O
N
Ph
Ph
3ad
1H NMR (400 MHz, CDCl3)
f1 (ppm)

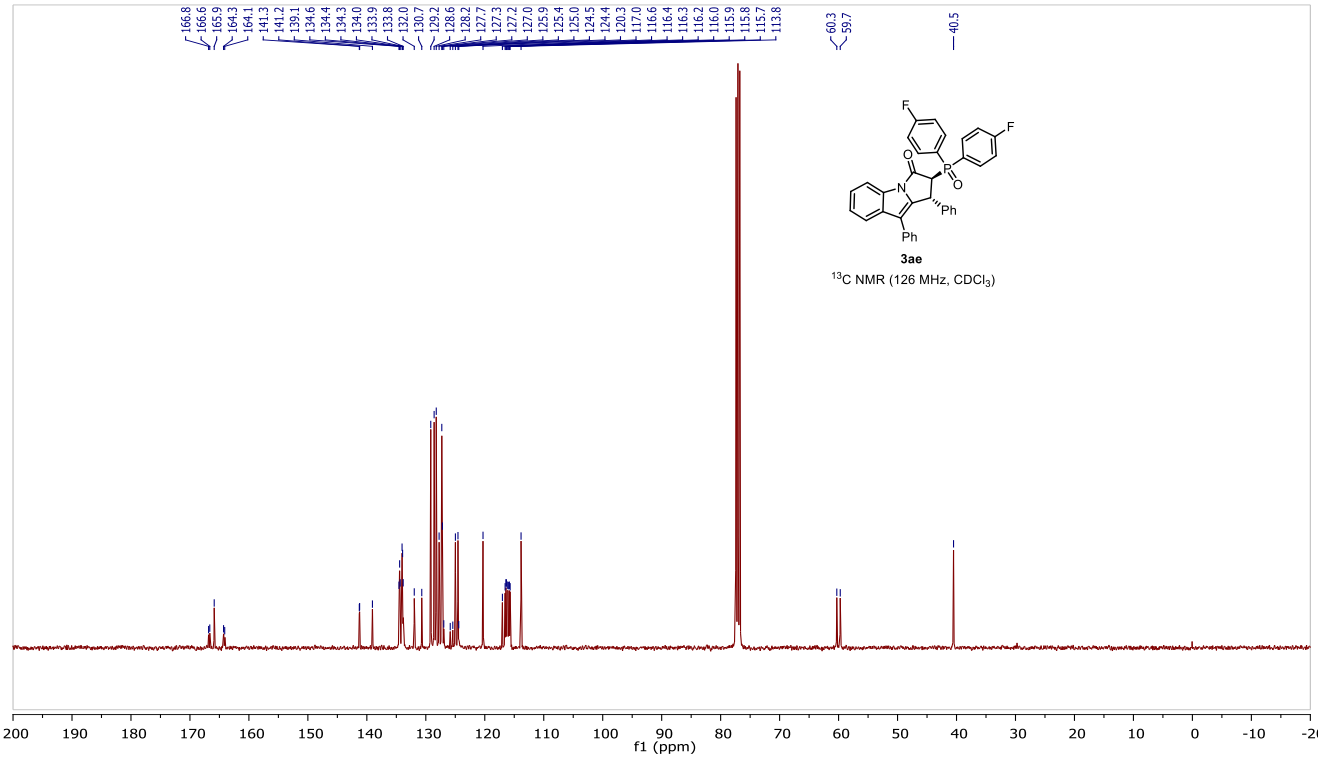

MeO
OMe
O
P
O
N
Ph
Ph
3ad
13C NMR (126 MHz, CDCl3)
f1 (ppm)

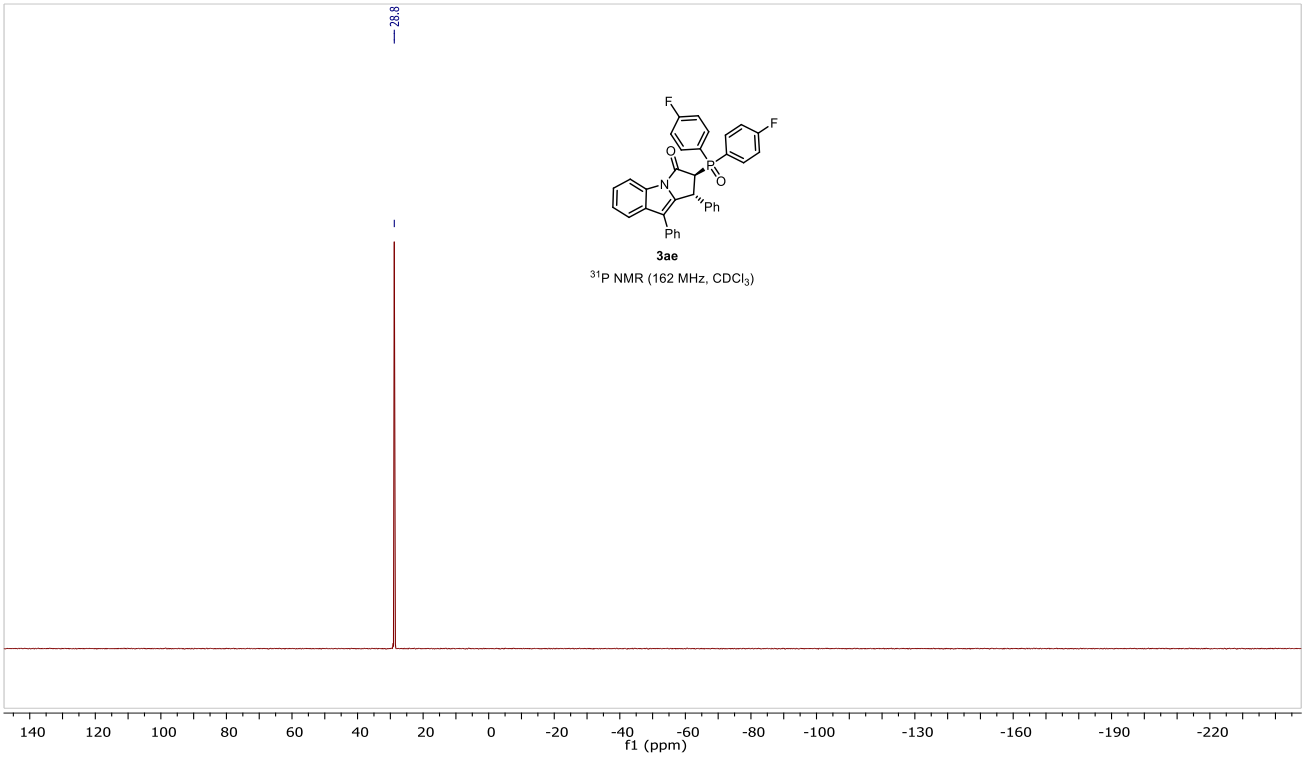


3ad

^{31}P NMR (162 MHz, $CDCl_3$)

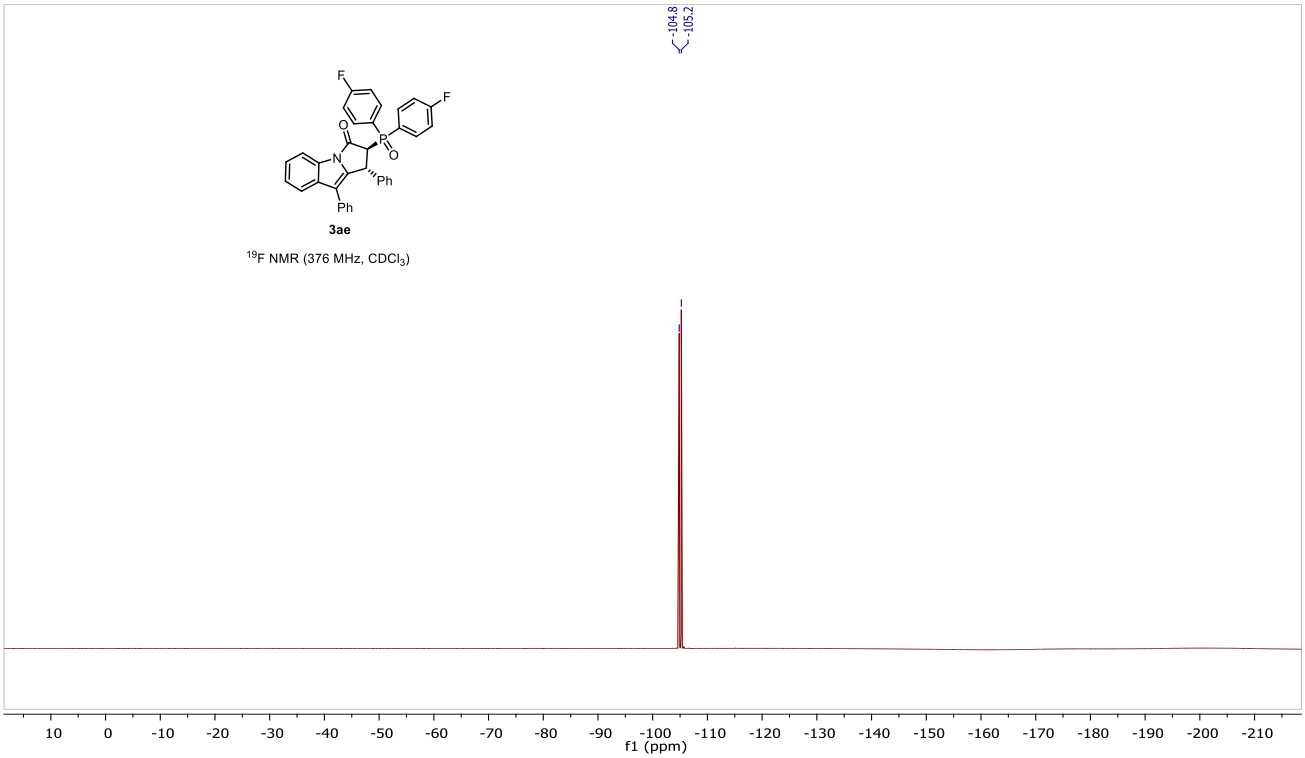

3ae
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


3ae
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)



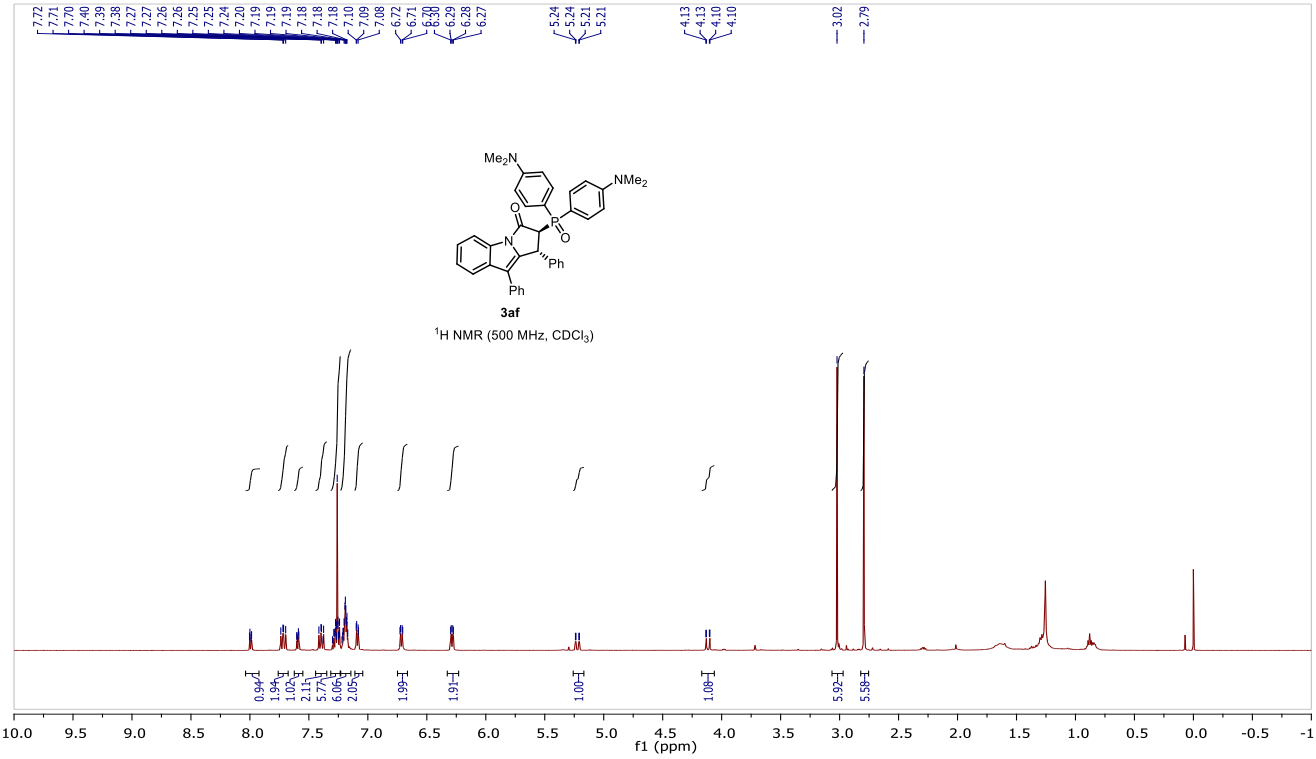
3ae

^{31}P NMR (162 MHz, $CDCl_3$)



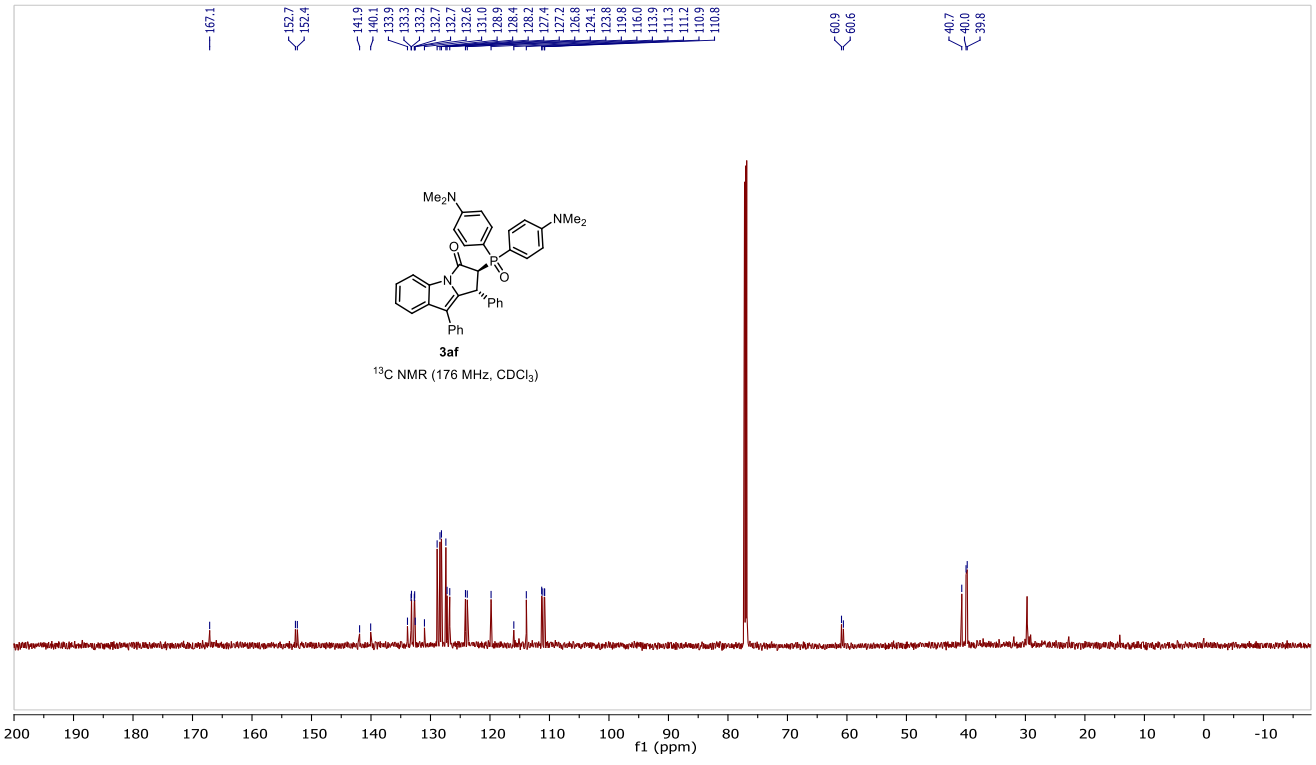
3ae

^{19}F NMR (376 MHz, $CDCl_3$)



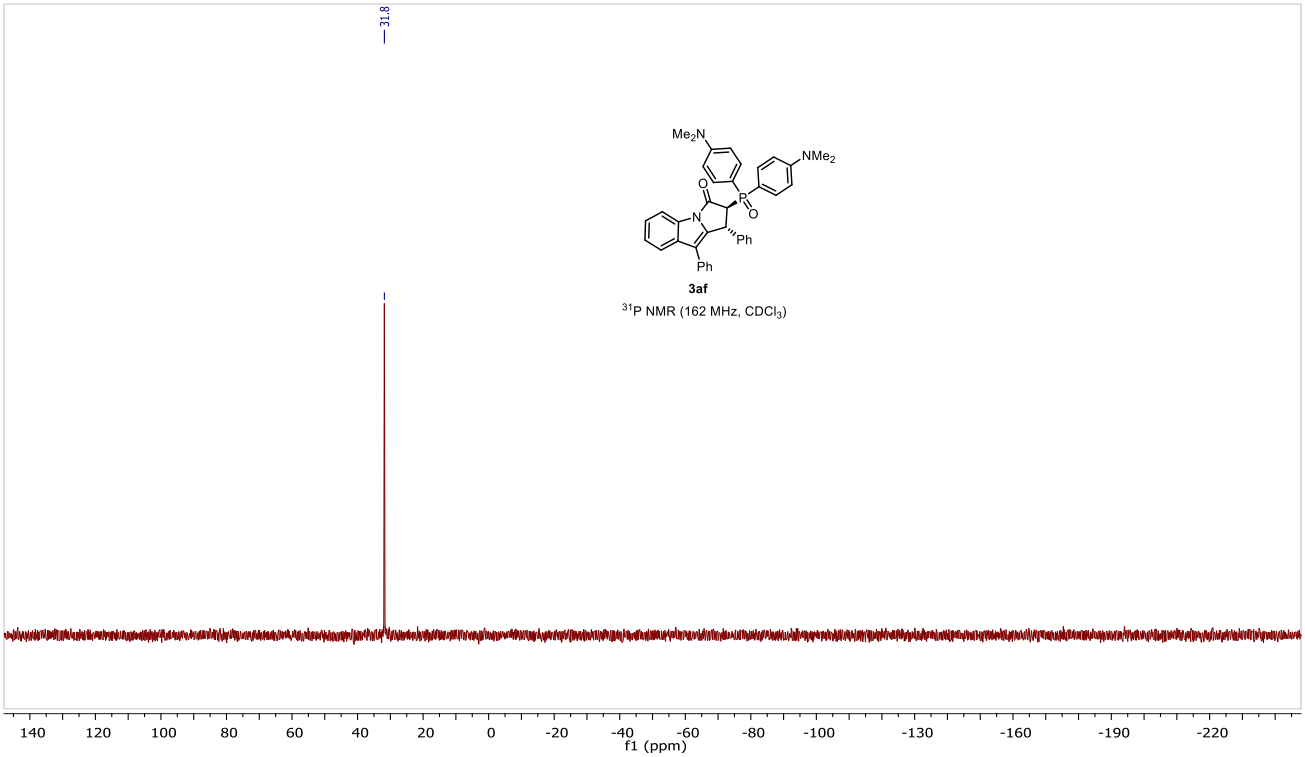
3af

^{1}H NMR (500 MHz, $CDCl_3$)



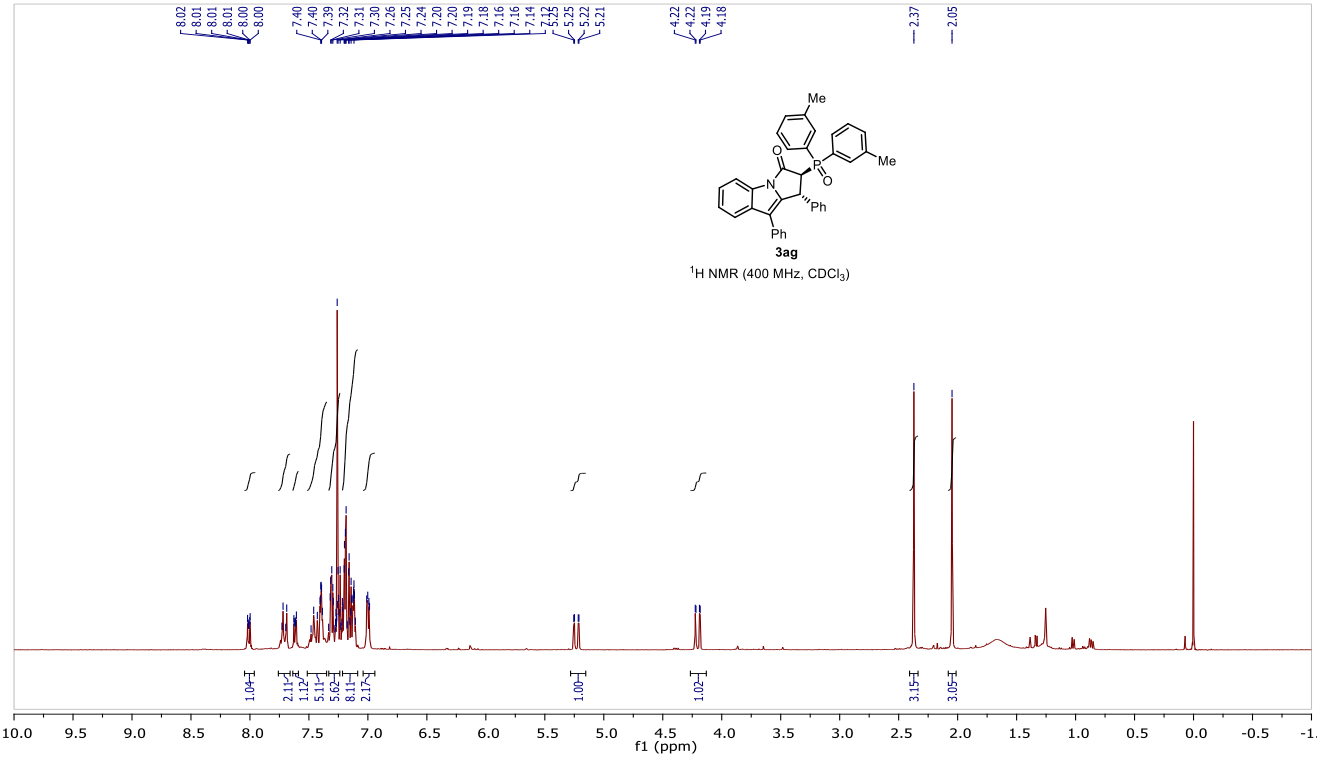
3af

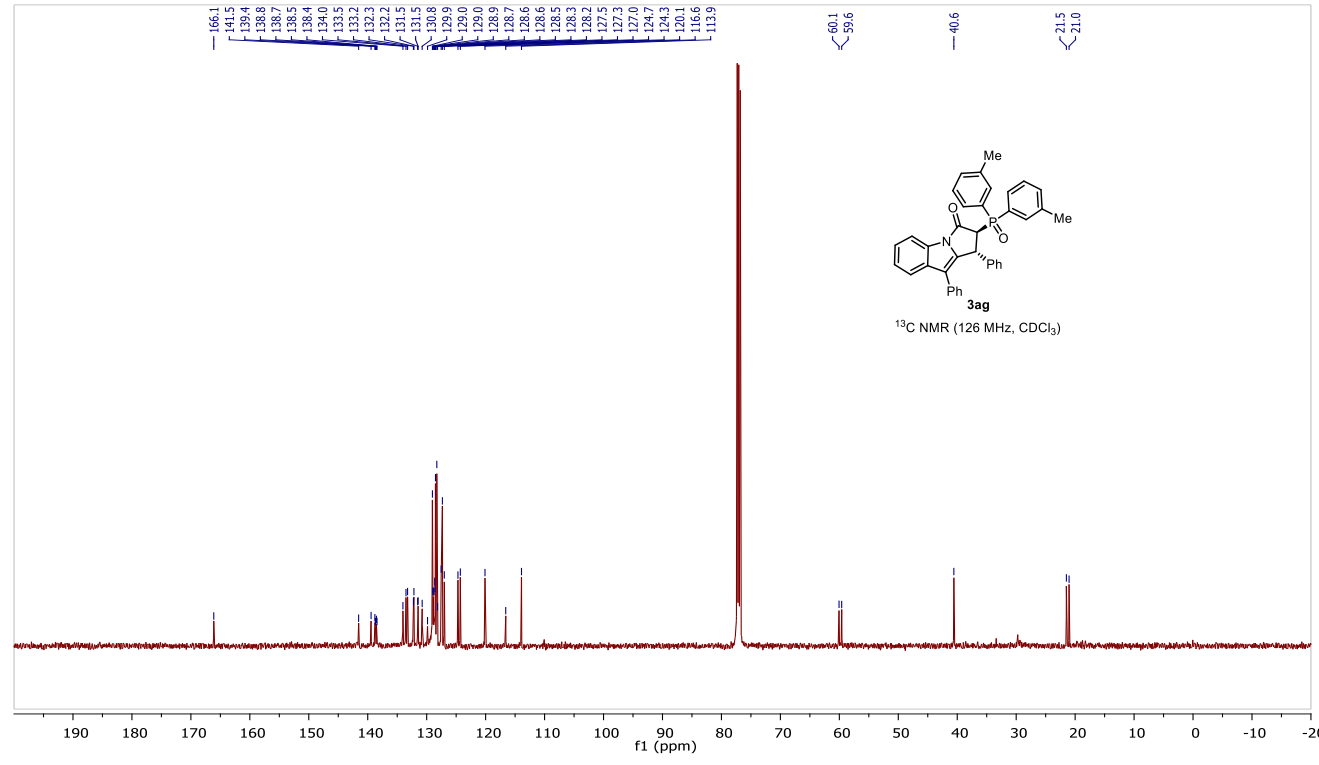
^{13}C NMR (176 MHz, $CDCl_3$)

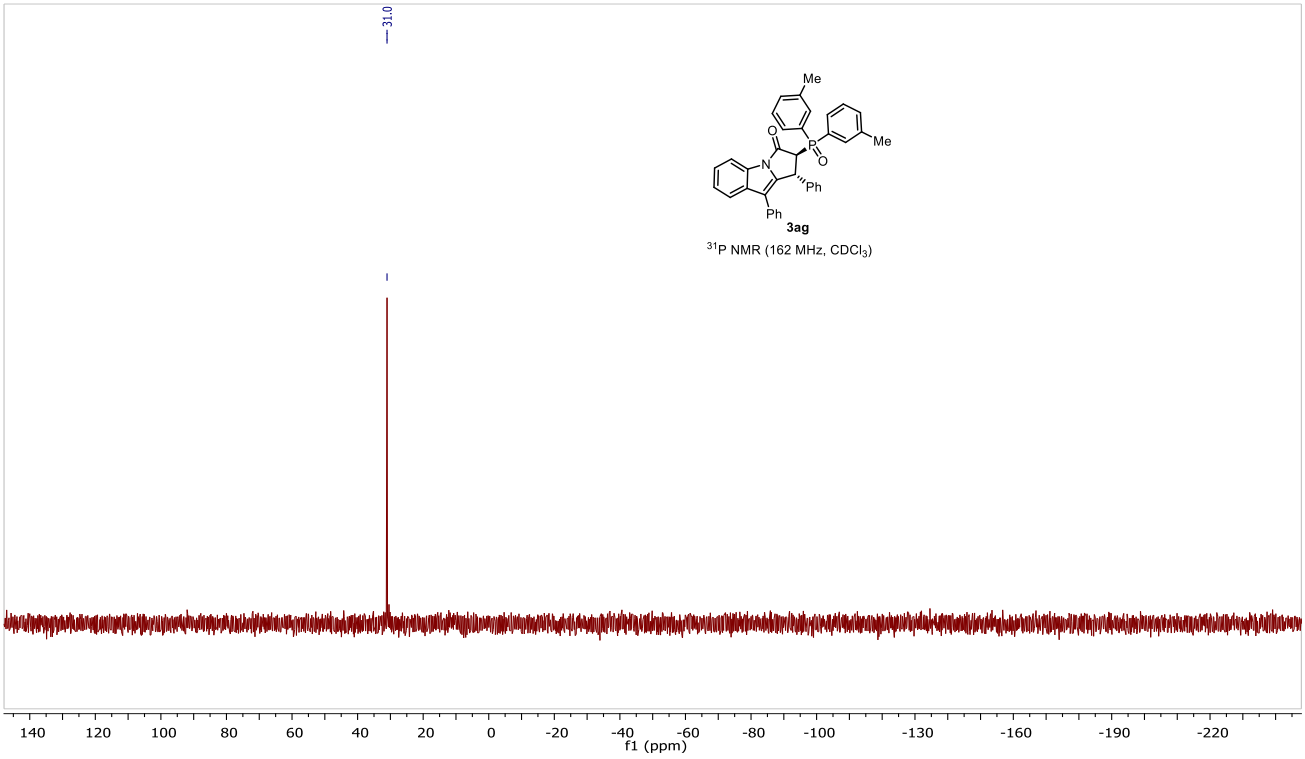


3af

^{31}P NMR (162 MHz, $CDCl_3$)

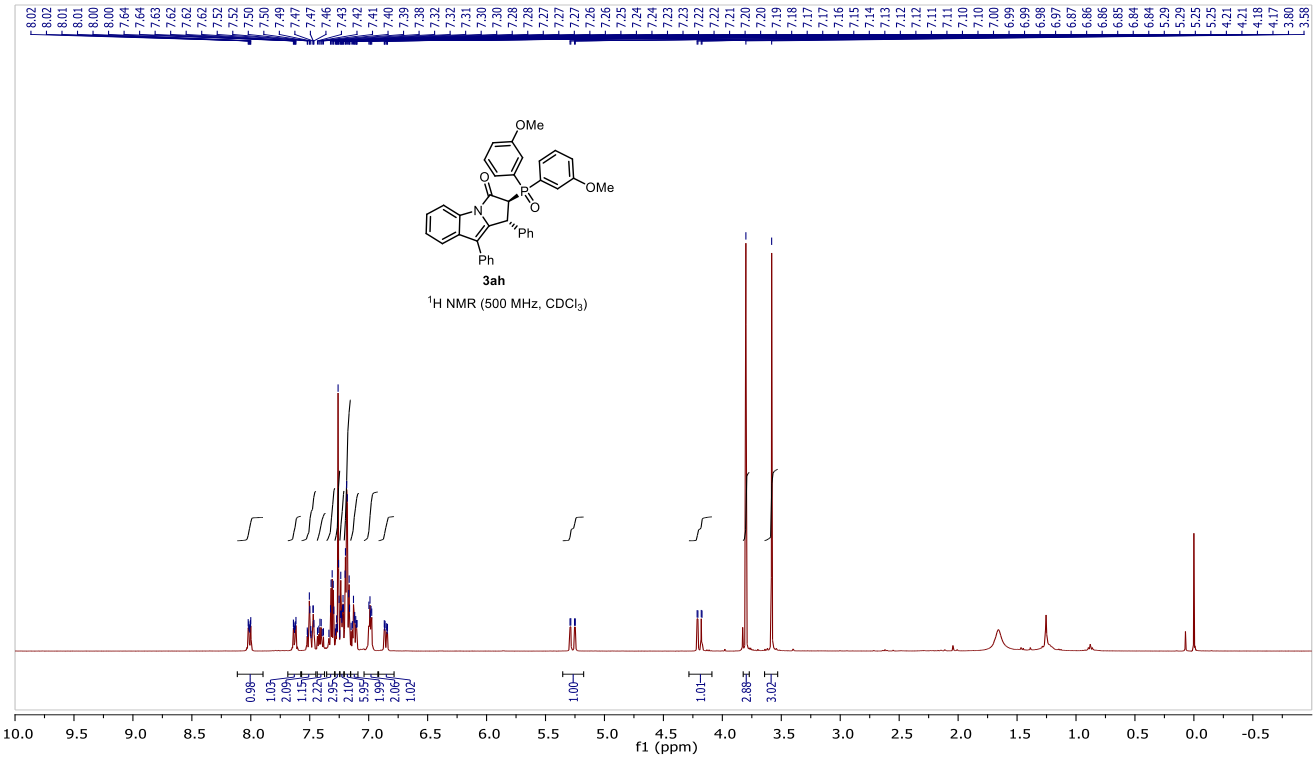

8.02
8.01
8.01
8.01
8.00
8.00
7.40
7.40
7.39
7.32
7.31
7.30
7.26
7.25
7.24
7.20
7.20
7.19
7.18
7.16
7.16
7.14
7.12
5.25
5.22
5.21
4.22
4.22
4.19
4.18
2.37
2.05
Me
Me
Ph
Ph
3ag
1H NMR (400 MHz, CDCl3)
1.04
2.15
1.12
5.11
5.62
8.11
2.17
1.00
1.02
3.15
3.05
f1 (ppm)

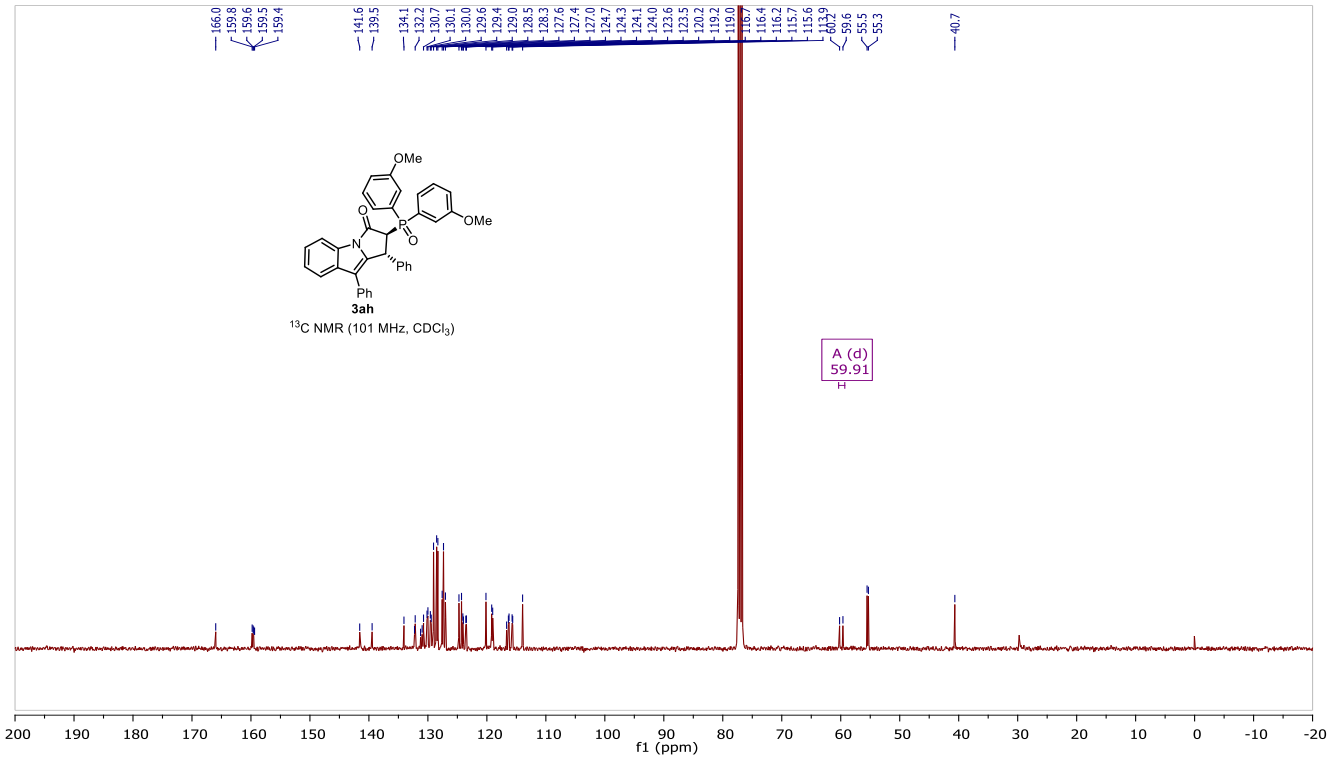

166.1
141.5
139.4
138.8
138.7
138.5
138.4
134.0
133.5
133.2
132.3
132.2
131.5
131.5
130.8
129.9
129.0
129.0
128.9
128.7
128.6
128.6
128.5
128.3
128.2
127.5
127.3
127.0
124.7
124.3
120.1
116.6
113.9
60.1
59.6
40.6
21.5
21.0
Me
Me
Ph
Ph
3ag
13C NMR (126 MHz, CDCl3)
f1 (ppm)

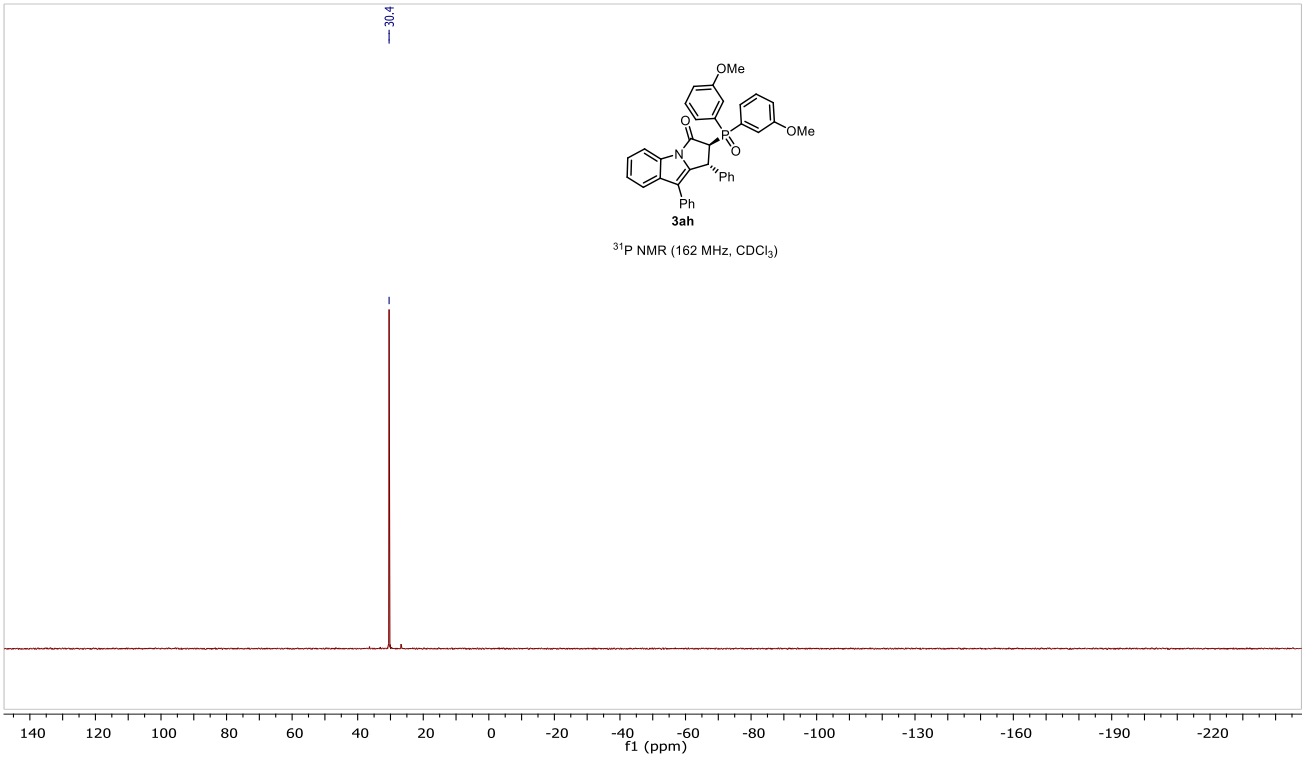


3ag

^{31}P NMR (162 MHz, $CDCl_3$)

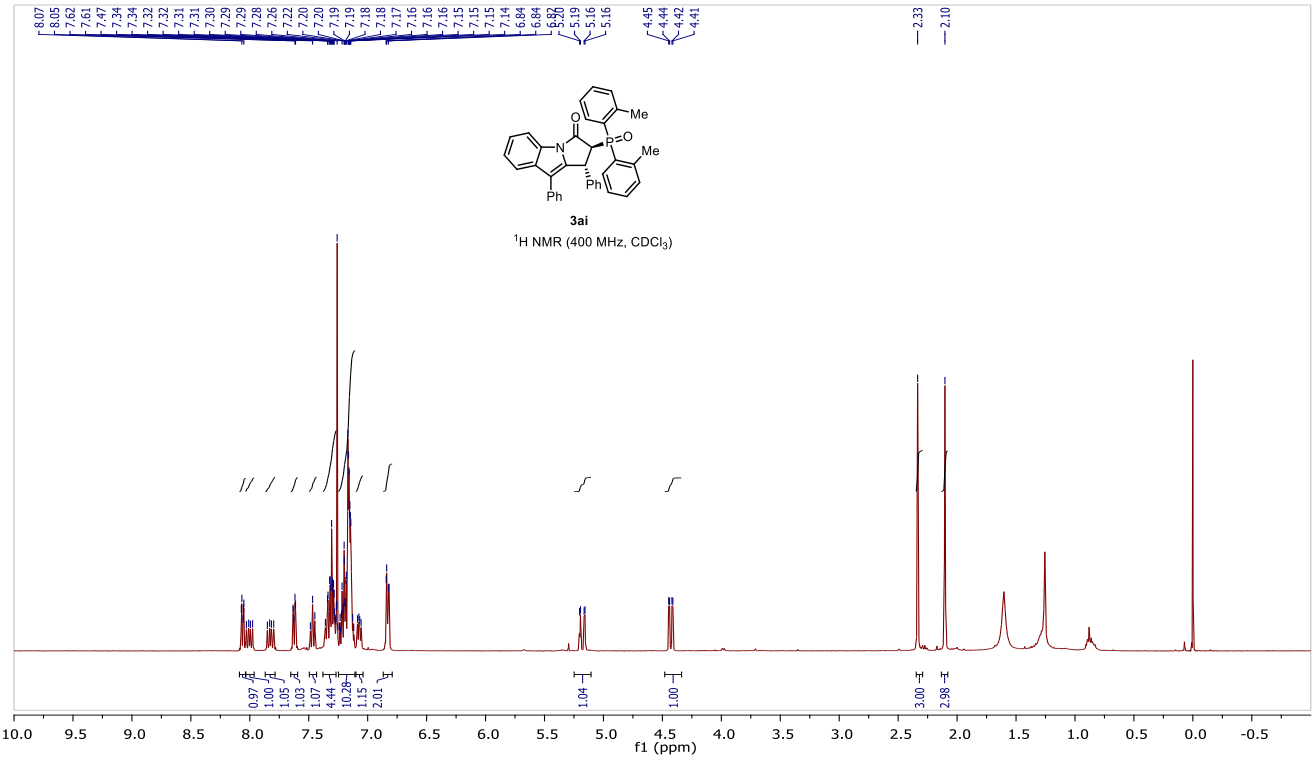

OMe
OMe
Ph
Ph
3ah
1H NMR (500 MHz, CDCl3)
f1 (ppm)

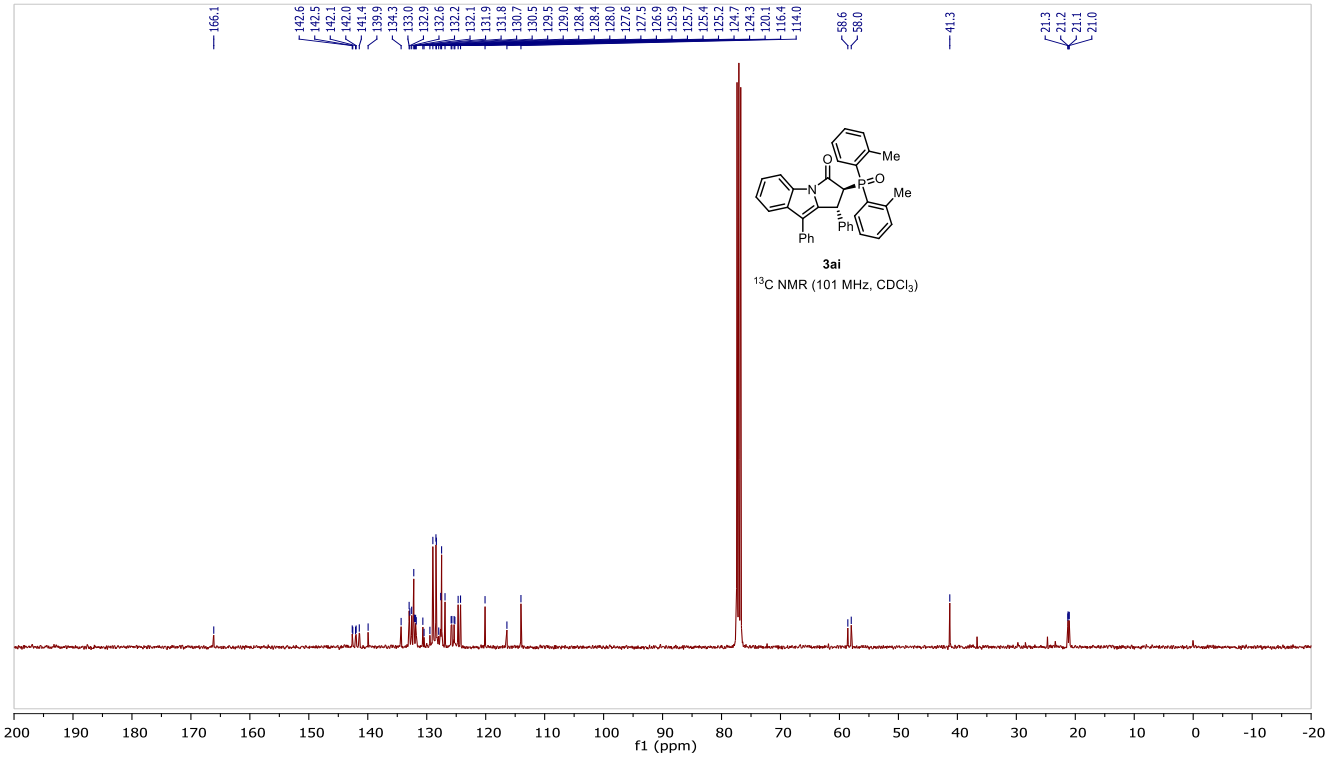

OMe
OMe
Ph
Ph
3ah
13C NMR (101 MHz, CDCl3)
A (d)
59.91
f1 (ppm)

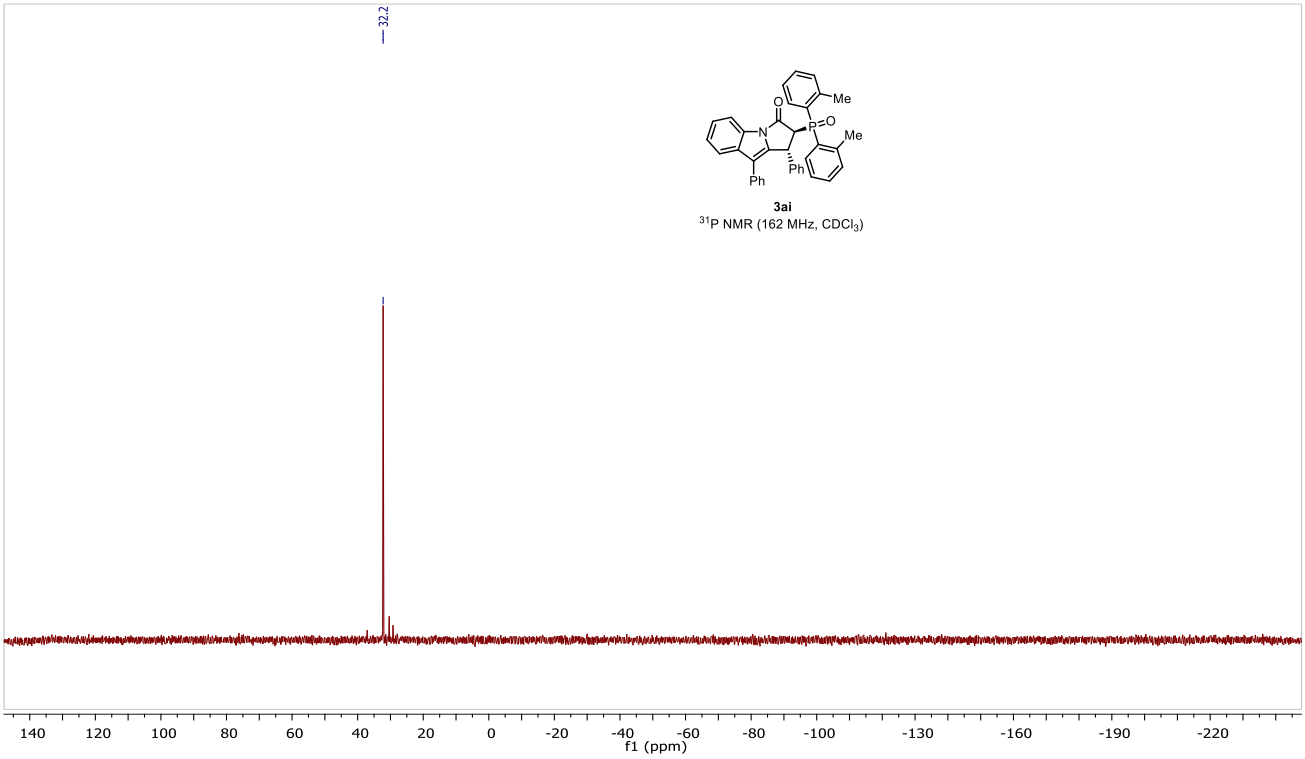


3ah

^{31}P NMR (162 MHz, $CDCl_3$)

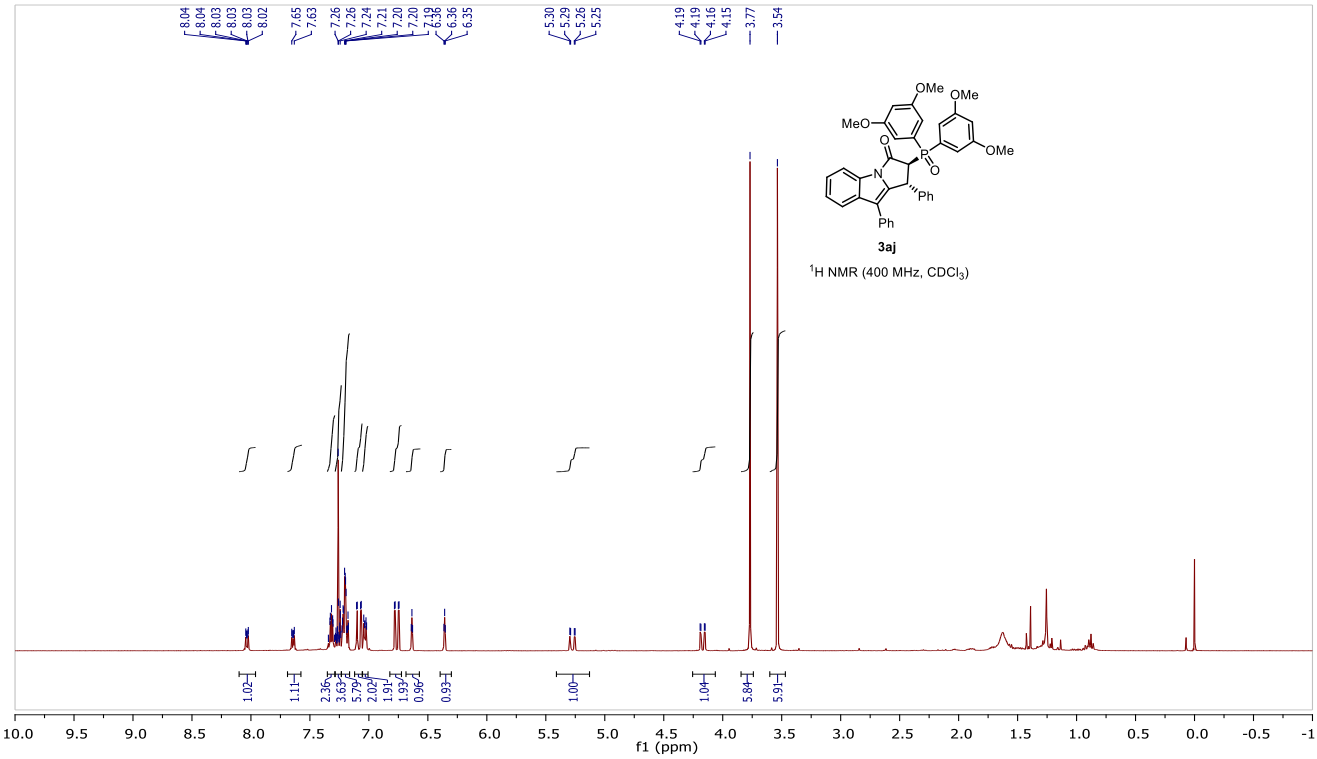

3ai
1H NMR (400 MHz, CDCl3)
f1 (ppm)

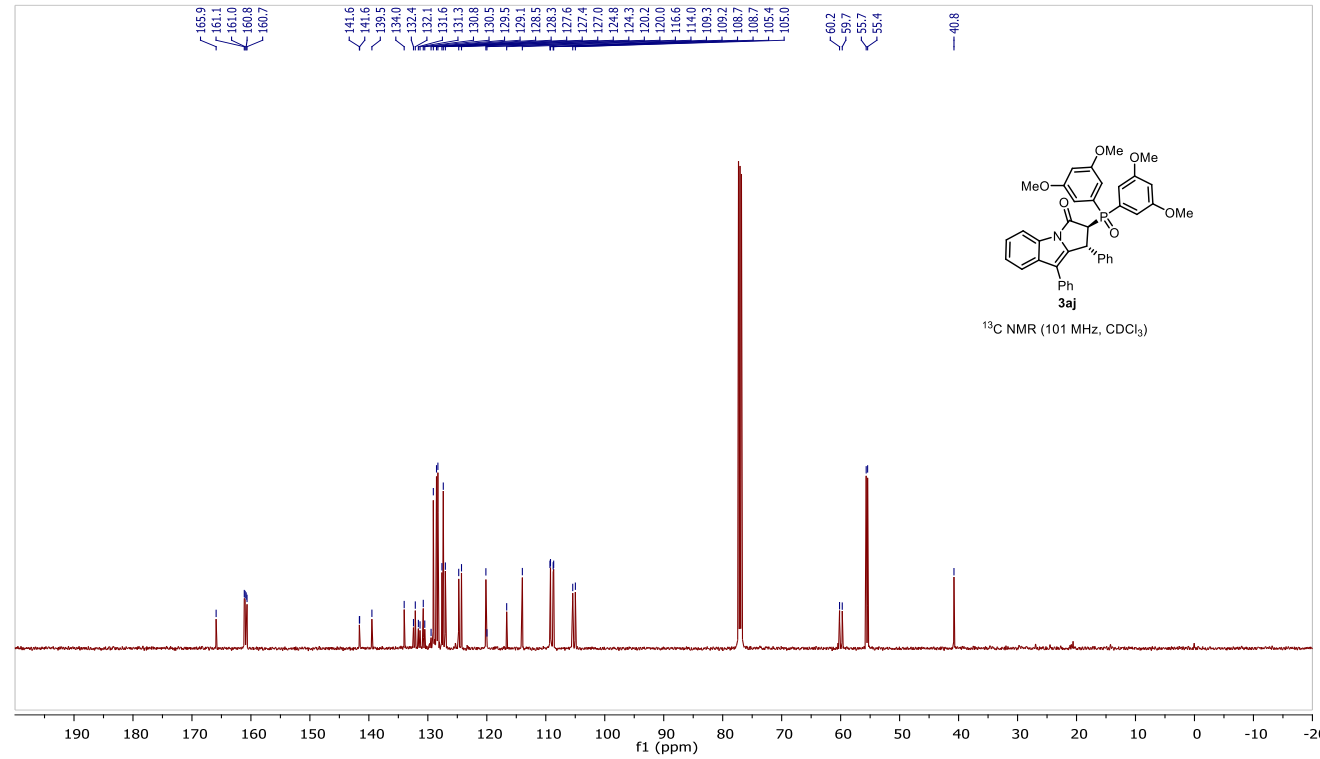

3ai
13C NMR (101 MHz, CDCl3)
f1 (ppm)

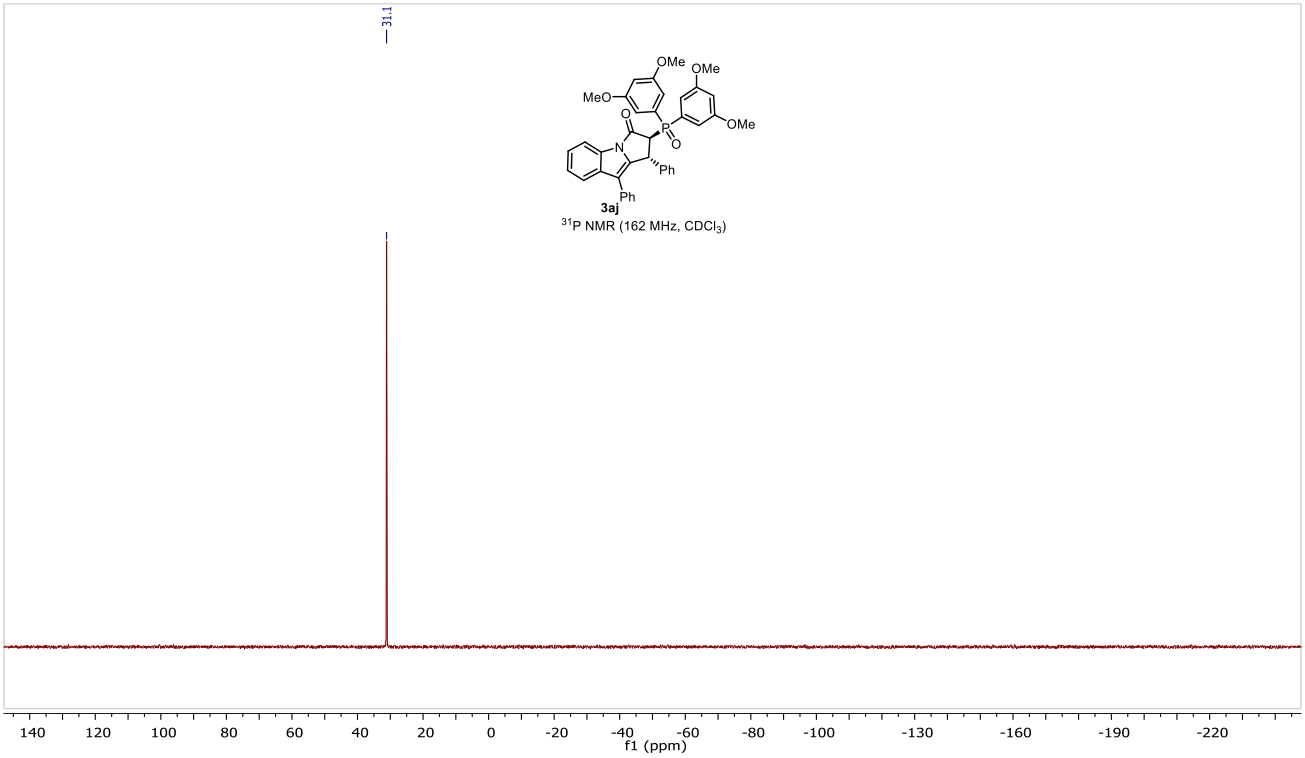


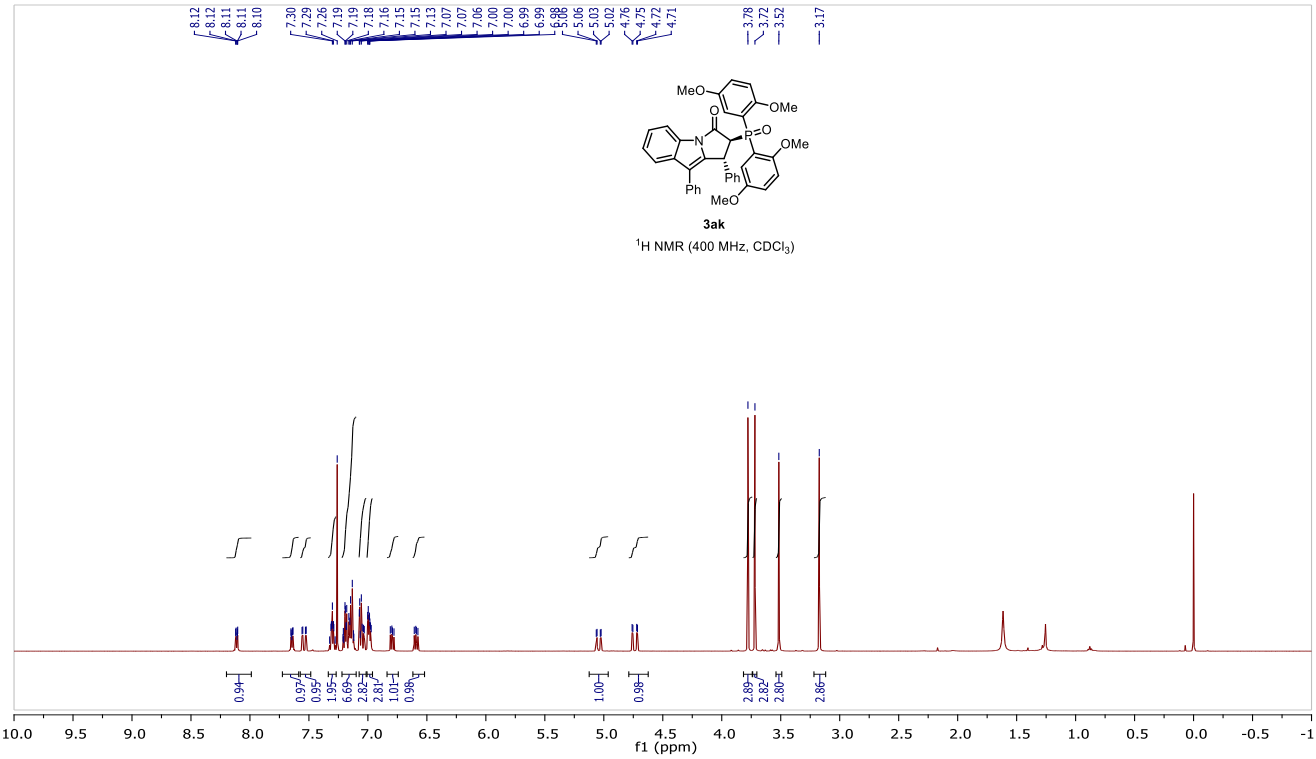
3ai

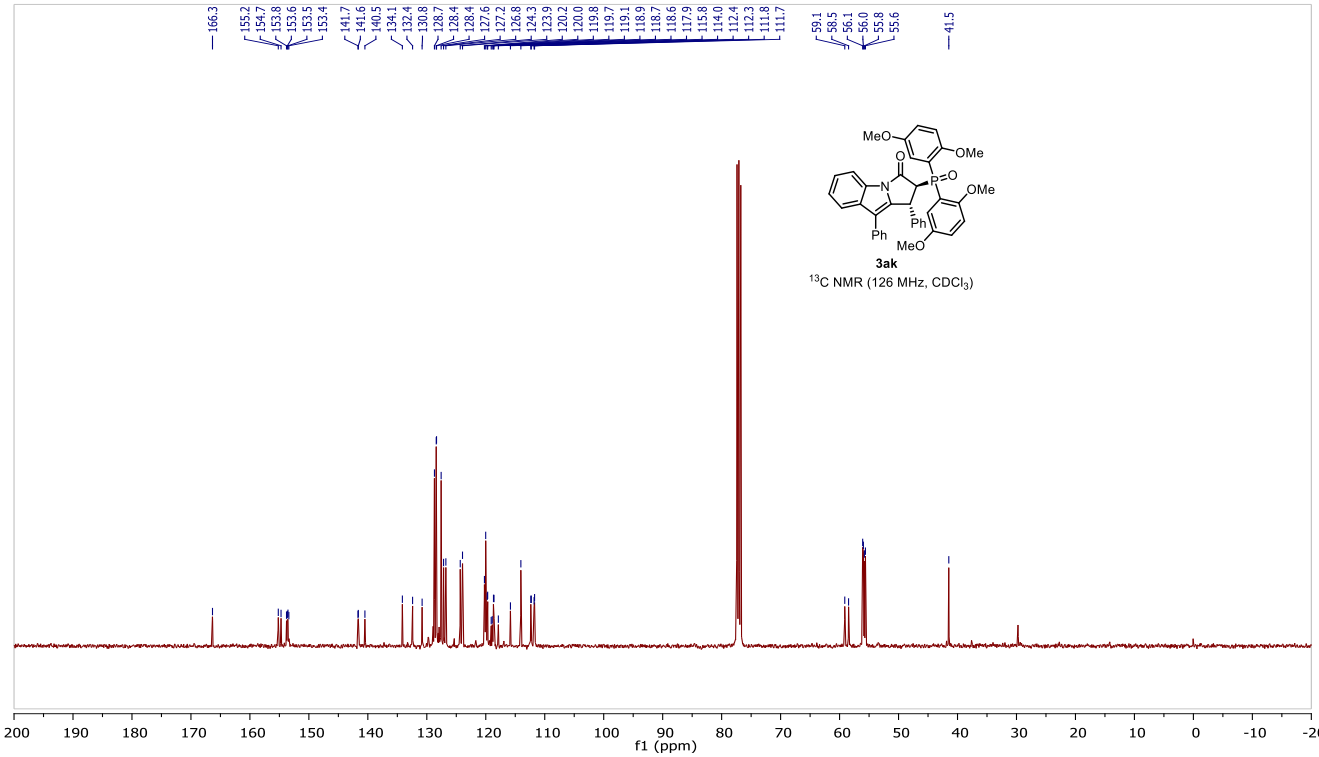
^{31}P NMR (162 MHz, $CDCl_3$)

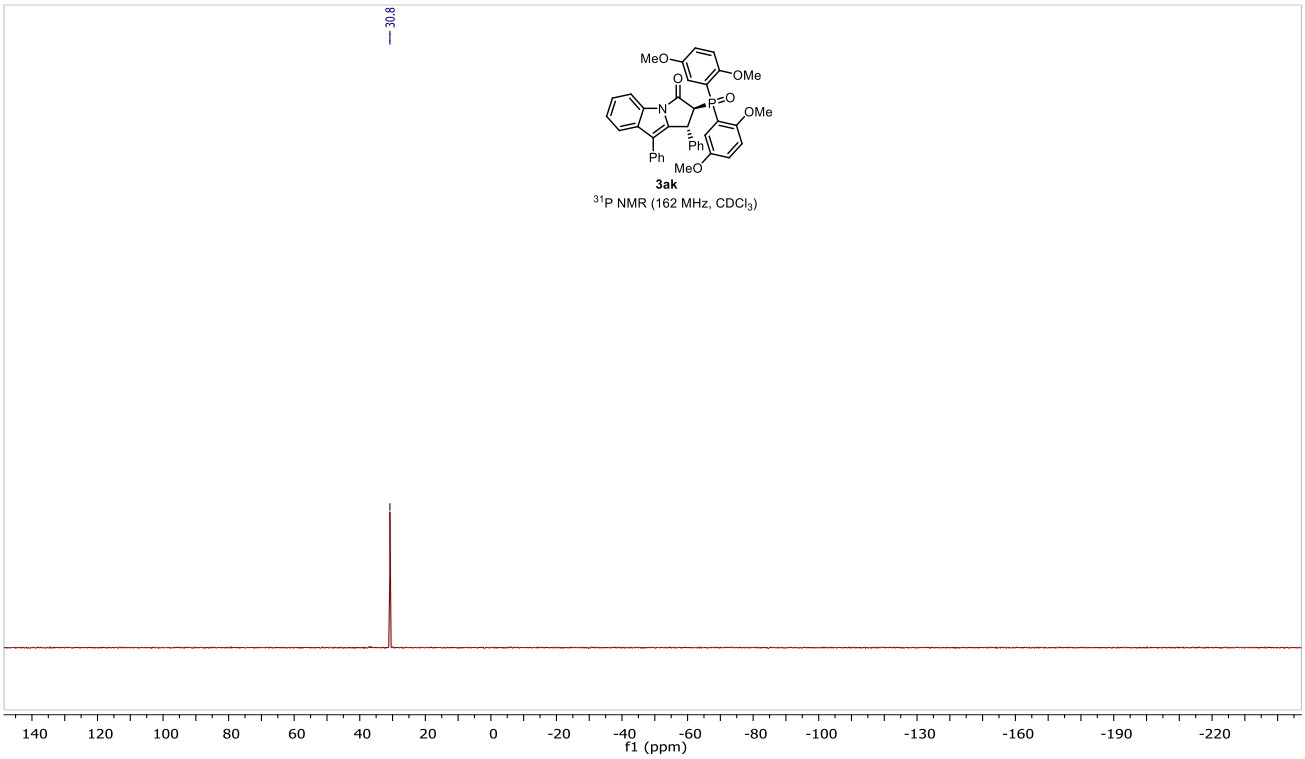

8.04
8.04
8.03
8.03
8.03
8.02
7.65
7.63
7.26
7.26
7.24
7.21
7.20
7.20
6.38
6.36
6.35
5.30
5.29
5.26
5.25
4.19
4.19
4.16
4.15
3.77
3.54
OMe
OMe
MeO
OMe
O
P
O
N
Ph
Ph
3aj
1H NMR (400 MHz, CDCl3)
1.02
1.11
2.36
3.63
5.79
2.02
1.91
1.93
0.96
0.93
1.00
1.04
5.84
5.91
f1 (ppm)


165.9
161.1
161.0
160.8
160.7
141.6
141.6
139.5
134.0
132.4
132.1
131.6
131.3
130.8
130.5
129.5
129.1
128.5
128.3
127.6
127.4
127.0
124.8
124.3
120.2
120.0
116.6
114.0
109.3
109.2
108.7
108.7
105.4
105.0
60.2
59.7
55.7
55.4
40.8
OMe
OMe
MeO
OMe
O
P
O
N
Ph
Ph
3aj
13C NMR (101 MHz, CDCl3)
f1 (ppm)


31.1
OMe
OMe
MeO
OMe
O
P
O
N
Ph
Ph
3aj
31P NMR (162 MHz, CDCl3)
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
f1 (ppm)

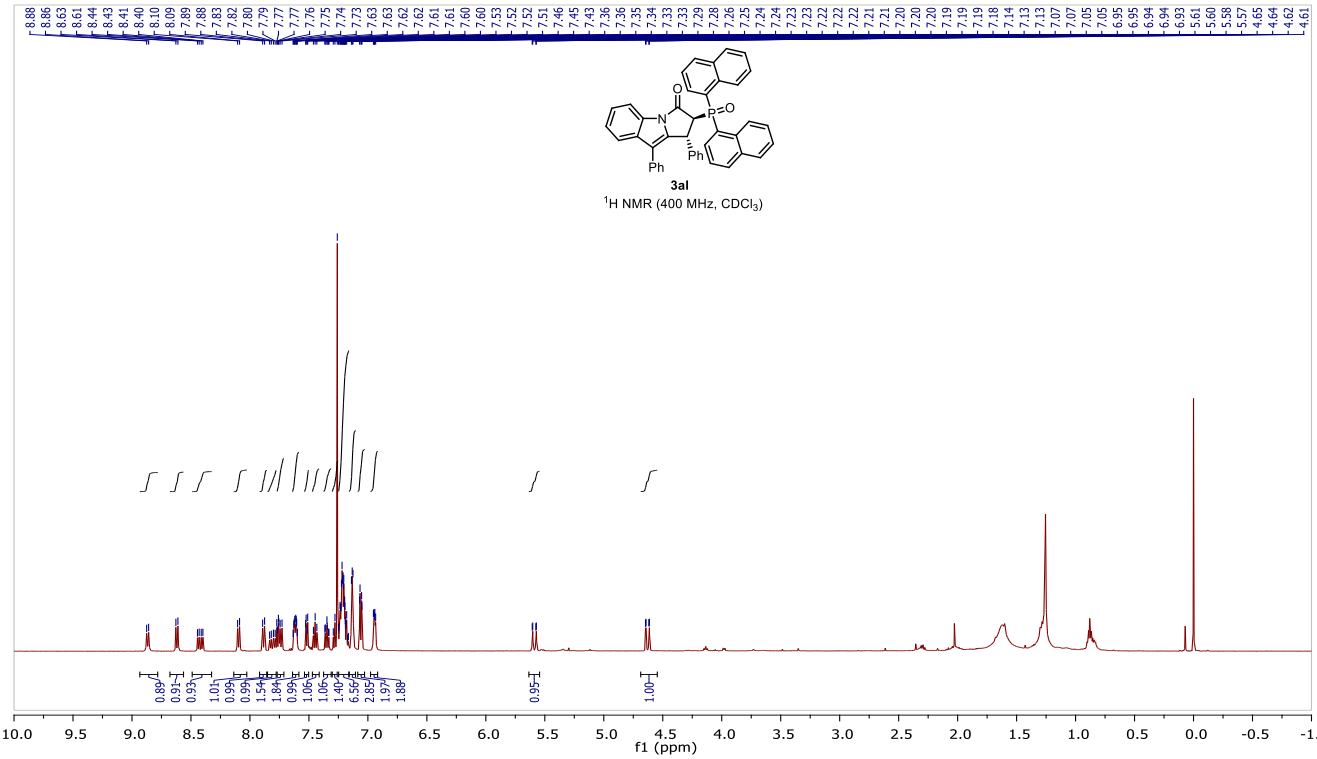

8.12
8.12
8.11
8.11
8.10
7.30
7.29
7.26
7.19
7.19
7.18
7.16
7.15
7.15
7.13
7.07
7.07
7.06
7.00
7.00
6.99
6.99
5.08
5.06
5.03
5.02
4.76
4.75
4.72
4.71
3.78
3.72
3.52
3.17
MeO
OMe
O
N
P=O
OMe
Ph
Ph
MeO
3ak
1H NMR (400 MHz, CDCl3)
0.94
0.97
0.99
1.95
6.69
2.82
2.81
1.01
0.98
1.00
0.98
2.89
2.82
2.80
2.86
10.0
9.5
9.0
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
-0.5
-1.0
f1 (ppm)

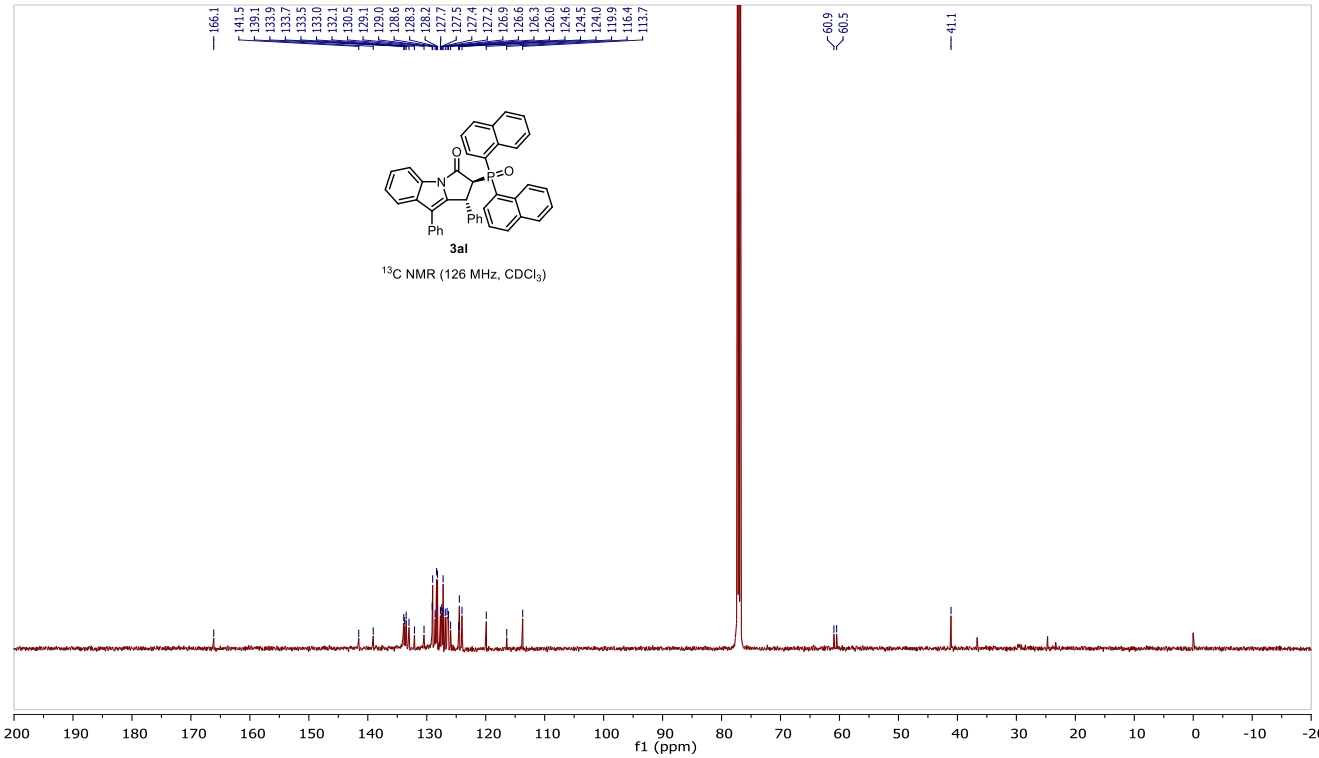

166.3
155.2
154.7
153.8
153.6
153.5
153.4
141.7
141.6
140.5
134.1
132.4
130.8
128.7
128.4
128.4
127.6
127.2
126.8
124.3
123.9
120.2
120.0
119.8
119.7
119.1
118.9
118.7
118.6
117.9
115.8
114.0
112.4
112.3
111.8
111.7
59.1
58.5
56.1
56.0
55.8
55.6
41.5
MeO
OMe
O
N
P=O
OMe
Ph
Ph
MeO
3ak
13C NMR (126 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

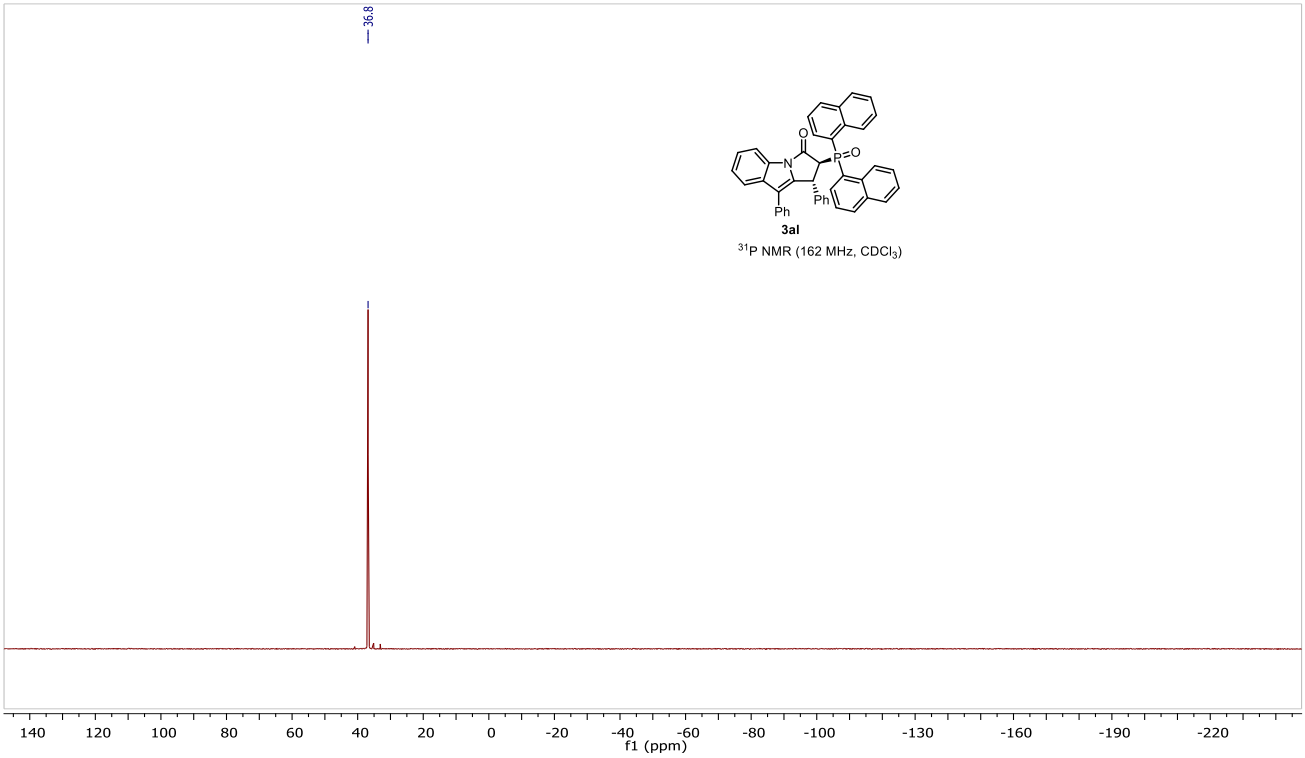


3ak

^{31}P NMR (162 MHz, $CDCl_3$)


3al
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


3al
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)


36.8
Ph
Ph
3al
31P NMR (162 MHz, CDCl3)
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
f1 (ppm)