Supplementary Information

DBU-promoted cascade phosphorylation/cyclization for the synthesis of phosphorylated 3-aminoindoles

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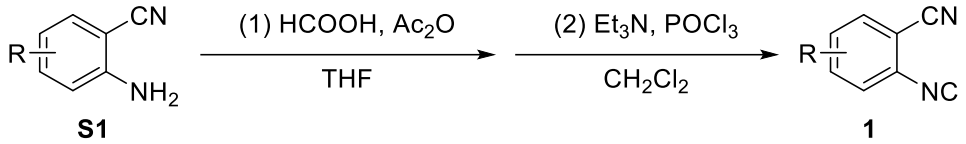
1. General Information

All reagents were commercially available and used without further purification, unless otherwise indicated. 2-Isocyanobenzonitriles[1] and diarylphosphine oxides[2] were prepared following the literature procedures. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Chromatography was carried out on flash silica gel (300−400 mesh). All new compounds were fully characterized. ^{1}H, ^{13}C, ^{19}F, ^{31}P NMR data were recorded on Bruker Avance 400 MHz or 500 MHz spectrometer at room temperature. All chemical shifts (δ) were given in ppm and coupling constants (*J*) were provided in Hz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), broad (br), doublet of doublet (dd), doublet of triplet (dt), triplet of doublet (td), and multiplet (m). Calibrated to $CDCl_3$ as the internal reference (7.26 and 77.16 ppm for ^{1}H and ^{13}C NMR spectra, respectively), DMSO-d_6 (2.50 and 39.52 ppm for ^{1}H and ^{13}C NMR spectra, respectively). Melting points were determined with X-4 micro melting point apparatus and uncorrected. High-resolution mass spectra (HRMS) were recorded on Agilent 6200 LC/MS TOF using ESI in positive mode. Data for X-ray crystal structure determinations were obtained with a Bruker SMART Bruker Platon II area detector diffractometer.

2. Preparation of Substrates

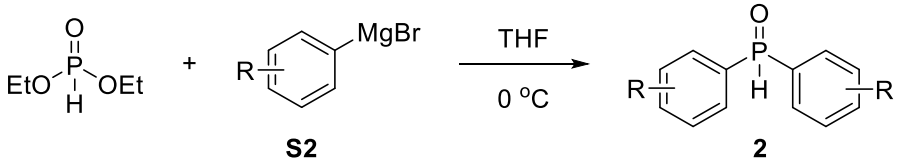
2.1 General procedure for the preparation of 2-isocyanobenzonitriles



S1 **1**

2-Isocyanobenzonitriles were prepared following the literature procedures.[1] To an oven-dried flask equipped with a dropping funnel, **S1** (5 mmol) and THF (15 mL) were cooled to 0 ℃. Acetic formic anhydride, which was prepared from the reaction of acetic anhydride (1.2 mL) with formic acid (0.6 mL) at 55 ℃ for 2 h, was transferred to the dropping funnel and dropped to the solution of **S1** at 0 ℃. After the addition was complete, the mixture was warmed to room temperature and stirred for 2 h. Then, the mixture was quenched by sat. aqueous solution of $NaHCO_3$ and extracted with EA three times. The extract was dried over Na_2SO_4 and concentrated under reduced pressure to give formamide. This formamide was used for the subsequent dehydration without further purification. To an oven-dried flask equipped with a dropping funnel, CH_2Cl_2 (20 mL), Et_3N (5 mL, 30 mmol) and the whole amount of formamide obtained above were added under Ar atmosphere and cooled to 0 ℃. $POCl_3$ (0.6 mL, 6 mmol) was added dropwise, and the mixture was stirred for 2 h at 0 ℃ after the addition was complete. Then, the mixture was quenched by sat. aqueous solution of Na_2CO_3 and stirred for 0.5 h. The mixture was extracted with CH_2Cl_2 three times, dried over Na_2SO_4 and evaporated under reduced pressure. The compound was purified by column chromatography (PE/EA = 6:1) to give the desired substrates **1**.

2.2 General procedure for the preparation of diarylphosphine oxides



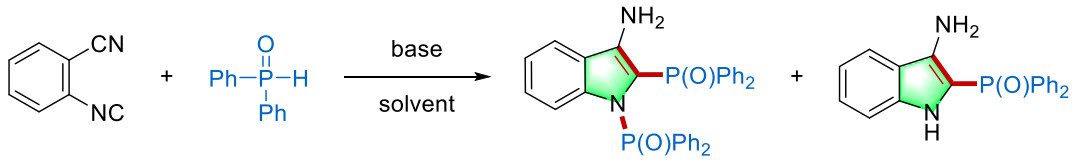
S2 **2**

Diarylphosphine oxides were prepared following the literature procedures.[2] A 100 mL dry bottom flask equipped with a magnetic stir bar was charged with aryl magnesium

bromide **S2** (32.6 mmol) in tetrahydrofuran under Ar atmosphere followed by the addition of diethylphosphite (1.29 mL, 10.0 mmol) dropwisely at 0 ^{o}C. This mixture was stirred at 0 ^{o}C for 15 minutes and at room temperature for another 2 h. After reaction was finished, the system was quenched by aqueous NH_4Cl solution slowly at 0 ^{o}C which was further extracted by chloroform. Organic phase was washed with brine, dried over Na_2SO_4. After the solvent had been removed under reduced pressure, the residue was purified by column chromatography (PE/EA = 1:1) to give the target diarylphosphine oxide **2**.

3. Detailed Screening Experiments

Table S1: Optimization of reaction conditions[a]



1a **2a** **3aa** **4aa**

Entry	Base (equiv.)	Solvent	**2a** (equiv.)	Time (h)	Temp. (°C)	Yield[b] (%) (**3aa**/**4aa**)
1	DBU (2.0)	DCE	2.0	5	RT	76/trace
2	DBU (2.0)	DMSO	2.0	5	RT	63/12
3	DBU (2.0)	Toluene	2.0	5	RT	60/11
4	DBU (2.0)	MeOH	2.0	5	RT	46/trace
5	DBU (2.0)	1,4-Dioxane	2.0	5	RT	58/16
6	DBU (2.0)	DCM	2.0	5	RT	67/ trace
7	DBU (2.0)	CH_3CN	2.0	5	RT	59/21
8	DBU (2.0)	EA	2.0	5	RT	56/14
9	DBU (2.0)	Acetone	2.0	5	RT	57/trace
10	Et_3N (2.0)	DCE	2.0	5	RT	23/trace
11	Py (2.0)	DCE	2.0	5	RT	NR
12	DIPEA (2.0)	DCE	2.0	5	RT	28/trace
13	DABCO (2.0)	DCE	2.0	5	RT	NR
14	Cs_2CO_3 (2.0)	DCE	2.0	5	RT	38/10
15	*t*-BuONa (2.0)	DCE	2.0	5	RT	43/trace
16	DBU (2.0)	DCE	1.0	5	RT	42/trace
17	DBU (1.0)	DCE	2.0	5	RT	48/trace
18	-	DCE	2.0	5	RT	0
19	**DBU (2.5)**	**DCE**	**2.5**	**5**	**RT**	**81/12**
20	DBU (2.5)	DCE	2.5	5	50	65/20
21	DBU (2.5)	DCE	2.5	3	RT	67/trace
22	DBU (2.5)	DCE	2.5	8	RT	69/23
23[c]	DBU (2.5)	DCE	2.5	5	RT	0
24	DBU (2.5)	CH_3CN	2.5	5	50	54/34
25	DBU (2.5)	CH_3CN	2.5	5	80	48/31
26	DBU (2.5)	CH_3CN	2.5	12	50	33/53
27	DBU (2.5)	CH_3CN	2.5	18	50	14/71
28	**DBU (2.5)**	**CH_3CN**	**2.5**	**24**	**50**	**trace/82**

[a] Reaction conditions: **1a** (0.1 mmol), **2a**, Base, Solvent (1.0 mL) under an argon atmosphere.
[b] Isolated yield. [c] Air atmosphere.

4. General Procedures

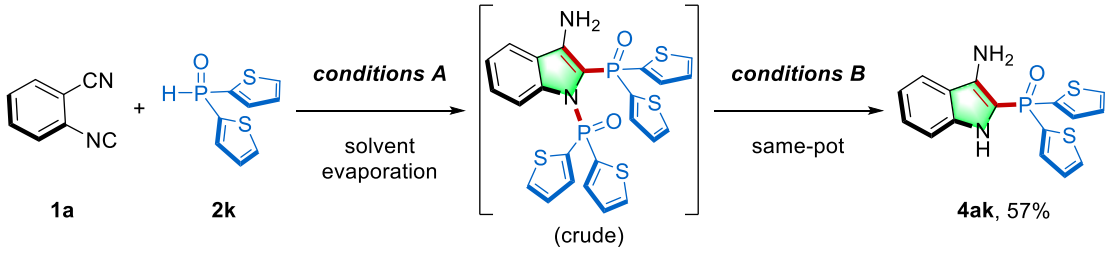
4.1 General procedure for the diphosphorylation cyclization of 2-isocyanobenzonitriles with diarylphosphine oxides (Conditions A)

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar was charged with **1** (0.1 mmol, 1.0 equiv.), **2** (0.25 mmol, 2.5 equiv.), and DBU (0.25 mmol, 2.5 equiv.), and then DCE (1.0 mL) was added into the mixture under argon atmosphere. Later, the reaction system was kept stirring at room temperature for 5 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (PE/EA = 1:3) to afford the desired products **3**.

4.2 General procedure for the monophosphorylation cyclization of 2-isocyanobenzonitriles with diarylphosphine oxides (Conditions B)

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar was charged with **1** (0.1 mmol, 1.0 equiv.), **2** (0.25 mmol, 2.5 equiv.), and DBU (0.25 mmol, 2.5 equiv.), and then CH_3CN (1.0 mL) was added into the mixture under argon atmosphere. Later, the reaction system was kept stirring at 50 ℃ for 24 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (PE/EA = 1:3) to afford the desired products **4**.

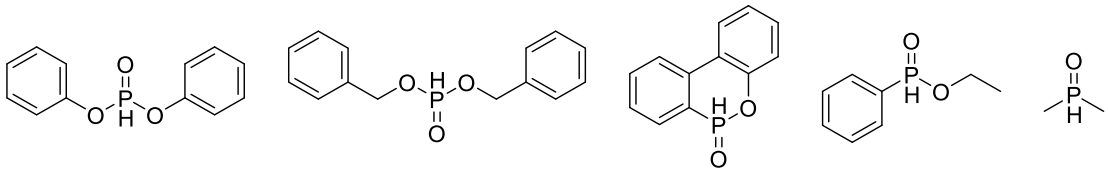
4.3 "Two-step-one-pot" process



An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar was

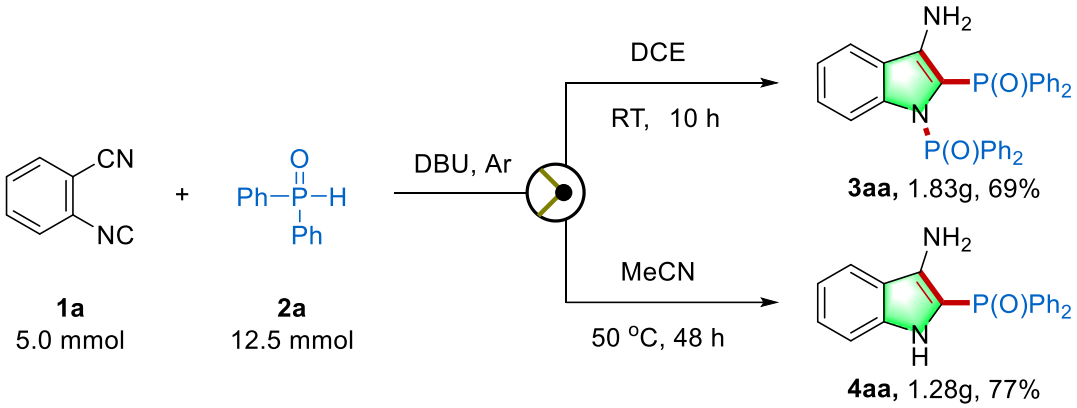
charged with **1a** (0.1 mmol, 1.0 equiv.), **2k** (0.25 mmol, 2.5 equiv.), and DBU (0.25 mmol, 2.5 equiv.), and then DCE (1.0 mL) was added into the mixture under argon atmosphere. After stirring for 5 h under argon at room temperature, the solvent was removed in vacuum. Without further purification, DBU (0.25 mmol, 2.5 equiv.) was added to a solution of the crude product in CH_3CN (1.0 mL) and stirred at 50 ℃ for 24 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (PE/EA = 1:3) to afford the desired product **4ak** (19.7 mg, 57%) for the two steps.

4.4 Unsuccessful substrates



5. Gram-Scale Synthesis and Further Transformations

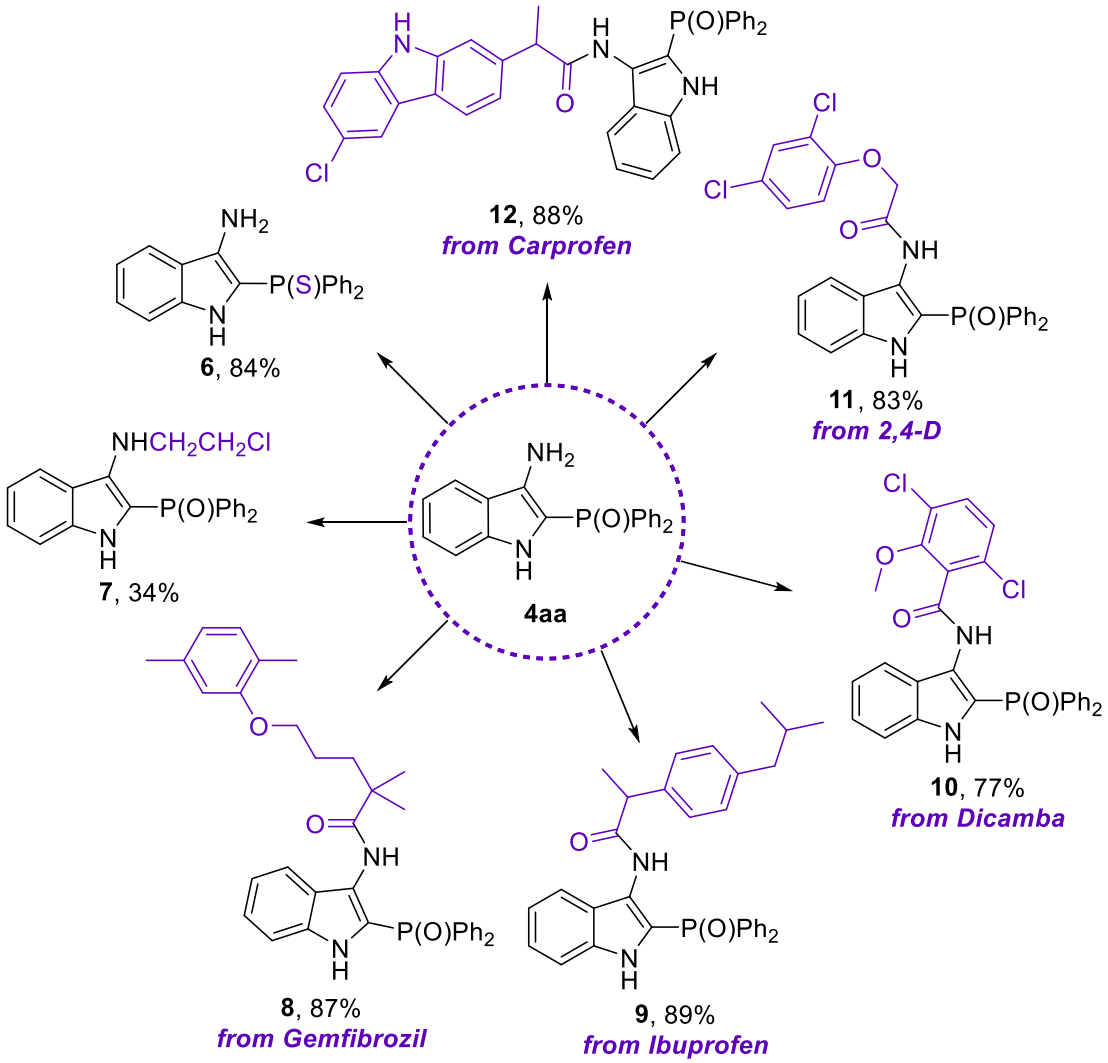
5.1 Gram-scale synthesis



An oven-dried Schlenk tube (100 mL) was equipped with a magnetic stir bar was charged with **1a** (5.0 mmol), **2a** (12.5 mmol), and DBU (12.5 mmol), and then DCE (50 mL) was added into the mixture under argon atmosphere. Later, the reaction system was kept stirring at room temperature for 10 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (PE/EA = 1:3) to afford the desired product **3aa** (1.83g, 69%).

An oven-dried Schlenk tube (100 mL) was equipped with a magnetic stir bar was charged with **1a** (5.0 mmol), **2a** (12.5 mmol), and DBU (12.5 mmol), and then CH_3CN (50 mL) was added into the mixture under argon atmosphere. Later, the reaction system was kept stirring at 50 ℃ for 48 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (PE/EA = 1:3) to afford the desired product **4aa** (1.28g, 77%).

5.2 Further transformations



5.2.1 Procedure for synthesis of derivative 6 [3]

A Schlenk tube was dried under vacuum and allowed to cool. The tube was then placed under argon atmosphere. To a stirred solution of (3-amino-1*H*-indol-2-yl)diphenylphosphine oxide (**4aa**, 0.2 mmol, 1.0 equiv.) in dry THF (2.0 mL) , triethylamine (1.0 mmol, 5.0 equiv.) was added. Trichlorosilane (1.0 mmol, 5.0 equiv.) was then added dropwise to the mixture at room temperature. The mixture was stirred at 80 ℃ for 5 h. Upon confirmation of reaction completion by ^{31}P NMR, S_8 (0.6 mmol, 3.0 equiv.) was added, and the mixture was stirred overnight. Upon confirmation of reaction completion by TLC, the mixture was cooled to 0 ℃ and quenched with NaOH. It was then heated to 60 ℃ for 30 minutes, cooled to room temperature, and extracted with DCM (3 times). The combined organic layers were dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to afford compound **6** (58.4 mg, 84%).

5.2.2 Procedure for synthesis of derivative 7

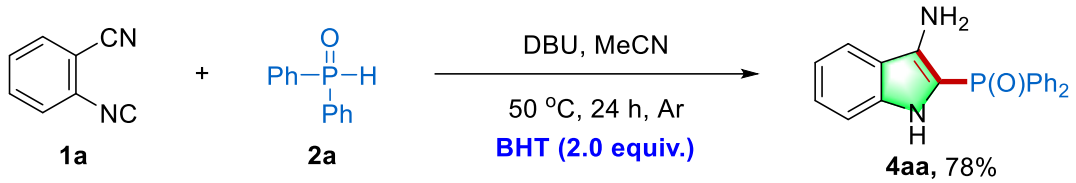
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar was charged with **4aa** (0.2 mmol, 1.0 equiv.), DBU (0.4 mmol, 2.0 equiv.), and then DCE (2.0 mL) was added into the mixture under argon atmosphere. Later, the reaction system was kept stirring at 50 ^{o}C for 24 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography to afford the desired product **7** (26.8 mg, 34%).

5.2.3 Procedure for synthesis of derivatives 8-12 [4]

Carboxylic acids (0.24 mmol, 1.2 equiv.), (3-amino-1*H*-indol-2-yl)diphenylphosphine oxide (**4aa**, 0.2 mmol, 1.0 equiv.) and DMAP (0.3 mmol, 1.5 equiv.) were dissolved in anhydrous DCM (1.0 mL) in a 10 mL Schlenk tube, followed by dropwise addition of EDCI (0.3 mmol, 1.5 equiv.) in DCM (1.0 mL) through dropping funnel at 0 ℃ under argon atmosphere. The mixture was gradually warmed to room temperature, then stirred overnight. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography to afford the desired products **8-12**.

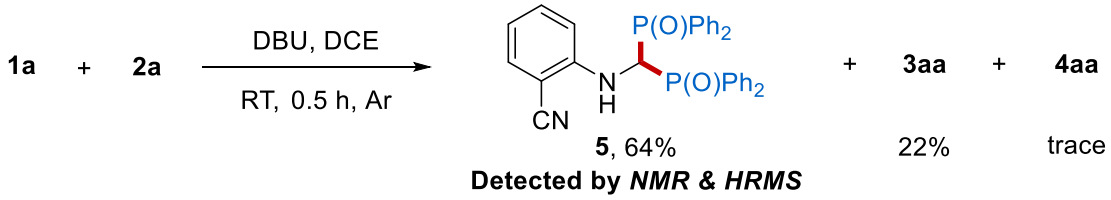
6. Control Experiments

6.1 Reaction with radical scavenger



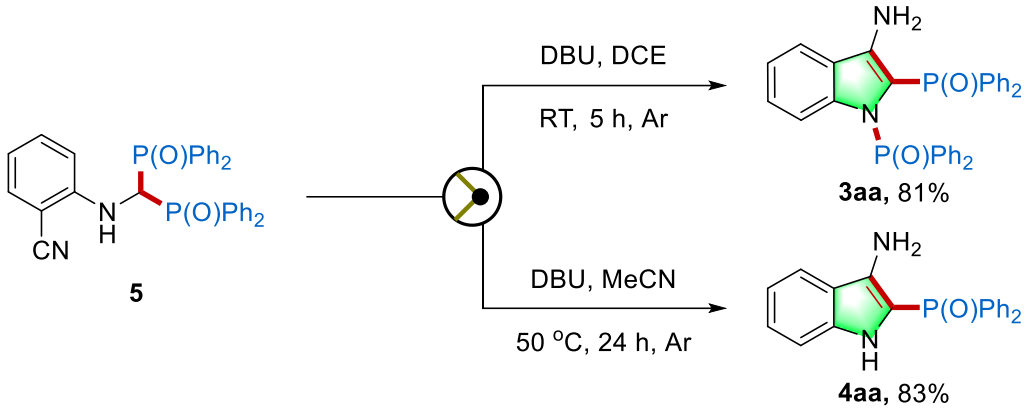
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar was charged with **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.25 mmol, 2.5 equiv.), 2,6-di-*tert*-butyl-4-methylphenol (BHT, 0.2 mmol, 2.0 equiv.), and DBU (0.25 mmol, 2.5 equiv.), and then CH_3CN (1.0 mL) was added into the mixture under argon atmosphere. Later, the reaction system was kept stirring at 50 ℃ for 24 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (PE/EA = 1:3) to afford the corresponding product **4aa** (25.8 mg, 78%).

6.2 Identifying possible reaction intermediate



An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar was charged with **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.25 mmol, 2.5 equiv.), and DBU (0.25 mmol, 2.5 equiv.), and then DCE (1.0 mL) was added into the mixture under argon atmosphere. The reaction system was kept stirring at room temperature under argon for 0.5 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (PE/EA = 1:3) to afford the corresponding products **5** (34.4 mg, 65%) and **3aa** (11.8 mg, 22%), respectively.

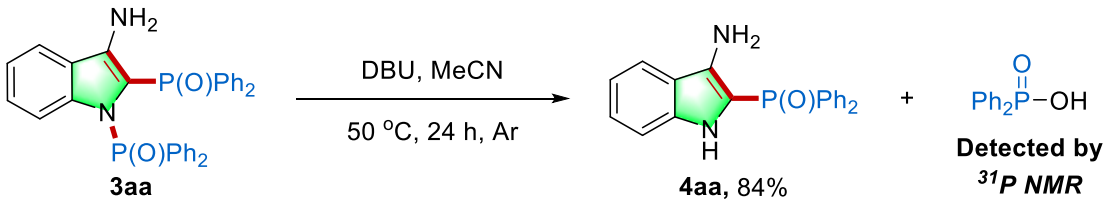
6.3 Further reactions involving intermediate 5



An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar was charged with **5** (0.1 mmol, 1.0 equiv.), DBU (0.25 mmol, 2.5 equiv.), and then DCE (1.0 mL) was added into the mixture under argon atmosphere. Later, the reaction system was kept stirring at room temperature for 5 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (PE/EA = 1:3) to afford the desired product **3aa** (43.2 mg, 81%).

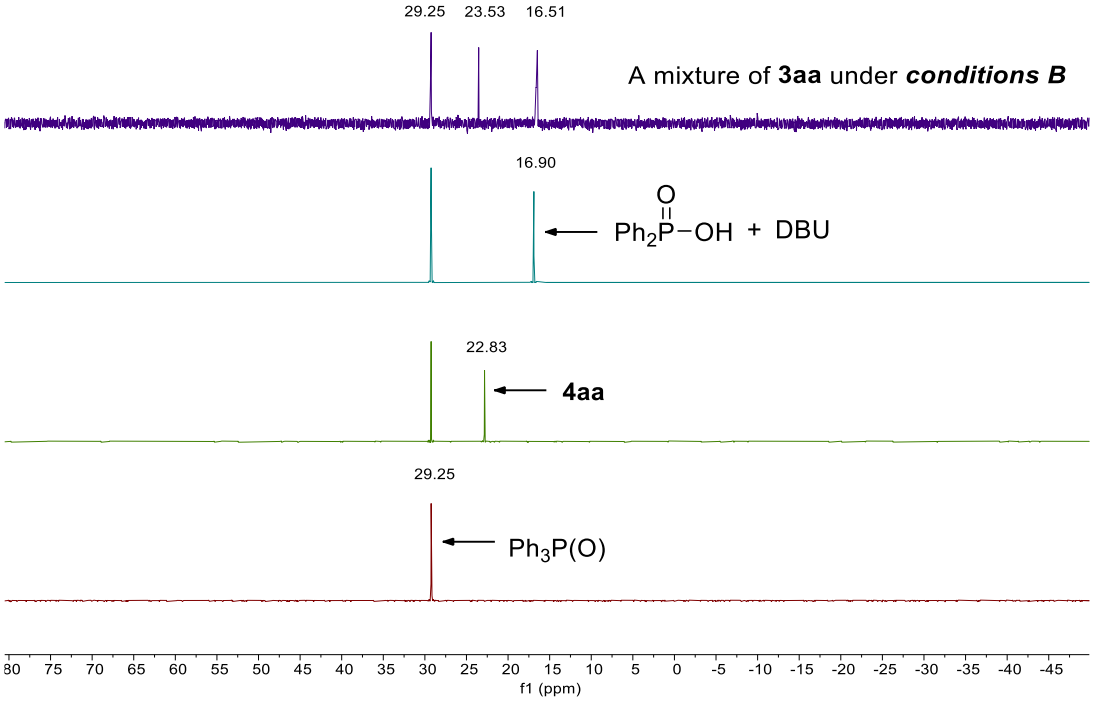
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar was charged with **5** (0.1 mmol, 1.0 equiv.), DBU (0.25 mmol, 2.5 equiv.), and then CH_3CN (1.0 mL) was added into the mixture under argon atmosphere. Later, the reaction system was kept stirring at 50 ℃ for 24 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (PE/EA = 1:3) to afford the desired product **4aa** (27.5 mg, 83%).

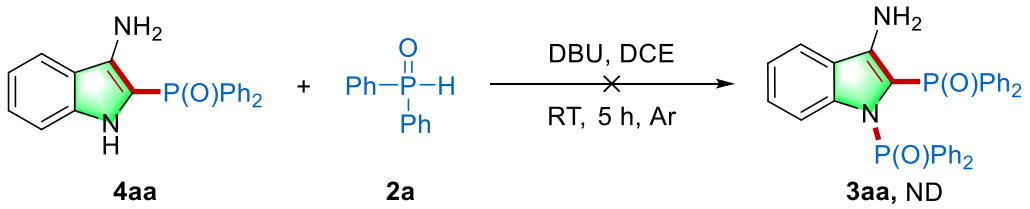
6.4 Identifying key reaction intermediates



An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar was

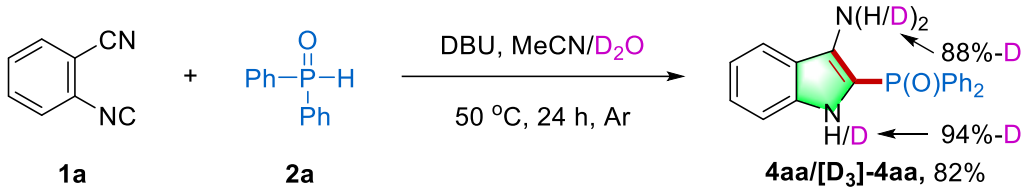
charged with **3aa** (0.1 mmol, 1.0 equiv.), DBU (0.25 mmol, 2.5 equiv.), and then CH_3CN (1.0 mL) was added into the mixture under argon atmosphere. Later, the reaction system was kept stirring at 50 ℃ for 24 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (PE/EA = 1:3) to afford the desired product **4aa** (28.0 mg, 84%). Meanwhile, the formation of $Ph_2P(O)OH$ was observed and monitored by ^{31}P NMR spectroscopy. Chemical shifts for ^{31}P are reported relative to an internal $Ph_3P(O)$ standard.



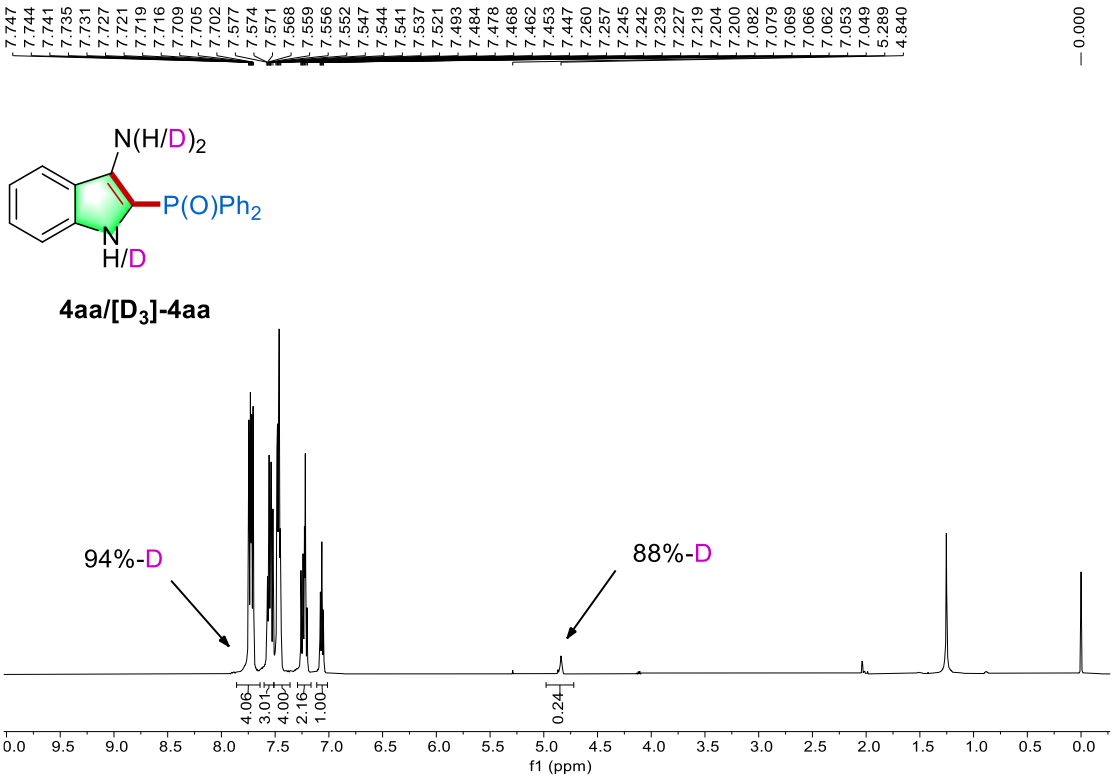


An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar was charged with **4aa** (0.1 mmol, 1.0 equiv.), **2a** (0.25 mmol, 2.5 equiv.), DBU (0.25 mmol, 2.5 equiv.), and then DCE (1.0 mL) was added into the mixture under argon atmosphere. Later, the reaction system was kept stirring at room temperature for 5 h. Compound **3aa** was not detected.

6.5 Deuterium labeling experiment

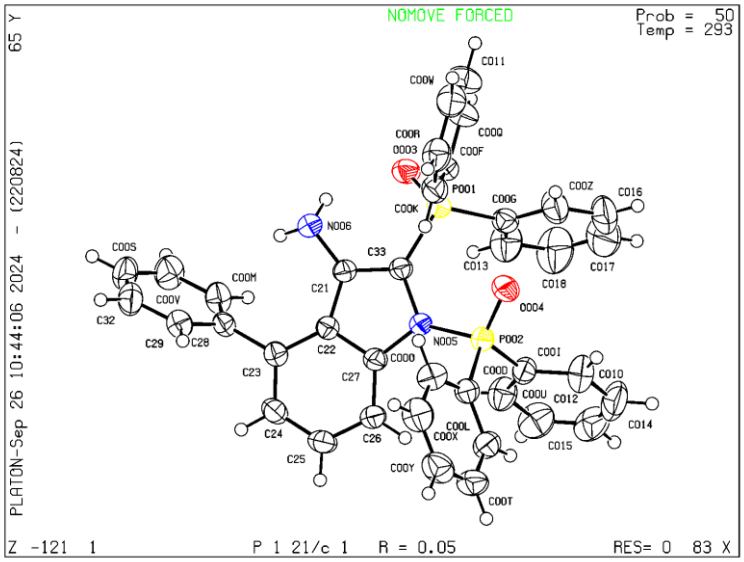


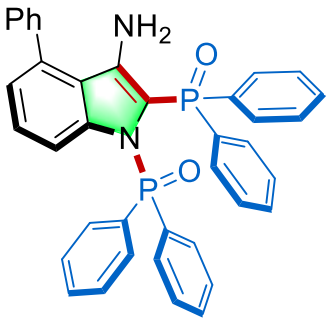
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar was charged with **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.25 mmol, 2.5 equiv.), and DBU (0.25 mmol, 2.5 equiv.), and then CH_3CN (1.0 mL)/D_2O (20 μL) was added into the mixture under argon atmosphere. Later, the reaction system was kept stirring at 50 ℃ for 24 h. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (PE/EA = 1:3) to afford the desired product **4aa**/D_3]-**4aa** (27.1 mg, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.85 – 7.65 (m, 4.06 H), 7.60 – 7.51 (m, 3H), 7.51 – 7.36 (m, 4H), 7.29 – 7.17 (m, 2H), 7.11 – 7.02 (m, 1H), 4.84 (br, 0.24H).



7. X-ray Crystallography Data of 3ja and 4ja

7.1 X-ray Crystallography Data of 3ja



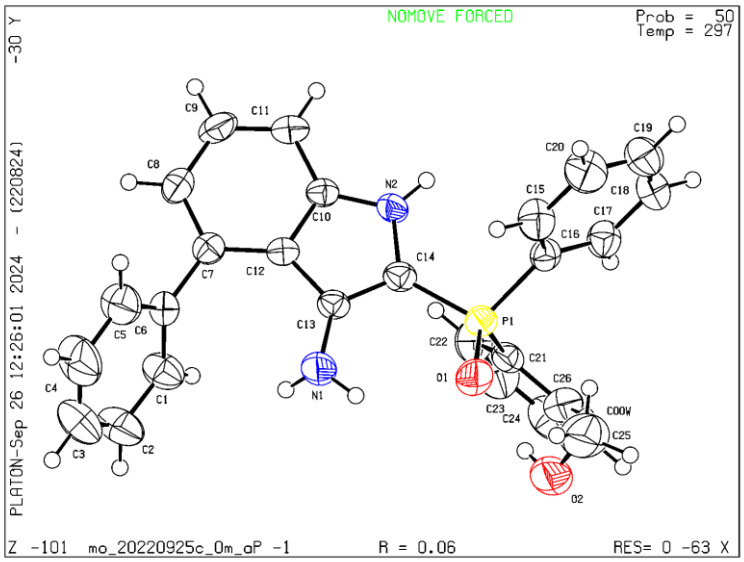


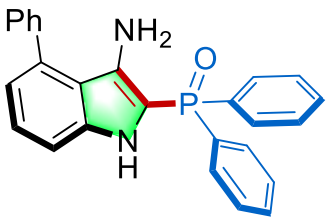
3ja
CCDC: 2387065

Identification code	1
Empirical formula	$C_{152}H_{120}N_8O_8P_8$
Formula weight	2434.31
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.300(8)
b/Å	17.905(10)
c/Å	12.534(7)
α/°	90
β/°	112.995(6)
γ/°	90
Volume/Å^3	3161(3)
Z	1
ρ_{calc}g/cm^3	1.279
μ/mm^{-1}	0.175
F(000)	1272.0
Crystal size/mm^3	0.22 × 0.21 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.892 to 57.208
Index ranges	-18 ≤ h ≤ 20, -23 ≤ k ≤ 23, -16 ≤ l ≤ 15

Reflections collected	28000
Independent reflections	7775 [R_{int} = 0.0577, R_{sigma} = 0.0676]
Data/restraints/parameters	7775/0/398
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0492, wR_2 = 0.1161
Final R indexes [all data]	R_1 = 0.0917, wR_2 = 0.1338
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.43

7.2 X-ray Crystallography Data of 4ja





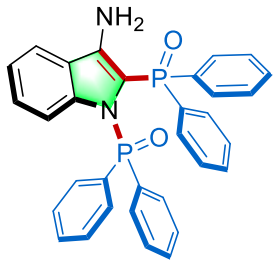
4ja
CCDC: 2387066

Identification code	mo_20220925c_0m_a
Empirical formula	$C_{27}H_{25}N_2O_2P$
Formula weight	440.46
Temperature/K	297.15
Crystal system	triclinic
Space group	P-1
a/Å	8.3695(12)
b/Å	10.144(2)
c/Å	14.956(3)
α/°	72.992(7)
β/°	78.674(6)
γ/°	80.115(6)
Volume/$Å^3$	1181.8(4)
Z	2
ρ_{calc}g/cm^3	1.238

μ/mm^{-1}	0.142
F(000)	464.0
Crystal size/mm^3	0.22 × 0.21 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.722 to 54.96
Index ranges	$-10 \leq h \leq 10$, $-13 \leq k \leq 13$, $-19 \leq l \leq 19$
Reflections collected	46840
Independent reflections	5408 [R_{int} = 0.0520, R_{sigma} = 0.0293]
Data/restraints/parameters	5408/0/292
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0621, wR_2 = 0.1422
Final R indexes [all data]	R_1 = 0.0853, wR_2 = 0.1649
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.45

8. Characterization Data of Products

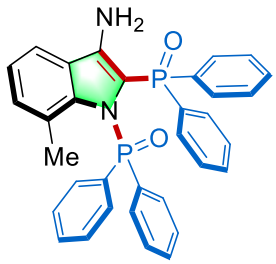
(3-amino-1*H*-indole-1,2-diyl)bis(diphenylphosphine oxide) (3aa)



3aa

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 43.1 mg, 81% yield; m.p. = 250 – 252 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.95 – 7.71 (m, 4H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 2H), 7.34 (td, *J* = 7.5, 1.5 Hz, 2H), 7.30 – 7.24 (m, 8H), 7.22 – 7.12 (m, 5H), 7.06 – 6.95 (m, 1H), 6.34 (d, *J* = 8.5 Hz, 1H), 5.85 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 147.1 (dd, *J* = 10.0 Hz, 7.5 Hz), 140.0 – 139.9 (m), 134.9 (d, *J* = 116.3 Hz), 132.6 (d, *J* = 2.5 Hz), 132.0 (dd, *J* = 93.8 Hz, 11.3 Hz), 131.4 -130.3 (m), 128.1 (dd, *J* = 142.5 Hz, 13.8 Hz), 126.7, 125.7 (dd, *J* = 11.3 Hz, 5.0 Hz), 121.4, 119.0, 114.4, 105.6 (d, *J* = 125.0 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 35.8, 26.8. **HRMS** (ESI): Calcd for $C_{32}H_{26}N_2O_2P_2$ $[M+H]^+$ 533.1542, found 533.1544.

(3-amino-7-methyl-1*H*-indole-1,2-diyl)bis(diphenylphosphine oxide) (3ba)

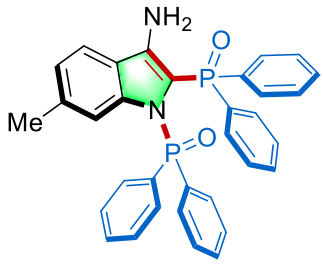


3ba

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 36.7 mg, 67% yield; m.p. = 219 – 221 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 12.5, 7.0 Hz, 4H), 7.49 (dd, *J* = 12.5, 7.5 Hz, 4H), 7.38 – 7.27 (m, 5H), 7.26 – 7.21 (m, 4H), 7.18 (td, *J* = 7.5, 3.5

Hz, 4H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.0 Hz, 1H), 4.74 (br, 2H), 1.96 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 145.6 (dd, *J* = 11.3 Hz, 6.3 Hz), 143.6 (d, *J* = 7.5 Hz), 134.6 – 131.2 (m), 130.6, 127.9 (dd, *J* = 12.5 Hz, 5.0 Hz), 127.2 (dd, *J* = 10.0 Hz, 3.8 Hz), 126.5, 122.8, 116.0, 110.2 (d, *J* = 130.0 Hz), 22.0. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 29.9, 28.6. **HRMS** (ESI): Calcd for $C_{33}H_{28}N_2O_2P_2$ $[M+H]^+$ 547.1699, found 547.1701.

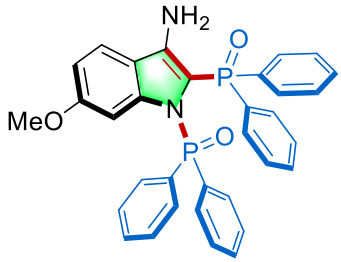
(3-amino-6-methyl-1*H*-indole-1,2-diyl)bis(diphenylphosphine oxide) (3ca)



3ca

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 44.6 mg, 82% yield; m.p. = 227 – 229 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 13.0, 7.0 Hz, 4H), 7.49 – 7.41 (m, 3H), 7.36 – 7.29 (m, 2H), 7.28 – 7.22 (m, 8H), 7.20 – 7.14 (m, 4H), 6.95 (d, *J* = 9.0 Hz, 1H), 6.04 (s, 1H), 5.80 (br, 2H), 2.07 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 147.3 (dd, *J* = 11.3 Hz, 7.5 Hz), 140.4 (dd, *J* = 7.5 Hz, 3.8 Hz), 136.8, 134.9 (d, *J* = 115.0 Hz), 132.5 – 130.4 (m), 128.0 (dd, *J* = 143.8 Hz, 12.5 Hz), 123.4 (dd, *J* = 11.3 Hz, 6.3 Hz), 123.0, 118.5, 114.5, 104.4 (dd, *J* = 125.0 Hz, 5.0 Hz), 22.0. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 35.6, 26.8. **HRMS** (ESI): Calcd for $C_{33}H_{28}N_2O_2P_2$ $[M+H]^+$ 547.1699, found 547.1695.

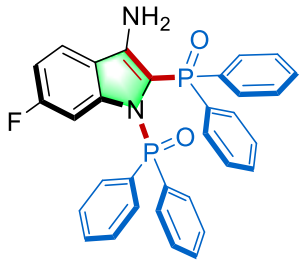
(3-amino-6-methoxy-1*H*-indole-1,2-diyl)bis(diphenylphosphine oxide) (3da)



3da

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 47.0 mg, 84% yield; m.p. = 224 – 226 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 13.0, 7.0 Hz, 4H), 7.48 – 7.44 (m, 3H), 7.35 – 7.16 (m, 14H), 6.76 (dd, *J* = 9.0, 2.0 Hz, 1H), 5.76 (s, 3H), 3.26 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.3, 147.5 (dd, *J* = 11.3 Hz, 7.5 Hz), 141.1 (dd, *J* = 6.3 Hz, 2.5 Hz), 135.0 (d, *J* = 115.0 Hz), 132.6 – 130.4 (m), 128.0 (dd, *J* = 162.5 Hz, 11.3 Hz), 119.6, 119.4 (dd, *J* = 11.3 Hz, 6.3 Hz), 111.5, 103.5 (d, *J* = 122.5 Hz), 97.7, 55.1. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 35.4, 26.5. **HRMS** (ESI): Calcd for $C_{33}H_{28}N_2O_3P_2$ $[M+H]^+$ 563.1648, found 563.1653.

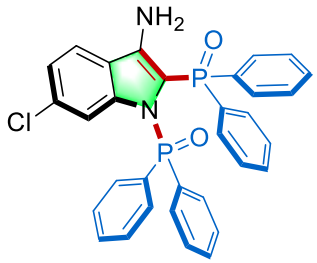
(3-amino-6-fluoro-1*H*-indole-1,2-diyl)bis(diphenylphosphine oxide) (3ea)



3ea

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 37.8 mg, 69% yield; m.p. = 202 – 204 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 13.0, 7.0 Hz, 4H), 7.57 – 7.46 (m, 3H), 7.38 – 7.24 (m, 10H), 7.17 (dd, *J* = 13.0, 7.5 Hz, 4H), 6.89 (td, *J* = 8.5, 2.5 Hz, 1H), 5.96 (dd, *J* = 11.0, 2.5 Hz, 1H), 5.80 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.0 (d, *J* = 242.5 Hz), 146.8 (dd, *J* = 10.0 Hz, 7.5 Hz), 140.3, 134.7 (d, *J* = 116.3 Hz), 133.0 – 131.0 (m), 130.4 (d, *J* = 123.8 Hz), 128.2 (dd, *J* = 160.0 Hz, 12.5 Hz), 122.1 (dd, *J* = 11.3 Hz, 6.3 Hz), 120.1 (d, *J* = 10.0 Hz), 110.2 (d, *J* = 25.0 Hz), 105.7 (d, *J* = 125.0 Hz), 101.2 (d, *J* = 28.8 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 35.4, 27.0. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -112.8. **HRMS** (ESI): Calcd for $C_{32}H_{25}FN_2O_2P_2$ $[M+H]^+$ 551.1448, found 551.1447.

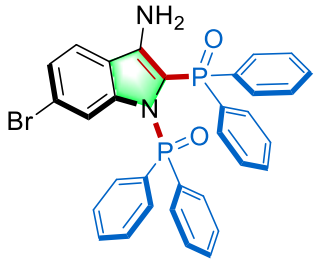
(3-amino-6-chloro-1*H*-indole-1,2-diyl)bis(diphenylphosphine oxide) (3fa)



3fa

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 40.9 mg, 72% yield; m.p. = 206 – 208 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 13.0, 7.5 Hz, 4H), 7.51 (t, *J* = 7.0 Hz, 3H), 7.37 – 7.23 (m, 10H), 7.22 – 7.08 (m, 5H), 6.21 (s, 1H), 5.65 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 146.6 (dd, *J* = 10.0 Hz, 7.5 Hz), 140.3, 134.5 (d, *J* = 116.3 Hz), 133.0 – 131.1 (m), 130.4 (d, *J* = 123.8 Hz), 128.2 (dd, *J* = 160.0 Hz, 13.8 Hz), 124.1 (dd, *J* = 11.3 Hz, 6.3 Hz), 122.2, 119.8, 114.5, 106.3 (d, *J* = 127.5 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 35.5, 27.1. **HRMS** (ESI): Calcd for $C_{32}H_{25}ClN_2O_2P_2$ $[M+H]^+$ 567.1153, found 567.1149.

(3-amino-6-bromo-1*H*-indole-1,2-diyl)bis(diphenylphosphine oxide) (3ga)

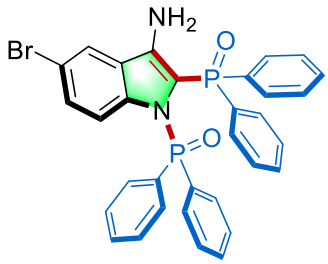


3ga

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 44.7 mg, 73% yield; m.p. = 210 – 212 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 13.0, 7.5 Hz, 4H), 7.55 – 7.41 (m, 3H), 7.39 – 7.21 (m, 11H), 7.15 (dd, *J* = 13.0, 7.5 Hz, 4H), 6.35 (s, 1H), 5.72 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 146.7 (dd, *J* = 11.3 Hz, 7.5 Hz), 140.6 (dd, *J* = 6.3 Hz, 3.8 Hz), 134.5 (d, *J* = 116.3 Hz), 133.0 – 131.1 (m), 130.3 (d, *J* = 123.8 Hz),

128.2 (dd, *J* = 161.3 Hz, 13.8 Hz), 124.7, 124.4 (dd, *J* = 11.3 Hz, 6.3 Hz), 120.6, 120.1, 117.4, 106.1 (dd, *J* = 123.8 Hz, 6.3 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 35.5, 27.1. **HRMS** (ESI): Calcd for $C_{32}H_{25}BrN_2O_2P_2$ $[M+H]^+$ 611.0647, found 611.0644.

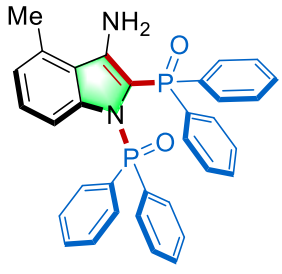
(3-amino-5-bromo-1*H*-indole-1,2-diyl)bis(diphenylphosphine oxide) (3ha)



3ha

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 42.3 mg, 69% yield; m.p. = 219 – 221 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 13.0, 7.0 Hz, 4H), 7.75 (s, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.34 (dt, *J* = 7.5, 2.0 Hz, 2H), 7.32 – 7.26 (m, 8H), 7.16 (dd, *J* = 13.5, 7.5 Hz, 4H), 7.07 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.18 (d, *J* = 9.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 146.0, 138.5, 134.5 (d, *J* = 116.3 Hz), 132.9 – 131.1 (m), 130.5 (d, *J* = 122.5 Hz), 129.5, 128.2 (dd, *J* = 151.3 Hz, 12.5 Hz), 127.3 (dd, *J* = 11.3 Hz, 5.0 Hz), 121.8, 115.7, 114.6, 107.1 (d, *J* = 127.5 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 35.6, 27.0. **HRMS** (ESI): Calcd for $C_{32}H_{25}BrN_2O_2P_2$ $[M+H]^+$ 611.0647, found 611.0644.

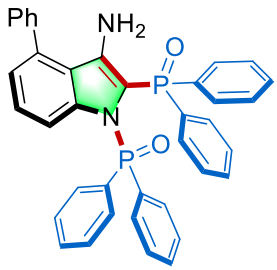
(3-amino-4-methyl-1*H*-indole-1,2-diyl)bis(diphenylphosphine oxide) (3ia)



3ia

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 42.4 mg, 78% yield; m.p. = 243 – 245 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 12.5, 7.5 Hz, 4H), 7.44 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.28 – 7.23 (m, 8H), 7.18 (dd, *J* = 13.0, 7.5 Hz, 4H), 6.92 – 6.72 (m, 2H), 6.28 – 6.22 (m, 1H), 6.05 (br, 2H), 2.81 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.5, 140.4 (dd, *J* = 10.0 Hz, 5.0 Hz), 135.1 (d, *J* = 116.3 Hz), 132.6 – 130.3 (m), 128.0 (dd, *J* = 137.5 Hz, 12.5 Hz), 126.2, 124.2 (dd, *J* = 10.0 Hz, 5.0 Hz), 123.4, 112.5, 104.7 (d, *J* = 128.8 Hz), 20.3. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 36.4, 27.1. **HRMS** (ESI): Calcd for $C_{33}H_{28}N_2O_2P_2$ $[M+H]^+$ 547.1699, found 547.1697.

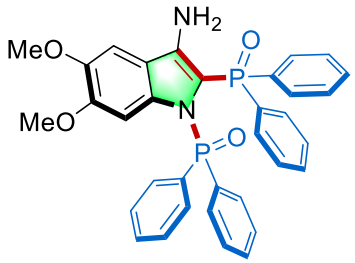
(3-amino-4-phenyl-1*H*-indole-1,2-diyl)bis(diphenylphosphine oxide) (3ja)



3ja

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 50.4 mg, 83% yield; m.p. = 236 – 238 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 13.0, 7.5 Hz, 4H), 7.58 – 7.40 (m, 7H), 7.36 – 7.18 (m, 14H), 7.00 – 6.88 (m, 2H), 6.45 (d, *J* = 8.0 Hz, 1H), 5.38 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 148.2 (dd, *J* = 11.3 Hz, 7.5 Hz), 140.5 (dd, *J* = 6.3 Hz, 3.8 Hz), 139.3, 137.0, 135.6, 134.7, 132.7 – 127.4 (m), 125.7, 123.5, 122.0 (dd, *J* = 11.3 Hz, 6.3 Hz), 113.7, 104.4 (dd, *J* = 125.0 Hz, 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ 35.9, 27.2. **HRMS** (ESI): Calcd for $C_{38}H_{30}N_2O_2P_2$ $[M+H]^+$ 609.1855, found 609.1857.

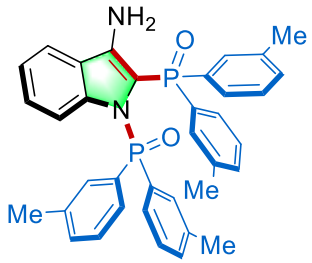
(3-amino-5,6-dimethoxy-1*H*-indole-1,2-diyl)bis(diphenylphosphine oxide) (3ka)



3ka

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 45.6 mg, 77% yield; m.p. = 234 – 236 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 12.5, 7.5 Hz, 4H), 7.47 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.45 – 7.23 (m, 10H), 7.15 (dd, *J* = 13.0, 7.5 Hz, 4H), 6.97 (s, 1H), 5.73 (s, 3H), 3.90 (s, 3H), 3.21 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.5, 147.6, 145.7, 134.9 (d, *J* = 115.0 Hz), 134.7, 132.6 – 130.6 (m), 128.0 (dd, *J* = 166.3 Hz, 13.8 Hz), 118.1 (dd, *J* = 11.3 Hz, 6.3 Hz), 103.7 (d, *J* = 127.5 Hz), 99.6, 97.4, 56.1, 55.5. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 35.2, 26.2. **HRMS** (ESI): Calcd for $C_{34}H_{30}N_2O_4P_2$ $[M+H]^+$ 593.1754, found 593.1752.

(3-amino-1*H*-indole-1,2-diyl)bis(di-m-tolylphosphine oxide) (3ab)

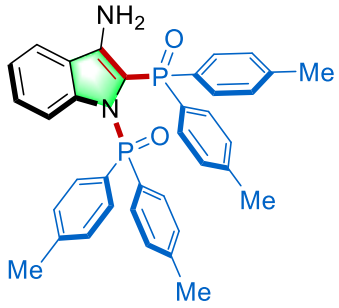


3ab

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 42.7 mg, 73% yield; m.p. = 221 – 223 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.74 – 7.66 (m, 4H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.20 (td, *J* = 7.5, 3.5 Hz, 2H), 7.17 – 7.13 (m, 5H), 7.06 – 6.99 (m, 3H), 6.95 (dd, *J* = 13.0, 7.5 Hz, 2H), 6.44 (d, *J* = 8.5 Hz, 1H), 2.22 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 146.8 (dd, *J* = 11.3 Hz, 7.5 Hz), 139.9, 137.7 (dd, *J* = 57.5 Hz, 12.5 Hz), 134.9 (d, *J* = 115.0 Hz), 133.4 (d, *J* = 3.8 Hz), 132.4 (dd, *J* = 81.3

Hz, 11.3 Hz), 131.7 (d, *J* = 2.5 Hz), 130.9 (d, *J* = 122.5 Hz), 129.1 (dd, *J* = 133.8 Hz, 11.3 Hz), 1277.8 (dd, *J* = 125.0 Hz, 15.0 Hz), 126.5, 125.6 (dd, *J* = 11.3 Hz, 5.0 Hz), 121.2, 118.8, 114.5, 105.8 (d, *J* = 120.0 Hz), 21.5, 21.5. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 36.5, 27.1. **HRMS** (ESI): Calcd for $C_{36}H_{34}N_2O_2P_2$ $[M+H]^+$ 589.2168, found 589.2172.

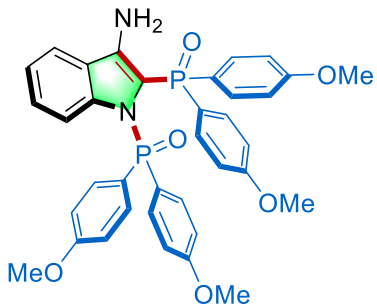
(3-amino-1*H*-indole-1,2-diyl)bis(di-*p*-tolylphosphine oxide) (3ac)



3ac

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 44.6 mg, 76% yield; m.p. = 228 – 230 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 12.8, 8.0 Hz, 4H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.09 – 6.94 (m, 13H), 6.36 (d, *J* = 8.4 Hz, 1H), 5.71 (br, 2H), 2.35 (s, 6H), 2.29 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.4 (dd, *J* = 10.0 Hz, 8.0 Hz), 142.9 (d, *J* = 2.0 Hz), 141.0 (d, *J* = 3.0 Hz), 139.9 (dd, *J* = 7.0 Hz, 4.0 Hz), 132.5 – 131.0 (m), 129.2 – 127.3 (m), 126.3, 125.4 (dd, *J* = 11.0 Hz, 6.0 Hz), 121.0, 118.7, 114.4, 106.6 (dd, *J* = 124.0 Hz, 5.0 Hz), 21.7, 21.6. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 35.8, 27.2. **HRMS** (ESI): Calcd for $C_{36}H_{34}N_2O_2P_2$ $[M+H]^+$ 589.2168, found 589.2173.

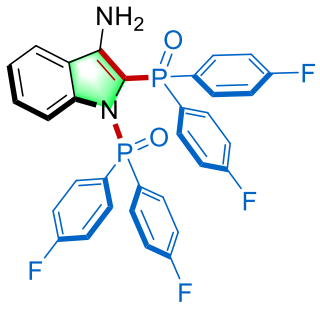
(3-amino-1*H*-indole-1,2-diyl)bis(bis(4-methoxyphenyl)phosphine oxide) (3ad)



3ad

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 53.9 mg, 83% yield; m.p. = 215 – 217 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 12.5, 9.0 Hz, 4H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.06 (m, 5H), 7.01 – 6.95 (m, 1H), 6.80 – 6.73 (m, 8H), 6.35 (d, *J* = 8.5 Hz, 1H), 3.80 (s, 6H), 3.77 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.7 (dd, *J* = 12.5 Hz, 2.5 Hz), 146.1, 140.0, 133.9 (dd, *J* = 105.0 Hz, 12.5 Hz), 127.0 – 125.9 (m), 125.5 (d, *J* = 6.3 Hz), 122.8 (d, *J* = 131.3 Hz), 121.1, 118.7, 114.4, 113.5 (dd, *J* = 140.0 Hz, 15.0 Hz), 107.1 (d, *J* = 120.0 Hz), 55.4, 55.2. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 34.7, 26.5. **HRMS** (ESI): Calcd for $C_{36}H_{34}N_2O_6P_2$ $[M+H]^+$ 653.1965, found 653.1961.

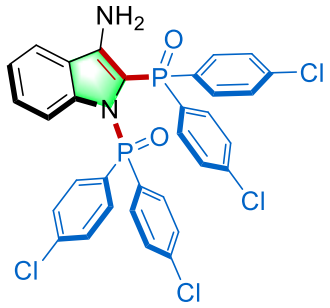
(3-amino-1*H*-indole-1,2-diyl)bis(bis(4-fluorophenyl)phosphine oxide) (3ae)



3ae

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 38.1 mg, 63% yield; m.p. = 208 – 210 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 – 7.80 (m, 4H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.12 (m, 5H), 7.08 – 6.93 (m, 9H), 6.26 (d, *J* = 8.4 Hz, 1H), 6.00 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.1 (dd, *J* = 116.3 Hz, 3.8 Hz), 164.1 (dd, *J* = 112.5 Hz, 3.8 Hz), 147.5 (d, *J* = 18.8 Hz), 139.9 (d, *J* = 18.8 Hz), 134.9 (dd, *J* = 12.5 Hz, 11.3 Hz), 134.1 (dd, *J* = 12.5 Hz, 8.8 Hz), 130.5 (dd, *J* = 120.0 Hz, 2.5 Hz), 127.3, 126.6 (dd, *J* = 127.5 Hz, 2.5 Hz), 125.5 (dd, *J* = 11.3 Hz, 6.3 Hz), 121.9, 119.3, 115.7 (ddd, *J* = 192.5, 21.3 Hz, 13.8 Hz), 114.1, 104.7 (d, *J* = 123.8 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 33.4, 25.2. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -103.9, -107.9. **HRMS** (ESI): Calcd for $C_{32}H_{22}F_4N_2O_2P_2$ $[M+H]^+$ 605.1165, found 605.1162.

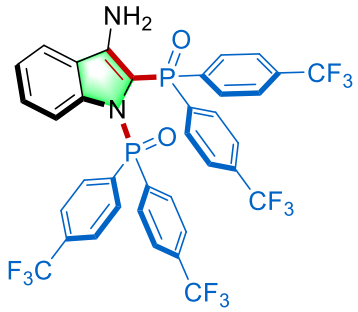
(3-amino-1*H*-indole-1,2-diyl)bis(bis(4-chlorophenyl)phosphine oxide) (3af)



3af

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 46.9 mg, 70% yield; m.p. = 204 – 206 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 12.4, 8.0 Hz, 4H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 8.4, 2.8 Hz, 4H), 7.27 – 7.17 (m, 5H), 7.11 – 7.06 (m, 5H), 6.29 (d, *J* = 8.8 Hz, 1H), 5.80 (br, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.8 (dd, *J* = 11.0 Hz, 8.0 Hz), 139.9 (d, *J* = 4.0 Hz), 139.7 (dd, *J* = 6.0 Hz, 4.0 Hz), 138.0 (d, *J* = 4.0 Hz), 133.8 – 132.2 (m), 129.4 – 127.5 (m), 125.3 (dd, *J* = 11.0 Hz, 6.0 Hz), 122.0, 119.3, 114.0, 103.8 (dd, *J* = 128.0 Hz, 6.0 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 33.7, 25.5. **HRMS** (ESI): Calcd for $C_{32}H_{22}Cl_4N_2O_2P_2$ $[M+H]^+$ 668.9983, found 668.9985.

(3-amino-1*H*-indole-1,2-diyl)bis(bis(4-(trifluoromethyl)phenyl)phosphine oxide) (3ag)

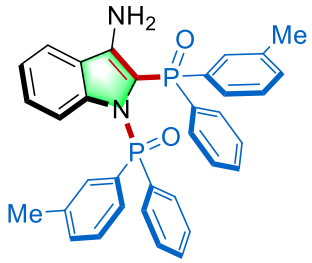


3ag

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 47.5 mg, 59% yield; m.p. = 217 – 219 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 12.8, 8.0 Hz, 4H), 7.73 – 7.51 (m, 9H), 7.36 – 7.20 (m, 5H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.26 (d, *J* = 8.4 Hz, 1H), 5.94

(br, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.0 (dd, *J* = 11.0 Hz, 8.0 Hz), 139.7 (dd, *J* = 6.0 Hz, 4.0 Hz), 139.0, 137.9, 135.2 (qd, *J* = 33.0 Hz, 4.0 Hz), 134.5, 133.2 (qd, *J* = 33.0 Hz, 4.0 Hz), 133.3, 132.3 (dd, *J* = 90.0 Hz, 10.0 Hz), 128.1, 126.0 (dq, *J* = 14.0 Hz, 4.0 Hz), 125.5 (dd, *J* = 11.0 Hz, 6.0 Hz), 124.6 (dq, *J* = 13.0 Hz, 4.0 Hz), 123.4 (qd, *J* = 271.0 Hz, 46.0 Hz), 122.5, 119.7, 113.8, 102.0 (dd, *J* = 129.0 Hz, 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ 33.2, 24.6. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -63.2, -63.6. **HRMS** (ESI): Calcd for $C_{36}H_{22}F_{12}N_2O_2P_2$ $[M+H]^+$ 805.1038, found 805.1042.

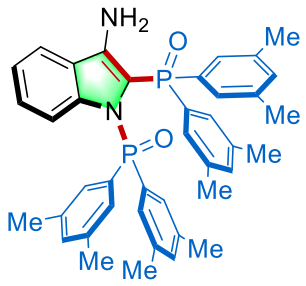
(3-amino-1-((R)-phenyl(m-tolyl)phosphoryl)-1*H*-indol-2-yl)(phenyl)(m-tolyl)phosphine oxide (3ah)



3ah

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 37.7 mg, 67% yield; m.p. = 215 – 217 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.96 – 7.80 (m, 2H), 7.73 – 7.64 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.38 – 7.34 (m, 1H), 7.33 – 7.25 (m, 5H), 7.22 – 7.12 (m, 6H), 7.07 – 6.92 (m, 3H), 6.39 (dd, *J* = 8.5, 4.5 Hz, 1H), 2.21 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 147.0, 139.9, 138.6, 137.1, 135.6 – 134.1 (m), 132.8 – 132.1 (m), 131.8, 131.6 (d, *J* = 10.0 Hz), 131.3, 130.9, 130.5 (d, *J* = 35.0 Hz), 129.7 (d, *J* = 10.0 Hz), 128.7 – 128.3 (m), 127.6 – 127.4 (m), 126.6, 125.7, 121.4, 118.9, 114.5, 105.7 (d, *J* =108.8 Hz), 21.5. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 36.1, 27.0. **HRMS** (ESI): Calcd for $C_{34}H_{30}N_2O_2P_2$ $[M+H]^+$ 561.1855, found 561.1851.

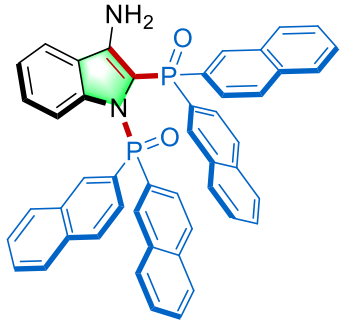
(3-amino-1*H*-indole-1,2-diyl)bis(bis(3,5-dimethylphenyl)phosphine oxide) (3ai)



3ai

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 50.7 mg, 79% yield; m.p. = 226 – 228 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 13.5 Hz, 4H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.07 – 7.02 (m, 3H), 6.96 (s, 2H), 6.80 (d, *J* = 13.0 Hz, 4H), 6.55 (d, *J* = 8.5 Hz, 1H), 5.58 (br, 2H), 2.21 (s, 12H), 2.17 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.5, 147.6 (d, *J* = 10.0 Hz), 145.7, 135.4 – 134.4 (m), 132.6 – 130.6 (m), 128.0 (dd, *J* = 166.3 Hz, 13.8 Hz), 118.1, 103.7 (d, *J* = 130.0 Hz), 99.6, 97.4, 56.1, 55.5. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 37.2, 27.4. **HRMS** (ESI): Calcd for $C_{40}H_{42}N_2O_2P_2$ $[M+H]^+$ 645.2794, found 645.2797.

(3-amino-1*H*-indole-1,2-diyl)bis(di(naphthalen-2-yl)phosphine oxide) (3aj)

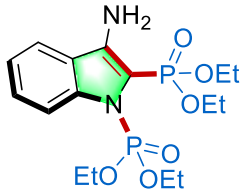


3aj

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 51.5 mg, 70% yield; m.p. = 249 – 251 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.50 (d, *J* = 14.5 Hz, 2H), 8.10 – 7.95 (m, 2H), 7.74 – 7.60 (m, 9H), 7.60 – 7.50 (m, 6H), 7.44 – 7.36 (m, 6H), 7.35 – 7.26 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.00 – 6.90 (m, 1H), 6.49 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 147.0, 140.1, 134.8 – 133.6 (m), 132.6 – 131.6 (m),129.1 – 126.8 (m), 126.1, 125.7 (d, *J* = 11.3 Hz), 121.5, 119.0, 114.4, 106.1 (d, *J* = 125.0 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ 35.9, 27.4. **HRMS** (ESI): Calcd for $C_{48}H_{34}N_2O_2P_2$ $[M+H]^+$ 733.2168, found 733.2168.

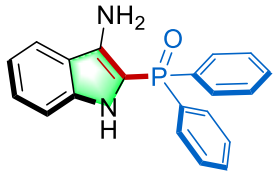
tetraethyl (3-amino-1*H*-indole-1,2-diyl)bis(phosphonate) (3ak)



3ak

According to the general procedure (**Conditions A**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 35.4 mg, 88% yield; m.p. = 158 – 160 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.5 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 4.23 – 4.06 (m, 6H), 4.06 – 3.94 (m, 2H), 1.34 (t, *J* = 7.0 Hz, 6H), 1.28 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 146.0134.3 (dd, *J* = 17.5 Hz, 10.0 Hz), 140.6 (dd, *J* = 10.0 Hz, 5.0 Hz), 127.8, 123.3 (dd, *J* = 12.5 Hz, 10.0 Hz), 121.7, 118.6, 115.9, 102.3 (d, *J* = 8.8 Hz), 100.6 (d, *J* = 7.5 Hz), 62.9 (dd, *J* = 170.0 Hz, 5.0 Hz), 16.1 (dd, *J* = 35.0 Hz, 7.5 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 12.7, -2.5. **HRMS** (ESI): Calcd for $C_{16}H_{26}N_2O_6P_2$ $[M+H]^+$ 405.1339, found 405. 1337.

(3-amino-1*H*-indol-2-yl)diphenylphosphine oxide (4aa)

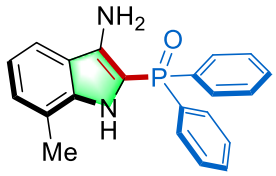


4aa

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 27.3 mg, 82% yield; m.p. = 242 – 244 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.87 (br, 1H), 7.73 (dd, *J* = 12.5, 7.5 Hz, 4H), 7.56 – 7.53 (m, 3H), 7.47 – 7.43 (m, 4H), 7.26 – 7.20 (m, 2H), 7.06 (t, *J* = 7.0 Hz, 1H), 4.27 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 138.2 (d, *J* = 8.8 Hz), 136.7 (d, *J* = 11.3 Hz), 132.8 (d, *J* = 107.5 Hz), 132.4, 131.8 (d, *J* = 11.3 Hz), 128.9 (d, *J* = 11.3 Hz), 125.5, 121.4 (d, *J* = 11.3 Hz), 119.0 (d, *J* = 56.3 Hz), 112.0, 105.8 (d, *J* = 130.0

Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 22.57. **HRMS** (ESI): Calcd for $C_{20}H_{17}N_2OP$ $[M+H]^+$ 333.1151, found 333.1152.

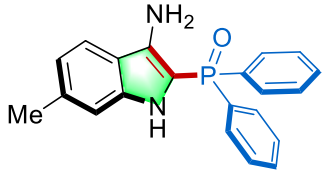
(3-amino-7-methyl-1*H*-indol-2-yl)diphenylphosphine oxide (4ba)



4ba

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 25.3 mg, 73% yield; m.p. = 256 – 258 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78 – 7.73 (m, 4H), 7.68 (br, 1H), 7.61 – 7.54 (m, 2H), 7.51 – 7.47 (m, 4H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 3.84 (br, 2H), 2.38 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.8 (d, *J* = 10.0 Hz), 136.4 (d, *J* = 11.3 Hz), 133.1 – 132.2 (m), 131.9 (d, *J* = 11.3 Hz), 129.0 (d, *J* = 12.5 Hz), 125.9, 121.4, 120.9 (d, *J* = 11.3 Hz), 119.5, 116.3, 105.8 (d, *J* = 130.0 Hz), 16.6. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 22.3. **HRMS** (ESI): Calcd for $C_{21}H_{19}N_2OP$ $[M+H]^+$ 347.1308, found 347.1311.

(3-amino-6-methyl-1*H*-indol-2-yl)diphenylphosphine oxide (4ca)

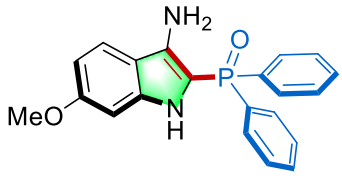


4ca

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 27.6 mg, 80% yield; m.p. = 248 – 250 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 – 7.62 (m, 5H), 7.57 – 7.50 (m, 2H), 7.48 – 7.35 (m, 5H), 6.98 (s, 1H), 6.89 (d, *J* = 10.0 Hz, 1H), 4.07 (br, 2H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.7 (d, *J* = 11.3 Hz), 137.0, 135.7, 133.5, 132.3 (d, *J* = 3.8 Hz), 131.8 (d, *J* = 13.8 Hz), 128.9 (d, *J* = 15.0 Hz), 121.2, 119.4 (d, *J* = 13.8 Hz), 118.4, 111.8 (d, *J* = 2.5 Hz), 104.8 (d, *J* = 163.8 Hz), 22.0. **^{31}P NMR** (162

MHz, $CDCl_3$): δ 22.5. **HRMS** (ESI): Calcd for $C_{21}H_{19}N_2OP$ $[M+H]^+$ 347.1308, found 347.1307.

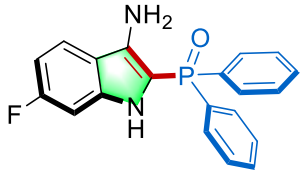
(3-amino-6-methoxy-1*H*-indol-2-yl)diphenylphosphine oxide (4da)



4da

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 30.3 mg, 84% yield; m.p. = 227 – 229 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78 – 7.68 (m, 4H), 7.65 (br, 1H), 7.57 – 7.51 (m, 2H), 7.45 (td, *J* = 7.5, 3.0 Hz, 4H), 7.38 (d, *J* = 8.5 Hz, 1H), 6.71 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.65 (d, *J* = 2.0 Hz, 1H), 4.08 (br, 2H), 3.75 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.1, 139.4 (d, *J* = 10.0 Hz), 137.4 (d, *J* = 11.3 Hz), 133.1 (d, *J* = 107.5 Hz), 132.3 (d, *J* = 2.5 Hz), 131.8 (d, *J* = 10.0 Hz), 128.9 (d, *J* = 12.5 Hz), 119.5, 115.8 (d, *J* = 10.0 Hz), 110.2, 104.0 (d, *J* = 132.5 Hz), 94.2, 55.5. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 22.2. **HRMS** (ESI): Calcd for $C_{21}H_{19}N_2O_2P$ $[M+H]^+$ 363.1257, found 363.1255.

(3-amino-6-fluoro-1*H*-indol-2-yl)diphenylphosphine oxide (4ea)

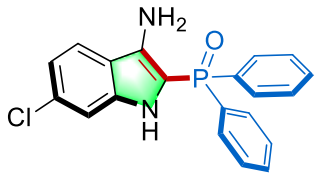


4ea

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 20.7 mg, 59% yield; m.p. = 251 – 253 ℃. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 10.34 (br, 1H), 7.74 – 7.64 (m, 5H), 7.64 – 7.59 (m, 2H), 7.58 – 7.50 (m, 4H), 6.95 (dd, *J* = 10.0, 2.5 Hz, 1H), 6.80 (td, *J* = 9.5, 2.5 Hz, 1H), 5.34 (br, 2H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 161.0 (d, *J* = 237.5 Hz), 139.4 (d, *J* = 11.3 Hz), 138.3 – 138.1 (m), 133.8 (d, *J* = 105.0 Hz), 132.03 (d, *J* = 2.5 Hz), 131.1 (d, *J* = 10.0 Hz), 128.7 (d, *J* = 12.5 Hz), 121.2 (d, *J* = 10.0 Hz), 117.0 (d, *J* = 11.3 Hz), 106.5 (d, *J* = 25.0 Hz), 102.4 (d, *J* = 130.0 Hz), 97.3 (d, *J* =

25.0 Hz). **^{31}P NMR** (202 MHz, DMSO-d_6): δ 21.7. **^{19}F NMR** (471 MHz, DMSO-d_6): δ -117.4. **HRMS** (ESI): Calcd for $C_{20}H_{16}FN_2OP$ $[M+H]^+$ 351.1057, found 351.1061.

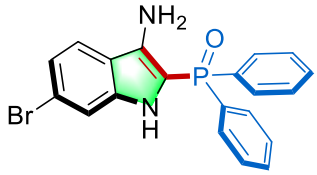
(3-amino-6-chloro-1*H*-indol-2-yl)diphenylphosphine oxide (4fa)



4fa

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 24.5 mg, 67% yield; m.p. = 263 – 265 ℃. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 10.40 (br, 1H), 7.70 – 7.64 (m, 5H), 7.62 (td, *J* = 7.5, 1.5 Hz, 2H), 7.56 (td, *J* = 7.5, 3.0 Hz, 4H), 7.23 (d, *J* = 1.5 Hz, 1H), 6.95 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.32 (br, 2H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 139.1 (d, *J* = 10.0 Hz), 138.3 (d, *J* = 10.0 Hz), 133.6 (d, *J* = 106.3 Hz), 132.1 (d, *J* = 2.5 Hz), 131.1 (d, *J* = 10.0 Hz), 129.5, 128.8 (d, *J* = 12.5 Hz), 121.2, 118.7 (d, *J* = 11.3 Hz), 117.9, 111.2, 103.0 (d, *J* = 131.3 Hz). **^{31}P NMR** (202 MHz, DMSO-d_6): δ 21.8. **HRMS** (ESI): Calcd for $C_{20}H_{16}ClN_2OP$ $[M+H]^+$ 367.0762, found 367.0765.

(3-amino-6-bromo-1*H*-indol-2-yl)diphenylphosphine oxide (4ga)

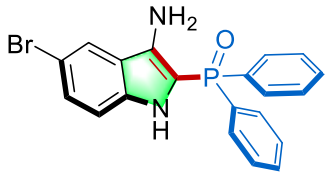


4ga

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 29.4 mg, 72% yield; m.p. = 253 – 255 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12 (br, 1H), 7.70 – 7.63 (m, 4H), 7.58 – 7.52 (m, 2H), 7.51 – 7.43 (m, 4H), 7.39 – 7.32 (m, 2H), 7.14 (dd, *J* = 8.8, 1.6 Hz, 1H), 4.12 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 138.7 (d, *J* = 10.0 Hz), 136.3 (d, *J* = 11.3 Hz), 132.6 (d, *J* = 3.8 Hz), 132.4 (d, *J* = 108.8 Hz), 131.8 (d, *J* = 10.0 Hz), 129.1 (d, *J* = 12.5 Hz), 122.6, 120.2 (d, *J* = 11.3 Hz), 120.0, 119.4, 115.0, 106.6 (d, *J* =

128.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ 22.3. **HRMS** (ESI): Calcd for $C_{20}H_{16}BrN_2OP$ $[M+H]^+$ 411.0256, found 411.0254.

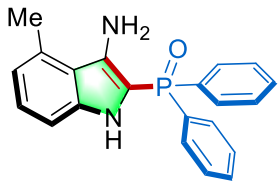
(3-amino-5-bromo-1*H*-indol-2-yl)diphenylphosphine oxide (4ha)



4ha

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 30.0 mg, 73% yield; m.p. = 255 – 257 ℃. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 10.46 (br, 1H), 7.94 (d, *J* = 2.0 Hz, 1H), 7.75 – 7.65 (m, 4H), 7.64 – 7.60 (m, 2H), 7.58 – 7.53 (m, 4H), 7.26 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 5.30 (br, 2H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 138.4 (d, *J* = 11.3 Hz), 136.7 (d, *J* = 10.0 Hz), 133.5 (d, *J* = 106.3 Hz), 132.2 (d, *J* = 2.5 Hz), 131.2 (d, *J* = 11.3 Hz), 128.8 (d, *J* = 12.5 Hz), 127.1, 122.1, 121.5 (d, *J* = 11.3 Hz), 113.9, 109.7, 103.8 (d, *J* = 130.0 Hz). **^{31}P NMR** (202 MHz, DMSO-d_6): δ 21.9. **HRMS** (ESI): Calcd for $C_{20}H_{16}BrN_2OP$ $[M+H]^+$ 411.0256, found 411.0253.

(3-amino-4-methyl-1*H*-indol-2-yl)diphenylphosphine oxide (4ia)

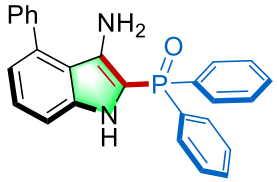


4ia

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 23.6 mg, 68% yield; m.p. = 271 – 273 ℃. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 10.26 (br, 1H), 7.73 – 7.66 (m, 4H), 7.64 – 7.60 (m, 2H), 7.59 – 7.52 (m, 4H), 7.06 – 7.03 (m, 1H), 7.02 – 6.95 (m, 1H), 6.65 – 6.57 (m, 1H), 5.16 (br, 2H), 2.66 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 141.3 (d, *J* = 11.3 Hz), 139.5 (d, *J* = 10.0 Hz), 134.6 (d, *J* = 105.0 Hz), 132.8, 132.5, 132.0 (d, *J* = 10.0 Hz), 129.5 (d, *J* = 12.5 Hz), 125.5, 120.0 (d, *J* = 10.0 Hz), 119.9,

110.6, 103.8 (d, J = 131.3 Hz), 20.4. **^{31}P NMR** (202 MHz, DMSO-d_6): δ 22.9. **HRMS** (ESI): Calcd for $C_{21}H_{19}N_2OP$ $[M+H]^+$ 347.1308, found 347.1306.

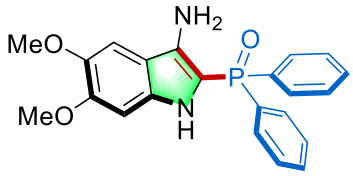
(3-amino-4-phenyl-1*H*-indol-2-yl)diphenylphosphine oxide (4ja)



4ja

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 33.0 mg, 81% yield; m.p. = 225 – 227 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.31 (br, 1H), 7.72 (dd, J = 12.5, 7.5 Hz, 4H), 7.57 – 7.48 (m, 4H), 7.47 – 7.35 (m, 7H), 7.24 – 7.15 (m, 2H), 6.90 (dd, J = 6.0, 2.0 Hz, 1H), 3.87 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.2, 138.7 (d, J = 2.5 Hz), 137.9 (d, J = 10.0 Hz), 136.3, 132.8 (d, J = 107.5 Hz), 132.2 (d, J = 2.5 Hz), 131.8 (d, J = 10.0 Hz), 129.3 – 127.5 (m), 124.8, 120.8, 117.4 (d, J = 10.0 Hz), 111.2, 104.7 (d, J = 132.5 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 22.9. **HRMS** (ESI): Calcd for $C_{26}H_{21}N_2OP$ $[M+H]^+$ 409.1464, found 409.1465.

(3-amino-5,6-dimethoxy-1*H*-indol-2-yl)diphenylphosphine oxide (4ka)

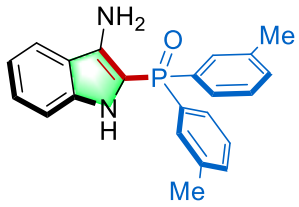


4ka

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 23.5 mg, 60% yield; m.p. = 238 – 240 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.71 (dd, J = 12.5, 8.0 Hz, 4H), 7.58 – 7.51 (m, 3H), 7.49 – 7.44 (m, 4H), 6.91 (s, 1H), 6.71 (s, 1H), 4.05 – 3.65 (m, 8H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 150.0, 145.0, 136.9 (d, J = 10.0 Hz), 133.1 (d, J = 107.5 Hz), 132.3 (d, J = 2.5 Hz), 131.8 (d, J = 11.3 Hz), 128.9 (d, J = 12.5 Hz), 114.0 (d, J = 11.3 Hz), 104.6 (d, J = 133.8 Hz), 99.4, 94.4, 56.2 (d, J = 40.0 Hz). **^{31}P NMR** (202

MHz, $CDCl_3$): δ 22.2. **HRMS** (ESI): Calcd for $C_{22}H_{21}N_2O_3P$ $[M+H]^+$ 393.1363, found 393.1365.

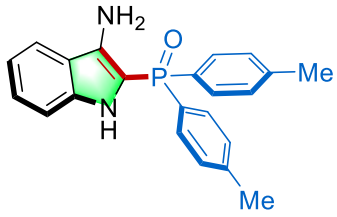
(3-amino-1*H*-indol-2-yl)di-m-tolylphosphine oxide (4ab)



4ab

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 26.7 mg, 74% yield; m.p. = 252 – 254 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69 (br, 1H), 7.62 (d, *J* = 13.0 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.39 – 7.29 (m, 4H), 7.27 – 7.19 (m, 2H), 7.08 – 7.05 (m, 1H), 4.14 (br, 2H), 2.35 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 138.9 (d, *J* = 12.5 Hz), 138.1 (d, *J* = 10.0 Hz), 136.7 (d, *J* = 11.3 Hz), 133.2 (d, *J* = 2.5 Hz), 133.1, 132.2 (d, *J* = 10.0 Hz), 128.9 – 128.7 (m), 125.4, 121.4 (d, *J* = 10.0 Hz), 118.9 (d, *J* = 46.3 Hz), 112.0, 106.1 (d, *J* = 130.0 Hz), 21.6. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 22.7. **HRMS** (ESI): Calcd for $C_{22}H_{21}N_2OP$ $[M+H]^+$ 361.1464, found 361.1469.

(3-amino-1*H*-indol-2-yl)di-p-tolylphosphine oxide (4ac)

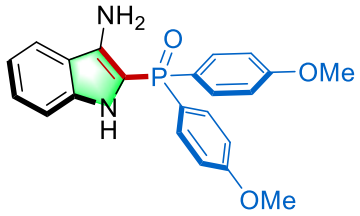


4ac

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 28.3 mg, 79% yield; m.p. = 247 – 249 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.99 (br, 1H), 7.60 (dd, *J* = 12.5, 8.0 Hz, 4H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.16 (m, 6H), 7.06 – 7.03 (m, 1H), 4.04 (br, 2H), 2.38 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 142.9, 138.0 (d, *J* = 10.0 Hz), 136.1, 131.8 (d, *J* = 11.3 Hz), 130.0 – 129.1 (m), 125.3, 121.3 (d, *J* = 10.0 Hz), 118.8 (d, *J* =

46.3 Hz), 112.0, 106.5 (d, *J* = 130.0 Hz), 21.7. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 22.6. **HRMS** (ESI): Calcd for $C_{22}H_{21}N_2OP$ $[M+H]^+$ 361.1464, found 361.1460.

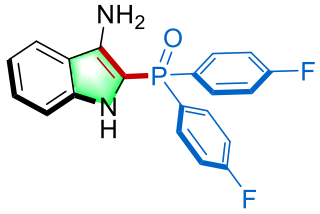
(3-amino-1*H*-indol-2-yl)bis(4-methoxyphenyl)phosphine oxide (4ad)



4ad

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 31.8 mg, 81% yield; m.p. = 231 – 233 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.27 (br, 1H), 7.61 (dd, *J* = 12.0, 8.5 Hz, 4H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 3.5 Hz, 2H), 7.04 – 7.00 (m, 1H), 6.89 (dd, *J* = 8.5 2.0 Hz, 4H), 4.16 (br, 2H), 3.78 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.7 (d, *J* = 2.5 Hz), 137.9 (d, *J* = 8.8 Hz), 135.5, 133.7 (d, *J* = 12.5 Hz), 125.2, 124.1 (d, *J* = 113.8 Hz), 121.3 (d, *J* = 11.3 Hz), 118.8 (d, *J* = 45.0 Hz), 114.4 (d, *J* = 13.8 Hz), 112.0, 107.1 (d, *J* = 130.0 Hz), 55.4. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 21.8. **HRMS** (ESI): Calcd for $C_{22}H_{21}N_2O_3P$ $[M+H]^+$ 393.1363, found 393.1360.

(3-amino-1*H*-indol-2-yl)bis(4-fluorophenyl)phosphine oxide (4ae)

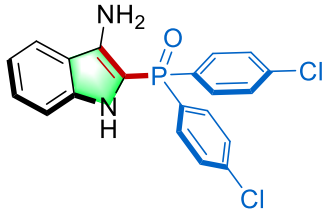


4ae

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 25.6 mg, 70% yield; m.p. = 253 – 255 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.39 (br, 1H), 7.71 – 7.66 (m, 4H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.12 – 7.02 (m, 5H), 4.10 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 165.4 (d, *J* = 2.5 Hz), 138.4 (d, *J* = 10.0 Hz), 137.0 (d, *J* = 10.0 Hz), 134.3 (dd, *J* = 12.5 Hz, 8.8 Hz), 128.6 (d, *J* = 112.5 Hz), 125.7, 121.1 (d, *J* =

10.0 Hz), 118.9 (d, *J* = 63.8 Hz), 116.4 (dd, *J* = 21.3 Hz, 13.8 Hz), 112.1, 104.9 (d, *J* = 133.8 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 21.2. **^{19}F NMR** (471 MHz, $CDCl_3$): δ -105.5. **HRMS** (ESI): Calcd for $C_{20}H_{15}F_2N_2OP$ $[M+H]^+$ 369.0963, found 369.0965.

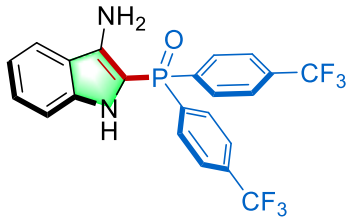
(3-amino-1*H*-indol-2-yl)bis(4-chlorophenyl)phosphine oxide (4af)



4af

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 29.8 mg, 75% yield; m.p. = 250 – 252 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.24 (br, 1H), 7.67 – 7.57 (m, 4H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 8.5, 2.0 Hz, 4H), 7.26 – 7.15 (m, 2H), 7.08 – 7.04 (m, 1H), 4.17 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 139.2 (d, *J* = 3.8 Hz), 138.5 (d, *J* = 8.8 Hz), 137.5 (d, *J* = 11.3 Hz), 133.1 (d, *J* = 11.3 Hz), 131.0 (d, *J* = 110.0 Hz), 129.3 (d, *J* = 13.8 Hz), 125.9, 121.1 (d, *J* = 11.3 Hz), 119. 0 (d, *J* = 68.8 Hz), 112.1, 104.2 (d, *J* = 133.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ 21.2. **HRMS** (ESI): Calcd for $C_{20}H_{15}Cl_2N_2OP$ $[M+H]^+$ 401.0372, found 401.0368.

(3-amino-1*H*-indol-2-yl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (4ag)

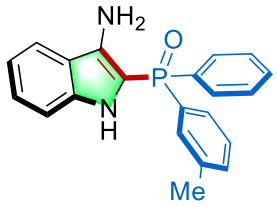


4ag

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). Yellow solid; 34.5 mg, 74% yield; m.p. = 185 – 187 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.16 (br, 1H), 7.83 (dd, *J* = 12.4, 8.0 Hz, 4H), 7.70 – 7.68 (m, 4H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.18 (m, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 4.30 (br, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.9 (d, *J* = 10.0 Hz), 138.5 (d, *J* = 11.0 Hz), 136.5 (d, *J* = 106.0 Hz), 134.4 (qd, *J* = 33.0 Hz, 3.0 Hz), 132.2 (d, *J* = 11.0 Hz), 126.3, 125.9 (dq, *J* = 12.0 Hz, 4.0 Hz), 123.5 (q, *J* = 271.0 Hz),

121.1 (d, *J* = 11.0 Hz), 119.2 (d, *J* = 73.0 Hz), 112.2 (d, *J* = 1.0 Hz), 103.0 (d, *J* = 135.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ 20.6. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -63.2. **HRMS** (ESI): Calcd for $C_{22}H_{15}F_6N_2OP$ $[M+H]^+$ 469.0899, found 469.0904.

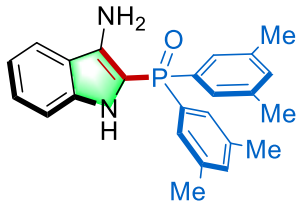
(S)-(3-amino-1*H*-indol-2-yl)(phenyl)(*m*-tolyl)phosphine oxide (4ah)



4ah

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 26.4 mg, 76% yield; m.p. = 252 – 254 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.98 (br, 1H), 7.72 (dd, *J* = 12.5, 7.5 Hz, 2H), 7.62 (d, *J* = 13.0 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.48 – 7.41 (m, 3H), 7.38 – 7.28 (m, 2H), 7.25 – 7.17 (m, 2H), 7.07 – 7.03 (m, 1H), 4.15 (br, 2H), 2.33 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 138.9 (d, *J* = 12.5 Hz), 138.1 (d, *J* = 8.8 Hz), 136.8 (d, *J* = 10.0 Hz), 133.4 – 133.0 (m), 132.5 – 132.2 (m), 131.8 (d, *J* = 10.0 Hz), 128.9 – 128.7 (m), 125.4, 121.3 (d, *J* = 10.0 Hz), 118.8 (d, *J* = 43.8 Hz), 112.0, 105.8 (d, *J* = 130.0 Hz), 21.5. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 22.7. **HRMS** (ESI): Calcd for $C_{21}H_{19}N_2OP$ $[M+H]^+$ 347.1308, found 347.1304.

(3-amino-1*H*-indol-2-yl)bis(3,5-dimethylphenyl)phosphine oxide (4ai)

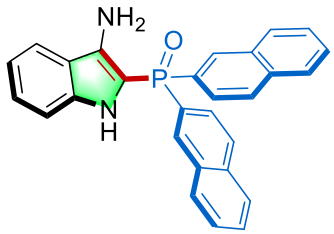


4ai

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 29.9 mg, 77% yield; m.p. = 255 – 257 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.64 (br, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J* = 13.0, 2.0 Hz, 4H), 7.25 – 7.20 (m, 2H), 7.17 (s, 2H), 7.08 – 7.04 (m, 1H), 4.07 (br, 2H), 2.30 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 138.7 (d, *J* = 13.8 Hz), 138.0 (d, *J* = 8.8 Hz), 136.5 (d, *J* = 10.0 Hz), 134.2 (d, *J* = 2.5 Hz), 132.6 (d, *J* =

106.3 Hz), 129.3 (d, *J* = 10.0 Hz), 125.3, 121.5 (d, *J* = 11.3 Hz), 118.9 (d, *J* = 36.3 Hz), 112.0, 106.4 (d, *J* = 128.8 Hz), 21.4. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 23.1. **HRMS** (ESI): Calcd for $C_{24}H_{25}N_2OP$ $[M+H]^+$ 389.1777, found 389.1772.

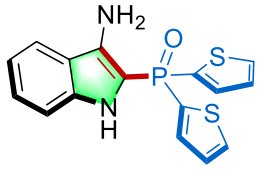
(3-amino-1*H*-indol-2-yl)di(naphthalen-2-yl)phosphine oxide (4aj)



4aj

According to the general procedure (**Conditions B**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 29.5 mg, 68% yield; m.p. = 268 – 270 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.32 (d, *J* = 14.5 Hz, 2H), 8.01 (br, 1H), 7.93 – 7.82 (m, 4H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.77 – 7.72 (m, 2H), 7.62 – 7.53 (m, 3H), 7.53 – 7.44 (m, 2H), 7.22 (d, *J* = 4.0 Hz, 2H), 7.09 – 7.05 (m, 1H), 4.36 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 138.3 (d, *J* = 8.8 Hz), 136.7, 135.0, 133.8 (d, *J* = 10.0 Hz), 132.6 (d, *J* = 13.8 Hz), 129.8 (d, *J* = 107.5 Hz), 129.2, 128.9 (d, *J* = 11.3 Hz), 128.3 (d, *J* = 65.0 Hz), 127.1, 126.5 (d, *J* = 11.3 Hz), 125.6, 121.4 (d, *J* = 10.0 Hz), 119.0 (d, *J* = 51.3 Hz), 112.1, 106.0 (d, *J* = 130.0 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 22.9. **HRMS** (ESI): Calcd for $C_{28}H_{21}N_2OP$ $[M+H]^+$ 433.1464, found 433.1464.

(3-amino-1*H*-indol-2-yl)di(thiophen-2-yl)phosphine oxide (4ak)

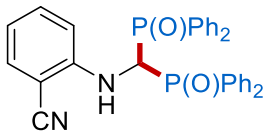


4ak

According to the general procedure (**3.3**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 19.7 mg, 57% yield; m.p. = 217 – 219 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.76 (t, *J* = 4.5 Hz, 2H), 7.71 (br, 1H), 7.64 – 7.58 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.22 (m, 2H), 7.21 – 7.18 (m, 2H), 7.10 – 7.05 (m, 1H), 4.24 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 138.2 (d, *J* = 10.0 Hz),

137.4 (d, *J* = 11.3 Hz), 136.8 (d, *J* = 11.3 Hz), 135.2 – 134.2 (m), 128.7 (d, *J* = 15.0 Hz), 126.0, 121.1 (d, *J* = 11.3 Hz), 119.1 (d, *J* = 36.3 Hz), 112.1, 105.8 (d, *J* = 145.0 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 5.4. **HRMS** (ESI): Calcd for $C_{16}H_{13}N_2OPS_2$ $[M+H]^+$ 345.0280, found 345.0275.

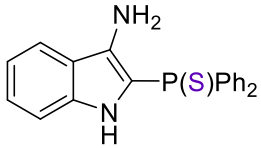
2-((bis(diphenylphosphoryl)methyl)amino)benzonitrile (5)



5

According to the control experiment (**5.1a**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 34.2 mg, 64% yield; m.p. = 189 – 191 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 – 7.78 (m, 8H), 7.47 – 7.27 (m, 12H), 7.15 (t, *J* = 8.0 Hz, 2H), 6.60 – 6.54 (m, 2H), 5.31 (s, 1H), 5.19 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 148.0, 133.8, 132.8, 132.3, 131.8 – 131.6 (m), 130.8 – 129.6 (m), 128.7 – 128.5 (m), 118.5, 116.9, 112.2, 97.5, 56.6 (t, *J* = 61.3 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 28.5. **HRMS** (ESI): Calcd for $C_{32}H_{27}N_2O_2P_2$ $[M+H]^+$ 533.1542, found 533.1540.

(3-amino-1*H*-indol-2-yl)diphenylphosphine sulfide (6)

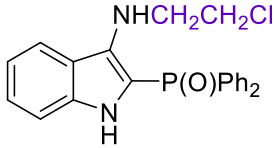


6

According to the further transformation (**4.2.1**), the product was purified by flash column chromatography (PE/EA = 6:1). Colorless oil; 58.4 mg, 84% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 14.0, 7.5 Hz, 5H), 7.59 – 7.39 (m, 7H), 7.29 – 7.16 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 3.84 (br, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.1 (d, *J* = 10.0 Hz), 134.9 (d, *J* = 10.0 Hz), 132.6 (d, *J* = 87.5 Hz), 132.0 (d, *J* = 2.5 Hz), 131.7 (d, *J* = 11.3 Hz), 128.9 (d, *J* = 12.5 Hz), 125.4, 121.7 (d, *J* = 10.0 Hz),

119.1, 118.5, 111.8, 103.8 (d, J = 111.3 Hz). **^{31}P NMR** (202 MHz, $CDCl_3$): δ 28.8. **HRMS** (ESI): Calcd for $C_{20}H_{17}N_2PS$ $[M+H]^+$ 349.0923, found 349.0922.

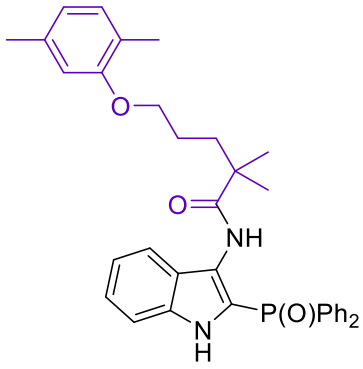
(3-((2-chloroethyl)amino)-1*H*-indol-2-yl)diphenylphosphine oxide (7)



7

According to the further transformation (**4.2.2**), the product was purified by flash column chromatography (PE/EA = 1:1). White solid; 26.8 mg, 34% yield; m.p. = 187 – 189 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.12 (br, 1H), 7.73 – 7.68 (m, 5H), 7.54 (td, J = 7.5, 1.5 Hz, 2H), 7.44 (td, J = 7.5, 3.0 Hz, 4H), 7.27 – 7.18 (m, 2H), 7.09 – 7.05 (m, 1H), 4.97 (br, 1H), 3.55 (t, J = 6.5 Hz, 2H), 3.47 (d, J = 6.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 138.3 (d, J = 8.8 Hz), 137.8, 133.0 – 132.2 (m), 131.8 (d, J = 11.3 Hz), 128.9 (d, J = 12.5 Hz), 125.2, 121.9 (d, J = 10.0 Hz), 120.6, 119.6, 112.4, 109.8 (d, J = 127.5 Hz), 49.8, 44.1. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 22.6. **HRMS** (ESI): Calcd for $C_{22}H_{20}ClN_2OP$ $[M+H]^+$ 395.1075, found 395.1074.

5-(2,5-dimethylphenoxy)-*N*-(2-(diphenylphosphoryl)-1*H*-indol-3-yl)-2,2-dimethyl pentanamide (8)

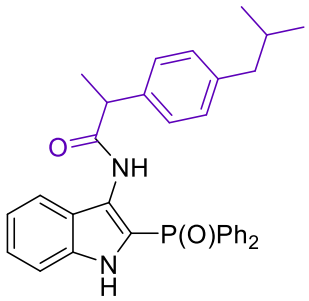


8

According to the further transformation (**4.2.3**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 97.8 mg, 87% yield; m.p. = 167 – 169 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.76 (br, 1H), 8.36 (br, 1H), 7.87 (d, J = 8.5

Hz, 1H), 7.71 – 7.66 (m, 4H), 7.54 (td, *J* = 7.5, 1.5 Hz, 2H), 7.44 (td, *J* = 7.5, 3.0 Hz, 4H), 7.31 – 7.19 (m, 2H), 7.16 – 7.08 (m, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.64 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.55 (s, 1H), 3.78 (t, *J* = 5.5 Hz, 2H), 2.29 (s, 3H), 2.13 (s, 3H), 1.84 – 1.53 (m, 4H), 1.20 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.0, 157.1, 137.7 (d, *J* = 10.0 Hz), 136.5, 132.9 (d, *J* = 3.8 Hz), 131.9 – 129.1 (m), 127.3 (d, *J* = 8.8 Hz), 125.4, 123.6, 123.0 (d, *J* = 8.8 Hz), 120.7, 120.6, 115.2 (d, *J* = 122.5 Hz), 112.0, 111.8, 68.0, 42.5, 37.8, 25.6, 25.3, 21.5, 15.9. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 23.1. **HRMS** (ESI): Calcd for $C_{35}H_{37}N_2O_3P$ $[M+H]^+$ 565.2615, found 565.2611.

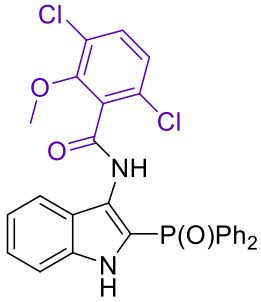
***N*-(2-(diphenylphosphoryl)-1*H*-indol-3-yl)-2-(4-isobutylphenyl)propenamide (9)**



9

According to the further transformation (**4.2.3**), the product was purified by flash column chromatography (PE/EA = 1:1). White solid; 92.2 mg, 89% yield; m.p. = 194 – 196 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.58 (br, 1H), 7.65 – 7.48 (m, 8H), 7.42 – 7.34 (m, 4H), 7.27 – 7.25 (m, 1H), 7.21 – 7.14 (m, 1H), 7.10 – 7.03 (m, 3H), 7.01 – 6.99 (m, 2H), 3.41 (q, *J* = 7.0 Hz, 1H), 2.42 (d, *J* = 7.0 Hz, 2H), 1.86 – 1.76 (m, 1H), 1.41 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.9, 140.6, 138.4, 137.5 (d, *J* = 10.0 Hz), 132.7 – 132.5 (m), 132.0 – 131.7 (m), 131.0 (d, *J* = 8.8 Hz), 129.6, 129.1 – 128.8 (m), 127.3, 125.0, 124.1 (d, *J* = 10.0 Hz), 123.5 (d, *J* = 10.0 Hz), 122.1, 120.5, 117.7 (d, *J* = 121.3 Hz), 112.2, 46.9, 45.1, 30.3, 22.5, 18.6. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 22.0. **HRMS** (ESI): Calcd for $C_{33}H_{33}N_2O_2P$ $[M+H]^+$ 521.2352, found 521.2349.

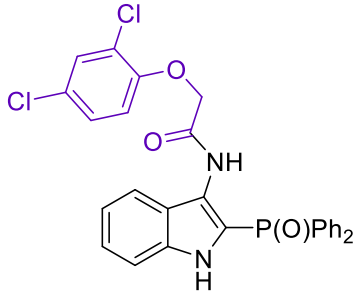
3,6-dichloro-*N*-(2-(diphenylphosphoryl)-1*H*-indol-3-yl)-2-methoxybenzamide (10)



10

According to the further transformation (**4.2.3**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 82.4 mg, 77% yield; m.p. = 233 – 235 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.67 (br, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.76 (br, 1H), 7.71 (dd, *J* = 13.0, 7.0 Hz, 4H), 7.54 – 7.45 (m, 2H), 7.44 – 7.34 (m, 5H), 7.33 – 7.23 (m, 2H), 7.22 – 7.15 (m, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.4, 153.9, 137.5 (d, *J* = 8.8 Hz), 133.0, 132.7, 132.0 (d, *J* = 10.0 Hz), 131.7 – 130.8 (m), 130.0, 129.0 (d, *J* = 12.5 Hz), 126.9, 126.0, 125.29, 123.3 – 123.1 (m), 122.5, 121.0, 118.1 (d, *J* = 120.0 Hz), 112.4, 62.5. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 22.1. **HRMS** (ESI): Calcd for $C_{28}H_{21}Cl_2N_2O_3P$ $[M+H]^+$ 535.0740, found 535.0735.

2-(2,4-dichlorophenoxy)-*N*-(2-(diphenylphosphoryl)-1*H*-indol-3-yl)acetamide (11)

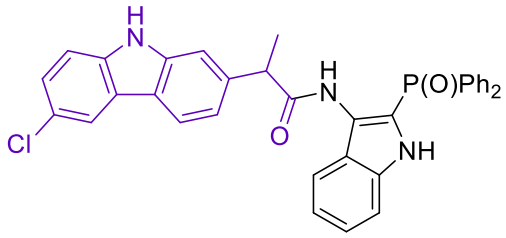


11

According to the further transformation (**4.2.3**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 88.4 mg, 83% yield; m.p. = 184 – 186 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 10.59 (br, 1H), 8.02 (br, 1H), 7.69 (dd, *J* = 13.0, 7.0 Hz, 4H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.42 – 7.33 (m, 5H),

7.30 – 7.26 (m, 1H), 7.19 – 7.12 (m, 2H), 6.70 (d, *J* = 9.0 Hz, 1H), 4.29 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.1, 151.4, 137.6 (d, *J* = 10.0 Hz), 132.6 (d, *J* = 2.5 Hz), 132.0 (d, *J* = 11.3 Hz), 131.3 (d, *J* = 110.0 Hz), 130.3, 128.9 (d, *J* = 12.5 Hz), 128.0, 127.5, 125.1, 123.9 (d, *J* = 8.8 Hz), 123.9, 121.1, 120.9, 120.4 – 120.1 (m), 114.4, 112.9, 68.1. **^{31}P NMR** (202 MHz, $CDCl_3$): δ 21.1. **HRMS** (ESI): Calcd for $C_{28}H_{21}Cl_2N_2O_3P$ $[M+H]^+$ 535.0740, found 535. 0735.

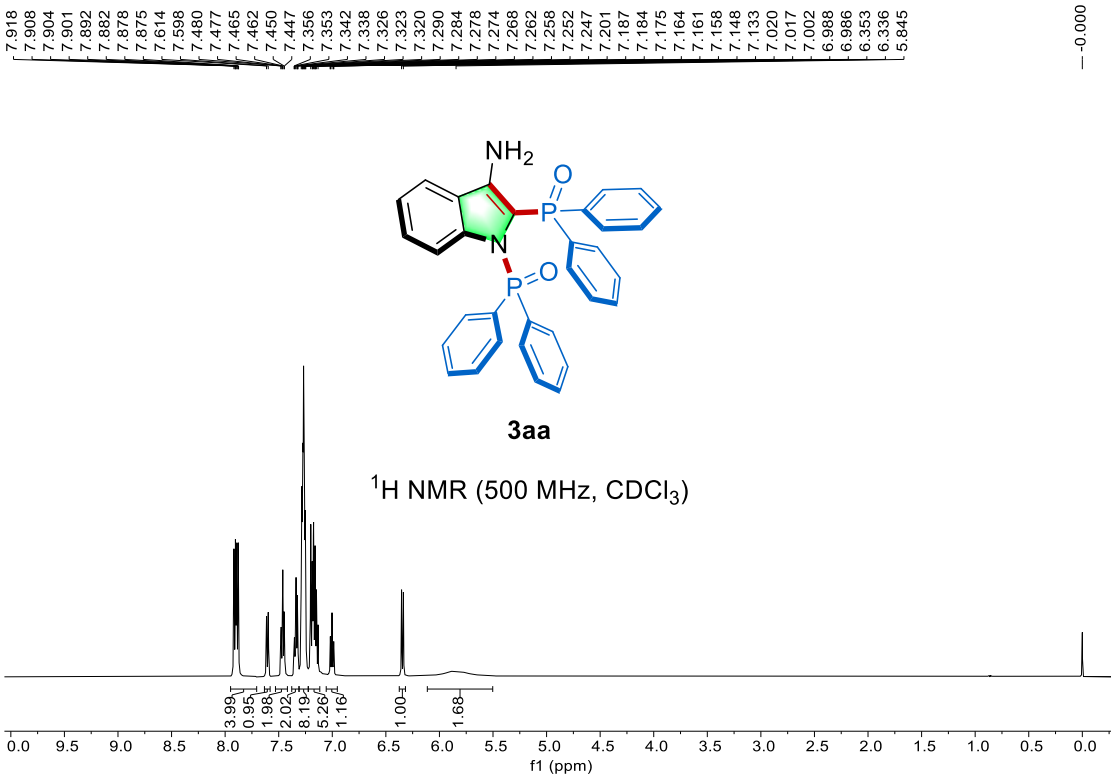
2-(6-chloro-9*H*-carbazol-2-yl)-*N*-(2-(diphenylphosphoryl)-1*H*-indol-3-yl)propanamide (12)

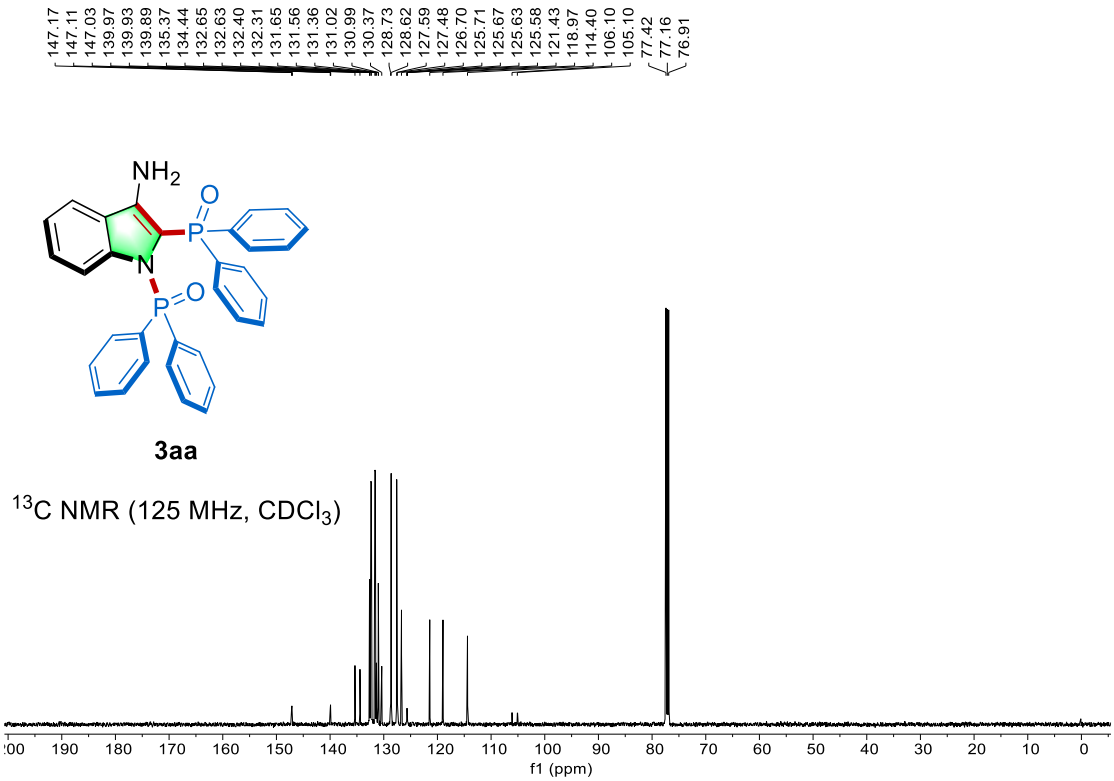


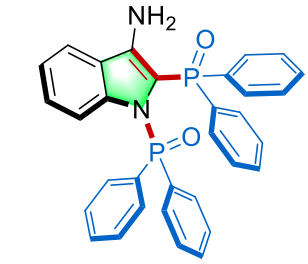
12

According to the further transformation (**4.2.3**), the product was purified by flash column chromatography (PE/EA = 1:3). White solid; 103.0 mg, 88% yield; m.p. = 210 – 212 ℃. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 11.53 (s, 1H), 11.46 (s, 1H), 9.38 (s, 1H), 8.23 (d, *J* = 2.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.64 (m, 4H), 7.64 – 7.55 (m, 2H), 7.55 – 7.44 (m, 6H), 7.44 – 7.36 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.17 (m, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 3.67 (q, *J* = 7.0 Hz, 1H), 1.32 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 173.0, 140.7, 138.5, 137.3 (d, *J* = 10.0 Hz), 132.8 – 131.5 (m), 128.7 (dd, *J* = 12.5 Hz, 8.8 Hz), 125.1 – 123.0 (m), 120.8 – 118.9 (m), 112.6, 112.5, 110.0, 45.8, 19.1. **^{31}P NMR** (202 MHz, DMSO-d_6): δ 18.9. **HRMS** (ESI): Calcd for $C_{35}H_{28}ClN_3O_2P$ $[M+H]^+$ 588.1602, found 588. 1598.

9. ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR Spectra of Compounds

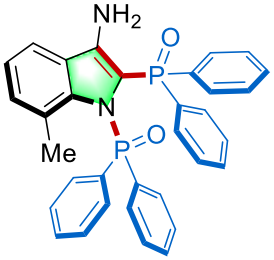






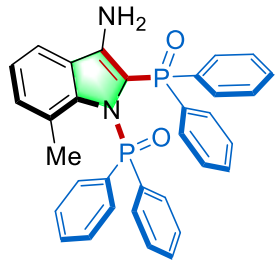
3aa

^{31}P NMR (202 MHz, $CDCl_3$)



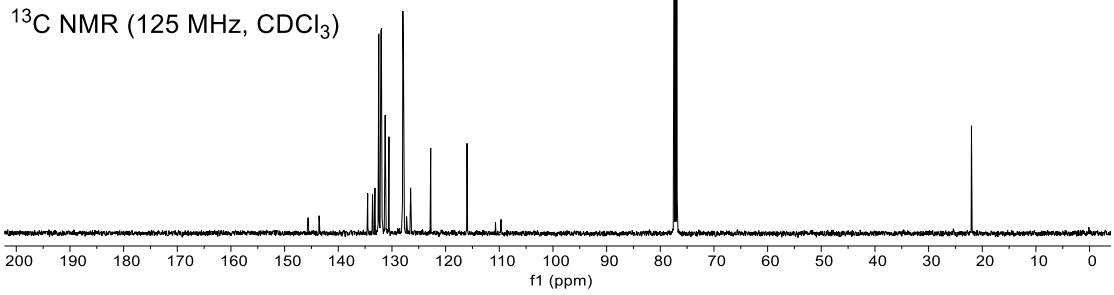
3ba

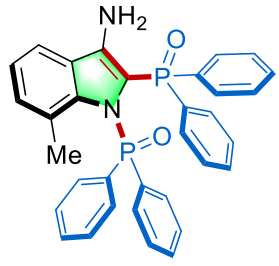
^{1}H NMR (500 MHz, $CDCl_3$)



3ba

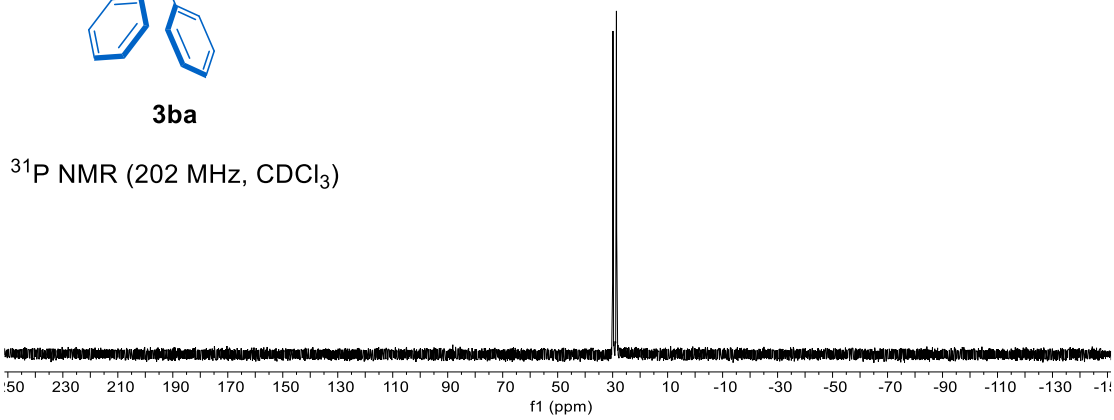
^{13}C NMR (125 MHz, $CDCl_3$)

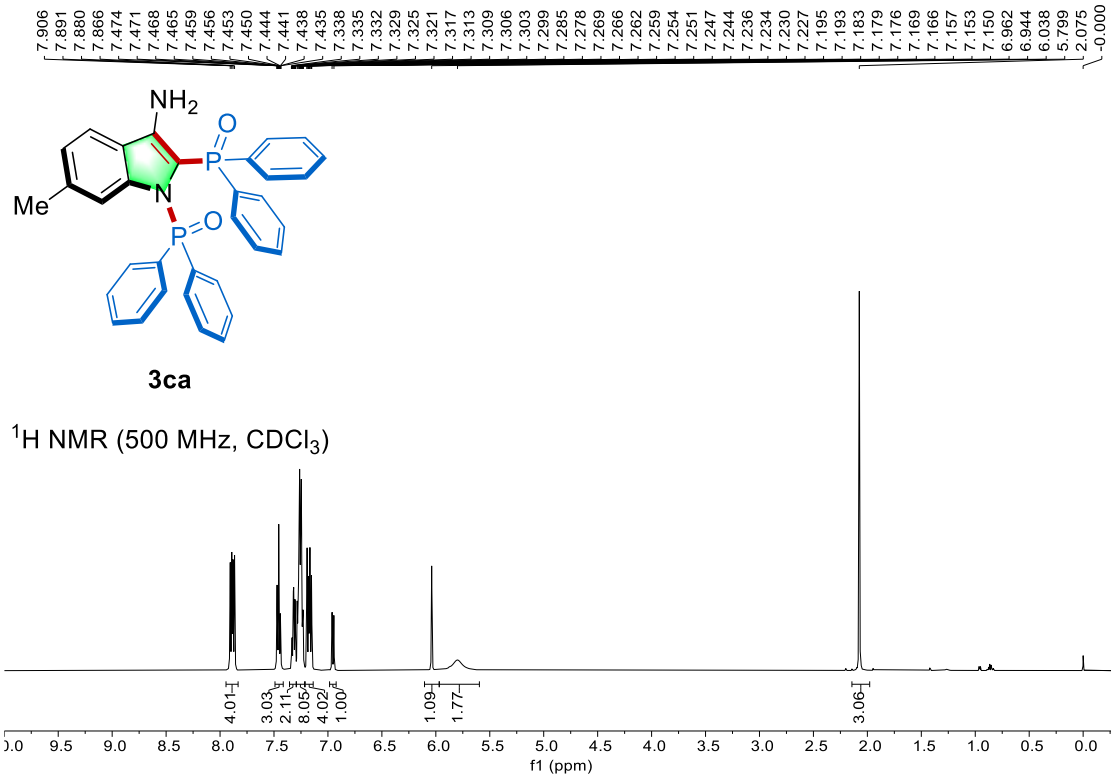




3ba

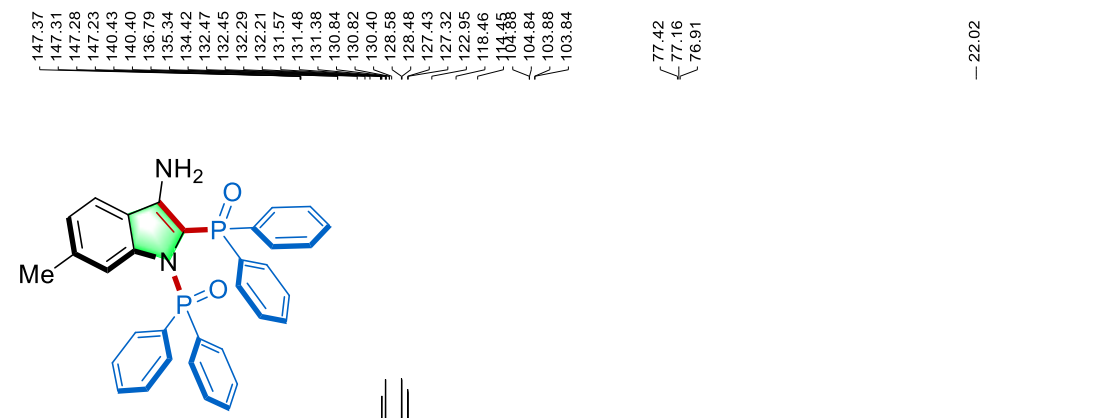
^{31}P NMR (202 MHz, $CDCl_3$)





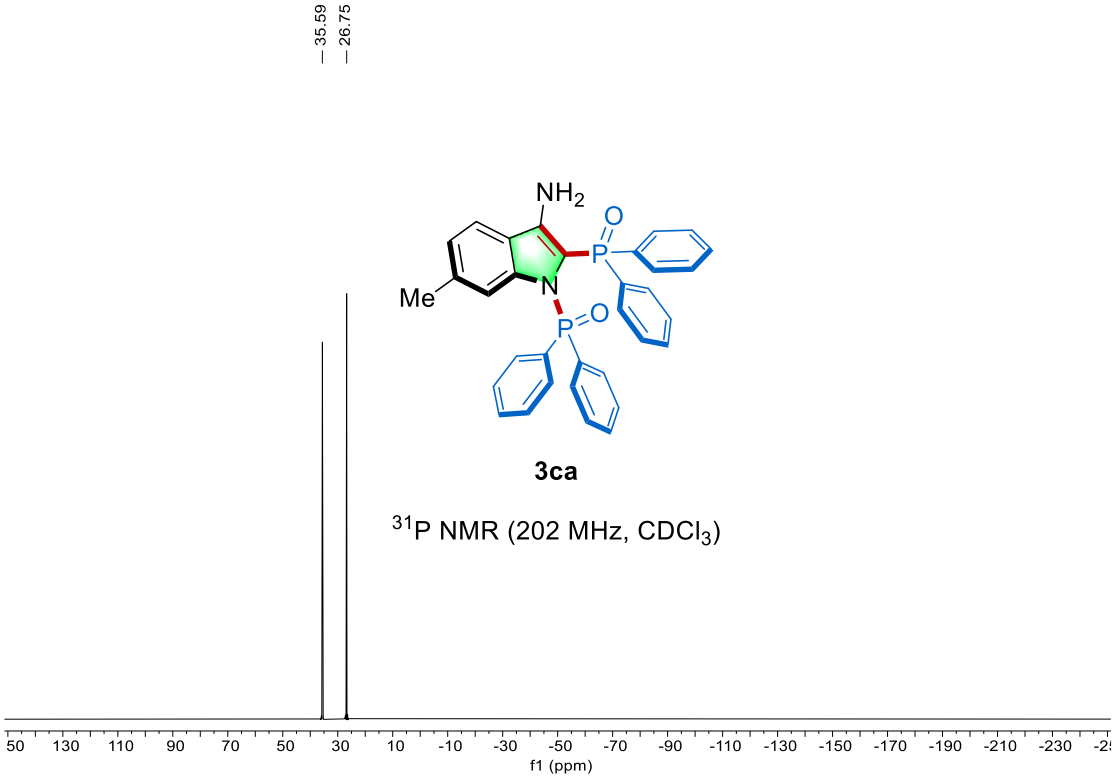
3ca

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



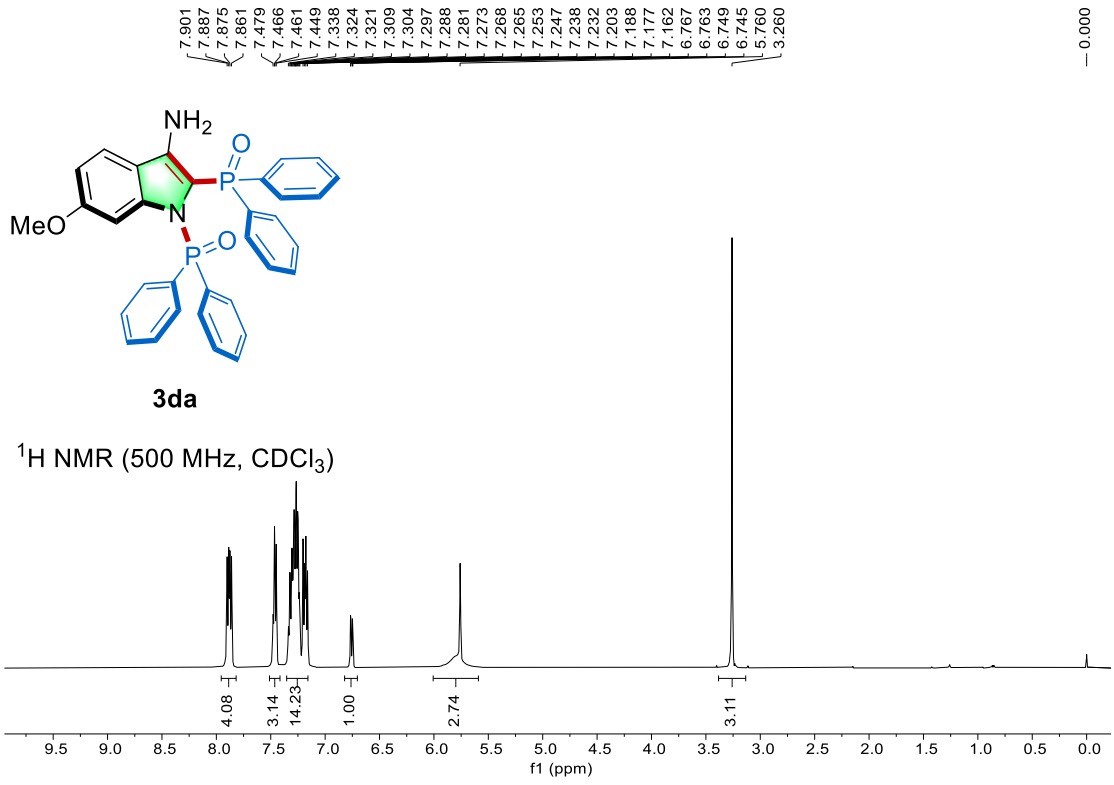
3ca

^{13}C NMR (125 MHz, $CDCl_3$)



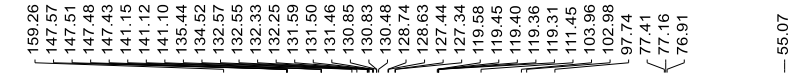
3ca

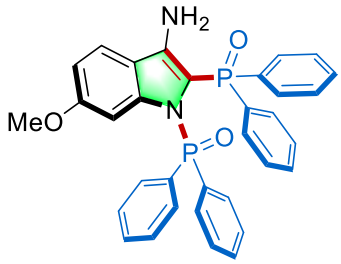
^{31}P NMR (202 MHz, $CDCl_3$)



3da

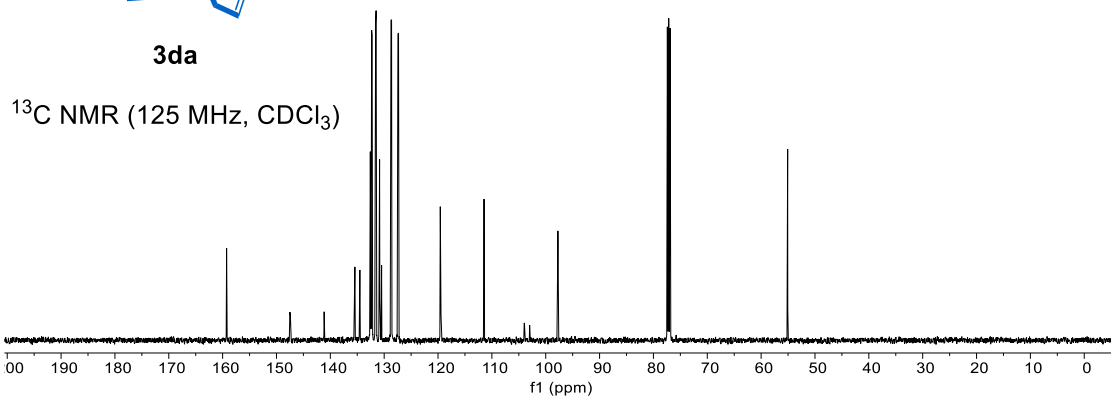
^{1}H NMR (500 MHz, $CDCl_3$)

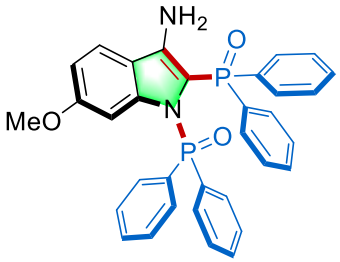




3da

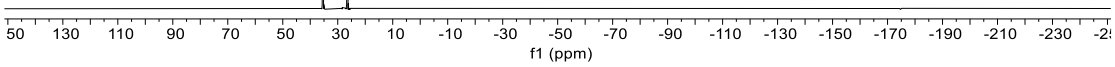
^{13}C NMR (125 MHz, $CDCl_3$)

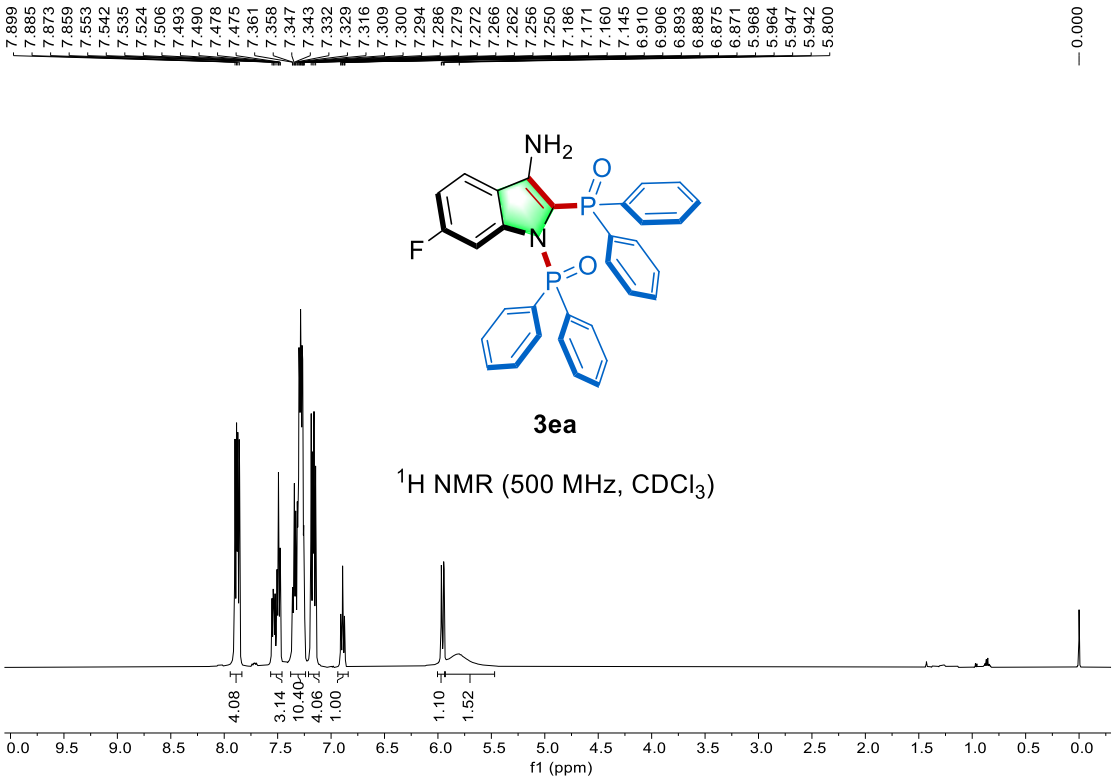


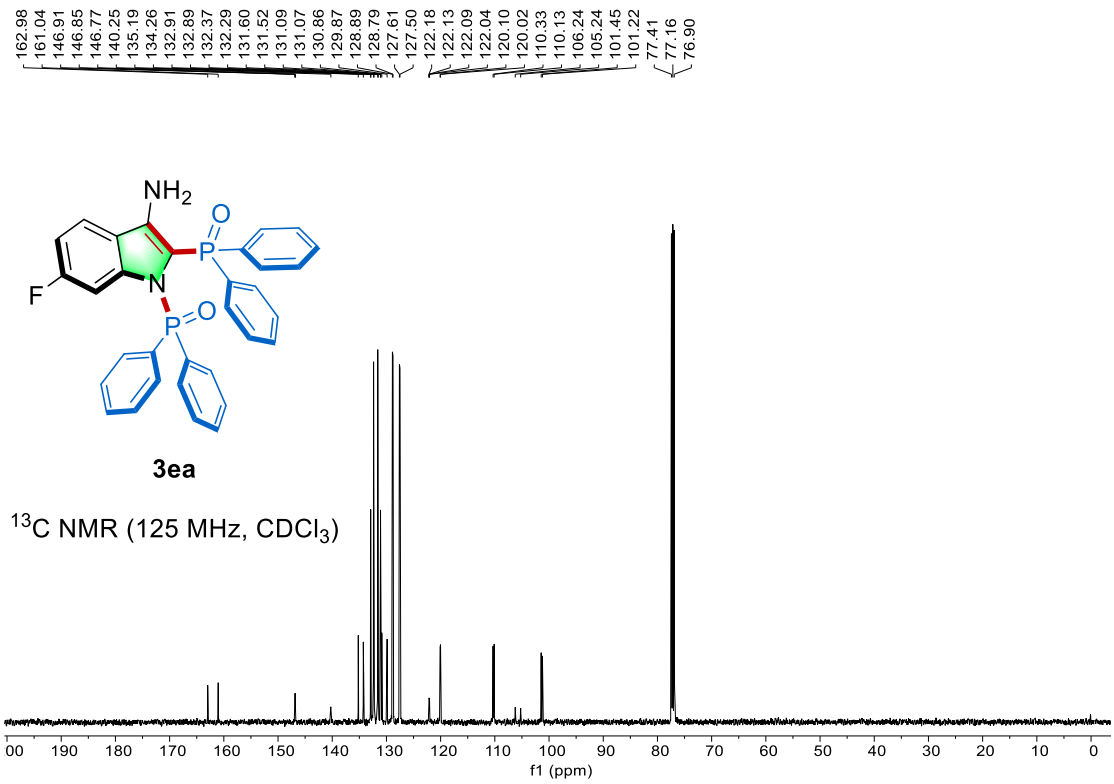


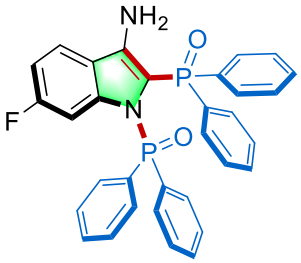
3da

^{31}P NMR (202 MHz, $CDCl_3$)



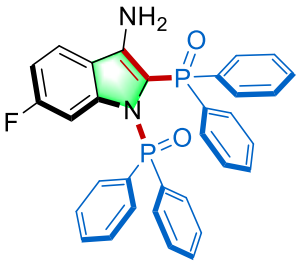

7.899
7.885
7.873
7.859
7.553
7.542
7.535
7.524
7.506
7.493
7.490
7.478
7.475
7.361
7.358
7.347
7.343
7.332
7.329
7.316
7.309
7.300
7.294
7.286
7.279
7.272
7.266
7.262
7.256
7.250
7.186
7.171
7.160
7.145
6.910
6.906
6.893
6.888
6.875
6.871
5.968
5.964
5.947
5.942
5.800
0.000
NH2
O
P
F
N
P
O
3ea
1H NMR (500 MHz, CDCl3)
4.08
3.14
10.40
4.06
1.00
1.10
1.52
0.0
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
f1 (ppm)


162.98
161.04
146.91
146.85
146.77
140.25
135.19
134.26
132.91
132.89
132.37
132.29
131.60
131.52
131.09
131.07
130.86
129.87
128.89
128.79
127.61
127.50
122.18
122.13
122.09
122.04
120.10
120.02
110.33
110.13
106.24
105.24
101.45
101.22
77.41
77.16
76.90
NH2
O
P
F
N
P
O
3ea
13C NMR (125 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



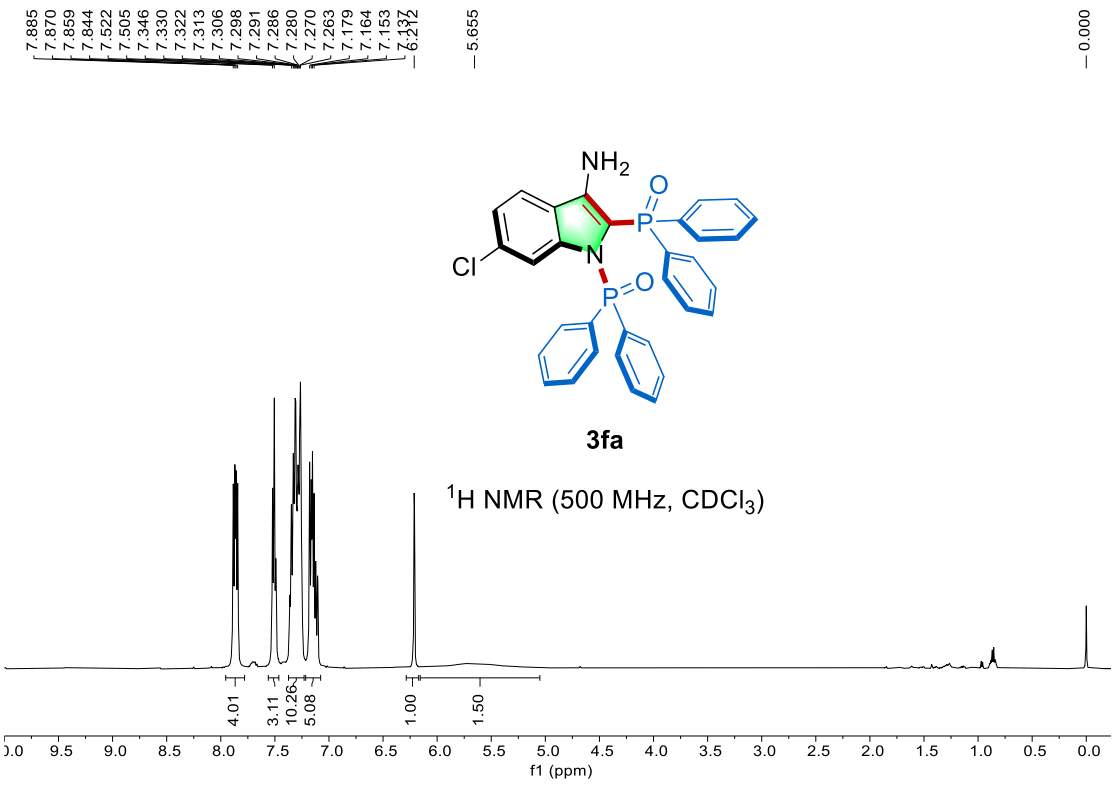
3ea

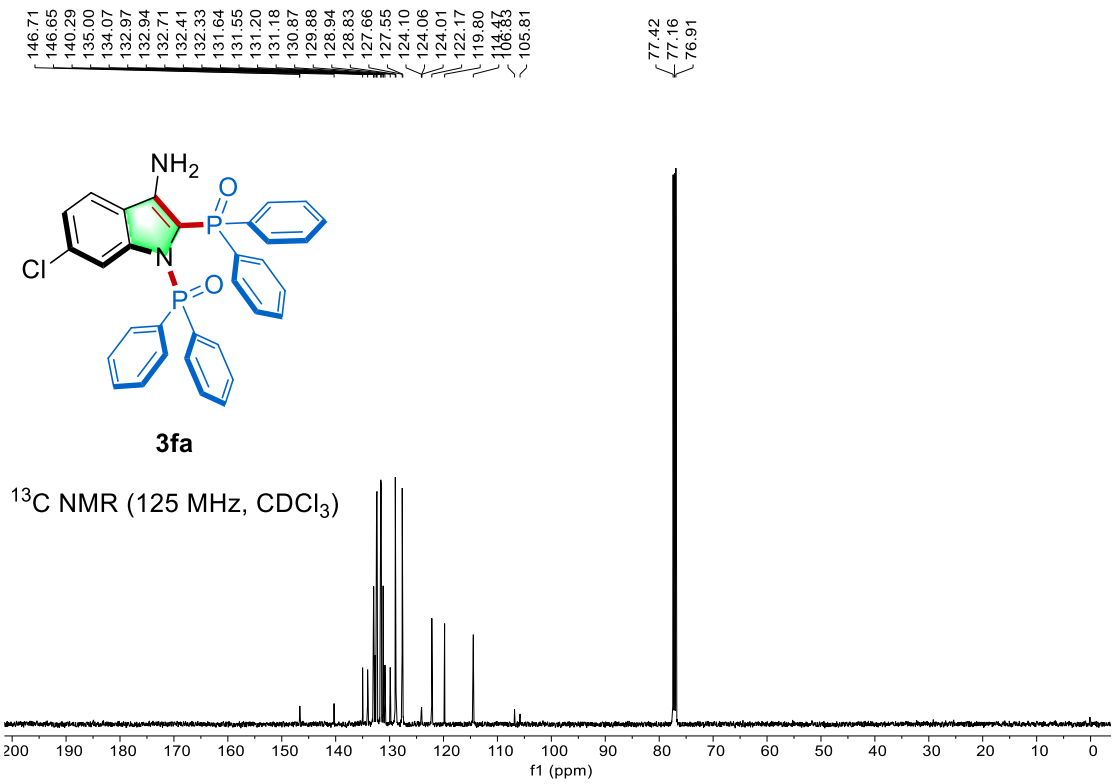
^{31}P NMR (202 MHz, $CDCl_3$)

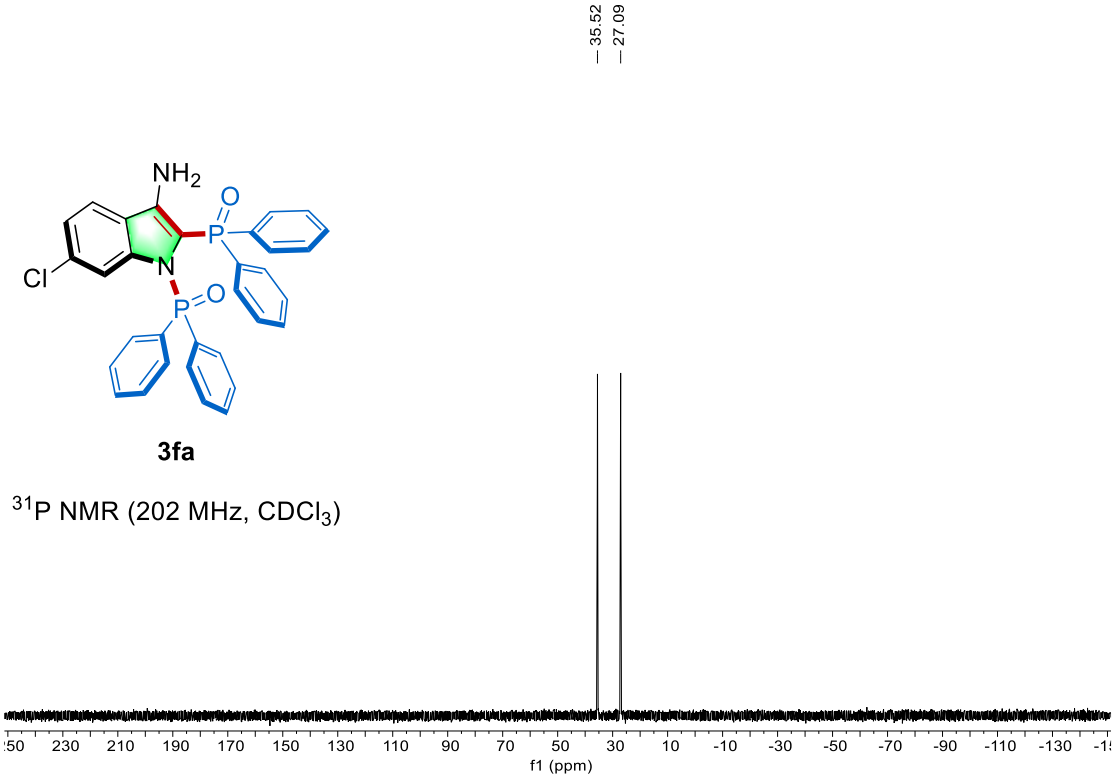


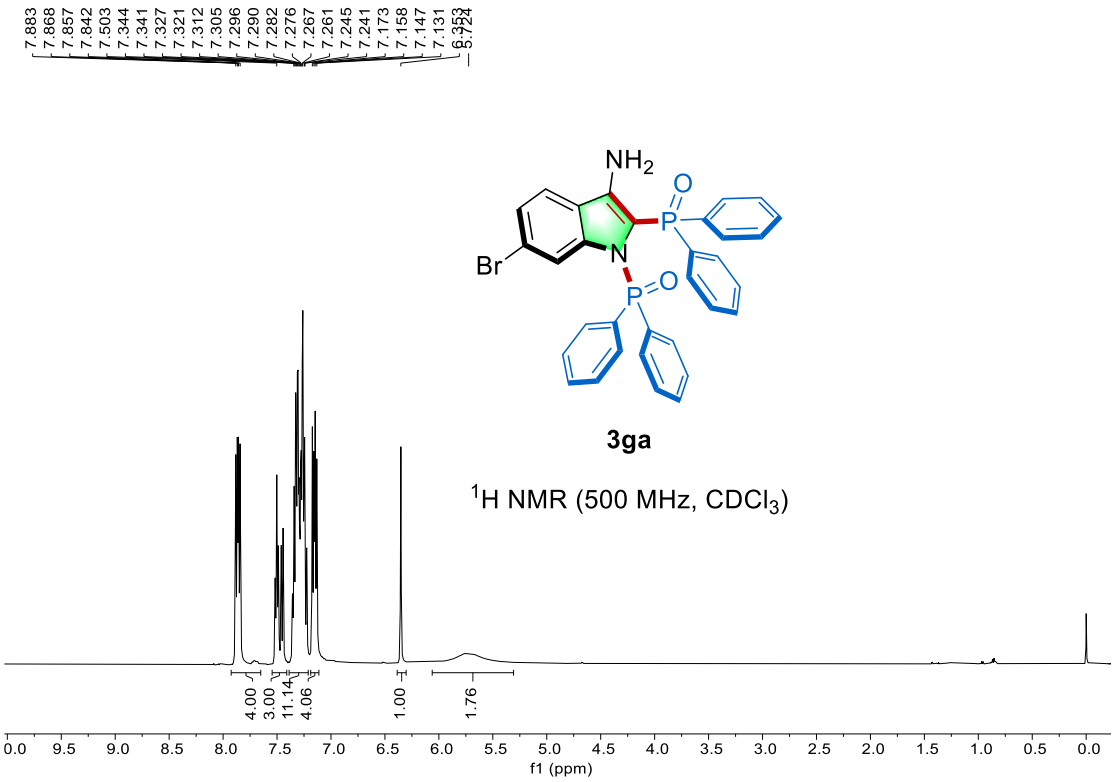
3ea

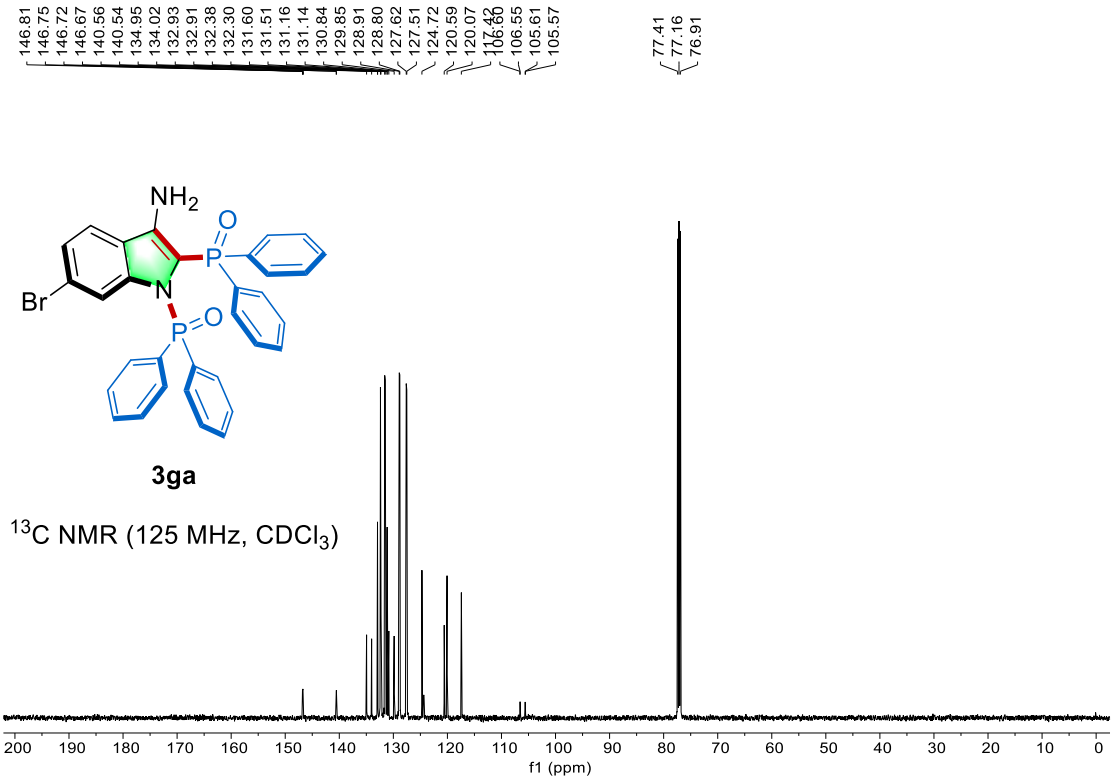
^{19}F NMR (376 MHz, $CDCl_3$)

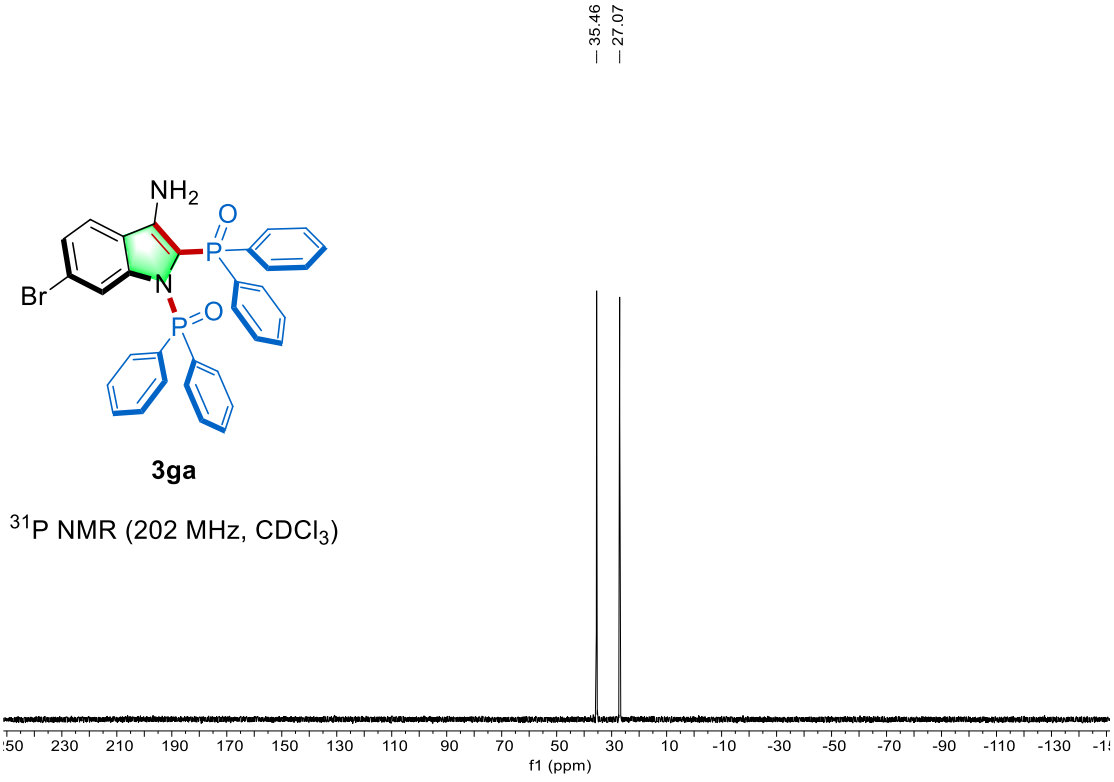

7.885
7.870
7.859
7.844
7.522
7.505
7.346
7.330
7.322
7.313
7.306
7.298
7.291
7.286
7.280
7.270
7.263
7.179
7.164
7.153
7.137
7.132
5.655
0.000
NH2
O
P
Cl
N
P
O
3fa
1H NMR (500 MHz, CDCl3)
4.01
3.11
10.26
5.08
1.00
1.50
f1 (ppm)

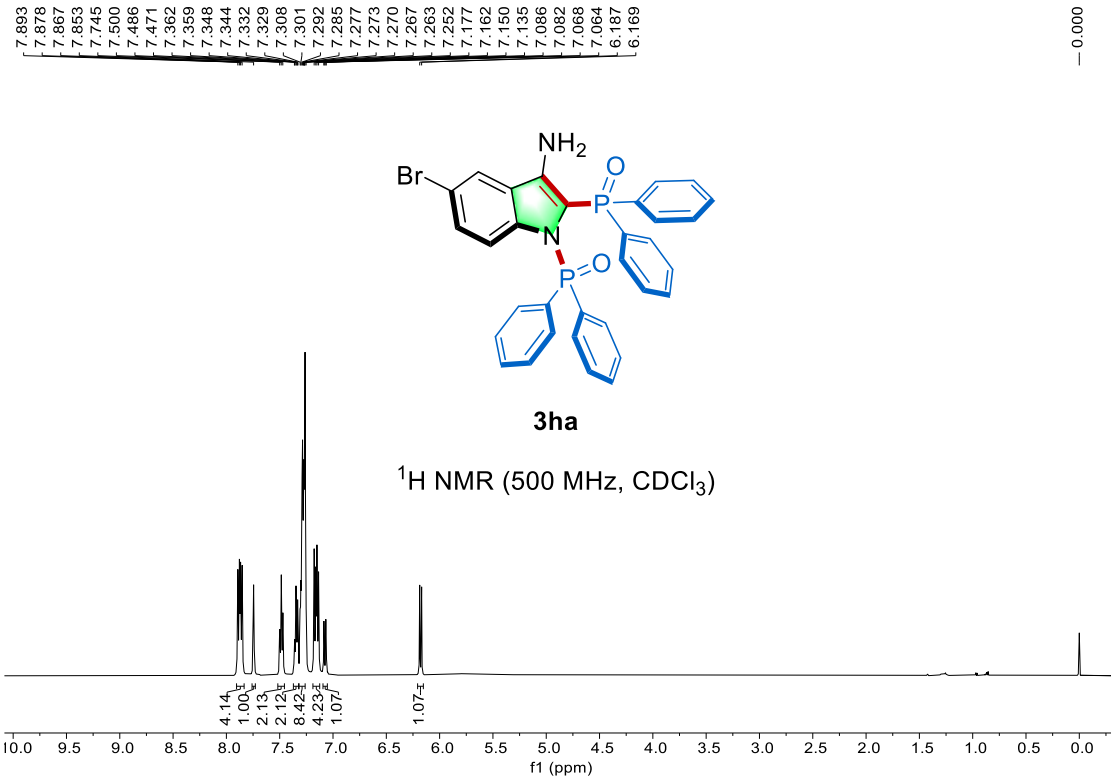

146.71
146.65
140.29
135.00
134.07
132.97
132.94
132.71
132.41
132.33
131.64
131.55
131.20
131.18
130.87
129.88
128.94
128.83
127.66
127.55
124.10
124.06
124.01
122.17
119.80
114.47
106.83
105.81
77.42
77.16
76.91
NH2
O
P
Cl
N
P
O
3fa
13C NMR (125 MHz, CDCl3)
f1 (ppm)

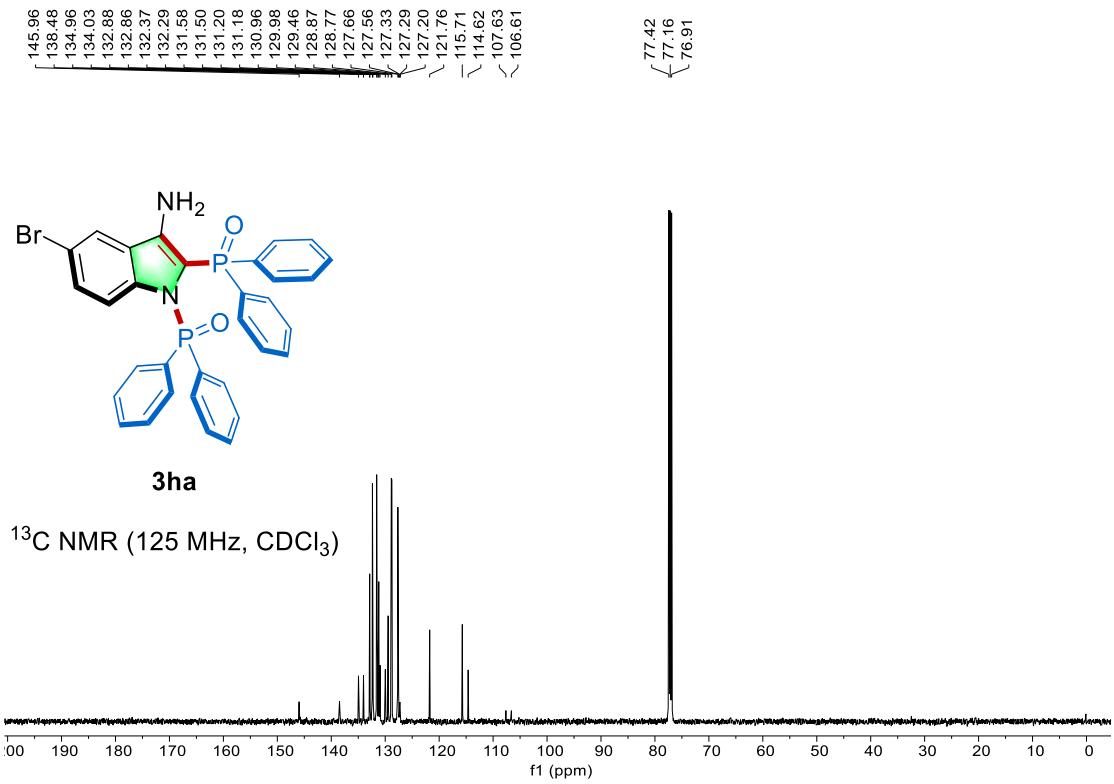

35.52
27.09
NH2
O
P
Cl
N
P
O
3fa
31P NMR (202 MHz, CDCl3)
f1 (ppm)

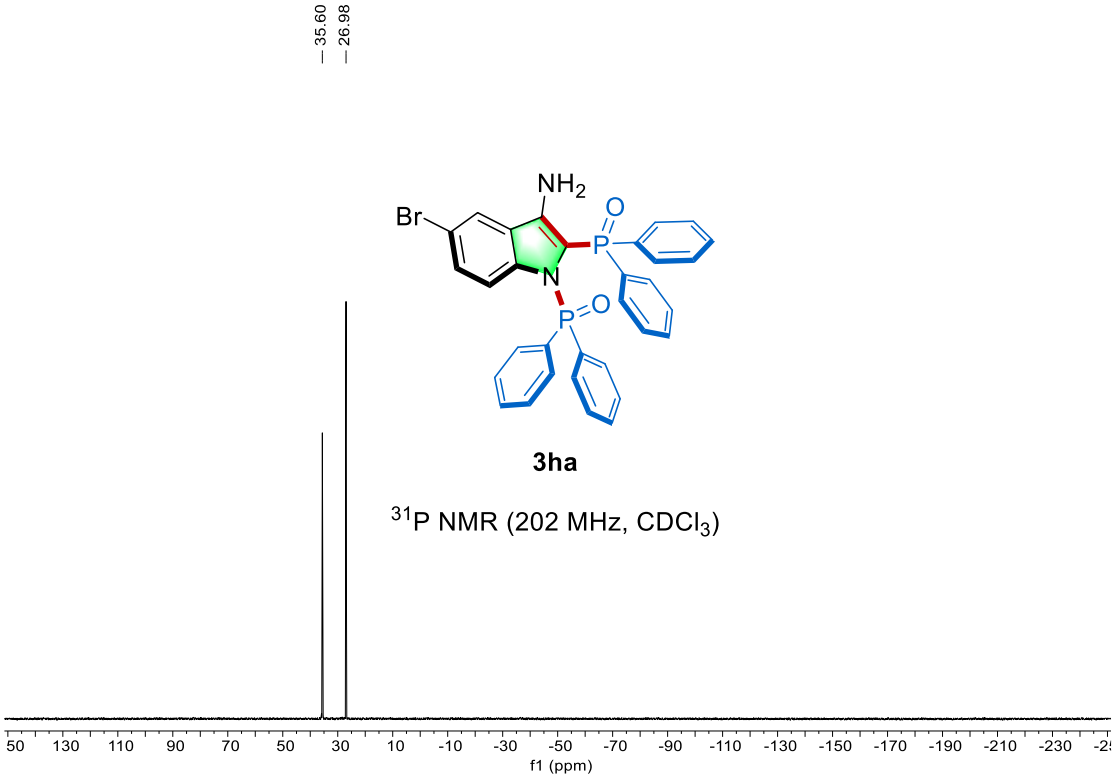

7.883
7.868
7.857
7.842
7.503
7.344
7.341
7.327
7.321
7.312
7.305
7.296
7.290
7.282
7.276
7.267
7.261
7.245
7.241
7.173
7.158
7.147
7.131
6.353
5.724
NH2
O
P
Br
N
P
O
3ga
1H NMR (500 MHz, CDCl3)
4.00
3.00
11.14
4.06
1.00
1.76
f1 (ppm)

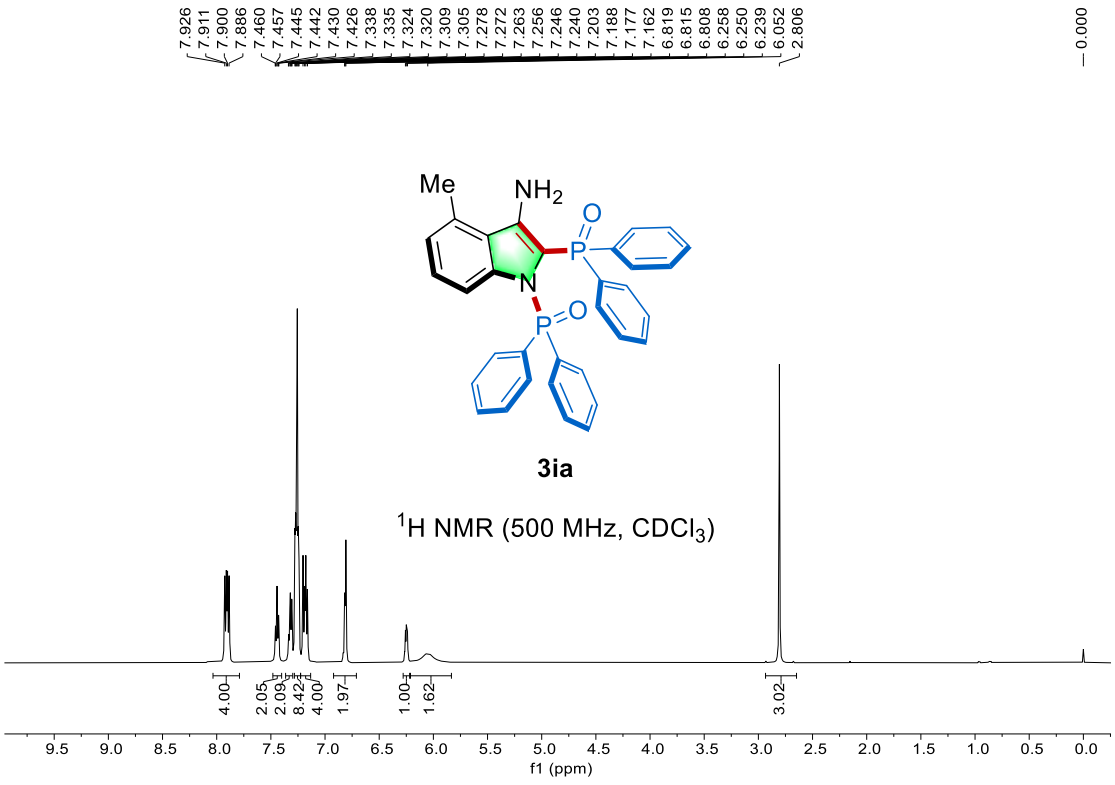

146.81
146.75
146.72
146.67
140.56
140.54
134.95
134.02
132.93
132.91
132.38
132.30
131.60
131.51
131.16
131.14
130.84
129.85
128.91
128.80
127.62
127.51
124.72
120.59
120.07
117.42
106.66
106.55
105.61
105.57
77.41
77.16
76.91
NH2
O
P
Br
N
P
O
3ga
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

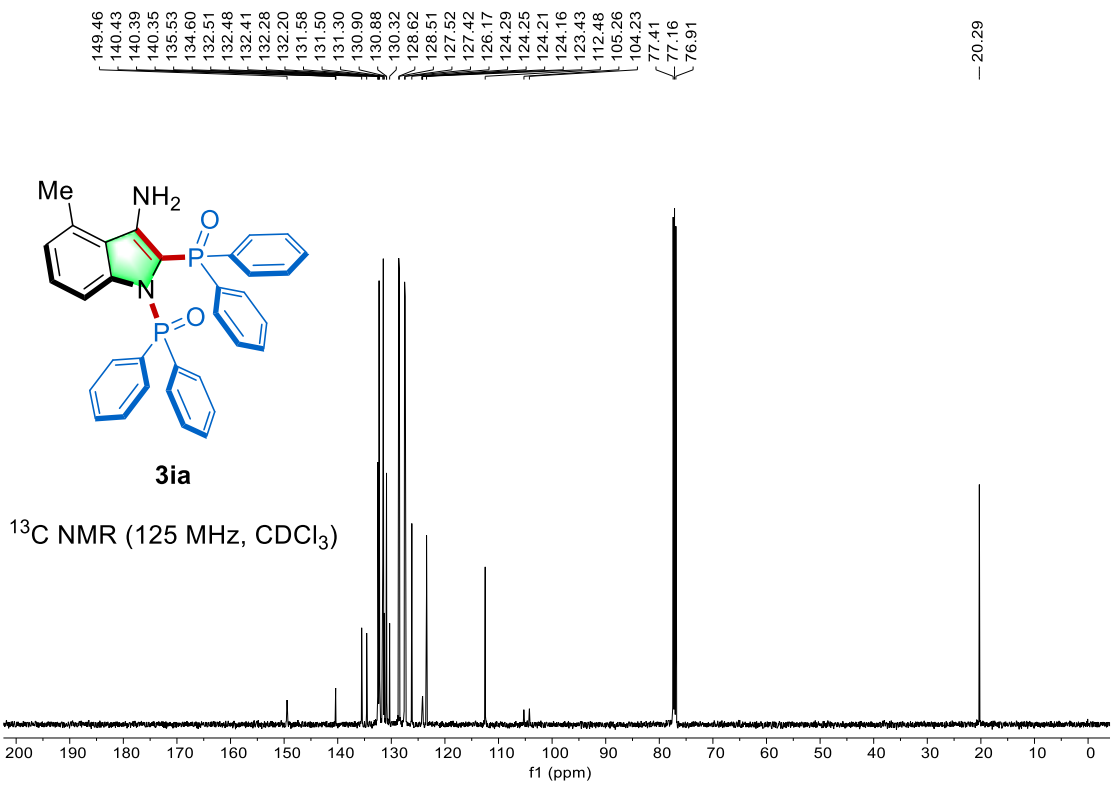

35.46
27.07
NH2
O
P
Br
N
P
O
3ga
31P NMR (202 MHz, CDCl3)
50
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
f1 (ppm)


7.893
7.878
7.867
7.853
7.745
7.500
7.486
7.471
7.362
7.359
7.348
7.344
7.332
7.329
7.308
7.301
7.292
7.285
7.277
7.273
7.270
7.267
7.263
7.252
7.177
7.162
7.150
7.135
7.086
7.082
7.068
7.064
6.187
6.169
0.000
NH2
Br
O
P
N
P
O
3ha
1H NMR (500 MHz, CDCl3)
4.14
1.00
2.13
2.12
8.42
4.23
1.07
1.07
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
f1 (ppm)


145.96
138.48
134.96
134.03
132.88
132.86
132.37
132.29
131.58
131.50
131.20
131.18
130.96
129.98
129.46
128.87
128.77
127.66
127.56
127.33
127.29
127.20
121.76
115.71
114.62
107.63
106.61
77.42
77.16
76.91
NH2
Br
O
P
N
P
O
3ha
13C NMR (125 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

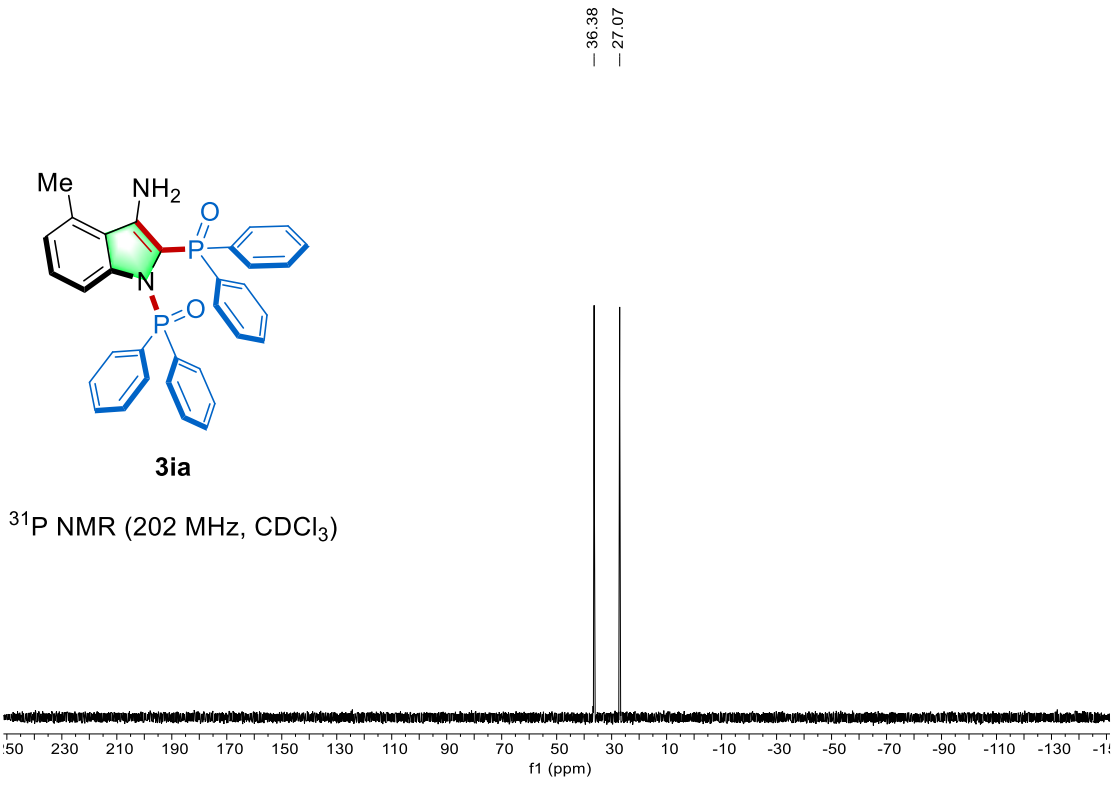

35.60
26.98
NH2
Br
O
P
N
P
O
3ha
31P NMR (202 MHz, CDCl3)
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


7.926
7.911
7.900
7.886
7.460
7.457
7.445
7.442
7.430
7.426
7.338
7.335
7.324
7.320
7.309
7.305
7.278
7.272
7.263
7.256
7.246
7.240
7.203
7.188
7.177
7.162
6.819
6.815
6.808
6.258
6.250
6.239
6.052
2.806
0.000
Me
NH2
O
P
N
P
O
3ia
1H NMR (500 MHz, CDCl3)
4.00
2.05
2.09
8.42
4.00
1.97
1.00
1.62
3.02
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
f1 (ppm)



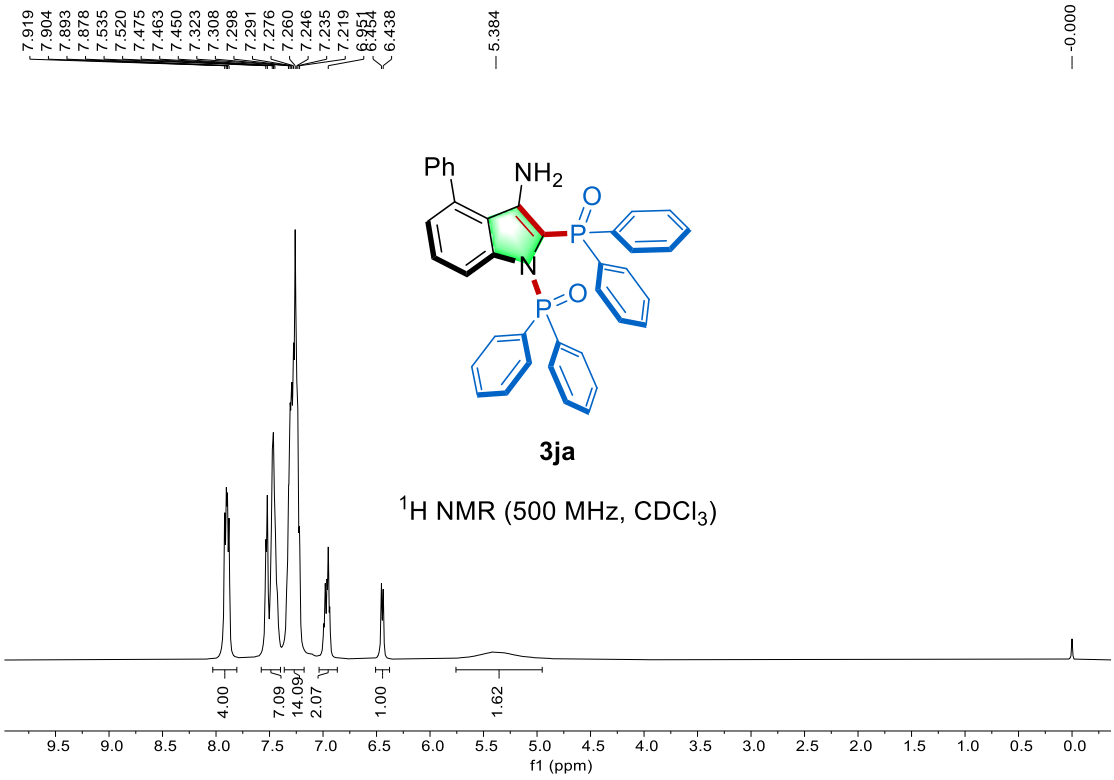
3ia

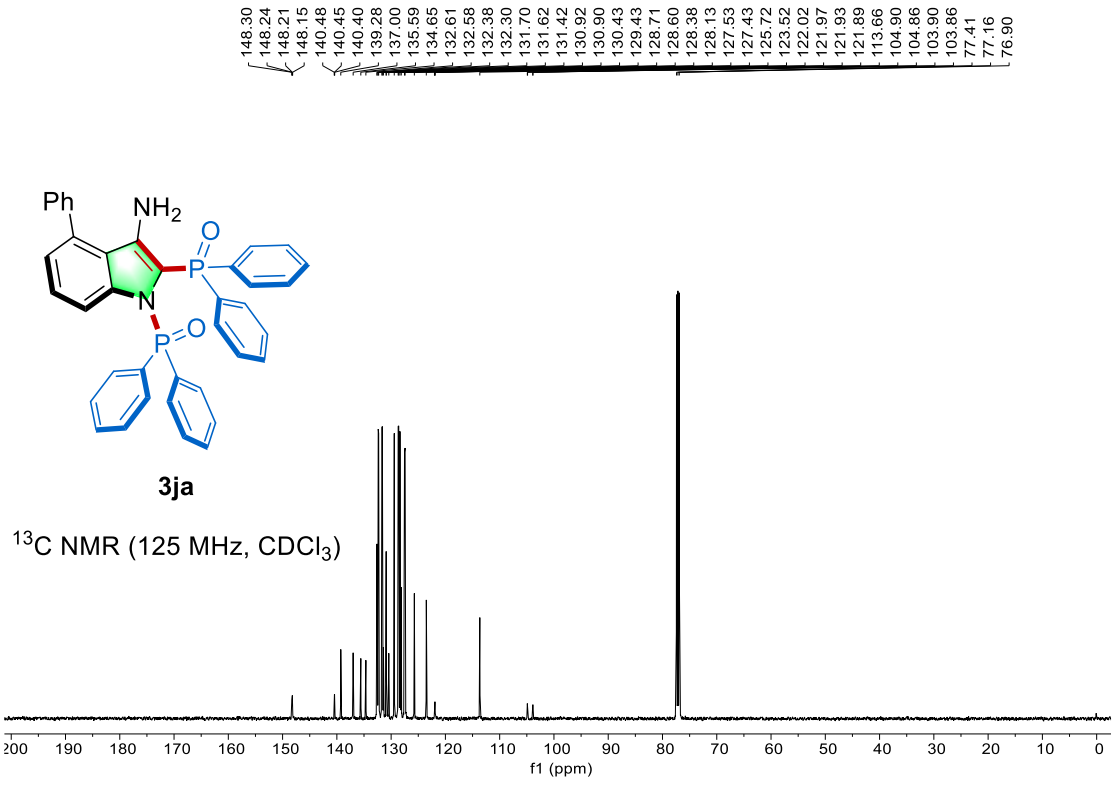
^{13}C NMR (125 MHz, $CDCl_3$)

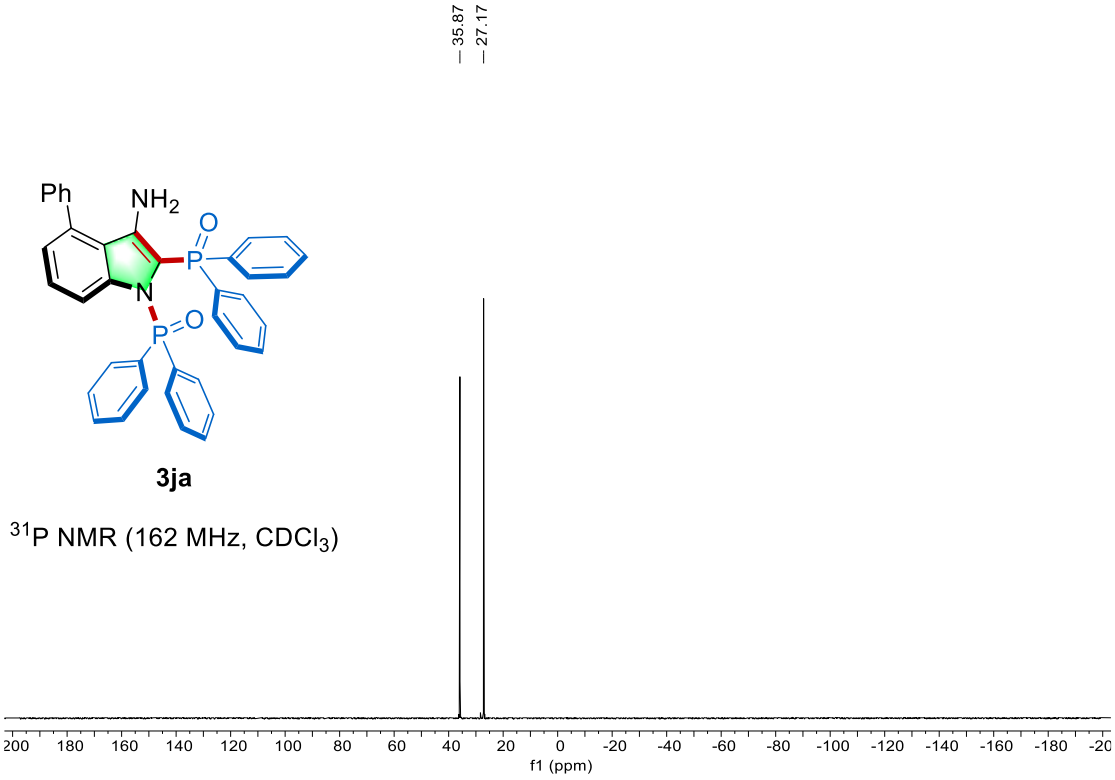


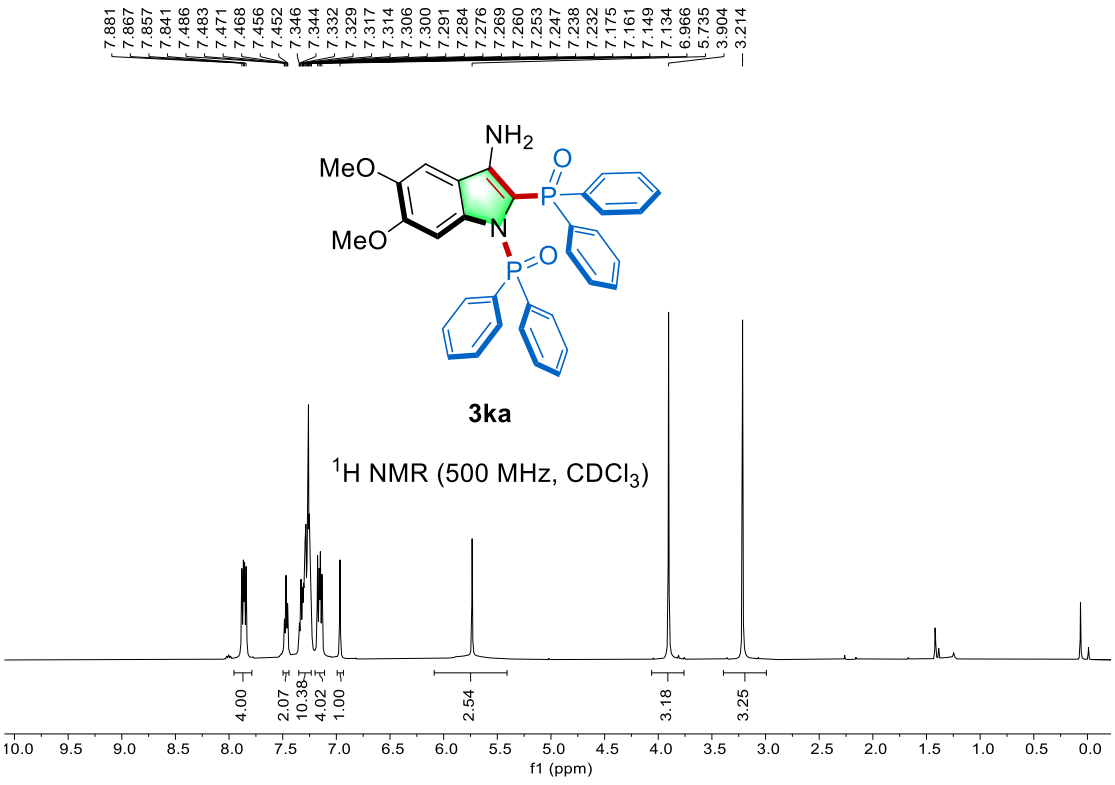
3ia

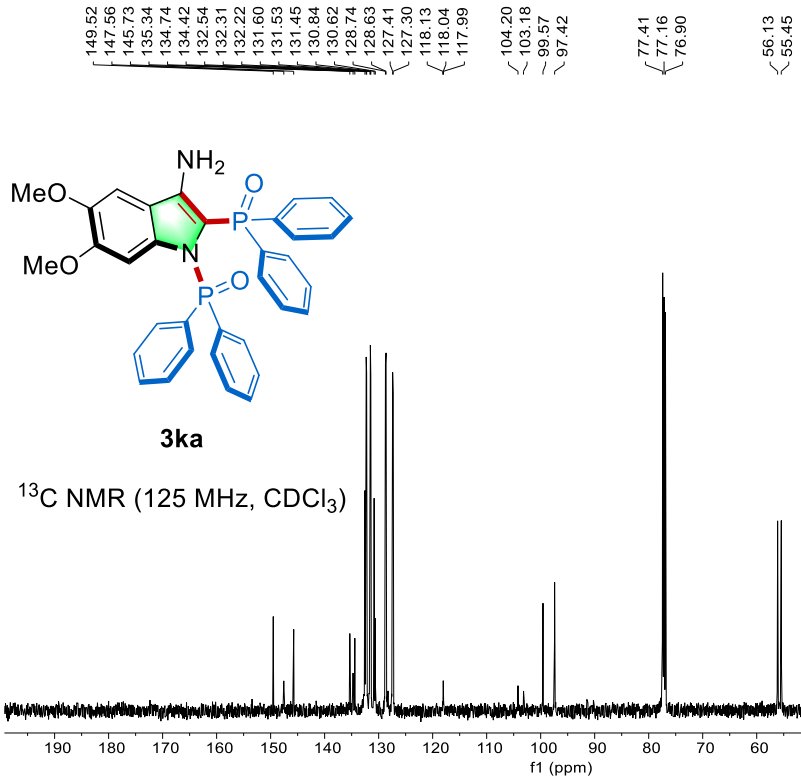
^{31}P NMR (202 MHz, $CDCl_3$)

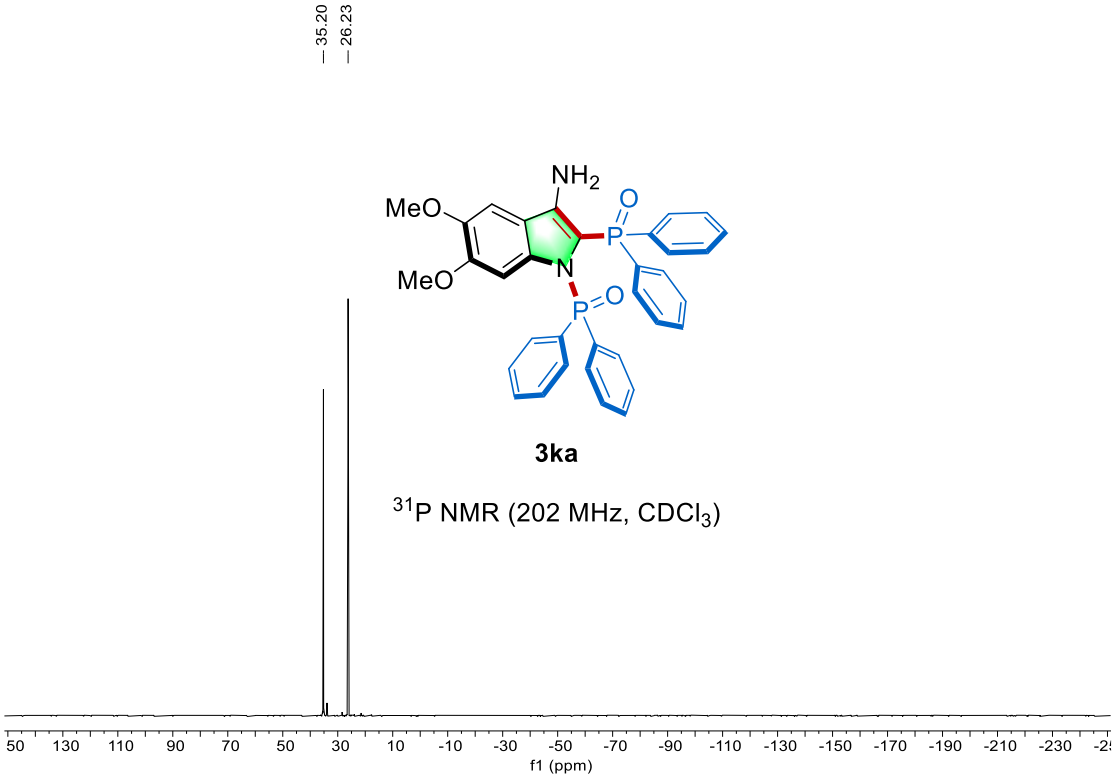

7.919
7.904
7.893
7.878
7.535
7.520
7.475
7.463
7.450
7.323
7.308
7.298
7.291
7.276
7.260
7.246
7.235
7.219
6.951
6.454
6.438
5.384
-0.000
Ph
NH2
O
P
N
P
O
3ja
1H NMR (500 MHz, CDCl3)
4.00
7.09
14.09
2.07
1.00
1.62
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

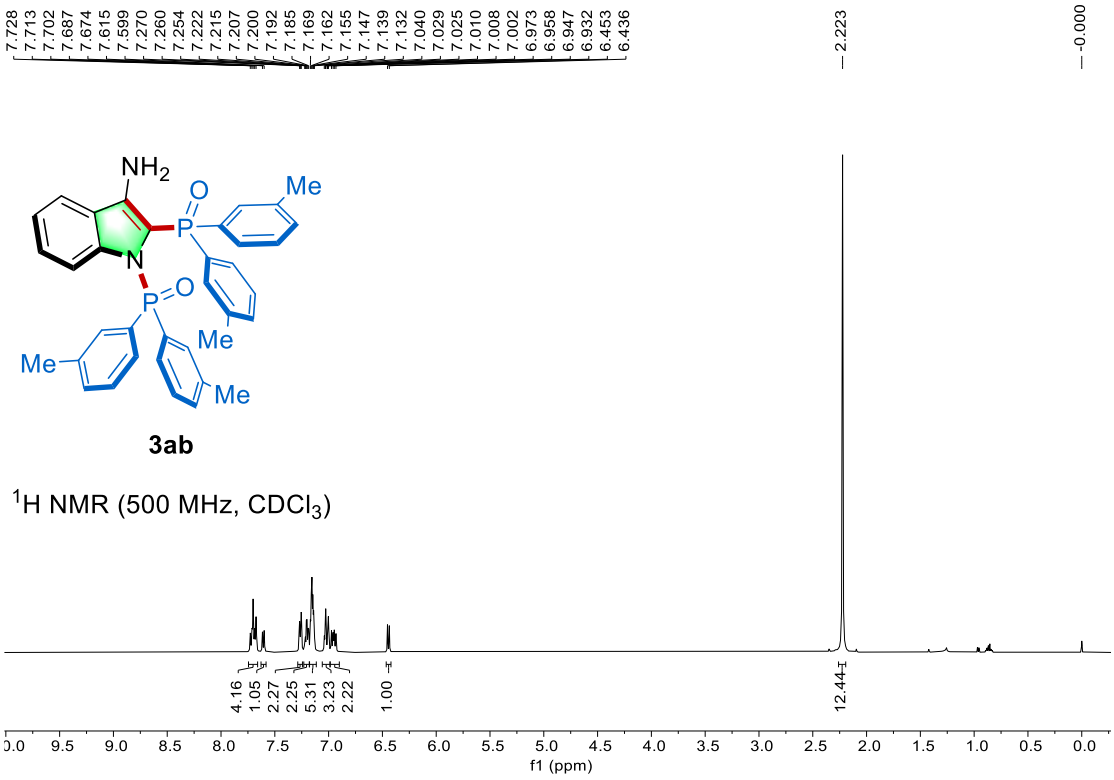

148.30
148.24
148.21
148.15
140.48
140.45
140.40
139.28
137.00
135.59
134.65
132.61
132.58
132.38
132.30
131.70
131.62
131.42
130.92
130.90
130.43
129.43
128.71
128.60
128.38
128.13
127.53
127.43
125.72
123.52
122.02
121.97
121.93
121.89
113.66
104.90
104.86
103.90
103.86
77.41
77.16
76.90
Ph
NH2
O
P
N
P
O
3ja
13C NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


35.87
27.17
Ph
NH2
O
P
N
P
O
3ja
31P NMR (162 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -20
f1 (ppm)


7.881
7.867
7.857
7.841
7.486
7.483
7.471
7.468
7.456
7.452
7.346
7.344
7.332
7.329
7.317
7.314
7.306
7.300
7.291
7.284
7.276
7.269
7.260
7.253
7.247
7.238
7.232
7.175
7.161
7.149
7.134
6.966
5.735
3.904
3.214
NH2
MeO
MeO
O
P
N
P
O
3ka
1H NMR (500 MHz, CDCl3)
4.00
2.07
10.38
4.02
1.00
2.54
3.18
3.25
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
f1 (ppm)

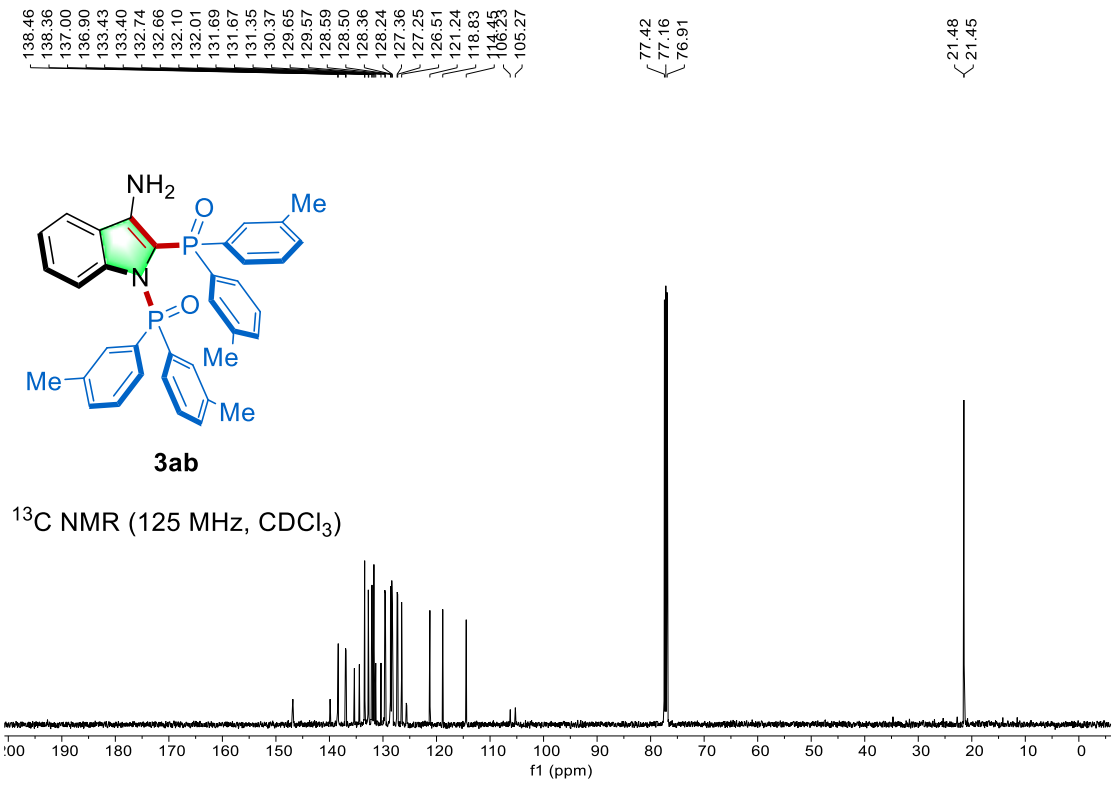

149.52
147.56
145.73
135.34
134.74
134.42
132.54
132.31
132.22
131.60
131.53
131.45
130.84
130.62
128.74
128.63
127.41
127.30
118.13
118.04
117.99
104.20
103.18
99.57
97.42
77.41
77.16
76.90
56.13
55.45
NH2
MeO
MeO
O
P
N
P=O
3ka
13C NMR (125 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


35.20
26.23
NH2
MeO
MeO
O
P
N
P=O
3ka
31P NMR (202 MHz, CDCl3)
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)



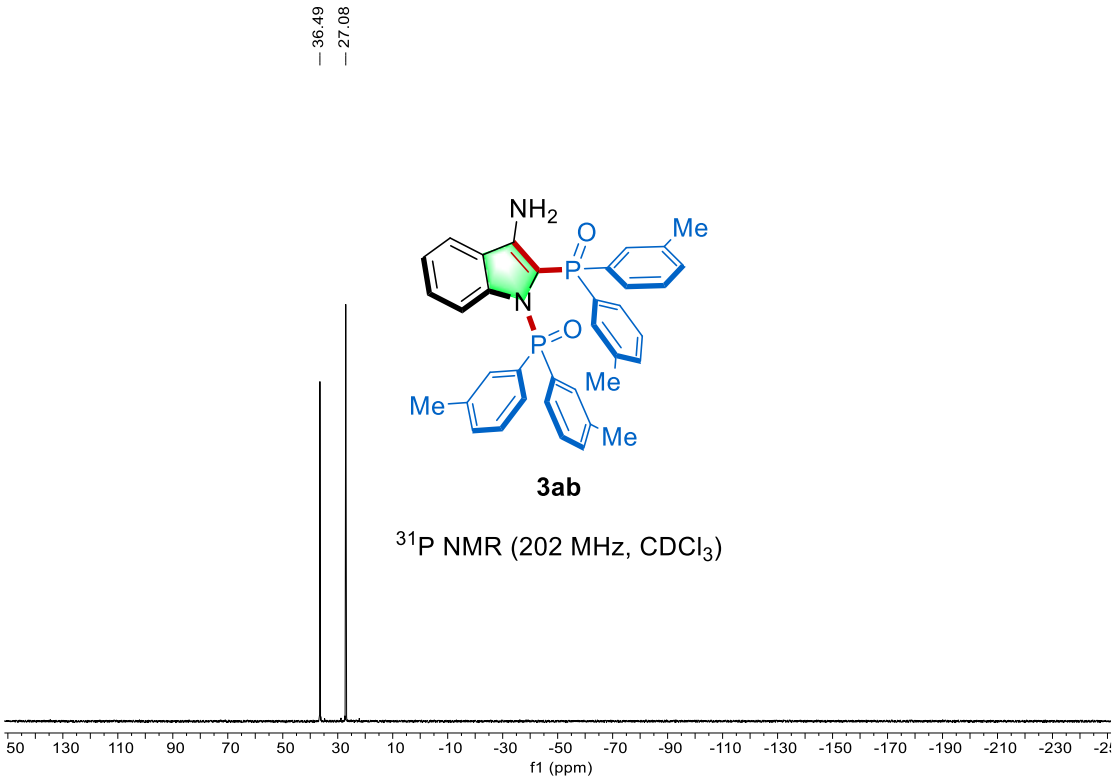
3ab

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



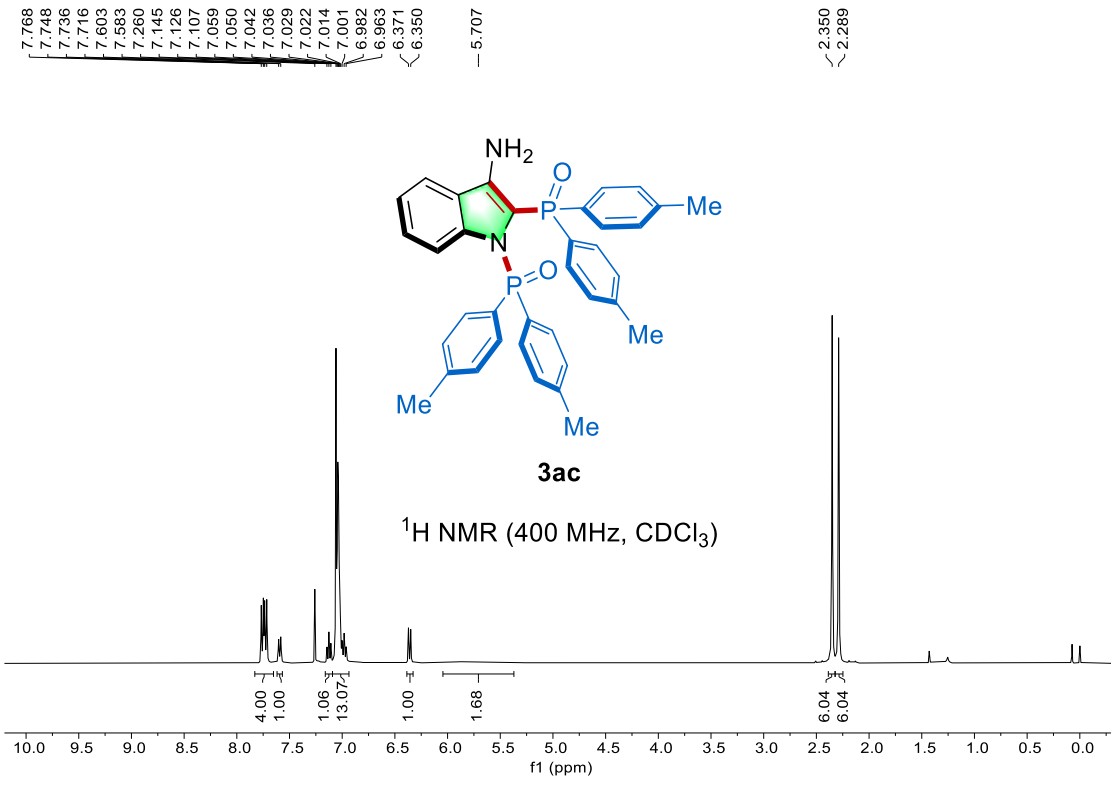
3ab

^{13}C NMR (125 MHz, $CDCl_3$)



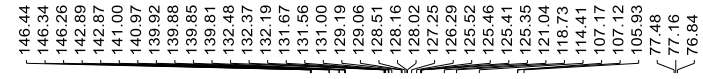
3ab

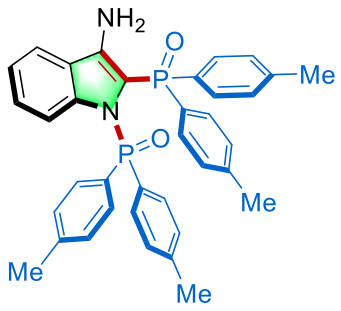
^{31}P NMR (202 MHz, $CDCl_3$)



3ac

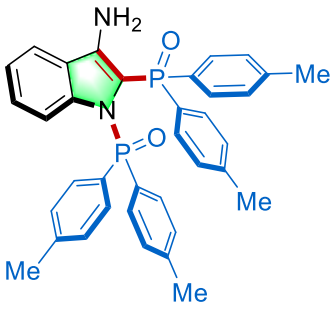
^{1}H NMR (400 MHz, $CDCl_3$)





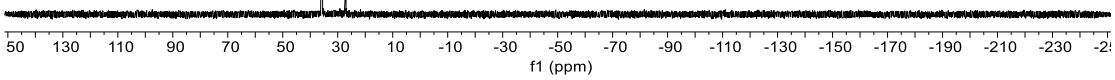
3ac

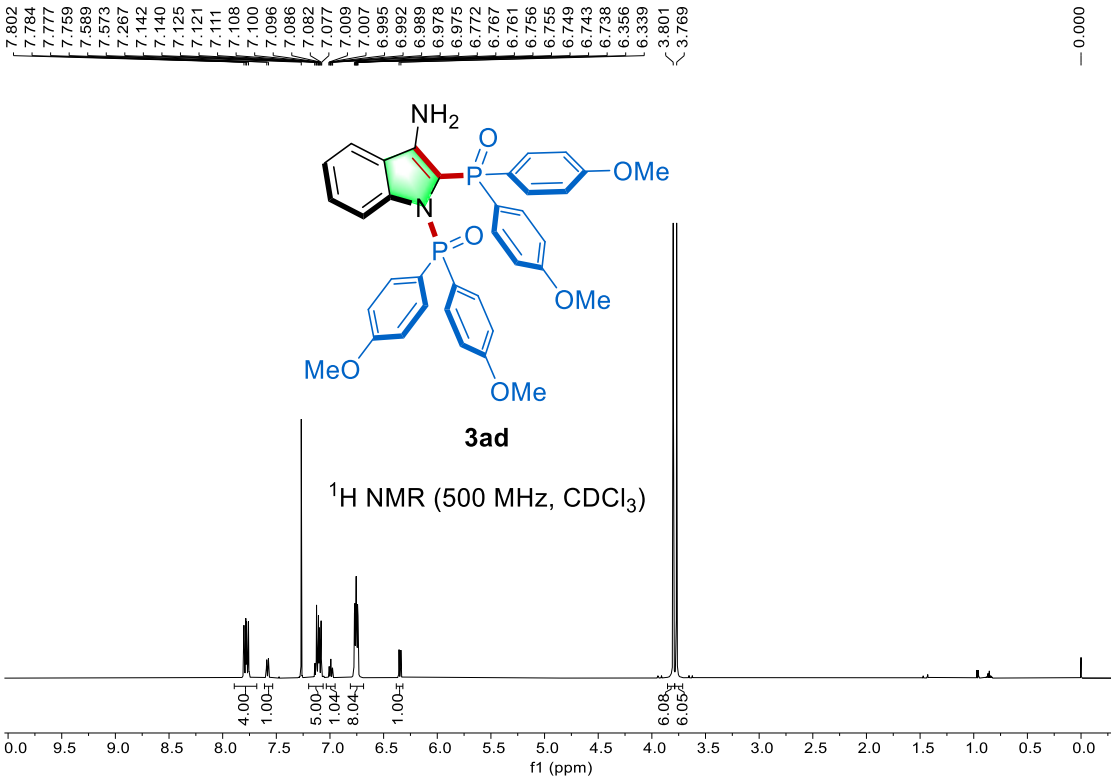
^{13}C NMR (100 MHz, $CDCl_3$)

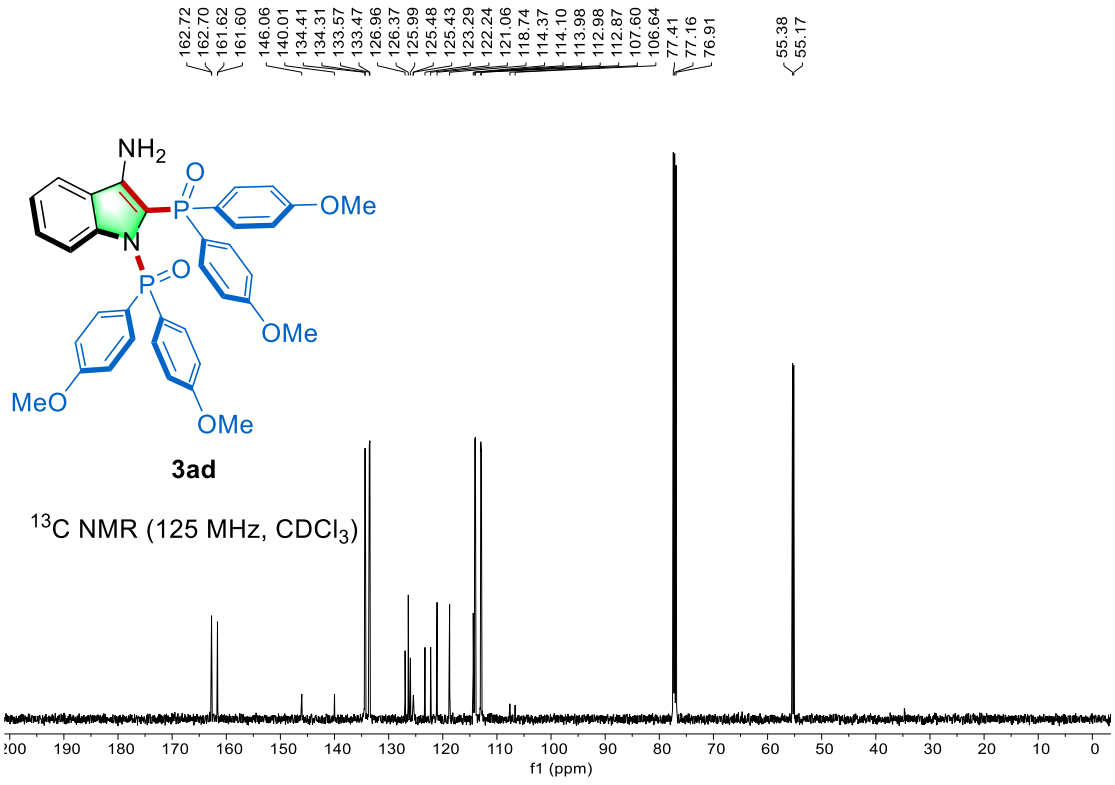


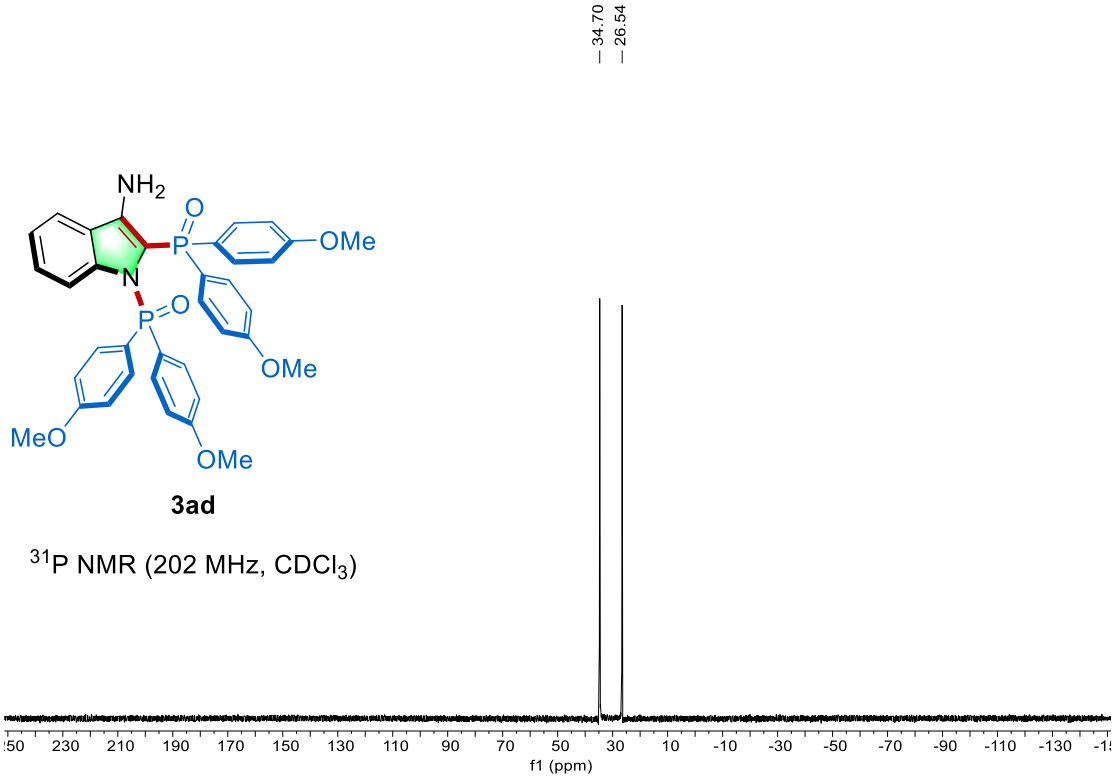
3ac

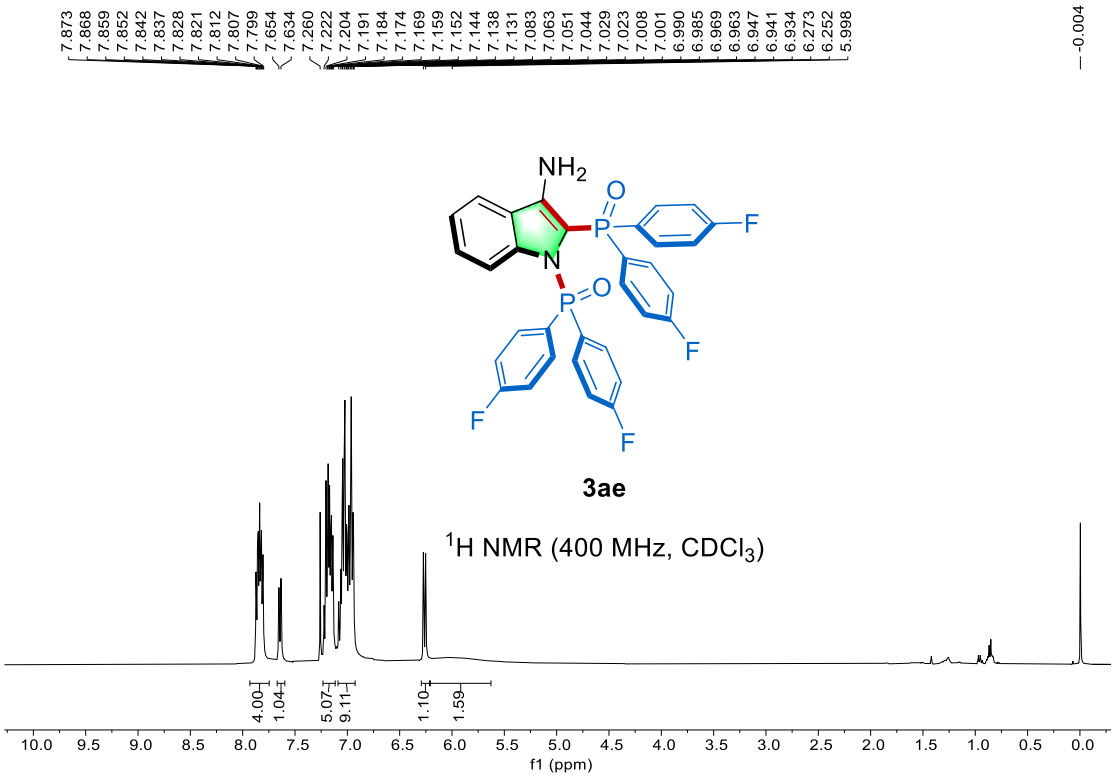
^{31}P NMR (202 MHz, $CDCl_3$)

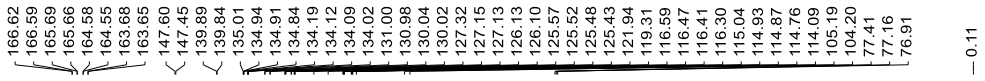


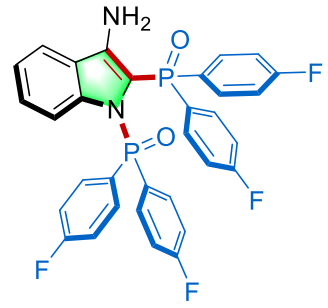

7.802
7.784
7.777
7.759
7.589
7.573
7.267
7.142
7.140
7.125
7.121
7.111
7.108
7.100
7.096
7.086
7.082
7.077
7.009
7.007
6.995
6.992
6.989
6.978
6.975
6.772
6.767
6.761
6.756
6.755
6.749
6.743
6.738
6.356
6.339
3.801
3.769
0.000
NH2
O
P
OMe
N
P
O
OMe
MeO
OMe
3ad
1H NMR (500 MHz, CDCl3)
4.00
1.00
5.00
1.04
8.04
1.00
6.08
6.05
f1 (ppm)


162.72
162.70
161.62
161.60
146.06
140.01
134.41
134.31
133.57
133.47
126.96
126.37
125.99
125.48
125.43
123.29
122.24
121.06
118.74
114.37
114.10
113.98
112.98
112.87
107.60
106.64
77.41
77.16
76.91
55.38
55.17
NH2
O
P
OMe
N
P
O
OMe
MeO
OMe
3ad
13C NMR (125 MHz, CDCl3)
f1 (ppm)


34.70
26.54
NH2
O
P
OMe
N
P
O
OMe
MeO
OMe
3ad
31P NMR (202 MHz, CDCl3)
f1 (ppm)

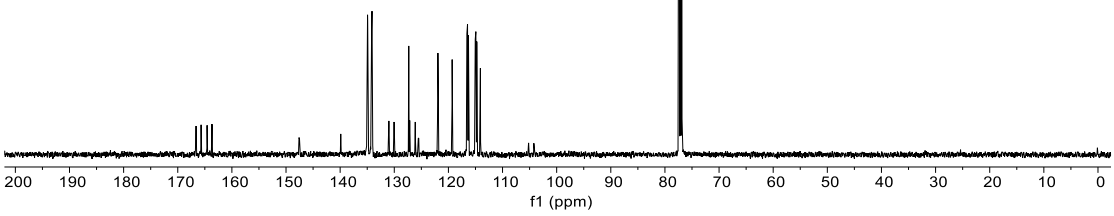

7.873
7.868
7.859
7.852
7.842
7.837
7.828
7.821
7.812
7.807
7.799
7.654
7.634
7.260
7.222
7.204
7.191
7.184
7.174
7.169
7.159
7.152
7.144
7.138
7.131
7.083
7.063
7.051
7.044
7.029
7.023
7.008
7.001
6.990
6.985
6.969
6.963
6.947
6.941
6.934
6.273
6.252
5.998
-0.004
NH2
O
P
F
N
P
O
F
F
F
3ae
1H NMR (400 MHz, CDCl3)
4.00
1.04
5.07
9.11
1.10
1.59
f1 (ppm)

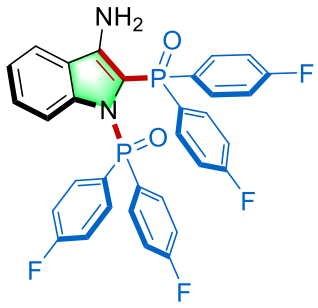




3ae

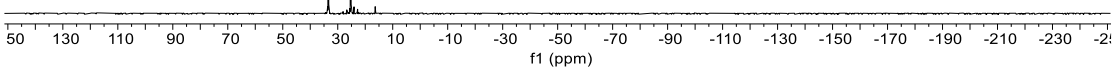
^{13}C NMR (125 MHz, $CDCl_3$)

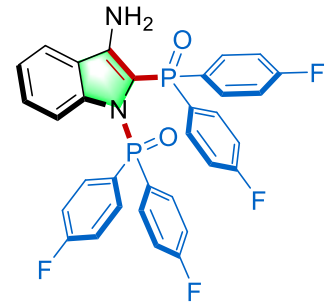




3ae

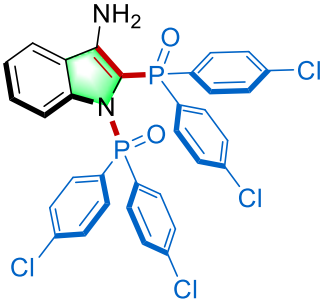
^{31}P NMR (202 MHz, $CDCl_3$)





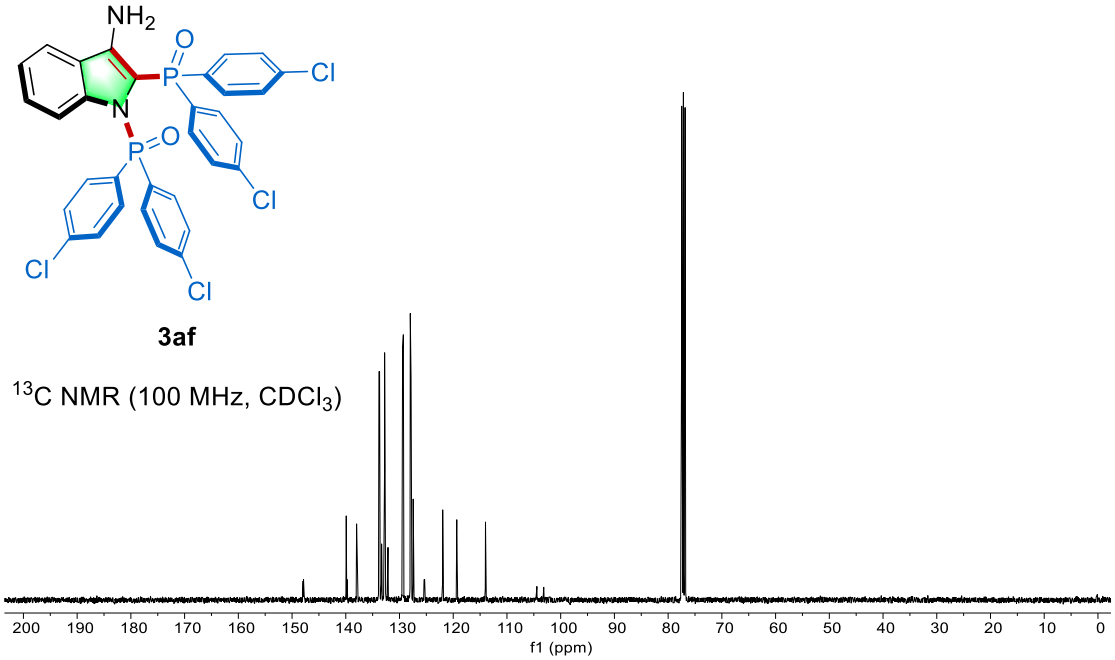
3ae

^{19}F NMR (471 MHz, $CDCl_3$)



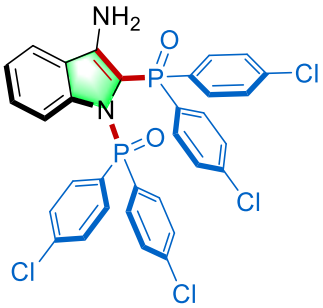
3af

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



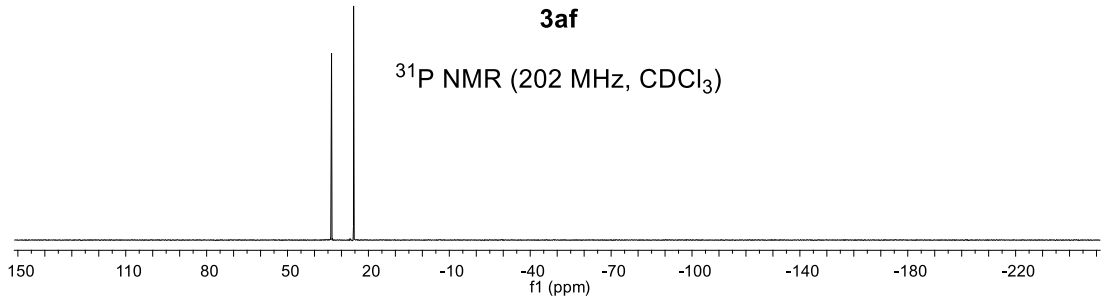
3af

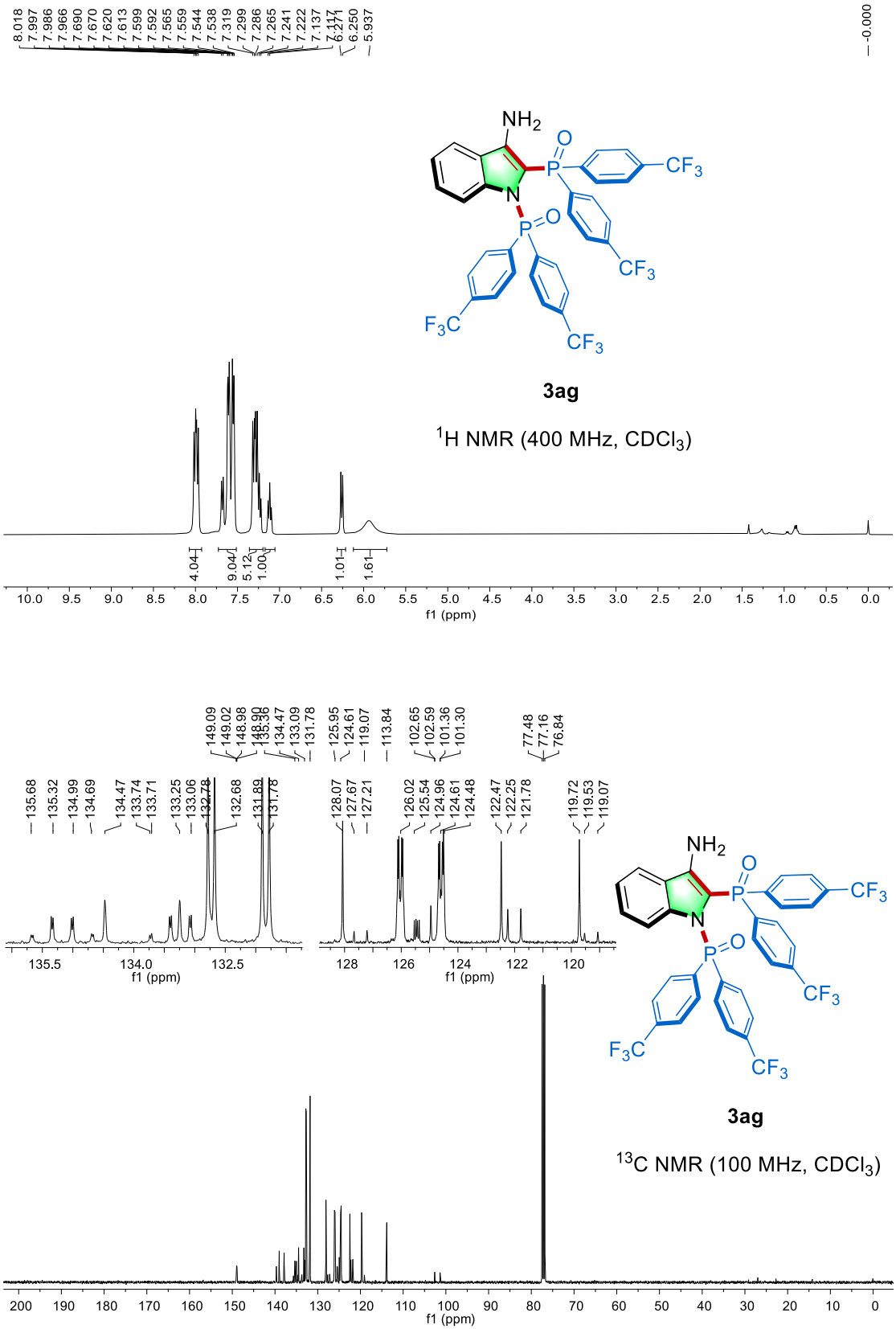
^{13}C NMR (100 MHz, $CDCl_3$)

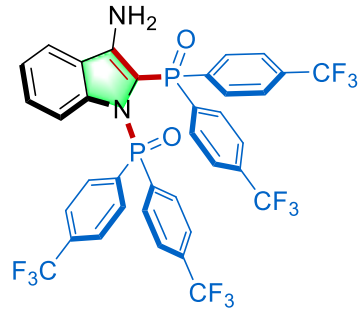


3af

^{31}P NMR (202 MHz, $CDCl_3$)

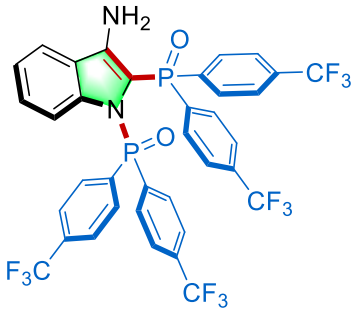



8.018
7.997
7.986
7.966
7.690
7.670
7.620
7.613
7.599
7.592
7.565
7.559
7.544
7.538
7.319
7.299
7.286
7.265
7.241
7.222
7.137
6.250
5.937
-0.000
NH2
O
P
CF3
N
P=O
CF3
F3C
CF3
3ag
1H NMR (400 MHz, CDCl3)
4.04
9.04
5.12
1.00
1.01
1.61
f1 (ppm)
149.09
149.02
148.98
135.36
134.47
133.09
131.78
125.95
124.61
119.07
113.84
102.65
102.59
101.36
101.30
77.48
77.16
76.84
135.68
135.32
134.99
134.69
134.47
133.74
133.71
133.25
133.06
132.78
132.68
131.89
131.78
128.07
127.67
127.21
126.02
125.54
124.96
124.61
124.48
122.47
122.25
121.78
119.72
119.53
119.07
f1 (ppm)
f1 (ppm)
NH2
O
P
CF3
N
P=O
CF3
F3C
CF3
3ag
13C NMR (100 MHz, CDCl3)
f1 (ppm)



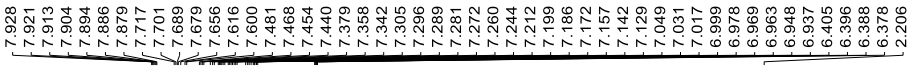
3ag

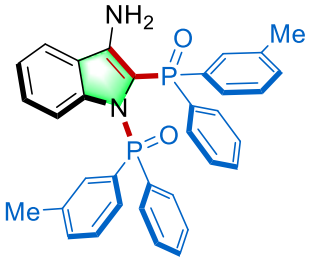
^{31}P NMR (162 MHz, $CDCl_3$)



3ag

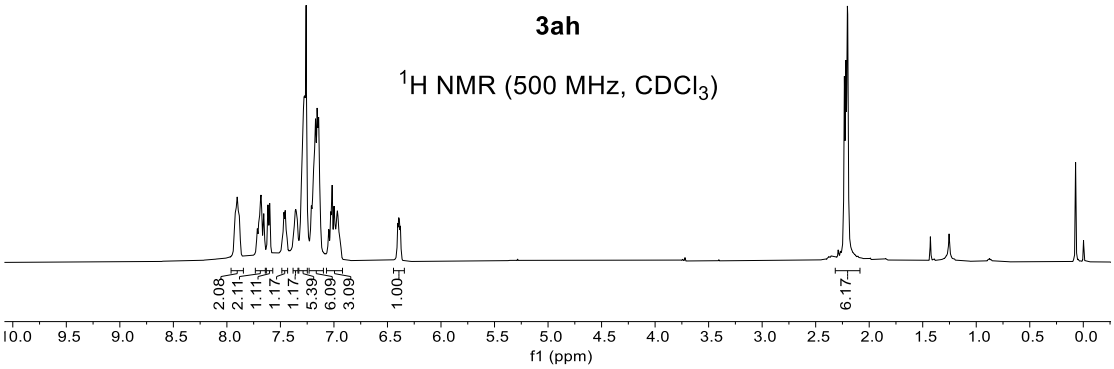
^{19}F NMR (376 MHz, $CDCl_3$)

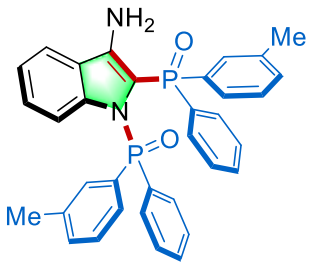




3ah

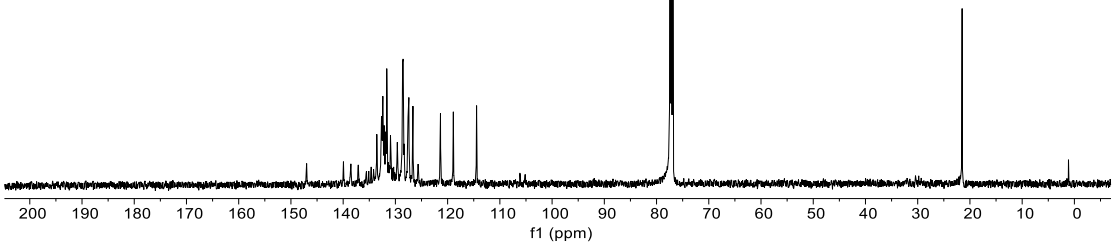
^{1}H NMR (500 MHz, $CDCl_3$)

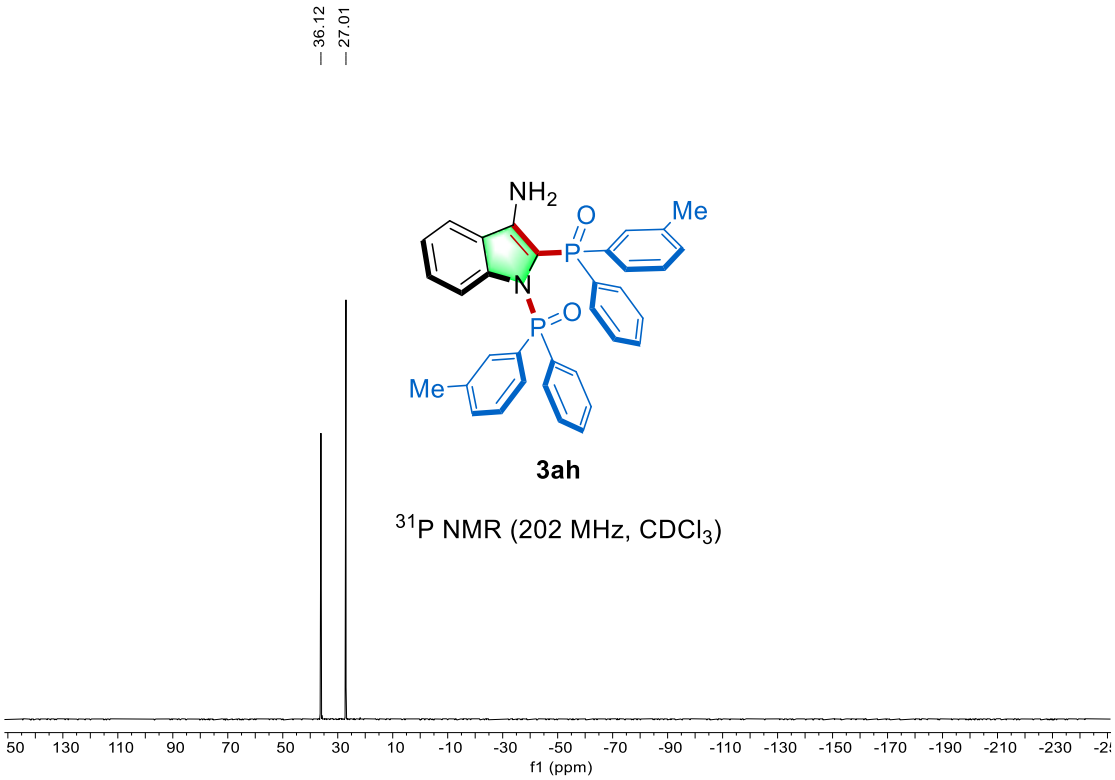




3ah

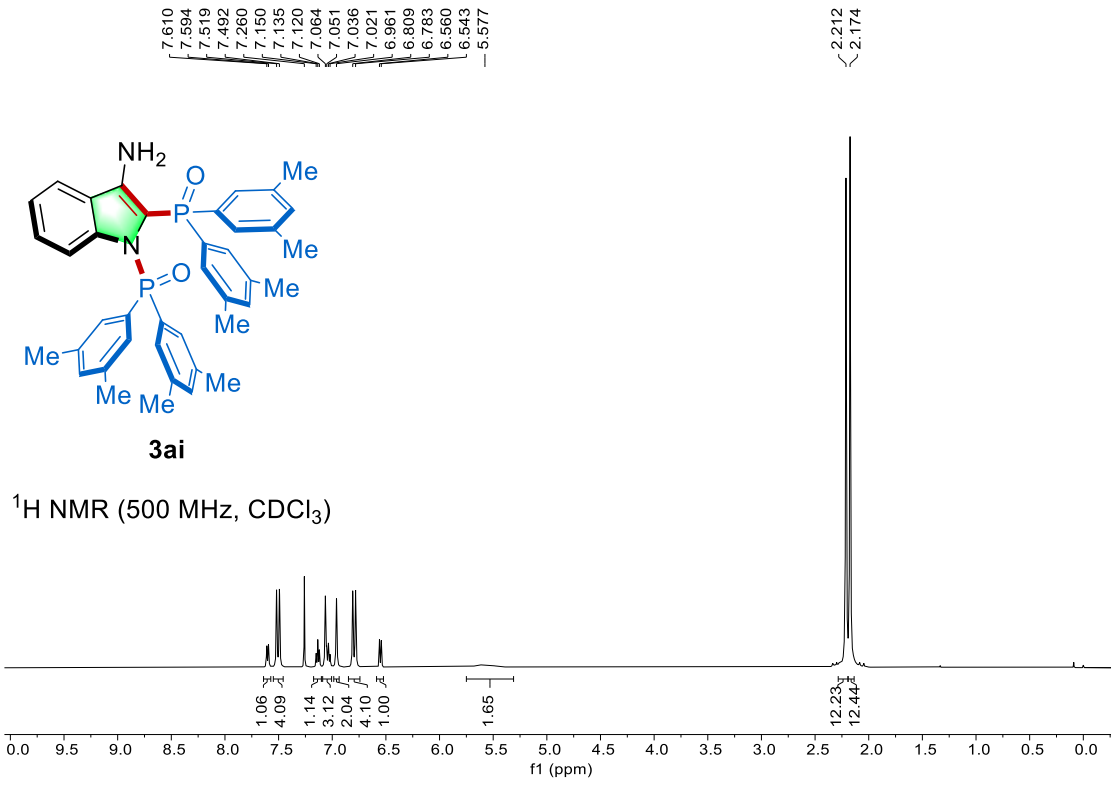
^{13}C NMR (125 MHz, $CDCl_3$)





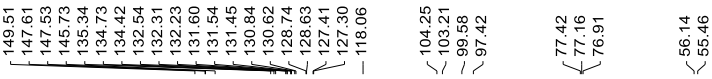
3ah

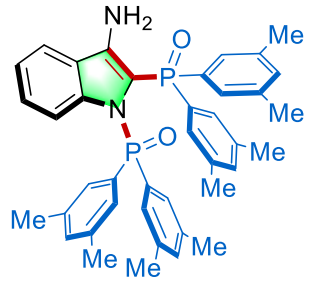
^{31}P NMR (202 MHz, $CDCl_3$)



3ai

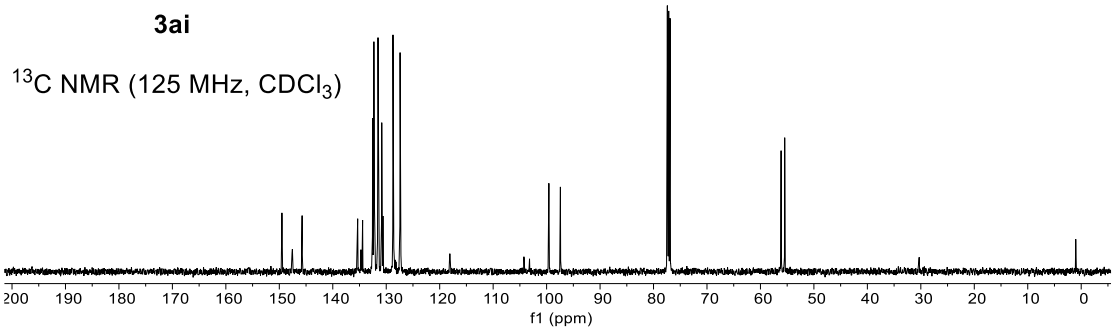
^{1}H NMR (500 MHz, $CDCl_3$)

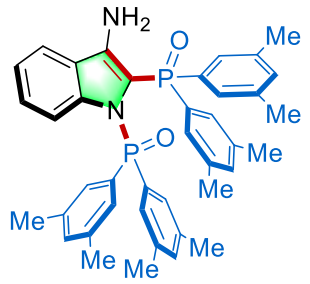




3ai

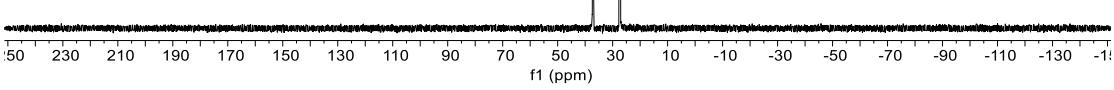
^{13}C NMR (125 MHz, $CDCl_3$)

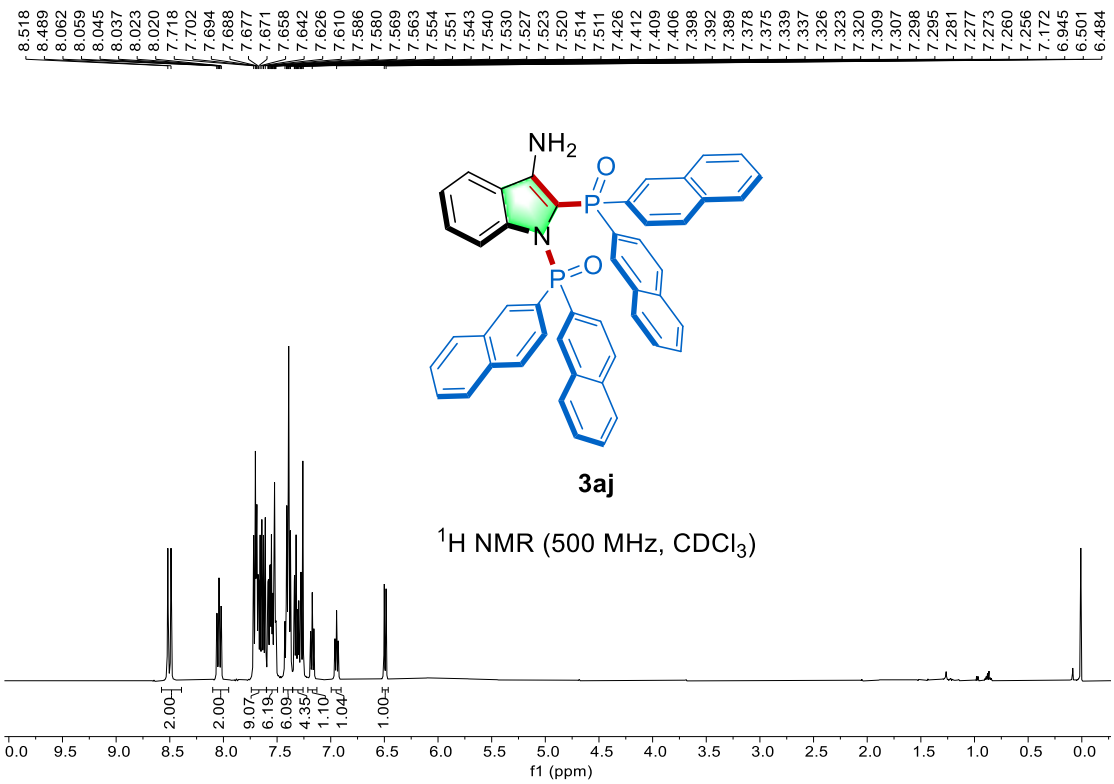


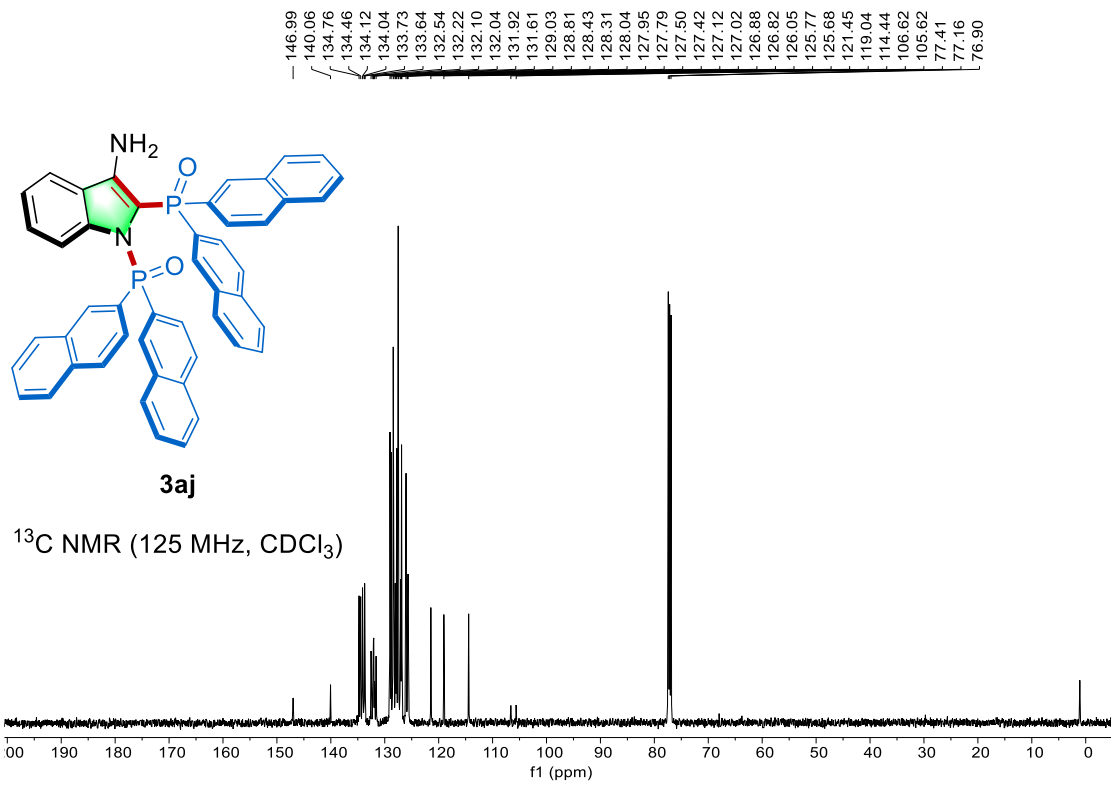


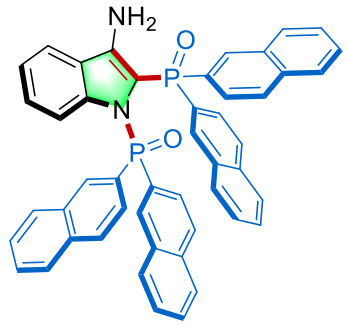
3ai

^{31}P NMR (202 MHz, $CDCl_3$)



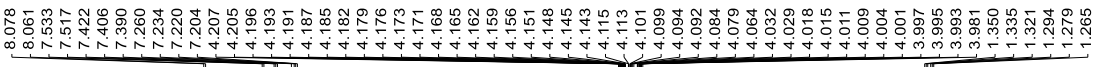

8.518
8.489
8.062
8.059
8.045
8.037
8.023
8.020
7.718
7.702
7.694
7.688
7.677
7.671
7.658
7.642
7.626
7.610
7.586
7.580
7.569
7.563
7.554
7.551
7.543
7.540
7.530
7.527
7.523
7.520
7.514
7.511
7.426
7.412
7.409
7.406
7.398
7.392
7.389
7.378
7.375
7.339
7.337
7.326
7.323
7.320
7.309
7.307
7.298
7.295
7.281
7.277
7.273
7.260
7.256
7.172
6.945
6.501
6.484
NH2
O
P
N
P
O
3aj
1H NMR (500 MHz, CDCl3)
2.00
2.00
9.07
6.19
6.09
4.35
1.10
1.04
1.00
0.0
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
f1 (ppm)

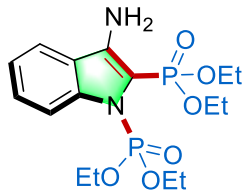

146.99
140.06
134.76
134.46
134.12
134.04
133.73
133.64
132.54
132.22
132.10
132.04
131.92
131.61
129.03
128.81
128.43
128.31
128.04
127.95
127.79
127.50
127.42
127.12
127.02
126.88
126.82
126.05
125.77
125.68
121.45
119.04
114.44
106.62
105.62
77.41
77.16
76.90
NH2
O
P
N
P
O
3aj
13C NMR (125 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3aj

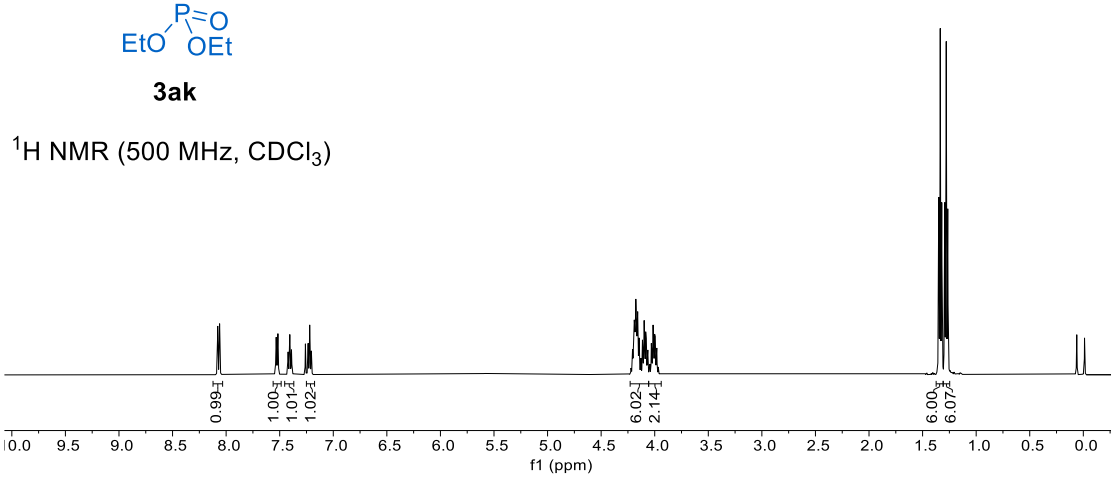
^{31}P NMR (202 MHz, $CDCl_3$)

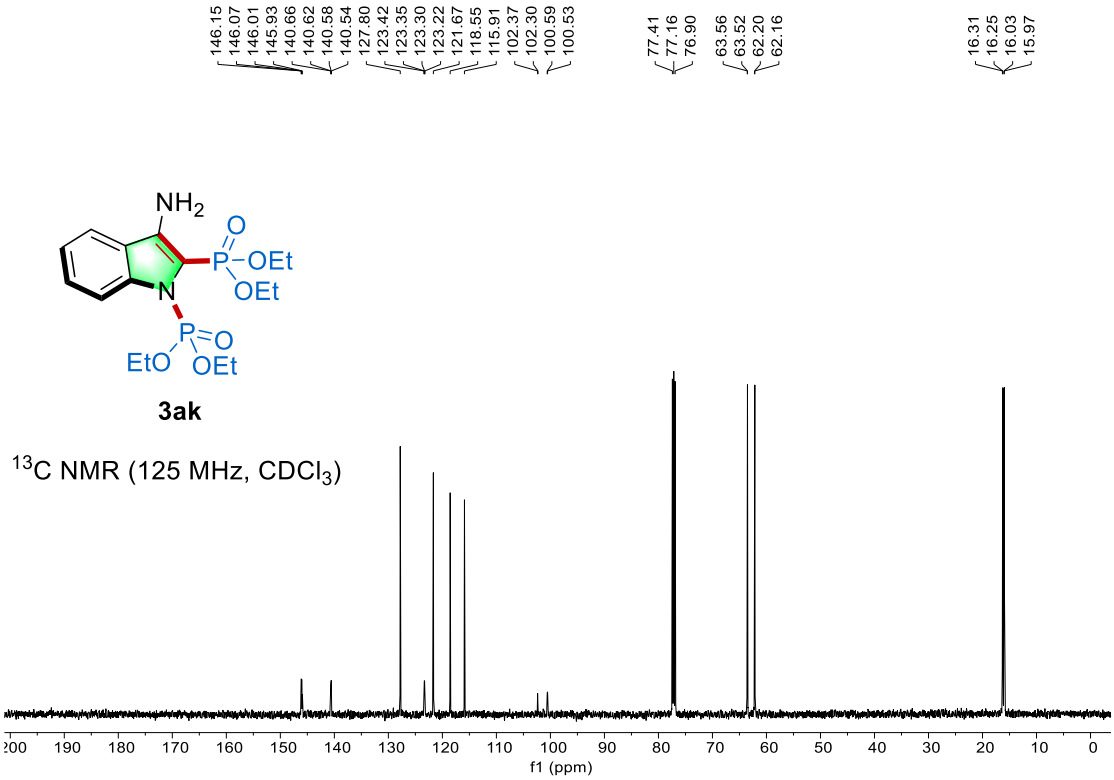


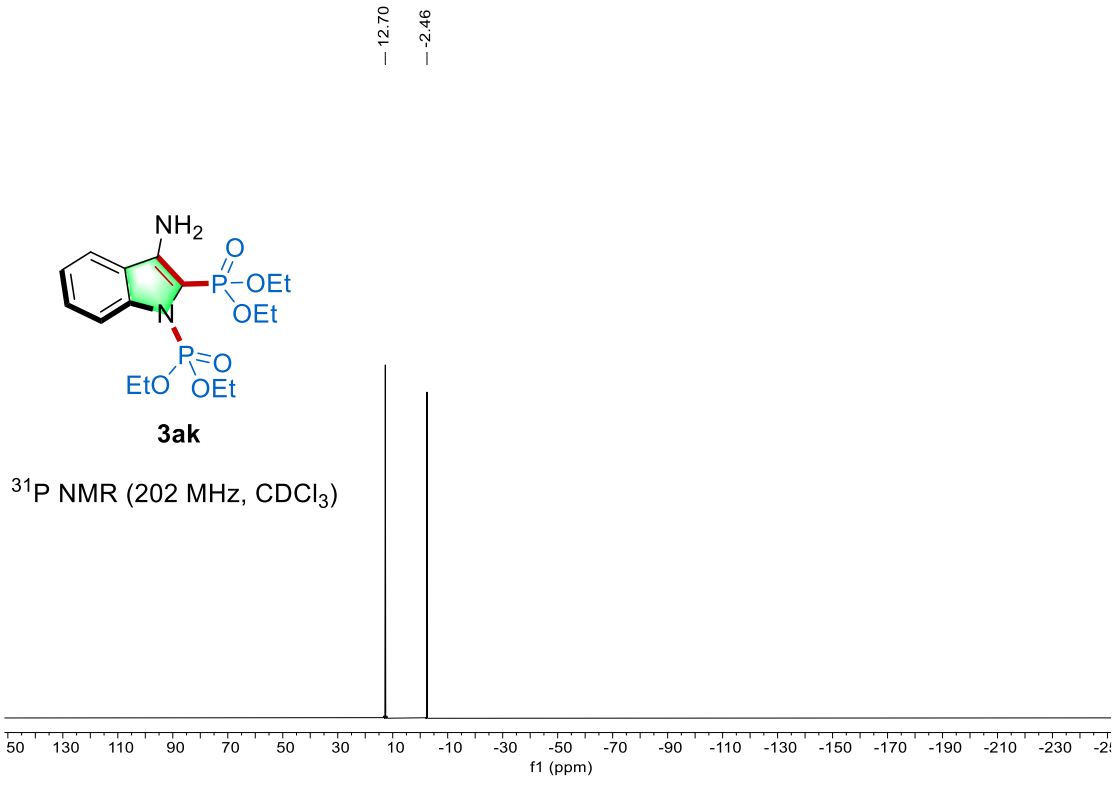


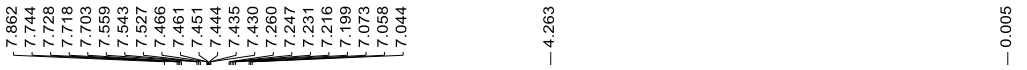
3ak

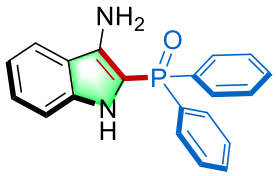
^{1}H NMR (500 MHz, $CDCl_3$)




146.15
146.07
146.01
145.93
140.66
140.62
140.58
140.54
127.80
123.42
123.35
123.30
123.22
121.67
118.55
115.91
102.37
102.30
100.59
100.53
77.41
77.16
76.90
63.56
63.52
62.20
62.16
16.31
16.25
16.03
15.97
NH2
O
P
OEt
OEt
N
P
O
EtO
OEt
3ak
13C NMR (125 MHz, CDCl3)
f1 (ppm)

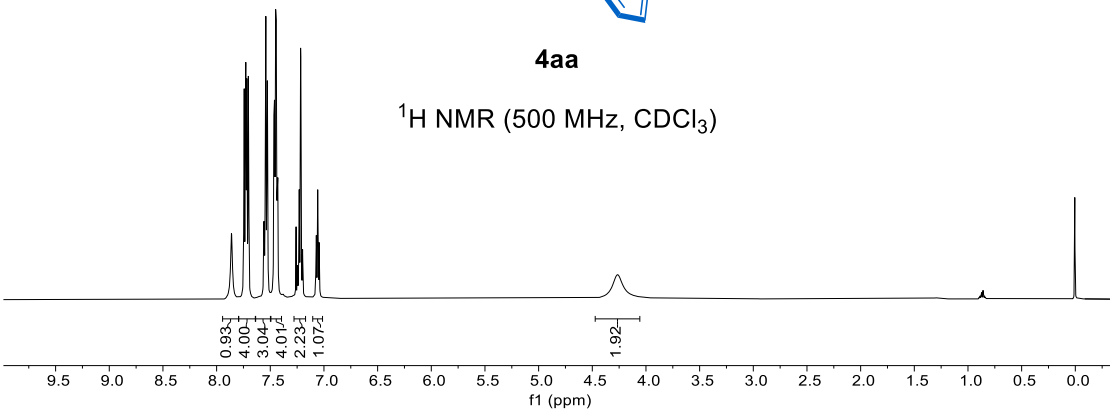

12.70
-2.46
NH2
O
P
OEt
OEt
N
P
O
EtO
OEt
3ak
31P NMR (202 MHz, CDCl3)
f1 (ppm)

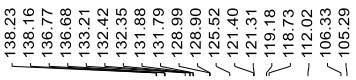


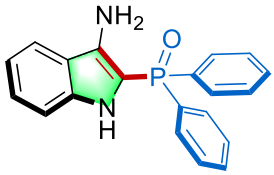


4aa

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

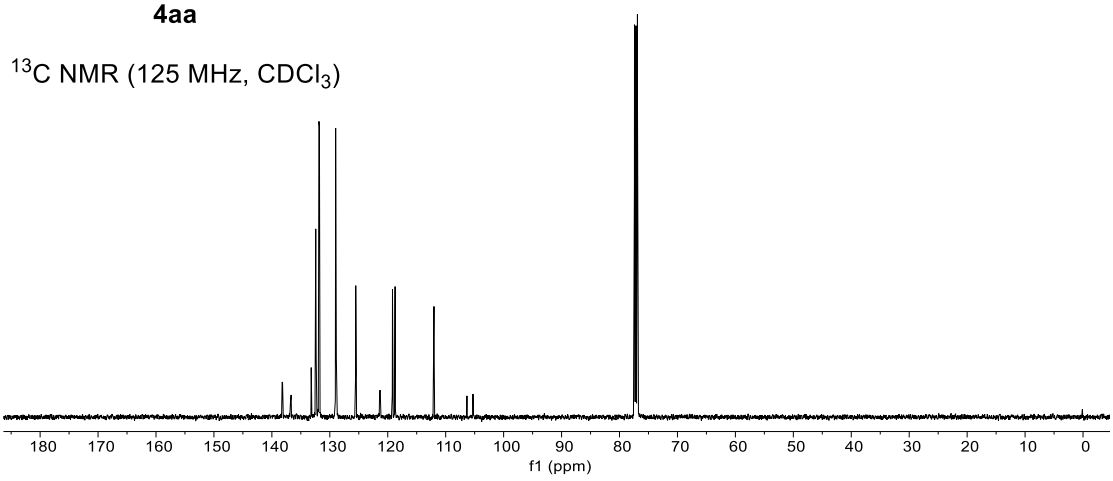


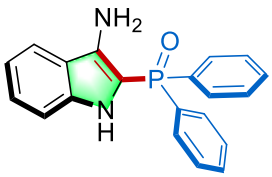




4aa

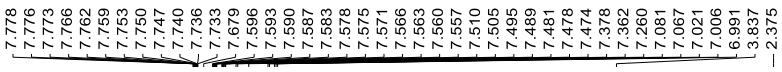
^{13}C NMR (125 MHz, $CDCl_3$)

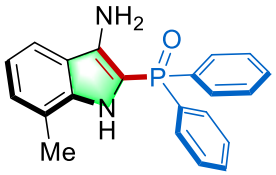




4aa

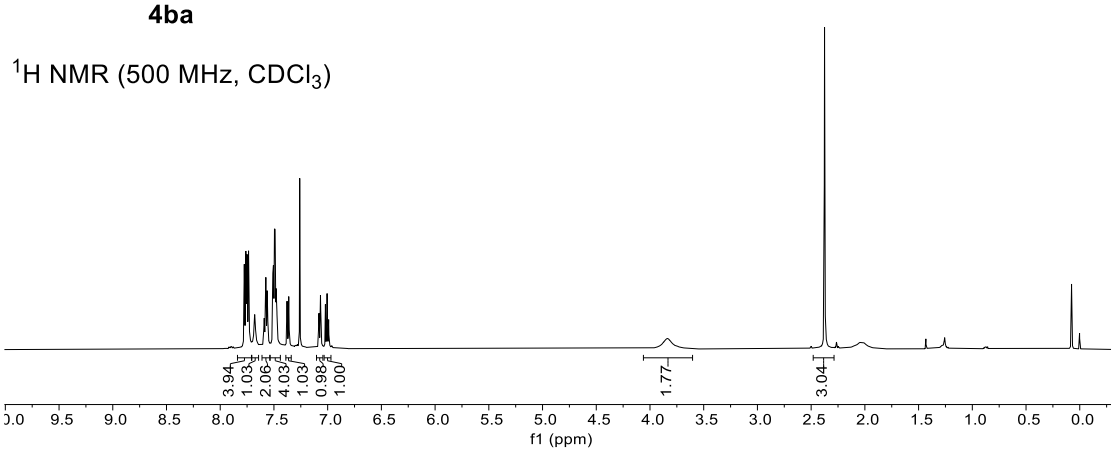
^{31}P NMR (202 MHz, $CDCl_3$)

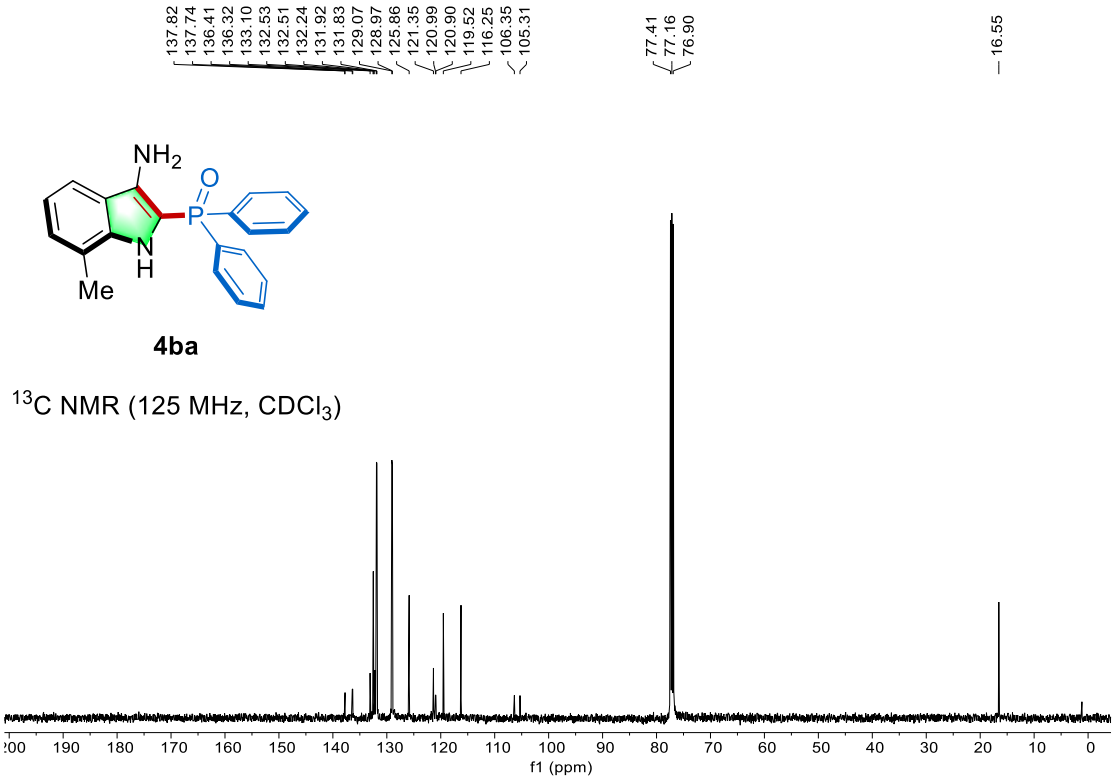




4ba

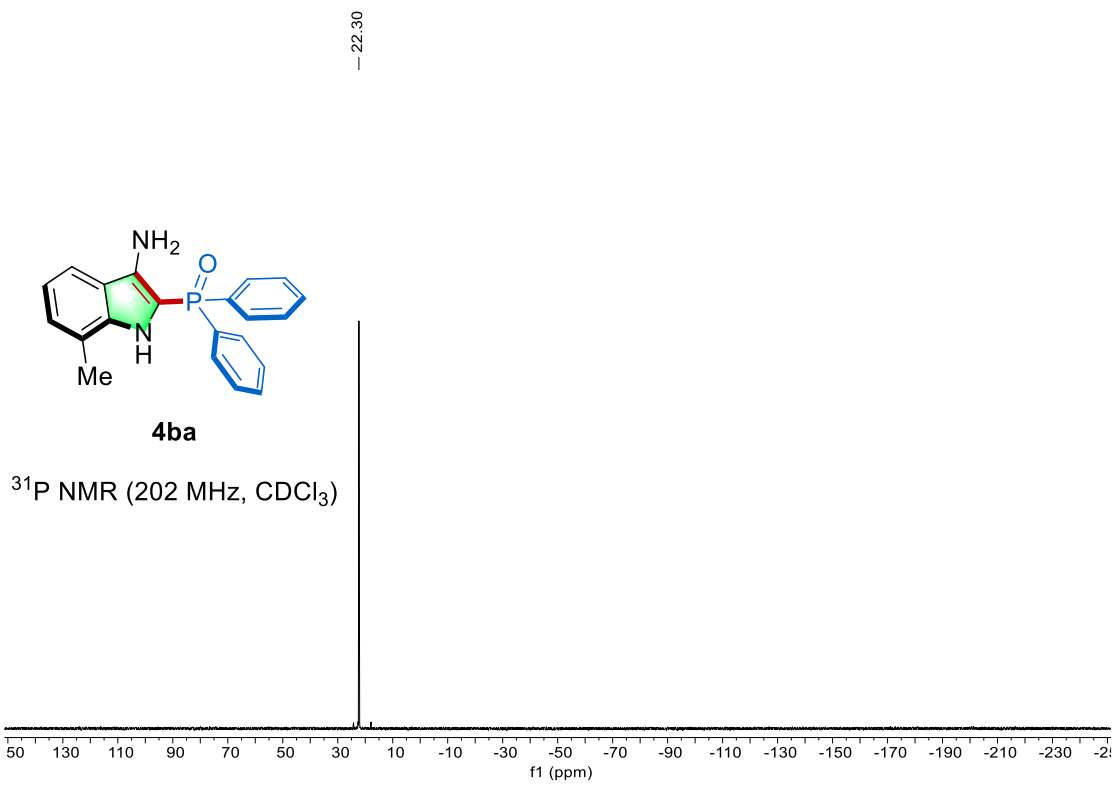
^{1}H NMR (500 MHz, $CDCl_3$)





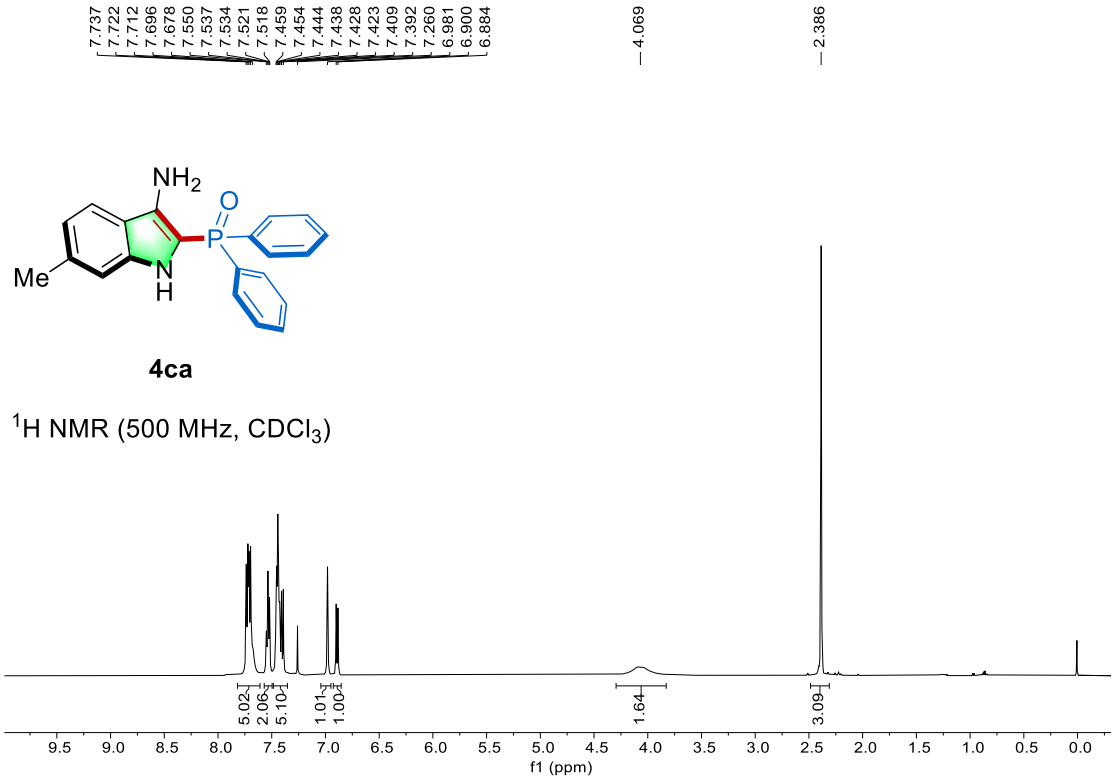
4ba

^{13}C NMR (125 MHz, $CDCl_3$)



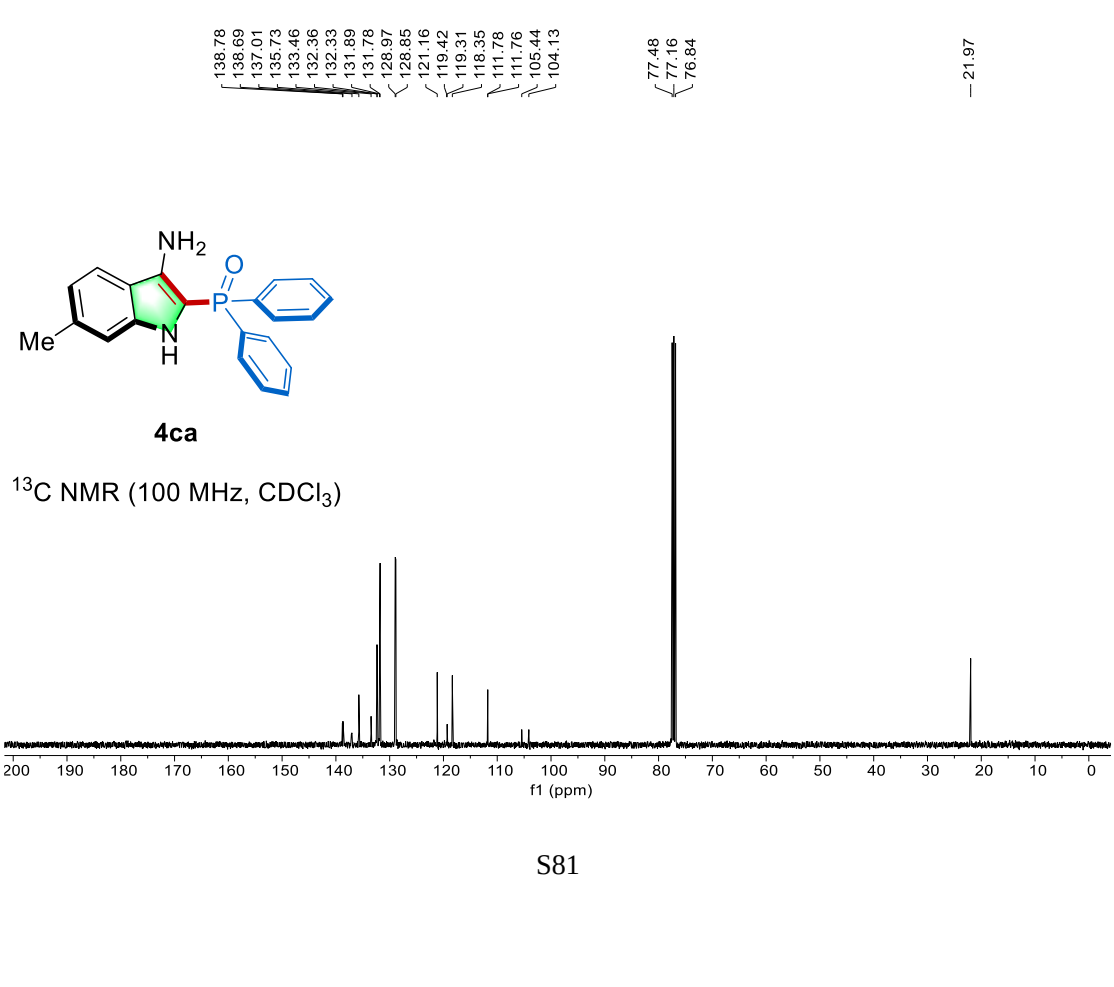
4ba

^{31}P NMR (202 MHz, $CDCl_3$)



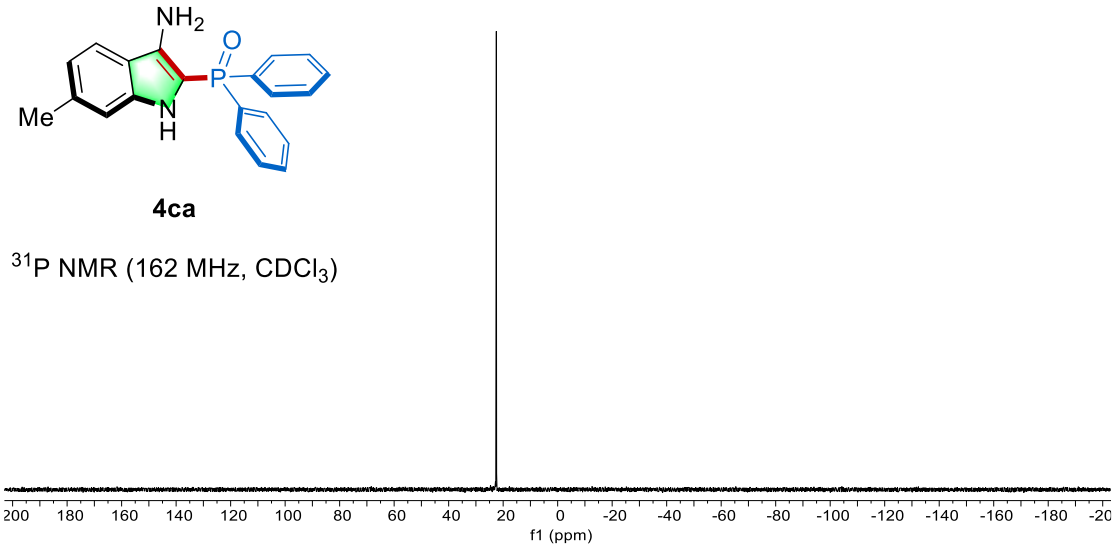
4ca

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



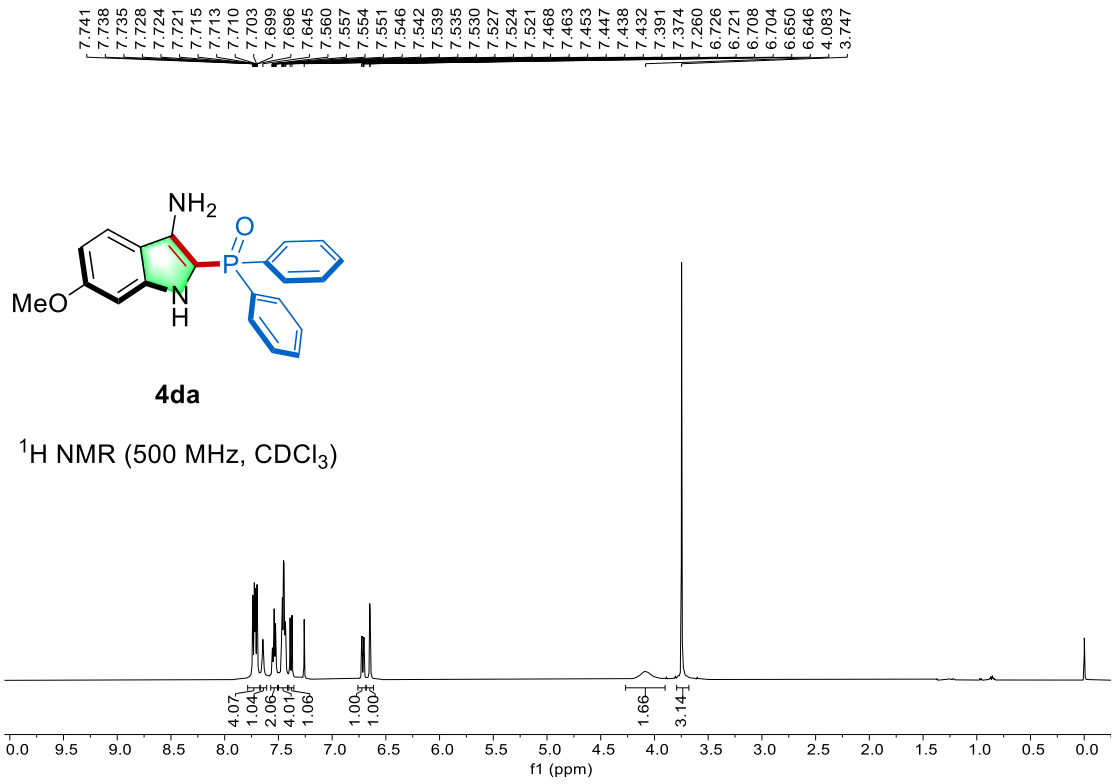
4ca

^{13}C NMR (100 MHz, $CDCl_3$)



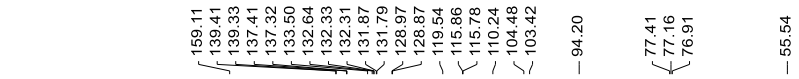
4ca

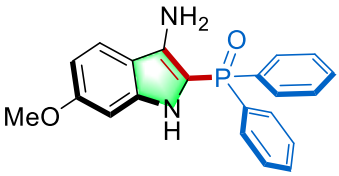
^{31}P NMR (162 MHz, $CDCl_3$)



4da

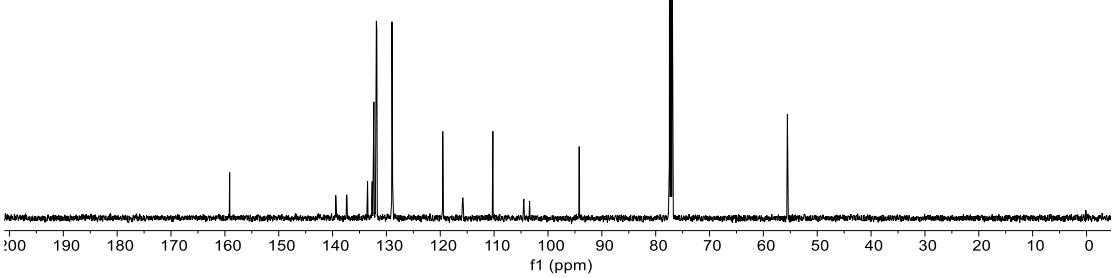
^{1}H NMR (500 MHz, $CDCl_3$)

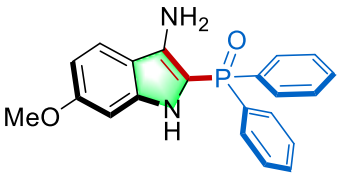




4da

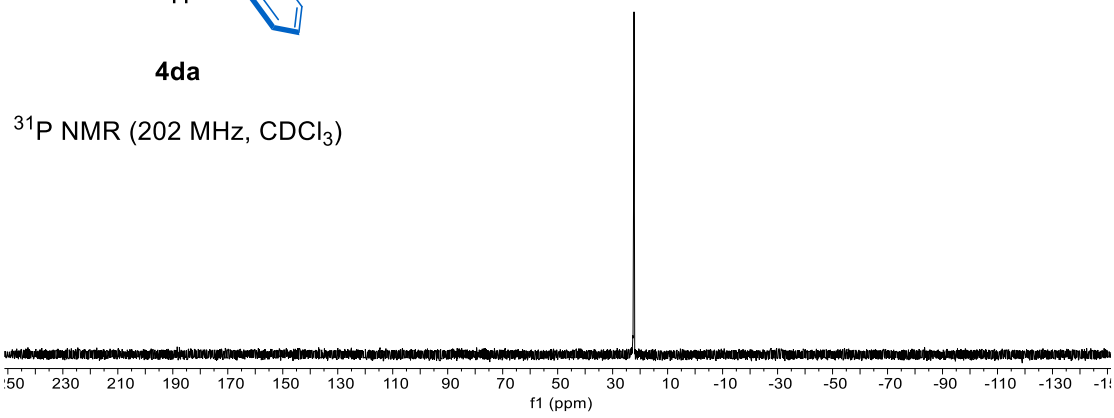
^{13}C NMR (125 MHz, $CDCl_3$)

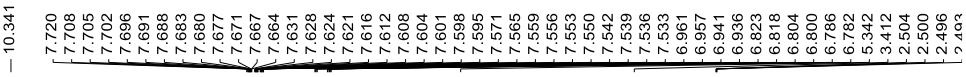


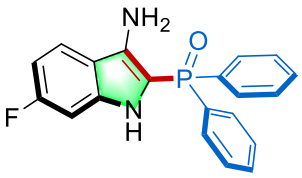


4da

^{31}P NMR (202 MHz, $CDCl_3$)

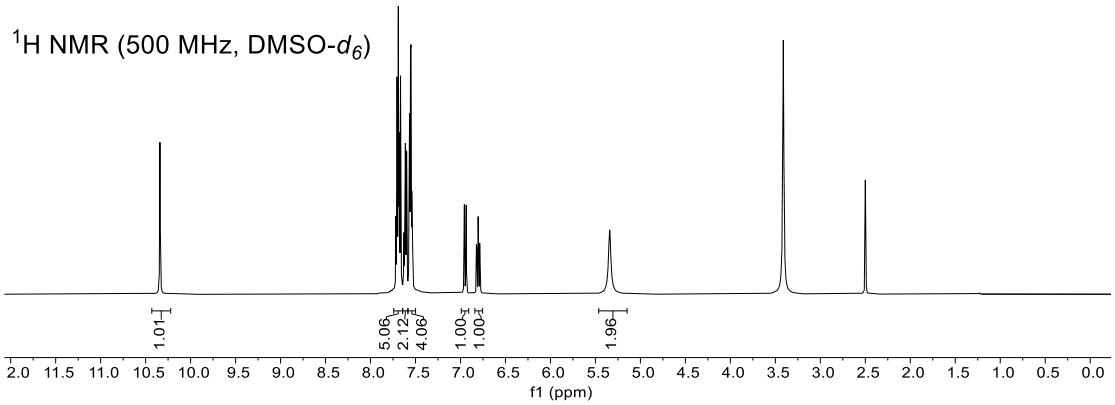


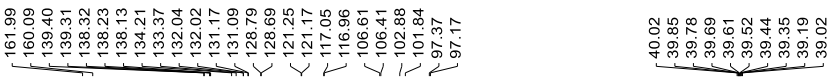


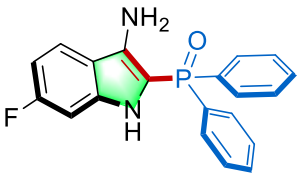


4ea

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

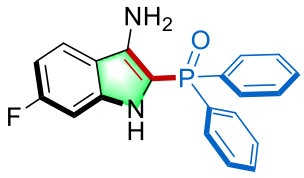






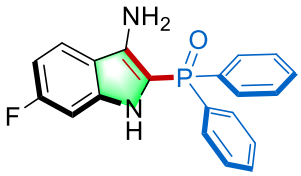
4ea

^{13}C NMR (125 MHz, DMSO-d_6)



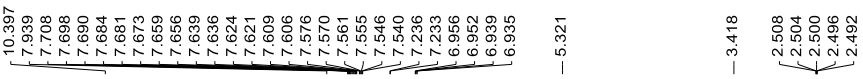
4ea

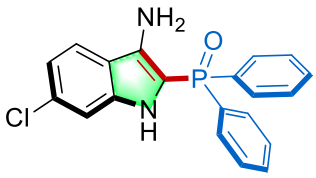
^{31}P NMR (202 MHz, DMSO-d_6)



4ea

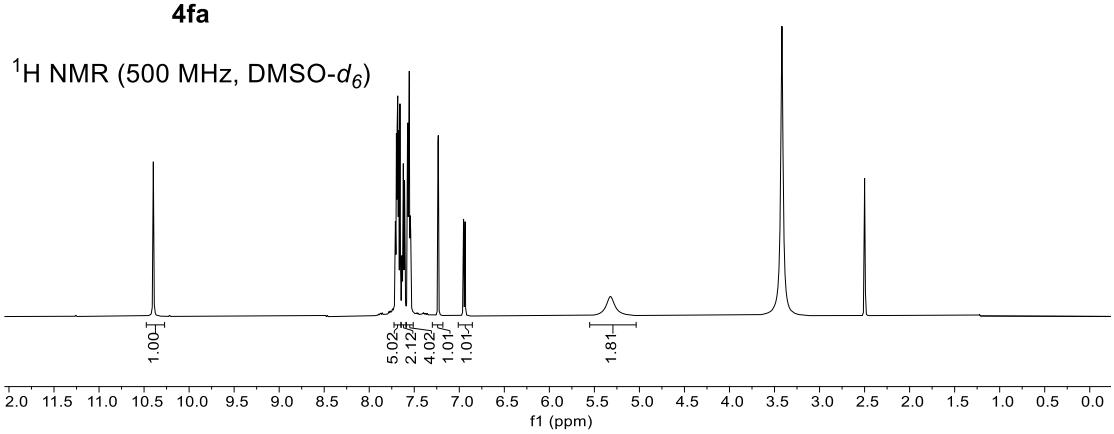
^{19}F NMR (471 MHz, DMSO-d_6)

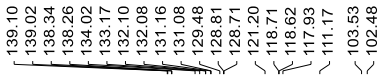


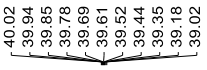


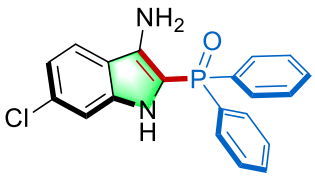
4fa

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



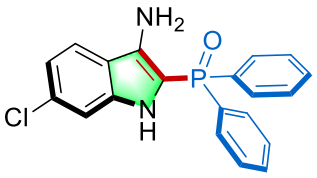






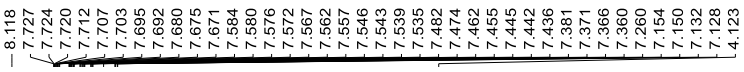
4fa

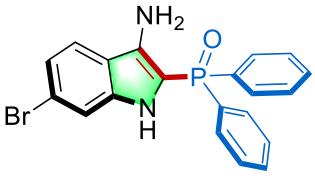
^{13}C NMR (125 MHz, DMSO-d_6)



4fa

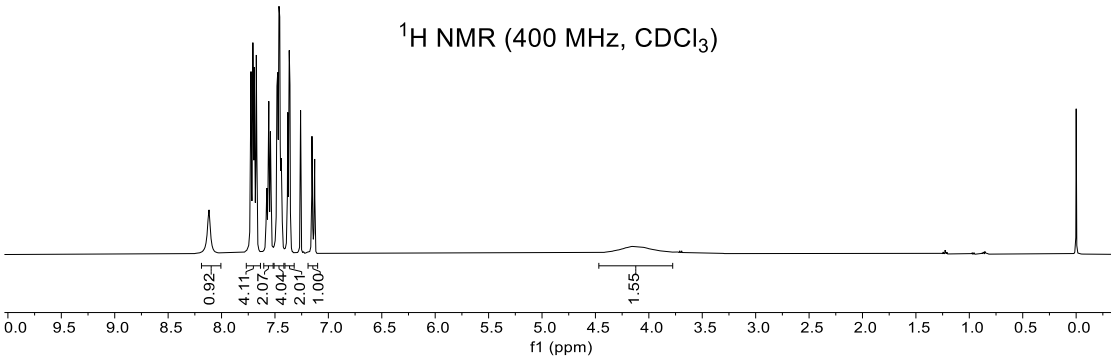
^{31}P NMR (202 MHz, DMSO-d_6)

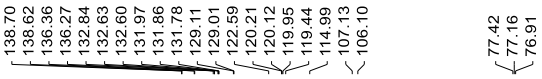


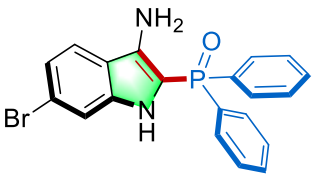


4ga

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

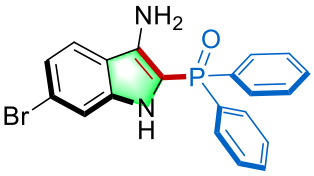






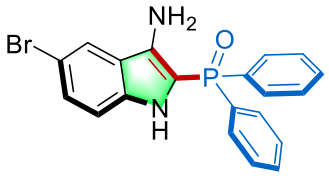
4ga

^{13}C NMR (125 MHz, $CDCl_3$)



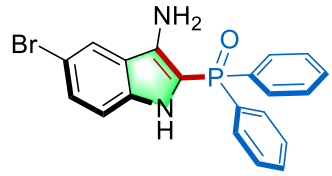
4ga

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



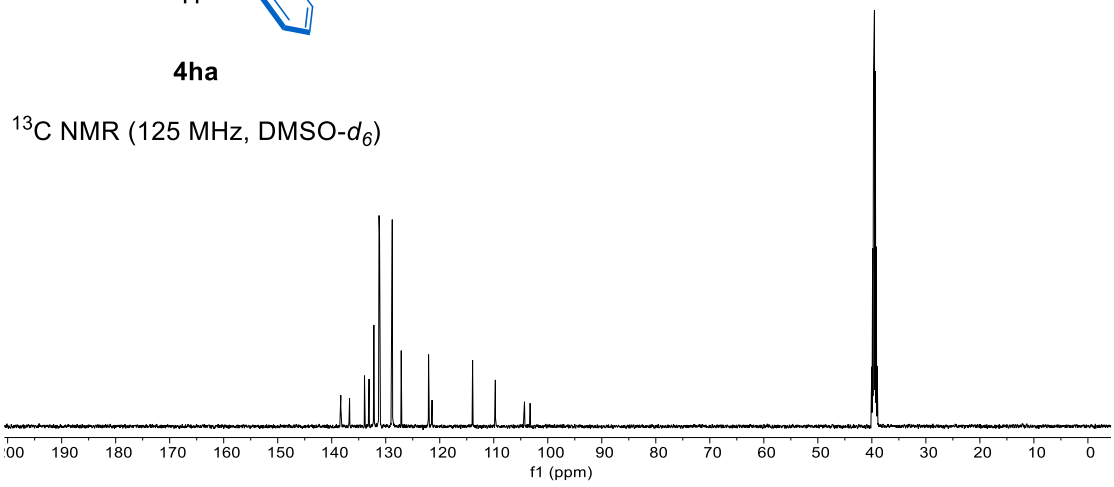
4ha

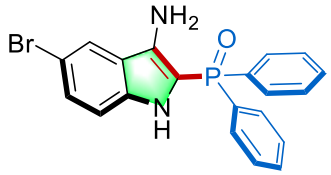
^{1}H NMR (500 MHz, DMSO-d_6)



4ha

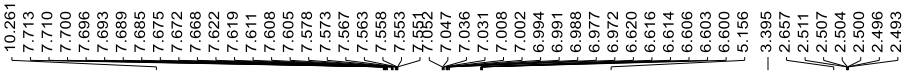
^{13}C NMR (125 MHz, DMSO-d_6)

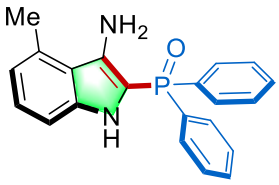




4ha

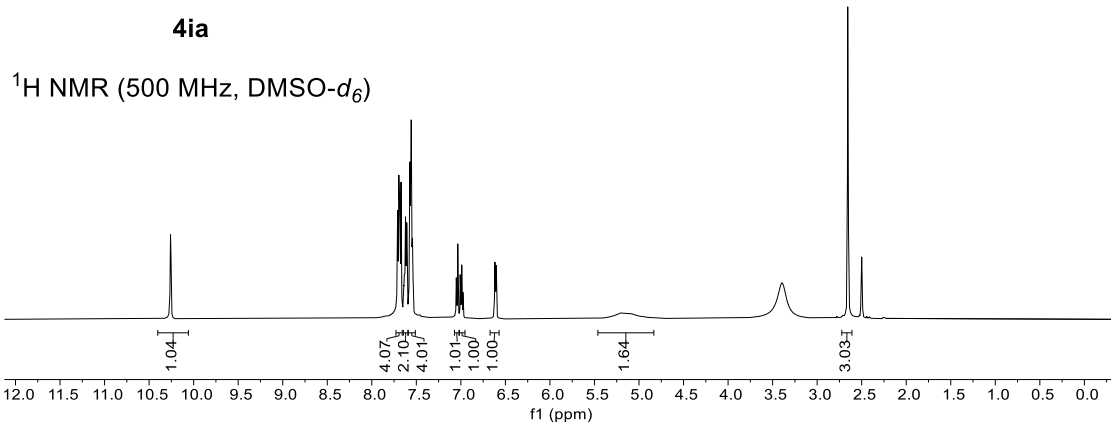
^{31}P NMR (202 MHz, DMSO-d_6)

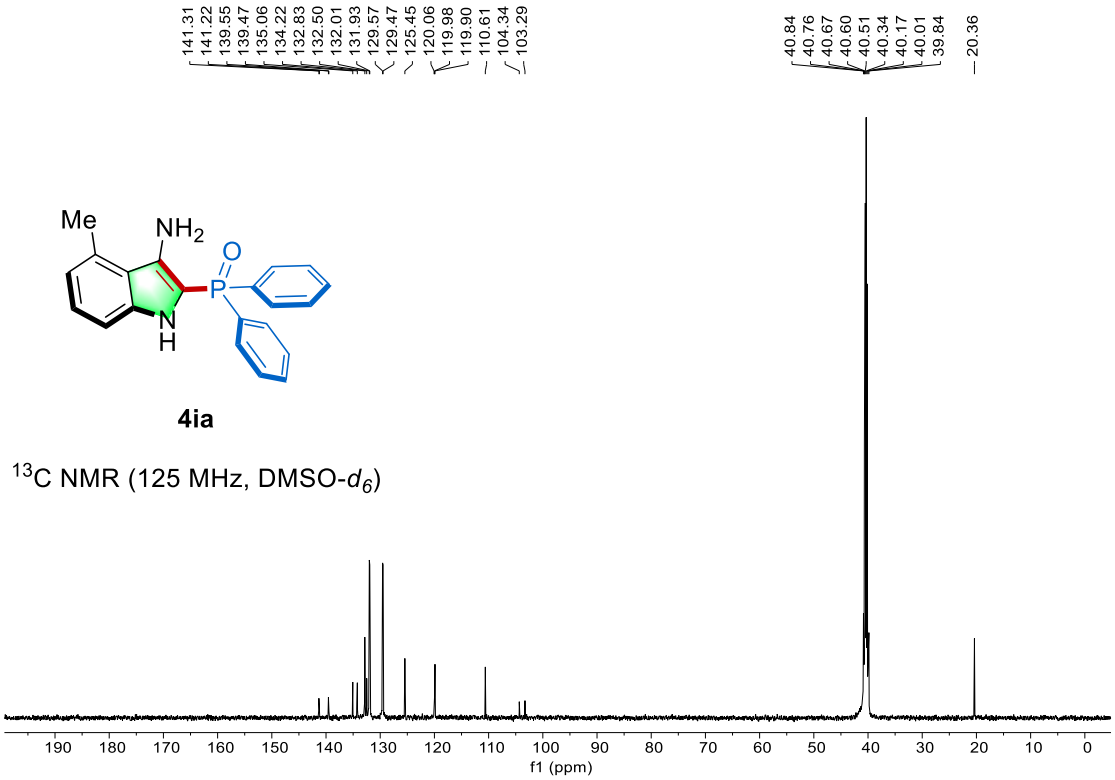




4ia

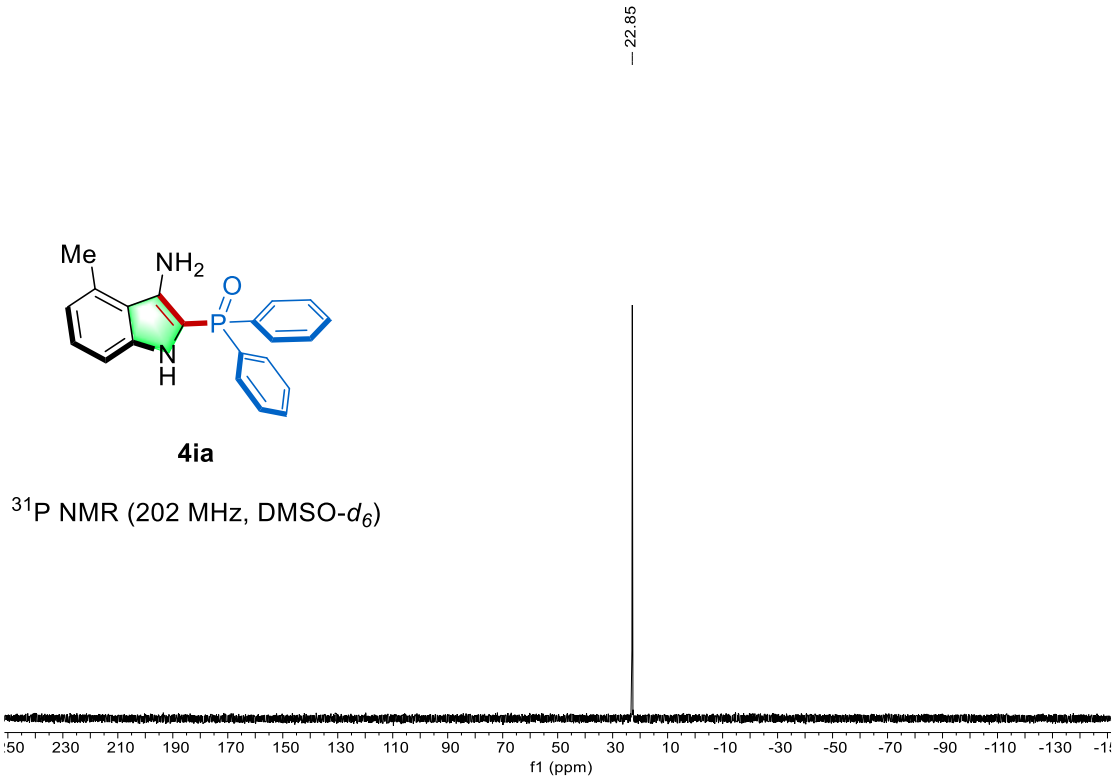
^{1}H NMR (500 MHz, DMSO-d_6)





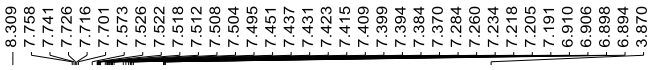
4ia

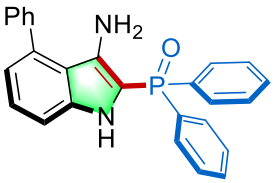
^{13}C NMR (125 MHz, DMSO-d_6)



4ia

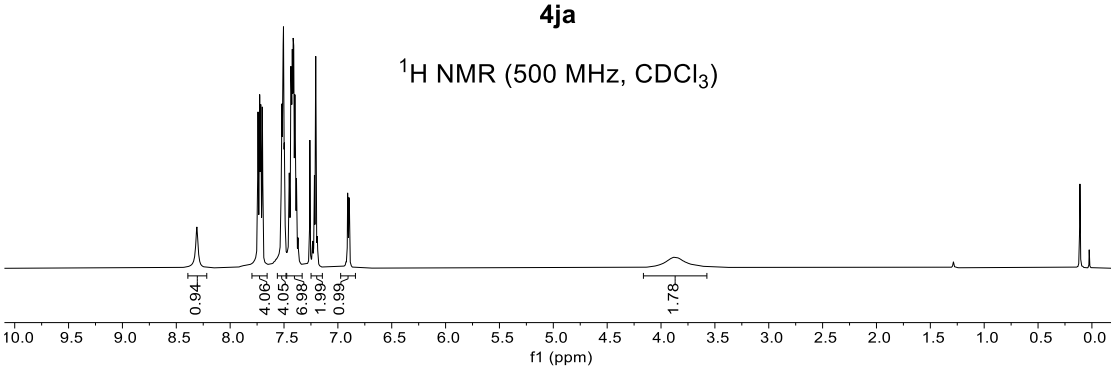
^{31}P NMR (202 MHz, DMSO-d_6)

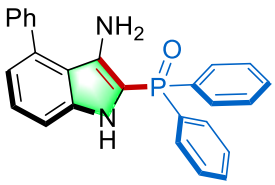




4ja

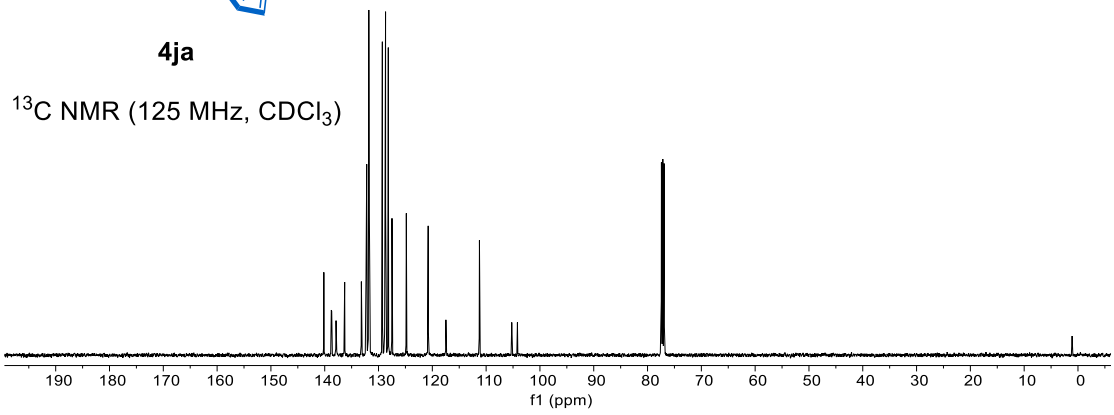
^{1}H NMR (500 MHz, $CDCl_3$)

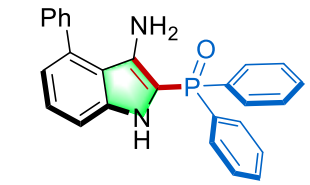




4ja

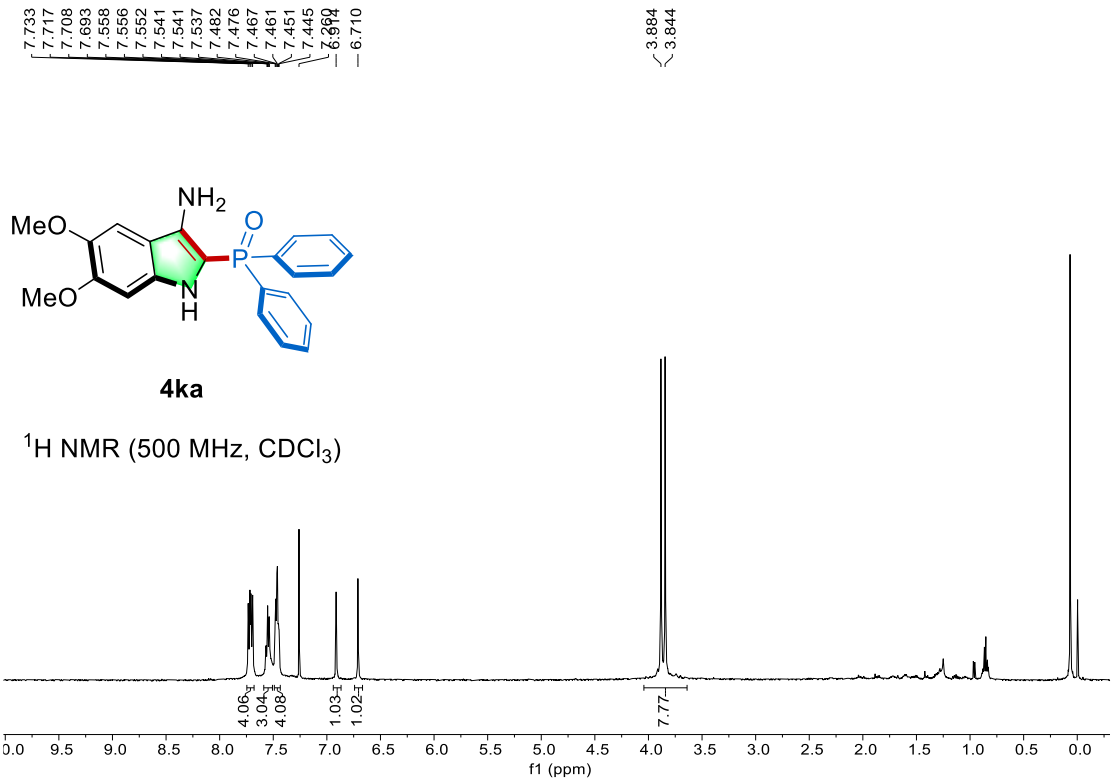
^{13}C NMR (125 MHz, $CDCl_3$)





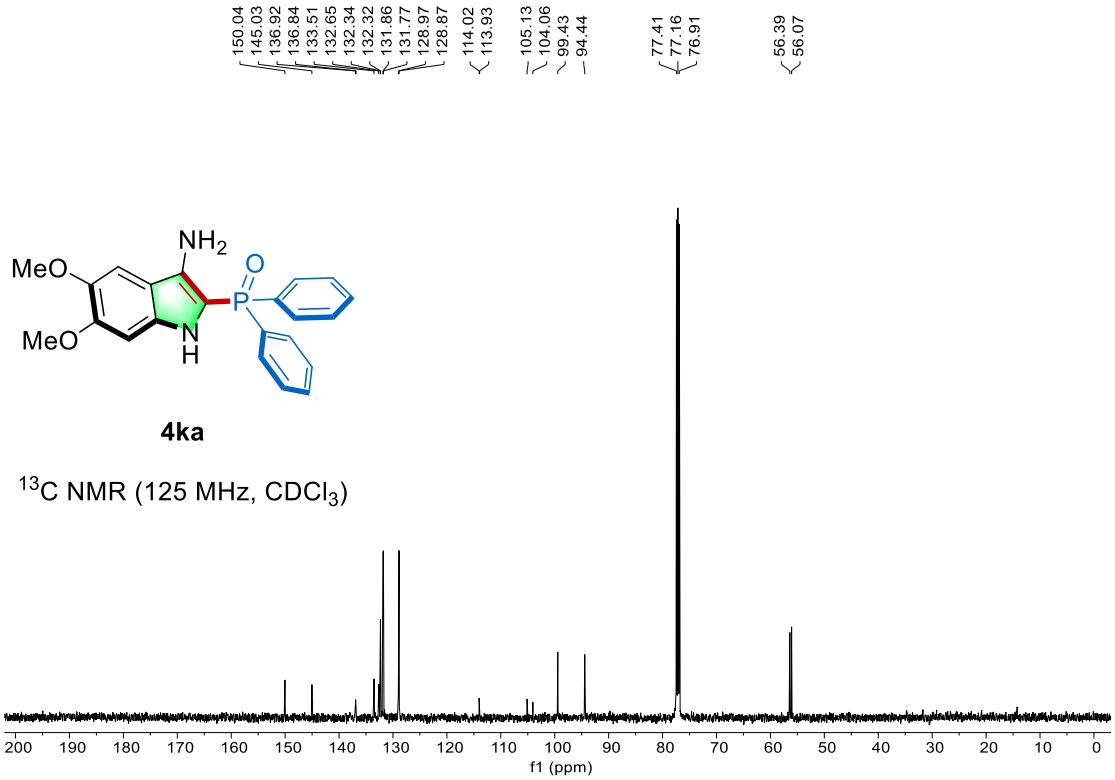
4ja

^{31}P NMR (202 MHz, $CDCl_3$)



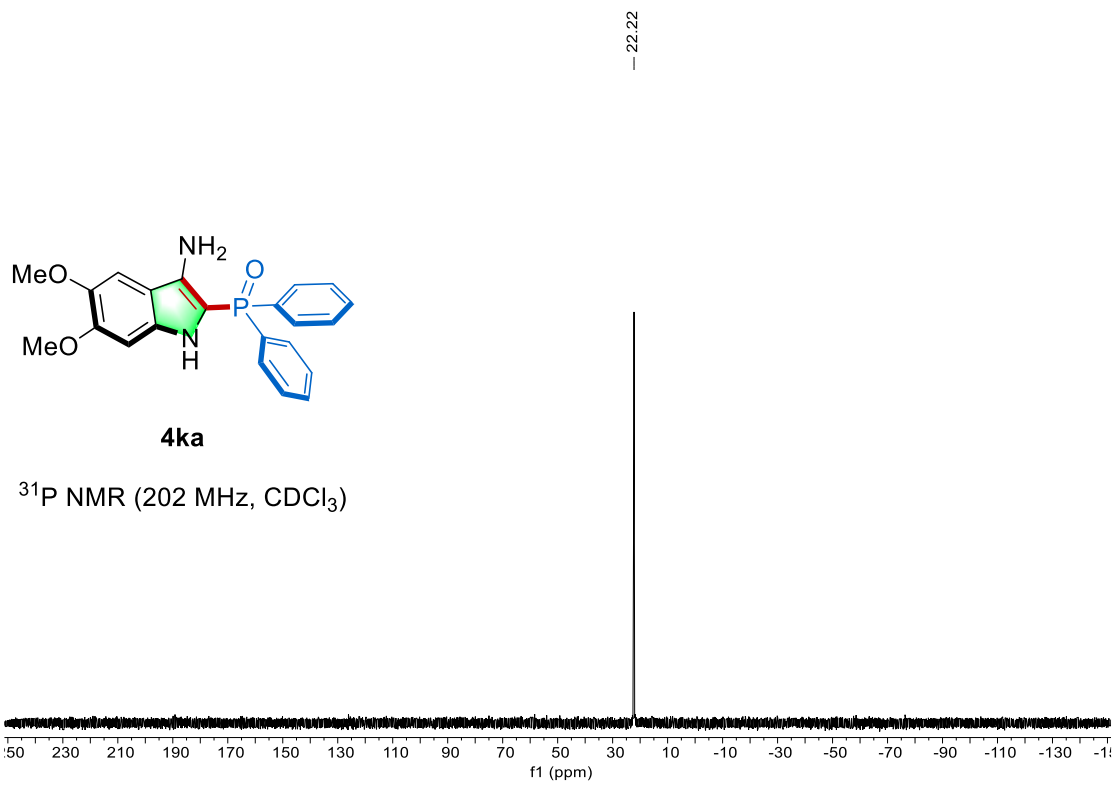
4ka

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



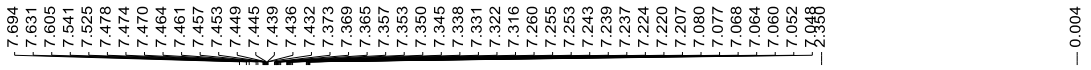
4ka

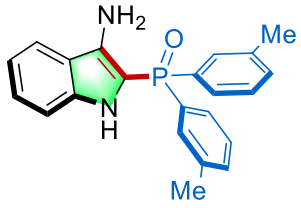
^{13}C NMR (125 MHz, $CDCl_3$)



4ka

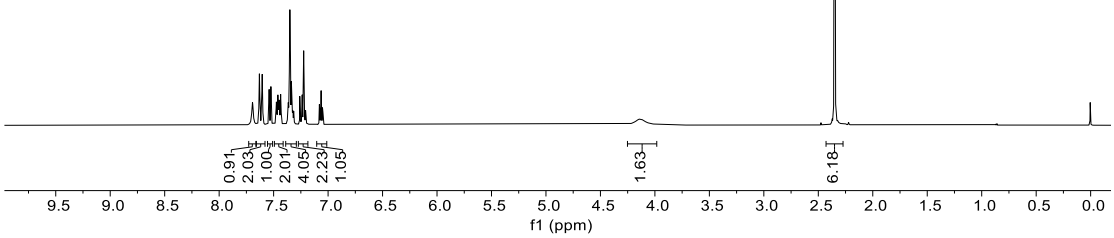
^{31}P NMR (202 MHz, $CDCl_3$)

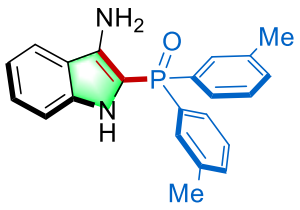




4ab

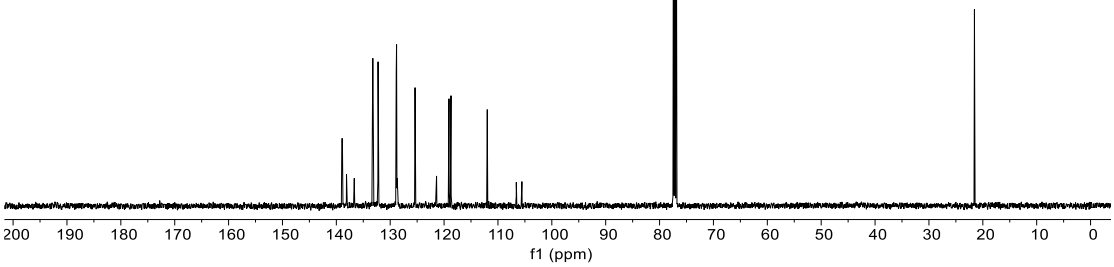
^{1}H NMR (500 MHz, $CDCl_3$)

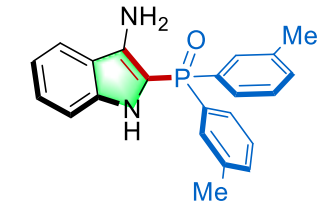




4ab

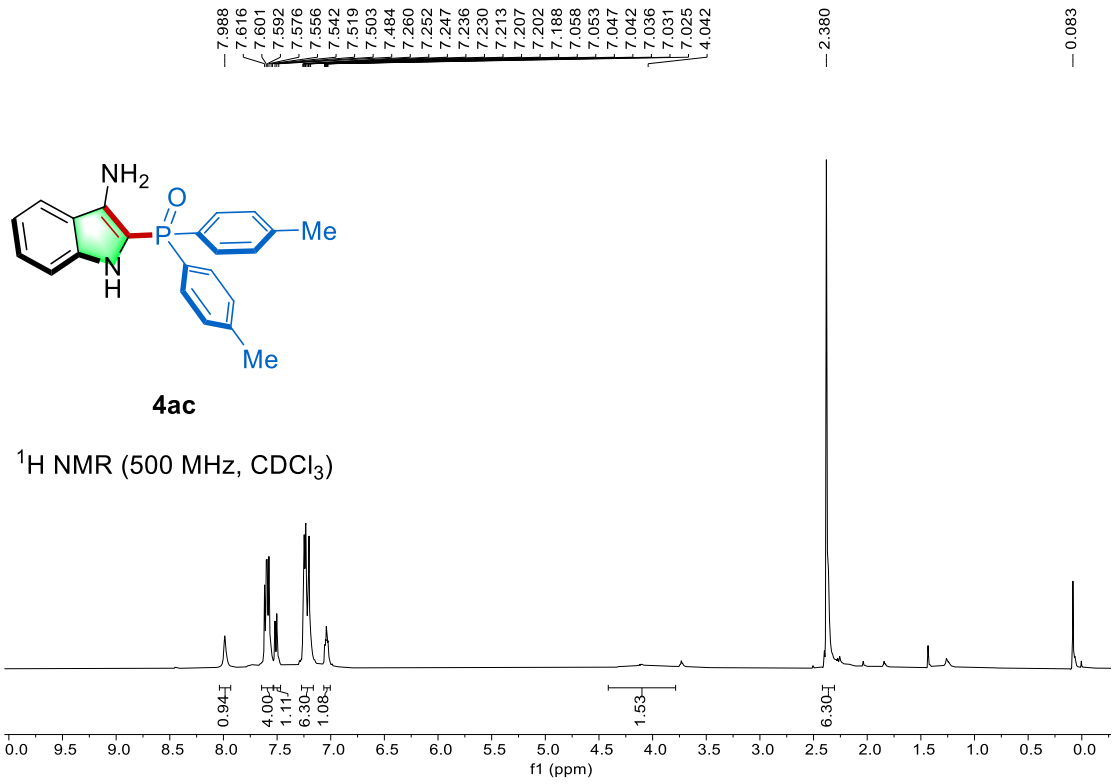
^{13}C NMR (125 MHz, $CDCl_3$)





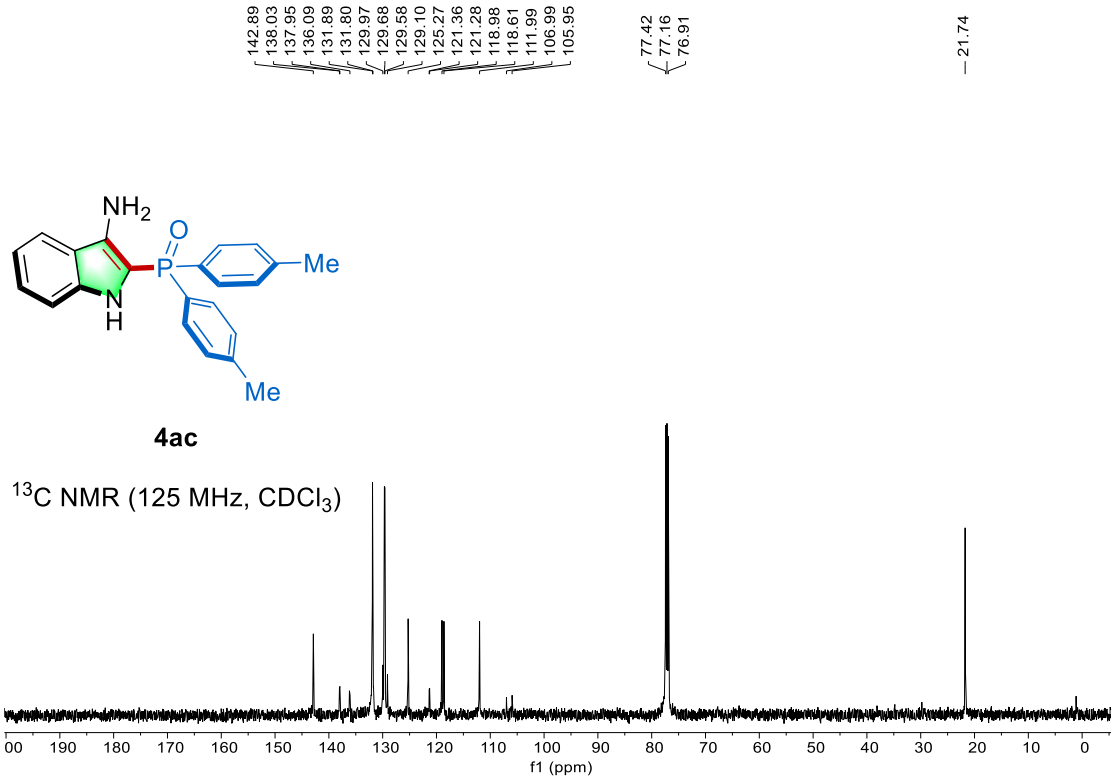
4ab

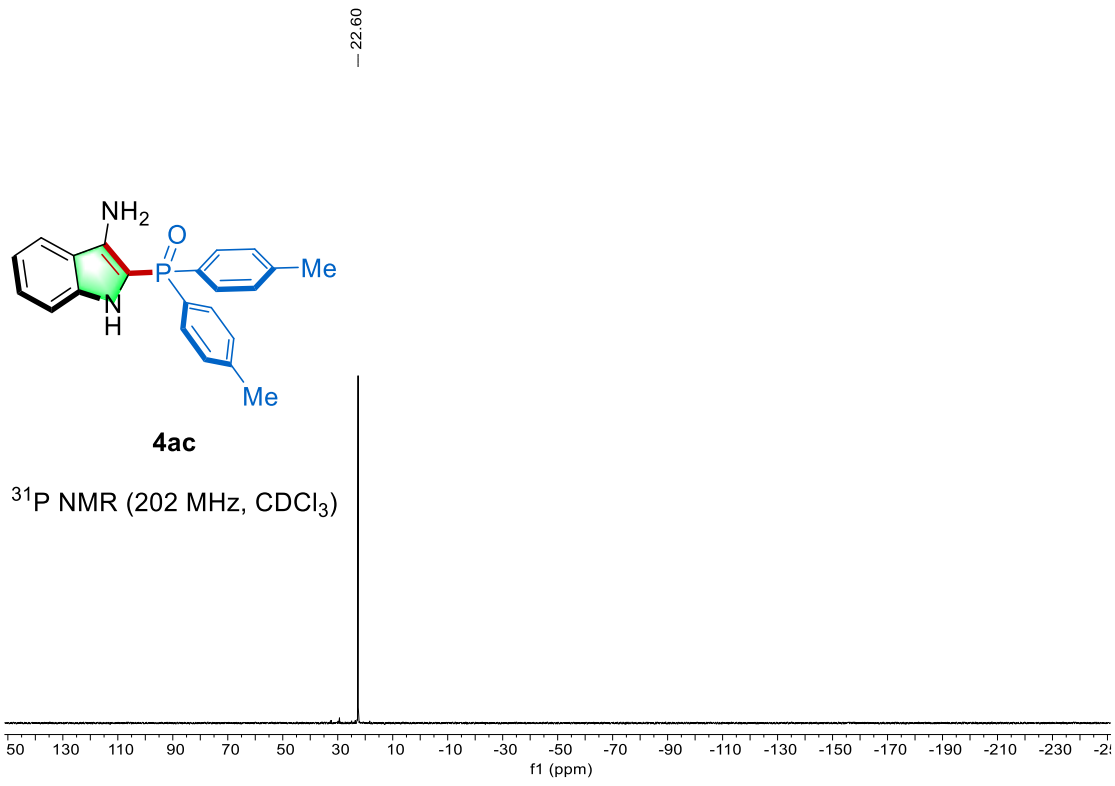
^{31}P NMR (202 MHz, $CDCl_3$)

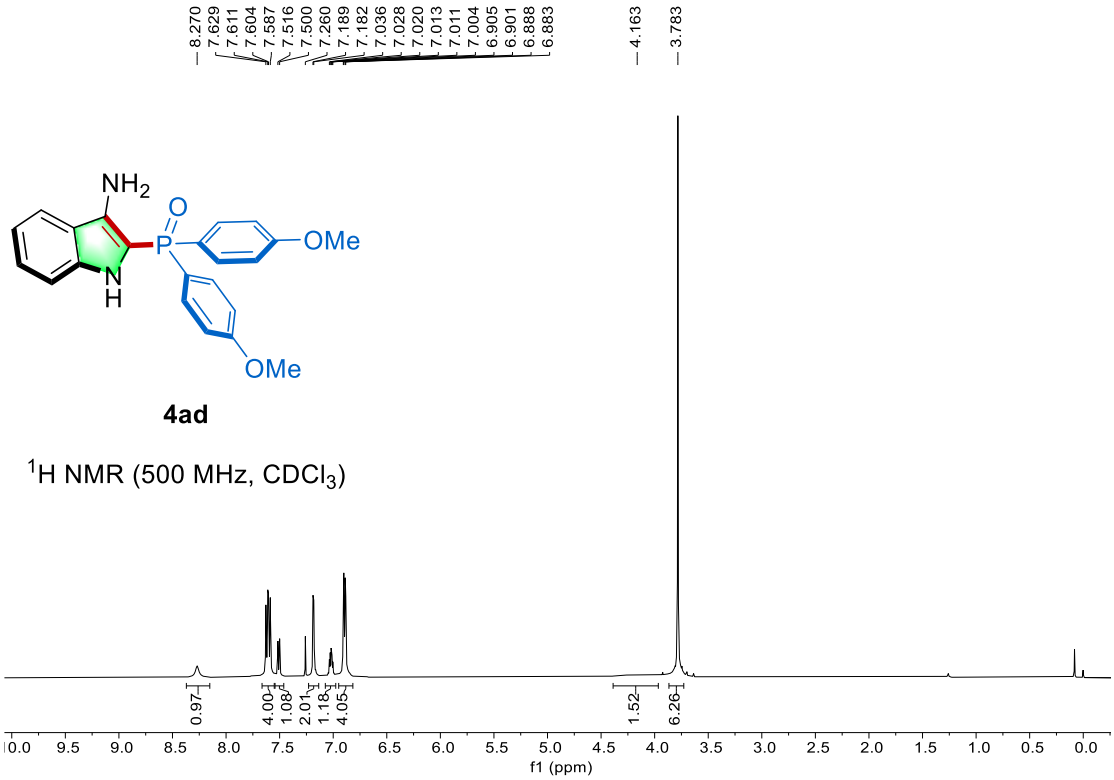


4ac

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

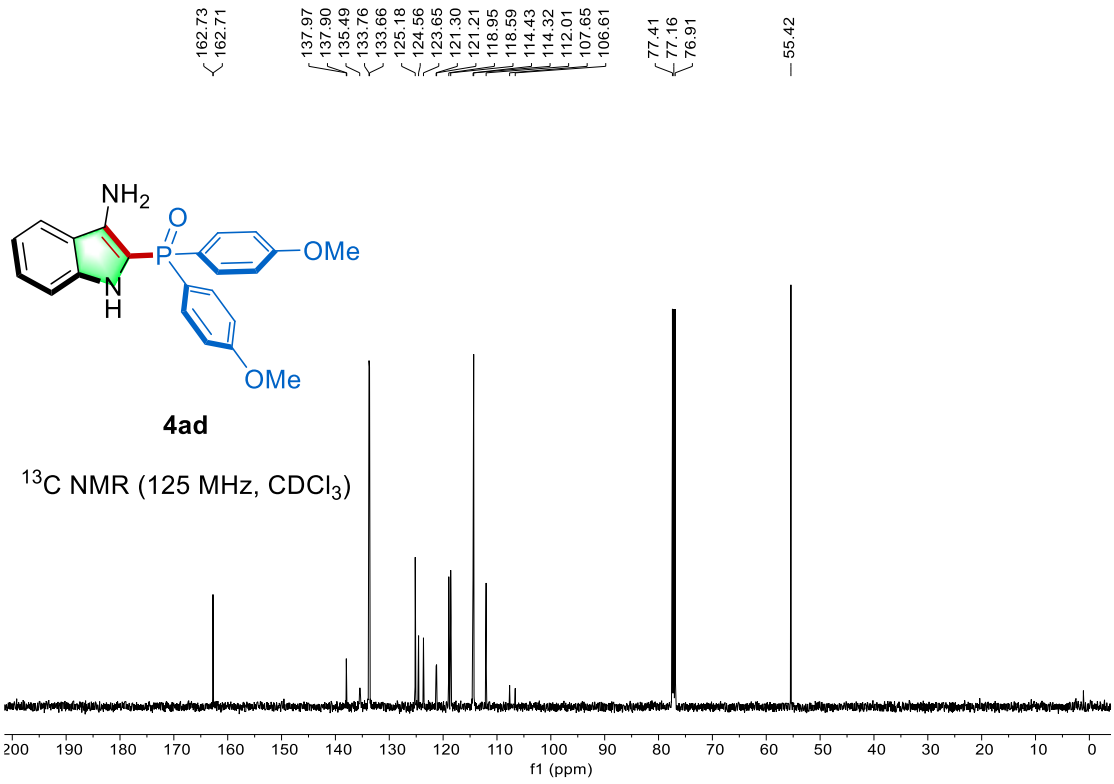

142.89
138.03
137.95
136.09
131.89
131.80
129.97
129.68
129.58
129.10
125.27
121.36
121.28
118.98
118.61
111.99
106.99
105.95
77.42
77.16
76.91
21.74
NH2
O
P
Me
N
H
Me
4ac
13C NMR (125 MHz, CDCl3)
f1 (ppm)


22.60
NH2
O
P
Me
N
H
Me
4ac
31P NMR (202 MHz, CDCl3)
f1 (ppm)



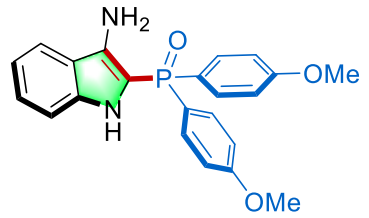
4ad

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



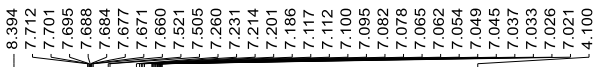
4ad

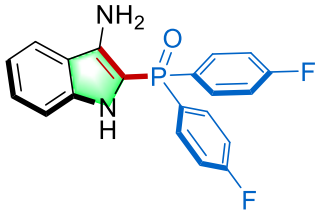
^{13}C NMR (125 MHz, $CDCl_3$)



4ad

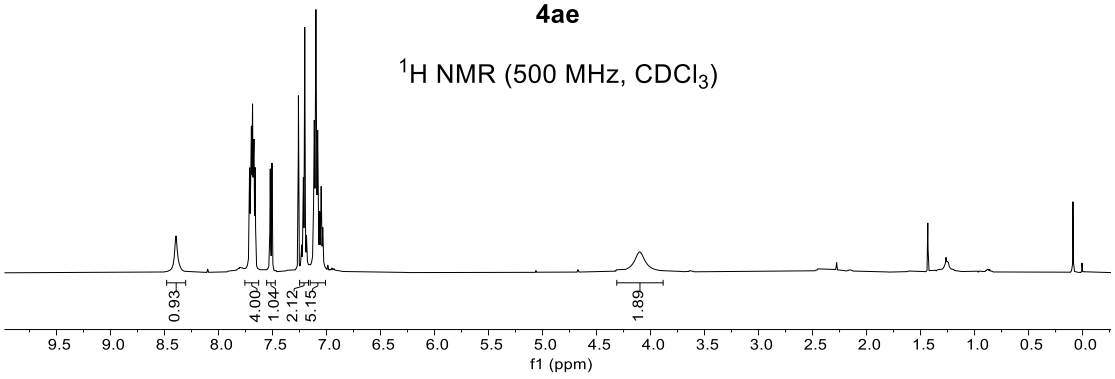
^{31}P NMR (202 MHz, $CDCl_3$)

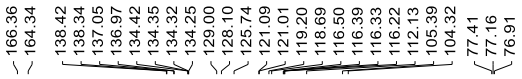


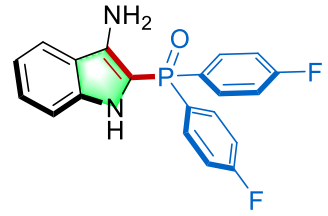


4ae

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

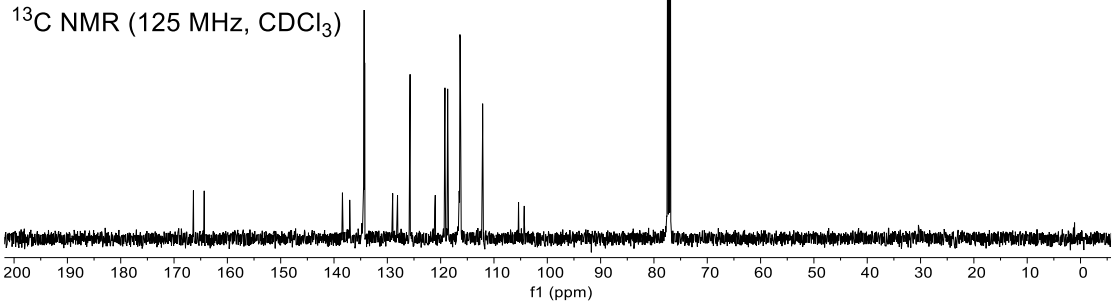


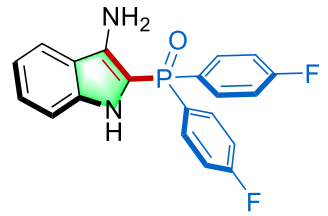




4ae

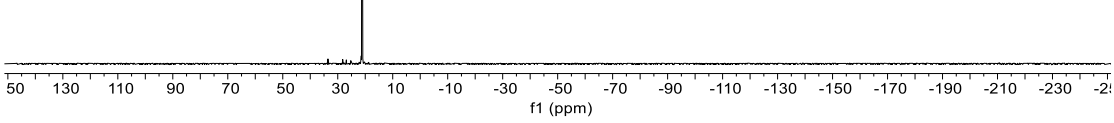
^{13}C NMR (125 MHz, $CDCl_3$)

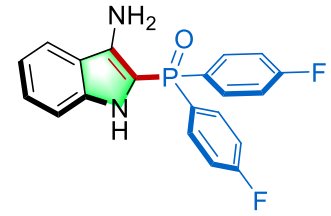




4ae

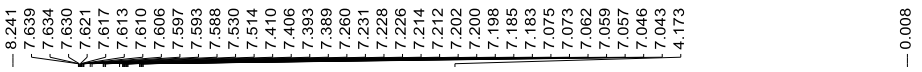
^{31}P NMR (202 MHz, $CDCl_3$)

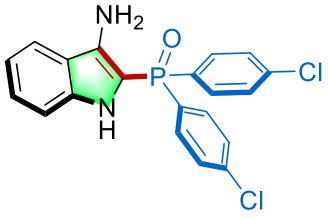




4ae

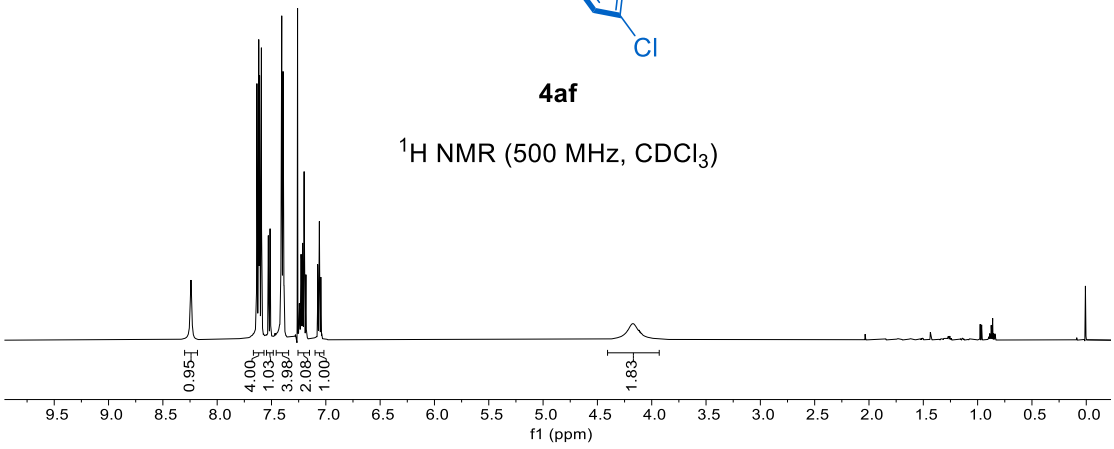
^{19}F NMR (471 MHz, $CDCl_3$)

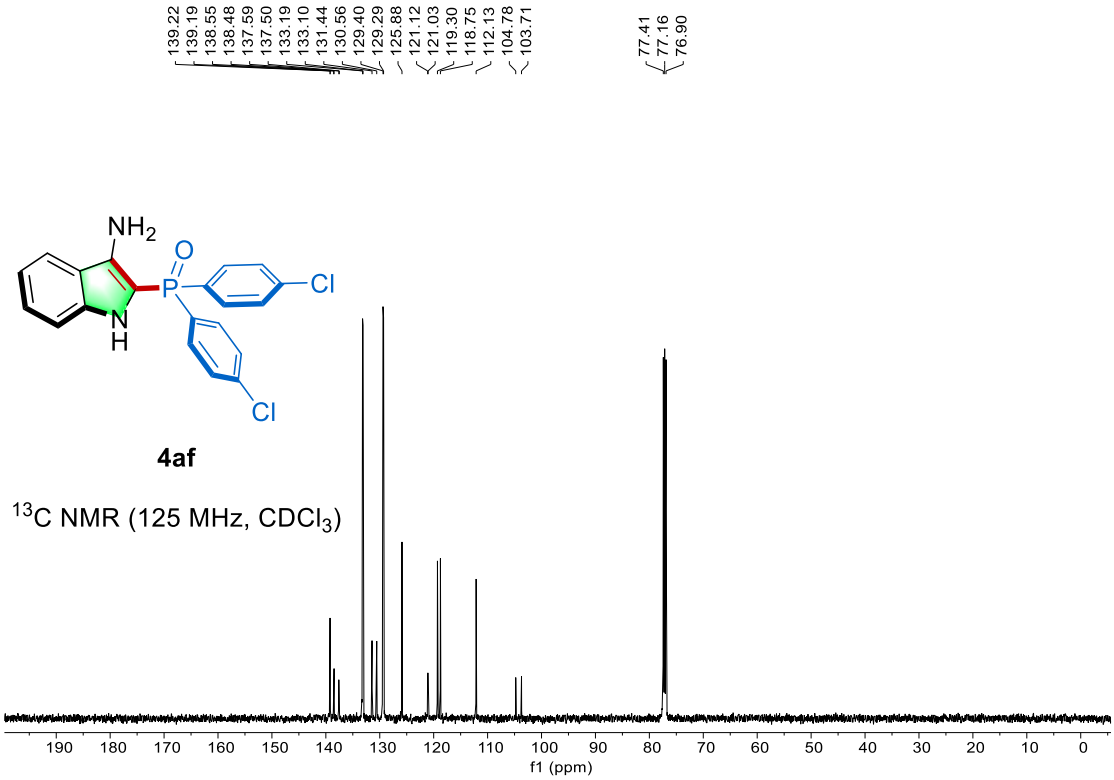




4af

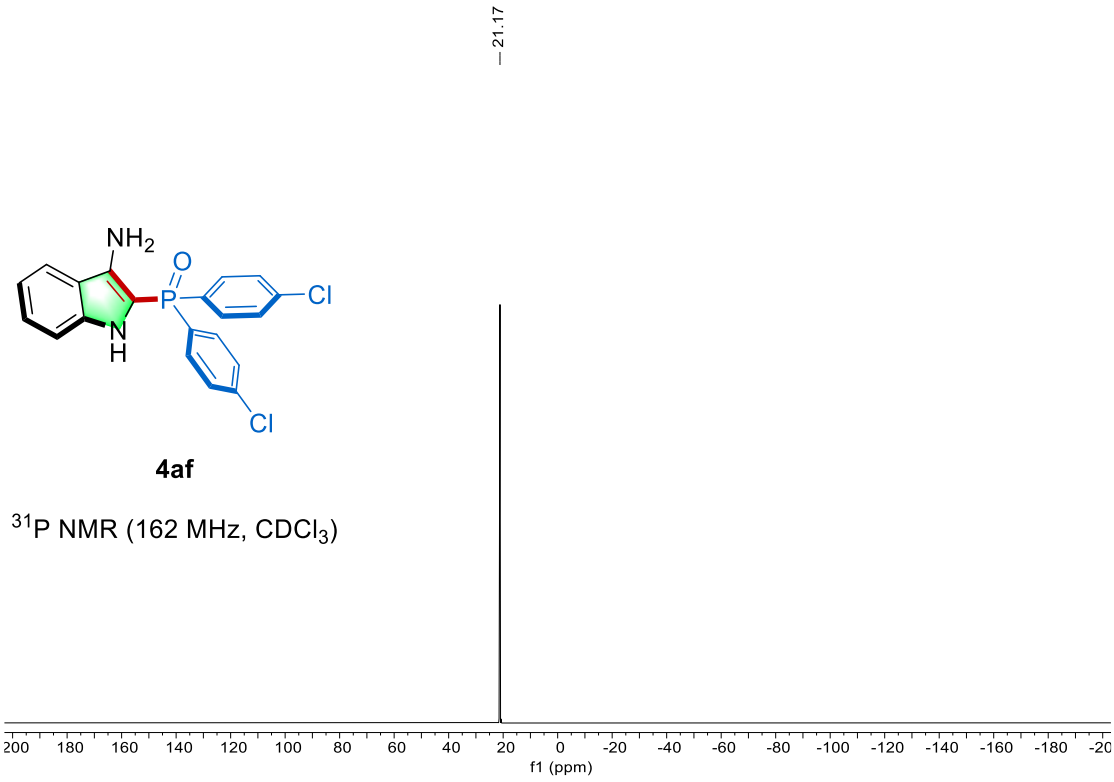
^{1}H NMR (500 MHz, $CDCl_3$)





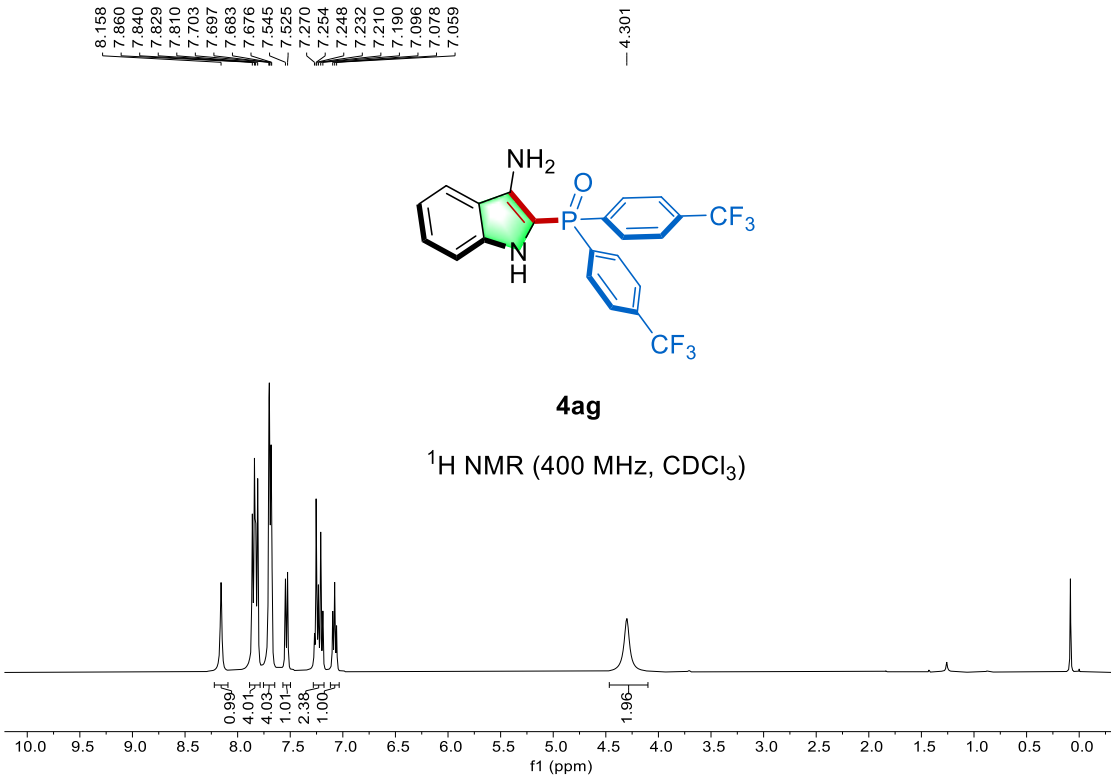
4af

^{13}C NMR (125 MHz, $CDCl_3$)



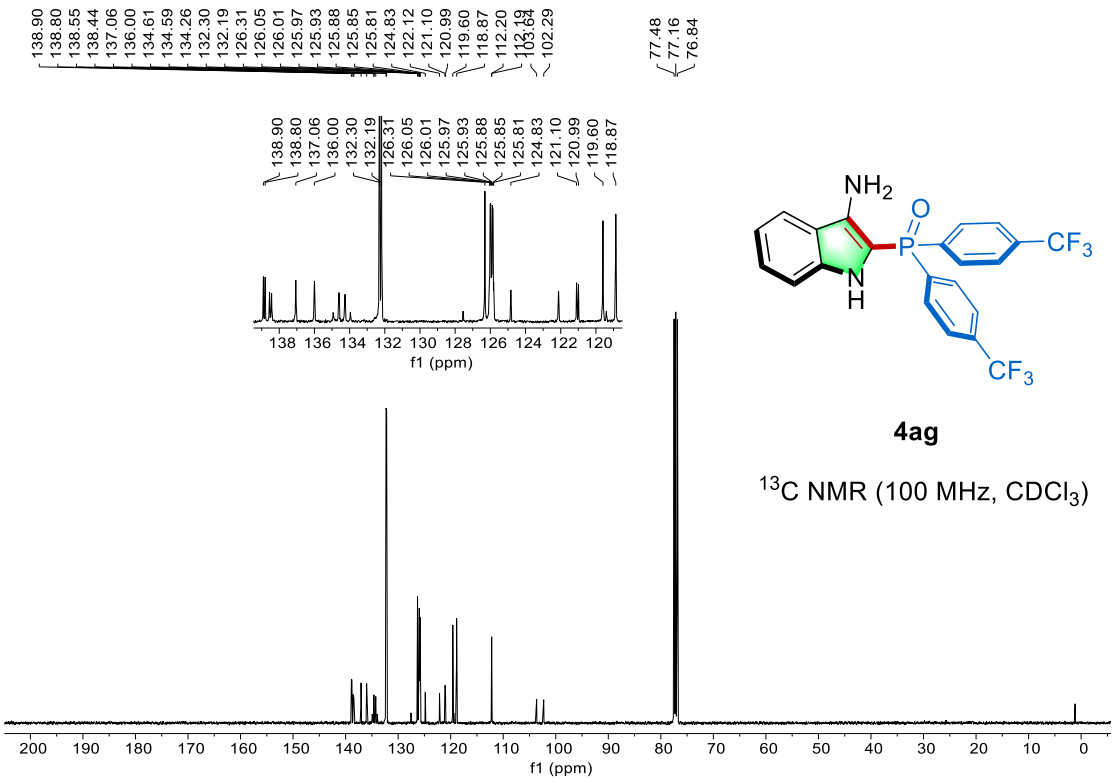
4af

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



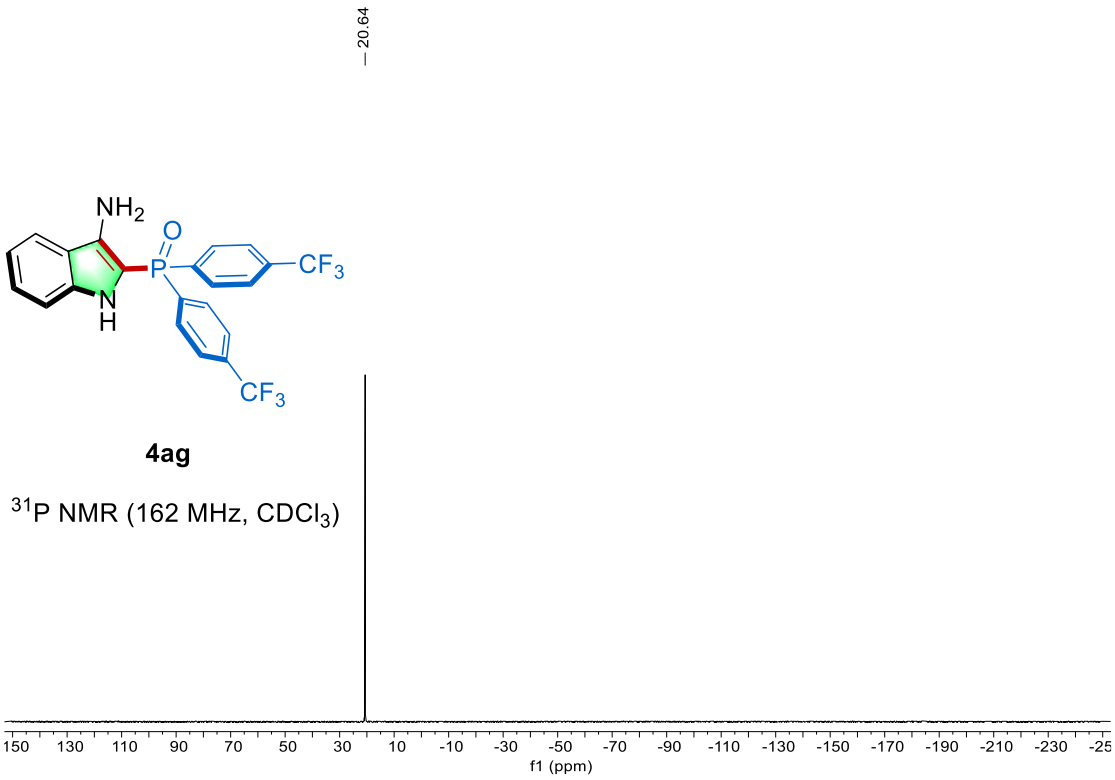
4ag

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



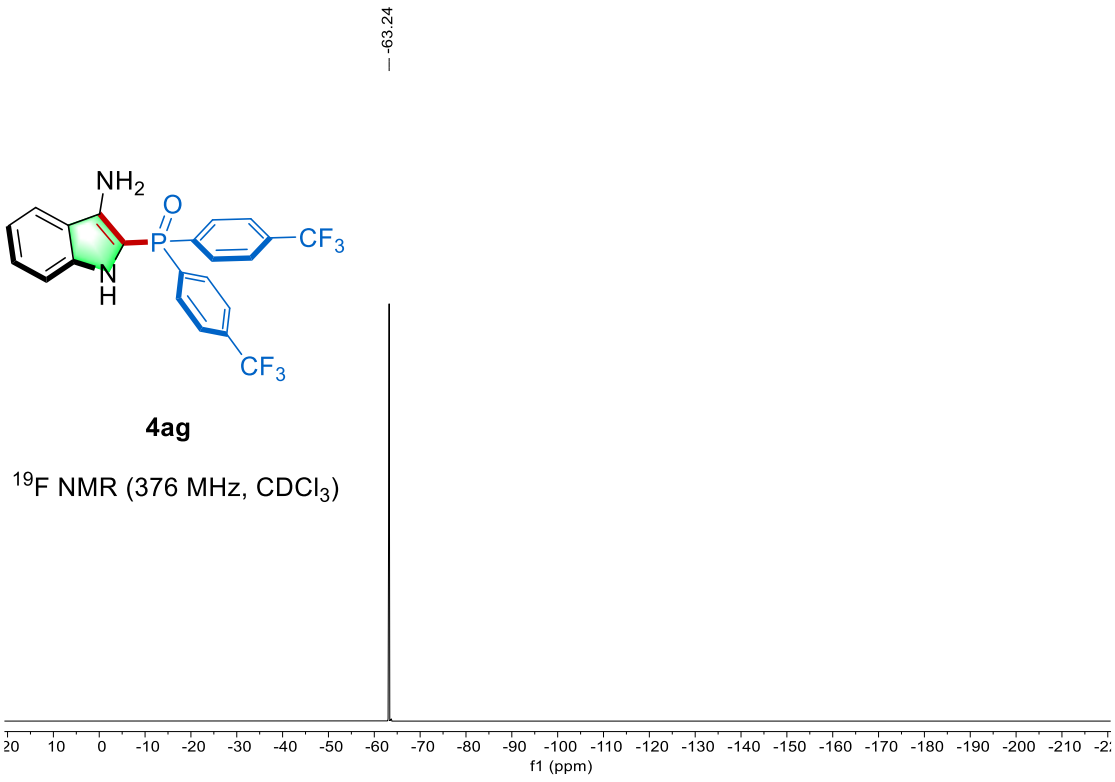
4ag

^{13}C NMR (100 MHz, $CDCl_3$)



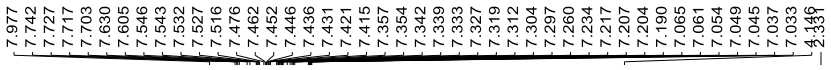
4ag

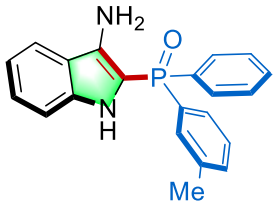
^{31}P NMR (162 MHz, $CDCl_3$)



4ag

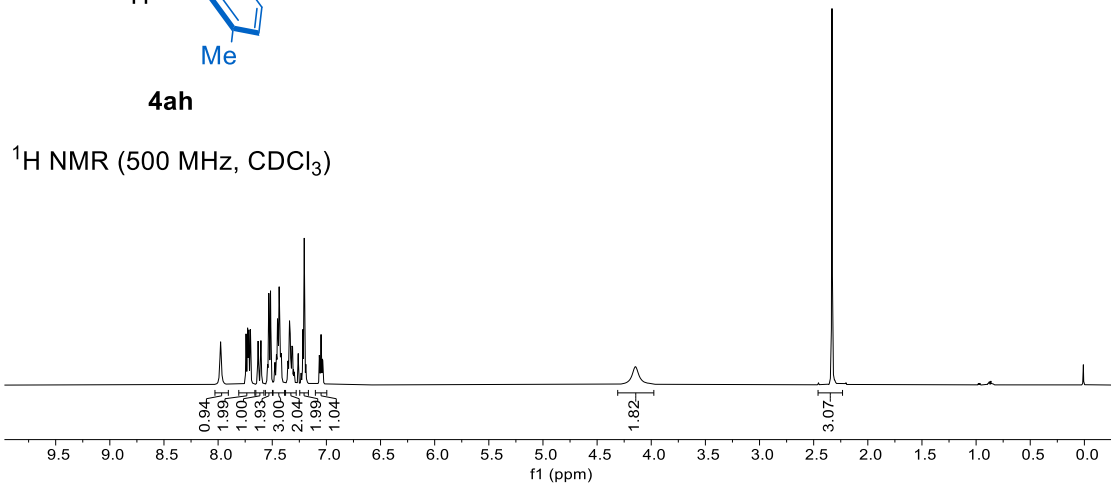
^{19}F NMR (376 MHz, $CDCl_3$)

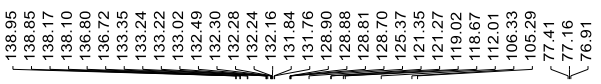


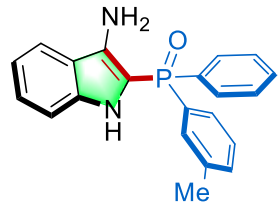


4ah

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

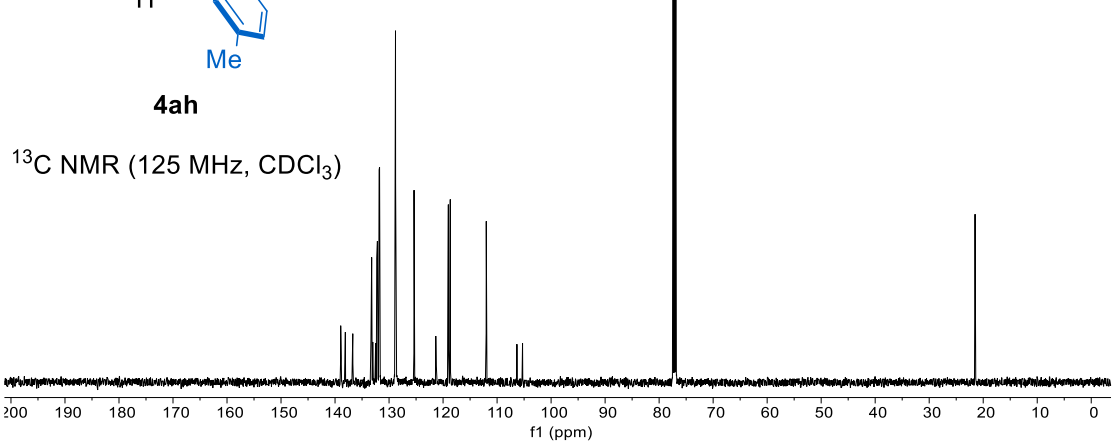


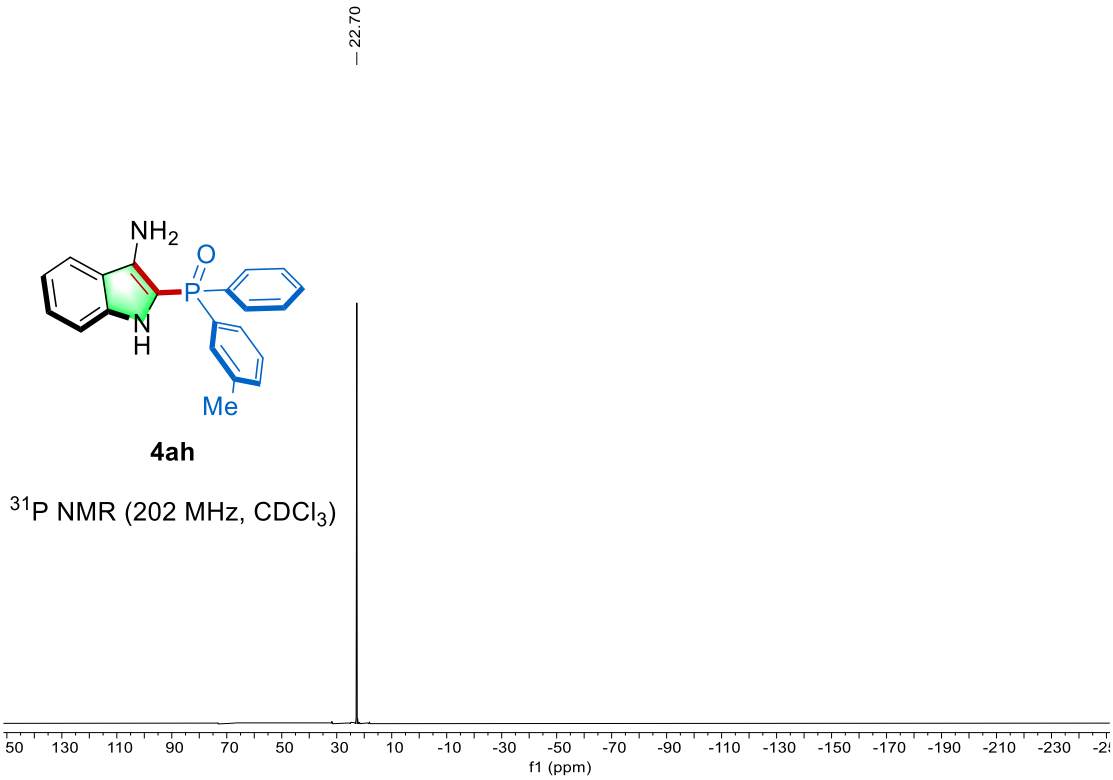




4ah

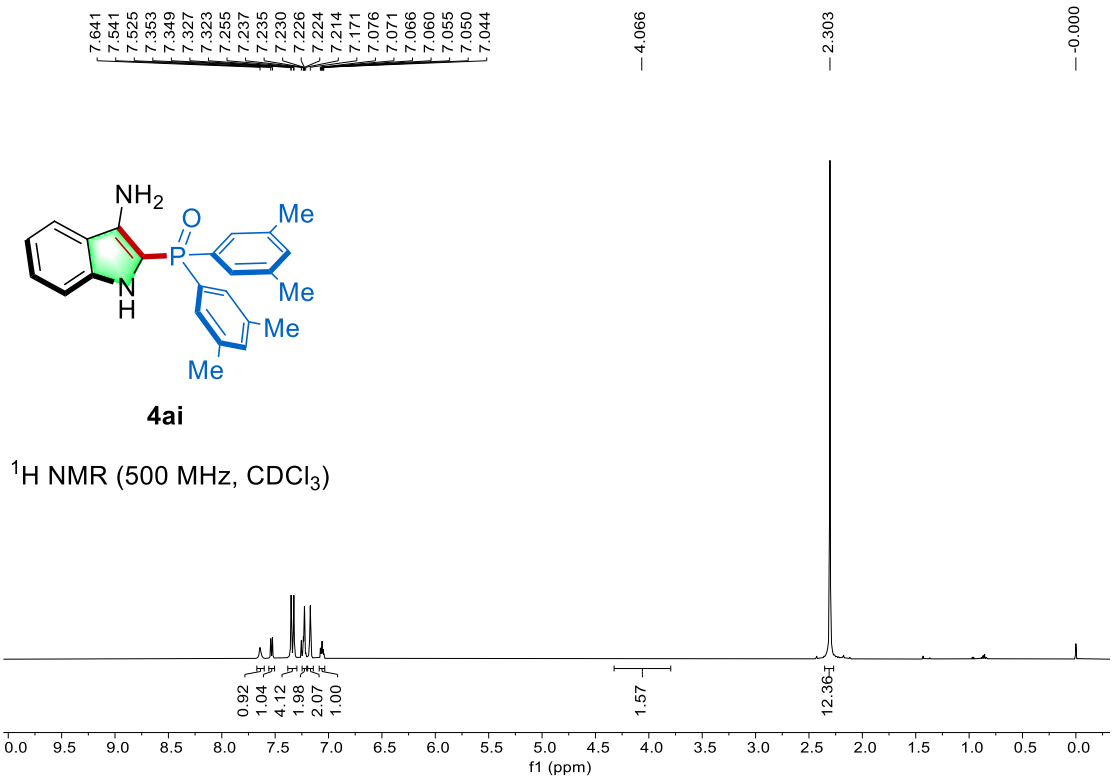
^{13}C NMR (125 MHz, $CDCl_3$)





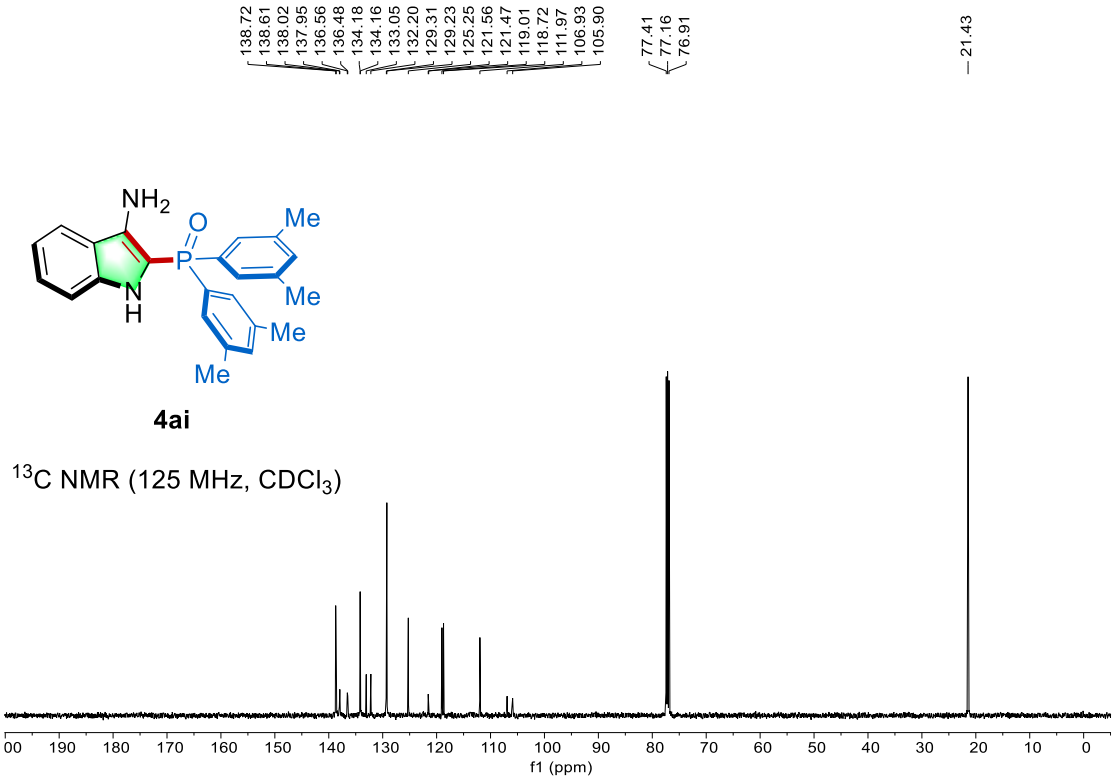
4ah

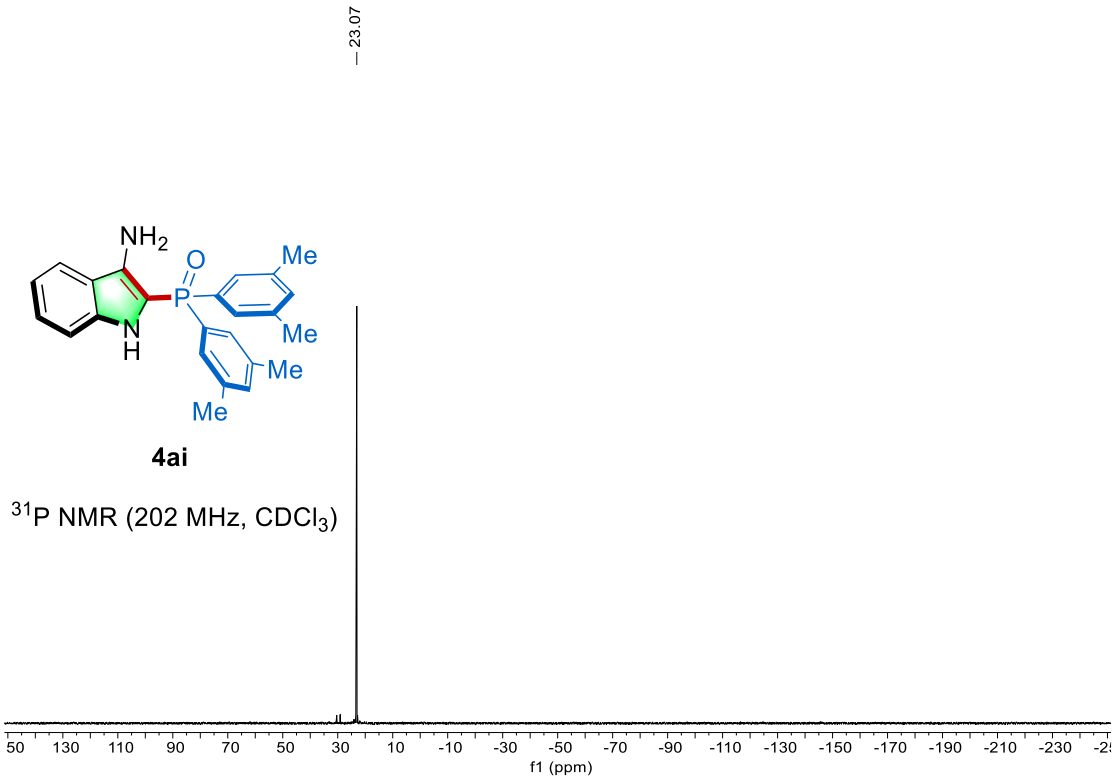
^{31}P NMR (202 MHz, $CDCl_3$)

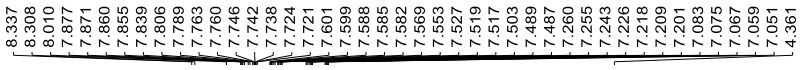


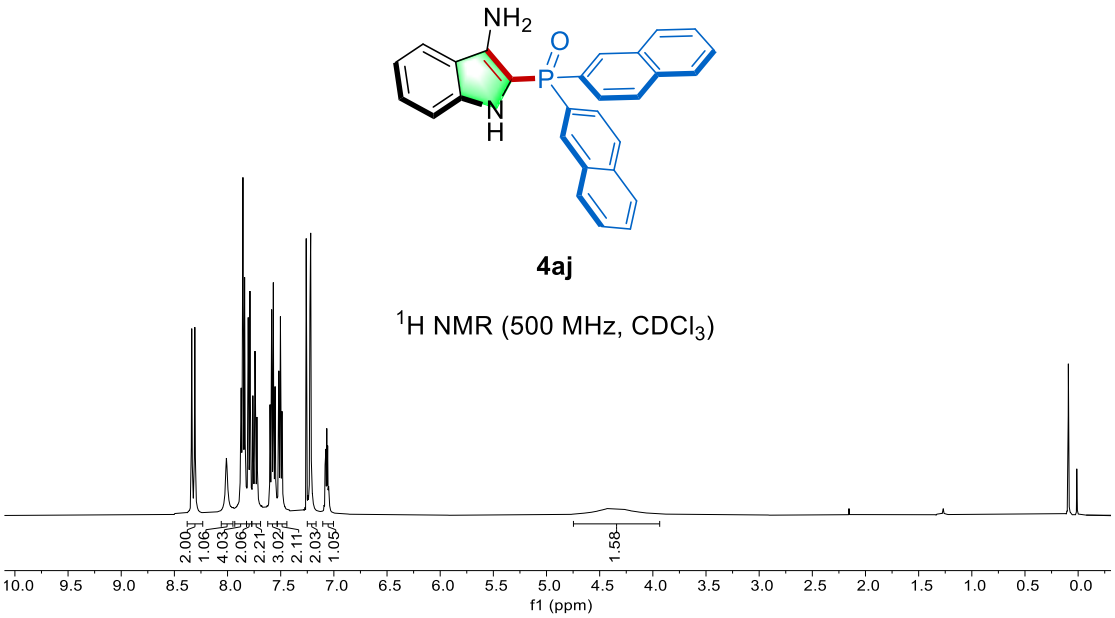
4ai

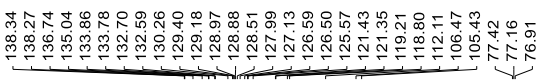
^{1}H NMR (500 MHz, $CDCl_3$)

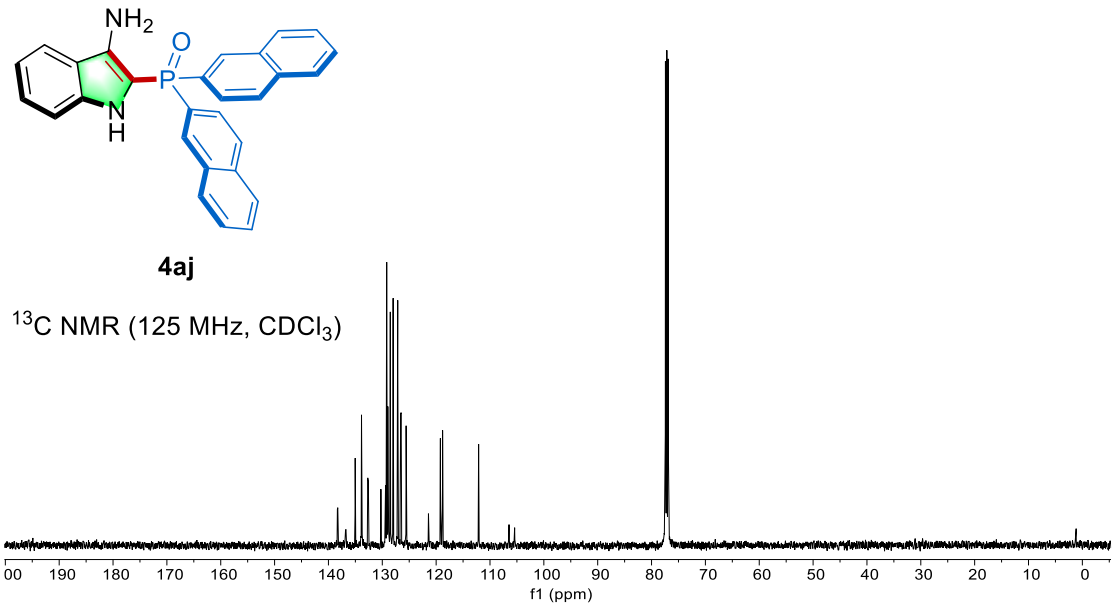

138.72
138.61
138.02
137.95
136.56
136.48
134.18
134.16
133.05
132.20
129.31
129.23
125.25
121.56
121.47
119.01
118.72
111.97
106.93
105.90
77.41
77.16
76.91
21.43
NH2
O
P
N
H
Me
Me
Me
Me
4ai
13C NMR (125 MHz, CDCl3)
f1 (ppm)

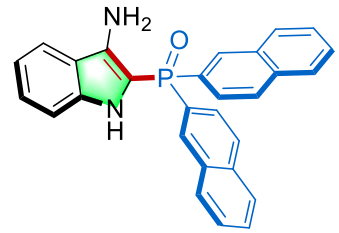

23.07
NH2
O
P
N
H
Me
Me
Me
Me
4ai
31P NMR (202 MHz, CDCl3)
f1 (ppm)


8.337
8.308
8.010
7.877
7.871
7.860
7.855
7.839
7.806
7.789
7.763
7.760
7.746
7.742
7.738
7.724
7.721
7.601
7.599
7.588
7.585
7.582
7.569
7.553
7.527
7.519
7.517
7.503
7.489
7.487
7.260
7.255
7.243
7.226
7.218
7.209
7.201
7.083
7.075
7.067
7.059
7.051
4.361


NH2
O
P
N
H
4aj
1H NMR (500 MHz, CDCl3)
2.00
1.06
4.03
2.06
2.21
3.02
2.11
2.03
1.05
1.58
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
f1 (ppm)

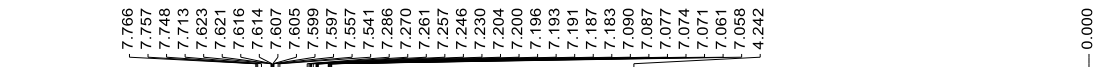

138.34
138.27
136.74
135.04
133.86
133.78
132.70
132.59
130.26
129.40
129.18
128.97
128.88
128.51
127.99
127.13
126.59
126.50
125.57
121.43
121.35
119.21
118.80
112.11
106.47
105.43
77.42
77.16
76.91

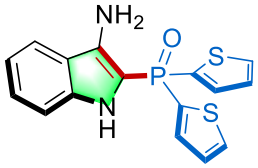

NH2
O
P
N
H
4aj
13C NMR (125 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



4aj

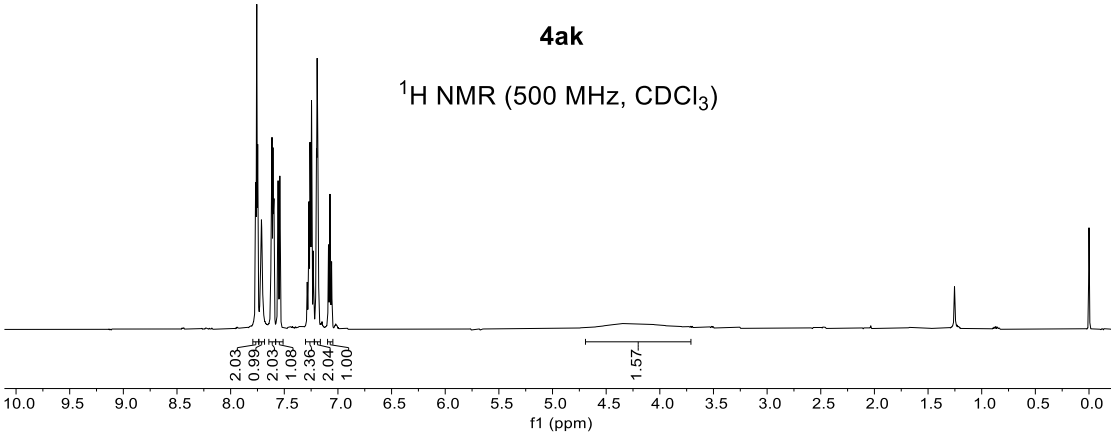
^{31}P NMR (202 MHz, $CDCl_3$)

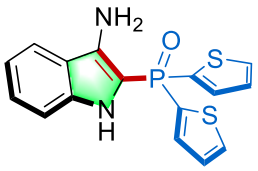




4ak

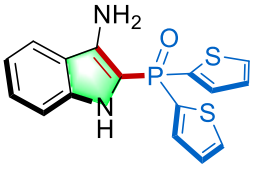
^{1}H NMR (500 MHz, $CDCl_3$)





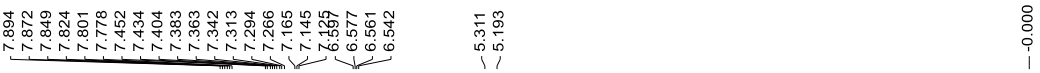
4ak

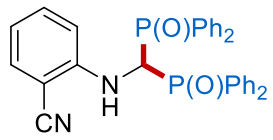
^{13}C NMR (125 MHz, $CDCl_3$)



4ak

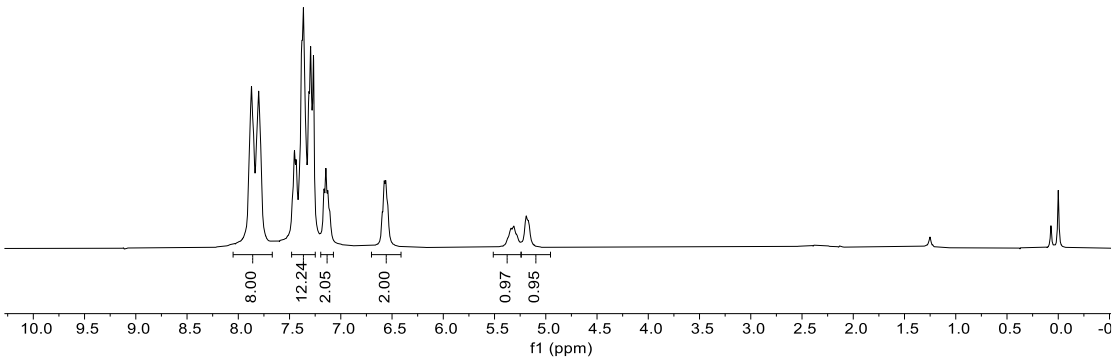
^{31}P NMR (202 MHz, $CDCl_3$)

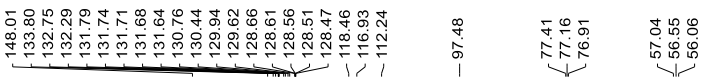


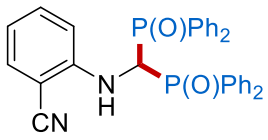


5

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

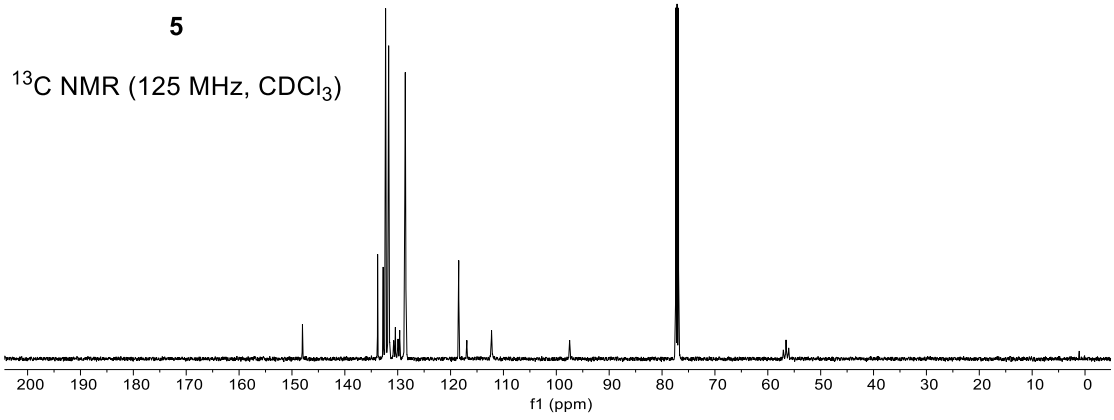


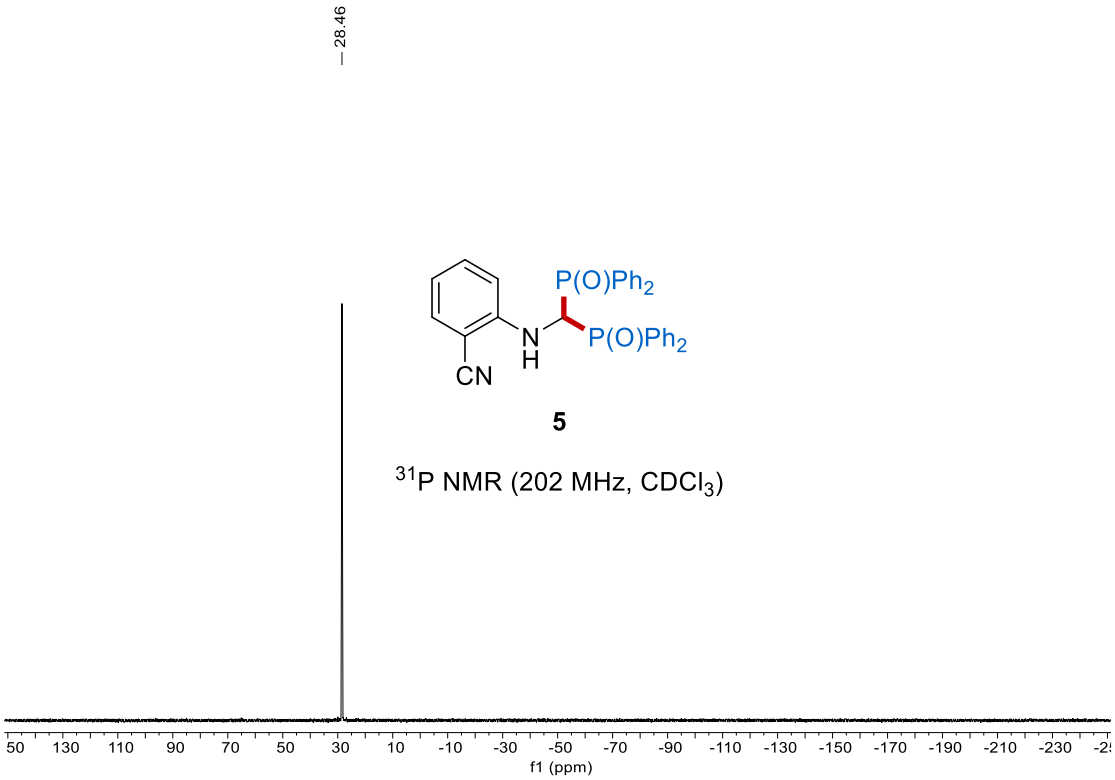


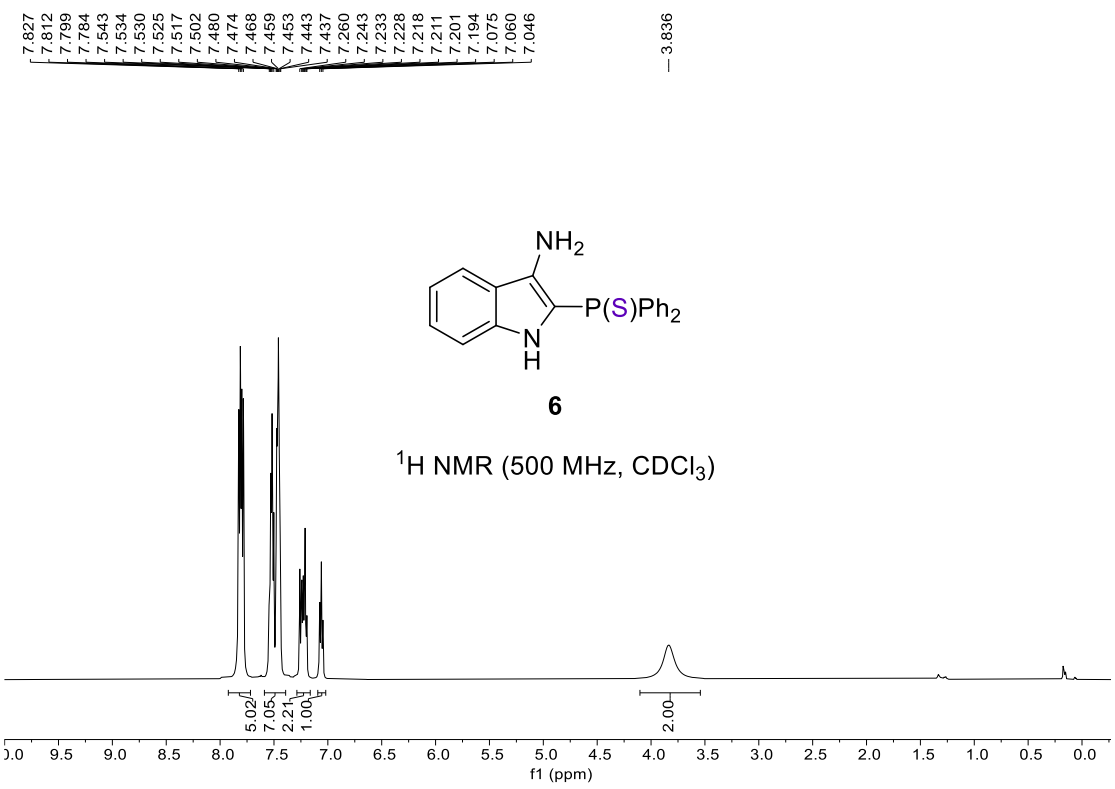


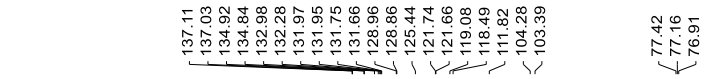
5

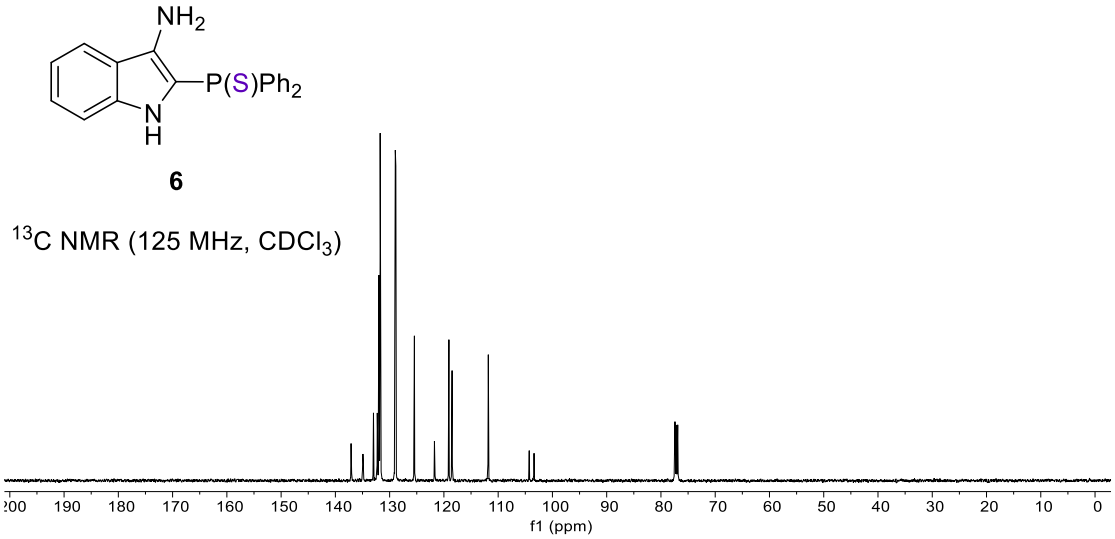
^{13}C NMR (125 MHz, $CDCl_3$)




28.46
P(O)Ph2
P(O)Ph2
N
H
CN
5
31P NMR (202 MHz, CDCl3)
f1 (ppm)

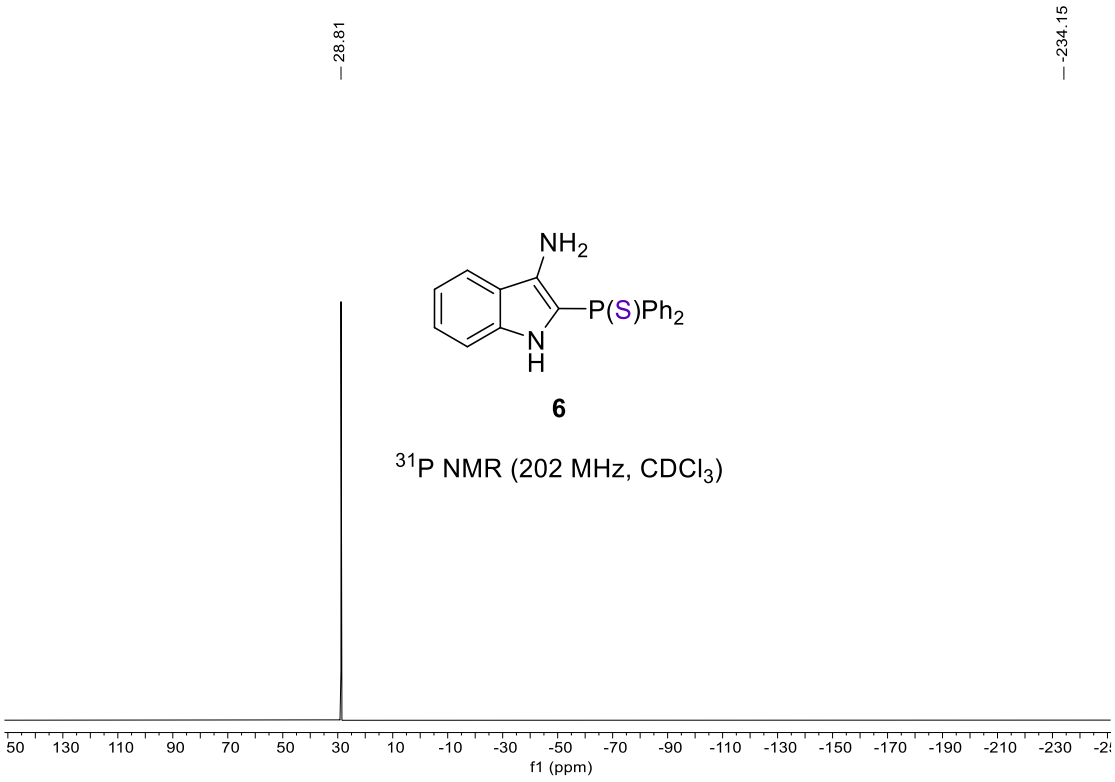

7.827
7.812
7.799
7.784
7.543
7.534
7.530
7.525
7.517
7.502
7.480
7.474
7.468
7.459
7.453
7.443
7.437
7.260
7.243
7.233
7.228
7.218
7.211
7.201
7.194
7.075
7.060
7.046
3.836
NH2
P(S)Ph2
N
H
6
1H NMR (500 MHz, CDCl3)
5.02
7.05
2.21
1.00
2.00
f1 (ppm)





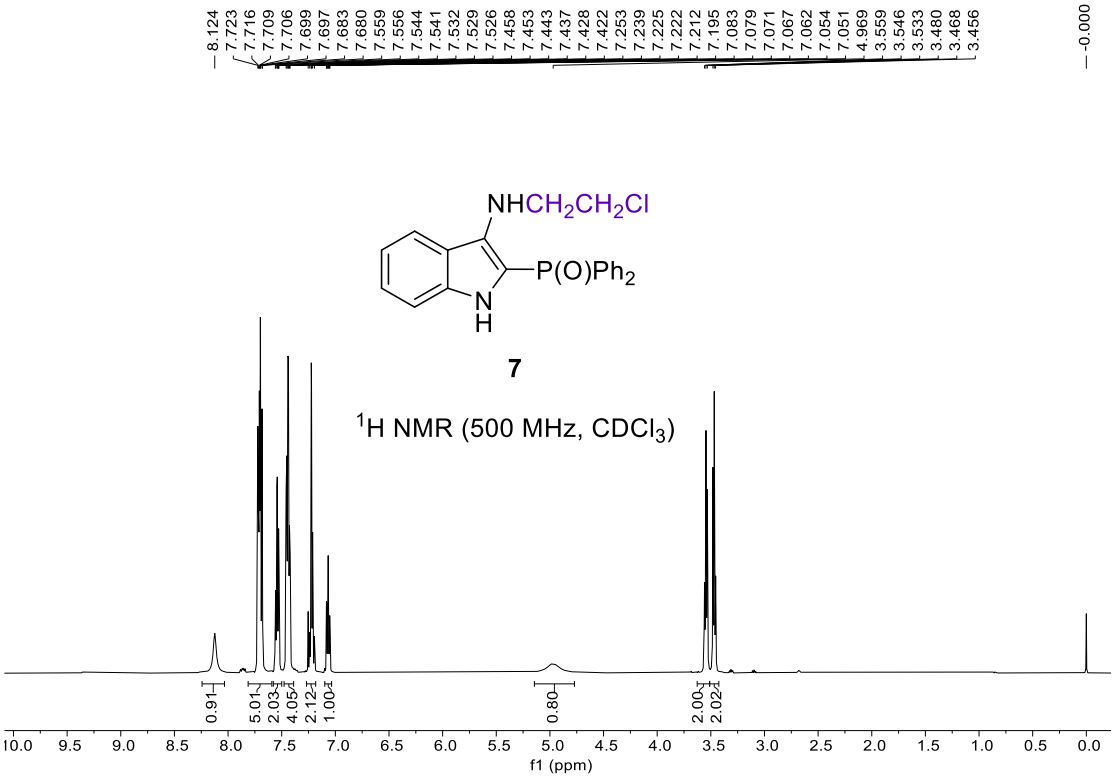
6

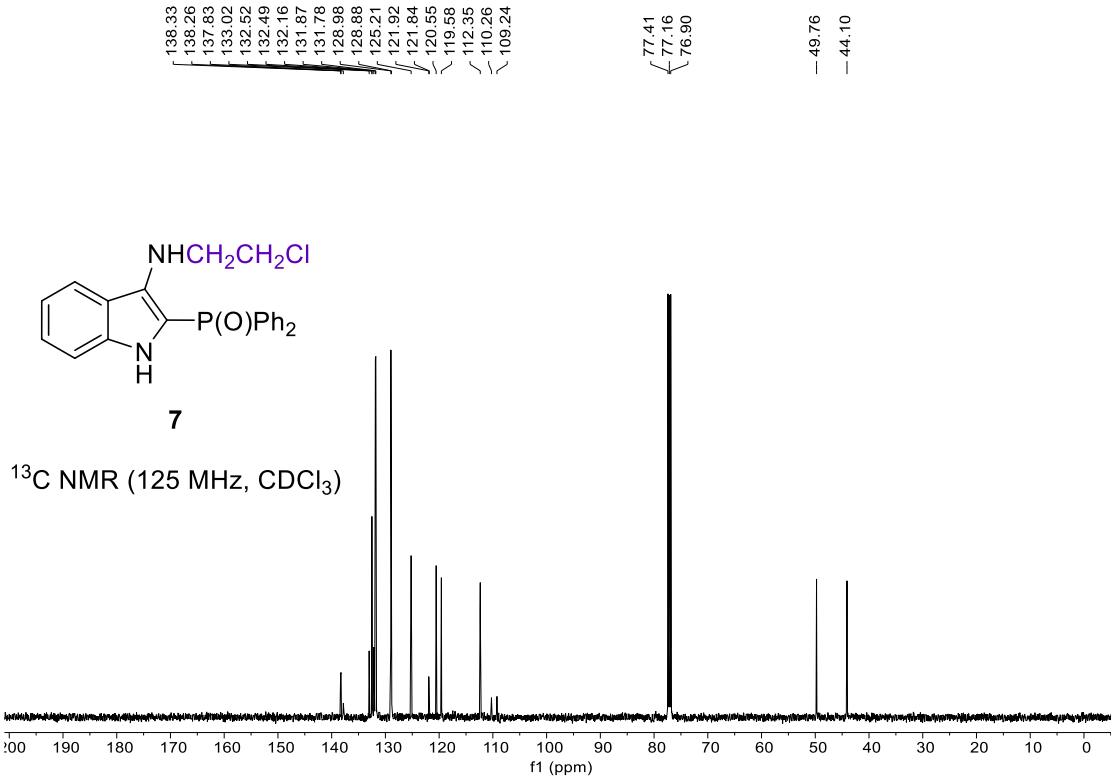
^{13}C NMR (125 MHz, $CDCl_3$)

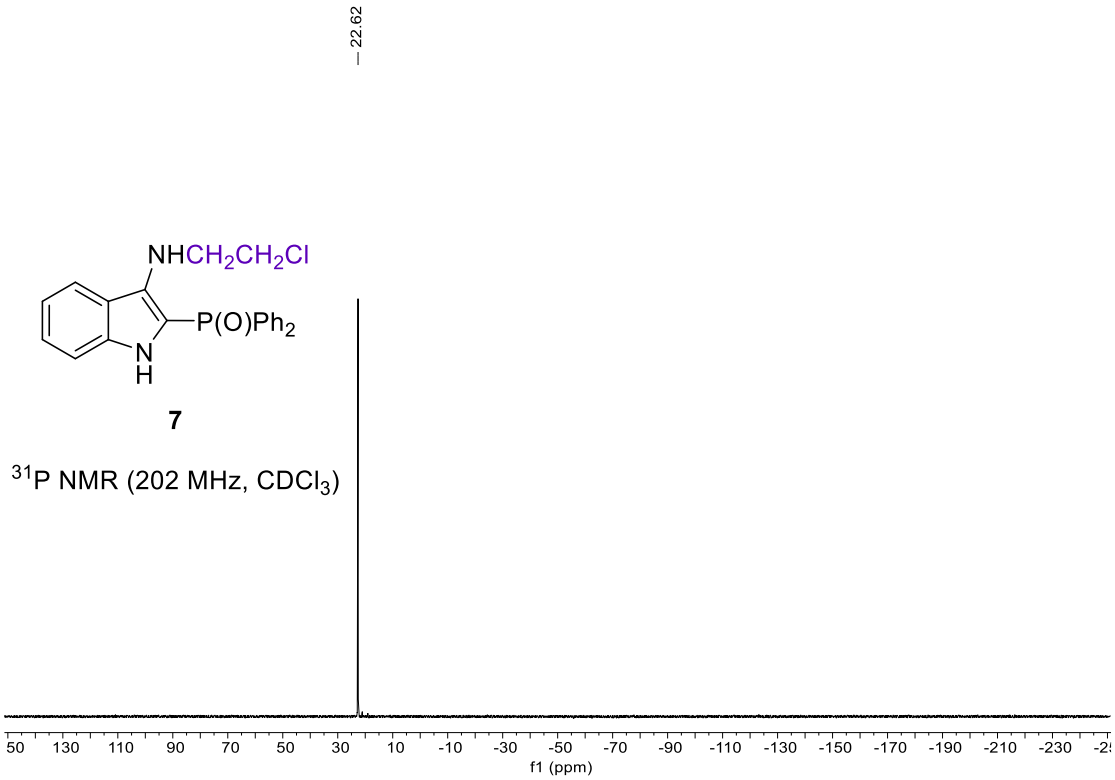


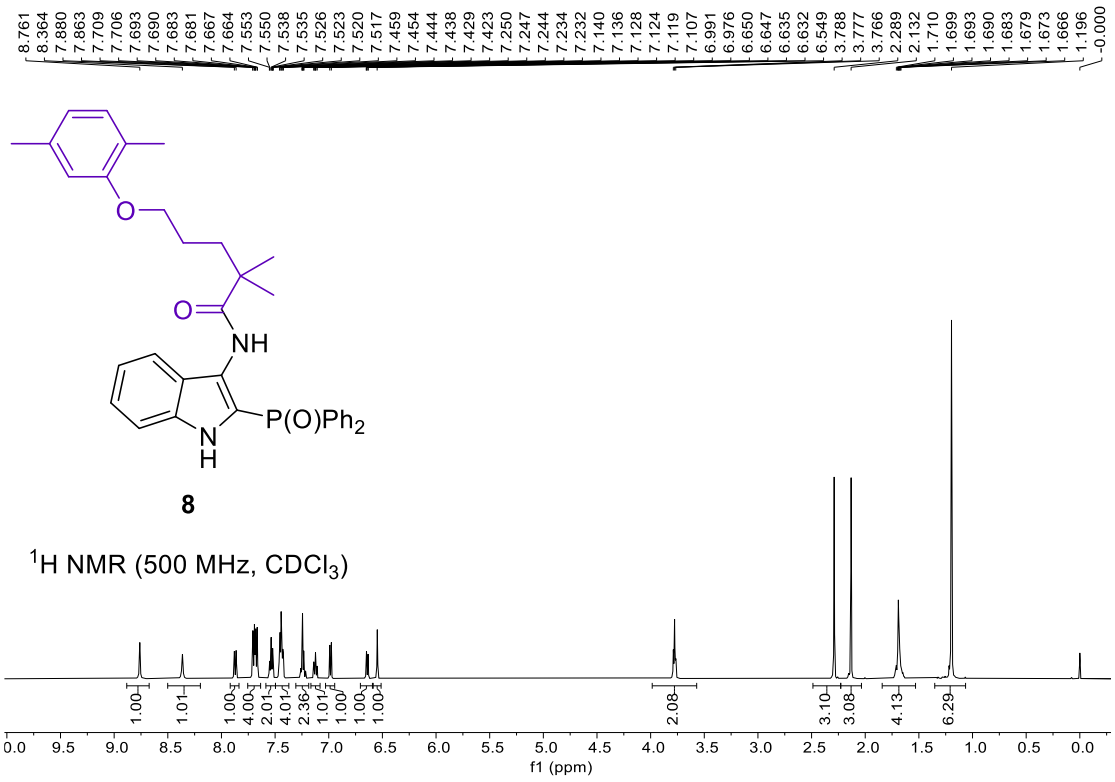
6

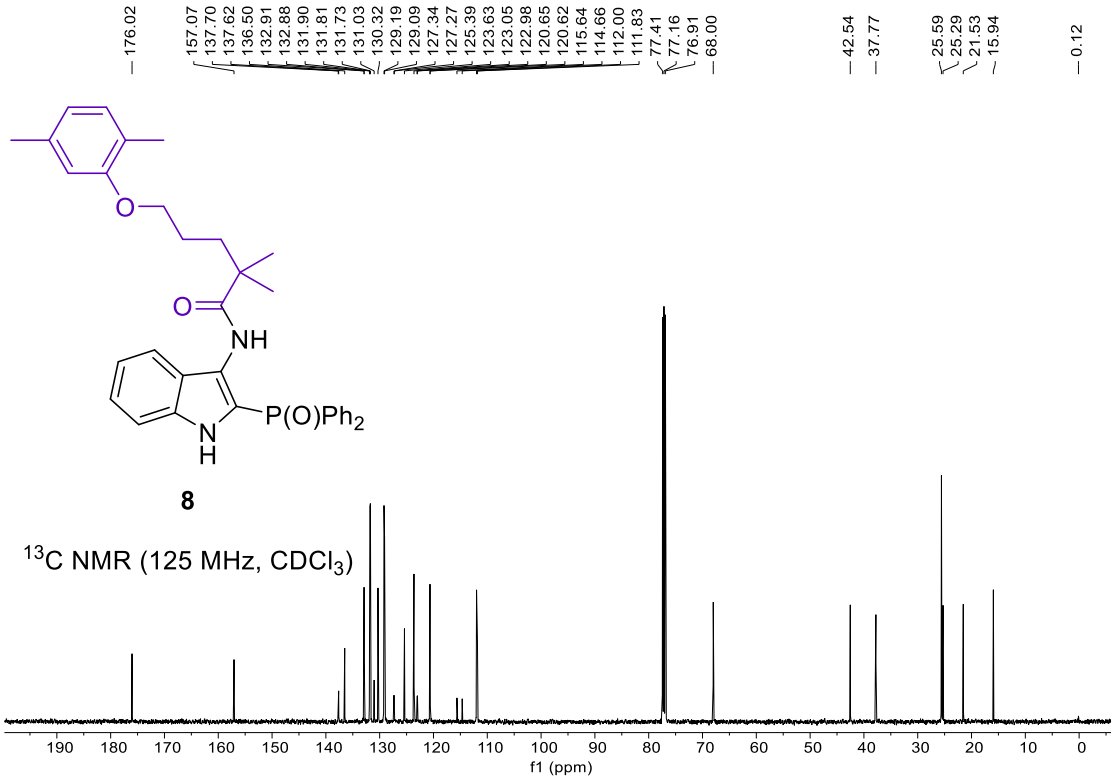
^{31}P NMR (202 MHz, $CDCl_3$)

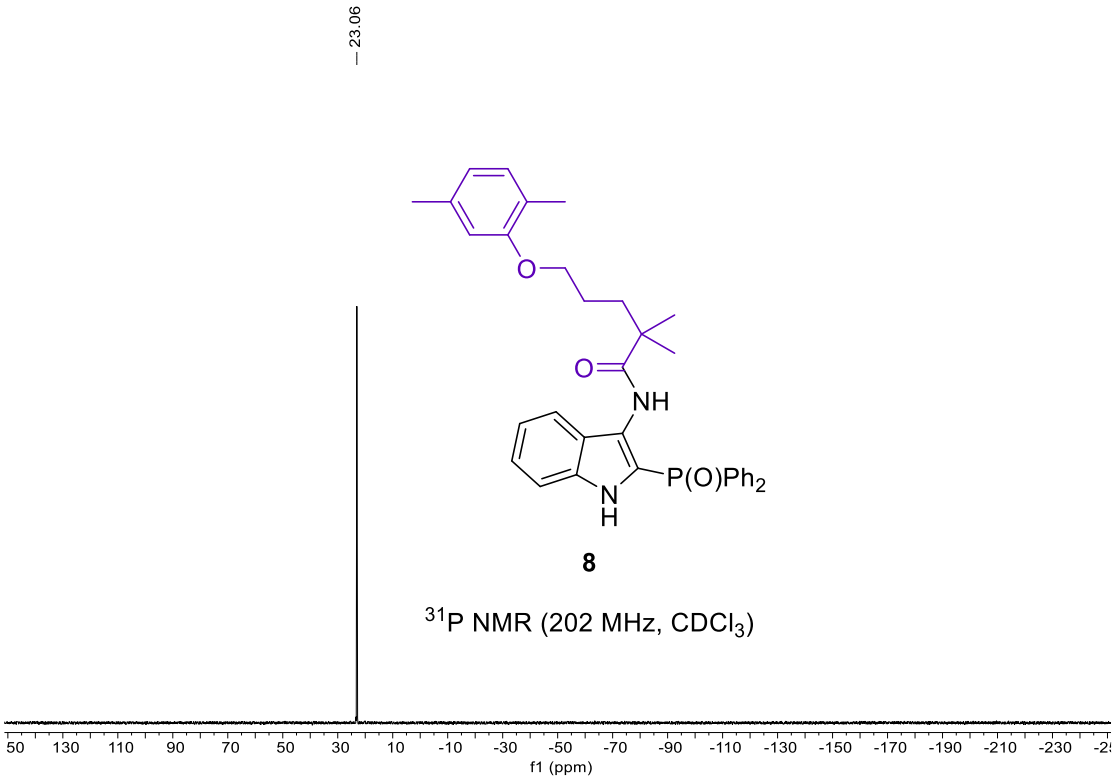

8.124
7.723
7.716
7.709
7.706
7.699
7.697
7.683
7.680
7.559
7.556
7.544
7.541
7.532
7.529
7.526
7.458
7.453
7.443
7.437
7.428
7.422
7.253
7.239
7.225
7.222
7.212
7.195
7.083
7.079
7.071
7.067
7.062
7.054
7.051
4.969
3.559
3.546
3.533
3.480
3.468
3.456
-0.000
NHCH2CH2Cl
P(O)Ph2
N
H
7
1H NMR (500 MHz, CDCl3)
0.91
5.01
2.03
4.05
2.12
1.00
0.80
2.00
2.02
f1 (ppm)

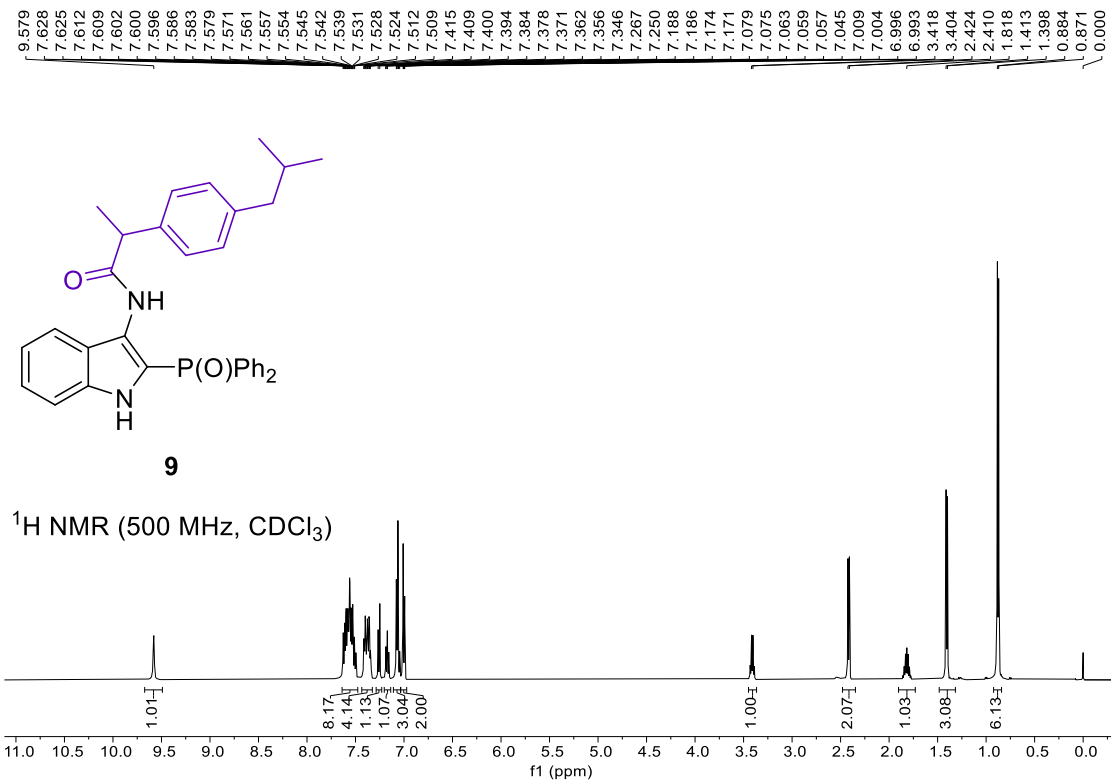

138.33
138.26
137.83
133.02
132.52
132.49
132.16
131.87
131.78
128.98
128.88
125.21
121.92
121.84
120.55
119.58
112.35
110.26
109.24
77.41
77.16
76.90
49.76
44.10
NHCH2CH2Cl
P(O)Ph2
N
H
7
13C NMR (125 MHz, CDCl3)
f1 (ppm)

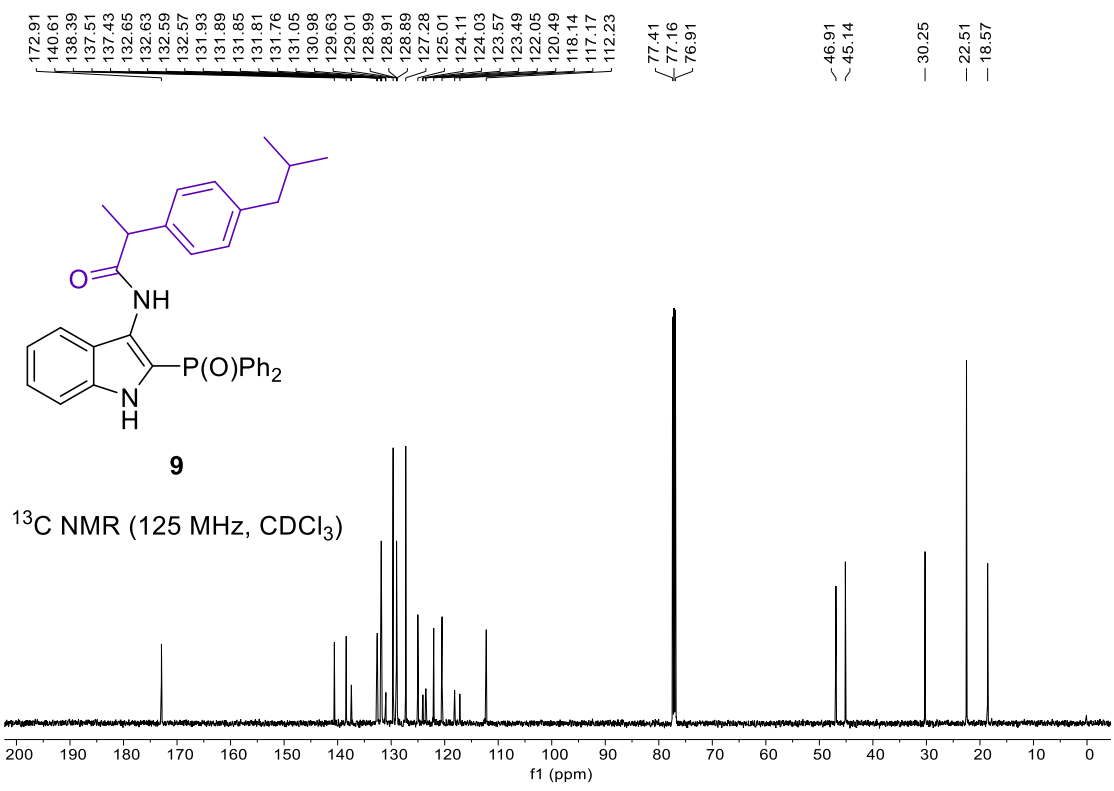

22.62
NHCH2CH2Cl
P(O)Ph2
N
H
7
31P NMR (202 MHz, CDCl3)
f1 (ppm)

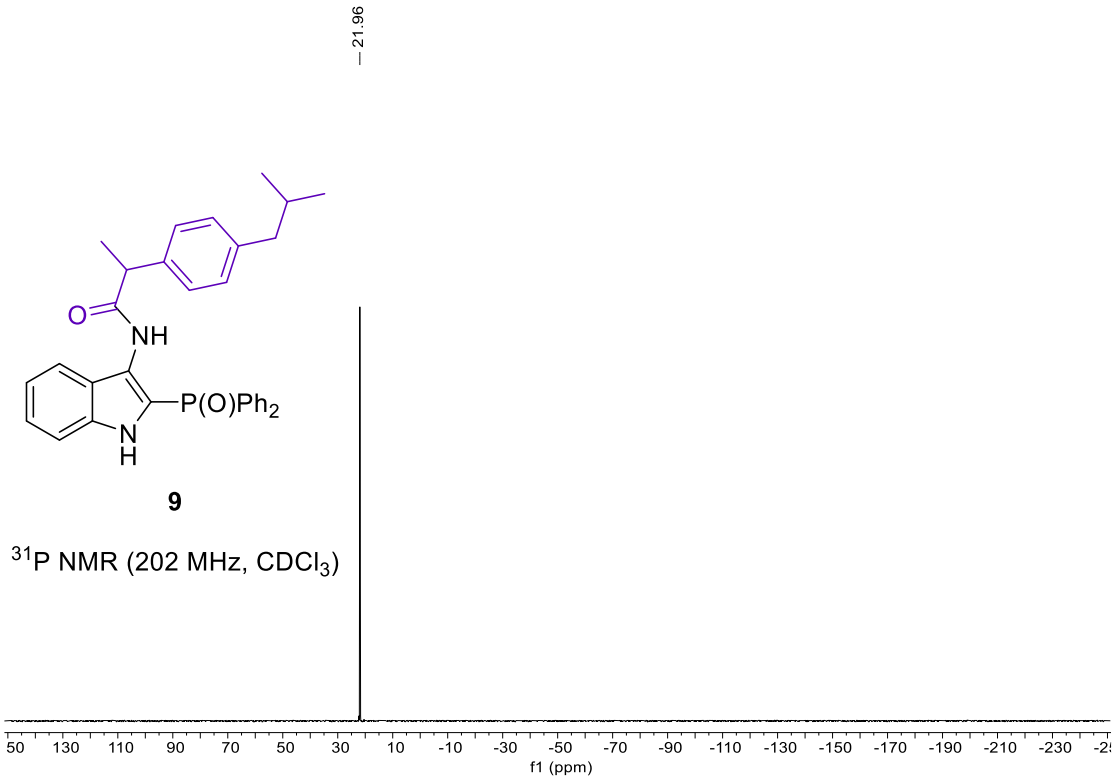

8.761
8.364
7.880
7.863
7.709
7.706
7.693
7.690
7.683
7.681
7.667
7.664
7.553
7.550
7.538
7.535
7.526
7.523
7.520
7.517
7.459
7.454
7.444
7.438
7.429
7.423
7.250
7.247
7.244
7.234
7.232
7.140
7.136
7.128
7.124
7.119
7.107
6.991
6.976
6.650
6.647
6.635
6.632
6.549
3.788
3.777
3.766
2.289
2.132
1.710
1.699
1.693
1.690
1.683
1.679
1.673
1.666
1.196
-0.000
O
O
NH
N
H
P(O)Ph2
8
1H NMR (500 MHz, CDCl3)
1.00
1.01
1.00
4.00
2.01
4.01
2.36
1.01
1.00
1.00
1.00
2.08
3.10
3.08
4.13
6.29
f1 (ppm)


176.02
157.07
137.70
137.62
136.50
132.91
132.88
131.90
131.81
131.73
131.03
130.32
129.19
129.09
127.34
127.27
125.39
123.63
123.05
122.98
120.65
120.62
115.64
114.66
112.00
111.83
77.41
77.16
76.91
68.00
42.54
37.77
25.59
25.29
21.53
15.94
0.12
O
O
NH
N
H
P(O)Ph2
8
13C NMR (125 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


23.06
O
O
NH
N
H
P(O)Ph2
8
31P NMR (202 MHz, CDCl3)
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

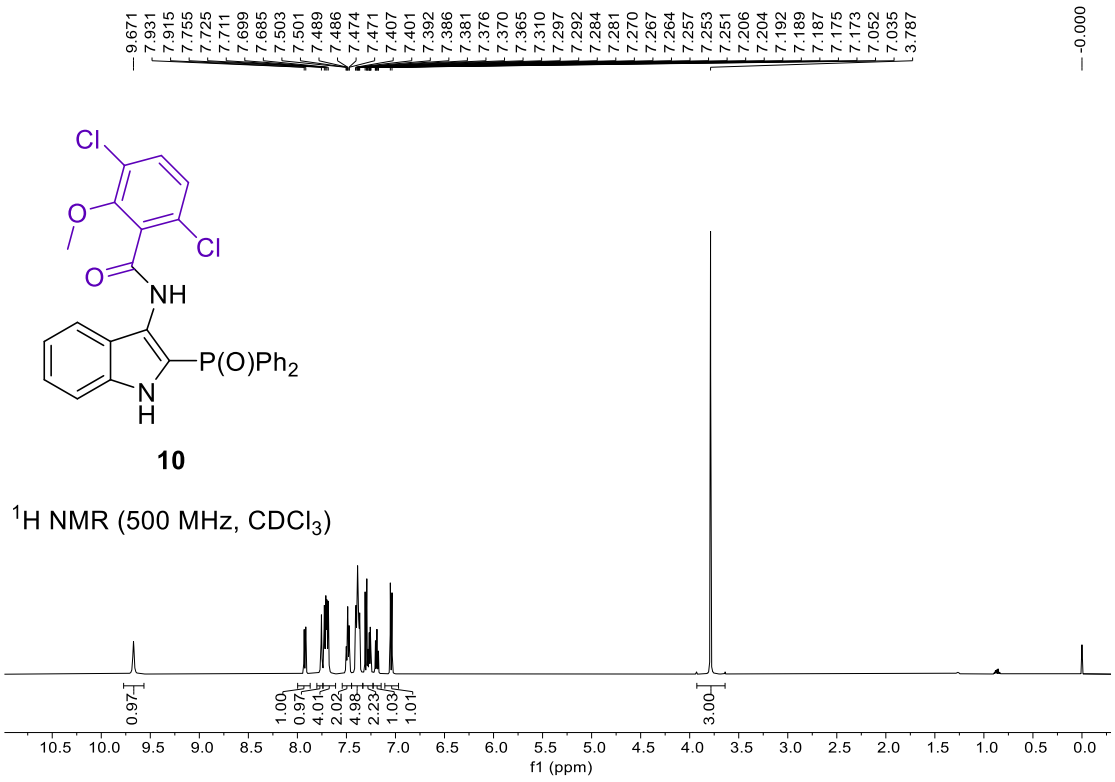

9.579
7.628
7.625
7.612
7.609
7.602
7.600
7.596
7.586
7.583
7.579
7.571
7.561
7.557
7.554
7.545
7.542
7.539
7.531
7.528
7.524
7.512
7.509
7.415
7.409
7.400
7.394
7.384
7.378
7.371
7.362
7.356
7.346
7.267
7.250
7.188
7.186
7.174
7.171
7.079
7.075
7.063
7.059
7.057
7.045
7.009
7.004
6.996
6.993
3.418
3.404
2.424
2.410
1.818
1.413
1.398
0.884
0.871
0.000
O
NH
P(O)Ph2
N
H
9
1H NMR (500 MHz, CDCl3)
1.01
8.17
4.14
1.13
1.07
3.04
2.00
1.00
2.07
1.03
3.08
6.13
11.0 10.5 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
f1 (ppm)


172.91
140.61
138.39
137.51
137.43
132.65
132.63
132.59
132.57
131.93
131.89
131.85
131.81
131.76
131.05
130.98
129.63
129.01
128.99
128.91
128.89
127.28
125.01
124.11
124.03
123.57
123.49
122.05
120.49
118.14
117.17
112.23
77.41
77.16
76.91
46.91
45.14
30.25
22.51
18.57
O
NH
P(O)Ph2
N
H
9
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



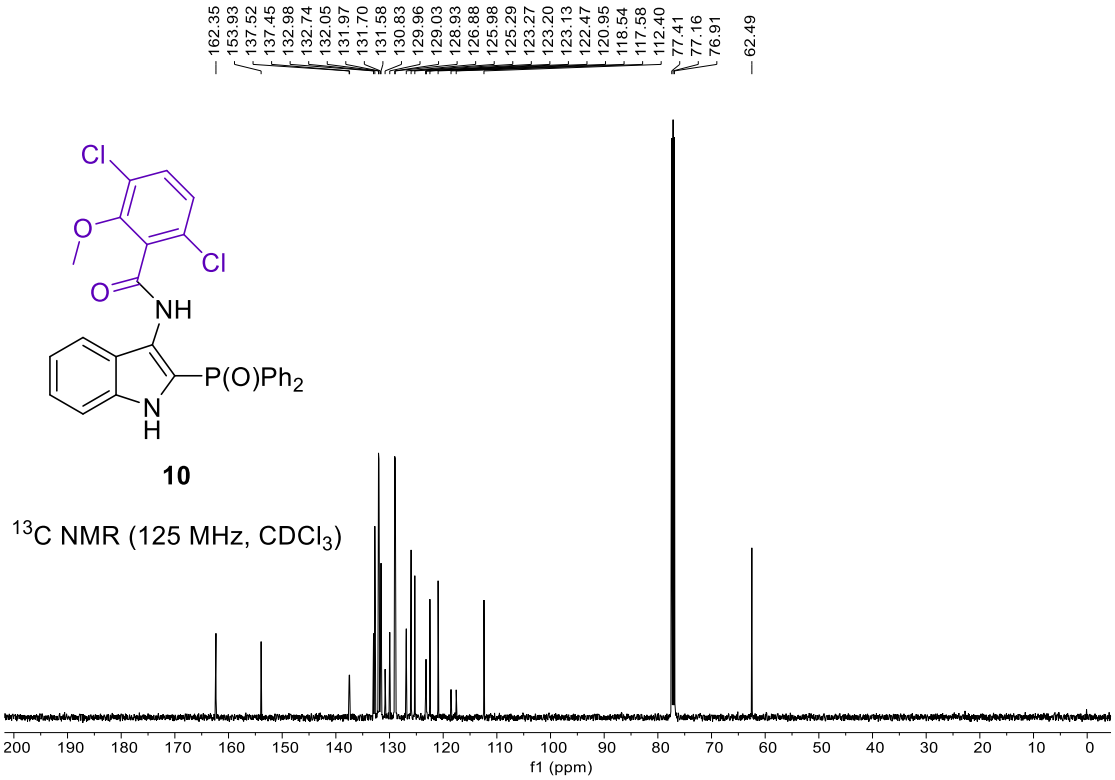
9

^{31}P NMR (202 MHz, $CDCl_3$)



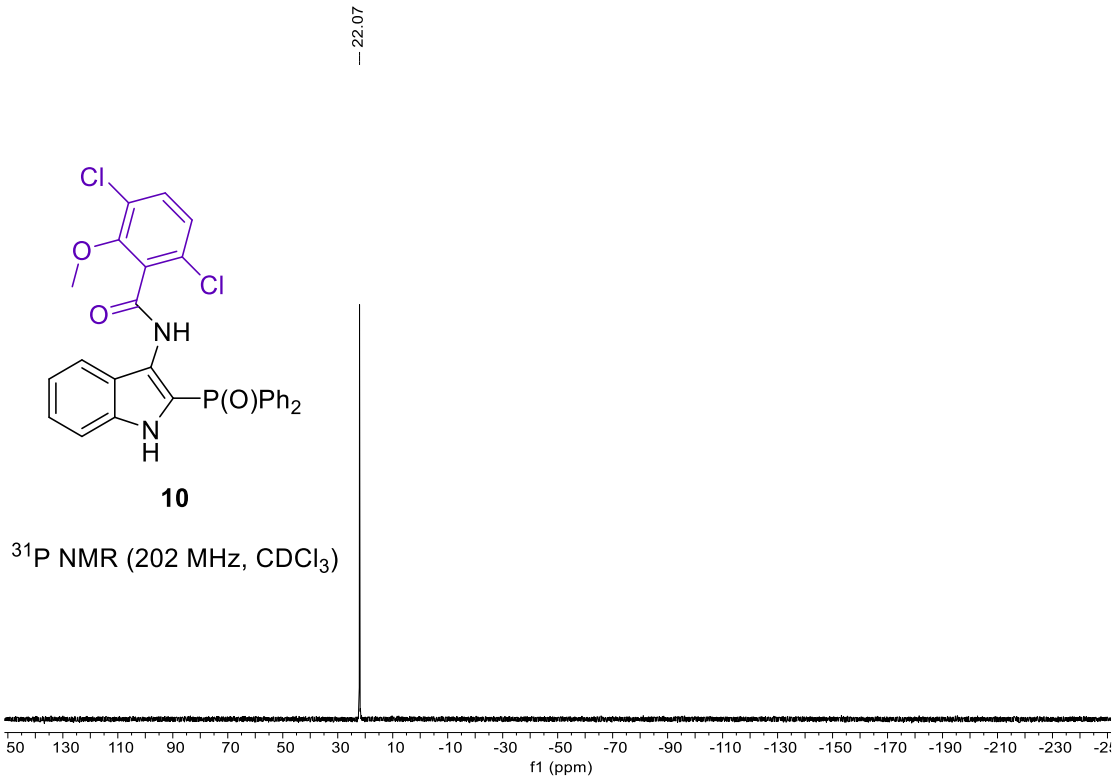
10

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



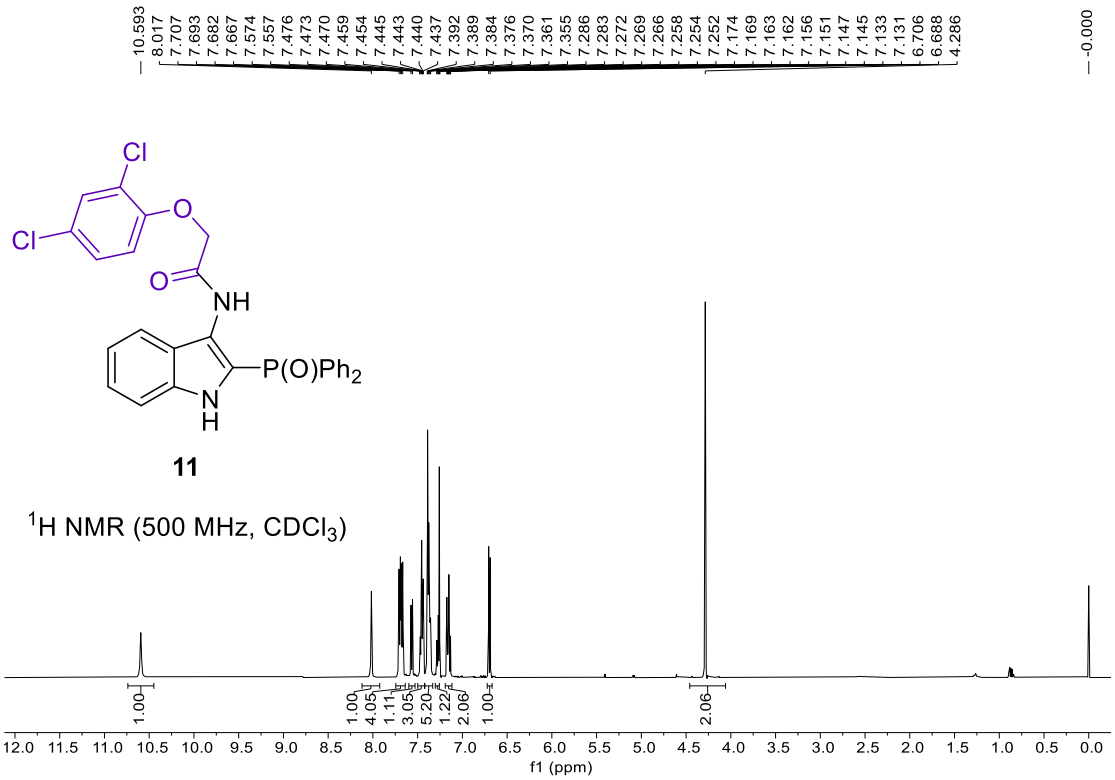
10

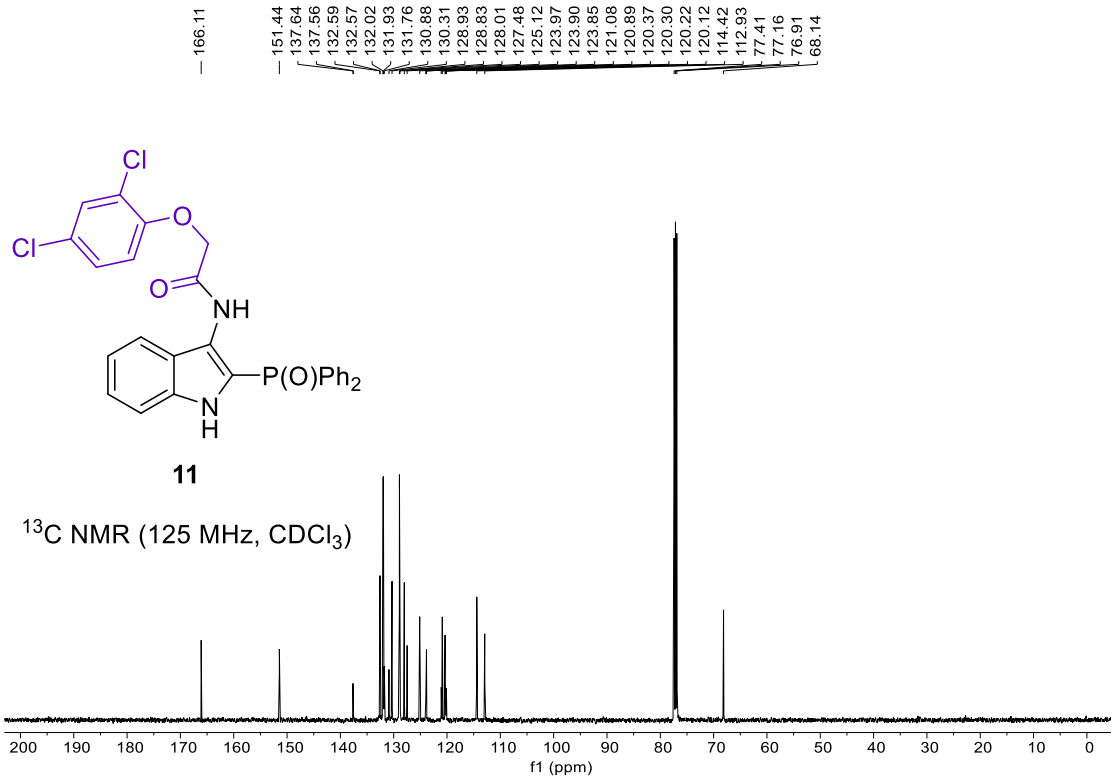
^{13}C NMR (125 MHz, $CDCl_3$)

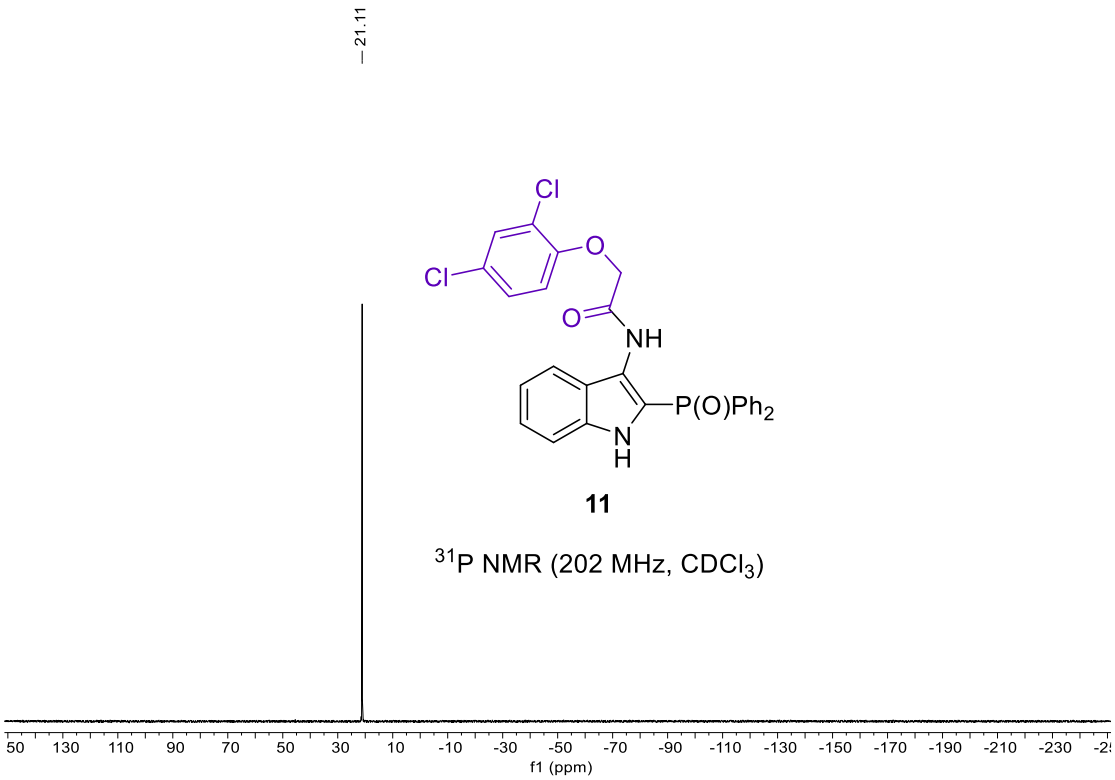


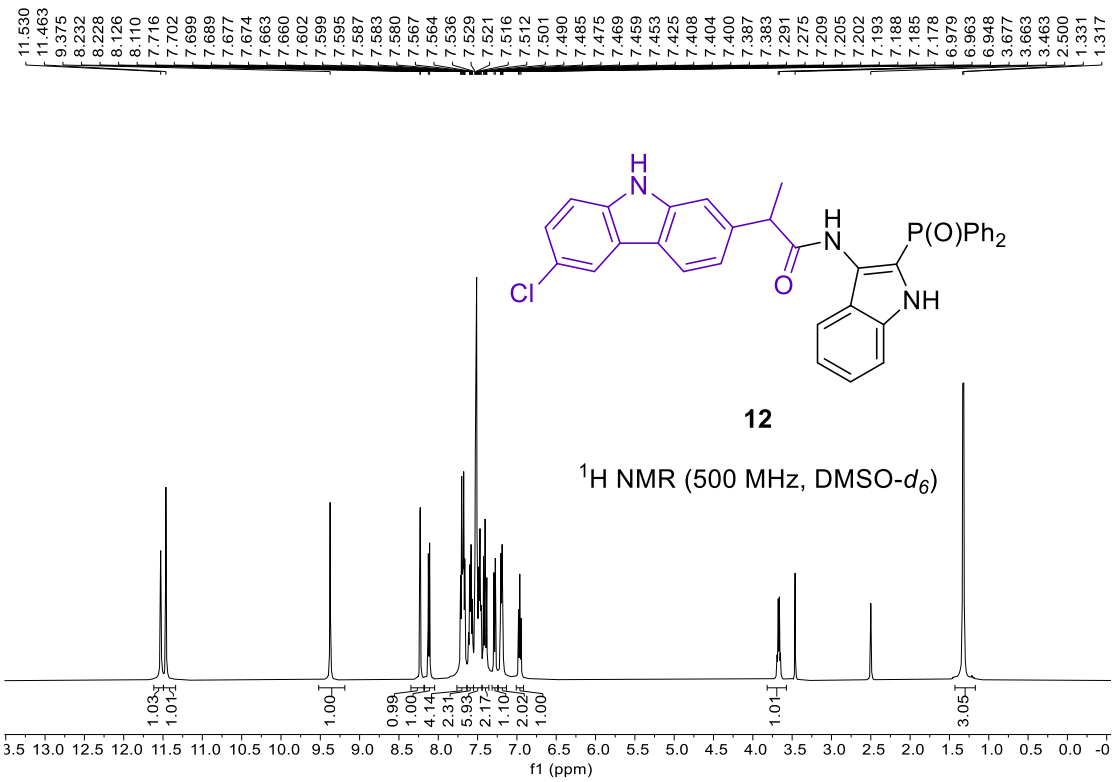
10

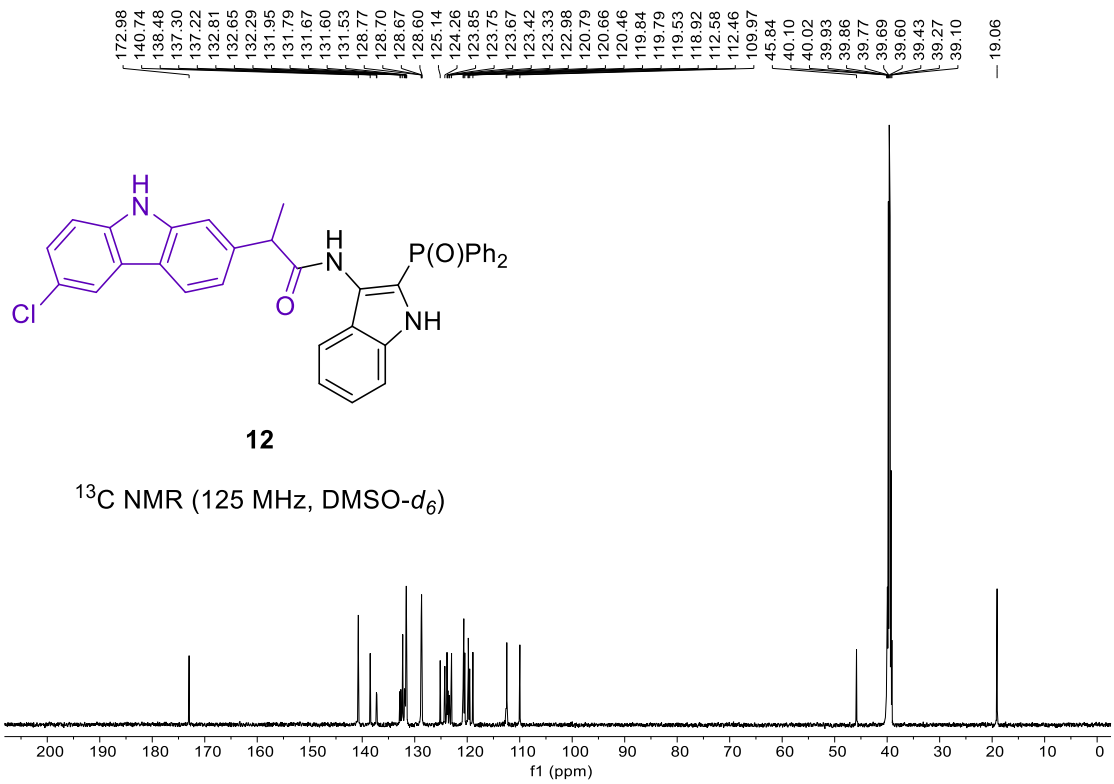
^{31}P NMR (202 MHz, $CDCl_3$)


10.593
8.017
7.707
7.693
7.682
7.667
7.574
7.557
7.476
7.473
7.470
7.459
7.454
7.445
7.443
7.440
7.437
7.392
7.389
7.384
7.376
7.370
7.361
7.355
7.286
7.283
7.272
7.269
7.266
7.258
7.254
7.252
7.174
7.169
7.163
7.162
7.156
7.151
7.147
7.145
7.133
7.131
6.706
6.688
4.286
-0.000
Cl
Cl
O
O
NH
P(O)Ph2
N
H
11
1H NMR (500 MHz, CDCl3)
1.00
1.00
4.05
1.11
3.05
5.20
1.22
2.06
1.00
2.06
12.0 11.5 11.0 10.5 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
f1 (ppm)


166.11
151.44
137.64
137.56
132.59
132.57
132.02
131.93
131.76
130.88
130.31
128.93
128.83
128.01
127.48
125.12
123.97
123.90
123.85
121.08
120.89
120.37
120.30
120.22
120.12
114.42
112.93
77.41
77.16
76.91
68.14
Cl
Cl
O
O
NH
P(O)Ph2
N
H
11
13C NMR (125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

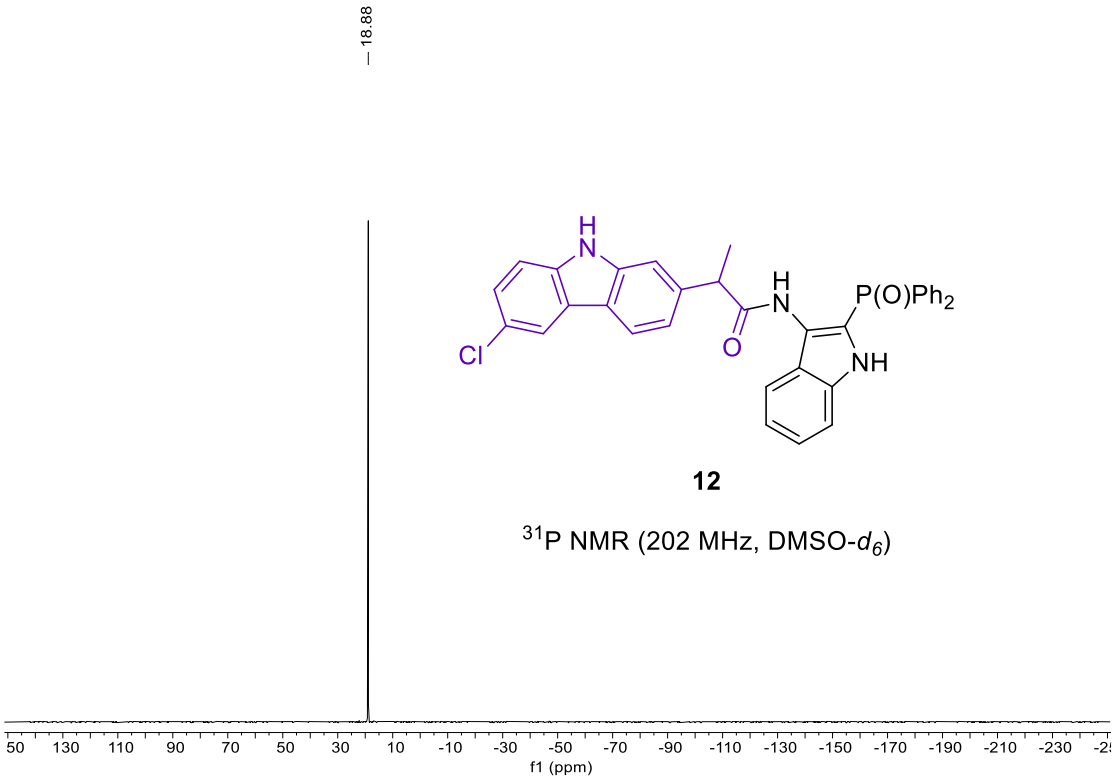

21.11
Cl
Cl
O
O
NH
P(O)Ph2
N
H
11
31P NMR (202 MHz, CDCl3)
f1 (ppm)


11.530
11.463
9.375
8.232
8.228
8.126
8.110
7.716
7.702
7.699
7.689
7.677
7.674
7.663
7.660
7.602
7.599
7.595
7.587
7.583
7.580
7.567
7.564
7.536
7.529
7.521
7.516
7.512
7.501
7.490
7.485
7.475
7.469
7.459
7.453
7.425
7.408
7.404
7.400
7.387
7.383
7.291
7.275
7.209
7.205
7.202
7.193
7.188
7.185
7.178
6.979
6.963
6.948
3.677
3.663
3.463
2.500
1.331
1.317
H
N
Cl
O
H
N
P(O)Ph2
NH
12
1H NMR (500 MHz, DMSO-d6)
1.03
1.01
1.00
0.99
1.00
4.14
2.31
5.93
2.17
1.10
2.02
1.00
1.01
3.05
f1 (ppm)



12

^{13}C NMR (125 MHz, DMSO-d_6)



12

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

10. References

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