Supporting Information

Cu/Pd cooperatively catalyzed tandem C−N and C-P bond formation: access to phosphorated 2*H*-indazoles

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Contents

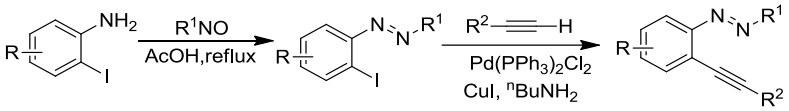
1. General Information

Reagents and Solvents: All solvents were purified and dried according to standard methods. PE refers to petroleum ether (b.p. 60–90 ℃) and EA refers to ethyl acetate. 2-Alkynyl azobenzenes derivatives were synthesized following the literature procedure.[1,2,3] P(O)H compounds **2b-2f, 2i, 2l** were commercially available and were used without further purification, and the other P(O)H compounds were synthesized following the literature procedure.[4,5]

Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they are listed as volume/volume ratios.

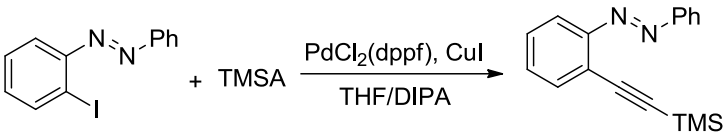
Data collection: ^{1}H and ^{13}C NMR spectra were collected on BRUKER AV-300 (300 MHz) spectrometer using $CDCl_3$ as solvent. Chemical shifts of ^{1}H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard ($CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$: δ = 77.0 ppm). High Resolution Mass measurement was performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m.p.) was measured on a microscopic melting point apparatus. Infrared spectra (IR) were recorded on a Thermo Scientific iS10 FT/IR spectrometer using a thin film supported on KBr disks. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}.

2. General procedure for preparation of 2-alkynyl azobenzenes

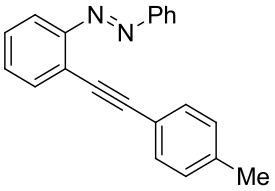


Substituted nitrosobenzene (1.0 equiv) was added to the substituted iodinated aniline (1.0 equiv) dissolved in AcOH (0.1 M). The solution was heated to 85 °C for 40 h. The resulting mixture was cooled to room temperature, diluted with DCM, and washed with brine and H_2O. The organic layer was dried through anhydrous Na_2SO_4, filtered over Celite, and concentrated in vacuo. Column chromatography on silica gel gave the corresponding 2-iodoazobenzenes. Then 2-iodoazobenzene (1.0 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (28.1 mg, 0.04 mmol, 0.04 equiv), CuI (15.2 mg, 0.08 mmol, 0.08 equiv) and $^nBuNH_2$ (497 μL, 6.0 mmol, 6.0 equiv) were dissolved in anhydrous THF (0.1 M) under Ar. To the resulting solution terminal alkyne (1.2 mmol, 1.2 equiv) was added dropwise. The mixture was stirred at room temperature. After the reaction was completed (detected by TLC) (2-7 h), saturated NH_4Cl aqueous solution was added. The organic layer was separated, and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel.

1l were synthesized according to the following procedure [1]:



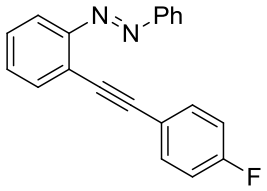
The 2-iodoazobenzene (1.0 equiv), $PdCl_2(dppf)$ (0.05 equiv), CuI (0.1 equiv), and (trimethylsilyl)acetylene (1.4 equiv) were dissolved in an amine base (0.1 M solution based on diazene). The mixture was immediately degassed by three successive freeze-pump-thaw cycles, and the flask was charged with Ar. The mixture was heated to 50 ℃ and stirred under Ar overnight. After cooling, the mixture was filtered over a short pad of silica (CH_2Cl_2) and concentrated in vacuo. Column chromatography on silica gel gave the desired product **1l**.



1-phenyl-2-(2-(p-tolylethynyl)phenyl)diazene (1c)

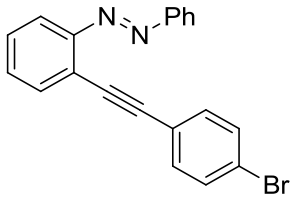
51% yield (151.1 mg); red solid; m. p. 56-58 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.0 Hz, 2H), 7.80-7.63 (m, 2H), 7.58-7.43 (m, 5H), 7.42-7.32 (m, 2H), 7.07 (d,

J = 7.8 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 152.9, 138.7, 133.3, 131.6, 131.3, 130.5, 129.2, 129.1, 128.7, 124.0, 123.3, 120.4, 116.2, 96.0, 86.3, 21.6. IR (KBr): $\tilde{\nu}$ =3128, 2218, 1400, 812, 772, 739, 680, 506 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{16}N_2+H]^+$ 297.1386, found 297.1389.



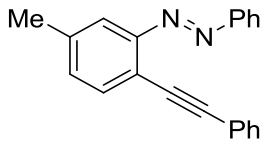
1-(2-((4-fluorophenyl)ethynyl)phenyl)-2-phenyldiazene（1e）

54% yield (162.0 mg); red solid; m. p. 65-67 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94-7.85 (m, 2H), 7.67-7.59 (m, 1H), 7.58-7.52 (m, 1H), 7.48-7.34 (m, 5H), 7.31-7.24 (m, 2H), 6.97-6.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 161.0, 153.1, 152.9, 133.6 (d, J = 8.4 Hz), 133.3, 131.4, 130.6, 129.2, 129.0, 123.3, 116.3, 115.9, 115.6, 94.6, 86.6. IR (KBr): $\tilde{\nu}$ =3127, 2360, 2336, 1400, 830,748, 686, 553 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{16}N_2+H]^+$ 301.1136, found 301.1138.



1-(2-((4-bromophenyl)ethynyl)phenyl)-2-phenyldiazene (1g)

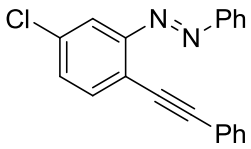
60% yield (216.2 mg); red solid; m. p. 61-63 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.80-7.60 (m, 2H), 7.56-7.45 (m, 5H), 7.44-7.28 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 152.9, 133.3, 133.0, 131.8, 131.7, 131.4, 130.5, 129.1, 123.3, 123.3, 122.7, 122.4, 116.3, 94.5, 88.0. IR (KBr): $\tilde{\nu}$ =3128, 2360, 2348, 1400, 818, 765,739, 683 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{16}N_2+H]^+$ 361.0335, found 361.0330.



1-(5-methyl-2-(phenylethynyl)phenyl)-2-phenyldiazene(1q)

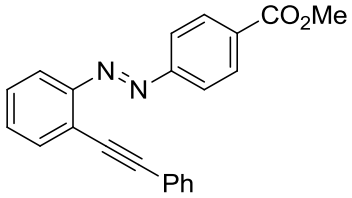
62% yield (183.5 mg); red solid; m. p. 50-52 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.56-7.38 (m, 4H), 7.38-7.25 (m, 3H), 7.18 (m, 3H), 7.07 (d, *J* = 8.2 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 139.4, 133.2, 131.7, 131.6, 131.3, 129.2, 129.0, 128.4, 128.4, 123.8, 123.3, 121.1, 116.6, 95.1, 87.2, 21.6.

IR (KBr): $\tilde{\nu}$ = 3133, 1400,863, 804,689 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{16}N_2+H]^+$ 297.1386, found 297.1391.



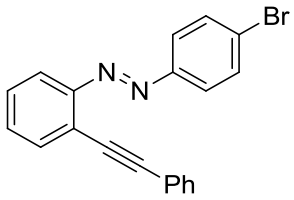
1-(5-chloro-2-(phenylethynyl)phenyl)-2-phenyldiazene(1r)

58% yield (183.3 mg); red solid; m. p. 60-62°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10-7.91 (m, 2H), 7.75 (d, *J* = 2.2 Hz, 1H), 7.66-7.55 (m, 3H), 7.53 (d, *J* = 6.7 Hz, 3H), 7.44-7.23 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 152.6, 135.1, 134.2, 131.8, 131.7, 130.4, 129.2, 128.6, 128.4, 123.4, 122.4, 116.5, 109.0, 96.6, 85.8. IR (KBr): $\tilde{\nu}$ = 3133, 2360, 2342, 1400, 854, 824, 754, 683 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{13}ClN_2+H]^+$ 317.0840, found 317.0843.



methyl 4-((2-(phenylethynyl)phenyl)diazenyl)benzoate(1s)

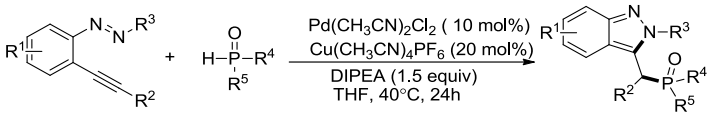
64% yield (217.6 mg); red solid; m. p. 92-94 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14-7.97 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.66-7.49 (m, 2H), 7.51-7.35 (m, 2H), 7.24 (m, 5H), 3.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 155.3, 152.8, 133.4, 132.0, 131.7, 131.3, 130.6, 128.9, 128.6, 128.5, 124.6, 123.3, 123.0, 116.1, 96.2, 86.8, 52.3. IR (KBr): $\tilde{\nu}$ =3132, 1724, 1714, 1493, 1435, 1402, 1278, 877, 777,761, 691, 512 cm^{-1} HRMS (ESI) calcd for $[C_{22}H_{16}N_2O_2+H]^+$ 341.1285, found 341.1289.



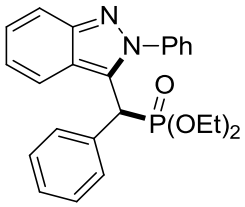
1-(4-bromophenyl)-2-(2-(phenylethynyl)phenyl)diazene(1t)

72% yield (259.2 mg); red solid; m. p. 81-83 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 2H), 7.76-7.61 (m, 2H), 7.67-7.60 (m, 2H), 7.60-7.52 (m, 2H), 7.47-7.38 (m, 2H), 7.37-7.30 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 151.6, 133.4, 132.4, 131.6, 130.9, 128.9, 128.6, 128.4, 125.8, 124.7, 124.0, 123.4, 116.1, 95.9, 86.8. IR (KBr): $\tilde{\nu}$ =3128, 2216, 1571, 1400, 1008, 837, 754, 686, 510 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{13}BrN_2+H]^+$ 361.0335, found 361.0336.

3. General procedure for synthesis and characterization of compounds

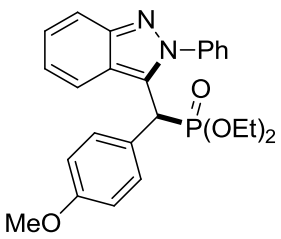


To a solution of the 2-alkynyl azobenzenes (0.2 mmol, 1.0 equiv), $Pd(CH_3CN)_2Cl_2$ (5.18mg, 0.02mmol, 10 mol%), $Cu(CH_3CN)_4PF_6$ (14.8mg, 0.04mmol, 20 mol%) and DIPEA (0.3 mmol, 1.5 equiv) in 2.0 mL anhydrous THF, the appropriate P(O)H compounds (0.24 mmol, 1.2 equiv) was added under Ar and the resulting mixture was stirred at 40 ^oC for 24 h. After the reaction was completed (detected by TLC), the solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the pure product (PE:EA= 2:1).



diethyl (phenyl(2-phenyl-2*H*-indazol-3-yl)methyl)phosphonate(3aa)

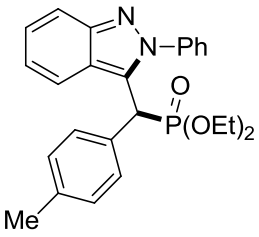
94% yield (80.1 mg); colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.7, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.57-7.48 (m, 3H), 7.46-7.38 (m, 4H), 7.37-7.23 (m, 4H), 7.19 (dd, *J* = 8.6, 6.6 Hz, 1H), 4.94 (d, *J* = 28.3 Hz, 1H), 4.02-3.65 (m, 4H), 1.09 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9 (d, *J* = 2.1 Hz), 139.3, 134.1 (d, *J* = 5.1 Hz), 130.5, 129.6, 129.3, 129.2 (d, *J* = 6.3 Hz), 128.8 (d, *J* = 2.1 Hz), 127.6 (d, *J* = 2.7 Hz), 126.8, 126.7, 122.8 (d, *J* = 1.3 Hz), 122.3, 121.2 (d, *J* = 3.0 Hz), 117.6, 63.3 (d, *J* = 7.1 Hz), 63.0 (d, *J* = 7.1 Hz), 43.9 (d, *J* = 143.2 Hz), 16.3 (d, *J* = 2.3 Hz), 16.2 (d, *J* = 2.3 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz): δ 22.1. IR (KBr): $\tilde{\nu}$ =3128, 1596, 1498, 1400, 1245, 1056, 1026, 759, 698 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{25}N_2O_3P+H]^+$ 421.1676, found 421.1681.



diethyl (phenyl(2-phenyl-2*H*-indazol-3-yl)methyl)phosphonate(3ba)

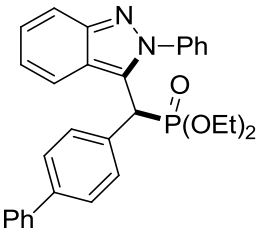
68% yield (61.2 mg); yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.52 (m, 3H), 7.39 (m, 2H), 7.36-7.25 (m, 3H), 7.18 (dd,

J = 8.6, 6.6 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.87 (d, *J* = 28.2 Hz, 1H), 4.03-3.62 (m, 7H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 148.9, 139.4, 130.8, 130.3, 130.3, 129.5, 129.3, 126.8, 126.7, 126.0, 122.8, 122.2, 121.1, 117.6, 114.2 (d, *J* = 1.9 Hz), 63.3 (d, *J* = 7.1 Hz), 63.0 (d, *J* = 7,1 Hz), 55.2, 43.0 (d, *J* = 143 Hz), 16.3 (t, *J* = 5.1 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 22.4. IR (KBr): $\tilde{\nu}$ =3134, 2360, 1508, 1400, 1252, 1051, 1026, 972, 674, 544 cm^{-1}. HRMS (ESI) calcd for $[C_{25}H_{27}N_2O_4P+H]^+$ 451.1781, found 451.1785.



diethyl ((2-phenyl-2*H*-indazol-3-yl)(p-tolyl)methyl)phosphonate(3ca)

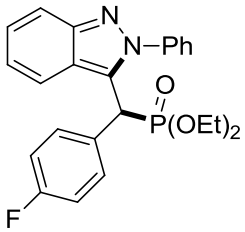
76% yield (66.0 mg); yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45(m, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.51 (m, 3H), 7.45-7.37 (m, 2H), 7.37-7.26 (m, 3H), 7.18 (dd, *J* = 8.7, 6.6 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 4.90 (d, *J* = 28.3 Hz, 1H), 4.03-3.62 (m, 4H), 2.29 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 139.4, 137.3 (d, *J* = 2.9 Hz), 131.0 (d, *J* = 5.0 Hz), 130.7, 129.5, 129.5, 129.3, 129.0 (d, *J* = 6.3 Hz), 126.8, 126.7, 122.9 (d, *J* = 1.4 Hz), 122.2, 121.2, (d, *J* = 2.9 Hz), 117.6, 63.1 (d, *J* = 7.1 Hz) , 63.0 (d, *J* =7,1 Hz), 43.5 (d, *J* = 143 Hz), 21.0, 16.3 (d, *J* = 4.2 Hz), 16.2 (d, *J* = 4.4 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 22.3. IR (KBr): $\tilde{\nu}$ =3132, 1641, 1400, 1257, 1163, 1057, 853, 539 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{27}N_2O_3P+H]^+$ 435.1832, found 435.1384.



diethyl ([1,1'-biphenyl]-4-yl(2-phenyl-2*H*-indazol-3-yl)methyl)phosphonate(3da)

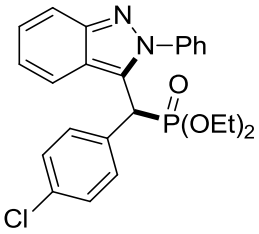
85% yield (84.2 mg); white solid; m. p. 57-59 ^{o}C;^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.61-7.47 (m, 9H), 7.47-7.41 (m, 2H), 7.42-7.13 (m, 5H), 5.00 (d, *J* = 28.3 Hz, 1H), 4.07-3.67 (m, 4H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$)) δ 149.0 (d, *J* = 2.2 Hz), 140.4 (d, *J* = 2.9 Hz), 140.3, 139.4, 133.2 (d, *J* = 5.1 Hz), 130.4, 129.6, 129.6 (d, *J* = 2.9 Hz), 129.4, 128.8, 127.5, 127.4, 127.0, 126.8, 126.7, 122.8, 122.3, 121.2 (d, *J* = 2.9

Hz), 118, 63.3 (d, *J* = 7.1 Hz), 63.0 (d, *J* = 7.1 Hz), 43.7 (d, *J* = 143.1 Hz), 16.3(d, *J* = 4.6 Hz), 16.2 (d, *J* = 4.1 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 22.0. IR(KBr): $\tilde{\nu}$ =3128, 1599, 1400, 1253, 1160, 1049, 1022, 966, 767, 697, 562 cm^{-1}; HRMS (ESI) calcd for $[C_{30}H_{29}N_2O_3P+H]^+$ 497.1989, found 497.1993.



diethyl ((4-fluorophenyl)(2-phenyl-2*H*-indazol-3-yl)methyl)phosphonate(3ea)

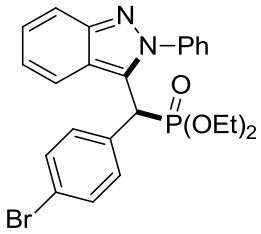
77% yield (67.5 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.6 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.53 (m, 3H), 7.45-7.25 (m, 5H), 7.19 (dd, *J* = 8.7, 6.6 Hz, 1H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.90 (d, *J* = 28.3 Hz, 1H), 4.07-3.63 (m, 4H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1 (d, *J* = 247.6 Hz), 149.0, 139.3, 130.8 (dd, *J* = 8.1, 6.2 Hz), 130.2, 130.1(m), 129.6, 129.4, 126.8, 122.5, 122.4, 121.0 (d, *J* = 2.8 Hz), 117.7, 115.9 (d, *J* = 2.1 Hz), 115.6 (d, *J* = 2.1 Hz), 63.37 (d, *J* = 7.1 Hz), 62.97 (d, *J* = 7.2 Hz), 43.1 (d, *J* = 144.2 Hz),16.3 (d, *J* = 3.8 Hz), 16.2 (d, *J* = 3.8 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.8, 21.8. IR (KBr): $\tilde{\nu}$ =3127, 1400, 1254, 1160, 1048, 1025, 969, 748, 571 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{24}FN_2O_3P+H]^+$ 439.1581, found 439.1584.



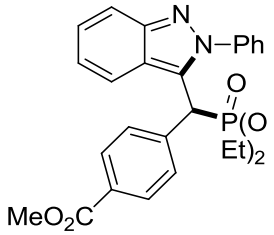
diethyl ((4-chlorophenyl)(2-phenyl-2*H*-indazol-3-yl)methyl)phosphonate(3fa)

73% yield (66.3 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.6 Hz, 1H), 8.08-7.97 (m, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.52 (m, 3H), 7.47-7.38 (m, 2H), 7.35 (m, 1H), 7.29-7.12 (m, 4H), 5.59 (d, *J* = 27.6 Hz, 1H), 4.14-3.69 (m, 4H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 139.6, 133.8 (d, *J* = 9.0 Hz), 132.4 (d, *J* = 3.9 Hz), 132.0 (d, *J* = 4.4 Hz), 130.3, 129.6 (d, *J* = 1.8 Hz), 129.4 (d, *J* = 5.7 Hz), 128.90 (d, *J* = 2.6 Hz), 127.2 (d, *J* = 2.7 Hz), 127.0, 126.5, 122.6 (d, *J* = 10.3 Hz), 121.3 (d, *J* = 2.6 Hz), 117.8, 63.3, 63.2, 39.8 (d, *J* = 146 Hz), 16.2, 16.1. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.7. IR (KBr): $\tilde{\nu}$ =3133, 2360, 2336, 1400, 1253, 1065, 1045, 1022, 969, 750, 692, 553 cm^{-1}; HRMS (ESI) calcd for

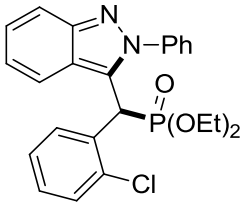
$[C_{24}H_{24}ClN_2O_3P+H]^+$ 455.1286, found 455.1293.



diethyl ((4-bromophenyl)(2-phenyl-2*H*-indazol-3-yl)methyl)phosphonate(3ga)
86% yield (85.7 mg); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.5 Hz,1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.59-7.47 (m, 3H), 7.46-7.31 (m, 5H), 7.32-7.24 (m, 2H), 7.19 (m, 1H), 4.88 (d, *J* = 28.4 Hz, 1H), 4.01-3.56 (m, 4H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 139.2, 133.28 (d, *J* = 5.1 Hz), 131.93 (d, *J* = 2.1 Hz), 130.79 (d, *J* = 6.2 Hz), 129.8, 129.7, 129.4, 126.8, 126.7, 122.5, 122.4, 121.84 (d, *J* = 3.5 Hz), 121.08 (d, *J* = 2.8 Hz), 117.8, 63.5(d, *J* = 7.1 Hz), 63.0 (d, *J* = 7.1 Hz), 43.3(d, *J* = 144 Hz), 16.3 (t, *J* = 5.4 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.4. IR (KBr): $\tilde{\nu}$ =3133, 2354, 2336, 1400, 1252, 1022, 966, 742,553 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{24}BrN_2O_3P+H]^+$ 499.0781, found 497.0788.

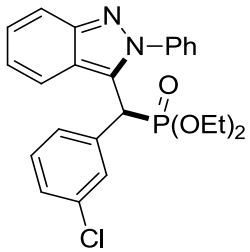


methyl 4-((diethoxyphosphoryl)(2-phenyl-*2H*-indazol-3-yl)methyl)benzoate(3ha)
78% yield (74.6 mg); yellow solid; m. p. 166-168 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.7 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.48-7.39 (m, 5H), 7.33-7.19 (m, 3H), 7.12 (dd, *J* = 8.7, 6.6 Hz, 1H), 4.90 (d, *J* = 28.6 Hz, 1H), 3.95-3.58 (m, 7H), 1.03 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 149.0 (d, *J* = 2.3 Hz), 139.3 (d, *J* = 5.0 Hz), 139.2, 130.0 (d, *J* = 2.1 Hz), 129.7, 129.6, 129.4, 129.2, 129.2, 126.8, 126.7, 122.6, 122.4, 121.2 (d, *J* = 2.9 Hz), 117.8, 63.5 (d, *J* =7.1 Hz), 63.1 (d, *J* =7.1 Hz), 52.2, 44. 0 (d, *J* =143 Hz), 16.3 (d, *J* =3.5 Hz), 16.2 (d, *J* =3.4 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.1. IR (KBr): $\tilde{\nu}$ =3127, 1716, 1400, 1282, 1253, 1017, 745, 701, 559 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{27}N_2O_5P+H]^+$ 479.1730, found 479.1731.



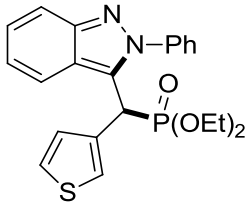
diethyl ((2-chlorophenyl)(2-phenyl-*2H*-indazol-3-yl)methyl)phosphonate(3ia)

62% yield (56.3 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.5 Hz, 1H), 8.07-8.00 (m, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.60-7.47 (m, 3H), 7.48-7.39 (m, 2H), 7.38-7.32 (m, 1H), 7.30-7.09 (m, 4H), 5.61 (d, *J* = 27.6 Hz, 1H), 4.12-3.74 (m, 4H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 139.6, 132.4, 132.0, 132.0, 130.3, 129.6 (d, *J* =1.7 Hz), 129.4, 129.3, 128.9 (d, *J* =2.7 Hz), 127.2 (d, *J* =2.7 Hz), 127.0, 126.5, 122.6, 122.5, 121.2, 117.8, 63.3, 63.2, 39.8 (d, *J* =145.7 Hz), 16.2, 16.1. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.7. IR (KBr): $\tilde{\nu}$ =3128, 2363, 1400, 1257, 1024, 967, 743, 551 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{24}ClN_2O_3P+H]^+$ 455.1286, found 455.1287.



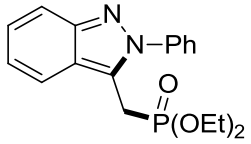
diethyl ((3-chlorophenyl)(2-phenyl-*2H*-indazol-3-yl)methyl)phosphonate(3ja)

55% yield (50.1 mg); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45-8.35 (m, 1H), 7.75 (d, *J* = 8.8, Hz, 1H), 7.61-7.46 (m, 3H), 7.45-7.34 (m, 4H), 7.34-7.30 (m, 1H), 7.28-7.14 (m, 3H), 4.90 (d, *J* = 28.4 Hz, 1H), 4.09-3.64 (m, 4H), 1.14 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 139.2, 136.2 (d, *J* = 4.6 Hz), 134.5, 130.04 (d, *J* = 2.1 Hz), 129.7, 129.6, 129.4, 129.2 (d, *J* = 6.4 Hz), 127.9 (d, *J* = 2.6 Hz), 127.4 (d, *J* = 6.1 Hz), 126.8, 126.7, 122.6, 122.4 (d, *J* = 1.3 Hz), 121.2 (d, *J* = 2.9 Hz), 117.7, 63.5 (d, *J* = 7.0 Hz), 63.1 (d, *J* = 7.2 Hz), 43.5 (d, *J* = 143.6 Hz), 16.3 (d, *J* = 3.9 Hz), 16.2 (d, *J* = 3.9 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.3. IR (KBr): $\tilde{\nu}$ =3128, 2354, 1400, 1163, 1054, 857, 750, 550 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{24}ClN_2O_3P+H]^+$ 455.1286, found 455.1288.



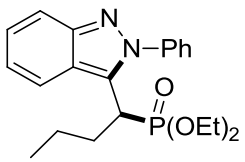
diethyl ((2-phenyl-*2H*-indazol-3-yl)(thiophen-3-yl)methyl)phosphonate(3ka)

83% yield (70.7 mg); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16-8.07 (m, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.50-7.43 (m, 3H), 7.43-7.36 (m, 2H), 7.31 – 7.22 (m, 1H), 7.22-7.12 (m, 2H), 7.10-6.97 (m, 2H), 4.98 (d, *J* = 27.9 Hz, 1H), 3.96-3.77 (m, 3H), 3.75-3.59 (m, 1H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 139.3, 133.5 (d, *J* = 4.9 Hz), 130.2, 129.5, 129.4, 128.2 (d, *J* = 5.4 Hz), 126.7, 126.7, 126.1, 123.9 (d, *J* = 8.2 Hz), 122.5 (d, *J* = 1.5 Hz), 122.0, 120.9 (d, *J* = 3.0 Hz), 117.7, 63.4 (d, *J* = 7.1 Hz), 62.9 (d, *J* = 7.2 Hz), 39.4 (d, *J* = 145.3 Hz), 16.3 (t, *J* = 5.5 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.8. IR (KBr): $\tilde{\nu}$ =3126, 1496, 1400, 1257, 1048, 1019, 966, 754, 544 cm^{-1}; HRMS (ESI) calcd for $[C_{22}H_{23}N_2O_3PS+H]^+$ 427.1240, found 427.1236.



diethyl ((2-phenyl-*2H*-indazol-3-yl)methyl)phosphonate(3la)

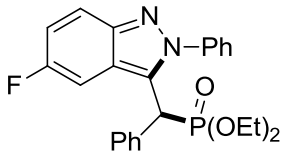
81% yield (55.7 mg); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, 1H), 7.69-7.56 (m, 3H), 7.54-7.37 (m, 3H), 7.30-7.18 (m, 1H), 7.07-7.01 (m, 1H), 4.02 – 3.78 (m, 4H), 3.53 (d, *J* = 21.6 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7 (d, *J* = 3.4 Hz), 139.4, 129.3, 129.1, 126.9, 126.5, 126.1 (d, *J* = 9.4 Hz), 121.8, 121.7 (d, *J* = 2.0 Hz), 120.8 (d, *J* = 2.3 Hz), 117.7, 62.5 (d, *J* = 6.9 Hz), 24.8 (d, *J* = 145.4 Hz), 16.4 (d, *J* = 6.0 Hz) ppm. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 22.1. IR (KBr): $\tilde{\nu}$ =3127, 1593, 1503, 1399, 1254, 1050, 1025, 969, 527 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{21}N_2O_3P+H]^+$ 345.1363, found 345.1368.



diethyl (1-(2-phenyl-2H-indazol-3-yl)butyl)phosphonate(3ma)

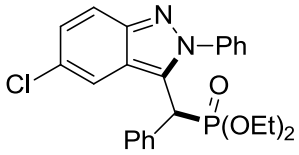
47% yield (36.3 mg); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.6 Hz, 1H), 7.78-7.68 (m, 1H), 7.65-7.58 (m, 2H), 7.58-7.47 (m, 3H), 7.41-7.23 (m, 1H), 7.15-7.06 (m, 1H), 4.17-3.93 (m, 3H), 3.93-3.75 (m, 1H), 3.67-3.49 (m, 1H), 2.45-2.21 (m,

1H), 2.14-1.96 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.09-0.91 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9 (d, *J* = 3.0 Hz), 139.6, 131.1 (d, *J* = 5.1 Hz), 129.3, 129.2, 127.1, 126.6, 121.8, 121.4 (d, *J* = 1.8 Hz), 120.3, 117.7, 62.8 (d, *J* = 7.1 Hz), 62.2 (d, *J* = 7.4 Hz), 37.30 (d, *J* = 144.5 Hz), 31.0, 21.0 (d, *J* = 14.9 Hz), 16.5 (d, *J* = 5.8 Hz), 16.3 (d, *J* = 5.6 Hz), 13.5. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 25.9. IR (KBr): $\tilde{\nu}$ =3417, 2926, 1597, 1379, 1250, 1024, 964, 748, 553 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{24}FN_2O_3P+H]^+$ 387.1832, found 387.1844.



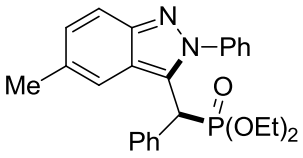
diethyl ((5-fluoro-2-phenyl-*2H*-indazol-3-yl)(phenyl)methyl)phosphonate(3na)

90% yield (78.9 mg); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 10.2, 2.4 Hz, 1H), 7.71 (dd, *J* = 9.4, 4.7 Hz, 1H), 7.59-7.45 (m, 3H), 7.43-7.34 (m, 4H), 7.32 -7.20 (m, 3H), 7.20-7.10 (m, 1H), 4.89 (d, *J* = 28.4 Hz, 1H), 4.05-3.71 (m, 4H), 1.07 (t, *J* = 13.9, 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4 (d, *J* = 240.2 Hz), 146.4, 139.2, 134.0 (d, *J* = 4.9 Hz), 130.9, 129.7, 129.4, 129.1 (d, *J* = 6.3 Hz), 128.9 (d, *J* = 2.1 Hz), 127.7 (d, *J* = 2.7 Hz), 126.7, 120.5 (dd, *J* = 2.9,2.8 Hz), 119.7 (d, *J* = 9.7 Hz), 118.5 (d, *J* = 29.1 Hz), 105.2 (d, *J* = 25.6 Hz), 63.28 (d, *J* = 7.1 Hz), 63.09 (d, *J* = 7.1 Hz), 43.69 (d, *J* = 143.3 Hz) 16.3, 16.2. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 22.0. IR (KBr): $\tilde{\nu}$ =3127, 1517, 1400, 1249, 1178, 1048, 1023, 963, 768, 698, 553 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{24}FN_2O_3P+H]^+$ 439.1581, found 439.1587.



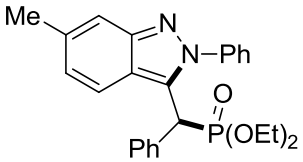
diethyl ((5-chloro-2-phenyl-*2H*-indazol-3-yl)(phenyl)methyl)phosphonate(3oa)

80% yield (72.7 mg); white solid; m. p. 128-129 ^{o}C;^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (d, *J* = 1.8 Hz, 1H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.59-7.46 (m, 3H), 7.42-7.34 (m, 4H), 7.34-7.22 (m, 4H), 4.90 (d, *J* = 28.4 Hz, 1H), 4.08-3.73 (m, 4H), 1.11 (d, *J* = 7.3 Hz, 3H), 1.06 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.3, 139.0, 133.8 (d, *J* = 5.2 Hz), 130.4, 129.8, 129.4, 129.0 (d, *J* = 6.3 Hz), 128.9 (d, *J* = 2.1 Hz), 128.2, 127.9, 127.8 (d, *J* = 2.6 Hz), 126.7, 121.5, 121.4, 119.2, 63.3 (d, *J* = 7.2 Hz), 63.2 (d, *J* = 7.1 Hz), 43.8 (d, *J* = 143.2 Hz), 16.3 (d, *J* = 1.5 Hz), 16.2 (d, *J* = 1.7 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.8. IR (KBr): $\tilde{\nu}$ =3128, 2360, 1502, 1400, 1246, 1052, 1030, 966, 695, 553 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{24}ClN_2O_3P+H]^+$ 455.1286, found 455.1291.



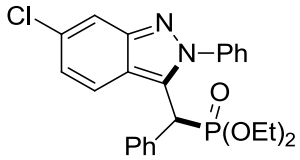
diethyl ((5-methyl-2-phenyl-2*H*-indazol-3-yl)(phenyl)methyl)phosphonate(3pa)

83% yield (72.1 mg); white solid; m. p. 100-102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.57-7.46 (m, 3H), 7.45-7.35 (m, 4H), 7.34-7.22 (m, 3H), 7.19 (dd, *J* = 8.9, 1.6 Hz, 1H), 4.90 (d, *J* = 28.5 Hz, 1H), 4.03-3.64 (m, 4H), 2.49 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 139.4, 134.25 (d, *J* = 4.9 Hz), 131.5, 129.7, 129.4, 129.3, 129.2, 129.1, 128.8 (d, *J* = 2.1 Hz), 127.56 (d, *J* = 2.7 Hz), 126.8, 121.5, 120.6, 117.3, 63.22 (d, *J* = 7.2 Hz), 62.93 (d, *J* = 7.1 Hz), 43.84 (d, *J* = 143.2 Hz), 22.2, 16.22 (t, *J* = 5.4 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 22.2. IR (KBr): $\tilde{\nu}$ =3128, 1596, 1496, 1400, 1251, 1022, 962, 777, 698, 556 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{27}N_2O_3P+H]^+$ 435.1832, found 435.1836.



diethyl ((6-methyl-2-phenyl-*2H*-indazol-3-yl)(phenyl)methyl)phosphonate(3qa)

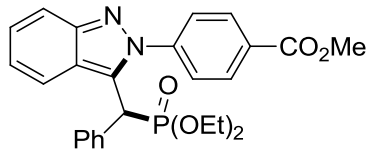
95% yield (82.5 mg); white solid; m. p. 94-96 °C;^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.54-7.45 (m, 4H), 7.45-7.35 (m, 4H), 7.31-7.20 (m, 3H), 7.03 (dd, *J* = 8.8, 1.4 Hz, 1H), 4.90 (d, *J* = 28.3 Hz, 1H), 3.99-3.67 (m, 4H), 2.47 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6, 139.4, 136.6, 134.2 (d, *J* = 5.1 Hz), 130.2, 129.4, 129.3,129.2 (d, *J* = 6.3 Hz), 128.74 (d, *J* = 2.2 Hz), 127.56 (d, *J* = 2.7 Hz), 126.8, 125.2, 122.3, 119.64 (d, *J* = 2.9 Hz), 115.9, 63.2 (d, *J* = 7.0 Hz), 62.9 (d, *J* = 7.1 Hz), 43.9 (d, *J* = 143.2 Hz), 22.1, 16.2, 16.2. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 22.2. IR (KBr): $\tilde{\nu}$ =3128, 1400, 1249, 1028, 971, 700, 559 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{27}N_2O_3P+H]^+$ 435.1382, found 435.1380.



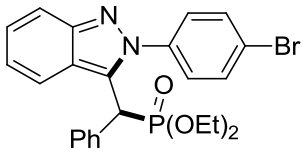
diethyl ((6-chloro-2-phenyl-*2H*-indazol-3-yl)(phenyl)methyl)phosphonate(3ra)

85% yield (77.2 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 9.1, 0.8 Hz, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.43-7.33 (m, 3H), 7.43-7.33 (m, 4H), 7.32-7.20 (m, 3H), 7.14 (dd, *J* = 9.1, 1.8 Hz, 1H), 4.89 (d, *J* = 28.1 Hz, 1H), 4.03-3.68 (m, 4H), 1.10

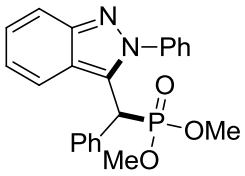
(t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 139.0, 133.8 (d, *J* = 5.0 Hz), 132.7, 131.3, 129.8, 129.4, 129.1 (d, *J* = 6.3 Hz), 128.9 (d, *J* = 2.1 Hz), 127.8 (d, *J* = 2.7 Hz), 126.7, 124.3 (d, *J* = 1.3 Hz), 123.8, 119.6 (d, *J* = 2.9 Hz), 116.5, 63.2 (t, *J* = 7.0 Hz), 43.8 (d, *J* = 143.5 Hz), 16.2 (d, *J* = 5.7 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.8. IR (KBr): $\tilde{\nu}$ =3128, 2363, 1504, 1400, 1250, 1050, 1025, 973, 767, 684, 559 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{24}ClN_2O_3P+H]^+$ 455.1286, found 455.1285.



methyl 4-(3-((diethoxyphosphoryl)(phenyl)methyl)-*2H*-indazol-2-yl)benzoate(3sa)
86% yield (82.2 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.7 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.46-7.24 (m, 6H), 7.24-7.13 (m, 1H), 4.91 (d, *J* = 28.5 Hz, 1H), 4.05-3.66 (m, 7H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 148.8, 142.5, 133.5 (d, *J* = 5.1 Hz), 130.5, 130.2, 130.1, 128.6 (d, *J* = 6.3 Hz), 128.4 (d, *J* = 2.1 Hz), 127.3 (d, *J* = 2.7 Hz), 126.6, 126.3, 122.3, 122.1, 121.0 (d, *J* = 3.0 Hz), 117.1, 62.8 (d, *J* = 7.2 Hz), 62.6 (d, *J* = 7.0 Hz), 52.0, 43.5 (d, *J* = 143.4 Hz), 15.7 (d, *J* = 3.2 Hz), 15.6 (d, *J* = 3.0 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.7. IR (KBr): $\tilde{\nu}$ =3127, 1725, 1605, 1401, 1283, 1019, 969, 757, 553 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{27}N_2O_5P+H]^+$ 479.1730, found 479.1735.

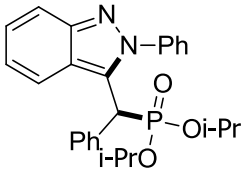


diethyl ((2-(4-bromophenyl)-*2H*-indazol-3-yl)(phenyl)methyl)phosphonate(3ta)
87% yield (86.7 mg); yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.8 Hz, 1H), 7.77-7.61 (m, 3H), 7.47-7.38 (m, 2H), 7.37-7.22 (m, 6H), 7.18 (dd, *J* = 8.8, 6.6 Hz, 1H), 4.87 (d, *J* = 28.4 Hz, 1H), 4.02-3.65 (m, 4H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 137.9, δ 133.5 (d, *J* = 5.1 Hz), 132.0, 130.1, 128.6 (d, *J* = 6.3 Hz), 128.35 (d, *J* = 2.1 Hz), 127.9, 127.2 (d, *J* = 2.6 Hz), 126.4, 123.1, 122.2 (d, *J* = 1.5 Hz), 122.0, 120.80 (d, *J* = 3.0 Hz), 117.1, 62.7 (d, *J* = 7.0 Hz), 62.6 (d, *J* = 7.0 Hz), 43.5 (d, *J* = 143.5 Hz), 15.7 (d, *J* = 3.6 Hz), 15.7 (d, *J* = 3.7 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.8. IR (KBr): $\tilde{\nu}$ =3128, 1494, 1399, 1246, 1051, 1014, 972, 835, 755, 701, 577, 549 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{24}BrN_2O_3P+H]^+$ 499.0781, found 499.0787.



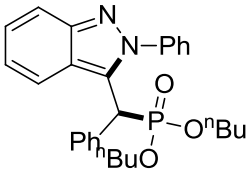
dimethyl (phenyl(2-phenyl-2*H*-indazol-3-yl)methyl)phosphonate(3ab)

85% yield (66.7 mg); yellow solid; m. p. 132-134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44-8.37 (m, 1H), 7.78-7.69 (m, 1H), 7.58-7.47 (m, 3H), 7.45-7.34 (m, 5H), 7.34-7.24 (m, 3H), 7.24-7.15 (m, 1H), 4.96 (d, *J* = 28.4 Hz, 1H), 3.54 (d, *J* = 10.9 Hz, 3H), 3.49 (d, *J* = 10.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 139.2, 133.85 (d, *J* = 5.0 Hz), 130.1, 129.6, 129.4, 129.2, 129.1, 128.92 (d, *J* = 2.0 Hz), 127.77 (d, *J* = 2.6 Hz), 126.8, 122.5, 121.2, 117, 53.82 (d, *J* = 7.1 Hz), 53.54 (d, *J* = 7.1 Hz), 43.38 (d, *J* = 143.6 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 24.4. IR (KBr): $\tilde{\nu}$ =3133, 1493, 1401, 1260, 1051, 1031, 830, 774, 748, 698, 548 cm^{-1}; HRMS (ESI) calcd for $[C_{22}H_{21}N_2O_3P+H]^+$ 393.1363, found 393.1368.



diisopropyl (phenyl(2-phenyl-2*H*-indazol-3-yl)methyl)phosphonate(3ac)

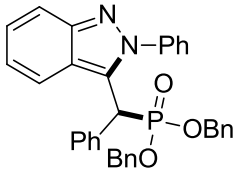
76% yield (68.1 mg); yellow solid; m. p. 105-107 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64-8.50 (m, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.59-7.47 (m, 3H), 7.46-7.33 (m, 5H), 7.33-7.24 (m, 3H), 7.19 (dd, *J* = 8.6, 6.5 Hz, 1H), 4.86 (d, *J* = 28.5 Hz, 1H), 4.55-4.38 (m, 2H), 1.19 (t, *J* = 6.2 Hz, 6H), 0.93 (d, *J* = 6.2 Hz, 3H), 0.66 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 139.4, 134.4 (d, *J* = 5.0 Hz), 130.9, 129.4 (d, *J* = 5.7 Hz), 129.3, 129.3, 128.7 (d, *J* = 2.2 Hz), 127.52 (d, *J* = 2.9 Hz), 126.8, 126.7, 123.1, 122.1, 121.2, 117.5, 72.11 (d, *J* = 7.3 Hz), 71.72 (d, *J* = 7.4 Hz), 23.7 (m). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 20.4. IR (KBr): $\tilde{\nu}$ =3128, 1496, 1400, 1252, 1008, 982, 742, 692, 550 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{29}N_2O_3P+H]^+$ 449.1989, found 479.1994.



dibutyl (phenyl(2-phenyl-*2H*-indazol-3-yl)methyl)phosphonate(3ad)

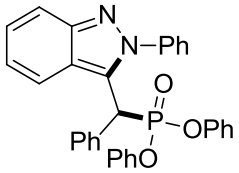
85% yield (80.9 mg); yellow solid; m. p. 61-63 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.6 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.60-7.46 (m, 3H), 7.46-7.36 (m, 4H),

7.35-7.23 (m, 4H), 7.21-7.14 (m, 1H), 4.94 (d, *J* = 28.4 Hz, 1H), 3.94-3.62 (m, 4H), 1.48-1.34 (m, 2H), 1.33-1.22 (m, 2H), 1.18-0.96 (m, 4H), 0.78 (t, *J* = 7.3 Hz, 3H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 139.3, 134.2 (d, *J* = 5.1 Hz), 129.5, 129.3, 129.2, 129.2, 128.8 (d, *J* = 2.2 Hz), 127.6 (d, *J* = 2.9 Hz), 126.8, 126.7, 122.8, 122.3, 121.3 (d, *J* = 2.6 Hz), 117.6, 66.9 (d, *J* = 7.3 Hz), 66.6 (d, *J* = 7.3 Hz), 43.9 (d, *J* = 143.2 Hz), 32.3 (d, *J* = 5.9 Hz), 32.2 (d, *J* = 5.9 Hz) 18.5, 18.4, 13.5, 13.4. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 21.9. IR (KBr): $\tilde{\nu}$ =3128, 2360, 1400, 1255, 1025, 692, 547 cm^{-1}; HRMS (ESI) calcd for $[C_{28}H_{33}N_2O_3P+H]^+$ 477.2302, found 477.2307.



dibenzyl (phenyl(2-phenyl-*2H*-indazol-3-yl)methyl)phosphonate(3ae)

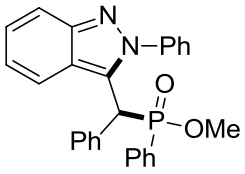
68% yield (84.0 mg); yellow solid; m. p. 100-102 ºC;^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.6 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.52-7.37 (m, 5H), 7.37-7.30 (m, 1H), 7.29-7.22 (m, 6H), 7.22-7.12 (m, 6H), 7.12-6.98 (m, 2H), 6.93-6.80 (m, 2H), 4.95 (d, *J* = 28.6 Hz, 1H), 4.88-4.57 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 139.2, 135.9 (dd, *J* = 6.0, 15.7 Hz) 133.9 (d, *J* = 5.1 Hz), 129.5, 129.3, 129.3, 128.9 (d, *J* = 2.1 Hz), 128.5, 128.4, 128.1, 127.9, 127.8 (d, *J* = 2.7 Hz), 126.8, 126.7, 122.8, 122.5,121.3 (d, *J* = 2.9 Hz), 117.8, 68.7 (d, *J* = 7.0 Hz), 68.4 (d, *J* = 7.1 Hz), 44.2 (d, *J* = 143.3 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 22.9. IR (KBr): $\tilde{\nu}$ =3126, 1593, 1454, 1401, 1378, 1247, 1056, 1020, 748, 696, 589, 544 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{29}N_2O_3P+H]^+$ 545.1989, found 545.1990.



diphenyl (phenyl(2-phenyl-*2H*-indazol-3-yl)methyl)phosphonate(3af)

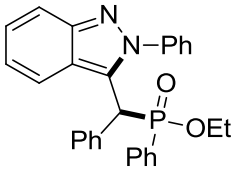
88% yield (90.8 mg); yellow solid; m. p. 142-145 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.56-7.44 (m, 5H), 7.39-7.25 (m, 6H), 7.23-7.10 (m, 5H), 7.09-7.00 (m, 2H), 6.82-6.62 (m, 4H), 5.30 (d, *J* = 28.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 150.1, 149.9, 149.0, 139.1, 133.1 (d, *J* = 5.6 Hz), 129.7, 129.6, 129.5, 129.4, 129.3, 129.1 (d, *J* = 2.3 Hz), 128.2 (d, *J* = 3.0 Hz), 126.8, 126.8, 125.3 (d, *J* = 2.3 Hz), 122.8, 122.4, 121.5, 120.3, 120.3 (d, *J* = 1.4 Hz), 120.3, 117.8, 43.97 (d, *J* = 144.1 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 14.4. IR (KBr): $\tilde{\nu}$ =

3128, 1590, 1488, 1451, 1401, 1278, 1201, 1183, 942, 698, 574, 526cm^{-1}; HRMS (ESI) calcd for $[C_{32}H_{25}N_2O_3P+H]^+$ 517.1676, found 517.1674.



methyl phenyl((S)-phenyl(2-phenyl-*2H*-indazol-3-yl)methyl)phosphinate(3ag)

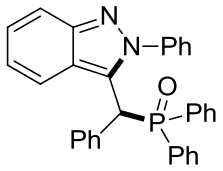
64% yield (56.1 mg); white solid; m. p. 182-184 ^{o}C;The ^{1}H NMR spectrum of the isolated product characterized as a 1.1:1 diastereomeric mixture. ^{1}H NMR (300 MHz, $CDCl_3$) a mixture: δ 8.67 (d, *J* = 8.6 Hz, 1H), 8.37 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.56-7.48 (m, 3H), 7.48-7.38 (m, 7H), 7.38-7.29 (m, 10H), 7.28-7.25 (m, 3H), 7.25-7.15 (m, 7H), 7.11-7.01 (m, 2H), 6.96-6.80 (m, 2H), 4.99 (d, *J* = 20.9 Hz, 1H),4.86(d, *J* = 20.3 Hz, 1H) 3.57 (d, *J* = 11.0 Hz, 3H), 3.52 (d, *J* = 10.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4 (d, *J* = 2.2 Hz), 148.4 (d, *J* = 2.6 Hz), 138.6, 138.5, 133.4,133.3,132.9, 132.8, 132.1 (d, *J* = 3.0 Hz), 132.0 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 9.5 Hz), 131.1 (d, *J* = 9.6 Hz), 128.4 (d, *J* = 2.1 Hz), 128.2 (d, *J* = 1.8 Hz), 128.1, 127.9, 127.9, 127.8, 127.2 (d, *J* = 2.3 Hz), 127.0 (d, *J* = 2.5 Hz), 126.3, 126.2, 122.6, 122.4, 121.9, 121.8, 121.02 (d, *J* = 3.1 Hz), 120.9 (d, *J* = 2.8 Hz), 117.3, 117.0, 51.64 (d, *J* = 6.9 Hz), 51.50 (d, *J* = 6.7 Hz), 47.41 (d, *J* = 31.5 Hz), 46.13 (d, *J* = 30.6 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 37.3. IR (KBr): $\tilde{\nu}$ =3133, 1496, 1400, 1240, 1025, 748, 691, 550, 488 cm^{-1}; HRMS (ESI) calcd for $[C_{27}H_{23}N_2O_2P+H]^+$ 439.1570, found 439.1570.



ethyl phenyl((S)-phenyl(2-phenyl-2H-indazol-3-yl)methyl)phosphinate(3ah)

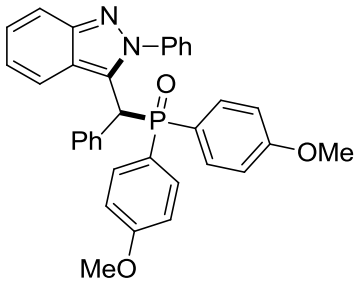
50% yield (45.2 mg); yellow solid; m. p. 55-57 ^{o}C; The ^{1}H NMR spectrum of the isolated product characterized as a 1.2:1 diastereomeric mixture. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.5 Hz, 0.45H), 8.42 (d, *J* = 8.6 Hz, 0.55H), 7.73 (d, *J* = 8.7 Hz, 0.57H), 7.62 (d, *J* = 8.5 Hz, 0.56H), 7.57-7.49 (m, 1H), 7.50-7.35 (m, 5H), 7.35-7.27 (m, 4H), 7.27-7.11 (m, 5H), 7.10-6.82 (m, 2H),4.99 (d, J = 20.8 Hz, 0.54H), 4.84 (d, J = 20.3 Hz, 0.45H), 4.06-3.75 (m, 2H), 1.16-1.07 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0 (d, *J* = 2.2 Hz), 148.9 (d, *J* = 2.2 Hz), 139.1, 139.0, 134.0 (d, *J* = 7.5 Hz), 133.5 (d, *J* = 4.0 Hz), 132.5 (d, *J* = 2.8 Hz), 132.3 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 9.5 Hz), 131.4

(d, *J* = 9.7 Hz), 130.7, 130.7, 130.6, 129.9 (d, *J* = 3.5 Hz), 129.7 (d, *J* = 5.0 Hz), 129.5 (d, *J* = 4.4 Hz), 129.3 (d, *J* = 5.7 Hz), 129.1 (d, *J* = 10.5 Hz), 128.8 (d, *J* = 2.0 Hz), 128.7 (d, *J* = 1.9 Hz), 128.4 (d, *J* = 9.6 Hz), 128.2 (d, *J* = 9.7 Hz), 127.6 (d, *J* = 2.5 Hz), 127.5 (d, *J* = 2.4 Hz), 126.7, 126.7, 126.6, 123.2 (d, *J* = 11.2 Hz), 122.2 (d, *J* = 15.8 Hz), 121.6 (d, *J* = 3.0 Hz), 121.4 (d, *J* = 2.8 Hz), 117.7, 117.5, 62.0 (d, *J* = 6.9 Hz), 61.7 (d, *J* = 6.6 Hz), 48.2 (d, *J* = 31.7 Hz), 46.9 (d, *J* = 31.0 Hz), 16.4 (d, *J* = 3.5 Hz), 16.3 (d, *J* = 3.1 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 37.1, 35.6. IR (KBr): $\tilde{\nu}$ =3127, 2361, 1593, 1400, 1237, 1120, 1026, 749, 696, 549 cm^{-1}; HRMS (ESI) calcd for $[C_{28}H_{25}N_2O_2P+H]^+$ 453.1726, found 453.1730.



diphenyl(phenyl(2-phenyl-*2H*-indazol-3-yl)methyl)phosphine oxide(3ai)

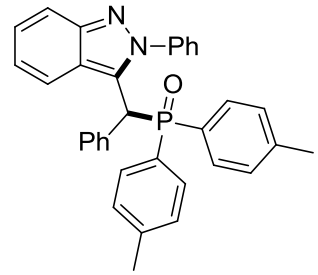
73% yield (70.7 mg); yellow solid; m. p. 243-244 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.6 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.56-7.45 (m, 4H), 7.46-7.35 (m, 4H), 7.35-7.23 (m, 7H), 7.23-7.14 (m, 5H), 7.09 (d, *J* = 7.2 Hz, 2H), 5.13 (d, *J* = 12.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 139.3, 134.0 (d, *J* = 4.9 Hz), 131.9, 131.9, 131.8, 131.40 (d, *J* = 8.7 Hz), 131.9, 131.9, 131.8, 130.0 (d, *J* = 5.0 Hz), 129.6, 129.2, 128.6 (d, *J* = 1.1 Hz), 128.4 (dd, *J* = 2.3, 11.6 Hz), 127.5 (d, *J* = 1.4 Hz), 126.9, 126.7, 123.8, 122.4, 121.6 (d, *J* = 2.5 Hz), 117.3, 47.7 (d, *J* = 65.6 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 29.0. IR (KBr): $\tilde{\nu}$ =3133, 2360, 1588, 1493, 1401, 1207, 1117, 742, 694, 539, 517 cm^{-1}; HRMS (ESI) calcd for $[C_{32}H_{25}N_2OP+H]^+$ 485.1777, found 485.1774.



bis(4-methoxyphenyl)(phenyl(2-phenyl-*2H*-indazol-3-yl)methyl)phosphine oxide(3aj)

56% yield (60.9 mg); yellow solid; m. p. 90-92 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.6 Hz, 1H), 7.65-7.58 (m, 1H), 7.55-7.43 (m, 3H), 7.41-7.23 (m, 8H), 7.22-7.13 (m, 4H), 7.14-7.03 (m, 2H), 6.80 (dd, *J* = 8.9, 2.4 Hz, 2H), 6.72 (dd, *J* = 8.9, 2.4 Hz, 2H), 5.03 (d, *J* = 12.6 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$)

13C NMR (75 MHz, $CDCl_3$) δ 162.3, 139.3, 134.4 (d, *J* = 4.7 Hz), 133.21 (d, *J* = 10.0 Hz), 132.7 (d, *J* = 10.3 Hz), 131.7, 130.0 (d, *J* = 5.0 Hz), 129.6, 129.1, 128.6 (d, *J* = 1.6 Hz), 127.3 (d, *J* = 2.0 Hz), 127.0, 126.7, 123.9, 122.2, 121.8, 121.6 (d, *J* = 2.8 Hz), 117.2e, 113.9 (d, *J* = 12.7 Hz), 55.2, 48.10 (d, *J* = 66.1 Hz). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 29.5. IR (KBr): $\tilde{\nu}$ =3129, 1596, 1401, 1257, 1116, 692, 541 cm^{-1}; HRMS (ESI) calcd for $[C_{34}H_{29}N_2O_3P+H]^+$ 545.1989 found 545.1989.



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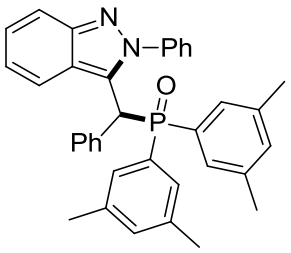
(phenyl(2-phenyl-*2H*-indazol-3-yl)methyl)di-p-tolylphosphine oxide(3ak)

64% yield (65.6 mg); yellow solid; m. p. 129-131 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89-8.82 (m 1H), 7.60 (d, *J* = 8.9 Hz, 1H), 7.55-7.41 (m, 3H), 7.38-7.22 (m, 7H), 7.21-7.13 (m, 4H), 7.13-7.05 (m, 4H), 7.01 (dd, *J* = 8.1, 2.9 Hz, 2H), 5.08 (d, *J* = 12.3 Hz, 1H), 2.28 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 142.2 (d, *J* = 2.7,5.3 Hz), 139.4, 134.3 (d, *J* = 4.8 Hz), 131.6, 131.4 (d, *J* = 9.0 Hz), 130.8 (d, *J* = 9.3 Hz), 130.0 (d, *J* = 5.0 Hz), 129.6, 129.2 (d, *J* = 3.1 Hz), 129.0, 128.6 (d, *J* = 1.7 Hz), 127.4 (d, *J* = 2.3 Hz), 127.0, 126.7, 123.9, 122.2, 121.6, 117.2, 47.8 (d, *J* = 65.4 Hz), 21.5, 21.4. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 29.5. IR (KBr): $\tilde{\nu}$ =3139, 2360, 1400, 1172, 759, 668, 538 cm^{-1}; HRMS (ESI) calcd for $[C_{34}H_{29}N_2OP+H]^+$ 513.2090, found 513.2093.



bis(3,5-dimethylphenyl)(phenyl(2-phenyl-*2H*-indazol-3-yl)methyl)phosphine oxide(3al)

75% yield (81.0 mg); yellow solid; m. p. 190 °C decomposed ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82-8.75 (m, 1H), 7.66-7.57 (m, 1H), 7.57-7.44 (m, 3H), 7.36-7.26 (m, 3H), 7.26-7.17 (m, 4H), 7.16-7.08 (m, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 10.6 Hz, 4H), 5.09 (d, *J* = 12.6 Hz, 1H), 2.18 (s, 6H), 2.13 (s, 6H).; ^{13}C NMR (75 MHz, $CDCl_3$)

δ 148.5 (d, *J* = 1.8 Hz), 138.8, 137.5 (d, *J* = 3.4 Hz), 137.3 (d, *J* = 3.6 Hz), 133.8 (d, *J* = 4.8 Hz), 133.0 (dd, *J* = 2.9 Hz, 8.0 Hz), 131.1, 131.0, 129.8 (d, *J* = 6.0 Hz), 129.5 (d, *J* = 4.8 Hz), 129.0, 128.7, 128.6, 128.1, 128.0, 127.9, 126.9 (d, *J* = 2.2 Hz), 126.5,126.2, 123.5, 121.7, 121.3 (d, *J* = 2.8 Hz). 116.6, 47.6, 46.7, 20.7, 20.6. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 29.9. IR (KBr): $\tilde{\nu}$ =3139, 1597, 1498, 1401, 1374, 1272, 1204, 1123, 877, 857, 776, 746, 695, 441 cm^{-1}; HRMS (ESI) calcd for $[C_{36}H_{33}N_2OP+H]^+$ 541.2403, found 541.2401.

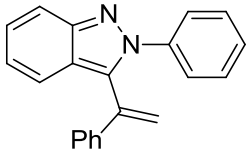
4. General Procedure for the Further Transformation of 3aa

4.1 *Transformation of* 3aa

a) General procedure

To a solution of **3aa** (0.1 mol, 1 equiv) in anhydrous THF was added slowly LDA (0.2 mmol, 2 equiv) at 0 ^{o}C under Ar atmosphere. After 10 min, paraformaldehyde (0.2 mmol, 2 equiv) was added. The reaction mixture was stirred at room temperature until the reaction was completed (detected by TLC). Then solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the pure product **5aa** (PE:EA= 50:1).

b) Characterization of the product



2-phenyl-3-(1-phenylvinyl)-2H-indazole (5aa)

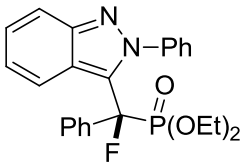
84% yield (24.9 mg); white solid; m. p. 96-98 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (dt, *J* = 8.8, 1.0 Hz, 1H), 7.57-7.43 (m, 3H), 7.40-7.33 (m, 1H), 7.32-7.21 (m, 3H), 7.20 -7.03 (m, 6H), 5.93 (d, *J* = 1.0 Hz, 1H), 5.52 (d, *J* = 1.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 140.3, 138.9, 138.5, 132.2, 128.7, 128.3, 128.2, 128.1, 126.9, 126.9, 125.3, 122.3, 120.7, 119.9, 117.7, 113.4. IR (KBr): $\tilde{\nu}$ =2953, 2850, 1597, 1499, 1361, 1024, 901, 831, 822,781, 691 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{16}N_2+H]^+$ 297.1386, found 297.1391.

4.1 The reaction of 3aa with NFSI

a) General procedure

A THF solution (1.0 mL) of **3aa** (0.1 mol, 1 equiv) was treated with LiHMDS (0.2 mmol, 2 equiv) at 0 ^{o}C for 10 min under Ar atmosphere before the addition of NFSI (0.2 mmol, 2 equiv).Then resulting solution was stirred at room tempreture until a complete consumption of **3aa** (detected by TLC). The solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the pure product **6aa** (PE:EA= 2:1).

b) Characterization of the product



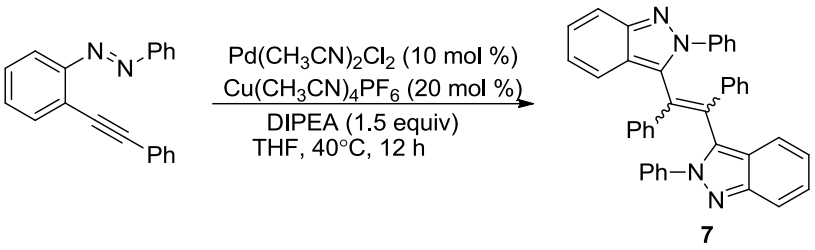
diethyl (fluoro(phenyl)(2-phenyl-2H-indazol-3-yl)methyl)phosphonate (6aa)

65% yield (28.4 mg); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 17.2, 8.8 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.41-7.31 (m, 1H), 7.30-7.24 (m, 1H), 7.24-7.10 (m, 7H), 7.04 (t, *J* = 8.7 Hz, 2H), 6.82 (t, *J* = 8.5 Hz, 1H), 4.24 - 3.73 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) 13C NMR (75 MHz, CDCl3) δ 147.3, 140.2 (d, J = 8.0 Hz), 135.5 (d, J = 21.7 Hz), 128.0, 127.8, 127.7, 126.9, 126.8, 126.6 (d, J = 2.2 Hz), 125.7, 125.6 (d, J = 1.6 Hz), 125.5, 125.4, 121.7 (dd, J = 10.0 Hz, 69 Hz), 116.8 (d, J = 5.4 Hz), 114.0 (dd, J=1.2 Hz, 22.5Hz), 63.7 (d, J = 7.5 Hz), 63.5 (d, J = 8.5 Hz), 15.3 (d, J = 5.7 Hz), 15.2 (d, J = 2.4 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 11.76 (d, J = 80.4 Hz).. IR (KBr): $\tilde{\nu}$ =2980, 2924, 2853, 1449, 1499, 1260, 1053, 1024, 975, 920, 791 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{24}FN_2O_3P+H]^+$ 439.1581, found 439.1600.

5. The trapping experiments of carbene intermediates

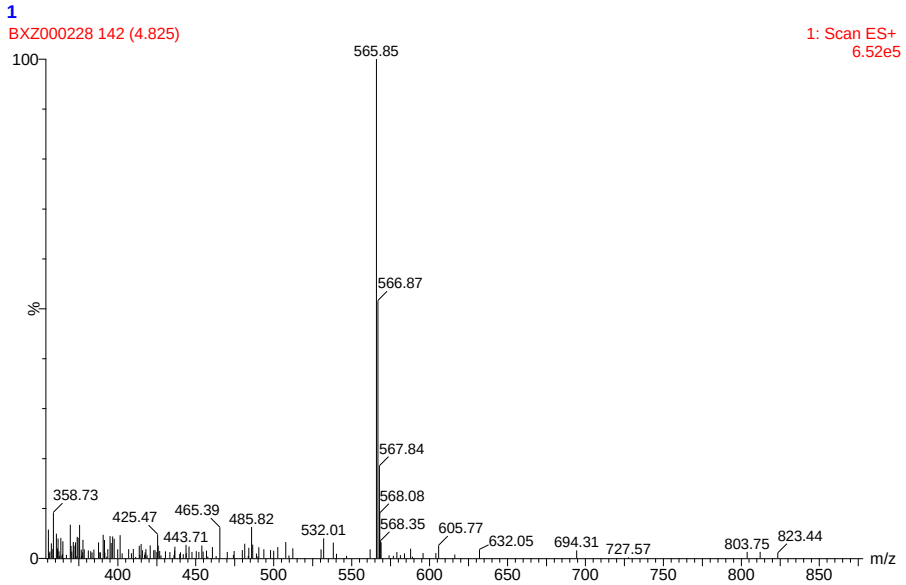
5.1 Formation of Dimmer 7

The reaction was carried out with **1a** at the absence of phosphonate **2a** at standard condition. After 12h, the dimer 6 was observed by LCMS. The results indicated that the carbene complex possibly formed during the process.[6]



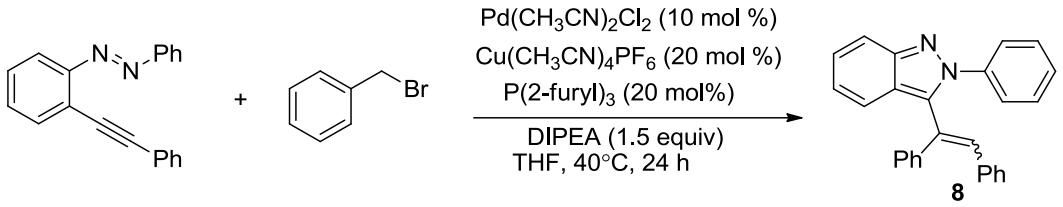
7

Exact Mass: 564.2314



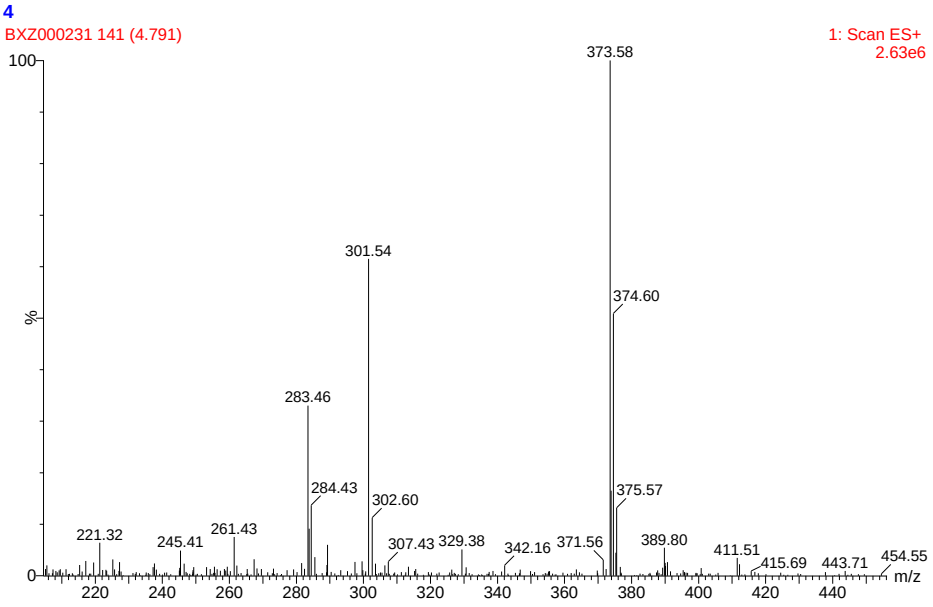
5.2 Trapping of palladium carbene

Benzyl bromide was added into reaction instead of phosphonate **2a** at standard condition. The product **8** was detected after 24h by LCMS and indicated that the palladium carbene may exist.[7]



8

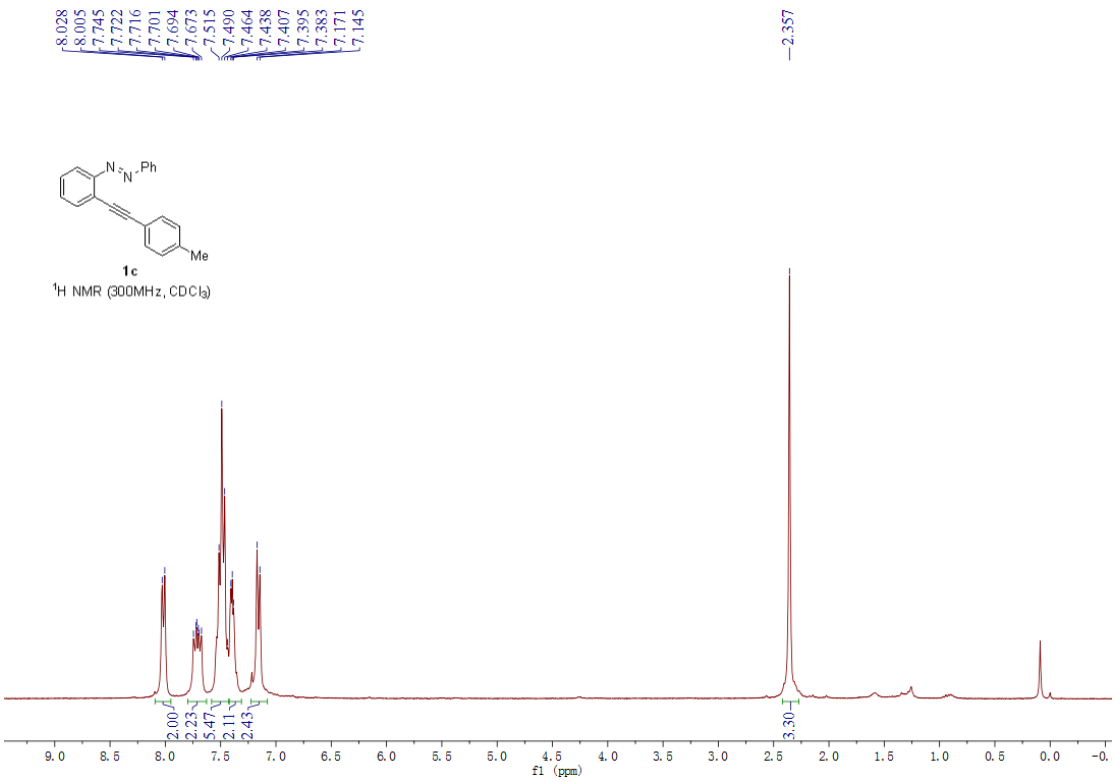
Exact Mass: 372.1626

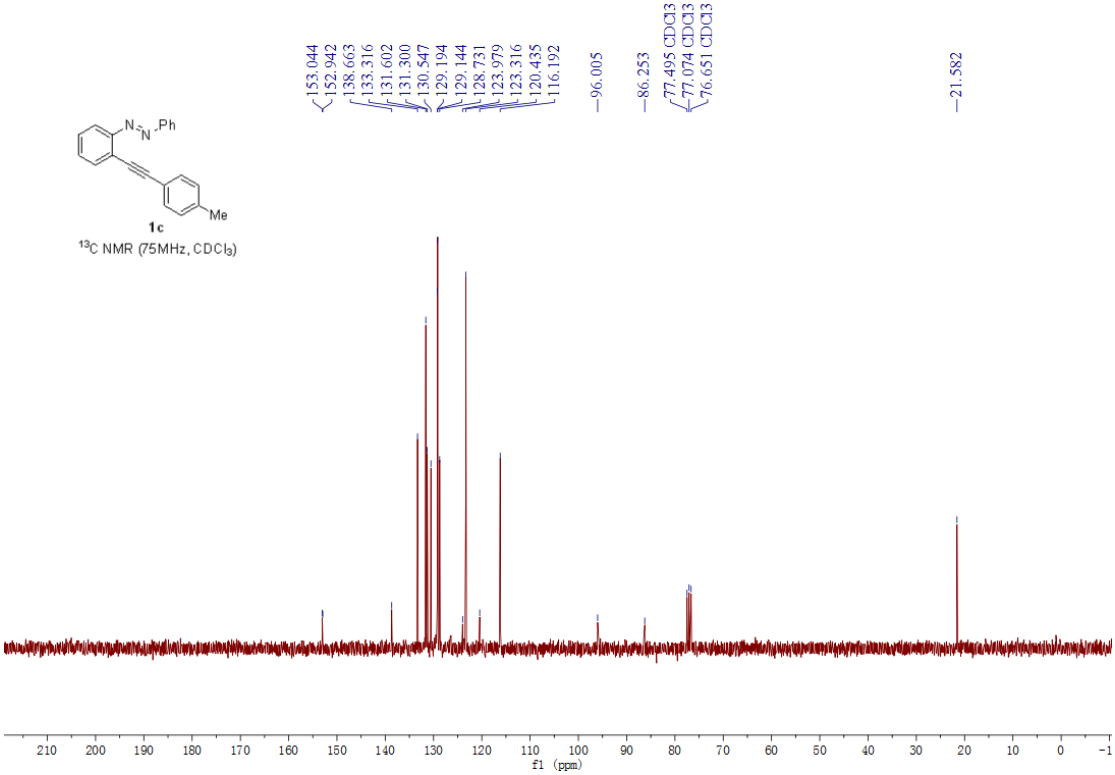


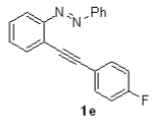
6. Reference

1. L. D. Shirtcliff, T. J. R. Weakley, M. M. Haley, F. Köhler, R. Herges, *J. Org. Chem.*, 2004, **69**, 6979.
2. C. Zhu, C. Feng, M. Yamane, *Chem. Commun.*, 2017, **53**, 2606.
3. G. K. S. Prakash, L. Gurung, P. C. Schmid, P. Wang, T. E. Thomas, C. Panja, T. Mathew, G. A. Olah, *Tetrahedron Lett*., 2009, **50**, 4279.
4. R. Shen, B. Luo, J. Yang, L. Zhang, L.-B. Han, *Chem. Commun.*, 2016, **52**, 6451.
5. C. C. Chen, J. Waser, *Chem. Commun.*, 2014, **50**, 12923.
6. H. Cao, H. Zhan, J. Cen, J. Lin, Y. Lin, Q. Zhu, M. Fu, H. Jiang, *Org. Lett.*, 2013, **15**, 1080.
7. Y. Zhou, F. Ye, X. Wang, S. Xu, Y. Zhang, J. Wang, *J. Org. Chem.*, 2015, **80**, 6109.

7. NMR Spectra

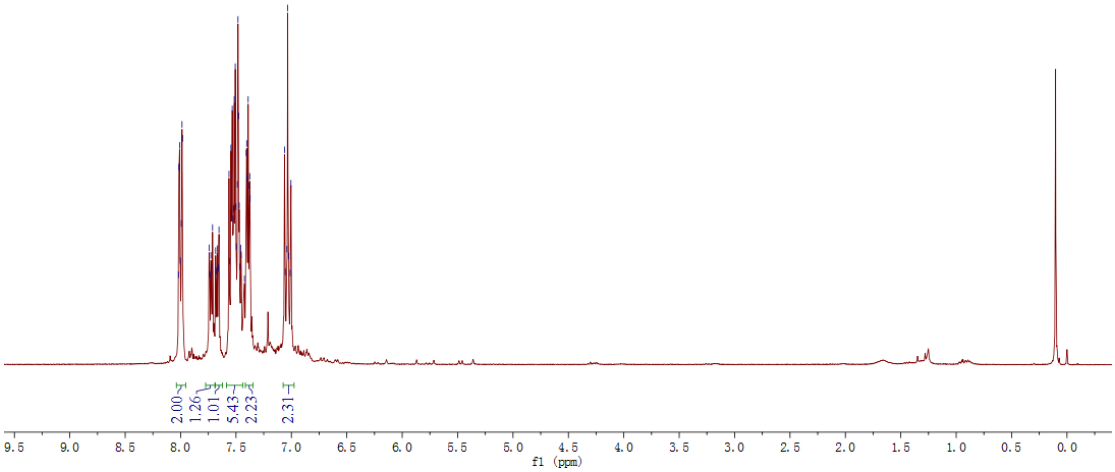


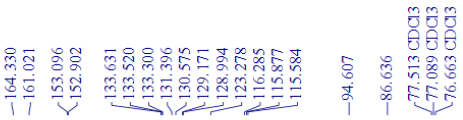


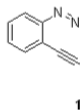


1e

^{1}H NMR (300MHz $CDCl_3$)

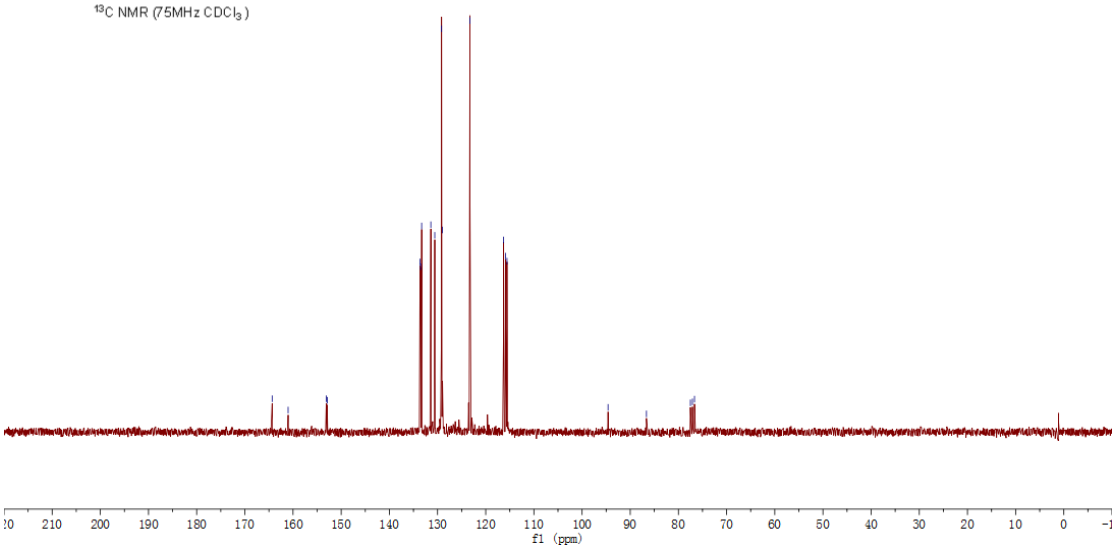


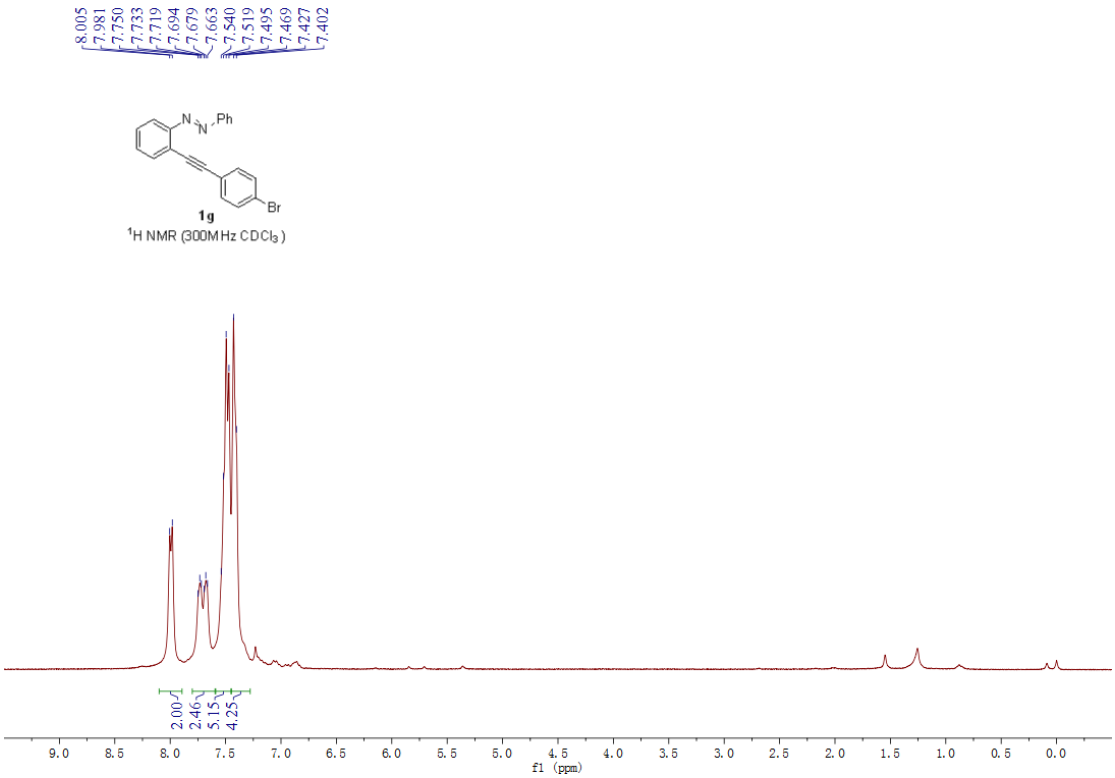




1e

^{13}C NMR (75MHz $CDCl_3$)

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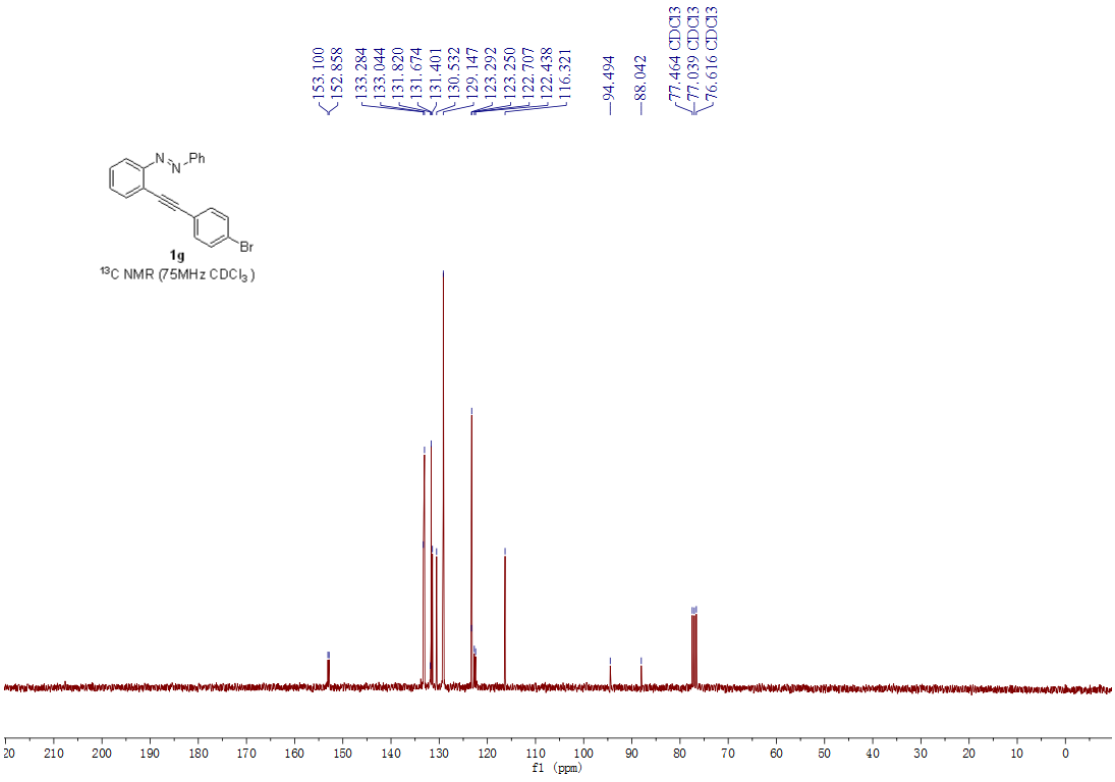
7.750
7.733
7.719
7.694
7.679
7.663
7.540
7.519
7.495
7.469
7.427
7.402
N
N
Ph
Br
1g
1H NMR (300MHz CDCl3)
2.00
2.46
5.15
4.25
f1 (ppm)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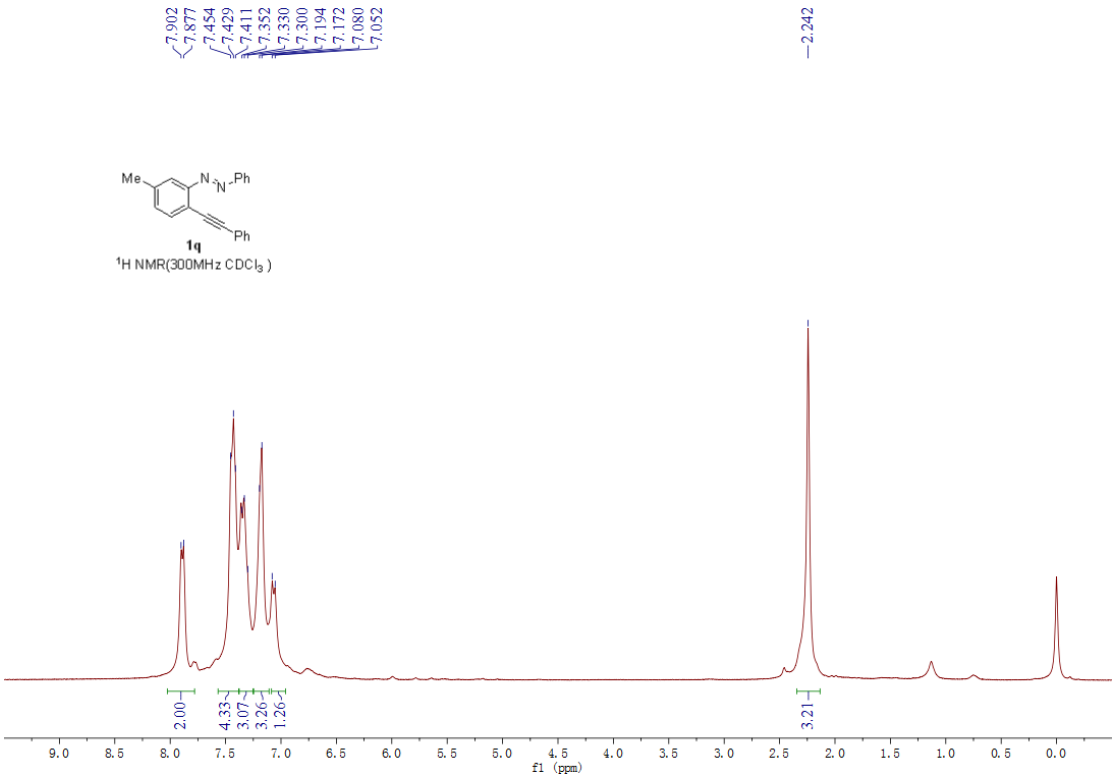
152.858
133.284
133.044
131.820
131.674
131.401
130.532
129.147
123.292
123.250
122.707
122.438
116.321
94.494
88.042
77.464 CDCl3
77.039 CDCl3
76.616 CDCl3
N
N
Ph
Br
1g
13C NMR (75MHz CDCl3)
f1 (ppm)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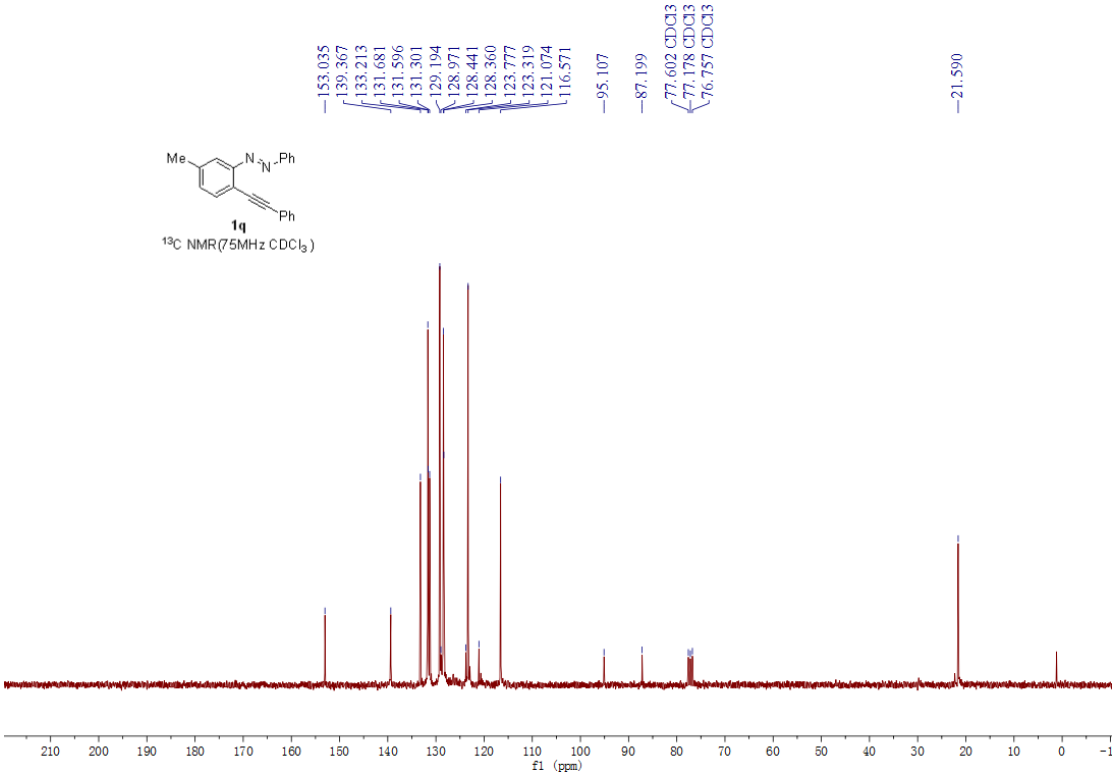
7.877
7.454
7.429
7.411
7.352
7.330
7.300
7.194
7.172
7.080
7.052
2.242
Me
N
N
Ph
Ph
1q
1H NMR(300MHz CDCl3)
2.00
4.33
3.07
3.26
1.26
3.21
f1 (ppm)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131.301
129.194
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128.360
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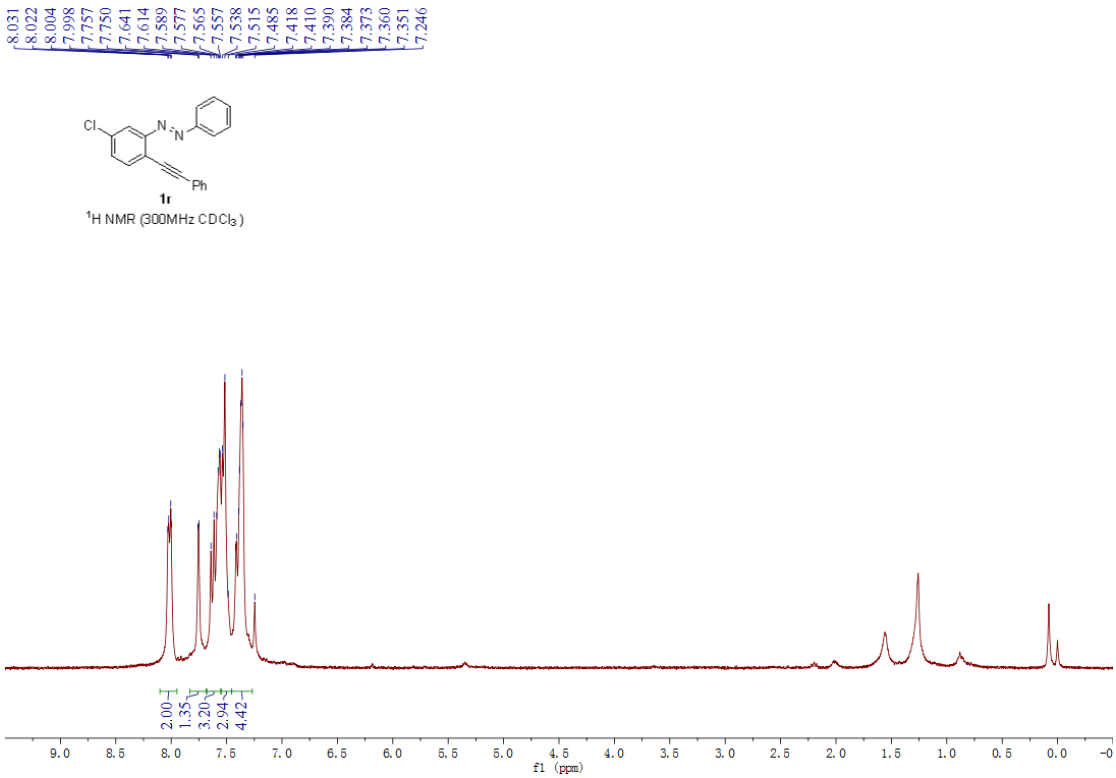
123.319
121.074
116.571
95.107
87.199
77.602 CDCl3
77.178 CDCl3
76.757 CDCl3
21.590
Me
N
N
Ph
Ph
1q
13C NMR(75MHz CDCl3)
f1 (ppm)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7.614
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7.577
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7.557
7.538
7.515
7.485
7.418
7.410
7.390
7.384
7.373
7.360
7.351
7.246
Cl
N
N
Ph
1r
1H NMR (300MHz CDCl3)
2.00
1.35
3.20
2.94
4.42
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
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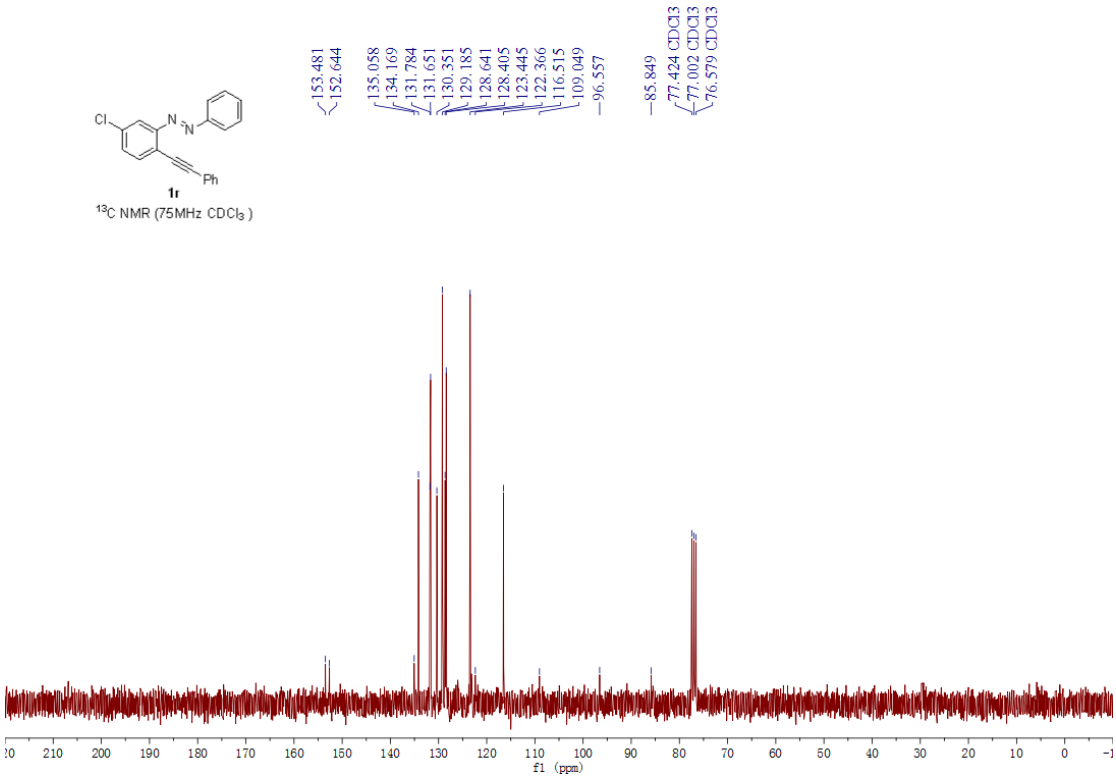
0.0
f1 (ppm)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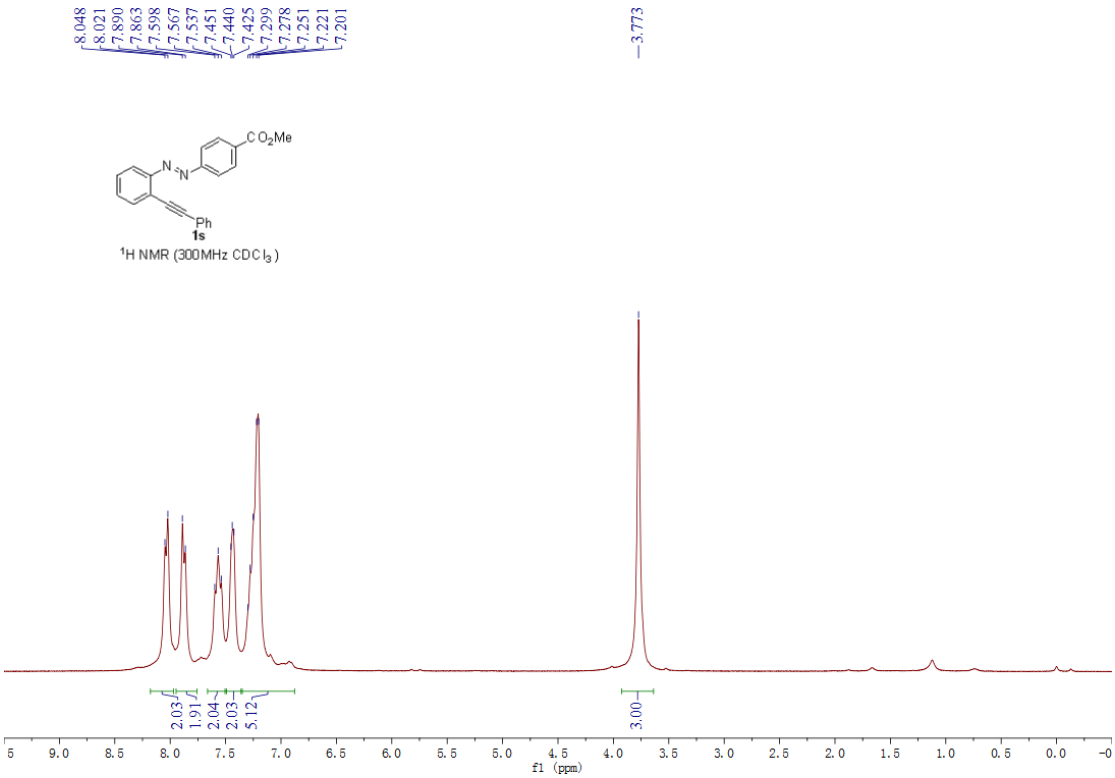
122.366
116.515
109.049
96.557
85.849
77.424 CDCl3
77.002 CDCl3
76.579 CDCl3
Cl
N
N
Ph
1r
13C NMR (75MHz CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.863
7.598
7.567
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7.451
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7.425
7.299
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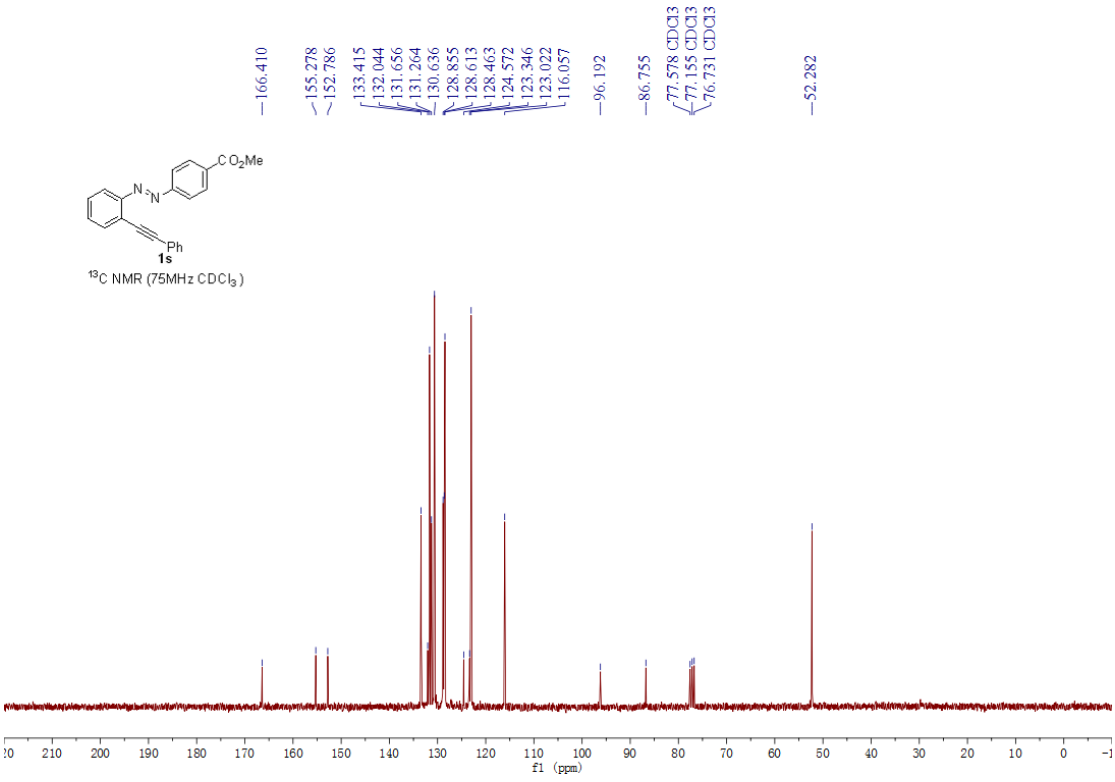
7.251
7.221
7.201
3.773
CO2Me
N
N
Ph
1s
1H NMR (300MHz CDCl3)
2.03
1.91
2.04
2.03
5.12
3.00
f1 (ppm)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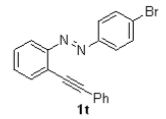
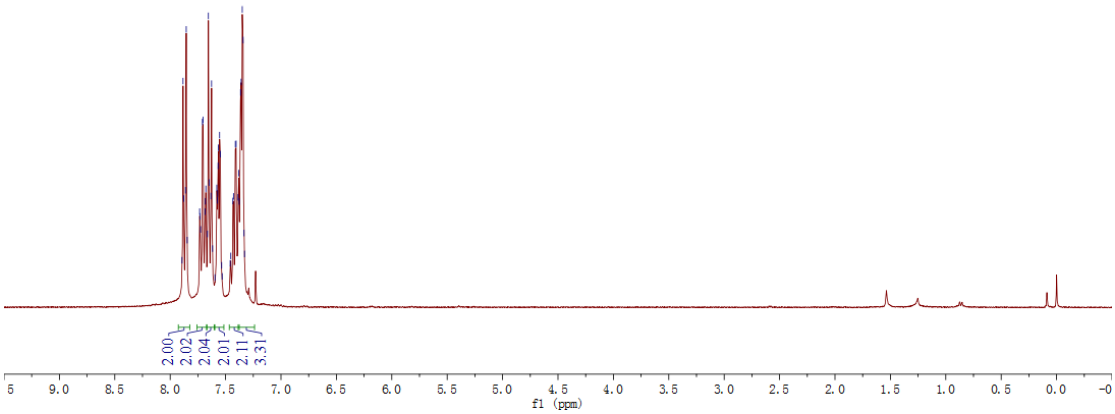
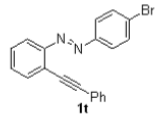
123.022
116.057
96.192
86.755
77.578 CDCl3
77.155 CDCl3
76.731 CDCl3
52.282
CO2Me
N
N
Ph
1s
13C NMR (75MHz CDCl3)
f1 (ppm)



1t

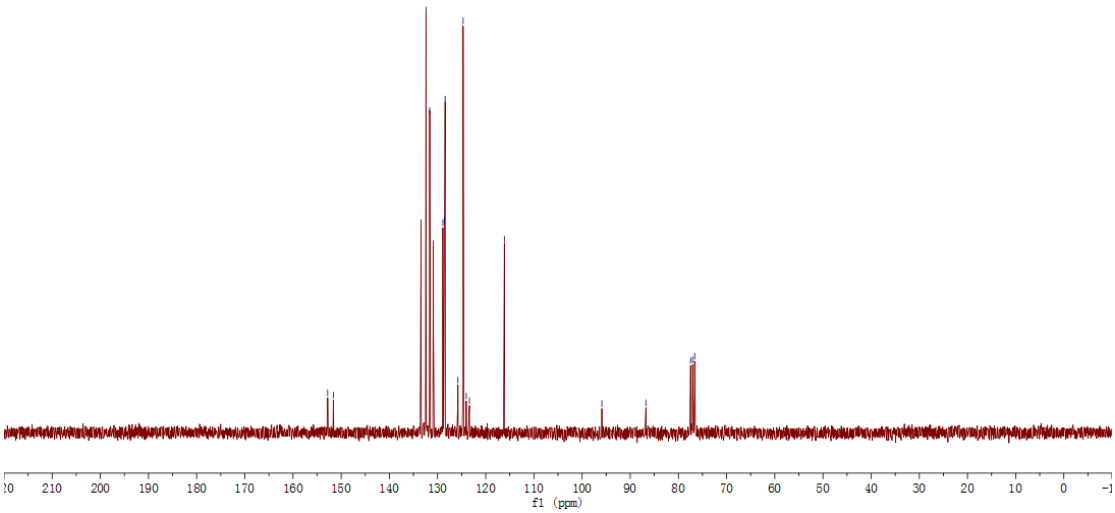
^{1}H NMR (300MHz $CDCl_3$)

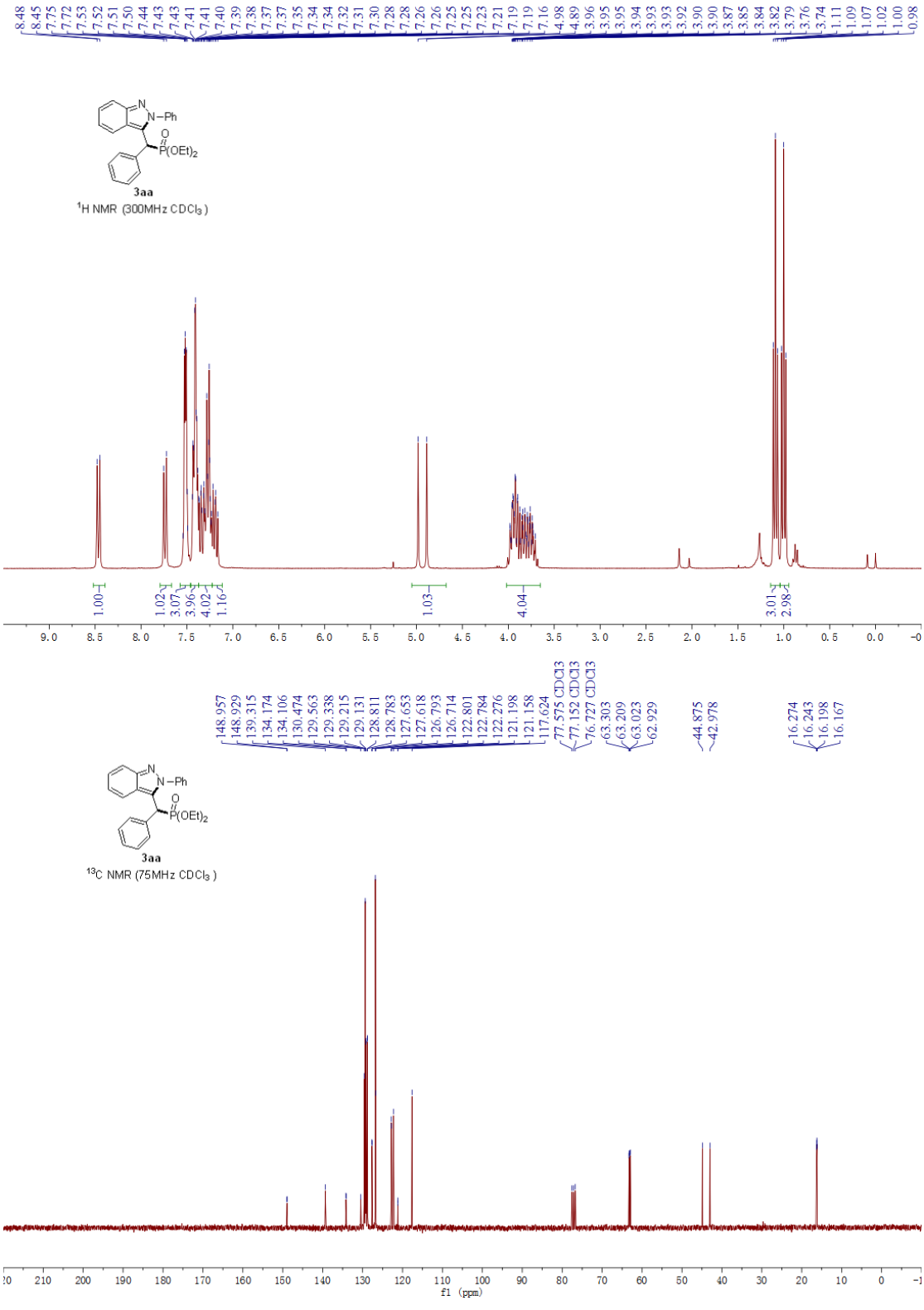


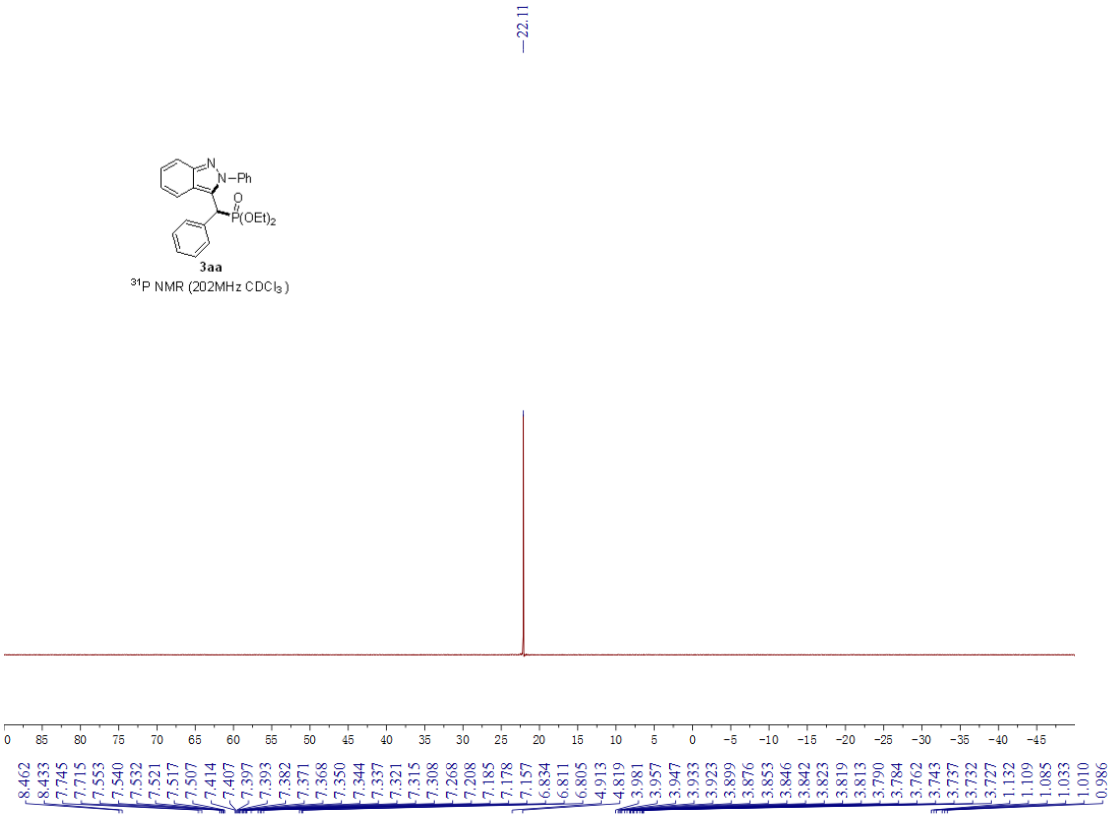


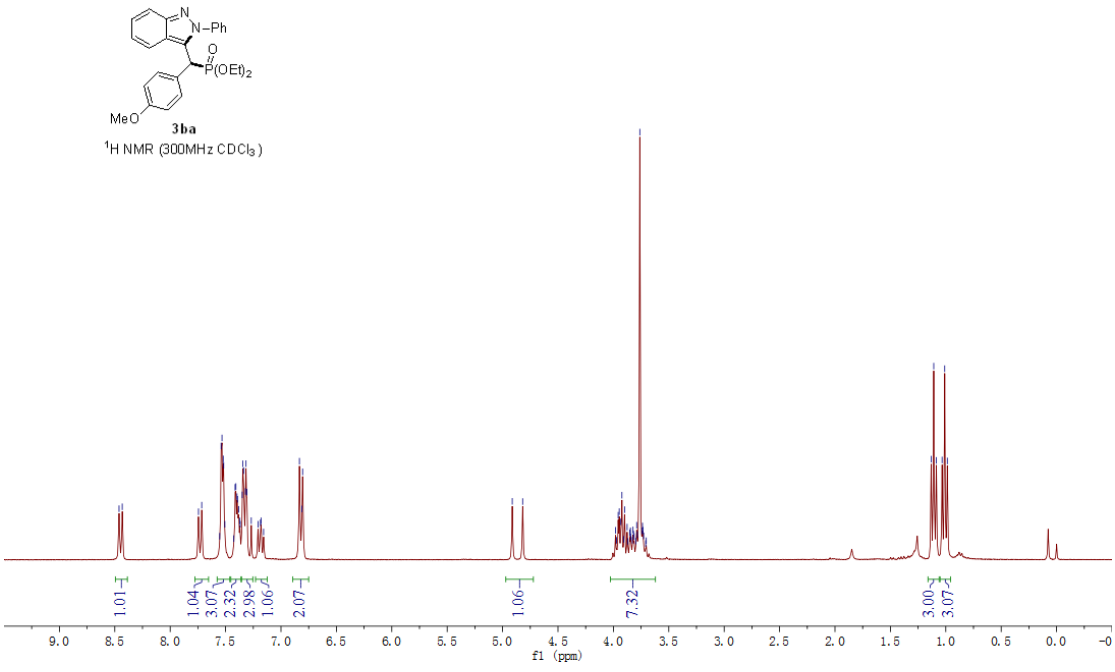
1t

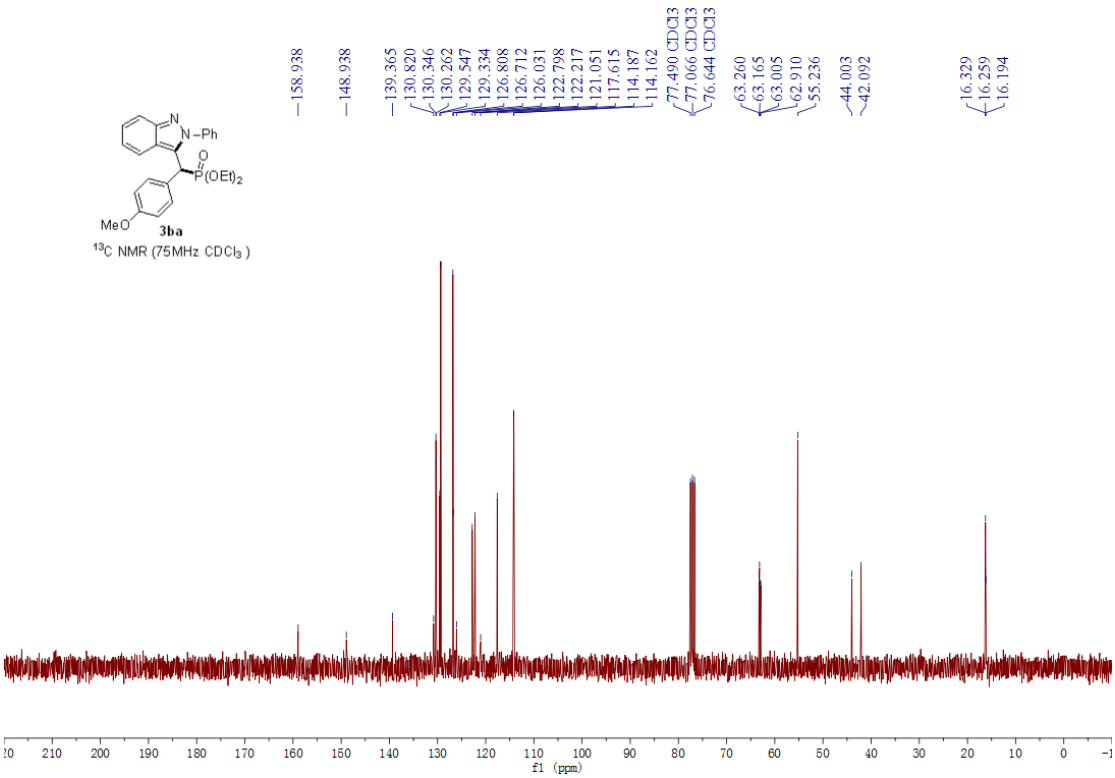
^{13}C NMR (75MHz $CDCl_3$)

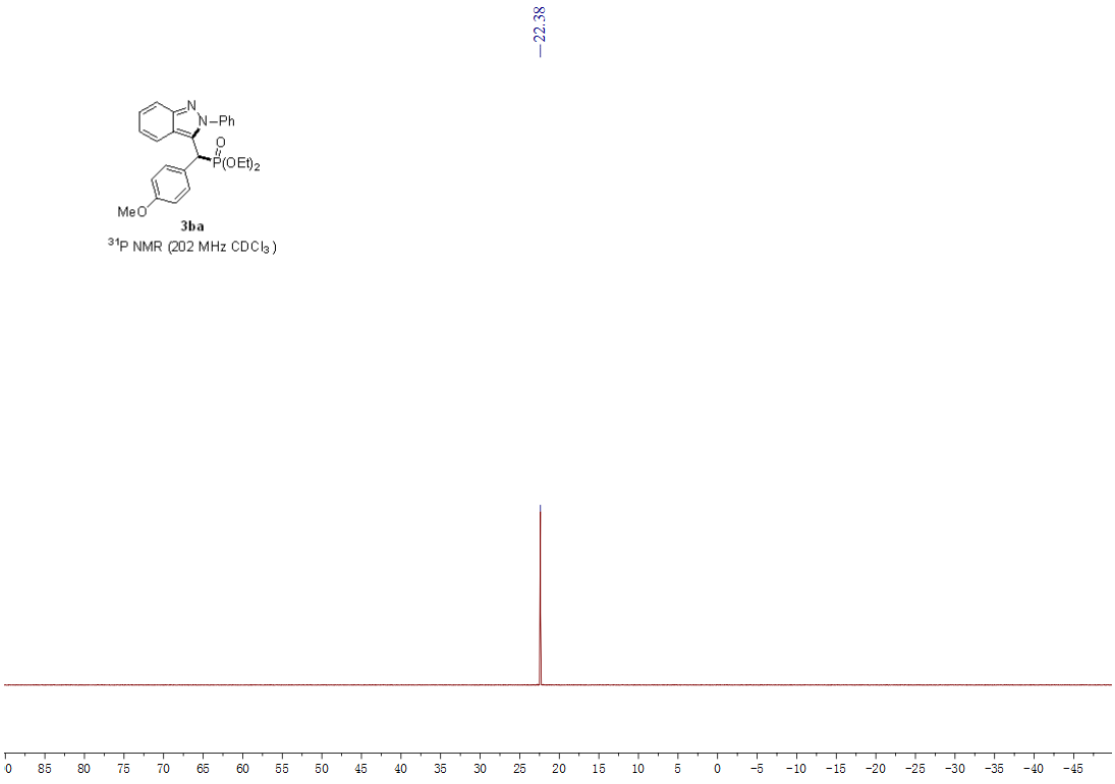


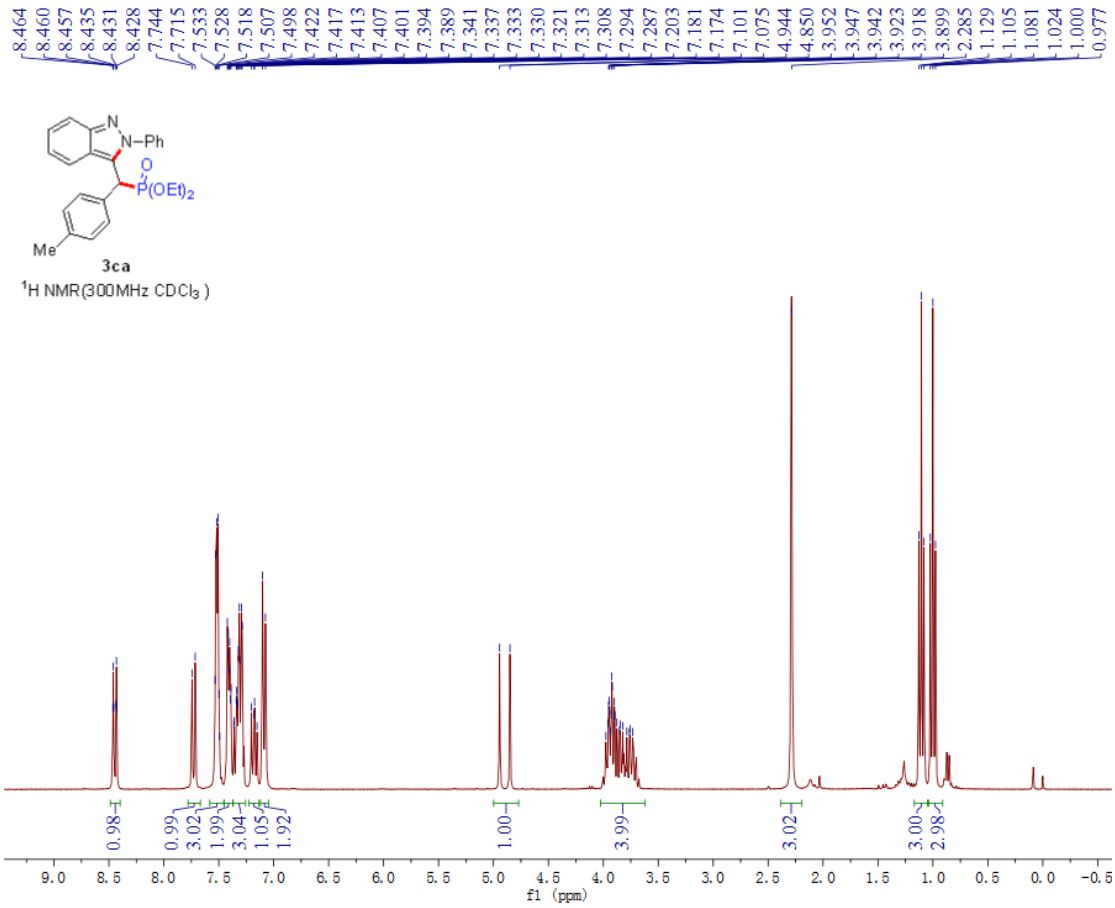

8.48 8.45 7.75 7.72 7.53 7.52 7.51 7.50 7.44 7.43 7.43 7.41 7.41 7.40 7.39 7.38 7.37 7.37 7.35 7.34 7.34 7.32 7.31 7.30 7.28 7.28 7.26 7.26 7.25 7.25 7.23 7.21 7.19 7.19 7.16 4.98 4.89 3.96 3.95 3.95 3.94 3.93 3.93 3.92 3.90 3.90 3.87 3.85 3.84 3.82 3.79 3.76 3.74 1.11 1.09 1.07 1.02 1.00 0.98
N–Ph
O
P(OEt)2
3aa
1H NMR (300MHz CDCl3)
1.00 1.02 3.07 3.96 4.02 1.16 1.03 4.04 3.01 2.98
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
148.957 148.929 139.315 134.174 134.106 130.474 129.563 129.338 129.215 129.131 128.811 128.783 127.653 127.618 126.793 126.714 122.801 122.784 122.276 121.198 121.158 117.624 77.575 CDCl3 77.152 CDCl3 76.727 CDCl3 63.303 63.209 63.023 62.929 44.875 42.978 16.274 16.243 16.198 16.167
N–Ph
O
P(OEt)2
3aa
13C NMR (75MHz CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

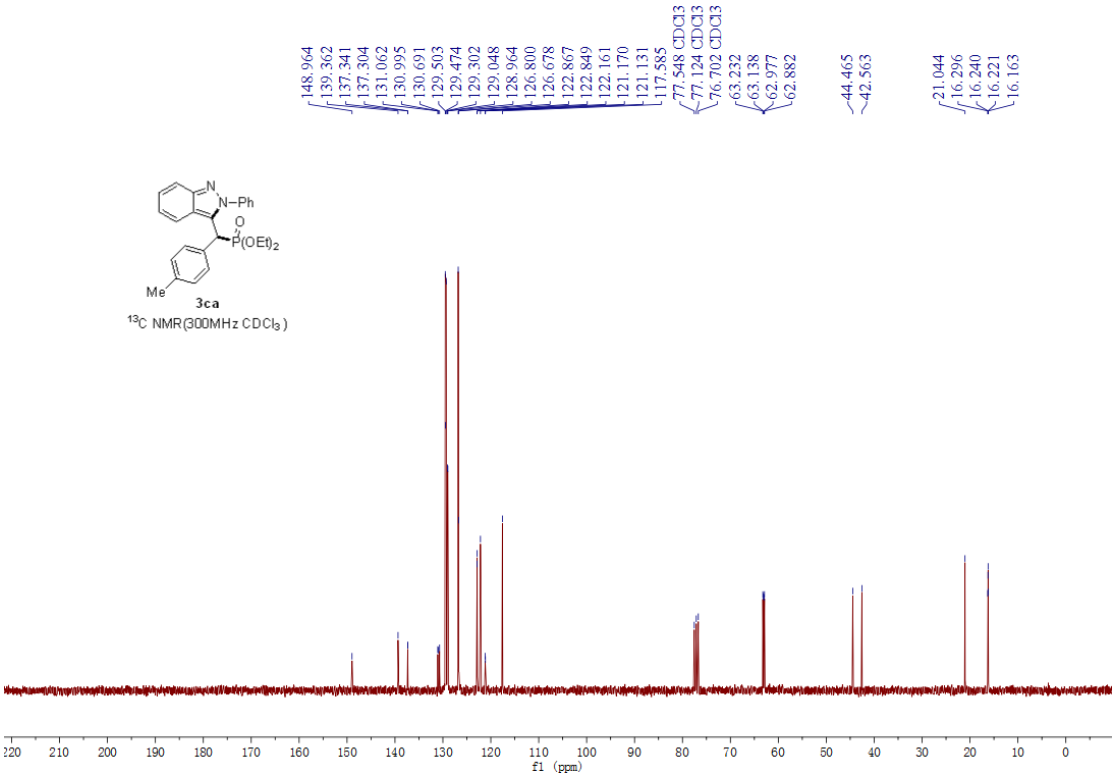

22.11
N–Ph
O
P(OEt)2
3aa
31P NMR (202MHz CDCl3)
8.462
8.433
7.745
7.715
7.553
7.540
7.532
7.521
7.517
7.507
7.414
7.407
7.397
7.393
7.382
7.371
7.368
7.350
7.344
7.337
7.321
7.315
7.308
7.268
7.208
7.185
7.178
7.157
6.834
6.811
6.805
4.913
4.819
3.981
3.957
3.947
3.933
3.923
3.899
3.876
3.853
3.846
3.842
3.823
3.819
3.813
3.790
3.784
3.762
3.743
3.737
3.732
3.727
1.132
1.109
1.085
1.033
1.010
0.986

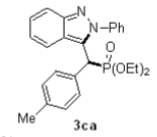

N–Ph
O
P(OEt)2
MeO
3ba
1H NMR (300MHz CDCl3)
1.01
1.04
3.07
2.32
2.98
1.06
2.07
1.06
7.32
3.00
3.07
f1 (ppm)


158.938
148.938
139.365
130.820
130.346
130.262
129.547
129.334
126.808
126.712
126.031
122.798
122.217
121.051
117.615
114.187
114.162
77.490 CDCl3
77.066 CDCl3
76.644 CDCl3
63.260
63.165
63.005
62.910
55.236
44.003
42.092
16.329
16.259
16.194
N
N–Ph
O
P(OEt)2
MeO
3ba
13C NMR (75MHz CDCl3)
f1 (ppm)


22.38
N
N–Ph
O
P(OEt)2
MeO
3ba
31P NMR (202 MHz CDCl3)

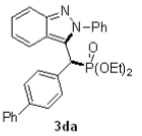

8.464
8.460
8.457
8.435
8.431
8.428
7.744
7.715
7.533
7.528
7.518
7.507
7.498
7.422
7.417
7.413
7.407
7.401
7.394
7.389
7.341
7.337
7.333
7.330
7.321
7.313
7.308
7.294
7.287
7.203
7.181
7.174
7.101
7.075
4.944
4.850
3.952
3.947
3.942
3.923
3.918
3.899
2.285
1.129
1.105
1.081
1.024
1.000
0.977
N
N–Ph
O
P(OEt)2
Me
3ca
1H NMR(300MHz CDCl3)
0.98
0.99
3.02
1.99
3.04
1.05
1.92
1.00
3.99
3.02
3.00
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


148.964
139.362
137.341
137.304
131.062
130.995
130.691
129.503
129.474
129.302
129.048
128.964
126.800
126.678
122.867
122.849
122.161
121.170
121.131
117.585
77.548 CDCl3
77.124 CDCl3
76.702 CDCl3
63.232
63.138
62.977
62.882
44.465
42.563
21.044
16.296
16.240
16.221
16.163
N
N–Ph
O
P(OEt)2
Me
3ca
13C NMR(300MHz CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



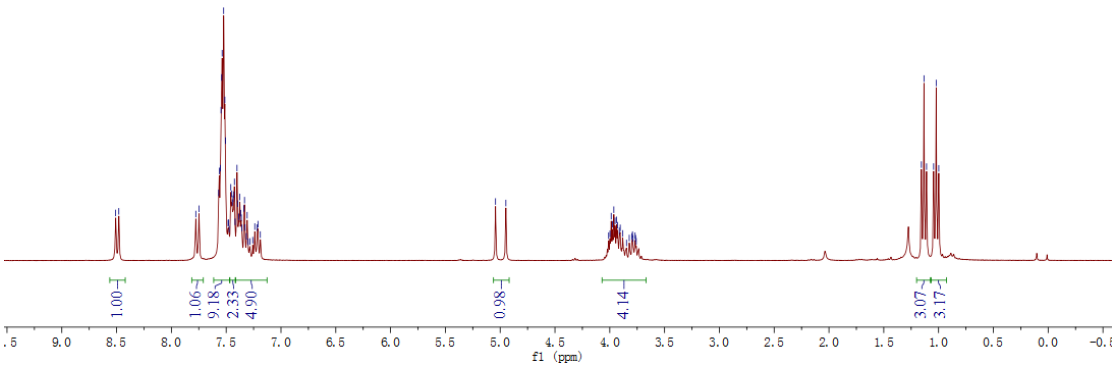
3ca

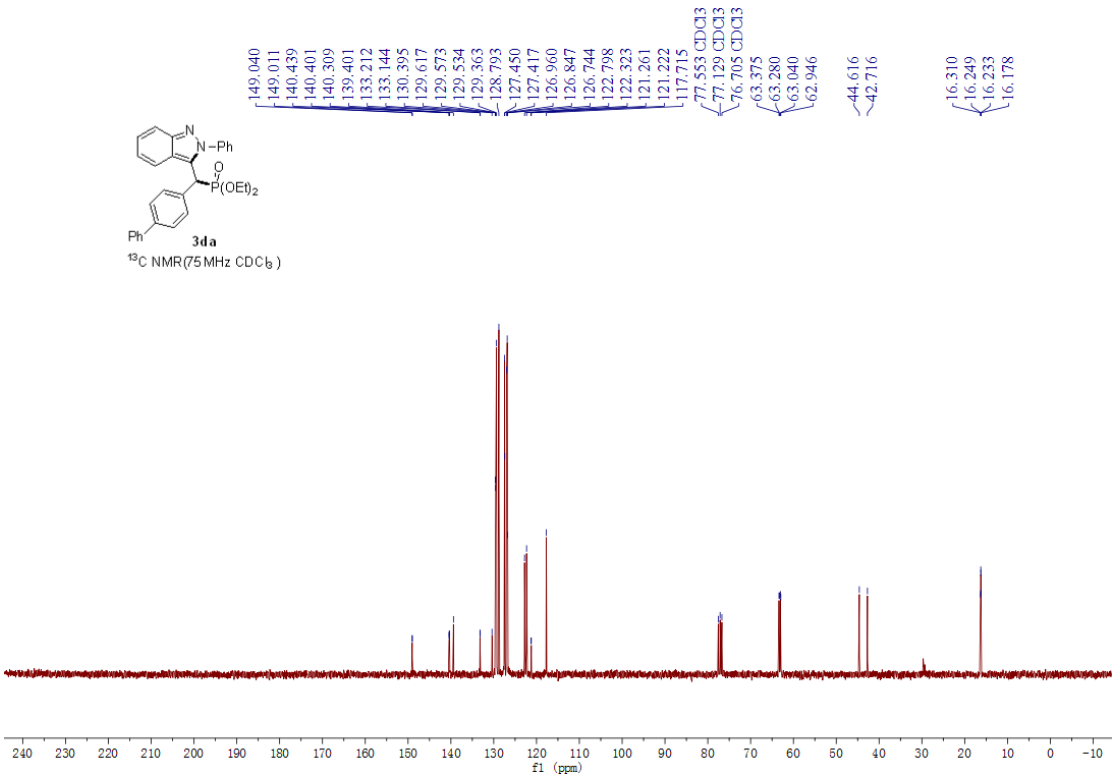
^{31}P NMR (202 MHz $CDCl_3$)

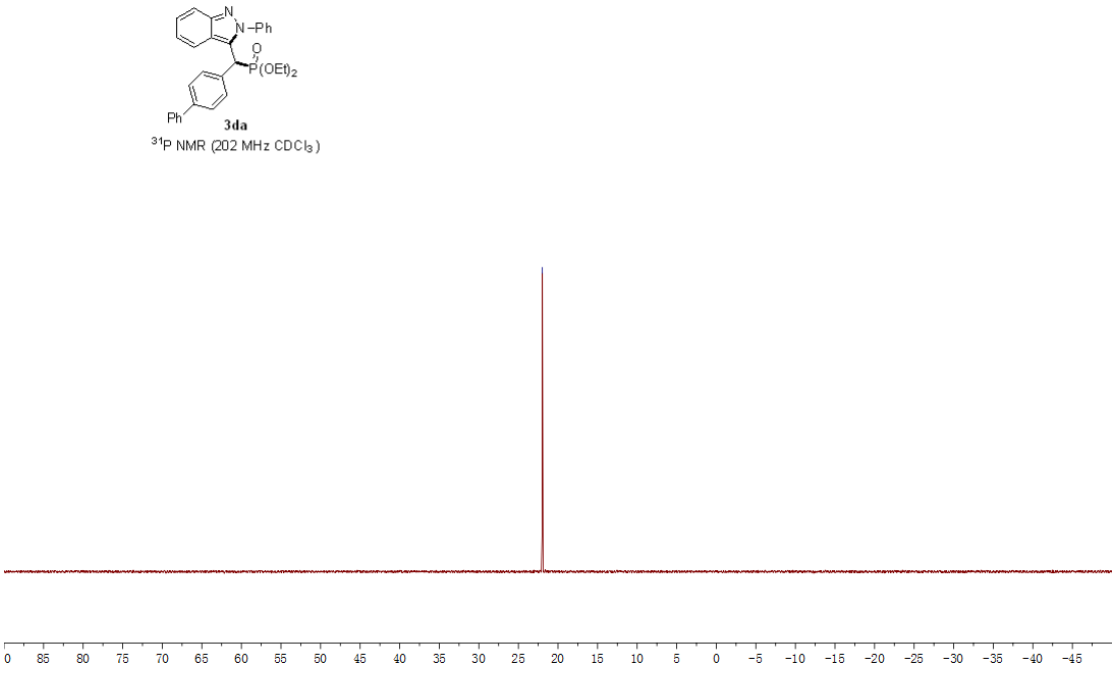


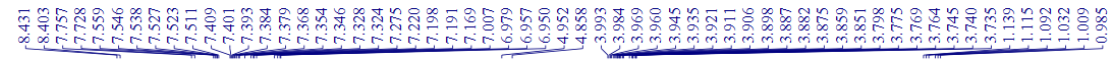
3da

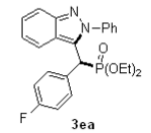
^{1}H NMR(300MHz $CDCl_3$)




149.040
149.011
140.439
140.401
140.309
139.401
133.212
133.144
130.395
129.617
129.573
129.534
129.363
128.793
127.450
127.417
126.960
126.847
126.744
122.798
122.323
121.261
121.222
117.715
77.553 CDCl3
77.129 CDCl3
76.705 CDCl3
63.375
63.280
63.040
62.946
44.616
42.716
16.310
16.249
16.233
16.178
N
N–Ph
O
P(OEt)2
Ph
3da
13C NMR(75 MHz CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

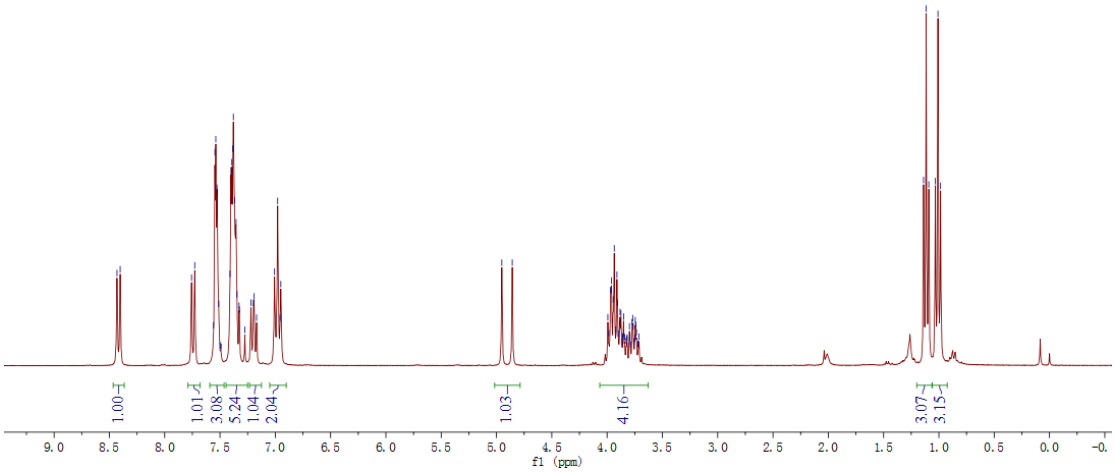

21.98
N
N–Ph
O
P(OEt)2
Ph
3da
31P NMR (202 MHz CDCl3)
0 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45

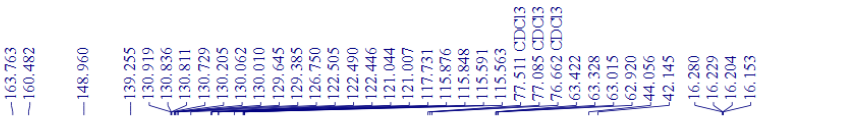


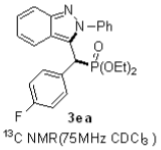


3ea

^{1}H NMR(300MHz $CDCl_3$)

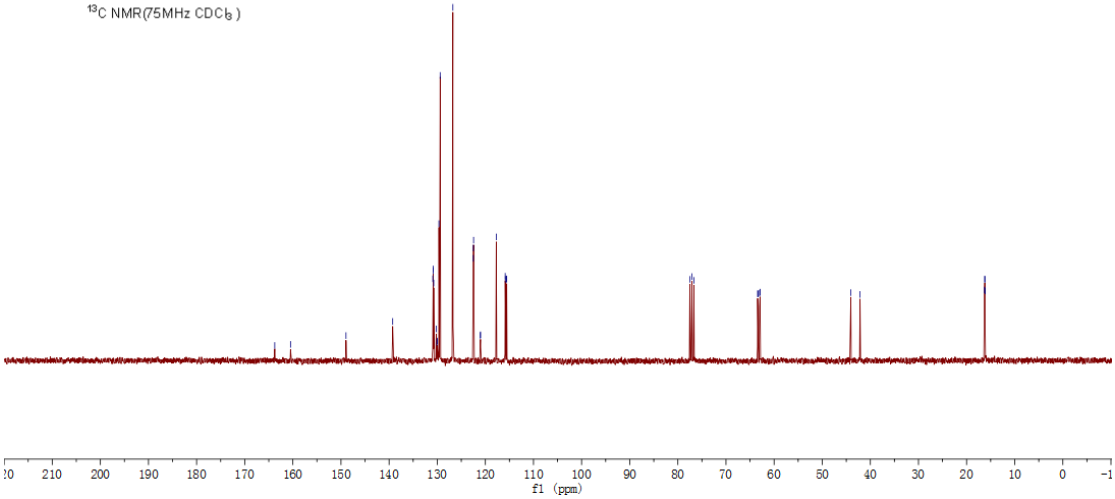


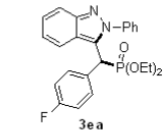




3ea

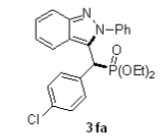
^{13}C NMR(75MHz $CDCl_3$)





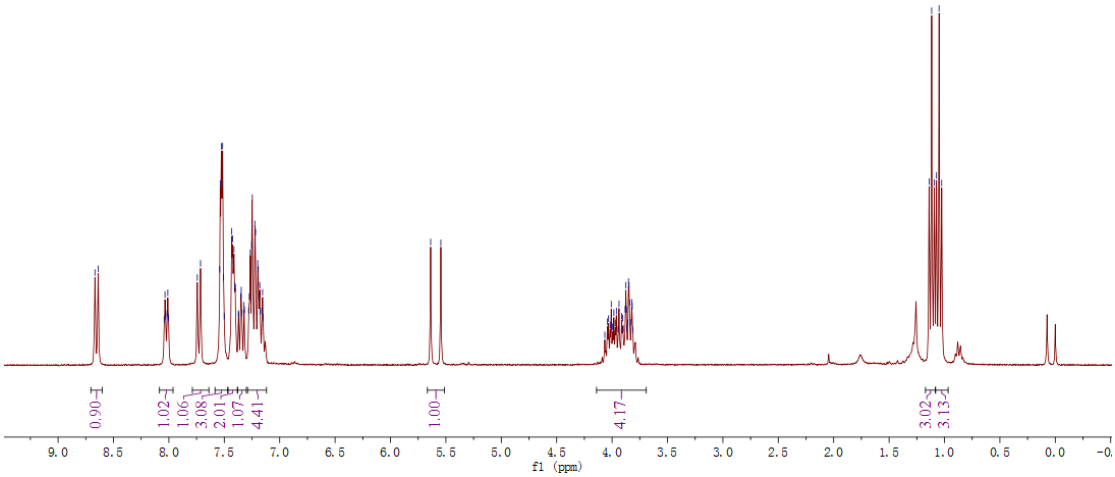
3ea

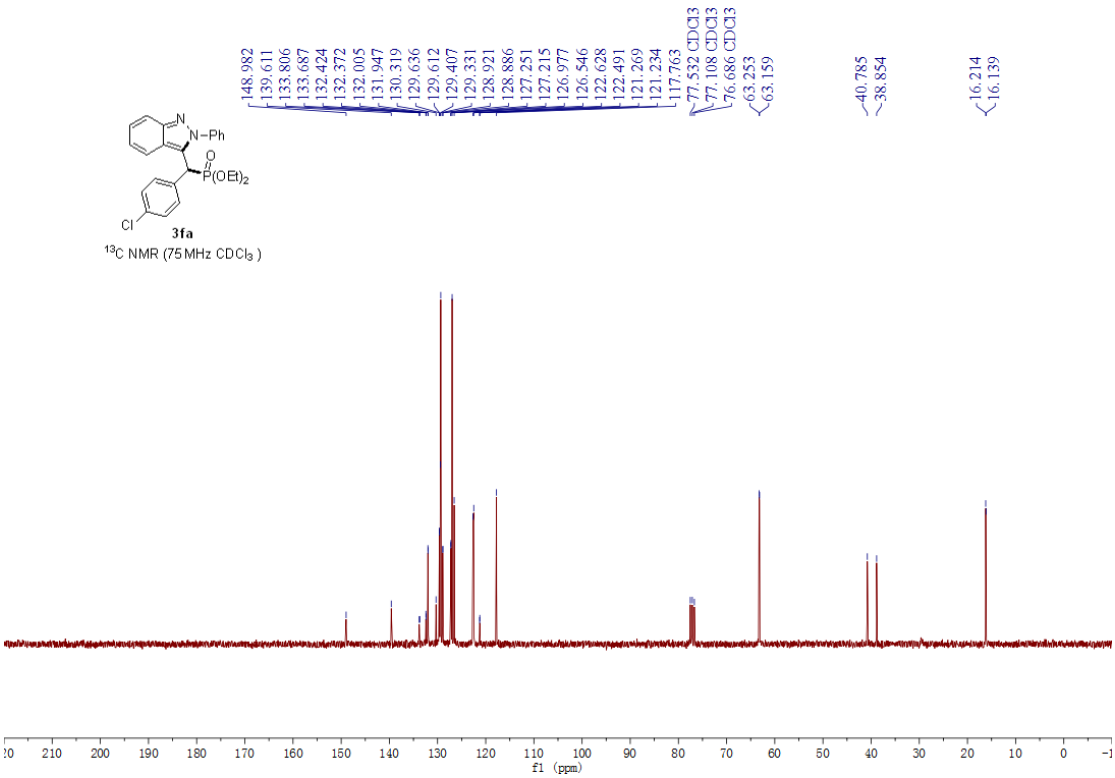
^{31}P NMR (202 MHz $CDCl_3$)

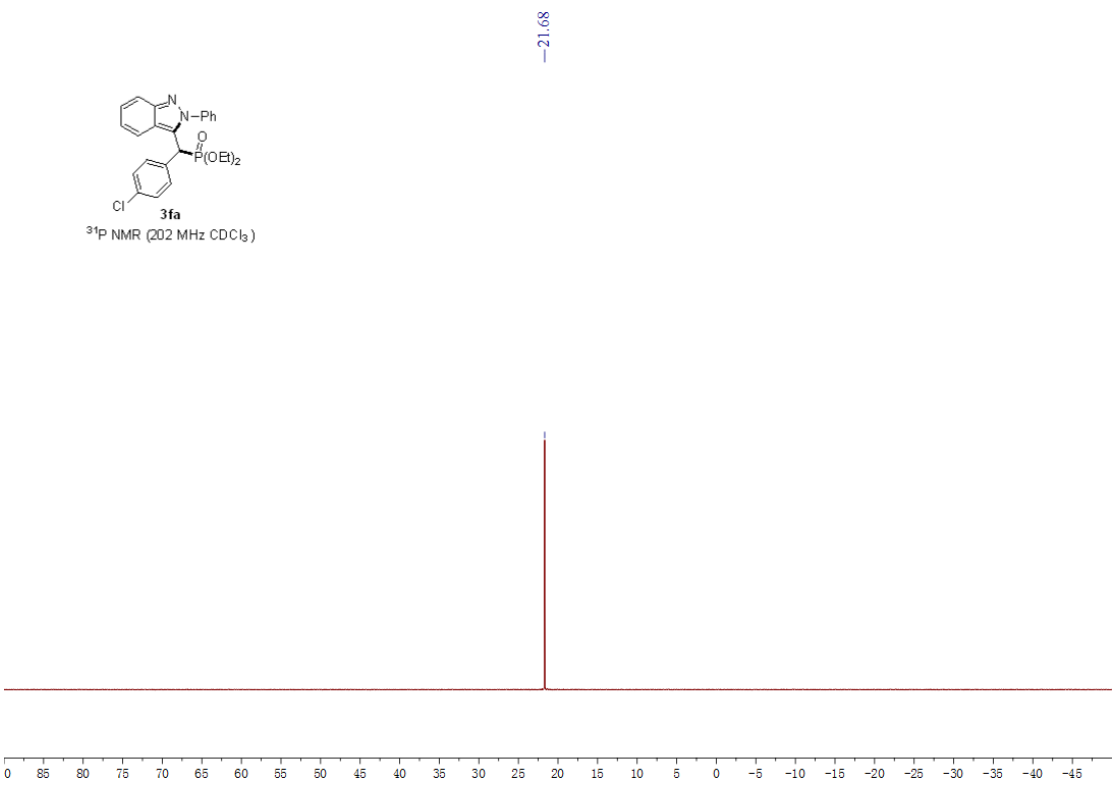


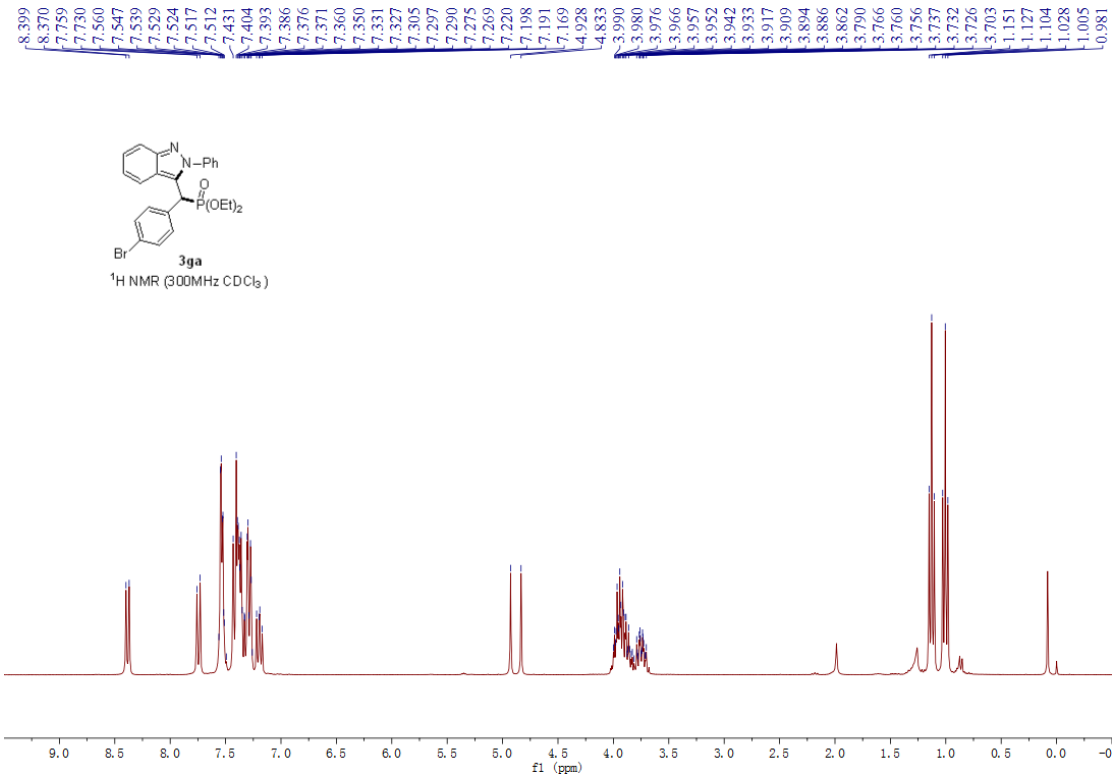
3fa

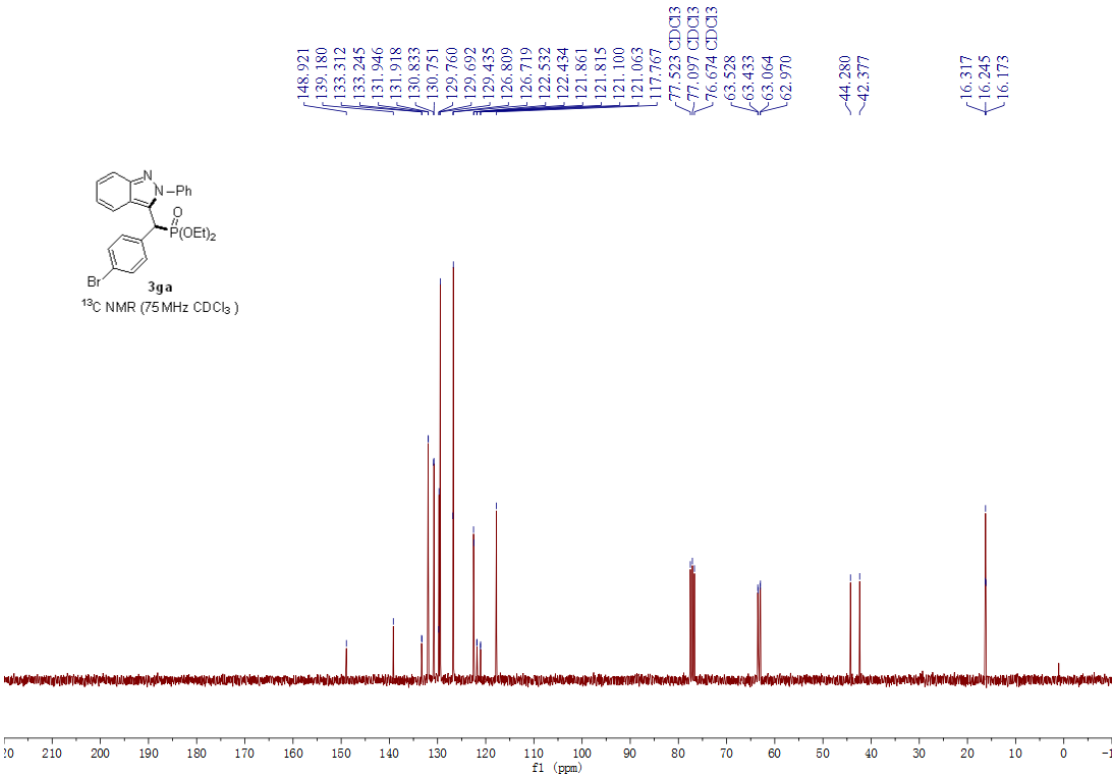
^{1}H NMR (300MHz $CDCl_3$)

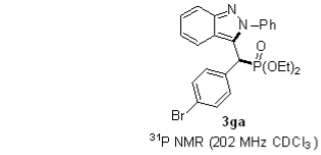



148.982
139.611
133.806
133.687
132.424
132.372
132.005
131.947
130.319
129.636
129.612
129.407
129.331
128.921
128.886
127.251
127.215
126.977
126.546
122.628
122.491
121.269
121.234
117.763
77.532 CDCl3
77.108 CDCl3
76.686 CDCl3
63.253
63.159
40.785
38.854
16.214
16.139
N
N–Ph
O
P(OEt)2
Cl
3fa
13C NMR (75 MHz CDCl3)
f1 (ppm)


21.68
N
N–Ph
O
P(OEt)2
Cl
3fa
31P NMR (202 MHz CDCl3)

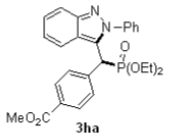

8.399
8.370
7.759
7.730
7.560
7.547
7.539
7.529
7.524
7.517
7.512
7.431
7.404
7.393
7.386
7.376
7.371
7.360
7.350
7.331
7.327
7.305
7.297
7.290
7.275
7.269
7.220
7.198
7.191
7.169
4.928
4.833
3.990
3.980
3.976
3.966
3.957
3.952
3.942
3.933
3.917
3.909
3.894
3.886
3.862
3.790
3.766
3.760
3.756
3.737
3.732
3.726
3.703
1.151
1.127
1.104
1.028
1.005
0.981
N
N–Ph
O
P(OEt)2
Br
3ga
1H NMR (300MHz CDCl3)
f1 (ppm)


148.921
139.180
133.312
133.245
131.946
131.918
130.833
130.751
129.760
129.692
129.435
126.809
126.719
122.532
122.434
121.861
121.815
121.100
121.063
117.767
77.523 CDCl3
77.097 CDCl3
76.674 CDCl3
63.528
63.433
63.064
62.970
44.280
42.377
16.317
16.245
16.173
N
N–Ph
O
P(OEt)2
Br
3ga
13C NMR (75MHz CDCl3)
f1 (ppm)



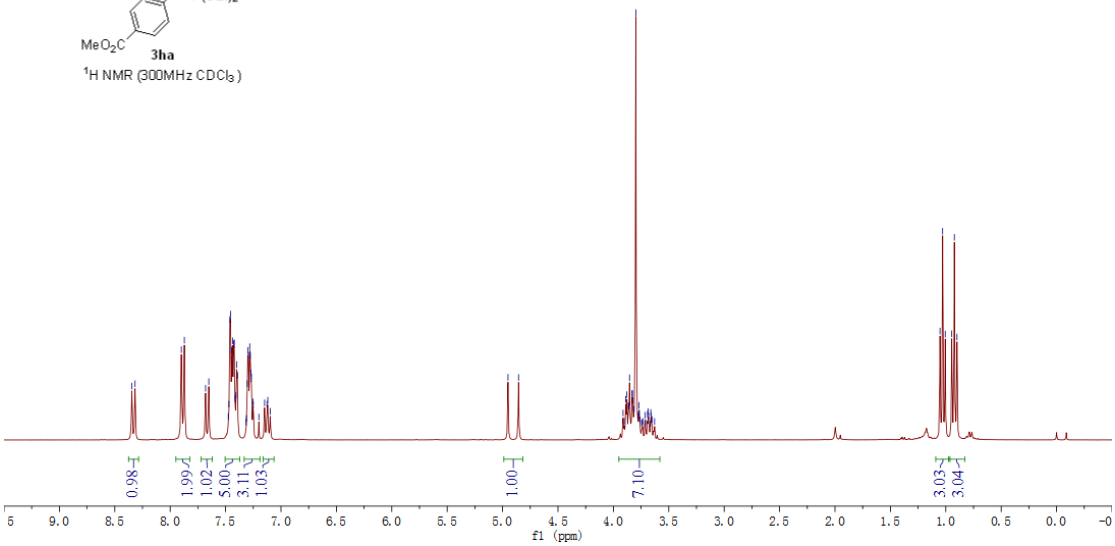
3ga

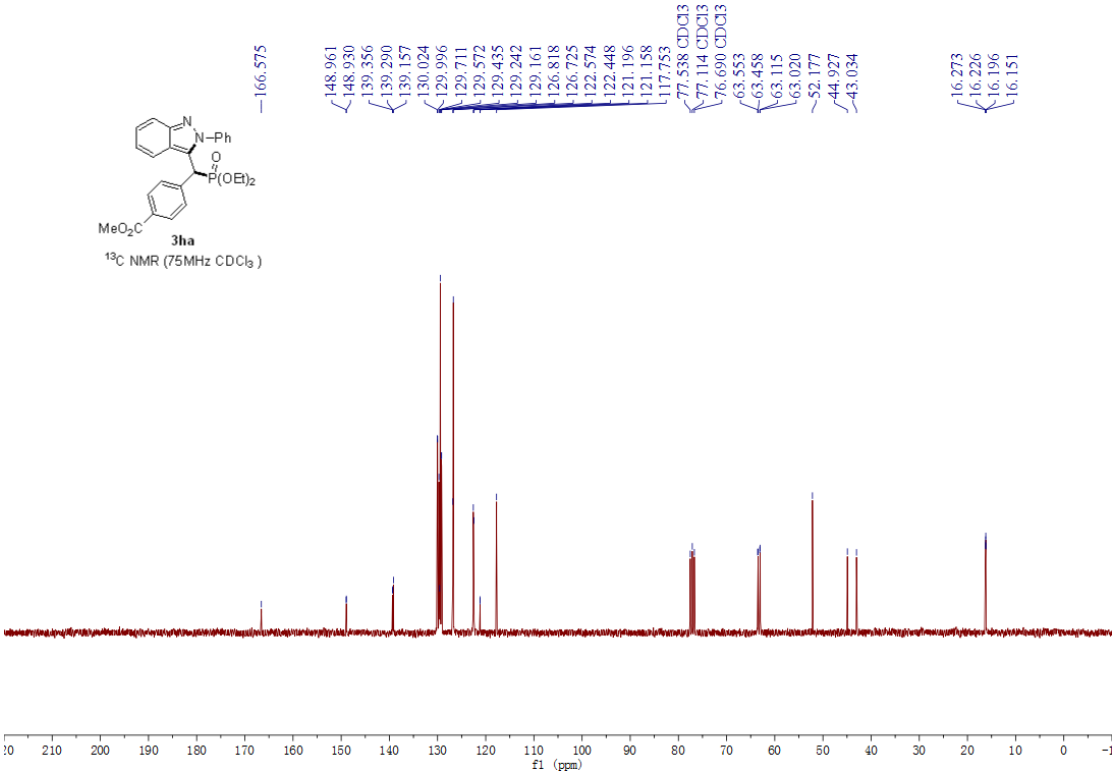
^{31}P NMR (202 MHz $CDCl_3$)

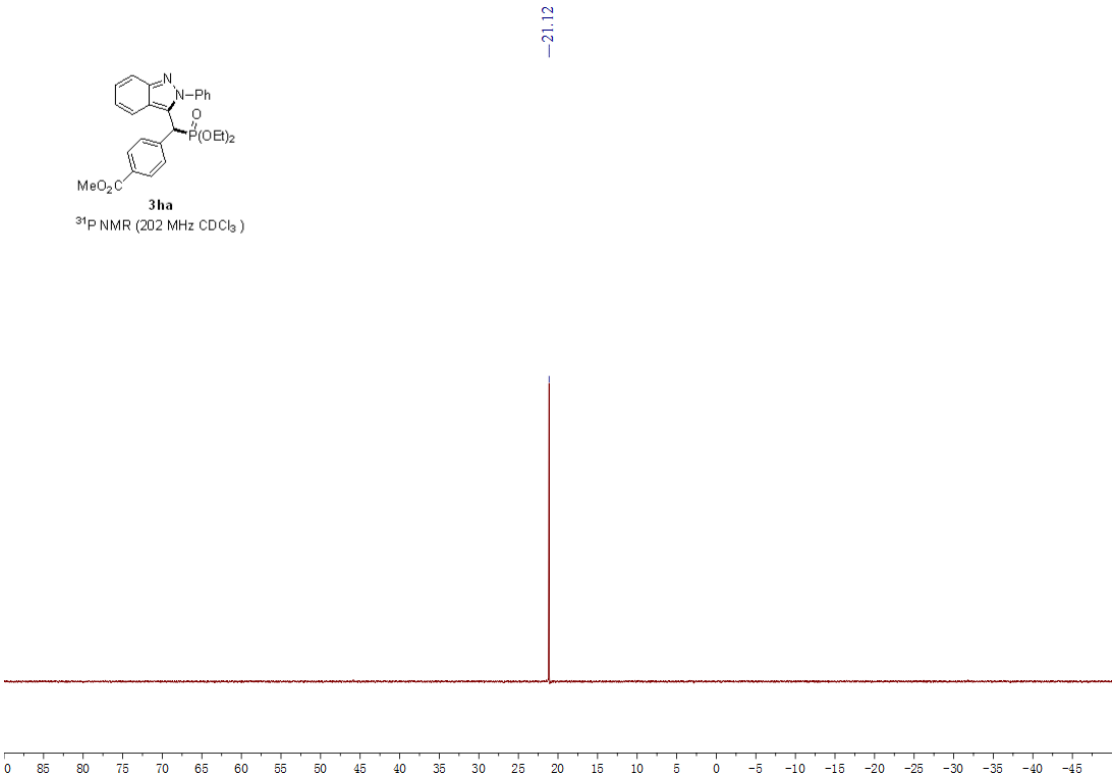


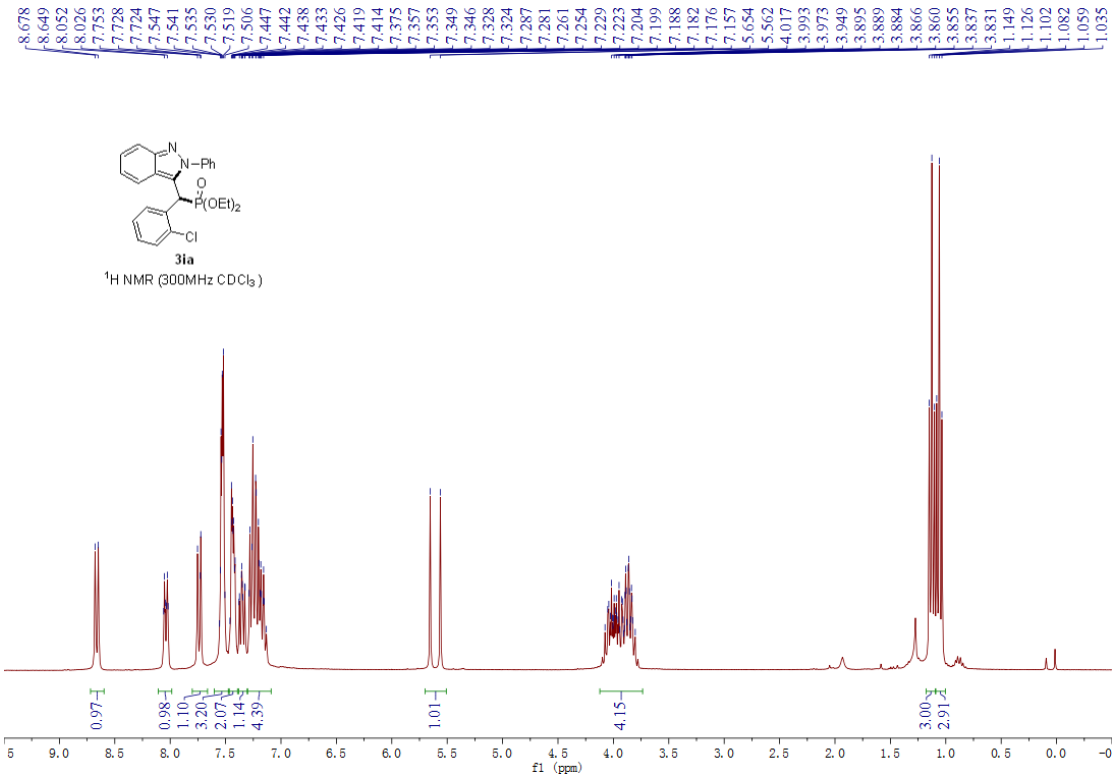
3ha

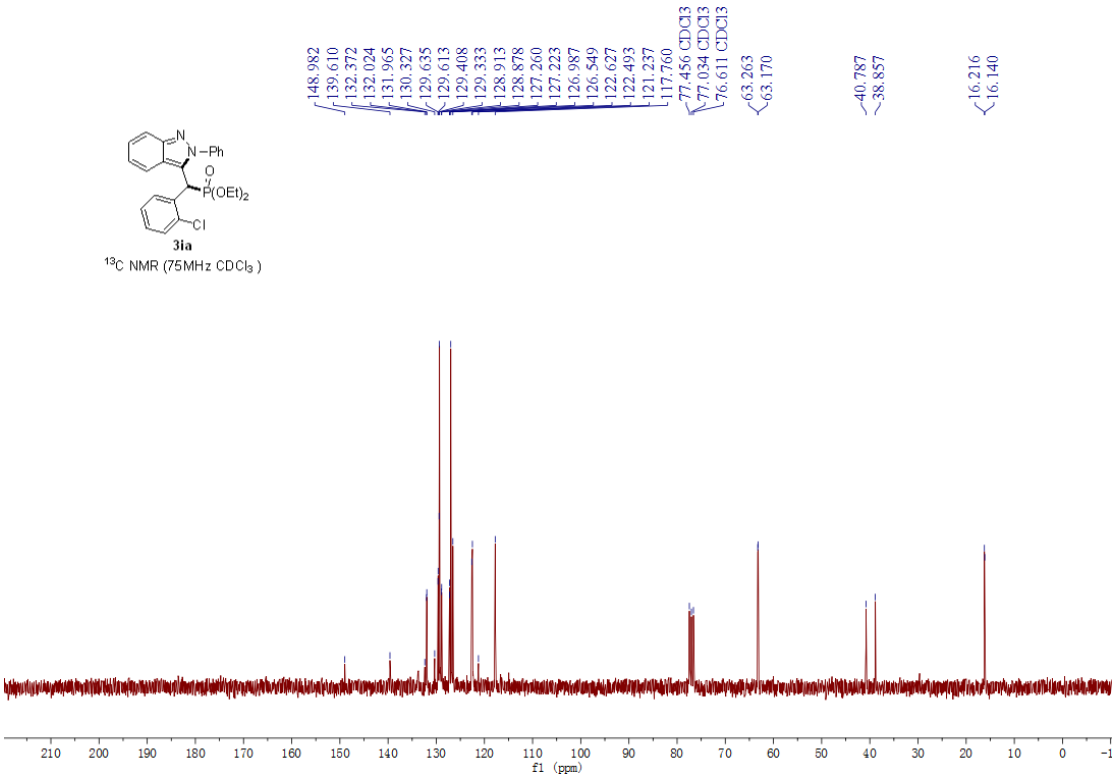
^{1}H NMR (300MHz $CDCl_3$)

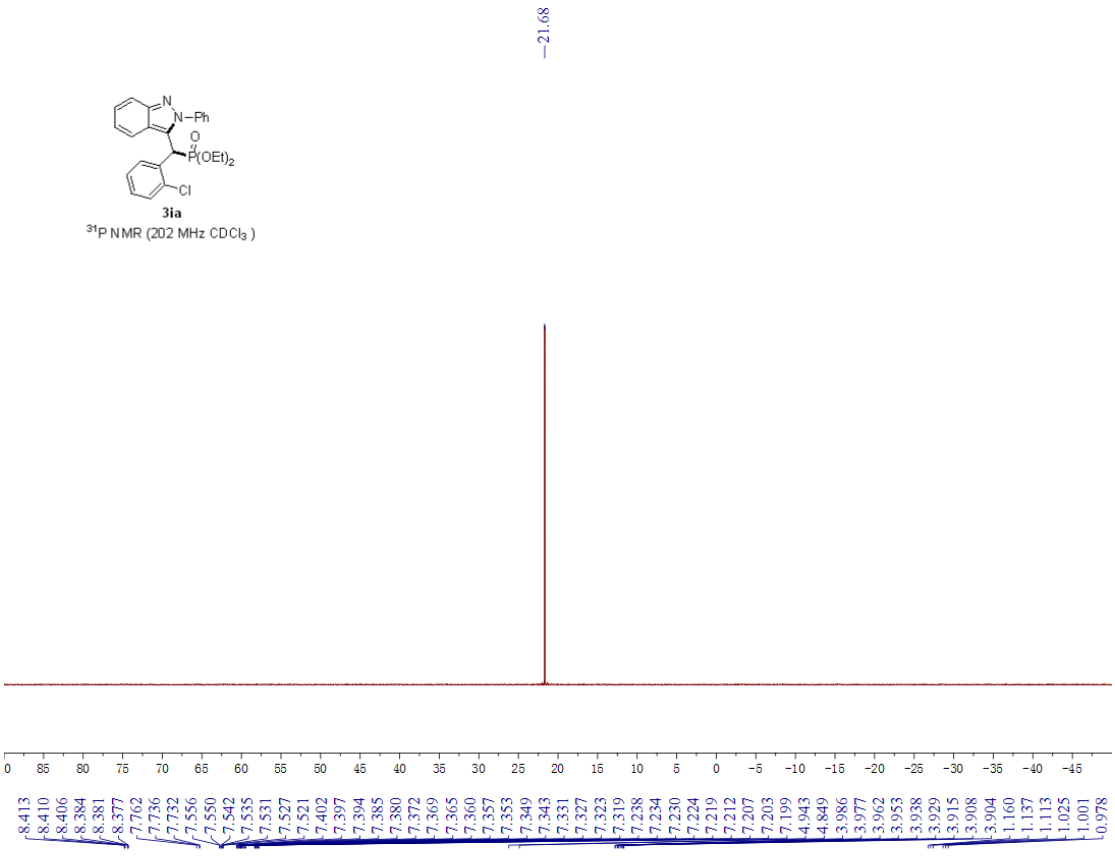


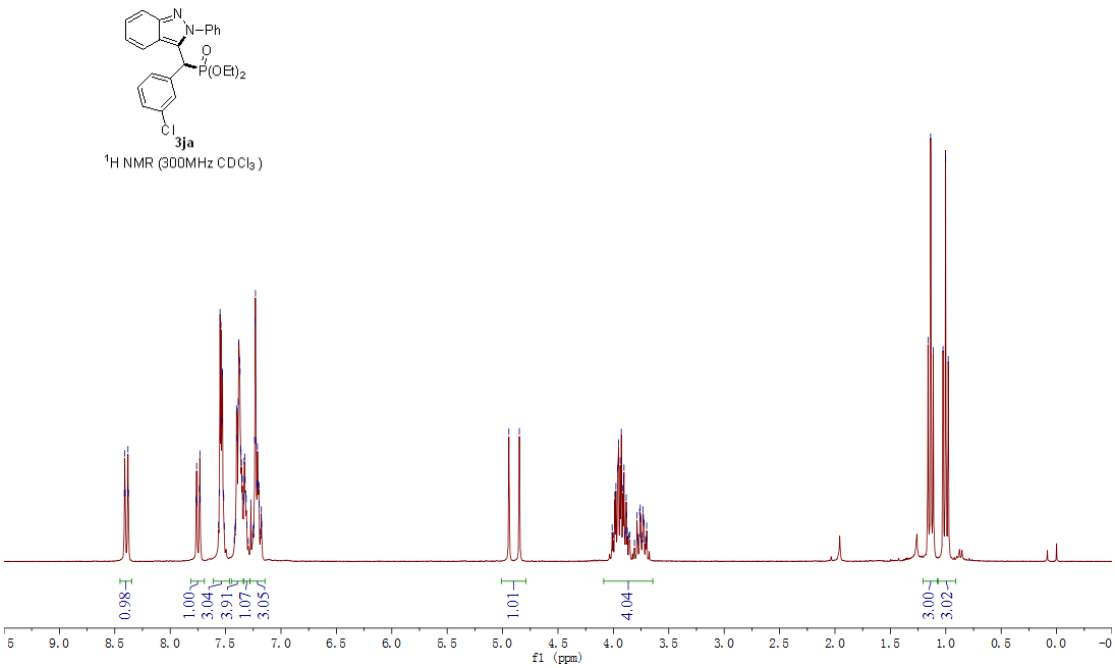

166.575
148.961
148.930
139.356
139.290
139.157
130.024
129.996
129.711
129.572
129.435
129.242
129.161
126.818
126.725
122.574
122.448
121.196
121.158
117.753
77.538 CDCl3
77.114 CDCl3
76.690 CDCl3
63.553
63.458
63.115
63.020
52.177
44.927
43.034
16.273
16.226
16.196
16.151
N
N–Ph
O
P(OEt)2
MeO2C
3ha
13C NMR (75MHz CDCl3)
f1 (ppm)

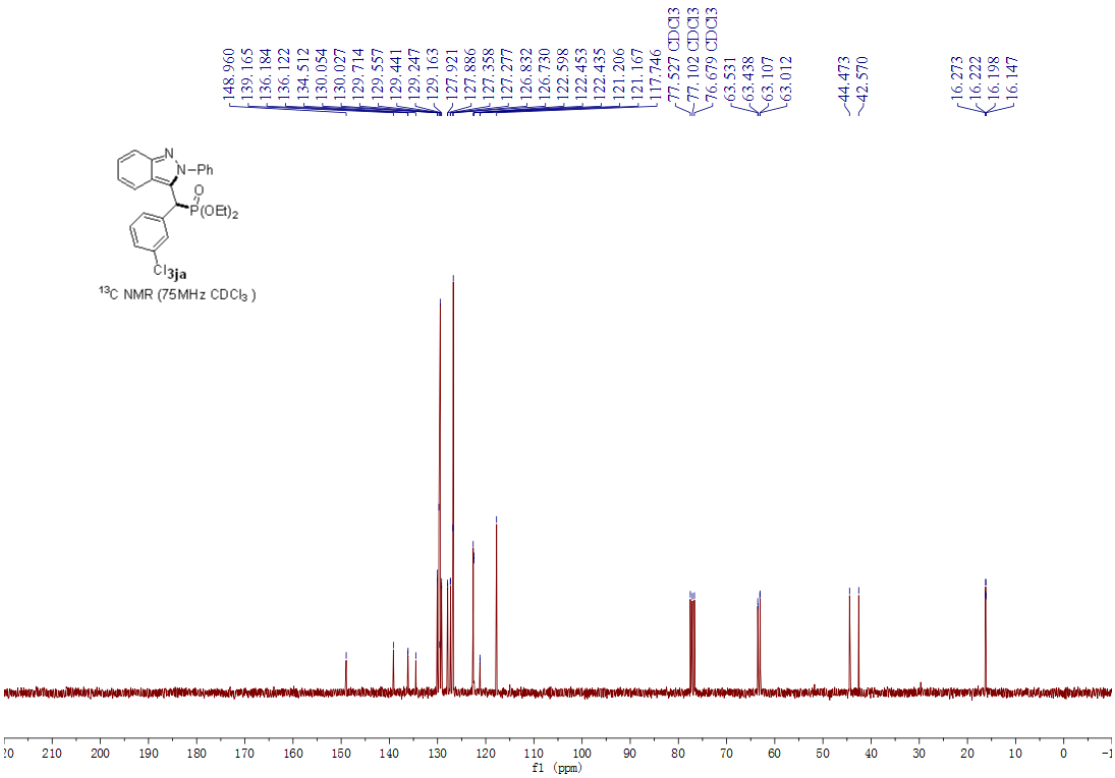

21.12
N
N–Ph
O
P(OEt)2
MeO2C
3ha
31P NMR (202 MHz CDCl3)

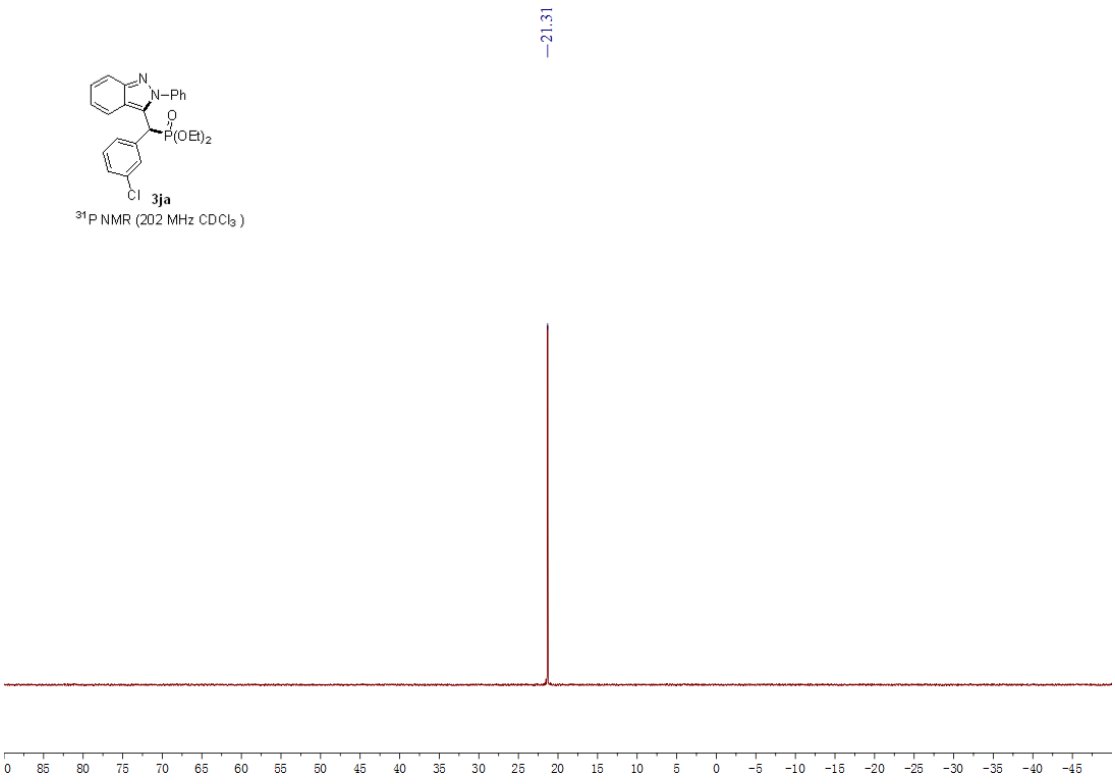

8.678
8.649
8.052
8.026
7.753
7.728
7.724
7.547
7.541
7.535
7.530
7.519
7.506
7.447
7.442
7.438
7.433
7.426
7.419
7.414
7.375
7.357
7.353
7.349
7.346
7.328
7.324
7.287
7.281
7.261
7.254
7.229
7.223
7.204
7.199
7.188
7.182
7.176
7.157
5.654
5.562
4.017
3.993
3.973
3.949
3.895
3.889
3.884
3.866
3.860
3.855
3.837
3.831
1.149
1.126
1.102
1.082
1.059
1.035
N
N–Ph
O
P(OEt)2
Cl
3ia
1H NMR (300MHz CDCl3)
0.97
0.98
1.10
3.20
2.07
1.14
4.39
1.01
4.15
3.00
2.91
f1 (ppm)

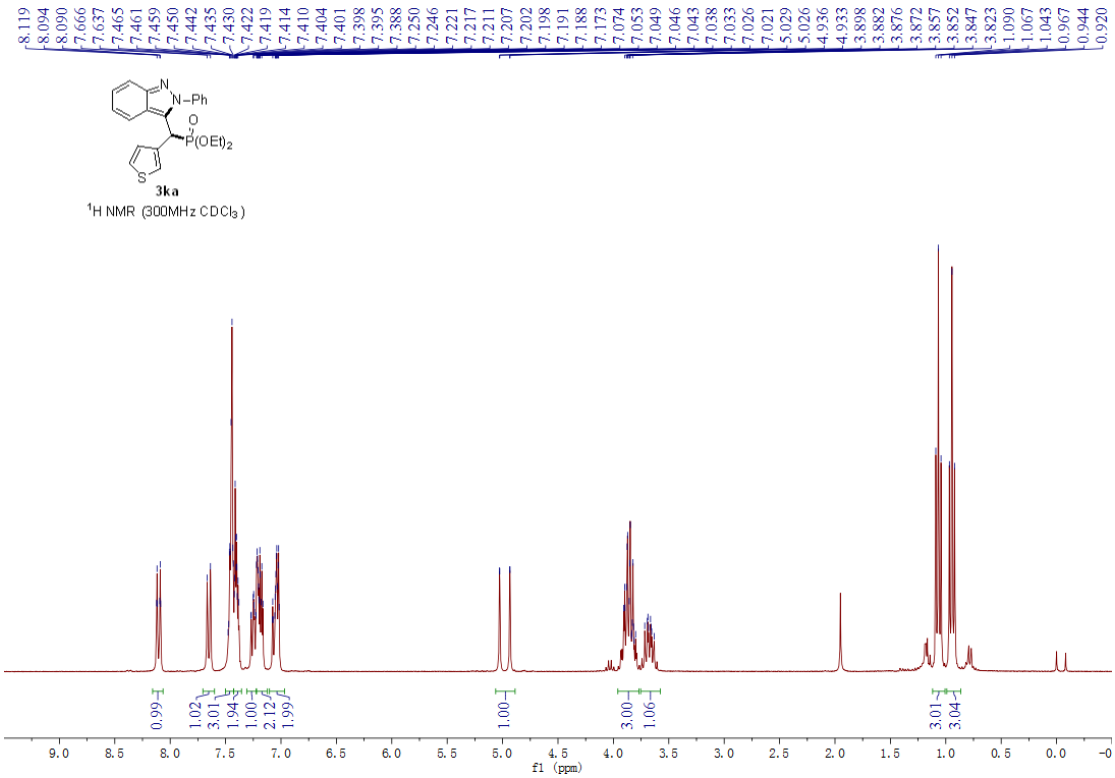

148.982
139.610
132.372
132.024
131.965
130.327
129.635
129.613
129.408
129.333
128.913
128.878
127.260
127.223
126.987
126.549
122.627
122.493
121.237
117.760
77.456 CDCl3
77.034 CDCl3
76.611 CDCl3
63.263
63.170
40.787
38.857
16.216
16.140
N
N–Ph
O
P(OEt)2
Cl
3ia
13C NMR (75MHz CDCl3)
f1 (ppm)

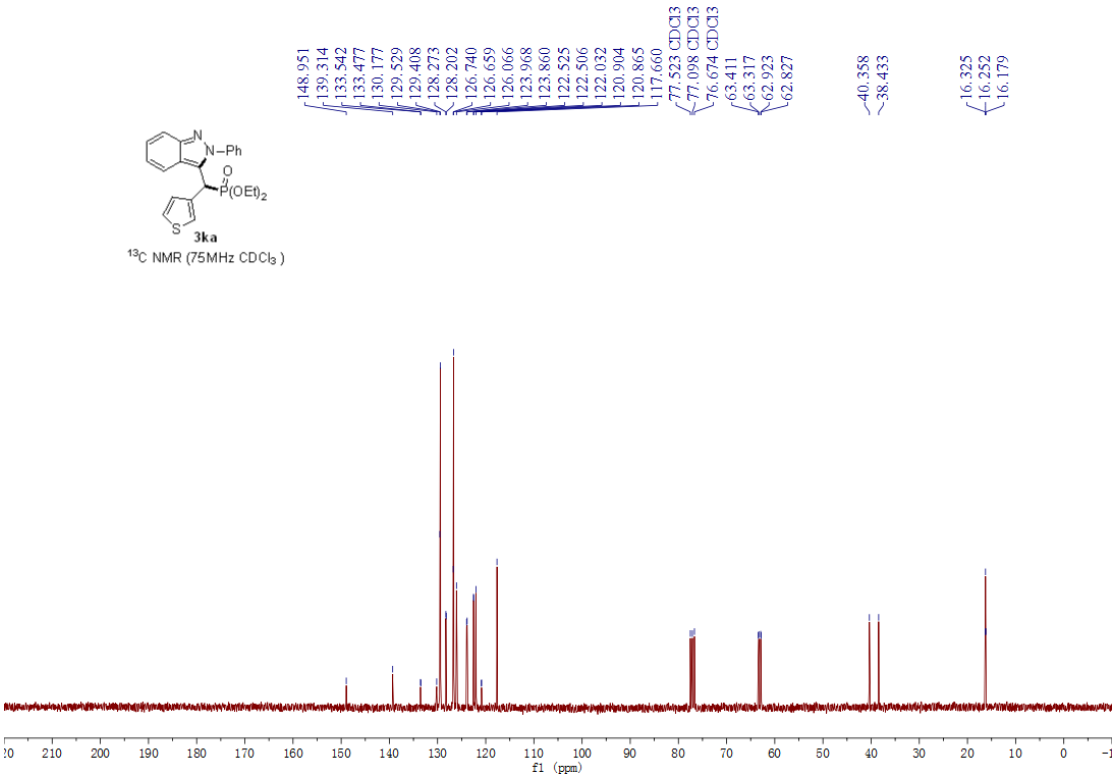

21.68
N
N–Ph
O
P(OEt)2
Cl
3ia
31P NMR (202 MHz CDCl3)
8.413
8.410
8.406
8.384
8.381
8.377
7.762
7.736
7.732
7.556
7.550
7.542
7.535
7.531
7.527
7.521
7.402
7.397
7.394
7.385
7.380
7.372
7.369
7.365
7.360
7.357
7.353
7.349
7.343
7.331
7.327
7.323
7.319
7.238
7.234
7.230
7.224
7.219
7.212
7.207
7.203
7.199
4.943
4.849
3.986
3.977
3.962
3.953
3.938
3.929
3.915
3.908
3.904
1.160
1.137
1.113
1.025
1.001
0.978

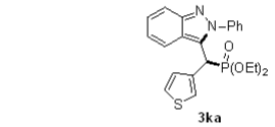

N
N–Ph
O
P(OEt)2
Cl
3ja
1H NMR (300MHz CDCl3)
0.98
1.00
3.04
3.91
1.07
3.05
1.01
4.04
3.00
3.02
f1 (ppm)


148.960
139.165
136.184
136.122
134.512
130.054
130.027
129.714
129.557
129.441
129.247
129.163
127.921
127.886
127.358
127.277
126.832
126.730
122.598
122.453
122.435
121.206
121.167
117.746
77.527 CDCl3
77.102 CDCl3
76.679 CDCl3
63.531
63.438
63.107
63.012
44.473
42.570
16.273
16.222
16.198
16.147
N
N–Ph
O
P(OEt)2
Cl
3ja
13C NMR (75MHz CDCl3)
f1 (ppm)


21.31
N
N–Ph
O
P(OEt)2
Cl
3ja
31P NMR (202 MHz CDCl3)

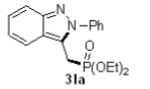

8.119
8.094
8.090
7.666
7.637
7.465
7.461
7.459
7.450
7.442
7.435
7.430
7.422
7.419
7.414
7.410
7.404
7.401
7.398
7.395
7.388
7.250
7.246
7.221
7.217
7.211
7.207
7.202
7.198
7.191
7.188
7.173
7.074
7.053
7.049
7.046
7.043
7.038
7.033
7.026
7.021
5.029
5.026
4.936
4.933
3.898
3.882
3.876
3.872
3.857
3.852
3.847
3.823
1.090
1.067
1.043
0.967
0.944
0.920
N–Ph
O
P(OEt)2
S
3ka
1H NMR (300MHz CDCl3)
0.99
1.02
3.01
1.94
1.00
2.12
1.99
1.00
3.00
1.06
3.01
3.04
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)


148.951
139.314
133.542
133.477
130.177
129.529
129.408
128.273
128.202
126.740
126.659
126.066
123.968
123.860
122.525
122.506
122.032
120.904
120.865
117.660
77.523 CDCl3
77.098 CDCl3
76.674 CDCl3
63.411
63.317
62.923
62.827
40.358
38.433
16.325
16.252
16.179
N–Ph
O
P(OEt)2
S
3ka
13C NMR (75MHz CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



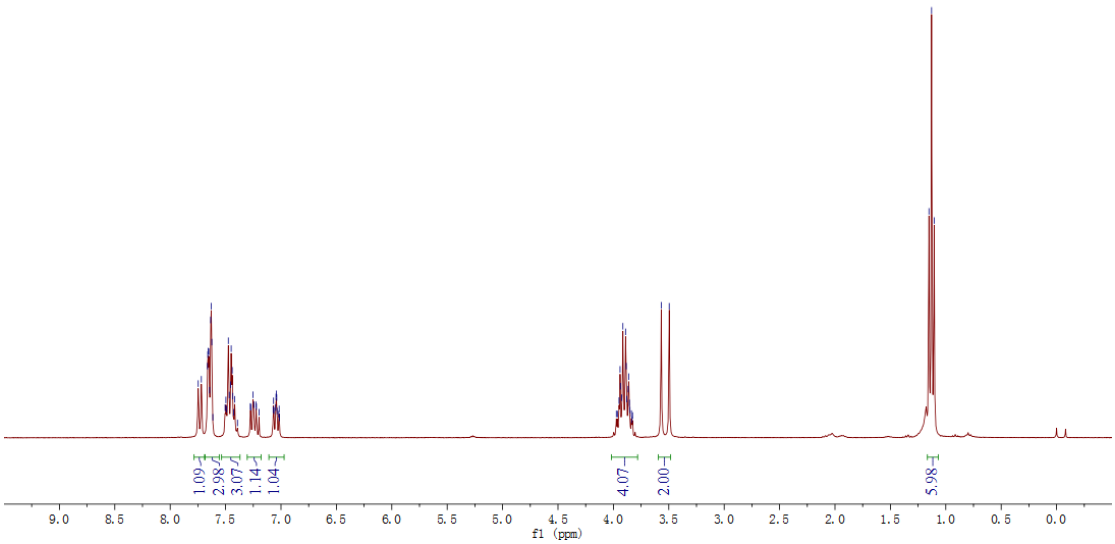
3ka

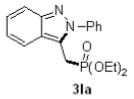
^{31}P NMR (202 MHz $CDCl_3$)



3la

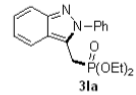
^{1}H NMR (300MHz $CDCl_3$)





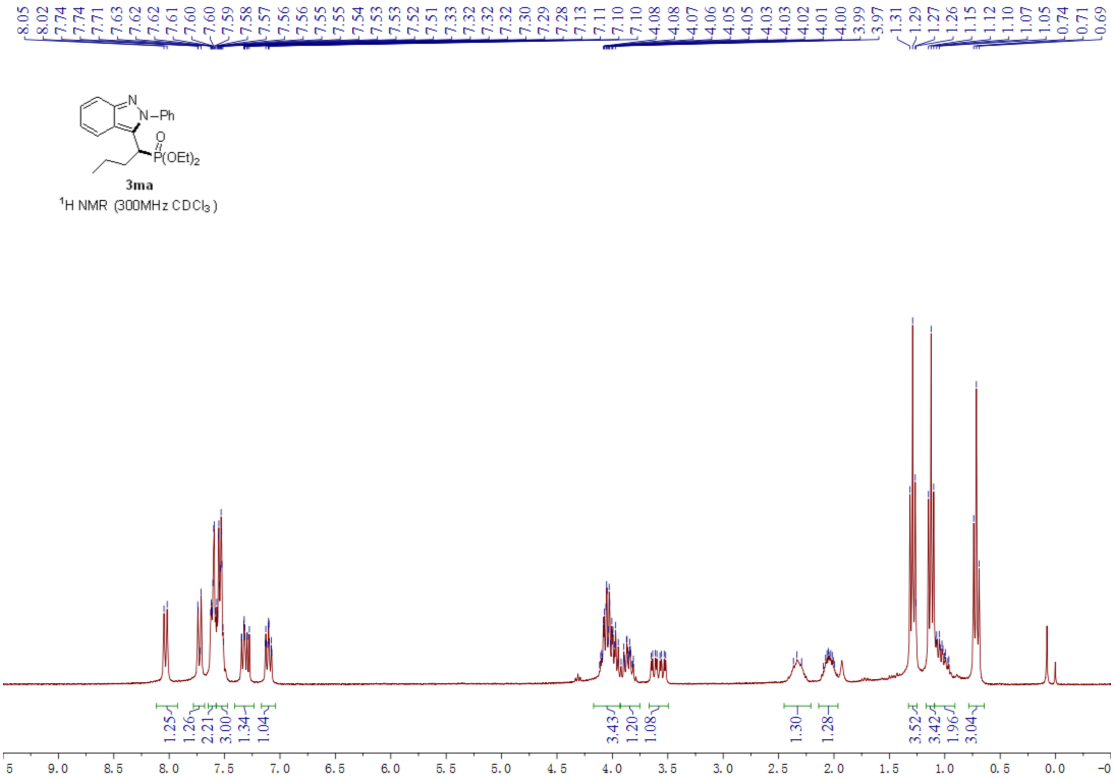
3la

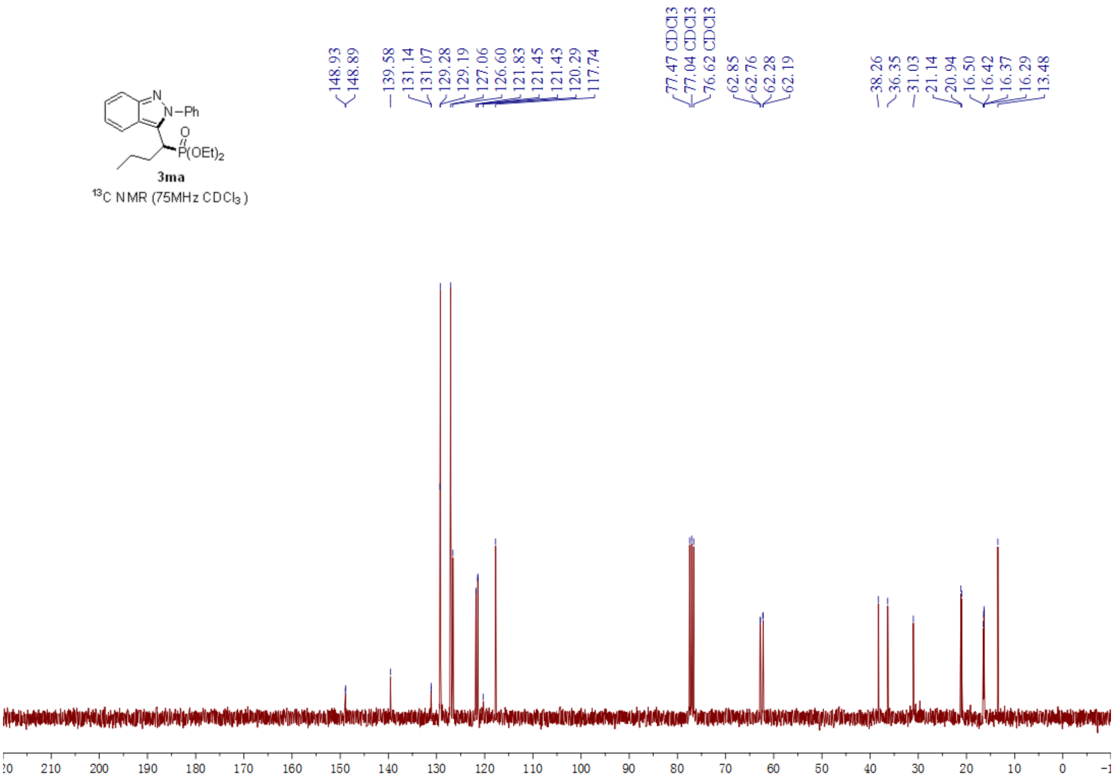
^{13}C NMR (75MHz $CDCl_3$)

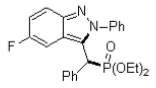


3la

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

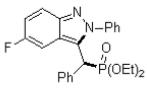

8.05 8.02 7.74 7.71 7.63 7.62 7.62 7.61 7.60 7.60 7.59 7.58 7.57 7.56 7.56 7.55 7.55 7.54 7.53 7.53 7.52 7.51 7.33 7.32 7.32 7.32 7.30 7.29 7.28 7.13 7.11 7.10 7.10 4.08 4.08 4.07 4.06 4.05 4.05 4.03 4.03 4.02 4.01 4.00 3.99 3.97 1.31 1.29 1.27 1.26 1.15 1.12 1.10 1.07 1.05 0.74 0.71 0.69
N
N–Ph
O
P(OEt)2
3ma
1H NMR (300MHz CDCl3)
1.25 1.26 2.21 3.00 1.34 1.04 3.43 1.20 1.08 1.30 1.28 3.52 3.42 1.96 3.04


148.93 148.89 139.58 131.14 131.07 129.28 129.19 127.06 126.60 121.83 121.45 121.43 120.29 117.74 77.47 CDCl3 77.04 CDCl3 76.62 CDCl3 62.85 62.76 62.28 62.19 38.26 36.35 31.03 21.14 20.94 16.50 16.42 16.37 16.29 13.48
N
N–Ph
O
P(OEt)2
3ma
13C NMR (75MHz CDCl3)



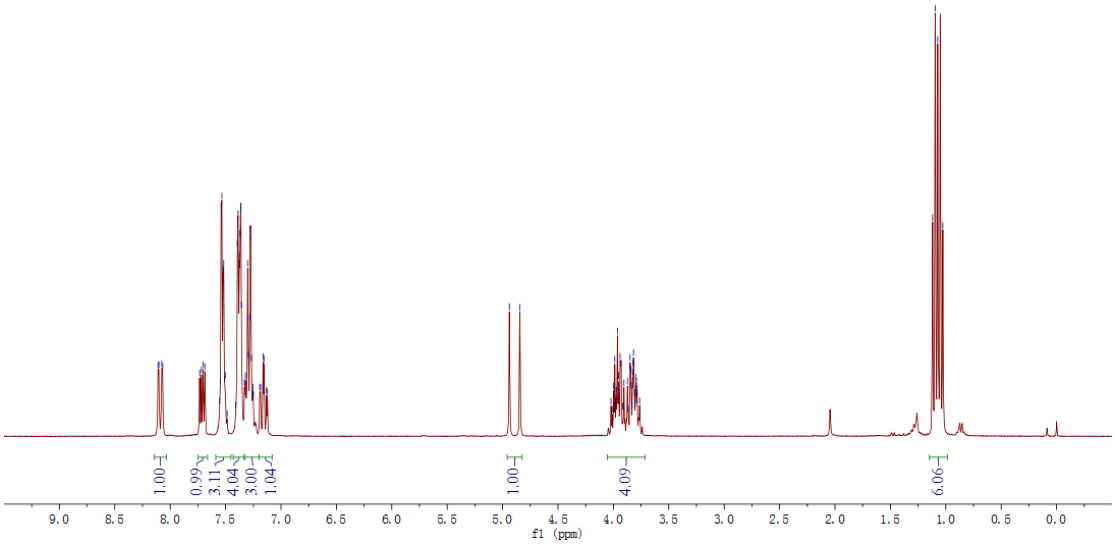
3ma

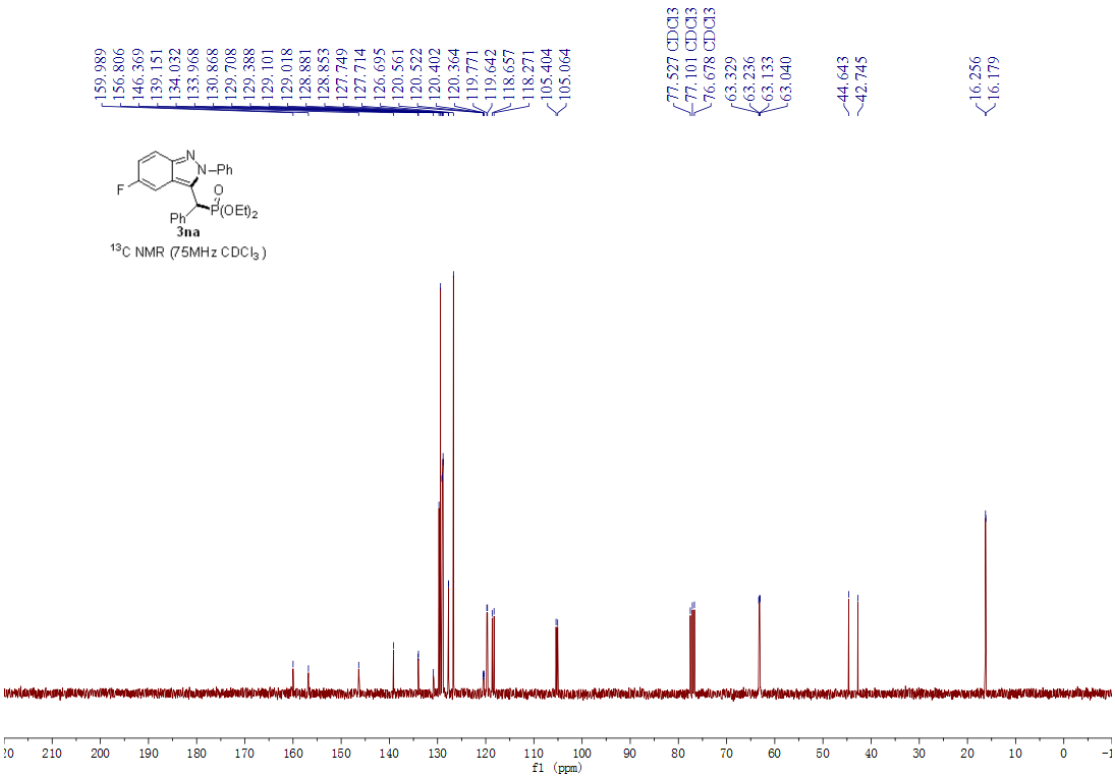
^{31}P NMR (202 MHz $CDCl_3$)

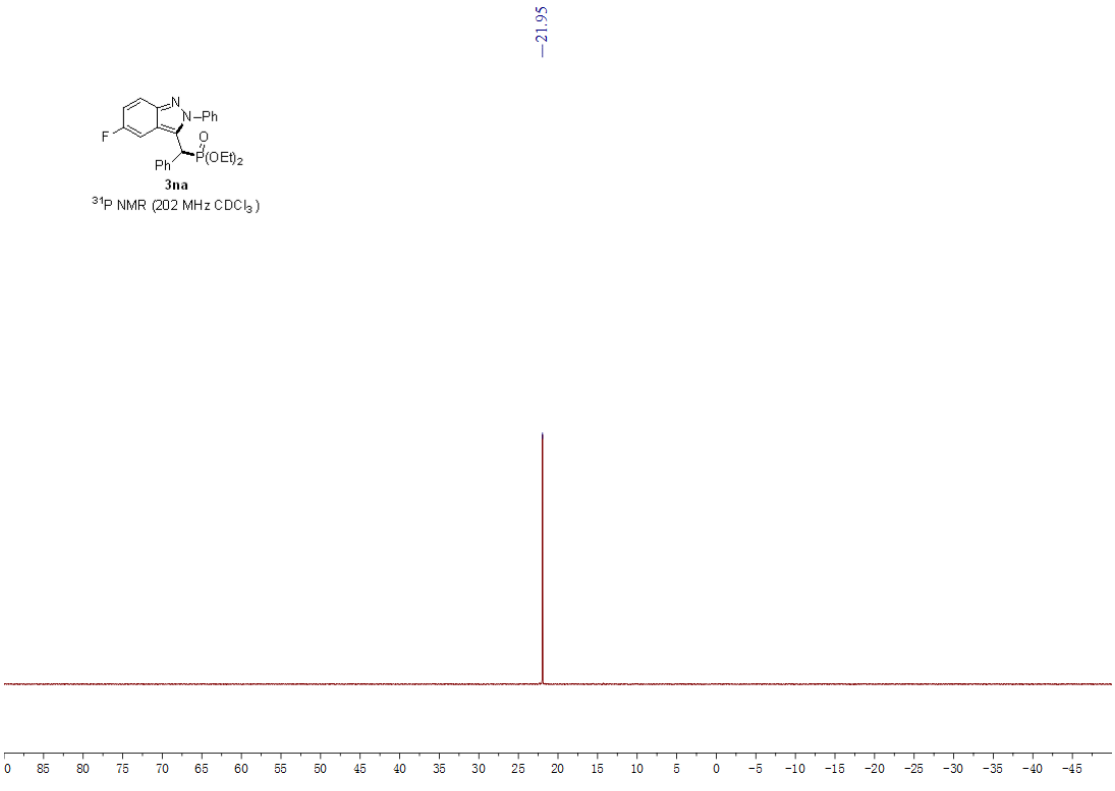


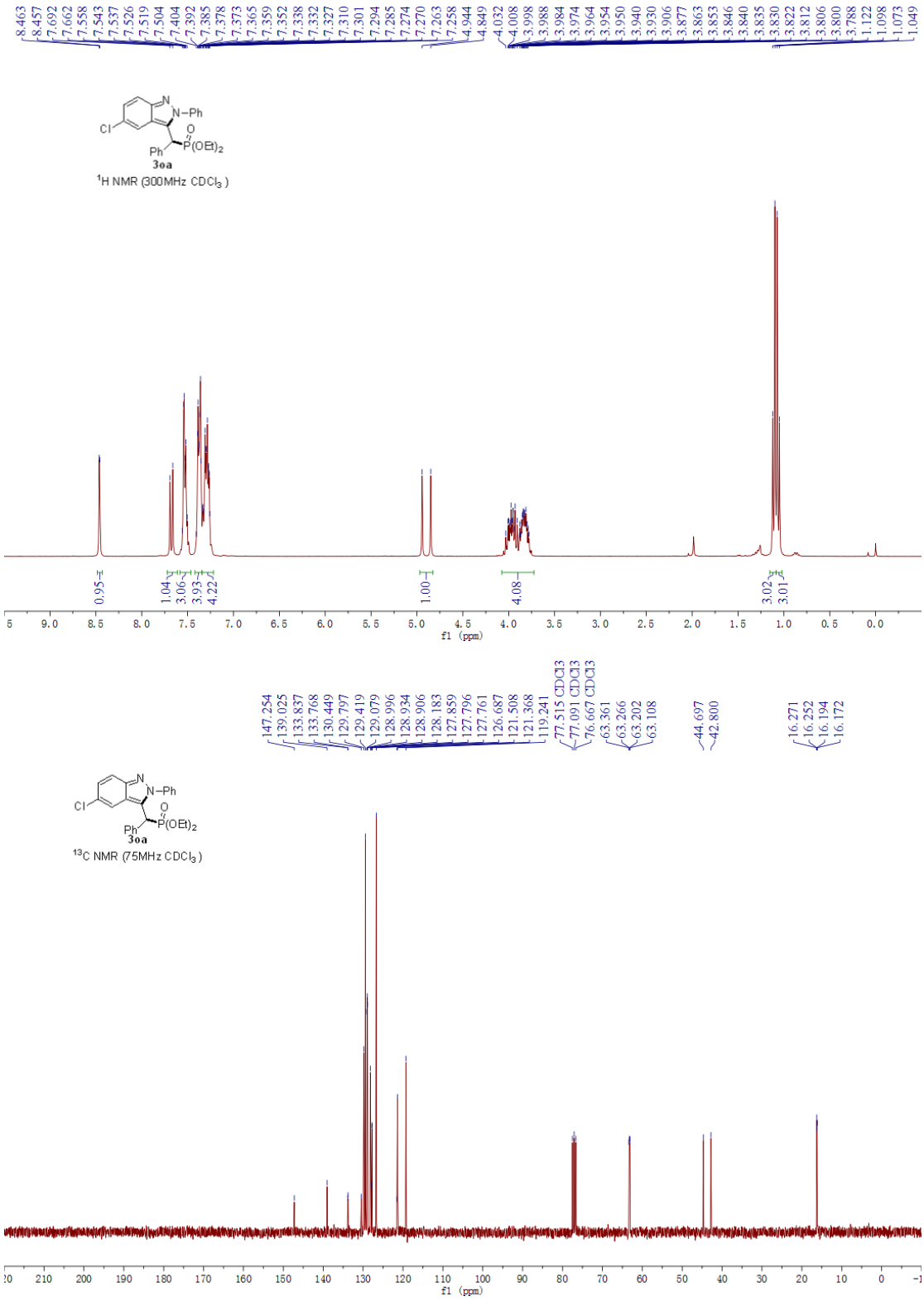
3na

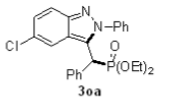
^{1}H NMR (300MHz $CDCl_3$)




159.989
156.806
146.369
139.151
134.032
133.968
130.868
129.708
129.388
129.101
129.018
128.881
128.853
127.749
127.714
126.695
120.561
120.522
120.402
120.364
119.771
119.642
118.657
118.271
105.404
105.064
77.527 CDCl3
77.101 CDCl3
76.678 CDCl3
63.329
63.236
63.133
63.040
44.643
42.745
16.256
16.179
3na
13C NMR (75MHz CDCl3)
f1 (ppm)

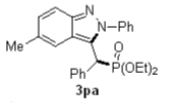

21.95
3na
31P NMR (202 MHz CDCl3)


8.463
8.457
7.692
7.662
7.558
7.543
7.537
7.526
7.519
7.504
7.404
7.392
7.385
7.378
7.373
7.365
7.359
7.352
7.338
7.332
7.327
7.310
7.301
7.294
7.285
7.274
7.270
7.263
7.258
4.944
4.849
4.032
4.008
3.998
3.988
3.984
3.974
3.964
3.954
3.950
3.940
3.930
3.906
3.877
3.863
3.853
3.846
3.840
3.835
3.830
3.822
3.812
3.806
3.800
3.788
1.122
1.098
1.073
1.049
Cl
N
N–Ph
O
P(OEt)2
Ph
3oa
1H NMR (300MHz CDCl3)
0.95
1.04
3.06
3.93
4.22
1.00
4.08
3.02
3.01
f1 (ppm)
147.254
139.025
133.837
133.768
130.449
129.797
129.419
129.079
128.996
128.934
128.906
128.183
127.859
127.796
127.761
126.687
121.508
121.368
119.241
77.515 CDCl3
77.091 CDCl3
76.667 CDCl3
63.361
63.266
63.202
63.108
44.697
42.800
16.271
16.252
16.194
16.172
13C NMR (75MHz CDCl3)
f1 (ppm)



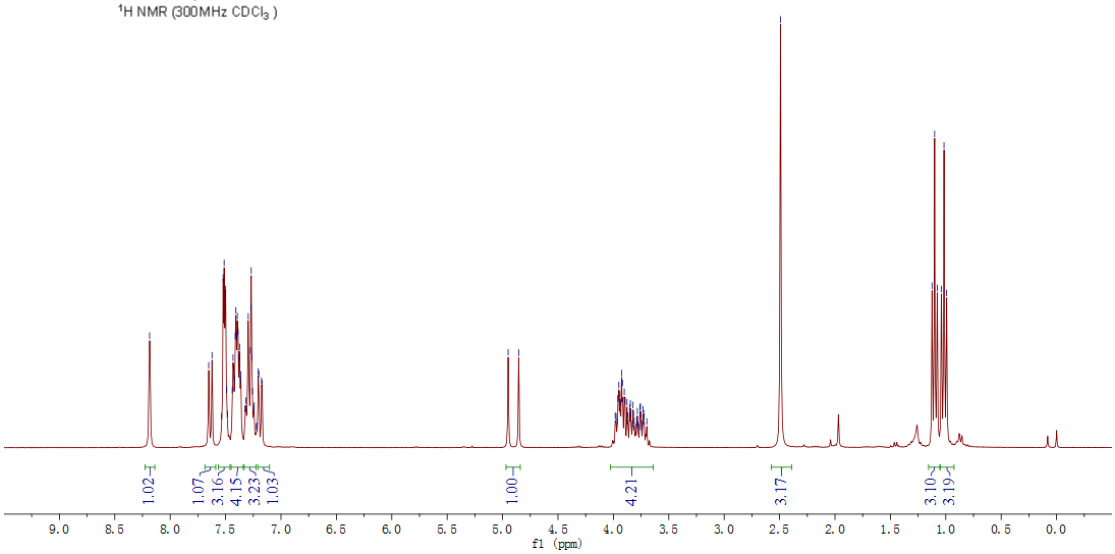
3oa

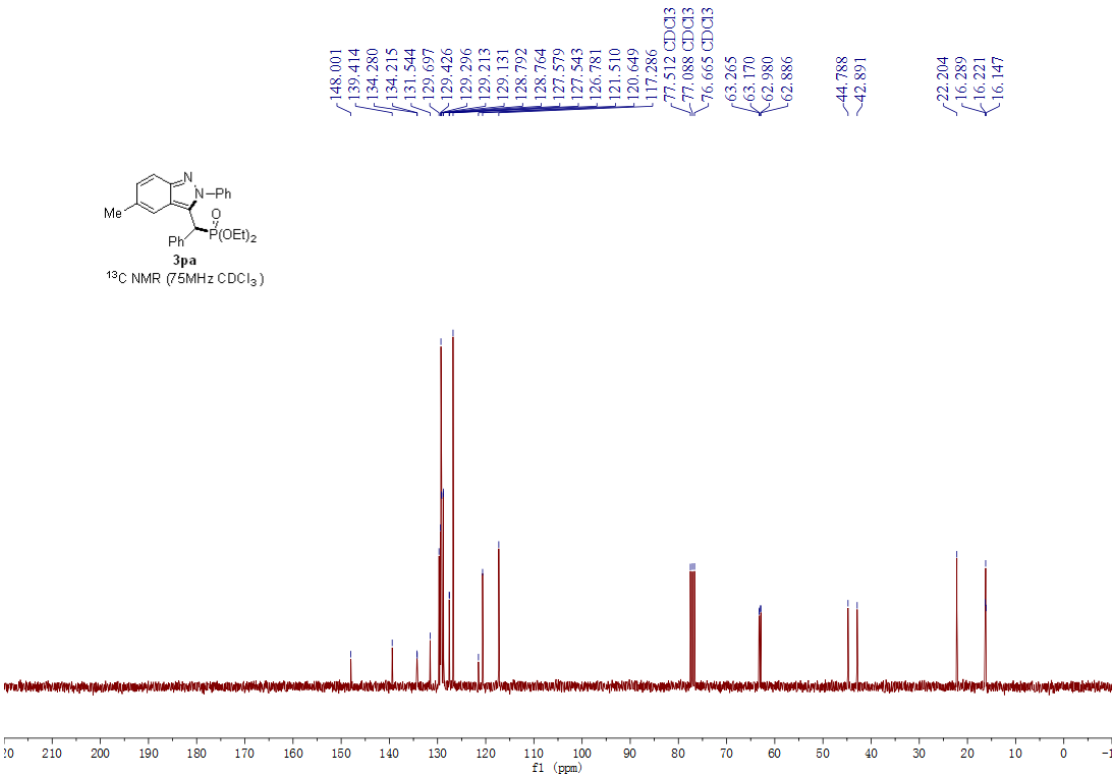
^{31}P NMR (202 MHz $CDCl_3$)

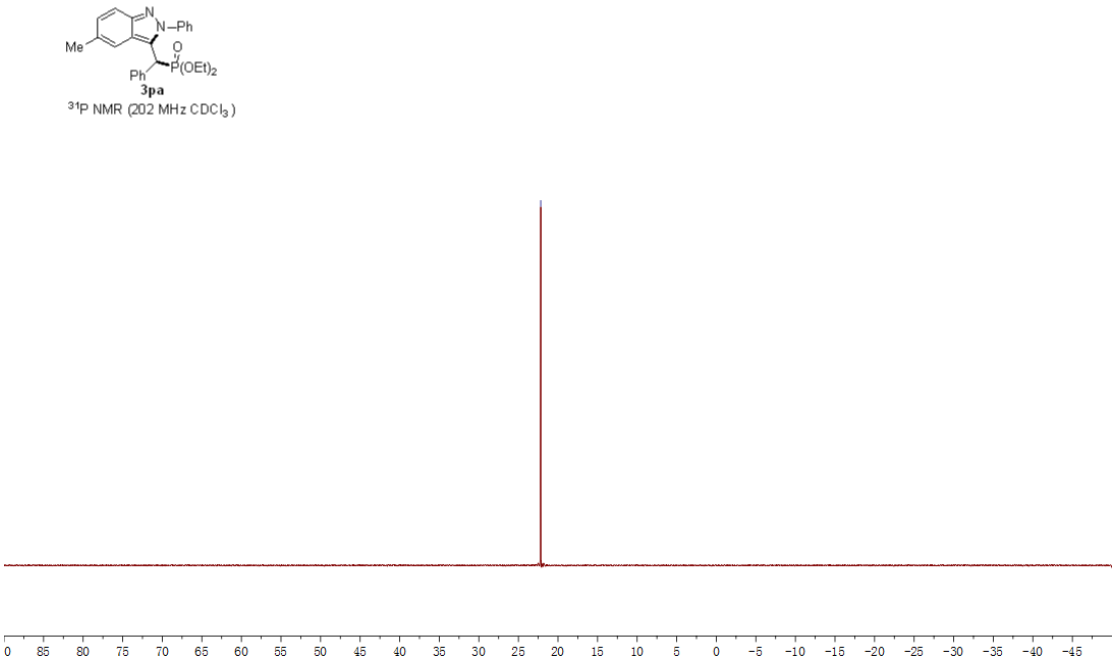


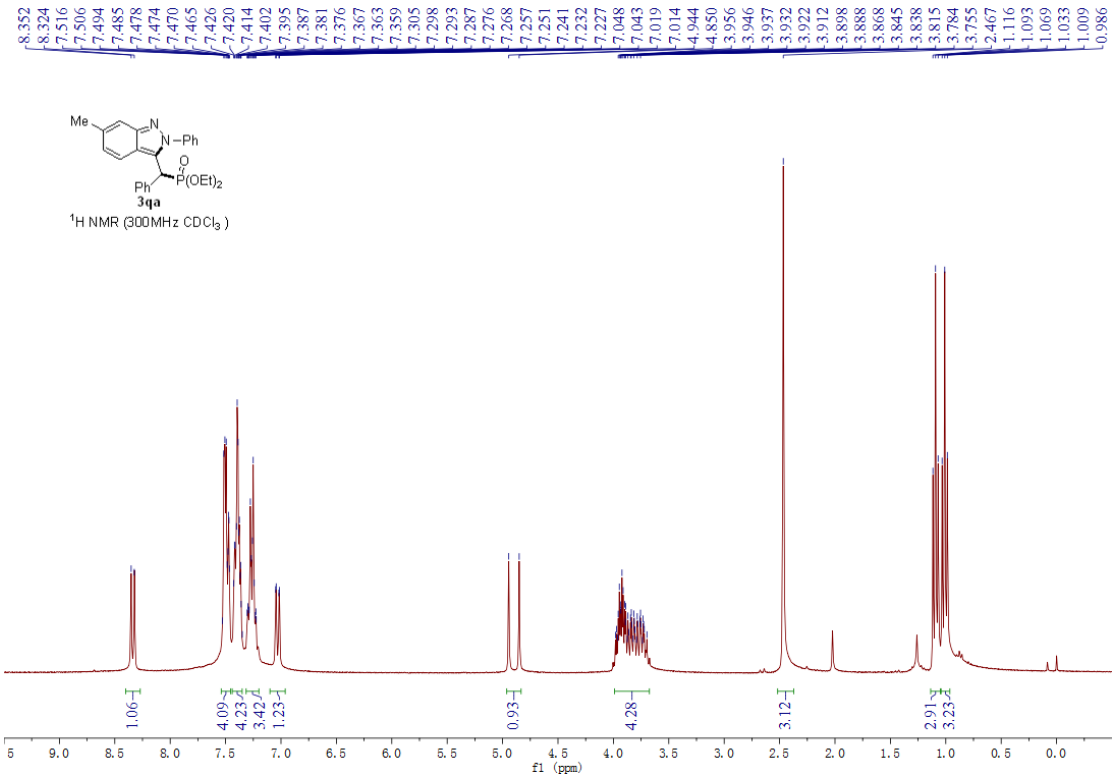
3pa

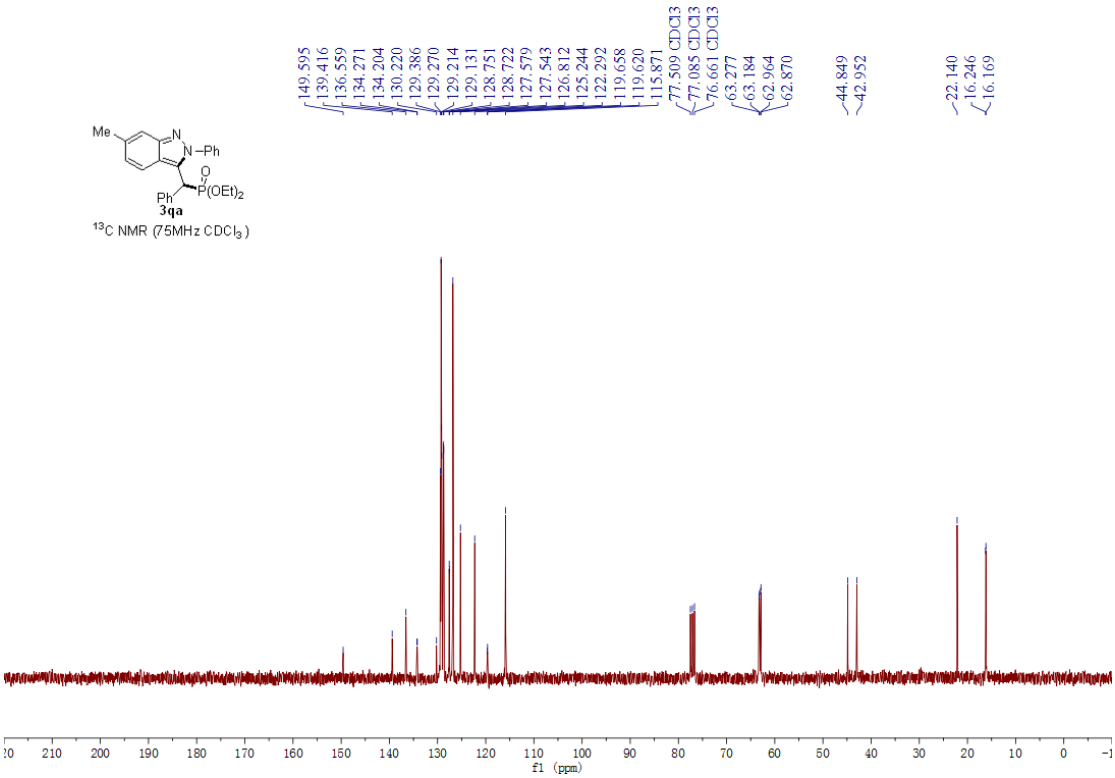
^{1}H NMR (300MHz $CDCl_3$)

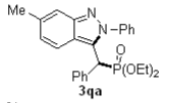



148.001
139.414
134.280
134.215
131.544
129.697
129.426
129.296
129.213
129.131
128.792
128.764
127.579
127.543
126.781
121.510
120.649
117.286
77.512 CDCl3
77.088 CDCl3
76.665 CDCl3
63.265
63.170
62.980
62.886
44.788
42.891
22.204
16.289
16.221
16.147
Me
N
N–Ph
O
P(OEt)2
Ph
3pa
13C NMR (75MHz CDCl3)
f1 (ppm)


22.18
Me
N
N–Ph
O
P(OEt)2
Ph
3pa
31P NMR (202 MHz CDCl3)

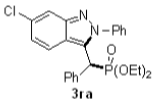

8.352
8.324
7.516
7.506
7.494
7.485
7.478
7.474
7.470
7.465
7.426
7.420
7.414
7.402
7.395
7.387
7.381
7.376
7.367
7.363
7.359
7.305
7.298
7.293
7.287
7.276
7.268
7.257
7.251
7.241
7.232
7.227
7.048
7.043
7.019
7.014
4.944
4.850
3.956
3.946
3.937
3.932
3.922
3.912
3.898
3.888
3.868
3.845
3.838
3.815
3.784
3.755
2.467
1.116
1.093
1.069
1.033
1.009
0.986
Me
N
N–Ph
O
Ph
P(OEt)2
3qa
1H NMR (300MHz CDCl3)
1.06
4.09
4.23
3.42
1.23
0.93
4.28
3.12
2.91
3.23
f1 (ppm)


149.595
139.416
136.559
134.271
134.204
130.220
129.386
129.270
129.214
129.131
128.751
128.722
127.579
127.543
126.812
125.244
122.292
119.658
119.620
115.871
77.509 CDCl3
77.085 CDCl3
76.661 CDCl3
63.277
63.184
62.964
62.870
44.849
42.952
22.140
16.246
16.169
Me
N
N–Ph
O
Ph
P(OEt)2
3qa
13C NMR (75MHz CDCl3)
f1 (ppm)



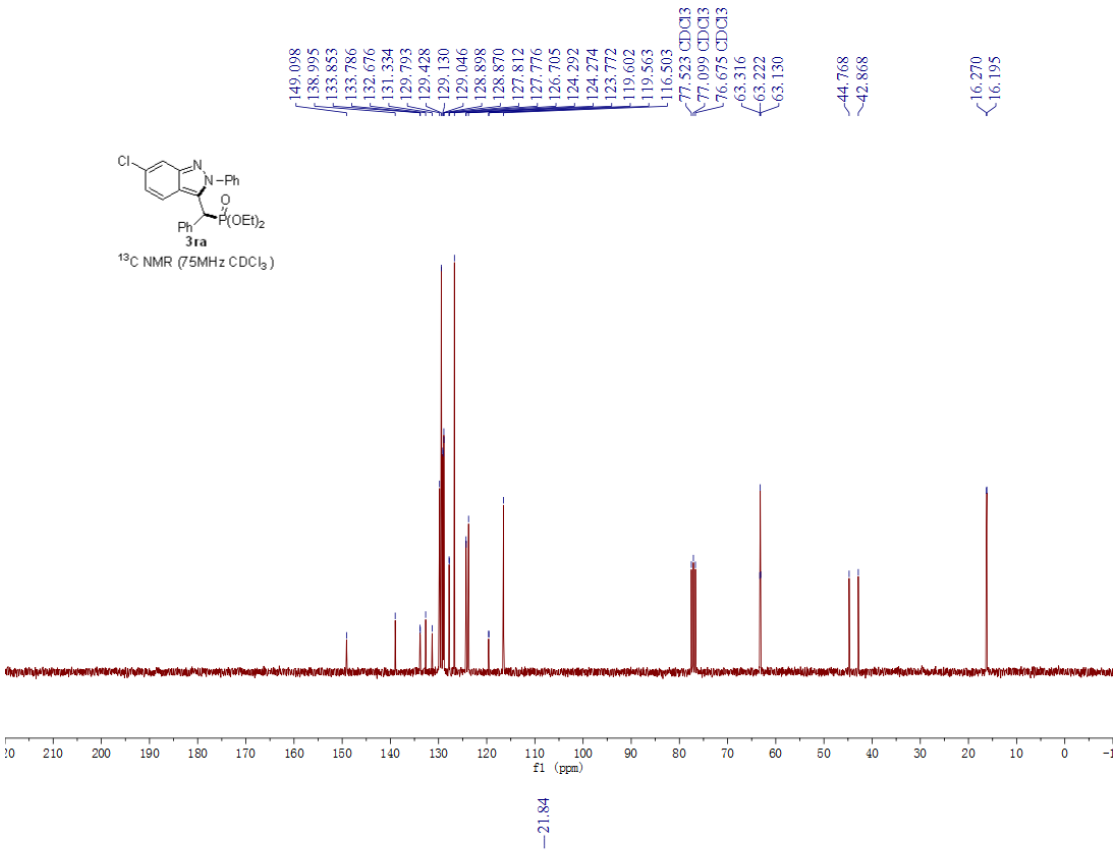
3qa

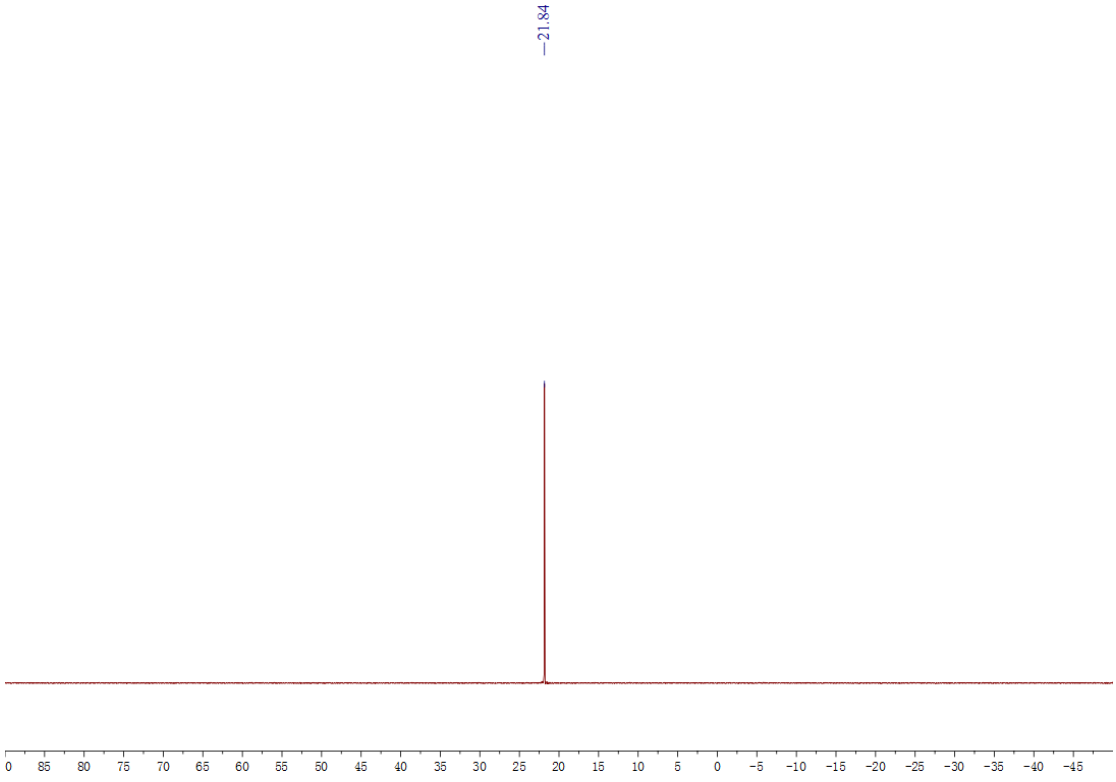
^{31}P NMR (202 MHz $CDCl_3$)

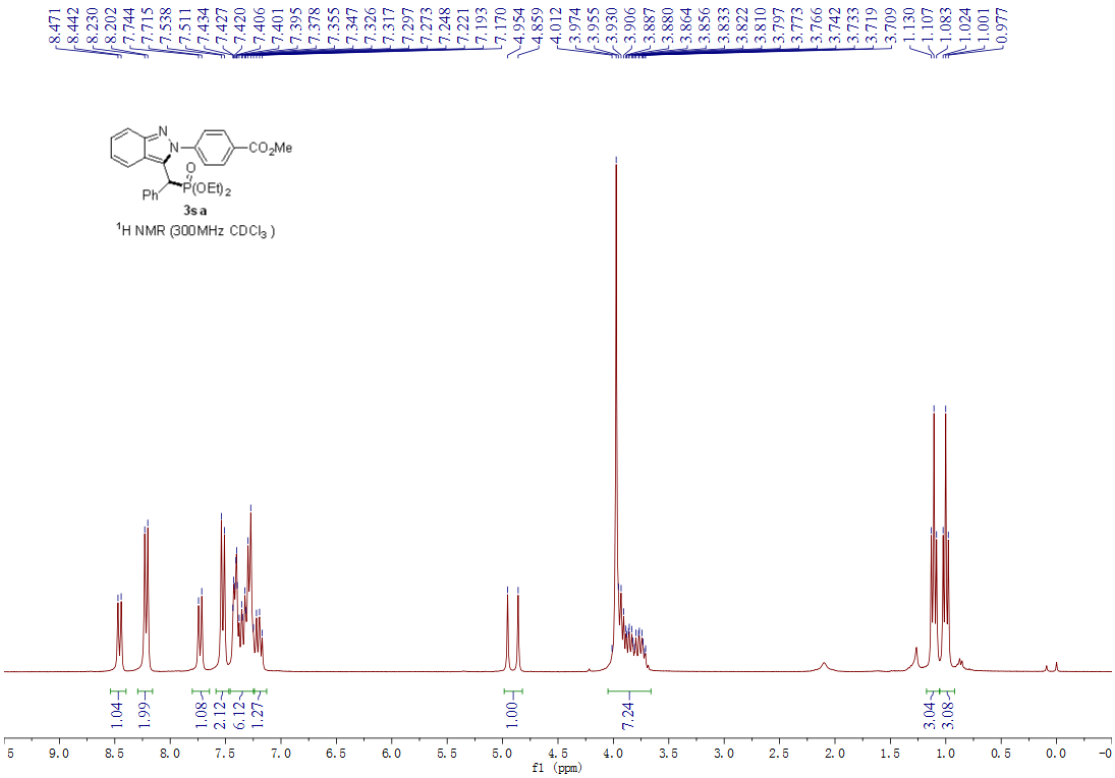


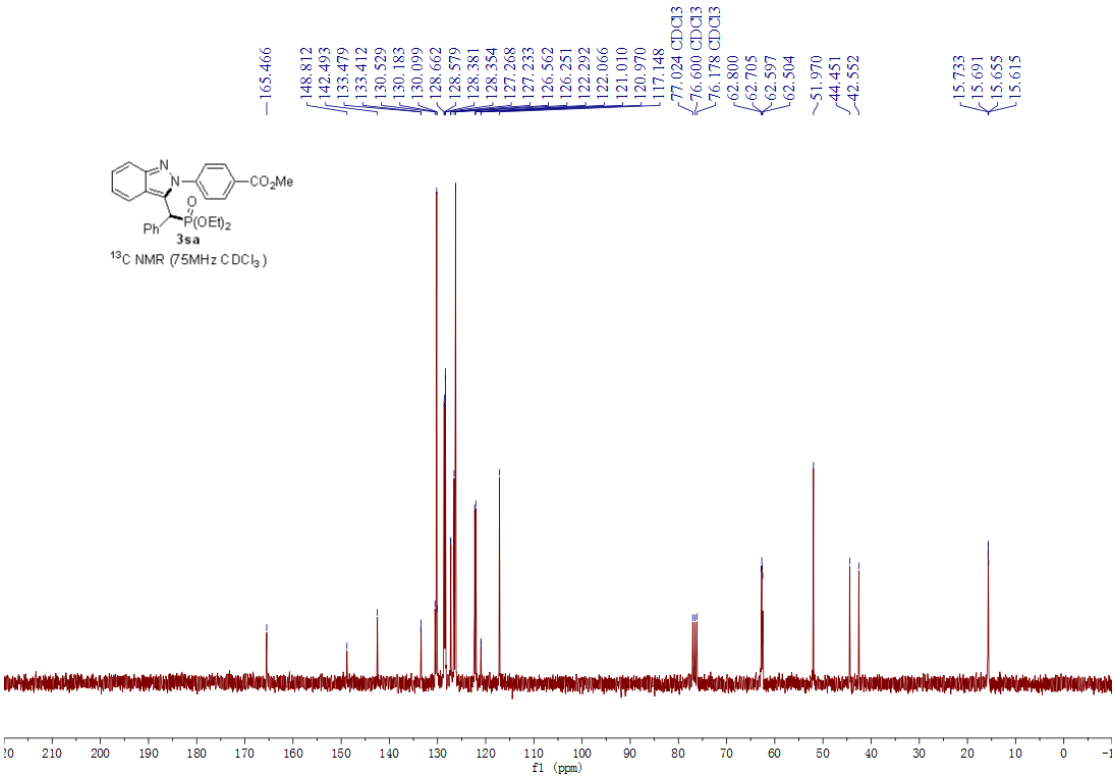
3ra

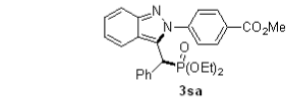
^{1}H NMR (300MHz $CDCl_3$)


149.098
138.995
133.853
133.786
132.676
131.334
129.793
129.428
129.130
129.046
128.898
128.870
127.812
127.776
126.705
124.292
124.274
123.772
119.602
119.563
116.503
77.523 CDCl3
77.099 CDCl3
76.675 CDCl3
63.316
63.222
63.130
44.768
42.868
16.270
16.195
Cl
N
N–Ph
O
P(OEt)2
Ph
3ra
13C NMR (75MHz CDCl3)
f1 (ppm)


21.84
f1 (ppm)

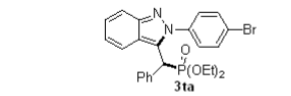

8.471
8.442
8.230
8.202
7.744
7.715
7.538
7.511
7.434
7.427
7.420
7.406
7.401
7.395
7.378
7.355
7.347
7.326
7.317
7.297
7.273
7.248
7.221
7.193
7.170
4.954
4.859
4.012
3.974
3.955
3.930
3.906
3.887
3.880
3.864
3.856
3.833
3.822
3.810
3.797
3.773
3.766
3.742
3.733
3.719
3.709
1.130
1.107
1.083
1.024
1.001
0.977
CO2Me
Ph
P(OEt)2
3sa
1H NMR (300MHz CDCl3)
1.04
1.99
1.08
2.12
6.12
1.27
1.00
7.24
3.04
3.08
f1 (ppm)


165.466
148.812
142.493
133.479
133.412
130.529
130.183
130.099
128.662
128.579
128.381
128.354
127.268
127.233
126.562
126.251
122.292
122.066
121.010
120.970
117.148
77.024 CDCl3
76.600 CDCl3
76.178 CDCl3
62.800
62.705
62.597
62.504
51.970
44.451
42.552
15.733
15.691
15.655
15.615
CO2Me
Ph
P(OEt)2
3sa
13C NMR (75MHz CDCl3)
f1 (ppm)



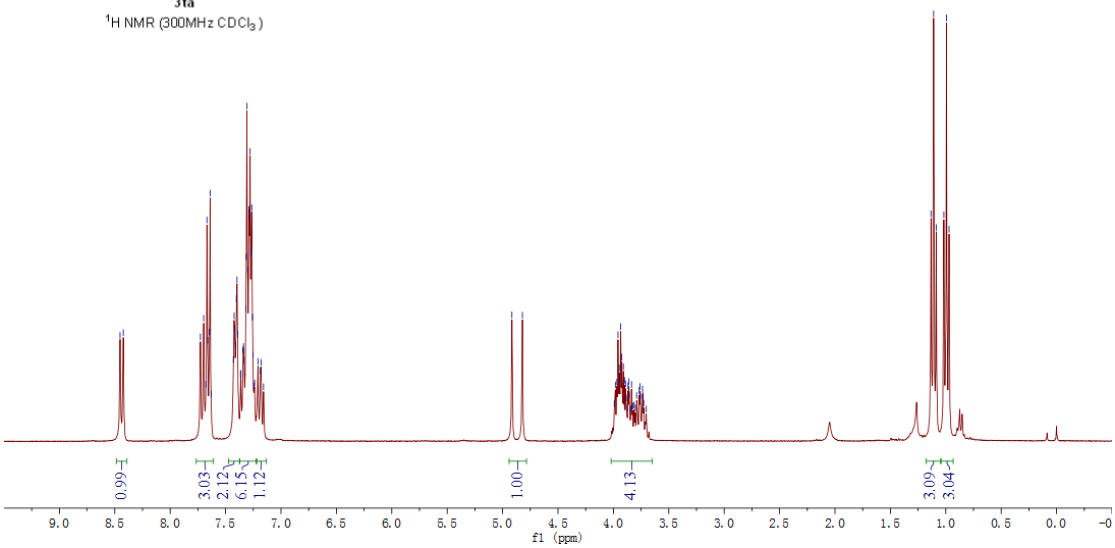
3sa

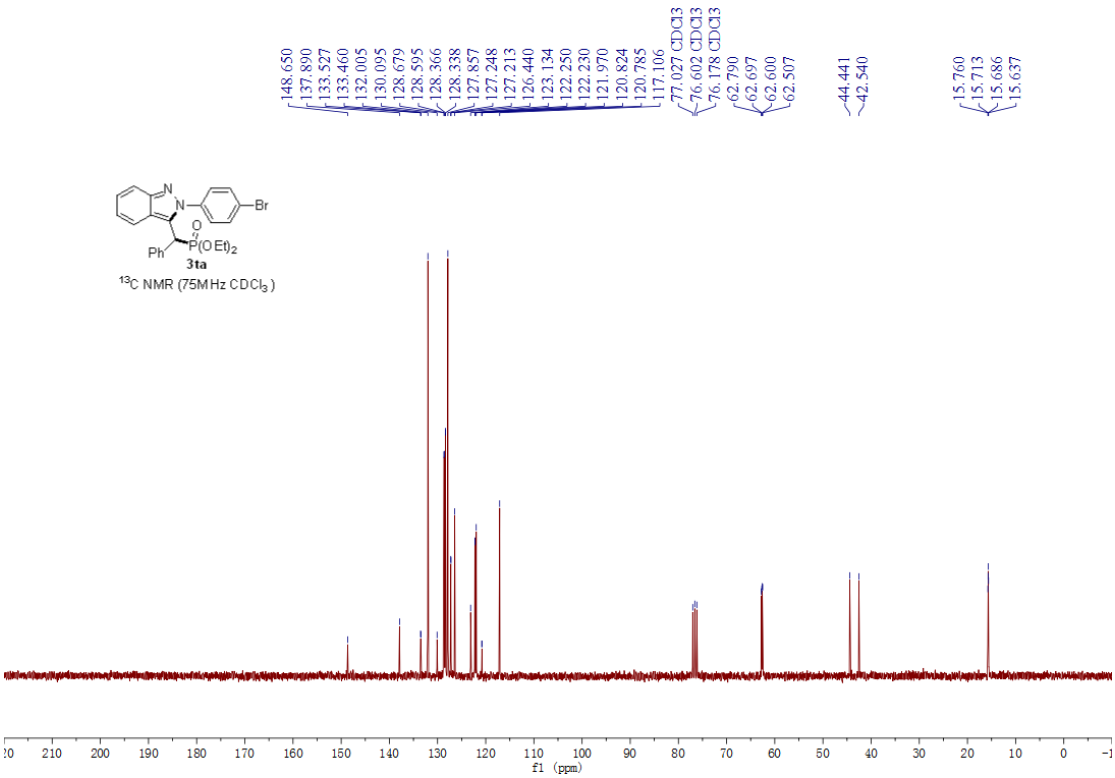
^{31}P NMR (202 MHz $CDCl_3$)

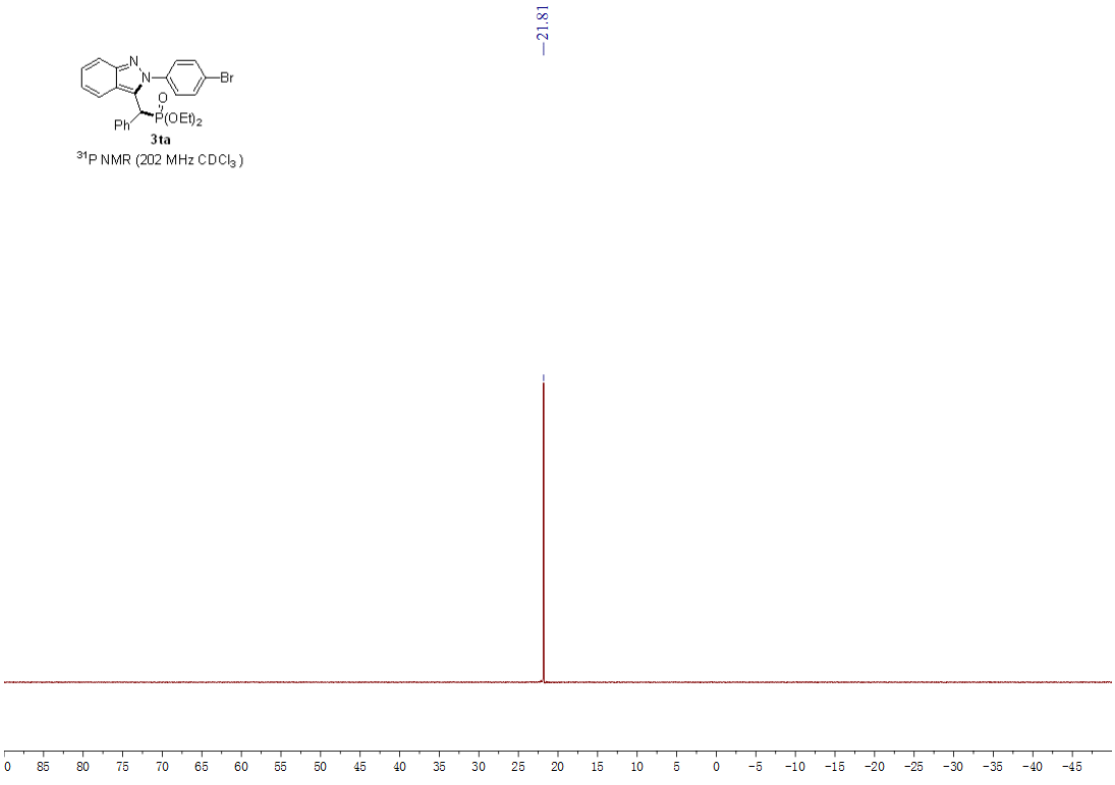


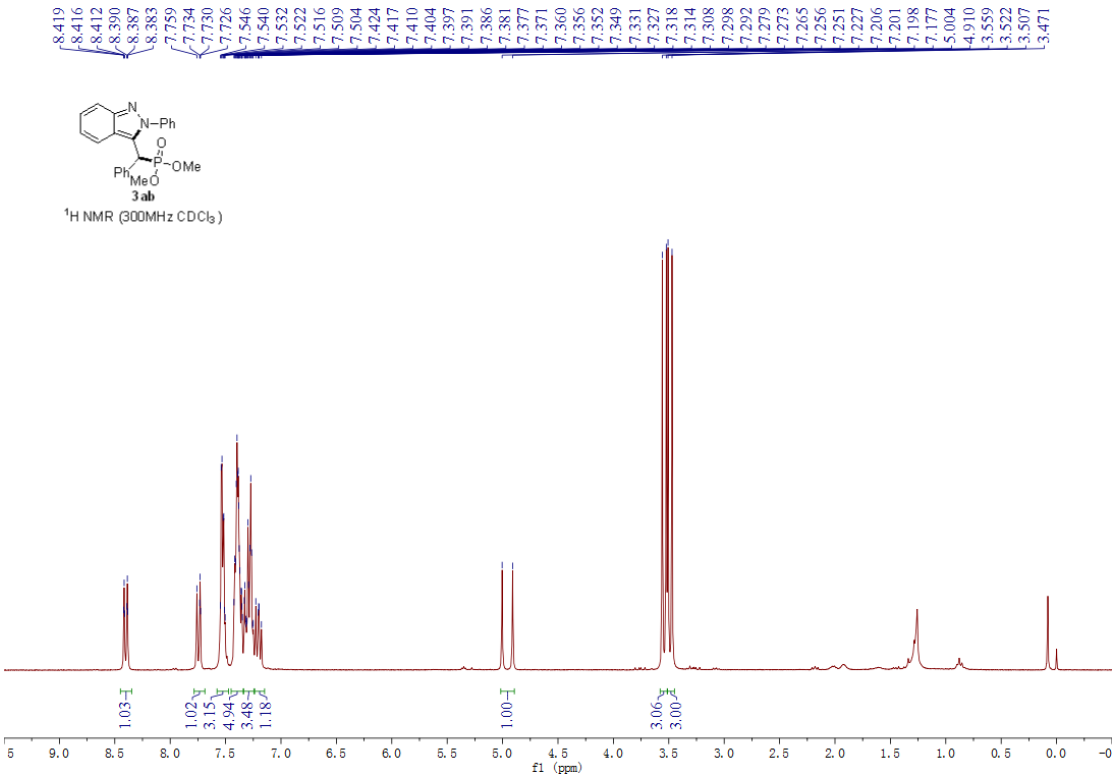
3ta

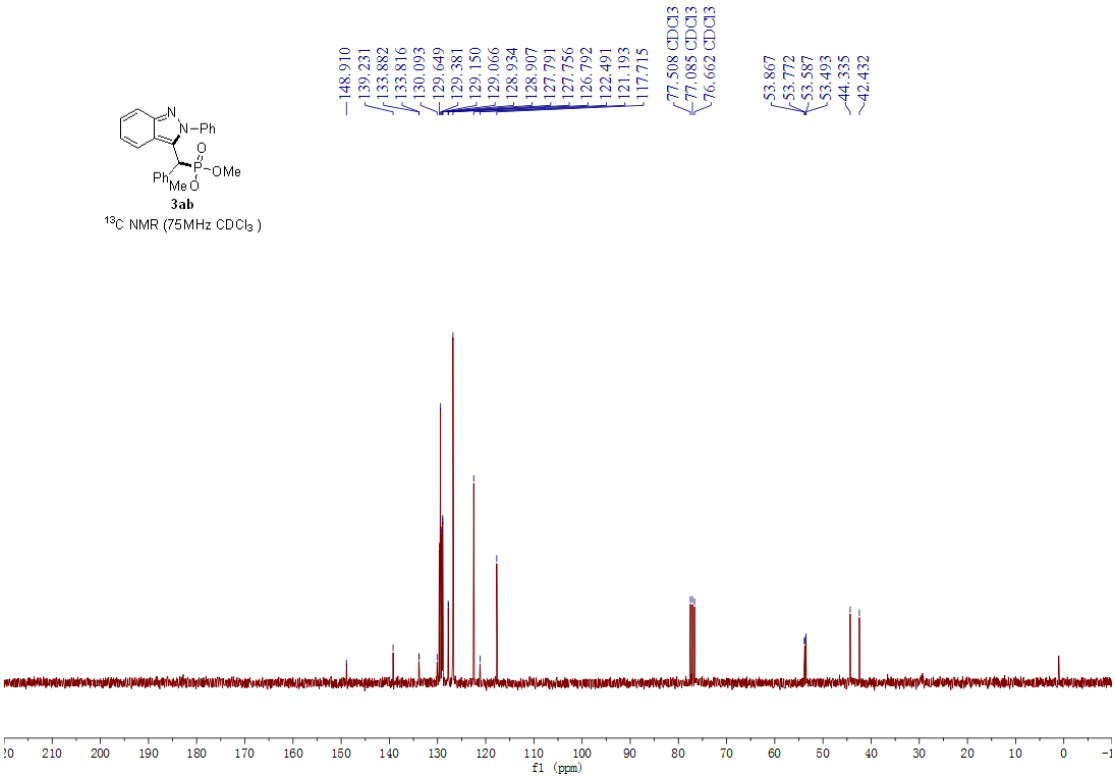
^{1}H NMR (300MHz $CDCl_3$)

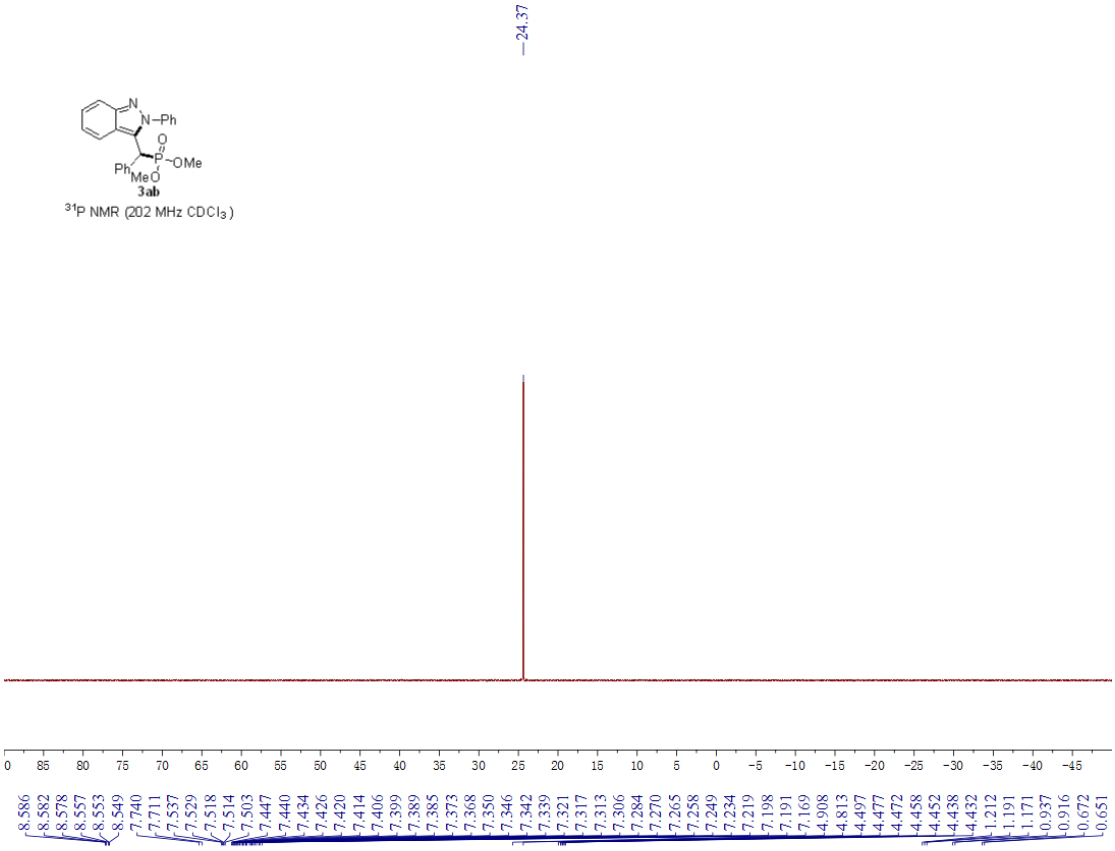


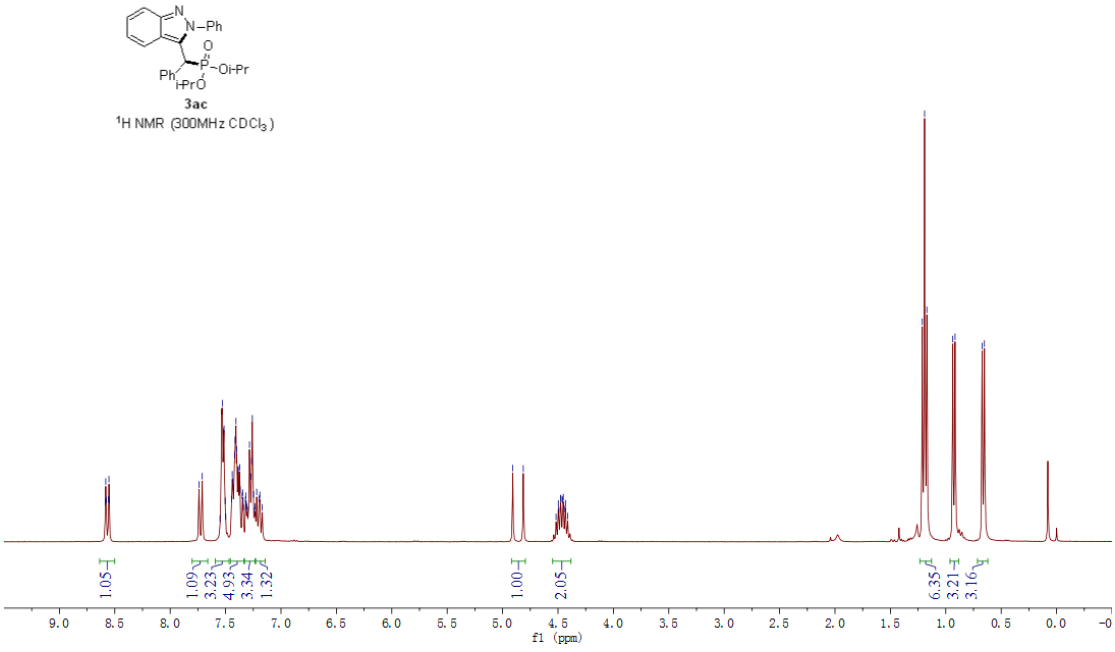

148.650
137.890
133.527
133.460
132.005
130.095
128.679
128.595
128.366
128.338
127.857
127.248
127.213
126.440
123.134
122.250
122.230
121.970
120.824
120.785
117.106
77.027 CDCl3
76.602 CDCl3
76.178 CDCl3
62.790
62.697
62.600
62.507
44.441
42.540
15.760
15.713
15.686
15.637
Br
O
P(OEt)2
Ph
3ta
13C NMR (75MHz CDCl3)
f1 (ppm)

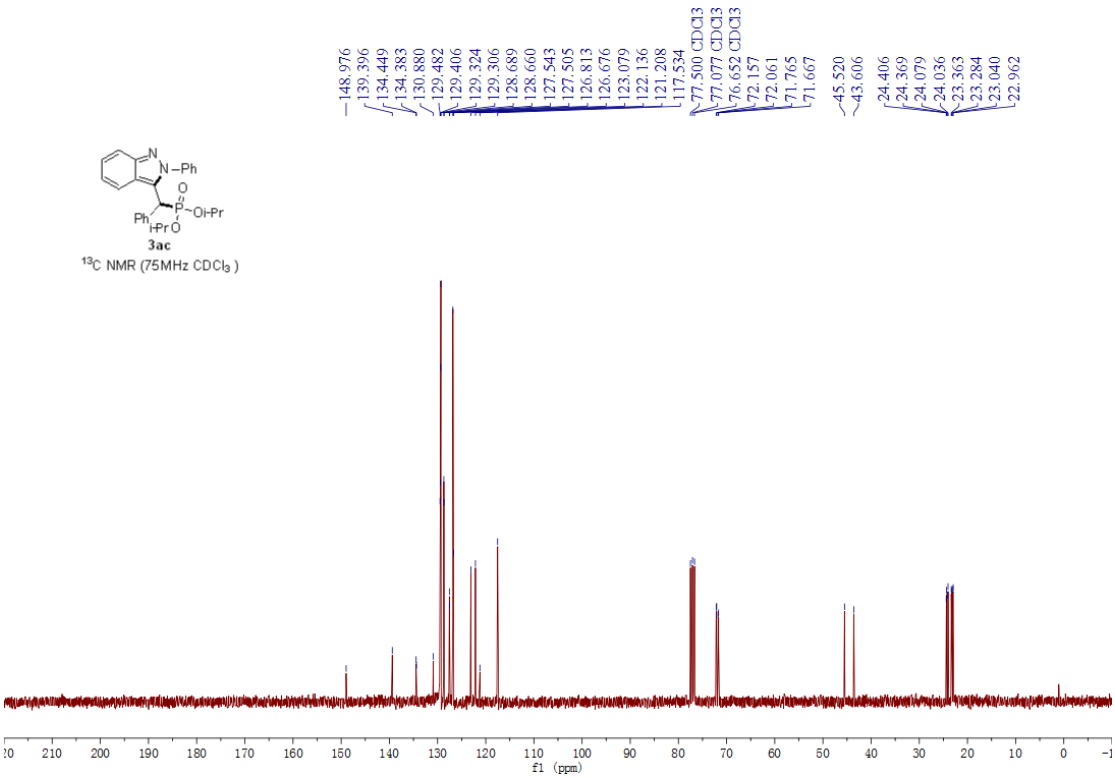

21.81
Br
O
P(OEt)2
Ph
3ta
31P NMR (202 MHz CDCl3)

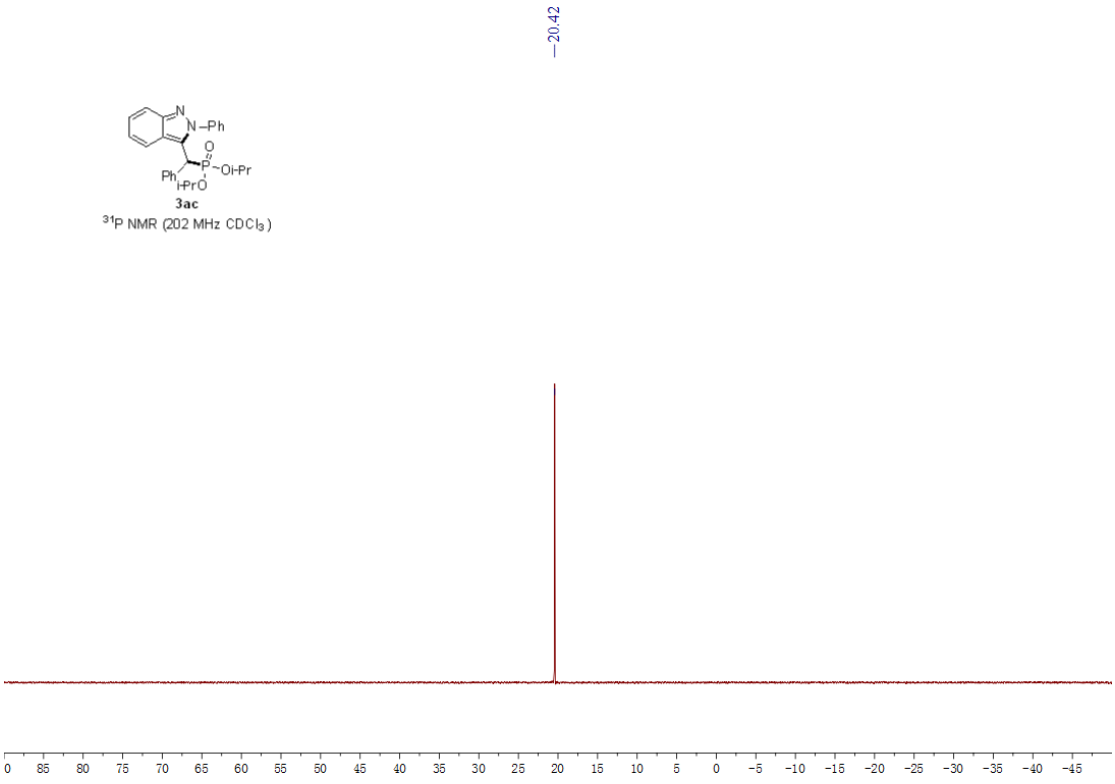

8.419
8.416
8.412
8.390
8.387
8.383
7.759
7.734
7.730
7.726
7.546
7.540
7.532
7.522
7.516
7.509
7.504
7.424
7.417
7.410
7.404
7.397
7.391
7.386
7.381
7.377
7.371
7.360
7.356
7.352
7.349
7.331
7.327
7.318
7.314
7.308
7.298
7.292
7.279
7.273
7.265
7.256
7.251
7.227
7.206
7.201
7.198
7.177
5.004
4.910
3.559
3.522
3.507
3.471
N–Ph
O
P
OMe
Ph
Me O
3ab
1H NMR (300MHz CDCl3)
1.03
1.02
3.15
4.94
3.48
1.18
1.00
3.06
3.00
f1 (ppm)

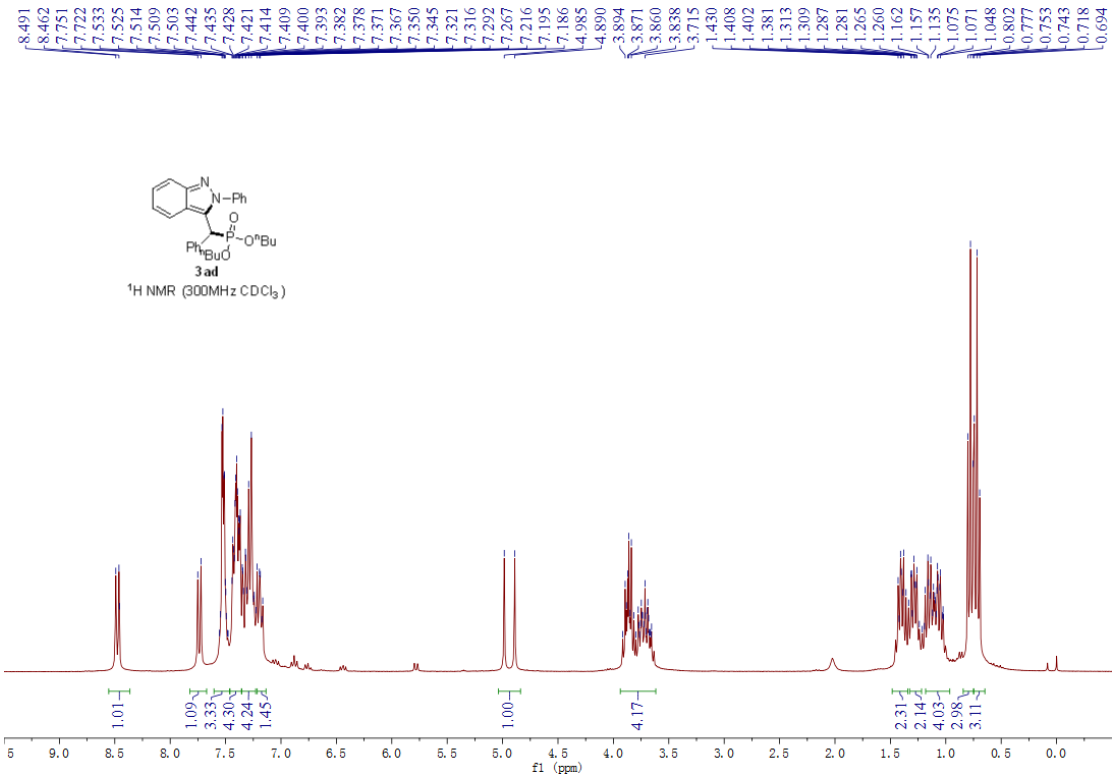

148.910
139.231
133.882
133.816
130.093
129.649
129.381
129.150
129.066
128.934
128.907
127.791
127.756
126.792
122.491
121.193
117.715
77.508 CDCl3
77.085 CDCl3
76.662 CDCl3
53.867
53.772
53.587
53.493
44.335
42.432
N–Ph
O
P
OMe
Ph
Me O
3ab
13C NMR (75MHz CDCl3)
f1 (ppm)

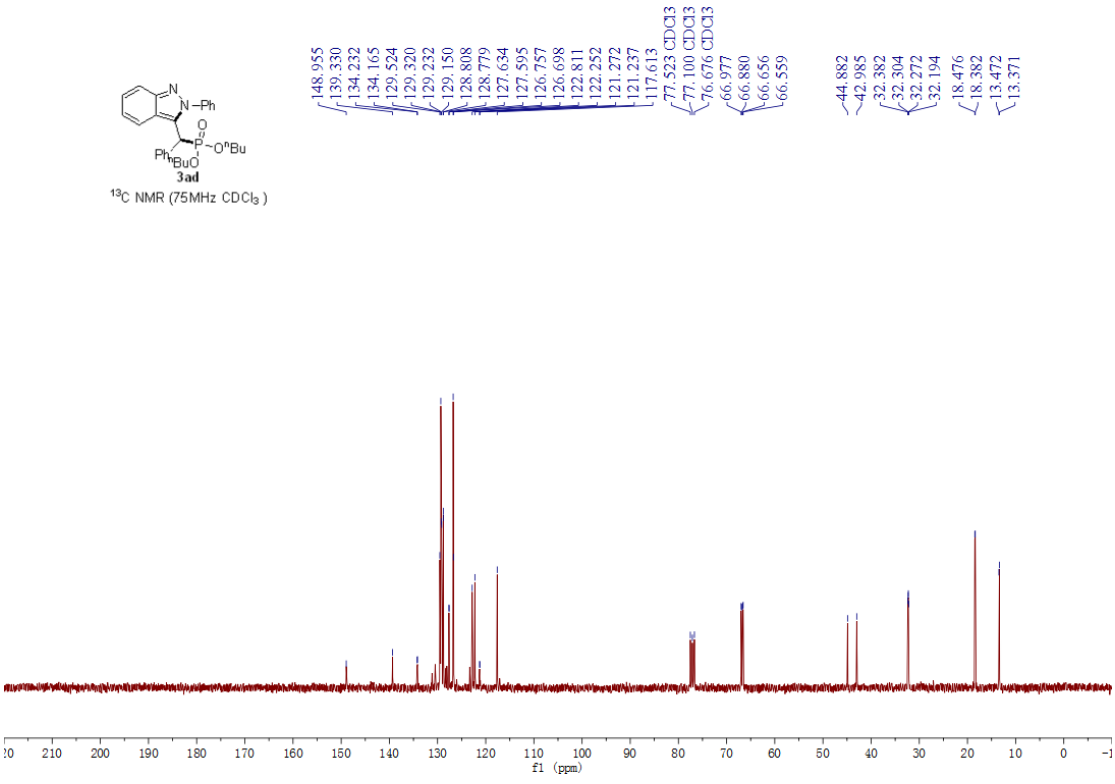

24.37
N
N–Ph
O
P
OMe
Ph
MeO
3ab
31P NMR (202 MHz CDCl3)
8.586
8.582
8.578
8.557
8.553
8.549
7.740
7.711
7.537
7.529
7.518
7.514
7.503
7.447
7.440
7.434
7.426
7.420
7.414
7.406
7.399
7.389
7.385
7.373
7.368
7.350
7.346
7.342
7.339
7.321
7.317
7.313
7.306
7.284
7.270
7.265
7.258
7.249
7.234
7.219
7.198
7.191
7.169
4.908
4.813
4.497
4.477
4.472
4.458
4.452
4.438
4.432
1.212
1.191
1.171
0.937
0.916
0.672
0.651

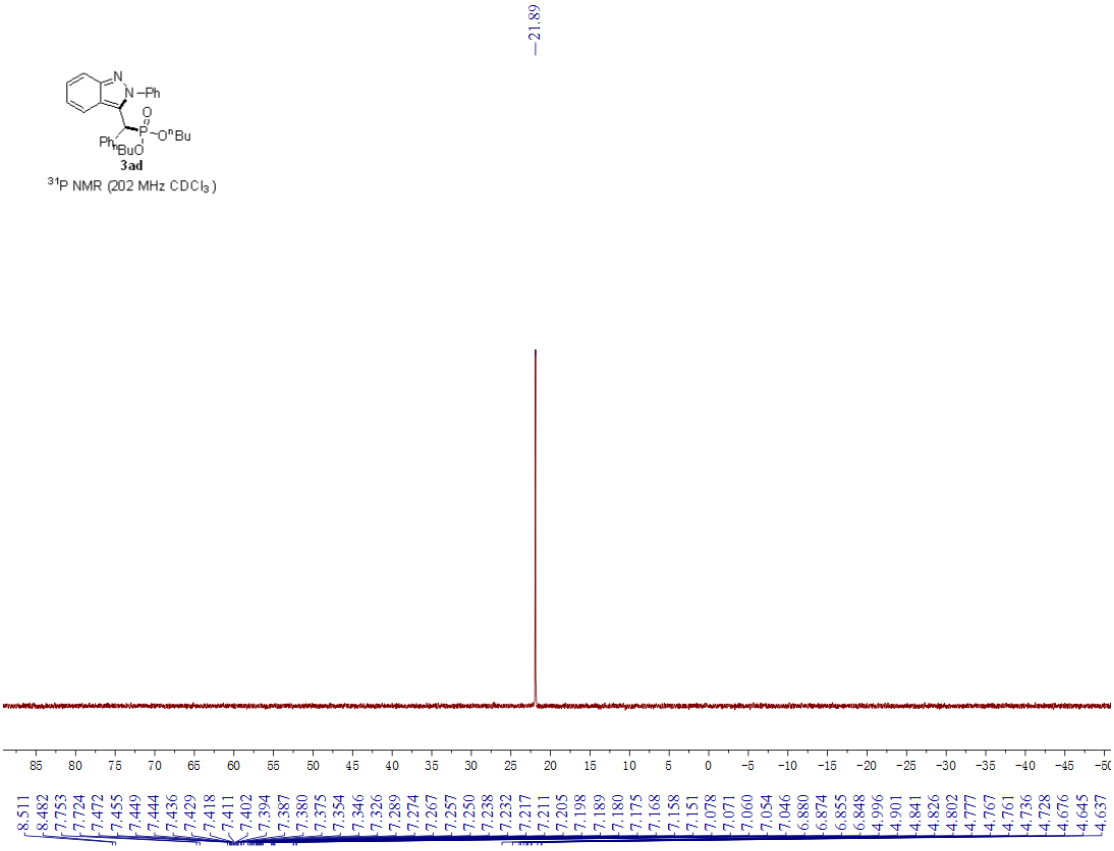

N
N–Ph
O
P
Oi-Pr
Ph
i-PrO
3ac
1H NMR (300MHz CDCl3)
1.05
1.09
3.23
4.93
3.34
1.32
1.00
2.05
6.35
3.21
3.16
f1 (ppm)

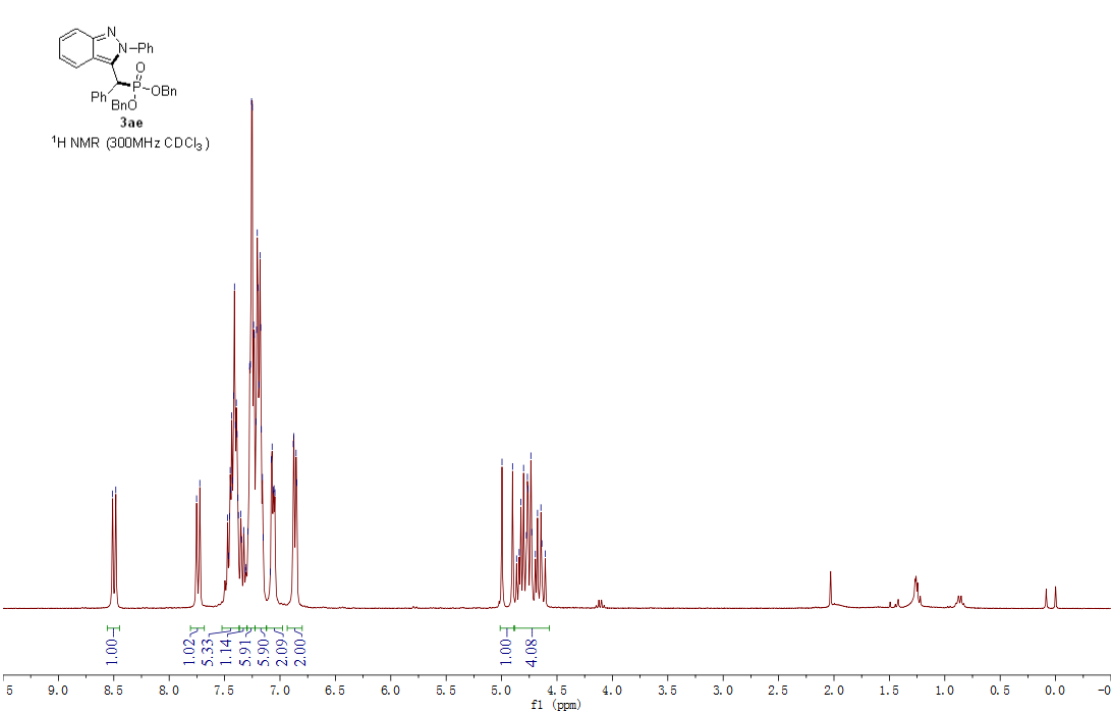

148.976
139.396
134.449
134.383
130.880
129.482
129.406
129.324
129.306
128.689
128.660
127.543
127.505
126.813
126.676
123.079
122.136
121.208
117.534
77.500 CDCl3
77.077 CDCl3
76.652 CDCl3
72.157
72.061
71.765
71.667
45.520
43.606
24.406
24.369
24.079
24.036
23.363
23.284
23.040
22.962
N–Ph
O
P
~Oi-Pr
Ph
i-PrO
3ac
13C NMR (75MHz CDCl3)
f1 (ppm)

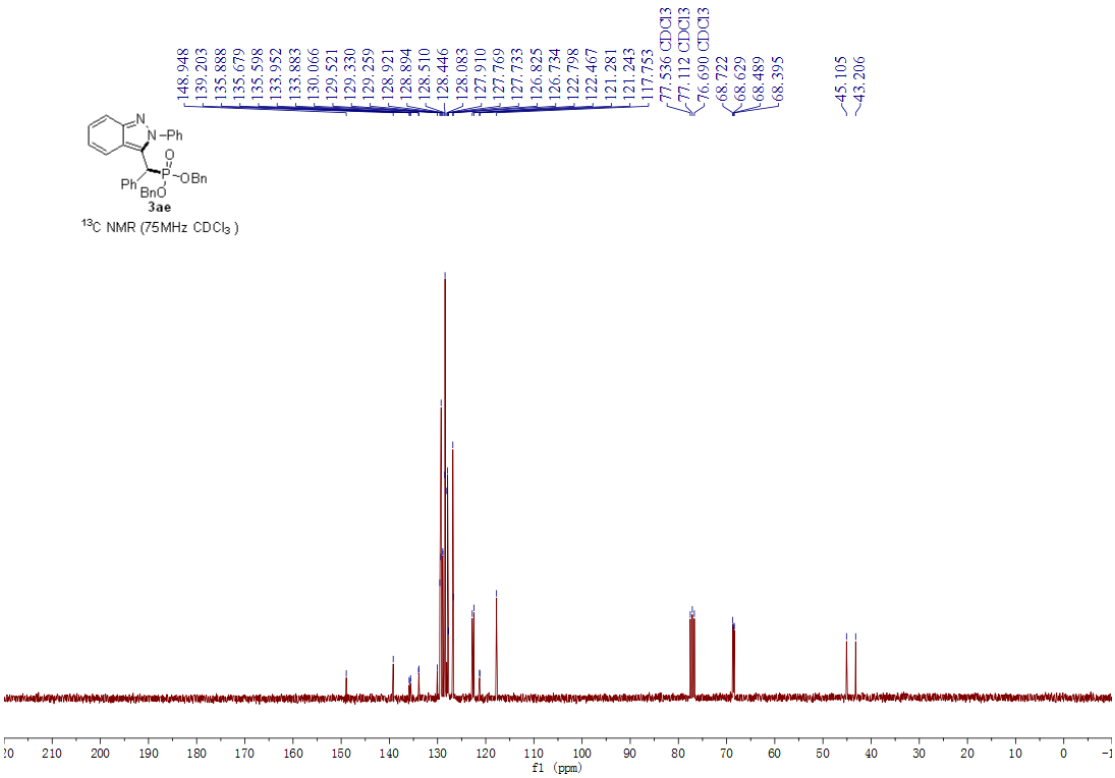

20.42
N–Ph
O
P
~Oi-Pr
Ph
i-PrO
3ac
31P NMR (202 MHz CDCl3)

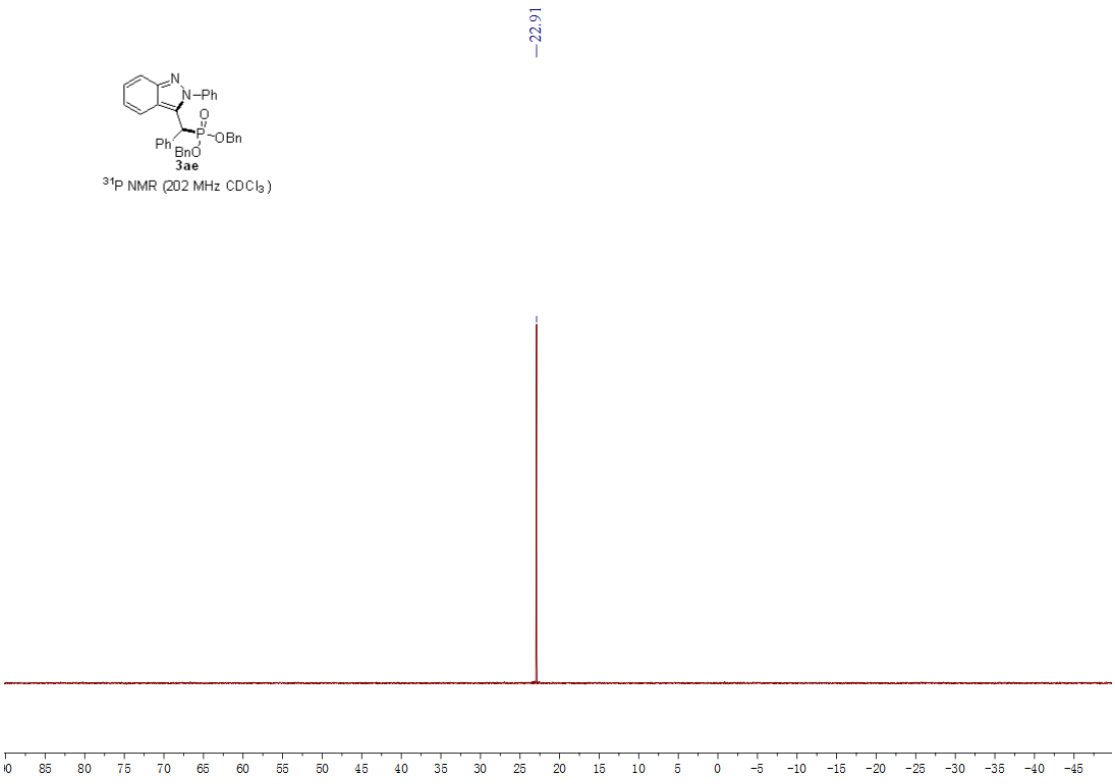

8.491
8.462
7.751
7.722
7.533
7.525
7.514
7.509
7.503
7.442
7.435
7.428
7.421
7.414
7.409
7.400
7.393
7.382
7.378
7.371
7.367
7.350
7.345
7.321
7.316
7.292
7.267
7.216
7.195
7.186
4.985
4.890
3.894
3.871
3.860
3.838
3.715
1.430
1.408
1.402
1.381
1.313
1.309
1.287
1.281
1.265
1.260
1.162
1.157
1.135
1.075
1.071
1.048
0.802
0.777
0.753
0.743
0.718
0.694
N–Ph
O
P
O^{n}Bu
Ph
^{n}BuO
3ad
^{1}H NMR (300MHz CDCl$_3$)
1.01
1.09
3.33
4.30
4.24
1.45
1.00
4.17
2.31
2.14
4.03
2.98
3.11
f1 (ppm)

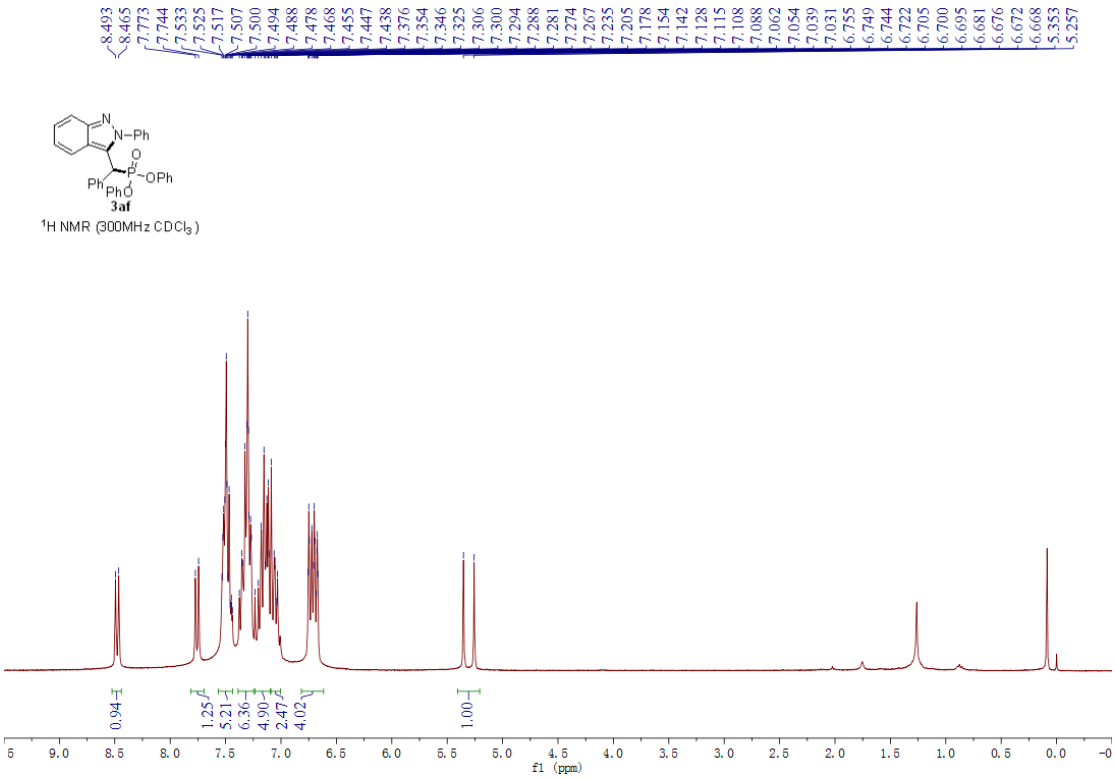

148.955
139.330
134.232
134.165
129.524
129.320
129.232
129.150
128.808
128.779
127.634
127.595
126.757
126.698
122.811
122.252
121.272
121.237
117.613
77.523 CDCl3
77.100 CDCl3
76.676 CDCl3
66.977
66.880
66.656
66.559
44.882
42.985
32.382
32.304
32.272
32.194
18.476
18.382
13.472
13.371
N–Ph
O
P
O^{n}Bu
Ph
^{n}BuO
3ad
^{13}C NMR (75MHz CDCl$_3$)
f1 (ppm)

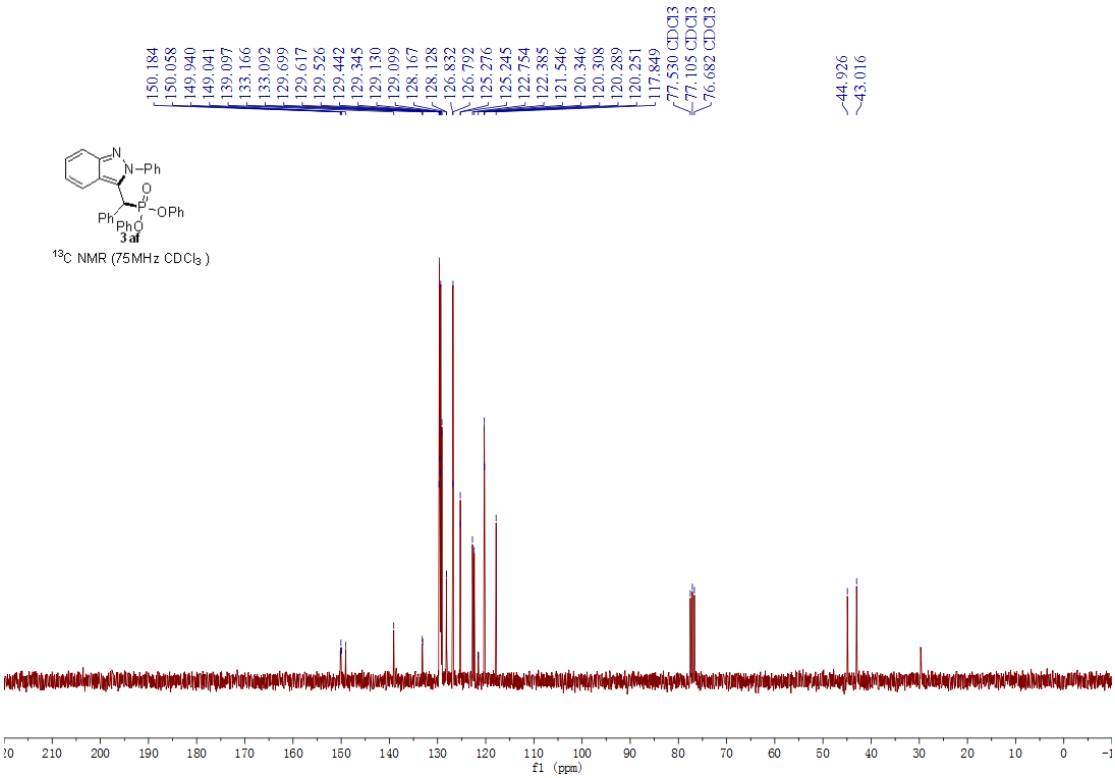

21.89
N
N–Ph
O
P
O^{n}Bu
Ph
BuO
3ad
^{31}P NMR (202 MHz CDCl$_3$)

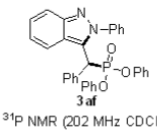

N
N–Ph
O
P
OBn
Ph
BnO
3ae
^{1}H NMR (300MHz CDCl$_3$)
f1 (ppm)


148.948
139.203
135.888
135.679
135.598
133.952
133.883
130.066
129.521
129.330
129.259
128.921
128.894
128.510
128.446
128.083
127.910
127.769
127.733
126.825
126.734
122.798
122.467
121.281
121.243
117.753
77.536 CDCl3
77.112 CDCl3
76.690 CDCl3
68.722
68.629
68.489
68.395
45.105
43.206
N
N–Ph
O
P
OBn
Ph
BnO
3ae
13C NMR (75MHz CDCl3)
f1 (ppm)


22.91
N
N–Ph
O
P
OBn
Ph
BnO
3ae
31P NMR (202 MHz CDCl3)

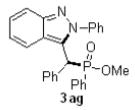

8.493
8.465
7.773
7.744
7.533
7.525
7.517
7.507
7.500
7.494
7.488
7.478
7.468
7.455
7.447
7.438
7.376
7.354
7.346
7.325
7.306
7.300
7.294
7.288
7.281
7.274
7.267
7.235
7.205
7.178
7.154
7.142
7.128
7.115
7.108
7.088
7.062
7.054
7.039
7.031
6.755
6.749
6.744
6.722
6.705
6.700
6.695
6.681
6.676
6.672
6.668
5.353
5.257
N
N–Ph
O
P
OPh
Ph
PhO
3af
1H NMR (300MHz CDCl3)
0.94
1.25
5.21
6.36
4.90
2.47
4.02
1.00
f1 (ppm)


150.184
150.058
149.940
149.041
139.097
133.166
133.092
129.699
129.617
129.526
129.442
129.345
129.130
129.099
128.167
128.128
126.832
126.792
125.276
125.245
122.754
122.385
121.546
120.346
120.308
120.289
120.251
117.849
77.530 CDCl3
77.105 CDCl3
76.682 CDCl3
44.926
43.016
N
N–Ph
O
P
OPh
Ph
PhO
3af
13C NMR (75MHz CDCl3)
f1 (ppm)



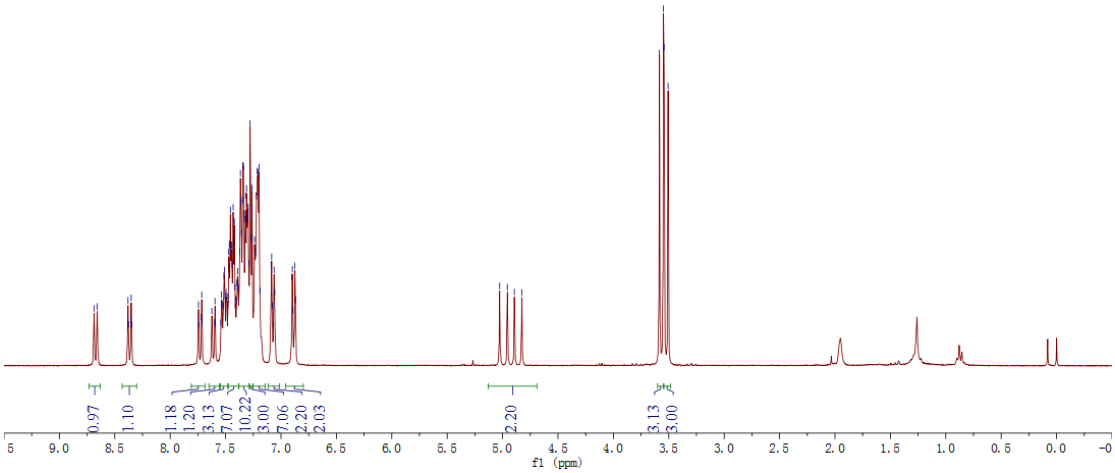
3af

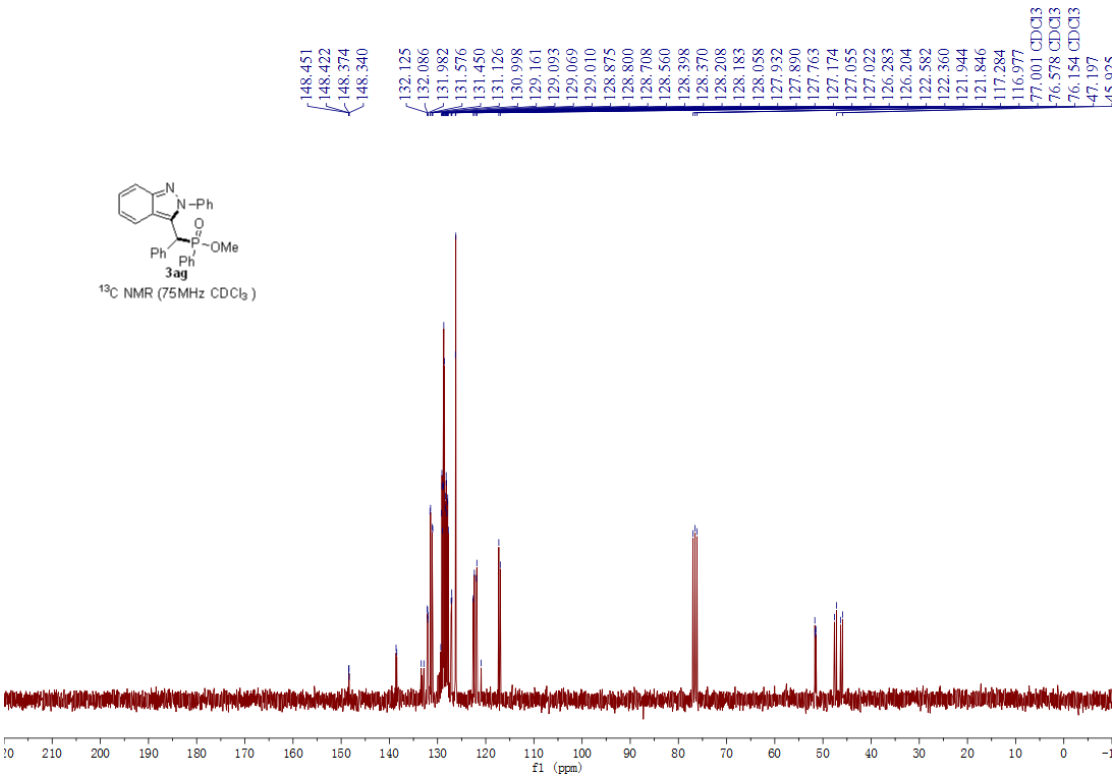
^{31}P NMR (202 MHz $CDCl_3$)

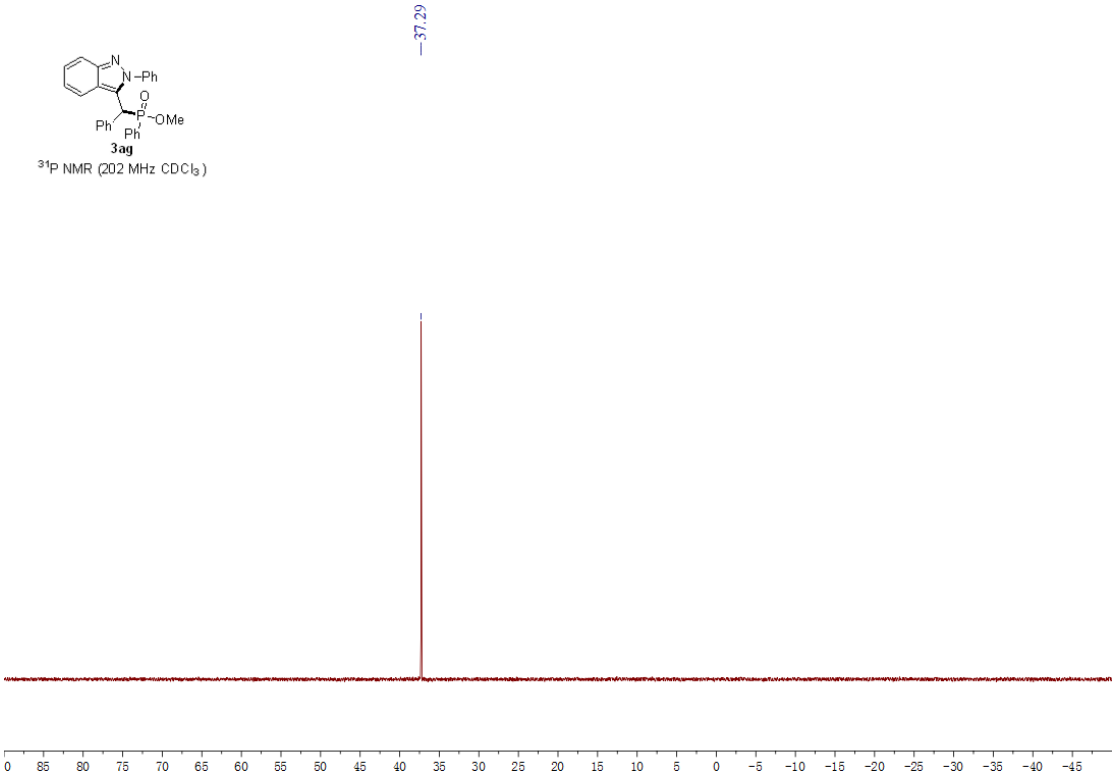


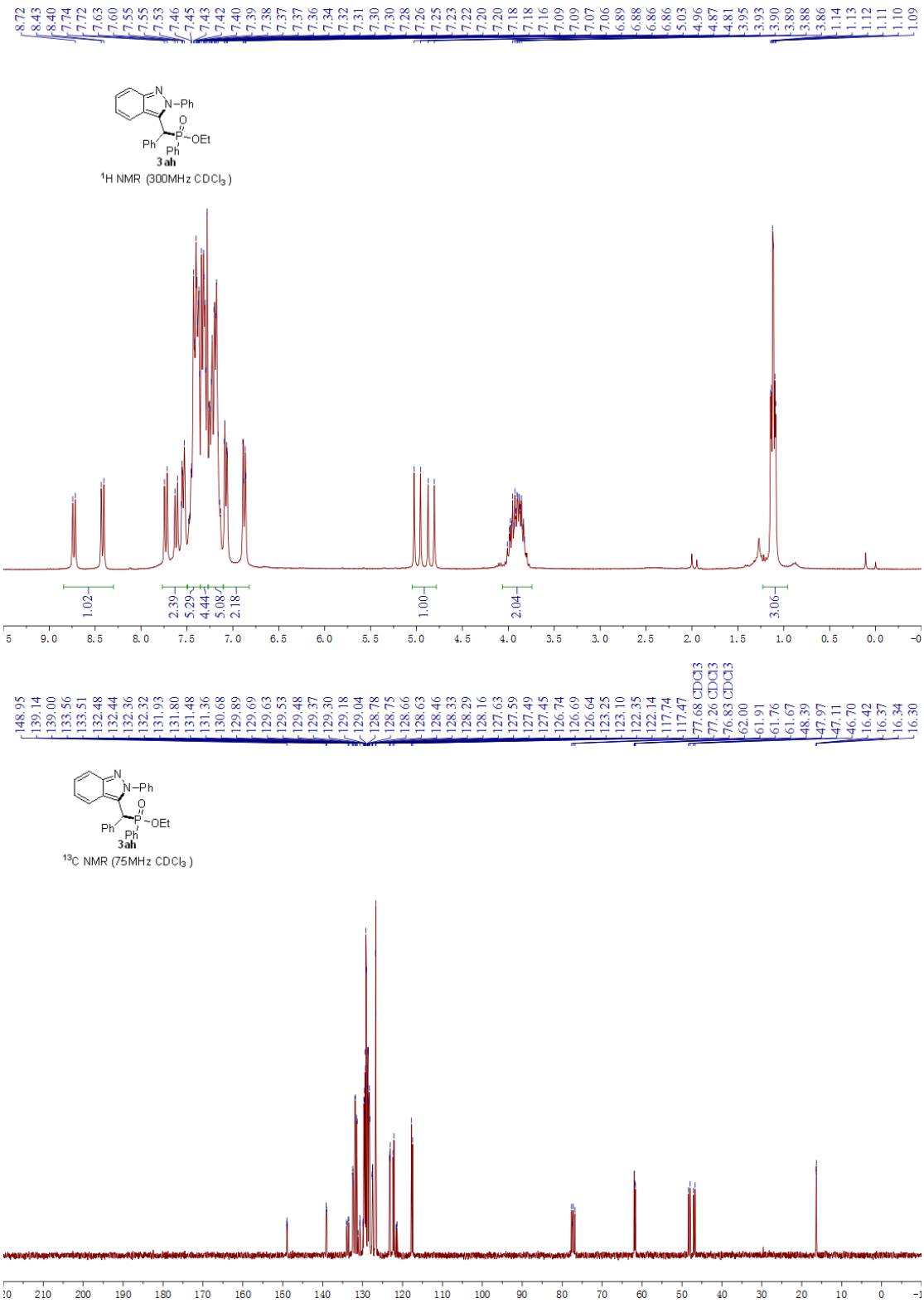
3ag

^{1}H NMR (300MHz $CDCl_3$)



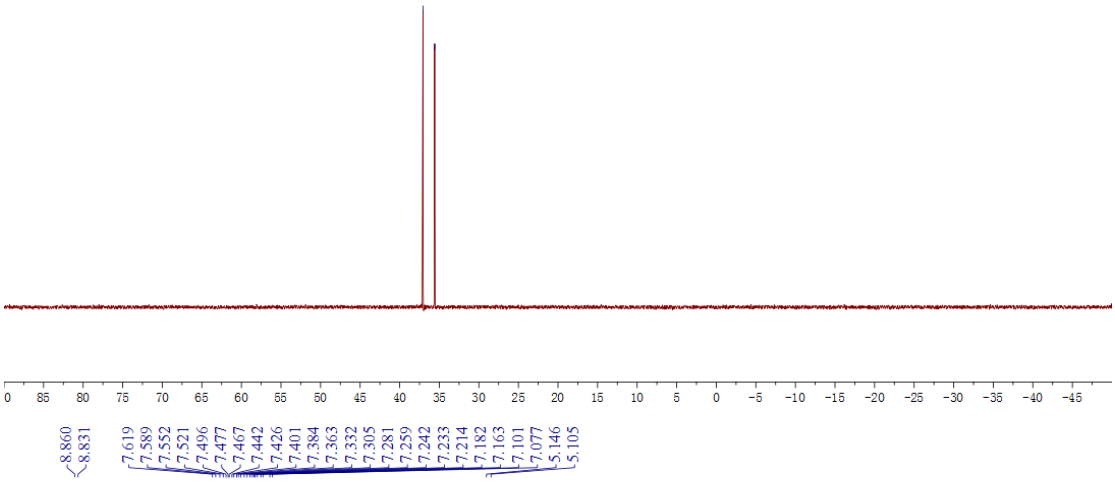

148.451
148.422
148.374
148.340
132.125
132.086
131.982
131.576
131.450
131.126
130.998
129.161
129.093
129.069
129.010
128.875
128.800
128.708
128.560
128.398
128.370
128.208
128.183
128.058
127.932
127.890
127.763
127.174
127.055
127.022
126.283
126.204
122.582
122.360
121.944
121.846
117.284
116.977
77.001 CDCl3
76.578 CDCl3
76.154 CDCl3
47.197
N
N–Ph
O
P
OMe
Ph
Ph
3ag
13C NMR (75MHz CDCl3)
f1 (ppm)

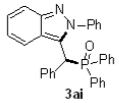

37.29
N
N–Ph
O
P
OMe
Ph
Ph
3ag
31P NMR (202 MHz CDCl3)


3ah
^{1}H NMR (300MHz CDCl$_3$)
3ah
^{13}C NMR (75MHz CDCl$_3$)

3ah

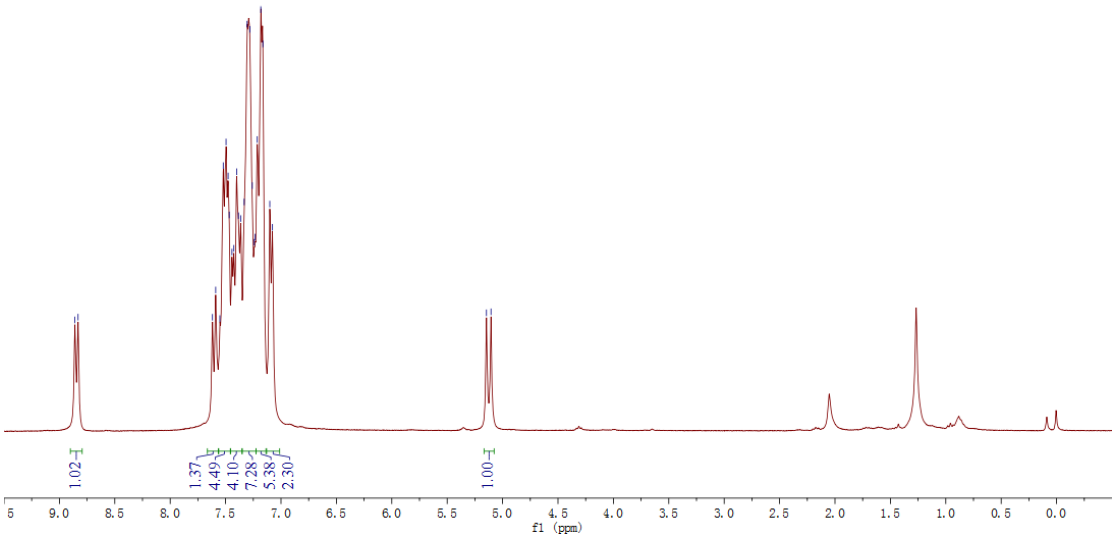
^{31}P NMR (202 MHz $CDCl_3$)

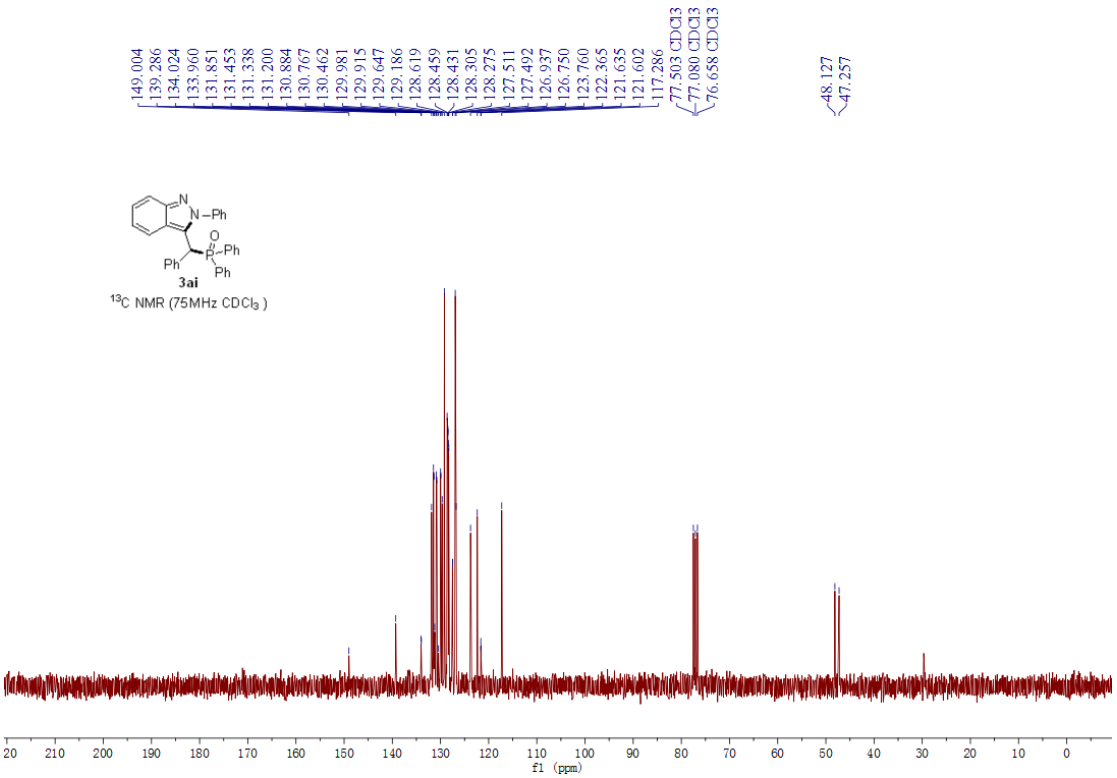


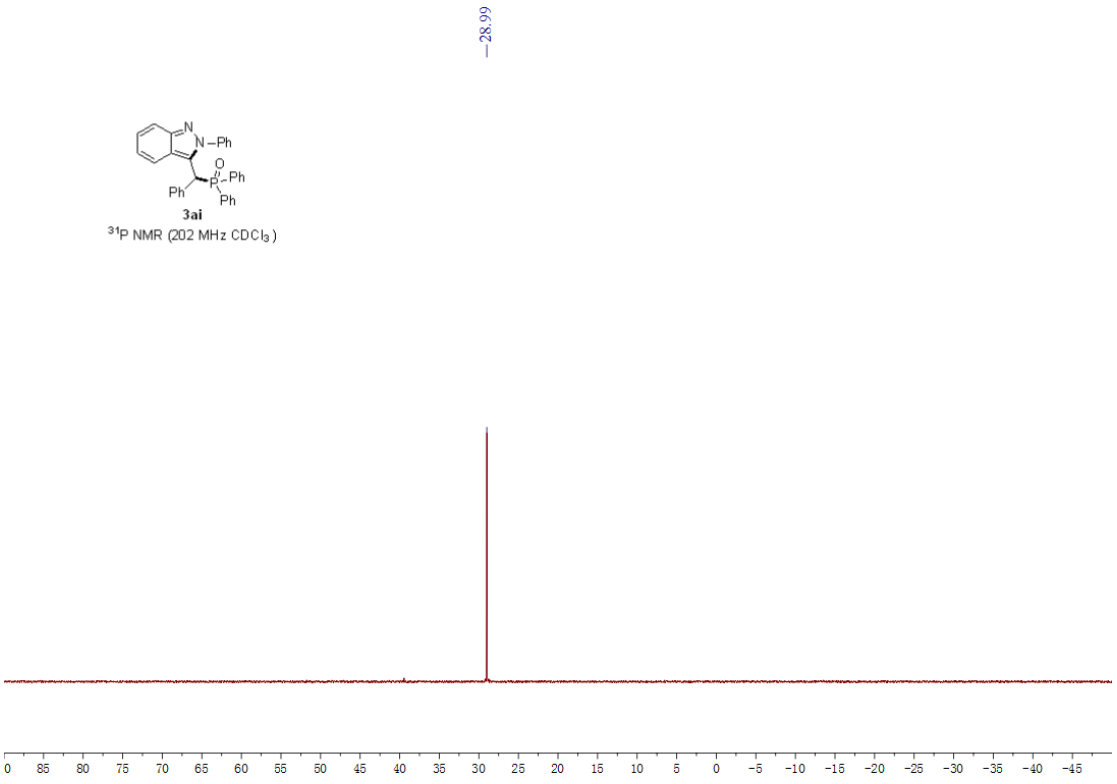


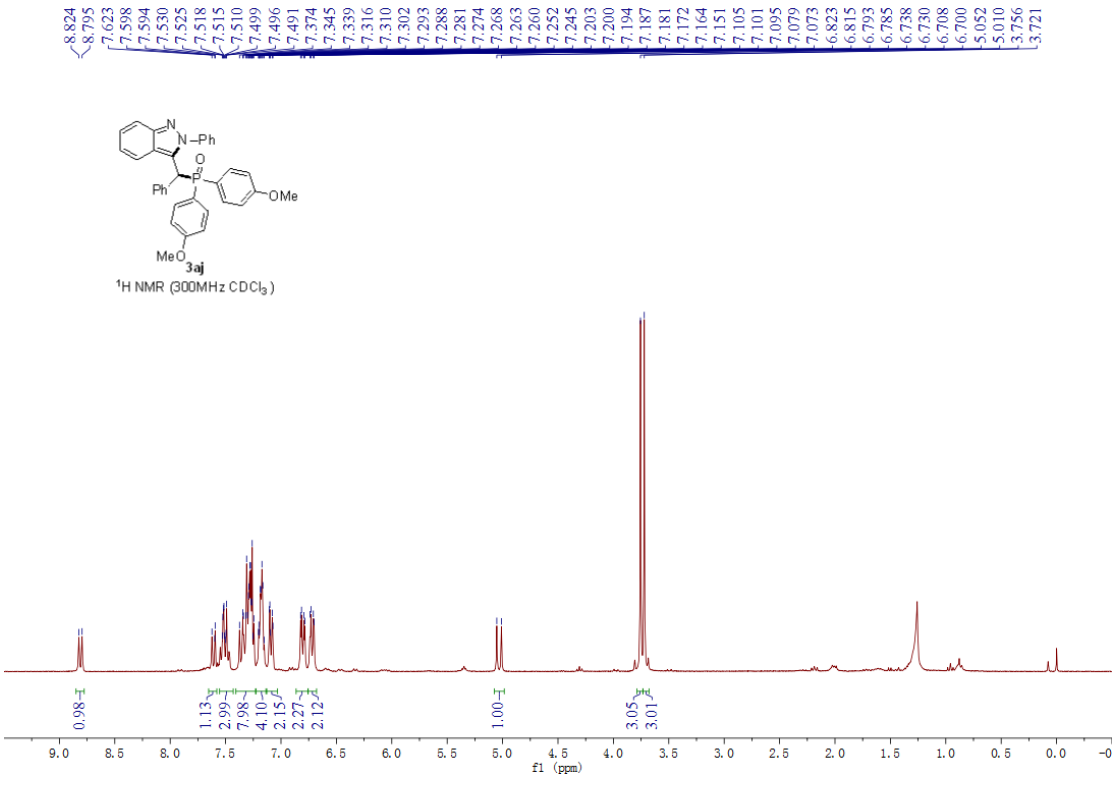
3ai

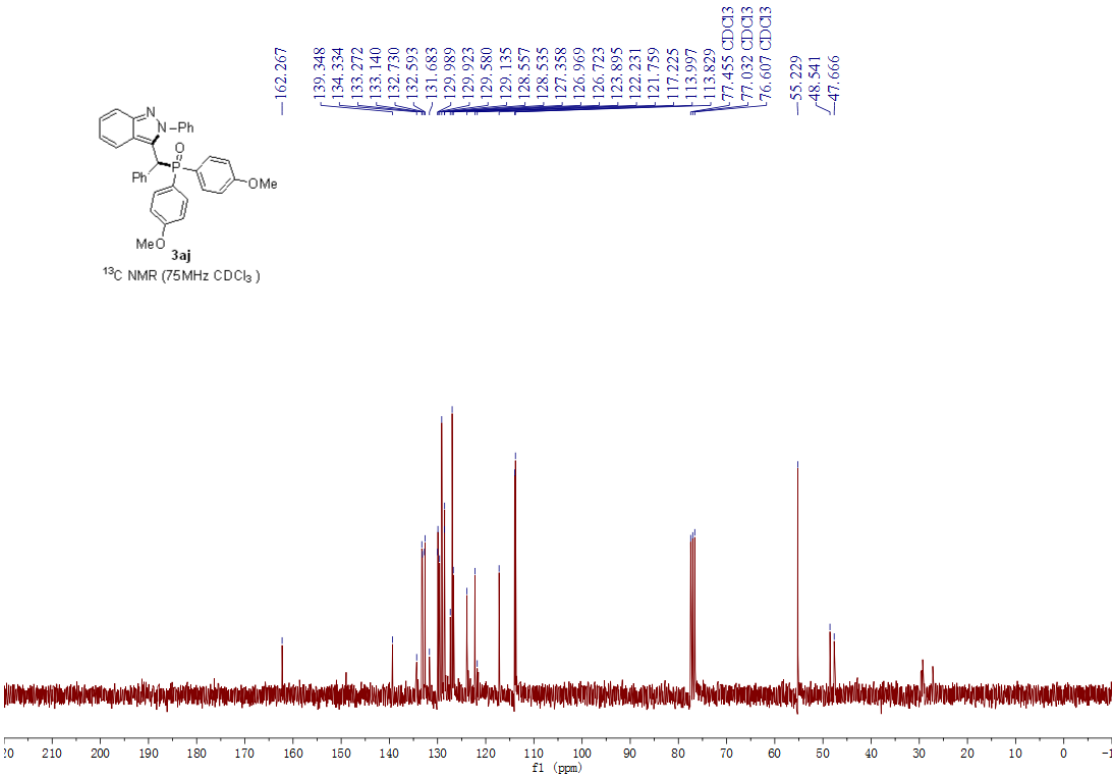
^{1}H NMR (300MHz $CDCl_3$)

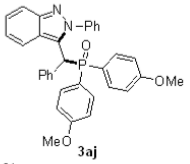



149.004
139.286
134.024
133.960
131.851
131.453
131.338
131.200
130.884
130.767
130.462
129.981
129.915
129.647
129.186
128.619
128.459
128.431
128.305
128.275
127.511
127.492
126.937
126.750
123.760
122.365
121.635
121.602
117.286
77.503 CDCl3
77.080 CDCl3
76.658 CDCl3
48.127
47.257
3ai
13C NMR (75MHz CDCl3)
f1 (ppm)


28.99
3ai
31P NMR (202 MHz CDCl3)

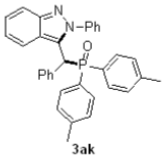

8.824
8.795
7.623
7.598
7.594
7.530
7.525
7.518
7.515
7.510
7.499
7.496
7.491
7.374
7.345
7.339
7.316
7.310
7.302
7.293
7.288
7.281
7.274
7.268
7.263
7.260
7.252
7.245
7.203
7.200
7.194
7.187
7.181
7.172
7.164
7.151
7.105
7.101
7.095
7.079
7.073
6.823
6.815
6.793
6.785
6.738
6.730
6.708
6.700
5.052
5.010
3.756
3.721
N
N–Ph
O
P
Ph
OMe
MeO
3aj
1H NMR (300MHz CDCl3)
0.98
1.13
2.99
7.98
4.10
2.15
2.27
2.12
1.00
3.05
3.01
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)


162.267
139.348
134.334
133.272
133.140
132.730
132.593
131.683
129.989
129.923
129.580
129.135
128.557
128.535
127.358
126.969
126.723
123.895
122.231
121.759
117.225
113.997
113.829
77.455 CDCl3
77.032 CDCl3
76.607 CDCl3
55.229
48.541
47.666
N
N–Ph
O
P
Ph
OMe
MeO
3aj
13C NMR (75MHz CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



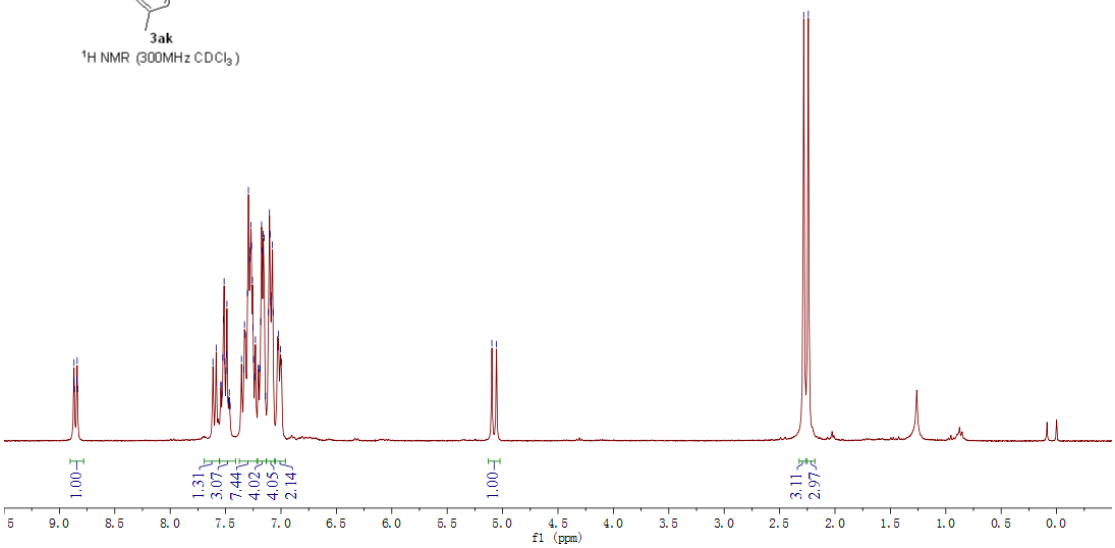
3aj

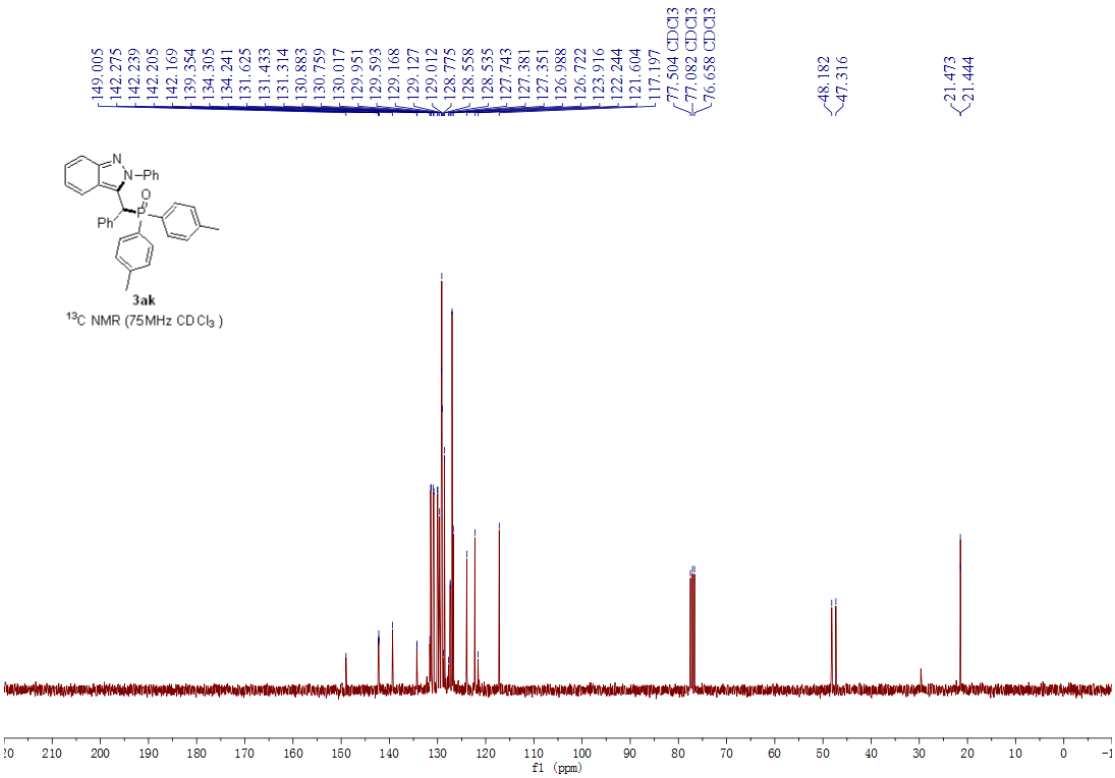
^{31}P NMR (202 MHz $CDCl_3$)

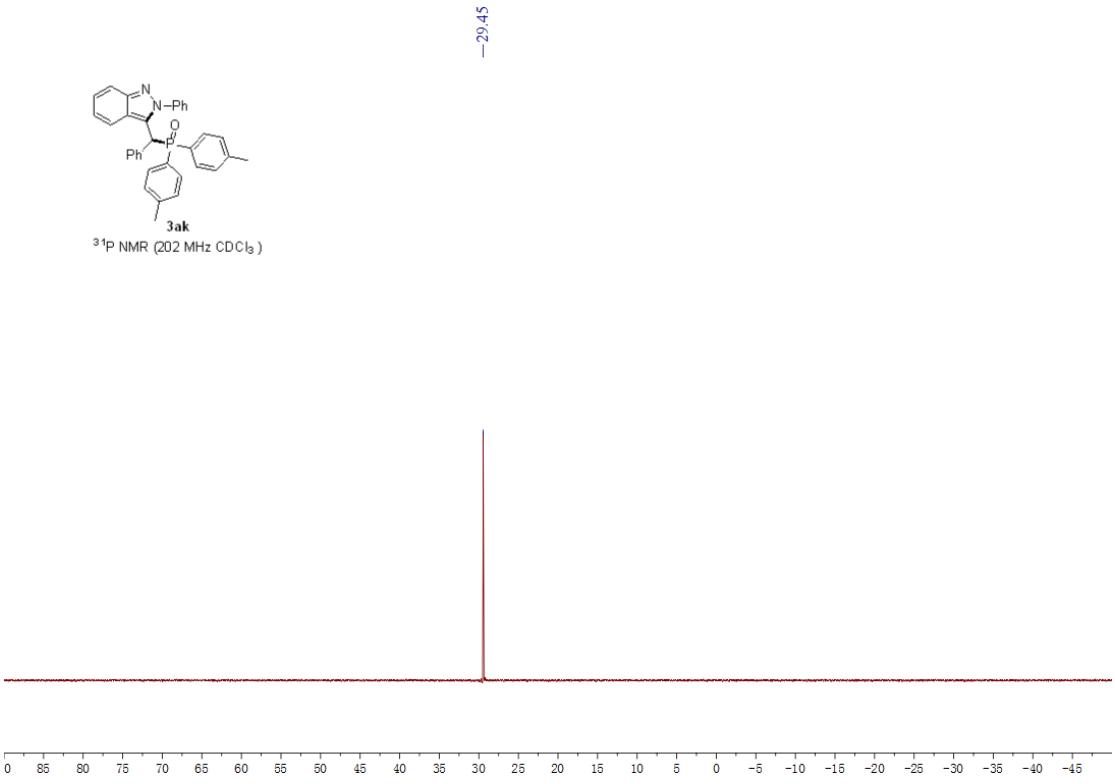


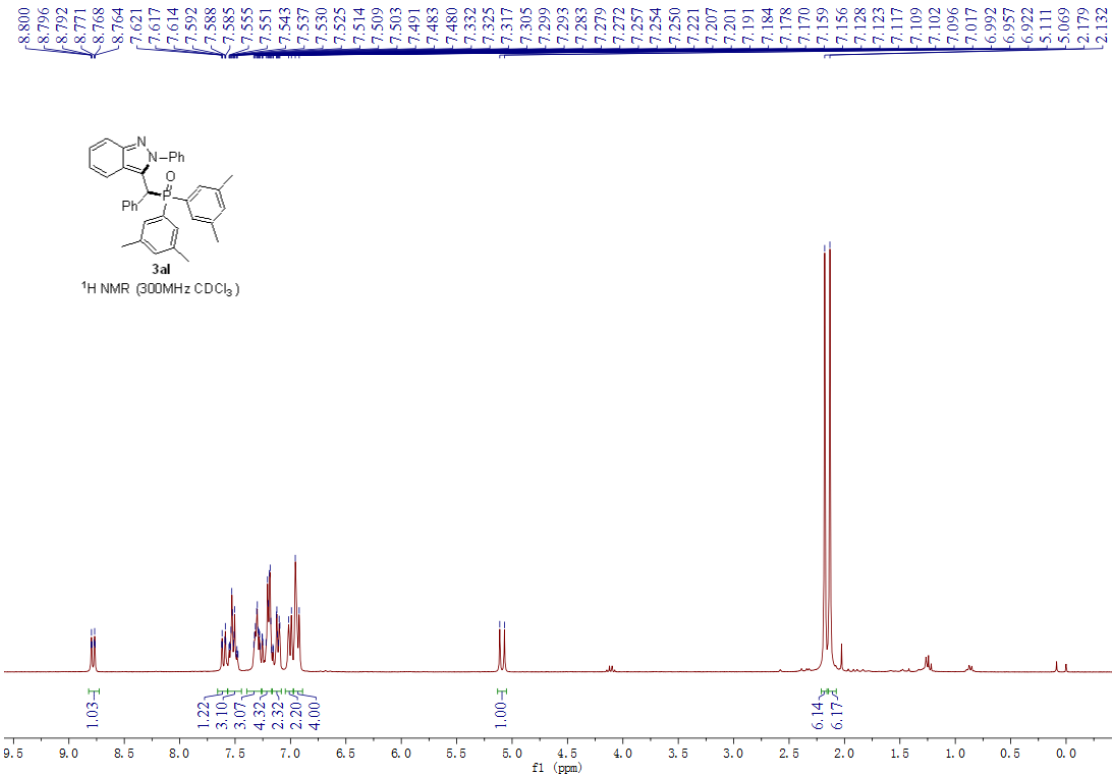
3ak

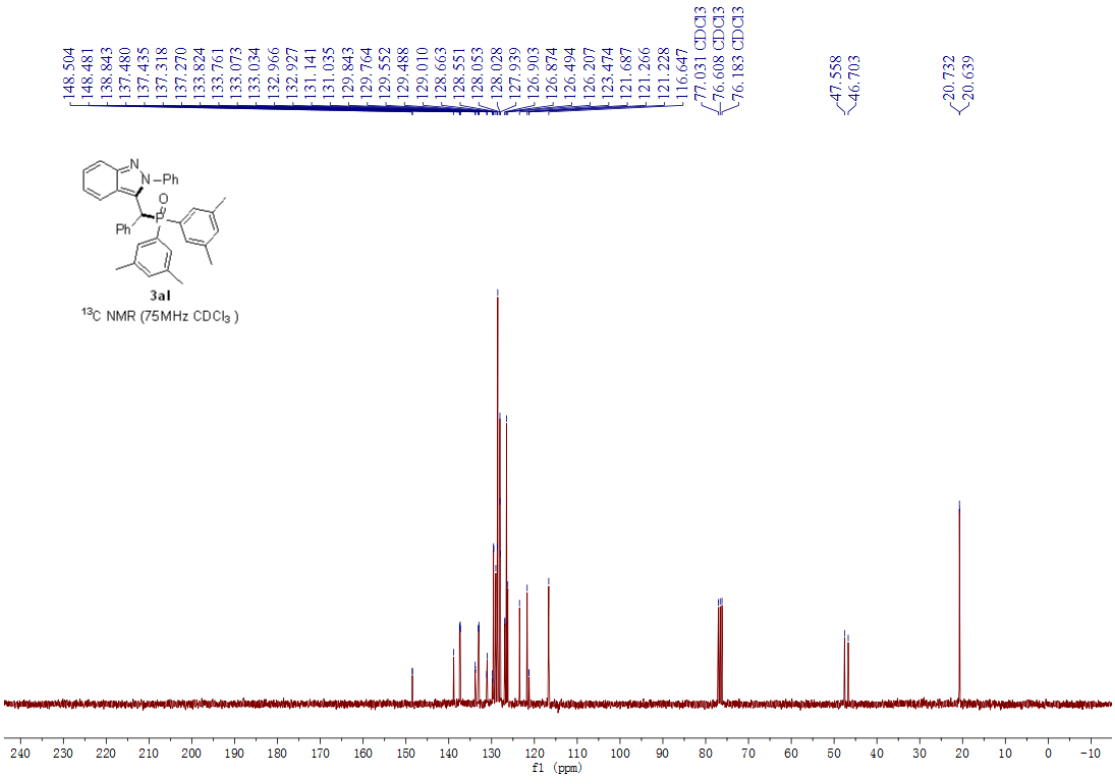
^{1}H NMR (300MHz $CDCl_3$)

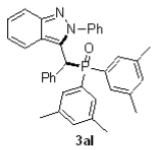



149.005
142.275
142.239
142.205
142.169
139.354
134.305
134.241
131.625
131.433
131.314
130.883
130.759
130.017
129.951
129.593
129.168
129.127
129.012
128.775
128.558
128.535
127.743
127.381
127.351
126.988
126.722
123.916
122.244
121.604
117.197
77.504 CDCl3
77.082 CDCl3
76.658 CDCl3
48.182
47.316
21.473
21.444
N–Ph
O
P
Ph
3ak
13C NMR (75MHz CDCl3)
f1 (ppm)


29.45
N–Ph
O
P
Ph
3ak
31P NMR (202 MHz CDCl3)

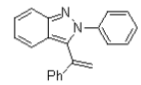

8.800
8.796
8.792
8.771
8.768
8.764
7.621
7.617
7.614
7.592
7.588
7.585
7.555
7.551
7.543
7.537
7.530
7.525
7.514
7.509
7.503
7.491
7.483
7.480
7.332
7.325
7.317
7.305
7.299
7.293
7.283
7.279
7.272
7.257
7.254
7.250
7.221
7.207
7.201
7.191
7.184
7.178
7.170
7.159
7.156
7.128
7.123
7.117
7.109
7.102
7.096
7.017
6.992
6.957
6.922
5.111
5.069
2.179
2.132
N
N–Ph
O
P
Ph
3al
1H NMR (300MHz CDCl3)
1.03
1.22
3.10
3.07
4.32
2.32
2.20
4.00
1.00
6.14
6.17
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)


148.504
148.481
138.843
137.480
137.435
137.318
137.270
133.824
133.761
133.073
133.034
132.966
132.927
131.141
131.035
129.843
129.764
129.552
129.488
129.010
128.663
128.551
128.053
128.028
127.939
126.903
126.874
126.494
126.207
123.474
121.687
121.266
121.228
116.647
77.031 CDCl3
76.608 CDCl3
76.183 CDCl3
47.558
46.703
20.732
20.639
N
N–Ph
O
P
Ph
3al
13C NMR (75MHz CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



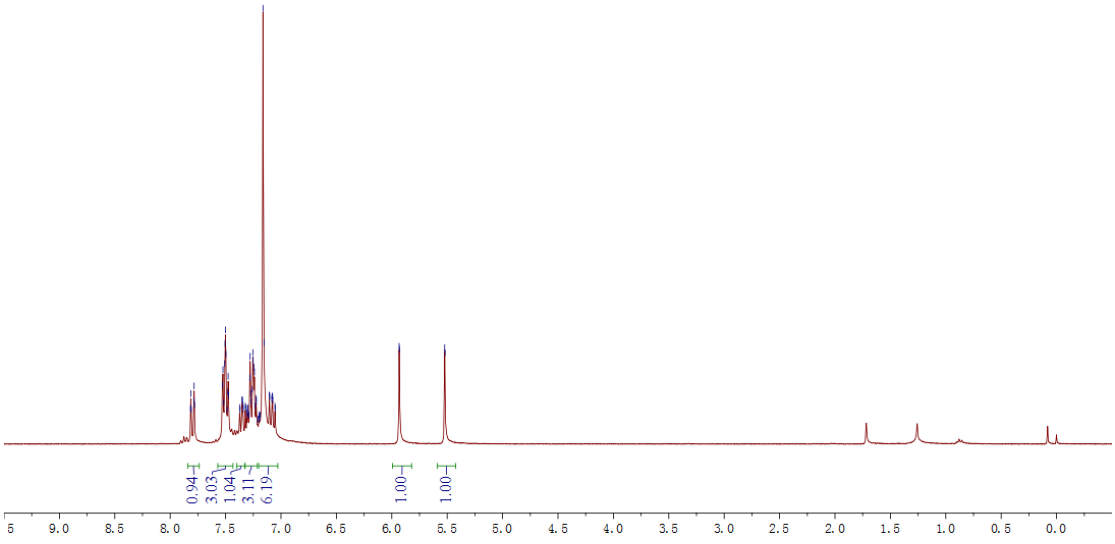
3al

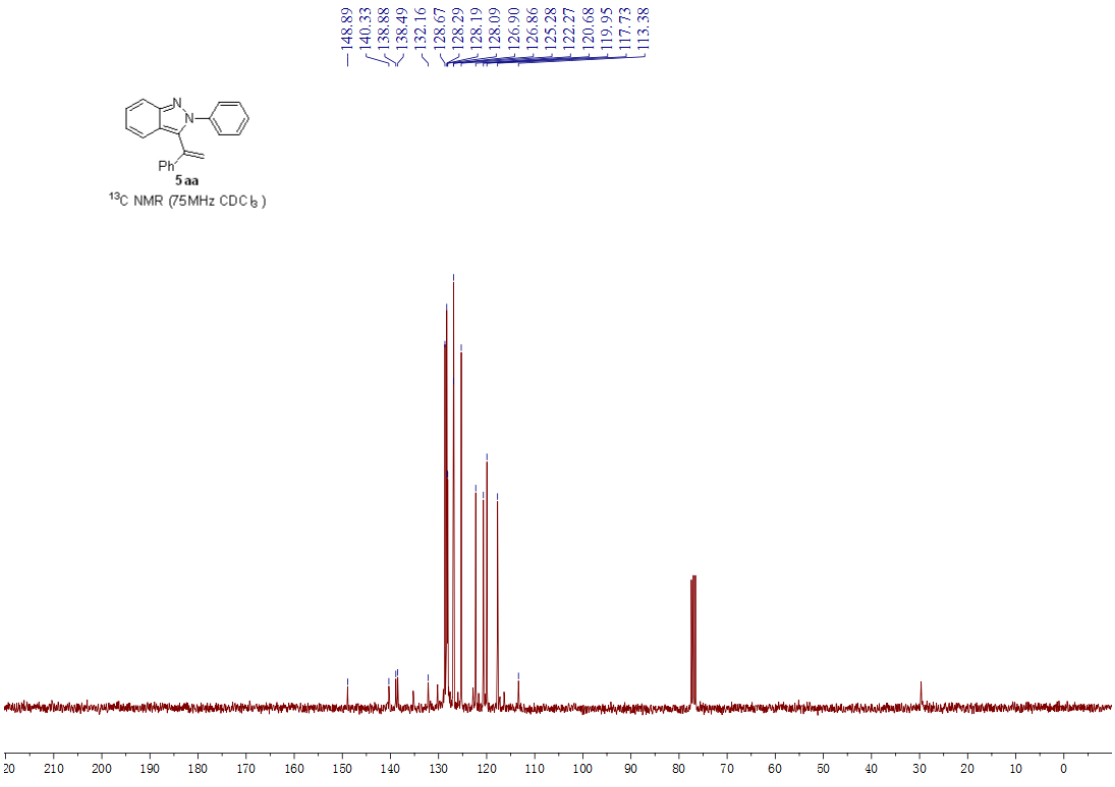
^{31}P NMR (202 MHz $CDCl_3$)

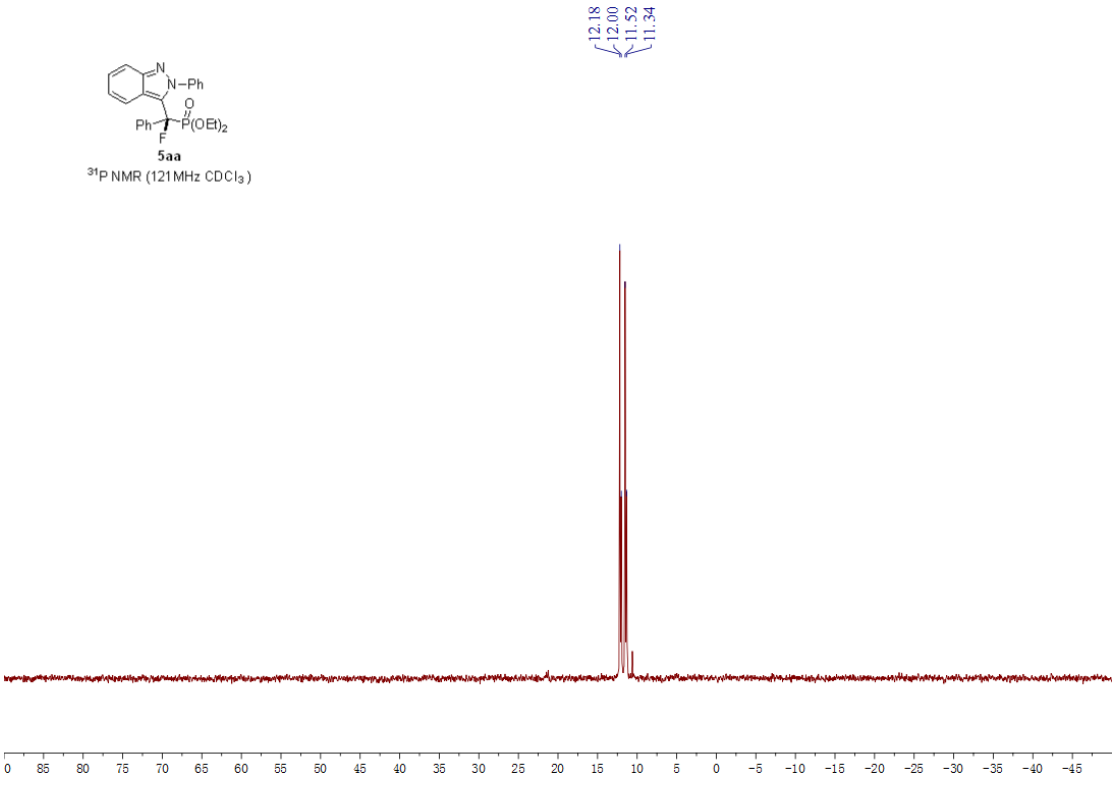


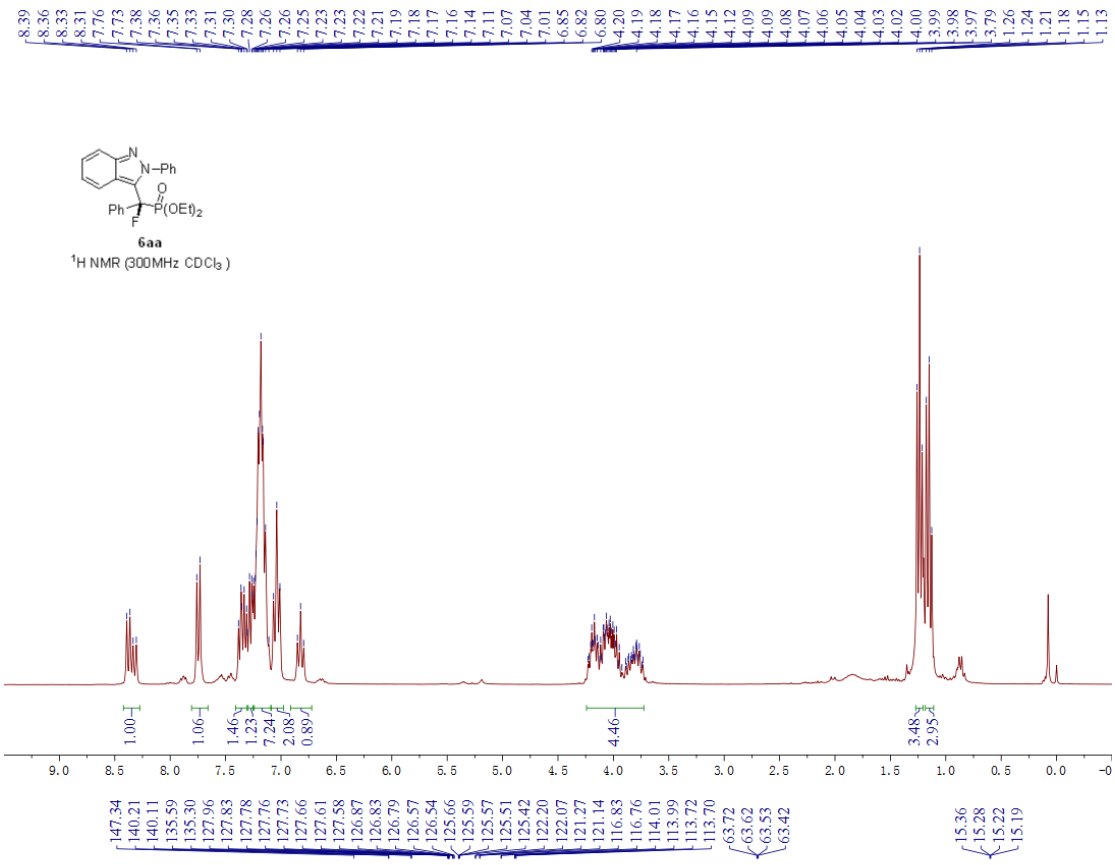
5aa

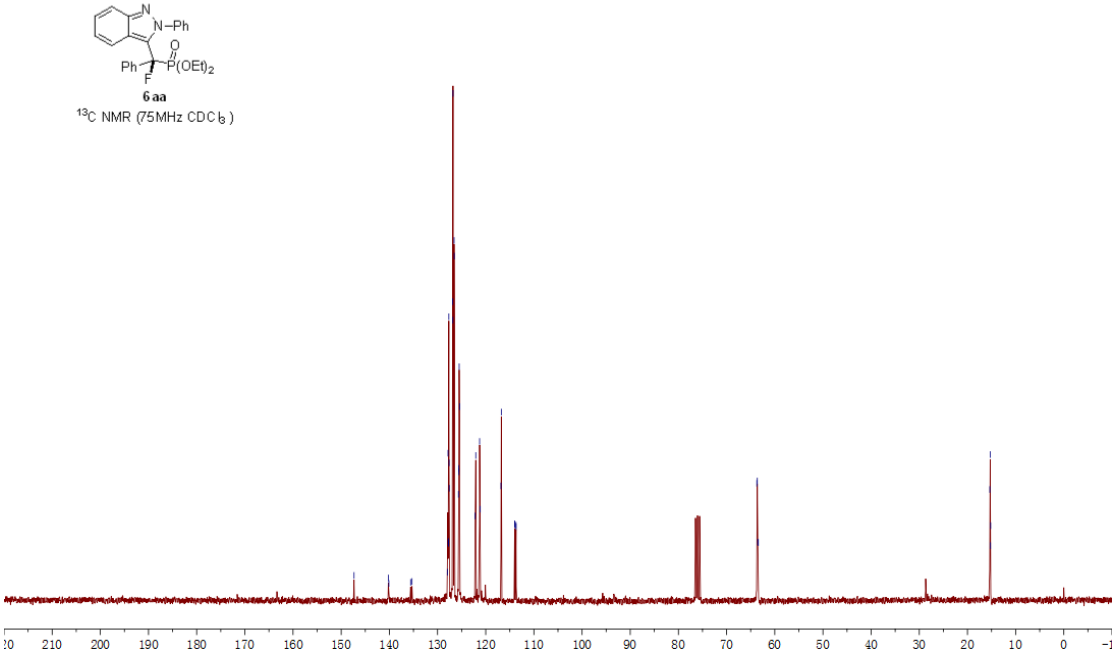
^{1}H NMR (300MHz $CDCl_3$)

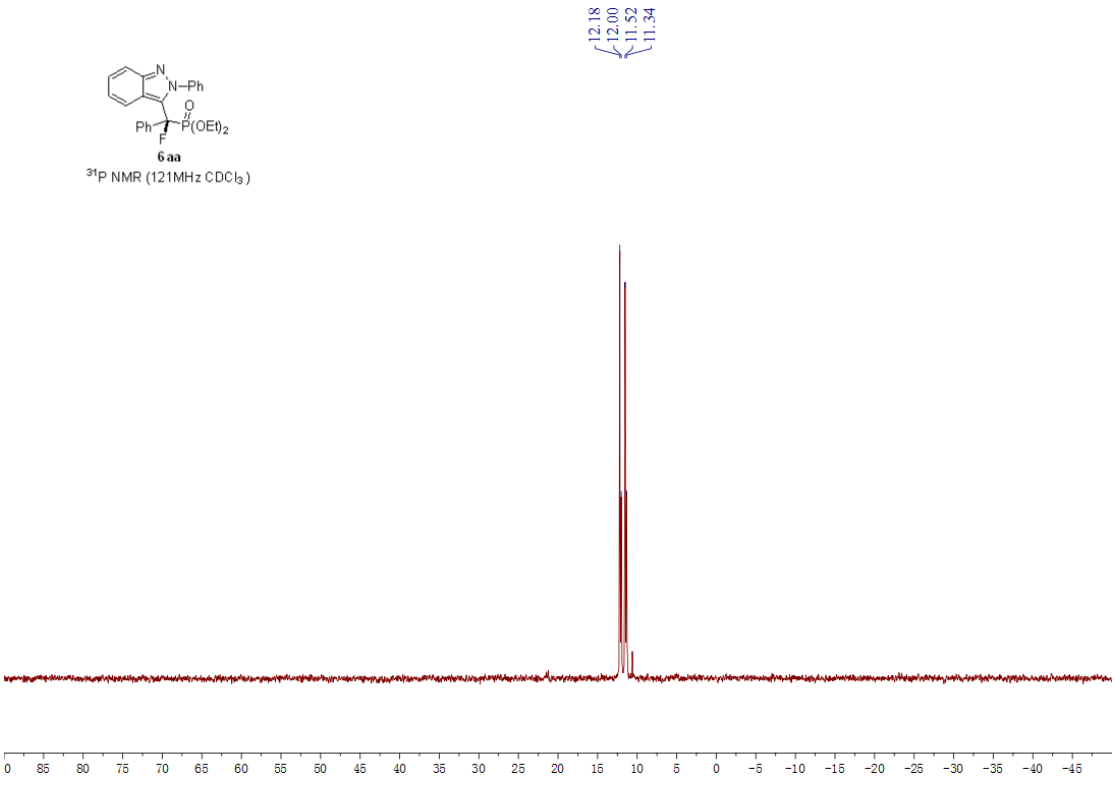



148.89
140.33
138.88
138.49
132.16
128.67
128.29
128.19
128.09
126.90
126.86
125.28
122.27
120.68
119.95
117.73
113.38
Ph
5aa
13C NMR (75MHz CDCl3)

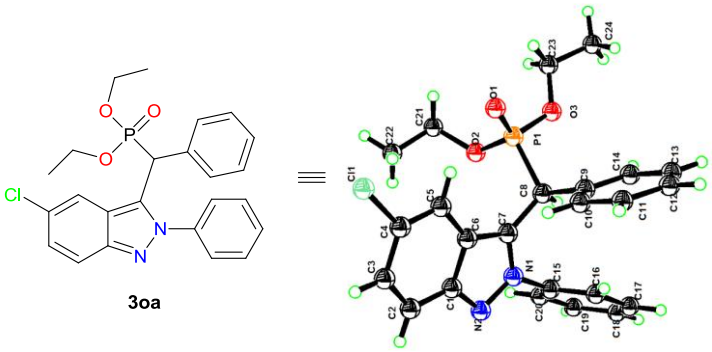

12.18
12.00
11.52
11.34
N–Ph
O
Ph
F
P(OEt)2
5aa
31P NMR (121MHz CDCl3)


8.39 8.36 8.33 8.31 7.76 7.73 7.38 7.36 7.35 7.33 7.31 7.30 7.28 7.26 7.26 7.25 7.23 7.23 7.22 7.21 7.19 7.18 7.17 7.16 7.14 7.11 7.07 7.04 7.01 6.85 6.82 6.80 4.20 4.19 4.18 4.17 4.16 4.15 4.12 4.09 4.09 4.08 4.07 4.06 4.05 4.04 4.03 4.02 4.00 3.99 3.98 3.97 3.79 1.26 1.24 1.21 1.18 1.15 1.13
N–Ph
O
Ph
F
P(OEt)2
6aa
1H NMR (300MHz CDCl3)
1.00 1.06 1.46 1.23 7.24 2.08 0.89 4.46 3.48 2.95
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
147.34 140.21 140.11 135.59 135.30 127.96 127.83 127.78 127.76 127.73 127.66 127.61 127.58 126.87 126.83 126.79 126.57 126.54 125.66 125.59 125.57 125.51 125.42 122.20 122.07 121.27 121.14 116.83 116.76 114.01 113.99 113.72 113.70 63.72 63.62 63.53 63.42 15.36 15.28 15.22 15.19


N–Ph
O
Ph
F
P(OEt)2
6aa
13C NMR (75MHz CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


12.18
12.00
11.52
11.34
N
N–Ph
O
P(OEt)2
Ph
F
6 aa
31P NMR (121MHz CDCl3)
0 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45

8. X-ray crystal structure of 3oa



CCDC−1553330 (**3oa**) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

```
Bond precision:  C-C = 0.0044 A          Wavelength=0.71073

Cell:            a=10.918(2)     b=14.453(3)         c=14.576(3)
                 alpha=90        beta=95.125(6)      gamma=90
Temperature:     205 K

                 Calculated                Reported
Volume           2290.9(8)                 2290.8(7)
Space group      P 21/n                    P 1 21/n 1
Hall group       -P 2yn                    -P 2yn
Moiety formula   C24 H24 Cl N2 O3 P        C24 H24 Cl N2 O3 P
Sum formula      C24 H24 Cl N2 O3 P        C24 H24 Cl N2 O3 P
Mr               454.87                    454.87
Dx,g cm-3        1.319                     1.319
Z                4                         4
Mu (mm-1)        0.265                     0.265
F000             952.0                     952.0
F000'            953.36
h,k,lmax         14,18,18                  13,18,18
Nref             5062                      5054
Tmin,Tmax        0.950,0.969               0.667,0.746
Tmin'            0.928

Correction method= # Reported T Limits: Tmin=0.667 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 27.116

R(reflections)= 0.0552( 2811)     wR2(reflections)= 0.1557( 5054)

S = 0.970                 Npar= 301
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