

Electronic Supplementary Information

Cu₂O-catalyzed cascade phosphinylation/cyclization of 2'- aminochalcones for the synthesis of hemi-indigo derivatives

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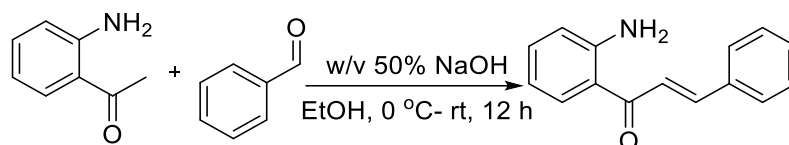
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1. General Experiment Information

All reagents were obtained from commercial sources and used as received without further purification unless otherwise stated. NMR spectra were recorded on a BrukerAvanceII 400 spectrometer and BrukerAvanceII 600 spectrometer in DMSO-*d*₆ or CDCl₃ with tetramethylsilane (TMS) as an internal standard; chemical shifts δ were given in ppm and coupling constants *J* in Hz. HRMS were measured on a QSTAR Pulsar I LC/TOF MS mass spectrometer.

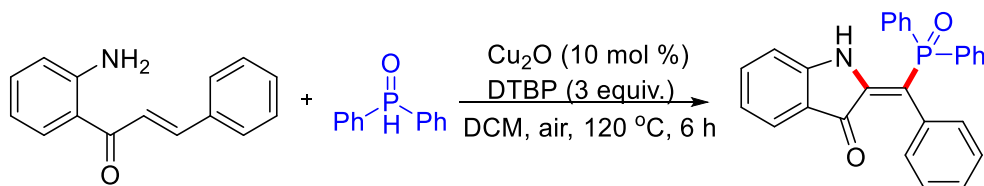
2. General Procedures

2.1 General procedure for Synthesis of 2'-amino Chalcones.



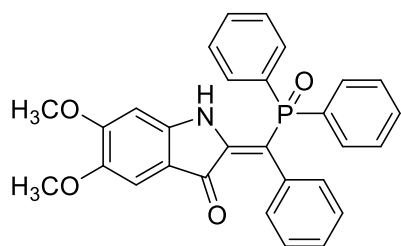
A round bottom flask containing a magnetic stirring bar was charged with 1-(2-aminophenyl)ethan-1-one (1 mmol, 1.0 equiv.) in ethanol and 50% w/v NaOH (5 mL). Then mixture was kept in 0 °C and corresponding benzaldehyde (1.1 mmol, 1.1 equiv.) was added. Then reaction mixture was stirred for 12 h. After the completion of the reaction (as monitored by TLC), water (15 mL) was added. The organic phase was extracted three times with 45 mL of ethyl acetate, dried over anhydrous sodium sulfate and filtered, and the solvent was evaporated under vacuum. Purification was performed by column chromatography on silica gel to obtain the desired products as a yellow solid.

2.2 General procedure for Synthesis of (Z)-2-((diphenylphosphoryl)(phenyl)methylene)indolin-3-one

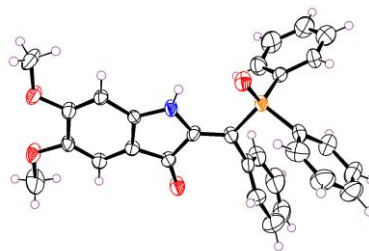


A mixture of 2'-amino Chalcones (0.2 mmol, 1.0 equiv.), diphenylphosphine oxide (0.3 mmol, 1.5 equiv.), Cu₂O (10 mol%) and DTBP (0.6 mmol, 3.0 equiv.) in DCM (2 mL) was stirred in sealed tubes at 120 °C for 6 h. After the completion of the reaction (TLC), H₂O (10 mL) was added. The mixture was extracted with DCM (3×10 mL), dried over anhydrous sodium sulfate and filtered, and the combined organic layers were concentrated by a rotary evaporator. Purification was performed by column chromatography on silica gel to provide the desired products.

2.3 Single crystal structure of 4a



4a

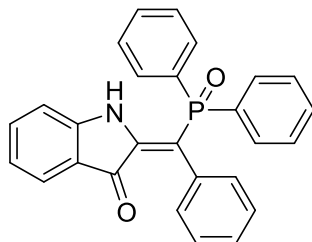


X-ray Single crystal structure of **4a**

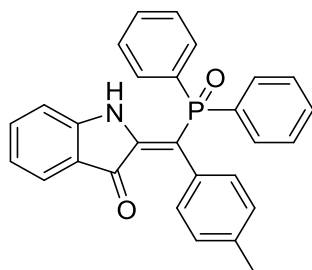
Empirical formula	$C_{29}H_{24}NO_4P$
Formula weight	481.1443
Temperature	294.00 K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 16.3847 (4) \text{ \AA}$ $\alpha = 90^\circ$ $b = 17.7511 (5) \text{ \AA}$ $\beta = 107.6320 (10)^\circ$ $c = 18.5322 (5) \text{ \AA}$ $\gamma = 90^\circ$
Volume	$5136.8 (2) \text{ \AA}^3$
Z	8
Density (calculated)	1.245 Mg/m^3
Absorption coefficient	1.229 mm^{-1}
F (000)	2016
Crystal size	$0.150 \times 0.090 \times 0.050 \text{ mm}^3$
Theta range for data collection	3.770 to 68.430°
Index ranges	$-19 \leq h \leq 19$, $-20 \leq k \leq 21$, $-22 \leq l \leq 21$
Reflections collected	58205
Independent reflections	4667 [R(int) = 0.0563]
Completeness to theta = 67.679°	98.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4667 / 187 / 354

Goodness-of-fit on F^2	1.095
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0475, wR2 = 0.1345
R indices (all data)	R1 = 0.0531, wR2 = 0.1447
Extinction coefficient	n/a
Largest diff. peak and hole	0.410 and -0.335 e. \AA^{-3}

3. Characterization of Materials

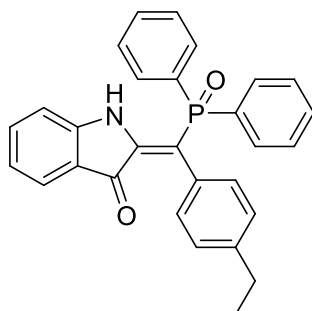


(Z)-2-((diphenylphosphoryl)(phenyl)methylene)indolin-3-one (3a): Compound **3a** was isolated as a red oil (64.1 mg, 76%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.28 (s, 1H), 7.60 (dd, $J = 8.5, 4.6$ Hz, 2H), 7.55 – 7.41 (m, 9H), 7.39 (d, $J = 7.5$ Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 1H), 7.18 (t, $J = 7.3$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 2H), 6.88 (t, $J = 7.4$ Hz, 1H), 6.67 (d, $J = 7.6$ Hz, 2H). ^{13}C NMR (151 MHz, DMSO) δ 185.35 (d, $J = 11.6$ Hz), 185.27 (d, $J = 11.6$ Hz), 153.10, 143.31, 137.59, 133.72 (d, $J = 6.3$ Hz), 133.68 (d, $J = 6.3$ Hz), 132.85 (d, $J = 1.8$ Hz), 132.84 (d, $J = 1.8$ Hz), 132.42 (d, $J = 9.7$ Hz), 132.36 (d, $J = 9.7$ Hz), 131.15 (d, $J = 104.2$ Hz), 130.97 (d, $J = 4.2$ Hz), 130.94 (d, $J = 4.2$ Hz), 130.46 (d, $J = 104.2$ Hz), 129.04 (d, $J = 11.6$ Hz), 128.96 (d, $J = 11.6$ Hz), 128.42, 127.64 (d, $J = 1.5$ Hz), 127.63 (d, $J = 1.5$ Hz), 124.61, 120.52, 119.71 (d, $J = 2.3$ Hz), 119.69 (d, $J = 2.3$ Hz), 113.16, 111.78 (d, $J = 90.1$ Hz), 111.18 (d, $J = 90.1$ Hz). ^{31}P NMR (243 MHz, DMSO) δ 31.76 (s). HRMS (EI): m/z $[M]^+$ calcd. for $\text{C}_{27}\text{H}_{20}\text{NO}_2\text{P}$: 421.1232. Found: 421.1234.

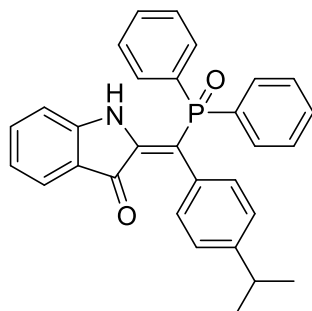


(Z)-2-((diphenylphosphoryl)(phenyl)methylene)indolin-3-one (3b): Compound **3b** was isolated as a red oil (69.7 mg, 80%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.34 (s, 1H), 7.60 (dd, $J = 8.5, 4.4$ Hz, 2H), 7.48 (dd, $J = 15.0,$

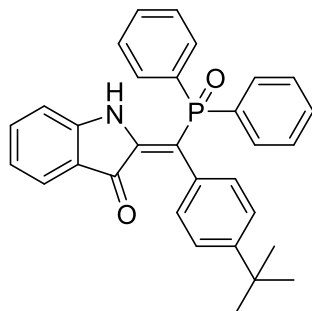
7.7 Hz, 9H), 7.38 (d, $J = 7.6$ Hz, 1H), 7.30 (d, $J = 8.1$ Hz, 1H), 6.95 – 6.82 (m, 3H), 6.55 (d, $J = 7.4$ Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 185.32 (d, $J = 11.5$ Hz), 185.24 (d, $J = 11.5$ Hz), 153.00, 143.41 (d, $J = 1.5$ Hz), 143.40 (d, $J = 1.5$ Hz), 137.52, 136.86 (d, $J = 2.1$ Hz), 136.85 (d, $J = 2.1$ Hz), 132.82 (d, $J = 2.7$ Hz), 132.81 (d, $J = 2.7$ Hz), 132.45 (d, $J = 9.7$ Hz), 132.39 (d, $J = 9.7$ Hz), 131.21 (d, $J = 104.5$ Hz), 130.91 (d, $J = 4.2$ Hz), 130.89 (d, $J = 4.2$ Hz), 130.52 (d, $J = 104.5$ Hz), 130.47, 129.07, 129.02 (d, $J = 12.1$ Hz), 128.94 (d, $J = 12.1$ Hz), 124.57, 120.44, 119.73 (d, $J = 2.4$ Hz), 119.71 (d, $J = 2.4$ Hz), 113.09, 111.89 (d, $J = 90.1$ Hz), 111.29 (d, $J = 90.1$ Hz), 21.25. ^{31}P NMR (243 MHz, DMSO) δ 31.66 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{28}\text{H}_{22}\text{NO}_2\text{P}$: 435.1388. Found: 435.1390.



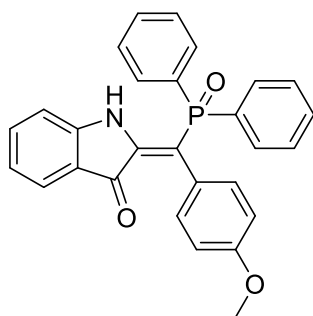
(Z)-2-((diphenylphosphoryl)(4-ethylphenyl)methylene)indolin-3-one (3c): Compound **3c** was isolated as a red oil (71.0 mg, 79%) by a column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.37 (s, 1H), 7.62 (t, $J = 6.4$ Hz, 2H), 7.57 – 7.45 (m, 9H), 7.42 (d, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 8.1$ Hz, 1H), 6.95 (d, $J = 7.8$ Hz, 2H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.60 (d, $J = 7.2$ Hz, 2H), 2.53 (q, $J = 7.5$ Hz, 2H), 1.14 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 185.32 (d, $J = 11.6$ Hz), 185.25 (d, $J = 11.6$ Hz), 153.04, 143.34, 143.23, 137.51, 132.79, 132.42 (d, $J = 9.5$ Hz), 132.36 (d, $J = 9.5$ Hz), 131.24 (d, $J = 104.0$ Hz), 130.93 (d, $J = 4.4$ Hz), 130.90 (d, $J = 4.4$ Hz), 130.80 (d, $J = 5.7$ Hz), 130.77 (d, $J = 5.7$ Hz), 130.55 (d, $J = 104.0$ Hz), 128.98 (d, $J = 12.1$ Hz), 128.90 (d, $J = 12.1$ Hz), 127.83, 124.58, 120.44, 119.74 (d, $J = 2.9$ Hz), 119.73 (d, $J = 2.9$ Hz), 113.10, 111.94 (d, $J = 90.1$ Hz), 111.35 (d, $J = 90.1$ Hz), 28.32, 16.03. ^{31}P NMR (243 MHz, DMSO) δ 31.81 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{29}\text{H}_{24}\text{NO}_2\text{P}$: 449.1545. Found: 449.1546.



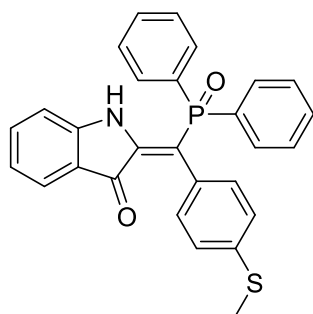
(Z)-2-((diphenylphosphoryl)(4-isopropylphenyl)methylene)indolin-3-one (3d): Compound **3d** was isolated as an orange solid (72.3 mg, 78%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1), m.p. 235.1–235.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.23 (s, 1H), 7.57 (dd, *J* = 13.6, 6.6 Hz, 7H), 7.50 – 7.39 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.68 (dd, *J* = 8.1, 1.6 Hz, 2H), 2.88 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 185.56 (d, *J* = 11.3 Hz), 185.49 (d, *J* = 11.3 Hz), 152.52, 148.29, 143.59, 136.90, 132.33 (d, *J* = 9.8 Hz), 132.27 (d, *J* = 9.8 Hz), 132.23, 130.58 (d, *J* = 105.2 Hz), 130.40 (d, *J* = 5.0 Hz), 130.36 (d, *J* = 5.0 Hz), 130.07 (d, *J* = 6.3 Hz), 130.02 (d, *J* = 6.3 Hz), 129.89 (d, *J* = 105.2 Hz), 128.29 (d, *J* = 12.2 Hz), 128.21 (d, *J* = 12.2 Hz), 126.31, 124.97, 120.13, 120.09, 111.90, 111.63 (d, *J* = 90.3 Hz), 111.30 (d, *J* = 90.3 Hz), 33.70, 23.93. ³¹P NMR (243 MHz, DMSO) δ 31.94 (s). HRMS (EI): *m/z* [M]⁺ calcd. for C₃₀H₂₆NO₂P: 463.1701. Found: 463.1699.



(Z)-2-((4-(tert-butyl)phenyl)(diphenylphosphoryl)methylene)indolin-3-one (3e): Compound **3e** was isolated as an orange solid (73.5 mg, 77%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1), m.p. 217.3–217.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.19 (s, 1H), 7.55 (dd, *J* = 12.2, 7.7 Hz, 7H), 7.50 – 7.45 (m, 1H), 7.41 (td, *J* = 7.7, 2.8 Hz, 4H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 6.9 Hz, 2H), 1.30 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 185.64 (d, *J* = 12.2 Hz), 185.56 (d, *J* = 12.2 Hz), 152.57, 150.60, 143.58, 136.93, 132.36 (d, *J* = 9.7 Hz), 132.29 (d, *J* = 9.7 Hz), 132.24 (d, *J* = 1.8 Hz), 132.23 (d, *J* = 1.8 Hz), 130.60 (d, *J* = 105.2 Hz), 130.10 (d, *J* = 4.1 Hz), 130.07 (d, *J* = 4.1 Hz), 129.91 (d, *J* = 105.2 Hz), 129.76 (d, *J* = 6.2 Hz), 129.72 (d, *J* = 6.2 Hz), 128.30 (d, *J* = 12.2 Hz), 128.22 (d, *J* = 12.2 Hz), 125.18, 125.02, 120.13, 111.92 (d, *J* = 90.6 Hz), 111.66, 111.32 (d, *J* = 90.6 Hz), 34.48, 31.30. ³¹P NMR (243 MHz, CDCl₃) δ 34.46 (s). HRMS (EI): *m/z* [M]⁺ calcd. for C₃₁H₂₈NO₂P: 477.1858. Found: 477.1856.

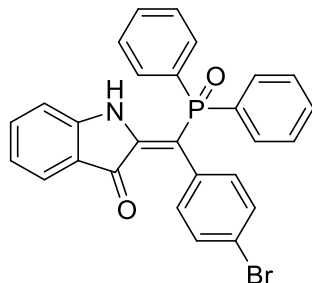


(Z)-2-((diphenylphosphoryl)(4-methoxyphenyl)methylene)indolin-3-one (3f): Compound **3f** was isolated as an orange oil (65.0 mg, 72%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 8:1). ^1H NMR (400 MHz, DMSO) δ 10.33 (s, 1H), 7.62 (dd, $J = 8.0, 4.7$ Hz, 2H), 7.55 – 7.46 (m, 9H), 7.41 (d, $J = 7.5$ Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 1H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.69 (d, $J = 8.6$ Hz, 2H), 6.59 (dd, $J = 8.5, 1.3$ Hz, 2H), 3.69 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 185.31 (d, $J = 11.8$ Hz), 185.23 (d, $J = 11.8$ Hz), 158.99, 152.91, 143.59, 137.52, 132.83 (d, $J = 1.8$ Hz), 132.82 (d, $J = 1.8$ Hz), 132.44 (d, $J = 9.4$ Hz), 132.38 (d, $J = 9.4$ Hz), 132.24 (d, $J = 4.2$ Hz), 132.21 (d, $J = 4.2$ Hz), 131.28 (d, $J = 104.0$ Hz), 130.59 (d, $J = 104.0$ Hz), 129.06 (d, $J = 12.1$ Hz), 128.98 (d, $J = 12.1$ Hz), 125.30 (d, $J = 6.3$ Hz), 125.26 (d, $J = 6.3$ Hz), 124.58, 120.42, 119.76 (d, $J = 2.1$ Hz), 119.75 (d, $J = 2.1$ Hz), 113.99, 113.06, 111.62 (d, $J = 67.6$ Hz), 111.02 (d, $J = 67.6$ Hz), 55.44. ^{31}P NMR (243 MHz, DMSO) δ 31.69 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{28}\text{H}_{22}\text{NO}_3\text{P}$: 451.1337. Found: 451.1339.

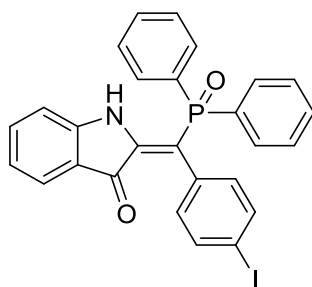


(Z)-2-((diphenylphosphoryl)(4-(methylthio)phenyl)methylene)indolin-3-one (3g): Compound **3g** was isolated as a red oil (65.5 mg, 70%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.34 (s, 1H), 7.66 – 7.59 (m, 2H), 7.57 – 7.45 (m, 9H), 7.41 (d, $J = 7.5$ Hz, 1H), 7.31 (d, $J = 8.1$ Hz, 1H), 6.99 (d, $J = 8.2$ Hz, 2H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.62 (d, $J = 7.2$ Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 185.36 (d, $J = 12.1$ Hz), 185.28 (d, $J = 12.1$ Hz), 153.00, 143.58, 137.80, 137.58, 132.90 (d, $J = 1.7$ Hz), 132.88 (d, $J = 1.7$ Hz), 132.47 (d, $J = 9.7$ Hz), 132.40 (d, $J = 9.7$ Hz), 131.56 (d, $J = 4.7$ Hz), 131.53 (d, $J = 4.7$ Hz), 131.15 (d, $J = 104.0$ Hz), 130.46 (d, $J = 104.0$ Hz), 130.00 (d, $J = 5.7$ Hz), 129.96 (d, $J = 5.7$ Hz), 129.08 (d, $J =$

12.1 Hz), 129.00 (d, $J = 12.1$ Hz), 125.73, 124.62, 120.52, 119.71 (d, $J = 2.3$ Hz), 119.69 (d, $J = 2.3$ Hz), 113.12, 111.19 (d, $J = 90.6$ Hz), 110.60 (d, $J = 90.6$ Hz), 14.98. ^{31}P NMR (243 MHz, DMSO) δ 31.62 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{28}\text{H}_{22}\text{NO}_2\text{PS}$: 467.1109. Found: 467.1107.

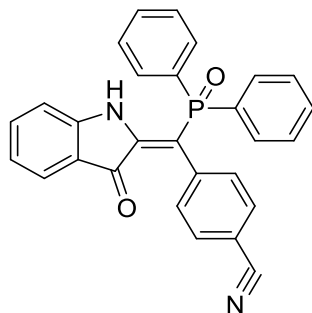


(Z)-2-((4-bromophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3h): Compound **3h** was isolated as an orange solid (69.0 mg, 69%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1), m.p. 249.7–250.4 °C. ^1H NMR (400 MHz, CDCl_3) δ 10.36 (s, 1H), 7.70 (dt, $J = 20.1, 10.2$ Hz, 6H), 7.66 – 7.50 (m, 6H), 7.41 (dd, $J = 9.6, 5.8$ Hz, 2H), 7.12 – 6.96 (m, 2H), 6.77 – 6.65 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 185.52 (d, $J = 11.3$ Hz), 185.45 (d, $J = 11.3$ Hz), 152.51, 143.74, 137.16, 132.54 (d, $J = 2.4$ Hz), 132.52 (d, $J = 2.4$ Hz), 132.38 (d, $J = 4.2$ Hz), 132.35 (d, $J = 4.2$ Hz), 132.32 (d, $J = 9.7$ Hz), 132.25 (d, $J = 9.7$ Hz), 132.02 (d, $J = 6.8$ Hz), 131.98 (d, $J = 6.8$ Hz), 131.48, 130.14 (d, $J = 105.4$ Hz), 129.44 (d, $J = 105.4$ Hz), 128.52 (d, $J = 11.9$ Hz), 128.44 (d, $J = 11.9$ Hz), 125.08, 121.97 (d, $J = 2.6$ Hz), 121.95 (d, $J = 2.6$ Hz), 120.39, 119.92 (d, $J = 2.4$ Hz), 119.91 (d, $J = 2.4$ Hz), 111.70, 109.94 (d, $J = 91.2$ Hz), 109.34 (d, $J = 91.2$ Hz). ^{31}P NMR (243 MHz, CDCl_3) δ 33.70 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{27}\text{H}_{19}\text{BrNO}_2\text{P}$: 499.0337. Found: 499.0341.

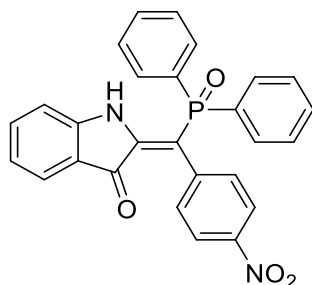


(Z)-2-((diphenylphosphoryl)(4-iodophenyl)methylene)indolin-3-one (3i): Compound **3i** was isolated as a red oil (78.8 mg, 72%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.30 (s, 1H), 7.65 – 7.57 (m, 2H), 7.56 – 7.42 (m, 11H), 7.39 (d, $J = 7.5$ Hz, 1H), 7.30 (d, $J = 8.1$ Hz, 1H), 6.87 (t, $J = 7.4$ Hz, 1H), 6.49 (d, $J = 7.0$ Hz, 2H). ^{13}C NMR (151 MHz, DMSO) δ 185.44 (d, $J = 11.2$ Hz), 185.36 (d, $J = 11.2$ Hz), 153.14, 143.42, 137.69, 137.26, 133.65 (d, $J = 5.9$ Hz), 133.61 (d, $J = 5.9$ Hz), 133.23 (d, $J = 4.2$ Hz), 133.20 (d, $J = 4.2$ Hz),

132.96, 132.45 (d, $J = 9.7$ Hz), 132.39 (d, $J = 9.7$ Hz), 130.96 (d, $J = 104.5$ Hz), 130.27 (d, $J = 104.5$ Hz), 129.14 (d, $J = 12.2$ Hz), 129.06 (d, $J = 12.2$ Hz), 124.66, 120.65, 119.63 (d, $J = 2.3$ Hz), 119.62 (d, $J = 2.3$ Hz), 113.22, 110.34 (d, $J = 90.3$ Hz), 109.74 (d, $J = 90.3$ Hz), 94.08 (d, $J = 2.6$ Hz), 94.06 (d, $J = 2.6$ Hz). ^{31}P NMR (243 MHz, DMSO) δ 31.38 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{27}\text{H}_{19}\text{INO}_2\text{P}$: 547.0198. Found: 547.0192.

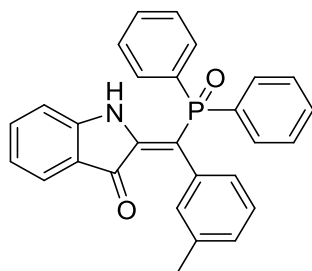


(Z)-4-((diphenylphosphoryl)(3-oxoindolin-2-ylidene)methyl)benzonitrile (3j): Compound **3j** was isolated as a red oil (60.7 mg, 68%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.28 (s, 1H), 7.65 – 7.59 (m, 2H), 7.58 – 7.46 (m, 11H), 7.40 (d, $J = 7.5$ Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 1H), 6.90 (dd, $J = 13.9, 7.2$ Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 185.53 (d, $J = 11.2$ Hz), 185.45 (d, $J = 11.2$ Hz), 153.34, 143.46, 140.08 (d, $J = 6.3$ Hz), 140.04 (d, $J = 6.3$ Hz), 137.77, 133.04, 132.45 (d, $J = 9.8$ Hz), 132.39 (d, $J = 9.8$ Hz), 132.25, 132.17 (d, $J = 4.1$ Hz), 132.14 (d, $J = 4.1$ Hz), 130.82 (d, $J = 104.5$ Hz), 130.13 (d, $J = 104.5$ Hz), 129.21 (d, $J = 11.8$ Hz), 129.13 (d, $J = 11.8$ Hz), 124.74, 120.81, 119.57 (d, $J = 1.8$ Hz), 119.55 (d, $J = 1.8$ Hz), 119.30, 113.35, 110.19 (d, $J = 2.0$ Hz), 110.18 (d, $J = 2.0$ Hz), 109.57 (d, $J = 90.1$ Hz), 108.98 (d, $J = 90.1$ Hz). ^{31}P NMR (243 MHz, DMSO) δ 31.38 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{28}\text{H}_{19}\text{N}_2\text{O}_2\text{P}$: 481.1443. Found: 481.1446.

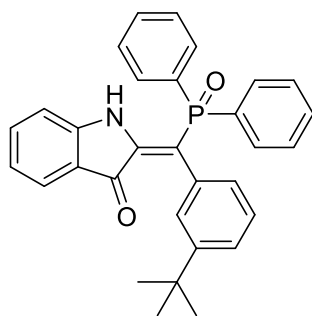


(Z)-2-((diphenylphosphoryl)(4-nitrophenyl)methylene)indolin-3-one (3k): Compound **3k** was isolated as a red oil (56.0 mg, 60%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.28 (s, 1H), 7.98 (d, $J = 8.7$ Hz, 2H), 7.67

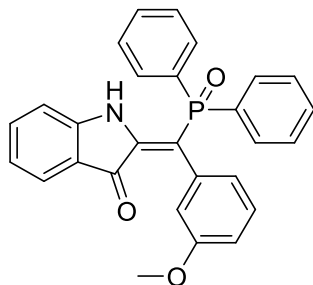
– 7.61 (m, 2H), 7.58 – 7.49 (m, 9H), 7.42 (d, $J = 7.5$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 1H), 7.01 (dd, $J = 8.7$, 1.5 Hz, 2H), 6.92 (t, $J = 7.4$ Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ 185.57 (d, $J = 11.0$ Hz), 185.50 (d, $J = 11.0$ Hz), 153.39, 146.79 (d, $J = 2.3$ Hz), 146.77 (d, $J = 2.3$ Hz), 143.45, 142.48 (d, $J = 6.2$ Hz), 142.44 (d, $J = 6.2$ Hz), 137.85, 133.09, 132.52 (d, $J = 4.2$ Hz), 132.49 (d, $J = 4.2$ Hz), 132.45 (d, $J = 10.1$ Hz), 132.39 (d, $J = 10.1$ Hz), 130.78 (d, $J = 104.5$ Hz), 130.08 (d, $J = 104.5$ Hz), 129.26 (d, $J = 12.4$ Hz), 129.18 (d, $J = 12.4$ Hz), 124.76, 123.46, 120.89, 119.50, 113.41, 109.14 (d, $J = 90.1$ Hz), 108.54 (d, $J = 90.1$ Hz). ^{31}P NMR (243 MHz, DMSO) δ 31.13 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{27}\text{H}_{19}\text{N}_2\text{O}_4\text{P}$: 466.1082. Found: 466.1085.



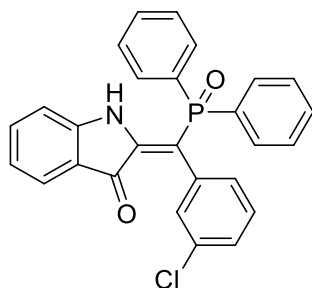
(Z)-2-((diphenylphosphoryl)(m-tolyl)methylene)indolin-3-one (31): Compound **31** was isolated as a red oil (65.3 mg, 75%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.30 (s, 1H), 7.63 (dd, $J = 8.4$, 4.5 Hz, 2H), 7.57 – 7.45 (m, 9H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 1H), 7.05 – 6.98 (m, 2H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.57 (d, $J = 5.1$ Hz, 1H), 6.37 (s, 1H), 2.04 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 185.33 (d, $J = 12.1$ Hz), 185.25 (d, $J = 12.1$ Hz), 153.08, 143.16, 137.57, 137.25, 133.46 (d, $J = 5.6$ Hz), 133.42 (d, $J = 5.6$ Hz), 132.81, 132.45 (d, $J = 9.5$ Hz), 132.38 (d, $J = 9.5$ Hz), 131.62 (d, $J = 4.1$ Hz), 131.59 (d, $J = 4.1$ Hz), 131.15 (d, $J = 102.7$ Hz), 130.47 (d, $J = 102.7$ Hz), 128.96 (d, $J = 11.8$ Hz), 128.89 (d, $J = 11.8$ Hz), 128.26 (d, $J = 8.6$ Hz), 128.21 (d, $J = 8.6$ Hz), 128.16 (d, $J = 4.4$ Hz), 128.13 (d, $J = 4.4$ Hz), 124.60, 120.48, 119.69, 113.14, 112.07 (d, $J = 89.4$ Hz), 111.48 (d, $J = 89.4$ Hz), 21.29. ^{31}P NMR (243 MHz, DMSO) δ 31.77 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{28}\text{H}_{22}\text{NO}_2\text{P}$: 435.1388. Found: 435.1391.



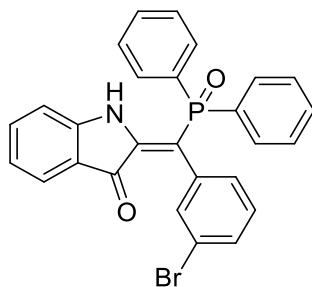
(Z)-2-((3-(tert-butyl)phenyl)(diphenylphosphoryl)methylene)indolin-3-one (3m): Compound **3m** was isolated as a red oil (70.7 mg, 74%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, DMSO) δ 10.37 (s, 1H), 7.61 (dd, *J* = 8.2, 4.6 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.48 (dd, *J* = 10.9, 5.9 Hz, 8H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 7.4 Hz, 1H), 6.58 (s, 1H), 1.00 (s, 9H). ¹³C NMR (151 MHz, DMSO) δ 185.32 (d, *J* = 11.9 Hz), 185.24 (d, *J* = 11.9 Hz), 153.05, 150.50, 143.09, 137.56, 132.98 (d, *J* = 5.1 Hz), 132.95 (d, *J* = 5.1 Hz), 132.75, 132.39 (d, *J* = 9.1 Hz), 132.33 (d, *J* = 9.1 Hz), 131.20 (d, *J* = 104.3 Hz), 130.51 (d, *J* = 104.3 Hz), 129.00 (d, *J* = 11.6 Hz), 128.93 (d, *J* = 11.6 Hz), 128.29, 128.16, 127.74, 124.62, 124.44, 120.44, 119.69, 113.09, 112.33 (d, *J* = 90.0 Hz), 111.73 (d, *J* = 90.0 Hz), 34.50, 31.25. ³¹P NMR (243 MHz, DMSO) δ 31.83 (s). HRMS (EI): *m/z* [M]⁺ calcd. for C₃₁H₂₈NO₂P: 477.1858. Found: 477.1855.



(Z)-2-((diphenylphosphoryl)(3-methoxyphenyl)methylene)indolin-3-one (3n): Compound **3n** was isolated as a red oil (64.1mg, 71%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 8:1). ¹H NMR (400 MHz, DMSO) δ 10.32 (s, 1H), 7.63 (dd, *J* = 8.5, 3.7 Hz, 2H), 7.58 – 7.46 (m, 9H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.33 (d, *J* = 7.4 Hz, 1H), 6.18 (s, 1H), 3.44 (s, 3H). ¹³C NMR (151 MHz, DMSO) δ 185.27 (d, *J* = 11.3 Hz), 185.19 (d, *J* = 11.3 Hz), 159.28, 153.10, 143.27, 137.57, 134.95 (d, *J* = 5.7 Hz), 134.91 (d, *J* = 5.7 Hz), 132.84, 132.44 (d, *J* = 9.5 Hz), 132.37 (d, *J* = 9.5 Hz), 131.15 (d, *J* = 104.2 Hz), 130.46 (d, *J* = 104.2 Hz), 129.45, 129.02 (d, *J* = 11.8 Hz), 128.95 (d, *J* = 11.8 Hz), 124.62, 123.43 (d, *J* = 4.5 Hz), 123.40 (d, *J* = 4.5 Hz), 120.51, 119.69, 116.21 (d, *J* = 4.2 Hz), 116.18 (d, *J* = 4.2 Hz), 113.59, 113.14, 111.47 (d, *J* = 90.1 Hz), 110.87 (d, *J* = 90.1 Hz), 55.11. ³¹P NMR (243 MHz, DMSO) δ 31.71 (s). HRMS (EI): *m/z* [M]⁺ calcd. for C₂₈H₂₂NO₃P: 451.1337. Found: 451.1335.

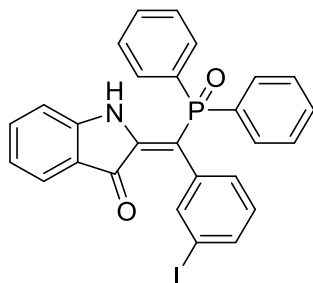


(Z)-2-((3-chlorophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3o): Compound **3o** was isolated as a red oil (59.3 mg, 65%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, DMSO) δ 10.27 (s, 1H), 7.69 – 7.61 (m, 2H), 7.53 (dd, *J* = 14.5, 8.8 Hz, 9H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.67 (s, 1H). ¹³C NMR (151 MHz, DMSO) δ 185.45 (d, *J* = 11.3 Hz), 185.38 (d, *J* = 11.3 Hz), 153.22, 143.58, 137.69, 136.19 (d, *J* = 6.2 Hz), 136.15 (d, *J* = 6.2 Hz), 132.99 (d, *J* = 1.7 Hz), 132.98 (d, *J* = 1.7 Hz), 132.94, 132.45 (d, *J* = 9.8 Hz), 132.39 (d, *J* = 9.8 Hz), 130.90 (d, *J* = 105.2 Hz), 130.82 (d, *J* = 4.2 Hz), 130.79 (d, *J* = 4.2 Hz), 130.20 (d, *J* = 105.2 Hz), 130.16, 129.80 (d, *J* = 4.1 Hz), 129.78 (d, *J* = 4.1 Hz), 129.13 (d, *J* = 12.1 Hz), 129.05 (d, *J* = 12.1 Hz), 127.50, 124.70, 120.69, 119.64 (d, *J* = 2.3 Hz), 119.63 (d, *J* = 2.3 Hz), 113.26, 109.63 (d, *J* = 90.4 Hz), 109.04 (d, *J* = 90.4 Hz). ³¹P NMR (243 MHz, DMSO) δ 31.75 (s). HRMS (EI): *m/z* [M]⁺ calcd. for C₂₇H₁₉ClNO₂P: 455.0842. Found: 455.0839.

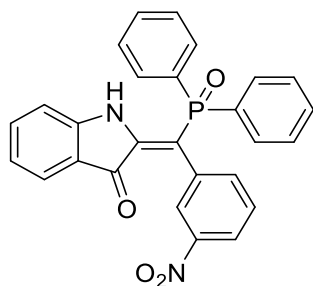


(Z)-2-((3-bromophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3p): Compound **3p** was isolated as a red oil (68.0 mg, 68%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, DMSO) δ 10.25 (s, 1H), 7.63 (dd, *J* = 8.6, 4.5 Hz, 2H), 7.58 – 7.44 (m, 9H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.07 (t, *J* = 8.1 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.75 (dd, *J* = 4.1, 2.1 Hz, 2H). ¹³C NMR (151 MHz, DMSO) δ 185.46 (d, *J* = 11.6 Hz), 185.39 (d, *J* = 11.6 Hz), 153.22, 143.55, 137.70, 136.42 (d, *J* = 6.3 Hz), 136.38 (d, *J* = 6.3 Hz), 133.61 (d, *J* = 4.7 Hz), 133.58 (d, *J* = 4.7 Hz), 133.00 (d, *J* = 1.8 Hz), 132.99 (d, *J* = 1.8 Hz), 132.45 (d, *J* = 9.8 Hz), 132.39 (d, *J* = 9.8 Hz), 131.57 (d, *J* = 105.2 Hz), 130.87 (d, *J* = 105.2 Hz), 130.40 (d, *J* = 5.4 Hz),

130.36 (d, $J = 5.4$ Hz), 130.23 (d, $J = 4.4$ Hz), 130.20 (d, $J = 4.4$ Hz), 129.13 (d, $J = 12.1$ Hz), 129.05 (d, $J = 12.1$ Hz), 124.70, 121.46, 120.69, 119.63 (d, $J = 2.4$ Hz), 119.62 (d, $J = 2.4$ Hz), 113.27, 109.60 (d, $J = 90.4$ Hz), 109.00 (d, $J = 90.4$ Hz). ^{31}P NMR (243 MHz, DMSO) δ 31.76 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{27}\text{H}_{19}\text{BrNO}_2\text{P}$: 499.0337. Found: 499.0331.

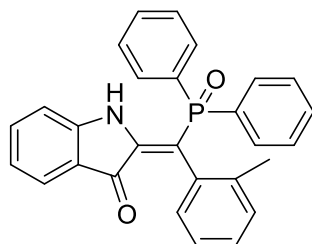


(Z)-2-((diphenylphosphoryl)(3-iodophenyl)methylene)indolin-3-one (3q): Compound **3q** was isolated as a red oil (76.6 mg, 70%) by a column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.28 (s, 1H), 7.66 – 7.58 (m, 2H), 7.56 – 7.44 (m, 10H), 7.41 (d, $J = 7.5$ Hz, 1H), 7.31 (d, $J = 8.1$ Hz, 1H), 6.96 – 6.85 (m, 3H), 6.81 (d, $J = 7.5$ Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ 185.48 (d, $J = 11.8$ Hz), 185.40 (d, $J = 11.8$ Hz), 153.20, 143.45, 139.44 (d, $J = 4.1$ Hz), 139.41 (d, $J = 4.1$ Hz), 137.66, 136.21, 136.17, 132.99, 132.46 (d, $J = 9.7$ Hz), 132.40 (d, $J = 9.7$ Hz), 130.84 (d, $J = 104.3$ Hz), 130.67 (d, $J = 4.4$ Hz), 130.64 (d, $J = 4.4$ Hz), 130.37, 130.15 (d, $J = 104.3$ Hz), 129.10 (d, $J = 11.8$ Hz), 129.02 (d, $J = 11.8$ Hz), 124.70, 120.67, 119.65 (d, $J = 2.0$ Hz), 119.64 (d, $J = 2.0$ Hz), 113.24, 109.80 (d, $J = 90.3$ Hz), 109.20 (d, $J = 90.3$ Hz), 94.47. ^{31}P NMR (243 MHz, DMSO) δ 31.79 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{27}\text{H}_{19}\text{INO}_2\text{P}$: 547.0198. Found: 547.0200.

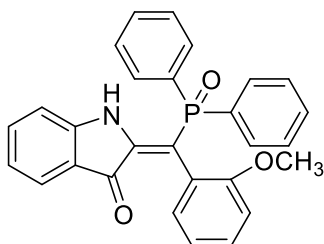


(Z)-2-((diphenylphosphoryl)(3-nitrophenyl)methylene)indolin-3-one (3r): Compound **3r** was isolated as a red oil (52.2 mg, 56%) by a column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.27 (s, 1H), 8.06 (d, $J = 8.1$ Hz, 1H), 7.65 (dd, $J = 10.0, 4.6$ Hz, 2H), 7.60 – 7.47 (m, 9H), 7.43 (dd, $J = 10.7, 4.9$ Hz, 3H), 7.36 (d, $J = 8.1$ Hz, 1H), 7.27 (d, $J = 7.6$ Hz, 1H), 6.93 (t, $J = 7.4$ Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ 185.63 (d, $J = 11.3$

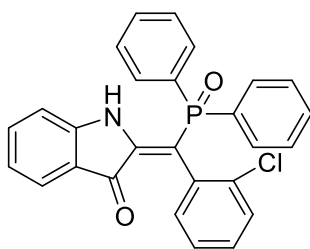
Hz), 185.56 (d, $J = 11.3$ Hz), 153.33, 147.76, 143.90, 138.38 (d, $J = 4.5$ Hz), 138.35 (d, $J = 4.5$ Hz), 137.81, 136.19 (d, $J = 6.6$ Hz), 136.14 (d, $J = 6.6$ Hz), 133.07, 132.49 (d, $J = 10.0$ Hz), 132.43 (d, $J = 10.0$ Hz), 130.73 (d, $J = 105.1$ Hz), 130.03 (d, $J = 105.1$ Hz), 129.96, 129.24 (d, $J = 12.2$ Hz), 129.16 (d, $J = 12.2$ Hz), 125.78 (d, $J = 4.1$ Hz), 125.76 (d, $J = 4.1$ Hz), 124.77, 122.47, 120.84, 119.61 (d, $J = 2.3$ Hz), 119.59 (d, $J = 2.3$ Hz), 113.35, 108.36 (d, $J = 90.8$ Hz), 107.76 (d, $J = 90.8$ Hz). ^{31}P NMR (243 MHz, DMSO) δ 31.61 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{27}\text{H}_{19}\text{N}_2\text{O}_4\text{P}$: 466.1082. Found: 466.1086.



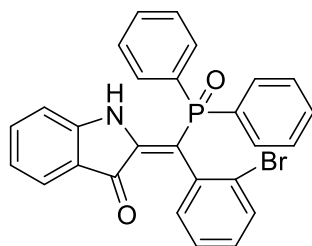
(Z)-2-((diphenylphosphoryl)(o-tolyl)methylene)indolin-3-one (3s): Compound **3s** was isolated as a red oil (63.6 mg, 73%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.30 (s, 1H), 7.74 – 7.63 (m, 3H), 7.56 (dt, $J = 15.3, 5.1$ Hz, 4H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.34 (t, $J = 8.9$ Hz, 3H), 7.13 (dd, $J = 18.6, 9.8$ Hz, 3H), 6.97 (dd, $J = 17.4, 7.8$ Hz, 2H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.64 (d, $J = 7.4$ Hz, 1H), 1.44 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 185.43 (d, $J = 11.8$ Hz), 185.35 (d, $J = 11.8$ Hz), 153.43, 143.06, 138.48 (d, $J = 4.5$ Hz), 138.45 (d, $J = 4.5$ Hz), 137.64, 133.30 (d, $J = 103.0$ Hz), 133.0 (d, $J = 1.8$ Hz), 132.99 (d, $J = 1.8$ Hz), 132.95 (d, $J = 4.5$ Hz), 132.92 (d, $J = 4.5$ Hz), 132.72, 132.61 (d, $J = 103.0$ Hz), 132.53 (d, $J = 8.5$ Hz), 132.47 (d, $J = 8.5$ Hz), 132.03 (d, $J = 10.7$ Hz), 131.96 (d, $J = 10.7$ Hz), 130.17, 129.88 (d, $J = 3.8$ Hz), 129.86 (d, $J = 3.8$ Hz), 129.56 (d, $J = 11.6$ Hz), 129.49 (d, $J = 11.6$ Hz), 128.40 (d, $J = 104.0$ Hz), 128.35 (d, $J = 11.3$ Hz), 128.28 (d, $J = 11.3$ Hz), 127.97 (d, $J = 1.5$ Hz), 127.96 (d, $J = 1.5$ Hz), 127.71 (d, $J = 104.0$ Hz), 126.03, 124.62, 120.49, 119.45 (d, $J = 2.3$ Hz), 119.43 (d, $J = 2.3$ Hz), 113.28, 110.72 (d, $J = 90.1$ Hz), 110.12 (d, $J = 90.1$ Hz), 19.54. ^{31}P NMR (243 MHz, DMSO) δ 30.21 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{28}\text{H}_{22}\text{NO}_2\text{P}$: 435.1388. Found: 435.1390.



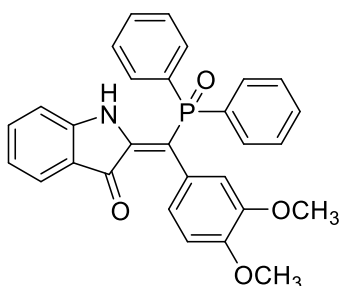
(Z)-2-((diphenylphosphoryl)(2-methoxyphenyl)methylene)indolin-3-one (3t): Compound **3t** was isolated as an orange oil (56.0 mg, 62%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 8:1). ¹H NMR (400 MHz, DMSO) δ 10.10 (s, 1H), 7.67 – 7.57 (m, 3H), 7.51 (t, *J* = 7.4 Hz, 4H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.25 (dd, *J* = 11.2, 7.6 Hz, 2H), 7.20 – 7.13 (m, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 4.9 Hz, 2H), 6.63 (d, *J* = 8.3 Hz, 1H), 3.06 (s, 3H). ¹³C NMR (151 MHz, DMSO) δ 185.26 (d, *J* = 12.2 Hz), 185.18 (d, *J* = 12.2 Hz), 157.68 (d, *J* = 4.8 Hz), 157.65 (d, *J* = 4.8 Hz), 153.25, 143.34, 137.52, 133.19 (d, *J* = 103.0 Hz), 132.71, 132.50 (d, *J* = 103.0 Hz), 132.31, 132.25, 132.07 (d, *J* = 10.7 Hz), 132.00 (d, *J* = 10.7 Hz), 131.27 (d, *J* = 4.2 Hz), 131.24 (d, *J* = 4.2 Hz), 130.20, 129.51, 129.31 (d, *J* = 11.6 Hz), 129.23 (d, *J* = 11.6 Hz), 128.08 (d, *J* = 11.9 Hz), 128.00 (d, *J* = 11.9 Hz), 124.53, 122.47 (d, *J* = 4.7 Hz), 122.44 (d, *J* = 4.7 Hz), 120.47, 119.70 (d, *J* = 2.0 Hz), 119.68 (d, *J* = 2.0 Hz), 113.22, 111.14, 108.94 (d, *J* = 92.9 Hz), 108.33 (d, *J* = 92.9 Hz), 54.97. ³¹P NMR (243 MHz, DMSO) δ 30.63 (s). HRMS (EI): *m/z* [M]⁺ calcd. for C₂₈H₂₂NO₃P: 451.1337. Found: 451.1335.



(Z)-2-((2-chlorophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3u): Compound **3u** was isolated as a red oil (55.6 mg, 61%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, DMSO) δ 10.30 (s, 1H), 7.74 (dd, *J* = 12.5, 7.4 Hz, 2H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.62 – 7.52 (m, 4H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.30 – 7.20 (m, 4H), 7.17 (dd, *J* = 13.7, 6.2 Hz, 1H), 6.96 – 6.87 (m, 2H). ¹³C NMR (151 MHz, DMSO) δ 185.31 (d, *J* = 12.0 Hz), 185.23 (d, *J* = 12.0 Hz), 153.52, 143.80, 137.78, 135.39 (d, *J* = 5.4 Hz), 135.36 (d, *J* = 5.4 Hz), 133.08, 133.02, 132.80 (d, *J* = 5.1 Hz), 132.77 (d, *J* = 5.1 Hz), 132.66, 132.51 (d, *J* = 8.9 Hz), 132.45 (d, *J* = 8.9 Hz), 132.39, 132.11 (d, *J* = 10.7 Hz), 132.04 (d, *J* = 10.7 Hz), 131.76 (d, *J* = 3.6 Hz), 131.73 (d, *J* = 3.6 Hz), 129.60 (d, *J* = 11.5 Hz), 129.53 (d, *J* = 11.5 Hz), 128.75 (d, *J* = 105.2 Hz), 128.34 (d, *J* = 11.9 Hz), 128.26 (d, *J* = 11.9 Hz), 128.06 (d, *J* = 105.2 Hz), 127.38, 124.73, 120.80, 119.38 (d, *J* = 2.1 Hz), 119.37 (d, *J* = 2.1 Hz), 113.43, 107.92 (d, *J* = 93.0 Hz), 107.31 (d, *J* = 93.0 Hz). ³¹P NMR (243 MHz, DMSO) δ 30.26 (s). HRMS (EI): *m/z* [M]⁺ calcd. for C₂₇H₁₉ClNO₂P: 455.0842. Found: 455.0839.



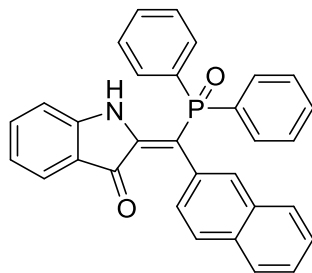
(Z)-2-((2-bromophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3v): Compound **3v** was isolated as an orange oil (63.0 mg, 63%) by a column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1). ¹H NMR (400 MHz, DMSO) δ 10.27 (s, 1H), 7.73 (dd, *J* = 12.5, 7.5 Hz, 2H), 7.67 (d, *J* = 6.9 Hz, 1H), 7.62 – 7.53 (m, 4H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.36 (ddd, *J* = 10.6, 7.7, 4.0 Hz, 4H), 7.25 – 7.12 (m, 4H), 6.97 – 6.85 (m, 2H). ¹³C NMR (151 MHz, DMSO) δ 185.20 (d, *J* = 11.6 Hz), 185.13 (d, *J* = 11.6 Hz), 153.51, 143.82, 137.79, 134.59 (d, *J* = 5.3 Hz), 134.55 (d, *J* = 5.3 Hz), 133.30 (d, *J* = 95.7 Hz), 133.03, 132.87, 132.68 (d, *J* = 8.3 Hz), 132.67 (d, *J* = 95.7 Hz), 132.62 (d, *J* = 8.3 Hz), 132.07, 132.00, 131.64 (d, *J* = 3.6 Hz), 131.61 (d, *J* = 3.6 Hz), 129.64, 129.56, 128.42 (d, *J* = 105.4 Hz), 128.29 (d, *J* = 11.5 Hz), 128.21 (d, *J* = 11.5 Hz), 127.97, 127.73 (d, *J* = 105.4 Hz), 126.84 (d, *J* = 5.6 Hz), 126.81 (d, *J* = 5.6 Hz), 124.75, 120.79, 119.38, 113.43, 109.71 (d, *J* = 93.0 Hz), 109.09 (d, *J* = 93.0 Hz). ³¹P NMR (243 MHz, DMSO) δ 30.06 (s). HRMS (EI): *m/z* [M]⁺ calcd. for C₂₇H₁₉BrNO₂P: 499.0337. Found: 499.0336.



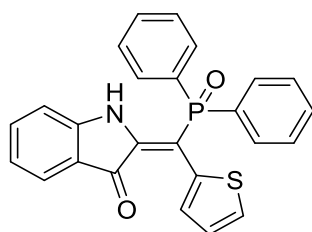
(Z)-2-((3,4-dimethoxyphenyl)(diphenylphosphoryl)methylene)indolin-3-one (3x): Compound **3x** was isolated as a red oil (67.4 mg, 70%) by a column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6:1). ¹H NMR (400 MHz, DMSO) δ 10.39 (s, 1H), 7.62 (t, *J* = 6.8 Hz, 2H), 7.58 – 7.46 (m, 9H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 6.35 (d, *J* = 8.2 Hz, 1H), 6.11 (s, 1H), 3.71 (s, 3H), 3.29 (s, 3H). ¹³C NMR (151 MHz, DMSO) δ 185.26 (d, *J* = 11.8 Hz), 185.19 (d, *J* = 11.8 Hz), 152.92, 148.61, 143.57, 137.47, 132.78, 132.51 (d, *J* = 9.5 Hz), 132.44 (d, *J* = 9.5 Hz), 131.32 (d, *J* = 103.9 Hz), 130.63 (d, *J* = 103.9 Hz), 129.02 (d, *J* = 11.6 Hz), 128.94 (d, *J* = 11.6 Hz), 125.44 (d, *J* = 6.2 Hz), 125.40 (d, *J* = 6.2 Hz), 124.61, 123.73 (d, *J* = 4.8 Hz), 123.69 (d, *J* = 4.8 Hz), 120.40, 119.79, 114.80 (d, *J* = 3.0 Hz), 114.78 (d, *J* = 3.0 Hz), 113.01, 111.81,

111.73 (d, $J = 90.4$ Hz), 111.13 (d, $J = 90.4$ Hz), 55.80, 55.35. ^{31}P NMR (243 MHz, DMSO) δ 31.63 (s).

HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{29}\text{H}_{24}\text{NO}_4\text{P}$: 481.1443. Found: 481.1446.

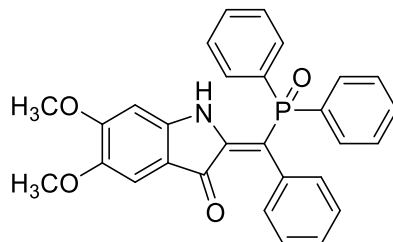


(Z)-2-((diphenylphosphoryl)(naphthalen-2-yl)methylene)indolin-3-one (3y): Compound **3y** was isolated as a red oil (52.8 mg, 56%) by a column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.37 (s, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.64 (d, $J = 8.5$ Hz, 1H), 7.59 (t, $J = 7.1$ Hz, 2H), 7.55 – 7.47 (m, 5H), 7.47 – 7.40 (m, 6H), 7.39 – 7.32 (m, 2H), 7.09 (s, 1H), 6.96 – 6.82 (m, 2H). ^{13}C NMR (151 MHz, DMSO) δ 185.42 (d, $J = 12.1$ Hz), 185.34 (d, $J = 12.1$ Hz), 153.15, 143.61, 137.65, 133.06, 132.89, 132.46 (d, $J = 10.0$ Hz), 132.40 (d, $J = 10.0$ Hz), 131.45 (d, $J = 5.6$ Hz), 131.41 (d, $J = 5.6$ Hz), 131.19 (d, $J = 104.3$ Hz), 130.50 (d, $J = 104.3$ Hz), 129.83 (d, $J = 5.3$ Hz), 129.80 (d, $J = 5.3$ Hz), 129.49 (d, $J = 3.8$ Hz), 129.46 (d, $J = 3.8$ Hz), 129.07 (d, $J = 12.1$ Hz), 128.99 (d, $J = 12.1$ Hz), 128.02, 127.87, 127.72, 126.56, 126.38, 124.63, 120.58, 119.68 (d, $J = 2.4$ Hz), 119.66 (d, $J = 2.4$ Hz), 113.22, 111.67 (d, $J = 90.1$ Hz), 111.08 (d, $J = 90.1$ Hz). ^{31}P NMR (243 MHz, DMSO) δ 31.64 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{31}\text{H}_{22}\text{NO}_2\text{P}$: 471.1388. Found: 471.1391.

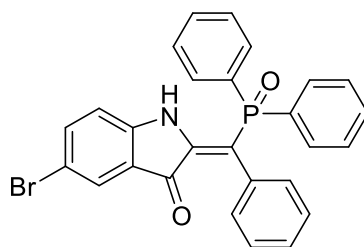


(Z)-2-((diphenylphosphoryl)(thiophen-2-yl)methylene)indolin-3-one (3z): Compound **3z** was isolated as a red oil (50.0 mg, 58%) by a column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.46 (s, 1H), 7.62 (dd, $J = 7.5, 4.5$ Hz, 2H), 7.55 – 7.46 (m, 9H), 7.42 (t, $J = 6.5$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 1H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.87 – 6.82 (m, 1H), 6.30 (d, $J = 2.7$ Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ 184.91 (d, $J = 11.0$ Hz), 184.84 (d, $J = 11.0$ Hz), 152.63, 144.92 (d, $J = 2.6$ Hz), 144.91 (d, $J = 2.6$ Hz), 137.73, 134.39 (d, $J = 6.2$ Hz), 134.35 (d, $J = 6.2$ Hz), 133.00, 132.28 (d, $J = 9.7$ Hz), 132.21 (d, $J = 9.7$ Hz), 131.10 (d, $J = 105.2$ Hz),

130.40 (d, $J = 105.2$ Hz), 129.27 (d, $J = 5.6$ Hz), 129.23 (d, $J = 5.6$ Hz), 129.12 (d, $J = 11.8$ Hz), 129.04 (d, $J = 11.8$ Hz), 128.31 (d, $J = 2.0$ Hz), 128.30 (d, $J = 2.0$ Hz), 127.45, 124.77, 120.93, 119.51 (d, $J = 2.3$ Hz), 119.49 (d, $J = 2.3$ Hz), 113.23, 102.93 (d, $J = 94.5$ Hz), 102.31 (d, $J = 94.5$ Hz). ^{31}P NMR (243 MHz, DMSO) δ 31.90 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{25}\text{H}_{18}\text{NO}_2\text{PS}$: 427.0796. Found: 427.0793.

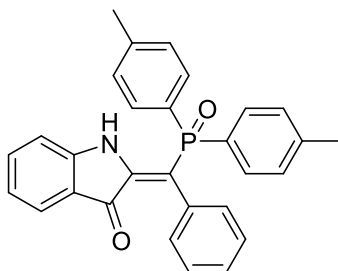


(Z)-2-((diphenylphosphoryl)(phenyl)methylene)-5,6-dimethoxyindolin-3-one (4a): Compound **4a** was isolated as a red solid (75.1 mg, 78%) by a column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6:1), m.p. 152.6–153.3 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.97 (s, 1H), 7.57 (dd, $J = 12.4, 7.5$ Hz, 6H), 7.46 – 7.39 (m, 4H), 7.24 (t, $J = 7.3$ Hz, 1H), 7.15 (t, $J = 7.5$ Hz, 2H), 6.96 (s, 1H), 6.75 (d, $J = 7.7$ Hz, 2H), 6.48 (s, 1H), 3.98 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 183.59 (d, $J = 11.8$ Hz), 183.51 (d, $J = 11.8$ Hz), 157.91, 150.35, 145.04, 144.33, 132.98 (d, $J = 6.2$ Hz), 132.94 (d, $J = 6.2$ Hz), 132.36, 132.35 (d, $J = 9.1$ Hz), 132.29 (d, $J = 9.1$ Hz), 130.66 (d, $J = 4.4$ Hz), 130.64 (d, $J = 4.4$ Hz), 130.54 (d, $J = 105.2$ Hz), 129.84 (d, $J = 105.2$ Hz), 128.35 (d, $J = 12.2$ Hz), 128.27 (d, $J = 12.2$ Hz), 128.17, 127.47, 111.56 (d, $J = 90.4$ Hz), 111.50 (d, $J = 1.8$ Hz), 111.49 (d, $J = 1.8$ Hz), 110.96 (d, $J = 90.4$ Hz), 105.87, 94.70, 56.39, 56.29. ^{31}P NMR (243 MHz, CDCl_3) δ 34.09 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{29}\text{H}_{24}\text{NO}_4\text{P}$: 481.1443. Found: 481.1446.

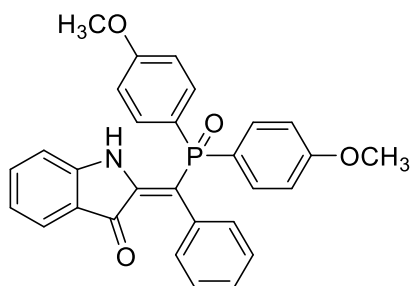


(Z)-5-bromo-2-((diphenylphosphoryl)(phenyl)methylene)indolin-3-one (4b): Compound **4b** was isolated as a red oil (72.1 mg, 72%) by a column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.43 (s, 1H), 7.69 (dd, $J = 8.6, 2.0$ Hz, 1H), 7.63 (dd, $J = 8.5, 4.9$ Hz, 2H), 7.54 – 7.44 (m, 9H), 7.37 (d, $J = 8.6$ Hz, 1H), 7.20 (t, $J = 7.3$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 2H), 6.69 (d, $J = 7.8$ Hz, 2H). ^{13}C NMR (151 MHz, DMSO) δ 184.08 (d, $J = 11.6$ Hz), 184.00 (d, $J = 11.6$ Hz), 152.03, 142.97, 139.56, 133.53 (d, $J = 5.6$ Hz), 133.50 (d, $J = 5.6$ Hz),

132.92, 132.45 (d, $J = 9.5$ Hz), 132.39 (d, $J = 9.5$ Hz), 130.96 (d, $J = 104.3$ Hz), 130.82 (d, $J = 4.7$ Hz), 130.79 (d, $J = 4.7$ Hz), 130.27 (d, $J = 104.3$ Hz), 129.06 (d, $J = 16.3$ Hz), 128.98 (d, $J = 16.3$ Hz), 128.47, 127.76, 126.66, 121.45 (d, $J = 2.4$ Hz), 121.44 (d, $J = 2.4$ Hz), 115.53, 113.20 (d, $J = 89.7$ Hz), 112.61 (d, $J = 89.7$ Hz), 111.99. ^{31}P NMR (243 MHz, DMSO) δ 31.52 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{27}\text{H}_{19}\text{BrNO}_2\text{P}$: 499.0337. Found: 499.0333.

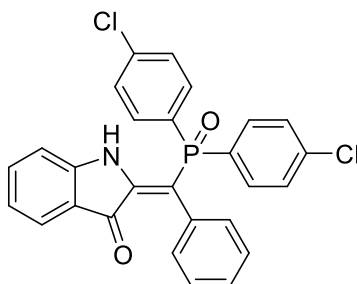


(Z)-2-((di-p-tolylphosphoryl)(phenyl)methylene)indolin-3-one (4d): Compound **4d** was isolated as an orange oil (74.6 mg, 83%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.54 (s, 1H), 7.49 – 7.37 (m, 6H), 7.28 (dd, $J = 14.0$, 7.7 Hz, 5H), 7.23 – 7.17 (m, 1H), 7.12 (t, $J = 7.3$ Hz, 2H), 6.85 (t, $J = 7.3$ Hz, 1H), 6.76 (d, $J = 7.3$ Hz, 2H), 2.32 (s, 6H). ^{13}C NMR (151 MHz, DMSO) δ 185.41 (d, $J = 11.6$ Hz), 185.34 (d, $J = 11.6$ Hz), 153.12, 143.17, 142.89, 137.43, 133.89 (d, $J = 4.7$ Hz), 133.86 (d, $J = 4.7$ Hz), 132.52 (d, $J = 9.7$ Hz), 132.46 (d, $J = 9.7$ Hz), 131.03, 129.57 (d, $J = 12.1$ Hz), 129.49 (d, $J = 12.1$ Hz), 128.41, 128.13 (d, $J = 106.5$ Hz), 127.60, 127.43 (d, $J = 106.5$ Hz), 124.59, 120.37, 119.81, 113.05, 112.48 (d, $J = 89.7$ Hz), 111.88 (d, $J = 89.7$ Hz), 21.60. ^{31}P NMR (243 MHz, DMSO) δ 31.78 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{29}\text{H}_{24}\text{NO}_2\text{P}$: 449.1545. Found: 449.1547.

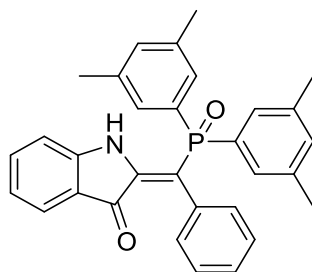


(Z)-2-((bis(4-methoxyphenyl)phosphoryl)(phenyl)methylene)indolin-3-one (4e): Compound **4e** was isolated as a red oil (78.0 mg, 81%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 6:1). ^1H NMR (400 MHz, DMSO) δ 10.49 (s, 1H), 7.53 – 7.40 (m, 6H), 7.31 (d, $J = 8.1$ Hz, 1H), 7.26 – 7.20 (m, 1H), 7.16 (t, $J = 7.4$ Hz, 2H), 7.04 (d, $J = 7.2$ Hz, 4H), 6.87 (t, $J = 7.4$ Hz, 1H), 6.76 (d, $J = 7.5$ Hz, 2H), 3.81 (s, 6H). ^{13}C NMR (151 MHz, DMSO) δ 185.47 (d, $J = 11.6$ Hz),

185.39 (d, $J = 11.6$ Hz), 162.73, 153.09, 142.78, 137.42, 134.43 (d, $J = 10.9$ Hz), 134.36 (d, $J = 10.9$ Hz), 134.09 (d, $J = 5.7$ Hz), 134.05 (d, $J = 5.7$ Hz), 130.97 (d, $J = 3.8$ Hz), 130.94 (d, $J = 3.8$ Hz), 128.40, 127.57, 124.56, 122.41 (d, $J = 111.0$ Hz), 121.67 (d, $J = 111.0$ Hz), 120.29, 119.82 (d, $J = 1.7$ Hz), 119.81 (d, $J = 1.7$ Hz), 114.56 (d, $J = 13.1$ Hz), 114.47 (d, $J = 13.1$ Hz), 113.19 (d, $J = 90.4$ Hz), 113.00, 112.59 (d, $J = 90.4$ Hz), 55.81. ^{31}P NMR (243 MHz, DMSO) δ 31.42 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{25}\text{H}_{18}\text{NO}_2\text{PS}$: 481.1443. Found: 481.1446.

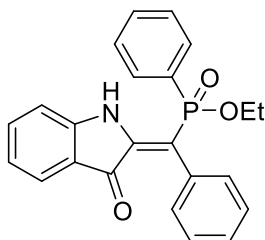


(Z)-2-((bis(4-chlorophenyl)phosphoryl)(phenyl)methylene)indolin-3-one (4f): Compound **4f** was isolated as a red oil (68.6 mg, 70%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.20 (s, 1H), 7.60 – 7.43 (m, 9H), 7.41 (d, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H), 7.24 – 7.18 (m, 1H), 7.14 (t, $J = 7.3$ Hz, 2H), 6.90 (t, $J = 7.4$ Hz, 1H), 6.73 (d, $J = 7.2$ Hz, 2H). ^{13}C NMR (151 MHz, DMSO) δ 185.35 (d, $J = 12.1$ Hz), 185.27 (d, $J = 12.1$ Hz), 153.15, 143.59, 138.14 (d, $J = 2.4$ Hz), 138.12 (d, $J = 2.4$ Hz), 137.62, 134.30 (d, $J = 10.4$ Hz), 134.23 (d, $J = 10.4$ Hz), 133.43 (d, $J = 5.9$ Hz), 133.39 (d, $J = 5.9$ Hz), 131.01 (d, $J = 4.2$ Hz), 130.99 (d, $J = 4.2$ Hz), 129.93 (d, $J = 106.9$ Hz), 129.30 (d, $J = 12.4$ Hz), 129.23 (d, $J = 106.8$ Hz), 129.21 (d, $J = 12.4$ Hz), 128.62, 127.79, 124.63, 120.68, 119.68, 113.27, 110.25 (d, $J = 92.9$ Hz), 109.63 (d, $J = 92.9$ Hz). ^{31}P NMR (243 MHz, DMSO) δ 30.36 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{27}\text{H}_{18}\text{Cl}_2\text{NO}_2\text{P}$: 489.0452. Found: 489.0448.

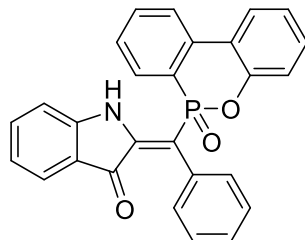


(Z)-2-((bis(3,5-dimethylphenyl)phosphoryl)(phenyl)methylene)indolin-3-one (4g): Compound **4g** was isolated as a red oil (78.3 mg, 82%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.53 (s, 1H), 7.48 (t, $J = 7.7$ Hz, 1H), 7.44

(d, $J = 7.6$ Hz, 1H), 7.31 (d, $J = 8.1$ Hz, 1H), 7.26 – 7.21 (m, 1H), 7.21 – 7.13 (m, 4H), 7.10 (d, $J = 12.1$ Hz, 4H), 6.87 (t, $J = 7.4$ Hz, 1H), 6.73 (d, $J = 7.5$ Hz, 2H), 2.21 (s, 12H). ^{13}C NMR (151 MHz, DMSO) δ 185.41 (d, $J = 11.9$ Hz), 185.33 (d, $J = 11.9$ Hz), 153.10, 143.19, 138.11 (d, $J = 12.5$ Hz), 138.03 (d, $J = 12.5$ Hz), 137.41, 134.16, 133.86 (d, $J = 5.7$ Hz), 133.83 (d, $J = 5.7$ Hz), 131.29 (d, $J = 3.8$ Hz), 131.27 (d, $J = 3.8$ Hz), 130.98 (d, $J = 103.4$ Hz), 130.29 (d, $J = 103.4$ Hz), 130.01 (d, $J = 9.5$ Hz), 129.95 (d, $J = 9.5$ Hz), 128.24, 127.51, 124.60, 120.32, 119.74, 113.04, 112.15 (d, $J = 88.9$ Hz), 111.56 (d, $J = 88.9$ Hz), 21.22. ^{31}P NMR (243 MHz, DMSO) δ 32.84 – 31.67 (m). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{31}\text{H}_{28}\text{NO}_2\text{P}$: 477.1858. Found: 477.1861.

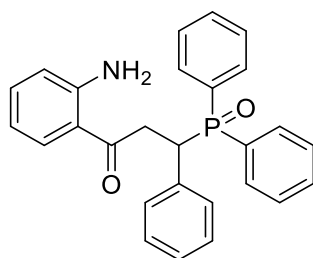


ethyl (Z)-((3-oxoindolin-2-ylidene)(phenyl)methyl)(phenyl)phosphinate (4h): Compound **4h** was isolated as a red oil (57.6 mg, 74%) by a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.18 (s, 1H), 7.59 – 7.35 (m, 9H), 7.24 – 7.16 (m, 3H), 6.90 (t, $J = 7.3$ Hz, 2H), 4.23 – 4.13 (m, 2H), 1.31 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 185.59 (d, $J = 13.7$ Hz), 185.50 (d, $J = 13.7$ Hz), 153.06, 142.76 (d, $J = 4.1$ Hz), 142.74 (d, $J = 4.1$ Hz), 137.64, 133.81 (d, $J = 5.3$ Hz), 133.77 (d, $J = 5.3$ Hz), 132.97, 131.80 (d, $J = 9.8$ Hz), 131.74 (d, $J = 9.8$ Hz), 131.00 (d, $J = 143.0$ Hz), 130.51 (d, $J = 3.0$ Hz), 130.49 (d, $J = 3.0$ Hz), 130.05 (d, $J = 143.0$ Hz), 128.85 (d, $J = 13.0$ Hz), 128.76 (d, $J = 13.0$ Hz), 128.37, 127.59, 124.60, 120.60, 119.81 (d, $J = 2.6$ Hz), 119.79 (d, $J = 2.6$ Hz), 113.15, 110.71 (d, $J = 119.4$ Hz), 109.92 (d, $J = 119.4$ Hz), 61.55 (d, $J = 5.6$ Hz), 61.51 (d, $J = 5.6$ Hz), 16.75 (d, $J = 6.6$ Hz), 16.71 (d, $J = 6.6$ Hz). ^{31}P NMR (243 MHz, DMSO) δ 32.88 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{23}\text{H}_{20}\text{NO}_3\text{P}$: 389.1181. Found: 389.1183.



(Z)-2-((6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)(phenyl)methylene)indolin-3-one (4i): Compound **4i** was isolated as a red oil (45.3 mg, 52%) by a column chromatography on silica gel (eluents:

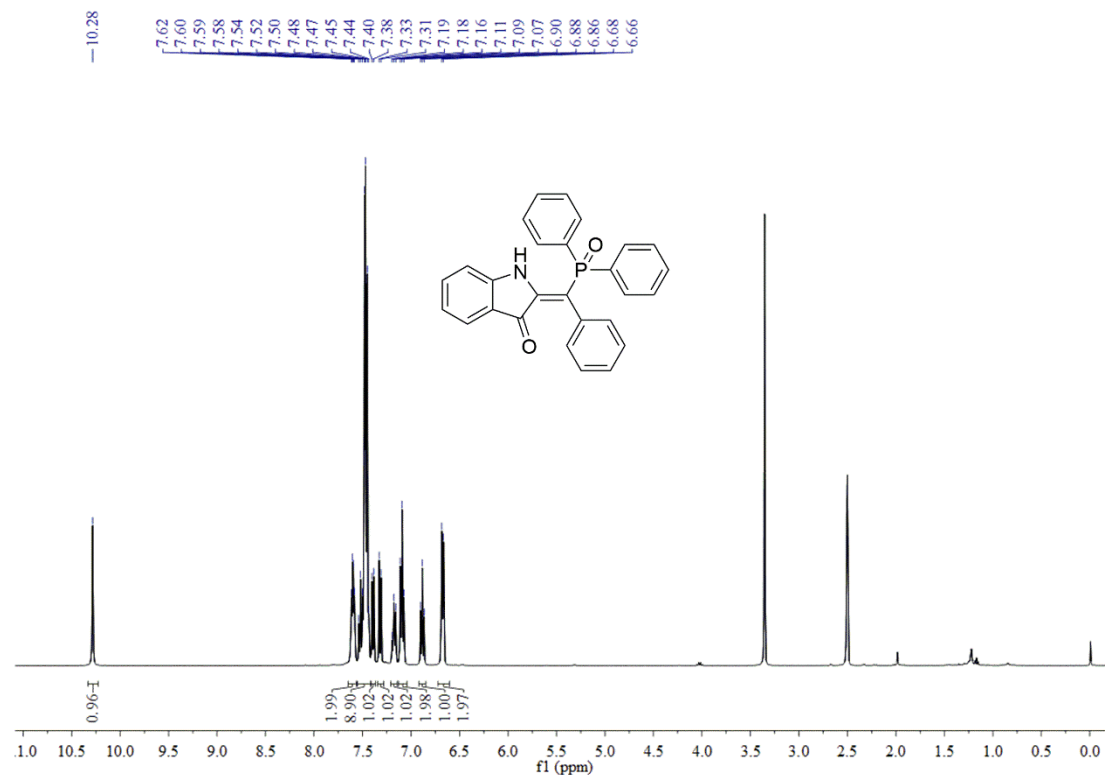
petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 10.21 (s, 1H), 8.17 – 8.10 (m, 1H), 8.02 (dd, J = 11.3, 7.0 Hz, 2H), 7.75 (t, J = 8.0 Hz, 1H), 7.59 (dd, J = 14.1, 6.4 Hz, 2H), 7.41 (dd, J = 14.1, 6.8 Hz, 3H), 7.30 – 7.17 (m, 3H), 7.09 – 6.89 (m, 5H). ^{13}C NMR (151 MHz, DMSO) δ 185.81 (d, J = 14.3 Hz), 185.72 (d, J = 14.3 Hz), 153.17, 149.69 (d, J = 9.5 Hz), 149.63 (d, J = 9.5 Hz), 142.97 (d, J = 4.8 Hz), 142.94 (d, J = 4.8 Hz), 137.83, 135.47 (d, J = 5.4 Hz), 135.44 (d, J = 5.4 Hz), 134.18, 131.34 (d, J = 12.4 Hz), 131.26 (d, J = 12.4 Hz), 131.11, 130.68 (d, J = 4.8 Hz), 130.65 (d, J = 4.8 Hz), 129.22 (d, J = 14.0 Hz), 129.13 (d, J = 14.0 Hz), 128.19, 127.52 (d, J = 1.8 Hz), 127.51 (d, J = 1.8 Hz), 125.72, 124.91, 124.69, 124.14 (d, J = 9.4 Hz), 124.07 (d, J = 9.4 Hz), 123.88 (d, J = 130.0 Hz), 123.02 (d, J = 130.0 Hz), 121.02, 120.89 (d, J = 10.7 Hz), 120.82 (d, J = 10.7 Hz), 120.18 (d, J = 5.9 Hz), 120.14 (d, J = 5.9 Hz), 119.67 (d, J = 3.8 Hz), 119.65 (d, J = 3.8 Hz), 114.81, 113.41, 107.67 (d, J = 131.7 Hz), 106.79 (d, J = 131.7 Hz). ^{31}P NMR (243 MHz, DMSO) δ 26.12 (d, J = 13.2 Hz). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{27}\text{H}_{18}\text{NO}_3\text{P}$: 435.1024. Found: 435.1021.



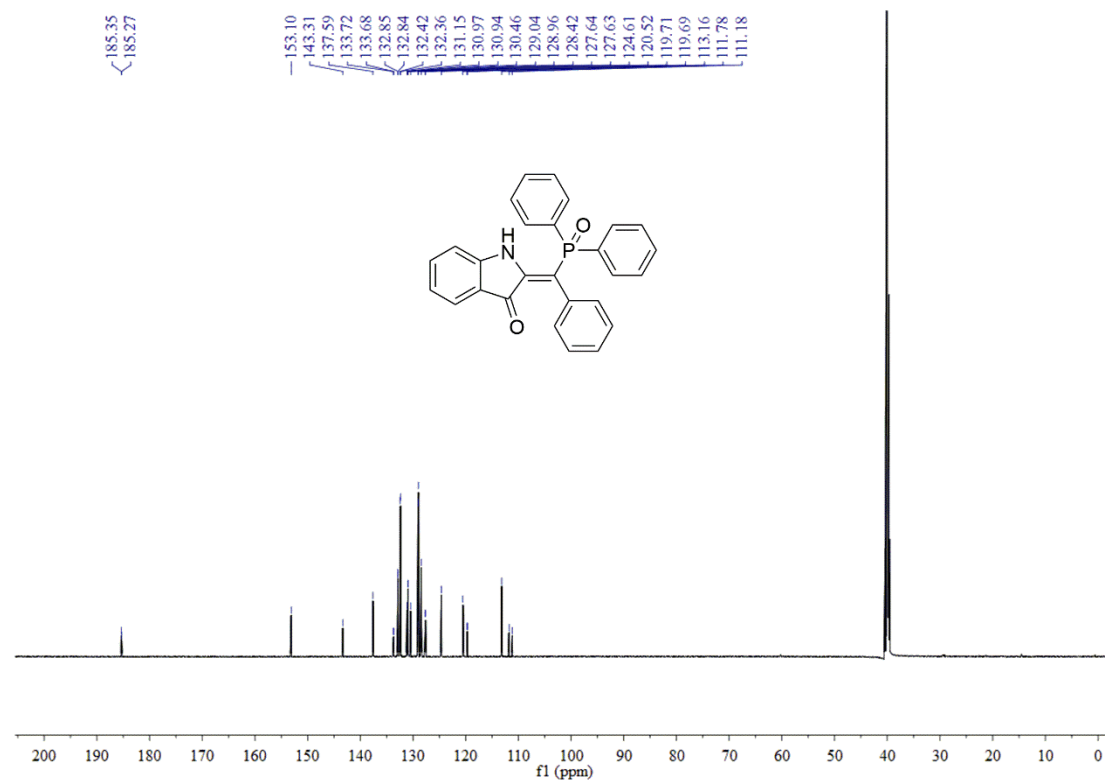
1-(2-aminophenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one (5a): Compound **5a** was isolated as a faint yellow oil (68.1 mg, 80%) by a column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1). ^1H NMR (400 MHz, DMSO) δ 8.08 (d, J = 5.9 Hz, 2H), 7.80 – 7.71 (m, 2H), 7.60 (d, J = 10.2 Hz, 4H), 7.45 – 7.32 (m, 5H), 7.22 – 7.09 (m, 5H), 7.08 – 7.02 (m, 1H), 6.71 (d, J = 8.3 Hz, 1H), 6.44 (t, J = 7.4 Hz, 1H), 4.72 – 4.61 (m, 1H), 3.99 – 3.86 (m, 1H), 3.10 (dd, J = 16.3, 10.5 Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ 198.16 (d, J = 13.9 Hz), 198.07 (d, J = 13.9 Hz), 151.60, 137.02 (d, J = 5.3 Hz), 136.98 (d, J = 5.3 Hz), 134.82, 133.37 (d, J = 92.6 Hz), 132.98 (d, J = 98.5 Hz), 132.76 (d, J = 92.6 Hz), 132.33 (d, J = 98.5 Hz), 132.29, 131.77, 131.39 (d, J = 7.4 Hz), 131.35 (d, J = 7.4 Hz), 131.34, 131.28 (d, J = 8.4 Hz), 131.23 (d, J = 8.4 Hz), 130.26 (d, J = 5.1 Hz), 130.23 (d, J = 5.1 Hz), 129.39 (d, J = 11.0 Hz), 129.31 (d, J = 11.0 Hz), 128.66 (d, J = 11.5 Hz), 128.59 (d, J = 11.5 Hz), 128.24, 127.02, 117.41, 116.57, 114.96, 41.11 (d, J = 68.1 Hz), 40.66 (d, J = 68.1 Hz), 38.73. ^{31}P NMR (243 MHz, DMSO) δ 32.45 (s). HRMS (EI): m/z $[\text{M}]^+$ calcd. for $\text{C}_{27}\text{H}_{24}\text{NO}_2\text{P}$: 425.1545. Found: 425.1543.

4. Copies of NMR Spectra

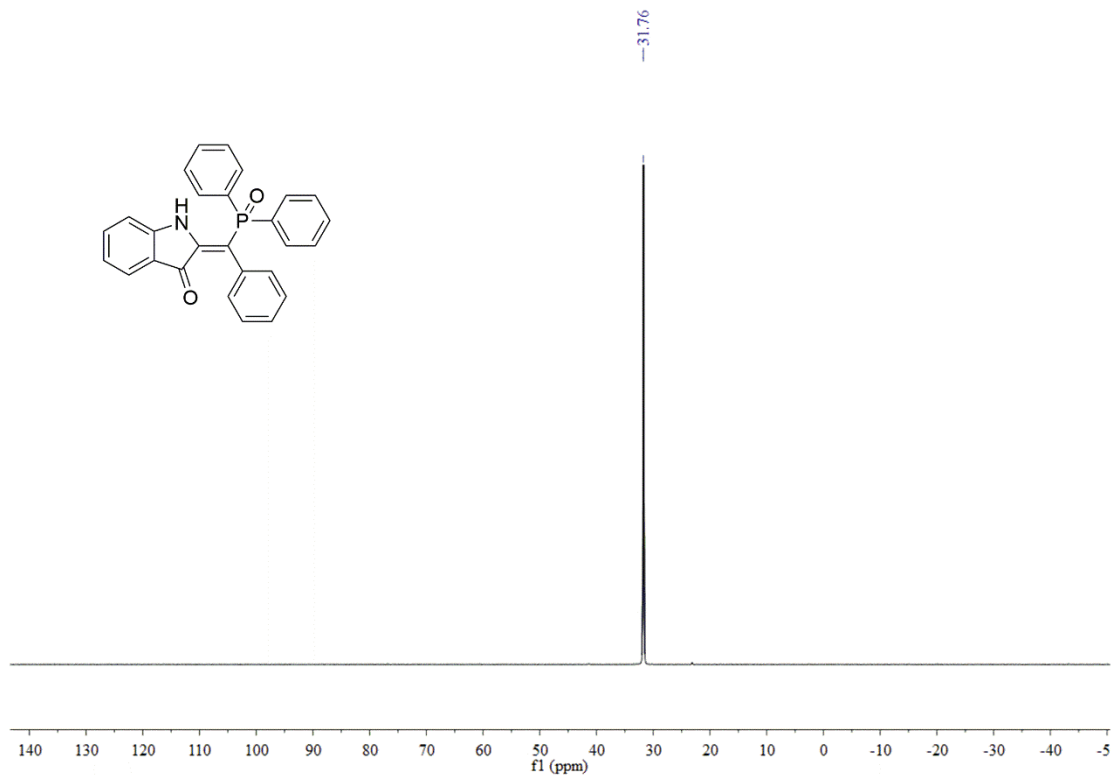
(Z)-2-((diphenylphosphoryl)(phenyl)methylene)indolin-3-one (3a): ^1H NMR



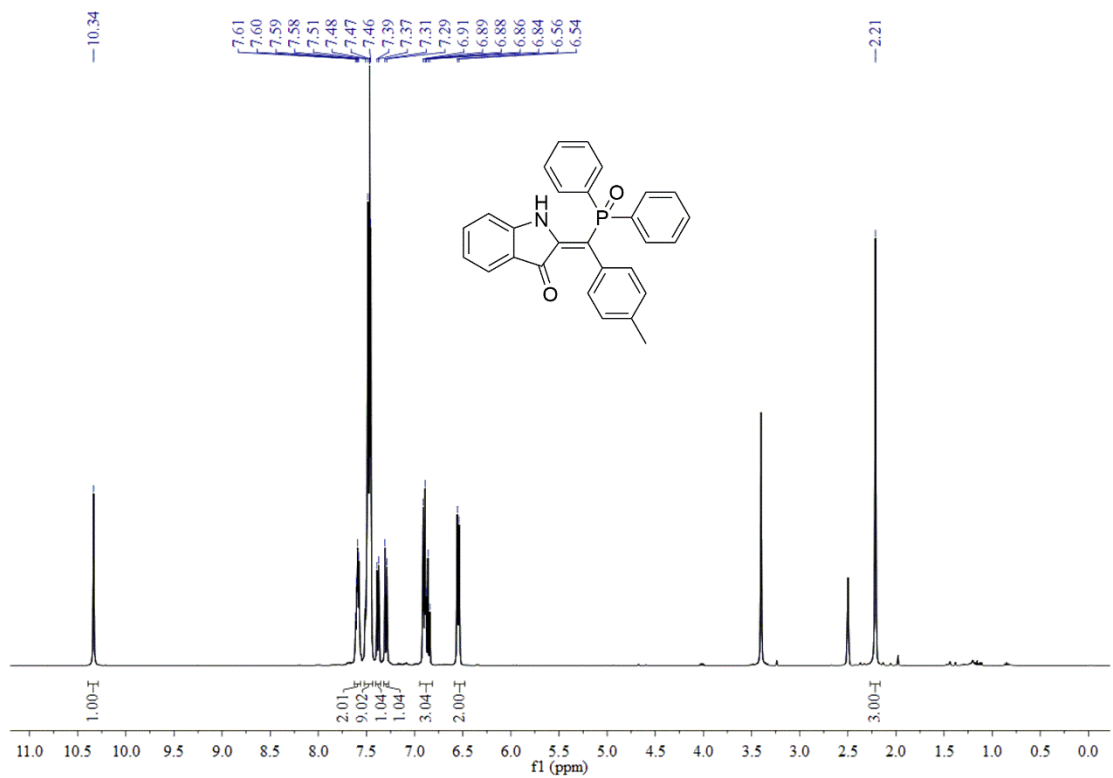
(Z)-2-((diphenylphosphoryl)(phenyl)methylene)indolin-3-one (3a): ^{13}C NMR



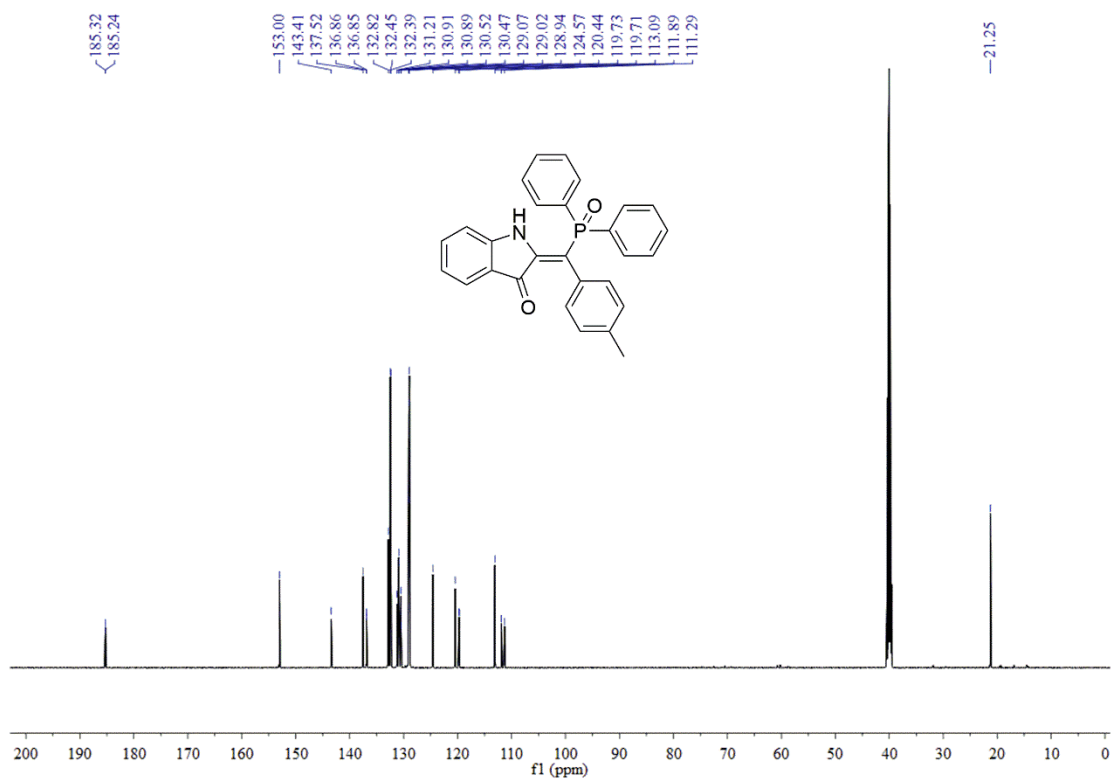
(Z)-2-((diphenylphosphoryl)(phenyl)methylene)indolin-3-one (3a): ³¹P NMR



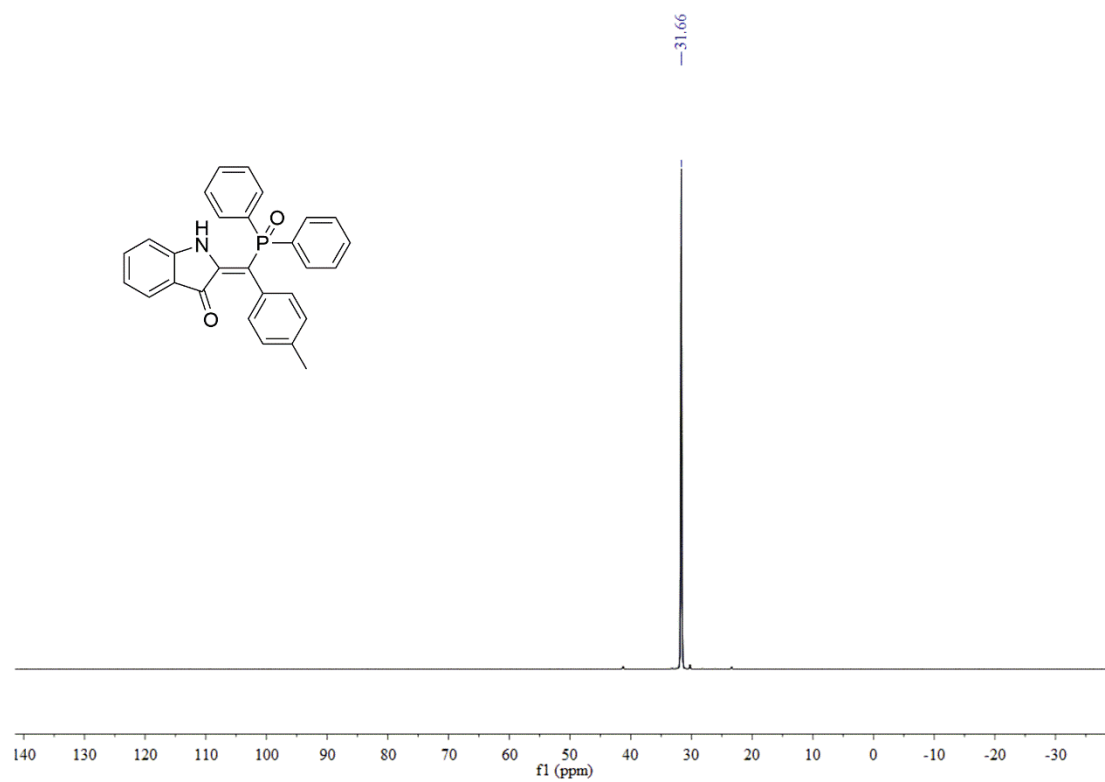
(Z)-2-((diphenylphosphoryl)(p-tolyl)methylene)indolin-3-one (3b): ¹H NMR



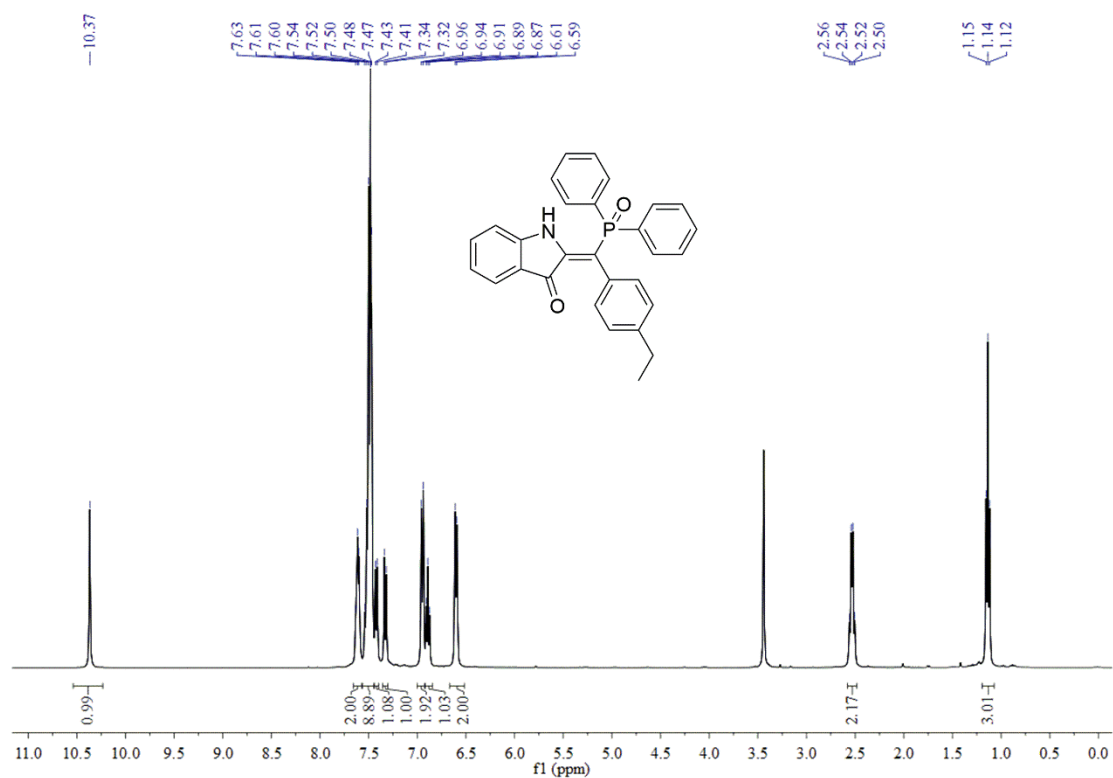
(Z)-2-((diphenylphosphoryl)(p-tolyl)methylene)indolin-3-one (3b): ^{13}C NMR



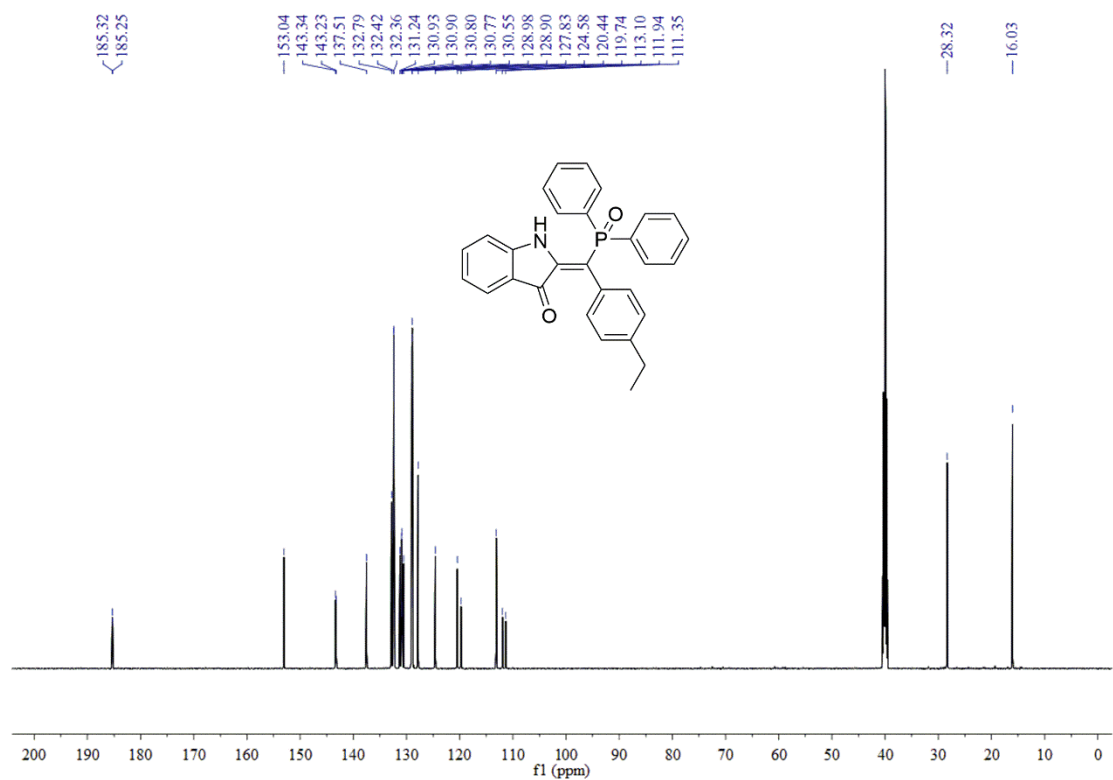
(Z)-2-((diphenylphosphoryl)(p-tolyl)methylene)indolin-3-one (3b): ^{31}P NMR



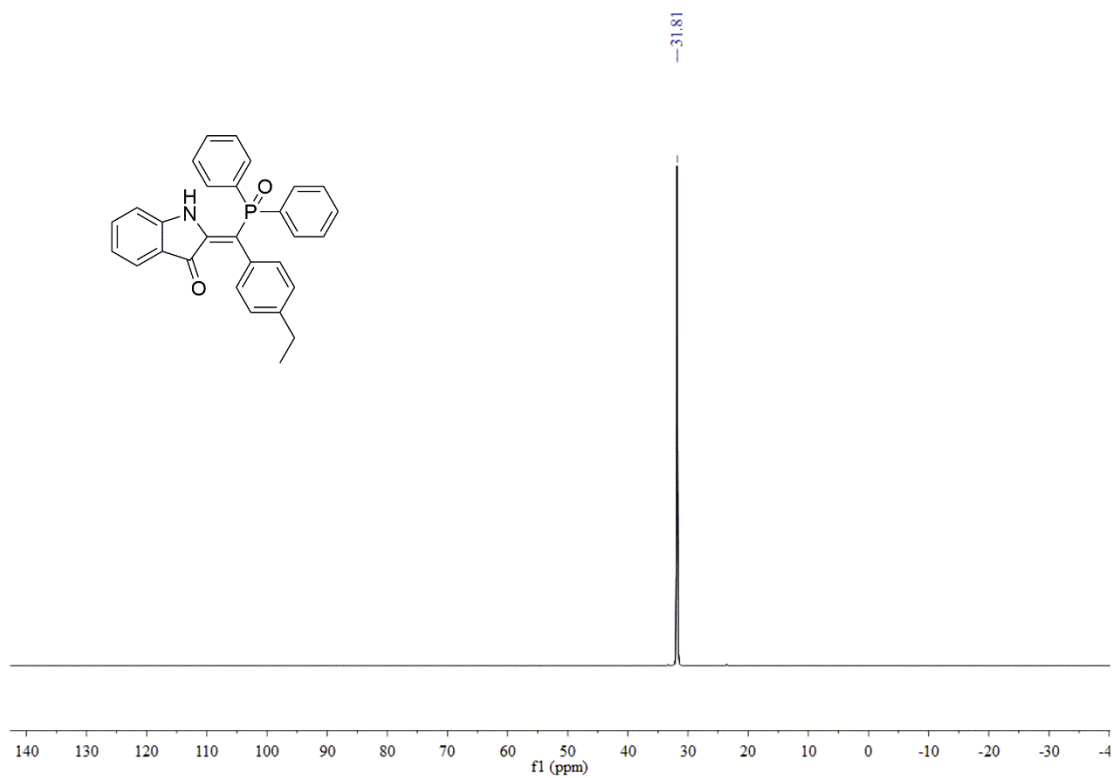
(Z)-2-((diphenylphosphoryl)(4-ethylphenyl)methylene)indolin-3-one (3c): ¹H NMR



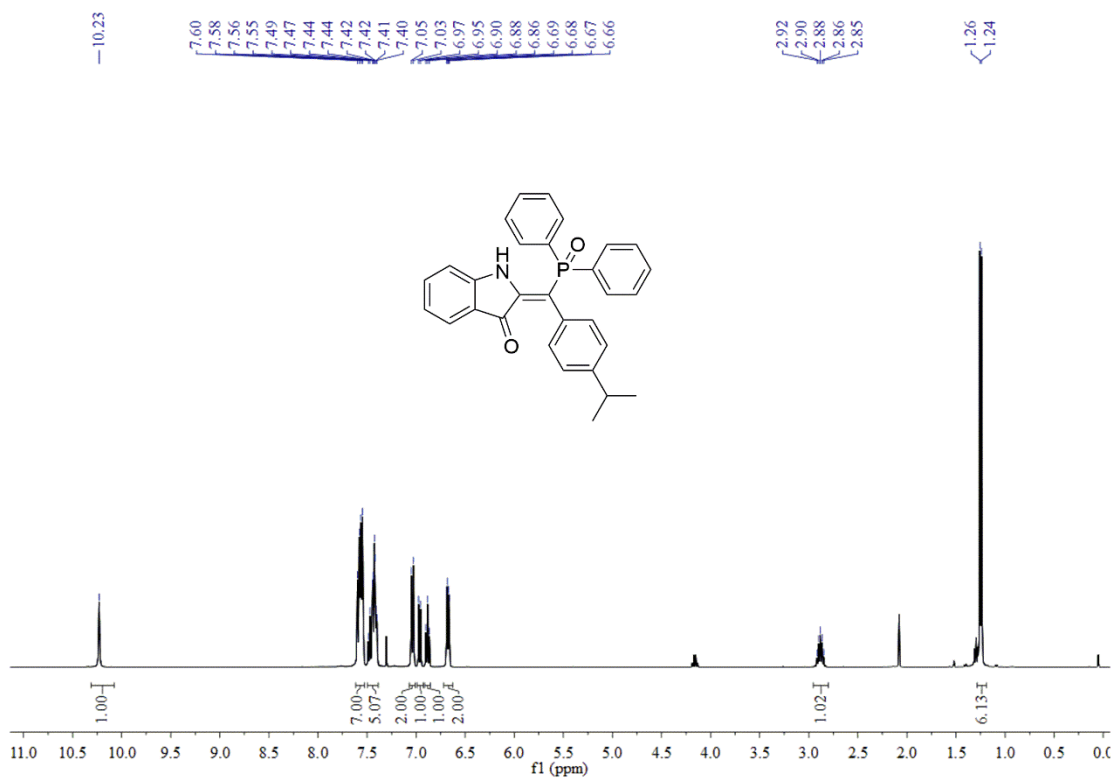
(Z)-2-((diphenylphosphoryl)(p-tolyl)methylene)indolin-3-one (3c): ¹³C NMR



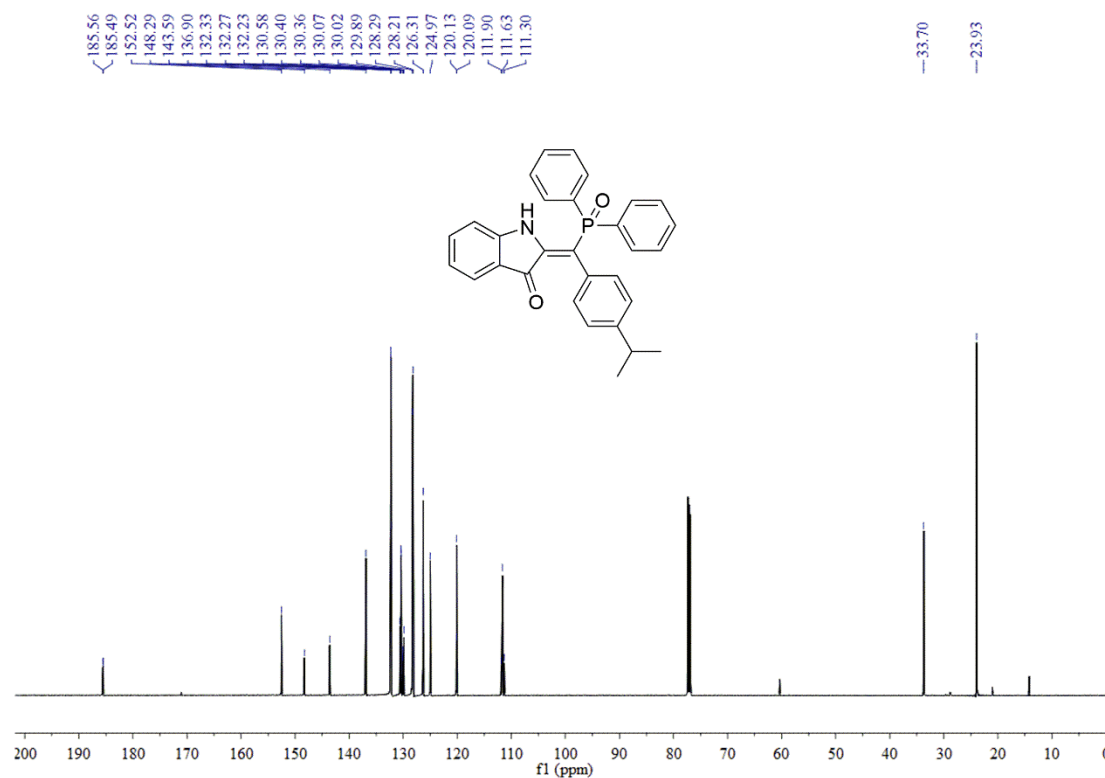
(Z)-2-((diphenylphosphoryl)(p-tolyl)methylene)indolin-3-one (3c): ³¹P NMR



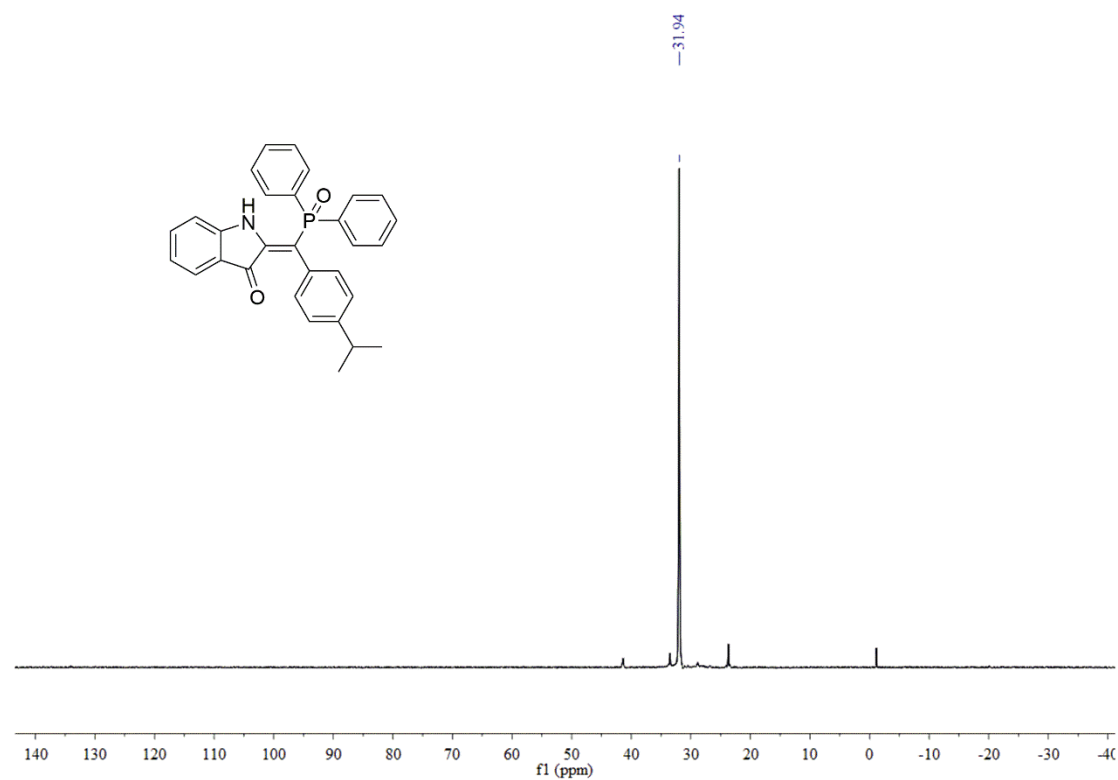
(Z)-2-((diphenylphosphoryl)(4-isopropylphenyl)methylene)indolin-3-one (3d): ¹H NMR



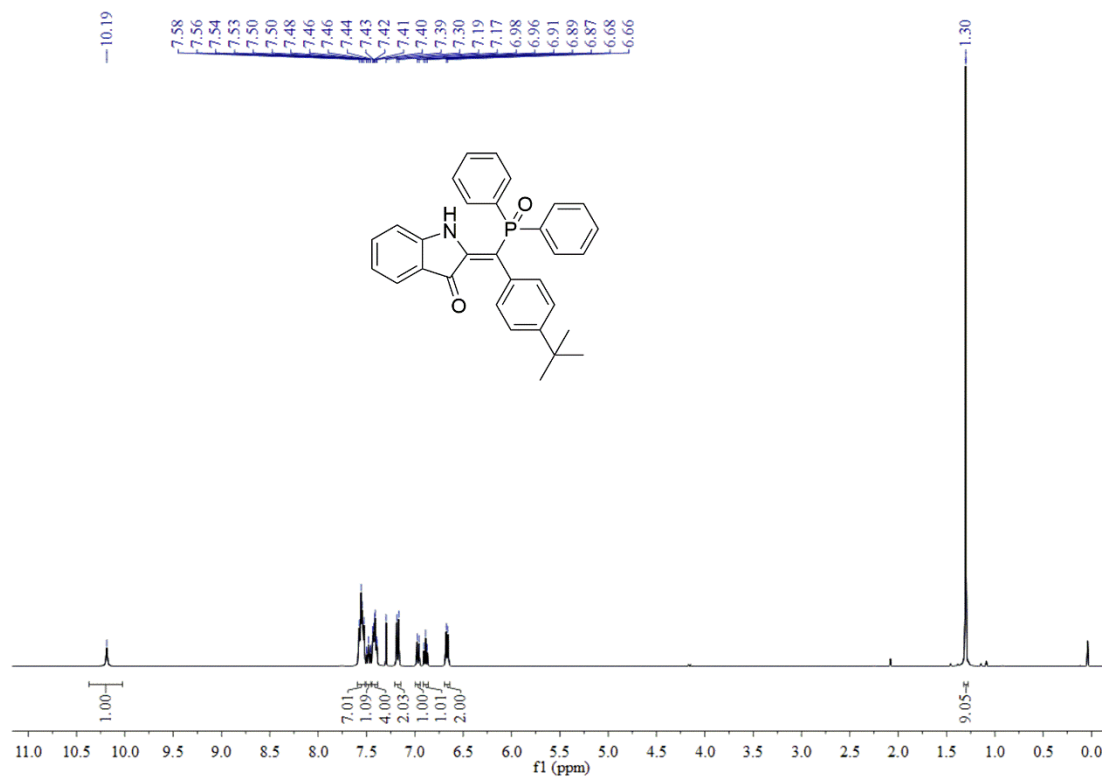
(Z)-2-((diphenylphosphoryl)(4-isopropylphenyl)methylene)indolin-3-one (3d): ¹³C NMR



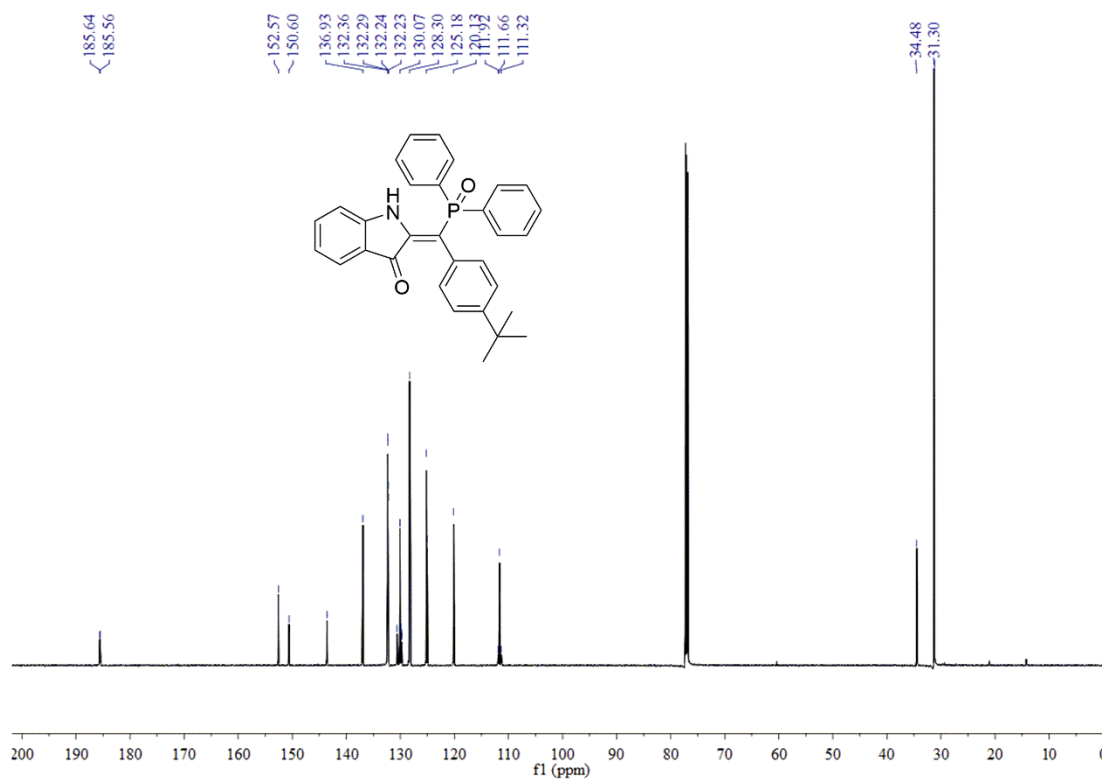
(Z)-2-((diphenylphosphoryl)(4-isopropylphenyl)methylene)indolin-3-one (3d): ³¹P NMR



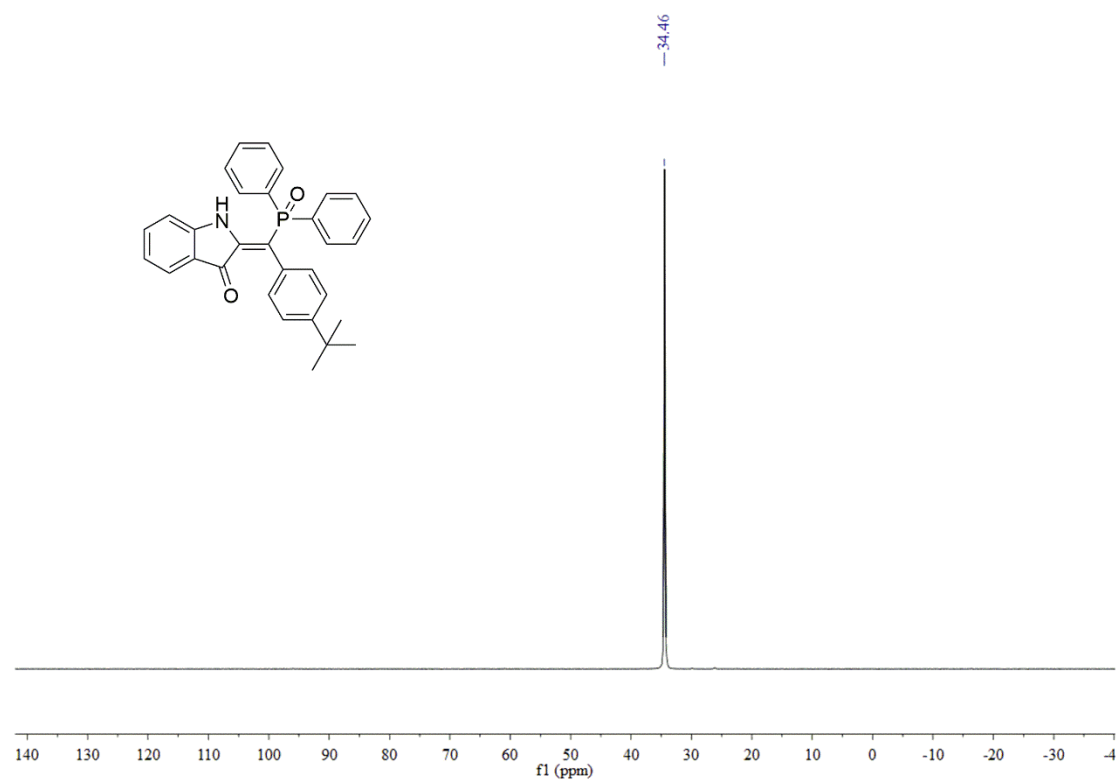
(Z)-2-((4-(tert-butyl)phenyl)(diphenylphosphoryl)methylene)indolin-3-one (3e): ¹H NMR



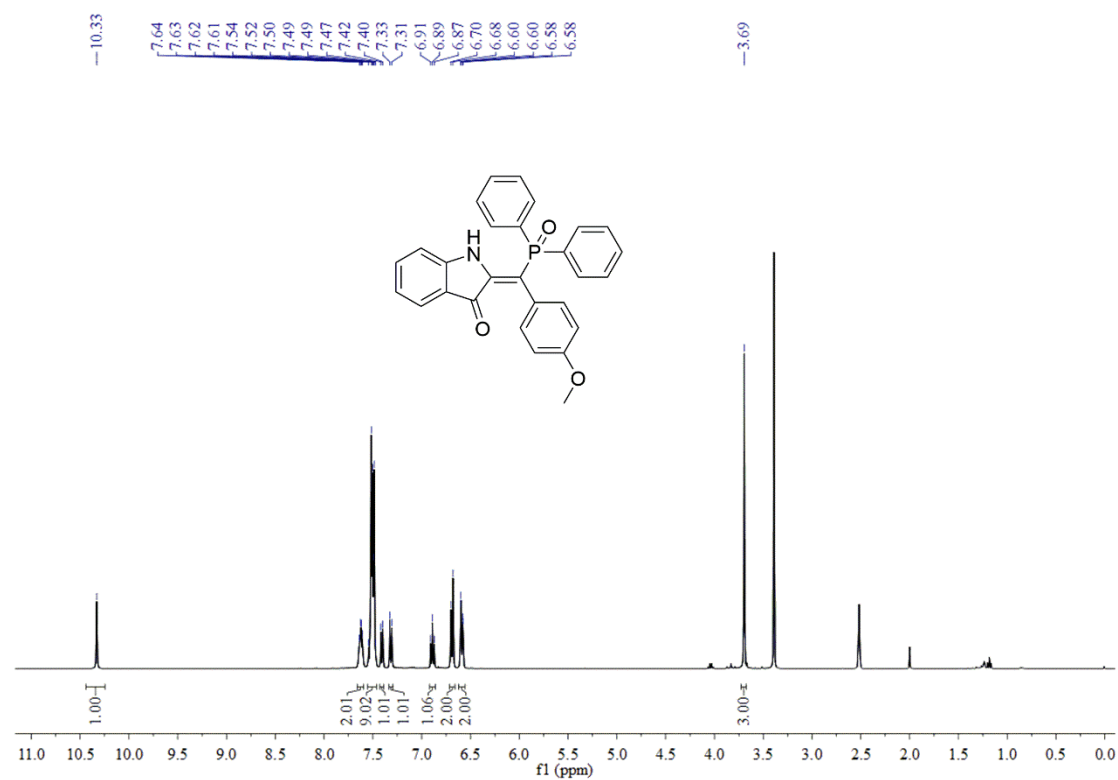
(Z)-2-((4-(tert-butyl)phenyl)(diphenylphosphoryl)methylene)indolin-3-one (3e): ¹³C NMR



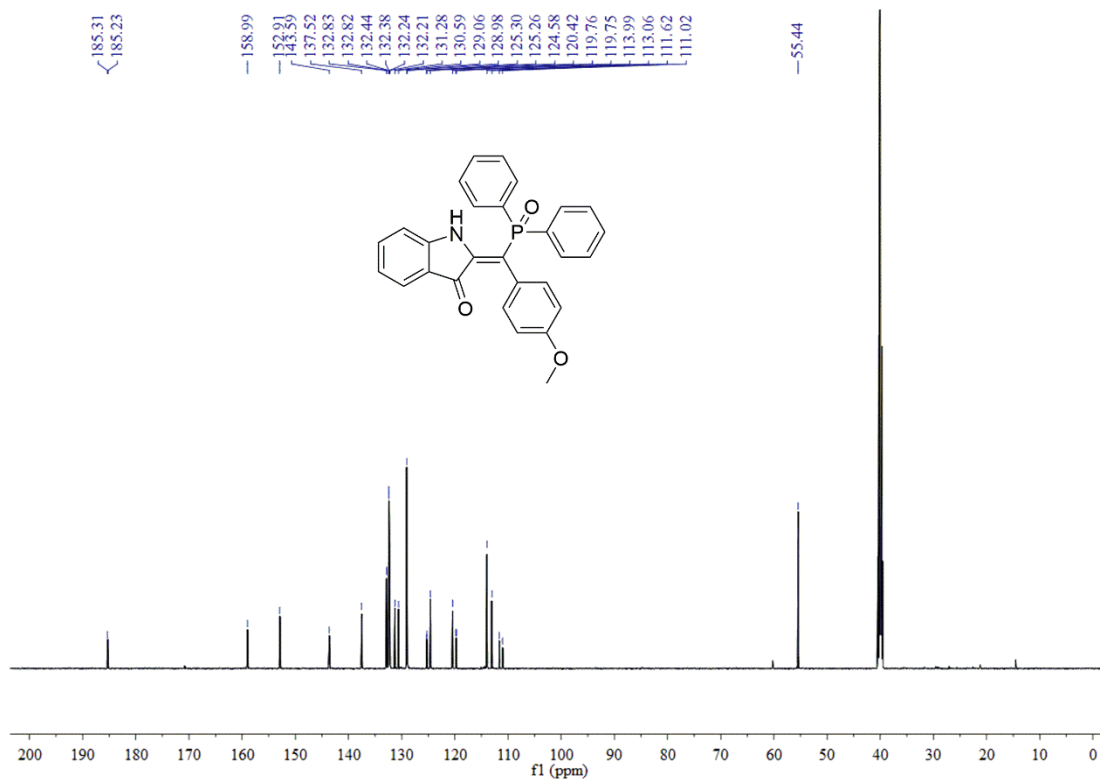
(Z)-2-((4-(tert-butyl)phenyl)(diphenylphosphoryl)methylene)indolin-3-one (3e): ³¹P NMR



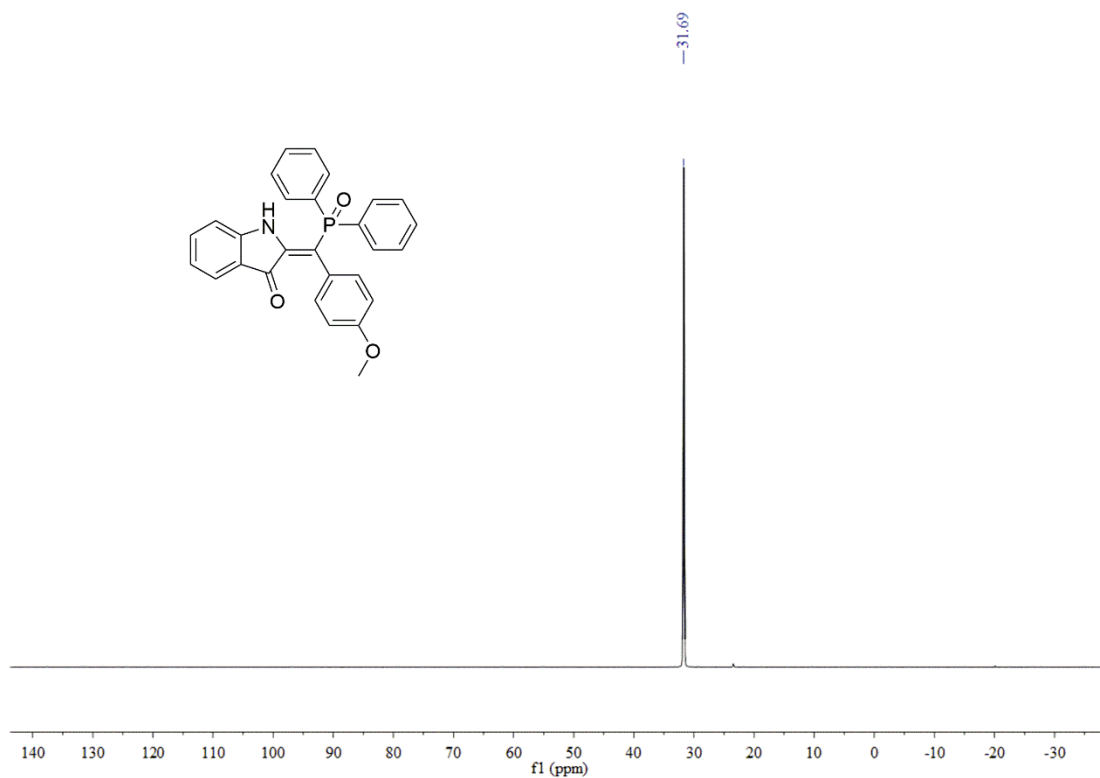
(Z)-2-((diphenylphosphoryl)(4-methoxyphenyl)methylene)indolin-3-one (3f): ¹H NMR



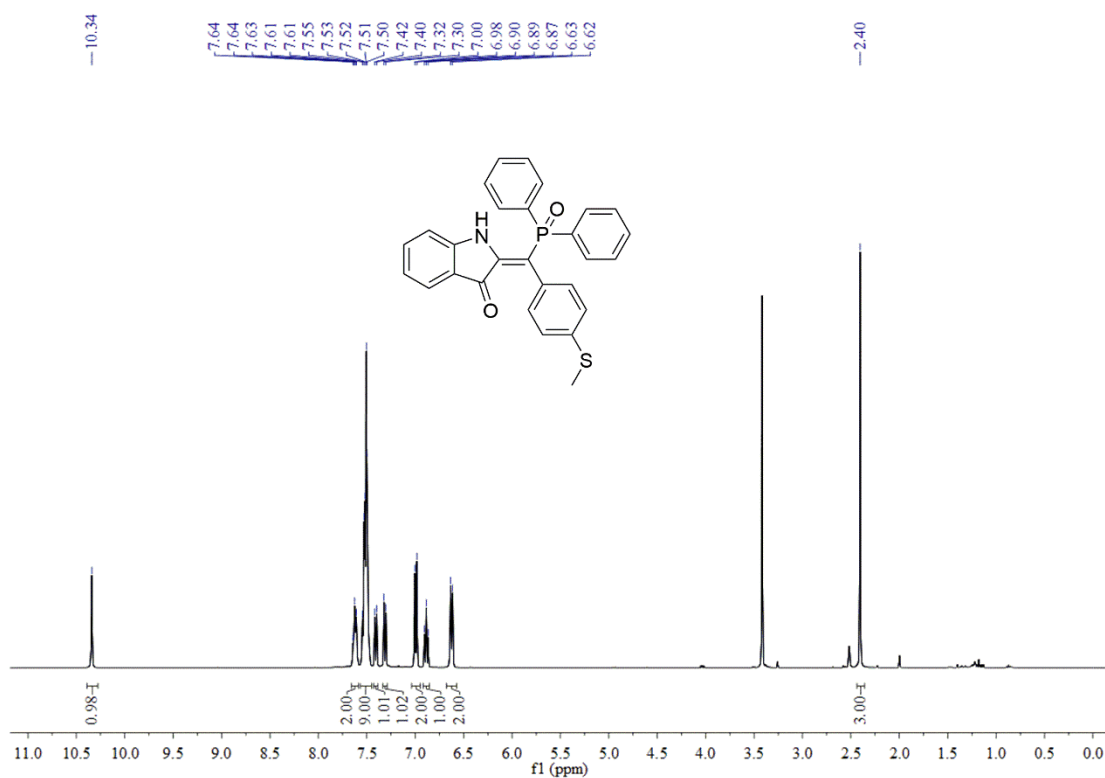
(Z)-2-((diphenylphosphoryl)(4-methoxyphenyl)methylene)indolin-3-one (3f): ¹³C NMR



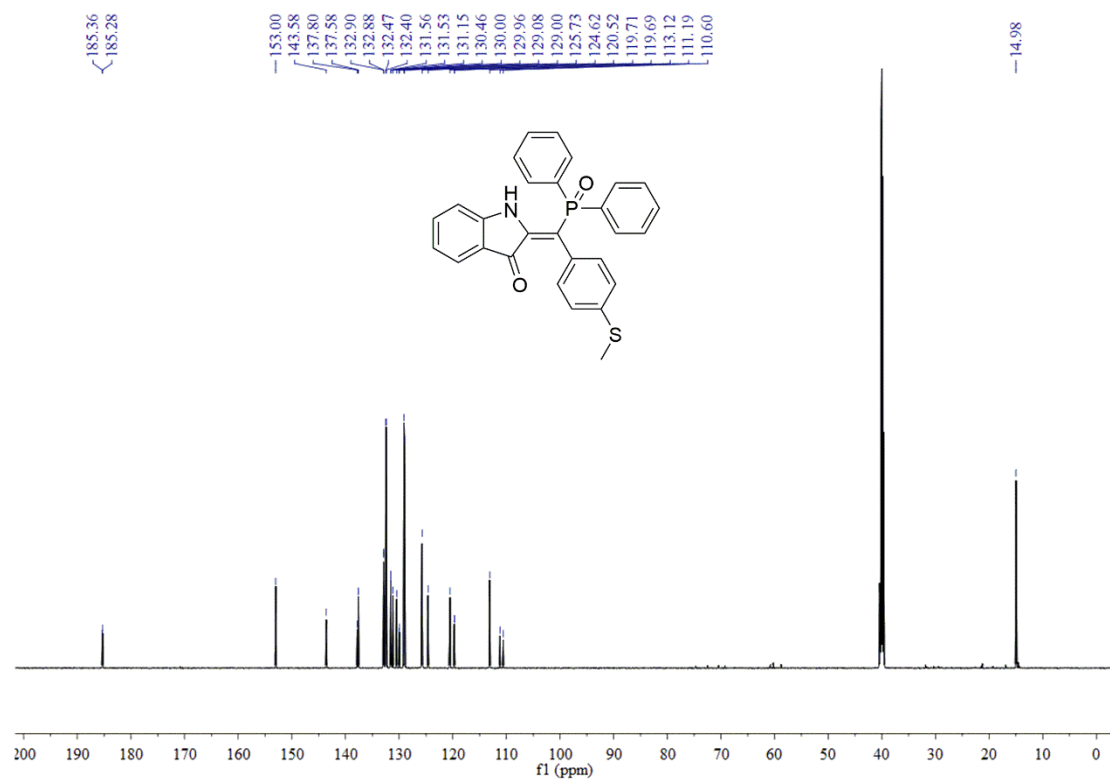
(Z)-2-((diphenylphosphoryl)(4-methoxyphenyl)methylene)indolin-3-one (3f): ³¹P NMR



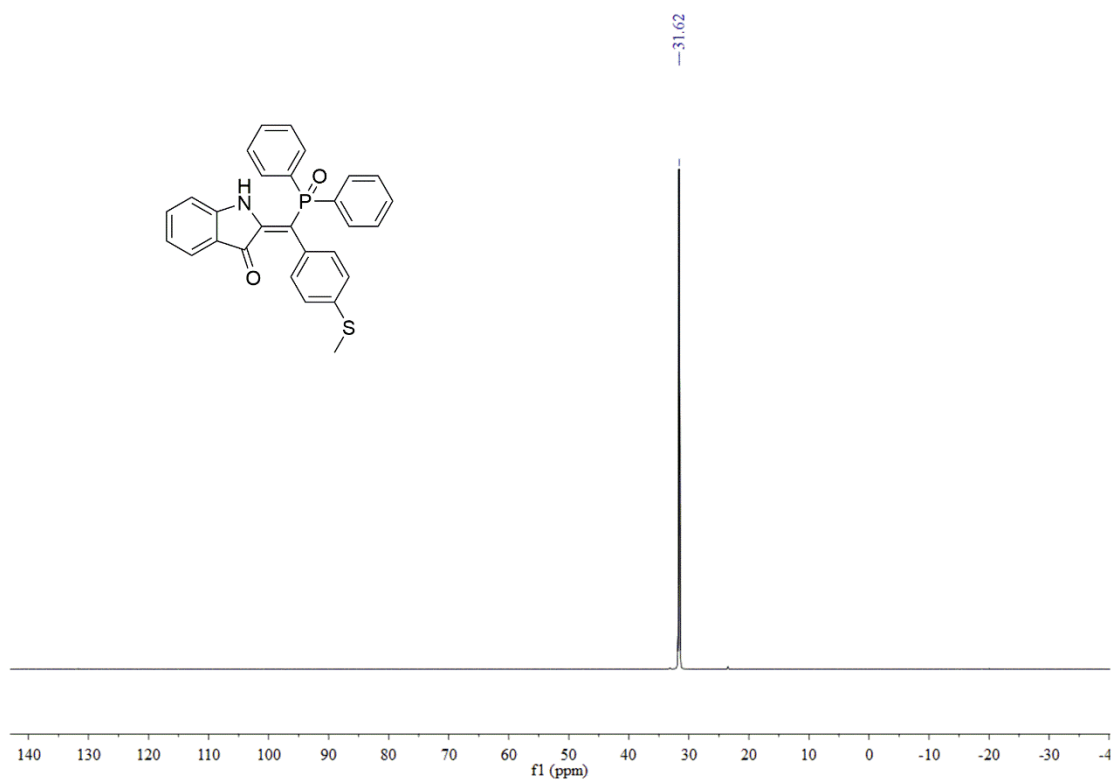
(Z)-2-((diphenylphosphoryl)(4-(methylthio)phenyl)methylene)indolin-3-one (3g): ¹H NMR



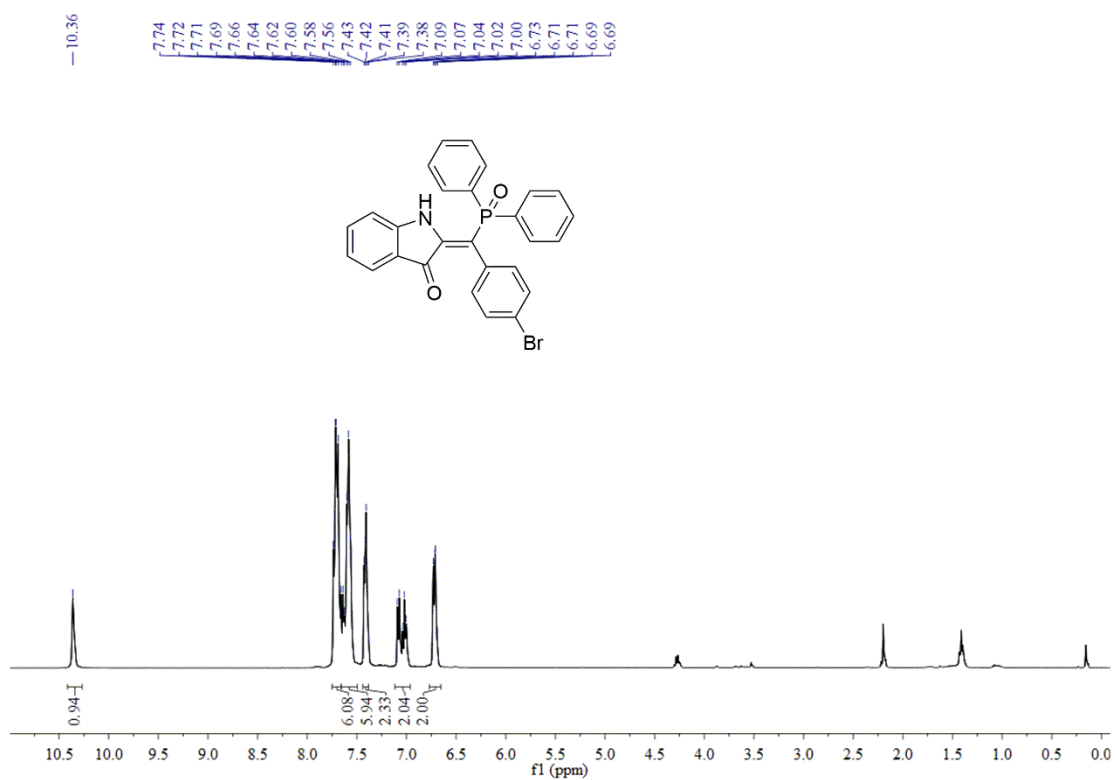
(Z)-2-((diphenylphosphoryl)(4-(methylthio)phenyl)methylene)indolin-3-one (3g): ¹³C NMR



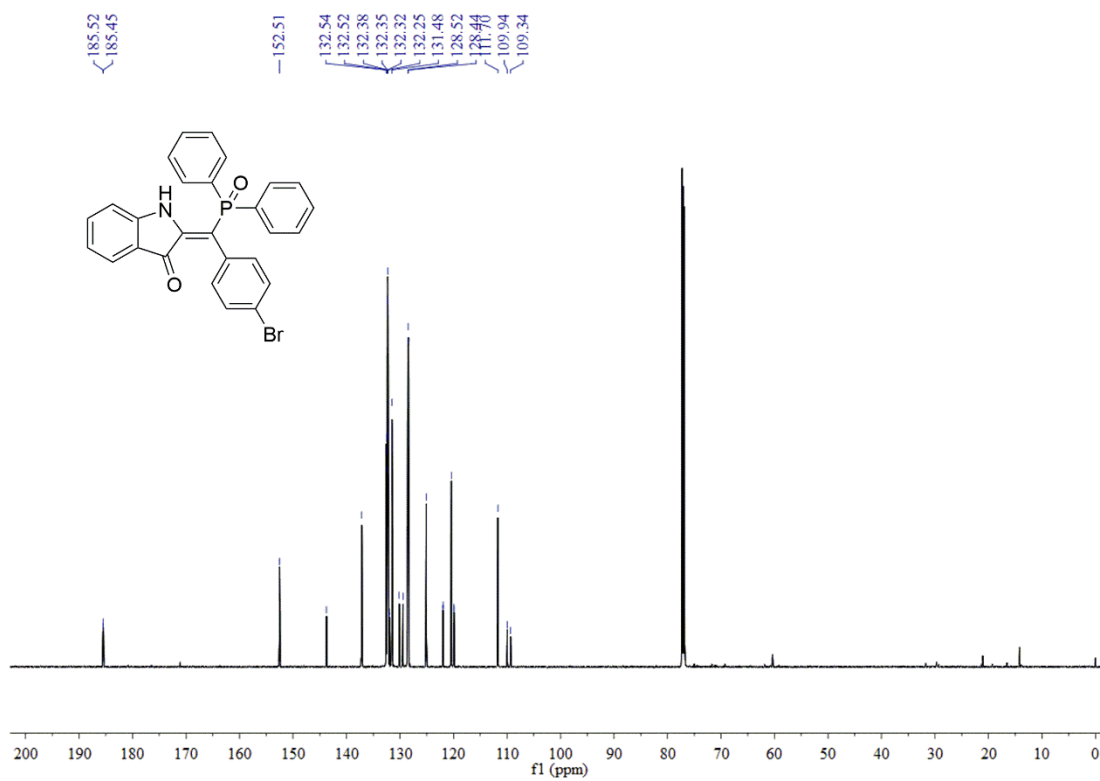
(Z)-2-((diphenylphosphoryl)(4-(methylthio)phenyl)methylene)indolin-3-one (3g): ³¹P NMR



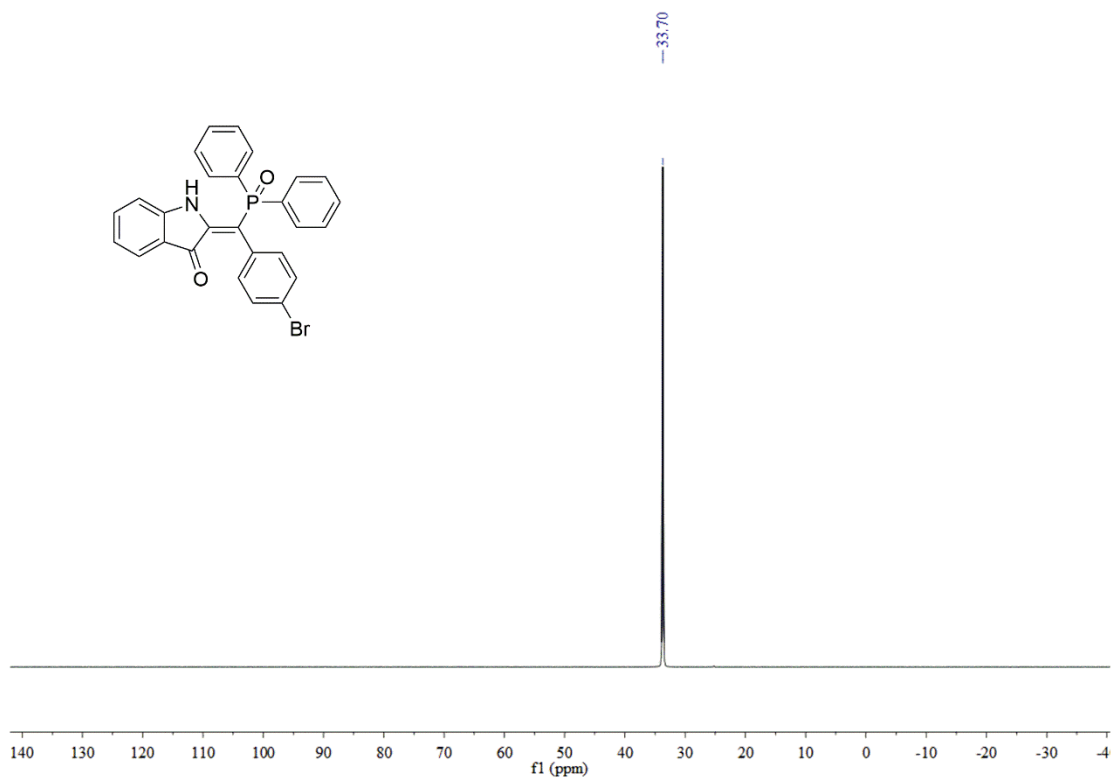
(Z)-2-((4-bromophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3h): ¹H NMR



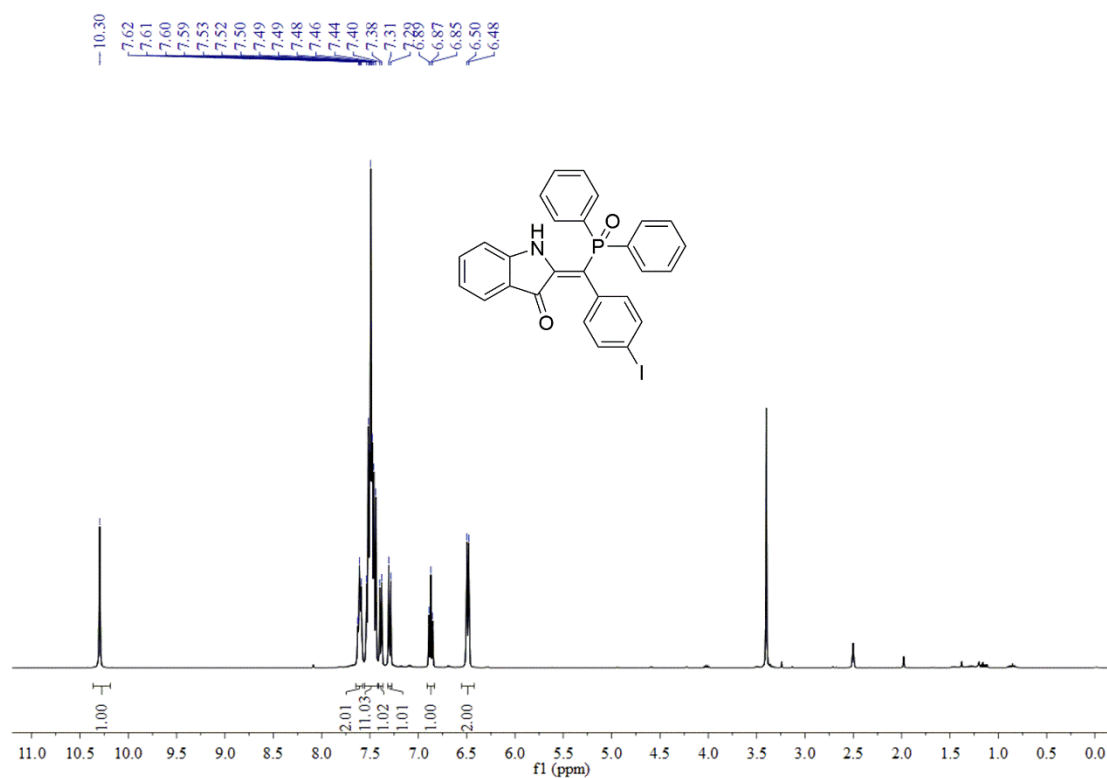
(Z)-2-((4-bromophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3h): ¹³C NMR



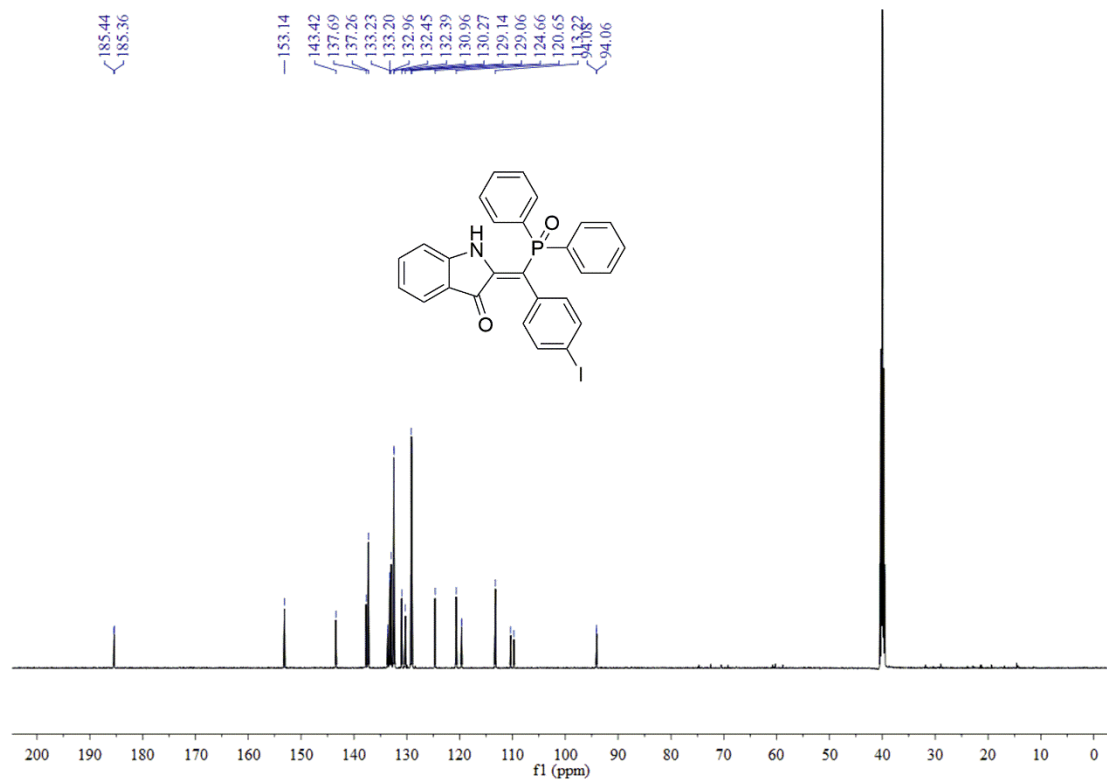
(Z)-2-((4-bromophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3h): ³¹P NMR



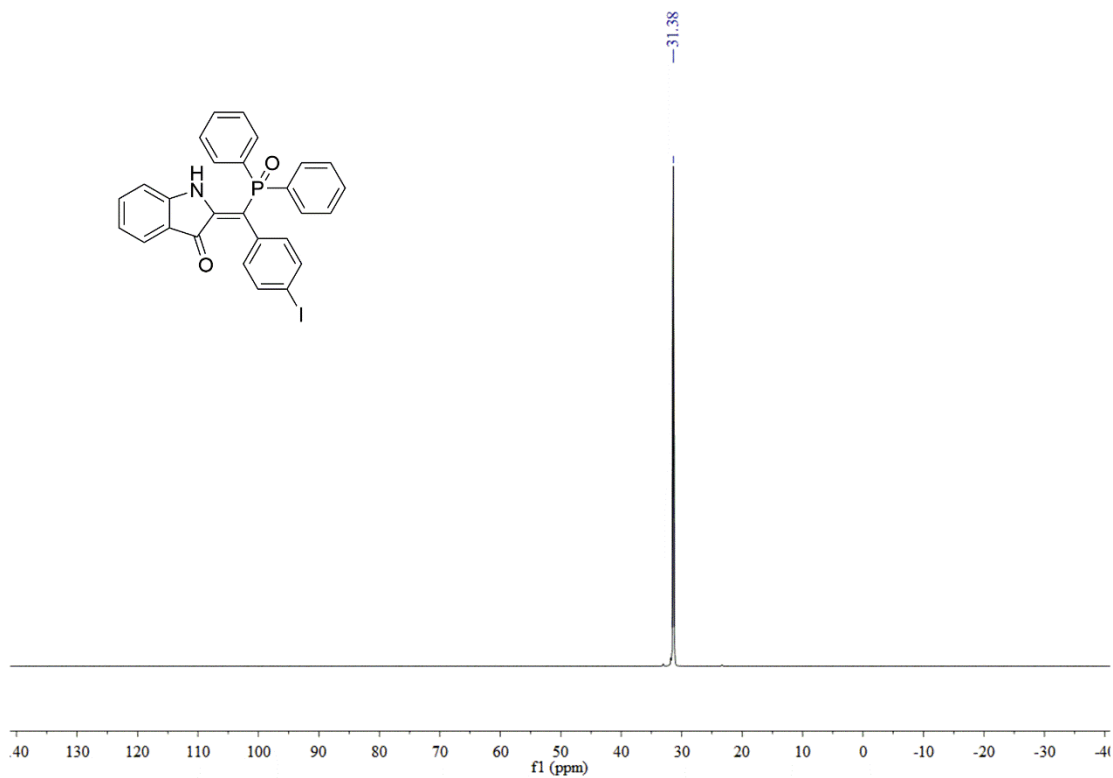
(Z)-2-((diphenylphosphoryl)(4-iodophenyl)methylene)indolin-3-one (3i): ¹H NMR



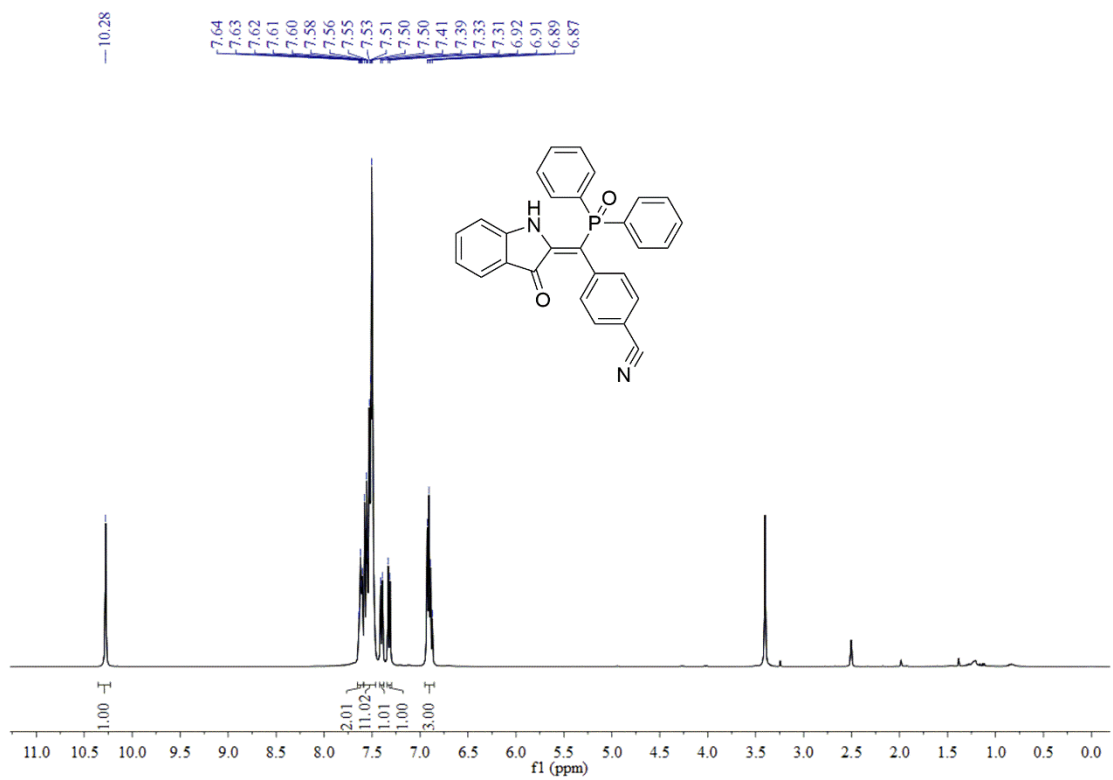
(Z)-2-((diphenylphosphoryl)(4-iodophenyl)methylene)indolin-3-one (3i): ¹³C NMR



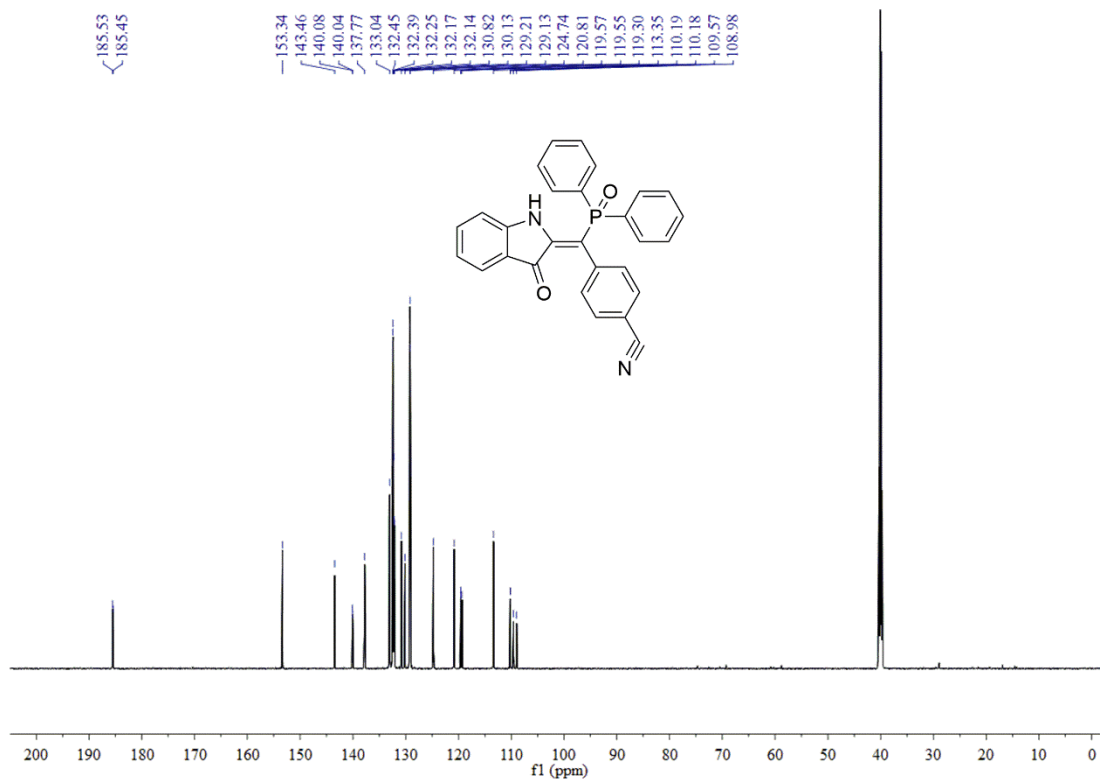
(Z)-2-((diphenylphosphoryl)(4-iodophenyl)methylene)indolin-3-one (3i): ³¹P NMR



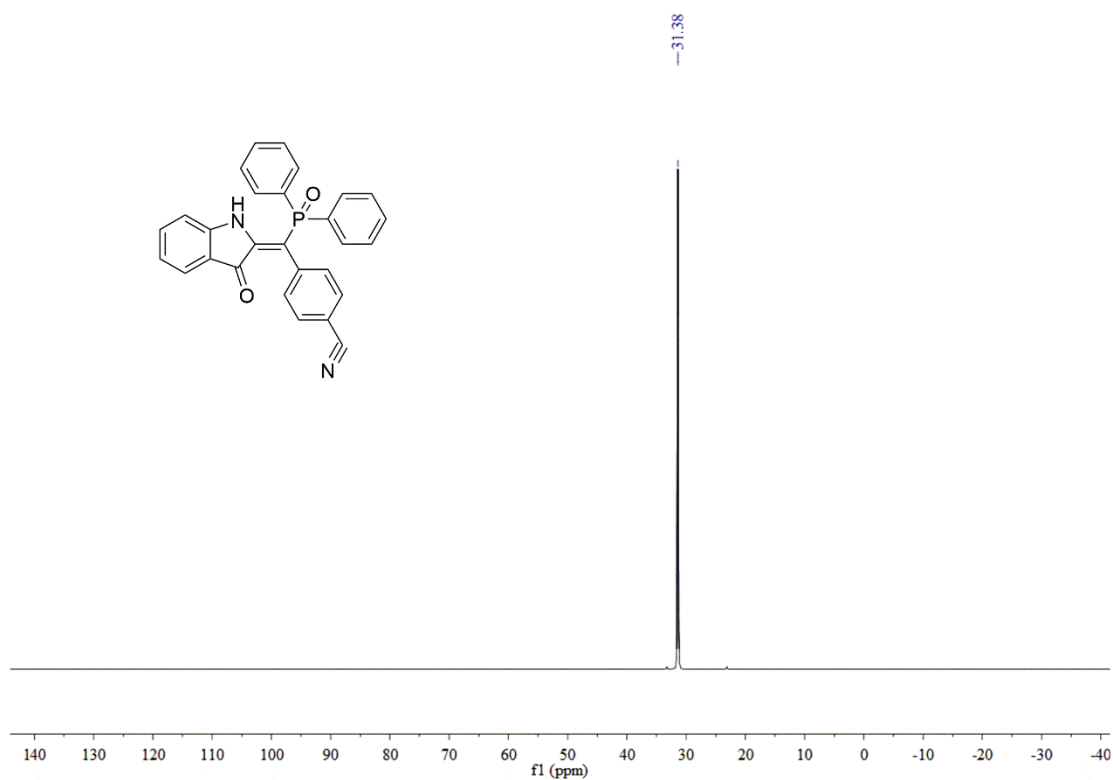
(Z)-4-((diphenylphosphoryl)(3-oxindolin-2-ylidene)methyl)benzotrile (3j): ¹H NMR



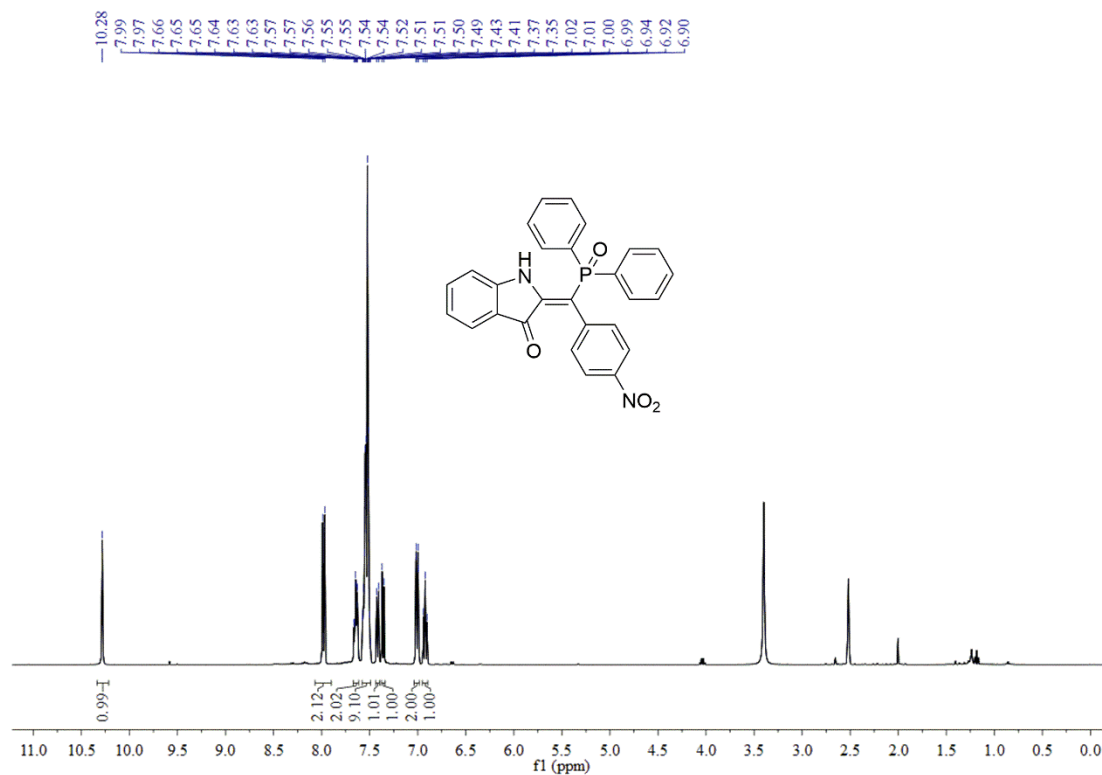
(Z)-4-((diphenylphosphoryl)(3-oxoindolin-2-ylidene)methyl)benzonitrile (3j): ¹³C NMR



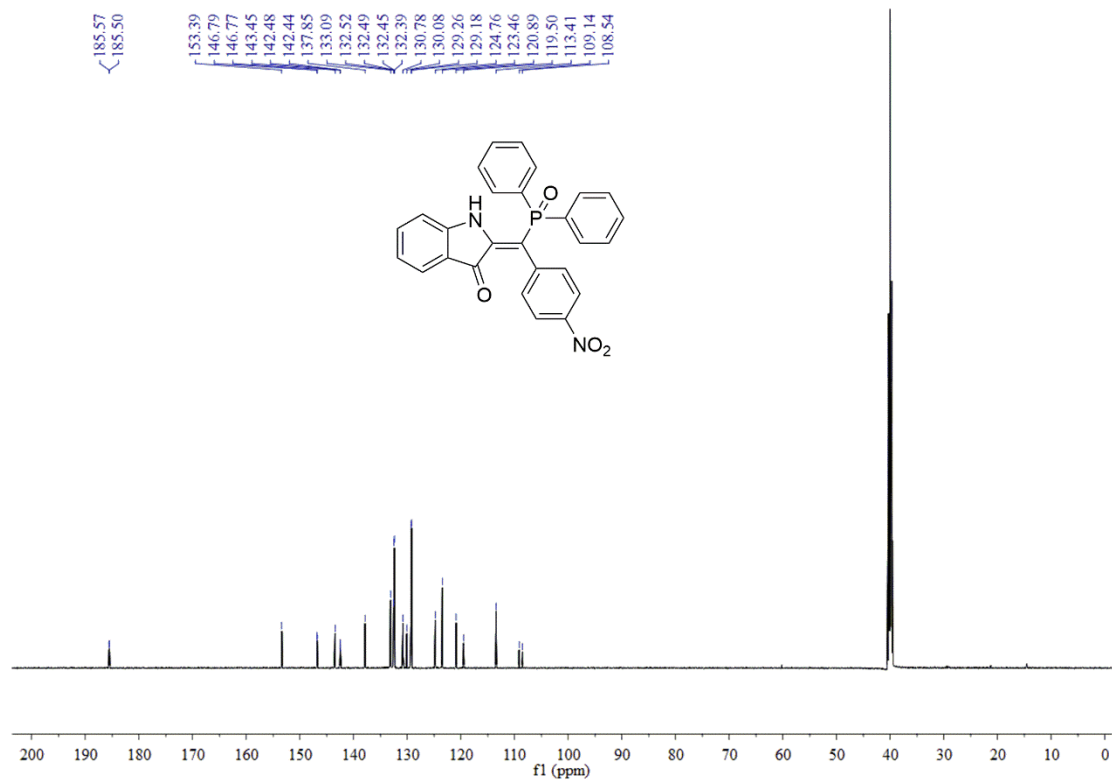
(Z)-4-((diphenylphosphoryl)(3-oxoindolin-2-ylidene)methyl)benzonitrile (3j): ³¹P NMR



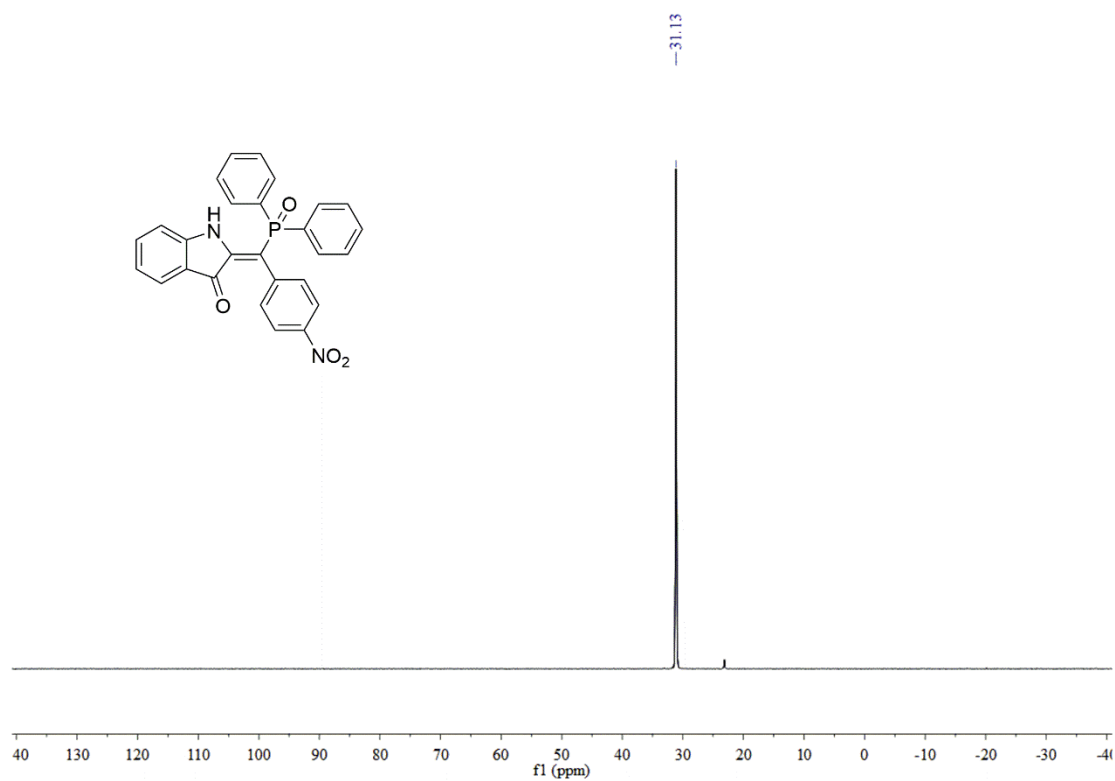
(Z)-2-((diphenylphosphoryl)(4-nitrophenyl)methylene)indolin-3-one (3k): ¹H NMR



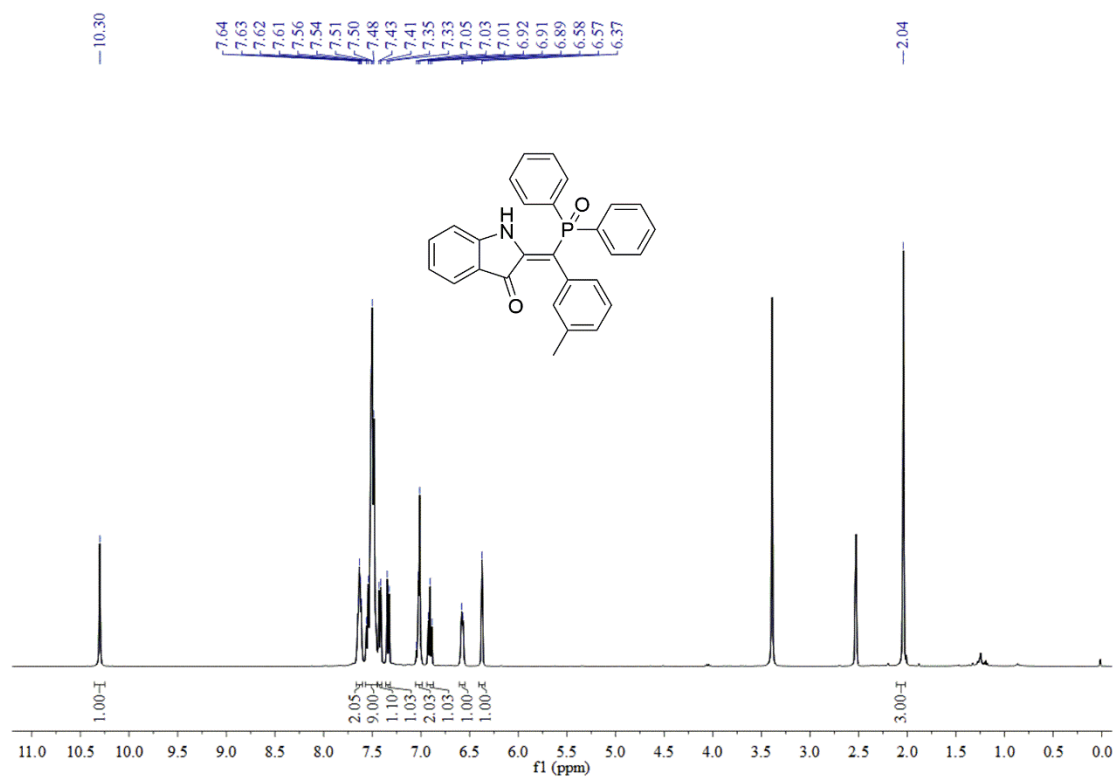
(Z)-2-((diphenylphosphoryl)(4-nitrophenyl)methylene)indolin-3-one (3k): ¹³C NMR



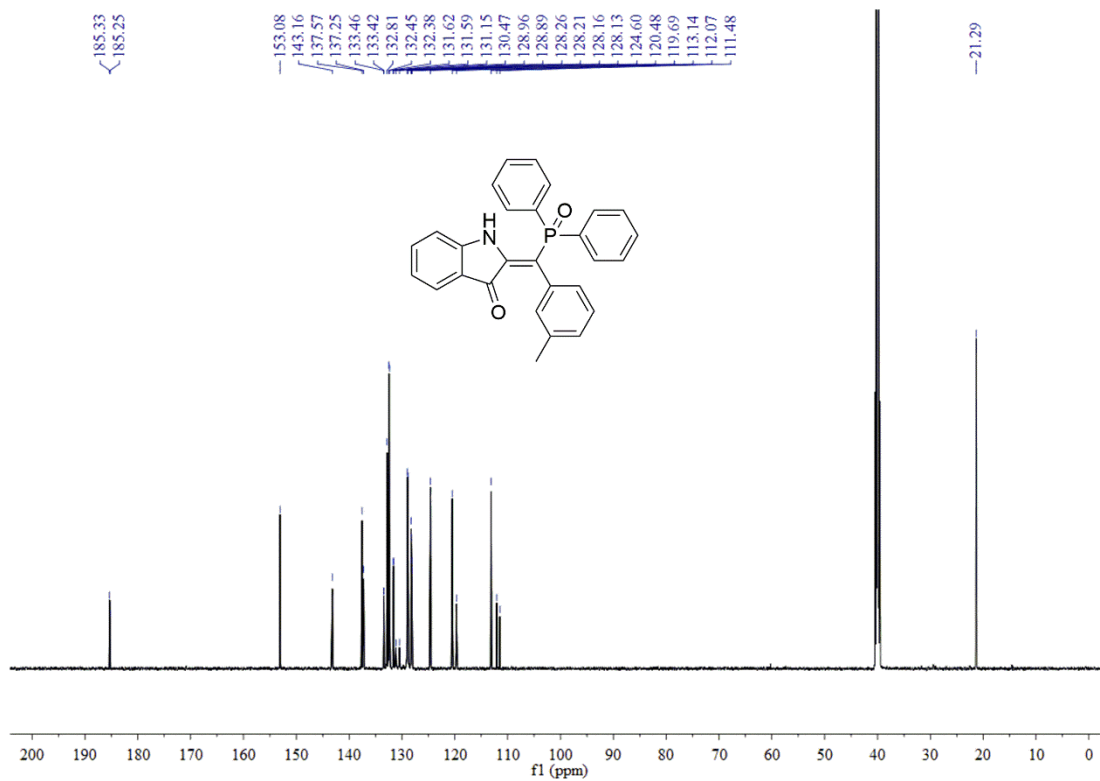
(Z)-2-((diphenylphosphoryl)(4-nitrophenyl)methylene)indolin-3-one (3k): ³¹P NMR



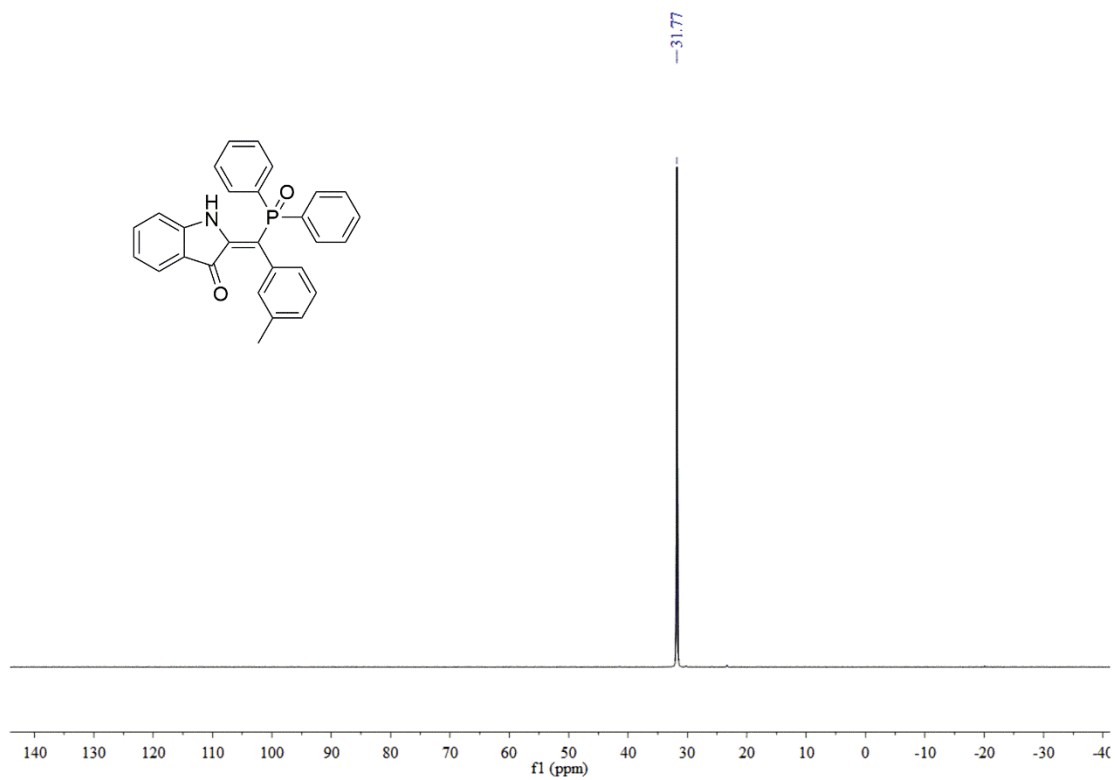
(Z)-2-((diphenylphosphoryl)(m-tolyl)methylene)indolin-3-one (3l): ¹H NMR



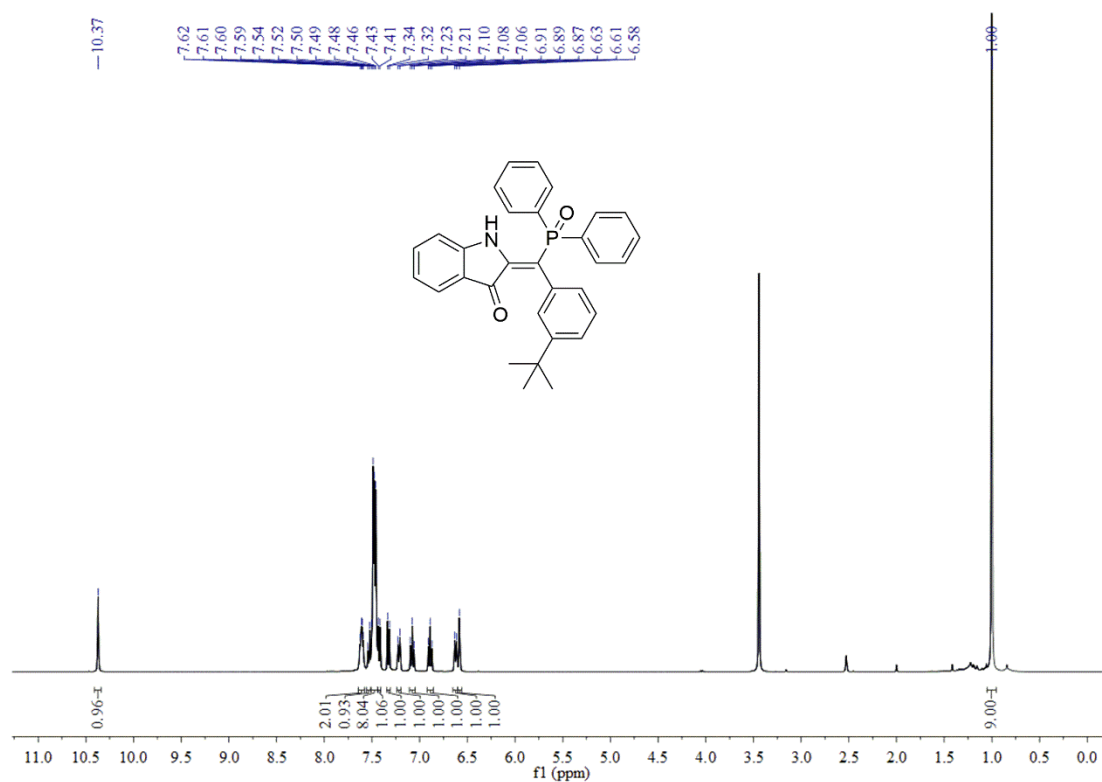
(Z)-2-((diphenylphosphoryl)(m-tolyl)methylene)indolin-3-one (3l): ¹³C NMR



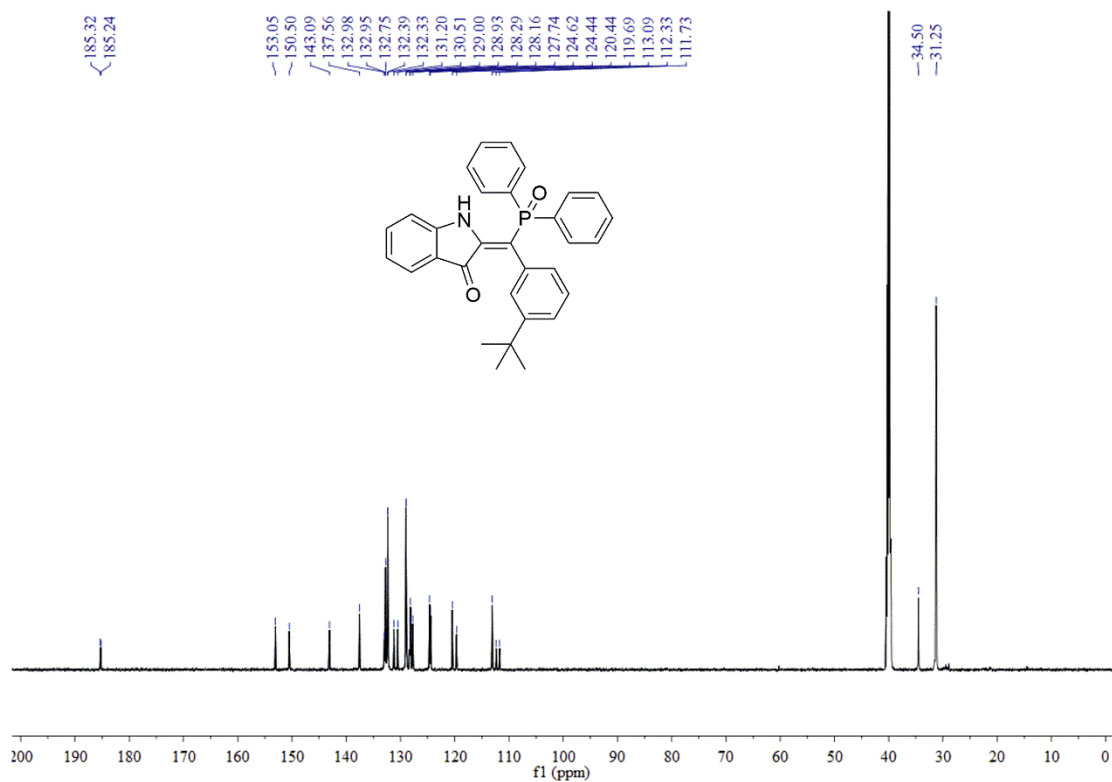
(Z)-2-((diphenylphosphoryl)(m-tolyl)methylene)indolin-3-one (3l): ³¹P NMR



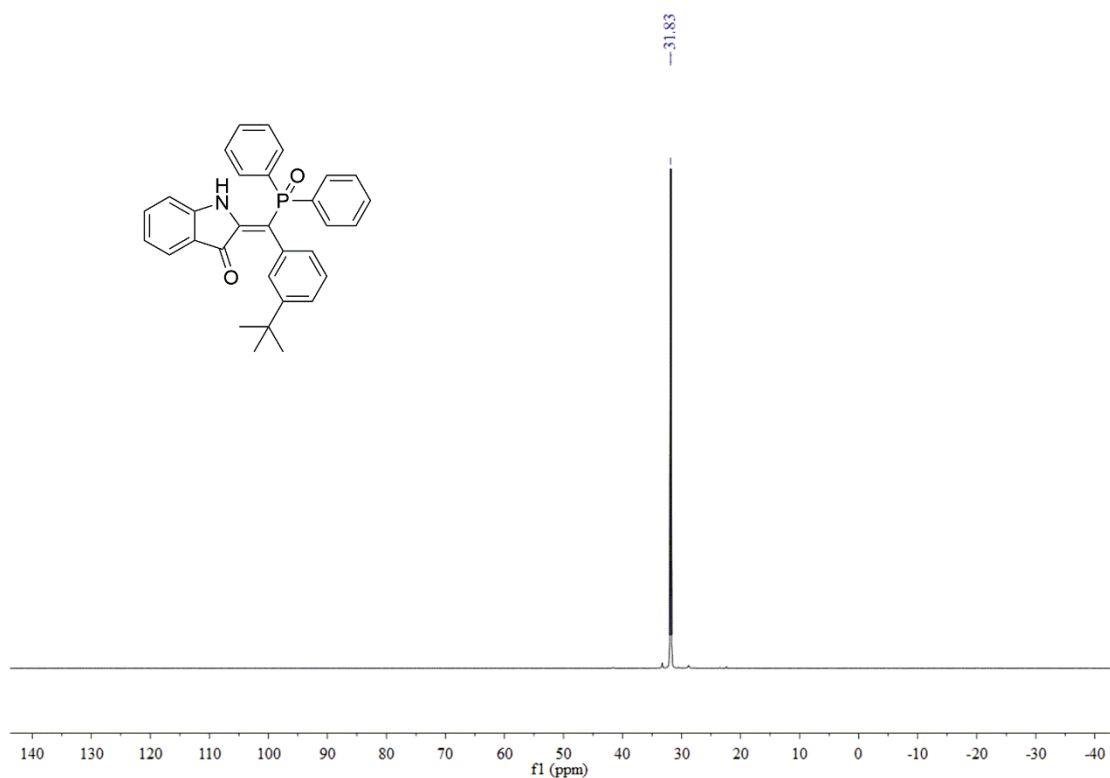
(Z)-2-((3-(tert-butyl)phenyl)(diphenylphosphoryl)methylene)indolin-3-one (3m): ¹H NMR



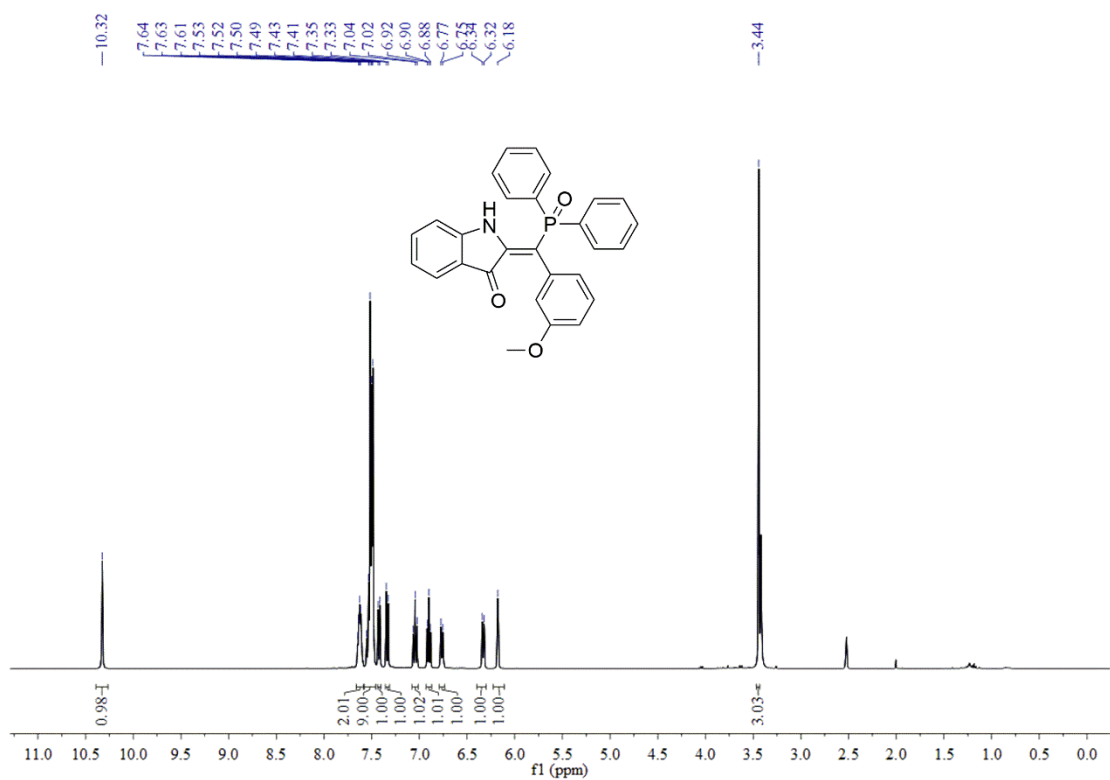
(Z)-2-((3-(tert-butyl)phenyl)(diphenylphosphoryl)methylene)indolin-3-one (3m): ¹³C NMR



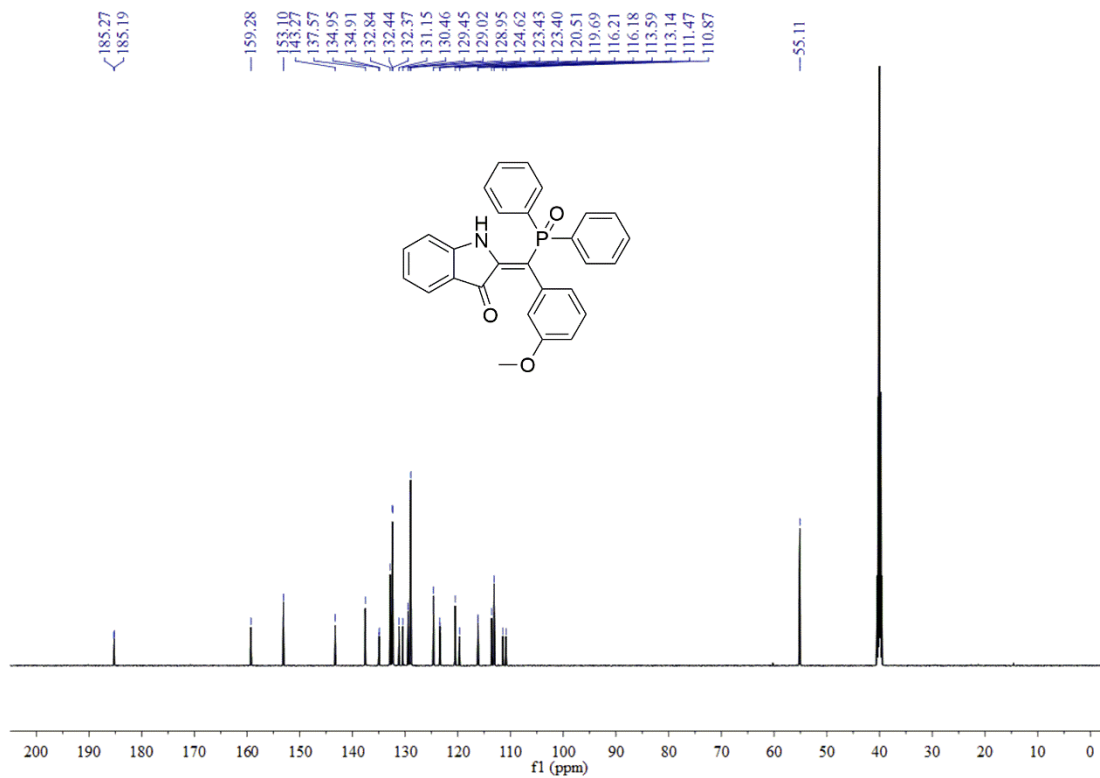
(Z)-2-((3-(tert-butyl)phenyl)(diphenylphosphoryl)methylene)indolin-3-one (3m): ^{31}P NMR



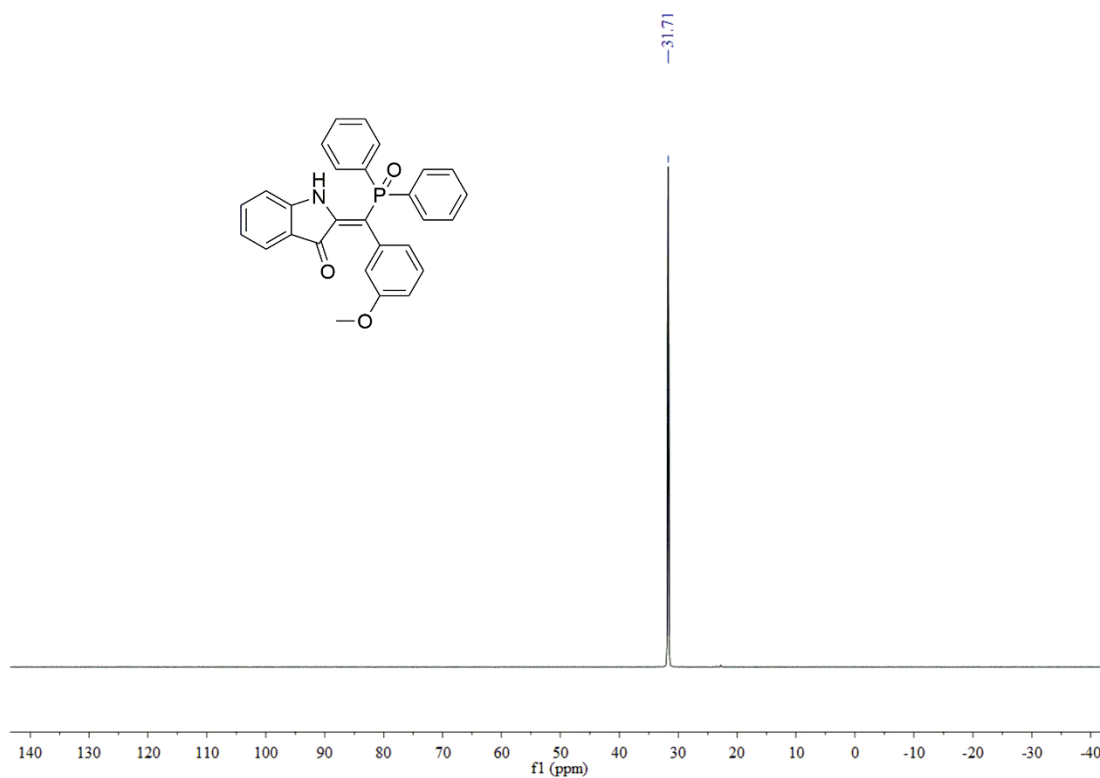
(Z)-2-((diphenylphosphoryl)(3-methoxyphenyl)methylene)indolin-3-one (3n): ^1H NMR



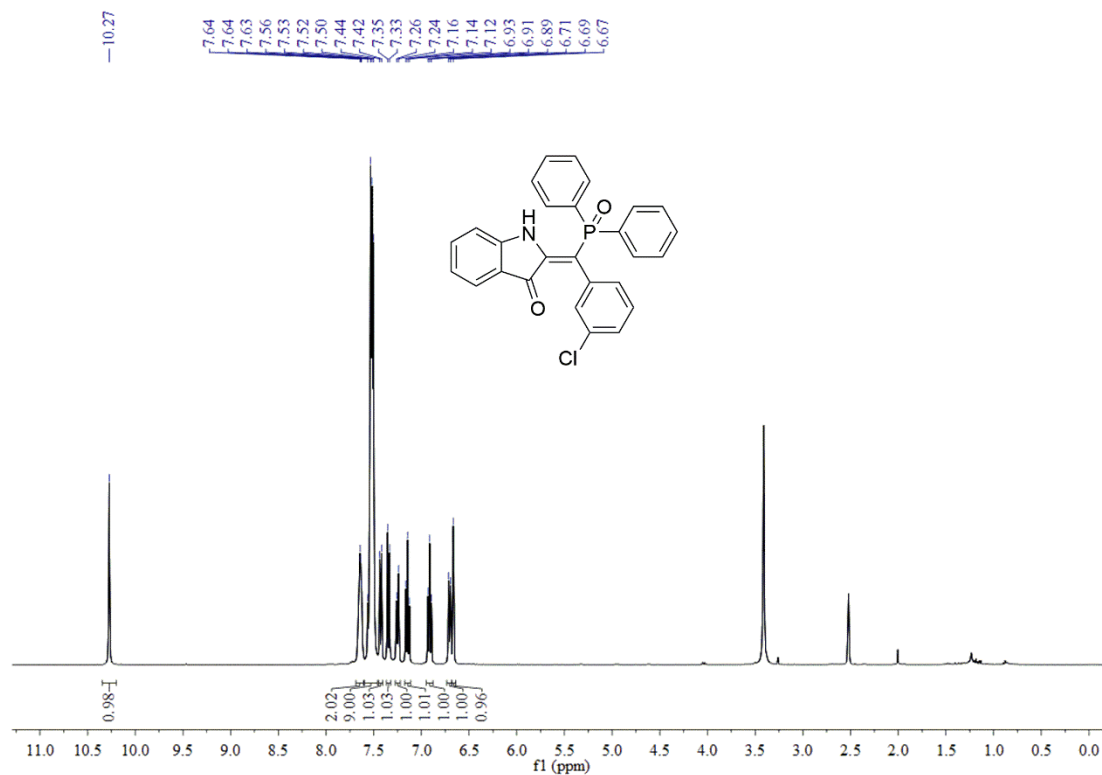
(Z)-2-((diphenylphosphoryl)(3-methoxyphenyl)methylene)indolin-3-one (3n): ¹³C NMR



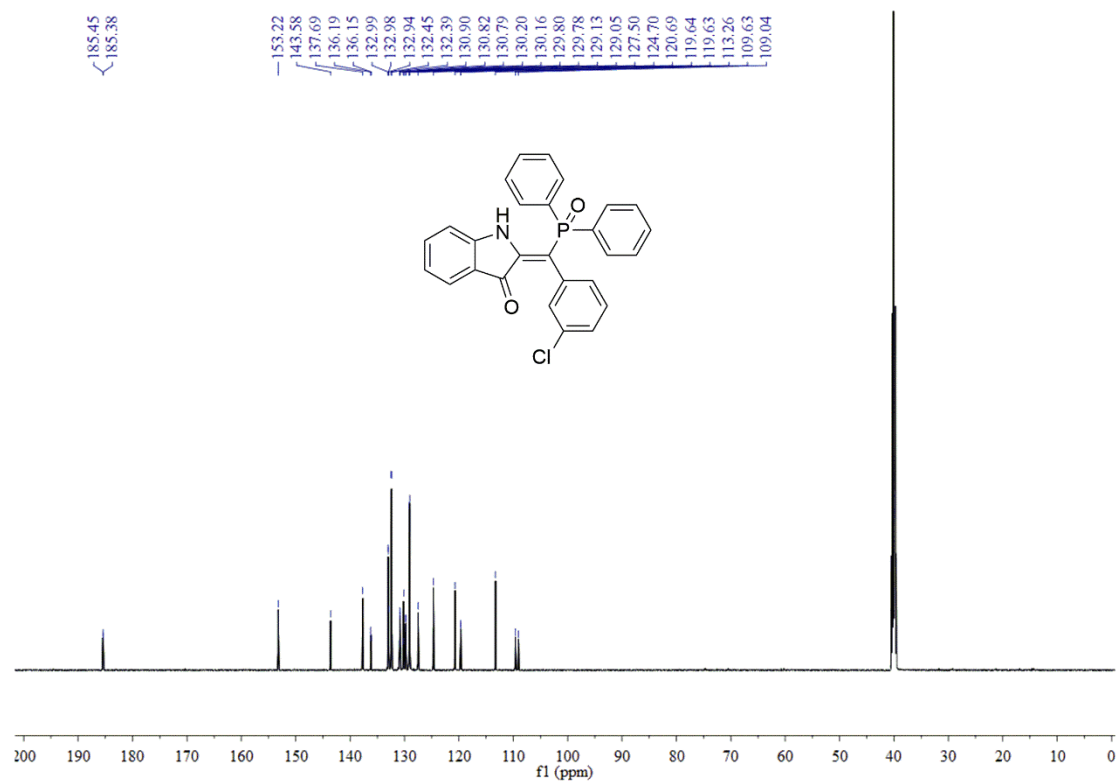
(Z)-2-((diphenylphosphoryl)(3-methoxyphenyl)methylene)indolin-3-one (3n): ³¹P NMR



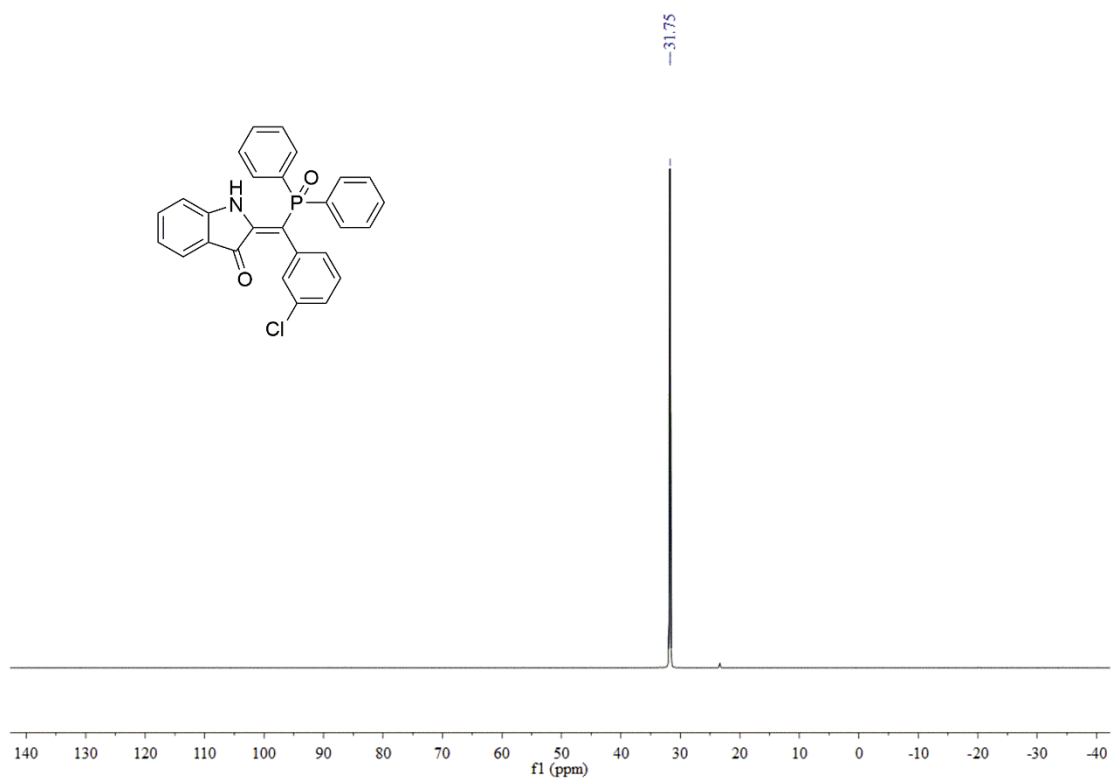
(Z)-2-((3-chlorophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3o): ¹H NMR



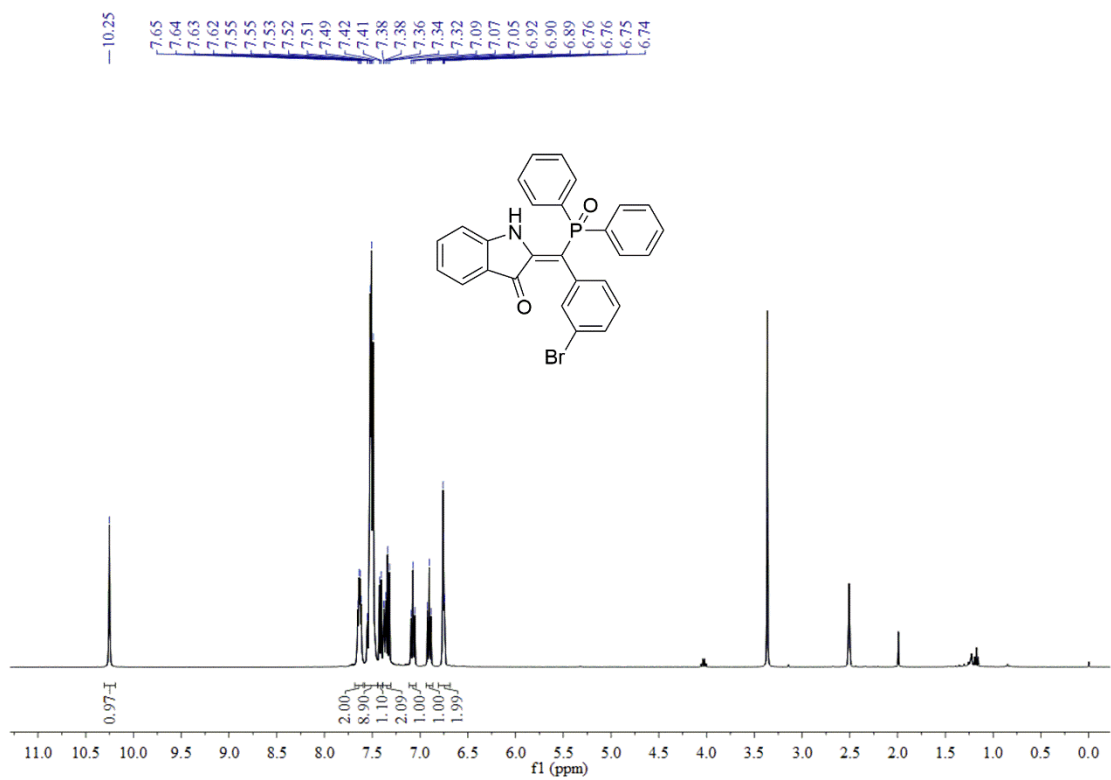
(Z)-2-((3-chlorophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3o): ¹³C NMR



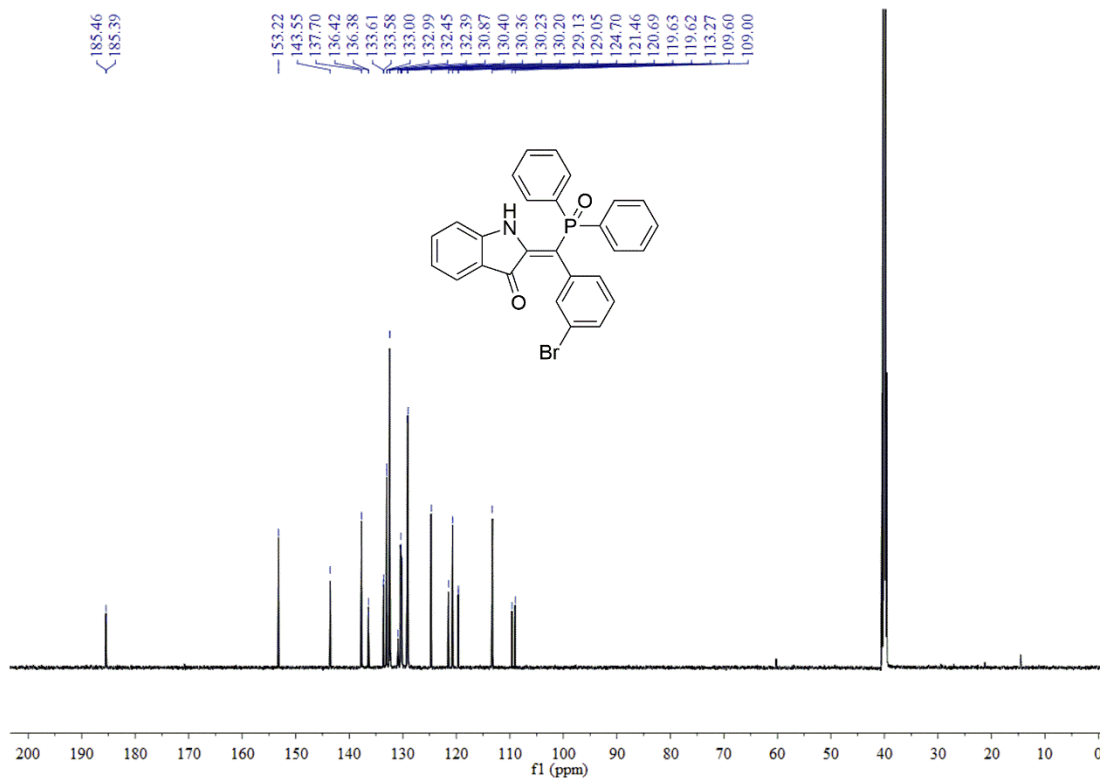
(Z)-2-((3-chlorophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3o): ³¹P NMR



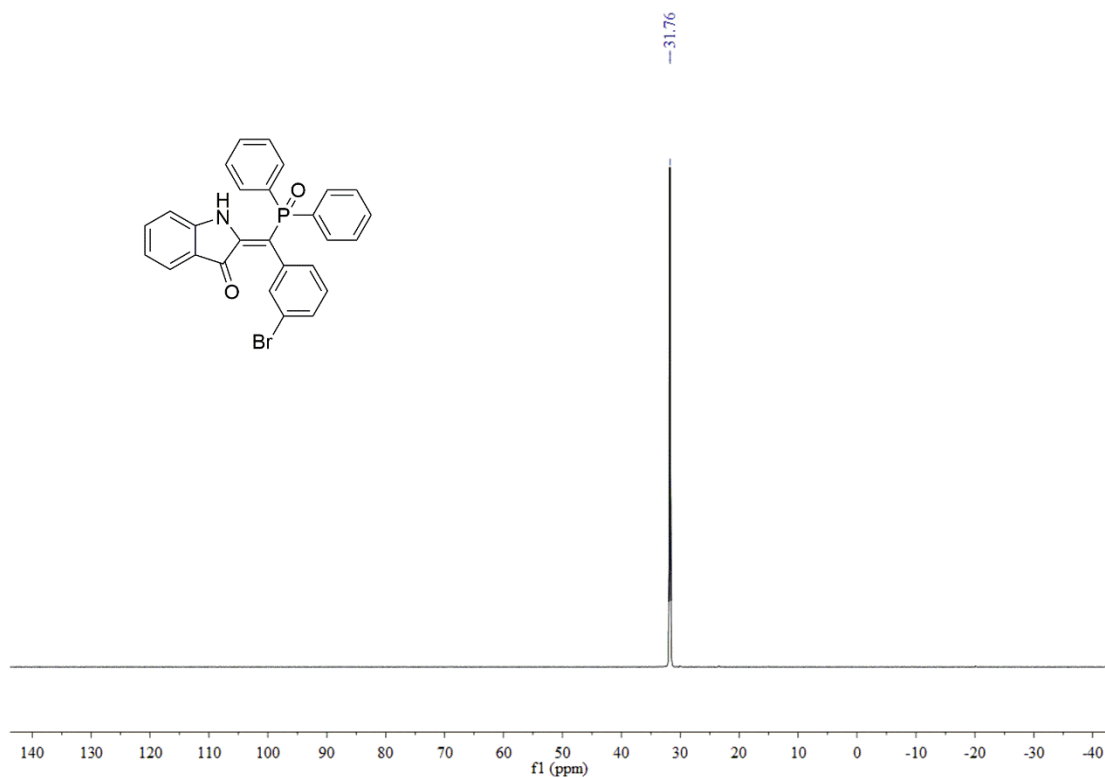
(Z)-2-((3-bromophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3p): ¹H NMR



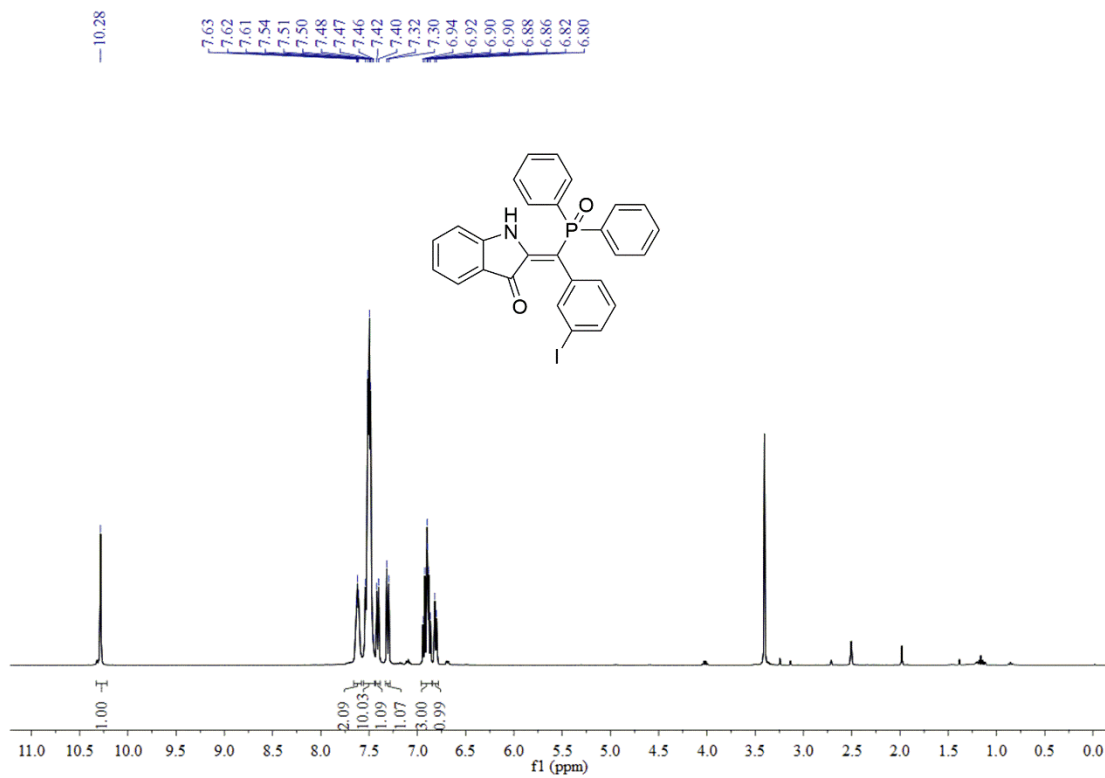
(Z)-2-((3-bromophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3p): ¹³C NMR



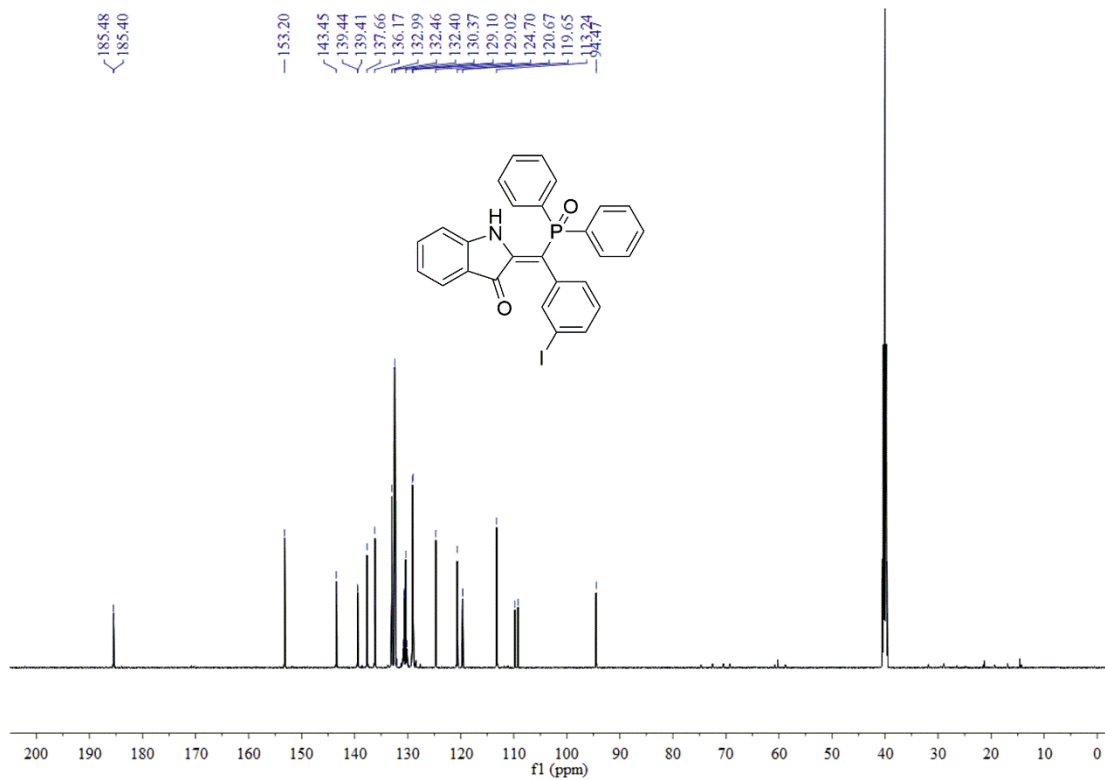
(Z)-2-((3-bromophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3p): ³¹P NMR



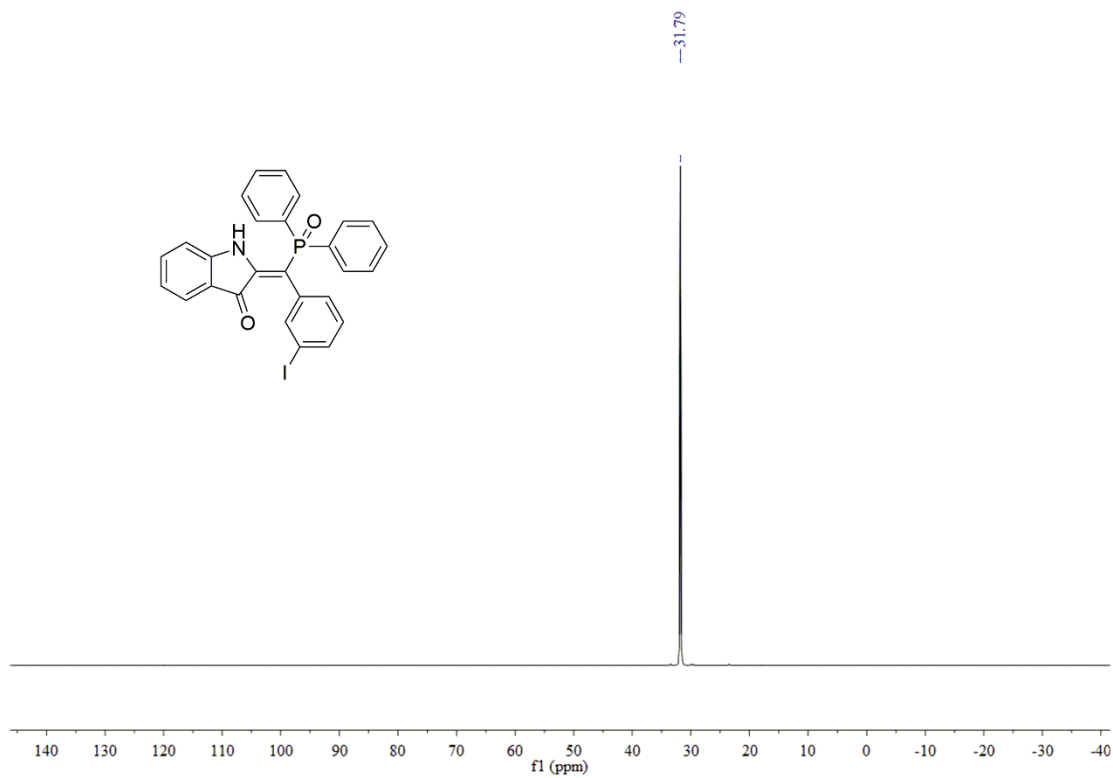
(Z)-2-((diphenylphosphoryl)(3-iodophenyl)methylene)indolin-3-one (3q): ¹H NMR



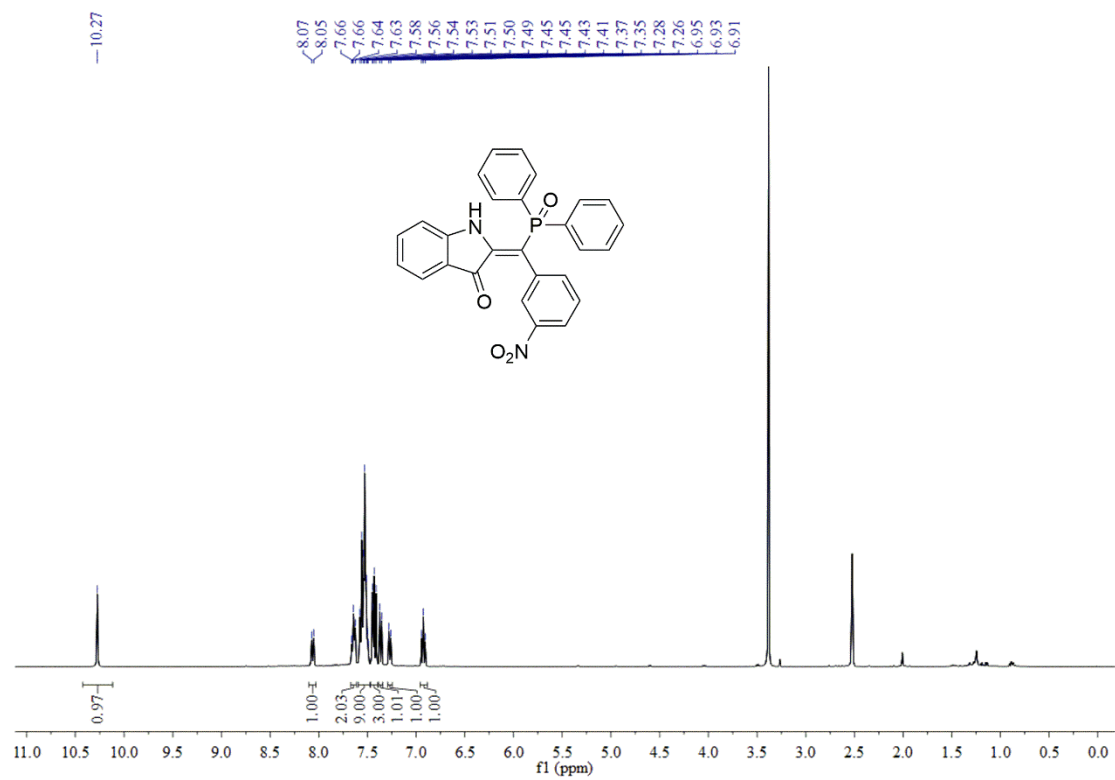
(Z)-2-((diphenylphosphoryl)(3-iodophenyl)methylene)indolin-3-one (3q): ¹³C NMR



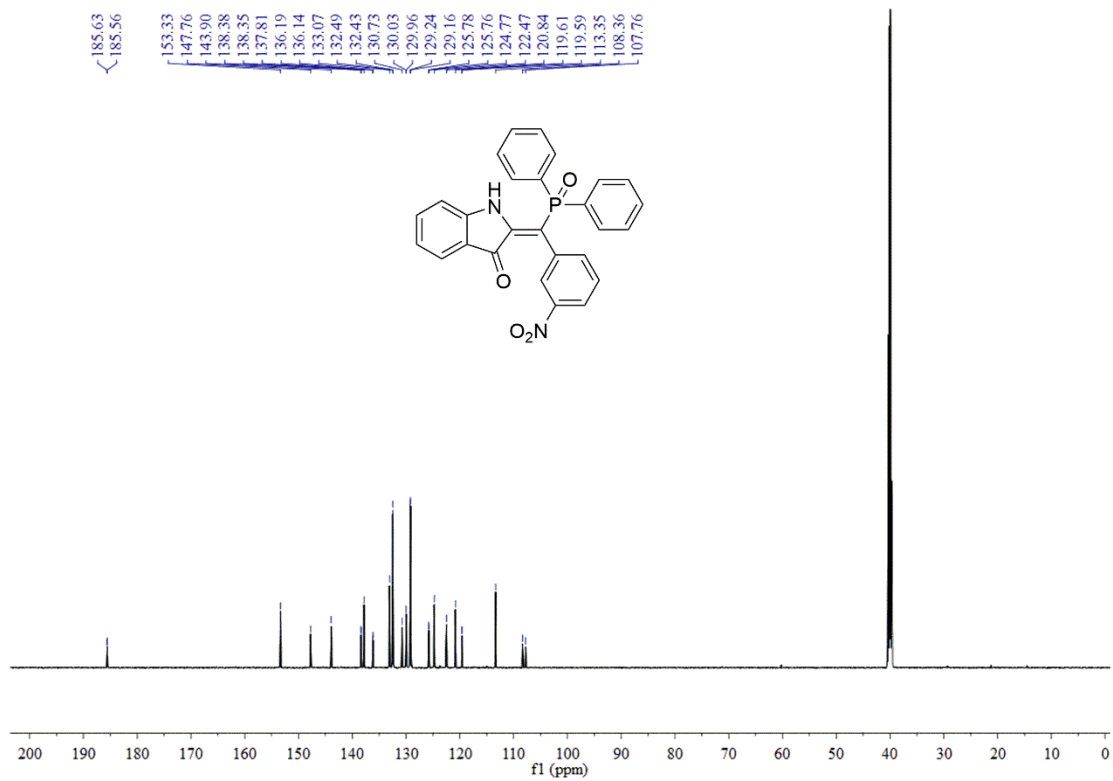
(Z)-2-((diphenylphosphoryl)(3-iodophenyl)methylene)indolin-3-one (3q): ³¹P NMR



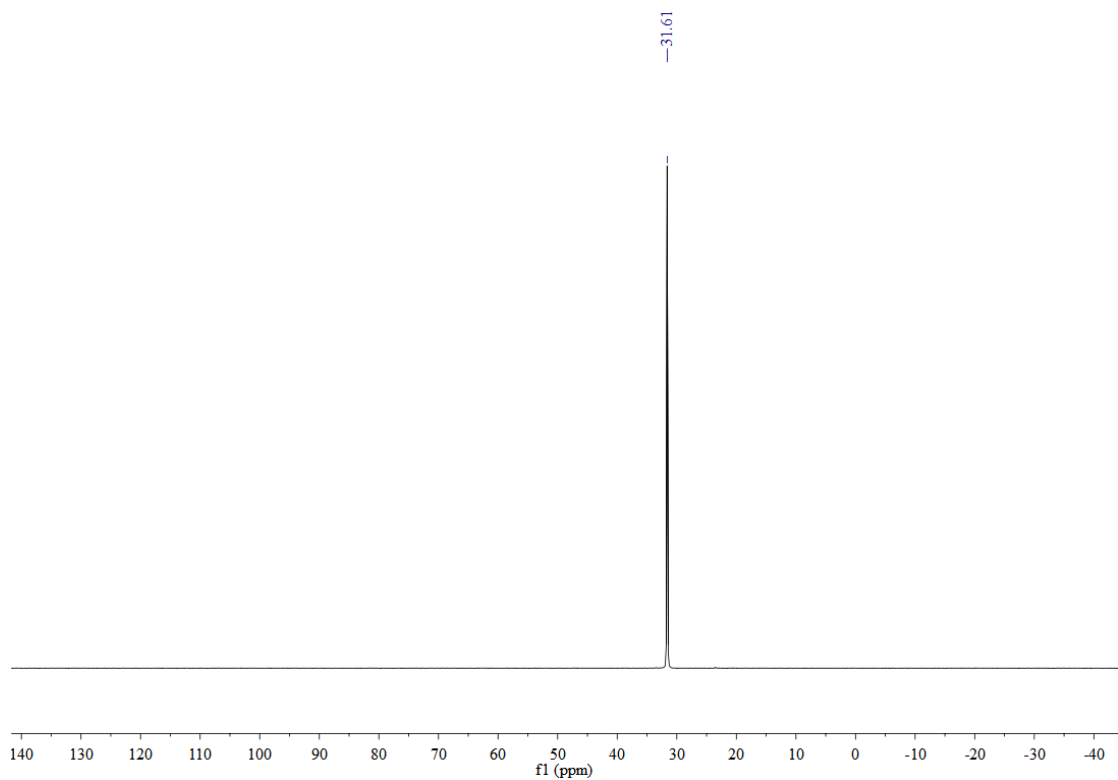
(Z)-2-((diphenylphosphoryl)(3-nitrophenyl)methylene)indolin-3-one (3r): ¹H NMR



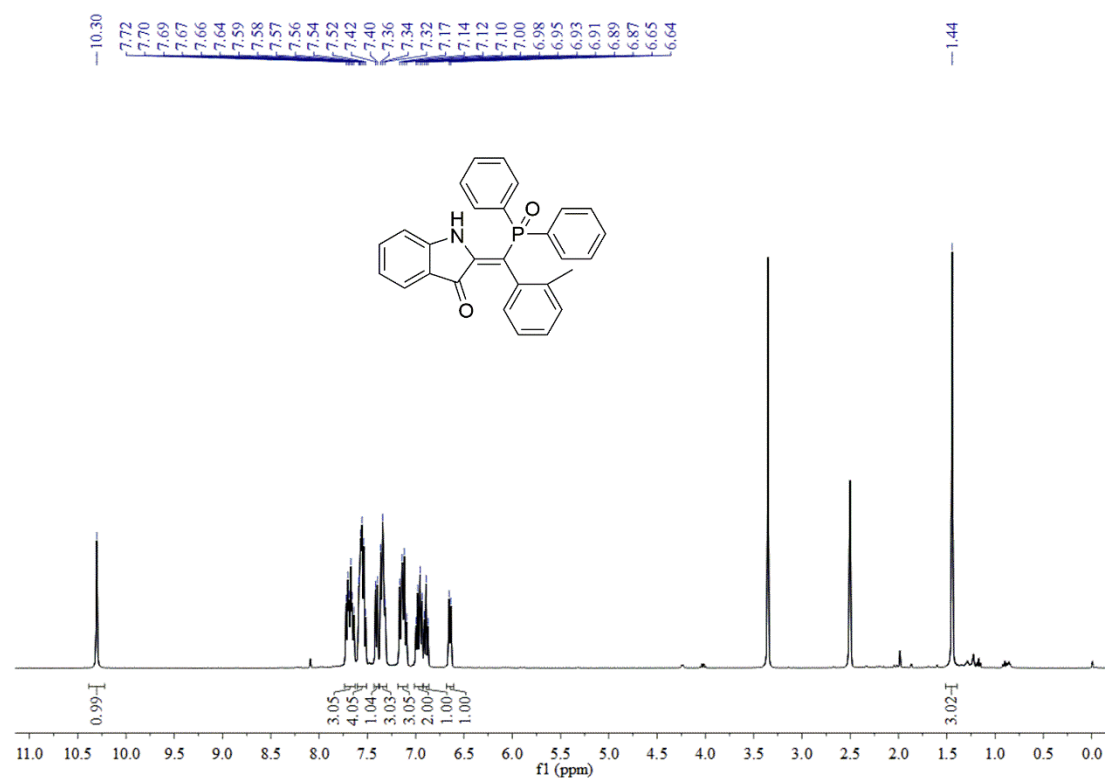
(Z)-2-((diphenylphosphoryl)(3-nitrophenyl)methylene)indolin-3-one (3r): ¹³C NMR



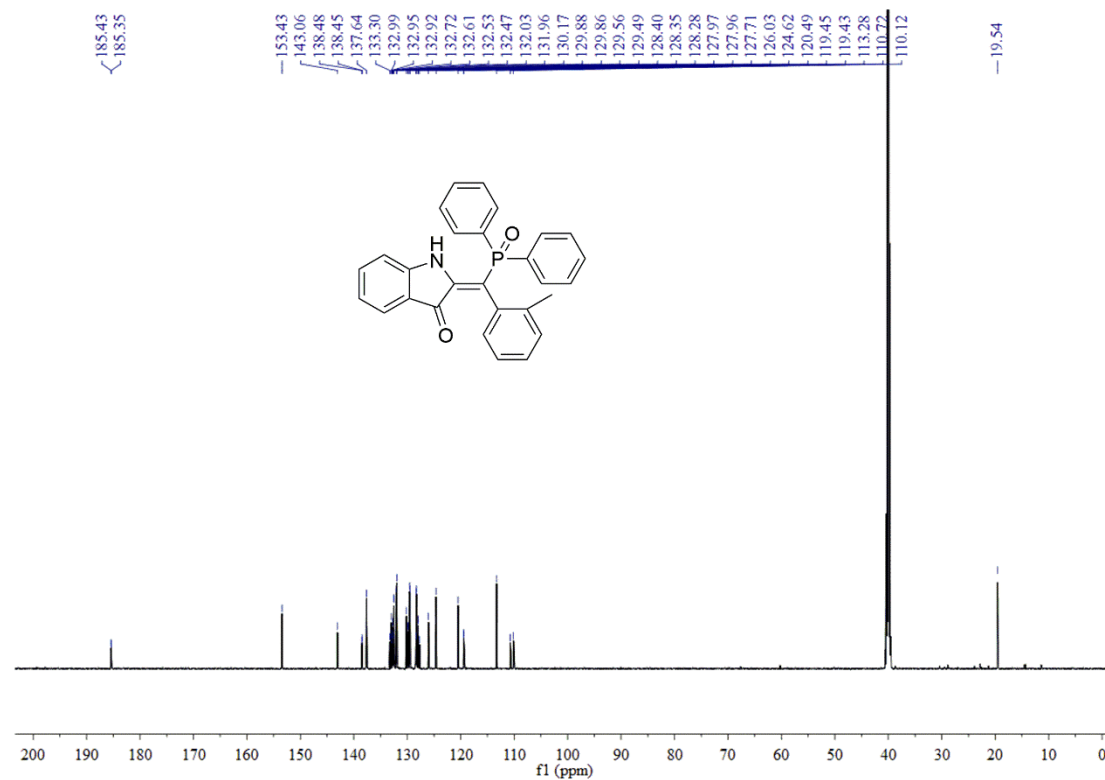
(Z)-2-((diphenylphosphoryl)(3-nitrophenyl)methylene)indolin-3-one (3r): ³¹P NMR



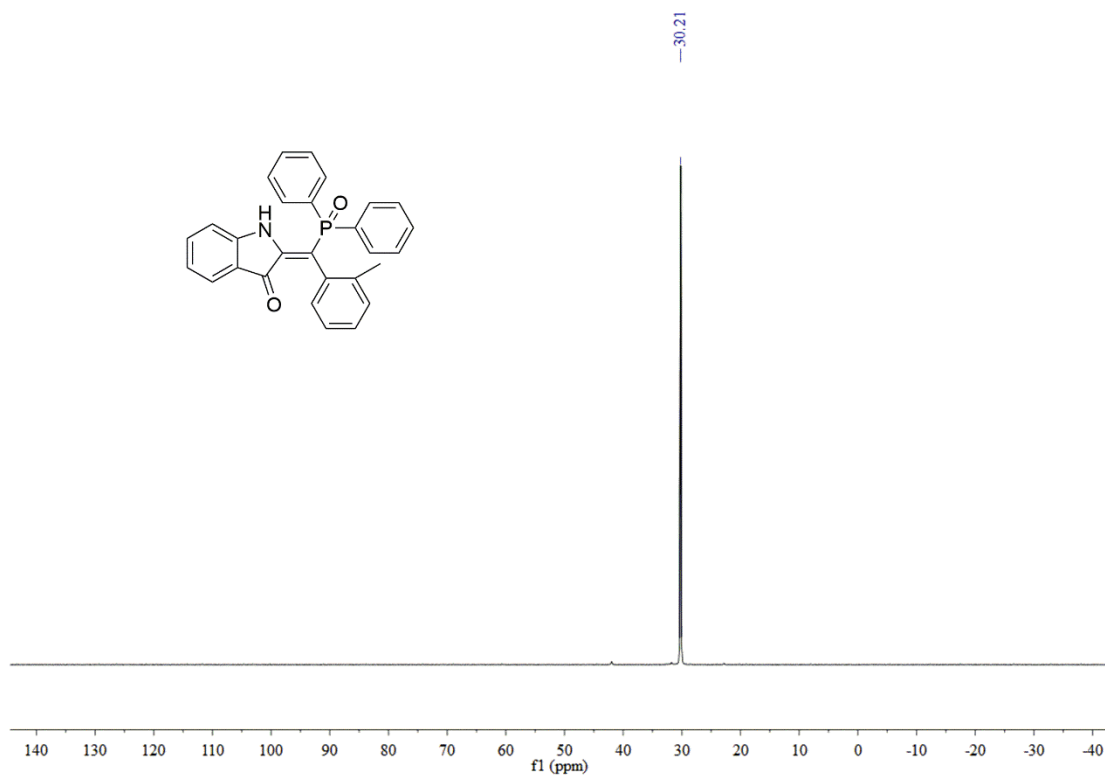
(Z)-2-((diphenylphosphoryl)(o-tolyl)methylene)indolin-3-one (3s): ¹H NMR



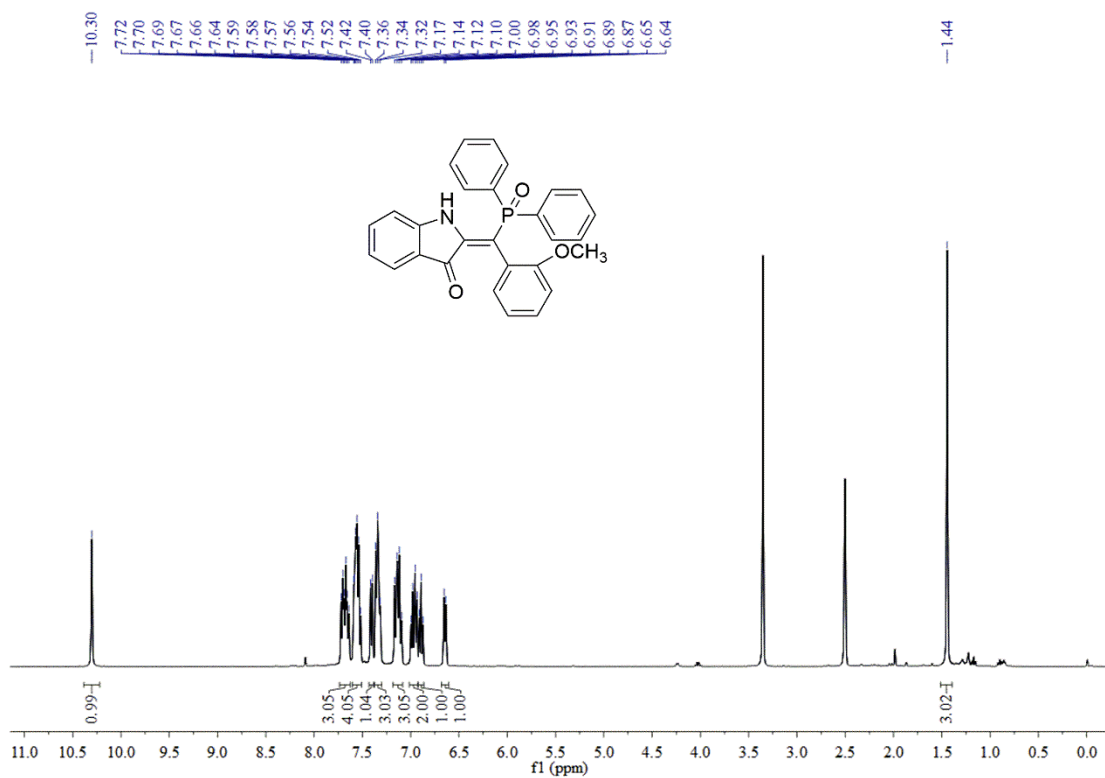
(Z)-2-((diphenylphosphoryl)(o-tolyl)methylene)indolin-3-one (3s): ¹³C NMR



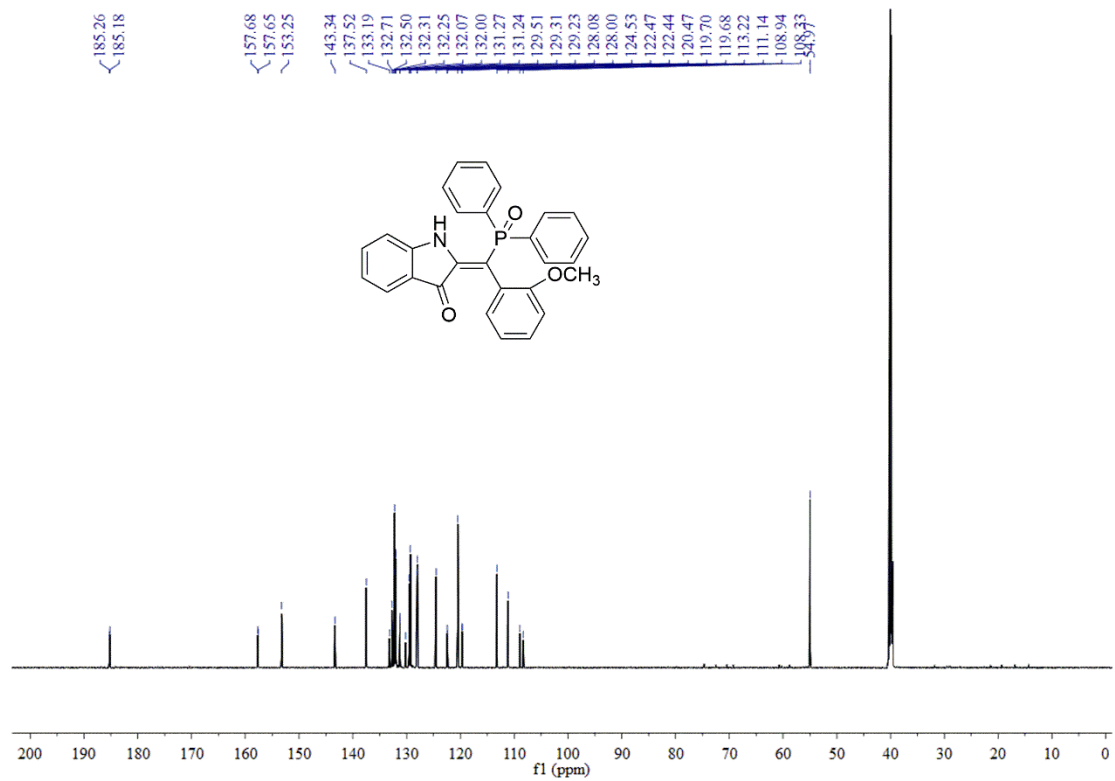
(Z)-2-((diphenylphosphoryl)(o-tolyl)methylene)indolin-3-one (3s): ³¹P NMR



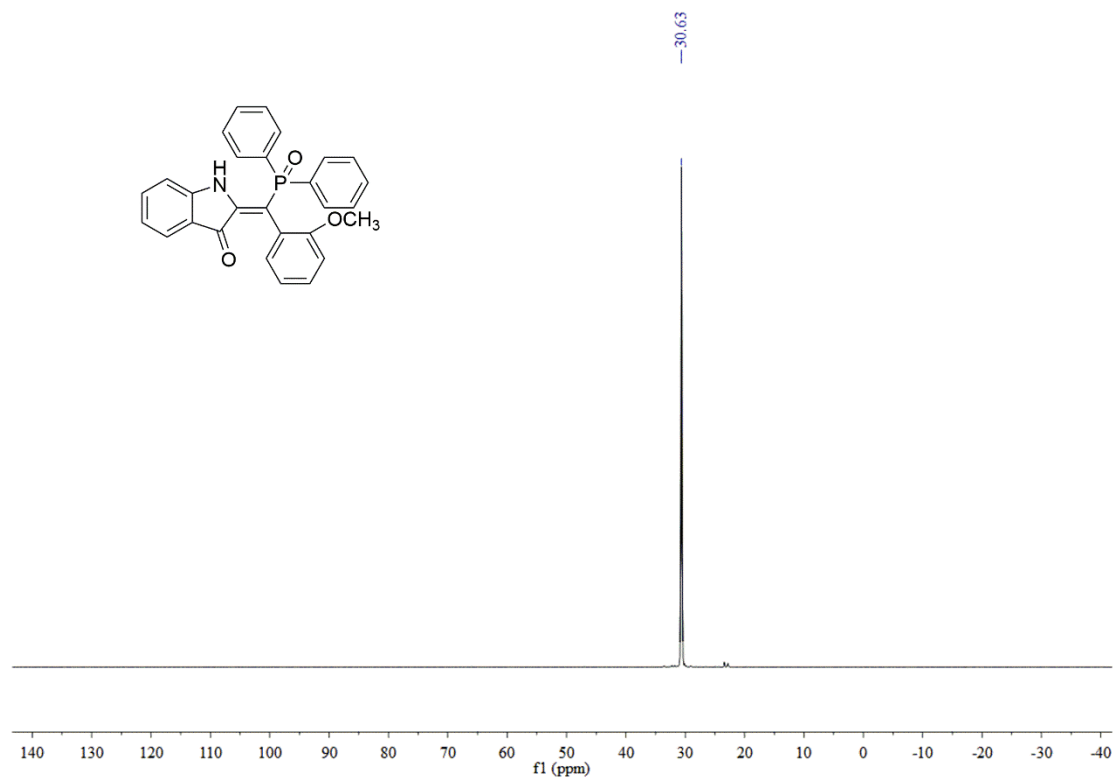
(Z)-2-((diphenylphosphoryl)(2-methoxyphenyl)methylene)indolin-3-one (3t): ¹H NMR



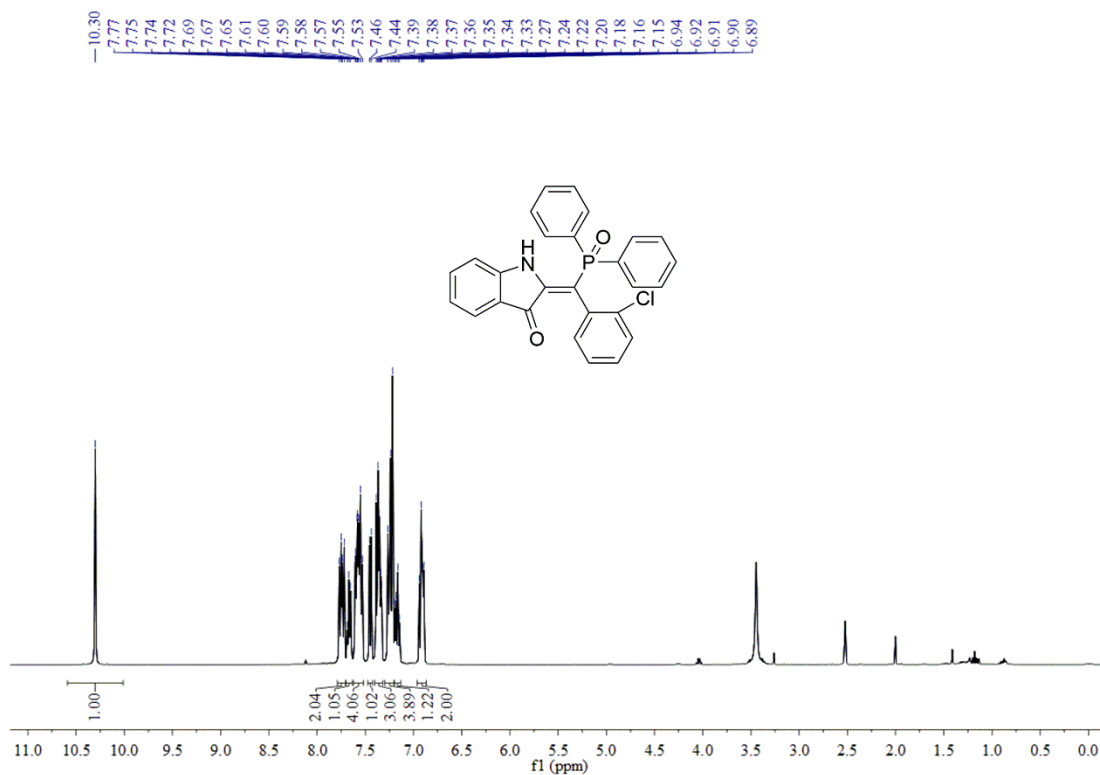
(Z)-2-((diphenylphosphoryl)(2-methoxyphenyl)methylene)indolin-3-one (3t): ¹³C NMR



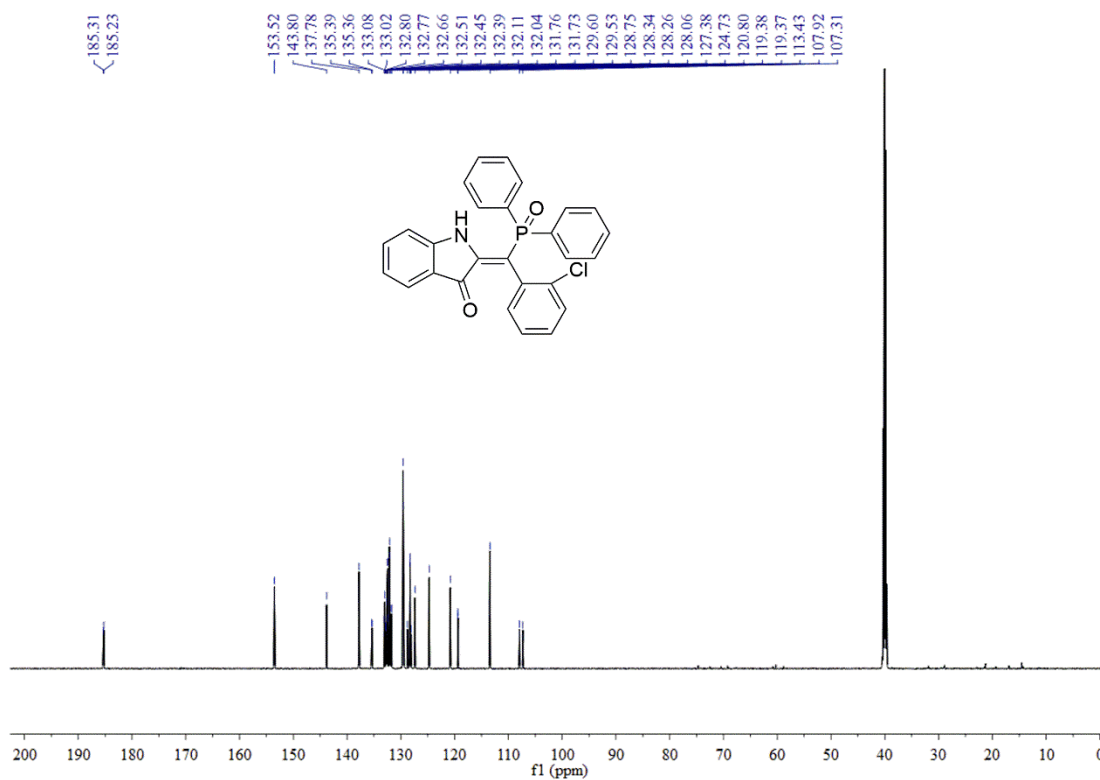
(Z)-2-((diphenylphosphoryl)(2-methoxyphenyl)methylene)indolin-3-one (3t): ³¹P NMR



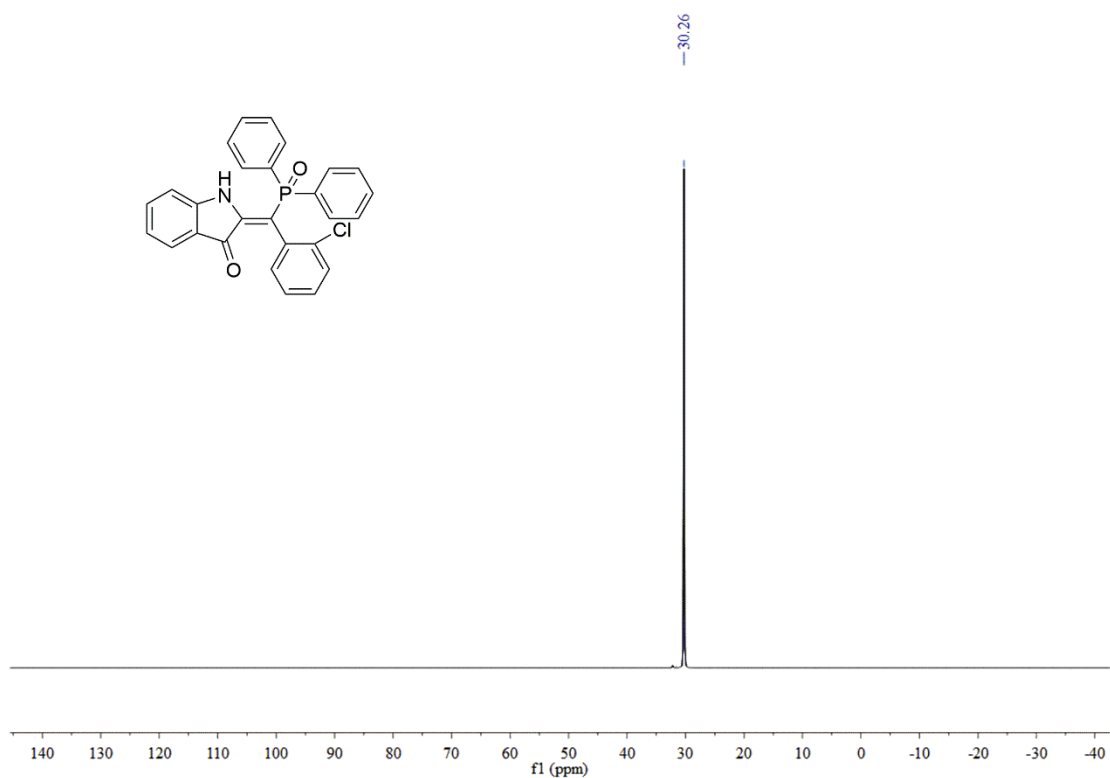
(Z)-2-((2-chlorophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3u): ¹H NMR



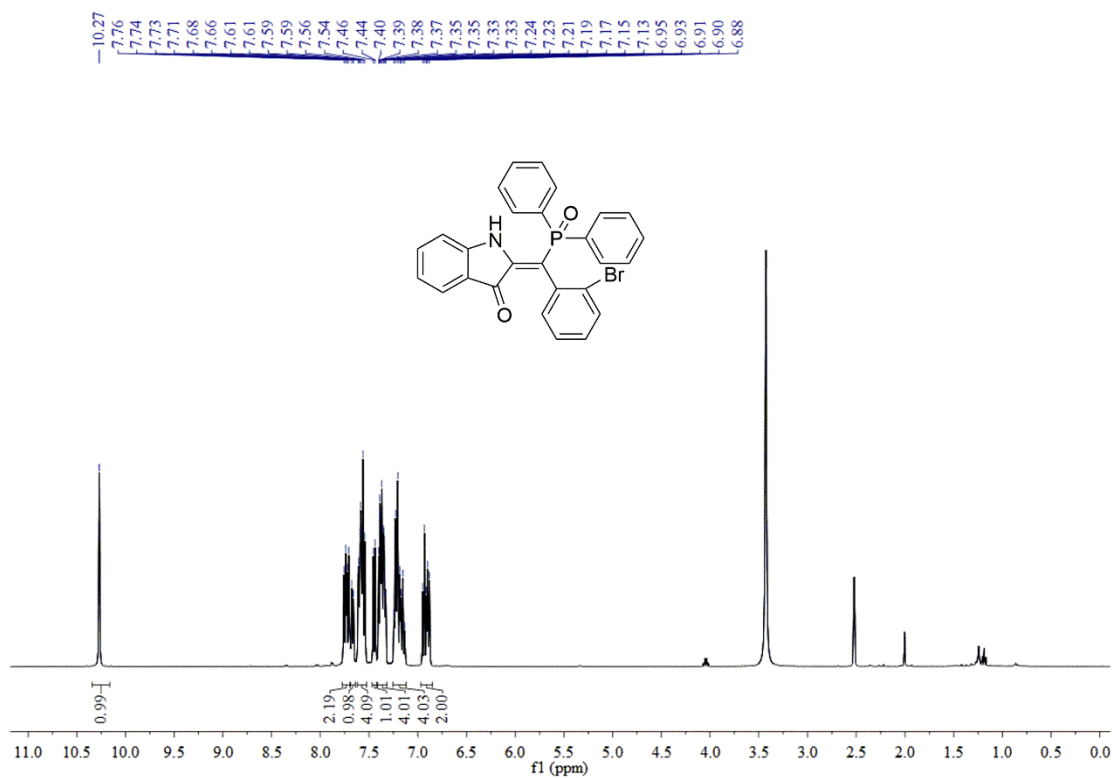
(Z)-2-((2-chlorophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3u): ¹³C NMR



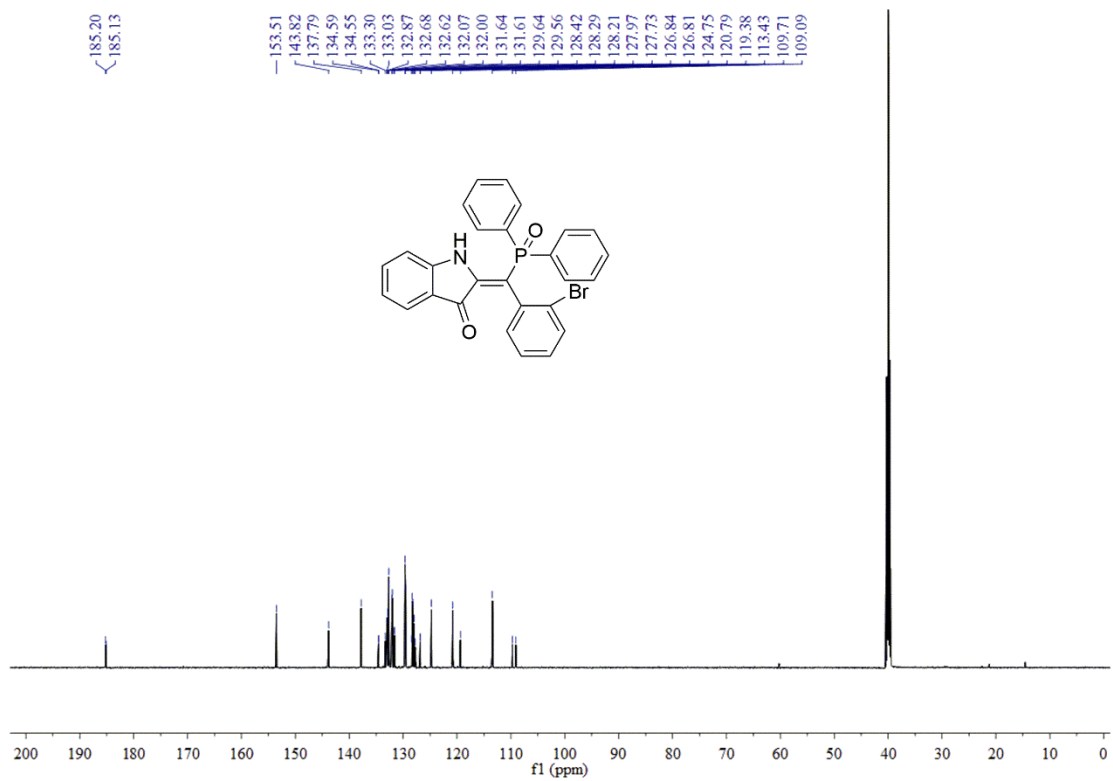
(Z)-2-((2-chlorophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3u): ³¹P NMR



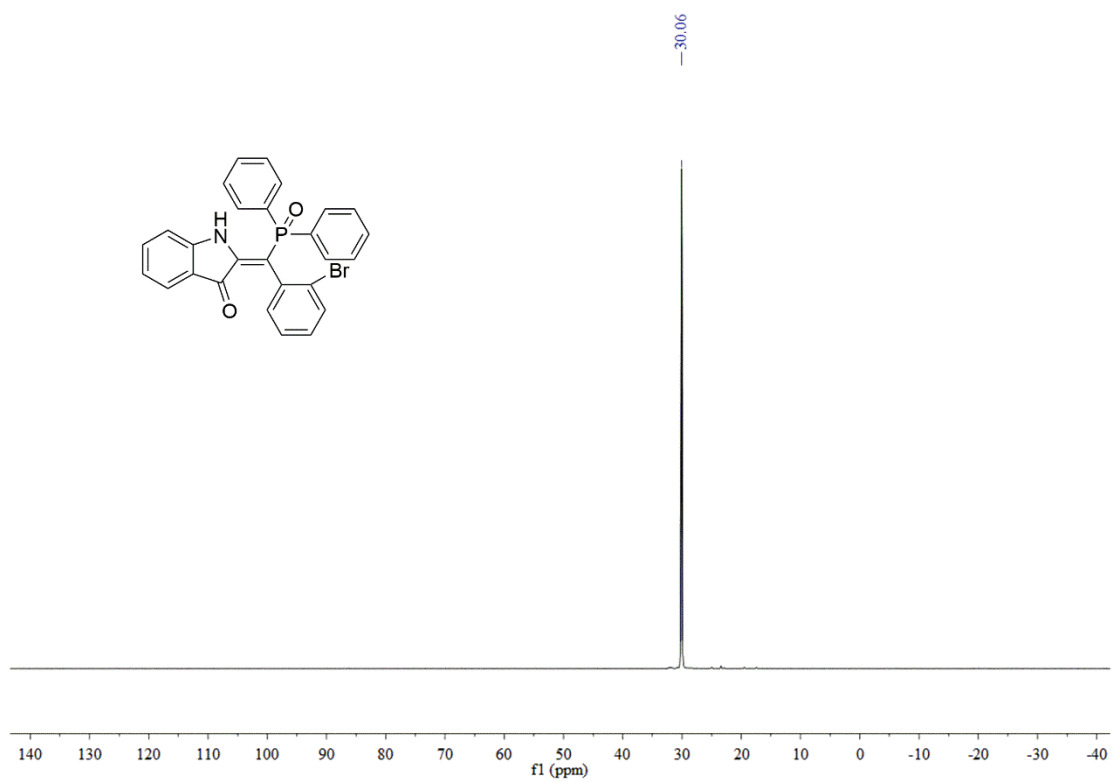
(Z)-2-((2-bromophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3v): ¹H NMR



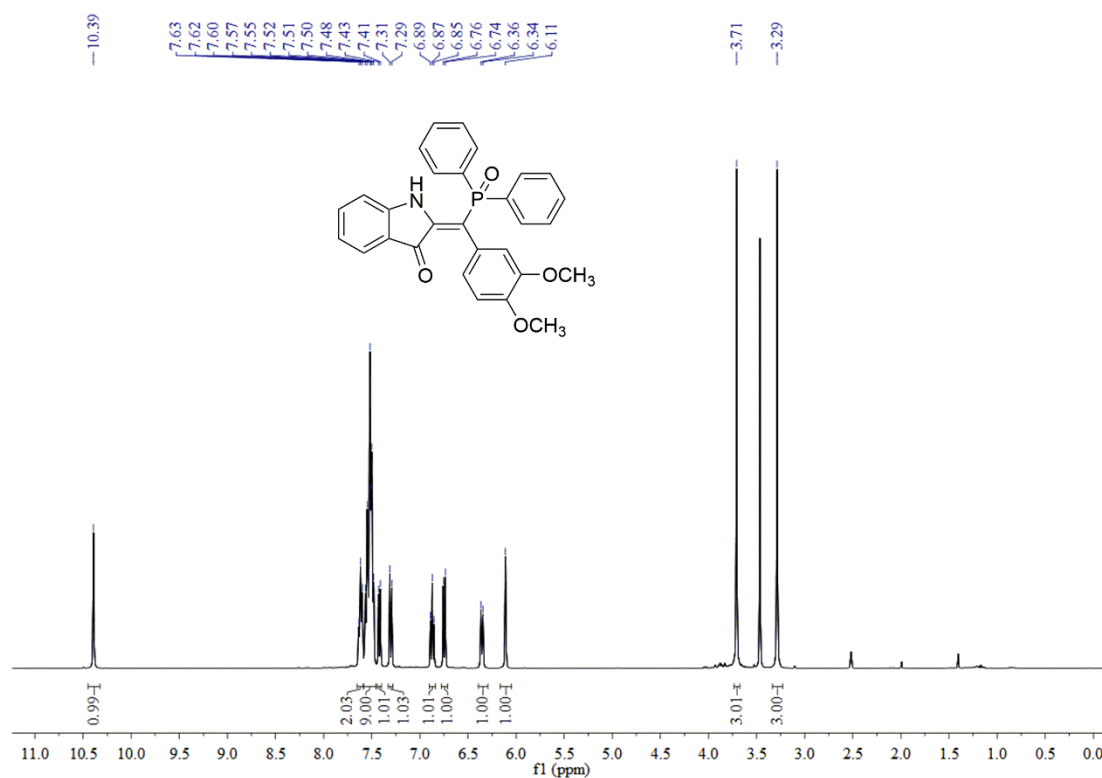
(Z)-2-((2-bromophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3v): ¹³C NMR



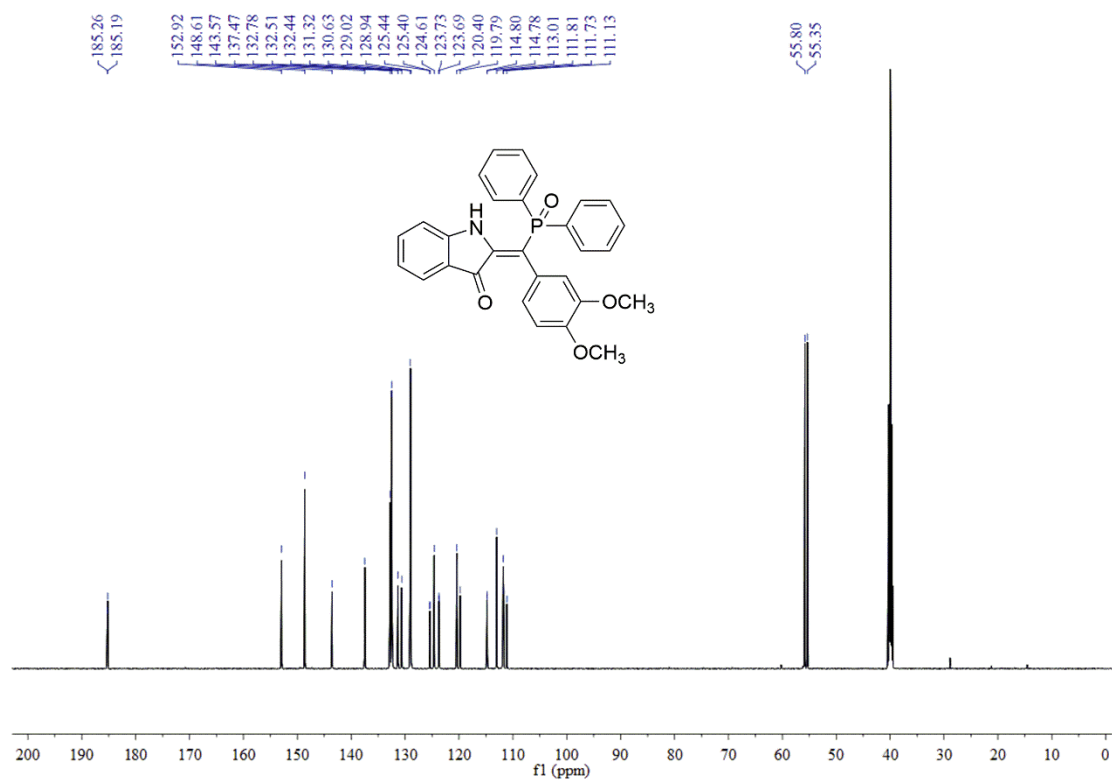
(Z)-2-((2-bromophenyl)(diphenylphosphoryl)methylene)indolin-3-one (3v): ³¹P NMR



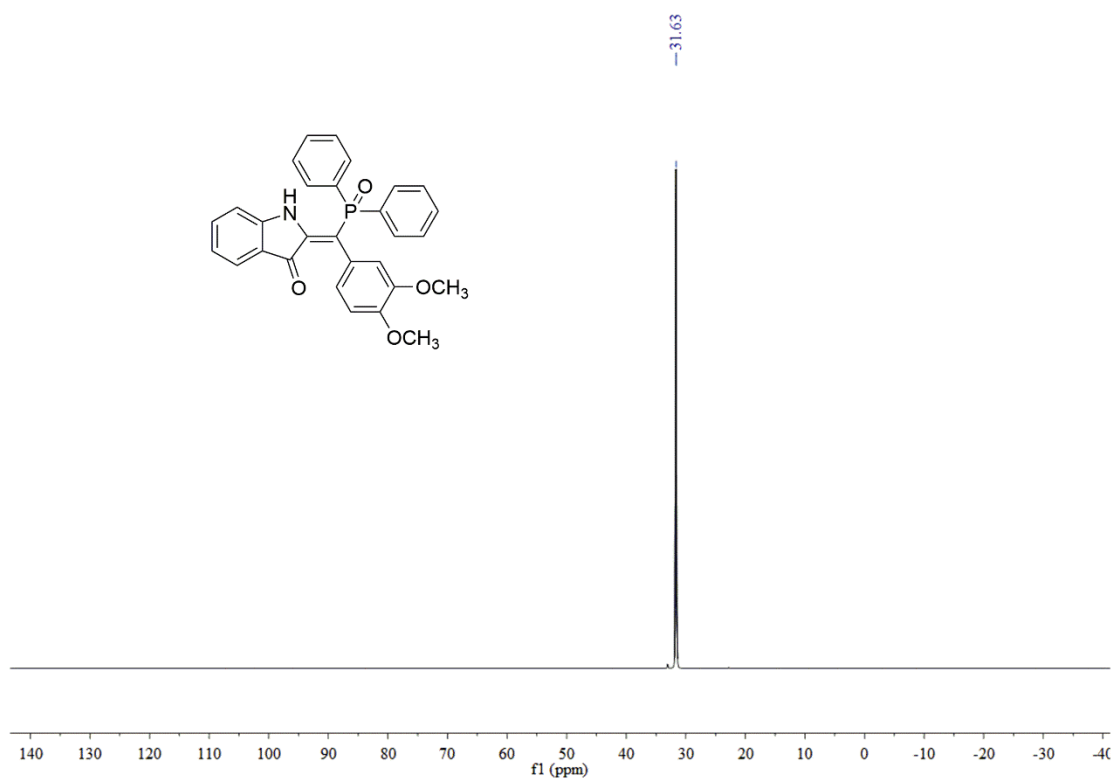
(Z)-2-((3,4-dimethoxyphenyl)(diphenylphosphoryl)methylene)indolin-3-one (3x): ¹H NMR



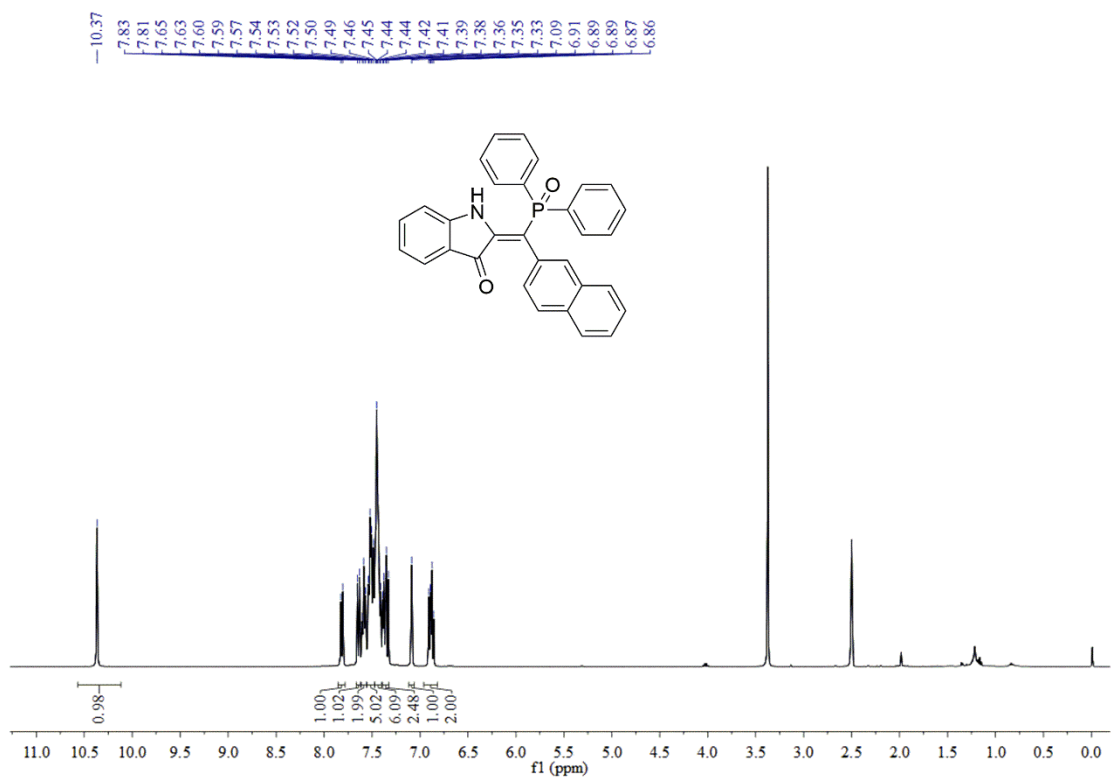
(Z)-2-((3,4-dimethoxyphenyl)(diphenylphosphoryl)methylene)indolin-3-one (3x): ¹³C NMR



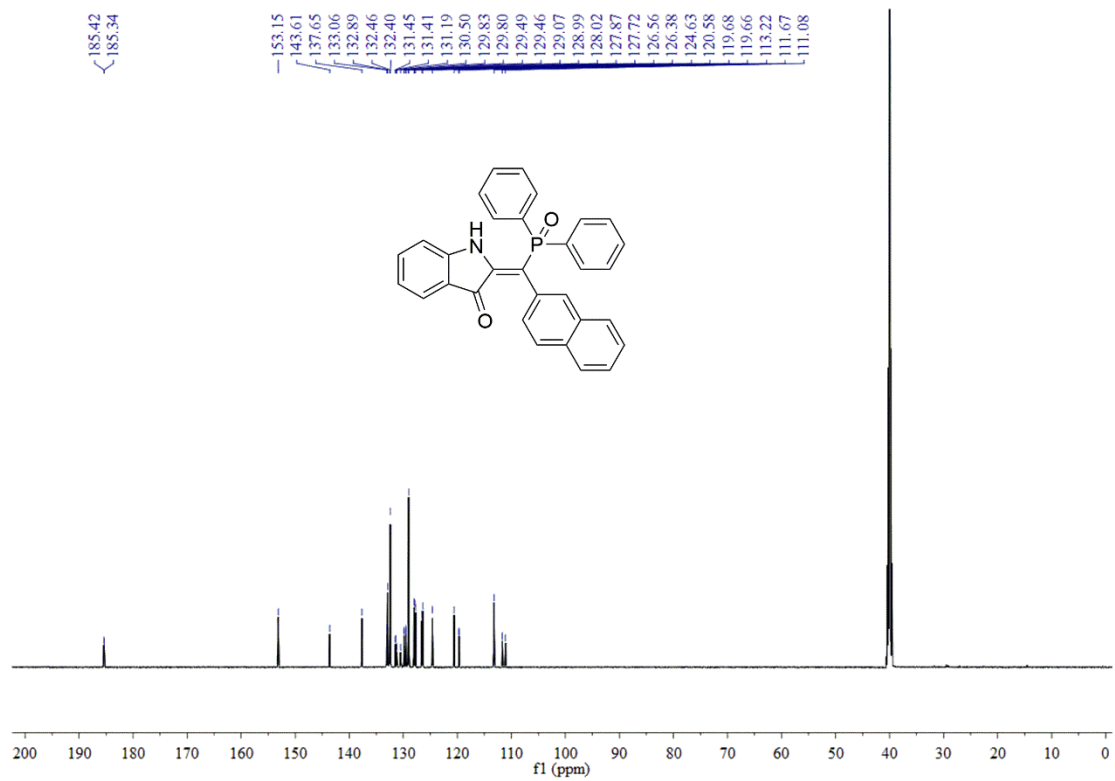
(Z)-2-((3,4-dimethoxyphenyl)(diphenylphosphoryl)methylene)indolin-3-one (3x): ³¹P NMR



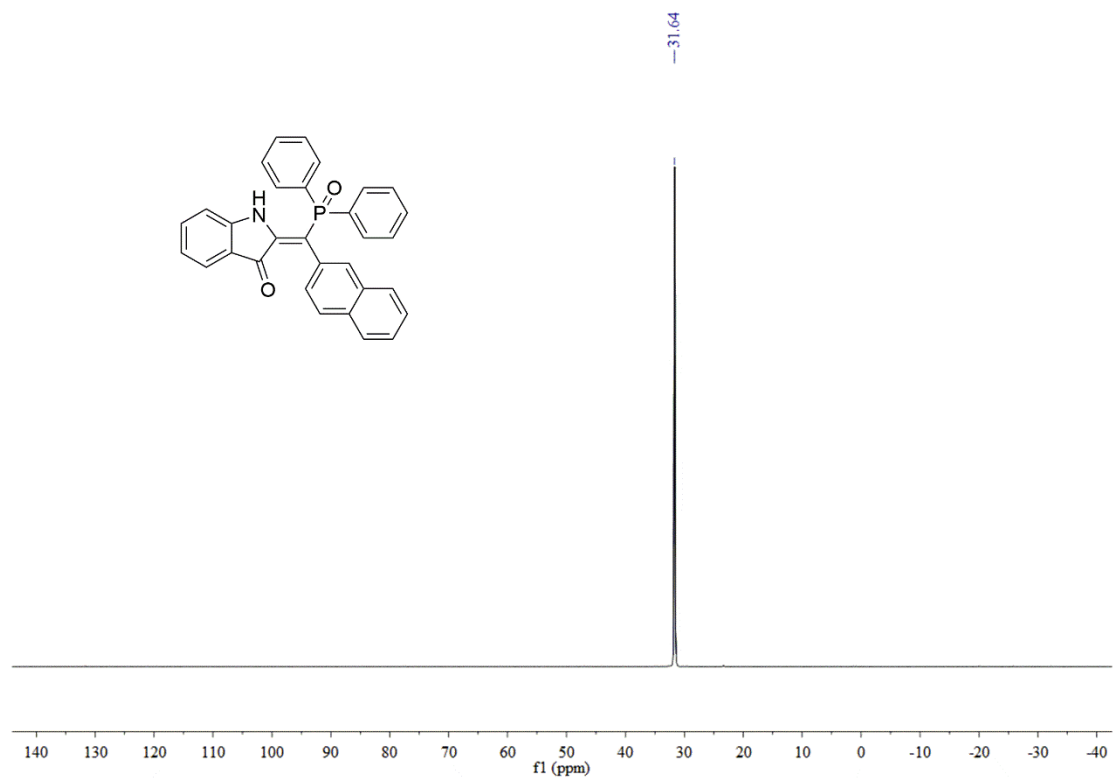
(Z)-2-((diphenylphosphoryl)(naphthalen-2-yl)methylene)indolin-3-one (3y): ¹H NMR



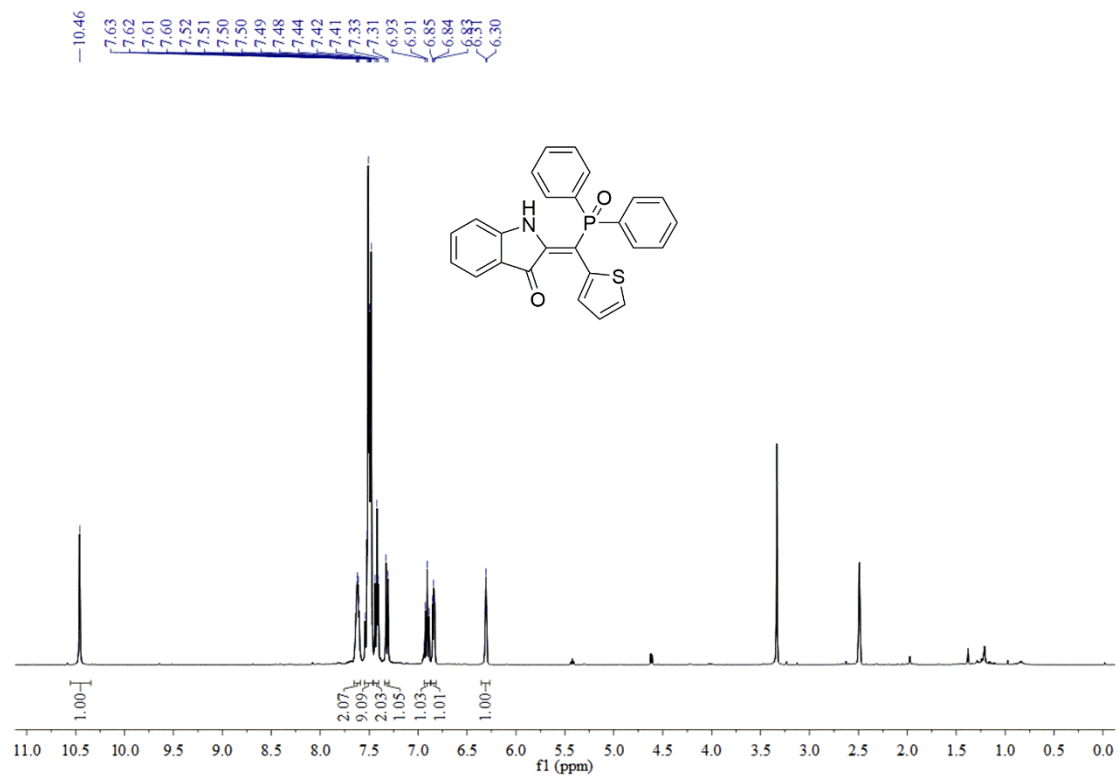
(Z)-2-((diphenylphosphoryl)(naphthalen-2-yl)methylene)indolin-3-one (3y): ¹³C NMR



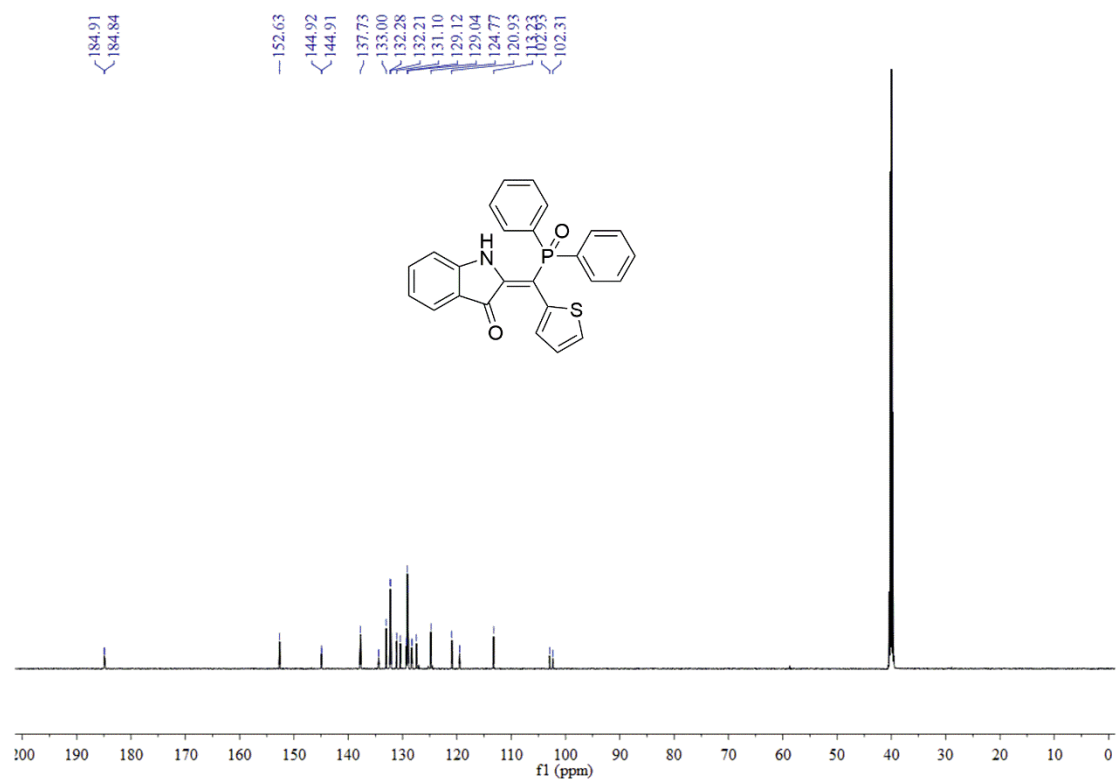
(Z)-2-((diphenylphosphoryl)(naphthalen-2-yl)methylene)indolin-3-one (3y): ³¹P NMR



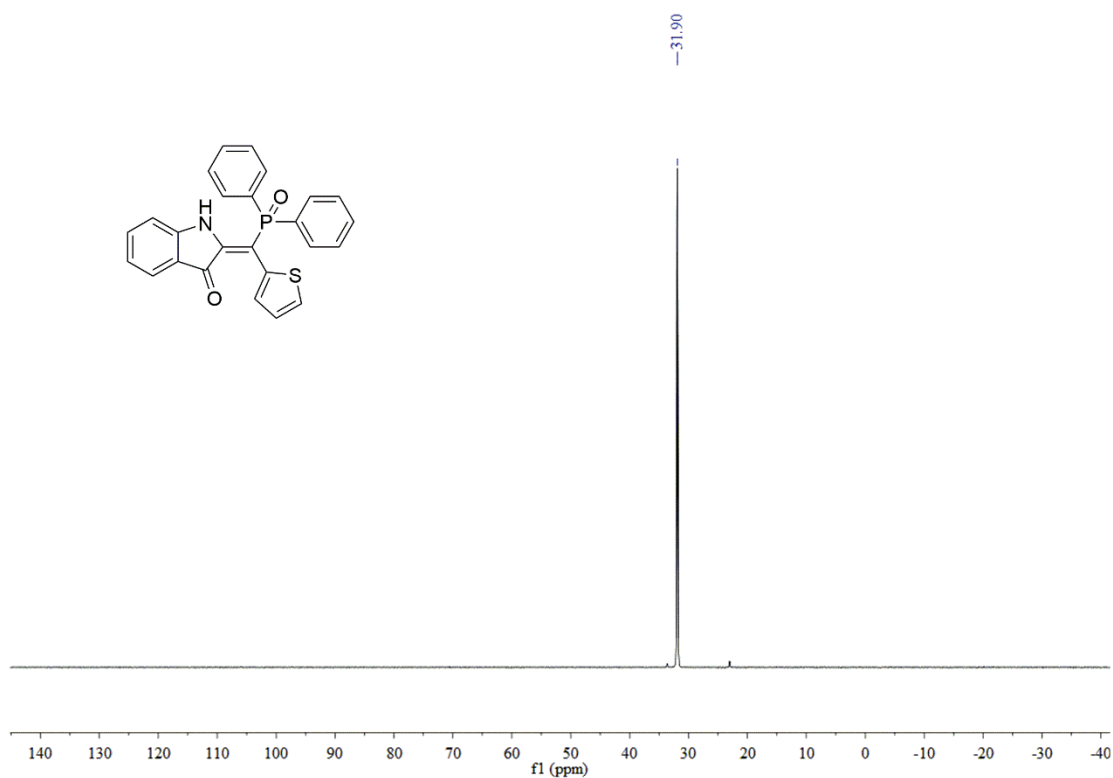
(Z)-2-((diphenylphosphoryl)(thiophen-2-yl)methylene)indolin-3-one (3z): ¹H NMR



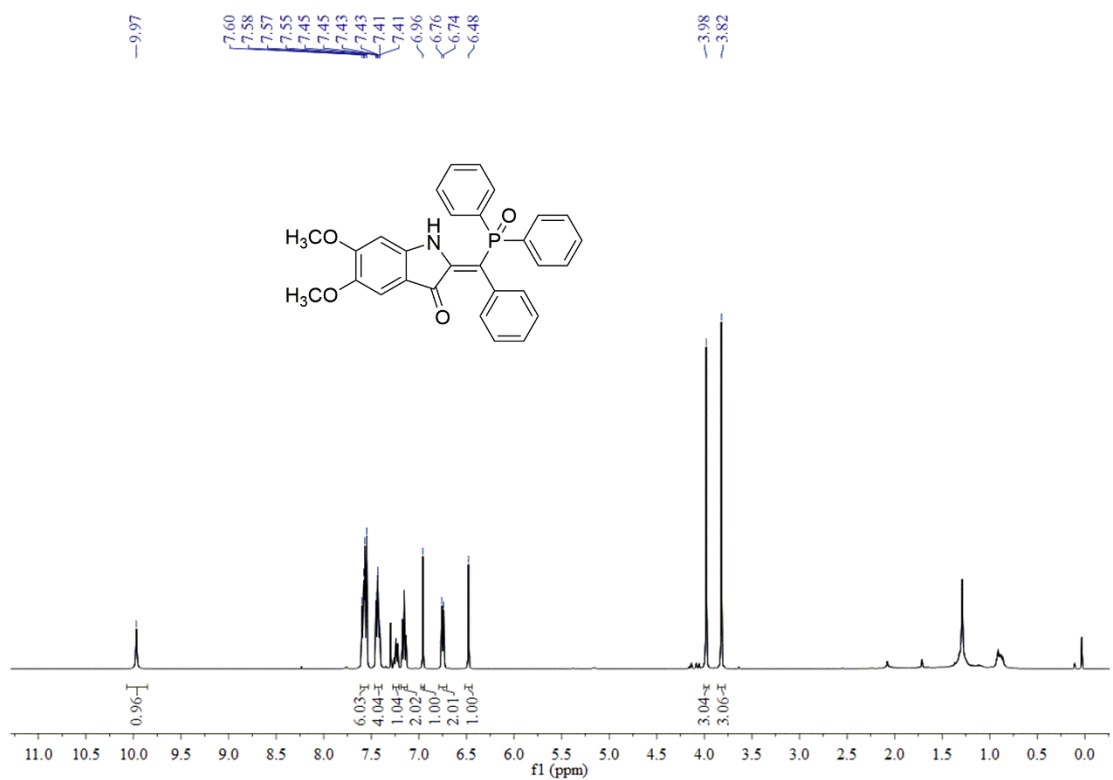
(Z)-2-((diphenylphosphoryl)(thiophen-2-yl)methylene)indolin-3-one (3z): ¹³C NMR



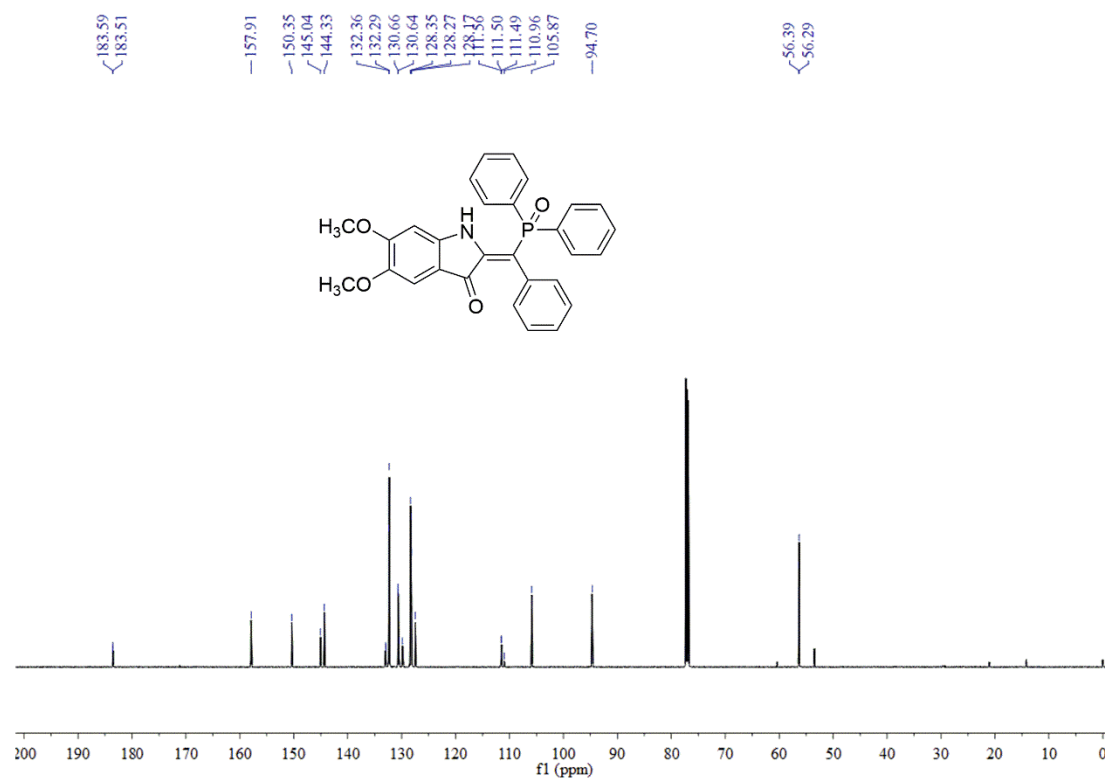
(Z)-2-((diphenylphosphoryl)(thiophen-2-yl)methylene)indolin-3-one (3z): ³¹P NMR



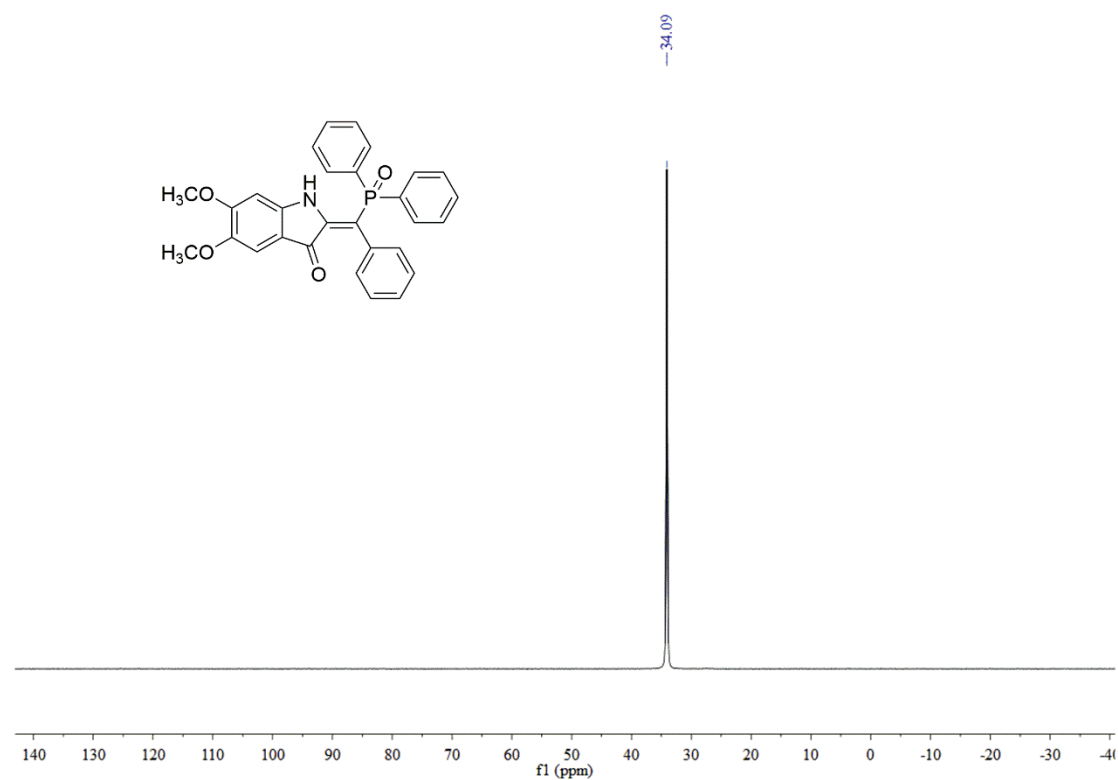
(Z)-2-((diphenylphosphoryl)(phenyl)methylene)-5,6-dimethoxyindolin-3-one (4a): ¹H NMR



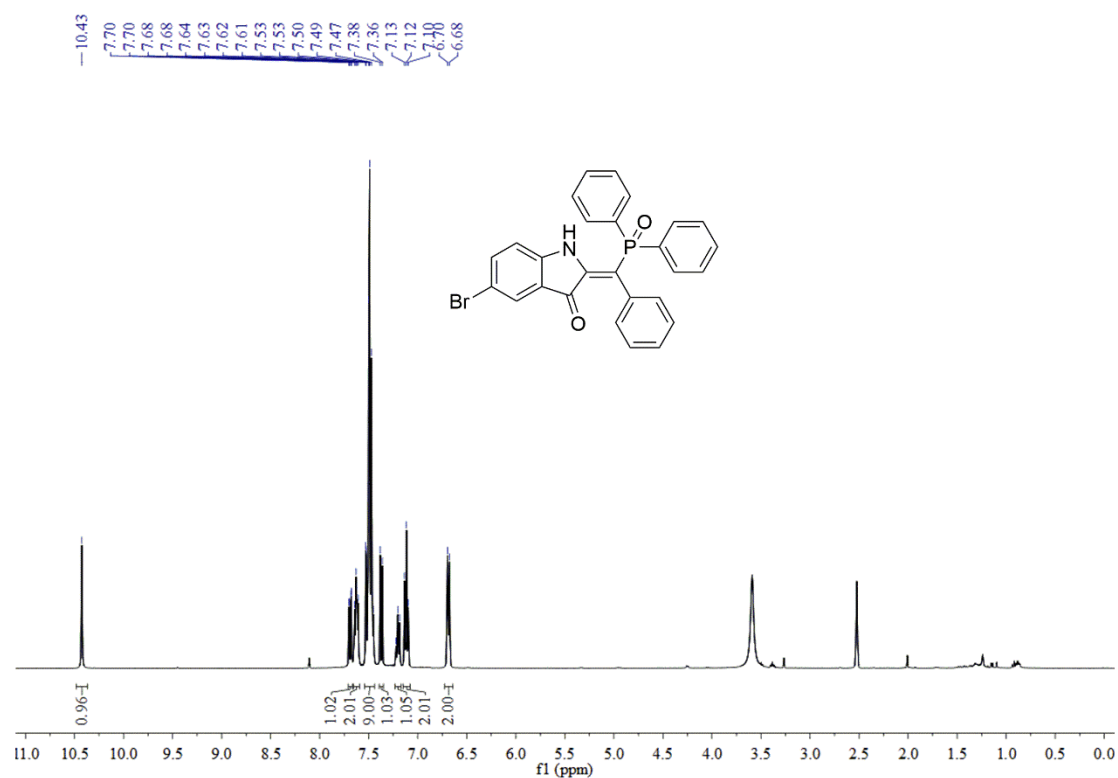
(Z)-2-((diphenylphosphoryl)(phenyl)methylene)-5,6-dimethoxyindolin-3-one (4a): ¹³C NMR



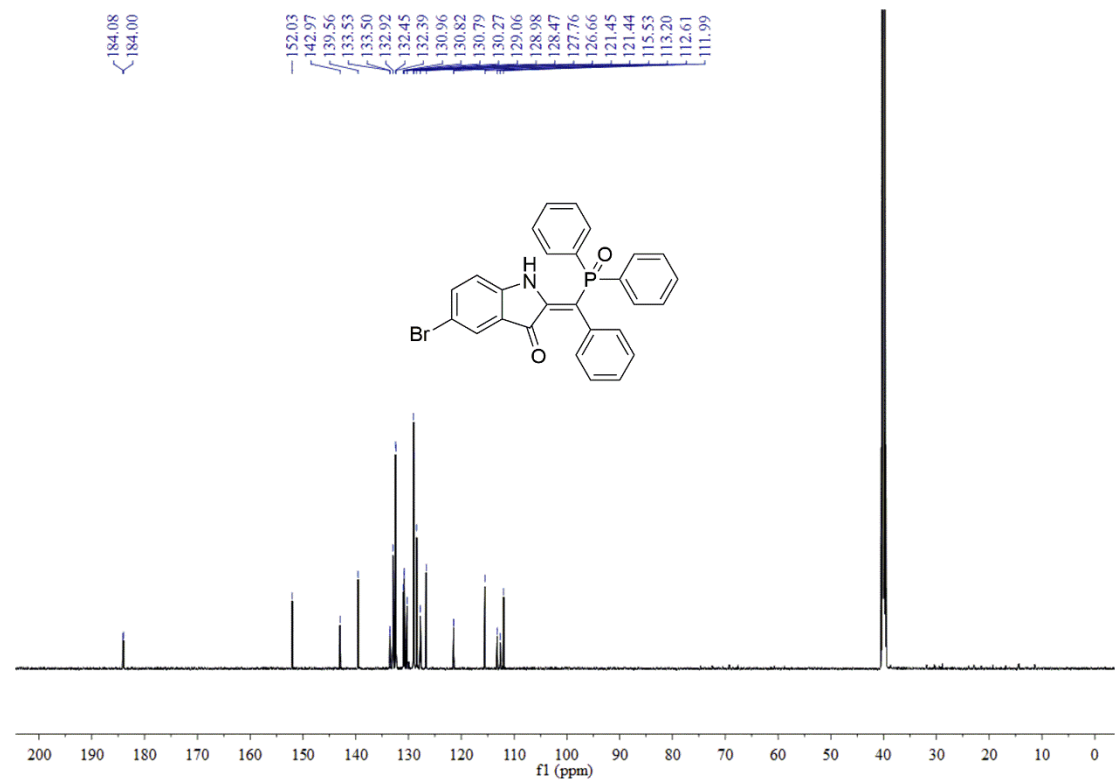
(Z)-2-((diphenylphosphoryl)(phenyl)methylene)-5,6-dimethoxyindolin-3-one (4a): ³¹P NMR



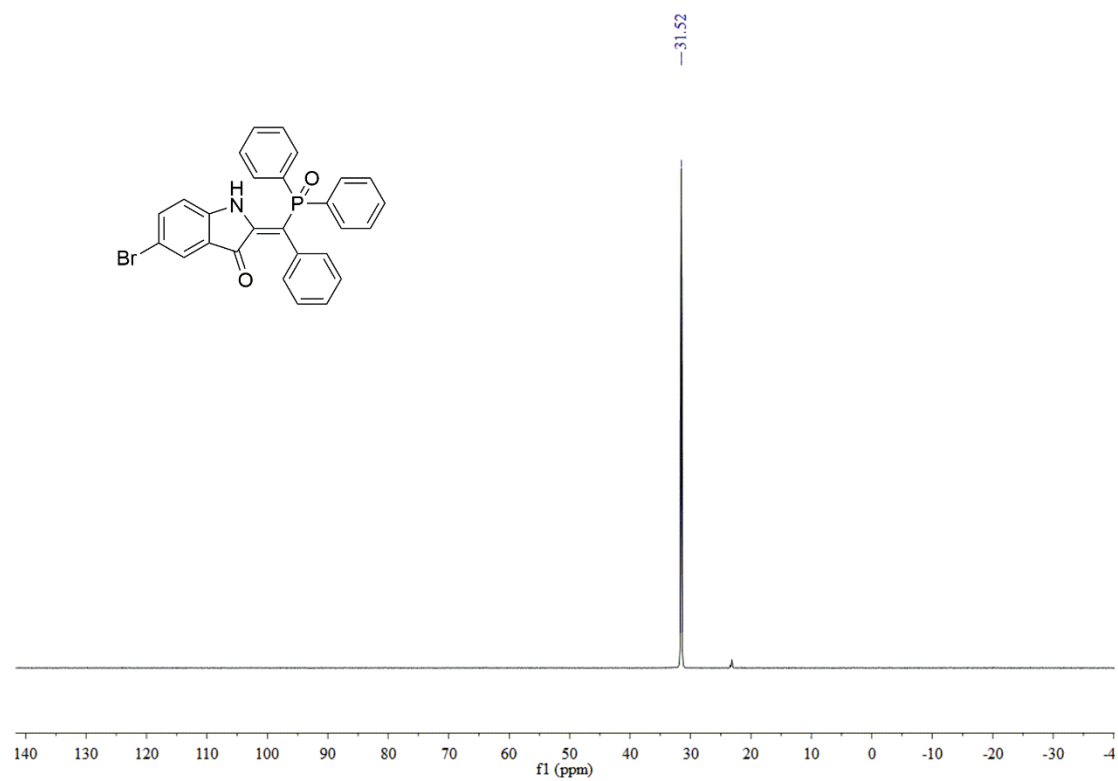
(Z)-5-bromo-2-((diphenylphosphoryl)(phenyl)methylene)indolin-3-one (4b): ¹H NMR



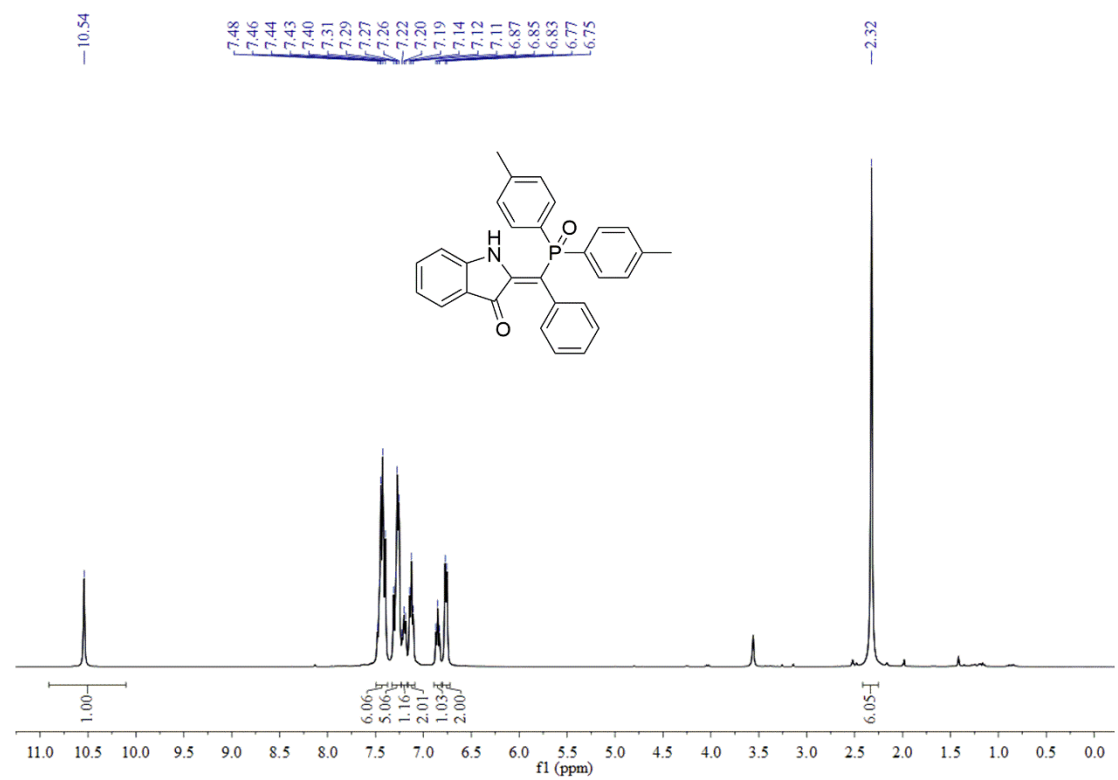
(Z)-5-bromo-2-((diphenylphosphoryl)(phenyl)methylene)indolin-3-one (4b): ¹³C NMR



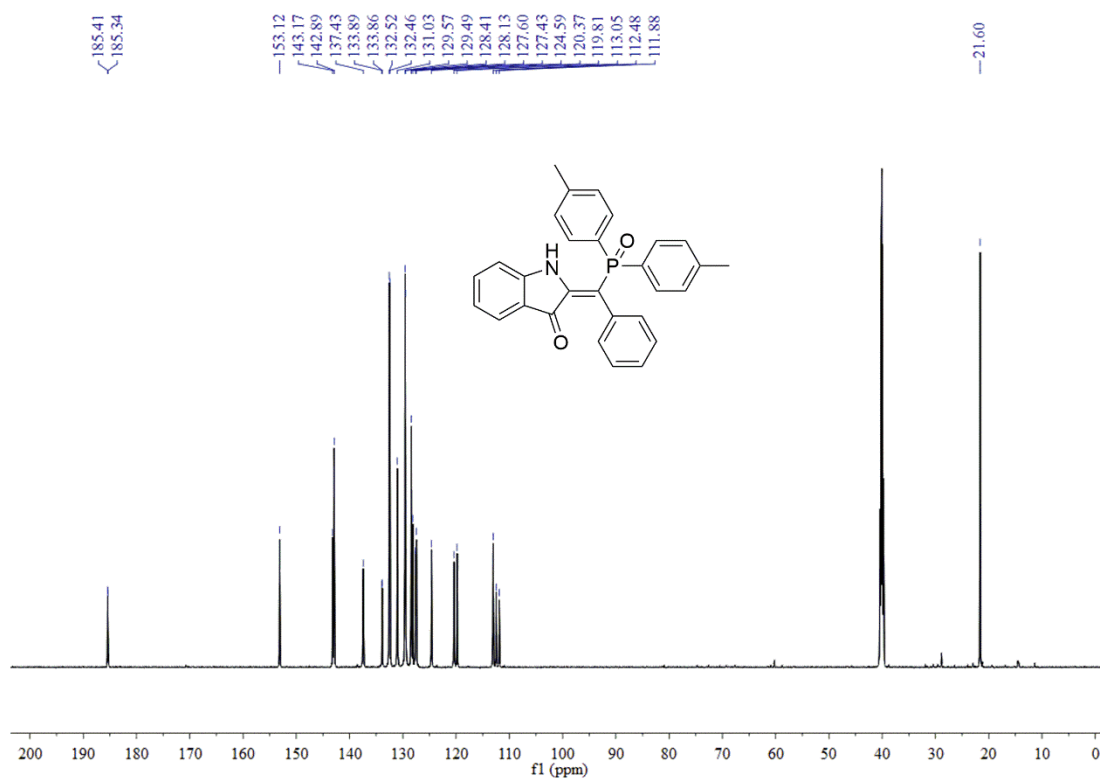
(Z)-5-bromo-2-((diphenylphosphoryl)(phenyl)methylene)indolin-3-one (4b): ^{31}P NMR



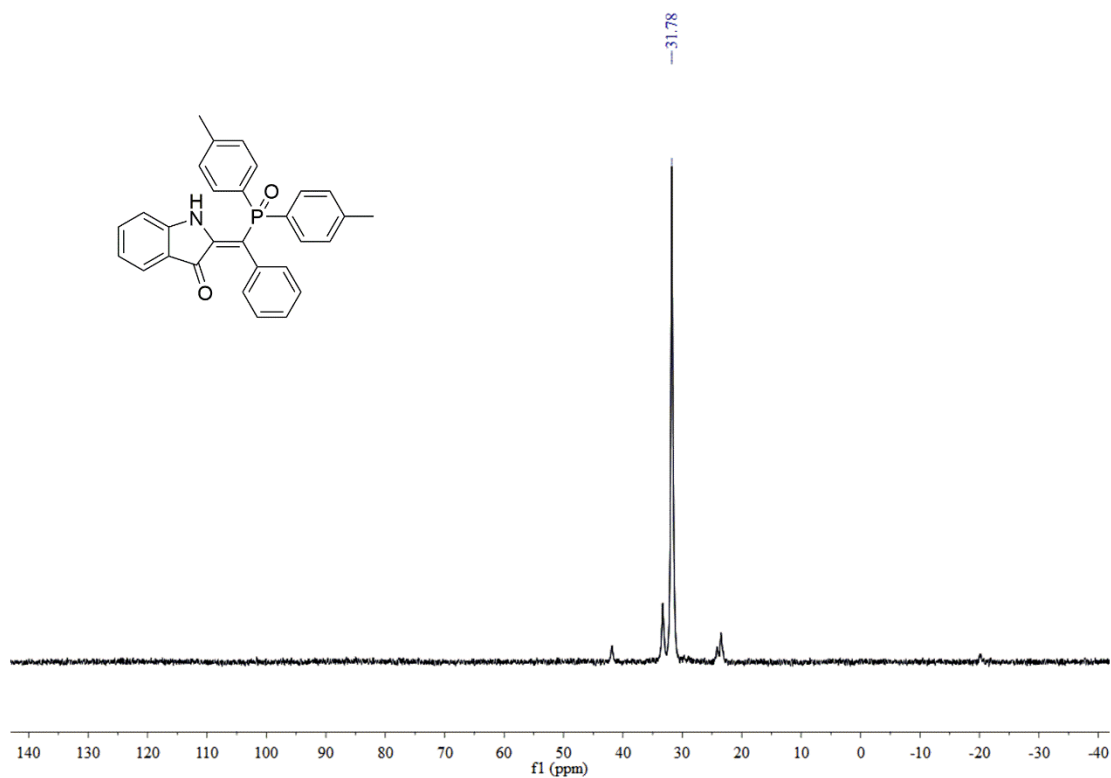
(Z)-2-((di-p-tolylphosphoryl)(phenyl)methylene)indolin-3-one (4d): ^1H NMR



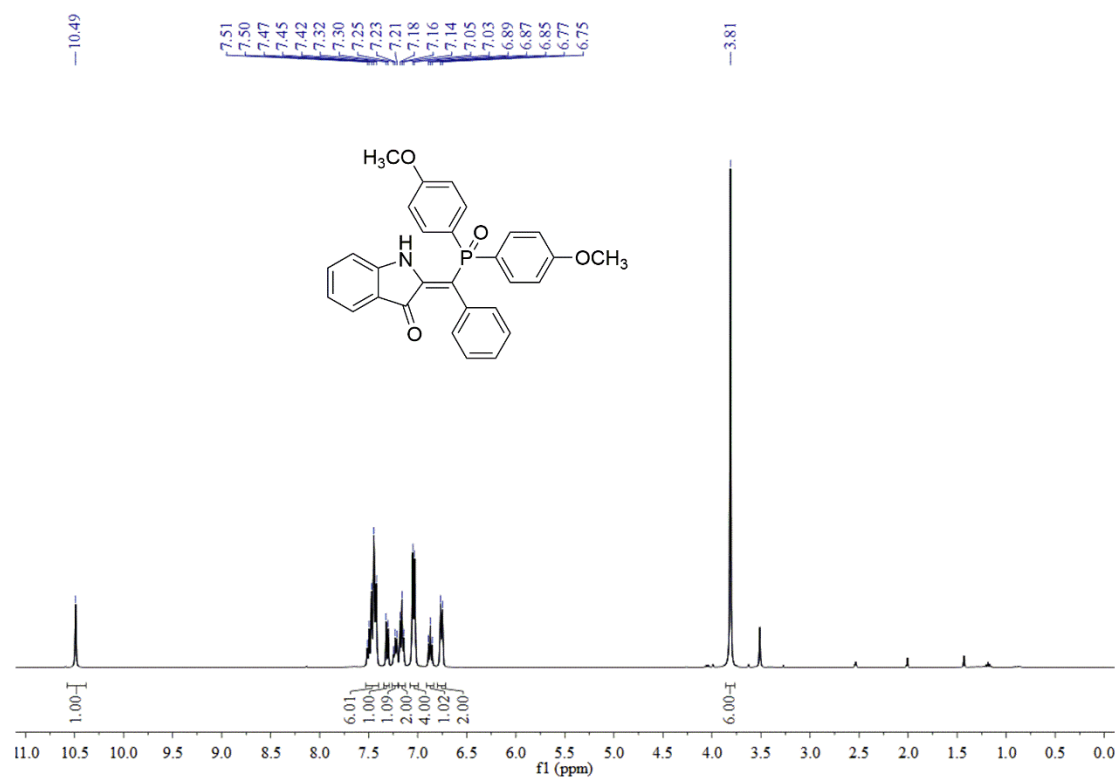
(Z)-2-((di-p-tolylphosphoryl)(phenyl)methylene)indolin-3-one (4d): ¹³C NMR



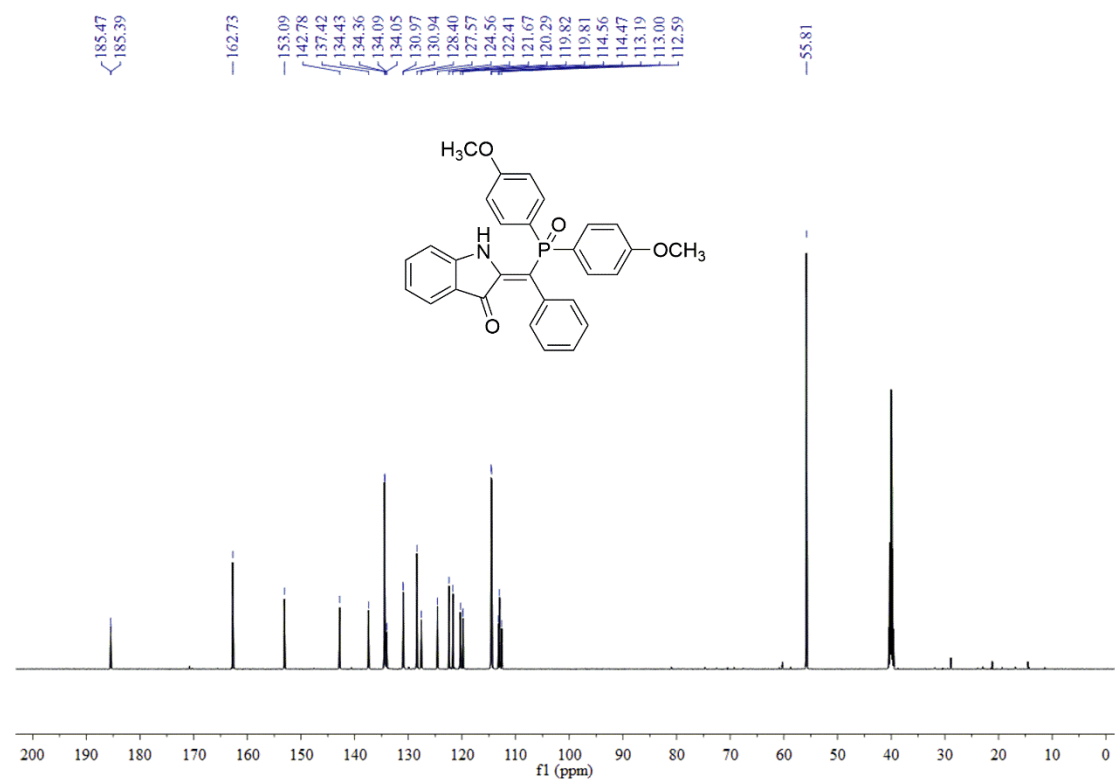
(Z)-2-((di-p-tolylphosphoryl)(phenyl)methylene)indolin-3-one (4d): ³¹P NMR



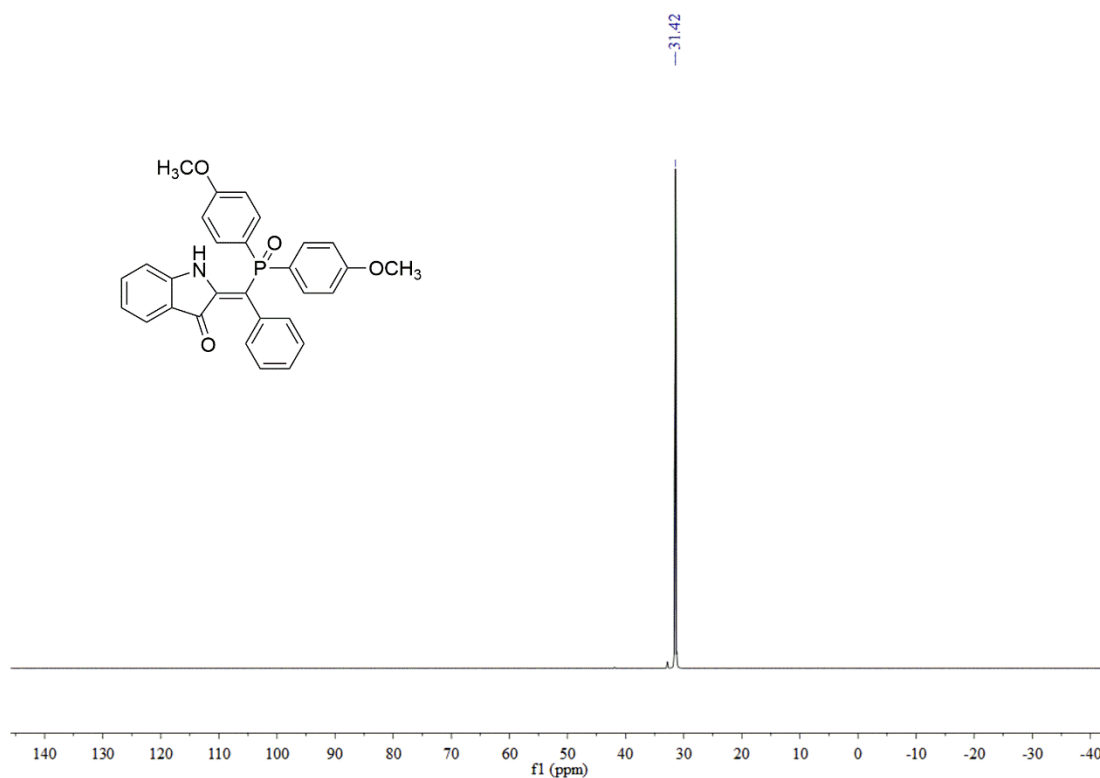
(Z)-2-((bis(4-methoxyphenyl)phosphoryl)(phenyl)methylene)indolin-3-one (4e): ¹H NMR



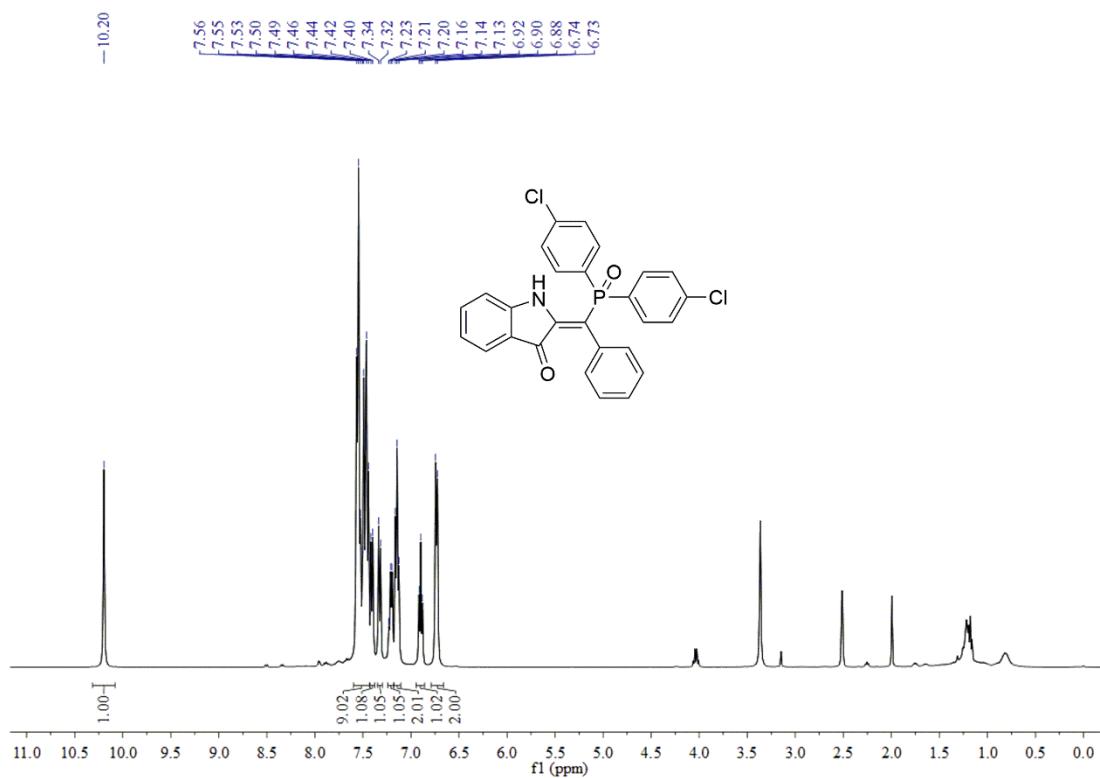
(Z)-2-((bis(4-methoxyphenyl)phosphoryl)(phenyl)methylene)indolin-3-one (4e): ¹³C NMR



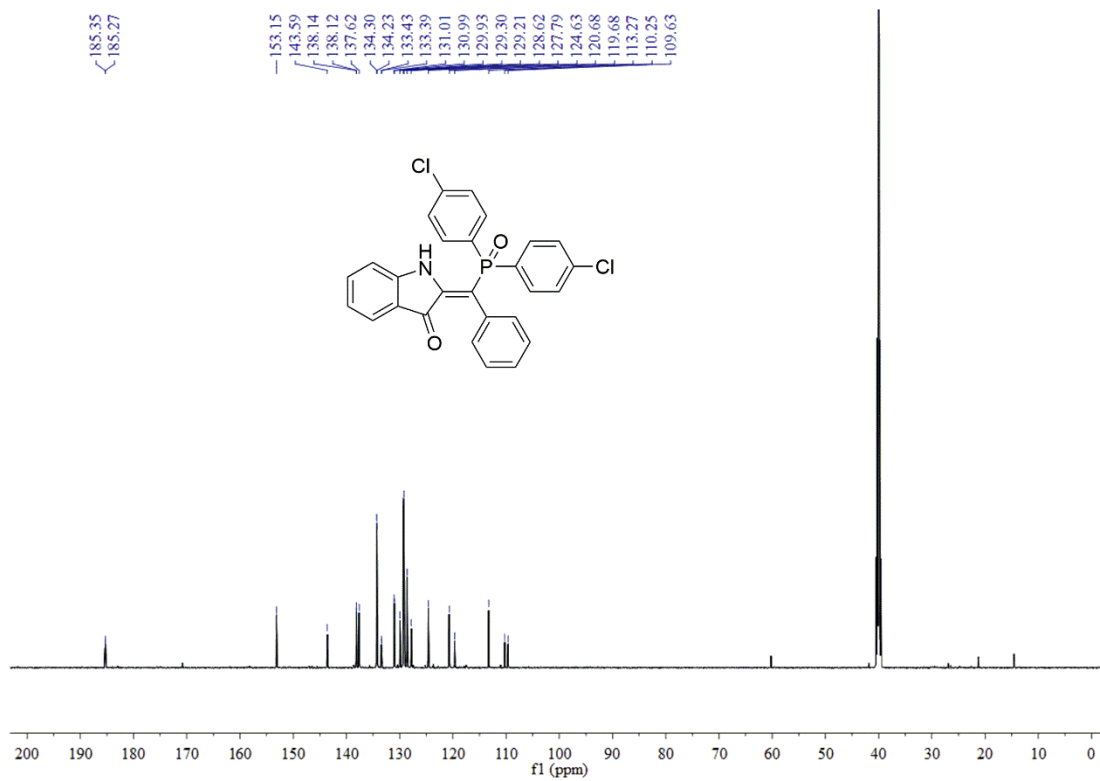
(Z)-2-((bis(4-methoxyphenyl)phosphoryl)(phenyl)methylene)indolin-3-one (4e): ³¹P NMR



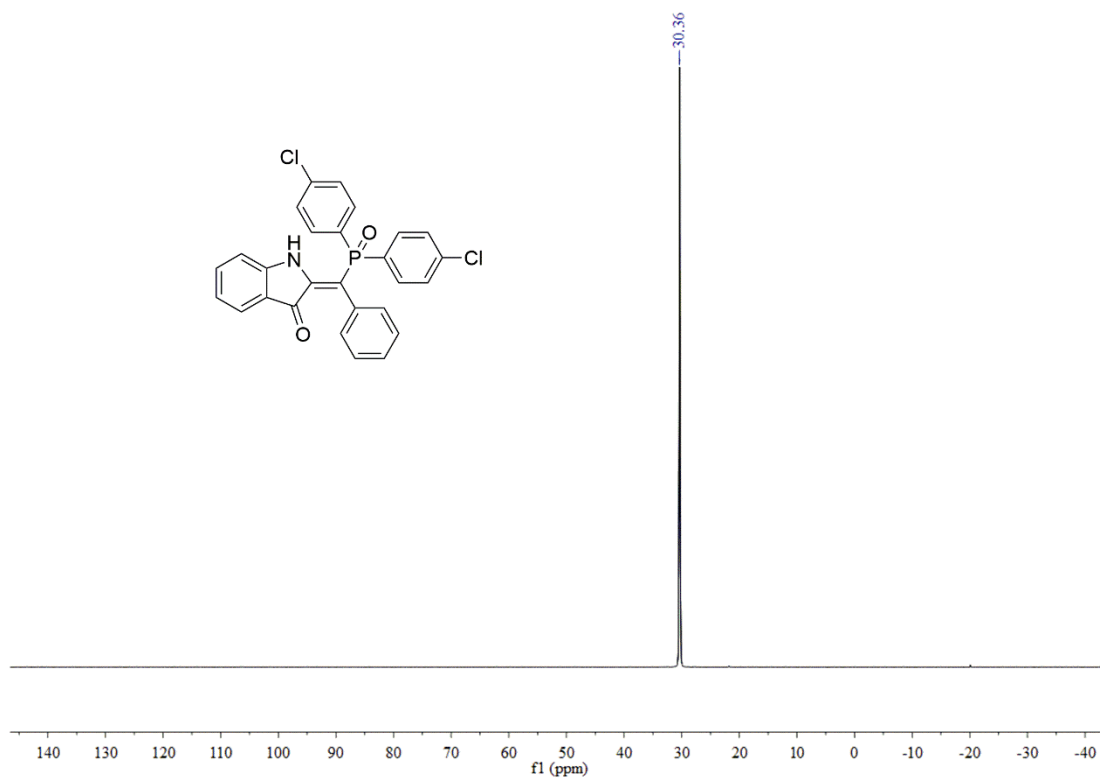
(Z)-2-((bis(4-chlorophenyl)phosphoryl)(phenyl)methylene)indolin-3-one (4f): ¹H NMR



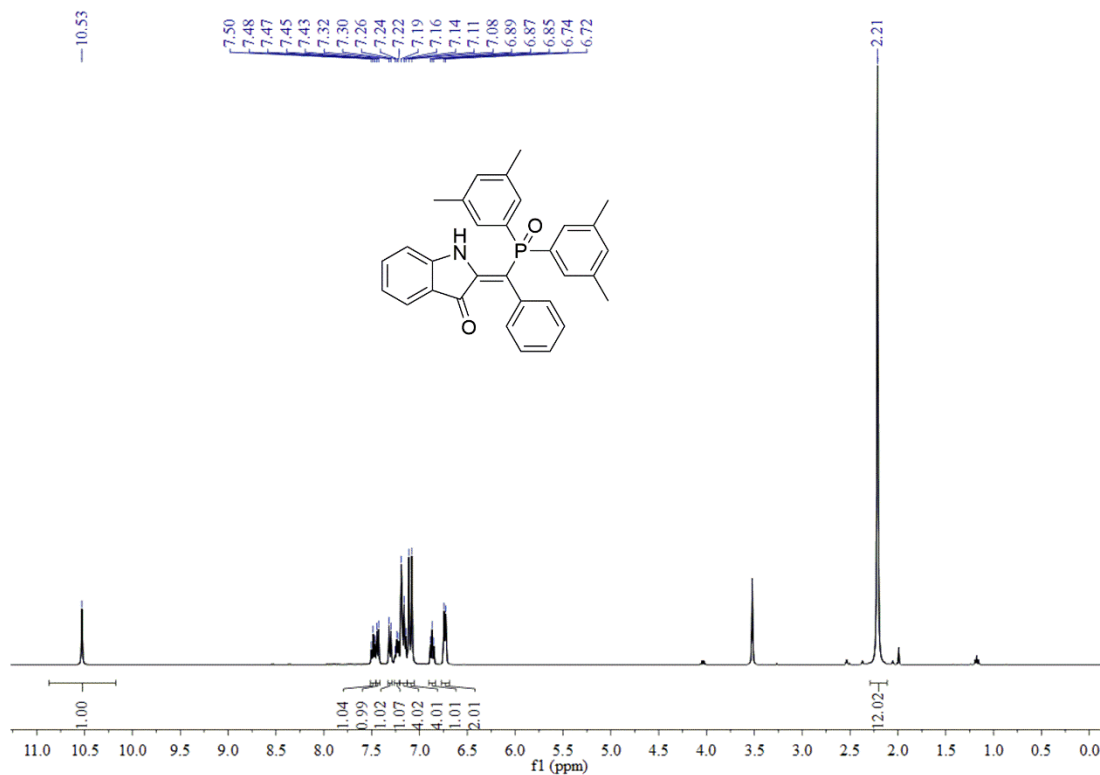
(Z)-2-((bis(4-chlorophenyl)phosphoryl)(phenyl)methylene)indolin-3-one (4f): ¹³C NMR



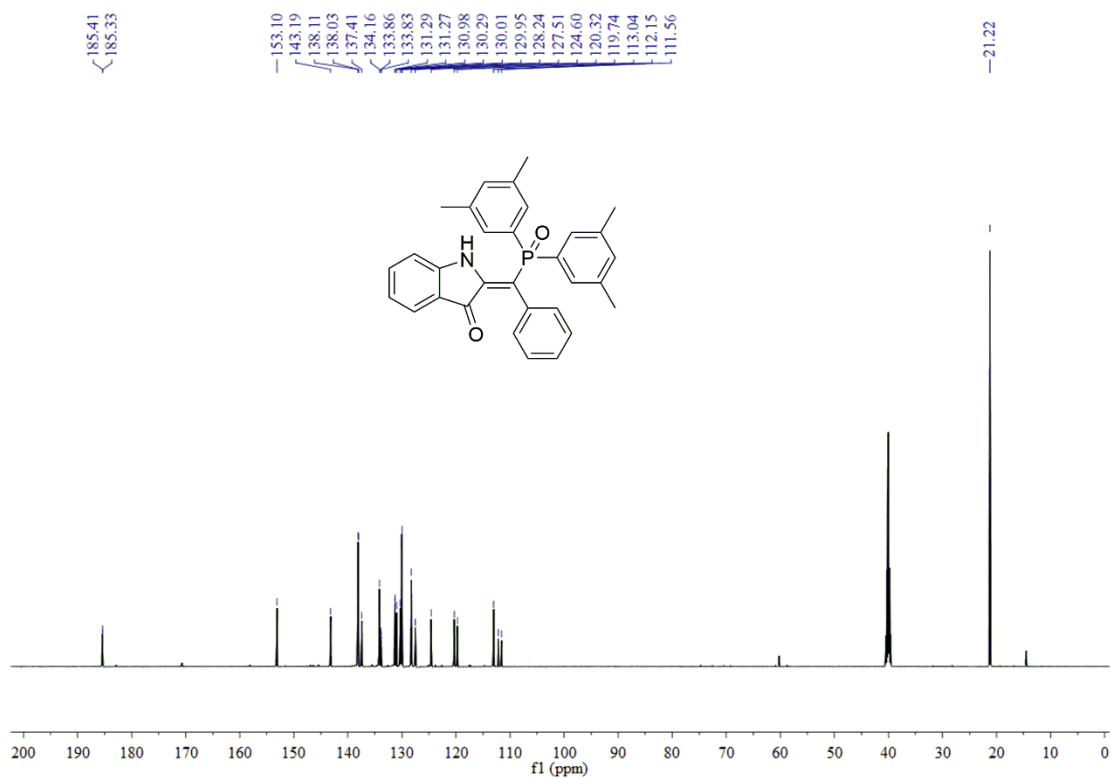
(Z)-2-((bis(4-chlorophenyl)phosphoryl)(phenyl)methylene)indolin-3-one (4f): ³¹P NMR



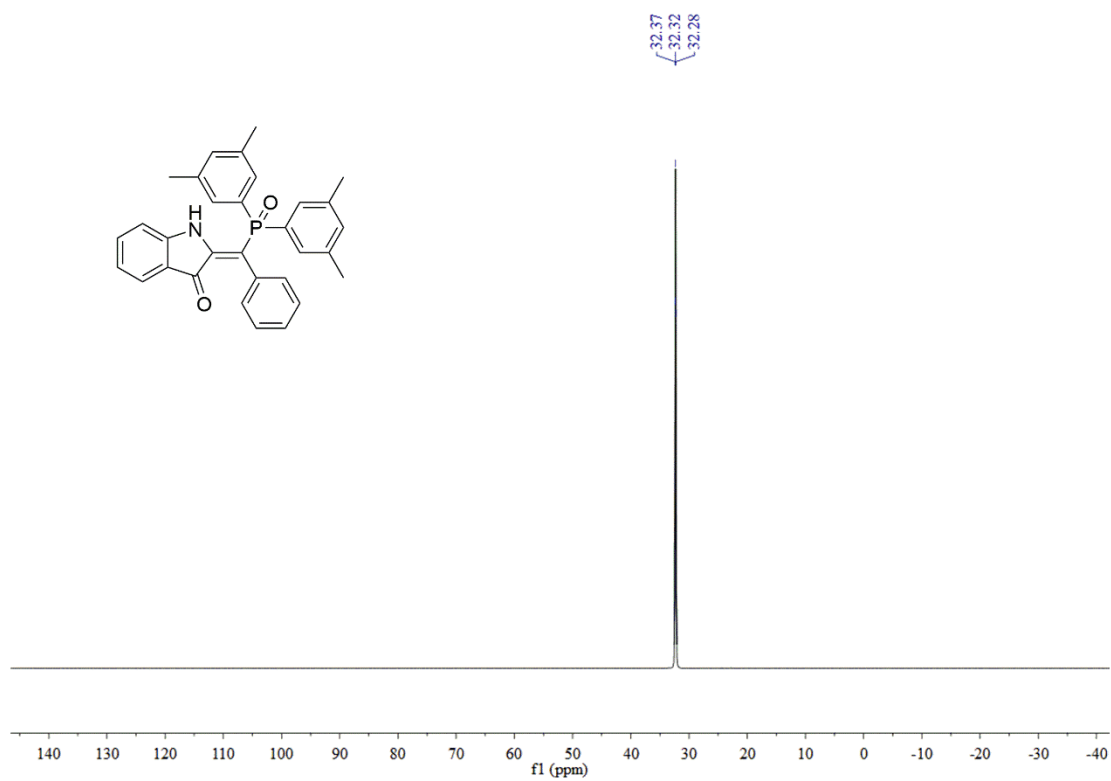
(Z)-2-((bis(3,5-dimethylphenyl)phosphoryl)(phenyl)methylene)indolin-3-one (4g): ¹H NMR



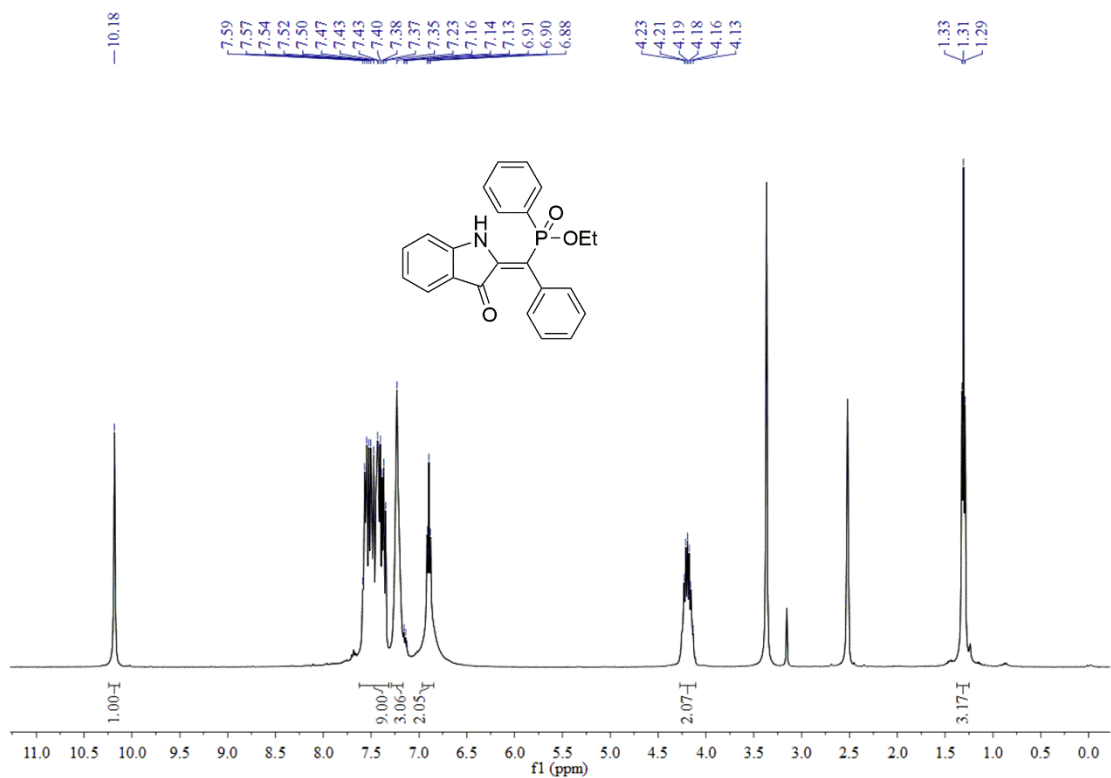
(Z)-2-((bis(3,5-dimethylphenyl)phosphoryl)(phenyl)methylene)indolin-3-one (4g): ¹³C NMR



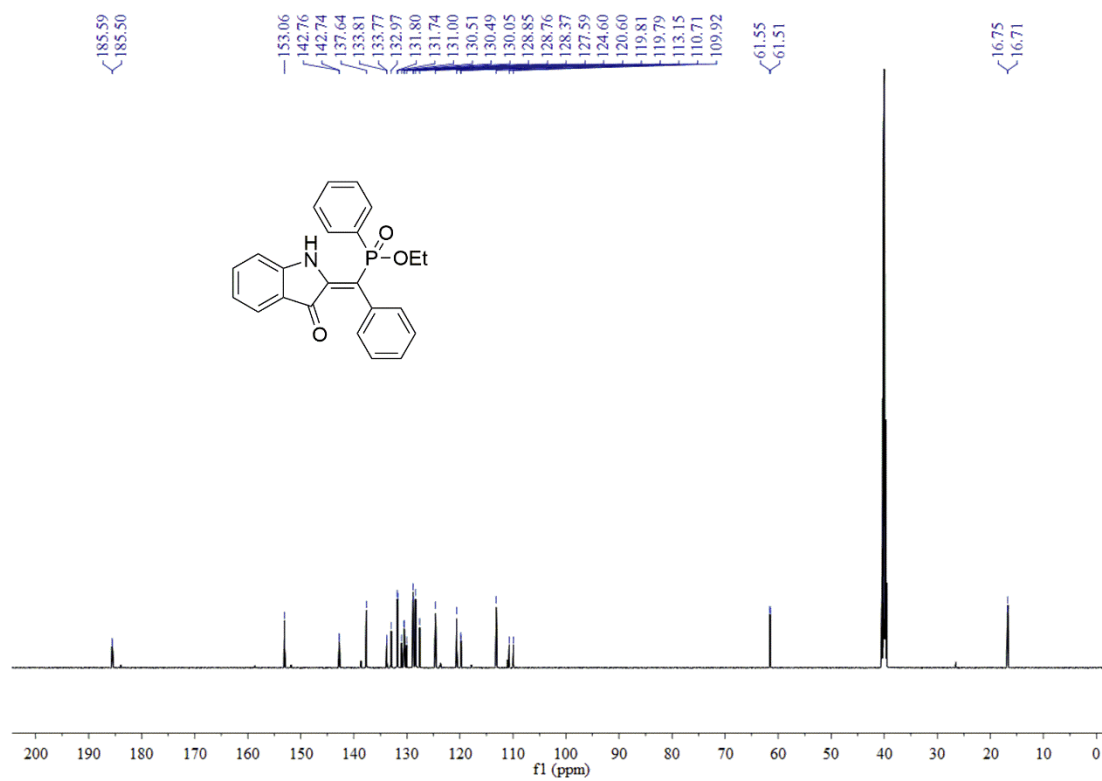
(Z)-2-((bis(3,5-dimethylphenyl)phosphoryl)(phenyl)methylene)indolin-3-one (4g): ³¹P NMR



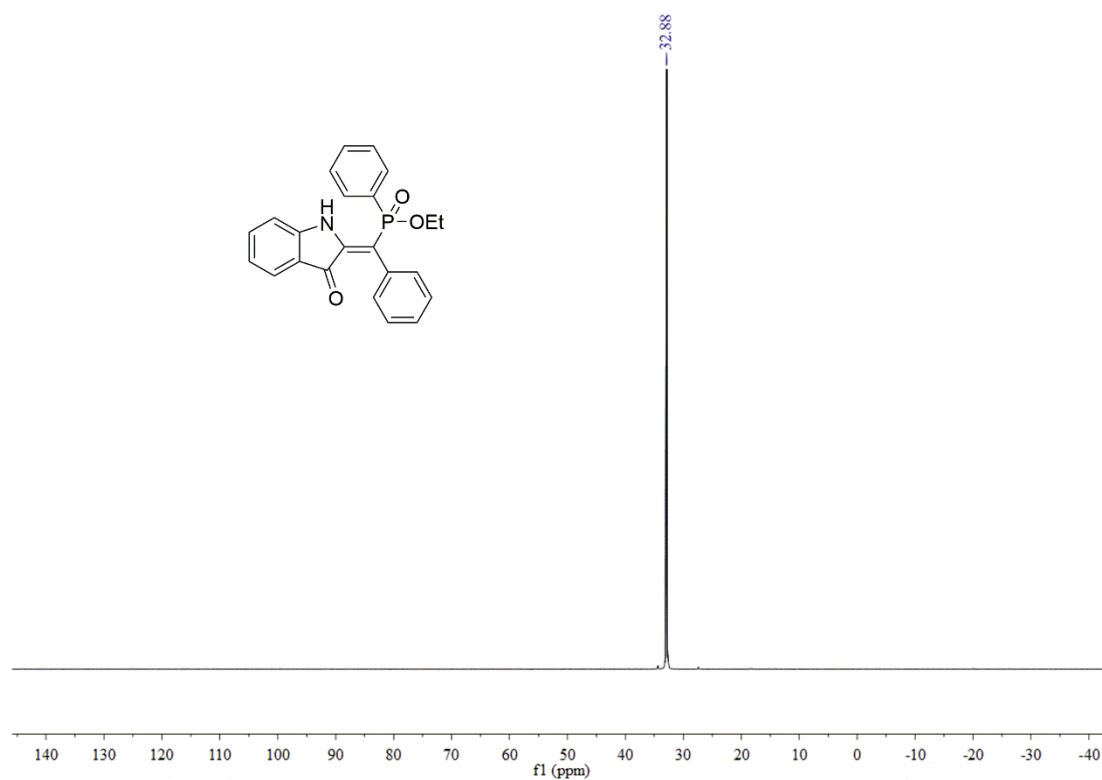
ethyl (Z)-((3-oxindolin-2-ylidene)(phenyl)methyl)(phenyl)phosphinate (4h): ¹H NMR



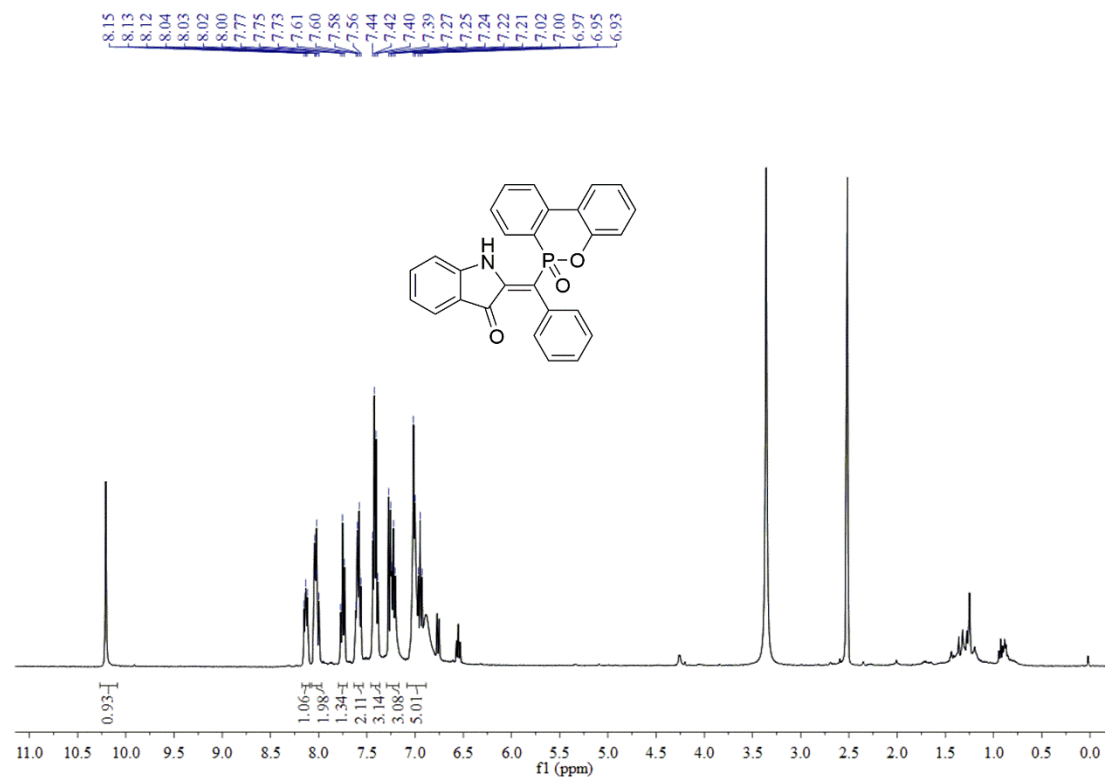
ethyl (Z)-((3-oxoindolin-2-ylidene)(phenyl)methyl)(phenyl)phosphinate (4h): ¹³C NMR



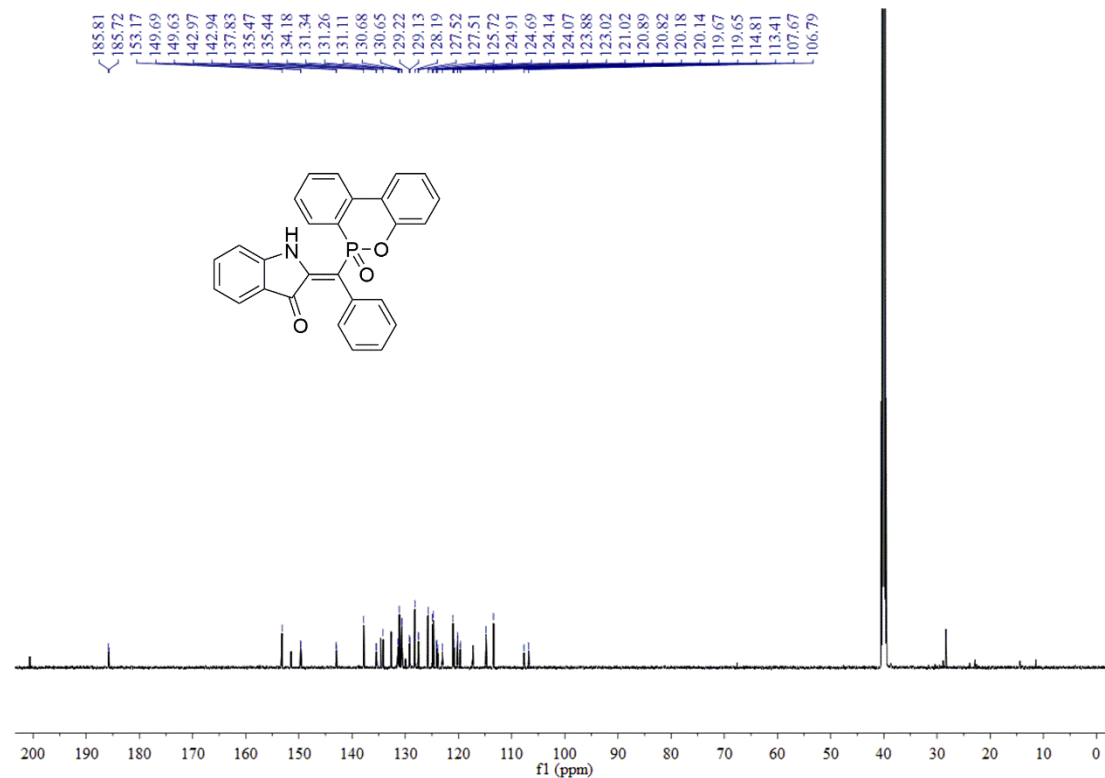
ethyl (Z)-((3-oxoindolin-2-ylidene)(phenyl)methyl)(phenyl)phosphinate (4h): ³¹P NMR



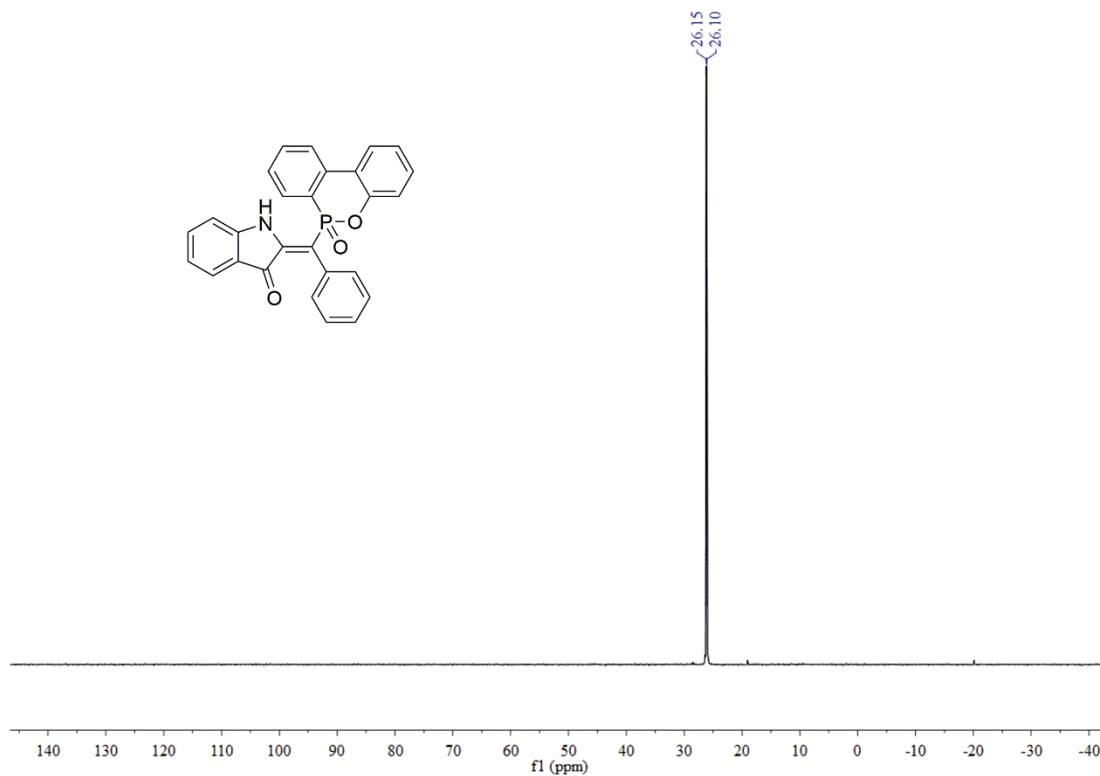
(Z)-2-((6-oxidodibenzo[*c,e*][1,2]oxaphosphinin-6-yl)(phenyl)methylene)indolin-3-one (4i): ¹H NMR



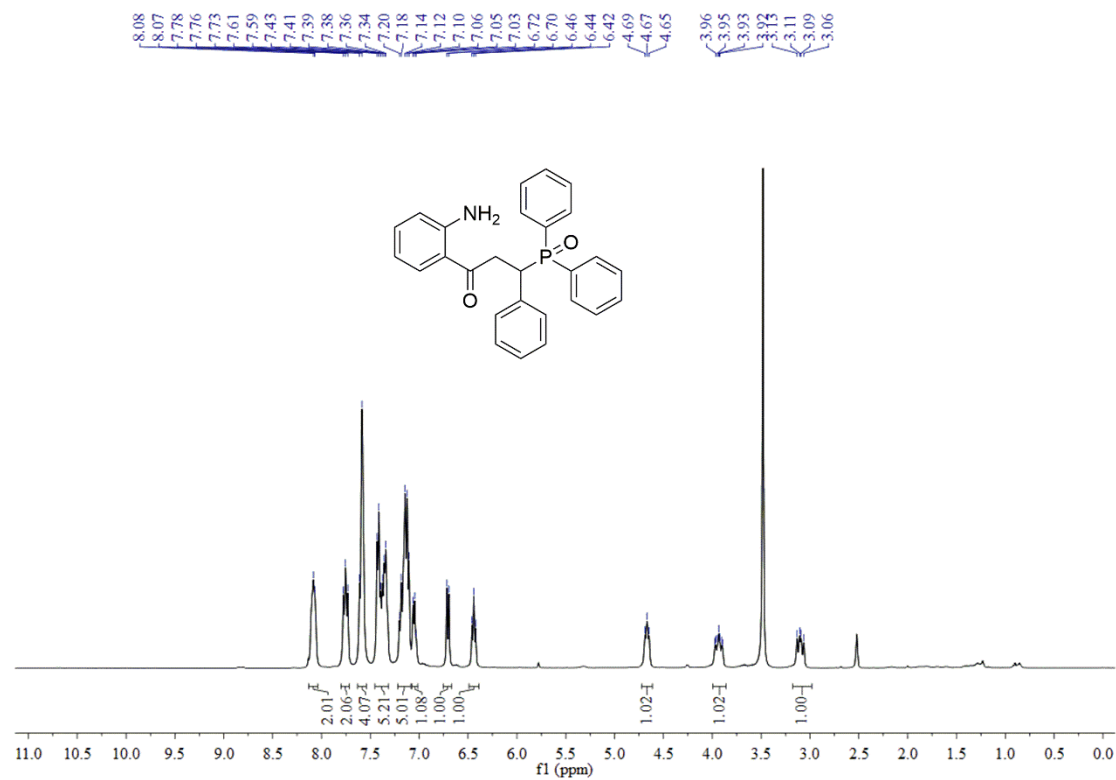
(Z)-2-((6-oxidodibenzo[*c,e*][1,2]oxaphosphinin-6-yl)(phenyl)methylene)indolin-3-one (4i): ¹³C NMR



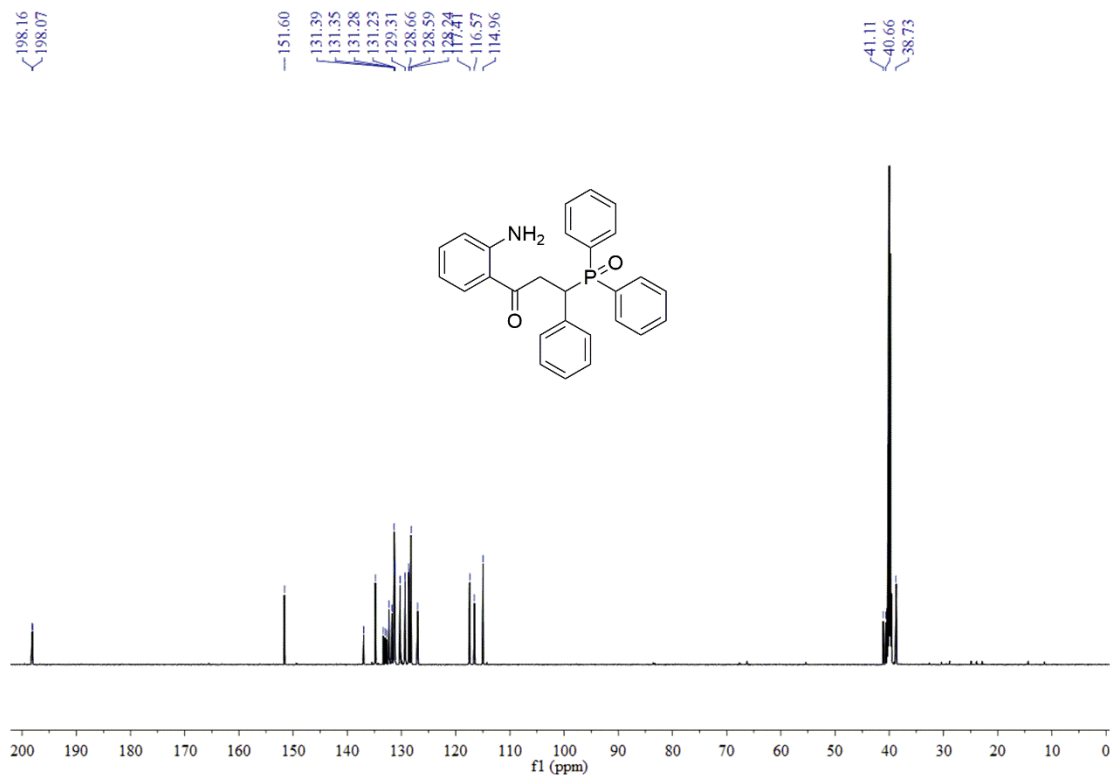
(Z)-2-((6-oxidodibenzo[*c,e*][1,2]oxaphosphinin-6-yl)(phenyl)methylene)indolin-3-one (4i): ³¹P NMR



1-(2-aminophenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one (5a): ¹H NMR



1-(2-aminophenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one (5a): ¹³C NMR



1-(2-aminophenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one (5a): ³¹P NMR

