

Supporting Information

Dy/Ho-encapsulated tartaric acid-functionalized tungstoantimonates: heterogeneous catalysts for isoindolinones synthesis

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1. General Information

Materials and Methods

All reagents were obtained from commercial sources and used without further purification.

The FT-IR spectrum was obtained by using a Fourier transform infrared (FT-IR) (4000-500 cm^{-1}) spectrometer (Thermo Nicolet iS5) at 0.5 cm^{-1} resolution and 16 scans. Thermogravimetric analyses (TGA) were performed under N_2 atmosphere on Mettler-Toledo TGA/SDTA 851^e thermal analyzer from 30 to 800 $^{\circ}\text{C}$. Powder X-ray diffraction (PXRD) was performed on a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature. Inductively coupled plasma optical emission spectrum (ICP-OES) data were obtained on an Agilent 725 ICP-OES spectrometer. Elemental analyses (EA) (C, H, and N) were obtained on Perkinelmer 240C analyzer. The solid-state ultraviolet diffuse reflection spectrum was acquired on a UV-8000 ultraviolet and visible spectrophotometer equipping an integrating sphere (Shanghai Metash Instruments Co., Ltd). The ^1H spectra were recorded on a Bruker ADVANCE III spectrometer at 500 MHz, and chemical shifts were reported in parts per million (ppm). Flash column chromatography was performed using silica gel of 200-300 mesh. The GC analysis was performed on Agilent 7890B equipped with a capillary column (HP-5, 30 m \times 0.25 μm) using a flame ionization detector. The HR-MS was recorded on Agilent Q-TOF 6520 equipment.

X-ray Crystallography

The single crystal X-ray diffraction data were collected on Bruker D8 Smart Apex II diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Intensities were collected by ω -scan and reduced on *APEX 3* and a multi-scan absorption correction was applied.¹ The structures were solved and refined on *Olex2* using *SHELX* package.² Parameters of the crystal data collection and refinement are given in Table S1. The CCDC numbers are 2362723 and 2362724.

2. Experimental

Synthesis of $[\text{H}_2\text{N}(\text{CH}_3)_2]_8\text{Na}_{12}[\text{Dy}_2(\text{H}_2\text{O})_6(\text{tar})(\text{Sb}_2\text{W}_{21}\text{O}_{72})]_2 \cdot 40\text{H}_2\text{O}$ (DySbW)

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (1.9791 g, 6 mmol), SbCl_3 (0.1825 g, 0.8 mmol), $\text{HN}(\text{CH}_3)_2 \cdot \text{HCl}$ (0.9785 g, 12 mmol), DL-tartaric acid (0.0451 g, 0.3 mmol), 1 M acetate buffer solution (10 mL) and deionized water (10 mL) were successively added to a 50 mL beaker and ultrasonicated for 10 min to dissolve them. The pH value of the solution was adjusted to 4.5 by 6 M HCl. The solution was stirred for 10 min, then $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ (0.2276 g, 0.6 mmol) was added, and the final pH of the solution was adjusted to 4.0 by 6 M HCl and was stirred for 30 min. Ultimately, the solution was

filtered. About 1 month later, colorless block crystals were obtained through evaporation (Yield based on W: ~0.40 g, 21.5%). Elemental analysis calculated (found %) for $[\text{H}_2\text{N}(\text{CH}_3)_2]_8\text{Na}_{12}[\text{Dy}_2(\text{H}_2\text{O})_6(\text{tar})(\text{Sb}_2\text{W}_{21}\text{O}_{72})]_2 \cdot 40\text{H}_2\text{O}$: C, 2.21 (2.24); H, 1.35 (1.28); N, 0.86 (0.87); W, 59.23 (59.33); Dy, 4.99 (5.05); Sb, 3.74 (3.78); Na, 2.12 (2.14).

Synthesis of $[\text{H}_2\text{N}(\text{CH}_3)_2]_6\text{Na}_{14}[\text{Ho}_2(\text{H}_2\text{O})_6(\text{tar})(\text{Sb}_2\text{W}_{21}\text{O}_{72})]_2 \cdot 25\text{H}_2\text{O}$ (HoSbW**)**

The synthesis of **HoSbW** was similar to that of **DySbW** except for the usage of $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ (0.2276 g, 0.6 mmol) instead of $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$. Colorless block crystals of **HoSbW** were collected after 1 month (Yield based on W: ~0.38 g, 20.9%). Elemental analysis calculated (found %) for $[\text{H}_2\text{N}(\text{CH}_3)_2]_6\text{Na}_{14}[\text{Ho}_2(\text{H}_2\text{O})_6(\text{tar})(\text{Sb}_2\text{W}_{21}\text{O}_{72})]_2 \cdot 25\text{H}_2\text{O}$: C, 1.89 (2.01); H, 1.00 (0.86); N, 0.66 (0.70); W, 60.66 (60.72); Ho, 5.18 (5.19); Sb, 3.83 (3.90); Na, 2.53 (2.52).

Typical procedure of the three-component reaction

To a 4 mL reaction vial, 2-acylbenzoic acid (**1**, 0.2 mmol), primary amines (**2**, 0.2 mmol), phosphine oxides (**3**, 0.2 mmol), **HoSbW** (0.5 mol%) and EtOH (1 mL) were added. Then the reaction was carried out in screw cap vials with a Teflon seal at 100 °C for 9 h. After the reaction, the mixture was purified by column chromatography (petroleum ether/EtOAc) to afford the desired products. After the reaction was completed, the catalyst was separated from the reaction solution by filtration, and then washed three times with EtOAc and EtOH, respectively, and finally the recovered catalyst was refreshed by drying in a vacuum drying oven at 40 °C for 3 hours.

3. Characterization

Table S1. Crystallographic data and structure refinement.

Code	DySbW	HoSbW
CCDC	2362723	2362724
Empirical formula	[H ₂ N(CH ₃) ₂] ₈ Na ₁₂ [Dy ₂ (H ₂ O) ₆ (tar)(Sb ₂ W ₂₁ O ₇₂)] ₂ ·40 H ₂ O	[H ₂ N(CH ₃) ₂] ₆ Na ₁₄ [Ho ₂ (H ₂ O) ₆ (tar)(Sb ₂ W ₂₁ O ₇₂)] ₂ ·25 H ₂ O
Fw	13117.81	12716.33
<i>T</i> (K)	100	100
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	24.7234(11)	24.7134(14)
<i>b</i> (Å)	25.8468(11)	25.8179(12)
<i>c</i> (Å)	26.5303(11)	26.5037(13)
α (°)	98.669(2)	98.714(2)
β (°)	110.256(2)	110.230(2)
γ (°)	111.317(2)	111.334(2)
<i>V</i> /Å ³	14055.2(11)	14016.5(13)
<i>F</i> (000)	10268.0	10171.0
<i>Z</i>	2	2
ρ_{calcd} (g·cm ⁻³)	2.831	2.815
μ (mm ⁻¹)	18.615	18.723
Reflections collected	171482	150869
Unique reflections	49332 (<i>R</i> _{int} = 0.0747)	48254 (<i>R</i> _{int} = 0.0632)
Parameter	2305	2170
GOOF on <i>F</i> ²	1.107	1.089
<i>R</i> ₁ ^a [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0477	0.0577
<i>wR</i> ₂ ^b (all data)	0.1303	0.1739

$${}^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad {}^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table S2. Selected bond lengths (Å).

DySbW					
Dy1-O1	2.427(8)	Dy3-O7W	2.393(9)	Sb1-O131	1.999(9)
Dy1-O1W	2.375(9)	Dy3-O8W	2.393(9)	Sb1-O144	1.961(8)
Dy1-O2W	2.440(8)	Dy3-O9W	2.455(9)	Sb1-O145	1.987(9)
Dy1-O3W	2.355(10)	Dy3-O69	2.365(9)	Sb2-O132	2.001(8)
Dy1-O5	2.350(8)	Dy3-O70	2.355(9)	Sb2-O133	1.972(8)
Dy1-O6	2.370(9)	Dy3-O97	2.331(9)	Sb2-O134	1.984(9)
Dy1-O33	2.324(9)	Dy3-O129	2.313(8)	Sb3-O135	1.992(9)
Dy1-O65	2.312(8)	Dy3-O142	2.432(8)	Sb3-O136	2.003(9)
Dy2-O2	2.357(8)	Dy4-O10W	3.6531(10)	Sb3-O137	1.985(8)
Dy2-O4W	2.345(9)	Dy4-O11W	2.375(9)	Sb4-O138	1.971(8)
Dy2-O5W	2.364(10)	Dy4-O12W	2.394(9)	Sb4-O149	1.979(9)
Dy2-O6W	2.492(8)	Dy4-O98	2.465(9)	Sb4-O140	1.999(9)
Dy2-O34	2.302(9)	Dy4-O101	2.314(9)		
Dy2-O37	2.344(9)	Dy4-O102	2.400(9)		
Dy2-O38	2.390(9)	Dy4-O130	2.389(9)		
Dy2-O66	2.398(8)	Dy4-O143	2.397(8)		

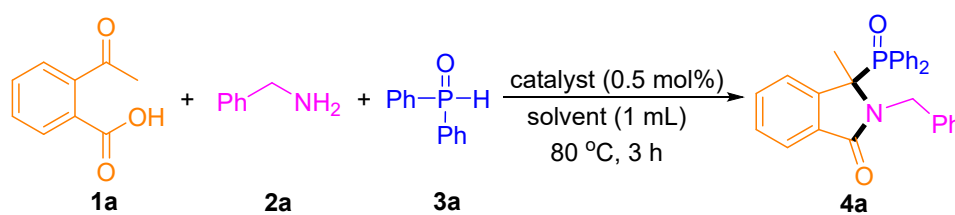
Symmetry transformations used to generate equivalent atoms: #1 2-X, -Y, 1-Z; #2 3-X, 1-Y, 2-Z; #3 2-X, 1-Y, 1-Z; #4 2-X, 1-Y, 2-Z.

HoSbW					
Ho1-O1	2.368(10)	Ho3-O7W	2.471(11)	Sb1-O133	1.974(10)
Ho1-O1W	2.475(11)	Ho3-O8W	2.369(11)	Sb1-O134	1.985(10)
Ho1-O2W	2.365(11)	Ho3-O9W	2.345(10)	Sb1-O135	1.962(10)
Ho1-O3W	2.371(11)	Ho3-O67	2.374(10)	Sb2-O136	1.954(11)
Ho1-O5	2.388(11)	Ho3-O71	2.382(11)	Sb2-O137	2.009(11)
Ho1-O6	2.336(11)	Ho3-O72	2.360(11)	Sb2-O138	1.988(10)
Ho1-O33	2.294(11)	Ho3-O99	2.304(10)	Sb3-O139	1.983(10)
Ho1-O66	2.348(10)	Ho3-O131	2.345(10)	Sb3-O140	1.992(10)
Ho2-O2	2.319(10)	Ho4-O10W	2.425(10)	Sb3-O141	1.968(10)
Ho2-O4W	2.391(10)	Ho4-O11W	2.388(11)	Sb4-O142	1.988(10)
Ho2-O5W	2.341(11)	Ho4-O12W	2.380(11)	Sb4-O143	2.044(11)
Ho2-O6W	2.405(10)	Ho4-O68	2.289(10)	Sb4-O144	2.007(10)
Ho2-O34	2.334(11)	Ho4-O100	2.302(10)		
Ho2-O37	2.367(11)	Ho4-O102	2.370(11)		
Ho2-O38	2.353(10)	Ho4-O103	2.343(11)		
Ho2-O65	2.402(10)	Ho4-O132	2.429(10)		

Symmetry transformations used to generate equivalent atoms: #1 2-X, 1-Y, 2-Z; #2 1-X, -Y, 1-Z; #3 2-X, 1-Y, 1-Z.

Table S3. Bond valence sum (BVS) calculations for **DySbW** and **HoSbW**.³

DySbW								
Atom	BVS	Valence	Atom	BVS	Valence	Atom	BVS	Valence
Dy1	2.98	+3	W14	6.02	+6	W31	6.13	+6
Dy2	2.95	+3	W15	6.00	+6	W32	6.40	+6
Dy3	2.89	+3	W16	6.14	+6	W33	6.06	+6
Dy4	2.85	+3	W17	6.05	+6	W34	6.14	+6
W1	6.04	+6	W18	6.01	+6	W35	6.06	+6
W2	5.97	+6	W19	6.05	+6	W36	6.03	+6
W3	6.02	+6	W20	6.09	+6	W37	6.06	+6
W4	5.95	+6	W21	6.15	+6	W38	5.92	+6
W5	5.84	+6	W22	5.99	+6	W39	6.19	+6
W6	6.14	+6	W23	6.15	+6	W40	5.92	+6
W7	5.94	+6	W24	6.15	+6	W41	6.03	+6
W8	6.20	+6	W25	6.07	+6	W42	6.14	+6
W9	6.18	+6	W26	5.92	+6	Sb1	2.92	+3
W10	6.16	+6	W27	5.95	+6	Sb2	2.91	+3
W11	6.23	+6	W28	6.14	+6	Sb3	2.85	+3
W12	6.05	+6	W29	6.09	+6	Sb4	2.92	+3
W13	6.01	+6	W30	6.20	+6			
HoSbW								
Atom	BVS	Valence	Atom	BVS	Valence	Atom	BVS	Valence
Ho1	3.19	+3	W14	5.85	+6	W31	5.94	+6
Ho2	3.21	+3	W15	6.11	+6	W32	6.17	+6
Ho3	3.18	+3	W16	6.41	+6	W33	5.95	+6
Ho4	3.21	+3	W17	5.84	+6	W34	5.81	+6
W1	6.15	+6	W18	6.04	+6	W35	6.01	+6
W2	5.94	+6	W19	6.09	+6	W36	6.12	+6
W3	6.24	+6	W20	6.10	+6	W37	6.01	+6
W4	5.98	+6	W21	5.95	+6	W38	5.97	+6
W5	6.02	+6	W22	6.03	+6	W39	5.99	+6
W6	5.94	+6	W23	6.12	+6	W40	6.24	+6
W7	6.00	+6	W24	5.98	+6	W41	6.18	+6
W8	6.08	+6	W25	5.95	+6	W42	6.11	+6
W9	6.12	+6	W26	6.04	+6	Sb1	2.99	+3
W10	5.88	+6	W27	6.07	+6	Sb2	2.92	+3
W11	6.33	+6	W28	6.15	+6	Sb3	2.93	+3
W12	6.16	+6	W29	6.14	+6	Sb4	2.69	+3
W13	6.28	+6	W30	6.00	+6			

Table S4. Optimization of reaction conditions.^a

Entry	Catalyst	Solvent	Tem (°C)	Time (h)	Yield ^b (%)
1	-	CH ₃ CN	80	3	8
2	DySbW	CH ₃ CN	80	3	26
3	HoSbW	CH ₃ CN	80	3	33
4	HoSbW	EtOH	80	3	53
5	HoSbW	PhCl	80	3	40
6	HoSbW	DMC	80	3	35
7	HoSbW	PC	80	3	29
8	HoSbW	EtOH	90	3	64
9	HoSbW	EtOH	100	3	71
10	HoSbW	EtOH	110	3	70
11	HoSbW	EtOH	100	5	79
12	HoSbW	EtOH	100	7	90
13	HoSbW	EtOH	100	9	98
14 ^c	HoSbW	EtOH	100	9	73
15 ^d	HoSbW	EtOH	100	9	97

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), **3a** (0.2 mmol), solvent (1.0 mL), catalyst (0.5 mol%), 80 °C for 3 h. ^b GC yields using biphenyl as internal standard. ^c Catalyst loading: 0.4 mol%. ^d Catalyst loading: 0.6 mol%.

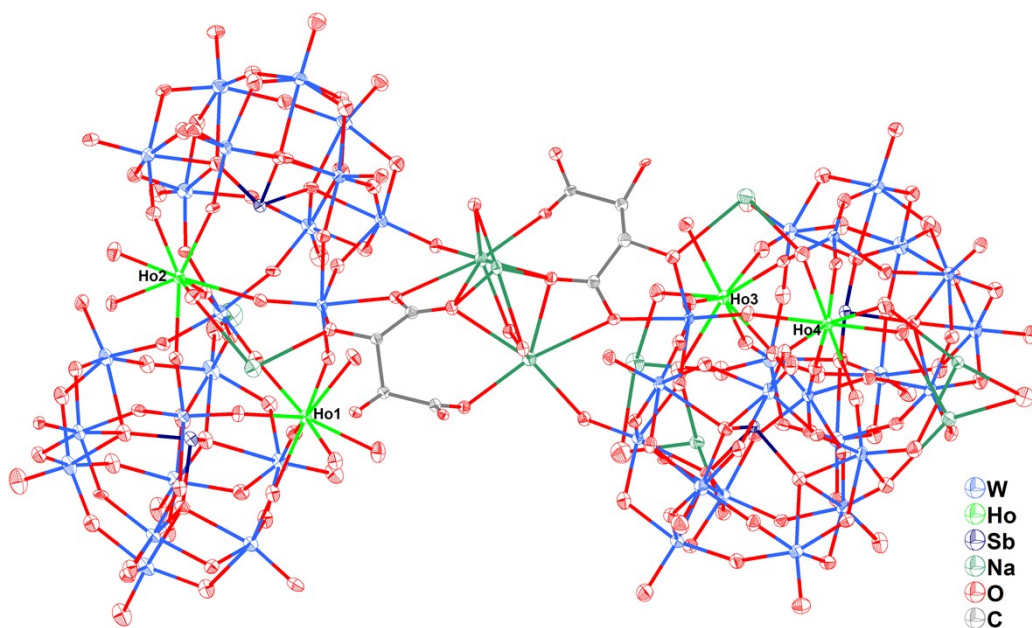


Fig. S1 View of the asymmetric unit of **HoSbW** in ellipsoid mode with 50% probability.

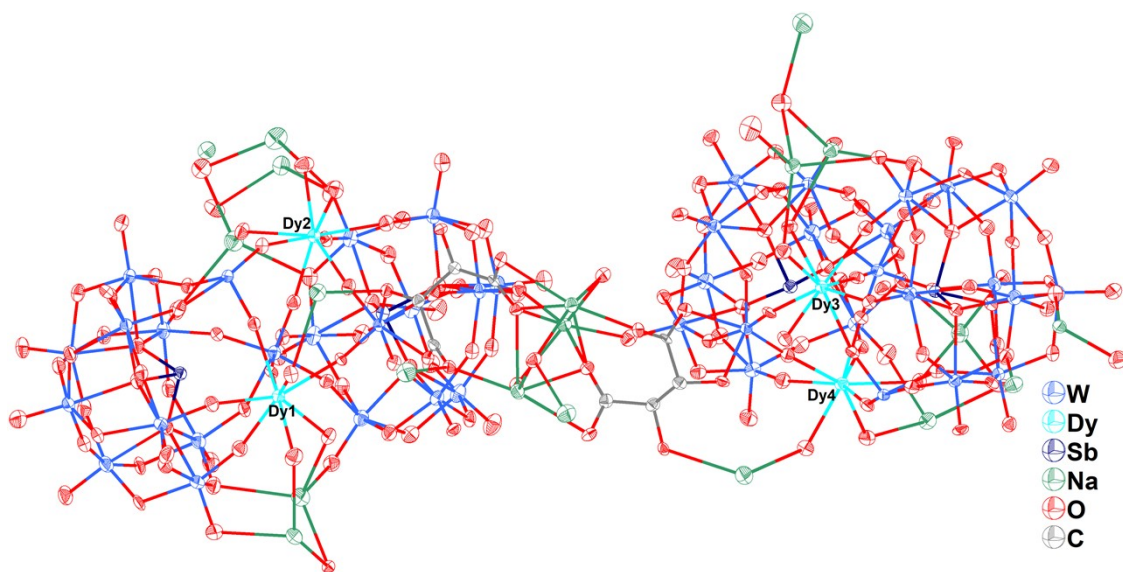


Fig. S2 View of the asymmetric unit of **DySbW** in ellipsoid mode with 50% probability.

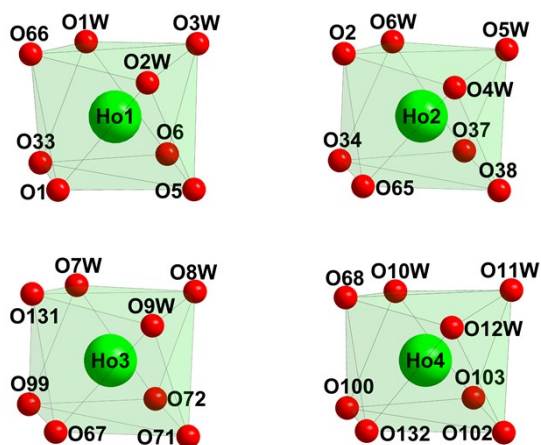


Fig. S3 The coordination environments of four Ho^{3+} ions in HoSbW . The symbol of “W” after oxygen atoms means water molecules.

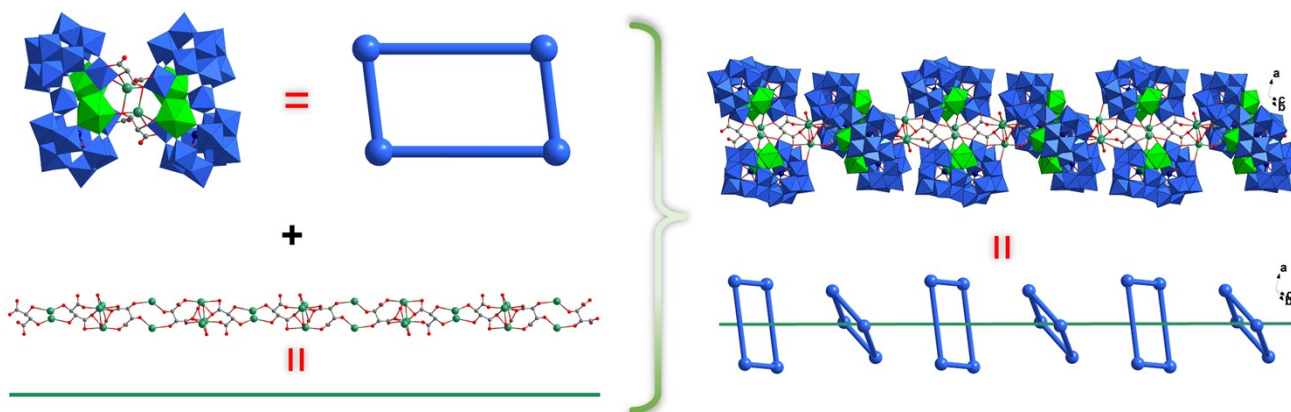


Fig. S4 View of the 2D structure of HoSbW .

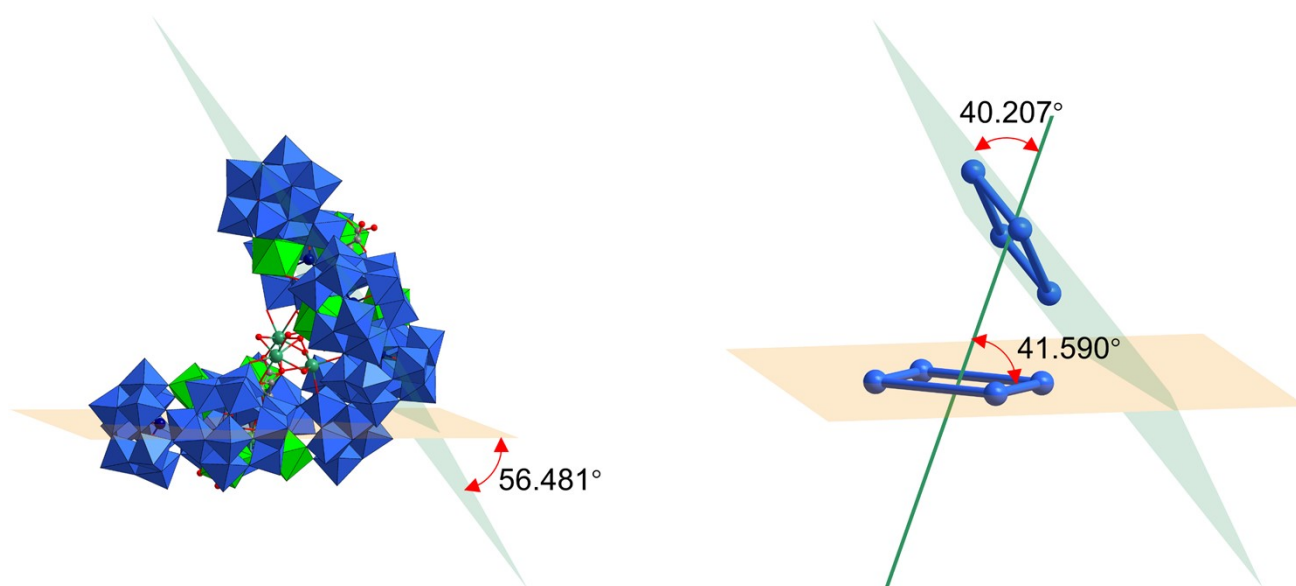


Fig. S5 Schematic diagram of the angles between adjacent $[\text{Ho}_2(\text{H}_2\text{O})_6(\text{tar})(\text{Sb}_2\text{W}_{21}\text{O}_{72})]^{20-}$ polyanions and the Na-tar chain.

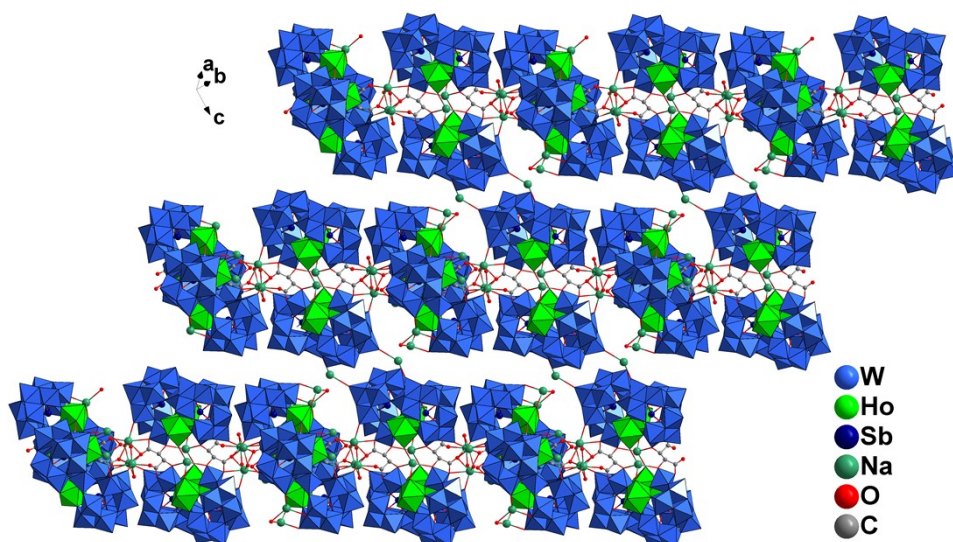


Fig. S6 View of the 2D structure of **HoSbW**.

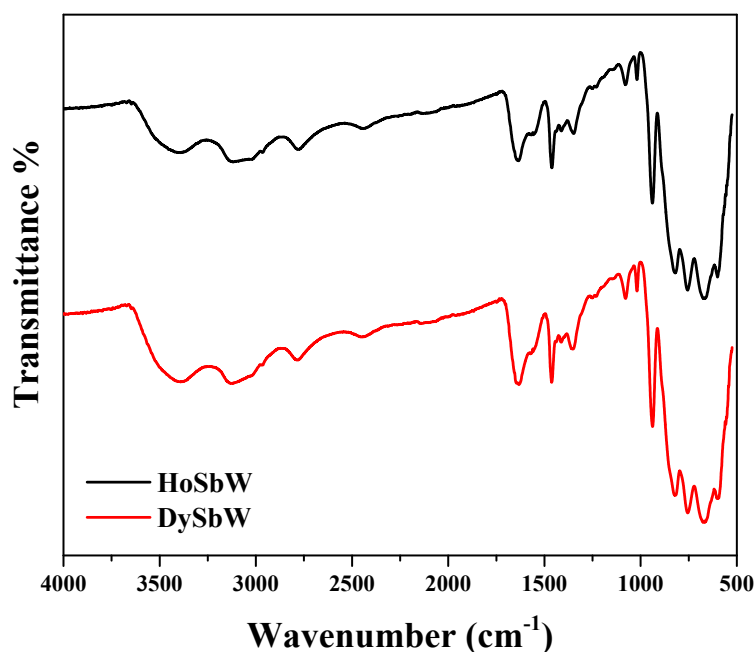


Fig. S7 FT-IR spectra of **HoSbW** and **DySbW**.

Due to the similarity of **HoSbW** and **DySbW**, the FT-IR spectra are almost the same. The broad absorption peak at about 3395 cm^{-1} and the bands around 1627 cm^{-1} are attributed to the $\nu(\text{O-H})$ stretching and bending vibration of water molecules, respectively. The $\nu(\text{N-H})$, $\nu(\text{C-H})$, and $\nu(\text{C-N})$ stretching vibrations appear at about 3130 , 2781 , 1351 , and 1019 cm^{-1} , respectively. Other bands between 1000 and 1750 cm^{-1} (1465 , 1414 , 1351 , 1078) are mainly assigned to be the vibrations from the C-C, C=O, and C-O bonds in mal ligands. The peaks that appear in the range of 500 to 1000 cm^{-1} can be attributed to the stretching vibrations of $\nu(\text{W-O}_t)$, $\nu(\text{Sb-O})$, $\nu(\text{W-O}_b)$, and $\nu(\text{W-O}_c)$, and the absorption peaks appearing at 935 , 822 , 755 , 671 , and 599 cm^{-1} , respectively.

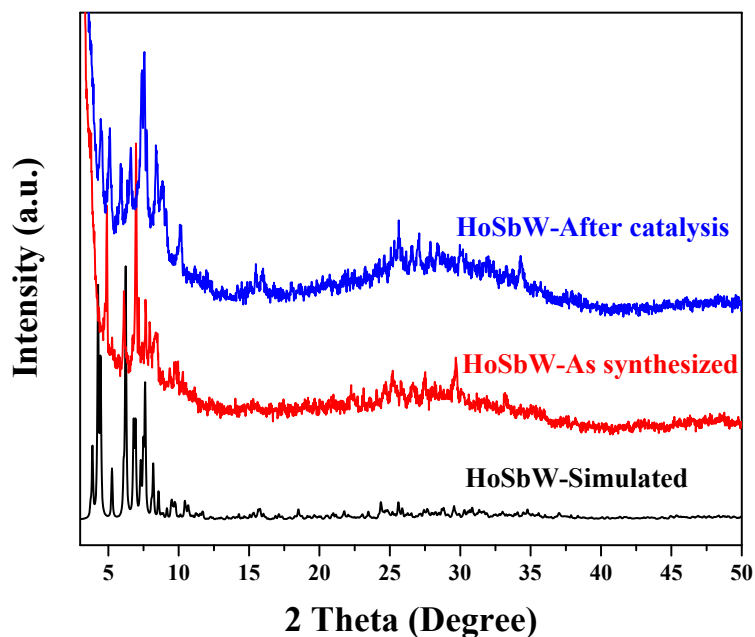


Fig. S8 PXRD patterns of **HoSbW**.

The diffraction peak positions of the experimental PXRD patterns are consistent with those of the simulated PXRD pattern, indicating the phase purity of the two compounds. The PXRD after catalysis also match well with the as synthesized and simulated patterns of **HoSbW**, indicating the stability of this catalyst. The excessive loss of water during the collection and recycling process may lead to the reduction of the crystallinity and the slight shift of peaks.

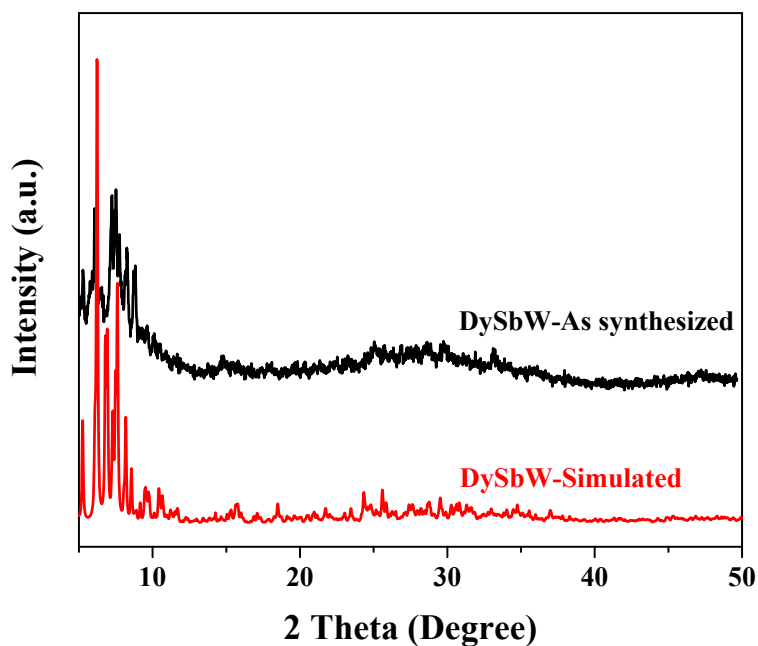


Fig. S9 PXRD patterns of **DySbW**.

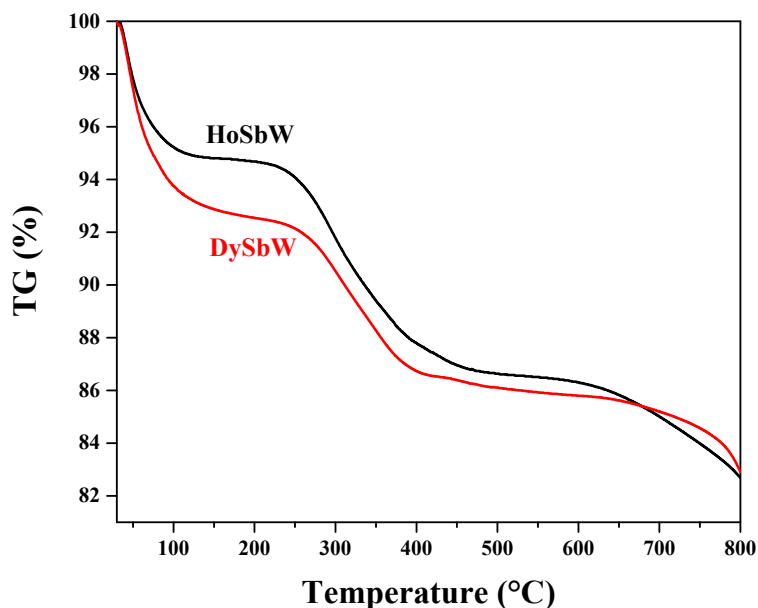


Fig. S10 TG curves of **HoSbW** and **DySbW**.

The weight losses are about 5.2% at 148°C for **HoSbW** and about 7.2% at 150°C for **DySbW**, which are corresponding to about 37 and 52 water molecules, respectively.

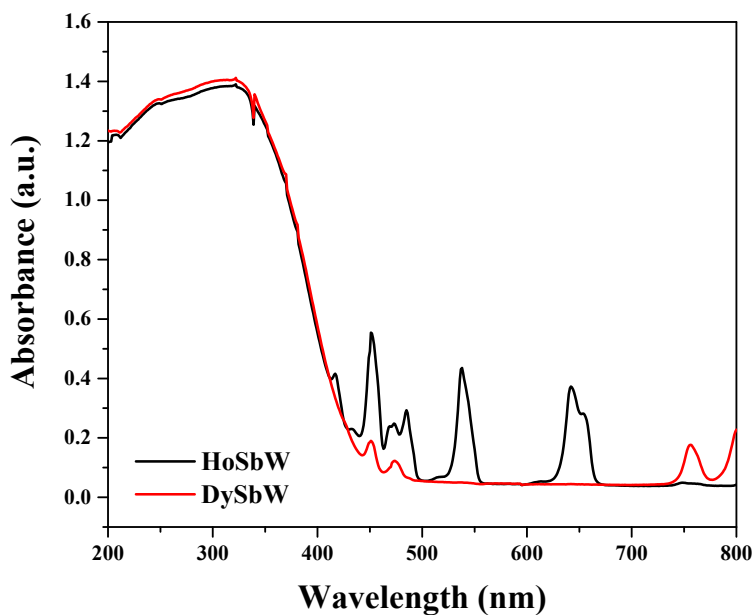


Fig. S11 Solid-state UV diffuse reflection spectra of **HoSbW** and **DySbW**.

The solid-state UV diffuse reflection spectra reveal a maximal peak at 319 nm, which is attributed to the absorption of the polytungstate moieties. The weak absorption peaks from 400 to 800 nm are mainly attributed to the weak absorption of Ho^{3+} and Dy^{3+} ions, which are consistent with the nearly colorless color of the samples.

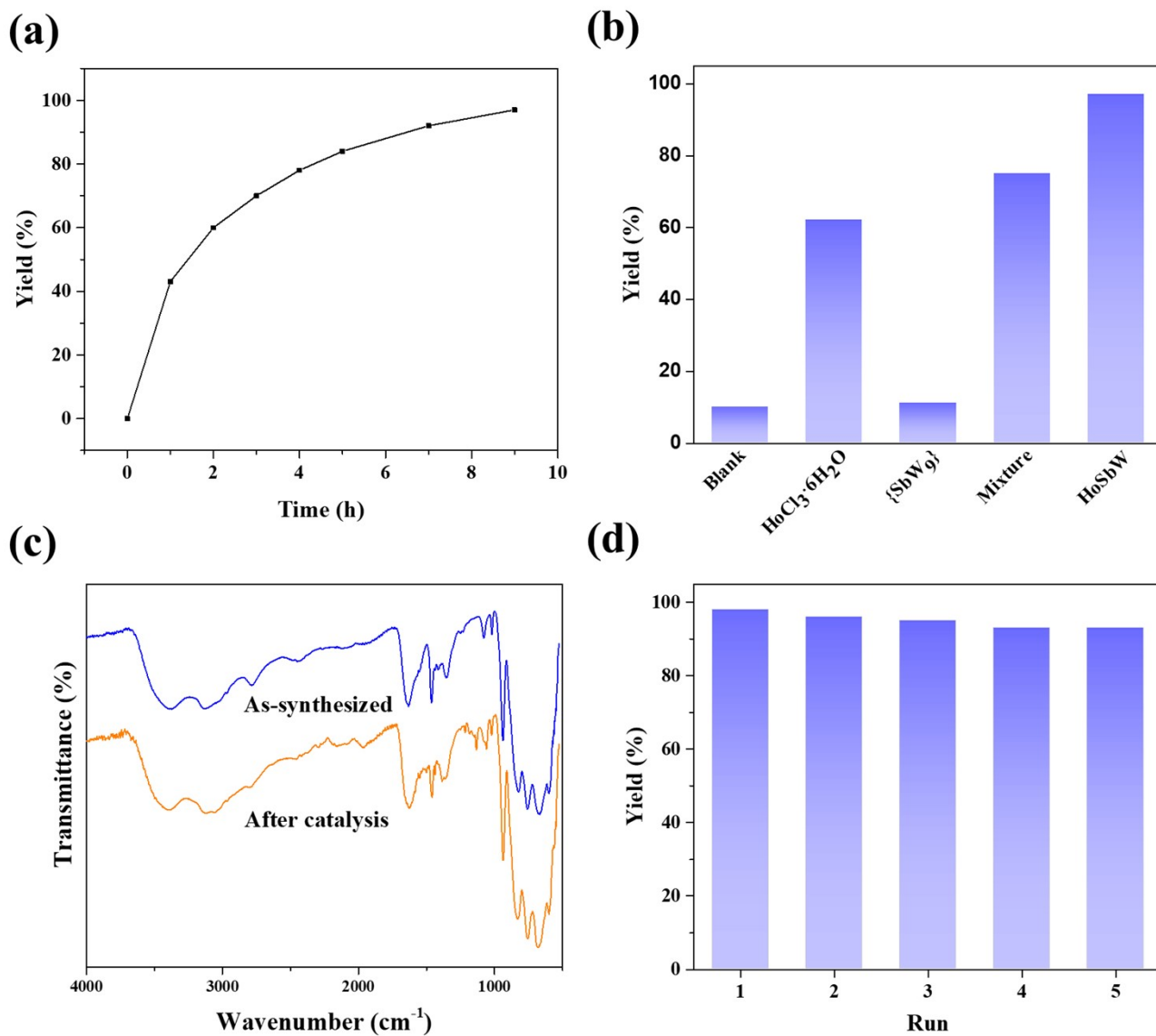
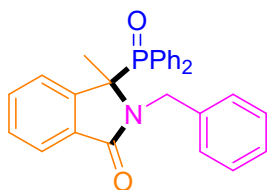


Fig. S12 (a) Reaction kinetics of the HoSbW -catalyzed reaction; (b) control experiments; (c) the FT-IR spectra of HoSbW before and after catalysis; (d) cycling experiments.

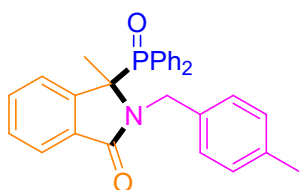
4. Characterization of Products⁴



2-benzyl-3-(diphenylphosphoryl)-3-methylisoindolin-1-one (4a)

¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.70 (dd, *J* = 10.4, 7.9 Hz, 2H), 7.57 – 7.48 (m, 3H), 7.45 (dd, *J* = 7.8 Hz, 3.2 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.26 (t, *J* = 5.7 Hz, 3H), 7.20 (dd, *J* = 12.7 Hz, 5.2 Hz, 4H), 6.64 (d, *J* = 7.7 Hz, 1H), 4.92 (dd, *J* = 106.5 Hz, 15.6 Hz, 2H), 1.74 (d, *J* = 12.1 Hz, 3H).

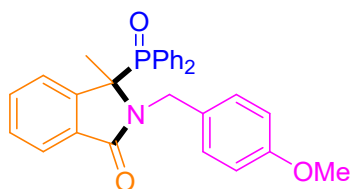
HRMS (ESI): *m/z*, calcd. for C₂₈H₂₄NO₂P [M+H]⁺ requires 438.1618, found 438.1621.



3-(diphenylphosphoryl)-3-methyl-2-(4-methylbenzyl)isoindolin-1-one (4b)

¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.58 – 7.52 (m, 2H), 7.50 – 7.43 (m, 3H), 7.40 – 7.34 (m, 3H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.66 (d, *J* = 7.7 Hz, 1H), 5.01 (d, *J* = 15.5 Hz, 1H), 4.79 – 4.66 (m, 1H), 2.27 (s, 3H), 1.76 (d, *J* = 12.1 Hz, 3H).

HRMS (ESI): *m/z*, calcd. for C₂₉H₂₆NO₂P [M+H]⁺ requires 452.1774, found 452.1779.

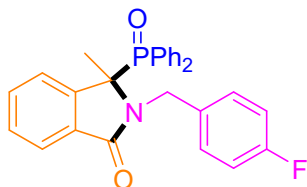


3-(diphenylphosphoryl)-2-(4-methoxybenzyl)-3-methylisoindolin-1-one (4c)

¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.56 – 7.43 (m, 5H), 7.38 – 7.32 (m, 3H), 7.22 (t, *J* = 8.3 Hz, 4H), 6.74 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 7.7 Hz, 1H), 4.98

(d, $J = 15.4$ Hz, 1H), 4.69 (d, $J = 15.3$ Hz, 1H), 3.74 (s, 3H), 1.75 (d, $J = 12.1$ Hz, 3H).

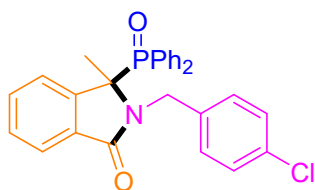
HRMS (ESI): m/z , calcd. for $C_{29}H_{26}NO_3P$ $[M+H]^+$ requires 468.1723, found 468.1720.



3-(diphenylphosphoryl)-2-(4-fluorobenzyl)-3-methylisoindolin-1-one (4d)

1H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, $J = 7.6$ Hz, 1H), 7.70 (dd, $J = 10.8$ Hz, 7.6 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.52 – 7.43 (m, 4H), 7.39 – 7.27 (m, 5H), 7.14 (dd, $J = 10.6$ Hz, 7.7 Hz, 2H), 6.91 – 6.85 (m, 2H), 6.56 (d, $J = 7.7$ Hz, 1H), 4.99 – 4.79 (m, 2H), 1.75 (d, $J = 12.0$ Hz, 3H).

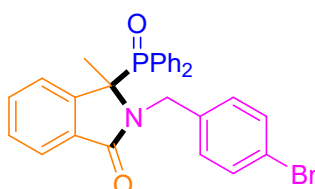
HRMS (ESI): m/z , calcd. for $C_{28}H_{23}FO_2P$ $[M+H]^+$ requires 456.1523, found 456.1520.



2-(4-chlorobenzyl)-3-(diphenylphosphoryl)-3-methylisoindolin-1-one (4e)

1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, $J = 7.6$ Hz, 1H), 7.74 – 7.68 (m, 2H), 7.61 – 7.57 (m, 1H), 7.53 – 7.45 (m, 4H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.33 (td, $J = 7.8$ Hz, 3.1 Hz, 2H), 7.25 (d, $J = 8.5$ Hz, 2H), 7.20 – 7.12 (m, 4H), 6.58 (d, $J = 7.7$ Hz, 1H), 4.98 – 4.83 (m, 2H), 1.76 (d, $J = 11.9$ Hz, 3H).

HRMS (ESI): m/z , calcd. for $C_{28}H_{23}ClNO_2P$ $[M+H]^+$ requires 472.1228, found 472.1231.

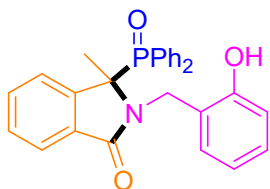


2-(4-bromobenzyl)-3-(diphenylphosphoryl)-3-methylisoindolin-1-one (4f)

1H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, $J = 7.6$ Hz, 1H), 7.71 (dd, $J = 10.9$ Hz, 7.7 Hz, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.54 – 7.45 (m, 4H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.34 (d, $J = 8.5$ Hz, 4H), 7.19 (d, $J = 8.1$

Hz, 2H), 7.16 – 7.11 (m, 2H), 6.56 (d, $J = 7.7$ Hz, 1H), 4.96 – 4.82 (m, 2H), 1.76 (d, $J = 12.0$ Hz, 3H).

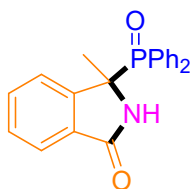
HRMS (ESI): m/z , calcd. for $C_{28}H_{23}BrNO_2P$ $[M+H]^+$ requires 516.0723, found 516.0720.



3-(diphenylphosphoryl)-2-(2-hydroxybenzyl)-3-methylisoindolin-1-one (4g)

1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, $J = 7.7$ Hz, 1H), 7.75 (dd, $J = 11.1$ Hz, 7.7 Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.52 (td, $J = 8.2$ Hz, 7.4 Hz, 4.9 Hz, 4H), 7.38 (t, $J = 8.0$ Hz, 2H), 7.33 (td, $J = 8.0$, 3.5 Hz, 2H), 7.18 – 7.11 (m, 3H), 6.90 (d, $J = 8.1$ Hz, 1H), 6.80 (t, $J = 7.4$ Hz, 1H), 6.45 (d, $J = 7.7$ Hz, 1H), 5.02 (d, $J = 15.3$ Hz, 1H), 4.80 (d, $J = 15.3$ Hz, 1H), 1.90 (d, $J = 11.9$ Hz, 3H).

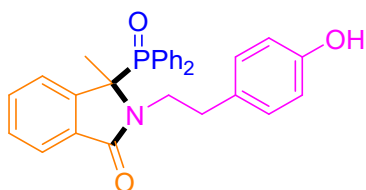
HRMS (ESI): m/z , calcd. for $C_{28}H_{24}NO_3P$ $[M+H]^+$ requires 454.1567, found 454.1564.



3-(diphenylphosphoryl)-3-methylisoindolin-1-one (4h)

1H NMR (500 MHz, $CDCl_3$) δ 8.43 – 8.26 (m, 2H), 8.00 (d, $J = 7.8$ Hz, 1H), 7.74 (t, $J = 7.5$ Hz, 1H), 7.70 – 7.56 (m, 4H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.38 – 7.27 (m, 3H), 7.14 (td, $J = 7.7$ Hz, 3.2 Hz, 2H), 1.90 (d, $J = 12.6$ Hz, 3H).

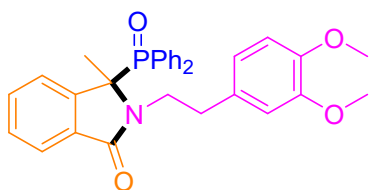
HRMS (ESI): m/z , calcd. for $C_{21}H_{18}NO_2P$ $[M+H]^+$ requires 348.1148, found 348.1145.



3-(diphenylphosphoryl)-2-(4-hydroxyphenethyl)-3-methylisoindolin-1-one (4i)

¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.71 (q, *J* = 7.9 Hz, 5.8 Hz, 3H), 7.60 (q, *J* = 10.1 Hz, 8.8 Hz, 2H), 7.49 (d, *J* = 4.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.30 (td, *J* = 7.8 Hz, 3.0 Hz, 2H), 7.10 (dd, *J* = 15.6 Hz, 8.8 Hz, 4H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.49 (d, *J* = 7.7 Hz, 1H), 4.02 – 3.68 (m, 2H), 2.97 – 2.76 (m, 2H), 1.94 (d, *J* = 12.0 Hz, 3H).

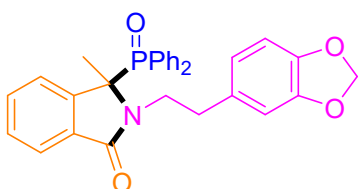
HRMS (ESI): *m/z*, calcd. for C₂₉H₂₆NO₃P [M+H]⁺ requires 468.1723, found 468.1721.



2-(3,4-dimethoxyphenethyl)-3-(diphenylphosphoryl)-3-methylisoindolin-1-one (4j)

¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.70 (dd, *J* = 12.4 Hz, 7.6 Hz, 3H), 7.58 (dd, *J* = 12.8 Hz, 5.4 Hz, 2H), 7.50 – 7.46 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.22 – 7.11 (m, 2H), 6.76 (d, *J* = 5.2 Hz, 2H), 6.62 (d, *J* = 7.8 Hz, 1H), 3.82 (d, *J* = 6.5 Hz, 6H), 2.89 (td, *J* = 11.8 Hz, 10.3 Hz, 6.4 Hz, 2H), 1.79 (d, *J* = 12.0 Hz, 3H).

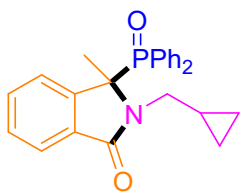
HRMS (ESI): *m/z*, calcd. for C₃₁H₃₀NO₄P [M+H]⁺ requires 512.1985, found 512.1981.



2-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-3-(diphenylphosphoryl)-3-methylisoindolin-1-one (4k)

¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.65 – 7.62 (m, 1H), 7.57 (d, *J* = 3.3 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.40 – 7.29 (m, 4H), 7.19 – 7.14 (m, 2H), 6.75 (s, 1H), 6.69 (s, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 5.88 (s, 2H), 3.91 – 3.55 (m, 2H), 3.00 – 2.72 (m, 2H), 1.84 (d, *J* = 12.0 Hz, 3H).

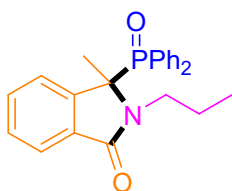
HRMS (ESI): *m/z*, calcd. for C₃₀H₂₆O₄P [M+H]⁺ requires 496.1672, found 496.1676.



2-(cyclopropylmethyl)-3-(diphenylphosphoryl)-3-methylisoindolin-1-one (4l)

¹H NMR (400 MHz, CDCl₃) δ 7.76 (t, *J* = 8.2 Hz, 1H), 7.71 (dd, *J* = 10.8 Hz, 7.9 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.53 – 7.41 (m, 4H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.31 (dt, *J* = 7.8 Hz, 3.5 Hz, 2H), 7.19 – 7.13 (m, 2H), 6.61 (d, *J* = 7.6 Hz, 1H), 3.72 – 3.19 (m, 2H), 2.08 (d, *J* = 12.0 Hz, 3H), 1.23 – 1.09 (m, 1H), 0.61 – 0.09 (m, 4H).

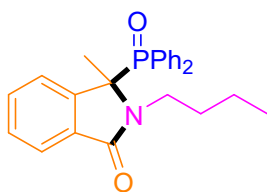
HRMS (ESI): *m/z*, calcd. for C₂₅H₂₄NO₂P [M+H]⁺ requires 402.1618, found 402.1617.



3-(diphenylphosphoryl)-3-methyl-2-propylisoindolin-1-one (4m)

¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.68 (m, 3H), 7.57 (td, *J* = 7.4 Hz, 1.5 Hz, 1H), 7.52 – 7.43 (m, 4H), 7.38 – 7.31 (m, 3H), 7.24 – 7.17 (m, 2H), 6.65 (d, *J* = 7.8 Hz, 1H), 3.59 – 3.39 (m, 2H), 2.00 (d, *J* = 12.0 Hz, 3H), 1.80 – 1.69 (m, 1H), 1.59 – 1.48 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H).

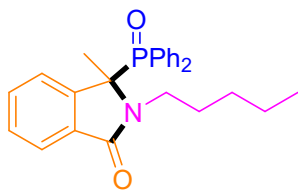
HRMS (ESI): *m/z*, calcd. for C₂₄H₂₄NO₂P [M+H]⁺ requires 390.1617, found 390.1612.



2-butyl-3-(diphenylphosphoryl)-3-methylisoindolin-1-one (4n)

¹H NMR (400 MHz, CDCl₃) δ 7.69 (dd, *J* = 18.2 Hz, 9.7 Hz, 3H), 7.55 – 7.50 (m, 1H), 7.47 – 7.38 (m, 4H), 7.31 (td, *J* = 7.4 Hz, 2.7 Hz, 3H), 7.21 (dd, *J* = 10.5 Hz, 7.7 Hz, 2H), 6.68 (d, *J* = 7.7 Hz, 1H), 3.75 – 3.24 (m, 2H), 1.98 (d, *J* = 12.0 Hz, 3H), 1.76 – 1.61 (m, 1H), 1.53 – 1.37 (m, 1H), 1.31 – 1.16 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H).

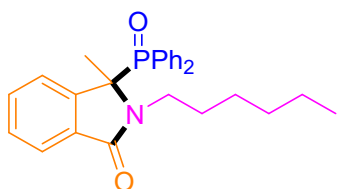
HRMS (ESI): *m/z*, calcd. for C₂₅H₂₆NO₂P [M+H]⁺ requires 404.1774, found 404.1776.



3-(diphenylphosphoryl)-3-methyl-2-pentylisoindolin-1-one (4o)

¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.67 (m, 3H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.38 – 7.32 (m, 3H), 7.24 (dd, *J* = 10.4 Hz, 7.9 Hz, 2H), 6.70 (d, *J* = 7.6 Hz, 1H), 3.58 – 3.42 (m, 2H), 2.01 (d, *J* = 11.9 Hz, 3H), 1.76 – 1.68 (m, 1H), 1.50 – 1.42 (m, 1H), 1.26 – 1.22 (m, 4H), 0.86 (t, *J* = 6.6 Hz, 3H).

HRMS (ESI): *m/z*, calcd. for C₂₆H₂₈NO₂P [M+H]⁺ requires 418.1930, found 418.1926.

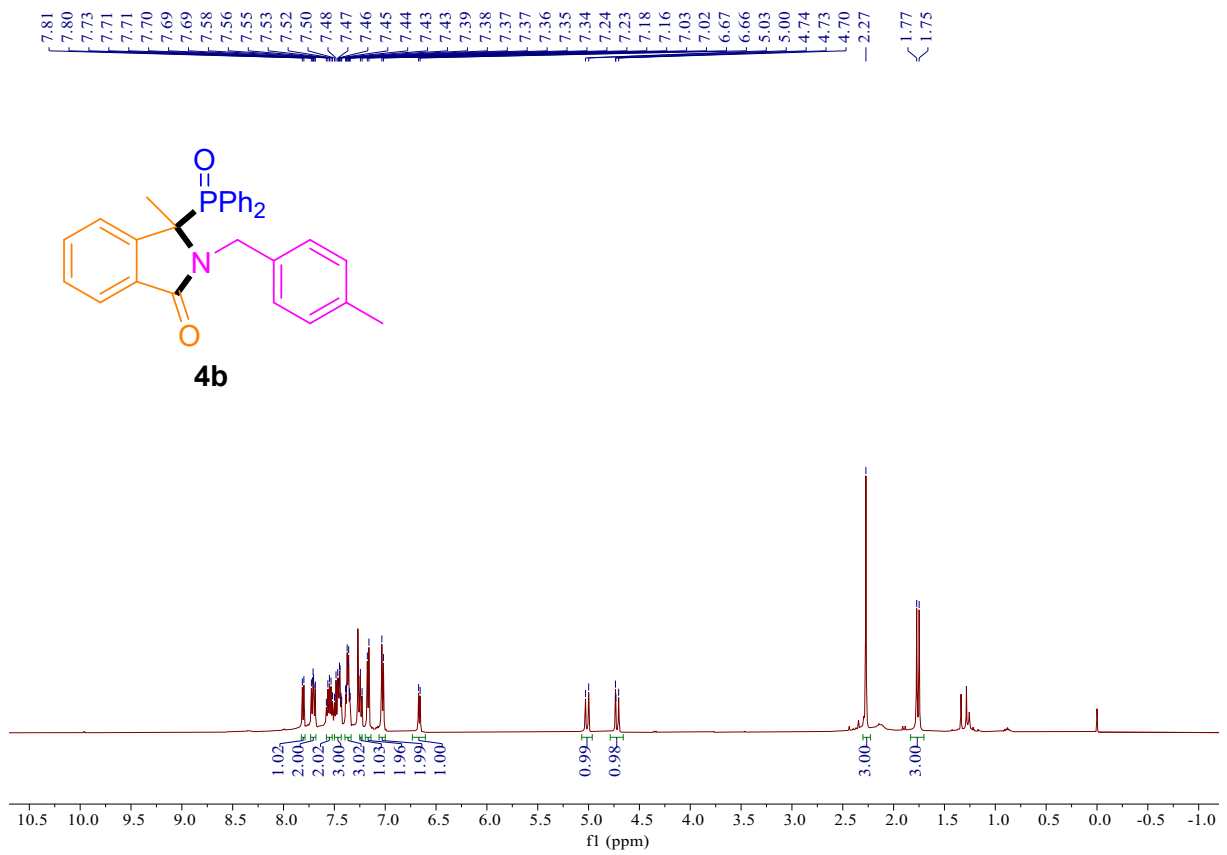
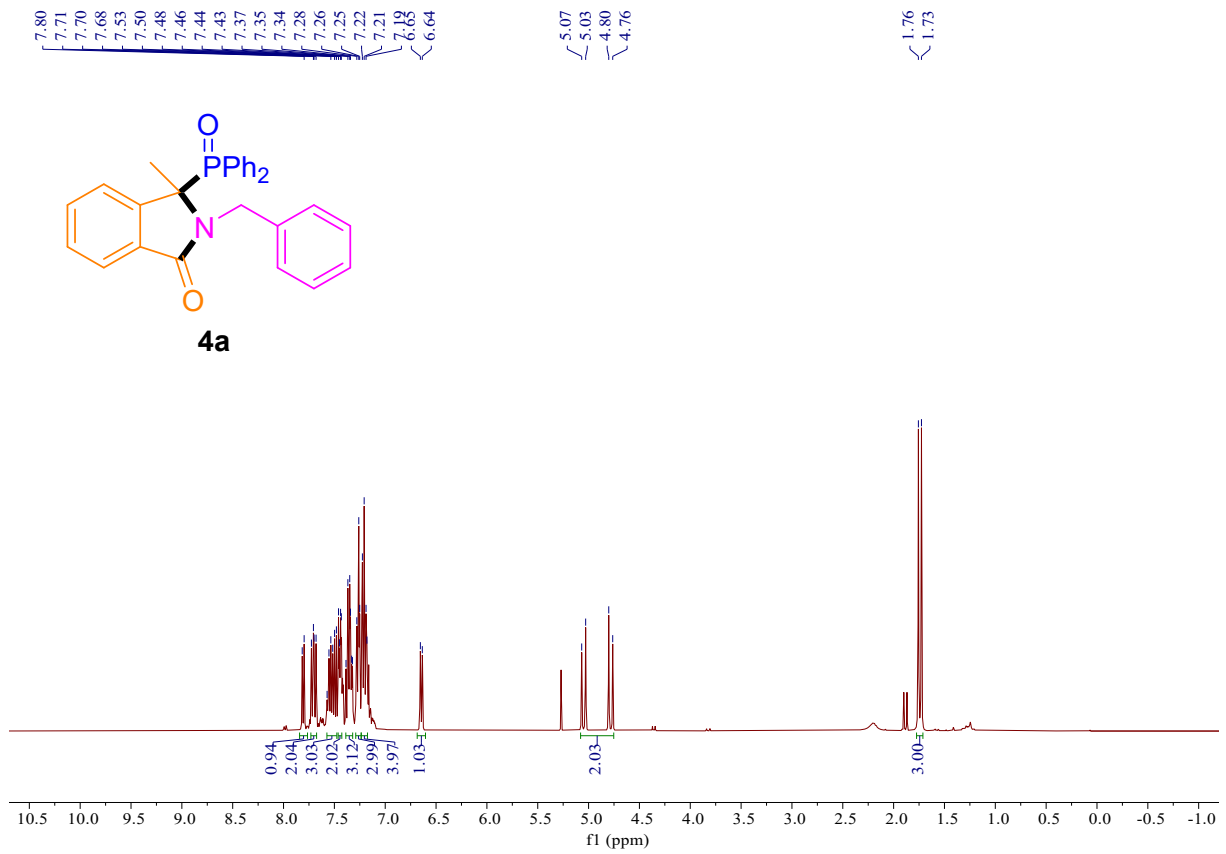


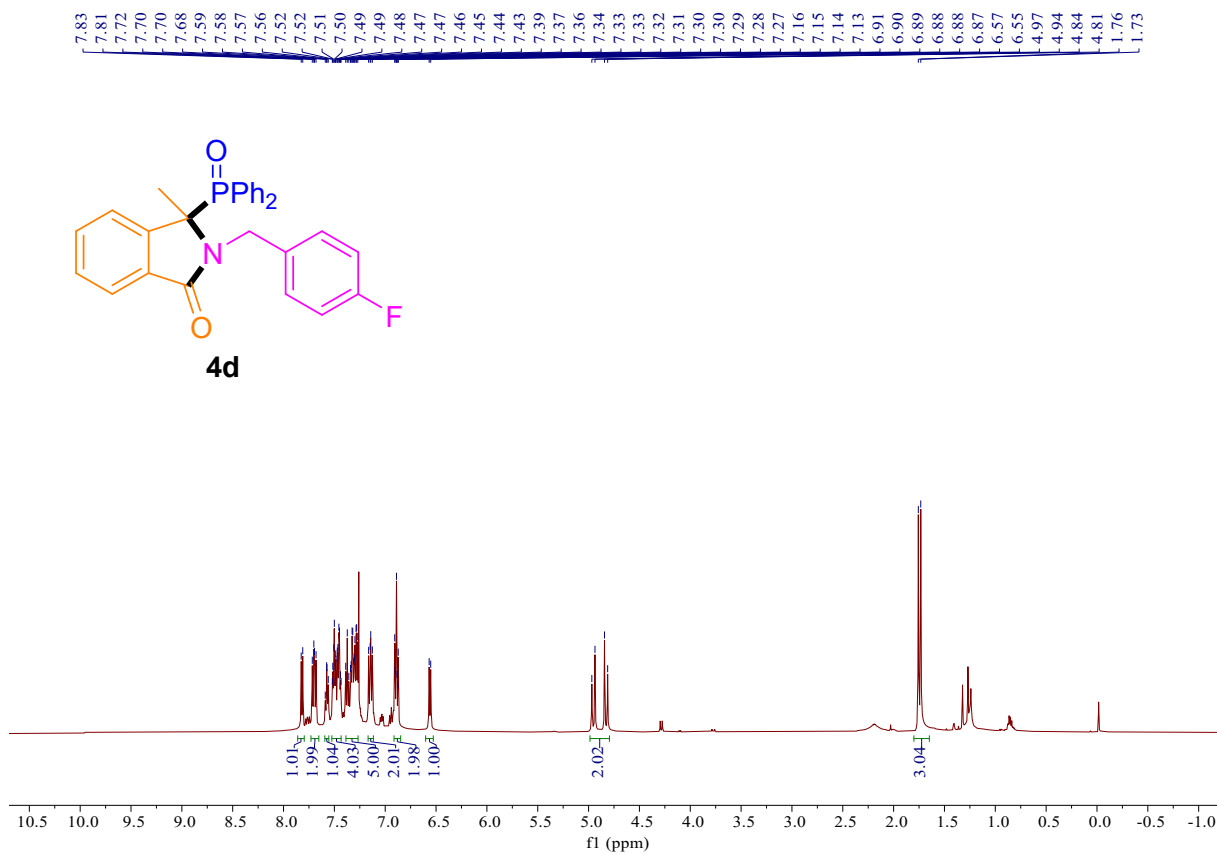
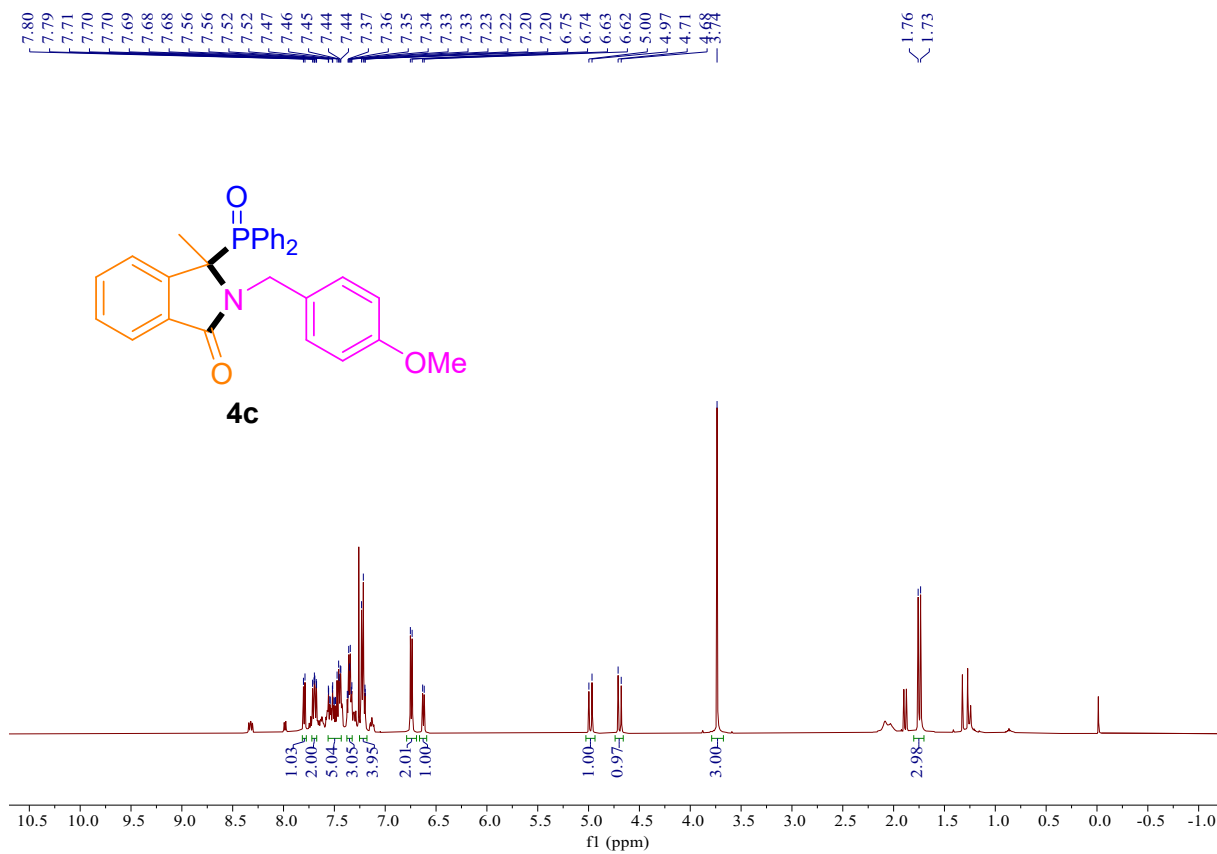
3-(diphenylphosphoryl)-2-hexyl-3-methylisoindolin-1-one (4p)

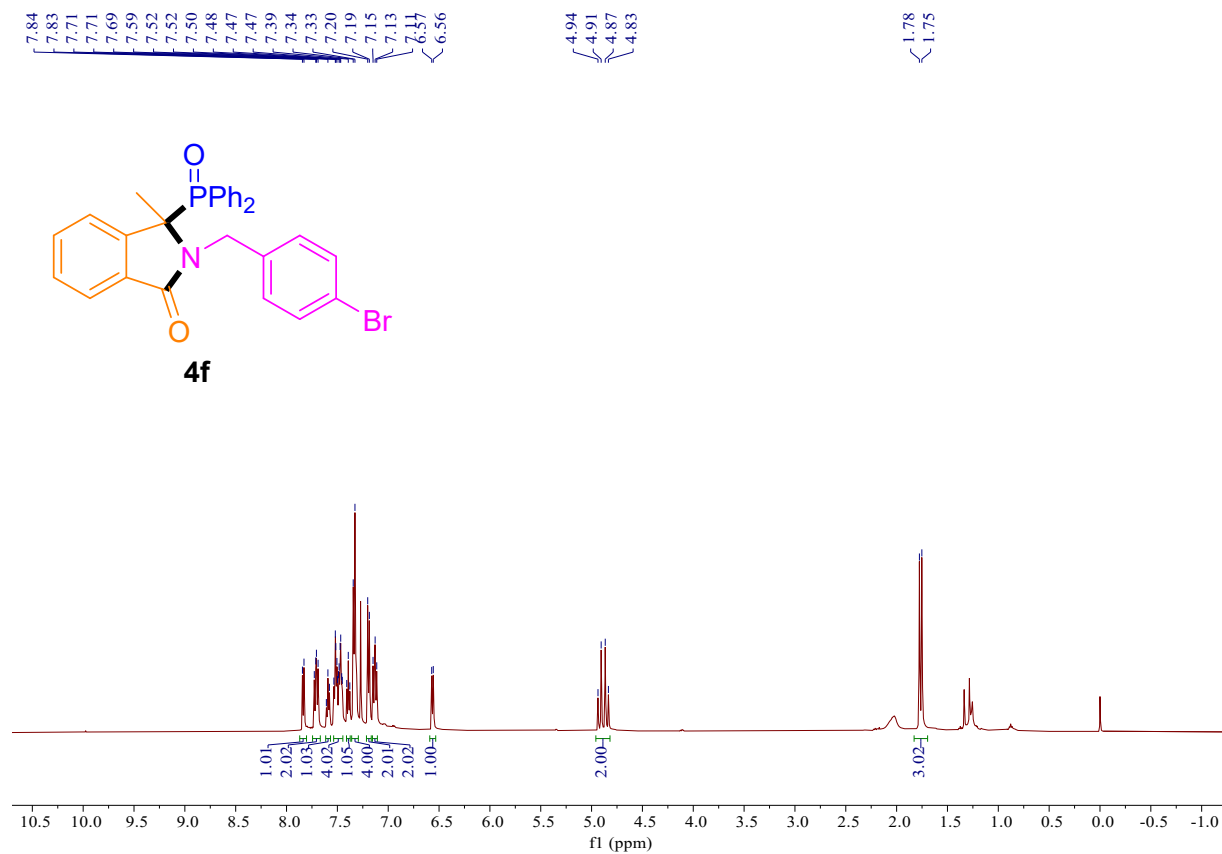
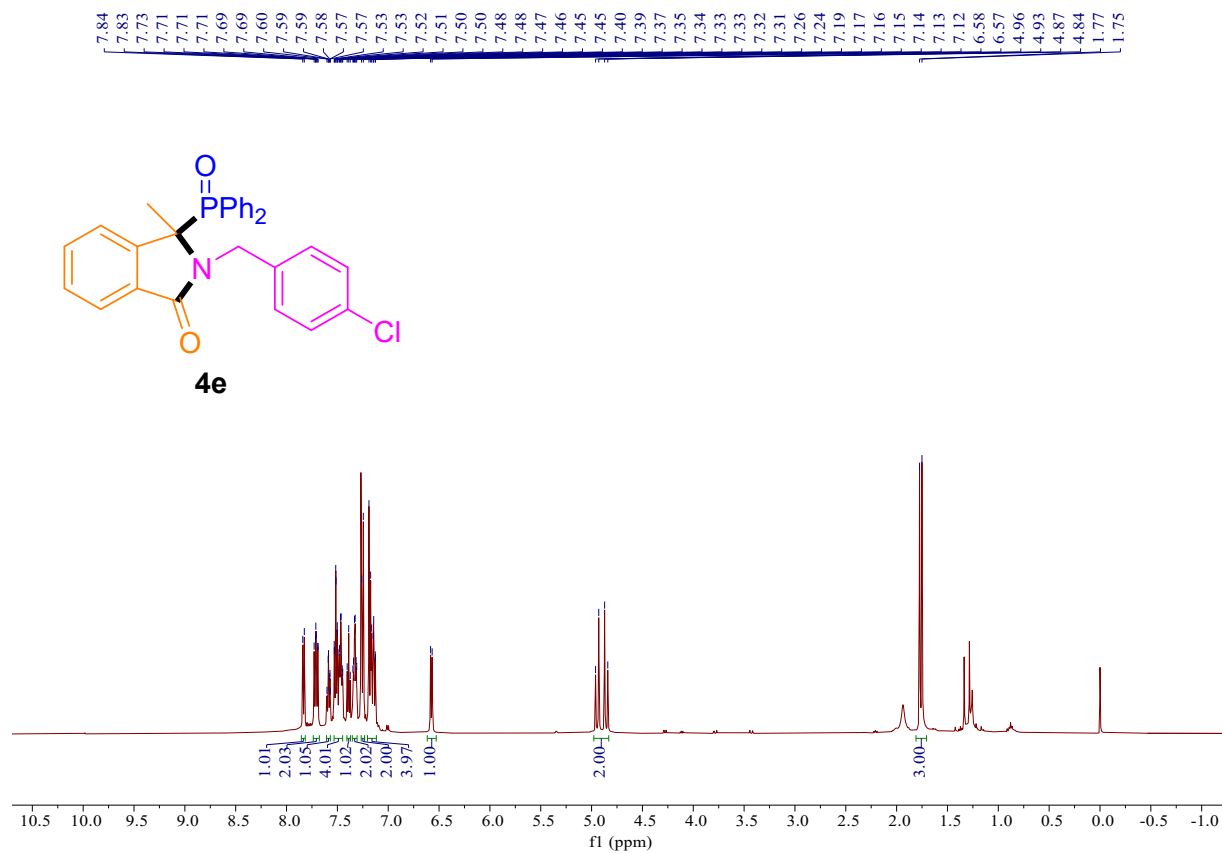
¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.66 (m, 3H), 7.58 – 7.54 (m, 1H), 7.53 – 7.49 (m, 1H), 7.48 – 7.40 (m, 3H), 7.39 – 7.30 (m, 3H), 7.27 – 7.18 (m, 2H), 6.70 (d, *J* = 7.7 Hz, 1H), 3.63 – 3.36 (m, 2H), 2.00 (d, *J* = 11.8 Hz, 3H), 1.78 – 1.67 (m, 1H), 1.51 – 1.43 (m, 1H), 1.24 (d, *J* = 7.9 Hz, 6H), 0.86 (t, *J* = 7.0 Hz, 3H).

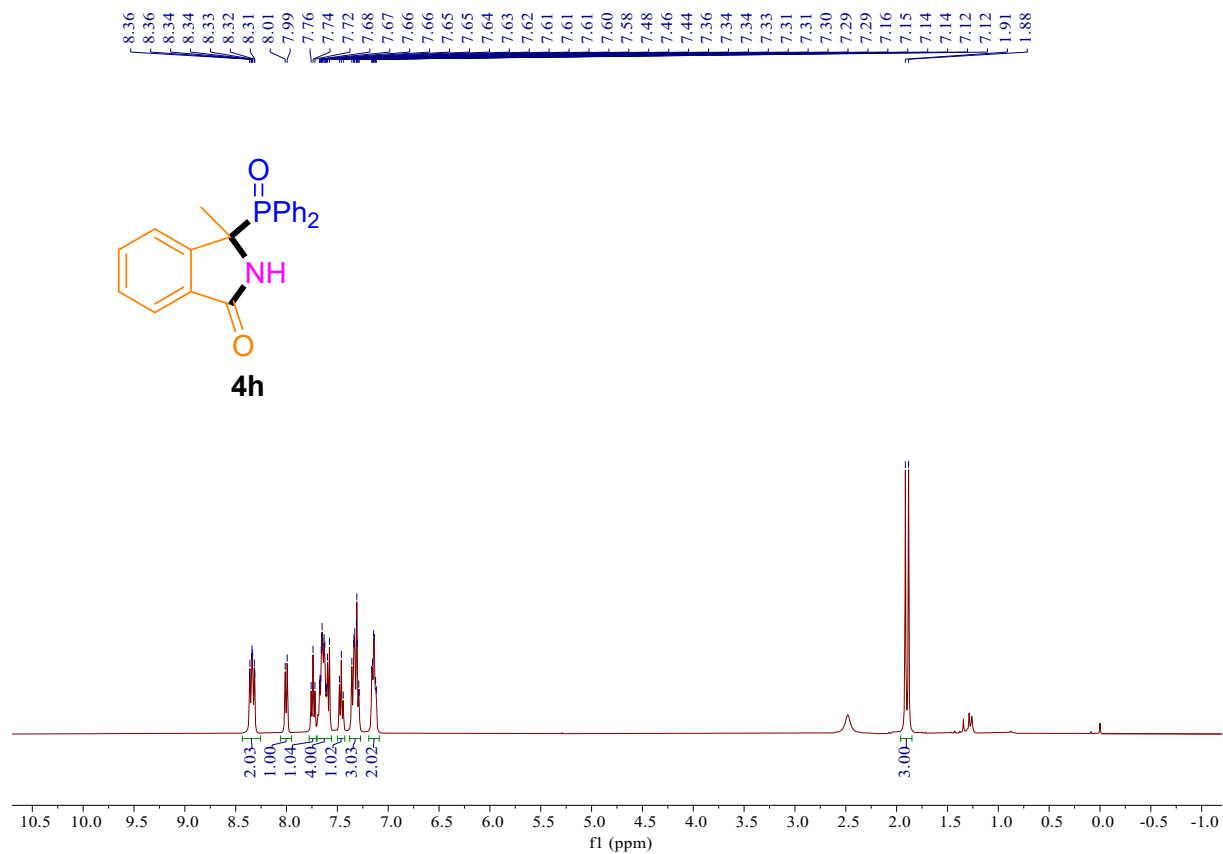
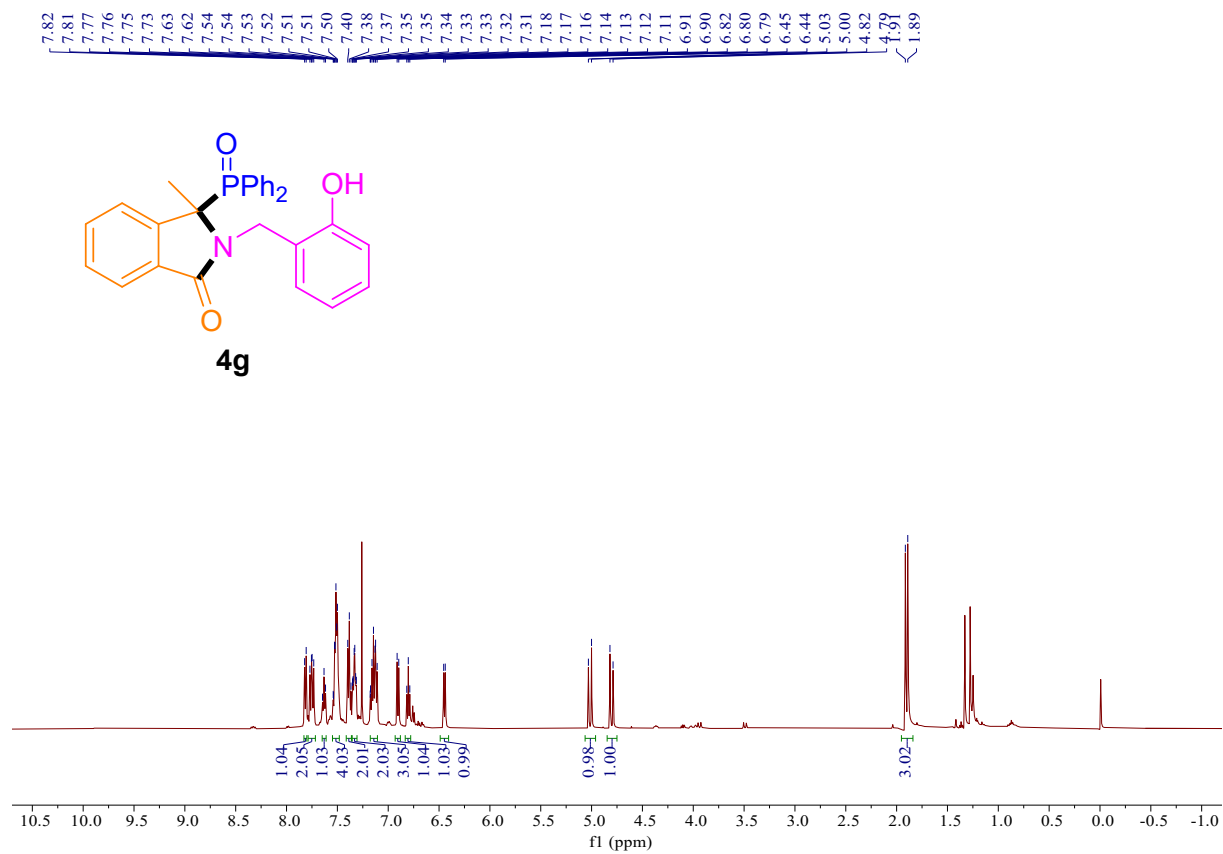
HRMS (ESI): *m/z*, calcd. for C₂₇H₃₀NO₂P [M+H]⁺ requires 432.2087, found 432.2084.

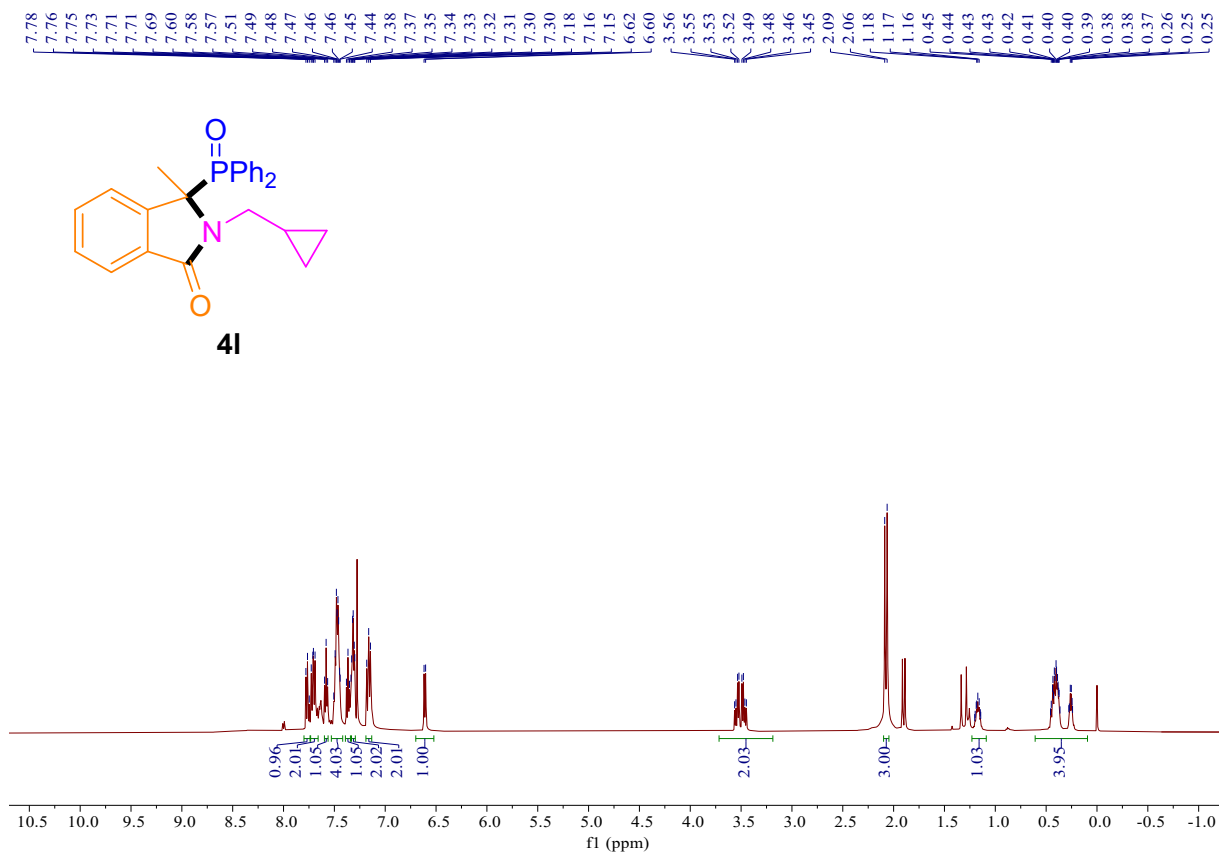
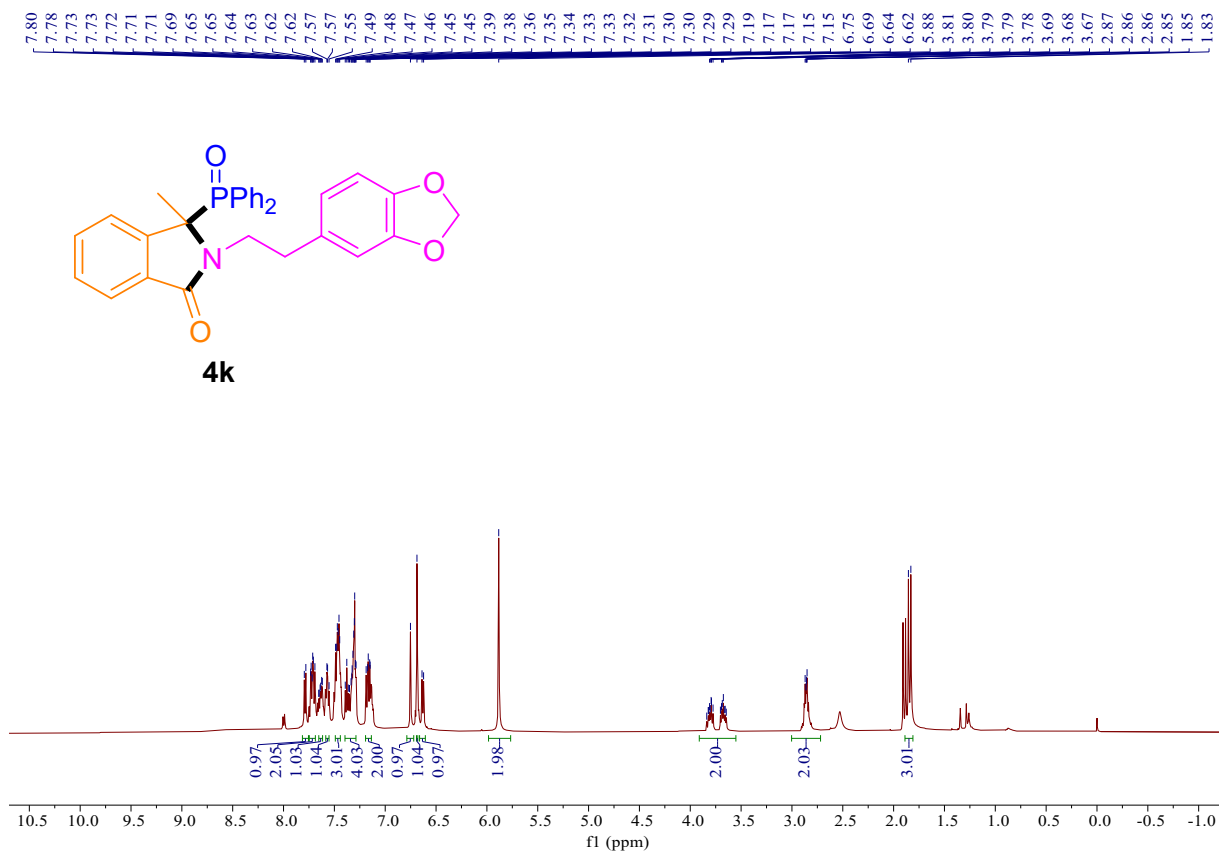
5. ¹H Spectra

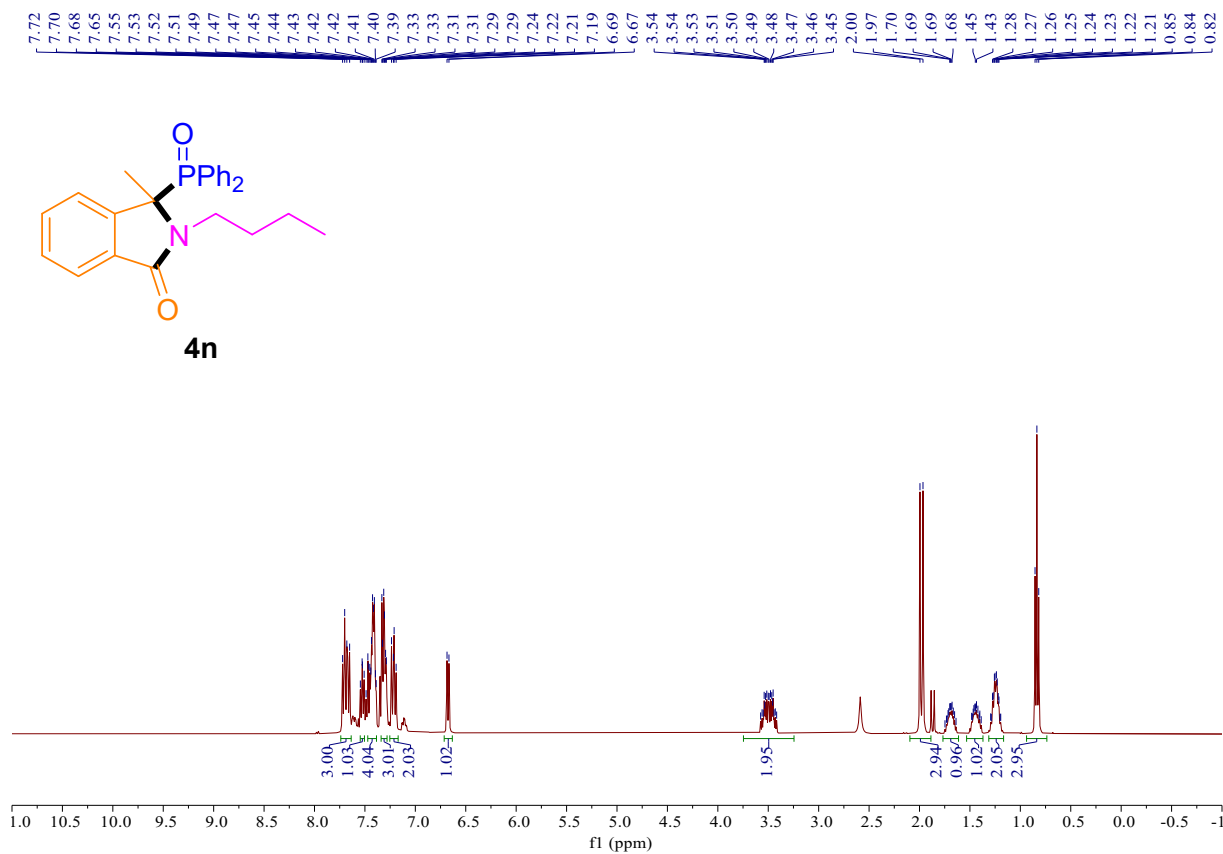
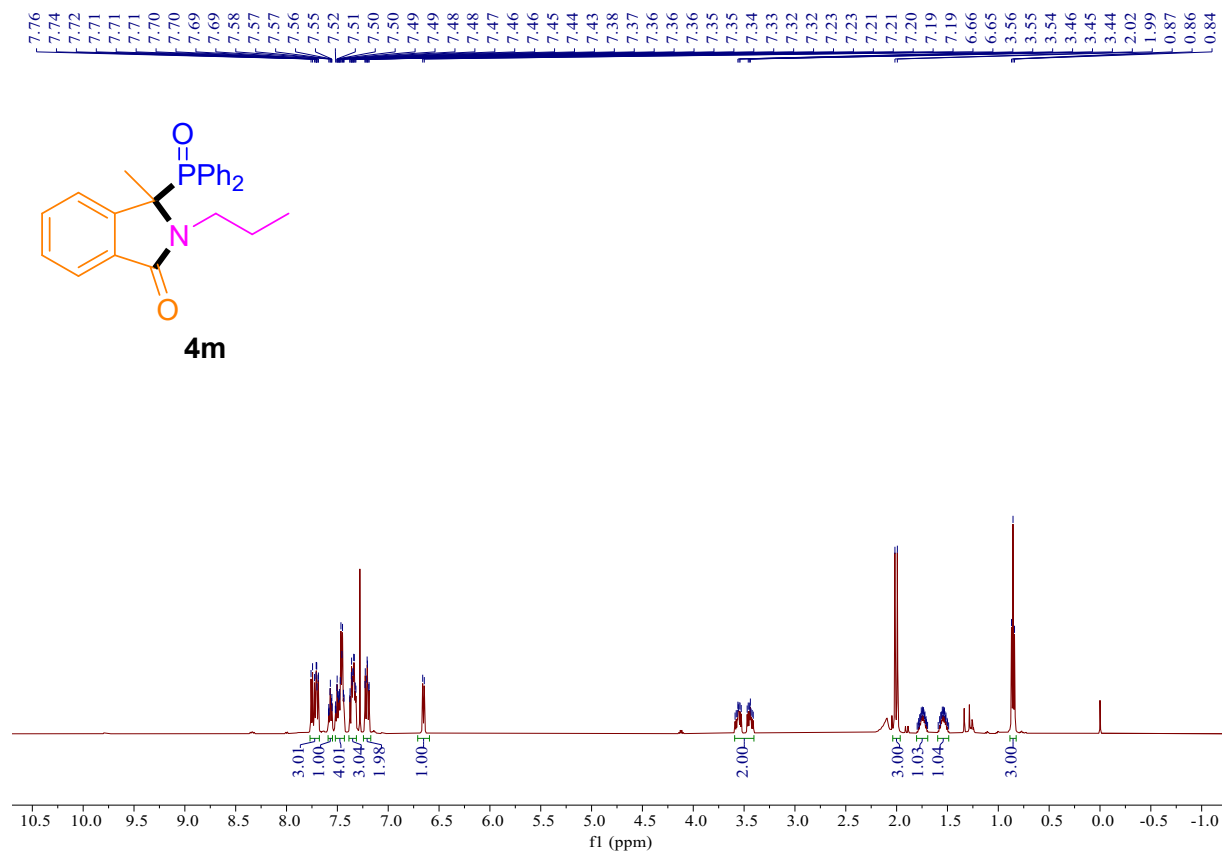


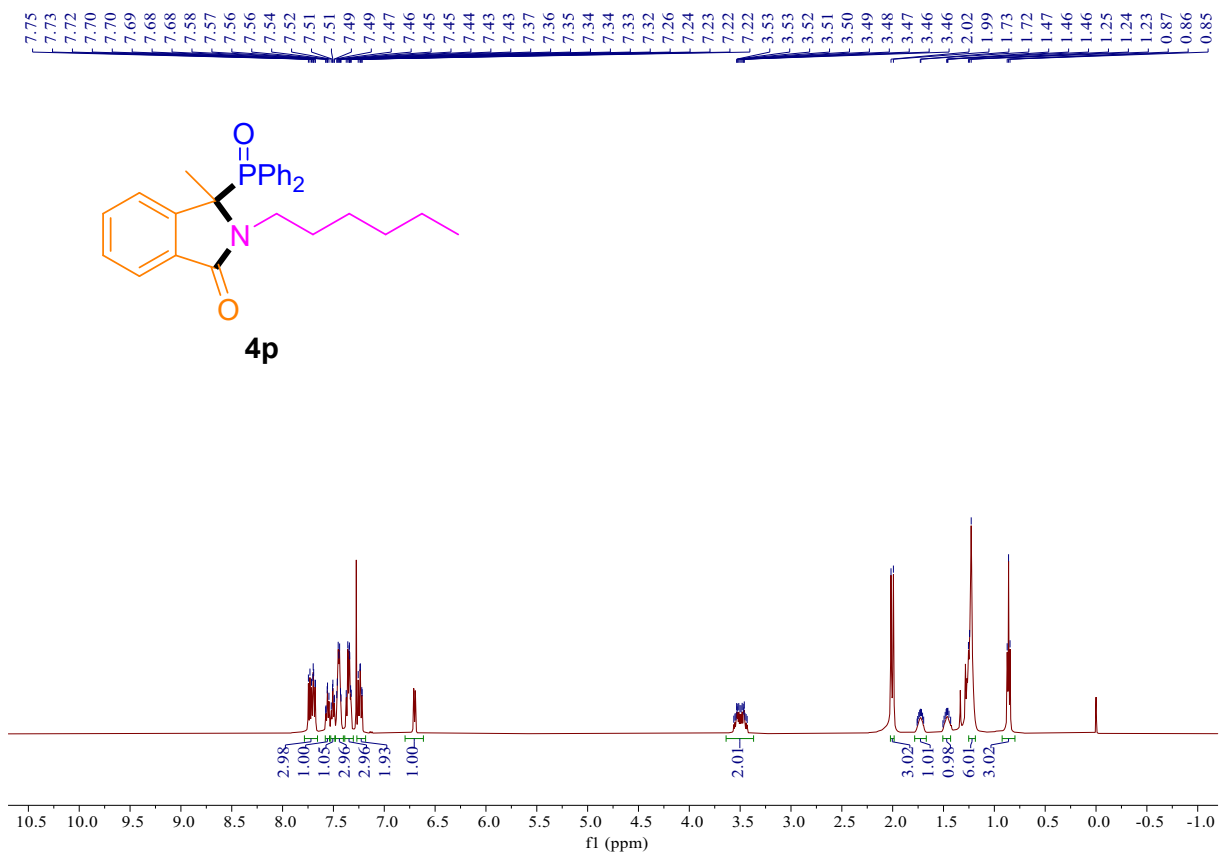
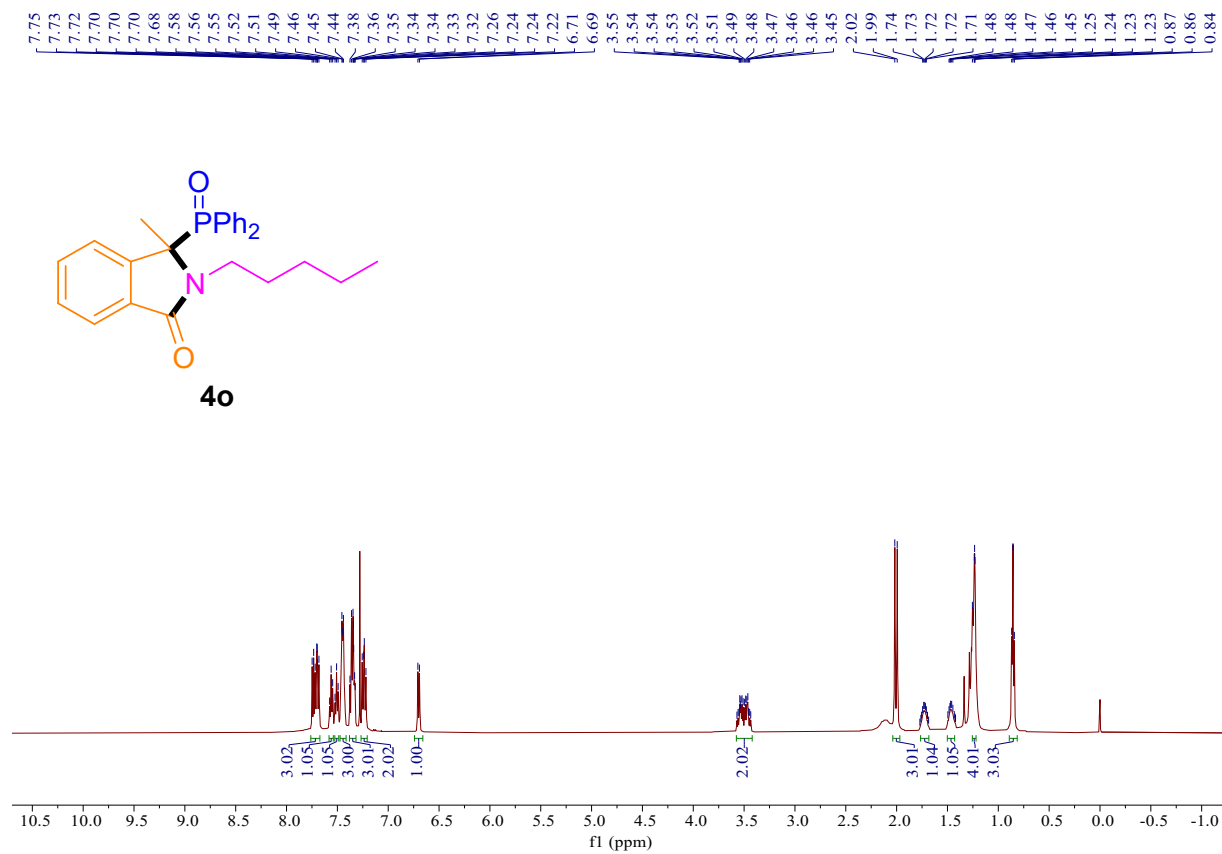












6. Notes and References

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- (2) (a) Spek, A. L. Single-Crystal Structure Validation with the Program *PLATON*. *J. Appl. Crystal.* **2003**, *36*, 7-13; (b) Spek, A. L. Structure Validation in Chemical Crystallography. *Acta Crystal.* **2009**, *D65*, 148-155; (c) Spek, A. L. What Makes a Crystal Structure Report Valid? *Inorg. Chim. Acta* **2018**, *470*, 232-237; (d) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H. *OLEX2*: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystal.* **2009**, *42*, 339-341; (e) Sheldrick, G. M. SHELXT—Integrated Space-Group and Crystal-Structure Determination. *Acta Crystal.* **2015**, *A71*, 3-8; (f) Sheldrick, G. M. Crystal Structure Refinement with *SHELXL*. *Acta Crystal.* **2015**, *C71*, 3-8.
- (3) (a) Brese, N.; O'keeffe, M. Bond-Valence Parameters for Solids. *Acta Crystal.* **1991**, *B47*, 192-197; (b) Brown, I.; Altermatt, D. Bond-Valence Parameters Obtained from a Systematic Analysis of the Inorganic Crystal Structure Database. *Acta Crystal.* **1985**, *B41*, 244-247.
- (4) Liu, Y. F.; Zeng, G. D.; Cheng, Y. T.; Chen, L.; Liu, Y. H.; Wei Y. G.; Yang, G. P. A $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ -catalyzed three-component tandem reaction for the synthesis of 3,3-disubstituted isoindolinones. *Chin. Chem. Lett.* **2024**, *35*, 108480