Supporting Information

A Porous Metal-Organic Cage Constructed from Dirhodium Paddle-Wheels: Synthesis, Structure and Catalysis

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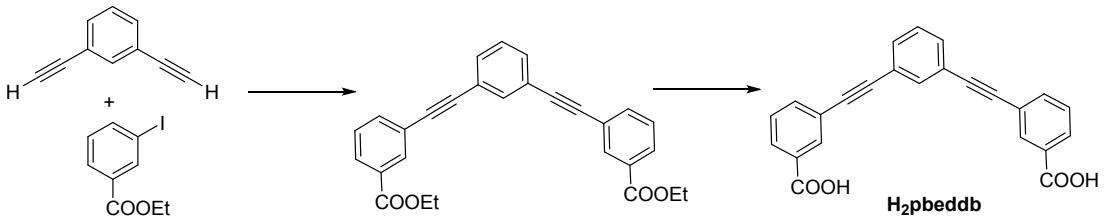
Contents

1. General Methods

All the reagents in the present work were obtained from the commercial source and used directly without further purification. The elemental analyses were performed with Perkin-Elmer 240 elemental analyzer. HRESI-MS was performed by using a Bruker Daltonics ESI-Q-TOF maXis4G. The data analyses of ESI-TOF mass spectra were processed on Bruker Data Analysis software and the simulations were performed on Bruker Isotope Pattern software. Infrared spectra on KBr pellets were collected with a Nicolet/Nexus-670 FT-IR spectrometer in the region of 4000-400 cm^{-1}. UV-vis spectra were tested on a Shimadzu/UV-3600 spectrophotometer. ^{1}H NMR were recorded on Varian/Mercury-Plus 300MHz or on Bruker AVANCE III 400MHz. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. PXRD patterns were recorded on SmartLab X-ray powder diffractometer (Rigaku Co.) at 40 kV and 30 mA with a Cu target tube. Thermogravimetric (TG) analyses were performed under an N_2 atmosphere at a heating rate of 10 $^{\circ}C$ min^{-1} by using a NETZSCH TG 209 system. X-ray photoelectron spectroscopy (XPS) was performed on a ULVAC PHI Quantera microprobe. Binding energies (BE) were calibrated by setting the measured BE of C 1s to 284.65 eV. ICP spectroscopy was conducted on a Spectro Ciros Vision ICP-OES spectrometer that is equipped with vacuum optics covering the spectral range from 175-777 nm, plasma power, 1300 w; coolant flow, 15.00 L/min; auxiliary flow, 0.80 L/min; nebulizer 0.70 L/min. The sorption isotherms for N_2 (77 K) and CO_2 (195 K) gas were measured with an Autosorb-iQ2-MP gas sorption analyzer (Quantachrome, USA). The samples are vacuumed at 110 °C for 6 h before the sorption examination.

Cautions! Although we have not experienced any problem in the handling of the azides (e.g. vinyl azides, dienyl azides and biaryl azides), extreme care should be taken when manipulating them due to their explosive nature.

2. Synthesis of the Ligand



The ligand was synthesized according to the reported procedure.[1] Under a nitrogen atmosphere, ethyl-3-iodobenzoate (3.0 mL, 15.75 mmol) was added to a solution of 1,3-diethynylbenzene (1.0 mL, 7.3 mmol) in deoxygenated distilled triethylamine (TEA, 25 mL) with $Pd(PPh_3)_4$ (250 mg, 0.22 mmol) and CuI (20.0 mg, 0.105 mmol) in a 100 mL Schlenk flask at room temperature. After stirred at reflux temperature for 48 hours, the reaction system was cooled to room temperature, to which a saturated aqueous solution of ammonium chloride and dichloromethane were added. The organic layer was separated and the aqueous layer was further extracted two times with dichloromethane. The combined organic layer was washed with brine and dried over sodium sulfate. After evaporation of the dichloromethane, the crude residue was purified by column chromatography on silica gel with ethyl acetate/hexane (20:1) as eluent to give 2.67 g of pure diethyl-3,3'-(1,3-phenylenebis(ethyne-2,1-diyl))dibenzoate as a white solid (87% yield based on 1,3-diethynylbenzene). Then the solid (2.0 g, 4.73 mmol) was dissolved in 30 mL of mixed solvent of THF and CH_3OH (v/v = 1:1), to which 15 mL of 3N NaOH aqueous solution was added. After the mixture was stirred at about 50 °C overnight, the organic phase was removed under reduced pressure. The aqueous phase was acidified with diluted hydrochloric acid to give white solid, which was filtered and washed with water to obtain pure 3,3'-[1,3-Phenylenebis(ethyne-2,1-diyl)]dibenzoic acid (yield: 1.58 g, 91%). ^{1}H NMR (400 MHz, DMSO-d^6) δ 13.30 (br s, 2H), 8.11 (s, 2H), 7.99 (d, 2H), 7.88 - 7.80 (m, 3H), 7.66 (d, 2H), 7.60 (t, 2H), 7.53 (t, 1H). FTIR (KBr) ν 2853(w), 2668(w), 1679(s), 1579(m), 1478(w), 1449(m), 1416(w), 1319(s), 1267(w), 917(w), 817(w), 754(m), 737(m), 679(m) cm^{-1}.

3. Synthesis, Crystal Structure and Characterizations of MOC-Rh-1

3.1 Synthesis

H_2pbeddb (18.3 mg, 0.05 mmol), $Rh_2(OAc)_4$ (8.8 mg, 0.02 mmol), Na_2CO_3 (6.0 mg 0.057 mmol) and 4 mL dimethylacetamide (DMAC) were placed in a glass vial, which was then sealed and heated to 100 ˚C in an oven. After 24 h, green block crystals were obtained (11.2 mg, 54% yield based on $Rh_2(OAc)_4$). Anal. Calcd. for $C_{124}H_{127}N_7O_{31}Rh_4$ (MOC-Rh-**1**·6H_2O·5DMAC): C, 56.78; H, 4.88, N, 3.74%; Found: C, 56.55; H,4.98; N, 3.85%. FTIR (KBr) *v* 3431 (s, br), 2919 (w), 1625 (m), 1606 (w), 1462 (w), 1425(w), 1387 (m), 1343 (w), 1082 (m. br), 784 (w) cm^{-1}.

3.2 Crystal Structure Determination

The X-ray diffraction data was collected with an Agilent Technologies SuperNova X-RAY diffractometer system for MOC-Rh-**1** equipped with $Cu_{k\alpha}$ radiation (λ = 1.54178 Å). The crystal was kept at 150.00(10) K during data collection. Using Olex2[2], the structure was solved with the ShelXS-97[3] structure solution program using Direct Methods and refined with the XL[4] refinement package using Least Squares minimization. The positions of the hydrogen atoms were generated geometrically. A summary of the crystal structure refinement data and selected bond angles and distances are listed in Table S1 and Table S2. Figures showing the three kinds of inter-cage π-π stacking interactions among the cages are shown in Figure S2. A summary of the interatomic distances in the inter-cage π-π stacking interactions is listed in Table S3.

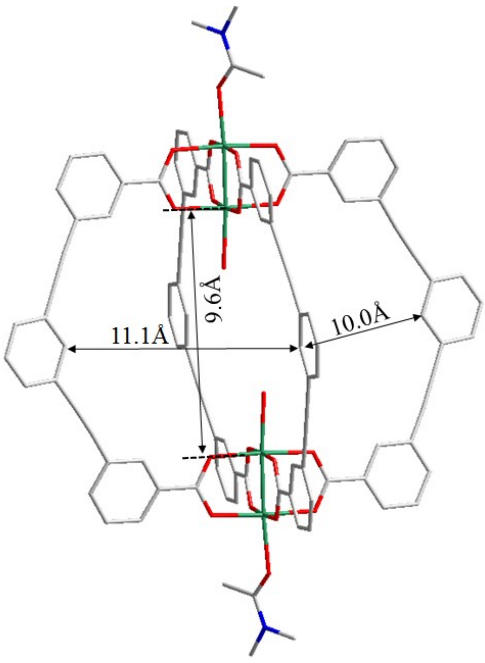
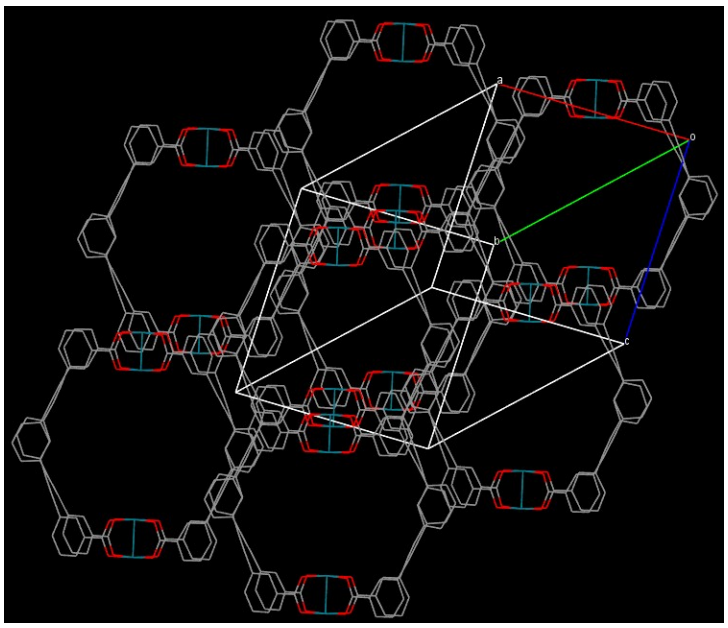


Figure S1. Representation of the window sizes of the cage.

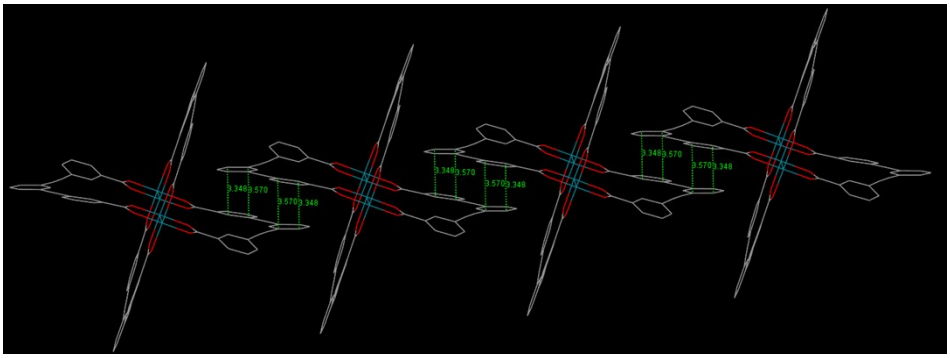
Table S1 Selected bond lengths (Å) and bond Angles (º) for MOC-Rh-**1**·2H_2O·3DMAC

Rh1-Rh2	2.3936(6)	O3-C40	1.273(7)
Rh1-O1	2.029(4)	O4-C40	1.263(8)
Rh1-O3	2.025(4)	O5-C34	1.263(8)
Rh1-O5	2.032(4)	O6-C34	1.274(8)
Rh1-O7	2.025(5)	O7-C1	1.268(9)
Rh1-O10	2.272(4)	O8-C1	1.265(9)
Rh2-O2	2.027(5)	O10-C55	1.173(9)
Rh2-O4	2.028(4)	N1-C55	1.297(10)
Rh2-O6	2.030(5)	N1-C56	1.433(13)
Rh2-O8	2.013(5)	N1-C57	1.424(12)
Rh2-O9	2.316(5)	O2-C16	1.267(8)
O1-C16	1.280(8)		
O1-Rh1- Rh2	88.67(12)	O4-Rh2-Rh1	88.34(12)
O1-Rh1-O5	176.37(16)	O4-Rh2-O6	88.51(18)
O1-Rh1- O10	87.58(17)	O4-Rh2-O9	94.28(18)
O3-Rh1 -Rh2	87.90(11)	O6-Rh2-Rh1	88.80(12)
O3-Rh1-O1	91.48(17)	O6-Rh2-O9	93.96(19)
O3-Rh1-O5	89.00(17)	O8-Rh2-Rh1	87.90(13)
O3-Rh1-O7	176.25(17)	O8-Rh2-O2	90.3(2)
O3-Rh1-O10	95.06(16)	O8-Rh2-O4	176.10(17)
O5-Rh1-Rh2	87.75(12)	O8-Rh2-O6	90.4(2)
O5-Rh1-O10	95.96(17)	O8-Rh2-O9	89.52(19)
O7-Rh1-Rh2	88.42(13)	O9-Rh2-Rh1	176.24(16)
O7-Rh1-O1	89.1(2)	C16-O1-Rh1	118.3(4)
O7-Rh1-O5	90.2(2)	C16-O2-Rh2	119.6(4)
O7-Rh1-O10	88.66(17)	C40-O3-Rh1	119.0(4)
O10-Rh1-Rh2	175.28(13)	C40-O4-Rh2	118.6(4)
O2-Rh2-Rh1	87.73(13)	C34-O5-Rh1	118.8(4)
O2-Rh2-O4	90.55(18)	C34-O6-Rh2	117.5(4)
O2-Rh2-O6	176.43(16)	C1-O7-Rh1	117.8(5)
O2-Rh2-O9	89.55(19)	C1-O8-Rh2	119.0(4)
		C55-O10-Rh1	133.5(5)

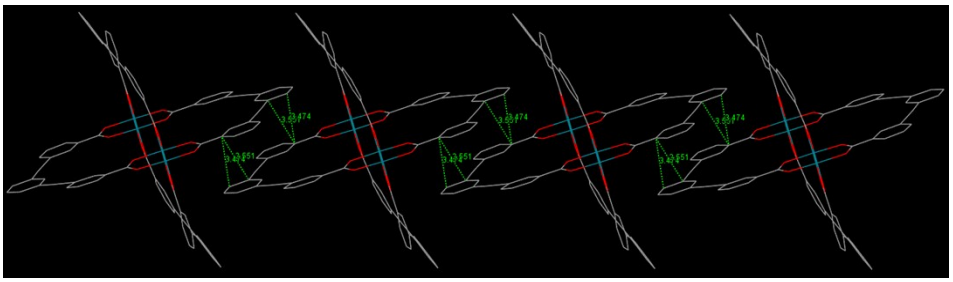
(a)



(b)



(c)



(d)

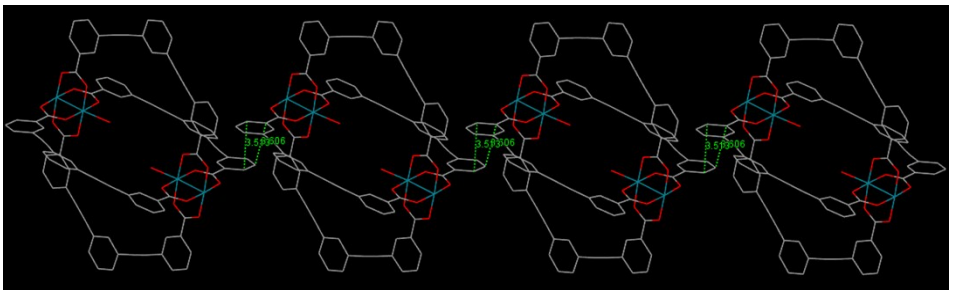


Figure S2. Solid-packing of discrete cages of MOC-Rh-**1** in the crystal lattice (a) and the three kinds of inter-cage π-π stacking interactions among the cages: type-I (b), type-II (c) and type-III (d). All hydrogen atoms and solvent molecules including those coordinated to Rh-Rh units are omitted for clarity.

Table S2 The interatomic distances (Å) in the inter-cage π-π stacking interactions observed in MOC-Rh-**1**.

Type-I		Type-II		Type-III	
C7···C13#	3.348	C17···C26#	3.474	C41···C43#	3.513
C6···C14#	3.570	C17···C25#	3.551	C42···C42#	3.606

3.3 Physical Characterizations

Table S3 Peaks in the solid UV-vis spectra of as-synthesized and activated samples of MOC-Rh-**1**.

	Peak1	Peak2
As-synthesized	453	587
Activated	452	595

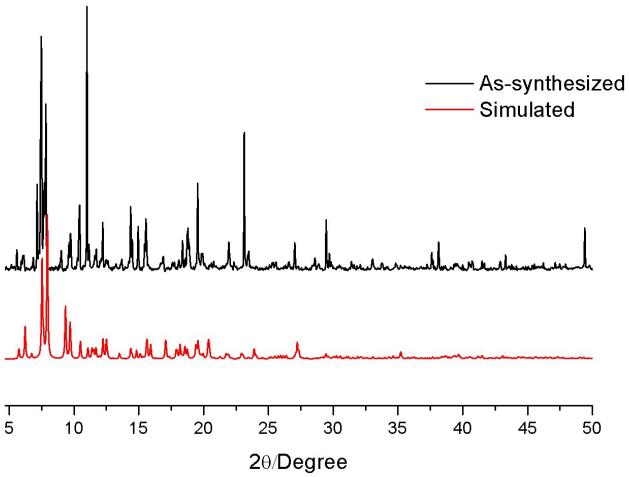


Figure S3. PXRD patterns of MOC-Rh-**1**.

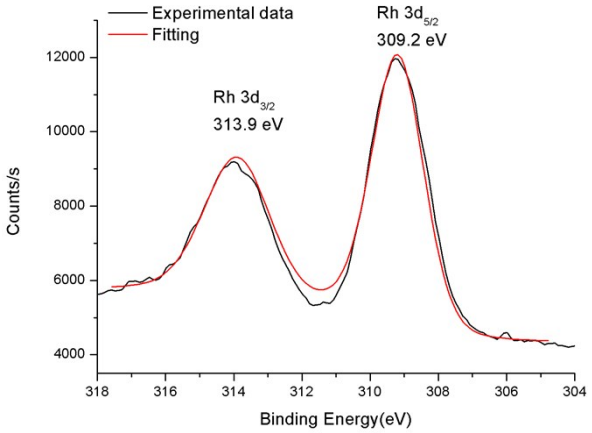
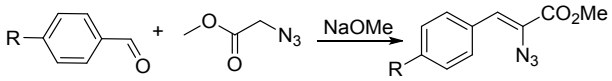


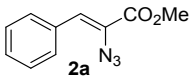
Figure S4. XPS spectra of Rh in MOC-Rh-**1** after catalysis.

4. Syntheses of Azides

4.1 Vinyl azides

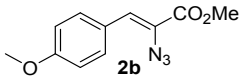


The vinyl azides were prepared in one step from the condensation of methyl azidoacetate and aromatic aldehydes following the method reported by Driver and co-workers:[5a] To a cooled (–20 °C) solution of NaOMe (0.601 g, 11.1 mmol, 1.52 equiv) in MeOH (4.0 mL) was added a solution of aldehyde (7.4 mmol, 1 equiv) and methyl azidoacetate (2.530 g, 22.3 mmol, 3 equiv) dropwise over 20 minutes. The resulting reaction mixture was warmed to –10 °C. After 4 h, the heterogeneous mixture was diluted with 20 mL of water and 20 mL of Et_2O. The phases were separated and the resulting aqueous phase was extracted with Et_2O (20 mL × 2). The combined organic phases were washed with distilled water (20 mL × 2) and brine (20 mL × 1). The resulting organic phase was dried over Na_2SO_4, concentrated under reduced pressure. The crude residue was purified by flash chromatography to afford pure product.



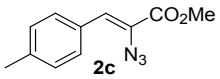
2a

(*Z*)-methyl 2-azido-3-phenylacrylate (**2a**). Light yellow low melting solid (0.67 g, 45%).[1]H NMR (400 MHz, $CDCl_3$) *δ* 7.81 (d, 2H), 7.31-7.41 (m, 3H), 6.92 (s, 1H), 3.92 (s, 3H).



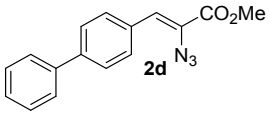
2b

(*Z*)-methyl 2-azido-3-(4-methoxyphenyl)acrylate (**2b**). Yellow solid (0.93 g, 54%). [1]H NMR (400 MHz, CDCl3) *δ* 7.78 (d, 2H), 6.91 (d, 2H), 6.88 (s, 1H), 3.90 (s, 3H), 3.83 (s, 3H).



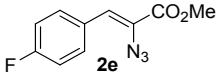
2c

(*Z*)-methyl 2-azido-3-(p-tolyl)acrylate (**2c**). Light yellow solid (0.78 g, 49%).[1]H NMR (400 MHz, $CDCl_3$) *δ* 7.71 (d, 2H), 7.20 (d, 2H), 6.90 (s, 1H), 3.90 (s, 3H), 2.37 (s, 3H).



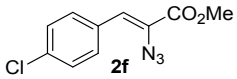
2d

(*Z*)-methyl 3-([1,1'-biphenyl]-4-yl)-2-azidoacrylate (**2d**). Pale yellow solid (0.80 g, 39%).[1]H NMR (400 MHz, $CDCl_3$) *δ* 7.93 (d, 2H), 7.66 (d, 4H), 7.49 (t, 2H), 7.40 (t, 1H), 6.99 (s, 1H), 3.96 (s, 3H).

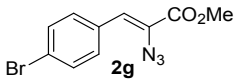


2e

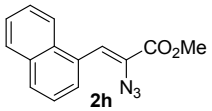
(*Z*)-methyl 2-azido-3-(4-fluorophenyl)acrylate (**2e**). Yellow solid (0.87 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84(d, 2H), 7.07 (d, 2H), 6.89 (s, 1H), 3.90 (s, 3H).



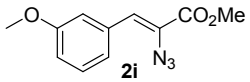
(*Z*)-methyl 2-azido-3-(4-chlorophenyl)acrylate (**2f**). Yellow solid (0.89 g, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, 2H), 7.35 (d, 2H), 6.84 (s, 1H), 3.91 (s, 3H).



(*Z*)-methyl 2-azido-3-(4-bromophenyl)acrylate (**2g**). Yellow solid (0.91 g, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, 2H), 7.52 (d, 2H), 6.84 (s, 1H), 3.92 (s, 3H).



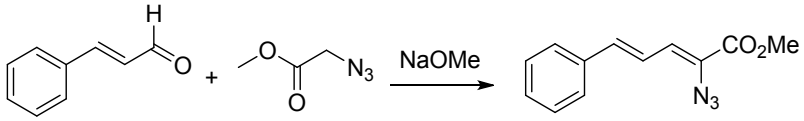
(*Z*)-methyl 2-azido-3-(naphthalen-1-yl)acrylate (**2h**). Yellow solid (0.83 g, 44%).^{1}H NMR 400 MHz, $CDCl_3$) δ 8.10 (d, 1H), 8.04 (d, 1H), 7.87 (t, 2H), 7.70 (s, 1H), 7.55 (m, 3H), 3.98 (s, 3H).



(*Z*)-methyl 2-azido-3-(3-methoxyphenyl)acrylate (**2i**). Yellow solid (0.88 g, 51%).^{1}H NMR 400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.37-7.27 (m, 2H), 6.87-6.93 (m, 2H), 3.92 (s, 3H), 3.84 (s, 3H).

4.2 Dienyl Azides

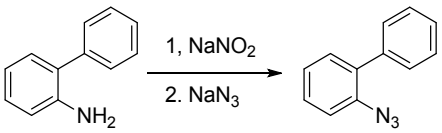
The dienyl azides were prepared following the method reported by Driver and co-workers.[5b]



To a cooled (–22 °C) solution of NaOMe (0.247 g, 4.57 mmol, 1.52 equiv) in .1.5 mL MeOH was added a solution of cinnamaldehyde (0.50 mL, 3.97 mmol, 1 equiv) and methyl azidoacetate (1.83 g, 15.9 mmol, 4 equiv) dropwise over 1 hour. The resulting reaction mixture was warmed to –10 °C. After 4 h, the heterogeneous mixture was diluted with 10 mL of water and 10 mL of Et_2O. The phases were separated and the resulting aqueous phase was extracted with Et_2O (10 mL × 2). The combined organic phases were washed with distilled water (10 mL × 2) and brine (10 mL × 1). The resulting organic phase was dried over Na_2SO_4, and the heterogeneous mixture was filtered. The filtrate was concentrated *in vacuo*. The crude residue was purified by flash chromatography (0:100 – 30:70 EtOAc:hexanes) to afford pure product as a yellow solid (0.391 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.50 (m, 2H), 7.28-7.38 (m, 3H),7.17(dd, 1H), 6.74-6.84 (m, 2H),3.88 (s, 3H).

4.3 Biaryl Azides

The biaryl azides were prepared following the method reported by Driver and co-workers.[5c]



In a 20 mL scintillation vial, 2-aminobiphenyl (3.00 g, 17.73 mmol, 1.0 equiv) was dissolved in 60 mL of HOAc and 30 mL of H_2O and chilled in an ice bath. $NaNO_2$ (1.61 g, 23.34 mmol, 1.4 equiv) was added slowly, and the resulting mixture was stirred at 0 °C for one hour. NaN_3 (1.63 g, 25.13 mmol, 1.5 equiv) was then added slowly, and the resulting mixture was warmed to ambient temperature, and stirred for 30 minutes. The solution was diluted with 20 mL of water and 20 mL of CH_2Cl_2 and basified by the slow addition of K_2CO_3 until bubbling ceased. The phases were separated and the aqueous phase was extracted with an additional 2 × 20 mL of CH_2Cl_2. The combined organic phases were washed 1 × 20 mL of water and 1 × 20 mL of brine. The resulting organic phase and dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo* to afford an oil. The crude product was purified by flash chromatography (0:100 – 30:70 EtOAc:hexanes) to afforded the product as a gray solid(3.12 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.36 (m, 7H), 7.30-7.23 (m, 2H);

5. Catalysis results of different catalyst

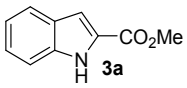
Table S4 Catalytic C-H amination results of different catalyst[a].

Entry	Catalyst	mol (%)	Conversion (%)
1	MOC-Rh-**1**	2	100
2	$Cu_4(pbeddb)_4$[b]	2	<1
3	$Rh_2(OAc)_4$	4	11
4	$RhCl_3$	8	< 1

[a]Reaction conditions: 2 mol% of the catalyst, 60 °C, 16 h, toluene. The yields are isolated yields. The conversions of the reactions were monitored by ^{1}H NMR. [b] The $Cu_4(pbeddb)_4$ sample was synthesized as reported by Lah and coworkers,[6] and activated by heating at 110 °C under vacuum for 6 h, the same as that of MOC-Rh-**1**.

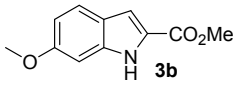
6. Substrate Scope

The typical procedure for the catalytic C-H amination is illustrated using the reaction with 2a as an example: A mixture of 2a (0.030 g, 0.15 mmol) and activated MOC-Rh-**1** (0.006 g, 0.003 mmol, 2 mol%) in toluene (0.75 mL) was heated to 60 °C. After 14 h, the reaction mixture was cooled to room temperature. The undissolved catalyst was removed through centrifugation, and washed with ethyl acetate (5 mL× 2). The combined supernatant was evaporated to dryness. The NMR yield was obtained through the addition of CH_2Br_2 (10.4 µL, 0.15 mmol) as the internal standard. After that, the reaction mixture was separated by flash chromatography (1:20 EtOAc:hexanes) to obtain pure product methyl 1*H*-indole-2-carboxylate (**3a**) as white solid (24.7 mg, 94%).



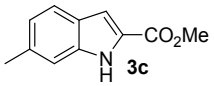
3a

Methyl 1*H*-indole-2-carboxylate (**3a**). White solid (24.7 mg, 94%). The spectral data matched that reported by Driver and co-workers:[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (br s, 1H), 7.70 (d, 1H), 7.43 (d, 1H), 7.33 (t, 1H), 7.23 (s, 1H), 7.16 (t, 1H), 3.95 (s, 1H). HR-MS (ESI$^-$) m/z calcd. for $C_{10}H_8NO_2$ $[M-H]^-$: 174.0561, found: 174.0535.

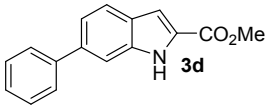


3b

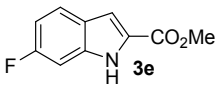
Methyl 6-methoxy-1*H*-indole-2-carboxylate (**3d**). White solid (27.9 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (br s, 1H), 7.55 (d, 1H), 7.16 (s, 1H), 6.83 (m, 2H), 3.92 (s, 3H), 3.86 (s, 3H). HR-MS (ESI$^-$) m/z calcd. for $C_{11}H_{10}NO_3$ $[M-H]^-$: 204.0666, found: 204.0656.



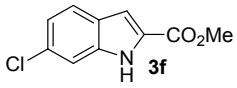
Methyl 6-methyl-1*H*-indole-2-carboxylate (**3b**). White solid (25.4 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (br s, 1H), 7.57 (d, 1H), 7.18 (m, 2H), 6.99 (d, 1H), 3.93 (s, 3H), 2.47 (s, 3H). HR-MS (ESI^-) m/z calcd. for $C_{11}H_{10}NO_2$ $[M-H]^-$: 188.0717, found: 188.0716.



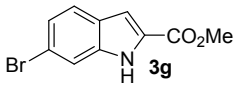
Methyl 6-phenyl-1*H*-indole-2-carboxylate (**3c**). White solid (23.3 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (br s, 1H), 7.74 (d, 1H), 7.65 (d, 2H), 7.61 (s, 1H), 7.44 (m, 3H), 7.36 (m, 1H), 7.25 (m, 1H), 3.96 (s, 3H). The spectral data matched that reported by Bonnamour and co-workers.[6] HR-MS (ESI^-) m/z calcd. for $C_{16}H_{12}NO_2$ $[M-H]^-$:250.0874, found: 250.0865.



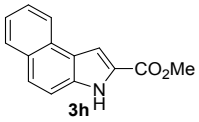
Methyl 6-fluoro-1*H*-indole-2-carboxylate (**3e**). White solid (26.6 mg, 92%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (br s, 1H), 7.62 (d, 1H), 7.20 (s, 1H), 7.09 (d, 1H), 6.94 (m, 1H), 3.94 (s, 3H). HR-MS (ESI^-) m/z calcd. for $C_{10}H_7FNO_2$ $[M-H]^-$:192.0466, found: 192.0469.



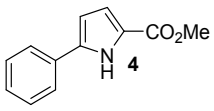
Methyl 6-chloro-1*H*-indole-2-carboxylate (**3f**). White solid (26.9 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (br s, 1H), 7.60 (d, 1H), 7.42 (s, 1H), 7.19 (s, 1H), 7.13 (d, 1H), 3.95 (s, 3H). HR-MS (ESI^-) m/z calcd. for $C_{10}H_7ClNO_2$ $[M-H]^-$:208.0171, found: 208.0174.



Methyl 6-bromo-1*H*-indole-2-carboxylate (**3g**). White solid (29.6 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (br s, 1H), 7.59 (s, 1H), 7.55 (d, 1H), 7.27 (d, 1H), 7.19 (s, 1H), 3.96 (s, 3H). HR-MS (ESI^-) m/z calcd. for $C_{10}H_7BrNO_2$ $[M-H]^-$: 251.9666, found: 251.9665.

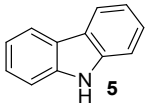


Methyl 3H-benzo[e]indole-2-carboxylate (**3h**). White solid (29.7 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (br s, 1H), 8.24 (d, 1H), 7.90(d, 1H), 7.72 (m,2H), 7.60 (t, 1H), 7.50(m, 2H), 3.99 (s, 3H);



4

Methyl 5-phenyl-1H-pyrrole-2-carboxylate (**4**). White solid (29.5 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (br s, 1H), 7.61 – 7.52 (m, 2H), 7.39-7.44 (m, 2H), 7.29-7.33 (m, 1H), 6.97-6.97 (m, 1H), 6.58 – 6.52 (m, 1H), 3.88 (s, 3H).



5

9*H*-Carbazole (**5**). White solid (23.0 mg, 92%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (br s, 1H), 7.96 (d, 2H), 7.55 – 7.25 (m, 4H), 7.09 (t, 2H).

7. Recycling Experiments

Table S5. Recycling experiments

Run	Conversion (%)
1	99
2	99
3	98
4	96
5	98
6	98
7	94
8	99
9	93
10	78

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1. J. R. Li, A. A. Yakovenko, W. G. Lu, D. J. Timmons, W. J. Zhuang, D. Q. Yuan and H. C. Zhou, *J. Am. Chem. Soc.*, 2010, **132**, 17599-17610
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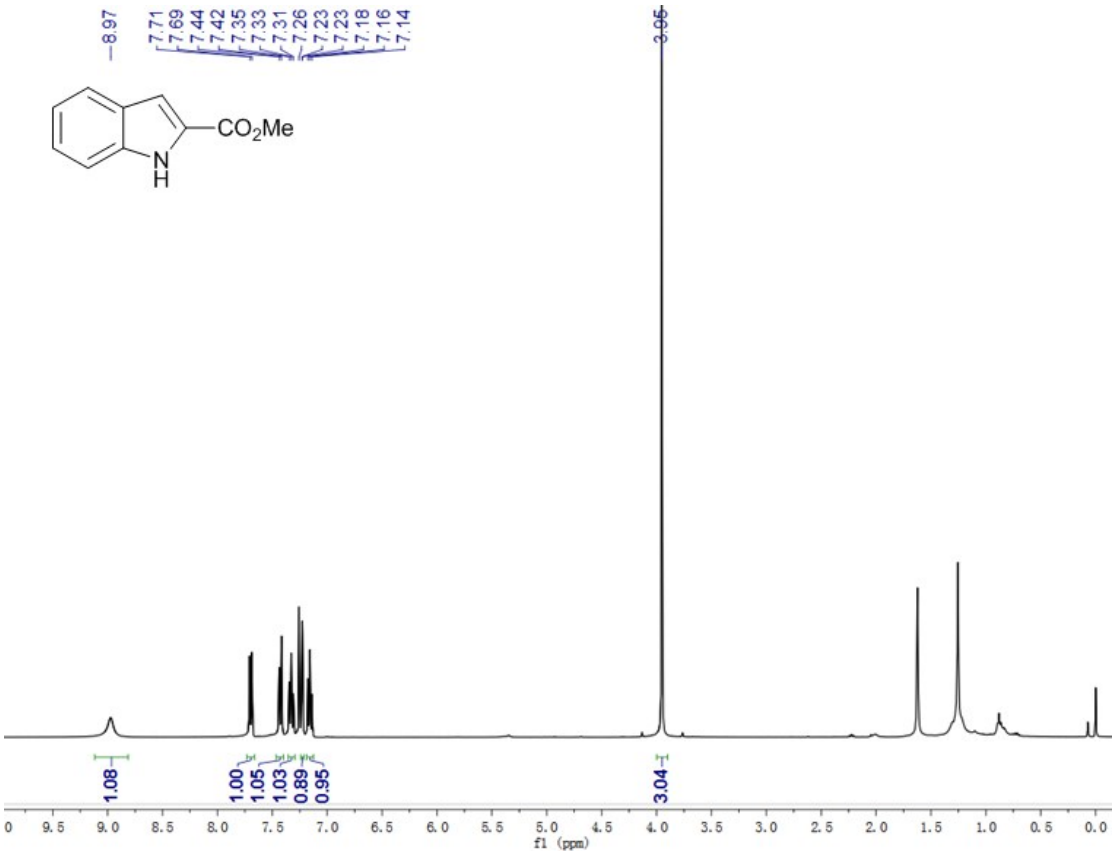
5. (a) B. J. Stokes, H. J. Dong, B. E. Leslie, A. L. Pumphrey and T. G. Driver, *J. Am. Chem. Soc.*, 2007, **129**, 7500-7501. (b) H. Dong, M. Shen, J. E. Redford, B. J. Stokes, A. L. Pumphrey and T. G. Driver, *Org. Lett.*, 2007, **9**, 5191-5194. (c) B. J. Stokes, B. Jovanovic, H. J. Dong, K. J. Richert, R. D. Riell and T. G. Driver, *J. Org. Chem.,* 2009, **74**, 3225-3228.
6. M. J. Prakash, M. Oh, X. Liu, K. N. Han, G. H. Seong and M. S. Lah, *Chem. Commun*., 2010, **46**, 2049-2051.
7. J. Bonnamour and C. Bolm, *Org. Lett.* 2011, **13**, 2012-2014.

Appendix I

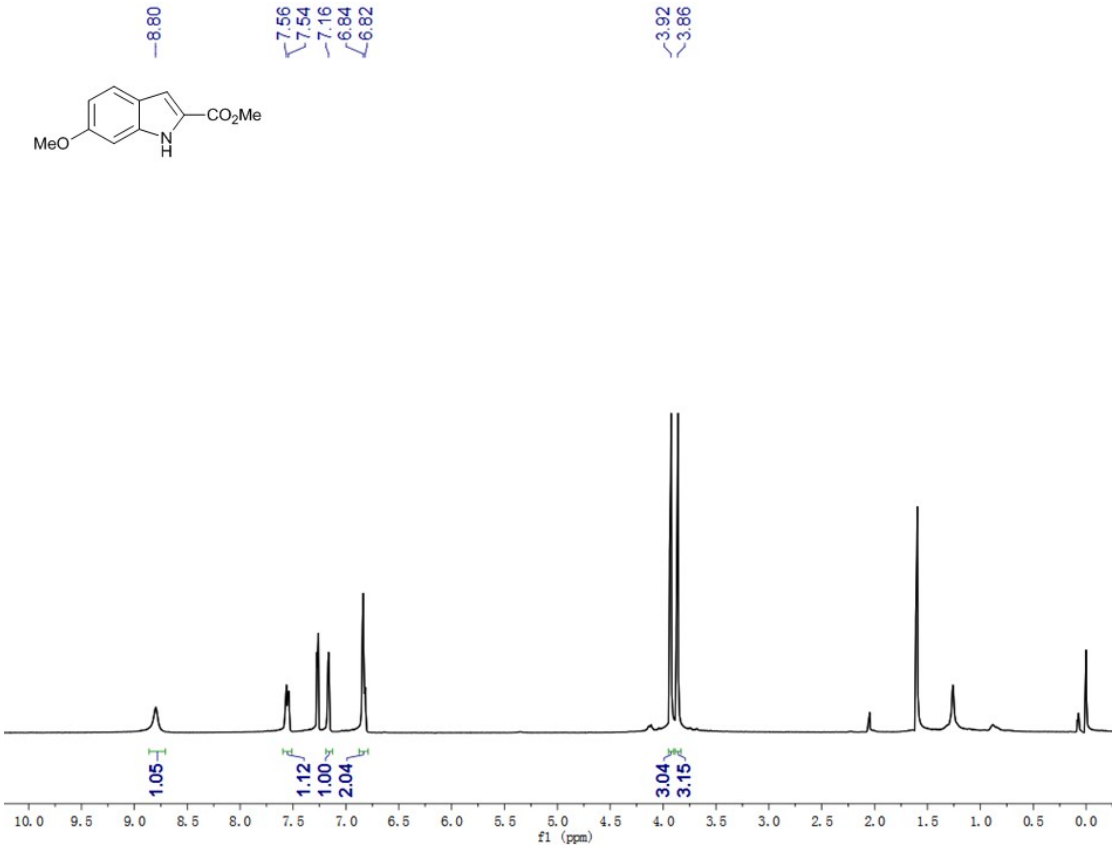
Spectral Copies of ^{1}H NMR of Catalysis products in this Study

Methyl 1*H*-indole-2-carboxylate



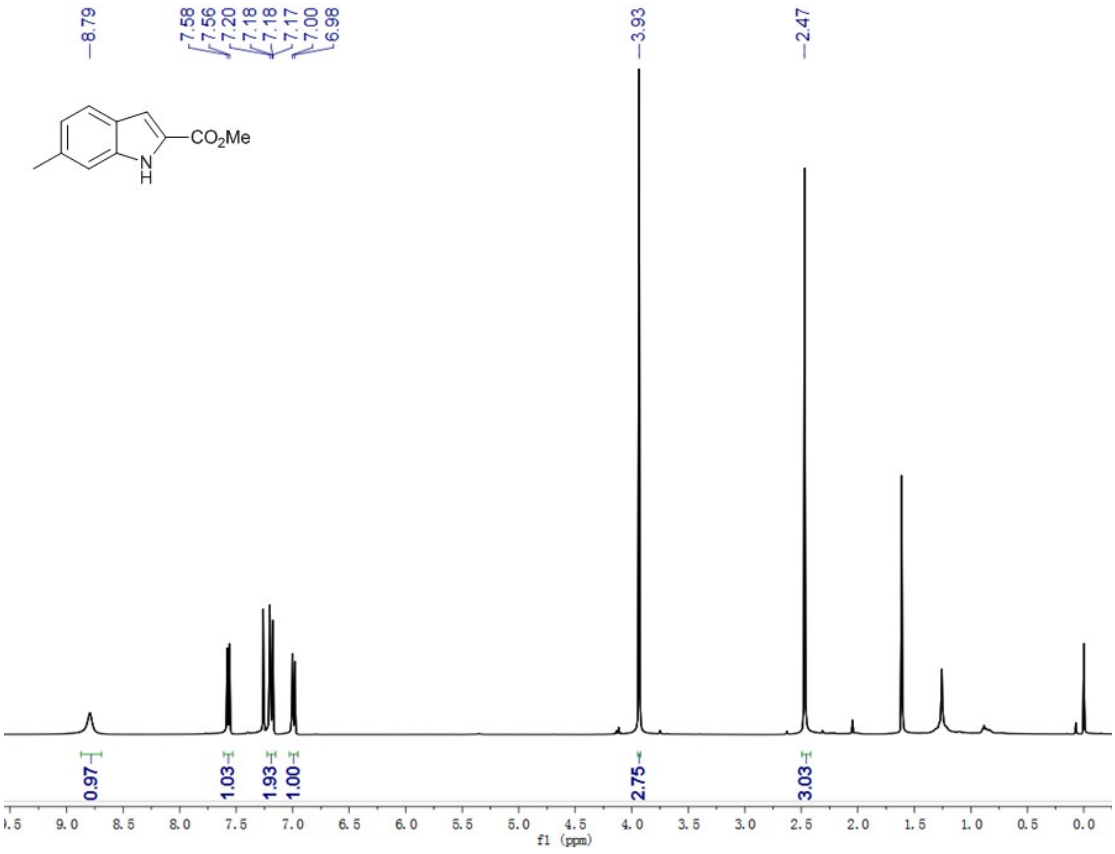
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **3a**.

Methyl 6-methoxy-1*H*-indole-2-carboxylate



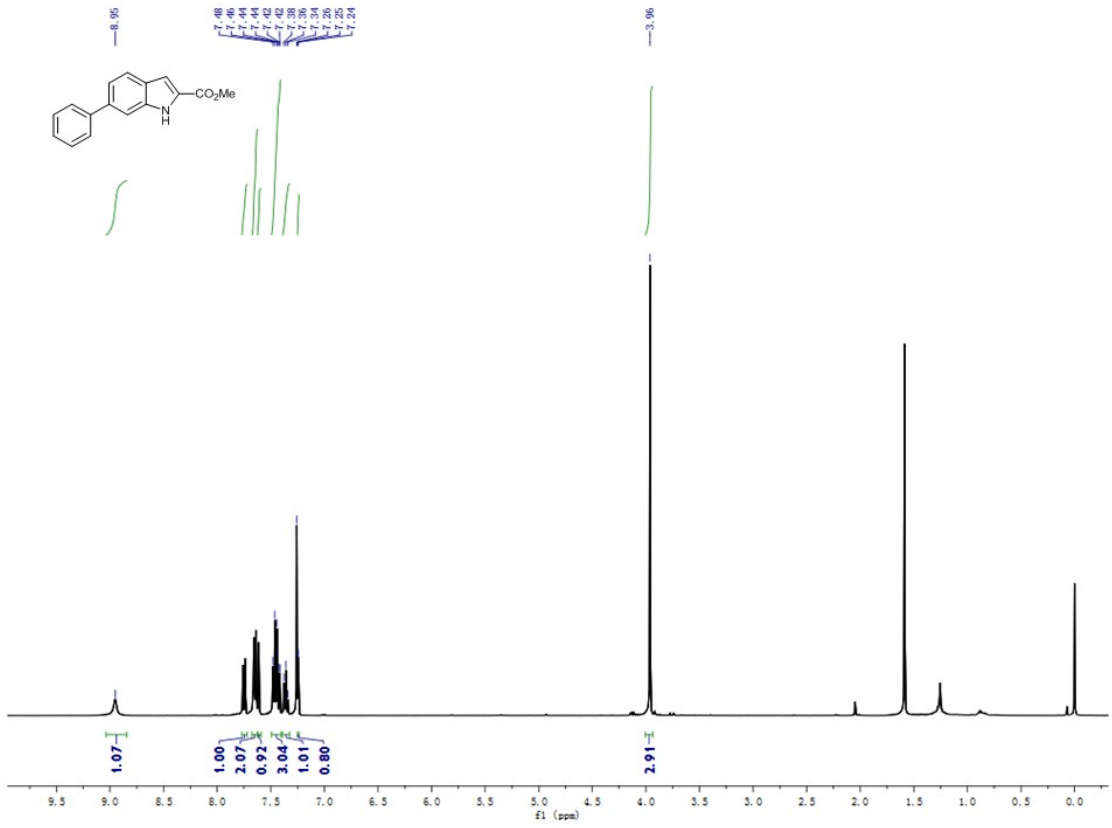
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **3b**.

Methyl 6-methyl-1*H*-indole-2-carboxylate



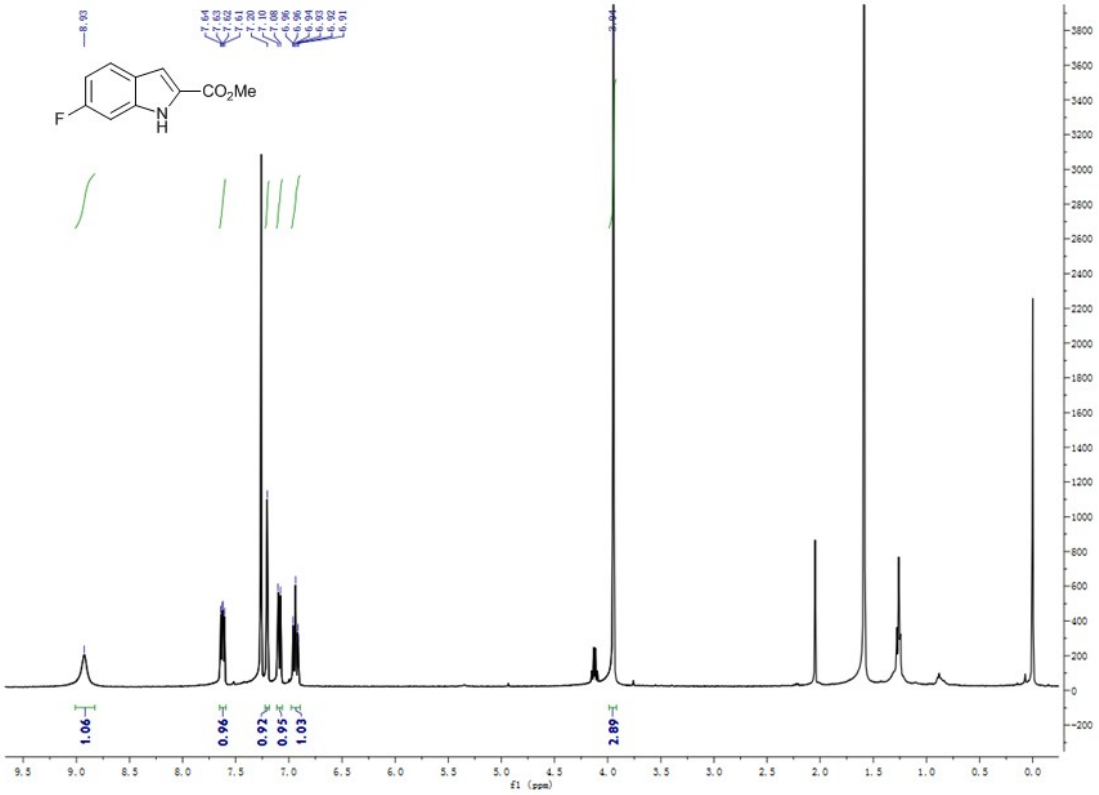
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **3c**.

Methyl 6-phenyl-1*H*-indole-2-carboxylate



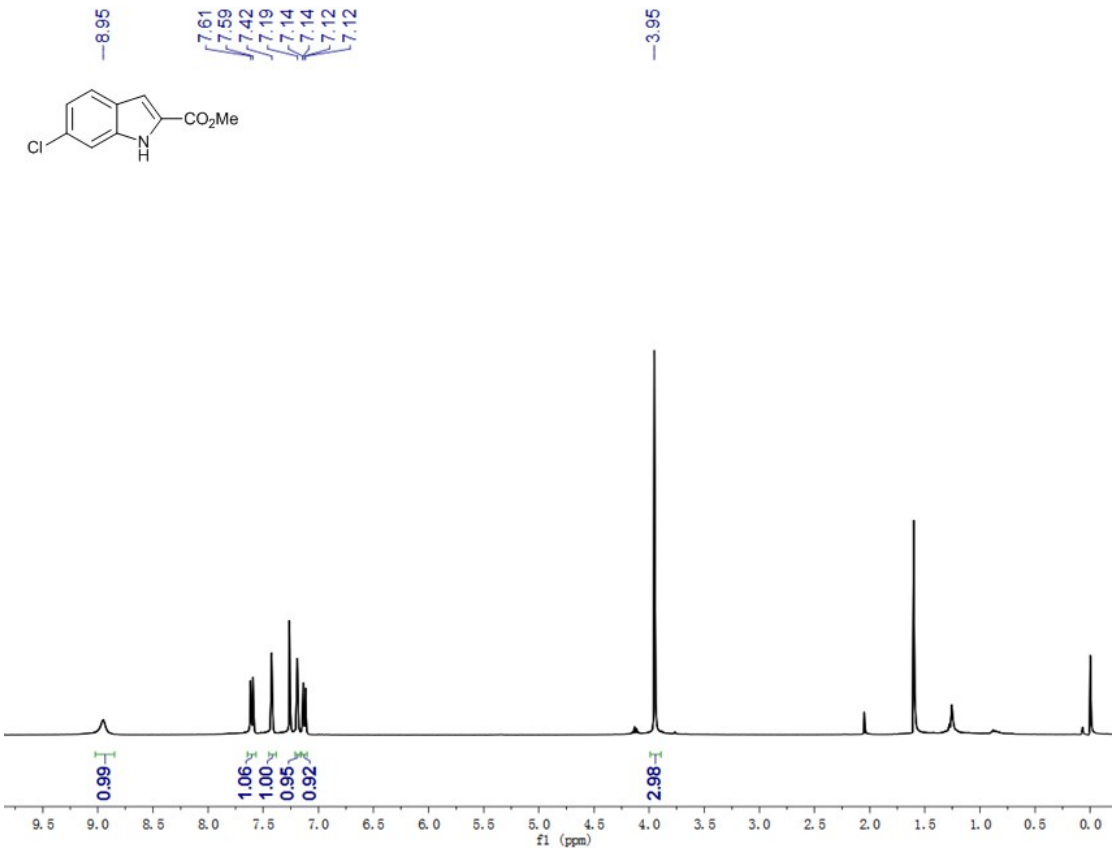
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **3d**.

Methyl 6-fluoro-1*H*-indole-2-carboxylate



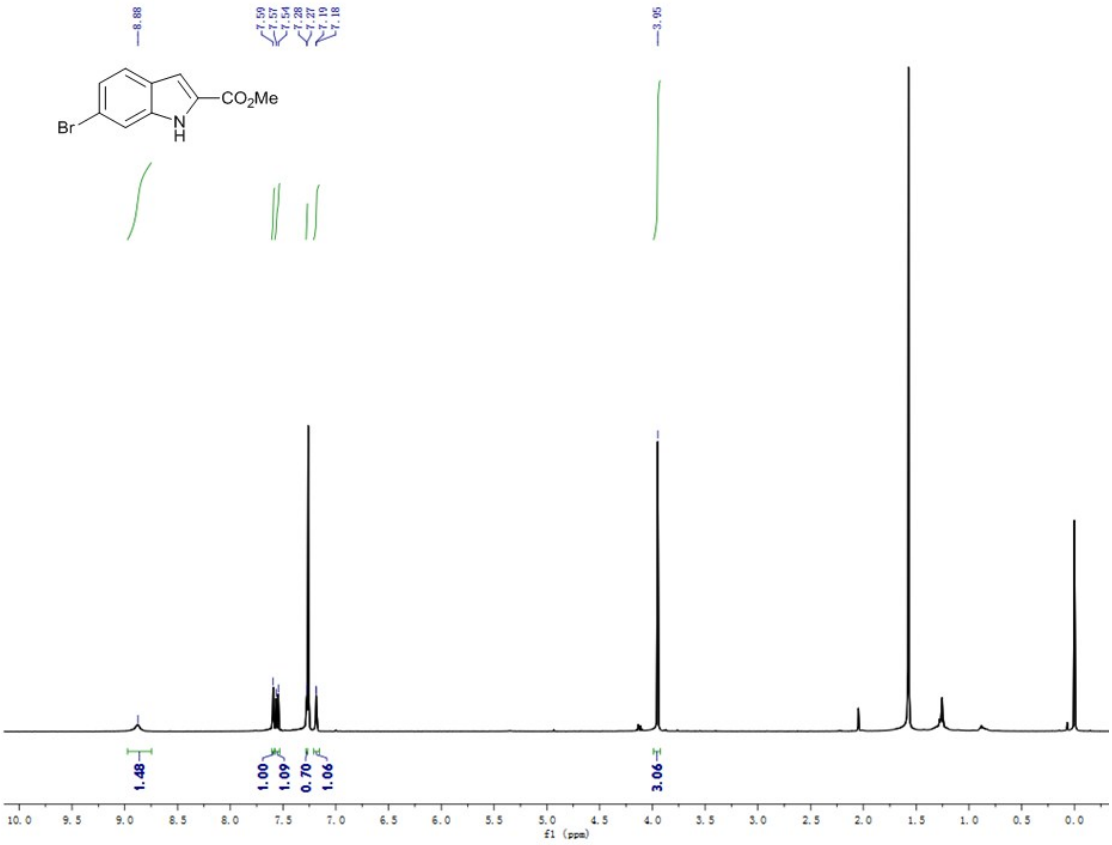
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **3e**.

Methyl 6-chloro-1*H*-indole-2-carboxylate



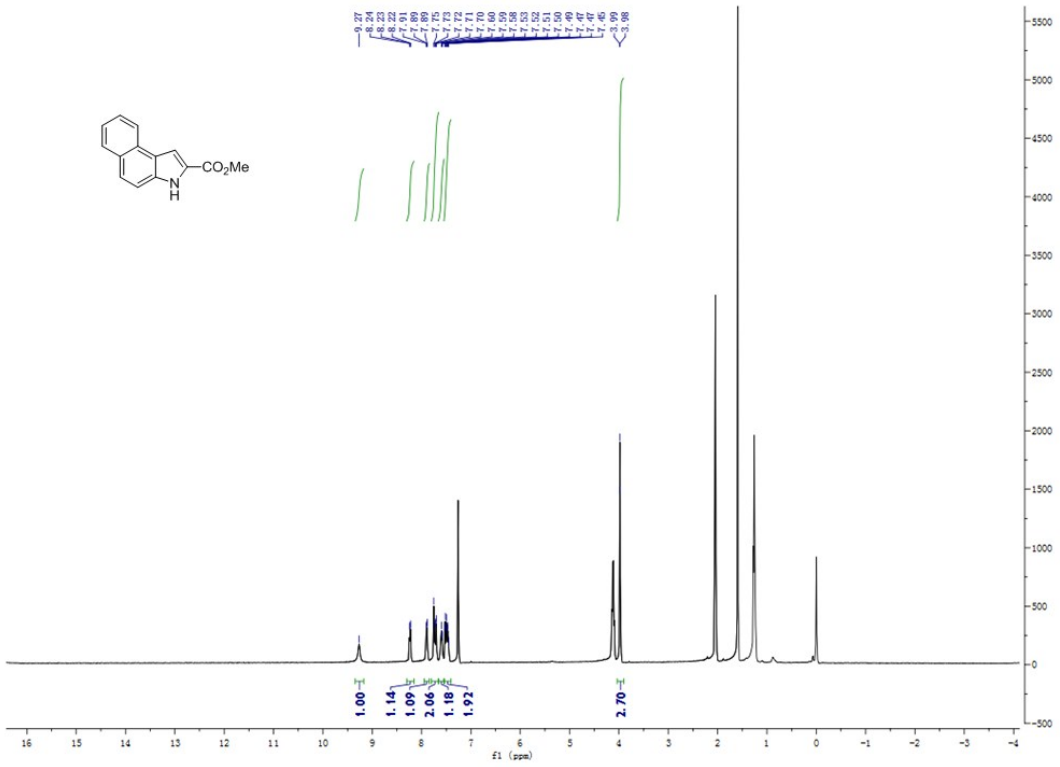
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **3f**.

Methyl 6-bromo-1*H*-indole-2-carboxylate



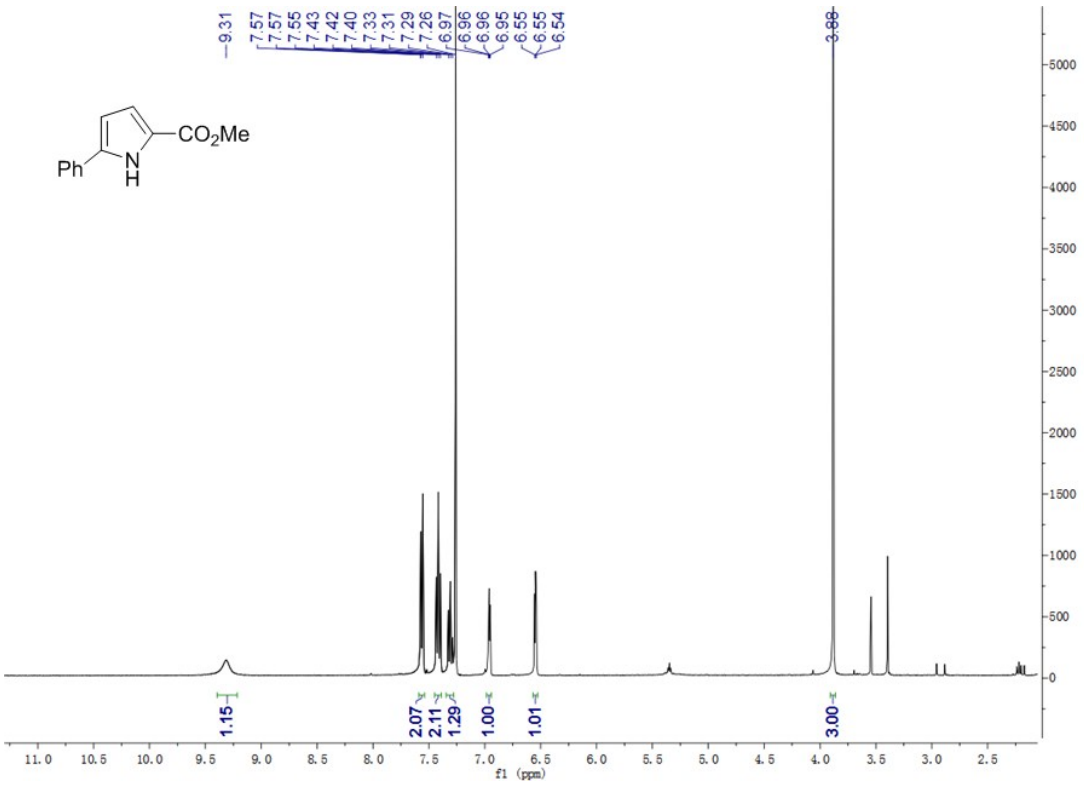
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **3g**.

Methyl 3H-benzo[e]indole-2-carboxylate



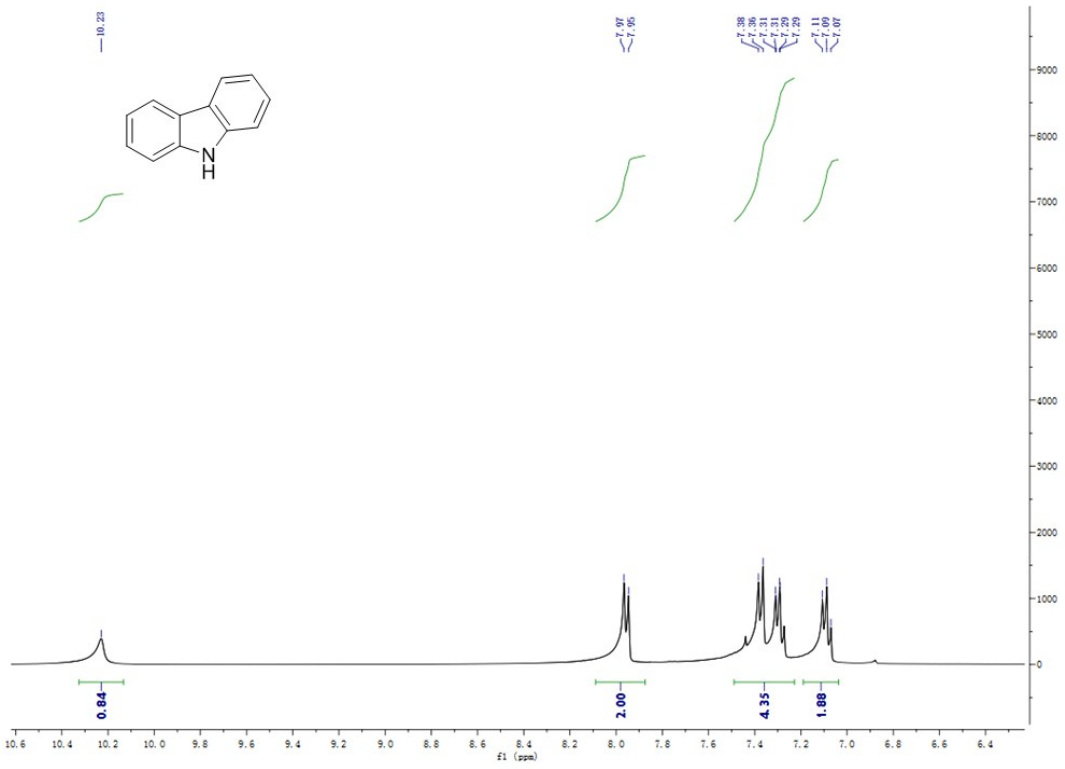
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **3h**.

Methyl 5-phenyl-1*H*-pyrrole-2-carboxylate



^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **4**.

9*H*-Carbazole



^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **5**.