

Electronic Supplementary Information (ESI) for New Journal of Chemistry.

# **Sustainable Aerobic Oxidative Coupling of Thiols and Amines for Selective Formation of Sulfenamides Using MOF-derived Cobalt Nanoparticles Supported on N-doped Carbon.**

Ya-Fei Guo<sup>a</sup>, Le Dong<sup>a</sup>, Jun-Ying Ma<sup>a\*</sup>, Shu-Xiao Feng<sup>a</sup>, Yong-Hua Duan<sup>a</sup>, Bao-Hua Xu<sup>b\*</sup>

<sup>a</sup> School of Chemical Engineering and Pharmaceutics, Henan University of Science and Technology, Luoyang 471023, Chin

<sup>b</sup> School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, PR China. E-mail: bhxu@bit.edu.cn.

[\*] Author to whom correspondence should be addressed; E-Mail: [majy39@163.com](mailto:majy39@163.com); [bhxu@bit.edu.cn](mailto:bhxu@bit.edu.cn).

## **Supporting Information**

### **Content**

**S1. Materials and Instrumentation.**

**S2. Preparation of the Catalysts.**

**S3. Characterization of the Catalysts.**

**S4. Control experiments to identify the catalytically active sites for the S-N oxidative coupling reaction.**

**S5. Preparation and characterization of Sulfenamides**

## S1. Materials and Instrumentation.

All reagents were acquired commercially and used without further purification. XRD powder patterns were recorded on a Bruker AXS D8 ADVANCE X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Processing and assignment of the powder patterns was done by comparing with the JCDs database. The TEM measurements were performed with an TECNAIG2 F20 high resolution transmission electron microscope. The catalyst was dispersed in ethanol with ultrasonic waves and then deposited on a transmission electron microscope carbon screen. TEM image and element mapping measurements were performed on a 200 kV bench. XPS data was obtained with a Thermo Fisher Scientific ESCALAB 250Xi spectrometer with monochromatic Al K $\alpha$  (1486.6 eV) radiation. To account for charging effects of carbonized samples, the binding energy values were referred to C 1s at 284.8 eV. Spectral analysis consisted in a Shirley + linear background subtraction and deconvolution using a mixed Gaussian and Lorentzian lineshapes for each spectral component. NMR spectra were recorded on a Bruker ASCEND spectrometer [ $^1\text{H}$ , 400 MHz;  $^{13}\text{C}\{^1\text{H}\}$  101 MHz]. For  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, the chemical shift ( $\delta$ ) was given relative to TMS and referenced to the solvent signal. Column chromatography was performed using silica gel. Analytical TLC was done using pre-coated silica gel 60 F<sub>254</sub> plates. GC analyses were performed on a GC-7890II gas chromatography device equipped with a flame ionization detector (GC-FID, GC-7890II, RB-1701 column length, 30 m; inner diameter, 0.32 mm; film thickness, 0.25  $\mu\text{m}$ ). GC-MS was performed using Trace GC Ultra-ISQ with TG-5MS (30 m $\times$ 0.25 mm) column. ESI-MS analysis were performed on a Bruker time of flight mass spectrometer microTOF-Q II using an electrospray ionization (ESI) source.

## S2. Preparation of the Catalysts.

### S2.1. Preparation of ZIF-67 and pyrolysis of the precursor to obtain Co-NC-T

In a 100 mL round bottomed flask, cobalt(II) nitrate hexahydrate (0.4802 g, 1.65mmol) was dissolved in 35 mL of deionized water. The mixture was stirred under room temperature for 5 min, marked as solution A. Then 2-methylimidazole (0.2709g, 3.3 mmol) was added into 35 mL deionized water under stirring for 5 min, marked as solution B. Then, solution A was poured into solution B slowly. The suspension was stirred for 2 h and was separated by centrifugation. The purple precipitate obtained was washed by methanol for three times, and then dried in a vacuum at 80°C for 12 h to obtain the ZIF-67. The powdered material was pyrolyzed at the defined temperature (600°C、700°C、800°C and 900°C ) with a heating rate of 5 °C/min for 3 h under N<sub>2</sub> atmosphere and then cooled to room temperature. The solid powders were grinded to obtain the final catalysts.

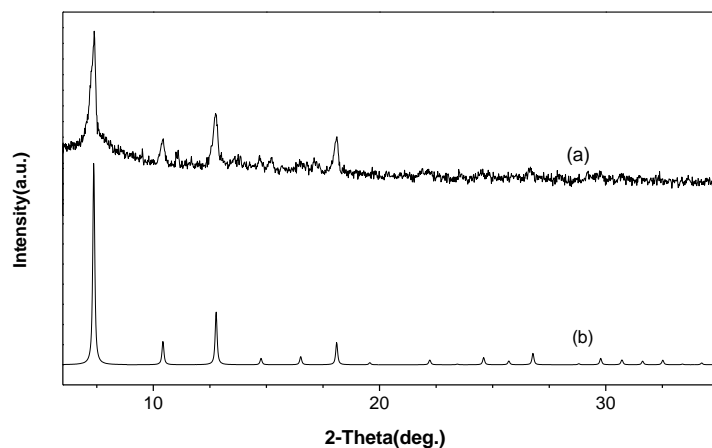
### S2.2 Preparation of the supported ZIF-67 and pyrolysis to obtain Co-NC/Al<sub>2</sub>O<sub>3</sub>-800 and Co-NC/C-800

In a 100 mL round bottomed flask, 2-methylimidazole (0.2709g, 3.3 mmol) were added into 35 mL deionized water following by stirring under room temperature for 5 min. To this mixture, the support (aluminium oxide (cat no. A140296) or carbon (cat no. C196580), 1.5 g) was added slowly. The round bottomed flask containing reaction mixture were allowed to stand stirring for 4 h at 100°C in order to slow evaporation of deionized water. After the evaporation of solvent, a solution of cobalt nitrate hexahydrate (0.4802 g, 1.65 mmol) in 35 mL deionized water was poured into the round bottomed flask. The mixture was again heated to 100°C under stirring until the solvent is almost dry. The obtained material was cooled to room temperature and dried in a vacuum at 80°C for 12 h and obtained the supported ZIF-67 precursor. The supported ZIF-67 was pyrolyzed at 800°C with a heating rate of 5 °C/min for 3 h under N<sub>2</sub> atmosphere and then cooled to room temperature. The solid powders were grinded to obtain the final catalysts.

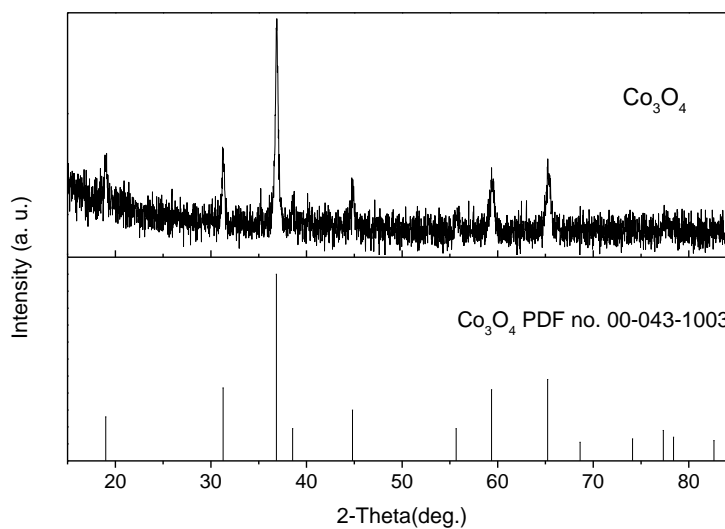
### S2.3 Impregnating Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O onto commercially nano-carbon and followed pyrolysis to prepare Co-C-800

In a 50 mL round bottomed flask, cobalt nitrate hexahydrate (0.4802 g, 1.65 mmol) and carbon support (1.5 g) were added into 35 mL deionized water following by stirring under 100°C for 4 h. After the evaporation of solvent, the material was cooled to room temperature and dried in a vacuum at 80°C for 12 h. The obtained material was pyrolyzed at 800°C with a heating rate of 5 °C/min for 3 hours under N<sub>2</sub> atmosphere and then cooled to room temperature after pyrolysis. The solid powders were grinded to obtain the final products.

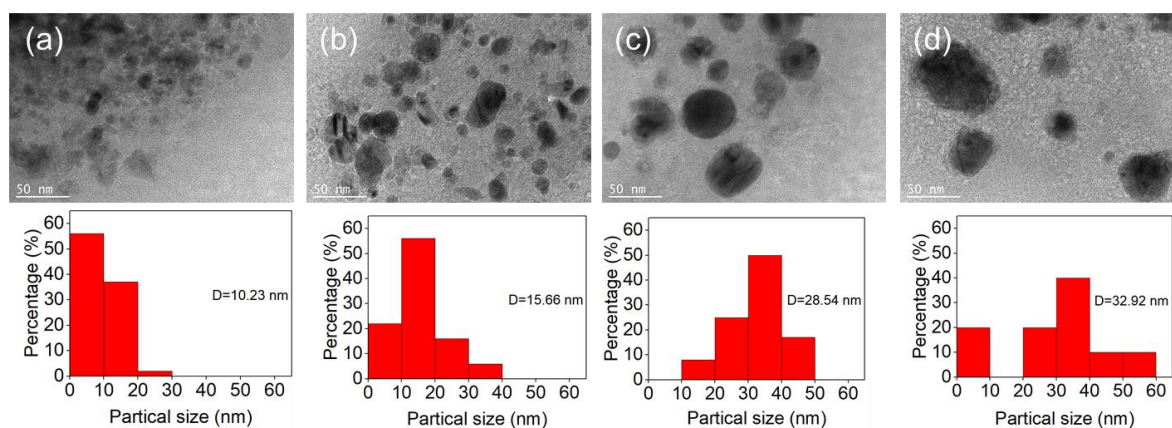
### S3. Characterization of the Catalysts.



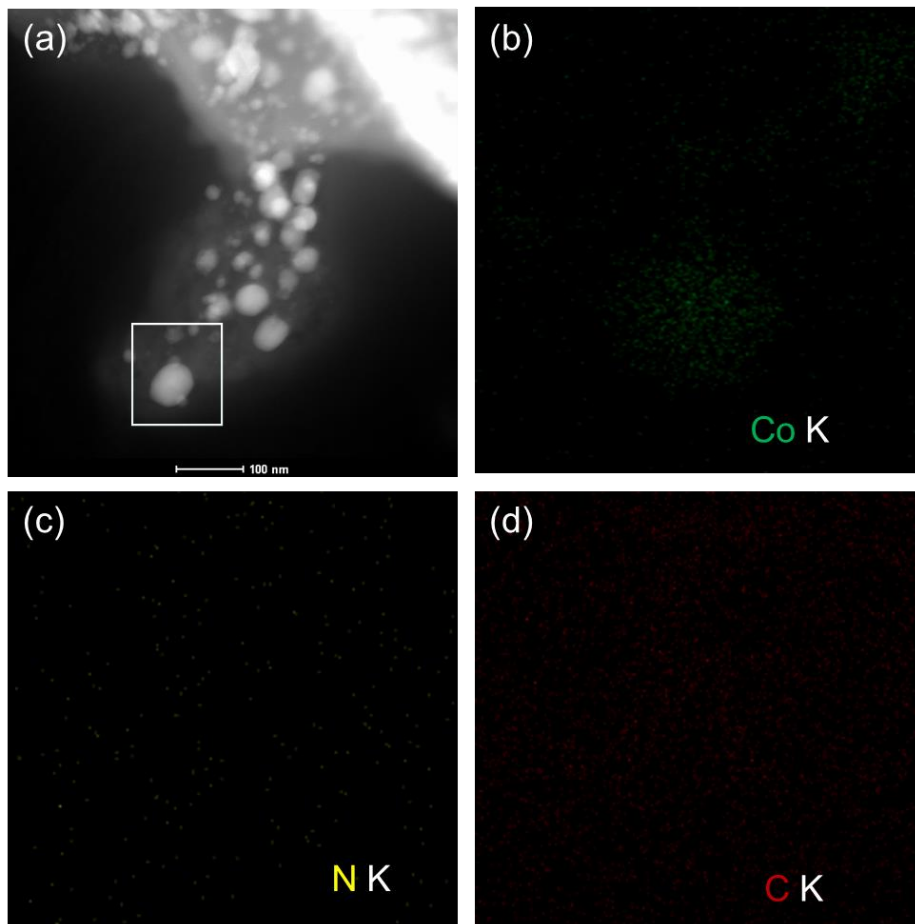
**Figure S1** Powder XRD of ZIF-67 synthesized (a) and simulated (b).



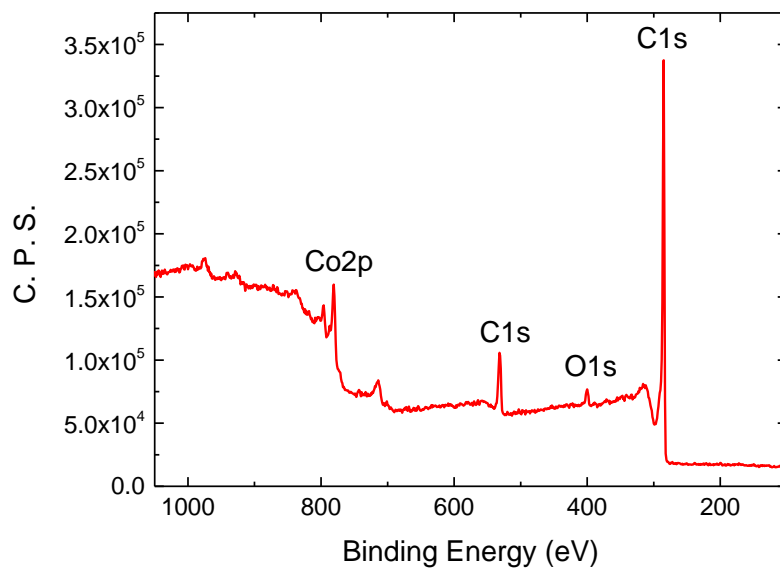
**Figure S2** Powder XRD of the commercial nano  $\text{Co}_3\text{O}_4$  catalysts.



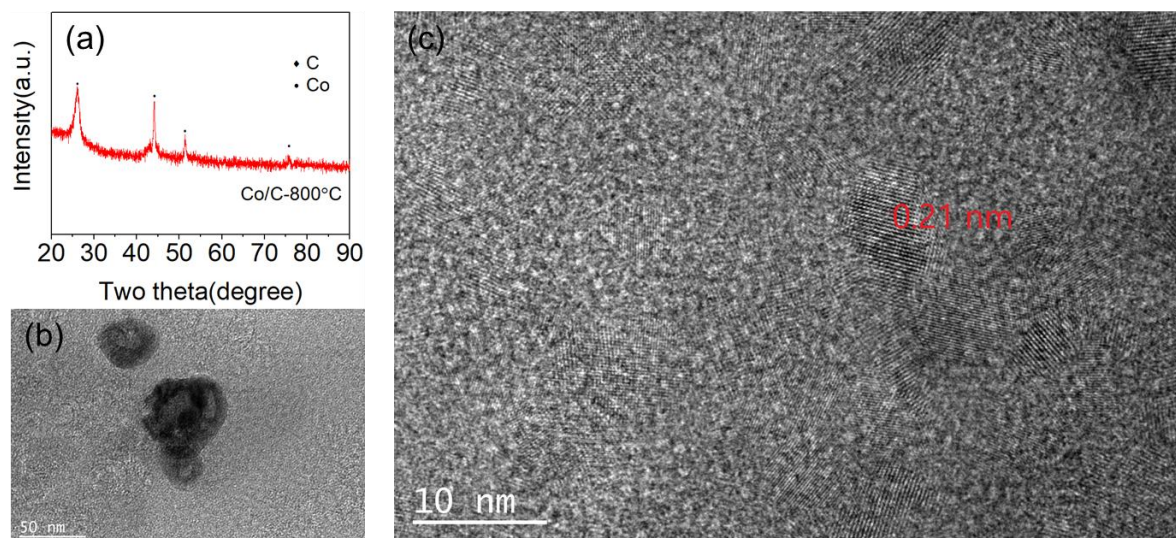
**Figure S3** The TEM image and particles size of the catalysts pyrolysed at different temperatures.



**Figure S4** STEM-EDS analysis of the Co-NC-800.

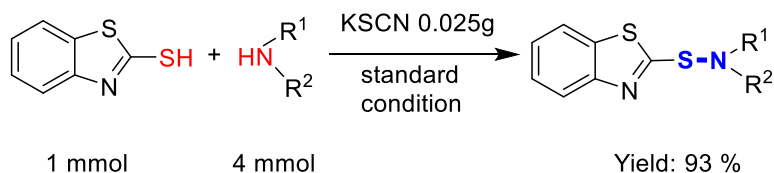


**Figure S5** The X-ray photoelectron spectroscopy (XPS) survey of the Co-NC-800 catalyst.

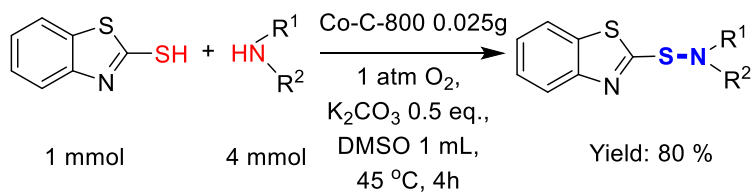


**Figure S6** The XRD and HRTEM characterization of the Co-C-800 catalyst.

**S4. Control experiments to identify the catalytically active sites for the S-N oxidative coupling reaction.**

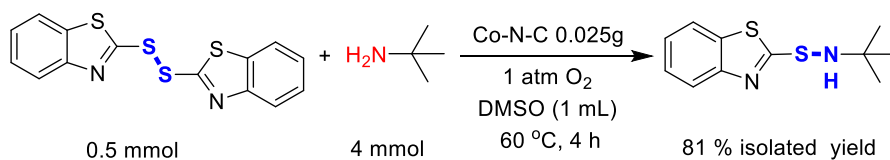


**Scheme S1.** Poisoning experiment with KSCN added as Co-N<sub>x</sub> binding molecule.

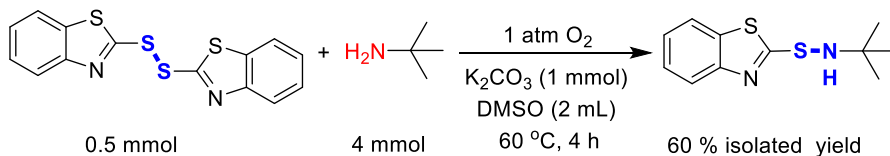


**Scheme S2.** Control experiment with modified catalyst (Co-C-800).

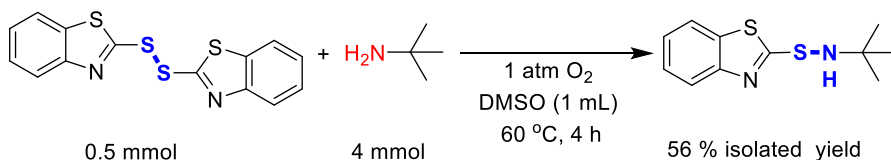
*a: control reaction without base*



*b: control reaction without catalyst*



*c: control reaction without base and catalyst*



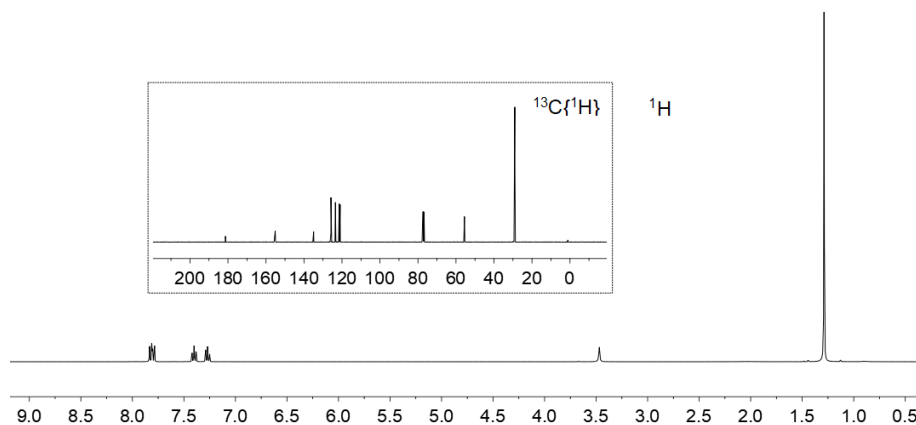
**Scheme S3.** Control experiments of 2,2'-di(2-benzothiazolyl)disulfide (**4aa**) to N-tert-butyl-2-benzothiazolesulphenamide (**3aa**).

## S5. Preparation of Sulfenamides

### General procedure for the oxidative coupling of thiols and amines.

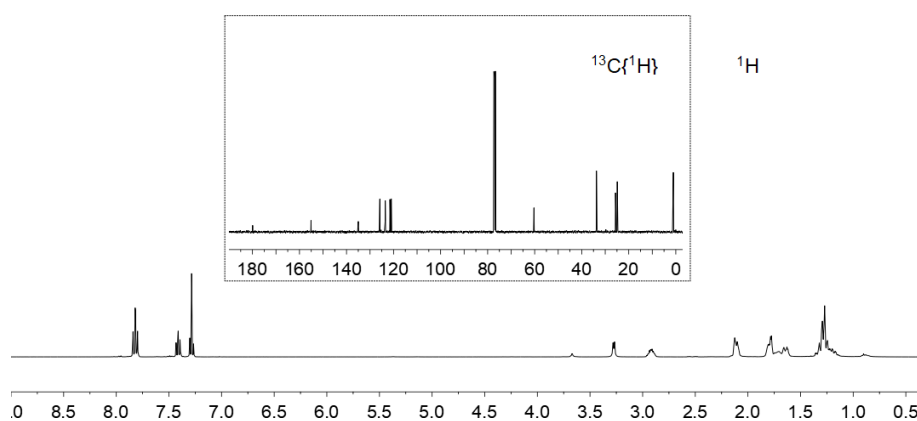
The cobalt catalysts (0.025 g), thiols (1 mmol), and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then amine (4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the filtrate. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography.

**Preparation of 3aa.** The cobalt catalysts (0.025 g), 2-mercaptobenzothiazole (0.167 g, 1 mmol), and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then tert-butylamine (0.293 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the filtrate. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3aa** (white solid) in a yield of 96% (229 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K)  $\delta$  7.81 (d,  $J = 8.2$  Hz, 1H), 7.78 (d,  $J = 8.1$  Hz, 1H), 7.40-7.36 (m, 1H), 7.27-7.24 (m, 1H), 3.44 (s, 1H), 1.27 (s, 9H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  181.4, 155.1, 134.9, 125.8, 123.5, 121.5, 121.0, 55.5, 29.0. HRMS (ESI)  $m/z$  calcd for  $C_{11}H_{14}N_2S_2$   $[M+H]^+$ : 239.0671, found 239.0674.

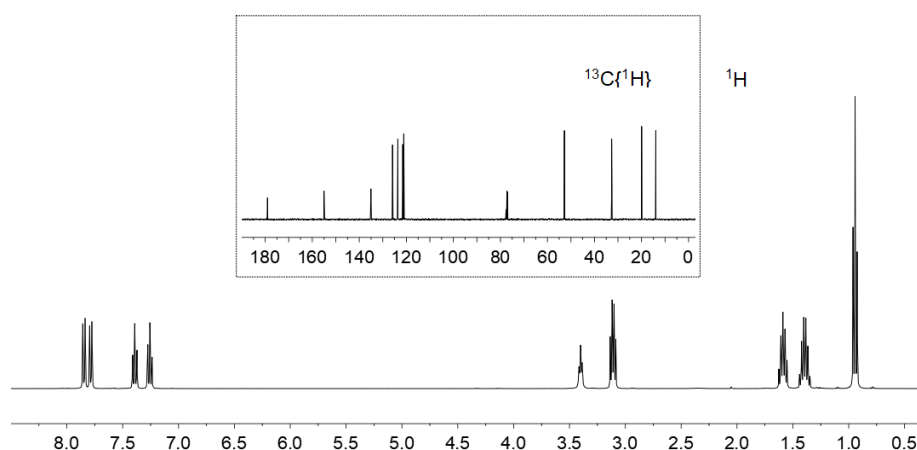


**Preparation of 3ab.** The cobalt catalysts (0.025 g), 2-mercaptobenzothiazole (0.167 g, 1 mmol), and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then cyclohexylamine (0.369 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the filtrate. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3ab** (white solid) in a yield of 92% (245 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K)  $\delta$  7.84-7.76 (m, 2H), 7.44-7.36 (m, 1H), 7.30-7.27 (m, 1H), 3.27 (d,  $J = 5.4$  Hz, 1H), 2.96-2.87 (m, 1H), 2.14-2.08 (m, 2H), 1.82-1.76 (m, 2H), 1.67-1.60 (m, 1H), 1.33-1.25 (m, 5H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  179.9, 155.1, 135.0, 125.8, 123.5, 121.5, 121.0, 60.3, 33.7, 25.6, 24.9. HRMS (ESI)  $m/z$  calcd for  $C_{13}H_{16}N_2S_2$   $[M+H]^+$ : 265.0825, found 265.0829.



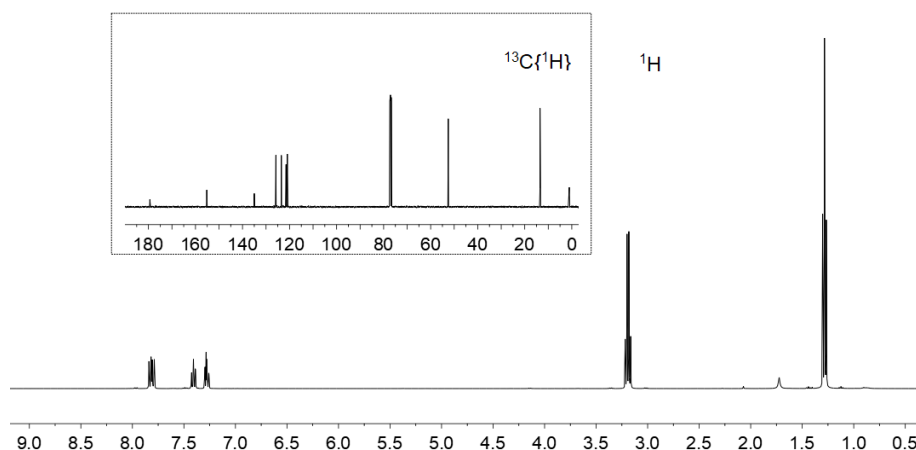


**Preparation of 3ac.** The cobalt catalysts (0.025g), 2-mercaptobenzothiazole (0.167 g, 1 mmol), and  $K_2CO_3$  (0.1381 g, 1 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then n-butylamine (0.173 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the filtrate. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3ac** (Light yellow oil) in a yield of 90% (216 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K)  $\delta$  7.82 (d,  $J = 8.1$  Hz, 1H), 7.76 (d,  $J = 8.1$  Hz, 1H), 7.39-7.35 (m, 1H), 7.25-7.21 (m, 1H), 3.38 (t,  $J = 5.8$ Hz, 1H), 3.11-3.05 (m, 2H), 1.61-1.52 (m, 2H), 1.41-1.31 (m, 2H), 0.94 (t,  $J = 7.3$  Hz, 3H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  179.0, 155.0, 146.8, 135.6, 125.9, 123.6, 121.5, 121.1, 52.8, 32.7, 20.0, 13.9. HRMS (ESI)  $m/z$  calcd for  $C_{11}H_{14}N_2S_2 [M+H]^+$ : 239.0671, found 239.0675.

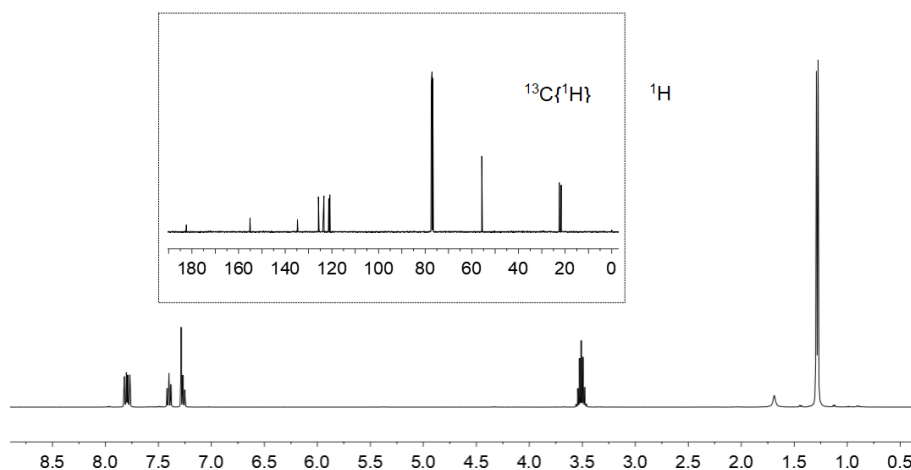


**Preparation of 3ad.** The cobalt catalysts (0.025 g), 2-mercaptobenzothiazole (0.167 g, 1 mmol) and  $K_2CO_3$  (0.1381 g, 1 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then diethylamine (0.293 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the filtrate. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column

chromatography (petroleum ether/ethyl acetate 25:1) provided **3ad** (white solid) in a yield of 85% (202 mg).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.80 (d,  $J = 8.1$  Hz, 1H), 7.77 (d,  $J = 8.1$  Hz, 1H), 7.40-7.36 (m, 1H), 7.27-7.23 (m, 1H), 3.16 (q,  $J = 7.1$  Hz, 4H), 1.26 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.4, 155.2, 135.0, 125.8, 123.5, 121.5, 120.9, 52.5, 13.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{S}_2$   $[\text{M}+\text{H}]^+$ : 239.0671, found 239.0676.

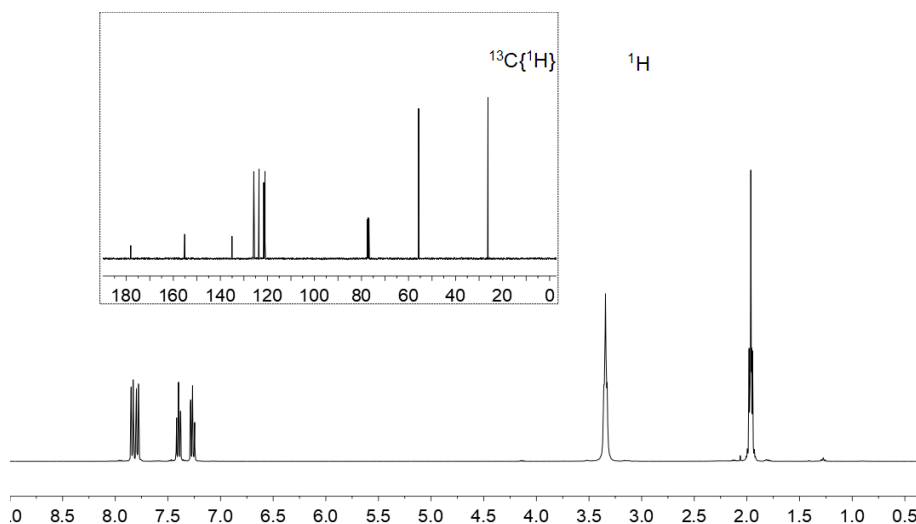


**Preparation of 3ae.** The cobalt catalysts (0.025 g), 2-mercaptobenzothiazole (0.167 g, 1 mmol), and  $\text{K}_2\text{CO}_3$  (0.0681 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $\text{O}_2$  for three times and closed with valve. Then diisopropylamine (0.404 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ\text{C}$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the filtrate. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $\text{Na}_2\text{SO}_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3ae** (white solid) in a yield of 86% (226 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.78 (d,  $J = 8.0$  Hz, 1H), 7.75 (d,  $J = 7.7$  Hz, 1H), 7.38-7.35 (m, 1H), 7.27-7.23 (m, 1H), 3.51-3.47 (m, 2H), 1.28-1.23 (m, 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  182.2, 155.1, 134.7, 125.7, 123.3, 121.3, 120.8, 55.7, 22.4, 21.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{18}\text{N}_2\text{S}_2$   $[\text{M}+\text{H}]^+$ : 267.0984, found 267.0988.

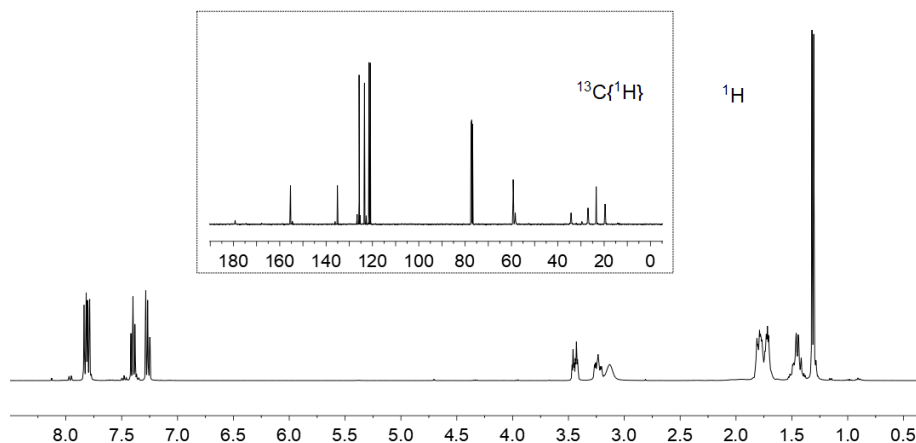


**Preparation of 3af.** The cobalt catalysts (0.025 g), 2-mercaptobenzothiazole (0.167 g, 1 mmol), and  $\text{K}_2\text{CO}_3$  (0.0681 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas

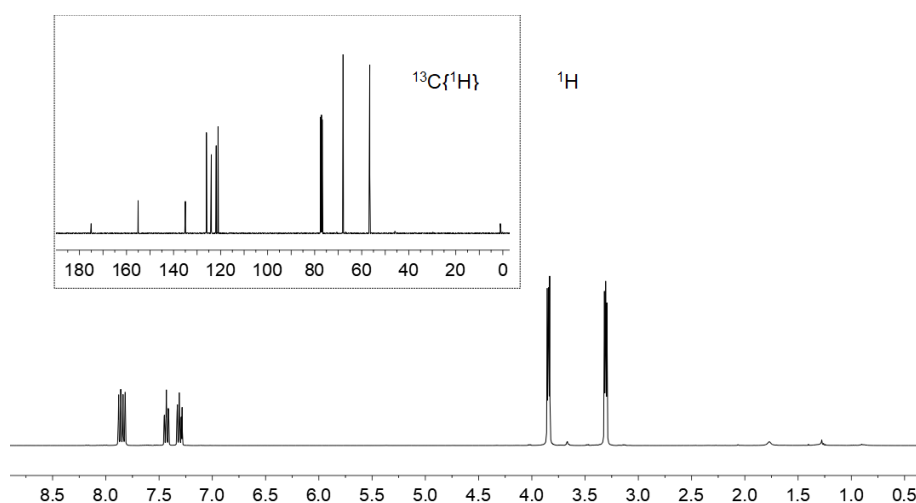
pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of O<sub>2</sub> for three times and closed with valve. Then pyrrolidine (0.284 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the 60°C and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the filtrate. The products were extracted by ethyl acetate (3×10 mL). The combined organic extract was dried by Na<sub>2</sub>SO<sub>4</sub> overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3af** (yellow oil) in a yield of 72% (170 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.8 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.42-7.37 (m, 1H), 7.30-7.23 (m, 1H), 3.34 (t, *J* = 6.5 Hz, 4H), 1.99-1.93 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 178.09, 155.17, 135.05, 125.78, 123.56, 121.57, 121.02, 55.70, 26.22. HRMS (ESI) *m/z* calcd for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 237.0515, found 237.0519.



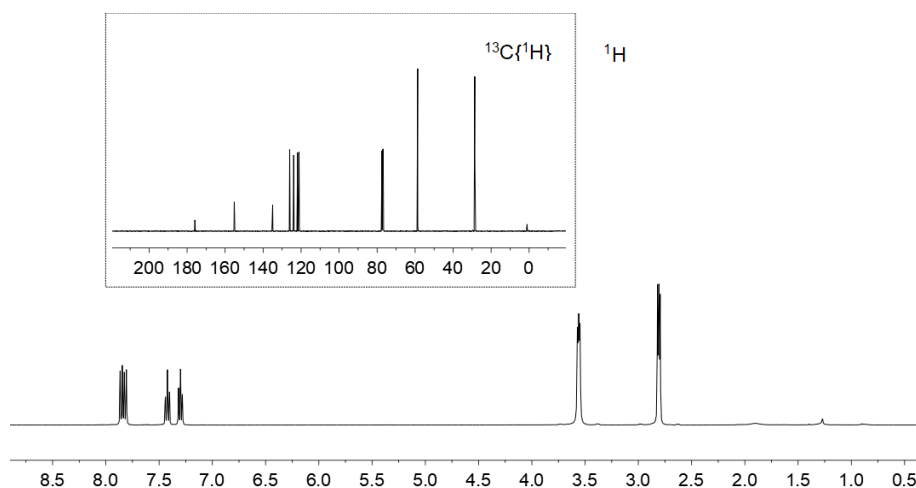
**Preparation of 3ag.** The cobalt catalysts (0.025 g), 2-mercaptobenzothiazole (0.168 g, 1 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of O<sub>2</sub> for three times and closed with valve. Then 2-methylpiperidine (0.397 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the 60°C and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the filtrate. The products were extracted by ethyl acetate (3×10 mL). The combined organic extract was dried by Na<sub>2</sub>SO<sub>4</sub> overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3ag** (white solid) in a yield of 84% (222 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.40-7.35 (m, 1H), 7.26-7.22 (m, 1H), 3.45-3.40 (m, 1H), 3.25-3.15 (m, 1H), 3.11 (s, 1H), 1.80-1.68 (m, 4H), 1.50-1.37 (m, 2H), 1.29 (d, *J* = 6.5 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 179.3, 155.4, 135.1, 125.8, 123.4, 121.5, 120.9, 59.3, 58.4, 34.3, 27.0, 23.4, 19.6. HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 265.0828, found 265.0832.



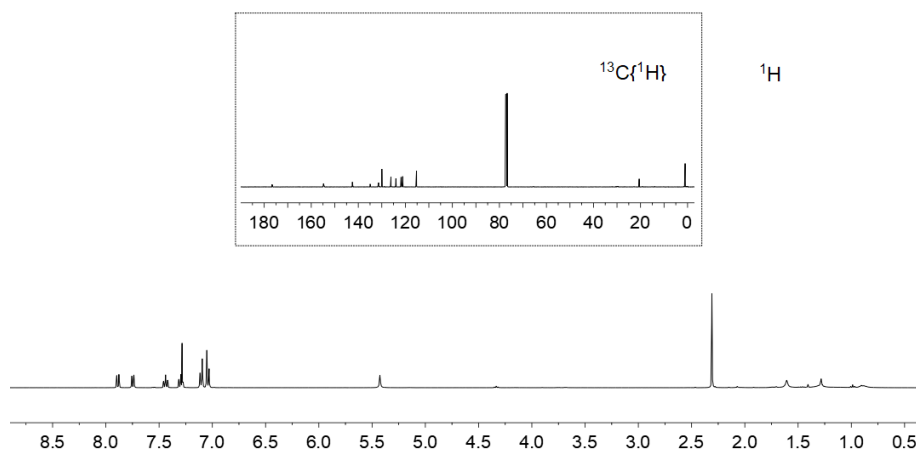
**Preparation of 3ah.** The cobalt catalysts (0.025 g), 2-mercaptobenzothiazole (0.168 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3ah** (white solid) in a yield of 97% (247 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K)  $\delta$  7.85 (d,  $J = 8.1$  Hz, 1H), 7.81 (d,  $J = 8.1$  Hz, 1H), 7.443-7.39 (m, 1H), 7.30-7.26 (m, 1H), 3.82 (t,  $J = 4.8$  Hz, 4H), 3.28 (t,  $J = 4.8$  Hz, 4H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  175.0, 155.1, 135.0, 126.0, 124.0, 121.89, 121.1, 67.9, 56.6. HRMS (ESI)  $m/z$  calcd for  $C_{11}H_{12}N_2OS_2$   $[M+H]^+$ : 253.0464, found 253.0469.



**Preparation of 3ai.** The cobalt catalysts (0.025 g), 2-mercaptobenzothiazole (0.168 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then thiomorpholine (0.412 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3ai** (white solid) in a yield of 97% (260 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K)  $\delta$  7.83 (d,  $J = 8.2$  Hz, 1H), 7.79 (d,  $J = 8.2$  Hz, 1H), 7.42-7.37 (m, 1H), 7.29-7.25 (m, 1H), 3.54 (t,  $J = 4.9$  Hz, 4H), 2.78 (t,  $J = 4.9$  Hz, 4H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  175.9, 155.2, 135.0, 126.0, 123.9, 121.9, 121.1, 58.6, 28.6. HRMS (ESI)  $m/z$  calcd for  $C_{11}H_{12}N_2S_3$   $[M+H]^+$ : 269.0235, found 269.0238.

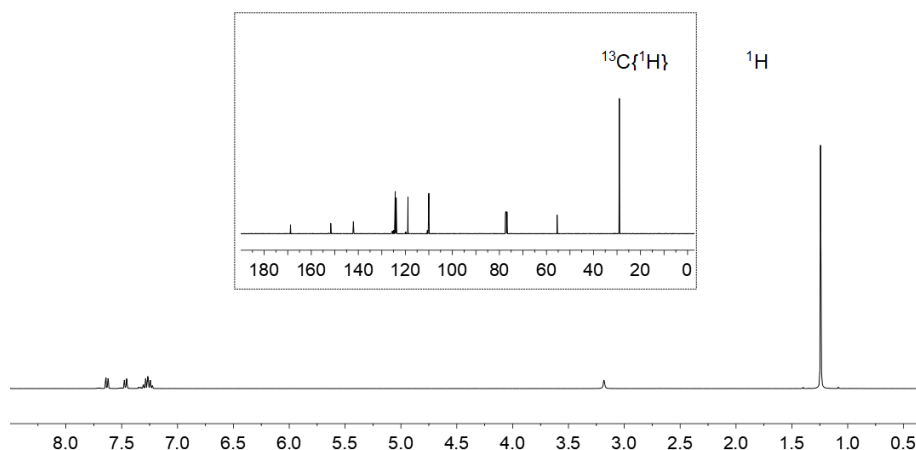


**Preparation of 3aj.** The cobalt catalysts (0.025 g), 2-mercaptobenzothiazole (0.168 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then paratoluidine (0.428 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3aj** (light yellow solid) in a yield of 45% (123 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K)  $\delta$  7.86 (d,  $J = 8.2$  Hz, 1H), 7.73 (d,  $J = 8.0$  Hz, 1H), 7.41 (t,  $J = 7.6$  Hz, 1H), 7.27 (t,  $J = 7.6$  Hz, 2H), 7.09-7.06 (m, 2H), 7.04-7.00 (m, 2H), 5.41 (s, 1H), 2.29 (s, 3H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  176.7, 154.8, 142.5, 135.0, 131.2, 130.0, 126.1, 124.0, 121.82, 121.1, 115.2, 20.5. HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{12}N_2S_2$   $[M+H]^+$ : 273.0515, found 273.0519.

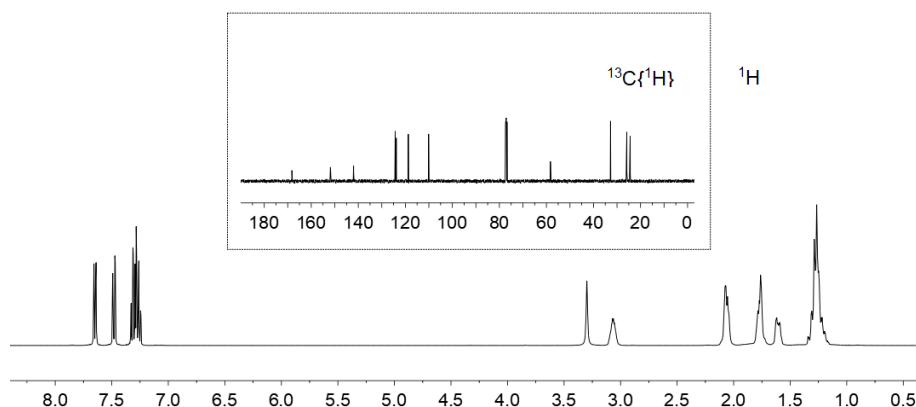


**Preparation of 3ba.** The cobalt catalysts (0.025 g), 2-mercaptobenzoxazole (0.157 g, 1 mmol), and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then tert-butylamine (0.293 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3ba** (white solid) in a yield of 75% (167 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K)  $\delta$  7.61 (d,  $J = 7.5$  Hz, 1H), 7.44 (d,  $J = 7.5$  Hz, 1H), 7.28-7.19 (m, 2H), 3.12 (s, 1H), 1.22 (s, 9H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  168.2, 151.9, 142.0, 124.3, 123.9, 118.7, 110.1, 58.3, 32.8, 25.8, 24.4. HRMS (ESI)

m/z calcd for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>OS [M+H]<sup>+</sup>:223.0900, found 223.0904.

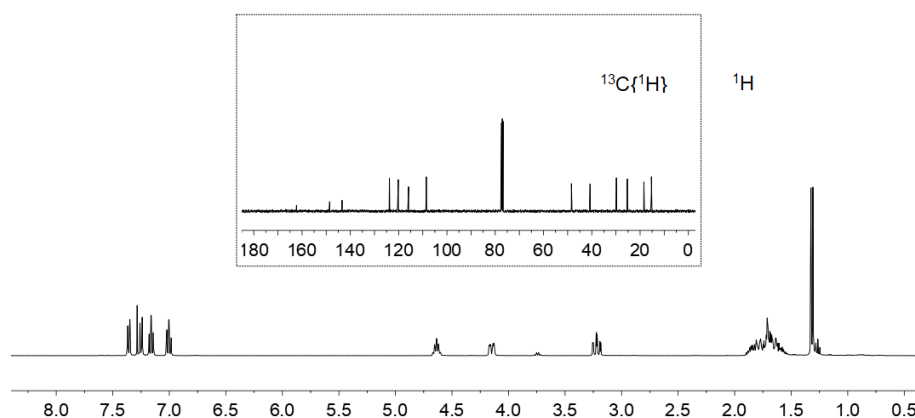


**Preparation of 3bb.** The cobalt catalysts (0.025 g), 2-mercaptobenzoxazole (0.167 g, 1 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of O<sub>2</sub> for three times and closed with valve. Then cyclohexylamine (0.369 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the 60°C and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate (3×10 mL). The combined organic extract was dried by Na<sub>2</sub>SO<sub>4</sub> overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3bb** (light yellow solid) in a yield of 63% (157 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.62 (d, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.29-7.20 (m, 2H), 3.27 (s, 1H), 3.04 (s, 1H), 2.28-2.00 (m, 2H), 1.79-1.72 (m, 2H), 1.62-1.55 (m, 1H), 1.32-1.20 (m, 5H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 168.2, 151.9, 142.0, 124.3, 123.9, 118.7, 110.1, 58.3, 32.8, 25.8, 24.4. HRMS (ESI) m/z calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>OS [M+H]<sup>+</sup>: 249.1056, found 249.1061.

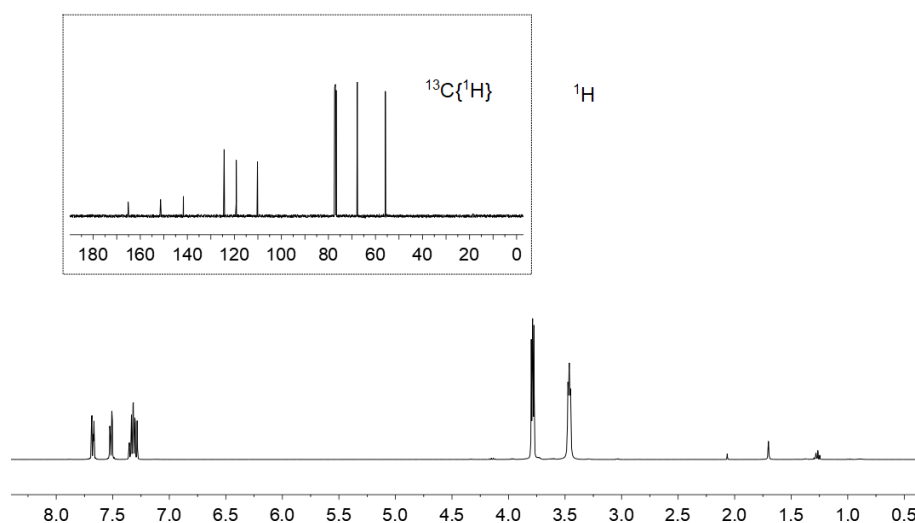


**Preparation of 3bg.** The cobalt catalysts (0.025 g), 2-mercaptobenzoxazole (0.168 g, 1 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of O<sub>2</sub> for three times and closed with valve. Then 2-methylpiperidine (0.397 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the 60°C and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate (3×10 mL). The combined organic extract was dried by Na<sub>2</sub>SO<sub>4</sub> overnight and concentrated, then purified by

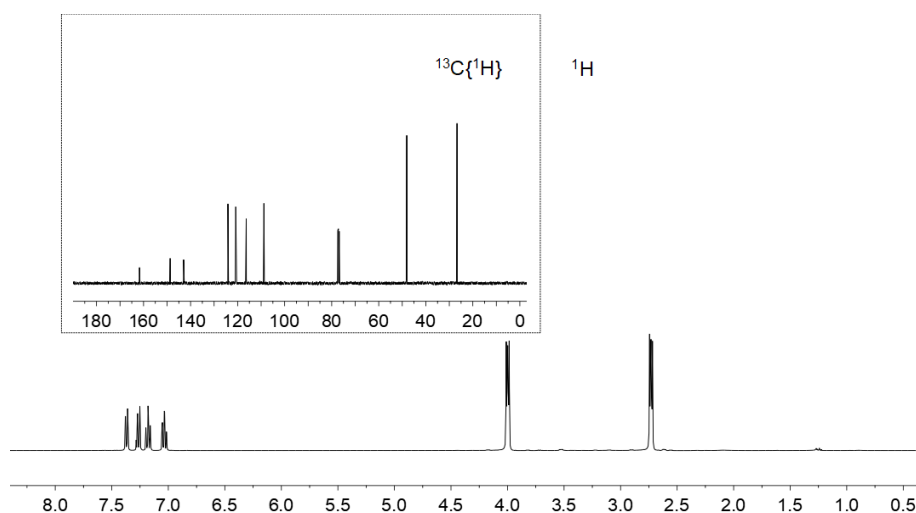
column chromatography (petroleum ether/ethyl acetate 25:1) provided **3bc** (white solid) in a yield of 64% (159 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.35-7.32 (d,  $J = 7.8$  Hz, 1H), 7.24-7.22 (d,  $J = 7.9$  Hz, 1H), 7.16-7.12 (m, 1H), 7.01-6.97 (m, 1H), 4.62-4.58 (m, 1H), 4.12 (d,  $J = 13.3$  Hz, 1H), 3.23-3.15 (m, 1H), 1.84-1.61 (m, 6H), 1.29 (d,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3, 148.6, 143.4, 123.8, 120.1, 115.9, 108.5, 48.4, 40.7, 29.8, 25.3, 18.4, 15.3. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{16}\text{N}_2\text{OS}$   $[\text{M}+\text{H}]^+$ : 249.1056, found 249.1059.



**Preparation of 3bh.** The cobalt catalysts (0.025 g), 2-mercaptobenzoxazole (0.168 g, 1 mmol) and  $\text{K}_2\text{CO}_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $\text{O}_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ\text{C}$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $\text{Na}_2\text{SO}_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3bd** (white solid) in a yield of 60% (142 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.65(d,  $J = 7.9$  Hz, 1H), 7.49 (d,  $J = 7.9$  Hz, 1H), 7.33-7.27 (m, 2H), 3.76 (t,  $J = 4.6$  Hz, 4H), 3.44 (t,  $J = 4.6$  Hz, 4H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.0, 155.1, 135.0, 126.0, 124.0, 121.9, 121.1, 67.9, 56.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 237.0692, found 237.0696.

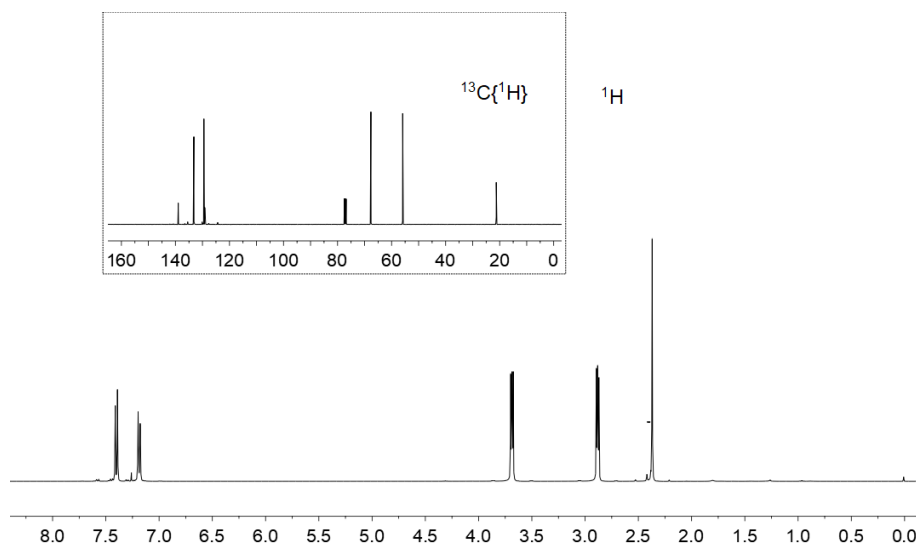


**Preparation of 3bi.** The cobalt catalysts (0.025 g), 2-mercaptobenzoxazole (0.168 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then Thiomorpholine (0.412 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3be** (white solid) in a yield of 68% (172 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K)  $\delta$  7.35 (d,  $J = 7.9$  Hz, 1H), 7.24 (d,  $J = 7.9$  Hz, 1H), 7.17-7.13 (m, 1H), 7.03-6.98 (m, 1H), 3.98 (t,  $J = 5.4$  Hz, 4H), 2.71 (t,  $J = 5.4$  Hz, 4H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  161.7, 148.7, 143.0, 124.1, 120.8, 116.3, 108.8, 48.1, 26.7. HRMS (ESI)  $m/z$  calcd for  $C_{11}H_{12}N_2OS$   $[M+H]^+$ : 253.0464, found 253.0468.

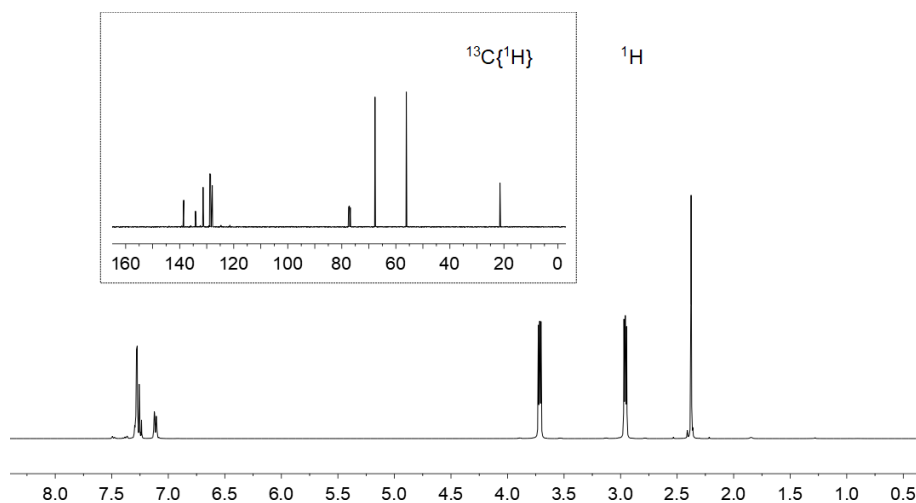


**Preparation of 3ch.** The cobalt catalysts (0.025 g), 4-methylbenzenethiol (0.124 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3ch** (yellow oil) in a yield of 88% (184 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K)  $\delta$  7.40 (d,  $J = 8.0$  Hz, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 3.69 (t,  $J = 4.8$  Hz, 4H), 2.88 (t,  $J = 4.8$  Hz, 4H), 2.37 (s, 3H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  139.0, 133.2, 129.5, 129.1, 67.7, 55.9, 21.3. HRMS (ESI)  $m/z$  calcd for  $C_{11}H_{15}NOS$   $[M+H]^+$ : 210.0947, found 210.0951.



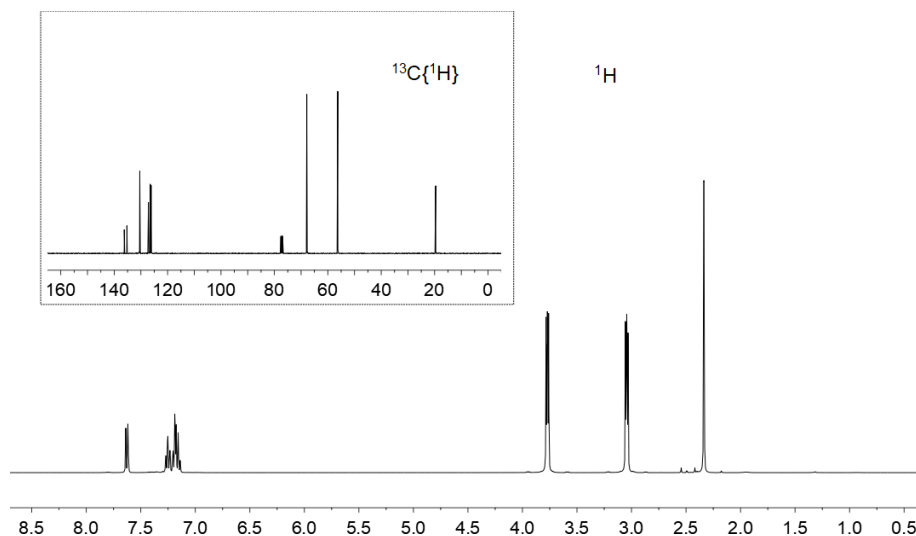


**Preparation of 3dh.** The cobalt catalysts (0.025 g), 3-methylbenzenethiol (0.124 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3dh** (yellow oil) in a yield of 84% (176 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K)  $\delta$  7.29-7.24 (m, 3H), 7.12 (d,  $J = 6.8$  Hz, 1H), 3.72 (t,  $J = 4.8$  Hz, 4H), 2.96 (t,  $J = 4.8$  Hz, 4H), 2.38 (s, 3H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  138.5, 134.1, 131.3, 128.9, 128.6, 127.9, 67.7, 56.1, 21.5. HRMS (ESI)  $m/z$  calcd for  $C_{11}H_{15}NOS$   $[M+H]^+$ : 210.0947, found 210.0952.

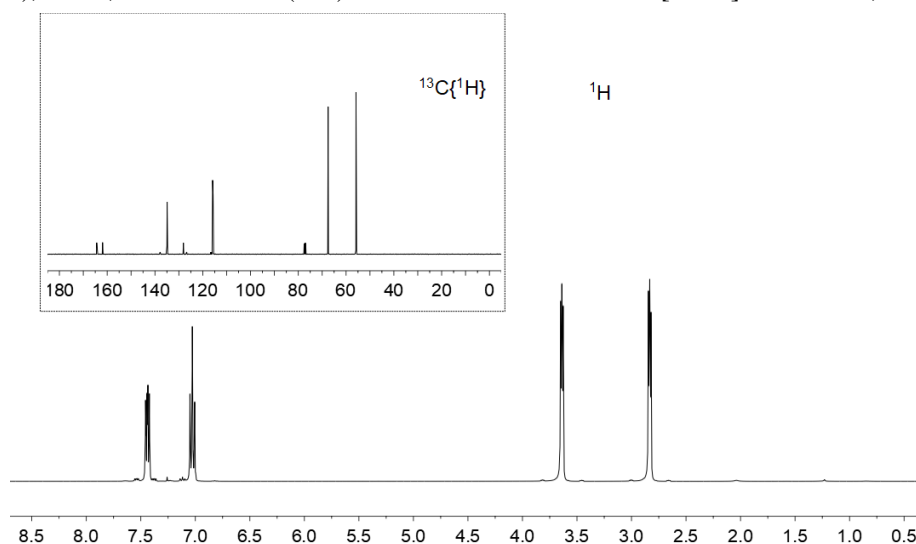


**Preparation of 3eh.** The cobalt catalysts (0.025 g), 2-methylbenzenethiol (0.124 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3eh** (yellow oil) in a yield of 76% (159 mg).  $^1H$  NMR (400

MHz,  $CDCl_3$ , 298 K)  $\delta$  7.64 (d,  $J = 7.6$  Hz, 1H), 7.28-7.23 (m, 1H), 7.22-7.14 (m, 2H), 3.78 (t,  $J = 4.8$  Hz, 4H), 3.05 (t,  $J = 4.8$  Hz, 4H), 2.34 (s, 3H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  136.2, 135.3, 130.4, 127.2, 126.5, 126.2, 67.9, 56.3, 19.6. HRMS (ESI)  $m/z$  calcd for  $C_{11}H_{15}NOS$   $[M+H]^+$ : 210.0947, found 210.0949.

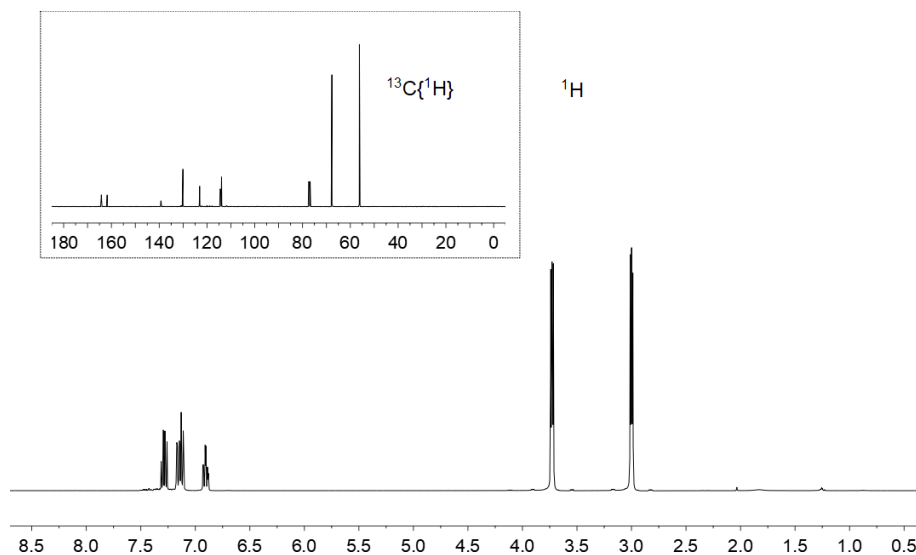


**Preparation of 3fh.** The cobalt catalysts (0.025 g), 4-fluorothiophenol (0.128 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3fh** (yellow oil) in a yield of 79% (168 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K)  $\delta$  7.44 (dd,  $J = 8.8$  Hz, 5.6 Hz, 2H), 7.03 (t,  $J = 8.8$  Hz, 2H), 3.64 (t,  $J = 4.8$  Hz, 4H), 2.83 (t,  $J = 4.8$  Hz, 4H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  163.16 (d,  $J = 248.8$  Hz), 134.95 (d,  $J = 8.3$  Hz), 128.07 (d,  $J = 3.4$  Hz), 115.77 (d,  $J = 21.7$  Hz), 67.52, 55.85. HRMS (ESI)  $m/z$  calcd for  $C_{10}H_{12}FNOS$   $[M+H]^+$ : 214.0696, found 214.0700.

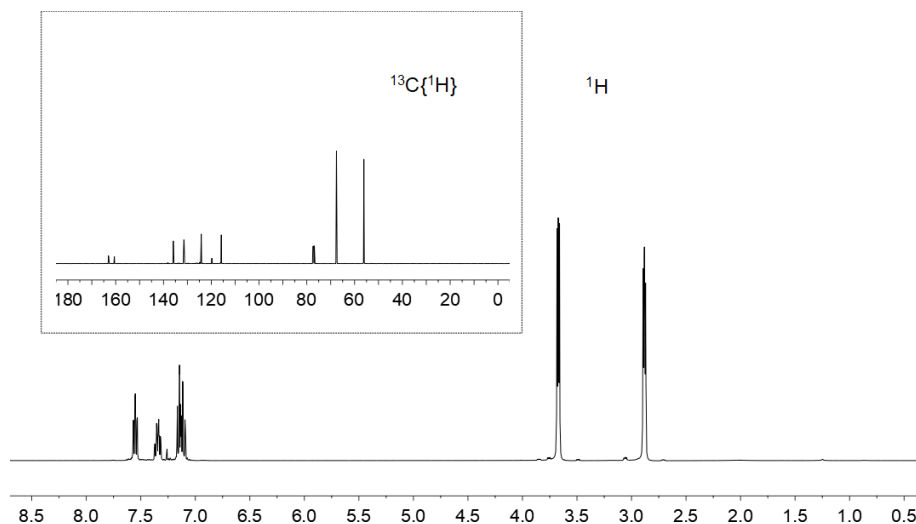


**Preparation of 3gh.** The cobalt catalysts (0.025 g), 3-fluorothiophenol (0.128 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction

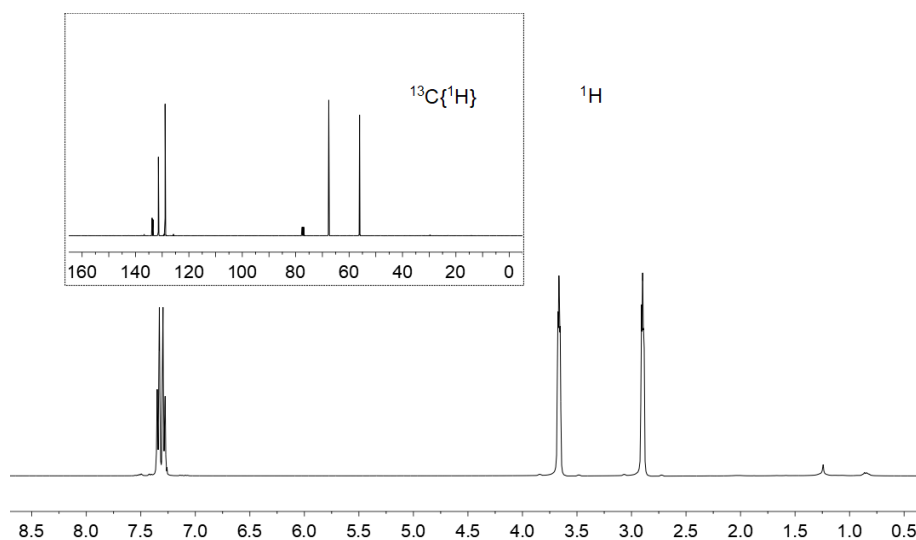
mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate (3×10 mL). The combined organic extract was dried by Na<sub>2</sub>SO<sub>4</sub> overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3gh** (yellow oil) in a yield of 93% (198 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.32-7.26 (m, 1H), 7.18-7.10 (m, 2H), 6.94-6.88 (m, 1H), 3.73 (t, *J* = 4.8 Hz, 4H), 3.00 (t, *J* = 4.8 Hz, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 163.0 (d, *J* = 248.3 Hz), 139.3 (d, *J* = 6.7 Hz), 130.1 (d, *J* = 8.3 Hz), 123.1 (d, *J* = 2.3 Hz), 114.4 (d, *J* = 23.0 Hz), 113.8 (d, *J* = 21.4 Hz), 67.7, 56.2. HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>12</sub>FNOS [M+H]<sup>+</sup>: 214.0696, found 214.0699.



**Preparation of 3hh.** The cobalt catalysts (0.025 g), 2-fluorothiophenol (0.128 g, 1 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of O<sub>2</sub> for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the 60°C and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate (3×10 mL). The combined organic extract was dried by Na<sub>2</sub>SO<sub>4</sub> overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3hh** (white solid) in a yield of 85% (181 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.57-7.52 (m, 1H), 7.38-7.31 (m, 1H), 7.17-7.09 (m, 2H), 3.67 (t, *J* = 4.8 Hz, 4H), 2.88 (t, *J* = 4.8 Hz, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 161.8, 135.9, 131.4 (d, *J* = 7.9 Hz), 124.2 (d, *J* = 3.7 Hz), 119.8 (d, *J* = 20.2 Hz), 115.9 (d, *J* = 23.5 Hz), 67.6, 56.1. HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>12</sub>FNOS [M+H]<sup>+</sup>: 214.0696, found 214.0698.

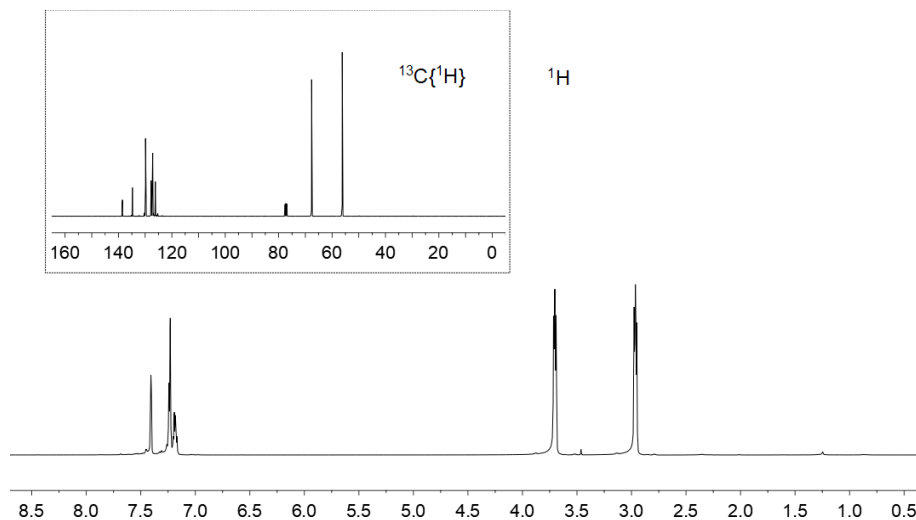


**Preparation of 3ih.** The cobalt catalysts (0.025 g), 4-chlorothiophenol (0.145 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3ih** (yellow oil) in a yield of 85% (195 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K)  $\delta$  7.34-7.29 (m, 2H), 7.28-7.24 (m, 2H), 3.64 (t,  $J = 4.8$  Hz, 4H), 2.87 (t,  $J = 4.8$  Hz, 4H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  133.8, 133.4, 131.4, 128.9, 67.6, 56.1. HRMS (ESI)  $m/z$  calcd for  $C_{10}H_{12}ClNOS$   $[M+H]^+$ : 230.0401, found 230.0404.

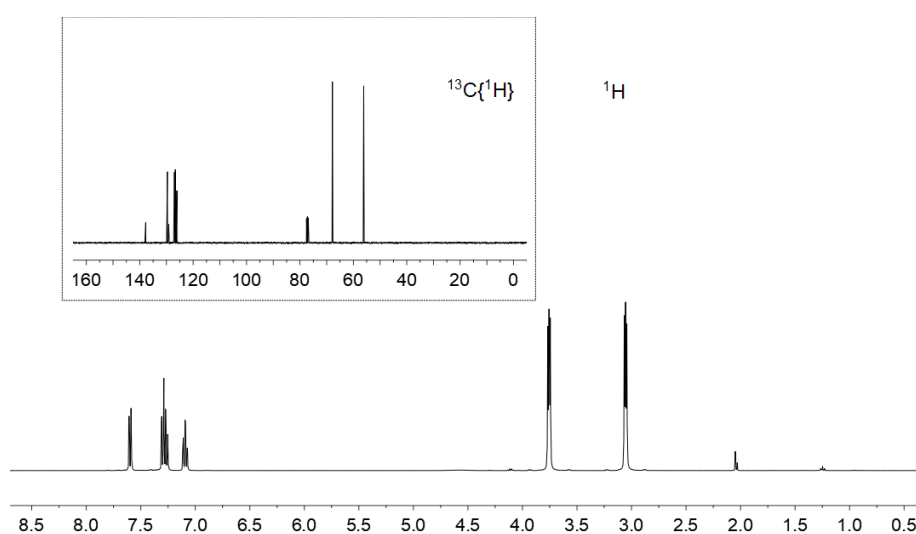


**Preparation of 3jh.** The cobalt catalysts (0.025 g), 3-chlorothiophenol (0.145 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate

(3×10 mL). The combined organic extract was dried by Na<sub>2</sub>SO<sub>4</sub> overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3jh** (yellow oil) in a yield of 82% (188 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.43-7.39 (m, 1H), 7.25-7.21 (m, 3H), 7.20-7.16 (m, 1H), 3.72 (t, *J* = 4.8 Hz, 4H), 2.96 (t, *J* = 4.8 Hz, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 138.5, 134.7, 129.9, 127.8, 127.2, 126.2, 67.7, 56.2. HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>12</sub>CINOS [M+H]<sup>+</sup>: 230.0401, found 230.0404.

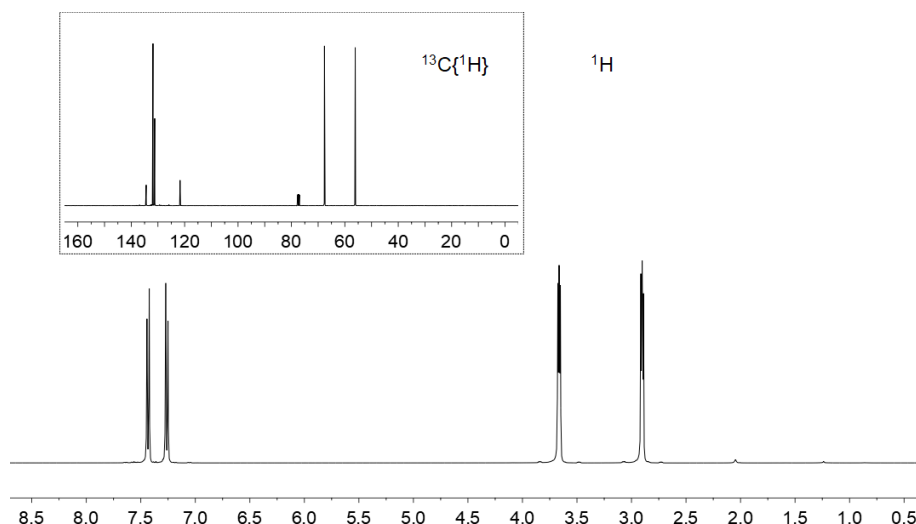


**Preparation of 3kh.** The cobalt catalysts (0.025 g), 2-chlorothiophenol (0.145 g, 1 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of O<sub>2</sub> for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the 60°C and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate (3×10 mL). The combined organic extract was dried by Na<sub>2</sub>SO<sub>4</sub> overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3kh** (yellow oil) in a yield of 88% (202 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ 7.60 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.34-7.23 (m, 2H), 7.15-7.05(m, 1H), 3.75 (t, *J* = 4.8 Hz, 4H), 3.05 (t, *J* = 4.8 Hz, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 137.8, 129.7, 129.1, 127.0, 126.7, 126.1, 67.9, 56.1. HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>12</sub>CINOS [M+H]<sup>+</sup>: 230.0401, found 230.0403.

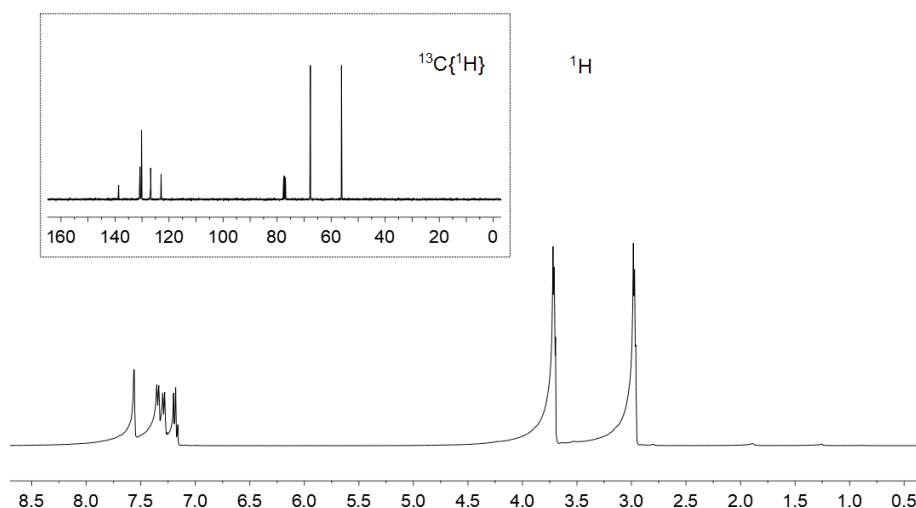


**Preparation of 3lh.** The cobalt catalysts (0.025 g), 4-bromothiophenol (0.189 g, 1 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of

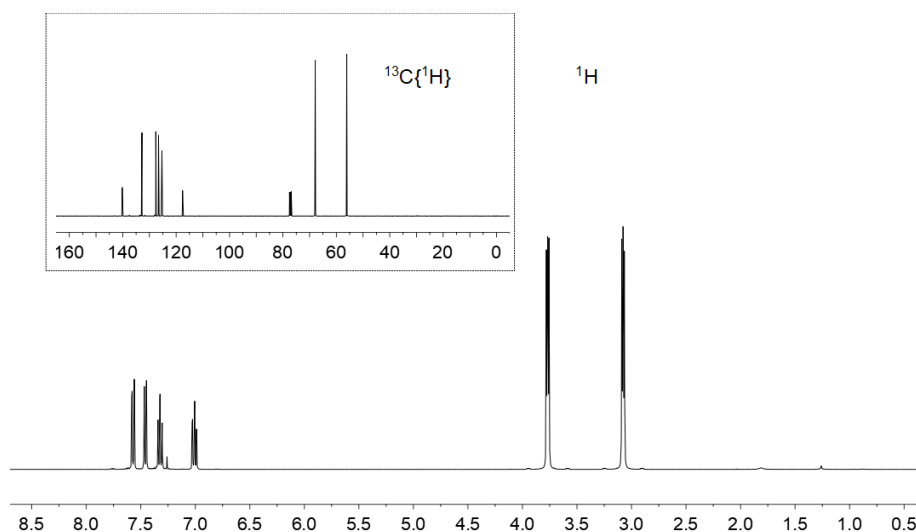
O<sub>2</sub> for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the 60°C and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate (3×10 mL). The combined organic extract was dried by Na<sub>2</sub>SO<sub>4</sub> overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3lh** (yellow oil) in a yield of 86% (222 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.66 (t, *J* = 4.8 Hz, 4H), 2.90 (t, *J* = 4.8 Hz, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 134.4, 131.9, 131.2, 121.7, 67.6, 56.1. HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>12</sub>BrNOS [M+H]<sup>+</sup>: 273.9896, found 273.9898.



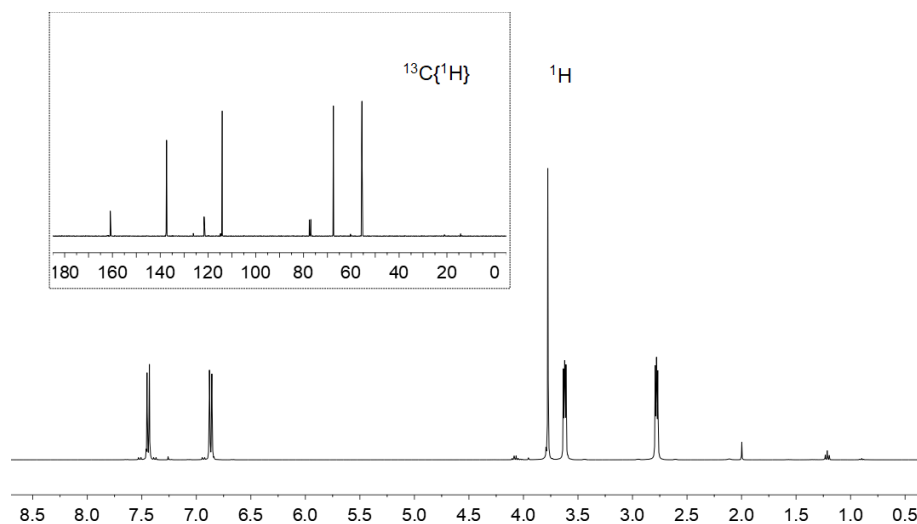
**Preparation of 3mh.** The cobalt catalysts (0.025 g), 3-bromothiophenol (0.189 g, 1 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of O<sub>2</sub> for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the 60°C and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate (3×10 mL). The combined organic extract was dried by Na<sub>2</sub>SO<sub>4</sub> overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3mh** (yellow oil) in a yield of 84% (217 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ 7.61-7.55 (m, 1H), 7.38-7.33 (m, 1H), 7.32-7.26 (m, 1H), 7.25-7.15 (m, 1H), 3.71 (t, *J* = 4.8 Hz, 4H), 2.97 (t, *J* = 4.8 Hz, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 138.6, 130.8, 130.2, 130.1, 126.8, 122.9, 67.7, 56.2. HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>12</sub>BrNOS [M+H]<sup>+</sup>: 273.9896, found 273.9901.



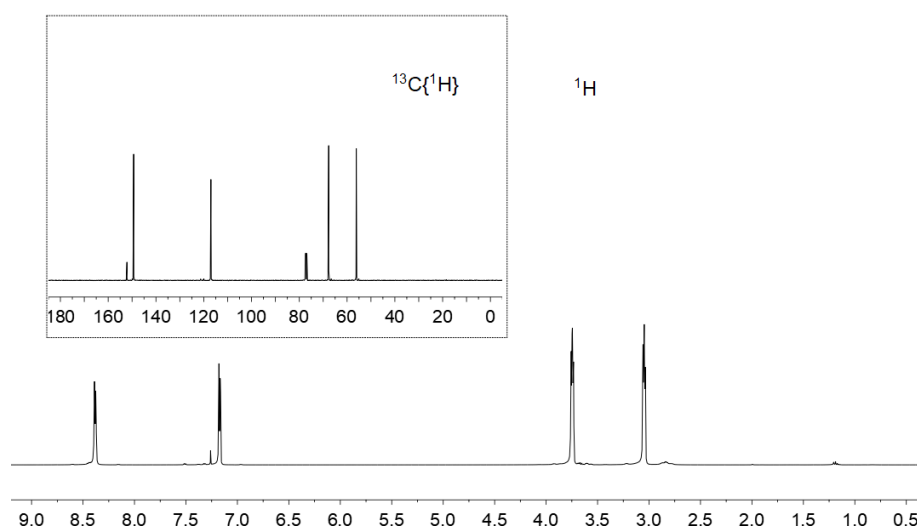
**Preparation of 3nh.** The cobalt catalysts (0.025 g), 2-bromothiophenol (0.189 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3nh** (yellow oil) in a yield of 91% (235 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298K)  $\delta$  7.57 (dd,  $J = 8.0$  Hz, 1.6 Hz, 1H), 7.46 (dd,  $J = 8.0$  Hz, 1.6 Hz, 1H), 7.36-7.29 (m, 1H), 7.04-6.97 (m, 1H), 3.77 (t,  $J = 4.8$  Hz, 4H), 3.08 (t,  $J = 4.8$  Hz, 4H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  140.2, 132.8, 127.6, 126.6, 125.3, 117.6, 67.9, 56.1. HRMS (ESI)  $m/z$  calcd for  $C_{10}H_{12}BrNOS$   $[M+H]^+$ : 273.9896, found 273.9899.



**Preparation of 3oh.** The cobalt catalysts (0.025 g), 4-methoxythiophenol (0.140 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. The metal block was heated to the reaction temperature and the reaction mixture was stirred for required time. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3oh** (yellow oil) in a yield of 80% (180 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298K)  $\delta$  7.44 (d,  $J = 8.8$  Hz, 2H), 6.87 (d,  $J = 8.8$  Hz, 2H), 3.78 (s, 3H), 3.62 (t,  $J = 4.8$  Hz, 4H), 2.78 (t,  $J = 4.8$  Hz, 4H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  160.9, 137.3, 121.6, 114.1, 67.5, 55.6, 55.3. HRMS (ESI)  $m/z$  calcd for  $C_{11}H_{15}NO_2S$   $[M+H]^+$ : 226.0896, found 226.0899.



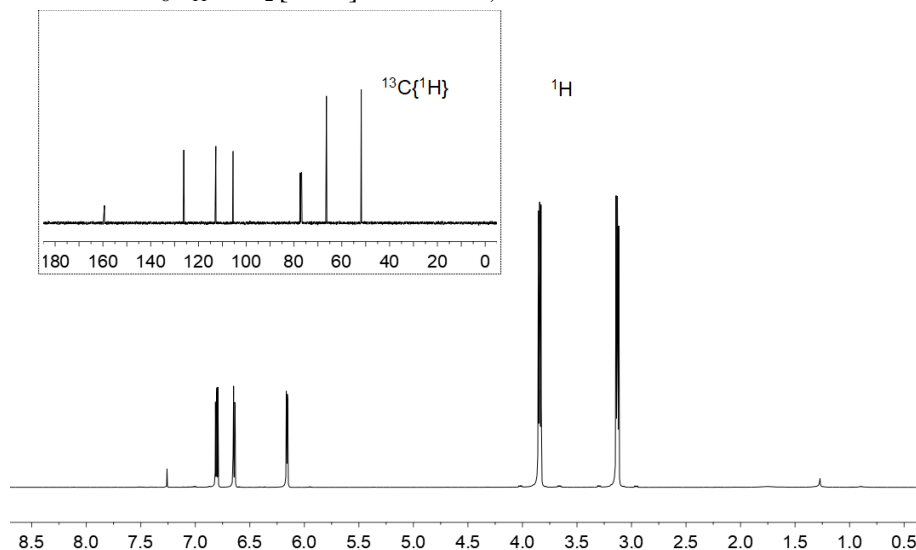
**Preparation of 3ph.** The cobalt catalysts (0.025 g), 4-mercaptopyridine (0.111 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3ph** (white solid) in a yield of 52% (102 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298K)  $\delta$  8.42-8.35 (m, 2H), 7.21-7.14 (m, 2H), 3.74 (t,  $J = 4.8$  Hz, 4H), 3.05 (t,  $J = 4.8$  Hz, 4H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  152.1, 149.3, 117.0, 67.7, 56.2. HRMS (ESI)  $m/z$  calcd for  $C_9H_{12}N_2OS$   $[M+H]^+$ : 197.0743, found 197.0747.



**Preparation of 3qh.** The cobalt catalysts (0.025 g), 2-thiophenethiol (0.116 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3qh** (yellow oil) in a yield of 49% (99 mg).  $^1H$  NMR (400



MHz,  $CDCl_3$ , 298K)  $\delta$  6.80 (dd,  $J = 5.6$  Hz, 1.2 Hz, 1H), 6.64 (dd,  $J = 5.6$  Hz, 1.2 Hz, 1H), 6.16 (dd,  $J = 3.6$  Hz, 1.2 Hz, 1H), 3.84 (t,  $J = 4.8$  Hz, 4H), 3.13 (t,  $J = 4.8$  Hz, 4H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  159.3, 126.2, 112.7, 105.5, 66.4, 51.9. HRMS (ESI)  $m/z$  calcd for  $C_8H_{11}NOS_2 [M+H]^+$ : 202.0355, found 202.0357.



**Preparation of 3rh.** The cobalt catalysts (0.025 g), 2-naphthalenethiol (0.106 g, 1 mmol) and  $K_2CO_3$  (0.069 g, 0.5 mmol) were added into a 38 mL screw-cap glass tube with a Teflon-coated stirring bar. The tube was fitted with the gas pipes and placed into a metal block on a parallel reactor with a reflux condenser. The reactor was evacuated, refilled with 0.1 MPa of  $O_2$  for three times and closed with valve. Then morpholine (0.348 g, 4 mmol) and DMSO (1 ml) were added into the reaction tube using syringes through a silicone pad on the cap. The metal block was heated to the  $60^\circ C$  and the reaction mixture was stirred for 16 h. At the end of the reaction, the solid was filtered off and washed thoroughly with ethyl acetate. Then saturated ammonium chloride solution (10 mL) was added to the liquids. The products were extracted by ethyl acetate ( $3 \times 10$  mL). The combined organic extract was dried by  $Na_2SO_4$  overnight and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate 25:1) provided **3rh** (yellow oil) in a yield of 84% (206 mg).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298K)  $\delta$  7.99 (d,  $J = 1.2$  Hz, 1H), 7.88-7.82 (m, 3H), 7.58-7.49 (m, 3H), 3.77 (t,  $J = 4.8$  Hz, 4H), 3.05 (t,  $J = 4.8$  Hz, 4H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  133.6, 132.9, 132.5, 129.2, 128.4, 128.1, 127.9, 126.7, 126.4, 67.8, 56.3. HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{15}NOS [M+H]^+$ : 246.0947, found 246.0949.

