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Catalytic O_2 Activation toward Oxidative N-S Bond Formation by a Thiolato Fe(III) Complex

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Electronic Supporting Information

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Materials and Methods

General Procedures. Commercially available chemicals were purchased from Aldrich or Acros, and used as received. All solvents except DMSO were distilled, dried, and stored in stored in dried N_2-filled reservoirs containing 4 Å molecular sieves before use. THF and hexane were distilled under nitrogen using sodium-benzophenone as a drying reagent. Ether and DMF were distilled under nitrogen using CaH_2 as a drying reagent. DMSO was purged under nitrogen and then stored in dried N_2-filled reservoirs containing 4 Å molecular sieves. The complexes[1] **1** and **1'**, substrates (**2b**, **2c**, **2d**, **2i**, **2m** and **2r**)[2] and products (**3b**, **3c**, **3e**, **3h**, **3l**, **3m**, **3p**, **3q** and **3r**)[3] was synthesized and identified by following the published procedures. ^{1}H, and ^{13}C NMR spectra were collected on an Avance 300 spectrometer. Chemical shifts for ^{1}H and ^{13}C{^{1}H} spectra were recorded in ppm relative to the residual proton and ^{13}C of $CDCl_3$ (^{1}H: δ 7.24; ^{13}C: δ 77.0) and DMSO-d_6 (^{1}H: δ 2.50; ^{13}C: δ 39.5). Infrared spectra were recorded on a Bruker Alpha instrument using ZnSe discs (0.2 mm, KBr windows). EPR spectra were monitored at X-band frequencies by using a Bruker EMSplus spectrometer with 8" magnet and 2.7 kW power supply. Elemental analyses and MS spectrometry were performed on a Heraeus CHN-OS Rapid Elemental Analyzer and JEOL JMX-SX/SX 102A Mass Spectrometer at the Instruments Center of National Chung Hsing University, Taiwan.

Crystallography

The crystals suitable for structure analysis were mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker APEX II with graphite monochromated Mo K_α radiation (λ = 0.71073 Å) at 150(2) K. All structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares methods against F^2 with SHELXL-97.[4] Tables of neutral atom scattering factors, f′ and f″, and absorption coefficients are from a standard source.[5] All atoms except for hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen atoms were fixed at calculated positions, and their positions were refined using a riding model. Crystallographic data collection and refinement parameters are given in Table S1-S6.

In situ time-dependant NMR experiment for the catalysis of S-N bond formation by complex 1' or complex 1 with oxygen

In the glove-box, a mixture of 1 equiv. of complex **1'** or complex **1** and 4 equiv. of $(LNHS)_2$ in DMSO-d_6 (400 μL) was transferred to a J. Young NMR tube. After collecting the first NMR spectrum of solution without adding oxygen, the J. Young NMR tube was degassed with the vacuum system and then filled with pure oxygen gas to conduct the in *situ* NMR experiment at 0.5, 2, 6, 12 and 24 hrs.

Synthesis of 2,2'-dithiobis[N-(methoxyphenyl)]benzamide (2e)

A solution of 0.25 g (2.1 mmol) of *o*-anisidine in 10 mL DCM was added dropwise to a solution of 0.35 g (1.0 mmol) of 2,2'-dithiosalicyl chloride in 20 mL DCM at 298 K. After 30 mins, the 0.5 mL NEt_3 was added to the above solution, and the solution was stirred for further 12 hrs. The resulting solution was washed with 50 mL H_2O three times, and the organic layer was collected, dried over with anhydrous $MgSO_4$ and filtrated. The solvent of the filtrate was removed by vacuum system to obtain the white solid 0.29 g (Yield: 55%). ^{1}H NMR

(DMSO-d_6): 9.73 (br, 2H), 7.83 (d, J = 7.4 Hz, 2H), 7.77 (d, J = 7.3 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.52 (t, J = 7.9 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.22 (t, J = 7.8 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 6.99 (t, J = 7.6 Hz, 2H), 3.84 (s, 6H). ^{13}C NMR: 165.64, 151.66, 136.95, 133.91, 131.51, 128.47, 126.45, 126.25, 126.13, 126.09, 124.50, 120.23, 111.59, 55.74.

Synthesis of 2,2'-dithiobis[N-(2-methyl)tetrahydrofuranyl)]benzamide (2f)

A solution of 0.21 g (2.1 mmol) of 2-(aminomethyl)tetrahydrofuran in 10 mL DCM was added dropwise to a solution of 0.35 g (1.0 mmol) of 2,2'-dithiosalicyl chloride in 20 mL DCM at 298 K. After 30 mins, the 0.5 mL NEt_3 was added to the above solution, and the solution was stirred for further 12 hrs. The resulting solution was washed with 50 mL H_2O three times, and the organic layer was collected, dried over with anhydrous $MgSO_4$ and filtrated. The solvent of the filtrate was removed by vacuum system to obtain the white solid 0.40 g (Yield: 86%). ^{1}H NMR (DMSO-d_6): 8.71 (t, J = 4.9 Hz, 2H), 7.62(d, J = 7.8 Hz, 4H), 7.44 (t, J = 8.0 Hz, 2H), 7.29 (t, J = 7.3 Hz, 2H), 3.99 (quin, J = 6.2 Hz, 2H), 3.79 (q, J = 6.9 Hz, 2H), 3.63 (q, J = 7.1 Hz, 2H), 3.32 (q, J = 6.1 Hz, 4H), 1.92 (m, 4H), 1.83 (m, 2H), 1.64 (m, 2H). ^{13}C NMR: 167.04, 136.68, 133.88, 131.09, 128.00, 125.97, 125.68, 77.02, 67.3, 43.33, 28.83, 25.18. IR (KBr): 3340 (br, ν_{NH}), 1629 (s, $\nu_{C=O}$) cm^{-1}. EA: C: 60.99, H: 5.97, N: 5.93; found: C: 60.89, H: 5.79, N: 5.66. HRMS m/z calcd for C24H28O4N2NaS2 $[M+Na]^+$: 495.1389; found: 495.1383.

Synthesis of 2,2'-dithiobis[N-2-(2-cyclohexenyl)-ethyl)]benzamide (2g)

A solution of 0.41 g (3.3 mmol) of 2-(1-cyclohexenyl)ethylamine in 10 mL DCM was added dropwise to a solution of 0.54 g (1.6 mmol) of 2,2'-dithiosalicyl chloride in 20 mL DCM at 298 K. After 30 mins, the 0.75 mL NEt_3 was added to the above solution, and the solution was stirred for further 12 hrs. The resulting solution was washed with 50 mL H_2O three times, and the organic layer was collected, dried over with anhydrous $MgSO_4$ and filtrated. The solvent of the filtrate was removed by vacuum system to obtain the white solid 0.50 g (Yield: 60%). ^{1}H NMR (DMSO-d_6): 8.55 (t, J = 5.6 Hz, 2H), 7.60 (d, J = 7.9 Hz, 2H), 7.57 (d, J = 7.3 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.29 (t, J = 7.4 Hz, 2H), 5.44 (s, 2H), 3.37 (s, 4H), 2.17 (t, J = 6.7 Hz, 4H), 1.95 (m, 8H), 1.54 (m, 8H). ^{13}C NMR: 166.75, 136.52, 134.92, 134.24, 130.95, 127.84, 125.98, 125.54, 122.26, 37.66, 37.47, 27.63, 24.82, 22.52, 22.03. IR (KBr): 3305 (br, ν_{NH}), 1632 (s, $\nu_{C=O}$) cm^{-1}. EA: C: 69.19, H: 6.97, N: 5.38; found: C: 68.86, H: 6.59, N: 5.30. HRMS m/z calcd for C30H36O2N2NaS2 $[M+Na]^+$: 543.2121; found: 543.2110.

Synthesis of 2,2'-dithiobis[N-(2-hydroxyethy)]benzamide (2h)

The solution of 0.35 g (1.0 mmol) of 2,2'-dithiosalicyl chloride in 20 mL DCM was slowly added to the flask contained 0.13 g (2.1 mmol) ethanolamine in an ice bath. After 30 mins, 0.5 mL NEt_3 was added to the above solution, and the solution was stirred for further 16 hrs. The precipitate of the resulting solution was filtrated, washed with 50 mL H_2O three times and 20 mL DCM twice, and then it was dried under vacuum to obtain the white product 0.25 g (Yield: 63%). ^{1}H NMR (DMSO-d_6): 8.62 (t, J = 4.8 Hz, 2H), 7.68 (d, J = 7.4 Hz, 2H), 7.63(d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.4 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 4.87 (t, J = 5.1 Hz, 2H), 3.55 (t, J = 6.0 Hz, 4H), 3.35 (q, J = 5.7 Hz, 4H). ^{13}C NMR: 167.28, 136.91, 133.90, 131.32, 128.25, 126.14, 125.87, 59.84, 42.35. IR (KBr): 3286(br, ν_{OH}), 1633(s, $\nu_{C=O}$) cm^{-1}. EA: C: 55.08, H: 5.14, N: 7.14; found: C: 55.07, H:

4.86, N: 7.32.

Synthesis of 2,2'-dithiolbis[N-(2-(dimethylamino)-ethyl)benzamide (2i)

The solution of 0.35 g (1.0 mmol) of 2,2'-dithiosalicyl chloride in 20 mL DCM was slowly added to the flask contained 0.18 g (2.0 mmol) N,N-dimethylethylenediamine in an ice bath. After 30 mins, 1.0 mL NEt_3 was added to the above solution, and the solution was stirred for further 12 hrs. The resulting solution was washed with 50 mL H_2O three times, and the organic layer was collected, dried over with anhydrous $MgSO_4$, filtrated and dried under vacuum system. The resident was washed with 15 mL ether twice and then dried under vacuum system to obtain the white product 0.24 g (Yield: 54%). ^{1}H NMR (DMSO-d_6): 8.60 (t, J = 5.6 Hz, 2H), 7.64 (d, J = 7.9 Hz, 4H), 7.43 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 3.38 (q, J = 6.2 Hz, 4H), 2.45 (t, J = 6.8 Hz, 4H), 2.19 (s, 6H). ^{13}C NMR: 166.98, 136.83, 133.92, 131.17, 128.04, 126.06, 125.77, 58.06, 45.30, 37.51. IR (KBr): 3310 (br, ν_{NH}), 1627 (s, $\nu_{C=O}$).

Synthesis of 2,2'-dithiobis[N-(2-chloroethyl)]benzamide (2j)

The solution of 0.35 g (1.0 mmol) of 2,2'-dithiosalicyl chloride in 20 mL THF was slowly added to the flask contained 0.24 g (2.1 mmol) 2-chloroethylamine hydrochloride in an ice bath. After 30 mins, 0.35 g (2.5 mmol) K_2CO_3 was added to the above solution, and the solution was stirred for further 16 hrs. The resulting solution was filtrated to remove salt, and the filtrate was dried under vacuum. The residues were washed by 15 mL DCM three times and then dried under vacuum to obtain the white solid 0.23 g (Yield: 53%). ^{1}H NMR (DMSO-d_6): 8.93 (t, J = 5.4 Hz, 2H), 7.68 (d, J = 7.0 Hz, 2H), 7.65 (d, J = 7.2 Hz, 2H), 7.47 (t, J = 7.7 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 3.77 (t, J = 5.9 Hz, 4H), 3.61 (q, J = 5.9 Hz, 4H). ^{13}C NMR: 167.18, 136.87, 133.32, 131.38, 128.07, 126.04, 125.78, 43.13, 41.33. IR (KBr): 3291 (br, ν_{NH}), 1626 (s, $\nu_{C=O}$) cm^{-1}. EA: C: 50.35, H: 4.23, N: 6.52; found: C: 50.29., H: 4.02, N: 6.19.

Synthesis of 2,2'-dithiobis[N-(2-methoxylethyl)]benzamide (2k)

The solution of 0.35 g (1.0 mmol) of 2,2'-dithiosalicyl chloride in 20 mL DCM was slowly added to the flask contained 0.16 g (2.1 mmol) 2-methoxyethanamine in an ice bath. After 30 mins, 0.5 mL NEt_3 was added to the above solution, and the solution was stirred for further 12 hrs. The resulting solution was washed with 50 mL H_2O three times, and the organic layer was collected, dried over with anhydrous $MgSO_4$ and filtrated. The solvent of the filtrate was removed by vacuum system to obtain the white solid 0.26 g (Yield: 61%). ^{1}H NMR (DMSO-d_6): 8.71 (t, J = 5.3 Hz, 2H), 7.64 (d, J = 6.9 Hz, 2H), 7.63 (d, J = 7.9 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 3.47 (m, 8H), 3.29 (s, 6H). ^{13}C NMR: 166.98, 136.75, 133.57, 131.13, 127.99, 125.93, 125.67, 70.33, 57.98, 39.03. IR (KBr): 3307 (br, ν_{NH}), 1627 (s, $\nu_{C=O}$) cm^{-1}. EA: C: 57.12, H: 5.75, N: 6.66; found: C: 56.70, H: 5.31, N: 6.52.

Synthesis of 2,2'-dithiobis[N-(methoxycarbonyl)-methyl)]benzamide (2l)

The solution of 0.35 g (1.0 mmol) of 2,2'-dithiosalicyl chloride in 20 mL DCM was slowly added to the flask contained 0.27 g (2.1 mmol) glycine methyl ester hydrochloride in an ice bath. After 30 mins, 1.0 mL NEt_3 was added to the above solution, and the solution was stirred for further 12 hrs. The resulting solution was washed with 50 mL H_2O three times, and the organic layer was collected, dried over with anhydrous $MgSO_4$

and filtrated. The solvent of the filtrate was removed by vacuum system to obtain the white solid 0.35 g (Yield: 78%). ^{1}H NMR (DMSO-d_6): 9.13(t, J = 6.1 Hz, 2H), 7.74 (d, J = 7.6 Hz, 2H), 7.67 (d, J = 7.9 Hz, 2H), 7.49, (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 4.06 (d, J = 5.7 Hz, 4H), 3.68 (s, 6H). ^{13}C NMR: 170.20, 167.35, 137.19, 132.51, 131.64, 128.23, 126.03, 125.75, 51.89, 41.17. IR (KBr): 3308 (br, ν_{NH}), 1756, 1636(s, $\nu_{C=O}$) cm^{-1}. EA: C: 53.56, H: 4.49, N: 6.25; found: C: 53.36, H: 4.42, N: 6.60.

Synthesis of 2,2'-dithiobis[N-(carboxyl)methyl)]benzamide (2m)

The 10 mL 2 M NaOH aqueous solution was transferred to the solution of 0.45 g (1.0 mmol) of 2,2'-dithiobis[N-(methoxycarbonyl)methyl)] benzamide in 30 mL MeOH at room temperature for 30 mins. The organic solvent was removed from the resulting solution by vacuum system. The aqueous layer was extracted with DCM (30 mL) twice to remove unreacted organic material. The gray solid was precipitated by adding 10 % HCl aqueous solution to the resulting aqueous layer (pH < 7). The solid was collected, washed with H_2O (10 mL) twice, and dried under vacuum system to obtain the product 0.37g (Yield: 88%). ^{1}H NMR (DMSO-d_6): 12.74 (br, 2H), 9.01 (t, J = 5.7 Hz, 2H), 7.73 (d, J = 7.5 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 3.96 (d, J = 5.8 Hz, 4H). ^{13}C NMR: 171.21, 167.27, 137.25, 132.70, 131.60, 128.24, 126.00, 125.77, 41.24. IR (KBr): 3285 (br, ν_{OH} and ν_{NH}), 1723, 1636 (s, $\nu_{C=O}$) cm^{-1}. EA: C: 51.42, H: 3.84, N: 6.66; found: C: 51.39, H: 3.66, N: 6.70.

Synthesis of 2,2'-dithiobis[N-(3-pyridinylmethyl)]benzamide (2n)

The solution of 0.35 g (1.0 mmol) of 2,2'-dithiosalicyl chloride in 20 mL DCM was slowly added to the flask contained 0.23 g (2.1 mmol) 3-picolylamine in an ice bath. After 30 mins, 1.0 mL NEt_3 was added to the above solution, and the solution was stirred for further 12 hrs. The resulting solution was washed with 50 mL H_2O three times, and the organic layer was collected, dried over with anhydrous $MgSO_4$ and filtrated. The solvent of the filtrate was removed by vacuum system to obtain the white solid 0.32 g (Yield: 66%). ^{1}H NMR (DMSO-d_6): 9.28 (t, J = 5.6 Hz, 2H), 8.60 (s, 2H), 8.48 (d, J = 3.2 Hz, 2H), 7.78 (d, J = 6.9 Hz, 2H), 7.70 (d, J = 7.1 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 5.2 Hz, 2H), 7.31 (t, J = 6.2 Hz, 2H), 4.52 (d, J = 5.1 Hz, 4H). ^{13}C NMR: 167.17, 148.87, 148.28, 136.85, 135.29, 134.85, 133.53, 131.43, 128.10, 126.22, 125.91, 123.66, 40.52. IR (KBr): 3266 (br, ν_{NH}), 1635 (s, $\nu_{C=O}$) cm^{-1}. EA: C: 64.18, H: 4.56, N: 11.51; found: C: 63.87, H: 4.66, N: 11.86.

Synthesis of 2,2'-dithiobis[N-(4-pyridinylmethyl)]benzamide (2o)

The solution of 0.35 g (1.0 mmol) of 2,2'-dithiosalicyl chloride in 20 mL DCM was slowly added to the flask contained 0.23 g (2.1 mmol) 4-picolylamine in an ice bath. After 30 mins, 1.0 mL NEt_3 was added to the above solution, and the solution was stirred for further 12 hrs. The resulting solution was washed with 50 mL H_2O three times, and the organic layer was collected, dried over with anhydrous $MgSO_4$ and filtrated. The solvent of the filtrate was removed by vacuum system to obtain the white solid 0. 31g (Yield: 64%). ^{1}H NMR (DMSO-d_6): 9.31 (t, J = 5.1 Hz, 2H), 8.52 (d, J = 5.0 Hz, 4H), 7.76 (d, J = 7.2 Hz, 2H), 7.65 (d, J = 7.9 Hz, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.36 (m, 6H), 4.52 (d, J = 5.7 Hz, 4H) . ^{13}C NMR: 167.36, 149.65, 148.38, 136.96, 133.44, 131.53, 128.20, 126.31, 125.97, 122.31, 41.86. IR (KBr): 3287 (br, ν_{NH}), 1639 (s, $\nu_{C=O}$) cm^{-1}. EA: C: 64.18, H: 4.56, N: 11.51; found: C: 64.12, H: 4.30, N: 11.89.

Synthesis of 2,2'-dithiobis[N-(2-propenyl)]benzamide (2p)

The solution of 0.72 g (2.1 mmol) of 2,2'-dithiosalicyl chloride in 20 mL DCM was slowly added to the flask contained 0.24 g (4.2 mmol) allylamine in an ice bath. After 30 mins, 1.0 mL NEt_3 was added to the above solution, and the solution was stirred for further 12 hrs. The resulting solution was washed with 50 mL H_2O three times, and the organic layer was collected, dried over with anhydrous $MgSO_4$ and filtrated. The solvent of the filtrate was removed by vacuum system to obtain the yellow solid 0.45 g (Yield: 56%). ^{1}H NMR (DMSO-d_6): 8.85 (t, *J* = 5.6 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 5.92 (m, 2H), 5.24 (dd, *J* = 17.2 and 1.4 Hz, 2H), 5.13 (dd, *J* = 10.2 and 1.2 Hz, 2H), 3.92 (t, *J* = 5.2 Hz, 4H) . ^{13}C NMR: 166.75, 136.15, 135.04, 133.75, 131.15, 127.99, 126.01, 125.71, 115.36, 41.49.

Synthesis of 2,2'-dithiobis[N-(2-propynyl)]benzamide (2q)

The solution of 0.35 g (1.0 mmol) of 2,2'-dithiosalicyl chloride in 20 mL DCM was slowly added to the flask contained 0.12 g (2.2 mmol) 2-propynylamine in an ice bath. After 30 mins, 0.5 mL NEt_3 was added to the above solution, and the solution was stirred for further 16 hrs. The precipitate of the resulting solution was filtrated, washed with 50 mL H_2O three times and 20 mL DCM twice, and then it was dried under vacuum to obtain the light yellow product 0.32 g (Yield: 84%). ^{1}H NMR (DMSO-d_6): 9.13 (t, *J* = 5.5 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 4.08 (dd, *J* = 5.3 and 2.3 Hz, 4H), 3.20 (t, *J* = 2.3 Hz, 2H). ^{13}C NMR: 166.59, 137.01, 132.84, 131.54, 128.14, 126.06, 125.80, 80.96, 73.25, 28.57.

Characterization of 2-(2-hydroxyphenyl)-1,2-benzisothiazol-3(2H)-one (3d)

^{1}H NMR (DMSO-d_6): 9.98 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR: 164.03, 154.14, 141.56, 132.07, 130.23, 130.13, 125.94, 125.45, 123.64, 123.03, 121.64, 119.25, 116.88. IR (KBr): 3224 (br, ν_{O-H}), 1643(s, $\nu_{C=O}$) cm^{-1}. EA: C: 64.18, H: 3.73, N: 5.76; found: C: 64.21, H: 3.70, N: 5.94. HRMS m/z calcd for C13H10O2NS $[M+H]^+$: 244.0421; found: 244.0427.

Characterization of 2-(2-tetrahydrofuranyl-methyl)-1,2-benzisothiazol-3(2H)-one (3f)

^{1}H NMR (DMSO-d_6): 7.94 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 4.11 (quin, *J* = 4.9 Hz, 1H), 3.92 (m, *J* = Hz, 2H), 3.79 (q, *J* = 7.1 Hz, 1H), 3.66 (q, *J* = 7.1 Hz, 1H), 1.94 (sext, *J* = 5.9 Hz, 1H), 1.79 (quin, *J* = 6.9 Hz, 2H), 1.55 (sext, *J* = 7.6 Hz, 1H). ^{13}C NMR: 164.74, 141.31, 131.78, 125.58, 125.31, 123.54, 121.53, 77.01, 67.45, 46.67, 28.00, 25.31. IR (KBr): 1654(s, $\nu_{C=O}$) cm^{-1}. EA: C: 61.25, H: 5.95, N: 5.57; found: C: 60.85, H: 5.78, N: 5.17. HRMS m/z calcd for C12H14O2NS $[M+H]^+$: 236.0740; found: 236.0749.

Characterization of 2-[2-(2-cyclohexenyl)ethyl]-1,2-benzisothiazol-3(2H)-one (3g)

^{1}H NMR (DMSO-d_6): 7.95 (d, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 7.1 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 5.38 (s, 1H), 3.89 (t, *J* = 6.5 Hz, 2H), 2.28 (t, *J* = 5.5 Hz, 2H), 1.97 (m, 2H), 1.84 (m, 2H), 1.56

(sext, J = 4.0 Hz, 2H), 1.46 (sext, J = 4.4 Hz, 2H). ^{13}C NMR: 164.17, 140.36, 133.80, 131.65, 125.49, 125.36, 124.10, 122.98, 121.73, 41.51, 37.13, 27.53, 24.69, 22.32, 21.76. IR (KBr): 1653(s, $\nu_{C=O}$) cm^{-1}. EA: C: 69.46, H: 6.61, N: 5.40; found: C: 69.71, H: 6.58, N: 5.36. HRMS m/z calcd for C15H18ONS $[M+H]^+$: 260.1113; found: 260.1104.

Characterization of 2-[N-(2-(dimethylamino)ethy)] -1,2-benzisothiazol-3(2H)-one (3i)

^{1}H NMR (DMSO-d_6): 7.94 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.66 (t, J = 7.8 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 3.91 (t, J = 5.9 Hz, 2H), 2.53 (t, J = 5.8 Hz, 2H), 2.21 (s, 6H). ^{13}C NMR: 164.45, 141.40, 131.63, 125.46, 125.27, 123.91, 121.62, 57.81, 45.00, 40.83. IR (KBr): 1652(s, $\nu_{C=O}$) cm^{-1}.

Characterization of 2-(2-chloroethyl)-1,2-benzisothiazol-3(2H)-one (3j)

^{1}H NMR (DMSO-d_6): 8.00 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 7.7 Hz, 1H), 7.69 (t, J = 7.1 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 4.18 (t, J = 5.8 Hz, 1H), 3.92 (t, J = 5.8 Hz, 2H). ^{13}C NMR: 164.72, 140.89, 132.05, 125.67, 125.57, 123.65, 123.97, 44.82, 43.00. IR (KBr): 1672(s, $\nu_{C=O}$) cm^{-1}. EA: C: 50.59, H: 3.77, N: 6.56; found: C: 50.64, H: 3.75, N: 6.19. HRMS m/z calcd for C9H9ONClS $[M+H]^+$: 214.0081; found: 214.0088.

Characterization of 2-(2-methoxylethyl)-1,2-benzisothiazol-3(2H)-one (3k)

^{1}H NMR (DMSO-d_6): 7.96 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.67 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.3 Hz, 1H), 3.99 (t, J = 5.2 Hz, 2H), 3.59 (t, J = 5.1 Hz, 2H), 3.28 (s, 3H). ^{13}C NMR: 184.49, 141.01, 131.81, 125.57, 125.42, 123.80, 121.73, 70.34, 58.08, 42.85. IR (KBr): 1652(s, $\nu_{C=O}$) cm^{-1}. EA: C: 57.40, H: 5.30, N: 6.69; found: C: 57.41, H: 4.99, N: 6.41.

Characterization of 2-(3-pyridinylmethyl)-1,2-benzisothiazol-3(2H)-one (3n)

^{1}H NMR (DMSO-d_6): 8.59 (s, 1H), 8.51 (d, J = 4.7 Hz, 1H), 7.95 (d, J = 8.7 Hz, 1H), 7.91 (d, J = 8.6 Hz, 1H), 7.68 (m, 2H), 7.41 (m, 2H), 5.08 (s, J = Hz, 2H). ^{13}C NMR: 164.73, 149.30, 149.22, 140.72, 136.04, 132.82, 132.24, 125.94, 125.86, 124.00, 123.89, 122.17, 44.09. IR (KBr): 1647 (s, $\nu_{C=O}$) cm^{-1}.

Characterization of 2-(4-pyridinylmethyl)-1,2-benzisothiazol-3(2H)-one (3o)

^{1}H NMR (DMSO-d_6): 8.54 (d, J = 6.2 Hz, 2H), 8.00 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 4.3 Hz, 2H), 5.09 (s, 2H). ^{13}C NMR: 165.13, 150.37, 146.33, 141.17, 132.62, 126.30, 126.17, 124.03, 122.81, 122.57, 45.61. IR (KBr): 1647 (s, $\nu_{C=O}$) cm^{-1}.

Synthesis of complex 4

Complex **1 (**0.06 g, 0.1 mmol) and $ONMe_3$ (0.008 g, 0.1 mmol) were dissolved in 5 mL DMF, and the solution was stirred for 1 hour. Then, 45 mL ether was added to the solution to form precipitates. The precipitates were collected and dried under the vacuum system. The residue was dissolved in 5 mL MeCN and layered by 40 mL ether slowly, and the dark green crystals 0.02 g (0.03 mmol) was obtained at -20˚C for 2 weeks (Crystal yield: 33%). IR (KBr): 1607, 1580 (s, $\nu_{C=O}$), 1023 (s, $\nu_{S=O}$) cm^{-1}. HRMS m/z calcd for C26H20O3N4FeS2 $[M]^-$: 556.0321; found: 556.0332. EPR (MeCN, 77K): 2.12.

The experiment for the catalysis of S-N bond formation by the ironic source with molecular oxygen

In the glove-box, a mixture of 2.5 (1, 5 or 10) mol% of ironic source (complex **1** or $FeCl_3$) and the disulfide substrate were loaded to the 50 mL flask and dissolved in THF/MeCN (1:1) (or DMF). The mixed solution was stirred for 24 or 48 hrs under O_2 atmosphere. The resulting solution was dried under vacuum, and the residues were dissolved in DMSO-d_6 to conduct the ^1H NMR experiment without further purification.

The experiment for the catalysis of S-N bond formation by the ironic source with $ONMe_3$

In the glove-box, a mixture of 2.5 (1, 5 or 10) mol% of ironic source (complex **1** or $FeCl_3$), the disulfide substrate and 5 fold of $ONMe_3$ were loaded to the 50 mL flask and dissolved in THF/MeCN (1:1) (or DMF). The mixed solution was stirred for 24 hrs in the closed system. The resulting solution was dried under vacuum, and the residues were dissolved in DMSO-d_6 to conduct the ^1H NMR experiment without further purification.

***In situ* NMR experiment for the oxidation of PPh_3 with $ONMe_3$**

In the glove-box, a mixture of 1 equiv. of PPh_3 and 1 equiv. of $ONMe_3$ in DMSO-d_6 (400 μL) was transferred to a J. Young NMR tube which conducted the *in situ* NMR experiment.

***In situ* NMR experiment for the oxidation of PPh_3 by complex 1 or $FeCl_3$ with $ONMe_3$**

In the glove-box, a mixture of 1 equiv. of complex **1** (or $FeCl_3$), 2 equiv. of PPh_3 and 2 equiv. of $ONMe_3$ in DMSO-d_6 (400 μL) was transferred to a J. Young NMR tube which conducted the *in situ* NMR experiment.

***In situ* NMR experiment for the oxidation of PPh_3 by complex 1 with O_2**

In the glove-box, a mixture of 1 equiv. of complex **1** and 2 equiv. of PPh_3 in DMSO-d_6 (400 μL) was transferred to a J. Young NMR tube. Then, the NMR tube was purged with O_2 for 10 seconds, and the tube was conducted the *in situ* NMR experiment after 24 hrs.

***In situ* NMR experiment for the reactivity of complex 4 with the disulfide substrates or PPh_3**

In the glove-box, a mixture of complex **4** and 4 fold of substrate **2a**, **2b** or PPh_3 in DMSO-d_6 (400 μL) was transferred to a J. Young NMR tube. The NMR tube was conducted the *in situ* NMR experiment after 24 hrs.

Supplementary Tables and Figures

Table S1. The summary of crystallographic data for the organic substrates (**2b**, **2c**, **2e**, **2f**).

	2b	**2c**	**2e**	**2f**
formula	C28H24N2O2S2	C22H28N2O2S2	C28H24N2O4S2	C24H28N2O4S2
fw	484.61	416.58	516.61	472.60
temp, K	296(2) K	150(2) K	150(2)	150(2)
cryst syst	Monoclinic	Triclinic	Monoclinic	Orthorhombic
space group	$P2_1/n$	P-1	C2/c	$P2_12_12_1$
a, Å	7.927(2)	11.2697(11)	11.532(2)	7.8446(2)
b, Å	18.115(5)	13.9696(13)	10.4494(19)	15.3529(4)
c, Å	16.886(5)	15.8362(14)	20.496(4)	18.7689(5)
α, º	90	113.646(6)	90	90
β, °	95.357(16)	92.993(6)	97.173(12)	90
γ, º	90	100.554(6)	90	90
Volume, $Å^3$ / *Z*	2414.1(12) / 4	2223.2(4) / 4	2450.4(7) / 4	2260.48(10) / 4
Density (cald.), Mg/m^3	1.333	1.245	1.400	1.389
Absorption coefficient, mm^{-1}	0.249	0.259	0.256	0.270
crystal size, mm	0.20 x 0.12 x 0.08	0.12 x 0.08 x 0.08	0.10 x 0.10 x 0.10	0.12 x 0.10 x 0.08
θ range, deg	2.42 to 28.29	1.418 to 28.280	2.00 to 28.28	1.71 to 28.82
no. of reflns collected	30128	25532	14783	31168
no. of indep reflns	5971	10716	3032	5592
max. and min. trans	0.982 and 0.960	0.978 and 0.967	0.9582 and 0.9582	0.973 and 0.959
no. of data /restraints /params	5971 / 0 / 307	10716 / 0 / 517	3030 / 0 / 164	5592 / 0 / 344
goodness-of-fit on F^2	0.732	0.921	1.164	0.898
final *R* indices [$I>2\sigma(I)$] R_1[a], wR_2[b]	0.0392, 0.1059	0.0476, 0.1166	0.0573, 0.1648	0.0441, 0.1182
R indices (all data), R_1[a] ,wR_2[b]	0.0778, 0.1434	0.0914, 0.1428	0.0782, 0.1798	0.0553, 0.1277
largest diff. peak and hole, e $Å^{-3}$	0.286 and -0.402	0.312 and -0.331	0.407 and -0.386	0.255 and -0.509

[a] $R_1 = \Sigma \left| F_0 \right| - \left| F_c \right| / \Sigma \left| F_0 \right|$

[b] $wR_2 = [\Sigma[\omega(F_0^2 - F_c^2)^2] / \Sigma[\omega(F_0^2)^2]]^{1/2}$

Table S2. The summary of crystallographic data for the organic substrates (**2i**, **2j**, **2n**, **2o**).

	2i	**2j**	**2n**	**2o**
formula	C22H30N4O2S2	C18H18Cl2N2O2S2	C27H26N4O3S2	C26H33N4O2S2
fw	446.62	429.36	518.64	486.59
temp, K	150(2)	150(2)	150(2)	150(2)
cryst syst	Monoclinic	Monoclinic	Triclinic	Orthorhombic
space group	$P2_1/n$	$P2_1/n$	P-1	$Pna2_1$
a, Å	7.767(3)	10.7004(4)	8.9627(17)	20.9157(11)
b, Å	19.185(6)	18.5647(4)	9.6003(15)	4.9145(3)
c, Å	15.494(5)	11.2176(2)	15.312(3)	23.0352(13)
α, º	90	90	101.184(13)	90
β, º	97.481(6)	118.2724(12)	95.225(12)	90
γ, º	90	90	101.995(12)	90
Volume, $Å^3$ / *Z*	2289.0(13) / 4	1962.54(7) / 4	1252.4(4) / 2	2367.8(2) / 4
Density (cald.), Mg/m^3	1.296	1.453	1.375	1.365
Absorption coefficient, mm^{-1}	0.258	0.559	0.250	0.257
crystal size, mm	0.12 x 0.04 x 0.01	0.15 x 0.12 x 0.10	0.20 x 0.04 x 0.04	0.35 x 0.12 x 0.06
θ range, deg	2.123 to 28.790	2.17 to 28.73	2.222 to 26.000	1.768 to 28.718
no. of reflns collected	14771	29522	13798	25741
no. of indep reflns	5928	5089	4890	5762
max. and min. trans	0.996 and 0.958	0.946 and 0.921	0.994 and 0.970	0.985 and 0.915
no. of data /restraints /params	5928 / 0 / 283	5089 / 0 / 254	4890 / 0 / 335	5762 / 1 / 307
goodness-of-fit on F^2	0.887	1.115	0.928	1.005
final *R* indices [$I>2\sigma(I)$] R_1[a], wR_2[b]	0.0630, 0.1434	0.0426, 0.1379	0.0703, 0.1596	0.0605, 0.1421
R indices (all data), R_1[a] ,wR_2[b]	0.1396, 0.1964	0.0546, 0.1512	0.1499, 0.2096	0.0812, 0.1554
largest diff. peak and hole, e $Å^{-3}$	0.323 and -0.397	0.793 and -0.661	0.300 and -0.436	1.210 and -0.376

[a] $R_1 = \Sigma \left| F_0 \right| - \left| F_c \right| / \Sigma \left| F_0 \right|$

[b] $wR_2 = [\Sigma[\omega(F_0^2 - F_c^2)^2] / \Sigma[\omega(F_0^2)^2]]^{1/2}$

Table S3. The summary of crystallographic data for the organic substrates (**2p**, **2q**, **2r**) and product (**3b**).

	2p	**2q**	**2r**	**3b**
formula	C20H20N2O2S2	C23H23N3O3S2	C26H20N2O2S2	C14H11NOS
fw	384.50	453.56	456.56	241.30
temp, K	150(2)	150(2)	150(2)	296(2) K
cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	Pn	$P2_1/c$	C2/c	$P2_1/c$
a, Å	9.0934(7)	11.755(16)	24.2458(18)	9.6442(4)
b, Å	11.9605(10)	7.717(10)	5.0506(4)	6.3275(2)
c, Å	17.7211(15)	24.95(3)	18.4959(14)	19.5922(7)
α, º	90	90	90	90
β, º	95.805(5)	93.228(17)	110.246(5)	96.247(2)°
γ, º	90	90	90	90
Volume, $Å^3$ / *Z*	1917.5(3) / 4	2259(5) / 4	2125.0(3) / 4	1188.49(8) / 4
Density (cald.), Mg/m^3	1.332	1.333	1.427	1.349
Absorption coefficient, mm^{-1}	0.294	0.265	0.279	0.253
crystal size, mm	0.23 x 0.10 x 0.02	0.12 x 0.04 x 0.02	0.25 x 0.04 x 0.02	0.15 x 0.12 x 0.08
θ range, deg	1.703 to 28.856	2.451 to 24.980	1.790 to 28.729	3.14 to 28.78
no. of reflns collected	23980	15094	10641	11850
no. of indep reflns	8693	3962	2722	3079
max. and min. trans	0.994 and 0.935	0.993 and 0.959	0.994 and 0.934	0.982 and 0.960
no. of data /restraints /params	8693 / 2 / 469	3962 / 0 / 282	2722 / 0 / 149	3079 / 0 / 154
goodness-of-fit on F^2	0.925	1.177	0.801	0.722
final *R* indices [$I>2\sigma(I)$] R_1[a], wR_2[b]	0.0589, 0.1410	0.0982, 0.2295	0.0466, 0.1162	0.0432, 0.1225
R indices (all data), R_1[a], wR_2[b]	0.0789, 0.1569	0.1613, 0.2685	0.0880, 0.1437	0.0654, 0.1469
largest diff. peak and hole, e $Å^{-3}$	1.261 and -0.515	0.814 and -0.743	0.266 and -0.357	0.294 and -0.312

[a] $R_1 = \Sigma \left| F_0 \right| - \left| F_c \right| / \Sigma \left| F_0 \right|$

[b] $wR_2 = [\Sigma[\omega(F_0^2 - F_c^2)^2] / \Sigma[\omega(F_0^2)^2]]^{1/2}$

Table S4. The summary of crystallographic data for the organic products (**3d**, **3e**, **3h**, **3j**).

	3d	**3e**	**3h**	**3j**
formula	C13H9NO2S	C14H11NO2S	C9H9NO2S	C9H8ClNOS
fw	243.27	257.30	195.23	213.67
temp, K	150(2)	150(2)	150(2)	150(2)
cryst syst	Monoclinic	Hexagonal	Monoclinic	Monoclinic
space group	Cc	$P6_122$	Pn	$P2_1/n$
a, Å	8.2595(4)	8.2970(4)	10.5437(4)	4.2898(4)
b, Å	18.2546(8)	8.2970(4)	7.8373(3)	10.1017(9)
c, Å	7.3234(4)	59.074(3)	10.7574(4)	21.2306(19)
α, º	90	90	90	90
β, °	102.049(4)	90	103.0875(18)	92.654(7)
γ, º	90	120	90	90
Volume, $Å^3$ / *Z*	1079.85(9) / 4	3521.8(3) / 12	865.84(6) / 4	919.03(14) / 4
Density (cald.), Mg/m^3	1.496	1.456	1.498	1.544
Absorption coefficient, mm^{-1}	0.286	0.267	0.335	0.597
crystal size, mm	0.09 x 0.03 x 0.03	0.12 x 0.10 x 0.08	0.35 x 0.20 x 0.04	0.12 x 0.02 x 0.02
θ range, deg	2.23 to 28.27	2.07 to 28.74	2.442 to 28.781	2.233 to 28.720
no. of reflns collected	6179	50743	11299	12819
no. of indep reflns	2582	3063	3902	2371
max. and min. trans	0.9915 and 0.9747	0.9651 and 0.9483	0.988 and 0.901	0.988 and 0.932
no. of data /restraints /params	2582 / 2 / 158	3063 / 0 / 164	3902 / 2 / 237	2371 / 0 / 118
goodness-of-fit on F^2	0.810	0.601	0.657	0.940
final *R* indices $[I>2\sigma(I)]$ $R_1{}^a$, $wR_2{}^b$	0.0453, 0.1145	0.0464, 0.1515	0.0265, 0.0771	0.0460, 0.1228
R indices (all data), $R_1{}^a$,$wR_2{}^b$	0.0775, 0.1397	0.0507, 0.1583	0.0280, 0.0815	0.0741, 0.1529
largest diff. peak and hole, e $Å^{-3}$	0.177 and -0.269	0.214 and -0.457	0.234 and -0.225	0.393 and -0.49

[a] $R_1 = \Sigma \left| F_0 \right| - \left| F_c \right| / \Sigma \left| F_0 \right|$

[b] $wR_2 = [\Sigma[\omega(F_0^2 - F_c^2)^2] / \Sigma[\omega(F_0^2)^2]]^{1/2}$

Table S5. The summary of crystallographic data for the organic products (**3l**, **3n**, **3q**, **3r**).

	3l	**3n**	**3q**	**3r**
formula	C10H9NO3S	C13H10N2OS	C10H7NOS	C13H10NOS
fw	223.24	242.29	189.23	227.27
temp, K	150(2)	150(2)	150(2)	150(2)
cryst syst	Monoclinic	Triclinic	Monoclinic	Monoclinic
space group	$P2_1/c$	P-1	$P2_1/n$	$P2_1/c$
a, Å	14.9647(9)	8.4192(5)	4.1297(3)	5.8819(4)
b, Å	12.5644(8)	8.7045(5)	14.1058(11)	14.3729(9)
c, Å	10.6636(6)	8.7097(5)	14.7610(11)	12.3134(9)
α, º	90	83.598(2)	90	90
β, °	93.300(3)	65.260(2)	93.338(5)	98.232(5)
γ, º	90	73.566(2)	90	90
Volume, $Å^3$ / *Z*	2001.7(2) / 8	556.00(6) / 2	858.41(11) / 4	1030.25(12) / 4
Density (cald.), Mg/m^3	1.482	1.447	1.464	1.465
Absorption coefficient, mm^{-1}	0.308	0.273	0.328	0.287
crystal size, mm	0.35 x 0.30 x 0.28	0.45 x 0.38 x 0.08	0.12 x 0.04 x 0.02	0.12 x 0.08 x 0.012
θ range, deg	2.801 to 27.875	2.912 to 27.886	1.999 to 28.802	2.191 to 28.733
no. of reflns collected	32183	11550	11263	13564
no. of indep reflns	4750	2639	2232	2662
max. and min. trans	0.897 and 0.874	0.963 and 0.815	0.993 and 0.963	0.994 and 0.943
no. of data /restraints /params	4750 / 0 / 273	2639 / 1 / 154	2232 / 0 / 118	2662 / 0 / 145
goodness-of-fit on F^2	1.240	0.920	0.933	0.989
final *R* indices [$I>2\sigma(I)$] R_1[a], wR_2[b]	0.0424, 0.1424	0.0308, 0.0806	0.0355, 0.1157	0.0422, 0.1282
R indices (all data), R_1[a] ,wR_2[b]	0.0533, 0.1629	0.0363, 0.0886	0.0448, 0.1260	0.0590, 0.1456
largest diff. peak and hole, e $Å^{-3}$	0.365 and -0.270	0.376 and -0.270	0.312 and -0.327	0.320 and -0.355

[a] $R_1 = \Sigma \left| F_0 \right| - \left| F_c \right| / \Sigma \left| F_0 \right|$

[b] $wR_2 = [\Sigma[\omega(F_0^2 - F_c^2)^2] / \Sigma[\omega(F_0^2)^2]]^{1/2}$

Table S6. The summary of crystallographic data for complex **4**.

	Complex 4
formula	C36H4 FeN6O3S2
fw	727.73
temp, K	150(2)
cryst syst	Triclinic
space group	P-1
a, Å	12.1106(7)
b, Å	12.3582(6)
c, Å	13.7051(8)
α, º	111.532(3)
β, °	99.093(3)
γ, º	108.092(3)
Volume, $Å^3$ / *Z*	1725.74(17) / 2
Density (cald.), Mg/m^3	1.401
Absorption coefficient, mm^{-1}	0.604
crystal size, mm	0.18 x 0.10 x 0.04
θ range, deg	1.859 to 24.998
no. of reflns collected	24083
no. of indep reflns	6088
max. and min. trans	0.958 and 0.822
no. of data /restraints /params	6088 / 16 / 539
goodness-of-fit on F^2	1.002
final *R* indices [$I>2\sigma(I)$] R_1[a], wR_2[b]	0.0364, 0.1177
R indices (all data), R_1[a] ,wR_2[b]	0.0438, 0.1264
largest diff. peak and hole, e $Å^{-3}$	0.454 and -0.411

[a] $R_1 = \Sigma \left| F_0 \right| - \left| F_c \right| / \Sigma \left| F_0 \right|$

[b] $wR_2 = [\Sigma[\omega(F_0^2 - F_c^2)^2] / \Sigma[\omega(F_0^2)^2]]^{1/2}$

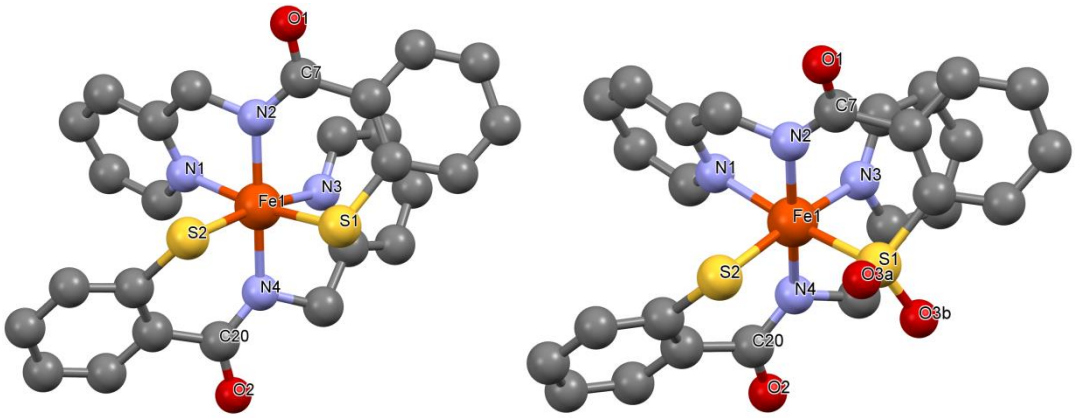

Table S7. The selected bond lengths and angles of complex **1** (left) and **4** (right).

	Complex **1**	Complex **4**		Complex **1**	Complex **4**
Fe1-N1	2.018(5)	1.9994(17)	N1-Fe1-N3	91.99(19)	91.54(7)
Fe1-N2	1.942(5)	1.9449(17)	N1-Fe1-N4	96.4(2)	93.74(7)
Fe1-N3	2.002(5)	2.0024(18)	N1-Fe1-S1	170.11(16)	172.20(5)
Fe1-N4	1.947(5)	1.9321(17)	N1-Fe1-S2	89.77(14)	90.37(5)
Fe1-S1	2.2641(18)	2.2294(6)	N2-Fe1-N3	95.6(2)	93.93(7)
Fe1-S2	2.2650(18)	2.2302(7)	N2-Fe1-N4	174.4(2)	173.43(8)
S1-O3A	n.d.	1.419(3)	N2-Fe1-S1	90.46(15)	90.67(5)
S1-O3B	n.d.	1.490(3)	N2-Fe1-S2	93.22(15)	91.57(6)
C7-O1	1.247(6)	1.245(3)	N3-Fe1-N4	80.5(2)	81.52(7)
C7-N2	1.348(7)	1.338(3)	N3-Fe1-S1	90.57(14)	89.88(5)
C20-O2	1.258(7)	1.249(3)	N3-Fe1-S2	171.22(15)	174.39(5)
C20-N4	1.332(7)	1.337(3)	N4-Fe1-S1	93.45(15)	94.05(6)
O1-C7-N2	123.5(6)	124.2(2)	N4-Fe1-S2	90.78(15)	93.09(6)
O2-C20-N4	123.0(6)	123.0(2)	S1-Fe1-S2	89.15(7)	88.94(2)
N1-Fe1-N2	79.8(2)	81.59(7)			

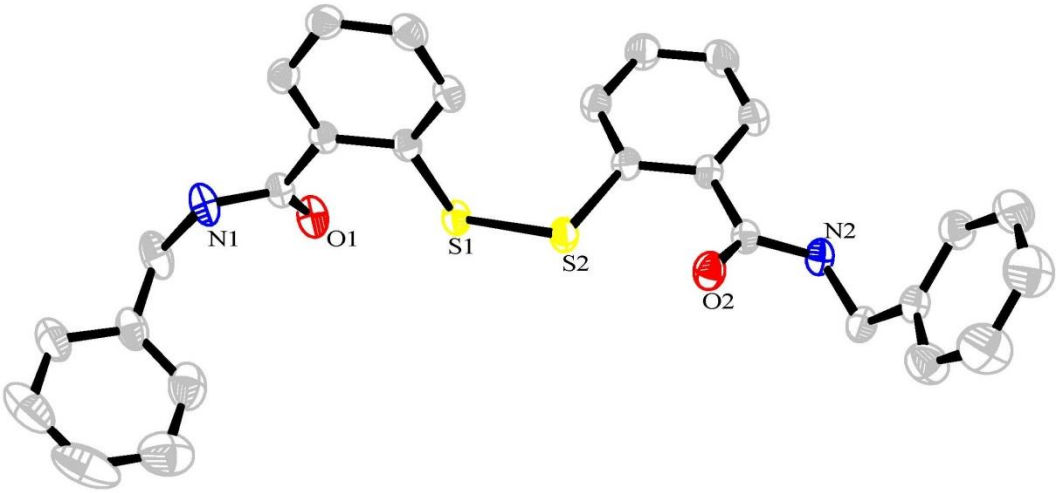

Figure S1. ORTEP drawings of **2b**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

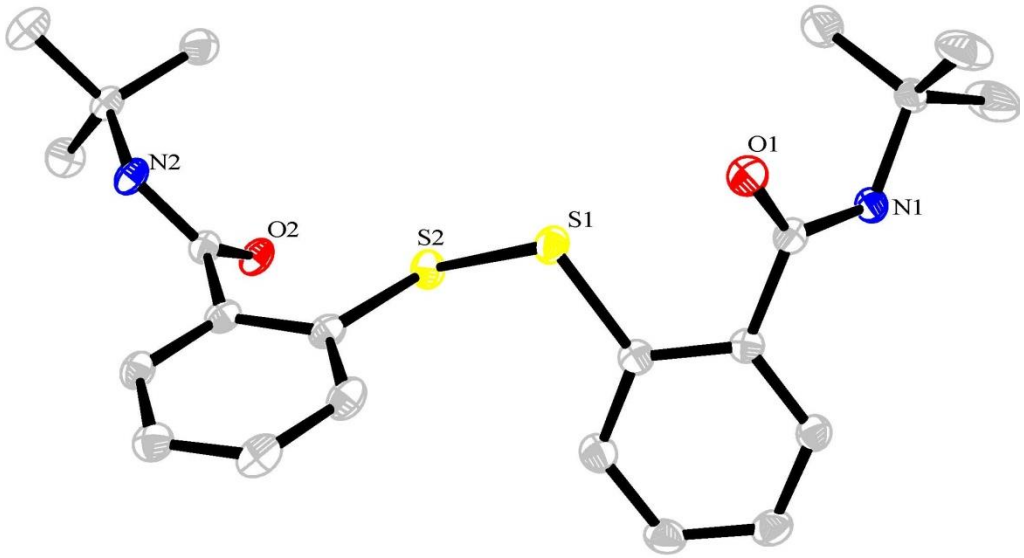

Figure S2. ORTEP drawings of **2c**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

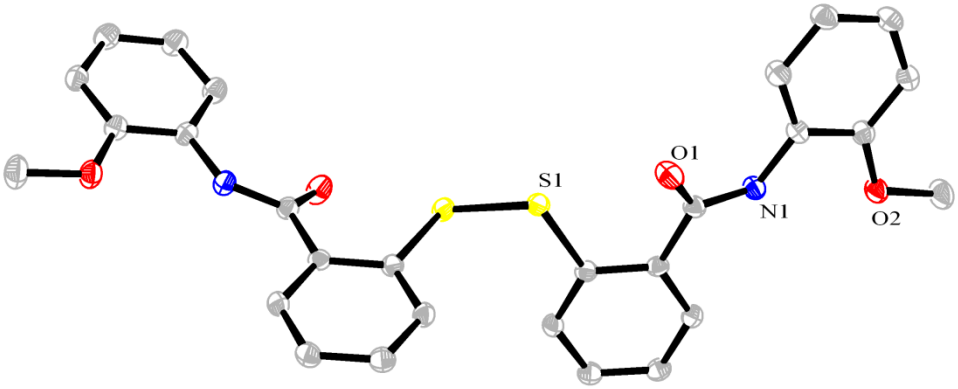

Figure S3. ORTEP drawings of **2e**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms and the disorder atoms are omitted for clarity.

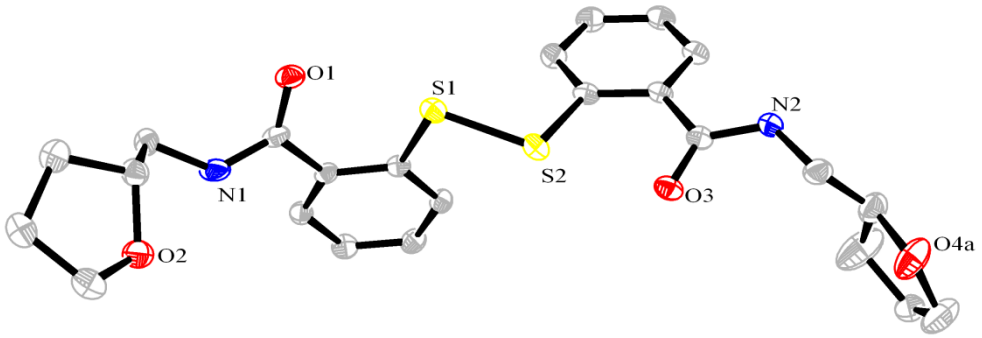

Figure S4. ORTEP drawings of **2f**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms and the disorder atoms are omitted for clarity.

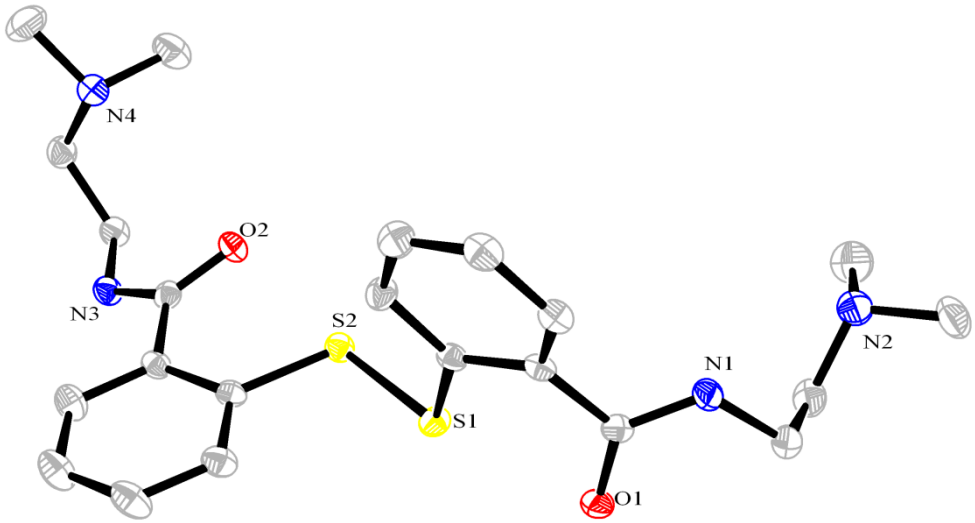

Figure S5. ORTEP drawings of **2i**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

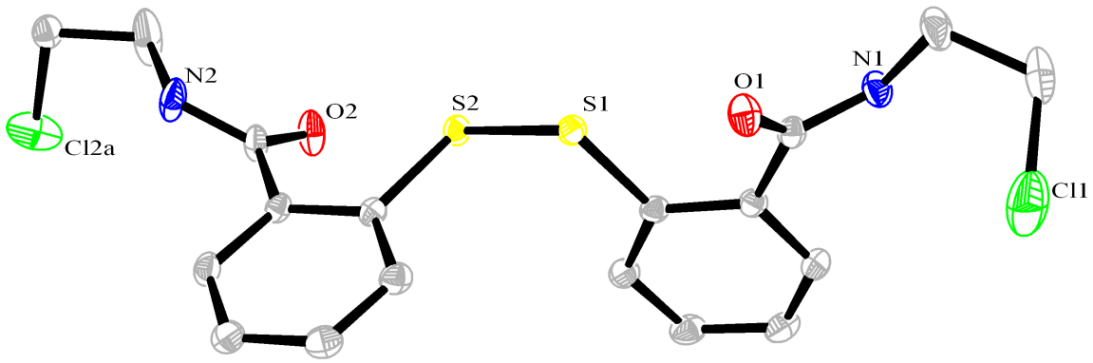

Figure S6. ORTEP drawings of **2j**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms and the disorder atoms are omitted for clarity.

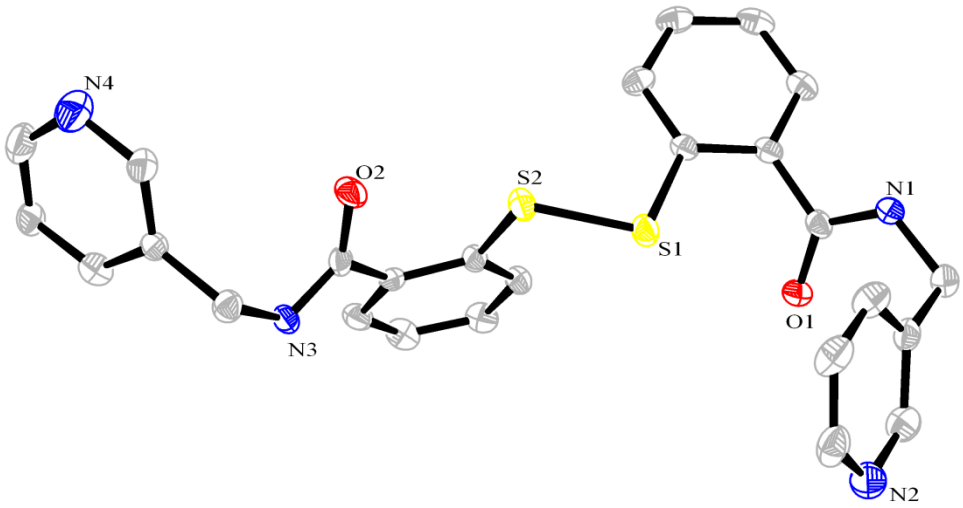

Figure S7. ORTEP drawings of **2n**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

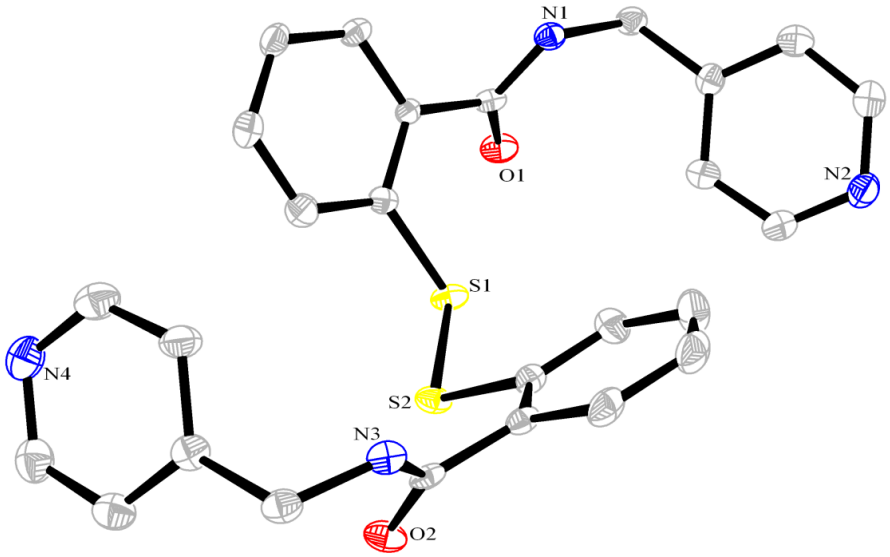

Figure S8. ORTEP drawings of **2o**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

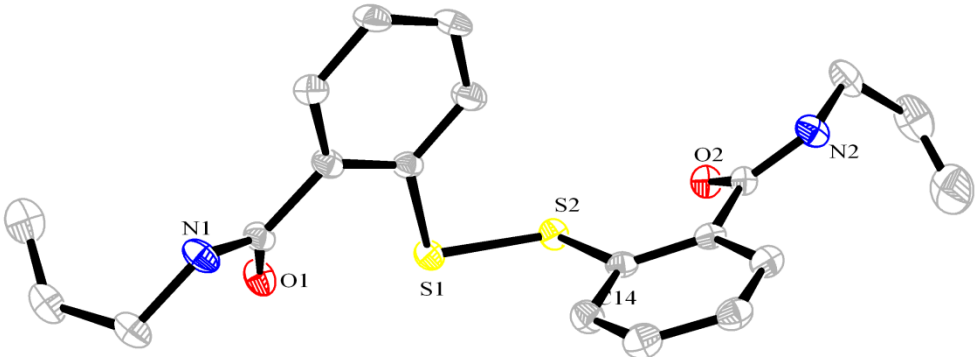

Figure S9. ORTEP drawings of **2p**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

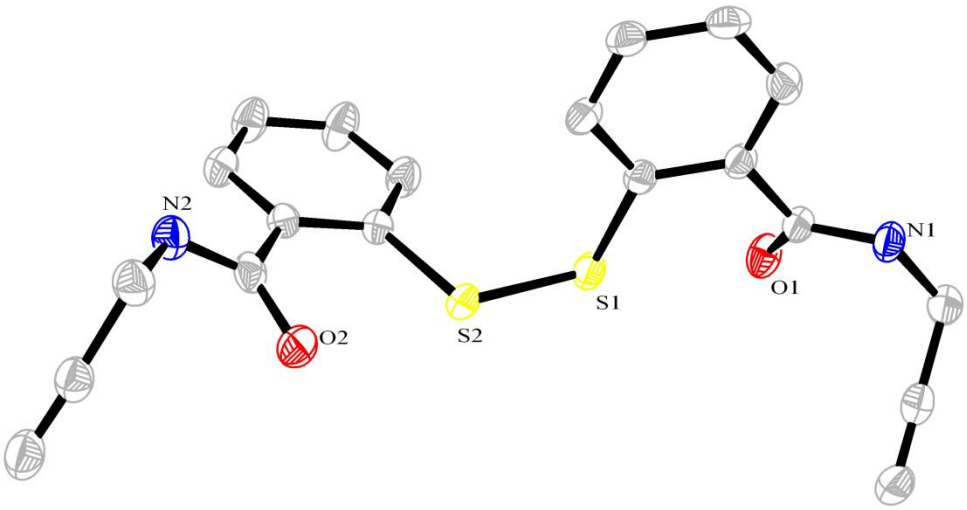

Figure S10. ORTEP drawings of **2q**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

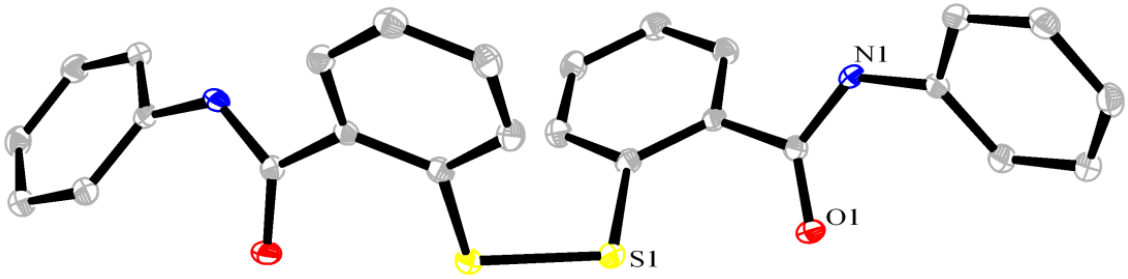

Figure S11. ORTEP drawings of **2r**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

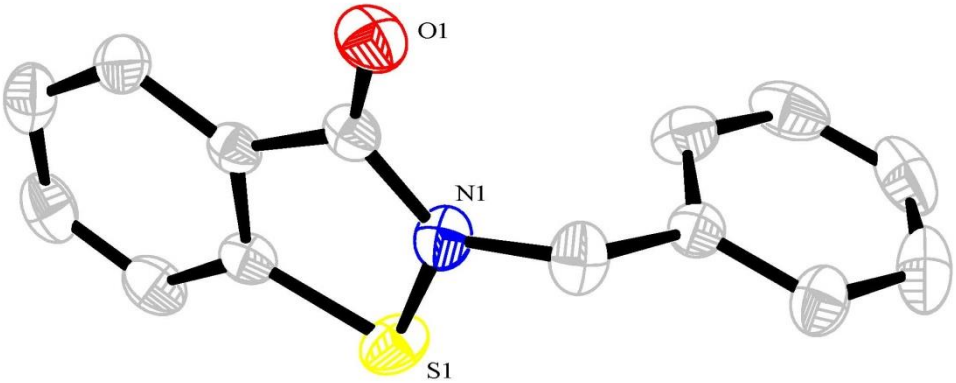

Figure S12. ORTEP drawings of **3b**. Thermal ellipsoids are drawn at the 35 % probability level and the hydrogen atoms are omitted for clarity.

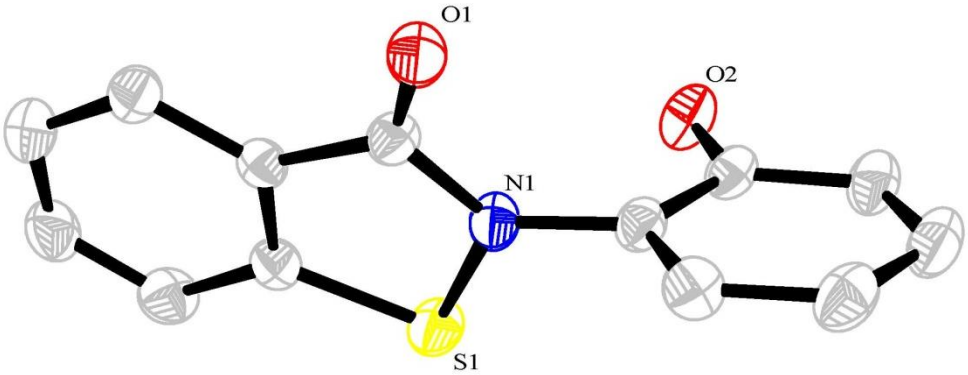

Figure S13. ORTEP drawings of **3d**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

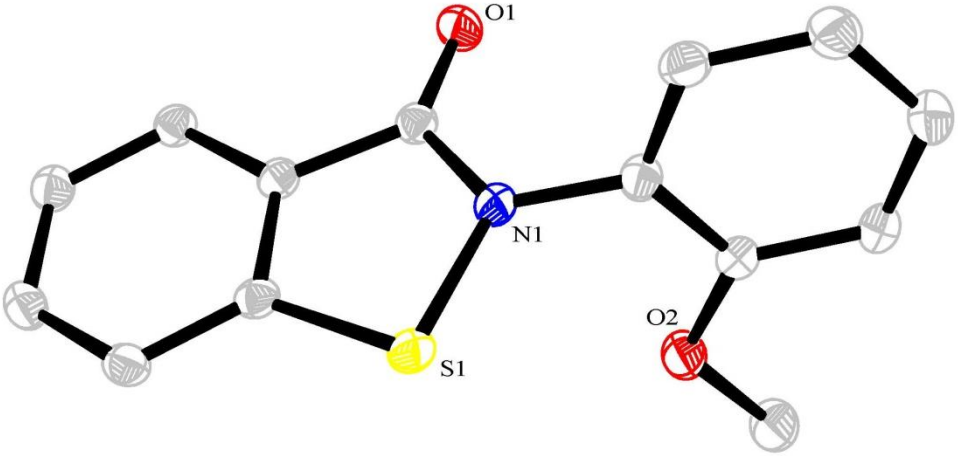

Figure S14. ORTEP drawings of **3e**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

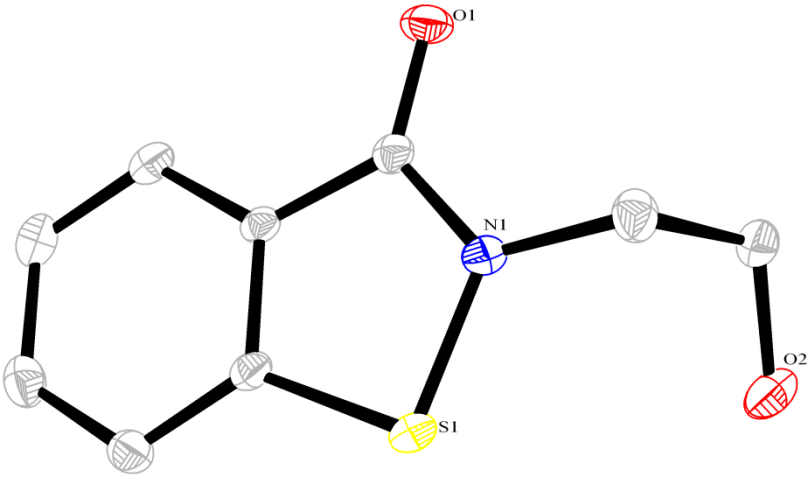

Figure S15. ORTEP drawings of **3h**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

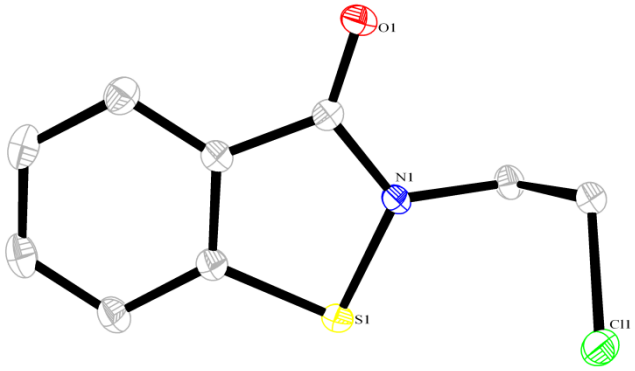

Figure S16. ORTEP drawings of **3j**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

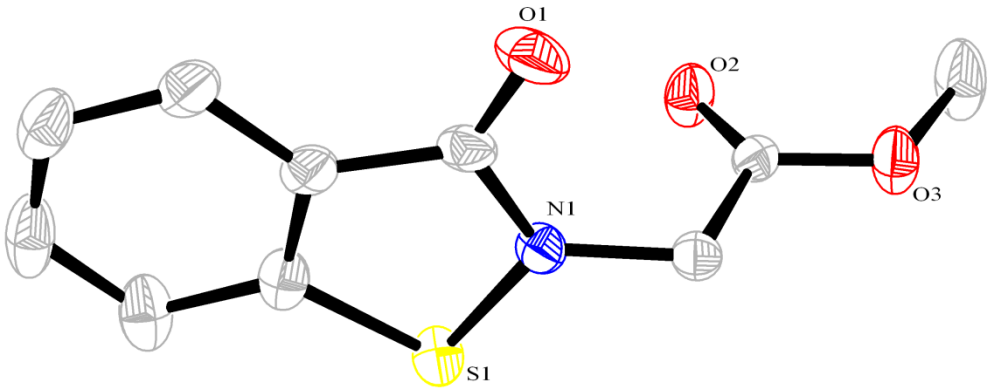

Figure S17. ORTEP drawings of **3l**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

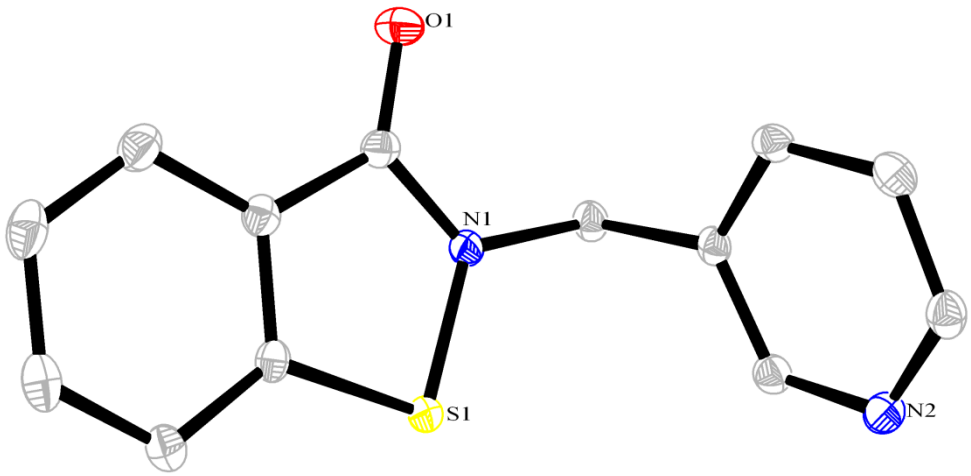

Figure S18. ORTEP drawings of **3n**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms and are omitted for clarity.

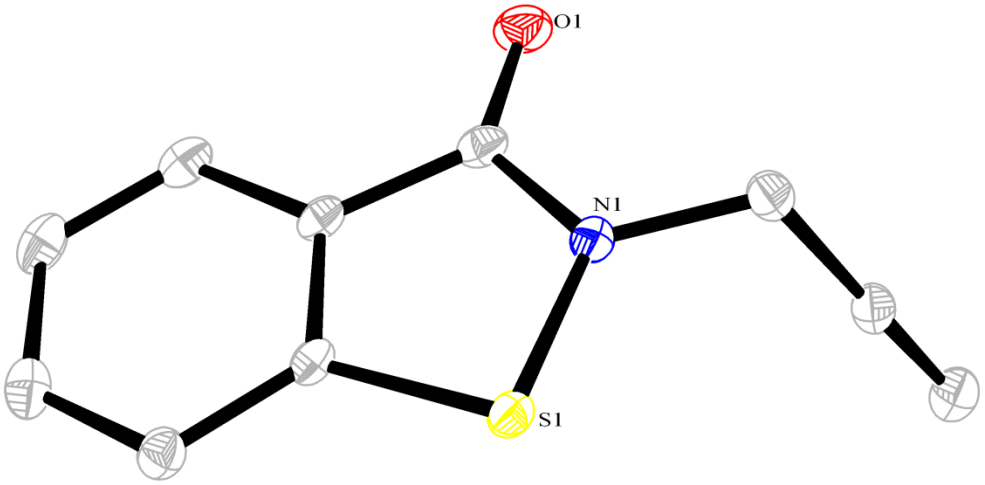

Figure S19. ORTEP drawings of **3q**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms are omitted for clarity.

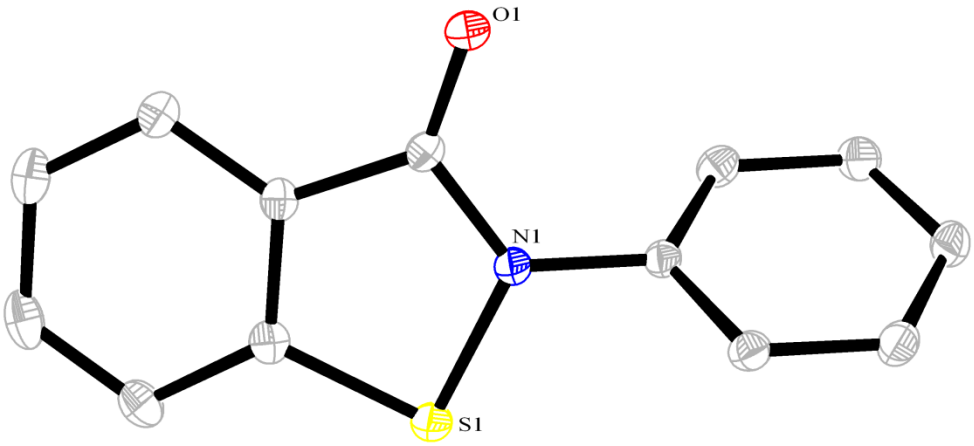

Figure S20. ORTEP drawings of **3r**. Thermal ellipsoids are drawn at the 35 % probability level, and the hydrogen atoms and the disorder atoms are omitted for clarity.

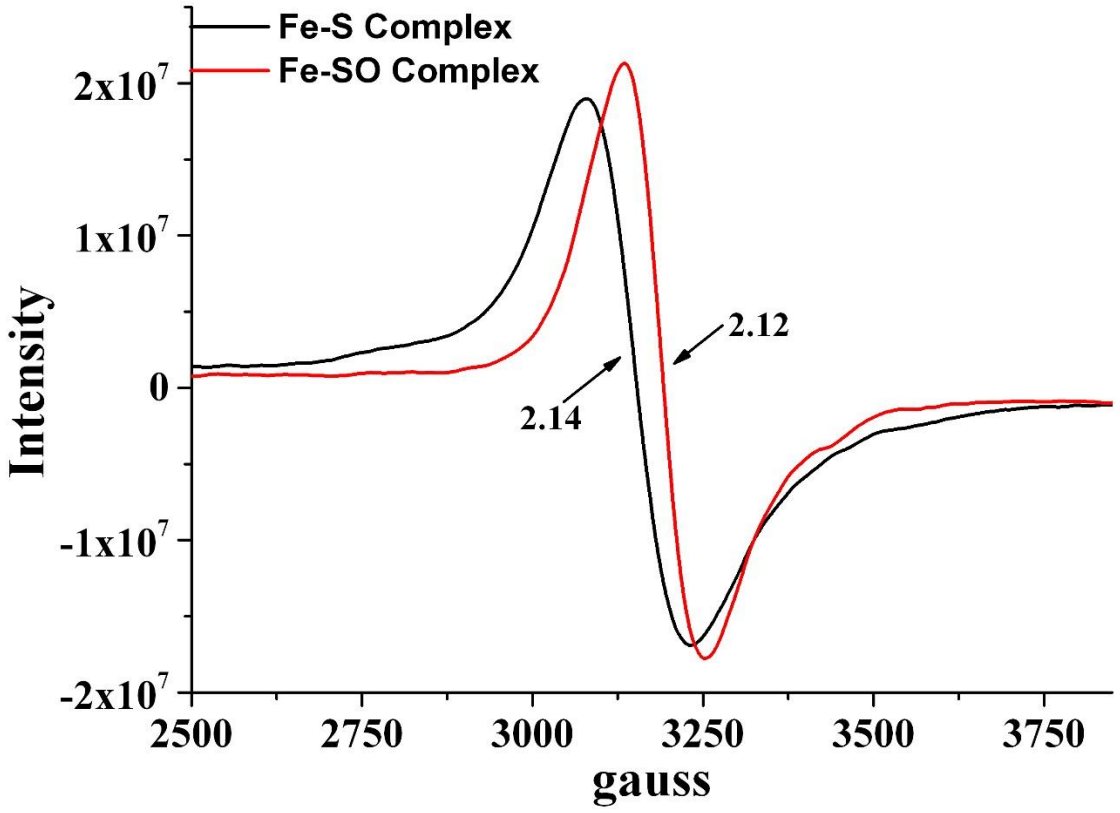

Figure S21. X-band EPR spectra (77K, CH_3CN) of complex **1** and **4**. Spectrometer settings: microwave frequency, 9.5 GHz; modulation frequency, 100 kHz; modulation amplitude, 10 G; time constant, 655.36 msec; conversion time, 40.96 msec; microwave power, 2 mW; receiver gain, 8.93×10^4.

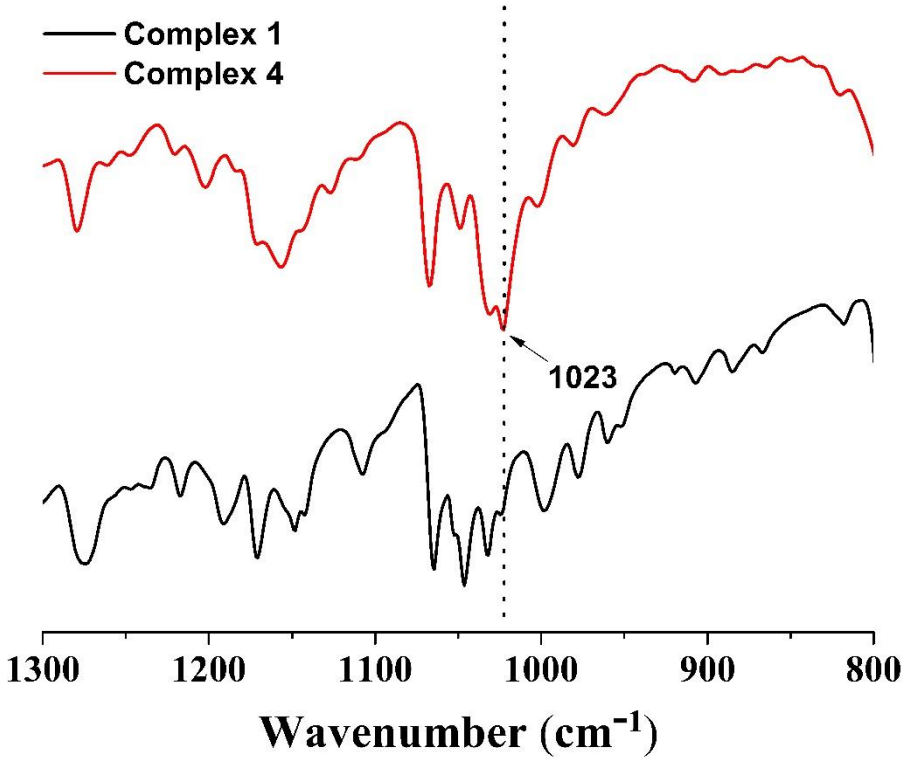

Figure S22. The solid IR spectra of complex **1** and **4**.

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