Persistent radical anions naphthalenediimide-based hybrid material for near-infrared photothermal conversion and photocatalytic oxidative organic transformations

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**Supplementary Methods:**

**General methods**

All air- and moisture-sensitive solutions and chemicals were handled under an argon atmosphere. Anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. Unless otherwise stated, all reagents were commercially available and used as received without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, TCI and Alfa-Aesar. TLC was performed with Merck TLC Silica gel60 F$_{254}$ plates with detection under UV light at 254 nm. Silica gel (200-300 mesh, Qingdao) was used for flash chromatography. Deactivated silica gel was prepared by addition of 15 mL Et$_3$N to 1 L of silica gel. Powder X-ray diffraction (XRD) measurements was recorded on a Bruker D8 ADVANCE X-Ray diffractometer at room temperature using a graphite monochromator Cu-target tube. UV-Vis spectra were performed on a Varian Cary 500 UV–Vis spectrophotometer. Thermostability of materials were performed on a Mettler Toledo TGA2 thermogravimetric system at N$_2$ atmosphere from 30 to 800 °C with a ramp rate of 10 °C/min. The electrochemical measurements were carried out using a Princeton 2273 electrochemical workstation. Fourier transform infrared (IR) spectra have been recorded on a Nicolet iS50 spectrometer using KBr disks dispersed with material powder. Nuclear magnetic resonance (NMR) spectrum was measured on a Bruker Avance III 400 M. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker A300 ESR spectrometer.

**Synthesis of SiMo-NDI**

A Teflon-lined steel autoclave (15 mL) was charged with H$_4$BNDI ligand (59.4 mg, 0.1 mmol), H$_4$SiMo$_{12}$O$_{40}$ (93.4 mg, 0.05 mmol), Ce(NO$_3$)$_3$·6H$_2$O (86.8 mg, 0.20 mmol), N,N-
dimethylacetamide (DMA, 4 mL), and acetonitrile (2 mL). The mixture was stirred under air for 5 min to achieve a homogenous dispersion. The autoclave was degassed by bubbling nitrogen for 5 min, was sealed and was heated at 100 °C for 2 days. After cooling to room temperature, the resulting precipitate was filtered and washed sequentially with DMA, acetonitrile and ethanol, and dried in air to provide light-yellow crystalline SiMo-NDI (approximate yield 62%). Anal. Calcd for C_{124}H_{164}Ce_{12}Mo_{12}N_{20}O_{80}Si: C 30.03, H 3.31, N 5.65%. Found: C 30.46, H 3.39, N 5.78%. IR (KBr, cm\(^{-1}\)): 3411(br), 3071(w), 2930(w), 1721(s), 1679(s), 1606(s), 1550(s), 1405(s), 1343(s), 1251(s), 1193(m), 973(s), 920(s), 801(s). Note that crystallographic data for SiMo-NDI have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 2348162.

**Photothermal conversion properties measurement.**

The 200 mg SiMo-NDI material was pressed into 5-mm-diameter pellet using a manual tablet press at the pressure of 3.0 Mpa. The obtained pellet was under continuous irradiation of a 808 nm laser until the sample reached a steady-state temperature. The temperature was monitored every 1 s by a Fluke (Ti400) thermal imaging camera. The 808 nm laser beam was irradiated at a power density from 0.2 to 1.0 W·cm\(^{-2}\).

**Electrochemical Measurements**

SiMo-NDI powder (10 mg) was ground with poly(vinylidene fluoride) (4 mg) and then ultrasonically dispersed in 3 mL of acetone. The resultant slurry was then drop-casted onto indium tin oxide (ITO) glass with an area of 0.5 × 0.5 cm\(^2\). A Pt wire (counter electrode), a Ag/AgCl electrode (reference electrode), and a coated ITO conductive glass (working
electrode) were assembled into a three-electrode system with 0.2 M Na₂SO₄ aqueous solution used as the electrolyte. The Mott-Schottky plots were collected in dark at different frequencies. The photocurrent measurements were conducted under the irradiation of a 300 W xenon lamp with a 420 nm cut-off filter under a nitrogen- or oxygen-saturated atmosphere.

**Methods of Transient Absorption Spectra**

Details of the femtosecond pump-probe TA measurements were similar to the literature procedures (Nat. Commun. 2023, 14, 4002). Briefly, the laser source was a regenerative amplified Ti:sapphire laser system (Coherent; 400 nm, 70 fs, 6 mJ/pulse, 1 kHz repetition rate). The 400 nm output pulse was split into two parts with a 50% beam splitter. One part was used to pump an OPA, which can generate a wavelength-tunable laser pulse from 250 nm to 2.5 μm using as a pump beam. Another part was attenuated with a neutral density filter and focused into a sapphire or CaF₂ crystal to generate a white light continuum for the probe beam. The pump pulses were chopped by a synchronised chopper at 500 Hz, and the absorbance change was calculated with two adjacent probe pulses (pump-blocked and pump-unblocked). The delay between the pump and probe pulses was controlled by a motorised delay stage. For fs TA measurements, SiMo-NDI single crystal (0.35*0.06*0.05) was filled in 1 mm airtight cuvettes prepared in a N₂-filled glove box and measured under ambient conditions, and the UV-visible (UV-vis) absorbances of all samples were adjusted to 0.5 before further characterisation.
**Procedure and characterization for hydroxylation of arylboronic acids and C-3 thiocyanation of indoles**

**General Procedure A: hydroxylation of arylboronic acids**

In a dry 10 mL Schlenk tube equipped with a stirring bar, arylboronic acids (0.5 mmol), SiMo-NDI (5 mol%) and DMF (5 mL) were added in air. The mixture was exposed to radiation under a 50 W white LED at a distance of 10 cm and stirred for 24 hours at room temperature. The mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with saturated brine solution (20 mL), dried (MgSO₄), filtered and concentrated under reduced pressure. The crude products were purified by flash chromatography by loading them onto a deactivated silica gel column (eluted with ethyl acetate: petroleum ether = 2:1) to give the corresponding colorless liquid or solid products 2a-2p.

**General Procedure B: C-3 thiocyanation of indoles**

An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with indoles (0.5 mmol), ammonium thiocyanate (1.0 mmol), SiMo-NDI (5 mol%), and tetrahydrofuran (5 mL). The reaction system was then exposed to air and stirred at room temperature for a period of 24 hours, while being irradiated by a 50 W white LED at a distance of 10 cm. Once the reaction was complete, the mixture was diluted with H₂O and ethyl acetate, the layers were separated and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with saturated brine solution (20 mL), dried (MgSO₄), filtered and concentrated in vacuo. The crude products were purified by column chromatography on silica gel (eluting with ethyl acetate: petroleum ether =4:1) to give the corresponding C-3 thiocyanation products of indoles 5a-5i.
Fig. S1. IR spectrum of SiMo-NDI.
Fig. S2. TGA curve of SiMo-NDI.

Fig. S3. C 1s XPS core-level spectra of SiMo-NDI before and after irradiation.
Fig. S4. N 1s XPS core-level spectra of SiMo-NDI before and after irradiation.

Fig. S5. O 1s XPS core-level spectra of SiMo-NDI before and after irradiation.
Fig. S6. Si 2p XPS core-level spectra of SiMo-NDI before and after irradiation.

Fig. S7. Ce 3d XPS core-level spectra of SiMo-NDI before and after irradiation.
Fig. S8. Mo 3d XPS core-level spectra of SiMo-NDI before and after irradiation.

Fig. S9. Survey XPS core-level spectra of SiMo-NDI after irradiation.
Fig. S10. The VB-XPS spectrum of the SiMo-NDI.

Fig. S11. Cycle performance of (a) hydroxylation of benzeneboronic acid (b) C-3 thiocyanation of indole.
Fig. S12. The PXRD patterns of SiMo-NDI after photocatalysis.

Fig. S13. Solid-state UV-Vis-NIR spectra of SiMo-NDI original and after irradiation 1 min.
Fig. S14. PXRD patterns of SiMo-NDI treated in different solvents.

Fig. S15. EPR spectra of SiMo-NDI in different solvents with 50 W white LED light irradiation.
Fig. S16. EPR spectra of SiMo-NDI before and after photothermal conversion.

Fig. S17. EPR spectra of SiMo-NDI in DMF with phenylboronic acid and 50 W white LED light irradiation.
Photocatalytic product Characterization:

Phenol (2a)

![Phenol](image)

The reaction was performed following General Procedure A with 1a (61.03 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2a (42.32 mg, 90% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_{H}$: 9.58 (1H, s); 7.15 (2H, t, $J = 8.0$ Hz), 6.78-6.75(3H, m); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) $\delta_{C}$: 157.4, 129.9, 119.6, 115.7.

2-hydroxybenzonitrile (2b)

![2-Hydroxybenzonitrile](image)

The reaction was performed following General Procedure A with 1b (73.52 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2b (54.16 mg, 91% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_{H}$: 11.10 (1H, s); 7.61 (1H, d, $J = 6.8$ Hz), 6.78-6.75(3H, m); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) $\delta_{C}$: 157.4, 129.9, 119.6, 115.7.
Hz), 7.51 (1H, t, $J = 7.2$ Hz), 7.04 (1H, d, $J = 8.4$ Hz), 6.94 (1H, t, $J = 7.6$ Hz); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$: 160.6, 135.1, 133.7, 120.0, 117.5, 116.6, 99.3.

4-Hydroxybenzonitrile (2c)

![Image of 4-Hydroxybenzonitrile (2c)]

The reaction was performed following General Procedure A with 1c (73.52 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2c (54.76 mg, 92% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$: 10.71 (1H, s) 7.66 (2H, d, $J = 8.8$ Hz), 6.96 (2H, d, $J = 8.4$ Hz); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$: 162.0, 134.6, 120.0, 116.8, 101.5.

o-cresol (2d)

![Image of o-cresol (2d)]

The reaction was performed following General Procedure A with 1d (68.03 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2d (48.63 mg, 90% yield); $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$: 9.25 (1H, s), 7.04 (1H, d, $J = 7.2$ Hz), 6.98 (1H, td, $J = 7.6$, 1.2 Hz), 6.76 (1H, d, $J = 8.0$ Hz), 6.68 (1H, td, $J = 7.6$, 1.2 Hz), 2.11 (3H, s); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$: 155.8, 131.0, 127.1, 124.2, 119.2, 115.0, 16.5.

m-cresol (2e)

![Image of m-cresol (2e)]

The reaction was performed following General Procedure A with 1e (68.03 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2e (52.41 mg, 97% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$: 9.27 (1H, s), 7.10 (1H, t, $J = 8.0$ Hz), 6.72 (1H, dd, $J = 8.0$ Hz), 6.68 (1H, dd, $J = 8.0$ Hz), 6.65 (1H, dd, $J = 8.0$), 2.27 (3H, s);
$^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 157.8, 139.2, 129.6, 120.1, 116.4, 112.9, 21.5.

**p-cresol (2f)**

\[
\begin{array}{c}
\text{H}_3\text{C} - \text{C} - \text{C} - \text{OH} \\
\end{array}
\]

The reaction was performed following General Procedure A with 1f (68.03 mg, 0.5 mmol).

The crude material was purified by flash chromatography on silica gel to give the product 2f (51.33 mg, 95% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$H: 6.96 (2H, m), 6.66 (2H, m), 2.20 (3H, s); $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$C: 155.9, 130.8, 116.0, 129.6, 20.5.

**2,5-dimethylphenol (2g)**

\[
\begin{array}{c}
\text{CH}_3 - \text{H}_3\text{C} - \text{C} - \text{OH} \\
\end{array}
\]

The reaction was performed following General Procedure A with 1g (75.04 mg, 0.5 mmol).

The crude material was purified by flash chromatography on silica gel to give the product 2g (57.98 mg, 95% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$H: 9.10 (1H, s), 6.90 (1H, d, $J = 7.6$ Hz), 6.57 (1H, s), 6.48 (1H, d, $J = 7.6$ Hz), 2.17 (3H, s), 2.05 (3H, s); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$C: 155.6, 136.1, 130.7, 121.0, 119.8, 115.7, 21.2, 16.1.

**3,5-dimethylphenol (2h)**

\[
\begin{array}{c}
\text{CH}_3 - \text{H}_3\text{C} - \text{C} - \text{OH} \\
\end{array}
\]

The reaction was performed following General Procedure A with 1h (75.04 mg, 0.5 mmol).

The crude material was purified by flash chromatography on silica gel to give the product 2h (56.15 mg, 92% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$H: 9.15 (1H, s), 6.55 (1H, s); 6.45 (2H, d, $J = 9.6$ Hz), 2.22 (6H, m); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$C: 157.8, 138.8, 121.1, 113.6, 21.4.
naphthalen-2-ol (2i)

[Chemical Structure]

The reaction was performed following General Procedure A with 1i (86.03 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2i (68.48 mg, 95% yield). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta_{\text{H}}\): 9.83 (1H, s), 7.78 (1H, s); 7.76 (1H, s); 7.71 (1H, d, \(J = 8.4\) Hz), 7.40 (1H, t, \(J = 7.2\) Hz), 7.27 (1H, t, \(J = 7.2\) Hz), 7.21 (1H, s), 7.16 (1H, d, \(J = 8.8\) Hz); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta_{\text{C}}\): 155.8, 135.1, 129.8, 128.2, 128.0, 126.6, 126.5, 123.1, 119.1, 109.2.

[1,1'-biphenyl]-4,4'-diol (2j)

[Chemical Structure]

The reaction was performed following General Procedure A with 1j (121.05 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2j (83.73 mg, 90% yield). \(^1\)H NMR (400 MHz, CD3OD) \(\delta_{\text{H}}\): 7.35 (4H, m), 6.81 (4H, m); \(^{13}\)C NMR (100 MHz, CD3OD) \(\delta_{\text{C}}\): 157.3, 133.9, 128.4, 116.4.

[1,1'-biphenyl]-3-ol (2k)

[Chemical Structure]

The reaction was performed following General Procedure A with 1k (99.04 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2k (79.08 mg, 93% yield). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta_{\text{H}}\): 9.57 (1H, s), 7.59 (2H, d, \(J = 7.6\) Hz), 7.45 (2H, d, \(J = 7.6\) Hz), 7.35 (1H, t, \(J = 7.2\) Hz), 7.26 (1H, t, \(J = 8.0\) Hz), 7.06 (1H, d, \(J = 8.0\) Hz), 7.01 (1H, s), 6.77 (1H, dd, \(J = 8.0, 2.4\) Hz); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta_{\text{C}}\): 158.3, 142.1, 140.8, 130.4, 129.3, 127.9, 127.1, 117.9, 114.9, 113.9.
[1,1'-biphenyl]-4-ol (2l)

\[
\begin{array}{c}
\text{HO} \\
\text{C-C-C-C} \\
\text{C-C-C-C} \\
\text{HO}
\end{array}
\]

The reaction was performed following General Procedure A with 1l (99.04 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2l (79.08 mg, 93% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$: 9.58 (1H, s), 7.57 (2H, d, $J = 7.6$ Hz'), 7.49 (2H, d, $J = 8.8$ Hz), 7.41 (2H, t, $J = 7.2$ Hz), 7.27 (1H, t, $J = 7.2$ Hz), 6.85 (2H, d, $J = 8.8$ Hz); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$: 157.6, 140.7, 131.4, 129.3, 128.2, 126.8, 126.4, 116.2.

4-Methoxyphenol (2m)

\[
\begin{array}{c}
\text{HO} \\
\text{C-C-C-C} \\
\text{C-C-C-C} \\
\text{H}_3\text{CO}
\end{array}
\]

The reaction was performed following General Procedure A with 1m (76.03 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2m (58.30 mg, 94% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$: 8.97 (1H, s), 6.77 (2H, m), 6.76 (2H, m), 3.66 (3H, s); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$: 152.6, 151.6, 116.2, 115.0, 55.6.

2-Hydroxybenzaldehyde (2n)

\[
\begin{array}{c}
\text{CHO} \\
\text{C-C-C-C} \\
\text{C-C-C-C} \\
\text{HO}
\end{array}
\]

The reaction was performed following General Procedure A with 1n (75.02 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2n (59.19 mg, 97% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$: 10.81; 7.61 (1H, d, $J = 4.0$ Hz); 7.42 (1H, m); 6.97 (1H, d, $J = 8.0$ Hz); 6.88 (1H, m) $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$: 193.8, 161.2, 136.7, 119.8, 117.5.

3-Hydroxybenzaldehyde (2o)
The reaction was performed following General Procedure A with 1o (75.02 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2o (56.14 mg, 92% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 9.98 (1H, s), 9.91 (1H, d, $J = 3.6$ Hz), 7.37 (2H, m), 7.27 (1H, m), 7.11 (1H, m); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 193.5, 158.4, 138.1, 130.7, 122.3, 121.5, 115.1.

4-Hydroxybenzaldehyde (2p)

The reaction was performed following General Procedure A with 1p (75.02 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 2p (57.36 mg, 94% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 9.81 (1H, s); 7.78 (2H, m); 6.96 (2H, m); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 191.4, 163.8, 132.6, 128.8, 116.3.

3-thiocyanato-1H-indole (5a)

The reaction was performed following General Procedure B with 1H-indole (3a) (58.53 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 5a (81.79 mg, 94% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 12.03 (1H, s), 8.00 (1H, d, $J = 4.0$ Hz), 7.66 (1H, m), 7.54 (1H, m), 7.31-7.24 (2H, m); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 136.8, 133.7, 127.9, 123.4, 121.6, 118.2, 113.3, 112.8, 89.7.

2-methyl-3-thiocyanato-1H-indole (5b)
The reaction was performed following General Procedure B with 2-methyl-1H-indole (3b) (65.54 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 5b (84.62 mg, 90% yield). $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$: 11.97 (1H, s), 7.56 (1H, t, $J$ = 4.0 Hz), 7.43 (1H, m), 7.22-7.17 (2H, m), 2.54 (3H, s); $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$C: 143.5, 135.8, 128.7, 122.7, 121.3, 117.6, 112.7, 112.3, 87.1, 12.1.

**2-phenyl-3-thiocyanato-1H-indole (5c)**

The reaction was performed following General Procedure B with 2-phenyl-1H-indole (3c) (96.54 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 5c (120.03 mg, 96% yield). $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$: 12.42 (1H, s), 7.86 (1H, t, $J$ = 1.6 Hz), 7.85 (1H, br s), 7.72 (1H, dd, $J$ = 6.4, 1.6 Hz), 7.63 (2H, t, $J$ = 7.6 Hz), 7.55 (2H, t, $J$ = 7.6 Hz), 7.31 (2H, m); $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$C: 143.6, 136.3, 130.4, 129.8, 129.6, 129.4, 129.3, 123.9, 121.9, 118.5, 112.9, 112.9, 87.6.

**4-methyl-3-thiocyanato-1H-indole (5d)**

The reaction was performed following General Procedure B with 4-methyl-1H-indole (3d) (66.54 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 5d (83.68 mg, 89% yield). $^1$H NMR (400 MHz, CD$_3$Cl) $\delta$: 8.54 (1H, s), 7.46 (1H, t, $J$ = 4.0 Hz), 7.16 (1H, t, $J$ = 8.0 Hz), 6.59 (2H, m), 2.71 (3H, s); $^{13}$C NMR (100 MHz, CD$_3$Cl) $\delta$C: 143.8, 136.9, 130.5, 129.7, 128.8, 125.6, 123.2, 121.7, 118.4, 112.6, 112.5, 6.3. 
MHz, DMSO-$d_6$ $\delta_C$: 136.5, 132.3, 126.1, 124.0, 113.4, 123.5, 131.1, 120.9, 110.1, 19.3.

5-methyl-3-thiocyanato-1H-indole (5e)

The reaction was performed following General Procedure B with 4-methyl-1H-indole (3e) (65.54 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 5e (89.32 mg, 95% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$: 11.90 (1H, s), 7.93 (1H, d, $J = 2.8$ Hz), 7.45 (1H, d, $J = 0.8$ Hz), 7.41 (1H, d, $J = 8.0$ Hz), 7.10 (1H, dd, $J = 8.0$, 1.6 Hz), 2.45 (3H, s); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$: 135.1, 133.6, 130.5, 128.1, 125.0, 117.6, 113.0, 112.9, 88.9, 21.7.

5-bromo-3-thiocyanato-1H-indole (5f)

The reaction was performed following General Procedure B with 5-bromo-1H-indole (3f) (97.48 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 5f (117.15 mg, 93% yield). 5-bromo-3-thiocyanato-1H-indole; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$: 12.23 (1H, s), 8.07 (1H, br s), 7.82 (1H, br s), 7.52 (1H, d, $J = 8.8$ Hz), 7.41 (1H, d, $J = 8.8$ Hz); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$: 135.6, 135.2, 129.7, 126.1, 120.4, 115.4, 114.2, 112.7, 89.9.

4-methoxy-3-thiocyanato-1H-indole (5g)

The reaction was performed following General Procedure B with 5-methoxy-1H-indole (3g)
(73.53 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 5g (98.96 mg, 97% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$: 8.76 (1H, s), 7.42 (1H, d, $J = 2.8$ Hz), 7.28 (1H, d, $J = 8.8$ Hz), 7.17 (1H, d, $J = 2.4$ Hz), 6.93 (1H, dd, $J = 8.8, 2.4$ Hz), 3.90 (3H, s); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$: 155.7, 131.5, 130.9, 128.5, 114.5, 113.1, 112.2, 99.8, 91.2, 55.9.

**6-methyl-3-thiocyanato-1H-indole (5h)**

![Image of 6-methyl-3-thiocyanato-1H-indole (5h)](image)

The reaction was performed following General Procedure B with 6-methyl-1H-indole (3h) (65.54 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 5h (90.26 mg, 96% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$: 8.67 (1H, s), 7.62 (1H, d, $J = 8.4$ Hz), 7.27 (1H, d, $J = 2.8$ Hz), 7.13 (1H, br s), 7.09 (1H, d, $J = 8.4$ Hz), 2.43 (3H, s; $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$: 136.5, 133.9, 130.7, 125.5, 123.7, 118.2, 112.6, 112.1, 91.3, 21.7.

**methyl-3-thiocyanato-1H-indole (5i)**

![Image of methyl-3-thiocyanato-1H-indole (5i)](image)

The reaction was performed following General Procedure B with 7-methyl-1H-indole (3i) (65.54 mg, 0.5 mmol). The crude material was purified by flash chromatography on silica gel to give the product 5i (88.38 mg, 94% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$: 8.61 (1H, s, 7.64 (1H, d, $J = 8.0$ Hz), 7.50 (1H, d, $J = 2.8$ Hz), 7.23 (1H, m), 7.11 (1H, d, $J = 7.2$ Hz), 2.49 (3H, s; $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_C$: 135.6, 130.6, 127.3, 124.4, 122.1, 121.4, 116.4, 112.0, 92.7, 16.4.
NMR Spectra

2a: phenol

Fig. S19. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2a.

Fig. S20. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2a.
2b: 2-hydroxybenzonitrile

Fig. S21. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2b.

Fig. S22. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2b.
2c: 4-hydroxybenzonitrile

Fig. S23. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2c.

Fig. S24. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2c.
2d: o-cresol

Fig. S25. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2d.

Fig. S26. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2d.
2e: m-cresol

Fig. S27. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2e.

Fig. S28. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2e.
2f: p-cresol

Fig. S29. $^1$H NMR spectra (400 MHz, CD$_3$OD) of 2f.

Fig. S30. $^{13}$C NMR spectra (100 MHz, CD$_3$OD) of 2f.
2g: 2,5-dimethylphenol

Fig. S31. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2g.

Fig. S32. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2g.
2h: 3,5-dimethylphenol

Fig. S33. $^1$H NMR spectra (400 MHz, DMSO-$_d_6$) of 2h.

Fig. S34. $^{13}$C NMR spectra (100 MHz, DMSO-$_d_6$) of 2h.
2i: naphthalen-2-ol

Fig. S35. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2i.

Fig. S36. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2i.
2j: [1,1'-biphenyl]-4,4'-diol

Fig. S37. $^1$H NMR spectra (400 MHz, CD$_3$OD) of 2j.

Fig. S38. $^{13}$C NMR spectra (100 MHz, CD$_3$OD) of 2j.
2k: [1,1'-biphenyl]-4-ol

Fig. S39. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2k.

Fig. S40. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2k.
2l: [1,1'-biphenyl]-3-ol

Fig. S41. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2l.

Fig. S42. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2l.
2m: 4-methoxyphenol

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\begin{align*}
\text{H}_2\text{C} & \quad - \quad \text{O} \quad - \quad \text{OH} \\
& \\
\end{align*}
\]

Fig. S43. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2m.

Fig. S44. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2m.
2n: 2-hydroxybenzaldehyde

Fig. S45. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2n.

Fig. S46. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2n.
2o: 3-hydroxybenzaldehyde

Fig. S47. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2o.

Fig. S48. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2o.
2p: 4-hydroxybenzaldehyde

Fig. S49. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 2p.

Fig. S50. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 2p.
5a: 3-thiocyanato-1H-indole

Fig. S51 $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 5a.

Fig. S52 $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 5a.
5b: 2-methyl-3-thiocyanato-1H-indole

Fig. S53. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 5b.

Fig. S54. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 5b.
5c: 2-phenyl-3-thiocyanato-1H-indole

Fig. S55. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 5c.

Fig. S56. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 5c.
5d: 4-methyl-3-thiocyanato-1H-indole

Fig. S57. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 5d.

Fig. S58. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 5d.
5e: 5-methyl-3-thiocyanato-1H-indole

Fig. S59. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 5e.

Fig. S60. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 5e.
5f: 5-bromo-3-thiocyanato-1H-indole

Fig. S61. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 5f.

Fig. S62. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 5f.
5g: 5-methoxy-3-thiocyanato-1H-indole

Fig. S63. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 5g.

Fig. S64. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 5g.
5h: 6-methyl-3-thiocyanato-1H-indole

Fig. S65. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 5h.

Fig. S66. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 5h.
5i: 7-methyl-3-thiocyanato-1H-indole

Fig. S67. $^1$H NMR spectra (400 MHz, DMSO-$d_6$) of 5i.

Fig. S68. $^{13}$C NMR spectra (100 MHz, DMSO-$d_6$) of 5i.