Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

Acridinium-Based Photoredox Nanocatalysts for Site-Selective Arene C–H Amination in Water

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1. ^{1}H NMR spectra

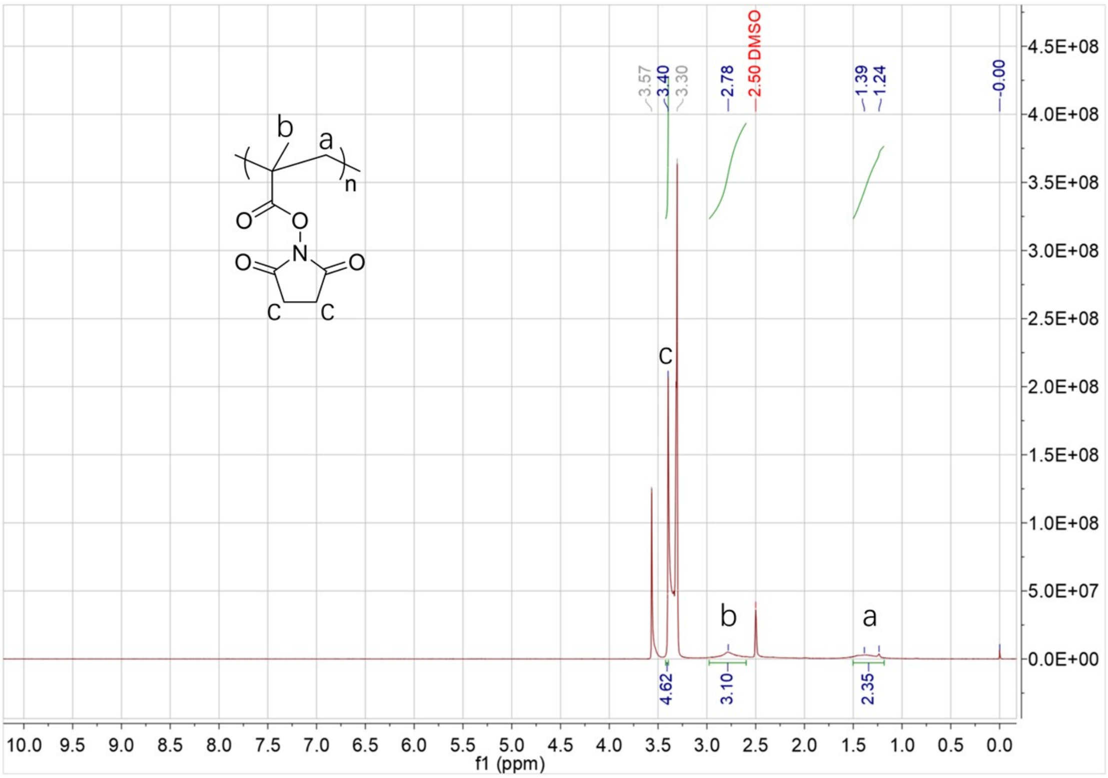

Figure S1. ^{1}H NMR spectrum in DMSO-d_6 of PNHSMA. The signals at 3.30 ppm and 3.57 ppm arise from water and 1,4-dioxane, respectively.

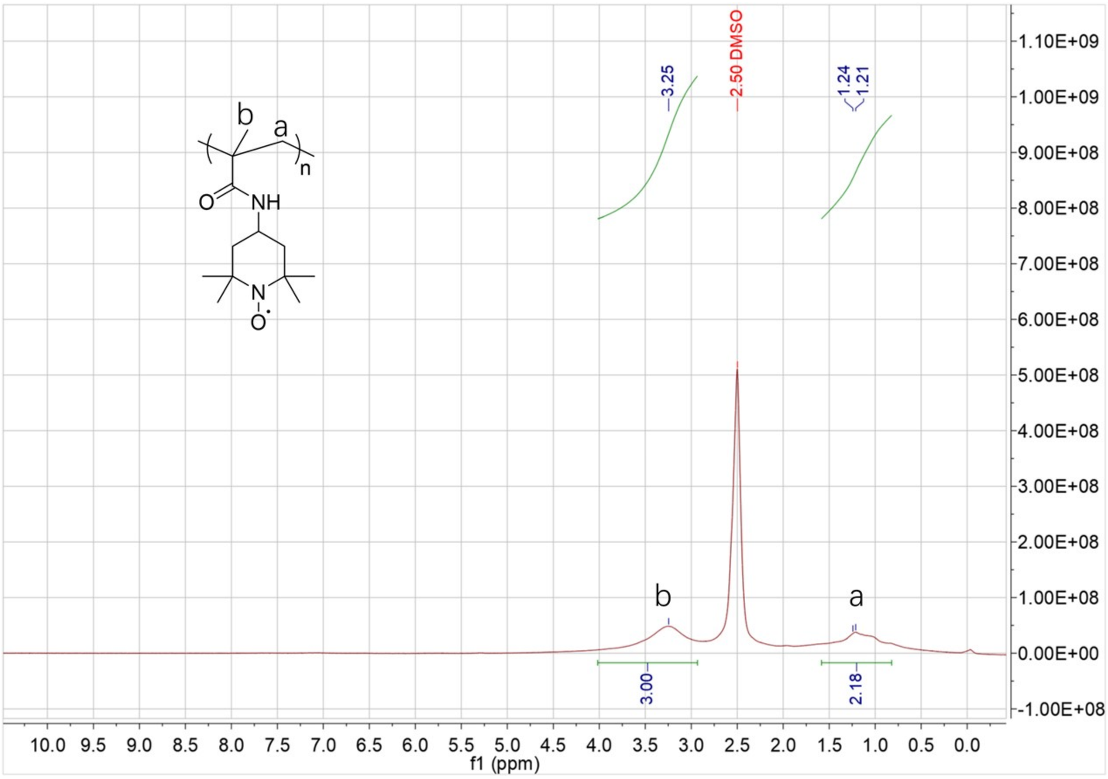

Figure S2. ^{1}H NMR spectrum in DMSO-d_6 of PMATE.

2. FT-IR spectra

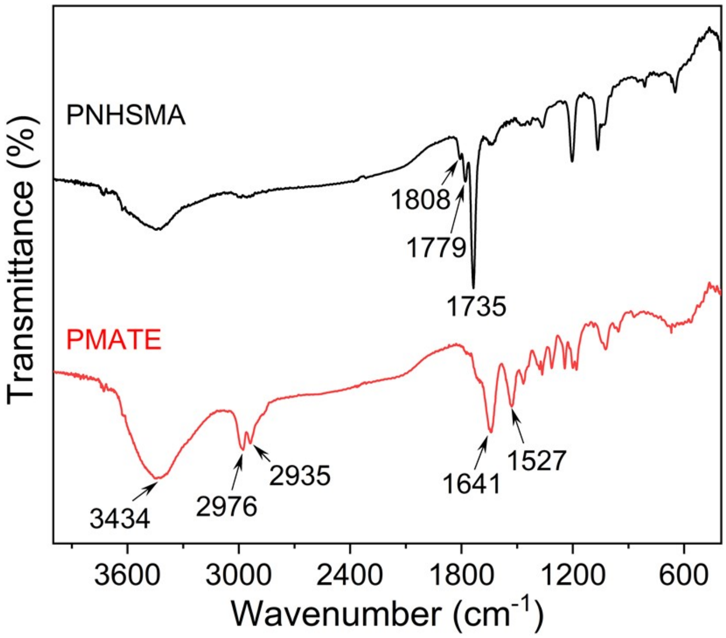

Figure S3. FT-IR spectra of PNHSMA and PMATE.

In the FT-IR spectrum of PNHSMA, three characteristic bands of carbonyl groups (i.e. the split ester carbonyl bands at 1808 and 1779 cm^{-1} and the succinimide carbonyl band at 1735 cm^{-1}) were observed at 1808, 1779, and 1735 cm^{-1}.[1-4] In the FT-IR spectrum of PMATE, the characteristic bands of N–H group was observed at 3434 cm^{-1}; the absorption bands at 2976 and 2935 cm^{-1} were ascribed to C–H vibrations; the characteristic bands of amide groups were observed at 1641 (amide I) and 1527 (amide II) cm^{-1}.

3. GPC trace of PMATE

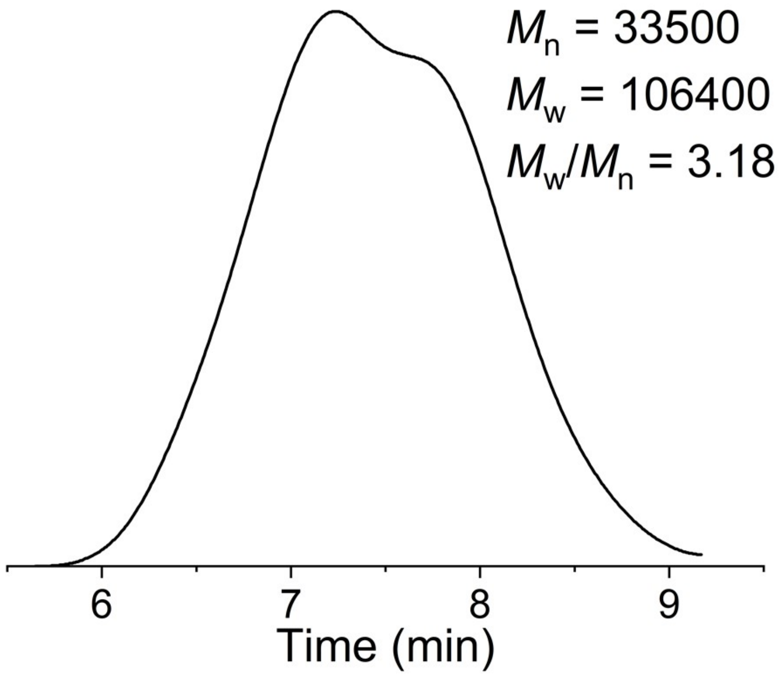

Figure S4. The GPC trace of PMATE.

4. EPR measurements

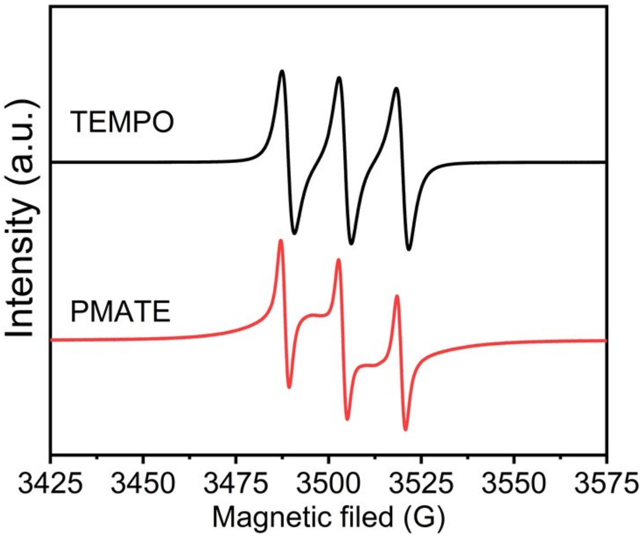

Figure S5. EPR measurements of TEMPO and PMATE in DMF (1.0 mg/mL) at room temperature.

5. Feed amount of the preparation of nanocatalysts

Table S1. Feed amount of the preparation of nanocatalysts through nanoprecipitation in water [a].

Nanocatalysts	Mes-Acr / mg	TEMPO / mg	PMATE / mg
Mes-Acr/TEMPO (5/10 mol%)	7	4	/
Mes-Acr/TEMPO (5/20 mol%)	7	8	/
Mes-Acr/TEMPO (5/40 mol%)	7	16	/
Mes-Acr/TEMPO (5/60 mol%)	7	24	/
Mes-Acr/PMATE (5/10 mol%)	7	/	6
Mes-Acr/PMATE (5/20 mol%)	7	/	12
Mes-Acr/PMATE (5/40 mol%)	7	/	24
Mes-Acr/PMATE (5/60 mol%)	7	/	36

[a] A solution of catalytic component in DMSO (0.5 mL) was added rapidly (<3 s) to de-ionized water (5.0 mL) at room temperature under stirring (500 r/min) to obtain the nanocatalyst.

6. TEM images and size distributions

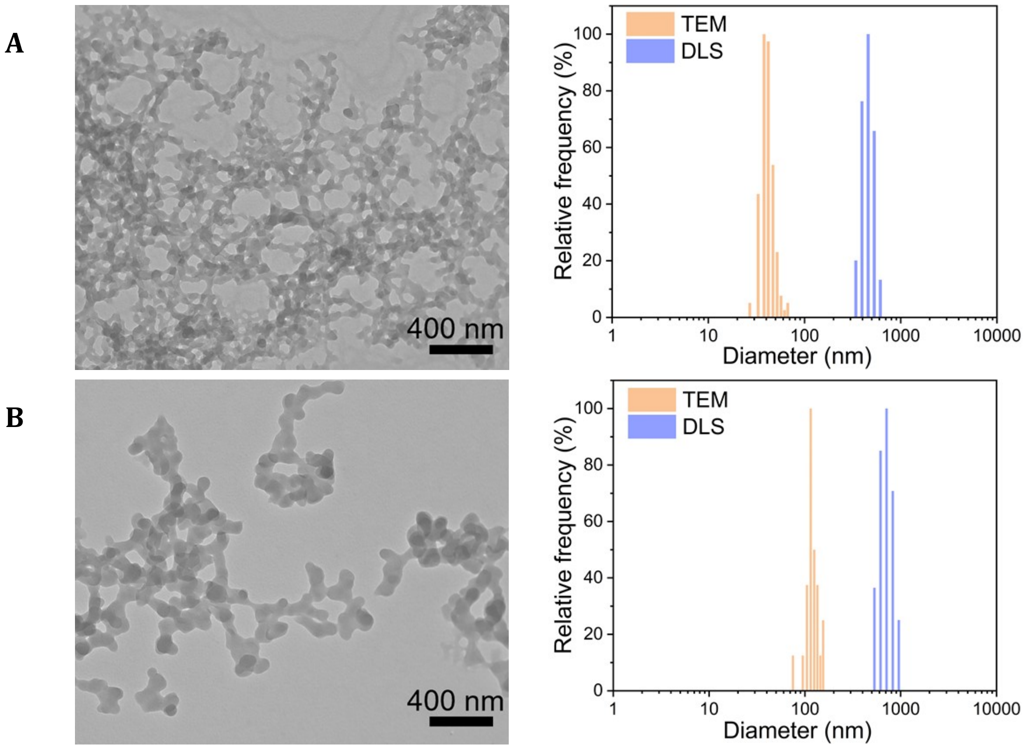

Figure S6. TEM images and size distributions determined by TEM and DLS of the (A) Mes-Acr/PMATE (5/10 mol%) and (B) Mes-Acr/PMATE (5/40 mol%) catalytic systems.

Table S2. Average diameters of nanocatalysts determined by TEM and DLS.

Nanocatalysts	D_{TEM} / nm	D_{DLS} / nm	PDI [a]
Mes-Acr/TEMPO (5/20 mol%)	216 ± 126	82 ± 30 (major) 4420 ± 920 (minor)	0.176
Mes-Acr/PMATE (5/10 mol%)	55 ± 27	422 ± 71	0.028
Mes-Acr/PMATE (5/20 mol%)	42 ± 26	458 ± 67	0.021
Mes-Acr/PMATE (5/40 mol%)	120 ± 46	710 ± 118	0.027

[a] Determined by DLS.

7. Estimation of the reaction order with respect to pyrazole

The reaction rate of products r_{product} can be determined by the following equation:

$$r_{\mathrm{product}} = k c_{\mathrm{anisole}}^{\alpha} c_{\mathrm{pyrazole}}^{\beta} c_{\mathrm{oxygen}}^{\gamma} \qquad (1)$$

Where k is the rate constant; c_{anisole}, c_{pyrazole}, and c_{oxygen} are the concentrations of anisole, pyrazole, and oxygen, respectively. α, β, and γ are the orders with respect to anisole, pyrazole, and oxygen, respectively.

$$\log r_{\mathrm{product}} = \log k + \alpha \log c_{\mathrm{anisole}} + \beta \log c_{\mathrm{pyrazole}} + \gamma \log c_{\mathrm{oxygen}} \qquad (2)$$

Due to the low yield (<10%) of products, the concentration of anisole c_{anisole} can be considered as a constant. The concentration of oxygen c_{oxygen} is a constant due to the exposure of the solution to open air. As such, the equation (2) can be simplified as the following equation:

$$\log r_{\mathrm{product}} = \log k_{\mathrm{c}} + \beta \log c_{\mathrm{pyrazole}} \qquad (3)$$

Where k_{c} is a constant. And the equation can be used for the determination the value of β by linear fitting of $\log r_{\mathrm{product}}$ vs $\log c_{\mathrm{pyrazole}}$.

The reaction rate r_{product} can be calculated according to the following equation:

$$r_{\mathrm{product}} = \frac{c_{\mathrm{pyrazole}}\left(y_{\mathrm{Ortho}} + y_{\mathrm{Para}}\right)}{t} \qquad (4)$$

Where y_{Ortho} and y_{Para} are the yields of ortho and para products; *t* is the reaction time.

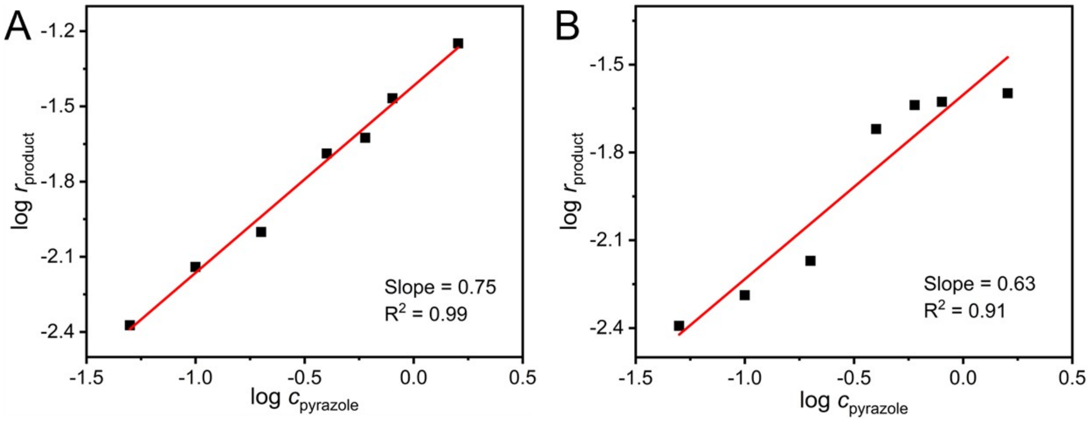

Figure S7. The fitting curves of $\log r_{\mathrm{product}}$ vs $\log c_{\mathrm{pyrazole}}$ in the case of (A) Mes-Acr/TEMPO and (B) Mes-Acr/PMATE as the catalytic systems. The reaction is 0.75 and 0.63 order in pyrazole when Mes-Acr/TEMPO and Mes-Acr/PMATE are used as the catalysts, respectively.

8. Typical ^{1}H NMR data of site-selective arene C–H amination

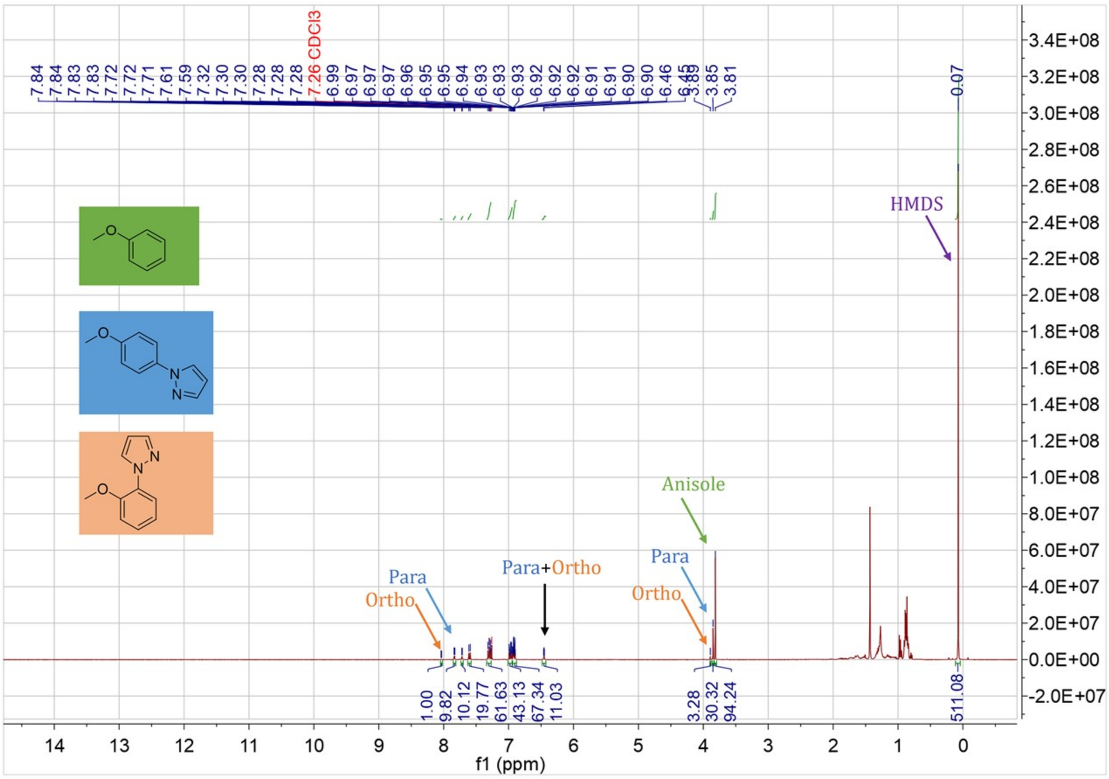

Figure S8. ^{1}H NMR spectrum in $CDCl_3$ of the extracted mixture of site-selective arene C–H amination of anisole with pyrazole over Mes-Acr/PMATE (5/20 mol%). HMDS was added as the internal standard. The yields of para and ortho products were 3.46% and 0.35%, respectively.

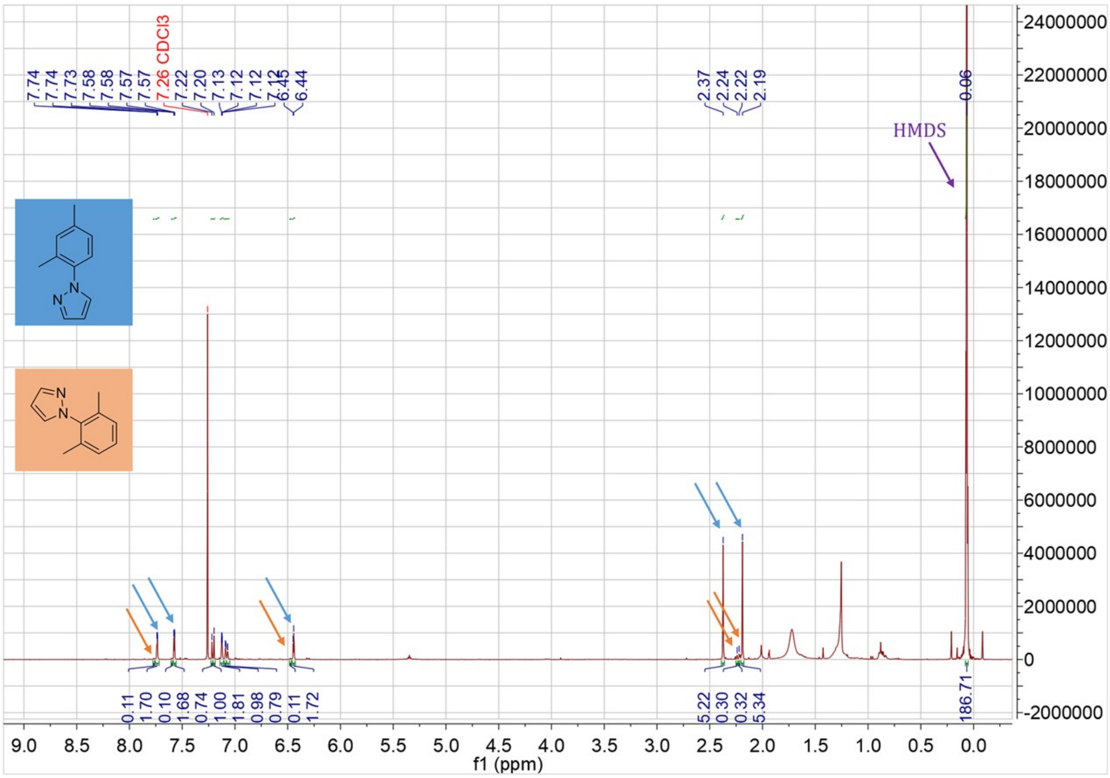

Figure S9. ^{1}H NMR spectrum in $CDCl_3$ of the extracted mixture of site-selective arene C–H amination of m-xylene with pyrazole over Mes-Acr/PMATE (5/20 mol%). HMDS was added as the internal standard. The yields of para and ortho products were 1.64% and 0.11%, respectively.

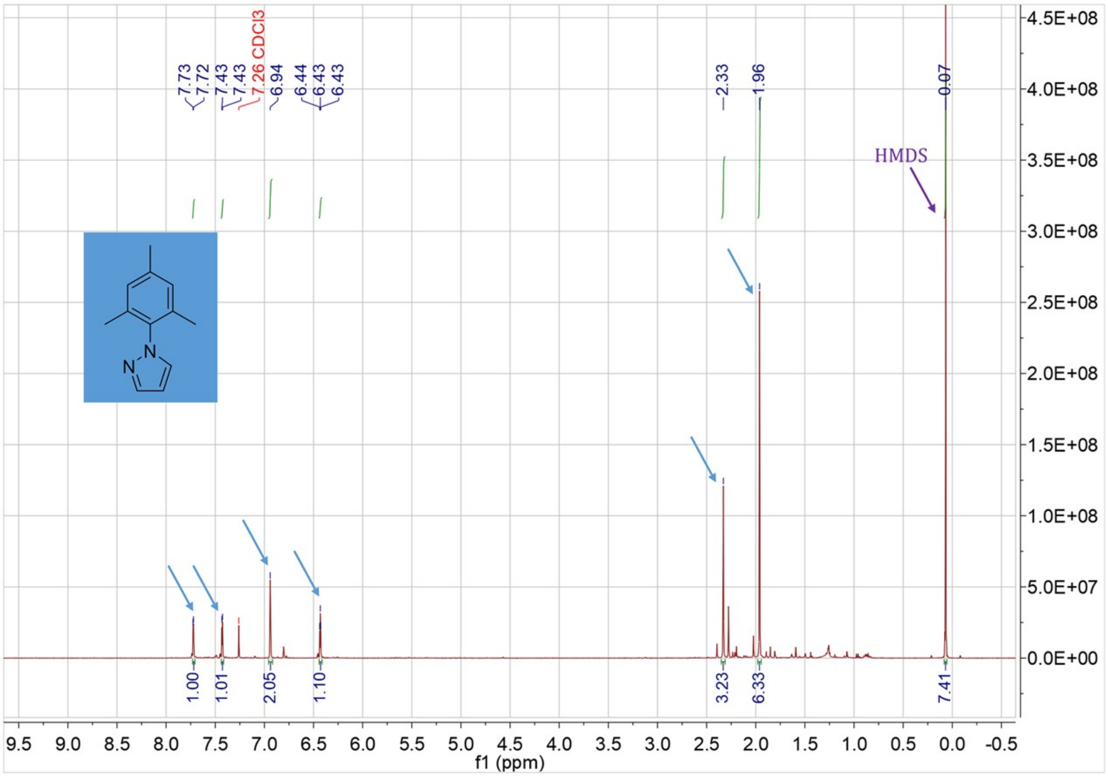

Figure S10. ^{1}H NMR spectrum in $CDCl_3$ of the extracted mixture of site-selective arene C–H amination of mesitylene with pyrazole over Mes-Acr/PMATE (5/20 mol%). HMDS was added as the internal standard. The yield of the product was 24.29%.

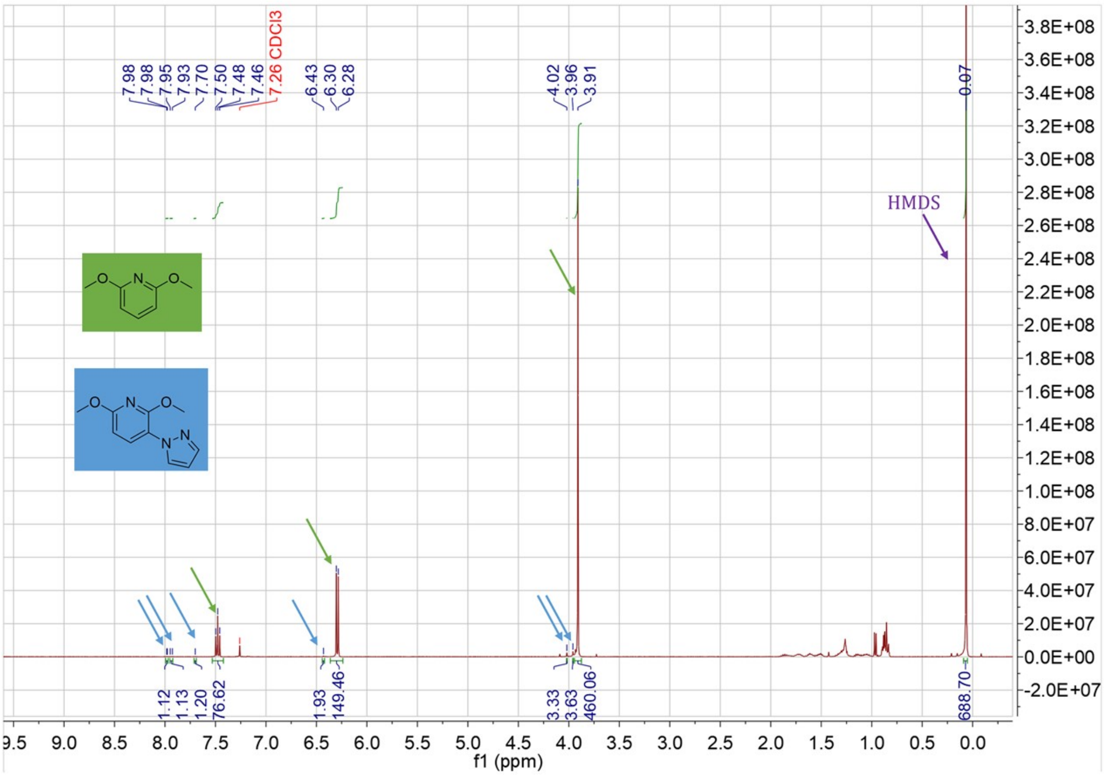

Figure S11. ^{1}H NMR spectrum in $CDCl_3$ of the extracted mixture of site-selective arene C–H amination of 2,6-dimethoxypyridine with pyrazole over Mes-Acr/PMATE (5/20 mol%). HMDS was added as the internal standard. The yield of the product was 0.29%.

9. Yields of site-selective arene C–H amination

Table S3. Yields of site-selective arene C–H amination of anisole with pyrazole over various nanocatalysts [a].

Nanocatalysts	Yield of the ortho product / %	Yield of the para product / %
Mes-Acr/TEMPO (5/10 mol%)	0.71	5.87
Mes-Acr/TEMPO (5/20 mol%)	0.41	3.69
Mes-Acr&TEMPO (5/20 mol%)	0.31	2.75
Mes-Acr/TEMPO (5/40 mol%)	0.15	1.32
Mes-Acr/TEMPO (5/60 mol%)	0.04	0.40
Mes-Acr/PMATE (5/10 mol%)	0.56	5.53
Mes-Acr/PMATE (5/20 mol%)	0.35	3.46
Mes-Acr&PMATE (5/20 mol%)	0.12	0.99
Mes-Acr/PMATE (5/40 mol%)	0.06	0.48
Mes-Acr/PMATE (5/60 mol%)	0.02	0.18

[a] Determined by ^{1}H NMR.

10. Stability of acridinium-based photoredox nanocatalysts

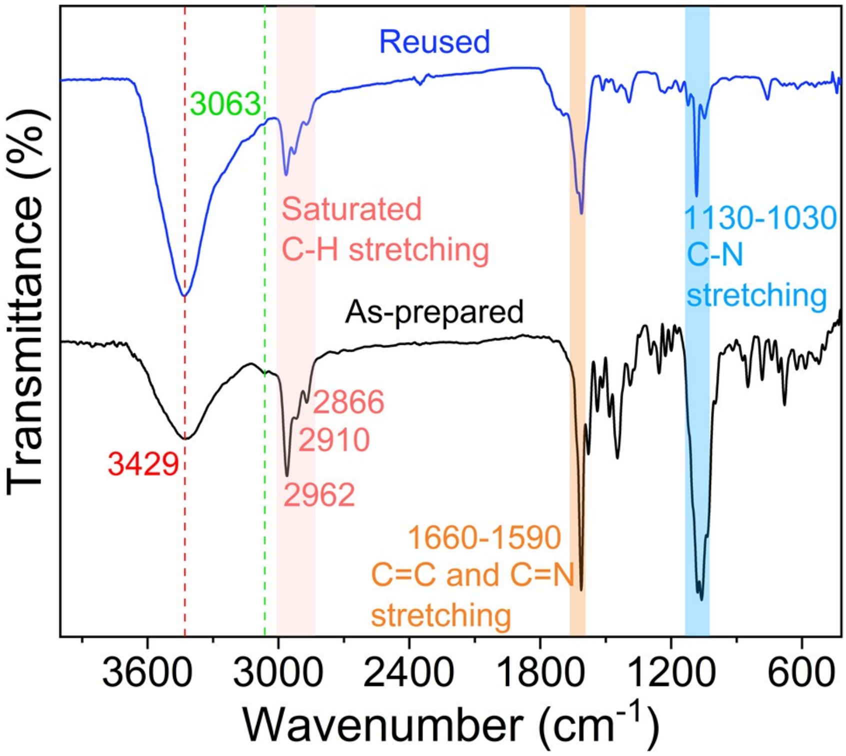

Figure S12. FT-IR spectra of the as-prepared and reused Mes-Acr/TEMPO (5/20 mol%) nanocatalysts.

The absorption band at 3429 cm^{-1} was ascribed to O–H vibration of water; the characteristic band of aromatic C-H groups was observed at 3063 cm^{-1}. The absorption bands at 2962, 2910, and 2866 cm^{-1} were ascribed to saturated C–H vibrations. The characteristic bands of C=C and C=N groups were observed at 1660-1590 cm^{-1}; the characteristic bands of C-N groups were observed at 1130-1030 cm^{-1}. The significant changes in shape and intensity of the characteristic bands of C=C and C=N groups and C-N groups after reuse suggest the degradation of Mes-Acr.

11. References

1. Feng, C. L.; Zhang, Z.; Förch, R.; Knoll, W.; Vancso, G. J.; Schönherr, H., Reactive Thin Polymer Films as Platforms for the Immobilization of Biomolecules. *Biomacromolecules* **2005,** *6* (6), 3243-3251.
2. Feng, C. L.; Vancso, G. J.; Schönherr, H., Fabrication of Robust Biomolecular Patterns by Reactive Microcontact Printing on N-Hydroxysuccinimide Ester-Containing Polymer Films. *Adv. Funct. Mater.* **2006,** *16* (10), 1306-1312.
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4. Rathfon, J. M.; Tew, G. N., Synthesis of thermoresponsive poly(N-isopropylmethacrylamide) and poly(acrylic acid) block copolymers via post-functionalization of poly(N-methacryloxysuccinimide). *Polymer* **2008,** *49* (7), 1761-1769.