

Supporting Information

Light-fuelled nitro-reduction via cascaded electron donor-acceptor complexes in aqueous media

Xiaohui Zhuang,^a Haijing Song,^a Jiayin Wang,^a Zhaokang Zhang,^a Jiayang Wang,^b Bin Sun,^{*a, c}
Weike Su^{a, c} and Can Jin^{*a, c}

^a College of Pharmaceutical Sciences, Collaborative Innovation Center of Yangtze River Delta Region Green Pharmaceuticals, Zhejiang University of Technology, Hangzhou 310014, P. R. China.

^b School of Life Sciences, HuZhou University, HuZhou, Zhejiang, PR China.

^c Key Laboratory for Green Pharmaceutical Technologies and Related Equipment of Ministry of Education and Key Laboratory of Pharmaceutical Engineering of Zhejiang Province.

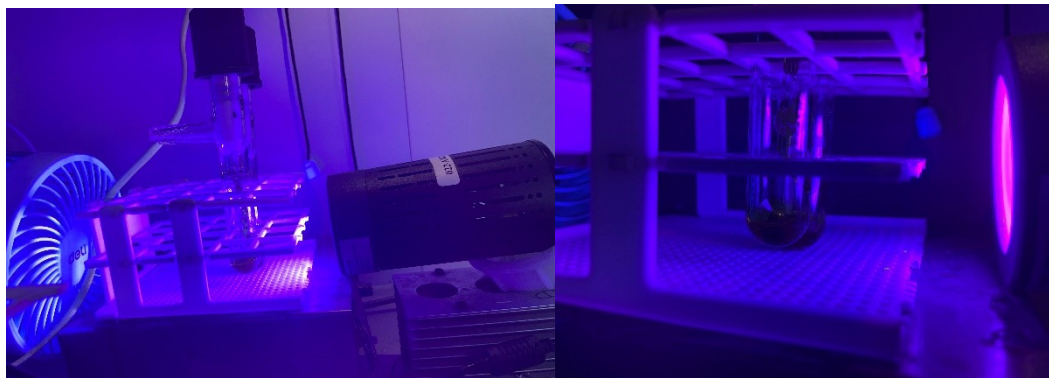
jincan@zjut.edu.cn; sunbin@zjut.edu.cn;

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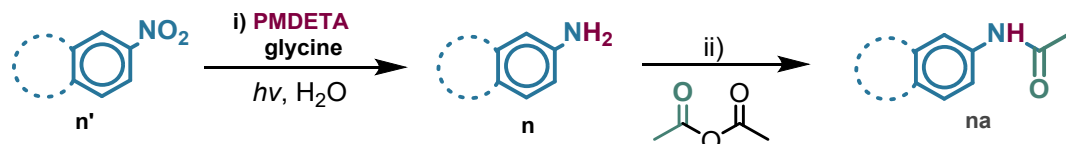
I. General Information

All reactions were run in a tube under air atmosphere. All commercially available reagent grade chemicals and solvents were used as received without further purification. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra are reported relative to chemical shift of tetramethylsilane (TMS). Chemical shifts (δ) are reported in ppm and coupling constants (J) in hertz (Hz). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet. For HRMS (ESI) measurements, the mass analyzer is micrOTOF-Q.



II. General procedure for the reduction of nitroarenes

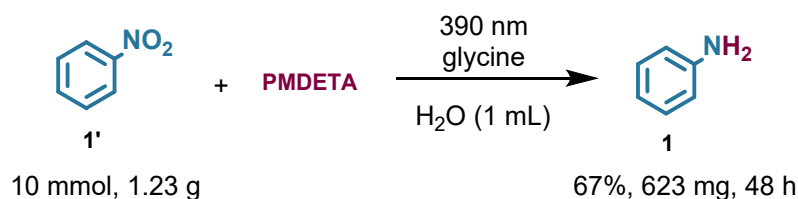
(1) With the scale of 0.2 mmol



(i) A 10 mL tube was charged with nitroarenes **n'** (0.2 mmol), pentamethyldiethylenetriamine PMDETA (3.0 equivalent), glycine (1.0 equivalent) in H_2O (0.5 mL) upon irradiation of 100 W 390 nm LEDs at room temperature under N_2 atmosphere for 24 h. (Notice: for the insoluble nitroarenes, EA may be added as appropriate to promote dissolution.) The reaction was monitored by TLC. After completion, the reaction mixture was quenched with water (10 mL) and extracted with dichloromethane for three times. The combined organic phase was dried over anhydrous Na_2SO_4 , filtered, and evaporated to leave a residue, which was purified by silica gel column chromatography with petroleum ether/ ethyl acetate (from 10 :1) to give the pure desired product **38A-38B, 39-61**.

(ii) A 25 mL round bottom flask was charged with acetic anhydride (2.0 equivalent), DMAP (20% mmol) and concentrated solution, which is extracted from the previous step, in DCM (5 mL) at rt to 80 °C temperature for 30 min to 10 h. The reaction was monitored by TLC. After completion, the reaction mixture was quenched with water (10 mL) and extracted with dichloromethane for three times. The combined organic phase was dried over anhydrous Na_2SO_4 , filtered, and evaporated to leave a residue, which was purified by silica gel column chromatography with petroleum ether/ ethyl acetate (from 5 :1) to give the pure desired product **1a-37a**.

(2) With the scale of 10 mmol (gram scale)



A 10 mL tube was charged with **1'** (10.0 mol), pentamethyldiethylenetriamine PMDETA (3.0 equivalent), glycine (1.0 equivalent) in H₂O (1 mL) upon irradiation of 100 W 390 nm LEDs at room temperature under N₂ atmosphere for 48 h. The reaction was monitored by TLC. After completion, the reaction mixture was quenched with water (15 mL) and extracted with dichloromethane for three times. The combined organic phase was dried over anhydrous Na₂SO₄, filtered, and evaporated to leave a residue, which was purified by silica gel column chromatography with petroleum ether/ ethyl acetate (from 10 :1) to give the pure desired product **1** in a yield of 67%.

III. Calculation of Ecoscale score

(1) Table S1. Calculation of Ecoscale score for this work

Eco Scale = 100 -Sum of individual penalties
Score on Eco Scale: >75, Excellent; >50, Acceptable; <50, Inadequate

A. Calculation of Penalty Points:

Parameters	Penalty Points
1. Yield: (100- % of yield)/2 = (100-85)/2	7.5
2. Price of reaction components (To obtain 10 mmol of end product, 60)	
a. ethyl <i>p</i> -nitrobenzoate (60') = 11.76 mmol = 2.295 g = USD 0.6	
b. pentamethyldiethylenetriamine (PMDETA) = 35.28 mmol = 6.114 g = USD 1.22	
c. glycine = 11.76 mmol = 0.882 g = USD 0.066	
Total cost of synthesis of 60 = (0.6 + 1.22 + 0.066) = USD 1.886	
Thus inexpensive, since (total cost of synthesis of 10 mmol of 60) < \$ 10:	0
3. Safety	
PMDETA (T)	5
4. Technical Setup	
photochemical activation	2
5. Temperature/time	
Room temperature, 24 h	1
6. Workup and purification	
Liquid-liquid extraction	3
Classical chromatography	10
Total penalty points:	28.5

B. Ecoscale calculation:

EcoScale score: (100-28.5) = **71.5 (> 50; it is an acceptable synthesis)**

(2) Table S2. Calculation of Ecoscale score for the site-selective nitro reduction method involved metal-loaded catalysts¹

Eco Scale = 100 -Sum of individual penalties

Score on Eco Scale: >75, Excellent; >50, Acceptable; <50, Inadequate

A. Calculation of Penalty Points:

Parameters	Penalty Points
1. Yield: (100- % of yield)/2 = (100-99.9)/2	0.05
2. Price of reaction components (To obtain 10 mmol of end product, 60)	
a. ethyl <i>p</i> -nitrobenzoate (60') = 11.76 mmol = 2.295 g = USD 0.6	
b. catalyst (10Cu-5Ni/AISBA-R) = not considered	
c. H ₂ = not considered	
Due to the difficulty of estimating the amount of hydrogen gas, the parameters for the price of components are not being considered for the time being	0
3. Safety	
Ni(NO ₃) ₂ ·6H ₂ O (N)	5
Na ₂ SiO ₃ (N)	5
Pluronic P123 (T)	5
H ₂ (F ⁺)	10
THF (F)	5
4. Technical Setup	
Pressure equipment, 2.5 MPa	3
5. Temperature/time	
Heating (95 °C), 3 h	3
6. Workup and purification	
Liquid-liquid extraction	3
Classical chromatography	10
Total penalty points:	49.05

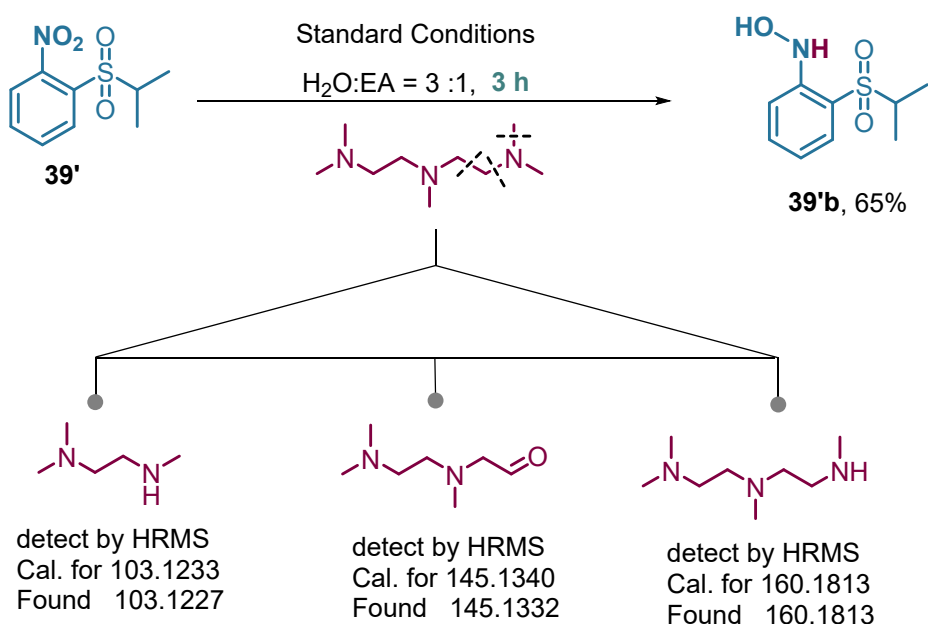
B. Ecoscale calculation:

EcoScale score: (100-49.05) = **50.95 (> 50; it is an acceptable synthesis)**

The result unveiled that this EDA complex-based strategy demonstrated higher economic and ecology benefits (71.5) compare to the reported metal-catalyzed hydrogenation (50.95).

IV. Mechanism study

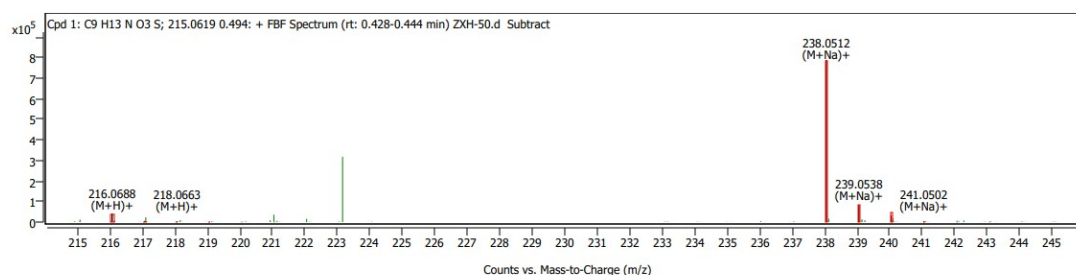
(1) Intermediates investigation



A 10 mL tube was charged with **39'** (0.2 mol), pentamethyldiethylenetriamine PMDETA (3.0 equivalent), glycine (1.0 equivalent) in mix solvent ($\text{H}_2\text{O}:\text{EA}=3:1$) upon irradiation of 100 W 390 nm LEDs at room temperature under N_2 atmosphere for 3 h. The reaction was monitored by TLC. After completion, the reaction mixture was quenched with water (10 mL) and extracted with dichloromethane for three times. The combined organic phase was dried over anhydrous Na_2SO_4 , filtered, and evaporated to leave a residue, which was purified by silica gel column chromatography with petroleum ether/ ethyl acetate (from 10 :1) to give the pure desired product **39'b**.

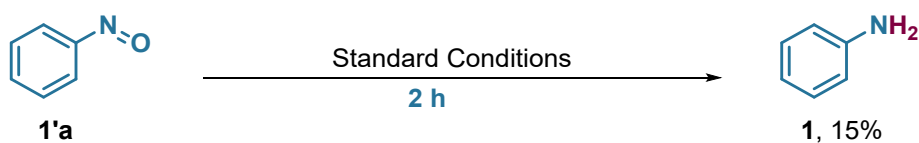
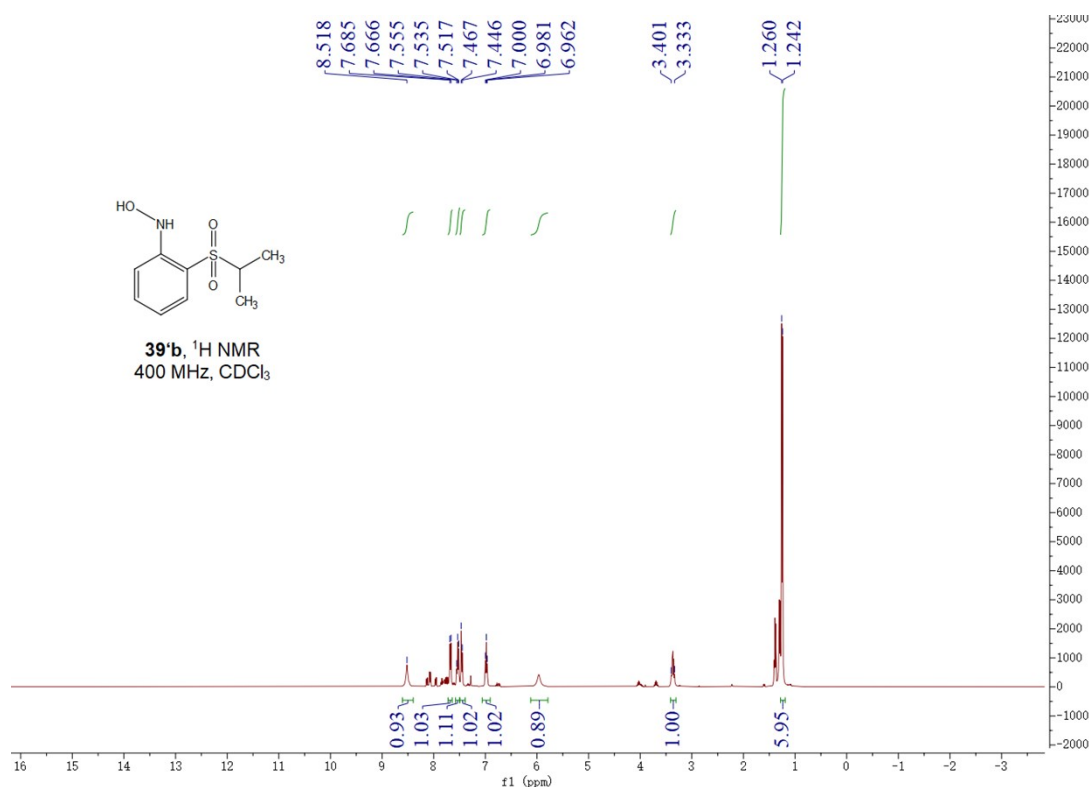
Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ 8.52 (s, 1H), 7.68 (d, $J = 7.6$ Hz, 1H), 7.54 (t, $J = 8.0$ Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 1H), 6.98 (t, $J = 7.6$ Hz, 1H), 5.96 (s, 1H), 3.40–3.33 (m, 1H), 2.16 (d, $J = 7.2$ Hz, 6H).

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_9\text{H}_{13}\text{NO}_3\text{SNa}$ 238.0514; Found: 238.0512.



Compound ID Table

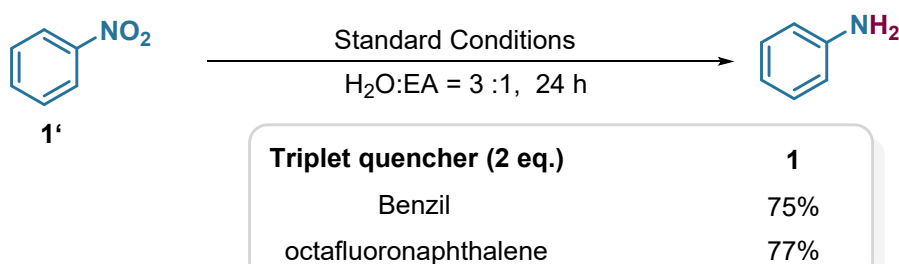
Name	Formula	Species	RT	RT Diff	Mass	CAS	ID Source	Score	Score (Lib)	Score (Tgt)
	$\text{C}_9\text{H}_{13}\text{N O}_3\text{S}$	$(\text{M}+\text{H})^+$ $(\text{M}+\text{Na})^+$	0.494		215.0619		FBF	99.14		99.14



A 10 mL tube was charged with **1'a** (0.2 mol), pentamethyldiethylenetriamine PMDETA (3.0 equivalent), glycine (1.0 equivalent) in (H_2O : EA=3:1) upon irradiation of 100 W 390 nm LEDs at room temperature under N_2 atmosphere for 2 h. The reaction was monitored by TLC. After completion, the reaction mixture was quenched with water (10 mL) and extracted with dichloromethane for three times. The combined organic phase was dried over anhydrous Na_2SO_4 , filtered, and evaporated to leave a residue, which was purified by silica gel column chromatography with petroleum ether/ ethyl acetate (from 10 :1) to give the pure desired product **1**.

The results indicate that hydroxylamine and nitrosoarene are potential intermediates.

(2) Triplet state quench experiment²⁻³



The triplet state quench experiments were conducted with nitrobenzene **1'**, PMDETA and glycine under the standard conditions using two different triplet quenchers (benzill, octafluoronaphthalene), respectively. However, these quenching studies did not reduce the reaction yield, indicating that the T_1 excited state of nitrobenzene is not the active species for triggering reaction.

The results rule out the possibility of nitroarene itself absorbing light to initiate the reaction.

(3) UV-vis experiment

UV-vis experiments were performed to analyse the potential association of PMDETA, glycine with electron acceptors (nitroarene, nitrosoarene, or hydroxylamine compounds).

(i) Various combinations of **8'**, PMDETA and glycine in DMF

- a) **8'** (1 mmol) was dissolved in DMF (5 mL).
- b) **8'** (1 mmol) and PMDETA (250 μ L) were dissolved in DMF (4.75 mL).
- c) **8'** (1 mmol) and glycine (250 μ L) were dissolved in DMF (4.75 mL).
- d) **8'** (1 mmol), PMDETA (250 μ L) and glycine (250 μ L) were dissolved in DMF (4.5 mL).

(ii) Various combinations of **1'a**, PMDETA and glycine in DMF

- e) **1'a** (1 mmol) was dissolved in DMF (5 mL)
- f) **1'a** (1 mmol) and PMDETA (250 μ L) were dissolved in DMF (4.75 mL)
- g) **1'a** (1 mmol) and glycine (250 μ L) were dissolved in DMF (4.75 mL)
- h) **1'a** (1 mmol), PMDETA (250 μ L) and glycine (250 μ L) were dissolved in DMF (4.5 mL)

(iii) Various combinations of **39'b**, PMDETA and glycine in DMF

- i) **39'b** (1 mmol) was dissolved in DMF (5 mL)
- j) **39'b** (1 mmol) and PMDETA (250 μ L) were dissolved in DMF (4.75 mL)
- k) **39'b** (1 mmol) and glycine (250 μ L) were dissolved in DMF (4.75 mL).
- l) **39'b** (1 mmol), PMDETA (250 μ L) and glycine (250 μ L) were dissolved in DMF (4.5 mL)
- m) PMDETA (250 μ L) and glycine (250 μ L) was dissolved in DMF (4.5 mL).
- n) PMDETA (250 μ L) was dissolved in DMF (4.75 mL)
- o) glycine (250 μ L) was dissolved in DMF (4.75 mL)

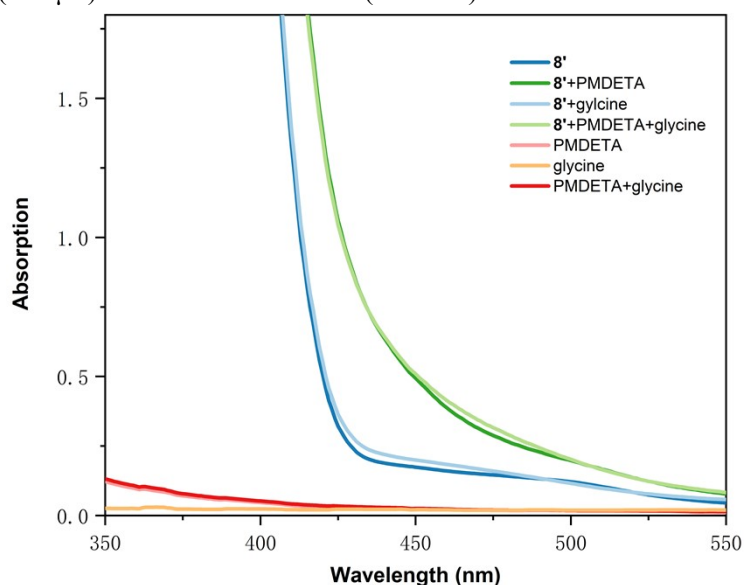


Figure S1: UV-vis spectra of various combinations of **8'**, PMDETA and glycine in DMF

The results revealed that PMDETA can associate with **8'** to form the EDA complex I, resulting a bathochromic shifted compared to the spectra of the individual components.

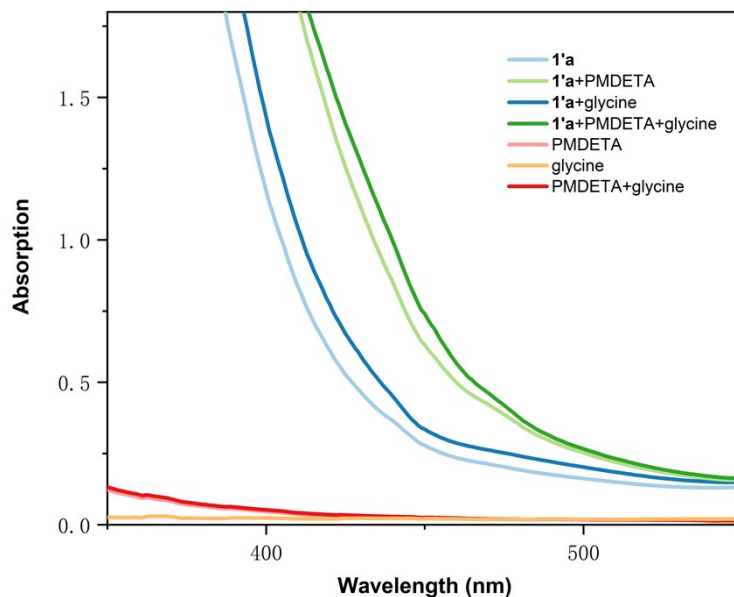


Figure S2: UV-vis spectra of various combinations of **1'a**, PMDETA and glycine in DMF

The results revealed that the addition of PMDETA resulted in a bathochromic shift in the absorbance of the nitroso compounds, with a slight modulation observed upon the addition of glycine. Based on these findings, it can be inferred that the formation of EDA complex II occurs between PMDETA and nitroso compounds.

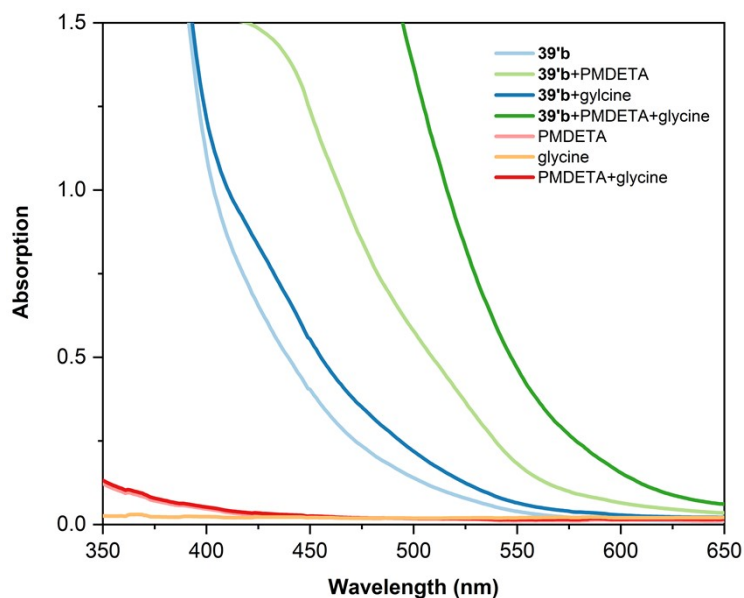


Figure S3: UV-vis spectra of various combinations of **39'b**, PMDETA and glycine in DMF

The results indicated that the absorbance of the hydroxylamine compounds underwent a bathochromic shift upon the introduction of PMDETA, while the addition of glycine further accentuated this red-shift. Based on these findings, it can be inferred that the

formation of EDA complex III occurs between PMDETA, glycine and hydroxylamine compounds.

(4) NMR titration⁴⁻⁵

The NMR sample of electron acceptors (**8'**, **1'a**, and **39'b**·glycine adduct) with different excesses of PMDETA in CDCl₃ or DMSO-*d*₆ was prepared.

(i) **EDA complex I: 8'** (0.25 M) with PMDETA (0.025 M to 0.075 M) in CDCl₃ (Figure S4).

(ii) **EDA complex II: 1'a** (0.25 M) with PMDETA (0.025 M to 0.075 M) in CDCl₃ (Figure S5).

(iii) **EDA complex III': 39'b** (0.25 M) with PMDETA (0.025 M to 0.075 M) in CDCl₃ (Figure S6).

(iv) **EDA complex III: 39'b**·glycine adduct (0.025 M) with PMDETA (0.025 M to 0.075 M) in DMSO-*d*₆ (Figure S7).

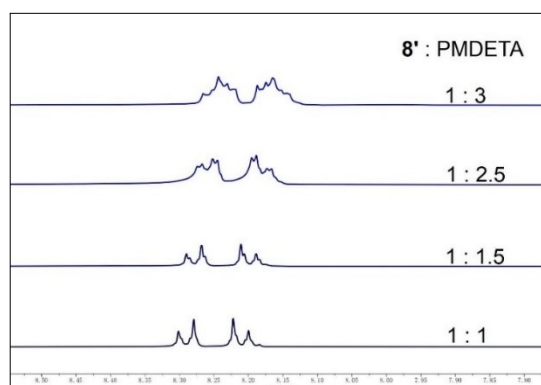


Figure S4: NMR titration of **8'** and PMDETA

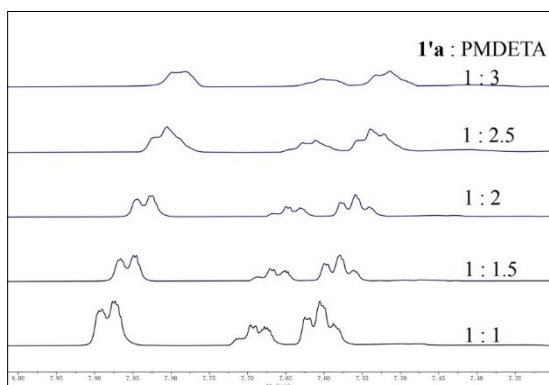


Figure S5: NMR titration of **1'a** and PMDETA

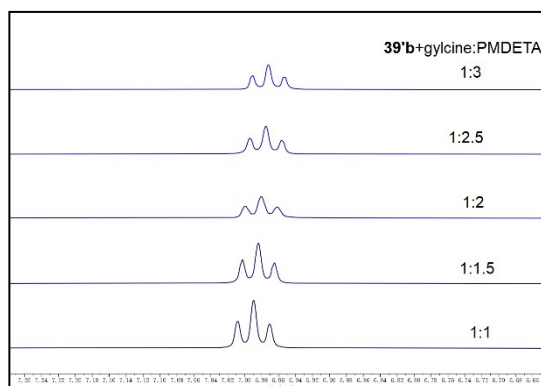
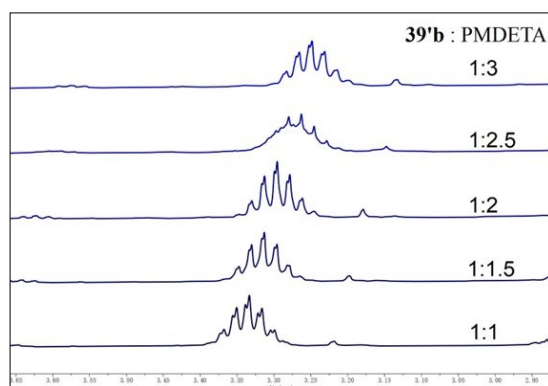


Figure S6: NMR titration of **39'b** and PMDETA**Figure S7:** NMR titration of **39'b**·glycine adduct and PMDETA

The change in chemical shift (in ppm) of each peak of electron acceptor was calculated by comparing the 0.25 M electron acceptor' solution. The association constants K_{EDA} were measured from the slope and intercept of the plots.

Table S3: Data obtained by ^1H NMR spectra for EDA complex I in CDCl_3 , with **8'** = 0.025 mol/L.

[PMDETA](M)	1/[PMDETA](M^{-1})	δ_0	$\delta_{\text{EDA-I}}$	$\Delta\delta$	1/ $\Delta\delta$
0.025	40	8.326	8.302	0.024	41.7
0.0375	26.7	8.326	8.290	0.036	27.8
0.0625	16	8.326	8.274	0.052	19.2
0.075	13.3	8.326	8.266	0.082	12.2

Table S4: Data obtained by ^1H NMR spectra for EDA complex II in CDCl_3 , with **1'a** = 0.025 mol/L.

[PMDETA](M)	1/[PMDETA](M^{-1})	δ_0	$\delta_{\text{EDA-II}}$	$\Delta\delta$	1/ $\Delta\delta$
0.025	40.0	7.918	7.877	0.041	24.4
0.0375	26.7	7.918	7.850	0.068	14.7
0.05	20.0	7.918	7.829	0.089	11.2
0.0625	16.0	7.918	7.805	0.113	8.4
0.075	13.3	7.918	7.778	0.140	7.1

Table S5: Data obtained by ^1H NMR spectra for EDA complex III' in CDCl_3 , with **39'b** = 0.025 mol/L.

[PMDETA](M)	1/[PMDETA](M^{-1})	δ_0	$\delta_{\text{EDA-III'}}$	$\Delta\delta$	1/ $\Delta\delta$
0.025	40.0	7.918	7.877	0.041	24.4
0.0375	26.7	7.918	7.850	0.068	14.7
0.05	20.0	7.918	7.829	0.089	11.2
0.0625	16.0	7.918	7.805	0.113	8.4
0.075	13.3	7.918	7.778	0.140	7.1

Table S6: Data obtained by ^1H NMR spectra for EDA complex III in DMSO, with **39'b**·glycine adduct = 0.025 mol/L.

[PMDETA](M)	1/[PMDETA](M ⁻¹)	δ_0	$\delta_{\text{EDA-III}}$	$\Delta\delta$	1/ $\Delta\delta$
0.025	40.0	7.001	9.9894	0.0107	93.5
0.0375	26.7	7.001	6.9840	0.0161	62.1
0.05	20.0	7.001	6.9804	0.0197	50.8
0.0625	16.0	7.001	6.9751	0.250	40
0.075	13.3	7.001	6.9721	0.0280	35.7

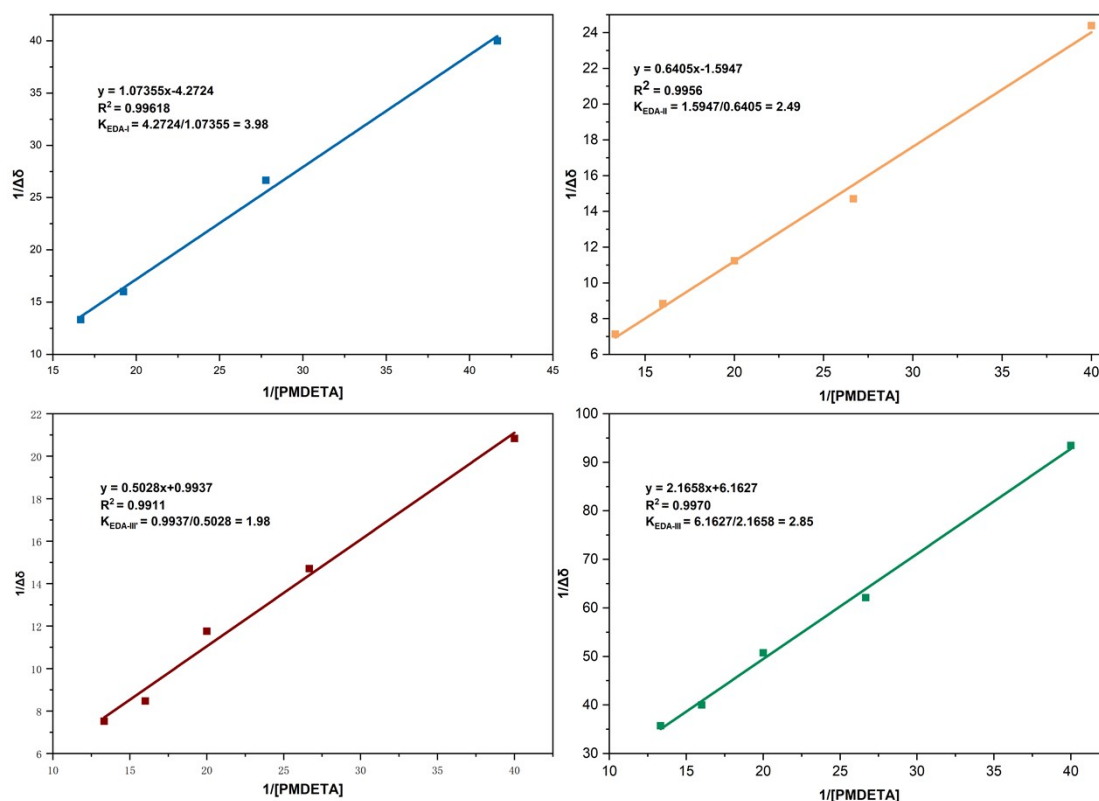


Figure S8: The association constants K_{EDA}

The results indicated that the value of K were decrease progressively in the absence of glycine ($K_{\text{EDA I}}=3.98 > K_{\text{EDA II}}=2.49 > K_{\text{EDA III}}=1.98$). Furthermore, the $K_{\text{EDA-III}}$ was measured at 2.85, suggesting that glycine could enhance the ability of **39'b** to associate with PMDETA.

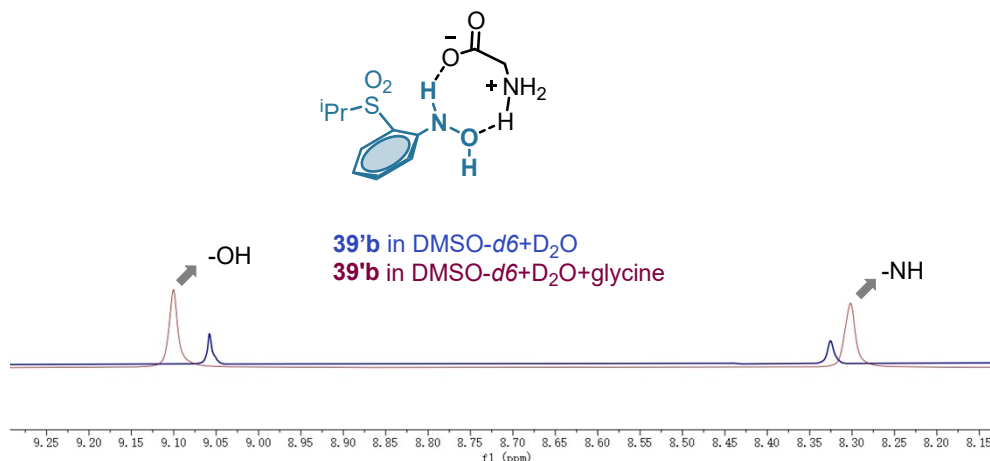


Figure S9: ^1H NMR shift of **39'b** and glycine

Based on the effect of electron-cloud density in chemical shift of protons, the following conclusions can be draw:

(a) the downfield shift of -OH proton indicates a reduced electron-cloud density of hydrogen atom, which is caused by the lone pair of electrons of O (oxygen in the **39'b**) to be biased toward H of $-\text{NH}_3^+$ to form the intermolecular hydrogen bonding between $-\text{NH}_3^+$ of glycine and **39'b** (-OH).

(b) the upfield of -NH proton suggests an increased electron-cloud density of hydrogen atom, which is caused by the presence of intermolecular hydrogen bonding between $-\text{COO}^-$ of glycine and **39'b** (-NH).

(5) Preliminary kinetic investigation

(i) A 10 mL tube was charged with 1-(isopropylsulfonyl)-2-nitrobenzene **39'** (0.2 mol), pentamethyldiethylenetriamine PMDETA (3.0 equivalent) in H_2O : EA (150 μL : 50 μL) upon irradiation of 100 W 390 nm LEDs at room temperature under N_2 atmosphere. Five parallel reactions were respectively illuminated under 390 nm for different time 1 h, 3 h, 5 h, 10 h, 24 h. The yield of **39** was obtained by ^1H NMR using 1,3,5-trimethoxybenzene (0.05 mmol) as an internal standard.

The results (blue lines) showed that in the absence of glycine, the **39'** was almost completely converted within 5 h, with 64.5% of **39'b** and 21.5% of **39** being formed, and thereafter the rate of conversion of **39'b** to **39** decreased dramatically, with only 36.5% of **39** being formed, accompanied by 55.5% of **39'b** remaining even after 24 h of reaction.

(ii) A 10 mL tube was charged with **39'** (0.2 mol), pentamethyldiethylenetriamine PMDETA (3.0 equivalent), glycine (1.0 equivalent) in H_2O : EA (150 μL : 50 μL) upon irradiation of 100 W 390 nm LEDs at room temperature under N_2 atmosphere. Five parallel reactions were respectively illuminated under 390 nm for different time 1 h, 3 h, 5 h, 10 h, 24 h. The yield of **39** was obtained by ^1H NMR using 1,3,5-trimethoxybenzene (0.05 mmol) as an internal standard.

The results (orange lines) showed that upon addition of glycine, the **39'** was almost completely converted within 3 h, with 82% of **39'b** and 8% of **39** being formed, and the

yield of **39** after 24 hours of reaction was 78%, accompanied by 12% **39'b** remaining.

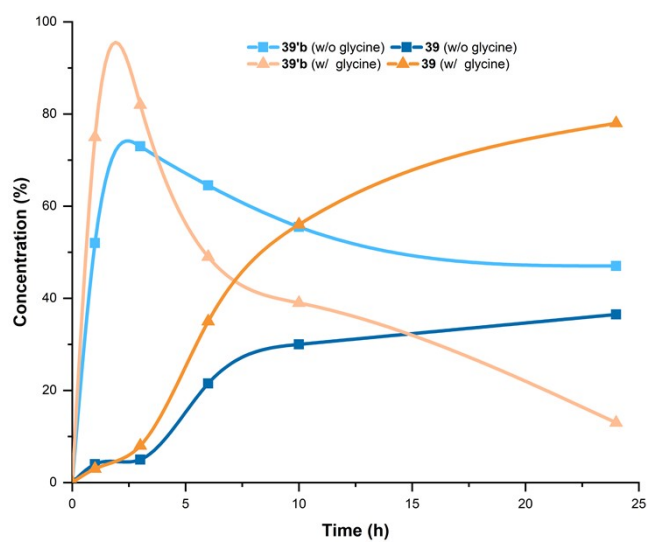
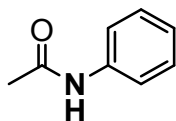


Figure S10: ^1H NMR of reaction solution

V. Characterization data for the products (reactions was conducted at 0.2 mmol scale).

***N*-phenylacetamide (1a)**



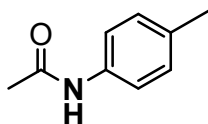
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (81% yield, 21.9 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.17 (s, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 2.16 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 169.1, 138.1, 128.9, 124.3, 120.2, 24.4.

(Known compound: *ACS Sustainable Chem. Eng.*, 2023, **11**, 9047-9056.).

***N*-(*p*-tolyl)acetamide (2a)**



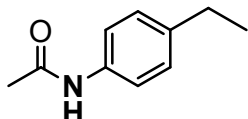
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (88% yield, 26.2 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.63 (s, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.11 (t, *J* = 8.1 Hz, 2H), 2.32 (s, 3H), 2.16 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.6, 135.4, 133.9, 129.4, 120.2, 24.4, 20.9.

(Known compound: *ACS Sustainable Chem. Eng.*, 2023, **11**, 9047-9056.).

***N*-(4-ethylphenyl)acetamide (3a)**



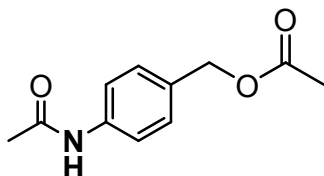
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (86% yield, 28.1 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.46-7.41 (m, 3H), 7.15 (d, *J* = 8.2 Hz, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.17 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.4, 140.4, 135.5, 128.3, 120.2, 28.3, 24.6, 15.6.

(Known compound: *ChemSusChem* 2022, **15**, e202200227.)

4-acetamidobenzyl acetate (4a)



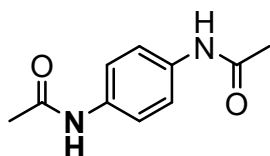
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (85% yield, 35.2 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.55-7.51 (m, 3H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.07 (s, 2H), 2.19 (s, 3H), 2.11 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.0, 168.5, 138.0, 131.7, 129.2, 119.9, 65.9, 24.6, 21.0.

(Known compound: *Eur. J. Org. Chem.*, 2012, **2012**, 6127-6131.)

***N,N'*-(1,4-phenylene)diacetamide (5a)**



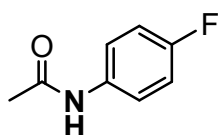
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (36% yield, 13.8 mg).

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.86 (d, *J* = 16.4 Hz, 2H), 7.50 (d, *J* = 16.8 Hz, 4H), 2.05-2.01 (m, 6H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 168.4, 135.1, 119.8, 24.3.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₀H₁₃N₂O₂ 193.0977, Found: 193.0974.

***N*-(4-fluorophenyl)acetamide (6a)**



Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (80% yield, 24.5 mg).

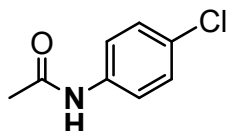
¹H NMR (400 MHz, CDCl₃) δ 7.55 (s, 1H), 7.48 (dd, *J* = 9.0 Hz, *J* = 4.8 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 2.18 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.6, 159.4 (d, *J*_{F-C} = 242.1 Hz), 133.87, 121.9 (d, *J*_{F-C} = 7.4 Hz), 115.6 (d, *J*_{F-C} = 22.3 Hz), 24.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -118.0

(Known compound: *Angew. Chem. Int. Ed.*, 2021, **60**, 7936-7940.)

***N*-(4-chlorophenyl)acetamide (7a)**



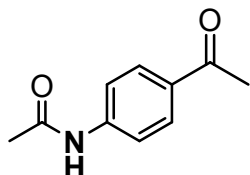
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (81% yield, 27.4 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.7 Hz, 2H), 7.46-7.31 (m, 3H), 2.19 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.3, 136.4, 129.3, 129.0, 121.1, 24.6.

(Known compound: *J. Am. Chem. Soc.*, 2022, **144**, 15437-15442.)

***N*-(4-acetylphenyl)acetamide (8a)**



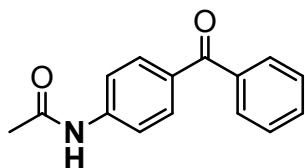
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (81% yield, 28.9 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.86 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 2.59 (s, 3H), 2.24 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 197.2, 168.8, 142.4, 132.8, 129.8, 118.9, 26.5, 24.8.

(Known compound: *J. Am. Chem. Soc.*, 2022, **144**, 15437-15442.)

***N*-(4-benzoylphenyl)acetamide (9a)**



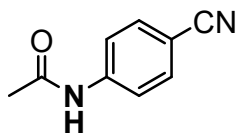
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (79% yield, 37.8 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.07 (s, 1H), 7.83-7.77 (m, 4H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 2.23 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 195.8, 168.8, 142.1, 137.8, 132.9, 132.3, 131.6, 129.8, 128.3, 118.8, 24.7.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₅H₁₄NO₂ 240.1028, Found: 240.1025.

***N*-(4-cyanophenyl)acetamide (10a)**



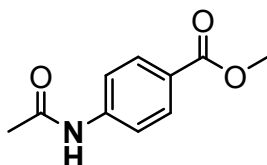
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (81% yield, 25.9 mg).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.37 (s, 1H), 7.77-7.72 (m, 4H), 2.09 (s, 3H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 169.6, 143.9, 133.7, 119.5, 119.4, 105.1, 24.7.

(Known compound: *ACS Sustainable Chem. Eng.*, 2023, **11**, 9047-9056.).

methyl 4-acetamidobenzoate (11a)



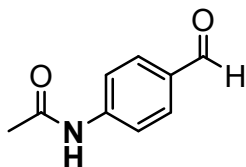
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (83% yield, 32.1 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.02-8.00 (m, 2H), 7.67 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 3H), 2.22 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.7, 166.7, 142.2, 130.8, 125.5, 118.8, 52.1, 24.8.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₀H₁₂NO₃ 194.0819, Found: 194.0814.

***N*-(4-formylphenyl)acetamide (12a)**



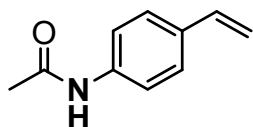
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (79% yield, 25.8 mg).

¹H NMR (400 MHz, CDCl₃) δ 9.93 (s, 1H), 8.01 (s, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 2.25 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 191.2, 169.0, 143.7, 132.2, 131.2, 119.3, 24.8.

(Known compound: *Angew. Chem. Int. Ed.*, 2021, **60**, 7935-7940.)

***N*-(4-vinylphenyl)acetamide (13a)**



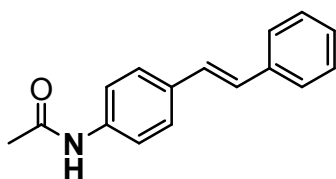
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (80% yield, 25.8 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.63 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.68 (dd, *J* = 17.6 Hz, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 10.8 Hz, 1H), 2.19 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.4, 137.5, 136.1, 133.7, 126.8, 119.8, 113.1, 24.6.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₀H₁₂NO 160.0921, Found: 160.0915.

***(E)*-N-(4-styrylphenyl)acetamide (14a)**



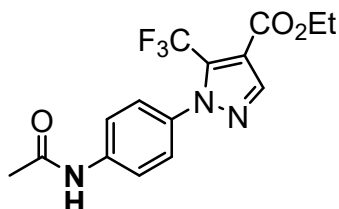
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (82% yield, 38.9 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.60 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.27-7.21 (m, 7H), 6.61-6.53 (m, 2H), 2.18 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.4, 137.3, 136.8, 133.2, 129.9, 129.6, 129.6, 128.8, 128.3, 127.1, 119.5, 24.6

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₆H₁₆NO 238.1232, Found: 238.1230.

ethyl 1-(4-acetamidophenyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate (15a)



Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (71% yield, 48.4 mg).

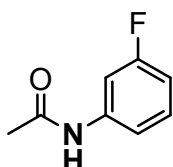
¹H NMR (400 MHz, CDCl₃) δ 8.12 (s, 1H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.53 (s, 1H), 7.38 (d, *J* = 8.7 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 2.24 (s, 3H), 1.40 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.8 (d, *J*_{F-C} = 8.5 Hz), 161.8, 142.4, 139.5 (d, *J*_{F-C} = 4.4 Hz), 134.8, 132.6 (q, *J*_{F-C} = 39.8 Hz), 126.5, 119.8 (d, *J*_{F-C} = 2.5 Hz), 119.1 (q, *J*_{F-C} = 269.9 Hz), 116.6, 61.4, 24.6, 14.10.

¹⁹F NMR (376 MHz, CDCl₃) δ -55.42

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₅H₁₅F₃N₃O₃ 342.1065, Found: 342.1069.

***N*-(3-fluorophenyl)acetamide (16a)**



Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (83% yield, 25.4 mg).

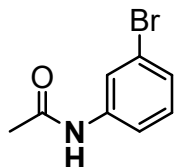
¹H NMR (400 MHz, CDCl₃) δ 7.69 (s, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.29-7.23 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.81 (t, *J* = 8.4 Hz, 1H), 2.20 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.8, 162.9 (d, *J*_{F-C} = 243.2 Hz), 139.4 (d, *J*_{F-C} = 10.8 Hz), 130.0 (d, *J*_{F-C} = 9.3 Hz), 115.0 (d, *J*_{F-C} = 2.8 Hz), 110.9 (d, *J*_{F-C} = 21.2 Hz), 107.4 (d, *J*_{F-C} = 26.1 Hz), 24.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -111.52.

(Known compound: *Angew. Chem. Int. Ed.*, 2021, **60**, 7935-7940.)

***N*-(3-bromophenyl)acetamide (17a)**



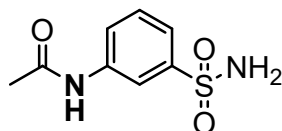
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (85% yield, 36.2 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.17 (s, 1H), 7.79 (s, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 2.18 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 169.1, 139.3, 130.2, 127.3, 123.0, 122.5, 118.5, 24.5.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₈H₉BrNO 213.9868, Found: 213.9862.

***N*-(3-sulfamoylphenyl)acetamide (18a)**



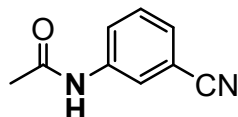
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (51% yield, 21.8 mg).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.24 (s, 1H), 8.15 (s, 1H), 7.75-7.70 (m, 1H), 7.49-7.48 (m, 2H), 7.35 (s, 2H), 2.07 (s, 3H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 169.2, 145.0, 140.1, 129.9, 122.2, 120.5, 116.4, 24.5.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₈H₁₁N₂O₃S 215.049; Found: 215.0501.

***N*-(3-cyanophenyl)acetamide (19a)**



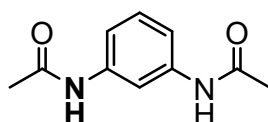
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (67% yield, 21.4 mg)

¹H NMR (400 MHz, CDCl₃) δ 8.11 (s, 1H), 7.97 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.45-7.38 (m, 2H), 2.22 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 169.2, 139.0, 130.0, 127.6, 124.0, 123.0, 118.7, 112.7, 24.5.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₉H₉N₂O 161.0715, Found: 161.0708.

***N,N'*-(1,3-phenylene)diacetamide (20a)**



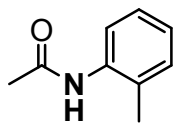
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (74% yield, 28.4 mg).

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.89 (s, 2H), 7.87 (s, 1H), 7.27-7.25 (m, 2H), 7.19-7.15 (m, 1H), 2.03 (s, 6H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 168.7, 140.0, 129.2, 114.3, 110.2, 24.5.

(Known compound: *Org. Chem. Front.*, 2022, **9**, 311-319.)

***N*-(*o*-tolyl)acetamide (21a)**



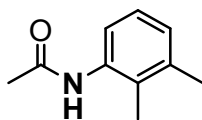
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (82% yield, 24.4 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.72 (s, 1H), 7.23-7.19 (m, 3H), 7.10 (t, *J* = 7.2 Hz, 1H), 2.26 (s, 3H), 2.20 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.6, 135.6, 130.5, 126.7, 125.4, 123.7, 123.7, 24.2, 17.8.

(Known compound: *ACS Sustainable Chem. Eng.*, 2023, **11**, 9047-9056.).

***N*-(2,3-dimethylphenyl)acetamide (22a)**



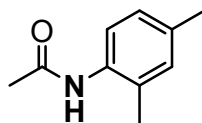
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (79% yield, 25.8mg).

¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 7.8 Hz, 1H), 7.15-7.09 (m, 2H), 7.03 (d, *J* = 7.4 Hz, 1H), 2.31 (s, 3H), 2.21 (s, 3H), 2.15 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.7, 137.5, 135.2, 129.9, 127.7, 125.9, 122.7, 24.0, 20.6, 13.9.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₀H₁₄NO 164.1075; Found: 164.1069.

***N*-(2,4-dimethylphenyl)acetamide (23a)**



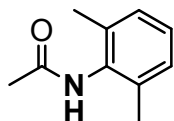
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (80% yield, 26.1 mg)

¹H NMR (400 MHz, CDCl₃) δ 7.53-7.51 (m, 1H), 7.10-7.02 (m, 3H), 2.30 (s, 3H), 2.22 (s, 3H), 2.19 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.7, 135.3, 132.9, 131.2, 130.3, 127.2, 124.1, 24.0, 20.9, 17.8.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₀H₁₄NO 164.1075; Found: 164.1070.

***N*-(2,6-dimethylphenyl)acetamide (24a)**



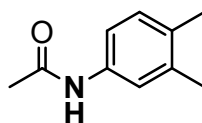
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (82% yield, 26.7 mg).

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.23 (s, 1H), 7.06 (s, 3H), 2.14 (s, 6H), 2.05 (s, 3H).

¹³C NMR (100 MHz, DMSO *d*₆) δ 168.2, 135.9, 135.6, 128.0, 126.7, 23.0, 18.6.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₀H₁₄NO 164.1075; Found: 164.1071.

***N*-(3,4-dimethylphenyl)acetamide (25a)**



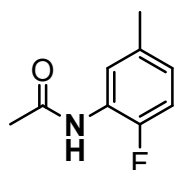
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (90% yield, 29.4 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.55 (s, 1H), 7.30 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 2.24 (s, 3H), 2.23 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 168.4, 137.2, 135.6, 132.7, 129.9, 121.5, 117.6, 24.5, 19.9, 19.2.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{10}\text{H}_{14}\text{NO}$ 164.1075; Found: 164.1068.

***N*-(2-fluoro-5-methylphenyl)acetamide (26a)**



Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (68% yield, 22.7 mg).

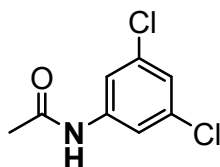
^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, $J = 7.4$ Hz, 1H), 7.41 (s, 1H), 6.96 (dd, $J = 10.6$ Hz, $J = 8.4$ Hz, 1H), 6.86-6.83 (m, 1H), 2.33 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 168.4, 150.6 (d, $J_{\text{F-C}} = 238.7$ Hz), , 134.2 (d, $J_{\text{F-C}} = 3.6$ Hz), 125.8 (d, $J_{\text{F-C}} = 10.5$ Hz), 124.6 (d, $J_{\text{F-C}} = 7.3$ Hz), 122.2, 114.2 (d, $J_{\text{F-C}} = 19.1$ Hz), 24.7, 21.1.

^{19}F NMR (376 MHz, CDCl_3) δ -136.19.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_9\text{H}_{11}\text{FNO}$ 168.0824; Found: 168.0817.

***N*-(3,5-dichlorophenyl)acetamide (27a)**



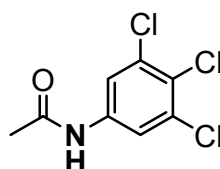
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (79% yield, 32.1 mg).

^1H NMR (400 MHz, $\text{MeOH-}d_4$) δ 7.60 (s, 2H), 7.14-7.13 (m, 1H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, $\text{MeOH-}d_4$) δ 174.4, 144.8, 138.7, 126.9, 121.4, 26.5.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_8\text{H}_8\text{Cl}_2\text{NO}$ 203.9983; Found: 203.9977.

***N*-(3,4,5-trichlorophenyl)acetamide (28a)**



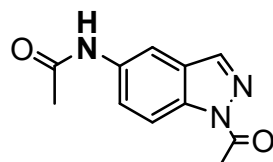
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (80% yield, 38.0 mg).

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 10.31 (s, 1H), 7.84-7.82 (m, 2H), 2.07. (s, 3H)

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 169.6, 139.7, 133.2, 123.4, 119.3, 24.6.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_8\text{H}_7\text{Cl}_3\text{NO}$ 237.9593; Found: 237.9585.

***N*-(1-acetyl-1*H*-indazol-5-yl)acetamide (29a)**



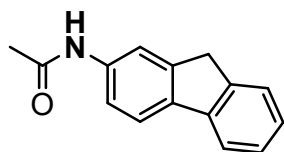
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (82% yield, 35.6 mg).

^1H NMR (400 MHz, CDCl_3) δ 8.35 (d, $J = 8.8$ Hz, 1H), 8.26 (s, 1H), 8.10 (s, 1H), 7.55 (s, 1H), 7.36 (dd, $J = 8.8$ Hz, $J = 1.9$ Hz, 1H), 2.80 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 168.6, 139.9, 135.9, 134.5, 126.8, 122.4, 115.8, 111.6, 24.6, 22.9.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_{12}\text{N}_3\text{O}_2$ 218.0929; Found: 218.0922.

***N*-(9H-fluoren-2-yl)acetamide (30a)**



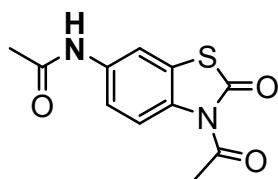
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (89% yield, 39.7 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.88 (s, 1H), 7.72 (t, *J* = 8.7 Hz, 2H), 7.60-7.49 (m, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 3.88 (s, 2H), 2.23 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.5, 144.3, 143.2, 141.3, 138.1, 136.7, 126.8, 126.3, 125.0, 120.1, 119.5, 118.7, 117.0, 37.0, 24.7.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₄NO 224.1075; Found: 224.1069.

***N*-(3-acetyl-2-oxo-2,3-dihydrobenzo[d]thiazol-6-yl)acetamide (31a)**



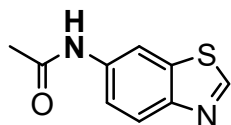
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (77% yield, 38.5 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 9.2 Hz, 1H), 8.00 (d, *J* = 2.4 Hz, 1H), 7.60 (s, 1H), 7.11 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 2.75 (s, 3H), 2.14 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.2, 170.8, 168.6, 135.5, 130.8, 122.6, 118.2, 118.1, 113.3, 27.3, 24.6.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₁H₁₁N₂O₃S 251.049; Found: 251.0489.

***N*-(benzo[d]thiazol-6-yl)acetamide (32a)**



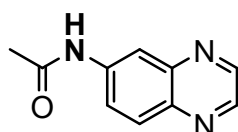
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (79% yield, 30.3 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.92 (s, 1H), 8.54 (d, *J* = 1.6 Hz, 1H), 8.03-7.99 (m, 2H), 7.35 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 2.23 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.9, 153.5, 149.8, 135.9, 134.8, 123.4, 119.1, 112.7, 24.6.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₉H₉N₂OS 193.0435; Found: 193.0430.

***N*-(quinoxalin-6-yl)acetamide (33a)**



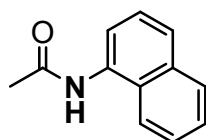
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (64% yield, 23.9 mg).

¹H NMR (400 MHz, MeOH-*d*₄) δ 8.78 (d, *J* = 2.0 Hz, 1H), 8.73 (d, *J* = 1.6 Hz, 1H), 8.47 (d, *J* = 2.0 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.87 (dd, *J* = 9.2 Hz, *J* = 2.4 Hz, 1H), 2.22 (s, 3H).

¹³C NMR (100 MHz, MeOH-*d*₄) δ 170.7, 145.3, 143.5, 143.1, 140.4, 139.5, 128.9, 123.9, 115.8, 22.7.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₀H₁₀N₃O 188.0824; Found: 188.0818.

***N*-(naphthalen-1-yl)acetamide (34a)**



Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (81% yield, 30.0 mg)

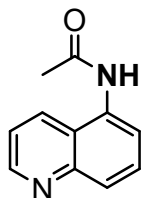
¹H NMR (400 MHz, DMSO-*d*₆) δ 9.94 (s, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.95-7.93 (m, 1H), 7.75 (d, *J*

= 8.0 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.58-7.47 (m, 3H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 169.4, 134.2, 128.6, 128.1, 126.4, 126.2, 126.0, 125.5, 123.2, 122.0, 24.0.

(Known compound: *ACS Sustainable Chem. Eng.*, 2023, **11**, 9047-9056.).

N-(quinolin-5-yl)acetamide (35a)



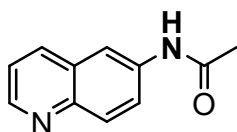
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (73% yield, 27.2 mg)

^1H NMR (400 MHz, DMSO- d_6) δ 10.07 (s, 1H), 8.92 (dd, J = 4.0 Hz, J = 1.2 Hz, 1H), 8.51 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.73 (t, J = 8.0 Hz, 1H), 7.56 (dd, J = 8.8 Hz, J = 4.0 Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 169.6, 150.9, 148.6, 134.5, 132.0, 129.5, 126.4, 123.2, 121.8, 121.3, 24.0.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}$ 187.0871; Found: 187.0876.

N-(quinolin-6-yl)acetamide (36a)



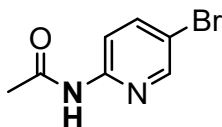
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (69% yield, 25.7 mg).

^1H NMR (400 MHz, DMSO- d_6) δ 10.26 (s, 1H), 8.77 (dd, J = 4.0 Hz, J = 1.2 Hz, 1H), 8.36, 8.36 (d, J = 2.0 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 9.2 Hz, 1H), 7.78 (dd, J = 8.8 Hz, J = 2.0 Hz, 1H), 7.46 (dd, J = 8.0 Hz, J = 4.0 Hz, 1H), 2.13 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 169.6, 150.9, 148.6, 134.6, 131.9, 129.5, 126.4, 123.2, 121.8, 121.3, 24.0.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}$ 187.0871; Found: 187.0869.

N-(5-bromopyridin-2-yl)acetamide (37a)



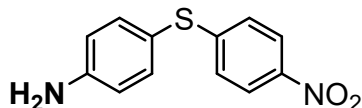
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (57% yield, 24.4 mg).

^1H NMR (400 MHz, DMSO- d_6) δ 8.33-8.27 (m, 2H), 8.18 (d, J = 8.8 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 168.7, 150.0, 148.4, 141.0, 115.3, 114.5, 24.8.

(Known compound: *Org. Biomol. Chem.*, 2020, **18**, 9292-9299)

4-((4-nitrophenyl)thio)aniline (38A)



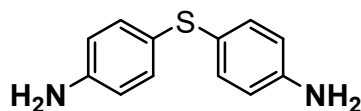
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, yellow solid (41% yield, 20.2 mg)

¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 9.2 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.11 (t, *J* = 9.2 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 3.56 (br, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 151.0, 148.3, 144.8, 137.3, 125.2, 123.9, 116.5, 116.2.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₂H₁₁N₂O₂S 247.0541; Found: 247.0543

4,4'-thiodianiline (38B)¹¹



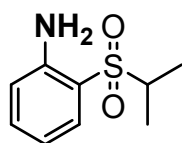
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, yellow solid (53% yield, 15.1 mg)

¹H NMR (400 MHz, CDCl₃) δ 7.18 (d, *J* = 8.4 Hz, 4H), 6.62 (d, *J* = 8.4 Hz, 4H), 3.65 (br, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 145.7, 132.8, 125.0, 115.8.

(Known compound: *Org. Lett.*, 2010, **12**, 2430-2433.)

2-(isopropylsulfonyl)aniline (39)



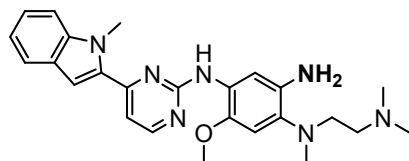
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (78% yield, 31 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.67 (br, 2H), 3.40-3.30 (m, 1H), 1.32 (d, *J* = 6.8 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 147.2, 135.0, 131.2, 118.1, 117.6, 117.5, 54.1, 15.3.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₉H₁₄NO₂S 200.0745; Found: 200.0736.

*N*¹-(2-(dimethylamino)ethyl)-5-methoxy-*N*¹-methyl-N⁴-(4-(1-methyl-1H-indol-2-yl)pyrimidin-2-yl)benzene-1,2,4-triamine (40)



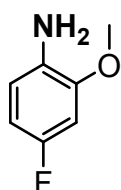
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (DCM/MeOH = 3:1) as eluant, white solid (45% yield, 40.1 mg)

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.44 (d, *J* = 7.6 Hz, 1H), 8.30 (s, 1H), 8.28 (d, *J* = 5.6 Hz, 1H), 7.80 (s, 1H), 7.52-7.50 (m, 2H), 7.25 (t, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 5.2 Hz, 1H), 6.77 (s, 1H), 4.58 (s, 2H), 3.87 (s, 3H), 3.75 (s, 3H), 2.89 (t, *J* = 6.8 Hz, 2H), 2.64 (s, 3H), 2.36 (t, *J* = 6.4 Hz, 2H), 2.17 (s, 6H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ 162.5, 160.9, 157.4, 142.2, 138.1, 137.2, 133.8, 133.3, 126.0, 125.7, 122.7, 122.6, 121.4, 112.9, 110.8, 109.5, 107.2, 105.7, 57.9, 56.9, 54.5, 46.2, 42.1, 40.6, 33.5.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₅H₃₂N₇O 446.2668; Found: 446.2660.

4-fluoro-2-methoxyaniline (41)



Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 10:1) as eluant, white solid (85% yield, 24.0 mg).

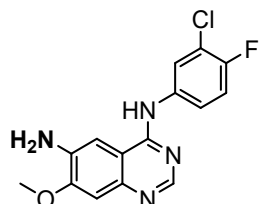
¹H NMR (400 MHz, CDCl₃) δ 6.64 (t, *J* = 7.6 Hz, 1H), 6.58 (dd, *J* = 10.4 Hz, *J* = 2.4 Hz, 1H), 6.53 (t, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.58 (br, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 156.4 (d, *J*_{F-C} = 234.1 Hz), 147.8 (d, *J*_{F-C} = 9.4 Hz), 132.0 (d, *J*_{F-C} = 2.6 Hz), 114.7 (d, *J*_{F-C} = 9.1 Hz), 106.4 (d, *J*_{F-C} = 21.7 Hz), 99.1 (d, *J*_{F-C} = 16.7 Hz), 55.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -124.19.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₇H₉FNO 142.0668; Found: 142.0662.

***N*⁴-(3-chloro-4-fluorophenyl)-7-methoxyquinazoline-4,6-diamine (42)**



Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (67% yield, 42.6 mg).

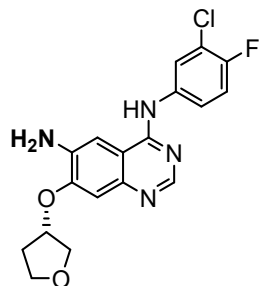
¹H NMR (400 MHz, DMSO) δ 9.40 (s, 1H), 8.39 (s, 1H), 8.21-8.19 (m, 1H), 7.83-7.80 (m, 1H), 7.42-7.38 (m, 2H), 7.11 (s, 1H), 5.40 (br, 2H), 3.97 (s, 3H).

¹³C NMR (100 MHz, DMSO) δ 155.5, 153.1 (d, *J*_{F-C} = 240.3 Hz), 153.2, 150.7, 145.3, 139.0, 138.0, 122.9, 121.9 (d, *J*_{F-C} = 6.7 Hz), 119.0 (d, *J*_{F-C} = 18.1 Hz), 116.8 (d, *J*_{F-C} = 21.4 Hz), 110.9, 106.4, 101.3, 56.3.

¹⁹F NMR (376 MHz, DMSO) δ -124.36.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₃ClFN₄O 319.0762; Found: 319.0757.

(*S*)-*N*⁴-(3-chloro-4-fluorophenyl)-7-((tetrahydrofuran-3-yl)oxy)quinazoline-4,6-diamine (43)



Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (78% yield, 58.4 mg).

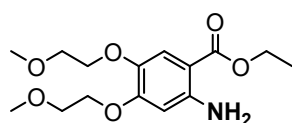
¹H NMR (400 MHz, CDCl₃) δ 8.58 (s, 1H), 7.92-7.90 (m, 2H), 7.52-7.48 (m, 2H), 7.36 (s, 1H), 7.14 (t, *J* = 8.4 Hz, 1H), 7.11, 7.09 (s, 1H), 7.00 (s, 1H), 5.09-5.07 (m, 1H), 4.28 (br, 2H), 4.11-4.08 (m, 1H), 4.05-4.01 (m, 2H), 3.96-3.90 (m, 1H), 2.37-2.28 (m, 1H), 2.25-2.19 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 154.5 (d, *J*_{F-C} = 244.3 Hz), 155.23, 151.9, 150.9, 145.5, 137.9, 135.5, 123.7, 121.1 (d, *J*_{F-C} = 6.7 Hz), 121.1 (d, *J*_{F-C} = 18.5 Hz), 116.5 (d, *J*_{F-C} = 21.9 Hz), 110.1, 108.1, 100.8, 78.6, 73.0, 67.3, 32.8.

¹⁹F NMR (376 MHz, CDCl₃) δ -121.30.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₈H₁₇ClFN₄O₂ 375.1024; Found: 375.1021.

ethyl 2-amino-4,5-bis(2-methoxyethoxy)benzoate (44)



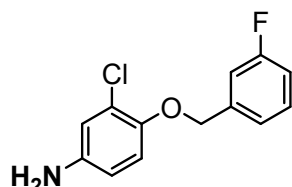
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (81% yield, 50.7 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.45 (s, 1H), 6.17 (s, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.13 (t, *J* = 4.4 Hz, 2H), 4.09 (t, *J* = 4.4 Hz, 2H), 3.78 (t, *J* = 4.8 Hz, 2H), 3.74 (t, *J* = 4.8 Hz, 2H), 3.45 (d, *J* = 3.2 Hz, 6H), 1.37 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 167.7, 155.2, 147.4, 139.7, 118.2, 103.2, 100.9, 71.2, 70.7, 70.1, 68.0, 60.1, 59.2, 59.1, 14.5.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₂₄NO₆ 314.1603; Found: 314.1602.

3-chloro-4-((3-fluorobenzyl)oxy)aniline (45)



Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 10:1) as eluant, white solid (83% yield, 41.7 mg)

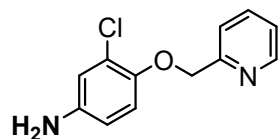
¹H NMR (400 MHz, CDCl₃) δ 7.38-7.33 (m, 1H), 7.24-7.20 (m, 2H), 7.04-7.00 (m, 1H), 6.81-6.78 (m, 2H), 6.52 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1H), 5.05 (br, 2H), 3.53 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 163.0 (d, *J*_{F-C} = 244.4 Hz), 146.9, 141.6, 139.7 (d, *J*_{F-C} = 7.3 Hz), 130.0 (d, *J*_{F-C} = 8.1 Hz), 124.5, 122.7, 122.6, 117.1 (d, *J*_{F-C} = 29.7 Hz), 114.7 (d, *J*_{F-C} = 21.1 Hz), 114.2 (d, *J*_{F-C} = 21.9 Hz), 114.2, 71.4 (d, *J*_{F-C} = 1.8 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ -112.93.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₃H₁₂ClFNO 252.0591; Found: 252.0587.

3-chloro-4-(pyridin-2-ylmethoxy)aniline (46)



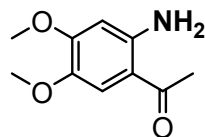
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 10:1) as eluant, white solid (81% yield, 37.9 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.58 (d, *J* = 8.8 Hz, 1H), 7.74 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.25-7.22 (m, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 2.8 Hz, 1H), 6.53 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1H), 5.20 (br, 2H), 3.27 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 157.3, 149.0, 146.8, 141.3, 136.9, 123.9, 122.6, 121.3, 117.2, 115.9, 114.3, 72.3.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₂H₁₂ClN₂O 235.0638; Found: 235.0633.

1-(2-amino-4,5-dimethoxyphenyl)ethan-1-one (47)



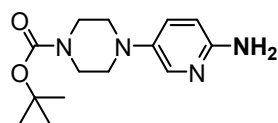
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 10:1) as eluant, white solid (79% yield, 30.8 mg)

¹H NMR (400 MHz, CDCl₃) δ 7.12 (s, 1H), 6.47-6.14 (m, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 2.54 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 198.4, 155.4, 147.5, 140.1, 114.1, 110.6, 99.3, 56.8, 55.8, 27.8.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₀H₁₄NO₃ 196.0973; Found: 196.0969.

tert-butyl 4-(6-aminopyridin-3-yl)piperazine-1-carboxylate (48)



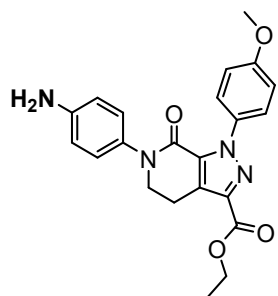
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 10:1) as eluant, white solid (73% yield, 40.6 mg)

¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 2.8 Hz, 1H), 7.19 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 6.51 (d, *J* = 8.8 Hz, 1H), 4.29 (s, 2H), 3.58 (t, *J* = 4.8 Hz, 4H), 2.97 (t, *J* = 4.4 Hz, 4H), 1.49 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 154.7, 153.3, 140.6, 137.2, 129.8, 109.3, 80.0, 51.0, 28.4.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₄H₂₃N₄O₂ 279.1821; Found: 279.1817.

Ethyl 6-(4-aminophenyl)-1-(4-methoxyphenyl)-7-oxo-4,5,6,7-tetrahydro-1H-pyrazolo[3,4-c]pyridine-3-carboxylate (49)



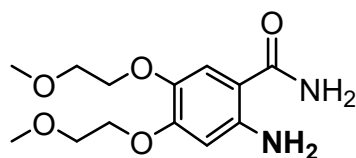
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 10:1) as eluant, white solid (61% yield, 49.6 mg)

¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 4.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 9.2 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 4.50 (q, *J* = 7.2 Hz, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 3.82 (s, 3H), 3.32-3.19 (m, 4H), 1.45 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 162.2, 159.8, 157.4, 144.7, 138.9, 133.3, 132.9, 132.6, 127.0, 126.7, 126.6, 115.5, 113.6, 61.2, 55.5, 51.4, 21.5, 14.4.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₃N₄O₄ 407.1719; Found: 407.1716.

2-amino-4,5-bis(2-methoxyethoxy)benzamide (50)



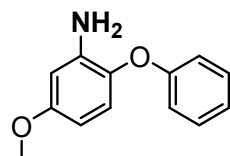
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 10:1) as eluant, white solid (75% yield, 42.6 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.05 (s, 1H), 6.40-6.02 (m, 3H), 5.28 (br, 2H), 4.05-4.01 (m, 4H), 3.72 (t, *J* = 5.2 Hz, 2H), 3.64 (t, *J* = 4.8 Hz, 2H), 3.38 (d, *J* = 7.2 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 171.5, 154.2, 146.8, 139.1, 117.3, 105.8, 101.6, 71.29, 70.7, 70.6, 67.8, 59.1, 58.9.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₃H₂₁N₂O₅ 285.1450; Found: 285.1461.

5-methoxy-2-phenoxyaniline (51)



Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 15:1) as eluant, white solid (75% yield, 32.3 mg).

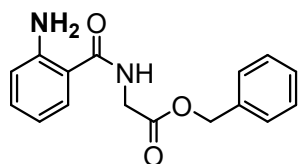
¹H NMR (400 MHz, CDCl₃) δ 7.31 (t, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.42 (d, *J* = 2.8 Hz, 1H), 6.31 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1H), 3.80 (s, 3H),

3.62 (br, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.3, 157.2, 139.8, 136.5, 129.7, 122.2, 121.9, 116.1, 103.7, 102.2, 55.5.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_{14}\text{NO}_2$ 216.1024; Found: 216.1020.

benzyl (2-aminobenzoyl)glycinate (52)



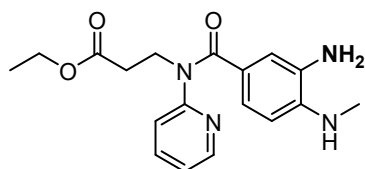
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (80% yield, 45.5 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.44-7.37 (m, 6H), 7.26-7.22 (m, 1H), 6.71-6.65 (m, 3H), 5.25-5.03 (m, 4H), 4.25 (d, J = 4.8 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 169.2, 148.6, 135.2, 132.7, 128.7, 128.6, 128.4, 127.5, 117.4, 116.8, 115.2, 67.3, 41.6.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_3$ 285.1239; Found: 285.1237.

ethyl 3-(3-amino-4-(methylamino)-*N*-(pyridin-2-yl)benzamido)propanoate (53)



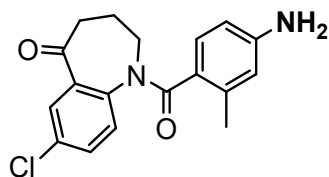
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (62% yield, 42.4 mg).

^1H NMR (400 MHz, CDCl_3) δ 8.43 (s, 1H), 7.42-7.36 (m, 1H), 7.03-6.98 (m, 1H), 6.86-6.82 (m, 1H), 6.76-6.70 (m, 2H), 6.35-6.28 (m, 1H), 4.41-4.35 (m, 2H), 4.10-4.03 (m, 2H), 3.46 (s, 3H), 2.81-2.73 (m, 5H), 1.23-1.17 (m, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 171.0, 156.8, 148.6, 141.6, 137.0, 132.5, 124.2, 123.4, 122.5, 120.5, 117.5, 108.3, 60.4, 44.5, 33.5, 30.5, 14.1.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{23}\text{N}_4\text{O}_3$ 343.1770; Found: 343.1773

1-(4-amino-2-methylbenzoyl)-7-chloro-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (54)



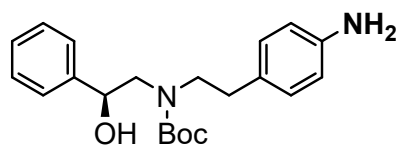
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 10:1) as eluant, white solid (77% yield, 50.5 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 2.4 Hz, 1H), 7.21 (d, J = 7.2 Hz, 1H), 6.77 (s, 1H), 6.64 (d, J = 6.0 Hz, 1H), 6.45 (d, J = 1.6 Hz, 1H), 6.24 (d, J = 7.6, 1H), 3.99-3.63 (m, 4H), 2.89 (t, J = 6.8 Hz, 2H), 2.34 (s, 3H), 2.14 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 200.5, 171.2, 147.4, 141.8, 138.0, 135.1, 132.6, 129.9, 129.2, 129.0, 125.1, 116.8, 111.7, 47.4, 40.1, 23.1, 20.0.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{18}\text{ClN}_2\text{O}_2$ 329.1057; Found: 329.1054.

***tert*-butyl (*S*)-(4-aminophenethyl)(2-hydroxy-2-phenylethyl)carbamate (55)**



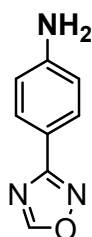
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 3:1) as eluant, white solid (85% yield, 60.6 mg)

¹H NMR (400 MHz, CDCl₃) δ 7.37-7.36 (m, 5H), 6.92 (d, *J* = 6.8 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 2H), 4.89 (d, *J* = 6.4 Hz, 1H), 3.54-3.21 (m, 7H), 2.70-2.56 (m, 2H), 1.49 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 158.1, 144.7, 142.5, 129.6, 128.9, 128.4, 127.5, 125.9, 115.4, 80.5, 74.4, 56.7, 51.7, 34.1, 28.4.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₉N₂O₃ 357.2178; Found: 357.2165.

4-(1,2,4-oxadiazol-3-yl)aniline (56)



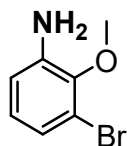
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 10:1) as eluant, white solid (67% yield, 21.6 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.69 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 4.02 (br, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 167.6, 164.2, 149.4, 129.1, 116.0, 114.8.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₈H₈N₃O 162.0667; Found: 162.0662.

3-bromo-2-methoxyaniline (57)



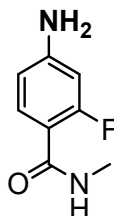
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 15:1) as eluant, white solid (79% yield, 31.8 mg)

¹H NMR (400 MHz, CDCl₃) δ 6.93 (d, *J* = 8.0 Hz, 1H), 6.80 (t, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 3.85 (s, 3H), 3.73 (br, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 144.2, 141.3, 125.8, 122.5, 117.1, 115.1, 59.6.

HRMS (ESI-TOF) *m/z*: [M - H]⁺ Calcd for C₇H₇BrNO 199.9703; Found: 199.9708.

4-amino-2-fluoro-*N*-methylbenzamide (58)



Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 5:1) as eluant, white solid (66% yield, 22.2 mg).

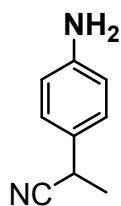
¹H NMR (400 MHz, CDCl₃) δ 7.91 (t, *J* = 8.8 Hz, 1H), 6.63 (s, 1H), 6.49 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 6.33 (dd, *J* = 14.4 Hz, *J* = 2.0 Hz, 1H), 4.18 (br, 2H), 3.00 (dd, *J* = 4.8 Hz, *J* = 0.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 164.4 (d, *J*_{F-C} = 3.7 Hz), 162.2 (d, *J*_{F-C} = 243.1 Hz), 151.4 (d, *J*_{F-C} = 12.7 Hz), 133.3 (d, *J*_{F-C} = 4.3 Hz), 110.8 (d, *J*_{F-C} = 1.8 Hz), 110.2 (d, *J*_{F-C} = 1.7 Hz), 100.8 (d, *J*_{F-C} = 28.5 Hz), 26.6

¹⁹F NMR (376 MHz, CDCl₃) δ -112.86.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₈H₁₀FN₂O 169.0778; Found: 169.0771.

2-(4-aminophenyl)propanenitrile (59)



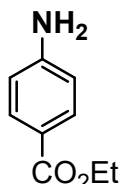
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 10:1) as eluant, white solid (76% yield, 22.2 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.14 (d, *J* = 8.4 Hz, 2H), 6.71-6.68 (m, 2H), 3.84-3.78 (m, 2H), 1.61 (d, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 146.2, 127.7, 126.8, 122.2, 115.4, 30.5, 21.5.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₉H₁₁N₂ 147.0922; Found: 147.0917.

ethyl 4-aminobenzoate (60)



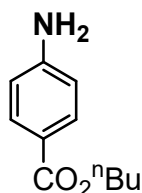
Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 10:1) as eluant, white solid (85% yield, 28.1 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 4.36 (br, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 166.8, 150.8, 131.6, 120.0, 113.8, 60.3, 14.4.

HRMS (ESI) m/z: [M + H]⁺ Calcd for C₉H₁₂NO₂ 166.0868; Found: 166.0863.

butyl 4-aminobenzoate (61)



Purified by column chromatography using the mixture of petroleum ether and ethyl acetate (PE/EA = 10:1) as eluant, white solid (81% yield, 31.3 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 4.28 (t, *J* = 6.8 Hz, 2H), 4.00 (br, 2H), 1.78-1.71 (m, 2H), 1.53-1.44 (m, 2H), 0.99 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 166.8, 150.5, 131.6, 120.3, 113.9, 64.3, 30.9, 19.3, 13.8.

HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₁H₁₆NO₂ 194.1182; Found: 194.1177.

Reference

- [1] X. Li, Y. Tan, Z. Liu, J. Su, Y. Xiao, B. Qiao, Y. Ding, *J. Catal.*, 2022, **416**, 332-343.
- [2] D. E. Wise, E. S. Gogarnoiu, A. D. Duke, J. M. Paolillo, T. L. Vacala, W. A. Hussain and M. Parasram, *J. Am. Chem. Soc.*, 2022, **144**, 15437-15442.
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VI. Copies of NMR Spectra

