

Supporting Information

A Versatile CO-assisted Direct Reductive Amination of 5-Hydroxymethylfurfural Catalyzed by Supported Gold

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1. Chemicals and materials

5-Hydroxymethylfurfural (HMF 99 %) was supplied by Aladdin. Titanium tetrachloride (TiCl_4) was supplied by Aladdin. Metal oxide CeO_2 and TiO_2 -P25 were supplied from the Evonik. Anatase TiO_2 was supplied from Hao tian nano technology (Shanghai) co., LTD. Palladium chloride (PdCl_2), ruthenium chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), rhodium chloride hydrate ($\text{RhCl}_3 \cdot \text{H}_2\text{O}$), chloroiridic acid hexahydrate ($\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$) and chloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), were supplied by Aldrich and used without further purification. 1 wt% $\text{Au}/\text{Al}_2\text{O}_3$ (catalogue number 79-0160) was supplied by Mintek. Au^0 colloid was supplied by Dao King technology (Beijing) co., LTD.

2. Catalyst preparation.

2.1 Preparation of rutile TiO_2

Rutile TiO_2 (TiO_2 -R) was prepared according to previous literature.^[S1] Under stirring, TiCl_4 was added dropwise into ethanol. Then the formed transparent yellow sol was slowly added into deionized water under vigorously stirring. The molar ratio of ethanol, TiCl_4 , and deionized water was 10:1:140. Subsequently, the solution was further stirred for 30 min. Finally, the solution was maintained in an oven at 50 °C for 24 h. After that, the formed white precipitate was separated by centrifugation, washed with deionized water for several times and dried at 50 °C. After that the sample was calcined at 400 °C for 3 h with the heating rate of 2 °C·min⁻¹. The BET surface area of the rutile support was 65 m²·g⁻¹.

2.2 Preparation of Au/TiO_2 catalysts

Au/TiO_2 -P25 was prepared by a modified deposition-precipitation (DP) method according to our previous work.^[S2] Briefly, 2 mL aqueous solutions of HAuCl_4 (10 mg/mL) was added into 100mL H_2O . The pH was adjusted to 7 by dropwise addition of NaOH (0.2 M), and then 1.0 g TiO_2 -P25 (Evonik P25, specific surface area: 50 m²·g⁻¹ nonporous, 70% anatase and 30% rutile) was dispersed in the solution, the pH of the solution was adjusted to 7. The mixture was stirred at 80 °C for 2 h, after which the

suspension was cooled to RT. Extensive washing with deionized water was then followed until it was free of Cl⁻ ions. The sample was dried under vacuum at room temperature for 12 h and then calcined in air at 350 °C for 4 h. By using anatase TiO₂ (BET surface area: 112 m²·g⁻¹) and rutile TiO₂ as the support, similar Au/TiO₂-A, Au/TiO₂-R were prepared by the same method as Au/TiO₂-P25.

2.3 Preparation of ZrO₂

ZrO₂ powders were prepared by a conventional precipitation method following the reported procedure.^[S3] Briefly, 12.9 g ZrOCl₂·8H₂O was dissolved in 200 mL deionized water at 25 °C, the pH was adjusted to 9.0 by dropwise addition of 2.5 M NH₃·H₂O. After 6 h stirring at 25 °C, the resultant hydro gel was washed with deionized water until free of chloride ions. The precipitate was then dried at 110 °C overnight and calcined at 400 °C for 2 h in air. The BET surface area of the resultant material was 115 m²·g⁻¹.

2.4 Preparation of Au/ZrO₂ catalyst

A modified deposition-precipitation (DP) method was employed to prepared the Au/ZrO₂ catalysts as follows: Initially, by mixing ZrO₂ powders (1 g) with 100 mL aqueous solutions of HAuCl₄ (0.2 mg/mL), the pH was adjusted to 9.0 by dropwise addition of 0.25 M NH₃·H₂O. After 6 h continuous stirring at 25 °C the catalyst was washed five times with deionized water and separated by filtration. The samples were dried at 110 °C in air for 1 h, followed by reduction with a stream of 5 vol% H₂/Ar at 350 °C for 2 h. Safety note: The mixing of gold chloride and ammonia solutions may lead to the formation of explosive gold compounds (fulminating gold).^[S4] Based on our experimental observations, mixing of ammonia solution (not concentrated, 0.25 M) with gold chloride solution with very low concentration (0.2 mg/mL) at RT does not result in explosive and friction-sensitive gold compounds.

2.5 Preparation of Au/CeO₂ catalyst

The Au/CeO₂ sample was prepared according to a routine DP procedure described previously.^[S2] 2 mL aqueous solutions of HAuCl₄ (10 mg/mL) was heated to 75 °C under vigorous stirring. The pH was adjusted to 8 by dropwise addition of NaOH (0.2 M), and then suitable amount of CeO₂ (Evonik, Ad Nano 90, specific surface area: 90 m²·g⁻¹) was dispersed in the solution. The mixture was aged for 2 h at 80 °C, after which the suspension was cooled to room temperature. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were dried under vacuum at room temperature for 12 h, and then calcined in air at 400 °C for 4 h.

2.6 Preparation of Au/SiO₂ catalyst

1.0 wt% Au/SiO₂ catalyst was prepared by the procedure as described elsewhere.^[S3] Typically, 1.0 g of SiO₂ (Degussa, Aerosil 380, specific surface area: 380 m²·g⁻¹) was introduced into the 100 mL aqueous solutions of HAuCl₄ (0.2 mg/mL) in order to prepare catalysts with 1.0 wt% gold content. After stirring at 75 °C for 1 h the solution was cooled down to room temperature and 0.2 M NH₃·H₂O was added to the solution under stirring. After 6 h stirring at room temperature the catalyst was washed five times with deionized water and separated by centrifugation. The samples were dried at 110 °C in a forced air oven for 1 h and reduced in flowing 5 vol% H₂/Ar at 300 °C for 2 h.

2.7 Preparation of Pd/TiO₂-R, Pt/TiO₂-R, Ru/TiO₂-R, Rh/TiO₂-R and Ir/TiO₂-R catalysts

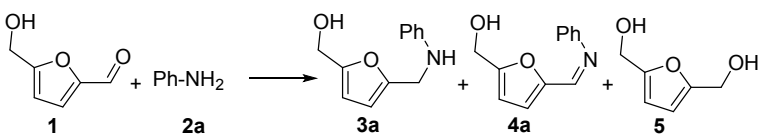
Pd/TiO₂-R, Pt/TiO₂-R, Ru/TiO₂-R, Rh/TiO₂-R and Ir/TiO₂-R catalysts were prepared by incipient-wetness impregnation (IWI) of the support (rutile TiO₂), with aqueous solution of PdCl₂, H₂PtCl₆·6H₂O, RuCl₃·xH₂O, RhCl₃·H₂O and H₂IrCl₆·6H₂O precursors of appropriate concentrations (typically 1.0 mL·g⁻¹ support). After a perfect mixing of the corresponding slurries, the resulting mixture was vigorously stirred at 80 °C for 4 h. Then samples were dried under vacuum at room temperature for 12 h and then reduced in 5 vol% H₂/Ar (80 mL·min⁻¹) at 400 °C for 2 h.

3. Leaching and reusability test

For the leaching test, the Au/TiO₂-R was removed from the reaction system after HMF reacted with aniline under CO for 1 h. Subsequently, the reaction was continued for another 1.5 h. The products can be sampled at 90 min, 120 min, and 150 min during the reaction, respectively. For the reusability test, the following procedure was employed to minimize possible experiment errors arising from the possible loss of catalyst during the RA of HMF. The same amount of catalyst (68 mg of 0.72% Au/TiO₂-R, for example) was added into seven different identical reactor for RA of HMF (0.5 mmol HMF, 60 °C). After the reaction run for 2.5 h, the spent Au/TiO₂-R was recovered by filtration and washed thoroughly with acetone, then dried under vacuum at 60 °C for 12 h before the next cycle. Typically, they were combined, and the same procedure as the ones described above was performed in six reactor, with each containing 68 mg of the recovered Au/TiO₂-R.

4. Supplementary data

Table S1. Screening of solvents. ^{a,b}



The reaction scheme shows the reaction of HMF (1) with aniline (2a) to form three products: 3a (N-phenyl-2-(hydroxymethyl)furan-3-carbaldehyde), 4a (N-phenyl-2-(hydroxymethyl)furan-3-carboxamide), and 5 (2-(hydroxymethyl)furan-3,5-diol).

Entry	Solvent	Conversion [%]	Yield [%]		
			3a	4a	5
1	Hexane/H ₂ O (1:1)	>99	81	19	0
2	Toluene/H ₂ O (1:1)	>99	90	10	0
3	THF/H ₂ O (1:1)	>99	94	6	0
4	Ethanol/H ₂ O (1:1)	>99	96	4	0
5	Acetonitrile/H ₂ O (1:1)	>99	97	3	0
6	Methanol/H ₂ O (1:1)	>99	>99	0	0
7	Methanol	95	14	81	0
8 ^c	Methanol	98	0	98	0
9	Methanol/H ₂ O (2:1)	96	88	12	0
10	Methanol/H ₂ O (1:2)	91	84	16	0
11	H ₂ O	89	94	6	0

^a Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), Au/TiO₂-R (Au 0.5 mol%), Solvent (3 mL), CO (20 bar), 60 °C, 2.5 h. ^b GC yields using anisole as internal standard. ^c In the presence of molecular sieves (4 Å).

Table S2. Control Experiments. ^{a,b}

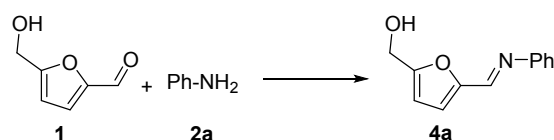
Entry	Au/TiO ₂ -R	CO	H ₂ O	Yield of 3a [%]
1 ^c	☒	☒	☒	0
2 ^d	☒	☒	☒	0
3 ^e	☒	☒	☒	0

^a Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), Au/TiO₂-R (Au 0.5 mol%), MeOH-H₂O (1:1 v/v, 3 mL), CO (20 bar), 60 °C, 2.5 h. ^b GC yields using anisole as internal standard. ^c Without Au/TiO₂-R. ^d N₂ (20 bar), no CO. ^e 3 mL methanol as solvent in the presence of molecular sieves (4 Å).

Table S3. Screening of Metal. ^{a,b}

Entry	Catalysts	Conversion [%]	Yield [%]		
			3a	4a	5
1	Pd/TiO ₂ -R	82	1	81	0
2	Pt/TiO ₂ -R	84	1	83	0
3	Ir/TiO ₂ -R	84	8	76	0
4	Ru/TiO ₂ -R	80	1	79	0
5	Rh/TiO ₂ -R	82	1	81	0

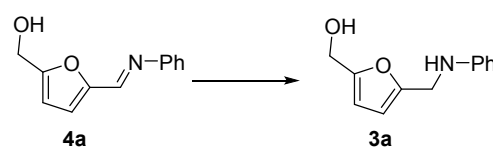
^a Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), M/TiO₂-R (metal 0.5 mol%), MeOH-H₂O (1:1 v/v, 3 mL), CO (20 bar), 60 °C, 2.5 h. ^b GC yields using anisole as internal standard.

Table S4. Direct imine condensation of 5-HMF with aniline. ^a

Entry	Catalysts	r (mmol·g ⁻¹ ·h ⁻¹) ^b
1	Au/TiO ₂ -R	6.504
2	TiO ₂ -R	6.423
3	TiO ₂ -A	6.423
4	TiO ₂ -P25	6.260
5	ZrO ₂	4.715
6	CeO ₂	5.935
7	Al ₂ O ₃	5.285
8	SiO ₂	5.041

^a Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), Au (0.5 mol%), MeOH-H₂O (1:1 v/v, 3 mL), N₂ (20 bar), 60 °C, 15 min. ^b Initial reaction rates (r) calculated for various catalyst based on GC yields.

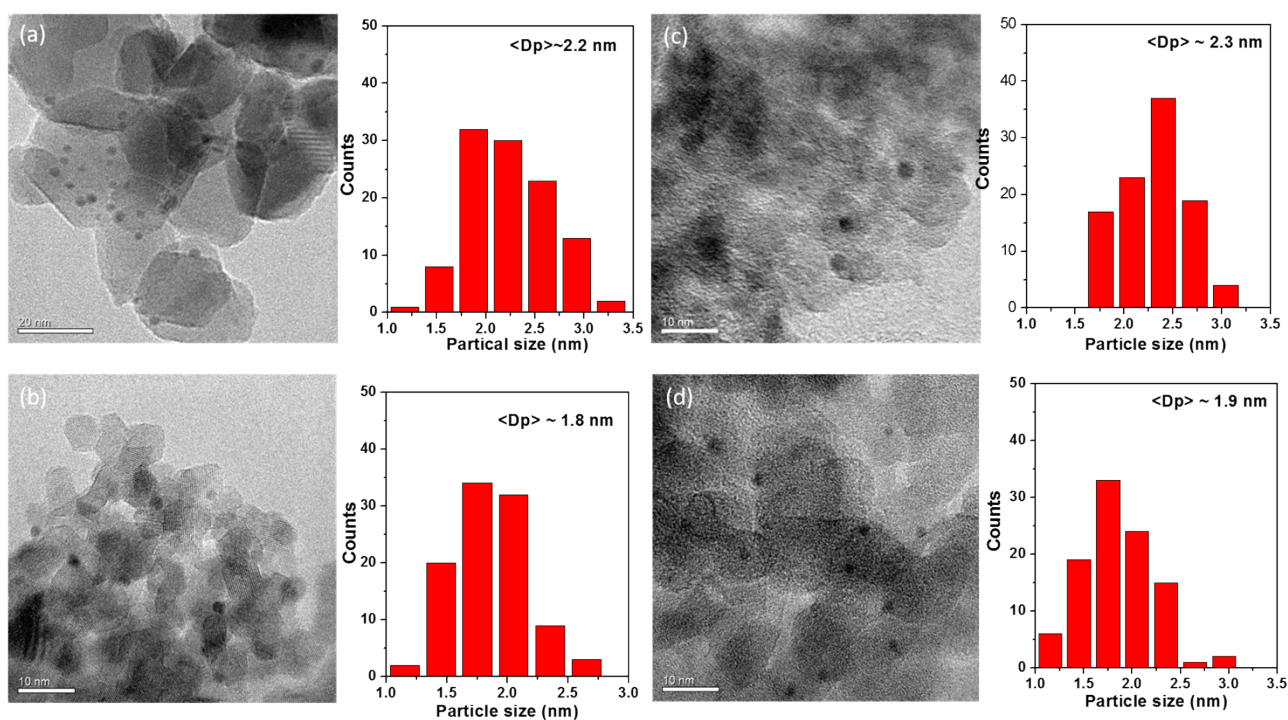
Table S5. Reduction of imine to the corresponding aminoalkylfuran with CO over Au catalysts ^a



4a $\xrightarrow{\text{CO}}$ **3a**

Entry	Catalysts	r (mmol·g ⁻¹ ·h ⁻¹) ^b
1	Au/TiO ₂ -R	0.154
2	TiO ₂ -R	0
3	Au/TiO ₂ -A	0.073
4	Au/TiO ₂ -P25	0.137
5	Au/ZrO ₂	0.046
6	Au/CeO ₂	0.085
7	Au/Al ₂ O ₃	0.005
8	Au/SiO ₂	0.002

^a Reaction conditions: **4a** (0.5 mmol), Au (0.5 mol%), MeOH-H₂O (1:1 v/v, 3 mL), CO (20 bar), 60 °C, 15 min. ^b Initial reaction rates (r) calculated for various catalyst based on GC yields.

**Figure S1.** TEM images and particle size distributions of various supported Au catalysts. (a) Au/TiO₂-P25, (b) Au/TiO₂-A, (c) Au/Al₂O₃, (d) Au/SiO₂.

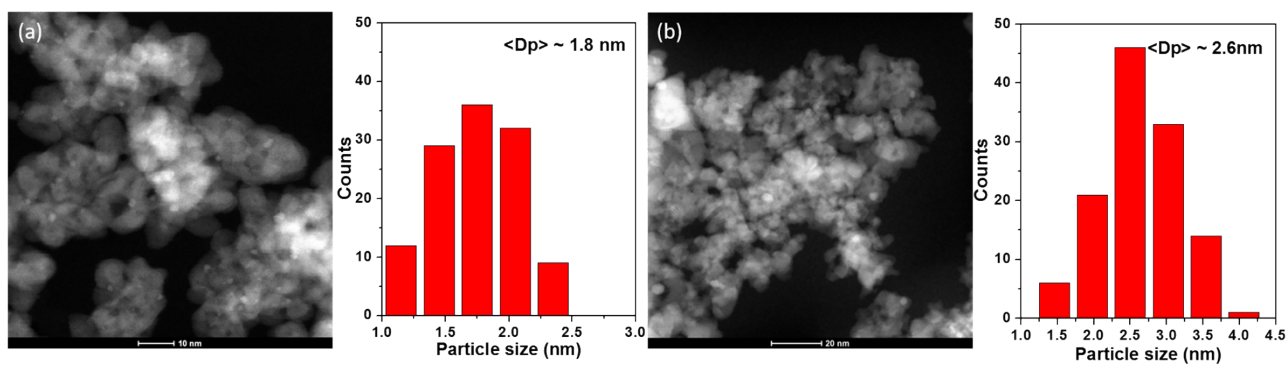


Figure S2. HAADF-STEM images and particle size of (a) Au/ZrO₂, (b) Au/CeO₂.

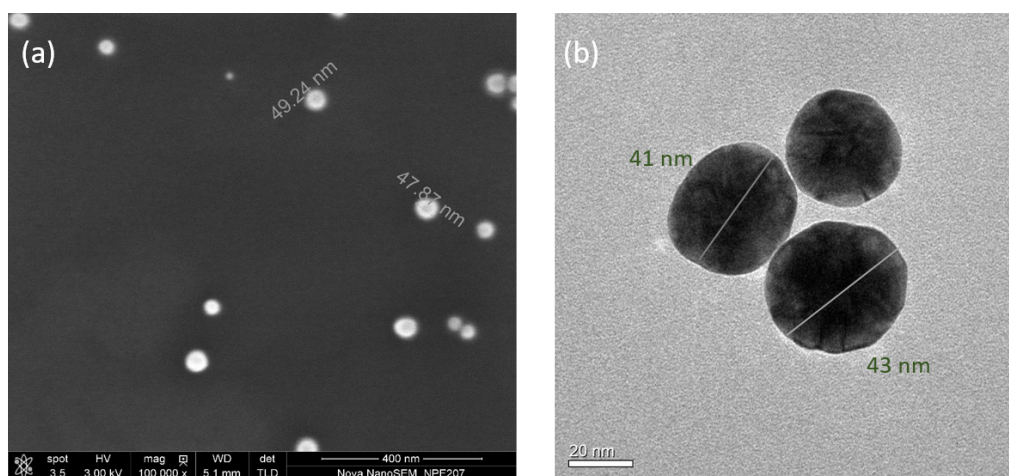


Figure S3. (a) FESEM image and (b) TEM image of Au⁰ colloid.

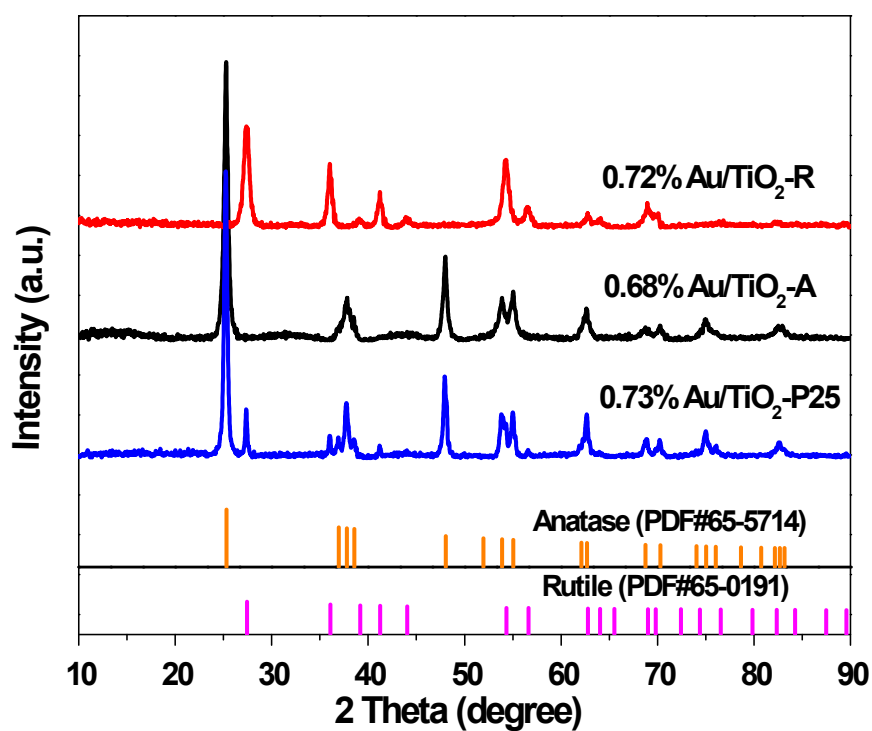


Figure S4. XRD of different Au/TiO₂ catalysts.

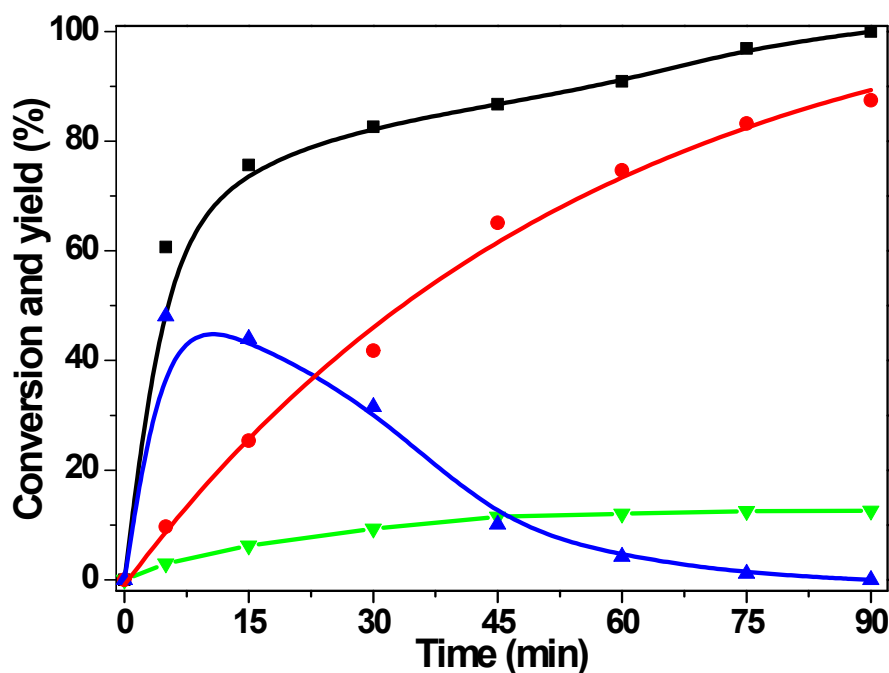


Figure S5. Reaction profile for aminoalkylfuran formation from HMF and aniline under H_2 atmosphere. (■) conversion of **1**, (●) yield of **3a**, (▲) yield of **4a**, (▼) yield of **5**. Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), MeOH- H_2O (1:1 v/v, 3 mL), Au/ TiO_2 -R (Au: 0.5 mol%), H_2 (20 bar), 60 °C.

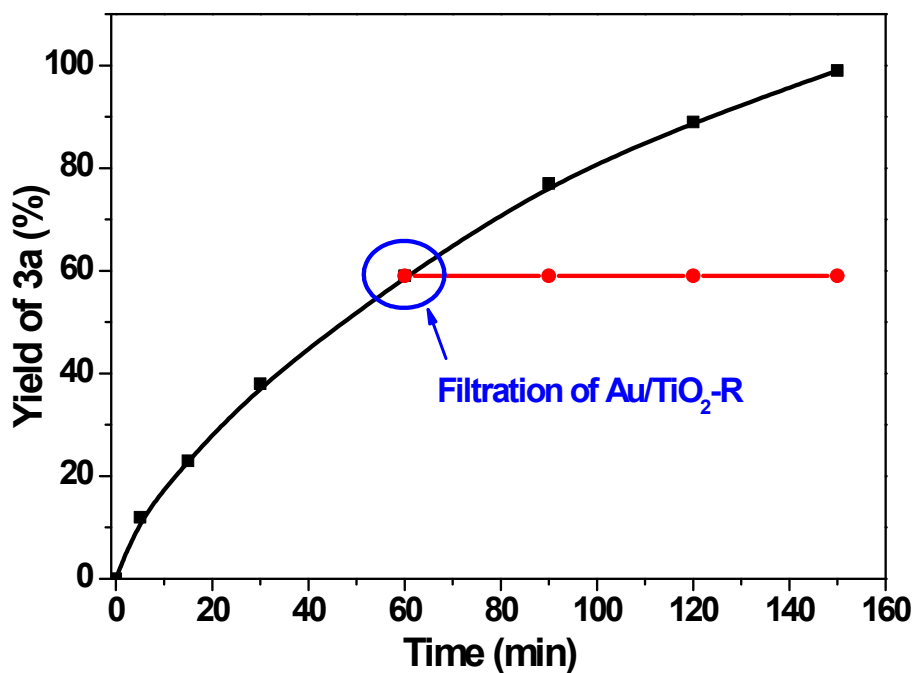


Figure S6. **3a** yield as a function of time in the leaching test. Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), MeOH- H_2O (1:1 v/v, 3 mL), Au/ TiO_2 -R (Au: 0.5 mol%), H_2 (20 bar), 60 °C. The black profile denotes the normal reaction in HMF conversion, while the red profile represents the leaching test in which the catalyst has been removed from the system. (The leached Au of the catalyst-removed liquid

phase of the reacted mixture was undetectable by ICP-AES.)

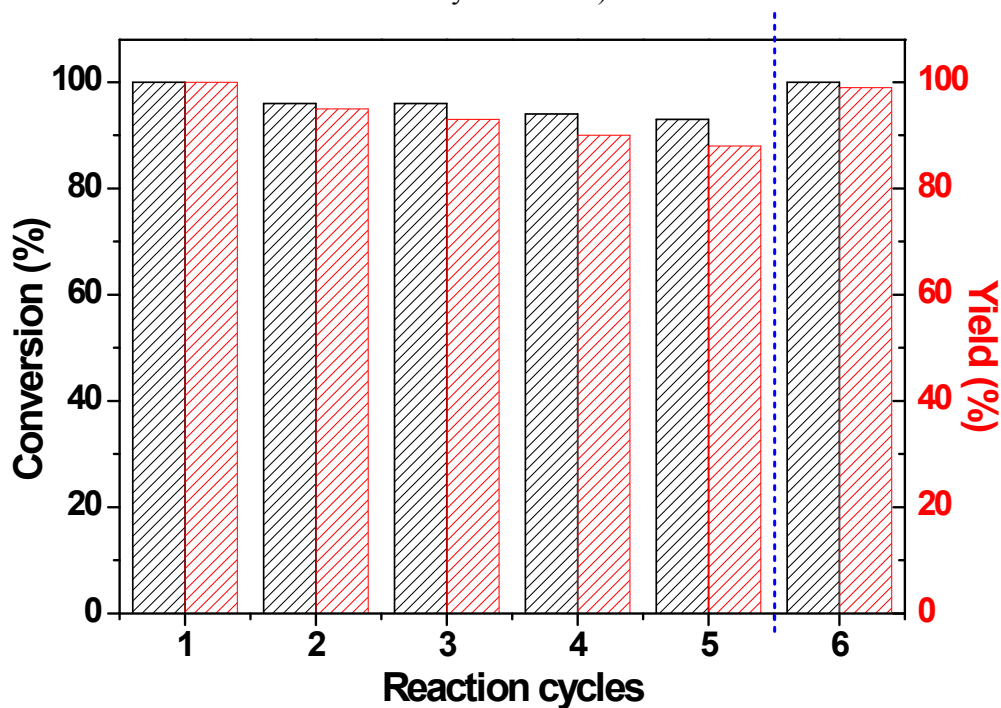
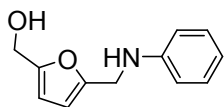


Figure S7. Reuse of Au/TiO₂-R catalyst in the direct RA of HMF with Aniline. Reaction conditions : **1** (0.5 mmol), **2a** (0.5 mmol), MeOH-H₂O (1:1 v/v, 3 mL), Au/TiO₂-R (Au: 0.5 mol%), H₂ (20 bar), 60 °C, 2.5 h. Note: Time for 6th run is 3 h.

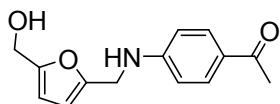


Scheme S1. Tentative mechanism for CO-assisted direct RA of HMF catalyzed by supported gold.

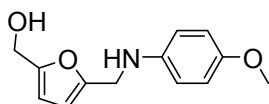
4. ¹H-NMR and ¹³C-NMR spectra of products



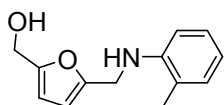
(Table 2, 3a).^[S5] ¹H-NMR (CDCl₃, 400 MHz): δ 7.17 (dd, *J* = 8.4 Hz, 7.6 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.18 (d, *J* = 2.8 Hz, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 4.51 (s, 2H), 4.26 (s, 2H), 3.08 (br s, 1H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.4, 152.7, 147.5, 129.2, 118.1, 113.2, 108.5, 107.7, 57.3, 41.4.



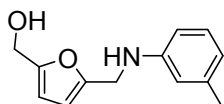
(Table 2, 3b).^[S5] ¹H-NMR (d₆-DMSO, 400 MHz): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.05 (t, *J* = 5.6 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.24 (d, *J* = 3.2 Hz, 1H), 6.19 (d, *J* = 3.2 Hz, 1H), 5.17 (t, *J* = 5.6 Hz, 1H), 4.30-4.35 (m, 4H), 2.39 (s, 3H); ¹³C-NMR (d₆-DMSO, 100 MHz): δ 195.5, 155.2, 152.8, 151.9, 130.8, 125.7, 111.5, 108.3, 108.0, 56.1, 26.3, 0.5.



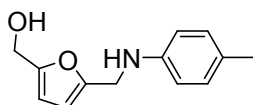
(Table 2, 3c).^[S5] ¹H-NMR (CDCl₃, 400 MHz): δ 6.76 (d, *J* = 9.2 Hz, 2H), 6.62 (d, *J* = 9.2 Hz, 2H), 6.17 (d, *J* = 3.2 Hz, 1H), 6.13 (d, *J* = 2.8 Hz, 1H), 4.51 (s, 2H), 4.21 (s, 2H), 3.72 (s, 3H), 3.03 (br s, 2H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.4, 152.9, 152.5, 141.6, 114.7, 114.6, 108.4, 107.7, 57.3, 55.6, 42.4.



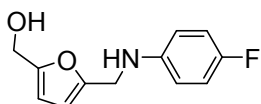
(Table 2, 3d).^[S5] ¹H-NMR (CDCl₃, 400 MHz): δ 7.14-7.06 (m, 2H), 6.71-6.67 (m, 2H), 6.22 (d, *J* = 2.8 Hz, 1H), 6.19 (d, *J* = 2.8 Hz, 1H), 4.57 (s, 2H), 4.35 (s, 2H), 2.16 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.4, 152.9, 145.5, 130.1, 127.0, 122.4, 117.7, 110.2, 108.7, 107.8, 57.5, 41.5, 17.5.



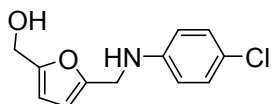
(Table 2, 3e).^[S5] ¹H-NMR (CDCl₃, 400 MHz): δ 7.07 (t, *J* = 8.0 Hz, 1H), 6.58-6.47 (m, 3H), 6.20 (d, *J* = 2.8 Hz, 1H), 6.16 (d, *J* = 3.2 Hz, 1H), 4.55 (s, 2H), 4.28 (s, 2H), 2.67 (br s, 1H), 2.27 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.3, 152.9, 147.5, 139.0, 129.1, 119.0, 114.0, 110.3, 108.6, 107.7, 57.4, 41.5, 21.6.



(Table 2, 3f).^[S5] ¹H-NMR (CDCl₃, 400 MHz): δ 6.76 (d, *J* = 9.2 Hz, 2H), 6.62 (d, *J* = 9.2 Hz, 2H), 6.17 (d, *J* = 3.2 Hz, 1H), 6.13 (d, *J* = 2.8 Hz, 1H), 4.51 (s, 2H), 4.21 (s, 2H), 3.72 (s, 3H), 3.03 (br s, 2H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.4, 152.9, 152.5, 141.6, 114.7, 114.6, 108.4, 107.7, 57.3, 55.6, 42.4.

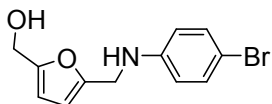


(Table 2, 3g).^[S5] ¹H-NMR (CDCl₃, 400 MHz): δ 6.90-6.85 (m, 2H), 6.60-6.57 (m, 2H), 6.18 (d, *J* = 2.8 Hz, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 4.52 (s, 2H), 4.22 (s, 2H), 3.12 (br s, 2H); ¹³C-NMR (CDCl₃, 100 MHz): δ 157.3, 155.0, 153.4, 152.5, 143.7, 115.7, 115.5, 114.2, 114.1, 108.6, 107.9, 57.3, 42.1.

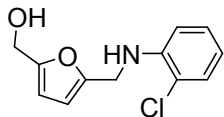


(Table 2, 3h).^[S5] ¹H-NMR (CDCl₃, 400 MHz): δ 7.14-7.10 (m, 2H), 6.61-6.57 (m, 2H), 6.21 (d, *J* = 2.8 Hz, 1H), 6.17 (d, *J* = 3.2 Hz, 1H), 4.57 (s, 2H), 4.27 (s, 2H), 2.59 (br s, 2H); ¹³C-NMR

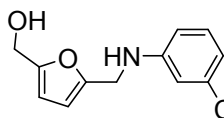
(CDCl₃, 100 MHz): δ 153.5, 152.3, 145.9, 129.0, 122.8, 114.3, 108.7, 108.0, 57.7, 41.6.



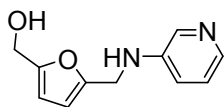
(Table 2, 3i). ^[S5] ¹H-NMR (CDCl₃, 400 MHz): δ 7.27-7.25 (m, 2H), 6.58-6.56 (m, 2H), 6.21 (d, *J* = 2.8 Hz, 1H), 6.17 (d, *J* = 3.2 Hz, 1H), 4.57 (s, 2H), 4.27 (s, 2H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.6, 151.9, 146.0, 132.0, 115.1, 110.2, 108.7, 108.2, 57.4, 41.7.



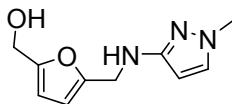
(Table 2, 3j). ¹H-NMR (CDCl₃, 400 MHz): ¹H-NMR (CDCl₃, 400 MHz): δ 7.28-7.25 (m, 1H), 7.15-7.11 (m, 1H), 6.74-6.65 (m, 2H), 6.21 (d, *J* = 3.2 Hz, 1H), 6.20 (d, *J* = 3.2 Hz, 1H), 4.59 (s, 2H), 4.37 (s, 2H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.6, 152.2, 143.3, 129.2, 127.7, 119.5, 117.9, 111.6, 108.7, 108.0, 57.5, 41.2; HRMS (ESI) calculated for C₁₂H₁₂ClNO₂ [M+H]⁺ 238.0629, observed 238.0629.



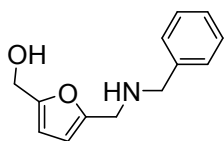
(Table 2, 3k). ¹H-NMR (CDCl₃, 400 MHz): δ 7.08 (t, *J* = 8.0 Hz, 1H), 6.72-6.65 (m, 2H), 6.55-6.53 (m, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 6.19 (d, *J* = 3.2 Hz, 1H), 4.58 (s, 2H), 4.29 (s, 2H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.6, 152.0, 148.4, 135.0, 130.2, 118.1, 113.0, 111.6, 108.7, 108.2, 57.5, 41.4; HRMS (ESI) calculated for C₁₂H₁₂ClNO₂ [M+H]⁺ 238.0629, observed 238.0613.



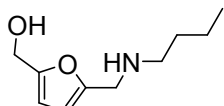
(Table 2, 3l). ¹H-NMR (d₆-DMSO, 400 MHz): δ 8.03 (d, *J* = 2.4 Hz, 1H), 7.78 (d, *J* = 4.4 Hz, 1H), 7.08-6.97 (m, 2H), 6.37-6.19 (m, 3H), 5.20 (s, 1H), 4.35 (d, *J* = 4.0 Hz, 2H), 4.25 (d, *J* = 6.0 Hz, 2H); ¹³C-NMR (d₆-DMSO, 100 MHz): δ 155.1, 152.3, 144.8, 137.6, 135.9, 124.0, 118.2, 108.2, 108.0, 56.1; HRMS (ESI) calculated for C₁₁H₁₂N₂O₂ [M+H]⁺ 205.0972, observed 205.0962.



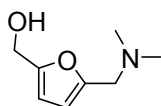
(Table 2, 3m). ¹H-NMR (CDCl₃, 400 MHz): δ 7.09 (d, *J* = 2.0 Hz, 1H), 6.19 (d, *J* = 3.2 Hz, 1H), 6.15 (d, *J* = 2.8 Hz, 1H), 5.55 (d, *J* = 2.0 Hz, 1H), 4.55 (s, 2H), 4.27 (s, 2H), 3.70 (s, 3H), 3.29 (br s, 2H); ¹³C-NMR (CDCl₃, 100 MHz): δ 156.5, 153.5, 153.2, 131.2, 108.4, 107.5, 91.2, 57.2, 42.4, 38.4; HRMS (ESI) calculated for C₁₀H₁₃N₃O₂ [M+H]⁺ 208.1081, observed 208.1079.



(Table 2, 3n).^[S7] ¹H-NMR (CDCl₃, 400 MHz): δ 7.34-7.23 (m, 5H), 6.17 (d, *J* = 2.8 Hz, 1H), 6.11 (d, *J* = 2.8 Hz, 1H), 4.51 (s, 2H), 3.76 (s, 2H), 3.74 (s, 2H), 2.66 (s, 2H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.7, 153.1, 139.3, 128.4, 128.3, 127.1, 108.1, 108.1, 57.1, 52.6, 45.2.

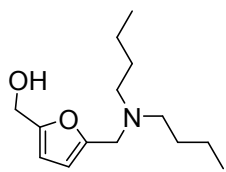


(Table 2, 3o).^[S7] ¹H-NMR (CDCl₃, 400 MHz): δ 6.19 (d, *J* = 2.8 Hz, 1H), 6.13 (d, *J* = 3.2 Hz, 1H), 4.55 (s, 2H), 3.76 (s, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.31 (s, 2H), 1.53-1.46 (m, 2H), 1.38-1.29 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.6, 153.4, 108.2, 107.9, 57.3, 48.7, 46.1, 31.7, 20.4, 13.9.



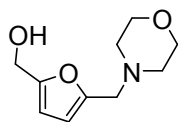
(Table 3, 3p).^[S8] ¹H-NMR (CDCl₃, 400 MHz): δ 6.22 (d, *J* = 3.2 Hz, 1H), 6.16 (d, *J* = 3.2 Hz,

1H), 4.58 (s, 2H), 3.47 (s, 2H), 2.278 (s, 6H), 2.24 (s, 1H); ¹³C-NMR (CDCl₃, 100 MHz): δ 154.0, 151.8, 109.5, 108.2, 57.5, 55.8, 44.8.



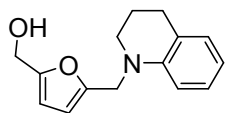
(Table 3, 3q). ^[S5] ¹H-NMR (CDCl₃, 400 MHz): δ 6.20 (d, *J* = 3.2 Hz, 1H), 6.11 (d, *J* =

2.8 Hz, 1H), 4.56 (s, 2H), 3.62 (s, 2H), 2.43 (t, *J* = 7.6 Hz, 4H), 2.35 (br s, 1H), 1.50-1.42 (m, 4H), 1.34-1.24 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 6H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.5, 152.7, 109.1, 108.2, 57.5, 53.5, 50.2, 28.9, 20.6, 14.0.



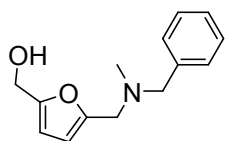
(Table 3, 3r). ^[S5] ¹H-NMR (CDCl₃, 400 MHz): δ 6.21 (d, *J* = 3.2 Hz, 1H), 6.16 (d, *J* = 2.8

Hz, 1H), 4.56 (s, 2H), 3.71 (t, *J* = 4.8 Hz, 4H), 3.50 (s, 2H), 3.05 (br s, 1H), 2.47 (t, *J* = 4.4 Hz, 4H); ¹³C-NMR (CDCl₃, 100 MHz): δ 154.3, 150.6, 110.0, 108.0, 66.6, 57.1, 55.2, 53.1.



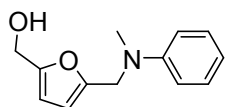
(Table 3, 3s). ¹H-NMR (CDCl₃, 400 MHz): δ 7.04-7.00 (m, 1H), 6.95 (d, *J* = 7.2 Hz,

1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.61-6.57 (m, 1H), 6.17 (d, *J* = 3.2 Hz, 1H), 6.08 (d, *J* = 3.2 Hz, 1H), 4.53 (s, 2H), 4.39 (s, 2H), 3.35 (t, *J* = 6.0 Hz, 2H), 2.76 (t, *J* = 6.4 Hz, 2H), 1.99-1.93 (m, 2H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.2, 152.4, 144.9, 129.1, 127.0, 122.8, 116.4, 111.3, 108.6, 107.8, 57.5, 49.6, 48.6, 28.0, 22.2; HRMS (ESI) calculated for C₁₅H₁₇NO₂ [M+H]⁺ 244.1332, observed 244.1330.



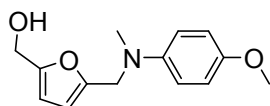
(Table 3, 3t). ^[S5] ¹H-NMR (CDCl₃, 400 MHz): δ 7.33-7.24 (m, 5H), 6.21 (d, *J* = 3.2 Hz,

1H), 6.16 (d, *J* = 3.2 Hz, 1H), 4.56 (s, 2H), 3.55 (s, 2H), 3.54 (s, 2H), 2.23 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.9, 151.9, 138.0, 129.2, 128.2, 127.1, 109.5, 108.1, 61.1, 57.3, 53.2, 41.8.



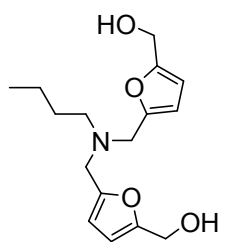
(Table 3, 3u). ^[S5] ¹H-NMR (CDCl₃, 400 MHz): δ 7.17 (dd, *J* = 8.8 Hz, 7.2 Hz, 2H), 6.81

(d, *J* = 8.0 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.17 (d, *J* = 3.2 Hz, 1H), 6.06 (d, *J* = 2.8 Hz, 1H), 4.52 (s, 2H), 4.43 (s, 2H), 2.98 (s, 3H), 2.02 (br s, 1H); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.3, 152.3, 149.2, 129.1, 117.2, 113.0, 108.5, 108.0, 57.4, 50.0, 38.3.



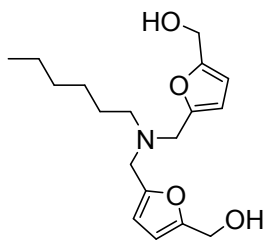
(Table 3, 3v). ^[S5] ¹H-NMR (d₆-DMSO, 400 MHz): δ 6.79-6.77 (m, 4H), 6.15 (d, *J* =

2.8 Hz, 1H), 6.08 (d, *J* = 3.2 Hz, 1H), 5.14 (t, *J* = 5.6 Hz, 1H), 4.32 (s, 2H), 4.31 (d, *J* = 5.6 Hz, 2H), 3.66 (s, 3H), 2.84 (s, 3H); ¹³C-NMR (d₆-DMSO, 100 MHz): δ 155.0, 151.9, 151.8, 144.0, 115.1, 114.8, 108.6, 107.9, 56.1, 55.6, 50.1, 39.1.

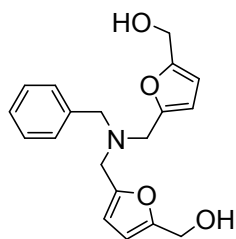


(Scheme 3, 6a). ^[S6] ¹H-NMR (CDCl₃, 400 MHz): δ 6.20 (d, *J* = 3.2 Hz, 2H), 6.15 (d, *J* =

2.8 Hz, 2H), 4.55 (s, 4H), 3.64 (s, 4H), 2.66 (br s, 2H), 2.47 (t, $J = 7.6$ Hz, 2H), 1.56-1.48 (m, 2H), 1.34-1.25 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 153.8, 151.7, 109.8, 108.2, 57.4, 53.2, 49.9, 28.7, 20.5, 13.9.



(Scheme 3, 6b). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 6.19 (d, $J = 2.8$ Hz, 2H), 6.14 (d, $J = 3.2$ Hz, 2H), 4.54 (s, 4H), 3.62 (s, 4H), 3.06 (br s, 2H), 2.44 (t, $J = 7.6$ Hz, 4H), 1.52-1.48 (m, 2H), 1.31-1.25 (m, 6H), 0.87 (t, $J = 6.8$ Hz, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 153.8, 151.8, 109.7, 108.1, 57.2, 53.5, 49.8, 31.6, 27.1, 26.6, 22.6, 14.0; HRMS (ESI) calculated for $\text{C}_{18}\text{H}_{27}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 322.2013, observed 322.2010.



(Scheme 3, 6c). $^{[S6]}$ $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 7.36-7.22 (m, 5H), 6.19 (d, $J = 2.8$ Hz, 2H), 6.15 (d, $J = 2.8$ Hz, 2H), 4.54 (s, 4H), 3.63 (s, 4H), 3.63 (s, 2H), 2.80 (br s, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 153.6, 152.0, 138.2, 129.1, 128.2, 127.1, 109.7, 108.3, 57.30, 57.2, 49.6.

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