Supplementary Information (SI) for Journal of Materials Chemistry A.

Regulating hydrogen spillover in Pt/M-ZrO_2 catalysed reductive methylation of aniline under mild conditions

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Table S1. Catalytic results of N-methylation of aniline using Pt/M-ZrO_2 with different methylating agents.

S. No.	C_1 source	Aniline Conv. (%)	NNDMA Yield (%)
1[a]	Formalin (formaldehyde)	99.7	68.4
2[b]	Paraformaldehyde	25.4	1.2
3[c]	Methanol	19.3	--
4[d]	CO_2	18.1	--

Reaction conditions: 0.5 mmol aniline, 25 mg Pt/M-ZrO_2 (0.003 mmol Pt), 15 g MeOH, 50 ˚C, 20 bar H_2, 0.5h. [a]150 mg formalin. [b]70 mg paraformaldehyde. [c] methanol solvent used as an alkylating agent. [d]10 bar CO_2.

Table S2. Comparison of the catalytic efficiency of the present study with the existing studies.

Entry	Catalyst	Conditions	Yield	TOF (h^{-1})	Ref.
1	Ru/C	70 ˚C, 8h, 25 bar H_2	>99	13	1
2	Pt/C	70 ˚C, 8h, 25 bar H_2	95	17	1
3	Pd/C	70 ˚C, 8h, 25 bar H_2	99	32	1
4	Rh/C	70 ˚C, 8h, 25 bar H_2	76	13	1
5	Raney Ni	70 ˚C, 8h, 25 bar H_2	99	-	1
6	Raney Co	70 ˚C, 8h, 25 bar H_2	99	-	1
7	Raney Ni (6)	180 ˚C, 7h, 17 bar H_2	65	31.0	2
8	CuAlOx	120 ˚C, 5h, 10 bar H_2	95 (N)	1.2	3
9	Ni/NiO@C	80 ˚C, 6h, 20 bar H_2	99	0.6	4
10	Pt/M-ZrO_2	0.5 mmol, 50 ˚C, 0.5h, 20 bar H_2	68.4	622	**This work**
11	Pt/M-ZrO_2	4 mmol, 50 ˚C, 2h, 20 bar H_2	81.6	1484	**This work**

Table S3: Physicochemical properties of parent and Pt supported on ZrO_2.

S. No.	Catalyst	Surface Area (m²/g)	BJH Pore Size (D=nm)	Total Pore Volume (cc/g)
1	M-ZrO_2	106.8	31.0	0.60
2	Pt/M-ZrO_2	116.3	17.3	0.58
3	T-ZrO_2	6.9	0.1	0.01
4	Pt/T-ZrO_2	7.3	1.7	0.15

Table S4: Metal dispersion and particle size of Pt supported on ZrO_2.

S. No.	Catalyst	Dispersion (%)	Particle size (nm)
		CO-pulse	HAADF-STEM/HRTEM
1	Pt/M-ZrO_2	27.7	0.72
2	Pt/T-ZrO_2	4.8	27.5

Table S5: Surface composition of elements of parent and Pt supported on ZrO_2 based on XPS analysis.

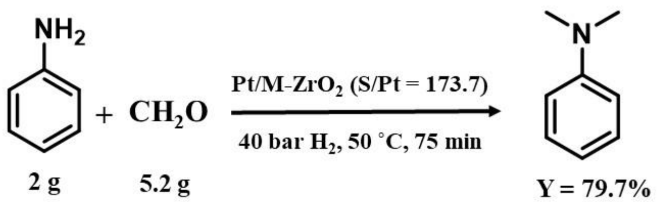
S. No.	Catalyst	Zr 3d; B.E (eV)		O 1s; B.E (eV)		Pt 4f; B.E (eV)			
		$3d_{5/2}$	$3d_{3/2}$	O_L	O_A	Pt^0 $4f_{5/2}$	Pt^{n+} $4f_{5/2}$	Pt^0 $4f_{3/2}$	Pt^{n+} $4f_{3/2}$
1	M-ZrO_2	181.5	183.9	529.5 (66.3)	531.1 (33.7)	-	-	-	-
2	T-ZrO_2	181.9	184.3	529.7 (77.4)	531.4 (22.6)	-	-	-	-
3	Pt/M-ZrO_2	181.6	184.0	529.5 (62.1)	531.1 (37.9)	71.5 (64.5)	73.1	75.0	76.5
4	Pt/T-ZrO_2	181.8	184.2	529.6 (73.7)	531.3 (26.3)	70.6 (68.4)	71.9	73.9	75.3
5*	Pt/M-ZrO_2	181.6	184.0	529.4 (66.1)	531.0 (33.9)	71.3 (62.2)	72.8	74.9	76.6

*Spent catalyst, Values in the parenthesis are the percentage of corresponding species.

Table S6: Catalytic activity of $Pt/M\text{-}ZrO_2$ towards the synthesis of NNDMA from nitrobenzene via a one-pot two-step process.

Entry	substrate	product	Time (h)	conversion	Yield
1. Step 1	Nitrobenzene	Aniline	1.5	>99	94.8
2. Step 2*	Aniline	NNDMA	1.25	>99	89.6
3. One-pot	Nitrobenzene	NNDMA	4	95.6	56.0
4. One-pot[#]	Nitrobenzene	NNDMA	4	>99	89.7

Reaction conditions: 0.5 mmol Nitrobenzene, 25 mg $Pt/M\text{-}ZrO_2$ (0.003 mmol Pt), 50 °C, 20 bar H_2. *reaction mixture from entry 1 was directly used for entry 2, [#]100 °C.



Scheme S1: Scale up experiment of the N, N-dimethylation of aniline using $Pt/M\text{-}ZrO_2$.

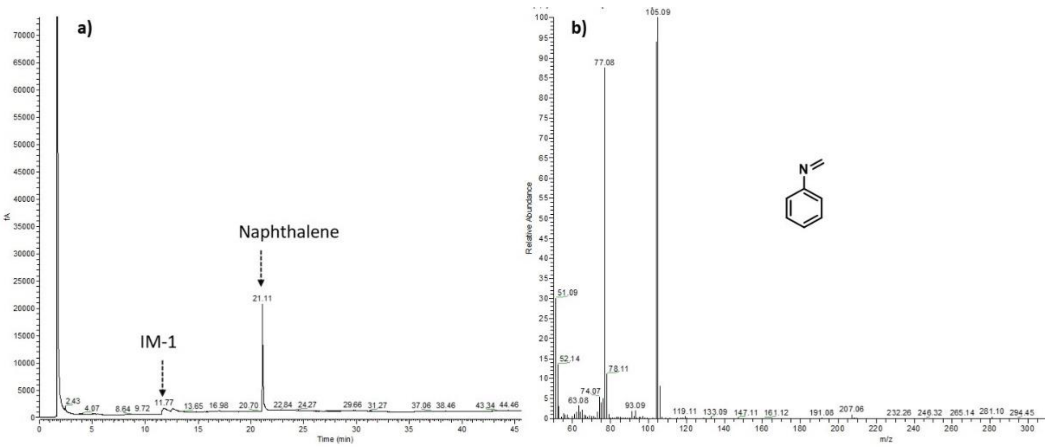


Figure S1: a) GC chromatogram of blank reaction without a catalyst (Table 1, entry 1) and b) GC-MS fragmentation of imine intermediate (IM-1).

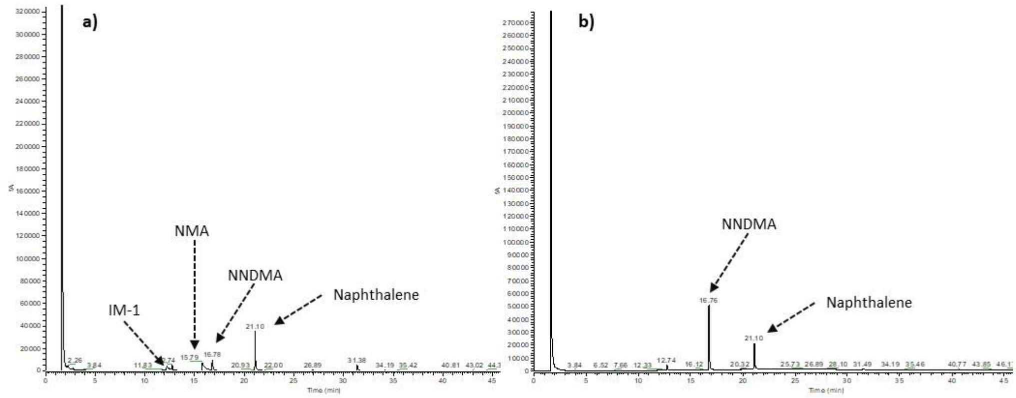


Figure S2: GC chromatograms of the reaction mixture with Pt/M-ZrO_2 as a catalyst after a) 0.5h and b) 1.25h.

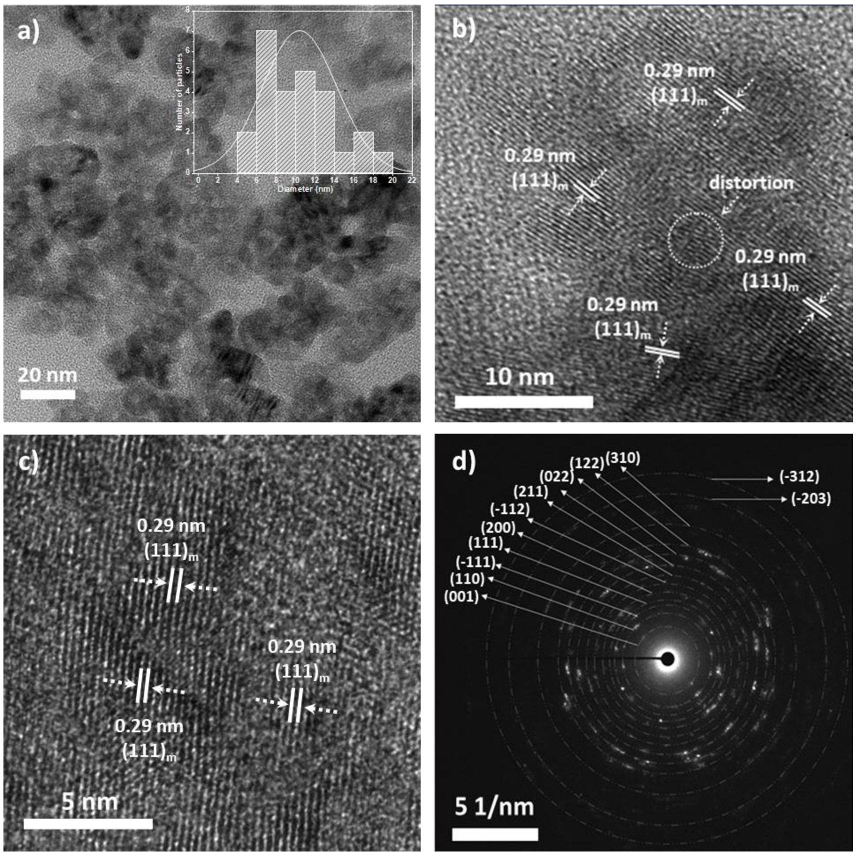


Figure S3: a-c) HRTEM images and d) SAED pattern of M-ZrO_2.

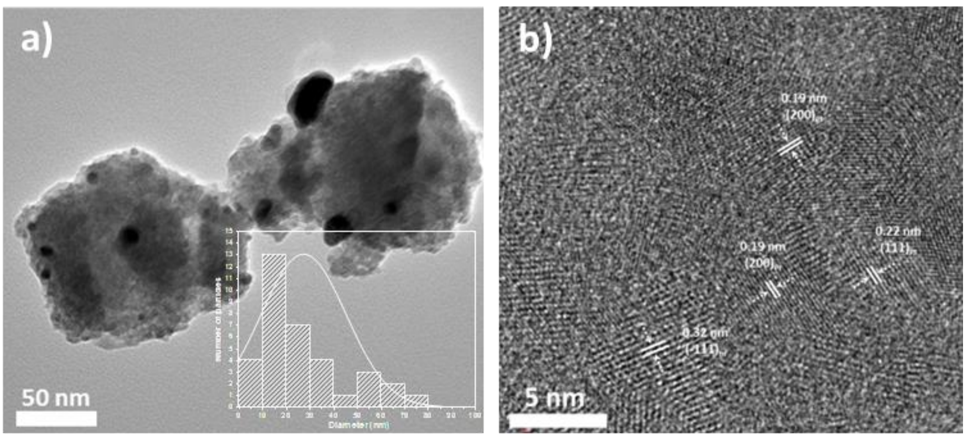


Figure S4: HRTEM images of Pt/T-ZrO_2.

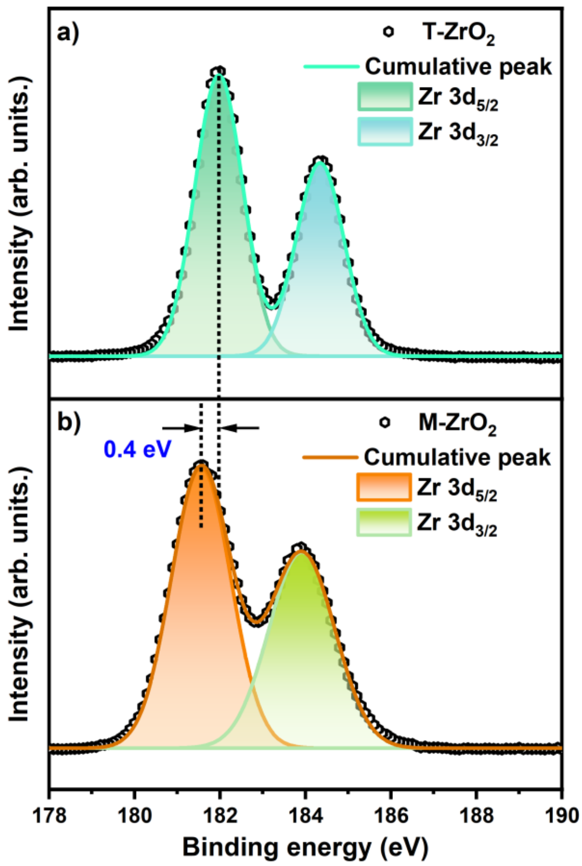


Figure S5: Zr 3d XPS spectra of a) T-ZrO_2; b) M-ZrO_2.

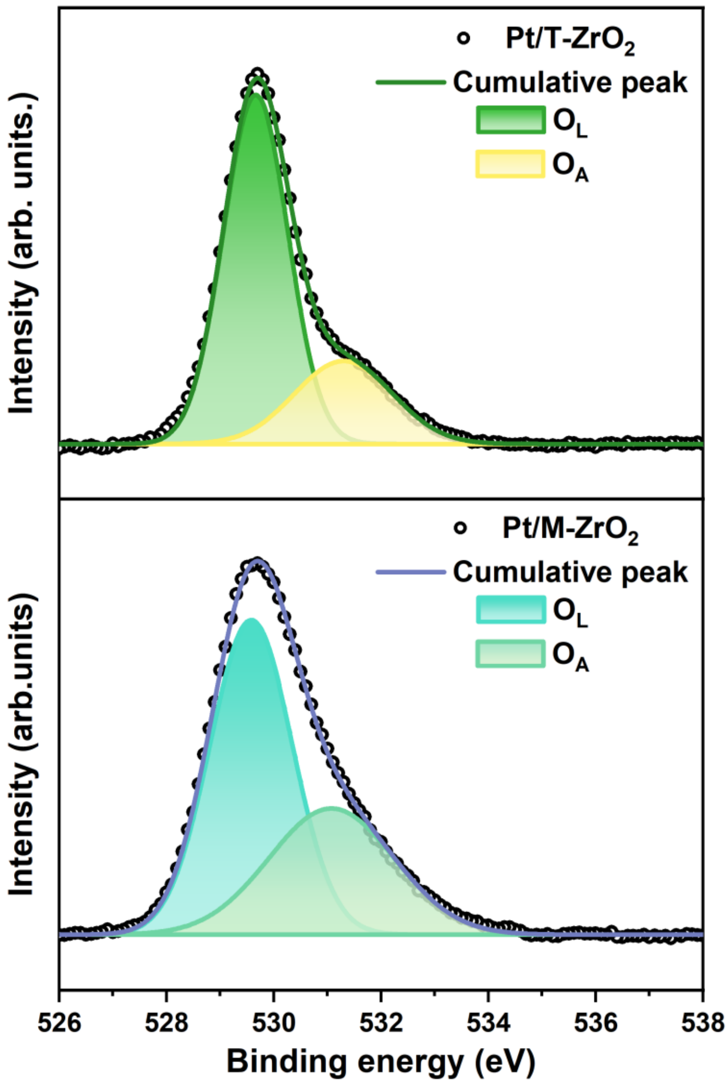


Figure S6: O 1s XPS spectra of a) T-ZrO_2; b) M-ZrO_2.

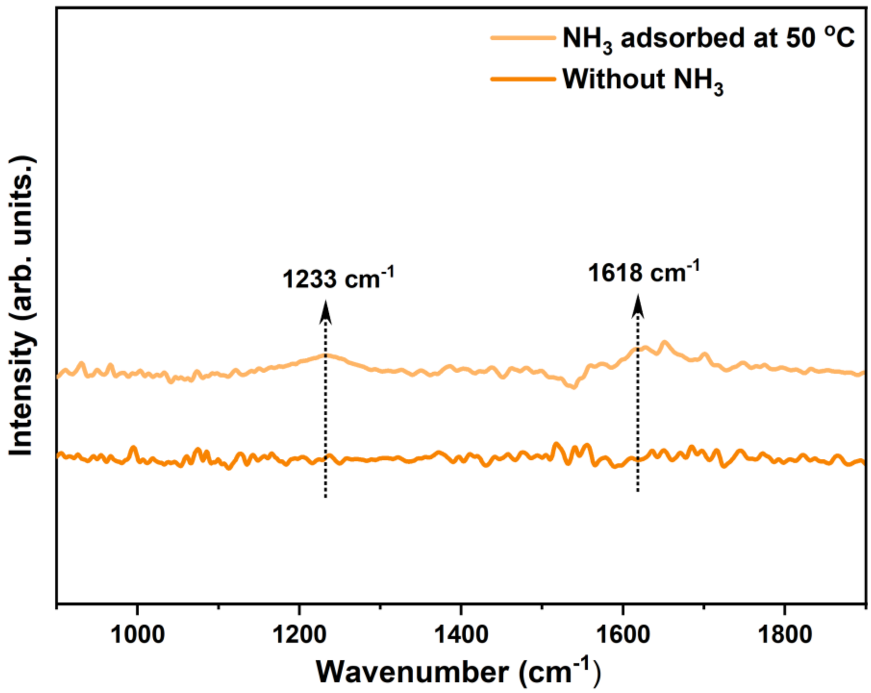


Figure S7: NH_3-DRIFT spectra of Pt/T-ZrO_2.

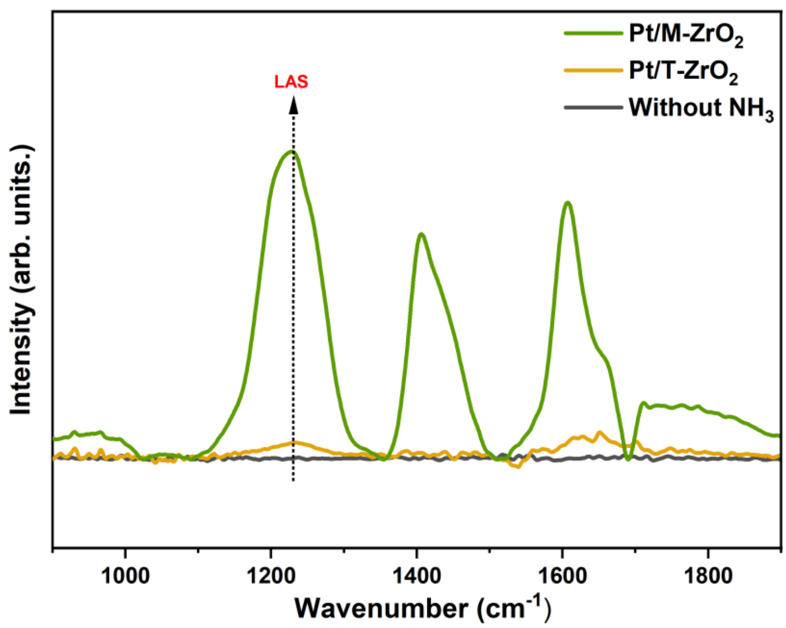


Figure S8: NH_3-DRIFT spectra of Pt supported on ZrO_2 catalyst at 50 °C.

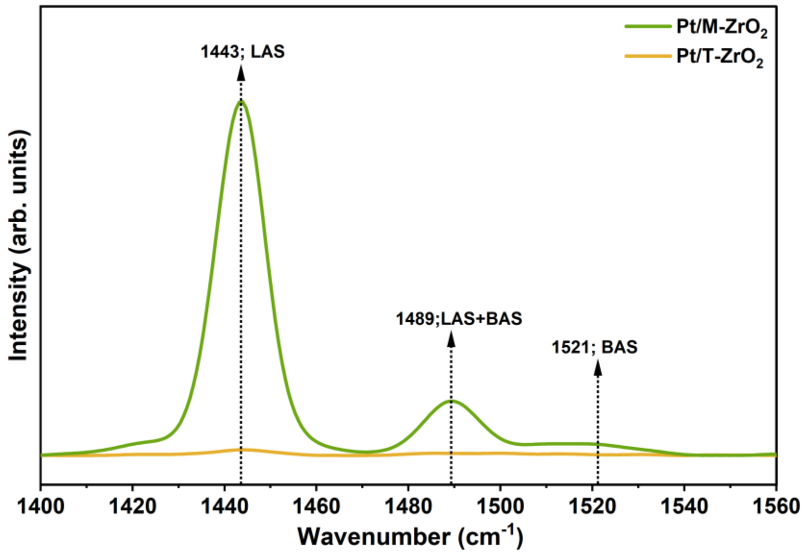


Figure S9. Pyridine DRIFT spectra of Pt/M-ZrO_2 and Pt/T-ZrO_2.

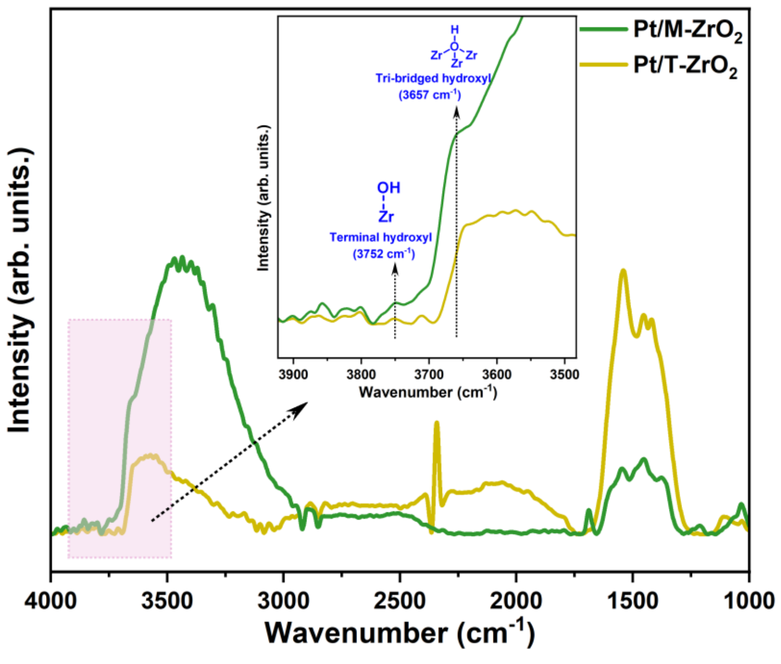


Figure S10: DRIFT spectra of Pt supported on ZrO_2 catalyst.

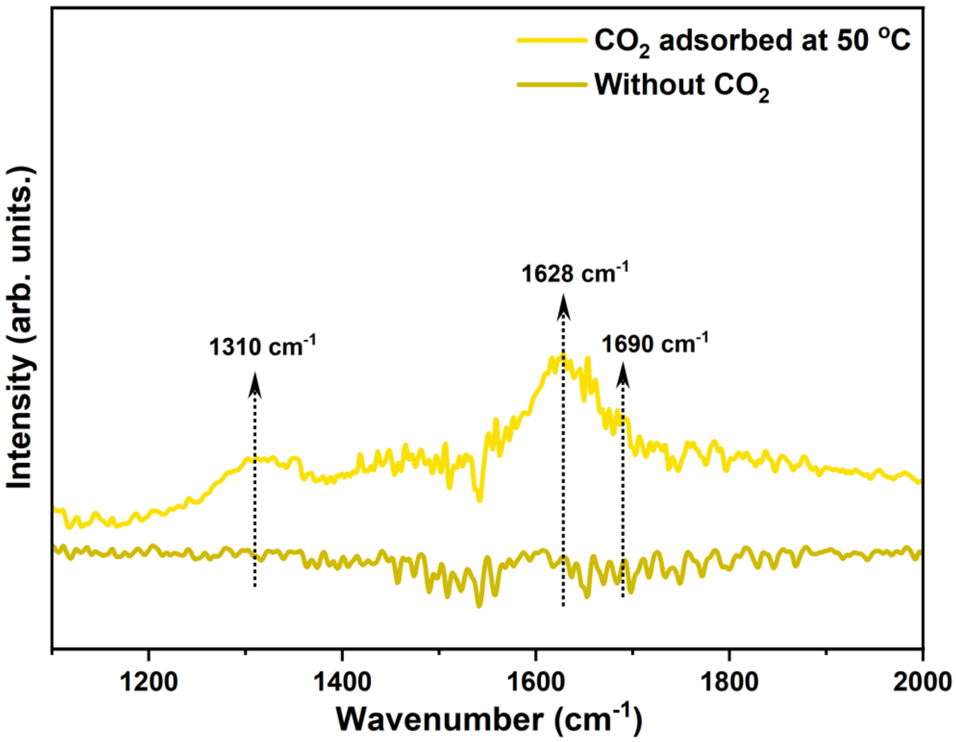


Figure S11: CO_2-DRIFT spectra of Pt/T-ZrO_2.

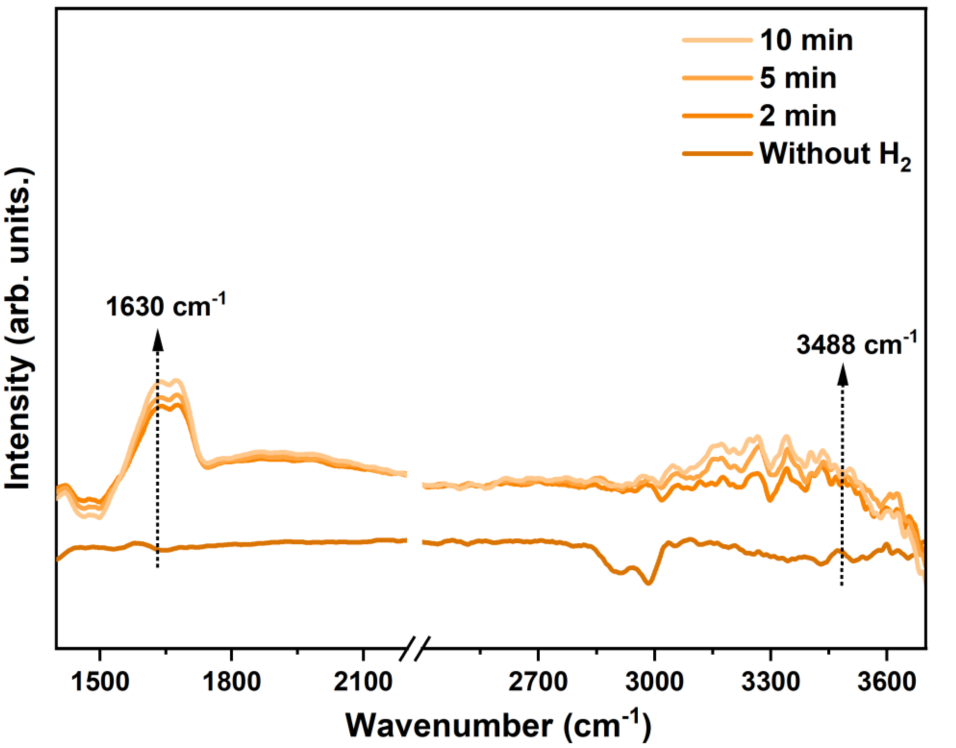


Figure S12: H_2-DRIFT spectra of M-ZrO_2.

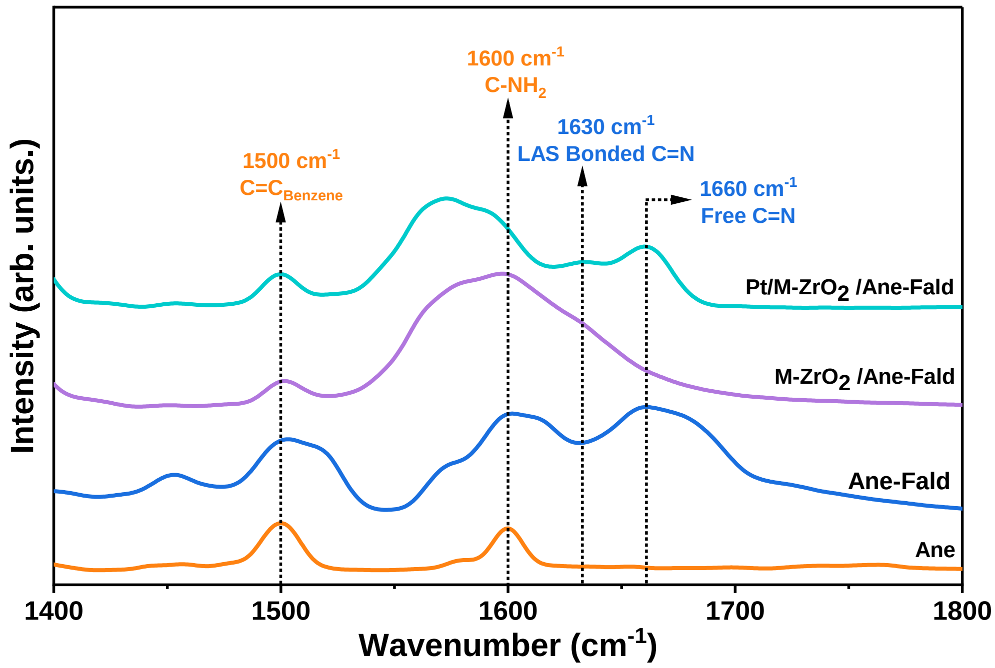


Figure S13: In-situ DRIFT spectra of aniline-formaldehyde mixture adsorbed over M-ZrO_2 and Pt/M-ZrO_2. Ane: aniline; Fald: formaldehyde; Ane-Fald: aniline-formaldehyde mixture.

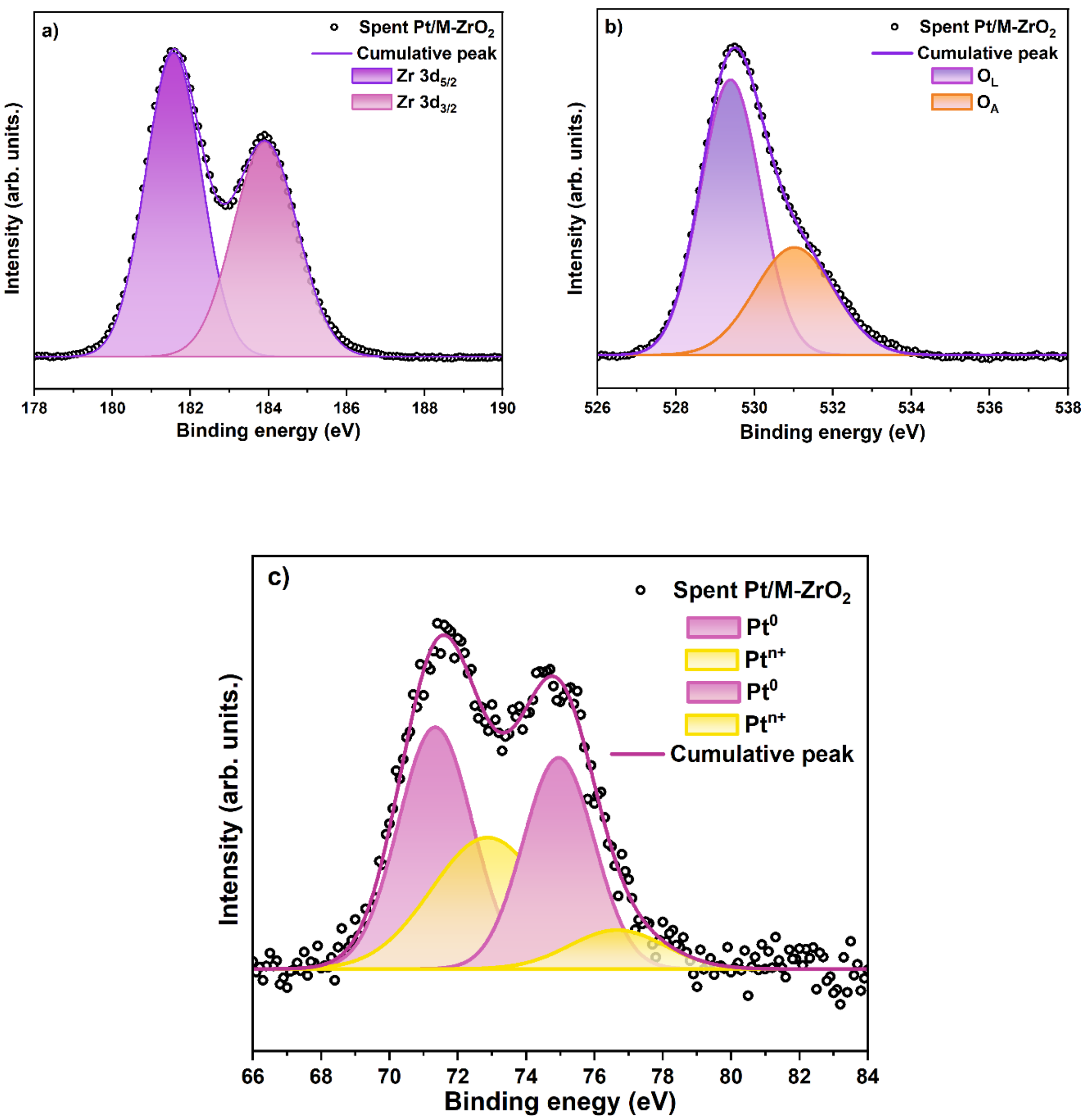


Figure S14: XPS spectra of a) Zr 3d, b) O 1s, c) Pt 4f of spent Pt/M-ZrO_2 (After 4^{rth} run).

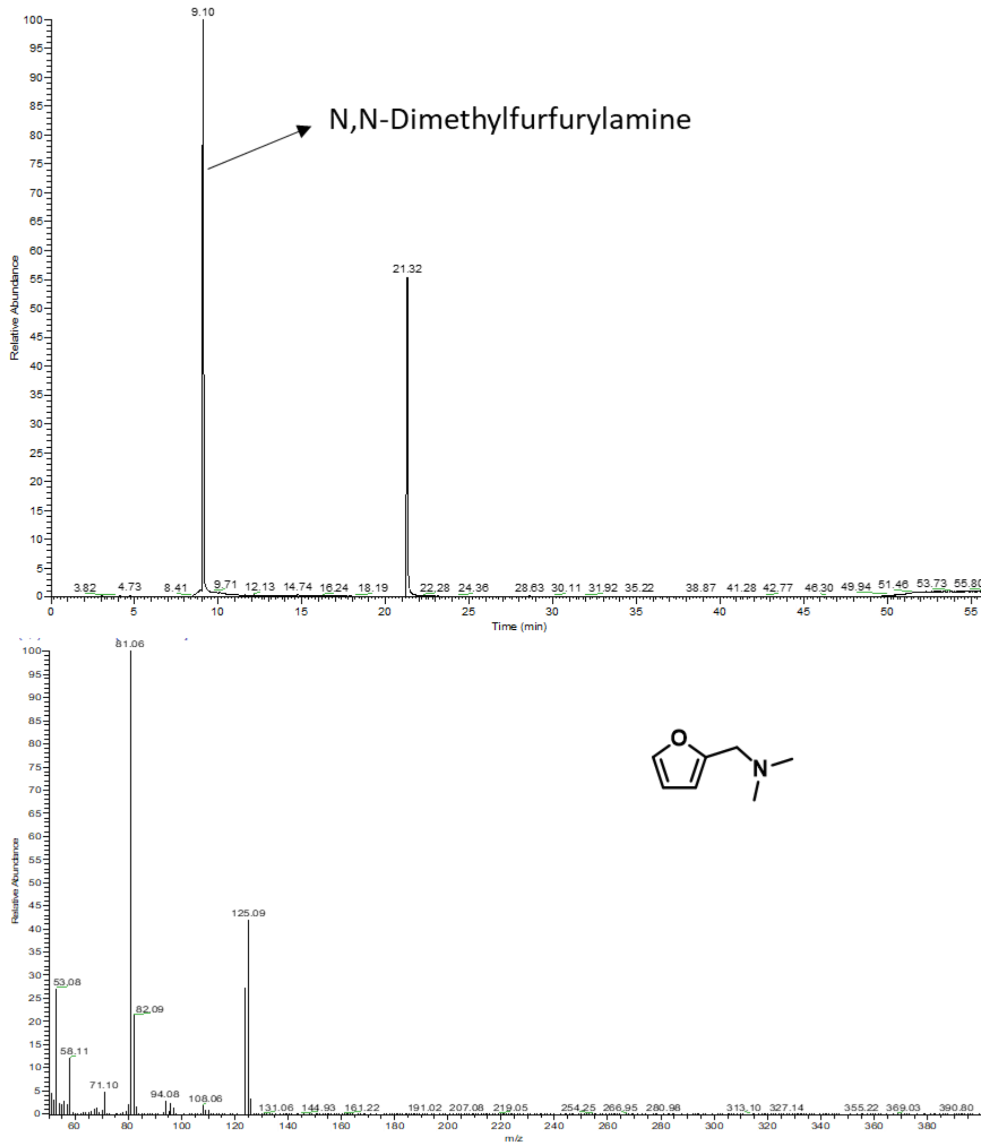


Figure S15: GC chromatograms of N-methylation of furfurylamine.

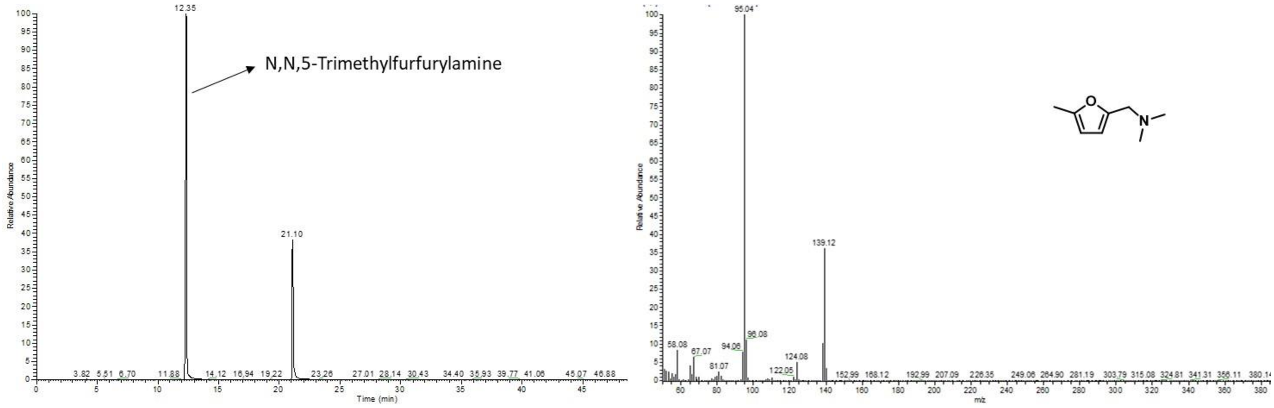


Figure S16: GC chromatograms of N-methylation of 5-methylfurfurylamine.

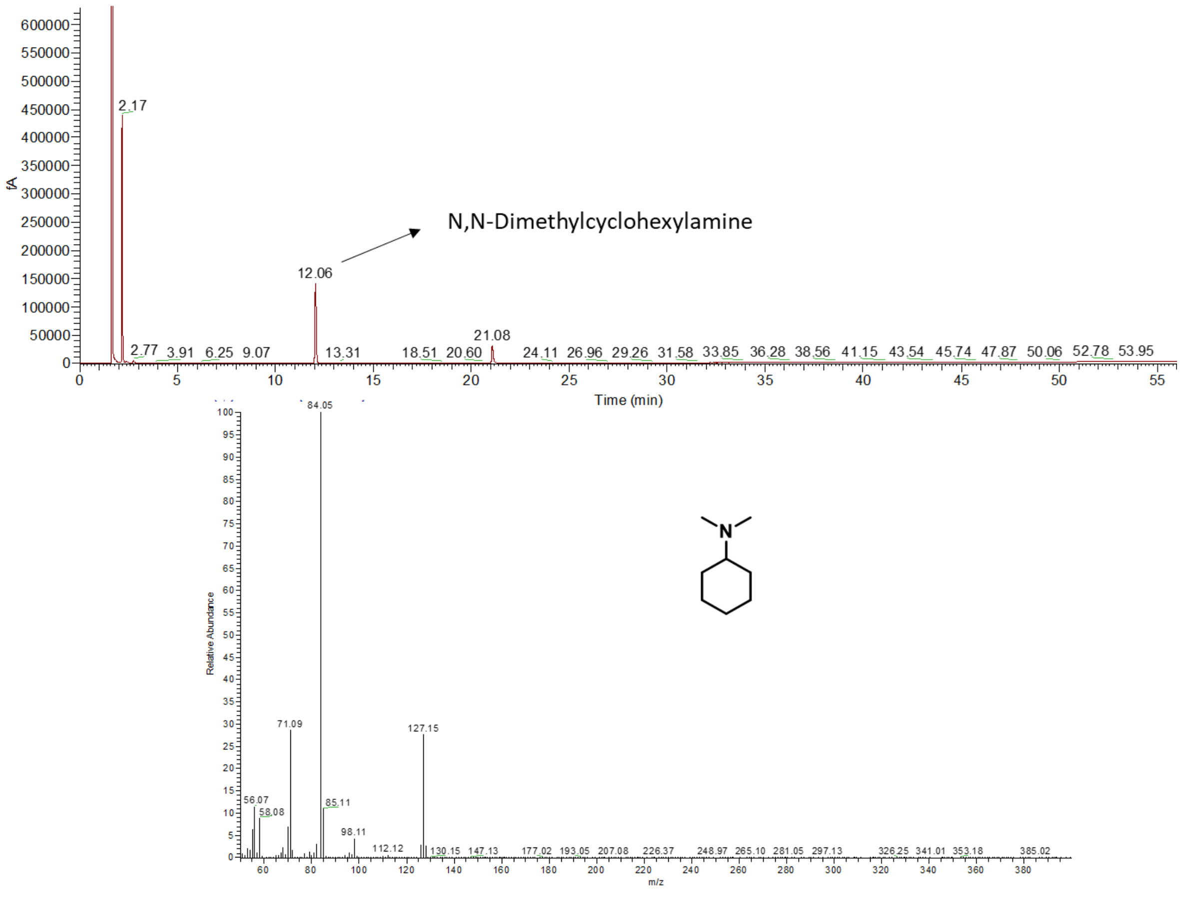


Figure S17: GC chromatograms of N-methylation of cyclohexylamine.

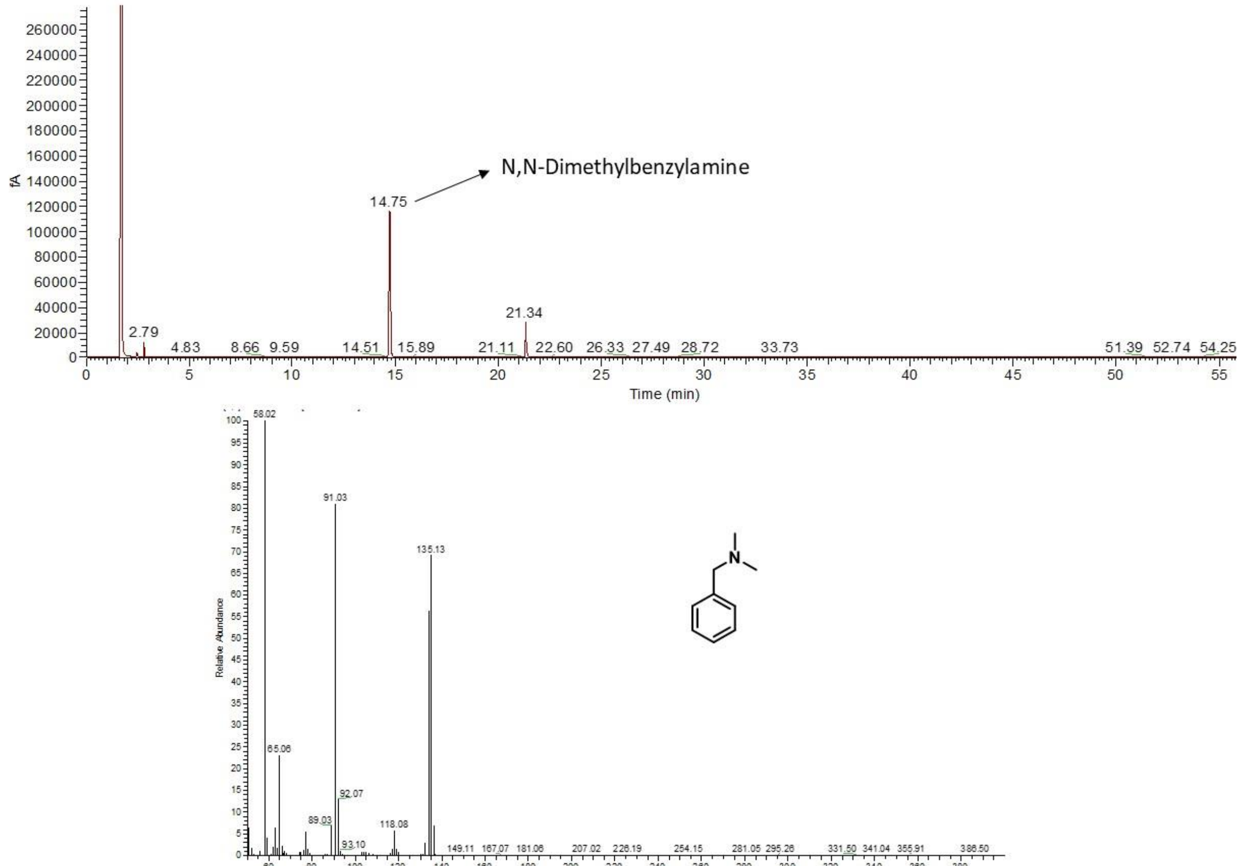


Figure S18: GC chromatograms of N-methylation of benzylamine.

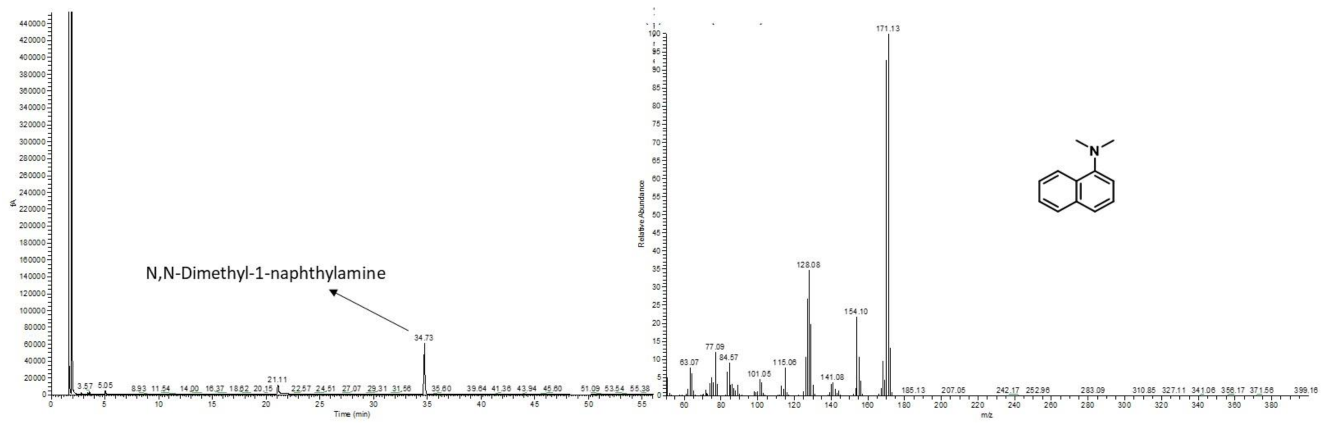


Figure S19: GC chromatograms of N-methylation of naphthylamine.

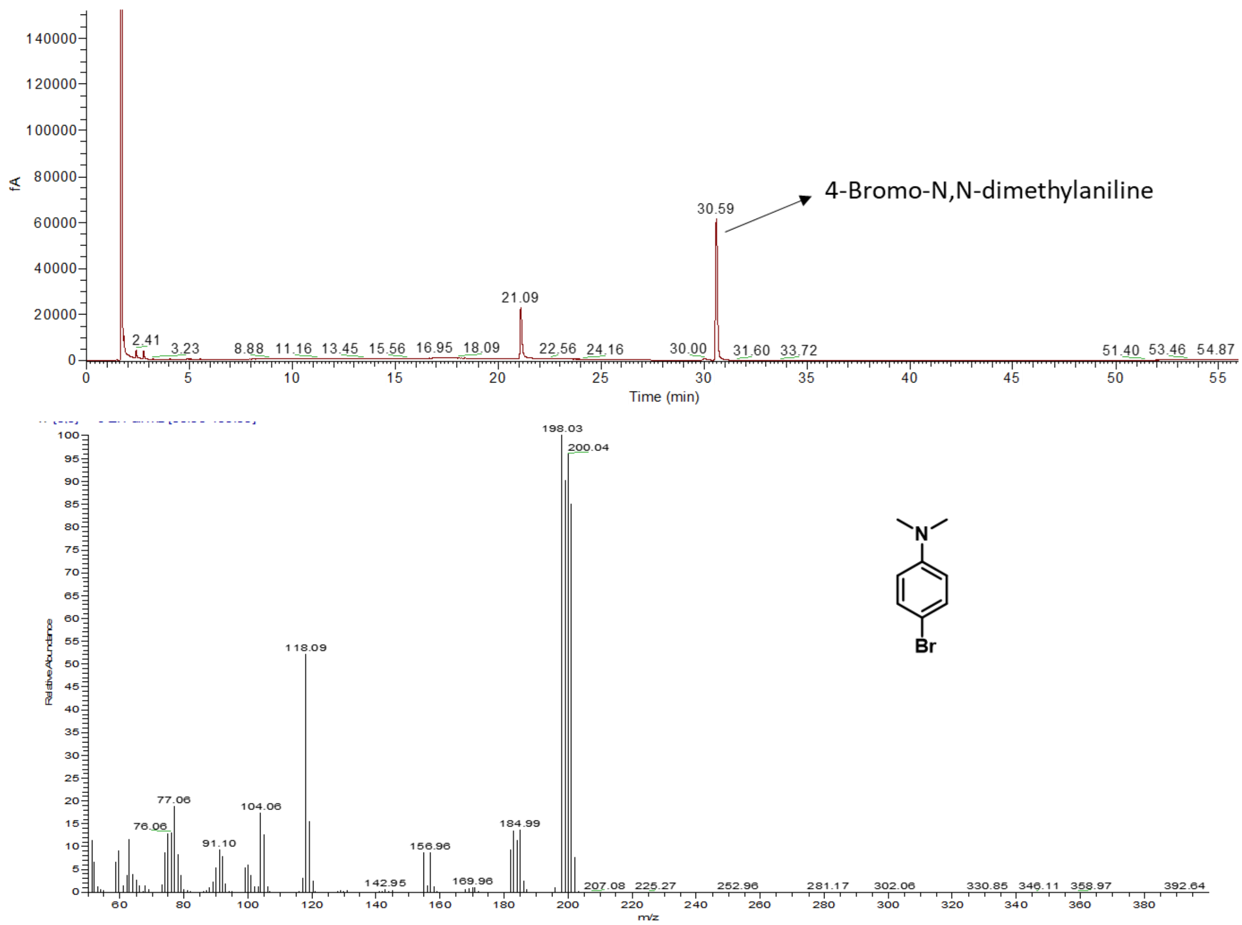


Figure S20: GC chromatograms of N-methylation of 4-bromoaniline.

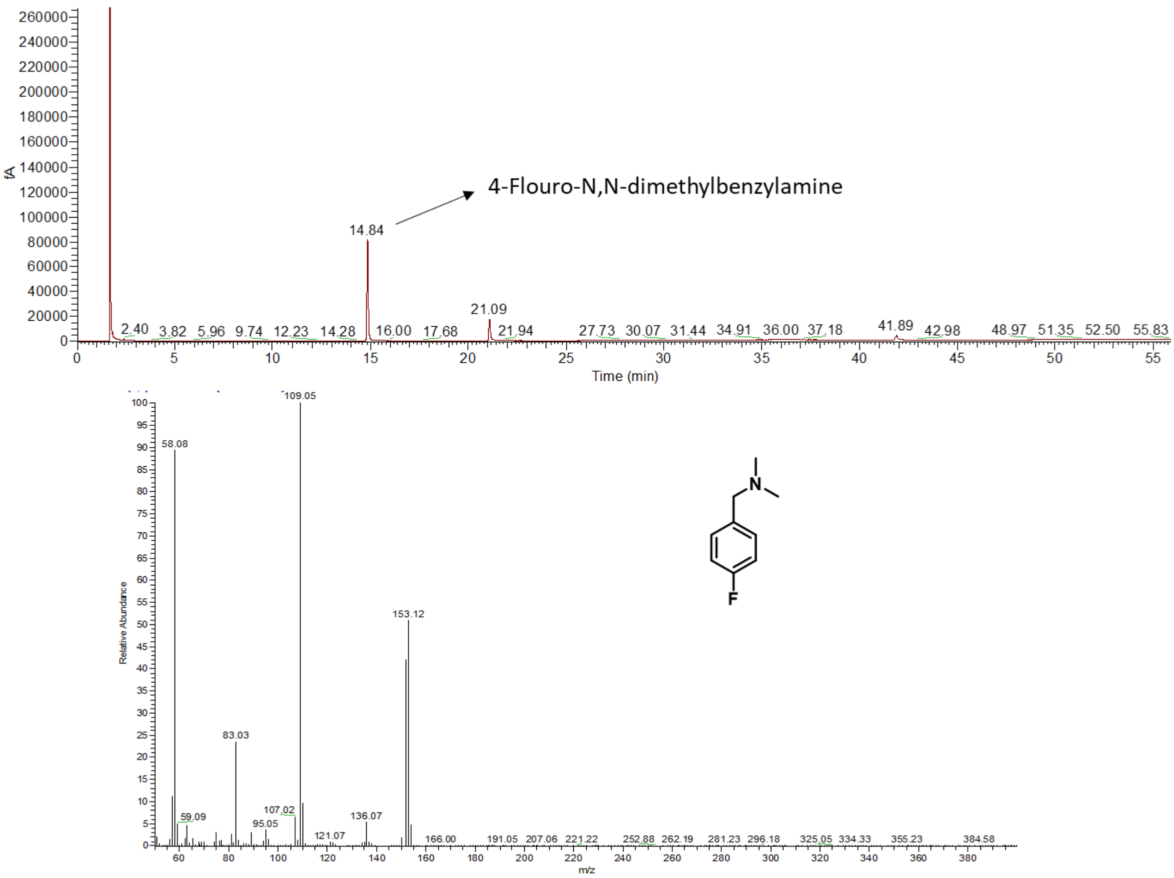


Figure S21: GC chromatograms of N-methylation of 4-flouro-benzylamine.

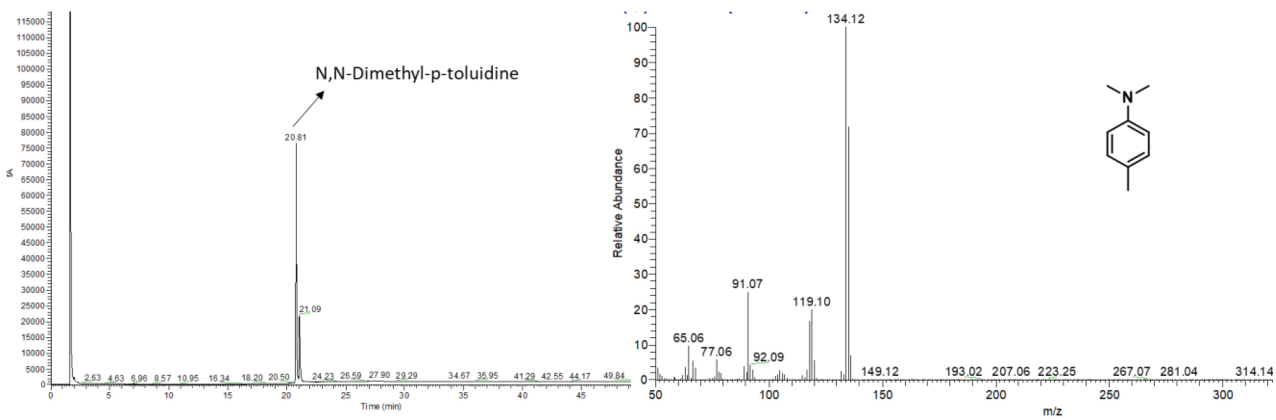


Figure S22: GC chromatograms of N-methylation of p-toluidine.

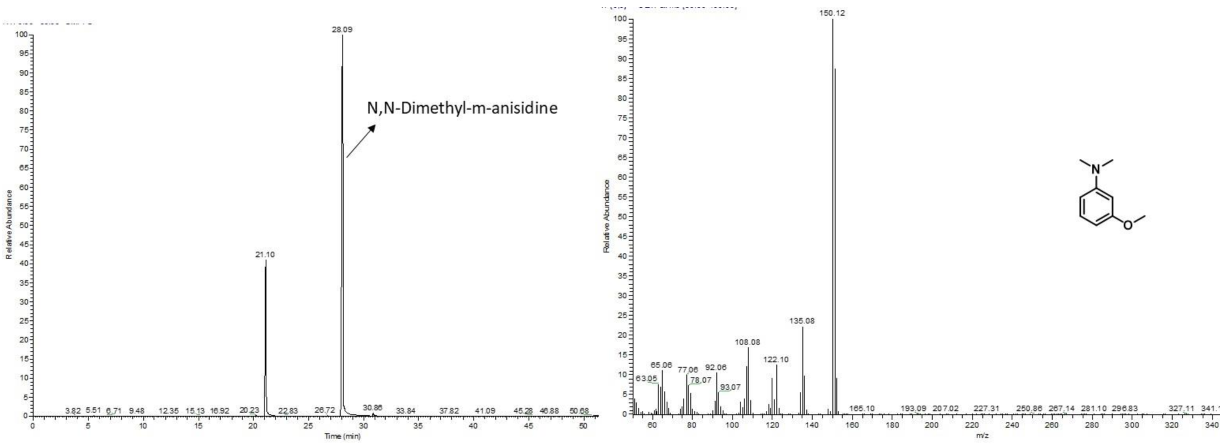


Figure S23: GC chromatograms of N-methylation of m-anisidine.

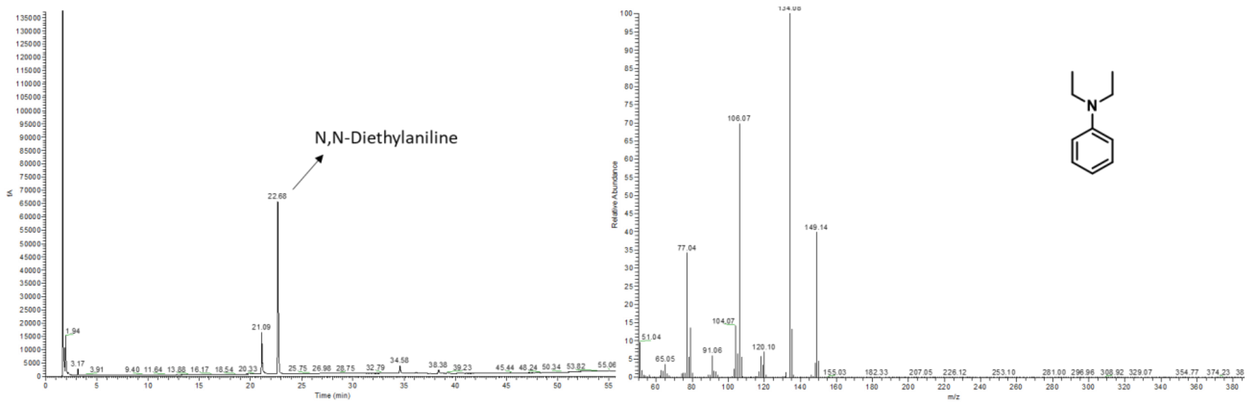


Figure S24: GC chromatograms of N-ethylation of aniline.

References:

(1) Liu, J.; Song, Y.; Wu, X.; Ma, L. *ACS Omega* **2021**, *6* (35), 22504–22513.

(2) Ge, X.; Luo, C.; Qian, C.; Yu, Z.; Chen, X. *RSC Adv.* **2014**, *4* (81), 43195–43203.

(3) Wang, H.; Huang, Y.; Dai, X.; Shi, F. *Chem. Comm.* **2017**, *53* (40), 5542–5545.

(4) Liu, J.; Song, Y.; Zhuang, X.; Zhang, M.; Ma, L. *Green Chem.* **2021**, *23* (12), 4604–4617.