Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Accelerated H_2 activation over Pt/M-ZrO_2 for the reductive amination of levulinic acid esters under benign conditions

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Table S1. Catalytic reductive amination of MLevu to OMP with metals supported on ZrO_2.

Entry	Catalyst	MLevu Conversion (%)	OMP Yield (%)	OMP Selectivity (%)
1	Ru/M-ZrO_2	97.9	18.0	18.4
2	Ir/M-ZrO_2	98.0	32.1	32.8
3	Ni/M-ZrO_2	89.1	6.2	6.9
4	Mn/M-ZrO_2	95.5	22.8	23.8
5	Ce/M-ZrO_2	94.9	10.2	10.8
6	Co/M-ZrO_2	93.7	10.4	11.1
7	Fe/M-ZrO_2	96.7	8.9	9.2

Reaction Conditions: 1 mmol MLevu, $mole_{substrate:Pt}$ = 81, 2 mmol octylamine, 19 ml methanol, 120 ˚C, 30 bar H_2, 4 h.

Table S2. Physicochemical properties of parent and Pt incorporated ZrO_2 catalysts.

Entry	Catalyst	Surface area (m^2/g)[a]	Pore size (nm)[b]	Pore volume (cm^3/g)[c]
1	M-ZrO_2	105	17.5	0.423
2	Pt-M-ZrO_2	93	17.4	0.393
3	T-ZrO_2	45	3.4	0.045
4	Pt-T-ZrO_2	6	3.8	0.006

[a]calculated from the BET method, [b]calculated from the BJH method, [c]obtained from the amount of N_2 adsorbed at a relative pressure of around 0.99.

Table S3. XPS data of parent and Pt incorporated ZrO_2 catalysts.

Catalyst	O-1s			Pt-4f		
	Gaussian peak	Peak Position (eV)	Area (%)	Gaussian peak	Peak Position (eV)	Area (%)
M-ZrO_2	O_L	529.7	96.8	Pt^0	--	--
	O_V	--	--	Pt^{2+}		
	O_A	532.4	3.1	Pt^{4+}		
T-ZrO_2	O_L	529.8	90.1	Pt^0	--	--
	O_V	--	--	Pt^{2+}		
	O_A	531.9	9.8	Pt^{4+}		
Pt/M-ZrO_2	O_L	529.8	94.5	Pt^0	71.8, 75.5	25.5
	O_V	531.8	2.5	Pt^{2+}	73.5, 76.2	37.7
	O_A	532.6	2.8	Pt^{4+}	74.6, 77.9	36.7
Reduced Pt/M-ZrO_2	O_L	529.5	82.0	Pt^0	71.4, 75.3	46.5
	O_V	531.3	15.3	Pt^{2+}	72.8, 76.3	41.3
	O_A	532.7	2.5	Pt^{4+}	74.2, 78.8	12.1
Pt/T-ZrO_2	O_L	529.8	90.1	Pt^0	71.3, 74.4	79.0
	O_V	--	--	Pt^{2+}	73.1, 77.2	6.0
	O_A	532.1	9.8	Pt^{4+}	75.4, 78.1	14.8

Table S4: The influence of platinum loading on the product yield

Entry	Catalyst	MLevu Conversion (%)	OMP Yield (%)	OMP Selectivity (%)
1	1wt% Pt/M-ZrO_2	58.2	3.2	5.5
2	2wt% Pt/M-ZrO_2	54.4	21.1	38.8
3	3wt% Pt/M-ZrO_2	63.7	27.5	43.2
4	4wt% Pt/M-ZrO_2	67.9	19.3	28.5

Reaction condition:1 mmol MLevu, $mole_{substrate:Pt}$ = 81, 2 mmol octylamine, 19 ml methanol, 30 ˚C, 30 bar H_2, 30 min.

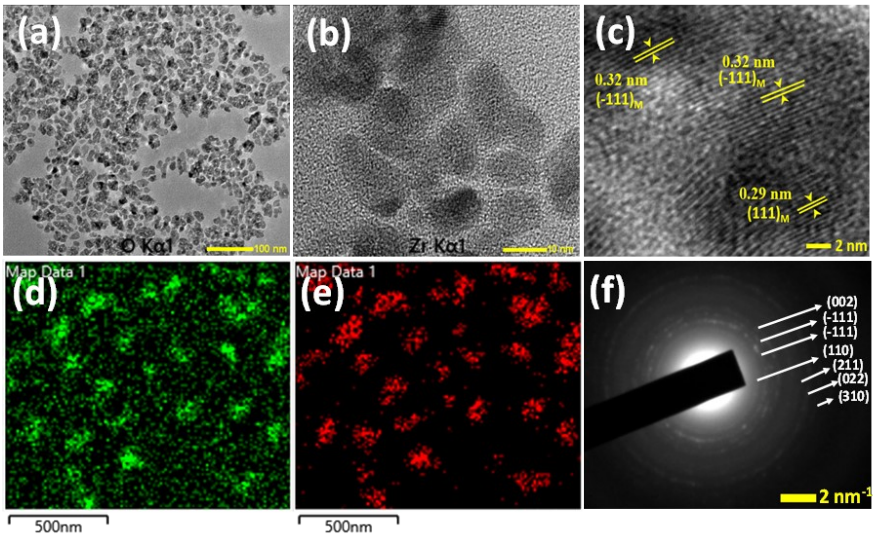


Figure S1. HR-TEM images (a-c), TEM-EDX elemental mapping(d,e) and SAED (f) of M-ZrO_2.

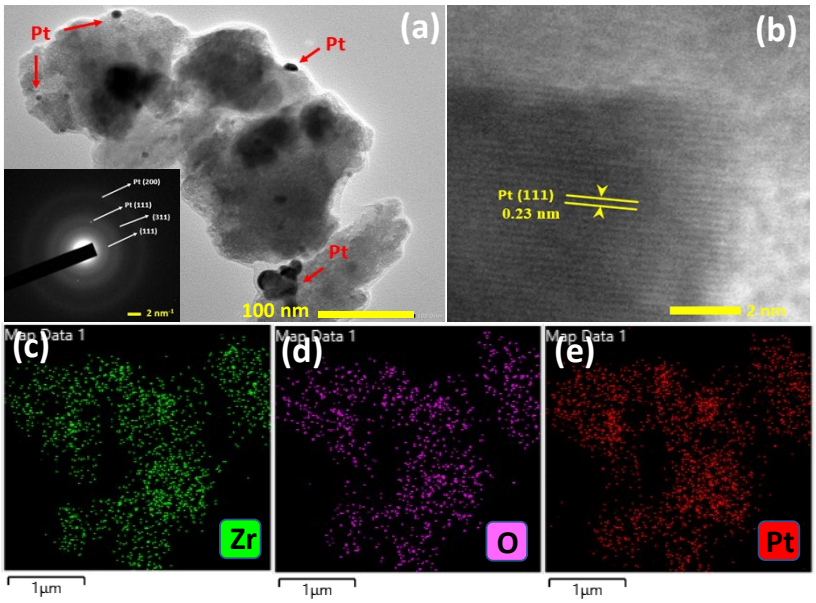


Figure S2. HR-TEM images (insert:SAED) (a, b) and TEM-EDX elemental mapping (c-e) of Pt/T-ZrO_2

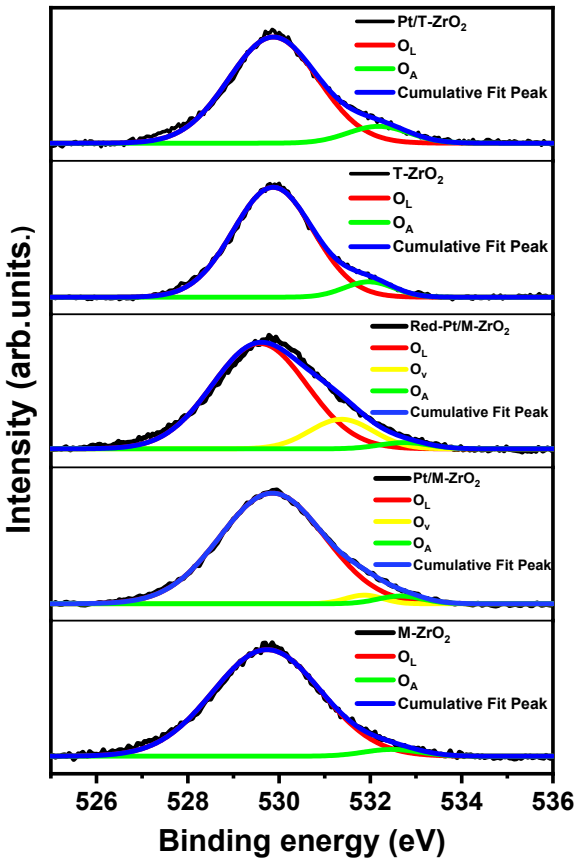


Figure S3. XPS spectra of O 1s of a) M-ZrO_2, b) Pt/M-ZrO_2, c) Reduced Pt/M-ZrO_2, d)T-ZrO_2, e) Pt/T-ZrO_2 after deconvolution.

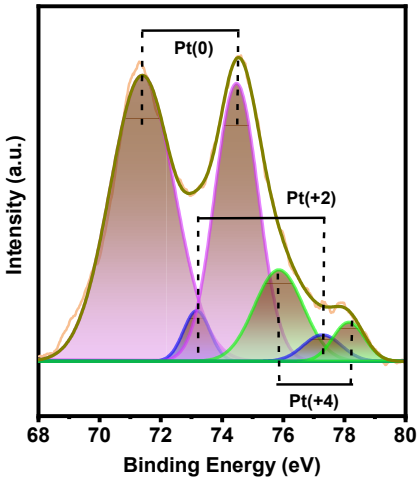


Figure S4. XPS spectra of Pt 4f of Pt/T-ZrO_2 after deconvolution.

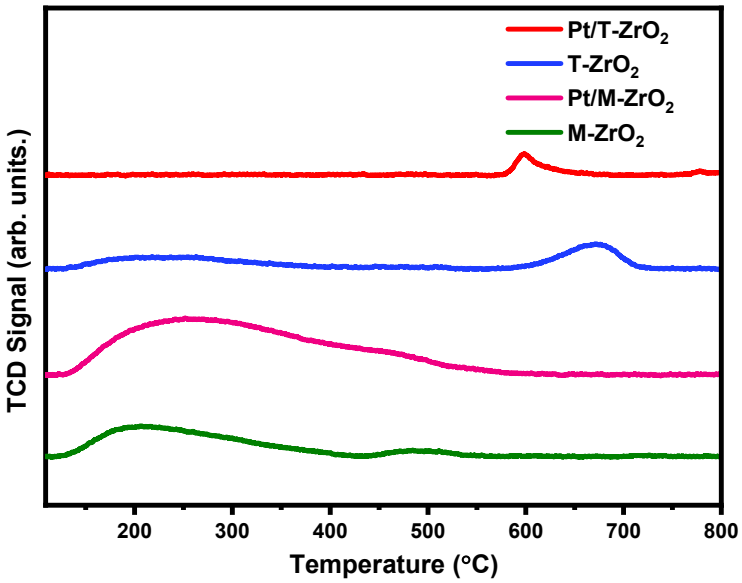


Figure S5. NH_3-TPD profile of parent and Pt incorporated ZrO_2 catalysts.

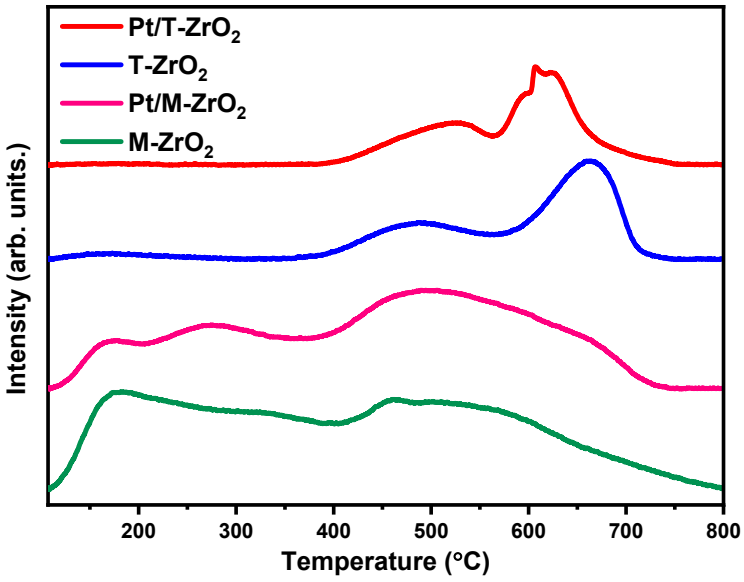


Figure S6. CO_2-TPD profile of parent and Pt incorporated ZrO_2 catalysts.

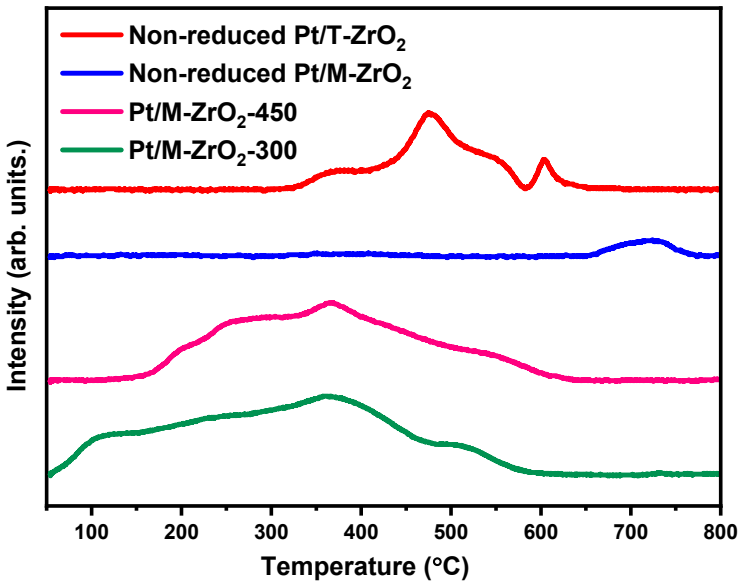


Figure S7. H_2-TPD profile of reduced and nonreduced Pt/ZrO_2 catalysts ($Pt/M\text{-}ZrO_2$-300: reduced at 300 ˚C; $Pt/M\text{-}ZrO_2$-450: reduced at 450 ˚C).

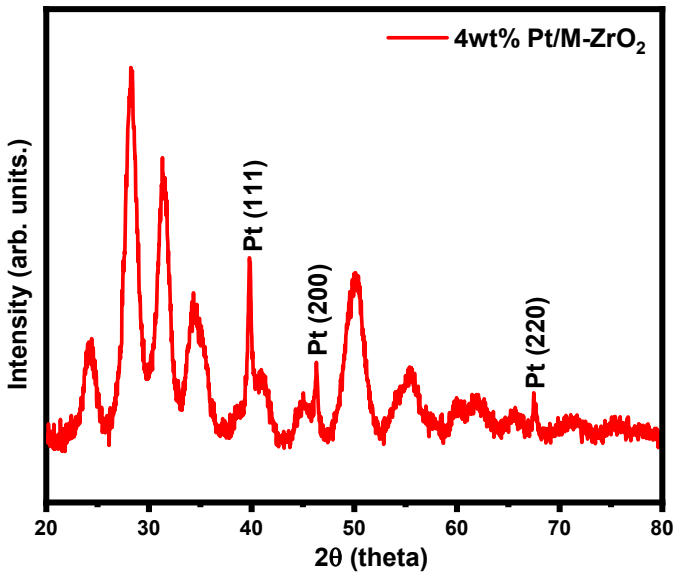


Figure S8. XRD pattern of 4 wt% $Pt/M\text{-}ZrO_2$ catalyst.

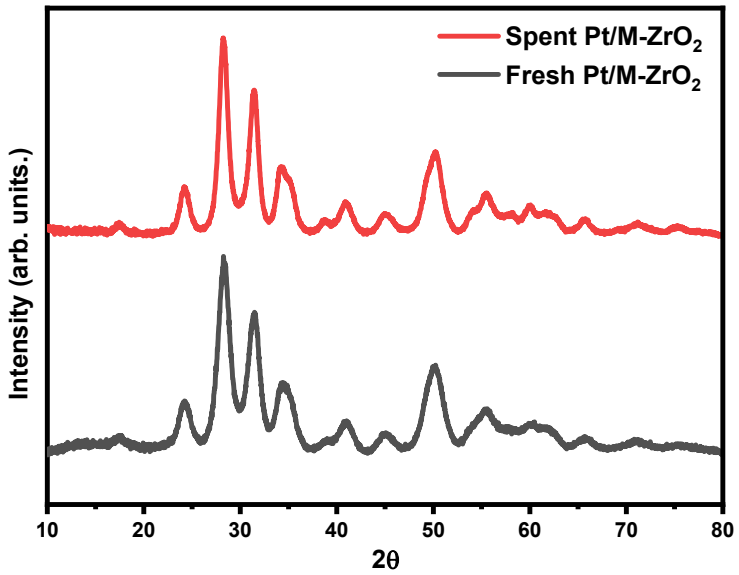


Figure S9. XRD pattern of fresh and spent (after four runs) Pt/M-ZrO_2 catalyst.

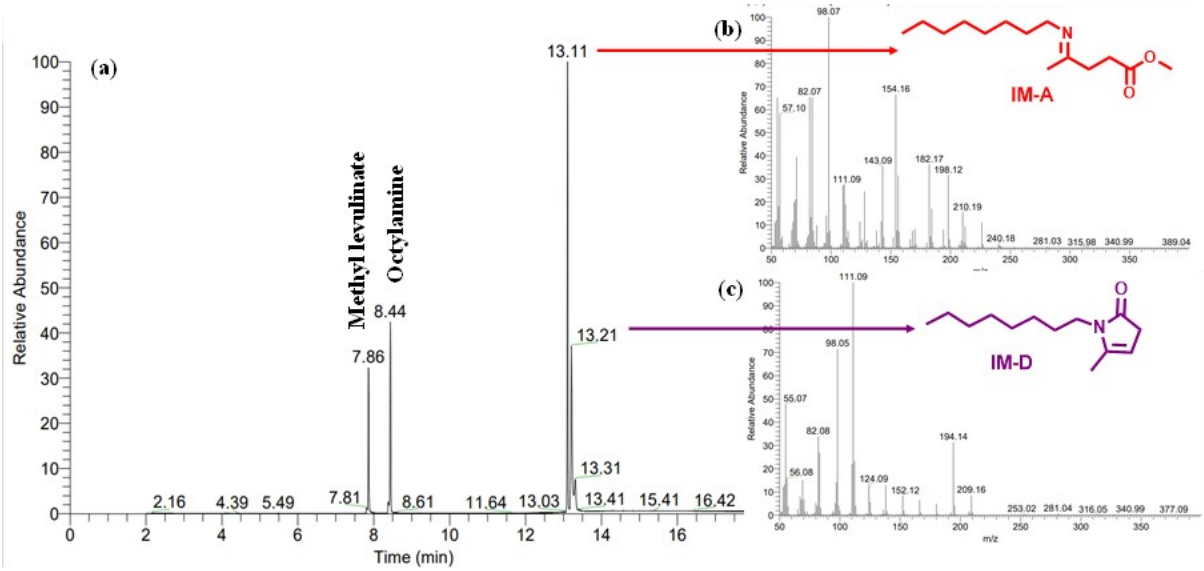
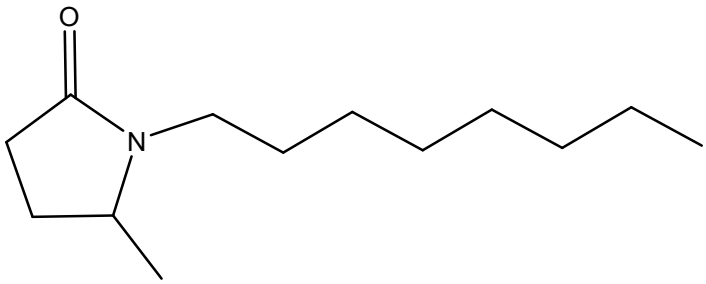


Figure S10. GC chromatogram and MS spectra of the reaction mixture. The GC-MS data of the intermediates has been compared with the literature data (Xie et al., J. Am. Chem. Soc. 2019, 141, 9, 4002–4009).[38]

Characterization of isolated products using IR, ^{1}H NMR, ^{13}C NMR, and HRMS:

The ^{1}H and ^{13}C{H} NMR spectra of all compounds have been recorded in 400 and ~101 MHz spectrometers using TMS as an internal standard, respectively. The HRMS analysis data of samples reported here were obtained from QTOF mass analyzer by the ESI method. The IR spectra of samples reported here were recorded as neat or thin films. Column chromatography purification of crude reaction mixtures/samples was carried out on alumina. Thin layer chromatography (TLC) analyses were carried out on alumina or silica gel plates. The components of TLC analysis were visualized by observation under iodine vapor.



5-Methyl-1-octylpyrrolidin-2-one:

The compound 5-methyl-1-octylpyrrolidin-2-one was obtained after purification by column chromatography on alumina (EtOAc : hexane = 10 : 90) as yellow color liquid (137 mg, 65%, 1 mmol scale);

R_f (10% EtOAc/hexane) 0.5;

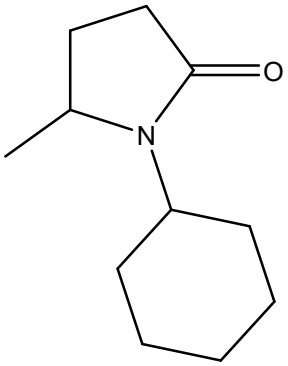
IR (DCM): 2920, 1746, 1185 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.73-3.65 (1H, m), 3.62-3.54 (1H, m), 2.94-2.87 (1H, m), 2.45-2.28 (2H, m), 2.22-2.13 (1H, m), 1.61-1.49 (2H, m), 1.46-1.39 (1H, m), 1.27-1.27 (10H, m), 1.20 (3H, d, J = 6.3 Hz), 0.88 (3H, t, J = 6.3 Hz).

^{13}C NMR (~101 MHz, $CDCl_3$): δ_C 173.8, 52.5, 39.2, 31.0, 29.5, 28.5, 28.5, 26.7, 26.2, 26.1, 21.9, 19.0, 13.3.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{13}H_{26}NO$: 212.2014 found 212.2019.

The compound is known in the literature, and the characterization data of this compound was compared with the literature data (Wei et al., ***Green Chem.*** **2014**, ***16***, 1093-1096).



1-Cyclohexyl-5-methylpyrrolidin-2-one:

The compound 1-cyclohexyl-5-methylpyrrolidin-2-one was obtained after purification by column chromatography on alumina (EtOAc : hexane = 10 : 90) as yellow color liquid (72 mg, 40%, 1 mmol scale);

R_f (10% EtOAc/hexane) 0.5;

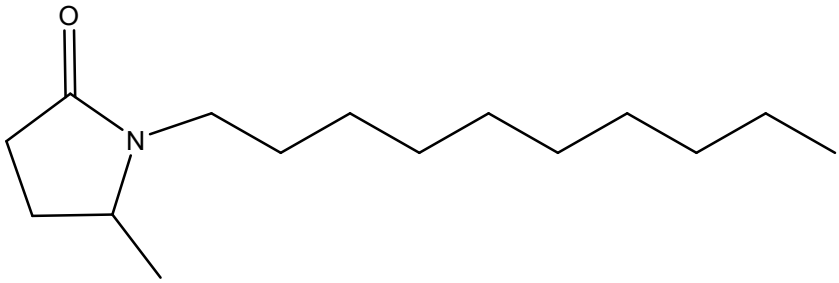
IR (DCM): 2927, 1748, 1187 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ_H 3.83-3.66 (2H, m), 2.52-2.42 (1H, m), 2.32-2.22 (1H, m), 2.19-2.09 (1H, m), 1.85-1.75 (3H, m), 1.70-1.63 (3H, m), 1.61-1.55 (1H, m), 1.53-1.46 (1H, m), 1.38-1.32 (2H, m), 1.27-1.24 (3H, m), 1.19-1.08 (1H, m).

^{13}C NMR (~101 MHz, $CDCl_3$): δ_C 174.4, 52.8, 52.4, 31.8, 30.3, 30.0, 27.4, 25.9, 25.8, 25.5, 22.4.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{11}H_{20}NO$: 182.1545 found 182.1549.

The compound is known in the literature, and the characterization data of this compound was compared with the literature data (Wei et al., ***Green Chem.*** **2014**, ***16***, 1093-1096).



1-Decyl-5-methylpyrrolidin-2-one:

(Sample code: KS-P-62)

The compound 1-decyl-5-methylpyrrolidin-2-one was obtained after purification by column chromatography on alumina (EtOAc : hexane = 10 : 90) as yellow color liquid (205 mg, 86%, 1 mmol scale);

R_f (10% EtOAc/hexane) 0.5;

IR (DCM): 2929, 1748, 1185 cm^{-1};

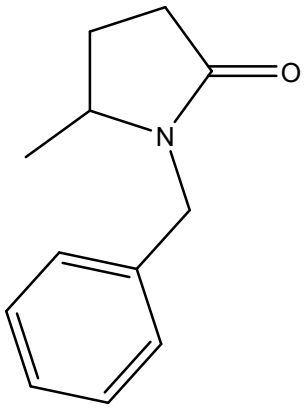
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.72-3.63 (1H, m), 3.60-3.52 (1H, m), 2.94-2.84 (1H, m), 2.44-2.26 (2H, m), 2.23-2.11 (1H, m), 1.60-1.37 (3H, m), 1.25-1.15 (17H, m), 0.88-0.85 (3H, m).

Proton count: 29

^{13}C NMR (~101 MHz, $CDCl_3$): δ_C 174.3, 52.9, 39.7, 31.7, 30.0, 29.2, 29.2, 29.0, 29.0, 27.1, 26.8, 26.5, 22.4, 19.5, 13.8.

HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{15}H_{29}NNaO$: 262.2147 found 262.2156.

The compound is known in the literature, and the characterization data of this compound was compared with the literature data (Barbaro et al., *Adv. Sustainable Syst.* **2020**, *4*, 1900117).



1-Benzyl-5-methylpyrrolidin-2-one:

The compound 1-benzyl-5-methylpyrrolidin-2-one was obtained after purification by column chromatography on alumina (EtOAc : hexane = 10 : 90) as yellow color liquid (131 mg, 69%, 1 mmol scale);

R_f (20% EtOAc/hexane) 0.5;

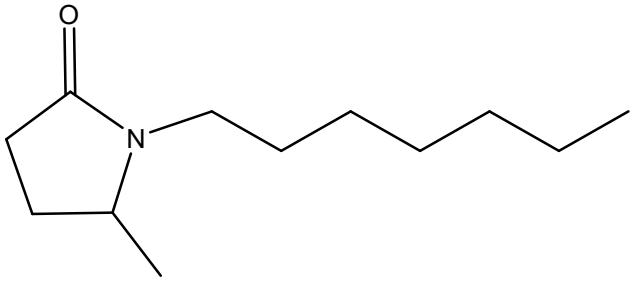
IR (DCM): 3146, 2925, 1738, 1180, 851 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.34-7.23 (5H, m), 3.99 (1H, d, J = 15.0 Hz), 4.00 (1H, d, J = 15.0 Hz), 3.56-3.48 (1H, m), 2.54-2.36 (2H, m), 2.20-2.11 (1H, m), 1.64-1.55 (1H, m), 1.16 (3H, d, J = 6.3 Hz).

^{13}C NMR (~101 MHz, $CDCl_3$): δ_C 174.3, 136.3, 128.0, 127.4, 126.8, 52.3, 43.3, 29.7, 26.1, 19.1.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{12}H_{16}NO$: 190.1232 found 190.1241.

The compound is known in the literature, and the characterization data of this compound was compared with the literature data (Wei et al., ***Green Chem.*** **2014**, ***16***, 1093-1096).



1-Heptyl-5-methylpyrrolidin-2-one:

The compound 1-heptyl-5-methylpyrrolidin-2-one was obtained after purification by column chromatography on alumina (EtOAc : hexane = 10 : 90) as yellow color liquid (121 mg, 61%, 1 mmol scale);

R_f (10% EtOAc/hexane) 0.5;

IR (DCM): 2929, 1748, 1185 cm^{-1};

^1H NMR (400 MHz, $CDCl_3$): δ_H 3.71-3.60 (1H, m), 3.58-3.48 (1H, m), 2.93-2.82 (1H, m), 2.42-2.24 (2H, m), 2.20-2.07 (1H, m), 1.57-1.34 (3H, m), 1.31-1.13 (11H, m), 0.90-0.79 (3H, m).

^{13}C NMR (~101 MHz, $CDCl_3$): δ_C 174.4, 53.0, 39.8, 31.5, 30.1, 28.8, 27.2, 26.7, 26.5, 22.3, 19.5, 13.8.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{12}H_{24}NO$: 198.1858 found 198.1858.