

PdGa/TiO₂ an efficient heterogeneous catalyst for direct methylation of N-methylaniline with CO₂/H₂

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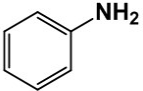
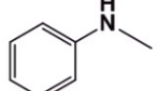
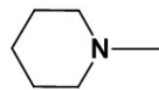
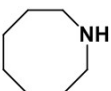
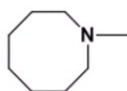
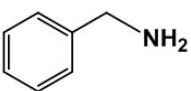
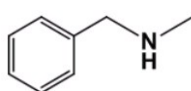
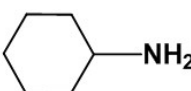
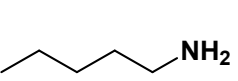
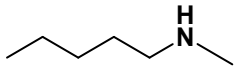
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Table S1 Comparison the catalytic performance with literature for the N-Methylation of N-methylaniline with CO₂/H₂.

Entry	Catalyst	Temp./Time (°C/h)	Yield (%)	Ref.
1	PdGa/TiO ₂	170/10	94	Present work
2	CuAlO _x	160/24	86	Chem. Sci., 2014, 5, 649 [12]
3	Pt-MoO _x /TiO ₂	200/24	82	Chem. Eur. J., 2014, 20, 6264 [14]
4	Pd/CuZrO _x	150/30	71	Chem. Commun., 2014, 50, 13521 [13]
5	[RuCl ₂ (dmsO) ₄]	100/16	98	Angew. Chem. Int. Ed., 2013, 52, 9568 [9]
6	NHC	50/24	87	Angew. Chem. Int. Ed., 2014, 53, 12876 [10]
7	[Ru(acac) ₃]	140/16	96	Angew. Chem. Int. Ed., 2013, 52, 12156 [11]

Table S2 Methylation of amines with CO₂ and H₂ over PdGa/TiO₂ catalyst

Entry	Substrates	Products	Yield/%
1			80.3
2			83.6
3			73.1
4			52
5			43
6			29

Reaction conditions: 1 mmol amine, catalyst 0.3 mol % Pd to amine, 2 mL hexane, 5 MPa CO₂, 5 MPa H₂, 180 °C, 8 h. The yields were obtained by GC-FID using biphenyl as the external standard material.