Supporting Information

Efficient Aerobic Oxidation of Amines to Imines by Cesium Promoted Mesoporous Manganese Oxide

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Chemicals

Manganese (II) nitrate tetrahydrate ($Mn(NO_3)_2.4H_2O$, ≥ 97.0) cesium nitrate ($CsNO_3$, ≥ 99.0), 1-butanol (anhydrous, 99.8%), and poly (ethylene glycol)- block- Poly(propylene glycol)-block-Poly(ethylene glycol) PEO_{20}-PPO_{70}-PEO_{20} (Pluronic P123), benzyl amine, 4-methylbenzylamine, 4-chlorobenzyl amine, 4-methoxybenzylamine, 1-napthalenemethylamine, 2-thiophenemethylamine, 4-(trifluoromethyl)benzylamine, butylamine, dodecylamine, dibenzylamine, 1,2,3,4-tetrahydroisoquinoline, manganese(III) oxide, toluene, hexane, methanol, dioxane were purchased from Sigma-Aldrich. Concentrated nitric acid (HNO_3, 68-70 %) was purchased from J. T. Baker. All chemicals were used as received without further purification. K-OMS-2, birnessite and amorphous manganese oxide were prepared by using reported procedures[1-3].

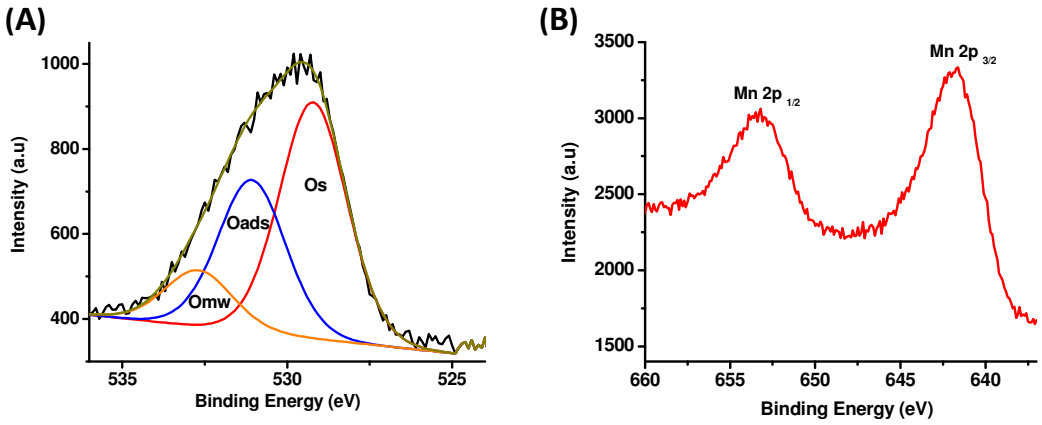


Figure S1. XPS of meso Cs/MnO_x. (A) Deconvoluted O1S spectra. Three different oxygen species were identified: Structural or lattice oxygen (O_s), surface adsorbed oxygen (O_{ads}) and adsorbed water or hydroxyl group (O_{mw}) and (B) Mn 2p spectra. The binding energy values fall in the binding energy of the Mn^{3+} oxidation state.

Table S1. XPS results of meso Cs/MnO_x

Materials	Mn (eV)		O_s		O_{ads}		O_{mw}	
	$2p_{3/2}$	$2p_{1/2}$	BE (eV)	%Area	BE (eV)	%Area	BE (eV)	%Area
UCT-18-Cs	641.5	653.2	529.2	55.3	531.0	32.1	532.5	12.6

O_s = Structural or lattice oxygen, O_{ads} = surface adsorbed oxygen, O_{mw} = adsorbed water or hydroxyl group.

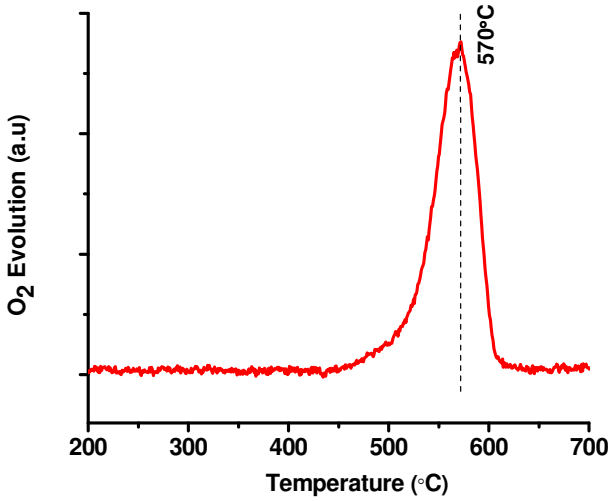


Figure S2. O_2-TPD of meso Cs/MnO_x. The peak around 570°C can be ascribed as the lattice or structural oxygen desorption from the material.

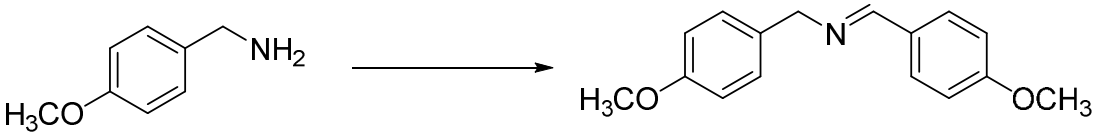


Table S2. The catalytic results using different catalysts[a]

Entry	Catalyst	Time (h)	Conversion[b] (%)	Selectivity[c] (%)	TON[d]
1	Meso Cs/MnOx	5	100	96	3.33
2	Meso MnOx	5	100	78	3.33
3	K-OMS-2[e]	5	100	42	0.87
4	Amorphous manganese oxide[e]	5	100	57	0.87
5	Birnessite[e]	8	94	96	0.82
6	C-Mn_2O_3	8	10	100	n/a
7	no	8	10	100	n/a

[a] Reaction conditions: 4-methoxy benzyl amine (0.5 mmol), catalyst (25 mg), solvent (5 mL), air balloon, 5-8 h. [b] Conversions were determined by GC-MS based on concentration of amines. [c] The side products were aldehyde and cyanide. [d]TON = moles of amines converted per mole of catalyst. [e] Catalyst: 50 mg.

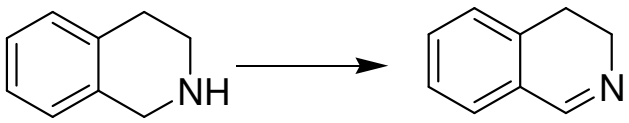


Table S3. Oxidation of 1,2,3,4-tetrahydroisoquinoline by meso Cs/MnOx with different Cs loading[a]

Entry	Catalyst	Mn/Cs[b] (nominal)	Mn/Cs[b] (ICP)	Conversion[c] (%)	Selectivity[c] (%)
1	Meso MnOx[d]	0	0	12	96
2	Meso Cs/MnOx	200/1	1767/1	87	96
3	Meso Cs/MnOx	150/1	1536/1	92	96
4	Meso Cs/MnOx	100/1	604/1	94	96

[a] Reaction conditions: 1,2,3,4-tetrahydroisoquinoline (0.5 mmol), catalyst (50 mg), solvent (5 mL), air balloon, 1 h. [b] Referred to molar ratio. [c] Determined by GC-MS. [d] 75% conversion after 24 h.

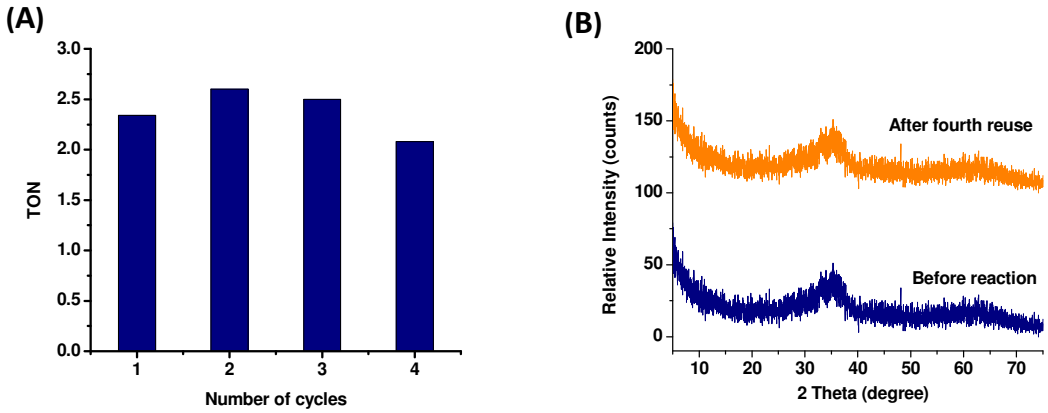


Figure S3. (A) Reusability test of the catalyst. Reaction condition: 4-methoxybenzylamine (0.5 mmol), catalyst (15 mg), solvent (5 mL), 110°C, air balloon, 4 h. Turnover number (TON) = [reacted mol amine]/[total mol catalyst]. (B) PXRD of meso Cs/MnOx before and after fourth reuse. The diffraction patterns without noticeable change were observed after fourth reuse.

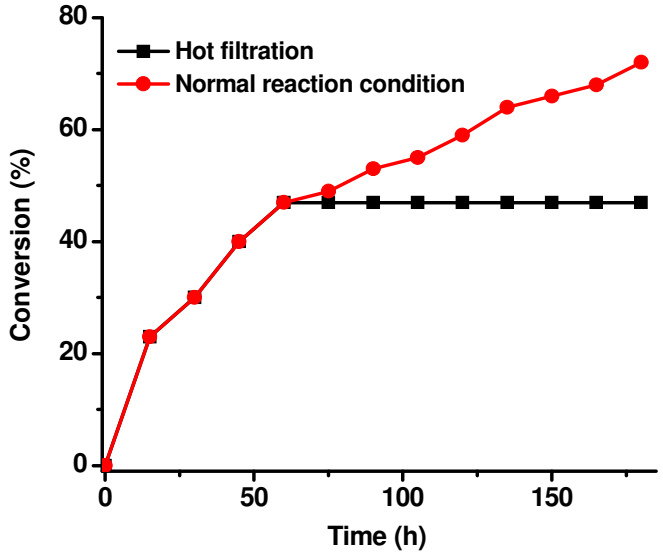


Figure S4. Test of heterogeneity. Catalyst was removed after 47% conversion, no change of conversion was observed thereafter. Reaction condition: 4-methoxybenzylamine (0.5 mmol), meso Cs/MnO_x (25 mg), solvent (5 mL), 110°C, air balloon, 3 h.

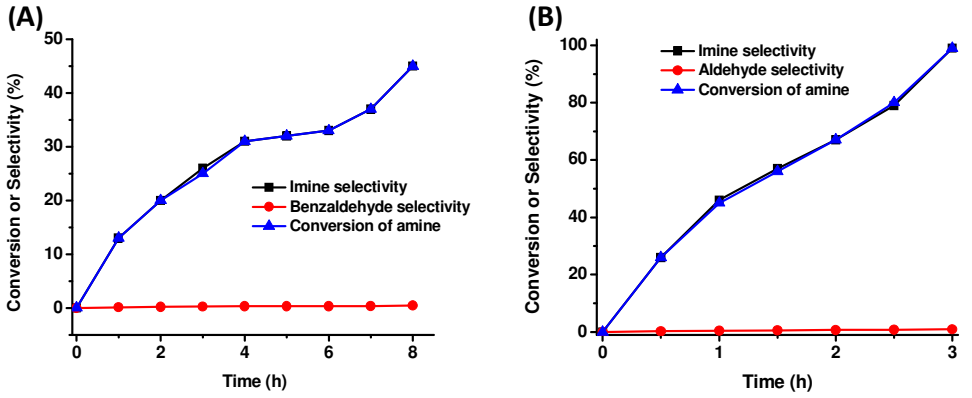


Figure S5. Time dependent studies of 4-methoxybenzylamine by meso Cs/MnOx : (A) at 80°C and (B) at 110°C. Reaction condition: 4-methoxybenzylamine (0.5 mmol), catalyst (25 mg), solvent (5 mL), O_2 balloon, 3/8 h. The formation of benzaldehyde was clearly observed in both cases.

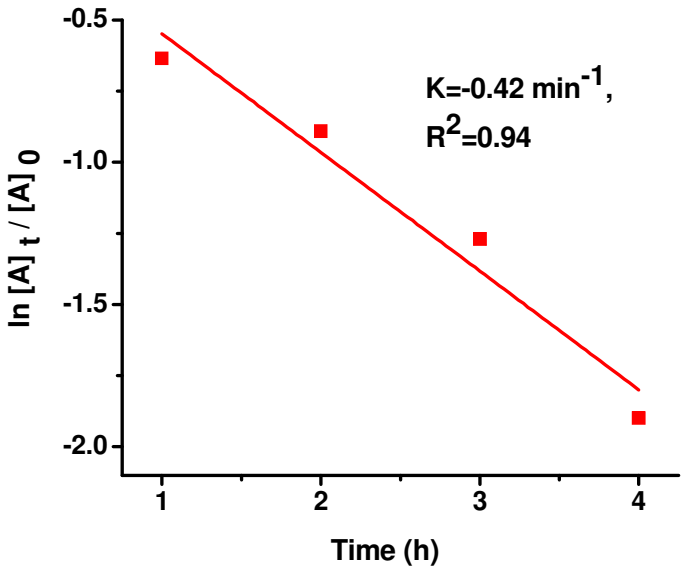


Figure S6. Kinetic study for the oxidation of amine by meso Cs/MnO_x. The reaction exhibited a first order rate dependence with respect to amine having the rate constant of 0.42 min^{-1}. Reaction condition: 4-Methoxybenzylamine (0.5 mmol), catalyst (50 mg), solvent (5 mL), air balloon. A_0: original concentration of substrate. A_t: concentration of substrate at time t. K: rate constant.

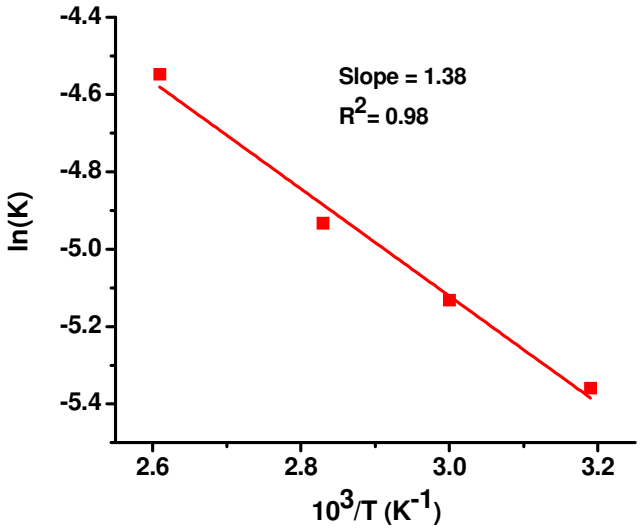


Figure S7. Arrhenius plot for the oxidation of amine by meso Cs/MnO_x. The apparent activation energy was estimated as 11.5 $KJmol^{-1}$. Reaction condition: 4-Methoxybenzylamine (0.5 mmol), catalyst (50 mg), solvent (5 mL), air balloon, 1 h. K: rate constant.

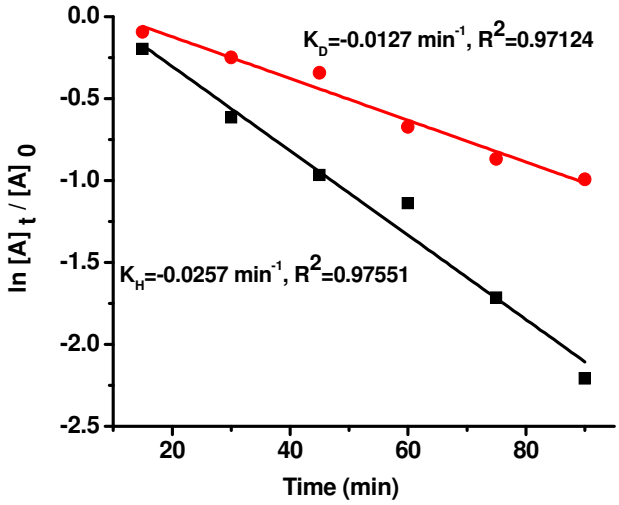


Figure S8. Kinetic plot of oxidation of benzylamine and benzylamine-α,α-d_2. The ratio of K_H/K_D = 2.02; which signified the oxidative dehydrogenation of benzylamine was the rate determining step. Reaction condition: amine (0.5 mmol), catalyst (25 mg), solvent (5 mL), 110°C, air balloon, 3 h. A_0: original concentration of substrate. A_t: concentration of substrate at time t. k: rate constant.

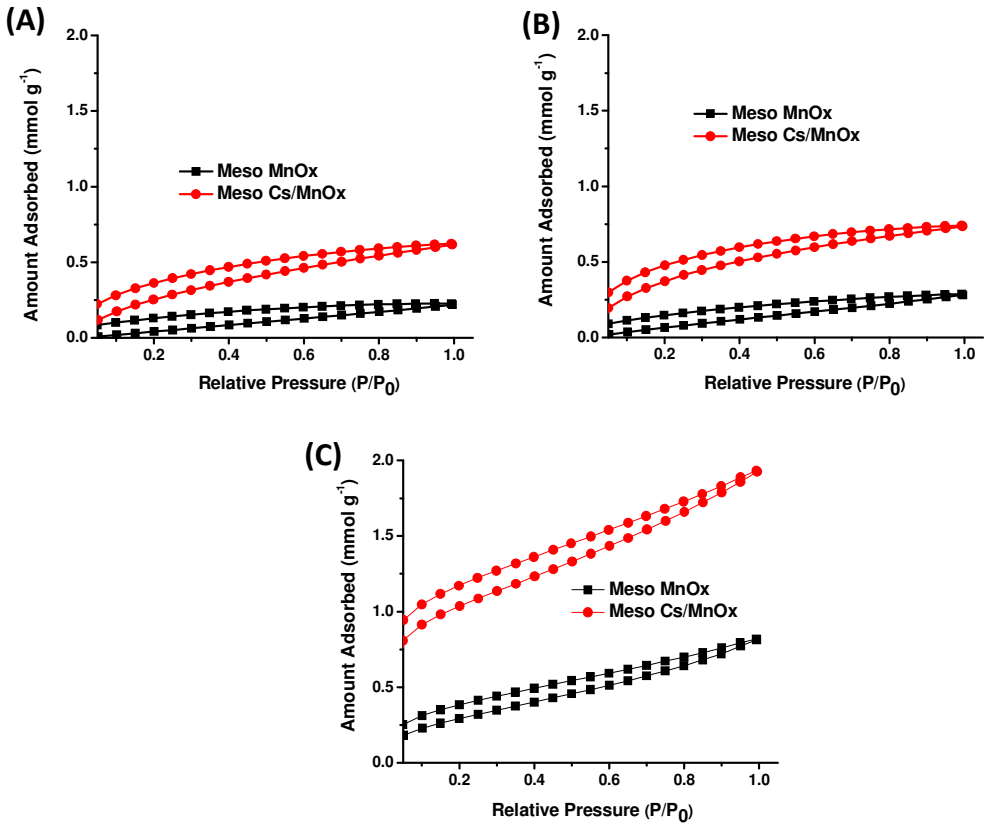
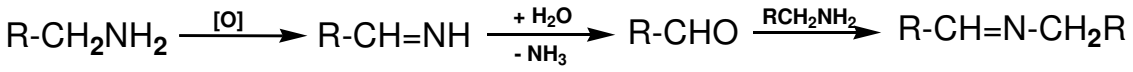
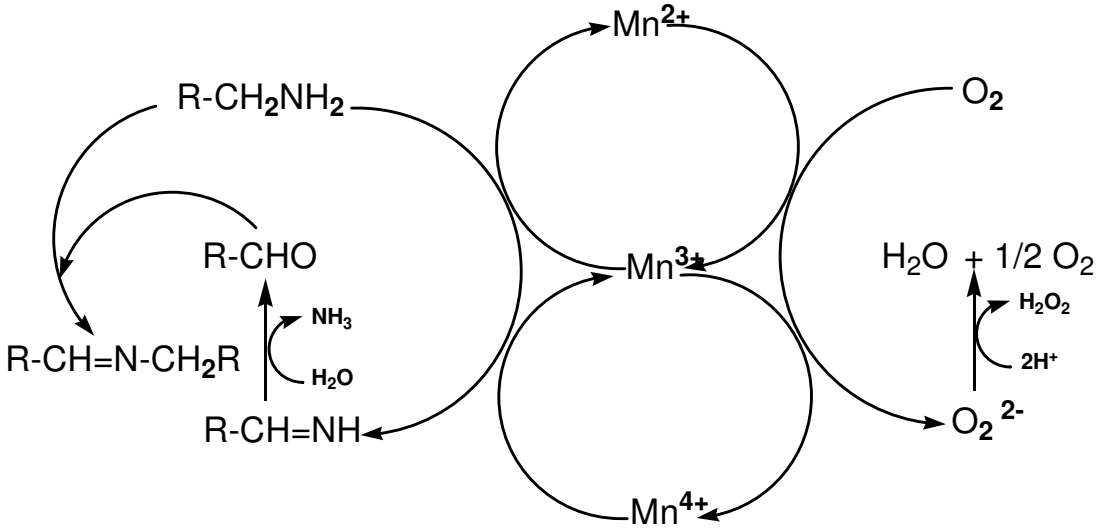


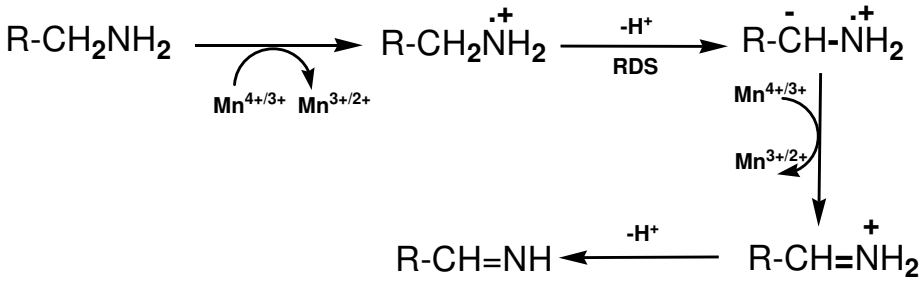
Figure S9. CO_2 adsorption experiment of meso MnOx and meso Cs/MnOx at three different temperatures: (A) room temperature, (B) 0 °C, and (C) -78 °C.



Scheme S1. Reaction pathways of oxidative coupling of amines over metal oxides

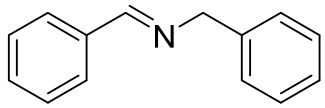


Scheme S2. Suggested overall mechanism of oxidation of amines over meso Cs/MnO_x following Mars-Van-Krevelen mechanism.



Scheme S3. Proposed reaction pathways of Mn mediated RCH=NH formation from amine. The forming of negatively charged intermediate due to abstraction of proton by oxidative dehydrogenation is the rate determining step (RDS).

Characterization of typical products

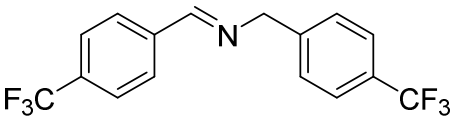


N-benzylidene benzylamine

Appearance: Yellow oil

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.41 (s, 1H), 7.80 (d, *J* = 4.2 Hz, 2H), 7.43 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.37 (s, 4H), 7.27 (s, 1H), 4.85 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.78, 130.56, 128.41, 128.30, 128.09, 127.79, 126.79, 64.86.

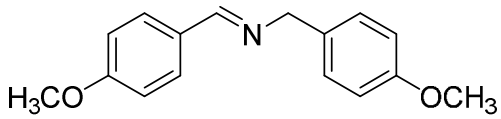


N-(4-(trifluoromethyl)benzylidene)(4-(trifluoromethyl)phenyl)methanamine

Appearance: Yellow oil

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.47 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 4.90 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.91, 142.85, 138.83, 128.34, 127.94, 125.39 (dd, *J* = 16.5, 3.6 Hz), 64.22.



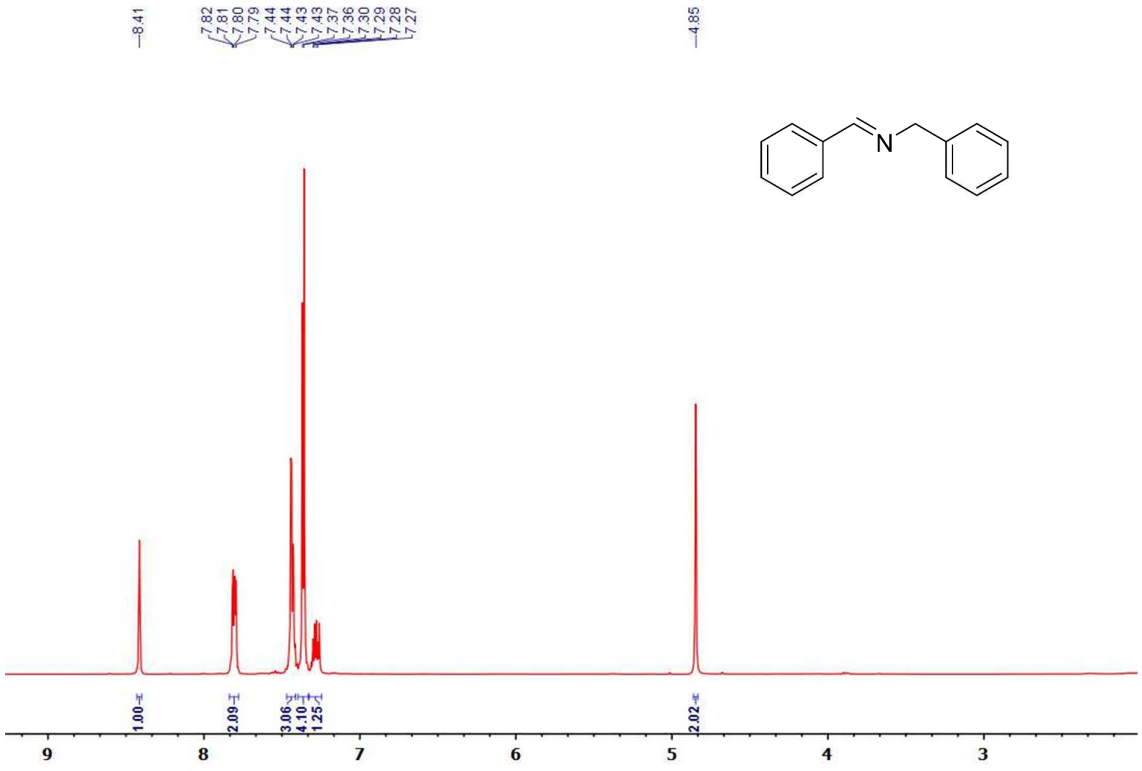
N-(4-methoxybenzylidene)(4-methoxyphenyl)methanamine

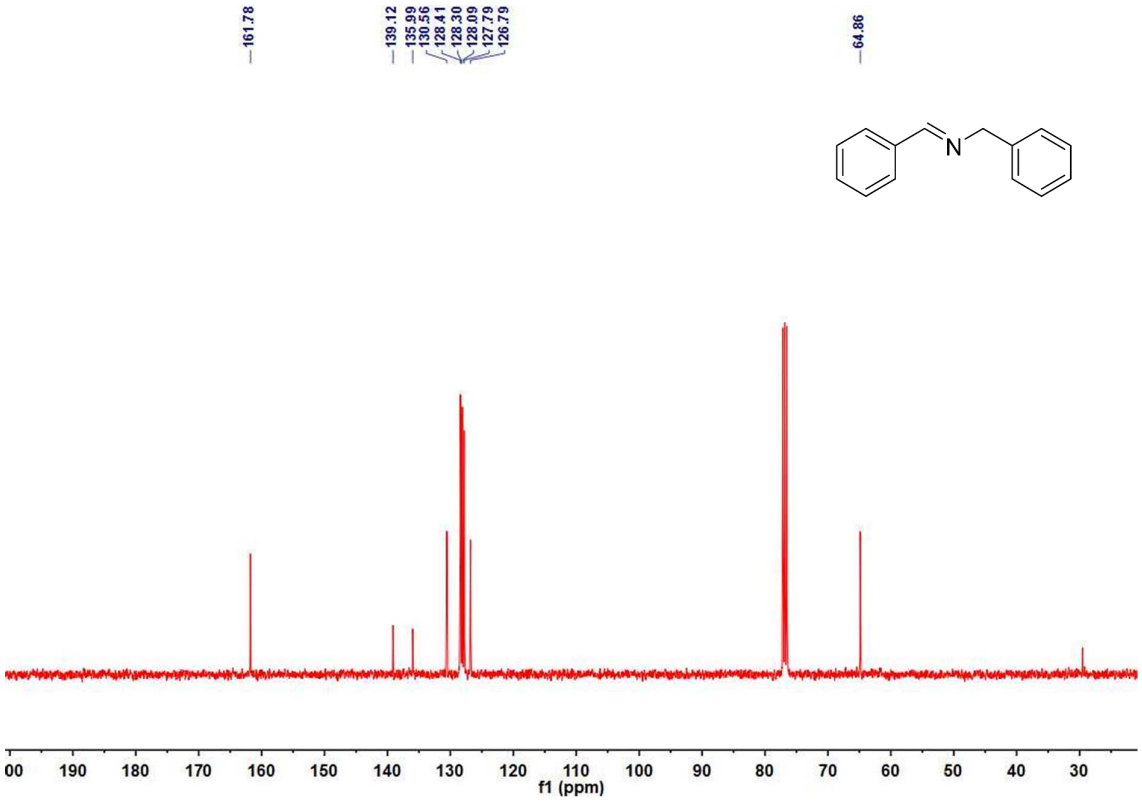
Appearance: Yellow oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.68 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.22 (m, 4H), 5.11 (s, 2H), 4.20 (d, *J* = 14.6 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.06, 161.28, 159.04, 132.09, 130.19, 129.55, 114.33 (d, *J* = 6.7 Hz), 64.79, 55.72.

[1]HNMR and [13]CNMR of typical products

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100
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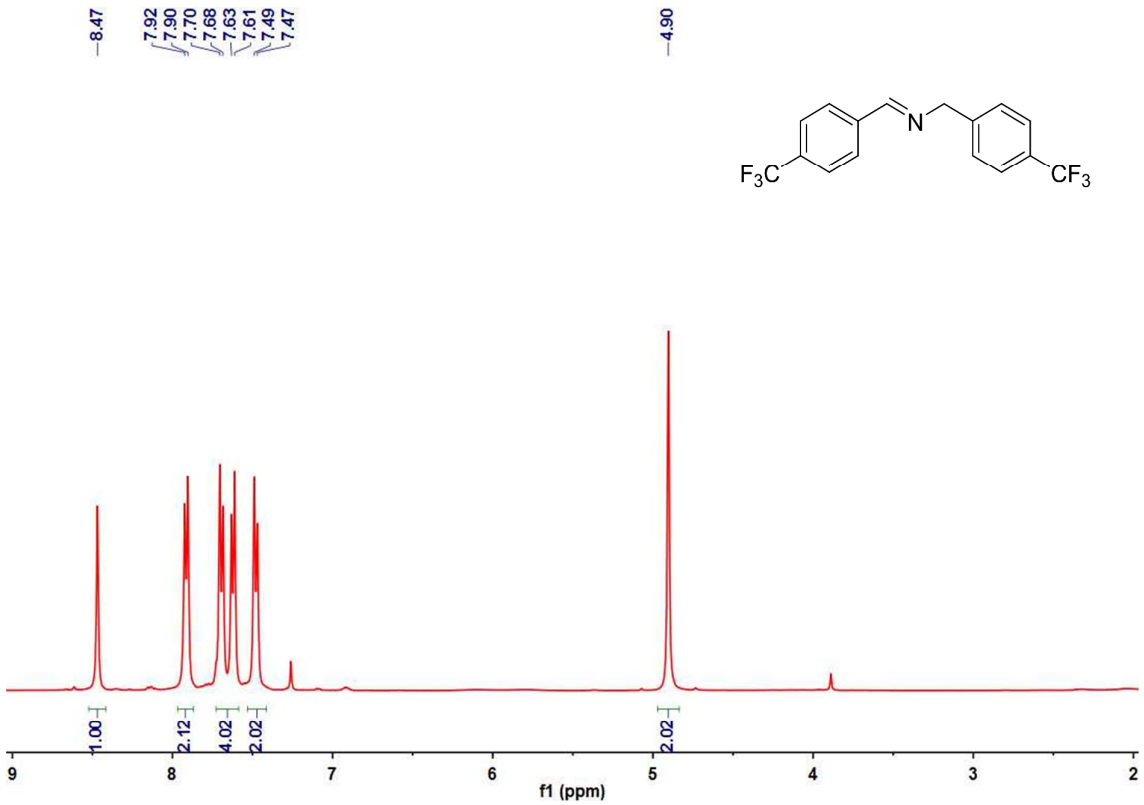
f1 (ppm)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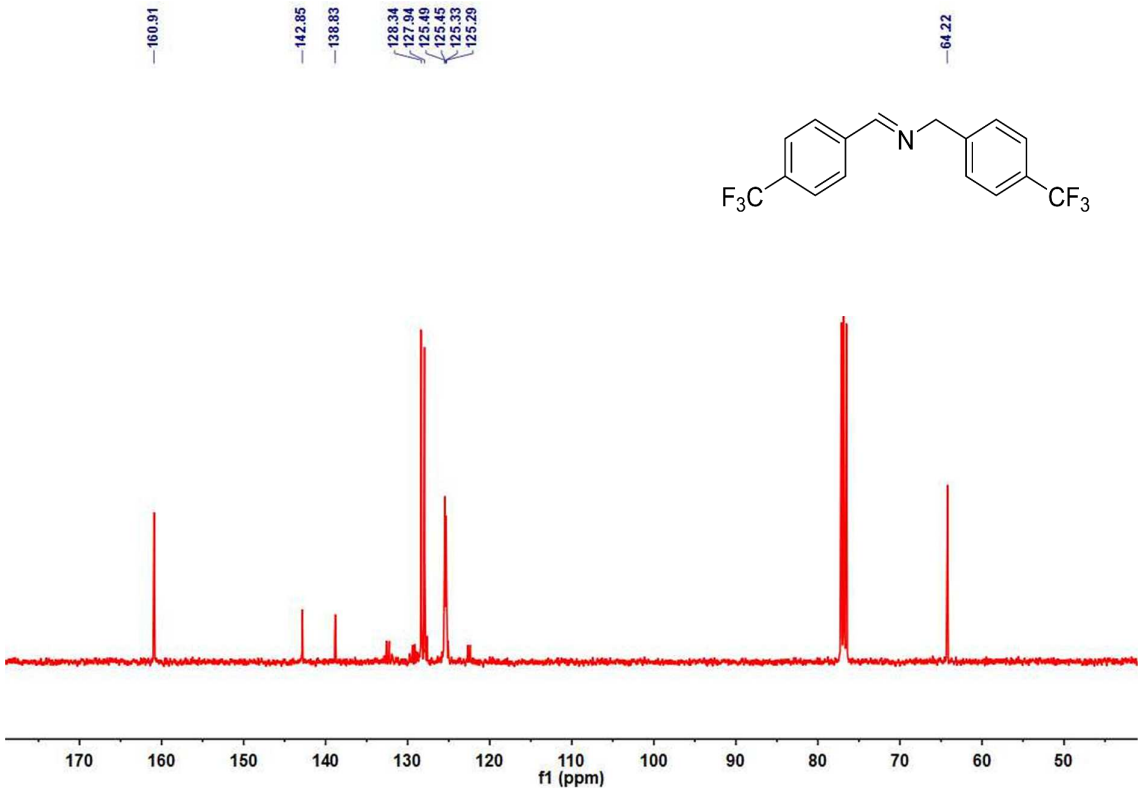
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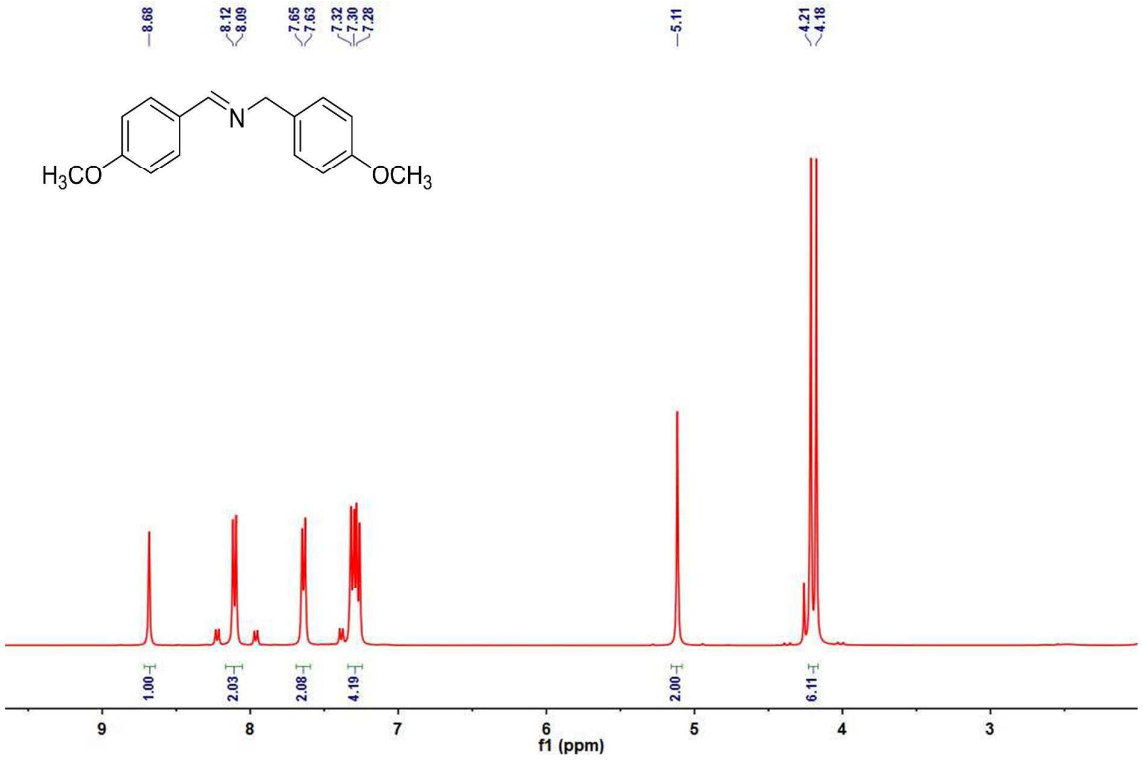
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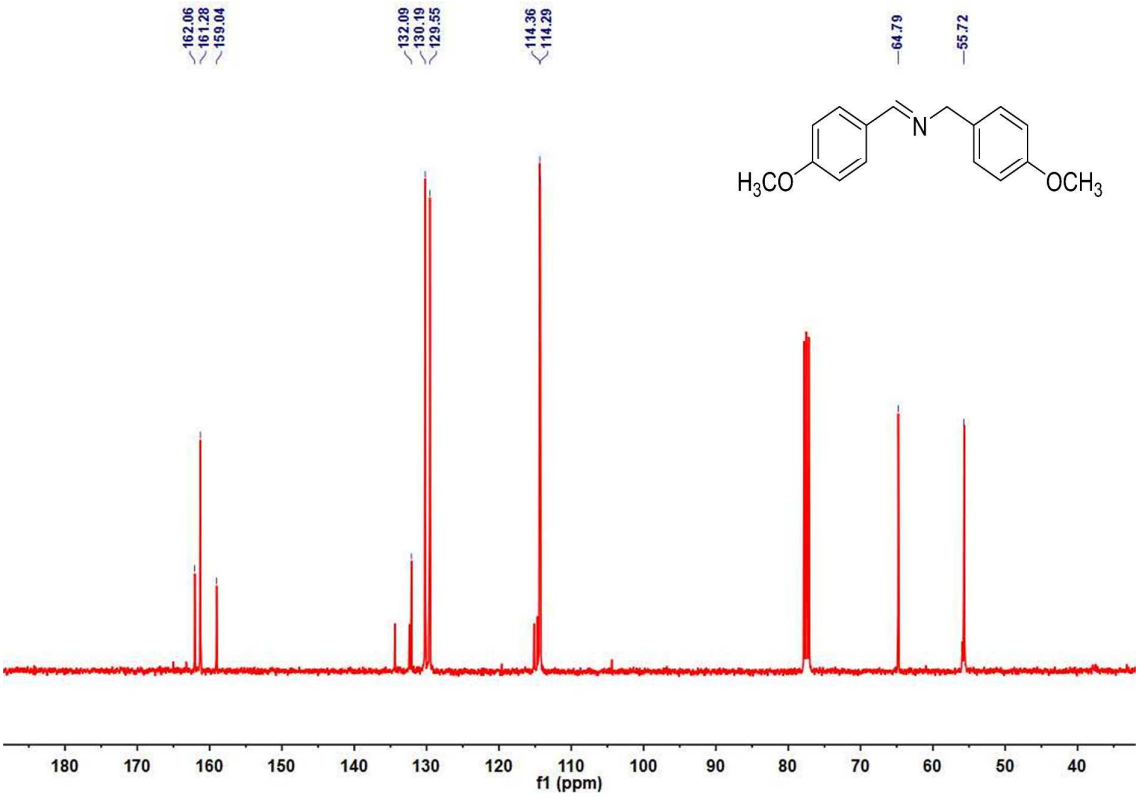

References:

(1) DeGuzman, R. N.; Shen, Y.-F.; Neth, E. J.; Suib, S. L.; O'Young, C.-L.; Levine, S.; Newsam, J. M. *Chem. Mat.* **1994**, *6*, 815-821.

(2) Kuo, C. H.; Li, W.; Pahalagedara, L.; El-Sawy, A. M.; Kriz, D.; Genz, N.; Guild, C.; Ressler, T.; Suib, S. L.; He, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 2345-2350.

(3) Cao, H.; Suib, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 5334-5342.