Supporting Information

Methylation of Amines, Nitrobenzenes and Aromatic Nitriles with Carbon Dioxide and Molecular Hydrogen

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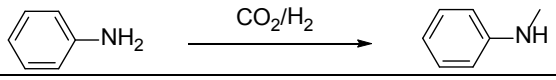
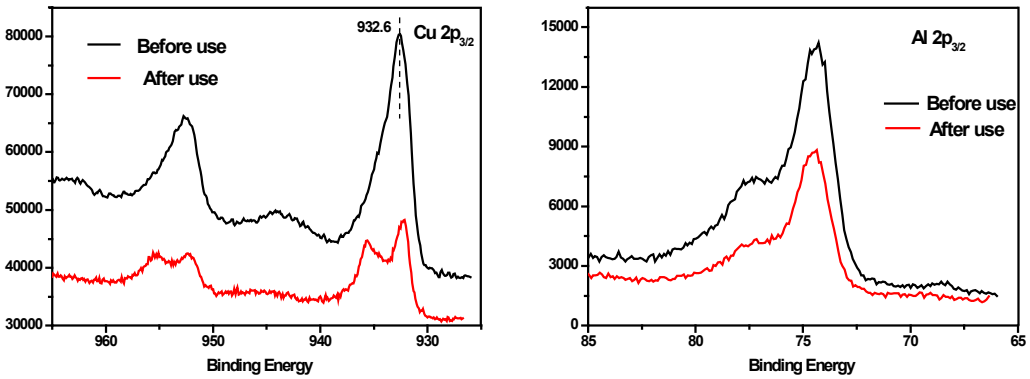
1. Table S1. Catalyst screening using mono-methylation of aniline as model reaction



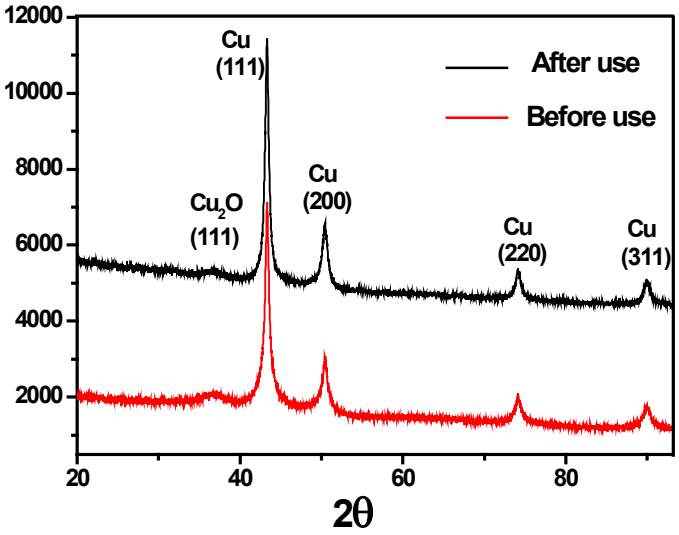
Entry	Catalyst	Al : Cu/mol : mol	Con./%	Yield/%
1	---	---	0	0
2	Al_2O_3	---	0	0
3	Cu	---	1	0
4	CuO	---	3	2
5	Cu_2O	---	4	<1
6	Al_2O_3-Cu	1 : 1	3	<1
7	Al_2O_3-CuO	1 : 1	6	2
8	Al_2O_3-Cu_2O	1 : 1	3	<1
9	Al_2O_3-Cu-Cu_2O	1 : 0.9 : 0.1	4	2
10	CuAlOx	1 : 1	95 (97[a])	86(82[a])

Reaction conditions: 1.0 mmol aniline, 50 mg catalyst, 2 mL hexane, 3.0 MPa CO_2, 6.0 MPa H_2, 160 °C, 24 h. The yields were obtained by GC-FID using biphenyl as external standard. [a] yield at the 3rd run.

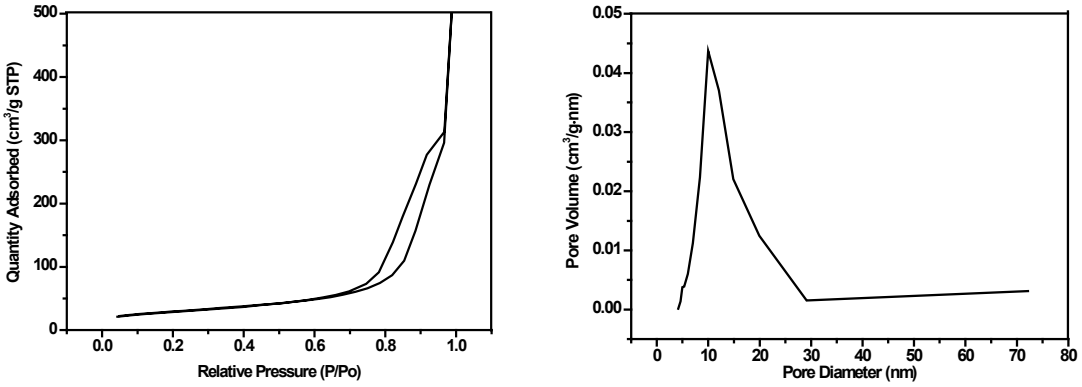
2. Figure S1. XPS diffraction patterns of prepared CuAlOx



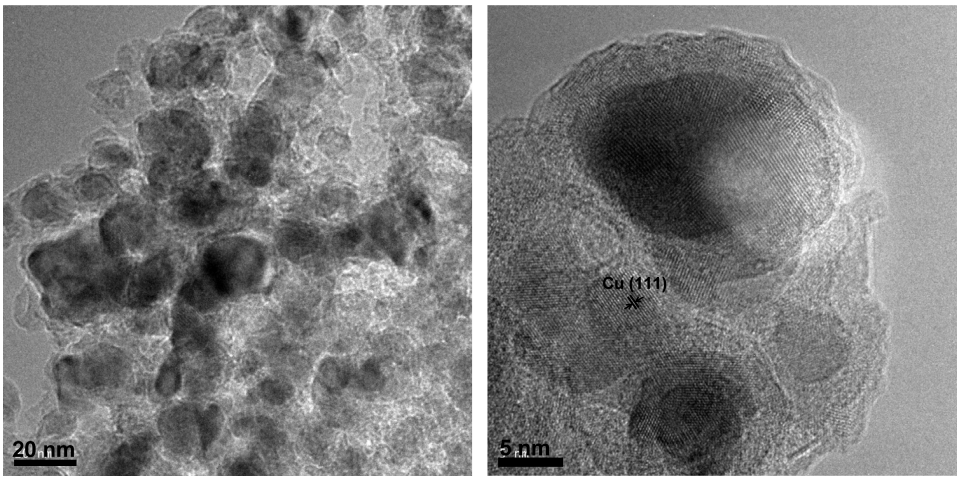
3. Figure S2. XRD diffraction patterns of prepared Cu-Al-Ox



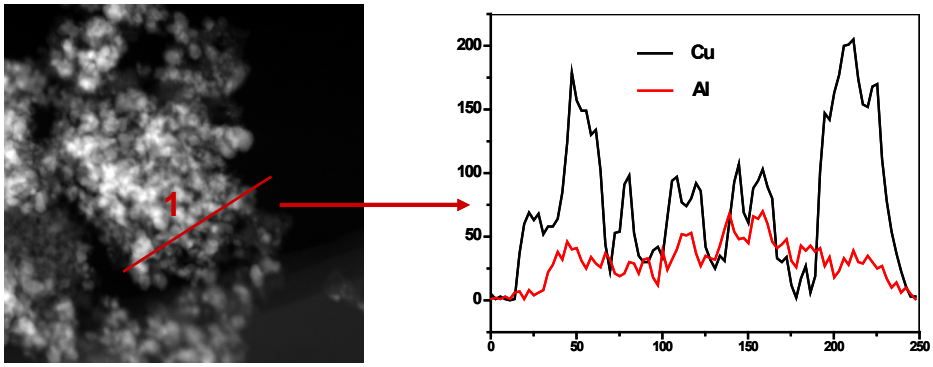
4. Figure S3. BJH Desorption patterns of prepared Cu-Al-Ox



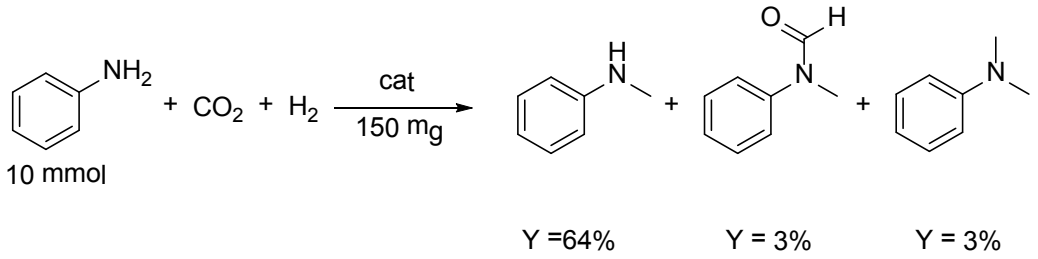
5. Figure S4. TEM (left) and HR-TEM (right) images of CuAlOx catalyst sample after use.



6. Figure S5. Line-scan EDS analysis across the catalyst after use.

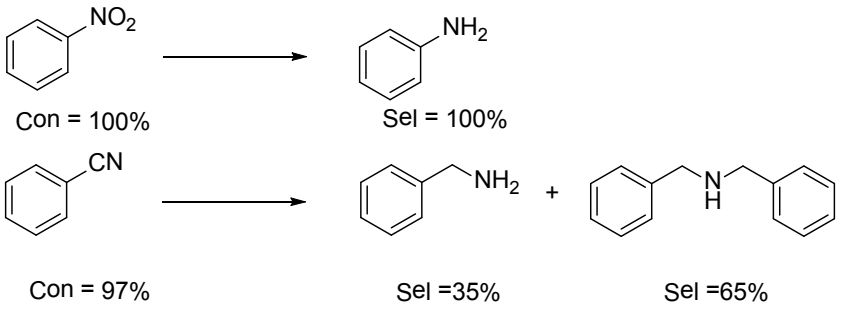


7. Scheme S1. The methylation reaction of aniline in a large scale.



Reaction conditions: 10 mmol amine, 150 mg catalyst, 5 mL hexane, 3.0 MPa CO_2, 6.0 MPa H_2, 160 ^oC, 24 h.

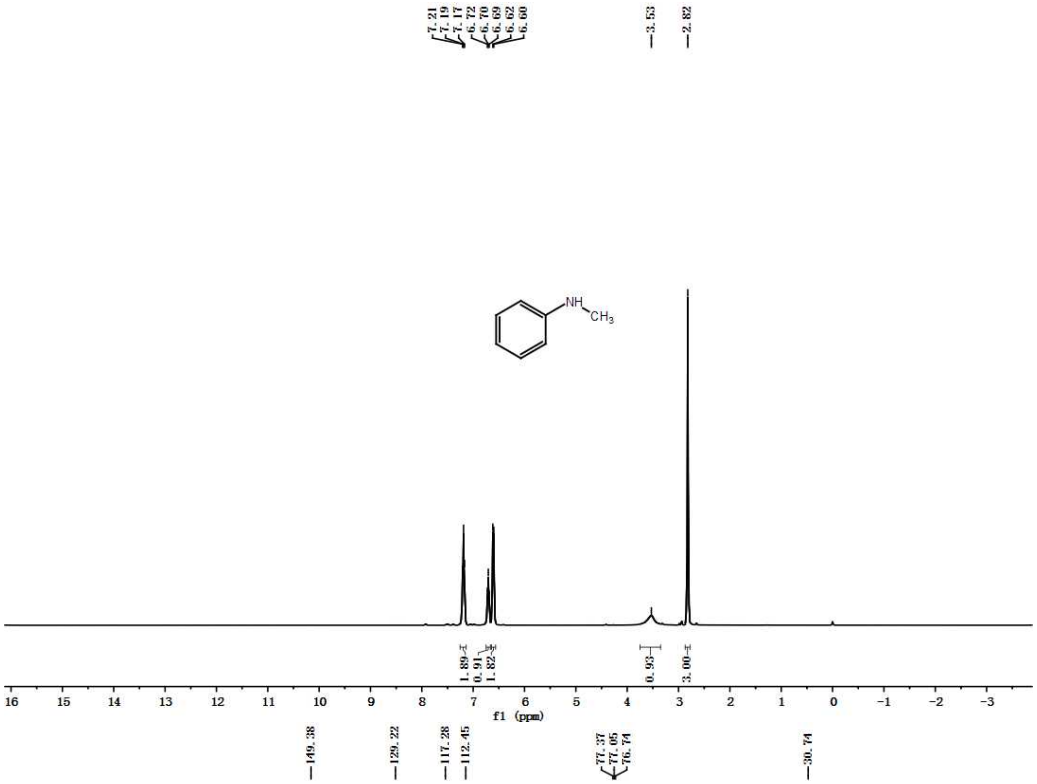
8. Scheme S2. The hydrogenation of nitrobenzene and benzonitrile.

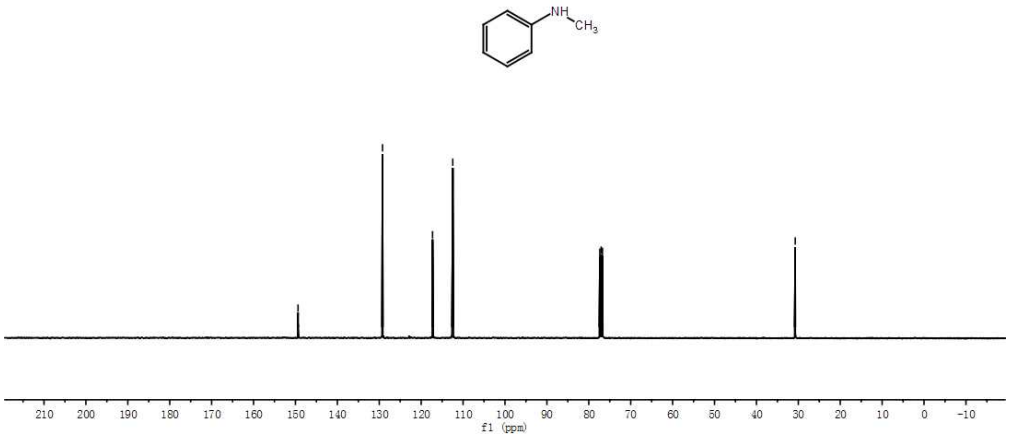


Reaction conditions: 1.0 mmol nitrobenzene or nitrile, 50 mg catalyst, 2 mL hexane, 6.0 MPa H_2, 160 ^oC, 12 h.

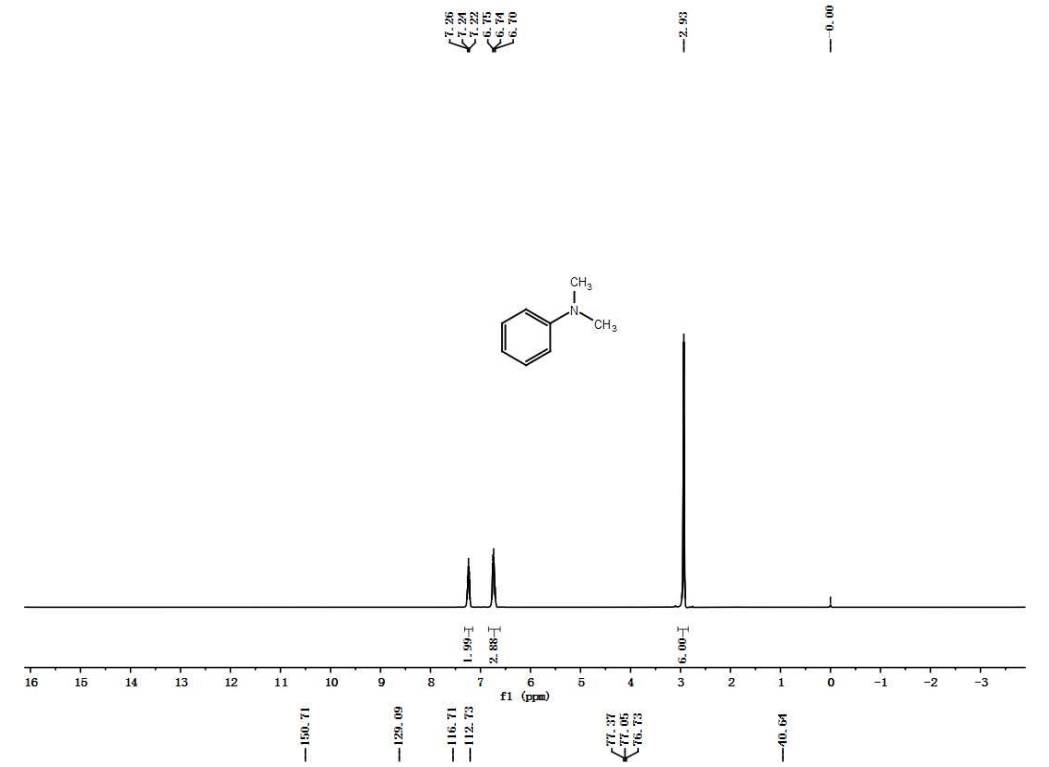
9. ^{1}H and ^{13}C NMR spectra of the isolated compounds

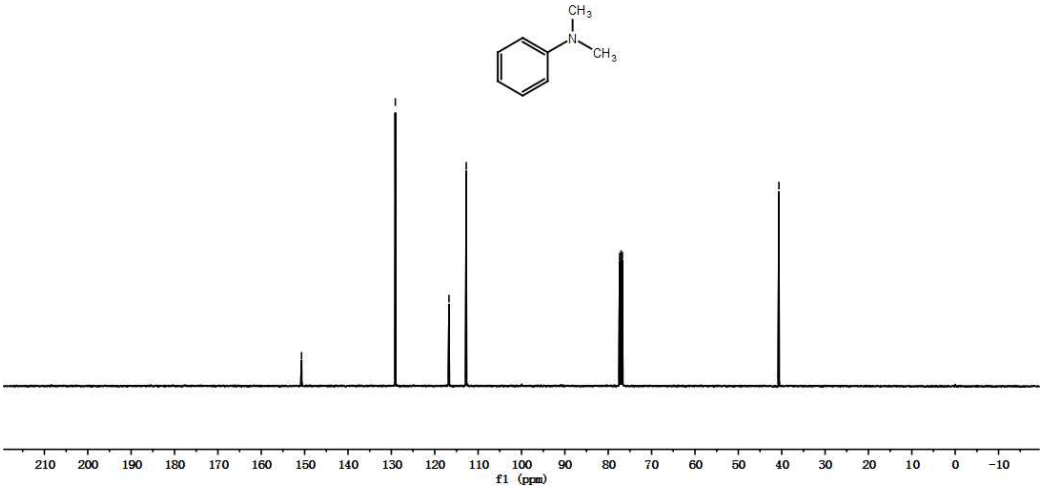
N-methylaniline: (Table 1, Entry 1) (GC purity 98%); The typical procedure for the N-methylation of aniline was followed: 95 mg aniline, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 3.0 MPa CO_2 and 6.0 MPa H_2 were introduced. The reaction was reacted at 160 ^{o}C for 24 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ethyl acetate (150 : 1) to give a brown liquid (88.5 mg, 81% yield).

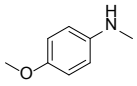




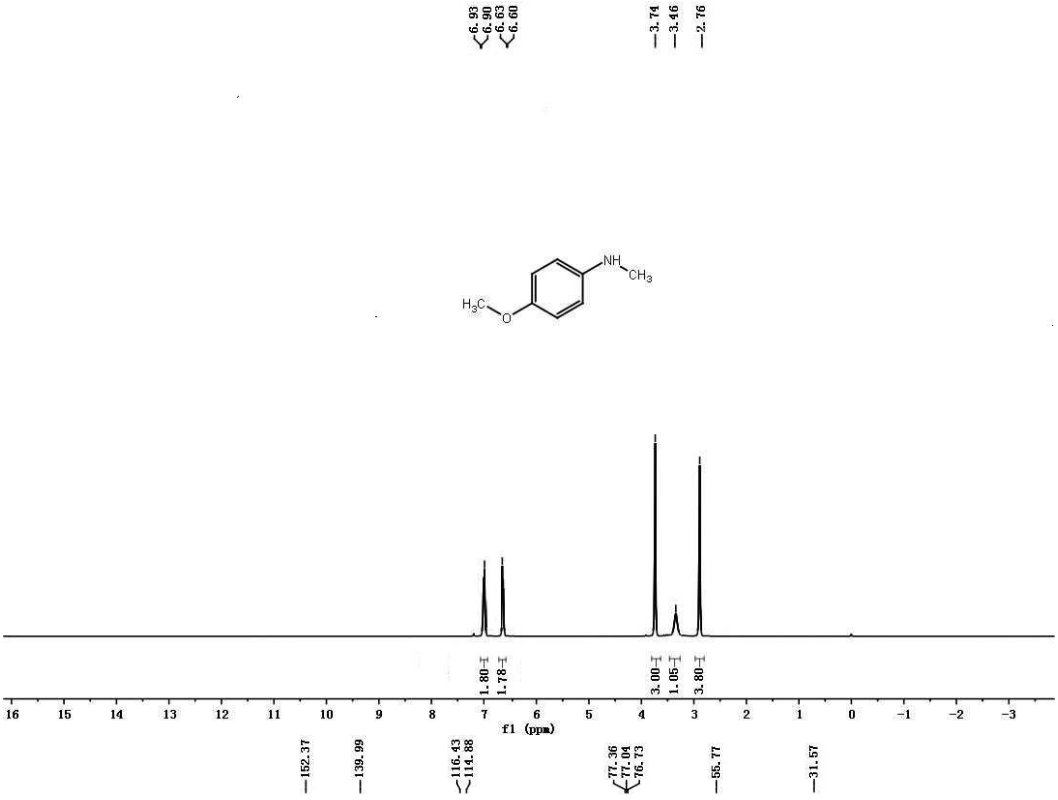
N,N-dimethylaniline: (Table 1, Entry 8) (GC purity 99%); The typical procedure for the N,N-dimethylation of aniline was followed: 94 mg aniline, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 3.0 MPa CO_2 and 7.0 MPa H_2 were introduced. The reaction was reacted at 160 ^oC for 48 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ethyl acetate (200 : 1) to give a brown liquid (94 mg, 77% yield).

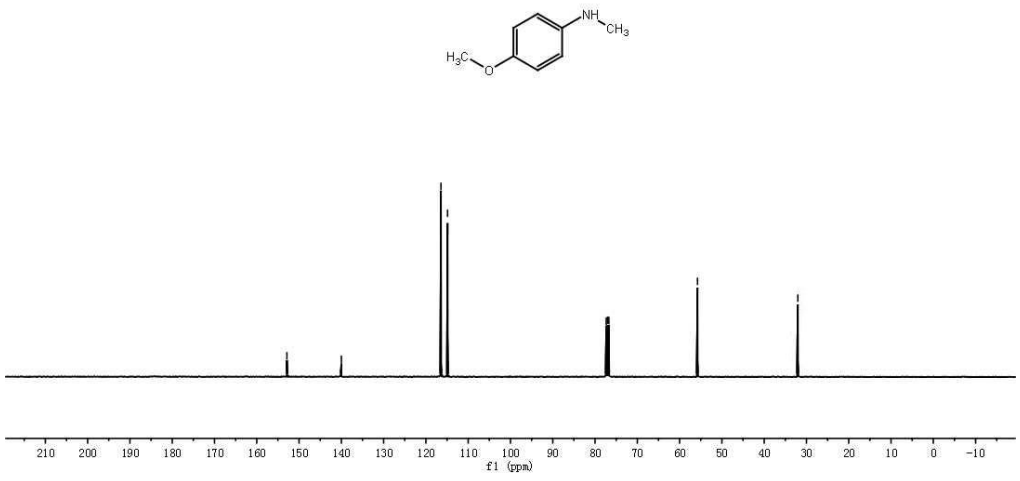


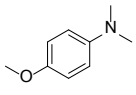




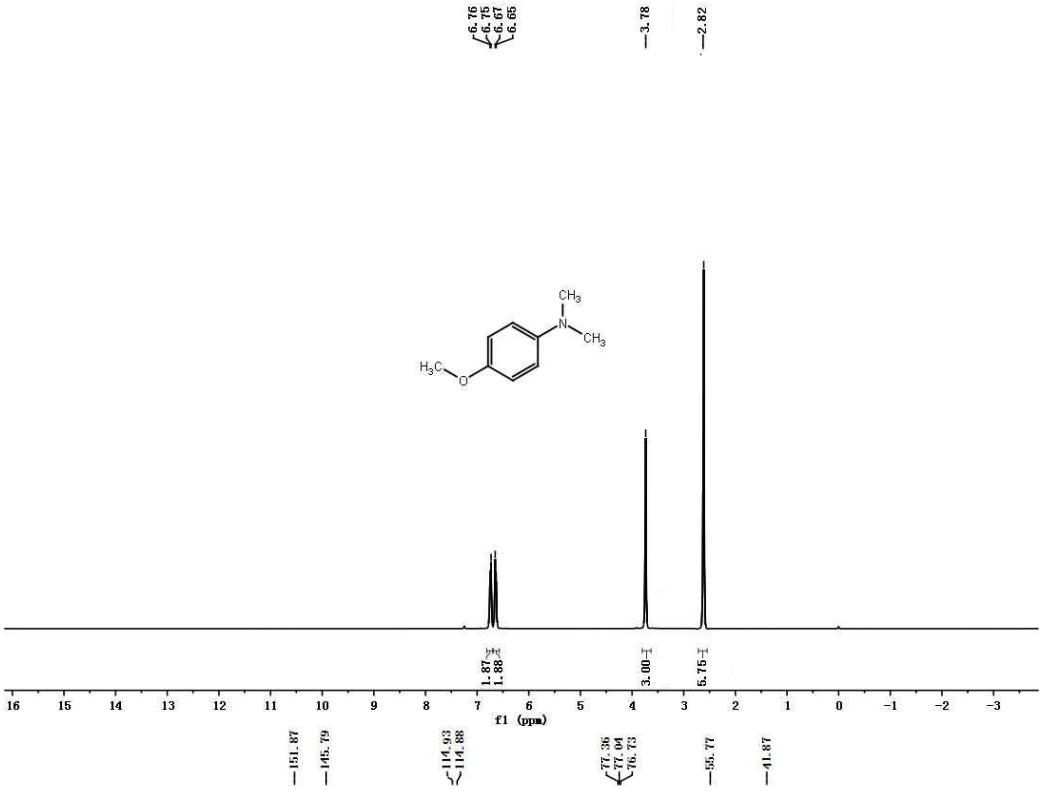
4-methoxy-N-methoxylaniline: (Table 1, Entry 3) (GC purity 98%); The typical procedure for the N-methylation of 4-methoxyaniline was followed: 125 mg 4-methoxyaniline, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 3.0 MPa CO_2 and 6.0 MPa H_2 were introduced. The reaction was reacted at 160 ^oC for 24 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ethyl acetate (130 : 1) to give a brown solid (103 mg, 74% yield).

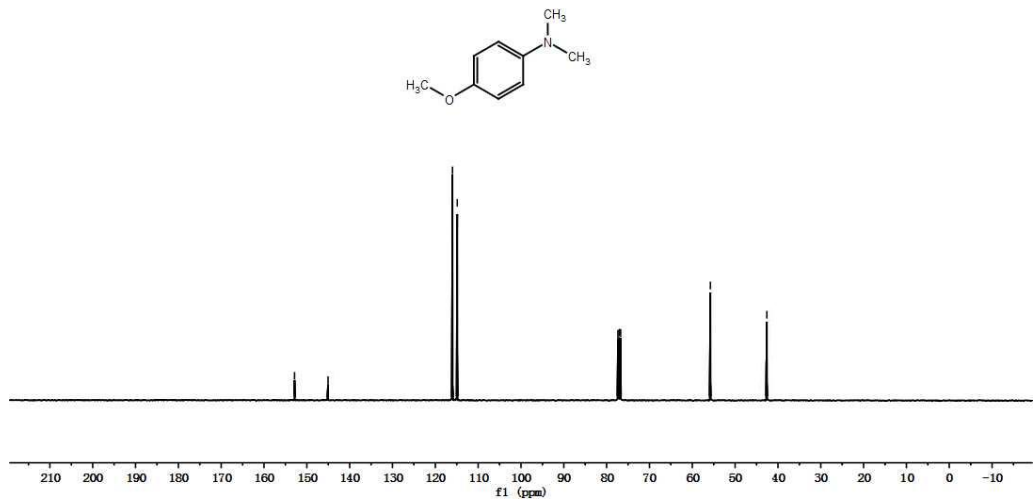


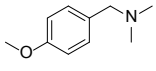




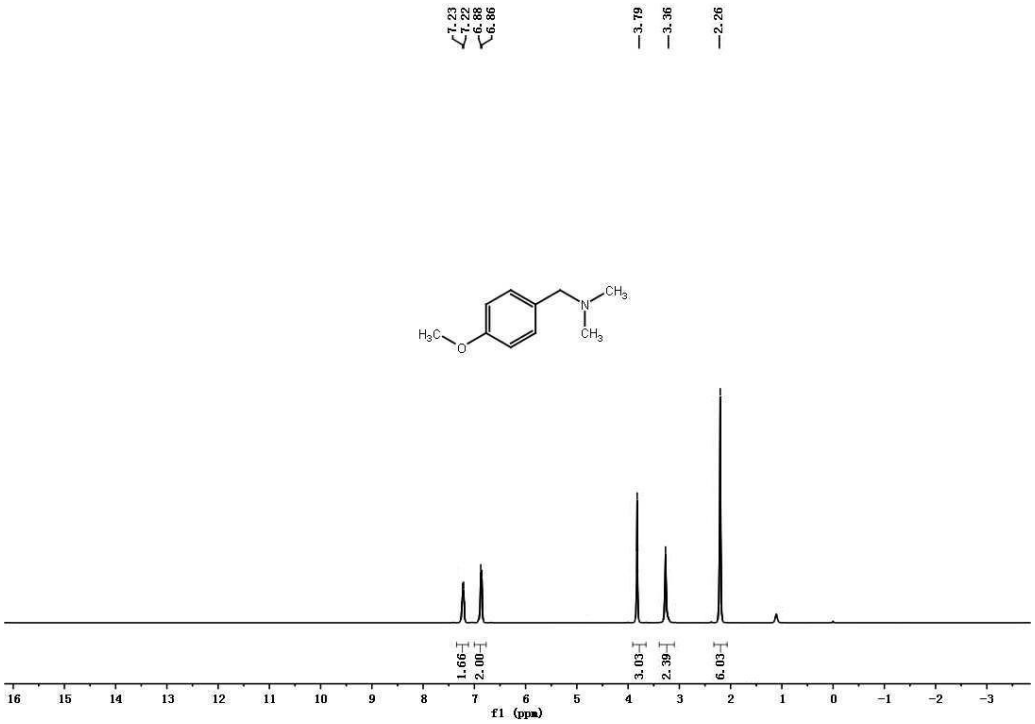
4-methoxy-N,N-dimethoxylaniline: (Table 1, Entry 10) (GC purity 99%); The typical procedure for the N,N-dimethylation of 4-methoxyaniline was followed: 122 mg 4-methoxyaniline, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 3.0 MPa CO_2 and 7.0 MPa H_2 were introduced. The reaction was reacted at 160 ^oC for 48 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ethyl acetate (185 : 1) to give a brown solid (123 mg, 82% yield).

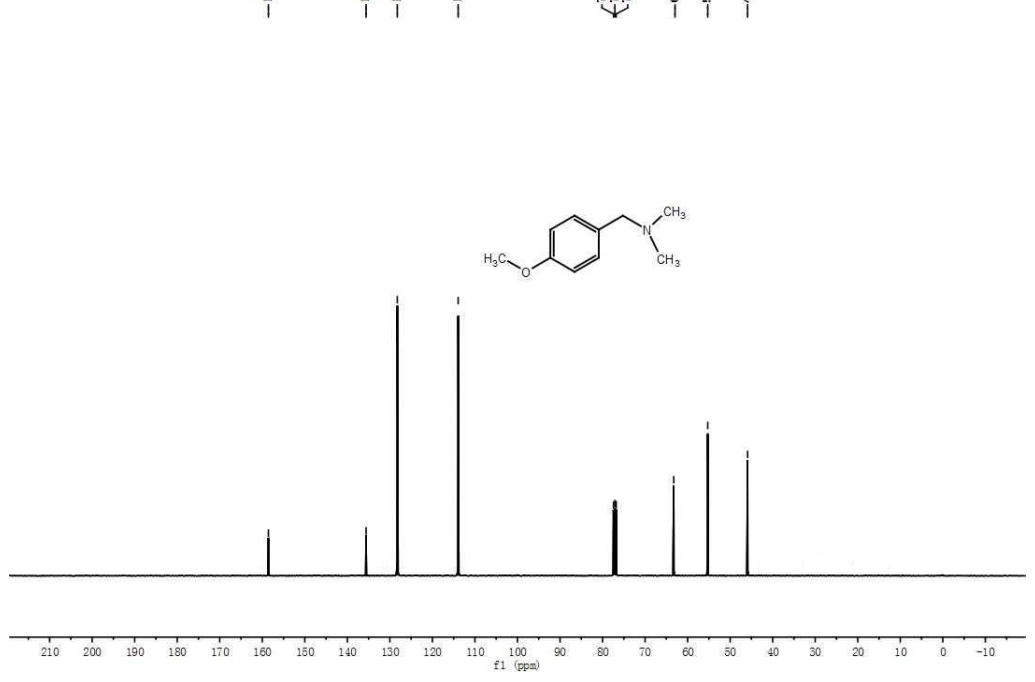


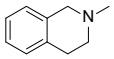




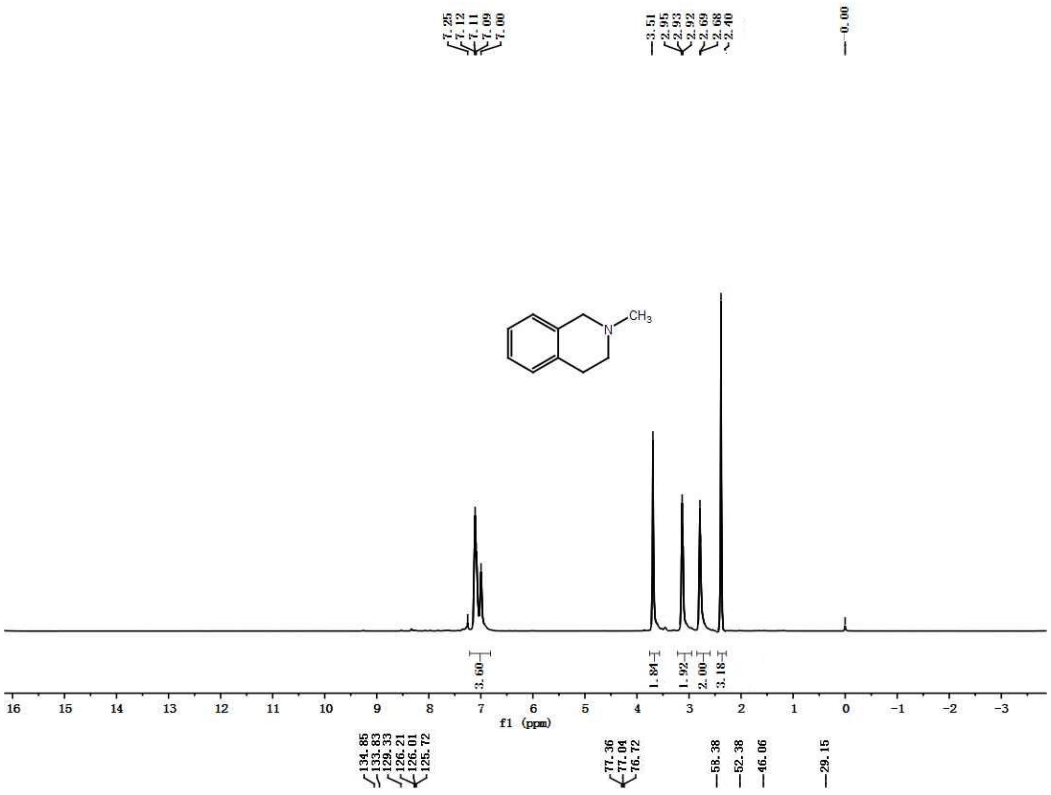
1-(4-methoxyphenyl)-N,N-dimethylmethanamine: (Table 1, Entry 14) (GC purity 97%); The typical procedure for the N,N-dimethylation of (4-methoxyphenyl)methanamine was followed: 140 mg (4-methoxyphenyl)methanamine, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 3.0 MPa CO_2 and 7.0 MPa H_2 were introduced. The reaction was reacted at 160 ^{o}C for 48 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ ethyl acetate (5 : 1) to give a brown liquid (116 mg, 69% yield).

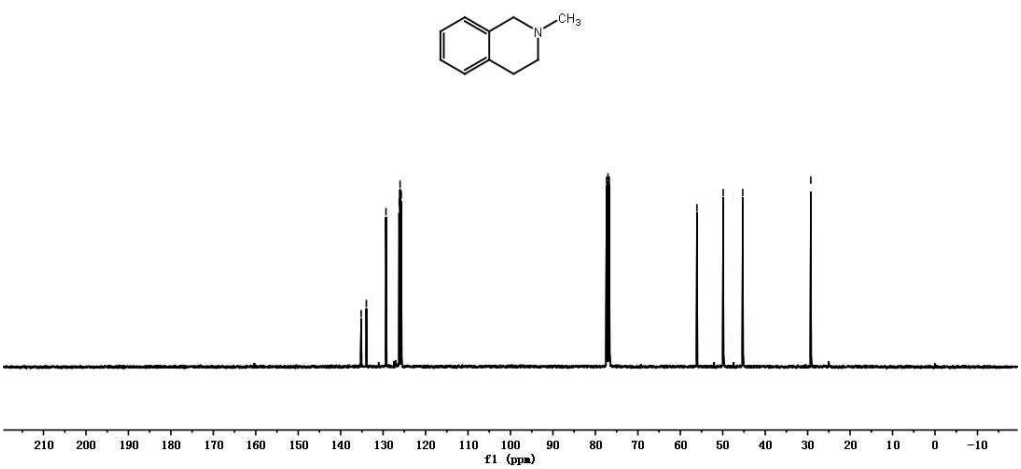


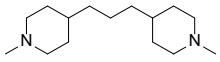




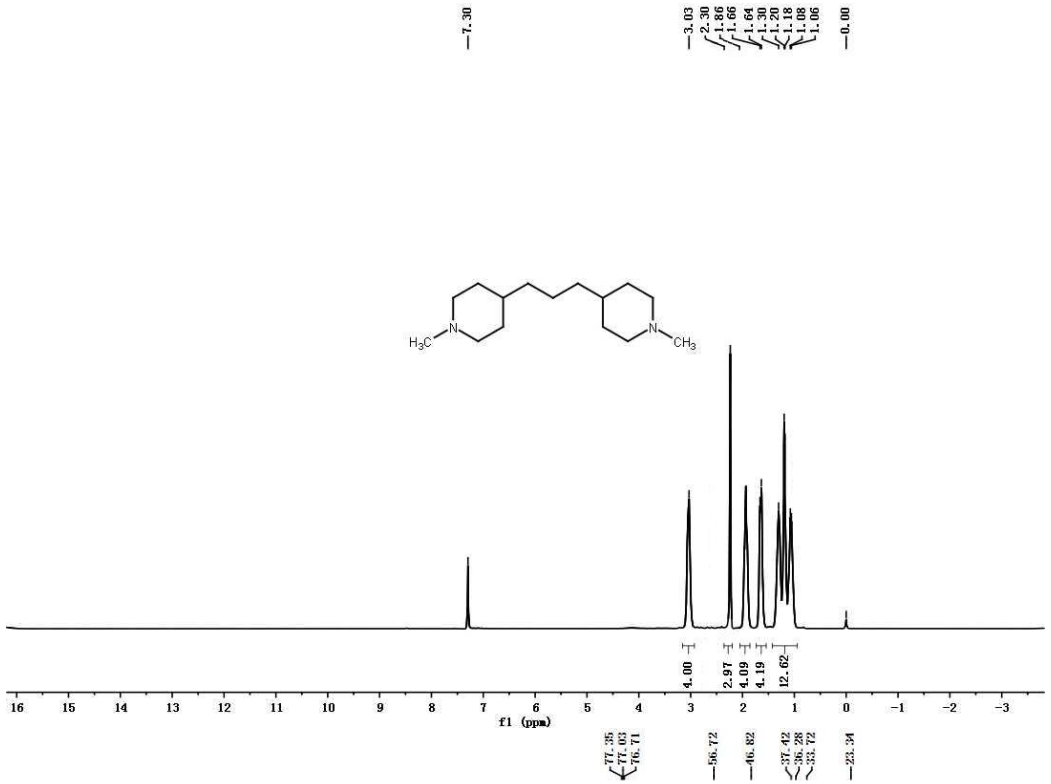
2-methyl-1,2,3,4-tetrahydroisoquinoline: (Table 2, Entry 8) (GC purity 97%); The typical procedure for the N-methylation of 1,2,3,4-tetrahydroisoquinoline was followed: 134 mg 1,2,3,4-tetrahydroisoquinoline, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 3.0 MPa CO_2 and 7.0 MPa H_2 were introduced. The reaction was reacted at 160 ^oC for 24h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ ethyl acetate (5 : 1) to give a brown liquid (130 mg, 87% yield).

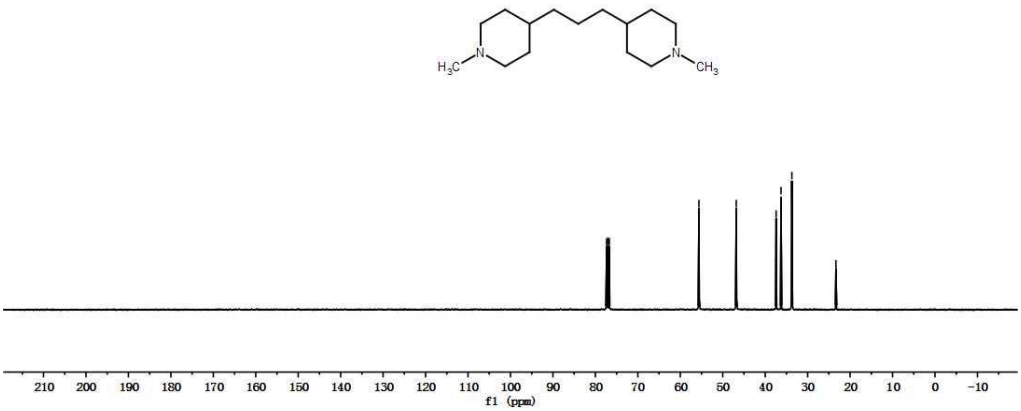




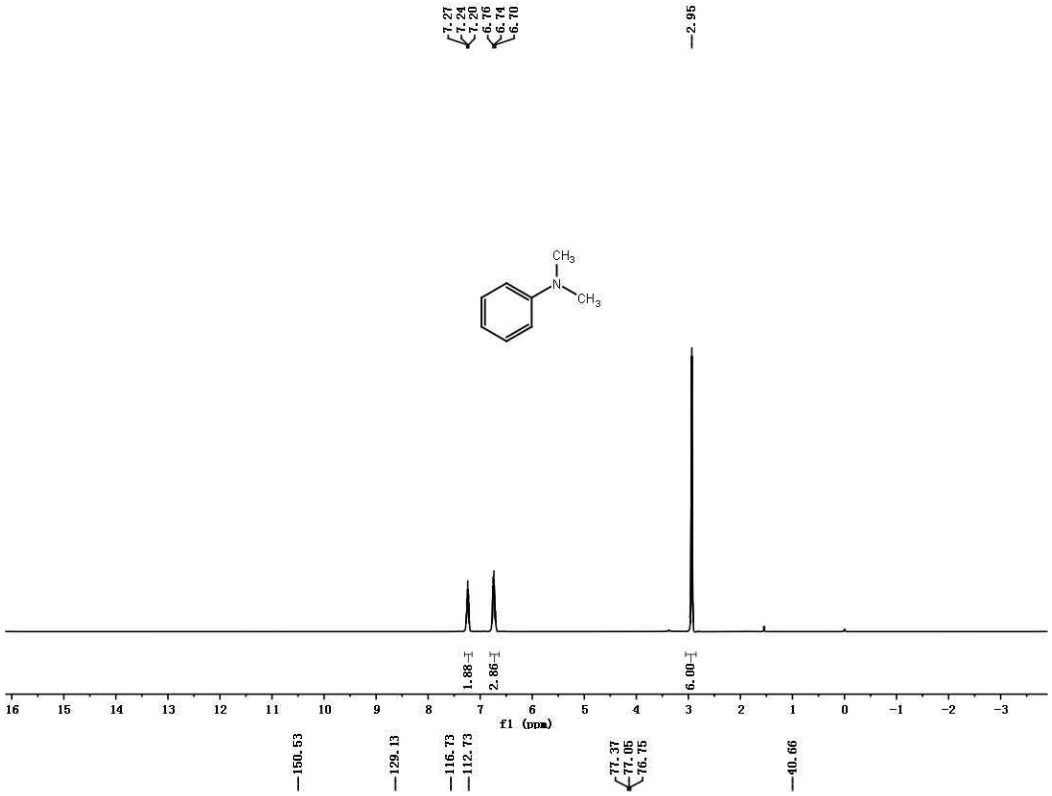


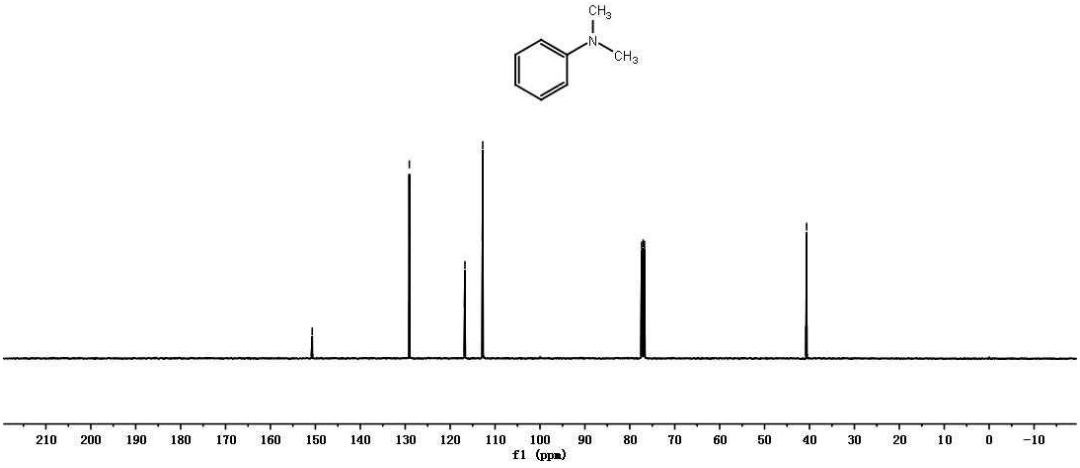
1,3-bis(1-methylpiperidin-4-yl)propane: (Table 2, Entry 12) (GC purity 97%); The typical procedure for the N-methylation of 1,3-di(piperidin-4-yl)propane was followed: 213 mg 1,2,3,4-tetrahydroisoquinoline, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 3.0 MPa CO_2 and 7.0 MPa H_2 were introduced. The reaction was reacted at 160 ^oC for 24h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ ethyl acetate (3 : 1) to give a brown liquid (181 mg, 75% yield).

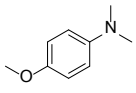




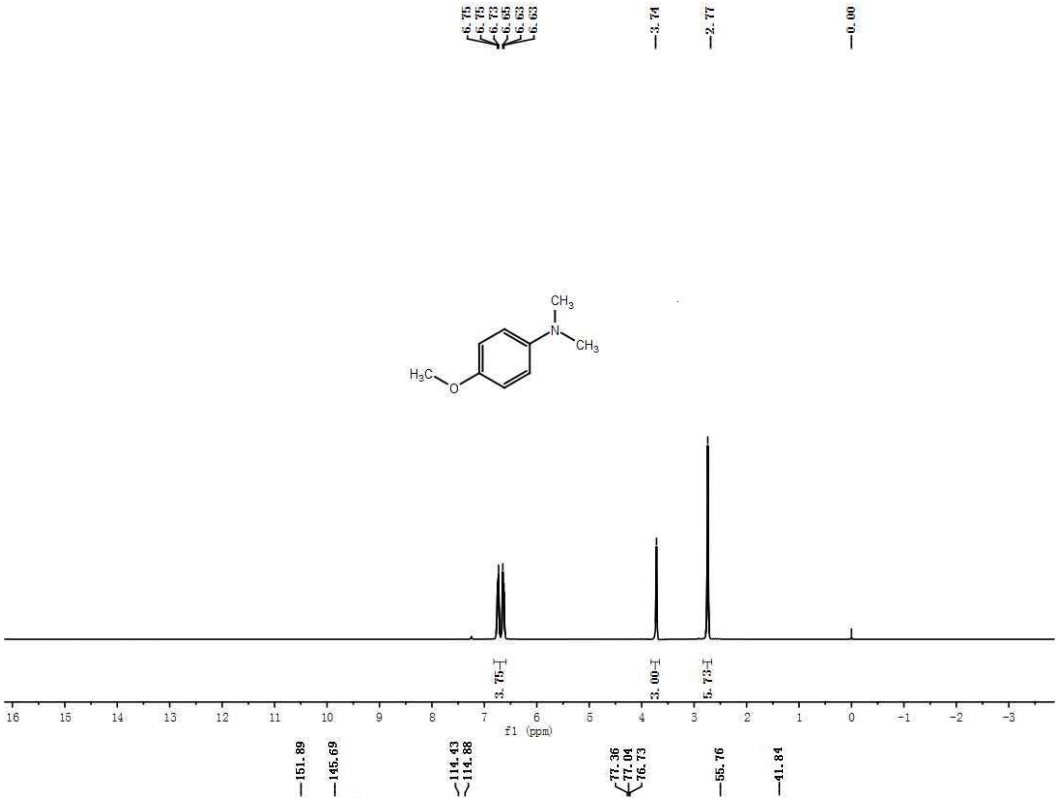
N-methylaniline: (Table 3, Entry 1) (GC purity 98%); The typical procedure for the N,N-dimethylation of nitrobenzene was followed: 125 mg nitrobenzene, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 3.0 MPa CO_2 and 7.0 MPa H_2 were introduced. The reaction was reacted at 170 ^{o}C for 48 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ethyl acetate (200 : 1) to give a brown liquid (98 mg, 80% yield).

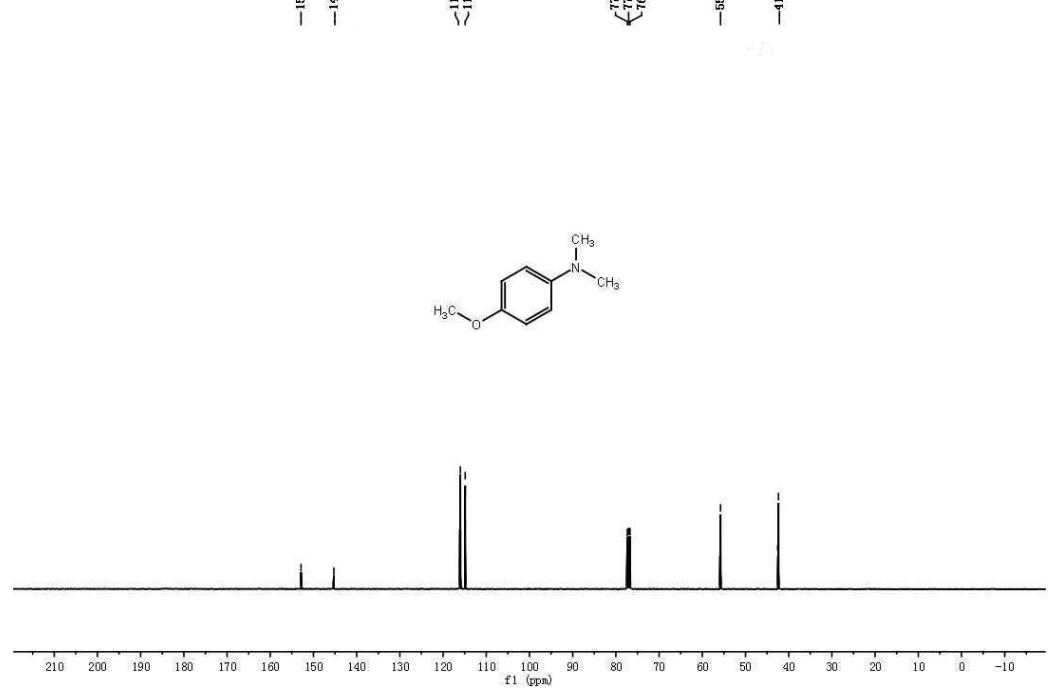


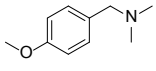




N-methylaniline: (Table 3, Entry 3) (GC purity 98%); The typical procedure for the N,N-dimethylation of 1-methoxy-4-nitrobenzene was followed: 155 mg 1-methoxy-4-nitrobenzene, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 3.0 MPa CO_2 and 7.0 MPa H_2 were introduced. The reaction was reacted at 170 ^{o}C for 48 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ethyl acetate (185 : 1) to give a brown liquid (125 mg, 82% yield).







1-(4-methoxyphenyl)-N,N-dimethylmethanamine: (Table 3, Entry 6) (GC purity 98%); The typical procedure for the N,N-dimethylation of 4-methoxybenzonitrile was followed: 135 mg 4-methoxybenzonitrile, 50 mg CuAlOx catalyst and 2 mL hexane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 3.0 MPa CO_2 and 7.0 MPa H_2 were introduced. The reaction was reacted at 170 ^{o}C for 48 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ethyl acetate (5 : 1) to give a brown liquid (65 mg, 39% yield).