$B(C_6F_5)_3$-catalyzed methylation of amines using CO_2 as a C1 building block

Zhenzhen Yang, Bo Yu, Hongye Zhang, Yanfei Zhao, Guipeng Ji, Zhishuang Ma, Xiang Gao and Zhimin Liu*

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: liuzm@iccas.ac.cn

Table of contents

1. General experimental methods

Materials

All reagents and solvents were purchased from commercial sources (J&K®, Beijing InnoChem Science & Technology Co., Sigma-Aldrich®) and were used without further purification, unless indicated otherwise.

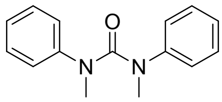
Instrumentation

Liquid NMR spectra was recorded on Bruck 400 spectrometer using $CDCl_3$ as solvent. The composition of the reaction mixture was analyzed by means of GC (Agilent 4890D) with a FID detector and a nonpolar capillary column (DB-5) (30 m × 0.25 mm × 0.25 μm). The column oven was temperature-programmed with a 2 min initial hold at 323 K, followed by the temperature increase to 538K at a rate of 20 K/min and kept at 538 K for 10 min. High purity nitrogen was used as a carrier gas.

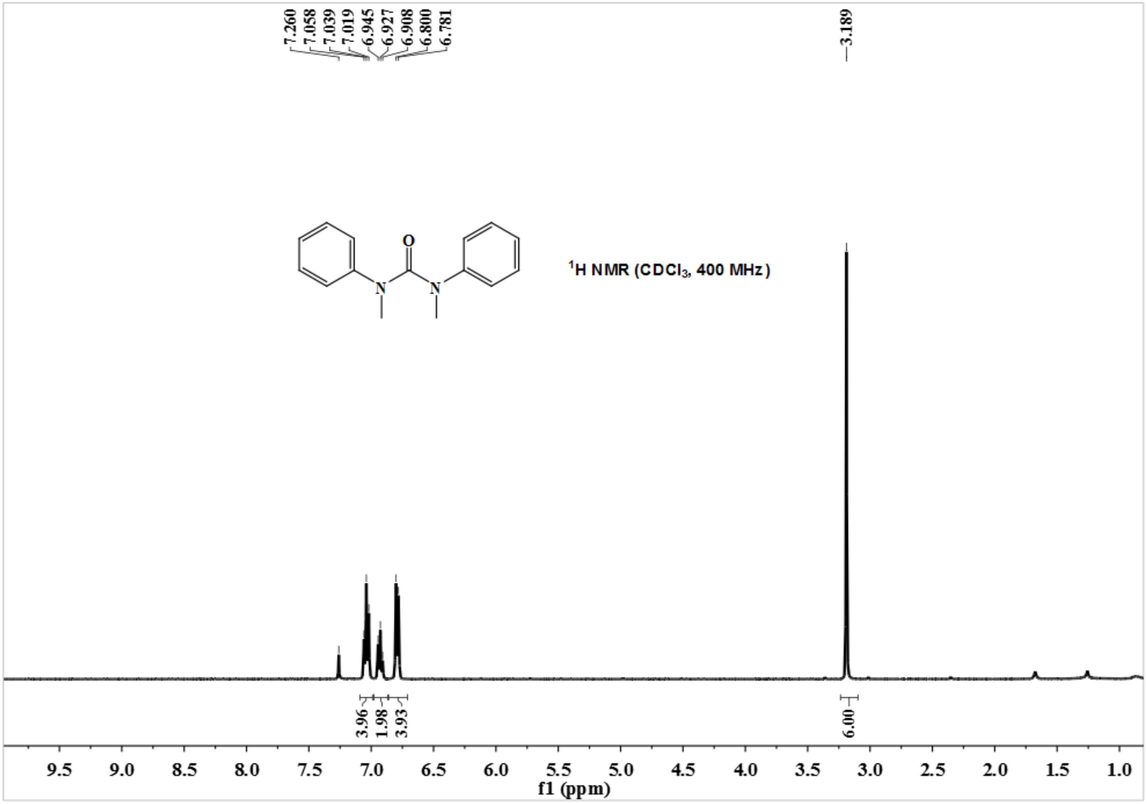
2. Typical procedures for the methylation reaction of N-methylaniline catalyzed by $B(C_6F_5)_3$ in the presence of CO_2 and $PhSi_3H$

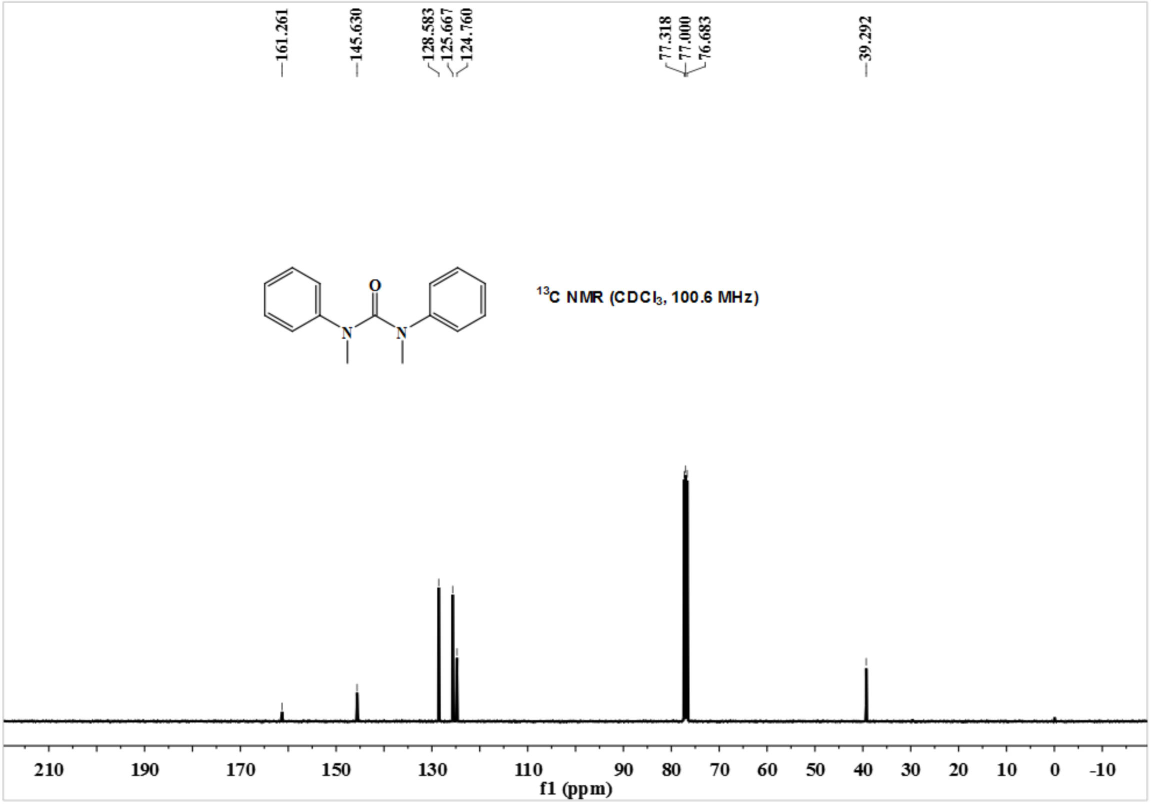
To a stainless steel autoclave (25 mL inner volume), $B(C_6F_5)_3$ (5 mol%), CH_3CN 2 mL, $PhSiH_3$ (1 mmol) and N-methylaniline (0.5 mmol) were added successively. CO_2 was then charged into the reactor up to a desired pressure (e.g., 0.5 MPa) at room temperature. The autoclave was heated at 140 ^oC for 24 h. After reaction, the autoclave was cooled to room temperature, and then CO_2 was vented. The product yields were determined by GC with a flame ionization detector and were further identified using GC-MS by comparing retention times and fragmentation patterns with authentic samples. The products were also isolated by column chromatography on silica gel (eluent: petroleum ether and dichloromethane) and identified by NMR spectra for substrate scope screening.

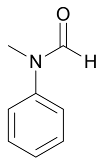
3. Characterization (NMR) of the methylamine products and byproducts



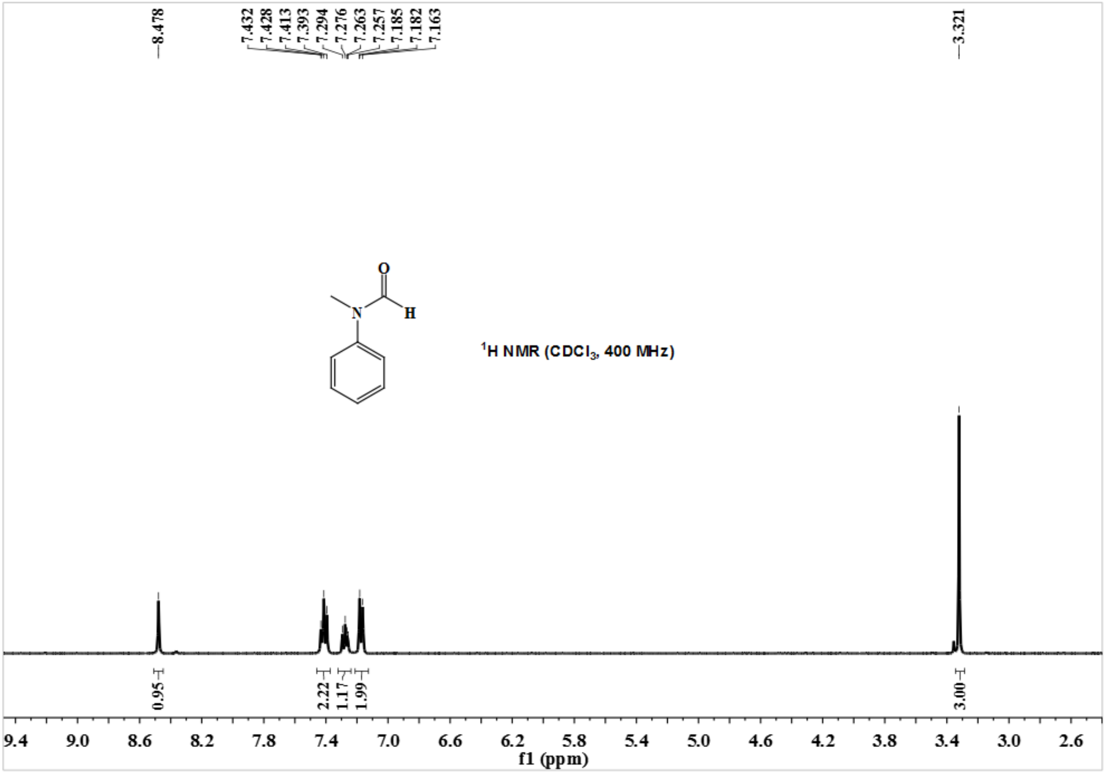
^1H NMR ($CDCl_3$, 400 MHz) δ 3.19 (s, 6H), 6.80 (d, ^3J = 7.6 Hz, 4H), 6.93 (t, ^3J = 7.2 Hz, 2H), 7.04 (t, ^3J = 7.6 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ39.29, 124.76, 125.67, 128.58, 145.63, 161.26.

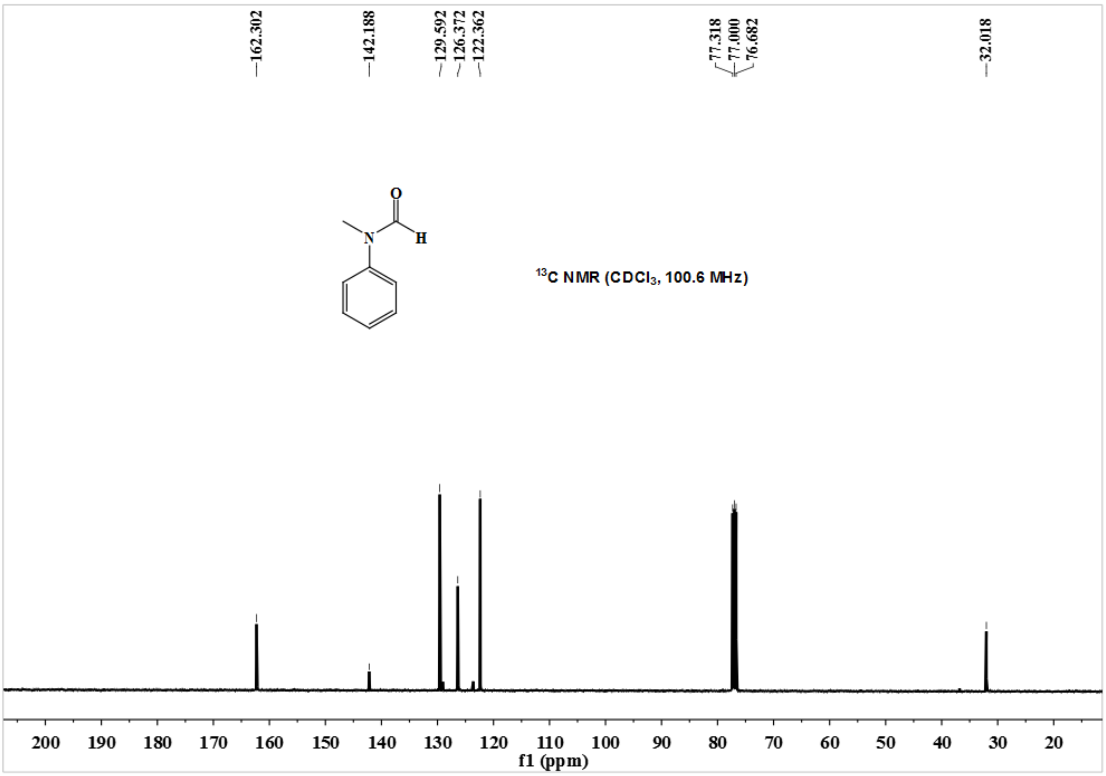


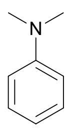




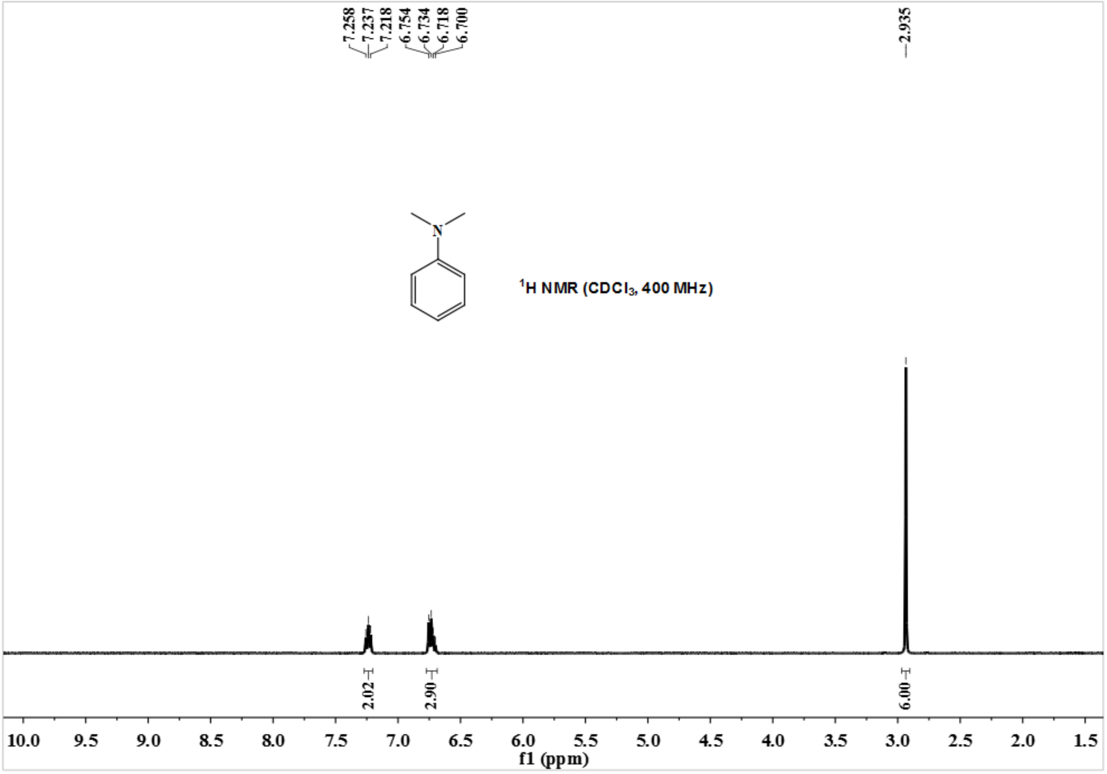
[1]H NMR ($CDCl_3$, 400 MHz) δ 3.32 (s, 3H), 7.16-7.18 (m, 2H), 7.26-7.29 (m, 1H), 7.39-7.43 (m, 2H), 8.48 (s, 1H); [13]C NMR ($CDCl_3$, 100.6 MHz) δ 32.02, 122.36, 126.37, 129.59, 142.19, 162.30.

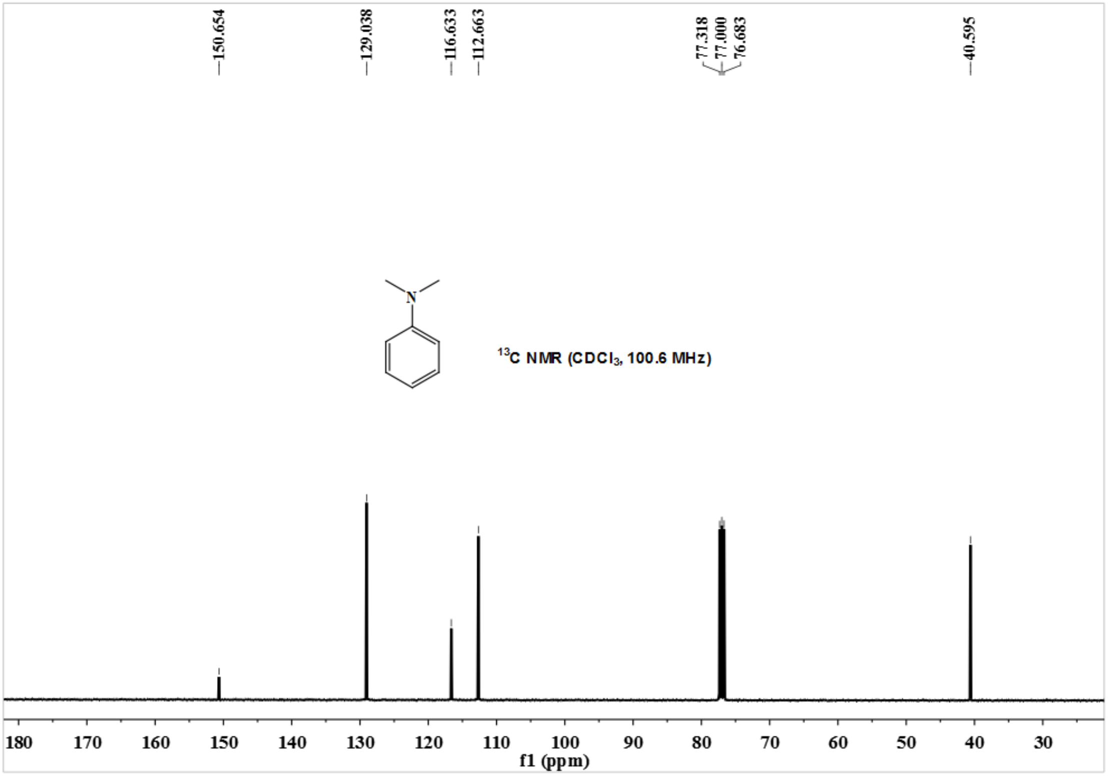


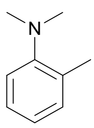




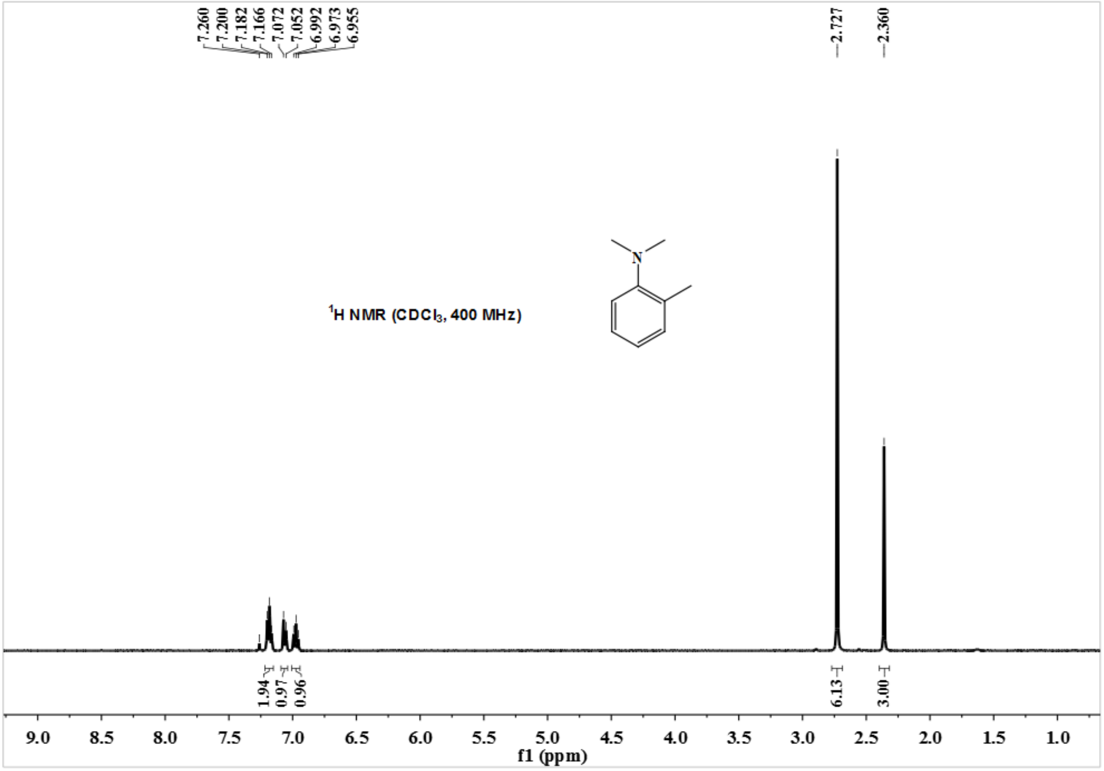
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.93 (s, 6H), 6.70-6.75 (m, 3H), 7.24 (t, ^3J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 40.59, 112.66, 116.63, 129.04, 150.65.

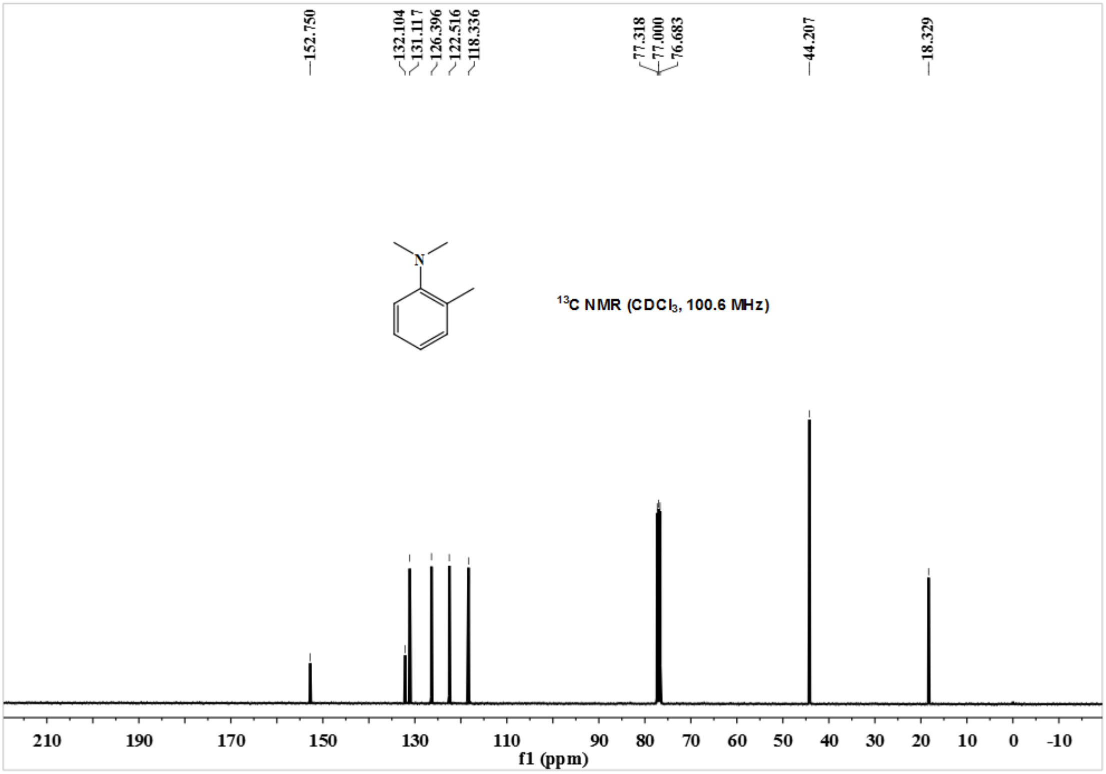


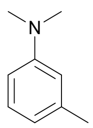




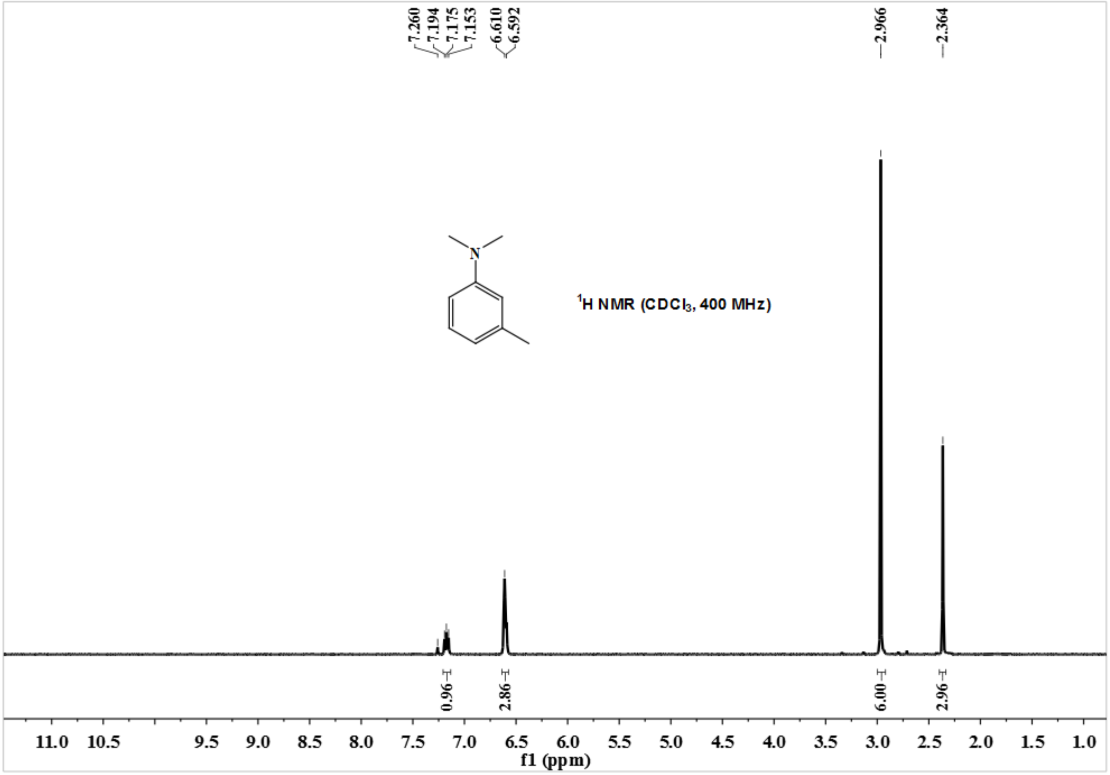
^{1}H NMR (CDCl$_3$, 400 MHz) δ 2.36 (s, 3H), 2.73 (s, 6H), 6.97 (t, ^3J = 7.2 Hz, 1H), 7.06 (t, ^3J = 8 Hz, 1H), 7.18 (t, ^3J = 7.2 Hz, 2H); ^{13}C NMR (CDCl$_3$, 100.6 MHz) δ 18.33, 44.21, 118.34, 122.52, 126.40, 131.12, 132.10, 152.75.

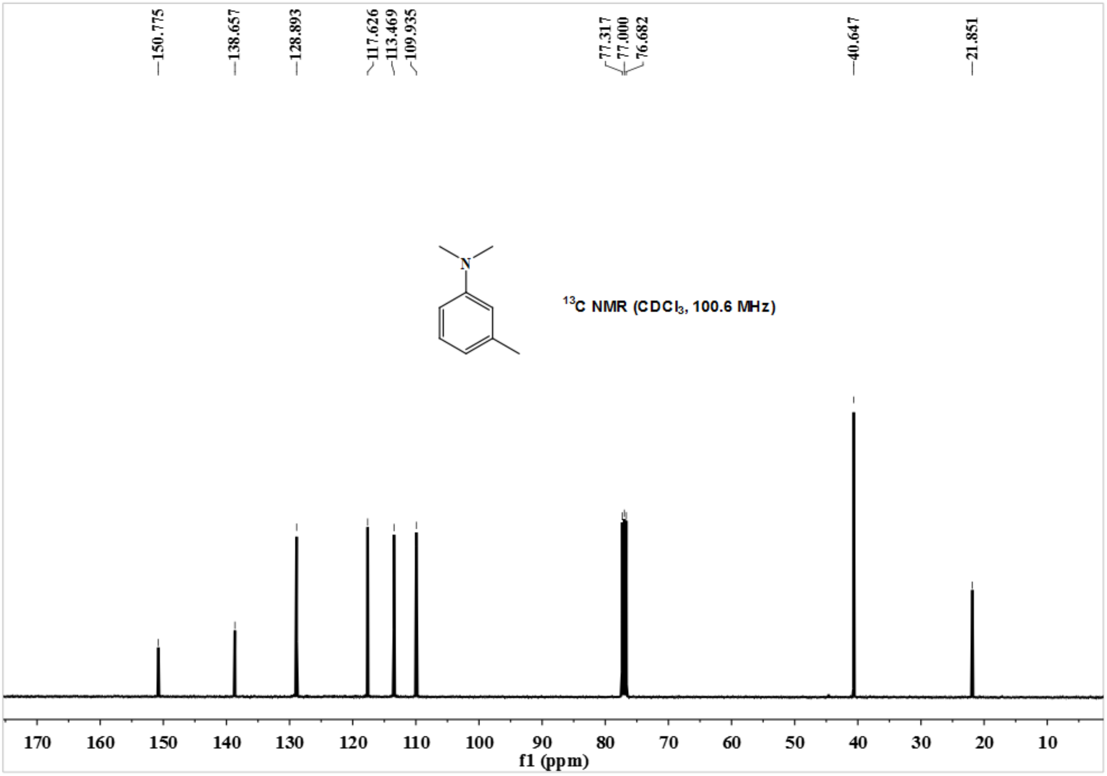


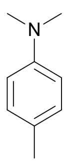




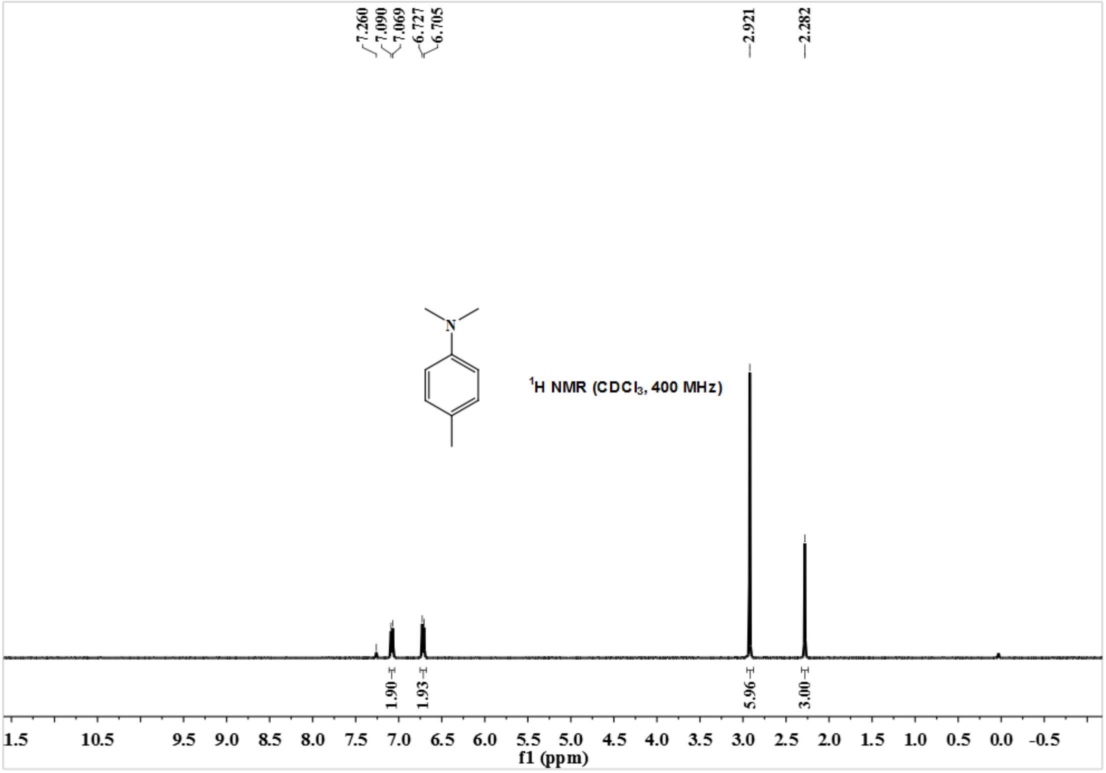
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3H), 2.97 (s, 6H), 6.59-6.61 (m, 3H), 7.17 (t, ^{3}J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.85, 40.65, 109.93, 113.47, 117.63, 128.89, 138.66, 150.77.

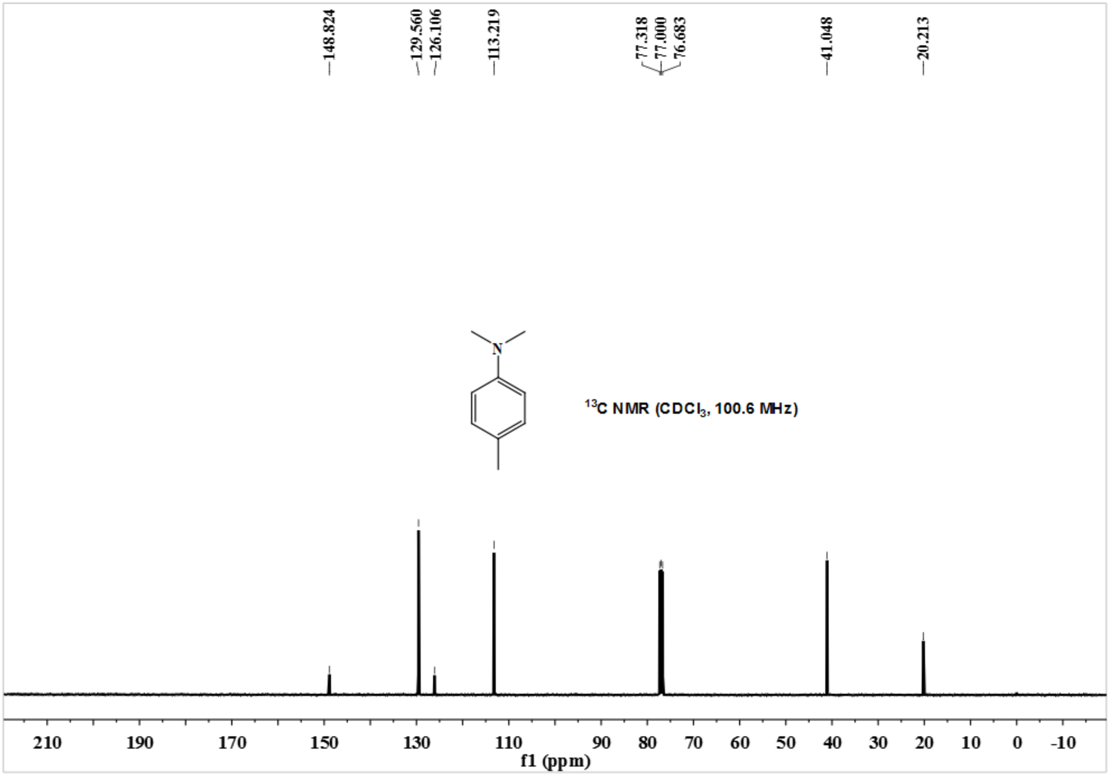


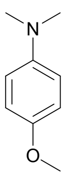




^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H), 2.92 (s, 6H), 6.72 (d, ^3J = 8.8 Hz, 2H), 7.08 (d, ^3J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.21, 41.05, 113.21, 126.11, 129.56, 148.82.

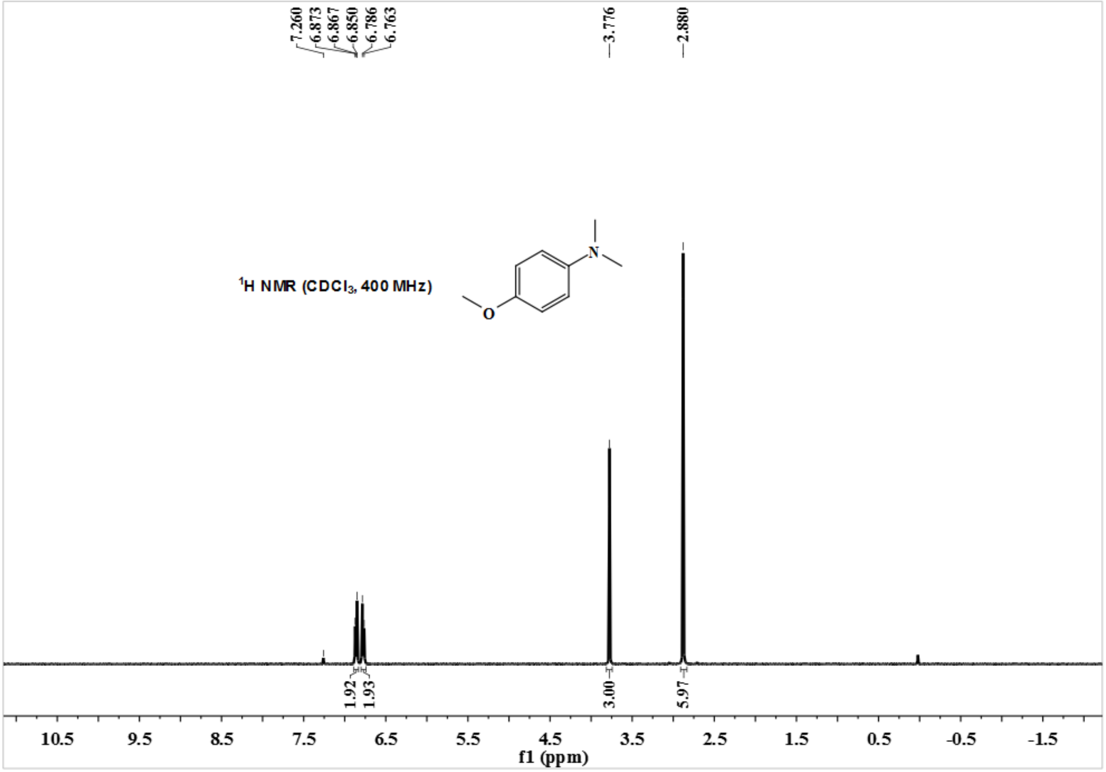


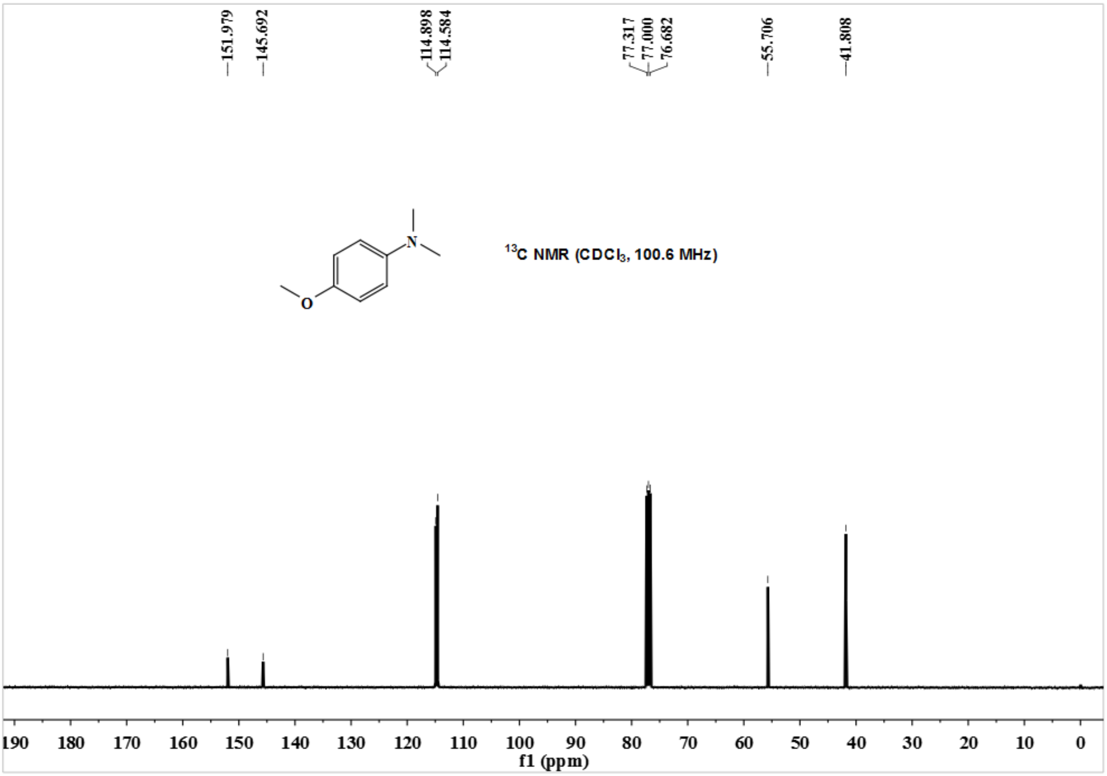


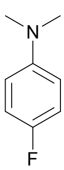


^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.88 (s, 6H), 3.78 (s, 3H), 6.76-6.79 (m, 2H), 6.85-6.87 (m, 2H);

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 41.81, 55.71, 114.58, 114.90, 145.69, 151.98.

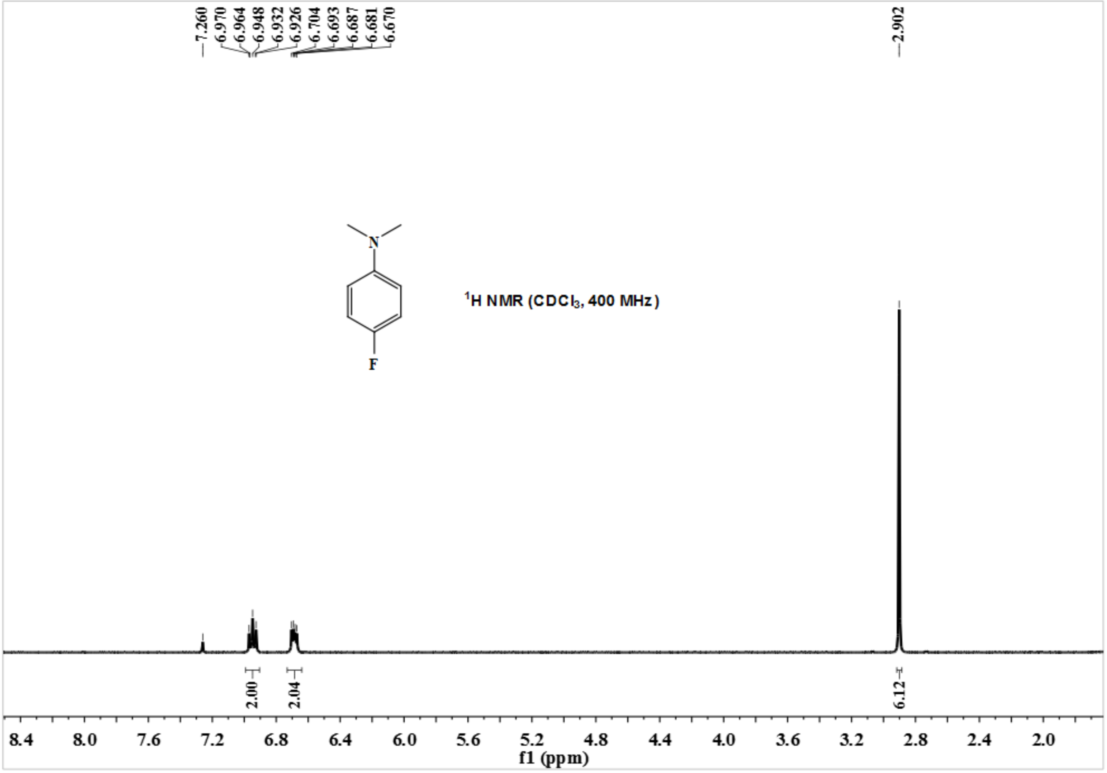


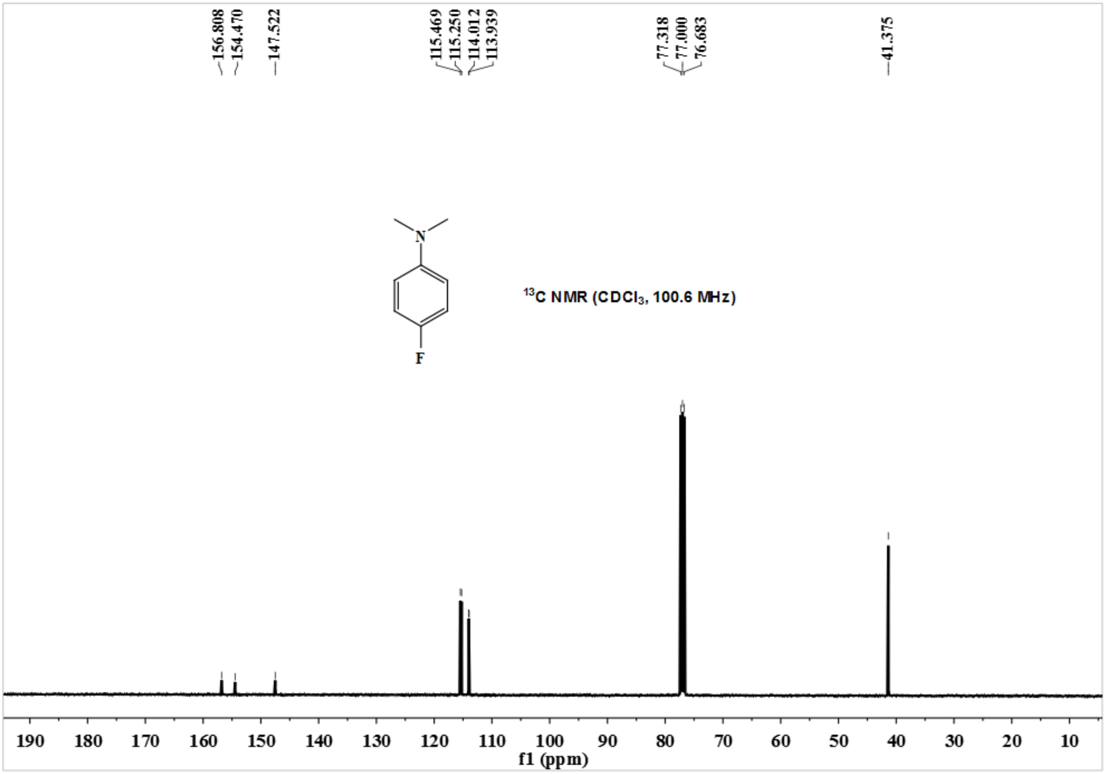


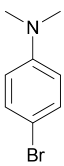


^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.90 (s, 6H), 6.67-6.70 (m, 2H), 6.93-6.97 (m, 2H); ^{13}C NMR

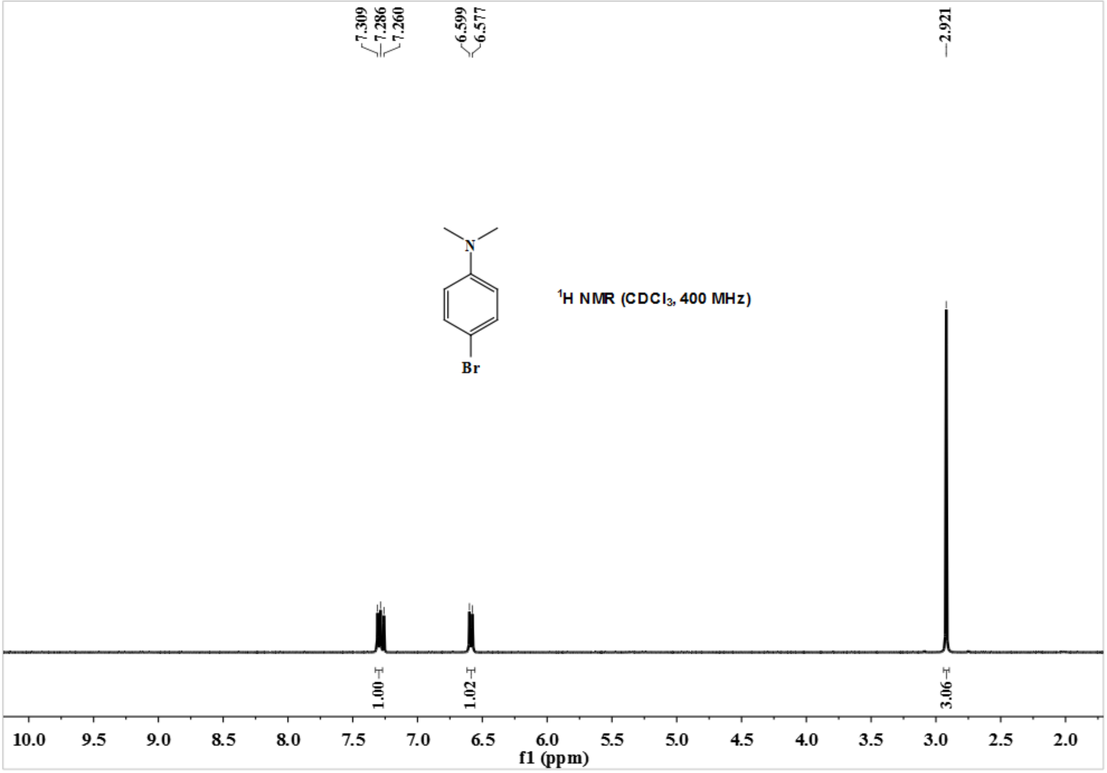
(CDCl$_3$, 100.6 MHz) δ 41.37, 113.8 (d, ^3J = 7.3 Hz), 115.36 (d, ^3J = 22.0 Hz), 147.52, 154.47, 156.81.

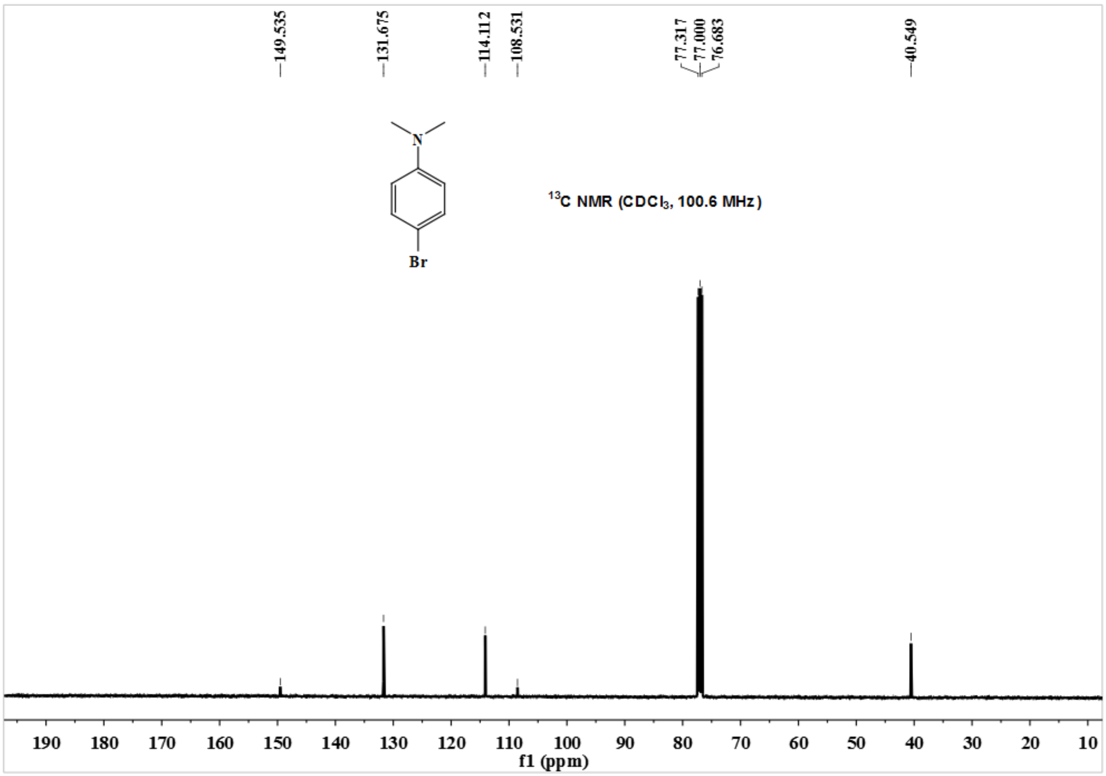


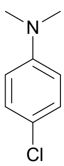




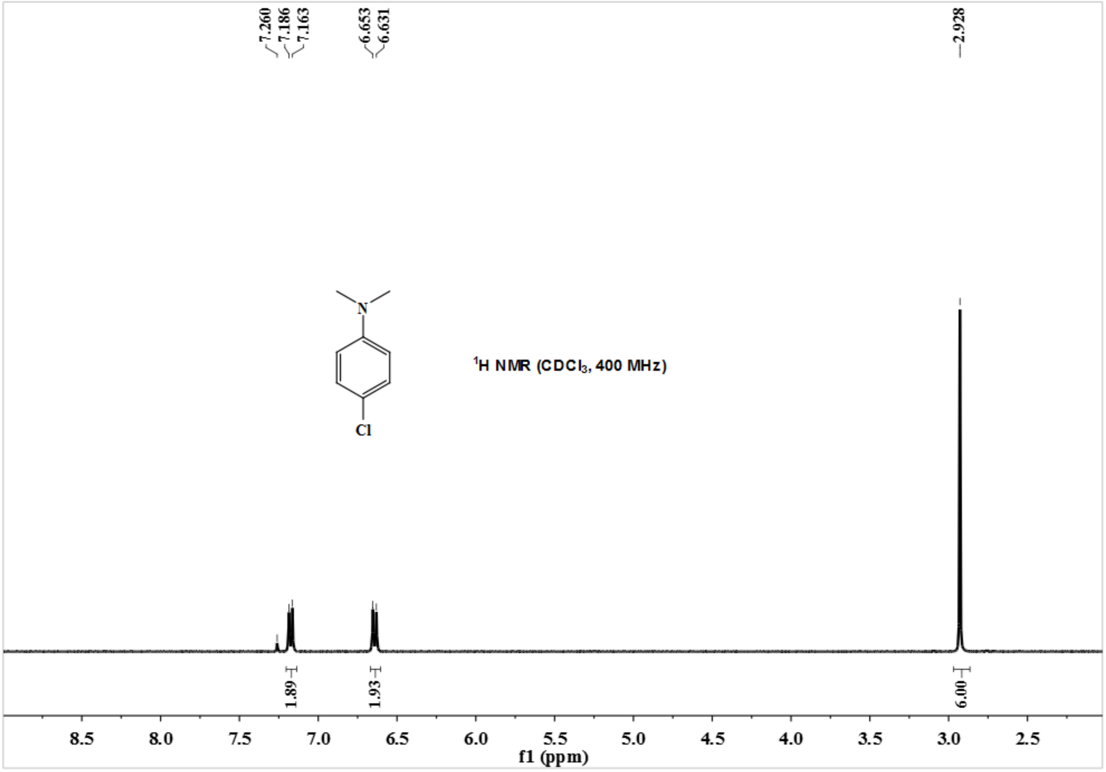
[1]H NMR ($CDCl_3$, 400 MHz) δ 2.92 (s, 3H), 6.59 (d, ^3J = 8.8 Hz, 2H), 7.28 (d, ^3J = 9.2 Hz, 2H); [13]C NMR ($CDCl_3$, 100.6 MHz) δ 40.55, 108.53, 114.11, 131.67, 149.53.

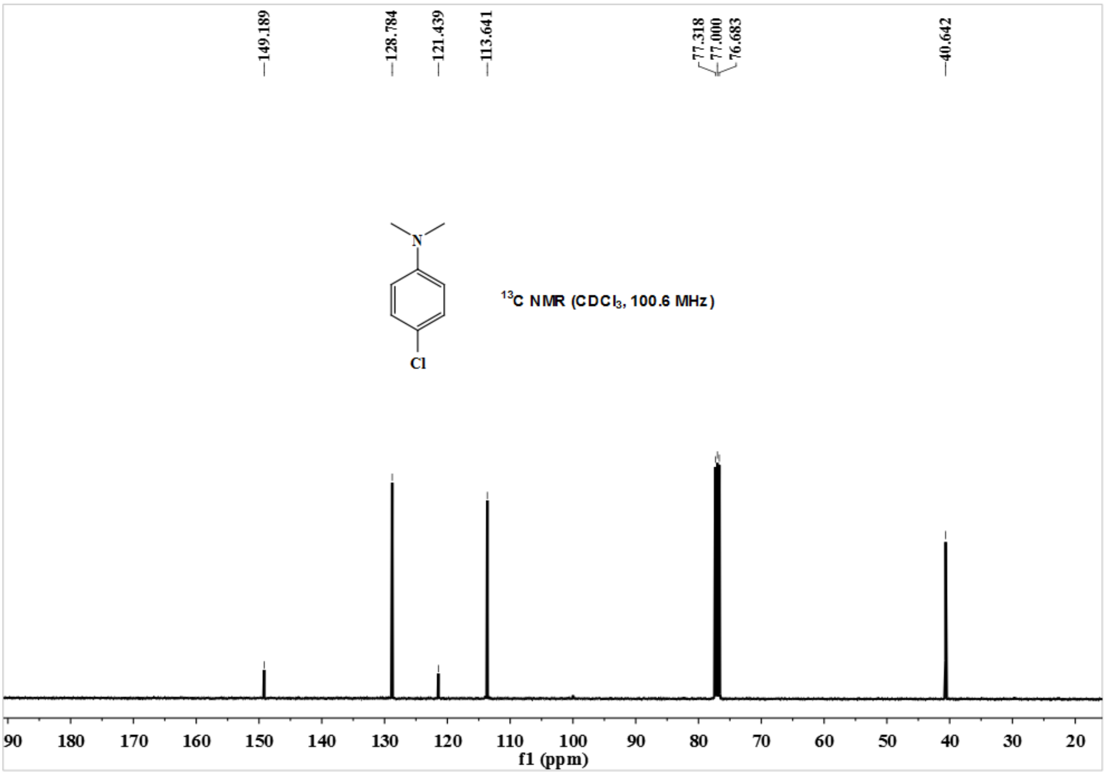


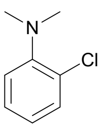




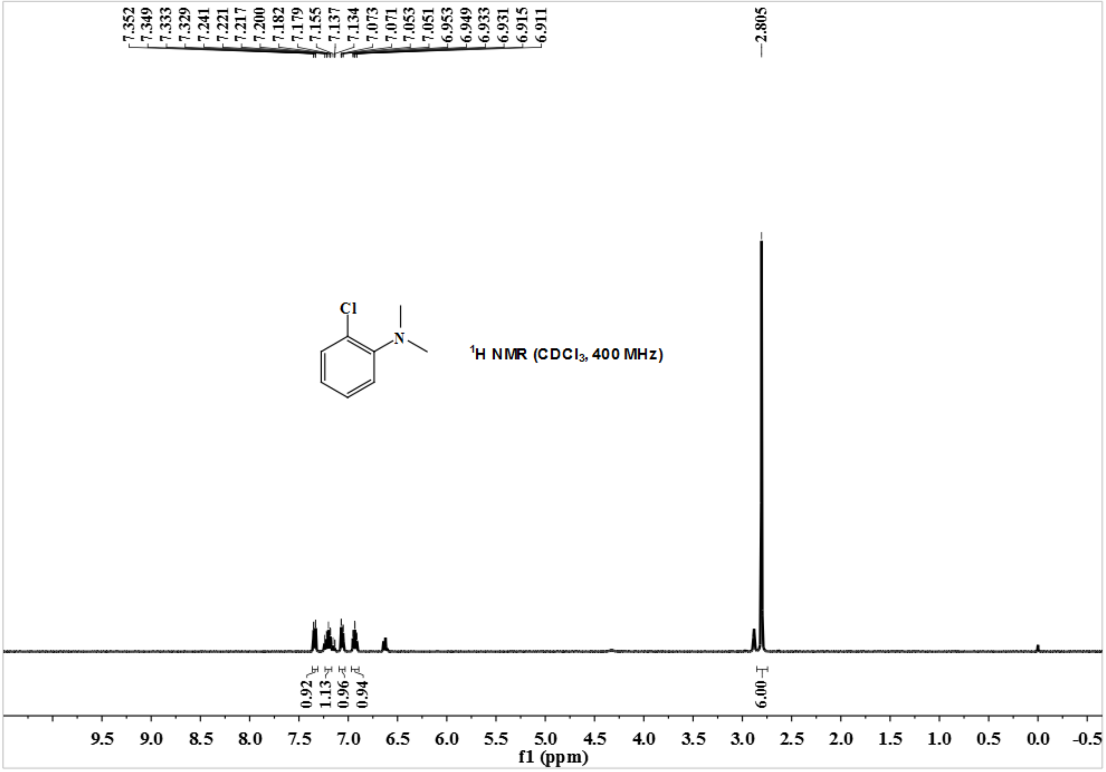
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.93 (s, 6H), 6.64 (d, 3J= 8.8 Hz, 2H), 7.17 (d, 3J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 40.64, 113.64, 121.44, 128.78, 149.19.

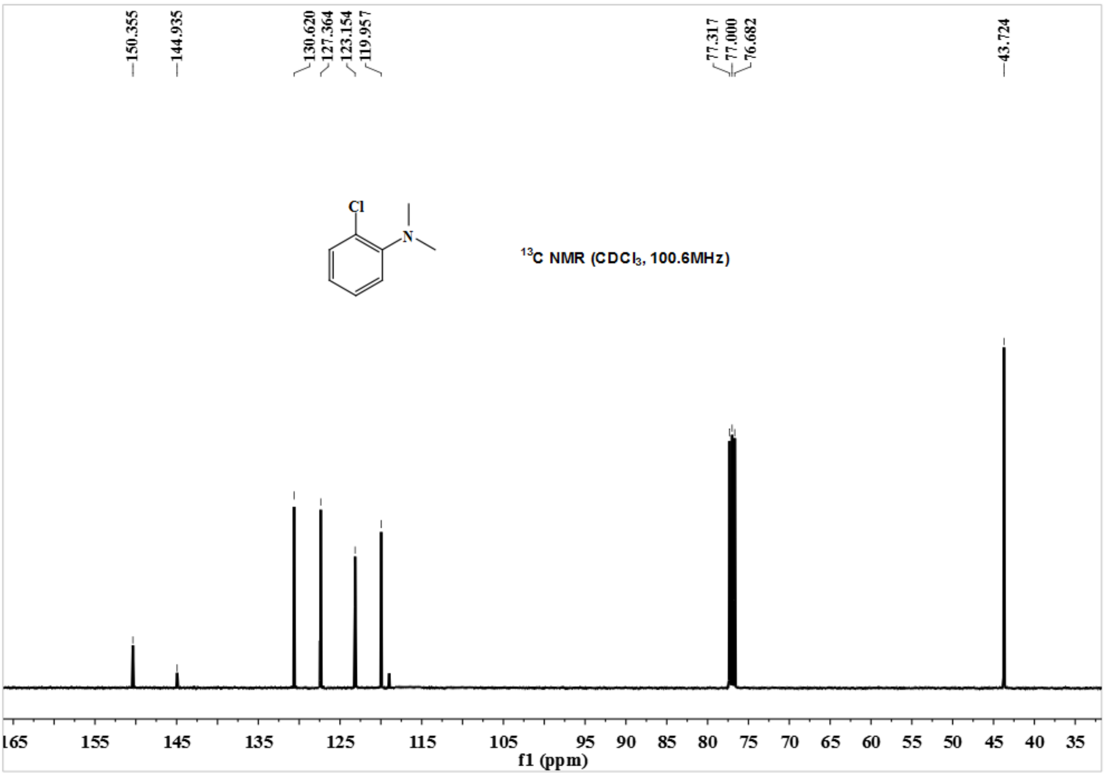


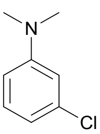




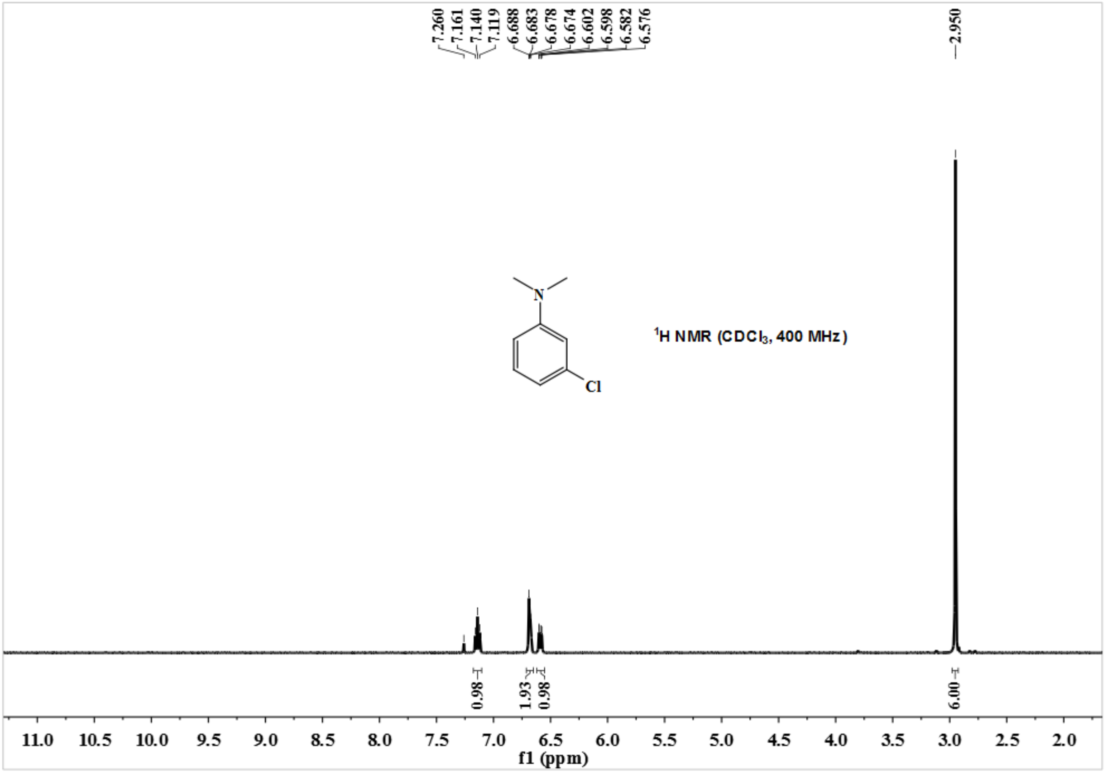
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.81 (s, 1H), 6.91-6.95 (m, 1H), 7.05-7.07 (m, 1H), 7.13-7.24 (m, 1H), 7.33-7.35 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 43.72, 119.96, 123.15, 127.36, 130.62, 144.94, 150.36.

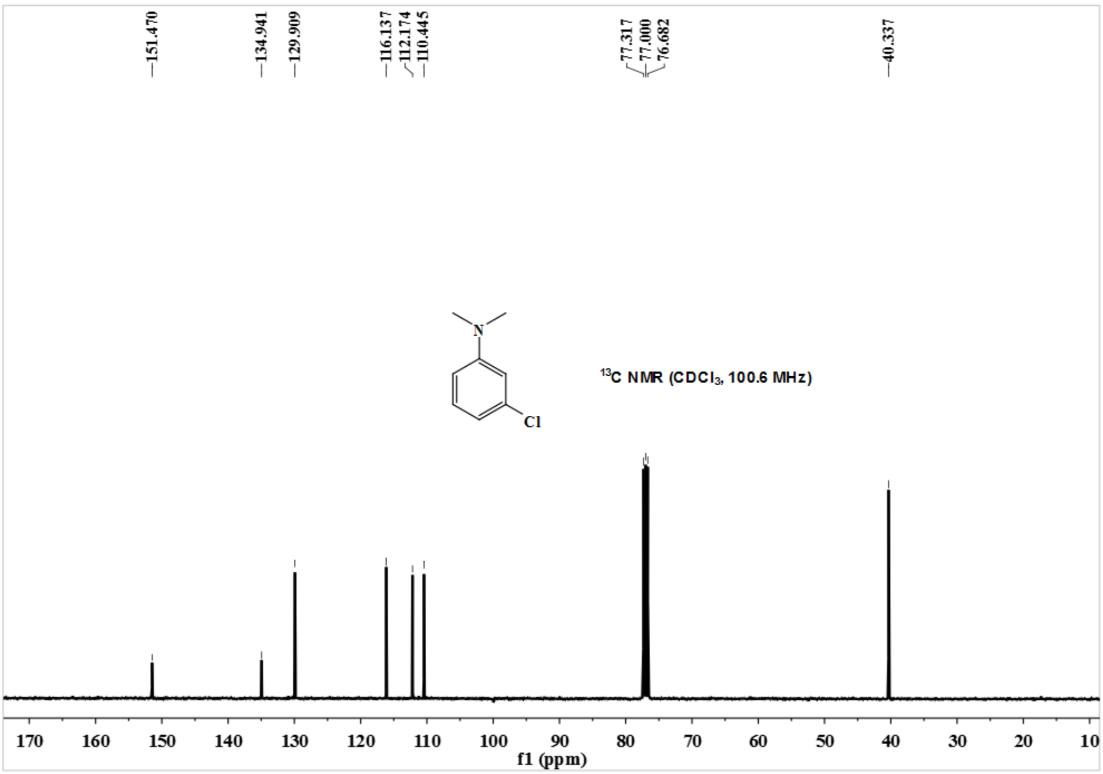


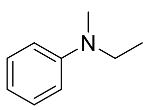




^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.95 (s, 1H), 6.58-6.60 (m, 1H), 6.67-6.69 (m, 2H), 7.14 (t, ^{3}J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 40.34, 110.44, 112.17, 116.14, 129.91, 134.94, 151.47.

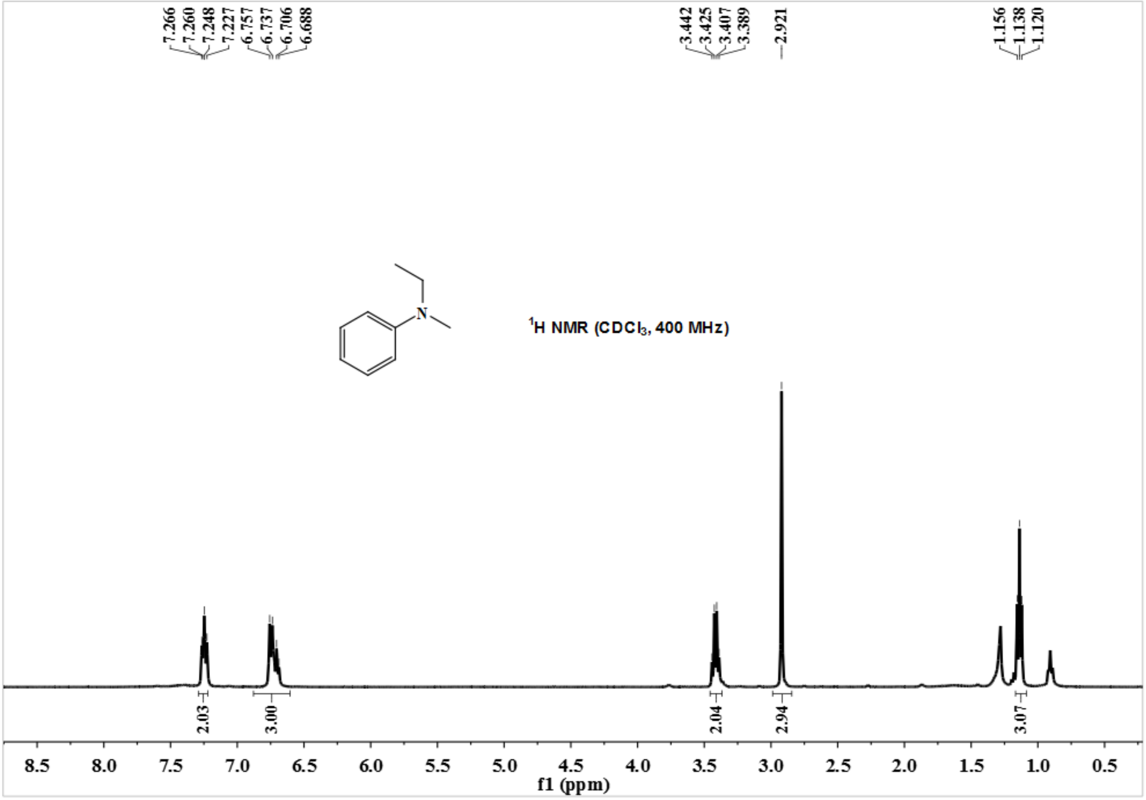


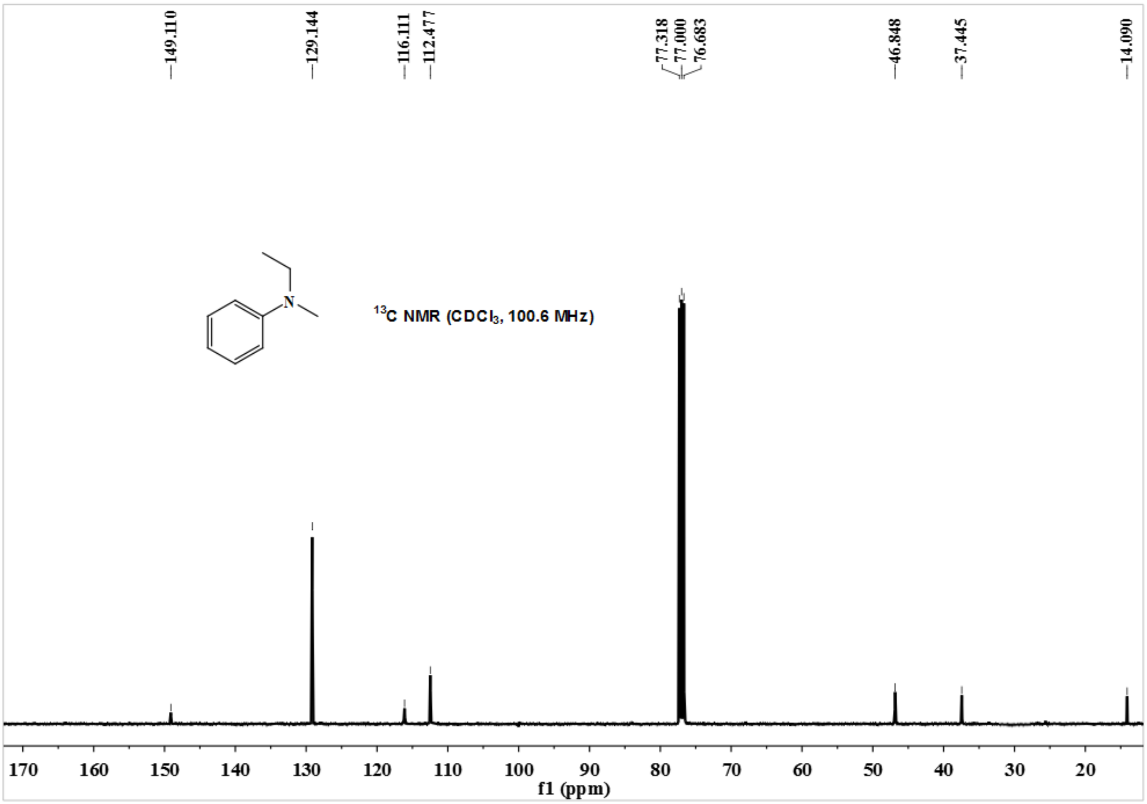


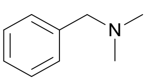


^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.14 (t, ^{3}J = 7.2 Hz, 3H), 2.92 (s, 3H), 3.39-3.44 (m, 2H), 6.69-6.76

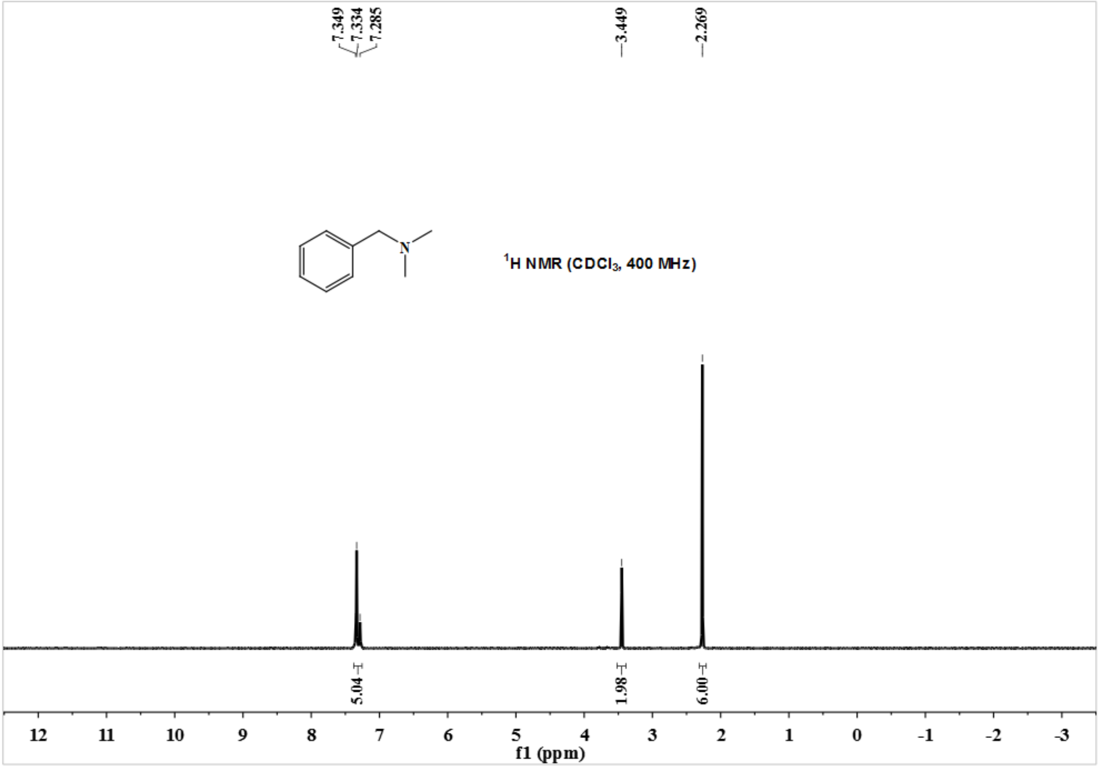
(m, 3H), 7.25 (t, ^{3}J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 14.09, 37.45, 46.85, 112.48, 116.11, 129.14, 149.11.

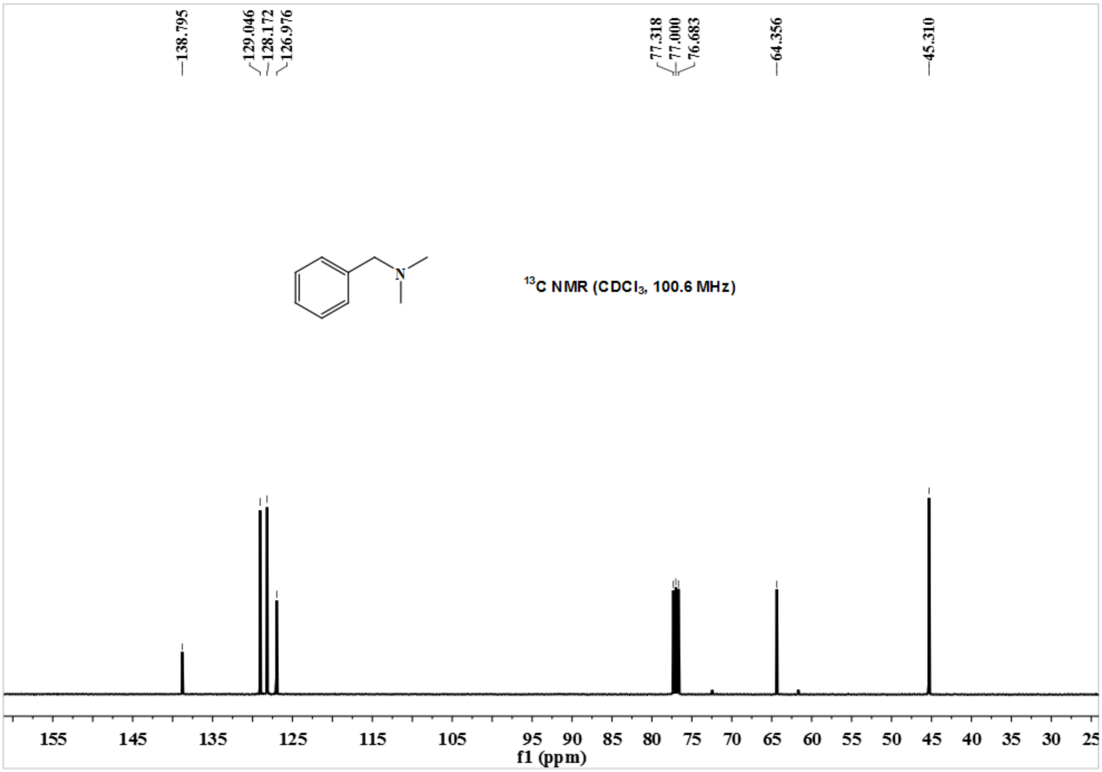


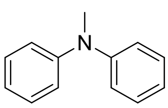




^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.27 (s, 6H), 3.45 (s, 2H), 7.29-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 45.31, 64.36, 126.98, 128.17, 129.05, 138.80.







^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.33 (s, 3H), 6.97 (t, ^{3}J = 7.6 Hz, 2H), 7.04 (d, ^{3}J = 8 Hz, 4H), 7.29

(t, 3J = 8 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 40.22, 120.45, 121.26, 129.17, 149.04.