Co-N-C supported on SiO_2: A Facile, Efficient Catalyst for Aerobic Oxidation of Amines to Imines

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Contents

General experimental information

The products were determined by using Lquid Chromatograph Mass Spectrometer (LC-MS, G6224A), C H N S Elemental Analyzer, Fourier Transform Infrared Spectrometer (FT-IR, Nicolet 380), and Melting Point Determination (Ry-1G). ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance II 400 (^{1}H: 400MHz, ^{13}C: 400MHz) spectrometer. The chemical shifts for the NMR spectra are reported in ppm relative to the solvent residual peak.1 Coupling constants J are reported in hertz (Hz). The following abbreviations are used for the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; st, sextet; m, multiplet; br, broad; dd, doublet of doublet. The products (3f, 3g, 3i, 3j, 3k, 3l) were determined by using Agilent GC-MS 7890. The yield was determined by Shimadzu GC-2000 Plus.

General procedure for the preparation of imines

All reactions were performed on a 0.50mmol scale relative to the amine. The procedure for the synthesis of 3a is given as an example:
In a typical amine oxidation reaction, a mixture of benzylamine (1a; 0.5mmol), catalyst (Co-N-C/SiO_2, 10wt% loading Co) was added in a 10mL round bottom flask equipped with a condenser. The reaction mixture was heated to 110°C under vigorous stirring for specific time under an air atmosphere. After reaction, the mixture was cooled to 80°C, 15mL of ethanol was added to the mixture which was vigorously stirred to completely dissolution of product, and the catalyst was removed by filtration. The filtrate was determined by Shimadzu GC-2000 Plus and Agilent GC-MS 7890 to obtain characteristic and yield of product. The solvent evaporated under reduced pressure to gain crude product which was purified by silica gel flash chromatography using dichloromethane and petroleum ether as eluent to afford the product.

Characterization of Products

N-Benzylidenebenzylamine (3a). Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H),7.80-7.77 (m, 2H), 7.43-7.42 (m, 3H), 7.34 (d, J = 4.4 Hz, 4H), 7.27-7.25 (m, 1H), 4.83 (s, 2H). ^{13}CNMR (400 MHz, $CDCl_3$): δ 162.0, 139.4, 136.5, 130.8, 128.6, 128.5, 128.3, 128.0, 127.0, 65.2. HRMS(ESI/APCI): m/z(%) calcd for $C_{14}H_{14}N$ $[M+H]^+$ 196.1121 Found 196.1115. FT-IR: ν = 3028/3061, 2822/2735/2723, 1644, 1600 cm^{-1}. Elemental Analysis: Calcd. For $C_{14}H_{13}N$: C, 86.12; H, 6.71; N, 7.17 Found: C, 84.78; H, 6.13; N, 6.97. This compound was known: E. Zhang, H. Tian, S. Xu, X. Yu, Q. Xu, *Org. Lett.*, 2013, **15**, 2704-2707.

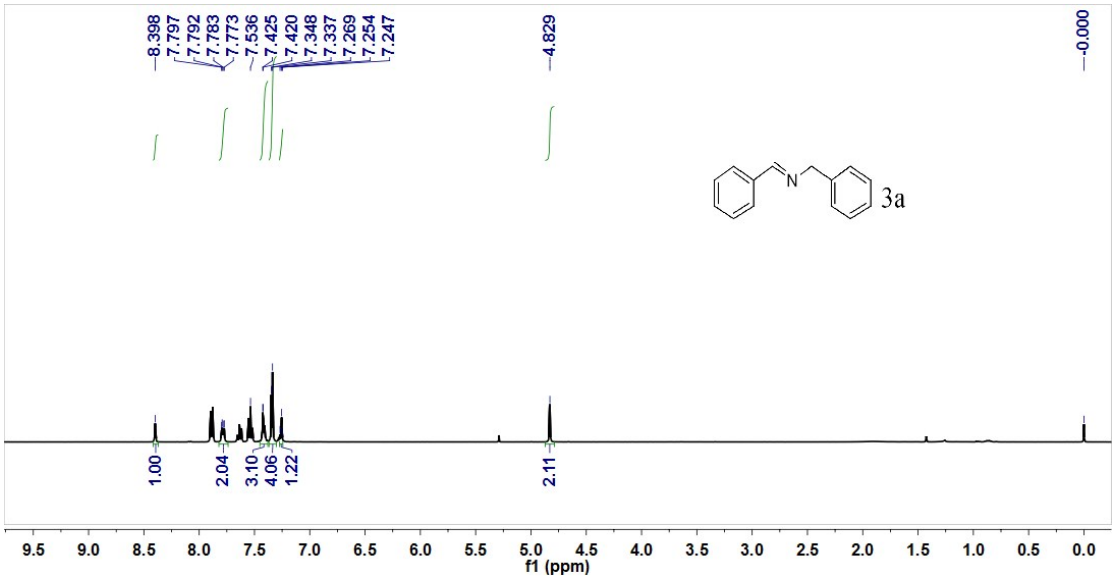
N-(4-Methylbenzylidene)-4-methylphenylmethylamine (3b). White solid; mp 84-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.22-7.20 (m, 4H), 7.15-7.13 (m, 2H), 4.76 (s, 2H), 2.37 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 161.7, 141.0, 136.5, 136.4, 133.7, 129.3, 129.2, 128.3, 128.0, 64.8, 21.5, 21.1. HRMS(ESI/APCI): m/z(%) calcd for $C_{16}H_{18}N$ $[M+H]^+$ 224.1434 Found 224.1436. FT-IR: ν = 3046/3017, 2914/2855/2813, 1643, 1605, 815, 796 cm^{-1}. Elemental Analysis: Calcd. For $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27 Found: C, 85.37; H, 6.22; N, 5.72. This compound was known: E. Zhang, H. Tian, S. Xu, X. Yu, Q. Xu, *Org. Lett.*, 2013, **15**, 2704-2707.

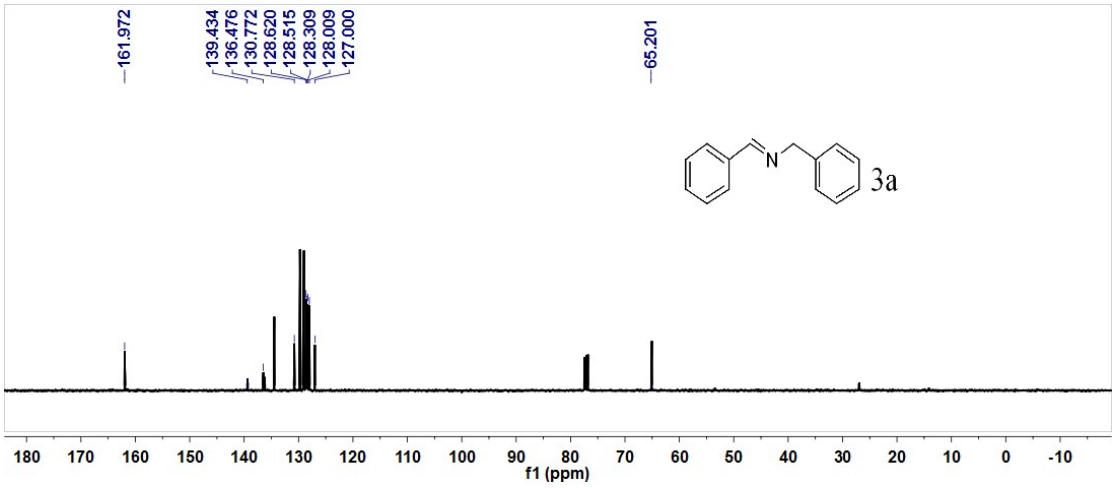
N-(4-Chlorobenzylidene)-4-chlorophenylmethylamine (3c). White solid; mp 65-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.71 (d, J = 8.4 Hz 2H), 7.39 (d, J = 8.4 Hz 2H), 7.31 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 8 Hz 2H), 4.76 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 160.8, 137.7, 136.9, 134.5, 132.8, 129.5, 129.3, 128.9, 128.7, 64.2. HRMS(ESI/APCI): m/z(%) calcd for $C_{14}H_{12}Cl_2N$ $[M+H]^+$ 264.0341 Found 264.0344. FT-IR: ν = 3045, 2854/2815, 1641, 1590, 827, 806 cm^{-1}. Elemental Analysis: Calcd For $C_{14}H_{11}Cl_2N$: C, 63.66; H, 4.20; N, 5.30 Found: C, 61.83; H, 3.89; N, 5.07. This compound was known: E. Zhang, H. Tian, S. Xu, X. Yu, Q. Xu, *Org. Lett.*, 2013, **15**, 2704-2707.

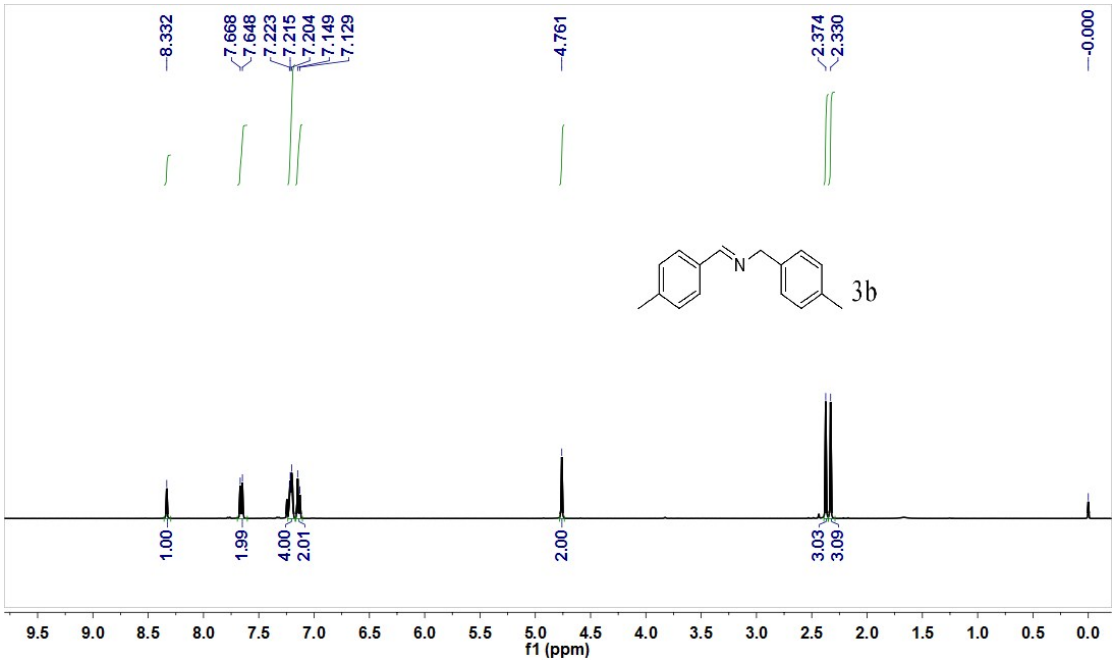
N-(2-Chlorobenzylidene)-2-chlorophenylmethylamine (3d). Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 8.12 (dd, J = 7.2, 1.2 Hz, 1H), 7.44-7.22 (m, 7H), 4.95 (s, 2H); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 159.7, 136.9, 135.1, 133.4, 133.2, 131.7, 129.8, 129.7, 129.4, 128.5, 128.3, 127.0, 126.9, 62.2. HRMS(ESI/APCI): m/z(%) calcd for $C_{14}H_{12}Cl_2N$ $[M+H]^+$ 264.0341 Found 264.0345. FT-IR: ν = 3066/3012, 2866/2751, 1698, 1638, 754, 712 cm^{-1}. Elemental Analysis: Calcd For $C_{14}H_{11}Cl_2N$: C, 63.66; H, 4.20; N, 5.30 Found: C, 62.10; H, 3.96; N, 5.15. This compound was known: E. Zhang, H. Tian, S. Xu, X. Yu, Q. Xu, *Org. Lett.*, 2013, **15**, 2704-2707.

N-(3-Chlorobenzylidene)-3-chlorophenylmethylamine (3e). Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.81 (t, J = 1.6 Hz, 1H), 7.63-7.61 (m, 1H), 7.40 (m, 1H), 7.37-7.33 (m, 2H), 7.30-7.21 (m, 3H), 4.78 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 160.9, 141.1, 137.8, 134.9, 134.4, 130.9, 130.4, 129.9, 128.0, 128.0, 127.3, 126.7, 126.1, 64.2. HRMS(ESI/APCI): m/z(%) calcd for $C_{14}H_{12}Cl_2N$ $[M+H]^+$ 264.0341 Found 264.0350. FT-IR: ν = 3063/3003, 2844/2727, 1702, 1646, 783, 727 cm^{-1}. Elemental Analysis: Calcd For $C_{14}H_{11}Cl_2N$: C, 63.66; H, 4.20; N, 5.30 Found: C, 61.08; H, 4.02; N, 4.94. This compound was known: E. Zhang, H. Tian, S. Xu, X. Yu, Q. Xu, *Org. Lett.*, 2013, **15**, 2704-2707.

^{1}H NMR and ^{13}C NMR spectra of imines and aromatic aldehydes



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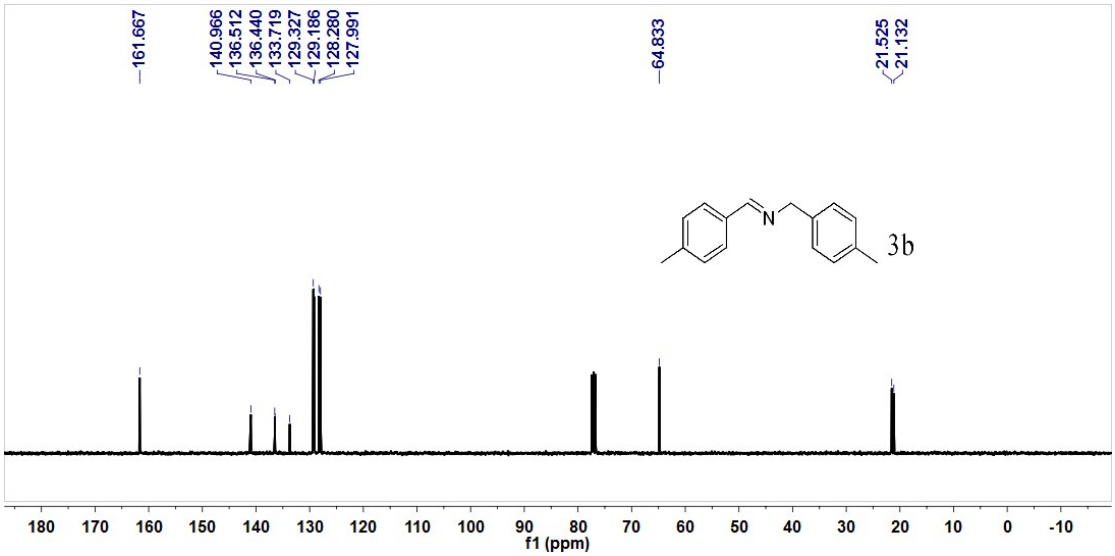
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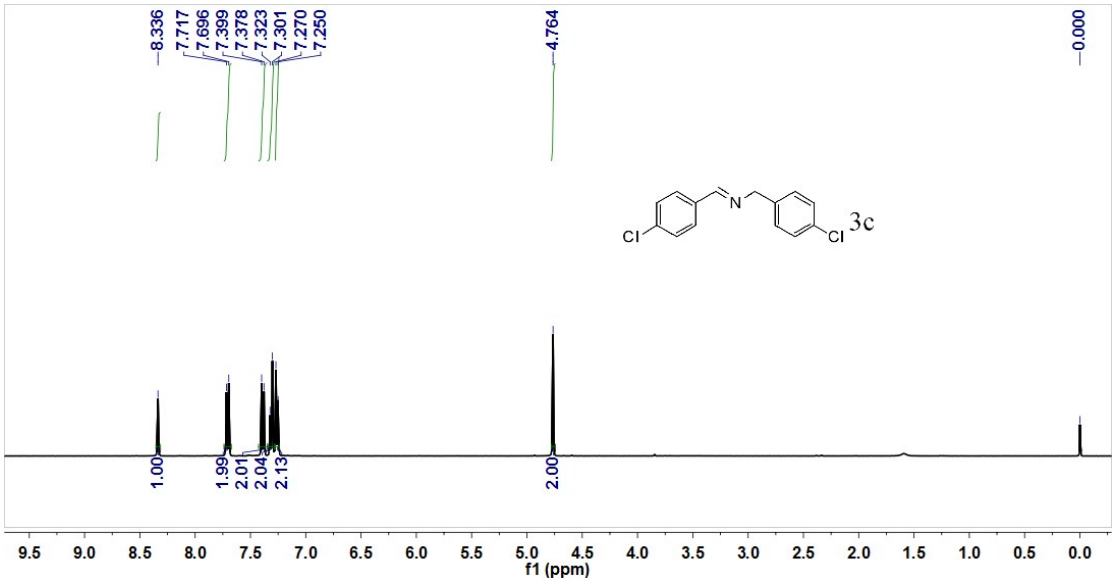
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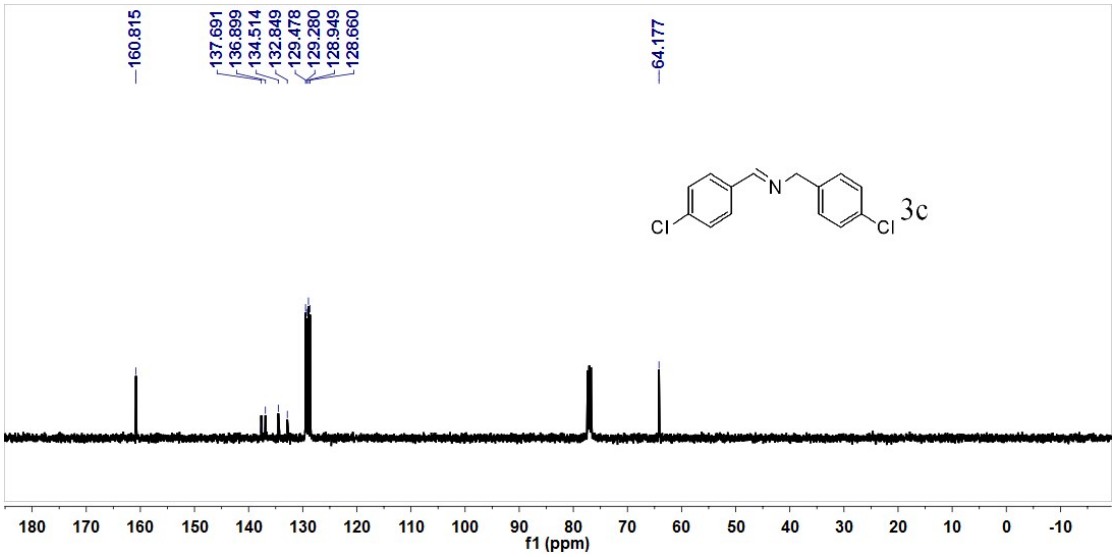
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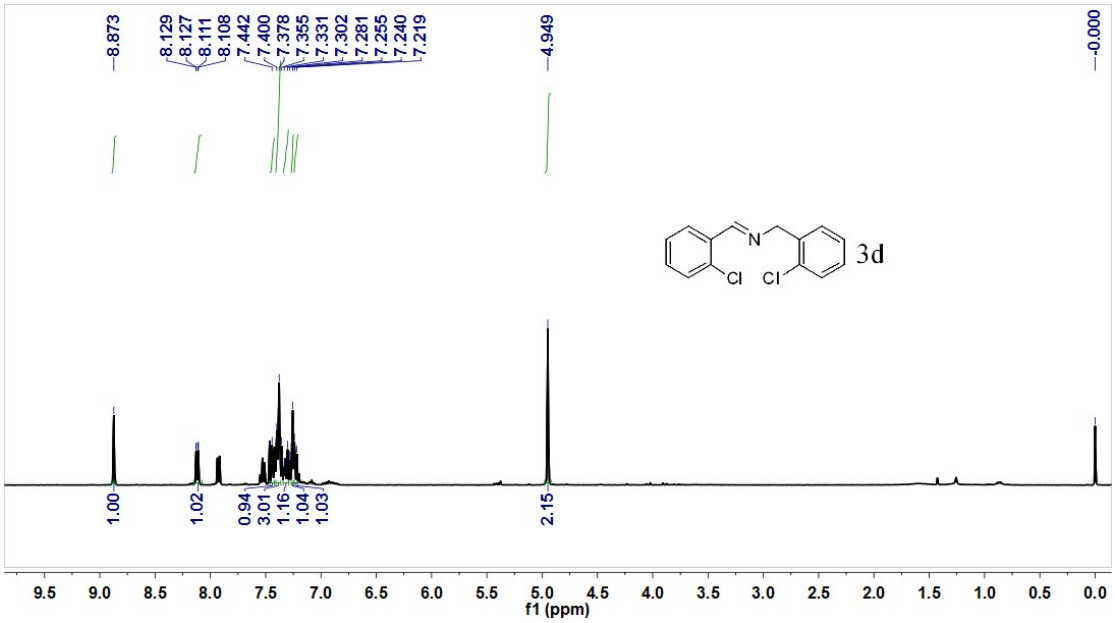
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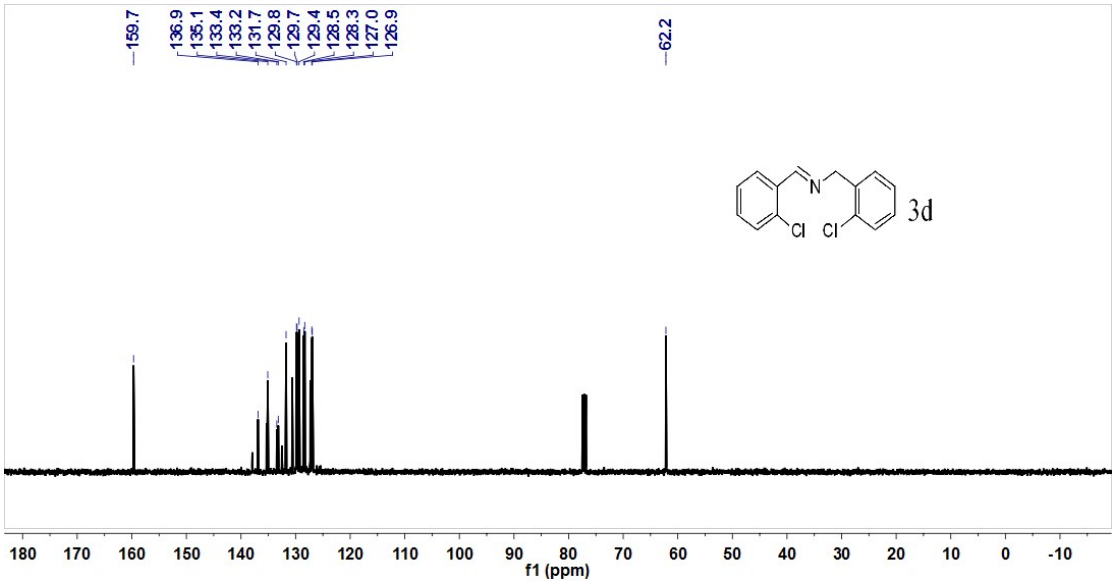
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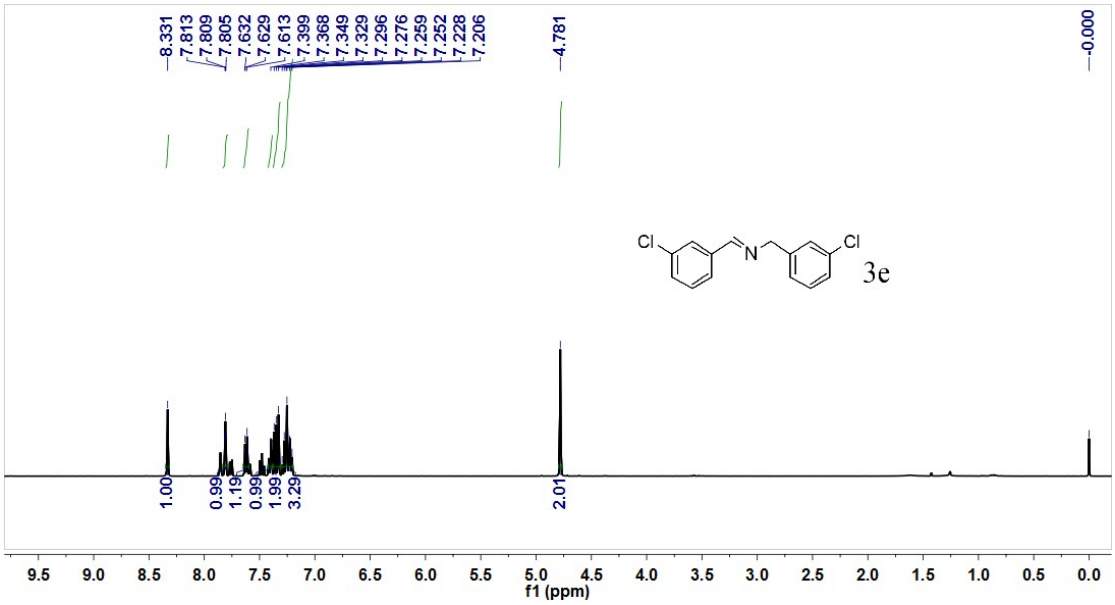
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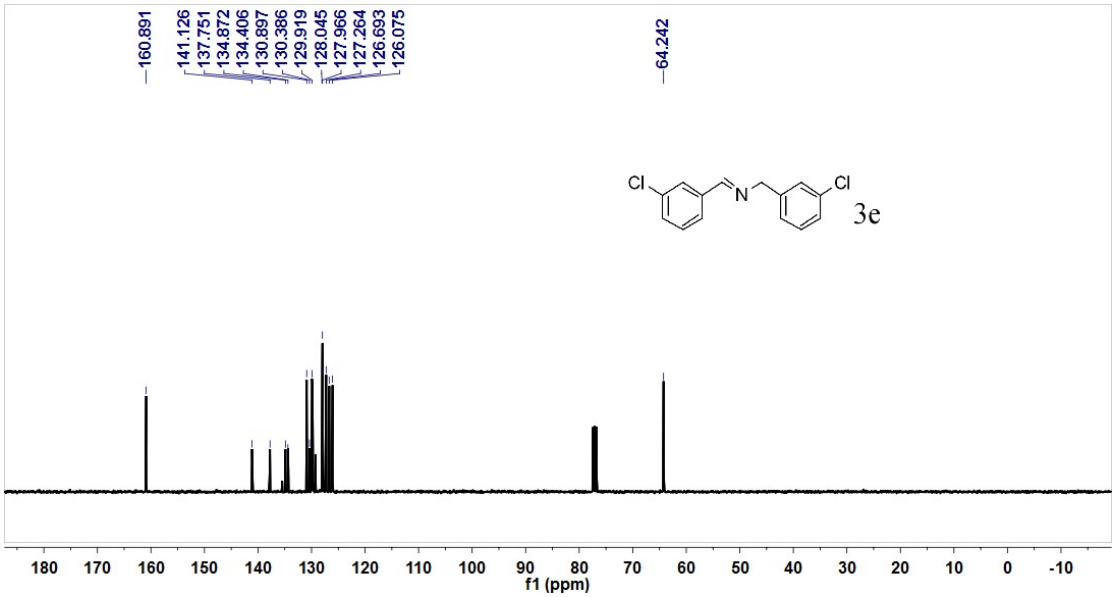
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