

Supporting Information

Heterogeneous Recyclable Nano-Palladium Catalyzed Amidation of Esters Using Formamides as Amine Sources

Yong-Sheng Bao, Lili Wang, Meilin Jia, Aiju Xu, Bao Agula,*

*Menghe Baiyin, and Bao Zhaorigetu**

*College of Chemistry and Environmental Science, Inner Mongolia Key
Laboratory of Green Catalysis, Inner Mongolia Normal University, Hohhot,
Inner Mongolia 010022, China*

**(Y.B.) E-mail: sbbys197812@163.com.*

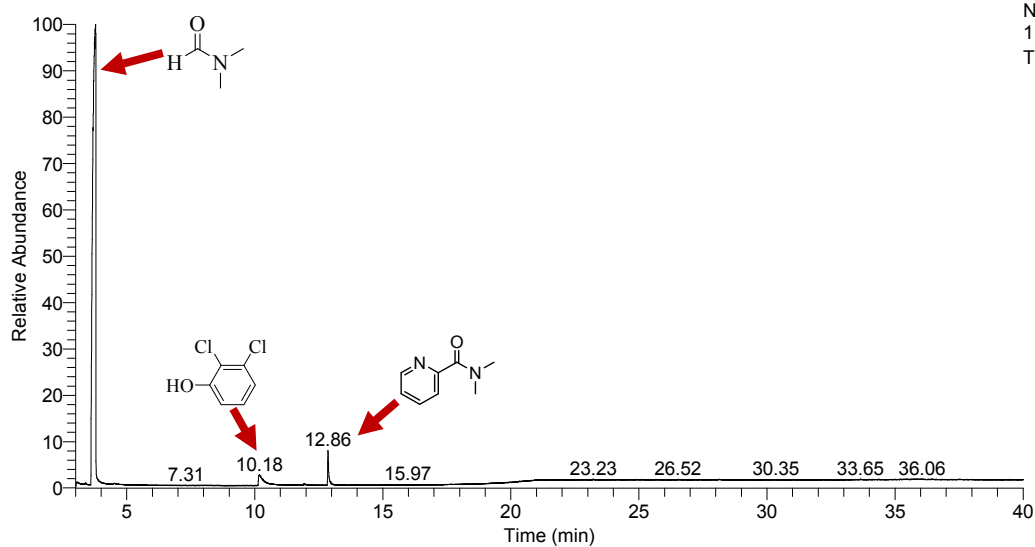
**(B.Z.) E-mail: zrgt@imnu.edu.cn.*

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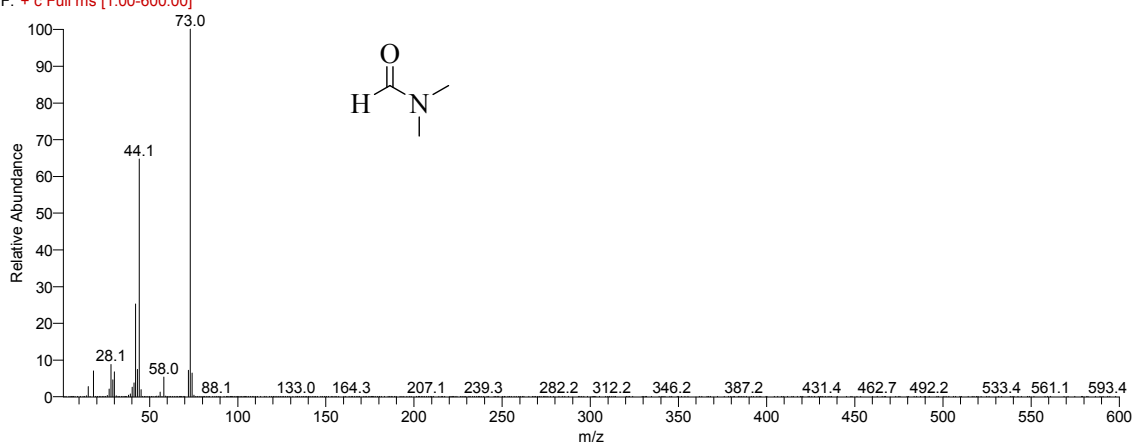
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1. GCMS Analysis of Reaction of 1a with DMF 2a

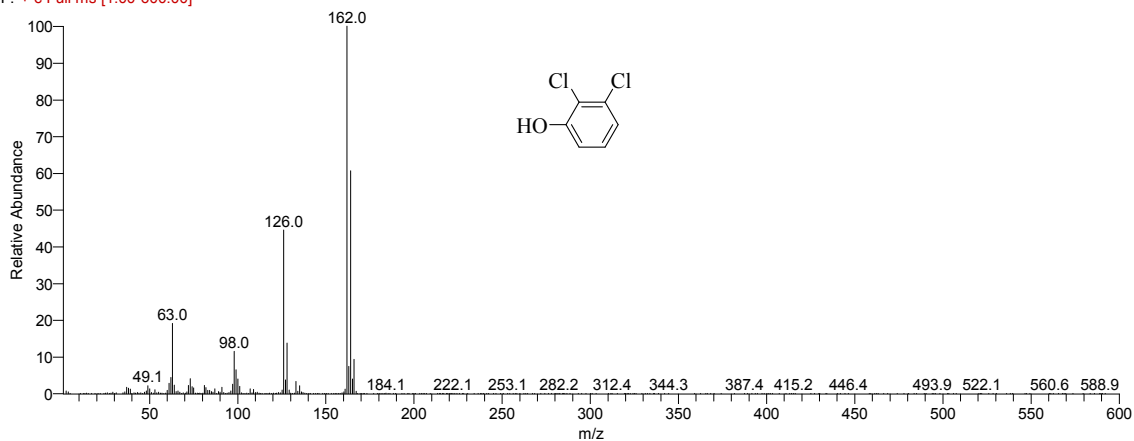
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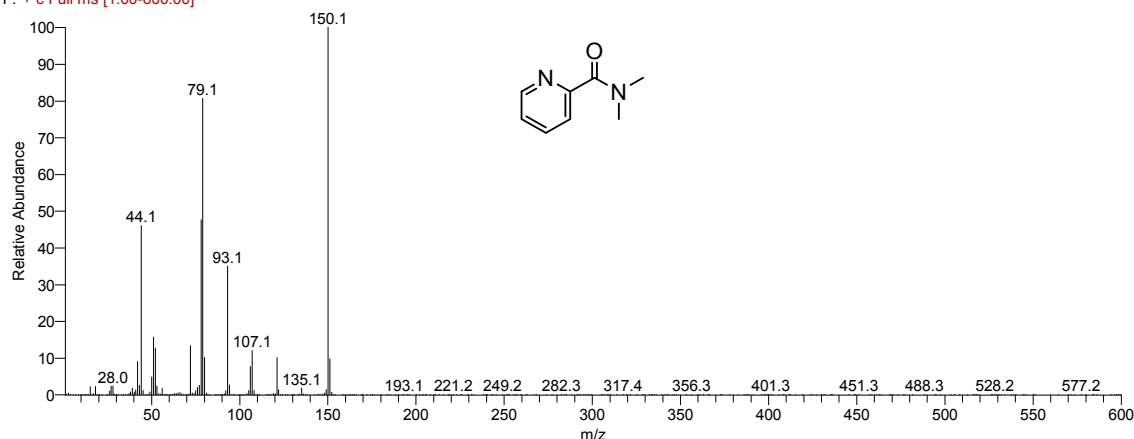
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2. Characterization Data for the Products

N,N-dimethylpicolinamide **3aa**.¹ Yield: 90% (27.0 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.60 (s, 1H), 7.82 (td, *J* = 7.7, 1.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.33 (m, 1H), 3.15 (s, 3H), 3.08 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.9, 154.2, 148.1, 137.3, 124.5, 123.7, 39.0, 35.8.

N,N-dimethylpyrazine-2-carboxamide **3ja**.² Yield: 87% (26.3 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.95 (d, *J* = 1.3 Hz, 1H), 8.64 (d, *J* = 2.5 Hz, 1H), 8.55 (dd, *J* = 2.4, 1.6 Hz, 1H), 3.17 (s, 3H), 3.13 (s, 3H).

N,N-dimethylfuran-2-carboxamide **3ka**.³ Yield: 90% (25.0 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.49 (d, *J* = 0.9 Hz, 1H), 7.01 (d, *J* = 3.4 Hz, 1H), 6.47 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.29 (s, 3H), 3.10 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 160.5, 147.9, 143.9, 116.4, 111.2, 38.4, 36.6.

N,N-dimethylthiophene-2-carboxamide **3la**.⁴ Yield: 91% (28.2 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.42 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.34 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.02 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.16 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 164.5, 137.8, 129.2, 128.8, 126.7, 39.5, 36.6.

2-(1*H*-indol-2-yl)-*N,N*-dimethylacetamide **3ma**.⁵ Yield: 83% (33.5 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.18 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.1 Hz, 1H), 7.13 (d, *J* = 7.1 Hz, 1H), 7.11 – 7.08 (m, 1H), 3.83 (s, 2H), 3.03 (s, 3H), 2.98 (s, 3H).

N,N-dimethylbenzamide **3na**.⁶ Yield: 85% (25.3 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.32 (m, 5H), 3.10 (s, 3H), 2.96 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 171.8, 136.1, 129.6, 128.3, 127.0, 39.6, 35.4.

4-cyano-*N,N*-dimethylbenzamide **3oa**.⁶ Yield: 92% (32.0 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.81 – 7.67 (m, 2H), 7.63 – 7.46 (m, 2H), 3.13 (s, 3H), 2.96 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.6, 140.6, 132.4, 127.8, 118.1, 113.4, 39.4, 35.4.

4-bromo-*N,N*-dimethylbenzamide **3pa**.⁶ Yield: 88% (39.9 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.63 – 7.45 (m, 2H), 7.31 – 7.27 (m, 2H), 3.09 (s, 3H), 2.97 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.6, 135.1, 131.6, 128.8, 123.8, 39.6, 35.4.

N,N-dimethyl-4-(trifluoromethyl)benzamide **3qa**.⁴ Yield: 87% (37.8 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 3.13 (s, 3H), 2.96 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.2, 139.8, 131.5 (q, *J*_{C-F} = 32.6 Hz), 127.4, 125.5 (q, *J*_{C-F} = 3.8 Hz), 123.7 (q, *J*_{C-F} = 272.5 Hz), 39.4, 35.3.

*piperidin-1-yl(pyridin-2-yl)methanone 3bb.*⁷ Yield: 79% (30.0 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.59 (s, 1H), 7.82 (t, *J* = 7.4 Hz, 1H), 7.69 (d, *J* = 7.3 Hz, 1H), 7.36 (s, 1H), 3.88 – 3.76 (m, 4H), 3.76 – 3.61 (m, 6H).

morpholino(pyridin-2-yl)methanone **3bc.**⁸ Yield: 81% (31.1 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.60 (d, *J* = 3.7 Hz, 1H), 7.84 (t, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.33 (m, 1H), 3.91 – 3.76 (m, 4H), 3.76 – 3.59 (m, 4H).

N-methylpicolinamide **3bd.**⁹ Yield: 91% (24.9 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.53 (d, *J* = 4.5 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 8.09 (s, 1H), 7.89 – 7.66 (m, 1H), 7.41 (dd, *J* = 7.1, 5.1 Hz, 1H), 3.03 (d, *J* = 5.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 165.2, 149.8, 148.1, 137.4, 126.2, 122.1, 26.1.

N-phenylpicolinamide **3be.**¹⁰ Yield: 74% (29.3 mg). ¹H NMR (500 MHz, CDCl₃) δ 10.04 (s, 1H), 8.62 (d, *J* = 4.3 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.55 – 7.45 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H).

4-cyano-*N*-methylbenzamide **3od.**¹¹ Yield: 89% (28.5 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 6.34 (s, 1H), 3.04 (d, *J* = 4.8 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 166.4, 138.5, 132.5(2C), 127.6(2C), 118.0, 115.0, 27.1.

4-cyano-*N*-phenylbenzamide **3oe.**¹² Yield: 63% (28.0 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.84 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 163.9, 138.9, 137.3, 132.7, 129.3, 127.8, 125.3, 120.4, 117.9, 115.5.

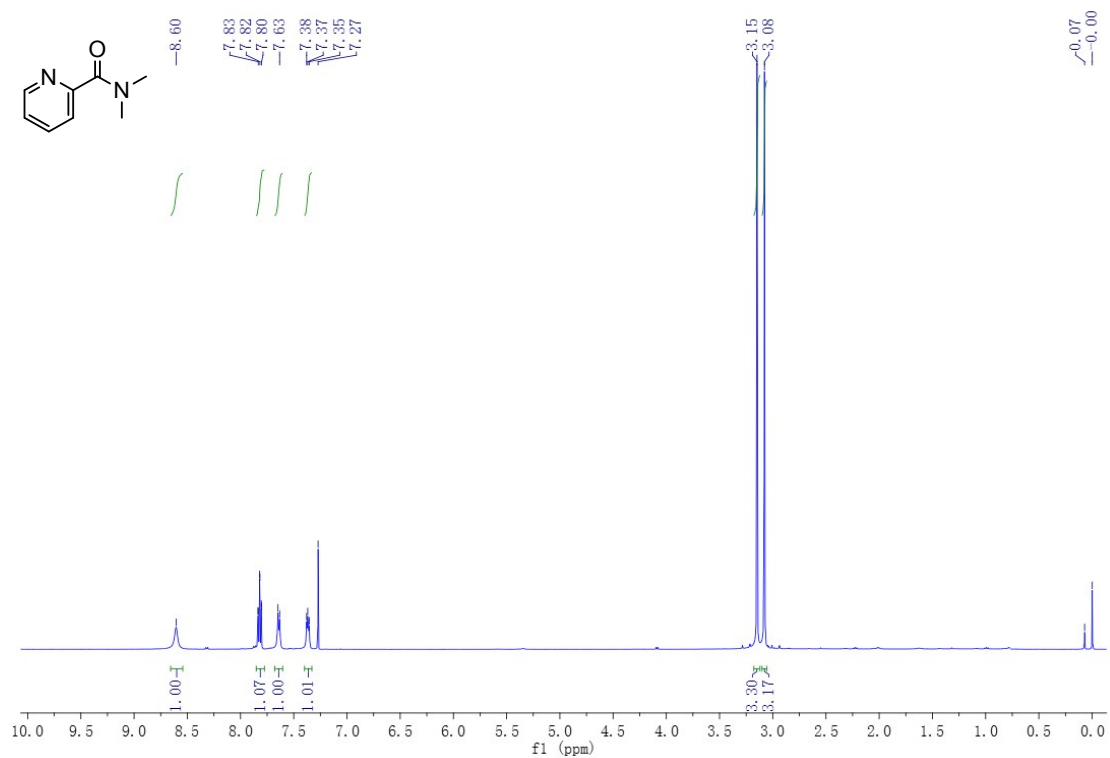
4-cyano-*N,N*-diethylbenzamide **3of.**¹³ Yield: 72% (29.1 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 3.56 (q, *J* = 6.9 Hz, 2H), 3.21 (q, *J* = 6.8 Hz, 2H), 1.29 – 1.24 (m, 3H), 1.12 (t, *J* = 5.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 169.4, 141.4, 132.4, 127.1, 118.2, 113.1, 43.3, 39.6, 14.2, 12.8.

References:

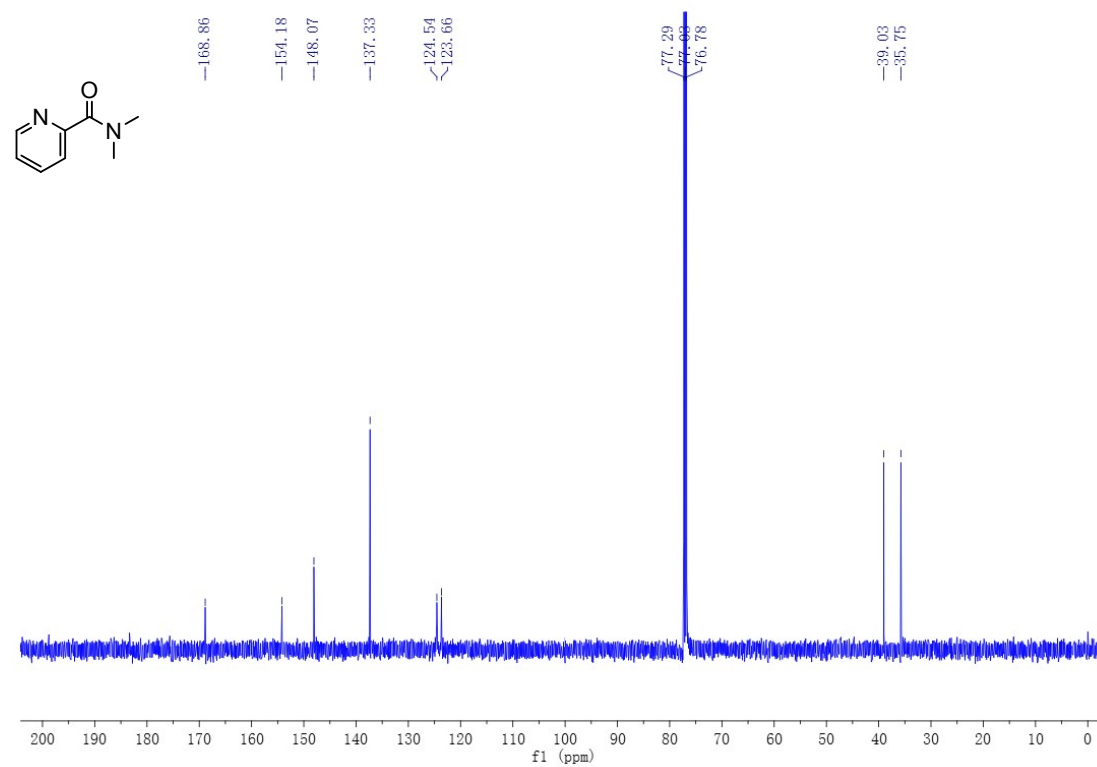
- [1] I. Okamoto, M. Terashima, H. Masu, M. Nabeta, K. Ono, N. Morita, K. Katagiri, I. Azumaya, O. Tamura *Tetrahedron* 2011, 67, 8536.
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3. ¹H NMR and ¹³C NMR Spectra of the Products

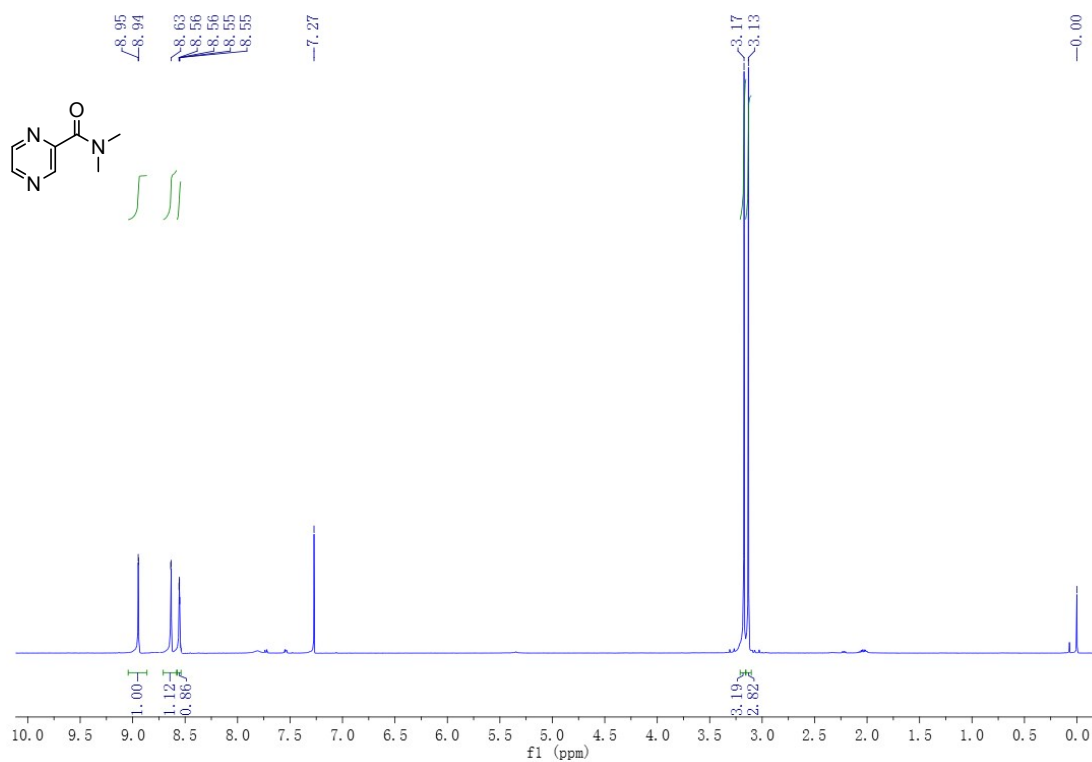
¹H NMR of *N,N*-dimethylpicolinamide **3aa**



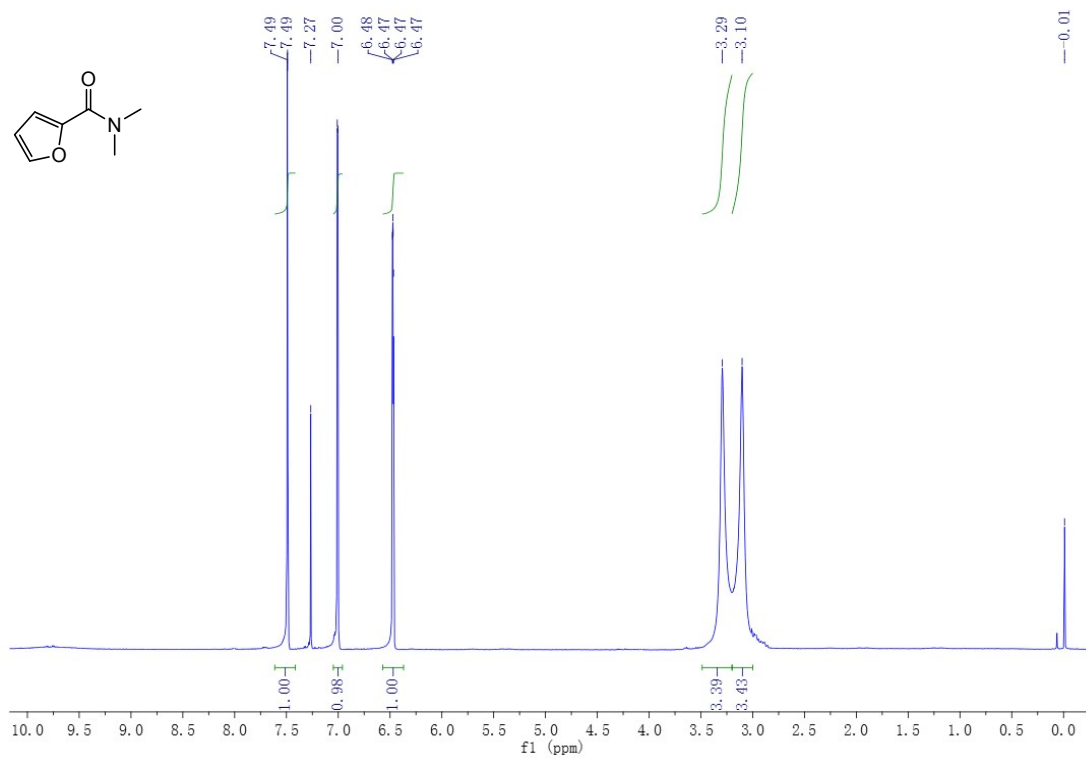
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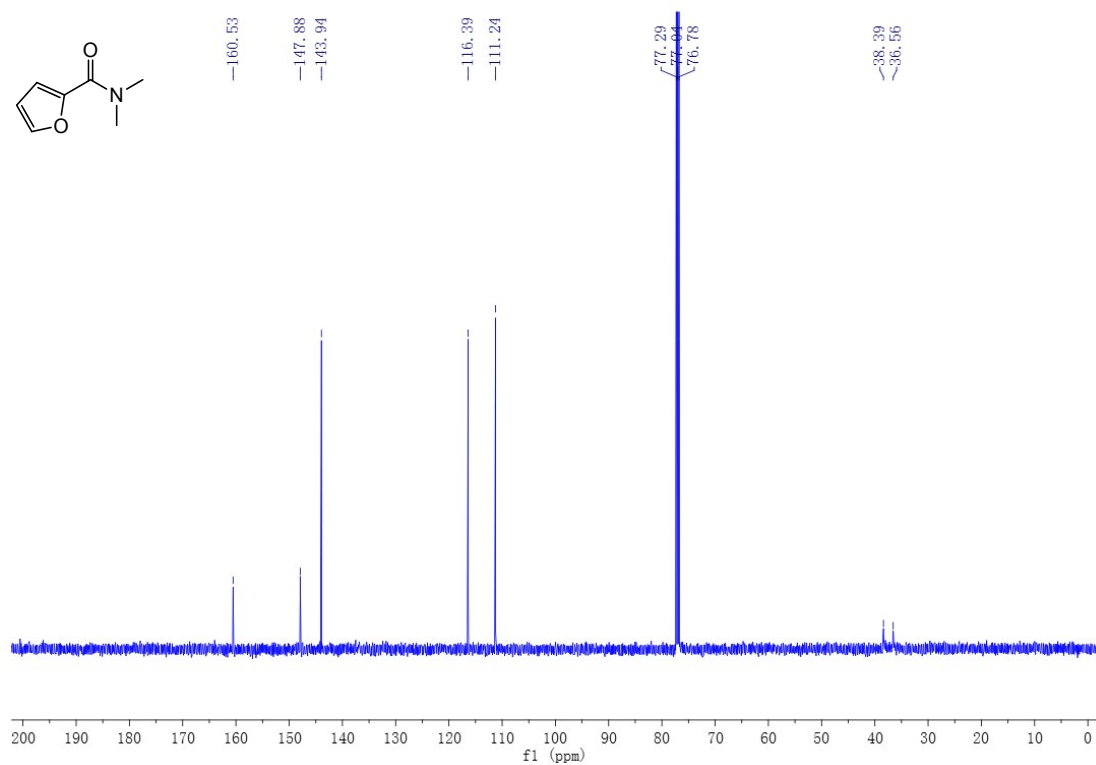
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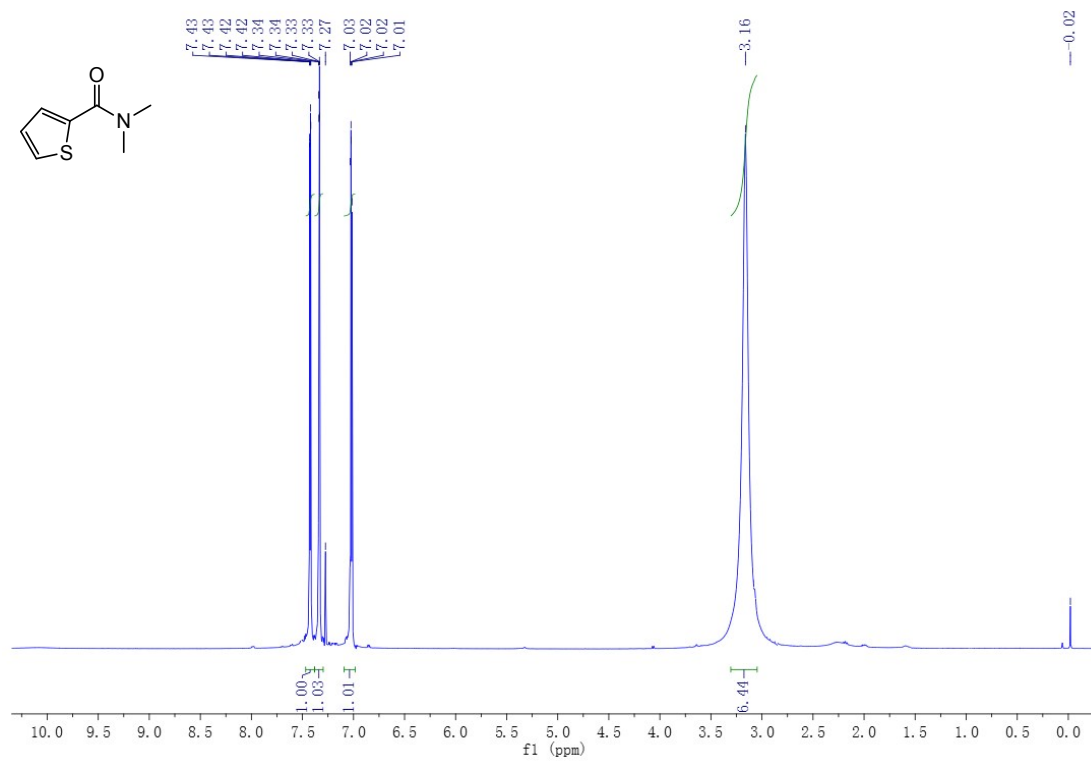
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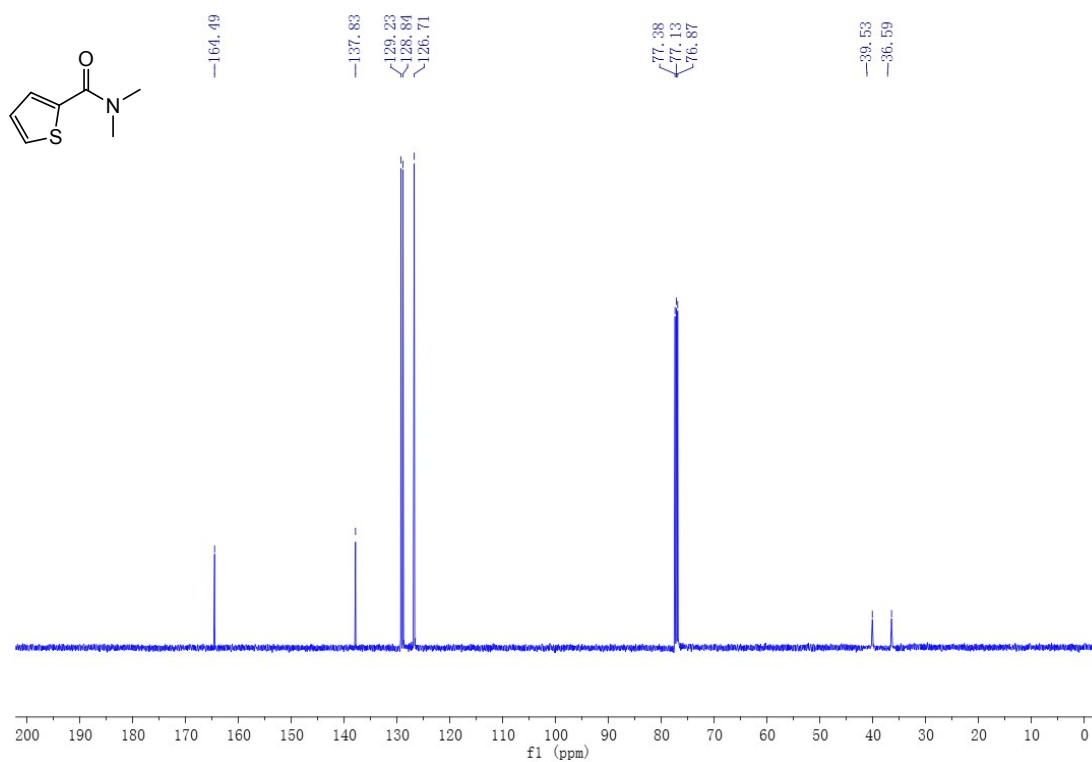
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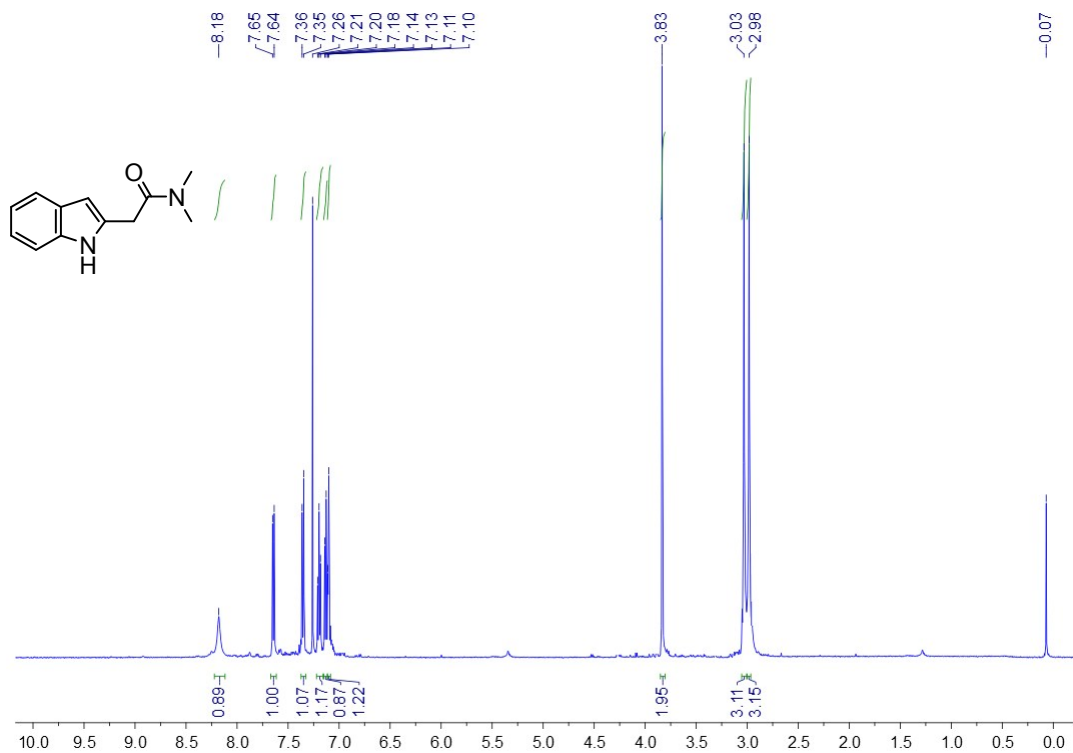
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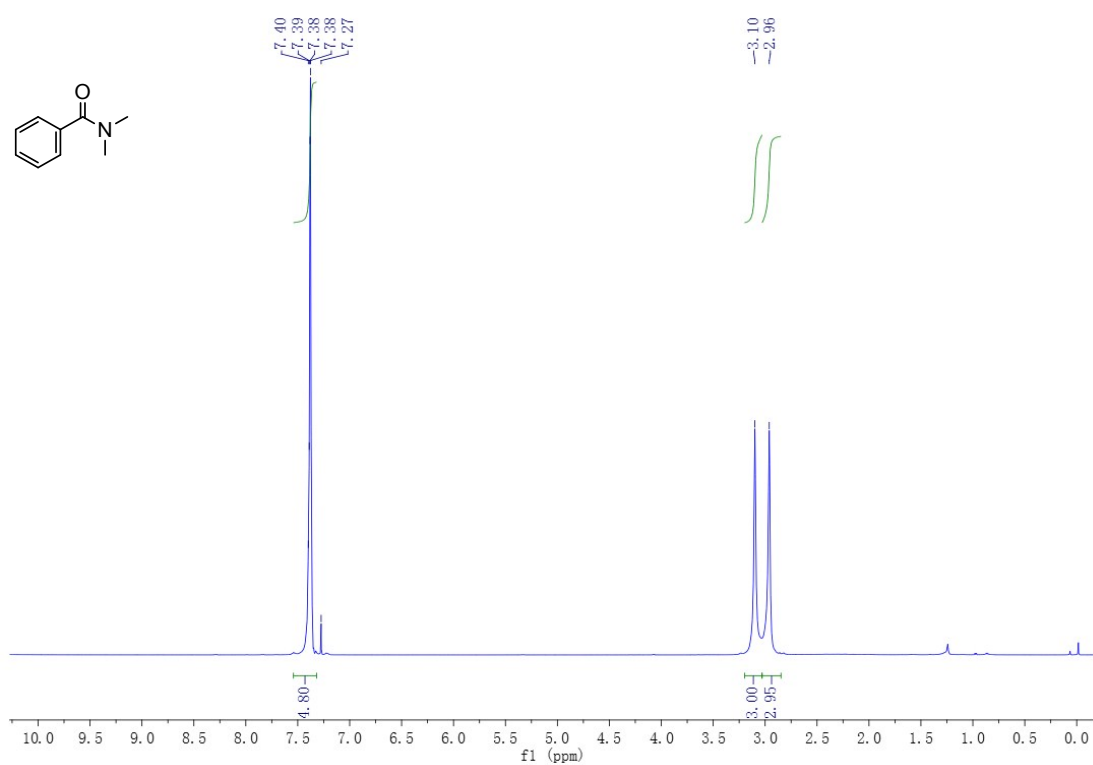
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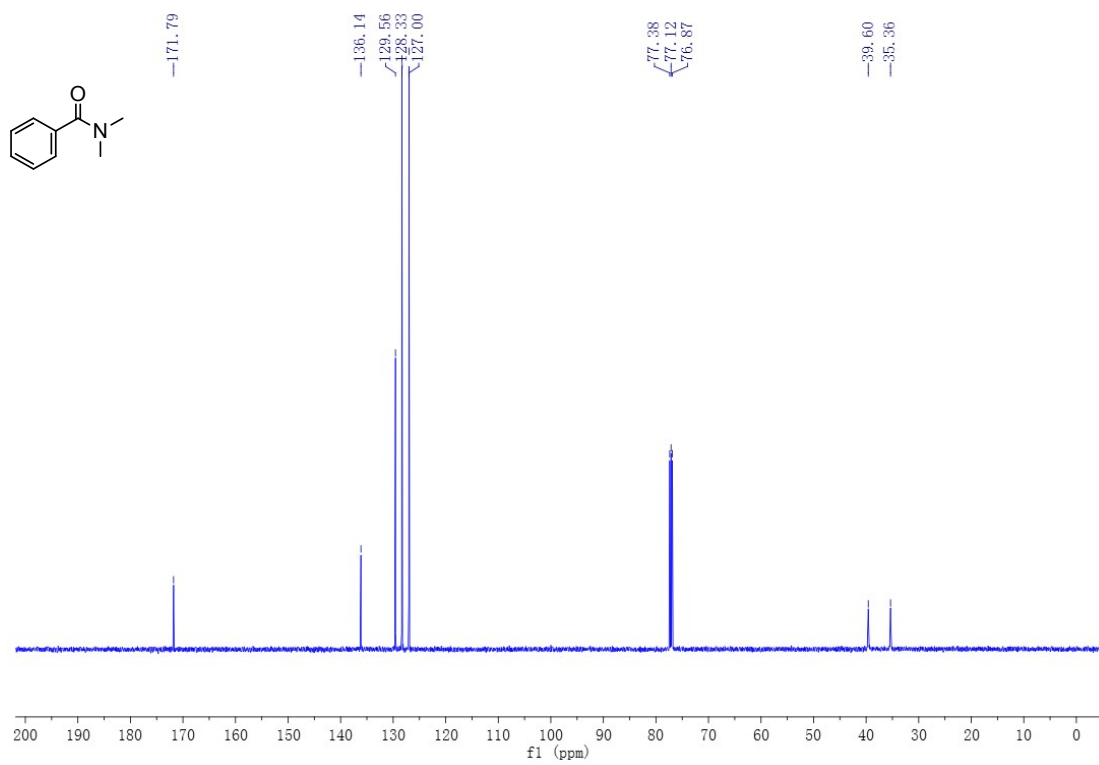
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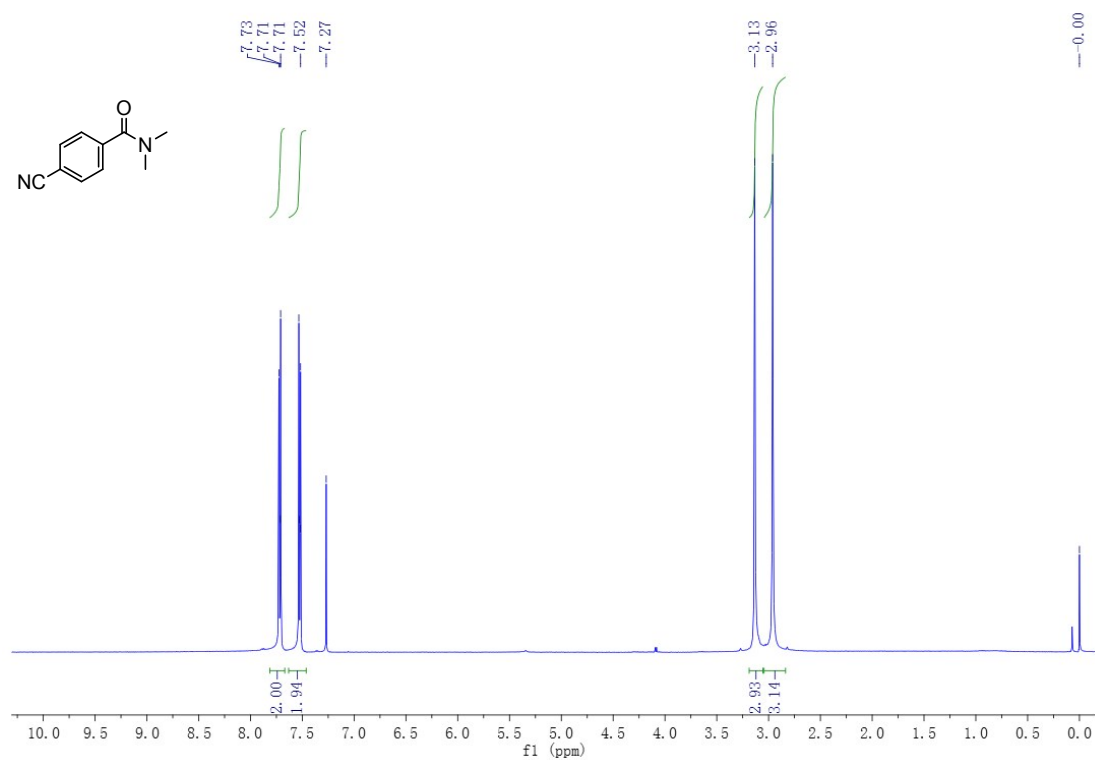
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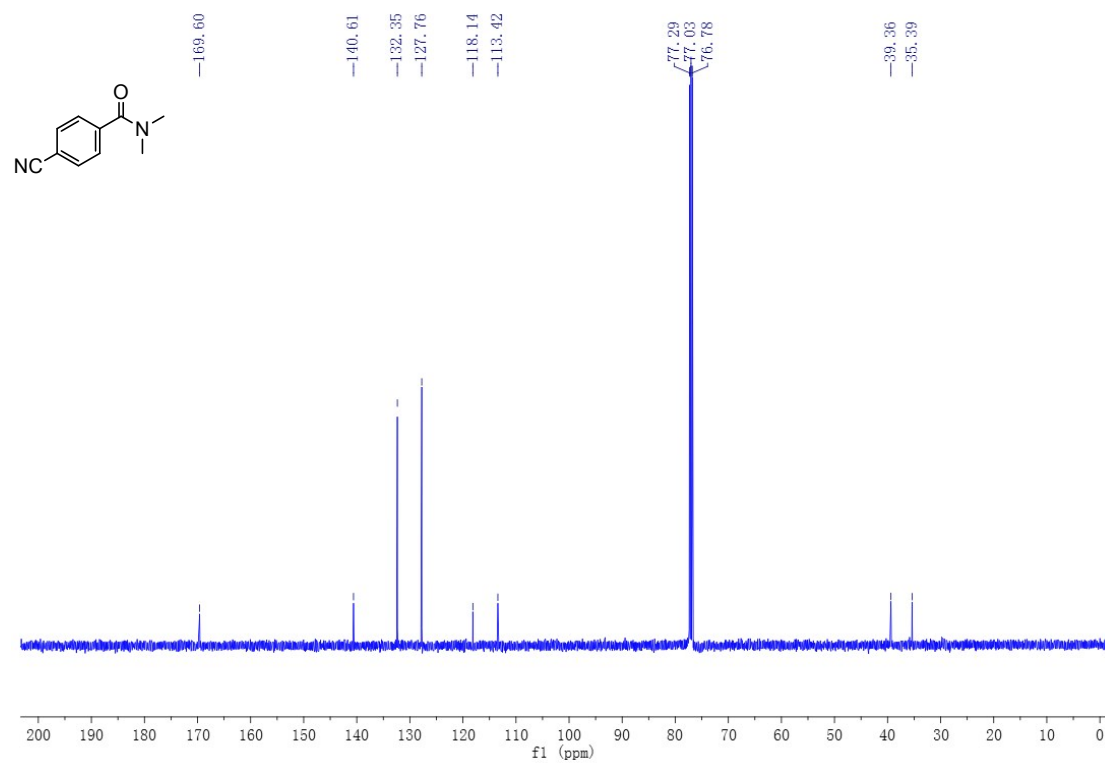
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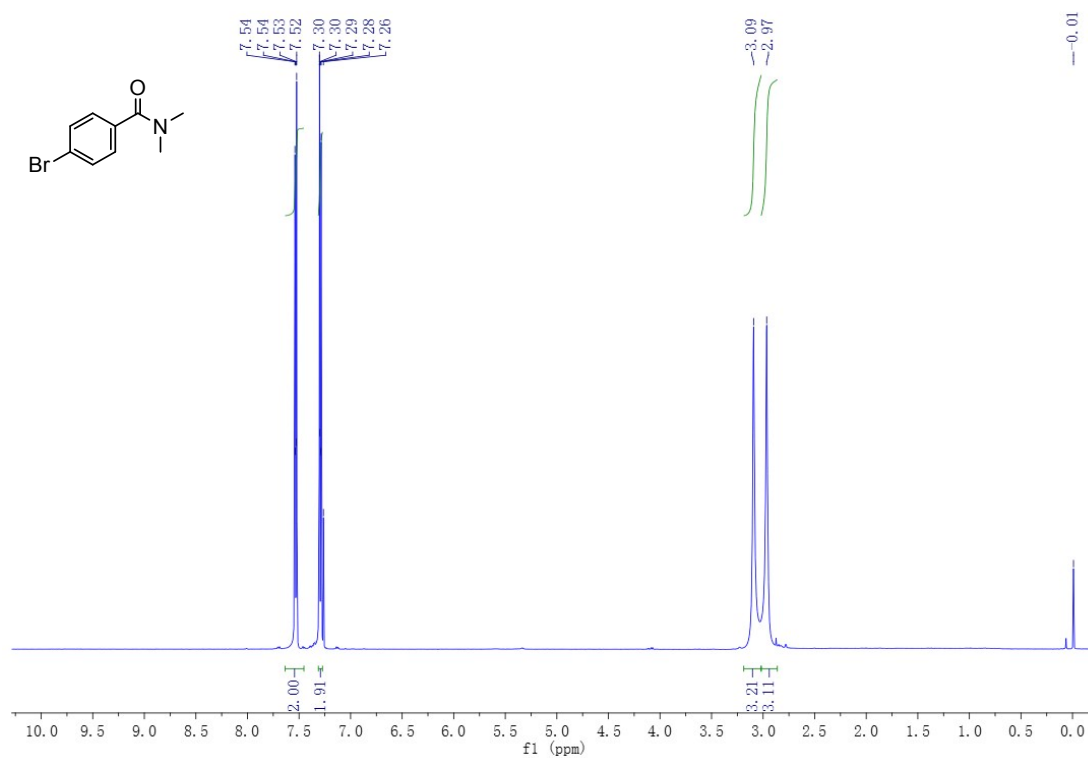
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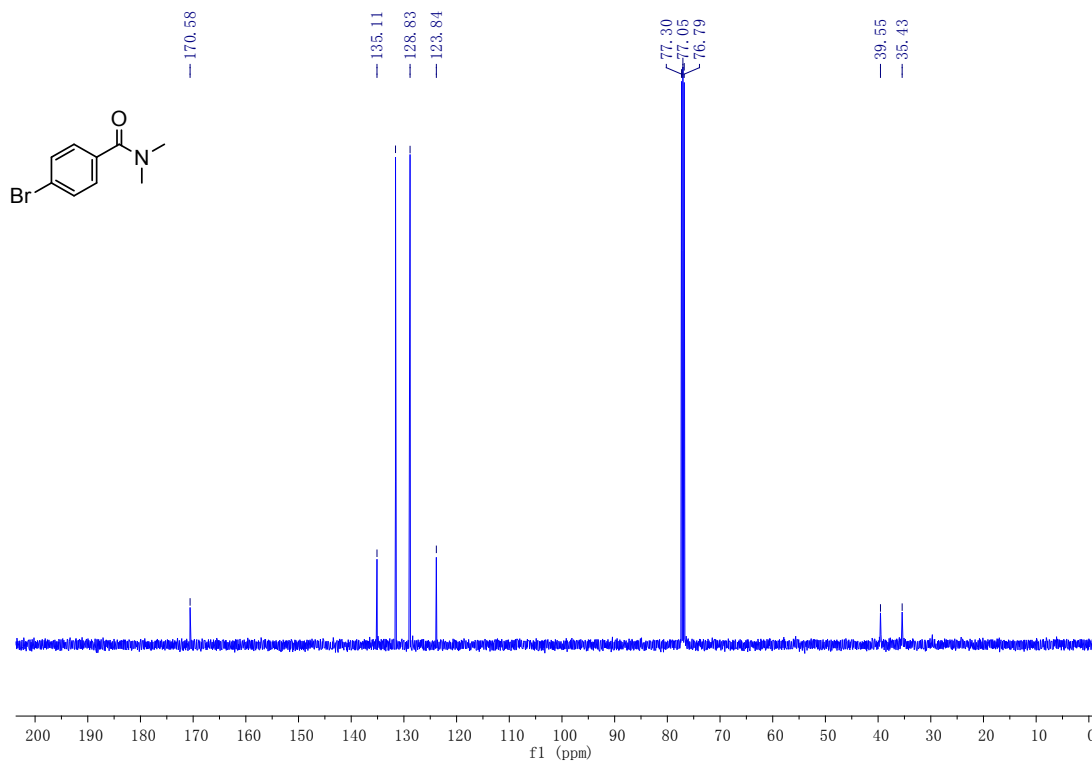
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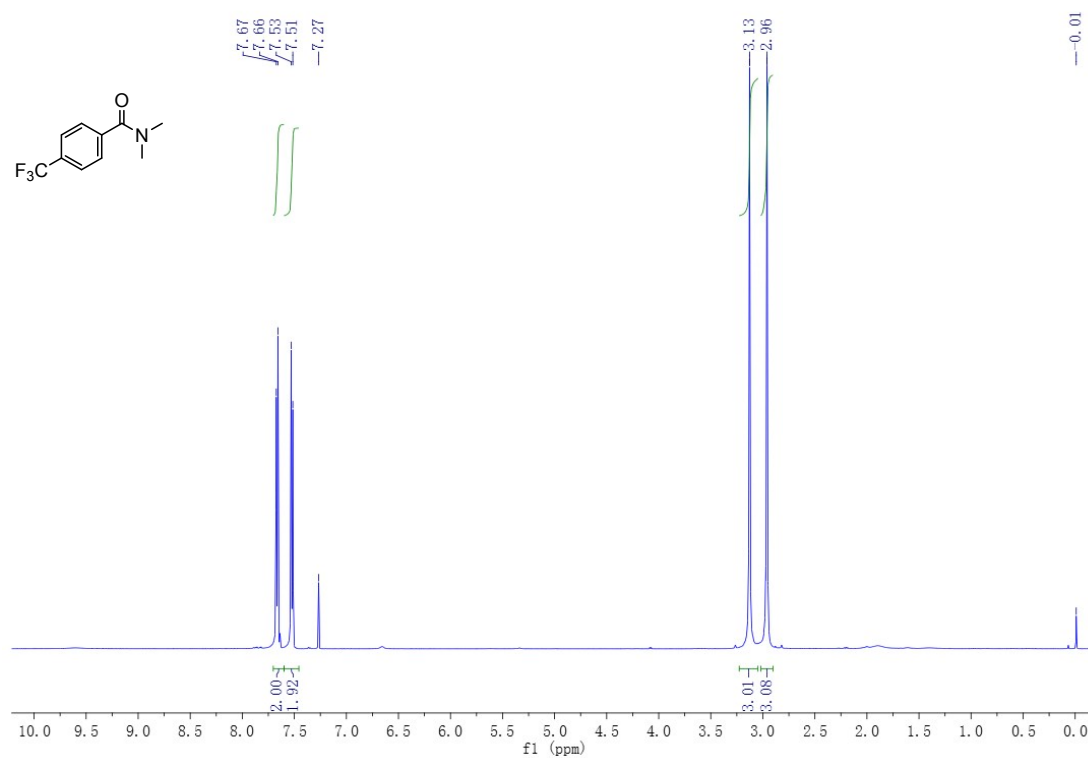
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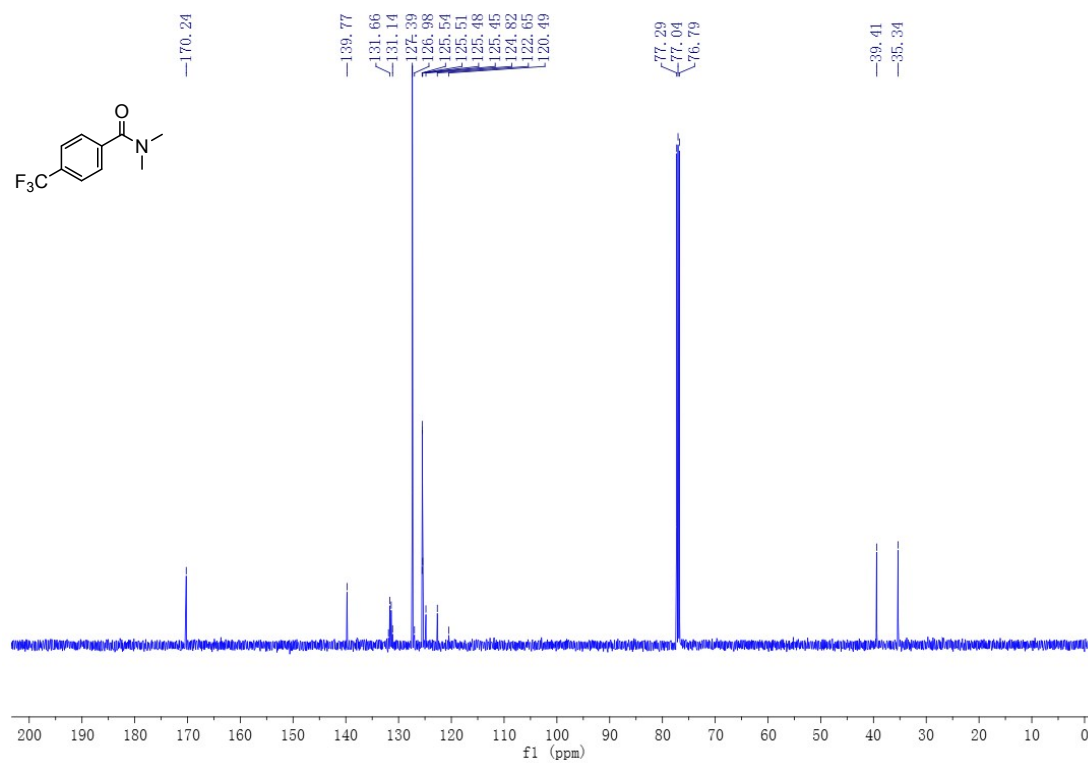
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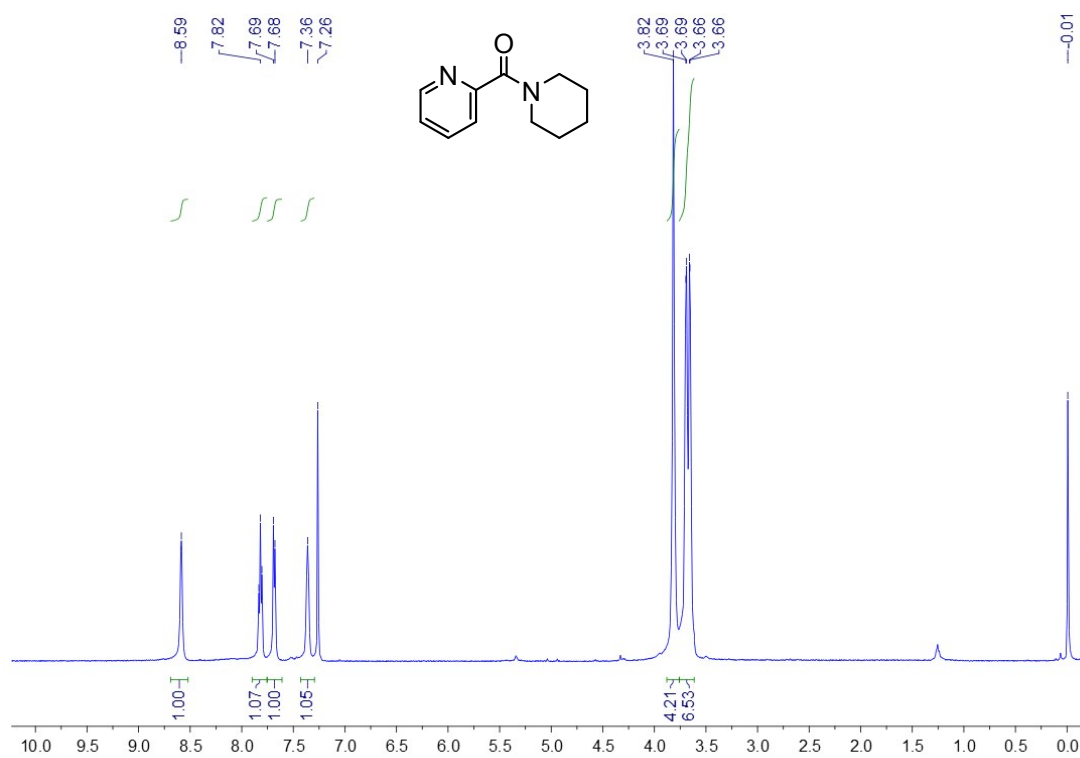
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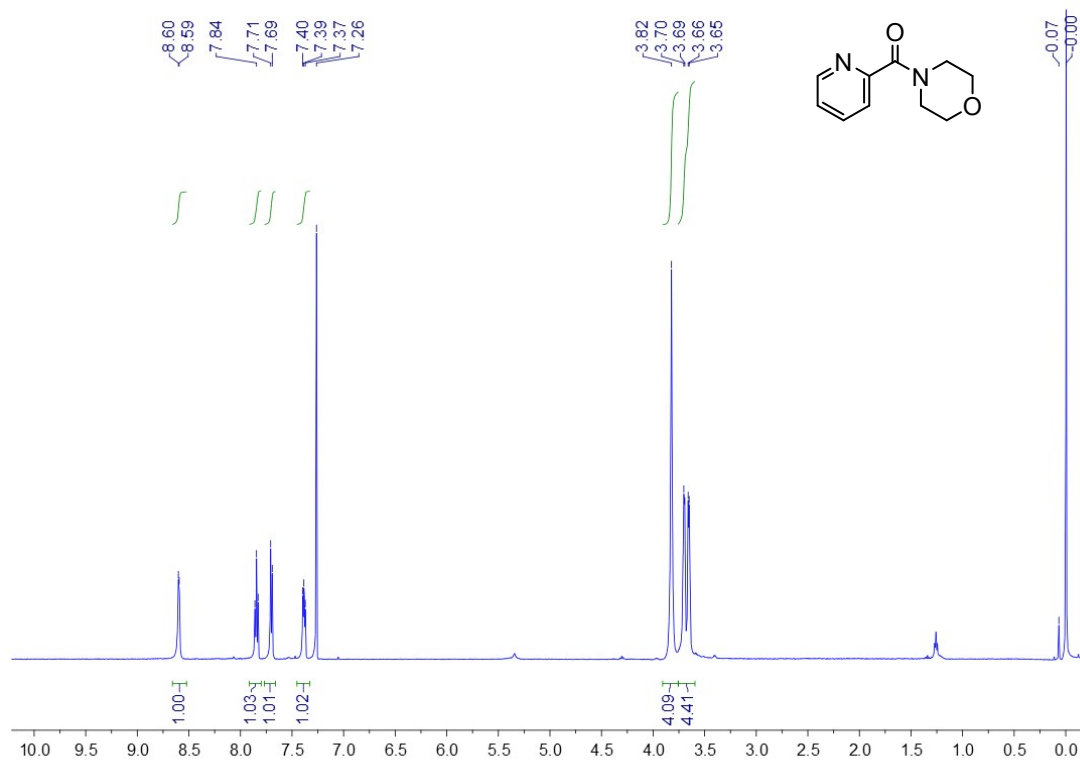
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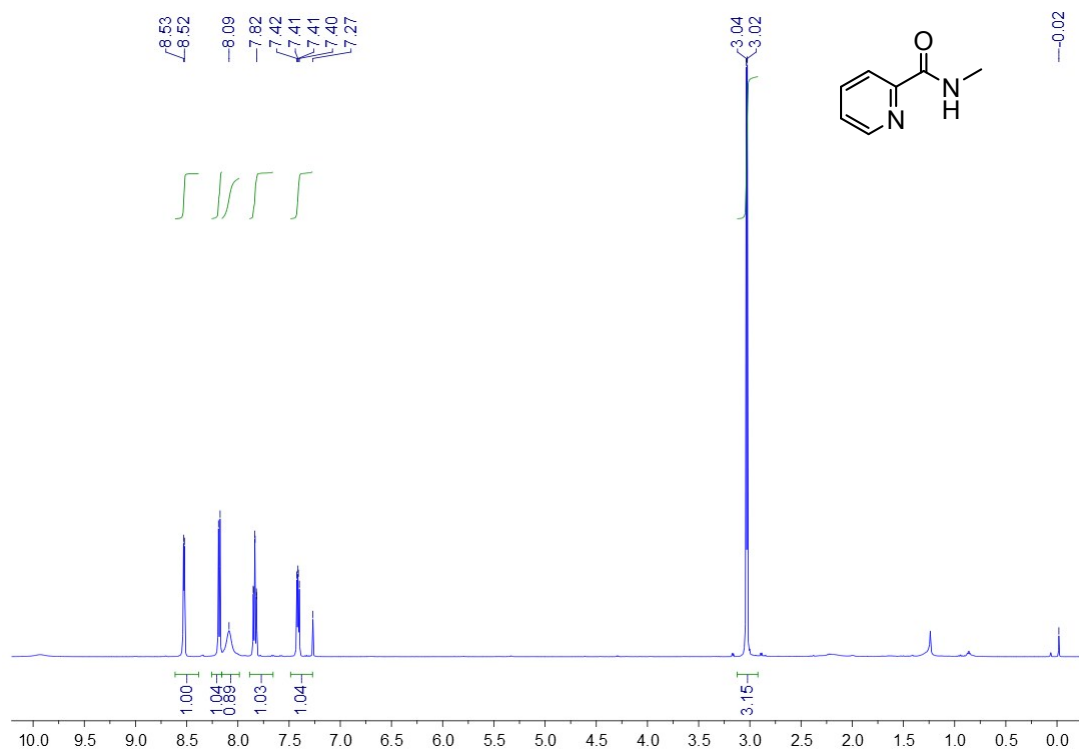
¹H NMR of piperidin-1-yl(pyridin-2-yl)methanone **3bb**



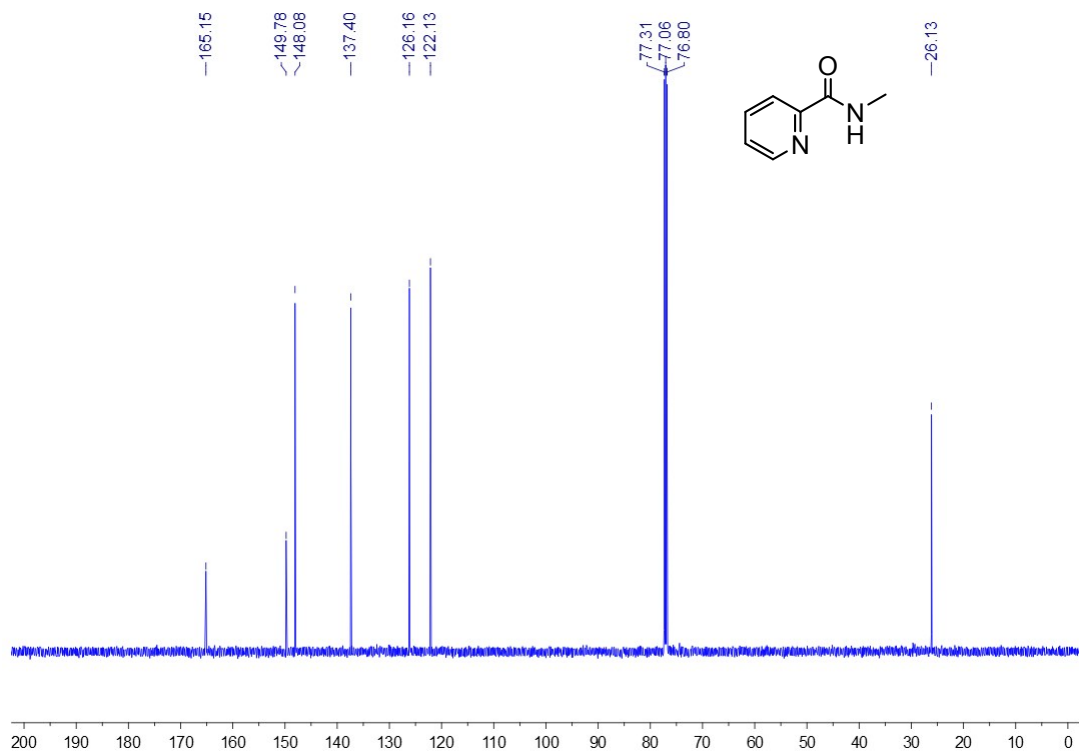
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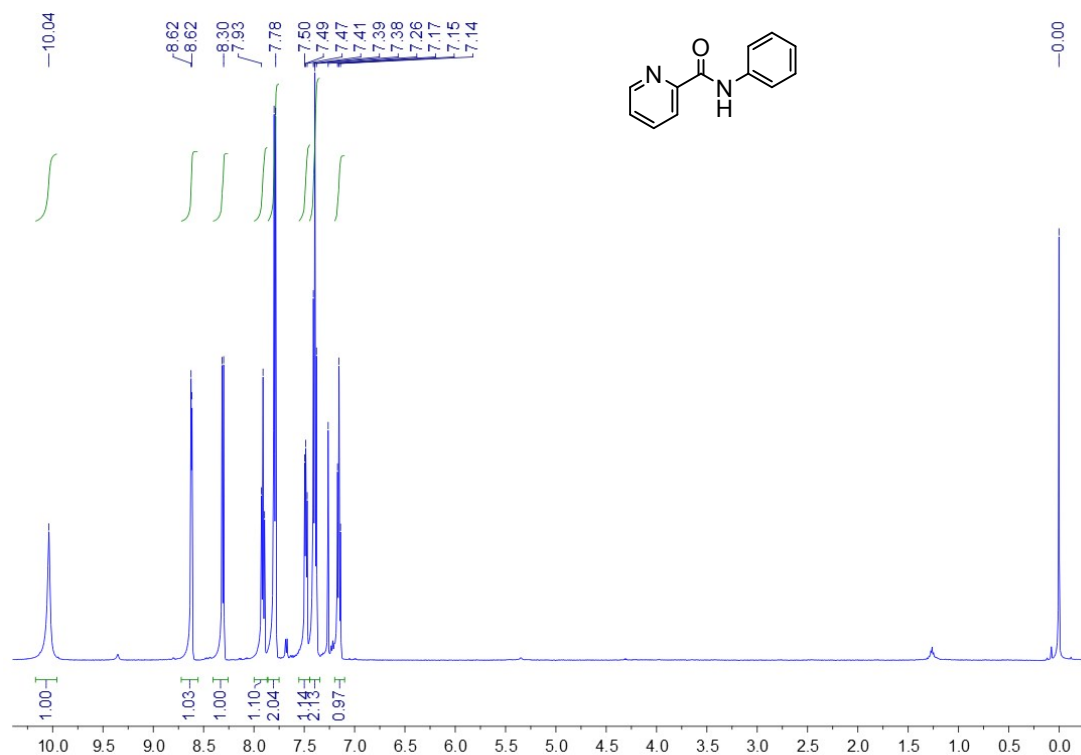
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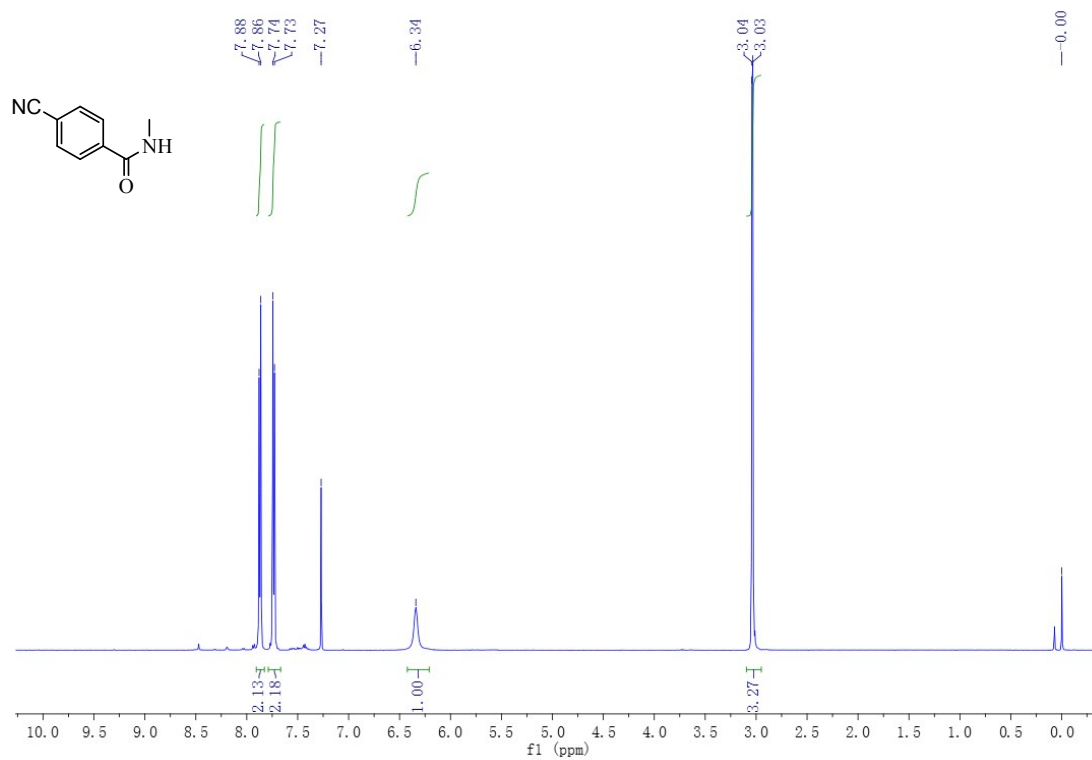
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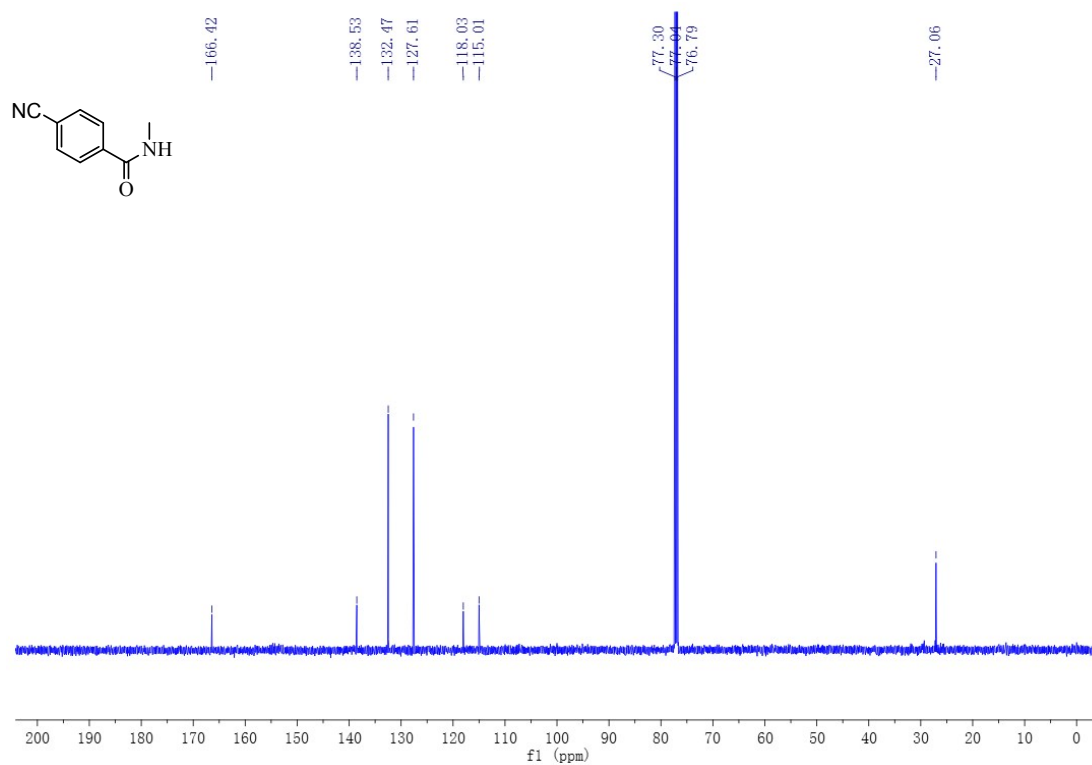
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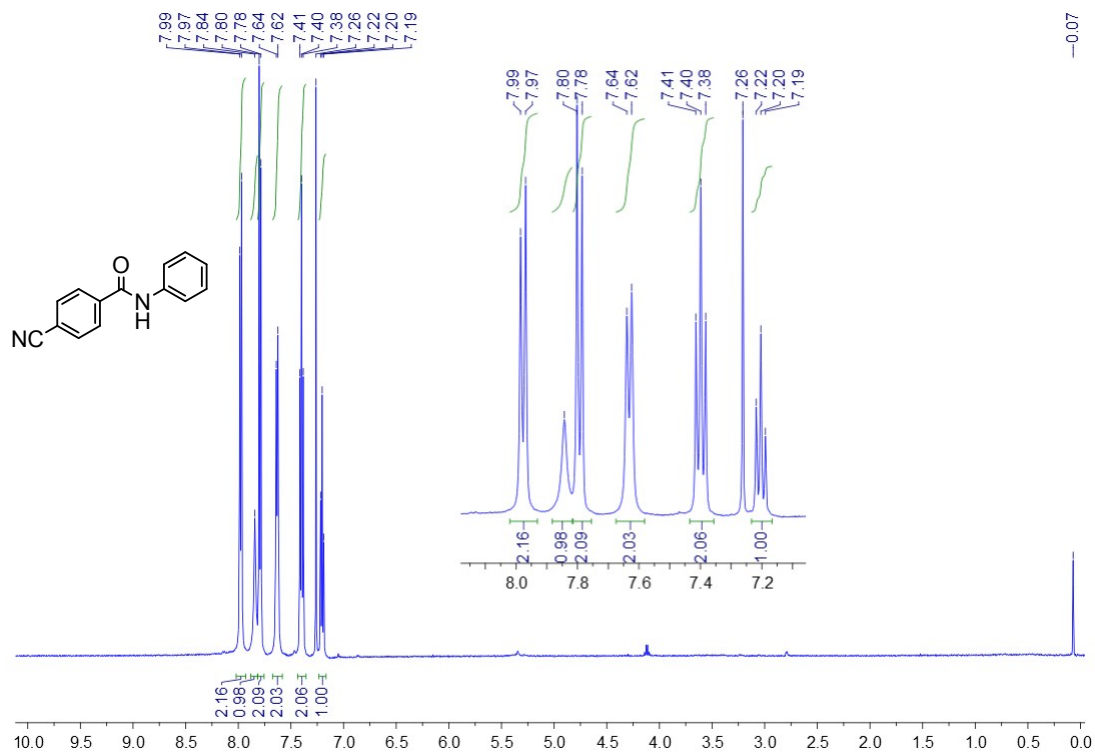
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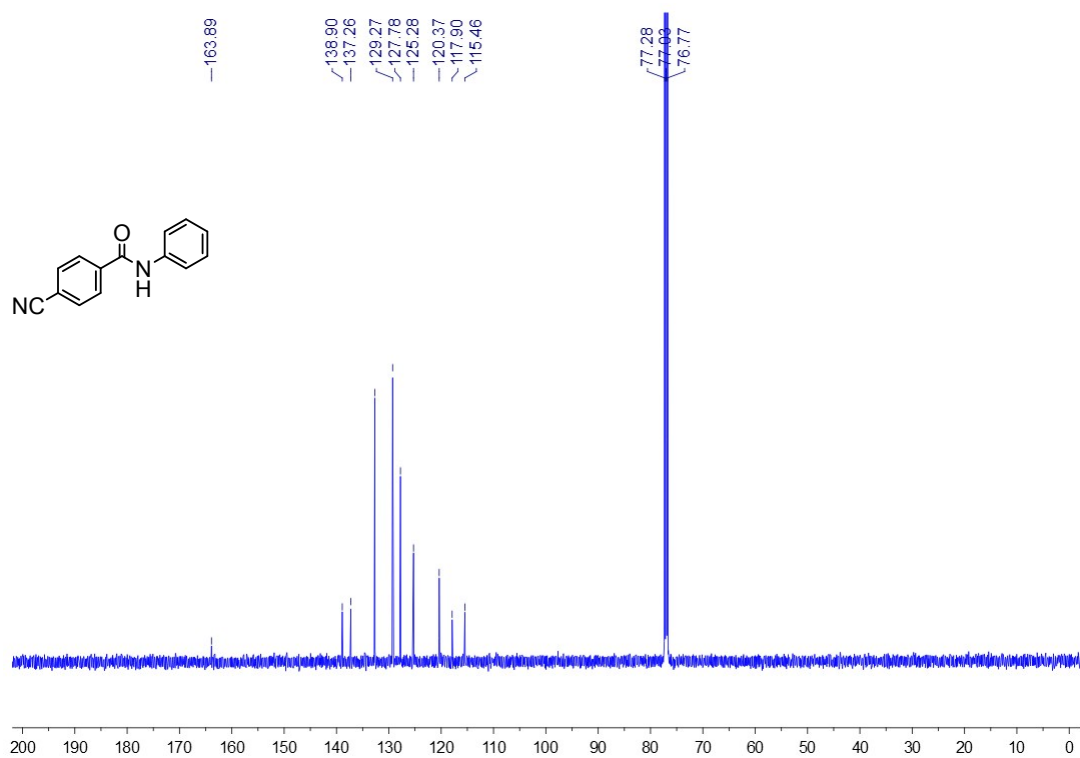
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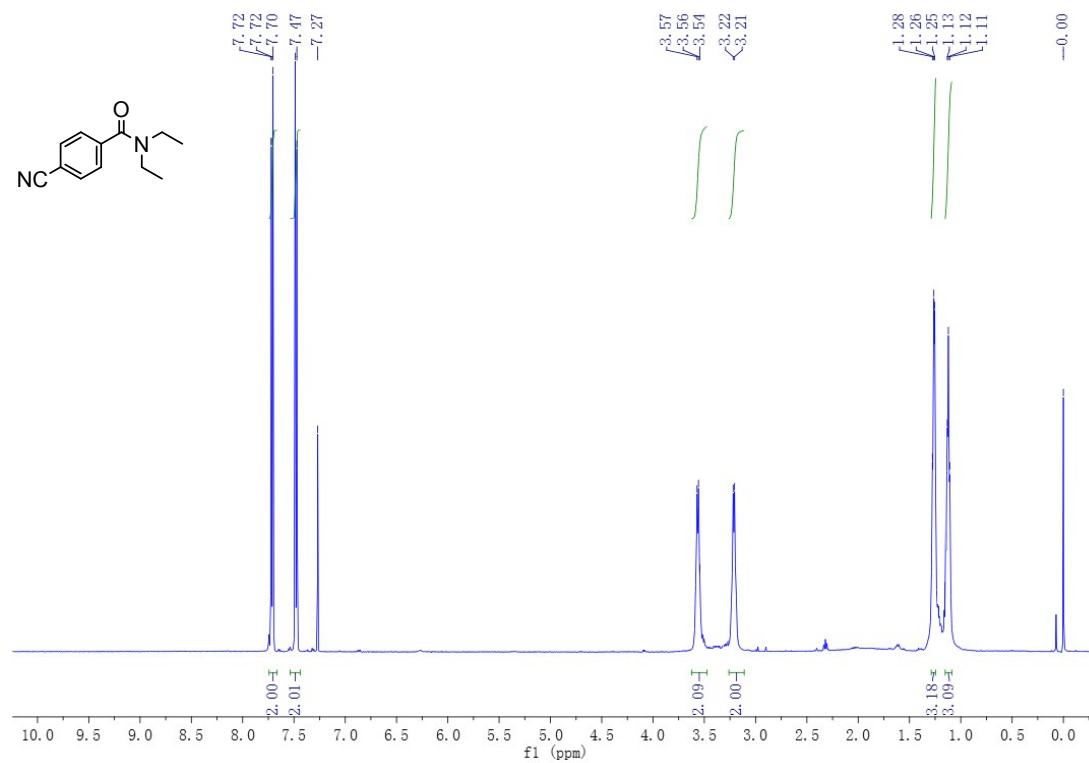
¹H NMR of 4-cyano-N-phenylbenzamide **3ne**



¹³C NMR of 4-cyano-N-phenylbenzamide **3ne**



¹H NMR of 4-cyano-N,N-diethylbenzamide **3nf**



¹³C NMR of 4-cyano-N,N-diethylbenzamide **3nf**

