Supporting Information for

Mild Transition Metal-Free Amination of Fluoroarenes Catalyzed by Fluoride Ions

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Characterization Data

1-(4-Nitrophenyl)-1*H*-imidazole (Table 2, entry 1).[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 (s, 1H), 7.37 (s, 1H), 7.49–7.64 (m, 2H), 7.97 (s, 1H), 8.33–8.38 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 117.7, 121.1, 125.8, 131.7, 135.4, 142.0, 146.3. Anal. calcd for $C_9H_7N_3O_2$ (189.17): C, 57.14; H, 3.73; N, 22.21. Found: C, 57.41; H, 3.81; N, 22.25.

4-(1*H*-Imidazol-1-yl)benzonitrile (Table 2, entry 2).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (s, 1H), 7.35 (s, 1H), 7.52–7.57 (m, 2H), 7.78–7.83 (m, 2H), 8.03 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 111.2, 117.6, 117.9, 121.5, 131.6, 134.2, 135.4, 140.6. Anal. calcd for $C_{10}H_7N_3$ (169.18): C, 70.99; H, 4.17; N, 24.84. Found: C, 71.08; H, 4.35; N, 24.59.

3-(1*H*-Imidazol-1-yl)benzonitrile (Table 2, entry 3).[3] ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.26 (s, 1H), 7.31 (s, 1H), 7.61–7.74 (m, 4H), 7.93 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 114.3, 117.5, 117.9, 124.6, 125.6, 130.9, 131.1, 131.4, 135.4, 138.1. Anal. calcd for $C_{10}H_7N_3$ (169.18): C, 70.99; H, 4.17; N, 24.84. Found: C, 70.89; H, 4.40; N, 24.56.

2-(1*H*-Imidazol-1-yl)benzonitrile (Table 2, entry 4).[4] ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.27 (s, 1H), 7.36 (s, 1H), 7.43–7.59 (m, 2H), 7.70–7.79 (m, 1H), 7.81–7.85 (m, 1H), 7.87 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 108.2, 115.9, 119.7, 125.7, 128.5, 130.9, 134.4, 134.6, 136.8, 139.4. Anal. calcd for $C_{10}H_7N_3$ (169.18): C, 70.99; H, 4.17; N, 24.84. Found: C, 70.82; H, 4.06; N, 24.53.

Methyl-4-(1*H*-imidazol-1-yl)benzoate (Table 2, entry 5).[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.87 (s, 3H), 7.16 (s, 1H), 7.29 (s, 1H), 7.38–7.43 (m, 2H), 7.89 (s, 1H), 8.04–8.11 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 52.3, 117.6, 120.4, 128.8, 131.0, 131.4, 135.3, 140.6, 165.9. Anal. calcd for $C_{11}H_{10}N_2O_2$ (202.21): C, 65.34; H, 4.98; N, 13.85. Found: C, 65.34; H, 4.91; N, 13.70.

1-(2,4-Dichlorophenyl)-1*H*-imidazole (Table 2, entry 6). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05 (s, 1H), 7.12 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.29 (dd, *J* = 2.2, 8.4 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H), 7.59 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 120.3, 128.1, 128.4, 129.7, 130.6, 130.7, 133.8, 135.0, 137.4. Anal. calcd for $C_9H_6Cl_2N_2$ (213.06): C, 50.74; H, 2.84; N, 13.15. Found: C, 50.71; H, 2.89; N, 13.05. HRMS: *m/z* [M^+] calcd for $C_9H_6Cl_2N_2$: 211.9908; found: 211.9900.

1-(4-Bromophenyl)-1*H*-imidazole (Table 2, entry 7).[1] ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.25 (s, 1H), 7.29 (s, 1H), 7.29–7.35 (m, 2H), 7.61–7.68 (m, 2H), 7.88 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 118.1, 121.0, 123.0, 130.8, 133.1, 135.5, 136.4. Anal. calcd for $C_9H_7BrN_2$ (223.07): C, 48.46; H, 3.16; N, 12.56. Found: C, 48.67; H, 3.36; N, 12.30. HRMS: *m/z* [M^+] calcd for $C_9H_7BrN_2$: 221.9793; found: 221.9789.

1-(4-Nitrophenyl)pyrrolidine (Table 4, entry 1).[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.03–2.10 (m, 4H), 3.36–3.43 (m, 4H), 6.42–6.51 (m, 2H), 8.07–8.15 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 25.5, 48.0, 110.5, 126.4, 136.6, 151.9. Anal. calcd for $C_{10}H_{12}N_2O_2$ (192.21): C, 62.49; H, 6.29; N, 14.57. Found: C, 62.65; H, 6.40; N, 14.54.

4-(Pyrrolidin-1-yl)benzonitrile (Table 4, entry 2).[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99–2.07 (m, 4H), 3.30–3.34 (m, 4H), 6.47–6.51 (m, 2H), 7.41–7.46 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 25.5, 47.6, 96.7, 111.5, 121.1, 133.5, 150.1. Anal. calcd for $C_{11}H_{12}N_2$ (172.23): C, 76.71; H, 7.02; N, 16.27. Found: C, 76.73; H, 7.01; N, 16.18.

Methyl-4-(pyrrolidin-1-yl)benzoate (Table 4, entry 3).[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.98–2.06 (m, 4H), 3.32–3.35 (m, 4H), 3.85 (s, 3H), 6.47–6.52 (m, 2H), 7.85–7.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 25.5, 47.7, 51.4, 110.9, 116.7, 131.5, 151.1, 167.7. Anal. calcd for $C_{12}H_{15}NO_2$ (205.25): C, 70.22; H, 7.37; N, 6.82. Found: C, 69.96; H, 7.20; N, 6.58.

(1) Ahrens, S.; Herdtweck, E.; Goutal, S.; Strassner, T. *Eur. J. Inorg. Chem.* **2006**, 1268-1274.
(2) Zhu, L.; Cheng, L.; Zhang, Y.; Xie, R.; You, J. *J. Org. Chem.* **2007**, *72*, 2737-2743.
(3) Suresh, P.; Pitchumani, K. *J. Org. Chem.* **2008**, *73*, 9121-9124.
(4) Ma, H.; Jiang, X. *J. Org. Chem.* **2007**, *72*, 8943-8946.
(5) Liu, J.; Chen, J.; Zhao, J.; Zhao, Y.; Li, L.; Zhang, H. *Synthesis* **2003**, 2661-2666.
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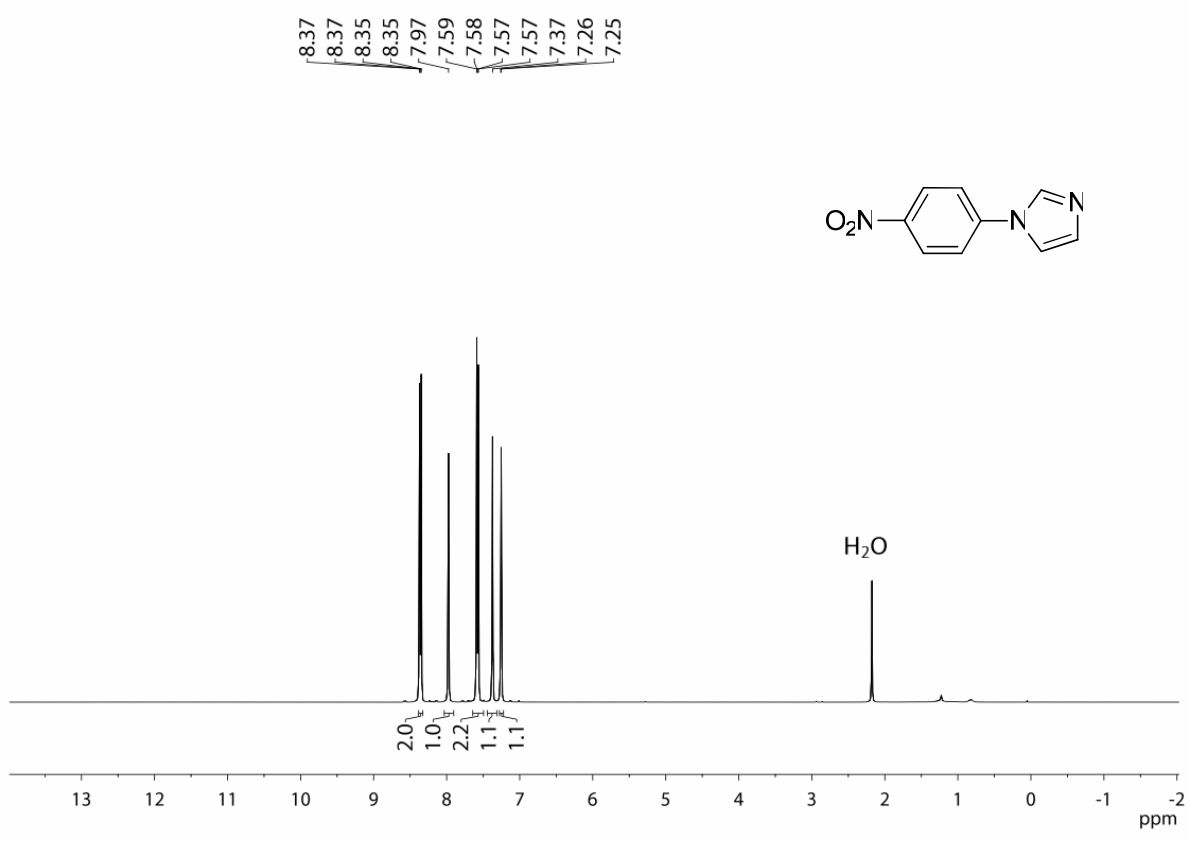
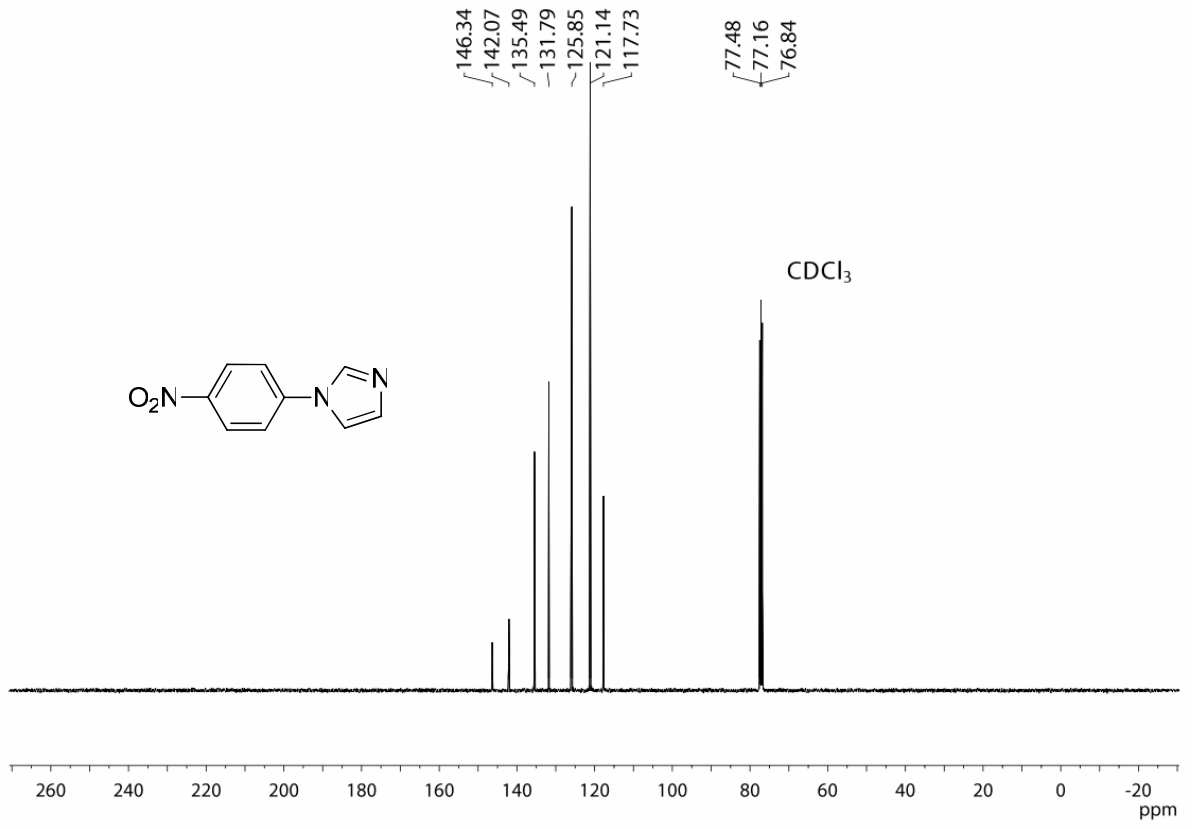
(7) Desmarets, C.; Schneider, R.; Fort, Y. *J. Org. Chem.* **2002**, *67*, 3029-3036.
(8) Hamid, M. H. S. A.; Allen, C. L.; Lamb, G. W.; Maxwell, A. C.; Maytum, H. C.; Watson, A. J. A.; Williams, J. M. J. *J. Am. Chem. Soc.* **2009**, *131*, 1766-1774.

NMR Spectra

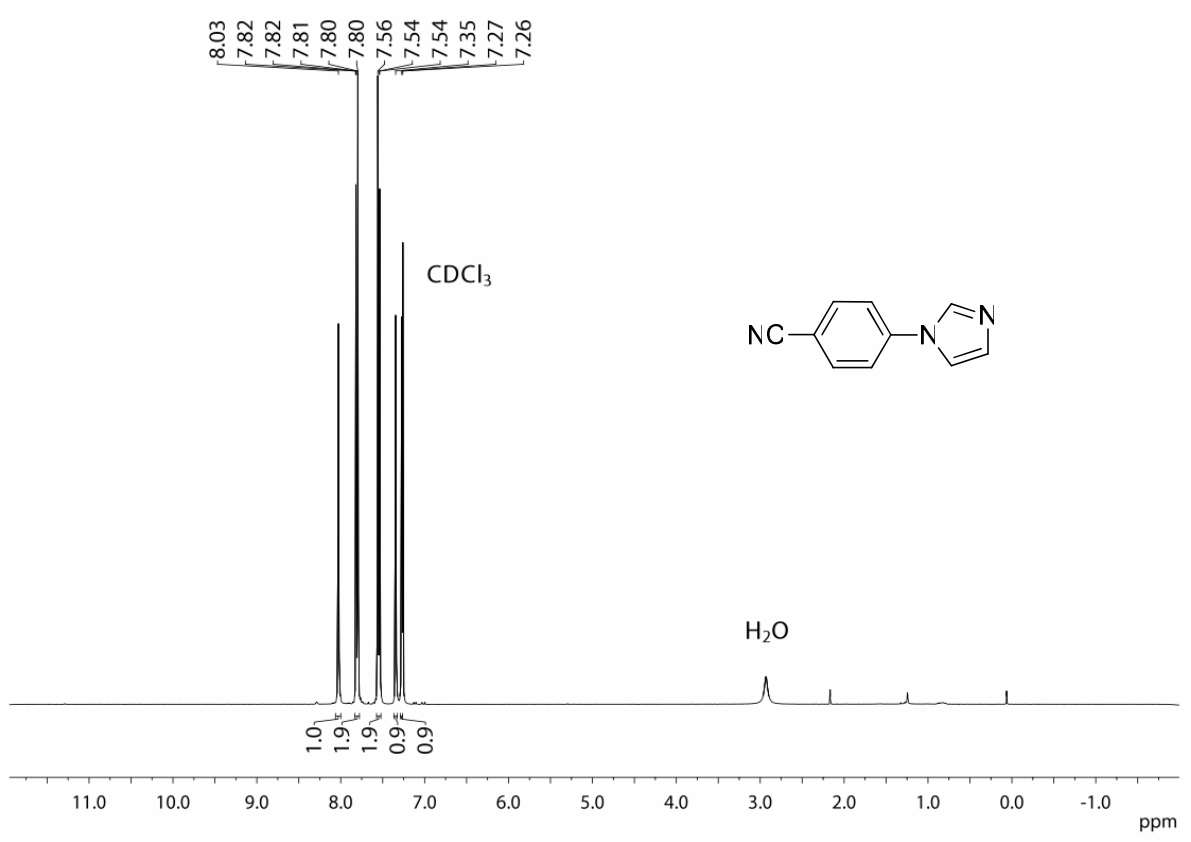
^{1}H-NMR spectrum 1-(4-Nitrophenyl)-1*H*-imidazole (Table 2, entry 1)



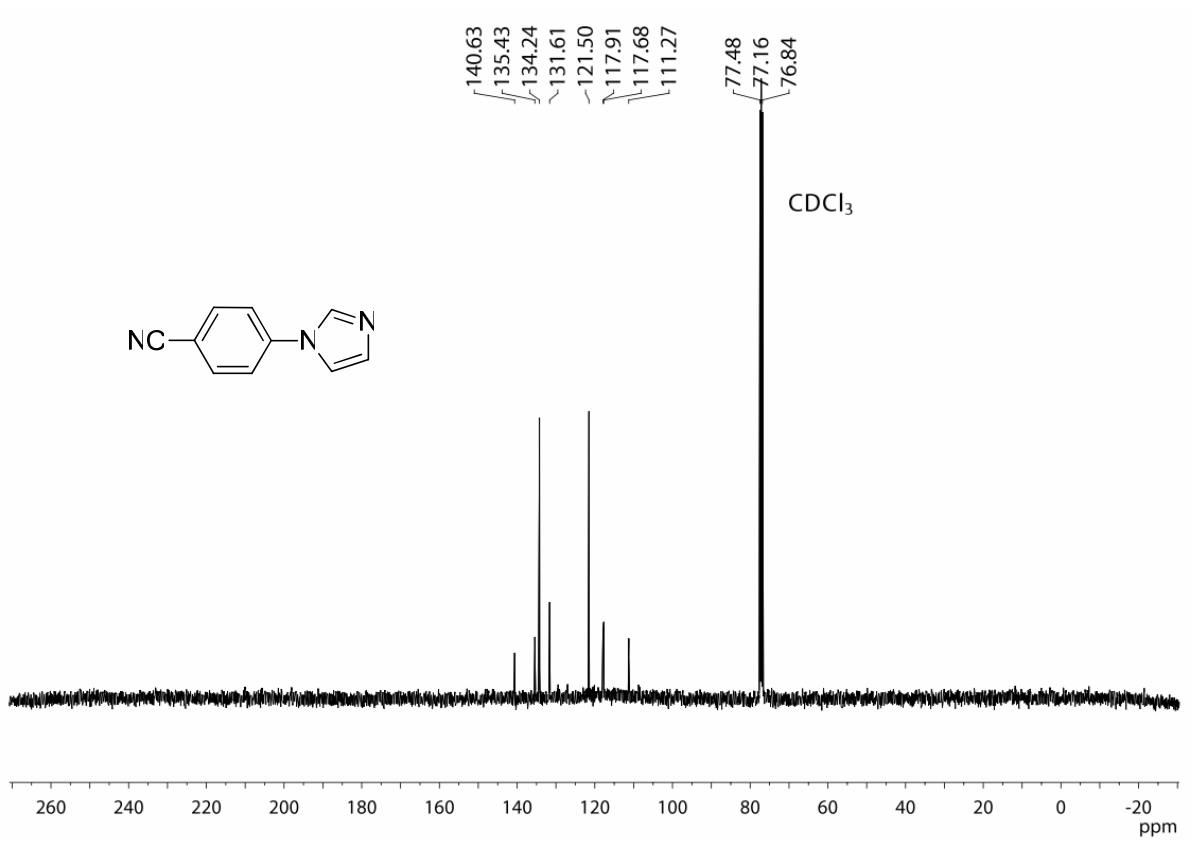
^{13}C-NMR spectrum 1-(4-Nitrophenyl)-1*H*-imidazole (Table 2, entry 1)



[1]H-NMR spectrum 4-(1*H*-Imidazol-1-yl)benzonitrile (Table 2, entry 2)



[13]C-NMR spectrum 4-(1*H*-Imidazol-1-yl)benzonitrile (Table 2, entry 2)



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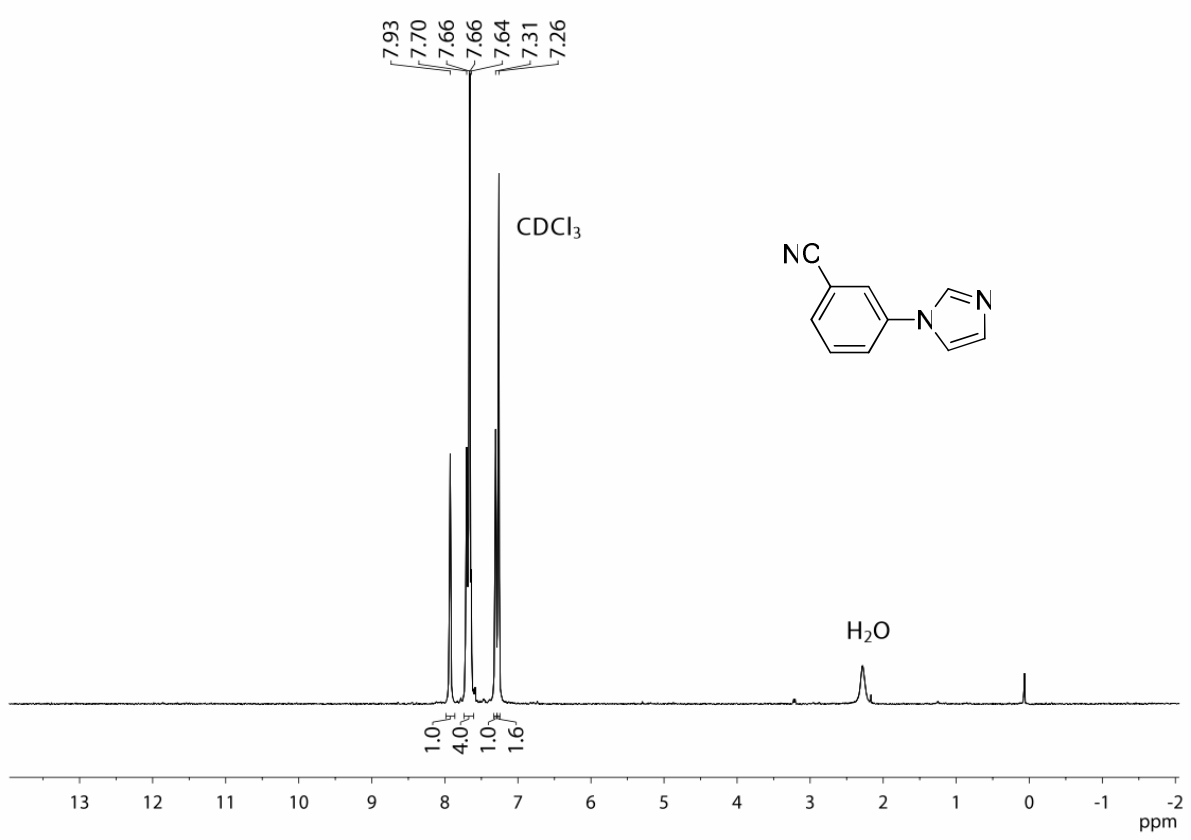
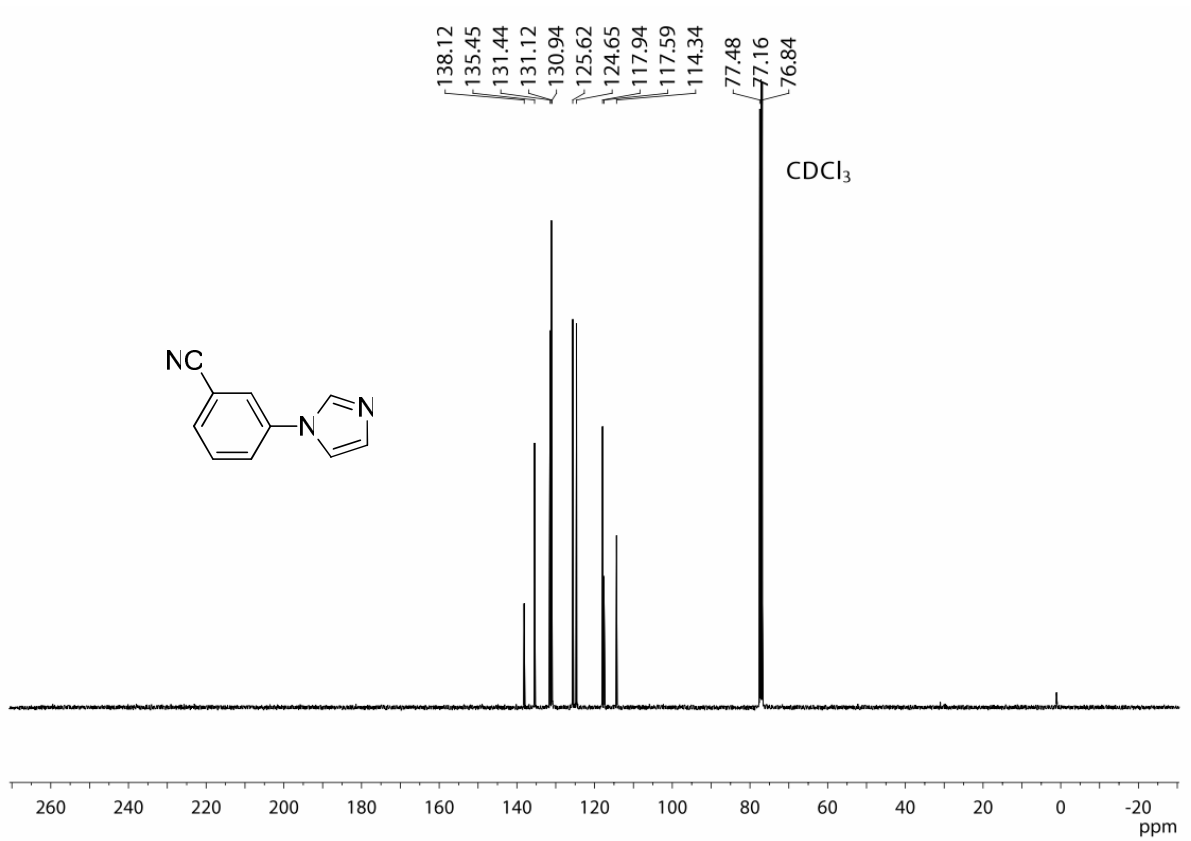


[13]C-NMR spectrum 3-(1*H*-Imidazol-1-yl)benzonitrile (Table 2, entry 3)



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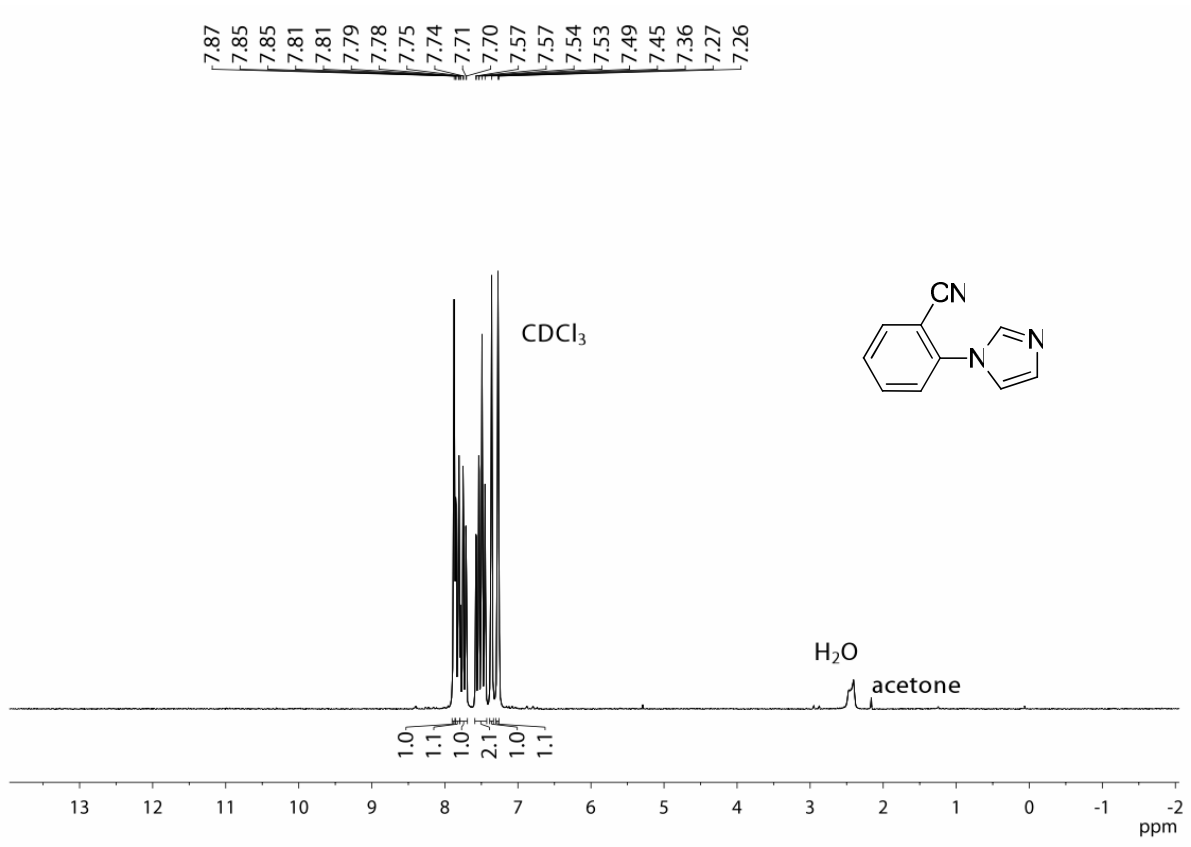

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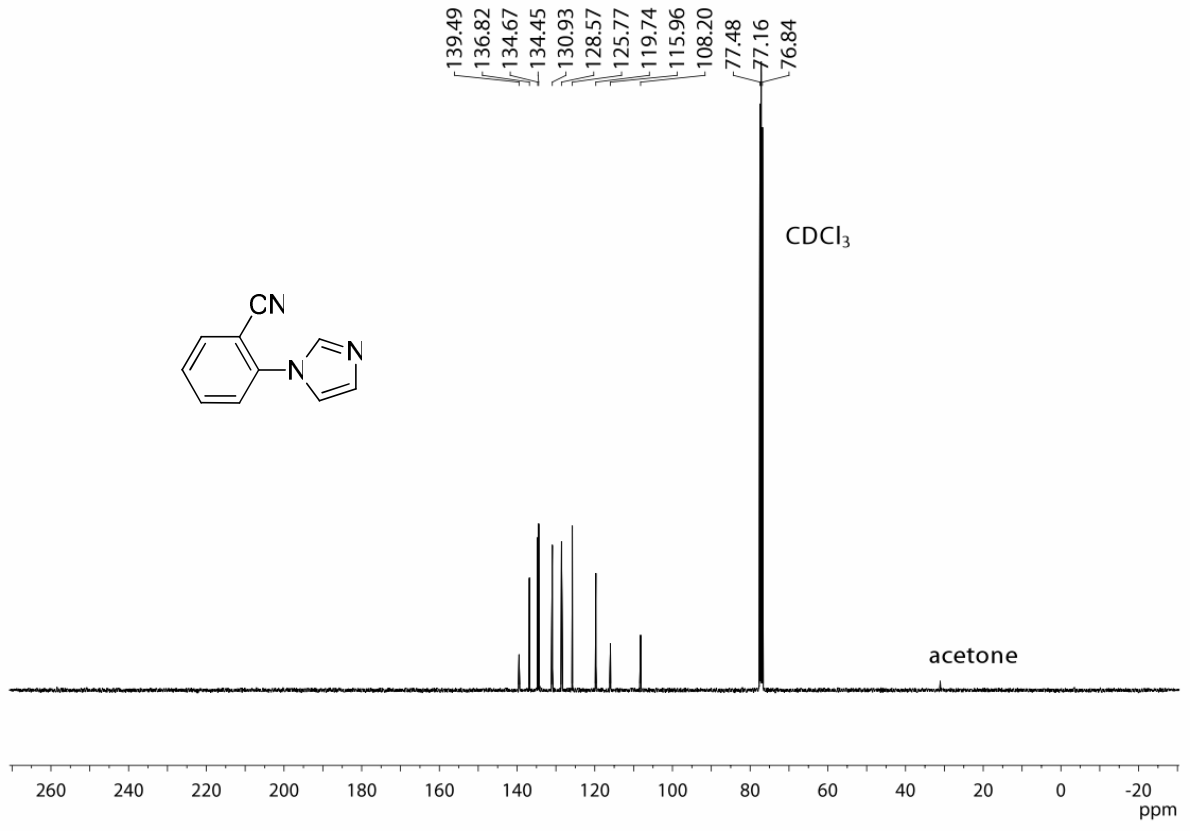
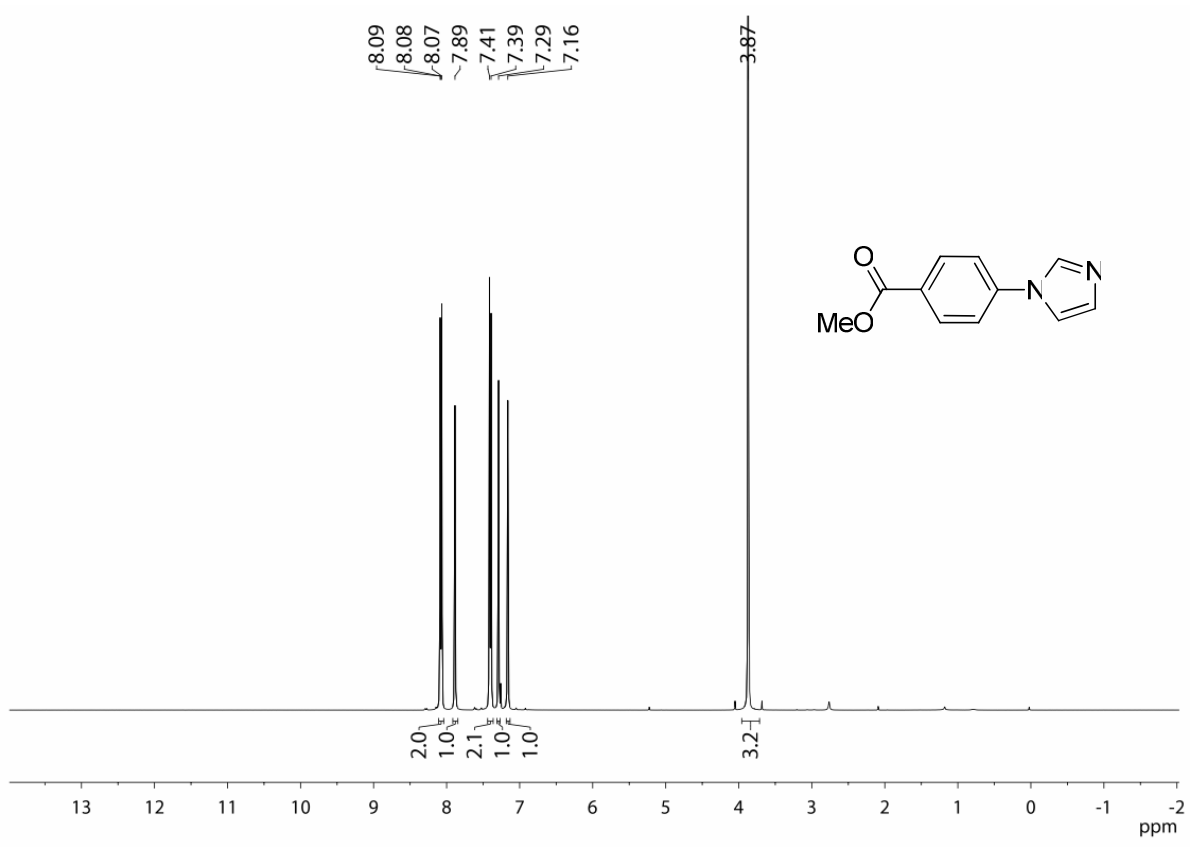
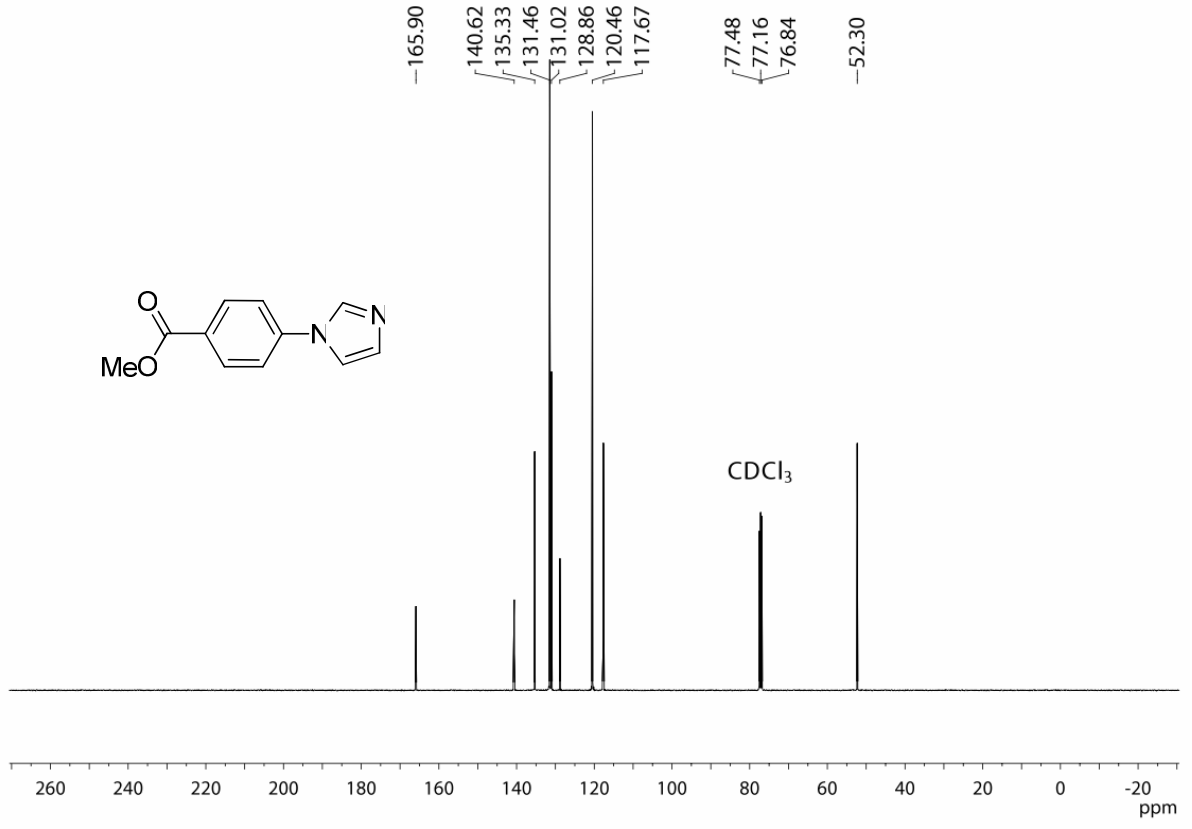


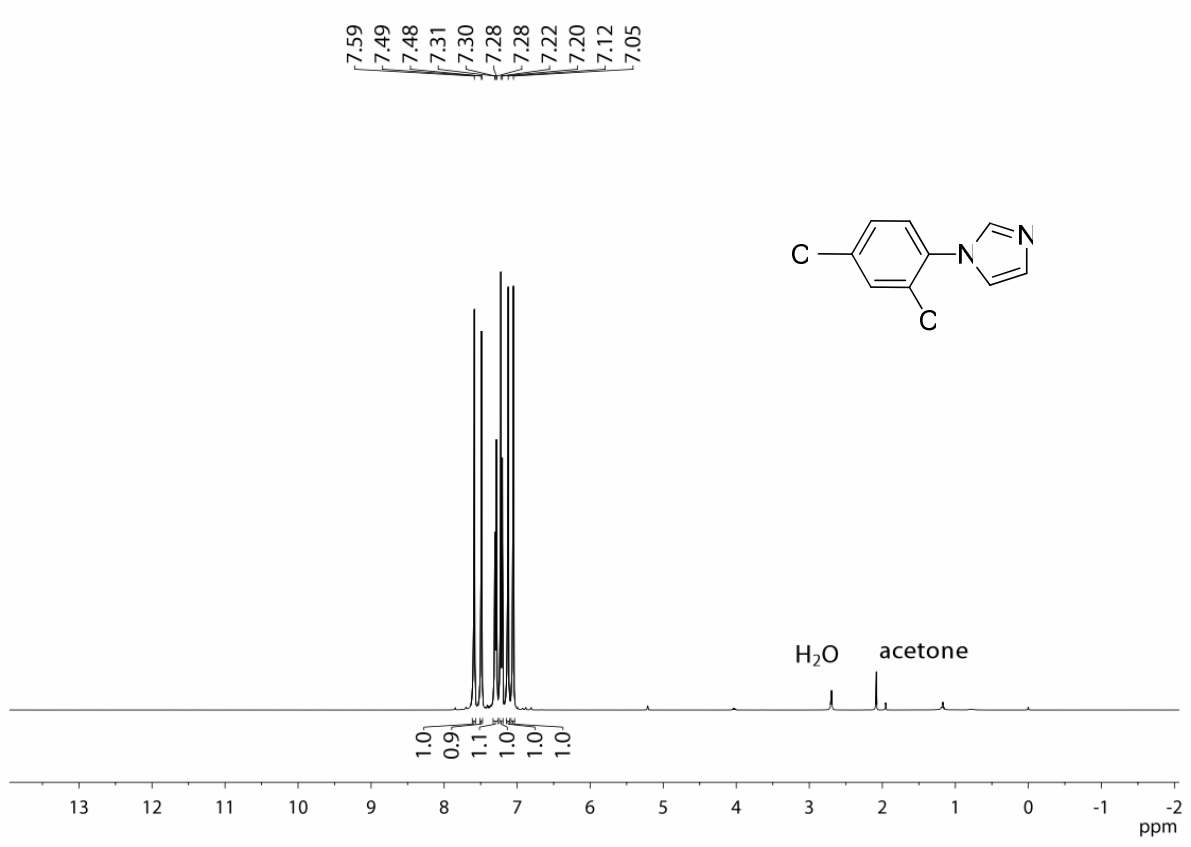
[1]H-NMR spectrum Methyl-4-(1*H*-imidazol-1-yl)benzoate (Table 2, entry 5)



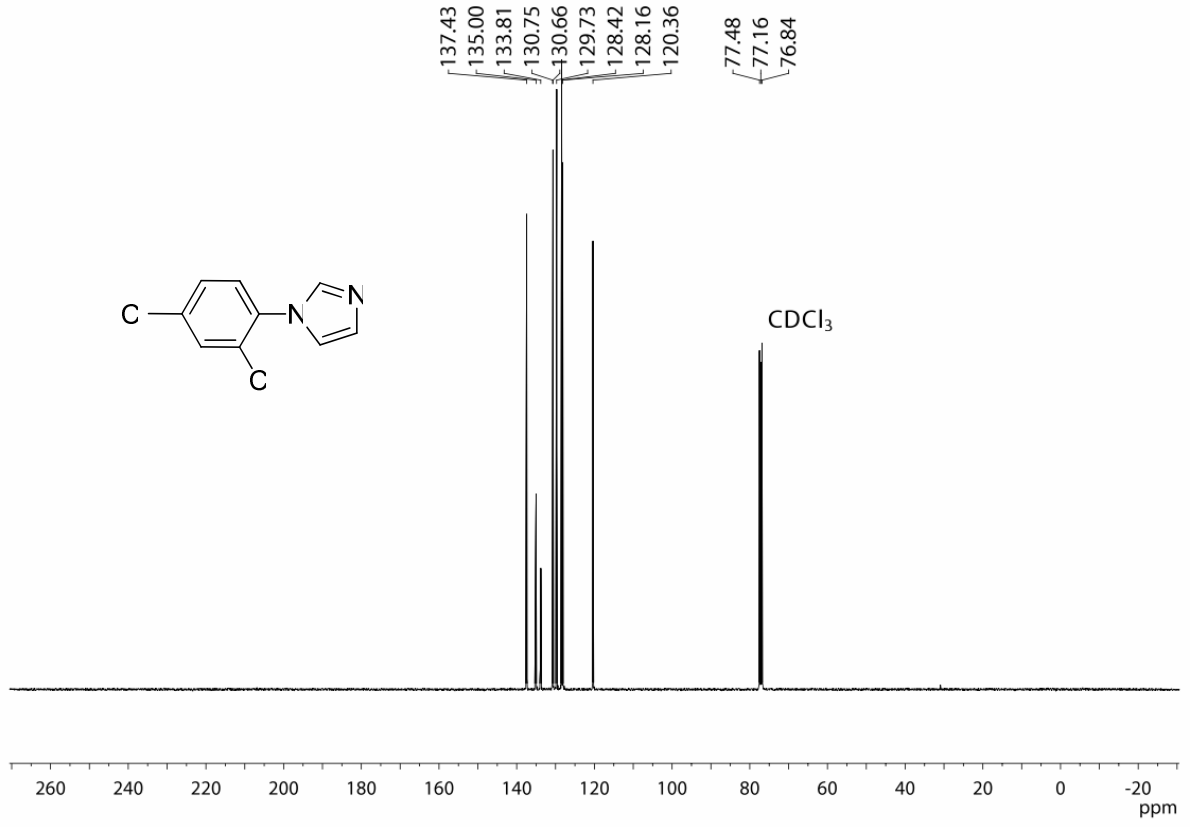
[13]C-NMR spectrum Methyl-4-(1*H*-imidazol-1-yl)benzoate (Table 2, entry 5)



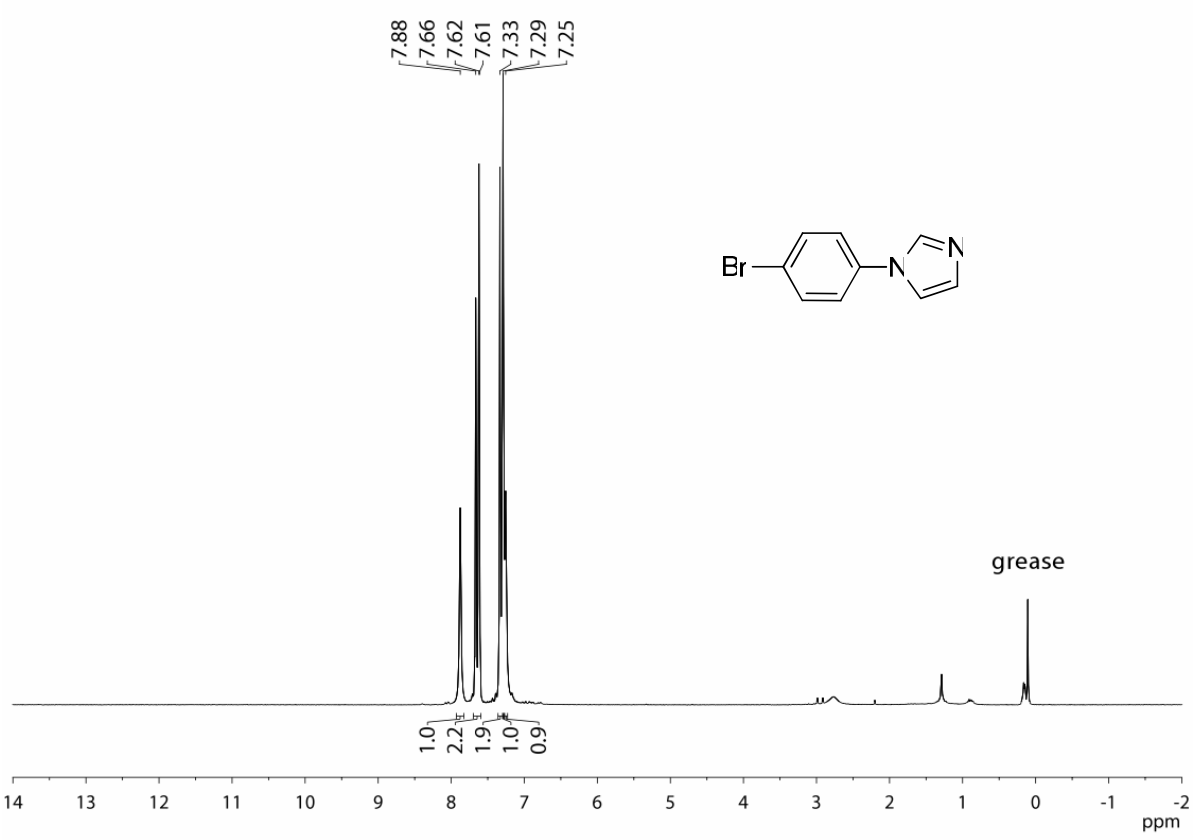
[1]H-NMR spectrum 1-(2,4-Dichlorophenyl)-1*H*-imidazole (Table 2, entry 6)



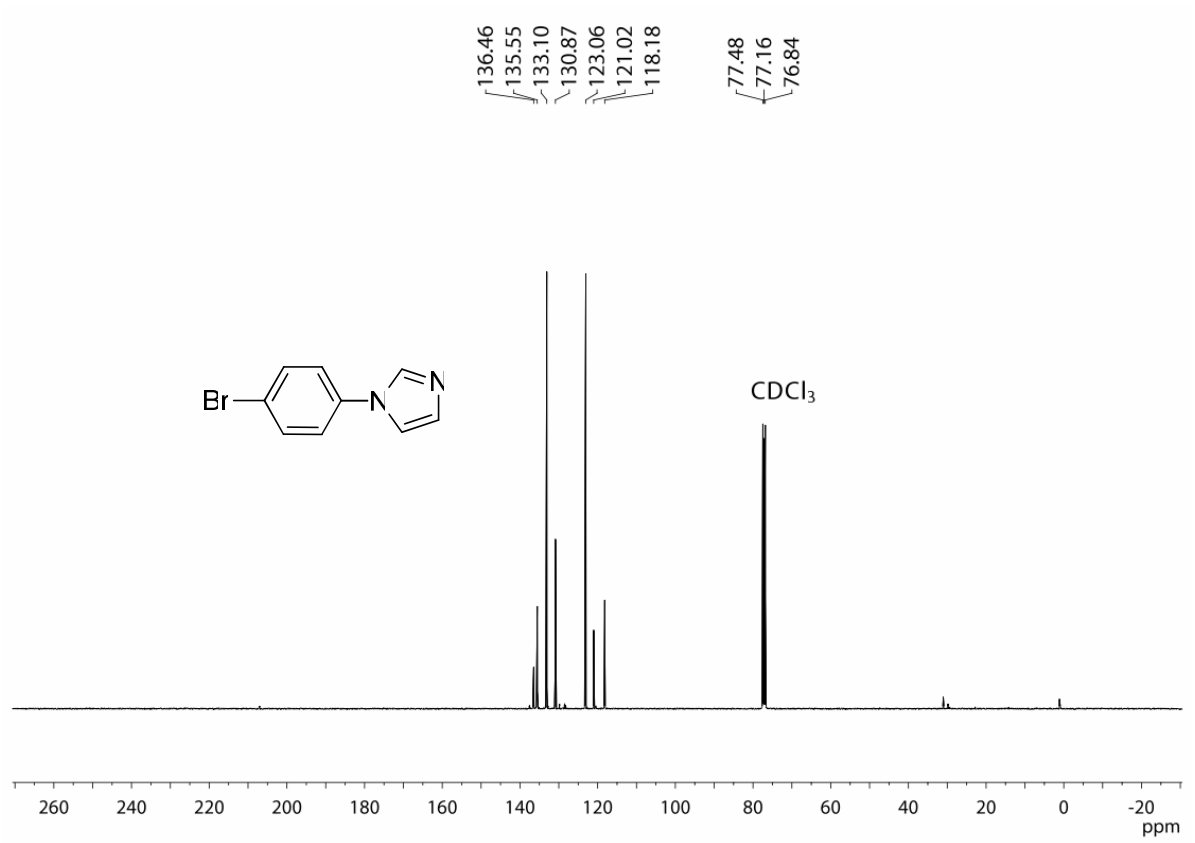
[13]C-NMR spectrum 1-(2,4-Dichlorophenyl)-1*H*-imidazole (Table 2, entry 6)



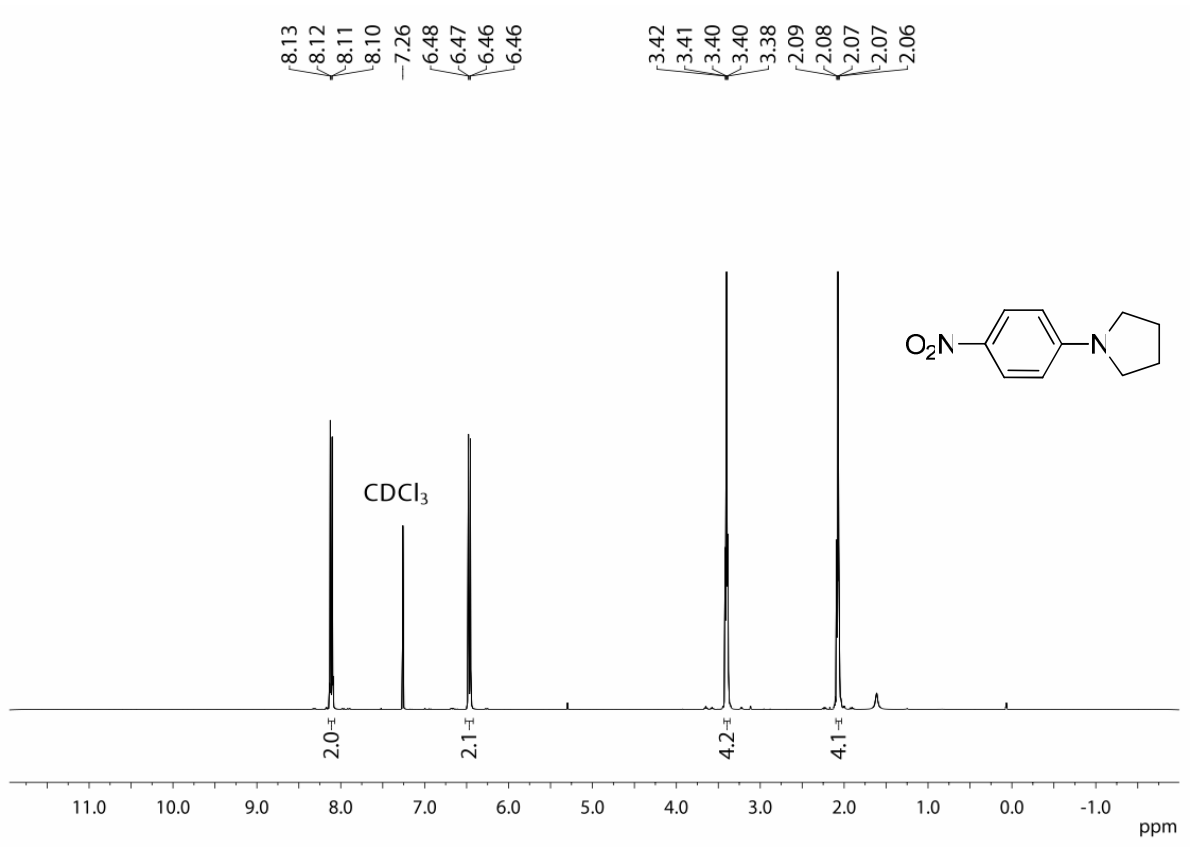
[1]H-NMR spectrum 1-(4-Bromophenyl)-1*H*-imidazole (Table 2, entry 7)



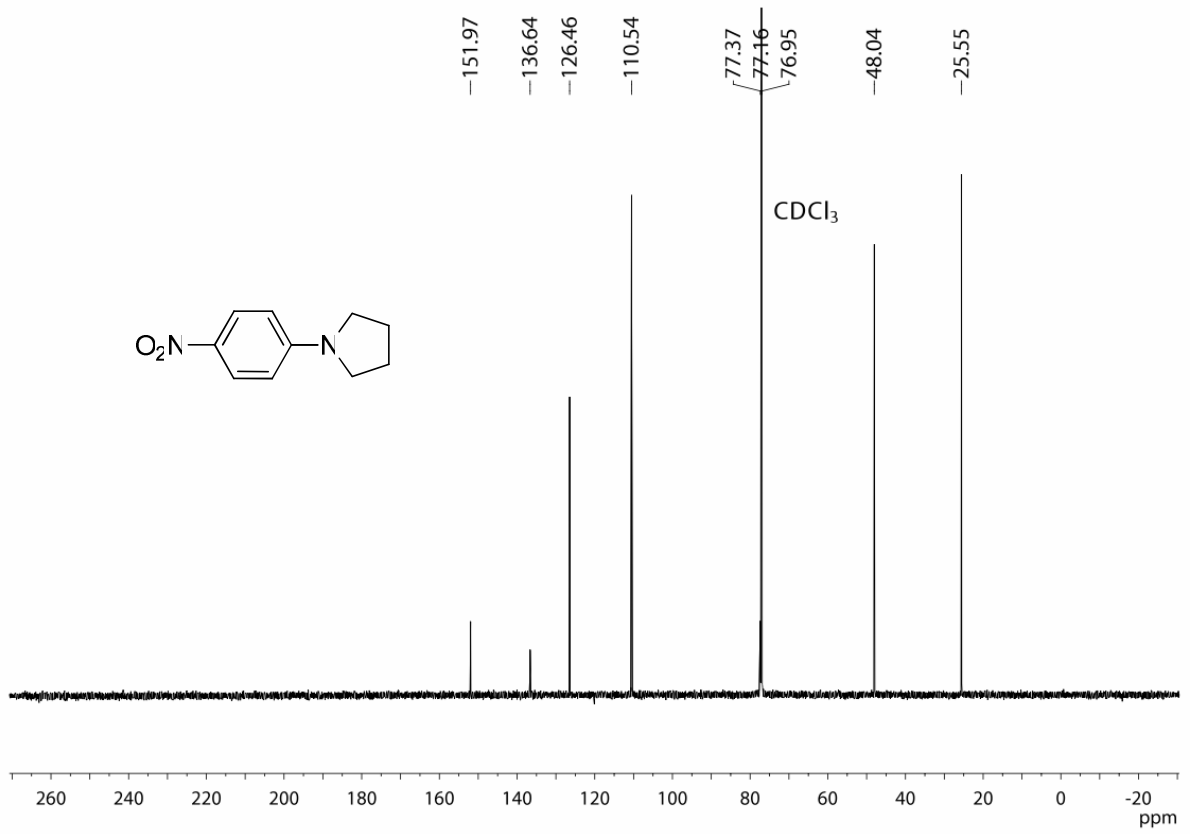
[13]C-NMR spectrum 1-(4-Bromophenyl)-1*H*-imidazole (Table 2, entry 7)



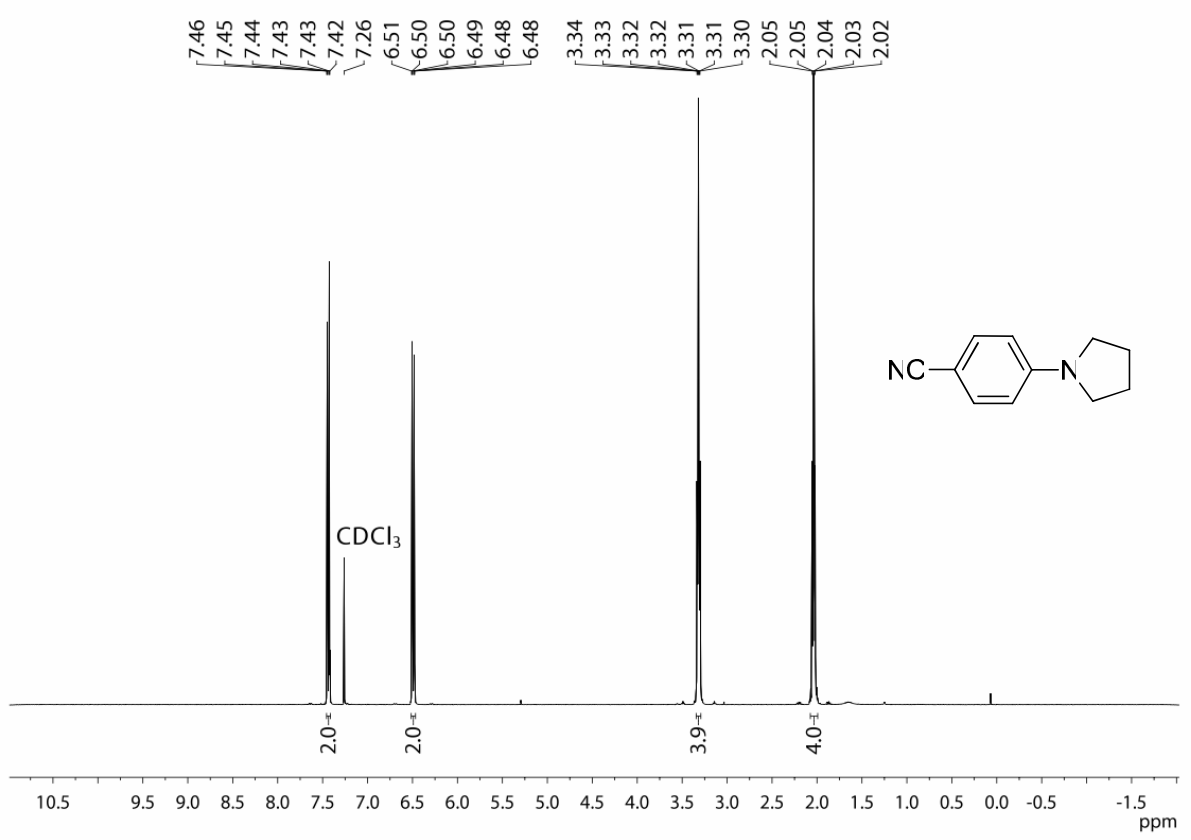
[1]H-NMR spectrum 1-(4-Nitrophenyl)pyrrolidine (Table 4, entry 1)



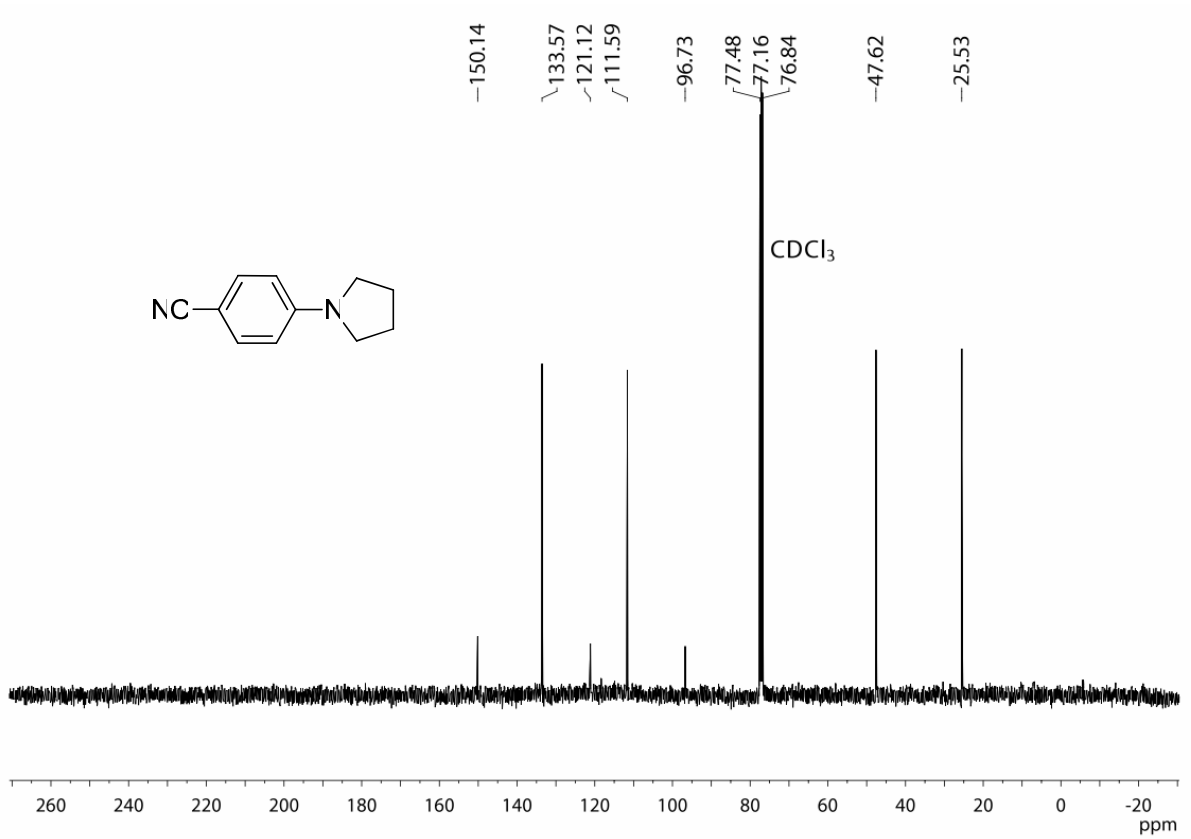
[13]C-NMR spectrum 1-(4-Nitrophenyl)pyrrolidine (Table 4, entry 1)



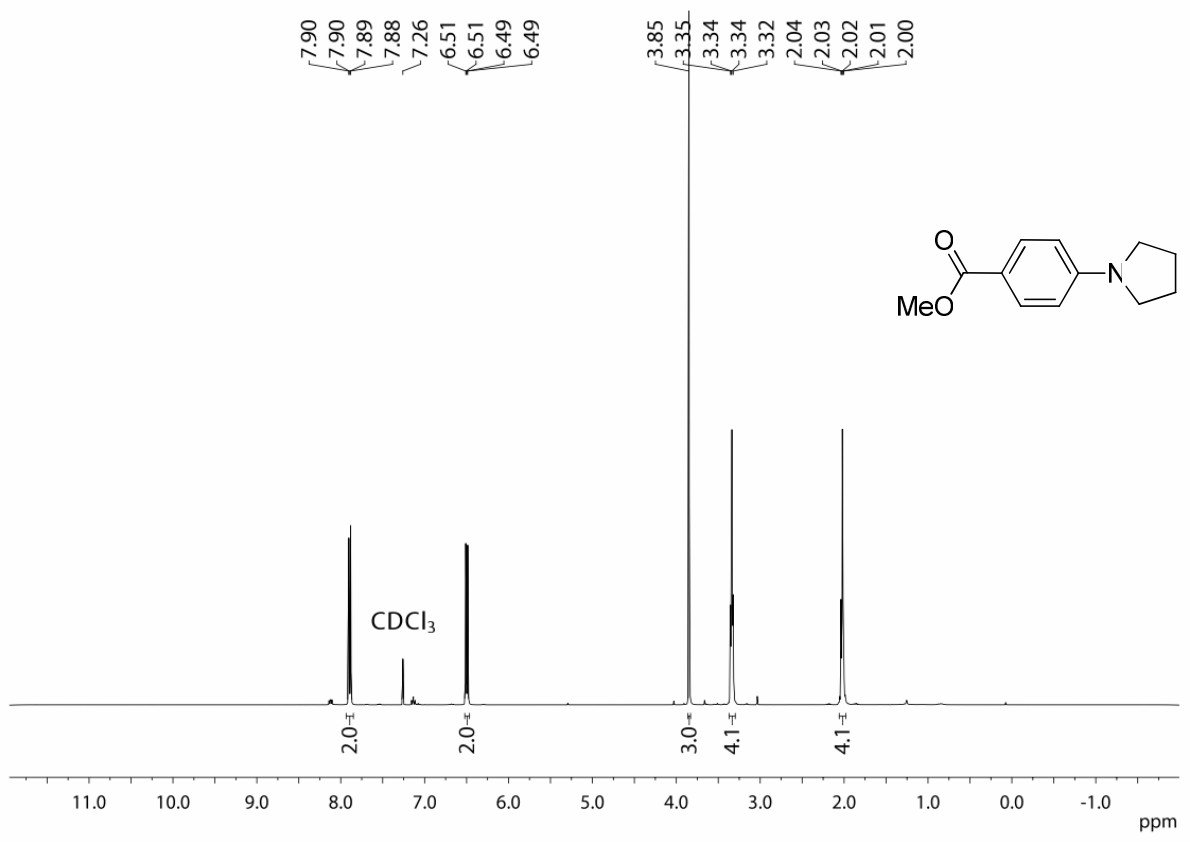
[1]H-NMR spectrum 4-(Pyrrolidin-1-yl)benzonitrile (Table 4, entry 2)



[13]C-NMR spectrum 4-(Pyrrolidin-1-yl)benzonitrile (Table 4, entry 2)



[1]H-NMR spectrum Methyl-4-(pyrrolidin-1-yl)benzoate (Table 4, entry 3)



[13]C-NMR spectrum Methyl-4-(pyrrolidin-1-yl)benzoate (Table 4, entry 3)