Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary file

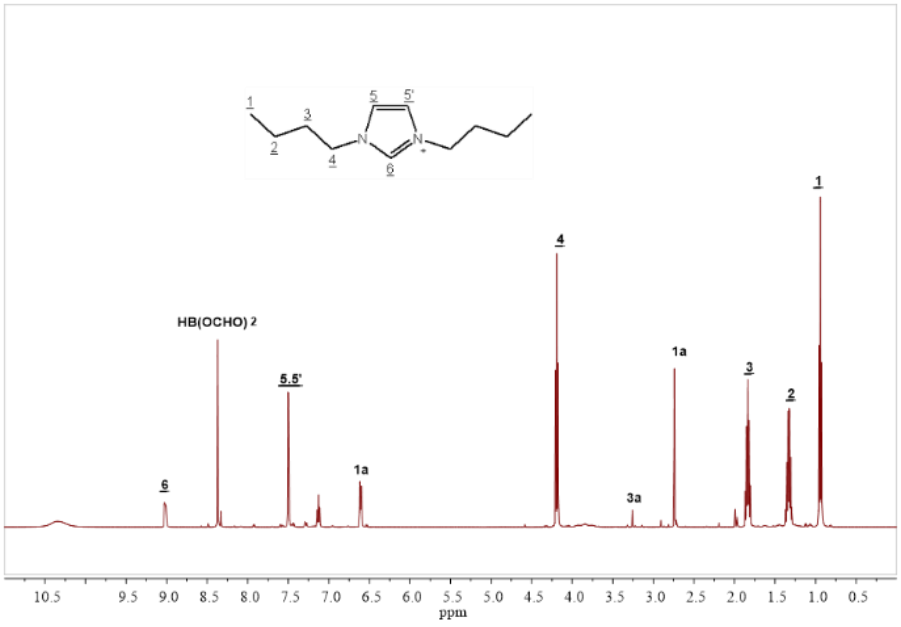
Reduction of CO_2 with ammonia borane and selective formylation of amines in the presence of imidazolium halides.

A. Skarżyńska, A.M. Trzeciak*

Table S1. Yield of products **2a** and **3a** in the experiment shown on Fig. 4.

Lp	Time [min, h]	Conversion **1a** [%]	Yield [%]	
			2a	**3a**
1	30 min.	2	-	2
2	1 h	12	4	8
3	2 h	16	5	11
4	3 h	17	5	12
5	3 h 20 min.	80	16	64
6	3 h 45 min.	81	23	58
7	4 h	84	22	62
8	5 h	84	21	63

Reaction conditions: 0.02 g $NH_3.BH_3$, 0.25 mmol **1a**, 5 bar CO_2, 0.6 mL CD_3CN, 80 ^oC



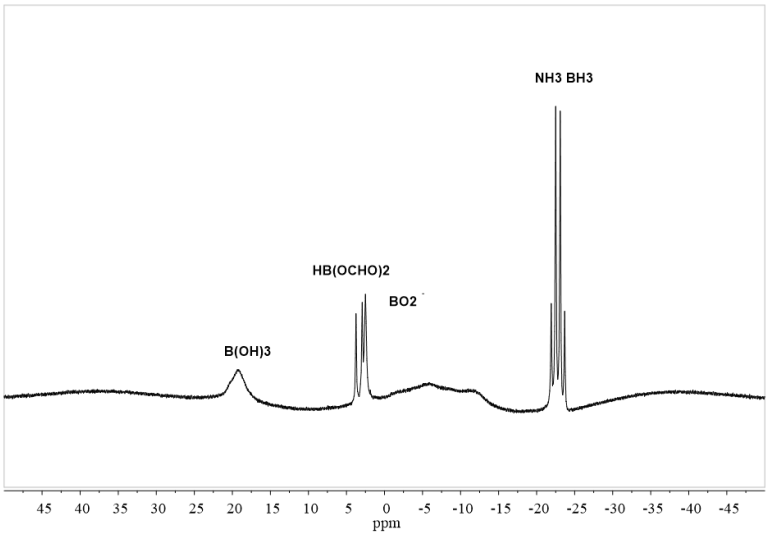


Figure S1. ^{1}H NMR and ^{11}B NMR spectra for the reaction **1a** + AB + [dbim]Cl + CO_2 (5 bar) at 80 °C after 2 h.

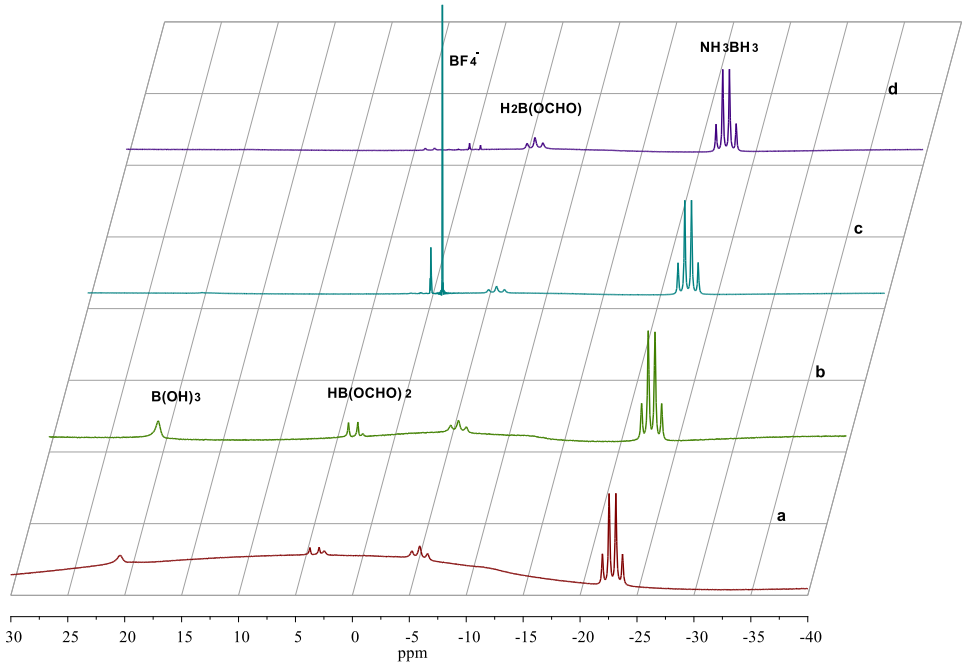


Figure S2. ^{11}B NMR spectra of AB + [IL]X + CO_2 (5 bar) after 2 h at 80°C; [IL]X = a) [dbim]Cl, b) [bmim]Br, c) [bmim]BF_4, d) [bmim]PF_6

Products characterization

N-phenylformamide[1] A mixture of two rotamers in a ratio of ca 1:1. **^{1}H NMR (500 MHz, $CDCl_3$)**: major rotamer (51%) δ 8.37 (ws, 1H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 2H) ppm; minor rotamer (49%) δ 8.66 (d, *J* = 11.4 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H) ppm; **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 169.5, 129.8, 129.2, δ 126.3, 122.1, 119.9, 119.0 ppm; **GC-MS**: C_7H_7NO, M = 121.1 m/z (%): 121 (100), 93 (99), 66 (85), 51 (15), 39 (40).

N-benzylformamide[2] A mixture of two rotamers in a ratio of ca 13:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.27 (ws, 1H), 8.20 (d, *J* = 12 Hz, 0.1H), 7.34-7.28 (m, 6.2), 4.49 (d, *J* = 5.9 Hz, 2.2H), 4.42 (d, *J* = 6.4 Hz, 0.3H) ppm; **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 160.9, 137.6, 129.1, 128.91, 128.1, 127.9, 127.9, 127.0, 42.3 ppm; **GC-MS**: C_8H_9NO, M = 135.2 m/z (%): 135 (100), 106 (42), 91 (48), 77 (37), 51 (33), 39 (18).

N-o-tolylformamide[2] A mixture of two rotamers in a ratio of ca 2:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.53 (d, *J* = 11.3 Hz, 1H), 8.44 (ws, 0.51H), 7.90 (d, *J* = 7.9 Hz, 0.6H), 7.20 (m, 3.86H), 7.14 (t, *J* = 6.2 Hz, 2.4H), 7.08 (t, *J* = 7.8 Hz, 0.5H), 2.27 (ws, 6H) ppm; **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 162.8, 131.4, 130.7, 129.4, 127.3, 127.0, 126.1, 125.6, 123.0, 120.5, 17.8, 17.7 ppm; **GC-MS**: C_8H_9NO, M = 135.2 m/z (%): 135 (38), 106 (100), 77 (27), 51 (15), 39 (15).

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[1] Siddique M., Boity B., Rit A., *Organometallics*, **2023,** 42, 1395-1403.

[2] Shirvani G., Shockravi A., Amini M., Saemian N., *J Label Compd Radiopharm*., **2017**, 60 130–134.

N-(3-chlorophenyl)formamide[3] A mixture of two rotamers in a ratio of ca 3:1. **^{1}H NMR (500 MHz, $CDCl_3$)** major rotamer (62%) δ 8.37 (s, 1.6H), 7.65 (t, *J* = 9 Hz, 1.5H), 7.37 (d, *J* = 8.5 Hz, 1.9H), 7.11 (d, *J* = 8.0 Hz, 1.5H), 7.12 (d, *J* = 8.3 Hz, 2.3H) ppm, minor rotamer (38%) δ 8.66 (d, *J* = 11.3 Hz, 1.6H), 7.28-7.26 (m, 1.65H), 7.07 (t, *J* = 2 Hz, 1.6H), 6.94 (d, *J* = 8.7 Hz, 1.05H) ppm; **^{13}C{^{1}H} (125 MHz, $CDCl_3$)** δ 158.8, 134.9, 131.1, 130.2, 125.5, 125.0, 120.1, 119.0, 117.9, 116.9 ppm; **GC-MS**: C_7H_6ClNO, M = 156.6 m/z (%): 157 (22), 155 (67), 127 (100), 100 (23), 92 (38), 73 (12), 65 (54), 50 (10), 39 (22).

N-(4-chlorophenyl)formamide[1]: A mixture of two rotamers in a ratio of ca 3:2. **^{1}HNMR (500 MHz, $CDCl_3$)**: major rotamer (64%), δ 8.36 (ws, 1.8H), 7.47 (d, *J* = 9 Hz, 3.8H), 7.29 (d, *J* = 9 Hz, 3.9H) ppm; minor rotamer (36%) δ 8.63 (d, *J* = 11 Hz, 1H), 7.31 (d, *J* = 9 Hz, 2.7H), 7.0 (d, *J* = 9 Hz, 2.1H) ppm; **^{13}C{^{1}H} (125 MHz, $CDCl_3$)** major rotamer δ 158.7, 129.2, 121.1 ppm, minor rotamer δ 161.9, 129.9, 120.2 ppm; **GC-MS**: C_7H_6ClNO, M = 156.6 m/z (%): 155 (61), 127 (100), 99 (29), 92 (37), 73 (22), 65 (52), 50 (14), 39 (25).

benzoxazole ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm: 8.08 (s, 1H), 7.78 (d, *J* = 10 Hz, 1H), 7.56 (d, *J* = 10 Hz, 1H), 7.37 (m, 2H); **GC-MS**: C_7H_5NO, M = 119.04 m/z (%): 119.04 (100), 120.04 (7.7).

N,N-dihexylformamide[4] **^{1}HNMR (500 MHz, $CDCl_3$)**: δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.98 (s, 1H), 4.22 (t, *J* = 7,2 Hz, 4H), 3.23 (m, 2H), 3.14 (t, *J* = 7.1 Hz, 2H), 1.82 (m, 4H), 1.48 (m, 4H), 133 (m, 4H), 1.24 (s, 14H), 0.90 (t, *J* = 7.3 Hz, 6H), 0.83 (m, 6H) ppm; **GC-MS**: $C_{13}H_{27}NO$, M = 213.3 m/z (%): 213 (2), 142 (88), 72 (100), 43 (35), 43 (35), 41 (26).

benzimidazole ^{1}H NMR (500 MHz, CD_3CN): *δ* 8.04 (s, 1H, NCHN), 7.53 (m, 2H, Ph), 7.03 (m, 2H, Ph). **^{13}C{^{1}H} NMR (125 MHz, CD_3CN)** 141.3, 122, 119.5, 115.4, 109.8. **GC-MS**: $C_7H_6N_2$, M = 118.1 m/z (%): 118 (100), 91 (40), 63 (20).

N,N-diethylformamide [5] **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.07 (s, 1H), 3.35 (q, *J* = 7.0 Hz, 2H), 3.26 (q, *J* = 7.0 Hz, 2H), 1.18 (t, *J* = 7.0 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 162.3, 41.9, 36.6, δ 14.9, 12.8, ppm; **GC-MS**: C_7H_7NO, M = 101.15 m/z (%): 101 (46), 86 (25), 72 (15), 58 (100), 44 (67).

The signals marked on spectra with *correspond to the $CH_3COOC_2H_5$ signals, used in purification process.

[3] Wei Y., Wu J., Xue D., Wang C., Liu Z., Zhang Z., Chen G., Xiao J., *Synlett* **2014**, 25, 1295-1298.

[4] Yu X., Yang Z., Guo S., Liu Z., Zhang H., Yu B., Zhaoa Y., Liu Z., *Chem. Commun*., **2018**, 54, 7633-7636.

[5] Z Song, J. Liu, S. Xing, X. Shao, J. Li, J. Peng, Y. Bai, *Org. Biomol. Chem.*, **2023**, 21, 832-837.

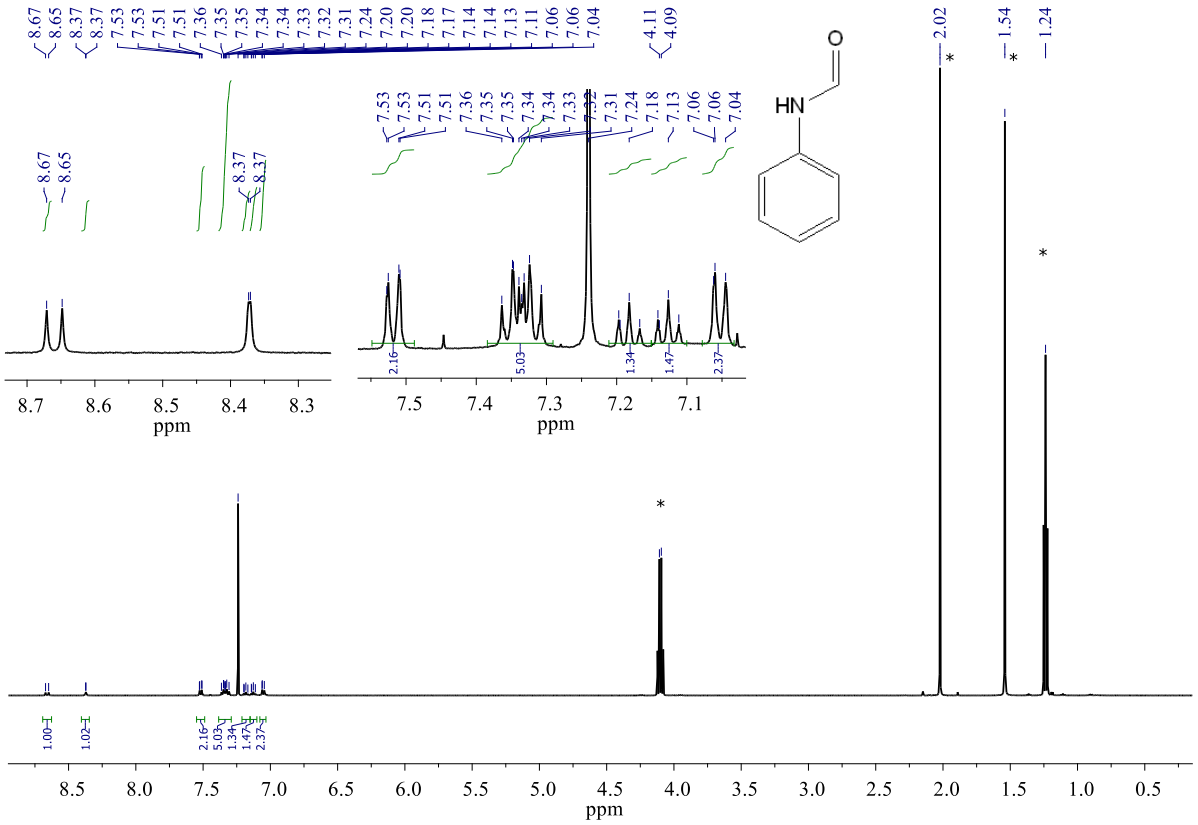

Figure 1. ^{1}H NMR spectrum for N-phenylformamide

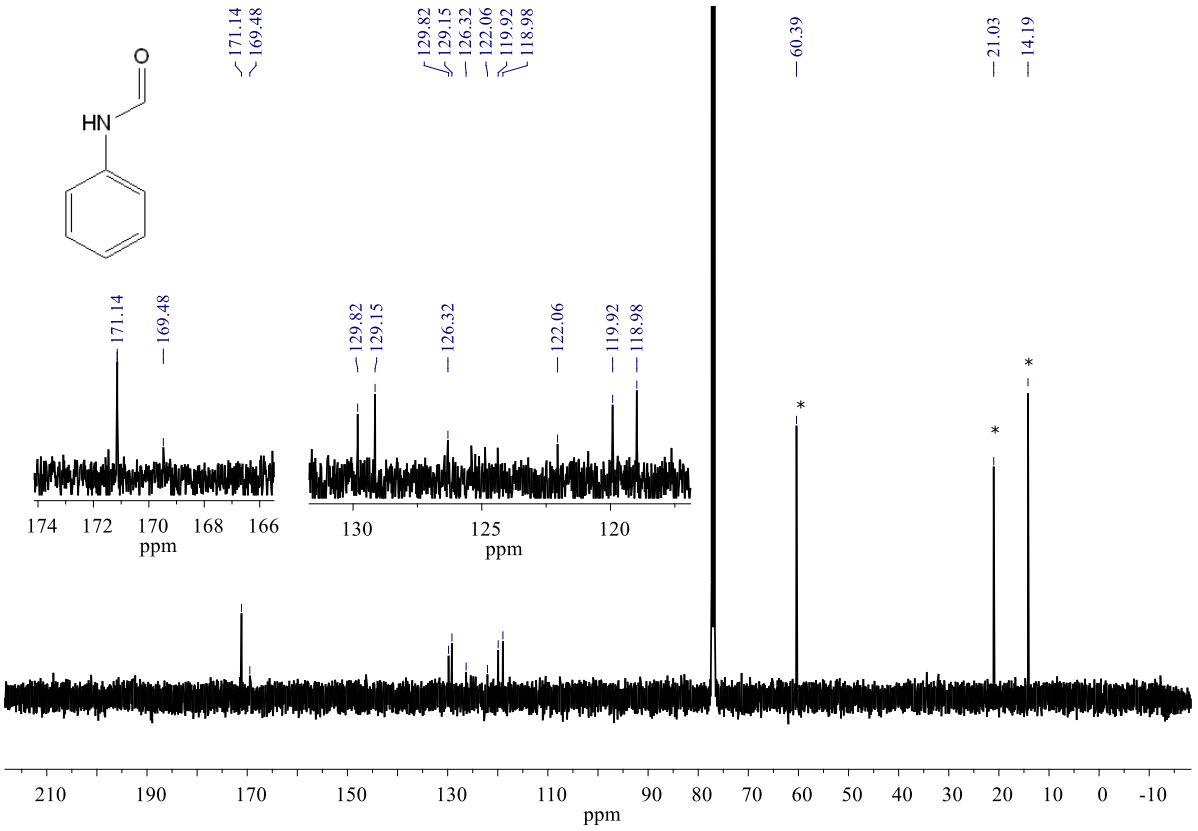

Figure 2. $^{13}C\{^{1}H\}$ NMR spectrum for N-phenylformamide

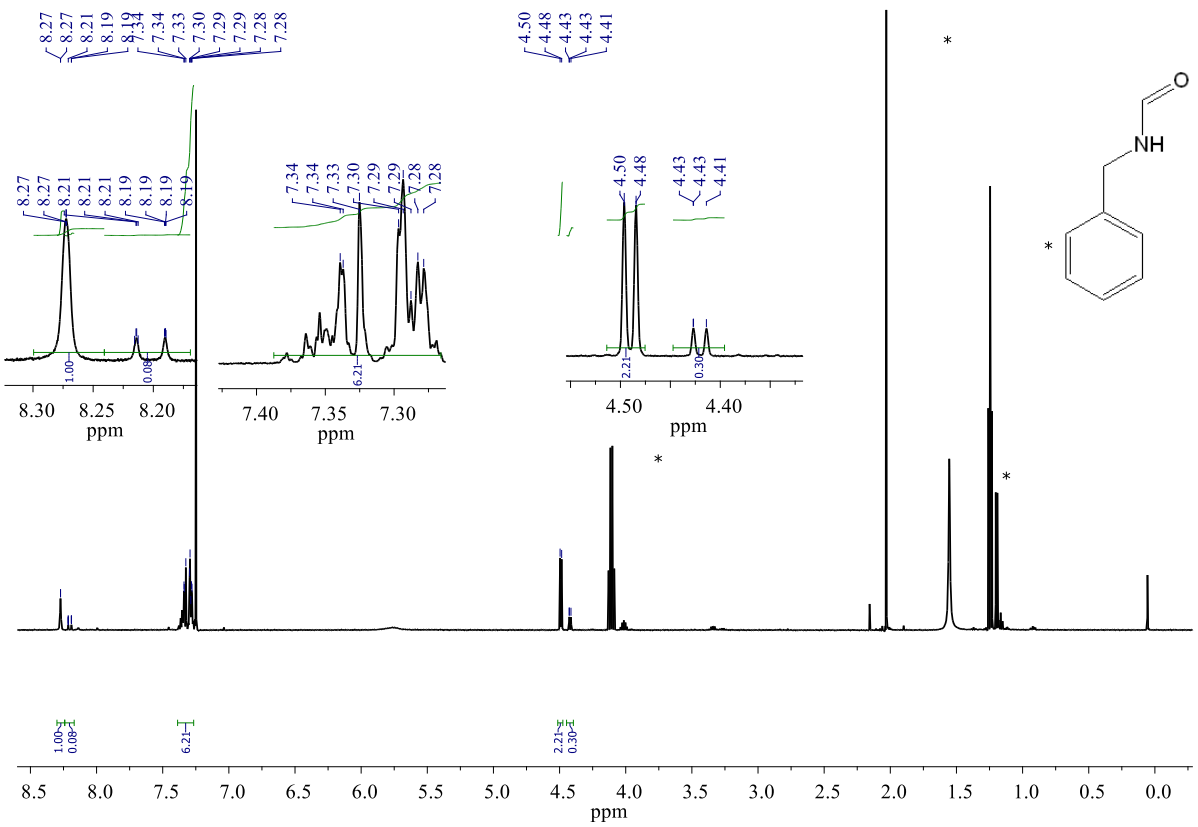

Figure 3. ^{1}H NMR spectrum for N-benzylformamide

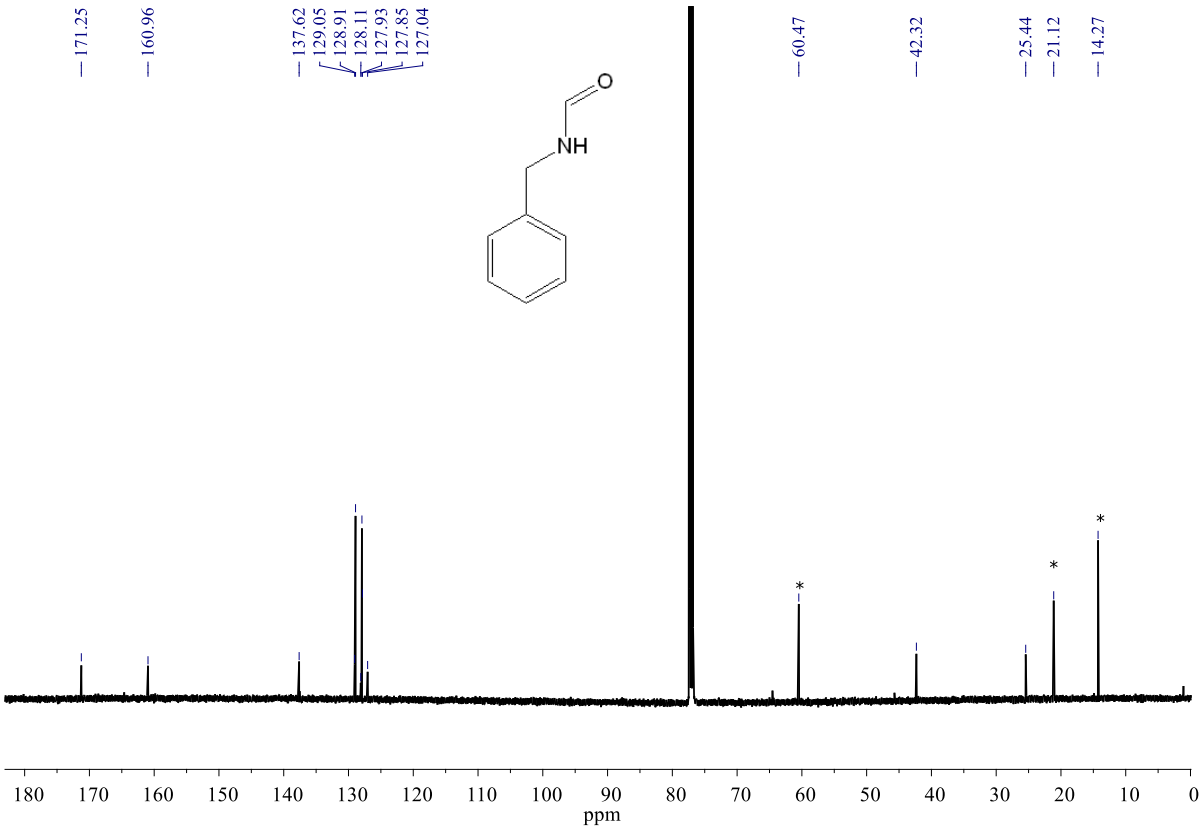

Figure 4. ^{13}C{^{1}H} NMR spectrum for N-benzylformamide

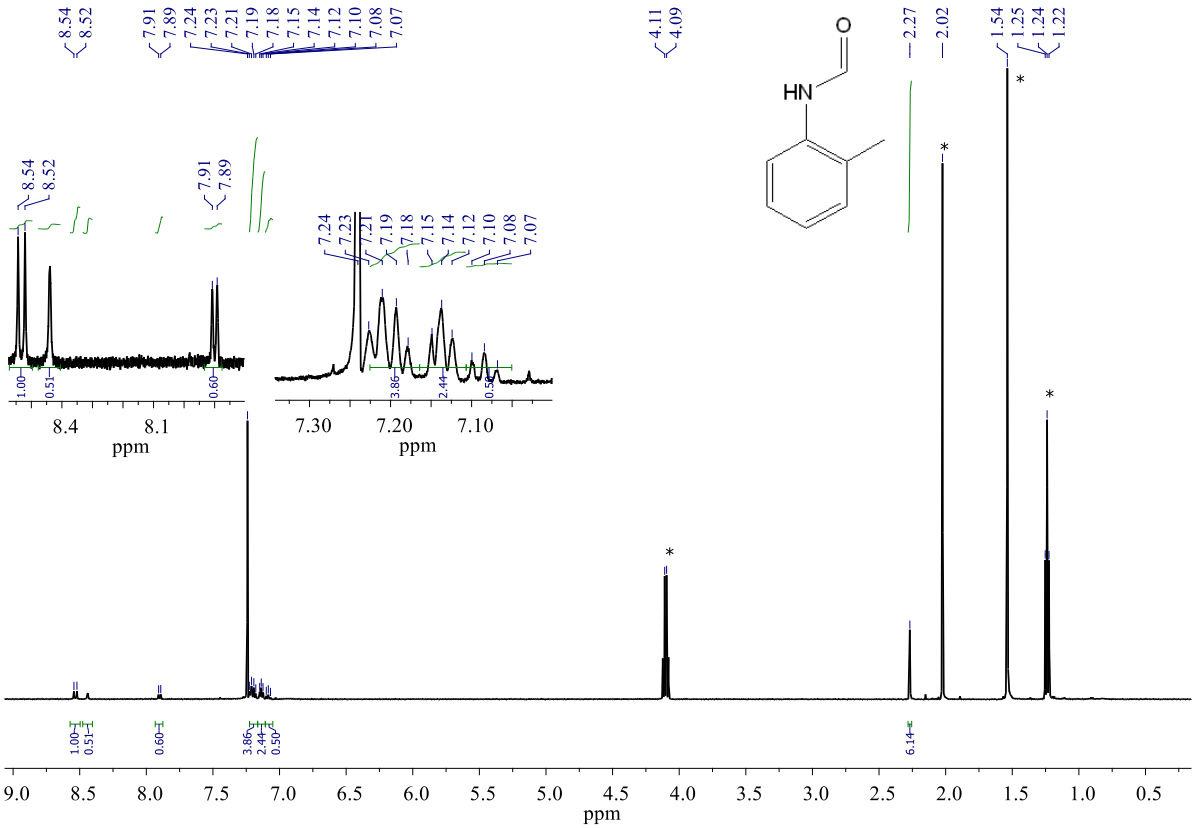

Figure 5. ^{1}H NMR spectrum for N-*o*-tolylformamide

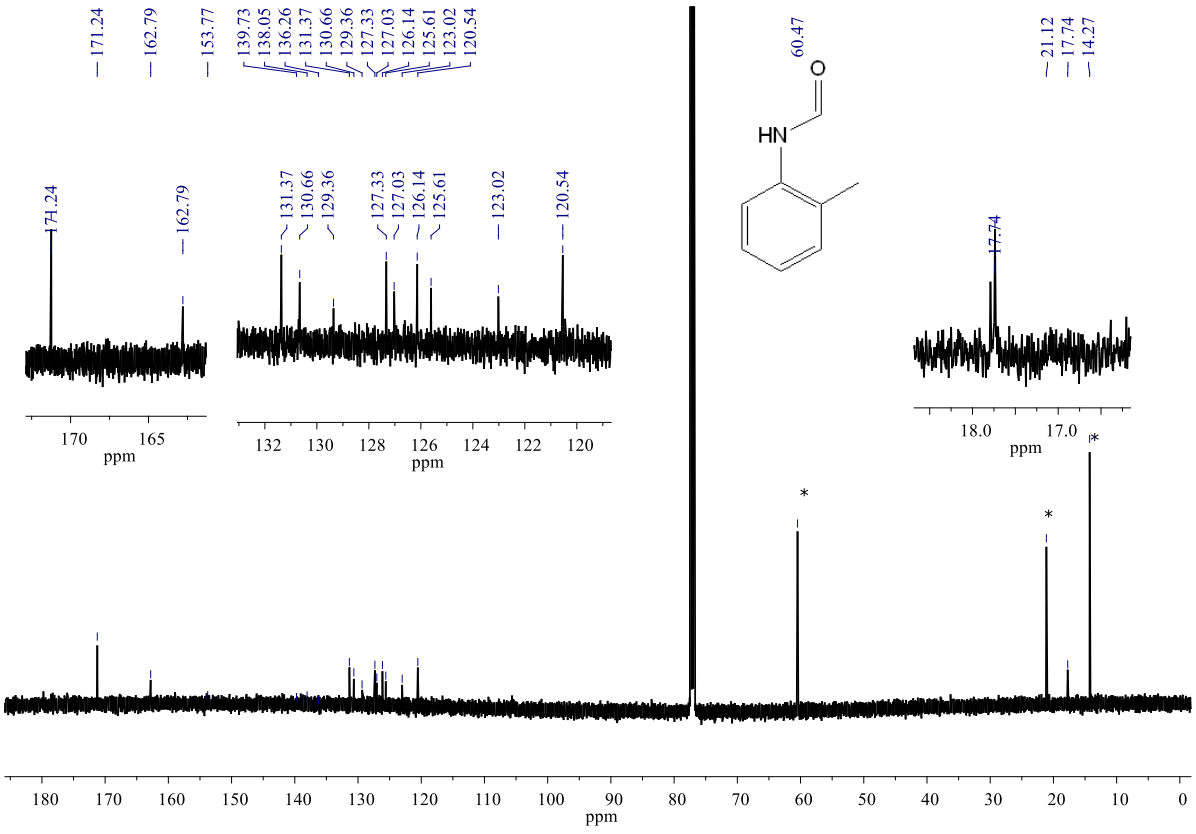

Figure 6. ^{13}C{^{1}H} NMR spectrum for N-*o*-tolylformamide

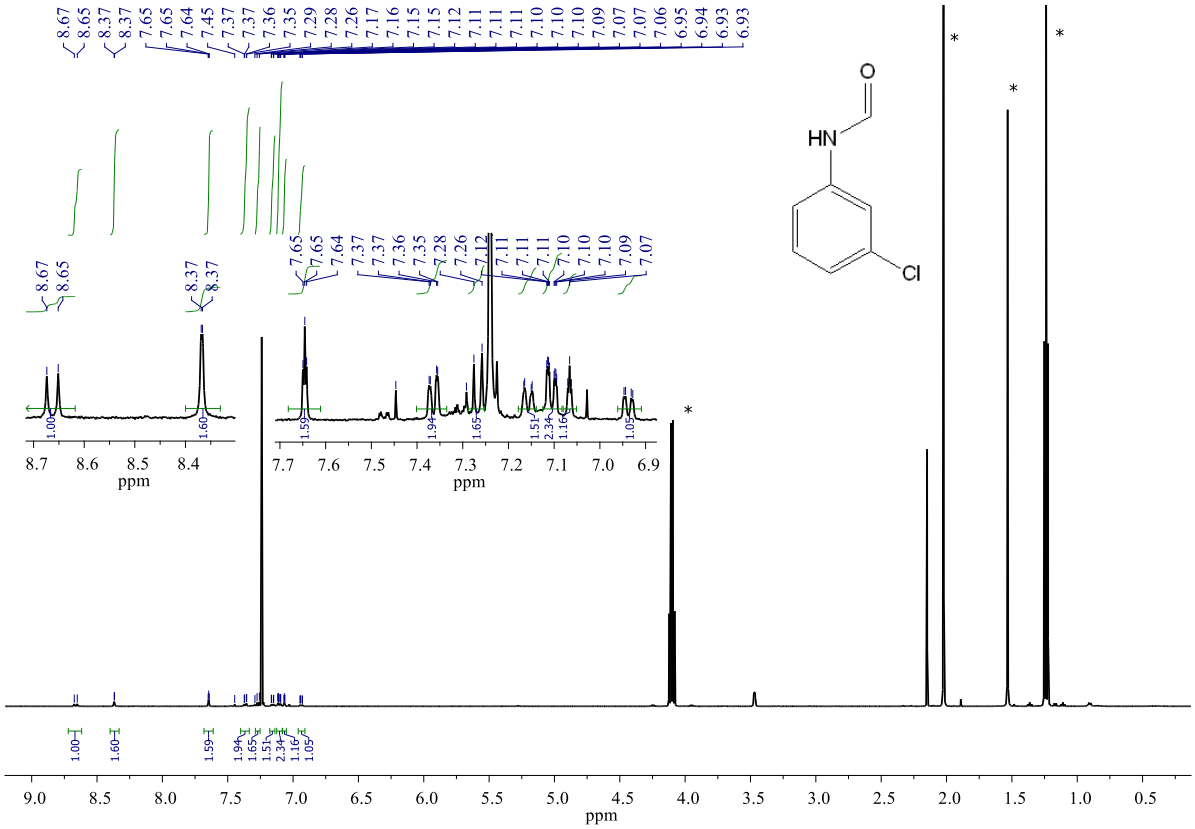

Figure 7. ^{1}H NMR spectrum for N-(3-chlorophenyl)formamide

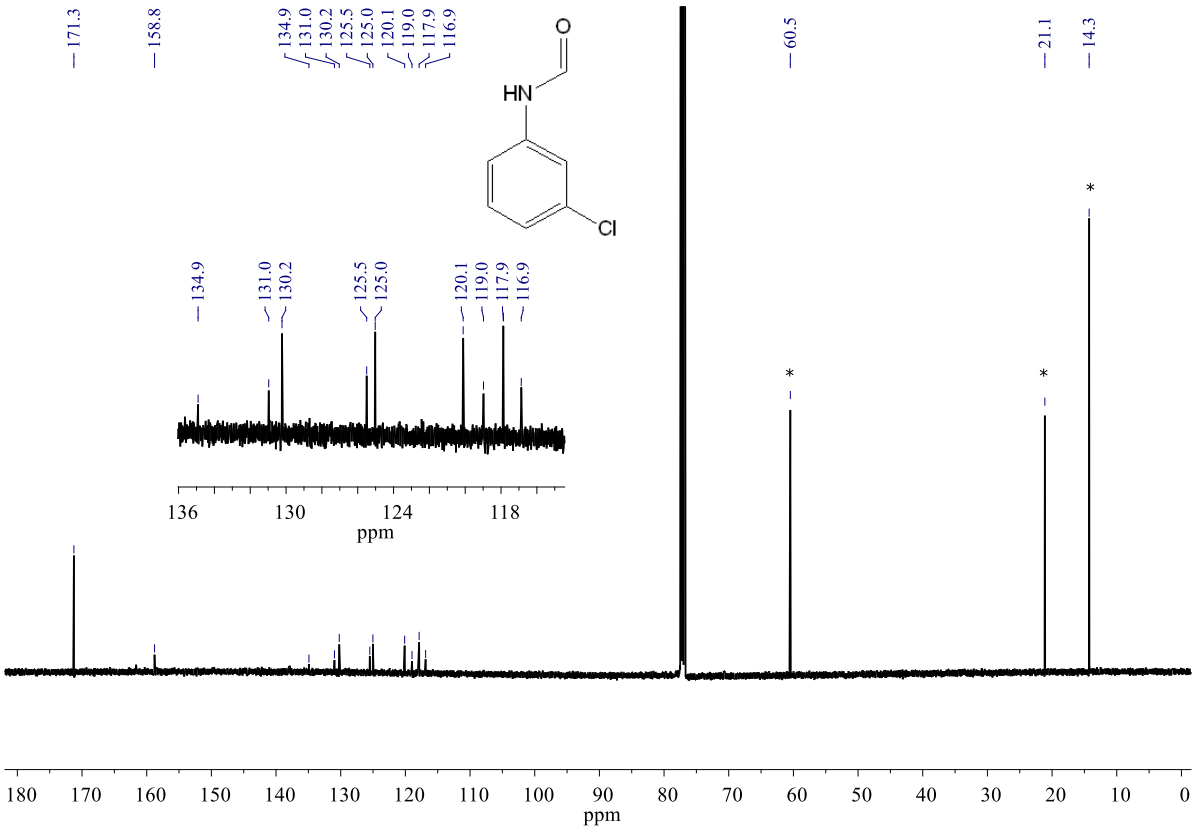

Figure 8. ^{13}C{^{1}H} NMR spectrum for N-(3-chlorophenyl)formamide

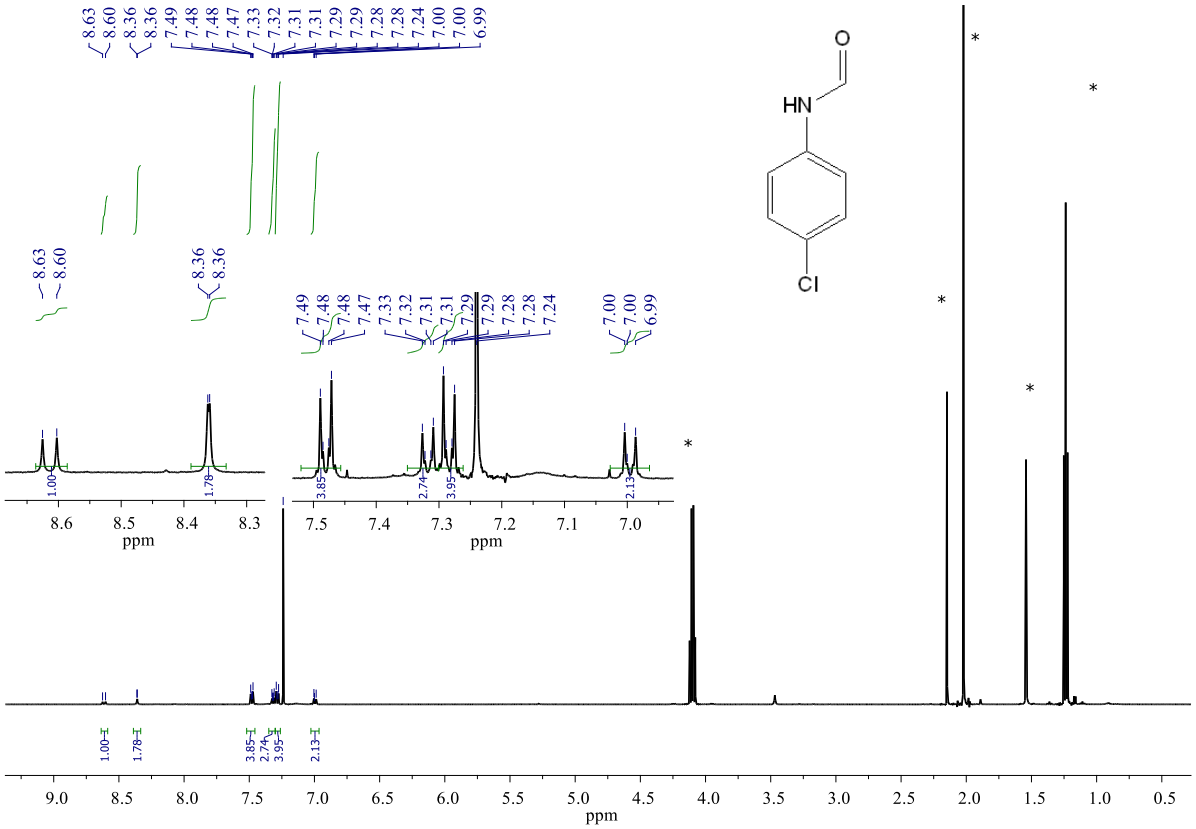

Figure 9. ^{1}H NMR spectrum for N-(4-chlorophenyl)formamide

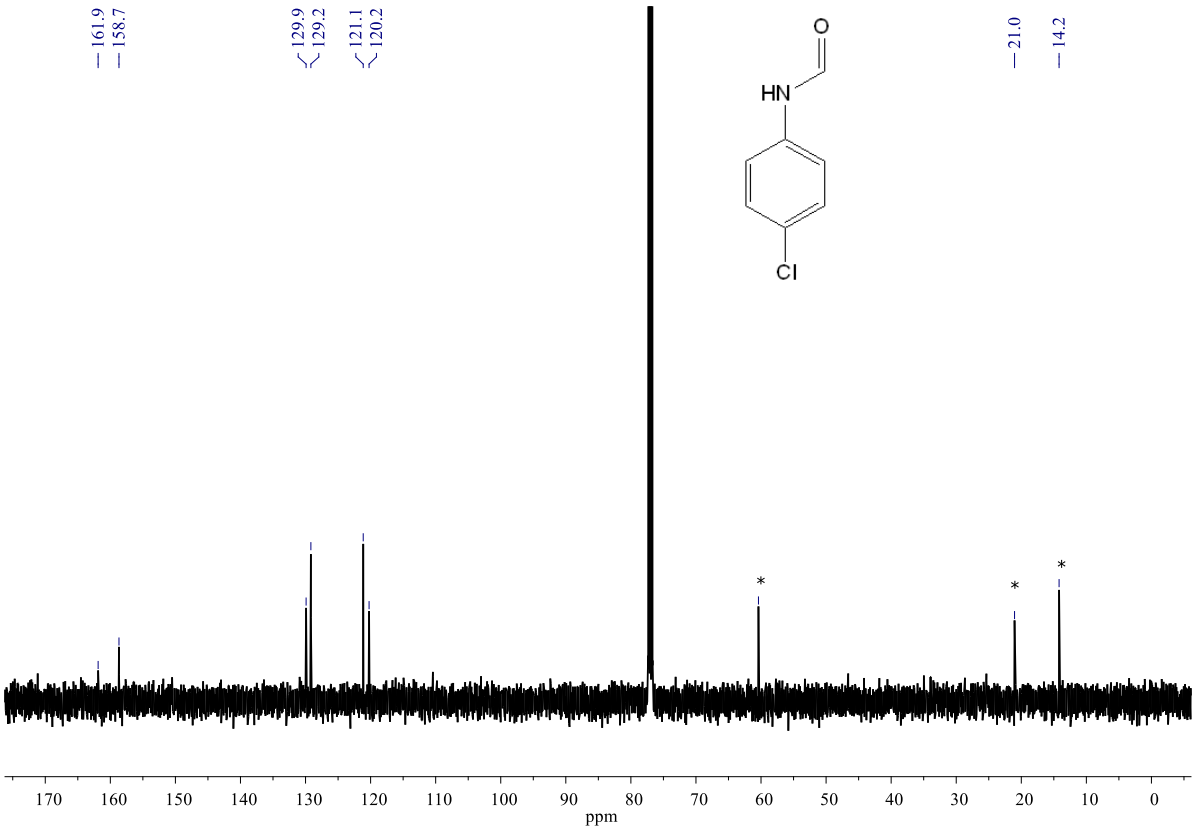

Figure 10. $^{13}C\{^{1}H\}$ NMR spectrum for N-(4-chlorophenyl)formamide

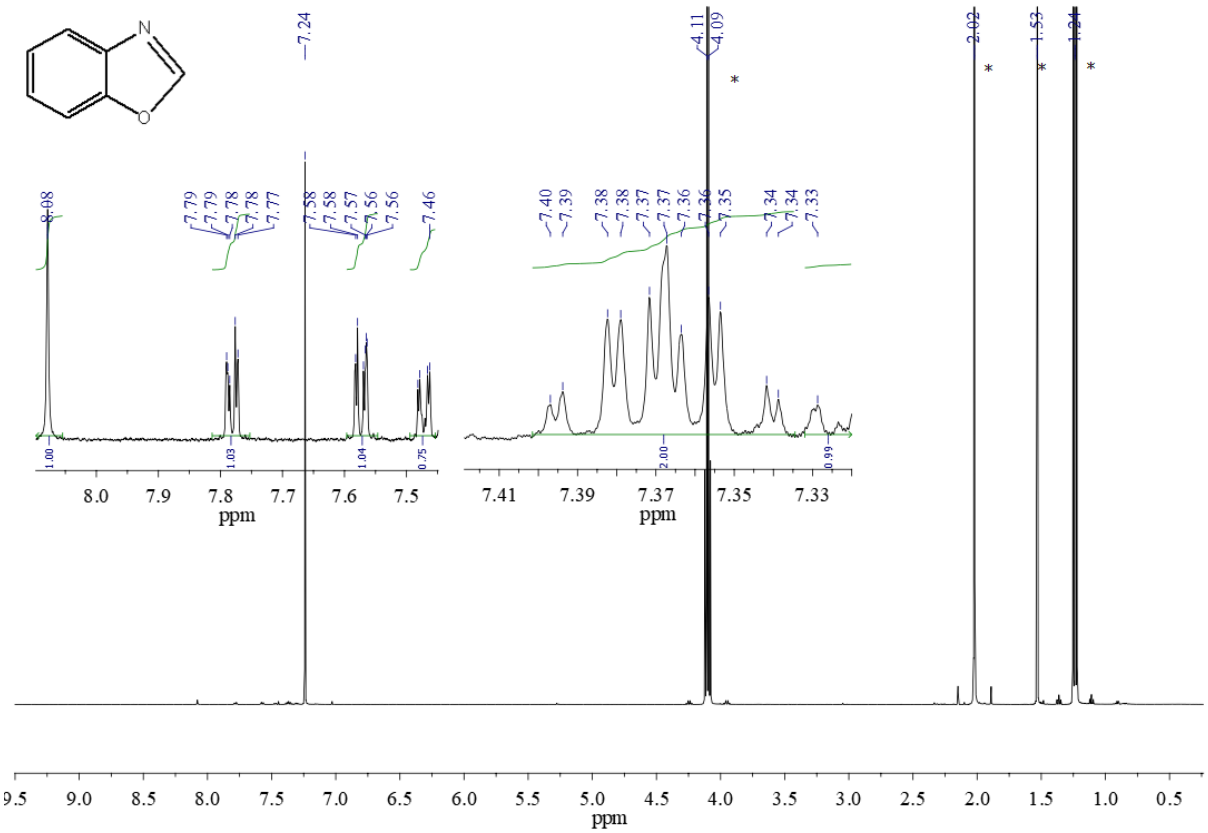

Figure 11. ^{1}H NMR spectrum for benzoxazole

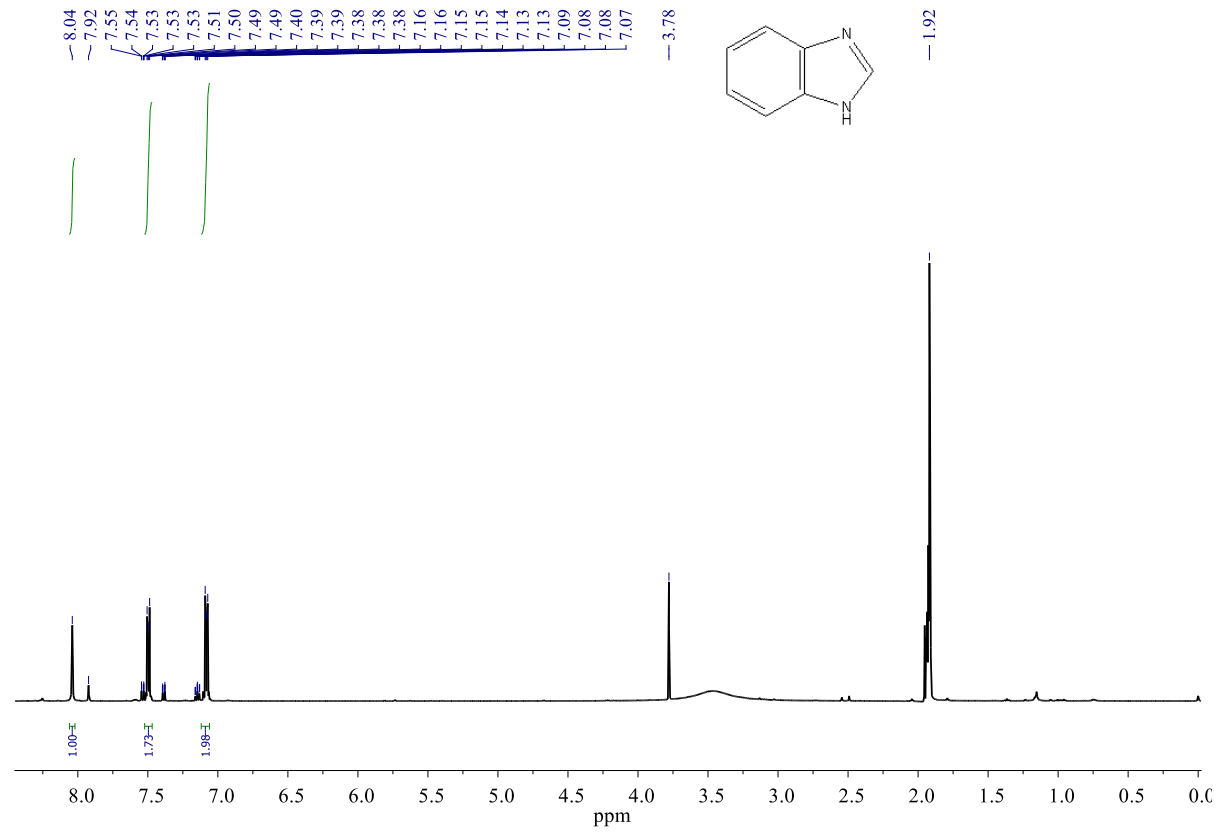

Figure 12. ^{1}H NMR spectrum for benzimidazole.

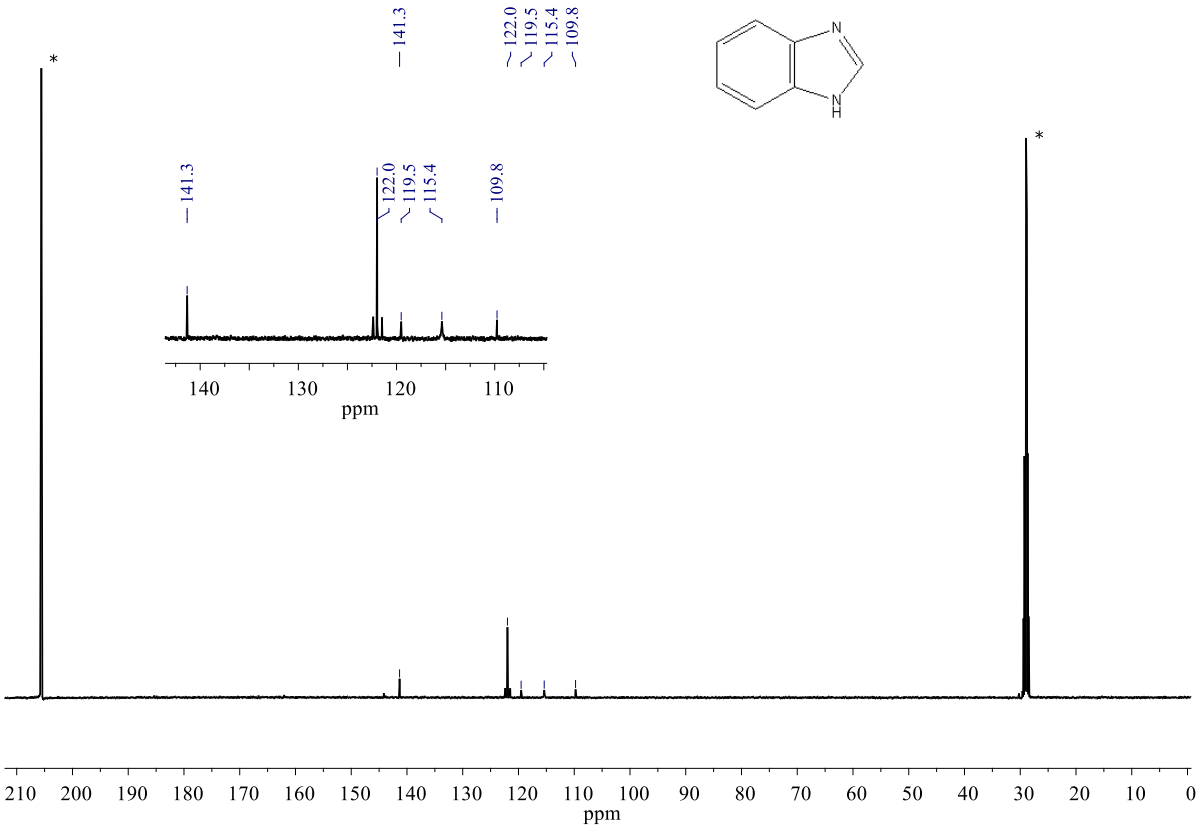

Figure 13. ^{13}C NMR spectrum for benzimidazole.

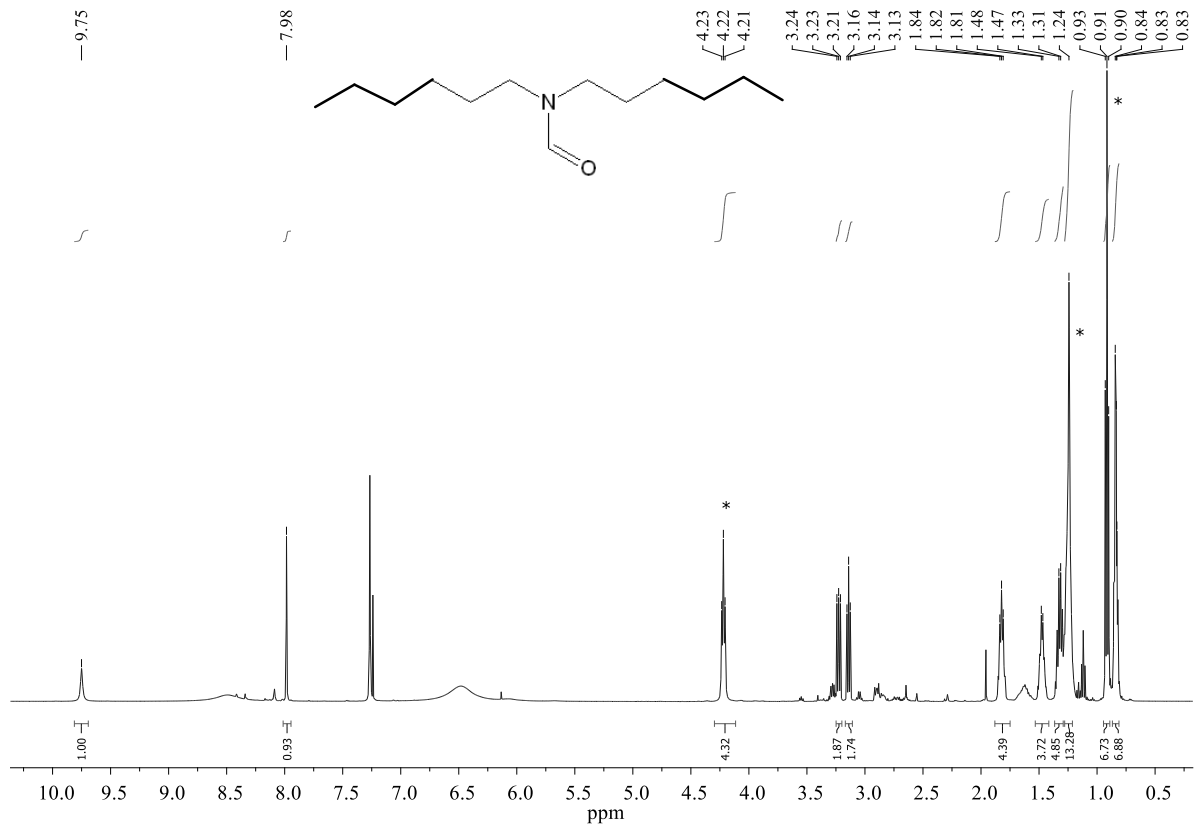

Figure 14. ^{1}H NMR spectrum for dihexylamine.

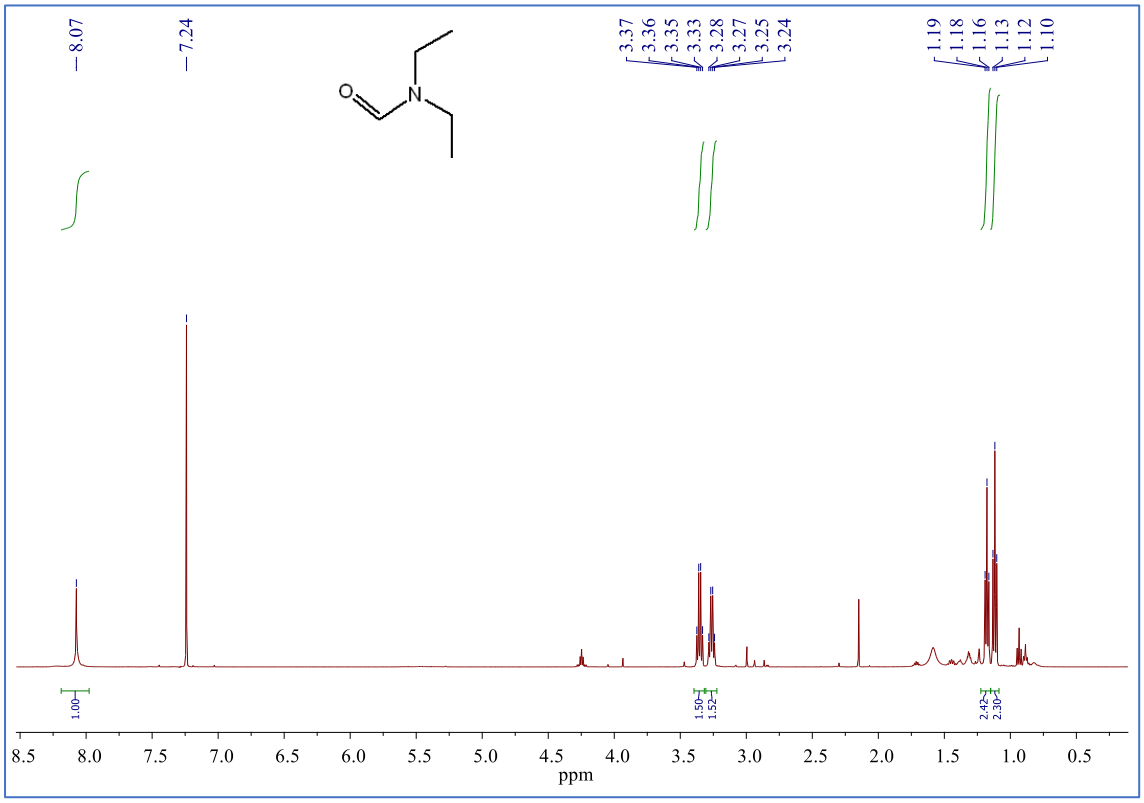

Figure 15. ^{1}H NMR spectrum for diethylformamide.

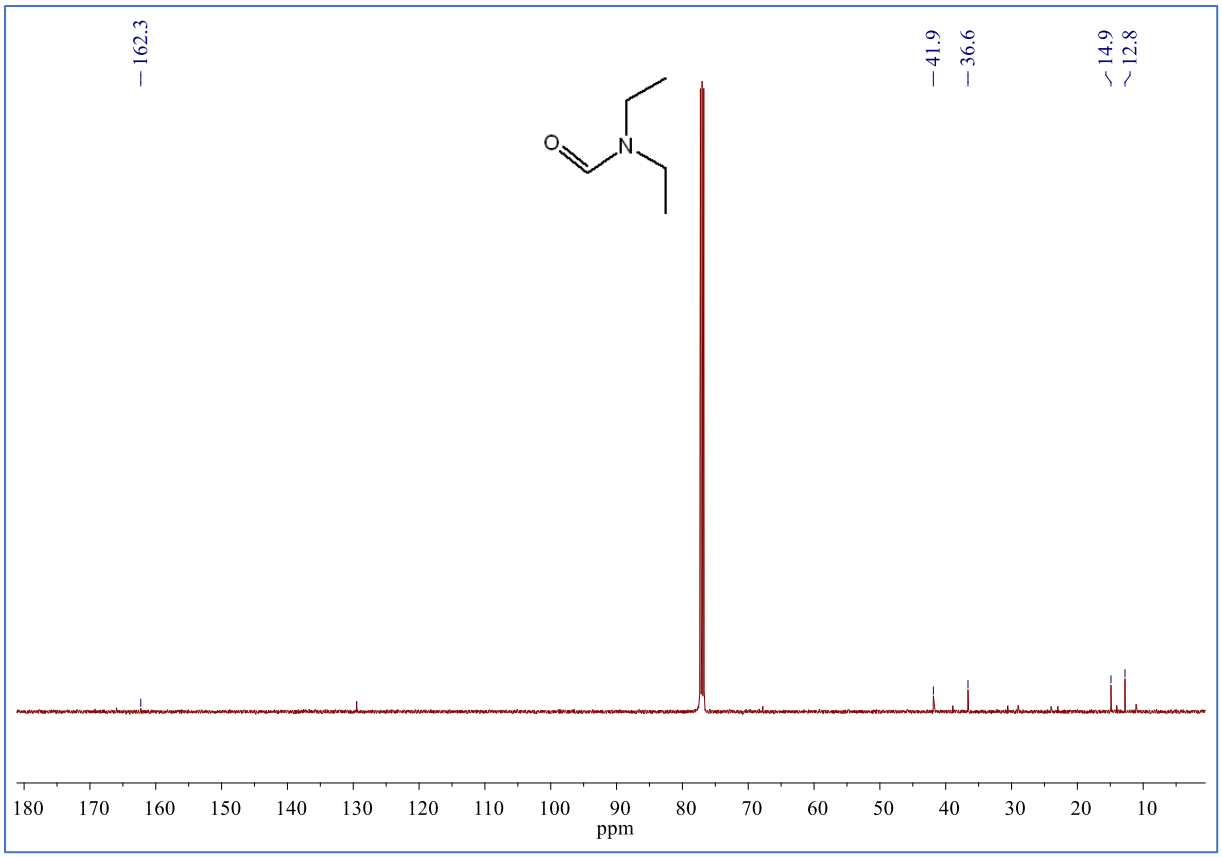

Figure 16. $^{13}C\{^{1}H\}$ NMR spectrum for diethylformamide.