A Copper-Catalyzed Synthesis of 2-Unsubstituted N-Substituted Benzimidazoles

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Supporting Information

1. General information

All reactions were carried out in flame-dried reaction vessels. Reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel. All new compounds were fully characterized. The commercially available chemicals were used without further purification.

NMR-spectra were recorded on a Bruker ARX-300, AV-300, or AV-400 MHz. Chemical shifts (δ) are quoted in ppm downfield of tetramethylsilane. Coupling constants (*J*) are quoted in Hz.

Infrared spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}. ESI mass spectra were recorded on a Bruker Daltonics MicroTof. Elemental analyses were recorded on Vario EL III of Fa. Elementar Analysensysteme GmbH, Hanau.

GC-MS Spectra were recorded on an Agilent Technologies 7890A GC-system with Agilent 5975C VL MSD or 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm x 30 m, Film: 0.25 μm). For control of the conversion and characterization of the products, two methods were used (Table 1). The method used starts with the injection temperature T_0, after holding this temperature for 3 min, the column is heated to the temperature T_1 (ramp) and holds the final temperature for the indicated time.

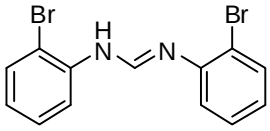
Table 1: GC-MS methods.

method	T_0 [°C]	ramp/K·min^{-1}	T_1[°C] /holding time[min]
A	**50**	**40**	**290 / 3**
B	**50**	**20**	**320 / 8**

2. Synthesis and Characterization of Formamidines

The formamidines were synthesized following the reported procedure by Grubbs et al., which was not further optimized.[1]

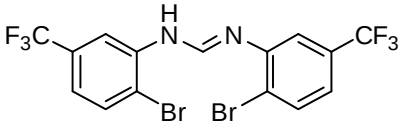
N,N'-Bis-(2-bromophenyl)-formamidine (1a)



2-Bromoaniline (3.44 g, 2.18 mL, 20 mmol, 2.0 eq.) and glacial acetic acid (30 mg, 29 µL, 0.5 mmol, 0.05 eq.) were mixed with triethylorthoformate (1.48 g, 1.67 mL, 10 mmol, 1.0 eq.). The mixture was stirred for 10 h at 140 °C and allowed to cool to rt. The resulting viscous oil solidified on standing. The solid was washed with *n*-pentane (2 × 10 mL) and recrystallized from EtOH to afford **1a** as a white solid (2.67 g, 75%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.46-7.14 (m, 5H), 7.00-6.89 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 147.3 (br), 142.9 (br), 132.9, 128.4, 124.5, 119.0 (br), 115.2 (br); **IR (ATR):** ν/cm^{-1} = 2989, 2918, 2855, 1653, 1580, 1498, 1468, 1448, 1435, 1379, 1307, 1281, 1260, 1226, 1206, 1122, 1028, 1001, 937, 909, 855, 820, 745, 681, 659, 626, 610, 543; **R_f (*n*-pentane/EtOAc 1:1):** 0.78; **t_R (50_40):** 10.56 min; **MS (GC-MS):** *m/z* (%) = 351 (6), 273 (52), 198 (1), 182 (12), 171 (100), 155 (23), 91 (13), 77 (10); **EM (ESI):** *m/z* [M + Na$^+$] calcd. for $C_{13}H_{10}Br_2NaN_2$: 374.9103, found: 374.9114.

N,N'-Bis-(2-bromo-5-trifluoromethylphenyl)-formamidine (1b)



The mixture of 2-bromo-5-(trifluoromethyl)aniline (1.0 g, 4.17 mmol, 2.0 eq.), triethylorthoformate (378 mg, 415 µL, 2.52 mmol, 1.0 eq.) and glacial acetic acid (6.3 mg, 6.0 µL, 0.104 mmol, 0.05 eq.) were stirred for 24 h at 150 ˚C. The resulting viscous oil solidified during cooling to rt. The brown solid was triturated in cold *n*-pentane (2 mL) and the supernatant was removed by decantation. This operation was repeated three times and dried under reduced pressure. The product **1b** was obtained as a white solid (726.2 mg, 71%). The exact assignment was not possible due to the complexity of the NMR spectra.

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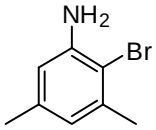
[1] Kuhn, K. M.; Grubbs, R. H. *Org. Lett.* **2008**, *10*, 2075.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (br s, 1H), 7.78-7.66 (m, 2H), 7.32-7.17 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 147.1, 133.6, 131.2 (q, *J* = 33 Hz), 123.7 (q, *J* = 272 Hz), 121.5 (m), 116.5 (m); **^{19}F NMR (282 MHz, $CDCl_3$):** δ –62.7; **IR (ATR):** ν/cm^{-1} = 3378, 3073, 1647, 1588, 1575, 1540, 1426, 1379, 1324, 1276, 1259, 1203, 1170, 1121, 1078, 1027, 959, 903, 882, 818, 746, 727, 682, 612, 586; **R_f (*n*-pentane/EtOAc 1:1):** 0.81; **t_R (50_40):** 9.77 min; **MS (GC-MS):** *m/z* (%) = 488 (4), 469 (1), 421 (1), 409 (41), 331 (1), 250 (18), 239 (100), 223 (18), 170 (3), 160 (12), 144 (37), 80 (1), 75 (10), 69 (5); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{15}H_9Br_2F_6N_2$: 490.9011, found: 490.9001.

2-Bromo-3,5-dimethylphenylamine[2]

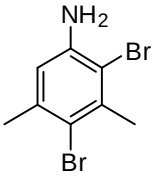


Following the procedure by Futagawa,[2] 3,5-dimethylaniline (6.38 g, 52.7 mmol, 1.0 eq.) was dissolved in CCl_4 (30 mL) and cooled to 0 ˚C. NBS (9.38 g, 52.7 mmol, 1.0 eq.) was added portionwise to the vigorously stirred solution at 0 ˚C and the residual NBS was rinsed with a small amount of CH_2Cl_2 in the reaction. The resulting brown suspenstion was stirred for 2.5 h at 0 °C and quenched by addition of H_2O (20 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were dried over Na_2SO_4 and the volatiles were removed under removed pressure. The brown residue was purified by column chromatography (Ø 5 cm, SiO_2: 16.5 cm, *n*-pentane/EtOAc 19:1) to yield the product as a greenish solid (1.78 g, 17%). As a byproducts 2,4-dibromo-3,5-dimethylphenylamine (1.99 g, 14%, an off-white solid) and 2,4,6-tribromo-3,5-dimethylphenylamine (696.7 mg, 4%, colorless needles) were obtained additionally and used for the synthesis of the symmetrically substituted formamidines. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.48-6.45 (m, 1H, Ar-H), 6.45-6.42 (m, 1H, Ar-H), 4.00 (br s, 2H, NH_2), 2.32 (s, 3H, CH_3), 2.18 (s, 3H, CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 143.9, 138.3, 137.3, 121.4, 113.8, 108.9, 23.4, 20.8; **IR (ATR):** ν/cm^{-1} = 3398, 3300, 3194, 3018, 2979, 2952, 2919, 2858, 2734, 1617, 1587, 1469, 1439, 1416, 1375, 1333, 1295, 1257, 1174, 1117, 1018, 965, 872, 836, 722, 693, 570; **R_f (*n*-pentane/EtOAc 19:1):** 0.27; **t_R (50_40):** 7.45 min; **MS (GC-MS):** *m/z* (%) = 201 (100), 184 (10), 120 (59), 105 (4), 91

[2] Futagawa, T. *Jpn. Kokai Tokkyo Koho* **1995**, JP 07330690 A.

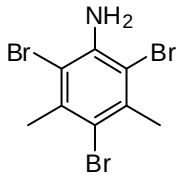
(24), 79 (3), 77 (16); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_8H_{11}BrN$: 200.0069, found: 200.0077.

2,4-Dibromo-3,5-dimethylphenylamine[2]



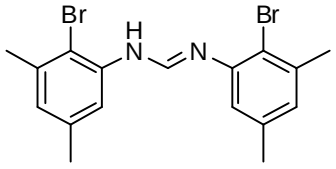
^{1}H NMR (300 MHz, DMSO-d6): δ 6.67 (s, 1H, Ar-H), 5.36 (s, 2H, NH_2), 2.46 (s, 3H, CH_3), 2.20 (s, 3H, CH_3); **^{13}C NMR (75 MHz, DMSO-d6):** δ 146.0, 137.7, 137.0, 115.5, 113.1, 108.9, 25.5, 24.6; **IR (ATR):** ν/cm^{-1} = 3390, 3293, 3191, 3053, 2987, 2948, 2918, 2847, 1618, 1567, 1454, 1426, 1394, 1376, 1331, 1280, 1219, 1134, 1041, 973, 859, 846, 718, 691, 642, 605, 589, 560; **R_f (*n*-pentane/EtOAc 19:1):** 0.20; **t_R (50_40):** 8.51 min; **MS (GC-MS):** *m/z* (%) = 279 (100), 198 (22), 118 (28), 104 (5), 91 (19), 77 (4); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_8H_{10}Br_2N$: 277.9175, found: 277.9165.

2,4,6-Tribromo-3,5-dimethylphenylamine[2]



^{1}H NMR (300 MHz, $CDCl_3$): δ 4.68 (br s, 2H, NH_2), 2.59 (s, 6H, 2×CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 141.2, 136.6, 114.6, 108.6, 25.6; **IR (ATR):** ν/cm^{-1} = 3416, 3294, 3191, 2921, 1604, 1547, 1432, 1394, 1373, 1264, 1101, 1026, 971, 711, 653; **R_f (*n*-pentane/EtOAc 19:1):** 0.58; **t_R (50_40):** 9.15 min; **MS (GC-MS):** *m/z* (%) = 357 (100), 342 (1), 278 (29), 197 (18), 184 (1), 168 (1), 91 (11), 90 (12), 78 (4), 77 (3); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_8H_9Br_3N$: 355.8280, found: 355.8281.

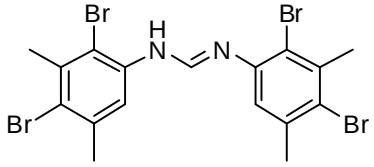
***N,N'*-Bis-(2-bromo-3,5-dimethylphenyl)-formamidine (1c)**



2-Bromo-3,5-dimethylphenylamine (1.5 g, 7.5 mmol, 1.0 eq.) and glacial acetic acid (11.3 mg, 10.7 µL, 0.189 mmol, 0.025 eq.) were mixed with triethylorthoformate (680.0 mg, 747.2 µL, 5.7 mmol, 0.75 eq.). The mixture was stirred for 4 h at 150 ˚C and allowed to cool to rt. The resulting brown viscous oil was scratched in *n*-pentane (2 mL) to afford the solid. The supernatant was removed by a pipette and this procedure was repeated five times using *n*-pentane (5 mL). The product was obtained as an off-white solid (1.10 g, 72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.07-6.65 (m, 5H), 2.40 (s, 6H), 2.28 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 147.4, 138.8, 137.5, 126.4, 116.9 (br), 23.6, 21.0; **IR (ATR):** ν/cm^{-1} = 3027, 2977, 2950, 2918, 2857, 2733, 1651, 1629, 1571, 1458, 1435, 1402, 1376, 1327, 1280, 1262, 1246, 1202, 1170, 1027, 999, 950, 845, 837, 729, 704, 639, 600, 583, 575, 568, 533; **R_f (*n*-pentane/EtOAc 1:1):** 0.84; **t_R (50_40):** 11.34 min; **MS (GC-MS):** *m/z* (%) = 357 (100), 342 (1), 278 (29), 197 (18), 184 (1), 168 (1), 91 (11), 90 (12), 78 (4), 77 (3); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{17}H_{19}Br_2N_2$: 408.9910, found: 408.9899.

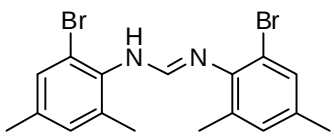
***N*,*N*'-Bis-(2,4-dibromo-3,5-dimethylphenyl)-formamidine (1d)**



2,4-Dibromo-3,5-dimethylphenylamine (1.67 g, 6.0 mmol, 1.0 eq.), glacial acetic acid (9.0 mg, 8.6 µL, 0.15 mmol, 0.025 eq.) and triethylorthoformate (544.0 mg, 597.8 µL, 4.5 mmol, 0.75 eq.) were suspended in *para*-xylene (4 mL) and the mixture was stirred for 11 h at 150 ˚C. After cooling to rt the resulting brown viscous oil was scratched in *n*-pentane (2 mL) to afford the solid. The supernatant was removed by a pipette and this procedure was repeated five times using *n*-pentane (5 mL). The product was obtained as a white solid (1.02 g, 60%). The measurement of ^{13}C NMR was not successful.

^{1}H NMR (400 MHz, DMSO-d6): δ 9.06 (s, 1H), 8.31 (s, 1H), 7.95 (s, 1H), 2.60 (s, 6H, CH_3), 2.34 (s, 6H, CH_3); **IR (ATR):** ν/cm^{-1} = 3377, 2920, 1636, 1577, 1554, 1487, 1449, 1397, 1375, 1357, 1317, 1267, 1244, 1203, 1032, 984, 955, 849, 824, 760, 717, 698, 661, 627, 600, 575, 557, 519; **R_f (*n*-pentane/EtOAc 1:1):** 0.79; **t_R (50_20_320_8ISO):** 21.90 min; **MS (GC-MS):** *m/z* (%) = 568 (8), 487 (78), 406 (1), 327 (4), 279 (100), 198 (12), 119 (12), 118 (14), 117 (8), 103 (22), 91 (13), 77 (12); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{17}H_{17}Br_4N_2$: 564.8120, found: 564.8106.

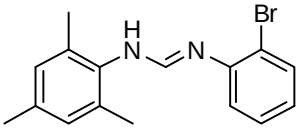
***N*,*N*'-Bis-(2-bromo-4,6-dimethylphenyl)-formamidine (1e)**



^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.24 (s, 2H), 6.95 (s, 2H), 6.21 (br s, 1H), 2.31 (br s, 6H), 2.25 (s, 6H);

^{13}C-NMR (75 MHz, $CDCl_3$): δ 130.8 (br), 130.6 (br), 20.5, 19.3 (br); **IR (ATR):** ν/cm^{-1} = 3143, 3011, 2976, 2948, 2918, 2844, 2732, 1644, 1600, 1556, 1470, 1438, 1371, 1315, 1264, 1216, 1170, 1122, 1110, 991, 846, 824, 810, 651; **R_f (*n*-Pentan/EtOAc 1:1):** 0.76; **t_R (50_40):** 12.13 min; **MS (GC-MS):** *m/z* (%) = 408 (2), 329 (18), 211 (2), 210 (5), 199 (100), 198 (11), 132 (3), 131 (25), 120 (25), 119 (5), 104 (18), 103 (15), 91 (10), 79 (2), 77 (16); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_{17}H_{19}Br_2N_2$: 408.9910, found: 408.9910.

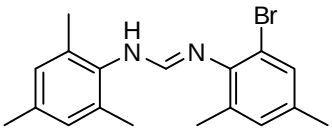
***N*-(2-Bromophenyl)-*N*'-(2,4,6-trimethylphenyl)-formamidine (1f)**



The mixture of 2,4,6-trimethylaniline (13.52 g, 14.08 mL, 100 mmol, 1.0 eq.), triethylorthoformate (14.82 g, 16.65 mL, 100 mmol, 1.0 eq.) and glacial acetic acid (300.3 mg, 287 µL, 5 mmol, 0.05 eq.) were stirred for 2.5 h at 120 °C, then cooled to rt. *ortho*-bromoaniline (17.20 g, 10.89 mL, 100 mmol, 1.0 eq.) was added to the reaction and the resulting mixture was stirred for 1.5 h at 140 °C, then for 14 h at 160 °C. After cooling to rt, the solidified crude product was triturated in *n*-pentane (10 mL) and the supernatant was removed by a pipette. The residue was recrystallized from acetone to yield the first fraction of the pure product. The mother liquor was concentrated and recrystallized fractionally from EtOAc to afford several pure fractions. The rest was purified by column chromatography (Ø 5 cm, SiO_2: 13 cm, CH_2Cl_2). The product **1f** was obtained as a white solid (6.84 g in total, 22%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.65 (m, 1H), 7.58-7.43 (m, 1H), 7.35-7.14 (m, 2H), 6.96-6.68 (m, 3H), 2.32-2.07 (m, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 133.0 (br), 129.0, 128.4 (br), 123.7 (br), 20.8, 18.6 (br); **IR (ATR):** ν/cm^{-1} = 3187, 2974, 2914, 2854, 2733, 1624, 1608, 1579, 1547, 1467, 1433, 1367, 1321, 1256, 1216, 1179, 1156, 1117, 1044, 1024, 993, 918, 843, 751, 728, 696, 648, 583; **R_f (*n*-pentane/EtOAc 1:1):** 0.67; **t_R (50_40):** 10.31 min; **MS (GC-MS):** *m/z* (%) = 316 (24), 237 (17), 170 (100), 154 (4), 146 (80), 135 (20), 131 (24), 120 (23), 118 (7), 103 (11), 92 (8), 91 (39), 77 (22); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_{16}H_{18}BrN_2$: 317.0648, found: 317.0641.

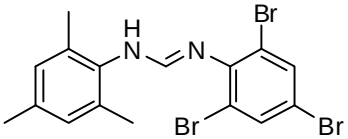
***N*-(2-Bromo-4,6-dimethylphenyl)-*N*'-(2,4,6-trimethylphenyl)-formamidine (1g)**



2,4,6-Trimethylaniline (2.45 g, 2.55 mL, 18.1 mmol, 1.0 eq.) and glacial acetic acid (54.3 mg, 52 µL, 0.905 mmol, 0.05 eq.) were mixed with triethylorthoformate (2.68 g, 3.01 mL, 18.1 mmol, 1.0 eq.) and the mixture was stirred for 1.5 h at 120 ˚C. The reaction vessel was removed from the oil bath and 2-bromo-4,6-dimethylaniline (3.62 g, 18.1 mmol, 1.0 eq.) was added. The resulting mixture was stirred for 20 h at 140 °C and cooled to rt. The obtained brown viscose oil solidified and the solid was triturated in *n*-pentane (10 mL), then the supernatant was removed with a pipette. The crude product was washed twice in the same fashion and recrystallized from EtOH. The further purification was performed by column chromatography (Ø 5 cm, SiO_2: 32 cm, CH_2Cl_2 → CH_2Cl_2/EtOAc 4:1 → 2:3 → 1:4) to deliver the product **1g** as a white solid (1.02 g, 16%). The symmetrical formamidine from 2-bromo-4,6-dimethylaniline, *N*,*N*'-bis-(2-bromo-4,6-dimethylphenyl)-formamidine **1e**, was obtained additionally as a white solid (465.6 mg, 6%) and used for the corresponding benzimidazole synthesis.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.09 (m, 2H), 7.05-6.79 (m, 3H), 6.20 (br s, 1H), 2.37-2.14 (m, 15H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 148.1(br), 134.0 (br), 130.7, 130.4, 129.0 (br), 20.8, 20.4, 19.2 (br), 18.6 (br); **IR (ATR):** ν/cm^{-1} = 3143, 2971, 2917, 2852, 1638, 1601, 1551, 1469, 1370, 1320, 1258, 1214, 1176, 1113, 847, 813; **R_f (*n*-pentane/EtOAc 1:1):** 0.68; ***t*$_R$ (50_40):** 11.06 min; **MS (GC-MS):** *m/z* (%) = 344 (11), 265 (17), 199 (86), 146 (55), 145 (17), 135 (100), 134 (26), 132 (3), 120 (47), 119 (12), 118 (6), 104 (16), 91 (25), 79 (6), 77 (21); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{18}H_{22}BrN_2$: 345.0961, found: 345.0959.

***N*-(2,4,6-Tribromophenyl)-*N*'-(2,4,6-trimethylphenyl)-formamidine (1h)**

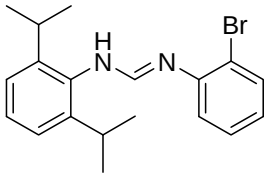


2,4,6-Tribromoaniline (3.30 g, 10 mmol, 2.0 eq.) and triethylorthoformate (741.0 mg, 832.6 µL, 5 mmol, 1.0 eq.) were dissolved in *para*-xylene (4 mL) and glacial acetic acid (15.0 mg, 14.3 µL, 0.25 mmol, 0.05 eq.) was added. The reaction was stirred for 2.5 h at 150 °C and cooled to rt. 2,4,6-Trimethylaniline (676.1 mg, 704.2 µL, 5 mmol, 1 eq.) was added to the mixture and it was stirred for 17.5 h at 140 °C. The mixture was diluted

with *n*-pentane (4 mL) after being cooled to rt. The obtained solid was filtered and washed with *n*-pentane (3 × 4 mL). The crude product was pre-adsorbed on silica gel and purified by column chromatography (Ø 4 cm, SiO_2: 14 cm, CH_2Cl_2) to give the product **1h** as a light violet solid (413.0 mg, 17%).

^{1}H NMR (300 MHz, DMSO-d6): δ 9.24-6.66 (m, 6H), 2.36-2.17 (m, 9H); **^{13}C NMR (75 MHz, DMSO-d6):** δ 153.2, 136.4 (br), 134.6 (br), 129.2, 21.5, 19.3; **IR (ATR):** ν/cm^{-1} = 2956, 2918, 2854, 1639, 1606, 1549, 1525, 1482, 1434, 1412, 1366, 1323, 1296, 1241, 1216, 1178, 1128, 1106, 1059, 1033, 1013, 995, 920, 850, 798, 757, 734, 712, 617; **R_f (*n*-pentane/EtOAc 1:1):** 0.82; **t_R (50_20_320):** 17.45 min; **MS (GC-MS):** *m/z* (%) = 472 (1), 457 (1), 393 (5), 327 (5), 315 (3), 311 (1), 237 (2), 170 (1), 146 (100), 135 (19), 134 (16), 120 (22), 119 (6), 105 (2), 91 (13), 79 (4), 77 (8); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{16}H_{16}Br_3N_2$: 472.8858, found: 472.8877.

***N*-(2-Bromophenyl)-*N*'-(2,6-diisopropylphenyl)-formamidine (1i)**

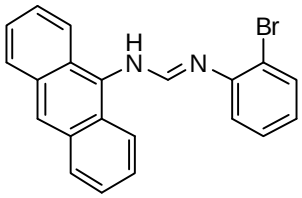


The mixture of 2,6-diisopropylamine (8.87 g, 9.43 mL, 50 mmol, 1.0 eq.), triethylorthoformate (7.41 g, 8.33 mL, 50 mmol, 1.0 eq.) and glacial acetic acid (150.1 mg, 143,2 µL, 2.5 mmol, 0.05 eq.) were stirred for 3 h at 120 °C. The reaction vessel was removed from the oil bath, *ortho*-bromoaniline (8.60 g, 5.44 mL, 50 mmol, 1 eq.) was added and the resulting mixture was stirred for 3 h at 140 ˚C. The reaction was cooled to rt and diluted with *n*-pentane (15 mL). The brown solution was cooled to 0 °C and stirred for 10 min to afford an off-white solid. The solid was filtered and washed with *n*-pentane (3 × 5 mL) and recrystallized from acetone subsequently. Two pure batches of the product **1i** were obtained as a white solid (3.98 g in total, 22%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04-6.66 (m, 9H), 3.32-2.96 (m, 2H), 1.27-1.15 (m, 12H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 148.1 (br), 142.1, 141.9, 141.2 (br), 138.5, 136.9, 133.2, 133.0 (br), 128.7, 128.5 (br), 124.7 (br), 124.3, 123.7, 123.5, 123.4, 123.2 (br), 117.3 (br), 115.1, 112.0, 28.0, 28.0 (br), 23.7 (br), 23.6, 23.5; **IR (ATR):** ν/cm^{-1} = 3191, 2165, 2970, 2960, 2937, 2869, 1632, 1579, 1557, 1463, 1438, 1375, 1361, 1340, 1252, 1204, 1150, 1115, 1043, 1025, 995, 939, 850, 797, 768, 748, 717, 707, 651; **R_f (*n*-pentane/EtOAc 1:1):** 0.76; **t_R (50_40):** 10.31 min; **MS (GC-MS):** *m/z* (%) = 358 (7),

315 (6), 279 (1), 273 (1), 189 (15), 188 (100), 182 (2), 171 (32), 147 (12), 146 (98), 132 (5), 119 (2), 91 (10), 79 (2), 77 (7); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_{19}H_{24}BrN_2$: 359.1117, found: 359.1124.

_N_-Anthracen-9-yl-_N'_-(2-bromophenyl)-formamidine (1j)

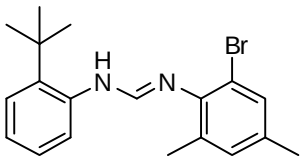


Anthracen-9-ylamine (3.87 g, 20 mmol, 1.0 eq.) and glacial acetic acid (60.1 mg, 55.3 µL, 1 mmol, 0.05 eq.) were mixed with triethylorthoformate (2.96 g, 3.33 mL, 20 mmol, 1.0 eq.). The reaction was stirred for 1.5 h at 120 ˚C and the reaction vessel was removed from the oil bath. 2-Bromoaniline (3.44 g, 2.18 mL, 20 mmol, 1.0 eq.) was added and the resulting mixture was stirred for 11 h at 140 °C. After cooling to rt the solid *n*-pentane (10 mL) was added to the mixture, the solid was triturated and the supernatant was removed by decantation. The crude mixture was washed twice in the same fashion and pre-adsorbed on silica gel. The first purification by column chromatography (Ø 5 cm, SiO_2: 37 cm, CH_2Cl_2/*n*-pentane 3:2 → 4:1 → CH_2Cl_2 → CH_2Cl_2/EtOAc 4:1) did not afford the pure product. Therefore the fractions containing the product were collected and concentrated. The residue was suspended in hot EtOH (10 mL) and cooled to rt. The yellow supernatant was decanted off and the solid was washed twice in the same manner. The still contaminated product was pre-adsorbed on silica gel and purified by column chromatography (Ø 5 cm, SiO_2: 32 cm, CH_2Cl_2/*n*-Pentan 9:1). The obtained slightly contaminated product was recrystallized from EtOAc and subsequently purified by another column chromatography (Ø 5 cm, SiO_2: 15 cm, CH_2Cl_2/*n*-Pentan 4:1) to afford the product **2j** (792 mg, 11%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27-8.17 (m, 3H), 8.13 (br s, 1H), 8.05-7.97 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.53-7.42 (m, 5H), 7.31-7.23 (m, 2H), 6.97 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 150.2 (br), 137.9 (br), 133.1, 131.9, 128.6, 128.3, 125.4, 125.1, 124.4, 124.2, 123.9, 122.3, 117.7 (br), 112.9; **IR (ATR):** ν/cm^{-1} = 1652, 1577, 1533, 1474, 1436, 1409, 1352, 1306, 1265, 1214, 1174, 1045, 1025, 1002, 957, 934, 886, 845, 787, 755, 735, 667, 658, 611, 535; **R_f (*n*-pentane/EtOAc 1:1):** 0.75; ***t*$_R$ (50_20_320-8ISO):** 20.12 min; **MS (GC-MS):** *m/z* (%) = 374 (39), 295 (8), 205 (4), 204

(22), 193 (100), 192 (9), 182 (2), 177 (25), 171 (5), 155 (3), 91 (5), 77 (2); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_{21}H_{16}BrN_2$: 375.0491, found: 375.0491.

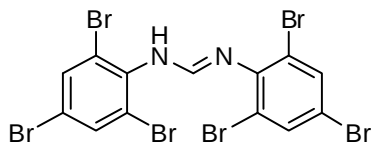
***N*-(2-Bromophenyl)-*N*'-(2-*tert*-butylphenyl)-formamidine (1k)**



The mixture of 2-*tert*-butylaniline (1.70 g, 1.78 mL, 11.4 mmol, 1.0 eq.), triethylorthoformate (1.69 g, 1.90 mL, 11.4 mmol, 1.0 eq.) and glacial acetic acid (34.2 mg, 32.7 µL, 0.57 mmol, 0.05 eq.) were stirred for 1.5 h at 120 ˚C. The reaction vessel was removed from the oil bath and 2-bromo-4,6-dimethylaniline (2.29 g, 11.4 mmol, 1.0 eq.) was added. The resulting mixture was stirred for 20 h at 140 °C and then cooled to rt. The black oil was purified by column chromatography (Ø 5 cm, SiO_2: 18 cm, CH_2Cl_2). The fractions containing the product were collected and concentrated. The resulting solid was washed with *n*-pentane (2 mL). The product **2k** was obtained as a dark purple solid (946.8 mg, 23%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90-6.25 (m, 8H), 2.50-1.06 (m, 15H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 150.9, 145.1, 142.6, 141.8, 138.9, 137.4, 135.6, 134.2, 133.8, 131.1, 130.9, 130.6, 127.3, 127.0, 126.4, 124.2, 122.0 (br), 119.6, 118.7, 35.1, 34.1, 30.4, 30.2, 20.5, 19.3, 18.5; **IR (ATR):** ν/cm^{-1} = 2964, 2919, 2863, 1661, 1590, 1566, 1476, 1437, 1360, 1303, 1260, 1196, 1122, 1089, 1051, 993, 851, 820, 754, 691, 623, 602, 539; **R_f (*n*-pentane/EtOAc 1:1):** 0.80; ***t*$_R$ (50_40):** 10.83 min; **MS (GC-MS):** *m/z* (%) = 358 (9), 301 (13), 279 (3), 223 (2), 200 (15), 199 (100), 161 (10), 160 (82), 149 (15), 133 (4), 132 (13), 120 (15), 119 (6), 105 (5), 104 (15), 91 (25), 79 (4), 77 (16), 57 (1); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_{19}H_{24}BrN_2$: 359.1117, found: 359.1118.

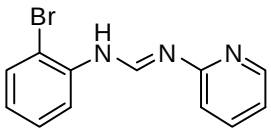
***N*,*N*'-Bis-(2,4,6-tribromophenyl)-formamidine (1l)**



2,4,6-Tribromoaniline (3.30 g, 10 mmol, 2.0 eq.) and triethylorthoformate (741.0 mg, 832.6 µL, 5 mmol, 1.0 eq.) were dissolved in *para*-xylene (4 mL) and three drops of conc. sulfuric acid were added. The reaction was stirred for 17 h at 150 °C and allowed to cool to rt. The mixture was diluted with CH_2Cl_2 (20 mL) and H_2O (20 mL) was added. The organic phase was separated, washed with H_2O (2 × 20 mL) and dried

over Na_2SO_4. The crude product was pre-adsorbed on silica gel and purified by column chromatography (Ø 4 cm, SiO_2: 16 cm, CH_2Cl_2/*n*-pentane 1:19). The product **1l** was obtained as a purple solid (272.8 mg, 8%). **^{1}H NMR (400 MHz, DMSO-d6):** δ 9.89-9.18 (m, 1H), 8.11-7.58 (m, 5H); **^{13}C NMR (100 MHz, DMSO-d6):** δ 152.8 (br), 135.3 (br), 134.8 (br), 126.6, 119.0; **IR (ATR):** ν/cm^{-1} = 3359, 3095, 3070, 2356, 2329, 1643, 1555, 1532, 1496, 1437, 1433, 1363, 1287, 1221, 1189, 1152, 1101, 1059, 988, 855, 830, 792, 737, 698, 658, 601, 564; **R_f (*n*-pentane/EtOAc 1:1):** 0.78; ***t*$_R$ (50_20_320_8ISO):** 22.14 min; **MS (GC-MS):** *m/z* (%) = 585 (4), 429 (1), 338 (3), 327 (34), 311 (3), 261 (5), 260 (3), 248 (10), 247 (4), 233 (3), 182 (1), 170 (15), 169 (9), 155 (14), 79 (7); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{13}H_7Br_6N_2$: 664.5704, found: 664.5694.

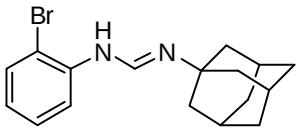
***N*-(2-Bromophenyl)-*N*'-pyridin-2-yl-formamidine (1m)**



To a 10 mL round bottom flask fitted with a distillation apparatus was taken the *o*-bromoaniline (3.66 g, 21.25 mmol, 1 eq.) and triethylorthoformate (3.5 mL, 21.25 mmol, 1 eq.). To this stirred solution was added acetic acid (60 μL, 1.06 mmol, 0.05 eq.). The reaction mixture was heated to 140 °C and kept stirring for 2 h. It was subsequently cooled and then 2-aminopyridine (2 g, 21.25 mmol) was added. The mixture was heated to 140 °C again and stirred for 12 h. It was then cooled and the residue was washed with *n*-hexane (3x 10 mL). The crude residue upon recrystallization using CH_2Cl_2-*n*-hexane afforded the *N*-(2-bromophenyl)-*N*'-pyridin-2-yl-formamidine **1m** as a light brown solid (3.58 g, 61%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.78 (s, 0.5H), 9.42 (s, 0.5 H), 877-8.28 (m, 2H), 7.73-6.59 (m, 7H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.7, 160.2, 149.7, 147.4, 138.2, 132.5, 128.5, 119.3, 118.2, 115.8, 111.9, 109.3; **IR (ATR):** ν/cm^{-1} = 2957, 2916, 2876, 1664, 1598, 1572, 1503, 1473, 1415, 1354, 1293, 1236, 1205, 1157, 1115, 1096, 1045, 1028, 1013, 990, 865; **R_f (*n*-pentane/EtOAc 1:1):** 0.50; ***t*$_R$ (50_40):** 10.05 min; **MS (GC-MS):** *m/z* (%) = 275 (9), 197 (14), 196 (100), 173 (24), 171 (25), 155 (9), 94 (92), 79 (19), 78 (42), 76 (13), 67 (33); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{12}H_{10}N_3BrH$: 276.0131, found: 276.0133.

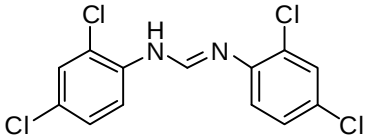
***N*-Adamantan-2-yl-*N*'-(2-bromophenyl)-formamidine (1n)**



To a 10 mL round bottom flask fitted with a distillation apparatus was taken the *o*-bromoaniline (2.274 g, 13.22 mmol, 1 eq.) and triethylorthoformate (2.2 mL, 13.22 mmol, 1 eq.). To this stirred solution was added acetic acid (37 µL, 0.66 mmol, 0.05 eq.). The reaction mixture was heated to 140 °C and kept stirring for 2 h. It was subsequently cooled and then adamantylamine (2 g, 13.22 mmol, 1 eq.) added. The mixture was heated to 140 °C again and stirred for 12 h. It was cooled and the residue was washed with *n*-hexane (3 × 10 mL). The crude residue upon recrystallization using CH_2Cl_2-*n*-hexane afforded *N*-adamantan-2-yl-*N*'-(2-bromo-phenyl)-formamidine **1n** as a white crystalline solid (3.17 g, 72%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.56-7.47 (m, 1H), 7.18 (s, 1H), 6.85 (d, *J* = 7.4 Hz, 2H), 2.11 (s, 4H), 1.82 (s, 7H), 1.69 (m, 4H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 132.9, 128.2, 123.7, 121.0, 44.0, 42.8, 36.1, 35.8, 29.5, 29.3; **IR (ATR):** ν/cm^{-1} = 2917, 2890, 2850, 1665, 1578, 1483, 1357, 1321, 1302, 1255, 1211, 1186, 1136, 1113, 1043, 1027, 992, 933, 863, 815, 754; **R_f (*n*-pentane/EtOAc 1:1):** 0.62; **t_R (50_40):** 11.44 min; **MS (GC-MS):** *m/z* (%) = 333 (18), 332 (51), 331 (8), 252 (21), 253 (100), 236 (17), 201 (12), 199 (19), 173 (56), 171 (57), 163 (23), 162 (56), 157 (19), 155 (18), 135 (92), 119 (41), 118 (30), 93 (65), 79 (64); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{17}H_{21}N_2BrH$: 333.0961, found: 333.0967.

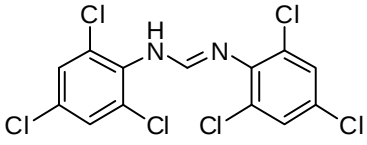
***N*,*N*'-Bis-(2,4-dichlorophenyl)-formamidine (1o)**



2,4-Dichloroaniline (4.86 g, 30 mmol, 2.0 eq.), triethylorthoformate (2.22 g, 2.5 mL, 15 mmol, 1.0 eq.) and glacial acetic acid (45.0 mg, 42.9 µL, 0.75 mmol, 0.05 eq.) were mixed and stirred for 14 h at 150 ˚C. After cooling to rt addition of *n*-pentane (10 mL) induced solidification of the crude product. The resulting solid was triturated in *n*-pentane, filtered and washed with *n*-pentane (5 mL). Subsequently the solid was recrystallized from acetone to afford the product **1o** as an off-white crystalline solid (2.72 g, 54%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (br s, 1H), 7.62-7.09 (m, 7H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 147.0 (br), 140.1 (br), 129.4, 128.8, 127.8, 125.4 (br), 120.0 (br); **IR (ATR):** ν/cm^{-1} = 3394, 3095, 2165, 1642, 1576, 1525, 1472, 1394, 1326, 1217, 1140, 1100, 1051, 961, 912, 875, 864, 834, 822, 729, 710, 688, 646, 627, 572, 555, 534; **R_f (*n*-pentane/EtOAc 1:1):** 0.82; **t_R (50_40):** 11.39 min; **MS (GC-MS):** *m/z* (%) = 332 (7), 297 (15), 173 (2), 172 (17), 161 (100), 125 (3), 110 (3), 90 (5); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{13}H_9Cl_4N_2$: 332.9514, found: 332.9532.

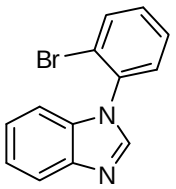
***N*,*N*'-Bis-(2,4,6-trichlorophenyl)-formamidine (1p)**



The mixture of 2,4,6-trichloroaniline (5.89 g, 30 mmol, 2.0 eq.), triethylorthoformate (2.22 g, 2.5 mL, 15 mmol, 1.0 eq.) and glacial acetic acid (45 mg, 42.9 µL, 0.75 mmol, 0.05 eq.) were stirred for 2.5 h at 150 °C. The temperature was elevated to 160 °C due to sluggish conversion. After 30 min no reaction progress was observed based on GC-MS. Three drops of sulfuric acid were added and the mixture was stirred for 2.5 h at 160 °C. The crude mixture was soluted with *n*-pentane (20 mL) after cooling to rt and the solid was formed. This solid was filtered, washed with cold *n*-pentane and subsequently recrystallized from acetone. The product **1p** was obtained as colorless needles (1.47 g, 24%). The measurement of ^{13}C NMR was not successful. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.79 (br s, 1H), 7.42 (br s, 1H), 7.38 (s, 4H); **IR (ATR):** ν/cm^{-1} = 3367, 3080, 2360, 2327, 1722, 1654, 1553, 1549, 1494, 1446, 1416, 1382, 1369, 1289, 1214, 1179, 1131, 1078, 979, 917, 855, 818, 796, 745, 709, 606, 565; **R_f (*n*-pentane/EtOAc 1:1):** 0.82; **t_R (50_20_320_8ISO):** 17.32 min; **MS (GC-MS):** *m/z* (%) = 400 (2), 365 (13), 331 (1), 206 (14), 195 (100), 194 (2), 179 (10), 159 (4), 145 (5), 125 (1), 110 (1); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{13}H_7Cl_6N_2$: 400.8735, found: 400.8739.

3. Synthesis of Characterization of 2-Unsubstituted, N-Substituted Benzimidazoles

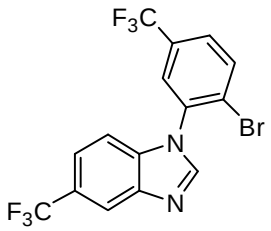
1-(2-Bromophenyl)-1*H*-benzoimidazole (2a)



Formamidine **1a** (177 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 1 h 20 min at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layers were treated with brine and dried over Na_2SO_4. The purification by column chromatography (Ø 2 cm, SiO_2: 14 cm, *n*-pentane/EtOAc 3:1) yielded the benzimidazole **2a** as a colorless oil (135 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H, NCHN), 7.89 (dd, *J* = 7.2, 1.1 Hz, 1H, Ar-H), 7.81 (dd, *J* = 8.0, 1.3 Hz, 1H, Ar-H), 7.54-7.48 (m, 1H, Ar-H), 7.45 (dd, *J* = 7.9, 1.8 Hz, 1H, Ar-H), 7.43-7.38 (m, 1H, Ar-H), 7.37-7.28 (m, 2H, 2×Ar-H), 7.21-7.17 (m, 1H, Ar-H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.2, 142.9, 135.1, 134.3, 134.2, 130.6, 129.1, 128.6, 123.7, 122.7, 121.4, 120.4, 110.5; **IR (ATR):** ν/cm^{-1} = 3061, 1731, 1614, 1587, 1493, 1454, 1306, 1288, 1260, 1230, 1203, 1158, 1142, 1056, 1030, 1007, 977, 889, 865, 786, 743, 716, 654, 634, 581, 553, 535; **R_f (*n*-pentane/EtOAc 1:1):** 0.29; **t_R (50_40):** 9.46 min; **MS (GC-MS):** *m/z* (%) = 272 (100), 193 (86), 155 (5), 77 (5), 76 (18); **EM (ESI):** *m/z* [M + H$^+$] calc. for $C_{13}H_{10}BrN_2$: 273.0022, found: 273.0028; **Elemental analysis:** calcd. (%) for $C_{13}H_9BrN_2$ (273.13): C 57.17, H 3.32, N 10.26, found: C 57.27, H 3.26, N 10.04.

1-(2-Bromo-5-trifluoromethylphenyl)-5-trifluoromethyl-1*H*-benzoimidazole (2b)

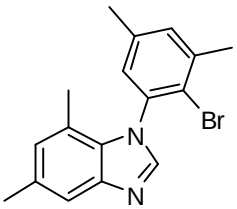


Formamidine **1b** (245 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 1 h 15 min at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layers were

treated over brine and dried with Na_2SO_4. The crude mixture was purified by column chromatography (Ø 2 cm, SiO_2: 18 cm, *n*-pentane/EtOAc 5:1) to afford the benzimidazole **2b** as a white crystalline solid (188 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H, Ar-H), 8.17 (s, 1H, NCHN), 8.01 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.75-7.70 (m, 2H, 2×Ar-H), 7.59 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.28 (d, *J* = 8.4 Hz, 1H, Ar-H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.4 (br), 143.0 (br), 135.4, 135.2, 131.7 (q, *J* = 34 Hz), 127.8 (q, *J* = 3.5 Hz), 126.0 (q, *J* = 3.6 Hz), 125.9 (q, *J* = 33 Hz), 125.7, 124.5 (q, *J* = 273 Hz), 122.9 (q, *J* = 273 Hz), 121.1 (q, *J* = 3.6 Hz), 118.6 (q, *J* = 4.1 Hz), 110.9; **^{19}F NMR (282 MHz, $CDCl_3$):** δ −60.84, −62.79; **R_f (*n*-pentane/EtOAc 1:1):** 0.68; **IR (ATR):** ν/cm^{-1} = 3134, 3098, 3032, 2961, 1628, 1611, 1499, 1488, 1444, 1425, 1355, 1317, 1302, 1256, 1224, 1187, 1158, 1138, 1107, 1081, 1048, 997, 976, 959, 916, 895, 934, 825, 805, 758, 729, 715, 671, 652; **t_R (50_40):** 8.96 min; **MS (GC-MS):** *m*/*z* (%) = 408 (100), 389 (13), 329 (45), 261 (8), 145 (5), 69 (8); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{15}H_8BrF_6N_2$: 408.9770, found: 408.9769; **Elemental analysis:** calcd. (%) for $C_{15}H_7BrF_6N_2$ (409.12): C 44.04, H 1.72, N 6.85, found: C 43.99, H 1.74, N 6.69.

1-(2-Bromo-3,5-dimethylphenyl)-5,7-dimethyl-1*H*-benzoimidazole (2c)



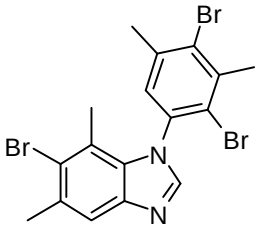
Formamidine **1c** (205 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 23 h 15 min at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL), the combined organic layers were treated with brine and dried over Na_2SO_4. The crude mixture was purified by column chromatography (Ø 2 cm, SiO_2: 15 cm, *n*-pentane/EtOAc 3:1) to yield the benzimidazole **2c** as a white solid (147 mg, 89%).

A scale-up reaction: Formamidine **1c** (811 mg, 1.98 mmol, 1 eq.) was dissolved in 7.9 mL DMSO. CuI (75.3 mg, 0.40 mmol, 20 mol%) and DBU (0.59 mL, 602 mg, 3.95 mmol, 2 eq.) were added and the reaction was stirred for 25 h 30 min at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL), the combined organic layers were treated

with brine and dried over Na_2SO_4. The crude mixture was purified by column chromatography (Ø 3 cm, SiO_2: 13 cm, *n*-pentane/EtOAc 3:1) to afford the benzimidazole **2c** (602 mg, 93%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (s, 1H, NCHN), 7.50 (br s, 1H, Ar-H), 7.24-7.20 (m, 1H, Ar-H), 7.13-7.09 (m, 1H, Ar-H), 6.85 (br s, 1H, Ar-H), 2.48 (s, 3H, Ar-CH_3), 2.45 (s, 3H, Ar-CH_3), 2.35 (s, 3H, Ar-CH_3), 1.96 (s, 3H, Ar-CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 143.8, 143.3, 139.3, 137.4, 136.8, 132.5, 132.1, 131.1, 128.2, 126.9, 122.7, 121.3, 117.9, 23.5, 21.3, 20.7, 17.3; **IR (ATR):** ν/cm^{-1} = 3081, 2956, 2916, 2858, 1597, 1575, 1493, 1460, 1441, 1385, 1345, 1308, 1270, 1247, 1229, 1209, 1163, 1135, 1082, 1063, 1036, 951, 892, 865, 841, 798, 760, 721, 645, 617, 605, 592, 569, 542, 530, 523, 513, 505, 499, 483; **R_f (*n*-pentane/EtOAc 1:1):** 0.29; **t_R (50_40):** 10.62 min; **MS (GC-MS):** *m*/*z* (%) = 328 (100), 315 (11), 313 (12), 249 (85), 207 (4), 117 (23), 117 (23), 91 (8), 77 (17); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{17}H_{18}BrN_2$: 329.0648, found: 329.0643; **Elemental analysis:** calcd. (%) for $C_{17}H_{17}BrN_2$ (329.23): C 62.02, H 5.20, N 8.51, found: C 62.05, H 5.04, N 8.31.

6-Bromo-1-(2,4-dibromo-3,5-dimethylphenyl)-5,7-dimethyl-1*H*-benzoimidazole (2d)

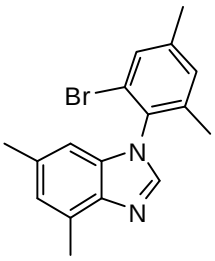


Formamidine **1d** (284 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 24 h 10 min at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layers were treated with brine and dried over Na_2SO_4. The purification by column chromatography (Ø 2 cm, SiO_2: 15 cm, *n*-pentane/EtOAc 3:1) yielded the benzimidazole **2d** as an off-white solid (242 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (br s, 1H, NCHN), 7.62 (s, 1H, Ar-H), 7.23 (s, 1H, Ar-H), 2.74 (s, 3H, Ar-CH_3), 2.54 (s, 3H, Ar-CH_3), 2.46 (s, 3H, Ar-CH_3), 2.10 (s, 3H, Ar-CH_3); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.6, 138.7, 135.7, 132.8, 129.3, 128.6, 123.9, 123.5, 121.8, 119.2, 25.4, 24.8, 24.1, 17.8; **IR (ATR):** ν/cm^{-1} = 3016, 2952, 2921, 2859, 2736, 1736, 1690, 1582, 1494, 1465, 1437, 1412, 1398, 1380, 1326, 1304, 1246, 1226,

1192, 1156, 1066, 1049, 997, 978, 913, 855, 815, 753, 724, 695, 645, 626, 577; **R_f (*n*-pentane/EtOAc 1:1):** 0.38; **t_R (50_20_320):** 18.31 min; **MS (GC-MS):** *m*/*z* (%) = 484 (35), 405 (24), 328 (12), 313 (21), 247 (21), 208 (5), 115 (5), 77 (6); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_{17}H_{16}Br_3N_2$: 484.8858, found: 484.8891; **Elemental analysis:** calcd. (%) for $C_{17}H_{15}Br_3N_2$ (487.03): C 41.92, H 3.10, N 5.75, found: C 42.25, H 2.95, N 5.61.

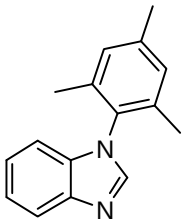
1-(2-Bromo-4,6-dimethylphenyl)-4,6-dimethyl-1*H*-benzoimidazole (2e)



Formamidine **1e** (205 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 1 h 10 min at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layers were treated with brine and dried over Na_2SO_4. The crude mixture was purified by column chromatography (Ø 2 cm, SiO_2: 15 cm, *n*-pentane/EtOAc 3:1) to afford the benzimidazole **2e** as an offwhite solid (160 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H, NCHN), 7.43 (s, 1H, Ar-H), 7.14 (s, 1H, Ar-H), 6.96 (s, 1H, Ar-H), 6.64 (s, 1H, Ar-H), 2.70 (s, 3H, Ar-CH_3), 2.40 (s, 3H, Ar-CH_3), 2.39 (s, 3H, Ar-CH_3), 1.99 (s, 3H, Ar-CH_3); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 141.5, 141.0, 140.5, 138.4, 133.6, 133.6, 131.5, 131.5, 130.8, 129.7, 124.7, 123.1, 107.4, 21.7, 20.9, 18.1, 16.5; **IR (ATR):** ν/cm^{-1} = 3109, 3017, 2955, 2922, 2855, 1739, 1699, 1610, 1561, 1497, 1455, 1378, 1337, 1301, 1275, 1245, 1207, 1149, 1130, 1037, 990, 940, 854, 833, 821, 807, 772, 677, 643; **R_f (*n*-pentane/EtOAc 1:1):** 0.46; **t_R (50_40):** 10.19 min; **MS (GC-MS):** *m*/*z* (%) = 328 (100), 313 (24), 299 (1), 249 (15), 235 (2), 221 (2), 145 (1), 130 (1), 116 (4), 91 (3), 79 (1), 77 (5); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_{17}H_{17}BrN_2$: 329.0648, found: 329.0649; **Elemental analysis:** calcd. (%) for $C_{17}H_{18}BrN_2$ (329.23): C 62.02, H 5.20, N 8.51, found: C 62.16, H 5.11, N 8.41.

1-(2,4,6-Trimethylphenyl)-1*H*-benzoimidazole (2f)[3]



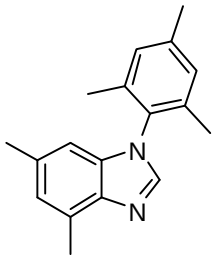
Formamidine **1f** (159 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 4 h 20 min at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layers were treated with brine and dried over Na_2SO_4. The crude mixture was purified by column chromatography (Ø 2 cm, SiO_2: 13 cm, *n*-pentane/EtOAc 3:1) to yield the benzimidazole **2f** as a yellow oil (100 mg, 85%).

A scale-up reaction: Formamidine **1f** (890 mg, 2.81 mmol, 1 eq.) was dissolved in 11.0 mL DMSO. CuI (107 mg, 0.52 mmol, 20 mol%) and DBU (0.84 mL, 854 mg, 5.61 mmol, 2 eq.) were added and the reaction was stirred for 2 h 20 min at 110 °C. H_2O (100 mL) and EtOAc (100 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 100 mL) and the combined organic layers were treated with brine and dried with Na_2SO_4. The crude mixture was purified by column chromatography (Ø 3 cm, SiO_2: 15 cm, *n*-pentane/EtOAc 3:1) to yield the benzimidazole **2f** as a yellow oil (644 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.0 Hz, 1H, Ar-H), 7.87 (s, 1H, NCHN), 7.35-7.29 (m, 1H, Ar-H), 7.29-7.23 (m, 1H, Ar-H), 7.04 (s, 2H, 2×Ar-H), 7.02 (d, J = 8.1 Hz, 1H, Ar-H), 2.39 (s, 3H, Ar-CH_3), 1.92 (s, 6H, 2×Ar-CH_3); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.3, 143.0, 139.2, 136.3, 134.1, 131.0, 129.3, 123.4, 122.3, 120.4, 110.2, 21.1, 17.4; **IR (ATR):** ν/cm^{-1} = 3079, 3062, 3051, 3032, 3020, 2970, 2951, 2920, 2859, 1614, 1591, 1492, 1455, 1379, 1341, 1305, 1281, 1226, 1207, 1173, 1137, 1105, 1035, 1006, 980, 941, 886, 854, 785, 766, 743, 645; **R_f (*n*-pentane/EtOAc 1:1):** 0.34; **t_R (50_40):** 9.14 min; **MS (GC-MS):** *m/z* (%) = 236 (96), 221 (7), 207 (3), 193 (6), 119 (2), 117 (3), 91 (8), 77 (8); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{16}H_{17}N_2$: 237.1386, found: 237.1381.

[3] Chan, A.; Scheidt, K. A. *J. Am. Chem. Soc.* **2007**, *129*, 5334.

4,6-Dimethyl-1-(2,4,6-trimethylphenyl)-1*H*-benzoimidazole (2g)

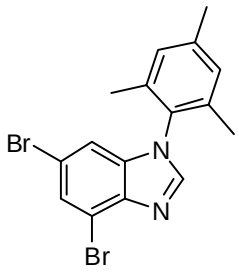


Formamidine **1g** (173 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 1 h 30 min at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layers were treated with brine and dried over Na_2SO_4. The crude mixture was purified by column chromatography (Ø 2 cm, SiO_2: 16 cm, *n*-pentane/EtOAc 3:1) to afford the benzimidazole **2g** as a yellowish solid (131 mg, 99%).

A scale-up reaction: Formamidine **1g** (716 mg, 2.07 mmol, 1 eq.) was dissolved in 8.3 mL DMSO. CuI (79.0 mg, 0.41 mmol, 20 mol%) and DBU (0.62 mL, 631 mg, 4.15 mmol, 2 eq.) were added and the reaction was stirred for 1 h 45 min at 110 °C. H_2O (80 mL) and EtOAc (80 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layers were treated with brine and dried over Na_2SO_4. The crude mixture was purified by column chromatography (Ø 3 cm, SiO_2: 15 cm, *n*-pentane/EtOAc 3:1) yielded the benzimidazole **2g** as an off-white solid (558 mg, quant.).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H, NCHN), 7.04 (s, 2H, 2×Ar-H), 6.95 (s, 1H, Ar-H), 6.64 (s, 1H, Ar-H), 2.71 (s, 3H, Ar-CH_3), 2.38 (s, 6H, 2×Ar-CH_3), 1.93 (s, 6H, 2×Ar-CH_3); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 141.6, 140.7, 139.0, 136.3, 134.0, 133.4, 131.3, 129.6, 129.2, 124.4, 107.4, 21.6, 21.1, 17.4, 16.5; **IR (ATR):** ν/cm^{-1} = 3105, 3018, 2954, 2920, 2858, 1718, 1614, 1594, 1496, 1457, 1381, 1339, 1299, 1267, 1248, 1206, 1132, 1035, 981, 933, 855, 835, 813, 769, 742, 677, 650; **R_f (*n*-pentane/EtOAc 1:1):** 0.35; **t_R (50_40):** 9.46 min; **MS (GC-MS):** *m*/*z* (%) = 264 (100), 249 (41), 235 (2), 221 (3), 207 (2), 193 (1), 145 (2), 119 (2), 105 (1), 91 (7), 77 (6); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_{18}H_{21}N_2$: 265.1699, found: 265.1697.

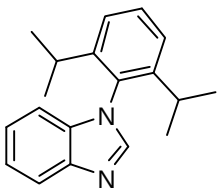
4,6-Dibromo-1-(2,4,6-trimethylphenyl)-1*H*-benzoimidazole (2h)



Formamidine **1h** (238 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 1 h 15 min at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layers were treated with brine and dried over Na_2SO_4. The purification by column chromatography (Ø 2 cm, SiO_2: 21 cm, *n*-pentane/EtOAc 3:1) yielded the benzimidazole **2h** as a white solid (193 mg, 98%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (s, 1H, NCHN), 7.63 (d, *J* = 1.6 Hz, 1H, Ar-H), 7.12 (d, *J* = 1.6 Hz, 1H, Ar-H), 7.04 (s, 2H, 2×Ar-H), 2.37 (s, 3H, Ar-CH_3), 1.90 (s, 6H, 2×Ar-CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 144.0, 141.2, 140.0, 135.9, 135.3, 130.1, 129.5, 128.2, 116.8, 114.6, 112.6, 21.1, 17.4; **IR (ATR):** ν/cm^{-1} = 3076, 2976, 2952, 2920, 2860, 1735, 1604, 1561, 1489, 1447, 1412, 1379, 1342, 1326, 1281, 1250, 1186, 1136, 1066, 1037, 913, 838, 759, 742, 722, 650, 596; **R_f (*n*-pentane/EtOAc 1:1):** 0.62; **t_R (50_40):** 11.18 min; **MS (GC-MS):** *m*/*z* (%) = 392 (52), 379 (2), 377 (2), 364 (2), 313 (22), 299 (6), 286 (2), 285 (2), 235 (5), 207 (9), 119 (3), 117 (14), 91 (16), 79 (3), 77 (13); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{16}H_{15}Br_2N_2$: 392.9597, found: 392.9595; **Elemental analysis:** calcd. (%) for $C_{16}H_{14}Br_2N_2$ (394.10): C 48.76, H 3.58, N 7.11, found: C 48.83, H 3.37, N 6.87.

1-(2,6-Diisopropylphenyl)-1*H*-benzoimidazole (2i)

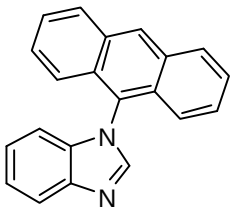


Formamidine **1i** (180 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 5 h 15 min at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layers were treated with brine and dried over Na_2SO_4. The purification by column chromatography (Ø 2 cm, SiO_2: 16 cm, *n*-pentane/EtOAc 3:1) yielded the benzimidazole **2i** as a white crystalline solid (127 mg, 91%).

An scale-up reaction: Formamidine **1i** (1.65 g, 4.58 mmol, 1 eq.) was dissolved in 18.5 mL DMSO. CuI (174 mg, 0.92 mmol, 20 mol%) and DBU (1.37 mL, 1.39 g, 9.16 mmol, 2 eq.) were added and the reaction was stirred for 3 h 20 min at 110 °C. H_2O (160 mL) and EtOAc (160 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL), the combined organic layers were treated with brine and dried over Na_2SO_4. The crude mixture was purified by column chromatography (Ø 3 cm, SiO_2: 19 cm, *n*-pentane/EtOAc 3:1) to afford the benzimidazole **2i** (1.22 g, 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.84 (m, 2H, NCHN, Ar-H), 7.51 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.36-7.30 (m, 1H, Ar-H), 7.33 (d, *J* = 7.8 Hz, 2H, 2×Ar-H), 7.29-7.23 (m, 1H, Ar-H), 7.04 (d, *J* = 7.8 Hz, 1H, Ar-H), 2.27 (sept, *J* = 6.9 Hz, 2H, 2×C*H*$(CH_3)_2$), 1.10 (d, *J* = 6.9 Hz, 6H,CH(C*H*$_3$)CH_3), 1.02 (d, *J* = 6.9 Hz, 6H, CH(CH_3)C*H*$_3$); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 147.5, 130.6, 130.2, 124.1, 123.6, 122.4, 120.3, 110.4, 28.2, 24.7, 23.9; **IR (ATR):** ν/cm^{-1} = 3080, 2964, 2927, 2869, 1788, 1616, 1592, 1485, 1461, 1443, 1383, 1363, 1308, 1287, 1248, 1222, 1182, 1158, 1142, 1058, 1008, 977, 938, 890, 848, 809, 789, 765, 758, 743, 649; **R_f (EtOAc/*n*-pentane 1:1):** 0.56; **t_R (50_40):** 9.30 min; **MS (GC-MS):** *m/z* (%) = 278 (100), 263 (58), 248 (9), 235 (10), 221 (8), 206 (7), 193 (4), 117 (5), 91 (6), 77 (7), 43 (3); **EM (ESI):** *m/z* [M + H$^+$] calcd. for $C_{19}H_{23}N_2$: 279.1856, found: 279.1848; **Elemental analysis:** calcd. (%) for $C_{19}H_{22}N_2$ (278.39): C 81.97, H 7.97, N 10.06, found: C 81.86, H 7.81, N 9.88.

1-Anthracen-9-yl-1*H*-benzoimidazol (2j)

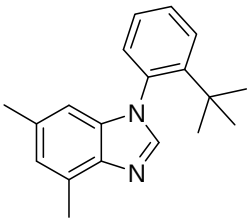


Formamidine **1j** (188 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 2 h at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL), the combined organic layers were treated with brine and dried over Na_2SO_4. The crude mixture was purified by column chromatography (Ø 2 cm, SiO_2: 14 cm, *n*-pentane/EtOAc 3:1) to afford the benzimidazole **2j** as a yellow-green solid (136 mg, 92%).

A scale-up reaction: Formamidine **1j** (477 mg, 1.27 mmol, 1 eq.) was dissolved in 5.0 mL DMSO. CuI (48.4 mg, 0.25 mmol, 20 mol%) and DBU (0.38 mL, 387 g, 2.54 mmol, 2 eq.) were added and the reaction was stirred for 24 h at 110 °C. H_2O (40 mL) and EtOAc (40 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL), the combined organic layers were treated with brine and dried over Na_2SO_4. The purification by column chromatography (Ø 3 cm, SiO_2: 16 cm, *n*-pentane/EtOAc 3:1) yielded the benzimidazole **2j** (323 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H, Ar-H), 8.17 (s, 1H, NCHN), 8.14 (d, *J* = 8.6 Hz, 2H, 2×Ar-H), 8.05 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.56-7.51 (m, 2H, 2×Ar-H), 7.44-7.37 (m, 3H, 3×Ar-H), 7.36-7.32 (m, 2H, 2×Ar-H), 7.23-7.18 (m, 1H, Ar-H), 6.86 (d, *J* = 8.1 Hz, 1H, Ar-H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.8, 143.2, 136.3, 131.5, 129.1, 128.9, 128.6, 127.7, 126.8, 125.9, 123.8, 122.7, 122.4, 120.5, 110.8; **IR (ATR):** ν/cm^{-1} = 3081, 3055, 3030, 1625, 1612, 1487, 1453, 1443, 1416, 1385, 1306, 1279, 1218, 1196, 1144, 1089, 1011, 961, 918, 887, 852, 791, 775, 764, 743, 731; **R_f (EtOAc/*n*-pentane 1:1):** 0.29; **t_R (50_40):** 12.78 min; **MS (GC-MS):** *m*/*z* (%) = 294 (100), 267 (7), 177 (3); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_{21}H_{15}N_2$: 295.1230, found: 295.1226; **Elemental analysis:** calcd. (%) for $C_{21}H_{14}N_2$ (294.35): C 85.69, H 4.79, N 9.52, found: C 85.59, H 4.67, N 9.65.

1-(2-*tert*-Butylphenyl)-4,6-dimethyl-1*H*-benzoimidazol (2k)

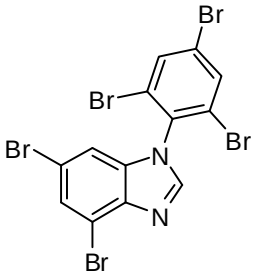


Formamidine **1k** (180 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 96 h 30 min at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL), the combined organic layers were treated with brine and dried over Na_2SO_4. The purification by column chromatography (Ø 2 cm, SiO_2: 22 cm, *n*-pentane/EtOAc 3:1) afforded the benzimidazole **2k** as a yellowish solid (118 mg, 85%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (s, 1H, NCHN), 7.67 (dd, *J* = 8.2, 1.4 Hz, 1H, Ar-H), 7.52-7.44 (m, 1H, Ar-H), 7.30 (dt, *J* = 7.4, 1.4 Hz, 1H, Ar-H), 7.02 (dd, *J* = 7.7,

1.4 Hz, 1H, Ar-H), 6.94 (s, 1H, Ar-H), 6.66 (s, 1H, Ar-H), 2.70 (s, 3H, Ar-CH_3), 2.38 (s, 3H, Ar-CH_3), 1.16 (s, 9H, $C(CH_3)_3$); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 148.3, 143.4, 140.3, 136.9, 134.3, 133.4, 131.3, 129.6, 129.4, 128.5, 127.0, 124.4, 108.5, 35.8, 31.8, 21.7, 16.6; **IR (ATR):** ν/cm^{-1} = 3009, 2963, 2917, 2873, 1715, 1614, 1597, 1491, 1447, 1396, 1364, 1338, 1280, 1265, 1246, 1204, 1196, 1169, 1131, 1103, 1054, 1036, 978, 953, 875, 860, 841, 814, 766, 759, 736, 671, 650, 615; **R_f (*n*-pentane/EtOAc 1:1):** 0.51; ***t*$_R$ (50_40):** 9.62 min; **MS (GC-MS):** *m/z* (%) = 278 (100), 263 (58), 249 (6), 235 (3), 221 (4), 207 (4), 193 (3), 145 (2), 132 (2), 117 (7), 91 (6), 77 (6); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_{19}H_{23}N_2$: 279.1856, found: 279.1855.

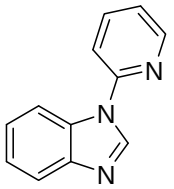
4,6-Dibrom-1-(2,4,6-tribromphenyl)-1*H*-benzoimidazol (2l)



Formamidine **1l** (200 mg, 0.30 mmol, 1 eq.) was dissolved in 1.2 mL DMSO. CuI (11.4 mg, 0.06 mmol, 20 mol%) and DBU (89.2 µL, 91 mg, 0.60 mmol, 2 eq.) were added and the reaction was stirred for 1 h 10 min at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL), the combined organic layers were treated with brine and dried over Na_2SO_4. The crude mixture was purified by column chromatography (Ø 2 cm, SiO_2: 17 cm, *n*-pentane/EtOAc 5:1) to yield the benzimidazole as a white solid (164 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 2H, 2×Ar-H), 7.92 (s, 1H, NCHN), 7.69 (d, *J* = 1.6 Hz, 1H, Ar-H), 7.16 (d, *J* = 1.6 Hz, 1H, Ar-H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.0, 141.1, 135.6, 134.1, 132.7, 129.1, 125.4, 124.6, 117.5, 114.9, 112.7; **IR (ATR):** ν/cm^{-1} = 3114, 3081, 1722, 1606, 1566, 1542, 1487, 1463, 1449, 1410, 1373, 1359, 1343, 1326, 1287, 1254, 1223, 1185, 1150, 1116, 1101, 1086, 1066, 1048, 986, 914, 877, 857, 839, 778, 756, 743, 735, 713, 640, 586; **R_f (*n*-pentane/EtOAc 1:1):** 0.70; ***t*$_R$ (50_20_320):** 18.68 min; **MS (GC-MS):** *m/z* (%) = 584 (10), 505 (2), 349 (12), 271 (3), 232 (2), 155 (7); **EM (ESI):** *m/z* [M + Na^+] calcd. for $C_{13}H_5Br_5N_2Na$: 606.6262, found: 606.6258; **Elemental analysis:** calcd. (%) for $C_{13}H_5Br_5N_2$ (588.71): C 26.52, H 0.86, N 4.76, found: C 26.80, H 1.02, N 4.64.

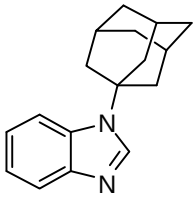
1-Pyridin-2-yl-1*H*-benzoimidazole (2m)



To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the *N*-(2-Bromophenyl)-*N*'-pyridin-2-yl-formamidine (138.1 mg, 0.5 mmol, 1.0 eq.) followed by the addition of 2 mL of DMSO. To this stirring mixture was added CuI (19.0 mg, 0.1 mmol, 0.2 eq.) and DBU (149 µL, 2.0 eq.). The reaction mixture was then stirred in a pre-heated oil bath at 110 °C for 1 h. Processing of the reaction mixture followed by flash column chromatography on silica gel (*n*-pentane/EtOAc 7:3) afforded the 1-pyridin-2-yl-1*H*-benzoimidazole as a white solid (85 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56-8.37 (m, 2H), 7.99-7.91 (m, 1H), 7.81-7.70 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.32-7.21 (m, 2H), 7.19-7.12 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.9, 149.4, 144.7, 141.4, 139.0, 132.1, 124.2, 123.3, 121.8, 120.6, 114.3, 112.7; **IR (ATR):** ν/cm^{-1} = 3081, 3022, 2974, 1587, 1498, 1473, 1451, 1437, 1371, 1336, 1301, 1279, 1242, 1204, 1172, 1156, 1145, 1097, 1054, 1011, 998, 983; **R_f (*n*-pentane/EtOAc 1:1):** 0.13. ***t*$_R$ (50_40):** 9.23 min; **MS (GC-MS):** *m/z* (%) = 195 (100), 194 (51), 169 (43), 170 (6), 84 (10), 78 (14); **EM (ESI)**: *m/z* [M + H$^+$] calcd. for $C_{12}H_9N_3H$: 196.0869, found: 196.0864.

1-Adamantan-2-yl-1*H*-benzoimidazole (2n)

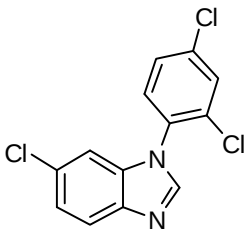


To an oven-dried screw-capped test tube equipped with a magnetic stir bar was added the *N*-adamantan-2-yl-*N*'-(2-bromophenyl)-formamidine (166.4 mg, 0.5 mmol, 1.0 eq.) followed by the addition of 2 mL of DMSO. To this stirred mixture was added CuI (19.0 mg, 0.1 mmol, 0.2 eq.) and DBU (149 µL, 2.0 eq.). The reaction mixture was then stirred in a pre-heated oil bath at 140 °C for 6 h. Processing of the reaction mixture followed by flash column chromatography on silica gel (*n*-pentane/EtOAc 1:1) afforded the 1-adamantan-2-yl-1*H*-benzimidazole as a white solid (120 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (br s, 1H, NCHN), 7.80 (m, 2H, 2×Ar-H), 7.24 (m, 2H, 2×Ar-H), 2.35 (m, 10H, adamantyl), 1.85 (d, *J* = 2.8 Hz, 5H, adamantyl); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 121.9, 121.2, 120.9, 41.9, 36.0, 29.4; **IR (ATR):** ν/cm^{-1} = 3047, 2922, 2905, 2851, 1612, 1485, 1452, 1363, 1311, 1280, 1227, 1181, 1154, 1105, 1091,

1013, 985, 888, 863, 818, 777; **R_f (*n*-pentane: EtOAc 1:1):** 0.16; **t_R (50_40):** 10.94 min; **MS (GC-MS):** *m/z* (%) = 252 (46), 136 (12), 135 (100), 107 (8), 93 (16), 91 (10), 79 (18); E**M (ESI)**: *m/z* [M + H^+] calcd. for $C_{17}H_{20}N_2H$: 253.1699, found: 253.1696.

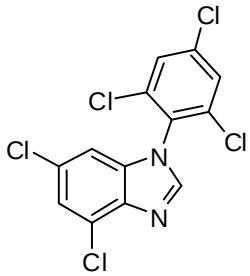
6-Chloro-1-(2,4-dichlorophenyl)-1*H*-benzoimidazole (2o)



Formamidine **1o** (167 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 190 h at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL), the combined organic layers were treated with brine and dried over Na_2SO_4. The crude mixture was purified by column chromatography (Ø 2 cm, SiO_2: 13 cm, *n*-pentane/EtOAc 3:1) to yield the benzimidazole **2o** as a slightly orange solid (79 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H, NCHN), 7.78 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.67 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.46 (dd, *J* = 8.5, 2.2 Hz, 1H, Ar-H), 7.39 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.31 (dd, *J* = 8.6, 2.0 Hz, 1H, Ar-H), 7.18 (d, *J* = 2.0 Hz, 1H, Ar-H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.4, 141.8, 136.1, 134.7, 132.3, 131.7, 131.0, 129.9, 129.4, 128.5, 123.7, 121.5, 110.5; **IR (ATR):** ν/cm^{-1} = 3090, 3018, 1779, 1615, 1584, 1564, 1489, 1459, 1386, 1335, 1303, 1279, 1227, 1198, 1175, 1142, 1110, 1071, 1056, 977, 936, 913, 893, 874, 836, 816, 805, 719, 670, 609, 595, 573, 517; **R_f (*n*-pentane/EtOAc 1:1):** 0.30; **t_R (50_40):** 10.10 min; **MS (GC-MS):** *m/z* (%) = 296 (100), 261 (18), 227 (7), 145 (4), 124 (5), 117 (6), 111 (6); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_{13}H_8Cl_3N_2$: 296.9748, found: 296.9739; **Elemental analysis:** calcd. (%) for $C_{13}H_7Cl_3N_2$ (297.57): C 52.47, H 2.37, N 9.41, found: C 52.47, H 2.33, N 9.32.

4,6-Dichlor-1-(2,4,6-trichlorphenyl)-1*H*-benzoimidazol (2p)



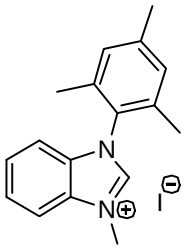
Formamidine **1p** (201 mg, 0.50 mmol, 1 eq.) was dissolved in 2 mL DMSO. CuI (19.0 mg, 0.1 mmol, 20 mol%) and DBU (149.3 µL, 152 mg, 1.0 mmol, 2 eq.) were added and the reaction was stirred for 171 h at 110 °C. H_2O (20 mL) and EtOAc (20 mL) were added

and the layers were separated. The aqueous layer was extracted with EtOAc (2 × 20 mL), the combined organic layers were treated with brine and dried over Na_2SO_4. The purification by preparative TLC (*n*-pentane/EtOAc 1:1) yielded the benzimidazole **2p** as a white solid (90 mg, 49%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (s, 1H, NCHN), 7.59 (s, 2H, 2×Ar-H), 7.39 (d, *J* = 1.8 Hz, 1H, Ar-H), 6.98 (d, *J* = 1.8 Hz, 1H, Ar-H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 143.5, 139.3, 137.2, 135.3, 134.5, 130.2, 129.4, 129.3, 126.2, 123.8, 109.2; **IR (ATR):** ν/cm^{-1} = 3123, 3079, 2924, 2853, 1733, 1685, 1610, 1574, 1555, 1495, 1470, 1457, 1390, 1374, 1347, 1328, 1289, 1268, 1252, 1201, 1179, 1166, 1146, 1092, 1071, 1046, 999, 929, 864, 853, 841, 826, 807, 766, 756, 725, 655, 638, 600, 596; **R_f (*n*-pentane/EtOAc 1:1):** 0.68; **t_R (50_40):** 11.75 min; **MS (GC-MS):** *m/z* (%) = 364 (62), 329 (11), 294 (25), 259 (8), 158 (6), 144 (5), 109 (14); **EM (ESI):** *m/z* [M + H^+] calcd. for $C_{13}H_5Cl_5N_2$: 386.8788, found: 386.8786.

4. Synthesis and Characterization of Benzimidazolium Salts

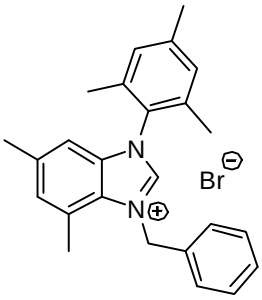
1-Methyl-3-(2,4,6-trimethylphenyl)-3*H*-benzimidazol-1-ium iodide (3f)[3]



The benzimidazole **2f** (686 mg, 2.90 mmol, 1 eq.) was treated with 11.6 mL MeI in a sealed tube at 40 °C. After complete conversion, MeI was removed in high vacuum and the solid was washed with Et_2O to furnish the salt **3f** as a white solid (1.03 g, 94%). In a scale-up reaction, Benzimidazole **2f** (4.867 g, 20 mmol, 1 eq.) was treated with 50 mL MeI in a sealed tube at 40 °C. After full conversion, MeI was removed in high vacuum and the solid was washed with Et_2O to yield the salt **3f** as a white solid (6.572 g, 87%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.81 (s, 1H, NCHN), 7.89 (d, 1H, *J* = 8.3 Hz, Ar-H), 7.76-7.69 (m, 1H, Ar-H), 7.66-7.59 (m, 1H, Ar-H), 7.28-7.23 (m, 1H, Ar-H), 7.07 (s, 2H, 2×Ar-H), 4.56 (s, 3H, NCH_3), 2.38 (s, 3H, Ar-CH_3), 2.03 (s, 6H, 2×Ar-CH_3); **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 142.1, 141.5, 135.2, 131.7, 131.1, 129.9, 128.0, 127.6, 127.5, 113.4, 112.8, 35.0, 21.0, 17.9. **EM (ESI):** *m/z* [M − I^-] calculated for $C_{17}H_{19}N_2$: 251.1543, Found: 251.1535.

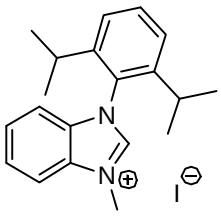
1-Benzyl-5,7-dimethyl-3-(2,4,6-trimethylphenyl)-3*H*-benzimidazol-1-iumbromide (3g)



The benzimidazole **2g** (403 mg, 1.52 mmol, 1 eq.) was dissolved in 3 mL EtOAc. Benzyl bromide (0.18 mL, 261 mg, 1.52 mmol, 1 eq.) was added, and the reaction mixture was stirred first 24 h at r.t., than at 60 °C. The solid obtained was filtered and washed with Et_2O to yield the salt **3g** as a white solid (637 mg, 96%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 11.07 (s, 1H, NCHN), 7.37-7.28 (m, 3H, 3×Ar-H), 7.14-7.09 (m, 3H, 3×Ar-H), 7.07 (s, 2H, 2×Ar-H_{Mes}), 6.80 (s, 1H, Ar-H), 6.43 (s, 2H, NCH_2Ph), 2.53 (s, 3H, Ar-CH_3), 2.39 (s, 3H, Ar-CH_3), 2.38 (s, 3H, Ar-CH_3), 2.05 (s, 6H, 2×Ar-CH_3); **^{13}C-NMR (75 MHz, DMSO-d6):** δ 143.9, 140.8, 138.5, 135.2, 135.2, 132.4, 131.0, 129.7, 129.2, 128.4, 128.1, 127.7, 126.1, 125.2, 110.2, 51.7, 20.7, 20.7, 17.6, 16.9; **IR (ATR):** ν/cm^{-1} = 3108, 3030, 3006, 2967, 2954, 2914, 2857, 2773, 1882, 1608, 1557, 1499, 1486, 1467, 1456, 1389, 1369, 1353, 1319, 1236, 1200, 1158, 1139, 1084, 1052, 1029, 976, 946, 921, 837, 764, 752, 719, 696, 666, 644; **EM (ESI):** *m/z* [M − Br^-] calcd. for $C_{25}H_{27}N_2$: 355.2169, found: 355.2173.

3-(2,6-Diisopropylphenyl)-1-methyl-3*H*-benzimidazol-1-ium iodide (3i)

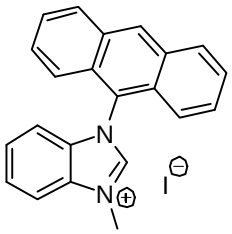


The benzimidazole **2i** (1.29 g, 4.65 mmol, 1 eq.) was treated with 18.6 mL MeI in a sealed tube at 40 °C. After complete conversion, MeI was removed in high vacuum and the solid was washed with Et_2O to yield the salt **3i** as an off-white solid (1.92 g, 98%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.83 (s, 1H, NCHN), 8.01 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.79-7.71 (m, 1H, Ar-H), 7.66-7.55 (m, 2H, 2×Ar-H), 7.35 (d, *J* = 7.9 Hz, 2H, 2×Ar-H), 7.20 (d, *J* = 8.4 Hz, 1H, Ar-H), 4.62 (s, 3H, NCH_3), 2.14 (sept, *J* = 6.8 Hz, 2H, C*H*(CH_3)CH_3), 1.20 (d, *J* = 6.8 Hz, 6H, 2×CH(C*H*$_3$)CH_3), 0.96 (d, *J* = 6.8 Hz, 6H, 2×CH(CH_3)C*H*$_3$); **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 146.3, 141.9, 132.7, 132.2, 131.6, 128.2, 127.9, 126.9, 125.0, 113.7, 112.9, 35.1, 28.6, 24.7, 23.9; **IR (ATR):** ν/cm^{-1} = 3116, 2965, 2935, 2872, 2361, 2343, 1613, 1560, 1478, 1459, 1451, 1382, 1360, 1321, 1279, 1251, 1217, 1180, 1148, 1129, 1104, 1059, 1043, 1005, 941, 899, 816, 787, 757, 641, 617, 598,3 575, 564, 529, 519, 508, 497, 491; **EM (ESI):** *m/z* [M − I^-] calculated

$C_{20}H_{25}N_2$: 293.2012, found: 293.2014; **Elemental Analysis:** calcd. (%) for $C_{20}H_{25}IN_2$ (420.33): C 57.15, H 5.99, N 6.66, found: C 57.13, H 5.90, N 6.64.

3-Anthracen-9-yl-1-methyl-3*H*-benzimidazol-1-ium iodide (3j)

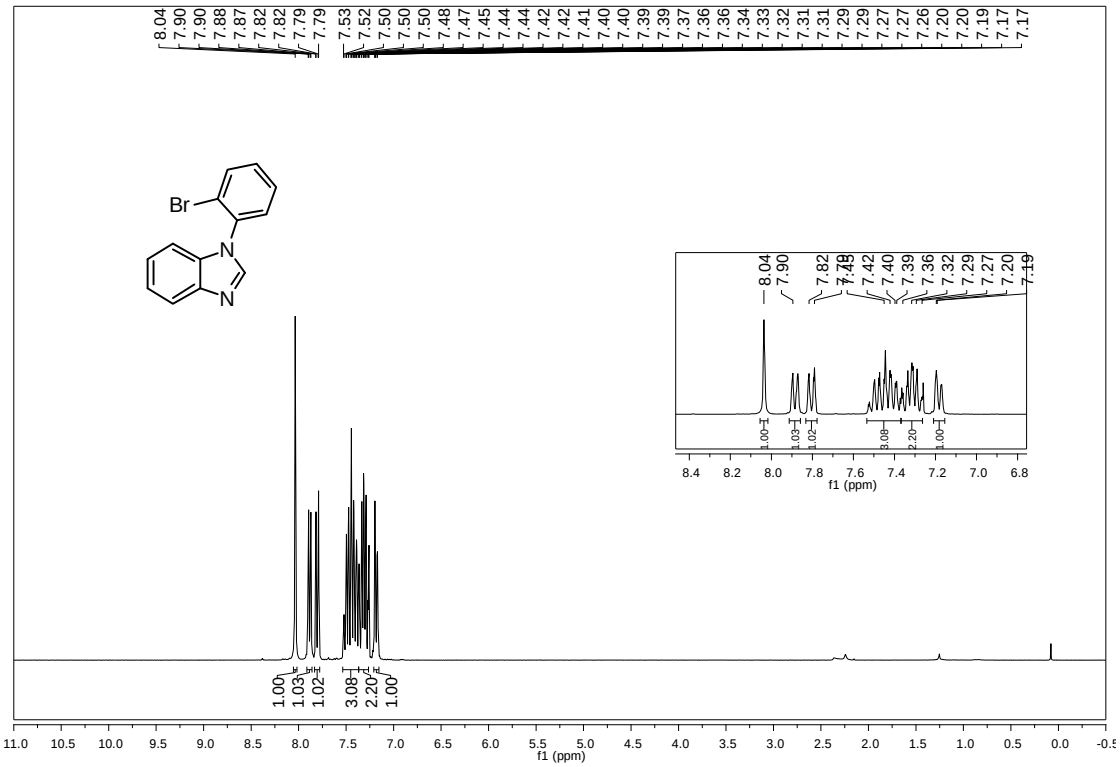


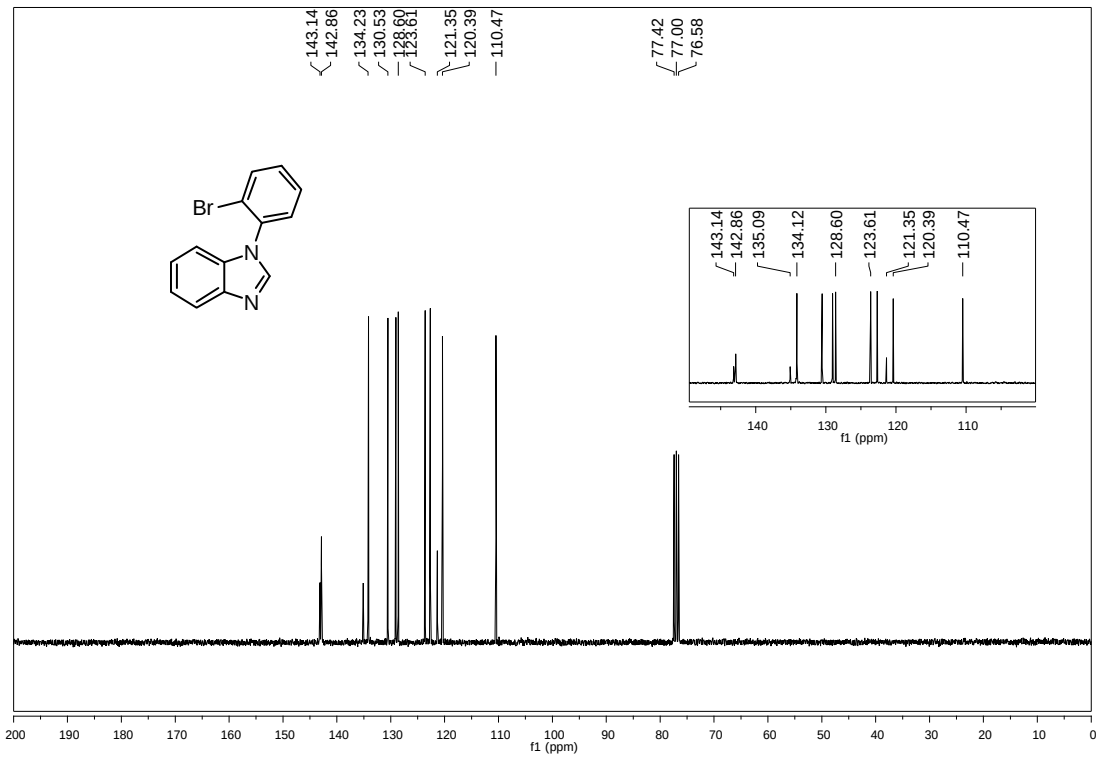
The benzimidazole **2j** (348 mg, 1.18 mmol, 1 eq.) was treated with 4.73 mL MeI in a sealed tube at 40 °C. After complete conversion, MeI was removed in high vacuum and the solid was washed with Et_2O to yield the salt **3j** as a yellow solid (520 mg, 100%).

^{1}H-NMR (400 MHz, DMSO-d6): δ 10.32 (s, 1H, NCHN), 9.16 (s, 1H, Ar-H), 8.39 (d, *J* = 8.5 Hz, 2H, 2×Ar-H), 8.34 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.85-7.80 (m, 1H, Ar-H), 7.73-7.67 (m, 2H, 2×Ar-H), 7.66-7.60 (m, 2H, 2×Ar-H), 7.59-7.52 (m, 3H, 3×Ar-H), 7.11 (d, *J* = 8.4 Hz, 1H, Ar-H), 4.32 (s, 3H, CH_3); **^{13}C-NMR (100 MHz, DMSO-d6):** δ 146.0, 133.9, 133.2, 132.2, 131.9, 130.0, 129.9, 128.9, 128.6, 128.1, 127.4, 123.8, 122.5, 115.4, 114.0, 35.2; **IR (ATR):** ν/cm^{-1} = 3122, 3059, 2984, 2959, 2760, 1626, 1613, 1560, 1487, 1457, 1446, 1420, 1363, 1307, 1254, 1202, 1172, 1132, 1018, 1006, 912, 856, 821, 786, 774, 765, 752, 731, 662, 643, 602, 578; **EM (ESI):** *m/z* [M − I¯] calcd. for $C_{22}H_{17}N_2$: 309.1386, found: 309.1376.

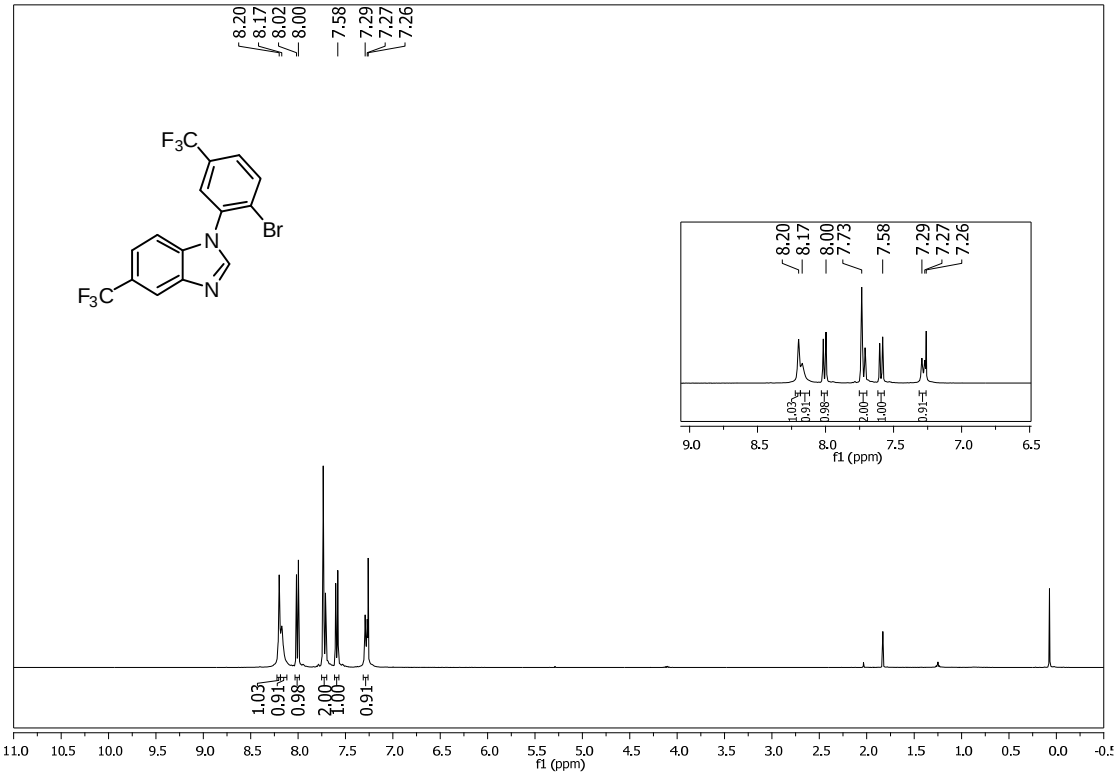
5. ^{1}H and ^{13}C NMR Spectra of Compounds

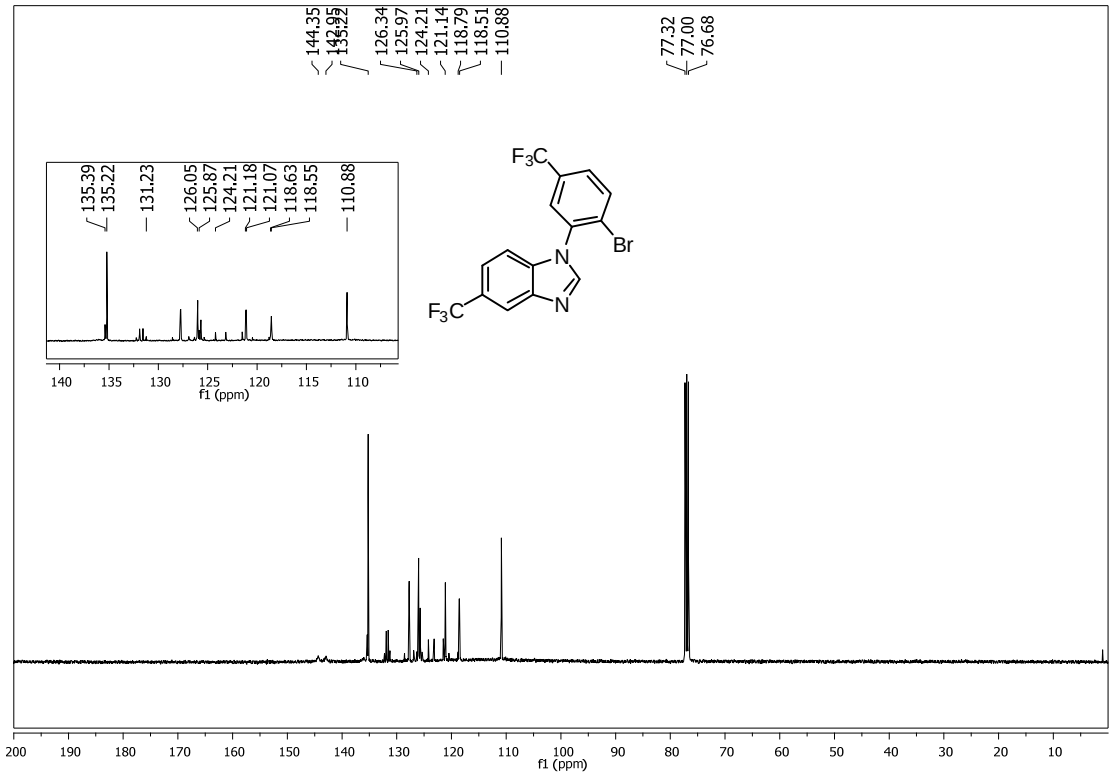
1-(2-Bromophenyl)-1*H*-benzoimidazole (2a)



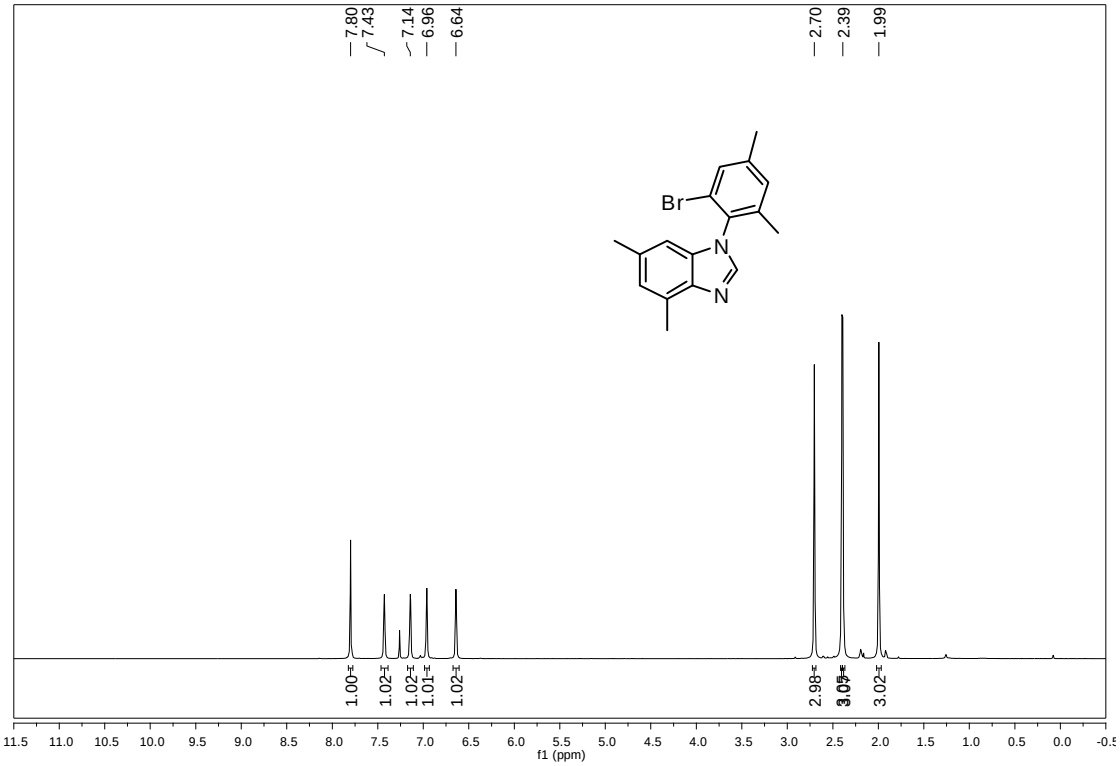


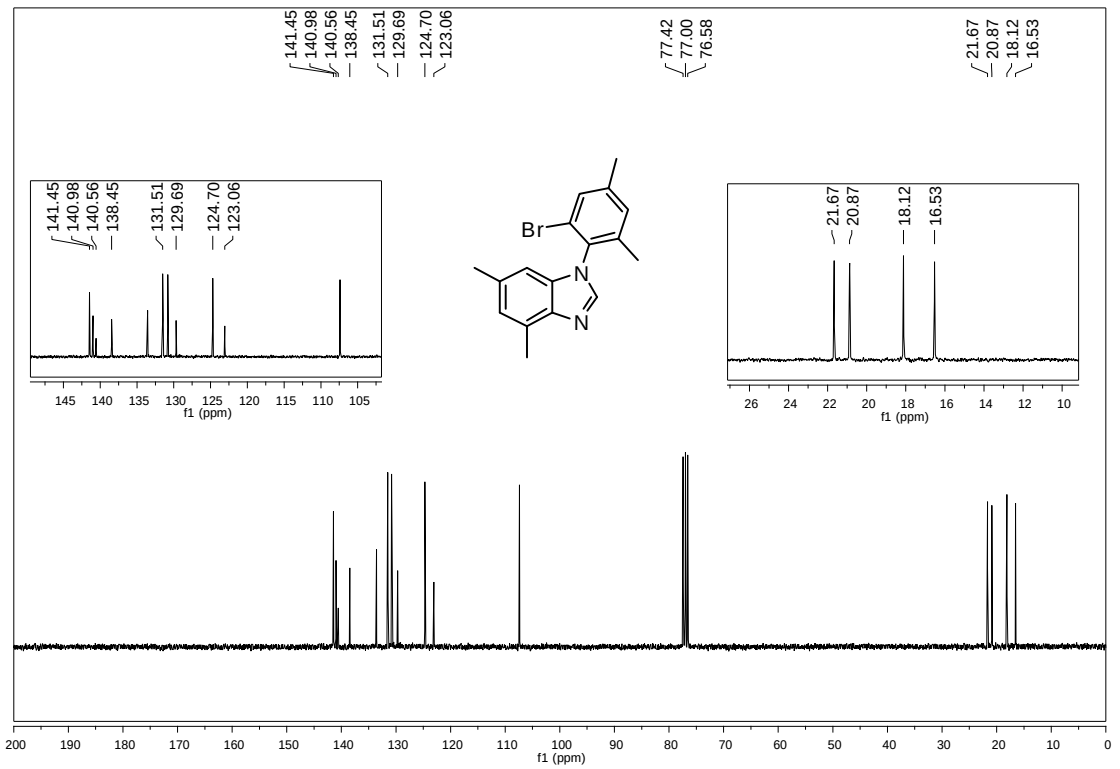
1-(2-Bromo-5-trifluoromethylphenyl)-5-trifluoromethyl-1*H*-benzoimidazole (2b)



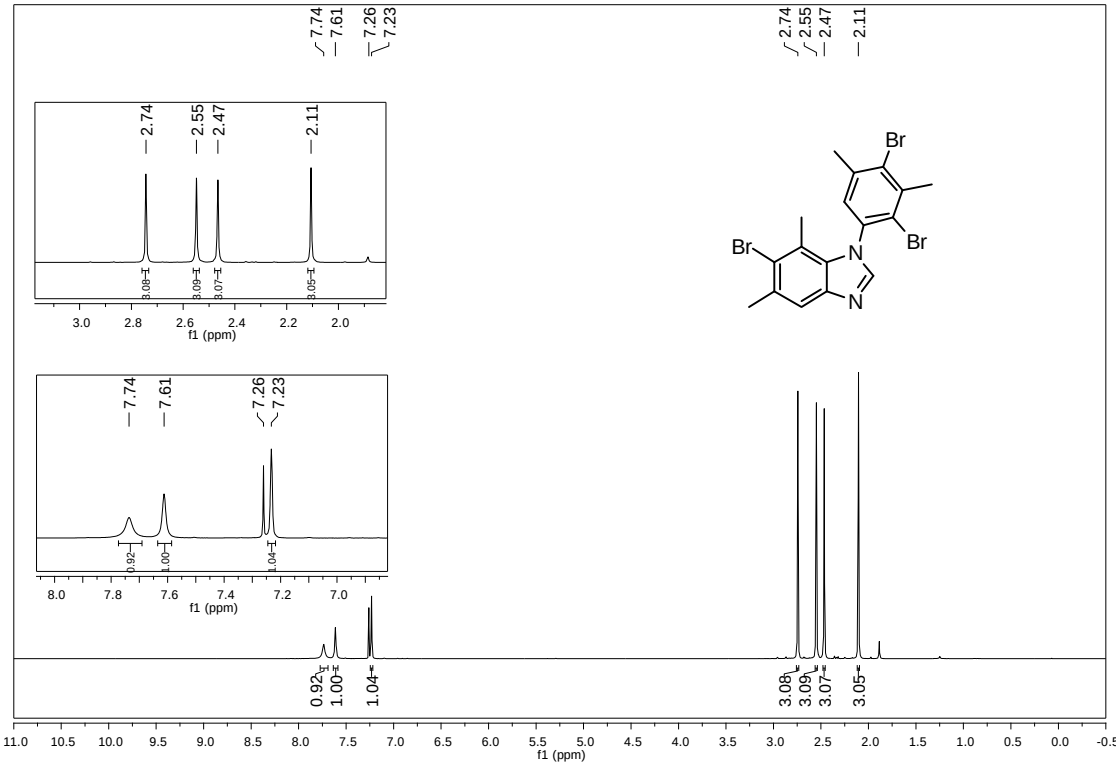


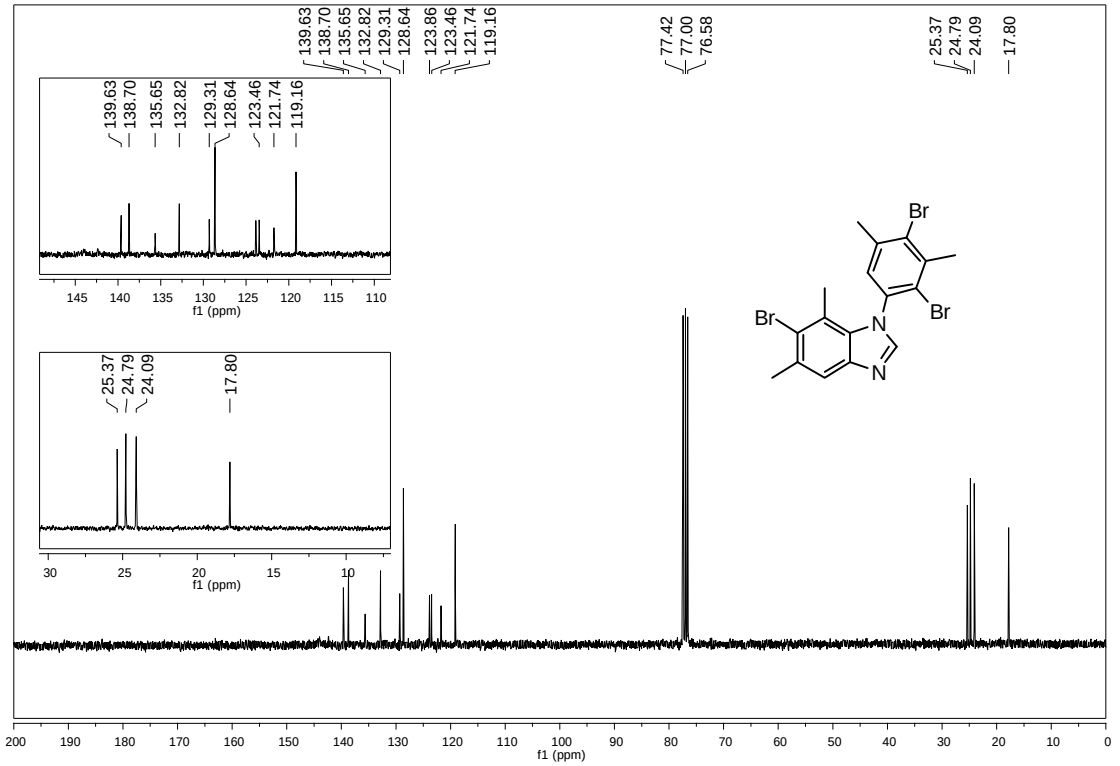
1-(2-Bromo-3,5-dimethylphenyl)-5,7-dimethyl-1*H*-benzoimidazole (2c)



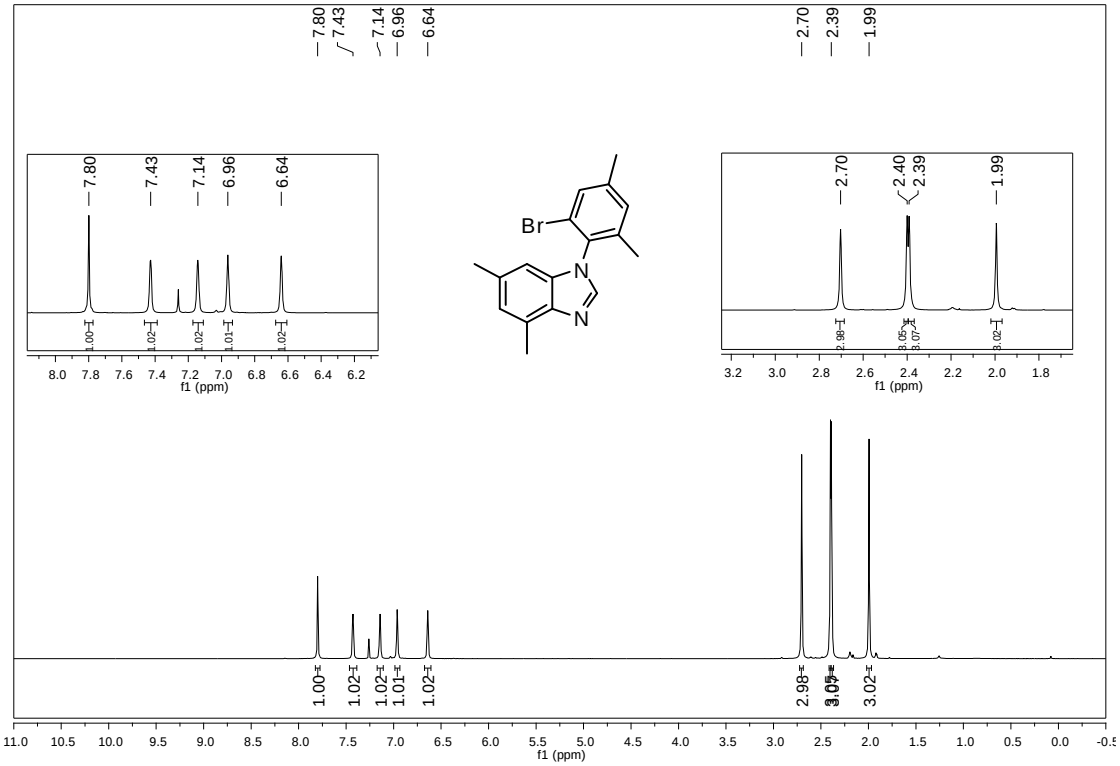


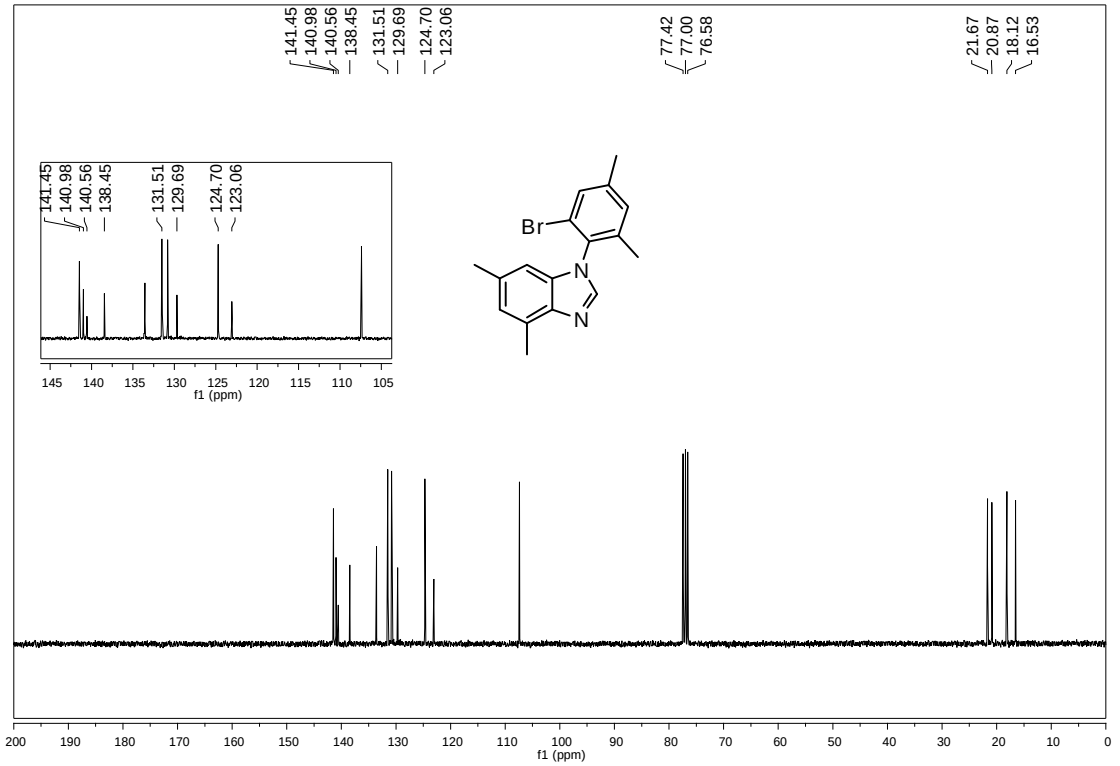
6-Bromo-1-(2,4-dibromo-3,5-dimethylphenyl)-5,7-dimethyl-1*H*-benzoimidazole (2d)



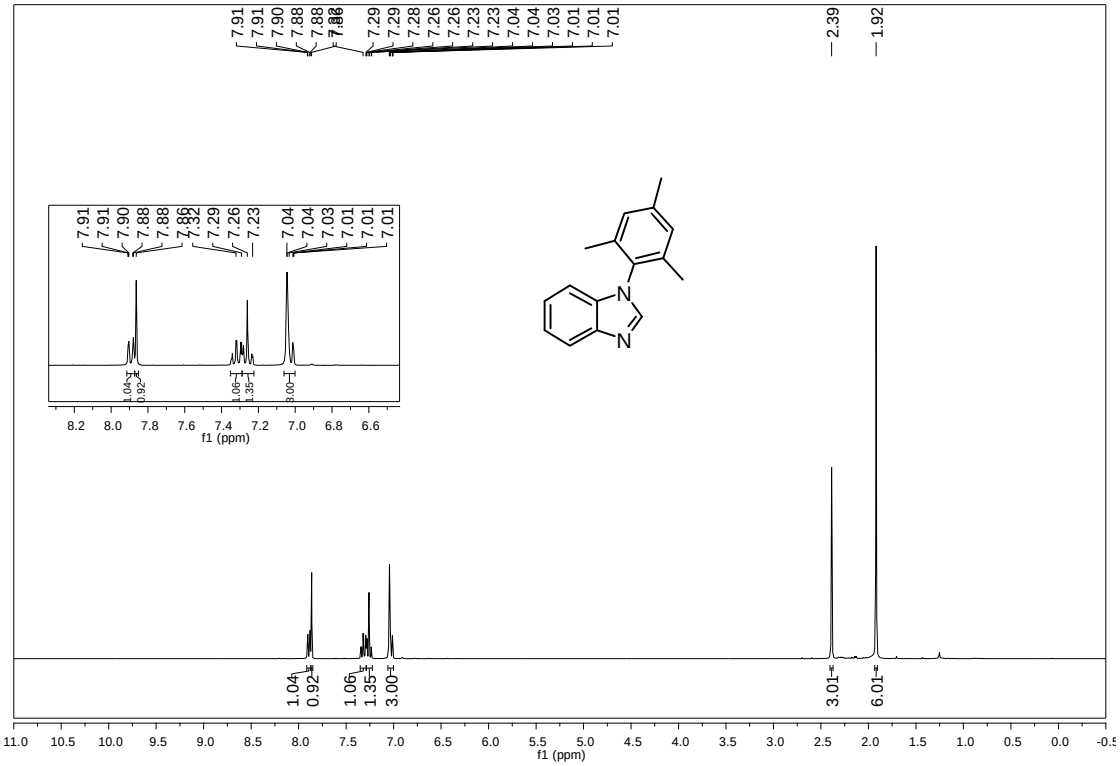


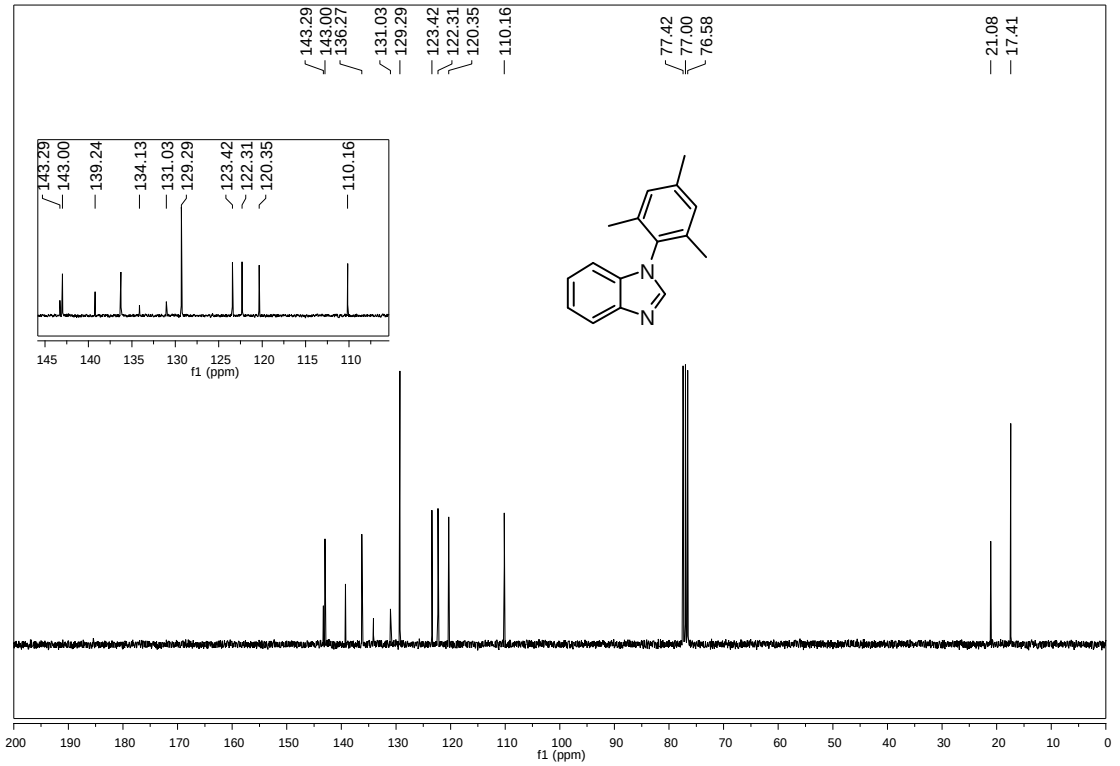
1-(2-Bromo-4,6-dimethylphenyl)-4,6-dimethyl-1*H*-benzoimidazole (2e)



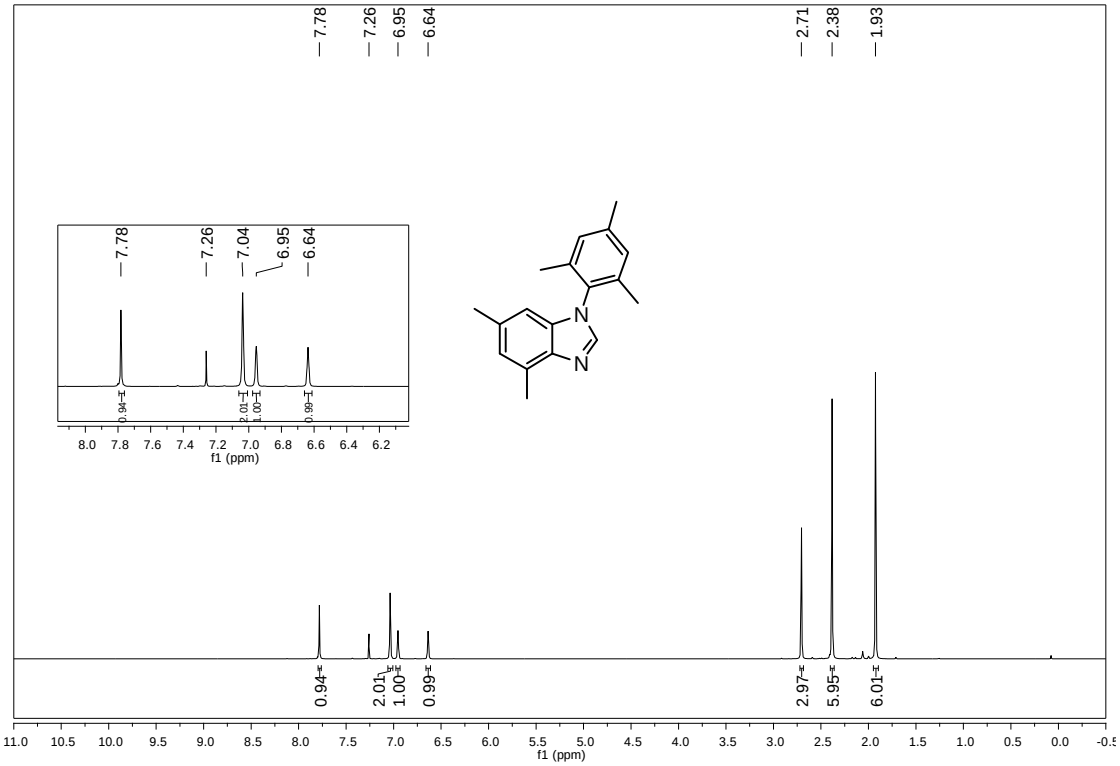


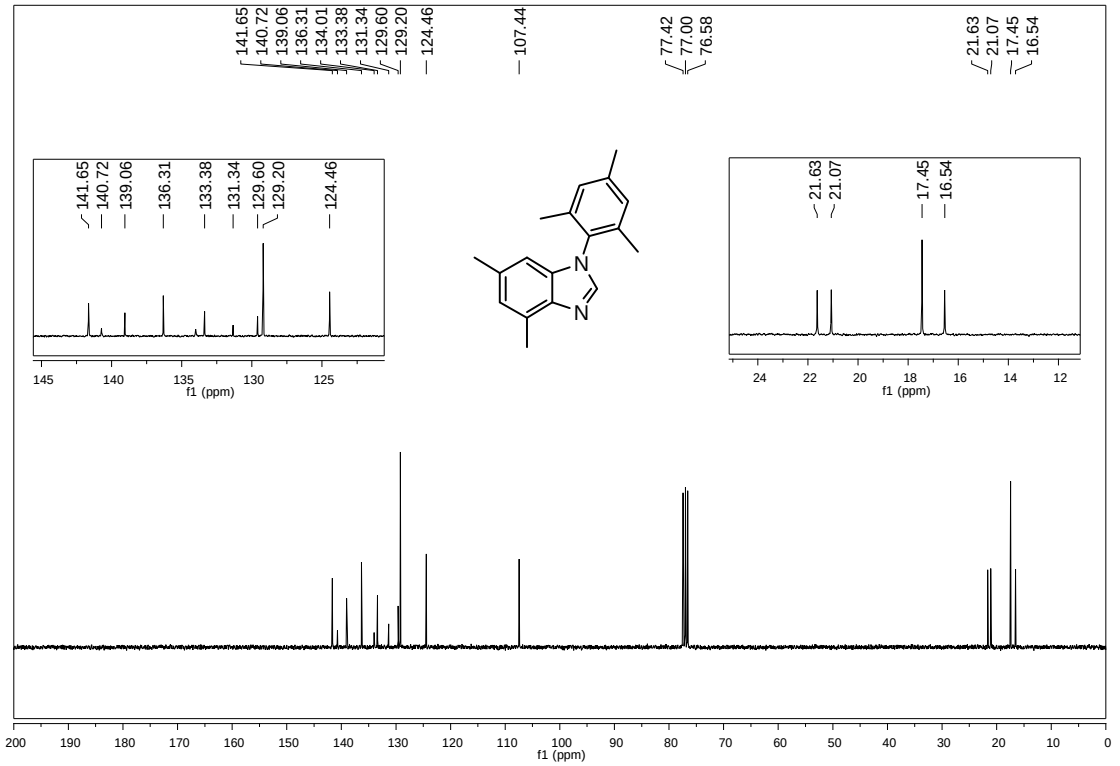
1-(2,4,6-Trimethylphenyl)-1*H*-benzoimidazole (2f)



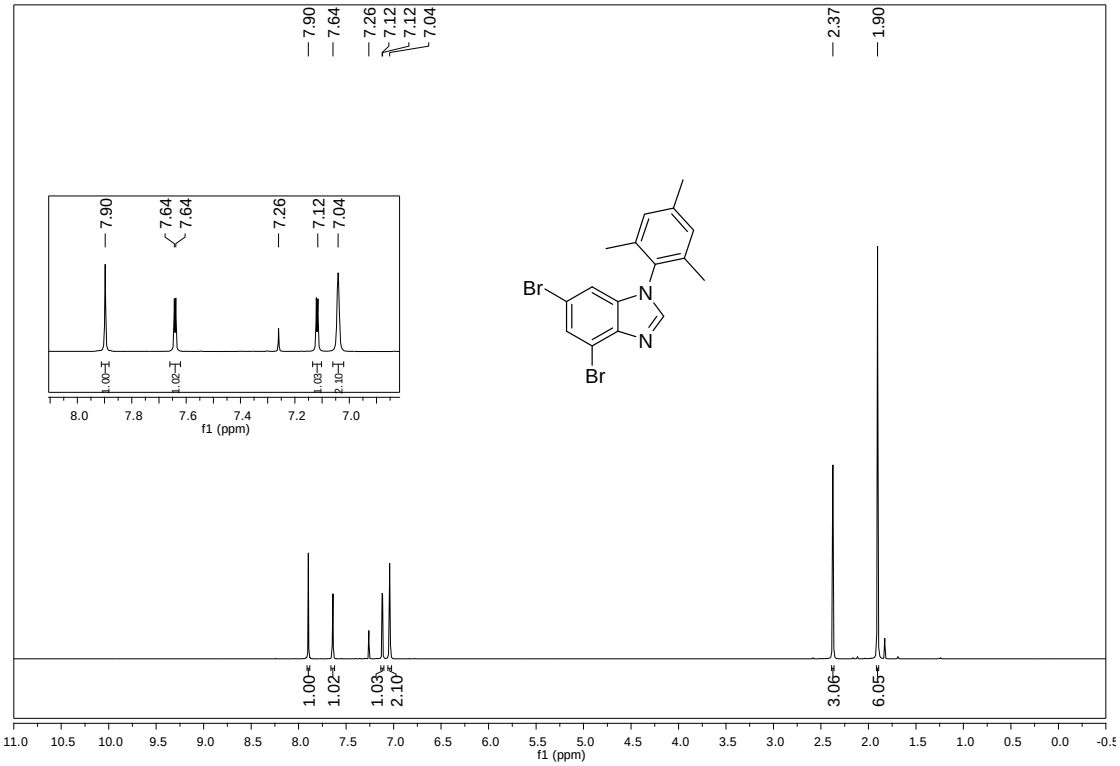


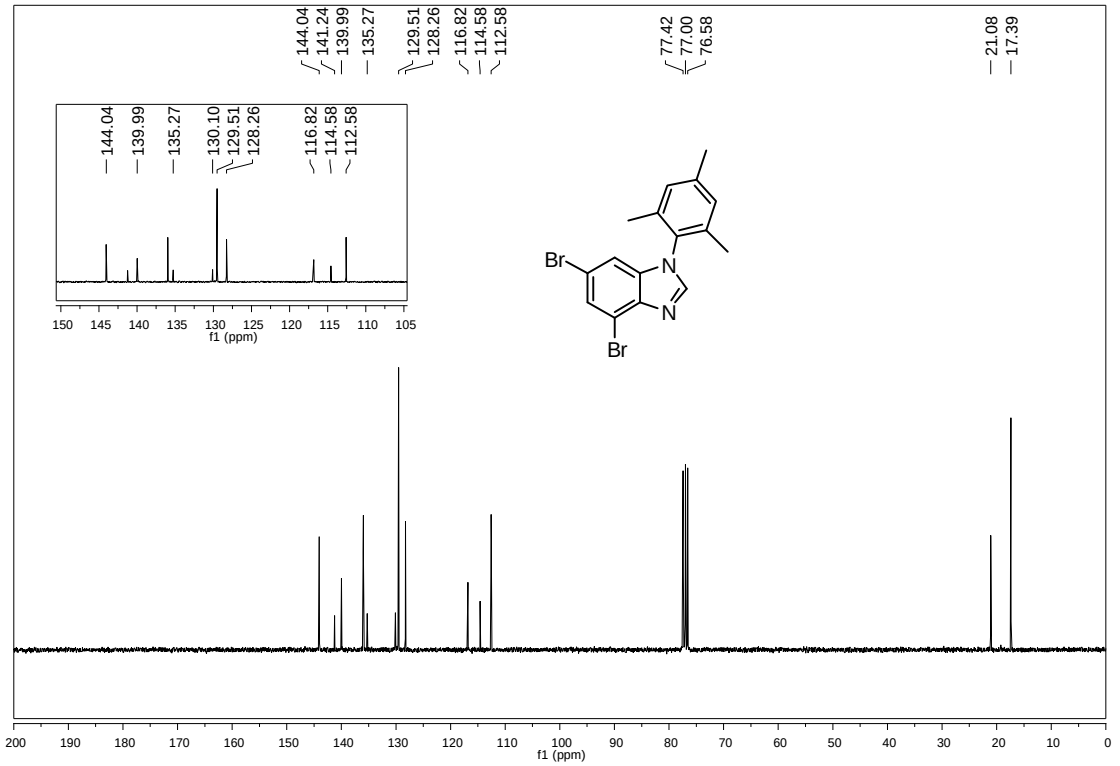
4,6-Dimethyl-1-(2,4,6-trimethylphenyl)-1*H*-benzoimidazole (2g)



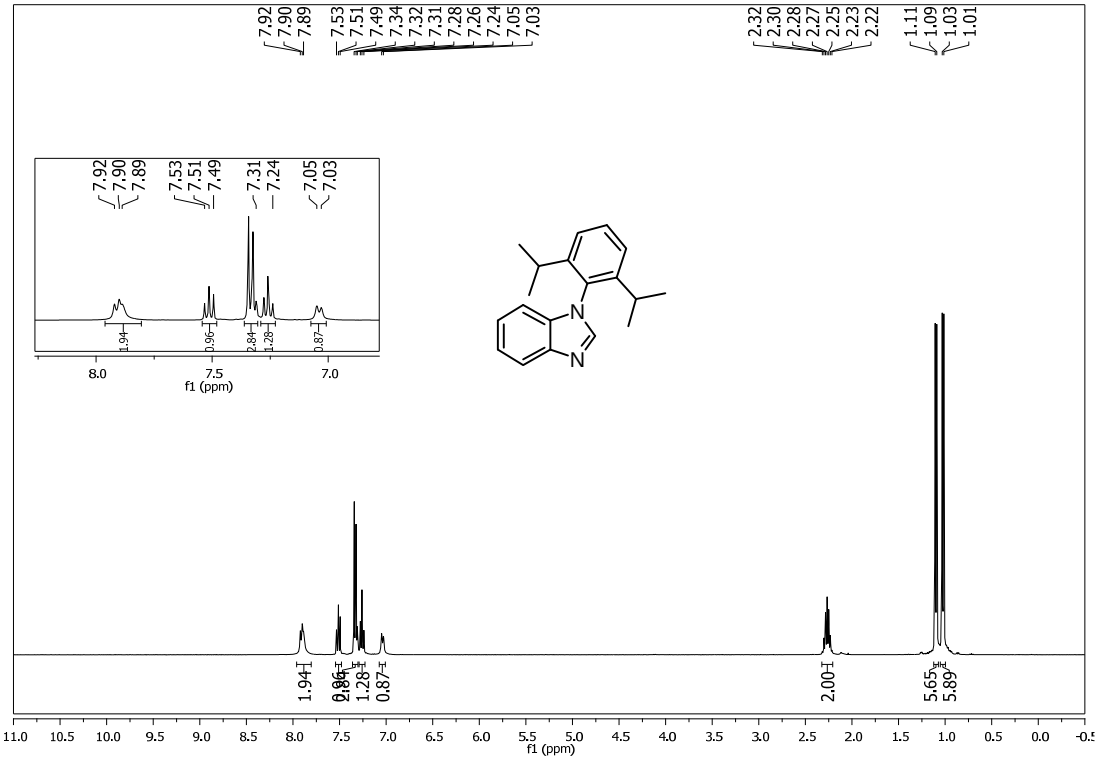


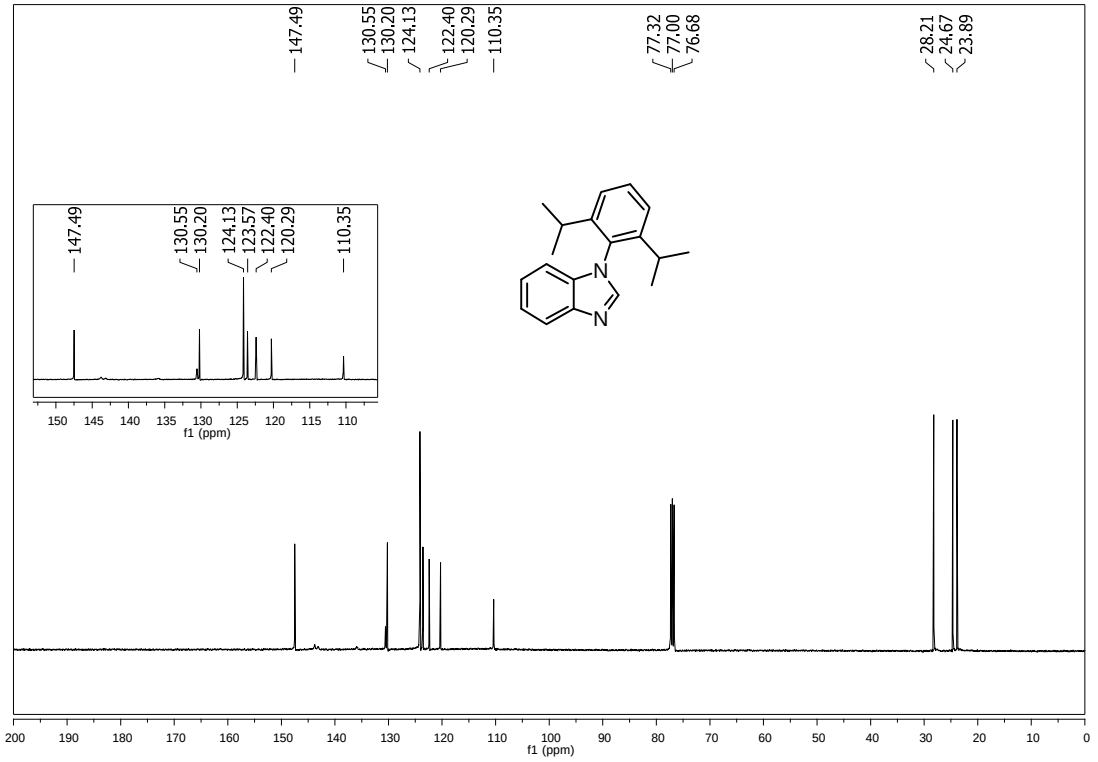
4,6-Dibromo-1-(2,4,6-trimethylphenyl)-1*H*-benzoimidazole (2h)



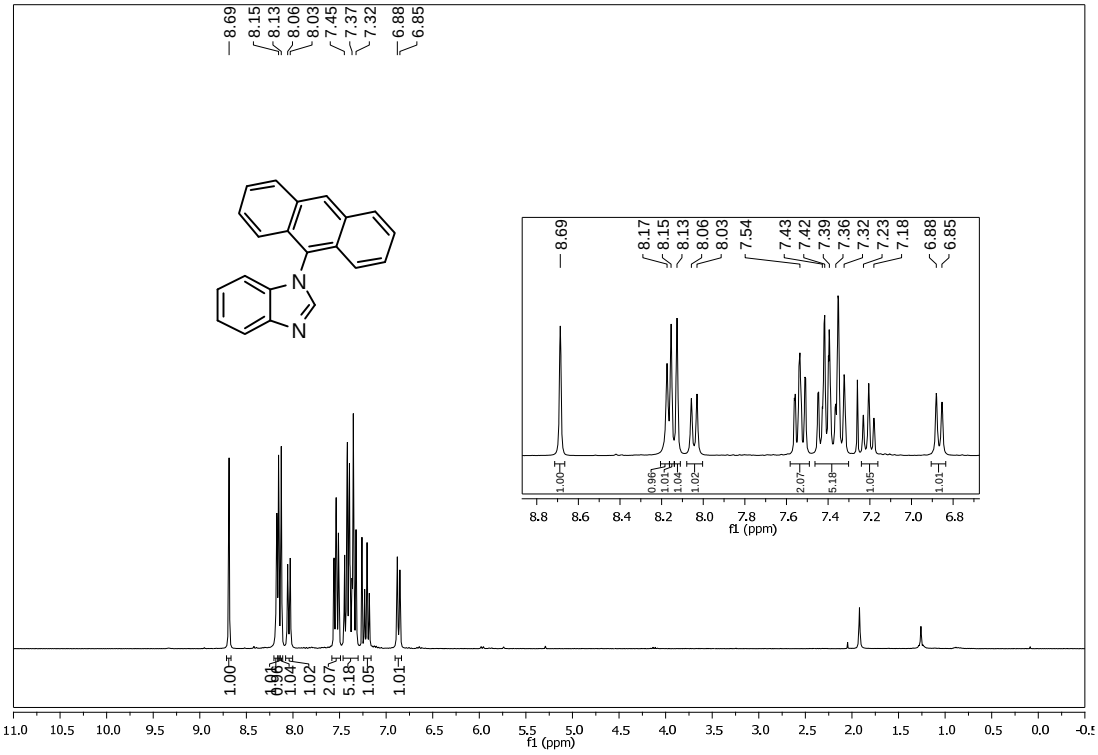


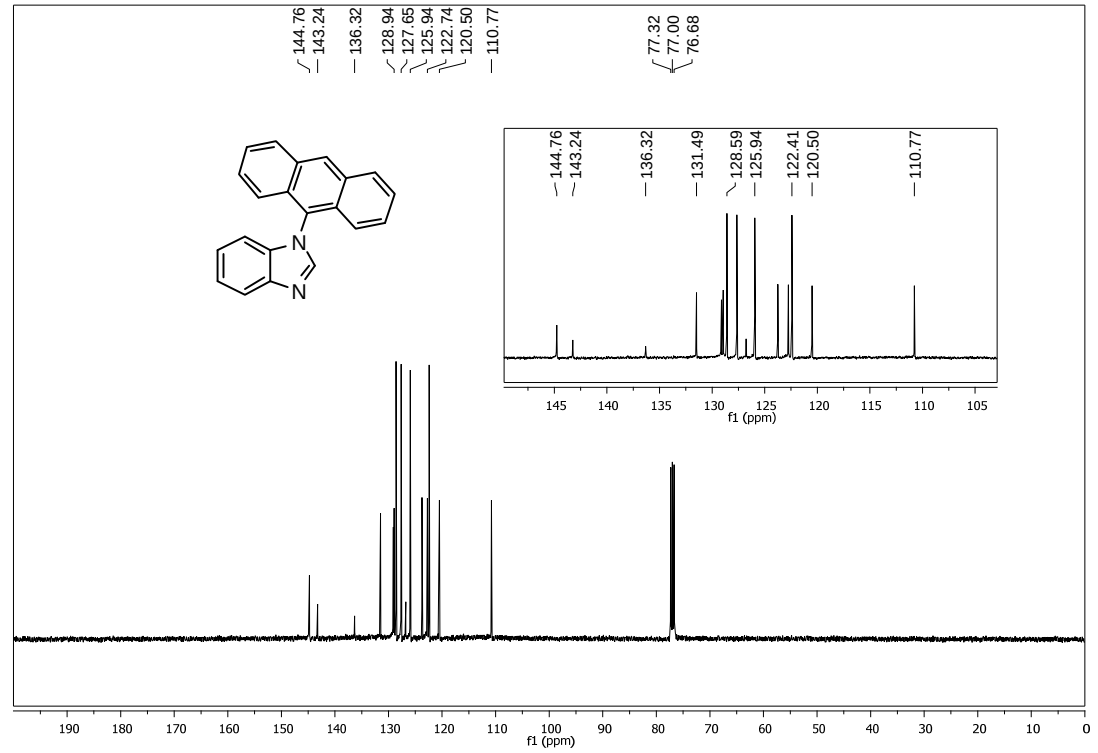
1-(2,6-Diisopropylphenyl)-1*H*-benzoimidazole (2i)



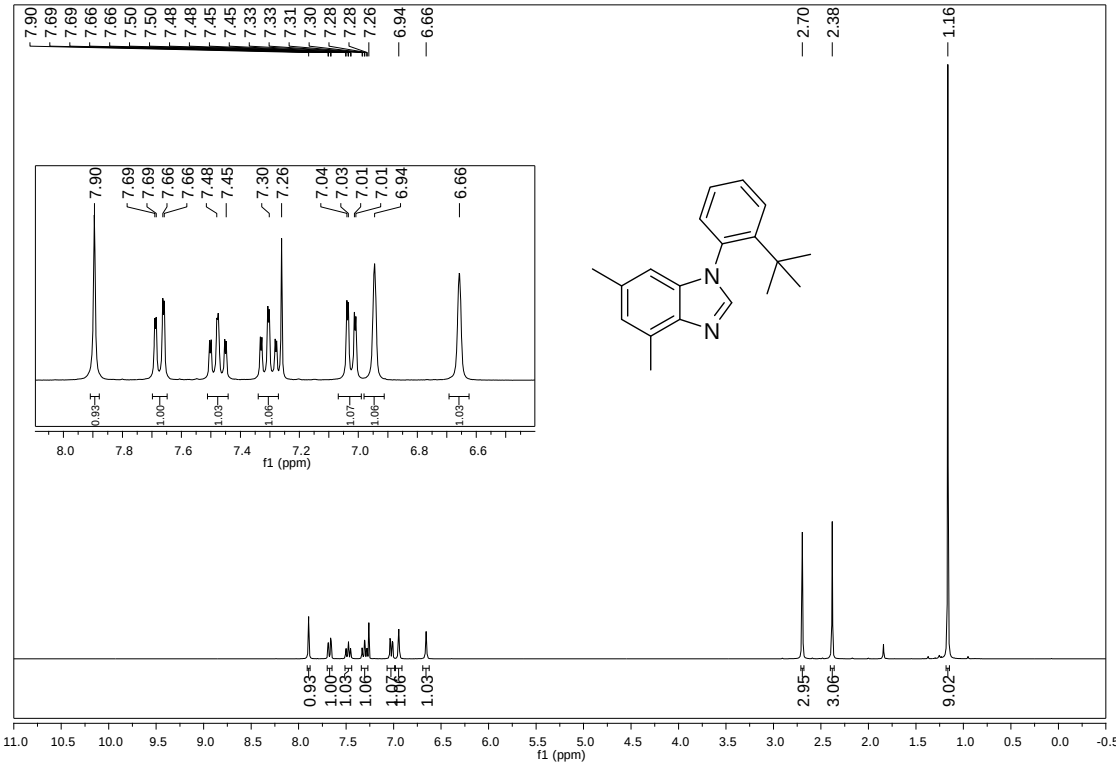


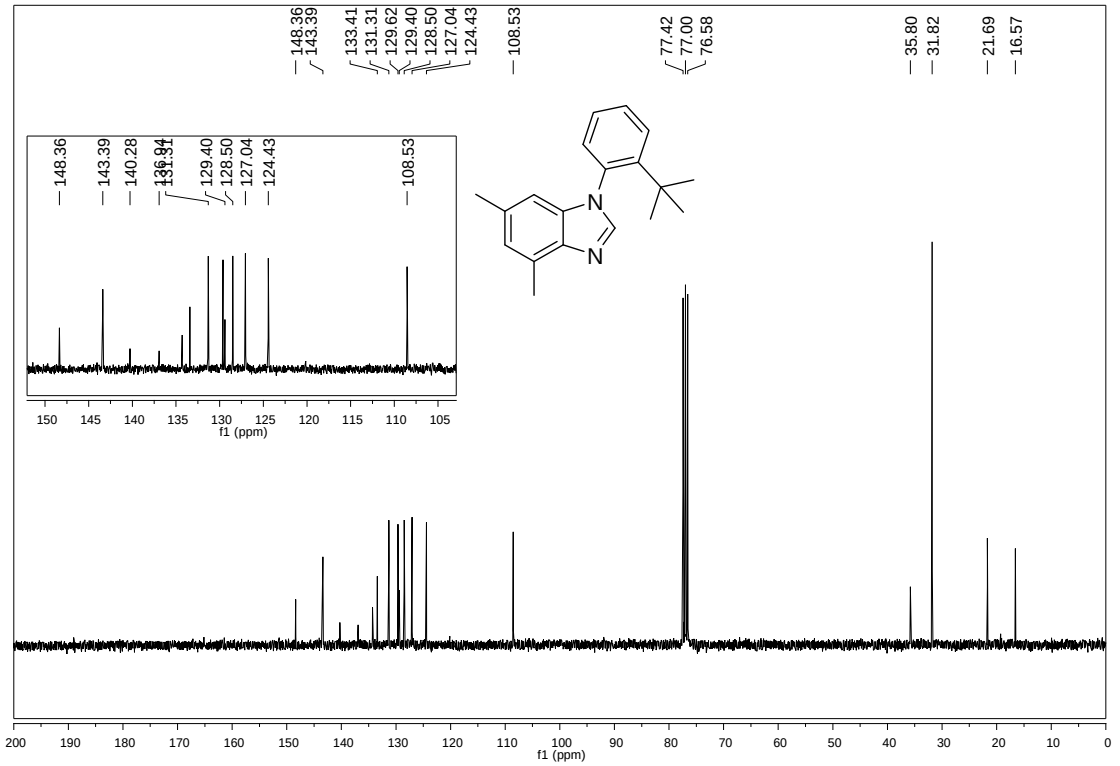
1-Anthracen-9-yl-1*H*-benzoimidazol (2j)



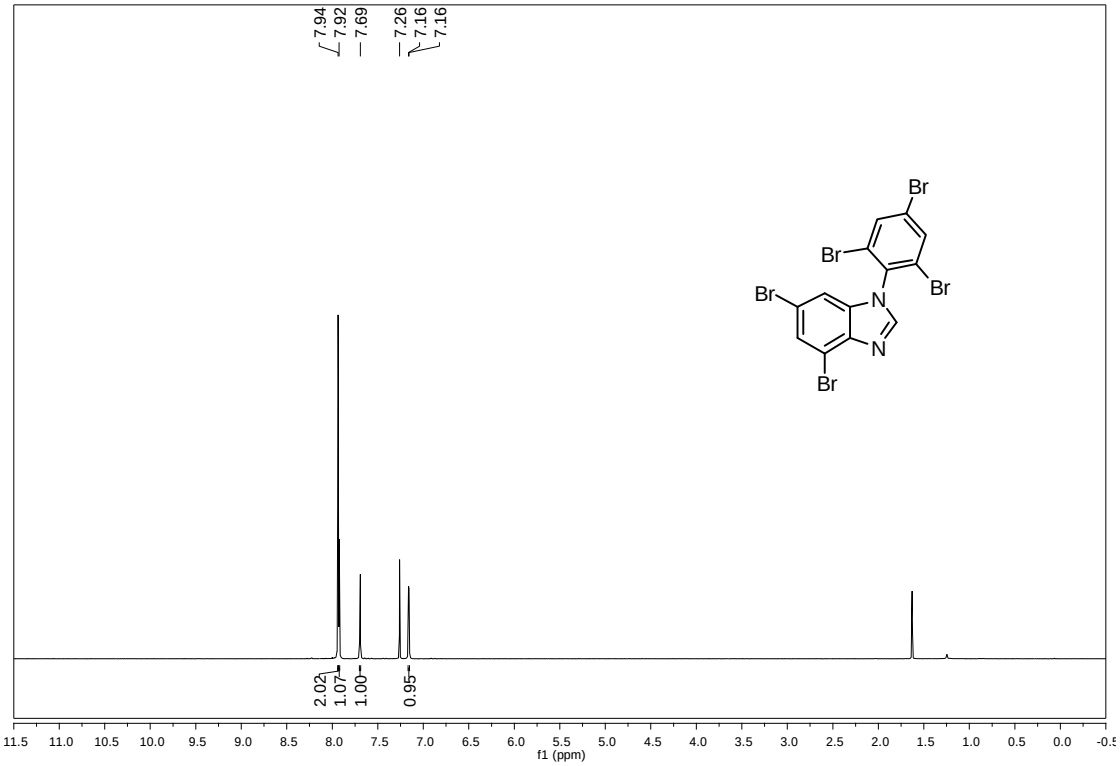


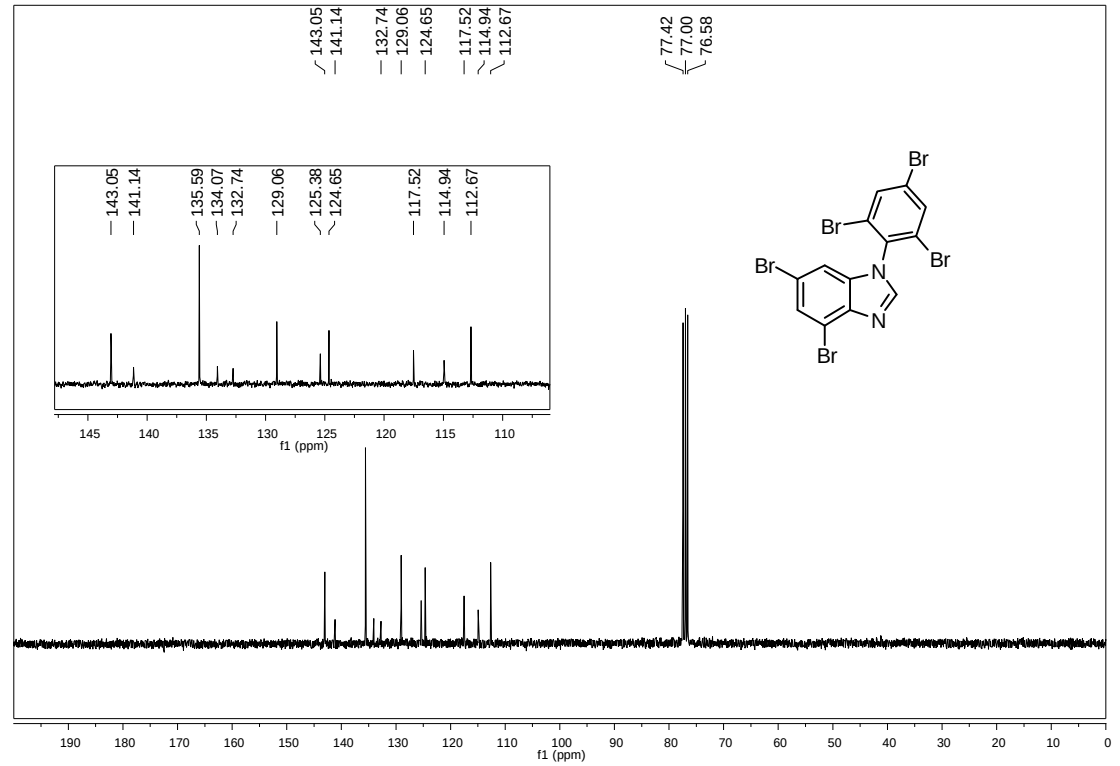
1-(2-*tert*-Butylphenyl)-4,6-dimethyl-1*H*-benzoimidazol (2k)



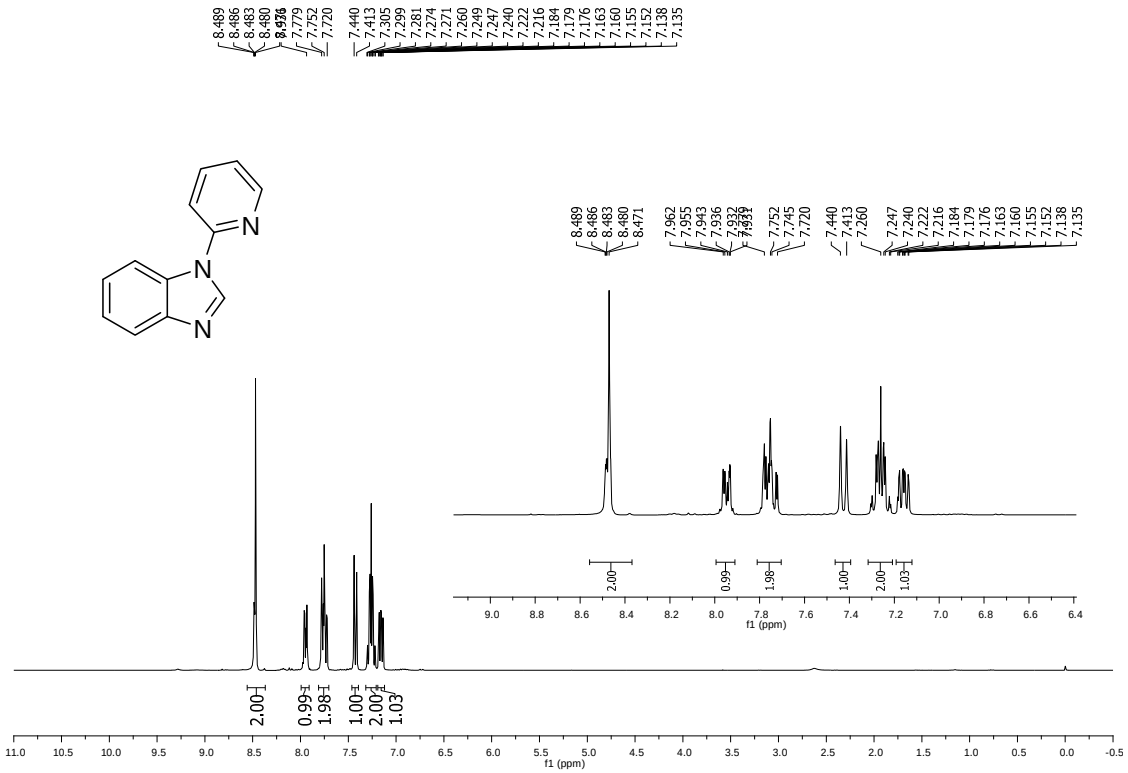


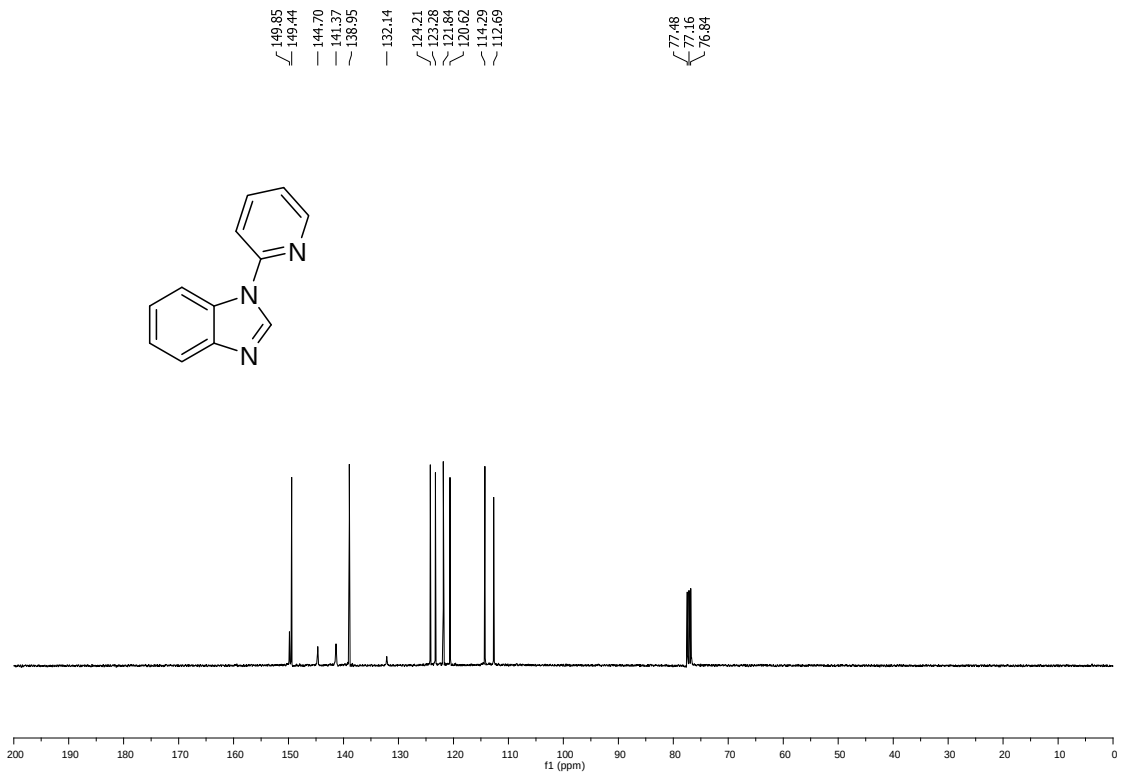
4,6-Dibrom-1-(2,4,6-tribromphenyl)-1*H*-benzoimidazol (2l)



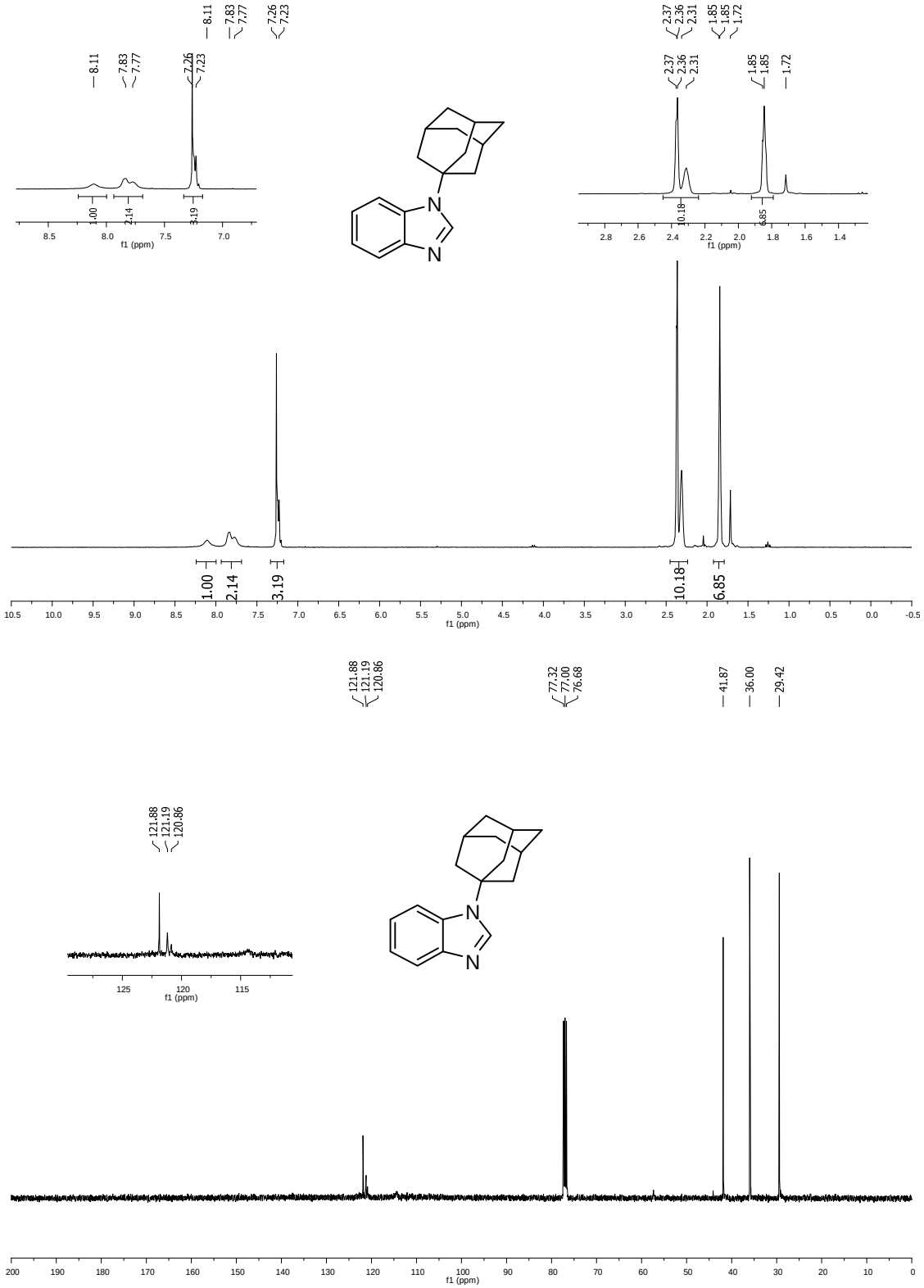


1-Pyridin-2-yl 1*H* Benzimidazole (2m)

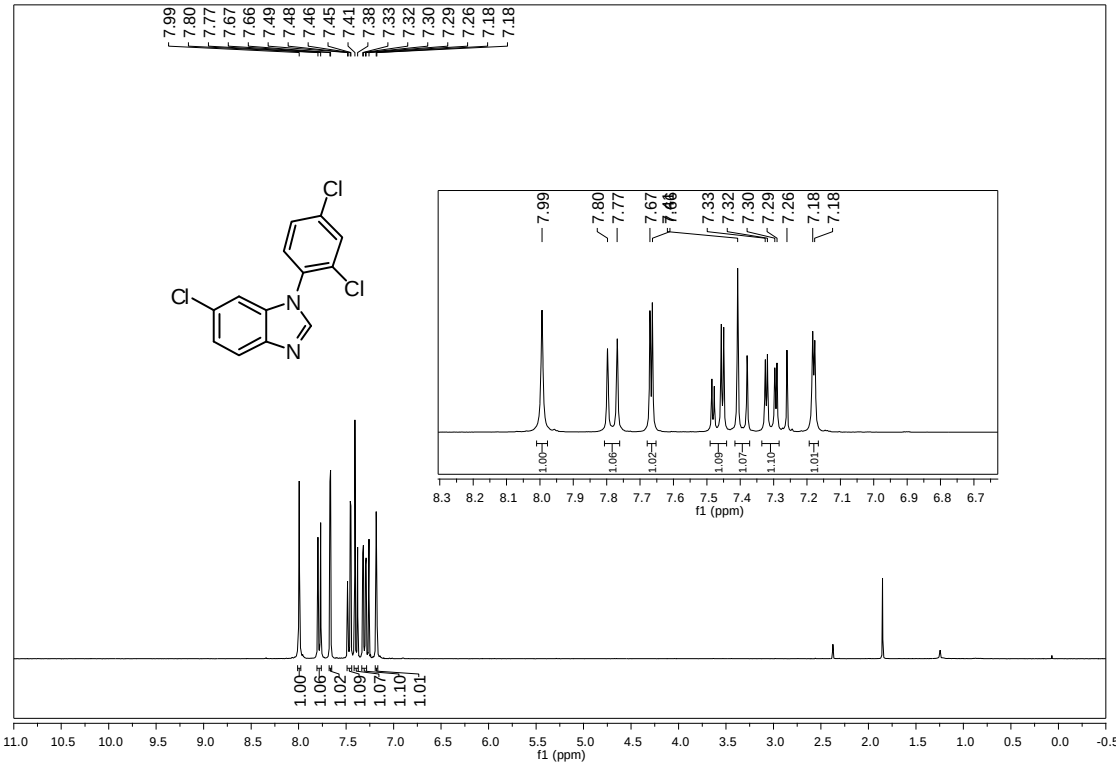


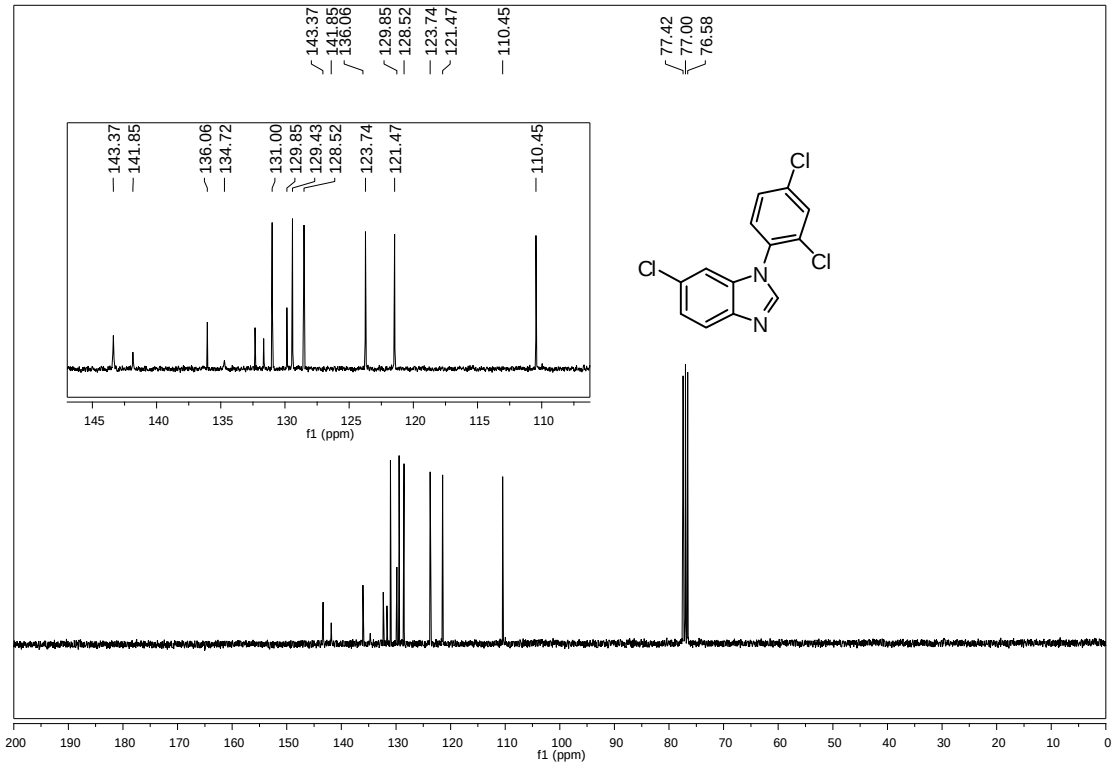


1-Adamantan-2-yl-1*H*-benzoimidazole (2n)

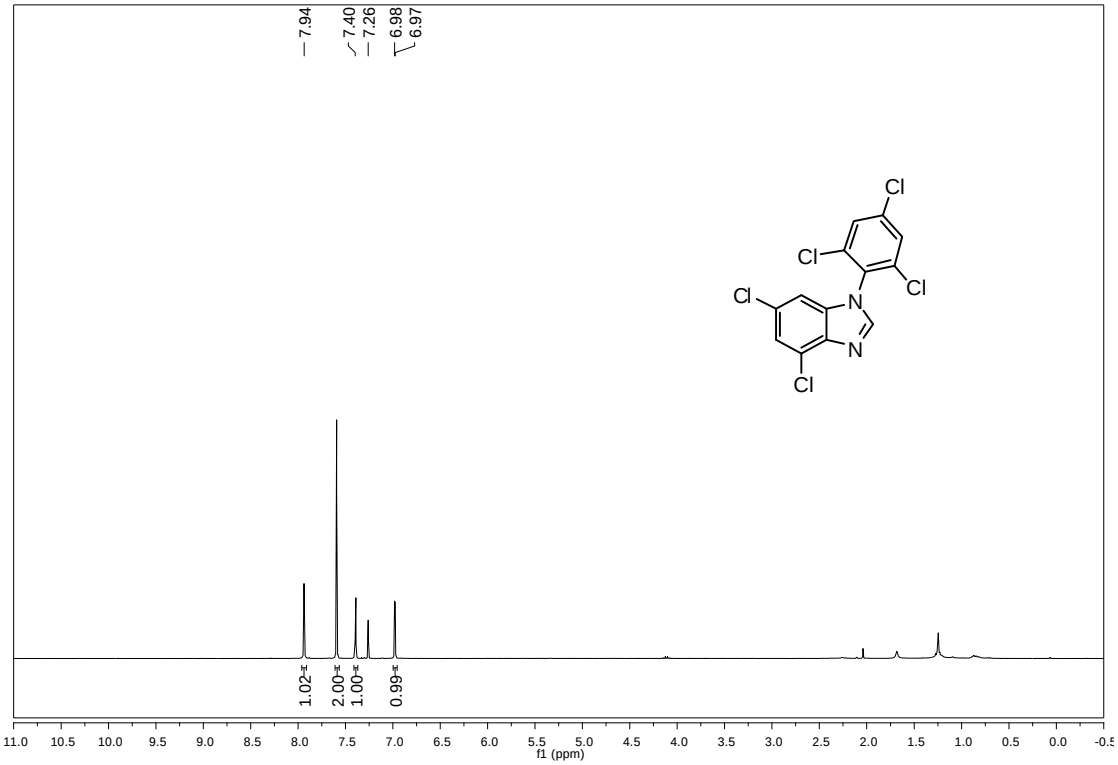


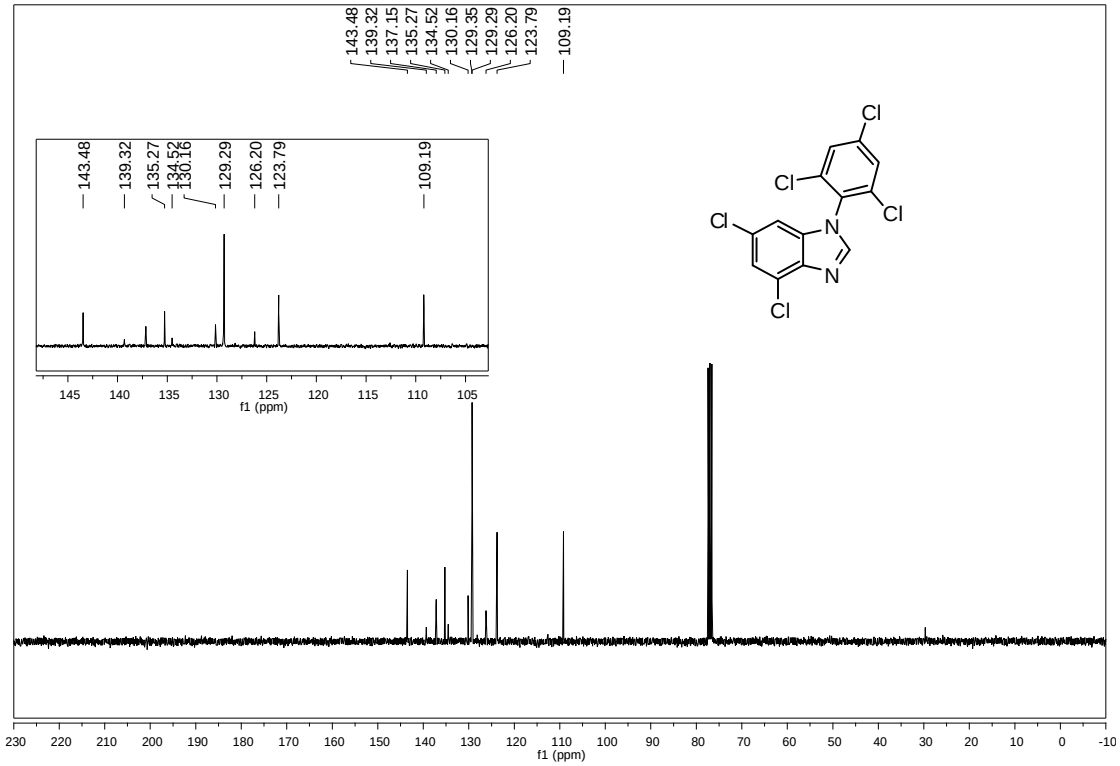
6-Chloro-1-(2,4-dichlorophenyl)-1*H*-benzoimidazole (2o)



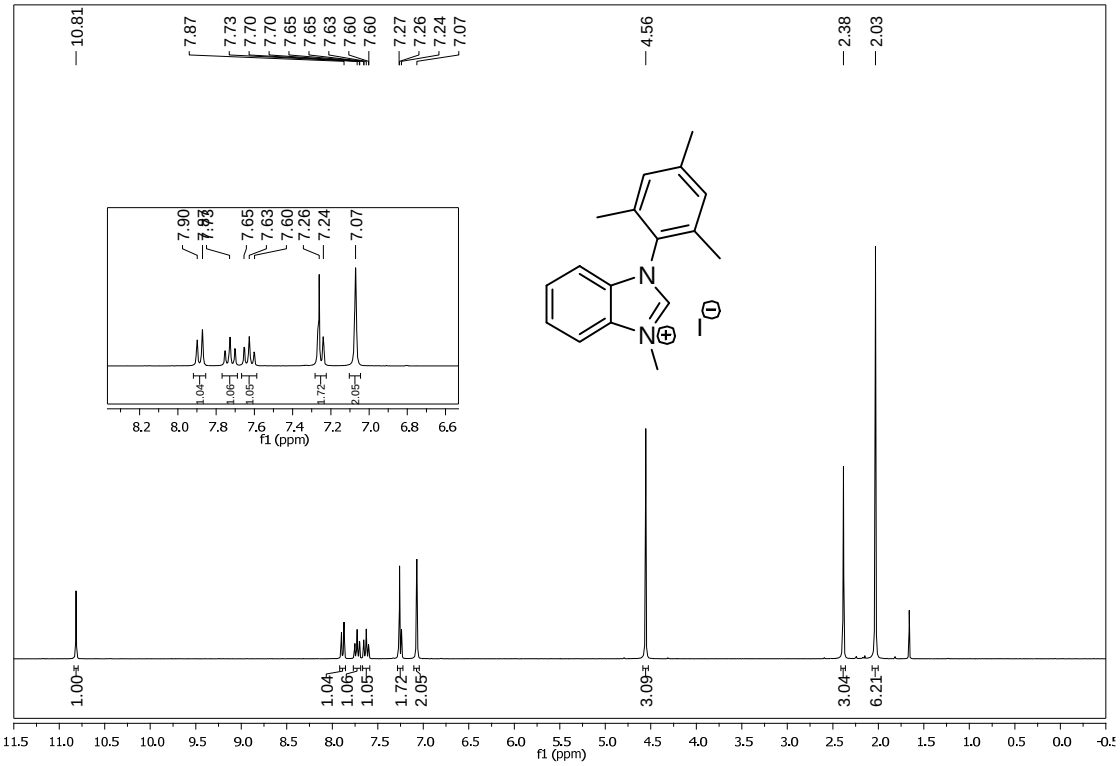


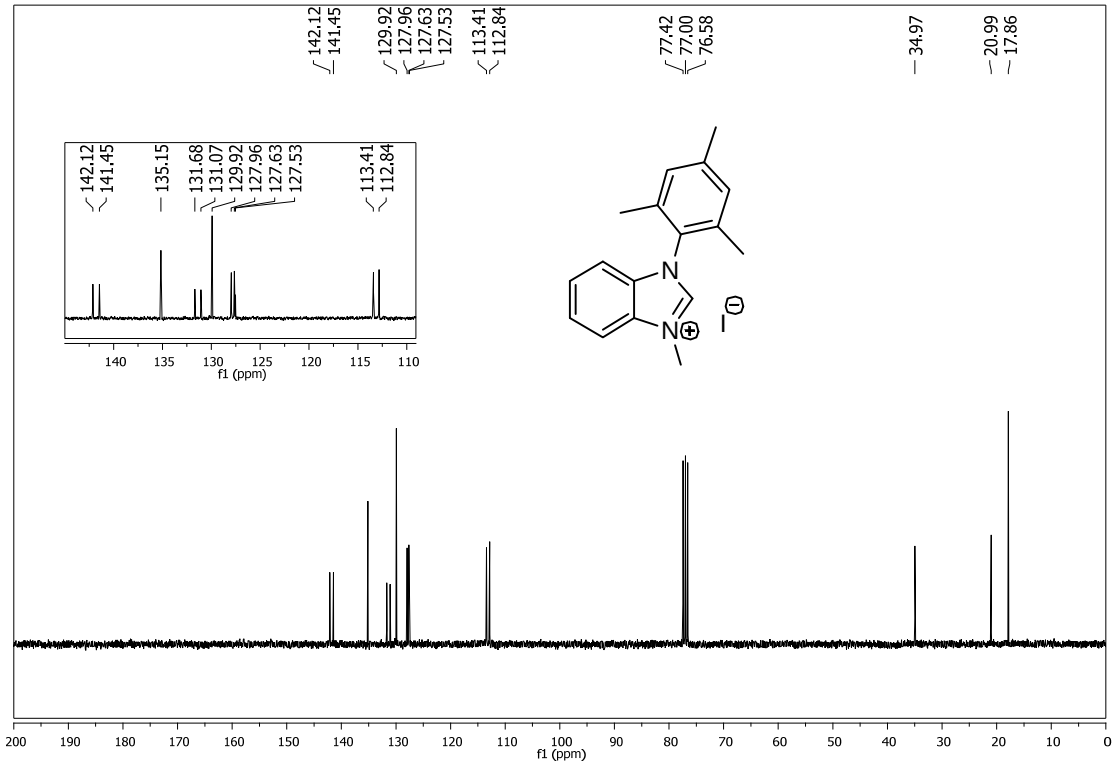
4,6-Dichlor-1-(2,4,6-trichlorphenyl)-1*H*-benzoimidazol (2p)



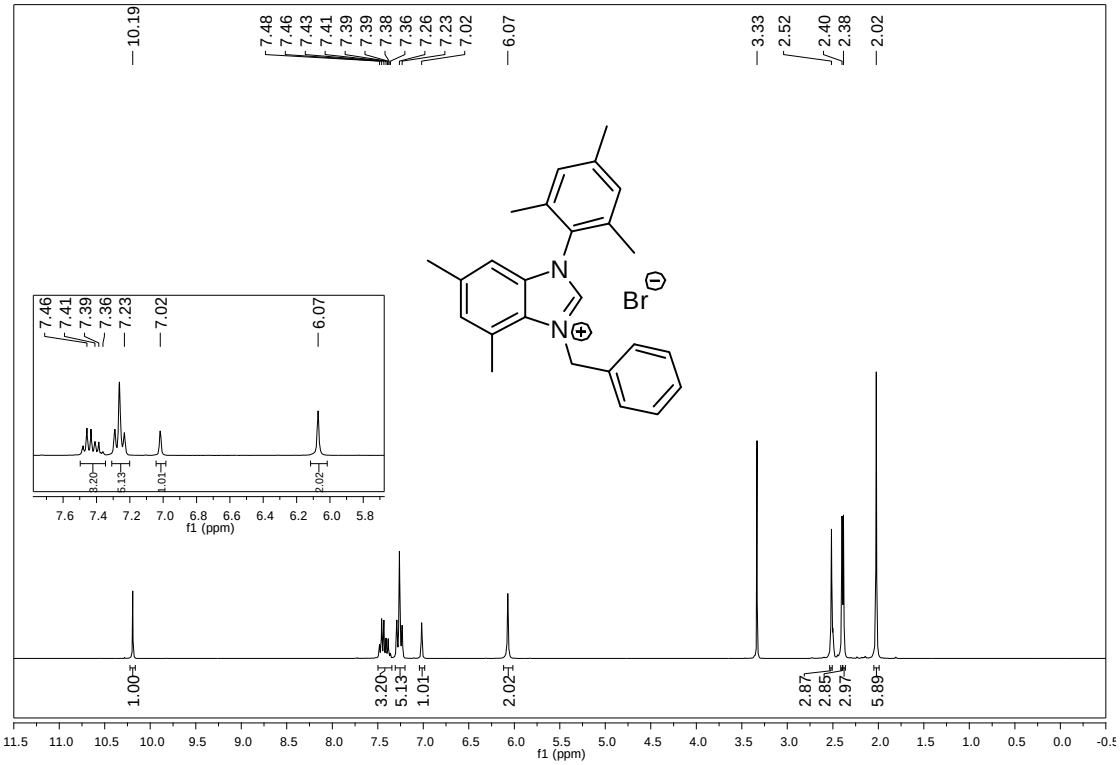


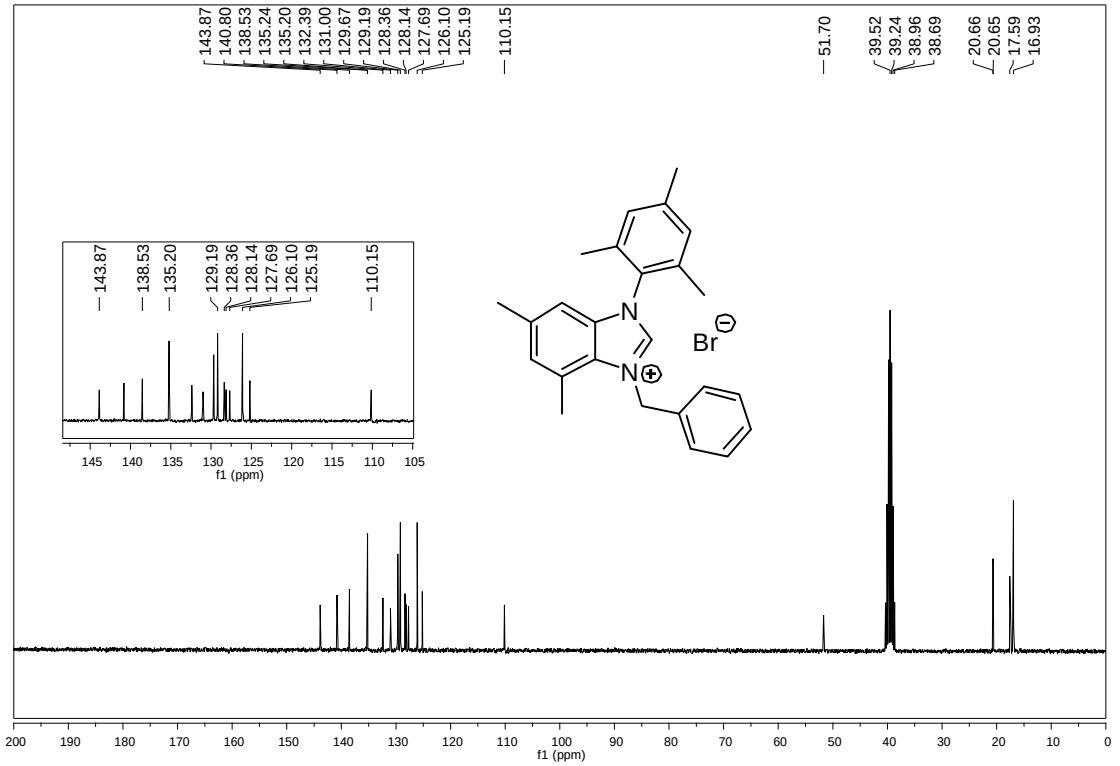
1-Methyl-3-(2,4,6-trimethylphenyl)-3*H*-benzimidazol-1-ium iodide (3f)



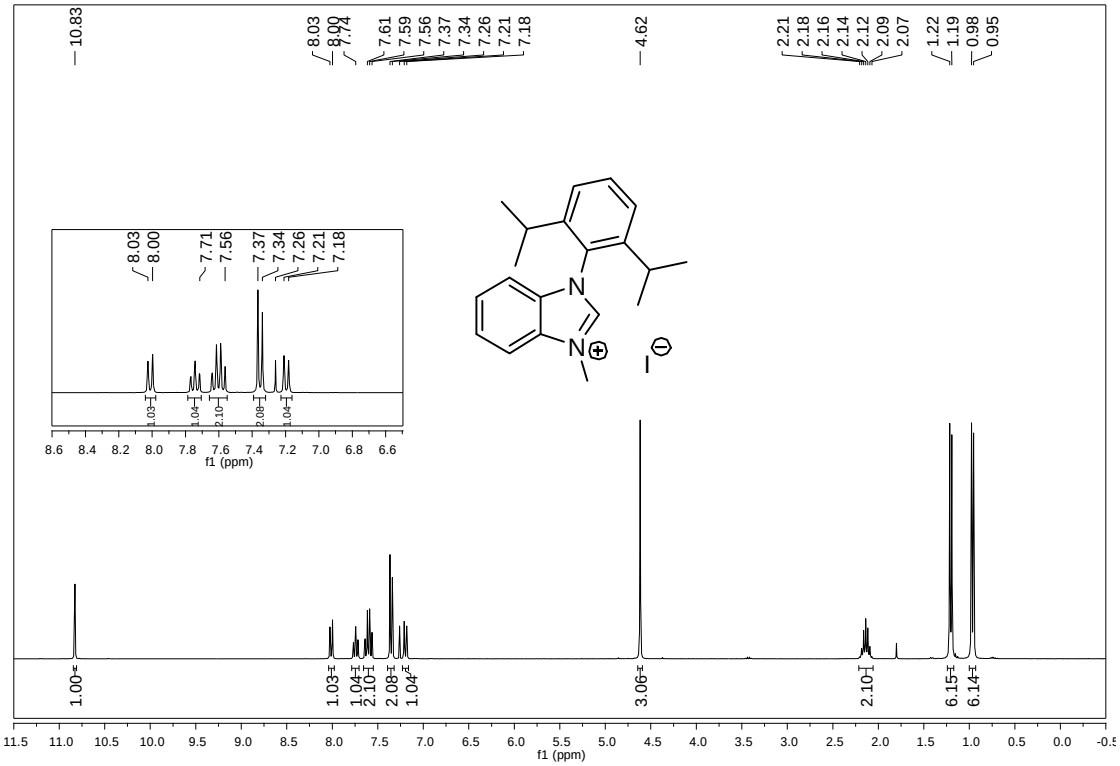


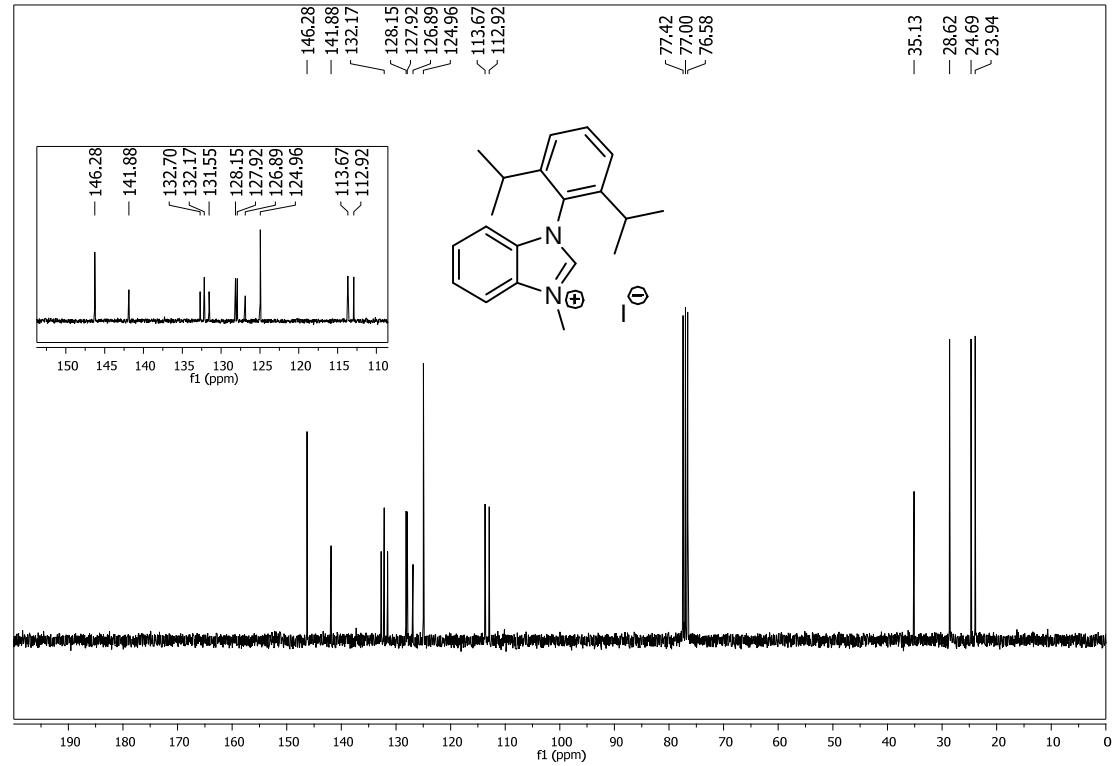
1-Benzyl-5,7-dimethyl-3-(2,4,6-trimethylphenyl)-3*H*-benzimidazol-1-iumbromide (3g)





3-(2,6-Diisopropylphenyl)-1-methyl-3*H*-benzimidazol-1-ium iodide (3i)





3-Anthracen-9-yl-1-methyl-3*H*-benzimidazol-1-ium iodide (3j)