Supporting Information

Direct Synthesis of Benzimidazoles by Dehydrogenative Coupling of Aromatic Diamines and Alcohols Catalyzed by Cobalt

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1. General Procedure

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques under argon atmosphere. All solvents were reagent grade or better. Non-deuterated solvents were dried over sodium/benzophenoneketyl (tetrahydrofuran, n-pentane, 1,4-dioxane, and toluene), and distilled under argon atmosphere. All solvents were degassed with argon and kept in the glove box over activated 4Å molecular sieves. Deuterated solvents were purchased from Aldrich, purged with argon and stored over activated 4Å molecular sieves in the glove box. ^{1}H, and ^{13}C NMR spectra were recorded using Bruker AMX-300 and 500 NMR spectrometer. All spectra were recorded at 295 K, unless otherwise noted. ^{1}H NMR and $^{13}C\{H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to the residual signals of an appropriate deuterated solvent. NMR spectroscopy abbreviations: br, broad; s, singlet; d, doublet; m, multiplet. GCMS was carried out on HP 6890 (flame ionization detector and thermal conductivity detector) and HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas. Most of the commercially available reagents were used as received.

2. Experimental

a) General procedure for the catalytic reactions

For Table 1: To 0.025 mmol of the pre-catalyst (**1-4)** in 2 mL THF was added 0.025 mmol $NaHBEt_3$ in 1mL THF dropwise at room temperature while stirring. After stirring for 20 min, the solvent was evaporated under vacuum. To the residue were added. 0.5 mmol of 1,2-diaminobenzene, and 0.5 mmol of 1-hexanol (and according to Table 1, in some cases a specified amount of ^{t}BuOK was also added) and the mixture was dissolved in 2 mL of toluene (or 1,4-dioxane or THF; Table 1, entries 10, 11, respectively) and placed in a Teflon Schlenk tube containing 4Å molecular sieves (750 mg) under N_2. The tube was heated at 150 ºC (or 120 ºC, Table 1, entry 3) with stirring for 24 h. The reaction mixture was then cooled down in an ice bath and the formed H_2 was vented off.

The reaction products were analyzed by GC-MS and ^{1}H NMR. The formation of 2-pentylbenzimidazole was determined by GC followed by the isolated yield of the product was determined after column chromatography.

For Table 2: 0.025 mmol of pre-catalyst **1** was dissolved in 2 mL THF and a solution of 0.025 mmol of $NaHBEt_3$ in 1 mL THF was added dropwise at room temperature while stirring. After stirring the reaction mixture for 20 min, the solvent was evaporated under vacuum. Then 0.5 mmol of 1,2-diaminobenzene and 0.5 mmol of the primary alcohol were added to the residue. The mixture was dissolved in 2 mL of toluene and transferred to a high pressure Teflon Schlenk tube containing 4Å molecular sieves (750 mg) under N_2. The tube was placed in a pre-heated oil bath at 150 ºC (bath temperature) with stirring for 24h (Table 2). The reaction mixture was then cooled down in an ice bath and the formed H_2 was vented off. The reaction products were analyzed by GC-MS. Pure benzimidazole derivatives were isolated by column chromatography using silica and the isolated yields are given in Table 2.

Reaction time was 36h for 3,4 dimethoxy benzylalcohol (entry 8, Table 2). 0.025 mmol of *t*BuOK was added to the reaction mixture of 4-cyanobenzyl alcohol (entry 14, Table 2). 0.067 g (1 mmol) crotononitrile was added to the reaction mixture of 3-phenyl-2-en-1-propanol as substrate (entry 15, Table 2).

b) Procedure for detection of H_2

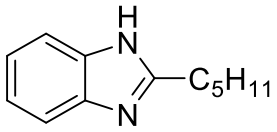
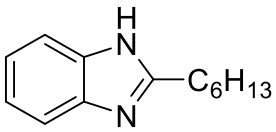
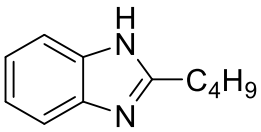
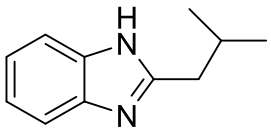
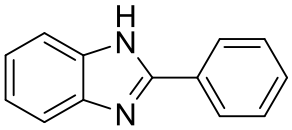
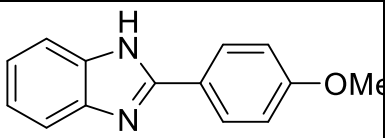
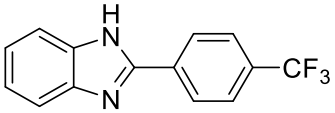
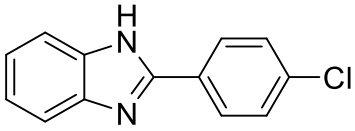
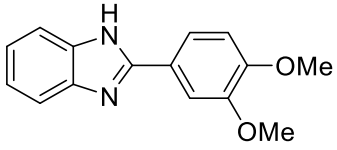
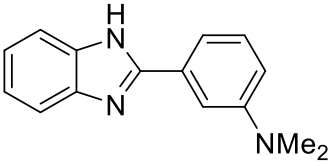
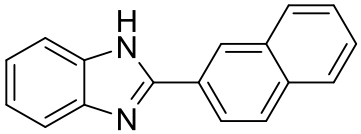
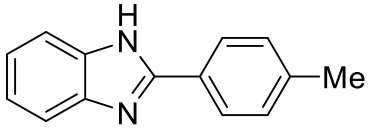
To a solution of 0.025 mmol pre-catalyst **1** in THF (2 mL) was added dropwise a solution of 0.025 mmol of $NaHBEt_3$ in 1 mL THF at room temperature while stirring. After stirring the reaction mixture for 20 min, the solvent was evaporated under vacuum. 0.5 mmol of 1,2-diaminobenzene and 0.5 mmol of 1-hexanol were added to the residue and the mixture was dissolved in 2 mL of toluene and placed in a Young Schlenk tube containing 4Å molecular sieves (750 mg). The tube was heated at 150 ºC (bath temperature) with stirring for the 24 h. The reaction mixture was then cooled down to room temperature and the gas mixture was injected in a thermal conductivity detector GC chromatograph showing formation of H_2.

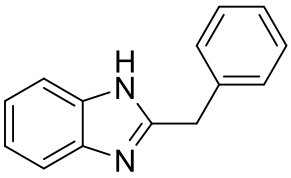
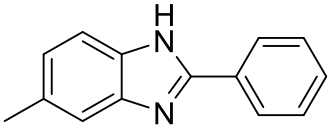
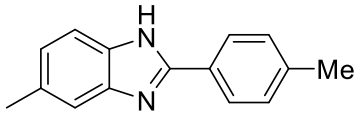
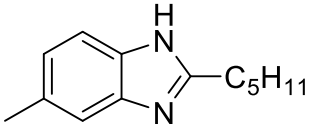
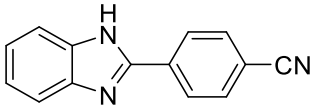
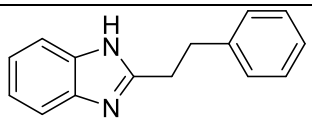
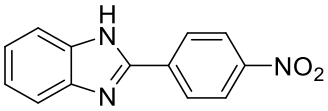
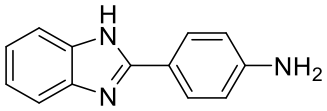
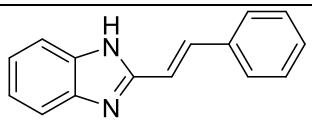
c) Preparation of the complexes

The Co-PNNH complexes **1**, **1-Cl**, Co-PNP complexes **2a** and **2b**, and Co-PNN complexes **3** and **4** were prepared according to literature procedures.[1-3]

3. GC-MS data of the benzimidazole products

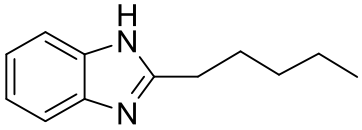
Table S1: GC-MS data of the benzimidazole products was obtained using an HP 6890 GC chromatograph equipped with flame ionization and thermal conductivity detectors, and a HP 5973 (MS detector) instruments, equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas with a flow rate of 1 ml/min):

 t_r = 17.80 min m/z = 188	 t_r = 18.51 min m/z = 202	 t_r = 17.14 min m/z = 174
 t_r = 16.59 min m/z = 174	 t_r = 19.75 min m/z = 194	 t_r = 20.66 min m/z = 224
 t_r = 19.69 min m/z = 262	 t_r = 21.19 min m/z = 228	 t_r = 22.76 min m/z = 254
 t_r = 22.60 min m/z = 237	 t_r = 23.43 min m/z = 244	 t_r = 20.87 min m/z = 208

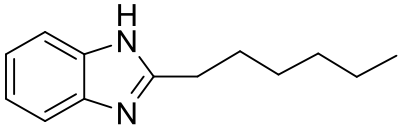
 t_r = 19.66 min m/z = 208	 t_r = 20.40 m/z = 208	 t_r = 21.13 min m/z = 222
 t_r = 18.49 min m/z = 202	 t_r = 23.14 min m/z = 219	 t_r = 20.30 min m/z =222
 t_r = 24.09 min m/z = 239	 t_r = 23.02 min m/z = 209	 t_r = 22.16 min m/z = 220/219

t_r = retention time

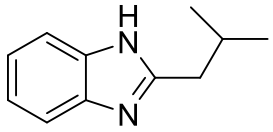
4. ^{1}H and ^{13}C{^{1}H} NMR data of isolated benzimidazoles[4]



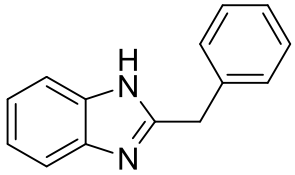
^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.91 (t, J = 6.65 Hz, 3H), 1.40 (m, 4H), 1.89 (p, J = 7.4Hz, 2H), 2.94 (t, J= 7.7 Hz, 2H), 7.24 (dd, J = 3.1, 2H), 7.57 (b, 2H), 9.4 (b, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 13.8, 22.3, 27.9, 29.3, 31.5, 122.2, 154.9.



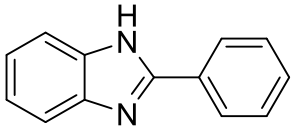
^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.89 (t, J = 6.8 Hz, 3H), 1.32 (m, 4H), 1.43 (m, 2H), 1.88 (p, J = 7.3 Hz, 2H) 2.94 (t, J= 8.4Hz, 2H), 7.24 (dd, J = 3.0 Hz, 2H), 7.57 (b, 2H), 9.5 (b, 1H); (500 MHz, DMSO-d_6) δ: 0.87 (t, J = 6.6 Hz, 3H), 1.30 (m, 6H), 1.76 (p, J = 7.8 Hz, 2H) 2.78 (t, J= 7.6Hz, 2H), 7.11 (dd, J = 2.9 Hz, 2H), 7.45 (b, 2H), 12.14 (b, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 14.0, 22.5, 28.2, 29.0, 29.4, 31.4, 114.7, 122.1, 155.3.



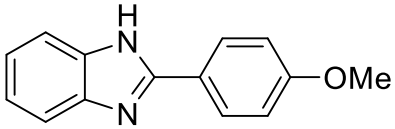
^{1}H NMR 500 MHz, $CDCl_3$) δ: 1.02 (d, J= 6.8 Hz, 6H), 2.27 (m, 1H), 2.83 (d, J= 7.25Hz 2H), 5.63 (b, 1H), 7.24 (dd, J= 3.75 Hz, 2H), 7.58 (dd, J= 3.25 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 22.5, 28.5, 38.5, 114.6, 122.1, 138.4, 154.4.



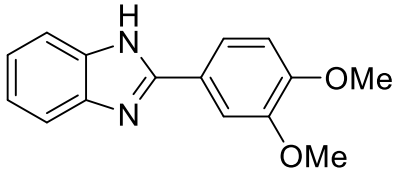
^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.29 (s, 2H), 7.24(dd, J = 3.2 Hz, 2H), 7.29-7.32 (m, 3H), 7.35 (m, 2H), 7.54 (b, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 35.9, 114.8, 122.4, 127.3, 129.0, 136.2, 153.2.



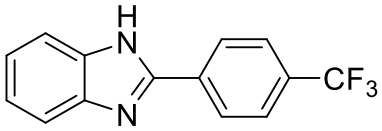
^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.11 (b, 2H), 7.45(d, J= 7.2Hz, 2H), 7.50 (d, 3H), 8.09 (d, J= 6.5Hz, 2H), 12.83 (b, 1H); ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): 122.5, 126.9, 129.4, 130.3, 130.6, 151.6.



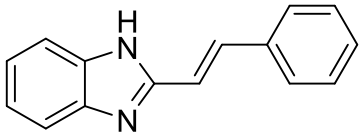
^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.62 (s, 3H), 7.68-7.59(m, 2H), 7.79(s, 2H), 7.96 (b, 1H), 8.20 (b, 2H), 9.13 (d, J= 6.18Hz, 1H), 11.29 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 55.9, 111.5, 114.9, 121.7, 122.8, 130.2, 131.5, 137.6, 149.6, 156.9.



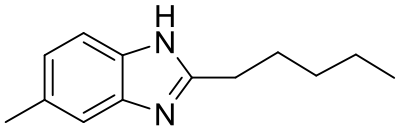
^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.85 (s, 3H), 3.90(s, 3H), 7.17(d, J= 8.3 Hz, 1H), 7.22 (dd, J = 2.9Hz, 2H), 7.59 (dd, J = 3.3Hz, 2H), 7.77 (d, J= 8.3Hz, 1H), 7.79 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 55.7, 55.9, 109.8, 111.2, 114.7, 119.7, 121.6, 123.1, 138.3, 149.4, 151.0, 151.9.



^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.12 (b, 2H), 7.59(b, 2H), 7.87 (d, J= 7.17Hz, 2H), 8.33 (d, J= 7.2Hz, 2H), 13.09 (b, 1H); ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): 115.6, 123.1, 126.4, 127.4, 134.4, 150.1; ^{19}F NMR (DMSO-d_6): -61.95 (CF_3)

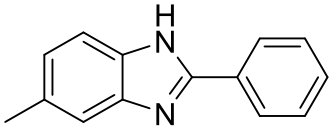


^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.16 (d, J = 16.5 Hz, 1H), 7.29-7.31(bm, 3H), 7.34-7.39 (b, 3H), 7.52 (d, J= 7.7 Hz, 2H), 7.64-7.67 (m, 2H), 10.13 (b, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 116.5, 123.1, 127.1, 128.3, 128.7, 128.7, 129.1, 135.5, 135.6, 150.8.

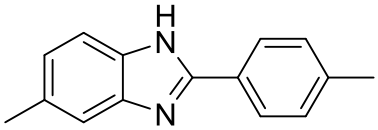


^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.80 (b, 3H), 1.29 (m, 4H), 1.85 (m, 2H), 2.44 (s, 3H), 2.94 (m, 2H), 7.04 (d, J= 7.65Hz, 1H), 7.34 (s, 1H), 7.44 (d, J= 7.89Hz, 1H), 9.5 (b, 1H);

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): 13.8, 21.5, 22.3, 28.1, 29.2, 31.4, 114.1, 114.4, 123.5, 131.8, 136.8, 138.2, 155.4.



^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.43 (s, 3H), 6.18 (b, 1H), 7.07(d, J= 7.47Hz, 1H), 7.39 (s, 4H), 7.52 (d, J= 7.44Hz, 1H), 8.09 (s, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): 21.6, 114.4, 115.1, 124.7, 126.7, 129.1, 130.2, 133.2, 137.0, 138.1, 151.3.



^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.40 (s, 3H), 2.48(s, 3H), 7.09 (d, J= 8.2 Hz, 1H), 7.26 (d, J= 7.7 Hz, 2H), 7.39 (s, 1H), 7.54 (d, J= 6.7 Hz, 1H), 7.98 (d, J= 8.0 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): 21.4, 21.7, 114.4, 115.1, 124.3, 126.4, 127.1, 129.7, 132.7, 137.8, 140.2, 151.6.

Selected ^{1}H and ^{13}C NMR spectra of isolated pyrroles

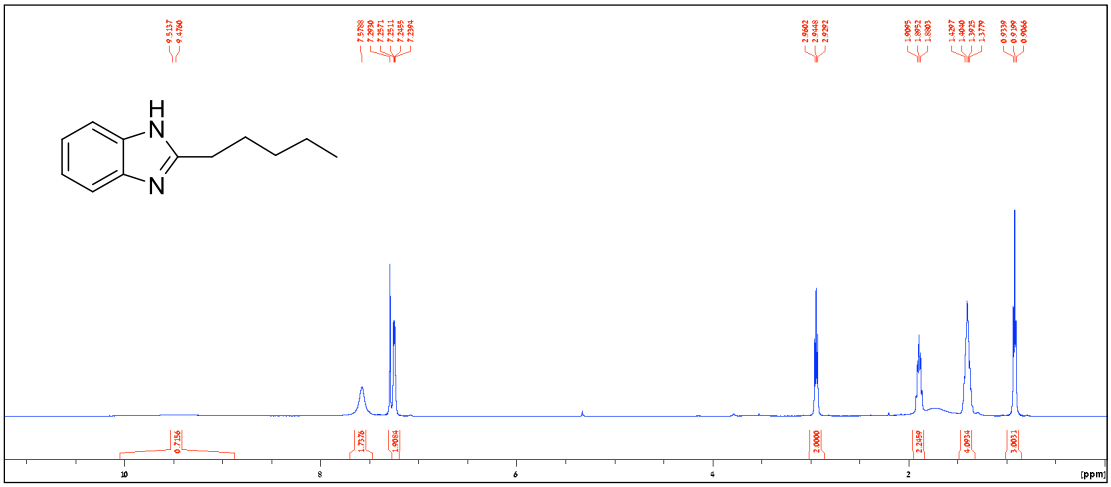


Figure S1. ^{1}H NMR of 2-pentylbenzimidazole in $CDCl_3$.

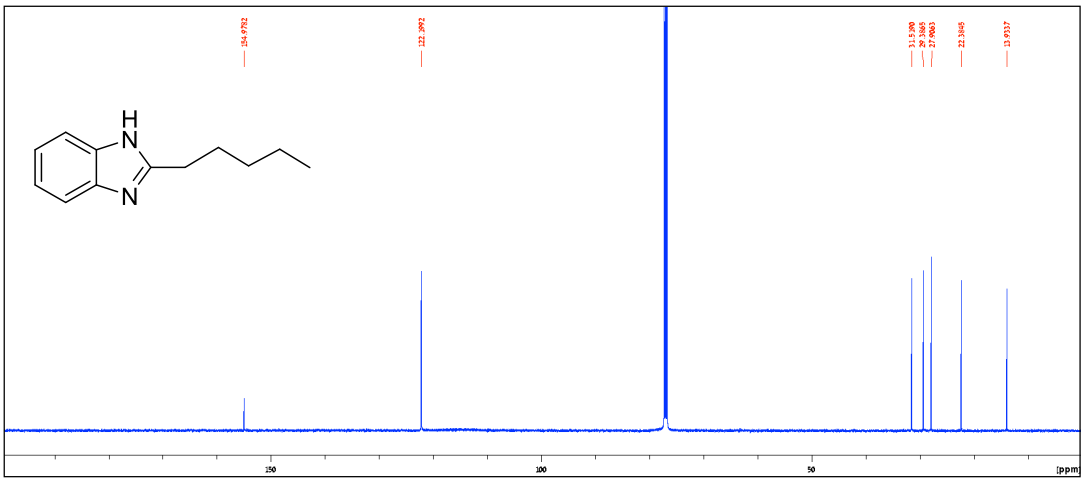


Figure S2. ^{13}C NMR of 2-pentylbenzimidazole in $CDCl_3$.

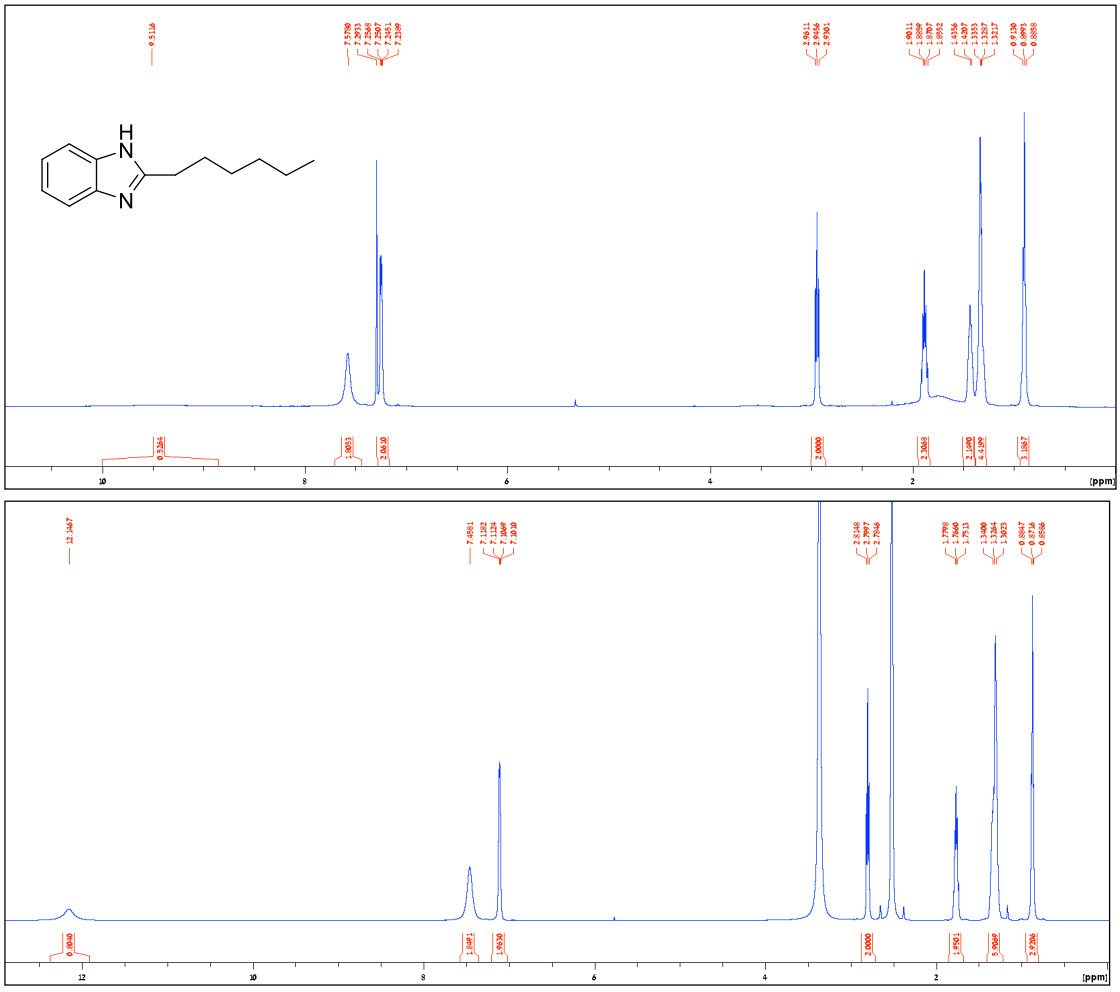


Figure S3. ^{1}H NMR of 2-hexylbenzimidazole in $CDCl_3$ and DMSO-d_6.

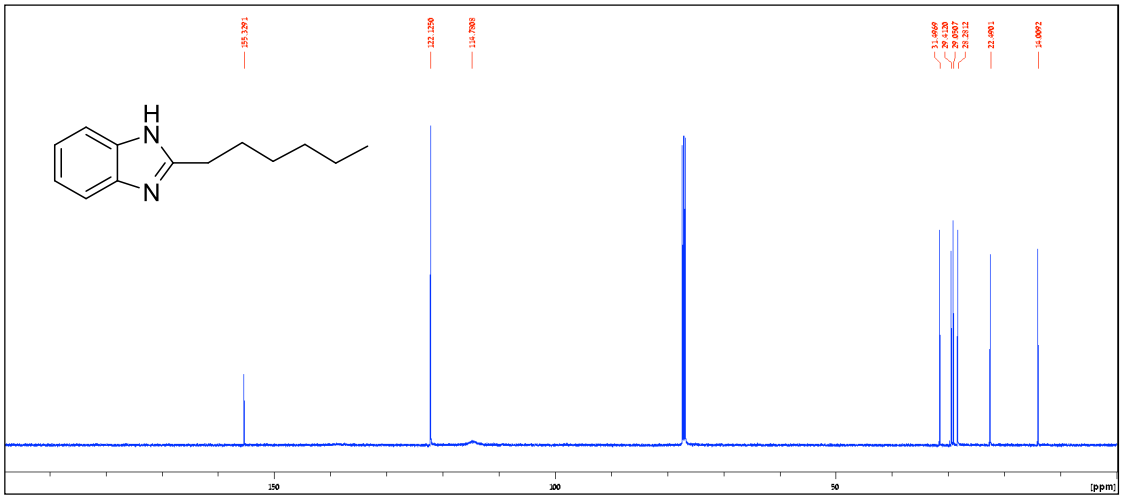


Figure S4. ^{13}C NMR of 2-hexylbenzimidazole in $CDCl_3$.

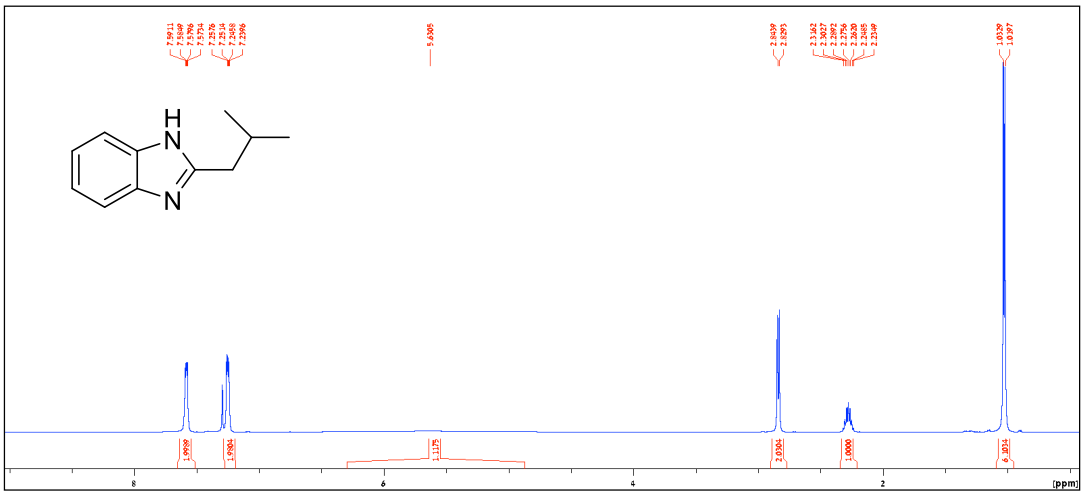


Figure S5. ^{1}H NMR of 2-isobutylbenzimidazole in $CDCl_3$.

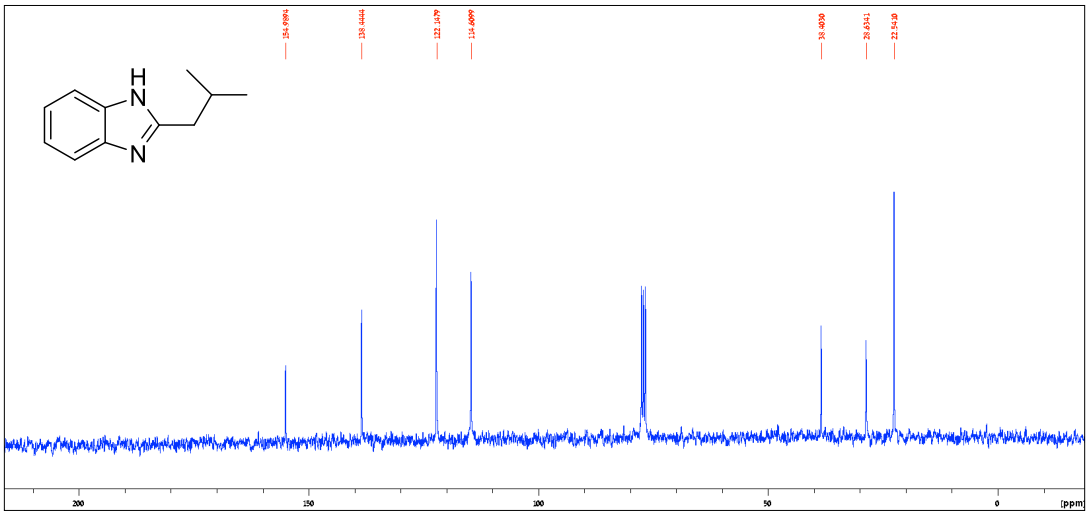


Figure S6. ^{13}C NMR of 2-isobutylbenzimidazole in $CDCl_3$.

Figure S7. ^{1}H NMR of 2-benzylbenzimidazole in $CDCl_3$.

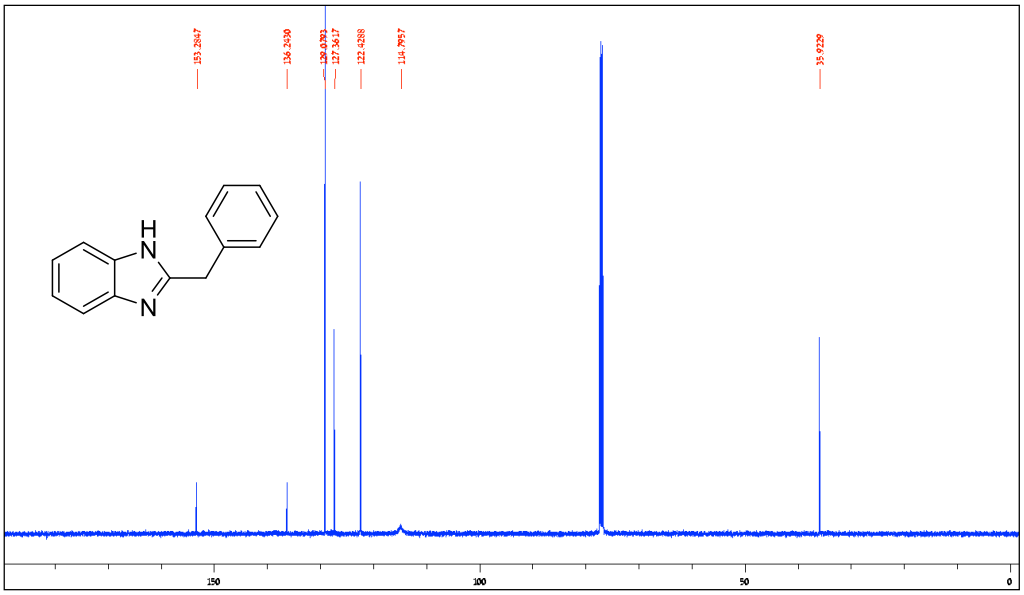


Figure S8. ^{13}C NMR of 2-benzylbenzimidazole in $CDCl_3$.

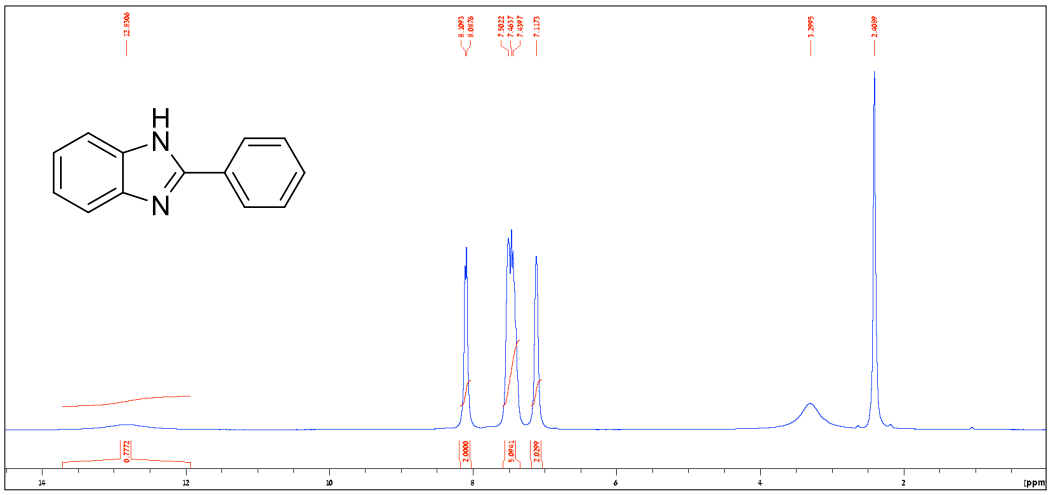


Figure S9. ^{1}H NMR of 2-phenylbenzimidazole in DMSO-d_6.

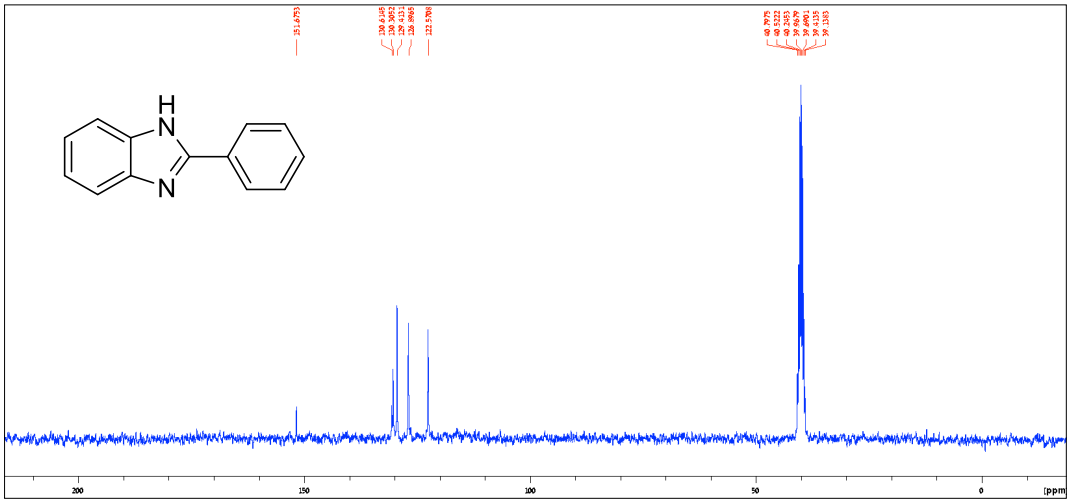


Figure S10. ^{13}C NMR of 2-phenylbenzimidazole in DMSO-d_6.

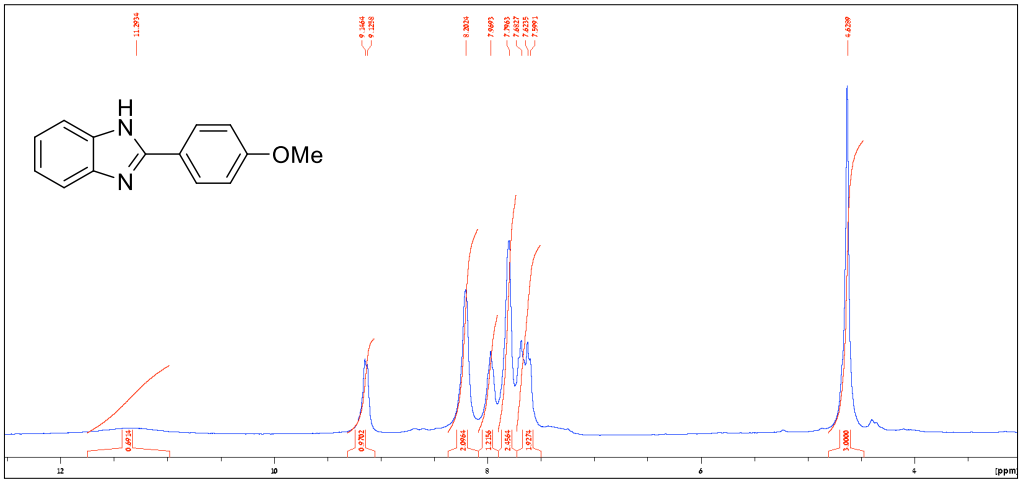


Figure S11. ^{1}H NMR of 2-(p-methoxyPhenyl)-benzimidazole in $CDCl_3$.

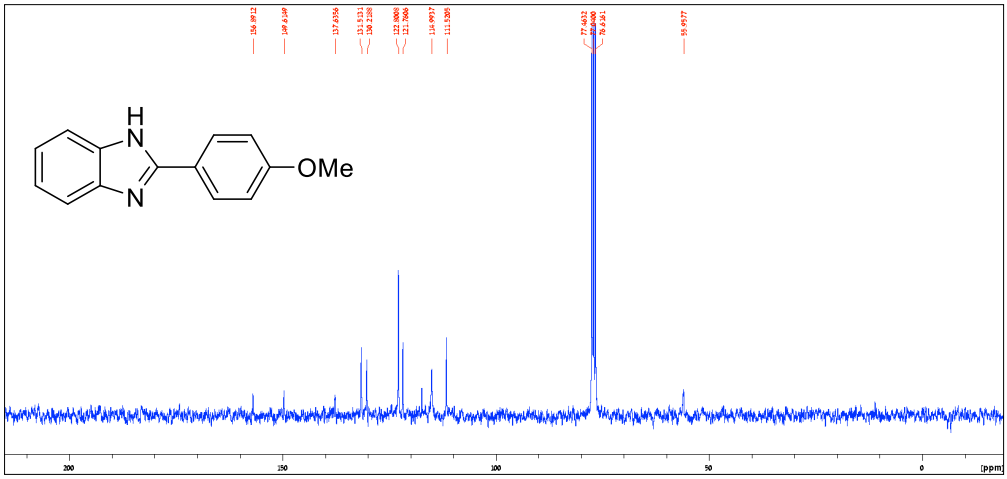


Figure S12.^{13}C NMR of 2-(p-methoxyphenyl)benzimidazole in $CDCl_3$

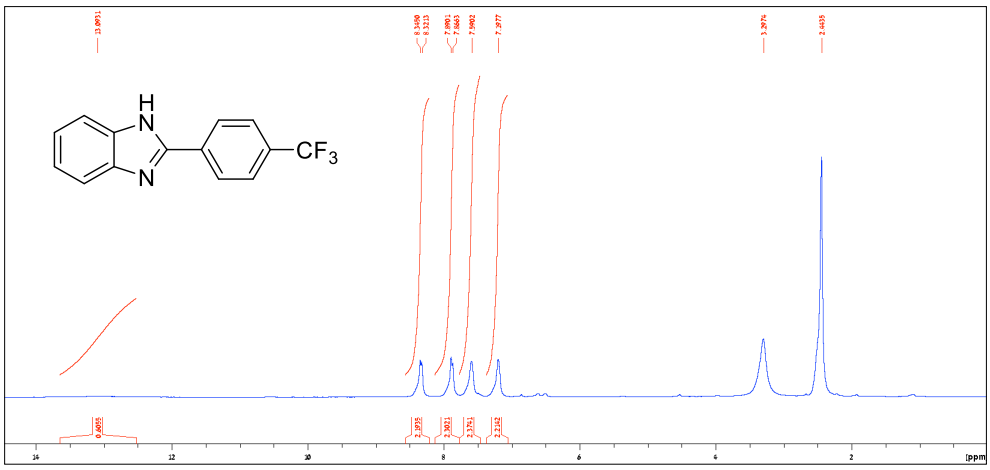


Figure S13. ^{1}H NMR of 2-(p-trifluoromethylphenyl)-benzimidazole in DMSO-d_6.

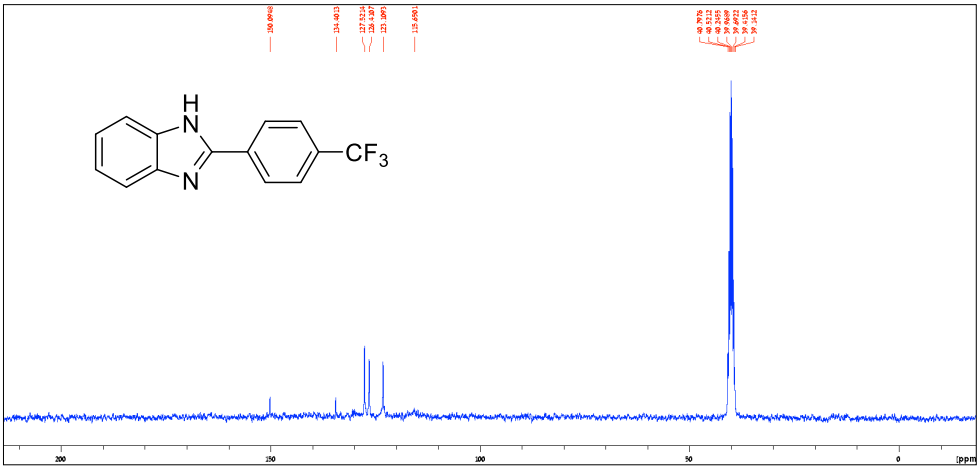


Figure S14. ^{13}C NMR of 2-(p-trifluoromethylphenyl)-benzimidazole in DMSO-d_6.

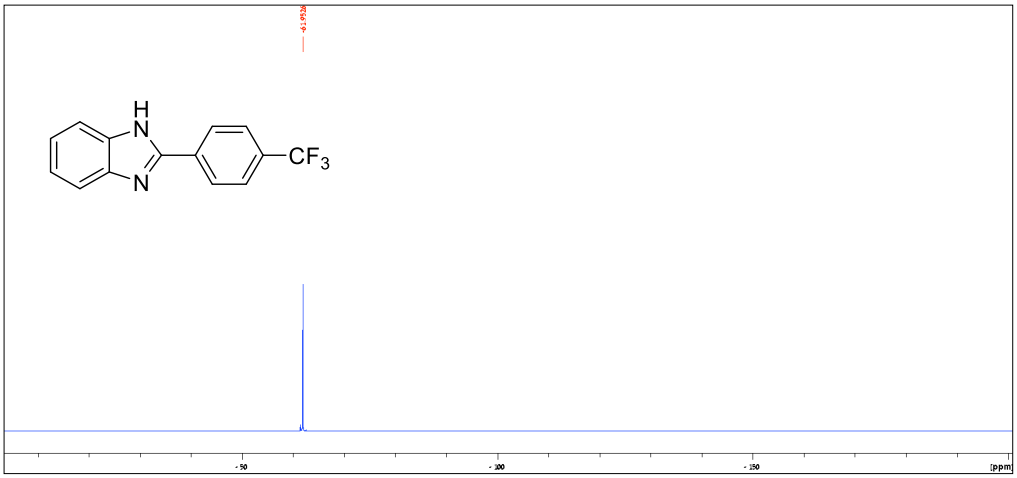


Figure S15. ^{19}F NMR of 2-(p-trifluoromethylphenyl)-benzimidazole in DMSO-d_6.

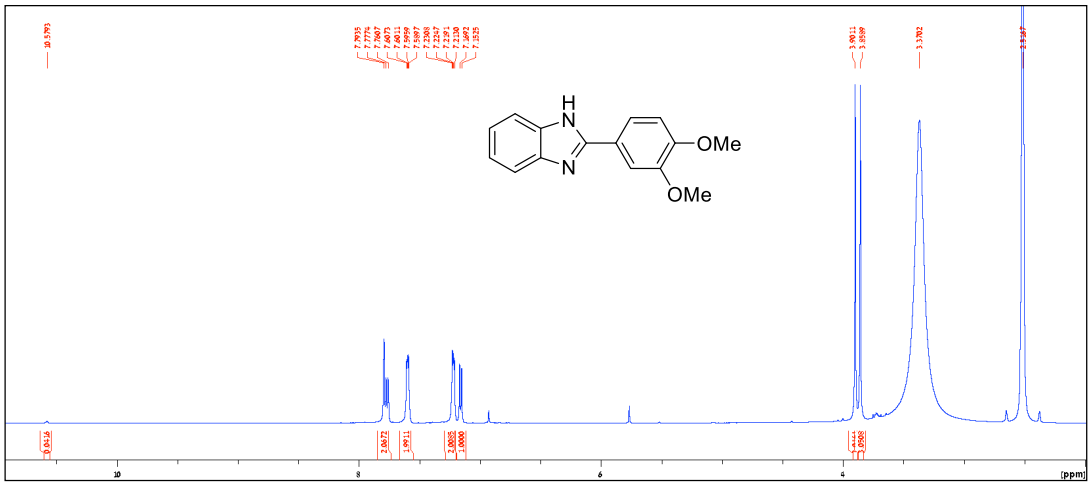


Figure S16. ^{1}H NMR of 2-(m,p-dimethoxyphenyl)-benzimidazole in DMSO-d_6.

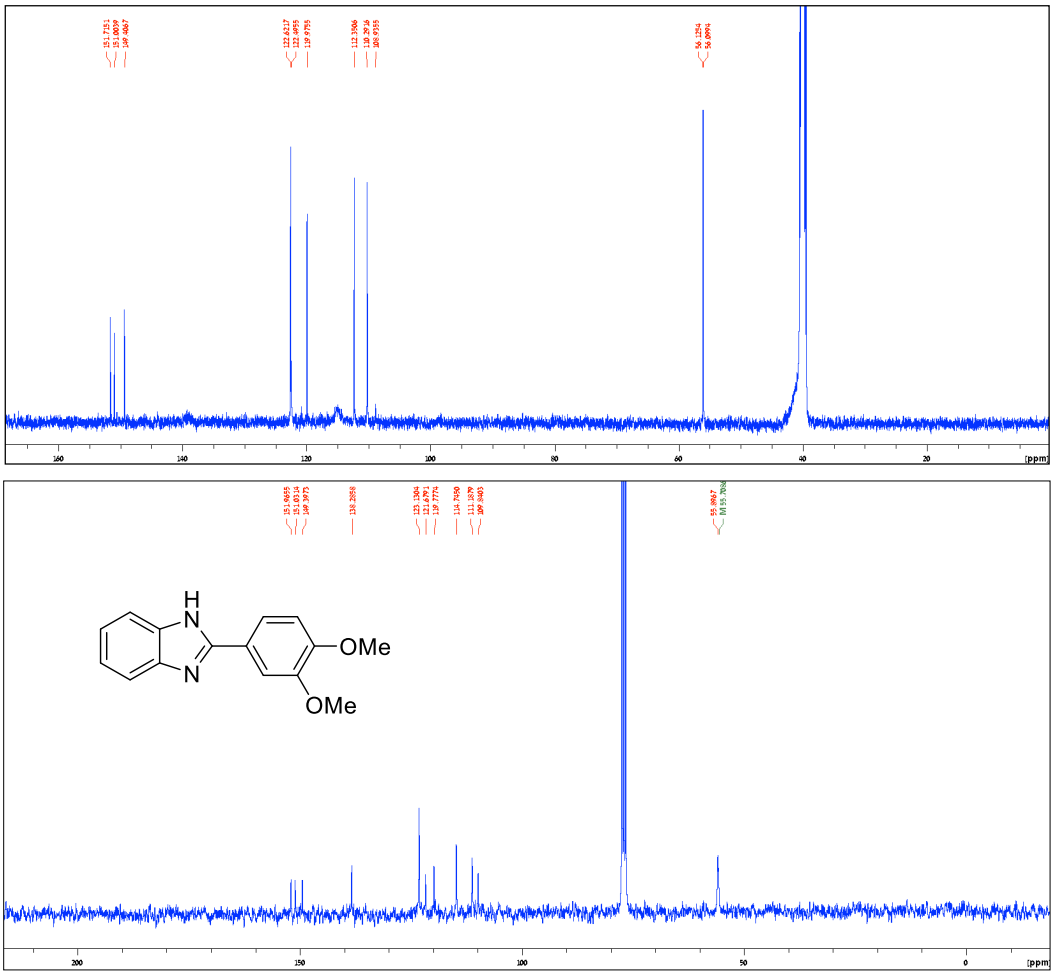


Figure S17. ^{13}C NMR of 2-(m,p-dimethoxyphenyl)-benzimidazole in DMSO-d_6 and $CDCl_3$.

Figure S18. ^{1}H NMR of 5-methyl-2-pentyl-benzimidazole in $CDCl_3$.

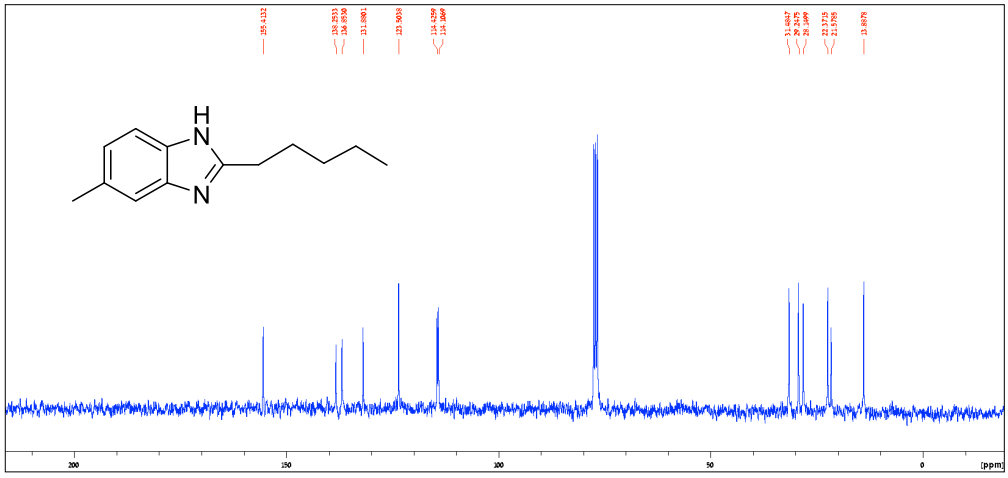


Figure S19. ^{13}C NMR of 5-methyl-2-pentylbenzimidazole in $CDCl_3$.

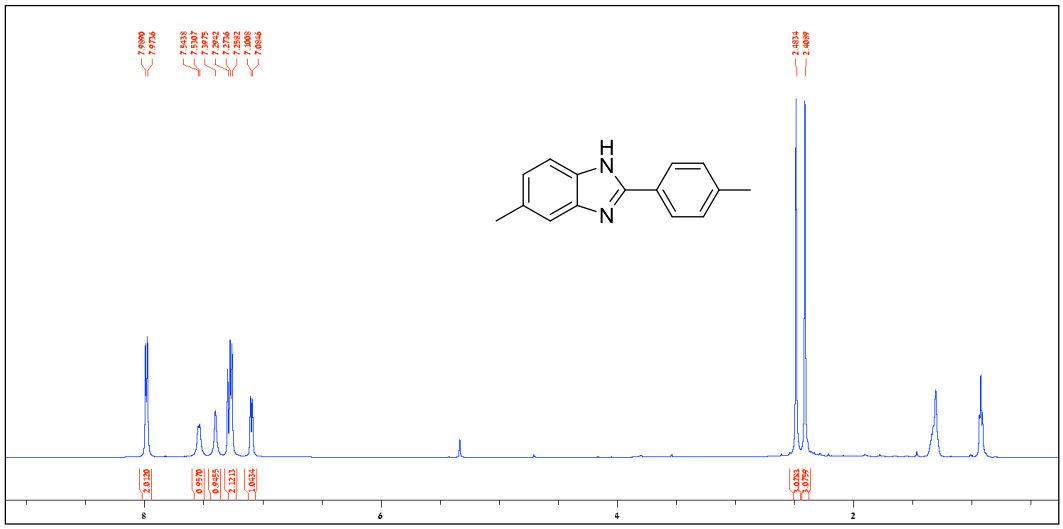


Figure S20. ^{1}H NMR of 5-methyl-2-(p-methylphenyl)-benzimidazole in $CDCl_3$.

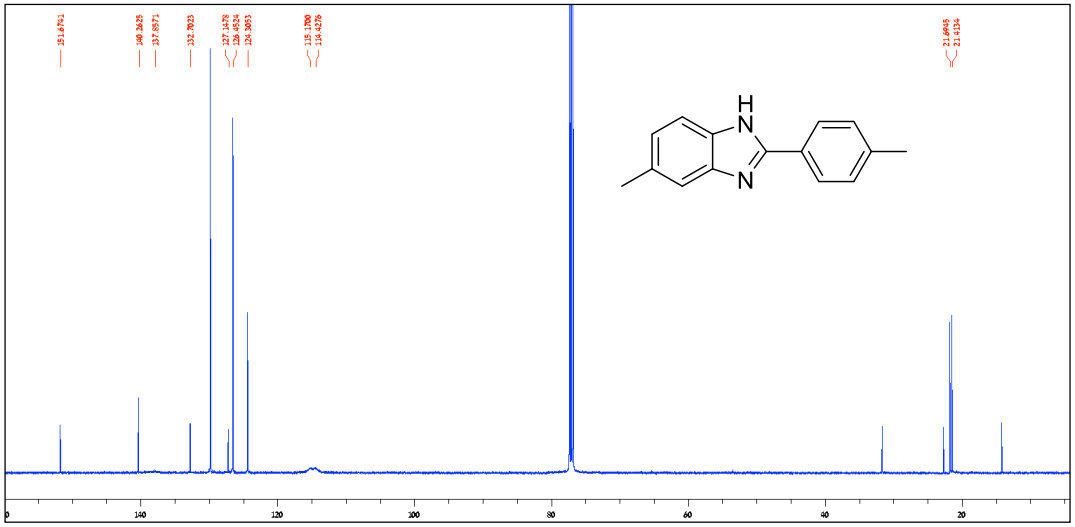


Figure S21. ^{13}C NMR of 5-methyl-2-(p-methylphenyl)-benzimidazole in $CDCl_3$.

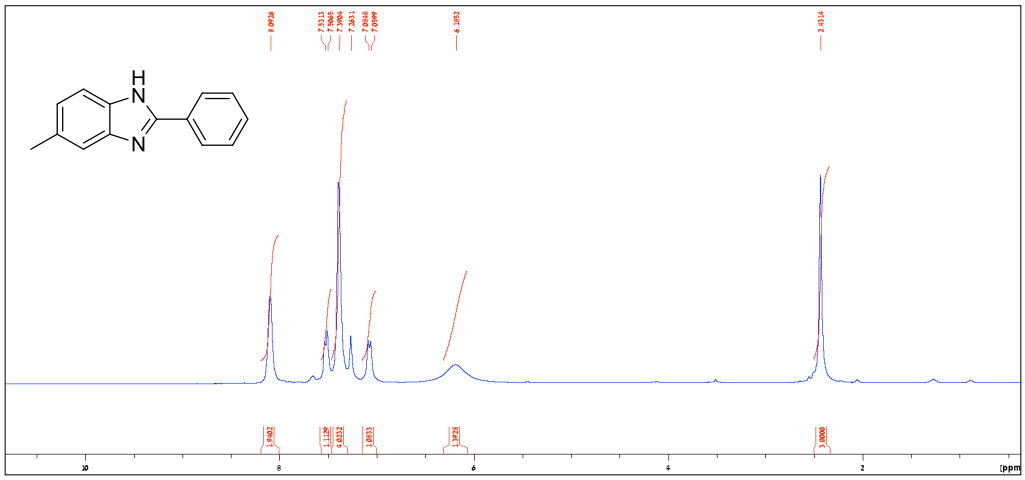


Figure S22. ^{1}H NMR of 5-methyl-2-phenyl-benzimidazole in $CDCl_3$.

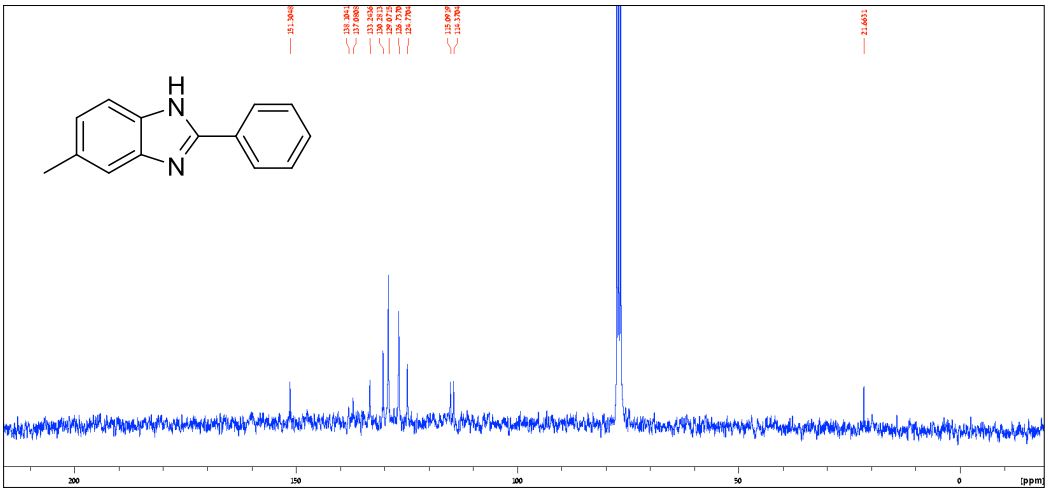


Figure S23. ^{13}C NMR of 5-methyl-2-phenyl-benzimidazole in $CDCl_3$.

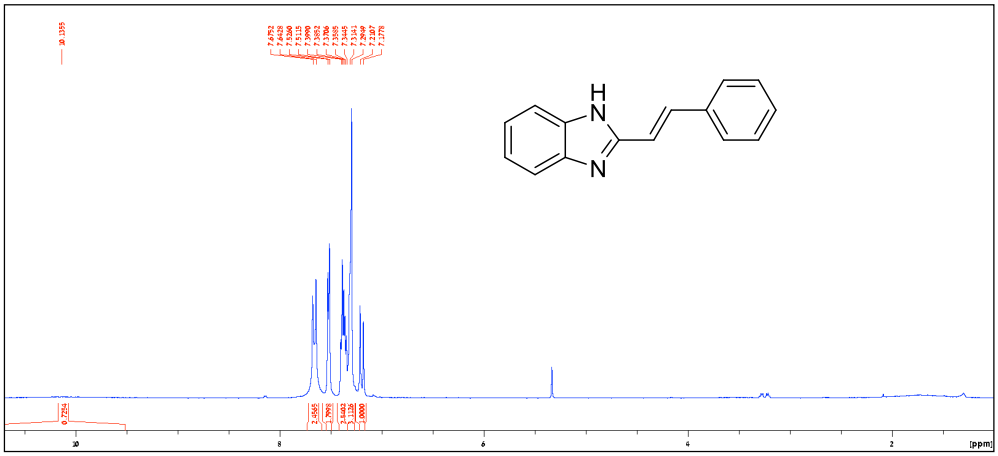


Figure S24. ^{1}H NMR of 2-styrylbenzimidazole in $CDCl_3$.

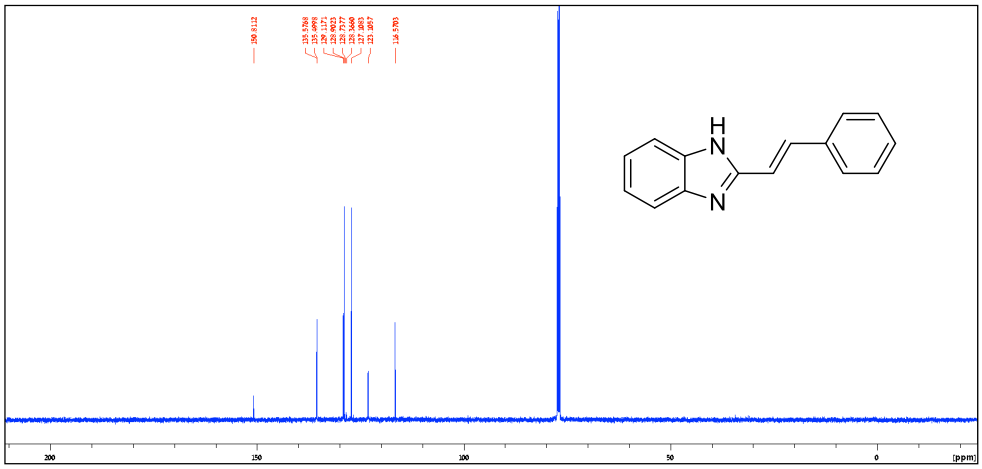


Figure S25. ^{13}C NMR of 2-styrylbenzimidazole in $CDCl_3$.

6. REFERENCES

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(3) Zhang, L.; Zuo, Z.; Leng, X.; Huang, Z. *Angew. Chem. Int. Ed.* **2014**, *53*, 2696-2700.

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