Supporting Information

Design strategy for arranging aromatic cyclic trimer in molecule

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Contents

Experimental Section

General experimental methods.

All starting materials and products were found to be stable in moisture and air. Starting materials such as 2-thiophenecarboxaldehyde, furan-2-carboxaldehyde, mesitylene, *o*-phenylenediamine and dimethylformamide were purchased from commercial sources and used as received. The ligands 2-thiophene-2-bezimidazole, 2-furan-2-benzimidazole and 1,3,5-tri(bromomethyl)-2,4,6-trimethylbenzene can be easily prepared, by a similar procedure to that reported earlier.[S1,S2] Elemental analyses were performed on a ElementarAnalysensysteme GmbH Vario EL-III instrument. ^{1}H and ^{13}C NMR spectra were recorded on an JEOL ECX 400 NMR spectrometer operating at 400 and 100.5 MHz, respectively. The chemical shifts are reported in parts per million (ppm) relative to residual solvent signal. Melting points for compounds were recorded in BUCHI laboratory equipment-Melting point M-560.

Synthesis of 1,3,5-tris(2-thiophenebenzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (1). A mixture of 2-thiophene-2-benzimidazole (889 mg, 4.44 mmol) and KOH (501 mg, 8.93 mmol) was stirred in dimethylformamide (10 mL) at room temperature for 1 h. The 1,3,5-tri(bromomethyl)-2,4,6-trimethylbenzene (592 mg, 1.48 mmol) was added to the reaction mixture and continuously allowed to stir for 72 h. The reaction was quenched by adding 200 mL of water. The white powders was collected by filtration and dissolved in hot methanol. Colourless crystals **1** were obtained at room temperature after few days. Yield: 90 % (1051 mg, 1.33 mmol). Mp. : 275 ºC (dec.). Anal. Calcd. for $C_{45}H_{36}N_6S_3 \cdot CH_3OH$ (M.wt. 789.04): C, 70.02; H, 5.11; N, 10.65; S, 12.19%. Found: C, 69.80; H, 5.28; N, 10.74; S, 12.37. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.84–7.83 (m, 6 H, $H^{4',5'}$, thiophene), 7.59 (d, 3 H, J_{HH} = 8.24 Hz, H^4, benzimidazolyl), 7.27 (t, 3 H, J_{HH} = 4.36 Hz, $H^{3'}$, thiophene), 7.12 (t, 3 H, J_{HH} = 7.8 Hz, H^5, benzimidazolyl), 6.64 (t, 3 H, J_{HH} = 7.8 Hz, H^6, benzimidazolyl), 6.29 (d, 3 H, J_{HH} = 8.28 Hz, H^7, benzimidazolyl), 5.74 (s, 6 H, methylene), and 1.99 (s, 9 H, H^9, –CH_3).

Synthesis of 1,3,5-tris(2-furanbenzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (2). A mixture of 2-furan-2-benzimidazole (807 mg, 4.38 mmol) and KOH (512 mg, 9.12 mmol) was stirred in dimethylformamide (10 mL) at room temperature for 1 h. The 1,3,5-tri(bromomethyl)-2,4,6-trimethylbenzene (591 mg, 1.48 mmol) was added to the reaction mixture and continuously allowed to stir for 72 h. Workup procedure was followed as **1**. Pale brown needle type crystals of **2** were obtained by crystallization from hot methanol after few

days at room temperature. Yield: 74 % (796 mg, 1.10 mmol). Mp: 278 ºC (dec.). Anal. Calcd for $C_{45}H_{36}N_6O_3 \cdot H_2O$ (M.wt. 726.82): C, 74.36; H, 5.27; N, 11.56%. Found: C, 74.09; H, 5.43; N, 11.48. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97 (d, 3 H, J_{HH} = 1.48 Hz, $H^{5'}$, furan), 7.59 (d, 3 H, J_{HH} = 8.08 Hz, H^4, benzimidazolyl), 7.28 (d, 3 H, J_{HH} = 3.64 Hz, $H^{3'}$, furan), 7.13 (t, 3 H, J_{HH} = 7.68 Hz, H^5, benzimidazolyl), 6.76-6.75 (m, 3 H, $H^{4'}$, furan), 6.64 (t, 3 H, J_{HH} = 7.7 Hz, H^6, benzimidazolyl), 6.35 (d, 3 H, J_{HH} = 8.04 Hz, H^7, benzimidazolyl), 5.83 (s, 6 H, methylene), and 2.09 (s, 9 H, H^9, –CH_3). ^{13}C NMR (100.5 MHz, DMSO-d_6): δ 145.17 (*C*H$^{5'}$, furan), 144.71 (*C*), 144.43 (*C*), 142.84 (*C*), 138.27 (*C*), 134.61 (*C*), 131.30 (*C*), 122.70 (*C*H^6, benzimidazolyl), 121.92 (*C*H^5, benzimidazolyl), 119.30 (*C*H^4, benzimidazolyl), 113.71 (*C*H$^{3'}$, furan), 112.10 (*C*H$^{4'}$, furan), 111.17 (*C*H^7, benzimidazolyl), 45.60 (*C*H$_2$) and 16.35 (*C*H$_3$).

X-ray Crystallography. Intensity data of suitably sized crystal of **1** was collected on an Oxford Xcalibur S diffractometer (4-circle *κ* goniometer, Sapphire-3 CCD detector, ω scans, graphite monochromator, and a single wavelength Enhance X-ray source with MoKα radiation).[S3] Pre-experiment, data collection, data reduction and absorption corrections were performed with the CrysAlisPro software suite.[S4] The structures were solved by direct methods using SIR 92,[S5] which revealed the atomic positions, and refined using the SHELX-97 program package[S6] and SHELXL97 (within the WinGX program package).[S7,S8] Non-hydrogen atoms were refined anisotropically. C–H hydrogen atoms were placed in geometrically calculated positions by using a riding model.

Reference

S1 X. Han, H. Ma and Y. Wang, *Rus. J. Org. Chem.* 2008, **44**, 863.

S2 A. W. van der Made and R. H. van der Made, *J. Org. Chem.* 1993, **58**, 1262.

S3 *ENHANCE, Oxford Xcalibur Single Crystal Diffractometer*, version 1.171.34.40; Oxford Diffraction Ltd: Oxford, U.K., 2006.

S4 *CrysAlisPro*, version 1.171.34.40; Oxford Diffraction Ltd: Oxford, U.K., 2006.

S5 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.* 1994, **27**, 435.

S6 G. M. Sheldrick, *SHELXL-97, Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.

S7 G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.

S8 L. J. Farrugia, *J. Appl. Crystallogr*. 1999, **32**, 837.

Table S1. The crystallographic data of **1**.

	1
formula	$C_{46}H_{40}N_6OS_3$
M_r	789.02
crystal system	orthorhombic
space group	*Pbca*
a (Å)	24.0070(17)
b (Å)	13.3108(7)
c (Å)	24.2954(14)
β (deg)	90.00
V (Å^3)	7763.7(8)
Z	8
T (K)	293 (2)
λ (Å)	0.71073
D_{calc} (g cm^{-3})	1.350
μ(Mo Kα) (mm^{-1})	0.237
no. of reflns collected	33730
no. of reflns used	6812
R_1 [$I > 2\sigma(I)$][a]	0.0909
wR_2 (all data)[b]	0.1479
GooF[c]	1.133
largest diff peak/hole (e Å^{-3})	0.23/–0.30

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;

[c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$

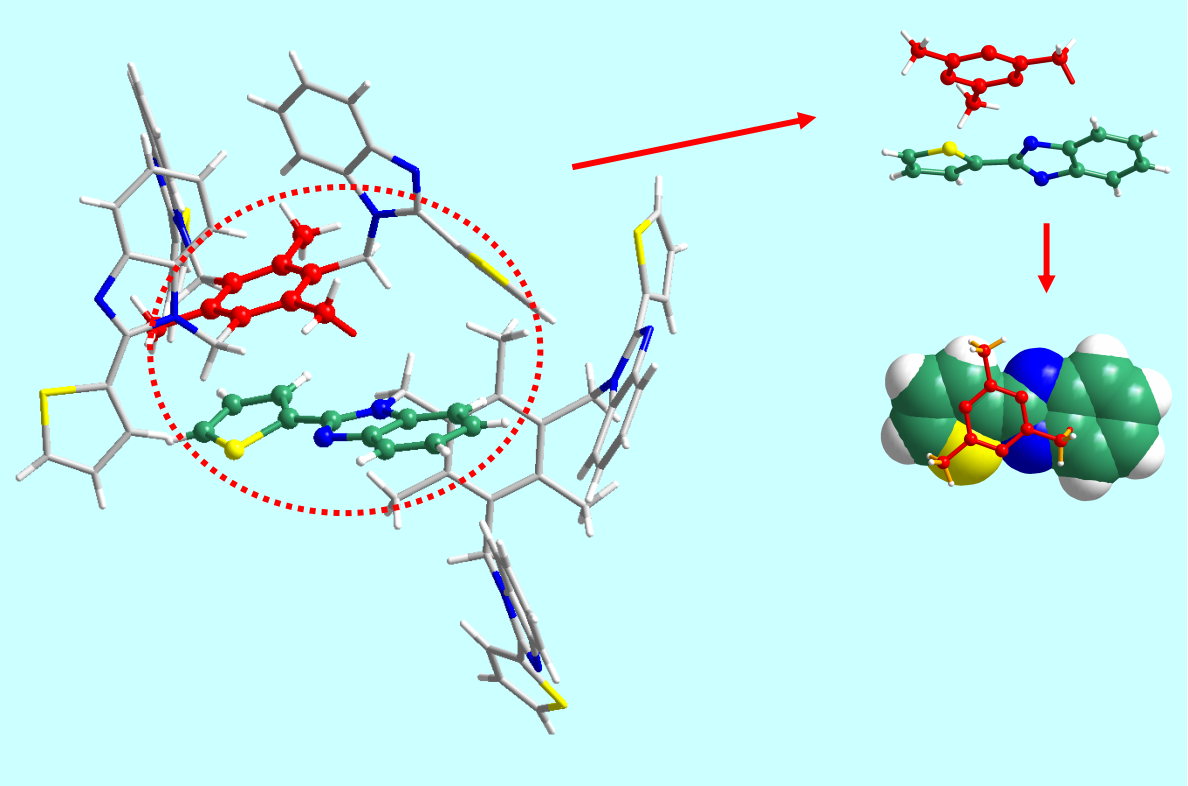


Fig. S1 Two adjacent molecules of **1** showing the π···π and C–H···π interactions.

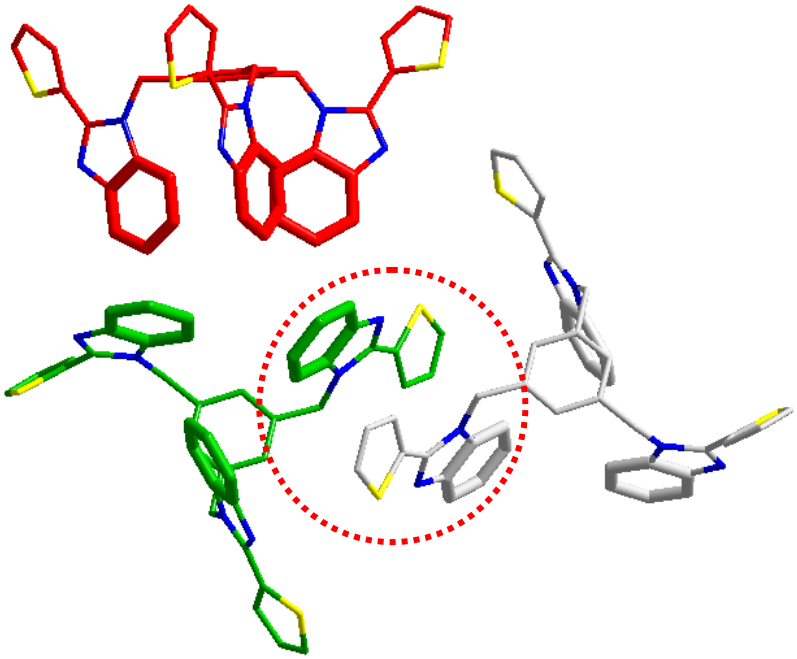


Fig. S2 Three adjacent molecules of **1** showing the *anti*-cofacial arrangement of two thiophene benzimidazolyl units. The methyl groups attached to the central aromatic ring are not shown for clarity.

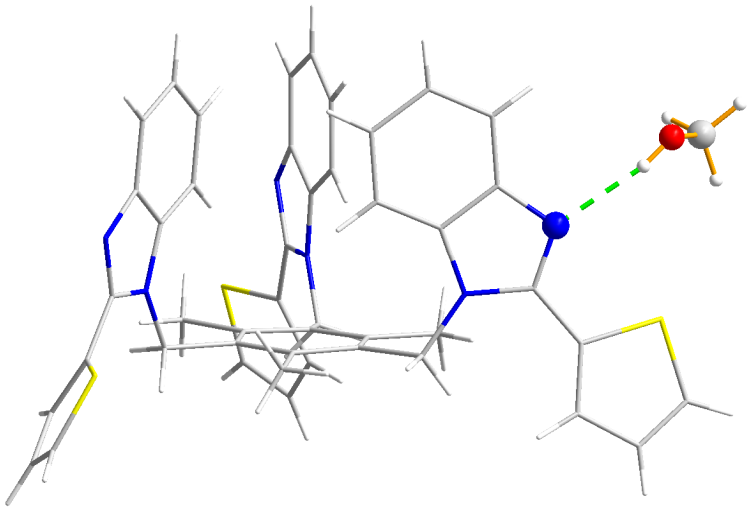


Fig. S3 Hydrogen bonding interaction between **1** and lattice methanol molecule.

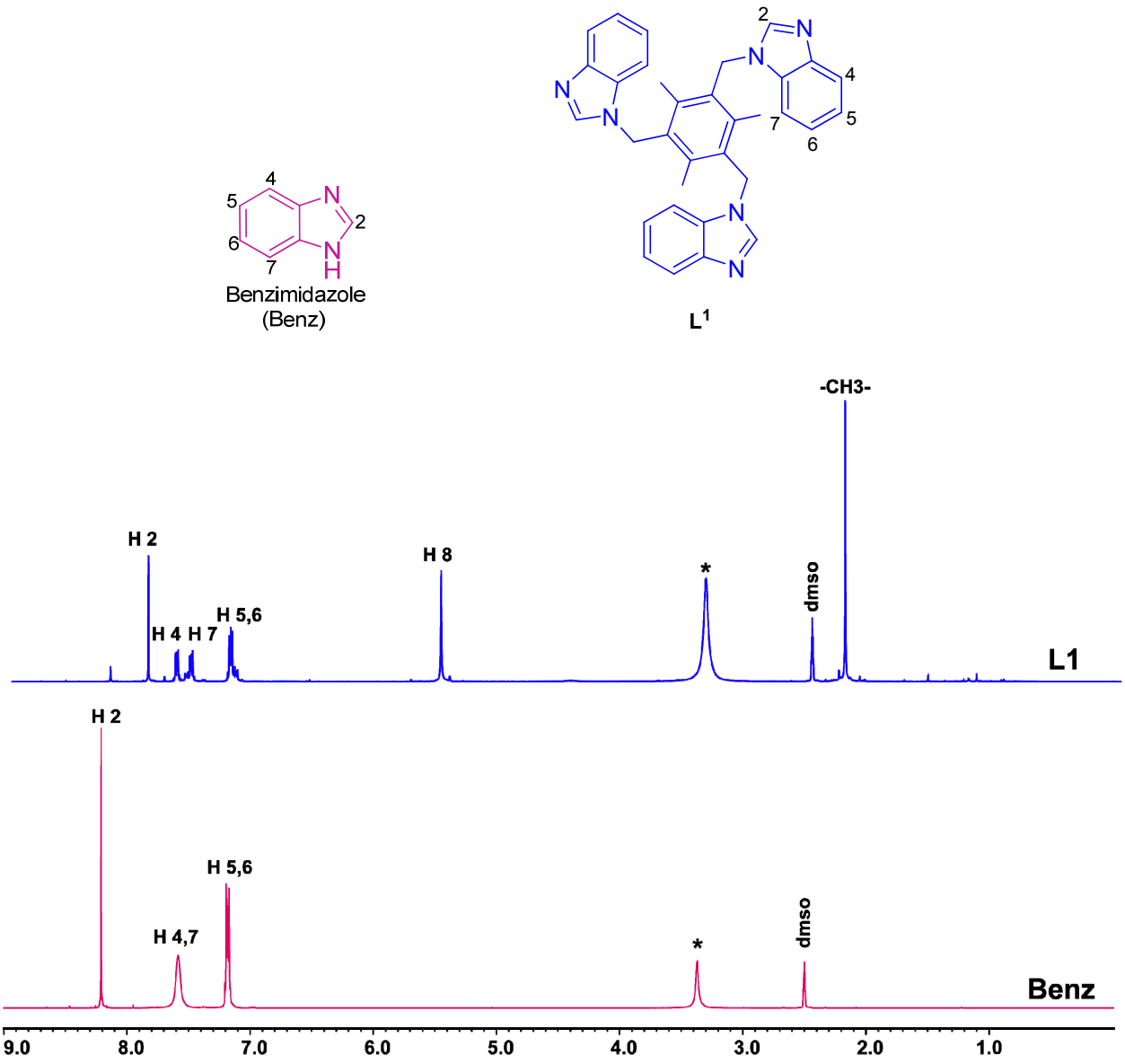
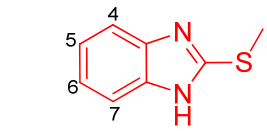
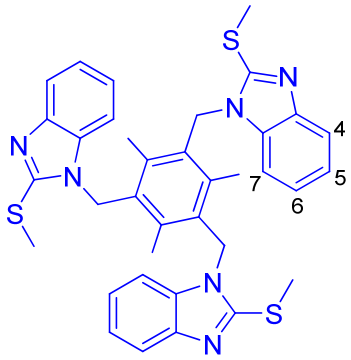


Fig. S4 The ^{1}H NMR spectra of benzimidazole and $\mathbf{L}^{1}$ in d_6-DMSO.



2-(Methylthio)bezimidazole
(Tbenz)



L^2

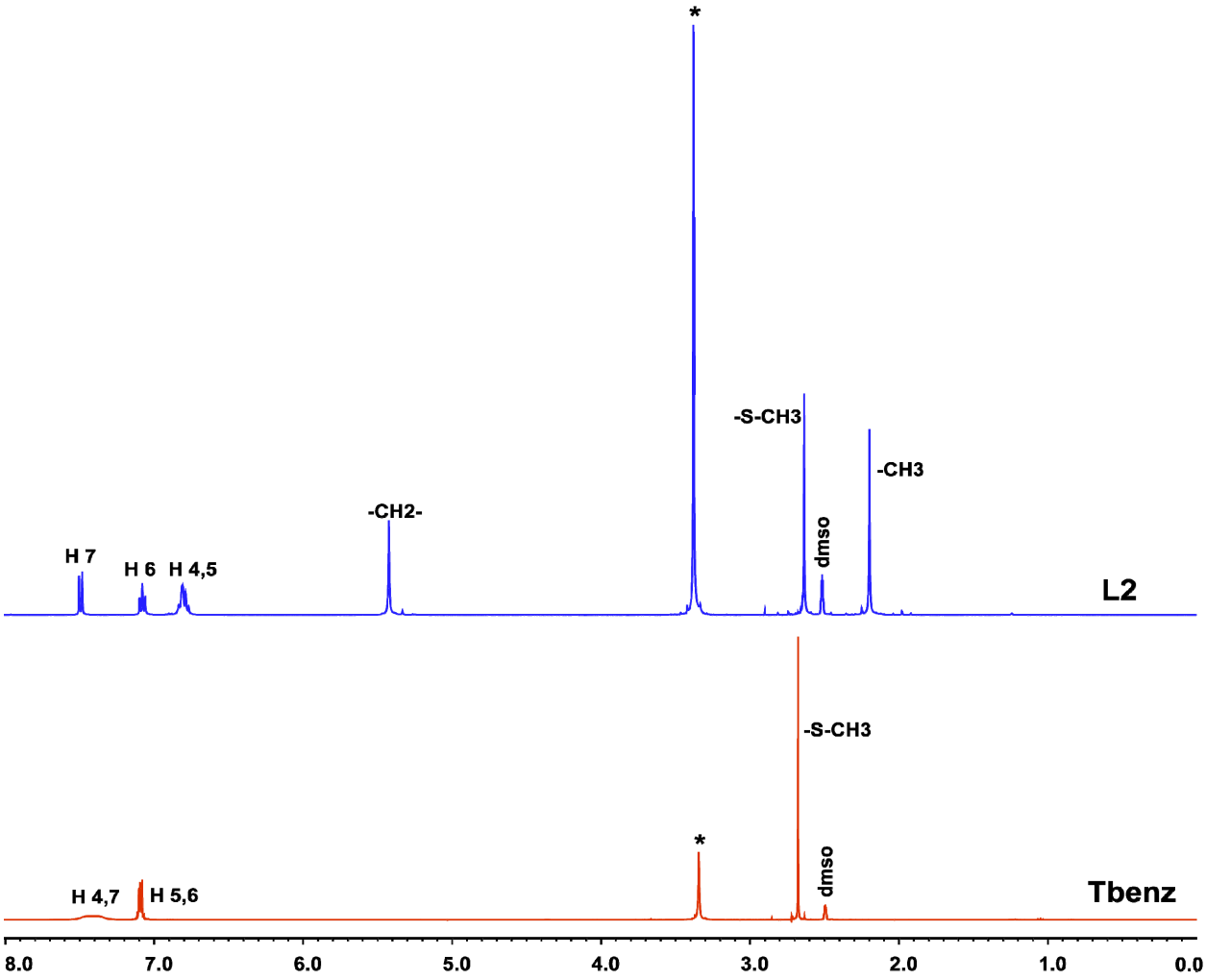


Fig. S5 The ^{1}H NMR spectra of 2-(methylthio)benzimidazole and $\mathbf{L^2}$ in d_6-DMSO.

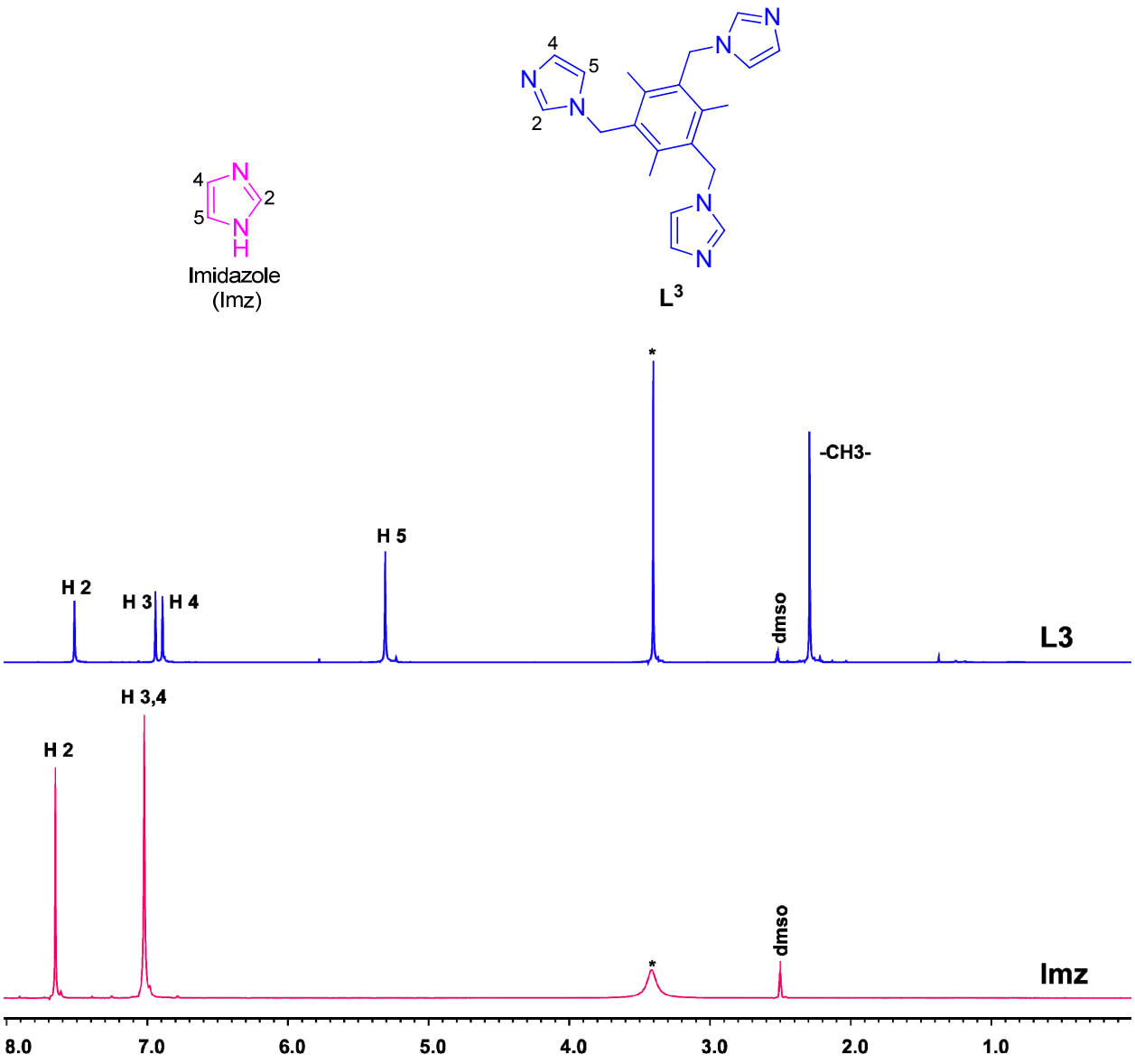


Fig. S6 The ^{1}H NMR spectra of imidazole and $\mathbf{L}^{3}$ in d_6-DMSO.