Supplementary Information

for

One step formation of amino derivative of *closo*-decaborate anion with *exo*-polyhedral benzimidazole groups during cadmium(II) complexation

Table S1. Crystal data and structure refinement for all compounds studied.

Compound	**1**	**5**	L^1
CCDC	2500848	2500849	2500850
Empirical formula	$C_{38}H_{56}B_{20}Cd_2N_{12}$	$C_{22}H_{38}B_{10}CdN_6O$	$C_{17}H_{15}N_5$
Formula weight	1121.94	623.08	289.34
Temperature, K	100.00	100	100.00
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$Pbca$	$P2_1/n$
a, Å	11.7328(6)	11.5923(7)	6.3413(7)
b, Å	16.9377(7)	20.2261(9)	7.4223(7)
c, Å	12.8151(7)	25.0151(16)	29.993(3)
β, °	101.554(2)	90	93.188(4)
Volume, $Å^3$	2495.1(2)	5865.2(6)	1409.5(2)
Z	2	8	4
d_{calc}, g/cm^3	1.493	1.411	1.363
μ, mm^{-1}	0.898	0.774	0.086
$F(000)$	1128.0	2544.0	608.0
Radiation	Mo$K\alpha$ ($\lambda = 0.71073$)	Mo$K\alpha$ ($\lambda = 0.71073$)	Mo$K\alpha$ ($\lambda = 0.71073$)
Index ranges	$-15 \le h \le 13$, $-21 \le k \le 18$, $-16 \le l \le 16$	$-14 \le h \le 15$, $-25 \le k \le 24$, $-19 \le l \le 32$	$-7 \le h \le 7$, $-8 \le k \le 8$, $-35 \le l \le 35$
Reflections collected	11251	30523	9727
Independent reflections	5513 [$R_{int} = 0.0563$]	6873 [$R_{int} = 0.0769$]	2491 [$R_{int} = 0.0869$]
Goodness-of-fit on F^2	1.033	1.022	1.036
Final R indexes [I>=2σ (I)]	$R_1 = 0.0528$, $wR_2 = 0.1097$	$R_1 = 0.0411$, $wR_2 = 0.0791$	$R_1 = 0.0823$, $wR_2 = 0.1876$
Final R indexes [all data]	$R_1 = 0.0872$, $wR_2 = 0.1242$	$R_1 = 0.0715$, $wR_2 = 0.0948$	$R_1 = 0.1479$, $wR_2 = 0.2238$

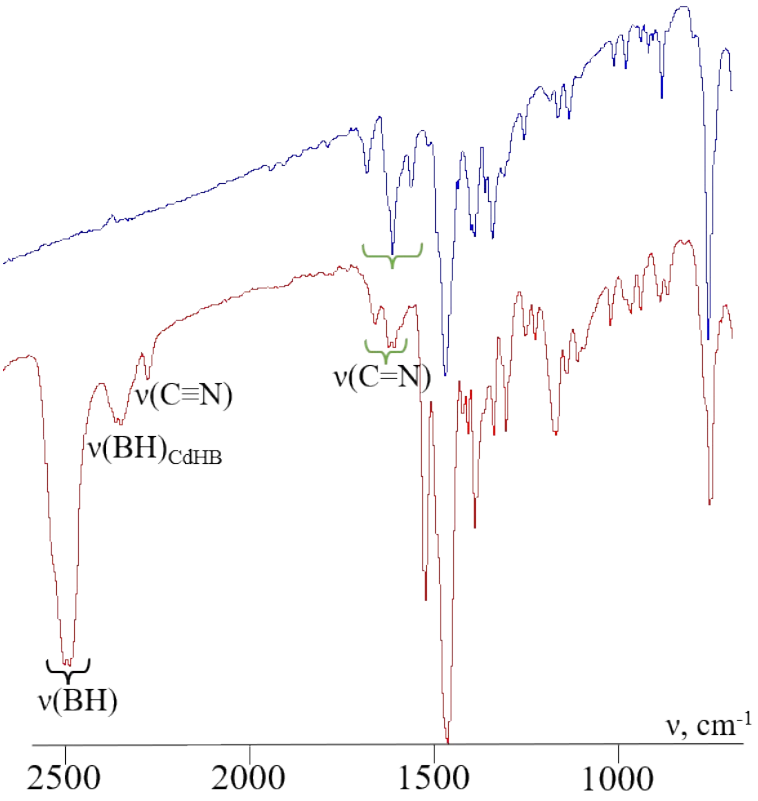

Fig. S1. Fragments of IR spectra of L^1 (blue) and complex **1** (red).

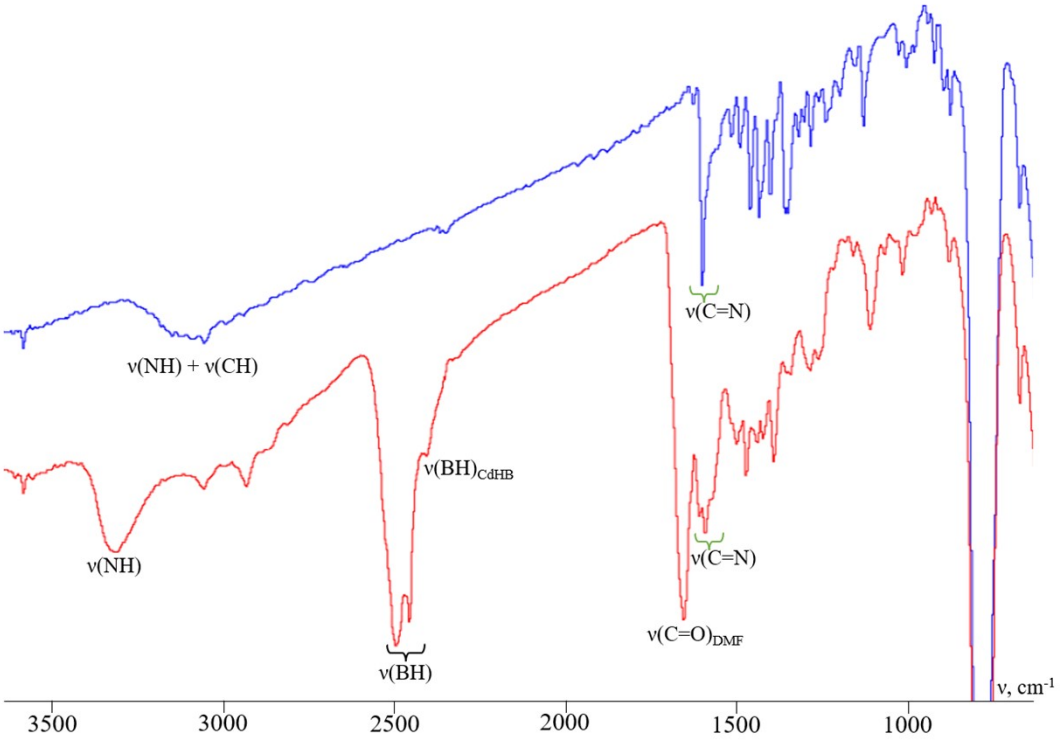

Fig. S2. IR spectra of L^2 (blue) and complex **2** (red).

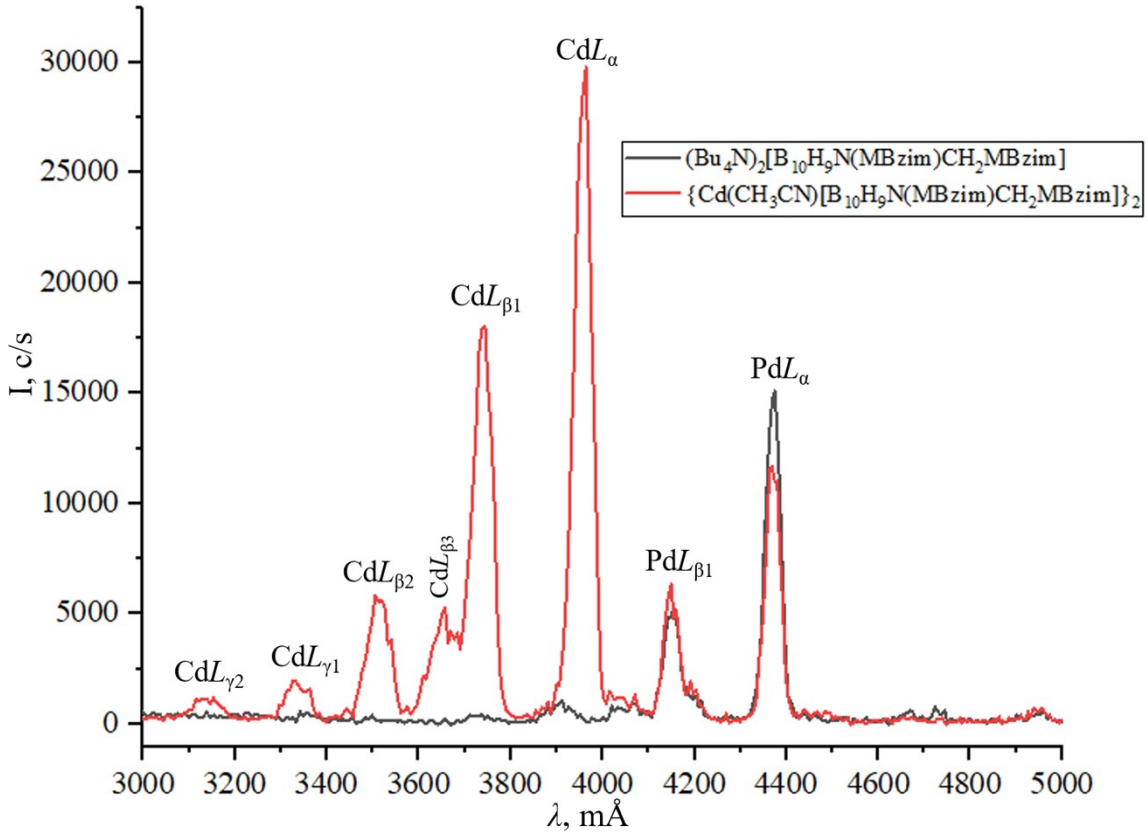

Fig. S3. X-ray spectral fluorescence spectra of $\{Cd(CH_3CN)[B_{10}H_9N(MBzim)CH_2MBzim]\}_2$ (**1**) (red) and $(Bu_4N)_2[B_{10}H_9N(MBzim)CH_2MBzim]$ (**3**) (black).

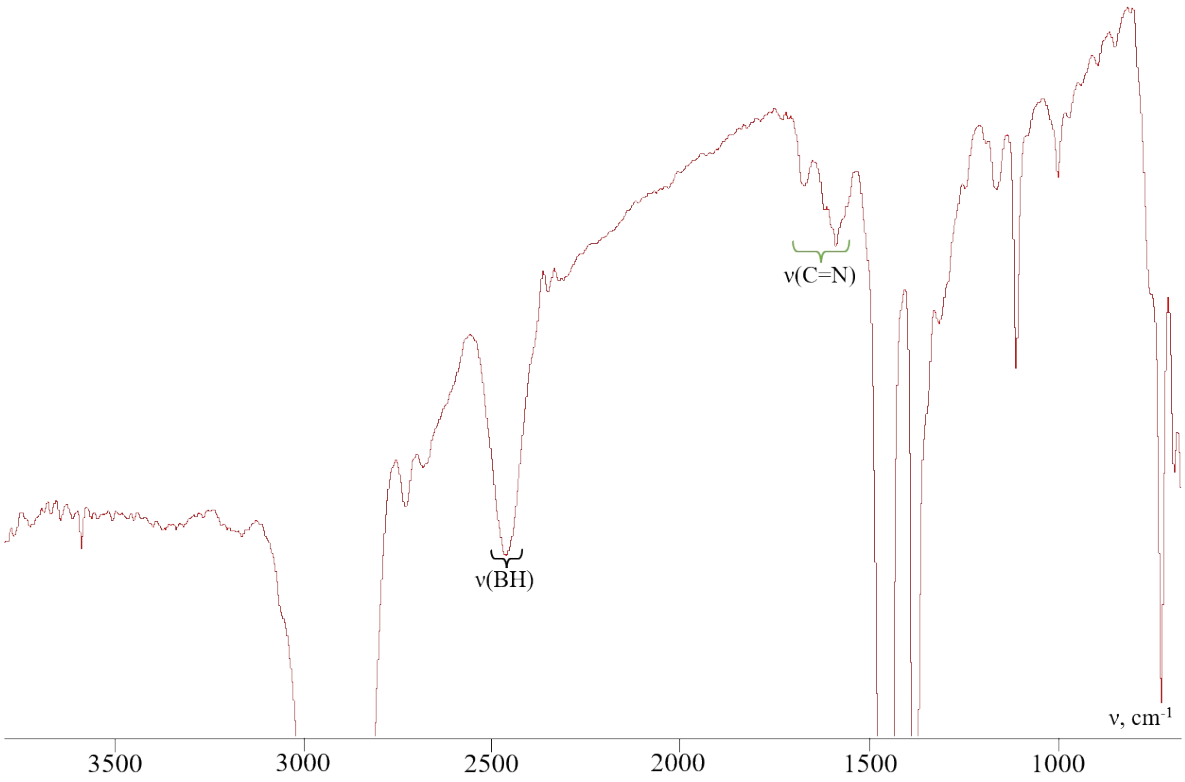

Fig. S4. IR spectrum of $(Bu_4N)_2[B_{10}H_9N(MBzim)CH_2MBzim]$ (**3**).

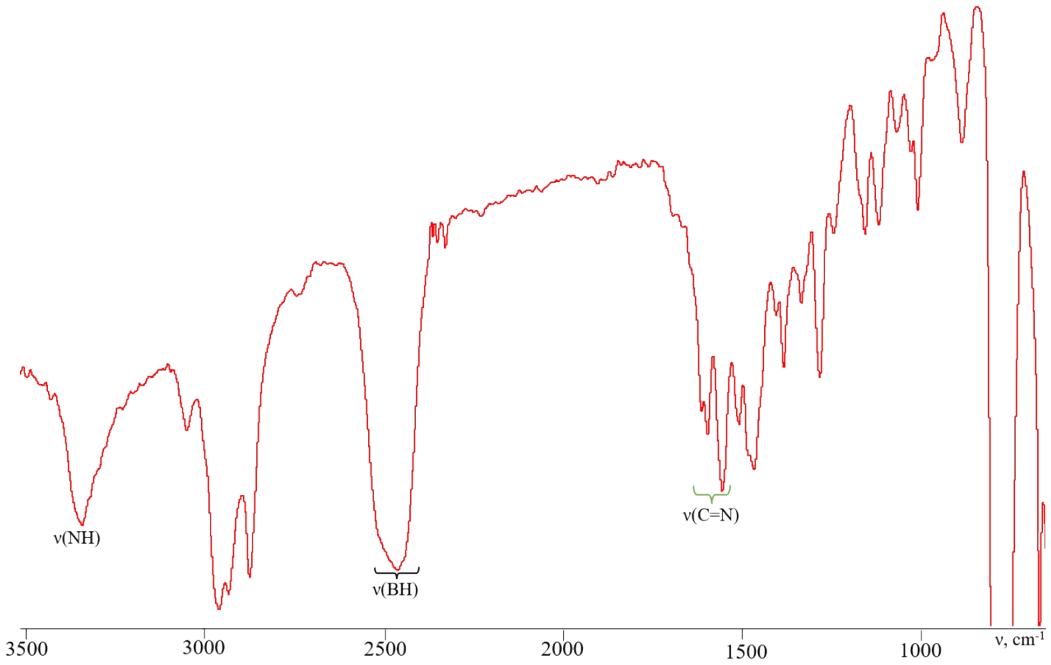

Fig. S5. IR spectrum of $(Bu_4N)_2[B_{10}H_9HN^+B(MBzim)CH_2Bzid^-]$ (**4**).

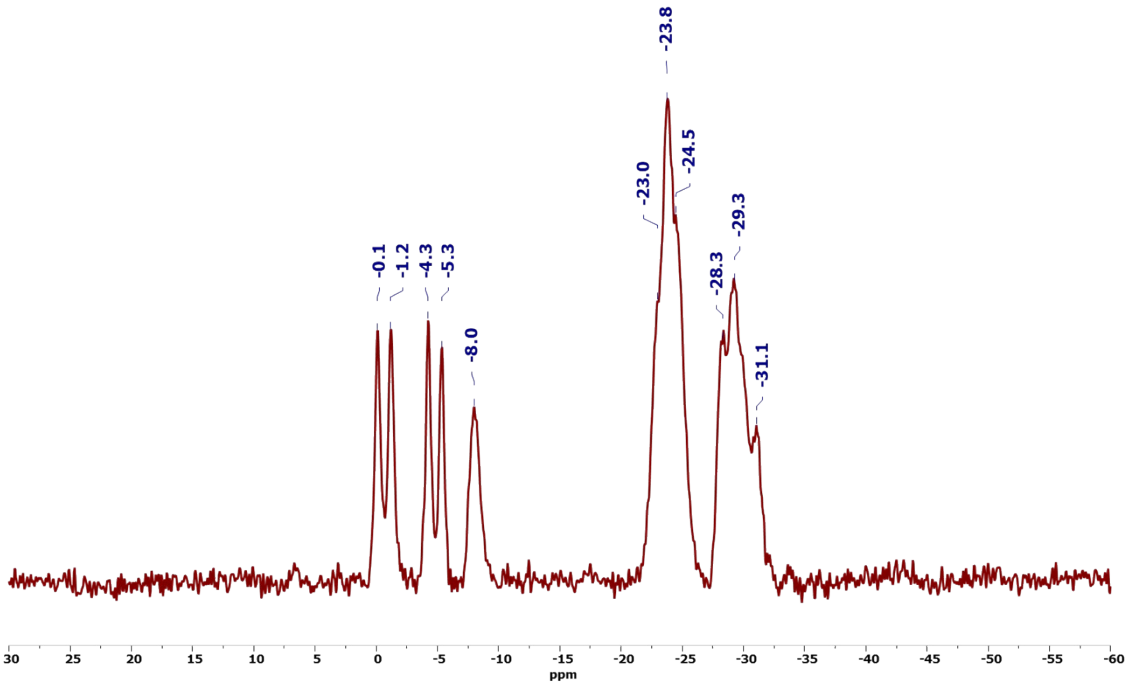

Fig. S6. ^{11}B NMR spectrum of $(Bu_4N)_2[B_{10}H_9N(MBzim)CH_2MBzim]$ (**3**) in $(CD_3)_2CO$.

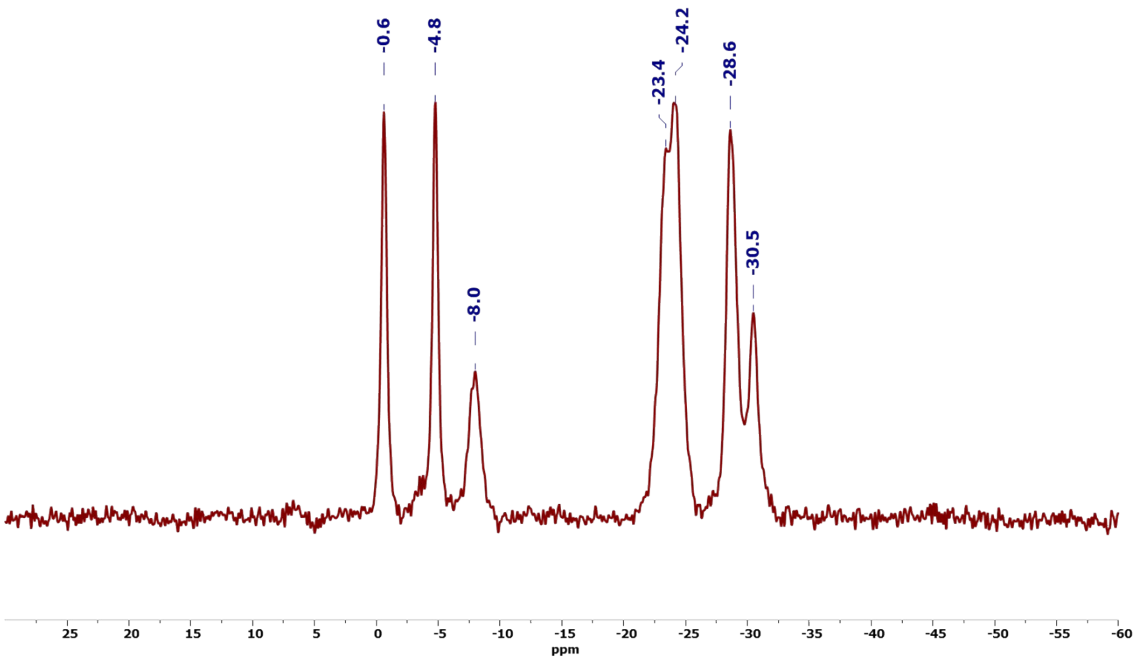

Fig. S7. $^{11}B\{^{1}H\}$ NMR spectrum of $(Bu_4N)_2[B_{10}H_9N(MBzim)CH_2MBzim]$ (**3**) in $(CD_3)_2CO$.

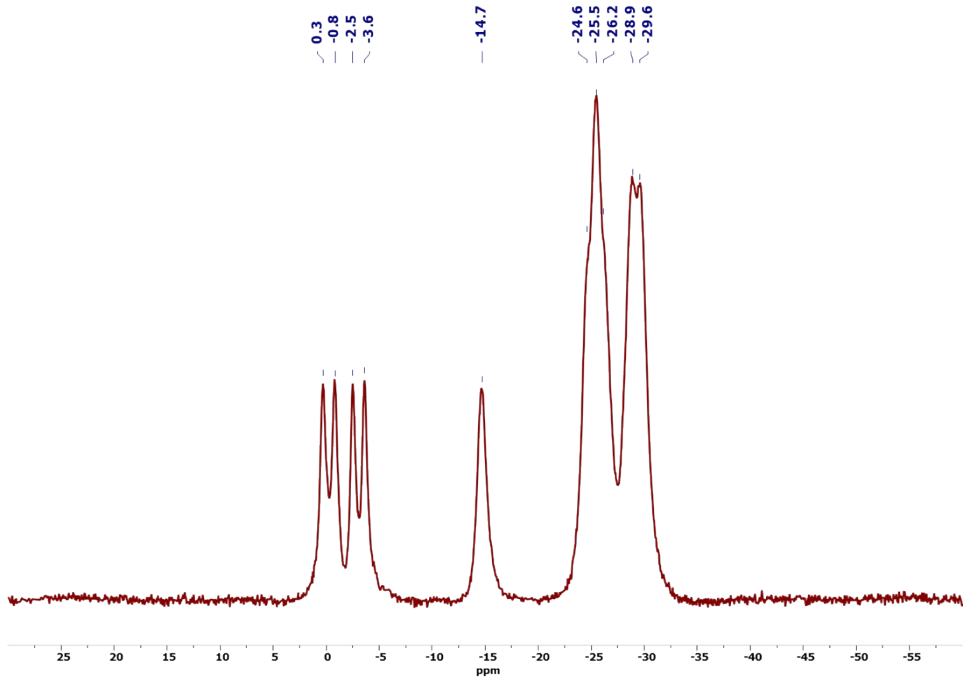

Fig. S8. ^{11}B NMR spectrum of $(Bu_4N)_2[B_{10}H_9HN^{+}B(MBzim)CH_2Bzid^{-}]$ (**4**) in $(CD_3)_2CO$.

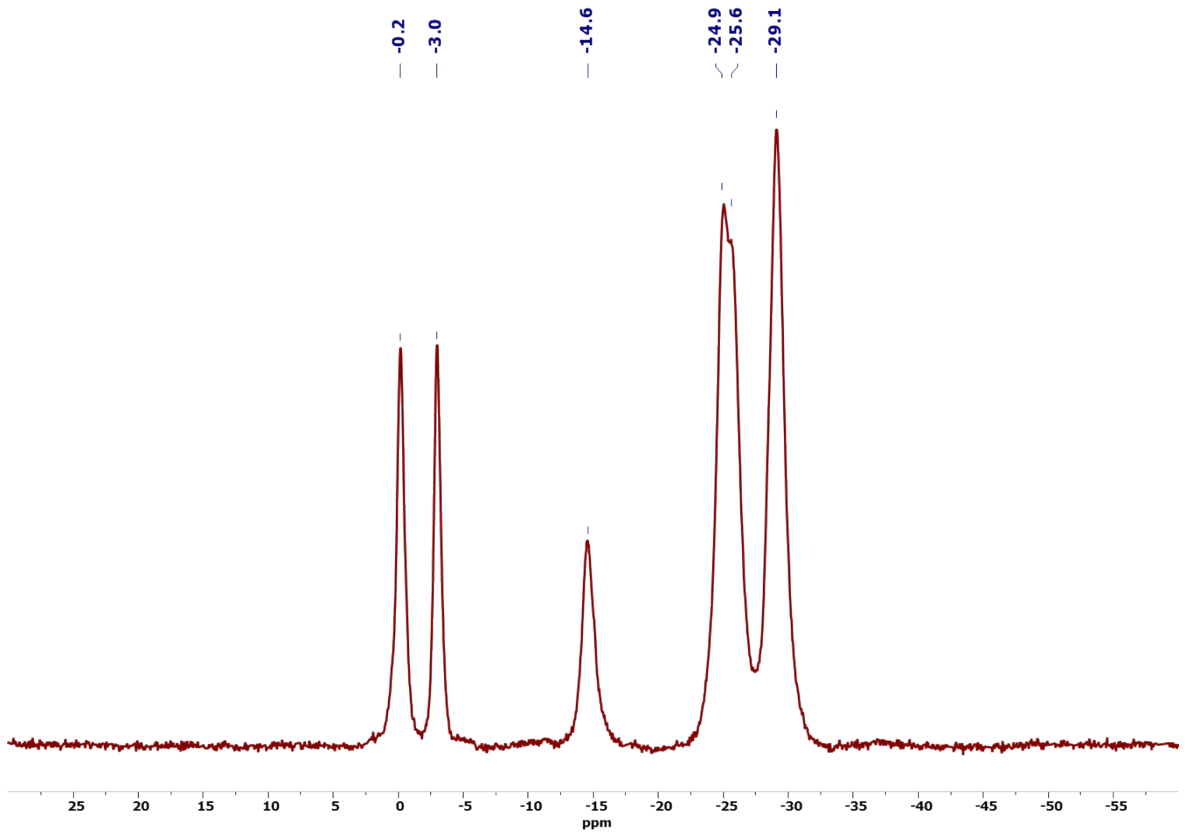

Fig. S9. $^{11}B\{^{1}H\}$ NMR spectrum of $(Bu_4N)_2[B_{10}H_9HN^{+}B(MBzim)CH_2Bzid^{-}]$ (**4**) in $(CD_3)_2CO$.

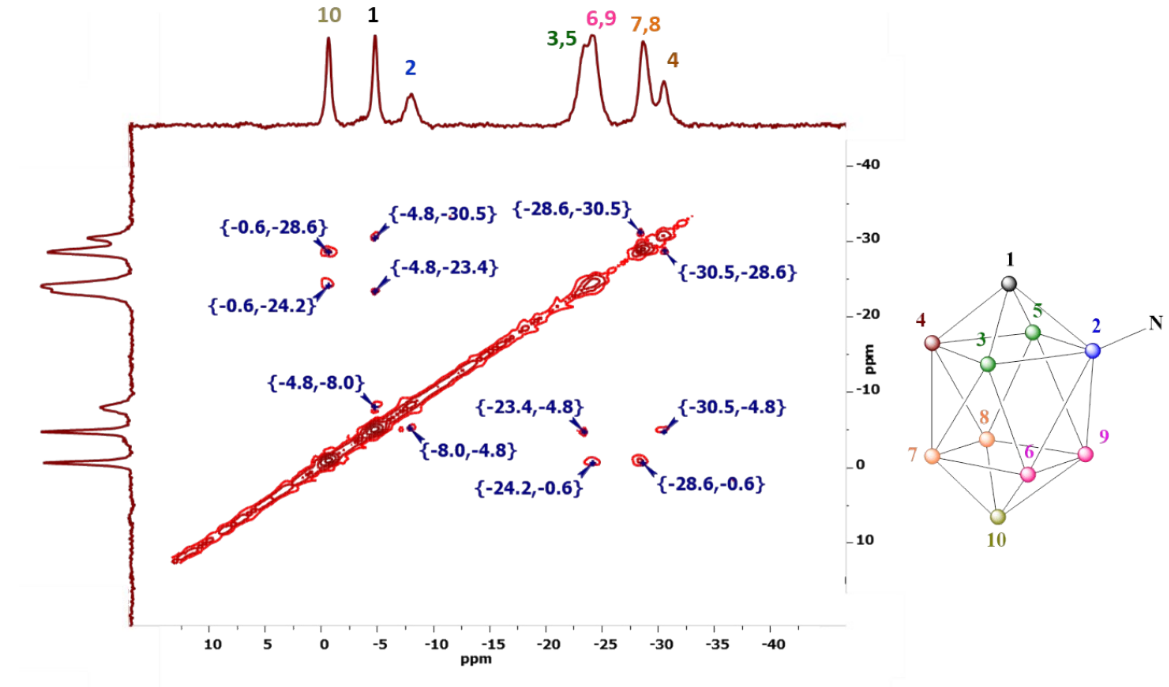

Fig. S10. COSY $^{11}B\{^{1}H\}$–$^{11}B\{^{1}H\}$ NMR spectrum of $(Bu_4N)_2[B_{10}H_9N(MBzim)CH_2MBzim]$ (**3**) in $(CD_3)_2CO$ using additional symmetry function.

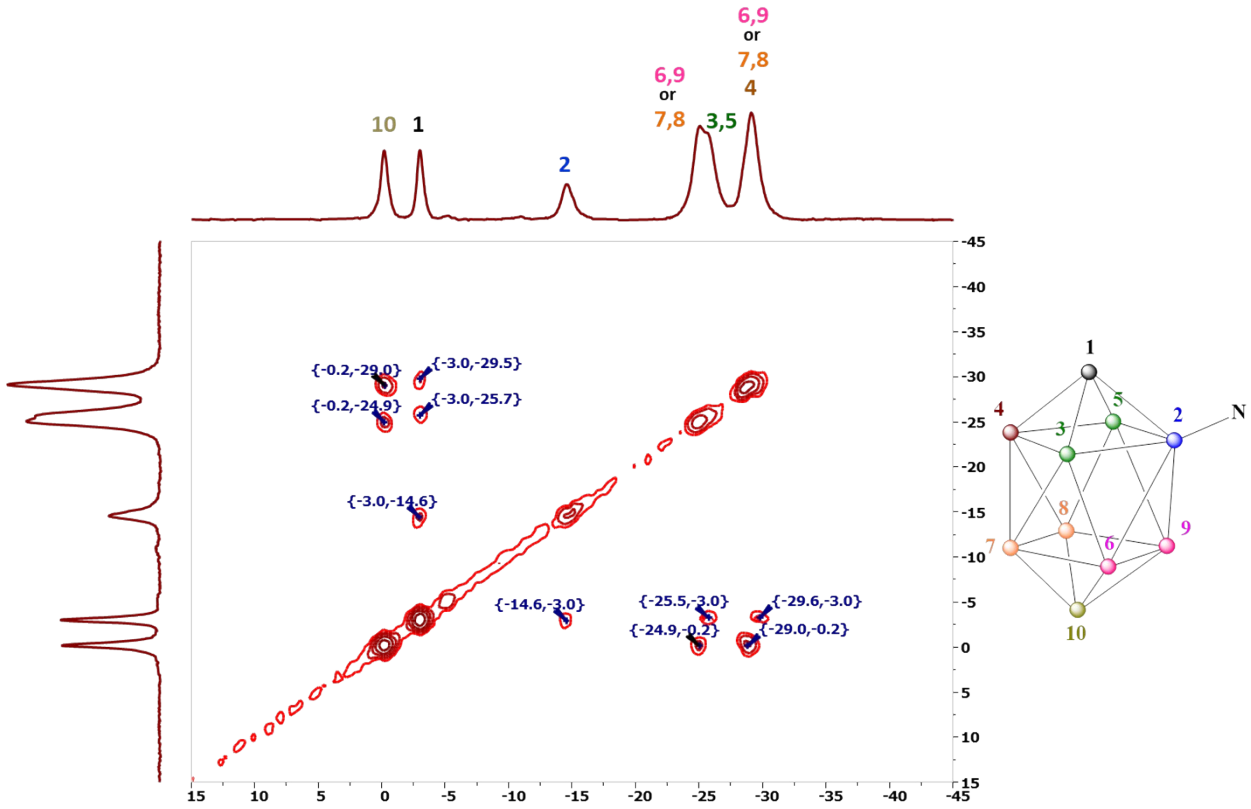

Fig. S11. COSY $^{11}B\{^1H\}$–$^{11}B\{^1H\}$ NMR spectrum of $(Bu_4N)_2[B_{10}H_9HN^+B(MBzim)CH_2Bzid^-]$ (**4**) in $(CD_3)_2CO$.

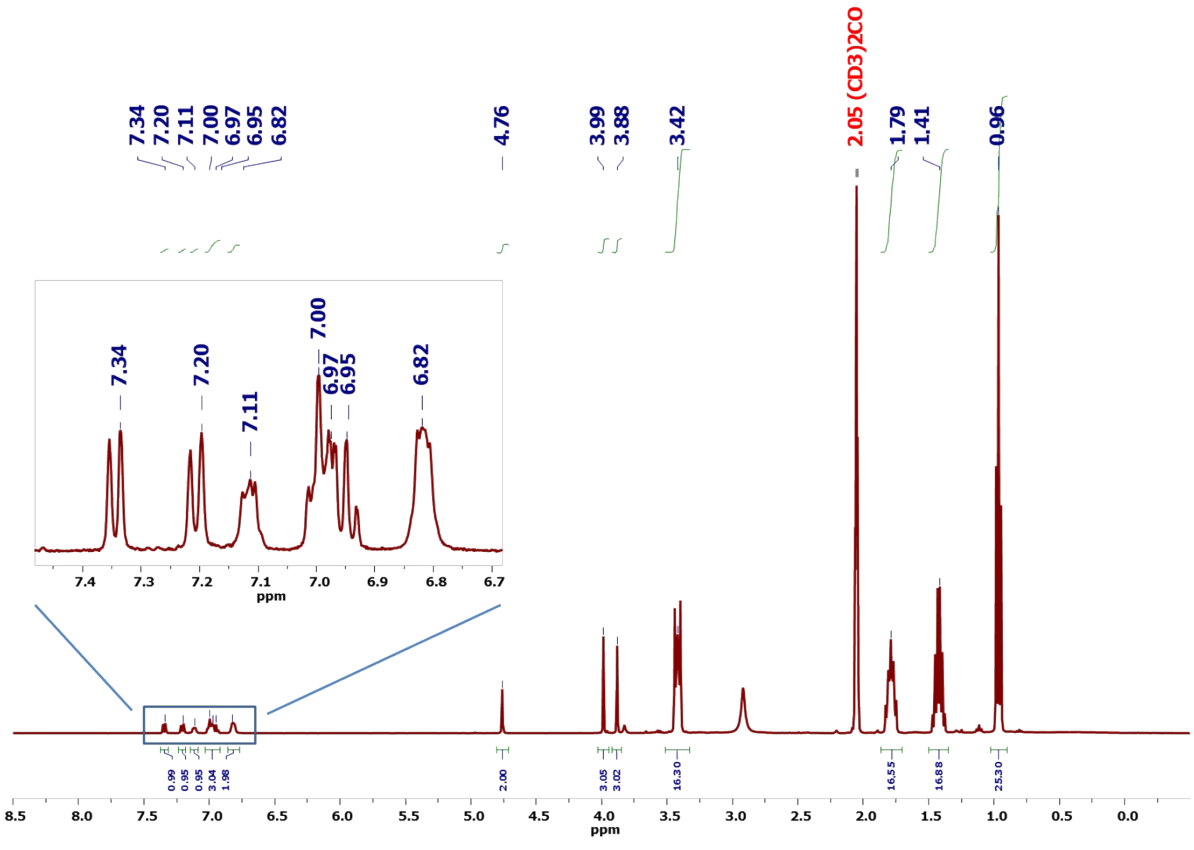

Fig. S12. ^1H NMR spectrum of $(Bu_4N)_2[B_{10}H_9N(MBzim)CH_2MBzim]$ (**3**) in $(CD_3)_2CO$.

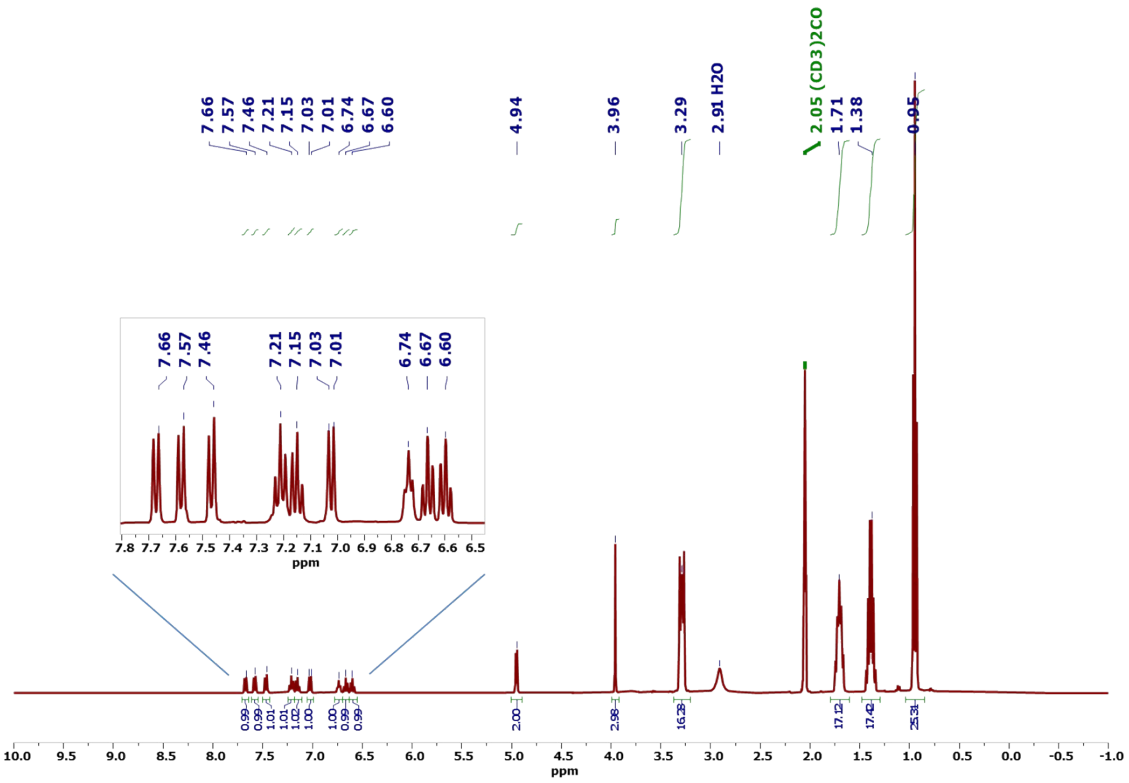

Fig. S13. ^{1}H NMR spectrum of $(Bu_4N)_2[B_{10}H_9HN^{+}B(MBzim)CH_2Bzid^{-}]$ (**4**) in $(CD_3)_2CO$.

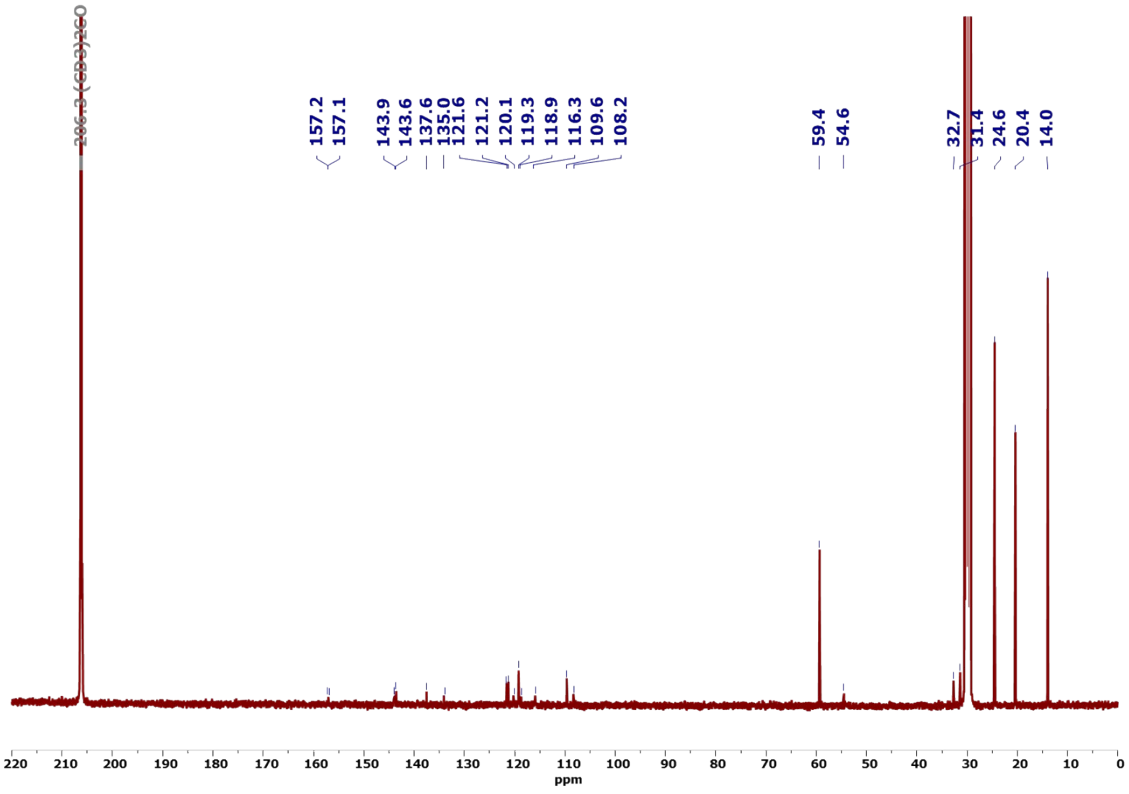

Fig. S14. $^{13}C\{^{1}H\}$ NMR spectrum of $(Bu_4N)_2[B_{10}H_9N(MBzim)CH_2MBzim]$ (**3**) in $(CD_3)_2CO$.

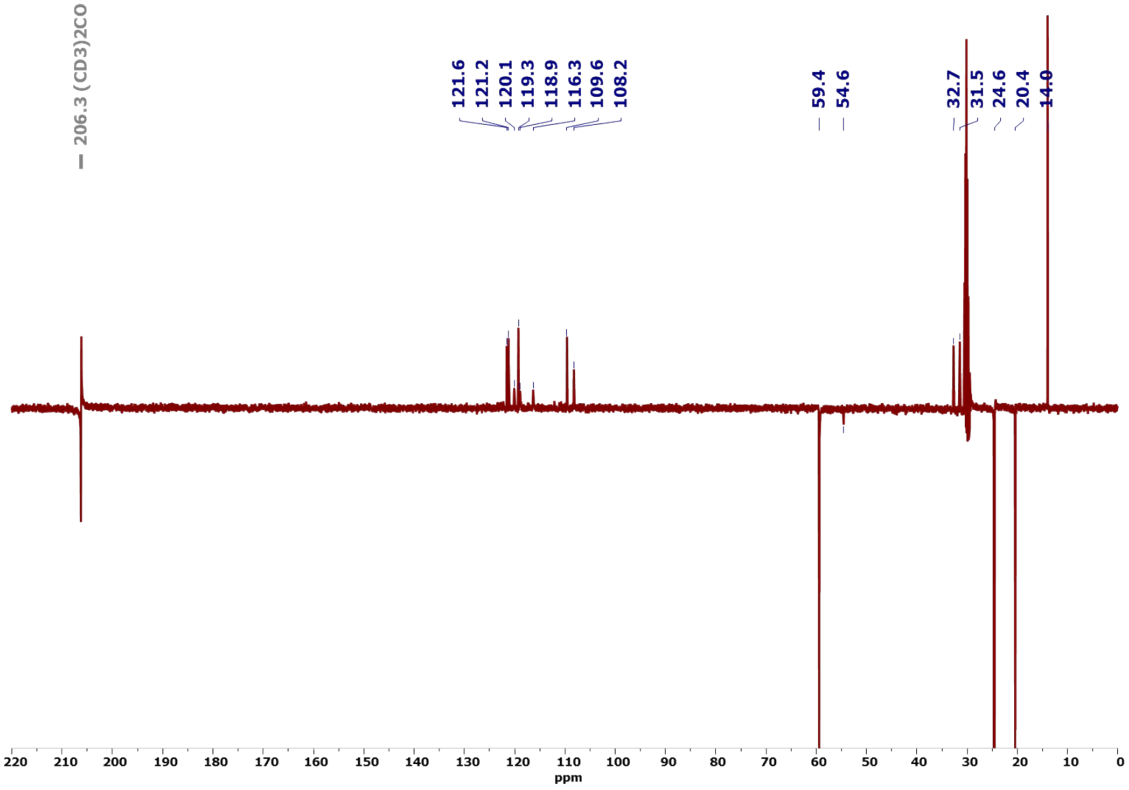

Fig. S15. $^{13}C\{^{1}H\}$-DEPT135 NMR spectrum of $(Bu_4N)_2[B_{10}H_9N(MBzim)CH_2MBzim]$ (**3**) in $(CD_3)_2CO$.

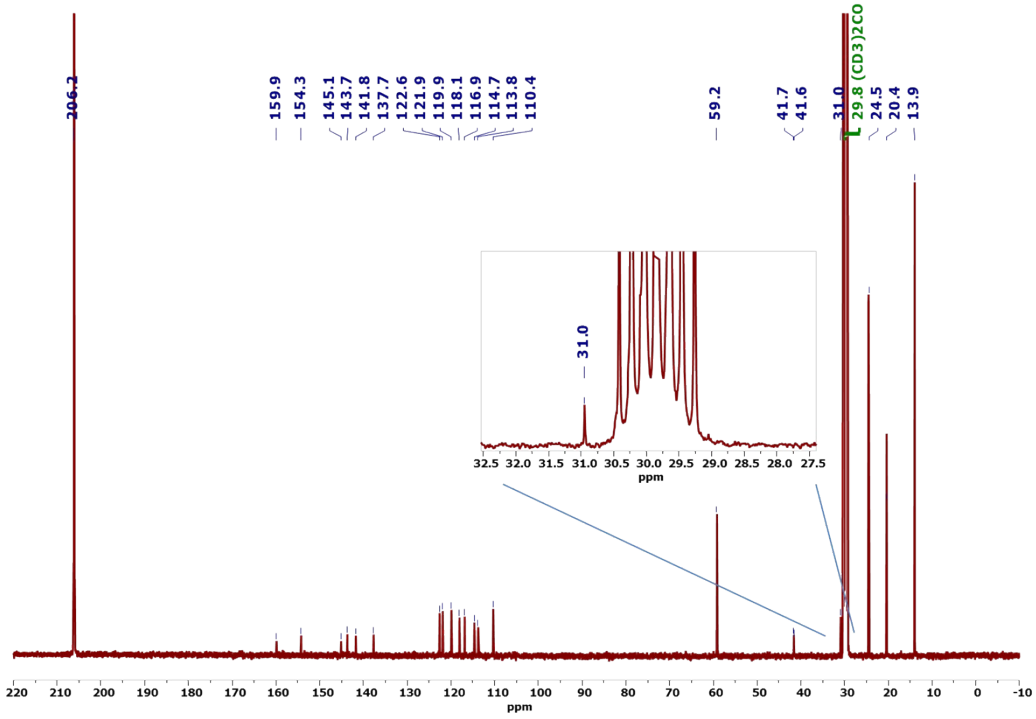

Fig. S16. $^{13}C\{^{1}H\}$ NMR spectrum of $(Bu_4N)_2[B_{10}H_9HN^{+}B(MBzim)CH_2Bzid^{-}]$ (**4**) in $(CD_3)_2CO$.

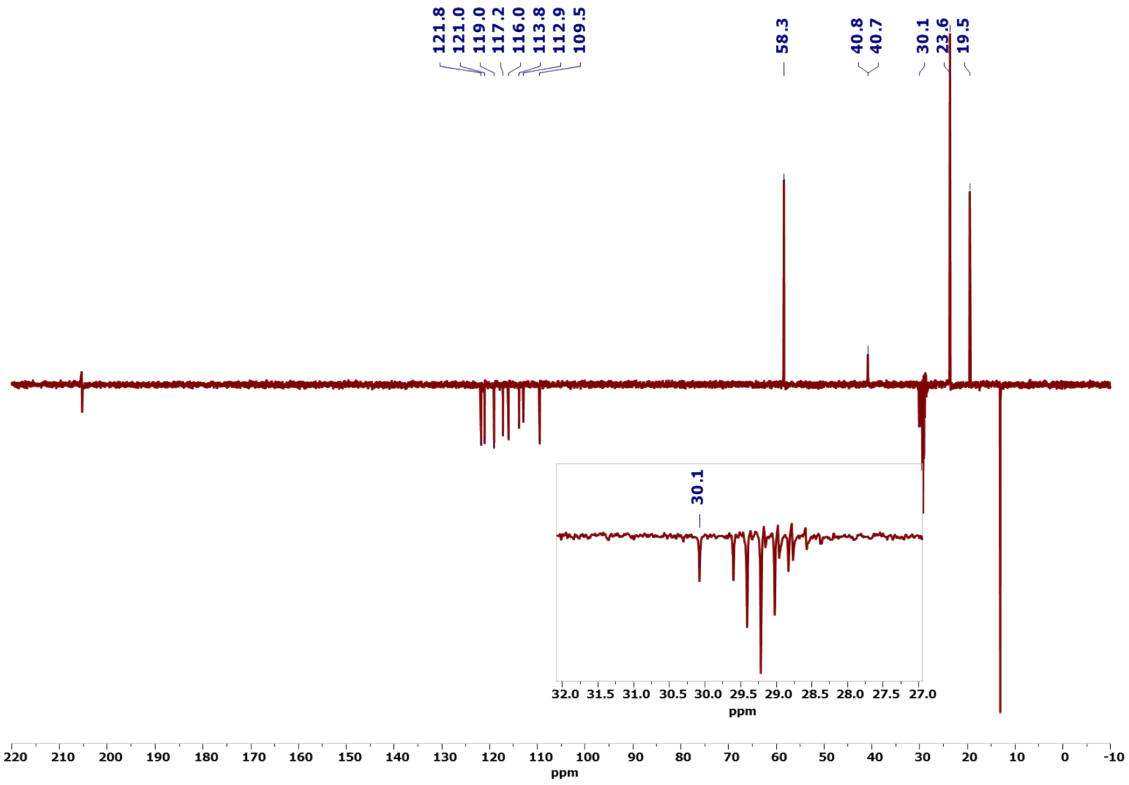

Fig. S17. $^{13}C\{^{1}H\}$-DEPT135 NMR spectrum of $(Bu_4N)_2[B_{10}H_9HN^{+}B(MBzim)CH_2Bzid^{-}]$ (**4**) in $(CD_3)_2CO$.

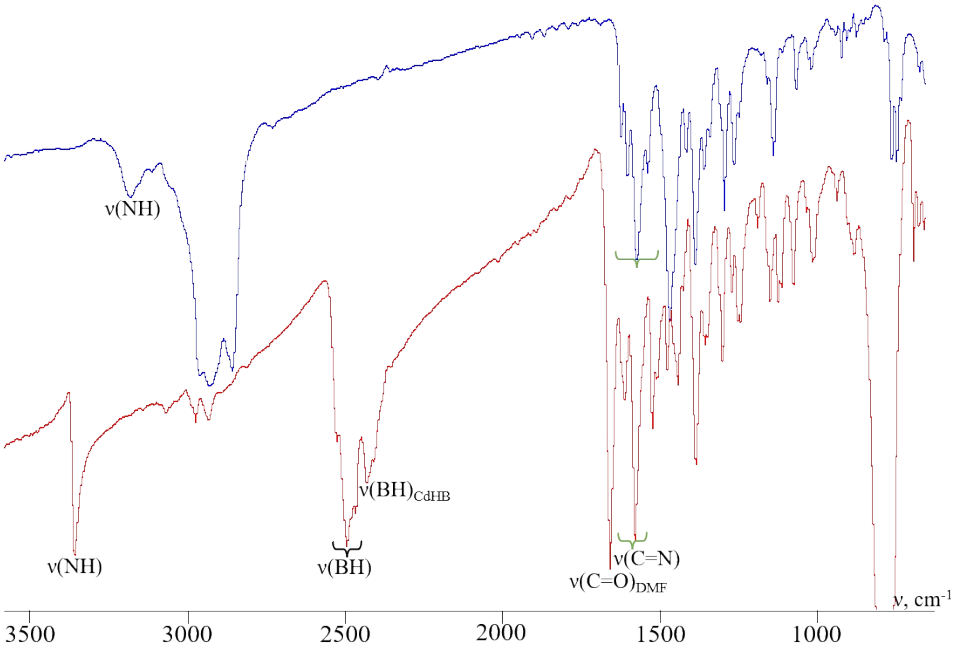

Fig. S18. IR spectra of L^3 (blue) and complex **5** (red).

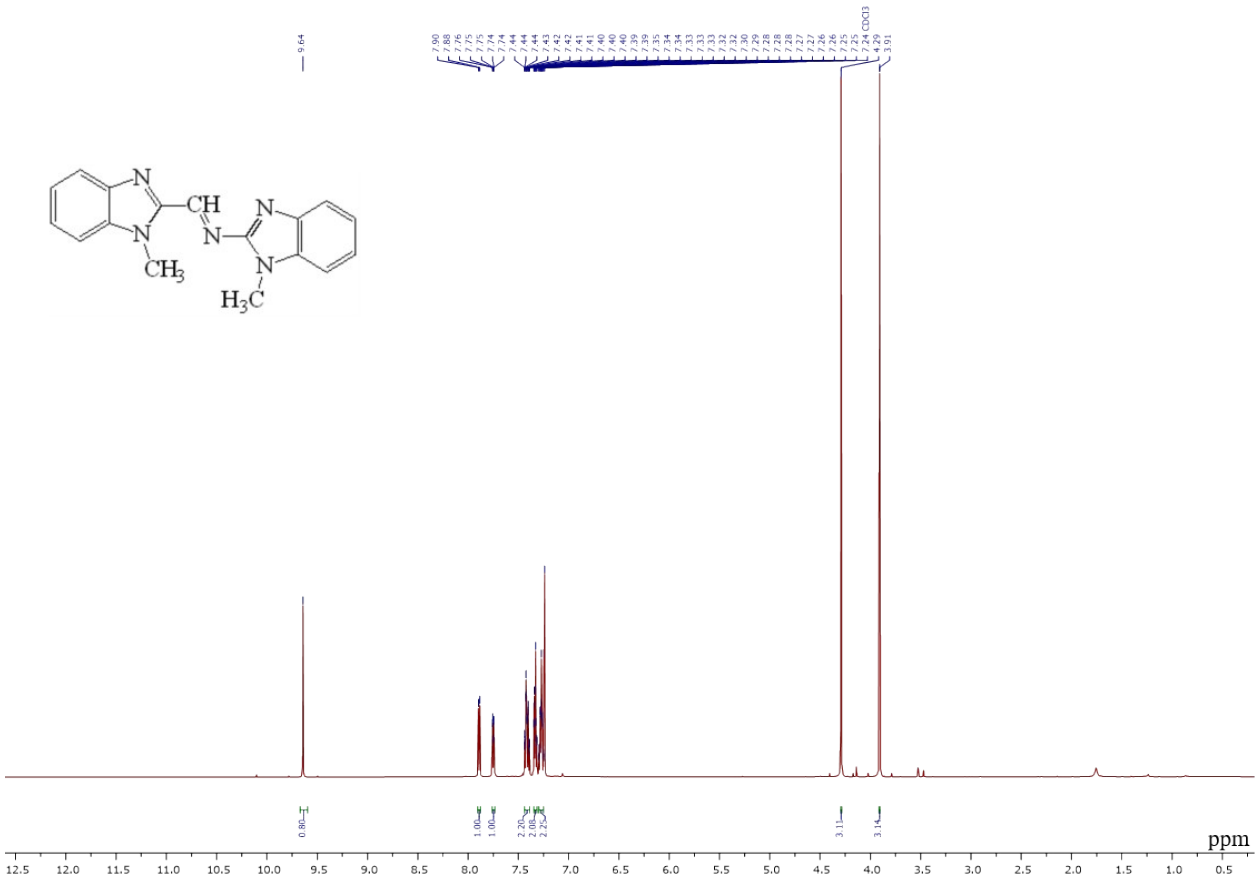

Fig. S19. ^{1}H NMR spectrum of *N,*1-bis(1-methylbenzimidazol-2-yl)methanimine (L^1).

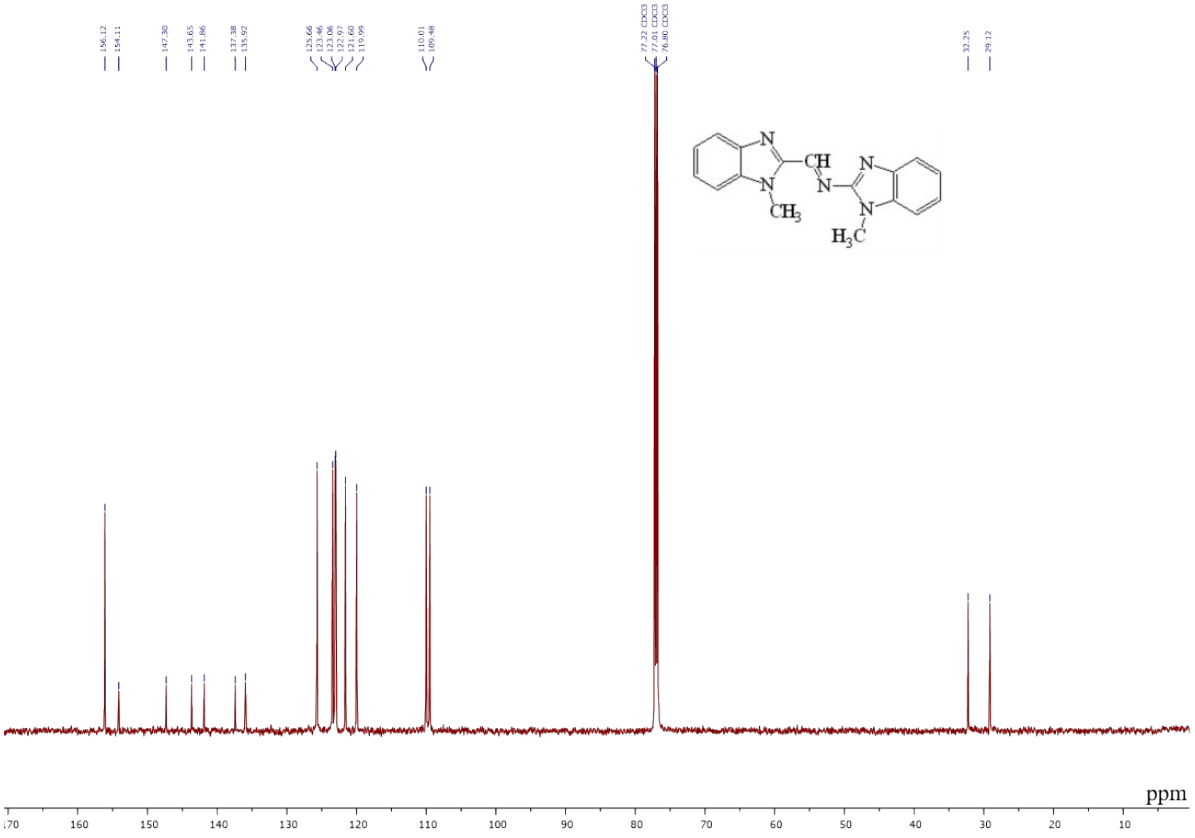

Fig. S20. ^{13}C NMR spectrum of *N,*1-bis(1-methylbenzimidazol-2-yl)methanimine (L^1).

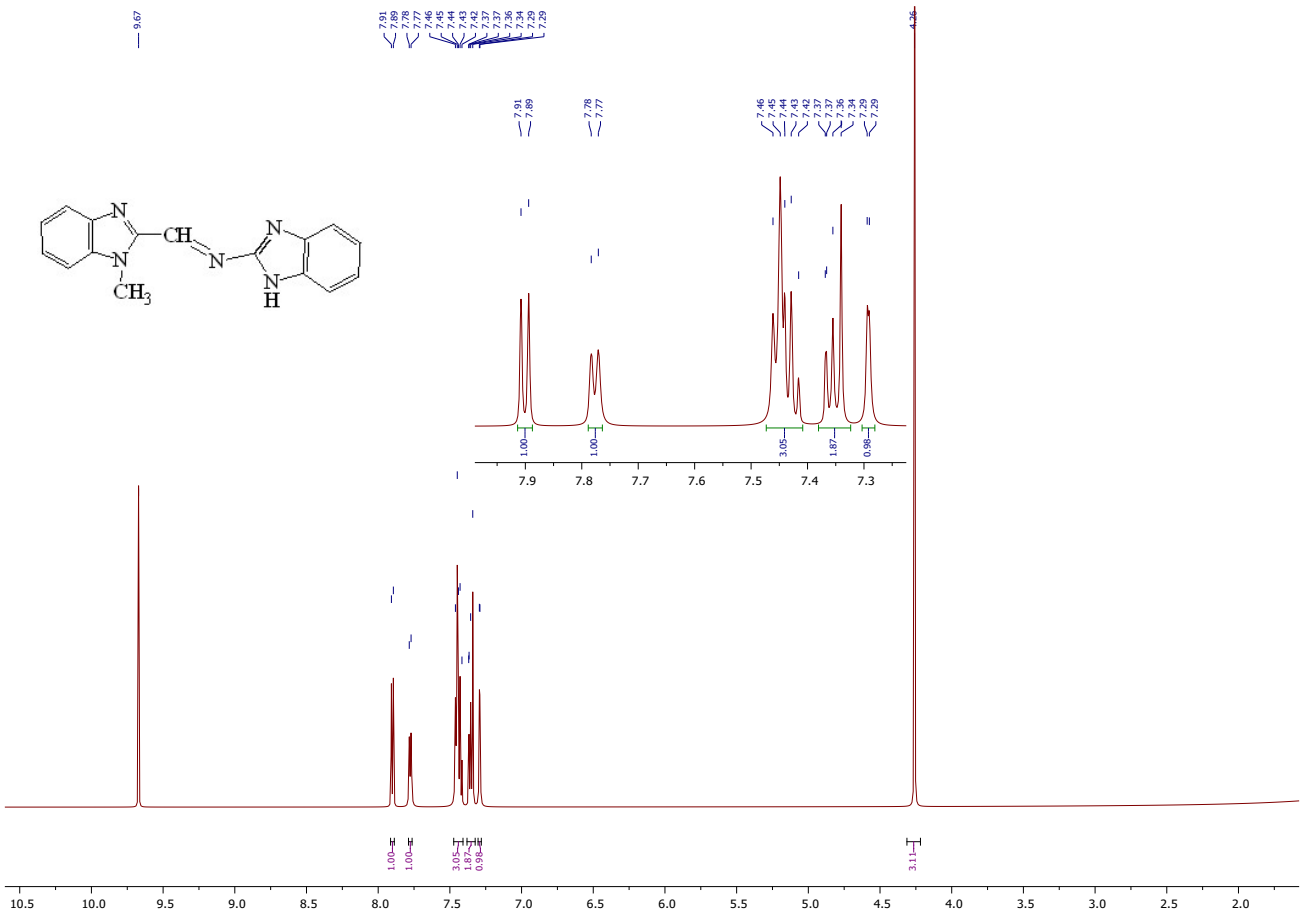

Fig. S21. ^{1}H NMR spectrum of *N*-(benzimidazol-2-yl)-1-(1-methylbenzimidazol-2-yl)methanimine (L^2).

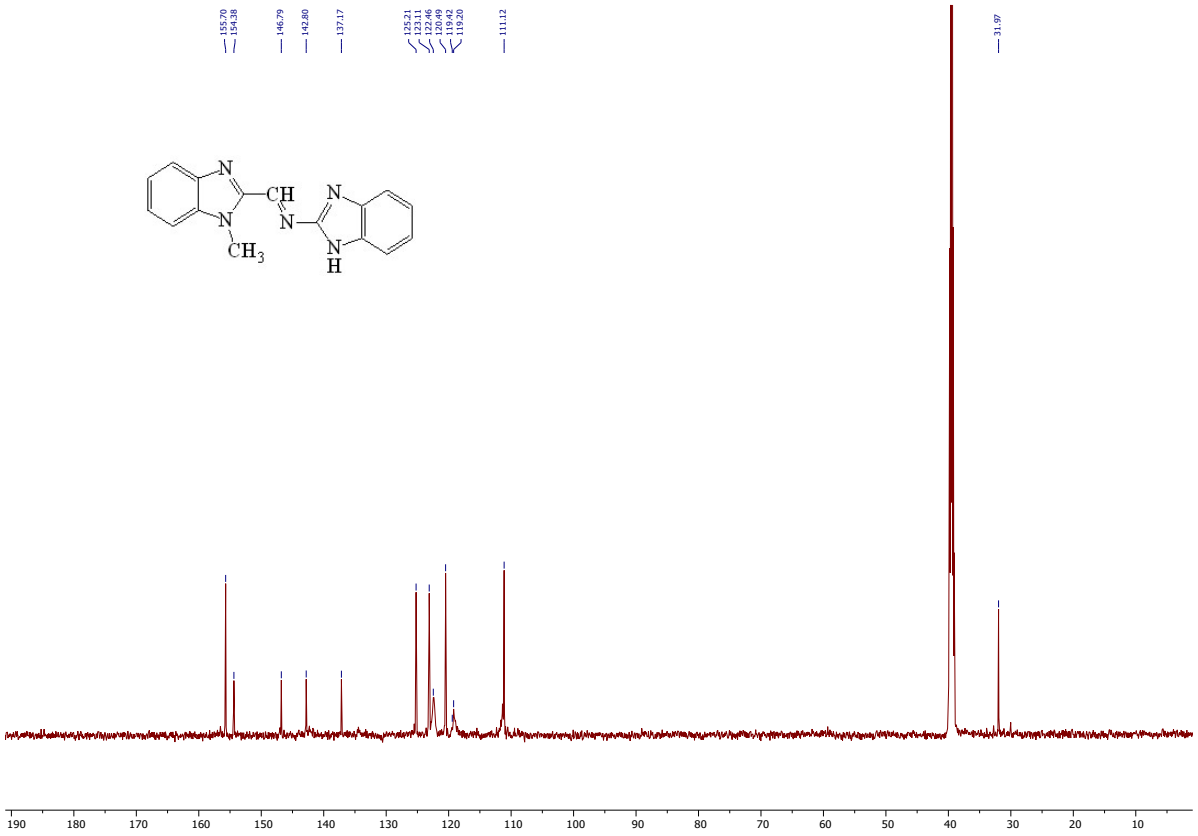

Fig. S22. ^{13}C NMR spectrum of *N*-(benzimidazol-2-yl)-1-(1-methylbenzimidazol-2-yl)methanimine (L^2).