Supplementary Information

Synthesis, Characterization, and Properties of a Benzofuran-based Cage-shaped Borate: Photo Activation of Lewis Acid Catalysts

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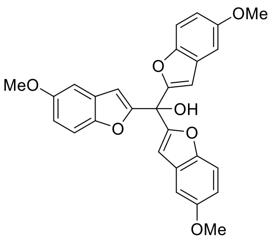
1. General. IR spectra were recorded as thin films or as solids in KBr pellets on a HORIBA FT-720 spectrophotometer. ^{1}H and ^{13}C spectra were obtained with a 400 and 100 MHz spectrometer, respectively, with TMS as internal standard. ^{11}B NMR spectra were obtained with a 127 MHz spectrometer with $BF_3{\cdot}OEt_2$ as external standard. Mass spectra were recorded on a JEOL JMSDS303. All reactions were carried out under nitrogen. Data collection for X-ray crystal analysis was performed on Rigaku/ R-AXIS RAPID diffractometer (CuK_α $\lambda = 1.54187$ Å). The structure was solved with direct methods and refined with full-matrix least squares(teXsan).Synthesis of boron complexes was performed in nitrogen-filled glove box.

2. Materials. Dehydrated dichloromethane, THF, acetonitrile, diethylether and hexane were purchased and used as obtained. The borates **2**·L (L = THF or Py) were prepared according to our previous report.[1] All other reagents are commercially available. The Mukaiyama aldol product is known in the literature.[2]

3. Computational Method. We applied the HF/DFT hybrid method originally proposed by Becke[3] referenced as B3PW91 three parameter hybrid functional. All calculations were performed with Gaussian 09, Revision C.01.[4] 6-31+G(d,p) were used for basis sets. All molecular geometries were fully optimized and the pyridine-complexation energy was calculated including zero point energy correction by the normal mode analysis for each structure.

4. Synthetic procedures for 4-12

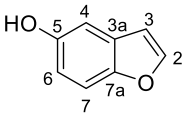
Tris(5-methoxy-2-benzofuranyl)methanol 6



A solution of BuLi in hexane (3.0 mmol, 1.86 mL, 1.6 M), *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (0.348 g, 3.0 mmol), and trimethylamine (0.303 g, 3.0 mmol) was introduced in the flask. 5-methoxybenzofuran (0.40 g, 2.7 mmol) was slowly added to the flask at rt with stirring. After stirring for 2 h at rt, the flask was cooled to 0 °C. Ethyl chloroformate (0.097 g, 0.9 mmol) in THF (0.5 mL) was slowly added to the flask. The stirring was kept for 1 h at rt. H_2O (10 mL) was added to quench the reaction and the mixture was extracted with diethylether (3 x 50 mL). The organic layer was dried ($MgSO_4$) and evaporated to give the desired product (0.45 g, 36%).

^{1}H NMR: (400 MHz, $CDCl_3$) 7.37 (d, J = 9.2 Hz, 3H), 7.01 (d, J = 2.4 Hz, 3H), 6.91 (dd, J = 9.2 Hz, 2.4 Hz, 3H), 6.73 (s, 3H), 3.83 (s, 9H, OMe). (OH signals were not detected.)

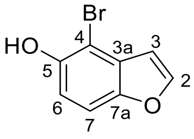
5-Hydroxybenzofuran 7



A procedure from the literature[5] was modified as follows: To the solution of 5-methoxybenzofuran (5.0 g, 33.74 mmol) in dichloromethane (50 mL) was added BBr_3 (1M in dichloromethane, 43.8 mL, 43.8 mmol) at -78 °C. After stirring for 2 h, warming up to ambient temperature and stirring for 1 h, saturated $NaHCO_3$aq (50 mL) was added to the mixture at 0 °C. The mixture was extracted with Et_2O (3 x 40 mL) and organic layer was extracted with NaOHaq (1 M, 3 x 50 mL). The aqueous layer was neutralized by HClaq (1M, 150 mL) and extracted with Et_2O (3 x 40 mL). The obtained organic layer was washed with brine and then dried ($MgSO_4$) and evaporated to give a brown solid, which was purified by column chromatography (hexane:EtOAc = 70:30, column length 150 mm, diameter 26 mm silicagel) to give the product (3.8 g, 85%) as a white solid.

mp: 58-59 °C; IR (KBr): 3273 cm^{-1} (OH); ^{1}H NMR: (400 MHz, $CDCl_3$) 7.59 (d, J = 2.0 Hz, 1H, 2-H), 7.34 (d, J = 8.8 Hz, 1H, 7-H), 7.01 (d, J = 2.4 Hz, 1H, 4-H), 6.81 (dd, J = 8.8, 2.4 Hz, 1H, 6-H), 6.68 (d, J = 2.4 Hz, 1H, 3-H), 4.63 (s, 1H, OH); ^{13}C NMR: (100 MHz, $CDCl_3$) 151.3 (s, C-5), 150.2 (s, C-7a), 146.1 (d, C-2), 128.4 (s, C-3a), 113.1 (d, C-6), 111.9 (d, C-7), 106.6 (d, C-3), 106.3 (s, C-4); MS: (EI, 70 eV) *m/z* 134 (M^+, 100), 105 (14), 78 (30), 77 (14), 51 (13); HRMS: (EI, 70 eV) Calculated ($C_8H_6O_2$) 134.0368 (M^+) Found: 134.0368; Analysis: $C_8H_6O_2$ (134.134) Calcd: C, 71.64; H, 4.51, O, 23.86 Found:C, 71.54, H, 4.39.

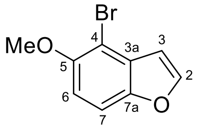
4-Bromo-5-hydroxybenzofuran 8



A procedure from the literature[6] was modified as follows: The flask equipped with a Soxhlet extractor was charged the solution of 5-hydroxybenzofuran (3.7 g, 27 mmol) and diisopropylamine (0.27 g, 2.7 mmol) in dichloromethane (150 mL). The thimble was filled with *N*-bromosuccinimide (4.4 g, 25 mmol) and the system was heated to reflux for 16 h. After cooling to ambient temperature, 2 M sulfuric acid (50 mL) was added to the mixture at 0 °C. The mixture was extracted with dichloromethane (3 x 50 mL) and the obtained organic layer was washed with brine and then dried ($MgSO_4$). The solution was evaporated to give a brown liquid, which was purified by column chromatography (hexane:EtOAc = 97:3, column length 150 mm, diameter 26 mm silicagel) to give the product (3.7 g, 70 %) as a white solid.

mp: 44-46 °C; IR (KBr): 3251 cm^{-1} (OH), 1227 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.61 (d, J = 2.2 Hz, 1H, 2-H), 7.33 (d, J = 8.8 Hz, 1H, 7-H), 6.99 (d, J = 8.8 Hz, 1H, 6-H), 6.70 (d, J = 2.2 Hz, 1H, 3-H), 5.43 (s, 1H, OH): ^{13}C NMR: (100 MHz, $CDCl_3$) 149.2 (s, C-7a), 148.6 (s, C-5), 146.4 (d, C-2), 129.0 (s, C-3a), 113.0 (d, C-6), 111.5 (d, C-7), 106.8 (d, C-3), 100.1 (s, C-4); MS: (EI, 70 eV) *m/z* 214 (M+2, 94), 212 (M^+, 100), 132 (M-Br, 13), 105 (36), 104 (19), 77 (24), 76 (35), 51 (18), 50 (17); HRMS: (EI, 70 eV) Calculated ($C_8H_5BrO_2$) 211.9473 (M^+) Found: 211.9470; Analysis: $C_8H_5BrO_2$ (213.03) Calcd: C, 45.11; H, 2.37, Br, 37.51, O, 15.02 Found:C, 45.02, H, 2.37, Br, 37.49.

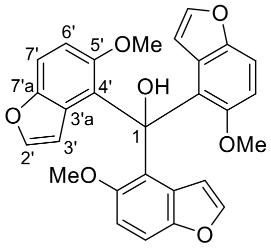
4-Bromo-5-methoxybenzofuran 9



To the solution of 4-bromo-5-hydroxybenzofuran (2.2 g, 10.4 mmol) and K_2CO_3 (2.9 g, 20.9 mmol) in *N*,*N*-dimethylformamide (40 mL) was added methyl iodide (1.8 g, 12.5 mmol) at ambient temperature. After stirring for 8 h, H_2O (50 mL) was added to the mixture at 0 °C. The mixture was extracted with CH_2Cl_2 (3 x 100 mL) and washed with H_2O (3 x 50 mL) and brine (100 mL). The obtained organic layer was dried ($MgSO_4$) and evaporated to give a white solid, which was purified by column chromatography (hexane:EtOAc = 98:2, column length 150 mm, diameter 26 mm silicagel) to give the product (1.7 g, 73%) as a white solid.

mp: 82-83 °C; IR (KBr): 1240 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.63 (d, *J* = 2.8 Hz, 1H, 2-H), 7.38 (dd, *J* = 8.8, 1.2 Hz, 1H, 7-H), 6.92 (d, *J* = 8.8 Hz, 1H, 6-H), 6.78 (dd, *J* = 2.8, 1.2 Hz, 1H, 3-H), 3.92 (s, 3H, OCH_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 152.3 (s, C-5), 149.6 (s, C-7a), 146.5 (d, C-2), 130.4 (s, C-3a), 110.5 (d, C-7), 110.0 (d, C-6), 107.2 (d, C-3), 102.5 (s, C-4), 57.6 (q, OCH_3); MS: (EI, 70 eV) *m/z* 228 (M+2, 94), 226 (M^+, 100), 213 ($M-CH_3+2$, 58), 211 ($M-CH_3$, 62), 185 (24), 183 (24), 76 (21); HRMS: (EI, 70 eV) Calculated ($C_9H_7BrO_2$) 225.9629 (M^+) Found: 225.9632; Analysis: $C_9H_7BrO_2$ (227.057) Calcd: C, 47.61; H, 3.11, Br, 35.19, O, 14.09 Found: C, 47.55, H, 3.01, Br, 35.12.

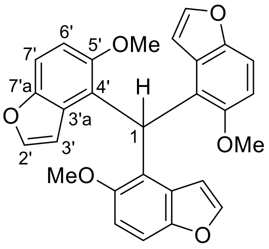
Tris(5-methoxy-4-benzofuranyl)methanol 10



To the solution of 4-bromo-5-methoxybenzofuran (3.46 g, 15.2 mmol) in Et_2O (30 mL) was added *n*-BuLi (1.6 M in hexane, 22.8 mmol, 14.3 mL) at -78 °C. After stirring for 3 h, warming up to 0 °C. The dropping funnel was charged with ethyl chloroformate (0.50 g, 4.57 mmol) and Et_2O (20 mL). The solution was slowly added to the flask at 0 °C, then mixture was stirred at ambient temperature for 14 h. H_2O (50 mL) was added to quench the reaction and the mixture was extracted with dichloromethane (3 x 50 mL). The obtained organic layer was washed with brine and dried ($MgSO_4$) and evaporated to give a white solid, then it was recrystallized (Et_2O/hexane = 1/1) to give the product (1.02 g, 47%).

mp: 220-225 °C; IR(KBr): 3519 cm^{-1} (OH), 1234 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.39 (d, *J* = 8.8 Hz, 3H, 7’-H), 7.32 (d, *J* = 2.4 Hz, 3H, 2’-H), 6.88 (d, *J* = 8.8 Hz, 3H, 6’-H), 6.24 (s, 1H, OH, D_2O-exchangeable), 6.10 (br, 3H, 3’-H), 3.12 (s, 9H, OCH_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 153.9 (s, C-5’), 150.7 (s, C-7’a), 144.6 (d, C-2’), 129.3 (s, C-4’), 127.9 (s, C-3’a), 112.1 (d, C-6’), 110.7 (d, C-7’), 108.5 (d, C-3’), 80.5 (s, C-1), 57.7 (q, OCH_3); MS: (EI, 70 eV) *m/z* 470 (M^+, 24), 323 (M^+-$C_9H_4O_2$, 19), 175 (M^+-2 x $C_9H_4O_2$, 100); HRMS: (EI, 70 eV) Calculated ($C_{28}H_{22}O_7$) 470.1366 (M^+) Found: 470.1368; Analysis: $C_{28}H_{22}O_7$ (470.477) Calcd: C, 71.48; H, 4.71, O, 23.8 Found: C, 71.65; H, 4.67.

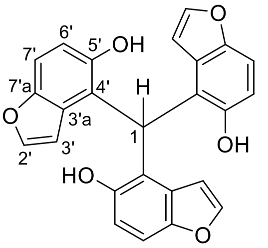
Tris(5-methoxy-4-benzofuranyl)methane 11



To the solution of tris(5-methoxy-4-benzofuranyl)methanol (0.92 g, 1.96 mmol) in acetonitrile (12 mL) and THF (18 mL) was added TsOH･H_2O (0.41 g, 2.2 mmol) at 0 °C. After stirring with warming up to ambient temperature for 14 h, H_2O (50 mL) was added to the mixture at 0 °C. The mixture was extracted with dichloromethane (3 x 50 mL) and the obtained organic layer was washed with brine and then dried ($MgSO_4$), which was purified by column chromatography (hexane:EtOAc = 80:20, column length 150 mm, diameter 26 mm silicagel) to give the product (0.64 g, 72%) as a white solid.

mp: 176-178 °C; IR (KBr): 1234 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.38 (d, *J* = 8.8 Hz, 3H, 7’-H), 7.24 (d, *J* = 2.4 Hz, 3H, 2’-H), 7.00 (s, 1H, 1-H), 6.93 (d, *J* = 8.8 Hz, 3H, 6’-H), 5.37 (br, 3H, 3’-H), 3.54 (s, 9H, OCH_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 154.1 (s, C-5’), 150.5 (s, C-7’a), 145.2 (d, C-2’), 128.3 (s, C-3’a), 125.3 (s, C-4’), 110.6 (d, C-6’), 109.7 (d, C-7’), 106.1 (d, C-3’), 57.8 (q, OCH_3), 38.1 (d, C-1); MS: (EI, 70 eV) *m/z* 454 (M^+, 100), 423 (M^+-OCH_3, 65), 161 (39), 131 (42); HRMS: (EI, 70 eV) Calculated ($C_{28}H_{22}O_6$) 454.1416 (M^+) Found: 454.1414; Analysis: $C_{28}H_{22}O_6$ (412.12) Calcd: C, 74.00; H, 4.88 Found: C, 73.97; H, 4.81.

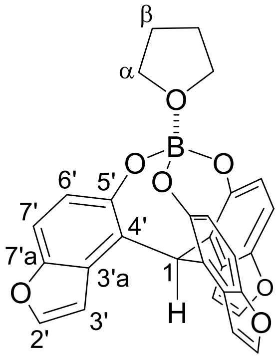
Tris(5-hydroxy-4-benzofuranyl)methane 12



To the solution of tris(5-methoxy-4-benzofuranyl)methane (0.54 g, 1.18 mmol) in dichloromethane (30 mL) was added BBr_3 (1M in dichloromethane, 3.9 mL, 3.9 mmol) at -78 °C. After stirring with warming up to at rt for 14 h, saturated $NaHCO_3$aq (30 mL) was added to the mixture at 0 °C. The mixture was extracted with Et_2O (30 mL) and the ether solution was extracted with NaOHaq (1 M, 3 x 50 mL). The aqueous layer was neutralized by HClaq (1M, 150 mL) and extracted with Et2O (2 x 30 mL). The obtained organic layer was washed with saturated NaClaq (2 x 20 mL) and then dried ($MgSO_4$) and evaporated to give a brown solid. The solid was washed with hexane to give the product (0.36 g, 74%).

mp: 209-213 °C; IR(KBr): 3487 cm^{-1} (OH); ^{1}H NMR: (400 MHz, $CDCl_3$) 7.39 (d, J = 8.2 Hz, 3H, 7’-H), 7.37 (d, J = 2.0 Hz, 3H, 2’-H), 6.85 (d, J = 8.2 Hz, 3H, 6’-H), 6.69 (s, 1H, 1-H), 5.83 (d, J = 2.0 Hz, 3H, 3’-H), 4.93 (s, 3H, OH, D_2O-exchangeable); ^{13}C NMR: (100 MHz, $CDCl_3$) 150.3 (s), 150.1 (s), 145.9 (d, C-2’), 128.0 (s, C-3’a), 117.7 (s, C-4’), 114.3 (d, C-6’), 111.6 (d, C-7’), 105.3 (d, C-3’), 38.9 (s, C-1); MS: (EI, 70 eV) m/z 412 (M^+, 11), 279 (15), 261 (100), 134 (7); HRMS: (EI, 70 eV) Calculated ($C_{25}H_{16}O_6$) 412.0947 (M^+) Found: 412.0948; Analysis: $C_{25}H_{16}O_6$ (412.12) Calcd: C, 72.81; H, 3.91 Found: C, 72.53; H, 4.16.

4·THF



In a nitrogen-filled glove box, to a suspension of tris(5-hydroxy-4-benzofuranyl)methane (0.1 mmol) in dichloromethane (3 mL) was added BH_3·THF in THF (0.11 mmol, 0.9 M) at room temperature with stirring for 3 h under release of H_2 gas. Evaporation of volatiles gave a viscous liquid, which was washed by hexane to give the product as a white solid almost quantitatively.

^{1}H NMR: (400 MHz, $CDCl_3$) 7.58 (d, J = 2.0 Hz, 3H, 2’-H), 7.24 (dd, J = 8.8, 0.8 Hz, 3H, 7’-H), 6.91 (d, J = 2.0 Hz, 3H, 3’-H), 6.88 (d, J = 8.8 Hz, 3H, 6’-H), 6.32 (s, 1H, 1-H), 4.49 (brs, 4H, α-H_2), 2.19 (brs, 4H, β-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 152.0 (s, C-5’), 150.4 (s, C-7’a), 145.6 (d, C-2’), 128.0 (s, C-3’a), 120.3 (s, C-4’), 117.6 (d, C-6’), 110.3 (d, C-7’), 104.9 (d, C-3’), 72.3 (t, C-α), 43.2 (s, C-1), 25.2 (t, C-β); ^{11}B NMR (127 MHz, $CDCl_3$) (BF_3·Et_2O in $CDCl_3$ as external standard) 5.79.

5. X-ray crystallographic data of 4·THF

Empirical Formula	$C_{29}H_{21}BO_7$
Formula Weight	492.29
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.800 x 0.800 x0.600 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 14.2762(3) Å
	b = 10.1806(2) Å
	c = 17.0287(3) Å
	β = 109.886(1) °
	V = 2327.38(8) $Å^3$
Space Group	$P2_1/n$ (#14)

Z value	4
D_{calc}	1.405 g/cm^3
F_{000}	1024.00
μ(CuK$_\alpha$)	8.253 cm^{-1}
Temperature	-150.0 °C
Function Minimized	$\Sigma\ w\ (F_o^2 - F_c^2)^2$
Least Squares Weights	$1/\sigma^2(F_o^2) = 1/\sigma^2(F_o)/(4F_o^2)$
No. Observations (I > 2.00σ(I))	3757
No. Variables	418
Reflection/Parameter Ratio	8.99
Residuals: $R1$ (I > 2.00σ(I))	0.0526
Residuals: $wR2$ (I > 2.00σ(I))	0.1067
Goodness of Fit Indicator	3.326
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.82 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.52 e$^-$/Å^3

6. NMR and IR measurements of the complex of borates 4 with 2,6-dimethyl-γ-pyrone 13

In a glove box, to a suspension of ligand (0.1 mmol) in dichloromethane (3 mL) was added BH_3·THF in THF (0.11 mmol, 1.0 M) at rt with stirring for 2 h under release of H_2 gas. Volatile was removed under reduced pressure and the residue was washed with hexane. The evaporated residue was resolved with dichloromethane (3 mL) and 2,6-dimethyl-γ-pyrone (0.1 mmol) was added to the solution. After stirring for 1 h, volatile was removed under reduced pressure to afford the product. NMR date of **1**·Pyrone, and **2**·Pyrone by our previous paper[7]. Infrared spectra of the borate complex with **13** were recorded as CH_2Cl_2 solutions and the average values of five times measurements were employed.

The δ(^{13}C) of C3 and C=O stretching in **13**(Boron free): 165.432 ppm and 1670.05 cm^{-1}.

7. DFT calculations

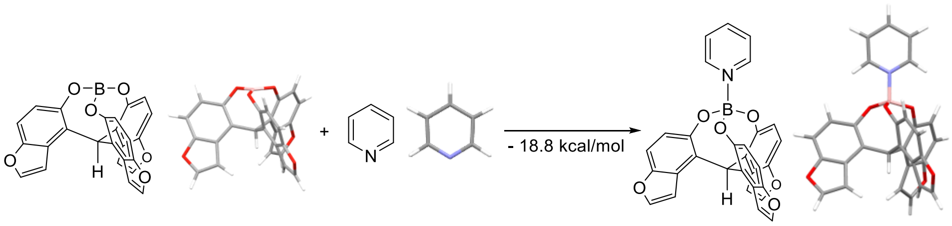
7-1. Optimized structures

Table S1. Theoretical calculation of cage-shaped and planar borates.

entry	borate		dihedral angle θ (C-O-B-O)	next-LUMO energy level (kcal/mol)	ΔE in pyridine -complexation (kcal/mol)
1[a]	$B(OPh)_3$	**1**	2.0°	-12.46	-5.0
2[a]	$B(OC_6H_4)_3CH$	**2**	48.4°	-18.26	-19.2
3[b]	$B(OC_6H_4)_3SiMe$	**3c**	45.4°	-16.81	-13.2
4	$B(Obenzofuran)_3CH$	**4**	47.9°	-21.58	-18.8

[a] ref. 1, [b] ref. 7

7-2. Estimation of the pyridine-complexation energy of 4

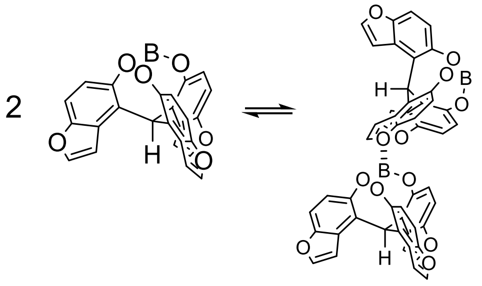


Scheme S1. Estimation of the pyridine-complexation energy of **4**.

Table S2. Total energies for borate **4** and **4**·Py.

compounds	Total energy (in hartree)
Benzofuran complex **4**	-1435.948154
Benzofuran-Py complex **4**·Py	-1684.092907
Pyridine (Py)	-248.11478

7-3. Estimation of self-dimerization energy of 4



Scheme S2. Estimation of the self-dimerization energy of **4**.

Table S3. Total energies for borate **4** and **4**-dimer.

compounds	Total energy (in hartree)
Benzofuran-complex **4**	-1436.27665257
Benzofuran-complex **4**×2	-2872.553305
Benzofuran-dimer	-2872.55524762

7-4. Electrostatic potential maps

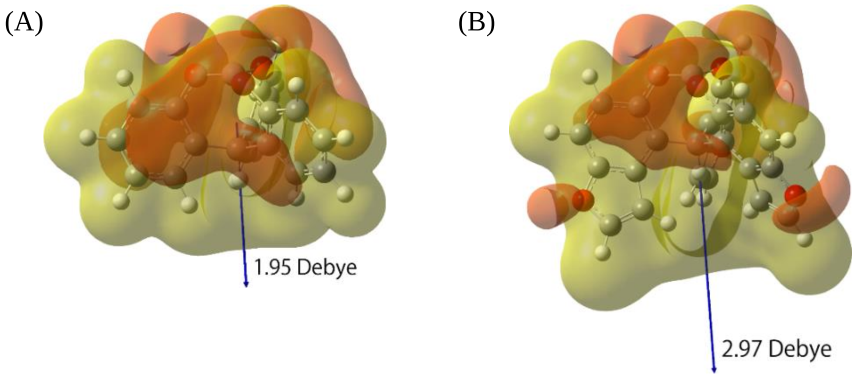


Figure S1. Electrostatic potential maps of (A) **2** and (B) **4** with dipole moments. Yellow and red meshes represent the positive and negative charged isosurface, respectively.

7-5. Mulliken charge distribution

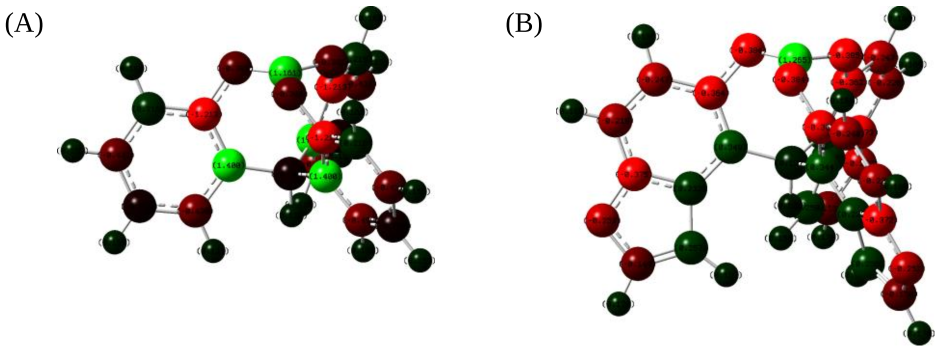
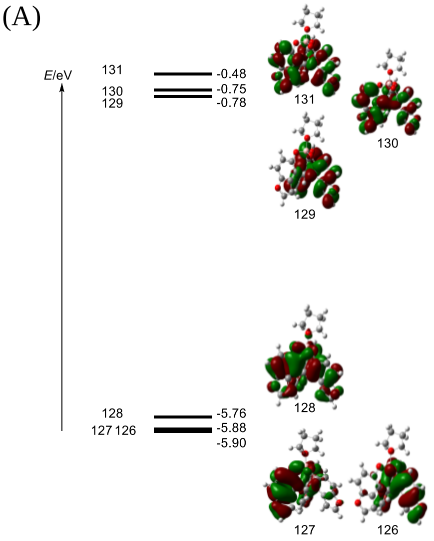


Figure S2. Mulliken charge distribution of (A) **2** and (B) **4**.

7-6. TD-DFT calculation for 4·THF

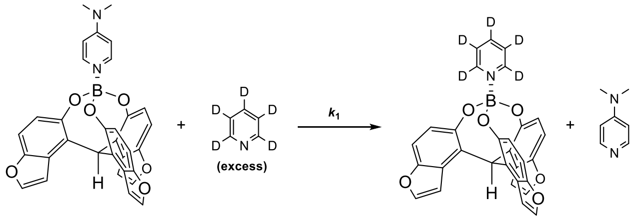


(B)

Excited State	Excitation Energy / eV (wavelenght / nm)	Excitation Amplitudes		Oscillator strength
1	4.3922 eV (282.28 nm)	125 ->129 128 ->129	-0.10161 0.67322	0.0565
2	4.4200 eV (280.51 nm)	127 ->129 128 ->130	0.11553 0.65448	0.0584
3	4.5026 eV (275.36 nm)	124 ->129 125 ->129 126 ->129 127 ->129 128 ->130	0.13405 -0.11103 0.16342 0.62990 -0.10897	0.0247

Figure S3. (A) Energy diagram and frontier orbitals for **4**·THF. (B) Excitation Energies of **4**·THF calculated at the TD-B3PW91/6-31+G(d,p) level.

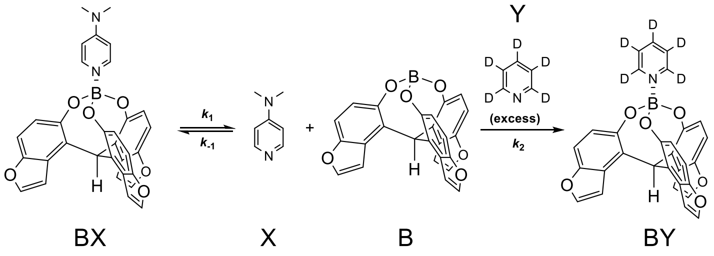
8. Kinetic investigations



To a solution of tris(5-hydroxy-4-benzofuranyl)methane (0.1 mmol) in dichloromethane (3 mL) was added BH_3·THF (0.11 mmol, 0.9 M) at rt with stirring for 2 h under release of H_2 gas. To the solution was added *N*, *N*-dimethylanimopyridine (0.1 mmol) at rt. After stirring for 2 h, solvent was removed under the reduced pressure. The obtained material was washed with hexane to give the pure complex. The complex (0.01 mmol) and pyridine-*d*$_5$ (5 mL) were added to the flask. The rate constants were determined by observing the reaction at 50, 70, 85, 90, 95 and 100 °C.

8-1. First-order rate equation

A pyridine exchange can be descried below. B; cage-shaped borate, X; DMAP, Y; pyridine-d_5. Excess amount of pyridine-d_5 (Y) was used as solvent and eq 2 is considered to be irreversible. BX and X can be observed by DMAP signals by NMR.



$$\mathrm{BX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} + \mathrm{X} \qquad (1) \qquad\qquad \mathrm{B} + \underset{\text{exess}}{\mathrm{Y}} \xrightarrow{k_2} \mathrm{BY} \qquad (2)$$

No ligand-free borate B is observed.

$$[\mathrm{BX}]_0 = [\mathrm{BX}] + [\mathrm{X}]$$

$$[\mathrm{X}] = [\mathrm{BY}]$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{BX}] - k_{-1}[\mathrm{B}][\mathrm{X}] - k_2[\mathrm{B}][\mathrm{Y}] = 0$$

$$[\mathrm{B}](k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]) = k_1[\mathrm{BX}]$$

$$-\frac{d[\mathrm{BX}]}{dt} = k_1[\mathrm{BX}] - k_{-1}[\mathrm{B}][\mathrm{X}]$$

$$= k_1[\mathrm{BX}] - \frac{k_{-1}[\mathrm{X}]\, k_1[\mathrm{BX}]}{k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]}$$

$$= k_1[\mathrm{BX}]\left(1 - \frac{k_{-1}[\mathrm{X}]}{k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]}\right)$$

$$k_{-1}[\mathrm{B}][\mathrm{X}] << k_2[\mathrm{B}][\mathrm{Y}]$$

$$k_{-1}[\mathrm{X}] << k_2[\mathrm{Y}]$$

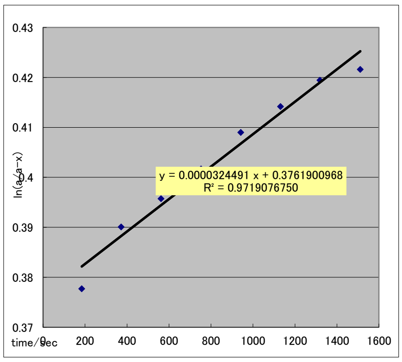
$$-\frac{d[\mathrm{BX}]}{dt} = k_1[\mathrm{BX}]$$

$$-\int \frac{d[\mathrm{BX}]}{[\mathrm{BX}]} = \int k_1 dt$$

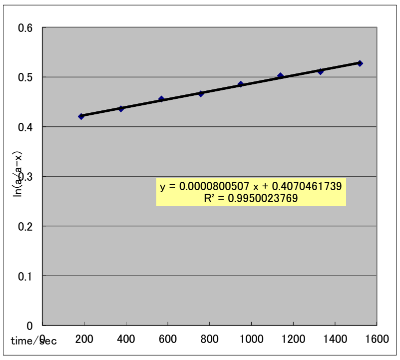
$$\boxed{-\ln \frac{[\mathrm{BX}]}{[\mathrm{BX}]_{t_0}} = k_1(t - t_0)} \qquad (A)$$

For simplification, t_0 can be voluntarily set as zero (with considering stable temperature condition experimentally). Plots based on (A) furnish a linear plot (See below).

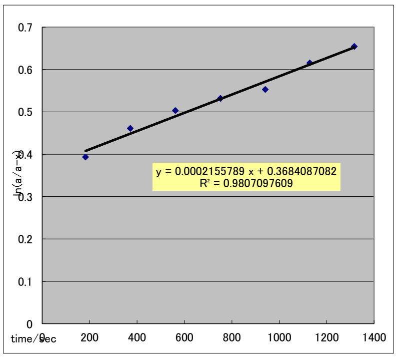
50 °C



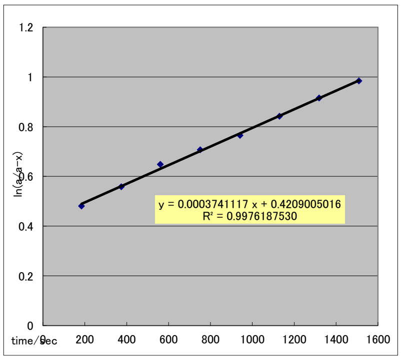
70 °C



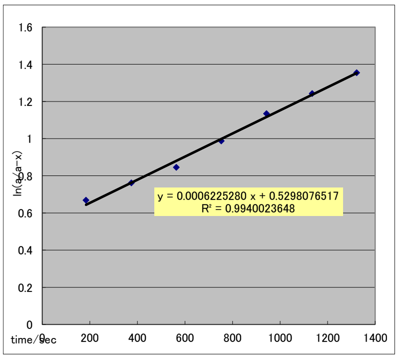
85 °C



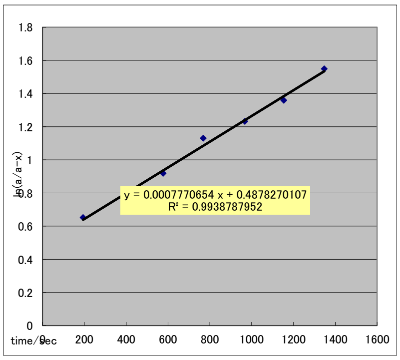
90 °C



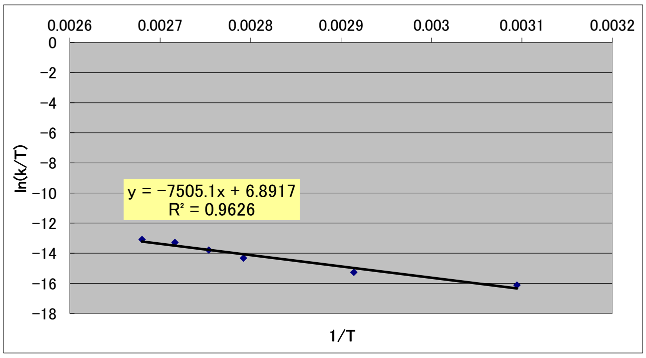
95 °C



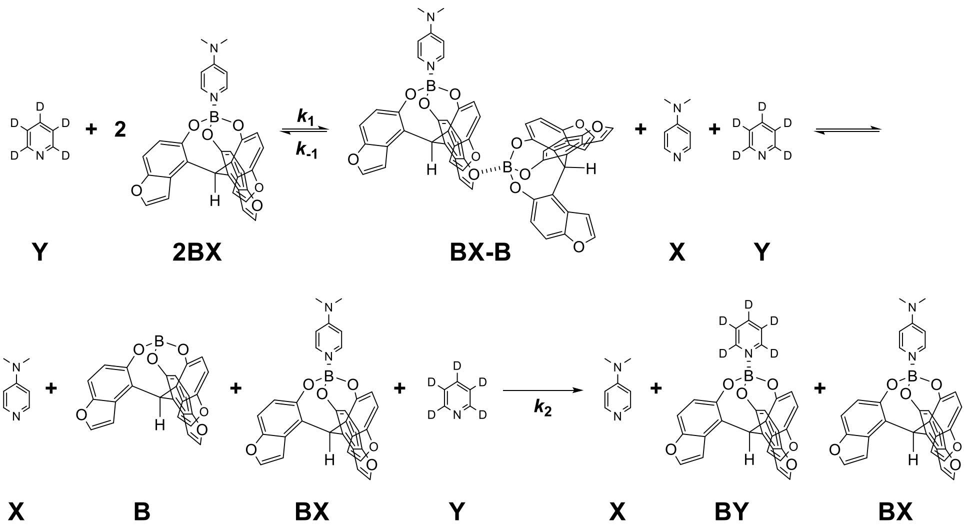
100 °C



Eyring plot



8-2. Second-order rate equation



A pyridine exchange can be descried below. B; cage-shaped borate, X; DMAP, Y;pyridine-d_5. Excess amount of pyridine-d_5 (Y) was used as solvent and eq 2 is considered to be irreversible. BX and X can be observed by DMAP signals by NMR.

$$\mathrm{Y} + 2\mathrm{BX} \xrightarrow{k'} \mathrm{X} + \mathrm{BY} + \mathrm{BX}$$

$$\frac{d[\mathrm{BY}]}{dt} = k'[\mathrm{BX}]^2[\mathrm{Y}] = k''[\mathrm{BX}]^2 \cdots \text{①}$$

$$2\mathrm{BX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{X} + \mathrm{B} + \mathrm{BX} \qquad \mathrm{B} + \mathrm{Y} \xrightarrow{k_2} \mathrm{BY}$$

No ligand-free borate B is observed.

$$\frac{d[\mathrm{BY}]}{dt} = k_2[\mathrm{B}][\mathrm{Y}] = k_2'[\mathrm{B}] \cdots \text{②}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{BX}]^2 - k_{-1}[\mathrm{B}][\mathrm{X}][\mathrm{BX}] - k_2'[\mathrm{B}] \approx 0 \quad \therefore\ [\mathrm{B}] = \frac{k_1[\mathrm{BX}]^2}{k_{-1}[\mathrm{X}][\mathrm{BX}] + k_2'} \cdots \text{③}$$

$$\text{By ①,②,③} \quad \frac{d[\mathrm{BY}]}{dt} = k''[\mathrm{BX}]^2 = \frac{k_2'k_1[\mathrm{BX}]^2}{k_{-1}[\mathrm{X}][\mathrm{BX}] + k_2'}$$

Ligand-free borate is unstaible, so complexation occurs very fast, which indicate large k_2 value.

$$k_{-1}[\mathrm{X}][\mathrm{BX}] << k_2' \quad \therefore\ k'' = k_1$$

$$\frac{d[\mathrm{BY}]}{dt} = k_1[\mathrm{BX}]^2$$

$$= k_1([\mathrm{BX}]_0 - [\mathrm{BY}])^2$$

$$\mathrm{c} - \mathrm{p} = [\mathrm{BX}]_0 - [\mathrm{BY}]$$

$$\frac{d[\mathrm{BY}]}{dt} = k_1(\mathrm{c} - \mathrm{p})^2$$

$$\mathrm{c} - \mathrm{p} = \mathrm{x}$$

$$\frac{d\mathrm{p}}{dt} = -\frac{d\mathrm{x}}{dt}$$

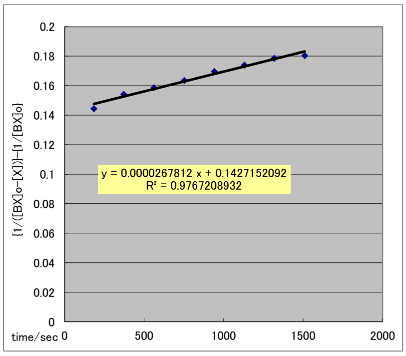
$$\frac{d\mathrm{x}}{dt} = -k_1\mathrm{x}^2$$

$$\therefore\ \frac{1}{\mathrm{c} - \mathrm{p}} - \frac{1}{\mathrm{c}} = k_1\mathrm{t}$$

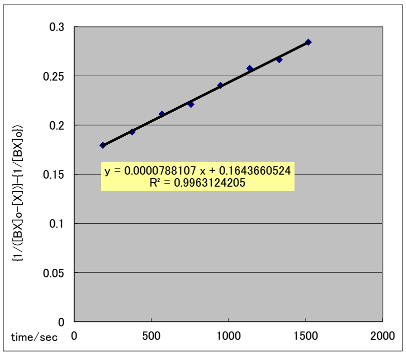
$$\boxed{\begin{array}{l} \therefore\ \dfrac{1}{[\mathrm{BX}]_0 - [\mathrm{BY}]} - \dfrac{1}{[\mathrm{BX}]_0} = k_1\mathrm{t} \\ \left(\therefore\ \dfrac{1}{[\mathrm{BX}]_0 - [\mathrm{X}]} - \dfrac{1}{[\mathrm{BX}]_0} = k_1\mathrm{t} \right) \end{array}} \begin{array}{l} \text{(B)} \\ \text{(B')} \end{array}$$

Plots based on (B´) furnish a linear plot (See below).

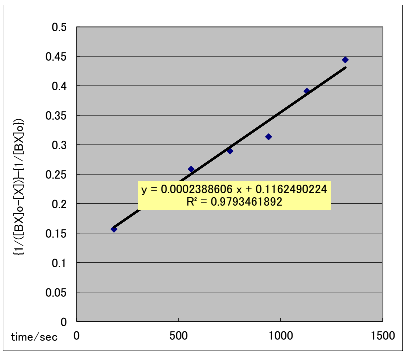
50 °C



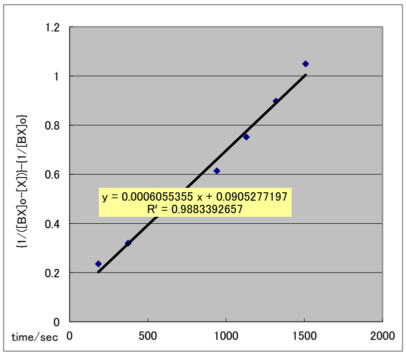
70 °C



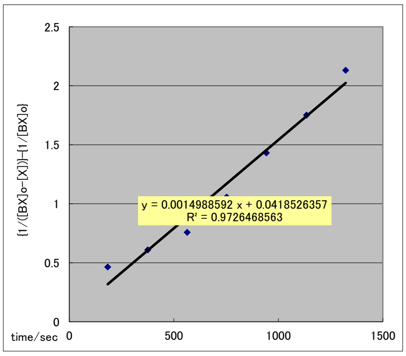
85 °C



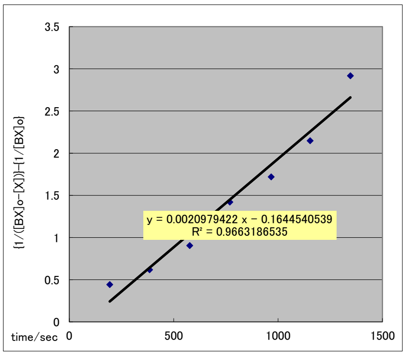
90 °C



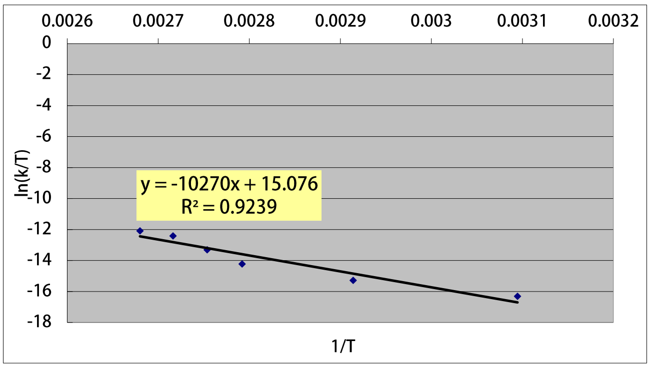
95 °C



100 °C

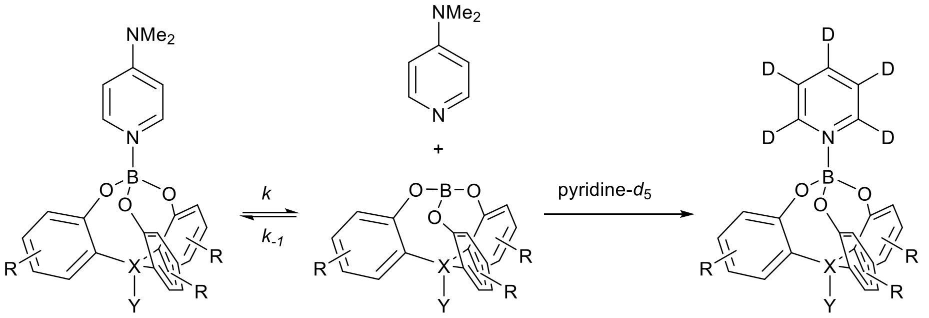


Eyring plot



8-3. Summary for kinetic investigations

Table S4. Kinetic parameters for ligand dissociation of the cage borates[a]



Entry	Borate	$\Delta H^‡$ (kcal/mol)	$\Delta S^‡$ (cal/K·mol)	$\Delta G^‡$ (kcal/mol)[b]	k (s^{-1})[b]
1[c]	**2**	35.1	22.3	28.6	2.32×10^{-9}
2[c]	**3a**	43.6	40.0	31.9	8.37×10^{-12}
3[c]	**3b**	31.2	7.5	29.0	1.16×10^{-9}
4[c]	**3c**	26.4	14.2	22.3	1.28×10^{-4}
5	**4**	14.9	-33.4	24.6	2.20×10^{-6}
6[d]	**4**	20.3	-17.2	25.4	6.31×10^{-7} [e]

[a] All entries except for entry 6 were calculated based on the first order of borate. [b] $\Delta G^‡$ and k are calculated at t = 20 °C. [c] ref. 7. [d] Each value was calculated based on the second order of borate.[e] The unit is [$s^{-1}M^{-1}$].

8. UV-spectra

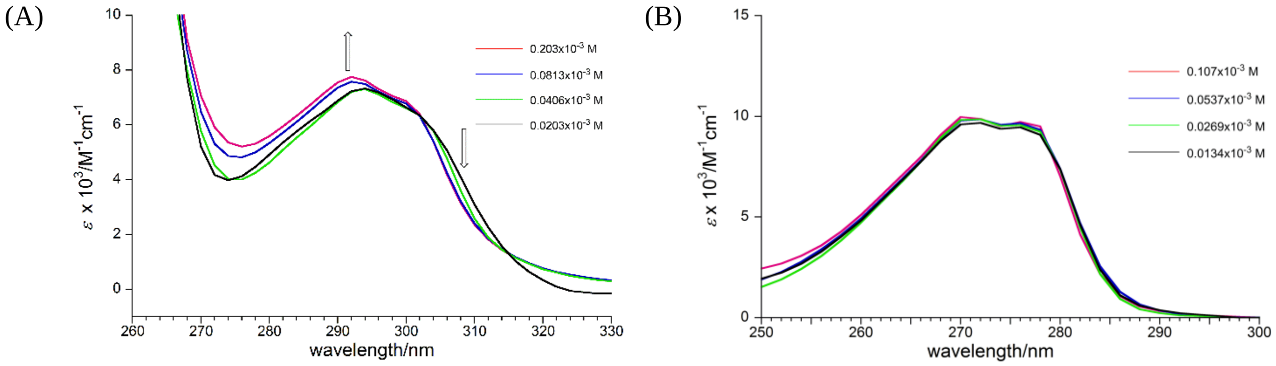


Figure S4. Absorption spectra of (A) **4**·THF and (B) **2**·THF recorded in CH_2Cl_2.

9. Concentration dependence of ^{1}H NMR

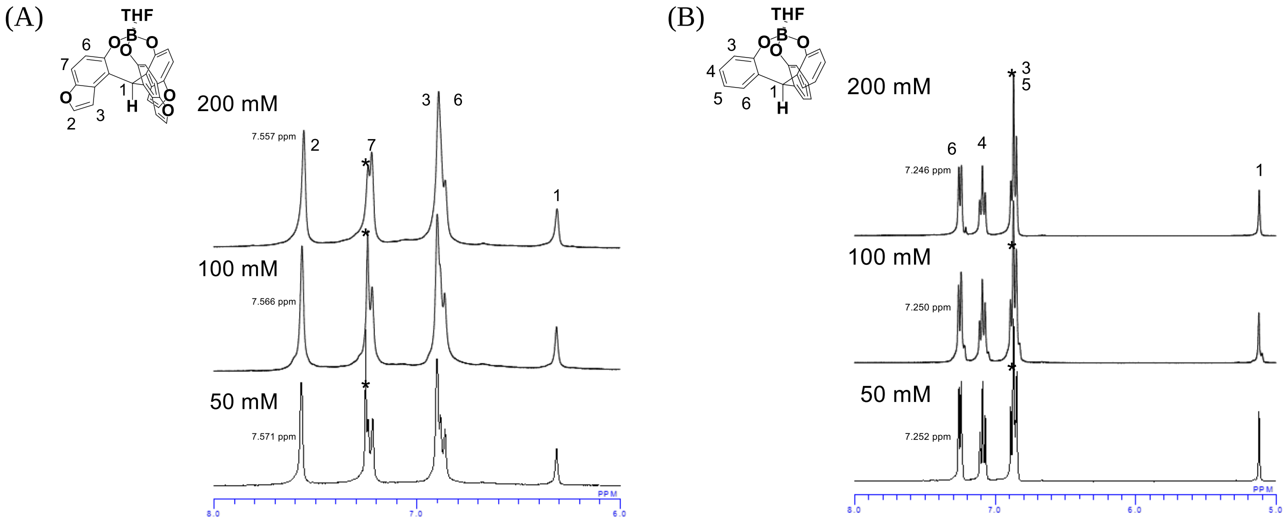


Figure S5. (A) **4**·THF and (B) **2**·THF in $CDCl_3$ at room temperature. Asterisks represent the residual solvents.

10. Mukaiyama Aldol Reaction

All products, **16a**[8], **16b**[9], **16c**[9], **16d**[10], and **16e**[11], were previously reported and were assigned by ^{1}H-NMR measurements.

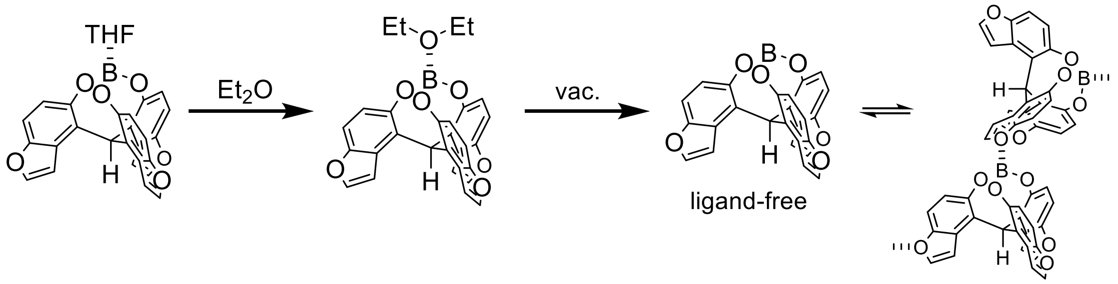
10-1. General procedure for Mukaiyama aldol reactiom

To a suspension of tris(2-hydroxyphenyl)methane or tris(5-hydroxy-4-benzofuranyl)methane (0.05 mmol) in dichloromethane (3 mL) was added BH_3·THF in THF (0.055 mmol, 0.9 M) at rt with stirring for 2 h under release of H_2 gas. To the solution was added dimethylketene methyl trimethylsilyl acetal (0.5 mmol) and aldehydes (0.5 mmol) at room temperature and the mixture was stirred at rt. After stirring for 1 h, $NaHCO_3$aq (10 mL) was added to the mixture, which was extracted with dichloromethane (3 x 10 mL). The organic layer was dried ($MgSO_4$) and evaporated to give a crude mixture, which was analyzed by NMR.

10-2. Black-light irradiation

To a suspension of tris(2-hydroxyphenyl)methane or tris(5-hydroxy-4-benzofuranyl)methane (0.025 mmol) in dichloromethane-*d₂* (3 mL) was added BH_3·THF in THF (0.028 mmol, 0.9 M) at rt with stirring for 2 h under release of H_2 gas. To the solution was added dimethylketene methyl trimethylsilyl acetal (0.5 mmol) and *p*-methylbenzaldehyde (0.5 mmol) at room temperature and the mixture was stirred at rt exposure to black-light (wavelength range of 300-400 nm centered at 365 nm,) irradiation. After stirring for 1 h, the reaction mixture was analyzed by NMR and the yield was determined on the basis of 1,1,2,2-tetrachloroethane as an internal standard.

11. Attempt to synthesize of the ligand-free 4



To a solution of tris(5-hydroxy-4-benzofuranyl)methane (0.1 mmol) in dichloromethane (3 mL) was added BH_3·THF (0.11 mmol, 0.9 M) at rt with stirring for 2 h under release of H_2 gas, then solvent was removed under the reduced pressure. The obtained material was washed with hexane to give the pure complex. To exchange for easily volatile ligand, complex is dissolved in little dichloromethane and then add much Et_2O with stirring. The mixture was evaporated but complex remain dissolved. Then mixture is added much Et_2O and evaporated many times, next added dichloromethane and evaporated repetitively in order to remove Et_2O by azeotropy. Finally solvent is perfectly removed with heating to give ligand-free complex.

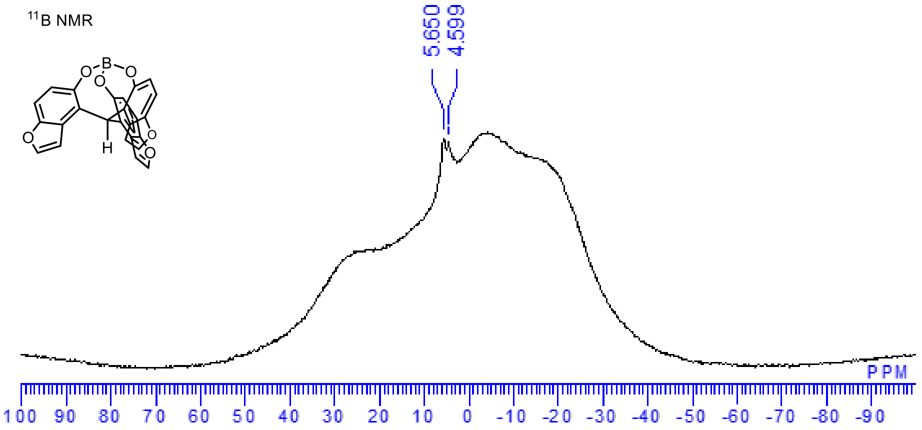
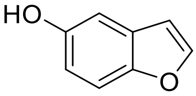


Figure S6. ^{11}B NMR (127 MHz, $CDCl_3$) of after the treatment of **4**·THF with washing with Et_2O.

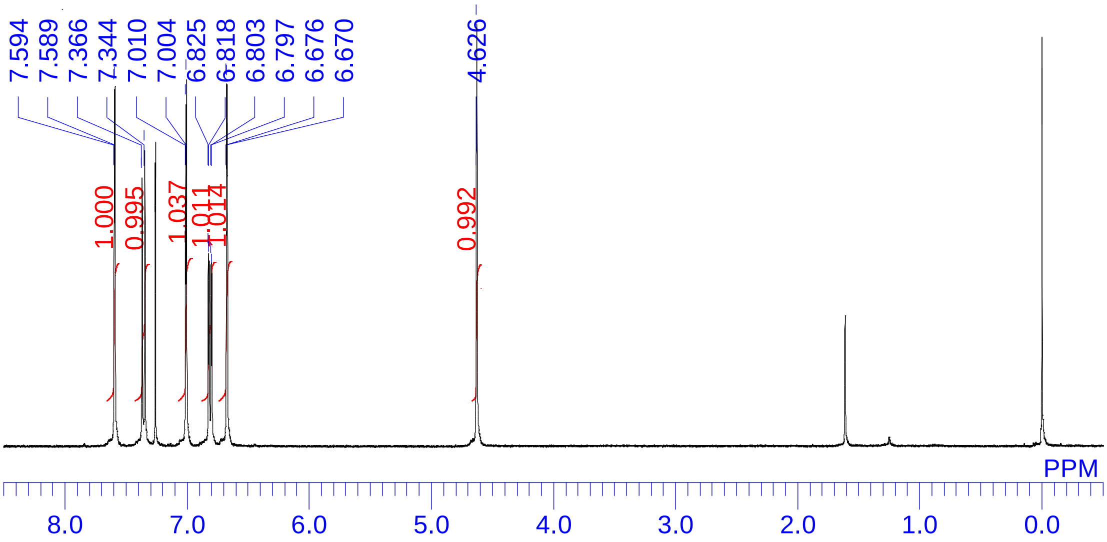
Since the dissociation of THF from the boron center should promote an intermolecular interaction, we attempted to observe the existence of the ligand-free complex under suitable conditions, although the normal cage-shaped borates always bear one equivalent of an external ligand. Actually, when the borate **2**·THF was set under reduced pressure for an extended period of time, it decomposed presumably because of the instability of the three-coordinated ligand-free structure. On the contrary, the complex of **4**·THF was dissolved in diethyl ether wherein the volatiles were evaporated under reduced pressure, and its caged shape remained. The ^{11}B-NMR spectrum of the residue showed two distinguishable peaks (5.65 and 4.60 ppm), which were assigned to solvent-coordinated or free borate. These results indicate that **4** easily released its own solvent-ligand and attained a stable assembly caused by the dipole-dipole interaction, which contributed to its high affinity to the substrate and to its high catalytic turnover during the catalyzing reaction course.

12. Spectrum charts

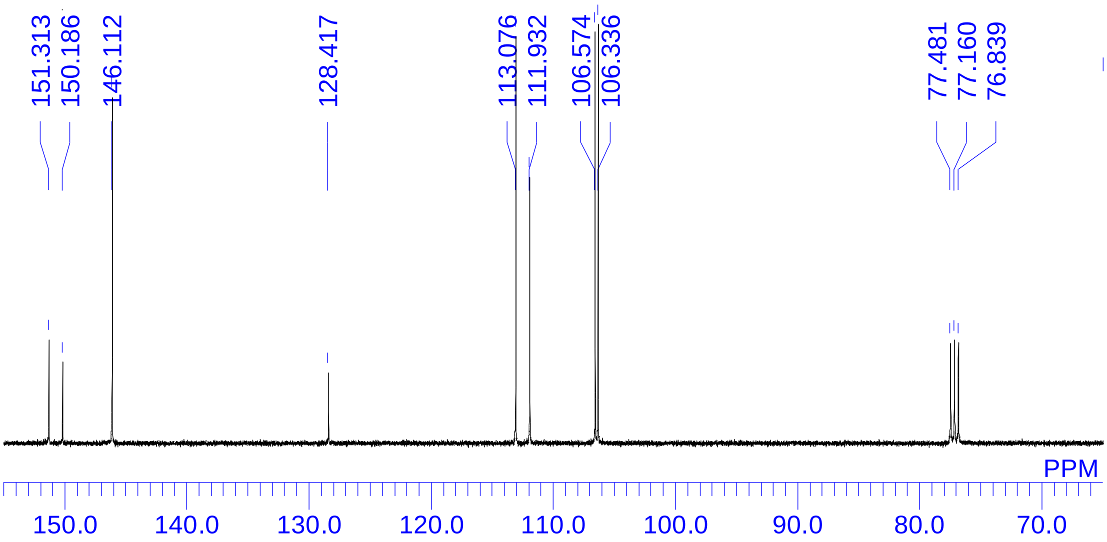
5-hydroxybenzofuran 7



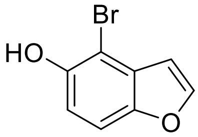
^{1}H NMR: (400 MHz, $CDCl_3$)



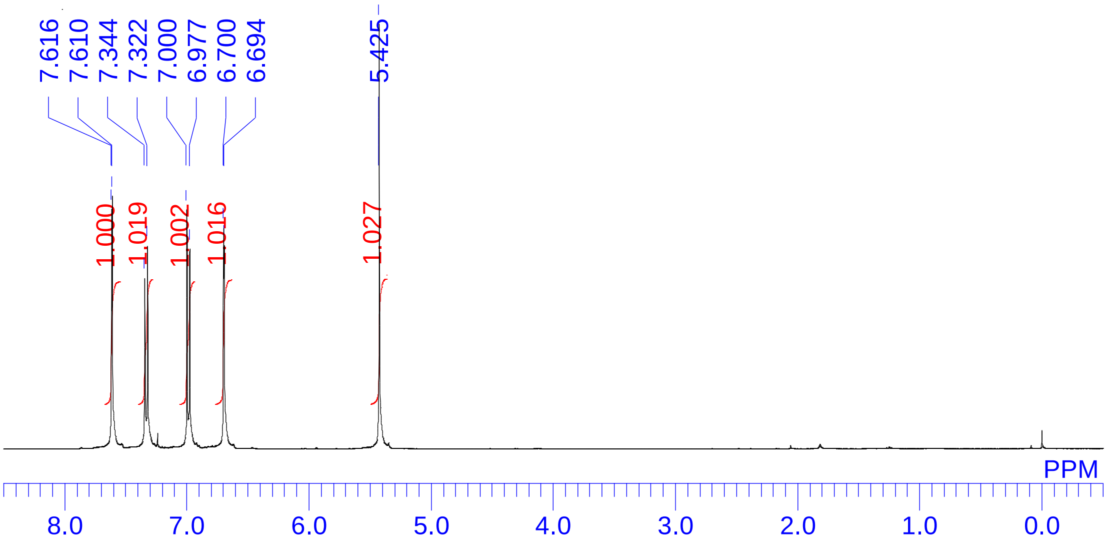
^{13}C NMR: (100 MHz, $CDCl_3$)



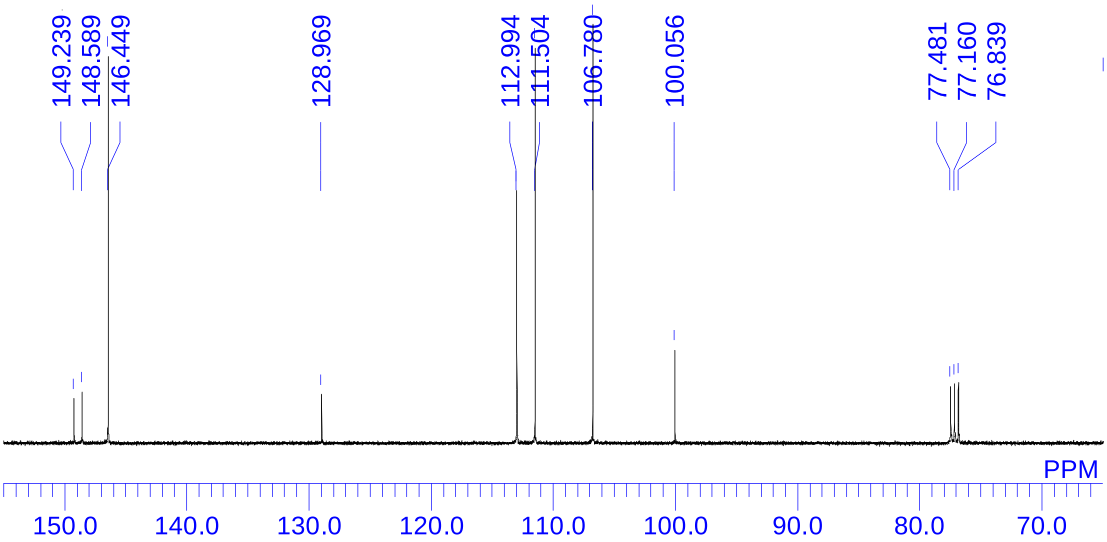
5-hydroxybenzofuran 8



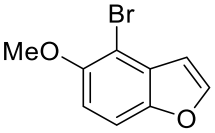
^{1}H NMR: (400 MHz, $CDCl_3$)



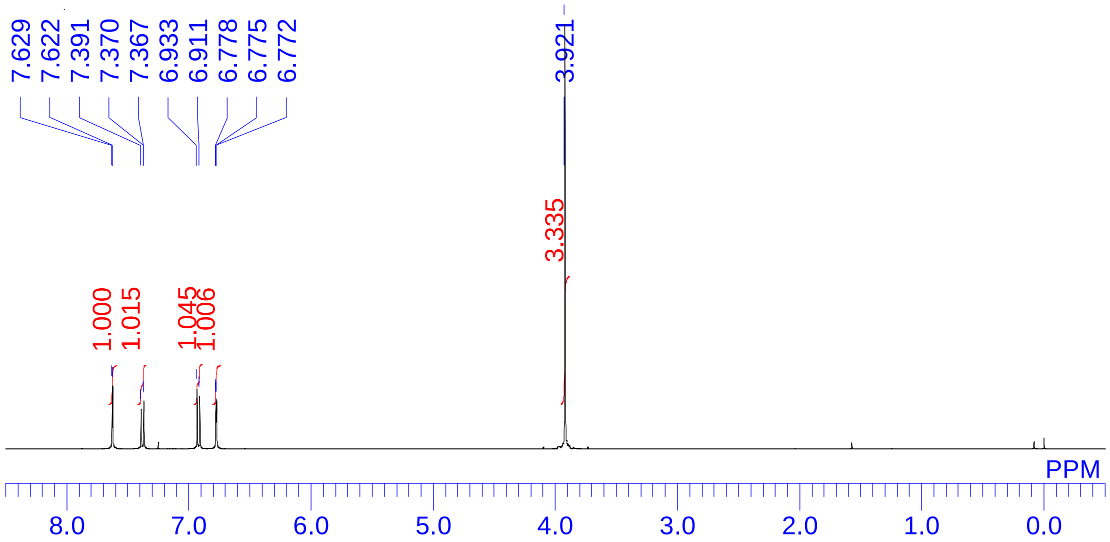
^{13}C NMR: (100 MHz, $CDCl_3$)



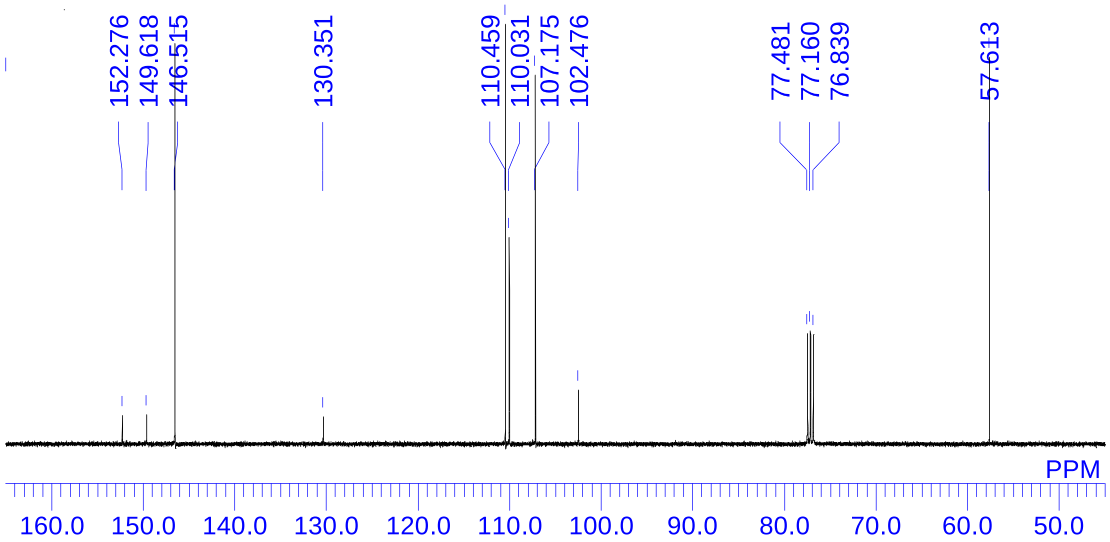
4-Bromo-5-methoxybenzofuran 9



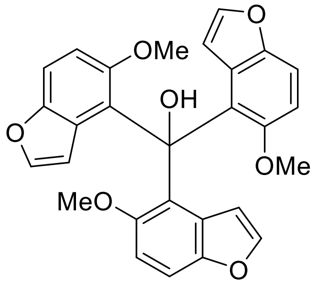
^{1}H NMR: (400 MHz, $CDCl_3$)



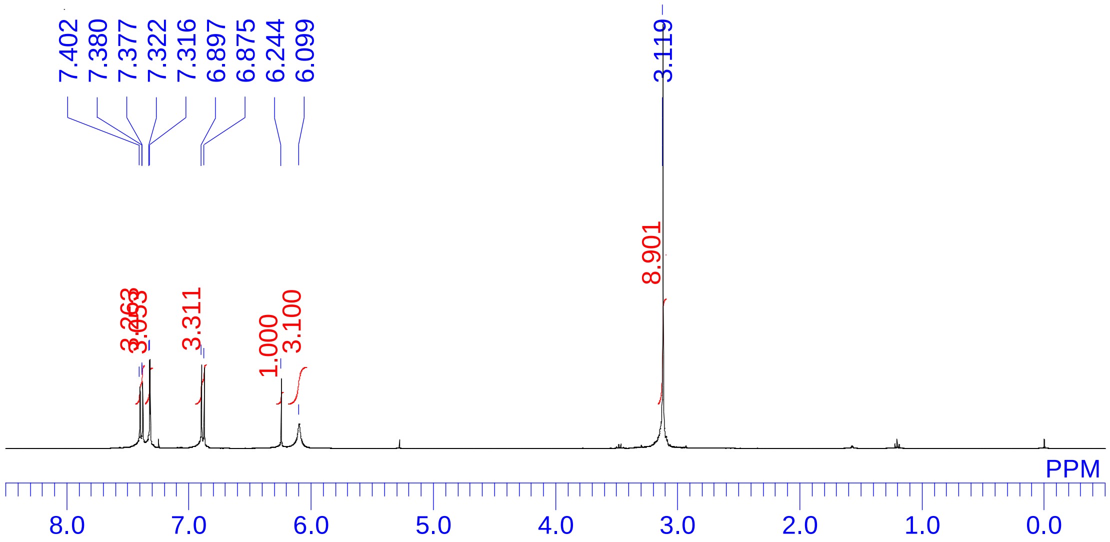
^{13}C NMR: (100 MHz, $CDCl_3$)



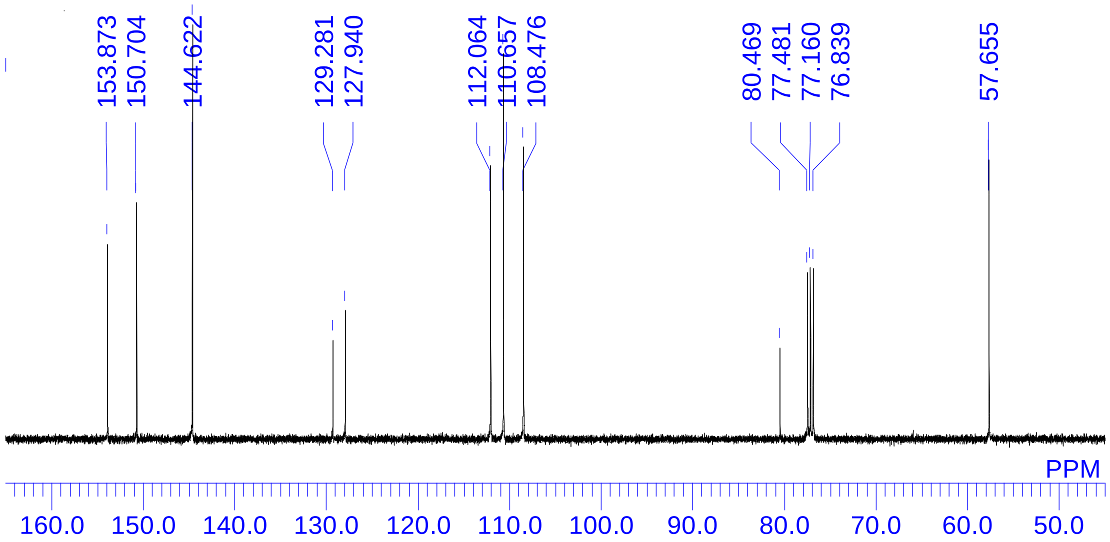
Tris(5-methoxy-4-benzofuranyl)methanol 10



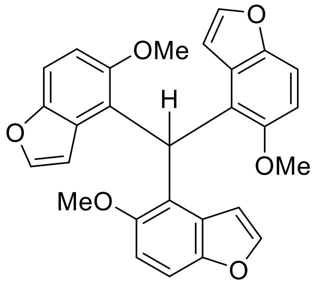
^{1}H NMR: (400 MHz, CDCl$_3$)



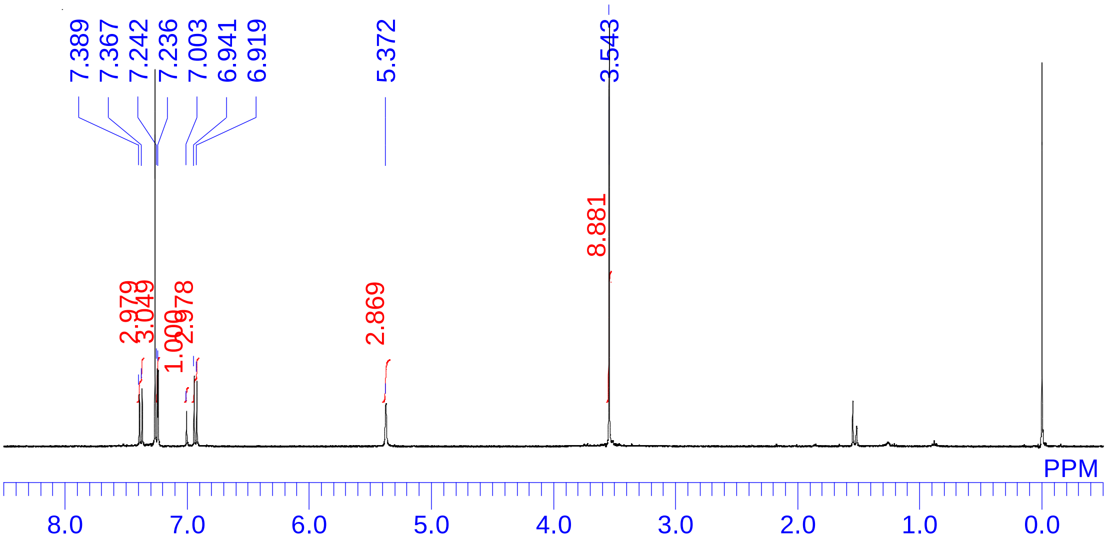
^{13}C NMR: (100 MHz, CDCl$_3$)



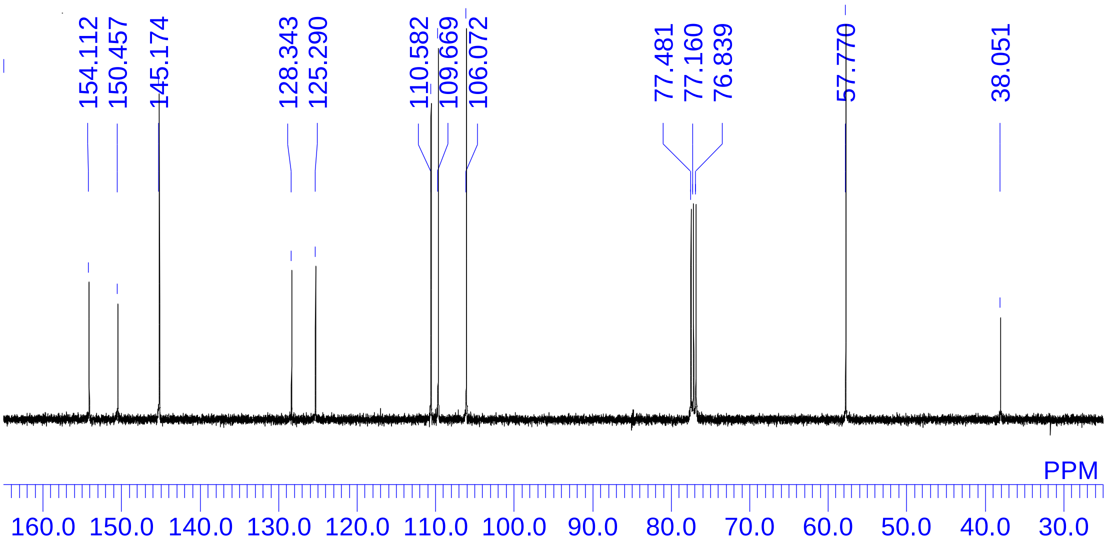
Tris(5-methoxy-4-benzofuranyl)methane 11



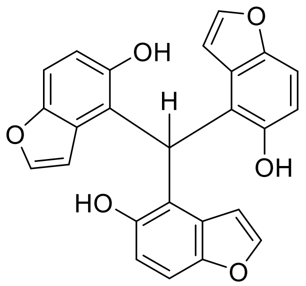
^{1}H NMR: (400 MHz, CDCl$_3$)



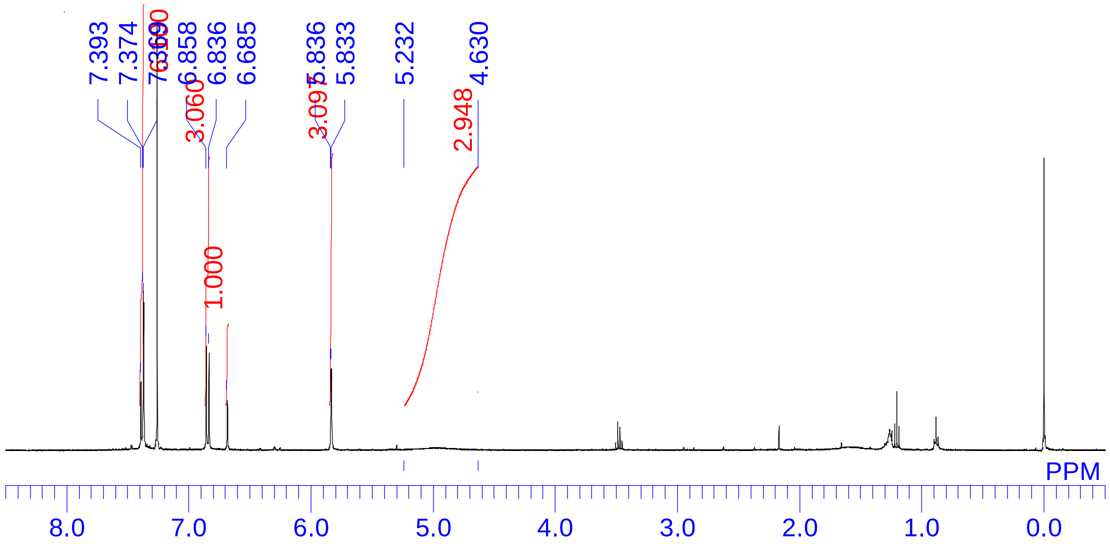
^{13}C NMR: (100 MHz, CDCl$_3$)



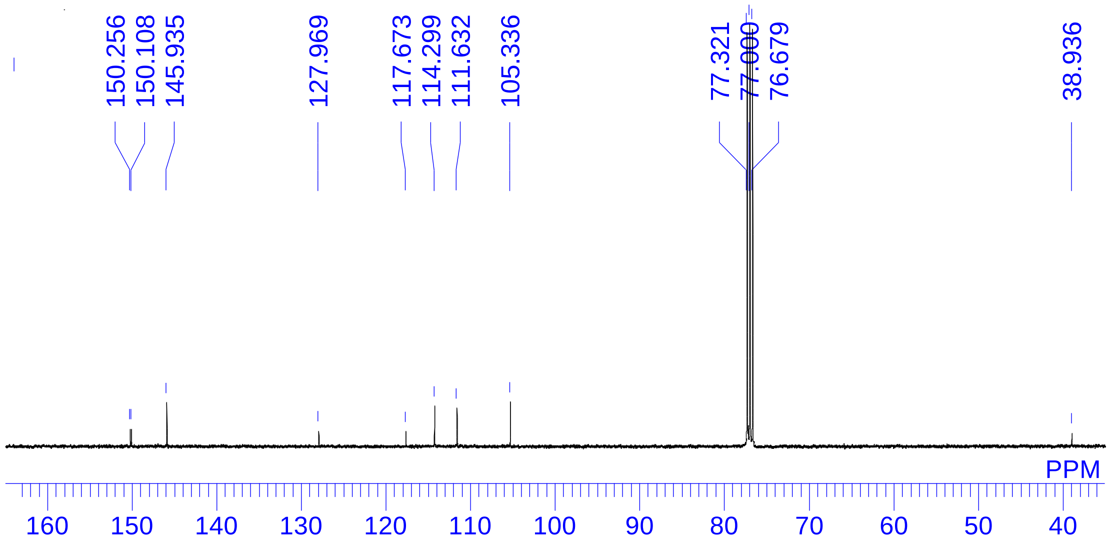
Tris(5-hydroxy-4-benzofuranyl)methane 12



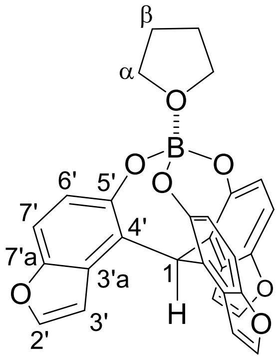
^{1}H NMR: (400 MHz, CDCl$_3$)



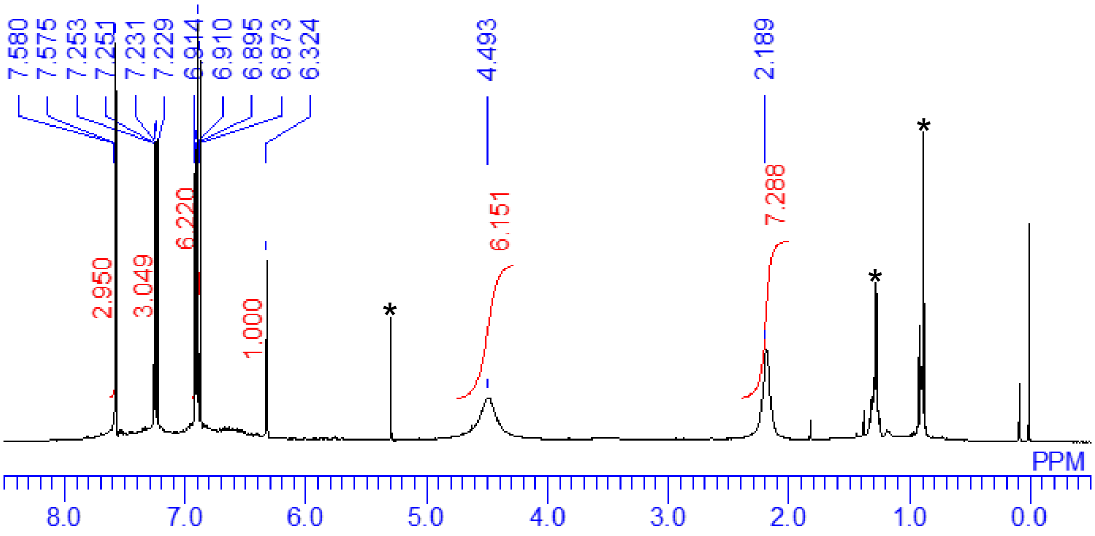
^{13}C NMR: (100 MHz, CDCl$_3$)



4·THF

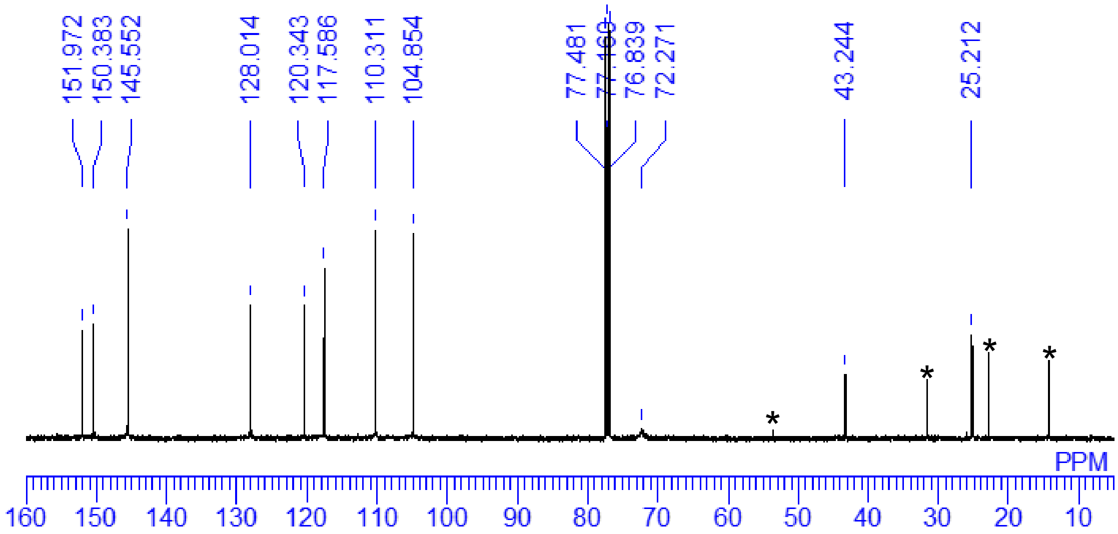


^{1}H NMR: (400 MHz, $CDCl_3$)



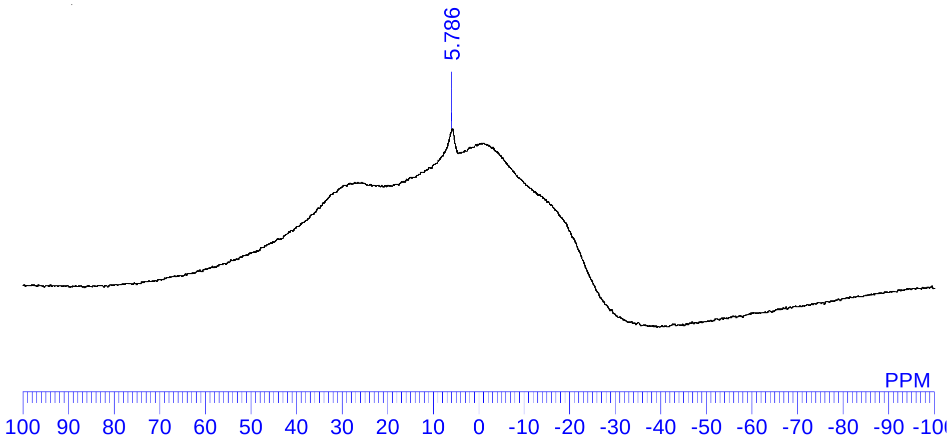
Asterisks represent the residual solvents.

^{13}C NMR: (100 MHz, $CDCl_3$)



Asterisks represent the residual solvents.

^{11}B NMR (127 MHz, $CDCl_3$)



13. Geometry (PDB) for DFT calculations

Benzofuran complex **4**

HETATM	1	O	0	-0.116	-1.369	-2.484	O
HETATM	2	O	0	1.243	0.583	-2.484	O
HETATM	3	O	0	-1.127	0.784	-2.484	O
HETATM	4	O	0	-1.028	4.495	1.516	O
HETATM	5	O	0	4.407	-1.357	1.517	O
HETATM	6	O	0	-3.380	-3.136	1.517	O
HETATM	7	C	0	-0.929	-1.172	-0.240	C
HETATM	8	C	0	-0.550	2.413	0.730	C
HETATM	9	C	0	-0.946	-1.821	-1.481	C
HETATM	10	C	0	-1.103	1.729	-1.482	C
HETATM	11	C	0	-1.123	3.661	0.437	C
HETATM	12	C	0	-0.075	2.527	2.087	C
HETATM	13	C	0	0.000	-0.000	0.114	C
HETATM	14	C	0	2.050	0.090	-1.481	C
HETATM	15	C	0	3.420	-0.041	-1.752	C
HETATM	16	C	0	3.733	-0.858	0.438	C
HETATM	17	C	0	4.296	-0.515	-0.783	C
HETATM	18	C	0	-1.702	3.977	-0.784	C
HETATM	19	C	0	2.365	-0.731	0.731	C
HETATM	20	C	0	-1.675	2.981	-1.752	C
HETATM	21	C	0	1.480	-0.219	-0.240	C
HETATM	22	C	0	-1.745	-2.942	-1.751	C
HETATM	23	C	0	-0.551	1.390	-0.241	C
HETATM	24	C	0	3.473	-1.553	2.491	C
HETATM	25	C	0	-3.083	-2.229	2.491	C

```
HETATM   26  C       0     2.227  -1.198   2.088        C
HETATM   27  C       0    -1.816  -1.681   0.731        C
HETATM   28  C       0    -2.151  -1.327   2.088        C
HETATM   29  C       0    -2.611  -2.802   0.438        C
HETATM   30  C       0    -0.390   3.784   2.489        C
HETATM   31  C       0    -2.595  -3.462  -0.782        C
HETATM   32  B       0     0.000  -0.001  -2.531        B
HETATM   33  H       0    -1.684  -3.387  -2.738        H
HETATM   34  H       0    -3.218  -4.329  -0.971        H
HETATM   35  H       0    -3.624  -2.350   3.417        H
HETATM   36  H       0    -1.782  -0.500   2.678        H
HETATM   37  H       0    -2.090   3.150  -2.740        H
HETATM   38  H       0    -2.142   4.950  -0.973        H
HETATM   39  H       0    -0.224   4.315   3.415        H
HETATM   40  H       0     0.456   1.794   2.678        H
HETATM   41  H       0     1.326  -1.291   2.679        H
HETATM   42  H       0     3.850  -1.961   3.417        H
HETATM   43  H       0     3.775   0.234  -2.739        H
HETATM   44  H       0     5.358  -0.621  -0.972        H
HETATM   45  H       0     0.000  -0.000   1.207        H
END
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Benzofuran-Py complex **4**·Py

```
HETATM    1  O       0     1.599   0.216   1.293        O
HETATM    2  O       0     1.520   1.077  -0.967        O
HETATM    3  O       0     1.503  -1.323  -0.581        O
HETATM    4  O       0    -2.688  -2.052  -4.008        O
HETATM    5  O       0    -2.459   4.595   0.315        O
HETATM    6  O       0    -2.324  -2.513   3.936        O
HETATM    7  C       0    -0.661  -0.615   1.362        C
HETATM    8  C       0    -1.795  -1.095  -2.143        C
HETATM    9  C       0     0.606  -0.454   1.934        C
HETATM   10  C       0     0.447  -1.491  -1.423        C
HETATM   11  C       0    -1.570  -1.960  -3.224        C
HETATM   12  C       0    -3.155  -0.639  -2.307        C
HETATM   13  C       0    -1.082   0.001   0.031        C
HETATM   14  C       0     0.507   1.927  -0.649        C
HETATM   15  C       0     0.739   3.296  -0.899        C
HETATM   16  C       0    -1.396   3.817  -0.058        C
```

HETATM	17	C	0	-0.210	4.269	-0.617	C
HETATM	18	C	0	-0.367	-2.619	-3.436	C
HETATM	19	C	0	-1.665	2.462	0.189	C
HETATM	20	C	0	0.640	-2.359	-2.517	C
HETATM	21	C	0	-0.713	1.472	-0.134	C
HETATM	22	C	0	0.908	-0.951	3.220	C
HETATM	23	C	0	-0.780	-0.861	-1.191	C
HETATM	24	C	0	-3.400	3.736	0.804	C
HETATM	25	C	0	-3.328	-2.455	3.014	C
HETATM	26	C	0	-2.992	2.443	0.757	C
HETATM	27	C	0	-1.599	-1.354	2.112	C
HETATM	28	C	0	-2.963	-1.775	1.898	C
HETATM	29	C	0	-1.265	-1.843	3.385	C
HETATM	30	C	0	-3.621	-1.243	-3.429	C
HETATM	31	C	0	-0.025	-1.648	3.975	C
HETATM	32	B	0	1.878	-0.020	-0.104	B
HETATM	33	H	0	1.906	-0.768	3.605	H
HETATM	34	H	0	0.204	-2.026	4.966	H
HETATM	35	H	0	-4.243	-2.956	3.295	H
HETATM	36	H	0	-3.582	-1.625	1.024	H
HETATM	37	H	0	1.616	-2.823	-2.626	H
HETATM	38	H	0	-0.221	-3.289	-4.276	H
HETATM	39	H	0	-4.571	-1.193	-3.940	H
HETATM	40	H	0	-3.704	0.066	-1.698	H
HETATM	41	H	0	-3.556	1.593	1.115	H
HETATM	42	H	0	-4.309	4.199	1.158	H
HETATM	43	H	0	1.694	3.571	-1.337	H
HETATM	44	H	0	-0.033	5.321	-0.816	H
HETATM	45	H	0	-2.173	0.010	0.082	H
HETATM	46	C	0	4.225	-1.172	-0.261	C
HETATM	47	C	0	4.183	1.135	0.023	C
HETATM	48	C	0	5.613	-1.189	-0.213	C
HETATM	49	H	0	3.620	-2.062	-0.395	H
HETATM	50	C	0	5.568	1.193	0.082	C
HETATM	51	H	0	3.552	2.013	0.104	H
HETATM	52	C	0	6.297	0.012	-0.040	C
HETATM	53	H	0	6.140	-2.132	-0.313	H
HETATM	54	H	0	6.059	2.151	0.219	H
HETATM	55	H	0	7.382	0.027	-0.001	H

HETATM	56	N	0	3.535	-0.028	-0.147	N

END

Pyridine

HETATM	1	C1	UNK	1	-1.141	0.722	0.000	C
HETATM	2	C2	UNK	1	-1.198	-0.672	0.000	C
HETATM	3	C3	UNK	1	0.000	-1.384	0.000	C
HETATM	4	C4	UNK	1	1.198	-0.672	0.000	C
HETATM	5	C5	UNK	1	1.141	0.722	0.000	C
HETATM	6	H6	UNK	1	-2.058	1.309	0.000	H
HETATM	7	H7	UNK	1	-2.157	-1.182	0.000	H
HETATM	8	H8	UNK	1	0.000	-2.471	0.000	H
HETATM	9	H9	UNK	1	2.157	-1.182	0.000	H
HETATM	10	H10	UNK	1	2.058	1.309	0.000	H
HETATM	11	N11	UNK	1	0.000	1.419	0.000	N

END

Benzofuran dimer **4-**dimer

O	5.14733900	1.39075200	-2.52652300
O	4.14954700	-0.77712900	-2.76368100
O	6.47332100	-0.58360500	-2.18864600
O	6.06347800	-4.17762700	1.95528300
O	-0.14289700	0.52664900	0.41665500
O	6.90829500	3.74966000	2.11997000
C	5.39708300	1.35274500	-0.12751100
C	5.42957400	-2.23424400	0.92057500
C	5.60439600	2.00643000	-1.35129300
C	6.38152500	-1.51022300	-1.13866300
C	6.27934000	-3.35617900	0.85179200
C	4.65472100	-2.39856500	2.13381400
C	4.63163400	0.02569500	0.04447600
C	3.04183600	-0.45180200	-1.97448000
C	1.77083500	-0.59562100	-2.54666900
C	0.83643400	0.14474600	-0.52618900
C	0.62030900	-0.30149400	-1.81831900
C	7.19016700	-3.58151500	-0.17015400
C	2.09465100	0.29852500	0.07495500
C	7.22382700	-2.63029400	-1.18506100
C	3.25663900	-0.03265000	-0.65064800

C	6.21231300	3.26440800	-1.46967900
C	5.48523900	-1.25163800	-0.09078000
C	0.53015300	0.93352300	1.59549400
C	6.54587800	2.76434400	3.03920600
C	1.86209500	0.80682800	1.41650100
C	5.89761800	2.01819400	1.01164600
C	5.93892300	1.71293700	2.42752700
C	6.51040900	3.27930300	0.87105700
C	5.06382400	-3.56064100	2.70840400
C	6.67455300	3.93426200	-0.34110900
B	5.27994700	0.01032200	-2.57008500
H	6.31347700	3.69161200	-2.45945100
H	7.14428700	4.90756200	-0.40198900
H	6.80426600	2.97509200	4.06243900
H	5.60145200	0.81281500	2.91757800
H	7.89109700	-2.73264500	-2.03160000
H	7.83029600	-4.45435800	-0.17835900
H	4.76887800	-4.08829700	3.59876100
H	3.87101300	-1.75841000	2.50791100
H	2.60800800	1.08332600	2.14519500
H	-0.12288600	1.27496800	2.37686800
H	1.70910300	-0.93336200	-3.57346200
H	-0.37363800	-0.38716600	-2.23458600
H	4.37078400	0.03064800	1.10662200
O	-2.29810100	0.96335600	1.45450900
O	-2.11579600	0.95170400	-0.98137800
O	-1.95503400	-1.12440700	0.25522800
O	-5.54798200	-3.68710800	-3.03186100
O	-6.58200400	4.09167300	-1.65766800
O	-6.51455300	-1.01317200	4.39253400
C	-4.50706700	-0.05050400	1.53482300
C	-5.01025500	-1.96949700	-1.61123800
C	-3.37746600	0.47117100	2.18009200
C	-2.87770700	-1.76511200	-0.56034400
C	-4.54750000	-3.15009200	-2.22226500
C	-6.36684200	-1.78353700	-2.08774700
C	-4.73602300	-0.04061200	0.01880300
C	-3.24946200	1.73501700	-1.15360300
C	-3.08357600	2.93796500	-1.86539800

C	-5.37741500	3.39477000	-1.56953200
C	-4.15662600	3.79222300	-2.09582400
C	-3.28061700	-3.67828100	-2.02032000
C	-5.57142400	2.19497200	-0.85944200
C	-2.44317100	-2.95349900	-1.17901200
C	-4.48856600	1.31215200	-0.65702800
C	-3.27686000	0.55509500	3.58210200
C	-4.17174100	-1.25387700	-0.72884900
C	-7.52736100	3.31374100	-0.98595100
C	-7.34658300	-1.45016800	3.35939400
C	-6.97423200	2.17379000	-0.49424800
C	-5.52149600	-0.55660100	2.37687900
C	-6.79980600	-1.19890400	2.14087900
C	-5.38945600	-0.46877900	3.77520500
C	-6.63770200	-2.82060500	-2.92334900
C	-4.29230200	0.09203200	4.41155300
B	-1.84753400	0.30302800	0.26584100
H	-2.37978300	0.99504500	4.00096000
H	-4.22995300	0.15584800	5.49055500
H	-8.26360000	-1.91602700	3.67615000
H	-7.23192500	-1.47224700	1.19077800
H	-1.43191500	-3.28427500	-0.97525000
H	-2.96353100	-4.59674600	-2.49804200
H	-7.49859500	-3.09194300	-3.50949800
H	-7.03419200	-0.96482900	-1.86739200
H	-7.48980400	1.42717300	0.08978400
H	-8.52014300	3.72790100	-0.95180500
H	-2.08999400	3.17835700	-2.22367100
H	-4.04779500	4.71925400	-2.64445800
H	-5.81821000	-0.17161700	-0.07100300

END

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