Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Selective Recognition between Aromatics and Aliphatics by Cage-Shaped Borates Supported by Machine Learning Approach

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1. General

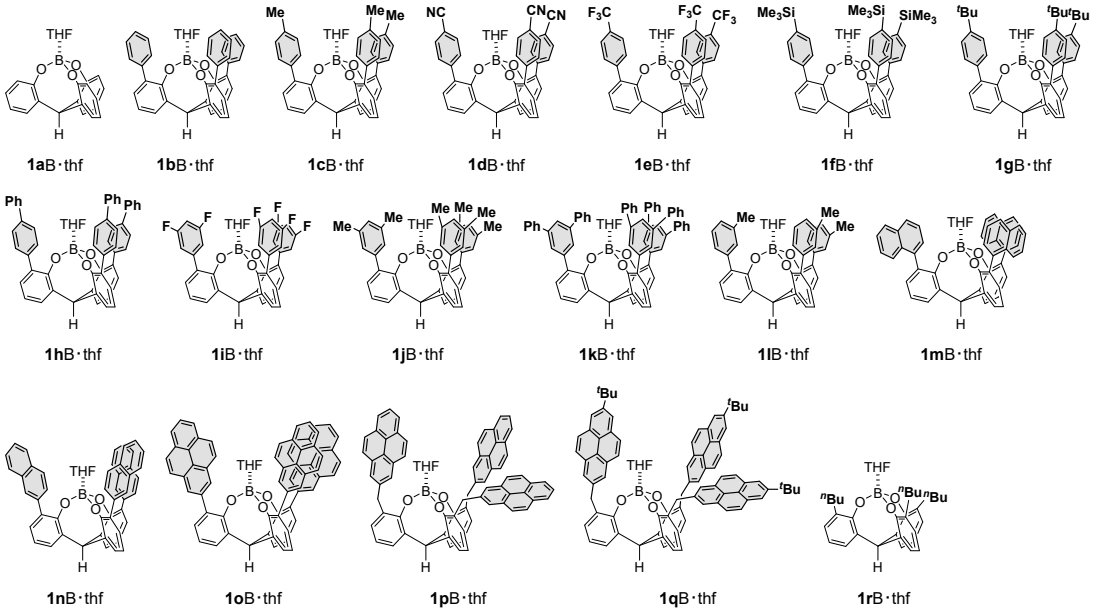
NMR spectra were recorded on JEOL-AL400, JEOL-ECS400 (400 MHz for ^{1}H, 100 MHz for ^{13}C, 127 MHz for ^{11}B NMR and 376 MHz for ^{19}F NMR) with TMS as an internal standard. ^{1}H and ^{13}C NMR signals of compounds were assigned using HMQC, HSQC, HMBC, COSY, and ^{13}C off-resonance techniques. Positive FAB, EI, MALDI-TOF mass spectra were recorded on a JEOL JMS-700, a Shimadzu GCMS-QP2010 Ultra, and a JEOL JMS-S3000, respectively. IR spectra were recorded as thin films or as solids in KBr pellets on a JASCO FT/IR 6200 spectrophotometer. Data collection for X-ray crystal analysis was performed on Rigaku/XtaLAB Synergy-S/Mo (MoK_α λ = 0.71075 Å), Rigaku/XtaLAB Synergy-S/Cu (CuK_α λ = 1.54187 Å) diffractometers. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed at calculated positions and refined "riding" on their corresponding carbon atoms by Olex2[1] program.

All apparatuses for flow synthesis were purchased from YMC. CO., LTD. Stainless steel (SUS316) T-shaped microreactor (YMC-P-0019) with inner diameters of 0.5 mm was used. The microreactor and gastight syringes were connected with PTFE tube (YMC-P-0025, inner diameter of 0.5 mm, OUW 1/16) equipped with PEEK fittings (YMC-P-0064, 1/16 OUW). Solutions were continuously introduced to the flow microreactor system via using syringe pumps (YSP-101), equipped with gastight syringes (YMC-P-1007, 5 mL).

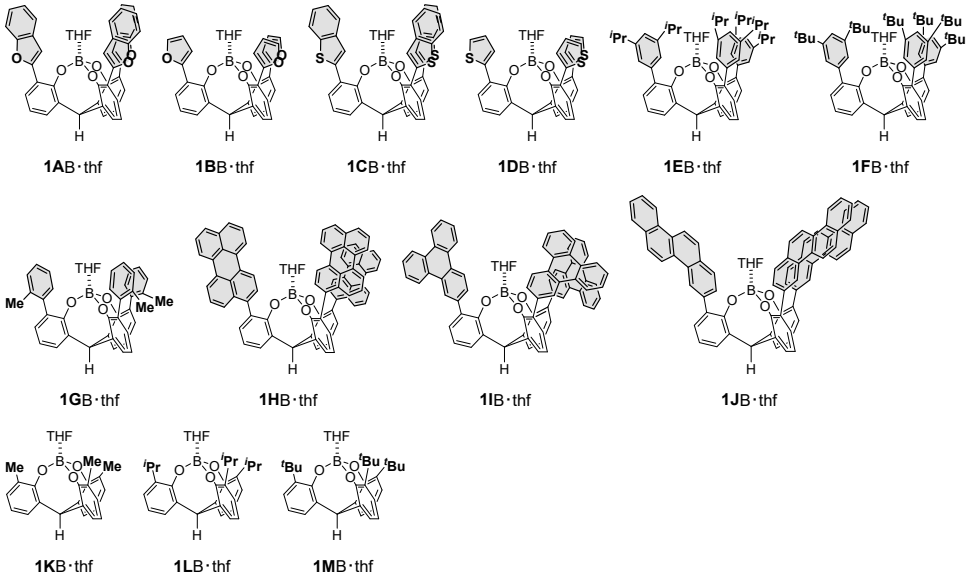
2. Materials

Anhydrous dichloromethane, THF, acetonitrile, diethylether, toluene and hexane were purchased and used as obtained. All reagents were obtained from commercial suppliers and used as received. Syntheses of cage-shaped borates and competitive hetero-Diels-Alder reactions were performed in a nitrogen-filled glove box. The products of model reactions, **4a**,[2] **4b**,[2] **4c**,[3] **4d**,[4] **4e**,[5] **4f**,[4] **4g**,[5] **4h**,[6] were known in literatures. The summary for the molecular structures of the cage-shaped borates described in the manuscript are shown in Figure S1.

A) Data collection



B) Prediction



C) Modified catalyst basd on 1AB

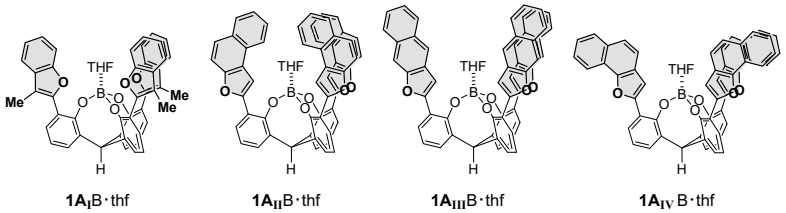
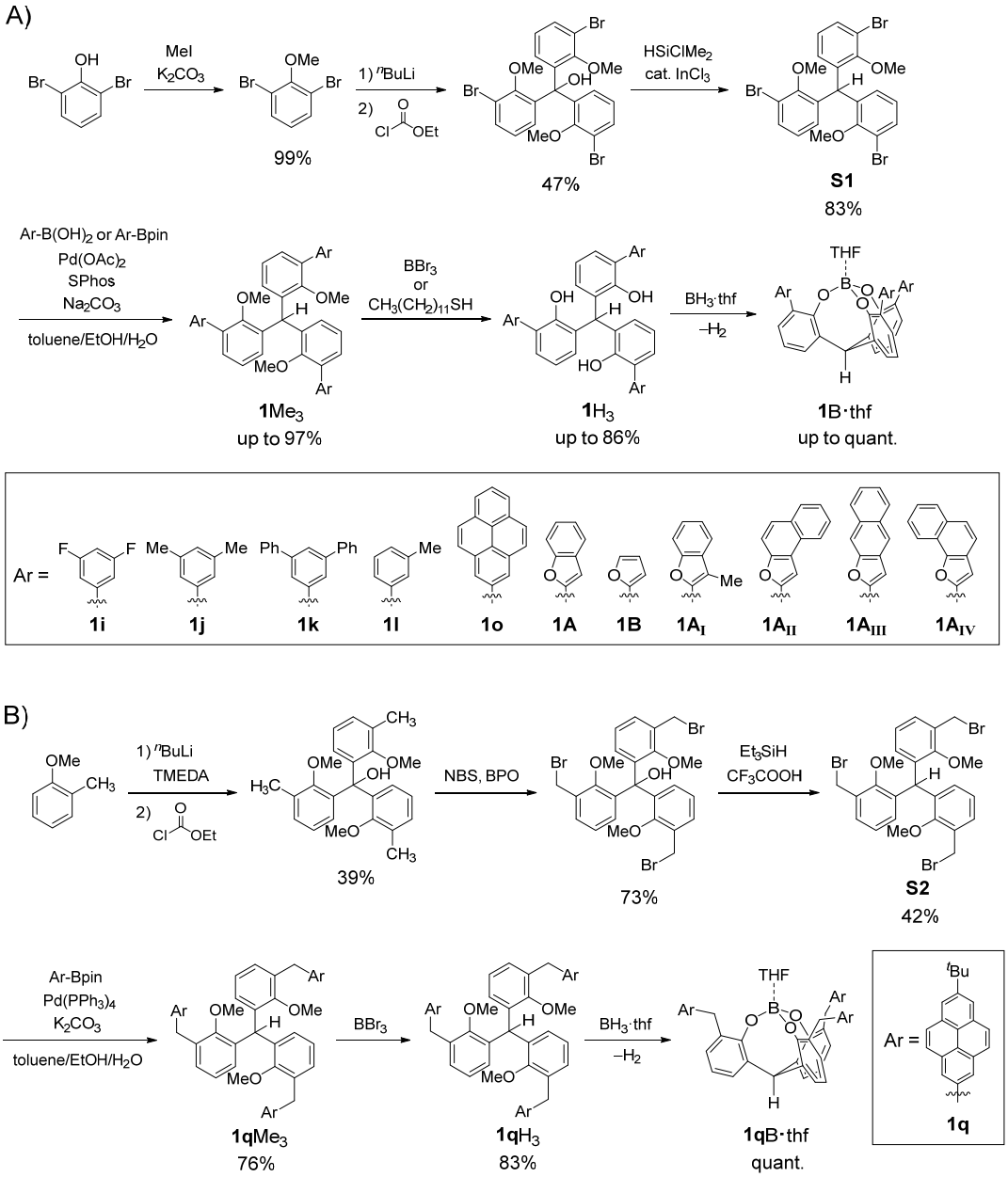


Figure S1. Summary for the molecular structures of the cage-shaped borates described in the manuscript. A) **1a**–**r**B·thf for data collection, B) **1A**–**M**B·thf for prediction, and C) Modified catalyst $\mathbf{1A_I}$–$\mathbf{A_{IV}}$B·thf.

3. Synthetic routes

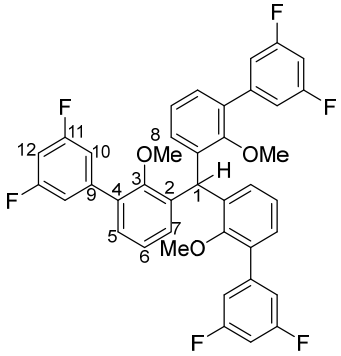
Cage-shaped borates (**1a**B·thf,[7] **1b**B·thf,[8] **1c**B·thf,[9] **1d**B·thf,[9] **1e**B·thf,[9] **1f**B·thf,[9] **1g**B·thf,[9] **1h**B·thf,[9] **1m**B·thf,[2] **1n**B·thf,[2] **1p**B·thf,[10] **1r**B·thf[10]) were synthesized according to our previous studies. The synthetic routes of borates **1i–l**B·thf, **1o**B·thf, **1q**B·thf, **1A**B·thf, **1B**B·thf, and **1A$_I$**–**A$_{IV}$**B·thf are summarized in Scheme S1.



Scheme S1. Synthetic routes to cage-shaped borates of A) **1i–l**B·thf, **1o**B·thf, **1A**B·thf, **1B**B·thf, and **1A$_I$**–**A$_{IV}$**B·thf and B) **1q**B·thf. TMEDA = *N*,*N*,*N*',*N*'-tetramethylethylenediamine, SPhos = 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl, NBS = *N*-bromosuccinimide, BPO = benzoyl peroxide.

4. Synthetic procedures

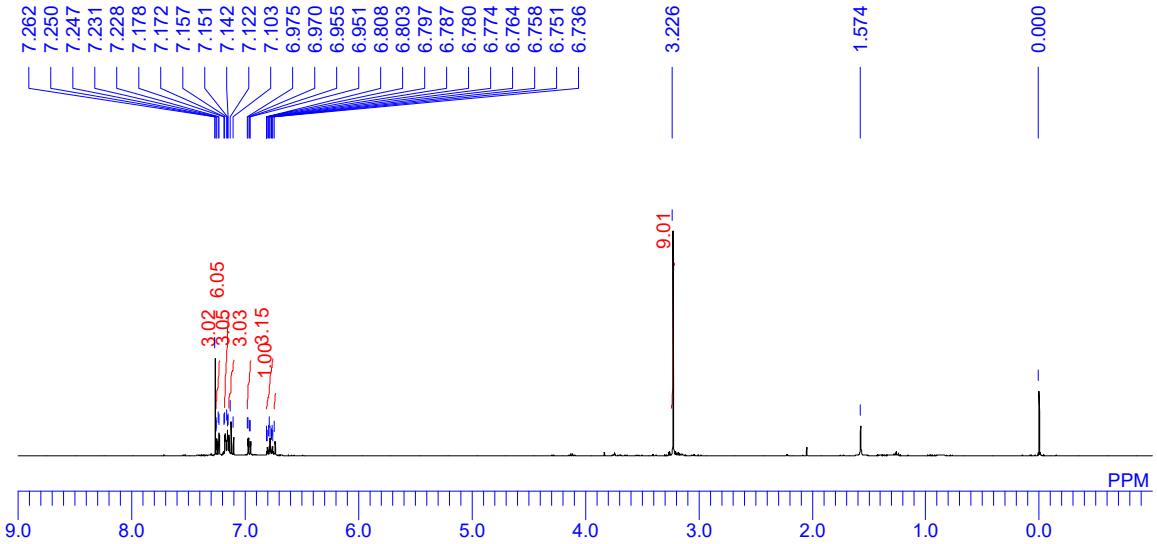
Tris{3',5'-difluoro-2-methoxy-(1,1'-biphenyl)-3-yl}methane 1iMe_3



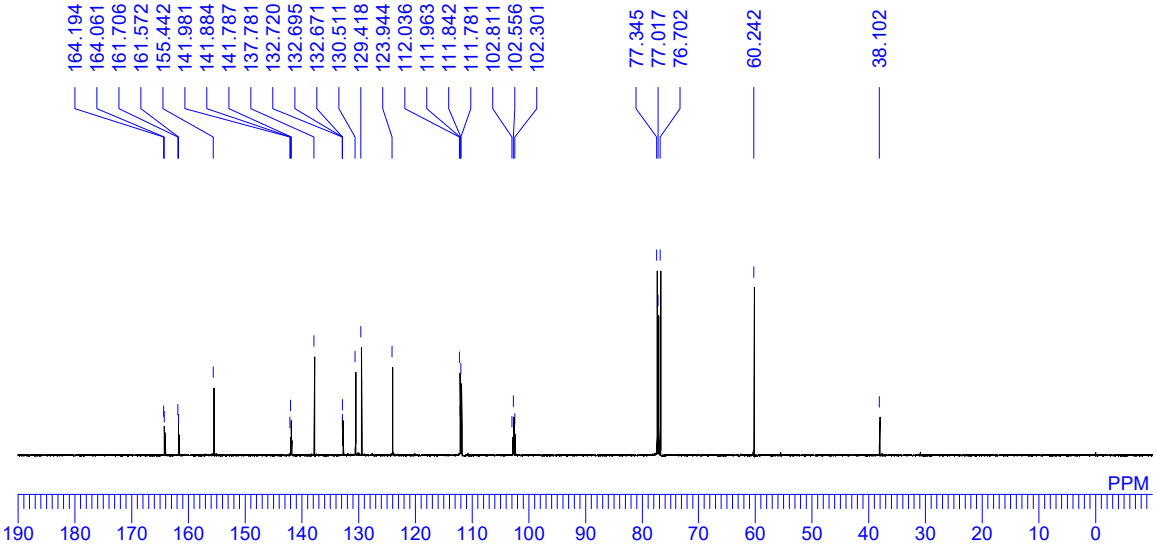
The mixture of **S1** (0.228 g, 0.40 mmol), 3,5-difluorophenylboronic acid (0.208 g, 1.32 mmol), palladium(II) acetate (9.0 mg, 0.04 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (32.8 mg, 0.08 mmol), and Na_2CO_3 (0.382 g, 3.60 mmol) in toluene (10 mL), ethanol (2.0 mL) and distilled water (2.0 mL) was heated at 100 °C for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3×10 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 90:10) on silica gel to give **1i**Me_3 as a colorless solid (0.205 g, 76%).

mp 117.2–117.6 °C; IR (KBr) ν = 3085 (w), 2941 (w), 1626 (s), 1597 (s), 1454 (m), 1410 (s), 1342 (m), 1248 (m), 1119 (s), 988 (s), 863 (m), 761 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.24 (dd, J = 7.6, 1.6 Hz, 3H), 7.16 (dd, $^3J_{H–F}$ = 8.6 Hz, $^4J_{H–H}$ = 2.6 Hz, 6H, 10-H), 7.12 (t, J = 8.0 Hz, 3H), 6.96 (dd, J = 7.8, 1.8 Hz, 3H), 6.78 (tt, $^3J_{H–F}$ = 9.2 Hz, $^4J_{H–H}$ = 2.4 Hz, 3H, 12-H), 6.74 (s, 1H, 1-H), 3.23 (s, 9H, 8-H); ^{13}C NMR (100 MHz, $CDCl_3$) 162.9 (s, dd, $^1J_{C–F}$ = 248.9 Hz, $^3J_{C–F}$ = 13.4 Hz, C-11), 155.4 (s), 141.9 (s, t, $^3J_{C–F}$ = 9.7 Hz, C-9), 137.8 (s), 132.7 (s, t, $^4J_{C–F}$ = 2.5 Hz, C-4), 130.5 (d), 129.4 (d), 123.9 (d), 111.9 (d, dd, $^2J_{C–F}$ = 18.8 Hz, $^4J_{C–F}$ = 6.7 Hz, C-10), 102.6 (d, t, $^2J_{C–F}$ = 25.5 Hz, C-12), 60.2 (q, C-8), 38.1 (d, C-1); ^{19}F NMR (376 MHz, $CDCl_3$, BF_3·OEt_2 (−153 ppm) in $CDCl_3$ used as an external standard; *i.e.* $CFCl_3$ (0 ppm)) −103.0; HRMS (MALDI-TOF MS) Calculated ($C_{40}H_{28}O_3F_6Na$): 693.1835 ([M+Na]$^+$), Found: 693.1860.

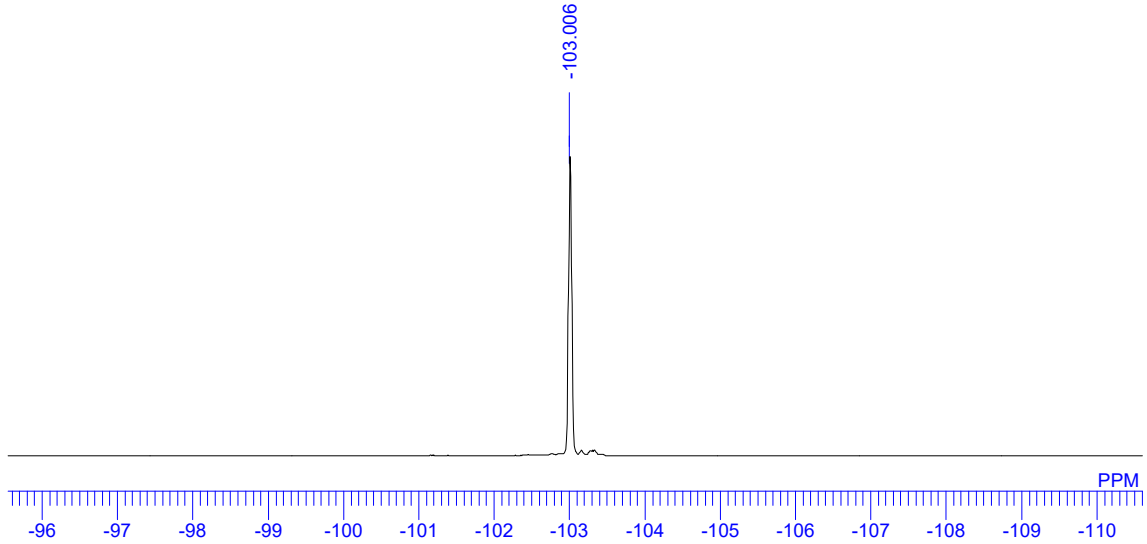
^{1}H NMR: (400 MHz, $CDCl_3$)



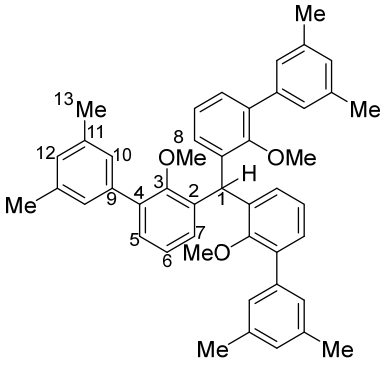
^{13}C NMR: (100 MHz, $CDCl_3$)



^{19}F NMR: (376 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ (−153 ppm) in $CDCl_3$ used as an external standard; *i.e.* $CFCl_3$ (0 ppm))



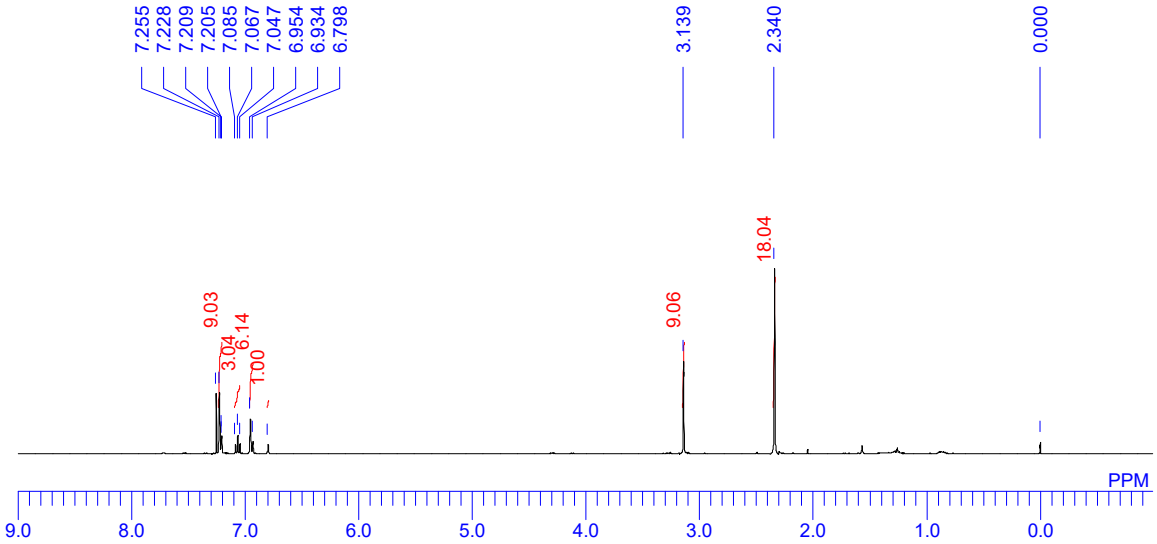
Tris{2-methoxy-3',5'-dimethyl-(1,1'-biphenyl)-3-yl}methane 1jMe_3



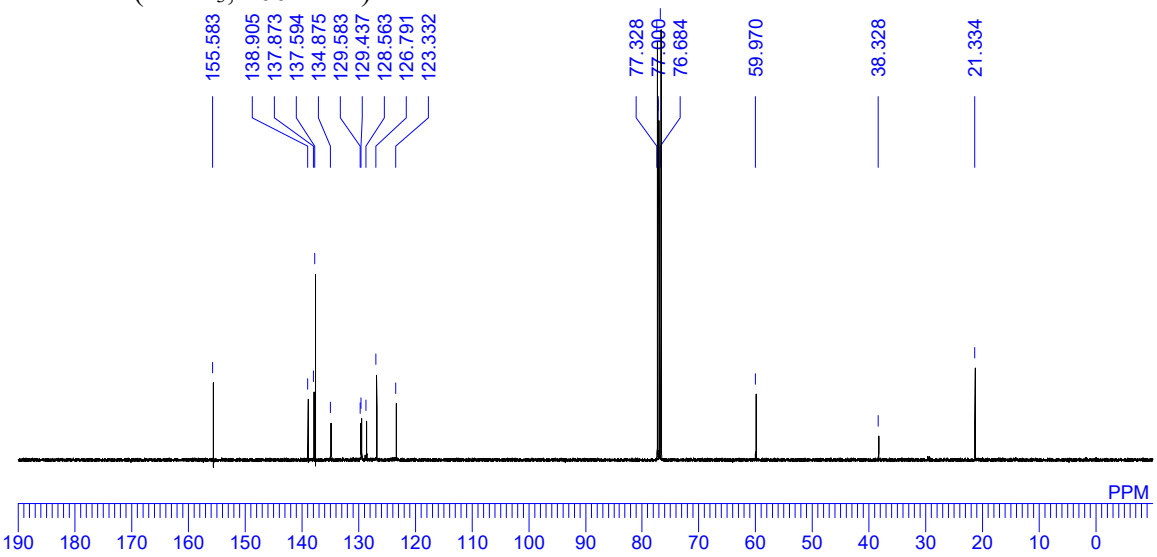
The mixture of **S1** (1.00 g, 1.75 mmol), 3,5-dimethylphenylboronic acid (0.87 g, 5.78 mmol), palladium(II) acetate (58 mg, 0.26 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (213 mg, 0.52 mmol), and Na_2CO_3 (1.85 g, 17.5 mmol) in toluene (6 mL), ethanol (2 mL) and distilled water (2 mL) was heated at 100 °C for 22 h. The reaction was quenched by HCl aq. at 0 °C. The mixture was extracted with dichloromethane (3×15 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 20:80) on silica gel to give **1j**Me_3 as a colorless solid (1.07 g, 94%).

mp 116.2–116.7 °C; IR (KBr) ν = 3017 (w), 2937 (m), 1603 (m), 1460 (s), 1406 (m), 1243 (m), 1228 (m), 1087 (w), 1010 (s), 852 (m), 774 (m), 761 (m), 706 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.23–7.21 (m, 9H), 7.07 (t, J = 7.6 Hz, 3H, 6-H), 6.95–6.93 (m, 6H), 6.80 (s, 1H, 1-H), 3.14 (s, 9H, 8-H), 2.34 (s, 18H, 13-H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.6 (s), 138.9 (s), 137.9 (s), 137.6 (s), 134.9 (s), 129.6 (d), 129.4 (d), 128.6 (d), 126.8 (d), 123.3 (d), 60.0 (q, C-8), 38.3 (d, C-1), 21.3 (s, C-13); MS (EI^+, 70 eV) *m/z* 646 (M^+, 100), 615 (74), 403 (15), 225 (67), 211 (46); HRMS (EI^+, 70 eV) Calculated ($C_{46}H_{46}O_3$): 646.3447 (M^+), Found: 646.3450.

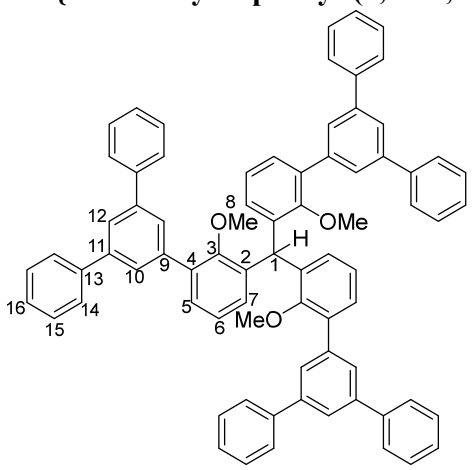
^{1}H NMR: ($CDCl_3$, 400 MHz)



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



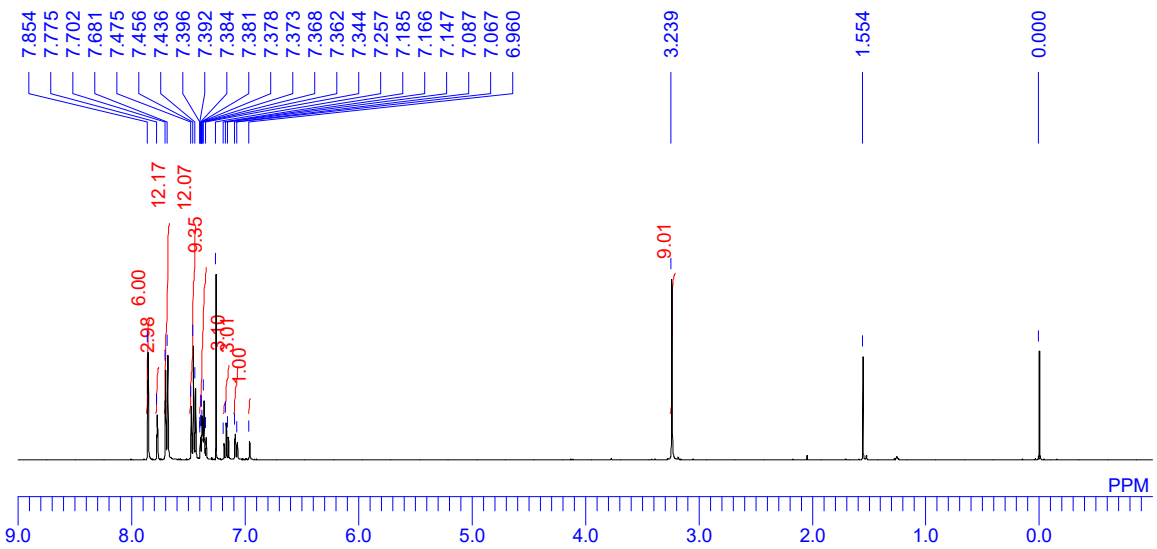
Tris{2-methoxy-5'-phenyl-(1,1':3',1''-terphenyl)-3-yl}methane 1kMe_3



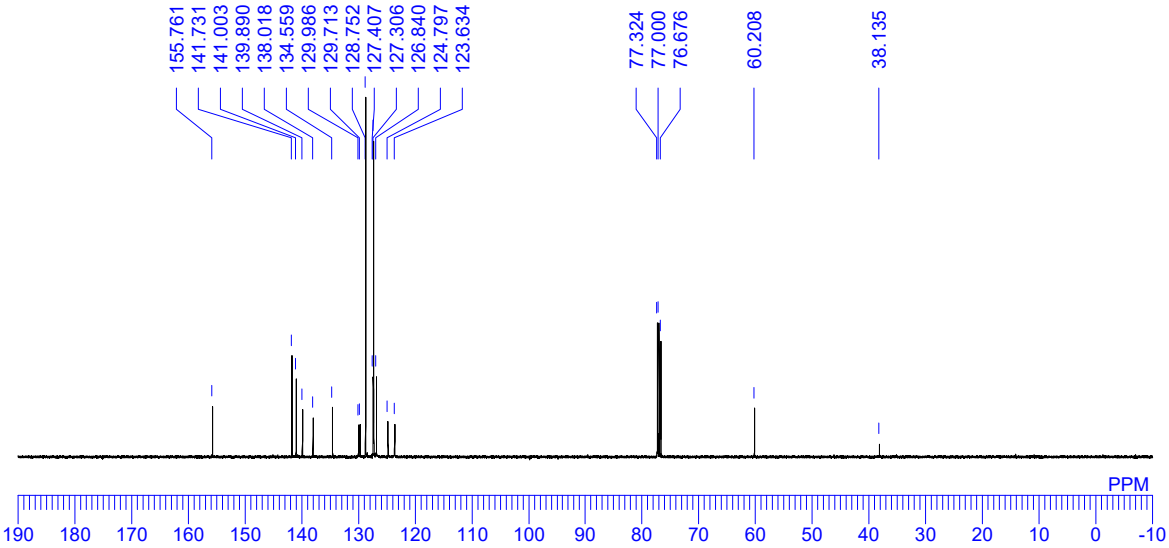
The mixture of **S1** (0.343 g, 0.60 mmol), 4,4,5,5-tetramethyl-2-(1,1′:3′,1″-terphenyl)-5′-yl-1,3,2-dioxaborolane (0.770 g, 2.16 mmol), palladium(II) acetate (13.5 mg, 0.06 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (49.3 mg, 0.12 mmol), and Na_2CO_3 (0.636 g, 6.00 mmol) in toluene (10 mL), ethanol (1.0 mL) and distilled water (1.0 mL) was heated at 100 ℃ for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3×20 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 10:90) on silica gel to give **1k**Me_3 as a colorless solid (0.601 g, 97%).

mp 138.5–139.1 ℃; IR (KBr) ν = 3033 (w), 2933 (w), 1595 (m), 1577 (m), 1497 (m), 1462 (m), 1402 (m), 1243 (w), 1220 (w), 1007 (m), 881 (w), 758 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.85 (s, 6H, 10-H), 7.78 (s, 3H, 12-H), 7.69 (d, J = 8.4 Hz, 12H, 14-H), 7.46 (t, J = 7.8 Hz, 12H, 15-H), 7.40–7.34 (m, 9H), 7.17 (t, J = 7.6 Hz, 3H, 6-H), 7.08 (d, J = 8.0 Hz, 3H), 6.96 (s, 1H, 1-H), 3.24 (s, 9H, 8-H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.8 (s), 141.7 (s), 141.0 (s), 139.9 (s), 138.0 (s), 134.6 (s), 130.0 (d), 129.7 (d), 128.8 (d), 127.4 (d), 127.3 (d), 126.8 (d), 124.8 (d), 123.6 (d), 60.2 (q, C-8), 38.1 (d, C-1); HRMS (MALDI-TOF MS) Calculated ($C_{76}H_{58}O_3Na$): 1041.4278 ($[M+Na]^+$), Found: 1041.4283.

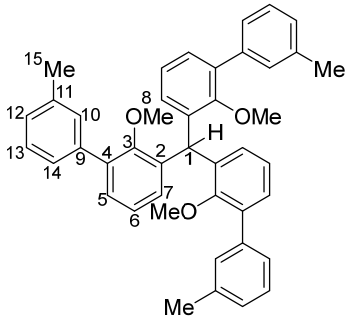
^{1}H NMR: ($CDCl_3$, 400 MHz)



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



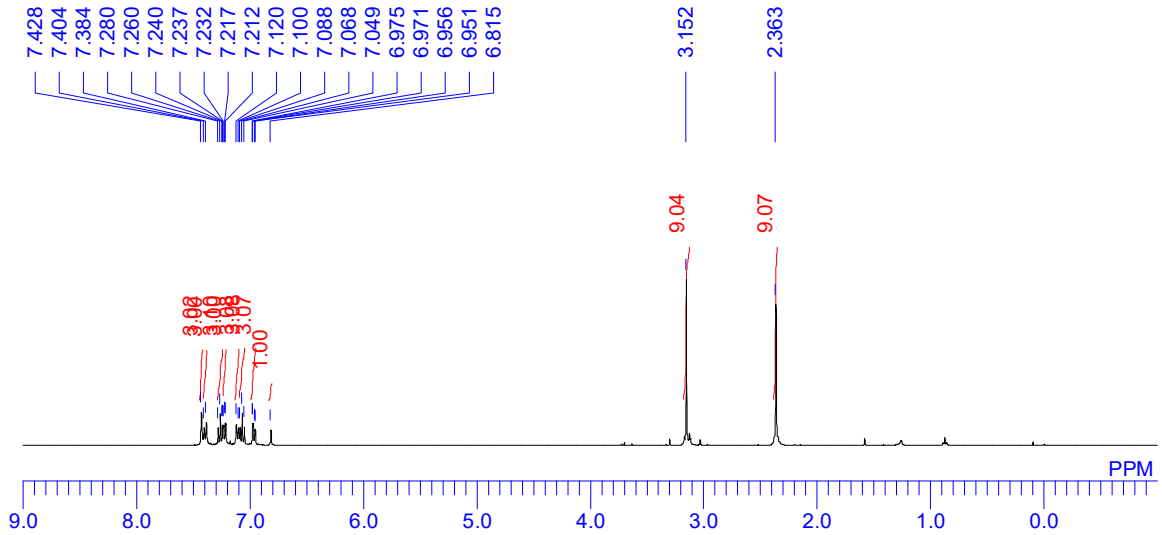
Tris{2-methoxy-3'-methyl-(1,1'-biphenyl)-3-yl}methane 1lMe$_3$



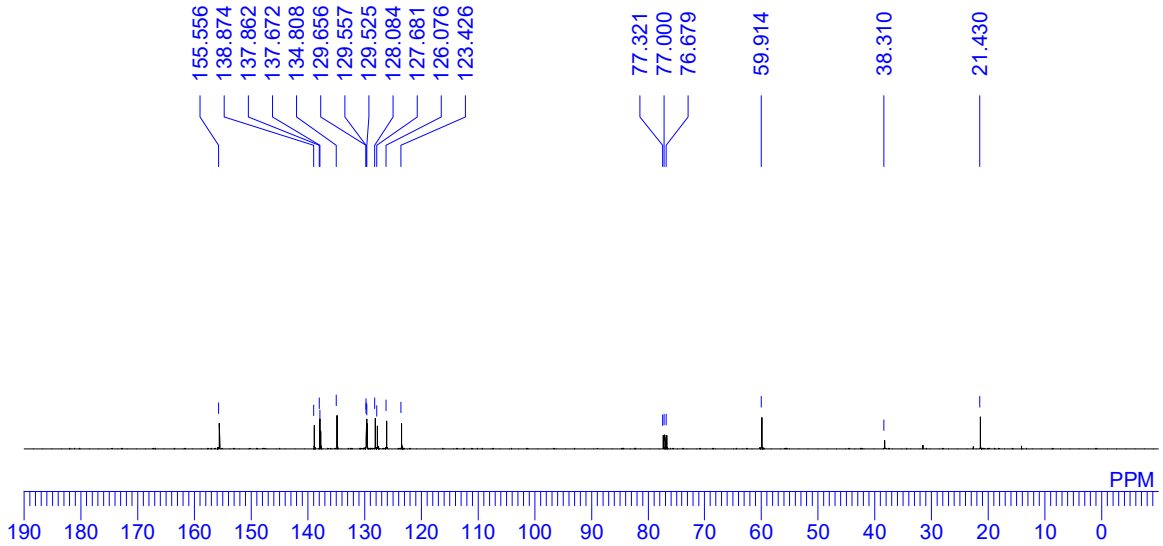
The mixture of **S1** (1.00 g, 1.75 mmol), 3-methylphenylboronic acid (0.87 g, 5.78 mmol), palladium(II) acetate (0.06 g, 0.26 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (0.22 g, 0.52 mmol), and sodium carbonate (1.85 g, 17.5 mmol) in toluene (6 mL), ethanol (6 mL) and distilled water (2 mL) was heated at 100 ℃ for 22 h. The reaction was quenched by HCl aq. at 0 ℃. The product was extracted with dichloromethane (3×15 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 90:10) on silica gel to give **1l**Me$_3$ as a colorless solid (1.07 g, 94%).

mp 96.1–96.7 ℃; IR (KBr) ν = 3026 (w), 2936 (w), 2921 (w), 1606 (w), 1576 (w), 1457 (s), 1400 (w), 1243 (m), 1223 (m), 1009 (s), 792 (m), 705 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.43 (s, 3H, 10-H), 7.39 (d, J = 8.0 Hz, 3H), 7.26 (t, J = 8.0 Hz, 3H), 7.22 (dd, J = 8.0, 2.0 Hz, 3H), 7.11 (d, J = 8.0 Hz, 3H), 7.07 (t, J = 7.8 Hz, 3H), 6.96 (dd, J = 7.8, 1.8 Hz, 3H), 6.82 (s, 1H, 1-H), 3.15 (s, 9H, 8-H), 2.36 (s, 9H, 15-H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.6 (s), 138.9 (s), 137.9 (s), 137.7 (s), 134.8 (s), 129.7 (d), 129.6 (d), 129.5 (d), 128.1 (d), 127.7 (d), 126.1 (d), 123.4 (d), 59.9 (q, C-8), 38.3 (d, C-1), 21.4 (q, C-15); MS (EI$^+$, 70 eV) m/z 604 (M$^+$, 100), 573 (69), 211 (62), 197 (42), 181 (28); HRMS (EI$^+$, 70 eV) Calculated ($C_{43}H_{40}O_3$): 604.2978 (M$^+$), Found: 604.2970.

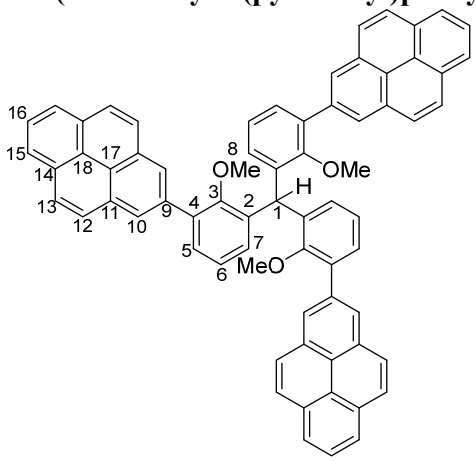
^{1}H NMR: (400 MHz, $CDCl_3$)



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



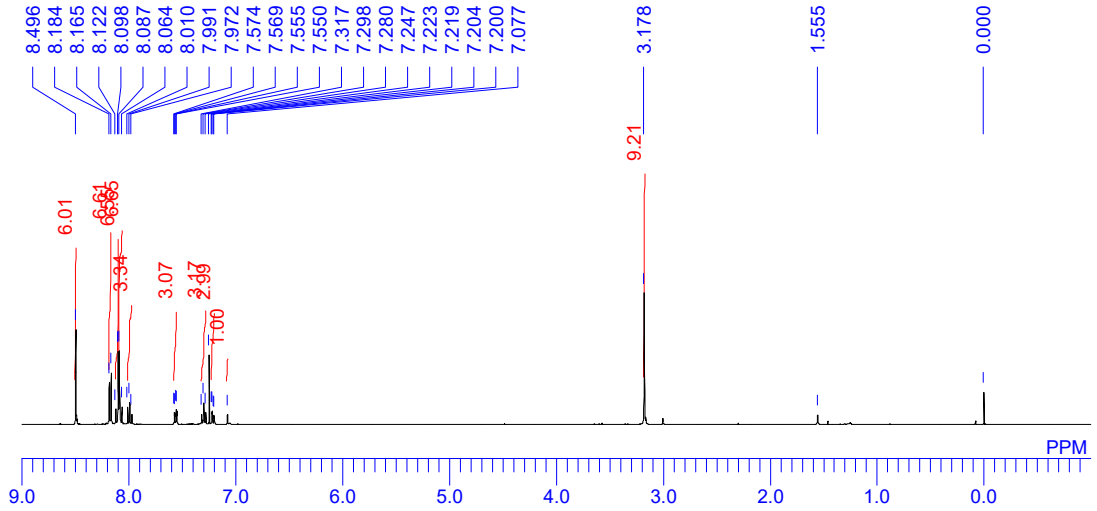
Tris(2-methoxy-3-(pyren-2-yl)phenyl)methane 1oMe$_3$



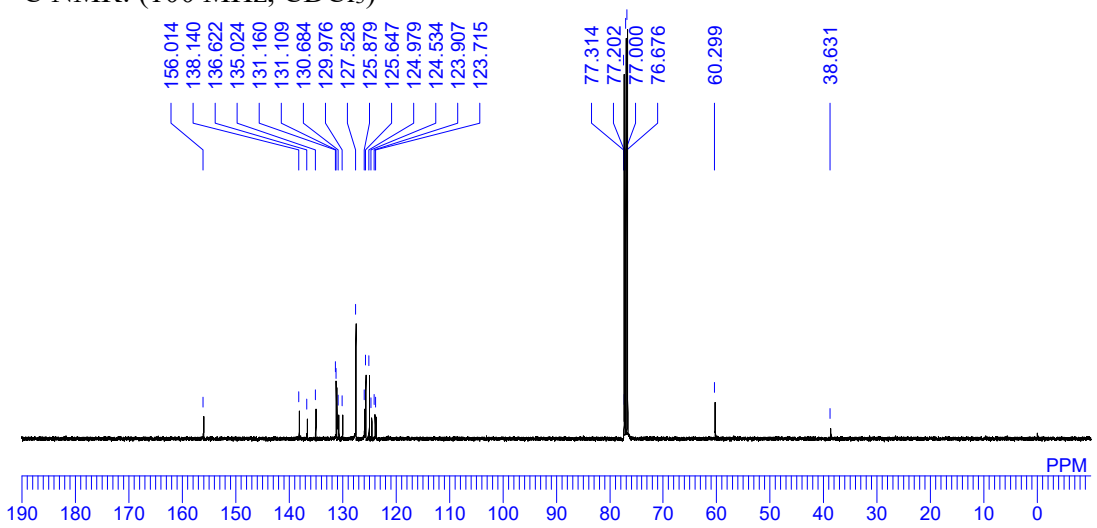
The mixture of **S1** (0.24 g, 0.42 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (0.46 g, 1.39 mmol), $Pd(PPh_3)_4$ (24 mg, 0.021 mmol), and K_2CO_3 (0.53 g, 3.81 mmol) in toluene (12 mL), ethanol (1.0 mL) and distilled water (1.0 mL) was heated at 90 ℃ for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3×20 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 60:40) on silica gel to give **1o**Me$_3$ as a colorless solid (0.28 g, 71%).

mp 239.5–240.2 ℃; IR (KBr) ν = 3038 (m), 2935 (m), 2824 (w), 1711 (m), 1601 (m), 1455 (s), 1414 (s), 1365 (m), 1227 (s), 1085 (m), 1007 (s), 820 (s), 714 (s), 665 (m), 497 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 8.50 (s, 6H, 10-H), 8.17 (d, J = 7.6 Hz, 6H), 8.11 (d, J = 9.6 Hz, 6H), 8.08 (d, J = 9.2 Hz, 6H), 7.99 (t, J = 7.6 Hz, 3H, 16-H), 7.56 (dd, J = 7.6, 2.0 Hz, 3H), 7.30 (t, J = 7.4 Hz, 3H, 6-H), 7.21 (dd, J = 7.6, 1.6 Hz, 3H), 7.08 (s, 1H, 1-H), 3.18 (s, 3H, 8-H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.0 (s), 138.1 (s), 136.6 (s), 135.0 (s), 131.2 (s), 131.1 (s), 130.7 (d), 130.0 (d), 127.5 (d), 125.9 (d), 125.6 (d), 125.0 (d), 124.5 (s), 123.9 (d), 123.7 (s), 77.2 (d), 60.3 (q), 38.6 (d); HRMS (MALDI-TOF MS) Calculated ($C_{70}H_{46}O_3$): 933.3442 (M^+), Found: 933.3424.

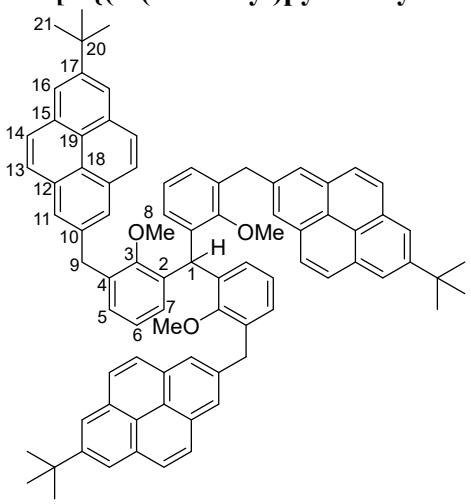
^{1}H NMR: (400 MHz, $CDCl_3$)



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



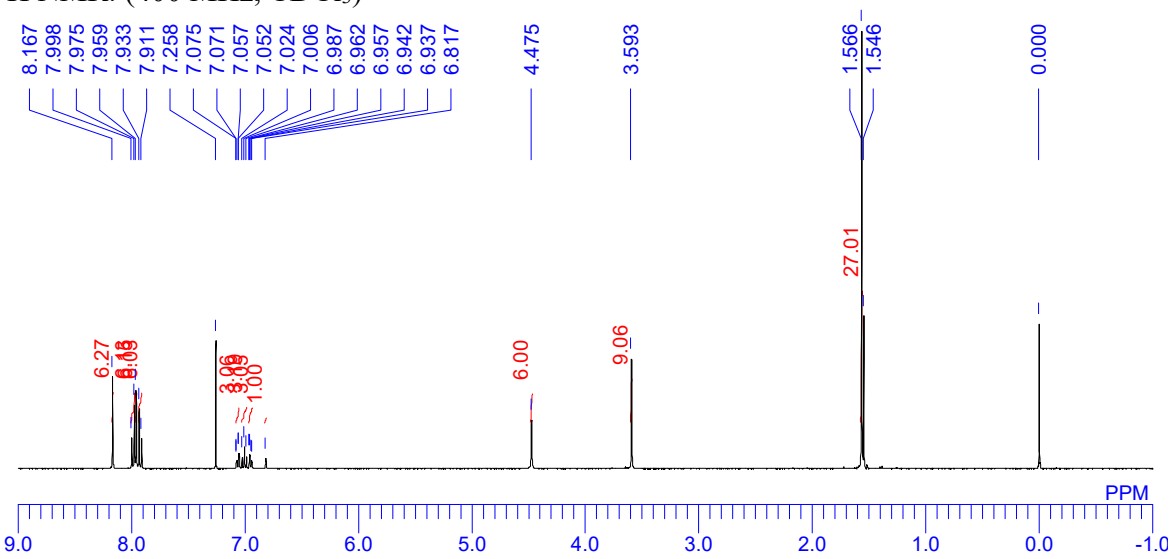
Tris[3-{(7-(*tert*-butyl)pyren-2-ylmethyl}-2-methoxyphenyl]methane 1rMe_3



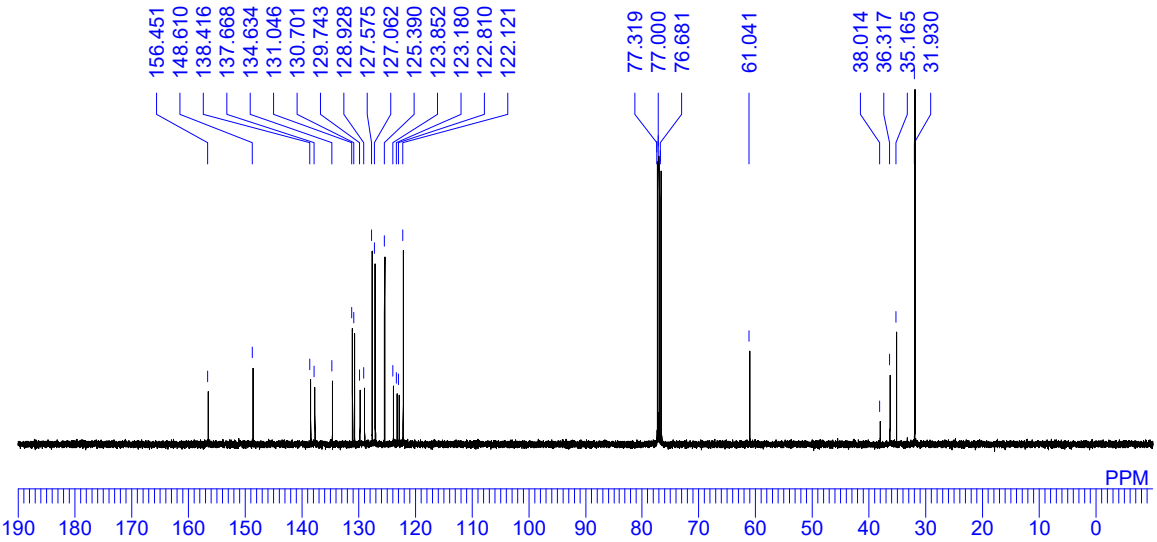
The mixture of **S1** (0.245 g, 0.40 mmol), 2-{7-(*tert*-butyl)pyren-2-yl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.507 g, 1.32 mmol), $Pd(PPh_3)_4$ (23.1 mg, 0.020 mmol), and K_2CO_3 (0.498 g, 3.60 mmol) in toluene (12 mL), ethanol (1.0 mL) and distilled water (1.0 mL) was heated at 90 ℃ for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3×20 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 40:60) on silica gel to give **1r**Me_3 as a colorless solid (0.350 g, 76%).

mp 186.9–187.7 ℃; IR (KBr) ν = 3038 (m), 2954 (s), 2867 (s), 2827 (m), 1754 (w), 1605 (s), 1461 (s), 1394 (m), 1226 (s), 1164 (m), 1085 (s), 1010 (s), 918 (w), 877 (s), 768 (s), 714 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.17 (s, 6H), 7.99 (d, J = 9.2 Hz, 6H), 7.96 (s, 6H), 7.92 (d, J = 8.8 Hz, 6H), 7.06 (dd, J = 7.4, 1.8 Hz, 3H), 7.01 (t, J = 7.4 Hz, 3H, 6-H), 6.95 (dd, J = 8.0, 2.0 Hz, 3H), 6.82 (s, 1H, 1-H), 4.48 (s, 6H, 9-H), 3.59 (s, 9H, 8-H), 1.57 (s, 27H, 21-H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.5 (s), 148.6 (s), 138.4 (s), 137.7 (s), 134.6 (s), 131.0 (s), 130.7 (s), 129.7 (d), 128.9 (d), 127.6 (d), 127.1 (d), 125.4 (d), 123.9 (d), 123.2 (s), 122.8 (s), 122.1 (d), 61.0 (q), 38.0 (d), 36.3 (t), 35.2 (s), 31.9 (q); HRMS (MALDI-TOF MS) Calculated ($C_{85}H_{76}O_3$): 1144.5789 (M^+), Found: 1144.5802.

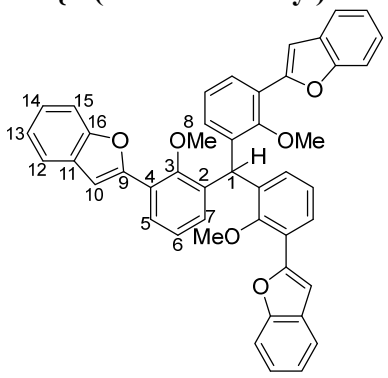
^{1}H NMR: (400 MHz, $CDCl_3$)



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



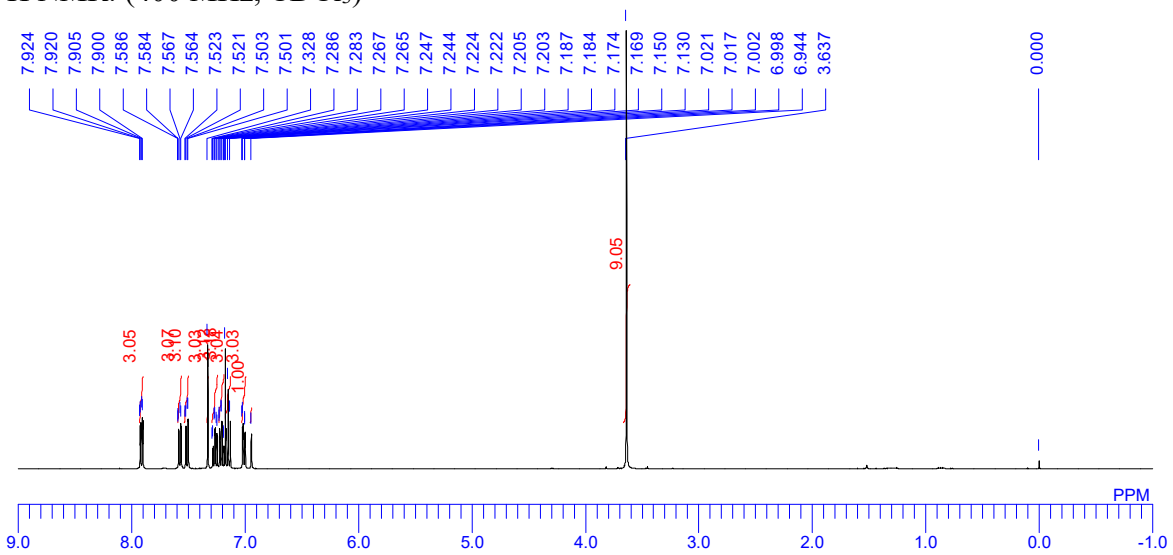
Tris{3-(benzofuran-2-yl)-2-methoxyphenyl}methane 1AMe$_3$



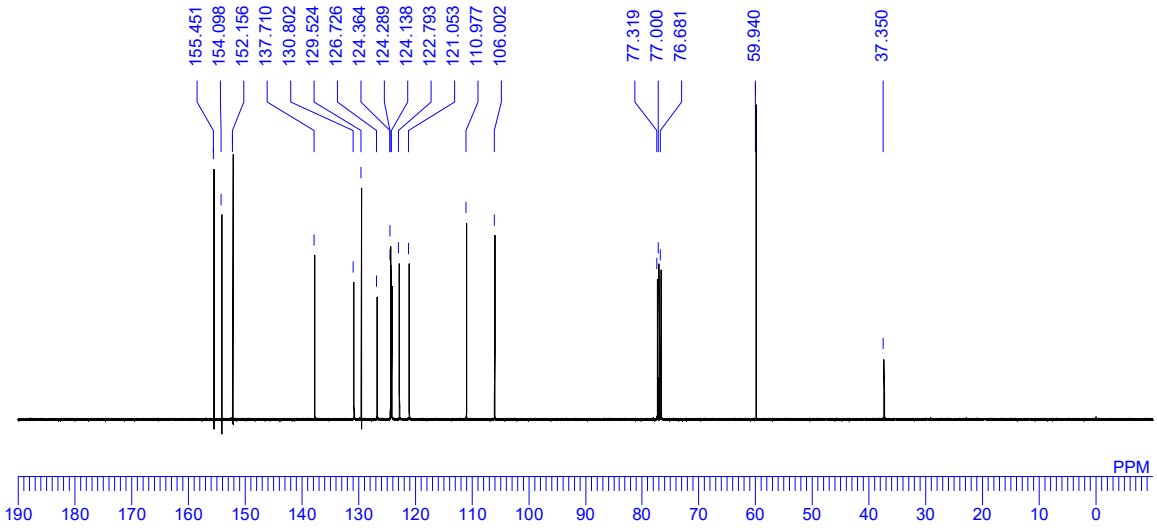
The mixture of **S1** (0.457 g, 0.80 mmol), benzofuran-2-boronic acid (0.428 g, 2.64 mmol), palladium(II) acetate (26.9 mg, 0.12 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (98.5 mg, 0.24 mmol), and Na_2CO_3 (0.848 g, 8.00 mmol) in toluene (12 mL), ethanol (1.0 mL) and distilled water (1.0 mL) was heated at 100 ℃ for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3×20 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 90:10) on silica gel to give **1A**Me$_3$ as a colorless solid (0.364 g, 67%).

mp 124.5–124.9 ℃; IR (KBr) ν = 3065 (w), 2941 (m), 2828 (w), 1589 (w), 1464 (s), 1447 (s), 1423 (m), 1305 (m), 1259 (s), 1228 (s), 1167 (m), 1088 (m), 1000 (s), 952 (m), 776 (m), 750 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.91 (dd, J = 7.8, 1.8 Hz, 3H), 7.58 (dd, J = 7.8, 1.2 Hz, 3H), 7.51 (dd, J = 8.0, 0.8 Hz, 3H), 7.33 (s, 3H, 10-H), 7.27 (td, J = 7.8, 1.2 Hz, 3H), 7.20 (td, J = 7.5, 1.2 Hz, 3H), 7.15 (t, J = 7.8 Hz, 3H), 7.01 (dd, J = 7.6, 1.6 Hz, 3H), 6.94 (s, 1H, 1-H), 3.64 (s, 9H, 8-H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.5 (s), 154.1 (s), 152.2 (s), 137.7 (s), 130.8 (d), 129.5 (s), 126.7 (d), 124.4 (d), 124.3 (s), 124.1 (d), 122.8 (d), 121.1 (d), 111.0 (d), 106.0 (d), 59.9 (q, C-8), 37.4 (d, C-1); MS (EI^+, 70 eV) m/z 682 (M^+, 100), 651 (18), 427 (11), 237 (31); HRMS (EI^+, 70 eV) Calculated ($C_{46}H_{34}O_6$): 682.2355 (M^+), Found: 682.2347.

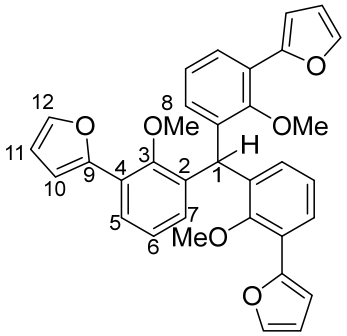
^{1}H NMR: (400 MHz, $CDCl_3$)



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

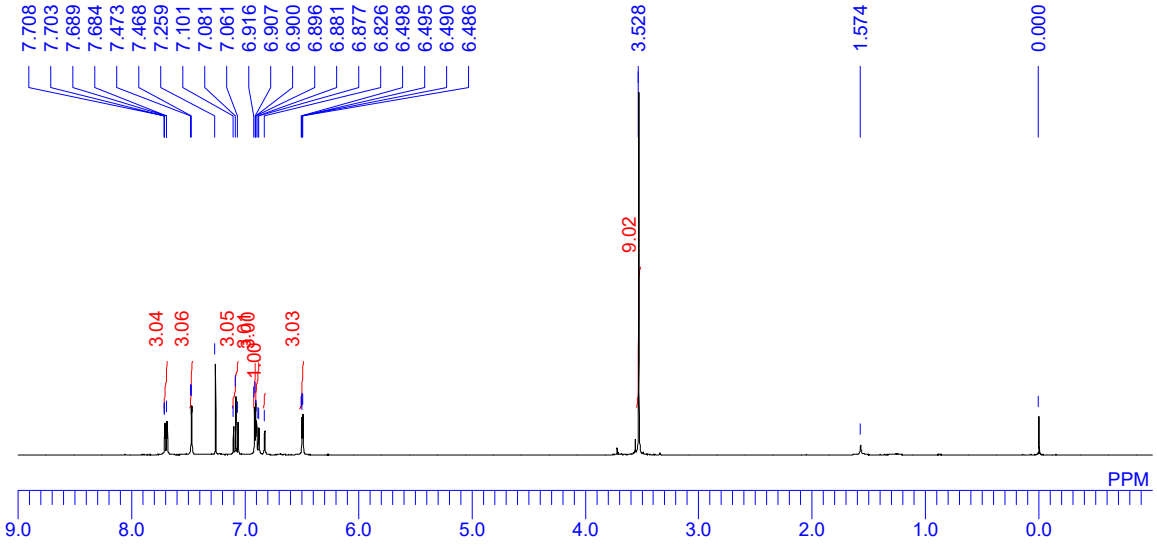


Tris{3-(furan-2-yl)-2-methoxyphenyl}methane 1BMe$_3$

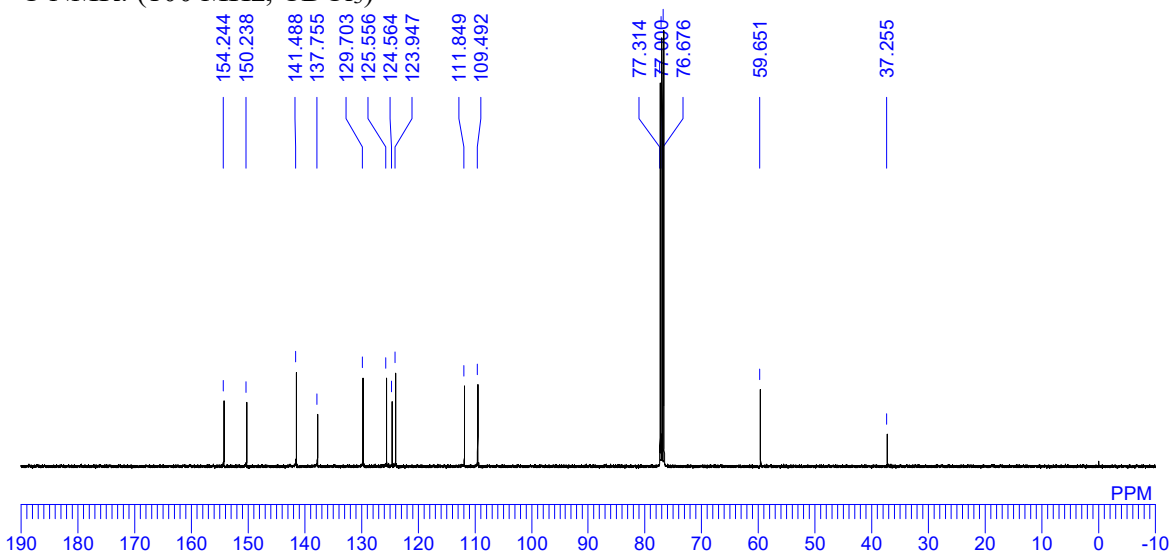


The mixture of **S1** (1.142 g, 2.00 mmol), 2-furylboronic acid (0.806 g, 7.20 mmol), palladium(II) acetate (67.4 mg, 0.30 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (246 mg, 0.60 mmol), and Na_2CO_3 (2.120 g, 20.0 mmol) in toluene (10 mL), ethanol (1.0 mL) and distilled water (1.0 mL) was heated at 100 ℃ for 7.5 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3×20 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 50:50) on silicagel to give **1B**Me$_3$ as a colorless solid (0.533 g, 50%).
mp 196.1–197.0 ℃ (decomp.); IR (KBr) ν = 3149 (w), 3119 (w), 3004 (w), 2960 (w), 2938 (m), 2825 (w), 1501 (m), 1461 (s), 1422 (m), 1372 (m), 1225 (s), 1160 (m), 1083 (s), 1017 (s), 995 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.70 (dd, J = 7.6, 2.0 Hz, 3H), 7.47 (d, J = 2.0 Hz, 3H), 7.08 (t, J = 8.0 Hz, 3H), 6.91 (d, J = 3.6 Hz, 3H), 6.89 (dd, J = 7.8, 1.8 Hz, 3H), 6.83 (s, 1H, 1-H), 6.49 (dd, J = 3.4, 1.4 Hz, 3H), 3.53 (s, 9H, 8-H); ^{13}C NMR (100 MHz, $CDCl_3$) 154.2 (s), 150.2 (s), 141.5 (d), 137.8 (s), 129.7 (d), 125.6 (d), 124.6 (s), 123.9 (d), 111.8 (d), 109.5 (d), 59.7 (q, C-8), 37.3 (d, C-1); HRMS (MALDI-TOF MS) Calculated ($C_{34}H_{28}O_6$): 532.1880 (M^+), Found: 532.1888.

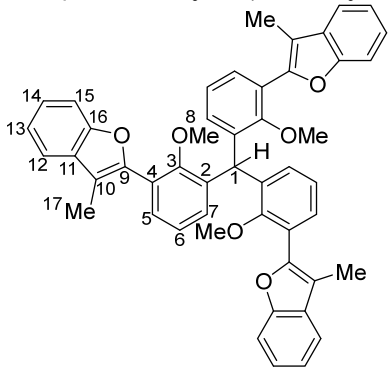
^{1}H NMR: (400 MHz, $CDCl_3$)



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



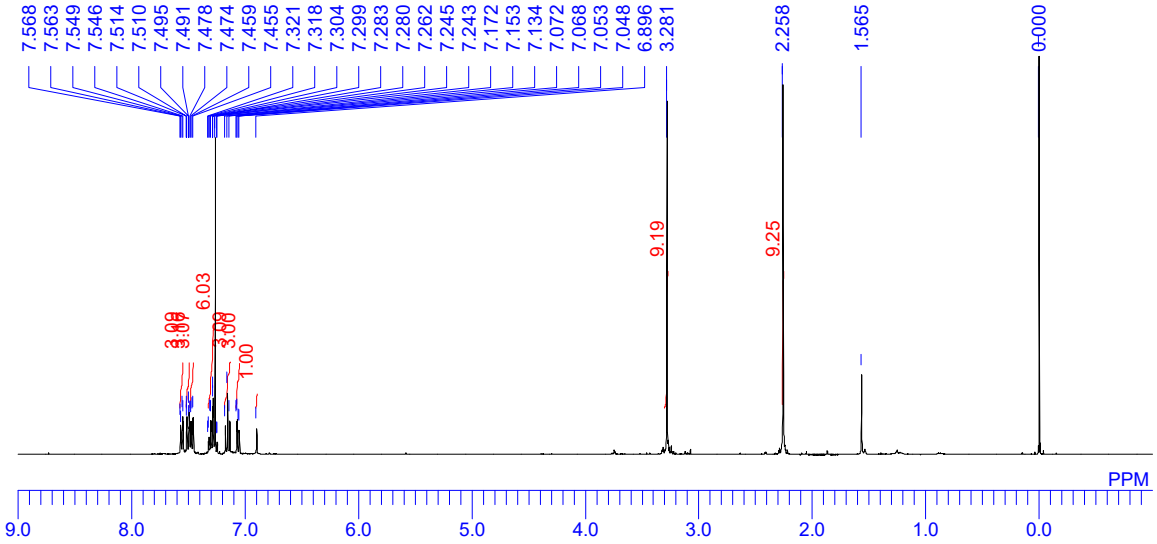
Tris{2-methoxy-3-(3-methylbenzofuran-2-yl)phenyl}methane 1A$_I$Me$_3$



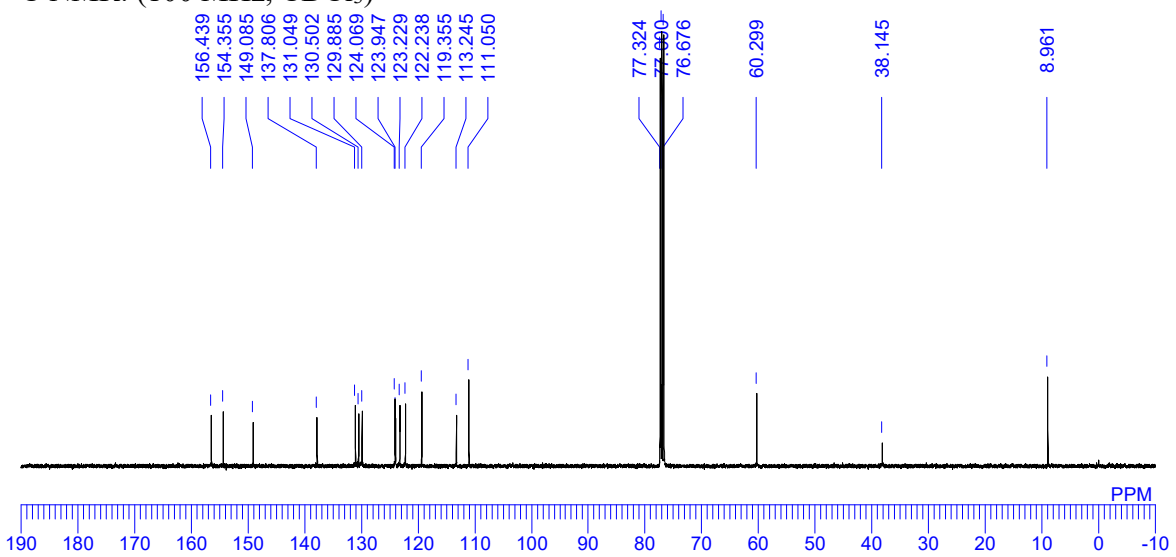
The mixture of **S1** (0.818 g, 1.43 mmol), 3-methylbenzofuran-2-boronic acid (1.22 g, 4.73 mmol), palladium(II) acetate (32.1 mg, 0.143 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (117 mg, 0.286 mmol), and Na_2CO_3 (1.52 g, 14.3 mmol) in toluene (12 mL), ethanol (2.0 mL) and distilled water (2.0 mL) was heated at 100 °C for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3×20 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 90:10) on silica gel to give **1A$_I$Me$_3$** as a colorless solid (0.747 g, 72%).

mp 90.2–90.9 °C; IR (KBr) ν = 3061 (w), 2922 (m), 2854 (m), 1587 (w), 1460 (s), 1451 (s), 1417 (s), 1266 (m), 1228 (s), 1214 (m), 1106 (m), 1078 (m), 1007 (s), 822 (w), 776 (m), 745 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.56 (dd, J = 7.2, 1.6 Hz, 3H), 7.50 (dd, J = 7.6, 1.6 Hz, 3H), 7.47 (dd, J = 7.8, 1.8 Hz, 3H), 7.32–7.24 (m, 6H), 7.15 (t, J = 7.6 Hz, 3H), 7.06 (dd, J = 7.6, 2.0 Hz, 3H), 6.90 (s, 1H, 1-H), 3.28 (s, 9H, 8-H), 2.26 (s, 9H, 17-H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.4 (s), 154.4 (s), 149.1 (s), 137.8 (s), 131.0 (d), 130.5 (s), 129.9 (d), 124.1 (d), 123.9 (s), 123.2 (d), 122.2 (d), 119.4 (d), 113.2 (s), 110.0 (d), 60.3 (q, C-8), 38.1 (d, C-1), 9.0 (q, C-17); HRMS (MALDI-TOF MS) Calculated ($C_{49}H_{40}O_6$): 724.2819 (M^+), Found: 724.2820.

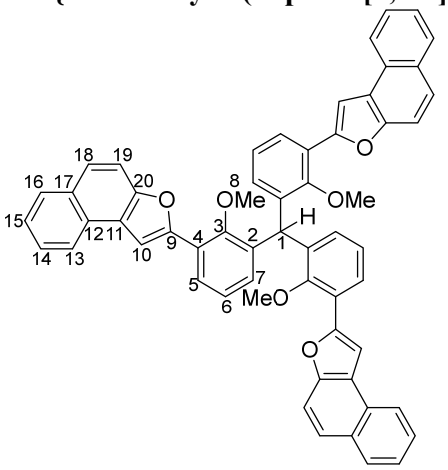
^{1}H NMR: (400 MHz, $CDCl_3$)



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



Tris{2-methoxy-3-(naphtho[2,1-*b*]furan-2-yl)phenyl}methane 1A$_{II}$Me$_3$

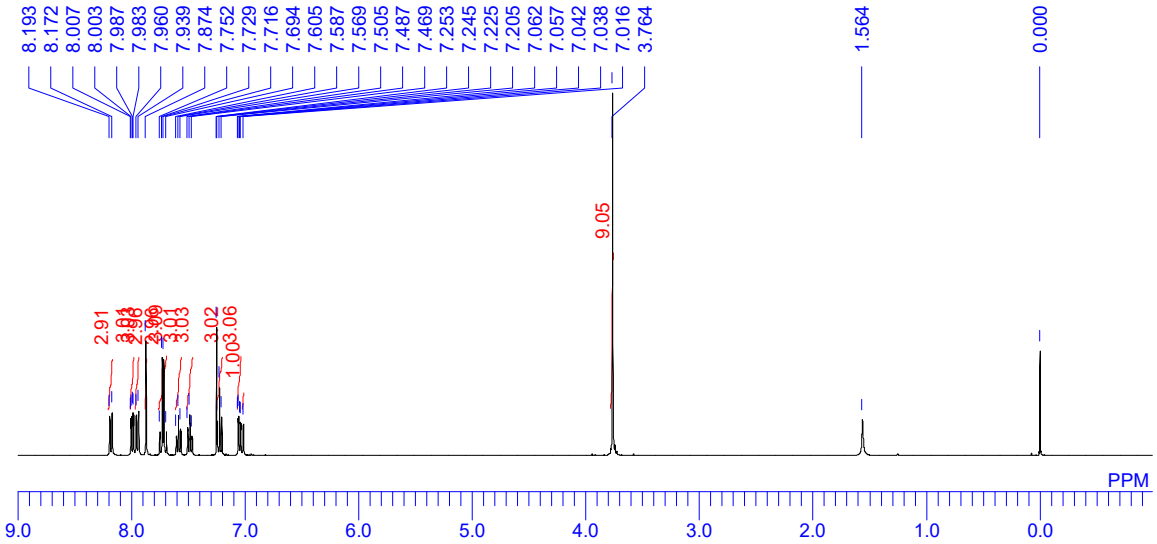


The mixture of **S1** (0.619 g, 1.08 mmol), naphtho[2,1-*b*]furan-2-ylboronic acid (0.758 g, 3.58 mmol), palladium(II) acetate (36.6 mg, 0.163 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (133 mg, 0.325 mmol), and Na_2CO_3 (1.15 g, 10.84 mmol) in toluene (10 mL), ethanol (1.0 mL) and distilled water (1.0 mL) was heated at 100 °C for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3×20 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 60:40) on silica gel to give **1A$_{II}$**Me$_3$ as a colorless solid (0.652 g, 72%).

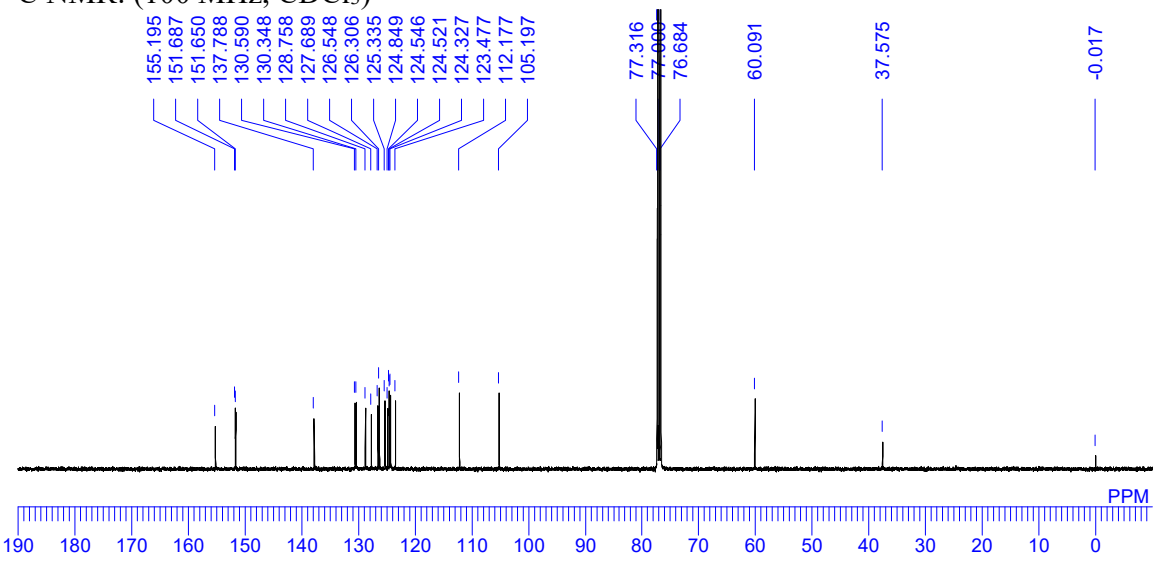
mp 248.5–249.5 °C (decomp.); IR (KBr) ν = 3056 (w), 2940 (w), 2827 (w), 1524 (w), 1462 (s), 1423 (m), 1385 (s), 1233 (s), 1164 (s), 1081 (m), 994 (s), 954 (w), 800 (s), 744 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 8.18 (d, J = 8.4 Hz, 3H), 8.00 (dd, J = 8.0, 1.6 Hz, 3H), 7.95 (d, J = 8.4 Hz, 3H), 7.87 (s, 3H, 10-H), 7.74 (d, J = 9.2 Hz, 3H), 7.71 (d, J = 8.8 Hz, 3H), 7.59 (t, J = 7.2 Hz, 3H), 7.49 (t, J = 7.2 Hz, 3H), 7.23 (t, J = 8.0 Hz, 3H), 7.05 (dd, J = 7.8, 1.8 Hz, 3H), 7.02 (s, 1H, 1-H), 3.76 (s, 9H, 8-H); ^{13}C NMR: (100 MHz, $CDCl_3$) 155.2 (s), 151.68 (s), 151.65 (s), 137.8 (s), 130.6 (d), 130.3 (s), 128.8 (d), 127.7 (s), 126.5 (d), 126.3 (d), 125.3 (d), 124.8 (s), 124.55 (d), 124.52 (s),

124.3 (d), 123.5 (d), 112.2 (d), 105.2 (d), 60.0 (q, C-8), 37.6 (d, C-1) HRMS (MALDI-TOF MS) Calculated ($C_{58}H_{40}O_6$): 832.2819 (M^+), Found: 832.2817.

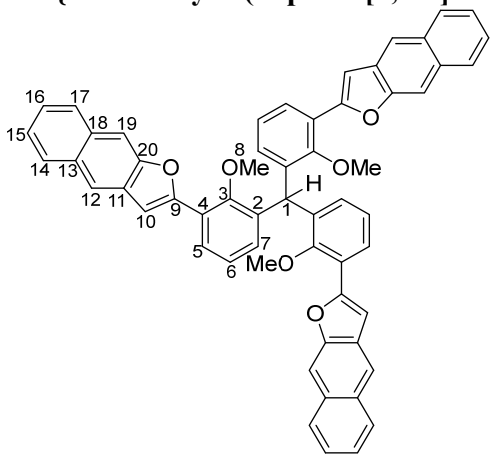
^{1}H NMR: (400 MHz, $CDCl_3$)



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



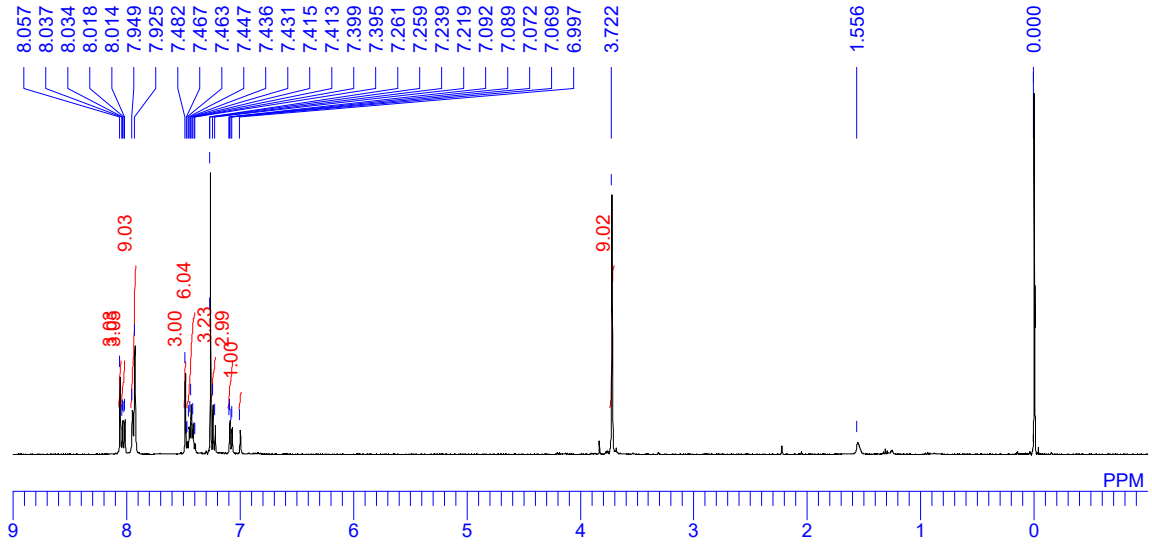
Tris{2-methoxy-3-(naphtho[2,3-*b*]furan-2-yl)phenyl}methane $\mathbf{1A_{III}Me_3}$



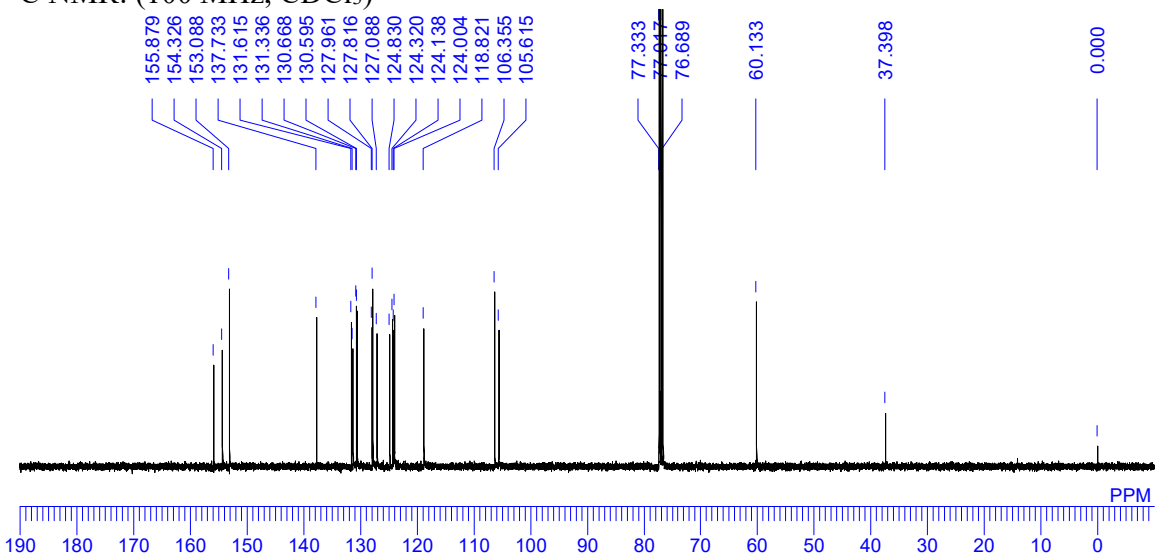
The mixture of **S1** (0.400 g, 0.700 mmol), naphtho[2,3-*b*]furan-2-ylboronic acid (0.445 g, 2.10 mmol), palladium(II) acetate (23.6 mg, 0.105 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (86.2 mg, 0.210 mmol), and Na_2CO_3 (0.742 g, 7.00 mmol) in toluene (10 mL), ethanol (1.0 mL) and distilled water (1.0 mL) was heated at 100 ℃ for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3×20 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 60:40) on silica gel. Further purification was conducted by a recycle GPC to give $\mathbf{1A_{III}}Me_3$ as a colorless solid (0.199 g, 39%).

mp 147.8–148.8 ℃; IR (KBr) ν = 3052 (w), 2941 (m), 2867 (w), 1589 (w), 1503 (m), 1464 (s), 1441 (m), 1257 (s), 1231 (s), 1150 (m), 1099 (s), 999 (s), 950 (m), 860 (s), 742 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.06 (s, 3H), 8.03 (dd, J = 7.8, 1.4 Hz, 3H), 7.95–7.93 (m, 9H), 7.48 (s, 3H), 7.47–7.40 (m, 6H), 7.24 (t, J = 8.0 Hz, 3H), 7.08 (dd, J = 8.0, 1.2 Hz, 3H), 7.00 (s, 1H, 1-H), 3.72 (s, 9H, 8-H); ^{13}C NMR: (100 MHz, $CDCl_3$) 155.9 (s), 154.3 (s), 153.1 (s), 137.7 (s), 131.6 (d), 131.3 (s), 130.7 (s), 130.6 (s), 128.0 (d), 127.8 (d), 127.1 (d), 124.8 (d), 124.3 (d), 124.1 (s), 124.0 (d), 118.8 (d), 106.4 (d), 105.6 (d), 60.1 (q, C-8), 37.4 (d, C-1); HRMS (MALDI-TOF MS) Calculated ($C_{58}H_{40}O_6$): 832.2819 (M^+), Found: 832.2852.

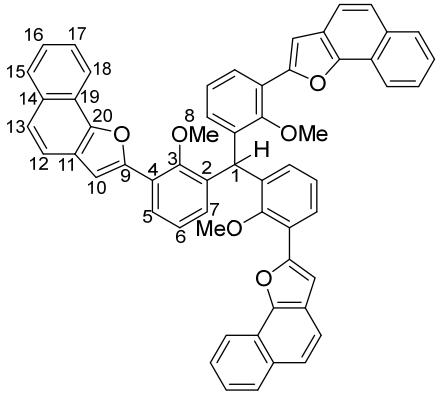
^{1}H NMR: (400 MHz, $CDCl_3$)



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

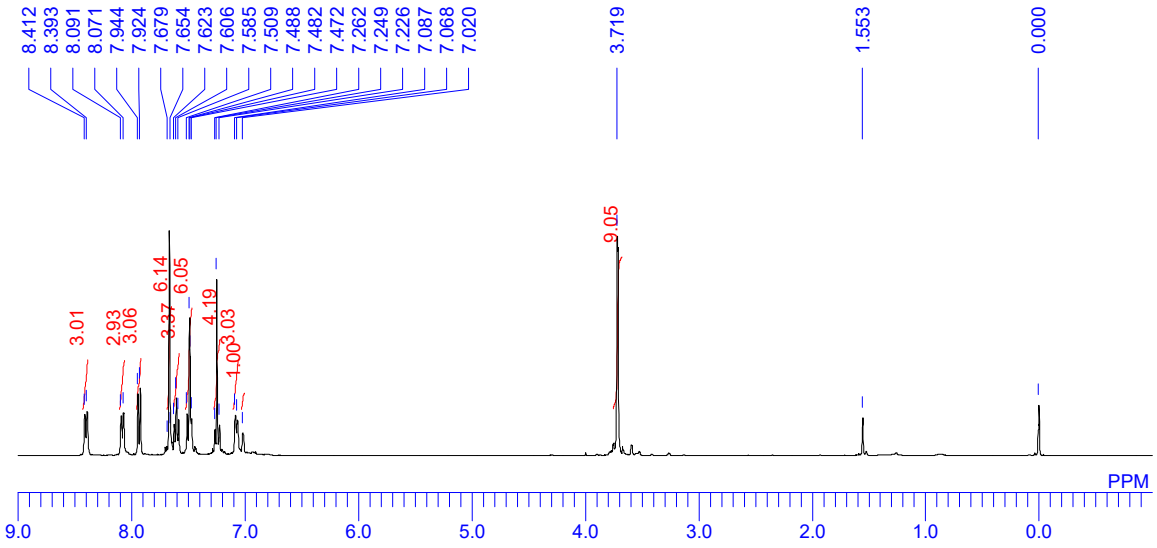


Tris{2-methoxy-3-(naphtho[1.2-*b*]furan-2-yl)phenyl}methane $\mathbf{1A_{IV}Me_3}$

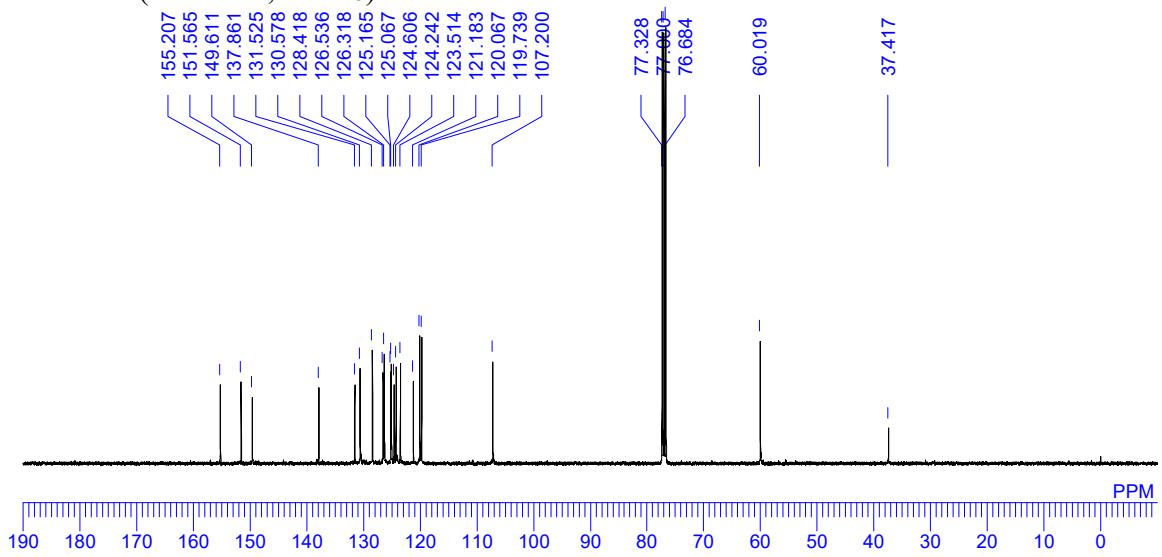


The mixture of **S1** (0.685 g, 1.20 mmol), naphtho[1,2-*b*]furan-2-ylboronic acid (0.916 g, 4.32 mmol), palladium(II) acetate (26.9 mg, 0.120 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (98.5 mg, 0.240 mmol), and Na_2CO_3 (1.27 g, 12.0 mmol) in toluene (10 mL), ethanol (1.0 mL) and distilled water (1.0 mL) was heated at 100 °C for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (3×20 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 60:40) on silica gel. Further purification was conducted by a recycle GPC to give $\mathbf{1A_{IV}Me_3}$ as a colorless solid (0.202 g, 20%).
mp 146.2–147.2 °C; IR (KBr) ν = 3059 (w), 3052 (w), 2932 (m), 2853 (w), 1590 (m), 1462 (s), 1377 (m), 1308 (w), 1248 (s), 1172 (w), 1110 (s), 1087 (m), 1002 (m), 886 (w), 811 (s), 740 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.40 (d, J = 7.6 Hz, 3H), 8.08 (d, J = 8.0 Hz, 3H), 7.93 (d, J = 8.0 Hz, 3H), 7.68–7.65 (m, 6H), 7.61 (t, J = 7.6 Hz, 3H), 7.51–7.47 (m, 6H), 7.24 (t, J = 7.2 Hz, 3H), 7.08 (d, J = 7.6 Hz, 3H), 7.02 (s, 1H, 1-H), 3.72 (s, 9H, 8-H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.2 (s), 151.6 (s), 149.6 (s), 137.9 (s), 131.5 (s), 130.6 (d), 128.4 (d), 126.5 (d), 126.3 (d), 125.2 (s), 125.1 (d), 124.6 (s), 124.2 (d), 123.5 (d), 121.2 (s), 120.1 (d), 119.7 (d), 107.2 (d), 60.0 (q, C-8), 37.4 (d, C-1); HRMS (MALDI-TOF MS) Calculated ($C_{58}H_{40}O_6$): 832.2819 (M^+), Found: 832.2804.

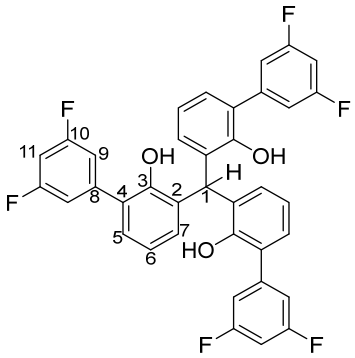
^1H NMR: (400 MHz, $CDCl_3$)



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

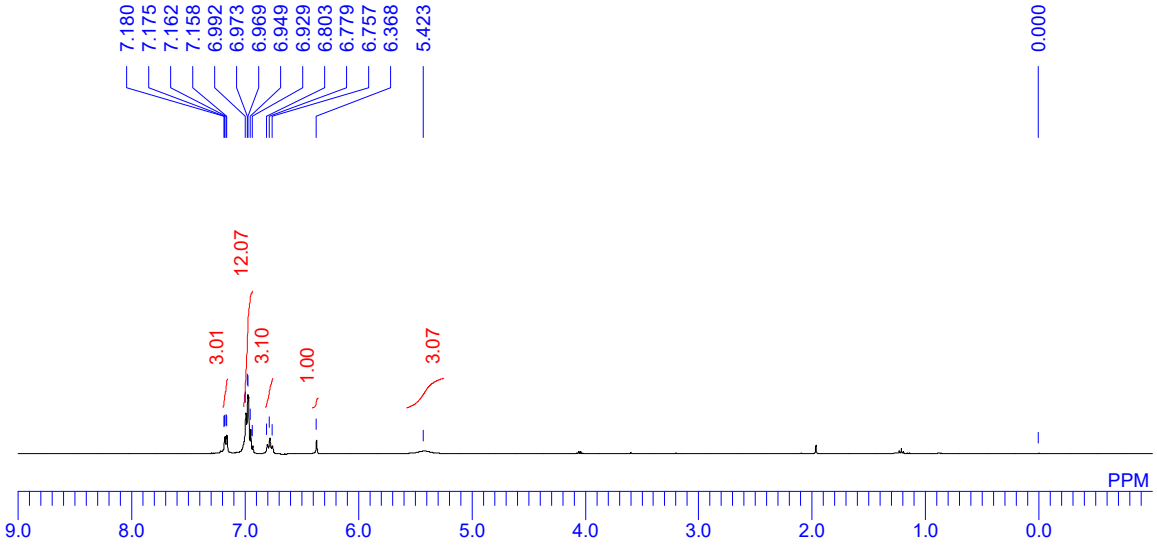


Tris{2-hydroxy-3',5'-difluoro-(1,1'-biphenyl)-3-yl}methane 1iH_3

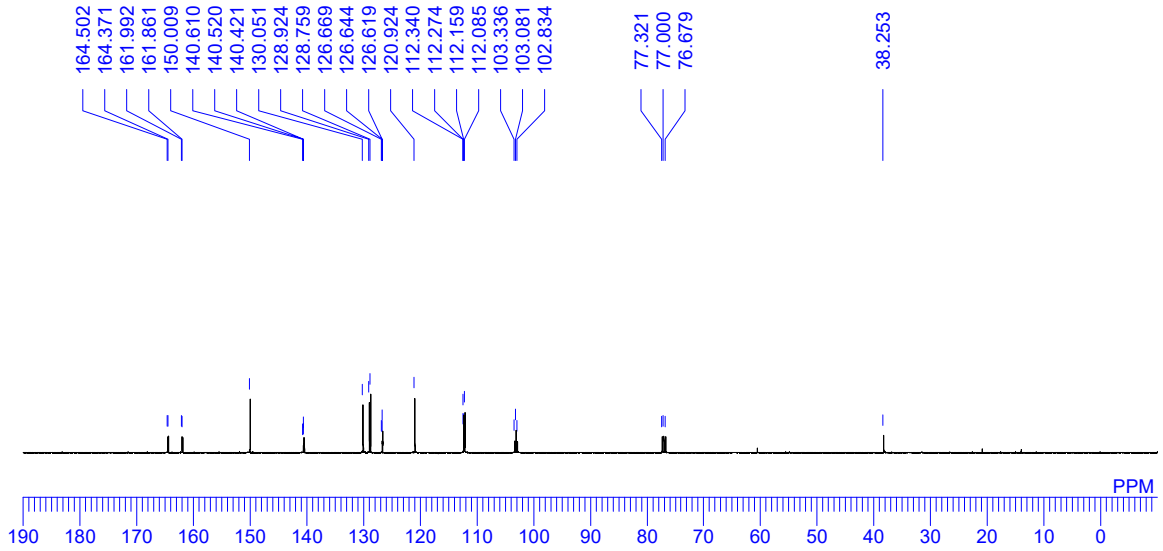


To the solution of **1i**Me_3 (0.628 g, 0.936 mmol) in dichloromethane (20 mL) was added BBr_3 (1.0 M in dichloromethane, 3.1 mL, 3.1 mmol) at −78 °C. The reaction mixture was stirred at room temperature for 19 h and water (10 ml) was added to the mixture at 0 °C. The mixture was extracted with dichloromethane (3×10 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 80:20) on silica gel to give **1i**H_3 as a colorless solid (0.504 g, 86%).
mp 109.9–110.5 °C; IR (KBr) ν = 3547 (s), 3090 (w), 1622 (s), 1597 (s), 1454 (s), 1419 (s), 1343 (m), 1320 (m), 1208 (m), 1190 (m), 1120 (s), 989 (s), 861 (s), 750 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.17 (dd, J = 7.0, 1.8 Hz, 3H), 6.99–6.93 (m, 12H), 6.78 (t, J = 9.2 Hz, 3H, 6-H), 6.37 (s, 1H, 1-H), 5.42 (brs, 3H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) 161.2 (s, dd, $^1J_{C–F}$ = 251.0 Hz, $^3J_{C–F}$ = 13.1 Hz, C-10), 150.0 (s), 140.5 (s, t, $^3J_{C–F}$ = 9.5 Hz, C-8), 130.1 (d), 128.9 (d), 128.8 (s), 126.6 (s, t, $^4J_{C–F}$ = 2.5 Hz, C-4), 120.9 (d), 112.2 (d, dd, $^2J_{C–F}$ = 18.5 Hz, $^4J_{C–F}$ = 7.0 Hz, C-9), 103.1 (d, t, $^2J_{C–F}$ = 25.1 Hz, C-11), 38.3 (d, C-1); ^{19}F NMR (376 MHz, $CDCl_3$, BF_3·OEt_2 (−153 ppm) in $CDCl_3$ used as an external standard; *i.e.* $CFCl_3$ (0 ppm)) −101.18–−101.22 (m); MS (EI^+, 70 eV) *m/z* 628 (M^+, 22), 421 (30), 405 (100), 309 (13); HRMS (EI^+, 70 eV) Calculated ($C_{37}H_{22}F_6O_3$): 628.1473 (M^+), Found: 628.1481.

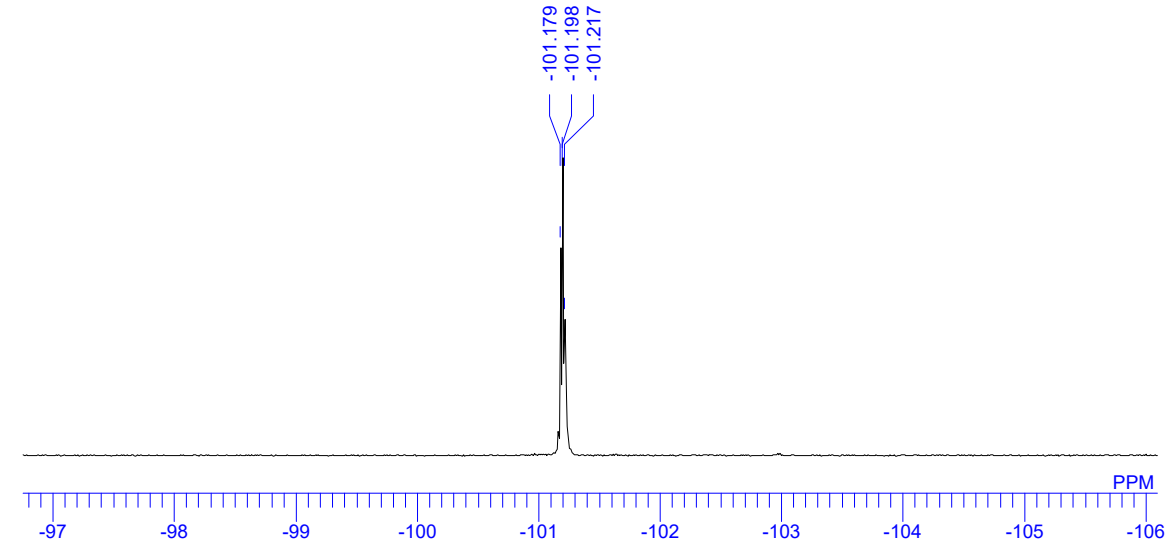
^{1}H NMR: (400 MHz, $CDCl_3$)



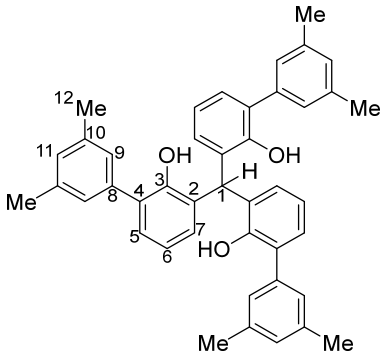
^{13}C NMR: (100 MHz, $CDCl_3$)



^{19}F NMR: (376 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ (−153 ppm) in $CDCl_3$ used as an external standard; *i.e.* $CFCl_3$ (0 ppm))



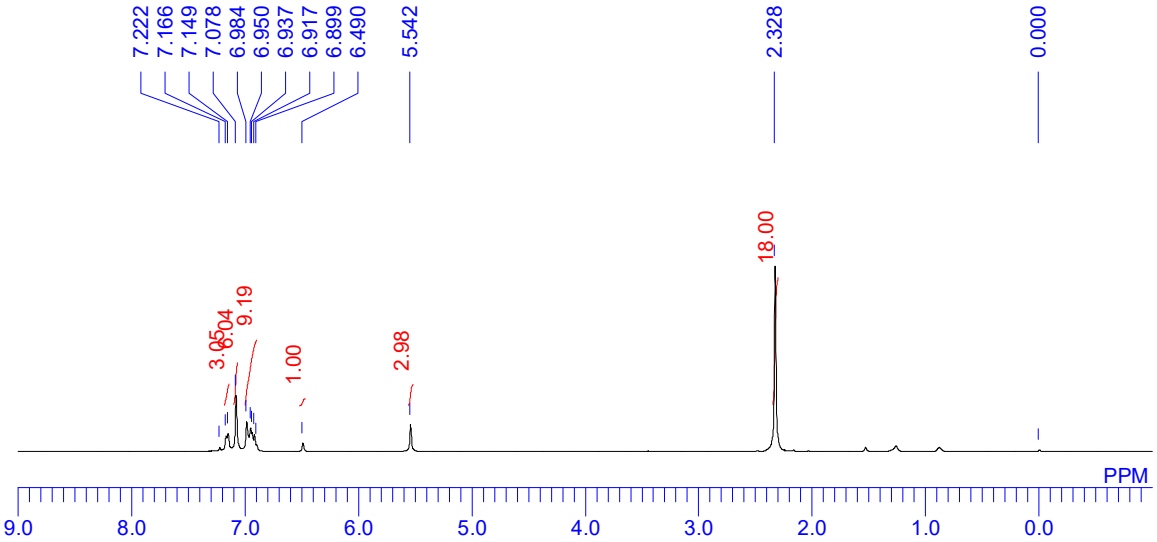
Tris{2-hydroxy-3',5'-dimethyl-(1,1'-biphenyl)-3-yl}methane 1jH_3



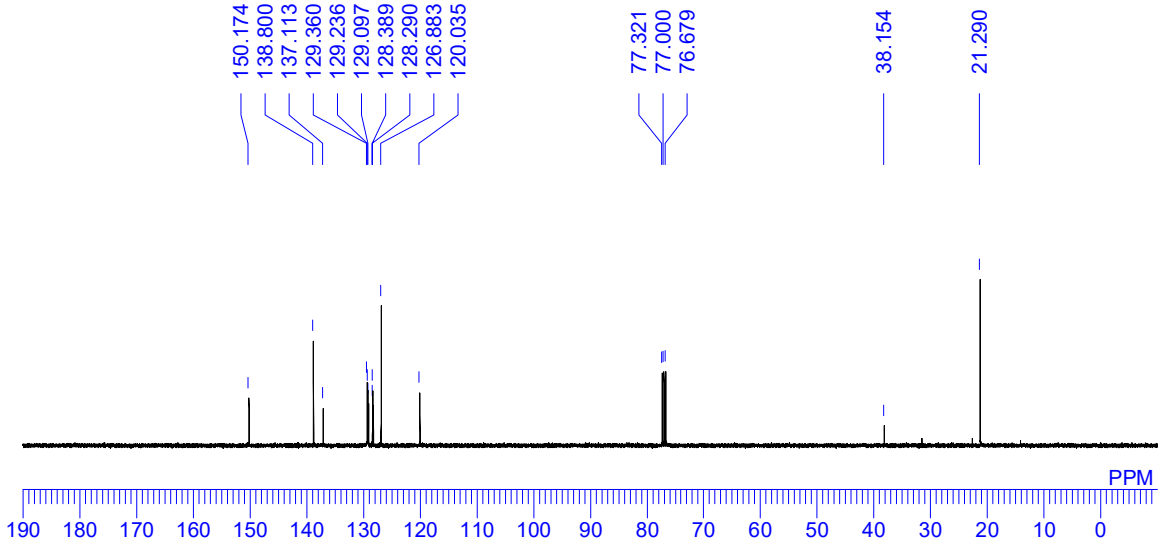
Sodium methoxide (1.06 g, 19.68 mmol) and 1-dodecanethiol (3.98 g, 19.68 mmol) were added to a solution of **1j**Me_3 (1.07 g, 1.64 mmol) in DMF (4 mL). After stirring at 100 °C for 4 h, water and diethyl ether (15 mL) were added to the reaction mixture at room temperature. The solution was neutralized by the addition of 1 M HCl aq., and the reaction mixture was extracted with diethyl ether (3×15 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 90:10) on silica gel to give **1j**H_3 as a white solid (0.39 g, 39%).

mp 216.1–216.3 °C; IR (KBr) ν = 3502 (m), 3026 (w), 2917 (w), 2858 (w), 1601 (m), 1451 (s), 1338 (m), 1327 (m), 1210 (m), 1189 (m), 852 (m), 747 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.16 (d, J = 6.8 Hz, 3H), 7.08 (s, 6H, 9-H), 6.98–6.90 (m, 9H), 6.49 (s, 1H, 1-H), 5.54 (s, 3H, OH), 2.33 (s, 18H, 12-H); ^{13}C NMR (100 MHz, $CDCl_3$) 150.2 (s), 138.8 (s), 137.1 (s), 129.4 (d), 129.2 (d), 129.1 (s), 128.4 (d), 128.3 (s), 126.9 (d), 120.0 (d), 38.2 (d, C-1), 21.3 (q, C-12); MS (EI^+, 70 eV) m/z 604 (M^+, 21), 407 (32), 389 (100), 301 (10), 203 (13); HRMS (EI^+, 70 eV) Calculated ($C_{43}H_{40}O_3$): 604.2978 (M^+), Found: 604.2976.

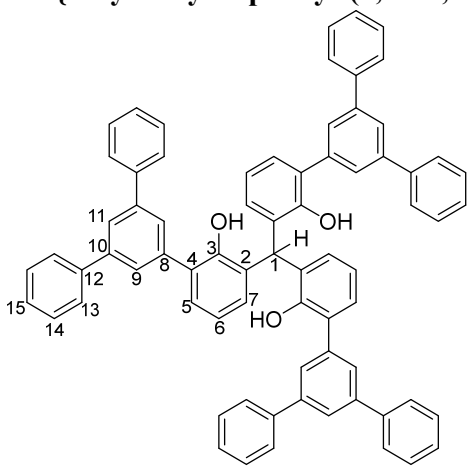
^1H NMR: (400 MHz, $CDCl_3$)



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



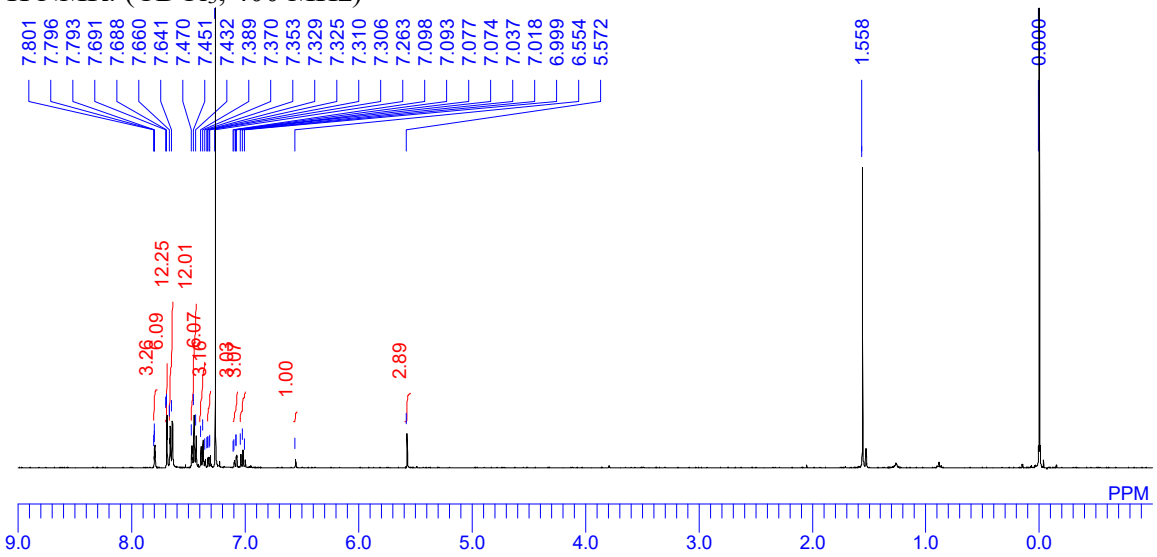
Tris{2-hydroxy-5'-phenyl-(1,1':3',1''-terphenyl)-3-yl}methane 1kH_3



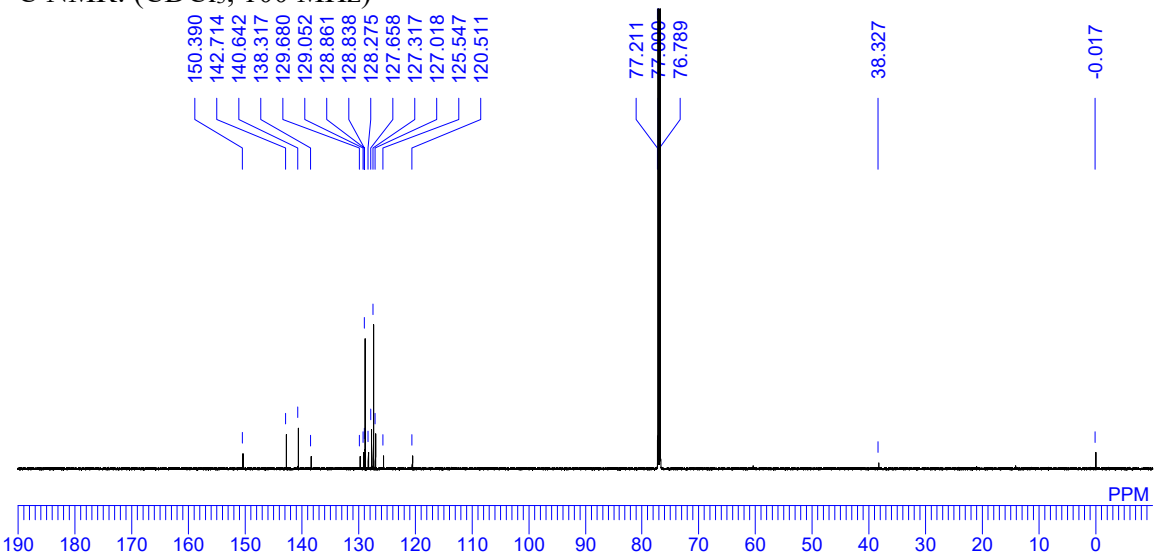
Sodium methoxide (1.06 g, 19.68 mmol) and 1-dodecanethiol (3.98 g, 19.68 mmol) were added to a solution of **1k**Me_3 (1.10 g, 1.64 mmol) in DMF (4 mL). After stirring at 100 ℃ for 16 h, water and diethyl ether (15 mL) were added to the reaction mixture at room temperature. The solution was neutralized by the addition of 1 M HCl aq., and the reaction mixture was extracted with diethyl ether (3×15 mL). The organic layer was dried over anhydrous $MgSO_4$, and the solvent was evaporated. The residue was purified by a silica gel column chromatography (hexane/ethyl acetate = 90:10) to give **1k**H_3 as a white solid (0.39 g, 39%).

mp 248.5–249.5 ℃ (decomp.); IR (KBr) ν = 3519 (s), 3030 (w), 2925 (w), 1594 (s), 1576 (m), 1496 (m), 1445 (s), 1408 (s), 1330 (m), 1222 (s), 1200 (m), 1077 (m), 883 (m), 827 (m), 763 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.80 (t, J = 1.6 Hz, 3H, 11-H), 7.69 (d, J = 1.2 Hz, 6H, 9-H), 7.65 (d, J = 7.6 Hz, 12H, 13-H), 7.45 (t, J = 7.6 Hz, 12H, 14-H), 7.37 (t, J = 7.2 Hz, 6H, 15-H), 7.32 (dd, J = 7.6, 1.6 Hz, 3H), 7.09 (dd, J = 8.0, 1.6 Hz, 3H), 7.02 (t, J = 7.6 Hz, 3H, 6-H), 6.55 (s, 1H, 1-H), 5.57 (s, 3H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) 150.4 (s), 142.7 (s), 140.6 (s), 138.3 (s), 129.7 (d), 129.1 (s), 128.9 (d), 128.8 (d), 128.3 (s), 127.7 (d), 127.3 (d), 127.0 (d), 125.5 (d), 120.5 (d), 38.3 (d); HRMS (MALDI-TOF MS) Calculated ($C_{73}H_{52}O_3Na$): 999.3809 ($[M+Na]^+$), Found: 999.3833.

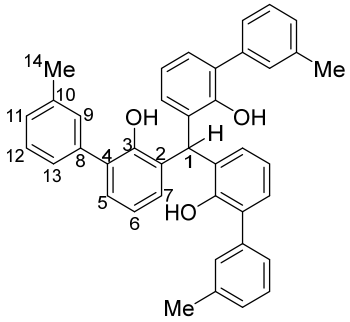
^{1}H NMR: ($CDCl_3$, 400 MHz)



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



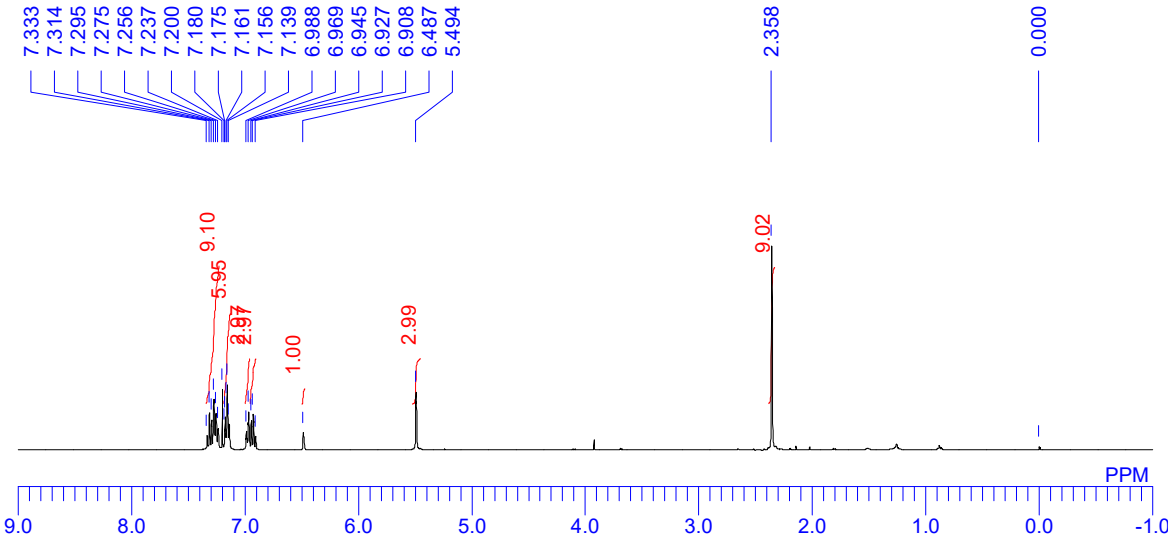
Tris{2-hydroxy-3'-methyl-(1,1'-biphenyl)-3-yl}methane 1lH$_3$



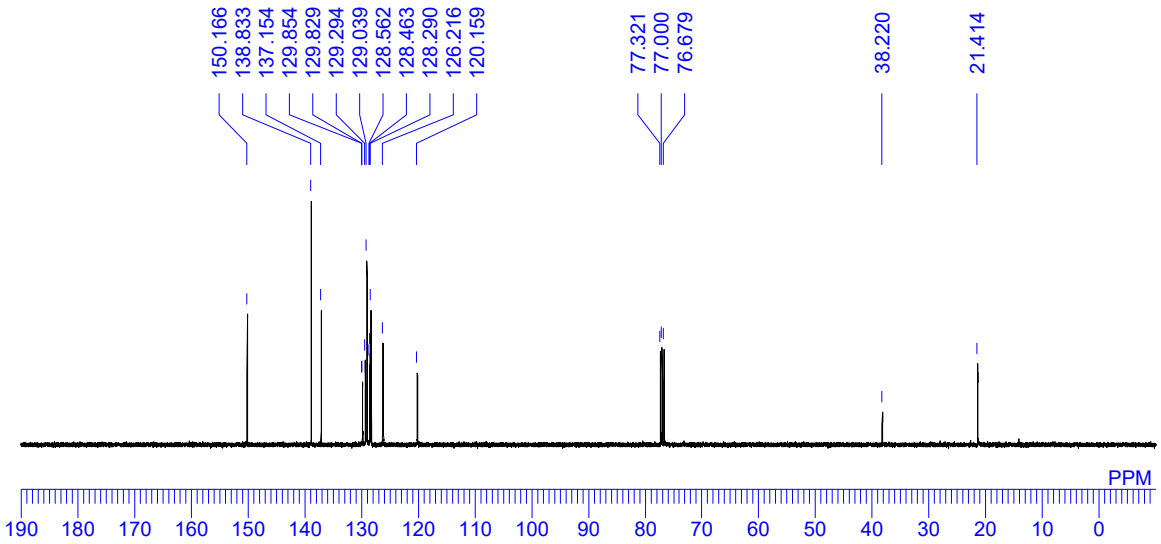
Sodium methoxide (1.06 g, 19.68 mmol) and 1-dodecanethiol (3.98 g, 19.68 mmol) were added to a solution of **1l**Me$_3$ (1.00 g, 1.64 mmol) in DMF (6 mL). After stirring at 100 °C for 4 h, water and diethyl ether (15 mL) were added to the reaction mixture at room temperature. The solution was neutralized by the addition of 1 M HCl aq., and the reaction mixture was extracted with diethyl ether (3×15 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 90:10) on silica gel to give **1l**H$_3$ as a white solid (0.35 g, 38%).

mp 97.2–98.0 °C; IR (KBr) ν = 3535 (m), 3032 (w), 2919 (w), 1606 (w), 1588 (w), 1446 (s), 1326 (m), 1227 (m), 1194 (m), 750 (m), 709 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.33–7.24 (m, 9H), 7.18–7.14 (m, 6H), 6.98 (d, J = 7.6 Hz, 3H), 6.93 (t, J = 7.4 Hz, 3H), 6.49 (s, 1H, 1-H), 5.49 (s, 3H, OH), 2.36 (s, 9H, 14-H); ^{13}C NMR (100 MHz, $CDCl_3$) 150.2 (s), 138.8 (s), 137.2 (s), 129.9 (d), 129.8 (d), 129.3 (d), 129.0 (s), 128.6 (d), 128.5 (d), 128.3 (s), 126.2 (d), 120.2 (d), 38.2 (d, C-1), 21.4 (q, C-14); MS (EI$^+$, 70 eV) m/z 562 (M$^+$, 18), 379 (24), 361 (100), 184 (14); HRMS (EI$^+$, 70 eV) Calculated ($C_{40}H_{34}O_3$): 562.2508 (M$^+$), Found: 562.2499.

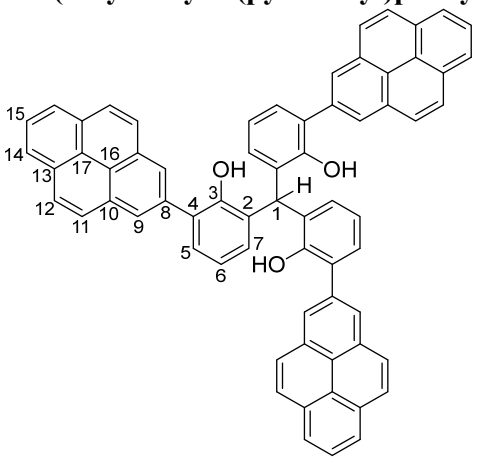
^{1}H NMR: ($CDCl_3$, 400 MHz)



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



Tris(2-hydroxy-3-(pyren-2-yl)phenyl)methane 1oH_3

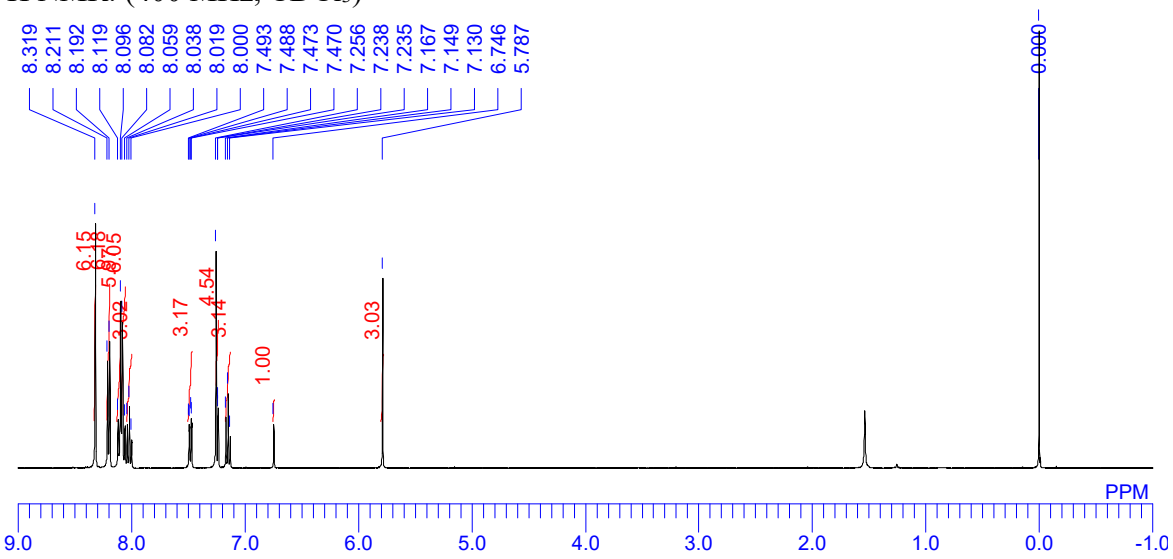


Sodium methoxide (0.39 g, 7.20 mmol) and 1-dodecanethiol (1.46 g, 7.20 mmol) were added to a solution of **1o**Me_3 (0.56 g, 0.60 mmol) in DMF (15 mL). After stirring at 100 °C for 16 h, water and diethyl ether (15 mL) were added to the reaction mixture at room temperature. The solution was neutralized by the addition of conc. HCl aq., and the reaction mixture was extracted with diethyl ether (3×15 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 50:50) on silica gel to give **1o**H_3 as a white solid (0.35 g, 65%).

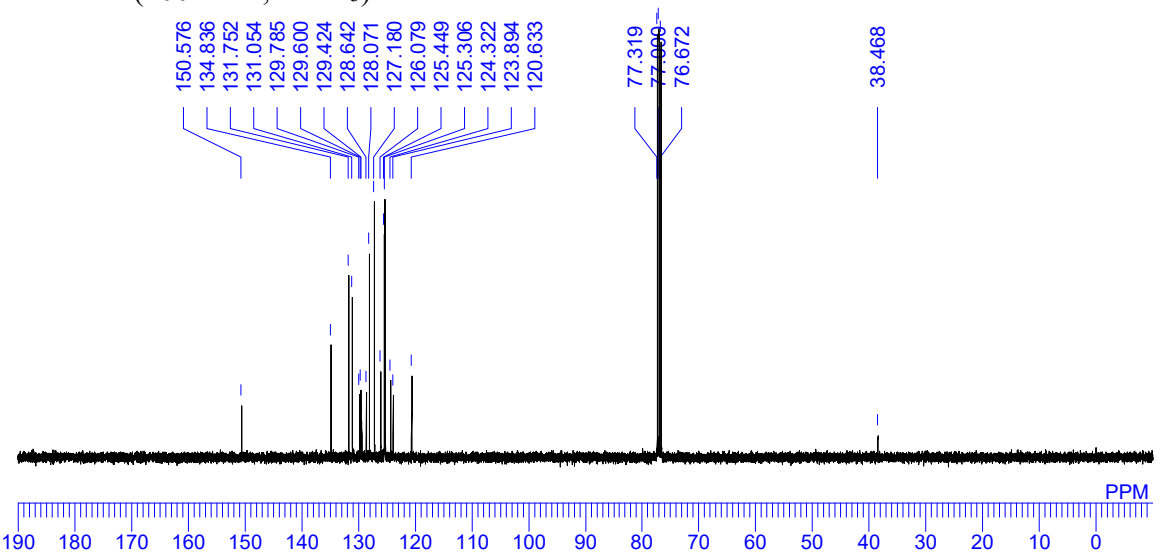
mp 256.1–256.5 °C; IR (KBr) ν = 3524 (m), 3036 (w), 1600 (m), 1436 (s), 1324 (m), 1233 (m), 1178 (m), 1095 (w), 883 (m), 842 (s), 821 (s), 754 (m), 734 (w), 714 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 8.32 (s, 6H, 9-H), 8.20 (d, J = 8.0 Hz, 6H), 8.11 (d, J = 9.2 Hz, 6H), 8.07 (d, J = 8.8 Hz, 6H), 8.02 (t, J = 7.6 Hz, 3H, 15-H), 7.48 (dd, J = 7.6, 1.6 Hz, 3H), 7.25 (dd, J = 7.4, 1.2 Hz, 3H), 7.15 (t, J = 7.4 Hz, 3H, 6-H), 6.75 (s, 1H, 1-H), 5.79 (s, 3H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) 150.6 (s), 134.8 (s), 131.8 (s), 131.1 (s), 129.8 (d), 129.6 (d), 129.4 (s), 128.6 (s), 128.1 (d), 127.2 (d), 126.1 (d), 125.4 (d), 125.3 (d), 124.3 (s), 123.9 (s), 120.6 (d), 38.5 (d, C-1); MS (FAB$^+$, 70 eV) m/z 892 (M$^+$, 4), 599 (9), 246 (24), 185 (98), 93 (100); HRMS (FAB$^+$, 70 eV) Calculated

($C_{67}H_{40}O_3$): 892.2978 (M^+), Found: 892.2980.

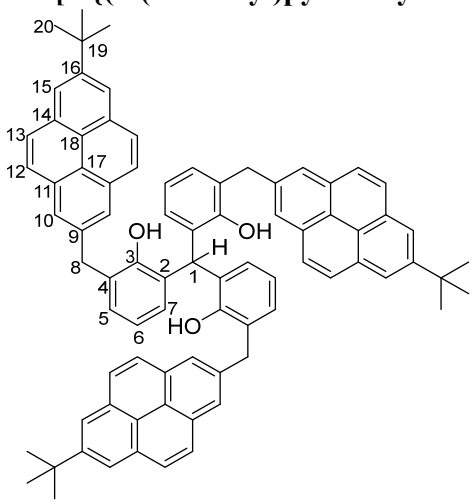
^{1}H NMR: (400 MHz, $CDCl_3$)



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

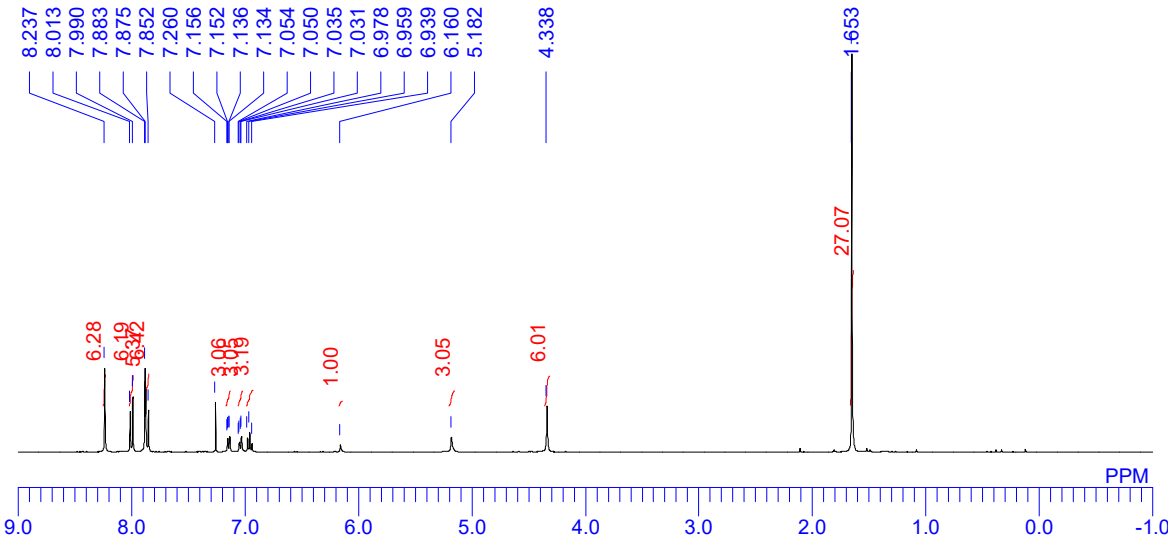


Tris[3-{(7-(*tert*-butyl)pyren-2-ylmethyl}-2-hydroxyphenyl]methane 1rH_3

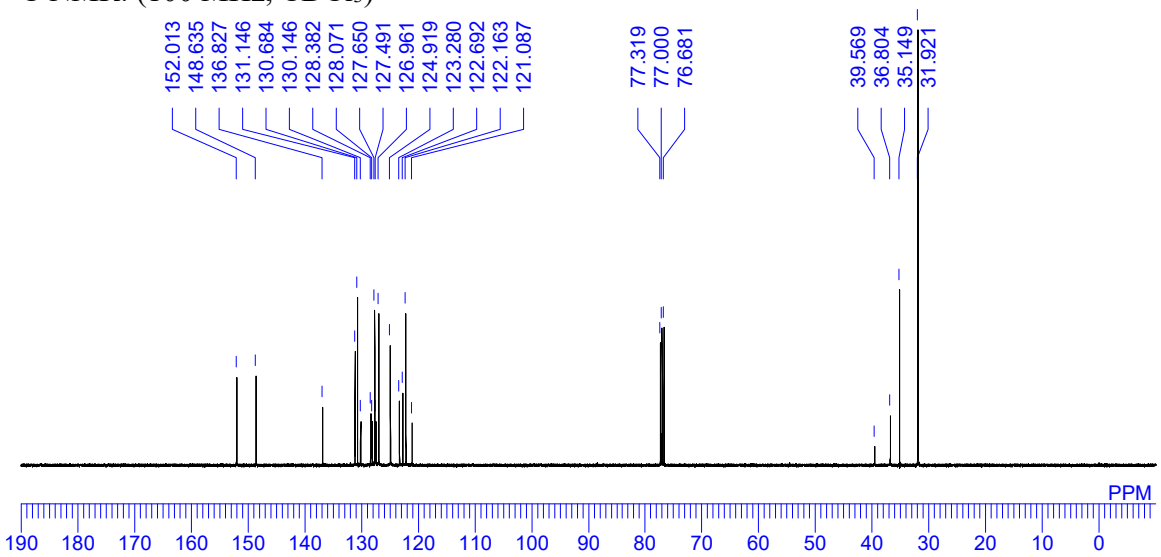


To the solution of **1r**Me_3 (0.350 g, 0.305 mmol) in dichloromethane (20 mL) was added BBr_3 (1.0 M in dichloromethane, 1.00 mL, 1.00 mmol) at −78 °C. The reaction mixture was stirred at room temperature for 14 h and water (10 ml) was added to the mixture at 0 °C. The mixture was extracted with dichloromethane (3×20 mL). The obtained organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (hexane/ethyl acetate = 60:40) on silica gel to give **1r**H_3 as a colorless solid (0.280 g, 83%).
mp 196.5–197.2 ℃; IR (KBr) ν = 3503 (m), 3038 (m), 2955 (s), 2867 (m), 1756 (w), 1605 (s), 1456 (s), 1360 (m), 1324 (w), 1254 (m), 1226 (s), 878 (s), 755 (s), 714 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.24 (s, 6H), 8.00 (d, J = 9.2 Hz, 6H), 7.88 (s, 6H), 7.86 (d, J = 9.2 Hz, 6H), 7.14 (dd, J = 7.6, 1.2 Hz, 3H), 7.04 (dd, J = 7.6, 1.6 Hz, 3H), 6.96 (t, J = 7.8 Hz, 3H, 6-H), 6.16 (s, 1H, 1-H), 5.18 (s, 3H, OH), 4.34 (s, 6H, 8-H), 1.65 (s, 27H, 20-H); ^{13}C NMR (100 MHz, $CDCl_3$) 152.0 (s), 148.6 (s), 136.8 (s), 131.1 (s), 130.7 (s), 130.1 (d), 128.4 (s), 128.1 (s), 127.7 (d), 127.5 (d), 127.0 (d), 124.9 (d), 123.3 (s), 122.7 (s), 122.2 (d), 121.1 (d), 39.6 (d, C-1), 36.8 (t, C-8), 35.1 (s, C-19), 31.9 (q, C-20); HRMS (MALDI-TOF MS) Calculated ($C_{82}H_{70}O_3$): 1102.5320 (M^+), Found: 1102.5332.

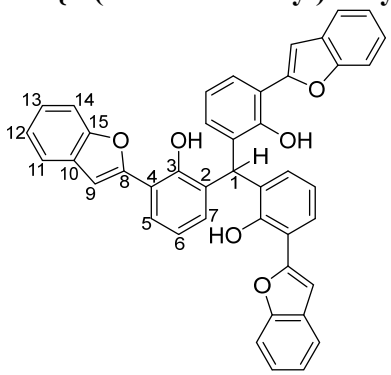
^{1}H NMR: (400 MHz, $CDCl_3$)



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



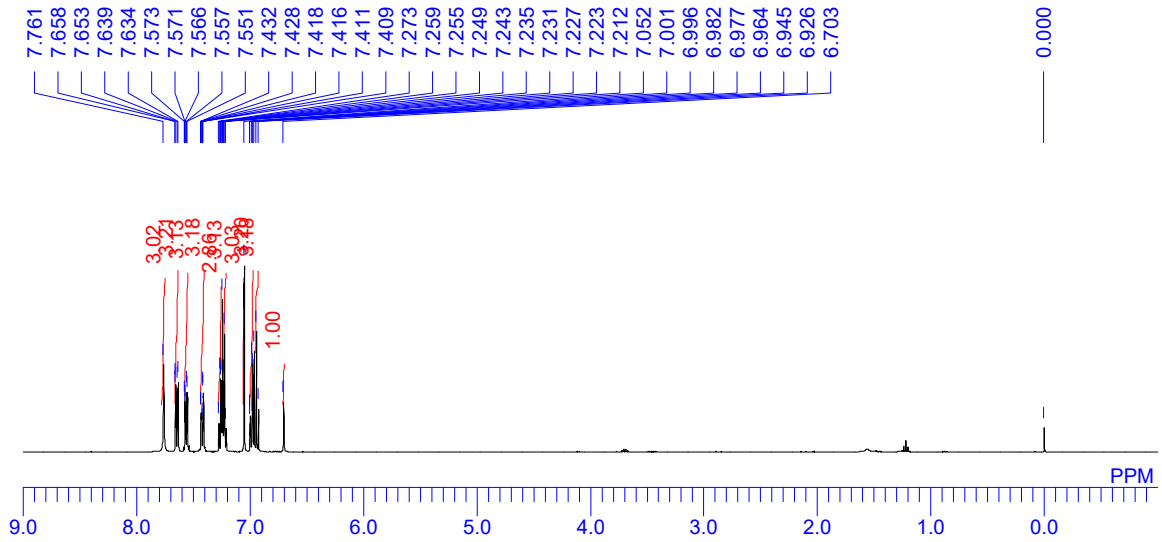
Tris{3-(benzofuran-2-yl)-2-hydroxyphenyl}methane 1AH$_3$



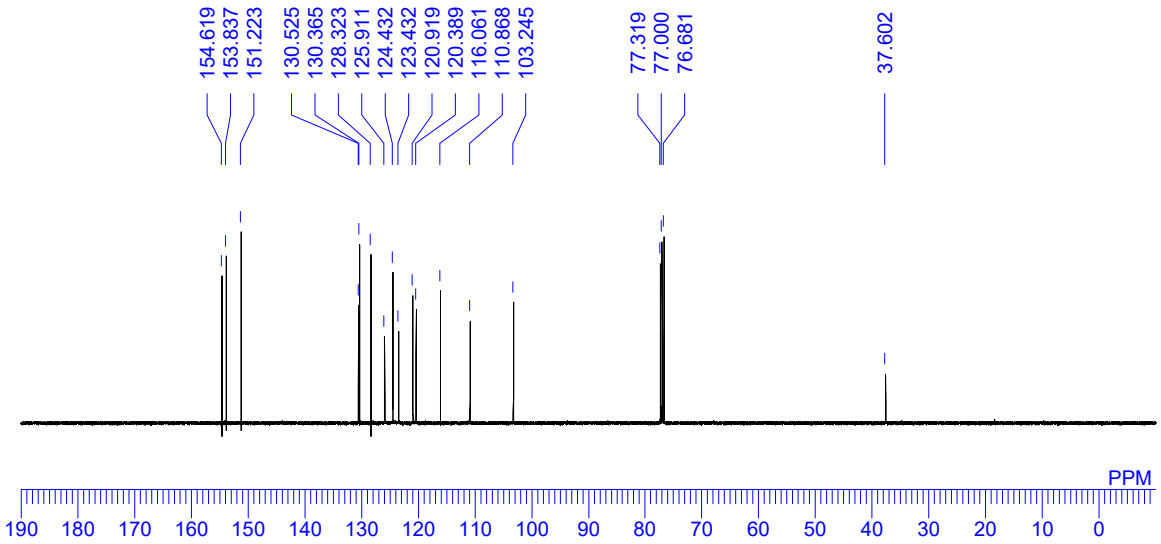
Sodium methoxide (0.376 g, 6.96 mmol) and 1-dodecanethiol (1.41 g, 6.96 mmol) were added to a solution of **1A**Me$_3$ (0.396 g, 0.580 mmol) in DMF (15 mL). After stirring at 100 °C for 16 h, water and diethyl ether (15 mL) were added to the reaction mixture at room temperature. The solution was neutralized by the addition of 1 M HCl aq., and the reaction mixture was extracted with diethyl ether (3×15 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 60:40) on silica gel to give **1A**H$_3$ as a white solid (0.158 g, 43%).

mp 248.2–248.9 °C; IR (KBr) ν = 3511 (s), 3103 (w), 3064 (w), 3015 (w), 1609 (w), 1591 (m), 1457 (s), 1435 (s), 1346 (s), 1303 (m), 1230 (s), 1166 (m), 953 (m), 833 (m), 748 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.76 (s, 3H), 7.65 (dd, J = 7.4, 1.8 Hz, 3H), 7.57–7.55 (m, 3H), 7.43–7.41 (m, 3H), 7.27–7.25 (m, 3H), 7.24–7.21 (m, 3H), 7.05 (s, 3H), 6.99 (dd, J = 7.8, 1.8 Hz, 3H), 6.95 (t, J = 7.6 Hz, 3H), 6.70 (s, 1H, 1-H); ^{13}C NMR (100 MHz, $CDCl_3$) 154.6 (s), 153.8 (s), 151.2 (s), 130.5 (d), 130.4 (s), 128.3 (s), 125.9 (d), 124.4 (d), 123.4 (d), 120.9 (d), 120.4 (d), 116.1 (s), 110.9 (d), 103.2 (d), 37.6 (d, C-1); HRMS (MALDI-TOF MS) Calculated ($C_{43}H_{28}O_6$): 640.1880 (M^+), Found: 640.1872.

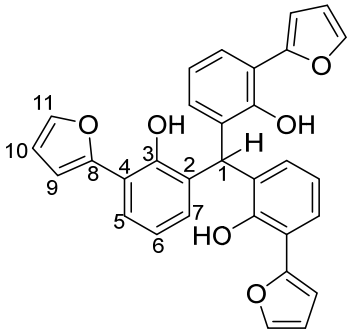
^{1}H NMR: (400 MHz, $CDCl_3$)



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



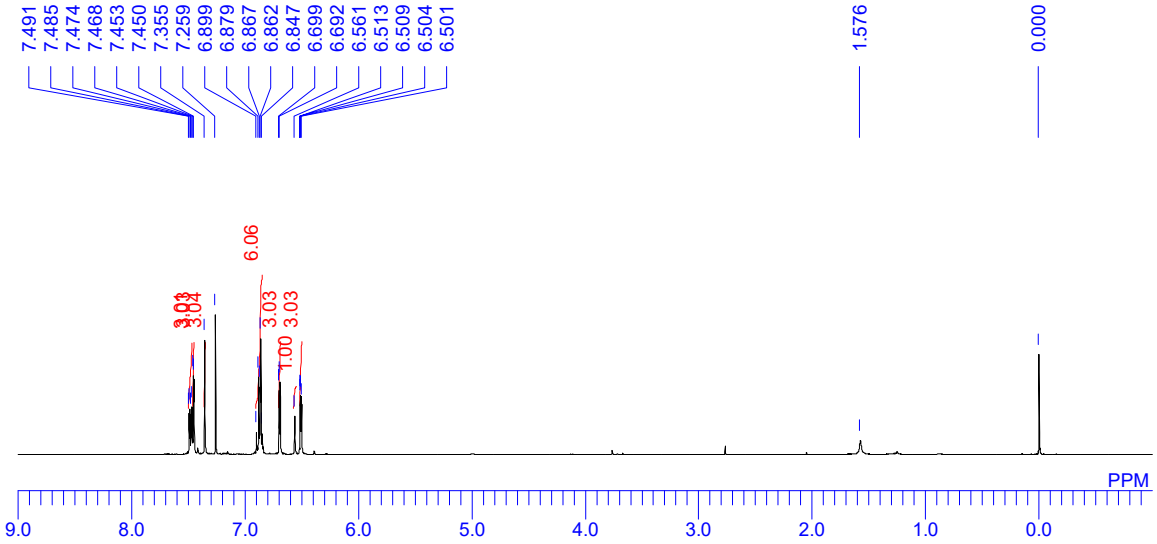
Tris{3-(furan-2-yl)-2-hydroxyphenyl}methane 1BH$_3$



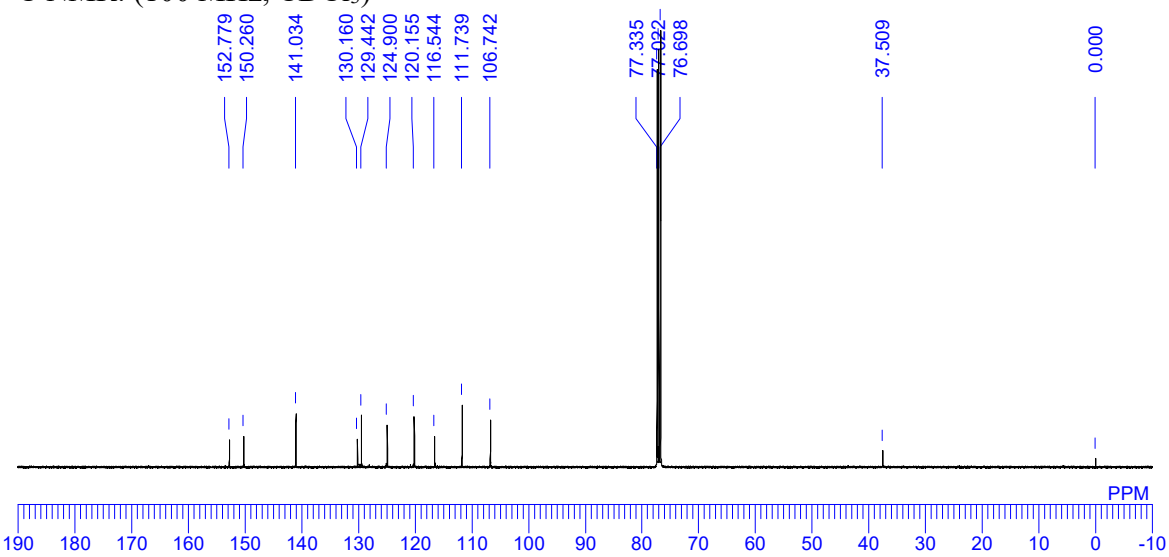
Sodium methoxide (0.648 g, 12.0 mmol) and 1-dodecanethiol (2.43 g, 12.0 mmol) were added to a solution of **1B**Me$_3$ (0.533 g, 1.00 mmol) in DMF (15 mL). After stirring at 100 °C for 7 h, water and ethyl acetate (15 mL) were added to the reaction mixture at room temperature. The solution was neutralized by the addition of 1 M HCl aq., and the reaction mixture was extracted with ethyl acetate (3×15 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 60:40) on silicagel to give **1B**H$_3$ as a colorless solid (0.173 g, 35%).

mp 184.6–185.4 °C (decomp.); IR (KBr) ν = 3473 (m), 3150 (w), 3120 (w), 3063 (w), 1590 (w), 1500 (m), 1460 (m), 1437 (s), 1335 (m), 1230 (m), 1184 (s), 1153 (s), 1068 (m), 1015 (m), 940 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.48 (dd, J = 6.8, 2.4 Hz, 3H), 7.45 (d, J = 1.6 Hz, 3H), 7.36 (s, 3H, OH), 6.90–6.85 (m, 6H), 6.70 (d, J = 2.8 Hz, 3H), 6.56 (s, 1H, 1-H), 6.51 (dd, J = 3.4, 1.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 152.8 (s), 150.3 (s), 141.0 (d), 130.2 (s), 129.4 (d), 124.9 (d), 120.2 (d), 116.5 (s), 111.7 (d), 106.7 (d), 37.5 (d, C-1); HRMS (MALDI-TOF MS) Calculated ($C_{31}H_{22}O_6Na$): 513.1309 ([M+Na]$^+$), Found: 513.1309.

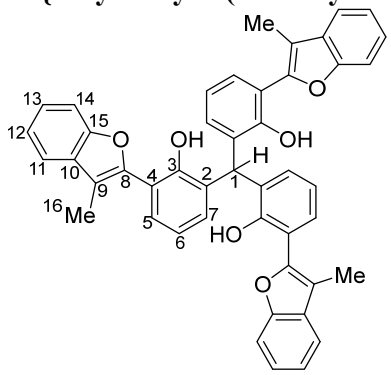
^{1}H NMR: (400 MHz, $CDCl_3$)



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



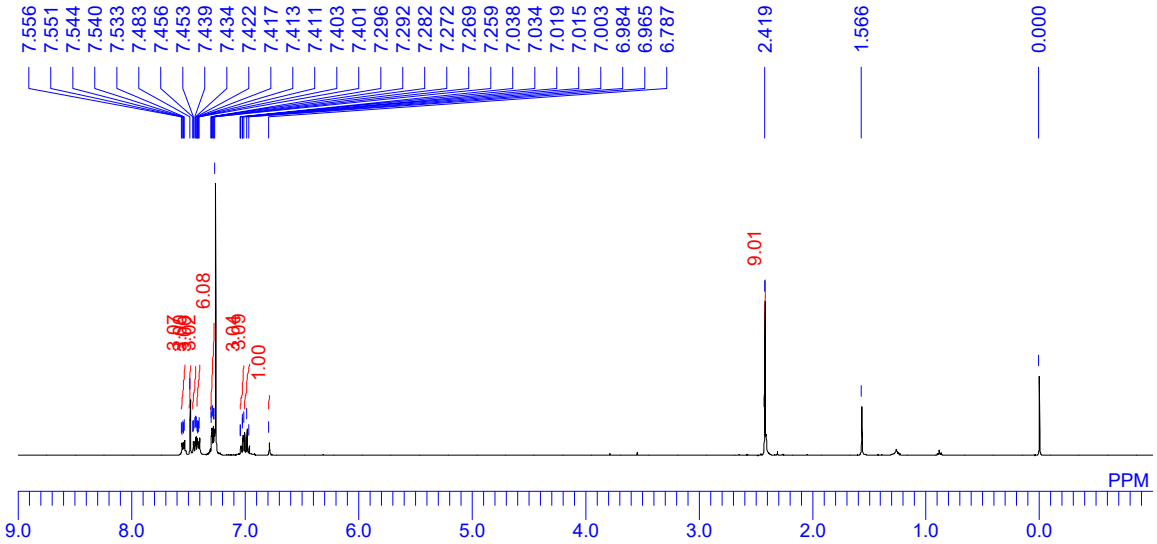
Tris{2-hydroxy-3-(3-methylbenzofuran-2-yl)phenyl}methane 1A$_I$H$_3$



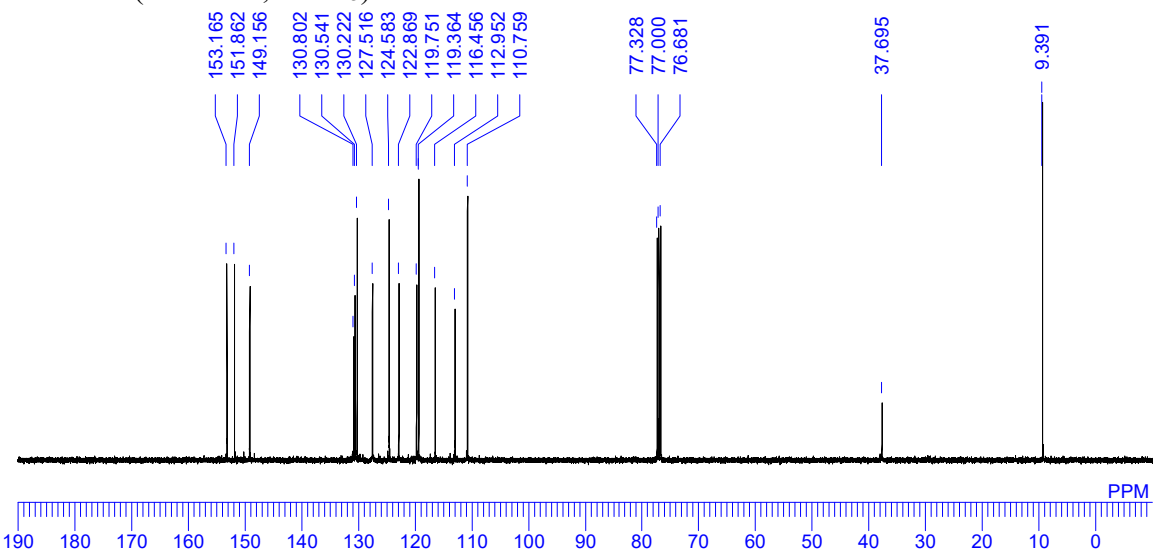
Sodium methoxide (0.698 g, 12.9 mmol) and 1-dodecanethiol (2.61 g, 12.9 mmol) were added to a solution of **1A$_I$**Me$_3$ (0.780 g, 1.08 mmol) in DMF (15 mL). After stirring at 100 °C for 16 h, water and diethyl ether (15 mL) were added to the reaction mixture at room temperature. The solution was neutralized by the addition of 1 M HCl aq., and the reaction mixture was extracted with diethyl ether (3×15 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 60:40) on silica gel to give **1A$_I$**H$_3$ as a white solid (0.110 g, 15%).

mp 118.9–119.8 °C; IR (KBr) ν = 3508 (m), 3051 (w), 2921 (m), 2853 (w), 1589 (m), 1451 (s), 1436 (s), 1343 (m), 1262 (m), 1230 (s), 1214 (s), 1070 (m), 1007 (w), 877 (w), 825 (m), 777 (m), 745 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.56–7.53 (m, 3H), 7.48 (s, 3H, OH), 7.44 (dd, J = 7.4, 1.8 Hz, 3H), 7.42–7.40 (m, 3H), 7.30–7.27 (m, 3H), 7.03 (dd, J = 7.6, 1.6 Hz, 3H), 6.98 (t, J = 7.6 Hz, 3H, 6-H), 6.79 (s, 1H, 1-H), 2.42 (s, 9H, 16-H); ^{13}C NMR (100 MHz, $CDCl_3$) 153.2 (s), 151.9 (s), 149.2 (s), 130.8 (s), 130.5 (d), 130.2 (s), 127.5 (d), 124.6 (d), 122.9 (d), 119.8 (d), 119.4 (d), 116.5 (s), 113.0 (s), 110.8 (d), 37.7 (d, C-1), 9.4 (d, C-16); HRMS (MALDI-TOF MS) Calculated ($C_{46}H_{34}O_6$): 682.2350 (M^+), Found: 682.2355.

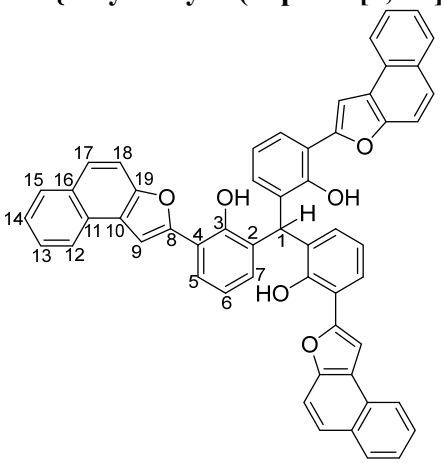
^{1}H NMR: (400 MHz, $CDCl_3$)



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



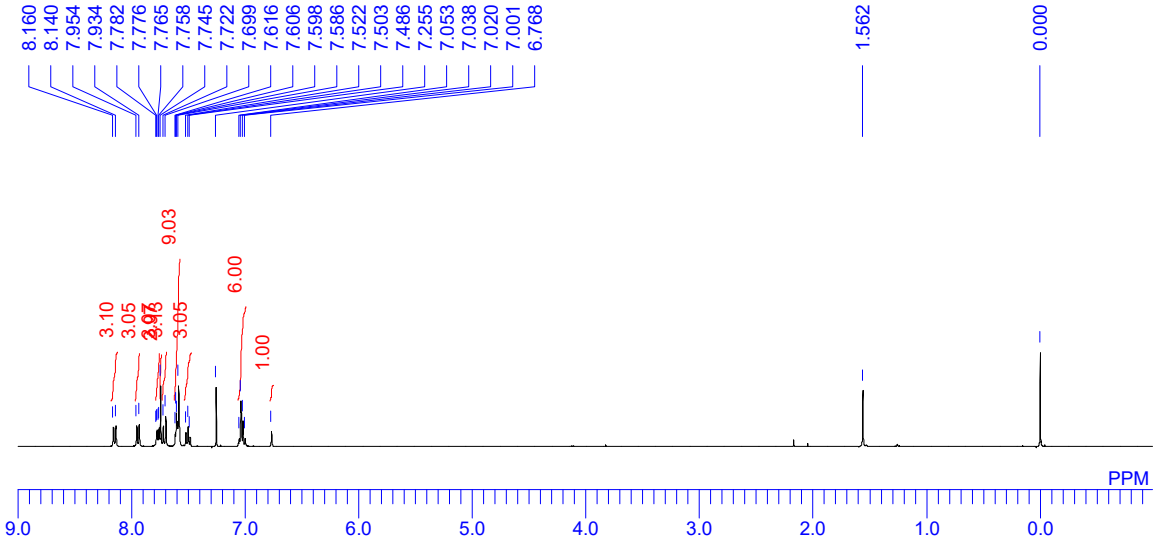
Tris{2-hydroxy-3-(naphtho[2,1-*b*]furan-2-yl)phenyl}methane $\mathbf{1A_{II}H_3}$



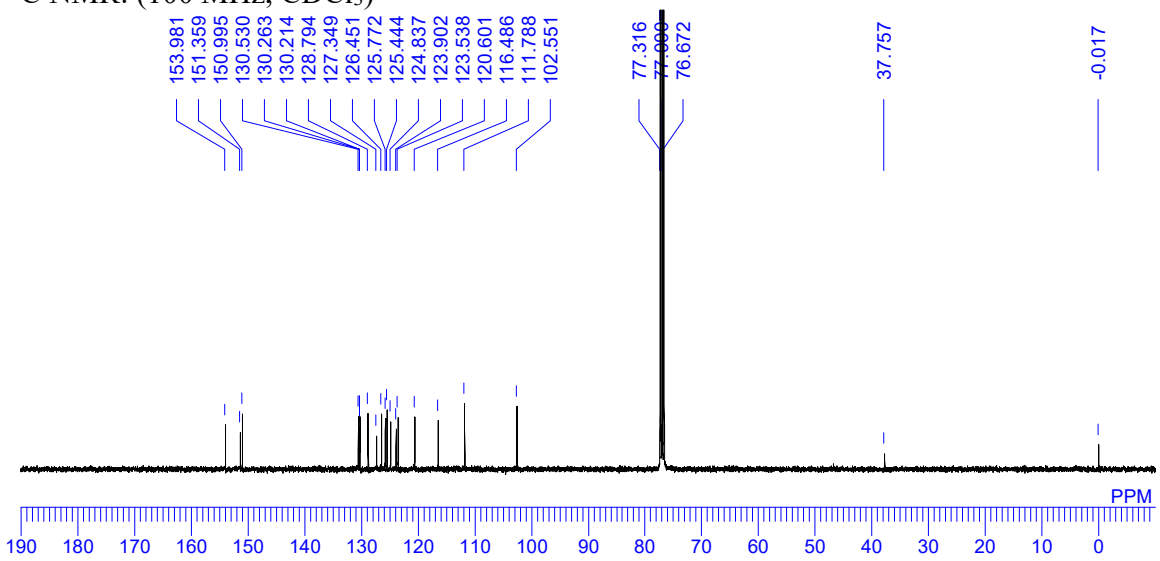
Sodium methoxide (0.674 g, 12.48 mmol) and 1-dodecanethiol (2.53 g, 12.48 mmol) were added to a solution of $\mathbf{1A_{II}}Me_3$ (0.866 g, 1.04 mmol) in DMF (15 mL). After stirring at 100 °C for 16 h, water and diethyl ether (15 mL) were added to the reaction mixture at room temperature. The solution was neutralized by the addition of 1 M HCl aq., and the reaction mixture was extracted with diethyl ether (3×15 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 60:40) on silica gel to give $\mathbf{1A_{II}}H_3$ as a white solid (0.420 g, 51%).

mp 260.5–261.0 °C (decomp.); IR (KBr) ν = 3520 (s), 3052 (w), 1592 (w), 1457 (s), 1433 (s), 1385 (s), 1350 (m), 1278 (m), 1233 (s), 1202 (m), 1163 (m), 1079 (w), 993 (m), 802 (s), 773 (s), 745 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.15 (d, J = 8.0 Hz, 3H), 7.94 (d, J = 8.0 Hz, 3H), 7.77 (dd, J = 7.0, 2.6 Hz, 3H), 7.75 (s, 3H), 7.71 (d, J = 9.2 Hz, 3H), 7.62–7.59 (m, 9H), 7.50 (t, J = 7.2 Hz, 3H), 7.05–7.00 (m, 6H), 6.77 (s, 1H, 1-H); ^{13}C NMR (100 MHz, $CDCl_3$) 154.0 (s), 151.4 (s), 151.0 (s), 130.5 (s), 130.3 (d), 130.2 (s), 128.8 (d), 127.3 (s), 126.5 (d), 125.8 (d), 125.4 (d), 124.8 (d), 123.9 (s), 123.5 (d), 120.6 (d), 116.5 (s), 111.8 (d), 102.6 (d), 37.8 (d, C-1); HRMS (MALDI-TOF MS) Calculated ($C_{55}H_{34}O_6$): 790.2350 (M^+), Found: 790.2357.

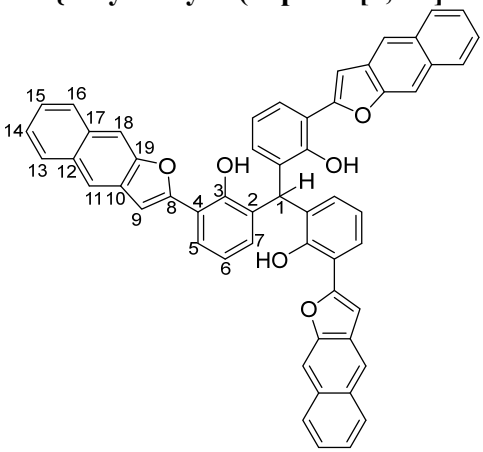
^1H NMR: (400 MHz, $CDCl_3$)



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



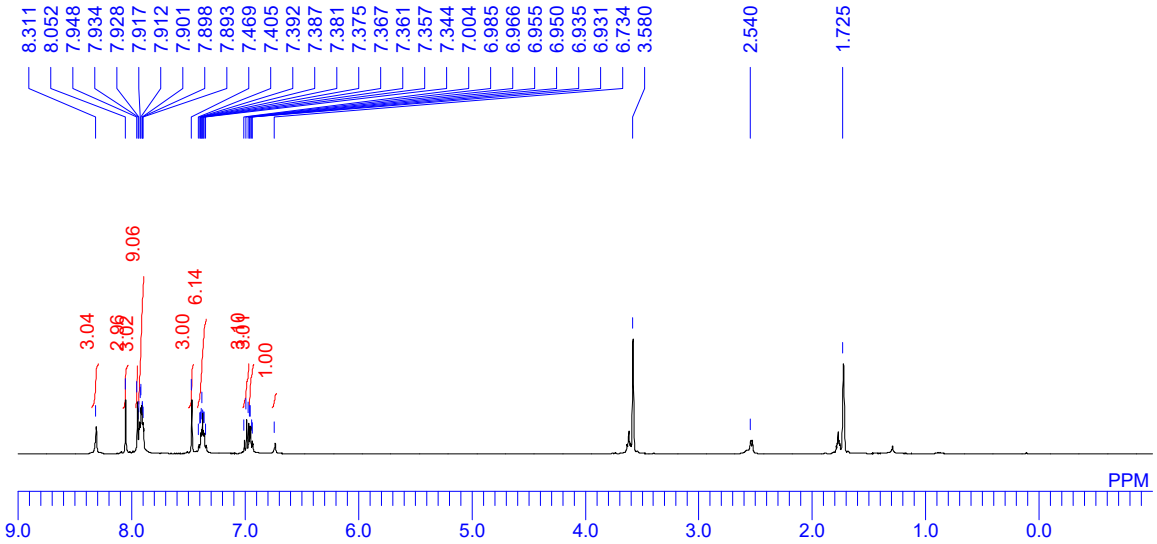
Tris{2-hydroxy-3-(naphtho[2,3-*b*]furan-2-yl)phenyl}methane $\mathbf{1A_{III}H_3}$



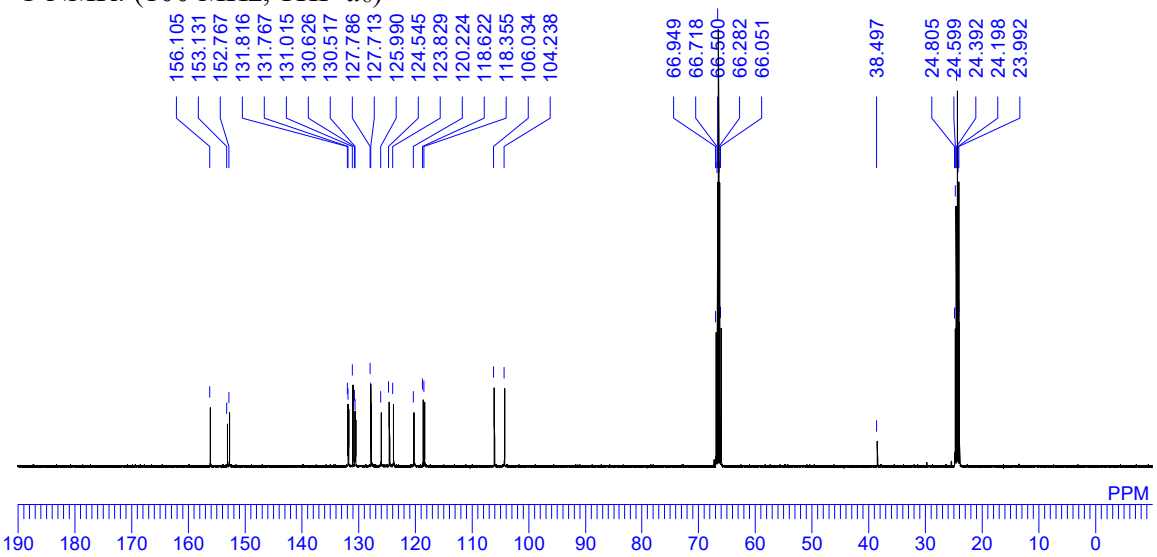
Sodium methoxide (0.214 g, 3.96 mmol) and 1-dodecanethiol (0.579 g, 3.96 mmol) were added to a solution of $\mathbf{1A_{III}}Me_3$ (0.275 g, 0.330 mmol) in DMF (10 mL). After stirring at 100 °C for 16 h, water and diethyl ether (15 mL) were added to the reaction mixture at room temperature. The solution was neutralized by the addition of 1 M HCl aq., and the reaction mixture was extracted with diethyl ether (3×15 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 20:80) on silica gel to give $\mathbf{1A_{III}}H_3$ as a white solid (0.124 g, 48%).

mp 247.9–248.6 °C; IR (KBr) ν = 3492 (s), 3052 (w), 2924 (w), 1732 (w), 1592 (m), 1503 (m), 1449 (s), 1435 (s), 1359 (m), 1256 (s), 1232 (s), 1149 (m), 1097 (m), 949 (m), 860 (s), 743 (s) cm^{-1}; ^{1}H NMR (400 MHz, THF-d_8) 8.31 (s, 3H), 8.05 (s, 3H), 7.95 (s, 3H), 7.93–7.89 (m, 9H), 7.47 (s, 3H), 7.41–7.34 (m, 6H), 6.99 (t, J = 7.6 Hz, 3H), 6.94 (dd, J = 7.8, 1.8 Hz, 3H), 6.73 (s, 1H, 1-H); ^{13}C NMR (100 MHz, THF-d_8) 156.1 (s), 153.1 (s), 152.8 (s), 131.82 (s), 131.77 (s), 131.0 (s), 130.6 (d), 130.5 (s), 127.8 (d), 127.7 (d), 126.0 (d), 124.5 (d), 123.8 (d), 120.2 (d), 118.6 (s), 118.4 (d), 106.0 (d), 104.2 (d), 38.5 (d, C-1); HRMS (MALDI-TOF MS) Calculated ($C_{55}H_{34}O_6$): 790.2350 (M^+), Found: 790.2334.

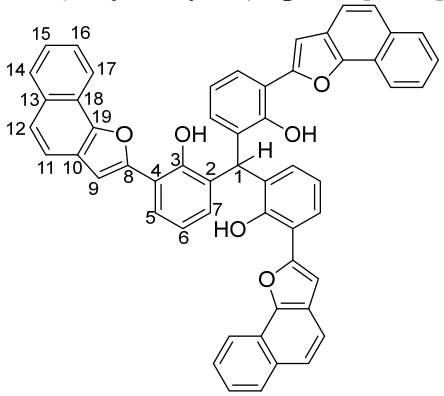
^{1}H NMR: (400 MHz, THF-d_8)



^{13}C NMR: (100 MHz, THF-d_8)



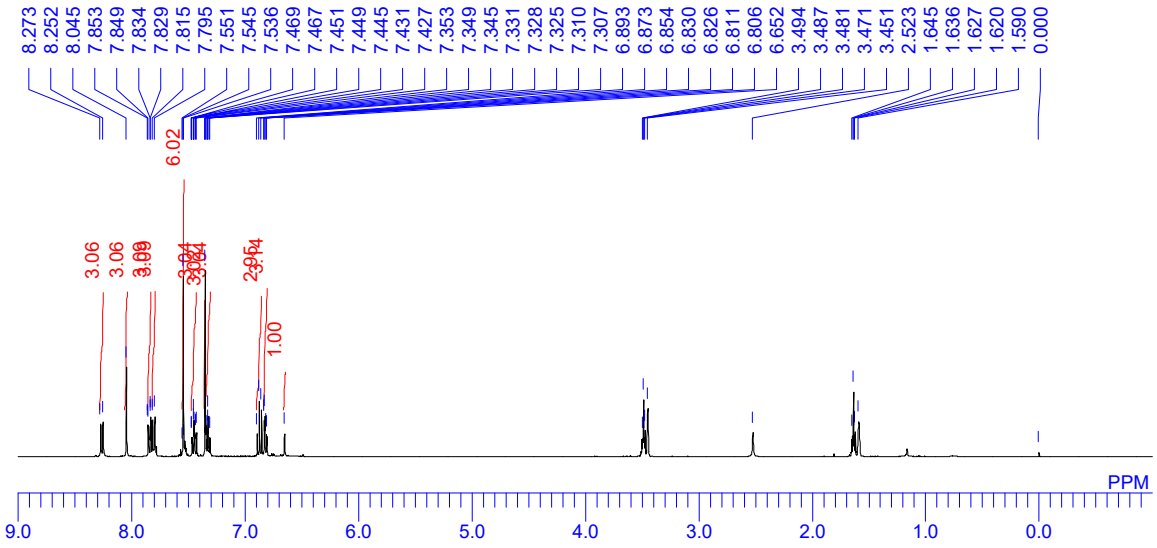
Tris{2-hydroxy-3-(naphtho[1,2-*b*]furan-2-yl)phenyl}methane $\mathbf{1A_{IV}H_3}$



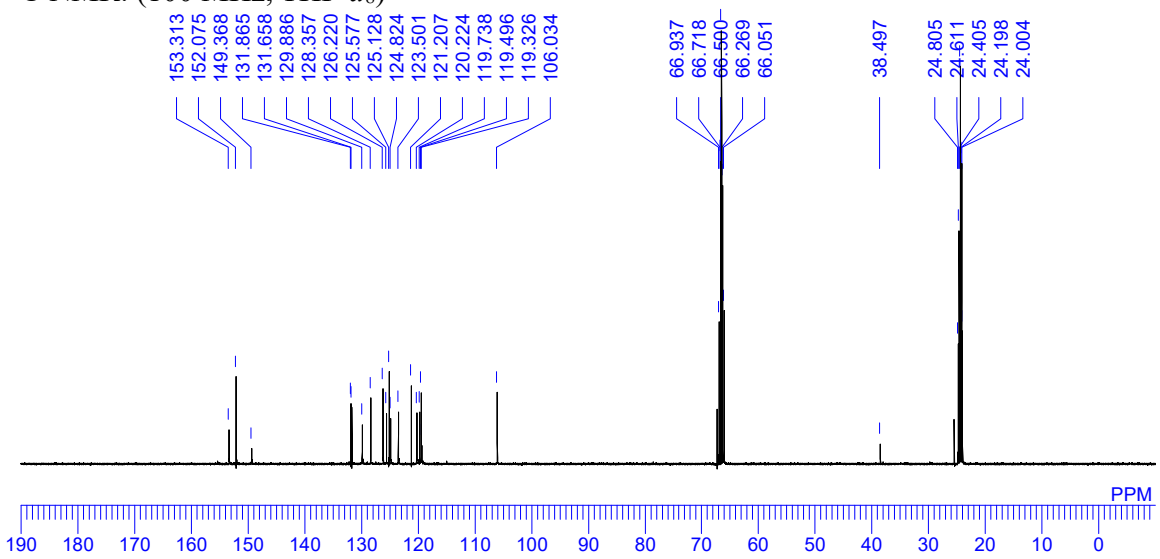
Sodium methoxide (0.095 g, 1.77 mmol) and 1-dodecanethiol (0.258 g, 1.77 mmol) were added to a solution of $\mathbf{1A_{IV}}Me_3$ (0.245 g, 0.294 mmol) in DMF (10 mL). After stirring at 100 °C for 16 h, water and diethyl ether (15 mL) were added to the reaction mixture at room temperature. The solution was neutralized by the addition of 1 M HCl aq., and the reaction mixture was extracted with diethyl ether (3×15 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The residue was purified by column chromatography (hexane/ethyl acetate = 40:60) on silica gel to give $\mathbf{1A_{IV}}H_3$ as a white solid (0.110 g, 47%).

mp 177.8–178.5 °C (decomp.); IR (KBr) ν = 3509 (s), 3060 (m), 1597 (m), 1523 (m), 1451 (s), 1433 (m), 1381 (m), 1313 (m), 1231 (m), 1169 (m), 1084 (m), 952 (w), 878 (w), 820 (s), 745 (s) cm^{-1}; ^1H NMR (400 MHz, THF-d_8) 8.26 (d, J = 8.4 Hz, 3H), 8.05 (s, 3H), 7.84 (dd, J = 7.8, 1.8 Hz, 3H), 7.81 (d, J = 8.0 Hz, 3H), 7.55–7.54 (m, 6H), 7.45 (td, J = 7.8, 1.2 Hz, 3H), 7.35 (s, 3H), 7.33 (td, J = 7.7, 1.3 Hz, 3H), 6.87 (t, J = 7.8 Hz, 3H), 6.82 (dd, J = 7.8, 1.8 Hz, 3H), 6.65 (s, 1H, 1-H); ^{13}C NMR (100 MHz, THF-d_8) 153.3 (s), 152.1 (s), 149.4 (s), 131.9 (s), 131.7 (s), 129.9 (d), 128.4 (d), 126.2 (d), 125.6 (d), 125.1 (s), 124.8 (d), 123.5 (d), 121.2 (s), 120.2 (d), 119.7 (d), 119.5 (d), 119.3 (s), 106.0 (d), 38.5 (d, C-1); HRMS (MALDI-TOF MS) Calculated ($C_{55}H_{34}O_6$): 790.2350 (M^+), Found: 790.2345.

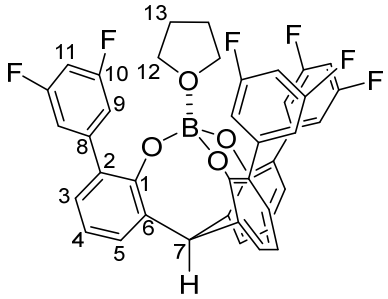
^1H NMR: (400 MHz, THF-d_8)



^{13}C NMR: (100 MHz, THF-d_8)



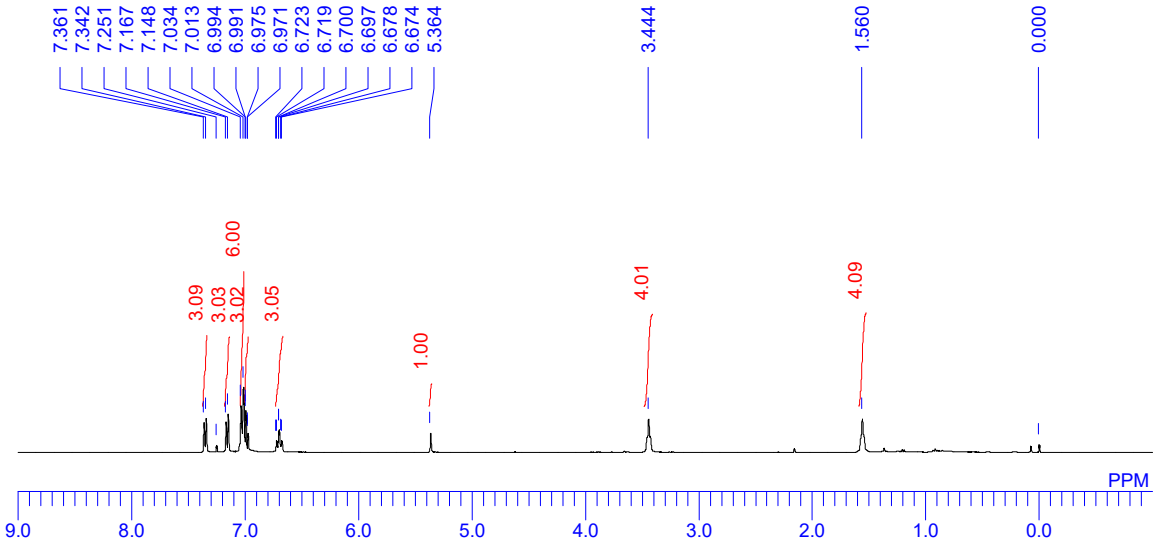
Cage-shaped borate 1iB·thf



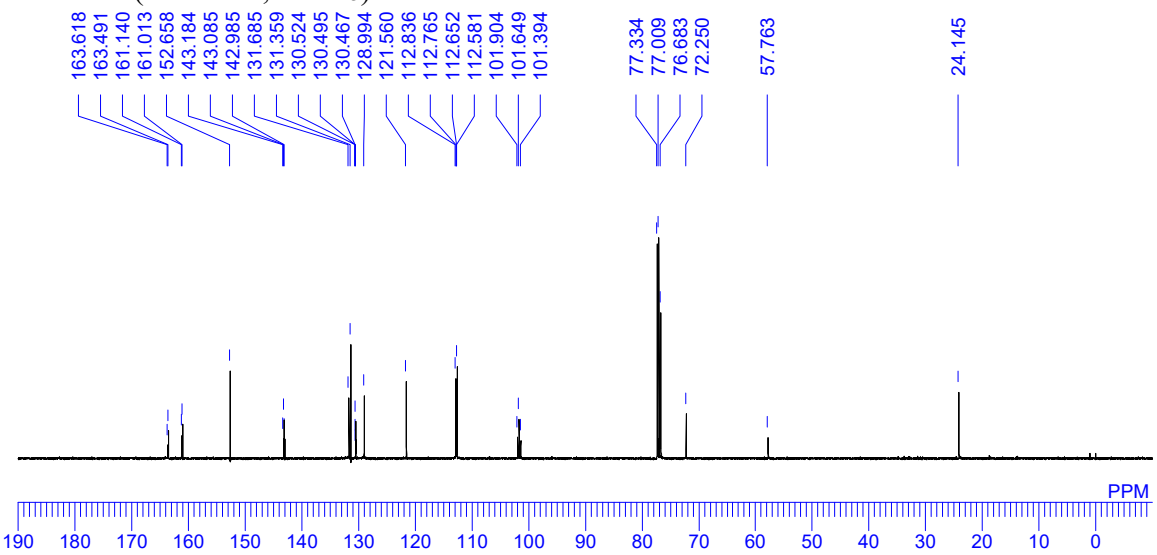
In a nitrogen-filled glove box, to a suspension of **1i**H$_3$ (420 mg, 0.668 mmol) in dichloromethane (3 mL) was added BH$_3$·THF in THF (0.734 mmol, 0.9 M) at room temperature with stirring for 2 h under release of H$_2$ gas. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give **1i**B·thf as a colorless solid (473 mg, quant.).

^{1}H NMR (400 MHz, CDCl$_3$) 7.35 (d, J = 7.6 Hz, 3H), 7.16 (d, J = 7.6 Hz, 3H), 7.02 (d, $^3J_{H–F}$ = 8.4 Hz, 6H, 9-H), 6.99 (td, J = 7.8, 1.4 Hz, 3H), 6.70 (td, $^3J_{H–F}$ = 9.0 Hz, $^4J_{H–H}$ = 1.4 Hz, 3H, 11-H), 5.36 (s, 1H, 7-H), 3.44 (brs, 4H, 12-H), 1.56 (brs, 4H, 13-H); ^{13}C NMR (100 MHz, CDCl$_3$) 162.3 (s, dd, $^1J_{C-F}$ = 247.8 Hz, $^3J_{C-F}$ = 12.7 Hz, C-10), 152.7 (s), 143.1 (s, t, $^3J_{C-F}$ = 10.0 Hz, C-8), 131.7 (d), 131.4 (s), 130.5 (s, t, $^4J_{C-F}$ = 2.9 Hz, C-2), 129.0 (d), 121.6 (d), 112.7 (d, dd, $^2J_{C-F}$ = 18.4 Hz, $^4J_{C-F}$ = 7.1 Hz, C-9), 101.6 (d, t, $^2J_{C-F}$ = 25.5 Hz, C-11), 72.3 (t, C-12), 57.8 (d, C-7), 24.1 (t, C-13); ^{11}B{^{1}H} NMR: (127 MHz, CDCl$_3$, BF$_3$·Et$_2$O in CDCl$_3$ as an external standard) 5.05 ^{19}F NMR (376 MHz, CDCl$_3$, BF$_3$·OEt$_2$ (−153 ppm) in CDCl$_3$ used as an external standard; *i.e.* CFCl$_3$ (0 ppm)) −103.87–−103.91 (m).

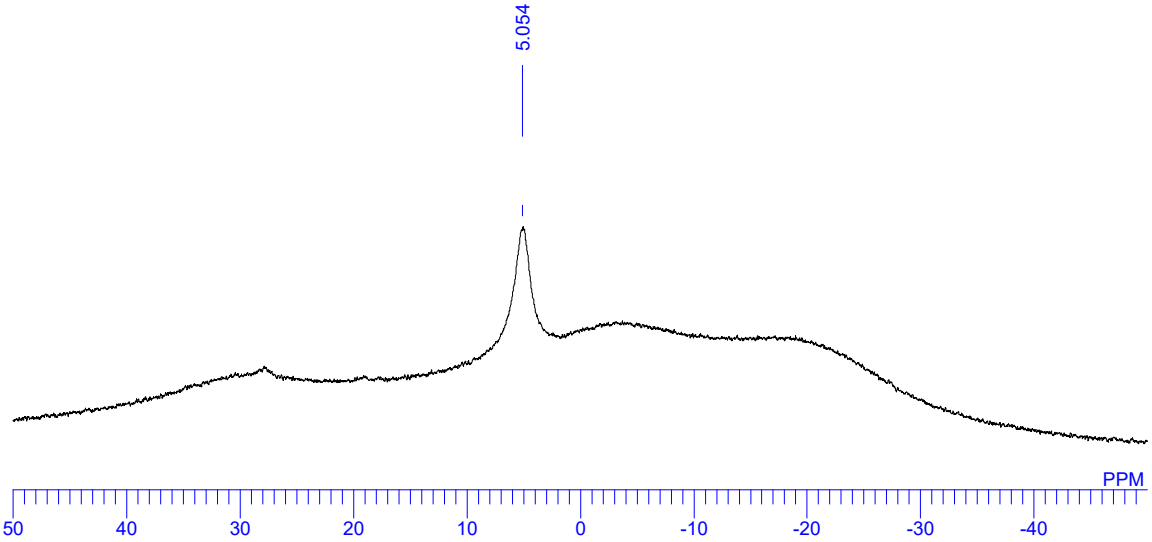
^{1}H NMR: (400 MHz, $CDCl_3$)



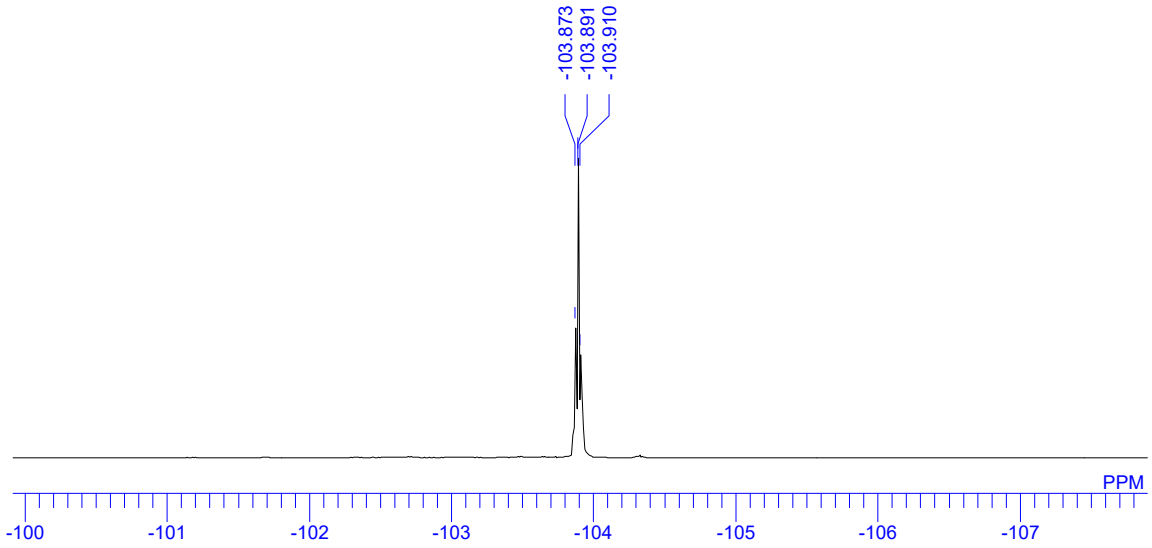
^{13}C NMR: (100 MHz, $CDCl_3$)



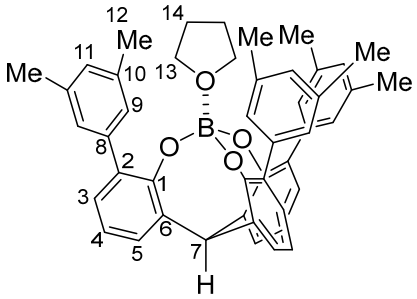
$^{11}B\{^{1}H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)



^{19}F NMR: (376 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ (−153 ppm) in $CDCl_3$ used as an external standard; *i.e.* $CFCl_3$ (0 ppm))

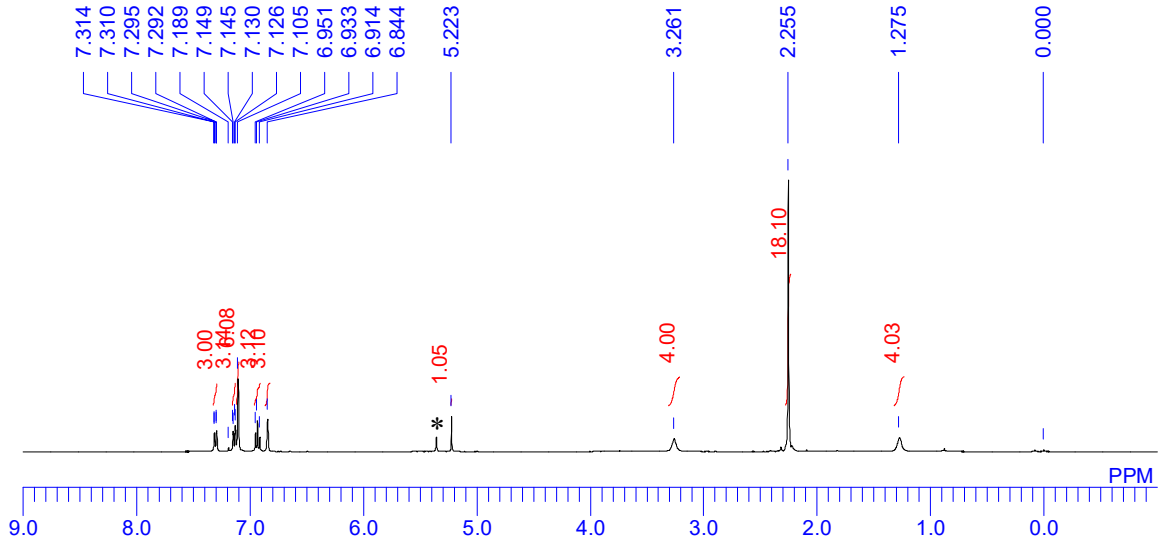


Cage-shaped borate 1jB·thf



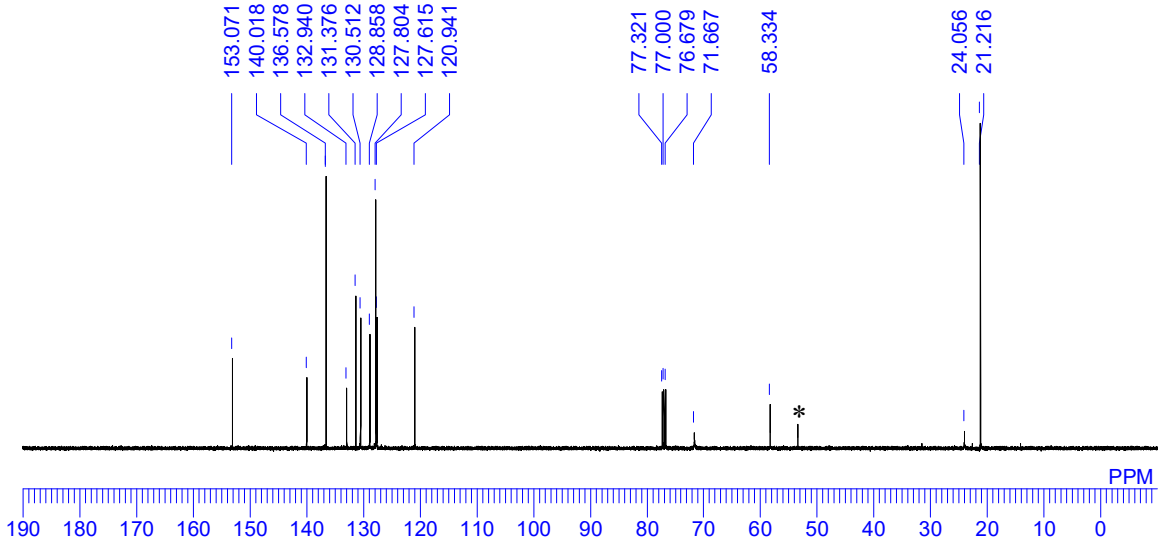
In a nitrogen-filled glove box, to a suspension of **1j**H_3 (390 mg, 0.644 mmol) in dichloromethane (3 mL) was added BH_3·THF in THF (0.708 mmol, 0.9 M) at room temperature with stirring for 2 h under release of H_2 gas. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give **1j**B·thf as a colorless solid (440 mg, quant.).
^{1}H NMR (400 MHz, $CDCl_3$) 7.30 (dd, J = 7.4, 1.4 Hz, 3H), 7.14 (dd, J = 7.6, 1.6 Hz, 3H), 7.11 (s, 6H, 9-H), 6.93 (t, J = 7.4 Hz, 3H, 4-H), 6.84 (s, 3H, 11-H), 5.22 (s, 1H, 7-H), 3.26 (brs, 4H, 13-H), 2.26 (s, 18H, 12-H), 1.55 (brs, 4H, 14-H); ^{13}C NMR (100 MHz, $CDCl_3$) 153.1 (s), 140.0 (s), 136.6 (s), 132.9 (s), 131.4 (s), 130.5 (d), 128.9 (d), 127.8 (d), 127.6 (d), 120.9 (d), 71.7 (t, C-13), 58.3 (d, C-7), 24.1 (t, C-14), 21.2 (q, C-12); ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, BF_3·Et_2O in $CDCl_3$ as an external standard) 5.44.

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



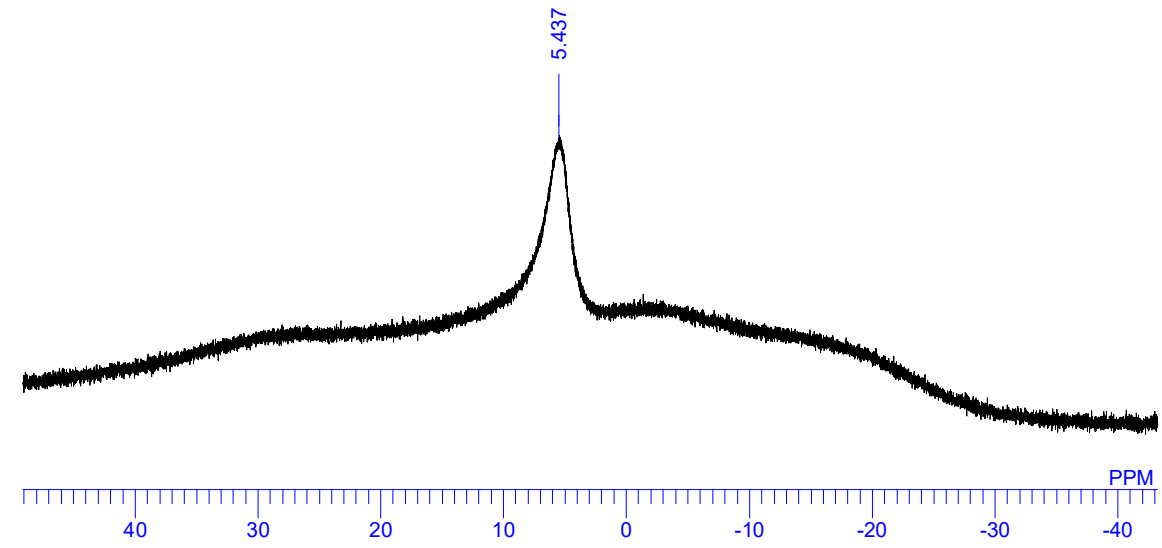
Asterisk represents residual dichloromethane.

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

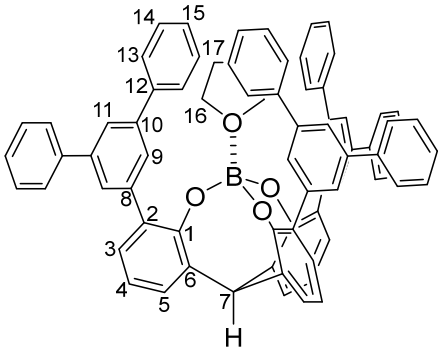


Asterisk represents residual dichloromethane.

$^{11}B\{^1H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)



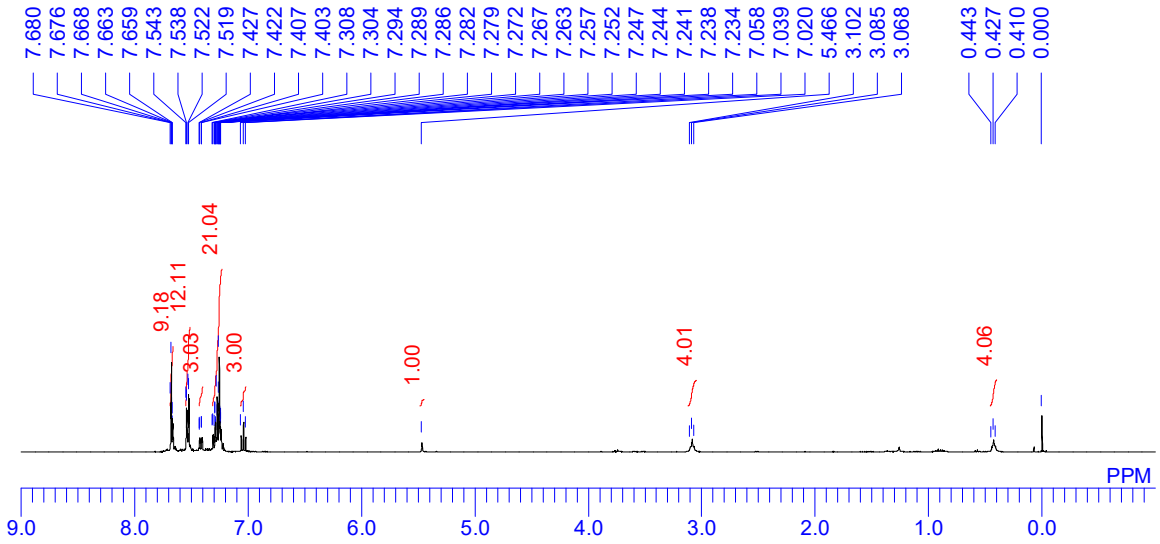
Cage-shaped borate 1kB·thf



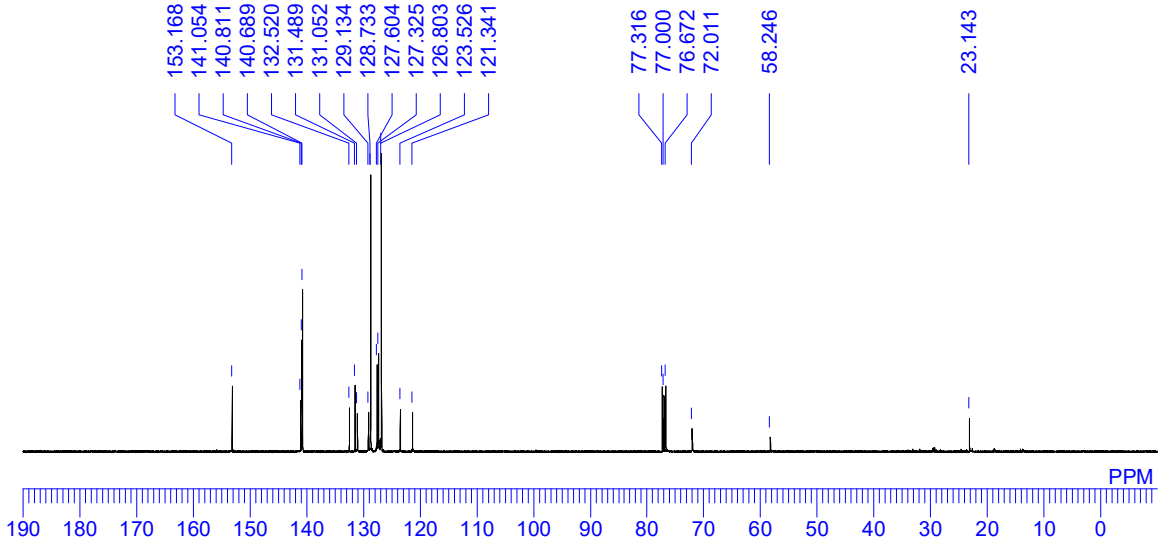
In a nitrogen-filled glove box, to a suspension of **1k**H_3 (528 mg, 0.539 mmol) in THF (4 mL) was added BH_3·THF in THF (0.648 mmol, 1.0 M) at room temperature with stirring for 2 h under release of H_2 gas. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give **1k**B·thf as a colorless solid (570 mg, quant.).

^{1}H NMR (400 MHz, $CDCl_3$) 7.68–7.66 (m, 9H), 7.54–7.52 (m, 12H), 7.41 (dd, J = 7.8, 1.8 Hz, 3H), 7.31–7.23 (m, 12H), 7.04 (t, J = 7.6 Hz, 3H), 5.47 (s, 1H, 7-H), 3.09 (t, J = 6.8 Hz, 4H, 16-H), 0.43 (t, J = 6.6 Hz, 4H, 17-H); ^{13}C NMR (100 MHz, $CDCl_3$) 153.2 (s), 141.1 (s), 140.8 (s), 140.7 (s), 132.5 (s), 131.5 (s), 131.1 (d), 129.1 (d), 128.7 (d), 127.6 (d), 127.3 (d), 126.8 (d), 123.5 (d), 121.3 (d), 72.0 (t, C-16), 58.2 (d, C-7), 23.1 (t, C-17); ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, BF_3·Et_2O in $CDCl_3$ as an external standard) 5.31.

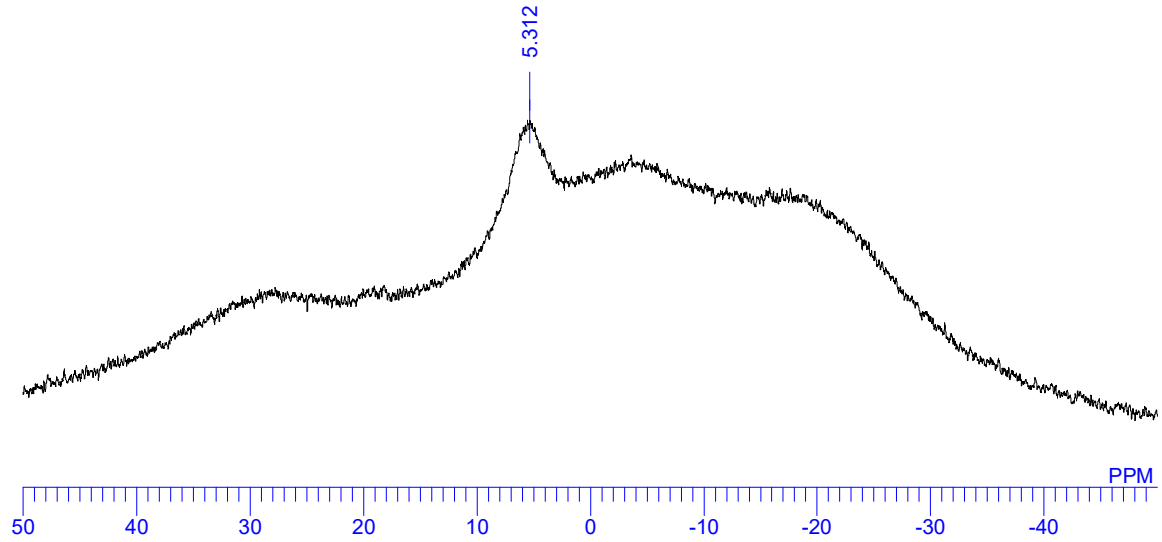
^{1}H NMR: (400 MHz, $CDCl_3$)



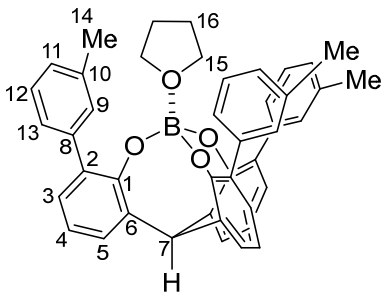
^{13}C NMR: (100 MHz, $CDCl_3$)



$^{11}B\{^{1}H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)

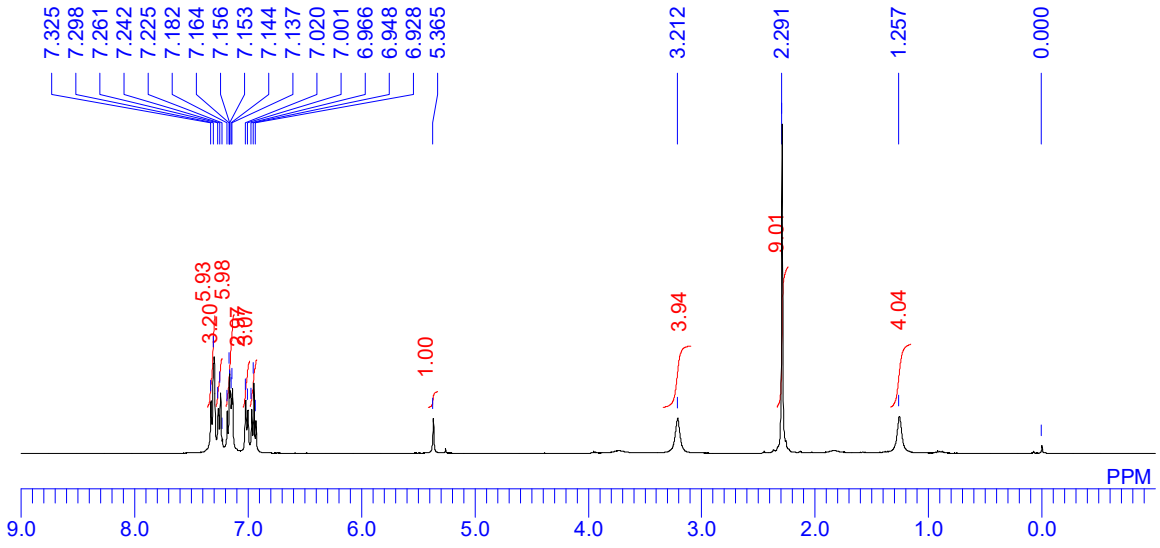


Cage-shaped borate 1lB·thf

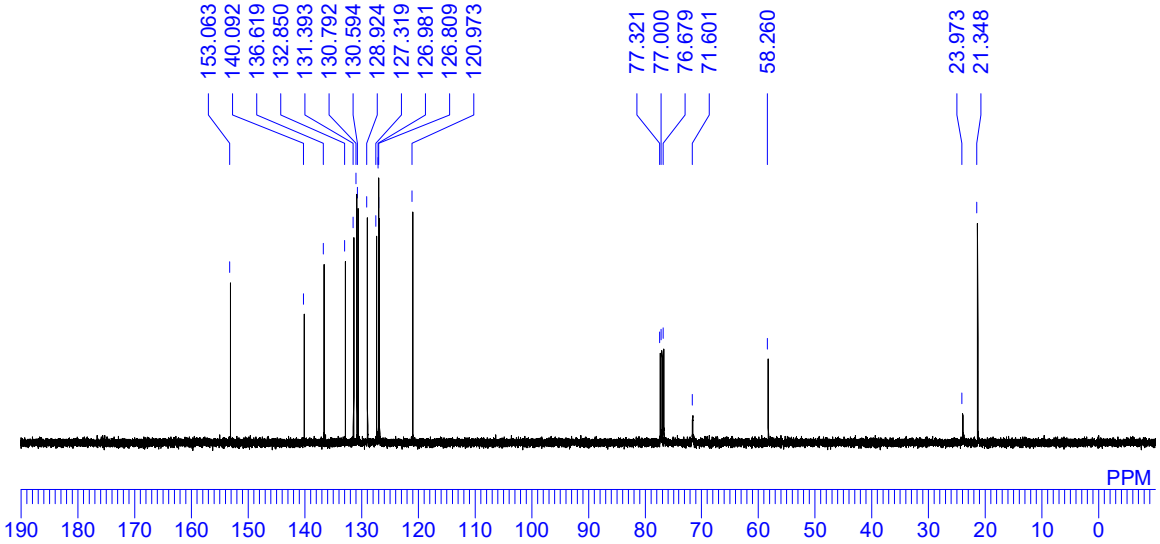


In a nitrogen-filled glove box, to a suspension of **1l**H_3 (347 mg, 0.616 mmol) in dichloromethane (6 mL) was added BH_3·THF in THF (0.677 mmol, 0.9 M) at room temperature with stirring for 2 h under release of H_2 gas. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give **1l**B·thf as a colorless solid (395 mg, quant.).
^{1}H NMR (400 MHz, $CDCl_3$) 7.33–7.30 (m, 6H), 7.25 (d, J = 7.6 Hz, 3H), 7.18–7.14 (m, 6H), 7.01 (d, J = 7.6 Hz, 3H), 6.95 (t, J = 7.6 Hz, 3H), 5.37 (s, 1H, 7-H), 3.21 (brs, 4H, 15-H), 2.29 (s, 9H, 14-H), 1.26 (brs, 4H, 16-H); ^{13}C NMR (100 MHz, $CDCl_3$) 153.1 (s), 140.1 (s), 136.6 (s), 132.9 (s), 131.4 (s), 130.8 (d), 130.6 (d), 128.9 (d), 127.3 (d), 127.0 (d), 126.8 (d), 121.0 (d), 71.6 (t, C-15), 58.3 (d, C-7), 24.0 (t, C-16), 21.3 (q, C-14); ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, BF_3·Et_2O in $CDCl_3$ as an external standard) 5.23.

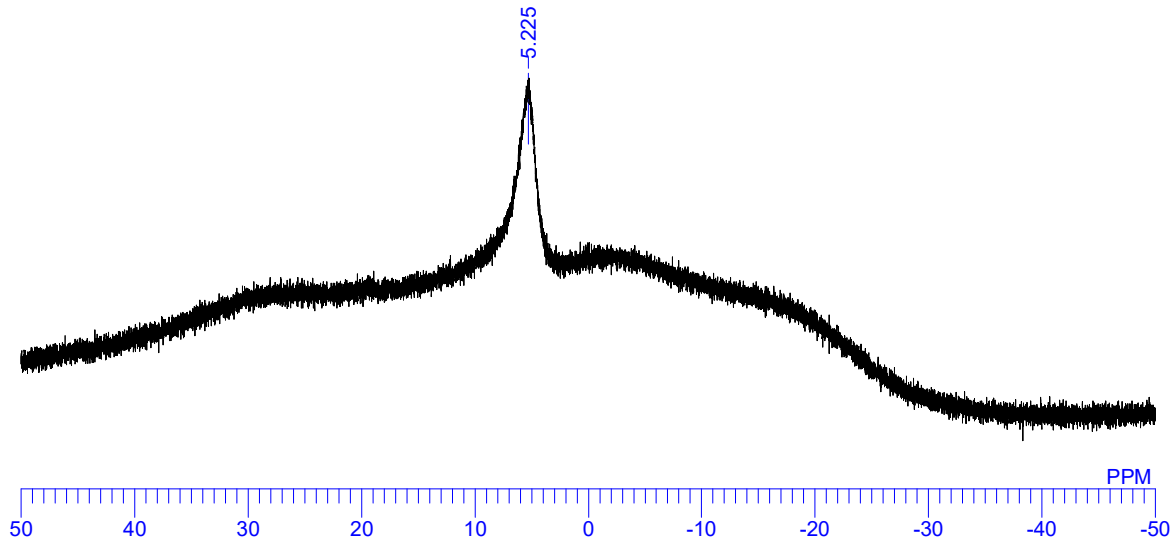
^{1}H NMR: (400 MHz, $CDCl_3$)



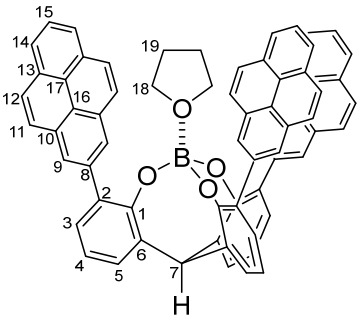
^{13}C NMR: (100 MHz, $CDCl_3$)



$^{11}B\{^{1}H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)

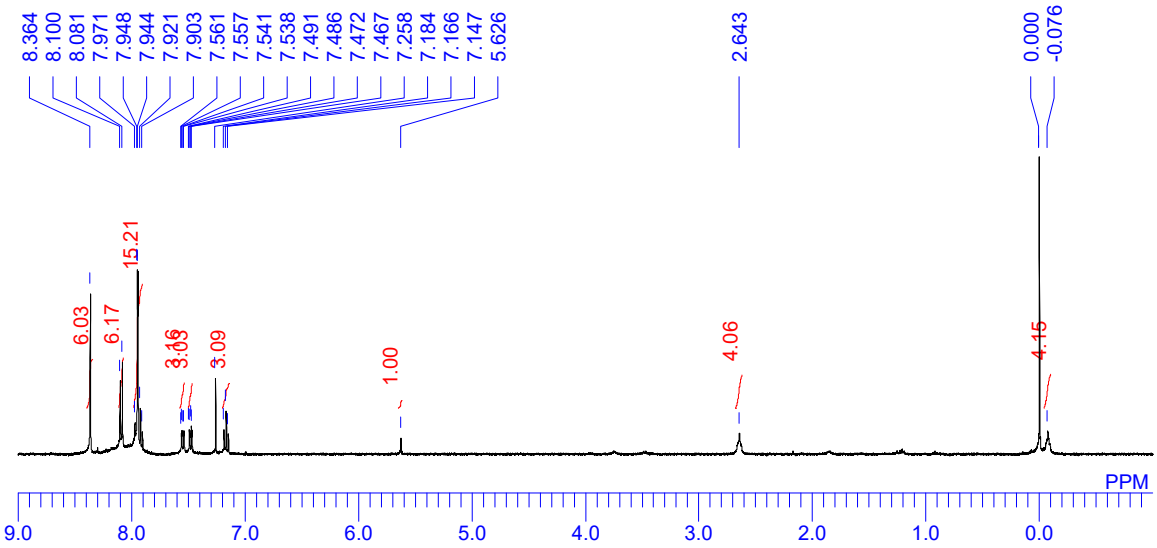


Cage-shaped borate 1oB·thf

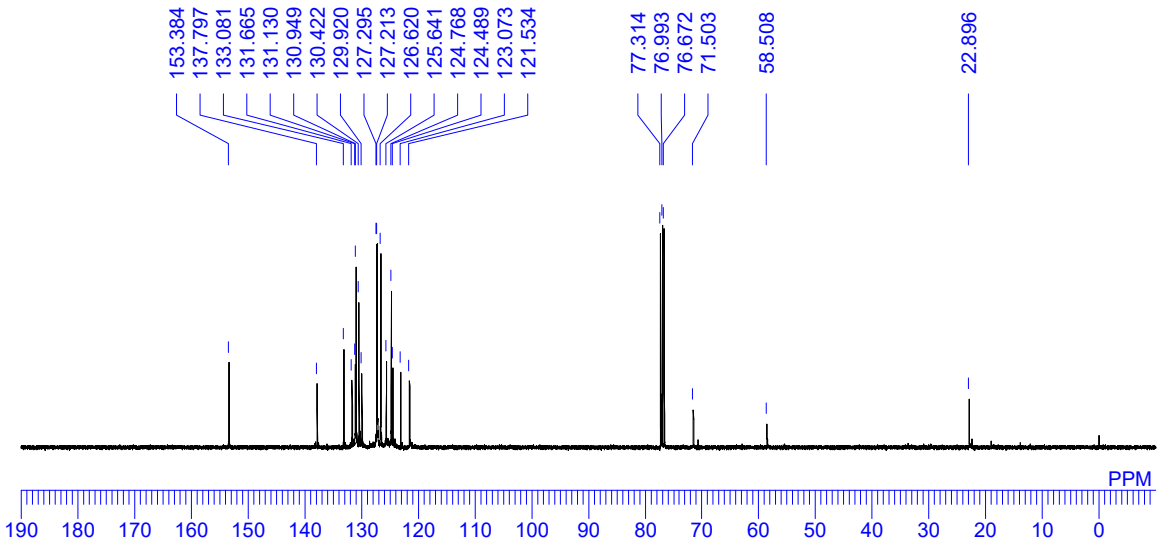


In a nitrogen-filled glove box, to a suspension of **1o**H_3 (123 mg, 0.138 mmol) in chloroform (5 mL) was added BH_3·THF in THF (0.138 mmol, 0.9 M) at room temperature with stirring for 1 h under release of H_2 gas. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give **1o**B·thf as a white solid. (134 mg, quant.).
^{1}H NMR (400 MHz, $CDCl_3$) 8.36 (s, 6H, 9-H), 8.09 (d, J = 7.6 Hz, 6H), 7.97–7.90 (m, 15H), 7.55 (dd, J = 7.8, 1.4 Hz, 3H), 7.48 (dd, J = 7.6, 2.0 Hz, 3H), 7.17 (t, J = 7.4 Hz, 3H, 4-H), 5.63 (s, 1H, 7-H), 2.64 (brs, 4H, 18-H), -0.08 (brs, 4H, 19-H); ^{13}C NMR (100 MHz, $CDCl_3$) 153.4 (s), 137.8 (s), 133.1 (s), 131.7 (s), 131.1 (d), 130.9 (s), 130.4 (s), 129.9 (d), 127.3 (d), 127.2 (d), 126.6 (d), 125.6 (d), 124.8 (d), 124.5 (s), 123.1 (s), 121.5 (d), 71.5 (t, C-18), 58.5 (d, C-7), 22.9 (t, C-19); ^{11}B{^{1}H} NMR: (127 MHz, $CDCl_3$, BF_3·Et_2O in $CDCl_3$ as an external standard) 5.22.

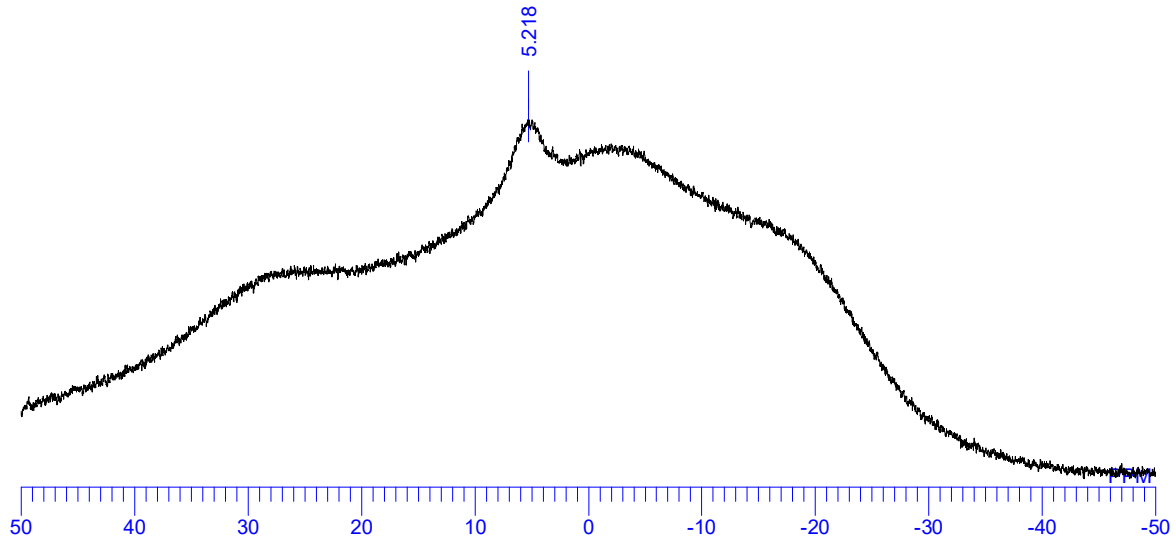
^{1}H NMR: (400 MHz, $CDCl_3$)



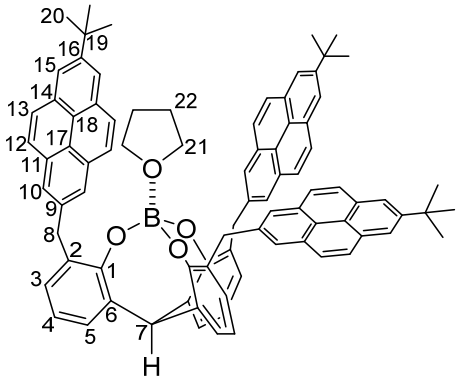
^{13}C NMR: (100 MHz, $CDCl_3$)



$^{11}B\{^1H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)



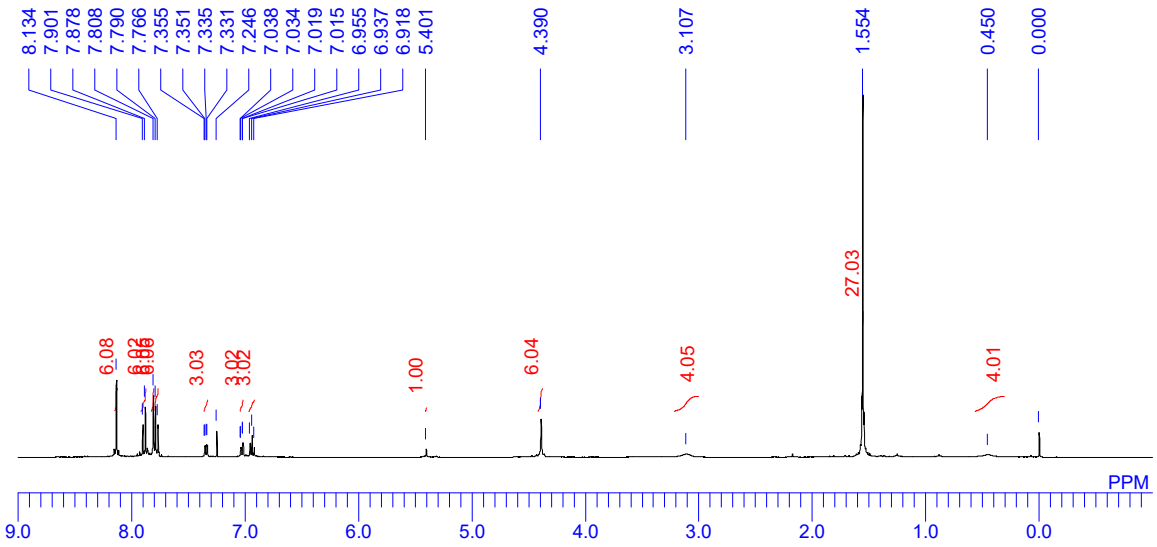
Cage-shaped borate 1rB·thf



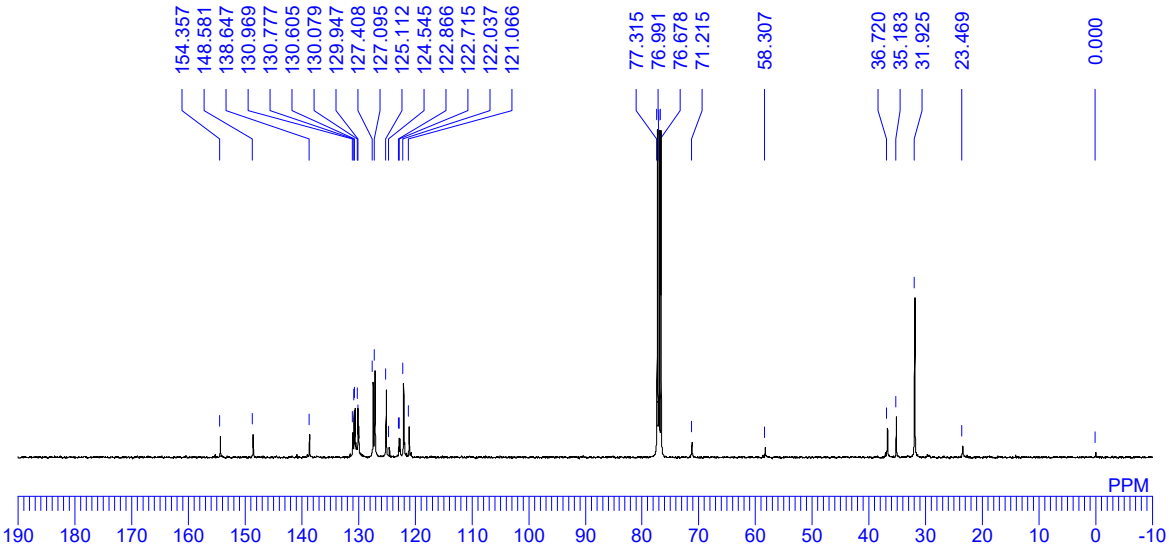
In a nitrogen-filled glove box, to a suspension of **1r**H_3 (510 mg, 0.445 mmol) in THF (5 mL) was added BH_3·THF in THF (0.0374 mmol, 0.9 M) at room temperature with stirring for 1 h under release of H_2 gas. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give **1r**B·thf as a colorless solid (526 mg, quant.).

^{1}H NMR (400 MHz, $CDCl_3$) 8.13 (s, 6H), 7.89 (d, J = 9.2 Hz, 6H), 7.81 (s, 6H), 7.78 (d, J = 9.6 Hz, 6H), 7.34 (dd, J = 8.0, 1.6 Hz, 3H), 7.03 (dd, J = 7.6, 1.6 Hz, 3H), 6.94 (t, J = 7.4 Hz, 3H, 4-H), 5.40 (s, 1H, 7-H), 4.39 (s, 6H. 8-H), 3.11 (brs, 4H, 21-H), 1.55 (s, 27H, 20-H), 0.45 (brs, 4H, 22-H); ^{13}C NMR (100 MHz, $CDCl_3$) 154.4 (s), 148.6 (s), 138.6 (s), 131.0 (s), 130.8 (s), 130.6 (s), 130.1 (d), 129.9 (d), 127.4 (d), 127.1 (d), 125.1 (d), 124.5 (s), 122.9 (s), 122.7 (s), 122.0 (d), 121.1 (d), 71.2 (t, C-21), 58.3 (d, C-7), 36.7 (t, C-8), 35.2 (s, C-8), 31.9 (q, C-20), 23.5 (t, C-22); ^{11}B{^{1}H} NMR: (127 MHz, $CDCl_3$, BF_3·Et_2O in $CDCl_3$ as an external standard) 3.92.

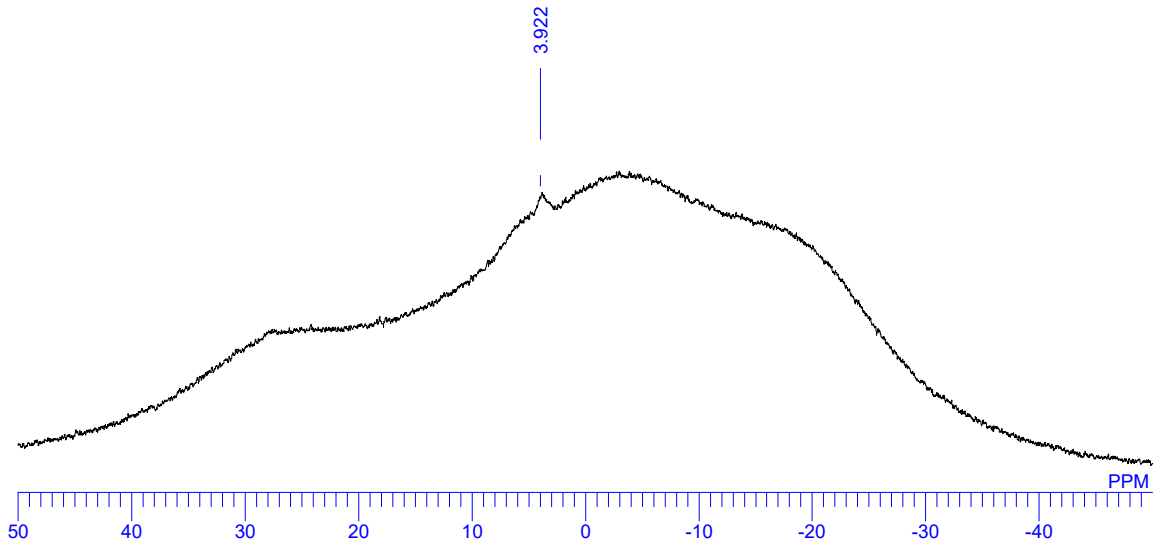
^{1}H NMR: (400 MHz, $CDCl_3$)



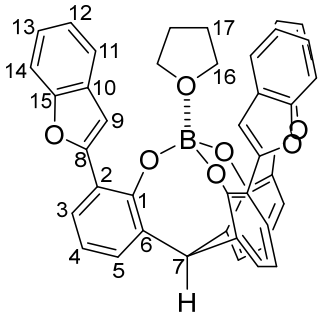
^{13}C NMR: (100 MHz, $CDCl_3$)



$^{11}B\{^1H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)

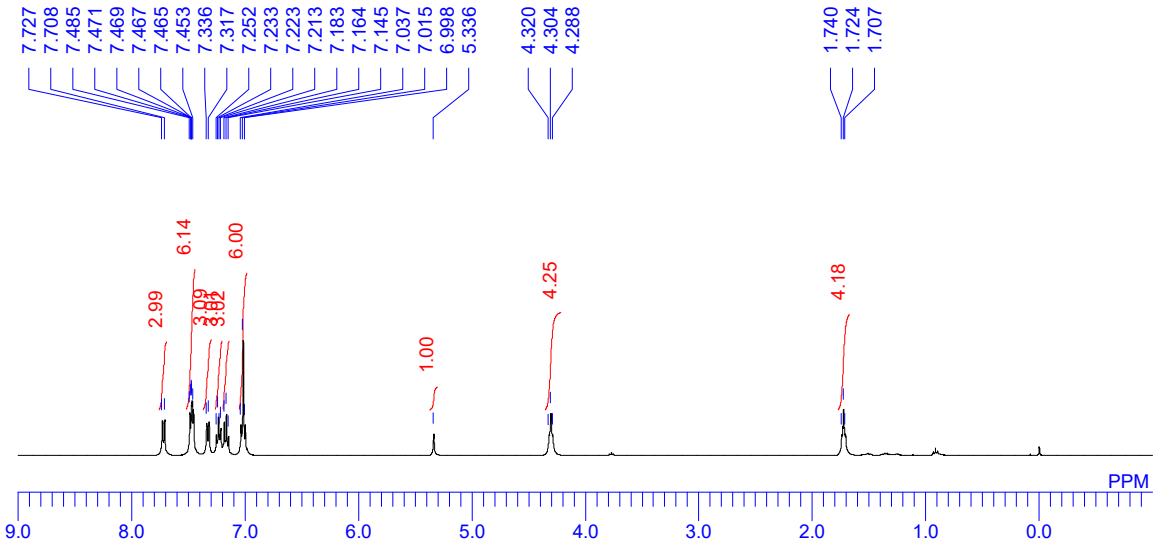


Cage-shaped borate 1AB·thf

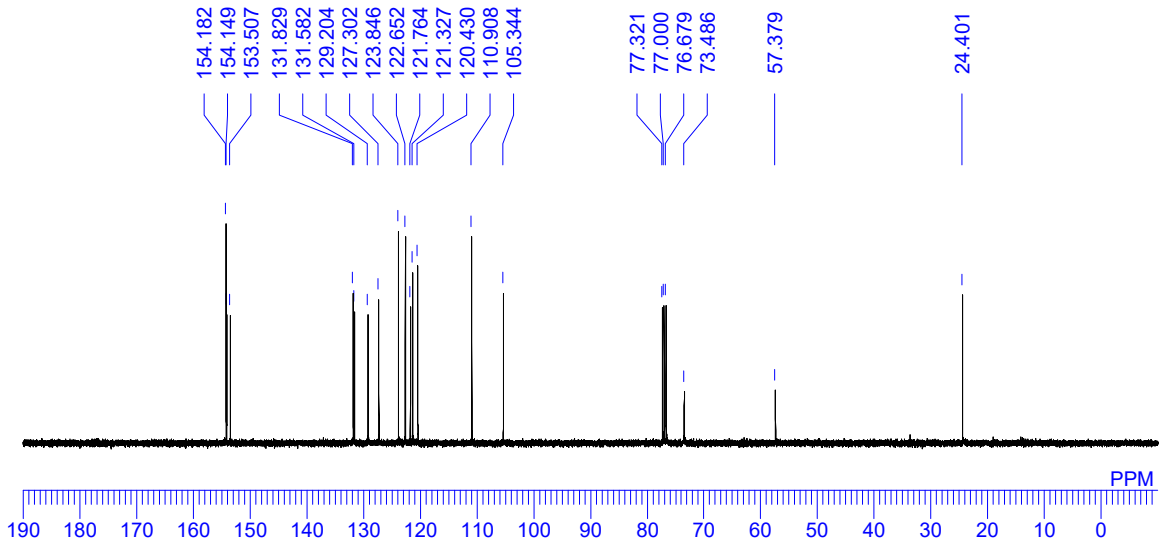


In a nitrogen-filled glove box, to a suspension of **1A**H_3 (95.6 mg, 0.149 mmol) in chloroform (5 mL) was added BH_3·THF in THF (0.179 mmol, 1.0 M) at room temperature with stirring for 1 h under release of H_2 gas. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give **1AB**·thf as a colorless solid (107 mg, quant.).
^{1}H NMR (400 MHz, $CDCl_3$) 7.72 (d, J = 7.6 Hz, 3H), 7.49–7.45 (m, 6H), 7.33 (d, J = 7.6 Hz, 3H), 7.23 (t, J = 7.8 Hz, 3H), 7.16 (t, J = 7.6 Hz, 3H), 7.04–7.00 (m, 6H), 5.34 (s, 1H, 7-H), 4.30 (t, J = 6.4 Hz, 4H, 16-H), 1.72 (t, J = 6.6 Hz, 4H, 17-H); ^{13}C NMR (100 MHz, $CDCl_3$) 154.2 (s), 154.1 (s), 153.5 (s), 131.8 (s), 131.6 (s), 129.2 (s), 127.3 (d), 123.8 (d), 122.7 (d), 121.8 (d), 121.3 (d), 120.4 (d), 110.9 (d), 105.3 (d), 73.5 (t, C-16), 57.4 (d, C-7), 24.4 (t, C-17); ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, BF_3·Et_2O in $CDCl_3$ as an external standard) 5.55.

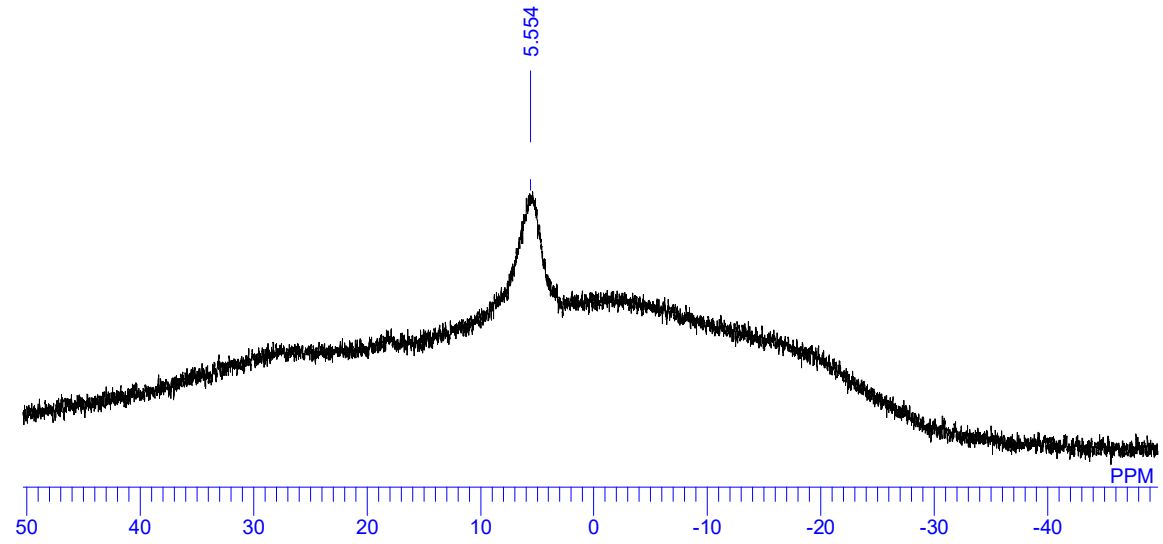
^{1}H NMR: (400 MHz, $CDCl_3$)



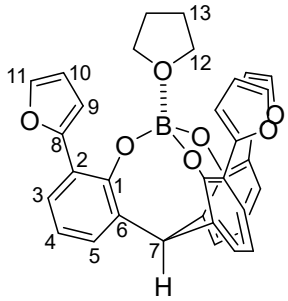
^{13}C NMR: (100 MHz, $CDCl_3$)



$^{11}B\{^{1}H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)



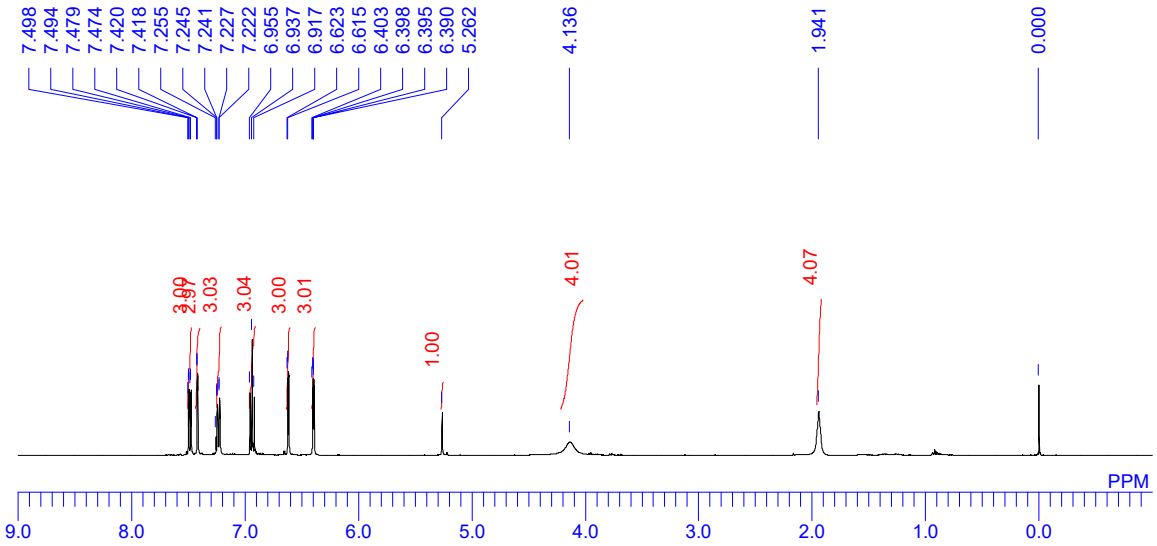
Cage-shaped borate 1BB·thf



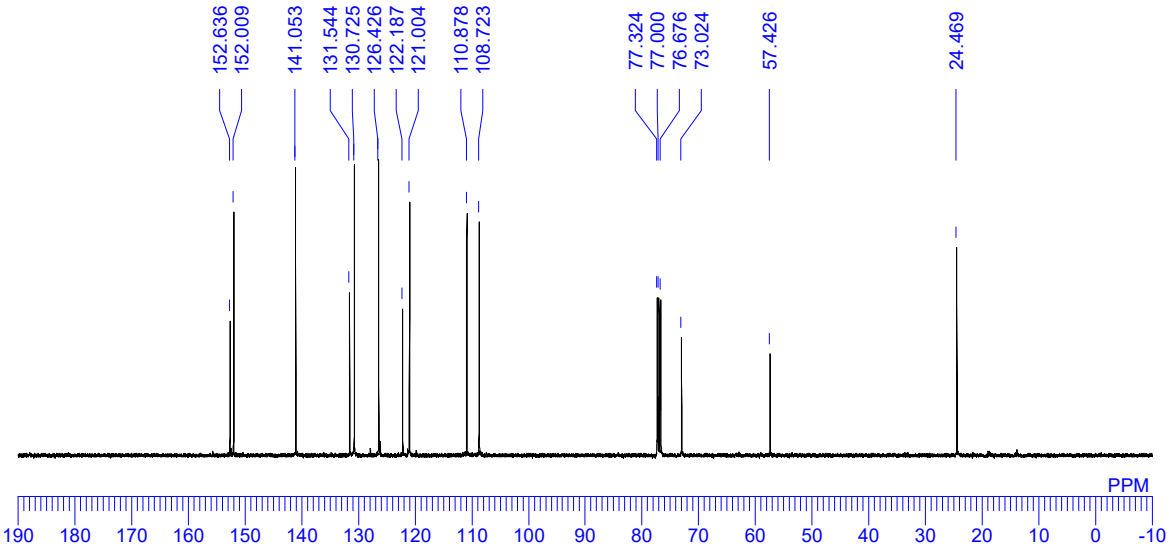
In a nitrogen-filled glove box, to a suspention of **1B**H_3 (173 mg, 0.352 mmol) in chloroform (5 mL) was added BH_3·THF in THF (0.422 mmol, 1.0 M) at room temperature with stirring for 2 h under release of H_2 gas. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give **1B**B·thf as a colorless solid (200 mg, quantatively).

^{1}H NMR (400 MHz, $CDCl_3$) 7.49 (dd, J = 7.8, 1.8 Hz, 3H, 3-H), 7.42 (d, J = 1.2 Hz, 3H, 11-H), 7.23 (dd, J = 7.8, 1.8 Hz, 3H, 5-H), 6.94 (t, J = 7.6 Hz, 3H, 4-H), 6.62 (d, J = 3.2 Hz, 3H, 9-H), 6.40 (dd, J = 3.2, 2.0 Hz, 3H, 10-H), 5.26 (s, 1H, 7-H), 4.14 (brs, 4H, 12-H), 1.94 (brs, 4H, 13-H); ^{13}C NMR (100 MHz, $CDCl_3$) 152.6 (s, C-1), 152.0 (s, C-8), 141.1 (d, C-11), 131.5 (s, C-6), 130.7 (d, C-5), 126.4 (d, C-3), 122.2 (s, C-2), 121.0 (d, C-4), 110.9 (d, C-10), 108.7 (d, C-9), 73.0 (t, C-12), 57.4 (d, C-7), 24.5 (t, C-13); ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, BF_3·Et_2O in $CDCl_3$ as an external standard) 5.35.

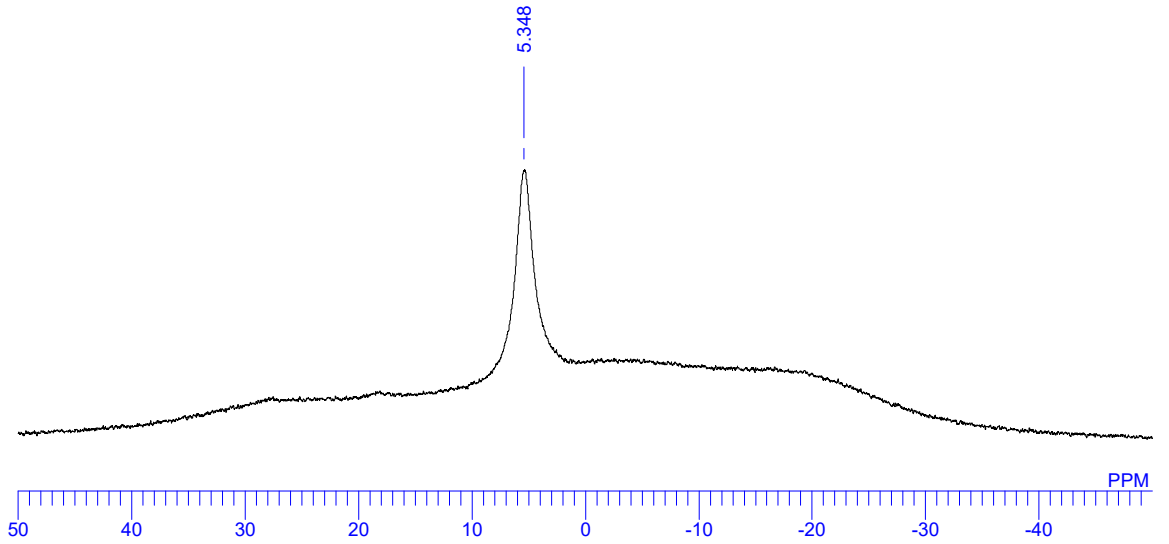
^{1}H NMR: (400 MHz, $CDCl_3$)



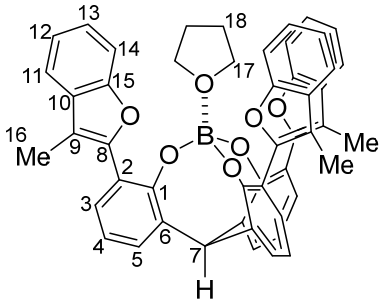
^{13}C NMR: (100 MHz, $CDCl_3$)



$^{11}B\{^{1}H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)

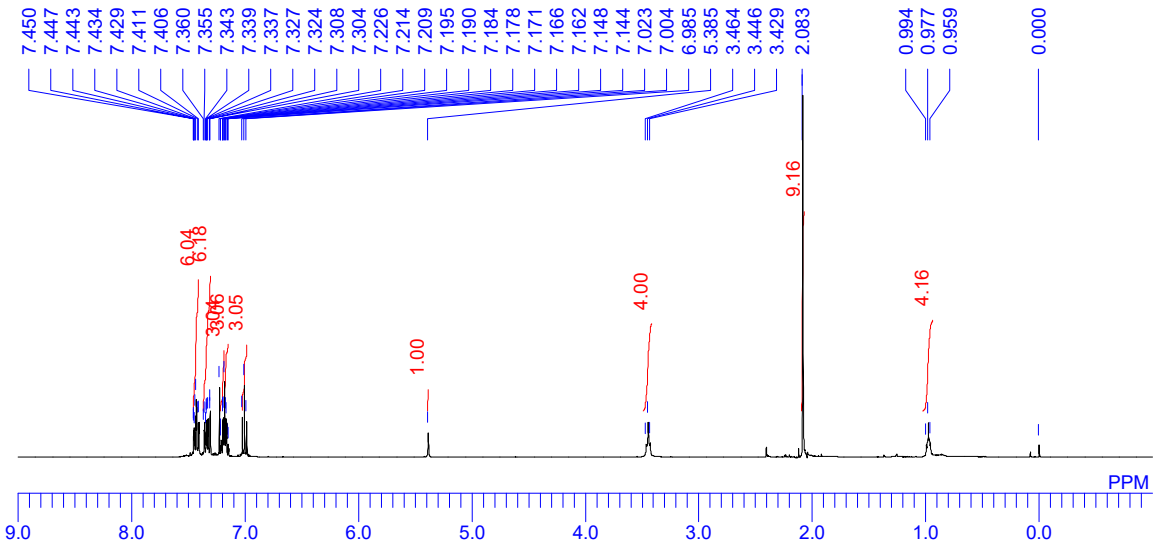


Cage-shaped borate 1A$_I$B·thf

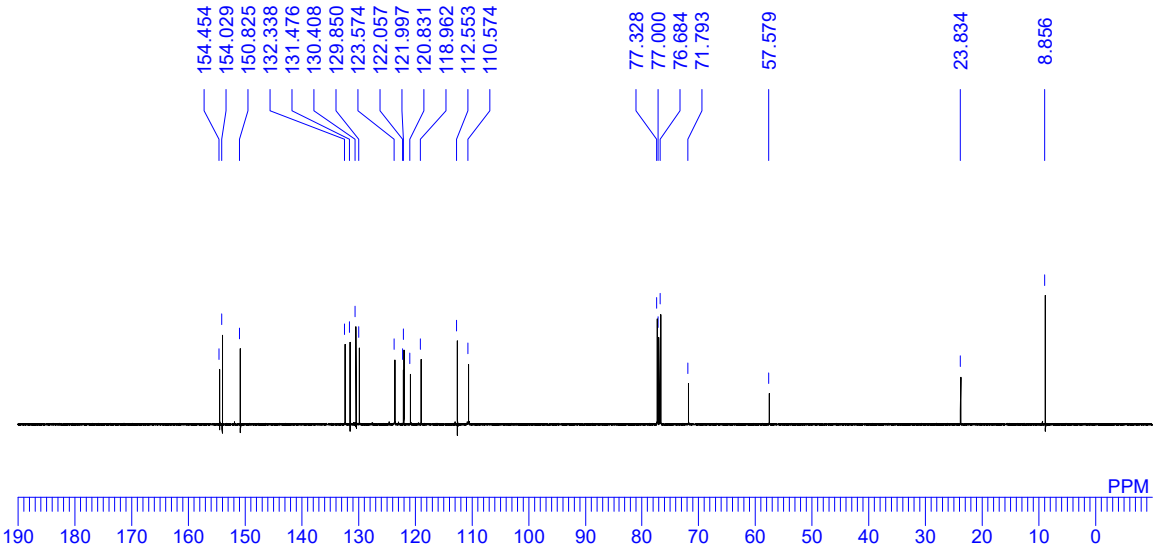


In a nitrogen-filled glove box, to a suspension of **1A$_I$H$_3$** (106 mg, 0.155 mmol) in chloroform (5 mL) was added BH$_3$·THF in THF (0.155 mmol, 0.9 M) at room temperature with stirring for 1 h under release of H$_2$ gas. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give **1A$_I$B**·thf as a colorless solid (118 mg, quant.).
^{1}H NMR (400 MHz, CDCl$_3$) 7.45–7.41 (m, 6H), 7.36–7.30 (m, 6H), 7.19 (td, J = 6.1, 2.0 Hz, 3H), 7.16 (td, J = 5.7, 1.6 Hz, 3H), 7.00 (t, J = 7.6 Hz, 3H), 5.39 (s, 1H, 7-H), 3.45 (t, J = 7.0 Hz, 4H, 17-H), 2.08 (s, 9H, 16-H), 0.98 (t, J = 7.0 Hz, 4H, 18-H); ^{13}C NMR (100 MHz, CDCl$_3$) 154.5 (s), 154.0 (s), 150.8 (s), 132.3 (d), 131.5 (s), 130.4 (d), 129.8 (s), 123.6 (d), 122.1 (s), 122.0 (d), 120.8 (d), 119.0 (d), 112.6 (s), 110.6 (d), 71.8 (t, C-17), 57.6 (d, C-7), 23.8 (t, C-18), 8.9 (d, C-16); ^{11}B{^{1}H} NMR: (127 MHz, CDCl$_3$, BF$_3$·Et$_2$O in CDCl$_3$ as an external standard) 4.78.

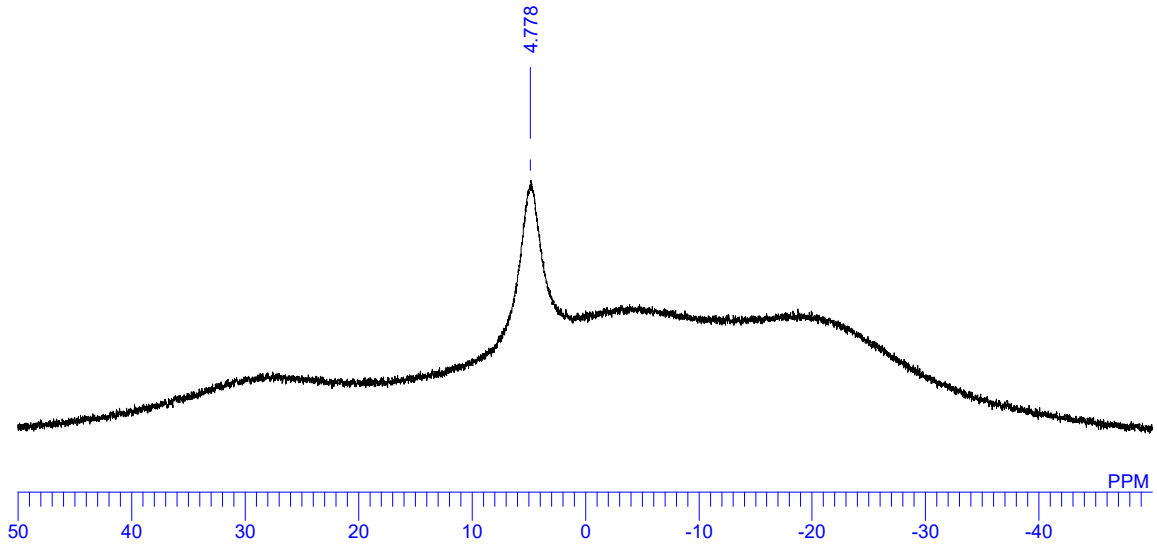
^{1}H NMR: (400 MHz, CDCl$_3$)



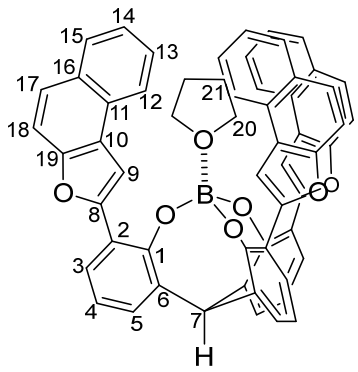
^{13}C NMR: (100 MHz, $CDCl_3$)



$^{11}B\{^1H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)

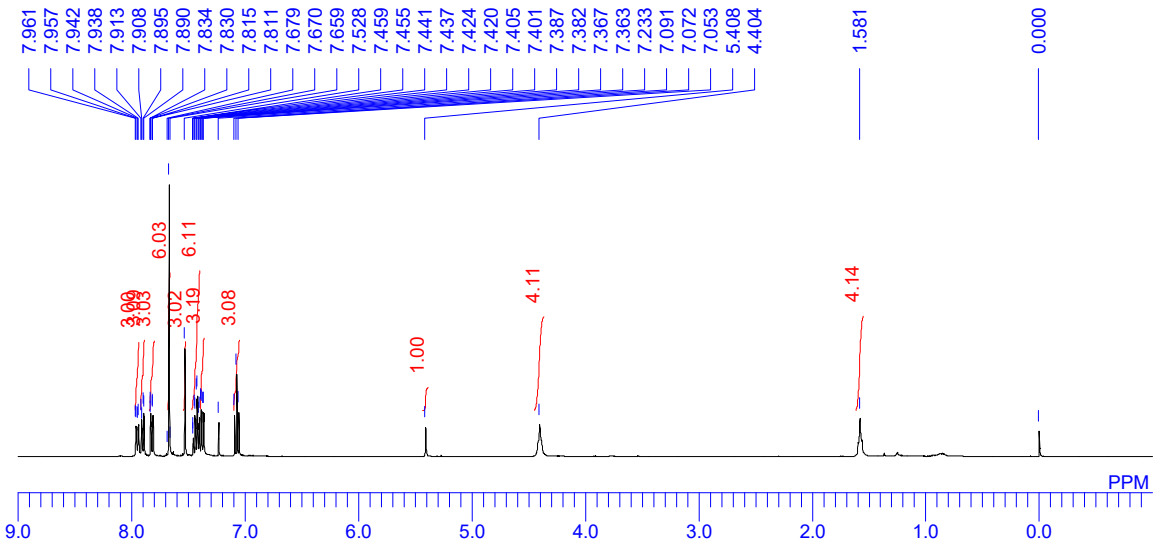


Cage-shaped borate $1A_{II}B$·thf

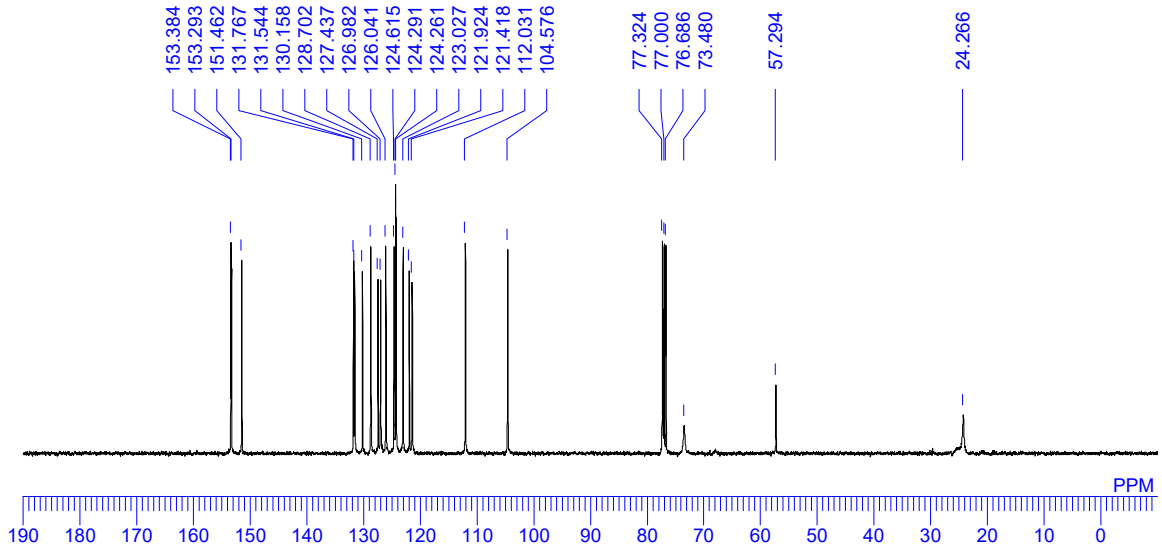


In a nitrogen-filled glove box, to a suspension of $\mathbf{1A_{II}}H_3$ (268 mg, 0.339 mmol) in chloroform (5 mL) was added BH_3·THF in THF (0.339 mmol, 0.9 M) at room temperature with stirring for 2 h under release of H_2 gas. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give $\mathbf{1A_{II}}B$·thf as a colorless solid (295 mg, quant.).
^{1}H NMR (400 MHz, $CDCl_3$) 7.95 (dd, J = 7.6, 1.6 Hz, 3H), 7.90 (dd, J = 7.2, 2.0 Hz, 3H), 7.82 (dd, J = 7.6, 1.6 Hz, 3H), 7.68–7.66 (m, 6H), 7.53 (s, 3H, 9-H), 7.46–7.40 (m, 6H), 7.37 (dd, J = 7.8, 1.8 Hz, 3H), 7.07 (t, J = 7.6 Hz, 3H), 5.41 (s, 1H, 7-H), 4.40 (brs, 4H, 20-H), 1.58 (brs, 4H, 21-H); ^{13}C NMR: (100 MHz, $CDCl_3$) 153.4 (s), 153.3 (s), 151.5 (s), 131.8 (s), 131.5 (d), 130.2 (s), 128.7 (d), 127.4 (s), 127.0 (d), 126.0 (d), 124.6 (d), 124.29 (s), 124.26 (d), 123.0 (d), 121.9 (s), 121.4 (d), 112.0 (d), 104.6 (d), 73.5 (t, C-20), 57.3 (d, C-7), 24.3 (t, C-21); ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, BF_3·Et_2O in $CDCl_3$ as an external standard) 5.43.

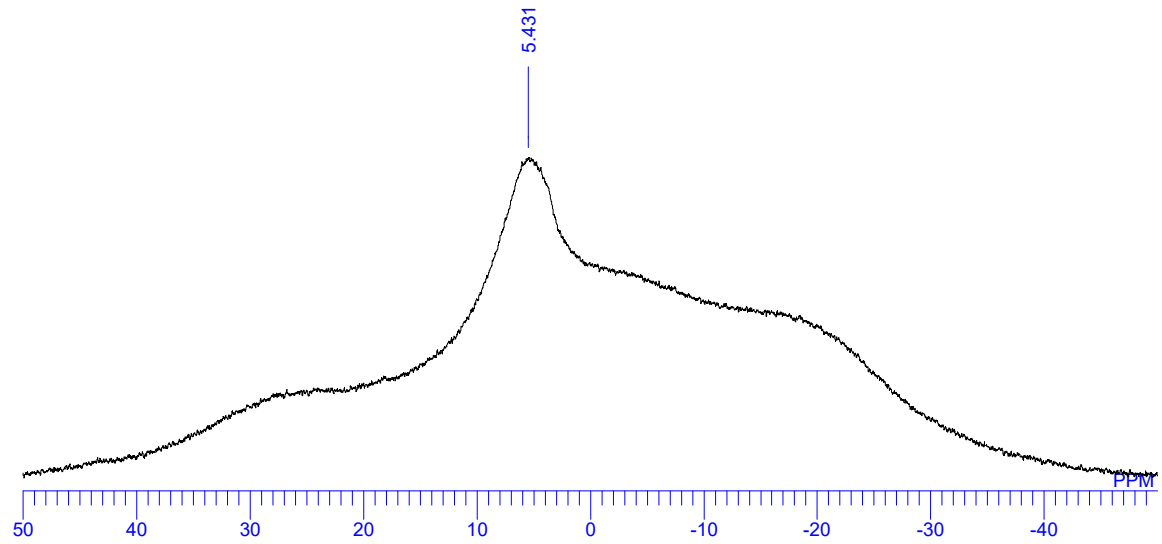
^{1}H NMR: (400 MHz, $CDCl_3$)



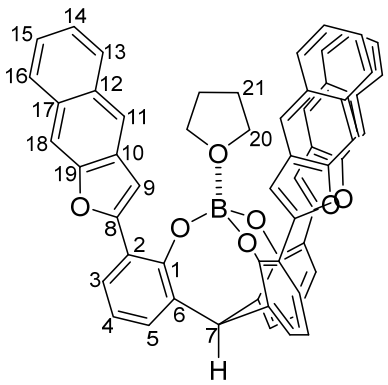
^{13}C NMR: (100 MHz, $CDCl_3$)



$^{11}B\{^1H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)

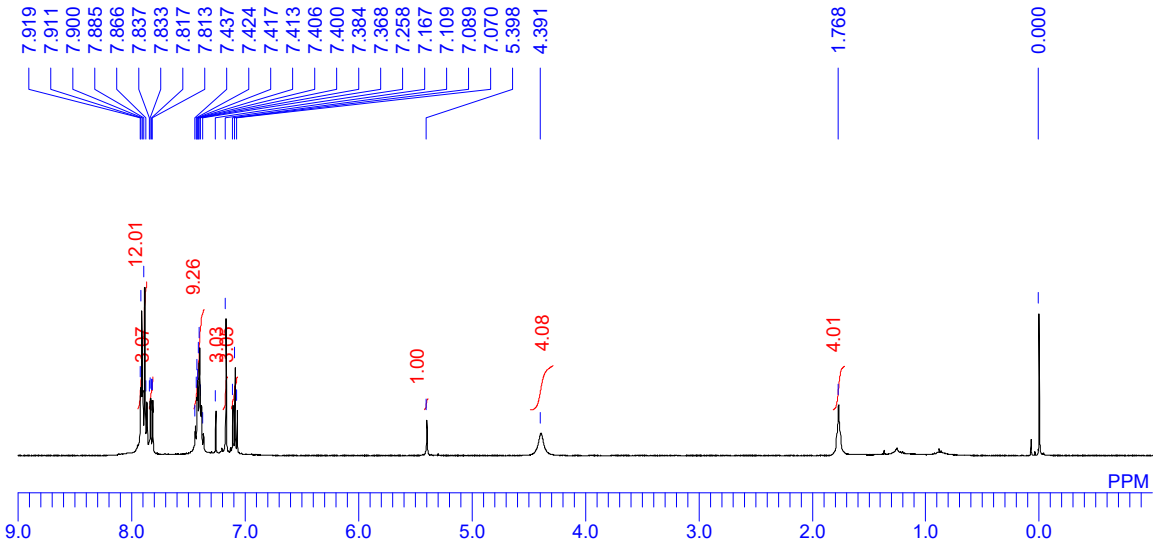


Cage-shaped borate $\mathbf{1A_{III}B}$·thf

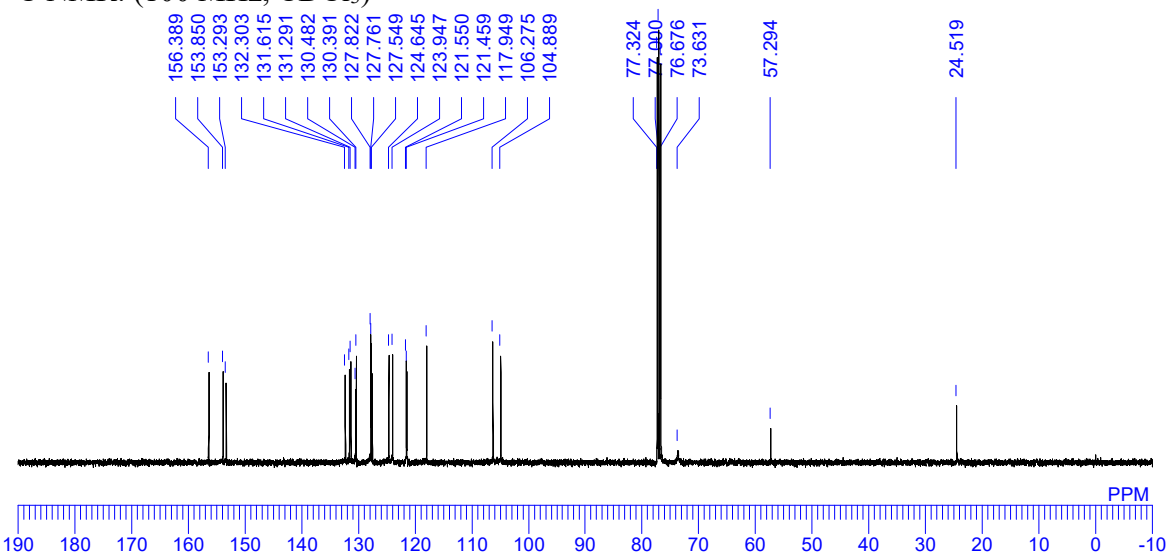


In a nitrogen-filled glove box, to a suspension of $\mathbf{1A_{III}}H_3$ (135 mg, 0.171 mmol) in chloroform (5 mL) was added BH_3·THF in THF (0.205 mmol, 0.9 M) at room temperature with stirring for 2 h under release of H_2 gas. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give $\mathbf{1A_{III}}B$·thf as a colorless solid (148 mg, quant.).
^{1}H NMR (400 MHz, $CDCl_3$) 7.92–7.87 (m, 12H), 7.83 (dd, J = 8.0, 1.6 Hz, 3H), 7.44–7.37 (m, 9H), 7.17 (s, 3H), 7.09 (t, J = 7.8 Hz, 3H), 5.40 (s, 1H, 7-H), 4.39 (brs, 4H, 20-H), 1.77 (brs, 4H, 21-H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.4 (s), 153.9 (s), 153.3 (s), 132.3 (d), 131.6 (s), 131.3 (s), 130.5 (s), 130.4 (s), 127.82 (d), 127.76 (d), 127.5 (d), 124.6 (d), 123.9 (d), 121.6 (s), 121.5 (d), 117.9 (d), 106.3 (d), 104.9 (d), 73.6 (t, C-20), 57.3 (d, C-7), 24.5 (t, C-21); ^{11}B{^{1}H} NMR: (127 MHz, $CDCl_3$, BF_3·Et_2O in $CDCl_3$ as an external standard) 5.53.

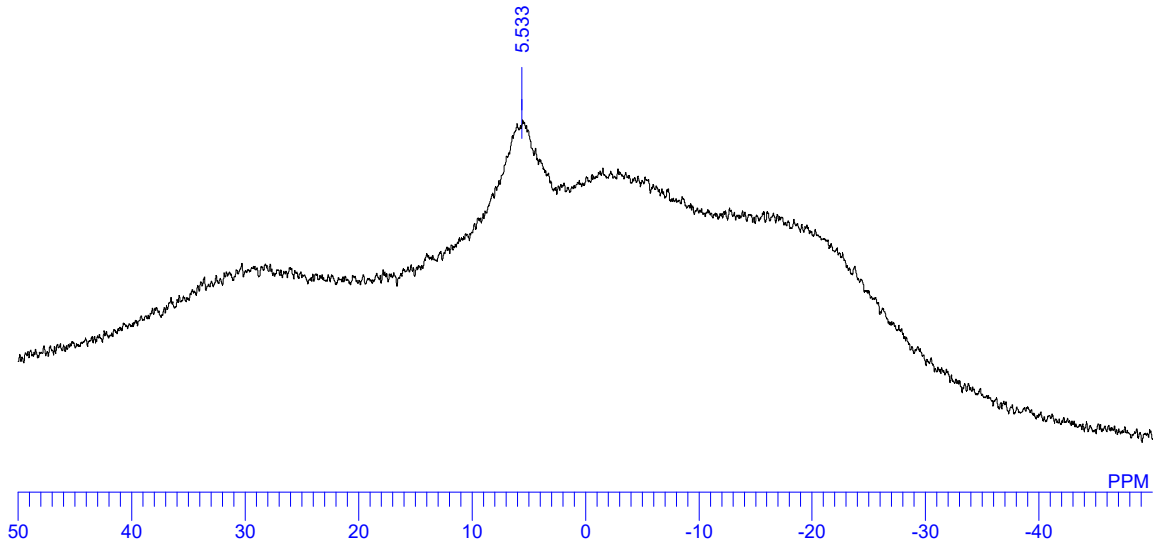
^{1}H NMR: (400 MHz, $CDCl_3$)



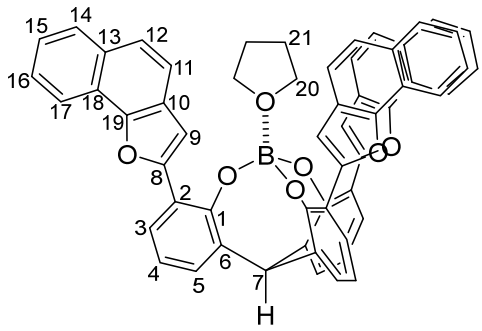
^{13}C NMR: (100 MHz, $CDCl_3$)



$^{11}B\{^1H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)

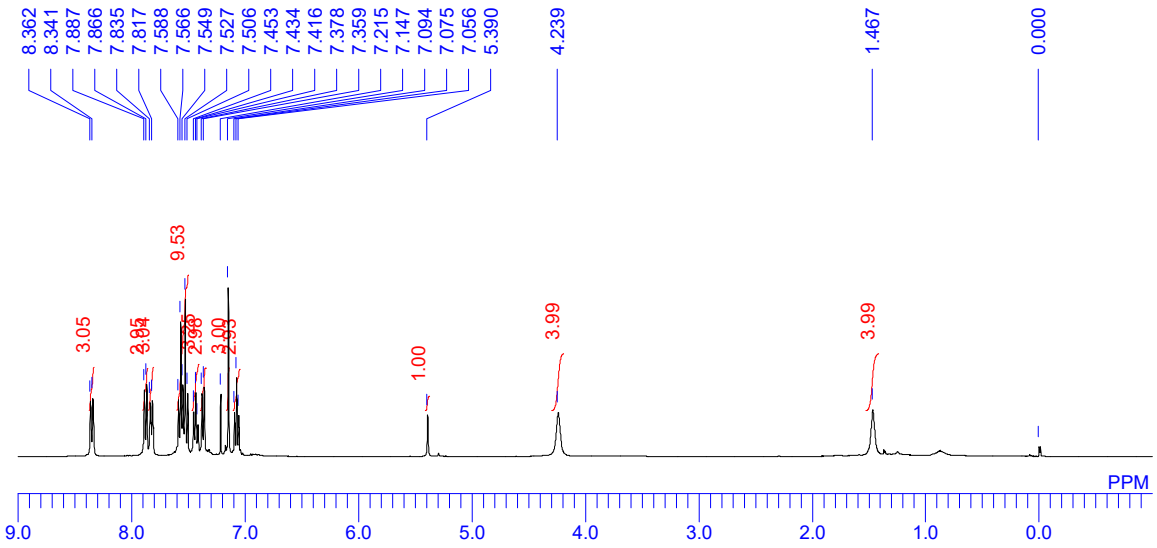


Cage-shaped borate $1A_{IV}B$·thf

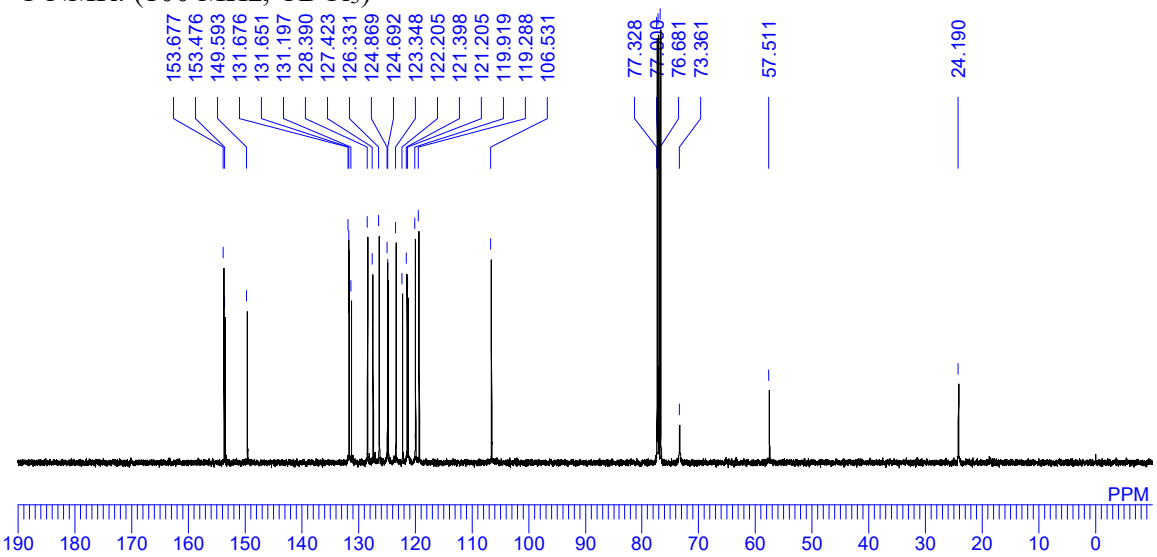


In a nitrogen-filled glove box, to a suspension of $\mathbf{1A_{IV}}H_3$ (110 mg, 0.139 mmol) in THF (5 mL) was added BH_3·THF in THF (0.153 mmol, 0.9 M) at room temperature with stirring for 2 h under release of H_2 gas. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give $\mathbf{1A_{IV}}B$·thf as a colorless solid (121 mg, quant.).
^{1}H NMR (400 MHz, $CDCl_3$) 8.35 (d, J = 8.4 Hz, 3H), 7.88 (d, J = 8.4 Hz, 3H), 7.83 (d, J = 7.2 Hz, 3H), 7.59–7.51 (m, 9H), 7.43 (t, J = 7.4 Hz, 3H), 7.37 (d, J = 7.6 Hz, 3H), 7.15 (s, 3H, 9-H), 7.08 (t, J = 7.6 Hz, 3H), 5.39 (s, 1H, 7-H), 4.24 (brs, 4H, 20-H), 1.47 (brs, 4H, 21-H); ^{13}C NMR (100 MHz, $CDCl_3$) 153.7 (s), 153.5 (s), 149.6 (s), 131.68 (d), 131.65 (s), 131.2 (s), 128.4 (d), 127.4 (d), 126.3 (d), 124.9 (d), 124.7 (s), 123.3 (d), 122.2 (s), 121.4 (d), 121.2 (s), 119.9 (d), 119.3 (d), 106.5 (d), 73.4 (t, C-20), 57.5 (d, C-7), 24.2 (t, C-21); ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, BF_3·Et_2O in $CDCl_3$ as an external standard) 5.86.

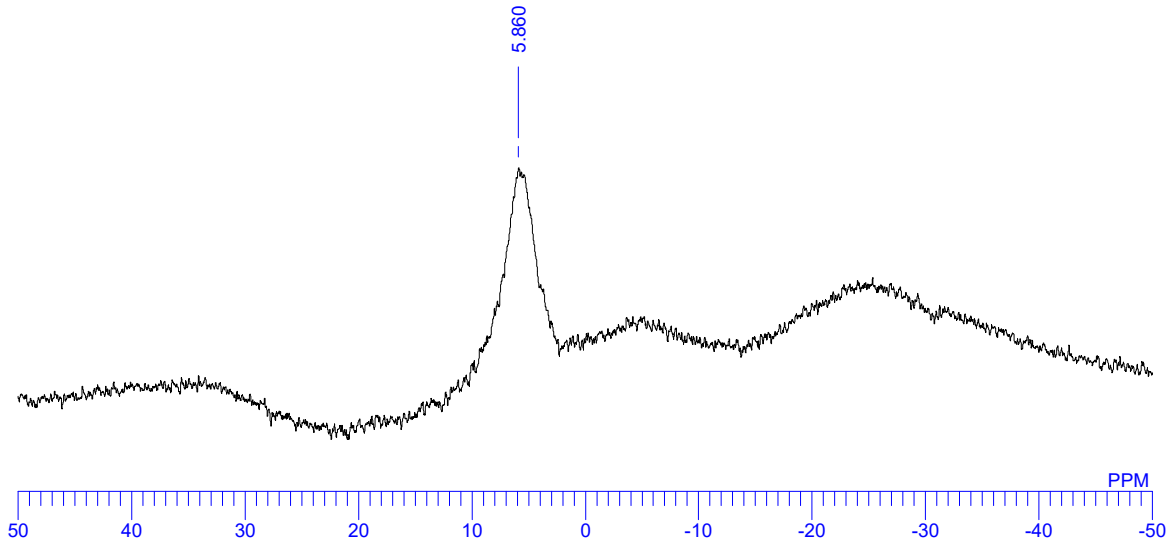
^{1}H NMR: (400 MHz, $CDCl_3$)



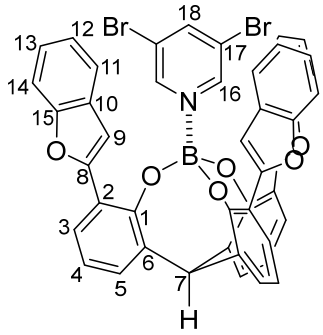
^{13}C NMR: (100 MHz, $CDCl_3$)



$^{11}B\{^1H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)



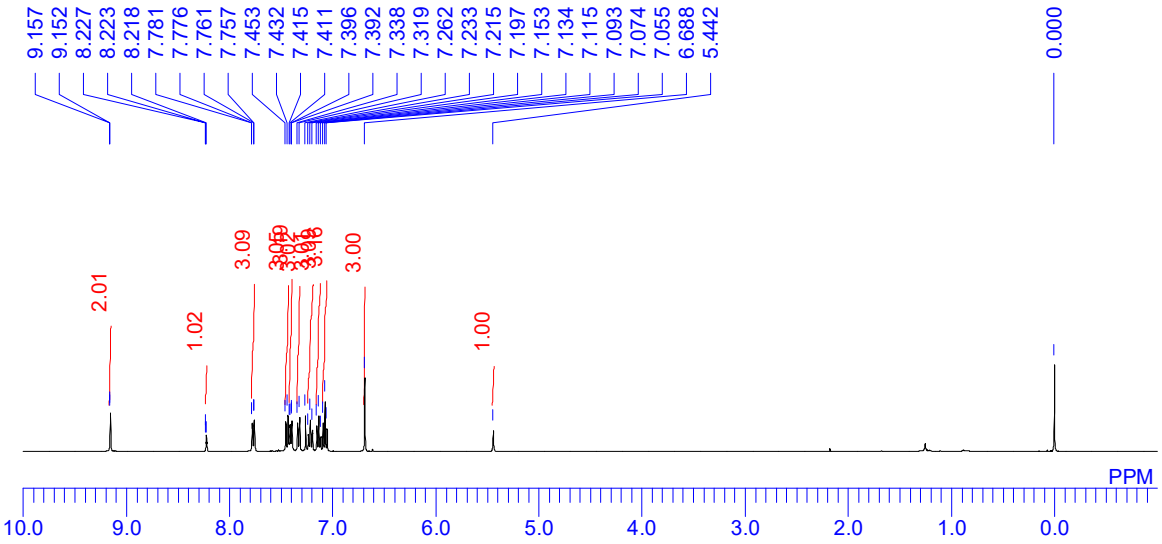
Cage-shaped borate 1AB·dbp



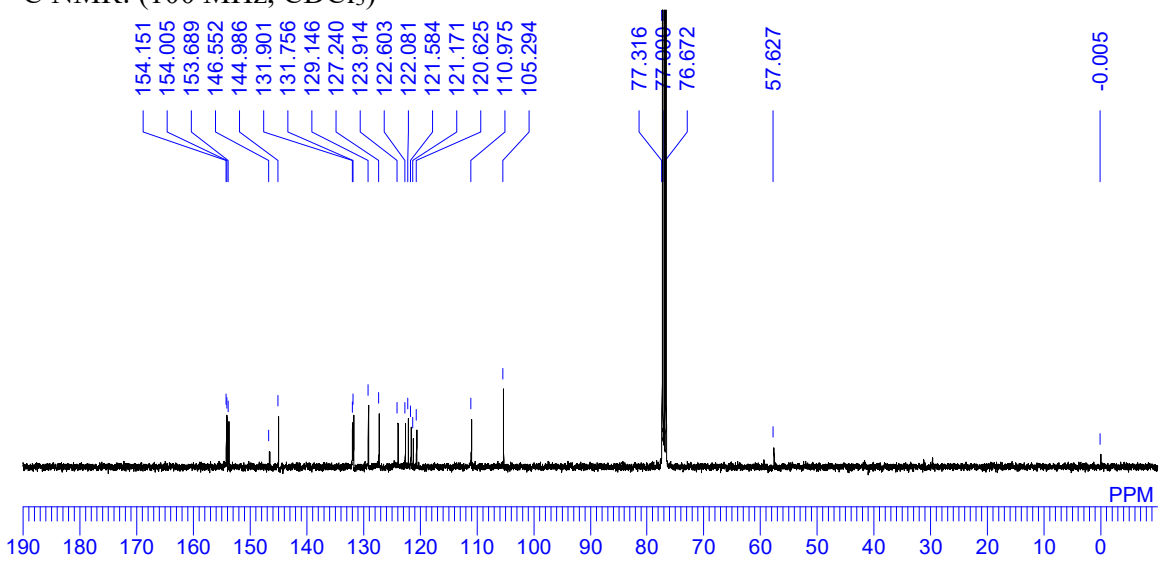
In a nitrogen-filled glove box, 3,5-dibromopyridine (5.9 mg, 0.0249 mmol) was added to the THF solution of **1AB**·thf (18.0 mg, 0.0249 mmol) and stirred 1 h at room temperature. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give **1AB**·dbp as a colorless solid (22.1 mg, quant.).

^{1}H NMR (400 MHz, $CDCl_3$) 9.15 (d, J = 2.0 Hz, 2H, 16-H), 8.22 (t, J = 1.8 Hz, 1H, 18-H), 7.77 (dd, J = 7.8, 1.8 Hz, 3H), 7.44 (d, J = 8.0 Hz, 3H), 7.40 (dd, J = 7.4, 1.4 Hz, 3H), 7.33 (d, J = 7.6 Hz, 3H), 7.22 (t, J = 7.2 Hz, 3H), 7.13 (t, J = 7.6 Hz, 3H), 7.07 (t, J = 7.6 Hz, 3H), 6.69 (s, 3H, 9-H), 5.44 (s, 1H, 7-H); ^{13}C NMR (100 MHz, $CDCl_3$) 154.2 (s), 154.0 (s), 153.7 (s), 146.6 (d), 145.0 (d), 131.9 (d), 131.8 (s), 129.1 (s), 127.2 (d), 123.9 (d), 122.6 (d), 122.1 (s), 121.6 (d), 121.2 (s), 120.6 (d), 111.0 (d), 105.3 (d), 57.6 (d, C-7); ^{11}B{^{1}H} NMR: (127 MHz, $CDCl_3$, BF_3·Et_2O in $CDCl_3$ as an external standard) 5.14.

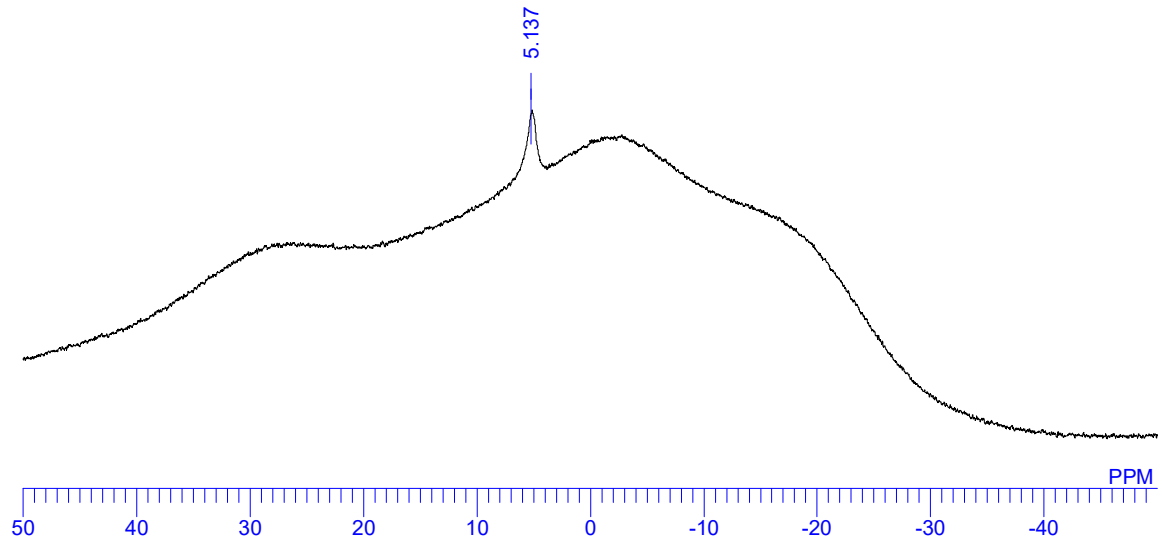
^{1}H NMR: (400 MHz, $CDCl_3$)



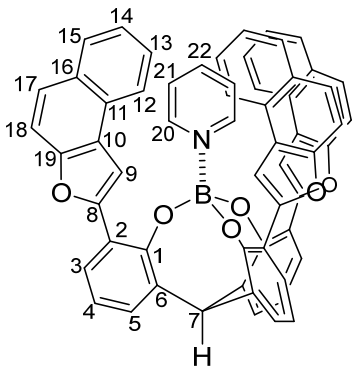
^{13}C NMR: (100 MHz, $CDCl_3$)



$^{11}B\{^1H\}$ NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)



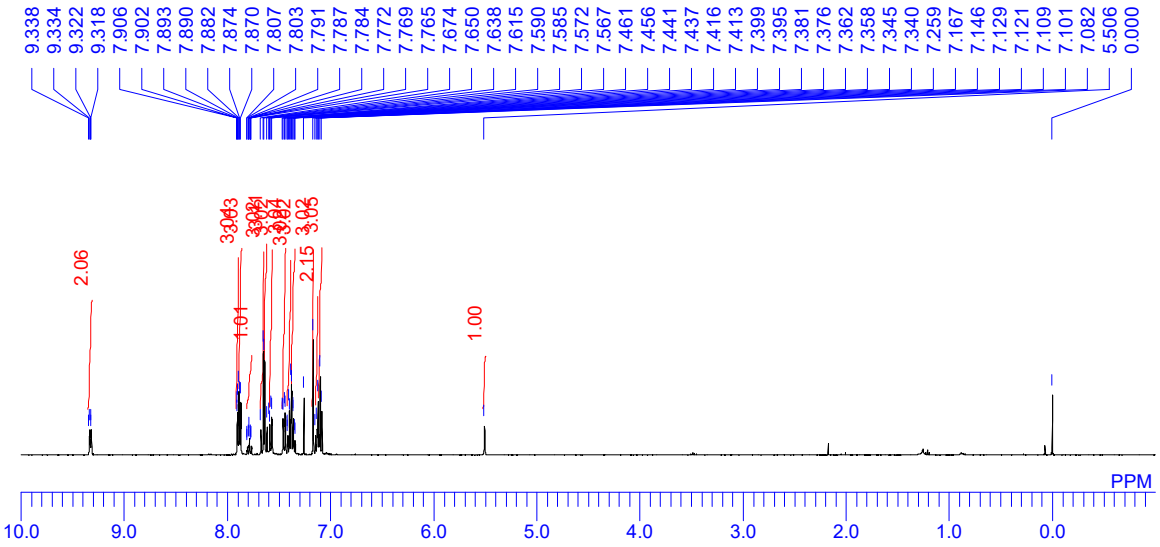
Cage-shaped borate 1A$_{II}$B·py



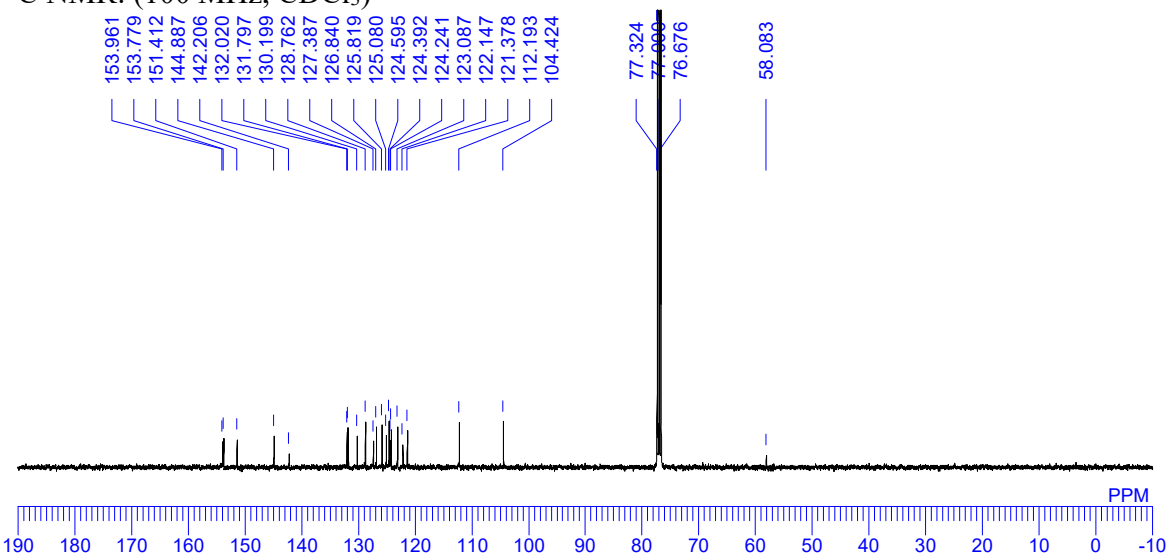
In a nitrogen-filled glove box, pyridine (6.0 mg, 0.0758 mmol) was added to the chloroform solution of **1A$_{II}$B**·thf (60.0 mg, 0.0689 mmol) and stirred 1 h at room temperature. Evaporation of volatiles gave a viscous residue, which was washed by hexane to give **1A$_{II}$B**·py as a colorless solid (60.5 mg, quant.).

^{1}H NMR (400 MHz, $CDCl_3$) 9.33 (dd, J = 6.4, 1.6 Hz, 2H, 20-H), 7.90 (dd, J = 5.0, 1.4 Hz, 3H), 7.88 (dd, J = 5.6, 1.6 Hz, 3H), 7.79 (tt, J = 7.6, 1.5 Hz, 1H, 22-H), 7.66 (d, J = 9.6 Hz, 3H), 7.63 (d, J = 9.2 Hz, 3H), 7.58 (dd, J = 7.2, 2.0 Hz, 3H), 7.45 (dd, J = 7.8, 1.8 Hz, 3H), 7.40 (td, J = 7.0, 1.4 Hz, 3H), 7.36 (td, J = 7.0, 1.8 Hz, 3H), 7.17 (s, 3H, 9-H), 7.13 (t, J = 7.4 Hz, 2H, 21-H), 7.10 (t, J = 7.8 Hz, 3H), 5.51 (s, 1H, 7-H); ^{13}C NMR (100 MHz, $CDCl_3$) 154.0 (s), 153.8 (s), 151.4 (s), 144.9 (d), 142.2 (d), 132.0 (s), 131.8 (d), 130.2 (s), 128.8 (d), 127.4 (s), 126.8 (d), 125.8 (d), 125.1 (d), 124.6 (d), 124.4 (s), 124.2 (d), 123.1 (d), 122.1 (s), 121.4 (d), 112.2 (d), 104.4 (d), 58.1 (d, C-7); ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, BF_3·Et_2O in $CDCl_3$ as an external standard) 5.13.

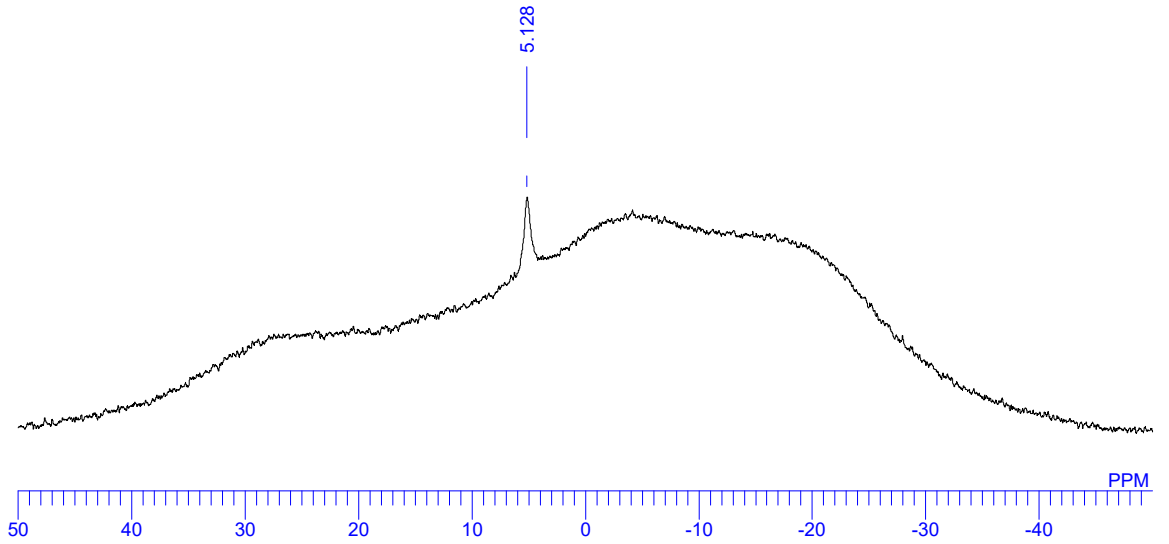
^{1}H NMR: (400 MHz, $CDCl_3$)



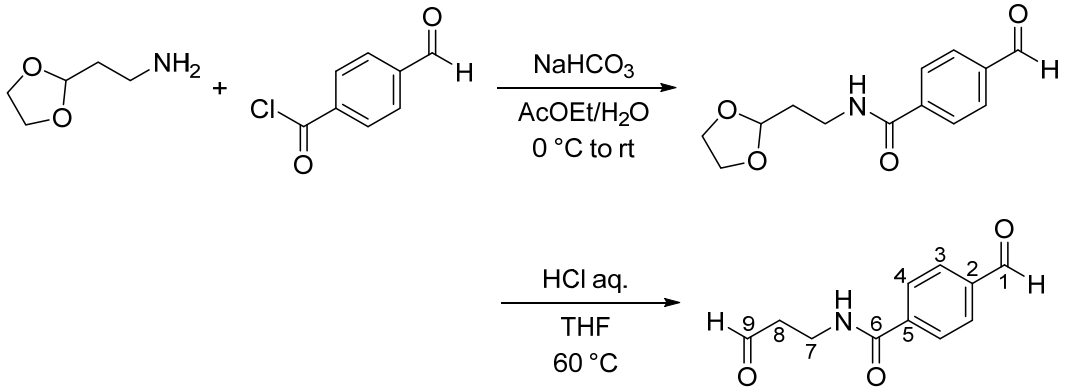
^{13}C NMR: (100 MHz, $CDCl_3$)



^{11}B{^{1}H} NMR: (127 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ in $CDCl_3$ as an external standard)



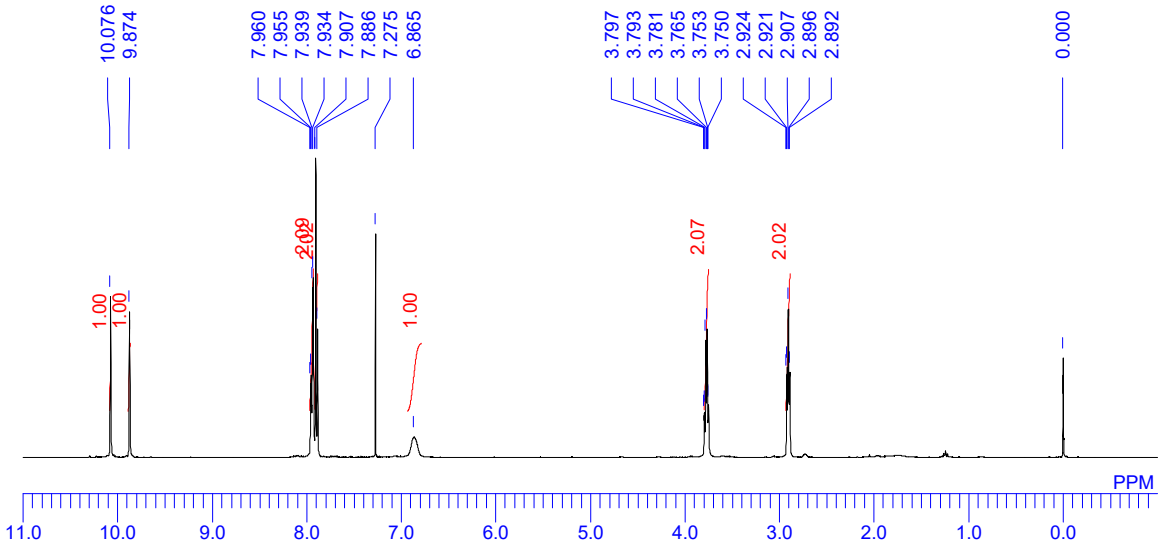
4-Formyl-*N*-(3-oxopropyl)benzamide 6



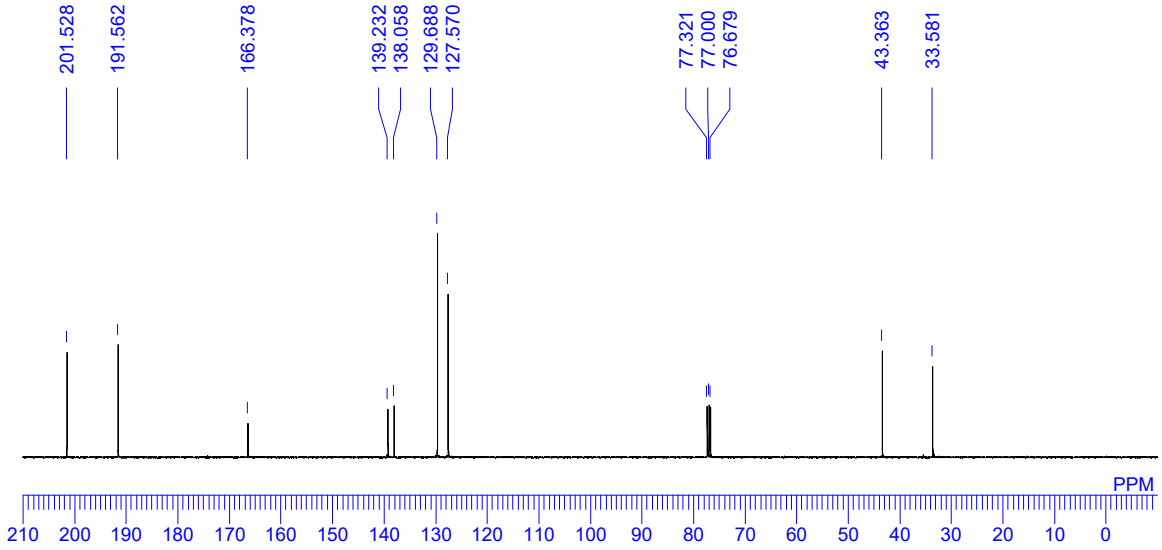
A procedure from the literature[11] was modified as follows: 4-Formylbenzoyl chloride (1.31 g, 7.76 mmol) was dropwisely added to a solution of 2-(2-aminoethyl)-1,3-dioxolane (1.00 g, 8.54 mmol), ethyl acetate (20 mL), H_2O (20 mL) and $NaHCO_3$ (2.00 g, 23.81 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 2 h, then extracted with ethyl acetate (3×20 mL). The reaction mixture was extracted with ethyl acetate (3×20 mL) and then washed with brine (3×20 mL). The obtained organic layer was dried over Na_2SO_4 and the solvent was removed in vacuum to provide the crude product which was used in the next step without further purification.
The crude product was dissolved in THF (20 mL) and 1 M HCl aq. (15 mL) was added to the solution. The mixture was heated to 60 ºC for 2 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (3×20 mL) and then washed with brine (3×20 mL). The obtained organic layer was dried over Na_2SO_4 and the solvent was removed in vacuum. The obtained residue was purified by column chromatography (ethyl acetate/methanol = 95:5) on silica gel to give **6** as a colorless oil (351 mg, 22%).

IR ν = 3585 (w), 3275 (m), 3069 (w), 2938 (w), 2848 (m), 2741 (w), 1704 (s), 1651 (m), 1541 (s), 1388 (m), 1319 (m), 1209 (m), 1103 (m), 1014 (w), 850 (m), 759 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 10.08 (s, 1H, 1-H), 9.87 (s, 1H, 9-H), 7.95 (dd, J = 8.4, 2.0 Hz, 2H, 4-H), 7.90 (d, J = 8.4 Hz, 2H, 3-H), 6.87 (brs, 1H, NH), 3.80–3.75 (m, 2H, 7-H), 2.91 (td, J = 5.7, 1.6 Hz, 2H, 8-H); ^{13}C NMR (100 MHz, $CDCl_3$) 201.5 (d, C-9), 191.6 (d, C-1), 166.4 (s, C-6), 139.2 (s, C-5), 138.1 (s, C-2), 129.7 (d, C-3), 127.6 (d, C-4), 43.4 (t, C-8), 33.6 (t, C-7); HRMS (MALDI-TOF MS) Calculated ($C_{11}H_{11}NO_3Na$): 228.0631 ($[M+Na]^+$), Found: 228.0634

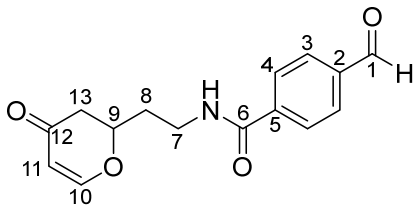
^{1}H NMR: ($CDCl_3$, 400 MHz)



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

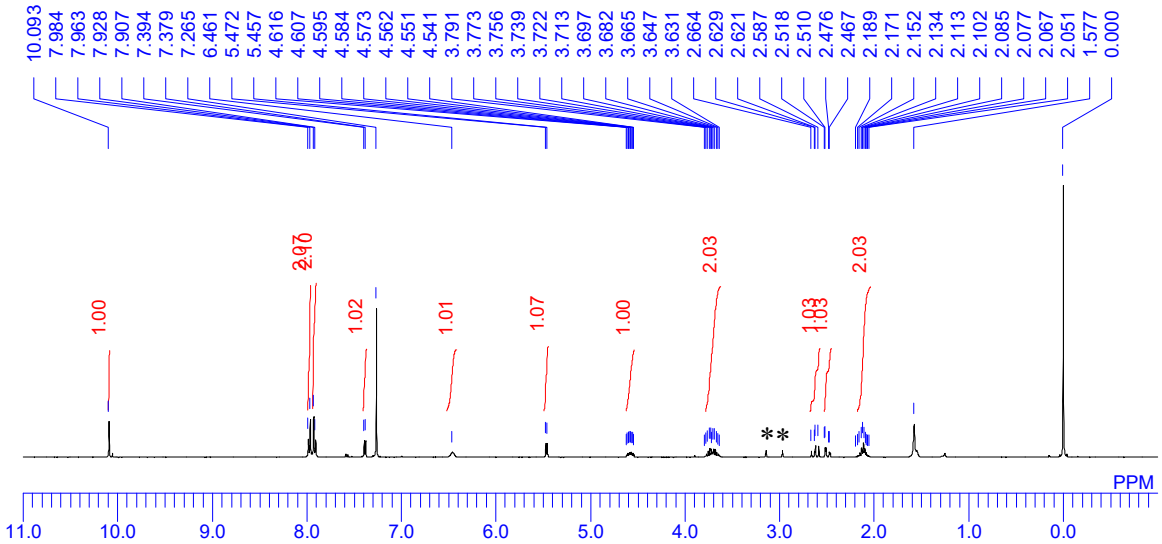


4-Formyl-*N*-(2-(4-oxo-3,4-dihydro-2*H*-pyran-2-yl)ethyl)benzamide 7a



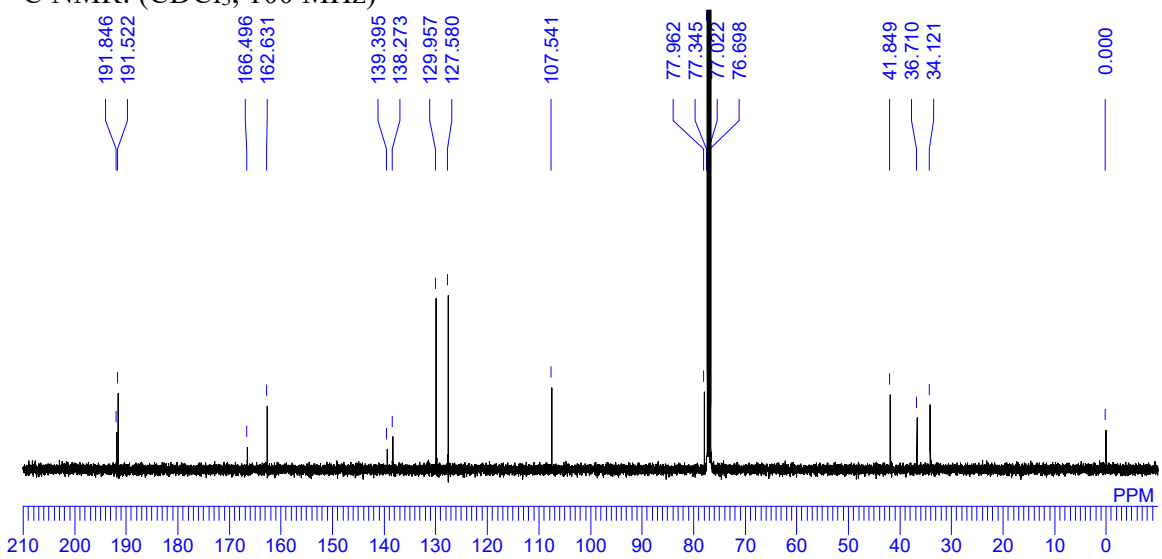
colorless oil; IR ν = 3348 (m), 3070 (w), 2927 (m), 2853 (w), 1702 (s), 1652 (s), 1592 (s), 1545 (s), 1412 (m), 1280 (s), 1211 (s), 1101 (m), 899 (w), 851 (m), 759 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 10.09 (s, 1H, 1-H), 7.97 (d, J = 8.4 Hz, 2H, 3-H), 7.92 (d, J = 8.4 Hz, 2H, 4-H), 7.39 (d, J = 6.0 Hz, 1H, 10-H), 6.46 (brs, 1H, NH), 5.46 (d, J = 6.0 Hz, 1H, 11-H), 4.62–4.54 (m, 1H, 9-H), 3.79–3.63 (m, 2H, 7-H), 2.63 (dd, J = 17.0, 13.8 Hz, 1H, 13-H), 2.49 (dd, J = 17.0, 3.4 Hz, 1H, 13-H), 2.19–2.05 (m, 2H, 8-H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.8 (s, C-12), 191.5 (d, C-1), 166.5 (s, C-6), 162.6 (d, C-10), 139.4 (s, C-5), 138.3 (s, C-2), 130.0 (d, C-3), 127.6 (d, C-4), 107.5 (d, C-11), 78.0 (d, C-9), 41.8 (t, C-13), 36.7 (t, C-7), 34.1 (t, C-8); HRMS (MALDI-TOF MS) Calculated ($C_{15}H_{15}NO_4Na$): 296.0893 ($[M+Na]^+$), Found: 296.0885

^1H NMR ($CDCl_3$, 400 MHz)

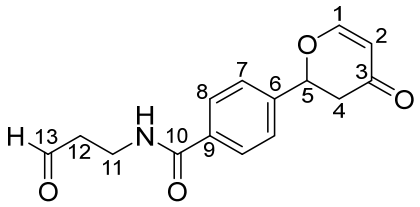


Asterisks represent inseparable impurities.

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

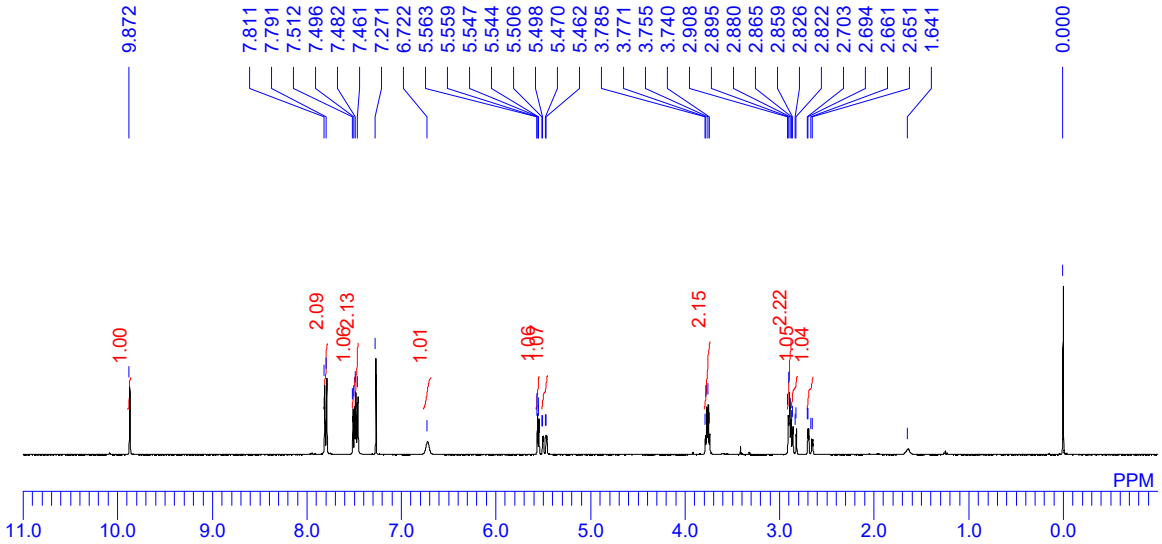


4-(4-Oxo-3,4-dihydro-2*H*-pyran-2-yl)-*N*-(3-oxoethyl)benzamide 7b

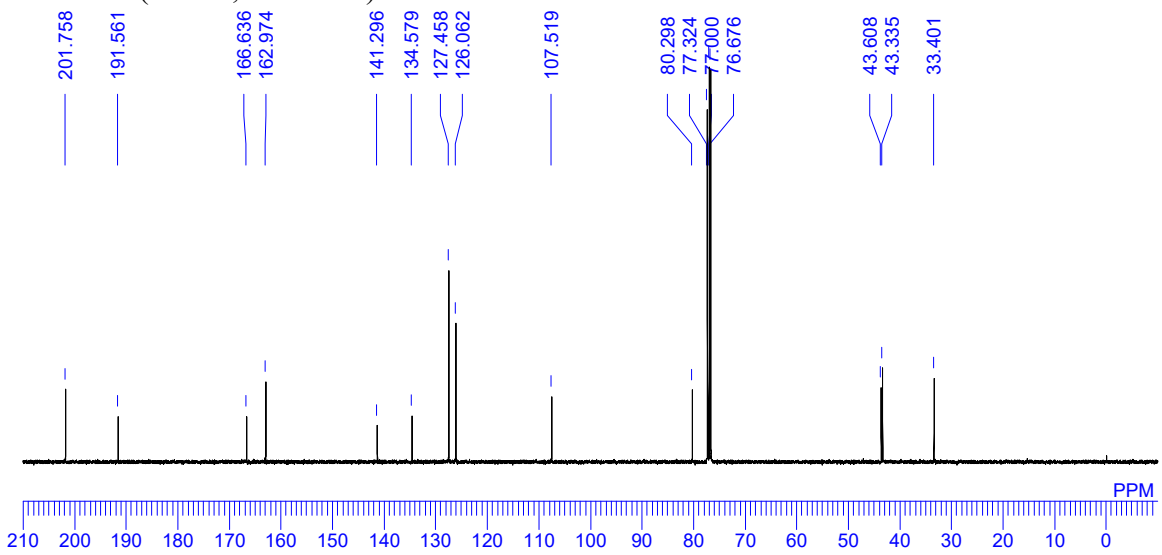


colorless oil; IR ν = 3567 (w), 3286 (m), 3069 (w), 2936 (w), 2901 (w), 1652 (s), 1592 (s), 1543 (s), 1506 (m), 1410 (m), 1231 (m), 1043 (m), 992 (m), 935 (m), 853 (m), 768 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 9.87 (s, 1H, 13-H), 7.80 (d, J = 8.0 Hz, 2H, 8-H), 7.50 (d, J = 6.4 Hz, 1H, 1-H), 7.47 (d, J = 8.4 Hz, 1H, 7-H), 6.72 (brs, 1H, NH), 5.55 (dd, J = 6.2, 1.4 Hz, 1H, 2-H), 5.48 (dd, J = 14.4, 3.2 Hz, 1H, 5-H), 3.76 (td, J = 6.1, 5.6 Hz, 2H, 11-H), 2.90 (t, J = 5.6 Hz, 3H, 12-H), 2.84 (dd, J = 15.2, 2.4 Hz, 1H, 4-H), 2.68 (dd, J = 17.0, 3.8 Hz, 1H, 4-H); ^{13}C NMR (100 MHz, $CDCl_3$) 201.8 (d, 13-C), 191.6 (s, 3-C), 166.6 (s, 10-C), 163.0 (d, 1-C), 141.3 (s, 6-C), 134.6 (s, 9-C), 127.5 (d, 8-C), 126.1 (d, 7-C), 107.5 (d, 2-C), 80.3 (d, 5-C), 43.6 (t, 12-C), 43.3 (t, 4-C), 33.4 (t, 11-C); HRMS (MALDI-TOF MS) Calculated ($C_{15}H_{15}NO_4Na$): 296.0893 ([M+Na]$^+$), Found: 296.0895

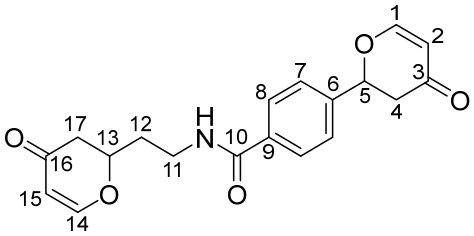
^{1}H NMR: ($CDCl_3$, 400 MHz)



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

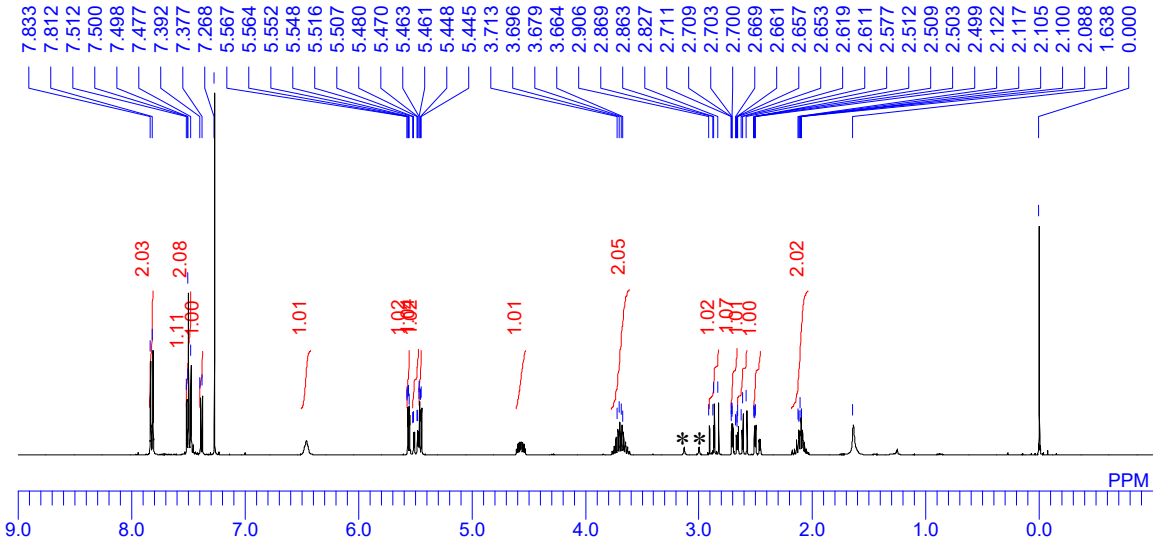


4-(4-Oxo-3,4-dihydro-2*H*-pyran-2-yl)-*N*-(2-{4-oxo-3,4-dihydro-2*H*-pyran-2-yl}ethyl)benzamide 7c



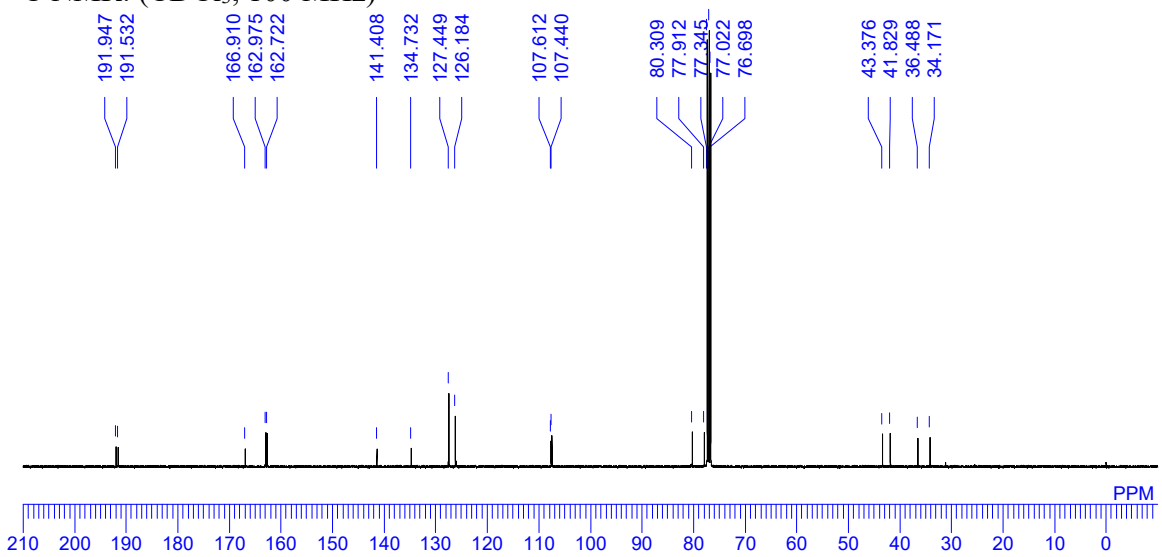
The product was isolated as a single diastereomer of colorless oil; IR ν = 3332 (m), 3064 (w), 2956 (w), 2926 (m), 1668 (s), 1652 (s), 1593 (s), 1547 (s), 1506 (m), 1408 (s), 1363 (m), 1277 (s), 1230 (s), 1040 (m), 993 (w), 935 (m), 852 (m), 797 (w), 768 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.82 (d, J = 8.4 Hz, 2H, 8-H), 7.51 (d, J = 4.8 Hz, 1H, 1-H), 7.49 (d, J = 8.4 Hz, 2H, 7-H), 7.38 (d, J = 6.0 Hz, 2H, 14-H), 6.46 (brs, 1H, NH), 5.56 (dd, J = 6.0, 1.2 Hz, 1H, 2-H), 5.49 (dd, J = 14.6, 3.8 Hz, 1H, 5-H), 5.45 (dd, J = 6.2, 1.4 Hz, 1H, 15-H), 4.61–4.53 (m, 1H, 13-H), 3.77–3.61 (m, 2H, 11-H), 2.87 (dd, J = 17.0, 14.6 Hz, 1H, 4-H), 2.68 (ddd, J = 17.0, 3.4, 1.2 Hz, 1H, 4-H), 2.62 (dd, J = 16.8, 13.6 Hz, 1H, 17-H), 2.48 (ddd, J = 16.9, 3.7, 1.3 Hz, 1H, 17-H), 2.18–2.03 (m, 2H, 12-H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.9 (s, C-16), 191.5 (s, C-3), 166.9 (s, C-10), 163.0 (d, C-1), 162.7 (d, C-14), 141.4 (s, C-6), 134.7 (s, C-9), 127.4 (d, C-8), 126.2 (d, C-7), 107.6 (d, C-2), 107.4 (d, C-15), 80.3 (d, C-5), 77.9 (d, C-13), 43.4 (t, C-4), 41.8 (t, C-17), 36.5 (t, C-11), 34.2 (t, C-12); HRMS (MALDI-TOF MS) Calculated ($C_{19}H_{19}NO_5Na$): 364.1155 ($[M+Na]^+$), Found: 364.1155

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



Asterisks represent inseparable impurities.

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



5. X-ray crystallographic data

5-1. Cage-shaped borate 1AB·dbp (CCDC 2297702)

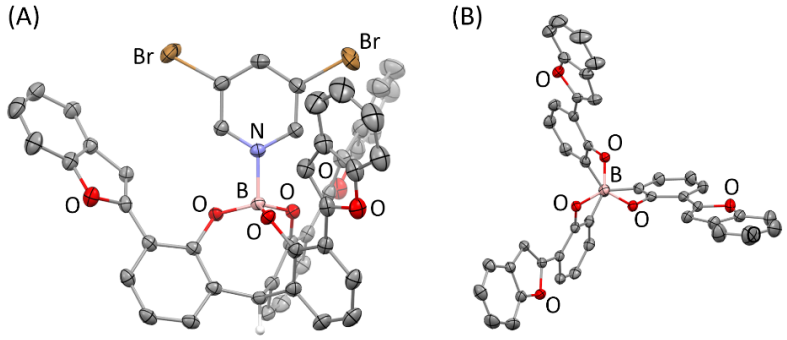


Figure S2. ORTEP drawings of **1AB**·dbp at the 50% probability level. (A) Side and (B) top views.

Empirical Formula	$C_{48}H_{28}BBr_2NO_6 + CHCl_3$	Space Group	$P2_1/c$ (#14)
Formula Weight	1004.71	Z value	4
Crystal Color	colorless	D_{calc}	1.588 g/cm^3
Crystal Dimensions	0.099 × 0.068 × 0.066 mm	F_{000}	2016.0
Crystal System	monoclinic	μ(CuK$_\alpha$)	4.642 mm^{-1}
Lattice Type	Primitive	Temperature	190 K
Lattice Parameters	a = 12.39030(10) Å	Data/restraints/parameters	8499/0/578
	b = 32.0048(2) Å	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0334
	c = 10.89300(10) Å	Residuals: wR_2 (all data)	0.0939
	β = 103.3290(10) °	Goodness of Fit Indicator	1.053
	V = 4203.25(6) Å^3		

5-2. Cage-shaped borate 1A$_{II}$B·py (CCDC 2297703)

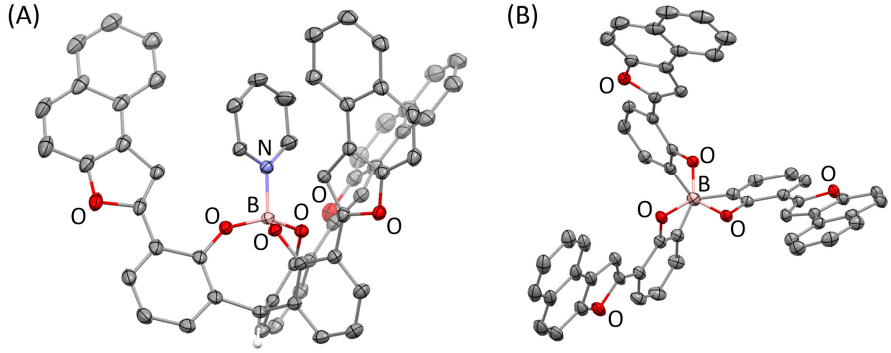
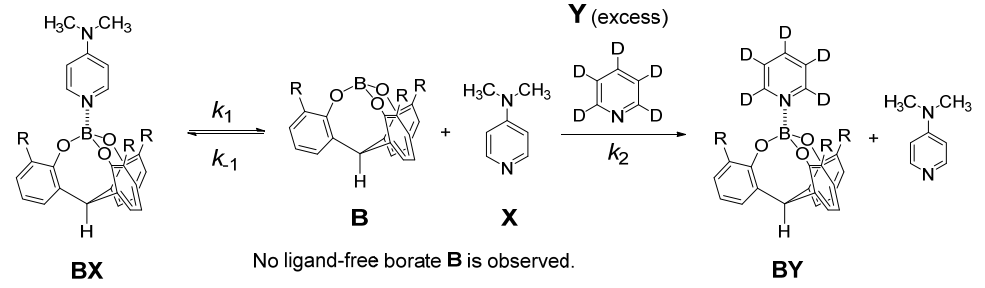


Figure S3. ORTEP drawings of **1A$_{II}$B**·py at the 50% probability level. (A) Side and (B) top views.

Empirical Formula	$C_{60}H_{36}BNO_6 + CH_2Cl_2$	Space Group	P-1 (#2)
Formula Weight	962.63	Z value	4
Crystal Color, Habit	colorless	D_{calc}	1.369 g/cm^3
Crystal Dimensions	0.262 × 0.221 × 0.159 mm	F_{000}	1992.0
Crystal System	triclinic	μ(MoK$_\alpha$)	1.715 mm^{-1}
Lattice Type	Primitive	Temperature	123 K
Lattice Parameters	a = 14.3033(2) Å	Date/restraints/parameters	18886/60/1307
	b = 16.7148(2) Å	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0576
	c = 20.3372(2) Å	Residuals: wR_2 (all data)	0.1683
	α = 87.3930(10) °	Goodness of Fit Indicator	1.037
	β = 77.1020(10) °		
	γ = 80.1780(10) °		
	V = 4669.87(10) Å^3		

6. Determination of ligand exchange rate of 1AB·dmap

A solution of **1A**B·dmap (14 μmol) in pyridine-d_5 (0.5 mL) was monitored via ^{1}H NMR measurements at 358 K, 363 K, 368 K and 373 K (Figure S3). Hexamethylbenzene was used as an internal standard. The obtained results were summarized in Table S19. 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. For simplification, t_0 can be voluntarily set as zero (with considering stable temperature condition experimentally). Plots based on the equation (A) furnish a linear plot (See below). Results with complex **1a**B and **1b**B have been previously reported.[8]



$$\mathbf{BX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{B} + \mathbf{X} \qquad (1)$$

$$\mathbf{B} + \underset{\text{excess}}{\mathbf{Y}} \xrightarrow{k_2} \mathbf{BY} \qquad (2)$$

$$[BX]_0 = [BX] + [X]$$

$$[X] = [BY]$$

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

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

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

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

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

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

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

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

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

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

Table S1. Kinetic parameters for ligand dissociation of the cage-shaped borate **1A**B, **1a**B and **1b**B.

entry	borate	$\Delta H^{\ddagger}$ [kcal mol^{-1}]	$\Delta S^{\ddagger}$ [cal K^{-1} mol^{-1}]	$\Delta G^{\ddagger}$ [kcal mol^{-1}] [a]	k [s^{-1}]
1	**1A**B	29.5	1.46	29.1	1.23×10^{-9}
2	**1a**B	35.1	22.3	28.6	2.32×10^{-9}
3	**1b**B	31.2	7.52	29.0	1.16×10^{-9}

[a] $\Delta G^{\ddagger}$ and k were calculated at 293 K.

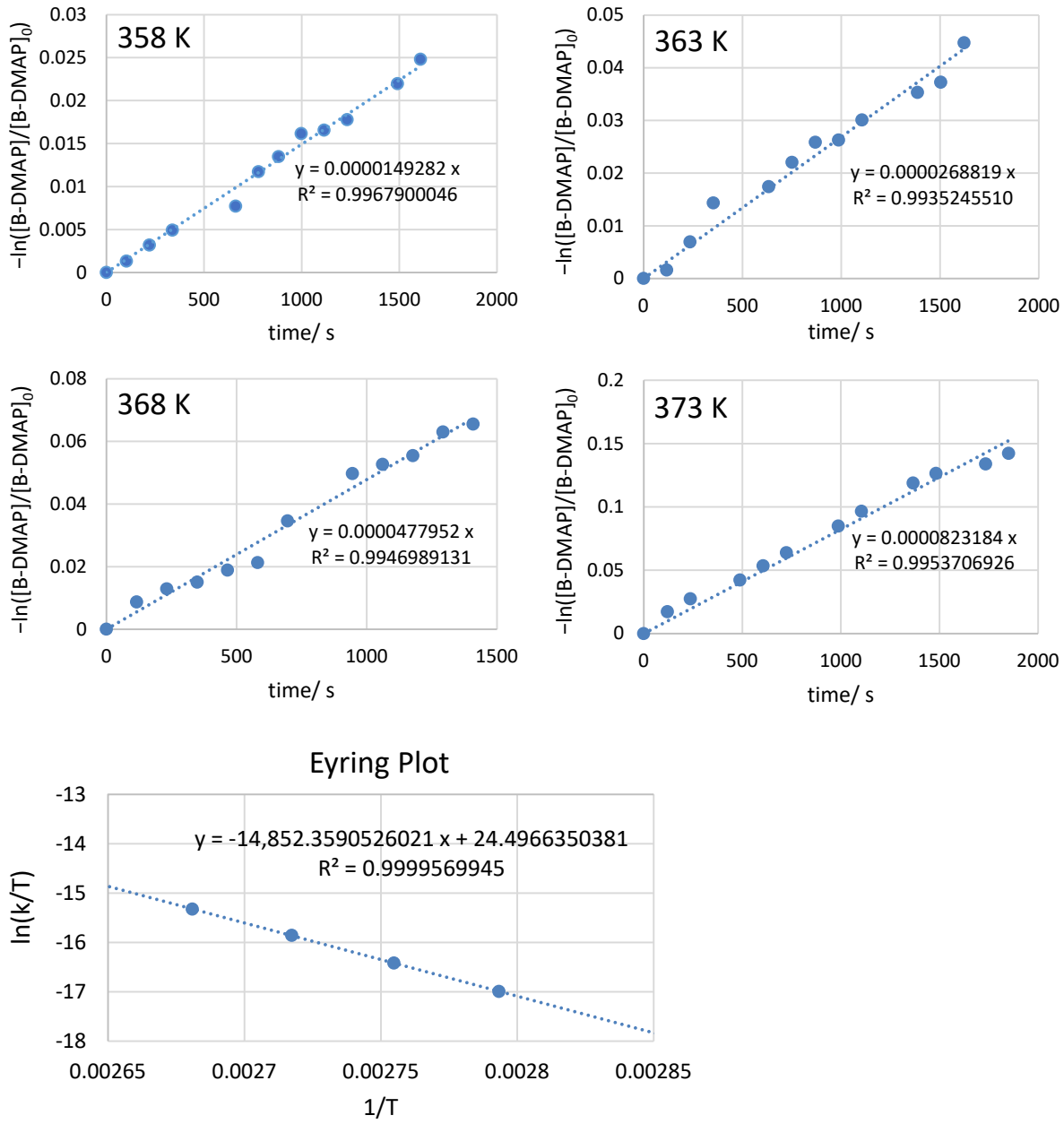
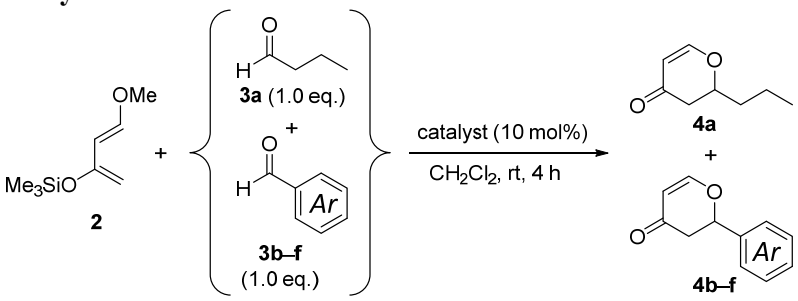


Figure S4. Kinetics plots and Eyring plot for dissociation of **1A**B·dmap.

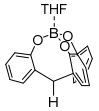
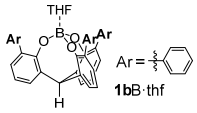
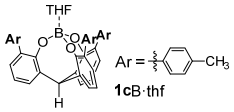
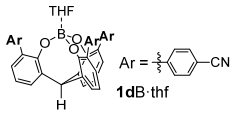
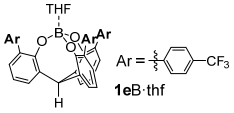
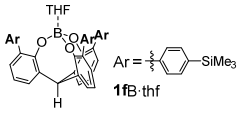
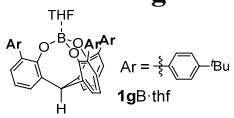
7. Intermolecular competitive hetero-Diels-Alder reaction of the Danishefsky's diene 2 with the mixture of aldehydes 3a and 3b–f

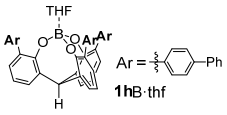
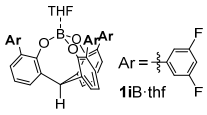
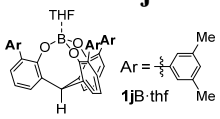
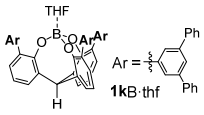
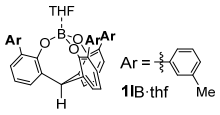
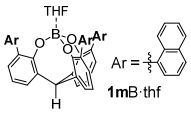
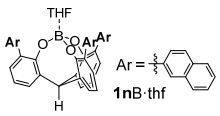


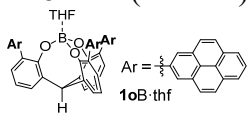
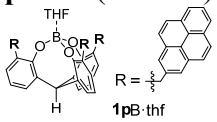
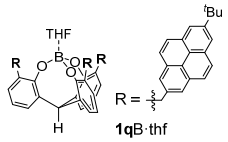
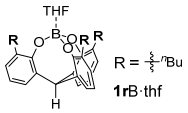
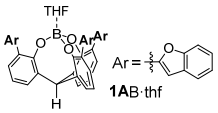
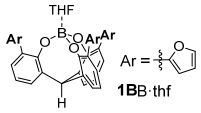
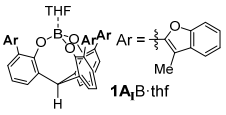
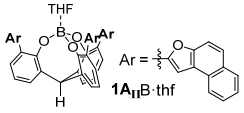
Ar = Ph (**b**), 4-$MeOC_6H_4$ (**c**), 4-MeC_6H_4 (**d**), C_6F_5 (**e**), 4-NCC_6H_4 (**f**)

In a nitrogen-filled glove box, to the solution of the borate catalyst (0.050 mmol) in CH_2Cl_2 (2 mL) was added Danishefsky's diene **2** (0.50 mmol), butanal **3a** (0.50 mmol), and benzaldehyde derivative **3b**–**f** (0.50 mmol) at room temperature. After stirring for 4 h at room temperature, HCl aq. (10 mL) was added to the mixture. The products were extracted with dichloromethane (3×10 mL). The organic layer was dried with $MgSO_4$ and evaporated to give a crude mixture, which was analyzed by NMR using 1,1,2,2-tetracholoroethane as an internal standard.

Table S2. Summary for the competitive cycloaddition of the **2** with **3a** and various benzaldehydes **3b**–**f**.

catalyst	benzaldehyde derivative **3**	total yield of **4**/ %		ratio of **4**	
1aB·thf 	**3b**	**4a**+**4b**	73	**4a**/**4b**	52:48
	3c	**4a**+**4c**	78	**4a**/**4c**	70:30
	3d	**4a**+**4d**	100	**4a**/**4d**	71:29
	3e	**4a**+**4e**	66	**4a**/**4e**	52:48
	3f	**4a**+**4f**	72	**4a**/**4f**	33:67
1bB·thf 	**3b**	**4a**+**4b**	71	**4a**/**4b**	30:70
	3c	**4a**+**4c**	79	**4a**/**4c**	49:51
	3d	**4a**+**4d**	93	**4a**/**4d**	36:64
	3e	**4a**+**4e**	66	**4a**/**4e**	14:86
	3f	**4a**+**4f**	79	**4a**/**4f**	10:90
1cB·thf 	**3b**	**4a**+**4b**	82	**4a**/**4b**	30:70
	3c	**4a**+**4c**	78	**4a**/**4c**	37:63
	3d	**4a**+**4d**	82	**4a**/**4d**	36:64
	3e	**4a**+**4e**	60	**4a**/**4e**	15:85
	3f	**4a**+**4f**	69	**4a**/**4f**	4:96
1dB·thf 	**3b**	**4a**+**4b**	98	**4a**/**4b**	35:65
	3c	**4a**+**4c**	76	**4a**/**4c**	59:41
	3d	**4a**+**4d**	75	**4a**/**4d**	40:60
	3e	**4a**+**4e**	45	**4a**/**4e**	27:73
	3f	**4a**+**4f**	91	**4a**/**4f**	21:79
1eB·thf 	**3b**	**4a**+**4b**	100	**4a**/**4b**	46:54
	3c	**4a**+**4c**	86	**4a**/**4c**	56:44
	3d	**4a**+**4d**	87	**4a**/**4d**	45:55
	3e	**4a**+**4e**	71	**4a**/**4e**	64:36
	3f	**4a**+**4f**	88	**4a**/**4f**	24:76
1fB·thf 	**3b**	**4a**+**4b**	71	**4a**/**4b**	34:66
	3c	**4a**+**4c**	74	**4a**/**4c**	49:51
	3d	**4a**+**4d**	78	**4a**/**4d**	40:60
	3e	**4a**+**4e**	68	**4a**/**4e**	28:72
	3f	**4a**+**4f**	70	**4a**/**4f**	20:80
1gB·thf 	**3b**	**4a**+**4b**	92	**4a**/**4b**	33:67
	3c	**4a**+**4c**	81	**4a**/**4c**	49:51
	3d	**4a**+**4d**	78	**4a**/**4d**	36:64
	3e	**4a**+**4e**	60	**4a**/**4e**	29:71
	3f	**4a**+**4f**	73	**4a**/**4f**	22:78

1hB·thf 	**3b**	**4a+4b**	81	**4a/4b**	30:70
	3c	**4a+4c**	85	**4a/4c**	41:59
	3d	**4a+4d**	76	**4a/4d**	30:70
	3e	**4a+4e**	66	**4a/4e**	18:82
	3f	**4a+4f**	78	**4a/4f**	10:90
1iB·thf 	**3b**	**4a+4b**	90	**4a/4b**	49:51
	3c	**4a+4c**	92	**4a/4c**	65:35
	3d	**4a+4d**	94	**4a/4d**	62:38
	3e	**4a+4e**	52	**4a/4e**	26:74
	3f	**4a+4f**	70	**4a/4f**	9:91
1jB·thf 	**3b**	**4a+4b**	79	**4a/4b**	30:70
	3c	**4a+4c**	68	**4a/4c**	43:57
	3d	**4a+4d**	77	**4a/4d**	36:64
	3e	**4a+4e**	54	**4a/4e**	28:72
	3f	**4a+4f**	64	**4a/4f**	4:96
1kB·thf 	**3b**	**4a+4b**	73	**4a/4b**	47:53
	3e	**4a+4e**	55	**4a/4e**	37:63
	3f	**4a+4f**	72	**4a/4f**	8:92
1lB·thf 	**3b**	**4a+4b**	72	**4a/4b**	26:74
	3c	**4a+4c**	68	**4a/4c**	39:61
	3d	**4a+4d**	83	**4a/4d**	31:69
	3e	**4a+4e**	57	**4a/4e**	15:85
	3f	**4a+4f**	61	**4a/4f**	13:87
1mB·thf 	**3b**	**4a+4b**	63	**4a/4b**	27:73
	3e	**4a+4e**	74	**4a/4e**	6:94
	3f	**4a+4f**	27	**4a/4f**	7:93
1nB·thf 	**3b**	**4a+4b**	60	**4a/4b**	22:78
	3c	**4a+4c**	93	**4a/4c**	42:58
	3d	**4a+4d**	73	**4a/4d**	35:65
	3e	**4a+4e**	63	**4a/4e**	14:86
	3f	**4a+4f**	57	**4a/4f**	4:96

1oB·thf (1 mol%) 	**3b**	**4a**+**4b**	86	**4a**/**4b**	43:57
	3e	**4a**+**4e**	52	**4a**/**4e**	24:76
	3f	**4a**+**4f**	72	**4a**/**4f**	8:92
1pB·thf (1 mol%) 	**3b**	**4a**+**4b**	93	**4a**/**4b**	43:57
1qB·thf (1 mol%) 	**3b**	**4a**+**4b**	94	**4a**/**4b**	51:49
1rB·thf 	**3b**	**4a**+**4b**	71	**4a**/**4b**	56:44
	3c	**4a**+**4c**	52	**4a**/**4c**	51:49
	3d	**4a**+**4d**	52	**4a**/**4d**	75:25
	3e	**4a**+**4e**	53	**4a**/**4e**	36:64
	3f	**4a**+**4f**	82	**4a**/**4f**	34:66
1AB·thf 	**3b**	**4a**+**4b**	91	**4a**/**4b**	26:74
	3c	**4a**+**4c**	84	**4a**/**4c**	45:55
	3d	**4a**+**4d**	87	**4a**/**4d**	35:65
	3e	**4a**+**4e**	32	**4a**/**4e**	16:84
	3f	**4a**+**4f**	82	**4a**/**4f**	9:91
1BB·thf 	**3b**	**4a**+**4b**	74	**4a**/**4b**	46:54
	3c	**4a**+**4c**	97	**4a**/**4c**	46:54
	3d	**4a**+**4d**	71	**4a**/**4d**	54:46
	3e	**4a**+**4e**	38	**4a**/**4e**	32:68
	3f	**4a**+**4f**	90	**4a**/**4f**	19:81
1A$_I$B·thf 	**3b**	**4a**+**4b**	76	**4a**/**4b**	34:66
	3c	**4a**+**4c**	84	**4a**/**4c**	43:57
	3d	**4a**+**4d**	76	**4a**/**4d**	38:62
	3e	**4a**+**4e**	51	**4a**/**4e**	47:53
	3f	**4a**+**4f**	66	**4a**/**4f**	22:78
1A$_{II}$B·thf 	**3b**	**4a**+**4b**	74	**4a**/**4b**	27:73
	3c	**4a**+**4c**	69	**4a**/**4c**	45:55
	3d	**4a**+**4d**	78	**4a**/**4d**	34:66
	3e	**4a**+**4e**	53	**4a**/**4e**	22:78
	3f	**4a**+**4f**	87	**4a**/**4f**	7:93

1A$_{III}$B·thf	**3b**	**4a+4b**	62	**4a/4b**	26:74
	3c	**4a+4c**	84	**4a/4c**	45:55
	3d	**4a+4d**	67	**4a/4d**	37:63
	3e	**4a+4e**	19	**4a/4e**	17:83
	3f	**4a+4f**	32	**4a/4f**	7:93
1A$_{IV}$B·thf	**3b**	**4a+4b**	86	**4a/4b**	26:74
	3c	**4a+4c**	81	**4a/4c**	41:59
	3d	**4a+4d**	77	**4a/4d**	35:65
	3e	**4a+4e**	28	**4a/4e**	10:90
	3f	**4a+4f**	80	**4a/4f**	9:91

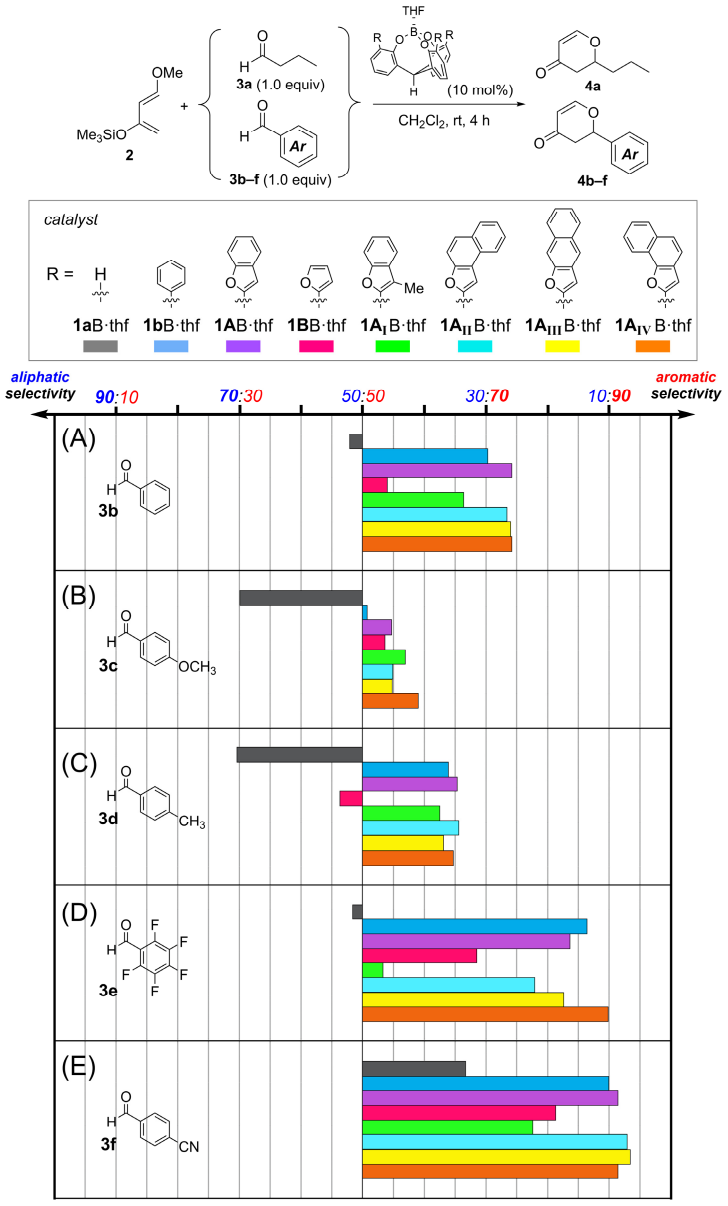
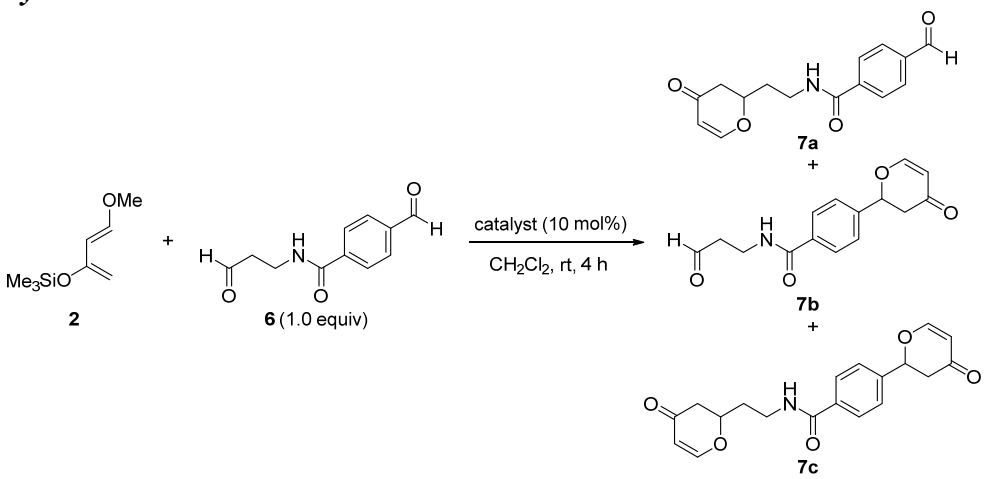


Figure S5. Observed chemoselectivity in the competitive hetero-Diels–Alder reactions between **3a** and various benzaldehyde derivatives **3b**–**f**.

8. Intramolecular competitive hetero-Diels-Alder reaction of the Danishefsky's diene 2 with the amide-based dialdehyde 6

Procedure for the intramolecular competitive hetero-Diels-Alder Reaction with 6

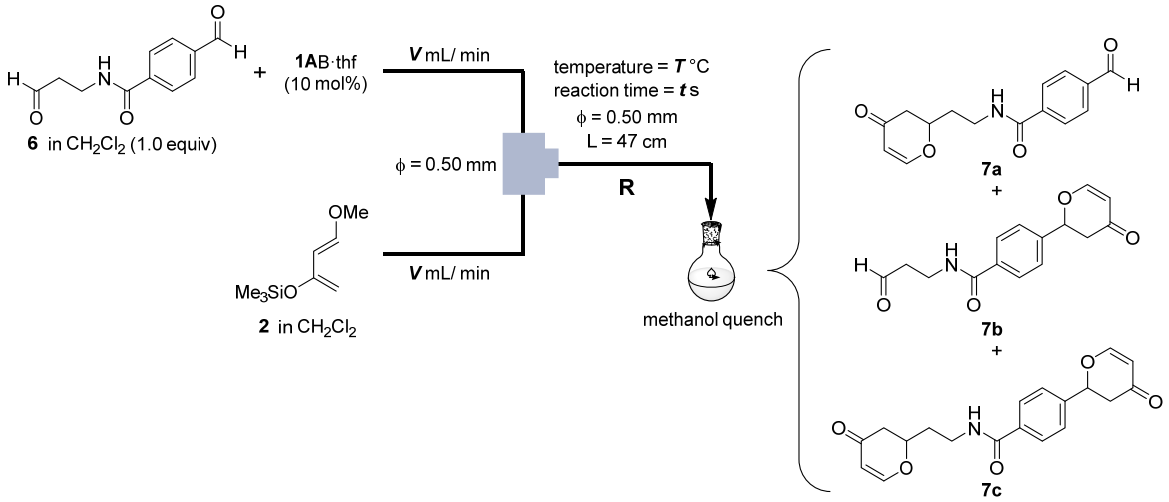
·In batch system



In a nitrogen-filled glove box, the dropwise solution of Danishefsky's diene **2** (34.5 mg, 0.20 mmol) in CH_2Cl_2 (2.0 mL) was gradually added to the solution of the dialdehyde **6** (41.0 mg, 0.20 mmol) and borate catalyst (0.020 mmol) in CH_2Cl_2 (2.0 mL) at room temperature via a syringe. After stirring for 4 h at room temperature, methanol (10 mL) was added to the mixture. The solvents were removed under vacuum. The obtained crude mixture was analyzed by NMR using 1,1,2,2-tetracholoroethane as an internal standard.

For the isolation of the products **7**, the crude mixture was purified by silica gel column chromatography (ethyl acetate/methanol = 95:5) followed by a recycle GPC, to give the three products **7a**–**c**.

·***In flow system***



A solution of **6** and **1A**B·thf (10 mol%) in CH_2Cl_2 (flow rate: *V* mL/min) and a solution of **2** in CH_2Cl_2 (flow rate: *V* mL/min) were introduced to a T-shaped microreactor (ϕ = 0.50 mm) by syringe pumps. The resulting solution was passed through R (ϕ = 0.50 mm, L = 47 cm). After a steady state (reaction time: *t* s) was reached, the outcoming solution was collected in a vessel containing methanol. The solvents were removed under vacuum. The obtained crude mixture was analyzed by NMR using 1,1,2,2-tetracholoroethane as an internal standard. The yields of the products and the selectivity with the increase in the flow rate were summarized in the following table.

entry	concentration /M	temperature ***T*** /°C	flow rate ***V*** /mL·min^{-1}	reaction time ***t*** /s	yield / % (**7a**+**7b**+**7c**)	ratio **7a**/**7b**/**7c**
1	0.050	rt	0.50	6	24	3 : 67 : 30
2	0.050	rt	1.00	3	25	8 : 90 : 2
3	0.050	rt	2.00	1.5	18	5 : 66 : 29

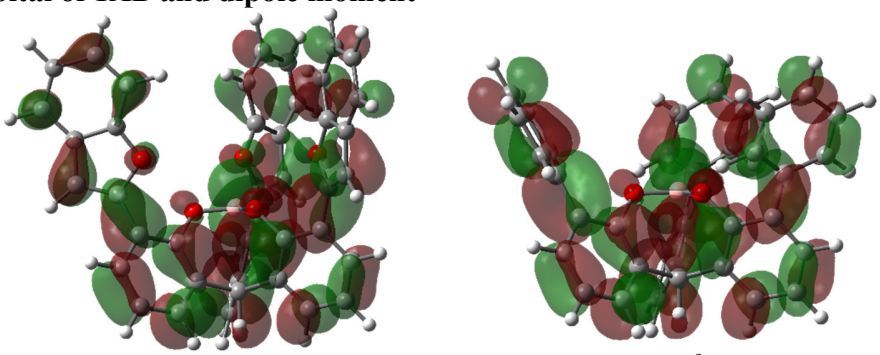
9. Computational method

All quantum chemical calculations were conducted using the Gaussian 16 Rev. C. 01 program.[12] The geometry of **1A**B and **1B**B were optimized at the ωB97X-D/Def2-SVP level, to afford the optimized structures as a local minimum structure giving all positive vibrational frequencies. The LUMO energy levels of the borates were calculated at the B3PW91/6-31+G** level using the optimized geometry. The dipole moments for **1A**B and **1B**B were estimated using the optimized structure at the ωB97X-D/Def2-SVP level including the solvent effect of the IEFPCM model (dichloromethane).

For the reaction profiles of the reaction of **2** with **3a** or **3b** catalyzed by the borate **1A**B, the ωB97X-D density functional and Def2-SVP were used. All molecular geometries were fully optimized and Gibbs free energies including contribution of vibrational entropy at an appropriate temperature were described in energy profiles. Solvation effect was introduced using the IEFPCM model and dichloromethane was used as a solvent.

Using the optimized structures of **1**B·**3**⊃**2** at the ωB97X-D/Def2-SVP level, Grimme's D3 dispersion correction with Becke–Johnson (BJ) damping[13] were estimated at the B3LYP/6-31G** level. Using the same optimized geometries of **1**B·**3**⊃**2**, non-covalent interactions (NCI) of inclusion complexes **1**B·**3**⊃**2** were computed using the non-covalent interaction index from the optimized electron density at the ωB97X-D/cc-pVTZ level of theory. The generation of the NCI plot surfaces were obtained by NCIPLOT program.[1415] The surfaces were colored on a blue-green-red (BGR) scale using VMD program[16] with a reduced density gradient (RDG) surfaces = 0.50 a.u. and the color range blue(attractive)-green-red(repulsive) for $-0.018 < \rho < +0.025$ a.u.. The blue region indicates strong attractive interactions, and the red region indicates strong repulsive interactions.

10. LUMO orbital of 1AB and dipole moment

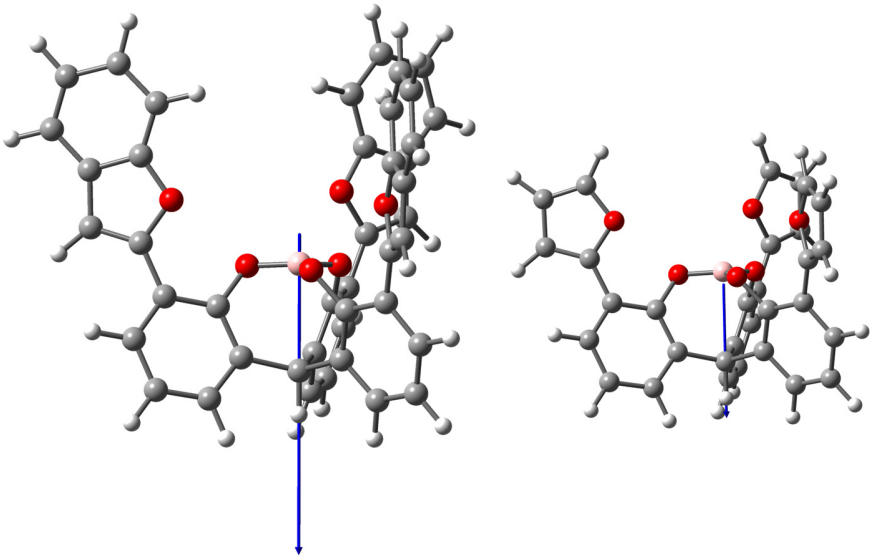


1AB
–1.44 eV (LUMO+1)

1bB[9]
–1.16 eV (LUMO)

Figure S6. The LUMO of **1A**B and **1b**B[9] calculated at the B3PW91/6-31+G** level.

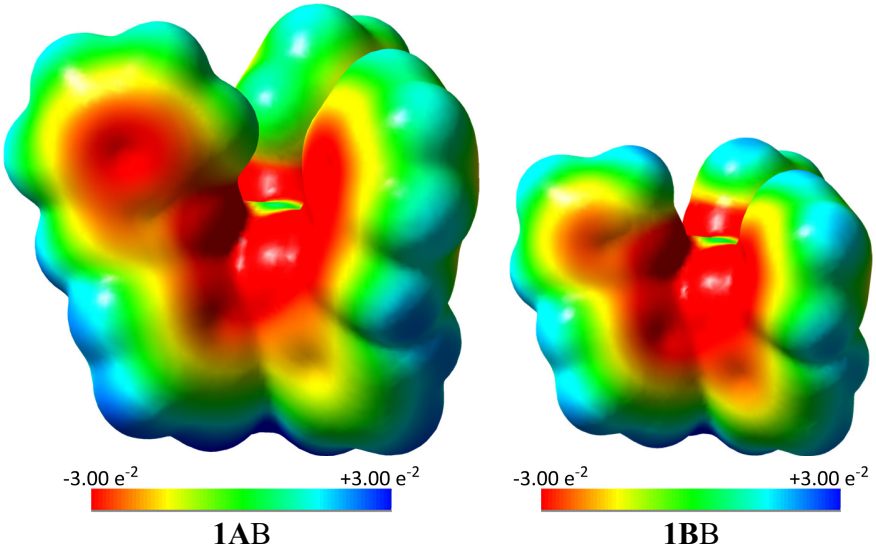
(A)



1AB
5.0108 Debye

1BB
2.4788 Debye

(B)



1AB **1B**B

Figure S7. (A) The dipole moment of **1A**B and **1B**B calculated at the ωB97X-D/Def2-SVP level including the solvent effect of the IEFPCM model (dichloromethane). (B) Electrostatic potential (ESP) map of **1A**B and **1B**B.

11. Summary for molecular geometries included in the estimated reaction pathway

The DFT calculations were performed using ωB97XD/def2svp. Solvation effect was introduced using the IEFPCM model, and dichloromethane was used as a solvent.

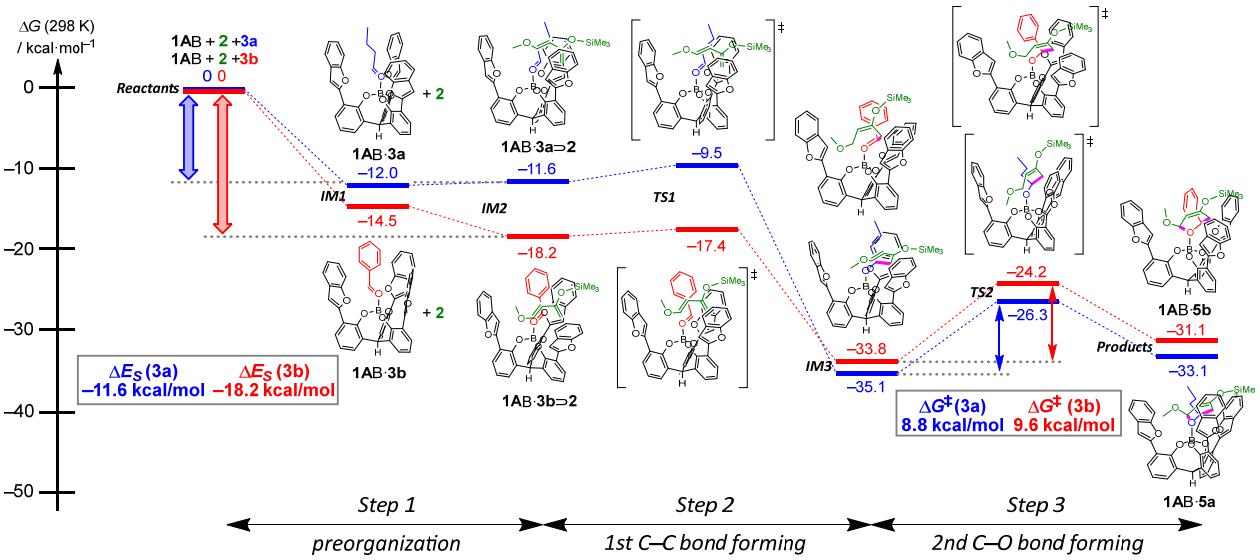


Figure S8. Energy profiles of the hetero-Diels–Alder reaction of **2** with **3a** or **3b** catalyzed by **1AB**. DFT calculations were performed at the wB97XD/def2svp level. Solvation effects were introduced by using the IEFPCM model, and dichloromethane was used as a solvent.

11-1. Reactants and products

Danishefsky's diene ***2***

total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-753.8749765	-753.650226	-753.693901

Table S3. Optimized Cartesian coordinates (Å) for **2** in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

C	0.14276594	1.40778479	-0.35609377	H	-0.29953210	-2.15777473	-0.75366411
O	-1.14311628	1.00970925	-0.54579080	C	0.40624341	2.62691511	0.14352192
Si	-1.87102193	-0.40012559	0.07512906	H	-0.40793388	3.27477347	0.47465132
C	-1.36026774	-0.57036086	1.86758844	H	1.43110626	2.99412511	0.20238248
H	-1.85240807	-1.44018922	2.33110402	C	1.17251560	0.43410599	-0.76002035
H	-0.27105535	-0.71195549	1.94915893	H	0.99588864	-0.15222351	-1.66699587
H	-1.63463792	0.32742170	2.44309392	C	2.28979779	0.22281649	-0.04841312
C	-3.70096083	-0.08458081	-0.11267109	H	2.46890125	0.74856128	0.89960687
H	-3.96590287	0.07077027	-1.17011062	O	3.24655856	-0.62579187	-0.44805832
H	-4.27902960	-0.94529117	0.25944505	C	4.25460012	-0.92265115	0.49566272
H	-4.00925589	0.80730718	0.45408551	H	4.98739596	-1.56522031	-0.00598870
C	-1.35798433	-1.90450253	-0.91566871	H	4.76000173	-0.00624342	0.84259080
H	-1.96612565	-2.77362430	-0.61615830	H	3.84224685	-1.45945232	1.36559817
H	-1.51315026	-1.73772749	-1.99324970				

butanal ***3a***

total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-232.2190702	-232.105585	-232.135505

Table S4. Optimized Cartesian coordinates (Å) for **3a** in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

C	2.39279303	-0.18148873	-0.05896228	C	-0.12025280	-0.42252012	0.23905857
H	2.43984857	-1.05859122	-0.72293120	H	0.03582695	-0.78030982	1.27401585
H	2.59337759	-0.52848376	0.96687479	H	-0.17372755	-1.30844194	-0.41225394
H	3.20341710	0.50322063	-0.34803591	C	-1.45556416	0.26643525	0.22377012
C	1.03459934	0.50407145	-0.15024591	H	-1.47867946	1.25359145	0.75350756
H	1.02318707	1.39332913	0.50265390	O	-2.45327555	-0.16840532	-0.29488523
H	0.87350172	0.87394095	-1.17647229				

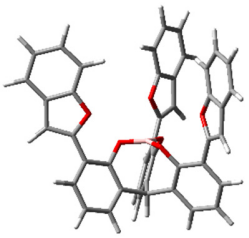
benzaldehyde ***3b***

total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-345.2097061	-345.098627	-345.129141

Table S5. Optimized Cartesian coordinates (Å) for **3b** in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

C	0.53348536	0.21287348	-0.00001182	H	-1.71154513	-2.35136785	0.00005294
C	0.04459473	-1.10063688	-0.00000429	H	-3.29094513	-0.43065109	0.00013886
C	-1.32675904	-1.32951474	0.00004891	H	-2.42879984	1.90160442	0.00013063
C	-2.21395137	-0.24843810	0.00009743	H	0.02959223	2.31444630	0.00003547
C	-1.73207974	1.06110163	0.00009252	C	1.99395927	0.46653874	-0.00007357
C	-0.35763209	1.29160154	0.00004052	O	2.83938873	-0.39671177	-0.00017255
H	0.75711239	-1.92830496	-0.00004181	H	2.27977289	1.54681334	-0.00007392

*Cage-shaped borate **1AB** (mmm)*

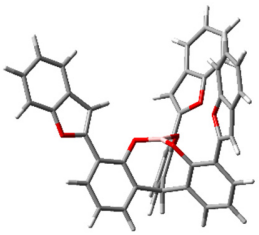


total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-2127.750852	-2127.172972	-2127.244271

Table S6. Optimized Cartesian coordinates (Å) for **1AB** in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

B	-0.00070764	-0.00749997	-0.72940255	C	3.58028530	-1.29642718	-3.81148204
O	-1.36247272	-0.07627327	-0.80586347	H	2.10830857	-0.31900653	-5.04103707
O	0.62093540	1.20510251	-0.81904657	H	4.86139442	-2.23182160	-2.34825182
C	-1.84176437	-0.90352838	-1.77850899	C	3.98094499	-3.36206731	0.18393897
O	0.73920280	-1.15305753	-0.80146278	O	2.87144587	-1.53882689	0.90257438
C	0.14767020	2.02141113	-1.80384026	H	-1.03519602	4.36687783	-4.64508285
C	-1.22435985	-0.89910088	-3.04211824	C	0.90616819	5.16922942	1.56480596
C	-2.96255320	-1.70092619	-1.50490496	H	1.35561059	5.85407396	-0.55960914
C	1.68677153	-1.16352340	-1.78239353	C	0.26215291	3.98492707	1.95791715
C	-0.15151452	1.46852102	-3.06189293	C	-5.91196336	-1.82274278	2.61819300
C	0.01565697	3.39394176	-1.54780604	C	-3.14813037	-1.75324508	3.33172875
C	-0.00507262	-0.02762744	-3.39854518	H	4.32127388	-1.34618684	-4.61081679
C	-1.77109991	-1.71788467	-4.03486807	C	4.02471385	-3.34574194	1.62464478
C	-3.48699777	-2.49305379	-2.53345817	H	4.40178607	-4.10566947	-0.48828080
C	-3.59291768	-1.70823306	-0.17898625	C	3.31748652	-2.19201832	1.99964128
C	1.36248921	-0.64429508	-3.04856939	C	1.35749123	6.05847232	2.55288554
C	2.94084964	-1.73109137	-1.51397056	C	0.03806552	3.63482019	3.28625781
C	-0.58251901	2.33879844	-4.06771742	C	-5.50885740	-1.83021483	3.94805090
C	-0.40316817	4.23117948	-2.58902013	H	-6.97079972	-1.84862267	2.35313479
C	0.31673266	3.95945760	-0.22682550	C	-4.14535594	-1.79638631	4.30071179
H	-0.00711855	-0.03587390	-4.49391128	H	-2.08822233	-1.72580635	3.58792998
C	-2.89552314	-2.50281170	-3.79152714	C	4.56785255	-4.16634364	2.62584477
H	-1.30716112	-1.73361889	-5.02416595	C	3.12128190	-1.80507428	3.32215989
H	-4.35385379	-3.12354250	-2.32676565	C	1.14332044	5.72723843	3.88536753
C	-4.90563151	-1.75548496	0.18168717	H	1.86354927	6.98672330	2.28022928
O	-2.77633991	-1.70562221	0.91351187	C	0.49204292	4.53176735	4.24782975
C	2.33581186	-0.71825487	-4.04956315	H	-0.46712434	2.70475797	3.55002446
C	3.87958716	-1.79964382	-2.55059255	H	-6.26145032	-1.86277683	4.73870972
C	3.27567159	-2.25649246	-0.18460775	H	-3.86513074	-1.80353988	5.35616881
C	-0.70110264	3.70802468	-3.84211171	C	4.38306158	-3.79730847	3.95278244
H	-0.82325106	1.93247682	-5.05318532	H	5.12149598	-5.07120704	2.36739147
H	-0.51705229	5.29961490	-2.39624298	C	3.66980929	-2.63217546	4.29696819
C	0.92731208	5.12545367	0.12418059	H	2.56576666	-0.90012391	3.57171870
O	-0.09300519	3.26205353	0.87139264	H	1.48560205	6.40484519	4.67041123
H	-3.30581056	-3.12994078	-4.58452577	H	0.34079715	4.30394141	5.30508347
C	-4.92294697	-1.78137888	1.62277136	H	4.79759883	-4.42073176	4.74783593
H	-5.75554994	-1.75342424	-0.49621481	H	3.54428118	-2.37299618	5.35035643
C	-3.57247428	-1.74648793	2.00615238				

*Cage-shaped borate **1AB** (mmp)*



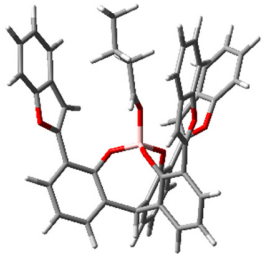
total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-2127.753746	-2127.17567	-2127.246438

Table S7. Optimized Cartesian coordinates (Å) for **1AB** in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

B	-0.03917038	0.01695358	-0.63086330	C	-3.97822355	-0.81004951	-3.39430133
O	1.05162189	0.82943757	-0.75461938	H	-2.31530180	-0.77945293	-4.76330171
O	0.09817187	-1.33111925	-0.78788227	H	-5.45318743	-0.71555210	-1.82539133
C	0.93713309	1.81672689	-1.68883641	C	-3.41512572	0.67592097	1.36717878
O	-1.29067120	0.56768889	-0.55984712	O	-5.29903185	-0.17178887	0.47139870
C	0.86179671	-1.70496617	-1.85566131	H	2.89582401	-2.86471823	-4.93469544
C	0.28048917	1.53429377	-2.89994588	C	2.30097304	-4.85534757	1.28259218
C	1.47446644	3.08436248	-1.41723725	H	2.11266376	-5.59969168	-0.86104400
C	-2.17905744	0.11451474	-1.49195239	C	2.20761249	-3.52871380	1.73320046
C	0.69622958	-1.02524714	-3.07467942	C	3.40337777	4.94017670	2.88836665
C	1.75497211	-2.77685319	-1.71962313	C	4.36974498	2.30078988	2.38515904
C	-0.28094064	0.14813050	-3.26965101	H	-4.68323584	-1.17522123	-4.14279970
C	0.13769139	2.57565908	-3.82194659	C	-4.43539205	0.66362963	2.38361435
C	1.31654216	4.09480268	-2.37368992	H	-2.39351930	1.02581068	1.45944398
C	2.14872326	3.38283774	-0.14776721	C	-5.57273354	0.12737700	1.76128535
C	-1.72510089	-0.11567865	-2.80291049	C	2.52114456	-5.87794716	2.21886521
C	-3.51879693	-0.08815061	-1.12229318	C	2.32497050	-3.15951685	3.07002835
C	1.44798704	-1.46117738	-4.16962210	C	4.28729355	4.31613712	3.76025681
C	2.47530935	-3.19195716	-2.84645359	H	3.03724887	5.94919463	3.08813548
C	1.94101293	-3.46233717	-0.43504841	C	4.76457023	3.01392547	3.51246290
H	-0.38181195	0.20695080	-4.35891583	H	4.72800879	1.29121607	2.17982482
C	0.64149270	3.84761431	-3.56361189	C	-4.51156519	1.04156542	3.73355822
H	-0.37434353	2.38019188	-4.76741767	C	-6.79041320	-0.05683475	2.40932794
H	1.74148499	5.08082384	-2.17645145	C	2.64108163	-5.53007196	3.55889481
C	2.11675272	4.50241496	0.62858128	H	2.59648509	-6.91976698	1.90109140
O	2.97393083	2.43500826	0.37962552	C	2.54496205	-4.18898141	3.97940314
C	-2.64752200	-0.58899001	-3.73989969	H	2.24702768	-2.11641299	3.37931274
C	-4.41088866	-0.55318831	-2.09986879	H	4.62061111	4.84238197	4.65723659
C	-3.99203894	0.16231243	0.24111682	H	5.45787340	2.55433773	4.22003047
C	2.32324214	-2.53956502	-4.06470370	C	-5.71860940	0.86633431	4.39945638
H	1.33861808	-0.94640429	-5.12731939	H	-3.64376514	1.46191913	4.24565816
H	3.17960237	-4.02028301	-2.74877234	C	-6.84314206	0.32442274	3.74656841
C	2.12217832	-4.78092398	-0.14588001	H	-7.65256047	-0.47799286	1.89066272
O	1.99251442	-2.69395026	0.69087469	H	2.81319620	-6.30945956	4.30421992
H	0.52456657	4.64226094	-4.30203013	H	2.64421321	-3.95245796	5.04088582
C	2.99228076	4.24020722	1.74290918	H	-5.80110787	1.15302293	5.44994759
H	1.52539187	5.39500418	0.44045023	H	-7.77581374	0.20055293	4.30093890
C	3.48475203	2.94346970	1.52412671				

11-2. Hetero-Diels-Alder reaction of 2 and 3a catalyzed by 1AB

*Intermediate **IM1***

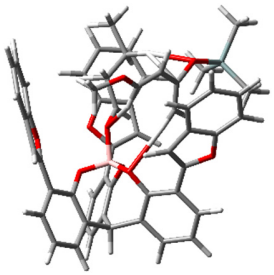


total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-2360.0188	-2359.32459	-2359.401104

Table S8. Optimized Cartesian coordinates (Å) for the intermediate **IM1** composed of **2**, **3a**, and **1A**B in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

B	0.57118151	0.65961423	0.08633276	C	-2.19632717	-1.50499583	-3.76180451
O	1.94797636	0.34319030	-0.01531399	H	-2.30066452	0.62066440	-4.58015889
O	-0.04658134	1.05010794	-1.13913972	C	-1.12539387	-2.09808169	-3.07382346
C	2.88496704	1.16627051	0.48705825	C	4.31062364	-4.20800102	2.84736208
O	0.23935427	1.51331695	1.18185312	C	3.72678279	-4.11464817	0.05504285
C	0.65891744	1.59383277	-2.14428144	H	-1.72023534	6.27386212	0.28904496
C	2.83044088	2.56260193	0.30435809	C	-3.35573536	0.22407145	2.95523927
C	3.93582162	0.58369809	1.22480770	H	-1.09829334	0.50455601	2.94754784
C	-0.25929349	2.73602872	0.92607513	C	-4.32141224	1.08344360	2.40775411
C	1.54783674	2.65875121	-1.93081180	C	-3.36570668	-2.25311792	-3.96996406
C	0.43185608	1.08136070	-3.43309054	C	-1.14466011	-3.40617319	-2.59788205
C	1.78115273	3.28160813	-0.55059112	C	4.15997752	-5.37156205	2.10177192
C	3.81802477	3.34484776	0.91311322	H	4.53303484	-4.25222370	3.91550560
C	4.90755781	1.40179591	1.81025645	C	3.87208173	-5.32636788	0.72374277
C	3.98534293	-0.86883647	1.44231498	H	3.50270004	-4.06161959	-1.01126087
C	0.46865636	3.65018606	0.14782605	C	-3.77126602	-0.97433257	3.55636907
C	-1.54475467	3.05572315	1.40611871	C	-5.68522255	0.80806191	2.41252146
C	2.19944066	3.19121241	-3.04868214	C	-3.41219873	-3.55554964	-3.48585345
C	1.08030930	1.65124833	-4.52910544	H	-4.21879484	-1.82094099	-4.49651886
C	-0.50125549	-0.05318956	-3.54867960	C	-2.31572333	-4.12670172	-2.81147479
H	2.24620247	4.25012586	-0.77286182	H	-0.28336144	-3.83350675	-2.08179430
C	4.84411054	2.78326680	1.66803567	H	4.26633293	-6.34220647	2.59102125
H	3.78265325	4.42958364	0.78082500	H	3.76044458	-6.26037673	0.16886315
H	5.71980280	0.93922346	2.37499255	C	-5.12942099	-1.26908790	3.56881591
C	4.23311370	-1.58516063	2.57497794	H	-3.04478100	-1.66032232	3.99721822
O	3.77878579	-1.68965030	0.37286672	C	-6.07384048	-0.39157823	3.00228848
C	-0.07465042	4.92096011	-0.05953989	H	-6.40542670	1.49722680	1.96977593
C	-2.05953656	4.33760023	1.17380500	H	-4.31503680	-4.15204585	-3.63179995
C	-2.37415018	2.01533255	2.02238216	H	-2.38468269	-5.15490254	-2.45046181
C	1.97070225	2.70530647	-4.33494569	H	-5.47474367	-2.19934668	4.02468898
H	2.89619460	4.02164578	-2.90566589	H	-7.13289910	-0.65633710	3.02691294
H	0.89607707	1.25317627	-5.52910547	O	-0.15007956	-0.72930859	0.48242012
C	-1.75108639	-0.16628537	-4.07020173	C	-1.28157278	-0.99249510	0.06748368
O	-0.10572414	-1.21749195	-2.94730411	C	-2.04153055	-2.16813988	0.53676901
H	5.60262422	3.42089388	2.12514217	H	-1.72441411	-0.31950441	-0.68954061
C	4.16973452	-2.97383770	2.19359839	C	-3.50658950	-2.14423423	0.11119630
H	4.41457590	-1.17101057	3.56363184	H	-1.91330823	-2.24756526	1.62936165
C	3.88170315	-2.96129352	0.81878533	H	-1.52402342	-3.05087484	0.11610621
C	-1.31940566	5.27324883	0.46019235	C	-4.24726099	-3.40954665	0.51846471
H	0.48687280	5.64680486	-0.65396089	H	-3.99666814	-1.26359830	0.55869218
H	-3.05474043	4.58677529	1.54556796	H	-3.55646663	-2.01884704	-0.98358753
C	-2.09055542	0.85823812	2.68936550	H	-5.30173478	-3.36189245	0.21171595
O	-3.72461679	2.16842187	1.86241028	H	-3.79743645	-4.29869689	0.04916472
H	2.48845993	3.15038049	-5.18630268	H	-4.22071552	-3.54873401	1.61027243

*Intermediate **IM2***

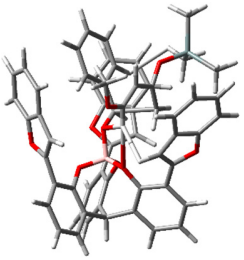


total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-3113.921718	-3112.999826	-3113.094246

Table S9. Optimized Cartesian coordinates (Å) for the intermediate **IM2** composed of **2**, **3a**, and **1A**B in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

B	-1.45946466	0.21847442	-0.58010708	H	-1.93000655	1.29491938	4.41956591
O	-2.75543444	0.34861392	-0.00771398	C	2.34472007	-4.94568373	0.27756328
O	-1.07373570	1.30949166	-1.42607701	C	3.99802697	-4.14051179	-1.90409600
C	-3.76802017	-0.45341586	-0.36455802	C	2.91273202	5.60787165	1.30866786
O	-1.19663726	-1.07339366	-1.15320705	H	3.42024119	5.24703716	-0.76349950
C	-1.99139815	2.13543684	-1.95823094	C	1.91989184	5.56369287	2.30629230
C	-4.13992347	-0.56242234	-1.71471422	H	-0.14705014	5.07492039	2.78810821
C	-4.44150752	-1.19501803	0.62797435	H	-1.86949630	-2.06906830	7.14695024
C	-1.19950043	-1.25269167	-2.48942669	H	-1.25807028	0.26819842	6.60794024
C	-3.12486196	1.63671190	-2.62181967	C	3.67993223	-5.32249922	0.20700355
C	-1.78063273	3.51972583	-1.84735263	H	1.72448954	-5.23373763	1.12792323
C	-3.37381461	0.14506887	-2.83103896	C	4.49796015	-4.92387664	-0.86841814
C	-5.22476770	-1.37705847	-2.04761190	H	4.61736479	-3.82259176	-2.74385427
C	-5.53441841	-1.99004862	0.25689213	H	3.91237644	5.96156817	1.56919812
C	-3.94378542	-1.26543034	2.00775554	H	2.16617098	5.88291428	3.32091134
C	-2.15486986	-0.64046770	-3.32932068	H	4.10980826	-5.93435729	1.00304374
C	-0.21043949	-2.08993001	-3.05111930	H	5.54465444	-5.23490329	-0.88993667
C	-4.03793539	2.55533098	-3.14696982	O	-0.52770671	0.32360258	0.70303647
C	-2.70780370	4.41114451	-2.39310124	C	0.38951086	1.14974666	0.84345129
C	-0.60239322	4.01352346	-1.10845464	C	1.48195823	-2.05041309	1.80219790
H	-4.06430765	0.11225284	-3.68268962	C	2.22373947	-0.39452106	-0.59681092
C	-5.93044059	-2.07865836	-1.07218365	C	0.99953532	1.36028328	2.17009768
H	-5.52323123	-1.46044644	-3.09605672	H	0.63140804	1.82085764	0.00235736
H	-6.07365918	-2.54527411	1.02725677	C	2.73652193	-1.69831204	1.47799481
C	-3.94143650	-2.32056215	2.87523246	O	1.21083258	-2.93440121	2.76827203
O	-3.33727057	-0.17712965	2.55848267	H	0.60993025	-1.65073718	1.27078624
C	-2.02151816	-0.79370273	-4.71295297	C	3.07358871	-0.78303343	0.38415124
C	-0.11023159	-2.21266772	-4.44244275	H	2.51826046	0.31519642	-1.36965042
C	0.71111508	-2.85880826	-2.20909935	H	1.26117689	-0.88463546	-0.71133208
C	-3.84241106	3.93071298	-3.03931544	C	2.38882895	1.98528598	2.18839525
H	-4.92398419	2.17801360	-3.66492255	H	0.93917719	0.42833888	2.75434749
H	-2.53389546	5.48528695	-2.29974955	H	0.27557332	2.05689350	2.64438596
C	0.67326293	4.28593034	-1.48633981	H	3.57388913	-2.10400895	2.04952115
O	-0.79098553	4.26232340	0.22518884	C	-0.12089428	-2.92790500	3.24778156
H	-6.78570501	-2.69677144	-1.35046344	O	4.33699341	-0.32650463	0.49418936
C	-3.26634921	-1.86463389	4.06190116	C	2.81226294	2.38881552	3.59422594
H	-4.33618600	-3.31349712	2.67592573	H	3.11590077	1.27364790	1.77678299
C	-2.91064613	-0.53362711	3.78897772	H	2.40087789	2.86442871	1.52616727
C	-0.99876861	-1.54960867	-5.27770143	H	-0.23381498	-3.79327350	3.91072545
H	-2.75311578	-0.30886495	-5.36496448	H	-0.84722829	-3.00723740	2.42170478
H	0.67381858	-2.84736302	-4.85885266	H	-0.33050712	-2.00903880	3.81959148
C	0.55223656	-3.53050375	-1.03512073	Si	5.29421406	0.53917333	-0.62750512
O	1.97790079	-3.01133190	-2.69970302	H	3.81141322	2.84777945	3.58356497
H	-4.57005946	4.62367122	-3.46502097	H	2.11260262	3.12009008	4.02788676
C	1.35231568	4.75875962	-0.30298448	H	2.84891424	1.51508268	4.26377308
H	1.07804919	4.16713049	-2.48795691	C	6.97193936	0.58642887	0.18668770
C	0.38551443	4.72155669	0.71454495	C	5.34702092	-0.41783610	-2.23366950
C	-2.89322652	-2.43020470	5.29135896	C	4.61455750	2.27361459	-0.82317703
C	-2.19229155	0.26678096	4.67222406	H	6.92147723	1.09590858	1.16128144
H	-0.91763601	-1.64616956	-6.36166041	H	7.69023519	1.13074741	-0.44659061
C	1.82137308	-4.15046400	-0.75270576	H	7.35956328	-0.43112236	0.34801889
H	-0.36151286	-3.56859083	-0.44929110	H	5.77733940	-1.41617653	-2.05755083
C	2.65838024	-3.77537334	-1.81415127	H	5.98294889	0.10443046	-2.96615783
C	2.64481529	5.21106700	0.00370616	H	4.34982928	-0.55282238	-2.67729631
C	0.63305316	5.11541705	2.02673225	H	3.59037285	2.29629065	-1.22390144
C	-2.17495201	-1.64697661	6.18723480	H	5.25839685	2.85042194	-1.50682116
H	-3.15235706	-3.46293430	5.53315145	H	4.60514734	2.79188599	0.14836434
C	-1.82604057	-0.31691557	5.88165055				

First transition state ***TS1***

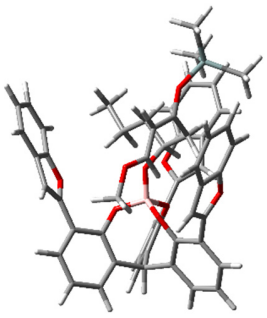


imaginary frequency / cm^{-1}	total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-242.4877	-3113.920641	-3112.998253	-3113.090984

Table S10. Optimized Cartesian coordinates (Å) for the transition state **TS1** composed of **2**, **3a**, and **1A**B in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

O	-2.72519627	0.32791560	0.59682203	C	2.12024098	-5.19940935	0.10632886
O	-1.61163634	0.98343291	-1.43840973	C	3.25994555	-4.41796402	-2.39003875
C	-3.74610856	-0.52944802	0.70805844	C	3.08204698	5.40693432	-1.49509894
O	-1.56806936	-1.30917937	-0.74583454	H	2.86314902	4.08623552	-3.19396881
C	-2.67329591	1.74622796	-1.73886115	C	2.46568779	6.01322973	-0.38367904
C	-4.52727619	-0.86498637	-0.40494901	H	0.63427838	6.24788243	0.77052671
C	-3.98910277	-1.11652267	1.96320027	H	1.06709307	0.00861645	6.76240311
C	-1.99331624	-1.67764365	-1.96883452	H	0.10560343	2.26179332	6.40049270
C	-3.95714826	1.18556119	-1.86856757	C	3.43537724	-5.51270410	-0.21516618
C	-2.47969316	3.12793920	-1.92029876	H	1.68725178	-5.49844764	1.06301470
C	-4.20902227	-0.31918857	-1.79287015	C	3.99821938	-5.12785518	-1.44767761
C	-5.57917929	-1.76890226	-0.22797481	H	3.68382166	-4.11157417	-3.34702764
C	-5.04164760	-2.02223246	2.10888017	H	4.13555863	5.61169797	-1.69725316
C	-3.02596995	-0.84116128	3.04163370	H	3.05103494	6.67361913	0.25940042
C	-3.18153866	-1.17296579	-2.54430420	H	4.04698691	-6.07017540	0.49758016
C	-1.21441360	-2.60595779	-2.69562232	H	5.03438962	-5.39212662	-1.66960151
C	-5.03230973	2.04223009	-2.11483920	O	-0.40938557	0.36179730	0.55321375
C	-3.57911784	3.95798796	-2.16065324	C	0.56989722	1.07791506	0.17445433
C	-1.11768201	3.68268193	-1.84360288	C	1.13478807	-2.11844774	1.39515877
H	-5.13691154	-0.46417466	-2.36133477	C	1.50628518	1.58713982	1.17113576
C	-5.84442992	-2.34155631	1.01496143	H	0.49891825	1.59439502	-0.79103528
H	-6.19852231	-2.03643123	-1.08870684	C	1.79644112	-0.49611406	-1.03825216
H	-5.22268271	-2.47986314	3.08395899	C	2.36914536	-1.63625483	1.12404569
C	-2.13196756	-1.65800810	3.66103748	H	0.27485004	-1.92325216	0.75241664
O	-2.89163398	0.45223116	3.45590728	O	0.79545688	-2.87433758	2.43008764
C	-3.47654549	-1.50944134	-3.86874178	C	1.44356455	1.16148450	2.50691337
C	-1.54139352	-2.91289505	-4.02145204	C	2.47770285	2.51686784	0.77655917
C	-0.08410642	-3.29638968	-2.06429392	C	2.67429624	-0.81328461	-0.02953469
C	-4.85841050	3.41933683	-2.24638852	H	2.13394893	0.10156565	-1.88534590
H	-6.03439545	1.61498309	-2.21143979	H	0.88221951	-1.07122518	-1.16997581
H	-3.41975461	5.03118491	-2.28603499	H	3.21332148	-1.82291523	1.78727673
C	-0.01676858	3.48340440	-2.61654571	C	1.78837217	-3.21439936	3.37591194
O	-0.86121899	4.56121529	-0.82873397	C	2.36057946	1.65694022	3.42902143
H	-6.67231412	-3.04381515	1.12824321	H	0.66718954	0.45934248	2.81708477
C	-1.35261856	-0.81055495	4.52873135	C	3.38679317	3.01270625	1.70334620
H	-2.00646355	-2.72146864	3.47772386	H	2.51150813	2.85573598	-0.26054513
C	-1.87597378	0.48035310	4.34631585	O	3.89224820	-0.28166853	0.03396487
C	-2.65792477	-2.34686904	-4.62178493	H	2.19750205	-2.31006979	3.85435757
H	-4.38712707	-1.10422749	-4.31862330	H	1.30167424	-3.84217776	4.13034269
H	-0.91189340	-3.61601087	-4.57058163	H	2.60655589	-3.77833730	2.89994277
C	0.02809782	-3.93693655	-0.86989845	C	3.33251070	2.57616799	3.02871690
O	1.06635928	-3.40448263	-2.79662070	H	2.30818741	1.32828666	4.46825245
H	-5.71732186	4.06560413	-2.43532131	H	4.13504555	3.74403669	1.39134709
C	1.02689077	4.29952635	-2.04804791	Si	5.02337831	0.12801795	-1.19455107
H	0.03847460	2.82951387	-3.48286995	H	4.04720610	2.96301352	3.75855716
C	0.43674154	4.92958388	-0.93971001	C	5.03127323	-1.27775579	-2.42242016
C	-0.27532572	-0.98805301	5.41006292	C	4.57988770	1.75313240	-2.00311231
C	-1.38593948	1.60734204	4.99946834	C	6.62358267	0.27586562	-0.25216661
H	-2.91260922	-2.58424084	-5.65604080	H	5.80514607	-1.10921454	-3.18799942
C	1.36135924	-4.47715434	-0.82615258	H	5.24503744	-2.23200726	-1.91695911
H	-0.74886074	-4.00463895	-0.11361900	H	4.06082881	-1.37542981	-2.93224437
C	1.94911866	-4.10509819	-2.04502115	H	4.62014083	2.58455241	-1.28385572
C	2.37658834	4.55384025	-2.33618655	H	5.30776195	1.96517402	-2.80328576
C	1.12510069	5.78732481	-0.08757106	H	3.57869720	1.74170735	-2.45849171
C	0.22924718	0.12606130	6.07149876	H	7.44339581	0.56416359	-0.92871196
H	0.15158914	-1.97833725	5.57807125	H	6.53955117	1.04555123	0.53074088
C	-0.31885604	1.40731867	5.86928130	H	6.89074960	-0.67796576	0.22740852
H	-1.81684164	2.59406802	4.82572980	B	-1.64437057	0.07881260	-0.31197559

*Intermediate **IM3***

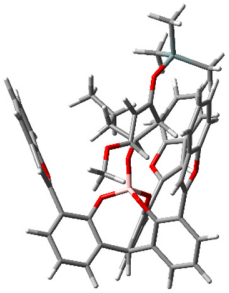


total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-3113.966469	-3113.039763	-3113.131804

Table S11. Optimized Cartesian coordinates (Å) for the intermediate **IM3** composed of **2**, **3a**, and **1A**B in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

B	1.25211761	-0.16844345	-0.39097382	H	0.38218332	-2.80164558	4.35735755
O	2.24153894	-0.61972324	0.58617127	C	-1.46073304	5.71440932	-0.49363139
O	1.15928353	-1.08034961	-1.53717913	C	-2.90780334	3.72782131	-1.94239786
C	3.43113686	-0.06483595	0.77495676	C	-4.31515962	-4.45228619	-1.68974302
O	1.59616951	1.20020253	-0.89755758	H	-3.85872408	-2.70706106	-2.88684567
C	2.05292793	-2.04466216	-1.76351693	C	-3.81345888	-5.52681868	-0.93102863
C	4.33224005	0.11448187	-0.29068882	H	-2.04048826	-6.53947968	-0.17234492
C	3.79386456	0.34778536	2.07858554	H	-0.63552234	-0.08322830	7.57056668
C	2.18330131	1.43471047	-2.07313900	H	-0.92939019	-2.25855699	6.42327844
C	3.43593856	-1.77308564	-1.79923539	C	-2.84857176	5.65319986	-0.44614466
C	1.59584676	-3.36640572	-1.97599527	H	-0.91452225	6.47712947	0.06473580
C	4.01017578	-0.36078470	-1.70362099	C	-3.56386501	4.67786021	-1.16671658
C	5.55468278	0.74409135	-0.04520030	H	-3.44499687	2.96375256	-2.50510000
C	5.02948832	0.97109905	2.28876002	H	-5.39577752	-4.33541666	-1.79657218
C	2.86372767	0.19007220	3.20405277	H	-4.51124460	-6.22436415	-0.46311840
C	3.29004537	0.69438199	-2.54067720	H	-3.39901471	6.37836140	0.15661529
C	1.69117000	2.50496607	-2.85273077	H	-4.65479532	4.66906599	-1.11459735
C	4.32475937	-2.83743196	-1.96779833	O	0.00189638	-0.07191231	0.32660238
C	2.51724148	-4.40840387	-2.13351254	C	-1.20486542	-0.58418764	-0.11484583
C	0.15778267	-3.64912847	-1.99299795	C	-0.61101231	2.50725887	1.00938824
H	4.99365758	-0.44730414	-2.18353376	C	-2.15961270	0.55062454	-0.60213669
C	5.90691210	1.18219663	1.23026967	C	-1.83204107	-1.46892891	0.95785810
H	6.25112697	0.88725412	-0.87649977	H	-1.03846984	-1.20291850	-1.00665797
H	5.30217627	1.28049557	3.30041535	C	-1.94526687	2.26590489	1.27587939
C	2.55918872	1.03914054	4.22870937	O	0.09278768	3.20910344	1.83249580
O	2.17184637	-0.97808914	3.31500647	H	-0.10284056	2.12372148	0.11858914
C	3.80764108	0.99649855	-3.80390599	C	-2.70987858	1.39519448	0.50007901
C	2.24539216	2.79116890	-4.10212521	H	-2.98856795	0.09220518	-1.15729314
C	0.59445340	3.33132355	-2.31506446	H	-1.58840096	1.16292699	-1.31217976
C	3.88225835	-4.15081671	-2.11713021	C	-0.89829111	-2.58272757	1.41854526
H	5.39795471	-2.62692451	-1.98783589	H	-2.75375385	-1.91119725	0.54690736
H	2.14691381	-5.42616197	-2.27352313	H	-2.12711332	-0.85722479	1.83058938
C	-0.89824635	-2.98878643	-2.54088832	H	-2.41683287	2.74195216	2.13638531
O	-0.25685399	-4.76124859	-1.30923056	C	1.48202096	3.42974231	1.55656637
H	6.87080068	1.66507723	1.40073872	O	-3.95384624	1.26927992	0.84380306
C	1.58043951	0.36001225	5.03927532	C	-1.58143734	-3.57498285	2.35108761
H	2.97314426	2.03320479	4.37985941	H	-0.50806464	-3.11488998	0.53748110
C	1.38855435	-0.88135385	4.41103312	H	-0.02100749	-2.13180988	1.90640756
C	3.29491987	2.02275875	-4.59403704	H	1.80610335	2.81423927	0.70665530
H	4.65880086	0.41528522	-4.17007039	H	2.03383779	3.14982567	2.46037179
H	1.84409245	3.62391033	-4.68422454	H	1.62011449	4.49765836	1.34821193
C	0.60311121	4.44958014	-1.54478745	Si	-5.44613556	0.61861046	0.20916871
O	-0.68615695	2.92566853	-2.58330552	H	-0.88439559	-4.35933626	2.68466003
H	4.60030535	-4.96328683	-2.24188745	H	-1.97575189	-3.07230130	3.24964234
C	-2.07901397	-3.70702834	-2.13832689	H	-2.42640732	-4.07379455	1.84860005
H	-0.83320648	-2.08020485	-3.13219697	C	-6.68631991	1.29818065	1.41430317
C	-1.60870128	-4.78919574	-1.37656655	C	-5.68333471	1.30009757	-1.50997296
C	0.84293593	0.65696849	6.19615054	C	-5.38443159	-1.24120933	0.23627554
C	0.50215823	-1.84895990	4.87408700	H	-6.48339858	0.93460707	2.43301128
H	3.72813376	2.23498785	-5.57294251	H	-7.70137300	0.97817012	1.13174562
C	-0.77800579	4.76484857	-1.26873583	H	-6.66213582	2.39828263	1.42563004
H	1.49195685	4.96898959	-1.19704202	H	-5.66563299	2.39998251	-1.50737186
C	-1.51862036	3.79155992	-1.95590995	H	-6.67149342	0.98110707	-1.87897188
C	-3.46263360	-3.53856513	-2.29975021	H	-4.92938487	0.93353067	-2.22230350
C	-2.44433519	-5.71634801	-0.76316390	H	-4.70303974	-1.66014540	-0.51837711
C	-0.05072345	-0.29545176	6.67283907	H	-6.39612763	-1.62110213	0.01868913
H	0.96655269	1.61385277	6.70757278	H	-5.08674221	-1.61999127	1.22551024
C	-0.21916038	-1.53272173	6.02130794				

Second transition state ***TS2***

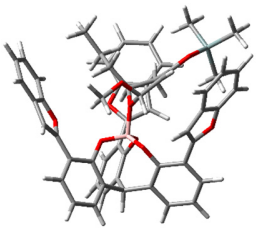


imaginary frequency / cm^{-1}	total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-203.0439	-3113.952055	-3113.026066	-3113.117719

Table S12. Optimized Cartesian coordinates (Å) for the transition state **TS2** composed of **2**, **3a**, and **1A**B in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

B	-1.42217250	-0.17778771	-0.29357855	H	-0.45057075	5.18276719	1.82117300
O	-2.24960032	0.94554742	0.12084220	C	1.28584242	-5.30957243	2.45548796
O	-1.13615851	-0.13918773	-1.71960903	C	2.54104724	-4.00114276	0.25301649
C	-3.52738742	0.82658412	0.47790513	C	4.85393214	1.46762996	-3.51039710
O	-1.98822966	-1.47124328	0.06167624	H	4.05118981	-0.53530926	-3.34746734
C	-1.85449421	0.59756907	-2.57623702	C	4.57884783	2.84151343	-3.65233629
C	-4.46020604	0.16103563	-0.33452599	H	3.04332605	4.37268381	-3.85114109
C	-3.93053239	1.37789793	1.71355920	H	0.91921728	4.41937000	5.85863891
C	-2.56451108	-2.27256517	-0.84416067	H	1.05627017	5.71930797	3.75496931
C	-3.26425908	0.56706719	-2.58023898	C	2.66609829	-5.15651149	2.39725771
C	-1.16520991	1.41637848	-3.49922371	H	0.81342032	-5.81265568	3.30144330
C	-4.09348331	-0.38315784	-1.71136251	C	3.28649914	-4.51697063	1.30729895
C	-5.76832581	0.01030647	0.13471562	H	3.00797347	-3.50269165	-0.59736744
C	-5.24586560	1.20825743	2.15390076	H	5.89243359	1.13697449	-3.44120291
C	-2.93823544	2.06826293	2.55086392	H	5.40681980	3.55239585	-3.68924875
C	-3.58580292	-1.82278775	-1.70178711	H	3.28538785	-5.54339617	3.20906582
C	-2.13692710	-3.61395970	-0.90609189	H	4.37444358	-4.42288637	1.29244747
C	-3.94498139	1.42032410	-3.45319552	O	-0.14267504	-0.05701301	0.49153851
C	-1.88326898	2.26129019	-4.35302682	C	0.97474800	0.60622754	-0.06066472
C	0.30056344	1.39133202	-3.55208377	C	0.22795164	-1.27524507	1.95374921
H	-5.05511748	-0.44423224	-2.23680738	C	2.14785406	-0.39082365	-0.10463196
C	-6.16514446	0.51391199	1.37186673	C	1.27393352	1.92301817	0.64949741
H	-6.49596078	-0.51292090	-0.49235113	H	0.72952304	0.82898704	-1.10305398
H	-5.54320656	1.63340536	3.11519016	C	1.62937393	-1.06220217	2.22805938
C	-2.53462110	1.84923838	3.83240809	O	-0.55716944	-1.00275409	2.95161723
O	-2.26188863	3.11257171	1.99019402	H	-0.11297755	-2.04923638	1.26492256
C	-4.17074447	-2.74355644	-2.57659116	C	2.55930420	-0.76667206	1.28666845
C	-2.75486140	-4.51199748	-1.77938507	H	2.98542943	0.05082704	-0.65978044
C	-0.99079667	-4.03915179	-0.08090408	H	1.81102570	-1.27447579	-0.66940002
C	-3.27224909	2.27703037	-4.32220637	C	2.06388515	2.87754401	-0.24507358
H	-5.03849665	1.40622829	-3.45390860	H	1.80574856	1.74661345	1.60037684
H	-1.33651279	2.90280310	-5.04702446	H	0.30841980	2.37773613	0.91759336
C	1.20159827	0.37468358	-3.46152462	H	1.92331529	-1.10923283	3.27772626
O	0.93044405	2.59675932	-3.70701323	C	-1.88454855	-1.52964935	2.99253256
H	-7.19309084	0.38343578	1.71462543	O	3.82521138	-0.66171483	1.65841724
C	-1.50150465	2.81913897	4.10009175	C	2.59367017	4.10458766	0.48407037
H	-2.90744217	1.07068460	4.49290958	H	2.90924505	2.34461188	-0.71066217
C	-1.39141354	3.56841264	2.91796433	H	1.41948389	3.18951312	-1.08378294
C	-3.77770323	-4.07930597	-2.61710871	H	-1.92651210	-2.50713542	2.49647403
H	-4.96727889	-2.39972088	-3.24230298	H	-2.57002107	-0.83443662	2.49450625
H	-2.41317990	-5.54903460	-1.80681249	H	-2.14132688	-1.62249225	4.05332957
C	-0.89490007	-4.72389446	1.08863312	Si	5.32617070	-0.45258008	0.84711699
O	0.24796926	-3.68279894	-0.54861706	H	3.14203592	4.76934458	-0.20012455
H	-3.83230246	2.93535117	-4.98856587	H	1.77506566	4.68353266	0.93713989
C	2.50448008	0.98172692	-3.53406882	H	3.27966891	3.81683921	1.29690614
H	0.95535821	-0.67324471	-3.31795899	C	6.56393640	-0.78506117	2.19731327
C	2.26259137	2.35668080	-3.68285169	C	5.45535192	-1.70500194	-0.53477909
C	-0.65877203	3.12647150	5.17929793	C	5.45112898	1.29976696	0.21444744
C	-0.49607232	4.62051164	2.75482299	H	6.44892253	-0.06449356	3.02142607
H	-4.26240580	-4.77511852	-3.30402787	H	7.58933755	-0.69634673	1.80557986
C	0.51351995	-4.79908953	1.40108008	H	6.43712034	-1.79982282	2.60435655
H	-1.73003540	-5.11216201	1.66628256	H	5.42963301	-2.73342304	-0.14421619
C	1.16008051	-4.14806142	0.33957831	H	6.41297441	-1.56837517	-1.06256728
C	3.83039499	0.52882742	-3.45333131	H	4.64960846	-1.59216835	-1.27489180
C	3.27208093	3.31139026	-3.74622358	H	4.88181490	1.45462563	-0.71396469
C	0.25178291	4.16681331	5.03188146	H	6.50594841	1.53216444	-0.00390416
H	-0.71480829	2.55997284	6.11110747	H	5.09387211	2.01779413	0.96877700
C	0.33106841	4.90674404	3.83628590				

*Adduct **1AB·5a***



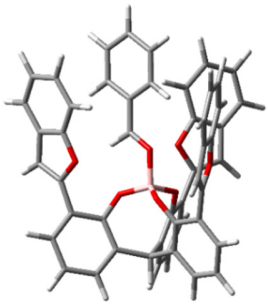
total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-3113.9665222	-3113.037692	-3113.128517

Table S13. Optimized Cartesian coordinates (Å) for **1AB·5a** in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

B	0.95728801	-0.91084355	0.44659322	H	3.38875913	3.64802697	-1.41648607
O	2.32818304	-0.56487700	0.23040533	C	-3.19821919	-3.69000063	-3.46776537
O	0.43035557	-0.41501015	1.68455313	C	-4.97294616	-2.86180523	-1.39340635
C	3.33638690	-1.44459069	0.33112394	C	-3.07812046	5.17406427	2.02310844
O	0.64577665	-2.27858777	0.17972495	H	-3.94927149	3.25674117	2.50895459
C	1.24359039	-0.15086990	2.72886549	C	-1.90357375	5.93891176	1.88736942
C	3.35022807	-2.44351747	1.32571358	H	0.26917738	5.96292075	2.02708492
C	4.41682070	-1.33816611	-0.57377316	H	4.81082770	3.70247337	-5.50785054
C	0.26944518	-3.09417884	1.18444705	H	3.79610165	4.86716036	-3.57312942
C	2.21518355	-1.07958514	3.14638906	C	-4.50051160	-3.29093426	-3.74752547
C	1.11139312	1.07590925	3.40832256	H	-2.52313438	-4.00020975	-4.26785973
C	2.38005134	-2.45797905	2.50809036	C	-5.37757504	-2.88295596	-2.72417705
C	4.37222483	-3.39628834	1.30211749	H	-5.63738847	-2.54894666	-0.58698702
C	5.43054457	-2.30401057	-0.55190260	H	-4.04444475	5.64237845	1.82483602
C	4.50215257	-0.24603981	-1.54978921	H	-1.97771379	6.98591266	1.58656504
C	1.06791827	-3.21446080	2.33241077	H	-4.85394202	-3.29249796	-4.78081176
C	-0.93689368	-3.80851135	1.07726372	H	-6.39340358	-2.57453679	-2.98046665
C	3.07389056	-0.73034774	4.19148410	O	0.14129542	-0.07856695	-0.70379929
C	1.99442230	1.39541371	4.44637670	C	-0.35558605	1.25887849	-0.40174056
C	0.06135141	2.04113600	3.05168775	C	-0.39405740	-0.71256494	-1.92178117
H	2.91475877	-3.03761853	3.27068862	C	-1.84897662	1.13000439	-0.14948724
C	5.39514023	-3.35249134	0.35833673	C	0.05189892	2.26913361	-1.46631563
H	4.37687379	-4.17937818	2.06517885	H	0.14380761	1.51899002	0.53582986
H	6.26385575	-2.21118119	-1.25152650	C	-1.85749078	-0.46488577	-2.04604656
C	4.97793210	-0.22416194	-2.82847098	O	0.25339118	-0.24675370	-3.03660892
O	4.04719294	0.98309655	-1.17344950	H	-0.17484346	-1.77445811	-1.74390042
C	0.62387070	-4.03605110	3.37139107	C	-2.53836941	0.36571011	-1.24694456
C	-1.35718368	-4.61481254	2.14120145	H	-2.28191524	2.13528594	-0.04877491
C	-1.77549688	-3.69091051	-0.12480873	H	-2.00439468	0.61655128	0.81133443
C	2.98345172	0.50103020	4.83448489	C	-0.02040431	3.69854754	-0.93243183
H	3.83484009	-1.44885359	4.50790752	H	-0.57522991	2.15938271	-2.36400880
H	1.88841333	2.35716343	4.95237966	H	1.08536070	2.04739125	-1.77424567
C	-1.29404129	1.94724613	3.01029549	H	-2.37148789	-1.00917497	-2.83863031
O	0.48164148	3.30913915	2.75546910	C	1.60774983	-0.62653365	-3.12957863
H	6.18554143	-4.10474257	0.36593283	O	-3.85807456	0.52246039	-1.41320944
C	4.78657505	1.12171079	-3.30520641	C	0.24528427	4.74407701	-2.00812677
H	5.37593676	-1.07423532	-3.37670532	H	-1.00896785	3.88849158	-0.48021966
C	4.20403673	1.81086068	-2.22947349	H	0.70780780	3.81038607	-0.11154362
C	-0.58174784	-4.72911243	3.28899080	H	1.71908568	-1.72516572	-3.11909092
H	1.23948567	-4.12940291	4.27019907	H	2.17938595	-0.20656195	-2.29201197
H	-2.30171599	-5.15594765	2.05528623	H	2.00077658	-0.22757395	-4.07223303
C	-1.53652978	-3.94873243	-1.43788738	Si	-5.10651148	1.20770878	-0.48031388
O	-3.06419160	-3.28188821	0.07672147	H	0.22545947	5.76049859	-1.58788774
H	3.66895403	0.75161230	5.64568163	H	1.22850588	4.58963615	-2.47906601
C	-1.77688612	3.25530810	2.64208173	H	-0.51370423	4.69307291	-2.80439099
H	-1.87040041	1.05152011	3.22655191	C	-6.66711437	0.59949344	-1.30042284
C	-0.62545824	4.04583485	2.50222947	C	-4.96406983	0.58226699	1.27836586
C	5.01076171	1.81014473	-4.50835113	C	-5.00564330	3.07245281	-0.59570602
C	3.83703296	3.15217188	-2.27879864	H	-6.67715736	0.87672644	-2.36578983
H	-0.90920601	-5.36264388	4.11506301	H	-7.54951976	1.05183031	-0.82070323
C	-2.76840141	-3.67041112	-2.13248424	H	-6.75981892	-0.49386937	-1.23025617
H	-0.59516141	-4.29766018	-1.85444889	H	-4.87282020	-0.51521532	1.28946676
C	-3.66577364	-3.25785085	-1.13537927	H	-5.86165823	0.85800557	1.85455723
C	-3.03119602	3.83795767	2.40347944	H	-4.08943493	0.99892337	1.79843719
C	-0.65069719	5.38618448	2.13082984	H	-4.07908523	3.47971724	-0.16509388
C	4.64666941	3.14963142	-4.58048935	H	-5.85102082	3.52873399	-0.05536093
H	5.45775867	1.30463534	-5.36671637	H	-5.06527748	3.39006264	-1.64848454
C	4.06875733	3.81365349	-3.48056668				

11-3. Hetero-Diels-Alder reaction of 2 and 3b catalyzed by 1AB

*Intermediate **IM1***

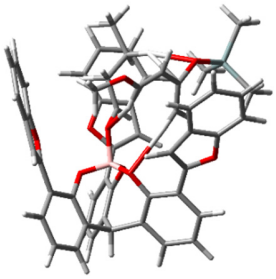


total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-3226.885284	-3225.968849	-3226.090344

Table S14. Optimized Cartesian coordinates (Å) for the intermediate **IM1** composed of **2**, **3b**, and **1A**B in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

O	-0.54632514	-0.07804845	0.12235662	O	-0.30622514	-3.20964444	-1.09588717
B	1.02897943	-0.05115432	-0.06833201	H	5.56730122	-2.11012648	-1.14903222
C	-1.31489692	-0.26153282	-0.83456527	C	3.98907570	2.99867394	-2.81729908
O	1.53325157	-0.75922962	1.05734560	H	2.44883457	4.48504979	-3.11158835
O	1.25886942	-0.70444917	-1.32307281	C	0.24966513	4.93908161	-1.18511572
O	1.36785199	1.33669759	-0.07870681	O	-0.57184957	2.85829256	-1.44573442
C	-2.74645687	-0.25567731	-0.68367124	H	5.31797243	1.38024829	-2.32504435
H	-0.88074265	-0.43940134	-1.83205662	H	-6.59707708	-0.19230394	-0.37078352
C	2.62747794	-0.33148077	1.70834096	H	5.75919253	0.65937601	3.78908666
C	2.22964337	-1.61849850	-1.47946306	C	-0.58382777	-1.15431718	4.86972217
C	2.23026835	1.82688536	-0.98169120	H	1.41077492	-2.24259981	5.06550045
C	-3.53994954	-0.40159995	-1.83271789	C	-0.86225573	-0.03055145	4.07419315
C	-3.33825524	-0.10097878	0.58232753	H	4.97095429	-4.26215945	-2.22083088
C	2.55051875	-0.26124820	3.11234258	C	-1.67851418	-3.51899734	-2.86581310
C	3.81901225	0.00608578	1.04060179	H	0.01780735	-3.29484434	-4.37446767
C	1.87370203	-2.85878469	-2.03718797	C	-1.58601708	-3.44811255	-1.46717682
C	3.55934333	-1.33929420	-1.13180267	H	4.68101064	3.44859586	-3.53125630
C	1.85626977	2.99605941	-1.67348206	C	-1.18297178	5.00026646	-1.04113645
C	3.48560375	1.23112952	-1.21064640	H	0.96475006	5.75382662	-1.10329393
C	-4.92441043	-0.37289375	-1.71777489	C	-1.62513431	3.67851558	-1.21305186
H	-3.06673187	-0.54092986	-2.80743357	C	-1.61819940	-1.71672116	5.63328147
C	-4.71989473	-0.08141590	0.68947618	C	-2.11292436	0.57747972	4.01114378
H	-2.70313148	-0.00301691	1.46390338	C	-2.93638219	-3.73615086	-3.45033851
C	3.68039710	0.07688446	3.85907326	C	-2.67348850	-3.59727501	-0.61125285
C	1.24805493	-0.50675156	3.75339124	C	-2.12514464	6.00767766	-0.78321816
C	3.98336361	-0.02245131	-0.48224475	C	-2.96529741	3.30704588	-1.14891772
C	4.92503805	0.36366983	1.82077384	C	-2.87933483	-1.13375841	5.57200052
C	2.86333343	-3.80254201	-2.31795548	H	-1.43720706	-2.59247411	6.25990026
C	0.44126687	-3.13616810	-2.24104325	C	-3.12402100	0.00043189	4.77421733
C	4.52443380	-2.31376645	-1.40716140	H	-2.28077073	1.46394876	3.39738826
C	2.74829375	3.57964531	-2.57938691	C	-4.03710639	-3.87846211	-2.61354535
C	0.55552368	3.63391144	-1.42047055	H	-3.04643360	-3.79260110	-4.53511976
C	4.34113059	1.83472238	-2.13823166	C	-3.90806627	-3.81317839	-1.21249450
C	-5.50881501	-0.21161551	-0.46017403	H	-2.55553687	-3.53189136	0.47108945
H	-5.55016133	-0.48419138	-2.60424677	C	-3.46771994	5.65475919	-0.71119154
H	-5.19027244	0.03557851	1.66720110	H	-1.80956905	7.04344020	-0.64249747
C	4.87356973	0.38698730	3.21245784	C	-3.88227116	4.32196835	-0.89297754
H	3.60774893	0.12039692	4.94793281	H	-3.27949117	2.27366996	-1.29180258
C	0.81400892	-1.43784302	4.64382657	H	-3.69757408	-1.55865621	6.15735629
O	0.24619052	0.35593283	3.40693820	H	-4.12411098	0.43912166	4.75712211
H	5.07005734	0.00637733	-0.62748026	H	-5.02490271	-4.04486052	-3.04843598
H	5.86010610	0.62286141	1.31668861	H	-4.79544860	-3.92643481	-0.58649527
C	4.19311233	-3.52671842	-2.00836049	H	-4.21734002	6.42327479	-0.51089198
H	2.58009186	-4.76166784	-2.75668505	H	-4.94461368	4.07635237	-0.83244330
C	-0.32983366	-3.31886166	-3.34486604				

*Intermediate **IM2***

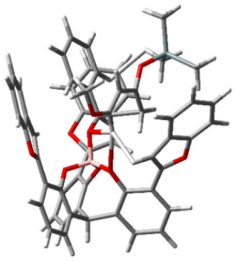


total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-3226.922324	-3226.002313	-3226.09634

Table S15. Optimized Cartesian coordinates (Å) for the intermediate **IM2** composed of **2**, **3b**, and **1A**B in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

B	1.52951266	0.67600268	0.26640687	H	-3.26252108	-2.09183518	5.21266931
O	1.62484423	-0.27935712	1.34490282	C	-3.35641995	4.59011177	-0.07381795
O	2.60876249	0.59635449	-0.67413474	C	-2.23334269	5.00343751	-2.66546036
C	2.03365870	0.10916712	2.57066242	C	0.78232788	-3.56458076	-5.44289900
O	1.25507935	2.00242152	0.74875440	H	0.28826476	-1.48640239	-5.09662664
C	3.75556915	-0.02006659	-0.35303007	C	1.60446023	-4.65463718	-5.09954225
C	1.38159068	-0.43986143	3.69665358	H	3.23606830	-5.37217139	-3.84748398
C	3.08299012	1.03726537	2.76118616	H	-3.23834169	-5.71190578	2.83693035
C	2.14643975	2.99196370	0.58122591	H	-4.37113548	-4.20173655	4.43855191
C	4.50252595	0.42946175	0.74460235	C	-4.16360942	4.81961681	-1.18235818
C	4.18144825	-1.12894936	-1.11170016	H	-3.79339493	4.42881617	0.91341519
C	1.68452908	0.02829032	4.98054749	C	-3.60990180	5.02117007	-2.46141701
C	0.39802231	-1.51836168	3.54829471	H	-1.79073365	5.15451119	-3.65069599
C	3.99763565	1.55390888	1.64332247	H	0.02656134	-3.69201134	-6.22092561
C	3.35744088	1.47440051	4.06047935	H	1.47112954	-5.60931075	-5.61268468
C	1.70346278	4.21334800	0.04105849	H	-5.24877908	4.84147164	-1.06234480
C	3.49537138	2.81054041	0.93266420	H	-4.27354602	5.19389899	-3.31112092
C	5.70374211	-0.21427974	1.04911524	C	-0.75386863	0.90900326	-0.73216275
C	5.39151759	-1.75267078	-0.77740654	C	-1.66803458	0.65698051	-1.82430058
C	3.34267120	-1.66486569	-2.18605164	O	0.31768172	0.26748613	-0.63407407
C	2.65489428	1.00331552	5.16608549	H	-0.92384875	1.77030181	-0.07042967
H	1.15215192	-0.39499200	5.83459378	C	-1.40811151	-0.35877073	-2.76047053
C	0.41780325	-2.67669146	2.83630365	C	-2.82610250	1.44017293	-1.93610659
O	-0.75223310	-1.40390773	4.28013384	C	-2.31240375	-0.59005999	-3.78935163
H	4.89391424	1.89444675	2.17727434	H	-0.49604534	-0.94966883	-2.66818717
H	4.15931694	2.20333172	4.20618465	C	-3.72194063	1.20895907	-2.97229752
C	2.63029370	5.22609076	-0.22618911	H	-3.01839580	2.23051868	-1.20820305
C	0.26970139	4.39646725	-0.23405682	C	-3.46742475	0.19026703	-3.89301709
C	4.39247799	3.84541673	0.65879617	H	-2.12170475	-1.38237496	-4.51592859
C	6.15384827	-1.29397998	0.29086226	H	-4.61972673	1.82327360	-3.06260790
H	6.29315307	0.13382505	1.90169134	H	-4.17388496	0.00486478	-4.70502188
H	5.72298898	-2.61205704	-1.36210285	C	-0.50560505	-2.51707672	-0.23325303
C	2.33467304	-1.13988470	-2.94063798	C	-1.83365103	-2.30148293	-0.33518455
O	3.58210927	-2.96942170	-2.52713933	O	0.21303162	-3.42074611	-0.89597925
H	2.89000305	1.36954854	6.16681438	H	0.12979186	-1.93000208	0.43086368
C	-0.83234273	-3.33711202	3.10736866	C	-2.54621135	-1.23364841	0.36465918
H	1.22630528	-3.00930668	2.19143054	H	-2.45364355	-2.89128905	-1.01068242
C	-1.50494170	-2.49591963	4.00761736	C	-0.43358540	-4.22626701	-1.85738895
C	3.97665792	5.03857785	0.06843636	C	-2.00832059	-0.38259850	1.27598473
H	2.28329085	6.16629991	-0.66005124	O	-3.81339365	-1.12301741	-0.06991396
C	-0.81808987	4.31166504	0.57819066	H	-1.20160985	-4.86317292	-1.38856197
O	-0.09077490	4.68543992	-1.52033605	H	-0.90279682	-3.60523602	-2.63803098
H	5.44577323	3.71365697	0.92183439	H	0.33938712	-4.85233857	-2.31707927
H	7.09705554	-1.78345914	0.54016516	H	-0.99298930	-0.52661381	1.64008770
C	1.89679002	-2.19434668	-3.81693711	H	-2.60647936	0.39925185	1.74426094
H	1.95037856	-0.12942424	-2.86041434	Si	-5.20957666	-0.46780799	0.66406247
C	2.70580877	-3.29787412	-3.50198183	C	-5.32387550	-1.14076317	2.40324020
C	-1.46012969	-4.51400122	2.67432051	C	-6.58920318	-1.08771217	-0.42752562
C	-2.77061349	-2.77065831	4.51484896	C	-5.17544467	1.40515323	0.65993704
H	4.70038526	5.82887147	-0.13825644	H	-4.51532313	-0.75809992	3.04350459
C	-1.96543386	4.55633771	-0.25856098	H	-6.28593467	-0.85339046	2.85685344
H	-0.79814467	4.08760004	1.64136238	H	-5.25580579	-2.23965430	2.40162224
C	-1.44216883	4.77034745	-1.54487711	H	-6.62920639	-2.18763360	-0.43037721
C	0.92000419	-2.33144791	-4.81535127	H	-7.56108578	-0.70812917	-0.07463050
C	2.58888491	-4.53792931	-4.12146348	H	-6.44388952	-0.74470098	-1.46385983
C	-2.72860090	-4.80288653	3.16345970	H	-4.26998389	1.81764125	1.12896212
H	-0.96592450	-5.17898187	1.96315260	H	-6.04489692	1.78072530	1.22405467
C	-3.37422745	-3.94444986	4.07424968	H	-5.24230947	1.80471409	-0.36284167

First transition state ***TS1***

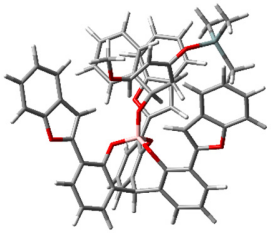


imaginary frequency / cm^{-1}	total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-157.9227	-3226.921973	-3226.002029	-3226.095059

Table S16. Optimized Cartesian coordinates (Å) for the transition state **TS1** composed of **2**, **3b**, and **1A**B in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

B	1.47461511	0.73313301	0.24612995	H	-3.18920865	-2.27169918	5.20244980
O	1.61902577	-0.21403893	1.33620512	C	-3.56910018	4.45455262	-0.01904578
O	2.57077942	0.69808303	-0.68250835	C	-2.49366363	4.96789801	-2.61265999
C	2.00077029	0.19947647	2.56075572	C	0.93559532	-3.58139708	-5.41395766
O	1.15278489	2.04995953	0.73834302	H	0.33042728	-1.53296468	-5.06611193
C	3.74012500	0.13438005	-0.35119366	C	1.81876364	-4.62401827	-5.07498247
C	1.36219354	-0.36936106	3.68513882	H	3.49617749	-5.24868111	-3.83365689
C	3.00713085	1.17352690	2.75447948	H	-2.95298934	-5.89832074	2.84872983
C	1.99860993	3.07655074	0.57213057	H	-4.16911596	-4.45032337	4.44665637
C	4.46311920	0.61932923	0.74798279	C	-4.39778852	4.67549045	-1.11339999
C	4.21828489	-0.95894031	-1.10227317	H	-3.98784760	4.25589616	0.96936052
C	1.63179890	0.11981217	4.96862031	C	-3.86743730	4.92615330	-2.39359250
C	0.43276219	-1.49432321	3.53315675	H	-2.06896733	5.15731553	-3.59916582
C	3.90669566	1.72365100	1.64037007	H	0.18273811	-3.75134743	-6.18665921
C	3.24979513	1.63050166	4.05317014	H	1.73479793	-5.58534325	-5.58618867
C	1.50210078	4.27968007	0.03626256	H	-5.48152995	4.65202061	-0.98114721
C	3.35435868	2.95510121	0.92354343	H	-4.54723148	5.09040803	-3.23216502
C	5.69056375	0.03065792	1.05924716	C	-0.84100115	0.83641826	-0.66083624
C	5.45386440	-1.52684269	-0.76169188	C	-1.72389869	0.60850457	-1.79642070
C	3.40708317	-1.53903783	-2.17453237	O	0.29523408	0.27979732	-0.63869702
C	2.55747443	1.13713321	5.15580394	H	-1.02098394	1.70226698	-0.01130804
H	1.11064579	-0.32070741	5.82088867	C	-1.40757878	-0.35488103	-2.76738960
C	0.51768500	-2.65273484	2.82570714	C	-2.89679754	1.36474846	-1.91642635
O	-0.72583948	-1.43921143	4.25879866	C	-2.27259113	-0.56567329	-3.83560978
H	4.78481945	2.10360221	2.17810300	H	-0.48124089	-0.92266993	-2.67390333
H	4.01781148	2.39461361	4.20123252	C	-3.75157002	1.15847628	-2.99302433
C	2.38438658	5.33085318	-0.23359137	H	-3.13361824	2.12048291	-1.16555449
C	0.05966406	4.40571868	-0.22371984	C	-3.44369280	0.18756861	-3.94789944
C	4.20603022	4.02706947	0.64788127	H	-2.03559241	-1.32067087	-4.58803005
C	6.19161988	-1.03059130	0.30687898	H	-4.65892702	1.75832328	-3.08757768
H	6.26056877	0.40815155	1.91259359	H	-4.11744921	0.02091650	-4.79115041
H	5.82484930	-2.37323735	-1.34157707	C	-0.33910852	-2.54137423	-0.23945713
C	2.36691309	-1.07184987	-2.92345974	C	-1.67774411	-2.38528249	-0.36106024
O	3.71694036	-2.82899243	-2.51684001	O	0.41652972	-3.43224827	-0.86557572
H	2.76711728	1.52008489	6.15594164	H	0.26328147	-1.91184109	0.41635710
C	-0.69477529	-3.38009491	3.09582796	C	-2.42811767	-1.32741328	0.29321780
H	1.34821973	-2.94565276	2.18973143	H	-2.26768325	-3.02108866	-1.02108542
C	-1.41505148	-2.57428935	3.99169448	C	-0.18326908	-4.28899120	-1.81642219
C	3.73857243	5.20063839	0.05655756	C	-1.90611085	-0.38452432	1.13942632
H	1.99629742	6.25606653	-0.66498866	O	-3.69574202	-1.27927147	-0.12098867
C	-1.01461274	4.25955334	0.59803482	H	-0.93445972	-4.94022324	-1.34125754
O	-0.32686567	4.71047563	-1.49847740	H	-0.65793008	-3.70524176	-2.62157076
H	5.26409437	3.94134371	0.91086287	H	0.62152493	-4.89767317	-2.24293911
H	7.15498627	-1.47632297	0.56119878	H	-0.91221286	-0.51082614	1.56401567
C	1.98351680	-2.14969273	-3.79655953	H	-2.55194967	0.36841407	1.59193589
H	1.92470228	-0.08590077	-2.83774902	Si	-5.13188424	-0.72231899	0.63633308
C	2.85458980	-3.20631524	-3.48631530	C	-5.14317582	-1.39000079	2.37919353
C	-1.25176389	-4.59529648	2.67132224	C	-6.47127990	-1.46114319	-0.42820010
C	-2.65956317	-2.92288899	4.50595773	C	-5.24332685	1.14536249	0.62474224
H	4.42739555	6.02097810	-0.15246507	H	-4.34562752	-0.94264542	2.99106054
C	-2.18019453	4.47896745	-0.21974773	H	-6.10890418	-1.16911355	2.86117549
H	-0.97313570	4.01290088	1.65558145	H	-4.99467952	-2.48070283	2.38332071
C	-1.68078029	4.74217359	-1.50638092	H	-6.42088825	-2.56053968	-0.42238726
C	1.00937007	-2.34173971	-4.78841950	H	-7.46507562	-1.15901772	-0.06206677
C	2.80211904	-4.45170951	-4.10393772	H	-6.37046041	-1.11565251	-1.46886854
C	-2.49876390	-4.95748612	3.16695615	H	-4.37699638	1.62990362	1.09870095
H	-0.71920637	-5.23484583	1.96447487	H	-6.14233342	1.44666336	1.18728013
C	-3.19174452	-4.13453718	4.07556027	H	-5.34000895	1.53817392	-0.39794610

*Intermediate **IM3***

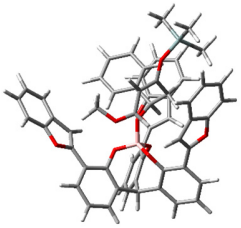


total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-3226.953386	-3226.029550	-3226.121117

Table S17. Optimized Cartesian coordinates (Å) for the intermediate **IM3** composed of **2**, **3b** and **1A**B in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

O	-2.53480422	-0.38059027	-0.22871987	C	3.35871818	-1.54078056	3.52341659
O	-0.82574442	-1.27380741	-1.70311823	C	4.52755292	-3.96538161	2.57571416
C	-3.55092274	-1.05691135	0.30182813	C	3.42786644	2.67451386	-4.42616454
O	-1.01017215	-2.07154129	0.55795315	H	3.84930546	0.64089199	-3.81274546
C	-1.74762790	-1.37114720	-2.66300836	C	2.44876777	3.61332781	-4.80169871
C	-3.87640965	-2.35480354	-0.13909023	H	0.33054895	3.99224077	-5.13182316
C	-4.32118297	-0.43907734	1.31621587	H	-2.57156707	5.96167739	3.75831527
C	-0.91838122	-3.31052856	0.08446540	H	-4.63901348	5.39844721	4.99909881
C	-2.88931266	-2.17846869	-2.49690380	C	4.65934291	-1.89705855	3.86494941
C	-1.56332680	-0.64428715	-3.86041730	H	2.91654968	-0.61330294	3.89290715
C	-3.11120347	-3.05225359	-1.26146543	C	5.23655402	-3.09327318	3.39858333
C	-4.95865967	-3.01479872	0.44652935	H	4.96240709	-4.89386201	2.20359602
C	-5.41045393	-1.12962626	1.86765439	H	4.47587035	2.98107823	-4.39464526
C	-3.97980833	0.89701256	1.81101221	H	2.75168473	4.63250814	-5.05096502
C	-1.88198093	-3.83853135	-0.80076635	H	5.24488923	-1.24080884	4.51251199
C	0.18480085	-4.10147709	0.48596041	H	6.26003440	-3.34237357	3.68606391
C	-3.85337790	-2.18483583	-3.50775650	O	-0.28812329	0.15481042	0.14343348
C	-2.55546049	-0.66663991	-4.84668137	C	0.80095197	0.64471586	-0.56718115
C	-0.33404594	0.13697472	-4.04619985	C	0.54405071	1.54010145	2.51144638
H	-3.80334498	-3.82932532	-1.61120194	C	0.58971204	2.10257504	-0.95332851
C	-5.72598243	-2.41380140	1.44304477	H	0.87388857	0.09232208	-1.51451437
H	-5.21075152	-4.02257037	0.10439330	C	2.13706659	0.33929930	0.12648376
H	-6.00240388	-0.64684130	2.64609584	C	1.90855583	1.67327853	2.37422915
C	-2.95990490	1.76940984	1.55524302	H	-0.05019903	0.95727176	1.79084881
O	-4.83226117	1.41205295	2.75566288	O	-0.17113332	2.04480952	3.46339352
C	-1.71963373	-5.14712158	-1.26029471	C	-0.70206075	2.51315017	-1.30279366
C	0.30604814	-5.41387278	0.00692517	C	1.63134502	3.03135237	-1.03896790
C	1.22349186	-3.53817905	1.35124956	C	2.64397775	1.09585468	1.32202303
C	-3.70589017	-1.42705526	-4.66911179	H	2.92305122	0.40127648	-0.63739442
H	-4.74613288	-2.80379830	-3.37967654	H	2.10435051	-0.72163116	0.43432232
H	-2.41073041	-0.08551695	-5.76004848	H	2.50685446	2.20377915	3.11578576
C	0.97362494	-0.18501427	-3.85138783	C	0.40482134	2.87842294	4.46608388
O	-0.46704224	1.42897149	-4.47415869	C	-0.94862042	3.82355108	-1.70593768
H	-6.57203720	-2.94578241	1.88214992	H	-1.52064227	1.79218240	-1.25680383
C	-3.18423895	2.91385516	2.39755209	C	1.38738270	4.34377591	-1.44234861
H	-2.14562539	1.59767488	0.86182451	H	2.65699600	2.74551102	-0.79760145
C	-4.35565082	2.62549061	3.11419244	O	3.92112173	1.21181424	1.43656154
C	-0.63933146	-5.93630810	-0.86541617	H	0.90604339	3.73957842	4.00239438
H	-2.46609243	-5.56169273	-1.94379936	H	-0.42943130	3.22124167	5.08530012
H	1.15897838	-6.01675966	0.32182656	H	1.11735135	2.30373589	5.07452920
C	1.31361293	-2.39833611	2.10097916	C	0.09505424	4.74674180	-1.77187146
O	2.38015043	-4.26841975	1.44116786	H	-1.96454953	4.12353443	-1.97238535
H	-4.47840921	-1.44708190	-5.43997144	H	2.21648583	5.05215616	-1.50263967
C	1.73088600	1.00391414	-4.13940604	Si	5.36169411	0.70047375	0.54822130
H	1.34071289	-1.15071581	-3.51518772	H	-0.09718524	5.77465054	-2.08724177
C	0.77635934	1.96346556	-4.51488179	C	6.68304986	0.98618043	1.81910691
C	-2.52771034	4.13269743	2.62643485	C	5.19719274	-1.09576244	0.09232200
C	-4.91212720	3.48655314	4.05498167	C	5.47046797	1.84968184	-0.91354218
H	-0.54122792	-6.95831278	-1.23599904	H	7.67028214	0.75032635	1.39230569
C	2.62680696	-2.40315294	2.69203831	H	6.69306083	2.03320529	2.15641577
H	0.53215912	-1.65310453	2.19368202	H	6.52205080	0.33490498	2.69152263
C	3.23120937	-3.58822797	2.24101224	H	4.52968140	-1.26943742	-0.76309426
C	3.08489605	1.36812729	-4.09606024	H	6.19660865	-1.47422271	-0.17666659
C	1.10084437	3.27170917	-4.85489547	H	4.83823954	-1.68597053	0.94884292
C	-3.06587310	5.00711562	3.56416833	H	6.41815632	1.66805532	-1.44535155
H	-1.61644929	4.38453316	2.07962783	H	4.65238531	1.69952739	-1.63443381
C	-4.24244188	4.68853027	4.27000379	H	5.45994804	2.90118203	-0.58834856
H	-5.82452841	3.22695231	4.59373949	B	-1.16764948	-0.90535261	-0.32753945

*Second transition state **TS2***

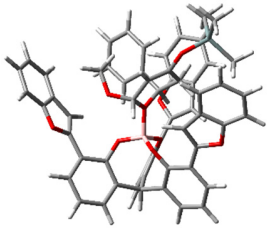


imaginary frequency / cm^{-1}	total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-232.7861	-3226.938355	-3226.014811	-3226.105858

Table S18. Optimized Cartesian coordinates (Å) for the transition state **TS2** composed of **2**, **3b**, and **1A**B in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

O	-2.37128671	0.33175857	0.04740631	C	3.32634142	2.85276003	-3.59755047
O	-0.76863313	1.09914903	1.66575128	C	4.71133106	3.29506134	-1.14068700
C	-3.47326782	0.98756610	-0.33143883	C	3.68589038	-2.88185702	4.32717866
O	-0.98597868	2.26738982	-0.41601272	H	3.99560511	-0.79124558	3.86046337
C	-1.71096017	0.99963644	2.61626671	C	2.75706894	-3.91308911	4.56411831
C	-3.82315921	2.23510656	0.22270418	H	0.65527966	-4.46564544	4.69906228
C	-4.32299704	0.38539910	-1.28664151	H	-3.52992312	-6.41599855	-3.02182028
C	-0.93807570	3.41039146	0.28308573	H	-4.61454748	-5.42620600	-5.01559377
C	-2.89035620	1.76380414	2.55048233	C	4.69496642	2.63771068	-3.49103253
C	-1.49837475	0.11346892	3.69196692	H	2.80221101	2.67520495	-4.53843335
C	-3.13725422	2.80941252	1.46159425	C	5.37959956	2.85640427	-2.27969169
C	-4.91365243	2.92518147	-0.31244133	H	5.22544661	3.46485371	-0.19371711
C	-5.40728358	1.10851262	-1.80023847	H	4.75360618	-3.10875394	4.36553871
C	-4.12493231	-1.00595698	-1.69370870	H	3.11903111	-4.92074406	4.77920384
C	-1.94746921	3.72786526	1.20862411	H	5.25395441	2.29230995	-4.36333865
C	0.15198720	4.28553968	0.10165494	H	6.45580024	2.67649453	-2.23168413
C	-3.87080960	1.56179363	3.52490609	O	-0.04072895	0.06493688	-0.38878187
C	-2.50704790	-0.07029331	4.64479473	C	1.10235602	-0.36475535	0.33068899
C	-0.22226483	-0.60074681	3.82325182	C	0.23654985	0.37016989	-2.15440730
H	-3.89735349	3.47045336	1.89797092	C	1.07635683	-1.87180625	0.49724949
C	-5.68505977	2.39026902	-1.34184371	H	1.03400570	0.08272786	1.32738159
H	-5.17522447	3.90075146	0.10696113	C	2.37354309	0.18949373	-0.33312147
H	-6.04194178	0.64122431	-2.55511439	C	1.42637152	-0.38941624	-2.50923609
C	-3.61482874	-2.09136755	-1.04657898	H	0.33824451	1.43869783	-1.96130364
O	-4.60447411	-1.35150420	-2.92955331	O	-0.90317531	0.12255583	-2.75608415
C	-1.84128773	4.91379362	1.93790672	C	-0.12189003	-2.57044884	0.32956057
C	0.23274000	5.46164437	0.85635882	C	2.21648573	-2.57930168	0.89267505
C	1.23781780	3.93024982	-0.82264960	C	2.51366941	-0.39780004	-1.70320589
C	-3.69808331	0.64108710	4.55671683	H	3.24466333	-0.01376742	0.29514525
H	-4.79445871	2.14474803	3.47159288	H	2.27323719	1.28364373	-0.38609609
H	-2.34082964	-0.77316178	5.46370699	H	1.43974798	-0.94774403	-3.44495636
C	1.06758939	-0.17444643	3.73529653	C	-1.16880736	-1.18583567	-3.24842246
O	-0.28465153	-1.92784809	4.14177238	C	-0.17806715	-3.94714550	0.54574108
H	-6.52839262	2.95134899	-1.74815846	H	-1.01303126	-2.02015231	0.02592395
C	-3.77337326	-3.20850594	-1.94080103	C	2.16379049	-3.95503865	1.10260765
H	-3.19093735	-2.08220637	-0.04763870	H	3.16011200	-2.05755418	1.06161652
C	-4.39107865	-2.68024619	-3.08586186	O	3.61048678	-1.02752553	-2.07495678
C	-0.76195193	5.78029162	1.77290796	H	-1.00041155	-1.93708128	-2.46387684
H	-2.62566708	5.16123978	2.65859527	H	-2.22023057	-1.18627339	-3.54801481
H	1.08836602	6.12545420	0.71526839	H	-0.54673876	-1.40770264	-4.12686616
C	1.25891275	3.59741067	-2.14113533	C	0.96531338	-4.64622326	0.92812408
O	2.49630665	3.89136620	-0.28341688	H	-1.12505086	-4.47503306	0.41521900
H	-4.48227504	0.49738615	5.30205821	H	3.06337462	-4.48673522	1.41957136
C	1.89189025	-1.32450000	4.00016453	Si	5.21314905	-1.38528762	-1.58701556
H	1.38333173	0.84155738	3.51382082	H	0.92212312	-5.72410242	1.09802343
C	0.99034611	-2.37364244	4.24073524	C	6.25788388	-0.89937156	-3.05171501
C	-3.45740478	-4.57600521	-1.91296429	C	5.72215753	-0.42942262	-0.06100596
C	-4.70896833	-3.43603855	-4.20942327	C	5.25344482	-3.22752375	-1.30202521
H	-0.70140054	6.70103707	2.35567929	H	7.31131745	-1.16749017	-2.87351987
C	2.63225697	3.29665137	-2.46191102	H	5.92029901	-1.41849196	-3.96162616
H	0.39490454	3.57021139	-2.79997332	H	6.20302270	0.18431565	-3.23094443
C	3.34143164	3.50366235	-1.26839843	H	5.23445169	-0.78523845	0.85957584
C	3.26965959	-1.58586780	4.04612620	H	6.80834432	-0.56152350	0.07261710
C	1.38675542	-3.67544715	4.52573229	H	5.52799975	0.64816801	-0.17526824
C	-3.76805653	-5.35023197	-3.02490309	H	6.27449512	-3.54614882	-1.03807712
H	-2.98122892	-5.02257876	-1.03822315	H	4.57712187	-3.52674530	-0.48809553
C	-4.38527409	-4.78884537	-4.15904722	H	4.95126350	-3.76676307	-2.21283043
H	-5.18659343	-2.98483758	-5.08012861	B	-1.09539102	0.98498641	0.26134569

*Adduct **1AB**·**5b***



total energy / hartree	total energy + ZPE / hartree	*G*(298 K) / hartree
-3226.953087	-3226.027208	-3226.116843

Table S19. Optimized Cartesian coordinates (Å) for **1AB**·**5b** in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

O	-2.25799586	0.91290466	-0.04387116	C	4.29497142	1.22048442	-3.21964996
O	-0.52892948	1.30412643	1.55882125	C	5.80874681	2.95163259	-1.52688027
C	-3.11834601	1.80878957	-0.55207006	C	2.62462589	-3.58754277	3.85711170
O	-0.34299539	2.29294433	-0.59805679	H	3.52376852	-1.63995817	3.56245779
C	-1.45055758	1.58567423	2.49986730	C	1.44415757	-4.31870630	4.09272229
C	-3.13218945	3.13595960	-0.09291863	H	-0.71144919	-4.24010559	4.38560592
C	-4.02757679	1.38573108	-1.54251201	H	-4.69193576	-5.50530715	-2.92304394
C	-0.00004998	3.44635891	0.01340132	H	-5.02082969	-4.43753192	-5.13270268
C	-2.37480689	2.63054790	2.31635078	C	5.68178062	1.27532884	-3.29612200
C	-1.46291715	0.81421143	3.68024727	H	3.72198624	0.54866437	-3.86073174
C	-2.32665066	3.59079902	1.12211221	C	6.42977584	2.12739295	-2.46095157
C	-3.97012427	4.05364935	-0.73243471	H	6.37350355	3.61648919	-0.87219000
C	-4.84761471	2.33382308	-2.16556200	H	3.57087961	-4.12326452	3.75467551
C	-4.15071557	-0.03510742	-1.87723799	H	1.49454843	-5.40715477	4.16388973
C	-0.92317422	4.11960262	0.83414518	H	6.20640102	0.64829655	-4.02024191
C	1.30183728	3.96410325	-0.16040023	H	7.51830201	2.14086344	-2.54623479
C	-3.35280153	2.82182709	3.29618536	O	-0.10723846	-0.11747441	-0.36916521
C	-2.46141946	1.03237175	4.63457520	C	0.65978860	-0.95859798	0.53547666
C	-0.43923770	-0.22465217	3.86874410	C	-0.03258187	-0.35818549	-1.83393290
H	-2.87267845	4.47342301	1.47808993	C	0.00381468	-2.31245423	0.67095336
C	-4.80247077	3.66975590	-1.78168475	H	0.55374454	-0.44876364	1.49135608
H	-3.97699921	5.09164212	-0.38859488	C	2.11506562	-0.90163288	0.13196061
H	-5.53442931	2.00545409	-2.94797468	C	1.30180149	-0.93207595	-2.19534976
C	-4.09582801	-1.15561008	-1.10782924	H	-0.15682247	0.66170040	-2.21988162
O	-4.44001327	-0.33833120	-3.17830346	O	-1.10588365	-1.04736330	-2.31784052
C	-0.53700200	5.31433793	1.44652644	C	-1.32610237	-2.33943391	1.10771488
C	1.64933271	5.16842704	0.46965069	C	0.65752924	-3.51612669	0.40997196
C	2.32255593	3.25700553	-0.93797201	C	2.29605466	-1.18256142	-1.33071250
C	-3.41518788	2.02489290	4.43799833	H	2.67588764	-1.60773626	0.75883230
H	-4.08256286	3.62472724	3.16086542	H	2.51009258	0.10398558	0.35418716
H	-2.47701277	0.41907694	5.53787589	H	1.44970444	-1.12267321	-3.25999790
C	0.91480297	-0.18305109	3.74815608	C	-1.11731615	-2.46224606	-2.36318173
O	-0.87615119	-1.49474570	4.12448985	C	-1.99529006	-3.54743568	1.26703931
H	-5.44327430	4.40491851	-2.27165694	H	-1.84104913	-1.39797286	1.31427039
C	-4.35683044	-2.26088849	-1.98937625	C	-0.01163104	-4.73024947	0.56995015
H	-3.87144607	-1.18387480	-0.04672411	H	1.69307481	-3.52302756	0.06585907
C	-4.54992138	-1.68506218	-3.25555397	O	3.46664802	-1.66343694	-1.75692111
C	0.73705320	5.84519320	1.26674103	H	-1.56886511	-2.87954053	-1.45332014
H	-1.25650726	5.83784139	2.08166840	H	-1.73642454	-2.74625414	-3.22417077
H	2.65624352	5.56280215	0.32912411	H	-0.10569787	-2.87554024	-2.48625175
C	2.28142239	2.31686786	-1.92322680	C	-1.33829155	-4.74932831	0.99416222
O	3.61737437	3.60915154	-0.65684587	H	-3.03252863	-3.55259297	1.60895439
H	-4.19363565	2.19587422	5.18344521	H	0.51010195	-5.66577714	0.35809123
C	1.37312448	-1.54278873	3.87603512	Si	4.92533083	-2.05221518	-0.94777760
H	1.50296865	0.70459504	3.53060789	H	-1.86118435	-5.70031558	1.11645855
C	0.21288748	-2.29954210	4.10475175	C	6.09770309	-2.43033461	-2.34425357
C	-4.41261308	-3.65691872	-1.86047101	C	5.49518314	-0.59493130	0.07458139
C	-4.79122974	-2.42716016	-4.40744729	C	4.64642755	-3.57214762	0.11348984
H	1.01679653	6.78303636	1.74966249	H	7.07775661	-2.73673935	-1.94622515
C	3.64770174	2.05026257	-2.29187543	H	5.71054902	-3.24800747	-2.97121050
H	1.38464746	1.89402226	-2.35455687	H	6.24552955	-1.54432997	-2.97860540
C	4.41948145	2.88886530	-1.47288253	H	4.90756563	-0.47167445	0.99639873
C	2.60598674	-2.20170517	3.75036454	H	6.54780602	-0.74189145	0.36560344
C	0.21315182	-3.68511635	4.22427739	H	5.43266477	0.33672903	-0.50825397
C	-4.65066768	-4.41658917	-2.99970795	H	5.61592790	-3.93077893	0.49587701
H	-4.25432326	-4.13320387	-0.89072367	H	4.00084378	-3.38214869	0.98534895
C	-4.83715557	-3.81061755	-4.25752511	H	4.19762870	-4.38570004	-0.47799850
H	-4.93046758	-1.94365785	-5.37537075	B	-0.88054587	1.21192313	0.17692683

Table S20. Optimized Cartesian coordinates (Å) for **1B**B in the singlet state at the ωB97XD/def2svp level including the IEFPCM solvent effect (CH_2Cl_2).

B	-0.00013100	-0.00124000	0.38549500	C	3.35045400	-1.78782300	-2.70363300
O	0.79631200	1.10599600	0.30845200	H	2.04334800	-0.58607600	-3.92196800
O	0.56059500	-1.24446100	0.31005100	H	4.47192900	-2.92471600	-1.25404600
C	0.45598000	1.99207300	-0.67230800	C	3.47347100	-3.94798100	1.25806800
O	-1.35736500	0.13496100	0.31142900	O	2.56872700	-2.06419800	2.01985800
C	1.49732800	-1.39460700	-0.67120000	H	-0.37213100	4.49900200	-3.50150900
C	0.07312500	1.49596900	-1.93172200	C	1.71668600	5.00765700	2.67967100
C	0.53933200	3.36807900	-0.41103100	H	2.18259200	5.66660300	0.56408500
C	-1.95735000	-0.60271400	-0.66775600	C	0.98081500	3.93545500	3.08380100
C	1.25691900	-0.81888300	-1.93188300	C	-3.22721400	-2.01535700	-2.69559100
C	2.64858700	-2.15254900	-0.40894300	H	-1.53285800	-1.48926900	-3.91639200
C	-0.00356300	-0.00338800	-2.27620000	H	-4.77251900	-2.41145200	-1.24410200
C	-0.22651900	2.42321000	-2.93417500	C	-5.15701800	-1.02282200	1.26335300
C	0.24396000	4.26005600	-1.45017900	O	-3.07355400	-1.18526000	2.02518500
C	0.94449300	3.88745000	0.90038000	H	4.07753800	-1.93952100	-3.50305000
C	-1.33972900	-0.68619200	-1.92882000	C	3.48910700	-3.97673000	2.68834300
C	-3.19030500	-1.21801200	-0.40332600	H	3.82714300	-4.71696200	0.57529300
C	2.20789000	-1.02627200	-2.93539200	C	2.92508700	-2.80343500	3.08827400
C	3.56709000	-2.34580000	-1.44899700	H	-3.72303800	-2.57120400	-3.49303600
C	2.89901700	-2.75709100	0.90464900	C	-5.18932100	-1.01665700	2.69362200
H	-0.00458500	-0.00420200	-3.37155600	H	-5.99979000	-0.94417600	0.58058600
C	-0.13676000	3.79344700	-2.70305400	C	-3.89146700	-1.11766700	3.09358100
H	-0.52999700	2.06052200	-3.91935300	H	0.71296000	3.54073000	4.05990100
H	0.29408600	5.33314400	-1.25567600	H	2.22006100	5.72768600	3.32022300
C	1.69374800	4.97828200	1.24955300	H	3.86431500	-4.76880400	3.33174700
O	0.51217400	3.25749200	2.01806400	H	2.71675700	-2.37083600	4.06283000
C	-1.99598200	-1.40846800	-2.92987100	H	-6.06247300	-0.94016300	3.33697000
C	-3.81820500	-1.91916500	-1.44102400	H	-3.41255900	-1.15156900	4.06815900
C	-3.83886100	-1.12652400	0.90999500				

12. Non-Covalent Interaction (NCI)-Plot

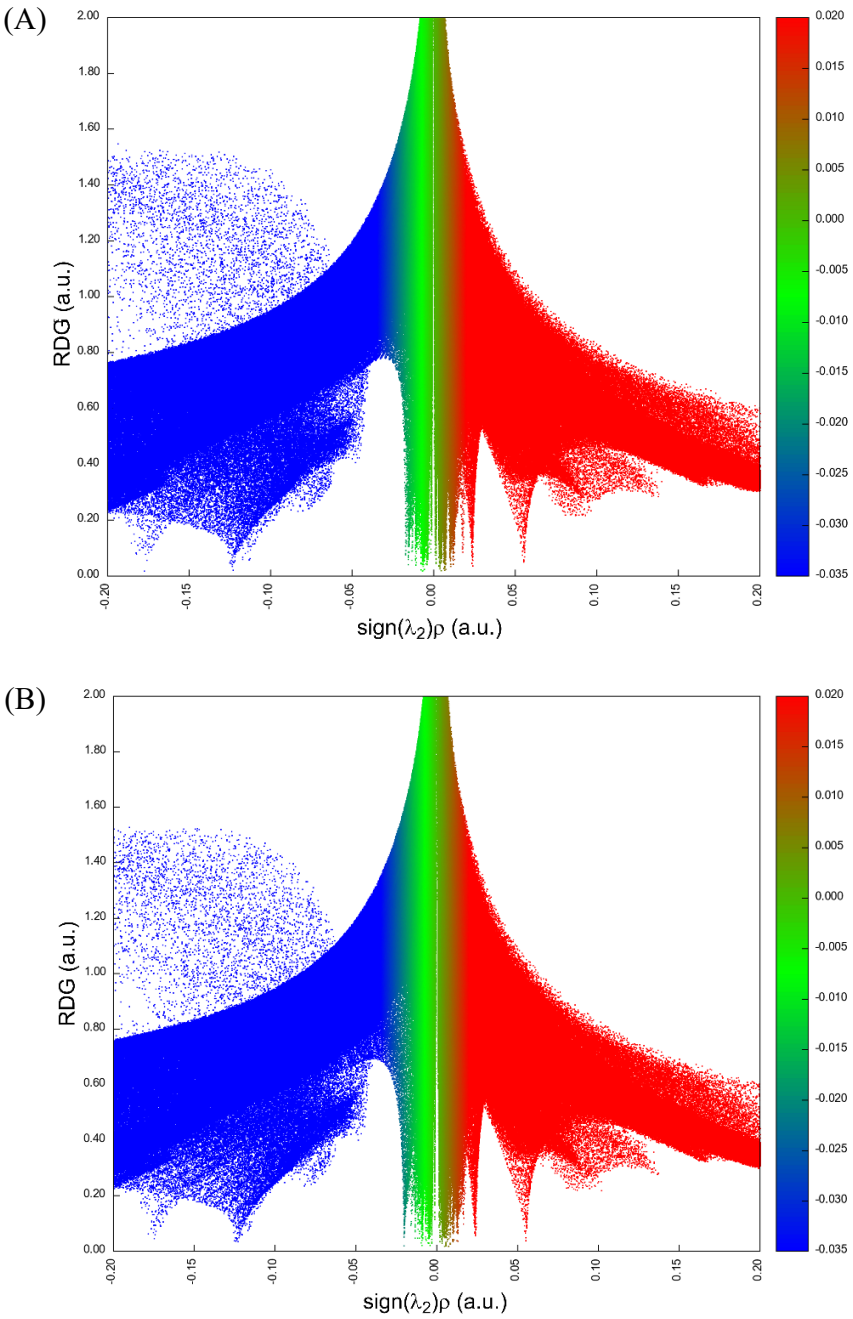


Figure S9. Scatter plots of the non-covalent interaction index within the inclusion complexes of (A) **1AB**·**3a**⊃**2** and (B) **1AB**·**3b**⊃**2** at the preorganized steps.

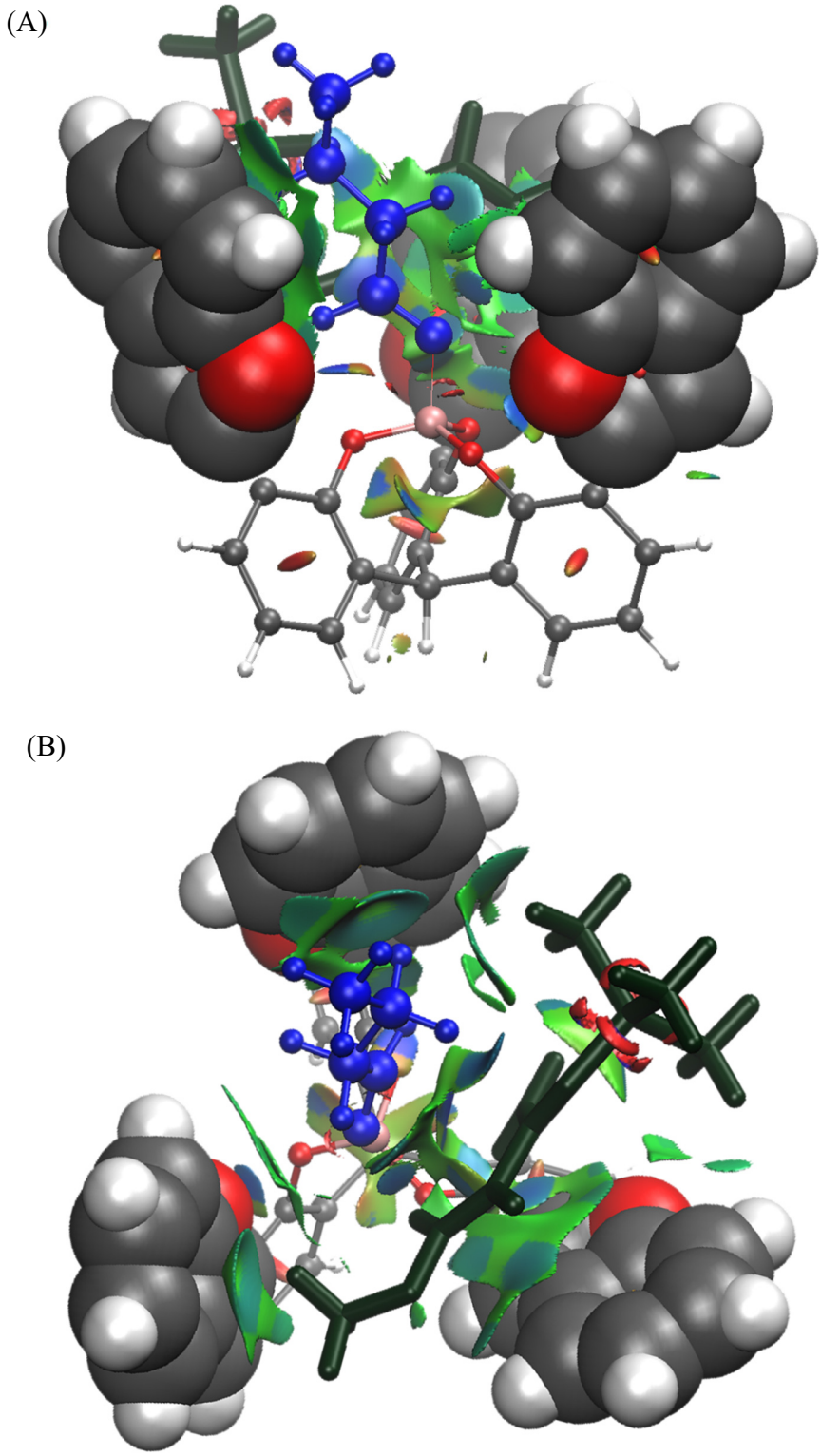


Figure S10. Non-covalent interaction (NCI) plots for **1A**B·**3a**⊃**2** (A) side view and (B) top view. (reduced density gradient (RDG) surfaces = 0.50 a.u. and the color range blue(attractive)-green-red(repulsive) for $-0.018 < \rho < +0.025$ a.u.)

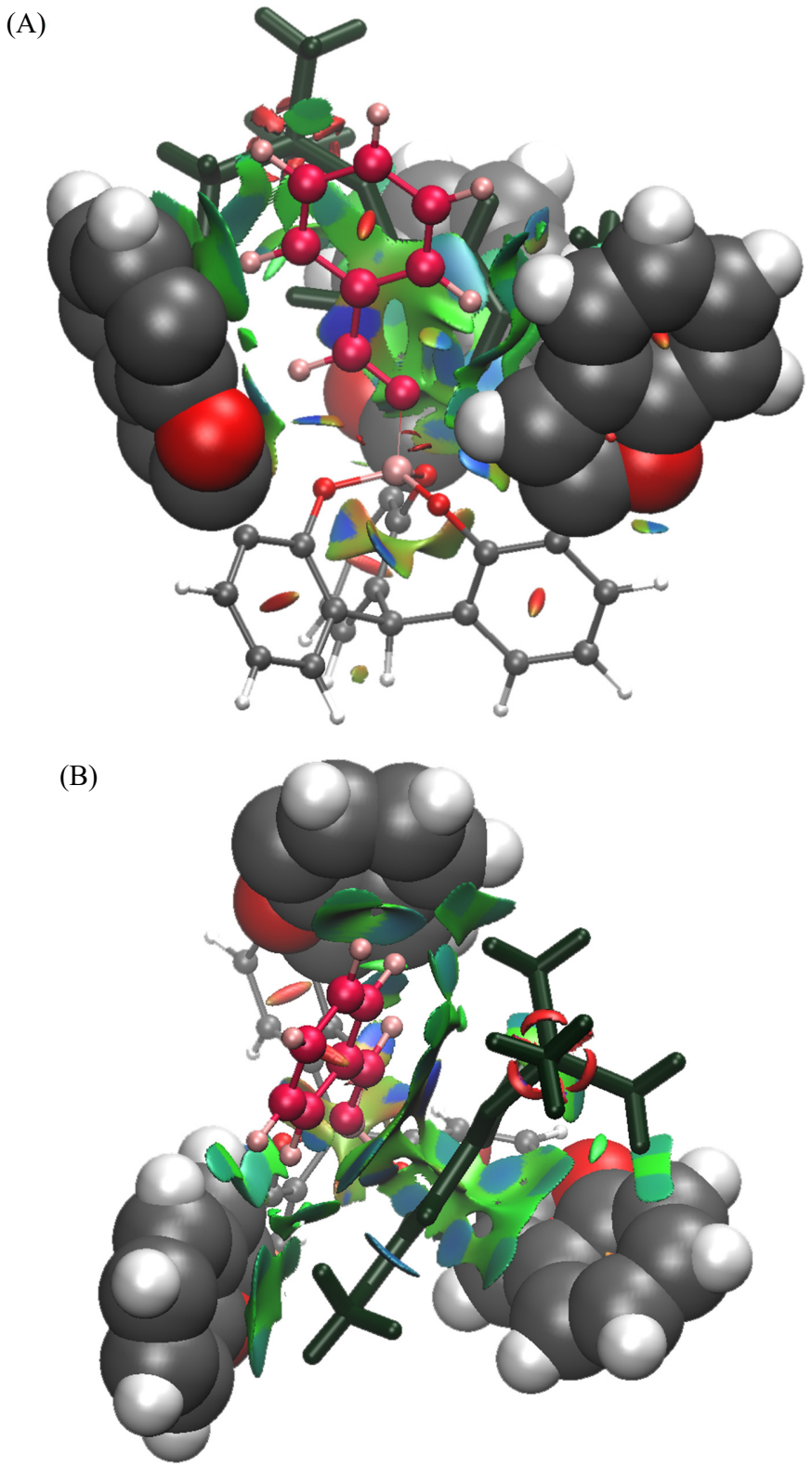


Figure S11. Non-covalent interaction (NCI) plots for **1A**B·**3b**⊃**2** (A) side view and (B) top view. (reduced density gradient (RDG) surfaces = 0.50 a.u. and the color range blue(attractive)-green-red(repulsive) for $-0.018 < \rho < +0.025$ a.u.)

13. Ensemble machine learning analysis

Proposed algorithm

We propose a method with stable and high performance by ensemble of multiple non-linear tree-based algorithms. The ensemble mean can be used to make stable and highly accurate forecasts, and the largest ensemble value can be considered as an optimistic forecast and the smallest as a pessimistic forecast.

$$\begin{aligned} feasible\ y &= Ave[y_i] \\ optimistic\ y &= Max[y_i] \\ pesimistic\ y &= Min[y_i] \end{aligned} \qquad (1)$$

where y is model output, subscripted *i* is each model.

Learning

As model reaction systems, the competitive hetero-Diels–Alder reactions of Danishefsky's diene **2** with a mixture of butanal **3a** and benzaldehyde derivatives **3b**–**h** catalyzed by cage-shaped Lewis acid **1a**–**r**B·thf were employed (Figure S12A). The explanatory variables for machine learning were 7963 variables including ordinary chemical descriptors generated from SMILES[17] by alvaDesc,[18] mulliken charge, 3D conformation, ovality (real surface area/minimum surface area), aspect ratio, and sterimol[19] of each aldehyde, catalyst, and solvent (Figure S12B). The aspect ratio is the ratio of the length L to the diameter D of the cylinder with the smallest diameter inscribed by the molecule. 1112 uniform variables were eliminated, then the number of the explanatory variables became 6851. The explanatory variables were normalized to mean zero and variance 1.

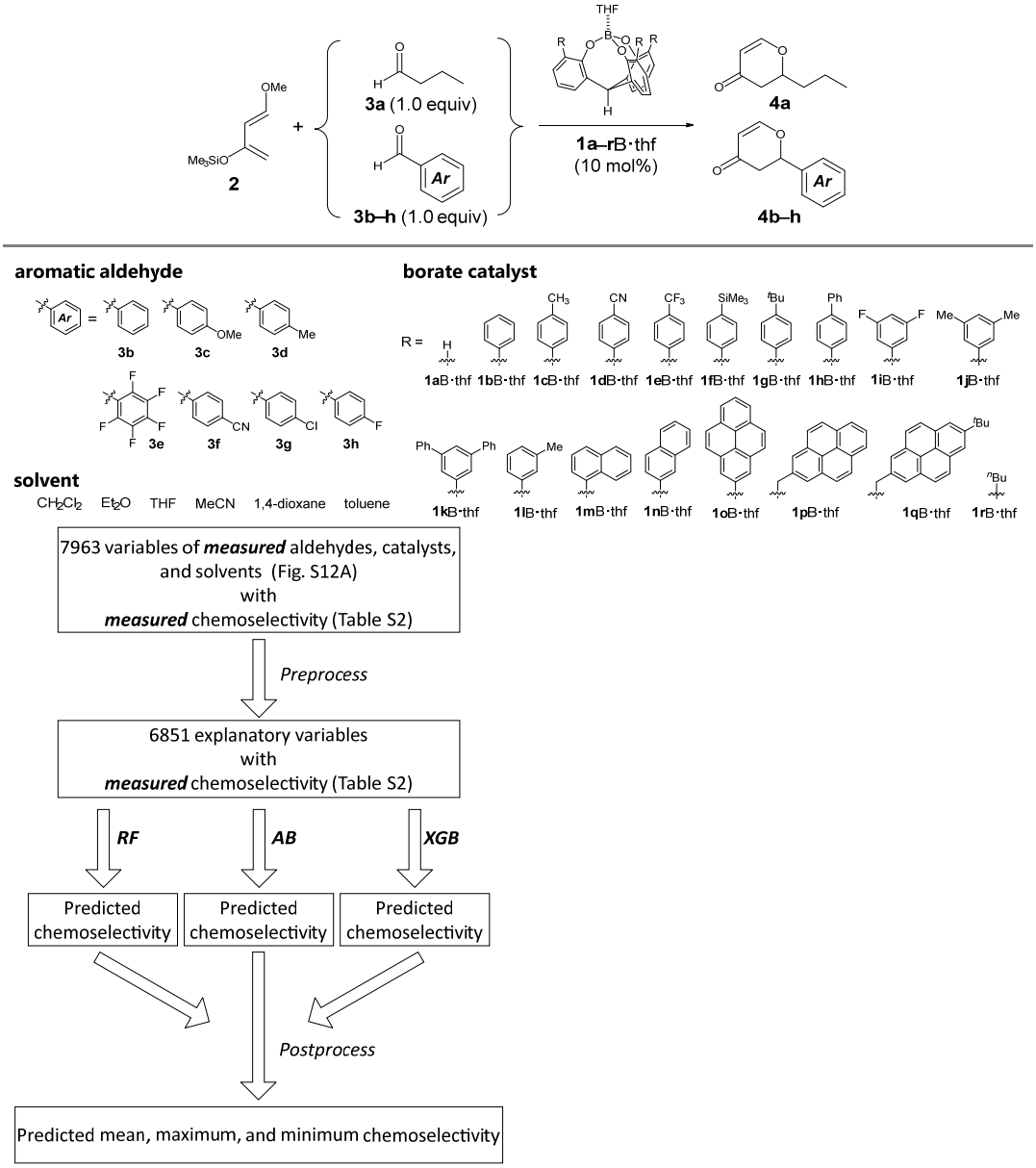
Cross-validation

4 linear algorithms (the Lasso,[20] the Ridge,[21] the PLS,[22] and the stochastic gradient descent (SDG)[23]), 4 non-linear non-tree-based algorithms (the BR,[24] the GP,[25] the MLP,[26] and the SVR[27]), and 4 non-linear tree-based algorithms (the DT,[28] the RF,[29] the AB,[30] and the XGB[31]), and the proposed algorithm were discussed. Figure S13 shows the cross-validation results for each regressor. The cross-validation consists of omitting one catalyst from all data sets three times. The Figure is a box plot of the root mean squared error for unlearned data (QRMSE) for the 13 regressors, where the orange line represents the 50%ile, the box represents the 25%ile to 75%ile, and the whiskers represents the minimum and maximum values. The flyers are not displayed. The linear and non-linear non-tree-based algorithms had large deviations. The non-linear tree-based algorithms, such as the RF, the AB, and the XGB had lower means and smaller deviations. The order in 50%ile was the RF, the AB, the XGB, and the DT. Then algorithm combined with the RF and the AB (RF_AB) had almost the same 50%ile of the RF and lower 75%ile than any of the non-linear tree-based algorithms. Further combined with the XGB (RF_AB_XGB) made lower 75%ile than the RF_AB. Although, further combined with the DT made higher 75%ile than the RF_AB_XGB. Therefore, the RF_AB_XGB was proposed as the best algorithm (Figure S14). The cross-validation results for each catalyst are shown in this section. For all the algorithms, the hyperparameters were tuned to give the best predictability rather than reproducibility.

The cross-validation results for the linear algorithms (the Lasso, the Ridge, the PLS, and the SGD) are shown in Figure S15. There is no method with a small QRMSE for all catalysts. The PLS became a particularly large QRMSE. The cross-validation results for the non-linear non-tree-based algorithms（the BR, the GP, the MLP, and the SVR） are shown in Figure S16. Among them, the largest QRMSE is shown with the GP. The cross-validation results for the non-linear tree-based algorithms (the DT, the RF, the AB, and the XGB) and the proposed algorithm are shown in Figure

S17. Among these non-linear tree-based algorithms, the largest QRMSE with the DT was indicated. Comparing linear algorithms, non-linear non-tree-based algorithms, and non-linear tree-based algorithms, the non-linear tree-based algorithms generally had a smaller QRMSE. This suggests that for discrete catalyst types, an algorithm such as nearest neighbor search would be more appropriate than a linear algorithm or a non-linear non-tree-based algorithm. On the other hand, there is no method with a small QRMSE for all catalysts. By using ensemble averaging, we were able to obtain QRMSEs that were consistently smaller than those of any single algorithm.

(A)



(B)

Figure S12. (A) Summary for the data sets of the competitive reactions between **3a** and **3b**–**h** catalyzed by **1a**–**r**B·thf for the machine learning. (B) Flow diagram of the proposed ensemble algorithm at learning phases.

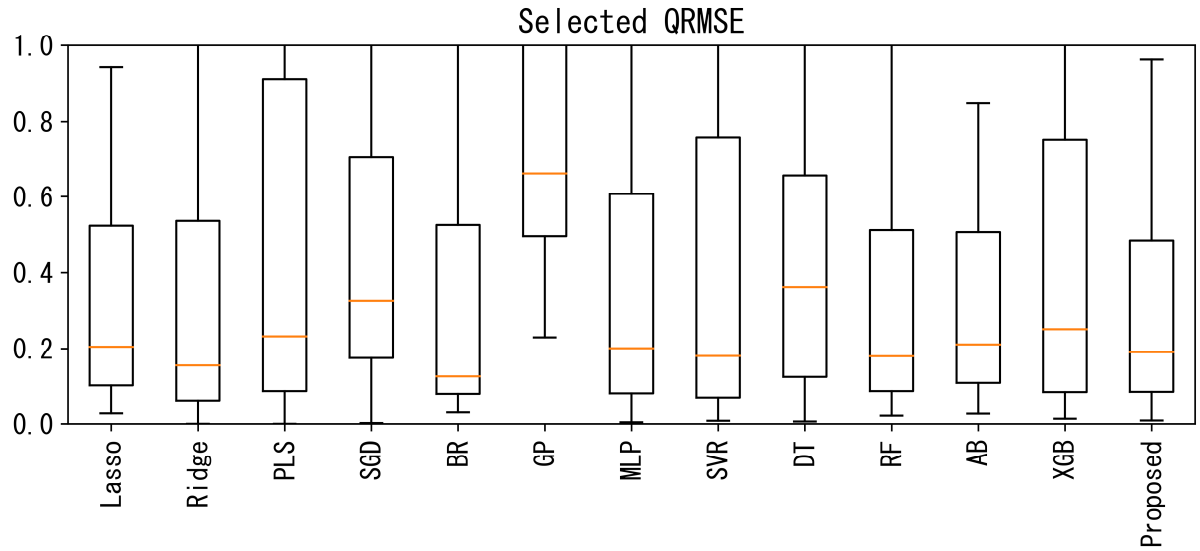


Figure S13. Cross-validation results for each regressor.

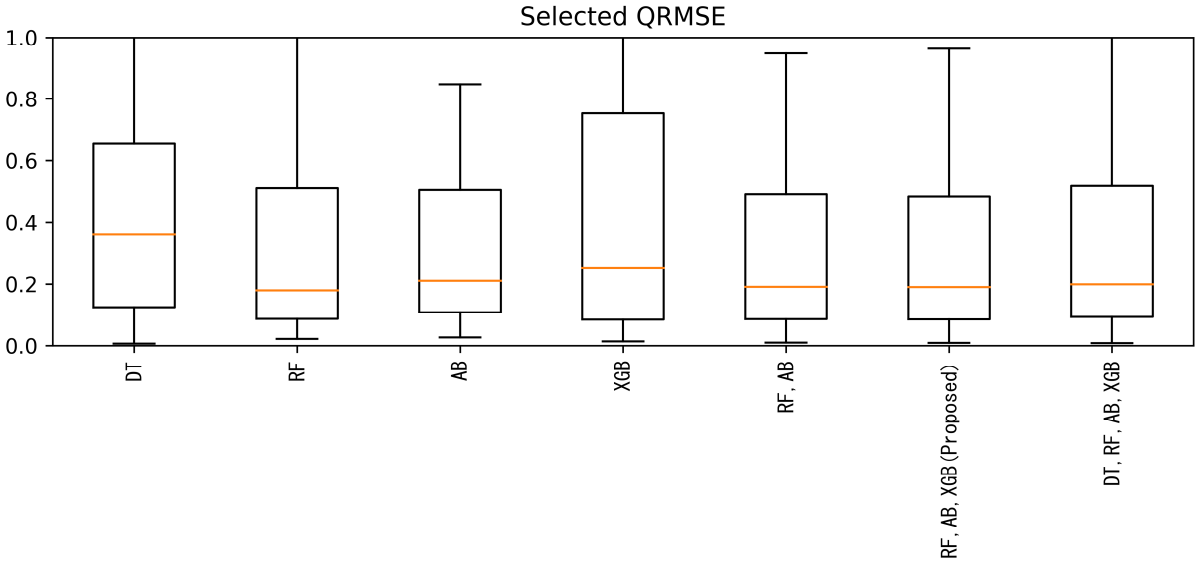


Figure S14. Cross-validation results for non-linear tree-based regressor and the combination.

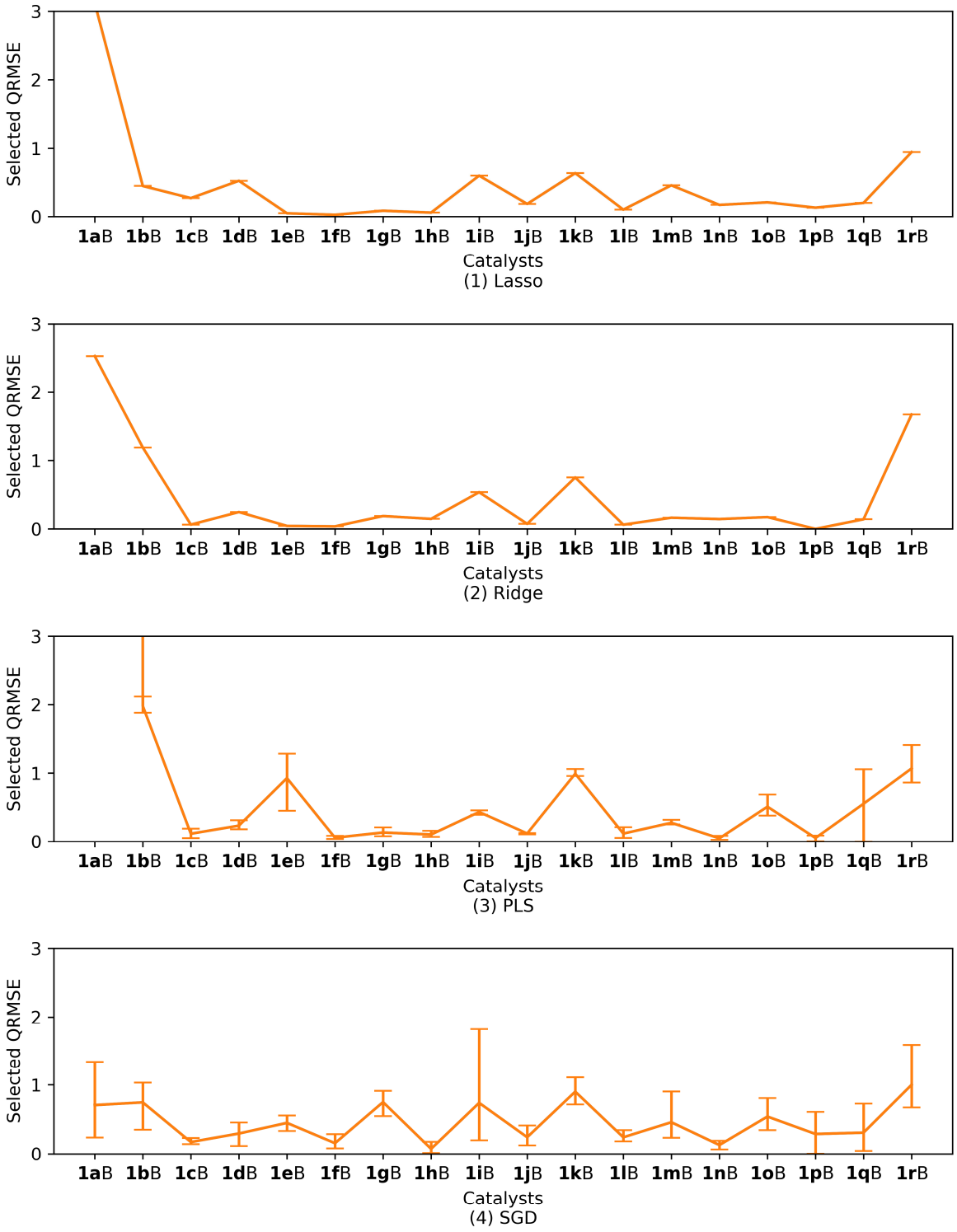


Figure S15. Cross-validation results for the linear algorithms.

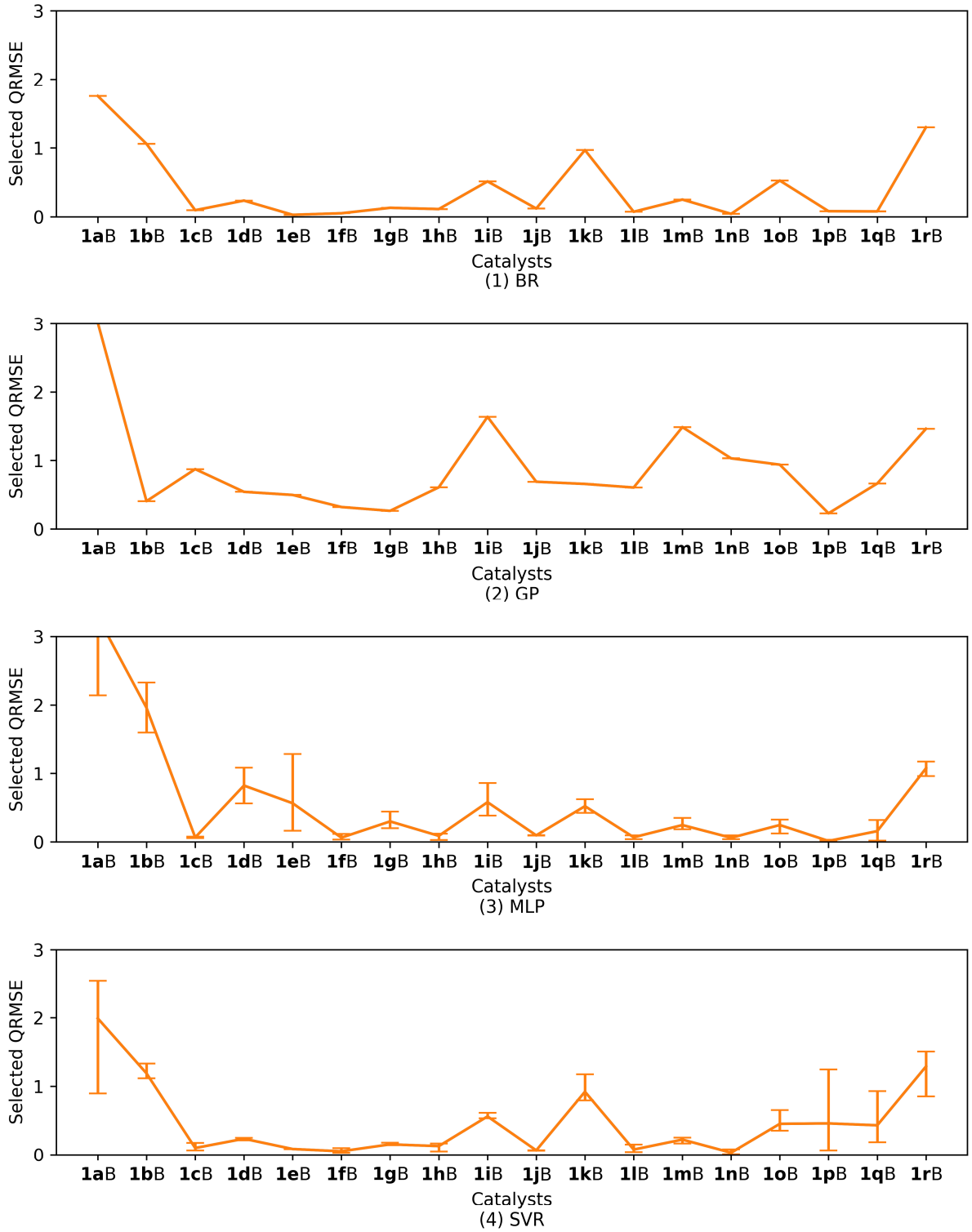


Figure S16. Cross-validation results for the non-linear non-tree-based algorithms.

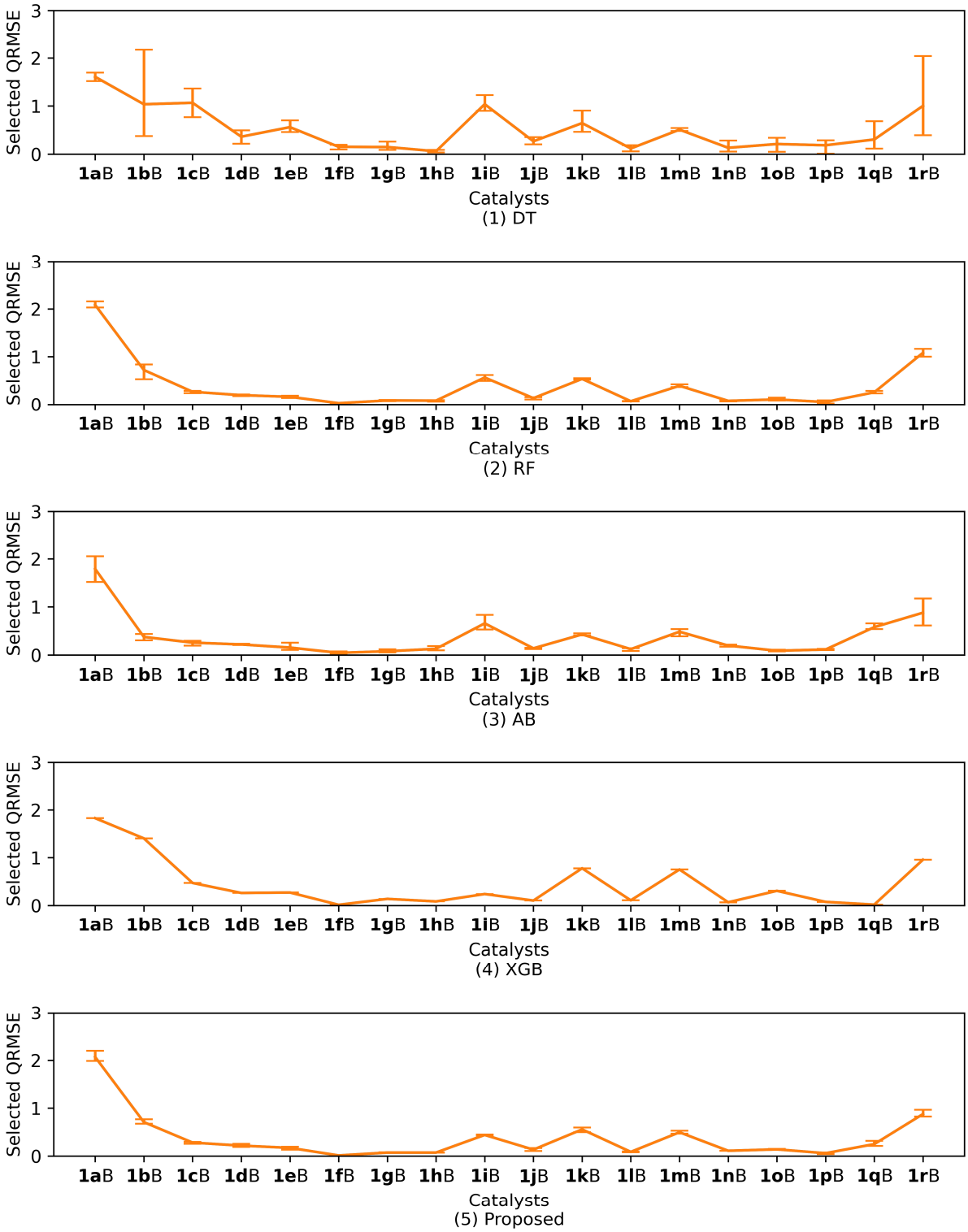


Figure S17. Cross-validation results for the non-linear tree-based algorithms.

Prediction

The proposed algorithm can also present "maximum" and "minimum" values through the model as well as ensemble averages. The "maximum value" can be interpreted as an optimistic expectation and the "minimum value" as a pessimistic expectation. The selectivity for unlearned 13 catalysts in Figure S18A was predicted by the proposed algorithm (Figure S18B). The prediction used all solvents and **2b** as the aromatic aldehyde. The ensemble mean, maximum and minimum values of the prediction are summarized in Figure S19 and Table S21. The catalysts can be divided into four categories based on the components of their π-pocket.

·*Category 1* (**1A**B–**1D**B) : Heteroaromatics are introduced as the components of their π-pocket.
·*Category 2* (**1E**B–**1G**B) : Alkylated aryl groups are introduced as the components of their π-pocket.
·*Category 3* (**1H**B–**1J**B) : Polycyclic aromatic hydrocarbons are introduced as the components of their π-pocket.
·*Category 4* (**1K**B–**1M**B) : Replacement of the aromatic moieties for the π-pocket with alkyl groups.

In Figure S19, the catalysts in *category 4* showed low estimated selectivity, supporting the importance of π-pocket constructed by aromatic substituents in the selectivity recognition of aromatic aldehyde. Other categories (*categories 1*, *2*, and *3*) were predicted to show similar high selectivity (**4a**/**4b** > 45:55). In these categories, the catalysts with the π-pocket composed by more π-extended or more substituted aromatic substituents tended to exhibit high predicted selectivity. A typical example is the comparison between **1A**B (**1C**B) and **1B**B (**1D**B). While the catalyst having a π-pocket consisting of simple heterole (furan (**1B**B) or thiophene (**1D**B)) shows a moderate selectivity (**4a**/**4b** = 43:57 (for **1B**B) or 41:59 (for **1D**B)), the predicted selectivity is improved in **1A**B (**4a**/**4b** = 33:67) or **1C**B (**4a**/**4b** = 34:66) through the benzo-fusions to the heterole moieties (beznfurane (**1A**B) and benzothiophene (**1B**B)). The benzo-fused effect in *category 1* on the predicted selectivity is more prominent. The higher selectivities of **1A**B and **1C**B are predicted than those of the catalysts in *categories 2* and *3*. It is interesting that such structurally minor changes can lead to significant improvements of the selectivity. The curiosity of the prediction, as well as the highly synthetic accessibility of the catalysts in *category 1*, strongly prompted us to experimentally investigate their selective recognition of aromatic aldehyde. In *category 1*, **1A**B having the π-pocket composed of 2-benzofuryl moieties had the highest predicted selectivity and the narrowest range between maximum and minimum prediction. Since the narrowest range can be interpreted as the most reliable prediction, **1A**B was selected as the target catalyst.

Figure S20 shows the estimated selectivity vs. the measured selectivity plots with and without **1A**B added to the training data. It was confirmed that adding **1A**B to the training data resulted in very high accuracy predictions. It was also confirmed that the prediction was also very accurate when it was not added to the training data.

Two-dimensional PCA (principal component analysis) plots of the explanatory variables are shown in Figure S21. Although this is not the non-linear space used in the proposed algorithm, it is a linear space with the PCA. The fact that **1A**B was within the range of the other experiments suggests that the selectivity was easy to predict.

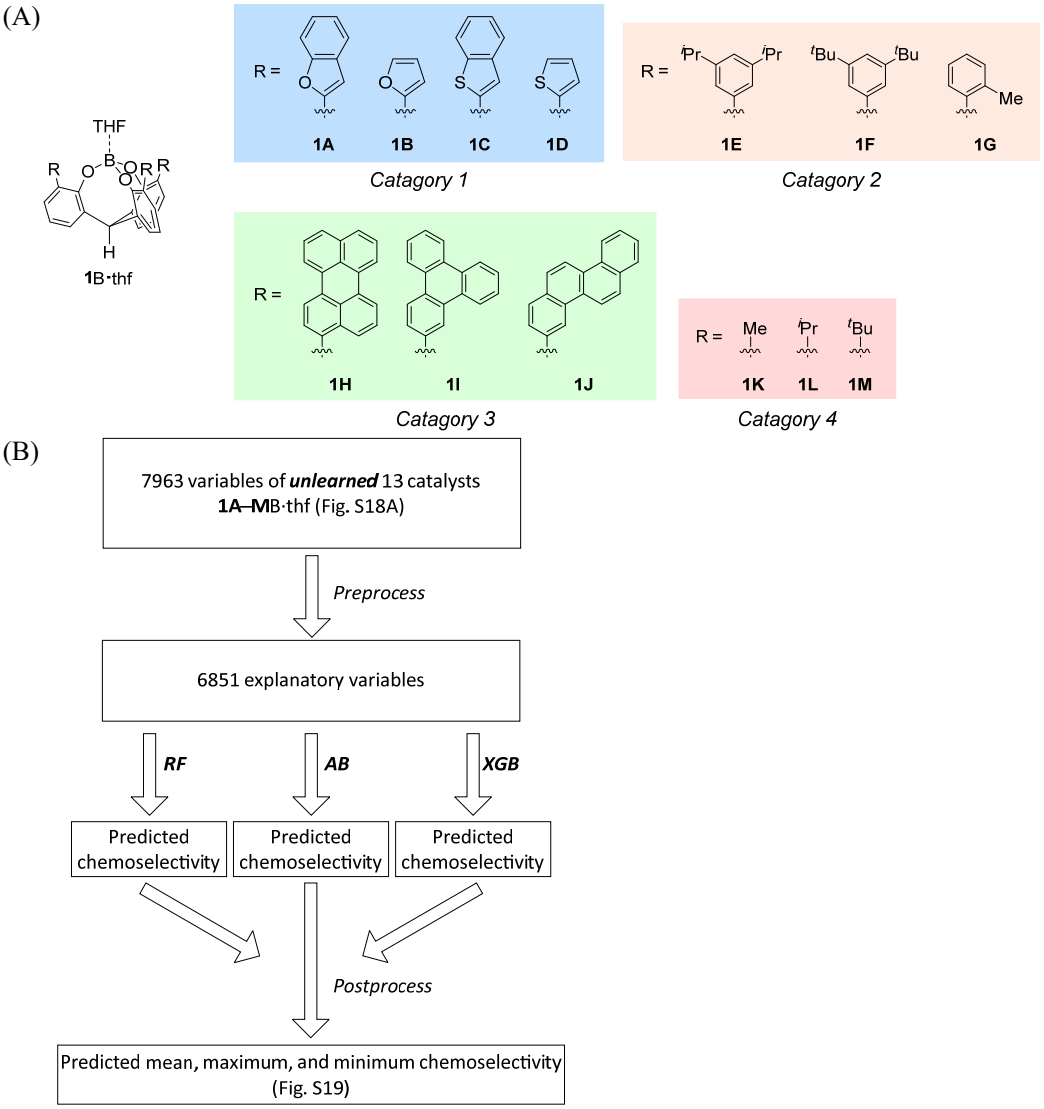


Figure S18. (A) Target unlearned borate catalysts. (B) Flow diagram of the proposed ensemble algorithm at predicting phase.

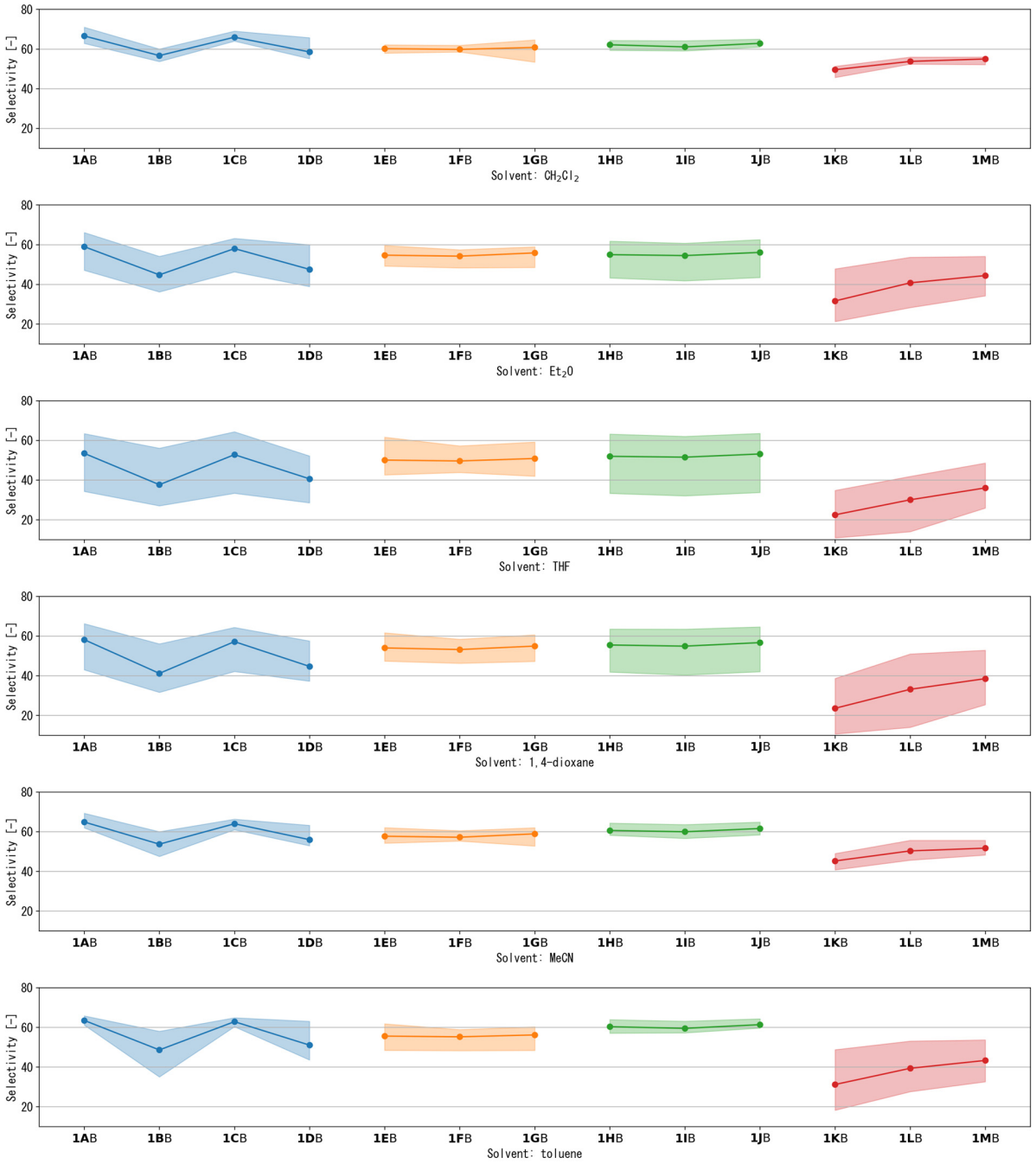


Figure S19. Ensemble mean, maximum and minimum selectivity of the prediction for each solvent and catalyst. Plots are ensemble means, hatched from maximum to minimum. Blue, orange, green, and red are *categories* 1–4, respectively.

Table S21. Summary for ensemble mean, maximum and minimum selectivity (**4a**/**4b**) of the prediction for each solvent and catalyst.

4a/**4b**	Solvent								
	CH_2Cl_2			Et_2O			THF		
cat.	mean	min	max	mean	min	max	mean	min	max
1AB	33/67	37/63	29/71	41/59	53/47	34/66	47/53	66/34	37/63
1BB	43/57	46/54	40/60	55/45	64/36	46/54	62/38	73/27	44/56
1CB	34/66	36/64	31/69	42/58	54/46	37/63	47/53	67/33	36/64
1DB	41/59	45/55	34/66	52/48	61/39	40/60	59/41	71/29	48/52
1EB	40/60	42/58	38/62	45/55	51/49	40/60	50/50	57/43	38/62
1FB	40/60	42/58	38/62	46/54	52/48	43/57	50/50	56/44	43/57
1GB	39/61	47/53	35/65	44/56	52/48	41/59	49/51	58/42	41/59
1HB	38/62	41/59	36/64	45/55	57/43	38/62	48/52	67/33	37/63
1IB	39/61	41/59	36/64	46/54	58/42	39/61	48/52	68/32	38/62
1JB	37/63	39/61	35/65	44/56	57/43	37/63	47/53	66/34	37/63
1KB	50/50	54/46	49/51	68/32	79/21	52/48	78/22	89/11	65/35
1LB	46/54	48/52	44/56	59/41	72/28	46/54	70/30	86/14	58/42
1MB	45/55	48/52	44/56	56/44	66/34	46/54	64/36	74/26	51/49

4a/**4b**	Solvent								
	1,4-dioxane			MeCN			toluene		
cat.	mean	min	max	mean	min	max	mean	min	max
1AB	42/58	57/43	34/66	35/65	38/62	31/69	37/63	39/61	34/66
1BB	59/41	68/32	44/56	46/54	52/48	40/60	51/49	65/35	42/58
1CB	43/57	58/42	36/64	36/64	39/61	34/66	37/63	40/60	35/65
1DB	55/45	63/37	43/57	44/56	47/53	37/63	49/51	56/44	37/63
1EB	46/54	53/47	38/62	42/58	46/54	38/62	44/56	52/48	38/62
1FB	47/53	54/46	42/58	43/57	45/55	40/60	45/55	52/48	41/59
1GB	45/55	53/47	39/61	41/59	47/53	38/62	44/56	52/48	40/60
1HB	45/55	58/42	37/63	39/61	42/58	36/64	40/60	43/57	36/64
1IB	45/55	60/40	37/63	40/60	43/57	36/64	41/59	43/57	37/63
1JB	43/57	58/42	35/65	38/62	42/58	35/65	39/61	40/60	36/64
1KB	76/24	89/11	61/39	55/45	59/41	51/49	69/31	82/18	51/49
1LB	67/33	86/14	49/51	50/50	54/46	44/56	61/39	72/28	47/53
1MB	62/38	75/25	47/53	48/52	52/48	44/56	57/43	67/33	46/54

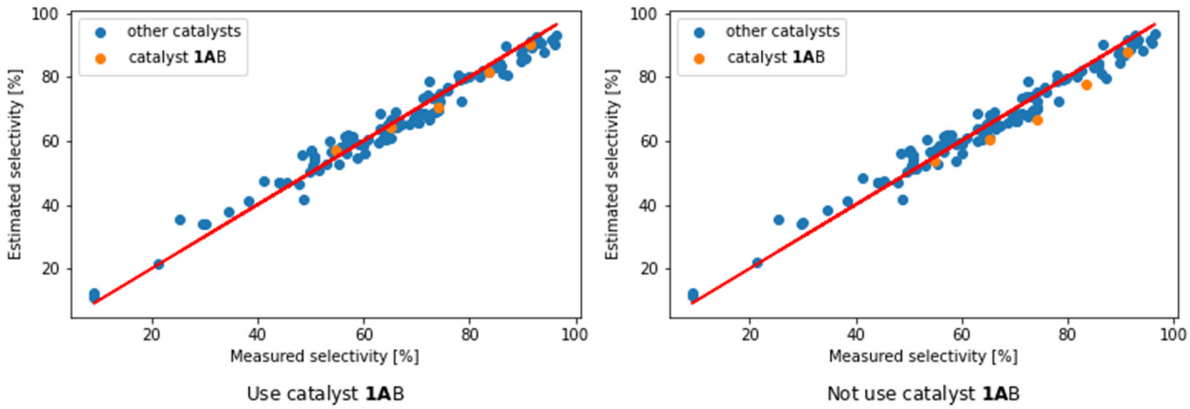


Figure S20. Estimated selectivity vs. the measured selectivity plots. The dots represent the estimated selectivity. The red line represents ideal estimation results. On the left is the prediction using experimental data of **1A**B and on the right is the prediction without it.

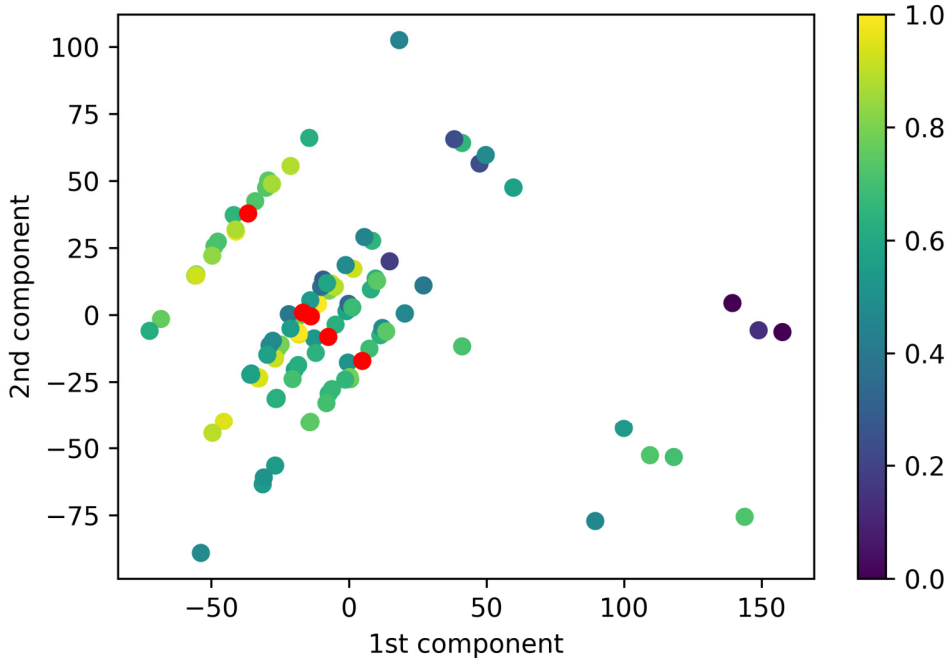


Figure S21. Two-dimensional PCA plots of the explanatory variables. The green gradation color represents selectivity from 0 to 1.0. The red dots represent **1A**B.

Interpretation

We evaluated each explanatory variable using shapley additive explanations (SHAP), a method that has introduced cooperative game theory to evaluate the contribution of each feature[32]. The contribution to the predicted chemoselectivity from 6851 explanation variables was evaluated using SHAP values. The higher the absolute SHAP value, the greater the contribution to the predicted chemoselectivity. Since SHAP values varied by dataset, the SHAP value was evaluated as the average of the absolute SHAP values of the training dataset with **1A**B and **1B**B. Figure S22 showed the average absolute SHAP values for the top 10 variables. Herein, the variable name prefix 2_ means a factor of the substrate, 4_ means a factor of the catalyst, and s_ means a factor of the solvent. The top two variables (2_SCBO and 4_TDB08p) contributed significantly to the predicted chemoselectivity, while the other variables contributed modestly. 2_SCBO is *the sum of conventional bond orders (H-depleted) of the substrate*, which corresponds to the three-dimensional substrate size weighted by the number of the composed covalent bonds. The insight nicely supported the experimental results; aromatic aldehydes having substituents and fewer hydrogen atoms, such as pentafluorobenzaldehyde **3e** and 4-cyanobenzaldehyde **3f** showed the high selectivity over butanal **3a**. From the viewpoint of molecular orbital theory, these aldehydes have the lower LUMO levels of the carbonyl that also promote the selective hetero-Diels-Alder reactions. On the other hand, 4_TDB08p is *the 3D Topological distance-based descriptors of the catalyst - lag 8 weighted by polarizability*, which corresponds to the three-dimensional size of a catalyst weighted by its molecular polarizability. The feature proposed the new insight into the design of the π-pocket as the molecular recognition site. We have already noticed that the catalysts having the π-pocket constructed by *meta*-substituted phenyl (**1l**B), or 1- (**1m**B)/2-naphthyl (**1n**B) moieties showed the higher selectivity of aromatic aldehydes than the catalysts having the π-pocket constructed by *para*-substituted or 3,5-disubstituted aromatic moieties. According to the SHAP analysis, the persistence of the molecular polarizability, which is mainly derived from the lower symmetric substituent patterns of the π-pocket, should contribute to the selectivity of aromatic aldehyde.

The other features after the third place were as follows.

s_Mp: *mean atomic polarizability (scaled on Carbon atom) of solvent*
4_WiA_G/D: *average Wiener-like index from distance/distance matrix of catalyst*
4_Sp: *sum of atomic polarizabilities (scaled on Carbon atom) of catalyst*
2_AVS_B(m): *average vertex sum from Burden matrix weighted by mass of reactant*
2_Mp: *mean atomic polarizability (scaled on Carbon atom) of reactant*
2_Se: *sum of atomic Sanderson electronegativities (scaled on Carbon atom) of reactant*
2_nBM: *number of multiple bonds of reactant*
4_CATS3D_04_AL: *CATS3D Acceptor-Lipophilic BIN 04 (4.000 – 5.000 Å) of catalyst*

The correlation between SHAP values and feature values of top 10 explanation variables were shown in Figure S23. The further to the right, the more it contributed to increasing the predicted selectivity, and the further to the left, the less it contributed to decreasing the predicted selectivity. The SHAP value was larger when 2_SCBO was large (in red) and smaller when 2_SCBO was small (in blue). These results indicated that increasing 2_SCBO, *i.e.*, increasing the number (*i.e.*, size) of the composed covalent bonds of the substrate, contributed significantly to higher predicted selectivity. The SHAP value was smaller when 4_TDB08p was small (in blue), but its absolute

value tended to be smaller than 2_SCBO when 4_TDB08p was high (in red), both positive and negative. These results suggested that a larger 4_TDB08p, *i.e.*, a larger three-dimensional size of the catalyst weighted by its polarizability, contributed to a higher predicted selectivity, but not to a large extent. However, it was suggested that a smaller 4_TDB08p contributes significantly to lower predicted selection rates. It was also shown that increasing 2_Mp and 2_nBM may contribute significantly to a higher predicted selectivity. Conversely, it was suggested that a larger 2_Se would contribute to a lower predicted selectivity. For a catalyst design, it should be noted that a larger 4_CATS3D_04_AL and a larger 4_Sp contributed to a higher predicted selectivity, but a smaller 4_Sp may also contributed to a higher predicted selectivity.

The correlations between SHAP values and each explanatory variable for **1A**B and **1B**B differed significantly. The 4_TDB08p increased the predicted selectivity in **1A**B, whereas 4_TDB08p decreased the predicted selectivity in **1B**B. Since s_Mp was an explanatory variable for solvent, the same trend was obtained for the same solvent. CH_2Cl_2, MeCN, and toluene increased the predicted selectivity, while Et_2O, THF, and 1,4-dioxane decreased the predicted selectivity. Therefore, the investigation of the SHAP values of the proposed ensemble prediction method provided many suggestions for improving the selectivity.

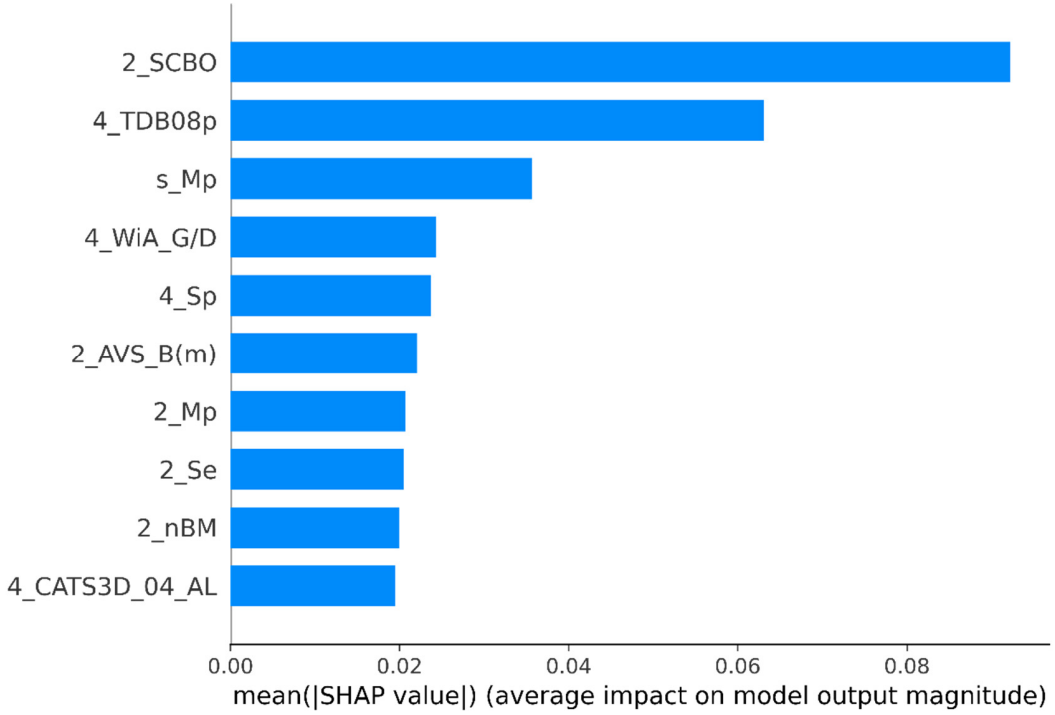


Figure S22. Mean absolute SHAP value of top 10 explanatory variables.

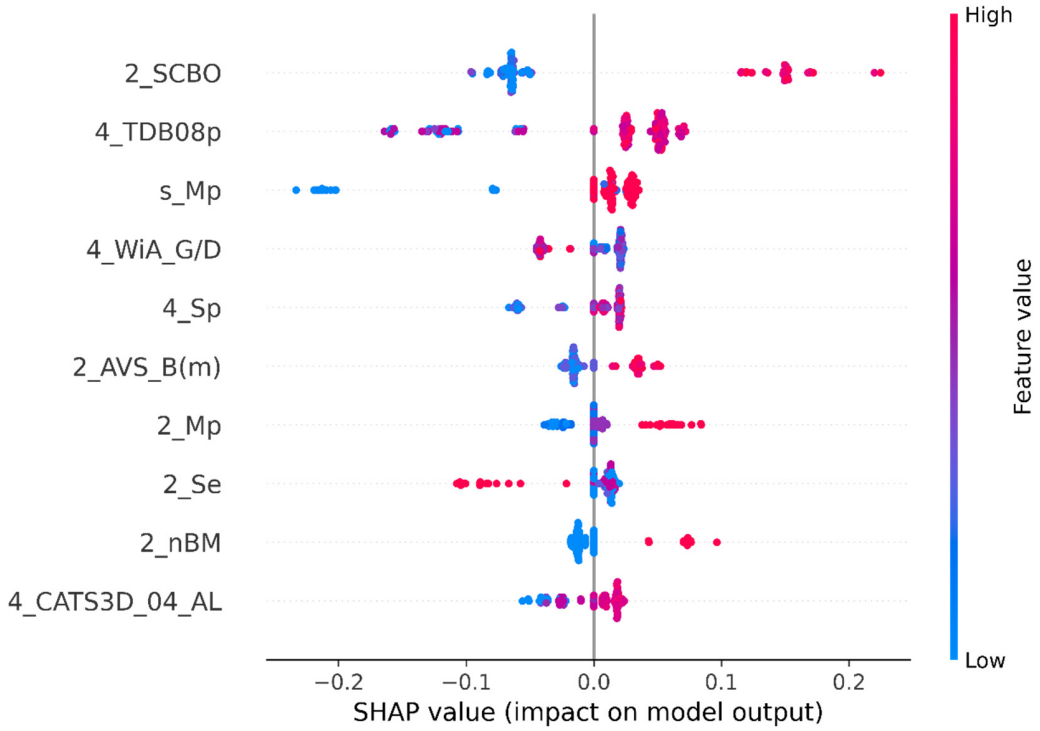


Figure S23. Correlation between SHAP value and feature value of top 10 explanation variables. Duplicated SHAP values are plotted by jitter. The dots are colored by feature value of each explanation variable.

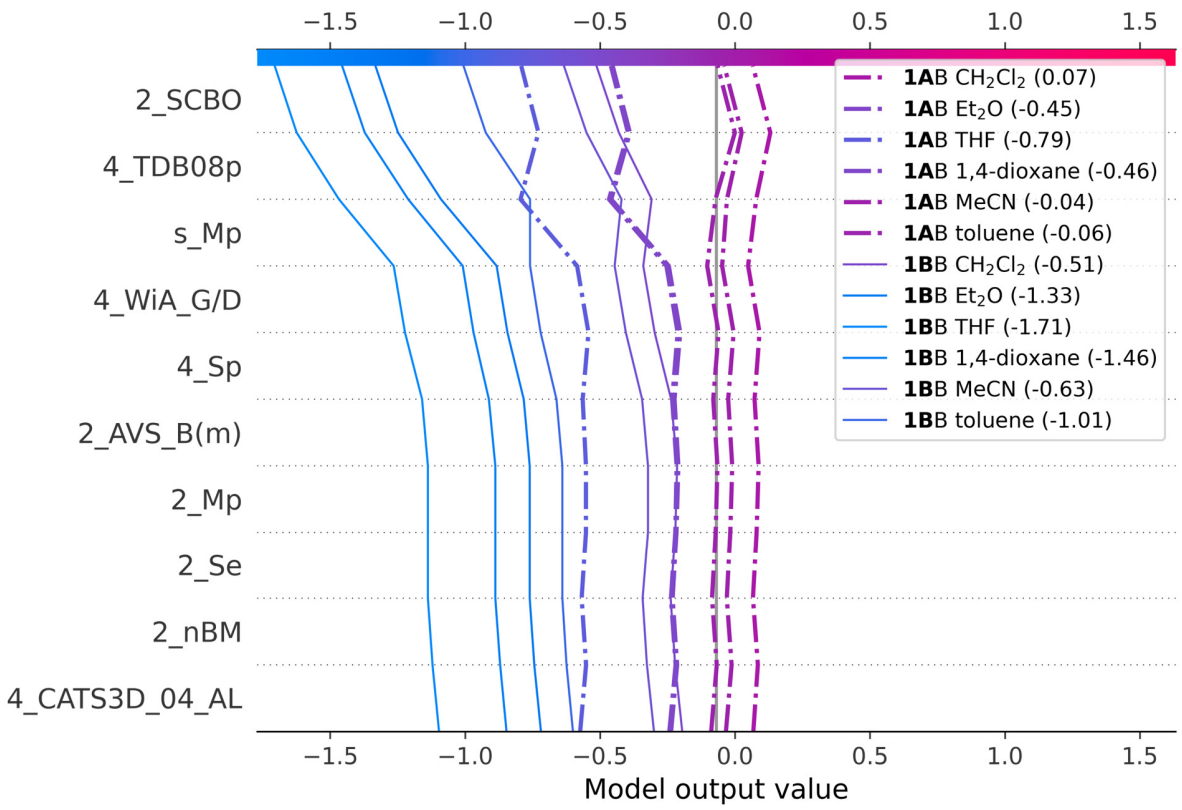


Figure S24. Contribution to standardized model output value by top 10 explanation variables. Lines are colored by the output value. Dash-dotted line represents **1A**B, solid line represents **1B**B. Each catalyst has 6 lines for 6 types of solvents.

Table S22. Summary for shap values of each explanation variables for each combination of catalyst (**1A**B or **1B**B) and solvent.

Catalyst Solvent	Explanation variables									
	2_SCBO	4_TDB08p	s_Mp	4_WiA_G/D	4_Sp	2_AVS_B(m)	2_Mp	2_Se	2_nBM	4_CATS3D_04_AL
1AB CH_2Cl_2	-0.0647	0.0524	0.0299	-0.0424	0.0185	-0.0151	0.0075	0.0135	-0.0181	0.0166
1AB Et_2O	-0.0636	0.0689	-0.2130	-0.0424	0.0211	-0.0142	0.0071	0.0141	-0.0165	0.0223
1AB THF	-0.0637	0.0665	-0.2098	-0.0421	0.0214	-0.0121	0.0000	0.0160	-0.0164	0.0218
1AB 1,4-dioxane	-0.0634	0.0706	-0.2129	-0.0416	0.0202	-0.0164	0.0048	0.0160	-0.0172	0.0231
1AB MeCN	-0.0645	0.0547	0.0179	-0.0427	0.0202	-0.0150	0.0072	0.0130	-0.0179	0.0210
1AB toluene	-0.0638	0.0719	0.0308	-0.0421	0.0197	-0.0156	0.0065	0.0136	-0.0176	0.0206
1BB CH_2Cl_2	-0.0829	-0.1213	0.0310	-0.0421	-0.0609	-0.0224	0.0068	0.0172	-0.0166	-0.0264
1BB Et_2O	-0.0836	-0.1591	-0.2061	-0.0402	-0.0602	-0.0222	0.0000	0.0000	-0.0169	-0.0247
1BB THF	-0.0812	-0.1566	-0.2029	-0.0419	-0.0632	-0.0216	0.0000	0.0000	-0.0171	-0.0242
1BB 1,4-dioxane	-0.0837	-0.1609	-0.2021	-0.0400	-0.0568	-0.0239	0.0000	0.0000	-0.0178	-0.0236
1BB MeCN	-0.0834	-0.1297	0.0254	-0.0415	-0.0602	-0.0218	0.0000	0.0199	-0.0160	-0.0261
1BB toluene	-0.0822	-0.1642	0.0000	-0.0392	-0.0586	-0.0219	0.0000	0.0000	-0.0153	-0.0239

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