**Supporting information**

# Cooperative Effects of *o*- and *m*-Methyl Groups on the Intramolecular Charge-Transfer Emission Properties of Dibenzoylmethanatoboron Difluorides

Mirai Tanaka[a], Shunsuke Muraoka[a], Yasunori Matsui[a,b], Eisuke Ohta[a,b], Takuya Ogaki[a,b], Kazuhiko Mizuno[a], and Hiroshi Ikeda[a,b,*]

[a] *Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan*
[b] *The Research Institute for Molecular Electronic Devices (RIMED), Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan*
*Corresponding author. *TEL and FAX*: +81-72-254-9289. *E-mail address*: ikeda@chem.osakafu-u.ac.jp

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## 1. $^{1}$H and $^{13}$C NMR spectra

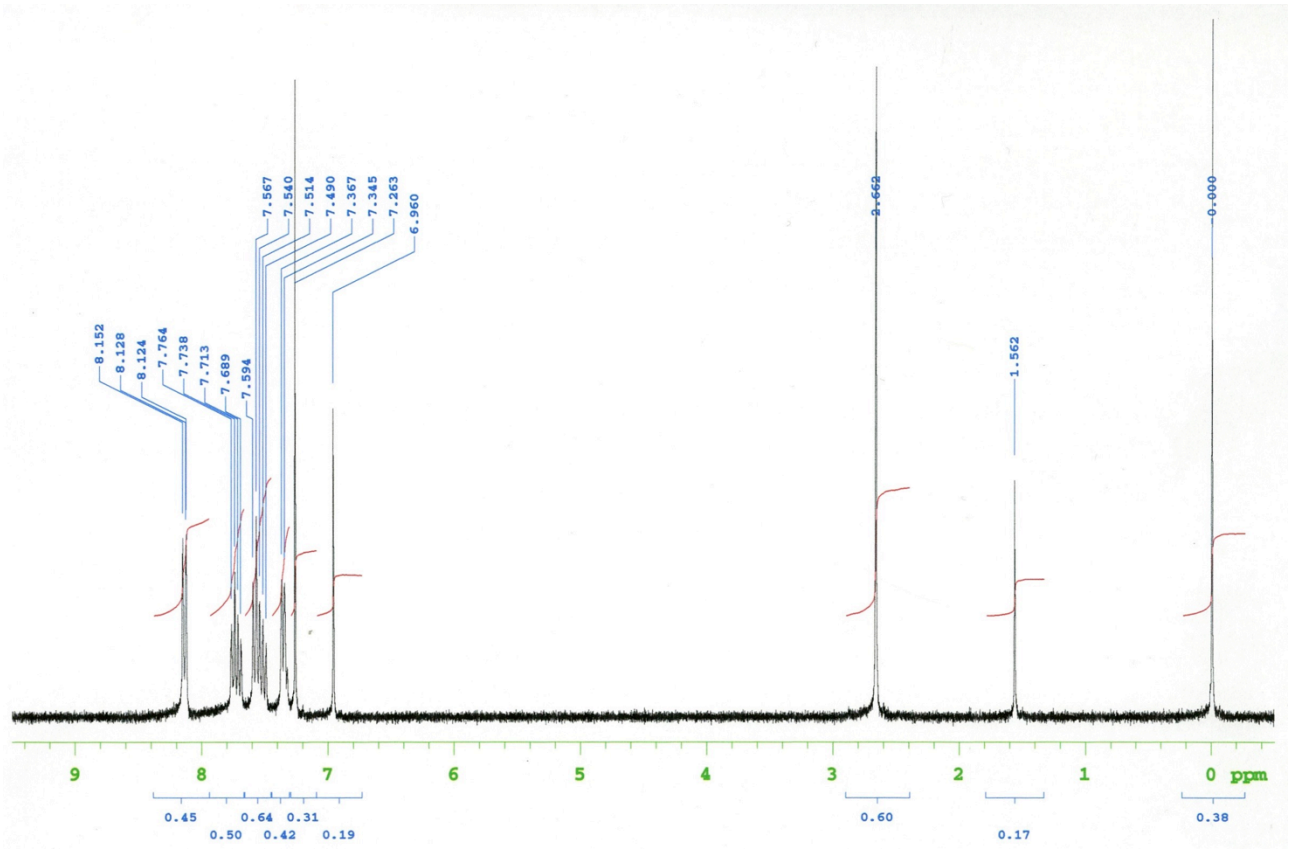


**Fig. S1.** $^{1}$H NMR spectrum of ***o*Tol-3** in $CDCl_3$.

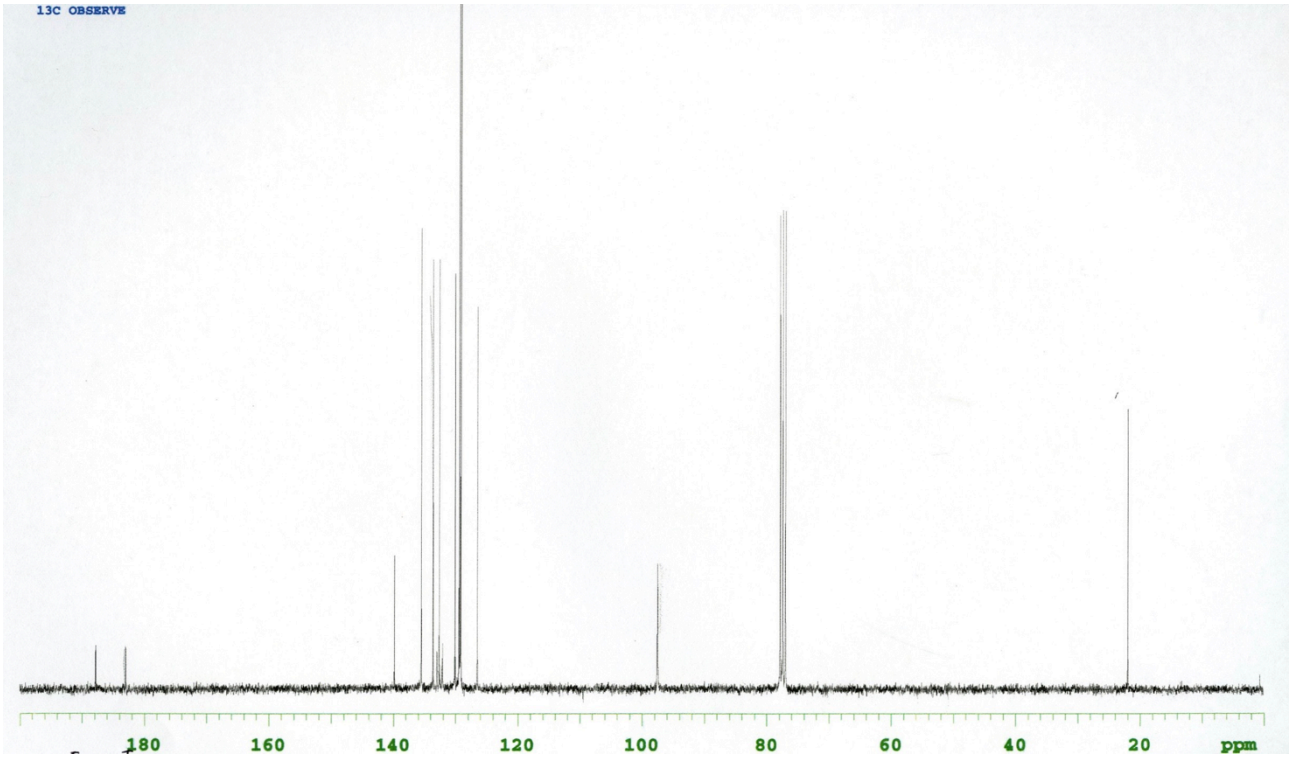


**Fig. S2.** $^{13}C$ NMR spectrum of ***o*Tol-3** in $CDCl_3$.

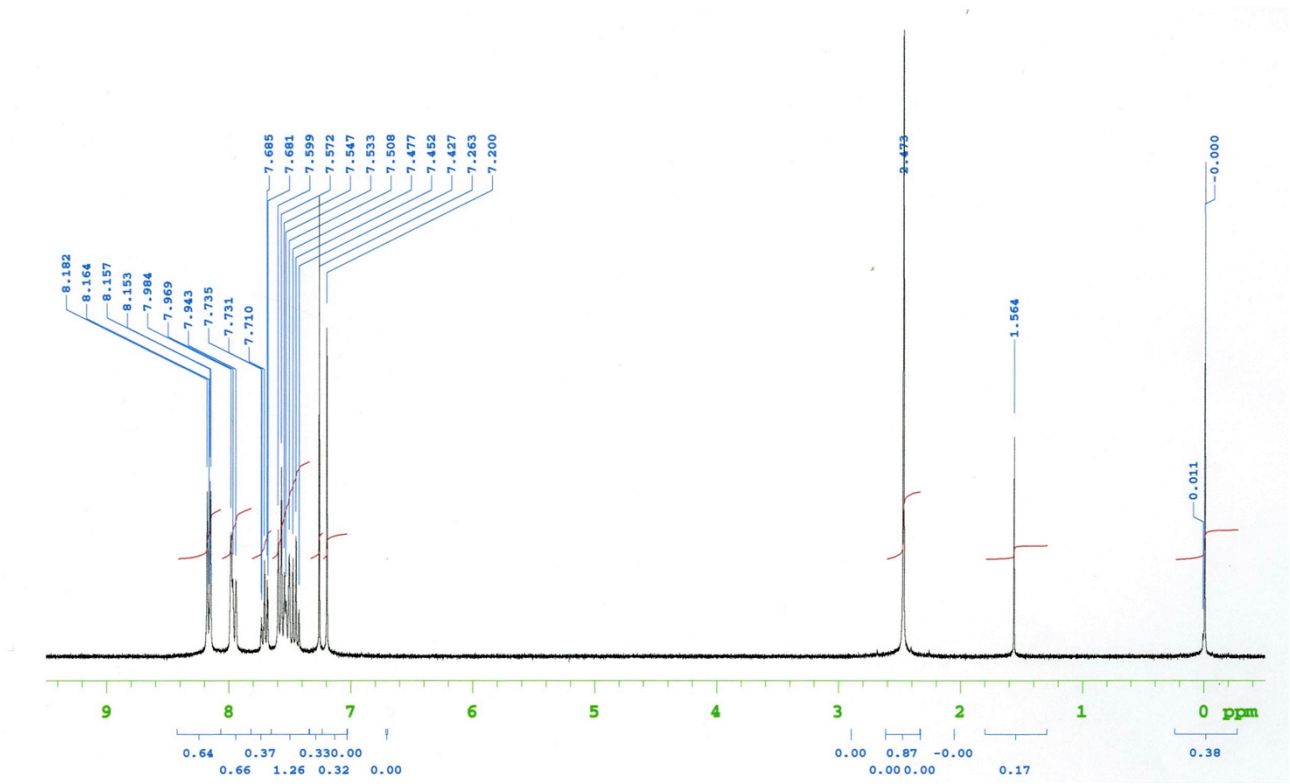


**Fig. S3.** $^{1}H$ NMR spectrum of ***m*Tol-3** in $CDCl_3$.

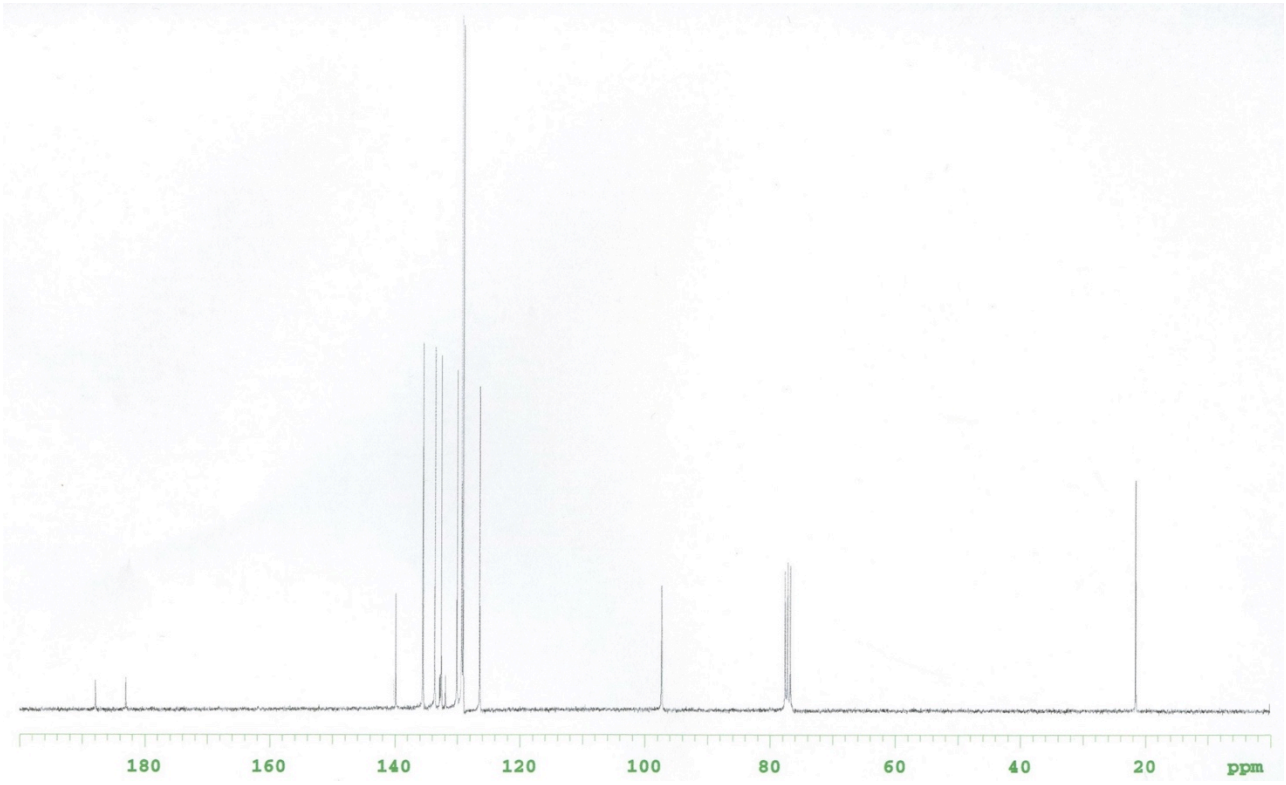


**Fig. S4.** $^{13}C$ NMR spectrum of ***m*Tol-3** in $CDCl_3$.

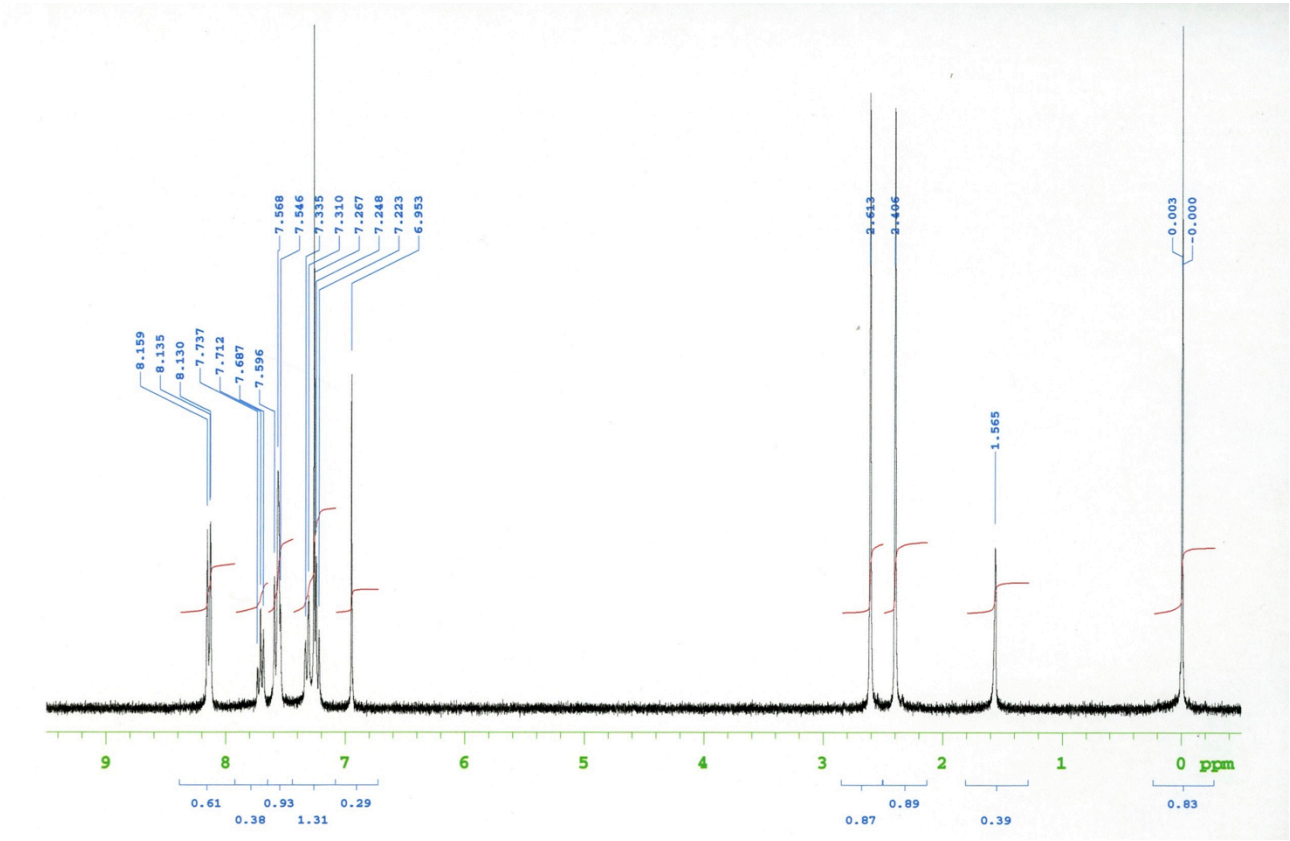


**Fig. S5.** $^{1}H$ NMR spectrum of **Xyl-4** in $CDCl_3$.

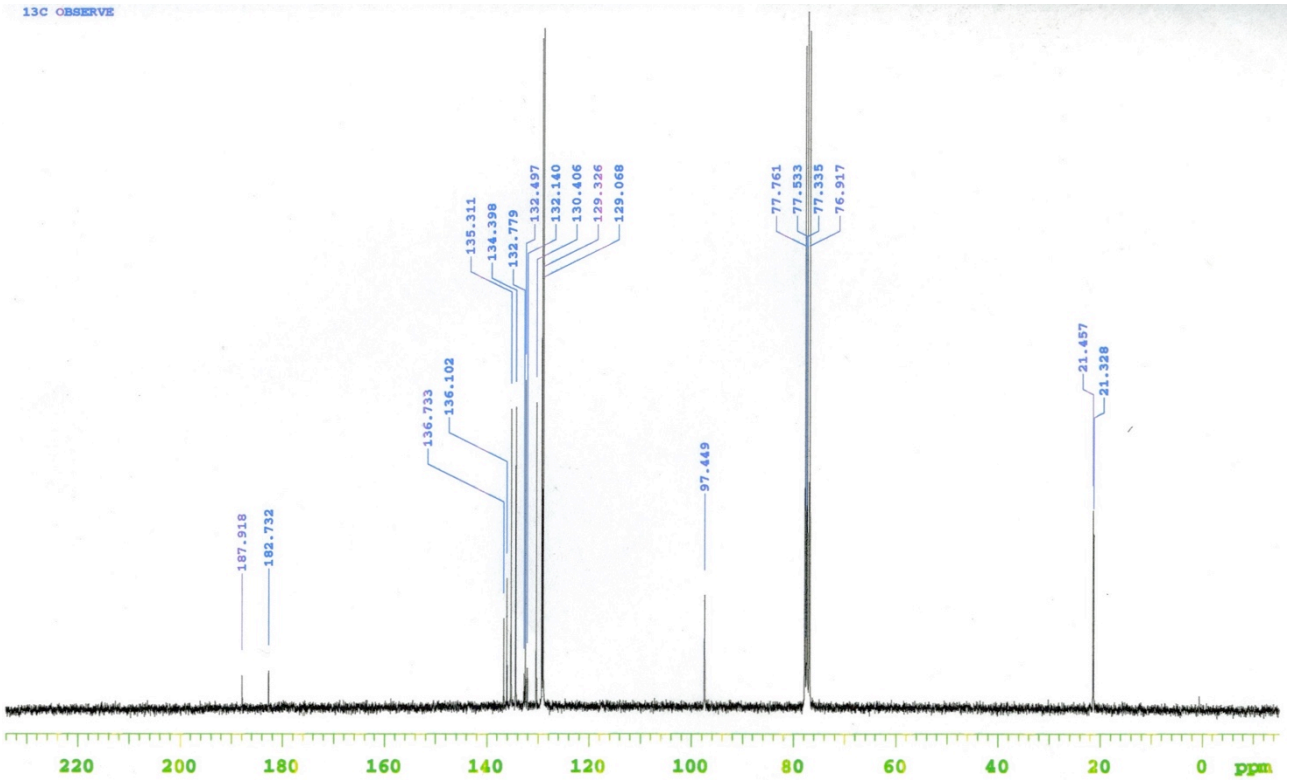


**Fig. S6.** $^{13}C$ NMR spectrum of **Xyl-4** in $CDCl_3$. The chemical shift at 77.335 ppm was used as an internal standard (77.160 ppm) of $^{13}CDCl_3$. Thus, all corrected chemical shifts of $^{13}C$ for **Xyl-4** shown in the Experimental Section were calculated to be (the chemical shift in Fig. S6) – 0.17 ppm.

## 2. Density functional theory calculation

**Table S1.** The Cartesian Coordinates (in Å) of ***o*Tol-3** Optimized by B3LYP/6-311G(d,p) (The sum of electronic and zero-point energies is –992.728878 Hartree.)

| Atoms | Coordinates | | |
|---|---|---|---|
| | x | y | z |
| C | –3.50097 | 0.00895 | –0.36445 |
| C | –4.66843 | –0.76065 | –0.38488 |
| C | –4.69201 | –2.08398 | 0.04344 |
| C | –3.52390 | –2.68747 | 0.50092 |
| C | –2.34614 | –1.95498 | 0.51400 |
| C | –2.31439 | –0.61536 | 0.09270 |
| C | –3.56715 | 1.43763 | –0.85081 |
| H | –5.58248 | –0.30443 | –0.74903 |
| C | –1.02664 | 0.10691 | 0.14419 |
| H | –5.62154 | –2.64148 | 0.01899 |
| H | –1.43876 | –2.41218 | 0.88933 |
| H | –4.48757 | 1.59450 | –1.41590 |
| H | –2.72016 | 1.70339 | –1.48403 |
| O | –1.07848 | 1.36189 | 0.44834 |
| C | 0.19436 | –0.52791 | –0.10626 |
| C | 1.38437 | 0.18018 | 0.07876 |
| B | 0.11479 | 2.27864 | 0.26335 |
| O | 1.37200 | 1.44141 | 0.37016 |
| H | 0.20781 | –1.55648 | –0.42318 |
| C | 2.72222 | –0.43380 | –0.03052 |
| F | 0.11636 | 3.20548 | 1.25815 |
| F | 0.04906 | 2.79815 | –1.00925 |
| C | 2.90268 | –1.82506 | –0.05979 |
| C | 3.84784 | 0.40120 | –0.10253 |
| C | 5.12043 | –0.14439 | –0.21376 |
| C | 4.17735 | –2.36631 | –0.16788 |
| C | 5.28866 | –1.52777 | –0.24804 |
| H | 3.70519 | 1.47305 | –0.07526 |
| H | 5.98227 | 0.50965 | –0.27492 |
| H | 2.05226 | –2.48984 | 0.02143 |
| H | 4.30572 | –3.44220 | –0.18408 |
| H | 6.28243 | –1.95230 | –0.33351 |
| H | –3.55492 | 2.13697 | –0.01191 |
| H | –3.53084 | –3.71417 | 0.84674 |

**Table S2.** The Cartesian Coordinates (in Å) of ***m*Tol-3** Optimized by B3LYP/6-311G(d,p) (The sum of electronic and zero-point energies is –992.733015 Hartree.)

| Atoms | Coordinates | | |
|---|---|---|---|
| | x | y | z |
| C | 3.34565 | 1.03276 | 0.12259 |
| C | 2.31760 | 0.08781 | 0.00995 |
| C | 2.64497 | –1.27536 | –0.06802 |
| C | 3.96773 | –1.70841 | –0.02694 |
| C | 4.97680 | –0.74391 | 0.09624 |
| C | 4.66877 | 0.61103 | 0.16900 |
| H | 3.09246 | 2.08265 | 0.17751 |

| | | | |
|---|---|---|---|
| C | 0.91937 | 0.55930 | –0.02881 |
| H | 5.46378 | 1.34165 | 0.26246 |
| C | 4.31499 | –3.17501 | –0.11649 |
| H | 1.86146 | –2.01406 | –0.18646 |
| H | 6.01430 | –1.06099 | 0.13079 |
| H | 3.42237 | –3.78977 | –0.24508 |
| H | 4.98235 | –3.37212 | –0.96036 |
| O | 0.76440 | 1.82446 | –0.24765 |
| C | –0.18235 | –0.28370 | 0.14437 |
| C | –1.46940 | 0.22737 | –0.03769 |
| B | –0.57162 | 2.52057 | –0.07612 |
| O | –1.66647 | 1.48677 | –0.25641 |
| H | –0.03954 | –1.32170 | 0.38841 |
| C | –2.68585 | –0.60923 | –0.00789 |
| C | –2.63099 | –2.00748 | –0.10931 |
| C | –3.93532 | 0.01668 | 0.11857 |
| C | –5.09891 | –0.74108 | 0.15744 |
| C | –3.79752 | –2.76105 | –0.07514 |
| C | –5.03354 | –2.13029 | 0.06176 |
| H | –3.97382 | 1.09531 | 0.19033 |
| H | –6.05816 | –0.24807 | 0.26280 |
| H | –1.68095 | –2.51000 | –0.23934 |
| H | –3.74433 | –3.83997 | –0.16143 |
| H | –5.94257 | –2.72022 | 0.08974 |
| F | –0.64309 | 2.99900 | 1.20841 |
| F | –0.69935 | 3.46570 | –1.04651 |
| H | 4.82726 | –3.51426 | 0.78880 |

**Table S3.** The Cartesian Coordinates (in Å) of **Xyl-4** Optimized by B3LYP/6-311G(d,p) (The sum of electronic and zero-point energies is –1032.030083 Hartree.)

| Atoms | Coordinates | | |
|---|---|---|---|
| | x | y | z |
| C | 3.25838 | –0.67205 | –0.43852 |
| C | 4.50753 | –0.04715 | –0.51533 |
| C | 4.69324 | 1.28643 | –0.17535 |
| C | 3.62167 | 2.07650 | 0.25348 |
| C | 2.36992 | 1.47480 | 0.31386 |
| C | 2.16777 | 0.12340 | –0.01737 |
| C | 3.14743 | –2.12716 | –0.82861 |
| H | 5.35794 | –0.62923 | –0.85369 |
| C | 0.80187 | –0.42741 | 0.09118 |
| C | 3.82475 | 3.52085 | 0.64125 |
| H | 5.68607 | 1.72010 | –0.24415 |
| H | 1.52625 | 2.05850 | 0.66385 |
| H | 4.03542 | –2.43022 | –1.38632 |
| H | 3.06215 | –2.76407 | 0.05470 |
| H | 4.50300 | 3.60913 | 1.49529 |
| H | 2.88128 | 3.99634 | 0.91545 |
| O | 0.70345 | –1.66122 | 0.46363 |
| C | –0.33804 | 0.33927 | –0.17659 |
| C | –1.60108 | –0.20329 | 0.06900 |
| B | –0.59786 | –2.42959 | 0.34696 |
| O | –1.73841 | –1.43832 | 0.43379 |
| H | –0.23273 | 1.34278 | –0.55114 |
| C | –2.85553 | 0.56566 | –0.05294 |
| F | –0.62781 | –3.01458 | –0.89855 |
| F | –0.68962 | –3.30064 | 1.38740 |
| C | –2.86412 | 1.96417 | –0.16779 |
| C | –4.07700 | –0.12523 | –0.04904 |
| C | –5.27538 | 0.56698 | –0.16878 |
| C | –4.06494 | 2.65255 | –0.28456 |
| C | –5.27293 | 1.95586 | –0.28805 |
| H | –4.06655 | –1.20284 | 0.04344 |
| H | –6.21259 | 0.02298 | –0.17051 |
| H | –1.93627 | 2.52138 | –0.14734 |
| H | –4.06024 | 3.73302 | –0.36751 |
| H | –6.20885 | 2.49499 | –0.38043 |
| H | 4.26274 | 4.09369 | –0.18145 |
| H | 2.26705 | –2.33044 | –1.43905 |

**Table S4.** The Cartesian Coordinates (in Å) of ***o*Tol-3*** Optimized by TD-B3LYP/6-31G(d) (The sum of electronic and zero-point energies is –992.344714 Hartree.)

| Atoms | Coordinates | | |
|---|---|---|---|
| | x | y | z |
| C | –3.11382 | –0.30693 | –0.89591 |
| C | –4.47307 | –0.75111 | –0.98839 |
| C | –5.04885 | –1.45872 | 0.03678 |
| C | –4.28044 | –1.74539 | 1.19850 |
| C | –2.94253 | –1.29985 | 1.31998 |
| C | –2.33861 | –0.60181 | 0.30185 |
| C | –2.49239 | 0.44479 | –1.99984 |
| H | –5.03268 | –0.52426 | –1.88967 |
| C | –0.96984 | –0.00127 | 0.43950 |
| H | –6.07495 | –1.80355 | –0.02834 |
| H | –2.38812 | –1.50825 | 2.22766 |
| H | –3.18557 | 0.65078 | –2.81676 |
| H | –1.62616 | –0.12353 | –2.37537 |
| O | –1.07287 | 1.28135 | 0.80959 |
| C | 0.19046 | –0.62528 | 0.12184 |
| C | 1.42021 | 0.12029 | 0.17960 |
| B | 0.04638 | 2.16015 | 0.30475 |
| O | 1.33494 | 1.43582 | 0.39853 |
| H | 0.19061 | –1.66790 | –0.17022 |
| C | 2.72688 | –0.44505 | 0.03338 |
| F | 0.09393 | 3.29063 | 1.07097 |
| F | –0.25020 | 2.44125 | –1.04458 |
| C | 2.95499 | –1.84299 | –0.09992 |
| C | 3.86780 | 0.40554 | 0.01901 |
| C | 5.14407 | –0.11435 | –0.13114 |
| C | 4.23773 | –2.34815 | –0.25171 |

| | | | |
|---|---|---|---|
| C | 5.34817 | –1.49393 | –0.27071 |
| H | 3.71307 | 1.47299 | 0.12303 |
| H | 5.99598 | 0.56152 | –0.14129 |
| H | 2.11913 | –2.53536 | –0.06976 |
| H | 4.37917 | –3.42200 | –0.35028 |
| H | 6.35045 | –1.89567 | –0.38727 |
| H | –2.01711 | 1.36953 | –1.63122 |
| H | –4.73043 | –2.31405 | 2.00615 |

**Table S5.** The Cartesian Coordinates (in Å) of ***m*Tol-3*** Optimized by TD-B3LYP/6-31G(d) (The sum of electronic and zero-point energies is –992.339284 Hartree.)

| Atoms | Coordinates | | |
|---|---|---|---|
| | x | y | x |
| C | 3.37998 | 1.03868 | –0.11887 |
| C | 2.31512 | 0.09983 | –0.04470 |
| C | 2.64040 | –1.28663 | 0.01706 |
| C | 3.95708 | –1.72867 | 0.01010 |
| C | 4.98784 | –0.77098 | –0.05907 |
| C | 4.69204 | 0.59960 | –0.12348 |
| H | 3.14057 | 2.09427 | –0.16645 |
| C | 0.95351 | 0.58322 | –0.04662 |
| H | 5.50207 | 1.32182 | –0.17605 |
| C | 4.28855 | –3.20119 | 0.07226 |
| H | 1.85005 | –2.02947 | 0.06202 |
| H | 6.02427 | –1.10026 | –0.06225 |
| H | 3.38454 | –3.81426 | 0.14005 |
| H | 4.84427 | –3.52128 | –0.81778 |
| O | 0.76560 | 1.87155 | –0.19340 |
| C | –0.17931 | –0.27446 | 0.09107 |
| C | –1.51269 | 0.24233 | –0.03253 |
| B | –0.56740 | 2.53480 | 0.07339 |
| O | –1.67600 | 1.53263 | –0.17712 |
| H | –0.03116 | –1.32498 | 0.28336 |
| C | –2.68607 | –0.59219 | –0.02826 |
| C | –2.62194 | –2.01445 | 0.06368 |
| C | –3.97015 | 0.01456 | –0.12885 |
| C | –5.11658 | –0.75963 | –0.13222 |
| C | –3.77994 | –2.77611 | 0.05795 |
| C | –5.03489 | –2.16051 | –0.03871 |
| H | –4.02708 | 1.09451 | –0.19904 |
| H | –6.08837 | –0.27934 | –0.20684 |
| H | –1.66422 | –2.51926 | 0.13548 |
| H | –3.71018 | –3.85812 | 0.12910 |
| H | –5.93945 | –2.76189 | –0.04101 |
| F | –0.61204 | 2.90433 | 1.39428 |
| F | –0.71667 | 3.55580 | –0.81415 |
| H | 4.91554 | –3.43073 | 0.94254 |

**Table S6.** The Cartesian Coordinates (in Å) of **Xyl-4** Optimized by TD-B3LYP/6-31G(d) (The sum of electronic and zero-point energies is –1031.643139 Hartree.)

| Atoms | Coordinates | | |
|---|---|---|---|
| | x | y | z |
| C | 2.80262 | –0.26865 | –1.17454 |
| C | 4.18239 | 0.04649 | –1.39549 |
| C | 4.86808 | 0.86586 | –0.53399 |
| C | 4.20918 | 1.41463 | 0.60274 |
| C | 2.83339 | 1.08786 | 0.83189 |
| C | 2.12563 | 0.28378 | –0.02078 |
| C | 2.07050 | –1.14529 | –2.11165 |
| H | 4.67599 | –0.36952 | –2.26773 |
| C | 0.72348 | –0.16449 | 0.28098 |
| C | 4.92667 | 2.30361 | 1.55778 |
| H | 5.91170 | 1.10635 | –0.70897 |
| H | 2.34287 | 1.48677 | 1.71390 |
| H | 2.71480 | –1.56593 | –2.88591 |
| H | 1.52380 | –1.93419 | –1.57286 |
| H | 4.98126 | 1.82022 | 2.54443 |
| H | 4.36756 | 3.23555 | 1.71278 |
| O | 0.73608 | –1.37550 | 0.85055 |
| C | –0.39779 | 0.50914 | –0.07523 |
| C | –1.68177 | –0.09244 | 0.17061 |
| B | –0.48771 | –2.20918 | 0.56198 |
| O | –1.69878 | –1.35624 | 0.60452 |
| H | –0.32582 | 1.48618 | –0.53619 |
| C | –2.94076 | 0.56703 | 0.00166 |
| F | –0.31493 | –2.73300 | –0.73437 |
| F | –0.58183 | –3.19074 | 1.50963 |
| C | –3.05583 | 1.93917 | –0.35691 |
| C | –4.15001 | –0.15753 | 0.19870 |
| C | –5.38356 | 0.45331 | 0.03567 |
| C | –4.29735 | 2.53593 | –0.51873 |
| C | –5.47675 | 1.80423 | –0.32620 |
| H | –4.08173 | –1.20288 | 0.47572 |
| H | –6.28953 | –0.12798 | 0.19094 |
| H | –2.16276 | 2.54087 | –0.49619 |
| H | –4.35128 | 3.58708 | –0.79294 |
| H | –6.44605 | 2.27773 | –0.45199 |
| H | 5.94049 | 2.54242 | 1.23054 |
| H | 1.26104 | –0.56500 | –2.58234 |

## 3. X-Ray crystallographic analysis

**Table S7.** Crystallographic data for ***o*Tol-3**, ***m*Tol-3**, and **Xyl-4**

| Parameter | ***o*Tol-3** | ***m*Tol-3** | **Xyl-4** |
|---|---|---|---|
| Molecular Formula | $C_{16}H_{13}BF_2O_2$ | $C_{16}H_{13}BF_2O_2$ | $C_{34}H_{30}B_2F_4O_4$ |
| Molecular Weight | 286.07 | 286.07 | 600.20 |
| Crystal Size | 0.5 × 0.4 × 0.3 | 0.5 × 0.5 × 0.2 | 0.9 × 0.9 × 0.3 |
| CCDC Number | 1524227 | 1524230 | 1524228 |
| Crystal System | Orthorhombic | Monoclinic | Monoclinic |
| Space Group | *Pbca* | $P2_1/c$ | $P2_1/a$ |
| *a* / Å | 8.2331(6) | 7.1998(17) | 14.2946(3) |
| *b* / Å | 13.1144(10) | 14.199(3) | 14.0130(10) |
| *c* / Å | 25.5836(19) | 14.276(4) | 15.2327(11) |
| α / degree | 90 | 90 | 90 |
| β / degree | 90 | 102.928(5) | 104.760(3) |
| γ / degree | 90 | 90 | 90 |
| *V* / Å$^3$ | 2762.32(4) | 1422.44(6) | 2980.58(4) |
| *Z* | 8 | 4 | 4 |
| $\rho_{calc}$ / g cm$^{-3}$ | 1.376 | 1.336 | 1.351 |
| Goodness of Fit | 1.088 | 0.801 | 0.876 |
| $R_1$ ($I > 2\sigma I$) | 0.0758 | 0.0788 | 0.0583 |
| $wR_2$ (all data) | 0.2586 | 0.2597 | 0.1931 |
| Reflections Measured | 24716 | 21581 | 27624 |
| Unique Reflections | 3121 | 3211 | 6671 |
| $R_{int}$ | 0.1021 | 0.0870 | 0.0813 |
| $\mu$ / mm$^{-1}$ | 0.094 | 0.094 | 0.094 |
| radiation source | Mo(Kα) | Mo(Kα) | Mo(Kα) |
| $\lambda$ / Å | 0.71075 | 0.71075 | 0.71075 |

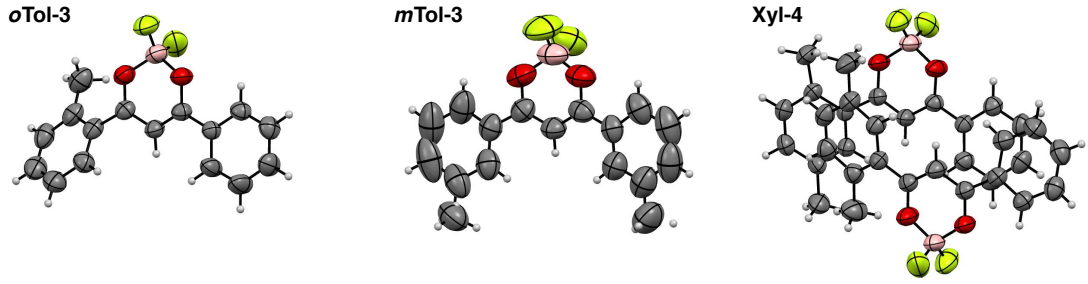


**Fig. S7.** ORTEP drawings of ***o*Tol-3**, ***m*Tol-3**, and **Xyl-4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

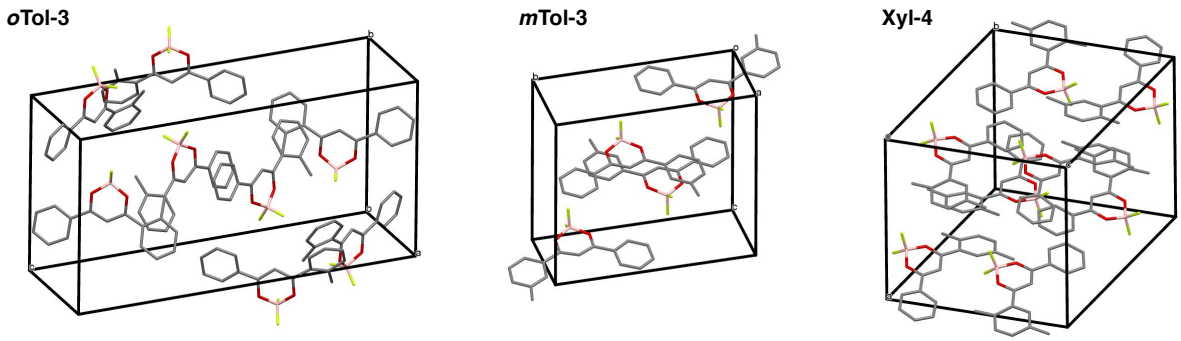


**Fig. S8.** Crystal packing structures of ***o*Tol-3**, ***m*Tol-3**, and **Xyl-4**.

(EOF)