Supporting Information

SYNTHESIS OF DIBENZOXAZONINES BY DOMINO (2+2) CYCLOADDITION—4π ELECTROCYCLIC RING OPENING REACTION OF CYCLIC IMINES WITH YNAMIDES

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Table of Contents

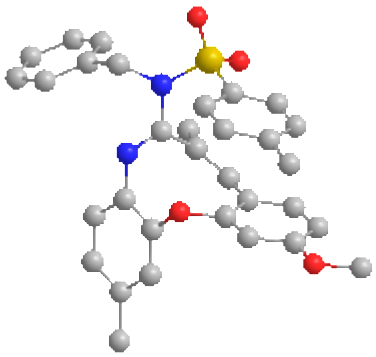

Figure S1. X-ray crystallographic structure of **4ab.** Hydrogen atoms are omitted for its clarity. One crystal unit has two molecules of **4ab**, whose structures are similar each other.

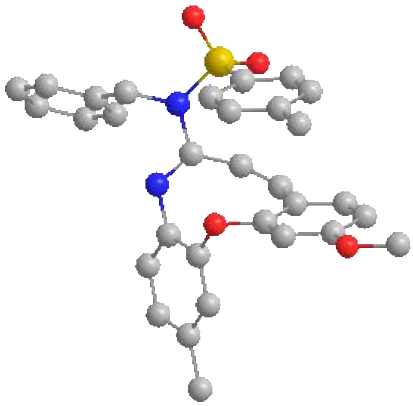

Figure S2. X-ray crystallographic structure of **4ac.** Hydrogen atoms are omitted for its clarity.

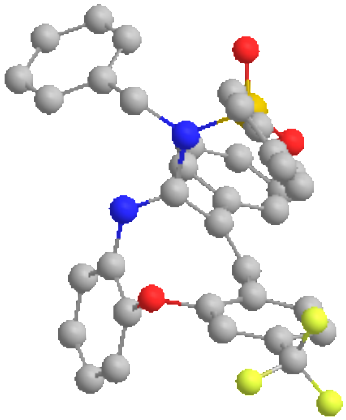

Figure S3. X-ray crystallographic structure of **4ba.** Hydrogen atoms are omitted for its clarity.

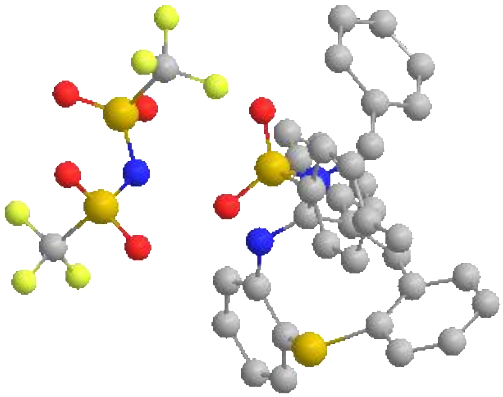

Figure S4. X-ray crystallographic structure of (**4da**)$_2$•(Tf_2NH)$_2$**.** Hydrogen atoms are omitted for its clarity. One crystal unit has two sets of **4da**•Tf_2NH, whose structures are similar each other.

General: All reactions were carried out under a positive atmosphere of Ar in dried glassware. Dehydrated solvents and materials were obtained from commercial suppliers and used without further purification unless otherwise noted. Column chromatography was performed on Fuji Silysia BW-200 silica gel or Kanto Kagaku Silica Gel 60 N (spherical, neutral) 100-210μm. Reactions and chromatography fractions were analyzed by thin-layer chromatography (TLC) carried out on Merck Silica Gel 60 F_{254} or Wako Silicagel 70 F254 TLC Plate-Wako with visualization by ultraviolet (UV) irradiation at 254 nm and/or indicated stains. IR spectra were measured on Shimadzu IRAffinity-1. The wave numbers of maximum absorption peaks of IR spectroscopy are presented in cm^{-1}. All melting points were determined using a Yamato MP-21 melting point apparatus MP-J3 and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on JEOL ECA-500 (^{1}H, 500 MHz; ^{13}C, 126 MHz). Chemical shifts are presented in ppm relative to tetramethylsilane (^{1}H, 0.00) or solvents as follows: $CDCl_3$ (^{13}C, 77.0) (^{1}H, 7.26). Abbreviations are as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; br s, broad singlet; br dd, broad doublet of doublets. High-resolution mass spectra (HRMS) were recorded on JEOL JMS-700 (FAB), or Shimadzu LCMS-IT-TOF (ESI) mass spectrometer using MeOH as a mobile phase. X-ray diffraction data were recorded on a RIGAKU R-AXIS RAPID system.

Synthesis of imines 1: Compounds **1** were prepared according as the reported procedure (Y. R. Jorapur, G. Rajagopal, P. J. Saikia, and R. R. Pal, *Tetrahedron Lett.*, 2008, **49**, 1495; Y.-C. Lin, N.-C. Li, and Y.-J. Cherng, *J. Heterocyclic Chem.,* 2014, **51**, 808).

3-Methoxy-7-methyldibenzo[b,f][1,4]oxazepine (**1a**): 94% yield (400 mg), Yellow solids. Mp 85–86 °C (recrystallization from AcOEt/hexane). ^{1}H NMR: δ 8.35 (s, 1H), 7.24–7.21 (m, 2H), 6.97 (d, J = 8.0 Hz, 1H), 6.91 (s, 1H), 6.73–6.70 (m, 1H), 6.65 (t, J = 2.2 Hz, 1H), 3.84 (s, 3H), 2.33 (s, 3H). ^{13}C NMR: δ 164.0, 161.7, 159.4, 152.0, 139.0, 138.1, 131.4, 129.0, 126.4, 121.8, 120.5, 111.0, 105.9, 55.6, 20.8. IR (neat): 1609, 1501, 1327, 1285, 1238, 1192, 1161, 1119, 1030. HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{15}H_{14}NO_2^+$ 240.1019; Found 240.1013.

Typical Procedure for (2+2) cycloaddition—4π Electrocyclization reaction: To a solution of **1** in dry CH_2Cl_2 (0.1 M) were added Tf_2NH (1.0 equiv) and, then, a solution of **2** (3.0 equiv) in CH_2Cl_2 (0.1 M) at ambient temperature. After stirred for 30 min at the same temperature, the resulting mixture was diluted

$CHCl_3$, quenched with water and extracted with $CHCl_3$ twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give **4**.

(5*E*,7*Z*)-6-(*N*-Benzyl-*N*-toluenesulfonyl)amino-11-methoxy-2-methyl-7-phenyldibenzo[*b*,*h*][1,4]oxazonine (4aa): 68% yield (170 mg), Colorless prisms. Mp 207–208 °C (recrystallization from AcOEt/hexane). ^{1}H NMR: δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 6.0 Hz, 2H), 7.22–7.17 (m, 4H), 7.11–7.08 (m, 4H), 6.92 (d, *J* = 8.6 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 2H), 6.72–6.68 (m, 3H), 6.61 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 6.42 (s, 1H), 4.97 (d, *J* = 14.9 Hz, 1H), 4.83 (d, *J* = 14.6 Hz, 1H), 3.89 (s, 3H), 2.39 (s, 3H), 2.14 (s, 3H). ^{13}C NMR: δ 160.5, 156.4, 155.5, 146.5, 143.7, 140.4, 137.9, 136.4, 136.1, 134.1, 133.6, 129.1, 128.9, 128.8, 128.3, 127.9, 128.8, 128.7, 127.2, 126.4, 125.3, 120.8, 119.9, 117.8, 109.5, 107.0, 55.5, 50.1, 21.6, 20.8. IR (neat): 1705, 1613, 1501, 1447, 1346, 1292, 1269, 1161, 1130. HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{37}H_{33}N_2O_4S^+$ 601.2156; Found 601.2149. X-ray: *orthorhombic*, *Pbca*; *a* = 10.0384(4), *b* = 20.7792(8), *c* = 28.4695(11); *V* = 5938.5(4), *Z* = 8, D_x = 1.331, *R* = 0.0559, $_wR_2$ = 0.1318, GOF = 1.018.

(5*E*,7*Z*)-6-(*N*-Benzyl-*N*-toluenesulfonyl)amino-11-methoxy-2,7-dimethyldibenzo[*b*,*h*][1,4]oxazonine (4ab): 75% yield (130 mg), Colorless prisms. Mp 166-167 °C (recrystallization from AcOEt/hexane). ^{1}H NMR: δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 8.6 Hz, 1H), 6.58–6.56 (m, 2H), 6.53 (s, 1H), 6.48 (dd, *J* = 8.3, 2.6 Hz, 1H), 5.97 (d, *J* = 14.3 Hz, 1H), 5.62 (d, *J* = 14.1 Hz, 1H), 5.45 (d, *J* = 14.9 Hz, 1H), 5.33 (d, *J* = 14.9 Hz, 1H), 3.85 (s, 3H), 2.22 (s, 3H), 2.16 (s, 3H). ^{13}C NMR: δ 160.8, 156.6, 155.4, 146.9, 143.3, 139.5, 137.5, 137.1, 134.6, 134.0, 131.2, 129.1, 128.8, 128.2, 127.3, 126.8, 125.1, 121.1, 120.8, 120.2, 119.0, 109.1, 107.8, 55.5, 49.8, 21.4, 20.9. IR (neat): 1701, 1609, 1497, 1350, 1292, 1234, 1161, 1126, 1092, 1030. HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{31}H_{29}N_2O_4S^+$ 525.1843; Found 525.1845. X-ray: *monoclinic*, *P2₁/n*; *a* = 18.0851(4), *b* = 6.2417(1), *c* = 22.8981(4); *β* = 93.973(2); *V* = 2578.57(8), *Z* = 2, D_x = 1.351, *R* = 0.0667, $_wR_2$ = 0.1542, GOF = 1.033.

(5*E*,7*Z*)-6-(*N*-Benzyl-*N*-toluenesulfonyl)amino-11-methoxy-2-methyldibenzo[*b*,*h*][1,4]oxazonine (4ac): 20% yield (52 mg), Colorless needles. Mp 165–166 °C (recrystallization from AcOEt/hexane). IR

(neat): 1701, 1613, 1497, 1443, 1412, 1354, 1262, 1188, 1088, 1034. HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{32}H_{31}N_2O_4S^+$ 533.1999; Found 533.1992. X-ray: *monoclinic*, *P2₁/c*; *a* = 14.2437(3), *b* = 12.0019(2), *c* = 32.2517(7); *β* = 98.183(2); *V* = 5457.3(2), *Z* = 8, D_x = 1.311, *R* = 0.0690, $_wR_2$ = 0.2035, GOF = 1.077.

(5*E*,7*Z*)-6-(*N*-Benzyl-*N*-toluenesulfonyl)amino-11-methoxy-2-methyl-7-(4-trifluoromethylphenyl)dibenzo[*b,h*][1,4]oxazonine (4ad): 57% yield (91 mg), Colorless prisms. Mp 153–154 °C (recrystallization from AcOEt/hexane). ^{1}H NMR: δ 7.35 (t, *J* = 8.6 Hz, 4H), 7.30–7.26 (m, 4H), 7.06–7.00 (m, 4H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.74–6.66 (m, 4H), 6.48–6.46 (m, 2H), 4.94–4.91 (m, 2H), 3.90 (s, 3H), 2.37 (s, 3H), 2.15 (s, 3H). ^{13}C NMR: δ 160.8, 155.7, 155.5, 146.3, 143.8, 141.6, 140.0, 136.2, 135.6, 134.4, 134.2, 132.6, 130.2, 129.5, 129.3, 129.1, 127.8, 127.4, 127.3, 126.6, 125.4, 125.0, 125.0, 120.8, 119.7, 117.5, 109.5, 107.1, 77.2, 55.4, 50.0, 21.4, 20.7. IR (neat): 1609, 1497, 1416, 1358, 1323, 1289, 1265, 1227, 1161, 1119, 1069, 1038, 1018. HRMS (ESI) *m/z* $[M + Na]^+$ Calcd for $C_{38}H_{31}F_3N_2NaO_4S^+$ 691.1849; Found 691.1850.

(5*E*,7*Z*)-3-(11-Methoxy-2-methyl-7-phenyldibenzo[*b,h*][1,4]oxazonin-6-yl)-4,4-dimethyloxazolidin-2-one (4ae): 35% yield (190 mg), Colorless Oil. ^{1}H-NMR: δ 7.34–7.28 (m, 4H), 7.25–7.21 (m, 2H), 7.06 (d, *J* = 8.9 Hz, 1H), 6.77–6.74 (m, 3H), 6.66–6.63 (m, 1H), 6.55 (s, 1H), 3.92 (d, *J* = 8.3 Hz, 1H), 3.86 (d, *J* = 8.3 Hz, 1H), 3.84 (s, 3H), 2.19 (s, 3H), 1.78 (s, 3H), 1.66 (s, 3H). ^{13}C-NMR: δ 163.9, 161.5, 159.3, 154.9, 151.8, 138.9, 137.9, 131.4, 131.3, 128.8, 128.1, 128.0, 126.2, 122.2, 121.7, 110.9, 105.8, 75.5, 73.3, 60.2, 55.5, 24.7, 20.7. IR (neat): 2249, 1767, 1605, 1501, 1404, 1389, 1327, 1277, 1238, 1177, 1115, 1072, 1022. HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{28}H_{27}N_2O_4^+$ 455.1965; Found 455.1963.

(5*E*,7*Z*)-6-(*N*-Benzyl-*N*-toluenesulfonyl)amino-11-trifluoromethyl-7-phenyldibenzo[*b,h*][1,4]oxazonine (4ba): 35% yield (170 mg), Colorless prisms. Mp 211–212 °C (recrystallization from AcOEt/hexane). ^{1}H NMR: δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.0 Hz, 2H), 7.25–7.20 (m, 4H), 7.13–7.09 (m, 5H), 6.98 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.93–6.87 (m, 4H), 6.84–6.82 (m, 2H), 6.56 (d, *J* = 7.2 Hz, 1H), 6.41 (s, 1H), 5.01 (d, *J* = 14.9 Hz, 1H), 4.83 (d, *J* = 14.9 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR: δ 155.5, 154.4, 146.2, 144.2, 143.0, 136.7, 136.1, 135.8, 133.5, 131.0, 129.2, 128.8, 128.5, 128.5, 127.9, 127.9, 127.7, 127.5, 126.5, 126.4, 125.2, 124.6, 124.5, 120.5, 50.2, 21.5. IR (neat): 1604, 1485, 1412, 1362, 1327, 1250, 1223, 1165, 1126, 1072. HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{36}H_{28}F_3N_2O_3S^+$ 625.1767; Found 625.1767. X-

ray: *monoclinic*, $P2_1/c$; a = 14.8185(11), b = 11.4831(8), c = 20.7989(14); β = 105.793(8); V = 2946.0(4), Z = 4, D_x = 1.408, R = 0.1343, $_wR_2$ = 0.3125, GOF = 1.051.

(5*E*,7*Z*)-6-(*N*-Benzyl-*N*-toluenesulfonyl)amino-2-chloro-7-phenyldibenzo[*b,h*][1,4]oxazonine (4ca): 70% yield (230 mg), Colorless prisms. Mp 207–208 °C (recrystallization from AcOEt/hexane). ^{1}H-NMR: δ 7.38–7.36 (m, 3H), 7.28 (d, J = 6.9 Hz, 2H), 7.24–7.19 (m, 5H), 7.13 (t, 7.8 Hz, 2H), 7.08 (d, J = 8.3 Hz, 3H), 6.93–6.88 (m, 3H), 6.86 (d, J = 7.2 Hz, 2H), 6.56 (d, J = 6.9 Hz, 1H), 6.47 (s, 1H), 5.00 (d, J = 14.9 Hz, 1H), 4.77 (d, J = 14.9 Hz, 1H), 2.39 (s, 3H). ^{13}C-NMR: δ 155.8, 154.8, 146.2, 144.1, 143.0, 137.0, 136.2, 135.8, 135.6, 134.3, 133.8, 129.2, 128.9, 128.2, 127.9, 127.7, 127.4, 127.0, 126.4, 125.1, 124.5, 123.4, 123.2, 121.8, 120.4, 50.2, 21.6. IR (neat): 1597, 1481, 1451, 1397, 1362, 1250, 1215, 1165, 1088, 1030. HRMS (ESI) *m/z* $[M + Na]^+$ Calcd for $C_{35}H_{27}ClN_2NaO_3S^+$ 613.1323; Found 613.1317.

(5*E*,7*Z*)-6-(*N*-Benzyl-*N*-toluenesulfonyl)amino7-phenyldibenzo[*b,h*][1,4]thiazonine (4da): 35% yield (10 mg), Yellow Oil. ^{1}H NMR: δ 7.33–7.30 (m, 4H), 7.29–7.27 (m, 3H), 7.25–7.23 (m, 2H), 7.19–7.13 (m, 5H), 7.11–7.04 (m, 8H), 6.45 (d, J = 7.5 Hz, 2H), 5.18 (s, 1H), 4.94 (d, J = 15.8 Hz, 1H), 4.65 (d, J = 15.8 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR: δ 158.8, 155.2, 149.3, 145.2, 145.1, 144.5, 143.1, 141.5, 140.9, 137.9, 136.3, 135.2, 134.7, 134.5, 134.2, 134.0, 131.4, 130.0, 129.2, 128.6, 128.5, 128.2, 128.2, 127.9, 127.8, 127.7, 127.4, 51.6, 21.6. IR (neat): 1751, 1620, 1593, 1485, 1451, 1412, 1366, 1331, 1250, 1219, 1169, 1126, 1072. HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{35}H_{29}N_2O_2S_2^+$ 573.1665; Found 573.1673. Single crystals were obtained from a solution of AcOEt and hexane in the presence of Tf_2NH. X-ray (co-crystallized with Tf_2NH): *triclinic*, *P-1*; a = 15.3464(9), b = 15.9425(8), c = 17.0757(8); α = 98.919(4), β = 109.695(5), γ = 98.545(4); V = 3794.1(4), Z = 4, D_x = 1.495, R = 0.0720, $_wR_2$ = 0.2087, GOF = 1.010.