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Practical Synthesis of Azobenzenophanes

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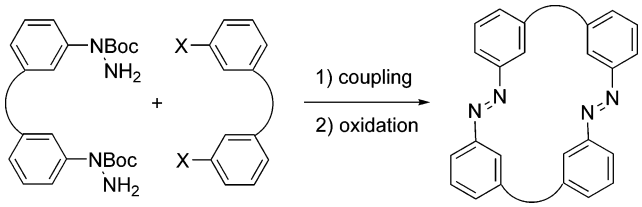

We devised a practical synthetic route to azobenzenophanes via successive Cu- and Pd-catalyzed coupling reaction of aryl hydrazide and aryl halide followed by Cu(I)-mediated oxidation reaction.

Azobenzenes have characteristic photoresponsive properties with potential applications in the areas of nonlinear optics, optical storage media, chemosensors, and photochemical switches.[1] Such photochemical response is exerted by reversible changes in the molecular geometry through the photochemical *E*/*Z* isomerization of the diazo bonds. The rates of the *E*/*Z* isomerization reactions can be modulated by changing the chemical structures or environment therein, although the exact mechanistic nature is not fully understood.[2] Azobenzenophanes in which two azobenzene units are linked together in a circular manner have additional interest as they can be used for the study to correlate the degree of steric distortion with the photochemical as well as thermal *E*/*Z* isomerization behavior.[3] Some of the notable azobenzenophanes, prepared and used for this purpose, are shown in Figure 1 (**1a** and **1b** reported by Rau and co-worker,[3a,e] **2a** and **2b** by Tamaoki and co-workers[3d,g]).

Synthetically, they are addressed by either annulation of properly functionalized azobenzenes or reductive coupling of bis(nitroarene) precursors, in general. However, neither synthetic approach is satisfactory because of the low product yield and functional group tolerance. For example, azobenzenophanes **2a** and **2c** were prepared from bis(nitroarene) **3a** and **3c** in 0.13% and 0.30% yield, respectively (Scheme 1).[3f,g] Synthesis of **1a** and **1b** fared no better.[3e]

Further exploitation of azobenzenophane to its full potential thus requires more efficient synthetic methods to ensure better availability as well as wider structural diversity. Previously, we reported an effective two-step synthetic protocol to azobenzenes, consisting of the Pd-catalyzed coupling reaction of aryl hydrazide **4** with aryl halide **5** and NBS/pyridine-mediated oxidation reaction of the resultant diaryl hydrazide into azobenzene **6** (Scheme 2).[4] The ineffectiveness of the current synthetic methods prompted us to use our method for construction of azobenzenophanes (Scheme 2).

We first studied the synthesis of [1,1](3,3′)-azobenzenophane **2a**, starting with diiodide **11**.[5] Its Cu(I)-catalyzed coupling reaction with $NHBocNH_2$ provided the bis-coupling product **12** in 81% yield. Subjection of **12** into the subsequent Pd-catalyzed coupling reaction with diiodide **11** afforded cyclic aryl hydrazide **13** in 53% yield. Oxidation of cyclic aryl hydrazide **13** into azobenzenophane **2a** was achieved with the CuI/Cs_2CO_3 system with an isolated yield of 61% after silica-gel flash column chromatography (Scheme 3).[4b] Oxidation with the NBS/pyridine system was ineffective in this case, resulting in production of a complex mixture.

[1,1′](3,3′)-Azobenzenophane **17** in which azobenzene units are directly connected each other at the 3,3′-positions represents the azobenzenophane member with the shortest carbon linker ever (none!). Synthesis commenced with 3,3′-diiodo-biphenyl **14** prepared according to the literature method.[6] Successive Cu(I)- and Pd-catalyzed coupling reactions provided cyclic hydrazide **16** in 40% overall yield from **14**. Cu(I)-mediated oxidation reaction furnished **17** in 60% isolated yield upon column chromatography (Scheme 4).

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(6) Inoue, A.; Kitagawa, K.; Shinokubo, H.; Oshima, K. *Tetrahedron* **2000**, *56*, 9601.

10.1021/jo062164p CCC: $37.00
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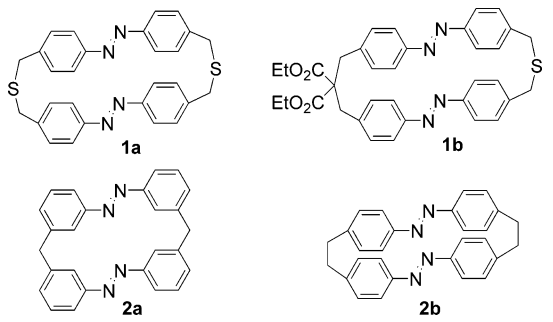
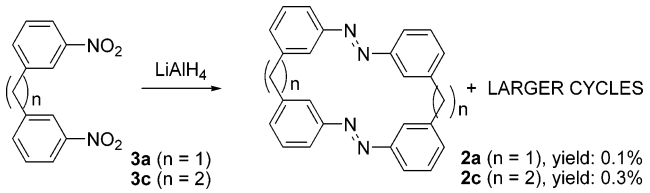
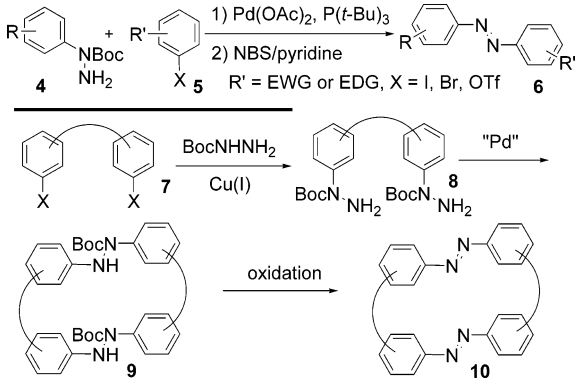


FIGURE 1. Representative azobenzenophanes.

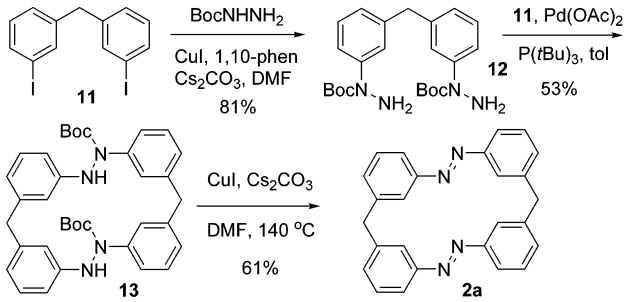
SCHEME 1. Synthesis of 2a and 2c



SCHEME 2

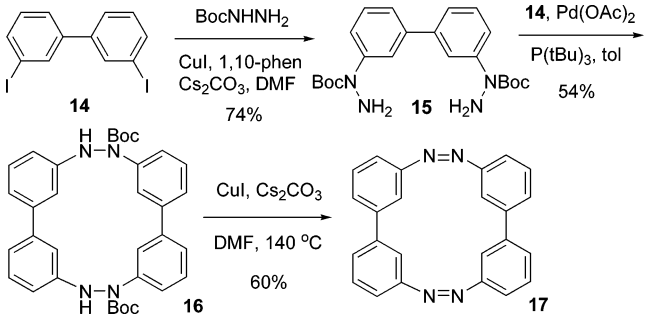


SCHEME 3. Synthesis of Azobenzenophane 2a

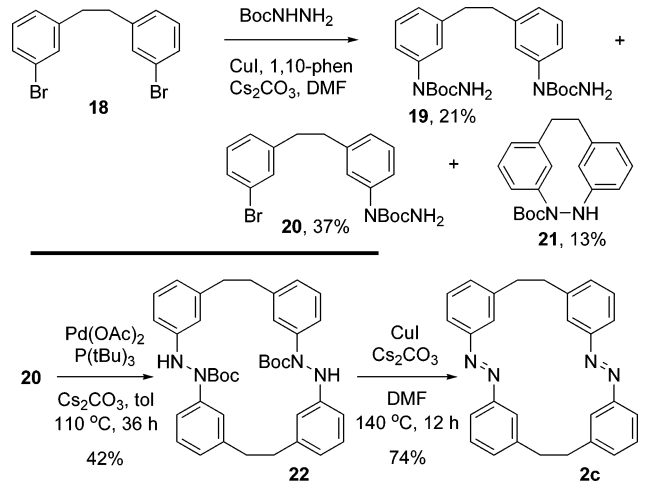


Synthesis of [1,1′](3,3′)-azobenzenophane with ethylene linkage **2c** required slight modification of the strategy because the Cu(I)-catalyzed coupling reaction of **18**[7] with $BocNHNH_2$ produced not only the desired bis-coupling product **19** but also mono-hydrazide **20** and cyclic hydrazide **21** in isolated yields of 21%, 37%, and 13%, respectively. No significant improvement in the total yield or product ratio was observed even with excess $BocNHNH_2$ (up to 10 equiv) in the coupling reaction and/or prolonged reaction time (Scheme 5). With careful control of $BocNHNH_2$ equivalents and reaction time, monocoupling

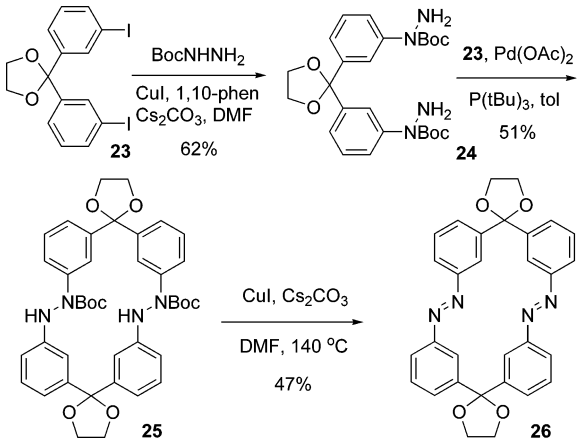
SCHEME 4. Synthesis of 17



SCHEME 5



SCHEME 6



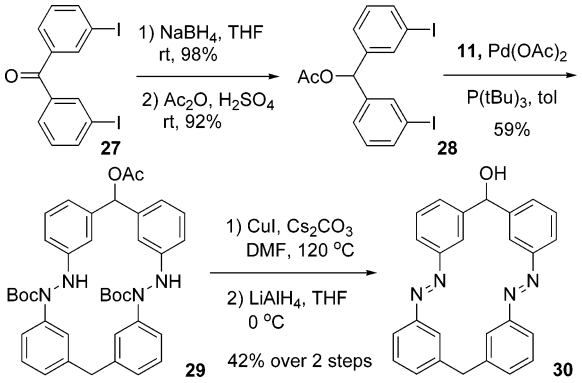
product **20** was obtained in 45% yield. Subsequent Cu(I)-catalyzed homocoupling followed by Cu(I)-mediated oxidation reaction provided azobenzenophane **2c** in 31% overall yield from **20**.

With the same reaction sequence azobenzenophane bearing ketal groups **26** was prepared from diiodide **23**[8] (Scheme 6). Protection of the ketone group proved to be essential because the unprotected form of **26** resulted in formation of a complex product mixture under the oxidation conditions. Installation of $BocNHNH_2$ followed by the coupling reaction with **23** provided bis-hydrazide **25** in good overall yield. After oxidation, azoben-

(7) Prepared from *m*-bromo-benzyl bromide via the Fe-mediated coupling reaction under the conditions reported: 79% yield. Vogtle, F.; Eisen, N.; Franken, S.; Bullesbach, P.; Puff, H. J. *Org. Chem.* **1987**, *52*, 5560.

(8) 3,3′-Diiodobenzophenone: Lulinski, P.; Skulski, L. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 951.

SCHEME 7



zenophane **26** was obtained in 47% isolated yield. Unfortunately, the ketal protecting groups in **26** are too robust to be unmasked under the conditions not affecting the azo groups (Scheme 6).

Azobenzenophane **30** bearing a hydroxyl group at the methylene linker was then prepared as a surrogate by following the route in Scheme 7.

In summary, we devised a new synthetic approach to azobenzenophane, consisting of Cu- and/or Pd-catalyzed coupling reaction of aryl hydrazide and aryl halide and Cu(I)-mediated oxidation reaction of the resultant cyclic aryl hydrazide. This new strategy would readily provide various other structurally and functionally useful cyclic azobenzenes for further exploitation of their interesting photochemical properties to full potential.

Experimental Section

12. To a sealed tube were added 200 mg (0.48 mmol) of **11**, 188 mg (3.0 equiv) of *tert*-butyl carbazate, 464 mg (3.0 equiv) of Cs_2CO_3, CuI (1.0 equiv), 1,10-phenanthroline (1.0 equiv), and DMF (5 mL) under Ar atmosphere. After 8 h at 80 °C, the reaction mixture was cooled to room temperature, diluted with ether, and washed with H_2O. The organic solution was dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography to give 167 mg of **12** (81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.20 (m, 6H), 6.94 (d, J = 8.0 Hz, 2H), 4.41 (bs, 4H), 3.96 (s, 2H), 1.46 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 143.0, 140.8, 128.1, 125.1, 124.0, 121.1, 81.7, 41.9, 28.4. FTIR (CH_2Cl_2) 3339, 2976, 2925, 2853, 1709, 1602, 1488, 1453, 1368, 1254, 1151 cm^{-1}. HRMS (M + Na)$^+$ calcd for $C_{23}H_{32}N_4NaO_4$ 451.2321, found 451.2312.

13. To a flask were added 112 mg (0.26 mmol) of **11**, 115 mg (0.26 mmol) of **12**, 262 mg (3.0 equiv) of Cs_2CO_3, 6 mg (10 mol %) of $Pd(OAc)_2$, 0.08 mL (10 mol %) of P(*t*-Bu)$_3$ dissolved in hexane, and 100 mL of anhydrous toluene under Ar atmosphere. After 36 h at 110 °C, the reaction mixture was cooled to room temperature and filtered through a plug of Celite. The filtrate was concentrated and chromatographed to give 85 mg of **13** (53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.0 Hz, 2H), 7.25−7.18 (m, 4H), 7.11 (t, J = 7.6 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 6.58 (dd, J = 8.0, 1.6 Hz, 2H), 6.41 (s, 2H), 6.25 (s, 2H), 3.88 (s, 2H), 3.75 (s, 2H), 1.33 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 148.3, 142.9, 142.6, 141.6, 128.9, 128.3, 124.8, 121.6, 121.0, 119.2, 112.4, 111.6, 82.1, 42.2, 42.1, 28.0. FTIR (CH_2Cl_2) 3336, 2977, 2925, 2852, 1713, 1606, 1449, 1368, 1252, 1156 cm^{-1}. HRMS (M + Na)$^+$ calcd for $C_{36}H_{40}N_4NaO_4$ 615.2947, found 615.2948.

2a. To a sealed tube were charged 87 mg (0.15 mmol) of **13**, 66 mg (2.4 equiv) of CuI, 150 mg (3.0 equiv) of Cs_2CO_3, and 3 mL of DMF. After 72 h at 140 °C, the reaction mixture was cooled to room temperature and partitioned into H_2O and ether. The separated organic solution was dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography to give 35 mg of **2a** (61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 4H), 7.66 (d, J = 7.7 Hz, 4H), 7.39 (t, J = 7.7 Hz, 4H), 7.35 (d, J = 7.7 Hz, 4H), 4.19 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 140.9, 131.1, 129.2, 126.0, 118.9, 40.2. FTIR (CH_2Cl_2) 2956, 2923, 1726, 1595, 1462, 1272, 1121, 1073 cm^{-1}. HRMS (M + 1)$^+$ calcd for $C_{26}H_{21}N_4$ 389.1766, found 389.1770.

15. 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 2H) 7.46−7.31 (m, 6H), 4.48 (bs, 4H), 1.53(s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 143.4, 141.1, 128.4, 123.4, 122.3, 122.2, 81.9, 28.3. FTIR (CH_2Cl_2) 3340, 2977, 2931, 1699, 1600, 1576, 1368, 1340, 1255 cm^{-1}. HRMS (M + Na)$^+$ calcd for $C_{22}H_{30}N_4NaO_4$ 437.2165, found 437.2155.

16. 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (bs, 2H), 7.43−7.33 (m, 8H), 7.25 (t, J = 7.6 Hz, 2H) 7.08 (dd, J = 8.0, 1.2 Hz, 2H), 6.84 (dd, J = 8.0, 2.0 Hz, 2H), 6.49 (bs, 2H), 1.34 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 149.0, 144.4, 143.4, 142.5, 128.6, 128.1, 124.5, 123.5, 123.2, 120.0, 116.0, 113.9, 82.3, 28.2. FTIR (CH_2Cl_2) 3305, 2977, 2928, 2854, 1699, 1607, 1582, 1482, 1368, 1328, 1255, 1152 cm^{-1}. HRMS (M + Na)$^+$ calcd for $C_{34}H_{36}N_4NaO_4$ 587.2634, found 587.2634.

17. 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (td, J = 8.0, 0.6 Hz, 4H), 7.10 (ddd, J = 8.0, 2.0, 1.2 Hz, 4H), 7.00 (ddd, J = 8.0, 2.0, 1.2 Hz, 4H), 6.51 (t, J = 1.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 139.3, 129.8, 124.7, 120.1, 119.7. FTIR (CH_2Cl_2) 2959, 2921, 2851, 1739, 1706, 1593, 1569, 1466, 1261, 1162, 1090, 1024 cm^{-1}. No parent ion peak was observed due to the decomposition.

19. 21% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.28 (m, 4H), 7.20 (t, J = 7.6 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 4.44 (bs, 4H), 2.91 (s, 4H), 1.51 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 143.1, 141.9, 128.1, 124.8, 123.5, 121.1, 81.7, 37.9, 28.3. FTIR (CH_2Cl_2) 3335, 2977, 2930, 2860, 1698, 1606, 1488, 1453, 1368, 1340, 1254, 1165, 1060 cm^{-1}. HRMS (M + Na)$^+$ calcd for $C_{24}H_{34}N_4NaO_4$ 465.2478, found 465.2466.

20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.06 (m, 7H), 6.89 (d, J = 7.2 Hz, 1H), 4.43 (bs, 2H), 2.87 (s, 4H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 143.8, 142.9, 141.1, 131.3, 129.7, 128.9, 128.0, 126.9, 124.5, 123.2, 122.2, 121.0, 81.7, 37.7, 37.8, 28.4. FTIR (CH_2Cl_2) 3337, 2977, 2930, 2861, 1698, 1598, 1488, 1475, 1368, 1341, 1293, 1254, 1070 cm^{-1}. HRMS (M + Na)$^+$ calcd for $C_{19}H_{23}BrN_2NaO_2$ 413.0841, found 413.0840.

22. 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.2 Hz, 2H), 7.19 (t, J = 7.6 Hz, 2H), 6.99 (t, J = 7.6 Hz, 2H), 6.94−6.90 (m, 4H), 6.50−6.42 (m, 6H), 6.13 (bs, 2H), 2.86 (d, J = 6.0 Hz, 4H), 2.81 (d, J = 6.8 Hz, 4H), 1.33 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 148.1, 142.3, 142.0, 141.7, 128.6, 128.0, 124.5, 122.1, 121.4, 119.3, 112.6, 111.0, 82.0, 37.9, 37.6, 28.2. FTIR (CH_2Cl_2) 3301, 3054, 2978, 2932, 1692, 1608, 1527, 1488, 1454, 1369, 1306, 1159 cm^{-1}. HRMS (M + Na)$^+$ calcd for $C_{38}H_{44}N_4NaO_4$ 643.3260, found 643.3272.

2c. 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.49 (m, 4H), 7.40 (t, J = 3.6 Hz, 4H), 7.33 (t, J = 7.6 Hz, 4H), 7.27−7.24 (m, 4H), 3.12 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 141.2, 131.1, 128.9, 124.2, 120.0, 35.9. FTIR (CH_2Cl_2) 2925, 2863, 1600, 1478, 1450, 1441, 1354, 1309, 1244, 1144, 1076 cm^{-1}. HRMS (M + 1)$^+$ calcd for $C_{28}H_{25}N_4$ 417.2079, found 417.2072.

23. Prepared from **27**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, J = 1.6 Hz, 2H), 7.62 (ddd, J = 7.6, 1.6, 1.2 Hz, 2H), 7.42 (td, J = 7.6, 1.2 Hz, 2H), 7.04 (t, J = 7.6 Hz, 2H), 4.03 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 137.3, 134.8, 130.0, 128.0, 125.4, 94.3, 65.0. FTIR (CH_2Cl_2) 3058, 2955, 2888, 1663, 1566, 1469, 1415, 1251 cm^{-1}. HRMS (M + 1)$^+$ calcd for $C_{15}H_{13}I_2O_2$ 478.9005, found 478.9015.

24. 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (bs, 2H), 7.43−7.25 (m, 6H), 4.42 (bs, 4H), 4.05 (s, 4H), 1.45 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 142.9, 142.0, 127.9, 122.8, 122.3, 121.3, 109.0, 81.7, 64.8, 28.2. FTIR (CH_2Cl_2) 3339, 2924, 2852, 1695, 1605, 1484, 1369, 1334, 1254, 1150, 1060 cm^{-1}. HRMS $(M + Na)^+$ calcd for $C_{25}H_{34}N_4NaO_6$ 509.2376, found 509.2363.

25. 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.14 (m, 12H), 6.75 (bs, 2H), 6.68−6.53 (m, 2H), 6.30 (bs, 2H), 4.00 (s, 4H), 3.92 (s, 4H), 1.35 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 147.9, 143.9, 143.0, 142.7, 128.9, 128.1, 121.8, 121.3, 118.9, 118.6, 113.4, 110.0, 109.2, 109.1, 82.3, 64.8, 64.7, 28.0. FTIR (CH_2Cl_2) 3331, 3058, 2979, 2892, 1714, 1607, 1478, 1443, 1369, 1321, 1254, 1152, 1087 cm^{-1}. HRMS $(M + Na)^+$ calcd for $C_{40}H_{44}N_4NaO_8$ 731.3057, found 731.3063.

26. 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (t, J = 1.6 Hz, 4H), 7.74−7.70 (m, 8H), 7.41 (t, J = 7.6 Hz, 4H), 4.24 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 142.9, 128.7, 126.6, 124.7, 120.8, 108.3, 65.3. FTIR (CH_2Cl_2) 2958, 2924, 2894, 2852, 1653, 1475, 1421, 1261, 1178, 1154, 1095, 1020 cm^{-1}. HRMS $(M + 1)^+$ calcd for $C_{30}H_{24}N_4NaO_4$ 527.1695, found 527.1696.

28. To a flame-dried 100 mL round-bottomed flask charged with **27** (1.07 g, 2.5 mmol) and 7 mL of dry THF was added $NaBH_4$ (0.11 g, 3.0 mmol) dissolved in 1.5 mL of THF slowly over 10 min at 0 °C. After addition, the mixture was warmed to room temperature and stirred for 1 h before quenching with H_2O. The reaction mixture was extracted with ether. The combined organic solution was dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography to give 1.05 g of the corresponding alcohol (98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, J = 1.6 Hz, 2H), 7.61 (td, J = 7.7 Hz, 1.6 Hz, 2H), 7.28 (d, J = 7.7 Hz, 2H), 7.06 (t, J = 7.7 Hz, 2H), 5.67 (d, J = 3.3 Hz, 1H), 2.37 (d, J = 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 136.8, 135.3, 130.3, 125.7, 94.6, 74.5. FTIR (CH_2Cl_2) 3374, 2158, 1647, 1582, 1562, 1464, 1419, 1174 cm^{-1}. HRMS $(M)^+$ calcd for $C_{13}H_{10}I_2O$ 435.8821, found 435.8815. To a flame-dried 10 mL round-bottomed flask charged with the alcohol (3.0 mmol), and acetic anhydride (6.0 mmol) in 15 mL of anhydrous $CHCl_3$ was added H_2SO_4 (4.5 mmol) at 0 °C. After addition, the reaction mixture was warmed to room temperature, stirred for 20 min, and quenched with H_2O. The product was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, concentrated, and chromatographed to give 1.41 g of **28** (92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, J = 1.5 Hz, 2H), 7.63 (td, J = 7.7 Hz, 1.5 Hz, 2H), 7.27 (d, J = 7.7 Hz, 2H), 7.08 (t, J = 7.7 Hz, 2H), 6.70 (s, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 142.5, 138.0, 136.5, 131.0, 127.0, 95.2, 75.7, 21.9. FTIR (CH_2Cl_2) 3056, 2922, 1744, 1584, 1568, 1467, 1425, 1371, 1228, 1178, 1065, 1023 cm^{-1}. HRMS $(M + Na)^+$ calcd for $C_{15}H_{12}I_2NaO_2$ 500.8825, found 500.8827.

29. 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.7 Hz, 2H), 7.21 (t, J = 7.7 Hz, 2H), 7.18−7.14 (m, 4H), 7.01 (d, J = 7.3 Hz, 2H), 6.91 (d, J = 7.3 Hz, 2H), 6.69 (s, 1H), 6.65 (dd, J = 8.1 Hz, 1.8 Hz, 2H), 6.54 (s, 2H), 6.29 (s, 2H), 3.90 (s, 2H), 2.05 (s, 3H), 1.33 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 154.4, 149.0, 143.5, 142.4, 142.3, 129.8, 129.1, 125.7, 121.7, 120.3, 120.0, 113.9, 110.8, 82.9, 77.3, 42.6, 28.7, 21.8. FTIR (CH_2Cl_2) 3342, 3050, 2974, 2922, 1703, 1610, 1478, 1450, 1370, 1262, 1148 cm^{-1}. HRMS $(M + Na)^+$ calcd for $C_{38}H_{42}N_4NaO_6$ 673.3002, found 673.3001.

30. To a sealed tube were charged 69 mg (0.11 mmol) of **29**, 49 mg (0.25 mmol) of CuI, 83 mg (0.25 mmol) of Cs_2CO_3, and 2.1 mL of DMF. After 12 h at 120 °C the reaction mixture was quenched with H_2O and extracted with ether. The organic solution was dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography. The purified azobenzenophane was then dissolved in 2 mL of dry THF and cooled to 0 °C. To this solution was added $LiAlH_4$ (6 mg, 0.16 mmol) suspended in 1.5 mL of THF at 0 °C. After 10 min at 0 °C, the reaction mixture was quenched with KOH (aq) and extracted with ether. The organic solution was dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography to give 18 mg of **30** (42% yield over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (t, J = 1.8 Hz, 2H), 8.19 (s, 2H), 7.73 (d, J = 8.1 Hz, 2H), 7.67 (td, J = 7.3 Hz, 1.8 Hz, 2H), 7.56 (d, J = 7.3 Hz, 2H), 7.43 (t, J = 7.7 Hz, 2H), 7.40−7.36 (m, 4H), 6.04 (s, 1H), 4.25 (d, J = 15.4 Hz, 1H), 4.13 (d, J = 15.4 Hz, 1H), 2.57 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 154.2, 144.6, 141.6, 131.8, 129.9, 129.8, 129.1, 126.6, 124.9, 121.2, 119.6, 75.8, 41.0. FTIR (CH_2Cl_2) 3394, 3055, 2920, 2852, 1595, 1476, 1436, 1261, 1145 cm^{-1}. HRMS $(M)^+$ calcd for $C_{26}H_{20}N_4O$ 404.1637, found 404.1638.

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Supporting Information Available: Spectral data for all unknown azobenzenophanes. This material is available free of charge via the Internet at http://pubs.acs.org.

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