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Metacyclo[2](2,5)thiophenophanes with extended π-systems

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Abstract: 12,13-Dibromometa[2](2,5)thiophenophane was subjected to Suzuki-Miyaura cross coupling to yield 12,13-diarylmeta[2](2,5)thiophenophanes, cyclophanes with extended π-systems.

Keywords: Cyclophane; metacyclophane; thiophenophane; Suzuki cross-coupling.

1. Introduction

Over the years, thiophenophanes[1-22] and their metal complexes[23,24] have been of considerable interest. Thiophenophanes have been used as study objects in the π-π-interaction[12] and σ-π-interaction[13] in closely spaced aromatic-heteroaromatic systems.[12,13] Thiophenophanes have been investigated as inclusion hosts[3] and have elicited attention as interesting optical material.[14,15] They have been used as starting materials for multi-functionalised arenophanes[16-18] via the corresponding thiophenophane *S*-oxides and for condensed heteroarenes.[19] Many, especially closely layered cyclophanes have interesting electronic properties due to the proximity of their areno/hetareno faces. These electronic properties can be modified by π-ring substitution. In this regard, extension of their π-

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systems due to suitable substitution is of interest. The following details a simple synthetic sequence to meta[2](2,5)thiophenophanes with extended π-systems as a first step to oligomers with heterocyclophane monomers bridged by π-units.[25-27]

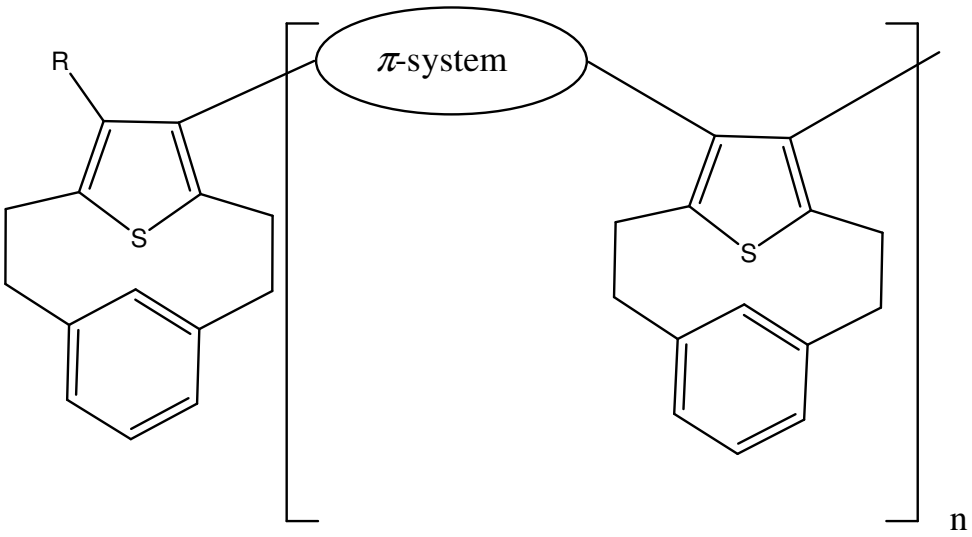
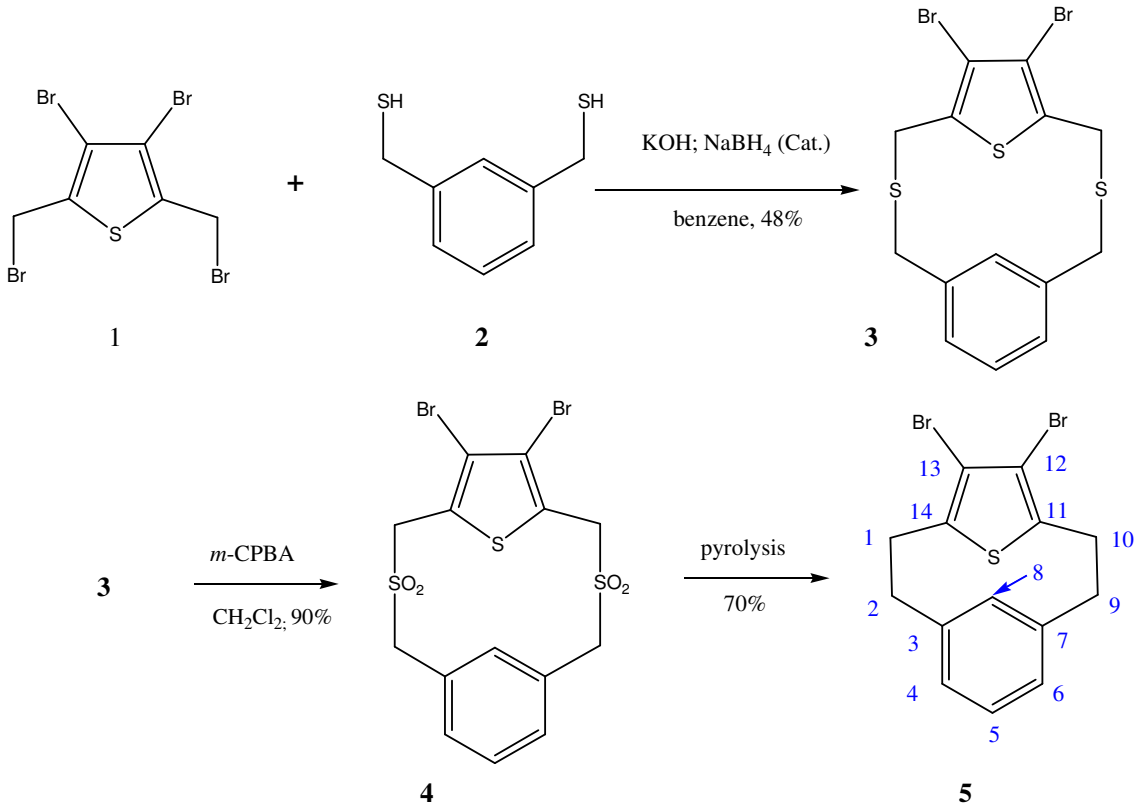


Figure 1. Schematic representation of oligomers with thiophenophane monomers bridged by π-systems

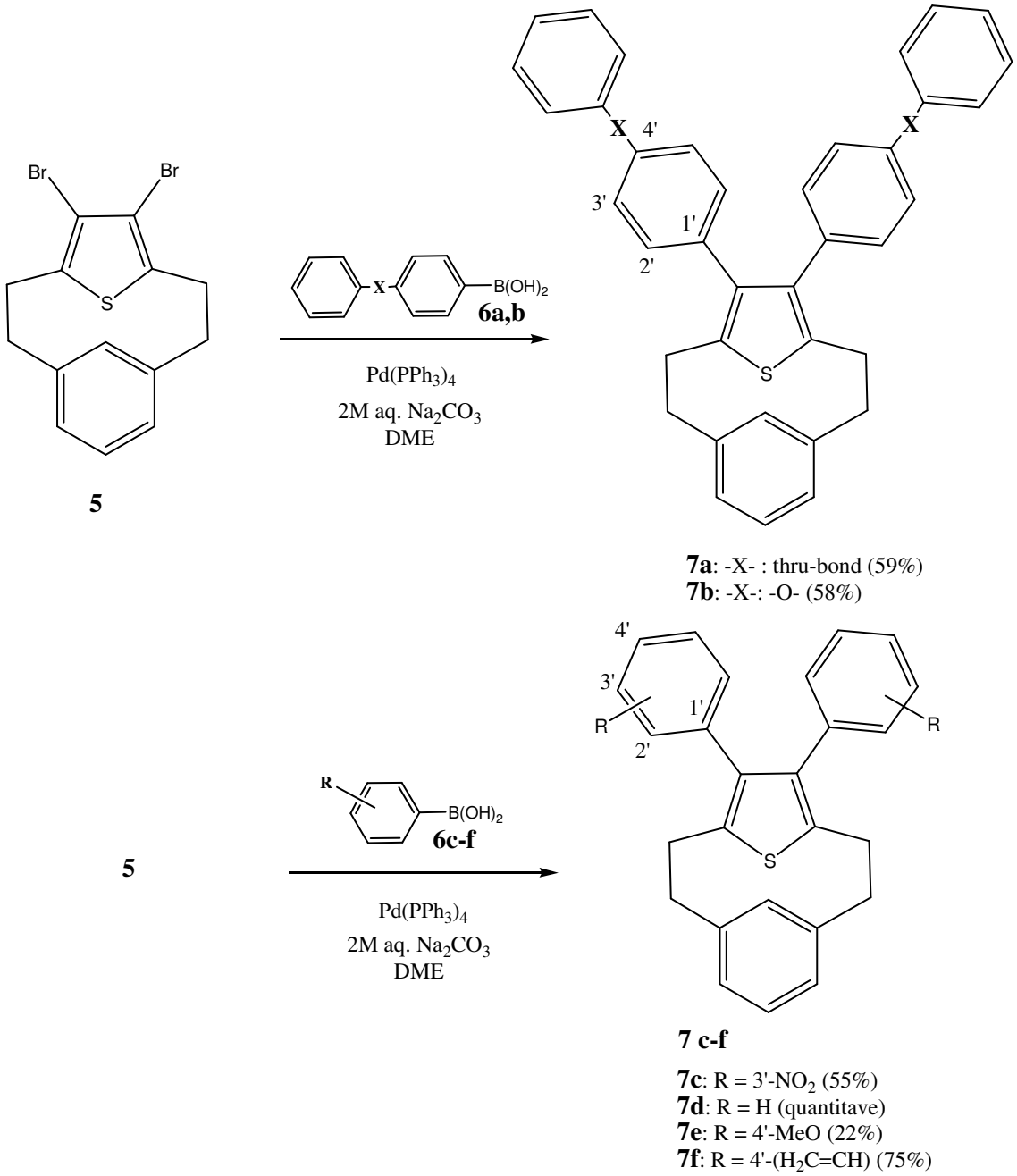
2. Results and Discussion

Synthesis. The key precursor, which was to be used as the substrate in Suzuki-Miyaura cross-coupling reactions, is 12,13-dibromo[2]metacyclo[2](2,5)thiophenophane (**5**), which is prepared by pyrolysis of disulfone **4**. The synthetic approach follows closely a sequence published previously.[16,21] At first, 3,4-dibromo-2,5-bis(bromomethyl)thiophene (**1**)[16] was prepared. The coupling reaction of 3,4-dibromo-2,5-bis(bromo)methylthiophene (**1**) with 1,3-bis(mercaptomethyl)benzene (**2**)[28] was carried out under high dilution conditions and afforded dithia[3]metacyclo[3](2,5)thiophenophane (**3**) in 48% yield. **3** was oxidized with *meta* chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 to sulfone **4** in 90% yield. Pyrolysis of **4** afforded dibromo[2.2](2,5)metathiophenophane **5**[16,21] in 70% yield (Scheme 1).



Scheme 1. Synthesis of 12,13-dibromometa[2](2,5)thiophenophane (**5**) [see also ref. 16 and 21]

Suzuki-Miyaura cross-coupling and characterization of the cyclophanes. **5** was subjected to Suzuki-Miyaura cross coupling reaction with a number of substituted aryl boronic acids **6** to yield the symmetric 14,15-diaryl[2]metacyclo[2](2,5)thiophenophanes **7** (Scheme 2). A two-phase reaction medium was chosen with a basic aqueous phase (aq. Na_2CO_3) and tetrakis(triphenylphosphino)palladium(0) [$Pd(PPh_3)_4$] as a catalyst.[29] In order to obtain the symmetric bis-coupled products **7**, it is necessary to use an excess of aryl boronic acid and a longer reaction time. Mono arylated cyclophanes form as by-products. They are separated from the desired diarylated products by column chromatography. In certain cases, as in the coupling reaction of **5** with 3-nitrophenylboronic acid (**6c**), the use of less arylboronic acid has led to the formation of the mono-arylated cyclophane (ie., to 14-bromo-15-(3-nitrophenyl)metacyclo[2](2,5)thiophenophane) as the major product.[30]



Scheme 2. Synthesis of symmetric 12,13-diarylmeta[2](2,5)thiophenophane (**7**) - Suzuki Miyaura cross coupling of thiophenophane **5**.

12,13-Dibromo[2]metacyclo[2](2,5)thiophenophane (**5**) consists of two layered π-systems, where the thienyl- and the phenylene ring are positioned almost in parallel. The X-ray crystal structure of **5**[31] shows the molecule to exhibit a conformation similar to 5-*tert*-butyl-12,13-dibromo-8-methyl[2]metacyclo[2](2,5)thiophenophane, of which the X-ray structure has already been

communicated.[21] At δ_H 5.97 ppm, H_8 (vs. δ_H 7.01 ppm for $H_{4,6}$ and δ_H 7.20 ppm for H_5) of the phenylene ring in **5** experiences a high field shift due to the vicinity of the overlying thienyl group. Although less pronounced, this high field shift of H_8 due to the anisotropy of the proximate thienyl group can be found in the π-extended cyclophanes as well. Only small differences in chemical shift values can be found for H_8, when comparing cyclophane **7c** with slightly electron withdrawing *m*-nitrophenyl substituents (δ_H 6.29) with cyclophane **7e** with slightly electron-donating *p*-anisyl substituents (δ_H 6.39). This may be due to a slightly different electronic interaction of the layered π-systems compensated by a slight difference in shielding, potentially due to a small change in interlayer distance.

3. Conclusion

A number of symmetric 14,15-diaryl[2]metacyclo[2](2,5)thiophenophanes **7** have been prepared successfully as a first step towards the synthesis of π-bridged heterophane oligomers. Currently, strategies utilizing aryldiboronic acids in the reaction with 12,13-dibromo[2]metacyclo[2](2,5) thiophenophane (**5**) and similar heterophanes are being investigated.

4. Experimental

General. – Melting points were measured on a Yanaco microscopic hotstage are uncorrected. Infrared spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer. The chemical shifts are relative to TMS (solvent $CDCl_3$, unless noted otherwise). Mass spectra were measured with a JMS-01-SG-2 spectrometer (EI, 70 eV or FAB-modus). UV-VIS spectra were performed with a Shimadzu UV-2401 PC spectrometer. UV-spectra of the cyclophanes were measured as solutions in cyclohexane (reagent grade ACS, ISO UV-VIS, Karl Fischer Titrations, Scharlau). Column chromatography was carried out with Wakogel 300.

12,13-Dibromo[2]metacyclo[2](2,5)thiophenophane (**5**) was prepared according to the literature.[16,21] Commercially available biphenylboronic acid (**6a**), *p*-phenoxyphenylboronic acid (**6b**), 3-nitrophenylboronic acid (**6c**), phenylboronic acid (**6d**), 4-methoxyphenylboronic acid (**6e**), and 4-vinylphenylboronic acid (**6f**) (all Aldrich) were used for this study.

12,13-Bis(*p*,*p*'-biphenyl)metacyclo[2](2,5)thiophenophane (**7a**). – A mixture of 12,13-dibromo[2]metacyclo[2](2,5)thiophenophane (**5**) (171 mg, 0.46 mmol), *p*,*p*'-biphenylboronic acid (228 mg, 1.15 mmol) and $Pd(PPh_3)_4$ (30 mg, $2.6 \cdot 10^{-2}$ mmol) in DME (4 mL) and 1.5 M aq. Na_2CO_3 (3 mL) was stirred at 60 ºC for 8h. Thereafter, the cooled solution was poured into water (50 mL) and extracted with $CHCl_3$ (3 X 15 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gel (hexane/$CHCl_3$ 20:3) gave **7a** (141 mg, 59%) as a pale yellow solid, mp. 210 ºC; IR (KBr) ν 2936, 1526, 1483, 841, 802, 764, 752, 735, 695 cm^{-1}; UV ($c = 3.4 \cdot 10^{-5}$ M in cyclohexane) λ_{max} nm (log ε) 280 (4.82), 251 (4.41), 204 (4.53); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.45 – 2.56 (m, 4H), 2.80 – 2.84 (m, 2H), 3.28 – 3.33 (m, 2H), 6.46 (s, 1H), 7.07 (d, 2H, ^3J 7.6 Hz), 7.23 – 7.62 (m, 19H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 32.20 (2C), 38.90 (2C), 126.41 (2C), 126.64 (4C), 126.91 (4C), 127.20 (2C), 128.72 (4C), 129.04, 130.39 (4C), 130.75, 136.04 (2C), 139.09 (2C), 140.63 (2C), 142.09 (4C), 142.67 (2C) MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 518 (M^+, 7.0). HRMS Calcd. for $C_{38}H_{30}S$: 518.2068. Found: 518.2065. Calcd. for $C_{38}H_{30}S \cdot 0.4H_2O$: C, 86.78; H, 5.90. Found: C, 86.88; H, 5.87%.

12,13-Bis(*p*-phenoxyphenyl)metacyclo[2](2,5)thiophenophane (**7b**). - A mixture of **5** (128 mg, 0.34(6) mmol), *p*-phenoxyphenylboronic acid (185 mg, 0.86 mmol) and $Pd(PPh_3)_4$ (30 mg, $2.6 \cdot 10^{-2}$ mmol) in DME (4 mL) and 1.5 M aq. Na_2CO_3 (3 mL) was stirred at 60ºC for 8h. Thereafter, the cooled solution was poured into water (50 mL) and extracted with $CHCl_3$ (3 X 15 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gel (hexane/$CHCl_3$ 20:3) gave **7b** (110 mg, 58%) as a colorless solid, mp. 167 ºC; IR (KBr) ν 1587, 1512, 1487, 1229, 1166, 867, 751, 695 cm^{-1}; UV ($c = 4.0 \cdot 10^{-5}$ M in cyclohexane) λ_{max} nm (log ε) 254 (4.53), 246 sh (4.36), 209 (4.88); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 32.09 (2C), 38.79 (2C), 118.23 (4C), 119.00 (4C), 123.32 (2C), 126.41 (2C), 129.04, 129.75 (4C), 130.64, 131.33 (4C), 132.00 (2C), 141.87 (2C), 142.03 (2C), 142.27 (2C), 155.99 (2C), 157.04 (2C); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 550 (M^+, 17.5). HRMS Calcd. for $C_{38}H_{30}O_2S$: 550.1967. Found: 550.1974. Calcd. for $C_{38}H_{30}O_2S$: C, 82.88; H, 5.49. Found: C, 82.74; H, 5.55%.

12,13-Bis(*m*-nitrophenyl)metacyclo[2](2,5)thiophenophane (**7c**).- A mixture of **5** (155 mg, 0.42 mmol), *m*-nitrophenylboronic acid (166 mg, 1.04 mmol) and $Pd(PPh_3)_4$ (30 mg, $2.6 \cdot 10^{-2}$ mmol) in DME (4 mL) and 1.5 M aq. Na_2CO_3 (3 mL) was stirred at 60ºC for 8h. Thereafter, the cooled solution was poured into water (50 mL) and extracted with $CHCl_3$ (3 X 15 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gel (hexane/$CHCl_3$/ether 8:2:1) gave **7c** (105 mg, 55%) as a pale yellow solid, mp. 196 ºC; IR (KBr) ν 2912, 1527, 1347, 1072, 813, 771, 730, 705, 691 cm^{-1}; UV ($c = 4.6 \cdot 10^{-5}$ M in cyclohexane) λ_{max} nm (log ε) 339 sh (3.26), 259 (4.48), 239 sh (4.38), 202 (4.68); ^1H NMR (270 MHz, $CDCl_3$) δ 2.35 – 2.50 (m, 4H), 2.89 (m, 2H), 3.19 (m, 2H), 6.29 (s, 1H), 7.08 (dd, 2H; ^3J 7.3 Hz, ^4J 1.6 Hz), 7.29 (dd, 1H, ^3J 8.1 Hz, ^3J 8.1 Hz), 7.43 – 7.54 (m, 4H), 8.11 – 8.18 (m, 4H), ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 32.06 (2C), 39.04 (2C), 122.05 (2C), 124.47 (2C), 126.69 (2C), 129.32 (2C), 129.55 (2C), 130.45 (2C), 135.98 (2C), 137.87 (2C), 139.17 (2C), 141.47 (2C), 145.18 (2C), 148.20; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 457 (MH^+, 6), 456 (6). HRMS Calcd. for $C_{26}H_{20}N_2O_4S$: 456.144. Found: 456.1146. Calcd. for $C_{26}H_{20}O_2N_4S$: C, 68.41; H, 4.42; N, 6.14. Found: C, 68.27; H, 4.43; N, 6.18%.

12,13-Diphenylmetacyclo[2](2,5)thiophenophane (**7d**). – A mixture of **5** (140 mg, 0.37(5) mmol), phenylboronic acid (110 mg, 0.82(5) mmol) and $Pd(PPh_3)_4$ (5.5 mg, 5.10-3 mmol) in DME (5 mL) and aq. Na_2CO_3 (250 mg Na_2CO_3 in 0.75 mL H_2O) was kept under reflux for 24h. Thereafter, the reaction mixture was extracted with CH_2Cl_2 (50 mL). The solution was dried over anhydrous $MgSO_4$, concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (hexane/ether 5:1) to give **7d** (153 mg, 0.37 mmol, quant.) as yellow prisms, mp. 199 ºC; IR (KBr) ν 3048, 3014, 2936, 2914, 2844, 1598, 1500, 1481, 1432, 1069, 913, 773, 731, 698 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.30 – 2.49 (m, 4H), 2.65 – 2.74 (m, 2H), 3.08 – 3.19 (m, 2H), 6.35 (s, 1H), 6.95 – 7.23 (m, 13H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 32.06, 38.81, 126.38, 126.52, 127.92, 129.00, 129.99, 130.69, 137.02, 142.10, 142.39, 142.53; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 366 (M^+, 100).

12,13-Bis(methoxyphenyl)metacyclo[2](2,5)thiophenophane (**7e**). – A mixture of **5** (140 mg, 0.37(5) mmol), 4-methoxyphenylboronic acid (125 mg, 0.82(5) mmol) and $Pd(PPh_3)_4$ (5.5 mg, 5.10^{-3} mmol) in DME (5 mL) and aq. Na_2CO_3 (250 mg Na_2CO_3 in 0.75 mL H_2O) was kept at reflux for 24h. Thereafter, the cooled reaction mixture was extracted with CH_2Cl_2 (100 mL). The solution was dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and the residue was subjected to column chromatography on silica gel (hexane/ether 2:1) to give **7e** (35 mg, 22%) as yellow prisms; mp. 175 ºC; IR (KBr) ν 3030, 2920, 2846, 1689, 1674, 1656, 1640, 1610, 1289, 1247, 1214, 1202, 1176 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.35 – 2.53 (m, 4H), 2.72 – 2.83 (m, 2H), 3.12- 3.25 (m, 2H), 3.79 (s, 6H, 2 OCH_3), 6.39 (s, 1H), 6.80 – 6.85 (m, 4H), 7.05 (d, 2H, ^3J 8.1 Hz), 7.14 – 7.27 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 32.56, 39.16, 55.60, 113.84, 126.77, 129.38, 130.01, 131.09, 131.52,

142.14, 142.61, 142.75, 158.60; MS (EI, 70 eV) *m/z* (%) 426 (M^+, 44). HRMS Found: 426.1651. Calcd. for $C_{28}H_{26}O_2S$: 426.1654 (M^+).

12,13-Bis(4-vinylphenyl)metacyclo[2](2,5)thiophenophane (**7f**). – A mixture of **5** (140 mg, 0.37(5) mmol), 4-vinylphenylboronic acid (122 mg, 0.82(5) mmol), $Pd(PPh_3)_4$ (5.5 mg, $5.0 \cdot 10^{-3}$ mmol) in DME (5 mL) and aq. Na_2CO_3 (250 mg Na_2CO_3 in 0.75 mL H_2O) was kept under reflux for 24h. Thereafter, the mixture was extracted with CH_2Cl_2 (100 mL). The organic phase was dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and the residue was purified by column chromatography on silica gel (hexane/ether 5:1) to give **7f** (118 mg, 75%) as yellow prisms; mp. 82 ºC; IR (KBr) ν 3080, 3014, 2916, 1627, 1604, 1517, 1432, 1400, 1329, 1261, 1206, 1167, 1112, 1068, 1028, 1015, 1006, 987, 910, 844, 807, 781, 711, 701, 473 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.29 – 2.46 (m, 4H), 2.63 – 2.75 (m, 2H), 3.04 – 3.19 (m, 2H), 5.01 – 5.19 (m, 4H), 5.60 - 5.69 (dd, 2H, ^3J 11.0 Hz, ^3J 10.5 Hz),. 6.38 (s, 1H), 6.52 – 7.30 (m, 11H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 31.30, 37.93, 112.72, 124.99, 125.05, 125.57, 128.17, 129.40, 129.86, 135.67, 135.90, 141.24, 141.33, 142.01; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 418 (M^+, 78).

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