Selective Halogenation of Bithiophenes Using 2-Halopyridazin-3(2*H*)-ones under Ambient Conditions

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Abstract: 2,2′-Bithiophene and halogenated-2,2′-bithiophenes were halogenated with 2-halo-4,5-dichloropyridazin-3(2*H*)-one in the presence of zinc halide to give selectively the corresponding dihalo-, trihalo-, and tetrahalo-2,2′-bithiophenes involving the same or different halogens in excellent yields, respectively.

Keywords: bithiophene, halogenation, chlorination, bromination, 2-halopyridazin-3(2*H*)-one

2,2′-Bithiophenes (**1**), oligothiophenes, and well-defined macromolecules bearing bithiophene rings have recently received remarkable attention due to their chemically and physically unique properties such as conductive, nonlinear optical, and liquid crystalline characteristics. Derivatives of the 2,2′-bithiophene are crucial components for synthesis of a myriad of useful materials in consideration of their numerous potential applications in electrochemistry, polymer science, semiconductor industry, nanotechnology, etc.[1] Especially halobithiophenes involving the different halogens, such as bromochloro- and dibromodichlorobithiophenes, are the key starting structure which allows one to readily synthesize various regioselectively substituted bithiophenes and well-defined oligothiophenes.[1a–1f,2] One of the most common method of preparing halobithiophenes is a coupling reaction of halothiophene using transition-metal-containing catalysts.[1c,e,f,2] While several direct halogenations of bithiophene were reported using bromine,[1d] *N*-bromosuccinimide,[3a,d,e] quaternary ammonium polyhalides,[3b] and thionyl chloride,[3c] these previously reported methods except for *N*-bromosuccinimide suffer the inconvenience of low selectivity, demanding additives, and/or low yields. In the chlorination for bithiophene using *N*-chlorosuccinimide, we also observed the low selectivity and the reactivity. Even though preparation of hexachloro- or the hexabromobithiophenes have been reported,[4,5] to the best of our knowledge, the highly selective halogenations for the synthesis of bromochloro-, bromotrichloro-, dibromodichloro- or chlorotribromobithiophene from bithiophene have not been reported yet and highlight this still very active research area.

Pyridazine is a heteroaromatic compound and has special properties such as different aromaticity, reactivity, and physical property, compared to general six-membered heteroaromatic compounds like pyridine, pyrimidine, and pyrazine because of the N–N unit.[6] Our group has focused on development of electrophilic synthons and reagents involving pyridazinone, and their applications.[6e,7] Our group has developed 2-chloropyridazin-3(2*H*)-ones as effective and eco-friendly electrophilic chlorinating agents for active methylene/methane compounds and also are superior to *N*-chlorosucinimide.[7b] The ease with which 4,5-dichloropyridazin-3(2*H*)-one can be removed and/or recycled spurred our interest in its utility as a synthetic auxiliary. Herein, we report the efficient direct halogenation of 2,2′-bithiophene and halogenated bithiophenes using 2-halopyridazin-3(2*H*)-ones.

2-Halopyridazin-3(2*H*)-ones **2** were easily prepared according to the literature methods.[7b,8] We first studied the direct chlorination of 2,2′-bithiophene (**1**) using 2,4,5-trichloropyridazin-3(2*H*)-one (**2a**). Compound **1** was treated with **2a** in the presence of metal chlorides (1 mol%) as the catalyst to give 5-chlorobithiophene (**3a**) and 5,5′-dichlorobithiophene (**4a**), whereas reaction of **1** with **2a** in the absence of metal chloride did not occur. Among six metal chlorides such as CuCl, $CuCl_2$, $AlCl_3$, $PdCl_2$, $FeCl_2$, $ZnBr_2$, and $ZnCl_2$, zinc chloride and zinc bromide (1 mol%) showed the best result. We also investigated the halogenation of 2,2′-bithiophene (**1**) with **2** in the presence of zinc halide in a variety of organic solvents such as CH_2Cl_2, MeCN, THF, MeOH, EtOAc, *n*-hexane, and acetone, and dichloromethane was found to be the most efficacious solvent. According to the literature,[7b,c] enhancement of the reactivity of halogen at N2-position of **2** may be due to the chelation of **2** with zinc halides.

From preliminary experiments for the halogenation of 2,2′-bithiophene (**1**), we selected the 2,2′-bithiophene (**1**, 1 equiv), zinc halide (1 mol%), **2** (1 equiv), CH_2Cl_2 system as the optimum conditions at room temperature. The halogenation of 2,2′-bithiophene (**1**) under the optimized conditions produced the products as the mixture of **3a** (or **3b**) and **4a** (or **4b**).[9] On the other hand, we observed four chlorinated products when 2,2′-bithiophene (**1**) was treat-

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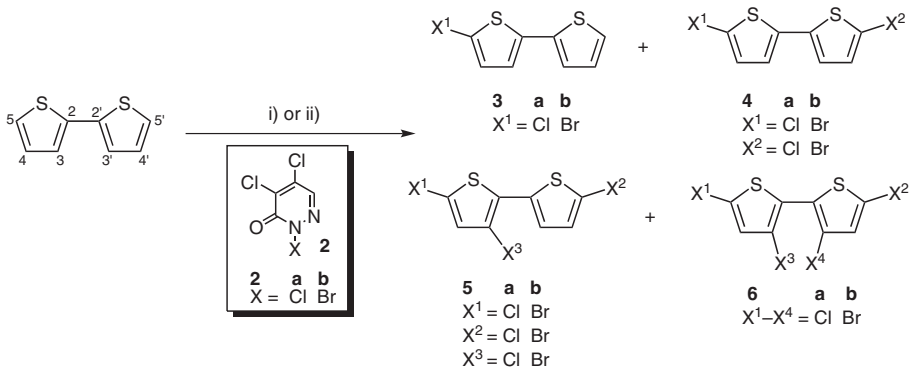


Scheme 1 Halogenation of 2,2′-bithiophene using 2-halo-4,5-dichloropyridazin-3(2*H*)-ones **2**. *Reagents and conditions*: i) **1** (1 equiv), **2a** (2.0, 3.0, 4.0, or 5.0 equiv), $ZnCl_2$, CH_2Cl_2, r.t.; ii) **1** (1 equiv), **2b** (2.0, 3.0, 4.0, or 5.0 equiv), $ZnBr_2$, CH_2Cl_2, r.t.

ed with an excess amount of **2a** at room temperature. According to TLC analysis, compound **1** was chlorinated in the following order: **1** → **3a** → **4a** → **5a** → **6a**. Thus, we attempted to synthesize selectively **4a–c** and **6a–f** by regulating the amounts of halogenating agents **2** under optimized conditions.

Based upon the screening experiments for optimizing catalytic conditions, 1 equivalent of 2,2′-bithiophene (**1**) was reacted with suitable amounts of **2a** or **2b** in the presence of $ZnCl_2$ or $ZnBr_2$ (1 mol%) in CH_2Cl_2 at room temperature to afford selectively **4a**, **4b**, **6a**, or **6b** in excellent yields (entries 2, 5, 8, and 10 in Table 1, Scheme 1).[9] Most interestingly, one equivalent of **3a** or **3b** was treated with 1.5 equivalents of **2b** or **2a** under the same conditions to give selectively 5-bromo-5′-chloro-2,2′-bithiophene (**4c**) in 95% yields, respectively (entries 11 and 13 in Table 1, Scheme 2). Halogenation of one equivalent of **3a** or **3b** with excess **2b** (4.5 equiv) or **2a** (3.5 equiv) afforded selectively 3,3′,5-tribromo-5′-chloro-2,2′-bithiophene (**6c**) or 5-bromo-3,3′5′-trichloro-2,2′-bithiophene (**6d**) in excellent yields (entries 12 and 14 in Table 1, Scheme 2). One equivalent of **4a** or **4b** was also reacted with excess of **2b** (3 equiv) or **2a** (2.5 equiv) under the same conditions to give selectively dibromodichlorobithiophene **6e** or **6f** in excellent yields, respectively (entries 15 and 16 in Table 1, Scheme 2). However, reaction of **3** with excess **2** under the same conditions did not yield pentahalo- or hexahalobithiophene.

Regioselectivity in the electrophilic halogenation of bithiophenes is well explained by a consideration of the Wheland intermediates.[14] Because of the delocalization of intermediate cation, the electrophilic attack from 2-position is more favorable than from 3-position in the thiophene ring. The cationic intermediates from both 3-position (or 3′-position) attack and 5-position (or 5′-position) attack in bithiophenes are also stabilized by the resonance contribution.

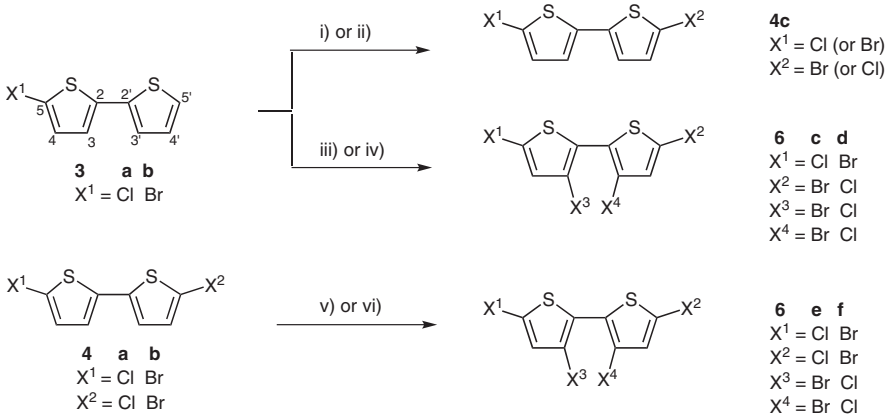
The chemical structures of the all products were characterized by high resolution mass spectrometry, FT-IR, ^1H NMR, and ^{13}C NMR spectroscopy. In addition, we confirmed that substitution took place at the 3-positions for **5a** and **5b** by using the NOESY NMR technique.

Table 1 Halogenation of **1**, **3a**,**b**, and **4a**,**b**[a]

Entry	**1**, **3**	**2** (equiv)	Time	Product (isolated yield, %)[b]			
				3	**4**	**5**	**6**
1	**1**	**2a** (1)	20 min	**3a** (75)	**4a** (17)	–	–
2	**1**	**2a** (2)	20 min	–	**4a** (95)	–	–
3	**1**	**2a** (3)	30 min	–	**4a** (12)	**5a** (60)	**6a** (15)
4	**1**	**2a** (4)	1 h	–	**4a** (2)	**5a** (65)	**6a** (20)
5	**1**	**2a** (5)	1 h	–	–	–	**6a** (94)
6	**1**	**2b** (1)	5 min	**3b** (82)	**4b** (9)	–	–
7	**1**	**2b** (2)	5 min	**3b** (66)	**4b** (27)	–	–
8	**1**	**2b** (3)	5 min	–	**4b** (94)	–	–
9	**1**	**2b** (4)	5 min	–	**4b** (45)	**5b** (38)	–
10	**1**	**2b** (5)	5 min	–	–	–	**6b** (95)
11	**3a**	**2b** (1.5)	5min	–	**4c** (95)	–	–
12	**3a**	**2b** (4.5)	1 h	–	–	–	**6c** (94)
13	**3b**	**2a** (1.5)	13 h	–	**4c** (95)	–	–
14	**3b**	**2a** (3.5)	14 h	–	–	–	**6d** (93)
15	**4a**	**2b** (3)	2 h	–	–	–	**6e** (96)
16	**4b**	**2a** (2.5)	16 h	–	–	–	**6f** (95)

[a] Reaction conditions: **1**, **3a**,**b**, or **4a**,**b** (1 equiv), **2**, $ZnCl_2$ or $ZnBr_2$ (1 mol%), CH_2Cl_2, r.t.
[b] Conversion ratio of bithiophenes is 100% in all reactions except for entries 1 (90% conversion) and 6 (88% conversion).

In summary, we have introduced a new and convenient halogenating agent for the direct halogenation of 2,2′-bithiophene derivatives under mild conditions using 2-halo-4,5-dichloropyridazin-3(2*H*)-ones (**2a** or **2b**). We demonstrated to produce selectively the corresponding dibromo-, dichloro-, bromochloro-, bromotrichloro, chlorotribromo-, dibromodichloro-, tetrabromo-, and tetrachloro-2,2′-bithiophenes from 2,2′-bithiophene (**1**) and halogenated-2,2′-bithiophenes, respectively. 2-Halo-4,5-



Scheme 2 Halogenation of **3a**,**b** and **4a**,**b** using compounds **2**. *Reagents and conditions*: i) **3a** (1 equiv), **2b** (1.5 equiv), $ZnBr_2$, CH_2Cl_2, r.t.; **3b** (1 equiv), **2a** (1.5 equiv), $ZnCl_2$, CH_2Cl_2, r.t.; iii) **3a** (1 equiv), **2b** (4.5 equiv), $ZnBr_2$, CH_2Cl_2, r.t.; iv) **3b** (1 equiv), **2a** (3.5 equiv), ZnC CH_2Cl_2, r.t.; v) **4a** (1 equiv), **2b** (3.0 equiv), $ZnBr_2$, CH_2Cl_2, r.t.; vi) **4b** (1 equiv), **2a** (2.5 equiv), $ZnCl_2$, CH_2Cl_2, r.t.

dichloropyridazin-3(2*H*)-ones are easily prepared from 4,5-dichloropyridazin-3(2*H*)-one, which is commercially available, stable, and reusable.[7] The present system is complementary to reported methods.[1d,3] We envision more selective halogenation of terthiophenes or oligothiophenes, and efforts in this direction are under way.

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(9) **General Procedure**

To a solution of zinc halide (1 mol%), 2-halo-4,5-dichloropyridazin-3 (2*H*)-one **2** (1–5 equiv), and CH_2Cl_2 (50 mL), bithiophenes (1 equiv) were added with stirring at r.t. Then, the reaction mixture was stirred until the **2** disappeared by TLC monitoring. The reaction mixture was filtered using Celite-545 pad, and washed with EtOAc (10–20 mL). The combined filtrate was evaporated under reduced pressure. The resulting residue was applied to the top of open-bed silica gel column (3 × 20 cm), and the column was eluted with *n*-hexane. Fractions containing the product were combined and evaporated under reduced pressure to give product.

5-Chloro-2,2′-bithiophene (3a)

Liquid; R_f = 0.56 (*n*-hexane). IR (KBr): 3070, 3043, 1507, 1421, 1065, 1001, 869, 789 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.21 (dd, 1 H, *J* = 1.2, 5.1 Hz), 7.09 (dd, 1 H, *J* = 1.2, 3.6 Hz), 6.99 (dd, 1 H, *J* = 3.6, 5.1 Hz), 6.92 (d, 1 H, *J* = 3.9 Hz), 6.82 (d, 1 H, *J* = 3.9 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.50, 136.03, 128.65, 127.86, 126.86, 124.76, 123.93, 122.86 ppm. HRMS (EI): *m/z* calcd for $C_8H_5ClS_2$: 199.9521; found: 199.9519. Anal. Calcd for $C_8H_5ClS_2$: C, 47.87; H, 2.51. Found: C, 47.90; H, 2.55.

5-Bromo-2,2′-bithiophene (3b)

Colorless crystals; mp 33 °C (recrystallization from $CHCl_3$; lit.[10] mp 32–33 °C), R_f = 0.51 (*n*-hexane). IR (KBr): 3099, 3082, 3066, 1501, 1439, 1414, 1350, 1198, 1074, 1051, 966, 879, 835, 820, 787, 690, 644, 611, 455 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.20 (dd, 1 H, *J* = 1.2, 5.1 Hz), 7.09 (dd, 1 H, *J* = 1.2, 3.6 Hz), 6.99 (dd, 1 H, *J* = 3.6, 5.1 Hz), 6.95 (d, 1 H, *J* = 3.8 Hz), 6.89 (d, 1 H, *J* = 3.8 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.93,136.42, 130.58, 127.85, 124.82, 124.06, 123.85, 110.93 ppm. HRMS (EI): *m/z* calcd for $C_8H_5BrS_2$: 243.9016; found: 243.9012. Anal. Calcd for $C_8H_5BrS_2$: C, 39.19; H, 2.06. Found: C, 39.21; H, 2.10.

5,5′-Dichloro-2,2′-bithiophene (4a)

Colorless crystals; mp 109 °C (recrystallization from $CHCl_3$; lit.[11] mp 109–110 °C); R_f = 0.64 (*n*-hexane). IR (KBr): 3095, 1504, 1418, 1137, 1075, 1012, 857, 816, 785 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ = 6.85 (d, 2 H, *J* = 3.9 Hz), 6.81 (d, 2 H, *J* = 3.9 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.03, 129.18, 126.91, 123.06 ppm. HRMS (EI): *m/z* calcd for $C_8H_4Cl_2S_2$: 233.9131; found: 233.9130. Anal. Calcd for $C_8H_4Cl_2S_2$: C, 40.86; H, 1.71. Found: C, 40.90; H, 1.74.

5,5′-Dibromo-2,2′-bithiophene (4b)

Colorless crystals; mp 141 °C (recrystallization from $CHCl_3$; lit.[1a] mp 147 °C, mp 146 °C,[12] mp 142 °C[13]); R_f = 0.59 (*n*-hexane). IR (KBr): 3090, 3067, 3036, 2922, 1732, 1535, 1497, 1454, 1412, 1317, 1196, 1057, 966, 864, 814, 789, 623, 604, 455 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.98 (d, 2 H, *J* = 3.9 Hz), 6.87 (d, 2 H, *J* = 3.9 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.81, 130.66, 124.16, 111.55 ppm. HRMS (EI): *m/z* calcd for $C_8H_4Br_2S_2$: 321.8121; found: 321.8126. Anal. Calcd for $C_8H_5Br_2S_2$: C, 29.65; H, 1.24. Found: C, 29.68; H, 1.29.

5-Bromo-5′-chloro-2,2′-bithiophene (4c)

Colorless crystals; mp 123 °C; R_f = 0.64 (*n*-hexane). IR (KBr): 3069, 3040, 1730, 1578, 1541, 1504, 1418, 1342, 1279, 1196, 1065, 999, 966, 868, 791, 633, 457 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.98 (d, 1 H, *J* = 3.8 Hz), 6.88 (d, 1 H, *J* = 3.9 Hz), 6.85 (d, 1 H, *J* = 4.0 Hz), 6.84 (d, 1 H, *J* = 4.0 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.90, 134.94, 130.65, 129.28, 126.95, 124.04, 123.18, 111.43 ppm. HRMS (EI): *m/z* calcd for $C_8H_4BrClS_2$: 277.8626; found: 277.8626. Anal. Calcd for $C_8H_4BrClS_2$: C, 34.36; H, 1.44. Found: C, 34.39; H, 1.50.

3,5,5′-Trichloro-2,2′-bithiophene (5a)

Colorless crystals; mp 99 °C (recrystallization from $CHCl_3$; lit.[3c] mp 102–103 °C), R_f = 0.69 (*n*-hexane). IR (KBr): 3097, 2925, 1499, 1402, 1305, 1136, 1012, 812 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.02 (d, 1 H, *J* = 4.0 Hz), 6.87 (d, 1 H, *J* = 4.0 Hz), 6.79 (s, 1 H) ppm. ^{13}C NMR(75 MHz, $CDCl_3$): δ = 131.35, 131.19, 128.56, 128.28, 127.86, 127.05, 126.24, 125.48, 120.06 ppm. HRMS (EI): *m/z* calcd for $C_8H_3Cl_3S_2$: 267.8742; found: 267.8742. Anal. Calcd for $C_8H_3Cl_3S_2$: C, 35.64; H, 1.12. Found: C, 35.68; H, 1.17.

3,5,5′-Tribromo-2,2′-bithiophene (5b)

Colorless crystals; mp 84 °C; R_f = 0.63 (*n*-hexane). IR (KBr): 3090, 2953, 2922, 2851, 1732, 1680, 1535, 1493, 1464, 1450, 1410, 1371, 1283, 1240, 1219, 1130, 1063, 1018, 974, 866, 814, 785, 638, 453 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.05 (d, 1 H, *J* = 3.9 Hz), 7.02 (d, 1 H, *J* = 3.9 Hz), 6.98 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.78, 133.80, 133.14, 130.03, 127.08, 113.79, 111.57, 107.32 ppm. HRMS (EI): *m/z* calcd for $C_8H_3Br_3S_2$: 399.7226; found: 399.7215. Anal. Calcd for $C_8H_3Br_3S_2$: C, 23.85; H, 0.75. Found: C, 23.87; H, 0.80.

3,3′,5,5′-Tetrachloro-2,2′-bithiophene (6a)

Colorless crystals; mp 113–114 °C (recrystallization from $CHCl_3$; lit.[3c] mp 120–121); R_f = 0.73 (*n*-hexane). IR (KBr): 3095, 2932, 1509, 1418, 1301, 1125, 1007, 811 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.88 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.09, 127.05, 124.33, 123.63 ppm. HRMS (EI): *m/z* calcd for $C_8H_2Cl_4S_2$: 301.8352; found: 301.8352. Anal. Calcd for $C_8H_2Cl_4S_2$: C, 31.60; H, 0.66. Found: C, 31.63; H, 0.69.

3,3′,5,5′-Tetrabromo-2,2′-bithiophene (6b)

Colorless crystals; mp 140 °C (recrystallization from $CHCl_3$; lit.[5] mp 138–140 °C); R_f = 0.66 (*n*-hexane). IR (KBr): 3097, 2920, 2851, 1537, 1479, 1447, 1393, 1288, 1126, 980, 920, 872, 827, 800, 739, 669, 584, 503, 469 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.07 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.01, 129.59, 114.82, 112.13 ppm. HRMS (EI): *m/z* calcd for $C_8H_2Br_4S_2$: 477.6331; found: 477.6335. Anal. Calcd for $C_8H_2Br_4S_2$: C, 19.94; H, 0.42. Found: C, 20.00; H, 0.48.

3,3′,5-Tribromo-5′-chloro-2,2′-bithiophene (6c)

Colorless crystals; mp 125 °C;, R_f = 0.69 (*n*-hexane). IR (KBr): 3099, 1539, 1485, 1452, 1396, 1315, 1292, 1230, 1198, 1128, 1011, 978, 874, 831, 798, 675, 586, 474 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.04 (s, 1 H), 6.92 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.98, 132.55, 129.56, 126.69, 114.80, 112.17, 111.47, 111.41 ppm. HRMS (EI): *m/z* calcd for $C_8H_2Br_3ClS_2$: 433.6837; found: 433.6841. Anal. Calcd for $C_8H_2Br_3ClS_2$: C, 21.97; H, 0.46. Found: C, 22.01; H, 0.49.

5-Bromo-3,3′,5′-trichloro-2,2′-bithiophene (6d)

Colorless crystals; mp 125 °C; R_f = 0.71 (*n*-hexane). IR (KBr): 3094, 2920, 2851, 1742, 1717, 1701, 1634, 1495, 1456, 1398, 1373, 1302, 1215, 1136, 1014, 982, 812, 685, 590, 465 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.98 (s, 1 H), 6.86 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ =

131.12, 130.52,127.15, 127.06, 124.40, 124.35, 123.62, 113.41 ppm. HRMS (EI): *m/z* calcd for $C_8H_2BrCl_3S_2$: 345.7847; found: 345.7845. Anal. Calcd for $C_8H_2BrCl_3S_2$: C, 27.57; H, 0.58. Found: C, 27.59; H, 0.62.

3,3′-Dibromo-5,5′-dichloro-2,2′-bithiophene (6e)

Colorless crystals; mp 103 °C; R_f = 0.69 (*n*-hexane). IR (KBr): 3101, 2952, 2922, 2851, 1537, 1489, 1455, 1419, 1401, 1295, 1131, 1074, 1016, 833, 799, 683, 588, 478, 460, 439 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.91 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.52, 129.55, 126.72, 111.47 ppm. HRMS (EI): *m/z* calcd for $C_8H_2Br_2Cl_2S_2$: 389.7342; found: 389.7340. Anal. Calcd for $C_8H_2Br_2Cl_2S_2$: C, 24.45; H, 0.51. Found: C, 24.47; H, 0.56.

5,5′-Dibromo-3,3′-dichloro-2,2′-bithiophene (6f)

Colorless crystals; mp 124 °C; R_f = 0.75 (*n*-hexane). IR (KBr): 3090, 2953, 2922, 2853, 1636, 1491, 1464, 1394, 1298, 1134, 980, 924, 814, 675, 590, 461 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.99 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.00, 130.53, 124.39, 113.46 ppm. HRMS (EI): *m/z* calcd for $C_8H_2Br_2Cl_2S_2$: 389.7342; found: 389.7346. Anal. Calcd for $C_8H_2Br_2Cl_2S_2$: C, 24.45; H, 0.51. Found: C, 24.48; H, 0.57.

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