Rhodium(I)-Mediated Synthesis of Benzo[2,1-*b*:3,4-*b*′:5,6-*c*″]trithiophenes and Naphtho[2,1-*b*:3,4-*b*′]dithiophenes

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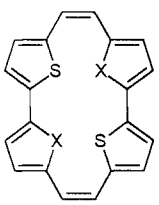
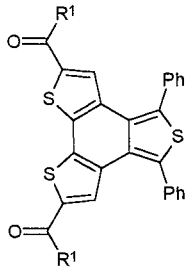
Dedicated with best wishes to Professor Dr. Gottfried Huttner, Heidelberg, on the occasion of his 60th birthday

The syntheses of carbonylated benzo[2,1-*b*:3,4-*b*′:5,6-*c*″]trithiophenes **2** and naphtho[2,1-*b*:3,4-*b*′]dithiophenes **3** are described. The treatment of 5,5′-dicarbonylated 3,3′-bis(phenylethynyl)-2,2′-bithiophenes **6** [readily available via Pd(II)-catalyzed alkynylation of the corresponding 3,3′-dibromo-2,2′-bithiophenes **5** in the presence of Cu(I) in (*i*-Pr)$_2$NH] with chlorotris(triphenylphosphine)rhodium(I) yields the cyclic rhodium complexes **7** which smoothly react with sulfur and acetylenes to give **2** and **3** in good yields.

During the course of our investigations directed towards the synthesis of novel sulfur-containing porphycene derivatives[1,2] as potential agents for use in photodynamic tumor therapy (PDT), we became interested in the introduction of benzo-fused bithiophene and trithiophene moieties as major components in the tetrathiaporphycene skeleton. Previously we have demonstrated that tetrathiaporphycene **1a**,[1] in contrast to 21,23-dithiaporphycene **1b**,[2] does not exhibit the typical paratropic [*n*]annulene structure of the porphycene species. This fact can be explained by the nonplanarity of the tetrathiaporphycenes due to the distortion caused by the steric demand of the four sulfur atoms. This distortion can be suppressed by fixing both thiophenes of the 2,2′-bithiophene unit through formation of a rigid benzo[2,1-*b*:3,4-*b*′]dithiophene moiety as represented by structure **2**.



1



2

1a X = S
1b X = NH
2 R^1 = H,CH_3,Ph

Presently, the most efficient method for the preparation of porphycenes[3] involves the intermolecular dimerization of dicarbonyl compounds with low-valent titanium under McMurry conditions.[4] Thus, we attempted a simple synthesis of dicarbonylated benzo[2,1-*b*:3,4-*b*′:5,6-*c*″]trithiophenes **2** and naphtho[2,1-*b*:3,4-*b*′]dithiophenes **3** as suitable precursors for planar tetrathiaporphycenes. Compounds **2** and **3** were also expected to exhibit favourable orientation of both carbonyl groups for the McMurry type cyclization.

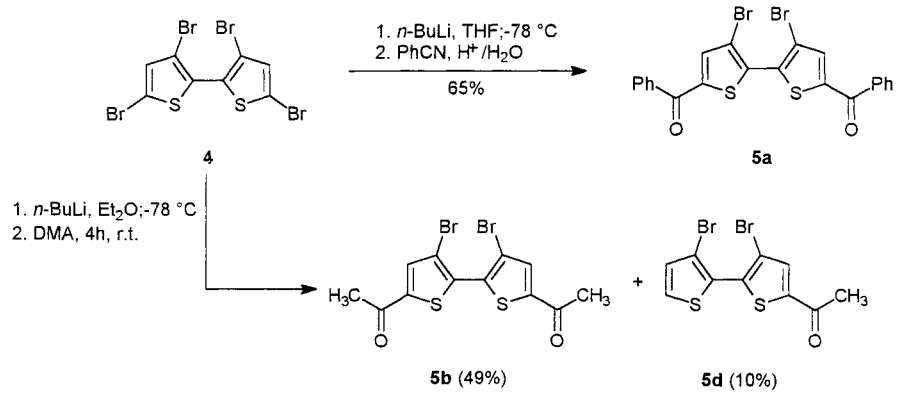
Benzodithiophene and benzotrithiophene derivatives are synthetically accessible by several routes.[5] However, prompted by the fundamental observation of Müller,[6] which presented the potential of rhodium(I)-mediated reactions with diynes for the controlled synthesis of arene systems, we recently described the preparation of condensed benzo[2,1-*b*:3,4-*b*′]dithiophenes and benzo[2,1-*b*:3,4-*b*′:5,6-*c*″]trithiophenes starting from 3,3′-bis(phenylethynyl)-2,2′-bithiophene derivatives using this method.[7] To transfer this strategy to the synthesis of target compounds **2** and **3** it was necessary to develop an efficient preparation of dicarbonylated 3,3′-bis(phenylethynyl)-2,2′-bithiophenes **6**.

In this direction, we have previously reported the synthesis of alkynylated 2,2′-bithiophene-5,5′-dicarbaldehydes[8] involving the palladium(II)-catalyzed alkynylation using the method of Hagihara and Whitesides.[9] Further investigations showed that this sequence is applicable to the preparation of the corresponding alkynylated 5,5′-dibenzoyl- and 5,5′-diacetyl-2,2′-bithiophenes **6a,b** starting from the 3,3′,5,5′-tetrabromo-2,2′-bithiophene **4**. The introduction of both carbonyl substituents in 5,5′-position can be accomplished by regioselective α-lithiation of **4** with 2 equivalents of BuLi. Reaction of the thienyllithium species with benzonitrile in THF at −78 °C affords, after acidic hydrolysis, the 5,5′-dibenzoyl-3,3′-dibromo-2,2′-bithiophene **5a** in good yield (Scheme 1).

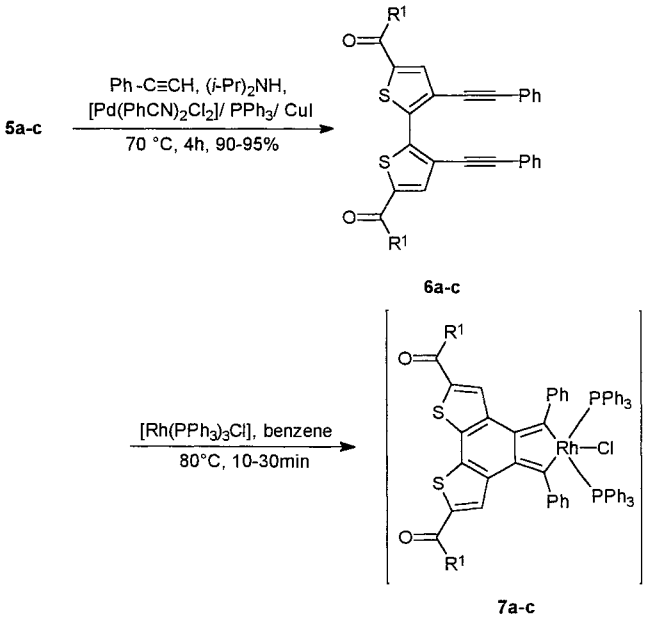
Analogous to the synthesis of the 3,3′-dibromo-2,2′-bithiophene-5,5′-dicarbaldehyde **(5c)**,[8] treatment of a solution of thienyllithium in Et_2O with dimethylacetamide (DMA) yields the corresponding diacetyl derivative **5b** as the major product after a reaction time of 4 hours at room temperature. Surprisingly, in addition to the major product, the monosubstituted 5-acetyl-3,3′-dibromo-2,2′-bithiophene **5d** (10%) and the 3,3′-dibromo-2,2′-bithiophene[8] (traces) were obtained (Scheme 1). The formation of these byproducts can be explained by the relatively high acidity of the α-protons of DMA, which allow the protonation of the thienyllithium intermediate. When the reaction was carried out in THF under the same reaction conditions, the desired product **5b** was obtained only in low yields (<5%) and **5c** was isolated as the major product.

These dicarbonylated 3,3′-dibromo-2,2′-bithiophenes **5a–c** are excellent starting materials for the preparation of the corresponding 3,3′-bisalkynylated derivatives **6a–c** (Scheme 2).

As shown for the synthesis of 3,3′-bis(phenylethynyl)-2,2′-bithiophene-5,5′-dicarbaldehyde **(6c)**,[8] the reaction of **5a,b** with an excess of phenylacetylene, using a catalyst[9] composed of dichlorobis(benzonitrile)palladium(II), triphenylphosphine and copper(I) iodide in boiling (*i*-Pr)$_2$NH, affords the dicarbonylated 3,3′-bis(phenylethy-



Scheme 1



5–7	R^1
a	Ph
b	Me
c	H

Scheme 2

nyl)-2,2′-bithiophene derivatives **6a,b** in moderate yields (Scheme 2). The heterogeneous reaction conditions caused by the low solubility of the starting materials **5a,b** in amine (ultrasonic bath) do not affect the yields [**6c**, so far synthesized in benzene/$(i\text{-Pr})_2$NH solution, is also obtainable from **5c** without decrease in yield]. The corresponding bis(trimethylsilylethynyl) derivatives **6e,f** are also obtained from **5a,b** by reaction with trimethylsilylacetylene under these conditions.

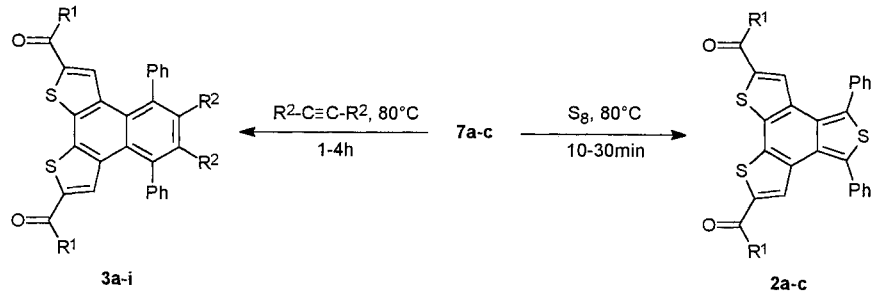
The 3,3′-bis(phenylethynyl)-2,2′-bithiophenes **6a–c** are excellent intermediates for the synthesis of the desired benzo[2,1-*b*:3,4-*b*′:5,6-*c*″]trithiophenes **2** and naphtho[2,1-*b*:3,4-*b*′]dithiophenes **3**. Thus, the reaction of **6a–c** with chlorotris(triphenylphosphine)rhodium(I) in deoxygenated benzene at 80 °C for ca 30 min (TLC monitoring) gives the corresponding rhodium complexes **7** as dark green (**7a,c**) or dark purple (**7b**) intermediates (Scheme 2). Because of their low stability, the complexes were not isolated but reacted directly with various acetylenes to give the substituted naphtho[2,1-*b*:3,4-*b*′]dithiophene compounds **3** (Scheme 3).

The conversion of **7a–c** with dried gaseous acetylene or dimethyl but-2-ynedioate to the corresponding 4,7-diphenyl-substituted naphtho[2,1-*b*:3,4-*b*′]dithiophenes **3a–c** and the dimethyl naphtho[2,1-*b*:3,4-*b*′]dithiophene-5,6-dicarboxylates **3d–f** required short reaction times and gave high yields. Due to the steric bulk of the phenyl substituents, treatment of the complexes **7a–c** with diphenylacetylene required longer reaction times and gave comparatively lower yields of the 4,5,6,7-tetraphenyl-substituted derivatives **3g–i**. For example, 4,5,6,7-tetraphenylnaphtho[2,1-*b*:3,4-*b*′]dithiophene-2,9-dicarbaldehyde (**3i**), was obtained in only 5% yield, the major product being the naphthodithiophene monoaldehyde **3j** (24%) (Scheme 4).

The product ratio was found to depend on the reaction time, as observed by terminating the conversion after shorter reaction times. In this way the desired product **3i** was isolated exclusively, but the overall yield decreased (< 5% of **3i**). Longer reaction times resulted in the production of not only the monocarbonylated material but also the completely decarbonylated 4,5,6,7-tetraphenylnaphtho[2,1-*b*:3,4-*b*′]dithiophene.[7] So far, these decarbonylation reactions cannot be explained conclusively.

As an alternative, Müller[6] also investigated the diyne reaction with chalcogens. According to this method the desired dicarbonylated 4,6-diphenylbenzo[2,1-*b*:3,4-*b*′:5,6-*c*″]trithiophenes **2a–c** were isolated in moderate yields after treatment of the rhodium complexes **7a–c** with elemental sulfur (Scheme 3).

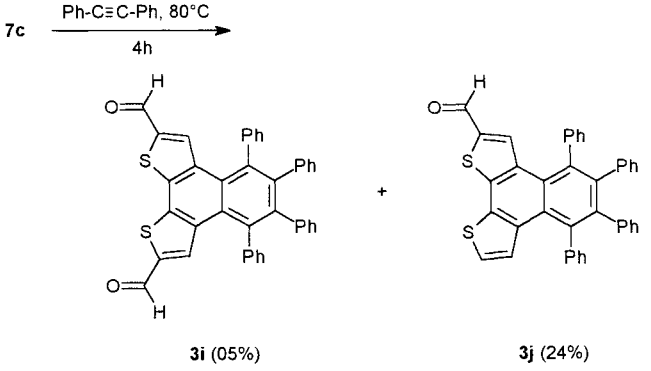
This synthesis of benzotrithiophenes **2** from 3,3′-dibromo-2,2′-bithiophenes **4a–c** is also applicable to the preparation of the 2-acetyl-4,6-diphenylbenzo[2,1-*b*:3,4-*b*′:5,6-*c*″]trithiophene (**2d**). After alkynylation of **5d** with phenylacetylene under the above stated reaction conditions, the reaction of the 5-acetyl-3,3′-bis(phenylethynyl)-2,2′-bithiophene (**6d**) with chlorotris(triphenylphosphine)rhodium(I) affords the blue rhodium complex **7d**, which smoothly reacts with elemental sulfur to give **2d** in 61% overall yields (Scheme 5).



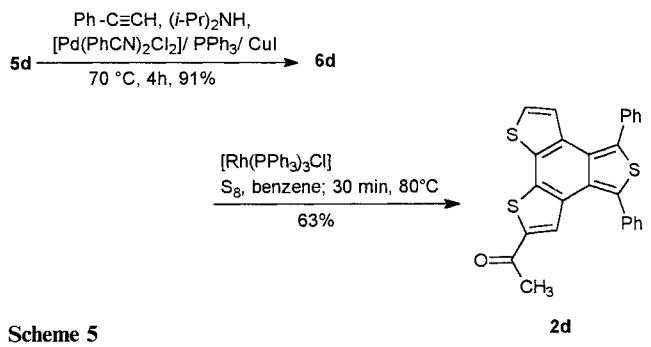
7	3	R^1	R^2
a	**a**	Ph	H
b	b	Me	H
c	**c**	H	H
a	**d**	Ph	CO_2Me
b	**l**	Me	CO_2Me
c	**f**	H	CO_2Me
a	**g**	Ph	Ph
b	**h**	Me	Ph
c	**i**	H	Ph

2	R^1
a	Ph
b	Me
c	H

Scheme 3



Scheme 4



Scheme 5

In conclusion, we have shown that the easily obtainable 3,3′-bis(phenylethynyl)-2,2′-bithiophenes **6a–d** are excellent precursors for the rhodium(I)-mediated synthesis of carbonylated naphtho[2,1-*b*:3,4-*b*′]dithiophenes **3a–j** and benzo[2,1-*b*:3,4-*b*′:5,6-*c*″]trithiophenes **2a–d**. Because of the rigidity of the arene skeleton and the favourable conformation of both carbonyl groups, compounds of structure **2** and **3** should be suitable synthetic intermediates for the synthesis of planar benzo-fused tetrathiaporphycenes.

All reactions were carried out under argon in flame-dried glassware. $(i\text{-Pr})_2NH$ was freshly distilled from KOH; Et_2O, THF and benzene were distilled from Na/benzophenone before use. Silica gel (60–200 mesh) for column chromatography (CC) was obtained from ICN-Biomedicals. Melting points were determined on a Reichert melting point microscope and are uncorrected. UV/VIS spectra were recorded in CH_2Cl_2 on a Hewlett Packard HP 8453 UV/VIS ChemStation and Hewlett Packard HP 8452A diode array spectrophotometer. IR spectra were recorded as KBr pellets on a Perkin-Elmer PE 1600 FT-IR spectrophotometer. ^1H NMR spectra were recorded on Bruker WM-250 (at 250.13 MHz), Bruker AM-360 (at 360.12 MHz) and Varian XL 300 spectrometers (at 299.95 MHz), δ in ppm relative to TMS, J in Hz. ^{13}C NMR spectra were obtained at 62.89 MHz, at 90.56 MHz and at 75.43 MHz on the same spectrometers (the degree of substitution was determined by J-modulated spin-echo experiments). Mass spectra were performed on a Varian MAT-311 A mass spectrometer at 70 eV. Elemental analyses were obtained on a Foss-Heraeus Vario EL; all compounds gave satisfactory microanalyses (C, H, S $\pm$ 0.3%).

The syntheses of 3,3′,5,5′-tetrabromo-2,2′-bithiophene **(4)**, 3,3′-dibromo-2,2′-bithiophene-5,5′-dicarbaldehyde **(5c)** and 3,3′-bis(phenylethynyl)-2,2′-bithiophene-5,5′-dicarbaldehyde **(6c)** are described in the literature.[8]

5,5′-Dibenzoyl-3,3′-dibromo-2,2′-bithiophene (5a):
To a solution of **4** (2.41 g, 5 mmol) in anhyd THF (150 mL) was added dropwise 2.5 M BuLi in hexane (4.4 mL, 11 mmol) over 30 min at −78 °C. After stirring for 1 h at the same temperature anhyd benzonitrile (1.1 mL, 11 mmol) was added in one portion. After stirring for an additional 2 h at −78 °C, the mixture was allowed to warm to r.t. The mixture was slowly added to ice water (300 mL), acidified with 10 N HCl (50 mL) under strong stirring for 30 min, then neutralized with K_2CO_3 and diluted with $CHCl_3$ (200 mL). The organic layer was separated, the aqueous phase extracted with $CHCl_3$ (100 mL), the combined organic phases washed with H_2O, dried ($MgSO_4$) and evaporated. The pure product was isolated after CC ($CHCl_3$) and recrystallization from toluene or

petroleum ether (100–120) as yellow needles; yield: 1.38 g (65%); mp 189–191 °C.

UV/VIS: λ (lg ε) = 265 (4.24), 342 nm (4.15).

IR: ν = 3080, 3055 (CH), 1641 (CO), 1595, 1576, 1496, 1444, 1366, 1316, 1280, 1179, 1156, 1111, 1104, 902, 865, 707, 689, 657 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.93–7.87 (m, 4H, arom), 7.69–7.61 (m, 2H, arom), 7.63 (s, 2H, $C^{4,4'}$–H), 7.59–7.51 (m, 4H, arom).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.44 (CO), 143.69 (arom C), 136.97 (arom CH), 136.68, 136.01 (arom C), 132.81, 129.00, 128.54 (arom CH), 112.78 ($C^{3,3'}$–Br).

MS (EI): *m/z* (%) = 532 (45, M^+), 455 (10, $M^+-C_6H_5$), 453 (5, $M^+-{}^{79}Br$), 348 (5, $M^+-{}^{79}Br-C_6H_5CO$), 105 (100, $C_6H_5CO^+$), 77 (65, $C_6H_5^+$).

HRMS: *m/z* calc. for $C_{22}H_{12}S_2O_2{}^{79}Br^{81}Br$: 531.8626, found: 531.8625.

5,5'-Diacetyl-3,3'-dibromo-2,2'-bithiophene (5b):

To a solution of **4** (2.41 g, 5 mmol) in anhyd Et_2O (150 mL) was added dropwise 2.5 M BuLi in hexane (4.4 mL, 11 mmol) over 30 min at −78 °C. After stirring for 1 h at the same temperature anhyd dimethylacetamide (DMA) (1.1 mL, 11 mmol) was added in one portion. After stirring for an additional 2 h at −78 °C, the mixture was allowed to warm to r.t. for 4 h. The mixture was hydrolyzed with 5 N HCl and diluted with 200 mL $CHCl_3$. The organic layer was separated, the aqueous phase extracted with $CHCl_3$ (100 mL), the combined organic phases washed with H_2O, dried ($MgSO_4$) and evaporated. The pure product was isolated after CC ($CHCl_3$, third fraction, R_f 0.38) and recrystallization from toluene as light yellow needles; yield: 1.00 g (49%); mp 265–266 °C.

UV/VIS: λ (lg ε) = 236 (4.08), 256 (4.08), 322 nm (4.06).

IR: ν = 3098 (CH), 2968, 2924 (CH_3), 1650 (CO), 1507, 1381, 1357, 1316, 1270, 1160, 1141, 940, 866, 810, 720, 608, 595 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.65 (s, 2H, $C^{4,4'}$–H), 2.58 (s, 6H, CH_3).

^{13}C NMR (91 MHz, $CDCl_3$): δ = 189.49 (CO), 144.61, 135.93 (arom C), 135.18 ($C^{4,4'}$–H), 113.08 ($C^{3,3'}$–Br), 26.57 ($COCH_3$).

MS (EI): *m/z* = 408 (60, M^+), 393 (60, M^+-CH_3), 284 (25, $M^+-COCH_3-{}^{81}Br$), 269 (20, $M^+-COCH_3-CH_3-{}^{81}Br$), 241 (5, $M^+-2COCH_3-{}^{81}Br$), 162 (30, $M^+-2COCH_3-{}^{79}Br-{}^{81}Br$), 43 (100, $COCH_3^+$).

HRMS: *m/z* calc. for $C_{12}H_8S_2O_2{}^{79}Br^{81}Br$: 407.8312, found: 407.8314.

5-Acetyl-3,3'-dibromo-2,2'-bithiophene **(5d)**:

Pure **5d** was obtained as a byproduct from the synthesis of **5b** after CC ($CHCl_3$, second fraction, R_f 0.53) and recrystallization from MeCN as colourless needles; yield: 180 mg (9.8%); mp 119–120 °C.

IR: ν = 3096 (CH), 2925 (CH_3), 1648 (CO), 1499, 1453, 1320, 1281, 1148, 867, 832, 799, 701, 593 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.63 (s, 1H, C^4–H), 7.45 (d, ^3J = 5.4 Hz, 1H, $C^{5'}$–H), 7.10 (d, ^3J = 5.4 Hz, 1H, $C^{4'}$–H), 2.56 (s, 3H, $COCH_3$).

^{13}C NMR (91 MHz, $CDCl_3$): δ = 189.43 (CO), 143.87 (arom C), 135.08, 131.23, 128.22 (arom CH), 113.11, 112.48 (C–Br), 26.44 ($COCH_3$).

MS (EI): *m/z* (%) = 366 (70, M^+), 351 (65, M^+-CH_3), 244 (40, $M^+-COCH_3-{}^{79}Br$), 163 (10, M^+-COCH_3-2Br), 43 (100, $COCH_3^+$).

HRMS: *m/z* calc. for $C_{10}H_6S_2O^{79}Br^{81}Br$: 365.8206, found: 365.8207.

Carbonylated 3,3'-Bisalkynyl-2,2'-bithiophenes 6a–f; General Procedure:

To a suspension (ultrasonic bath) of **5a–c** (0.5 mmol) in freshly distilled $(i\text{-Pr})_2NH$ (100 mL) were added dichlorobis(benzonitrile)-palladium(II) (0.2 mmol, 78 mg), Ph_3P (0.4 mmol, 106 mg) and CuI (0.2 mmol, 38 mg). The solution was degassed by passing a rapid stream of argon through it. An excess of the corresponding acetylene (2 mmol of phenylacetylene or trimethylsilylacetylene) was then added at r.t. After stirring for 30 min the suspension was heated at 70 °C for 4 h. During this time the solution rapidly turned bright yellow, then yellow brown and finally dark brown, with the formation of a precipitate. The solution was allowed to cool to r.t. and then filtered.

5,5'-Dibenzoyl-3,3'-bis(phenylethynyl)-2,2'-bithiophene **(6a)**:

After treatment of **5a** (266 mg) with phenylacetylene (0.2 mL), CC ($CHCl_3$) of the yellow brown precipitate followed by recrystallization from toluene gave pure **6a** as orange crystals; yield: 255 mg (89%); mp 228–230 °C.

UV/VIS: λ (lg ε) = 242 (4.46), 252sh (4.44), 305sh (4.68), 313 (4.71), 429 (4.28), 455sh nm (4.24).

IR: ν = 3056 (CH), 2199 (C≡C), 1630 (CO), 1599, 1576, 1511, 1489, 1447, 1402, 1346, 1314, 1283, 1233, 1110, 1025, 863, 854, 751, 704, 684, 661, 523 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3/CS_2$, 1:1): δ = 7.92–7.88 (m, 4H, arom), 7.72 (s, 2H, $C^{4,4'}$–H), 7.63–7.58 (m, 6H, arom), 7.55–7.48 (m, 4H, arom), 7.39–7.35 (m, 6H, arom).

^{13}C NMR (75 MHz, $CDCl_3/CS_2$, 1:1): δ = 186.91 (CO), 143.32, 141.18, 137.28 (arom C), 136.95, 132.31, 131.18, 128.94, 128.93, 128.39, 128.36 (arom CH), 122.22, 121.51 (arom C), 98.10, 84.89 (C≡C).

MS (EI): *m/z* (%) = 574 (100, M^+), 469 (10, $M^+-C_6H_5CO$), 364 (5, $M^+-2C_6H_5CO$), 105 (80, $C_6H_5CO^+$), 77 (50, $C_6H_5^+$).

HRMS: *m/z* calc. for $C_{38}H_{22}S_2O_2$: 574.1061, found: 574.1062.

5,5'-Diacetyl-3,3'-bis(phenylethynyl)-2,2'-bithiophene **(6b)**:

After treatment of **5b** (204 mg) with phenylacetylene (0.2 mL), CC ($CHCl_3$) of the yellow brown precipitate followed by recrystallization from toluene gave pure **6b** as yellow needles; yield: 203 mg (90%); mp 243–244 °C (dec).

UV/VIS: λ (lg ε) = 242 (4.39), 294sh (4.71), 302 (4.73), 416 (4.21), 434sh nm (4.15).

IR: ν = 3105, 3053 (CH), 2922 (CH_3), 2203 (C≡C), 1653 (CO), 1517, 1490, 1442, 1407, 1364, 1264, 1239, 1157, 853, 756, 686, 609, 599, 544, 528 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.75 (s, 2H, $C^{4,4'}$–H), 7.67–7.62 (m, 4H, arom), 7.44–7.39 (m, 6H, arom), 2.58 (s, 6H, $COCH_3$).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 190.39 (CO), 143.35, 142.29 (arom C), 135.21, 131.56, 129.14, 128.65 (arom CH), 122.47, 121.71 (arom C), 97.86, 84.64 (C≡C), 26.74 ($COCH_3$).

MS (EI): *m/z* (%) = 450 (100, M^+).

HRMS: *m/z* calc. for $C_{28}H_{18}O_2S_2$: 450.0748, found: 450.0746.

5-Acetyl-3,3'-bis(phenylethynyl)-2,2'-bithiophene **(6d)**:

Pure **6d** was obtained after treatment of **5d** (183 mg) with phenylacetylene (0.2 mL), filtration of the warm mixture, CC [petroleum ether (bp 40–60 °C) $CHCl_3$, 1:1] of the filtrate and recrystallization from toluene, as yellow needles; yield: 185 mg (90.7%); mp 193–194 °C.

UV/VIS: λ (lg ε) = 244 (4.41), 252 (4.40), 276 (4.44), 304 (4.54), 398 nm (4.21).

IR: ν = 3098, 3081, 3022 (CH), 2966, 2922 (CH_3), 2199 (C≡C), 1659 (CO), 1491, 1441, 1356, 1271, 856, 839, 759, 753, 738, 687, 592, 545, 525 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.72 (s, 1H, C^4–H), 7.66–7.56 (m, 4H, arom), 7.40–7.36 (m, 6H, arom), 7.35 (d, ^3J = 5.2 Hz, 1H, $C^{5'}$–H), 7.20 (d, ^3J = 5.2 Hz, 1H, $C^{4'}$–H), 2.56 (s, 3H, $COCH_3$).

^{13}C NMR (91 MHz, $CDCl_3$): δ = 190.35 (CO), 145.11, 140.63, 136.97 (arom C), 135.35, 131.59, 131.47, 130.83, 128.82, 128.76, 128.58, 128.52, 126.12 (arom CH), 122.97, 122.87, 121.49, 119.66 (arom C), 97.65, 95.93, 85.54, 84.93 (C≡C), 26.64 ($COCH_3$).

MS (EI): *m/z* (%) = 408 (100, M^+), 364 (25, M^+-COCH_3), 43 (15, $COCH_3^+$).

HRMS: *m/z* calc. for $C_{26}H_{16}OS_2$: 408.0643, found: 408.0643.

5,5'-Dibenzoyl-3,3'-bis[(trimethylsilyl)ethynyl]-2,2'-bithiophene (**6e**):

After the reaction of **5a** (266 mg) with trimethylsilylacetylene (0.2 mL), CC ($CHCl_3$) of the filtrate followed by recrystallization from MeCN gave pure **6e** as yellow needles; yield: 265 mg (94%); mp 219–221 °C.

UV/VIS: λ (lg ε) = 230sh (4.33), 283 (4.51), 333 (3.89), 349 (3.89), 409 (4.40), 431 nm (4.37).

IR: ν = 3045 (CH), 2957, 2900 (CH_3), 2148 (C≡C), 1635 (CO), 1512, 1447, 1387, 1284, 1250, 1180, 1118, 978, 896, 848, 757, 716, 694, 650 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, ^3J = 7.1 Hz, 4H, arom), 7.64 (s, 2H, $C^{4,4'}$–H), 7.59 (t, ^3J = 7.5 Hz, 2H, arom), 7.52 (t, ^3J = 7.5 Hz, 4H, arom), 0.34 [s, 18H, $Si(CH_3)_3$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.39 (CO), 144.46, 140.98, 137.22 (arom C), 137.13, 132.40, 128.90, 128.38 (arom CH), 121.33 (arom C), 105.54, 99.44 (C≡C), −0.59 [$Si(CH_3)_3$].

MS (EI): *m/z* (%) = 566 (40, M^+), 551 (5, M^+-CH_3), 461 (5, $M^+-C_6H_5CO$), 105 (65, $C_6H_5CO^+$), 73 [100, $Si(CH_3)_3^+$].

HRMS: *m/z* calc. for $C_{32}H_{30}O_2S_2Si_2$: 566.1226, found: 566.1223.

5,5'-Diacetyl-3,3'-bis[(trimethylsilyl)ethynyl]-2,2'-bithiophene (**6f**):

After treatment of **5b** (266 mg) with trimethylsilylacetylene (0.2 mL), CC ($CHCl_3$) of the filtrate followed by recrystallization from MeCN gave pure **6f** as yellow crystals; yield: 128 mg (58%); mp 247–248 °C.

UV/VIS: λ (lg ε) = 268 (4.57), 274 (4.58), 380sh (4.18), 396 (4.32), 418 nm (4.26).

IR: ν = 3079 (CH), 2961 (CH_3), 2146 (C≡C), 1662 (CO), 1518, 1389, 1360, 1262, 1180, 1039, 968, 931, 891, 847, 761, 660, 608, 586 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.66 (s, 2H, $C^{4,4'}$–H), 2.55 (s, 6H, $COCH_3$), 0.33 [s, 18H, $Si(CH_3)_3$].

^{13}C NMR (63 MHz, $CDCl_3$): δ = 190.16 (CO), 144.37, 141.93 (arom C), 135.18 (arom CH), 121.54 (arom C), 105.31, 99.43 (C≡C), 26.62 ($COCH_3$), −0.59 [$Si(CH_3)_3$].

MS (EI): *m/z* (%) = 442 (35, M^+), 427 (15, M^+-CH_3), 369 [5, $M^+-Si(CH_3)_3$], 73 [100, $Si(CH_3)_3^+$], 43 (20, $COCH_3^+$).

HRMS: *m/z* calc. for $C_{22}H_{26}O_2S_2Si_2$: 442.0913, found: 442.0911.

Chloro[3,3'-bis(phenylethynyl)-2,2'-bithiophene]bis(triphenylphosphine)rhodium(I) Complexes 7a–d; General Procedure:

To a solution of **6** (0.2 mmol) in deoxygenated benzene (80 mL) was added chlorotris(triphenylphosphine)rhodium(I) (186 mg, 0.2 mmol). The clear solution was heated at 80 °C for approximately 30 min (TLC monitoring). During this time the solution rapidly turned dark green (**7a** and **7c**), purple (**7b**) or blue (**7d**). The solutions of rhodium complexes were used for further reactions. The pure complexes were not isolated.

4,7-Diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophenes 3; General Procedure:

To a freshly prepared solution of complex **7a–c** (0.2 mmol, see above) was added an excess of the corresponding acetylene in one portion at 80 °C. After stirring for approximately 1–4 h at the same temperature, the solution turned brown (TLC monitoring). The mixture was allowed to cool to r.t., the solvent evaporated and the residue was chromatographed on silica gel. The products were purified further by recrystallization from appropriate solvent.

2,9-Dibenzoyl-4,7-diphenylnaphtho[2,1-b:3,4-b']dithiophene (**3a**):

A slow stream of dry acetylene was passed through a solution of **7a** (0.2 mmol, see above) for 10–20 min (TLC monitoring). CC ($CHCl_3$) and recrystallization from toluene gave pure **3a** as yellow needles; yield: 94 mg (78%); mp 278–280 °C.

UV/VIS: λ (lg ε) = 240sh (4.57), 258 (4.69), 330 (4.33), 376sh (4.21), 396 (4.33), 414 nm (4.36).

IR: ν = 3122, 3067, 3022 (CH), 1626 (CO), 1597, 1576, 1533, 1496, 1466, 1443, 1418, 1368, 1284, 1229, 1176, 1110, 910, 839, 718, 710, 705, 689, 673, 649, 562, 534 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.61–7.52 (m, 8H, arom), 7.48 (s, 2H, $C^{3,8}$–H), 7.45–7.33 (m, 12H, arom), 7.24 (s, 2H, $C^{5,6}$–H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 188.33 (CO), 143.50, 141.36, 139.56, 138.53, 137.15, 135.60 (arom C), 135.49, 132.08, 129.22, 129.14, 128.99, 128.58, 128.46 (arom CH), 128.03 (arom C), 127.96 (arom CH).

MS (EI): *m/z* (%) = 600 (75, M^+), 105 (100, $C_6H_5CO^+$), 77 (15, $C_6H_5^+$).

HRMS: *m/z* calc. for $C_{40}H_{24}S_2O_2$: 600.1218, found: 600.1218.

2,9-Diacetyl-4,7-diphenylnaphtho[2,1-b:3,4-b']dithiophene (**3b**):

A slow stream of dry acetylene was passed through a solution of complex **7b** (0.2 mmol, see above) for 10–20 min (TLC monitoring). CC ($CHCl_3$) and recrystallization from toluene gave pure **3b** as light yellow crystals; yield: 65 mg (68%); mp 352–353 °C.

UV/VIS: λ (lg ε) = 266 (4.62), 310 (4.32), 378 (4.33), 396 nm (4.33).

IR: ν = 3142, 3032 (CH), 1656 (CO), 1541, 1361, 1275, 1259, 1234, 1178, 1039, 1021, 933, 856, 828, 773, 761, 702, 607, 589, 539 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.61–7.57 (m, 6H, arom), 7.59 (s, 2H, $C^{3,8}$–H), 7.52–7.47 (m, 4H, arom), 6.97 (s, 2H, $C^{5,6}$–H), 2.19 (s, 6H, $COCH_3$).

^{13}C NMR (91 MHz, $CDCl_3$): δ = 191.46 (CO), 143.69, 141.44, 139.58, 138.62, 135.42 (arom C), 133.71, 129.55, 129.23, 128.56, 128.07 (arom CH), 26.06 ($COCH_3$).

MS (EI): *m/z* (%) = 476 (100, M^+), 461 (10, M^+-CH_3), 390 (25, $M^+-2COCH_3$), 43 (35, $COCH_3^+$).

HRMS: *m/z* calc. for $C_{30}H_{20}O_2S_2$: 476.0905, found: 476.0904.

4,7-Diphenylnaphtho[2,1-b:3,4-b']dithiophene-2,9-dicarbaldehyde (**3c**):

A slow stream of dry acetylene was passed through a solution of complex **7c** for 10–20 min (TLC monitoring). CC ($CHCl_3$) and recrystallization from toluene gave pure **3c** as light yellow crystals; yield: 28 mg (31%); mp 322 °C (dec).

UV/VIS: λ (lg ε) = 260 (4.62), 314 (4.30), 386 (4.31), 404 nm (4.33).

IR: ν = 3118, 3067, 3032 (CH), 2816 (CHO), 1671 (CO), 1540, 1495, 1442, 1420, 1365, 1255, 1223, 1195, 1168, 1123, 1075, 1023, 854, 832, 763, 712, 704, 664, 653, 620, 538, 400 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 9.62 (s, 2H, CHO), 7.61 (s, 2H, $C^{3,8}$–H), 7.61–7.57 (m, 6H, arom), 7.51–7.48 (m, 4H, arom), 7.06 (s, 2H, $C^{5,6}$–H).

^{13}C NMR (91 MHz, $CDCl_3$): δ = 183.65 (CHO), 143.22, 140.97, 139.73, 138.75 (arom C), 137.64 (arom C–H), 135.81 (arom C), 129.41, 129.16, 128.27 (arom C–H), 127.91 (arom C).

MS (EI): *m/z* (%) = 448 (100, M^+), 390 (20, $M^+ - 2CHO$), 314 (10, $M^+ - 2CHO - C_6H_4$).

HRMS: *m/z* calc. for $C_{28}H_{16}O_2S_2$: 448.0592, found: 448.0591.

Dimethyl 2,9-Dibenzoyl-4,7-diphenylnaphtho[2,1-b:3,4-b']bithiophene-5,6-dicarboxylate (**3d**):

Reaction of complex **7a** with dimethyl but-2-ynedioate (142 mg, 1 mmol) for 1 h, CC ($CHCl_3$) and recrystallization from toluene gave pure **3d** as yellow needles; yield: 132 mg (92%); mp 300–301 °C.

UV/VIS: λ (lg ε) = 246sh (4.52), 266 (4.66), 318sh (4.34), 328 (4.36), 386 (4.44), 406 nm (4.48).

IR: ν = 3119, 3057 (CH), 2950 (CH_3), 1734 (CO_2CH_3), 1630 (CO), 1598, 1577, 1529, 1496, 1458, 1370, 1304, 1284, 1261, 1231, 1179, 1114, 1096, 1076, 1030, 982, 929, 878, 846, 768, 718, 700, 650, 581 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.64–7.55 (m, 2H, arom), 7.53–7.35 (m, 16H, arom), 7.33–7.23 (m, 2H, arom), 6.94 (s, 2H, $C^{3,8}$–H), 3.46 (s, 6H, CO_2CH_3).

^{13}C NMR (91 MHz, $CDCl_3$): δ = 188.30 (CO), 168.33 (CO_2CH_3), 141.87, 140.05, 139.77, 137.35, 136.94 (arom C), 135.23 (arom CH), 135.02 (arom C), 132.24 (arom CH), 131.12 (arom C), 129.59 (arom CH), 129.18 (arom C), 129.13, 129.00, 128.81, 128.54 (arom CH), 52.34 (CO_2CH_3).

MS (EI): *m/z* (%) = 716 (100, M^+), 685 (5, M^+-OCH_3), 105 (40, $C_6H_5CO^+$), 77 (35, $C_6H_5^+$).

HRMS: *m/z* calc. for $C_{44}H_{28}S_2O_6$: 716.1327, found: 716.1326.

Dimethyl 2,9-Diacetyl-4,7-diphenylnaphtho[2,1-b:3,4-b']dithiophene-5,6-dicarboxylate (**3e**):

Reaction of complex **7b** with dimethyl but-2-ynedioate (142 mg, 1 mmol) for 1 h, CC (EtOAc) and recrystallization from MeCN gave pure **3e** as light yellow needles; yield: 85 mg (72%); mp 289–291 °C.

UV/VIS: λ (lg ε) = 240sh (4.39), 262sh (4.54), 274 (4.57), 306 (4.39), 316 (4.42), 354sh (4.14), 370 (4.34), 390 nm (4.37).

IR: ν = 3119, 3049 (CH), 2945 (CH_3), 1742 (CO_2CH_3), 1663 (CO), 1538, 1464, 1430, 1362, 1305, 1268, 1222, 1098, 763, 707, 589 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.63–7.58 (m, 6H, arom), 7.49–7.44 (m, 4H, arom), 6.65 (s, 2H, $C^{3,8}$–H), 3.54 (s, 6H, CO_2CH_3), 2.17 (s, 6H, $COCH_3$).

^{13}C NMR (91 MHz, $CDCl_3$): δ = 191.23 (CO), 168.27 (CO_2CH_3), 142.03, 140.17, 137.48, 134.94 (arom C), 133.55 (arom CH), 130.95 (arom C), 130.08, 129.27, 128.88 (arom CH), 52.46 (CO_2CH_3), 26.10 ($COCH_3$).

MS (EI): *m/z* (%) = 592 (100, M^+), 577 (5, M^+-CH_3), 561 (5, M^+-OCH_3), 388 (10, $M^+-2CO_2CH_3-2COCH_3$), 43 (20, $COCH_3^+$).

HRMS: *m/z* calc. for $C_{34}H_{24}O_6S_2$: 592.1014, found: 592.1015.

Dimethyl 2,9-Diformyl-4,7-diphenylnaphtho[2,1-b:3,4-b']dithiophene-5,6-dicarboxylate (**3f**):

Reaction of complex **7c** with dimethyl but-2-ynedioate (142 mg, 1 mmol) for 1 h, CC ($CHCl_3$) and recrystallization from toluene gave pure **3f** as light yellow needles; yield: 77 mg (68%); mp 286 °C (dec).

UV/VIS: λ (lg ε) = 242sh (4.48), 272 (4.62), 318 (4.41), 374 (4.37), 394 nm (4.39).

IR: ν = 3106, 3056, 3000 (CH), 2954 (CH_3), 2832 (CHO), 1743, 1730 (CO_2CH_3), 1680 (CO), 1534, 1438, 1374, 1360, 1303, 1227, 1094, 981, 814, 767, 702, 653, 582 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 9.57 (s, 2H, CHO), 7.62–7.54 (m, 6H, arom), 7.46–7.41 (m, 4H, arom), 6.71 (s, 2H, $C^{3,8}$–H), 3.53 (s, 6H, CO_2CH_3).

^{13}C NMR (91 MHz, $CDCl_3$): δ = 183.40 (CHO), 168.15 (CO_2CH_3), 141.32, 140.22, 139.58, 137.56 (arom C), 137.50 (arom CH), 135.25, 131.32 (arom C), 129.80, 129.44 (arom CH), 129.07 (arom C), 129.03 (arom CH), 52.46 (CO_2CH_3).

MS (EI): *m/z* (%) = 564 (100, M^+), 535 (5, M^+-CHO), 533 (20, M^+-OCH_3), 446 (5, $M^+-2CO_2CH_3$), 417 (5, $M^+-2CO_2CH_3-CHO$), 388 (10, $M^+-2CO_2CH_3-2CHO$).

HRMS: *m/z* calc. for $C_{32}H_{20}O_6S_2$: 564.0701, found: 564.0701.

2,9-Dibenzoyl-4,5,6,7-tetraphenylnaphtho[2,1-b:3,4-b']dithiophene (**3g**):

Reaction of complex **7a** with diphenylacetylene (178 mg, 1 mmol) for 4 h, CC ($CHCl_3$) and recrystallization from benzene gave pure **3g** as yellow cubes; yield: 115 mg (77%), mp > 350 °C.

UV/VIS: λ (lg ε) = 244sh (4.61), 264 (4.77), 334 (4.37), 398 (4.40), 416 nm (4.43).

IR: ν = 3136, 3056, 3023 (CH), 1630 (CO), 1598, 1576, 1526, 1495, 1453, 1442, 1398, 1353, 1305, 1285, 1215, 1178, 1112, 1078, 1025, 1001, 853, 758, 717, 698, 657, 561 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.59–7.46 (m, 6H, arom), 7.42–7.34 (m, 4H, arom), 7.19–7.05 (m, 8H, arom), 7.00–6.91 (m, 2H, arom), 6.89 (s, 2H, $C^{3,8}$–H), 6.85–6.80 (m, 6H, arom), 6.77–6.71 (m, 4H, arom).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 188.62 (CO), 141.81, 141.09, 140.84, 139.92, 138.95, 138.05, 137.27 (arom C), 136.00 (arom CH), 135.87 (arom C), 131.97, 131.07, 130.86, 129.03, 128.51, 128.44 (arom CH), 128.13 (arom C), 127.23, 126.60, 125.46 (arom CH).

MS (EI): *m/z* (%) = 752 (100, M^+), 105 (30, $C_6H_5CO^+$).

HRMS: calc. for $C_{52}H_{32}S_2O_2$: 752.1844, found: 752.1841.

2,9-Diacetyl-4,5,6,7-tetraphenylnaphtho[2,1-b:3,4-b']dithiophene (**3h**):

Reaction of complex **7b** with diphenylacetylene (178 mg, 1 mmol) for 2 h, CC ($CHCl_3$) and recrystallization from toluene gave pure **3h** as yellow needles; yield: 108 mg (86%); mp 332–333 °C.

UV/VIS: λ (lg ε) = 242sh (4.49), 270 (4.71), 314 (4.39), 380 (4.31), 400 nm (4.32).

IR: ν = 3137, 3057, 3024 (CH), 2922 (CH_3), 1659 (CO), 1535, 1496, 1455, 1441, 1354, 1271, 1219, 919, 852, 768, 761, 703, 587, 561 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.35–7.31 (m, 6H, arom), 7.26–7.22 (m, 4H, arom), 6.92–6.83 (m, 10H, arom), 6.58 (s, 2H, $C^{3,8}$–H), 2.12 (s, 6H, $COCH_3$).

^{13}C NMR (91 MHz, $CDCl_3$): δ = 191.56 (CO), 142.19, 141.05, 140.62, 139.80, 138.92, 137.99, 135.60 (arom C), 134.31, 131.15, 131.07, 128.64 (arom CH), 128.07 (arom C), 127.30, 126.67, 125.58 (arom CH), 26.06 ($COCH_3$).

MS (EI): *m/z* (%) = 628 (100, M^+), 542 (5, $M^+-2COCH_3$), 465 (5, $M^+-2COCH_3-C_6H_5$), 388 (5, $M^+-2COCH_3-2C_6H_5$), 43 (25, $COCH_3^+$).

HRMS: *m/z* calc. for $C_{42}H_{28}S_2O_2$: 628.1531, found: 628.1528.

4,5,6,7-Tetraphenylnaphtho[2,1-b:3,4-b']dithiophene-2,9-dicarbaldehyde (**3i**):

Reaction of complex **7c** with diphenylacetylene (178 mg, 1 mmol) for 4 h, CC ($CHCl_3$, second fraction, R_f 0.25) and recrystallization from toluene gave **3i** as yellow crystals; yield: 5–8 mg (ca 5%); mp > 350 °C.

UV/VIS: λ (lg ε) = 234 (4.55), 268 (4.70), 316 (4.37), 388 (4.17), 406 nm (4.31).

IR: ν = 3123, 3078, 3056, 3022 (CH), 1667 (CO), 1533, 1495, 1443, 1350, 1167, 1127, 772, 762, 700, 661, 559 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 9.53 (s, 2H, CHO), 7.33–7.17 (m, 10H, arom), 6.90–6.80 (m, 10H, arom), 6.63 (s, 2H, $C^{3,8}$–H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 183.61 (CHO), 141.76, 141.15, 140.62, 139.72, 139.11 (arom C), 138.39 (arom CH), 138.24, 136.08 (arom C), 131.06, 130.07, 128.84, 127.46, 126.72, 125.67 (arom C–H).

MS (EI): *m/z* (%) = 600 (100, M^+).

HRMS: *m/z* calc. for $C_{40}H_{24}S_2O_2$: 600.1218, found: 600.1218.

4,5,6,7-Tetraphenylnaphtho[2,1-b:3,4-b']dithiophene-2-carbaldehyde (**3j**):

The first fraction (R_f 0.58) from the CC of the above reaction was the major product and was identified as **3j**. Recrystallization from toluene afforded light yellow crystals; yield: 28 mg (25%); mp 349 °C.

UV/VIS: λ (lg ε) = 252sh (4.61), 268 (4.68), 304 (4.40), 370 (4.27), 384 nm (4.24).

IR: ν = 3054, 3021 (CH), 2823 (CHO), 1669 (CO), 1600, 1529, 1496, 1441, 1356, 1288, 1245, 1175, 1130, 1106, 1069, 1024, 844, 760, 698, 669, 644, 561 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.50 (s, 1H, CHO), 7.31–7.15 (m, 10H, arom), 7.11 (d, ^3J = 5.6 Hz, 1H, C^9–H), 6.91–6.78 (m, 10H, arom), 6.63 (s, 1H, C^3–H), 6.14 (d, ^3J = 5.6 Hz, 1H, C^8–H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 183.79 (CHO), 142.22, 142.19, 140.46, 140.25, 140.16, 140.13 (arom C), 139.18 (arom CH), 138.51, 138.25, 137.84, 137.06, 134.00, 133.22 (arom C), 131.23, 131.18, 129.06, 128.74, 128.33 (arom CH), 127.87, 127.80 (arom C), 127.23, 127.07, 126.64, 126.58, 125.48, 125.42, 124.03 (arom CH).

MS (EI): *m/z* (%) = 572 (100, M^+), 105 (70, $C_8H_9^+$), 77 (10, $C_6H_5^+$).

HRMS: *m/z* calc. for $C_{39}H_{24}OS_2$: 572.1269, found: 572.1268.

4,6-Diphenylbenzo[2,1-*b*:3,4-*b'*:5,6-*c''*]trithiophenes 2a–d; General Procedure:

To a freshly prepared solution of complex **7a–d** (0.2 mmol, see above) was added an excess (64 mg, 2 mmol) of sulfur in one portion at 80 °C. The mixture turned brown after stirring for ca 30 min (TLC monitoring) at the same temperature. The mixture was allowed to cool to r.t., evaporated and chromatographed on a silica gel column.

2,8-Dibenzoyl-4,6-diphenylbenzo[2,1-b:3,4-b':5,6-c'']trithiophene (**2a**):

The product was purified by CC ($CHCl_3$) and recrystallized from toluene to give pure **2a** as orange needles; yield: 92 mg (75.9%); mp 278–280°C.

UV/VIS: λ (lg ε) = 230 (4.60), 258sh (4.49), 268 (4.50), 349 (4.46), 449sh (4.23), 463 nm (4.26).

IR: ν = 3056 (CH), 1626 (CO), 1596, 1576, 1513, 1447, 1420, 1383, 1284, 1202, 1175, 1115, 1072, 1028, 1000, 854, 766, 744, 713, 705, 653 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3/CS_2$ 1:1): δ = 7.67–7.65 (m, 2H, arom), 7.65–7.63 (m, 2H, arom), 7.60–7.54 (m, 6H, arom), 7.57 (s, 2H, $C^{3,7}$–H), 7.52–7.36 (m, 10H, arom).

^{13}C NMR (75 MHz, $CDCl_3/CS_2$ 1:1): δ = 186.81 (CO), 142.02, 137.02, 136.89, 134.91, 133.58, 132.57 (arom C), 131.90, 131.24, 130.30 (arom CH), 129.19 (arom C), 128.82, 128.68, 128.67, 128.06 (arom CH).

MS (EI): *m/z* (%) = 606 (20, M^+), 529 (10, $M^+-C_6H_5$), 501 (5, $M^+-C_6H_5-CO$), 105 (100, $C_6H_5CO^+$), 77 (20, $C_6H_5^+$).

HRMS: *m/z* calc. for $C_{38}H_{22}S_3O_2$: 606.0782, found: 606.0780.

2,8-Diacetyl-4,6-diphenylbenzo[2,1-b:3,4-b':5,6-c'']trithiophene (**2b**):

The product **2b** was purified by CC ($CHCl_3$) and recrystallized from toluene to afford as orange crystals; yield: 86 mg (89.2%); mp 296°C.

UV/VIS: λ (lg ε) = 238 (4.43), 254 (4.52), 266sh (4.46), 334 (4.35), 444 nm (4.17).

IR: ν = 3114, 3047 (CH), 2922 (CH_3), 1651 (CO), 1516, 1447, 1359, 1270, 1206, 1178, 1152, 1074, 1041, 861, 767, 738, 702, 630, 607, 592 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.69–7.63 (m, 4H, arom), 7.61–7.56 (m, 6H, arom), 7.58 (s, 2H, $C^{3,7}$–H), 2.35 (s, 6H, $COCH_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.85 (CO), 142.02, 137.03, 135.14, 134.02, 132.86 (arom C), 130.75, 129.40, 129.24, 129.00 (arom CH), 26.33 ($COCH_3$).

MS (EI): *m/z* (%) = 482 (100, M^+), 439 (5, M^+-COCH_3), 396 (15, $M^+-2COCH_3$), 43 (10, $COCH_3^+$).

HRMS: *m/z* calc. for $C_{28}H_{18}S_3O_2$: 482.0469, found: 482.0470.

4,6-Diphenylbenzo[2,1-b:3,4-b':5,6-c'']trithiophene-2,8-dicarbaldehyde (**2c**):

The product was purified by CC ($CHCl_3$) and recrystallized from toluene to give pure **2c** as orange needles; yield: 68 mg (68%); mp 303–304°C (dec.).

UV/VIS: λ (lg ε) = 253 (4.56), 266sh (4.49), 340 (4.41), 455 nm (4.19).

IR: ν = 3056 (CH), 2823 (CHO), 1676 (CO), 1516, 1447, 1379, 1226, 1158, 1121, 860, 765, 749, 704, 658, 485 cm^{-1}.

^1H NMR (250 MHz, T = 323 K $CDCl_3$): δ = 9.78 (s, 2H, CHO), 7.68 (s, 2H, $C^{3,7}$–H), 7.67–7.61 (m, 4H, arom), 7.60–7.54 (m, 6H, arom).

^{13}C NMR (63 MHz, T = 323 K, $CDCl_3$): δ = 182.98 (CHO), 142.41, 137.75, 137.49, 135.05, 133.83, 133.30 (arom C), 132.89, 130.66, 129.39, 129.20 (arom CH).

MS (EI): *m/z* (%) = 454 (100, M^+), 396 (10, M^+-2CHO).

HRMS: *m/z* calc. for $C_{26}H_{14}S_3O_2$: 454.0156, found: 454.0157.

2-Acetyl-4,6-diphenylbenzo[2,1-b:3,4-b':5,6-c'']trithiophene (**2d**):

Purification of the product by CC [petroleum ether (bp 40–60°C, $CHCl_3$, 1:1] and recrystallization from nitromethane gave orange needles; yield: 55 mg (63%); mp 188–190°C.

UV/VIS: λ (lg ε) = 246 (4.46), 330 (4.15), 344sh (4.08), 416 nm (4.16).

IR: ν = 3054, 3022 (CH), 2967, 2922 (CH_3), 1652 (CO), 1512, 1419, 1270, 1145, 834, 756, 724, 718, 696 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 7.68–7.61 (m, 4H, arom), 7.59 (s, 1H, C^3–H), 7.57–7.50 (m, 6H, arom), 7.24 (d, ^3J = 5.3 Hz, 1H, C^8–H), 7.09 (d, ^3J = 5.3 Hz, 1H, C^7–H), 2.33 (s, 3H, $COCH_3$).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 190.82 (CO), 140.61, 138.36, 134.82, 134.45, 134.41, 134.13, 133.17, 131.32 (arom C), 130.84, 130.78 (arom CH), 130.40 (arom C), 129.77 (arom C–H), 129.62 (arom C), 128.96, 128.87, 128.75, 128.61, 125.21, 124.60 (arom CH), 26.14 ($COCH_3$).

MS (EI): *m/z* (%) = 440 (100, M^+), 396 (20, $M^+-H-COCH_3$), 364 (10, $M^+-H-COCH_3-S$).

HRMS: *m/z* calc. for $C_{26}H_{16}S_3O$: 440.0363, found: 440.0363.

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