Efficient One-Pot Synthesis of Dithieno(dibenzothieno)-Fused Cycloheptanones, Tropones, and Cyclooctanones

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The reactions of α,*β*-unsaturated amide/triflic anhydride complexes (generated in situ from the corresponding amides and triflic anhydride) with dithiophenes and dithienylmethanes proceed as tandem alkylation−Vilsmeier−Haack acylation to form dithieno- and dibenzothieno-fused cycloheptanones and cyclooctanones in moderate to good yields. The reactions of 2-bromo-*N*,*N*-dimethylacrylamide/triflic anhydride complex allow preparation of tropones in a simple one-pot procedure. The reaction of 2,2-dibenzothienylmethane with dimethylacrylamide/triflic anhydride complex proceeds unusually to afford dimethylaminonaphthalene in addition to the predictable fused cyclooctanone.

Introduction

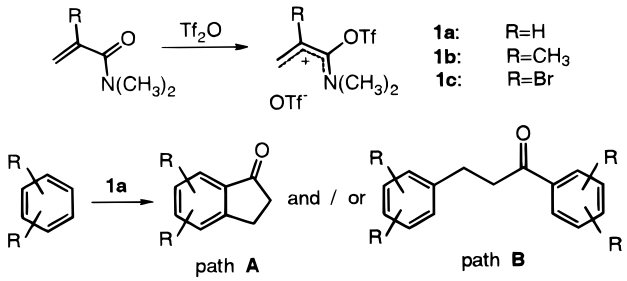
Application of triflic anhydride as a mild and effective activation reagent in Vilsmeier−Haack reaction is a subject of increasing interest.[1−4] In our previous papers,[5−8] we have reported the reaction of the *N*,*N*-dimethylacrylamide/triflic anhydride complex **1a** with electron-rich aromatics and heteroaromatics yielding the corresponding fused cyclopentanones and/or 1,3-diaryl(dihetaryl)-propanones.

The iminium triflates **1a**−**c** have two electrophilic centers—an iminium moiety and an activated double bond. The mechanism envisioned for the reaction of **1a** involves the initial alkylation of aromatic substrate followed by either intra- (path A) or intermolecular (path B) Vilsmeier acylation (Scheme 1).[5]

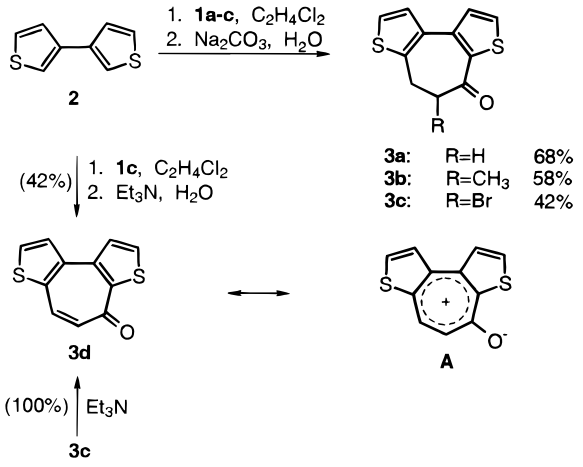
In this paper we explore the possibility to realize the third pathway for this tandem reaction. It is intramolecular (like the path A) but binds two different aromatic rings (like the path B). We suggested that the use of appropriately substituted and activated bis-aromatic compounds with different bridge lengths would provide an efficient and concise route to a number of fused seven- and eight-membered cyclic ketones. One can tune the reaction by modifying the structure and properties of the aromatic nuclei.

The present paper reports our investigation toward the synthesis of dithieno-fused seven- and eight-membered ring ketones by reaction of **1a**−**c** with 3,3′-dithiophenes and dibenzo[*b*]thiophenes.

Scheme 1



Scheme 2



Results and Discussion

We have found that **1a** smoothly reacts with 3,3-dithiophene (**2**) to give rise to the dithieno-fused cycloheptanone **3a** in 68% yield (Scheme 2). To study the behavior of other α,*β*-unsaturated amide/triflic anhydride complexes in seven-membered ring closure, we have carried out the reactions of **1b** and **1c** with **2** and obtained the corresponding fused cycloheptanones **3b** and **3c** in moderate yields. Notably, fused ketones **3a**−**c** have unusual C═O absorption bands in their IR spectra at 1630−1640 cm^{-1} which could be explained by the influence of electron-donating sulfur atom.

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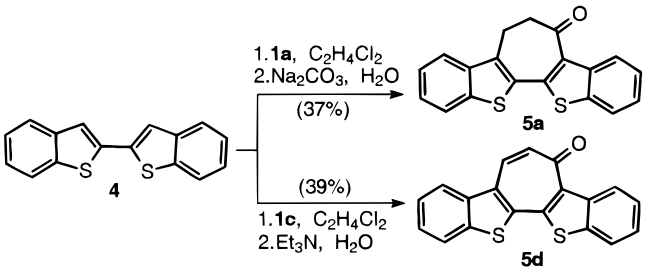
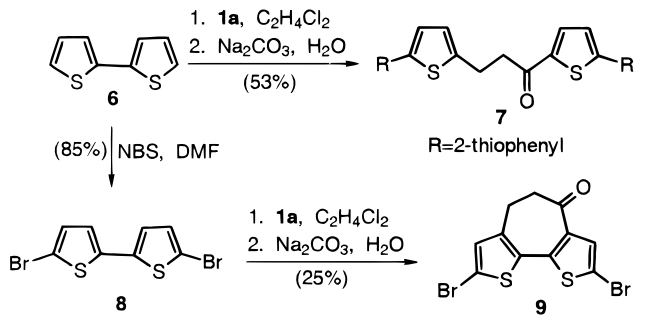
Scheme 3



Scheme 4



We have found that 2,2-dibenzo[*b*]thiophene (**4**) reacts with **1a** similarly to produce the corresponding fused cycloheptanone **5a** in 45% yield (Scheme 3). Our attempts to carry out the reaction of **4** with **1b** were unsuccessful due to the lower reactivity of **1b** compared to the reactivity of **1a**.[5]

The reactions of **1c** with **2** or **4** permit preparation of dithieno-fused tropone **3d** and dibenzo[*b*]thieno-fused tropone **5d** after quenching with aqueous Et_3N (Schemes 2, 3). It is also possible to convert **3c** to **3d** quantitatively by treatment with Et_3N in $CHCl_3$. The known literature approach to this class of fused systems involves complicated multistep synthesis with the overall yield near 1.5%.[9]

Tropones **3d** and **5d** were isolated as high-melting and far more polar (according to the TLC data) substances than **3a**−**c** and **5a**. This could be explained by considerable contribution of dipole resonance structure **A** (Scheme 2).

2,2-Dithiophene **6** reacts with **1a** to yield only the product of intermolecular reaction **7**. However, 5,5′-dibromo-2,2′-dithiophene **8** (easily obtained from **6** by direct bromination with NBS[10]) was found to react with **1a** giving rise to the cyclic ketone **9** (although in low yields and with a considerable recovery of the starting dibromide) (Scheme 4). Attempts to improve the yield of **9** by the variation of solvent, stoichiometry, and reaction time were unsuccessful.

To perform the eight-membered ring closure, two appropriate substrates—3,3-dithienylmethane (**10**) and 2,2-dibenzo[*b*]thienylmethane (**12**)—were synthesized and tested under the standard reaction conditions. The starting materials **10** and **12** were prepared by TMSI[11] reduction of diarylmethanols **10a** and **12a** in 62% and 31% yields, respectively. In the case of **12a**, a considerable amount of dimeric byproduct[11] **12b** was formed (Scheme 5). The methanols **10a** and **12a** were easily prepared from the corresponding aryllithium compounds and ethyl formate.

It was found that **10** reacts cleanly with **1a** and **1c** to afford the corresponding fused cyclooctanones **11a** and **11c** in moderate yields (Scheme 6).

We have also studied the reaction of **12** with **1a**. Surprisingly, naphthothiophene derivative **14** was isolated along with the desired eight-membered cyclic ketone **13** (Scheme 7). The formation of **14** proceeds via the Vilsmeier cyclization into the 4-position of the benzothiophene ring followed by an acid-catalyzed isomerization to the aromatic amine. In both cases the leaving group is OTf, but iminium salt B is stable under the reaction conditions and converts to the ketone **13** after quenching with base whereas the benzothiophene intermediate **C** undergoes the isomerization to the naphthalene system having greater aromatic delocalization energy (Scheme 7).

To test this supposition, we have investigated the behavior of 2-methylbenzo[*b*]thiophene **15** in the reaction with complex **1a**. Analogously, the product of cyclization into the benzene ring, dimethylamine **17**, was isolated in addition to the intermolecular reaction product **16** (Scheme 8). The reaction pathway and the yield of each product depend on the reaction conditions such as dilution and molar ratio of **15** and **1a**. It was found that yields of both **16** and **17** are in the range of 10−25%, with the total yield 34−36%.

We have also attempted to prepare a nine-membered cyclic ketone from 1,2-di(3-thieno)ethane **20**. However, our attempts were unsuccessful; monitoring of the reaction mixture by TLC showed only formation of numerous oligomers (Scheme 9).

Conclusion

In summary, we have studied the reactions of several α,*β*-unsaturated amide/triflic anhydride complexes **1a**−**c** with dithiophenes and dithienylmethanes. It was demonstrated that dithiophene- and dibenzothiophene-fused cycloheptanones, tropones, and cyclooctanones are easily prepared by this method in moderate to good yields. In addition to the expected products 2-alkyl-substituted benzothiophenes and 2,2-dibenzothienylmethane afforded dimethylaminonaphthalenes resulting from cyclization into the 4-position followed by acid-catalyzed isomerization of the benzothiophene aromatic system to the naphthalene aromatic system.

Experimental Section

Melting points were determined in sealed capillaries and are uncorrected. Column chromatography was performed on silica gel (63−200 mesh, Merck). All solvents were dried and distilled according to the standard procedures. Triflic anhydride was prepared according to the literature procedure[12] from trifluoromethanesulfonic acid (Merck). 5,5′-Dibromo-2,2′-dithiophene was synthesized from 2,2′-dithiophene by direct bromination with NBS[10] in 85% yield. 2-Methylbenzo[*b*]-thiophene and 2,2′-dibenzo[*b*]thiophene were synthesized from benzo[*b*]thienyllithium under known procedures.[13] 1,2-Di(3-thieno)ethane was prepared from 3-(bromomethyl)thiophene.[14]

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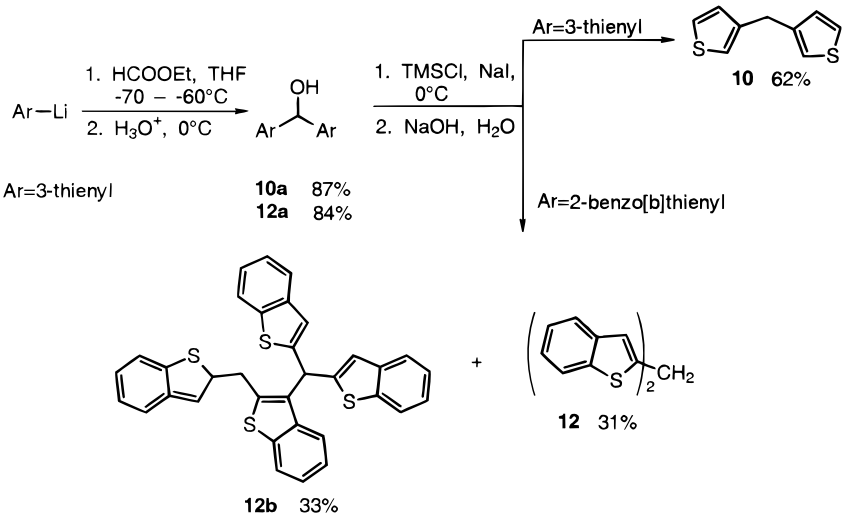
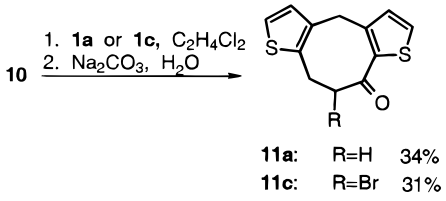
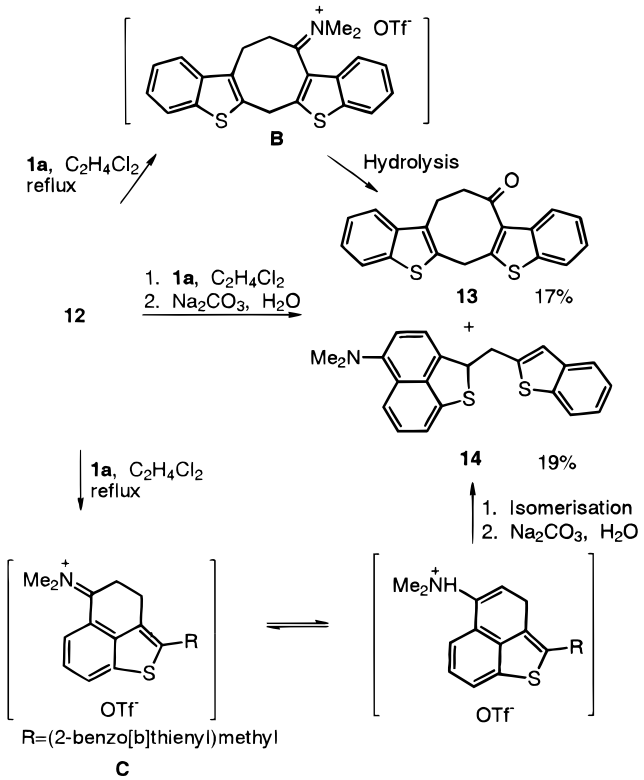
Scheme 5



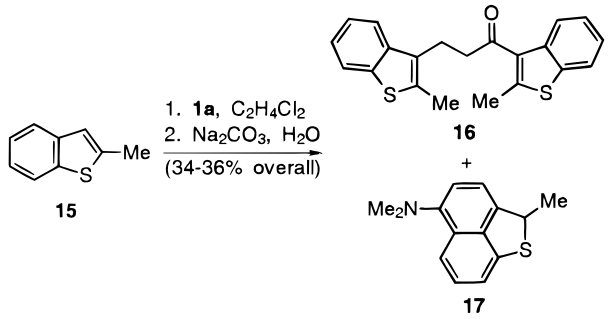
Scheme 6



Scheme 7



Scheme 8



Organolithium compounds were prepared according to the literature techniques.[13]

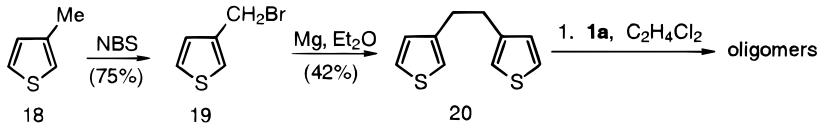
Preparation of Diarylmethanols. A solution of organolithium compound (60 mmol) in THF[13] was cooled to −70 °C, and a solution of the ethyl formate (30 mmol) in THF (10 mL) was added dropwise while maintaining the temperature between −70 and −60 °C. The mixture was then allowed to warm slowly (over ∼1 h) to 0 °C. The resulting mixture was hydrolyzed with 10% aq HCl (10 mL, 27 mmol) with cooling below 0 °C. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$ (2 × 10 mL). The combined solutions were dried with Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on a short silica gel column (benzene−ether 4:1) to yield pale-yellow viscous oils, which solidified upon standing.

Di(3-thienyl)methanol (10a). Yield 87%, mp 61−62 °C. IR (Nujol) 3480 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.19 (dd, 2H, J = 5.0, 3.0 Hz), 7.07 (m, 2H), 6.93 (dd, 2H, J = 5.0, 1.3 Hz), 5.76 (s, 1H), 3.10 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 144.71 (2C), 126.26 (2C), 125.94 (2C), 121.50 (2C), 68.67. Anal. Calcd for $C_9H_8OS_2$: C, 55.07; H, 4.11. Found: C, 54.85; H, 4.27.

Di(benzo[*b*]thiophen-2-yl)methanol (12a). Yield 84%, mp 133−136 °C. IR (Nujol) 3490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.79 (d, 2H, J = 7.8 Hz), 7.70 (d, 2H, J = 7.8 Hz), 7.37−7.29 (m, 4H), 7.25 (s, 2H), 6.40 (s, 1H), 3.16 (br.s, 1H); ^{13}C NMR ($CDCl_3$) δ 146.82 (2C), 139.79 (2C), 139.19 (2C), 124.49 (2C), 124.36 (2C), 123.77 (2C), 122.45 (2C), 121.69 (2C), 69.49. Anal. Calcd for $C_{17}H_{12}OS_2$: C, 68.89; H, 4.08. Found: C, 68.50; H, 4.00.

Reduction of Diarylmethanols by TMSI.[11] To a well-stirred solution of chlorotrimethylsilane (10.9 g, 100 mmol) in anhydrous CH_3CN (20 mL) was added NaI (15.0 g, 100 mmol) in one portion. The resulting slurry was stirred for 20 min at 0 °C, and then a solution of corresponding diarylmethanol (20 mmol) in CH_3CN (20 mL) was added dropwise over 30 min to maintain the reaction temperature below 10 °C. The reaction mixture was quenched with aqueous NaOH (3 g in 15 mL), extracted with ethyl acetate (2 × 40 mL), washed with a solution of $Na_2S_2O_3 \cdot 5H_2O$ (11.2 g in 50 mL), and dried over Na_2SO_4. Organic solvents were removed in vacuo, brown residue was purified by column chromatography (hexane) to yield the pure diarylmethanes as a white solid (**12**) or pale-yellow oil which solidified upon standing (**10**). In the case of **12a**, a considerable amount of dimeric product[11] **12b** was successively isolated by column chromatography.

Scheme 9



3-(3-Thienylmethyl)thiophene (10). Yield 62%, mp 35−36 °C. ^{1}H NMR ($CDCl_3$) δ 7.38 (m, 2H), 7.09 (m, 4H), 4.14 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 140.75 (2C), 128.21 (2C), 125.42 (2C), 121.00 (2C), 30.89. Anal. Calcd for $C_9H_8S_2$: C, 59.96; H, 4.47. Found: C, 59.68; H, 4.26.

2-(Benzo[*b*]thiophen-2-ylmethyl)benzo[*b*]thiophene (12). Yield 31%, mp 134−136 °C. ^{1}H NMR ($CDCl_3$) δ 7.79 (d, 2H, J = 7.8 Hz), 7.72 (d, 2H, J = 7.8 Hz), 7.36 (dd, 2H, J = 7.8, 7.6 Hz), 7.30 (dd, 2H, J = 7.8, 7.6 Hz), 7.18 (s, 2H), 4.51 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 142.99 (2C), 139.83 (4C), 124.23 (2C), 123.93 (2C), 123.15 (2C), 122.20 (4C), 31.94. Anal. Calcd for $C_{17}H_{12}S_2$: C, 72.82; H, 4.31. Found: C, 72.76; H, 4.45.

2-(Benzo[*b*]thiophen-2-ylmethyl)-3-[di(benzo[*b*]thiophen-2-yl)methyl]-1-benzo[*b*]thiophene (12b). Yield 33%, mp 201−203 °C. ^{1}H NMR ($CDCl_3$) δ 7.81 (d, 1H, J = 8.2 Hz), 7.76−7.70 (m, 3H), 7.62 (dd, 2H, J = 7.6, 1.6 Hz), 7.56 (dd, 1H, J = 7.6, 1.8 Hz), 7.34−7.24 (m, 9H), 7.22 (s, 2H), 7.05 (s, 1H), 6.52 (s, 1H), 4.54 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 145.15 (2C), 142.28, 140.24, 139.82 (2C), 139.77, 139.63, 139.36 (2C), 138.74, 138.70, 131.55, 124.28 (2C), 124.20 (4C), 124.14, 123.92, 123.43(2C), 123.34, 123.27 (2C), 123.14, 122.62, 122.37, 122.17 (2C), 122.13, 41.94, 30.17. Anal. Calcd for $C_{34}H_{22}S_4$: C, 73.08; H, 3.97. Found: C, 72.79; H, 4.08.

General Procedure for Cyclic Ketone Formation. A solution of α,β-unsaturated amide (8.5 mmol) in anhydrous $C_2H_4Cl_2$ (20 mL) was cooled to 0 °C. Triflic anhydride (2.4 g, 8.5 mmol) in $C_2H_4Cl_2$ (10 mL) was added dropwise over a period of 10 min, and then the corresponding thiophene (8.5 mmol) in $C_2H_4Cl_2$ (10 mL) was added. The reaction mixture was refluxed 0.5−8 h and then was added to a mixture of Et_2O and aqueous Na_2CO_3 and stirred for an additional 1 h. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 20 mL). The organic solvents were removed in vacuo. The residue was purified by column chromatography (silica gel, benzene for **3a**−**c**, **5a**, **5c**, **9**, **11a**, **11c**, **13**, **14**, **16**, **17**; hexane/diethyl ether 4:1 for **7**; benzene/diethyl ether 3:1 for **3d**, **5d**) to afford pure cyclic ketone and some of the unreacted aromatic substrate.

5,6-Dihydro-4*H*-thieno[3′,2′:3,4]cyclohepta[1,2-*b*]thiophen-4-one (3a). Yield 68% (85%),[15] mp 50−51 °C. IR (Nujol) 1635 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.50 (d, 1H, J = 5.0 Hz), 7.15 (d, 1H, J = 4.9 Hz), 7.13 (d, 1H, J = 5.0 Hz), 6.97 (d, 1H, J = 4.9 Hz), 2.95−2.90 (m, 2H), 2.81−2.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 192.38, 140.42, 139.19, 138.12, 133.45, 132.50, 128.34, 127.46, 121.54, 40.96, 21.83. Anal. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66. Found: C, 59.54; H, 3.40.

5-Methyl-5,6-dihydro-4*H*-thieno[3′,2′:3,4]cyclohepta[1,2-*b*]thiophen-4-one (3b). Yield 58% (79%),[15] mp 49−50 °C. IR (Nujol) 1635 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.55 (d, 1H, J = 5.0 Hz), 7.23 (d, 2H, J = 5.0 Hz), 7.05 (d, 1H, J = 5.0 Hz), 3.04−3.87 (m, 3H), 1.17 (d, 3H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 195.02, 139.13, 138.75, 138.29, 133.53, 132.64, 128.30, 127.39, 121.86, 44.07, 29.37, 15.12. Anal. Calcd for $C_{12}H_{10}OS_2$: C, 61.51; H, 4.30. Found: C, 62.02; H, 4.48.

5-Bromo-5,6-dihydro-4*H*-thieno[3′,2′:3,4]cyclohepta[1,2-*b*]thiophen-4-one (3c). Yield 42% (66%),[15] mp 119−121 °C. IR (Nujol) 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.73 (d, 1H, J = 5.0 Hz), 7.36 (d, 1H, J = 5.0 Hz), 7.34 (d, 1H, J = 4.9 Hz), 7.22 (d, 1H, J = 4.9 Hz), 4.88 (dd, 1H, J = 6.8, 1.8 Hz), 3.54 (dd, 1H, J = 16.5, 1.8 Hz), 3.43 (dd, 1H, J = 16.5, 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 186.13, 139.52, 137.04, 135.84, 135.62, 133.65, 128.75, 127.82, 123.17, 50.70, 30.55. Anal. Calcd for $C_{11}H_7BrOS_2$: C, 44.16; H, 2.36. Found: C, 44.70; H, 2.52.

4*H*-Thieno[3′,2′:3,4]cyclohepta[1,2-*b*]thiophen-4-one (3d). Method A. The reaction mixture obtained under the general procedure from 2-bromo-*N*,*N*-dimethylacrylamide (8.5 mmol), triflic anhydride (8.5 mmol), and **2** (8.5 mmol) was poured into the aqueous Et_3N (20 mmol) and stirred overnight. The product was isolated according to general procedure. Yield 42% (66%).[15] **Method B. 3c** (4 mmol) was dissolved in $CHCl_3$ (10 mL) and then aqueous Et_3N (10 mmol) was added, and the mixture was stirred for an additional 5 h. The organic layer was separated, dried over Na_2SO_4, and solvent was removed in vacuo to afford pure **3d**, yield 100%, mp 172 °C. IR (Nujol) 1575, 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.81 (d, 1H, J = 5.3 Hz), 7.74 (d, 1H, J = 5.3 Hz), 7.72 (d, 1H, J = 5.3 Hz), 7.68 (d, 1H, J = 12.2 Hz), 7.66 (d, 1H, J = 5.3 Hz), 6.86 (d, 1H, J = 12.2 Hz); ^{13}C NMR ($CDCl_3$) δ 180.86, 147.62, 138.55, 137.68, 136.70, 134.14, 131.96, 129.75, 128.17, 128.09, 127.12. Anal. Calcd for $C_{11}H_6OS_2$: C, 60.53; H, 2.77. Found: C, 60.20; H, 3.16.

6,7-Dihydro-5*H*-benzo[*b*]thieno[3′,2′:6,7]cyclohepta[1,2-*b*]benzo[*b*]thiophen-5-one (5a). Yield 37% (74%),[15] mp 177−179 °C. IR (Nujol) 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.79 (d, 1H, J = 8.0 Hz), 7.80−7.70 (m, 3H), 7.48−7.34 (m, 4H), 3.20−3.16 (m, 2H), 3.06−3.02 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 195.49, 146.63, 139.55, 139.53, 138.92, 137.64, 137.40, 131.83, 129.55, 126.49, 126.18, 126.17, 125.67, 124.93, 122.52, 122.46, 121.26, 42.47, 20.81. Anal. Calcd for $C_{19}H_{12}OS_2$: C, 71.22; H, 3.77. Found: C, 71.02; H, 4.01.

5*H*-Benzo[*b*]thieno[3′,2′:6,7]cyclohepta[1,2-*b*][1]benzothiophen-5-one (5d). The reaction mixture obtained under the general procedure from 2-bromo-*N*,*N*-dimethylacrylamide (8.5 mmol), triflic anhydride (8.5 mmol), and **4** (8.5 mmol) was poured into aqueous Et_3N (20 mmol) and stirred overnight. The product was isolated according to the general procedure. Yield 39% (68%),[15] mp 251−254 °C. IR (Nujol) 1585, 1615 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.29 (d, 1H, J = 7.8 Hz), 8.05 (m, 1H), 7.92 (d, 1H, J = 12.5 Hz), 7.88−7.74 (m, 2H), 7.57−7.48 (m, 3H), 7.38−7.30 (m, 1H), 7.23 (d, 1H, J = 12.5 Hz); ^{13}C NMR ($CDCl_3$) δ 183.11, 151.83, 139.51, 138.31, 138.16, 135.26, 131.71, 127.71, 127.52, 127.18, 126.68, 126.20, 125.75, 124.90, 123.70, 122.38, 122.18, 121.37, 121.12. Anal. Calcd for $C_{19}H_{10}OS_2$: C, 71.67; H, 3.17. Found: C, 71.27; H, 3.09.

1,3-Bis[5-(2-thienyl)-2-thienyl]-1-propanone (7). Yield 53% (84%),[15] mp 141−142 °C. IR (Nujol) 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.60 (d, 1H, J = 4.0 Hz), 7.33−7.30 (m, 2H), 7.16 (dd, 1H, J = 5.1, 1.2 Hz), 7.15 (d, 1H, J = 4.0 Hz), 7.09 (dd, 1H, J = 3.6, 1.2 Hz), 7.05 (dd, 1H, J = 5.0, 3.9 Hz), 6.98 (dd, 1H, J = 5.0, 3.6 Hz), 6.97 (d, 1H, J = 3.6 Hz), 6.80 (d, 1H, J = 3.6 Hz), 3.26 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 190.90, 145.74, 142.82, 141.67, 137.56, 136.23, 135.48, 132.76, 128.19, 127.65, 126.50, 125.64, 125.54, 124.12, 123.92, 123.45, 123.22, 40.48, 24.65. Anal. Calcd for $C_{19}H_{14}OS_4$: C, 59.04; H, 3.65. Found: C, 58.77; H, 3.74.

2,8-Dibromo-5,6-dihydro-4*H*-thieno[3′,2′:6,7]cyclohepta[1,2-*b*]thiophen-4-one (9). Yield 25% (78%),[15] mp 136−137 °C. IR (Nujol) 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.51 (s, 1H), 6.90 (s, 1H), 2.90−2.78 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 192.53, 143.50, 141.86, 136.12, 132.66, 132.50, 132.08, 112.97, 110.23, 41.17, 23.21. Anal. Calcd for $C_{11}H_6Br_2OS_2$: C, 34.94; H, 1.60. Found: C, 34.79; H, 1.86.

6,10-Dihydrothieno[3′,2′:4,5]cycloocta[1,2-*b*]thiophen-4(5*H*)-one (11a). Yield 34% (69%),[15] mp 134−135 °C. IR (Nujol) 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.47 (d, 1H, J = 4.9 Hz), 6.99 (d, 1H, J = 4.9 Hz), 6.97 (d, 1H, J = 5.0 Hz), 6.73 (d, 1H, J = 5.0 Hz), 4.28 (s, 2H), 3.45−3.40 (m, 2H), 3.35−3.30 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 194.36, 147.97, 140.94, 135.92, 134.48, 132.70, 131.20, 130.48, 122.00, 38.77, 30.54, 25.66. Anal. Calcd for $C_{12}H_{10}OS_2$: C, 61.51; H, 4.30. Found: C, 60.97; H, 4.18.

(15) Yield based on conversion of substrate.

5-Bromo-6,10-dihydrothieno[3′,2′:4,5]cycloocta[1,2-*b*]-thiophen-4(5*H*)-one (11c). Yield 31% (61%),[15] mp 163−164 °C (dec). IR (Nujol) 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.52 (d, 1H, J = 4.8 Hz), 7.10 (m, 2H), 6.73 (d, 1H, J = 5.2 Hz), 5.79 (dd, 1H, J = 12.0, 6.0), 4.31 (d, 1H, J = 16.0 Hz), 4.10 (d, 1H, J = 16.0 Hz), 3.79−3.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 188.82, 146.63, 137.68, 136.35, 133.36, 132.95, 130.76, 130.14, 123.25, 50.19, 36.09, 31.25. Anal. Calcd for $C_{12}H_9BrOS_2$: C, 46.02; H, 2.90. Found: C, 47.28; H, 3.15.

7,13-Dihydrobenzo[*b*]thieno[3′,2′:6,7]cycloocta[1,2-*b*]-benzo[*b*]thiophen-5(6*H*)-one (13). Yield 17%, mp 212−215 °C (dec). IR (Nujol) 1645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.53 (d, 1H, J = 8.2 Hz), 7.73 (dd, 2H, J = 8.2, 7.6 Hz), 7.62 (d, 1H, J = 7.6 Hz), 7.43 (ddd, 1H, J = 8.2, 7.2, 1.2 Hz), 7.38−7.28 (m, 3H), 4.70 (s, 2H), 3.59−3.55 (m, 2H), 3.40−3.35 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 197.74, 153.31, 144.49, 140.90, 138.98, 137.31, 136.80, 133.98, 129.24, 125.80, 125.24, 125.14, 124.55, 124.29, 121.97, 121.41, 121.16, 39.85, 30.07, 24.94. Anal. Calcd for $C_{20}H_{14}OS_2$: C, 71.83; H, 4.22. Found: C, 71.35; H, 4.07.

***N*-[2-(Benzo[*b*]thiophen-2-ylmethyl)-2*H*-naphtho[1,8-*bc*]thiophen-5-yl]-*N*,*N*-dimethylamine (14).** Yield 19%, mp 115−117 °C. ^1H NMR ($CDCl_3$) δ 7.78 (d, 1H, J = 7.6 Hz), 7.33 (m, 2H), 7.36−7.25 (m, 4H), 7.18 (s, 1H, CH-), 7.15 (d, 1H, J = 8.0 Hz), 6.97 (d, 1H, J = 7.6 Hz, CH-4), 5.43 (dd, 1H, J = 9.2, 5.2 Hz, CH-2), 3.66 (dd, 1H, J = 15.2, 5.2 Hz, CH_2), 3.44 (dd, 1H, J = 15.2, 9.2 Hz, CH_2), 2.90 (s, 6H, $N(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 148.21 (C-5), 143.95, 142.08, 139.81, 139.74, 137.84, 136.47, 127.79, 127.17, 124.25, 123.90, 123.15, 122.74, 122.23, 120.68, 117.99, 116.38, 114.60, 55.37 (C-2), 44.84 ($N(CH_3)_2$), 40.62 (CH_2). Anal. Calcd for $C_{22}H_{19}NS_2$: C, 73.09; H, 5.30. Found: C, 73.43; H, 5.55.

1,3-Bis(2-methylbenzo[*b*]thiophen-3-yl)-1-propanone (16). Method A. The reaction mixture obtained under the general procedure from *N*,*N*-dimethylacrylamide (4.2 mmol), triflic anhydride (4.2 mmol), and **15** (8.5 mmol) in $C_2H_4Cl_2$ (20 mL) was quenched by aqueous Na_2CO_3. Products were isolated according to the general procedure to give **16** as a white solid, yield 25%, mp 97−98 °C, and **17** as an yellow oil, yield 10%. **Method B.** Reaction mixture obtained under the general procedure from *N*,*N*-dimethylacrylamide (4.2 mmol), triflic anhydride (4.2 mmol) and **15** (3.5 mmol) in $C_2H_4Cl_2$ (150 mL) was quenched by aqueous Na_2CO_3. Products were isolated according to general procedure to give **16** in 11% yield and **17** in 23% yield. IR (Nujol) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.09 (d, 1H, J = 8.2 Hz), 7.82 (d, 1H, J = 7.9 Hz), 7.78 (d, 1H, J = 7.7 Hz), 7.70 (d, 1H, J = 7.9 Hz), 7.43−7.31 (m, 4H), 3.38−3.33 (m, 2H), 3.30−3.25 (m, 2H), 2.72 (s, 3H), 2.60 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 198.02, 148.26, 139.90, 138.42, 138.18, 137.34, 135.19, 132.87, 130.22, 125.17, 124.40, 123.99, 123.63, 123.47, 122.21, 121.71, 120.90, 43.16, 20.79, 16.84, 13.84. Anal. Calcd for $C_{20}H_{14}OS_2$: C, 71.96; H, 4.56. Found: C, 71.61; H, 4.82.

***N*,*N*-Dimethyl-*N*-(2-methyl-5a,8b-dihydro-2*H*-naphtho-[1,8-*bc*]thiophen-5-yl)amine (17).** ^1H NMR ($CDCl_3$) δ 7.66 (d, 1H, J = 8.4 Hz, CH-8), 7.33 (dd, 1H, J = 8.4 Hz, CH-7), 7.17 (dd, 1H, J = 7.7, 1.4 Hz, CH-3), 7.15 (d, 1H, J = 8.4 Hz, CH-6), 6.98 (d, 1H, J = 7.7 Hz, CH-4), 5.11 (dq, 1H, J = 6.8, 1.4 Hz, CH-2), 2.88 (s, 6H, $N(CH_3)_2$), 1.71 (d, 3H, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 148.68 (C-5), 143.42, 140.88, 136.10, 127.72, 127.20, 119.75, 117.77, 116.12, 114.73, 48.75 (C-2), 44.88 ($N(CH_3)_2$), 24.44 (CH_3). Anal. Calcd for $C_{14}H_{15}NS$: C, 73.32; H, 6.11. Found: C, 72.95; H, 6.15.

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