Efficient One-Pot Synthesis of Cyclopenta[*b*]thiophen-1-ones and 1,3-Di(2-thiophenyl)propan-1-ones from Thiophenes

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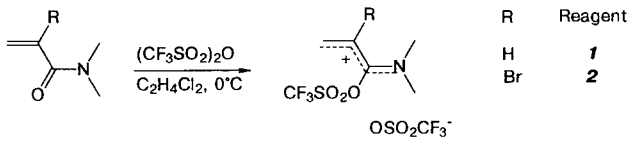
The reaction of *N,N*-dimethylacrylamide/triflic anhydride complex with substituted thiophenes led to the corresponding cyclopenta-[*b*]thiophen-1-ones and 1,3-di(2-thiophenyl)propan-1-ones. The application of 2-bromo-*N,N*-dimethylacrylamide in this reaction allows 2-bromo-substituted five- or seven-membered thiophene-fused cyclic ketones to be obtained.

Recently we have demonstrated the utility of *N,N*-dimethylacrylamide/triflic anhydride complex for one-step preparation of substituted indan-1-ones and 1,3-diarylpropan-1-ones.[1] Indanones are currently used in medicinal chemistry[2] and their synthetic preparation and chemical properties are well-known.[3] Cyclopentanones fused to thiophene and benzothiophene rings also possess some biological activity and can be applied in medicinal chemistry,[4,5] however, their preparation has frequently encountered difficulties due to some strains caused by greater angular requirements of the thiophene ring.[4,6,7]

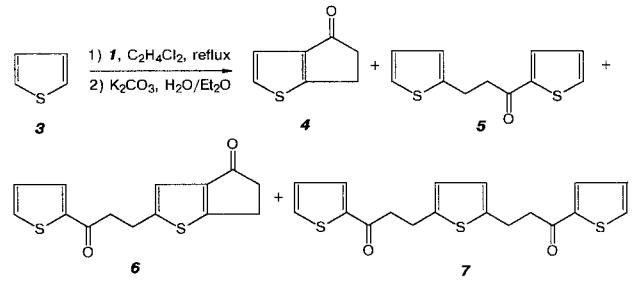
Now we have investigated the behavior of thiophene and some 2- or 3-substituted thiophenes in reactions with *N,N*-dimethylacrylamide/triflic anhydride complex **1** and *N,N*-dimethyl-2-bromoacrylamide/triflic anhydride complex **2**. The addition of the triflic anhydride in $C_2H_4Cl_2$ (1,2-dichloroethane) to the solution of the corresponding amide at 0 °C leads to formation of **1** as a white amorphous precipitate or **2** as a colorless oil (Scheme 1).



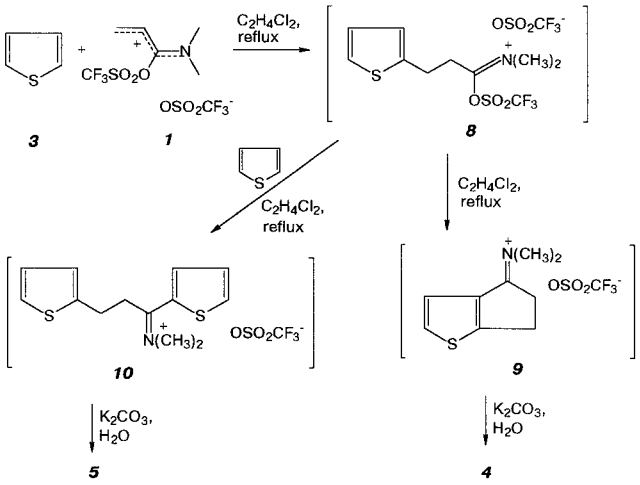
Scheme 1

The reaction of complex **1** with thiophene **(3)** followed by hydrolysis gives rise to a mixture of four products **4**–**7** in 60–65% overall yield (Scheme 2). Each product can be isolated in pure form by column chromatography [hexane/EtOAc (10:1) for **5**, benzene for **4** and **7**, benzene/diethyl ether (3:1) for **6**].

This reaction presumably proceeds via the formation of the iminium salt **8**, which can undergo cyclization to yield intermediate **9**. The latter is converted by hydrolysis (aqueous K_2CO_3) to the corresponding fused cyclopentanone **4** (Scheme 3). Alternatively, **8** can react with thiophene to form after hydrolysis the dithiophenylpropanone **5**. Iminium salt **10** contains the alkylthiophene fragment and therefore the succeeding reaction with complex **1** can take place. This results in the formation of **6** and/or **7** that have deactivated thiophene rings and do not take part in the subsequent cyclization reaction or linkage.



Scheme 2



Scheme 3

We succeeded in finding conditions for selective formation of the ketones **4**, **5** and **7**. To avoid the intermolecular reaction yielding **5** and **7**, a considerable amount of solvent (nearly 200 mL per gram of thiophene) was used (Method A). As a result, cyclopenta[*b*]thiophenone **(4)** was obtained in 45% yield (Table 1). On the other hand, if the reaction is conducted with two equivalents of thiophene and 25–30 mL of $C_2H_4Cl_2$ per gram of thiophene, the dithiophenylpropanone **5** was isolated in 55% yield as the major product (Method B). The application of a two-step addition of the reagent **1** to a solution of substrate **3** in a small amount of solvent (25–30 mL of $C_2H_4Cl_2$ per gram of thiophene) leads to predominant formation of ketones **5** (25%) and **7** (25%) (Method C).

The results of the reaction of complex **1** with monosubstituted thiophenes **3a–d**, as summarized in Table 2, show the predominant formation of the intermolecular reaction product **5a–d**. Moreover, dithiophenylpropanone **5c** was obtained as the sole product by reacting **3c** and **1**; **3a** also yielded only trace amounts of cyclic product.

Table 1. Reaction of Complex **1** with Thiophene

Reaction Conditions		Yield (%)			
Method	Substrate/Reagent Ratio	**4**	**5**	**6**	**7**
A	1:1	45	6	5	5
B	2:1	5	55	0	8
C	1:1	5	25	5	25

Table 2. Reaction of Complex **1** with Substituted Thiophenes

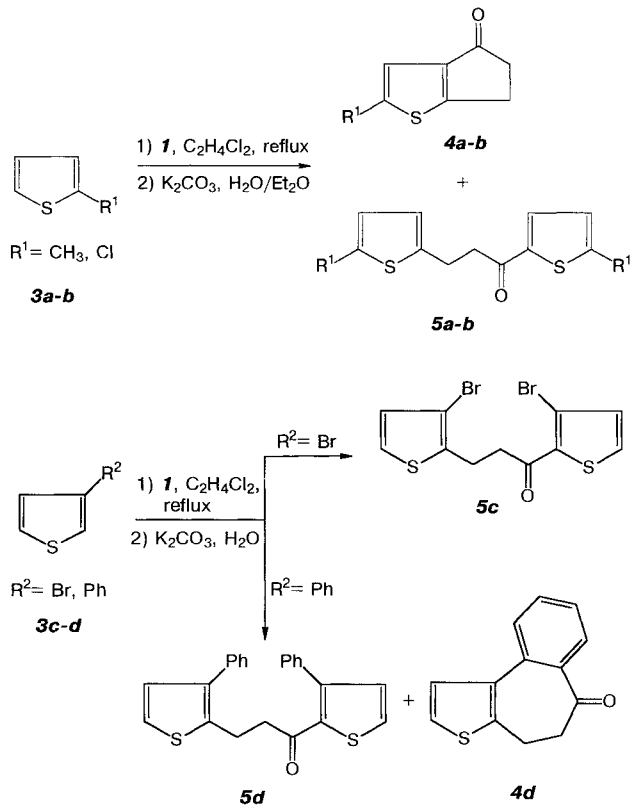
3, 4, 5	R^1	R^2	Yield (%)		Reaction Time (h)
			4	**5**	
a	Me	H	trace	52	3
b	Cl	H	10	46	6
c	H	Br	0	51	4
d	H	Ph	12	43	3

The first step of the reaction of **1** with thiophenes proceeds selectively at the most active position of the substrate. 2-Substituted thiophenes initially react exclusively at the 5-position, whereas in the case of 3-substituted thiophenes the attack occurs only at the 2-position (Scheme 4). The second step of the reaction is less selective and in the cases of **3b** and **3d** two types of products were formed.

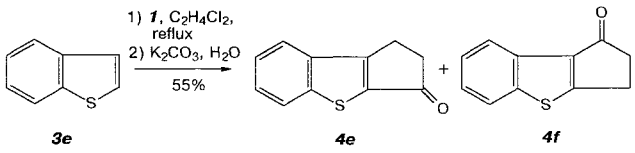
Surprisingly, 3-phenylthiophene **(3d)** was found to give the seven-membered ring product **4d**, in spite of the fact that the less active phenyl group is involved in the second step.

Prolonged reflux (nearly 10 h) of benzo[*b*]thiophene **(3e)** with complex **1** in $C_2H_4Cl_2$ followed by hydrolysis leads to a mixture of products **4e** and **4f** in a 4:1 ratio with an overall yield of 55% (Scheme 5), which was not separable by column chromatography. The predominant ketone **4e** was obtained as a result of the initial attack of **1** at the more active 3-position of **3e**; the attack at the less active 2-position leads to the formation of the minor product **4f**. These results are in accordance with the literature data.[8,9] It was known that benzo[*b*]thiophene is less active than thiophenes and sluggishly reacts with Vilsmeier-Haack reagent to produce 3-carbaldehyde with a low yield.[8] The 3-position in **3e** is insignificantly more active than 2-position, and the initial attack of electrophile can proceed at both positions.[9]

It would be interesting and useful if the method of activation by triflic anhydride was applicable not only to *N*,*N*-dimethylacrylamide but also to other α,β-unsaturated amides. Unfortunately, dimethylamides of methacrylic and crotonic acid were found to be inactive to the majority of aromatics, including thiophenes. Nevertheless, a complex of 2-bromo-substituted acrylamide and triflic anhydride **(2)** smoothly reacts with thiophenes **3**, **3b**, **3d** to afford the corresponding cyclic products **11**, **11b**, **11d**,

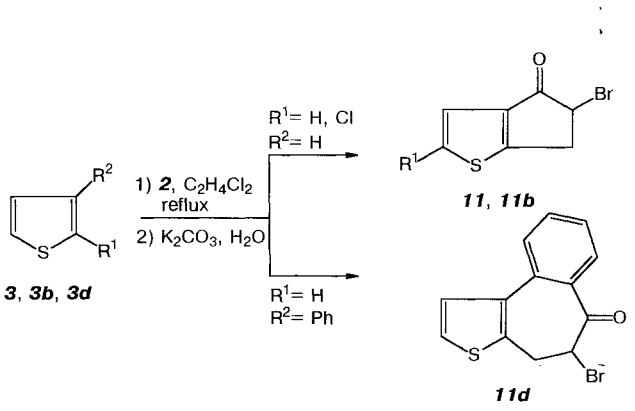


Scheme 4



Scheme 5

respectively (Scheme 6) in moderate yields (Table 3). In contrast to complex **1**, no intermolecular reaction products were detected. It should be mentioned, however, that **2** is less reactive than **1**, and the reaction with benzothiophene **(3e)** does not proceed.



Scheme 6

Table 3. Reaction of Complex **2** with Thiophenes

Product	R^1	R^2	Yield (%)	Reaction Time (h)
11	H	H	43	5
11b	Cl	H	35	5
11d	H	Ph	31	3

In conclusion, we have investigated the reactions of various thiophenes with two novel bifunctional electrophilic reagents, complexes of α,β-unsaturated amides with triflic anhydride. It was demonstrated that the corresponding cyclopenta[*b*]thiophenones and dithiophenylpropanones are easily prepared by this method in moderate yields.

Melting points were determined in sealed capillaries and are uncorrected. NMR spectra were recorded on Varian VXR-400 and Bruker AM 400C spectrometers with TMS as an internal standard. IR spectra were obtained with a UR-20 spectrometer as films. Column chromatography was performed on silica gel (63–200 mesh, Merck). All solvents used were dried and distilled according to the standard procedure. Triflic anhydride was prepared according to literature procedure[10] from trifluoromethanesulfonic acid (Merck).

Reaction of Thiophenes 3 with Complexes 1 or 2; General Procedure:
A solution of *N,N*-dimethylacrylamide (0.85 g, 8.5 mmol) or 2-bromo-*N,N*-dimethylacrylamide (1.50 g, 8.5 mmol) in anhyd $C_2H_4Cl_2$ (20 mL) was cooled to 0 °C. Over a period of 10 min triflic anhydride (2.4 g, 8.5 mmol) in $C_2H_4Cl_2$ (10 mL) was added dropwise. Then the corresponding substituted thiophene **3** (8.5 mmol) in $C_2H_4Cl_2$ (10 mL) was added and the mixture was refluxed 3–8 h. It was then added to a mixture of Et_2O (50 mL) and aq K_2CO_3 solution (50 mL) and stirred for an additional 1 h. The organic layer was separated and the aqueous layer extracted with Et_2O (2 × 50 mL). The solvents were removed in vacuo and the products were purified by column chromatography [silica gel, benzene or hexane/Et_2O (4:1) or benzene/Et_2O (3:1)].

5,6-Dihydro-4*H*-cyclopenta[*b*]thiophen-4-one (4):
Method A: The complex **1** was prepared as described in the general procedure from *N,N*-dimethylacrylamide (0.85 g, 8.5 mmol) and triflic anhydride (2.4 g, 8.5 mmol) in $C_2H_4Cl_2$ (100 mL), then thiophene (**3**; 0.71 g, 8.5 mmol) in $C_2H_4Cl_2$ (50 mL) was added. The mixture was refluxed 8 h and the product was isolated according to general procedure, column chromatography (benzene, R_f 0.17) to give **4** as a white solid; yield: 0.53 g (45%); mp 114 °C (Lit.[4] mp 115 °C).

IR (Nujol): $\nu = 1700\ cm^{-1}$ (CO).

^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.25$ (d, $^3J = 5.10$ Hz, 1 H, H-3), 7.08 (d, $^3J = 5.10$ Hz, 1 H, H-2). 3.15–3.11 (m, 2 H, CH_2), 2.95–2.91 (m, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.15$ (CO), 170.50, 145.55, 130.87, 119.05, 41.61, 24.30.

1,3-Di(2-thiophenyl)propan-1-one (5):
Method B: The complex **1** was prepared as described in general procedure from *N,N*-dimethylacrylamide (0.85 g, 8.5 mmol) and triflic anhydride (2.4 g, 8.5 mmol) in $C_2H_4Cl_2$ (20 mL), then thiophene (1.42 g, 17 mmol) in $C_2H_4Cl_2$ (20 mL) was added. The mixture was refluxed 2 h and the product was isolated according to the general procedure (column chromatography: hexane/EtOAc, 10:1; R_f 0.27) to give **5** as a pale yellow solid, yield 1.04 g (55%); mp 28 °C.

IR (Nujol): $\nu = 1670\ cm^{-1}$ (CO).

^1H NMR ($CDCl_3$): $\delta = 7.61$ (dd, $^3J = 3.8$ Hz, $^4J = 1.1$ Hz, 1 H, CH-3), 7.52 (dd, $^3J = 4.9$ Hz, $^4J = 1.1$ Hz, CH-5), 7.02 (m, 2 H, CH-4, CH-5′), 6.83 (dd, $^3J = 3.4$ Hz, $^3J = 5.1$ Hz, 1 H, CH-4′), 6.76 (dd, $^3J = 3.4$ Hz, $^4J = 1.1$ Hz, 1 H, CH-3′), 3.20 (s, 4 H, 2 CH_2).

^{13}C NMR ($CDCl_3$): $\delta = 191.24$ (CO), 143.79, 143.32, 133.55, 131.79, 127.98, 126.70, 124.60, 123.27, 40.89, 24.17.

$C_{11}H_{10}OS_2$: Calc. C 59.46, H 4.50; Found: C 59.18, H 4.47.

2-(3-Oxo-3-(2-thiophenyl)propyl)-5,6-dihydro-4H-cyclopenta[b]-thiophen-4-one **(6)**:

Method A; column chromatography: benzene/Et_2O (3:1), R_f 0.45; yellow solid; yield: 0.12 g (5%); mp 127–129 °C.

IR (Nujol): $\nu = 1670$ (CO, C-1), $1700\ cm^{-1}$ (CO, C-4).

^1H NMR ($CDCl_3$): $\delta = 7.73$ (dd, $^3J = 3.8$ Hz, $^4J = 1.0$ Hz, 1 H, CH-3′), 7.66 (dd, $^3J = 5.0$ Hz, $^4J = 1.0$ Hz, 1 H, CH-5′), 7.12 (dd, $^3J = 5.0$ Hz, $^3J = 3.8$ Hz, 1 H, CH-4′), 6.88 (s, 1 H, CH-3), 3.35–3.15 (m, 4 H, 2 CH_2-propyl), 3.15–3.05 (m, 2 H, CH_2), 2.93–2.83 (m, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): $\delta = 196.20$ (CO, C-4), 190.62 (CO propyl), 169.35, 149.66, 145.36, 143.60, 134.23, 131.98, 128.16, 116.29, 40.66, 40.15, 24.68, 24.51.

$C_{14}H_{12}O_2S_2$: Calc. C 59.60, H 4.44; Found: C 59.84, H 4.38.

3-(5-(3-Oxo-3-(2-thiophenyl)propyl)-2-thiophenyl)-1-(2-thiophenyl)-propan-1-one (7):
Method C: The complex **1** was prepared as described in the general procedure from *N,N*-dimethylacrylamide (0.42 g, 4.2 mmol) and triflic anhydride (1.2 g, 4.2 mmol) in $C_2H_4Cl_2$ (10 mL) and added to 2 equivalents of thiophene (**3**; 0.71 g, 8.5 mmol) in $C_2H_4Cl_2$ (10 mL). The mixture was refluxed for 1 h, then a second portion of the reaction complex **1** freshly prepared from *N,N*-dimethylacrylamide (0.42 g, 4.2 mmol) and triflic anhydride (1.2 g, 4.2 mmol) in $C_2H_4Cl_2$ (10 mL) was added and the mixture was refluxed 2 h. The product was isolated according to the general procedure; column chromatography: benzene; R_f 0.26; pale yellow solid, yield: 0.26 g (25%); mp 77–79 °C.

IR (Nujol): $\nu = 1670\ cm^{-1}$ (C=O).

^1H NMR ($CDCl_3$): $\delta = 7.71$ (dd, $^3J = 3.8$ Hz, $^4J = 0.9$ Hz, 2 H, CH-3′, CH-3″), 7.63 (dd, $^3J = 4.9$ Hz, $^4J = 0.6$ Hz, 2 H, CH-5′, CH-5″), 7.14 (m, 2 H, CH-4′, CH-4″), 6.65 (s, 2 H, CH-3, CH-4), 3.30–3.10 (m, 8 H, 4 CH_2).

^{13}C NMR ($CDCl_3$): $\delta = 191.49$ (2CO), 143.90, 141.60, 133.63, 131.86, 128.05, 124.37, 40.96, 24.50.

$C_{18}H_{16}O_2S_3$: Calc. C 59.97, H 4.44; Found: C 60.01, H 4.50.

1,3-Di(2-(5-methyl)thiophenyl)propan-1-one **(5a)**:

Prepared following the general procedure; column chromatography: hexane/EtOAc (10:1); R_f 0.34; pale brown solid; yield: 0.55 g (52%); mp 54–55 °C.

IR (Nujol): $\nu = 1670\ cm^{-1}$ (CO).

^1H NMR ($CDCl_3$): $\delta = 7.62$ (d, $^3J = 3.7$ Hz, 1 H, CH-3), 6.90 (d, $^3J = 3.7$ Hz, CH-4), 6.73 (d, $^3J = 3.3$ Hz, 1 H, CH-3′ or CH-4′), 6.65 (d, $^3J = 3.3$ Hz, 1 H, CH-3′ or CH-4′), 3.29 (s, 4 H, 2 CH_2), 2.63, 2.52 (2 s, 6 H, 2 CH_3).

^{13}C NMR ($CDCl_3$): $\delta = 190.91$ (CO), 149.41, 141.56, 141.07, 137.44, 132.19, 126.47, 124.45, 124.08, 40.36, 24.45, 15.69, 14.94.

$C_{13}H_{14}OS_2$: Calc. C 62.40, H 5.60; Found: C 62.72, H 5.95.

2-Chloro-5,6-Dihydro-[4H]-cyclopenta[b]thiophen-4-one **(4b)**:

Prepared following the general procedure; column chromatography: hexane/EtOAc (10:1); yield 0.15 g (10%) of **4b** (R_f 0.13); yellow solid; mp 105–107 °C; and 0.57 g (46%) of **5b** (R_f 0.36).

IR (Nujol): $\nu = 1720\ cm^{-1}$ (CO).

^1H NMR ($CDCl_3$): $\delta = 7.00$ (s, 1 H, CH-3), 3.22–3.11 (m, 2 H, CH_2), 2.96–2.85 (m, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): $\delta = 197.06$ (CO), 167.33, 143.75, 134.71, 118.35, 39.54, 24.79.

C_7H_5ClOS: Calc. C 48.70, H 2.90; Found: C 48.93, H 3.09.

1,3-Di(2-(5-chloro)thiophenyl)propan-1-one **(5b)**: pale yellow solid; mp 49–50 °C.

IR (Nujol): $\nu = 1670\ cm^{-1}$ (CO).

^{1}H NMR ($CDCl_3$): δ = 7.48 (d, ^3J = 4.0 Hz, 1 H, CH-3), 6.92 (d, ^3J = 4.0 Hz, CH-4), 6.70 (d, J = 3.6 Hz, 1 H, CH-3′ or CH-4′), 6.60 (d, ^3J = 3.6 Hz, 1 H, CH-3′ or CH-4′), 3.15 (s, 4 H, 2 CH_2).

^{13}C NMR ($CDCl_3$): δ = 190.22 (CO), 142.35, 142.08, 139.84, 131.50, 127.64, 126.87, 125.76, 124.28, 39.77, 24.51.

$C_{11}H_8Cl_2OS_2$: Calc. C 45.36, H 2.75; Found: C 45.26, H 2.70.

1,3-Di(2-(3-bromo)thiophenyl)propan-1-one (**5c**):

Prepared following the general procedure; column chromatography: hexane/EtOAc, 10:1; R_f 0.34; yield: 0.83 g (51 %); white solid; mp 86 °C.

IR (Nujol): ν = 1660 cm^{-1} (CO).

^{1}H NMR ($CDCl_3$): δ = 7.50 (d, ^3J = 5.2 Hz, 1 H), 7.12 (d, ^3J = 5.2 Hz, 1 H), 7.08 (d, ^3J = 5.2 Hz, 1 H). 6.90 (d, ^3J = 5.2 Hz, 1 H), 3.46–3.37 (s, 2 H, CH_2), 3.25–3.16 (s, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = 190.30 (CO), 137.26, 133.51, 132.25, 130.95, 129.86, 129.81, 123.67, 123.56, 41.70, 23.27.

$C_{11}H_8Br_2OS_2$: Calc. C 34.65, H 2.10, S 16.84; Found. C 34.71, H 2.09, S 16.93.

1,3-Di(2-(3-phenyl)thiophenyl)propan-1-one (**5d**):

Prepared following the general procedure; column chromatography: hexane/EtOAc (10:1); yield: 0.68 g (43 %) of **3d** (R_f 0.27); pale gray solid; mp 127 °C, and 0.22 g (12 %) of **6** (R_f 0.13).

IR (Nujol): ν = 1660 cm^{-1} (CO).

^{1}H NMR ($CDCl_3$): δ = 7.57 (d, ^3J = 5.5 Hz, 1 H), 7.50–7.27 (m, 10 H, 2C_6H_5), 7.12 (d, ^3J = 4.7 Hz, 1 H), 7.09 (d, ^3J = 5.5 Hz, 1 H), 7.00 (d, ^3J = 4.7 Hz, 1 H), 3.28–3.17 (s, 2 H, CH_2), 2.93–2.82 (s, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = 192.46 (CO), 146.27, 138.52, 138.37, 137.84, 136.15, 135.91, 131.61, 130.47, 128.86, 128.53 (2C), 128.31 (2C), 128.02 (4C), 127.88, 126.44, 121.57, 42.54, 22.66.

$C_{23}H_{18}OS_2$: Calc. C 73.76, H 4.84; Found: C 73.65, H 5.20.

5.6-Dihydro-4H-benzo[3,4]cyclohepta[b]thiophen-6-one (**4d**): Pale yellow solid; mp 50–52 °C.

IR (Nujol): ν = 1685 cm^{-1} (CO).

^{1}H NMR ($CDCl_3$): δ = 7.87 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1 H, CH-7), 7.52 (m, 1 H, CH-8 or CH-9), 7.45 (dd, ^3J = 7.8 Hz, 1 H, CH-10), 7.33 (m, 1 H, CH-8 or CH-9), 7.21 (d, ^3J = 5.2 Hz, 1 H, CH-1 or CH-2), 7.10 (d, ^3J = 5.2 Hz, 1 H, CH-1 or CH-2), 3.03 (s, 4 H, 2 CH_2).

^{13}C NMR ($CDCl_3$): δ = 203.83 (CO), 139.19, 137.44, 136.90, 134.57, 132.44, 130.49, 128.42, 128.34, 126.90, 122.09, 47.47, 22.56.

$C_{13}H_{14}OS$: Calc. C 72.87, H 4.70; Found: C 72.50, H 5.00

2,3-Dihydro-1H-benzo[b]cyclopenta[d]thiophen-3-one (**4e**) *and 2,3-Dihydro-1H-benzo[b]cyclopenta[d]thiophen-1-one* (**4f**):

Prepared following the general procedure, column chromatography: benzene, R_f 0.21, yield: 0.88 g (55 %); mixture **4f**/**4e** approximately 4:1; pale brown solid.

IR (Nujol): ν = 1710 cm^{-1} (CO).

^{1}H NMR ($CDCl_3$) for **4e**: δ = 7.85 (m, 2 H), 7.40 (m, 2 H), 3.15 (m, 2 H, CH_2), 2.90 (m, 2 H, CH_2) for **4f**: δ = 7.85 (m, 2 H), 7.40 (m, 2 H), 3.15 (m, 2 H, CH_2), 2.90 (m, 2 H, CH_2).

^{13}C NMR ($CDCl_3$) for **4e**: δ = 198.64 (CO), 165.20, 148.21, 140.60, 134.14, 128.14, 124.96, 124.37, 123.47, 39.67, 23.02; for **4f**: δ = 197.78 (CO), 174.30, 144.17, 139.66, 131.05, 125.59, 125.33, 122.86, 122.71, 41.08, 25.15.

$C_{11}H_8OS$: Calc. C 70.21, H 4.26; Found: C 70.50, H 4.52.

5-Bromo-5,6-dihydro-4H-cyclopenta[b]thiophen-4-one (**11**):

Prepared following the general procedure; column chromatography: benzene; R_f 0.31; yield: 0.79 g (43 %); pale grey solid; mp 75 °C.

IR (Nujol): ν = 1710 (CO).

^{1}H NMR ($CDCl_3$): δ = 7.42 (d, ^3J = 4.8 Hz, 1 H, CH-3), 7.20 (d, ^3J = 4.8 Hz, 1 H, CH-2), 4.87 (dd, ^3J = 6.8 Hz, ^3J = 2.4 Hz, 1 H, CH-5), 3.92 (dd, ^2J = 18.2 Hz, ^3J = 6.8 Hz, 1 H, CH_2-6), 3.46 (dd, ^2J = 18.2 Hz, ^3J = 2.4 Hz, 1 H, CH_2-6).

^{13}C NMR ($CDCl_3$): δ = 190.79 (CO), 166.76, 141.94, 131.85, 119.95, 48.03, 36.33.

C_7H_5BrOS: Calc. C 38.71, H 2.30; Found: C 39.09, H 2.69.

5-Bromo-2-chloro-5,6-dihydro-4H-cyclopenta[b]thiophen-4-one (**11b**):

Prepared following the general procedure, column chromatography: benzene; R_f 0.45; yield: 0.75 g (35 %); pale yellow solid; mp 79 °C.

IR (Nujol): ν = 1720 cm^{-1} (CO).

^{1}H NMR ($CDCl_3$): δ = 7.04 (s, 1 H, CH-3), 4.74 (dd, ^3J = 6.8 Hz, ^3J = 2.5 Hz, 1 H, CH-5), 3.85 (dd, ^2J = 18.3 Hz, ^3J = 6.8 Hz, 1 H, CH_2-6), 3.41 (dd, J = 18.3 Hz, ^3J = 2.5 Hz, 1 H, CH_2-6).

^{13}C NMR ($CDCl_3$): δ = 190.20 (CO), 163.92, 140.34, 135.89, 119.03, 45.75, 36.92.

$C_7H_4BrClOS$: Calc. C 33.40, H 1.59; Found: C 33.42, H 1.60.

5-Bromo-5,6-dihydro-4H-benzo[3,4]cyclohepta[b]thiophen-6-one (**11d**):

Prepared following the general procedure; column chromatography: benzene; R_f 0.55; yield: 0.77 g (31 %); pale grey solid; mp 42 °C.

IR (Nujol): ν = 1690 cm^{-1} (CO).

^{1}H NMR ($CDCl_3$): δ = 7.68 (dd, ^3J = 7.8 Hz, ^4J = 1.1 Hz, 1 H, CH-7), 7.48 (m, 1 H, CH-8 or CH-9), 7.35 (d, ^3J = 7.8 Hz, 1 H, CH-10), 7.30 (m, 1 H, CH-8 or CH-9), 7.13 (d, ^3J = 5.2 Hz, 1 H, CH-1 or CH-2), 7.11 (d, ^3J = 5.2 Hz, 1 H, CH-1 or CH-2), 4.77 (dd, ^3J = 10.1 Hz, ^3J = 4.5 Hz, 1 H, CH-5), 3.41 (dd, ^2J = 15.2 Hz, ^3J = 4.5 Hz, 1 H, CH_2-6), 3.41 (dd, ^2J = 15.2 Hz, ^3J = 10.1 Hz, 1 H, CH_2-6).

^{13}C NMR ($CDCl_3$): δ = 199.10 (CO), 138.98, 135.37, 134.06, 133.60, 132.55, 130.81, 127.98, 127.92, 127.56, 124.07, 52.72, 32.08.

$C_{13}H_9BrOS$: Calc. C 53.24, H 3.07; Found: C 53.82, H 2.92.

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