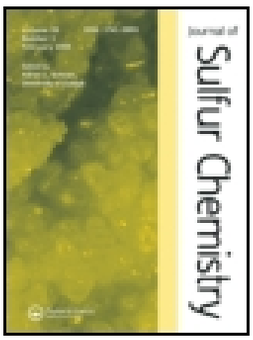

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Microwave-assisted reactions of α-diazoketones with hetaryl and ferrocenyl thioketones*

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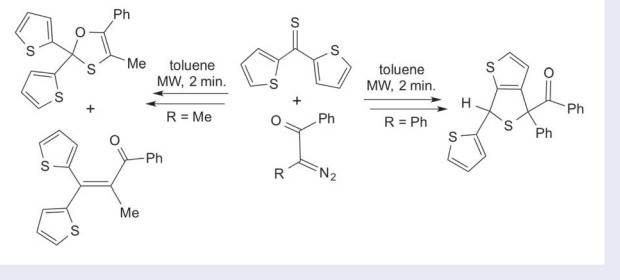
ABSTRACT

Differently substituted hetaryl thioketones react with less reactive diazoketones under microwave (MW) irradiation in toluene solution. After only 2 min, the reactions were complete and, depending on the type of the used diazoketone, α,β-unsaturated ketones, acyl substituted thiiranes or 1,3-oxathioles were obtained as final products. In the case of azibenzil and di(thiophen-2-yl) thioketone, a new type of 1,5-dipolar electrocyclization of the intermediate thiocarbonyl ylide involving a thiophene ring led to a fused sulfur heterocycle. In contrast to hetaryl thioketones, the ferrocenyl analogues decompose under MW irradiation. Alternatively, they react with diazopropanone and 2-diazo-1-phenylethanone in boiling THF in the presence of $LiClO_4$ to give α,β-unsaturated ketones as sole products. In these cases, the reactions require long reaction times.



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Diazo compounds; thioketones; microwave irradiation; thiocarbonyl ylides; sulfur heterocycles

1. Introduction

Reactions of diazomethane with 'superdipolarophilic' thioketones have extensively been studied, and it is well established that both cycloaliphatic and aromatic thioketones yield 1,3,4-thiadiazolines regioselectively even at low temperature. These [3+2]-cycloadducts extrude N_2 upon warming and reactive thiocarbonyl *S*-methanides are generated thereby

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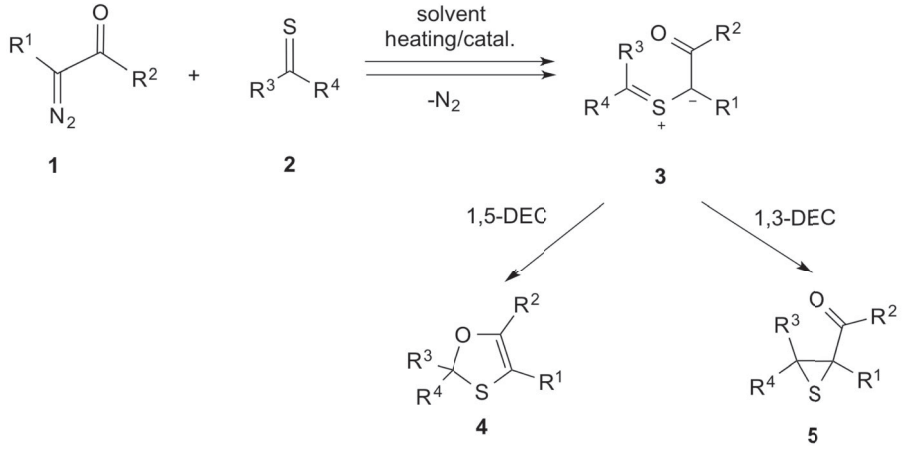
*Dedicated to Professor Zbigniew Kudzin (University of Łódź) on the occasion of his 70th birthday.



Scheme 1. *In situ* generation of α-acyl-substituted thiocarbonyl ylides **3** and their DEC.

[1–3]. In recent publications, we demonstrated that hetaryl thioketones react with diazomethane with immediate evolution of N_2 already below −70°C [4,5]. In these reactions, delocalized diradicals were postulated as intermediates, which either undergo dimerization or trap the starting thioketone to give 4,4,5,5-tetrasubstituted 1,3-dithiolanes in a regioselective manner. An analogous behavior of hetaryl thioketones was observed in reactions with alkyl- and trimethylsilyl-substituted diazomethanes. On the other hand, diphenyldiazomethane reacts with hetaryl thioketones only at ca. 0°C, and after spontaneous evolution of N_2 the corresponding tetra-substituted thiiranes or ethenes were obtained [6].

α-Diazoketones form an important class of propargyl-allenyl-type 1,3-dipoles [7,8], which are widely explored in the [3+2]-cycloaddition chemistry. Moreover, they are known as important precursors of carbenes and carbenoids generated photolytically or by treatment with metal salts, for example, rhodium(II) acetate [9]. The presence of an electron-withdrawing acyl group reduces the 1,3-dipolar reactivity and their [3+2]-cycloadditions require harsher reaction conditions, or Lewis acids are applied as catalyst [10]. In recent years, microwave (MW)-supported reactions have extensively been elaborated, and in many cases drastic reduction of reaction times and improvement of yields of products were reported also for [3+2]-cycloadditions performed with diverse 1,3-dipoles [11,12].

In our earlier studies, we described the reactions of some diazoketones **1** with cycloaliphatic and aromatic thioketones **2** (Scheme 1). In general, they were performed at enhanced temperature and, in some cases, $LiClO_4$ was used as an efficient catalyst. Depending on the substitution pattern, 1,3-oxathioles **4** or thiiranes **5** formed from the intermediate thiocarbonyl ylides **3** via 1,5- and 1,3-dipolar electrocyclization (DEC), respectively, were obtained [13–16]. Reactions leading to five membered heterocycles via 1,5-dipolar electrocyclizations of thiocarbonyl *S*-methanides bearing a C=X group at the α-position have been summarized in a recent review [17].

The reactivity of α-diazoketones **1** in [3+2]-cycloadditions with C=S dipolarophiles depends strongly on their structures and acyclic α-diazoketones were shown to be more reactive than cyclic analogues [10,18]. Due to our continuing interest in the chemistry of

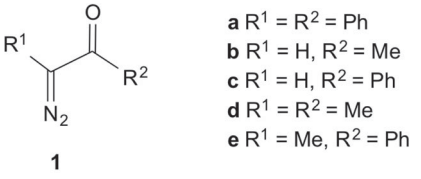
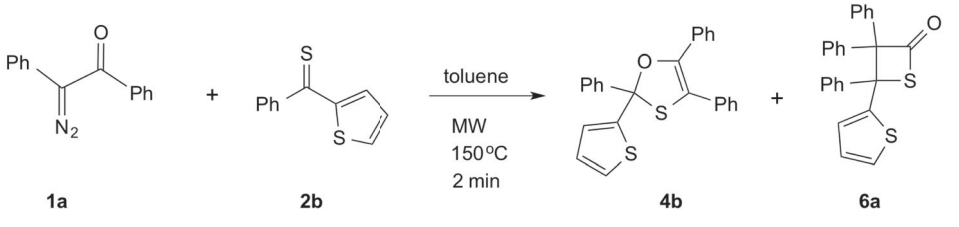


Figure 1. α-Diazoketones **1** selected for the reactions with hetaryl and ferrocenyl thioketones.

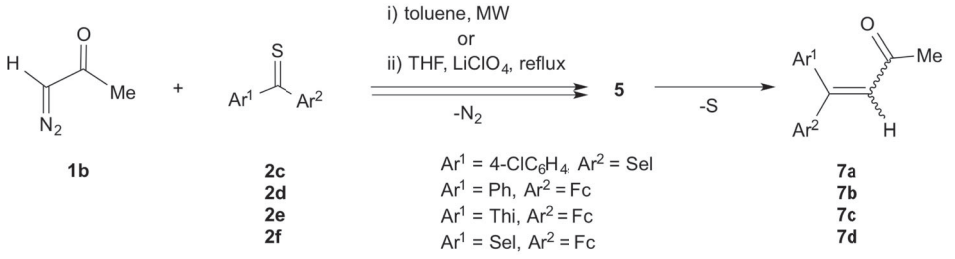
hetaryl and ferrocenyl thioketones as useful building blocks in the organic chemistry of sulfur [19], their reactions with diverse α-diazoketones **1** as representatives of diazo 1,3-dipoles should be compared with aromatic analogues. For this study, differently substituted α-diazoketones **1a**–**e**, presented in Figure 1, were selected in order to compare the influence of Me and Ph groups on the course of the investigated reactions.

2. Results and discussion

In an earlier publication, the reaction of thiobenzophenone (**2a**, $R^3 = R^4 = Ph$) with 2-diazo-1,2-diphenylethanone (azibenzil, **1a**) was reported to occur in Et_2O at room temperature within 96 h to give 2-benzoyl-2,3,3-triphenylthiirane (**5a**, $R^1 - R^4 = Ph$) in only 5% yield [16]. On the other hand, in THF in the presence of $LiClO_4$, the reaction was complete after 15 h, and the 1,3-oxathiole **4a** ($R^1 - R^4 = Ph$) was obtained in 51% yield [13]. The same reaction conditions were applied in a test experiment with **1a** and phenyl (thiophen-2-yl) thioketone (**2b**). Unexpectedly, no reaction was observed after 24 h. Moreover, even after 7 d, the main part of **1a** remained unchanged, whereas **2b** underwent slow decomposition. Similarly, the attempted reaction in boiling THF in the presence of $LiClO_4$ was unsuccessful. For that reason, the reaction conditions were changed, and the reaction was carried out in toluene under MW irradiation (200 W, 150°C). In that case, the characteristic green color of **2b** disappeared already after 2 min. After evaporation of the solvent, the ^{1}H NMR spectrum of the crude mixture suggested the presence of two products, which were separated and identified as 2,4,5-triphenyl-2-(thiophen-2-yl)-1,3-oxathiole (**4b**) and 3,3,4-triphenyl-4-(thiophen-2-yl)thietan-2-one (**6a**) (Scheme 2); the latter is a known compound [20]. In the case of **4b**, the structure was established based on ^{13}C NMR and IR data as well as the elemental analysis. In the ^{13}C NMR spectrum, the most characteristic signal of C(2) appeared at 96.2 ppm. Importantly, in the registered IR spectrum, no C=O absorption was observed.



Scheme 2. Reaction of hetaryl thioketone **2b** with azibenzil (**1a**) under MW irradiation.



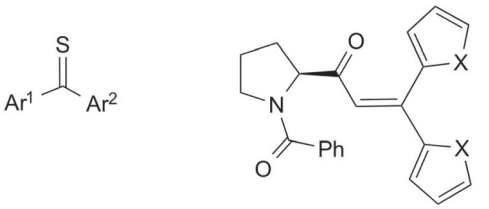
Scheme 3. Formation of α,β-unsaturated ketones **7** in reactions of diazopropanone (**1b**) with hetaryl and ferrocenyl thioketones **2** (Fc = ferrocenyl, Sel = selenophen-2-yl, Thi = thiophen-2-yl).

The formation of **4b** results from the 1,5-DEC of the *in situ* generated thiocarbonyl *S*-methanide **3b** (R^1 – R^3 = Ph, R^4 = thiophen-2-yl) according to the mechanistic explanation presented in Scheme 1. Very likely, the intermediate **3b** is formed via addition of the initially formed benzoyl(phenyl)carbene onto the C=S group of **2b** [3]. The reactive benzoyl(phenyl)carbene undergoes a competitive Wolff rearrangement to give diphenylketene, which is known to trap thioketones yielding thietan-2-ones, for example, **6a**, in a regioselective manner [20].

Prompted by these results, we decided to study reactions of the α-diazoketones **1a**–**e** with hetaryl and ferrocenyl thioketones **2** systematically. The first series of experiments comprises reactions of diazopropanone (**1b**) with thioketones **2c**–**f** (Scheme 3). In the experiment with **2c** under MW irradiation, the only product isolated after chromatographic workup was the α,β-unsaturated ketone **7a**. Remarkably, only one stereoisomer was obtained. The collected spectroscopic data did not allow determining the configuration of the product. In contrast, the attempted MW-assisted reactions with ferrocenyl thioketones **2d**–**f** were unsuccessful and only decomposition of the thioketones was observed. For that reason, the reactions of **1b** with **2d**–**f** were repeated in boiling THF in the presence of $LiClO_4$. After 16 h, the conversions were complete and the α,β-unsaturated ketones **7b**–**d** were obtained as single stereoisomers with unknown configuration in fair yields (Scheme 3).

The mechanistic explanation of the pathway leading to products **7** is based on the assumption that the intermediate thiocarbonyl ylides of type **3** bearing hetaryl or/and ferrocenyl groups undergo 1,3-DEC to give thiiranes of type **5**, which under the reaction conditions extrude sulfur immediately. The reaction sequence **1** + **2** → **7** corresponds formally with the 'two-fold extrusion reaction' [21], which belongs to the most useful olefinition reactions. These results point out that the presence of hetaryl or ferrocenyl substituents promotes the extrusion of sulfur from the initially formed thiiranes in analogy to results obtained in reactions with *N*-protected diazoproline performed in boiling THF in the presence of $LiClO_4$ [22]. In the present study, *N*-benzoyldiazoproline was reacted with di(thiophen-2-yl)- and di(selenophen-2-yl)thioketone (**2g**,**h**) under MW irradiation, and the corresponding α,β-unsaturated ketones **7e**,**f** were obtained in high yields (Figure 2).

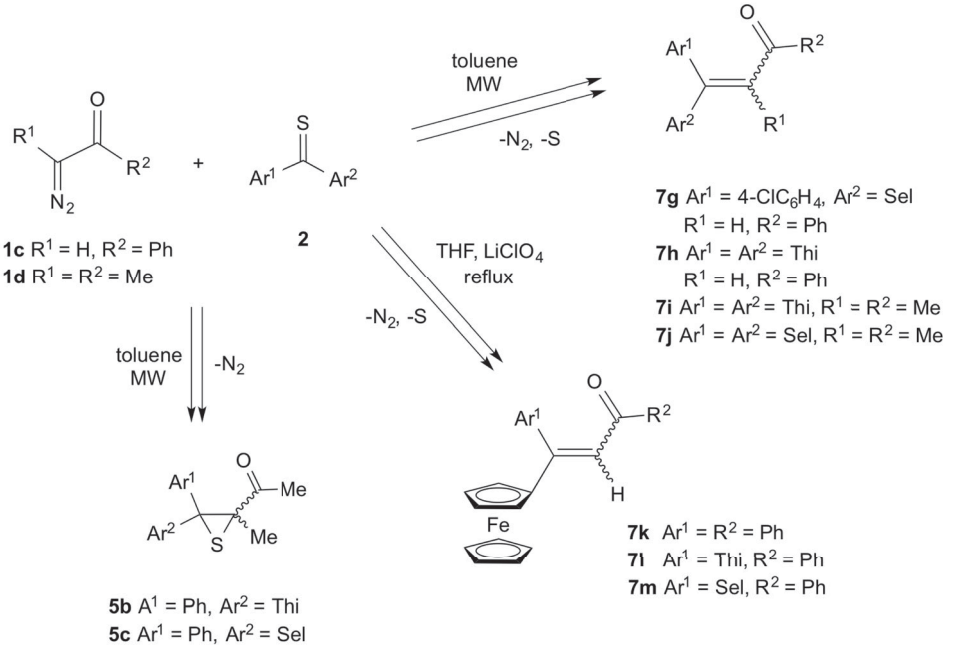
The MW-assisted reactions of diazoacetophenone (**1c**) and 3-diazobutan-2-one (**1d**) with diverse hetaryl thioketones **2** led, in most cases, to the corresponding α,β-unsaturated ketones of type **7** (Scheme 4). However, the initially formed thiiranes **5b**,**c** could be isolated in the reactions of **1d** with **2b** and **2i**, respectively.



2g $Ar^1 = Ar^2$ = Thi
2h $Ar^1 = Ar^2$ = Sel

7e X = S
7f X = Se

Figure 2. α,β-Unsaturated ketones obtained from *N*-benzoyldiazoproline and dihetaryl thioketones **2g** and **2h**.



1c R^1 = H, R^2 = Ph
1d $R^1 = R^2$ = Me

7g Ar^1 = 4-ClC_6H_4, Ar^2 = Sel
R^1 = H, R^2 = Ph
7h $Ar^1 = Ar^2$ = Thi
R^1 = H, R^2 = Ph
7i $Ar^1 = Ar^2$ = Thi, $R^1 = R^2$ = Me
7j $Ar^1 = Ar^2$ = Sel, $R^1 = R^2$ = Me

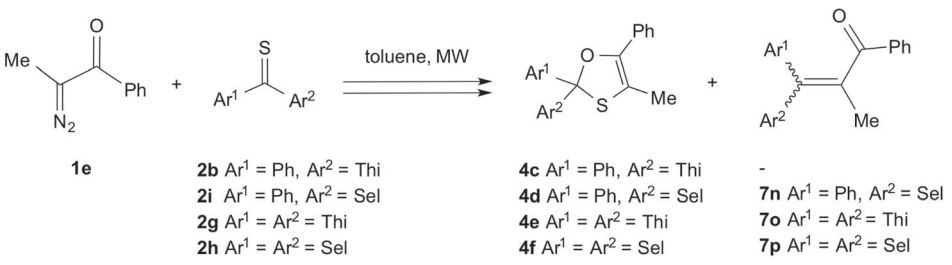
5b A^1 = Ph, Ar^2 = Thi
5c Ar^1 = Ph, Ar^2 = Sel

7k $Ar^1 = R^2$ = Ph
7l Ar^1 = Thi, R^2 = Ph
7m Ar^1 = Sel, R^2 = Ph

Scheme 4. Reactions of α-diazoketones **1c** and **1d** with hetaryl and ferrocenyl thioketones.

In analogy to the experiments performed with **1b**, the attempted reactions of **1c** with ferrocenyl thioketones **2d–f** led to α,β-unsaturated ketones **7k–m** only in boiling THF/$LiClO_4$.

The next diazocompound used was 2-diazo-1-phenylpropan-1-one (**1e**). The MW-assisted reactions carried out with hetaryl thioketones **2b**,**g–i** gave 1,3-oxathiole derivatives **4**, which in most cases were obtained side by side with the corresponding α,β-unsaturated ketones **7** (Scheme 5). Apparently, the presence of the benzoyl group in the intermediate thiocarbonyl ylide **3** enhances its ability to undergo the 1,5-DEC leading to 1,3-oxathioles **4** as major products. The competitive 1,3-DEC results in the formation of the corresponding benzoyl-substituted thiiranes, which subsequently extrude sulfur to give alkenes **7**.



Scheme 5. Formation of 1,3-oxathioles **4** and α,β-unsaturated ketones **7** in the reactions of 2-diazo-1-phenylpropan-1-one (**1e)** with hetaryl thioketones **2**.

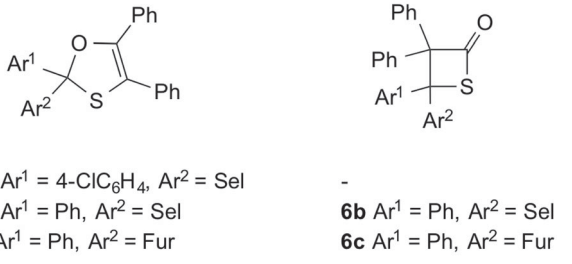
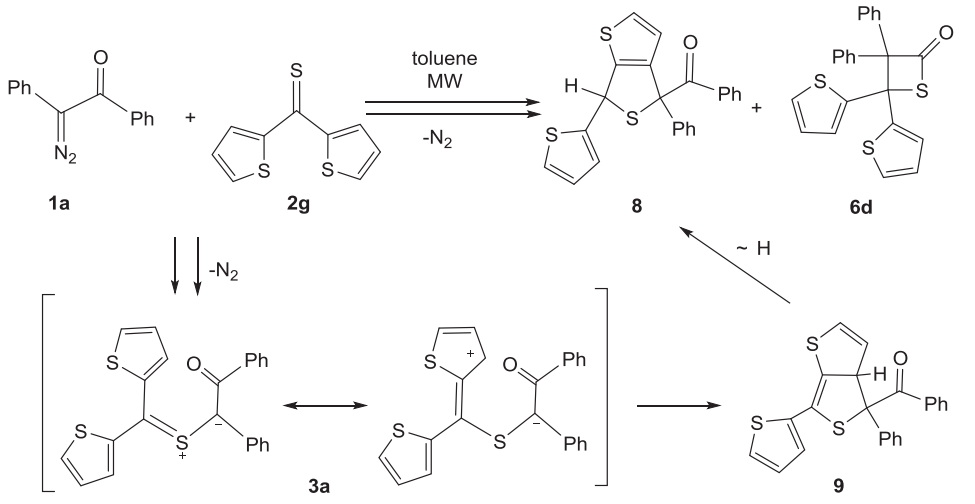


Figure 3. Products of the reaction of azibenzil (**1a**) with aryl hetaryl thioketones **2** (Fur = furan-2-yl).

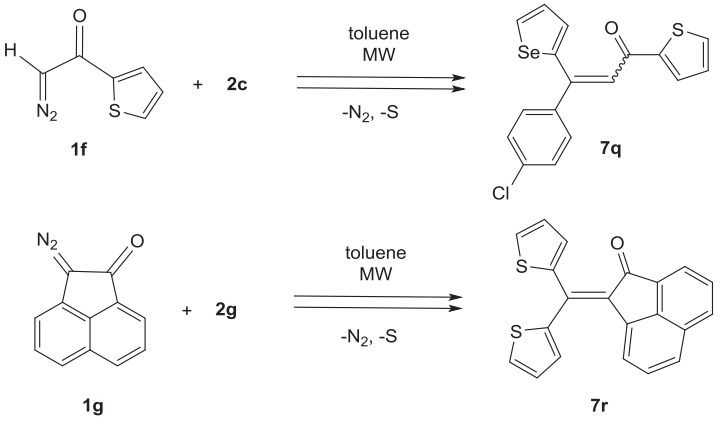
In extension of the study presented in Scheme 2, azibenzil (**1a**) was used for reactions with hetaryl thioketones **2c**,**g**,**i**, and **2j** (Ar^1 = Ph, Ar^2 = Fur). In this series, neither thiiranes **5** nor α,β-unsaturated ketones **7** were formed, and only 1,3-oxathioles **4** as well as thietan-2-ones **6** were isolated from the reaction mixtures. The reaction course is presented in Scheme 2, and the obtained products are depicted in Figure 3.

An unexpected result was obtained in the reaction of **1a** with **2g**. The chromatographic separation gave two products, and one of them was identified as the known 3,3-diphenyl-4,4-di(thiophen-2-yl)thietan-2-one **6d** [20]. The second product **8**, isolated in a comparable amount as a solid material, showed in the ^{13}C NMR spectrum the characteristic absorption of a keto group at 203.5 ppm. The corresponding IR absorption was found at 1682 cm^{-1}. In addition, the ^{1}H NMR spectrum revealed the presence of a singlet for a CH group at 5.60 ppm, which correlated with the signal of a sp^3-C atom in the ^{13}C NMR spectrum (42.2 ppm). Moreover, the presence of five signals for C_{arom} indicated that one of the former CH atoms of a thiophene ring was involved in the formation of a new σ-bond. Based on these data, the structure **8** was attributed to the new product isomeric with the expected thiirane or 1,3-dithiole (Scheme 6). An additional argument was found in the ^{1}H NMR spectrum, in which two doublets with J = 5.2 Hz localized at 6.22 and 7.09 ppm corresponded with two H-atoms in α- and β-positions of the fused thiophene ring.

The reaction pathway leading to **8** is presented in Scheme 6. The intermediate thiocarbonyl ylide **3a** undergoes a formal 1,5-DEC involving a thiophene ring. The resulting fused sulfur heterocycle **9** stabilizes via 1,3-H-shift to give **8** as the final product. This is the first example of a benzoyl-substituted thiocarbonyl ylide, which forms neither a 1,3-oxathiole nor a thiirane as products of dipolar electrocyclization.



Scheme 6. Reaction of azibenzil (**1a**) with di(thiophen-2-yl) thioketone (**2g**) leading to thieno[3,4-*b*]thiophene derivative **8**.



Scheme 7. Synthesis of α,β-unsaturated ketones **7q**,**r** from hetaryl thioketones **2c**,**g**.

In two additional experiments, 2-diazo-1-(thiophen-2-yl)ethanone (**1f**) and 2-diazoacenaphthen-1-one (**1g**) were reacted with thioketones **2c** and **2g**, respectively. In both cases, the corresponding α,β-unsaturated ketones **7q** and **r**, respectively, were obtained as the sole product (Scheme 7). Analogous to previously described examples (Scheme 3), only one stereoisomer of **7q** was formed.

3. Conclusions

The presented results show that the less reactive diazoketones can be used efficiently for reactions with hetaryl thioketones under MW irradiation. Under these conditions, the reaction time was reduced to 2 min in all cases. Depending on the type of substituents in the starting diazoketones, α,β-unsaturated ketones, acyl-substituted thiiranes

or 1,3-oxathioles were obtained as final products. Remarkably, the reaction of azibenzil and di(thiophen-2-yl) thioketone gave a fused sulfur heterocycle (thieno[3,4-*b*]thiophene skeleton) upon involvement of a thiophene ring in the electrocyclization process (1,5-dipolar electrocyclization). The presented method supplements the very few methods reported for the synthesis of thieno[3,4-*b*]thiophene derivatives, which are of current interest for materials chemistry [23]. Ferrocenyl thioketones are not suitable substrates for MW-supported reactions, but in the studied cases, α,β-unsaturated ketones were formed as sole products when the reactions with diazoketones **1b** and **1c** were carried out in boiling THF in the presence of $LiClO_4$. The mechanistic explanation for all these reactions is based on the assumption that acyl-substituted thiocarbonyl ylides are formed as reactive intermediates, which subsequently undergo DEC processes. The course of the latter reactions depends on the type of substituents in the diazoketone used. In contrast to known analogous reactions of aromatic and cycloaliphatic thioketones with diazomethanes, which proceed via initial [3+2]-cycloaddition, the generation of the thiocarbonyl ylides under MW-irradiation occur, very likely, via decomposition of the starting diazoketones. The carbene formed thereby adds to the thiocarbonyl group of the thioketone. A piece of evidence for this reaction sequence is the observed formation of diphenylketene in reactions performed with azibenzil, which led to the corresponding thietan-2-ones.

4. Experimental design

4.1. General

All solvents were dried over appropriate drying agents and distilled before use. The ^1H and ^{13}C NMR spectra were measured on a Bruker Avance III instrument (600 and 150 MHz, respectively), using the solvent ($CDCl_3$/residual $CHCl_3$) signal as reference. The IR spectra (KBr pellets) were recorded on a Nexus FT-IR spectrophotometer. The elemental analyses were determined on a Vario Micro Cube. Flash column chromatography (FCC) was carried out using Silica gel 60 (Sigma-Aldrich, 230–400 mesh). Melting points were determined in a capillary using a Stewart® SMP30. MW experiments were carried out with CEM-focused Microwave-type Discover SPD at 150 W. The notation Fc represents in this study 'ferrocenyl'.

4.2. Starting materials

The applied α-diazoketones **1** were obtained by known methods either via oxidation of the corresponding hydrazone [24] or by treatment of an acid chloride with excess diazomethane or diazoethane (Arndt-Eistert reaction) [25]. Aryl and hetaryl thioketones **2a**–**c**,**g**–**j** [4,26] as well as ferrocenyl-substituted thioketones **2d**–**f** [27] were prepared from parent ketones via thionation using Lawesson's reagent.

4.3. Reactions of α-diazoketones 1 with thioketones 2 under MW irradiation – general procedure

A solution of a diazocompound **1** (1 mmol) and a thioketone **2** (1 mmol) in anhydrous toluene (3 mL) was subjected to MW irradiation at 150°C for ca. 2 min. The reactions were

performed until the color of thioketone **2** disappeared. If necessary, additional portions of **1** were added to achieve full consumption of thioketone **2**. After complete reaction, the solvent was evaporated and the crude mixtures were purified chromatographically (SiO_2) using as eluent petroleum ether or hexane with increasing amounts of CH_2Cl_2. Analytically pure samples were obtained after crystallization from petroleum ether or hexane with small amounts of CH_2Cl_2.

4.3.1. 2,4,5-Triphenyl-2-(thiophen-2-yl)-1,3-oxathiole (4b)

Red crystals; m.p. 127.4–129.8°C; yield: 100 mg (25%). ^{1}H NMR: 6.98 (*dd*, $J_{H,H}$ = 5.0 Hz, $J_{H,H}$ = 3.7 Hz, 1CH_{arom}); 7.12 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 1.3 Hz, 1CH_{arom}); 7.24–7.34 (*m*, 8CH_{arom}); 7.37–7.48 (*m*, 6CH_{arom}); 7.73–7.76 (*m*, 2CH_{arom}). ^{13}C NMR: 96.2, 111.9 (C_{Thi}, C(4)); 126.1, 126.5, 127.0, 127.5, 127.7, 127.9, 128.1, 128.2, 128.3, 128.5, 128.7, 129.2 (18CH_{arom}); 130.7, 132.2, 141.2, 143.4 (4C_{arom}); 148.9 (C(5)). IR (KBr): 3082*m*, 3050*m*, 3015*m*, 1609*s*, 1496*s*, 1445*s*, 1223*s*, 1150*m*, 1065*s*, 965*m*, 954*m*, 831*m*, 748*vs*, 691*vs*. Anal. calcd for $C_{25}H_{18}OS_2$ (398.54): C 75.34, H 4.55, S 16.09; found: C 75.44, H 4.73, S 15.98.

4.3.2. 4-Methyl-2,5-diphenyl-2-(thiophen-2-yl)-1,3-oxathiole (4c)

Brown-orange crystals; m.p. 84–86°C; yield: 315 mg (94%). ^{1}H NMR: 2.14 (*s*, CH_3); 6.95 (*dd*, $J_{H,H}$ = 5.0 Hz, $J_{H,H}$ = 3.6 Hz, 1CH_{arom}); 7.06 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 1.4 Hz, 1CH_{arom}); 7.30–7.41 (*m*, 7CH_{arom}); 7.57–7.59 (*m*, 2CH_{arom}); 7.66–7.69 (*m*, 2CH_{arom}). ^{13}C NMR: 12.9 (CH_3); 95.8, 107.1 (C_{Thi}, C(4)); 126.0, 126.4, 126.8, 127.2, 127.3, 127.8, 128.0, 128.3, 128.4 (13CH_{arom}); 130.8, 141.3, 143.7 (3C_{arom}); 149.3 (C(5)). IR (KBr): 3098*m*, 2911*m*, 1635*m*, 1489*m*, 1442*m*, 1429*m*, 1233*s*, 1147*s*, 1071*m*, 1011*s*, 831*m*, 767*m*, 745*m*, 707*vs*, 694*v*. Anal. calcd for $C_{20}H_{16}OS_2$ (336.47): C 71.39, H 4.79, S 19.06; found: C 71.44, H 4.90, S 19.12.

4.3.3. 4-Methyl-2,5-diphenyl-2- (selenophen-2-yl)-1,3-oxathiole (4d)

Beige crystals; m.p. 90–92°C; yield: 210 mg (55%). ^{1}H NMR: 2.14 (*s*, CH_3); 7.20 (*d*, $J_{H,H}$ = 3.4 Hz, 2CH_{arom}); 7.31–7.42 (*m*, 6CH_{arom}); 7.59 (*d*, $J_{H,H}$ = 7.6 Hz, 2CH_{arom}); 7.71 (*d*, $J_{H,H}$ = 7.8 Hz, 2CH_{arom}); 8.05 (*dd*, $J_{H,H}$ = 6.0 Hz, $J_{H,H}$ = 3.4 Hz, 1CH_{arom}). ^{13}C NMR: 12.9 (CH_3); 97.4, 107.2 (C_{Sel}, C(4)); 126.0, 127.3, 127.8, 128.0, 128.2, 128.3, 129.0, 129.1, 132.3 (13CH_{arom}); 130.9, 141.2, 143.7 (3C_{arom}); 156.5 (C(5)). IR (KBr): 3056*s*, 2914*m*, 2851*m*, 1632*m*, 1492*s*, 1445*s*, 1382*m*, 1233*s*, 1144*s*, 1078*m*, 1011*s*, 834*m*, 767*m*, 736*s*, 694*vs*, 675*m*. Anal. calcd. for $C_{20}H_{16}OSSe$ (383.37): C 62.66, H 4.21, S 8.36; found C 62.65, H 4.40, S 8.56.

4.3.4. 4-Methyl-5-phenyl-2,2-di(thiophen-2-yl)-1,3-oxathiole (4e)

Beige crystals; m.p. 74.2–75.3°C; yield: 170 mg (50%). ^{1}H NMR: 2.15 (*s*, CH_3); 6.99 (*dd*, $J_{H,H}$ = 5.0 Hz, $J_{H,H}$ = 3.6 Hz, 2CH_{arom}); 7.20 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 1.1 Hz, 2CH_{arom}); 7.30–7.33 (*m*, 2CH_{arom}); 7.36–7.41 (*m*, 3CH_{arom}); 7.56–7.60 (*m*, 2CH_{arom}). ^{13}C NMR: 12.9 (CH_3); 93.0, 107.4 (C_{Thi}, C(4)); 126.0, 126.5, 127.0, 127.4, 127.9, 128.2 (11CH_{arom}); 130.6, 141.2 (3C_{arom}); 148.3 (C(5)). IR (KBr): 3088*m*, 1622*m*, 1594*m*, 1492*s*, 1429*m*, 1350*m*, 1233*s*, 1138*s*, 1071*m*, 1036*s*, 1005*s*, 843*m*, 827*m*, 777*m*, 764*s*, 707*vs*, 691*vs*. Anal. calcd for $C_{18}H_{14}OS_3$ (342.50): C 63.12, H 4.12, S 28.09; found: C 63.17, H 4.64, S 28.05.

4.3.5. 4-Methyl-5-phenyl-2,2-di(selenophen-2-yl)-1,3-oxathiole (4f)

Beige crystals; m.p. 87–89°C; yield: 150 mg (35%). ^{1}H NMR: 2.15 (*s*, CH_3); 7.23 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 3.8 Hz, $2CH_{arom}$); 7.30–7.33 (*m*, $1CH_{arom}$); 7.37–7.41 (*m*, $4CH_{arom}$); 7.54–7.58 (*m*, $2CH_{arom}$); 8.06 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 1.0 Hz, $2CH_{arom}$). ^{13}C NMR: 12.9 (CH_3); 96.2, 107.6 (C_{Sel}, C(4)); 127.4, 127.9, 128.2, 128.9, 129.0, 132.2 ($11CH_{arom}$); 130.6, 141.0 ($3C_{arom}$); 155.2 (C(5)). IR (KBr): 3098*m*, 3060*m*, 1625*m*, 1492*m*, 1442*s*, 1236*s*, 1230*s*, 1144*s*, 1125*s*, 1074*m*, 1027*m*, 1002*m*, 843*m*, 834*m*, 764*s*, 732*s*, 694*vs*, 618*m*. Anal. calcd for $C_{18}H_{14}OSSe_2$ (436.29): C 49.55, H 3.23, S 7.35; found: C 49.62, H 3.41, S 7.59.

4.3.6. 2-(4-Chlorophenyl)-4,5-diphenyl-2-(selenophen-2-yl)-1,3-oxathiole (4g)

Brown crystals; m.p. 128–130°C; yield: 150 mg (31%). ^{1}H NMR: 7.21–7.33 (*m*, $12CH_{arom}$); 7.37–7.40 (*m*, $2CH_{arom}$); 7.42–7.44 (*m*, $2CH_{arom}$); 7.68–7.71 (*m*, $2CH_{arom}$); 8.01 (*dd*, $J_{H,H}$ = 5.1 Hz, $J_{H,H}$ = 1.8 Hz, $1CH_{arom}$). ^{13}C NMR: 97.3, 112.1 (C_{Sel}, C(4)); 127.6, 127.9, 128.2, 128.3, 128.4, 128.7, 129.1, 129.2, 129.6, 132.9 ($17CH_{arom}$); 130.5, 132.0, 134.5, 141.2, 142.1 ($5C_{arom}$); 155.2 (C(5)). IR (KBr): 3053*m*, 3033*m*, 1616*s*, 1570*m*, 1486*s*, 1439*m*, 1391*m*, 1230*s*, 1214*m*, 1087*s*, 1052*m*, 983*m*, 954*m*, 812*m*, 758*vs*, 691*vs*. Anal. calcd for $C_{25}H_{17}ClOSSe$ (479.88): C 62.57, H 3.57, S 6.68; found: C 62.62, H 3.62, S 6.82.

4.3.7. 2,4,5-Triphenyl-2-(selenophen-2-yl)-1,3-oxathiole (4h)

Green-brown crystals; m.p. 141–143°C; yield: 50 mg (11%). ^{1}H NMR: 7.21–7.32 (*m*, $9CH_{arom}$); 7.36–7.46 (*m*, $6CH_{arom}$); 7.74–7.76 (*m*, $2CH_{arom}$); 8.08 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 1.0 Hz, $1CH_{arom}$). ^{13}C NMR: 97.8, 112.0 (C_{Sel}, C(4)); 126.1, 127.6, 127.8, 128.1, 128.2, 128.3, 128.5, 128.6, 129.1, 129.2, 129.4, 132.5 ($18CH_{arom}$); 130.7, 132.2, 141.1, 143.5 ($4C_{arom}$); 156.2 (C(5)). IR (KBr): 3085*m*, 3047*m*, 3018*m*, 3000*s*, 2958*s*, 1613*m*, 1489*m*, 1445*s*, 1264*s*, 1217*m*, 1144*m*, 1062*s*, 1027*s*, 967*m*, 808*m*, 755*s*, 698*vs*. Anal. calcd for $C_{25}H_{18}OSSe$ (445.43): C 67.41, H 4.07, S 7.20; found: C 67.36, H 4.22, S 7.21.

4.3.8. 2-(Furan-2-yl)-2,4,5-triphenyl-1,3-oxathiole (4i)

Pale-brown viscous oil; yield: 100 mg (26%). ^{1}H NMR: 6.39–6.40 (*m*, $1CH_{arom}$); 6.49 (*d*, $J_{H,H}$ = 3.3 Hz, $1CH_{arom}$); 7.17–7.22 (*m*, $1CH_{arom}$); 7.24–7.34 (*m*, $6CH_{arom}$); 7.38–7.47 (*m*, $6CH_{arom}$); 7.52–7.54 (*m*, $1CH_{arom}$); 7.69–7.72 (*m*, $2CH_{arom}$). ^{13}C NMR: 93.6, 111.4 (C_{Fur}, C(4)); 110.2, 110.5, 126.2, 127.7, 127.9, 128.2, 128.3, 128.4, 128.5, 128.6, 129.1, 129.3 ($18CH_{arom}$); 131.7, 132.2, 141.3, 141.7 ($4C_{arom}$); 154.9 (C(5)). IR (KBr): 3061*m*, 3024*m*, 2956*m*, 1676*m*, 1627*m*, 1599*m*, 1491*s*, 1448*s*, 1223*s*, 1153*s*, 1063*s*, 1017*m*, 882*m*, 851*m*, 746*vs*, 700*vs*, 592*m*. Anal. calcd for $C_{25}H_{18}O_2S$ (382.47): C 78.51, H 4.74, S 8.38; found: C 78.38, H 4.82, S 8.38.

4.3.9. 1-[2-Methyl-3-phenyl-3-(thiophen-2-yl)thiiran-2-yl]ethanone (5b)

Pale-orange crystals; m.p. 38.8–40.2°C; yield: 180 mg (66%). ^{1}H NMR: 1.69, 1.72 ($2CH_3$); 6.89–6.91 (*m*, $1CH_{arom}$); 6.99–7.01 (*m*, $1CH_{arom}$); 7.18–7.22 (*m*, $1CH_{arom}$); 7.27–7.34 (*m*, $3CH_{arom}$); 7.49–7.51 (*m*, $2CH_{arom}$). ^{13}C NMR: 21.1, 28.8 ($2CH_3$); 58.5, 60.7 (C(2),C(3)); 126.2, 126.9, 127.9, 128.0, 128.4, 129.3 ($8CH_{arom}$); 140.3, 145.2 ($2C_{arom}$); 207.2 (C=O). IR (KBr): 3075*m*, 3063*m*, 2933*m*, 1685*vs* (C=O), 1442*s* 1359*s*, 1347*s*, 1261*s*, 1233*s*, 1097*m*, 850*m*, 726*s*, 720*s*, 694*s*. Anal. calcd for $C_{15}H_{14}OS_2$ (342.50): C 65.66, H 5.14, S 23.37; found: C 65.54, H 5.58, S 23.41.

4.3.10. 1-[2-Methyl-3-phenyl-3-(selenophen-2-yl)thiiran-2-yl]ethanone (5c)

Pale-brown crystals; m.p. 42–44°C; yield: 160 mg (50%). ^{1}H NMR: 1.70, 1.78 ($2CH_3$); 7.14–7.16 (*m*, $2CH_{arom}$); 7.24–7.34 (*m*, $3CH_{arom}$); 7.48–7.50 (*m*, $2CH_{arom}$); 7.90 (*dd*, $J_{H,H}$ = 5.1 Hz, $J_{H,H}$ = 2.0 Hz, $1CH_{arom}$). ^{13}C NMR: 21.0, 28.8 ($2CH_3$); 60.6, 60.8 (C(2), C(3)); 128.1, 128.5, 129.2, 129.5, 130.0, 132.3 ($8CH_{arom}$); 140.7, 152.4 ($2C_{arom}$); 207.3 (C=O). IR (KBr): 3060*m*, 3003*m*, 2920*m*, 1685*vs* (C=O), 1492*m*, 1445*m*, 1356*s*, 1236*s*, 1097*m*, 1055*m*, 979*m*, 777*m*, 736*s*, 704*s*, 688*s*. Anal. calcd for $C_{15}H_{14}OSSe$ (321.30): C 56.07, H 4.39, S 9.98; found: C 56.30, H 4.73, S 9.98.

4.3.11. 3,3,4-Triphenyl-4-(thiophen-2-yl)thietan-2-one (6a)

Pale-yellow crystals; m.p. 145°C (dec) ([20]: 146°C (dec)); yield: 240 mg (60%). ^{1}H NMR: 6.59 (*dd*, $J_{H,H}$ = 3.8 Hz, $J_{H,H}$ = 1.2 Hz, $1CH_{arom}$); 6.67 (*dd*, $J_{H,H}$ = 5.0 Hz, $J_{H,H}$ = 3.8 Hz, $1CH_{arom}$); 7.04–7.10 (*m*, $6CH_{arom}$); 7.21–7.28 (*m*, $8CH_{arom}$); 7.43–7.46 (*m*, $2CH_{arom}$). ^{13}C NMR: 62.4, 94.2 (C(3),C(4)); 126.3, 126.9, 127.2, 127.6, 127.7, 127.9, 128.6, 129.2, 130.0, 130.2 (18 CH_{arom}); 137.2, 138.5, 140.1, 150.8 (4 C_{arom}); 193.5 (C=O).

4.3.12. 3,3,4-Triphenyl-4-(selenophen-2-yl)thietan-2-one (6b)

Pale-yellow solid; m.p. 162°C (dec) ([20]: 163°C (dec)); yield: 250 mg (56%). ^{1}H NMR: 6.75 (*d*, $J_{H,H}$ = 3.7 Hz, $1CH_{arom}$); 6.91 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 4.0 Hz, $1CH_{arom}$); 7.03–7.11 (*m*, $5CH_{arom}$); 7.21–7.29 (*m*, $8CH_{arom}$); 7.49–7.50 (*m*, $2CH_{arom}$); 7.79 (*d*, $J_{H,H}$ = 5.6 Hz, $1CH_{arom}$). ^{13}C NMR: 64.3, 94.3 (C(3),C(4)); 127.2, 127.3, 127.6, 127.7, 127.8, 127.9 128.9, 129.0, 129.2, 130.0, 132.0, 133.1 ($18CH_{arom}$); 137.2, 138.6, 140.7, 159.1 ($4C_{arom}$); 193.6 (C=O).

4.3.13. 4-(Furan-2-yl)-3,3,4-triphenylthietan-2-one (6c)

Pale-brown crystals; m.p. 146°C (dec); yield: 240 mg (63%). ^{1}H NMR: 5.85 (*d*, $J_{H,H}$ = 3.2 Hz, $1CH_{arom}$); 6.12 (*dd*, $J_{H,H}$ = 3.2 Hz, $J_{H,H}$ = 1.9 Hz, $1CH_{arom}$); 7.02–7.11 (*m*, $5CH_{arom}$); 7.19–7.22 (*m*, $3CH_{arom}$); 7.25–7.29 (*m*, $6CH_{arom}$); 7.46–7.48 (*m*, $2CH_{arom}$). ^{13}C NMR: 60.0, 92.5 (C(3),C(4)); 110.2, 112.6, 127.0, 127.3, 127.4, 127.5, 127.6, 127.7, 127.9, 129.0, 130.2, 143.1 ($18CH_{arom}$); 137.8, 138.2, 138.4, 154.8 ($4C_{arom}$); 193.4 (C=O). IR (KBr): 3060*m*, 3025*m*, 1746*vs* (C=O), 1609*s*, 1597*m*, 1486*s*, 1439*s*, 1198*m*, 1144*m*, 1049*s*, 1021*m*, 831*s*, 818*s*, 732*vs*, 691*vs*, 650*m*, 631*m*. Anal. calcd for $C_{25}H_{18}O_2S$ (382.47): C 78.51, H 4.74, S 8.38; found: C 78.48, H 4.73 S 8.30.

4.3.14. 4-(4-Chlorophenyl)-4-(selenophen-2-yl)but-3-en-2-one (7a)

Beige crystals: m.p. 62–64°C: yield: 120 mg (39%). ^{1}H NMR: 1.97 (CH_3); 6.61 (*s*, 1CH); 7.06 (*dd*, $J_{H,H}$ = 3.9 Hz, $J_{H,H}$ = 1.0 Hz, 1CH); 7.24–7.29 (*m*, 3CH); 7.43–7.45 (*m*, 2CH); 8.09 (*dd*, $J_{H,H}$ = 5.5 Hz, $J_{H,H}$ = 1.2 Hz, 1CH). ^{13}C NMR: 30.8 (CH_3); 125.4, 128.7, 130.3, 130.8, 133.0, 134.1 ($7CH_{arom}$, CH=); 134.9, 136.8, 148.2, 151.0 ($3C_{arom}$, C=); 197.9 (C=O). IR (KBr): 3104*m*, 2990*m*, 1679*s* (C=O), 1594*s*, 1572*s*, 1486*s*, 1429*m*, 1375*m*, 1350*m*, 1214*m*, 1176*s*, 1090*m*, 1014*s*, 970*m*, 840*s*, 777*s*, 717*s*, 574*s*. Anal. calcd for $C_{14}H_{11}ClOSe$ (309.65): C 54.30, H 3.58; found: C 54.43, H 3.66.

4.3.15. (S)-1-(1-Benzoylpyrrolidin-2-yl)-3,3-di(thiophen-2-yl)prop-2-en-1-one (7e)

Yellow viscous oil; yield: 330 mg (85%); mixture of two rotamers in the ratio *ca*. 80:20; according to ref. [22]. ^{1}H NMR (*major rotamer*): 1.84–2.25 (*m*, CH_2CH_2); 3.52–3.85 (*m*,

CH_2N); 4.85–4.92 (*m*, CHN); 6.87 (*s*, CH=); 7.04–7.59 (*m*, $11CH_{arom}$). ^{13}C NMR: 25.3 (CH_2); 28.7 (CH_2); 50.2 (CH_2N); 65.3 (CHN); 121.7 (CH=); 126.8, 127.3, 127.7, 127.8, 128.2, 128.4, 130.0, 130.2, 130.4 ($11CH_{arom}$); 136.4, 138.1, 141.1, 145.4 ($3C_{arom}$; C=); 169.5 (C=O); 196.9 (C=O).

4.3.16. (S)-(1-Benzoylpyrrolidin-2-yl)-3,3-di(selenophen-2-yl)prop-2-en-1-one (7f)

Yellow viscous oil; yield: 380 mg (78%); mixture of two rotamers in the ratio *ca*. 80:20; according to ref. [22]. ^1H NMR (*major rotamer*): 1.81–2.20 (*m*, CH_2CH_2); 3.46–3.80 (*m*, CH_2); 4.81–4.85 (*m*, CHN); 6.78 (*s*, CH=); 7.06–8.20 (*m*, $11CH_{arom}$). ^{13}C NMR: 25.3 (CH_2); 29.9 (CH_2); 49.8 (CH_2N); 65.3 (CHN); 121.6 (CH=); 127.9, 128.6, 129.2, 129.0, 130.5, 132.4, 132.7, 133.9, 134.0 ($11CH_{arom}$); 136.6, 144.2, 145.3, 151.7 ($3C_{arom}$; C=); 169.5 (C=O), 197.0 (C=O).

4.3.17. 3-(4-Chlorophenyl)-1-phenyl-3-(selenophen-2-yl)prop-2-en-1-one (7g)

Brown-orange crystals; m.p. 142–144°; yield: 165 mg (44%). ^1H NMR: 7.19–7.22 (*m*, 2CH); 7.30–7.34 (*m*, 1CH); 7.35–7.40 (*m*, 4CH); 7.55–7.64 (*m*, 5CH); 8.09 (*dd*, $J_{H,H} = 5.2$ Hz, $J_{H,H} = 1.6$ Hz, 1CH). ^{13}C NMR: 121.3, 128.3, 128.4, 128.5, 130.4, 130.8, 132.7, 132.8, 133.8 ($12CH_{arom}$, CH=); 134.5, 137.1, 138.6, 149.6, 151.4 ($4C_{arom}$, C=); 190.4 (C=O). IR (KBr): 3101*m*, 3053*m*, 1647*s* (C=O), 1568*s*, 1555*s*, 1486*s,* 1426*m*, 1385*m*, 1264*m*, 1220*s*, 1173*m*, 1087*m*, 1021*s*, 1011*s*, 907*m*, 780*s*, 723*s*, 691*s*, 631*s*. Anal. calcd for $C_{19}H_{13}ClOSe$ (371.72): C 61.39, H 3.53; found: C 61.37, H 3.56.

4.3.18. 1-Phenyl-3,3-di(thiophen-2-yl)prop-2-en-1-one (7h)

Yellow crystals; m.p. 82–84°C; yield: 230 mg (78%). ^1H NMR: 6.98 (*dd*, $J_{H,H} = 5.0$ Hz, $J_{H,H} = 3.6$ Hz, 1CH); 7.09 (*dd*, $J_{H,H} = 5.1$ Hz, $J_{H,H} = 3.8$ Hz, 1CH); 7.13 (*s*, 1CH); 7.16 (*d*, $J_{H,H} = 3.5$ Hz, $J_{H,H} = 1.1$ Hz, 1CH); 7.23 (*d*, $J_{H,H} = 3.8$ Hz, $J_{H,H} = 1.1$ Hz, 1CH); 7.35 (*d*, $J_{H,H} = 5.0$ Hz, $J_{H,H} = 1.1$ Hz, 1CH); 7.39–7.45 (*m*, 3CH); 7.45–7.51 (*m*, 1CH); 7.91 (*d*, $J_{H,H} = 1.2$ Hz, 1CH); 7.93 (*d*, $J_{H,H} = 1.2$ Hz, 1CH). ^{13}C NMR: 122.8, 126.8, 127.8, 127.9, 128.0, 128.4, 128.6, 129.8, 130.2, 132.6 ($11CH_{arom}$, CH=); 138.3, 138.8, 139.8, 145.0 ($3C_{arom}$, C=); 191.9 (C=O). IR (KBr): 3117*m*, 3094*m*, 3063*m,* 2920*m*, 1635*s* (C=O); 1568*s*, 1524*m*, 1445*m*, 1432*m*, 1315*m*, 1268*s*, 1242*m*, 1109*m*, 1059*m*, 1021*m*, 853*m*, 831*m*, 777*m*, 729*s,* 707*s*. Anal. calcd for $C_{17}H_{12}OS_2$ (296.41): C 68.89, H 4.08, S 21.64; found: C 68.89, H 4.20, S 21.49.

4.3.19. 3-Methyl-4,4-di(thiophen-2-yl)but-3-en-2-one (7i)

Pale viscous oil; yield: 130 mg (52%). ^1H NMR: 1.84, 2.09 ($2CH_3$); 6.90, 6.98 (2*d*, $J_{H,H} = 3.2$ Hz, $2CH_{arom}$); 7.31 (*m*, CH_{arom}). ^{13}C NMR: 19.1, 29.3 ($2CH_3$); 126.8, 127.1, 127.4, 128.3, 129.3, 130.0 ($6CH_{arom}$); 129.6, 139.7, 142.5, 143.1 ($2C_{arom}$, 2C=); 206.9 (C=O). IR (KBr): 2952*m*, 2920*m*, 1673*vs* (C=O), 1439*s* 1347*m*, 1277*m*, 1239*m*, 1179*m*, 1100*m*, 1033*m*, 983*m*, 856*m*, 840*m*, 770*m*, 685*s*. Anal. calcd for $C_{13}H_{12}OS_2$ (248.36): C 62.87, H 4.87, S 25.82; found: C 62.90, H 5.09, S 25.84.

4.3.20. 3-Methyl-4,4-di(selenophen-2-yl)but-3-en-2-one (7j)

Brown-orange crystals; m.p. 36.7–38.3°C; yield: 160 mg (47%). ^1H NMR: 2.00, 2.14 ($2CH_3$); 7.17–7.18 (*m*, $1CH_{arom}$); 6.21–7.23 (*m*, $1CH_{arom}$); 7.28–7.29 (*m*, $1CH_{arom}$); 7.30–7.32 (*m*, $1CH_{arom}$); 8.14 (*dt*, $J_{H,H} = 5.5$ Hz, $J_{H,H} = 0.8$ Hz, $2CH_{arom}$). ^{13}C NMR:

19.2, 29.3 ($2CH_3$); 129.2, 129.3, 131.1, 132.1, 133.3, 134.3 ($6CH_{arom}$); 133.8, 138.4, 149.0, 149.9 ($2C_{arom}$, 2C=); 207.2 (C=O). IR (KBr): 3107*m*, 2958*m*, 2914*m*, 1676*vs* (C=O), 1616*m*, 1578*m*, 1515*m*, 1420*s* 1353*s*, 1280*m*, 1239*m*, 1223*m*, 1100*m*, 1046*m*, 983*m*, 853*m*, 827*m*, 707*s*. Anal. calcd for $C_{13}H_{12}OSe_2$ (342.15): C 45.63, H 3.54; found: C 45.44, H 3.65.

4.3.21. (Z,E)-2-Methyl-1,3-diphenyl-3-(selenophen-2-yl)prop-2-en-1-one (7n)

Beige solid; m.p. 116°C (dec.); yield: 130 mg (37%). ^{1}H NMR: 2.06, 2.30 ($2CH_3$); 6.94 (*dd*, $J_{H,H} = 5.6$ Hz, $J_{H,H} = 3.8$ Hz, CH_{arom}); 6.99 (*dd*, $J_{H,H} = 3.8$ Hz, $J_{H,H} = 0.7$ Hz, CH_{arom}); 7.06–7.08 (*m*, CH_{arom}); 7.12–7.15 (*m*, CH_{arom}); 7.24–7.27 (*m*, CH_{arom}); 7.34 (*dd*, $J_{H,H} = 5.6$ Hz, $J_{H,H} = 3.8$ Hz, CH_{arom}); 7.37–7.50 (*m*, CH_{arom}); 7.73 (*dd*, $J_{H,H} = 5.6$ Hz, $J_{H,H} = 1.1$ Hz, CH_{arom}); 7.80 (*dd*, $J_{H,H} = 5.6$ Hz, $J_{H,H} = 1.1$ Hz, CH_{arom}); 7.85–7.87 (*m*, CH_{arom}); 7.92 (*dd*, $J_{H,H} = 5.6$ Hz, $J_{H,H} = 0.7$ Hz, CH_{arom}); 8.22 (*dd*, $J_{H,H} = 5.6$ Hz, $J_{H,H} = 0.7$ Hz, CH_{arom}). ^{13}C NMR: 19.8 (CH_3); 20.2 (CH_3); 127.7, 127.9, 128.1, 128.2, 128.4, 128.5, 129.0, 129.1, 129.2, 129.4, 130.1, 131.2, 131.4, 132.5, 133.0, 133.1 ($26CH_{arom}$); 134.2, 134.8, 135.9, 137.0, 137.7, 138.5, 141.1, 141.4, 149.1, 150.0 ($6C_{arom}$, 4C=); 200.6, 201.0 (2C=O). IR (KBr): 3091*m*, 3053*m*, 2939*m*, 2914*m*, 1651*s* (C=O), 1594*m*, 1578*m*, 1448*m*, 1309*m*, 1245*m*, 1217*m*, 1157*m*, 1005*m*, 948*m*, 783*m*, 701*vs*, 641*m*. Anal. calcd. for $C_{20}H_{16}OSe$ (351.30): C 68.38, H 4.59; found C 68.06, H 4.57.

4.3.22. 2-Methyl-1-phenyl-3,3-di(thiophen-2-yl)prop-2-en-1-one (7o)

Beige crystals; m.p. 115–117°C; yield: 240 mg (77%). ^{1}H NMR: 2.32 (*s*, CH_3); 6.71 (*dd*, $J_{H,H} = 5.4$ Hz, $J_{H,H} = 3.6$ Hz, $1CH_{arom}$); 6.88 (*dd*, $J_{H,H} = 3.6$ Hz, $J_{H,H} = 1.0$ Hz, $1CH_{arom}$); 7.11–7.14 (*m*, $2CH_{arom}$); 7.18 (*dd*, $J_{H,H} = 3.5$ Hz, $J_{H,H} = 1.1$ Hz, $1CH_{arom}$); 7.34–7.37 (*m*, $2CH_{arom}$); 7.44–7.47 (*m*, $2CH_{arom}$); 7.83–7.85 (*m*, $2CH_{arom}$) ^{13}C NMR: 20.2 (CH_3); 126.5, 126.8, 126.9, 127.5, 128.3, 129.0, 129.1, 129.7, 132.8 ($11CH_{arom}$); 132.8, 136.2, 137.0, 142.1, 143.0 ($3C_{arom}$, 2C=); 200.2 (C=O). IR (KBr): 3069*m*, 2946*m*, 2914*m*, 1651*s* (C=O), 1597*m*, 1575*m*, 1445*m*, 1366*m*, 1312*s*, 1249*s*, 1176*m*, 989*s*, 840*m*, 827*m*, 732*s*, 723*s*, 704*vs*, 647*s*. Anal. calcd for $C_{18}H_{14}OS_2$ (310.43): C 69.64, H 4.55, S 20.66; found: C 69.62, H 4.63, S 20.58.

4.3.23. 2-Methyl-1-phenyl-3,3-di(selenophen-2-yl)prop-2-en-1-one (7p)

Pale-brown crystals; m.p. 112–114°C; yield: 140 mg (35%). ^{1}H NMR: 2.27 (*s*, CH_3); 6.94 (*dd*, $J_{H,H} = 5.6$ Hz, $J_{H,H} = 3.8$ Hz, $1CH_{arom}$); 7.06 (*dd*, $J_{H,H} = 3.8$ Hz, $J_{H,H} = 1.0$ Hz, $1CH_{arom}$); 7.34–7.39 (*m*, $4CH_{arom}$); 7.46–7.48 (*m*, $1CH_{arom}$); 7.83–7.85 (*m*, $3CH_{arom}$); 8.16 (*dd*, $J_{H,H} = 5.6$ Hz, $J_{H,H} = 1.0$ Hz, $1CH_{arom}$). ^{13}C NMR: 20.3 (CH_3); 128.4, 128.9, 129.0, 129.3, 130.8, 131.8, 132.8, 132.9, 133.5 ($11CH_{arom}$); 133.1, 135.6, 136.1, 148.6, 149.8, ($3C_{arom}$, 2C=); 200.4 (C=O). IR (KBr): 3091*m*, 3075*m*, 3056*m*, 1647*vs* (C=O), 1591*m*, 1578*m*, 1448*m*, 1435*m*, 1312*m*, 1280*s*, 1242*m*, 1169*m*, 983*s*, 846*m*, 834*m*, 774*m*, 704*vs*, 653*m*. Anal. calcd for $C_{18}H_{14}OSe_2$ (404.22): C 53.48, H 3.49; found: C 53.06, H 3.70.

4.3.24. 3-(4-Chlorophenyl)-3-(selenophen-2-yl)-1-(thiophen-2-yl)prop-2-en-1-one (7q)

Brown crystals; m.p. 169°C (dec.); yield: 210 mg (56%). ^{1}H NMR: 7.16 (*dd*, $J_{H,H} = 5.0$ Hz, $J_{H,H} = 3.9$ Hz, 1CH); 7.20 (*dd*, $J_{H,H} = 3.9$ Hz, $J_{H,H} = 1.0$ Hz, 1CH); 7.28–7.31 (*m*, 4CH); 7.38–7.41 (*m*, 2CH); 7.64 (*dd*, $J_{H,H} = 5.0$ Hz, $J_{H,H} = 1.0$ Hz, 1CH); 7.78 (*dd*, $J_{H,H} = 3.9$ Hz, $J_{H,H} = 1.0$ Hz, 1CH); 8.14 (*dd*, $J_{H,H} = 5.6$ Hz, $J_{H,H} = 1.0$ Hz, 1CH). ^{13}C

NMR: 119.7, 128.2, 128.4, 130.3, 130.9, 131.5, 133.0, 133.7, 134.2 (9CH_{arom}, CH=); 134.5, 137.0, 146.5, 150.1, 151.4 (4C_{arom}, C=); 181.5 (C=O). IR (KBr): 3094*m*, 1628*s* (C=O), 1556*s*, 1483*s*, 1426*m*, 1413*s*, 1353*m*, 1350*m*, 1271*m*, 1226*s*, 1204*m*, 1055*m*, 986*m*, 891*m*, 853*m*, 834*m*, 720*s*, 634*s*. Anal. calcd for $C_{17}H_{11}ClOSSe$ (377.75): C 54.05, H 2.94, S 8.49; found: C 54.08, H 3.12, S 8.53.

4.3.25. 2-[Di(thiophen-2-yl)methylene]acenaphthylen-1-one (7r)

Orange crystals; m.p. 80–82°C; yield: 300 mg (87%). ^{1}H NMR: 6.62 (*d*, $J_{H,H}$ = 7.3 Hz, 1CH); 7.15 (*dd*, $J_{H,H}$ = 5.0 Hz, $J_{H,H}$ = 3.8 Hz, 1CH); 7.22 (*dd*, $J_{H,H}$ = 5.1 Hz, $J_{H,H}$ = 3.7 Hz, 1CH); 7.30 (*dd*, $J_{H,H}$ = 3.4 Hz, $J_{H,H}$ = 1.0 Hz, 1CH); 7.39 (*t*, $J_{H,H}$ = 7.4 Hz, 1CH); 7.59 (*dd*, $J_{H,H}$ = 5.2 Hz, $J_{H,H}$ = 0.7 Hz, 1CH); 7.61–7.63 (*m*, 2CH); 7.73 (*t*, $J_{H,H}$ = 7.2 Hz, 1CH); 7.78 (*d*, $J_{H,H}$ = 8.3 Hz, 1CH); 8.03 (*d*, $J_{H,H}$ = 7.0 Hz, 1CH); 8.07 (*d*, $J_{H,H}$ = 8.2 Hz, 1CH). ^{13}C NMR: 120.7, 121.4, 125.0, 127.0, 127.4, 127.8, 128.2, 128.6, 129.7, 130.6, 131.0, 133.5 (12CH_{arom}); 130.0, 131.7, 133.3, 135.6, 136.2, 138.5, 142.0, 143.1 (6C_{arom}, 2C=); 190.8 (C=O). IR (KBr): 3078*m*, 3047*m*, 1687*s* (C=O), 1622*m*, 1599*m*, 1547*s*, 1516*s*, 1489*s* 1457*m*, 1409*s*, 1359*s*, 1338*s*, 1270*s*, 1254*s*, 1222*s*, 1156*m*, 1135*m*, 1092*m*, 1024*vs*, 914*s*, 850*s*, 828*s*, 796*s*, 777*s*, 717*s*, 706*s*, 647*m*, 624*m*. Anal. calcd for $C_{21}H_{12}OS_2$ (344.45): C 73.23, H 3.51, S 18.62; found: C 73.35, H 3.52, S 18.58.

4.3.26. Phenyl-[4-phenyl-6-(thiophen-2-yl)-4,6-dihydrothieno[3,4-b]thiophen-4-yl]methanone (8)

Pink crystals; m.p. 152°C (dec.); yield: 195 mg (48%). ^{1}H NMR: 5.60 (*s*, 1CH); 6.22 (*d*, $J_{H,H}$ = 5.2 Hz, 1CH); 6.87–6.88 (*m*, 2CH); 7.00 (*dd*, $J_{H,H}$ = 5.1 Hz, $J_{H,H}$ = 3.7 Hz, 1CH); 7.09 (*d*, $J_{H,H}$ = 5.2 Hz, 1CH); 7.11–7.13 (*m*, 2CH); 7.16 (*d*, $J_{H,H}$ = 3.3 Hz, 1CH); 7.27–7.29 (*m*, 3CH); 7.36 (*d*, $J_{H,H}$ = 5.1 Hz, 1CH); 7.40–7.43 (*m*, 3CH). ^{13}C NMR: 42.2 (CH); 70.2 (C_q–Ph); 123.3, 126.8, 126.9, 127.4, 127.8, 128.3, 128.5, 128.9, 130.0, 130.1, 130.8 (15CH_{arom}); 137.2, 139.4, 139.5, 141.3, 142.8 (5C_{arom}); 203.5 (C=O). IR (KBr): 3063*m*, 3022*m*, 2923*m*, 1682*s* (C=O), 1594*m*, 1496*m*, 1445*m*, 1233*m*, 1040*m*, 995*m*, 834*m*, 742*m*, 726*m*, 694*s*, 634*m*. Anal. calcd for $C_{23}H_{16}OS_3$ (404.57): C 68.28, H 3.99, S 23.78; found: C 68.26, H 4.11, S 23.55.

4.4. Reactions of α-diazoketones 1b,c with ferrocenyl-substituted thioketones 2d–f – general procedure

To the solution of a thioketone **2** (1 mmol) in THF (10 mL), the corresponding α-diazoketone **1** (1 mmol) and a catalytic amount of $LiClO_4$ were added. The mixture was heated at reflux overnight. Then, the solvent was evaporated and the crude product was purified by FCC (petroleum ether/CH_2Cl_2 2:8).

4.4.1. 4-Ferrocenyl-4-phenylbut-3-en-2-one (7b)

Red crystals; m.p. 78.8–80.7°C; yield: 185 mg (56%). ^{1}H NMR: 1.73 (*s*, CH_3); 4.19 (*s*, 5CH(Fc)); 4.33 (*brs*, 2CH(Fc)); 4.43 (*brs*, 2CH(Fc)); 6.54 (*brs*, CH=); 7.28–7.31 (*m*, 2CH_{arom}); 7.41–7.48 (*m*, 3CH_{arom}). ^{13}C NMR: 30.2 (CH_3); 68.5, 70.9 (4CH(Fc)); 69.9 (5CH(Fc)); 83.9 (C(Fc)); 124.2, 128.1, 128.4 (6CH_{arom}); 138.9, 156.7 (C_{arom}, C=); 199.0 (C=O). IR (KBr): 3098*m*, 3088*m*, 1635*vs*, 1578*vs*, 1489*m*, 1435*m*, 1378*m*, 1356*s*, 1271*vs*,

1204*m*, 1154*m*, 1106*m*, 1055*m*, 998*m*, 941*m*, 843*m*, 821*s*, 720*s*, 704*s*, 603*w*, 489*s*. Anal. calcd for $C_{20}H_{18}FeO$ (330.20): C 72.75, H 5.49; found: C 72.56, H 5.48.

4.4.2. 4-Ferrocenyl-4-(thiophen-2-yl)but-3-en-2-one (7c)

Red crystals; m.p. 106.2–108.7°C; yield: 218 mg (65%). ^{1}H NMR: 1.88 (*s*, CH_3); 4.23 (*s*, 5CH(Fc)); 4.41–4.42 (*m*, 2CH(Fc)); 4.43–4.44 (*m*, 2CH(Fc)); 6.56 (brs, CH=); 7.03–7.05 (m, $1CH_{arom}$); 7.10 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 4.8 Hz, $1CH_{arom}$); 7.47 (*d*, $J_{H,H}$ = 5.4 Hz, $1CH_{arom}$). ^{13}C NMR: 29.5 (CH_3); 68.5, 70.9 (4CH(Fc)); 70.2 (5CH(Fc)); 84.1 (C(Fc)); 126.4, 126.8, 126.9, 128.7 ($3CH_{arom}$, CH=); 138.3, 148.2 (C_{arom}, C=); 199.2 (C=O). IR (KBr): 3077*w*, 3066*w*, 1628*vs*, 1584*s*, 1521*m*, 1451*w*, 1451*w*, 1363*m*, 1271*vs*, 1204*w*, 1103*w*, 1002*w*, 929*w*, 840*w*, 818*m*, 707*m*, 501*m*. Anal. calcd for $C_{18}H_{16}FeOS$ (336.23): C 64.30, H 4.80, S 9.54; found: C 64.28, H 4. 85, S 9.51.

4.4.3. 4-Ferrocenyl-4-(selenophen-2-yl)but-3-en-2-one (7d)

Red crystals; m.p. 107.9–111.0°C; yield: 241 mg (63%). ^{1}H NMR: 1.96 (*s*, CH_3); 4.34 (*s*, 5CH(Fc)); 4.51–4.64 (*m*, 4CH(Fc)); 6.51 (*brs*, 1CH=); 7.15 (*brs*, $1CH_{arom}$); 7.31 (*brs*, $1CH_{arom}$); 8.15 (*d*, $J_{H,H}$ = 4.8 Hz, $1CH_{arom}$). ^{13}C NMR: 29.7 (CH_3); 68.6, 70.8 (4CH(Fc)); 70.1 (5CH(Fc)); 84.1 (C(Fc)); 125.6, 129.1, 131.0, 132.9 ($3CH_{arom}$, CH=); 144.1, 150.4 (C_{arom}, C=); 199.4 (C=O). IR (KBr): 3104*m*, 3091*m*, 1638*vs*, 1591*s*, 1534*m*, 1464*m*, 1416*m*, 1366*m*, 1271*vs*, 1220*m*, 1201*m*, 1106*m*, 1002*m*, 843*m*, 824*m*, 793*m*, 704*s*. Anal. calcd for $C_{18}H_{16}FeOSe$ (383.12): C 56.43, H 4.21; found: C 56.24, H 4.23.

4.4.4. 3-Ferrocenyl-1,3-diphenylprop-2-en-1-one (7k)

Red crystals; m.p. 99.0–101.5°C; yield: 192 mg (49%). ^{1}H NMR: 4.23 (*s*, 5CH(Fc)); 4.43–4.46 (*m*, 4CH(Fc)); 7.23 (*brs*, CH=); 7.29–7.36 (*m*, $5CH_{arom}$); 7.37–7.41 (*m*, $2CH_{arom}$); 7.46–7.50 (*m*, $1CH_{arom}$); 7.86–7.88 (*m*, $2CH_{arom}$). ^{13}C NMR: 68.6, 70.8 (4CH(Fc)); 70.0 (5CH(Fc)); 84.2 (C(Fc)); 118.6, 127.6, 127.7, 128.2, 128.3, 128.4, 132.1 ($10CH_{arom}$, CH=); 139.1, 139.3, 157.7 ($2C_{arom}$, C=); 190.7 (C=O). IR (KBr): 3055*w*, 3033*w*, 3011*w*, 1638*m*, 1591*m*, 1578*s*, 1562*vs*, 1489*m*, 1445*s*, 1391*m*, 1277*m*, 1220*s*, 1100*m*, 1030*m*, 1014*s*, 964*m*, 818*m*, 767*m*, 717*m*, 694*s*, 631*s*, 476*s*. Anal. calcd for $C_{25}H_{20}FeO$ (392.27): C 76.55, H 5.14; found: C 76.44, H 5.16.

4.4.5. 3-Ferrocenyl-1-phenyl-3-(thiophen-2-yl)prop-2-en-1-one (7l)

Red crystals; m.p. 114.2–116.9°C; yield: 192 mg (61%). ^{1}H NMR: 4.33 (*s*, 5CH(Fc)); 4.50 (*brs*, 2CH(Fc)); 4.59 (*brs*, 2CH(Fc)); 6.90 (*brs*, CH=); 7.00 (*brs*, $1CH_{arom}$); 7.07 (*brs*, $1CH_{arom}$); 7.28–7.48 (*m*, $4CH_{arom}$); 7.84 (*d*, $J_{H,H}$ = 6.6 Hz, $2CH_{arom}$). ^{13}C NMR: 68.5, 70.7 (4CH(Fc)); 70.2 (5CH(Fc)); 84.4 (C(Fc)); 121.5, 126.4, 126.5, 128.1, 128.4, 128.7, 132.1 ($8CH_{arom}$, CH=); 138.8, 148.1 (C_{arom}, C=); 192.1 (C=O). IR (KBr): 1635*vs*, 1575*m*, 1524*w*, 1445*w*, 1315*w*, 1274*m*, 1103*w*, 1062*w*, 1033*w*, 998*w*, 824*m*, 710*m*, 495*m*. Anal. calcd for $C_{23}H_{18}FeOS$ (398.30): C 69.36, H 4.56, S 8.05; found: C 69.34, H 4.55, S 8.26.

4.4.6. 3-Ferrocenyl-1-phenyl-3-(selenophen-2-yl)prop-2-en-1-one (7m)

Red crystals; m.p. 95.6–98.7°C; yield: 235 mg (53%). ^{1}H NMR: 4.30 (*s*, 5CH(Fc)); 4.47 (*brs*, 2CH(Fc)); 4.60 (*brs*, 2CH(Fc)); 7.11 (*brs*, CH=); 7.15 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 5.4 Hz, $1CH_{arom}$); 7.17–7.19 (*m*, $1CH_{arom}$); 7.35–7.40 (*m*, $2CH_{arom}$); 7.44–7.48 (*m*, $1CH_{arom}$); 7.87 (*d*, $J_{H,H}$ = 7.2 Hz, $2CH_{arom}$); 8.02 (*d*, $J_{H,H}$ = 5.4 Hz, $1CH_{arom}$). ^{13}C NMR: 68.8, 70.5

(4CH(Fc)); 70.1 (5CH(Fc)); 84.7 (C(Fc)); 120.8, 128.2, 128.4, 128.8, 131.2, 132.1, 132.5 ($8CH_{arom}$, CH=); 138.9, 144.7, 150.3 ($2C_{arom}$, C=); 192.1 (C=O). IR (KBr): 3082*w*, 3053*w*, 3025*w*, 1632*vs*, 1594*m*, 1568*s*, 1530*m*, 1442*m*, 1315*m*, 1274*s*, 1223*m*, 1176*w*, 1103*m*, 1062*m*, 1033*m*, 998*m*, 859*s*, 821*s*, 767*s*, 704*vs*, 660*w*, 599*w*, 501*s*, 482*m*. Anal. calcd for $C_{23}H_{18}FeOSe$ (445.19): C 62.05, H 4.08; found: C 61.96, H 4.06.

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