Photochemical Behavior of Iodoheterocyclic Derivatives in the Presence of Electron-Poor Olefins

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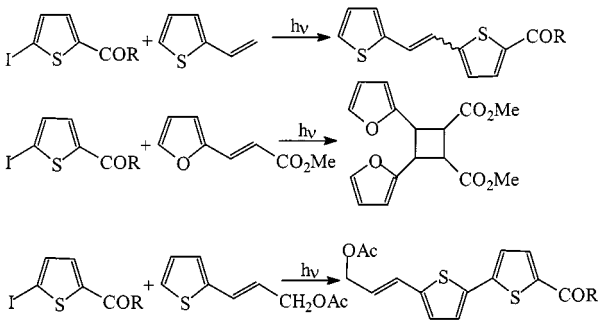
Photochemical reactions of some haloheterocycles bearing electron-withdrawing groups **1a–d** with electron-poor olefins **2a–c** gave the addition products **3a–f** and **3h–m** in good yields. Other products obtained were the corresponding olefins **4a–k** and the alkanes **3g**. These reactions involve homolytic cleavage of the carbon–halogen bond to give the corresponding radical. The nature of these radicals has been studied. Ab initio calculations at the MP2/6–31G* level are supportive of the formation of σ radicals. These radicals are electrophilic and interact with the HOMOs of the electron-poor olefins.

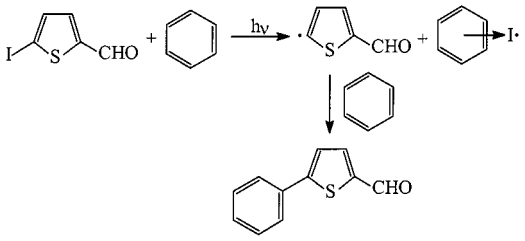
Introduction

Some years ago, we reported that haloheterocycles bearing electron-withdrawing substituents (such as $COCH_3$ or CHO) are capable of reacting with arylalkenes under irradiation conditions. This reaction allowed us to obtain the corresponding products of substitution at the alkene as *E*/*Z* mixtures (Scheme 1).[1] On the other hand, when the alkene was substituted with an electron-withdrawing group, we found that no coupling reaction with halo-substituted heterocycles occurred. In the latter case, dimerization of the alkene was in fact observed (Scheme 1).[2] When a weakly electron-withdrawing group (CH_2OAc) was present on the arylalkene, reaction did take place, but substitution was observed on the aromatic part of the molecule (Scheme 1).[3]



Scheme 1. Reactions of halogenothiophenes with arylalkenes

Mechanistic studies of the photochemical reaction of halo-substituted heterocycles in the presence of aromatic compounds have shown that the process involves cleavage of the C–X bond with subsequent formation of the corresponding heterocyclic radical and of halogen/arene complexes (Scheme 2).[4]



Scheme 2. Mechanism of the photochemical arylation of halogenothiophenes

In view of the fact that the 5-thienyl radical obtained in this reaction bears an electron-withdrawing group, we considered it to be an electrophilic radical, and thus capable of reacting with electron-rich olefins.[5] This is consistent with the aforementioned results. However, we recently found that halothiophene derivatives can also react with electron-poor olefins, such as acrylonitrile, to give the corresponding addition products in good yields.[6]

In this paper, we present the results obtained following a study of the photochemical behavior of 5-haloheterocycles bearing electron-withdrawing groups in the presence of electron-poor olefins. In particular, we studied whether the aforementioned reactivity of haloheterocyclic derivatives towards electron-poor olefins was general and, if so, whether this behavior could be rationalized in terms of the electrophilicities of the radicals generated in reactions of this type.

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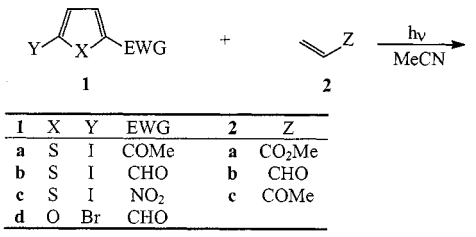
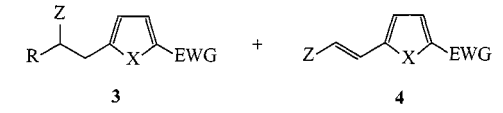
To this end, we studied the electronic properties of these radicals and of their parent species.

Results and Discussion

In this study, we used as halo-substituted heterocycles 2-acetyl-5-iodothiophene (**1a**), 5-iodothiophene-2-carbaldehyde (**1b**), 2-iodo-5-nitrothiophene (**1c**), and 5-bromofuran-2-carbaldehyde (**1c**). As olefins we used methyl acrylate (**2a**), acrolein (**2b**), 3-butenone (**2c**), cyclopentenone (**2d**), and cyclohexenone (**2e**) (Scheme 3).



1	X	Y	EWG	2	Z
a	S	I	COMe	a	CO_2Me
b	S	I	CHO	b	CHO
c	S	I	NO_2	c	COMe
d	O	Br	CHO		



3	R	X	Z	EWG	4	X	Z	EWG
a	I	S	CO_2Me	COMe	a	S	CO_2Me	COMe
b	I	S	CO_2Me	CHO	b	S	CO_2Me	CHO
c	I	S	CO_2Me	NO_2	c	S	CO_2Me	NO_2
d	Br	O	CO_2Me	CHO	d	O	CO_2Me	CHO
e	I	S	CHO	COMe	e	S	CHO	COMe
f	I	S	CHO	CHO	f	S	CHO	CHO
g	H	S	CHO	CHO	g	S	CHO	NO_2
h	I	S	CHO	NO_2	h	O	CHO	CHO
i	Br	O	CHO	CHO	i	S	COMe	COMe
j	I	S	COMe	COMe	j	S	COMe	CHO
k	I	S	COMe	CHO	k	S	COMe	NO_2
l	I	S	COMe	NO_2				
m	Br	O	COMe	CHO				

Scheme 3. Photochemical reactions of halogeno-substituted heterocycles with electron-poor olefins

Irradiation of these substrates in acetonitrile in the presence of **2a**, **2b**, or **2c** gave a mixture of the addition product (**3a–3f**, **3h–3m**) and the substitution product (**4a–4k**) (Scheme 3, Table 1).

It is interesting to note that the photochemical behavior is not constant, but rather depends on the nature of the haloheterocycle used and on the electron-poor olefin. In particular, when **1a** was used we obtained a mixture of the addition products **3a**, **3e**, and **3j** together with the substitution products **4a**, **4e**, and **4i**. Nevertheless, **4a** and **4i** were obtained only in very low yields, and the reaction gave appreciable yields of **4e**. The substitution product became predominant when the nitro-substituted iodothiophene **1c** was used as substrate. In this case, we observed an interesting dependence on the irradiation time. When the irradiation was maintained for 1 h, the addition products **3h** and **3l** predominated. However, after irradiation for 2–2.5 h, the main products were those of substitution, **4c** and **4g**. This behavior would seem to show that the substitution products

Table 1. Photochemical reactions of haloheterocyclic derivatives with electron-poor olefins

Heterocycle	Olefin	Reaction time [h]	Product	Yield [%][a]
1a	**2a**	1	**3a**	61
			4a	7
1b	**2a**	1	**3b**	64
			4b	29
1c	**2a**	2.5	**3c**	20
			4c	44
1d	**2a**	1	**3d**	57
			4d	16
1a	**2b**	1	**3e**	60
			4e	27
1b	**2b**	1	**3f**	23
			4f	44
			3g	23
		2	**3f**	26
			3g	57
1c	**2b**	1	**3h**	60
			4g	20
		2	**3h**	34
			4g	45
1d	**2b**	2	**3i**	56
			4h	26
1a	**2c**	1	**3j**	75
			4i	19
1b	**2c**	1	**3k**	72
			4j	20
1c	**2c**	1	**3l**	67
			4k	18
1d	**2c**	1	**3m**	17

[a] All yields refer to isolated chromatographically pure compounds.

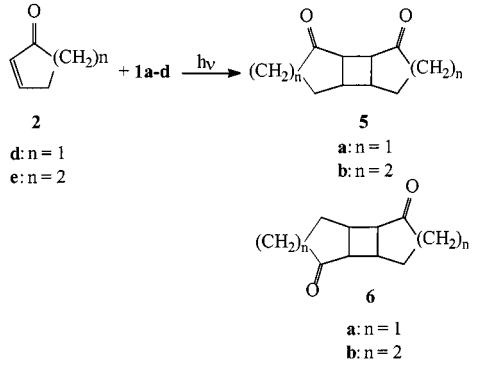
are derived from the addition products through photochemical elimination of HI.

Irradiation of 5-iodothiophene-2-carbaldehyde (**1b**) in the presence of methyl acrylate (**2a**) gave a 6:4 mixture of the addition product **3b** and the substitution product **4b**. When the same substrate was irradiated in the presence of 3-pentenone, a 2:1 mixture of the addition product **3k** and the olefin **4j** was obtained. When **1b** was irradiated for 1 h in the presence of acrolein, the main product was the olefin **4f**, which was accompanied by the dehalogenated product **3g**. When the same reaction was allowed to proceed for 2 h, **3g** became the main product and was accompanied by some addition product **3f**.

Finally, when the bromofuran derivative **1d** was irradiated in the presence of methyl acrylate, we obtained a 1:1 mixture of **3d** (the addition product) and **4d**. In the presence of acrolein, the olefin **4h** was obtained only as a by-product. When 3-butenone was used, only the addition product **3m** was obtained, albeit in low yields.

Irradiation of **1a–d** in the presence of cyclopentenone and cyclohexenone gave only the corresponding dimers **5a–b** and **6a–b** (Scheme 4). The photochemical dimerization of cyclopentenone and cyclohexenone is a well-known reaction.[7] In our project, we had hoped to observe some reaction of our substrates **1a–d** with **2d–e** in spite of this side reaction, but this was not the case.

Compounds **1a–d** cannot act as sensitizers in this reaction. The triplet energies (E_T) of our substrates can be estimated to be around 53–55 kcal mol^{-1},[4] while cyclopentenone and cyclohexenone show an E_T 70–72 kcal mol^{-1}.[7]



Scheme 4. Photochemical reactions of halogeno-substituted heterocycles with cyclopentenone and cyclohexenone

Cyclopentenone and cyclohexenone exhibit a weak absorption at λ 300 nm. Thus, direct absorption of these two substrates can account for the formation of the products. However, it is noteworthy that 3-butenone and acrolein also exhibit a weak absorption in this region of the spectrum, although we did not observe the formation of dimers in these cases.

From the aforementioned results, it is evident that the radical generated by homolytic cleavage of haloheterocyclic derivatives bearing electron-withdrawing groups reacts efficiently with electron-poor olefins giving a mixture of addition and substitution products. This behavior is apparently at variance with the supposed electrophilic properties of heterocyclic radicals bearing an electron-withdrawing group.

Calculations were performed out in order to help in understanding this behavior. The radicals presumably produced from cleavage of the iodothiophenes bearing $COCH_3$, CHO, CN, NO_2, and $COOCH_3$ were characterized theoretically, optimizing their geometries at the MP2/6–31G* level by means of the Gaussian94[8] package of programs on a K200 Pentium II/400 MHz SCSI system.

In the three cases where conformers are possible, i.e. when the substituent is $COCH_3$, CHO, or $COOCH_3$, the two species were found to differ in energy by 1.7 kcal mol^{-1}, 2.3 kcal mol^{-1}, and 0.2 kcal mol^{-1}, respectively (the preferred geometry having oxygen *cis* to sulfur in the first and second cases, and *trans* in the third). In all cases, the open-shell species was found to be a σ-type radical, with the singly-occupied orbital deeply embedded within the space of doubly-occupied *p* orbitals. This is also indicated by the phenyl-like spin density distribution observed around the ring, as reported in Table 2 along with the charge density. In the case of the three species where conformers exist, the reported values refer to the more stable form. All the radicals exhibit a spin density greater than unity at the C2 position and a strong negative density at the adjacent C3.

We have examined the reactivity patterns of the radicals in the light of previous results, as shown in Table 3. If we limit our comparison of theoretical results with experimental data to the addition/substitution ratio obtained for reaction of the radicals with $CH_2{=}CHCOCH_3$, the only substituted olefin for which the addition + substitution yield is reasonably close to 100% for three of the radicals investigated, we can tentatively correlate the charge density at the radical site with the addition/substitution ratio. It would appear that a greater negative charge at the site of attack favours the addition product. Of course, more experimental data are required to confirm this hypothesis.

Table 2. Charge density and spin density distributions in the examined radicals; the numbering scheme starts with the S atom, goes through the radical site (2), then completes the ring leaving out the H atoms, then proceeds to the heavy atoms of the substituent, the H atoms attached to the ring (in the same sequence as its heavy atoms), and ends with the H atoms of the substituents, where present

Substituent	Atomic index	Charge density	Spin density
$COCH_3$	S1	0.3451	–0.0588
	C2	–0.1386	1.5052
	C3	–0.2240	–0.5825
	C4	–0.1590	0.5217
	C5	–0.3406	–0.4152
	C6	0.5745	0.1948
	O7	–0.5274	–0.1824
	C8	–0.5775	–0.0157
	H9	0.2267	0.0445
	H10	0.2223	–0.0246
	H11	0.1917	0.0049
	H12	0.1917	0.0049
	H13	0.2151	0.0032
HCO	S1	0.3449	–0.0609
	C2	–0.1335	1.5129
	C3	–0.2216	–0.5875
	C4	–0.1570	0.5259
	C5	–0.3300	–0.4131
	C6	0.3527	0.2238
	O7	–0.4751	–0.2159
	H8	0.1620	–0.0048
	H9	0.2304	0.0445
	H10	0.2272	–0.0248
CN	S1	0.3607	–0.0520
	C2	–0.1249	1.5097
	C3	–0.2198	–0.5943
	C4	–0.1221	0.5271
	C5	–0.2591	–0.440
	C6	–0.2591	0.3468
	N7	–0.4409	–0.3185
	H8	0.2382	0.0461
	H9	0.2457	–0.0248
NO_2	S1	0.3967	–0.0725
	C2	–0.1227	1.5102
	C3	–0.2251	–0.5779
	C4	–0.1279	0.4971
	C5	–0.0326	–0.3708
	N6	0.4889	0.0932
	O7	–0.4562	–0.0400
	O8	–0.4419	–0.0627
	H9	0.2449	0.0450
	H10	0.2759	–0.0217
$COOCH_3$	S1	0.3489	–0.0639
	C2	–0.1381	1.5126
	C3	–0.2224	–0.5853
	C4	–0.1312	0.5140
	C5	–0.3542	–0.4036
	C6	0.8637	0.0968
	O7	–0.5918	–0.0932
	O8	–0.6422	0.0000
	C9	–0.1846	0.0010
	H10	0.2298	0.0446
	H11	0.2515	–0.0230
	H12	0.1902	0.0002
	H13	0.1903	–0.0001
	H14	0.1901	0.0002

Table 3. Comparison of spin density and charge density the 2-position with the addition/substitution (A/S) ratio for reaction of three of the investigated radicals with CH_2=$CHCOOCH_3$ (i), CH_2=CHCHO (ii), and CH_2=$CHCOCH_3$ (iii)

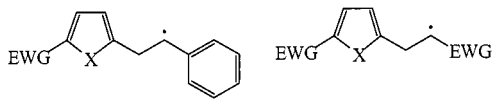
Substituent	Spin density at the 2-position of the radical	Charge density at the 2-position of the radical	A/S ratio i	ii	iii
$COCH_3$	1.5052	–0.1386	61:7	60:27	75:19
CHO	1.5129	–0.1335	64:29	23:44	72:20
NO_2	1.5102	–0.1227	20:44	60:20	67:18

The results reported herein present a picture of the radicals obtained upon homolytic cleavage of the carbon–halogen bonds in **1a–d** that is consistent with the hypothesis that the presence of an electron-withdrawing group renders them electrophilic. In fact, the substituent is seen to reduce both the charge and spin densities at the radical carbon. These results are in agreement with previously reported data on the photochemical behavior of the same substrates in the presence of acrylonitrile, where we concluded that the best interaction between the relevant frontier orbitals was that between the SOMO of the radicals and the HOMO of the electron-poor olefin.[6]

Conclusion

In conclusion, the radicals generated upon homolytic cleavage of the carbon–halogen bonds in haloheterocycles bearing electron-withdrawing groups are electrophilic and are thus capable of interacting with the HOMOs of olefins. Usually, electron-poor olefins react more rapidly with nucleophilic radicals and the interaction involves the LUMOs of the olefins. This work relates to an unusual case where the corresponding addition products are obtained in good yields.

Thus, the radicals described here react with both electron-rich and electron-poor olefins, the only difference being the nature of the observed products. In reactions with electron-rich olefins, we obtained olefins as the sole products, while in the present case the addition product predominates. This contrasting behavior can probably be explained in terms of the different natures of the likely radical intermediates (Scheme 5).



Scheme 5. Radicals from the attack of heterocyclic radicals on electron-rich and electron-poor olefins

In fact, while with electron-rich olefins a nucleophilic radical is generated, in the reactions reported here an electrophilic radical is produced, which can react with halogen atoms (or, more probably, with a complex of the halogen atom with the olefin, see ref.[4]) to give the addition product.

Experimental Section

General Remarks: Mass spectra were recorded using a Hewlett-Packard 5971 mass-selective detector on a Hewlett-Packard 5890 gas chromatograph [OV-1 capillary column in the range 70–250 °C (20 °C min^{-1})]. – NMR spectra were recorded with a Bruker 300 AM instrument. – Elemental analyses were carried out using a Carlo Erba 1106 elemental analyzer. – 2-Acetyl-5-iodothiophene (**1a**) was obtained from 2-iodothiophene by acylation with Ac_2O and H_3PO_4.[9] 2-Iodothiophene was obtained by reaction of thiophene with iodine and HgO.[10] 5-Iodothiophene-2-carbaldehyde (**1b**) was prepared from thiophene-2-carbaldehyde by reduction with $LiAlH_4$, iodination with iodine and HgO, and subsequent oxidation of the alcohol with PCC.[11] 2-Iodo-5-nitrothiophene (**1c**) was obtained from 2-iodothiophene by reaction with nitric acid and Ac_2O.[12] 5-Bromofuran-2-carbaldehyde (**1d**) was prepared from furan-2-carbaldehyde by reaction with bromine in dichloromethane.[13]

Photochemical Reactions of 1a–d with Electron-Poor Olefins – General Procedure: The iodoheterocyclic derivative **1a–d** (0.4 mmol) was dissolved in acetonitrile (70 mL) containing the olefin **2a–e** (3 g). The mixture was purged with a stream of nitrogen for 1 h and then irradiated with a 125 W high-pressure mercury arc (Helios-Italquartz). At the end of the reaction (for times, see Table 1), the mixture was washed with 0.1 N sodium thiosulfate solution, dried (Na_2SO_4), and the solvent was evaporated. Chromatography of the crude products on silica gel, eluting with *n*-hexane/ethyl acetate mixtures, gave the pure products as listed in Table 1 and detailed below.

Methyl 3-(5-Acetyl-2-thienyl)-2-iodopropionate (3a): Yield: 61%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.52 (s, 3 H, $COCH_3$), 3.46 (dd, 1 H, J_1 = 15 Hz, J_2 = 6 Hz, CH–CH_aH_b), 3.70 (dd, 1 H, J_1 = 15 Hz, J_2 = 9 Hz, CH–CH_aH_b), 3.76 (s, 3 H, OCH_3), 4.51 (dd, 1 H, J_1 = 9 Hz, J_2 = 6 Hz, C*H*–CH_2), 6.91 (d, 1 H, J = 3.8 Hz, thienyl H), 7.53 (d, 1 H, J = 3.8 Hz, thienyl H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 26.8 (CH_2), 30.4 ($CO*C*H_3$), 51.8 (CO_2*C*H_3), 53.2 (CHI), 128.1 (thienyl C), 134.6 (thienyl C), 136.4 (thienyl C), 143.3 (thienyl C), 159.1 ($*C*O_2CH_3$), 195.7 (CO). – MS: *m*/*z* (%) = 338 (2), 213 (5), 212 (10), 211 (100), 181 (10), 180 (8), 179 (67), 169 (18), 139 (30), 137 (55), 109 (13), 82 (5). – $C_{10}H_{11}IO_3S$ (338.2): calcd. C 35.52, H 3.28, S 9.48; found C 35.58, H 3.12, S 9.54.

Methyl 3-(5-Formyl-2-thienyl)-2-iodopropionate (3b): Yield: 64%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.50 (dd, 1 H, J_1 = 16.8 Hz, J_2 = 6 Hz, $CHCH_aH_b$), 3.74 (dd, 1 H, J_1 = 16.8 Hz, J_2 = 9 Hz, $CHCH_aH_b$), 3.76 (s, 3 H, OCH_3), 4.53 (dd, 1 H, J_1 = 9 Hz, J_2 = 6 Hz, C*H*CH_2), 7.01 (d, 1 H, J = 3.8 Hz, thienyl H), 7.63 (d, 1 H, J = 3.8 Hz, thienyl H), 9.58 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 27.2 (CH_2), 51.7 (CO_2*C*H_3), 54.1 (CHI), 128.5 (thienyl C), 135.2 (thienyl C), 136.2 (thienyl C), 145.2 (thienyl C), 159.4 ($*C*O_2CH_3$), 182.8 (CHO). – MS: *m*/*z* (%) = 324 (1), 293 (3), 199 (5), 198 (10), 197 (100), 167 (3), 166 (5), 138 (10), 137 (30), 127 (5), 125 (15), 109 (15), 97 (10). – $C_9H_9IO_3S$ (324.1): calcd. C 33.35, H 2.80, S 9.89; found C 33.40, H 2.70, S 9.58.

Methyl 2-Iodo-3-(5-nitro-2-thienyl)propionate (3c): Yield: 20%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.43 (dd, 1 H, J_1 =

17 Hz, J_2 = 6 Hz, CH–CH_aH_b), 3.67 (dd, 1 H, J_1 = 17 Hz, J_2 = 9 Hz, CH–CH_aH_b), 3.79 (s, 3 H, OCH_3), 4.52 (dd, 1 H, J_1 = 9 Hz, J_2 = 6 Hz, C*H*–CH_2), 6.88 (d, 1 H, J = 4 Hz, thienyl H), 7.78 (d, 1 H, J = 4 Hz, thienyl H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.6 (CH_2), 52.1 (CO_2CH_3), 53.8 (CHI), 129.9 (thienyl C), 130.3 (thienyl C), 132.6 (thienyl C), 152.7 (thienyl C), 159.7 (CO_2CH_3). – MS: *m*/*z* (%) = 310 (2), 216 (5), 215 (10), 214 (100), 182 (60), 172 (10), 142 (12), 109 (12), 69 (9), 66 (10), 59 (10). – $C_8H_8INO_4S$ (341.1): calcd. C 28.17, H 2.36, N 4.11, S 9.40; found C 28.25, H 2.28, N 4.07, S 9.50.

Methyl 2-Bromo-(5-formyl-2-furyl)propionate (3d): Yield: 57%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.38 (dd, 1 H, J_1 = 16 Hz, J_2 = 7.5 Hz, CH–CH_aH_b), 3.59 (dd, 1 H, J_1 = 16 Hz, J_2 = 7.5 Hz, CH–CH_aH_b), 3.79 (s, 3 H, OCH_3), 4.57 (dd, 1 H, J_1 = J_2 = 7.5 Hz, C*H*–CH_2), 6.41 (d, 1 H, J = 4 Hz, furyl H), 7.18 (d, 1 H, J = 4 Hz, furyl H), 9.55 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 30.2 (CH_2), 52.3 (CO_2CH_3), 74.3 (CHBr), 112.9 (furyl C), 121.7 (furyl C), 148.5 (furyl C), 153.3 (furyl C), 160.2 (CO_2CH_3), 178.2 (CHO). – MS: *m*/*z* (%) = 262 (1), 260 (1), 201 (2), 182 (3), 181 (35), 151 (6), 150 (10), 149 (100), 122 (10), 121 (12), 109 (12), 81 (5). – $C_9H_9BrO_4$ (261.1): calcd. C 41.41, H 3.47; found C 41.32, H 3.55.

3-(5-Acetyl-2-thienyl)-2-iodopropanal (3e): Yield: 60%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.53 (s, 3 H, CH_3), 3.42 (dd, 1 H, J_1 = 16 Hz, J_2 = 6 Hz, CH–CH_aH_b), 3.72 (dd, 1 H, J_1 = 16 Hz, J_2 = 7 Hz, CH–CH_aH_b), 4.74 (dd, 1 H, J_1 = 7 Hz, J_2 = 6 Hz, C*H*–CH_2), 6.94 (d, 1 H, J = 4 Hz, thienyl H), 7.54 (d, 1 H, J = 4 Hz, thienyl H), 9.43 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 28.5 (CH_2), 29.9 ($COCH_3$), 60.3 (CHI), 129.8 (thienyl C), 135.3 (thienyl C), 136.6 (thienyl C), 143.5 (thienyl C), 195.3 (CO), 199.2 (CHO). – MS: *m*/*z* (%) = 308 (2), 184 (5), 183 (10), 182 (78), 169 (5), 168 (10), 167 (90), 155 (3), 154 (10), 153 (58), 141 (7), 140 (40), 139 (54), 126 (20), 124 (20), 112 (10), 111 (100), 110 (10), 109 (10), 97 (50), 96 (20), 95 (15), 77 (18). – $C_9H_9IO_2S$ (308.1): calcd. C 35.08, H 2.94, S 10.40; found C 35.00, H 3.01, S 10.32.

5-(2-Formyl-2-iodoethyl)thiophene-2-carbaldehyde (3f): Yield: 26%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.45 (dd, 1 H, J_1 = 16 Hz, J_2 = 7 Hz, CH–CH_aH_b), 3.74 (dd, 1 H, J_1 = 16 Hz, J_2 = 7 Hz, CH–CH_aH_b), 4.76 (ddd, 1 H, J_1 = J_2 = 7 Hz, J_3 = 1.4 Hz, OHC–C*H*–CH_2), 7.02 (d, 1 H, J = 4 Hz, thienyl H), 7.63 (d, 1 H, J = 4 Hz, thienyl H), 9.32 (d, 1 H, J = 1.4 Hz, CHC*H*O), 9.84 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 29.3 (CH_2), 59.9 (CHI), 128.5 (thienyl C), 134.8 (thienyl C), 136.5 (thienyl C), 145.3 (thienyl C), 183.3 (CHO), 198.5 (CH*C*HO). – MS: *m*/*z* (%) = 294 (1), 167 (8), 166 (60), 139 (10), 138 (13), 137 (100), 111 (10), 110 (9), 109 (44), 69 (10), 65 (18). – $C_8H_7IO_2S$ (294.1): calcd. C 32.67, H 2.40, S 10.90; found C 32.64, H 2.45, S 11.01.

5-(2-Formylethyl)thiophene-2-carbaldehyde (3g): Yield: 57%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.92 (t, 2 H, J = 7 Hz, CH_2CH_2), 3.23 (t, 2 H, J = 7 H, CH_2CH_2), 6.96 (d, 1 H, J = 4 Hz, thienyl H), 7.62 (d, 1 H, J = 4 Hz, thienyl H), 9.84 (s, 2 H, 2 CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 28.5 (CH_2), 56.3 ($OHCCH_2$), 129.0 (thienyl C), 135.2 (thienyl C), 135.8 (thienyl C), 145.7 (thienyl C), 184.0 (CHO), 198.6 (CH_2CHO). – MS: *m*/*z* (%) = 170 (8), 169 (10), 168 (90), 160 (28), 140 (18), 139 (55), 137 (10), 133 (13), 128 (5), 127 (13), 126 (100), 125 (72), 113 (11), 112 (58), 111 (98), 109 (20), 97 (70), 96 (10), 95 (10), 85 (10), 78 (10), 77 (22), 71 (10), 69 (15), 67 (10), 65 (10). – $C_8H_8O_2S$ (168.2): calcd. C 57.12, H 4.79, S 19.06; found C 57.05, H 4.73, S 20.02.

2-Iodo-3-(5-nitro-2-thienyl)propanal (3h): Yield: 60%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.42 (dd, 1 H, J_1 = 16 Hz, J_2 = 7 Hz, CH–CH_aH_b), 3.70 (dd, 1 H, J_1 = 16 Hz, J_2 = 7 Hz, CH–CH_aH_b), 4.76 (ddd, 1 H, J_1 = J_2 = 7 Hz, J_3 = 1 Hz, OHC–C*H*–CH_2), 6.90 (d, 1 H, J = 4 Hz, thienyl H), 7.82 (d, 1 H, J = 4 Hz, thienyl H), 9.35 (d, 1 H, J = 1 Hz, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 29.5 (CH_2), 60.4 (CHI), 130.1 (thienyl C), 131.0 (thienyl C), 133.2 (thienyl C), 152.2 (thienyl C), 199.3 (CHO). – MS: *m*/*z* (%) = 311 (1), 186 (5), 185 (50), 156 (11), 143 (100), 142 (15), 139 (15), 129 (30), 112 (12), 111 (15), 110 (30), 99 (10), 97 (22), 96 (17), 95 (10), 77 (22), 71 (12), 70 (12), 69 (15), 67 (13), 66 (12), 65 (12). – $C_7H_6INO_3S$ (311.1): calcd. C 27.03, H 1.94, N 4.50, S 10.31; found C 27.09, H 2.00, N 4.46, S 10.35.

5-(2-Bromo-2-formylethyl)furan-2-carbaldehyde (3i): Yield: 56%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.31 (dd, 1 H, J_1 = 16 Hz, J_2 = 8 Hz, $CHCH_aH_b$), 3.64 (dd, 1 H, J_1 = 16 Hz, J_2 = 6 Hz, CH–CH_aH_b), 4.70 (ddd, 1 H, J_1 = 8 Hz, J_2 = 6 Hz, J_3 = 1 Hz, OHC–C*H*–CH_2), 6.46 (d, 1 H, J = 4 Hz, furyl H), 7.22 (m, 1 H, furyl H), 9.56 (m, 2 H, 2 CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 31.0 (CH_2), 75.1 (CHBr), 113.1 (furyl C), 122.0 (furyl C), 148.2 (furyl C), 154.2 (furyl C), 175.2 (CHO), 199.8 (CHBr*C*HO). – MS: *m*/*z* (%) = 232 (2), 230 (2), 201 (1), 152 (8), 151 (100), 121 (10), 109 (16), 95 (10), 81 (14), 65 (12). – $C_8H_7BrO_3$ (231.0): calcd. C 41.59, H 3.05; found C 41.63, H 3.01.

4-(5-Acetyl-2-thienyl)-3-iodo-2-butanone (3j): Yield: 75%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.51 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 3.37 (dd, 1 H, J_1 = 15.5 Hz, J_2 = 6.7 Hz, $CHCH_aH_b$), 3.67 (dd, 1 H, J_1 = 15.5 Hz, J_2 = 8.2 Hz, $CHCH_aH_b$), 4.70 (dd, 1 H, J_1 = 8.2 Hz, J_2 = 6.7 Hz, C*H*–CH_2), 6.88 (d, 1 H, J = 3.8 Hz, thienyl H), 7.52 (d, 1 H, J = 3.8 Hz, thienyl H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 29.0 (CH_2), 30.5 (CH_3), 32.5 (CH_3), 60.4 (CHI), 128.6 (thienyl C), 135.0 (thienyl C), 136.0 (thienyl C), 143.6 (thienyl C), 196.2 (CO), 199.4 (CO). – MS: *m*/*z* (%) = 322 (0.1), 197 (7), 196 (23), 195 (100), 194 (6), 181 (9), 153 (44), 152 (7), 151 (12), 139 (14), 137 (24), 111 (10), 109 (10). – $C_{10}H_{11}IO_2S$ (322.2): calcd. C 37.28, H 3.44, S 9.95; found C 37.33, H 3.40, S 10.01.

5-(2-Iodo-3-oxobutyl)thiophene-2-carbaldehyde (3k): Yield: 72%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.43 (s, 3 H, CH_3), 3.45 (dd, 1 H, J_1 = 16 Hz, J_2 = 6.5 Hz, $CHCH_aH_b$), 3.72 (dd, 1 H, J_1 = 16 Hz, J_2 = 8 Hz, $CHCH_aH_b$), 4.72 (dd, 1 H, J_1 = 8 Hz, J_2 = 6.5 Hz, C*H*CH_2), 6.98 (d, 1 H, J = 4 Hz, thienyl H), 7.62 (d, 1 H, J = 4 Hz, thienyl H), 9.84 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 29.0 (CH_2), 31.4 (CH_3), 60.7 (CHI), 128.7 (thienyl C), 135.5 (thienyl C), 135.8 (thienyl C), 145.0 (thienyl C), 183.3 (CHO), 199.5 (CO). – MS: *m*/*z* (%) = 308 (0.5), 183 (9), 182 (20), 181 (100), 180 (10), 165 (10), 151 (10), 139 (21), 137 (18), 125 (16), 111 (16), 109 (9), 97 (9). – $C_9H_9IO_2S$ (308.1): calcd. C 35.08, H 2.94, S 10.40; found C 35.00, H 2.99, S 10.34.

4-(5-Nitro-2-thienyl)-3-iodo-2-butanone (3l): Yield: 67%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.43 (s, 3 H, CH_3), 3.72 (m, 2 H, $CHCH_2$), 4.30 (dd, 1 H, J_1 = J_2 = 8 Hz, C*H*CH_2), 6.87 (d, 1 H, J = 4 Hz, thienyl H), 7.83 (d, 1 H, J = 4 Hz, thienyl H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 28.9 (CH_2), 32.3 (CH_3), 60.1 (CHI), 130.0 (thienyl C), 130.3 (thienyl C), 132.5 (thienyl C), 153.1 (thienyl C), 198.3 (CO). – MS: *m*/*z* (%) = 198 (11), 127 (10), 113 (12), 99 (18), 85 (53), 71 (66), 70 (12), 69 (10), 57 (100), 56 (12), 55 (15). – $C_8H_8IO_3NS$ (325.1): calcd. C 29.55, H 2.48, N 4.31, S 9.86; found C 29.49, H 2.50, N 4.34, S 9.80.

5-(2-Bromo-3-oxobutyl)furan-2-carbaldehyde (3m): Yield: 17%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.42 (s, 3 H, CH_3), 3.28 (dd, 1 H, J_1 = 16 Hz, J_2 = 8 Hz, $CHCH_aH_b$), 3.53 (dd, 1 H, J_1 = 16 Hz, J_2 = 7 Hz, $CHCH_aH_b$), 4.68 (dd, 1 H, J_1 = 8 Hz, J_2 =

7 Hz, C*H*CH_2), 6.41 (d, 1 H, *J* = 3.6 Hz, furyl H), 7.20 (d, 1 H, *J* = 3.6 Hz, furyl H), 9.56 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 29.3 (CH_2), 30.8 (CH_3), 75.0 (CHBr), 112.2 (furyl C), 122.7 (furyl C), 148.3 (furyl C), 153.8 (furyl C), 179.1 (CHO), 197.8 (CO). – MS: *m*/*z* (%) = 201 (0.1), 166 (16), 165 (100), 149 (10), 135 (23), 123 (74), 109 (10), 65 (15). – $C_9H_9BrO_3$ (245.1): calcd. C 44.11, H 3.70; found C 44.03, H 3.77.

Methyl (2*E*)-3-(5-Acetyl-2-thienyl)-2-propenoate (4a): Yield: 7%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.57 (s, 3 H, CH_3), 3.82 (s, 3 H, OCH_3), 6.39 (d, 1 H, *J* = 15.7 Hz, CH=C*H*), 7.26 (d, 1 H, *J* = 3.8 Hz, thienyl H), 7.61 (d, 1 H, *J* = 3.8 Hz, thienyl H), 7.77 (d, 1 H, *J* = 15.7 Hz, C*H*=CH). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 30.6 (CO*C*H_3), 51.7 (CO_2*C*H_3), 128.6 (thienyl C), 129.5 (CH), 130.8 (CH), 136.5 (thienyl C), 136.7 (thienyl C), 143.6 (thienyl C), 167.0 (*C*O_2CH_3), 196.1 (CO). – MS: *m*/*z* (%) = 212 (3), 211 (10), 210 (65), 195 (100), 179 (30), 167 (20), 152 (10), 151 (5), 139 (8), 137 (10), 135 (15), 109 (12), 108 (9), 82 (9). – $C_{10}H_{10}O_3S$ (210.2): calcd. C 57.13, H 4.79, S 15.25; found C 57.09, H 4.83, S 15.22.

Methyl (2*E*)-3-(5-Formyl-2-thienyl)-2-propenoate (4b): Yield: 29%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.82 (s, 3 H, OCH_3), 6.43 (d, 1 H, *J* = 16 Hz, CH=C*H*), 7.33 (d, 1 H, *J* = 3.8 Hz, thienyl H), 7.71 (d, 1 H, *J* = 3.8 Hz, thienyl H), 7.76 (d, 1 H, *J* = 16 Hz, C*H*=CH), 9.91 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 51.6 (CO_2*C*H_3), 128.7 (thienyl C), 130.6 (CH), 131.0 (CH), 136.3 (thienyl C), 136.7 (thienyl C), 145.7 (thienyl C), 166.8 (*C*O_2CH_3), 183.2 (CHO). – MS: *m*/*z* (%) = 198 (5), 197 (10), 196 (100), 195 (8), 167 (20), 165 (95), 137 (15), 109 (20), 108 (10), 65 (10). – $C_9H_8O_3S$ (196.2): calcd. C 55.09, H 4.11, S 16.34; found C 55.12, H 4.07, S 16.30.

Methyl (2*E*)-3-(5-Nitro-2-thienyl)-2-propenoate (4c): Yield: 44%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.83 (s, 3 H, OCH_3), 6.43 (d, 1 H, *J* = 16 Hz, CH=C*H*), 7.19 (d, 1 H, *J* = 4 Hz, thienyl H), 7.68 (d, 1 H, *J* = 16 Hz, C*H*=CH), 7.86 (d, 1 H, *J* = 4 Hz, thienyl H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 51.8 (CH_3), 129.8 (CH), 130.7 (CH), 131.1 (thienyl C), 131.3 (thienyl C), 132.4 (thienyl C), 153.0 (thienyl C), 167.3 (*C*O_2CH_3). – MS: *m*/*z* (%) = 215 (1), 214 (2), 213 (25), 183 (5), 182 (35), 169 (5), 168 (10), 167 (100), 152 (20), 139 (10), 136 (12), 124 (15), 108 (20), 96 (13), 82 (10), 69 (10), 63 (9). – $C_8H_7NO_4S$ (213.2): calcd. C 45.07, H 3.31, N 6.57, S 15.04; found C 45.12, H 3.28, N 6.60, S 16.00.

Methyl (2*E*)-3-(5-Formyl-2-furyl)-2-propenoate (4d): Yield: 16%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.80 (s, 3 H, CH_3), 6.63 (d, 1 H, *J* = 16 Hz, CH), 6.74 (d, 1 H, *J* = 4 Hz, furyl H), 7.22 (d, 1 H, *J* = 4 Hz, furyl H), 7.47 (d, 1 H, *J* = 16 Hz, CH), 9.66 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 51.8 (CH_3), 113.4 (furyl C), 122.0 (furyl C), 130.0 (CH), 130.2 (CH), 150.3 (furyl C), 153.5 (furyl C), 166.5 (CO_2CH_3), 178.5 (CHO). – MS: *m*/*z* (%) = 181 (5), 180 (35), 152 (10), 151 (100), 150 (9), 149 (70), 136 (11), 123 (15), 121 (12), 95 (10), 65 (20), 64 (10), 63 (16). – $C_9H_8O_4$ (180.2): calcd. C 60.00, H 4.48; found C 60.07, H 4.44.

(2*E*)-3-(5-Acetyl-2-thienyl)-2-propenal (4e): Yield: 27%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.59 (s, 3 H, CH_3), 6.63 (dd, 1 H, J_1 = 16 Hz, J_2 = 8 Hz, CH=C*H*–CHO), 7.37 (d, 1 H, *J* = 4 Hz, thienyl H), 7.56 (d, 1 H, *J* = 16 Hz, C*H*=CH), 7.66 (d, 1 H, *J* = 4 Hz, thienyl H), 9.68 (d, 1 H, *J* = 8 Hz, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 30.6 (CH_3), 128.3 (thienyl C), 135.0 (thienyl C), 136.3 (thienyl C), 136.6 (CH), 137.2 (CH), 143.6 (thienyl C), 192.2 (CHO), 196.0 (CO). – MS: *m*/*z* (%) = 180 (55), 165 (12), 137 (100), 109 (47), 65 (12). – $C_9H_8O_2S$ (180.2): calcd. C 59.98, H 4.47, S 17.79; found C 60.05, H 4.40, S 17.86.

(2*E*)-3-(5-Formyl-2-thienyl)-2-propenal (4f): Yield: 44%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.68 (dd, 1 H, J_1 = 15 Hz, J_2 = 7 Hz, CH=C*H*CHO), 7.44 (d, 1 H, *J* = 4 Hz, thienyl H), 7.60 (d, 1 H, *J* = 15 Hz, C*H*=CHCHO), 7.76 (d, 1 H, *J* = 4 Hz, thienyl H), 9.71 (d, 1 H, *J* = 7 Hz, CHC*H*O), 9.95 (s, 1 H, thienyl CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 129.0 (thienyl C), 136.3 (thienyl C), 137.0 (CH), 137.3 (CH), 137.7 (thienyl C), 145.6 (thienyl C), 183.0 (CHO), 192.4 (CHO). – MS: *m*/*z* (%) = 166 (65), 138 (12), 137 (100), 109 (48), 65 (20). – $C_8H_6O_2S$ (166.2): calcd. C 57.82, H 3.64, S 19.29; found C 57.78, H 3.69, S 19.21.

(2*E*)-3-(5-Nitro-2-thienyl)-2-propenal (4g): Yield: 45%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.64 (dd, 1 H, J_1 = 16 Hz, J_2 = 7.5 Hz, CH=C*H*–CHO), 7.29 (d, 1 H, *J* = 4 Hz, thienyl H), 7.34 (d, 1 H, *J* = 16 Hz, C*H*=CH), 7.88 (d, 1 H, *J* = 4 Hz, thienyl H), 9.70 (d, 1 H, *J* = 7.5 Hz, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 130.3 (thienyl C), 130.5 (thienyl C), 133.1 (thienyl C), 136.2 (CH), 137.0 (CH), 153.0 (thienyl C), 192.7 (CHO). – MS: *m*/*z* (%) = 183 (18), 138 (10), 137 (100), 109 (42), 108 (13), 82 (10), 69 (15), 65 (20). – $C_7H_5NO_3S$ (183.2): calcd. C 45.90, H 2.75, N 7.65, S 17.50; found C 45.86, H 2.81, N 7.59, S 17.53.

(2*E*)-3-(5-Formyl-2-furyl)-2-propenal (4h): Yield: 26%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.85 (dd, 1 H, J_1 = 14 Hz, J_2 = 9 Hz, CH=C*H*CHO), 6.92 (d, 1 H, *J* = 15 Hz, C*H*=CHCHO), 7.28 (d, 1 H, *J* = 2 Hz, furyl H), 7.33 (d, 1 H, *J* = 2 Hz, furyl H), 9.70 (d, 1 H, *J* = 9 Hz, CH=CHC*H*O), 9.74 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 113.7 (furyl C), 123.2 (furyl C), 136.6 (CH), 137.3 (CH), 151.3 (furyl H), 152.5 (furyl H), 182.2 (CHO), 193.0 (CHO). – MS: *m*/*z* (%) = 150 (8), 149 (100), 121 (5), 104 (6). – $C_8H_6O_3$ (150.1): calcd. C 64.00, H 4.03; found C 63.94, H 4.06.

(3*E*)-4-(5-Acetyl-2-thienyl)-3-buten-2-one (4i): Yield: 19%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.38 (s, 3 H, CH_3), 2.55 (s, 3 H, CH_3), 6.63 (d, 1 H, *J* = 16 Hz, CH), 6.82 (d, 1 H, *J* = 4 Hz, thienyl H), 7.49 (d, 1 H, *J* = 4 Hz, thienyl H), 7.57 (d, 1 H, *J* = 16 Hz, CH). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 30.8 (CH_3), 31.2 (CH_3), 128.1 (thienyl C), 130.5 (CH), 136.2 (thienyl C), 136.8 (thienyl C), 138.7 (CH), 143.7 (thienyl C), 195.8 (CO), 196.9 (CO). – MS: *m*/*z* (%) = 195 (7), 194 (60), 179 (39), 152 (8), 151 (100), 109 (18). – $C_{10}H_{10}O_2S$ (194.2): calcd. C 61.83, H 5.19, S 16.50; found C 61.77, H 5.12, S 16.57.

(1*E*)-5-(3-Oxo-1-butenyl)thiophene-2-carbaldehyde (4j): Yield: 20%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.40 (s, 3 H, CH_3), 6.70 (d, 1 H, *J* = 16 Hz, CH), 7.37 (d, 1 H, *J* = 4 Hz, thienyl H), 7.60 (d, 1 H, *J* = 16 Hz, CH), 7.72 (d, 1 H, *J* = 4 Hz, thienyl H), 9.92 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 31.4 (CH_3), 129.0 (thienyl C), 131.3 (CH), 136.4 (thienyl C), 136.7 (thienyl C), 139.2 (CH), 145.6 (thienyl C), 183.1 (CHO), 196.5 (CO). – MS: *m*/*z* (%) = 182 (7), 181 (12), 180 (100), 166 (8), 165 (91), 152 (10), 151 (72), 137 (23), 109 (38), 82 (12), 69 (14), 65 (22). – $C_9H_8O_2S$ (180.2): calcd. C 59.98, H 4.47, S 17.79; found C 60.05, H 4.40, S 17.71.

(3*E*)-4-(5-Nitro-2-thienyl)-3-buten-2-one (4k): Yield: 18%. Viscous oil. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.32 (s, 3 H, CH_3), 5.97 (d, 1 H, *J* = 16 Hz, CH), 6.13 (d, 1 H, *J* = 16 Hz, CH), 6.66 (d, 1 H, *J* = 4 Hz, thienyl H), 7.12 (d, 1 H, *J* = 4 Hz, thienyl H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 31.5 (CH_3), 130.6 (thienyl C), 130.9 (CH), 131.3 (thienyl C), 132.9 (thienyl C), 138.9 (CH), 153.1 (thienyl C), 196.7 (CO). – MS: *m*/*z* (%) = 198 (10), 197 (45), 137 (66), 124 (60), 119 (49), 109 (17), 99 (18), 98 (43), 97 (36), 95 (17), 93 (15), 83 (15), 81 (17), 71 (25), 55 (23), 44 (16), 43 (100). – $C_8H_7NO_3S$ (197.2): calcd. C 48.72, H 3.58, N 7.10, S 16.26; found C 48.78, H 3.62, N 7.17, S 16.30.

Reactions of Compounds 1a–d in the Presence of Cyclopentenone or Cyclohexenone: The reactions were carried out as described above. In this case, we observed the formation of cyclopentenone and cyclohexenone dimers as the only products. Cyclopentenone dimer **5a**: MS: *m*/*z* (%) = 165 (10), 164 (100), 136 (21), 135 (12), 122 (9), 121 (10), 109 (12), 108 (15), 107 (12), 95 (11), 94 (15), 93 (11), 91 (15), 83 (30), 82 (68), 81 (32), 80 (35), 79 (80), 77 (26). Cyclopentenone dimer **6a**: MS: *m*/*z* (%) = 165 (11), 164 (100), 136 (20), 135 (9), 122 (10), 121 (15), 120 (10), 109 (9), 108 (37), 107 (18), 94 (17), 93 (14), 92 (10), 91 (15), 83 (20), 82 (61), 81 (20), 80 (45), 79 (90), 77 (26), 68 (10), 67 (15), 66 (17), 65 (10), 55 (12), 54 (26), 53 (20). Cyclohexenone dimer **5b**: MS: *m*/*z* (%) = 192 (20), 163 (11), 150 (38), 136 (20), 135 (15), 121 (10), 119 (10), 97 (22), 96 (30), 81 (21), 80 (10), 79 (21), 68 (100). Cyclohexenone dimer **6b**: MS: *m*/*z* (%) = 192 (22), 174 (9), 164 (9), 137 (9), 136 (52), 135 (38), 121 (30), 110 (10), 109 (19), 108 (30), 107 (18), 97 (55), 96 (60), 95 (18), 94 (16), 93 (30), 92 (15), 93 (30), 81 (20), 80 (41), 79 (59), 77 (35), 68 (100), 67 (28).

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