Reactions of β-Ethylsulfanylpropionyl Tetrafluoroborate with Electron-Rich Aromatics: A Novel Synthesis of Aryl Vinyl Ketones

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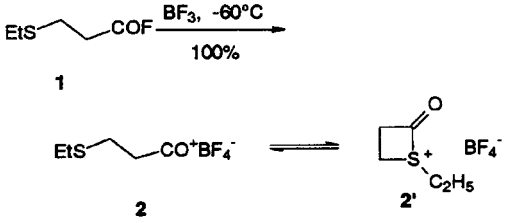
A new synthesis of aryl vinyl ketones is described. The acylation of active aromatics with the complex of β-ethylsulfanylpropionyl fluoride **1** and boron trifluoride leads to formation of 1-aryl-3-(ethylsulfanyl)propan-1-ones. Subsequent methylation with methyl triflate and elimination with an aqueous solution of $KHCO_3$ results in formation of aryl vinyl ketones in 86–99 % yield.

Vinyl ketones have been widely used in synthesis as excellent Michael acceptors, dienophiles and monomers.[1] Different aryl vinyl ketones and their derivatives such as $ArC(O)CH_2CH_2R$, R = Cl, Me_2N, MeS, Me_2S^+, Ph_3P^+, are effective as microbiocides with good environmental properties.[2]

There are different methods of synthesis of aryl vinyl ketones including pyrolysis of β-dialkylaminocarbonyl compounds and their quaternary salts, oxidation of allylic alcohols, base-induced elimination of HHal from β-halopropenones, and oxidative decarboxylation of γ-oxo carboxylic acids with lead tetraacetate in the presence of cupric acetate.[3] Nevertheless, the direct acylation of aromatics with acryloyl chloride leading to aryl vinyl ketones is not described.

Now we report a new efficient method of synthesis of aryl vinyl ketones. Recently we have proposed a new reagent, the complex of β-ethylsulfanylpropionyl fluoride and boron trifluoride, which is supposed to exist in the form of acylsulfonium salt (Scheme 1).[4,5]

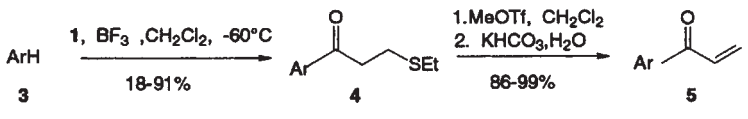


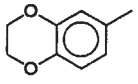
Scheme 1

When studying the properties of complex **2**, we have found that it reacts with different electron-rich aromatic compounds. We have performed the reaction of **2** with various aromatic and heteroaromatic compounds (Scheme 2).

The acylation takes place under mild conditions to give the corresponding 1-(2-aryl)-3-(ethylsulfanyl)propan-1-ones **4a–n** in high yields. We have found that the reaction proceeds regioselectively and it is very sensitive to electronic and steric factors. This can be illustrated by the reactions of anisole and *para*-methylanisole: the reaction with anisole afforded 83% of *para*-substituted anisole **4a** and no *ortho*-substituted product was observed, in the case of *para*-methylanisole the only product was *ortho*-(3-ethylsulfanylpropionyl)-*para*-methylanisole (**4e**), but it was obtained in 30% yield. Analogously, the reaction with 1,2- and 1,3-dimethoxybenzene proceeds in high yields whereas the reaction with 1,4-dimethoxybenzene, which has a similar structure and nucleophilicity, leads to formation of the corresponding ketone **4d** only in 18% yield. We believe that the reaction is regiospecific due to complex **2** being in the form of four-membered cyclic acylsulfonium salt **2′**, and therefore there are considerable steric requirements for the acylation transition state to occur.

Recently it has been found that acylsulfonium salts are efficient reagents for acylation[6] and perfluoroacylation[7] of various unsaturated hydrocarbons including the aromatic ones. It was reported that acetylsulfonium and trifluoroacetylsulfonium tetrafluoroborates react mildly with aro-



3-5	Ar	3-5	Ar	3-5	Ar
a	4-MeOPh	f	4-methoxynaphthyl-1	k	thienyl-1
b	3,4-diMeOPh	g		l	4-bromothienyl-1
c	2,4-diMeOPh	h[a]	4-PhOPh	m	selenophenyl-1
d[a]	2,5-diMeOPh	i[a]	4-PhSPh	n	ferrocenyl
e[a]	2-MeO-5-MePh	j	pyrenyl-1		

[a] - compounds **5d, 5e, 5h** and **5j** were not obtained

Scheme 2

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matic compounds to give the corresponding acetyl and trifluoroacetyl arenes and hetarenes. However, the authors[8] failed to introduce acetyl or trifluoroacetyl functions into anisole. The complex **2** is slightly more active than dimethylacylsulfonium salts, it reacts with anisole and *para*-methylanisole. Attempts to perform the acylation of less active aromatics such as toluene, xylenes, mesitylene and anthracene were unsuccessful. Perhaps in the last case the reaction does not take place because of steric reasons.

Our attempts to carry out the reaction with different pyrroles and indoles failed. The complex **2** quickly decomposes even at –60°C in the presence of nitrogen-containing heteroaromatic compounds. We suppose that the recoordination of boron trifluoride from the complex **2** to nitrogen of the substrate occurs.

We have investigated the transformation of the obtained 1-aryl 3-(ethylsulfanyl)propan-1-ones **4a–n** into the aryl vinyl ketones **5a–n**. As a result we elaborated the two-step synthesis of aryl vinyl ketones from the corresponding aromatics: the first step: acylation with β-ethylsulfanylpropionyl fluoride and boron trifluoride complex **2**; the second step: *S*-methylation of 1-aryl-3-(ethylsulfanyl)-propan-1-ones **4a–n** and elimination of ethyl methyl sulfide by treatment with an aqueous solution of $KHCO_3$.

It was found that yields of aryl vinyl ketones depended on the nature of the methylating reagent used. We have studied the methylation with methyl triflate, methyl sulfate and methyl iodide. The highest yields of aryl vinyl ketones were obtained when methyl triflate was used. In this case the target products were easily isolated after stirring with aqueous $KHCO_3$ (the products were purified by passing through a short column with silica gel). Methyl sulfate and methyl iodide also gave good yields, but reactions proceeded more slowly (two days) and the purification of products required column chromatography since the vinyl ketones had some impurities.

We have also investigated the possibility of one-pot synthesis of aryl vinyl ketones. Yield in the reaction with thiophene was 72% – close to that of the two-step synthesis. Therefore, the complex of β-(ethylsulfanyl)propionyl fluoride with boron trifluoride **2** can be considered as an acryloyl cation synthetic equivalent.

In conclusion, we have investigated the acylation of various aromatics with the complex of β-(ethylsulfanyl)propionyl fluoride/ boron trifluoride. This reaction leads to formation of 1-aryl-3-(ethylsulfanyl)propan-1-ones **4a–n** in good yields. The subsequent methylation with methyl triflate and elimination with aqueous $KHCO_3$ allows the synthesis of aryl vinyl ketones **5a–n** in excellent yields. The possibility of one-pot synthesis of aryl vinyl ketones was shown.

Melting points were determined in sealed capillaries and are uncorrected. All yields refer to pure isolated products. NMR spectra were recorded on Varian VXR-400 and Bruker AM 400C spectrometers in $CDCl_3$ with TMS as an internal standard. The IR spectra were obtained with UR-20 spectrometer. Column chromatography was performed on silica gel (63-200 mesh, Merck). All solvents used were dried and distilled according to the standard procedures. Methyl triflate was prepared according to the literature procedure[9] from trifluoromethanesulfonic acid (Merck). β-(Ethylsulfanyl)propionyl fluoride was prepared according to the literature procedure[4] from 3-sulfanylpropionic acid (Aldrich).

1-(2-Aryl)-3-(ethylsulfanyl)propan-1-ones; General Procedure:
A well-stirred solution of β-(ethylsulfanyl)propionyl fluoride (**1**) (2.72 g, 0.02 mol) in CH_2Cl_2 (40 mL) was saturated by gaseous BF_3 at –60 °C. A solution of aromatic compound **3a–n** (0.02 mol) in CH_2Cl_2 (10 mL) was added dropwise. After stirring for 15 min at –40 °C the temperature was allowed to rise to 0 °C and the mixture was stirred for 2 h at this temperature. Sat. aq $KHCO_3$ (40 mL) was then added. The organic layer was separated, the aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic phases were dried (Na_2SO_4), filtered and concentrated at reduced pressure. The crude product was purified by passing through a short column with silica gel in hexane/EtOAc (9/1).

3-(Ethylsulfanyl)-1-(4-methoxyphenyl)propan-1-one (**4a**): colorless oil, yield; 3.72 g (83%).

IR (Nujol): ν = 1690 (CO).

^{1}H NMR: δ = 1.27 (t, 3H, J = 7.2 Hz, CH_2CH_3), 2.58 (q, 2H, J = 7.2 Hz, CH_2CH_3), 2.90 (t, 2H, J = 7.2 Hz, CH_2CH_2S), 3.21 (t, 2H, J = 7.2 Hz, $COCH_2$), 3.85 (s, 3H, CH_3O), 6.92 (d, 2H, J = 8.8 Hz, H_{arom}-3, 5), 7.93 (d, 2H, J = 8.8 Hz, H_{arom}-2, 6).

^{13}C NMR: δ = 14.58, 25.87, 26.12, 38.43, 55.28, 113.59, 129.54, l30.11, 163.39, 196.76.

$C_{12}H_{16}O_2S$: Calc. C 64.25, H 7.19; Found: C 64.68, H 7.12.

1-(3,4-Dimethoxyphenyl)-3-(ethylsulfanyl)propan-1-one (**4b**): colorless needles, yield; 4.37 g (86%), mp 75–76 °C (hexane).

IR (Nujol): ν = 1690 (CO).

^{1}H NMR: δ = 1.28 (t, 3H, J = 7.2 Hz, CH_2CH_3), 2.59 (q, 2H, J = 7.2 Hz, CH_2CH_3), 2.92 (t, 2H, J = 7.2 Hz, CH_2CH_2S), 3.23 (t, 2H, J = 7.2 Hz, $COCH_2$), 3.93 (s, 3H, CH_3O), 3.94 (s, 3H, CH_3O), 6.89 (d, 1H, J = 8.4 Hz, H_{arom}-5), 7.52 (d, 1H, J = 2.0 Hz, H_{arom}-2), 7.56 (dd, 1H, J = 8.4 Hz, J = 2.0 Hz, H_{arom}-6).

^{13}C NMR: δ = 14.78, 26.17, 26.35, 38.49, 56.00, 56.05, 110.05, 122.70, 129.90, 149.07, 153.40, 196.97.

$C_{13}H_{18}O_3S$: Calc. C 61.39, H 7.13; Found: C 61.45, H 7.27.

1-(2,4-Dimethoxyphenyl)-3-(ethylsulfanyl)propan-1-one (**4c**): colorless oil, yield; 4.62 g (91%).

IR (Nujol): ν = 1680 (CO).

^{1}H NMR: δ = 1.25 (t, 3H, J = 7.2 Hz, CH_2CH_3), 2.55 (q, 2H, J = 7.2 Hz, CH_2CH_3), 2.84 (t, 2H, J = 7.2 Hz, CH_2CH_2S), 3.23 (t, 2H, J = 7.2 Hz, $COCH_2$), 3.78 (s, 3H, CH_3O), 3.80 (s, 3H, CH_3O), 6.42 (d, 1H, J = 2.0 Hz, H_{arom}-3), 6.51 (dd, 1H, J = 8.4, 2.0 Hz, H_{arom}-5), 7.80 (d, 1H, J = 8.4 Hz, H_{arom}-6).

^{13}C NMR: δ = 14.82, 26.23, 26.38, 43.99, 55.51, 55.53, 98.33, 105.37, 120.72, 132.78, 160.91, 164.62, 198.21.

$C_{13}H_{18}O_3S$: Calc, C 61.39, H 7.13; Found: C 61.17, H 7.57.

1-(2,5-Dimethoxyphenyl)-3-(ethylsulfanyl)propan-1-one (**4d**): yellow oil, yield; 0.91 g (18%).

IR (Nujol): ν = 1690 (CO).

^{1}H NMR: δ = 1.26 (t, 3H, J = 7.3 Hz, CH_2CH_3), 2.56 (q, 2H, J = 7.3 Hz, CH_2CH_3), 2.90 (t, 2H, J = 7.2 Hz, CH_2CH_2S), 3.27 (t, 2H, J = 7.2 Hz, $COCH_2$), 3.75 (s, 3H, CH_3O), 3.79 (s, 3H, CH_3O), 6.92 (d, 1H, J = 8,9 Hz, H_{arom}-3), 7.11 (dd, 1H, J = 8.9, 2.9 Hz, H_{arom}-4), 7. 16 (d, 1H, J = 2.9 Hz, H_{arom}-6).

^{13}C NMR: δ = 14.63, 25.54, 26.34, 38.66, 55.89, 112.26, 114.52, 119.35, 124.25, 151.68, 156.71, 203.82.

$C_{13}H_{18}O_3S$: Calc. C 61.39, H 7.13; Found: C 61.01, H 7.44.

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3-(Ethylsulfanyl)-1-(2-methoxy-5-methylphenyl)propan-1-one (**4e**): colorless oil, yield; 1.43 g (30%).

IR (Nujol): ν = 1690 (CO).

^{1}H NMR: δ = 1.26 (t, 3H, J = 7.6 Hz, CH_2CH_3), 2.28 (s, 3H, CH_3), 2.56 (q, 2H, J = 7.6 Hz, CH_2CH_3), 2.86 (t, 2H, J = 7.2 Hz, CH_2CH_2S), 3.26 (t, 2H, J = 7.2 Hz, $COCH_2$), 3.86 (s, 3H, CH_3O), 6.84 (d, 1H, J = 8.4 Hz, H_{arom}-3), 7.24 (dd, 1H, J = 8.4, 2.4 Hz, H_{arom}-4), 7.51 (d, 1H, J = 2.4 Hz, H_{arom}-6).

^{13}C NMR: δ = 14.76, 20.22, 26.14, 44.08, 55.58, 111.54, 127.42, 129.92, 130.60, 134.16, 156.68, 200.62.

$C_{13}H_{18}O_2S$: Calc. C 65.61, H 7.61; Found: C 65.34, H 7.71.

3-(Ethylsulfanyl)-1-(4-methoxy-1-naphthyl)propan-1-one (**4f**): colorless oil, yield; 3.68 g (67%).

IR (Nujol): ν = 1680 (CO).

^{1}H NMR: δ = 1.29 (t, 3H, J = 7.2 Hz, CH_2CH_3) 2.60 (q, 2H, J = 7.2 Hz, CH_2CH_3), 2.95 (t, 2H, J = 7.2 Hz, CH_2CH_2S), 3.28 (t, 2H, J = 7.2 Hz, $COCH_3$), 4.04 (s, 3H, CH_3O), 6.76 (d, 1H, J = 8.2 Hz, $C_{10}H_6$), 7.64–7.46 (m, 2H, $C_{10}H_6$), 7.96 (d, 1H, J = 8.2 Hz, $C_{10}H_6$), 8.30 (d, 1H, J = 8.2 Hz, $C_{10}H_6$), 8.91 (d, 1H, J = 8.2 Hz, $C_{10}H_6$).

^{13}C NMR: δ = 14.76, 26.33, 26.68, 41.26, 55.77, 102.0, 122.08, 125.78, 125.81, 125.98, 127.13, 128.66, 130.82, 131.95, 159.16, 200.44.

$C_{16}H_{18}O_2S$: Calc. C 70.04, H 6.61; Found: C 69.86, H 6.59.

1-(2,3-Dihydro-1,4-benzodioxin-6-yl)-3-(ethylsulfanyl)propan-1-one (**4g**): colorless oil, yield; 4.14 g (82%).

IR (Nujol): ν = 1690 (CO).

^{1}H NMR: δ = 1.21 (t, 3H, J = 7.4 Hz, CH_2CH_3), 2.59 (br s, 2H, CH_2CH_3), 2.92 (br s, 2H, CH_2CH_2S), 3.12 (t, 2H, J = 7.2 Hz, $COCH_2$), 4.30–4.15 (m, 4H, OCH_2CH_2O), 6.84 (d, 1H, J = 9.1 Hz, H_{arom}-5), 7.42 (d, 1H, J = 9.1 Hz, H_{arom}-6), 7.44 (s, 1H, H_{arom}-2).

^{13}C NMR: δ = 14.74, 25.99, 26.25, 38.63, 64.07, 64.65, 117.21, 117.49, 122.05, 130.45, 143.32, 148.10, 196.83.

$C_{13}H_{16}O_3S$: Calc. C 61.88, H 6.39; Found: C 62.03, H 6.17.

3-(Ethylsulfanyl)-1-(4-phenoxyphenyl)propan-1-one (**4h**): colorless oil, yield; 3.72 g (65%).

IR (Nujol): ν = 1690 (CO).

^{1}H NMR: δ = 1.25 (t, 3H, J = 7.4 Hz, CH_2CH_3), 2.56 (q, 2H, J = 7.4 Hz, CH_2CH_3), 2.89 (t, 2H, J = 7.2 Hz, CH_2CH_2S), 3.20 (t, 2H, J = 7.2 Hz, $COCH_2$), 7.39–6.96 (m, 7H, C_6H_5 and H_{arom}-3, 5), 7.91 (d, 2H, J = 8.9 Hz, H_{arom}-2, 6).

^{13}C NMR: δ = 14.54, 25.71, 26.07, 38.51, 117.05, 119.93, 124.41, l29.81, 130.08, 131.04, 155.13, 161.81, 196.70.
$C_{17}H_{18}O_2S$: Calc. C 71.30, H 6.33; Found: C 71.16, H 6.43.

3-(Ethylsulfanyl)-1-[4-(phenylsulfanyl)phenyl]propan-1-one **(4i)**: colorless oil, yield; 2.84 g (47%).

IR (Nujol): ν = 1690 (CO).

^{1}H NMR: δ = 1.25 (t, 3H, J = 7.2 Hz, CH_2CH_3), 2.57 (q, 2H, J = 7.2 Hz, CH_2CH_3), 2.89 (t, 2H, J = 7.2 Hz, CH_2CH_2S), 3.19 (t, 2H. J = 7.2 Hz, $COCH_2$), 7.19 (d, 2H, J = 8.40 Hz, H_{arom}-3, 5), 7.51–7.37 (m, 5H, C_6H_5), 7.81 (d, 2H, J = 8.40 Hz, H_{arom}-2, 6).

^{13}C NMR: δ = 14.75, 25.89, 26.35, 38.83, 127.43, 128.59, 128.82, 129.68, 131.95, 133.91, 145.16, 197.35.

$C_{17}H_{18}OS_2$: Calc. C 67.51, H 6.00; Found: C 67.87, H 5.58.

3-(Ethylsulfanyl)-1-(1-pyrenyl)propan-1-one (**4j**): yellow powder, yield; 2.87 g (45%), mp 90–93 °C (hexane).

IR (Nujol): ν = 1680 (Co).

^{1}H NMR: δ = 1.27 (t, 3H, J = 7.2 Hz, CH_2CH_3), 2.60 (br s, 2H, CH_2CH_3), 2.71 (br s, 2H, CH_2CH_2S), 3.42 (t, 2H, J = 7.2 Hz, $COCH_2$), 8.20–7.73 (m, 8H, $C_{16}H_9$), 8.89 (d, 1H, J = 9.4 Hz, H_{arom}-2).

^{13}C NMR: δ = 14.85, 26.37, 26.53, 42.51, 123.87, 124.08, 124.70, 124.80, 125.96, 126.09, 126.21, 126.28, 126.90, 129.35, 129.46, 129.57, 130.37, 130.91, 131.62, 133.73, 202.58.

$C_{21}H_{18}OS$: Calc. C 79.21, H 5.70; Found: C 79.24, H 5.66.

3-(Ethylsulfanyl)-1-(2-thienyl)propan-1-one (**4k**), colorless oil, yield; 3.45 g (86%).

IR (Nujol): ν = 1700 (CO).

^{1}H NMR: δ = 1.22 (t, 3H, J = 7.2 Hz, CH_2CH_3), 2.51 (q, 2H, J = 7.2 Hz, CH_2CH_3), 2.88 (t, 2H, J = 7.2 Hz, CH_2CH_2S), 3.23 (t, 2H, J = 7.2 Hz, $COCH_2$), 7.08 (dd, 1H, J = 4.9, 3.8 Hz, H_{arom}-4), 7.59 (dd, 1H, J = 4.9, 1.1 Hz, H_{arom}-5), 7.68 (dd, 1H, J = 3.8, 1.1 Hz, H_{arom}-3).

^{13}C NMR: δ = 14.66, 26.85, 26,15, 39.51, 128.14, 132.02, 133.83, 143.80, 191.14.

$C_9H_{12}OS_2$: Calc. C 53.97, H 6.04; Found: C 54.14, H 6.08.

1-(5-Bromo-2-thienyl)-3-(ethylsulfanyl)propan-1-one **(41)**: pale yellow oil, yield; 4.19 g (75%).

IR (Nujol): ν = 1670 (CO).

^{1}H NMR: δ = 1.26 (t, 3H, J = 7.2 Hz, CH_2CH_3), 2.57 (q, 2H, J = 7.2 Hz, CH_2CH_3), 2.89 (t, 2H, J = 6.8 Hz, CH_2CH_2S), 3.12 (t, 2H, J = 6.8 Hz, $COCH_2$), 7.11 (d, 1H, J = 4.0 Hz, H_{arom}-4), 7.46 (d, 1H, J = 4.0 Hz, H_{arom}-3).

^{13}C NMR: δ = 14.55, 25.71, 26.17, 38.83, 122.72, 131.12, 131.95, 145.18, 189.99.

$C_9H_{11}BrOS_2$: Calc. C 38.72, H 3.97; Found: C 38.69, H 3.81.

3-(Ethylsulfanyl)-1-(2-selenophenyl)propan-1-one (**4m**): colorless oil, yield; 3.56 g (72%).

IR (Nujol): ν = 1690 (CO).

^{1}H NMR: δ = 1.24 (t, 3H, J = 7.2 Hz, CH_2CH_3), 2.55 (q, 2H, J = 7.2 Hz, CH_2CH_3), 2.89 (t, 2H, J = 7.2 Hz, CH_2CH_2S), 3.20 (t, 2H, J = 7.2 Hz, $COCH_2$), 7.38 (dd, 1H, J = 5.5, 3.9 Hz, H_{arom}-4), 7.93 (dd, 1H, J = 5.5, 1.2 Hz, H_{arom}-5), 8.38 (dd, 1H, J = 3.9, 1.2 Hz, H_{arom}-3).

^{13}C NMR: δ = 14.73, 26.17, 26.27, 39.01, 130.78, 134.37, 140.13, l50.81, 192.19.

$C_9H_{12}OSSe$: Calc. C 43.47, H 4.89; Found: C 43.52, H 5.01.

3-(Ethylsulfanyl)-1-(ferrocenyl)propan-1-one (**4n**): brown viscous oil, yield; 4.84 g (80%).

IR (Nujol): ν = 1680 (CO).

^{1}H NMR: δ = 1.24 (t, 3H, J = 7.4 Hz, CH_2CH_3), 2.55 (q, 2H, J = 7.4 Hz, CH_2CH_3), 2.85 (t, 2H, J = 7.2 Hz, CH_2CH_2S), 2.95 (t, 2H, J = 7.2 Hz, $COCH_2$), 4.17 (s, 5H, C_5H_5), 4.46 (s, 2H, H_{arom}-3, 4), 4.75 (s, 2H, H_{arom}-2, 5).

^{13}C NMR: δ = 14.59, 26.68. 26.20, 39.58, 69.00, 69.58, 72.10, 78.41, 201.98.

$C_{15}H_{18}FeOS$: Calc. C 59.62, H 6.00; Found: C 59.55, H 6.02.

1-Arylprop-2-en-1-ones; General Procedure:

A solution of l-(2-aryl)-3-(ethylsulfanyl)propan-1-one **4a–n** (0.01 mol) in CH_2Cl_2 (15 mL) was cooled to 0 °C. Methyl triflate (1.64 g, 0.01 mol) dissolved in CH_2Cl_2 (5 mL) was added dropwise. The mixture was stirred at r.t. until the starting **4a–n** disappeared (controlled by TLC). Then sat. aq $KHCO_3$ (20 mL) was added and the mixture was stirred for an additional 2 h. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phases were dried (Na_2SO_4), filtered and

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concentrated at reduced pressure. The crude product was purified by passing through a short column with silica gel in hexane/EtOAc, (9/1).

1-(4-Methoxyphenyl)prop-2-en-1-one (**5a**): colorless oil, yield; 1.61 g (99%).

IR spectrum was identical to lit.[10]

^{1}H NMR: δ = 3.83 (s, 3H, CH_3O), 5.84 (dd, 1H, *J* = 10.5, 1.6 Hz, H-3), 6.39 (dd, 1H, *J* = 17.0, 1.6 Hz, H-3), 6.94 (d, 2H, *J* = 8.7 Hz, H_{arom}-3, 5), 7.16 (dd, 1H, *J* = 17.0, 10.5 Hz, H-2), 7.92 (d, 2H, *J* = 8.7 Hz, H_{arom}-2, 6).

^{13}C NMR: δ = 55.36, 113.77, 129.03, 130.89, 132.03, 163.48, 188.97.

1-(3,4-Dimethoxyphenyl)prop-2-en-1-one (**5b**): colorless oil, yield; 1.91 g (99%).

IR spectrum was identical to lit.[10]

^{1}H NMR: δ = 3.90 (s, 6H, 2xCH_3O), 5.86 (dd, 1H, *J* = 10.5, 1.8 Hz, H-3), 6.38 (dd, 1H, *J* = 17.0, 1.8 Hz, H-3), 6.85 (d, 1H, *J* = 9.2 Hz, H_{arom}-5), 7.14 (dd, 1H, *J* = 17.0, 10.5 Hz, H-2), 7.52 (s, 1H, H_{arom}-2), 7.56 (d, 1H, *J* = 9.2 Hz, H_{arom}-6).

^{13}C NMR: δ = 55.82, 55.91, 109.84, 110.59, 123.25, 129.01, 130.22, l31.75, 149.07, 153.26, 188.86.

1-(2,4-Dimethoxyphenyl)prop-2-en-1-one (**5c**): colorless oil, yield; l.88 g (98%).

IR spectrum was identical to lit.[10]

^{1}H NMR: δ = 3.80 (s, 3H, CH_3O), 3.82 (s, 3H, CH_3O), 5.68 (dd, 1H, *J* = 10.4, 2.0 Hz, H-3), 6.30 (dd, 1H, *J* = 17.2, 2.0 Hz, H-3), 6.44 (d, 1H, *J* = 2.4 Hz, H_{arom}-3), 6.52 (dd, 1H, *J* = 8.4, 2.4 Hz, H_{arom}-5), 7.12 (dd, 1H, *J* = 17.2, 10.4 Hz, H-2), 7.60 (d, 1H, *J* = 8.4 Hz, H_{arom}-6).

^{13}C NMR: δ = 55.46, 55.51, 98.37, 102.24, 121.18, 126.94, 132.87, 136.64, 160.57, 164.36, 190.54.

1-(4-Methoxy-1-naphthyl)prop-2-en-1-one (**5f**): colorless oil, yield; 2.10 g (99%).

IR (Nujol): ν = 1650 (CO).

^{1}H NMR: δ = 4.02 (s, 3H, CH_3O), 5.90 (dd, 1H, *J* = 9.0, 2.4 Hz, H-3), 6.38 (dd, 1H, *J* = 17.2, 2.4, H-3), 6.74 (d, 1H, *J* = 8.1), 7.08 (dd, 1H, *J* = 17.2, 9.0 Hz, H-2), 7.68–7.52 (m, 2H, $C_{10}H_6$), 7.85 (d, 1H, *J* = 8.1 Hz, $C_{10}H_6$), 8.38 (d, 1H, *J* = 8.6 Hz, $C_{10}H_6$), 8.72 (d, 1H, *J* = 8.6 Hz, $C_{10}H_6$).

^{13}C NMR: δ = 55.71, 102.06, 122.23, 125.78, 125.83, 127.71, 128.27, l29.49, 131.02, 132.19, 136.45, 158.79, 193.62.

$C_{14}H_{12}O_2$: Calc. C 79.23, H 5.70; Found: C 79.05, H 5.63.

1-(2,3-Dihydro-1,4-benzodioxin-6-yl)prop-2-en-1-one (**5g**): pale yellow oil, yield; 1.61 g (90%).

IR (Neat): ν = 1660 (CO).

^{1}H NMR: δ = 4.30–4.10 (m, 4H, OCH_2CH_2O), 5.86 (dd, 1H, *J* = 10.5, 1.7 Hz, H-3), 6.48 (dd, 1H, *J* = 17.1, 1.7 Hz, H-3), 6.83 (d, 1H, *J* = 8.2 Hz, H_{arom}-5), 7.30 (dd, 1H, *J* = 17.1, 10.5 Hz, H-2), 7.46–7.42 (m, 2H, H_{arom}-2, 6).

^{13}C NMR: δ = 64.07, 64.66, 117.25, 118.14, 122.80, 129.28, 130.94, 131.98, 143.40, 148.09, 188.95.

$C_{11}H_{10}O_3$: Calc. C 69.47, H 5.30; Found: C 69.51, H 5.35.

1-(1-Pyrenyl)propan-1-one (**5j**): yellow powder, yield; 2.21 g (86%). mp 52–54°C (toluene), lit.[11] yellow oil.

IR (Nujol): ν = 1650 (CO).

^{1}H NMR: δ = 5.86 (dd, 1H, *J* = 10.4, 1.2 Hz, H-3), 6.48 (dd, 1H, *J* = 17.2, 1.2 Hz, H-3), 7.04 (dd, 1H, *J* = 17.2 Hz, *J* = 10.4 Hz, H-2), 8.20–7.89 (m, 8H, $C_{16}H_9$), 8.61 (d, 1H, *J* – 9.2 Hz, H_{arom}-2).

^{13}C NMR: δ = 123.71, 124.12, 124.49. 124.68, 125.84, 126.02, l26.21, 126.44, 126.92, 129.04, 129.16, 129.44, 130.40, 130.88, 131.10, 132.24, 133.30, 137.05, 195.78.

$C_{19}H_{12}O$: Calc. C 89.04, H 4.72; Found: C 89.14, H 4.69.

1-(2-Thienyl)prop-2-en-1-one (**5k**): colorless oil, yield; 1.37 g (99%). IR (Neat): ν = 1660 (CO).

^{1}H NMR: δ = 5.86 (dd, 1H, *J* = 10.4, 1.6 Hz, H-3), 6.48 (dd, 1H, *J* = 16.9, 1.6 Hz, H-3), 7.08 (dd, 1H, *J* = 16.9, 10.4 Hz, H-2), 7.16 (dd, 1H, *J* = 4.9, 3.7 Hz, H_{arom}-4), 7.68 (dd, 1H, *J* = 4.9, 1.1 Hz, H_{arom}-5), 7.78 (dd, 1H, *J* = 3.7, 1.1 Hz, H_{arom}-3).

^{13}C NMR: δ = 128.13, 129.19, 131.69, 132.30, 134.17, 144.39, 182.20.

C_7H_6OS: Calc. C 60.84, H 4.38; Found: C 60.99, H 4.42.

1-(5-Bromo-2-thienyl)prop-2-en-1-one (**5l**): pale yellow oil, yield; 2.08 g (96%).

IR (Nujol): ν = 1660 (CO).

^{1}H NMR: δ = 5.86 (dd, 1H, *J* = 10.4, 1.6 Hz, H-3), 6.48 (dd, 1H, *J* = 16.4, 1.6 Hz, H-3), 7.04 (dd, 1H, *J* = 16.8, 10.4 Hz, H-2), 7.08 (d, 1H, *J* = 3.6 Hz, H_{arom}-4), 7.46 (d, 1H, *J* = 3.6 Hz, H_{arom}-3).

^{13}C NMR: δ = 123.19, 129.82, 130.73, 131.32, 132.40, 145.96, 181.08.

C_7H_5BrOS: Calc. C 38.73, H 2.32; Found: C 38.61, H 2.16.

1-(2-Selenophenyl)prop-2-en-1-one (**5m**): colorless oil, yield; 1.81 g (98%).

IR (Nujol): ν = 1660 (CO).

^{1}H NMR: δ = 5.86 (dd, 1H, *J* = 10.4, 1.6 Hz, H-3), 6.48 (dd, 1H, *J* = 18.2, 1.6 Hz, H-3), 7.04 (dd, 1H, *J* = 18.2, 10.4 Hz, H-2), 7.37 (dd, 1H, *J* = 4.0, 5.2 Hz, H_{arom}-4), 7.95 (d, 1H, *J* = 4.0 Hz, H_{arom}-5), 8.36 (d, 1H, *J* = 5.2 Hz, H_{arom}-3).

^{13}C NMR: δ = 129.12, 130.78, 131.07, 134.64, 140.51, 151.43, 183.32.

C_7H_6OSe: Calc. C 45.44, H 3.27; Found: C 45.72, H 3.39.

1-(Ferrocenyl)prop-2-en-1-one (**5n**): red powder, yield; 2.28 g (95%), mp 72–73°C (hexane), lit.[12] 71–74°C.

IR (Nujol): ν = 1660 (CO).

^{1}H NMR: δ = 4.11 (s, 5H, C_5H_5), 4.48 (t, 2H, *J* = 2.0 Hz, H_{arom}-3, 4), 4.76 (t, 2H, *J* = 2.0 Hz, H_{arom}-2, 5), 5.64 (dd, 1H, *J* = 10.4, 2.0 Hz, H-3), 6.36 (dd, 1H, *J* = 17.2, 2.0 Hz, H-3), 6.74 (dd, 1H, *J* = 17.2, 10.4 Hz, H-2).

^{13}C NMR: δ = 69.44, 69.49, 68.80, 72.59, 72.70, 79.38, 125.98, l32.77, 192.68.

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