Synthesis and Reactivity of π-Electron-Deficient (Arylsulfonyl)acetates

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

Different π-electron-deficient (arylsulfonyl)acetates **9** were synthesized (*Scheme 1*, *Table 1*), and their behavior as soft nucleophiles in the dialkylation reaction under phase-transfer catalysis conditions was studied (*Schemes 2* and *3*, *Tables 2* and *3*). The [3,5-bis(trifluoromethyl)phenyl]sulfonyl group was shown to be the best substituent for the stereoselective synthesis of (*E*)-aconitates **18** *via* an alkylation hydro-sulfonyl-elimination integrated process under very mild phase-transfer-catalysis conditions (*Scheme 5*, *Table 4*). Sulfonylacetates **9h**,**i** also underwent smooth *Diels-Alder* reactions with acyclic and cyclic dienes *via in situ* formation of the appropriate dienophile through a *Knoevenagel* condensation with paraformaldehyde (*Scheme 6*). Reductive desulfonylation with Zn and NH_4Cl in THF was shown to be an efficient method for removal of the synthetically useful sulfonyl moiety (*Scheme 7*).

1. Introduction. – The sulfonyl group is a well-established activating moiety introduced in an intermediate molecule for the construction of C–C bonds and other transformations [1]. During the last years, the use of sulfones in organic synthesis has been a common synthetic methodology in many total syntheses and in the preparation of an infinite collection of functionalized compounds. The ability of the sulfonyl group to stabilize carbanions is one of the best known features of these compounds [2], they can act also as radical stabilizers [3] and as cationic synthons [4]. Since removal of the sulfonyl group, generally by a reductive process or *via* a base-promoted β-elimination route [5], is simple, sulfones have become a very popular tool for organic chemists.

Electron-deficient sulfonyl groups are of particular interest in synthetic chemistry as they represent one of the strongest neutral electron-withdrawing functionalities known. The presence of electron-withdrawing substituents at the sulfonyl moiety increases to a large extent the acidity of H-atoms at the α position, facilitating deprotonation and subsequent desulfonylation steps.

(Perfluoroalkyl)sulfonyl groups [6], such as triflones (=(trifluoromethyl)sulfones), are used as electron-deficient sulfonyl moieties for the stabilization of carbanions [7], as a tool to activate olefins in nucleophilic additions or cycloaddition reactions, and as nucleofuge leaving groups [8]. However, they have to be prepared from sodium triflinate (=sodium trifluoromethanesulfinate)[1]), which is not commercially available, and have a great tendency to decompose by sulfur dioxide extrusion [5]. On the other hand, π-electron deficient arylsulfonyl derivatives are very stable compounds and are

[1]) Sodium triflinate is usually prepared from the unaccessible trifluorobromomethane [9].

usually prepared from commercially available starting materials. They have been successfully used as base-labile amino-protecting groups[2]) for peptide synthesis as an alternative to the most popular (9*H*-fluoren-9-ylmethoxy)carbonyl (Fmoc) group [11]. Some representative examples depicted in *Figure* are the 4-nitro- (Nsc) [12], 4-bromo- (Bsc) [13], 4-(methylsulfonyl)- (Mpc) [13][14], and 2,4-dinitro-substituted [15] [(phenylsulfonyl)ethoxy]carbonyl groups **1**–**4**. π-Electron-deficient arylsulfones have also been employed to improve the desulfonylation processes; the 4-fluorophenyl and 2-naphthyl sulfones have been shown to increase the rate and yield of the reaction under typical sodium-amalgam desulfonylation conditions when compared with phenyl or 4-methylphenyl sulfones [16]. Besides, the very efficient stannyl-radical-mediated cleavage of π-electron-deficient heterocyclic sulfones such as **5** (*Fig.*) has recently been developed for the synthesis of α-fluorinated esters and phosphonates [17]. Pyridin-2-yl sulfones such as **6** (*Fig.*) have been used as glycosylation agents in the presence of Sm^{II} and Sm^{III} species as reducing agents [18]. Although the ability of the sulfone group to stabilize carbanions is known, only a few examples of π-electron-deficient sulfones have been reported in the literature. Acetal carbanions derived from **7** substituted with an electron-withdrawing group (EWG) can be mainly dialkylated in the case of the (nitrophenyl)sulfonyl systems [19]. In the total synthesis of rhizoxin D, a natural macrolactone with potent antitumor and antifungal activity, the (3,4-dichlorophenyl)-sulfonyl group has been introduced to improve the yield in the alkylation of the lithium diisopropylamide generated carbanion derived from compound **8** and for the hydro-sulfonyl elimination step (1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 105°) in comparison with the phenylsulfonyl moiety [20].

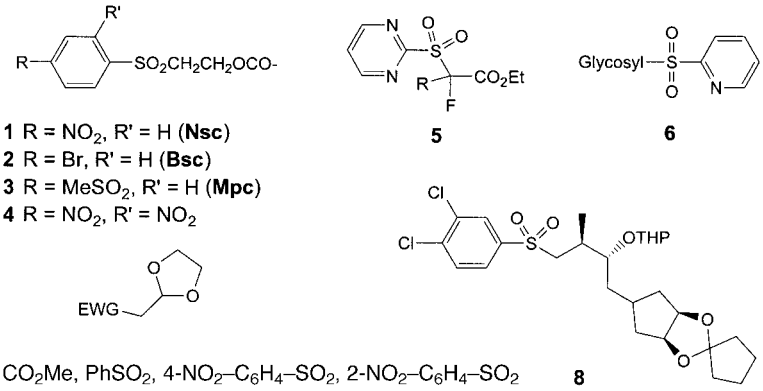

Figure. *π-Electron-deficient sulfones*

In a preliminary publication [21], we have recently reported the use of π-electron-deficient (arylsulfonyl)acetates **9** as soft nucleophiles for the stereoselective synthesis of (*E*)-aconitates *via* an alkylation/hydro-sulfonyl-elimination sequence under very mild phase-transfer-catalysis (PTC) conditions. Herein, we report the full account of the synthesis and reactivity of a complete series of π-electron-deficient (arylsulfonyl)-acetates **9**.

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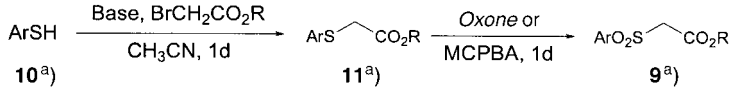
[2]) For a recent review on N-protecting groups, see [10].

2. Results and Discussion. – The series of π-electron deficient (arylsulfonyl)acetates **9** was synthesized *via* an alkylation/oxidation sequence of the corresponding arylthiols **10** (*Scheme 1*, *Table 1*). (Arylthio)acetates **11** were readily accessible and obtained in quantitative yields by reaction with alkyl bromoacetates with either NaH or Et_3N as the base in MeCN at room temperature for 1 d. Only the alkylation of pentafluorothiophenol with benzyl bromoacetate (*Table 1*, *Entry 3*) proceeded in low yield to give **11c** along with uncharacterizable by-products probably obtained from nucleophilic aromatic substitution reactions of the starting thiol with the reaction product[3]). The oxidation of (arylthio)acetates **11** was carried out with *Oxone*® in $MeOH/H_2O$ or 3-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 at room temperature for 1 d. A variety of π-electron-deficient (arylsulfonyl)acetates **9a–i** were prepared in good to excellent yields (*Table 1*, *Entries 1–9*) as well as the 4-methylphenyl derivative **9j**[4]) (*Table 1*, *Entry 10*).

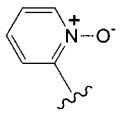
Scheme 1. *Synthesis of (Arylsulfonyl)acetates*



10[a]) **11**[a]) **9**[a])

[a]) See *Table 1* for Ar and R.

Table 1. *Synthesis of (Arylsulfonyl)acetates* **9**

Entry	Ar	Base	R	(Arylthio)acetate **11**		Oxidant	(Arylsulfonyl)acetate **9**	
				No.	Yield [%][a])		No.	Yield [%][b])
1	3-CF_3-C_6H_4	NaH	Bn	**11a**	90	*Oxone*	**9a**	83
2	4-NO_2-C_6H_4	NaH	Bn	**11b**	95	*Oxone*	**9b**	47
3	C_6F_5	NaH	Bn	**11c**	30	*Oxone*	**9c**	68
4		Et_3N	Bn	**11d**	90	*Oxone*	**9d**	30
5	Pyridin-2-yl	Et_3N	Bn	**11e**	80	MCPBA	**9e**	56
6	Pyrimidin-2-yl	Et_3N	Bn	**11f**	85	MCPBA	**9f**	62
7	3,4-$(Cl)_2C_6H_3$	Et_3N	^{i}Pr	**11g**	90	*Oxone*	**9g**	73
8	3,5-$(CF_3)_2C_6H_3$	NaH	Bn	**11h**	98	*Oxone*	**9h**	75
9	3,5-$(CF_3)_2C_6H_3$	NaH	^{i}Pr	**11i**	99	*Oxone*	**9i**	92
10	4-Me-C_6H_4	–	^{i}Pr	–		–	**9j**	80[c])

[a]) Isolated yield determined for the crude reaction mixture after 1 d reaction time. All the crude (arylthio)acetates **11** showed a high purity (> 95%) as determined by ^{1}H-NMR (300 MHz). [b]) Isolated yield after flash chromatography, based on starting **11** after 1 d reaction time. [c]) Isopropyl (4-methylphenyl)sulfonyl]acetate (**9j**) was prepared in 80% yield by reaction of the corresponding sodium 4-methylbenzene sulfinate with isopropyl bromoacetate in DMF at r.t. for 1 d.

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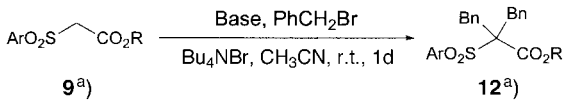
[3]) It is known that pentafluorophenyl compounds containing electron-withdrawing groups react with nucleophilic reagents to give 1,4-disubstituted compounds [22].

[4]) Isopropyl [(4-methylphenyl)sulfonyl]acetate (**9j**) was prepared in 80% yield by reaction of the corresponding sodium 4-methylbenzenesulfinate with isopropyl bromoacetate in DMF at room temperature for 1 d (see *Exper. Part*).

First, we studied the effect of the different electron-withdrawing groups in the alkylation reaction of the sulfonyl-substituted substrates under PTC conditions[5]). The reaction was studied treating the different (arylsulfonyl)acetates **9** with benzyl bromide in the presence of K_2CO_3 or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base and Bu_4NBr as phase-transfer catalyst in MeCN for 1 d at room temperature (*Scheme 2*, *Table 2*). In the case of the (4-methylphenyl)sulfonyl derivative **9j**, the alkylation

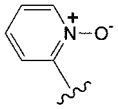
Scheme 2. *Dibenzylation of (Arylsulfonyl)acetates*



9[a]) **12**[a])

[a]) See *Table 2* for Ar and R.

Table 2. *Dibenzylation of (Arylsulfonyl)acetates* **9**

Entry	Ar	R	Base	Product	Yield [%][a])
1	3-CF_3-C_6H_4	Bn	K_2CO_3	**12a**	30
2	4-NO_2-C_6H_4	Bn	K_2CO_3	**12b**	66
3	C_6F_5	Bn	K_2CO_3	**12c**	28
4		Bn	K_2CO_3	**12d**	[b])
5	Pyridin-2-yl	Bn	K_2CO_3	**12e**	64
6	Pyrimidin-2-yl	Bn	K_2CO_3	**12f**	58
7	3,4-$(Cl)_2C_6H_3$	^{i}Pr	DBU	**12g**	30[c])
8	3,5-$(CF_3)_2C_6H_3$	Bn	K_2CO_3	**12h**	58
9	3,5-$(CF_3)_2C_6H_3$	^{i}Pr	K_2CO_3	**12i**	71
10	4-Me-C_6H_4	^{i}Pr	K_2CO_3	**12j**	50[d])

[a]) Isolated yield after flash chromatography, based on starting **9** after 1 d reaction time. [b]) Only decomposition products were detected by ^{1}H-NMR analysis (300 MHz) of the crude reaction mixture. [c]) The reaction did not work in the presence of inorganic bases such as K_2CO_3 and KOH. [d]) Monoalkylated isopropyl 2-[(4-methylphenyl)sulfonyl]-3-phenylpropanoate was also obtained in 50% yield.

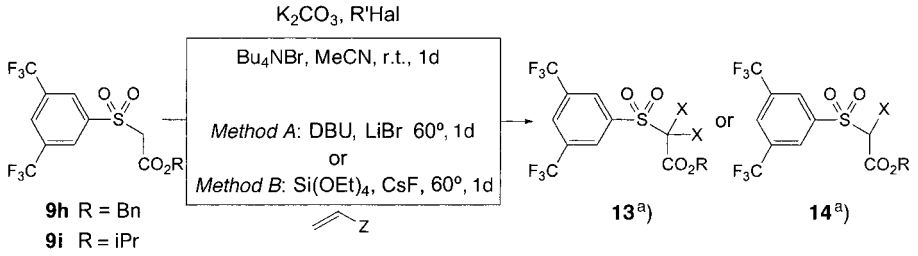
reaction afforded a 1:1 mixture of mono- and dibenzylated products (*Table 2*, *Entry 10*). Under the same conditions, π-electron-deficient (arylsulfonyl)acetates **9a**–**i** furnished the corresponding dialkylated products **12a**–**i** in good yields, except for the (1-oxidopyridin-2-yl)sulfonyl derivative **12d**, which decomposed (*Table 2*, *Entry 4*). In the case of [(pentafluorophenyl)sulfonyl]acetate **9c**, a very low 28% yield of dialkylated product was obtained. The dialkylation of the [(3,4-dichlorophenyl)sulfonyl]acetate **9g** was unproductive in the presence of K_2CO_3 and other inorganic bases such as KOH. When DBU was used as base, a very low 30% yield was obtained after 2 d

5) For a study of the substituent effects on the pK_a values of different substituted aryl phenacyl sulfones, see [23].

(*Table 2*, *Entry 7*). The best yields in the dialkylation reaction were obtained with the 4-nitrophenyl, pyridin-2-yl, pyrimidin-2-yl, and [3,5-bis(trifluoromethyl)phenyl]sulfonyl derivatives (*Table 2*, *Entries 2*, *5*, *6*, *8*, and *9*). The isopropyl acetate **9i** afforded the highest yield (71%) in the dialkylation process (*Table 2*, *Entry 9*).

A variety of electrophiles were found to undergo this useful dialkylation reaction under PTC conditions with the [3,5-bis(trifluoromethyl)phenyl]sulfonyl derivatives **9h**,**i**, which had been shown to contain the best activating group. These substrates underwent dialkylation upon deprotonation with 3 equiv. of K_2CO_3 in MeCN at room temperature to give functionalized π-electron-deficient arylsulfonyl derivatives in moderate to excellent yields (*Scheme 3*, *Table 3*). Different alkyl halides such as methyl iodide, allyl bromide, and prop-2-ynyl bromide furnished the corresponding products **13a**–**d** in good yields (*Table 3*, *Entries 1–4*). When the alkylation reaction was carried out with methyl (2*E*)-4-bromobut-2-enoate (*Scheme 3*, *Table 3*, *Entry 5*), a 42% isolated yield of the monoallylated product **14a** was obtained. When methyl 2-(bromomethyl)prop-2-enoate was used as electrophile, 6 equiv. of base had to be used to afford the dialkylated product in 58% yield (*Table 3*, *Entry 6*). Dialkylated sulfonyl derivatives **13c** and **13g** were subjected to a Pd^{II}-catalyzed cycloisomerization [24]. As shown in *Scheme 4*, palladium acetate (5 mol-%) catalyzed the cyclization of both 1,6-dienic sulfonyl derivatives in a HCl-saturated $CHCl_3$ solution at 60° to afford, after 12 h, the cyclopentene derivatives with high regio- and stereoselectivity and in moderate yields. The relative configuration of the cyclic sulfonyl derivatives **15** and **16** was determined by NOESY experiments. (Arylsulfonyl)cyclopentanecarboxylates were also synthesized in very good yields with 1,4-dihalides as electrophiles (*Table 3*, *Entries 9–12*). Cyclopentenecarboxylate **13i** with a phenylsulfonyl group has been used as starting material for the generation of ethyl 3-oxocyclopenta-1,4-diene-1-carboxylate, a very reactive dienophile [25].

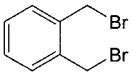
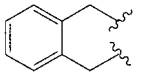
Scheme 3. *Dialkylation of {[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}acetates*



a) See *Table 3* for R and X.

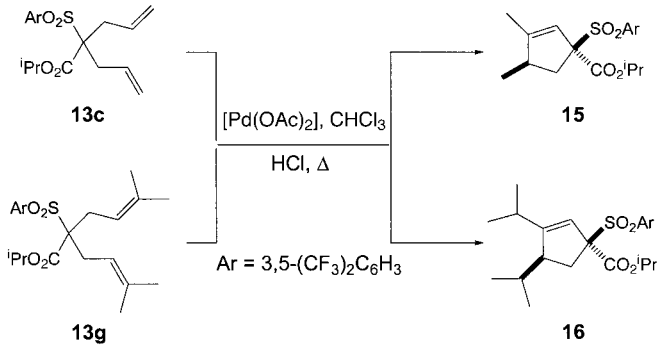
Michael diaddition of sulfonylacetate **9i** with different acceptors was studied under two different reaction conditions (*Scheme 3* and *Table 3*). *Method A* consisted in the use of substoichiometric amounts of DBU (0.2 equiv.) at 60° in MeCN for 1 d. *Method B* involved the use of $Si(OEt)_4$ and CsF as base at 60° for 1 d [26]. *Entries 13* and *14* of *Table 3* show that the *Michael* diaddition delivered better yields with *Method A* in the case of methyl and *tert*-butyl prop-2-enoates as electrophiles. Under the same reaction conditions, methyl vinyl ketone led to the expected dialkylated

Table 3. *Dialkylation of {[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}acetates* **9h**,**i**

Entry	R	E^+	Product **13** or **14**		
			No.	X	Yield [%][a])
1	Bn	MeI	**13a**	Me	89
2	Bn	CH_2=$CHCH_2Br$	**13b**	CH_2=$CHCH_2$	74
3	^{i}Pr	CH_2=$CHCH_2Br$	**13c**	CH_2=$CHCH_2$	81
4	Bn	HC≡CCH_2Br	**13d**	HC≡CCH_2	67
5	^{i}Pr	(*E*)-MeO_2CCH=$CHCH_2Br$	**14a**	(*E*)-MeO_2CCH=$CHCH_2$	42[b])
6	^{i}Pr	$MeO_2CC(=CH_2)CH_2Br$	**13e**	$MeO_2CC(=CH_2)CH_2$	58[c])
7	^{i}Pr	(*E*)-PhCH=$CHCH_2Br$	**13f**	(*E*)-PhCH=$CHCH_2$	48[b])
8	^{i}Pr	Me_2C=$CHCH_2Br$	**13g**	Me_2C=$CHCH_2$	78[b])
9	Bn	$I(CH_2)_4I$	**13h**	$(CH_2)_4$	73
10	Bn	(*Z*)-$BrCH_2CH$=$CHCH_2Br$	**13i**	(*Z*)-CH_2CH=$CHCH_2$	92
11	Bn		**13j**		57
12	^{i}Pr		**13k**		65
13	^{i}Pr	CH_2=$CHCO_2Et$	**13l**	$CH_2CH_2CO_2Et$	54[d]), 35[e])
14	^{i}Pr	CH_2=$CHCO_2{}^t$Bu	**13m**	$CH_2CH_2CO_2{}^t$Bu	74[d]), 62[e])
15	^{i}Pr	CH_2=CHCOMe	**13n**	CH_2CH_2COMe	58
16	^{i}Pr	CH_2=$CHCONH_2$	**14c**	$CH_2CH_2CONH_2$	47[b])

[a]) Isolated yield after flash chromatography based on starting sulfonylacetate after 1 d reaction time. [b]) 2 Equiv. of K_2CO_3 were used. [c]) 6 Equiv, of K_2CO_3 were used. With 3 equiv. of base, monoalkylated product **14b** (see *Exper. Part*) was obtained as the only product in 41% yield. [d]) *Method A:* DBU (0.2 equiv.), LiBr, THF, 60°, 1 d. [e]) *Method B:* $Si(OEt)_4$, CsF, 60°, 1 d.

Scheme 4. *Cycloisomerization Reactions*

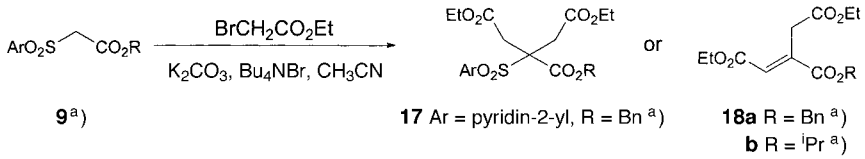


compound in 58% yield (*Table 3*, *Entry 15*). The reaction carried out with prop-2-enamide afforded only the monoalkylated derivative **14c** in 47% yield (*Table 3*, *Entry 16*).

When the dialkylation/reaction was carried out with ethyl bromoacetate as the electrophile under the same PTC conditions as described above but in the presence of 6 equiv. of base (*Scheme 5*, *Table 4*), sulfonylacetates **9a,b,f** cleanly underwent a dialkylation elimination process to provide stereoselectively the (*E*)-aconitate (=(1*E*)-

prop-1-ene-1,2,3-tricarboxylate **18a**[6]) in moderate yields (*Table 4*, *Entries 1*, *2*, and *4*)[7]). The 3,5-[bis(trifluoromethyl)phenyl]sulfonyl group showed again the best activating effect; thus sulfonylacetate **9h** gave aconitate **18a** after 3 d at room temperature with higher yield (*Table 4*, *Entry 5*). The integrated process was faster when the reaction was carried out with isopropyl {[3,5-bis(trifluoromethyl)phenyl]sulfonyl}acetate (**9i**). Aconitate **18b** was then obtained in 71% yield after 3 d at room temperature (*Table 4*, *Entry 6*) and in 60% yield when the mixture was warmed up to 60° for 1 d (*Table 4*, *Entry 7*)[8]). These results can be compared with those obtained with [(4-methylphenyl)sulfonyl]acetate **9j**, which afforded **18b** in a poor 35% isolated yield after 2 d at 60° (*Table 4*, *Entry 8*). The integrated process was unsuccessful in the case of [(pyridin-2-yl)sulfonyl]acetate **9e**, which afforded the corresponding dialkylated product **17** in moderate yield (*Scheme 5*, *Table 4*, *Entry 3*).

Scheme 5. *Synthesis of Aconitates* **18**



9[a]) **17** Ar = pyridin-2-yl, R = Bn[a]) **18a** R = Bn[a]) **b** R = ^{i}Pr[a])

[a]) For Ar, R, and yields, see *Table 4*.

Table 4. *Synthesis of Aconitates* **18**

Entry	Starting ester **9**			*T* [°]	Time [d]	Aconitate **18**	
	Ar	R	No.			No.	Yield [%][a])
1	3-CF_3-C_6H_4	Bn	**9a**	r.t.	4	**18a**	50
2	4-NO_2-C_6H_4	Bn	**9b**	r.t.	3	**18a**	20
3	Pyridin-2-yl	Bn	**9e**	r.t.	7	**17**	50
4	Pyrimidin-2-yl	Bn	**9f**	r.t.	7	**18a**	30
5	3,5-$(CF_3)_2C_6H_3$	Bn	**9h**	r.t.	3	**18a**	64
6	3,5-$(CF_3)_2C_6H_3$	^{i}Pr	**9i**	r.t.	3	**18b**	71
7	3,5-$(CF_3)_2C_6H_3$	^{i}Pr	**9i**	60	1	**18b**	60
8	4-Me-C_6H_4	^{i}Pr	**9j**	60	2	**18b**	35

[a]) Isolated yield after flash chromatography based on starting sulfonylacetate **9**.

(Arylsulfonyl)acetates **9** have been shown to be very efficient precursors of reactive methylenic dienophiles in a *Knoevenagel* condensation reaction with paraformaldehyde (*Scheme 6*). This is a very interesting transformation as the chemistry of 1,1-disubstituted alkenes containing two electron-withdrawing groups have received significant attention in recent years [29]. The *Knoevenagel* condensation of sulfony-

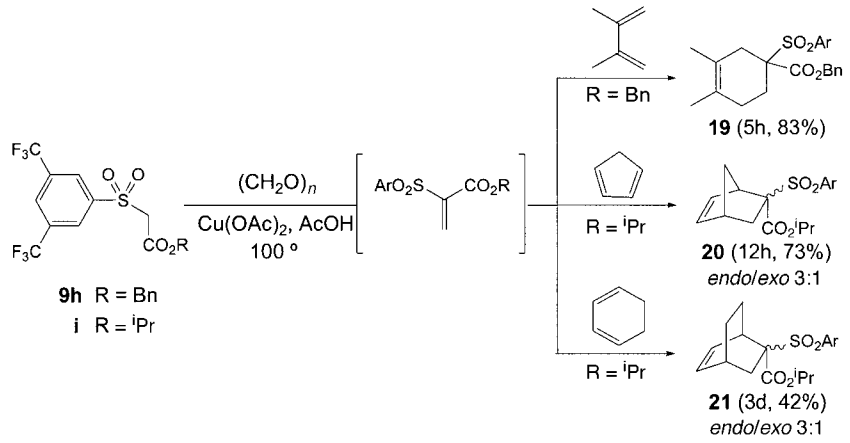
6) The configurations of aconitates **18** were determined with the aid of NOESY and non-decoupled ^{13}C-NMR experiments ($^{3}J(HC{=}C, CH_2C{=}C) = 7.7$ Hz for the (*E*) isomer and 5.5 Hz for the (*Z*) isomer.

7) Trimethyl aconitates have recently been used as versatile synthetic building blocks in the synthesis of heterocycles by means of domino reactions [27].

8) A similar synthesis of triethyl aconitates has been performed by reaction of sodium triflinate and ethyl bromoacetate in the presence of KI and $^{i}Pr_2EtN$ in *N*,*N*-dimethylacetamide at 80° for 145 h in 67% yield (see [28]).

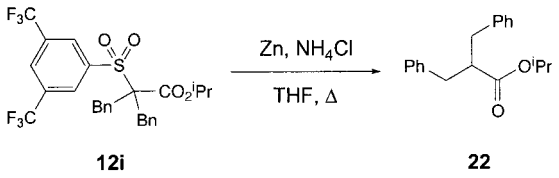
lacetate **9h** with paraformaldehyde in the presence of 2,3-dimethylbuta-1,3-diene gave the corresponding *Diels-Alder* adduct **19** in 83% yield after 5 h (*Scheme 6*). Under the same conditions, derivative **9i** reacted with paraformaldehyde in the presence of cyclic 1,3-dienes such as cyclopenta-1,3-diene and cyclohexa-1,3-diene, affording bicyclic *Diels-Alder* adducts **20** and **21** in good yields and moderate diastereoselectivity (*endo*/*exo* 3:1) (*Scheme 6*)[9]). The first step of the reaction is the formation of the corresponding dienophile intermediates, which are very unstable and were not isolated. The cycloaddition reactions were carried out in sealed tubes at 100° in AcOH as solvent and with $Cu(OAc)_2$ as catalyst [30].

Scheme 6. Diels-Alder *Cycloadditions*



Finally, the reduction of dibenzylated ester **12i** was carried out with Zn in the presence of ammonium chloride in refluxing THF for 1 d to give ester **22** in 70% yield (*Scheme 7*).

Scheme 7. *Reduction of Sulfonylacetate* **12i** *with Zinc*



In conclusion, of all synthesized π-electron-deficient (arylsulfonyl)acetates **9**, the [3,5-bis(trifluoromethyl)phenyl]sulfonyl group was shown to be the best substituent for the dialkylation of these acetates and the alkylation/hydro-sulfonyl-elimination sequence under very mild phase-transfer-catalysis conditions, allowing the stereoselective synthesis of (*E*)-aconitates. Sulfonylacetates **9h**,**i** also underwent smooth *Diels-Alder* reactions with acyclic and cyclic dienes *via in situ* formation of the appropriate dienophile by a *Knoevenagel* condensation with paraformaldehyde.

[9]) The configuration of bicyclic derivatives **20** and **21** was determined by NOESY experiments.

Reductive desulfonylation with Zn and NH_4Cl in THF was shown to be an efficient method for the removal of the synthetically useful sulfonyl moiety.

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Experimental Part

1. *General.* Commercial chemicals and solvents were used without further purification unless otherwise stated. Flash chromatography (FC): silica gel *60* (0.040–0.063 mm; *Merck*). TLC: *Polygram®-SIL-G/UV$_{254}$* plates; elution with hexane/AcOEt 2:1. M.p.: *Reichert Thermovar.* IR Spectra: *Nicolet Impact-400D-FT* spectrophotometer; in cm^{-1}. NMR Spectra: *Bruker AC-300* or *Avance-DRX-500* spectrometer; in $CDCl_3$; δ in ppm rel. to $SiMe_4$ (=0 ppm), *J* in Hz. EI-MS: mass-selective detector *G2579A* from *Agilent Technologies 5973N*; in *m/z* (rel. intensity in % of the base peak). HR-MS: *Finningan MAT95S* apparatus. Elemental analyses: *Carlo Erba EA 1108 (CHNS-O)*; performed by the corresponding services at the University of Alicante.

2. *(Arylthio)acetates* **11a–c**, **11h**, *and* **11i**. To a soln. of the corresponding thiol **10** (5 mmol) and 95% of NaH (150 mg, 6 mmol) in MeCN (15 ml) under N_2 was added at 0° the corresponding alkyl bromoacetate (5.5 mmol). The mixture was stirred at r.t. for 1 d. After quenching with H_2O (20 ml), the mixture was extracted with AcOEt (2 × 20 ml). The combined org. layers were dried (Na_2SO_4) and evaporated: (arylthio)acetates **11**, which were used for the next step without further purification.

Benzyl {[3-(Trifluoromethyl)phenyl]thio}acetate (**11a**). Yield 1.467 g (90%). R_f 0.70. IR: 1735, 1275, 1128. ^{1}H-NMR: 7.62 (*s*, 1 arom. H); 7.74 (*d*, *J* = 7.3, 1 arom. H); 7.40 (*d*, *J* = 7.9, 1 arom. H); 7.31–7.25 (*m*, 6 arom. H); 5.10 (*s*, CH_2O); 3.66 (*s*, CH_2S). ^{13}C-NMR: 168.81 (C=O); 136.39, 135.00 (arom. C); 131.12 (*q*, *J*(C,F) = 31.7, *C*CF_3); 132.35, 129.23, 128.36, 128.24, 128.11, 125.76, 123.23 (arom. CH); 120.02 (*q*, *J*(C,F) = 271.7, CF_3); 67.18 (CH_2O); 35.77 (CH_2S). EI-MS: 326 (10, M^+), 191 (40), 171 (10), 91 (100), 65 (11). HR-EI-MS: 326.0513 ($C_{16}H_{13}SO_2F_3^+$; calc. 326.0588).

Benzyl [(4-Nitrophenyl)thio]acetate (**11b**). Yield 1.439 g (95%). R_f 0.60. IR: 1735, 1517, 1342, 1267, 11.80. ^{1}H-NMR: 8.05 (*d*, *J* = 8.5, 2 arom. H); 7.36–7.25 (*m*, 7 arom. H); 5.17 (*s*, CH_2O); 3.79 (*s*, CH_2S). ^{13}C-NMR: 166.78 (C=O); 140.92, 140.79, 134.22 (arom. C); 131.38, 128.90, 128.72, 128.58, 128.51, 127.67, 127.01, 124.15 (arom. CH); 65.28 (CH_2O); 54.72 (CH_2S). EI-MS: 303 (5, M^+), 168 (19), 121 (12), 100 (100). HR-EI-MS: 303.0621 ($C_{15}H_{13}NO_4S^+$; calc. 303.0565).

Benzyl [(2,3,4,5,6-Pentafluorophenyl)thio]acetate (**11c**). Yield 522 mg (30%). R_f 0.65. IR: 1738, 1273, 1128. ^{1}H-NMR: 7.39–7.19 (*m*, 5 arom. H); 5.09 (*s*, CH_2O); 3.57 (*s*, CH_2S). ^{13}C-NMR: 168.19 (*C*=O); 134.81 (arom. C); 128.63, 128.57, 128.52 (arom. CH); 67.63 (CH_2O); 35.58 (CH_2S). EI-MS: 348 (19, M^+), 203 (22), 105 (18), 92 (17), 91 (100), 77 (19), 65 (32), 51 (17), 46 (10), 45 (37). HR-EI-MS: 348.0217 ($C_{15}H_9F_5O_2S^+$; calc. 348.0243).

Benzyl {[3,5-Bis(trifluoromethyl)phenyl]thio}acetate (**11h**). Yield 1.930 g (98%). R_f 0.69. IR: 1738, 1280, 1137. ^{1}H-NMR: 7.77 (*s*, 2 arom. H); 7.67 (*s*, 1 arom. H); 7.32–7.24 (*m*, 5 arom. H); 5.14 (*s*, CH_2O); 3.76 (*s*, CH_2S). ^{13}C-NMR: 168.17 (C=O); 138.75, 134.86 (arom. C); 132.43 (*q*, *J*(C,F) = 32.2, 2 *C*CF_3); 128.67, 128.56, 128.48, 127.70, 126.97 (arom. CH); 122.85 (*q*, *J*(C,F) = 271.7, 2 CF_3); 67.76 (CH_2O); 35.47 (CH_2S). EI-MS: 394 (4, M^+), 259 (10), 91 (100). HR-EI-MS: 394.0472 ($C_{17}H_{12}F_6O_2S^+$; calc. 394.0462).

Isopropyl {[3,5-Bis(trifluoromethyl)phenyl]thio}acetate (**11i**). Yield 1.713 g (99%). R_f 0.71. IR: 1735, 1282, 1138. ^{1}H-NMR: 7.82 (*s*, 2 arom. H); 7.70 (*s*, 1 arom. H); 5.11–5.01 (*m*, Me_2CH); 3.72 (*s*, CH_2S); 1.22 (*d*, *J* = 6.7, *Me*$_2$CH). ^{13}C-NMR: 168.17 (C=O); 139.19 (arom. C); 132.21 (*q*, *J*(C,F) = 32.2, 2 *C*CF_3); 128.27, 128.24, 119.99 (arom. CH); 122.95 (*q*, *J*(C,F) = 271.7, 2 CF_3); 69.91 (Me_2CH); 35.69 (CH_2S); 21.46 (*Me*$_2$CH). EI-MS: 346 (49, M^+), 285 (11), 260 (26), 259 (100), 239 (30). HR-EI-MS: 346.0479 ($C_{13}H_{12}F_6O_2S^+$; calc. 346.0462).

3. *(Arylthio)acetates* **11d–g**. To a soln. of the corresponding thiol **10** (5 mmol) and Et_3N (1425 µl, 10 mmol) in MeCN (15 ml) was added the corresponding alkyl bromoacetate. The mixture was stirred at r.t. for 1 d. After quenching the mixture with a sat. aq. NH_4Cl soln. (20 ml), the mixture was extracted with AcOEt (2 × 20 ml). The combined org. layers were dried (Na_2SO_4) and evaporated: (arylthio)acetates **11**, which were used in the next step without further purification.

Benzyl [(1-Oxidopyridin-2-yl)thio]acetate (**11d**). Yield 1.238 g (90%). M.p. 94–95°. IR: 1728, 1245, 1141. ^{1}H-NMR: 8.18 (*d*, *J* = 6.0, 1 arom. H); 7.35–7.18 (*m*, 7 arom. H); 7.14 (*t*, *J* = 8.5, 1 arom. H); 5.16 (*s*, CH_2O);

3.76 (*s*, CH_2S). ^{13}C-NMR: 168.81 (C=O); 150.25, 134.59 (arom. C); 128.21, 128.16, 128.00, 125.65, 121.83, 120.89, 113.89 (arom. CH); 67.18 (CH_2O); 35.77 (CH_2S). EI-MS: 275 (1, M^+), 168 (11), 127 (14), 125 (13), 124 (64), 120 (19), 111 (31), 91 (100), 79 (14), 78 (42), 77 (11), 65 (15), 51 (18). Anal. calc. for $C_{14}H_{13}NO_3S^+$ (275): C 61.08, H 4.76, N 5.09, S 11.64; found: C 60.74, H 5.00, N 5.14, S 11.46.

Benzyl (Pyridin-2-ylthio)acetate (**11e**). Yield 1.036 g (80%). R_f 0.69. IR: 1728, 1270, 1148. ^{1}H-NMR: 8.30 (*d*, *J* = 3.7, 1 arom. H); 7.60–7.31 (*m*, 6 arom. H); 7.19 (*d*, *J* = 7.9, 1 arom. H); 6.96–6.93 (*m*, 1 arom. H); 5.16 (*s*, CH_2O); 4.00 (*s*, CH_2S). ^{13}C-NMR: 169.40 (C=O); 135.42, 128.13 (arom. C); 149.07, 135.80, 128.22, 127.95, 127.90, 121.68, 119.54 (arom. CH); 66.82 (CH_2O); 32.02 (CH_2S). EI-MS: 259 (6, M^+), 168 (14), 125 (17), 124 (89), 120 (28), 111 (41), 91 (100), 79 (11), 78 (43), 65 (15), 51 (17). HR-EI-MS: 259.0681 ($C_{14}H_{13}NO_2S^+$; calc. 259.0667).

Benzyl (Pyrimidin-2-ylthio)acetate (**11f**). Yield 1.105 g (85%). R_f 0.60. IR: 1740, 1295, 1151. ^{1}H-NMR: 8.43 (*d*, *J* = 4.9, 2 arom. H); 7.36–7.29 (*m*, 5 arom. H); 6.95 (*t*, *J* = 4.9, 1 arom. H); 5.19 (*s*, CH_2O); 3.97 (*s*, CH_2S). ^{13}C-NMR: 168.92 (C=O); 170.44, 135.41 (arom. C); 157.07, 128.31, 128.08, 116.70 (arom. CH); 66.99 (CH_2O); 33.26 (CH_2S). EI-MS: 259 (6, M^+), 154 (19), 126 (11), 125 (68), 112 (40), 98 (11), 91 (100), 65 (13). HR-EI-MS: 260.0690 ($C_{13}H_{12}N_2O_2S^+$; calc. 260.0619).

Isopropyl [(3,4-Dichlorophenyl)thio]acetate (**11g**). Yield 1.251 g (90%). R_f 0.71. IR: 1730, 1282, 1141. ^{1}H-NMR: 7.56–7.19 (*m*, 3 arom. H); 5.06–4.97 (*m*, Me_2CH); 3.60 (*s*, CH_2S); 1.22 (*d*, *J* = 6.1, Me_2CH). ^{13}C-NMR: 168.40 (C=O); 135.33, 128.93, 126.55 (arom. C); 130.76, 130.44, 128.65 (arom. CH); 69.36 (Me_2CH); 36.40 (CH_2S); 21.50 (Me_2CH). EI-MS: 278 (73, M^+), 236 (13), 195 (13), 193 (68), 192 (13), 191 (100), 142 (18). HR-EI-MS: 277.9895 ($C_{11}H_{12}Cl_2O_2S^+$; calc. 277.9935).

4. *(Arylsulfonyl)acetates* **9a**–**d** *and* **9g**–**i**. To a soln. of the corresponding (arylthio)acetate **11** (5 mmol) in MeOH/H_2O 1:1 (40 ml) was added portionwise *Oxone*® (30.75 g, 50 mmol) at 0°. The mixture was stirred vigorously at r.t. for 1 d. The MeOH was evaporated and the residue diluted with CH_2Cl_2 (40 ml) and washed with brine (3 × 50 ml). The org. layer was dried (Na_2SO_4) and evaporated and the crude product purified by FC (hexane/AcOEt): (arylsulfonyl)acetates **9**.

Benzyl [[3-(Trifluoromethyl)phenyl]sulfonyl]acetate (**9a**). Yield 1.486 g (83%). R_f 0.38. IR: 1745, 1327, 1285, 1163, 1142. ^{1}H-NMR: 8.18 (*s*, 1 arom. H); 8.03 (*d*, *J* = 7.9, 1 arom. H); 7.85 (*d*, *J* = 7.9, 1 arom. H); 7.59 (*t*, *J* = 7.3, 1 arom. H); 7.33–7.21 (*m*, 5 arom. H); 5.09 (*s*, CH_2O); 4.21 (*s*, CH_2S). ^{13}C-NMR: 161.79 (C=O); 139.59, 134.15 (arom. C); 131.88, 130.65, 129.88, 128.57, 128.45, 128.36, 125.44 (arom. CH); 132.16 (*q*, *J*(C,F) = 30.5, *C*CF_3); 122.88 (*q*, *J*(C,F) = 271.7,CF_3); 67.93 (CH_2O); 60.39 (CH_2S). DIP-MS: 358 (6, M^+), 338 (29), 336 (45), 303 (12), 285 (13), 282 (18), 271 (17), 269 (100), 267 (78), 265 (35), 253 (22), 252 (42), 251 (25), 249 (16), 247 (12), 235 (12), 233 (40), 231 (74), 229 (68), 227 (16), 225 (10), 219 (15), 218 (11), 217 (17), 216 (10), 213 (27), 212 (17), 211 (36), 210 (28), 209 (15), 205 (33), 204 (85), 203 (68), 202 (10), 199 (18), 197 (62), 196 (21), 195 (34), 194 (75), 193 (39), 192 (20), 185 (20), 183 (43), 182 (17), 181 (43), 180 (15), 179 (12), 177 (46), 175 (56), 173 (12), 171 (13), 169 (16), 165 (39), 163 (18), 162 (26), 161 (59), 160 (29), 159 (40), 158 (18), 157 (18), 151 (10), 149 (59), 148 (25), 147 (75), 146 (31), 144 (12), 143 (25), 141 (20), 140 (12), 137 (17), 135 (28), 133 (22), 127 (36), 126 (46), 125 (35), 123 (21), 121 (29), 119 (52), 117 (46), 115 (19), 114 (27), 113 (41), 112 (58), 111 (69), 110 (38), 109 (69), 108 (12), 107 (53), 101 (15), 99 (40), 95 (75), 89 (26), 87 (22), 85 (65), 83 (71), 82 (10), 79 (22), 78 (16), 77 (81), 76 (59), 75 (57), 73 (13), 64 (11), 63 (21), 51 (27). HR-DIP-MS: 358.0486 ($C_{16}H_{13}F_3O_4S^+$; calc. 358.0486).

Benzyl [(4-Nitrophenyl)sulfonyl]acetate (**9b**). Yield 787 mg (47%). M.p. 83–84°. IR: 1734, 1533, 1341, 1308, 1276, 1158, 1108. ^{1}H-NMR: 8.23 (*d*, *J* = 8.5, 2 arom. H); 7.98 (*d*, *J* = 8.5, 2 arom. H); 7.38–7.23 (*m*, 5 arom. H); 5.10 (*s*, CH_2O); 4.22 (*s*, CH_2S). ^{13}C-NMR: 161.62 (C=O); 150.90, 143.64, 134.03 (arom. C); 130.05, 129.03, 128.90, 128.66, 124.18 (arom. CH); 68.33 (CH_2O); 60.58 (CH_2S). DIP-MS: 224 (1, [M – CH_2Ph]$^+$), 211 (18), 170 (78), 150 (36), 149 (85), 148 (27), 141 (28), 125 (22), 124 (10), 123 (10), 122 (55), 120 (74), 109 (18), 108 (51), 107 (100), 106 (72), 105 (85), 92 (12), 91 (31), 90 (49), 79 (84), 78 (12), 77 (57), 75 (30), 65 (24), 63 (17), 51 (46). Anal. calc. for $C_{15}H_{13}NO_6S$ (335): C 53.73, H 3.91, N 4.18, S 9.56; found: C 53.64, H 4.09, N 4.00, S 8.78.

Benzyl [(2,3,4,5,6-Pentafluorophenyl)sulfonyl]acetate (**9c**). Yield 1.292 g (68%). M.p. 119°. IR: 1758, 1354, 1286, 1120, 1158. ^{1}H-NMR: 7.36–7.23 (*m*, 5 arom. H); 5.14 (*s*, CH_2O); 4.33 (*s*, CH_2S). ^{13}C-NMR: 163.53 (C=O); 134.14 (arom. C); 128.89, 128.81, 128.58 (arom. CH); 68.02 (CH_2O); 56.86 (CH_2S). DIP-MS: 380 (100, M^+), 233 (29), 232 (12), 231 (66), 216 (17), 215 (63), 195 (12), 184 (15), 183 (63), 181 (35), 168 (73), 167 (36), 155 (15), 150 (77), 149 (37), 148 (37), 1121 (12), 120 (33), 119 (12), 177 (47), 109 (15), 108 (42), 107 (21), 106 (70), 105 (57), 104 (13), 99 (12), 93 (13), 92 (48), 91 (23), 90 (46), 89 (47), 80 (27), 79 (31), 78 (24), 77 (38), 65 (18), 64 (24), 63 (32), 52 (21), 51 (34). Anal. calc. for $C_{15}H_9F_5O_4S$ (380): C 47.38, H 2.39, S 8.43; found: C 47.83, H 2.59, S 7.99.

Benzyl [(1-Oxidopyridin-2-yl)sulfonyl]acetate (**9d**). Yield 460 mg (30%). R_f 0.20. IR: 1715, 1366, 1266, 1161, 1141. ^{1}H-NMR: 8.20 (*d*, *J* = 6.7, 1 arom. H); 7.92 (*dd*, *J* = 7.9, 1.2, 1 arom. H); 7.41 (*t*, *J* = 6.1, 1 arom. H); 7.34–7.20 (*m*, 6 arom. H); 5.06 (*s*, CH_2O); 4.89 (*s*, CH_2S). ^{13}C-NMR: 162.13 (C=O); 146.05, 134.10 (arom. C); 140.68, 129.67, 128.69, 128.58, 127.76, 125.49 (arom. CH); 68.02 (CH_2O); 57.09 (CH_2S). DIP-MS: 307 (0.3, M^+), 254 (10), 252 (22), 250 (13), 248 (39), 235 (25), 234 (10), 232 (10), 220 (40), 219 (18), 218 (30), 217 (21), 216 (24), 201 (10), 200 (38), 186 (22), 185 (73), 184 (10), 183 (10), 182 (16), 181 (13), 172 (12), 168 (52), 167 (32), 160 (17), 159 (53), 158 (70), 156 (49), 155 (42), 154 (43), 145 (19), 144 (53), 143 (25), 142 (26), 128 (11), 127 (49), 126 (56), 125 (11), 114 (11), 113 (14), 112 (100), 111 (10), 110 (60), 108 (16), 107 (51), 106 (34), 105 (81), 96 (86), 93 (14), 92 (26), 91 (36), 90 (79), 89 (78), 80 (37), 79 (15), 78 (17), 77 (29), 76 (18), 67 (11), 66 (36), 65 (22), 64 (44), 63 (71), 53 (11), 52 (50), 51 (15). HR-DIP-MS: 307.0536 ($C_{14}H_{13}NO_5S^+$; calc. 307.0514).

Isopropyl [(3,4-Dichlorophenyl)sulfonyl]acetate (**9g**). Yield 1.132 g (73%). M.p. 79–80°. IR: 1733, 1336, 1288, 1143, 1088. ^{1}H-NMR: 8.04 (*s*, 1 arom. H); 7.78 (*d*, *J* = 7.9, 1 arom. H); 7.67 (*d*, *J* = 7.9, 1 arom. H); 5.05–4.97 (*m*, Me_2CH); 4.11 (*s*, CH_2S); 1.22 (*d*, *J* = 6.1, Me_2CH). ^{13}C-NMR: 161.48 (C=O); 138.33, 133.92 (arom. C); 131.22, 130.70, 127.72 (arom. CH); 70.82 (CH_2O); 61.08 (CH_2S); 21.46 (Me_2CH). DIP-MS: 310 (9, M^+), 253 (44), 251 (75), 228 (25), 226 (43), 213 (14), 211 (88), 209 (100), 208 (12), 206 (91), 205 (12), 204 (90), 193 (11), 164 (26), 162 (44), 161 (25), 159 (34), 149 (12), 147 (83), 146 (12), 145 (94), 111 (21), 110 (17), 109 (60), 85 (10), 75 (29), 74 (23), 59 (27). Anal. calc. for $C_{11}H_{12}Cl_2O_4S$ (310): C 42.46, H 3.89, S 10.30; found: C 39.94, H 3.83, S 10.01.

Benzyl {[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}acetate (**9h**). Yield 1.598 g (75%). M.p. 96–98°. IR: 1732, 1318, 1294, 1148, 1135. ^{1}H-NMR: 8.37 (*s*, 2 arom. H); 8.12 (*s*, 1 arom. H); 7.35–7.22 (*m*, 5 arom. H); 5.12 (*s*, CH_2O); 4.25 (*s*, CH_2S). ^{13}C-NMR: 161.55 (C=O); 141.23, 132.89 (arom. C); 133.29 (*q*, *J*(C,F) = 35.4, 2 *C*CF_3); 128.68, 128.45 (arom. CH); 122.30 (*q*, *J*(C,F) = 271.7, 2 CF_3); 68.41 (CH_2O); 60.34 (CH_2S). DIP-MS: 426 (86, M^+), 407 (35), 365 (21), 335 (12), 279 (10), 277 (31), 262 (12), 261 (80), 214 (23), 183 (21), 182 (11), 163 (30), 150 (35), 149 (27), 148 (47), 147 (10), 144 (21), 121 (24), 120 (94), 109 (21), 108 (35), 107 (19), 106 (100), 105 (56), 103 (14), 92 (57), 91 (13), 90 (78), 89 (31), 79 (63), 78 (27, 77 (52)), 63 (16), 51 (42). Anal. calc. for $C_{17}H_{12}F_6O_4S$ (426): C 46.38, H 2.92, S 7.74; found: C 46.27, H 2.80, S 7.39.

Isopropyl {[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}acetate (**9i**). Yield 1.739 g (92%). M.p. 109–110°. IR: 1727, 1361, 1288, 1184, 1141. ^{1}H-NMR: 8.43 (*s*, 2 arom. H); 8.19 (*s*, 1 arom. H); 5.08–4.97 (*m*, Me_2CH); 4.19 (*s*, CH_2S); 1.21 (*d*, *J* = 6.7, Me_2CH). ^{13}C-NMR: 161.21 (C=O); 141.49 (arom. C); 133.09 (*q*, *J*(C,F) = 35.4, 2 *C*CF_3); 129.31, 127.82 (arom. CH); 122.32 (*q*, *J*(C,F) = 271.7, 2 CF_3); 71.18 (Me_2CH); 60.86 (CH_2S); 21.37 (Me_2CH). DIP-MS: 378 (12, M^+), 359 (35), 320 (36), 319 (100), 318 (13), 317 (41), 293 (10), 279 (30), 278 (11), 272 (58), 243 (10), 214 (13), 213 (22), 194 (24), 163 (23), 125 (19), 100 (10), 85 (20), 77 (10), 71 (10), 69 (15), 59 (33), 56 (10), 55 (18). Anal. calc. for $C_{13}H_{12}F_6O_4S$ (378): C 41.28, H 3.20, S 8.48; found: C 41.10, H 3.19, S 7.93.

5. *(Arylsulfonyl)acetates* **9e–f**. To a soln. of the corresponding (arylthio)acetate **11** (5 mmol) in CH_2Cl_2 (50 ml), was added portionwise $NaHCO_3$ (2.948 g, 35 mmol) and MCPBA (3.365 g, 15 mmol) at 0°. The mixture was stirred vigorously at r.t. for 2 h. The mixture was then washed with sat. aq. $Na_2S_2O_3$ soln. (2 × 60 ml), sat. aq. $NaHCO_3$ soln. (2 × 60 ml), and brine (2 × 60 ml). The org. layer was dried (Na_2SO_4) and evaporated and the crude product purified by FC (hexane/AcOEt): (arylsulfonyl)acetates **9e**,**f**.

Benzyl (Pyridin-2-ylsulfonyl)acetate (**9e**). Yield 815 mg (56%). R_f 0.33. IR: 1742, 1325, 1276, 1166, 1110. ^{1}H-NMR: 8.65 (*s*, *J* = 4.3, 1 arom. H); 7.95 (*d*, *J* = 7.9, 1 arom. H); 7.82 (2*d*, *J* = 7.9, 7.3, 1 arom. H); 7.48 (*dd*, *J* = 7.3, 4.9, 1 arom. H); 7.36–7.17 (*m*, 1 arom. H); 5.06 (*s*, CH_2O); 4.51 (*s*, CH_2S). ^{13}C-NMR: 162.05 (C=O); 156.19, 134.23 (arom. C); 149.90, 137.96, 128.42, 128.37, 128.29, 127.45, 122.10 (arom. CH); 67.67 (CH_2O); 55.89 (CH_2S). DIP-MS: 291 (2, M^+), 185 (29), 184 (100), 143 (65), 107 (17), 93 (73), 92 (11), 91 (16), 90 (26), 80 (32), 79 (14), 78 (52), 77 (64), 65 (78), 63 (11), 52 (33), 51 (45). HR-DIP-MS: 291.0546 ($C_{14}H_{13}NO_4S^+$; calc. 291.0565).

Benzyl (Pyrimidin-2-ylsulfonyl)acetate (**9f**). Yield 905 mg (62%). M.p. 99–100°. IR: 1742, 1333, 1273, 1140, 1123. ^{1}H-NMR: 8.80 (*d*, *J* = 4.9, 2 arom. H); 7.46 (*t*, *J* = 4.9, 1 arom. H); 7.31–7.18 (*m*, 5 arom. H); 5.07 (*s*, CH_2O); 4.64 (*s*, CH_2S). ^{13}C-NMR: 164.51 (C=O); 161.87, 133.98 (arom. C); 158.29, 128.37, 128.31, 128.27, 123.78 (arom. CH); 67.75 (CH_2O); 55.15 (CH_2S). DIP-MS: 292 (0.3, M^+), 186 (36), 169 (23), 107 (28), 106 (11), 94 (66), 92 (23), 91 (52), 89 (10), 81 (50), 80 (100), 78 (32), 77 (50), 65 (38), 53 (57), 52 (44), 51 (32). Anal. calc. for $C_{13}H_{12}N_2O_4S$ (292): C 53.42, H 4.41, N 9.58, S 10.97; found: C 51.77, H 3.99, N 9.50, S 10.55.

6. *Isopropyl [(4-Methylphenyl)sulfonyl]acetate* (**9j**). A DMF soln. (30 ml) of sodium 4-methylbenzenesulfinate (1.430 g, 8 mmol) and isopropyl bromoacetate (260 µl, 2 mmol) was stirred vigorously at r.t. for 1 d. The mixture was diluted with AcOEt (20 ml) and washed with H_2O (5 × 60 ml). The org. layer was dried (Na_2SO_4) and evaporated and the crude product purified by FC (hexane/AcOEt): 410 mg (80%) of pure **9j**. M.p. 62–63°. IR: 1733, 1325, 1288, 1151, 1104. ^{1}H-NMR: 7.82 (*d*, *J* = 7.9, 2 arom. H); 7.37 (*d*, *J* = 7.9, 2 arom. H); 5.01–4.92 (*m*, Me_2CH); 4.08 (*s*, CH_2S); 2.45 (*s*, MeC_6H_4); 1.17 (*d*, *J* = 6.1, Me_2CH). ^{13}C-NMR: 161.77 (C=O);

145.16, 135.65 (arom. C); 129.58, 128.36 (arom. CH); 70.09 (Me_2CH); 61.46 (CH_2S); 21.22 (Me_2CH). DIP-MS: 256 (6, M^+), 197 (50), 192 (50), 173 (55), 172 (28), 157 (32), 156 (52), 155 (64), 151 (52), 149 (77), 139 (74), 122 (14), 121 (18), 119 (14), 108 (29), 107 (46), 106 (32), 105 (51), 103 (20), 92 (34), 91 (66), 90 (35), 89 (55), 80 (10), 79 (69), 78 (45), 77 (52), 66 (39), 65 (52), 64 (42), 62 (13), 59 (100), 56 (19), 53 (17), 51 (14). Anal. calc. for $C_{12}H_{16}O_4S$ (256): C 5623, H 6.29, S 12.51; found: C 55.59, H 4.48, S 12.35.

7. *Dialkylation of (Arylsulfonyl)acetates with Alkyl Halides: General Procedure.* To a THF soln. (3 ml) of the corresponding (arylsulfonyl)acetate **9** (0.2 mmol), K_2CO_3 (87 mg, 0.6 mmol), and Bu_4NBr (7 mg, 0.02 mmol) was added the corresponding alkyl halide (0.44 mmol). The mixture was stirred at r.t. for 1 d and then the reaction quenched with sat. aq. NH_4Cl soln. The aq. phase was extracted with AcOEt (2 × 10 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the crude product purified by FC (hexane/AcOEt): alkylated compounds **12**–**14**.

Benzyl 2-Benzyl-3-phenyl-2-{[3-(trifluoromethyl)phenyl]sulfonyl}propanoate (**12a**). Yield 32 mg (30%). R_f 0.33. IR: 1735, 1326, 1278, 1177, 1140. ^{1}H-NMR: 8.04 (*s*, 1 arom. H); 7.80 (2*d*, *J* = 7.9, 2 arom. H); 7.44 (*t*, *J* = 7.9, 1 arom. H); 7.36–7.07 (*m*, 15 arom. H); 5.12 (*s*, CH_2O); 3.48, 3.41 (2*d*, *J* = 14.3, 2 CH_2C). ^{13}C-NMR: 167.42 (C=O); 139.24, 133.09, 131.28 (arom. C); 131.97 (*q*, *J*(C,F) = 35.4, *C*CF_3); 130.93, 130.26, 130.21, 129.05, 128.86, 128.68, 128.10, 127.82, 127.77, 127.32 (arom. CH); 122.30 (*q*, *J*(C,F) = 271.2, CF_3); 78.62 (CS); 68.17 (CH_2O); 39.10 (2 *C*H_2C). DIP-MS: 538 (0.06, M^+), 237 (30), 219 (16), 193 (21), 192 (20), 191 (15), 178 (13), 159 (20), 145 (33), 131 (11), 116 (10), 115 (40), 92 (37), 91 (100), 77 (11), 65 (19). HR-DIP-MS: 538.1462 ($C_{30}H_{25}F_3O_4S^+$; calc. 538.1426).

Benzyl 2-Benzyl-2-[(4-nitrophenyl)sulfonyl]-3-phenylpropanoate (**12b**). Yield 68 mg (66%). R_f 0.39. IR: 1735, 1532, 1349, 1280, 1144, 1140. ^{1}H-NMR: 8.02 (*d*, *J* = 9.2, 2 arom. H); 7.76 (*d*, *J* = 8.5, 2 arom. H); 7.39–7.12 (*m*, 15 arom. H); 5.11 (*s*, CH_2O); 3.50, 3.43 (2*d*, *J* = 14.0, 2 CH_2C). ^{13}C-NMR: 167.24 (C=O); 150.34, 143.48, 133.87, 133.64 (arom. C); 132.09, 130.93, 129.23, 129.13, 128.74, 128.19, 127.45, 123.12 (arom. CH); 78.94 (CS); 68.44 (CH_2O); 39.23 (2 *C*H_2C). DIP-MS: 515 (0.4, M^+), 75 (20), 76 (30), 79 (13), 105 (14), 107 (21), 115 (64), 116 (60), 117 (100), 118 (30), 119 (56), 135 (83), 145 (57), 146 (13), 190 (97), 191 (28). HR-DIP-MS: 515.1419 ($C_{29}H_{25}NO_6S^+$; calc. 515.1403).

Benzyl 2-Benzyl-2-[(2,3,4,5,6-pentafluorophenyl)sulfonyl]-3-phenylpropanoate (**12c**). Yield 31 mg (28%). R_f 0.74. IR: 1730, 1320, 1280, 1140, 1120. ^{1}H-NMR: 7.38–7.62 (*m*, 15 arom. H); 5.19 (*s*, CH_2O); 3.56, 3.46 (2*d*, *J* = 14.0, 2 CH_2C). ^{13}C-NMR: 166.69 (C=O); 133.72, 133.38, 129.21, 128.89, 128.82, 128.64, 128.11, 127.22 (arom. C, 5 CF); 130.83, 128.98, 128.69, 128.18, 128.04, 127.42 (arom. CH); 80.18 (CS); 68.96 (CH_2O); 37.32 (2 *C*H_2C). DIP-MS: 560 (2, M^+), 467 (22), 466 (95), 402 (16), 393 (17), 392 (80), 343 (10), 331 (43), 330 (17), 328 (15), 313 (20), 312 (17), 307 (10), 306 (12), 283 (20), 253 (11), 252 (34), 251 (50), 250 (17), 239 (33), 238 (12), 237 (34), 233 (19), 222 (17), 221 (28), 220 (35), 219 (32), 209 (10), 205 (23), 195 (15), 194 (58), 193 (19), 192 (27), 191 (32), 190 (17), 189 (32), 187 (21), 182 (15), 181 (27), 180 (45), 179 (57), 178 (64), 177 (35), 168 (77), 167 (27), 166 (25), 165 (40), 163 (11), 162 (18), 161 (18), 160 (41), 159 (17), 152 (12), 149 (15), 143 (14), 137 (12), 132 (11), 131 (53), 129 (10), 119 (19), 118 (26), 117 (33), 116 (32), 115 (32), 111 (10), 108 (10), 107 (58), 106 (17), 105 (100), 104 (11), 103 (48), 102 (35), 99 (30), 97 (11), 95 (15), 93 (17), 91 (26), 90 (74), 89 (55), 83 (14), 79 (25), 78 (20), 77 (55), 75 (11), 71 (17), 69 (16), 65 (38), 64 (71), 63 (27), 57 (25), 55 (15). HR-DIP-MS: 560.1065 ($C_{29}H_{21}F_5O_4S^+$; calc. 560.1081).

Benzyl 2-Benzyl-3-phenyl-2-(pyridin-2-ylsulfonyl)propanoate (**12e**). Yield 60 mg (64%). R_f 0.26. IR: 1735, 1318, 1266, 1189, 1155. ^{1}H-NMR: 8.43 (*d*, *J* = 4.3, 1 arom. H); 7.57–7.05 (*m*, 18 arom. H); 5.19 (*s*, CH_2O); 3.65, 3.55 (2*d*, *J* = 14.0, 2 CH_2C). ^{13}C-NMR: 167.58 (C=O); 157.23, 134.44, 134.31 (arom. C); 148.93, 137.36, 131.09, 128.83, 128.48, 128.45, 127.87, 126.95, 126.62, 124.07 (arom. CH); 76.85 (CS); 68.04 (CH_2O); 38.67 (2 *C*H_2C). DIP-MS: 471 (0.2, M^+), 407 (12), 316 (19), 298 (16), 219 (18), 192 (13), 191 (18), 178 (14), 159 (24), 115 (40), 103 (10), 91 (100), 79 (42), 78 (46), 77 (23), 65 (20), 52 (14). HR-DIP-MS: 472.1534 ($C_{28}H_{26}NO_4S^+$; calc. 472.1582).

Benzyl 2-Benzyl-3-phenyl-2-(pyrimidin-2-ylsulfonyl)propanoate (**12f**). Yield 55 mg (58%). R_f 0.28. IR: 1735, 1322, 1263, 1190, 1125. ^{1}H-NMR: 8.32 (*d*, *J* = 4.9, 2 arom. H); 7.37–7.03 (*m*, 16 arom. H); 5.21 (*s*, CH_2O); 3.70, 3.55 (2*d*, *J* = 14.0, 2 CH_2C). ^{13}C-NMR: 167.04 (C=O); 157.34, 131.38, 128.82, 128.45, 128.32, 127.87, 127.03, 122.65 (ArCH); 134.65, 133.82, 128.58, 128.53 (arom. C); 74.95 (CS); 67.75 (CH_2O); 38.46 (2 *C*H_2C). DIP-MS: 391 (0.06, $[M - pymSO_2]^+$), 408 (38), 329 (26), 299 (16), 273 (12), 237 (35), 222 (19), 221 (29), 200 (12), 219 (44), 209 (20), 195 (14), 194 (100), 193 (59), 192 (18), 191 (18), 186 (14), 183 (30), 181 (11), 180 (22), 179 (19), 178 (15), 177 (31), 169 (55), 161 (50), 159 (46), 157 (15), 145 (21), 131 (18), 126 (12), 117 (23), 116 (10), 115 (47), 92 (83), 91 (75), 81 (24), 80 (29), 77 (10), 65 (13), 64 (13), 51 (15). HR-DIP-MS: 472.1430 ($C_{27}H_{24}N_2O_4S^+$; calc. 472.1456).

Isopropyl 2-Benzyl-2-[(3,4-dichlorophenyl)sulfonyl]-3-phenylpropanoate (**12g**). Yield 29 mg (30%). R_f 0.38. IR: 1725, 1372, 1271, 1162, 1145. ^{1}H-NMR: 7.84 (*s*, 1 arom. H); 7.62, 7.52 (2*d*, *J* = 8.6, 2 arom. H); 7.22 (*m*, 15 arom. H); 5.05–4.99 (*m*, Me_2CH); 3.43 (*m*, 2 CH_2C); 1.19 (*d*, *J* = 6.1, Me_2CH). ^{13}C-NMR: 167.22 (C=O); 138.80, 137.82, 134.23, 132.96 (arom. C); 132.79, 130.97, 130.20, 129.94, 128.05, 127.35 (arom. CH); 78.62 (CS); 71.31 (CHO); 39.26 (2 CH_2C); 21.46 (Me_2CH). DIP-MS: 491 (4, $[M+1]^+$), 431 (20), 283 (15), 282 (81), 280 (33), 241 (13), 240 (42), 239 (48), 237 (24), 223 (17), 222 (53), 221 (15), 220 (33), 219 (39), 209 (11), 205 (16), 196 (11), 195 (58), 194 (34), 191 (42), 190 (20), 189 (37), 181 (54), 180 (12), 179 (96), 178 (39), 167 (25), 166 (23), 165 (64), 163 (12), 162 (88), 161 (27), 160 (100), 159 (45), 152 (20), 149 (26), 148 (47), 147 (66), 146 (56), 145 (76), 143 (12), 133 (95), 132 (37), 131 (63), 130 (12), 119 (30), 118 (46), 117 (41), 116 (28), 115 (14), 111 (16), 110 (16), 109 (26), 107 (87), 105 (95), 103 (91), 102 (34), 92 (23), 91 (62), 90 (13), 89 (20), 79 (24), 78 (33), 77 (42), 75 (12), 74 (16), 65 (68), 64 (12), 63 (13), 51 (12). HR-DIP-MS: 490.0730 ($C_{25}H_{24}Cl_2O_4S^+$; calc. 490.0772).

Benzyl 2-Benzyl-2-{[3,5-bis(trifluoromethyl)phenyl]sulfonyl}-3-phenylpropanoate (**12h**). Yield 70 mg (58%). R_f 0.60. IR: 1724, 1356, 1279, 1189, 1143. ^{1}H-NMR: 8.16 (*s*, 2 arom. H); 7.99 (*s*, 1 arom. H); 7.38–7.05 (*m*, 15 arom. H); 5.14 (*s*, CH_2O); 3.50, 3.42 (2*d*, *J* = 14.6, 2 CH_2C). ^{13}C-NMR: 167.32 (C=O); 141.32, 133.54, 131.73 (arom. C); 131.97 (*q*, *J*(C,F) = 35.4, 2 CCF_3); 130.97, 130.93, 128.92, 128.69, 128.63, 128.14, 127.56, 127.08 (arom. CH); 122.29 (*q*, *J*(C,F) = 271.7, 2 CF_3); 79.18 (CS); 68.28 (CH_2O); 39.47 (2 CH_2C). DIP-MS: 606 (0.2, M^+), 330 (23), 329 (96), 328 (40), 316 (16), 312 (12), 311 (60), 283 (14), 261 (10), 251 (18), 239 (11), 238 (85), 237 (49), 222 (22), 221 (88), 220 (69), 219 (29), 214 (16), 213 (33), 205 (16), 195 (18), 194 (41), 193 (94), 192 (94), 191 (77), 181 (30), 180 (10), 179 (34), 178 (70), 167 (17), 165 (24), 163 (11), 161 (88), 160 (24), 159 (91), 145 (11), 143 (13), 131 (66), 125 (12), 117 (31), 116 (41), 115 (98), 107 (15), 105 (20), 104 (10), 103 (40), 92 (100), 91 (42), 90 (13), 89 (15), 79 (11), 77 (27), 65 (65), 57 (22). HR-DIP-MS: 499.0793 ($C_{24}H_{17}F_6O_3S^+$, $[M-OBn]^+$; calc. 499.0803).

Isopropyl 2-Benzyl-2-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-3-phenylpropanoate (**12i**). Yield 79 mg (71%). R_f 0.57. IR: 1724, 1356, 1279, 1189, 1143. ^{1}H-NMR: 8.22 (*s*, 2 arom. H); 8.04 (*s*, 1 arom. H); 7.37–7.21 (*m*, 10 arom. H); 5.07–5.01 (*m*, Me_2CH); 3.52, 3.44 (2*d*, *J* = 14.4, 2 CH_2C); 1.18 (*d*, *J* = 6.1, Me_2CH). ^{13}C-NMR: 167.17 (C=O); 141.48, 136.52 (arom. C); 132.16 (*q*, *J*(C,F) = 30.5, 2 CCF_3); 131.10, 131.02, 130.94, 128.47, 128.14, 127.61 (arom. CH); 122.39 (*q*, *J*(C,F) = 271.50, 2 CF_3); 79.04 (CS); 71.64 (Me_2CH); 39.52 (2 CH_2C); 21.32 (Me_2CH). DIP-MS: 558 (0.24, M^+), 242 (100), 240 (11), 142 (73), 79 (17). HR-DIP-MS: 558.1300 ($C_{27}H_{24}F_6O_4S^+$; calc. 558.1299).

Isopropyl 2-Benzyl-2-[(4-methylphenyl)sulfonyl]-3-phenylpropanoate (**12j**)/*Isopropyl 2-[(4-Methylphenyl)sulfonyl]-3-phenylpropanoate.* Yield 44 mg (**12j**/monoalkylated product 1:1). R_f 0.58. IR: 1738, 1338, 1281, 1140, 1118. ^{1}H-NMR: 7.80, 7.74 (2*d*, *J* = 8.5, 4 arom. H); 7.34, 7.29 (2*d*, *J* = 8.5, 4 arom. H); 7.25–7.12 (*m*, 15 arom. H); 5.00–4.91, 4.85–4.76 (2*m*, 2 H, Me_2CH); 4.14 (*dd*, *J* = 11.1, 3.3, 1 H, CHS); 3.51–3.43 (*m*, 4 H, CH_2C); 3.42–3.37, 3.24–3.16 (2*m*, 2 H, CH_2CH), 1.13, 0.99, 0.92 (3*d*, *J* = 6.1, 12 H, 2 Me_2CH). ^{13}C-NMR: 167.53, 164.88 (C=O); 145.42, 144.85, 135.54, 134.89, 134.58, 130.96, 130.91, 129.66, 129.40, 129.03, 128.86, 128.63, 127.84, 127.14, 126.89 (arom. C, arom. CH); 77.74 (CS); 72.13 (CHS); 70.79, 69.90 (Me_2CH); 38.44 (2 CH_2C); 32.63 (2 CH_2CH); 21.66, 21.60, 21.35, 21.23, 21.15 (2 Me_2CH). DIP-MS (**12j**): 346 (0.4, M^+), 287 (60), 192 (29), 191 (28), 190 (13), 150 (100), 149 (20), 148 (49), 147 (32), 145 (33), 132 (24), 131 (62), 107 (56), 104 (35), 103 (48), 92 (26), 91 (26), 77 (33), 65 (92). DIP-MS (monoalkylated product): 436 (0.5, M^+), 91 (100). HR-DIP-MS: 346.1234 ($C_{19}H_{22}O_4S^+$; calc. 346.1239); 436.1706 ($C_{26}H_{28}O_4S^+$; calc. 436.1708).

Benzyl 2-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-2-methylpropanoate (**13a**). Yield 53 mg (58%). R_f 0.33 (hexane/AcOEt 3:1). IR: 1744, 1313, 1278, 1138, 1122. ^{1}H-NMR: 8.25 (*s*, 2 arom. H); 8.11 (*s*, 1 arom. H); 7.37–724 (*m*, 5 arom. H); 5.12 (*s*, CH_2O); 1.68 (*s*, 2 Me). ^{13}C-NMR: 168.16 (C=O); 138.70, 134.36 (arom. C); 132.47 (*q*, *J*(C,F) = 35.4, 2 CCF_3); 130.86, 130.81, 128.66, 127.89, 127.53 (arom. CH); 122.33 (*q*, *J*(C,F) = 271.7, 2 CF_3); 69.83 (CS); 68.18 (CH_2O); 20.02 (2 Me). DIP-MS: 454 (0.5, M^+), 176 (29), 107 (65), 91 (100), 70 (15). HR-DIP-MS: 347.0188 ($C_{12}H_9F_6O_3S^+$; $[M-OBn]^+$; calc. 347.0176).

Benzyl 2-Allyl-2-{[3,5-bis(trifluoromethyl)phenyl]sulfonyl}pent-4-enoate (**13b**). Yield 75 mg (74%). R_f 0.33 (hexane/AcOEt 3:1). IR: 3083, 1740, 1642, 1359, 1280, 1153, 1140. ^{1}H-NMR: 8.26 (*s*, 2 arom. H); 8.11 (*s*, 1 arom. H); 7.36–7.27 (*m*, 5 arom. H); 5.83–5.73 (*m*, 2 CH=); 5.19–5.13 (*m*, 2 CH_2=); 5.13 (*s*, CH_2O); 2.93 (*dd*, *J* = 14.6, 6.7, 1 CH_2C); 2.81 (*dd*, *J* = 14.6, 7.3, 1 CH_2C). ^{13}C-NMR: 166.82 (C=O); 139.37, 134.08 (arom. C); 132.43 (*q*, *J*(C,F) = 34.2, 2 CCF_3); 130.91, 130.20, 128.80, 128.68, 127.59 (arom. CH); 128.21 (2 CH=); 122.67 (*q*, *J*(C,F) = 271.4, 2 CF_3); 120.95 (2 CH_2=); 79.04 (CS); 68.35 (CH_2O); 35.04 (2 CH_2C). DIP-MS: 506 (4, M^+), 228 (15), 213 (23), 183 (12), 130 (19), 104 (11), 93 (17), 92 (100), 91 (11), 79 (23), 77 (26), 65 (36), 53 (11). HR-DIP-MS: 506.1018 ($C_{23}H_{20}F_6O_4S^+$; calc. 506.0986).

Isopropyl 2-Allyl-2-{[3,5-bis(trifluoromethyl)phenyl]sulfonyl}pent-4-enoate (**13c**). Yield 74 mg (81%). R_f 0.47 (hexane/AcOEt 3:1). IR: 3086, 1728, 1639, 1357, 1281, 1184, 1146. ^{1}H-NMR: 8.33 (*s*, 2 arom. H); 8.17 (*s*, 1 arom. H); 5.90–5.76 (*m*, 2 CH=); 5.23–5.17 (*m*, 2 CH_2=); 5.05–4.96 (*m*, Me_2CH); 2.89 (*dd*, *J* = 14.6, 6.7, 1 CH_2C); 2.79 (*dd*, *J* = 14.6, 7.3, 1 CH_2C); 1.25 (*d*, *J* = 6.1, Me_2CH). ^{13}C-NMR: 166.38 (C=O); 139.54 (arom. C); 132.39 (*q*, *J*(C,F) = 35.0, 2 *C*CF_3); 131.04, 127.64, 127.61 (arom. CH); 130.43 (2 CH=); 122.67 (*q*, *J*(C,F) = 271.4, 2 CF_3); 120.73 (2 CH_2=); 75.75 (CS); 71.24 (Me_2CH); 35.18 (2 *C*H_2C); 21.32 (Me_2CH). DIP-MS: 458 (1, M^+), 217 (10), 191 (10), 178 (12), 177 (11), 176 (40), 174 (16), 173 (53), 170 (33), 167 (10), 163 (15), 149 (24), 125 (19), 123 (47), 121 (13), 105 (13), 99 (10), 98 (19), 97 (48), 95 (24), 85 (15), 83 (46), 70 (23), 69 (34), 67 (19), 57 (100). HR-DIP-MS: 458.0916 ($C_{19}H_{20}F_6O_4S^+$; calc. 458.0986).

Benzyl 2-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-2-(prop-2-ynyl)pent-4-ynoate (**13d**). Yield 67 mg (67%). R_f 0.38 (hexane/AcOEt 3:1). IR: 3292, 2105, 1739, 1370, 1280, 1186, 1147. ^{1}H-NMR: 8.34 (*s*, 2 arom. H); 8.14 (*s*, 1 arom. H); 7.38–7.35 (*m*, 5 arom. H); 5.21 (*s*, CH_2O); 3.22 (*dd*, *J* = 17.1, 2.4, 1 CH_2C); 3.08 (*dd*, *J* = 17.1, 3.1, 1 CH_2C); 2.08 (*t*, *J* = 2.4, 2 CH≡C). ^{13}C-NMR: 165.30 (C=O); 138.42, 133.94 (arom. C); 132.77 (*q*, *J*(C,F) = 34.2, 2 *C*CF_3); 130.97, 130.92, 128.81, 128.61, 128.32 (arom. CH); 122.23 (*q*, *J*(C,F) = 271.7, 2 CF_3); 76.26 (2 *C*≡CH); 73.84 (2 *C*H≡C); 73.27 (CS); 69.09 (CH_2O); 21.68 (2 *C*H_2C). DIP-MS: 502 (2, M^+), 226 (15), 225 (100), 224 (89), 207 (11), 195 (28), 185 (30), 179 (45), 166 (15), 165 (17), 133 (10), 131 (31), 120 (92), 119 (18), 118 (54), 117 (14), 115 (20), 107 (76), 105 (15), 93 (17), 92 (38), 91 (35), 90 (58), 89 (38), 79 (23), 65 (21). HR-DIP-MS: 502.0674 ($C_{23}H_{16}F_6O_4S^+$; calc. 502.0673).

4-Isopropyl 2,6-Dimethyl 4-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}hepta-1,6-diene-2,4,6-tricarboxylate (**13e**). Yield 67 mg (58%). R_f 0.40 (hexane/AcOEt 3:1). IR: 3087, 1736, 1628, 1358, 1281, 1188, 1147. ^{1}H-NMR: 8.42 (*s*, 2 arom. H); 8.17 (*s*, 1 arom. H); 6.34 (*s*, 1 CH_2=C); 5.76 (*s*, 1 CH_2=C); 5.10–5.05 (*m*, Me_2CH); 3.75 (*s*, 2 MeO); 3.26, 3.11 (2*d*, *J* = 15.3, 2 CH_2C); 1.22 (*d*, *J* = 6.1, Me_2CH). ^{13}C-NMR: 167.09, 166.89 (C=O); 139.87, 134.35, 134.31 (arom. C, *C*=CH_2); 132.40 (*q*, *J*(C,F) = 34.2, 2 *C*CF_3); 131.53, 131.48, 127.73, 127.69, 127.59 (arom. CH); 129.42 (2 CH_2=); 122.30 (*q*, *J*(C,F) = 271.4, 2 CF_3); 76.68 (CS); 71.82 (Me_2CH); 52.22 (2 MeO); 32.49 (2 *C*H_2C); 21.21 (Me_2CH). DIP-MS: 531 (12, $[M - O^iPr]^+$), 500 (13), 493 (23), 469 (45), 465 (45), 436 (11), 298 (14), 297 (28), 261 (25), 255 (37), 238 (14), 237 (97), 261 (25), 255 (37), 224 (11), 223 (98), 222 (55), 213 (51), 209 (11), 206 (33), 205 (97), 205 (97), 195 (32), 194 (23), 192 (26), 191 (97), 179 (15), 178 (15), 177 (86), 164 (15), 163 (67), 152 (12), 151 (18), 149 (34), 147 (18), 146 (22), 145 (15), 139 (13), 137 (13), 135 (42), 134 (11), 125 (10), 121 (19), 119 (41), 118 (14), 107 (19), 105 (13), 92 (13), 91 (100), 79 (25), 77 (23), 69 (15), 65 (28), 59 (79), 55 (13), 53 (12). HR-DIP-MS: 574.1102 ($C_{23}H_{24}F_6O_8S^+$; calc. 574.1096).

*Isopropyl (4*E*)-2-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-5-phenyl-2-[(2*E*)-3-phenylprop-2-enyl]pent-4-enoate* (**13f**). Yield 59 mg (48%). R_f 0.44. IR: 3060, 1739, 1644, 1370, 1280, 1189, 1147. ^{1}H-NMR: 8.36 (*s*, 2 arom. H); 8.16 (*s*, 1 arom. H); 7.31–7.24 (*m*, 10 arom. H); 6.50 (*d*, *J* = 15.9, 2 PhCH=); 6.21 (*dt*, *J* = 15.9, 7.32, 2 CH_2C*H*=); 5.08–5.02 (*m*, Me_2CH); 3.10 (*dd*, *J* = 14.6, 6.71, 1 CH_2CH=); 3.00 (*dd*, *J* = 14.6, 7.3, 1 CH_2CH=); 1.26 (*d*, *J* = 6.7, Me_2CH). ^{13}C-NMR: 166.49 (C=O); 139.63, 136.54 (arom. C); 135.61, 131.02, 128.63, 126.27 (arom. CH); 132.52 (*q*, *J*(C,F) = 34.2, 2 *C*CF_3); 122.39 (*q*, *J*(C,F) = 271.7, 2 CF_3); 127.84, 121.75 (2 CH=CH); 76.38 (CS); 71.34 (Me_2CH); 34.83 (2 *C*H_2CH=); 21.46 (Me_2CH). DIP-MS: 551 (2, $[M - O^iPr]^+$), 548 (10), 332 (17), 291 (23), 290 (43), 289 (86), 273 (20), 272 (20), 271 (41), 245 (51), 244 (21), 243 (43), 241 (26), 229 (13), 228 (18), 213 (26), 206 (87), 205 (37), 204 (15), 200 (18), 199 (63), 198 (18), 187 (56), 186 (37), 181 (24), 180 (100), 179 (10), 170 (14), 169 (90), 168 (10), 167 (78), 165 (18), 156 (14), 155 (87), 154 (13), 153 (28), 143 (18), 142 (48), 141 (60), 129 (73), 128 (67), 127 (22), 118 (46), 117 (37), 116 (30), 115 (44), 105 (19), 104 (51), 103 (13), 92 (27), 86 (12), 77 (19). HR-DIP-MS: 610.1631 ($C_{31}H_{28}F_6O_4S^+$; calc. 610.1613).

Isopropyl 2-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-5-methyl-2-(3-methylbut-2-enyl)hex-4-enoate (**13g**). Yield 80 mg (78%). R_f 0.53 (hexane/AcOEt 8:1). IR: 3080, 1736, 1625, 1358, 1270, 1178, 1140. ^{1}H-NMR: 8.33 (*s*, 2 arom. H); 8.14 (*s*, 1 arom. H); 5.13–5.11 (*m*, 2 CH=); 5.06–4.97 (*m*, Me_2CH); 2.77 (*d*, *J* = 6.7, 2 CH_2C); 1.70, 1.58 (2*s*, 2 Me_2C=); 1.24 (*d*, *J* = 6.1, Me_2CH). ^{13}C-NMR: 167.05 (C=O); 140.23 (arom. C); 136.39 (Me_2*C*=); 132.23 (*q*, *J*(C,F) = 35.4, 2 *C*CF_3); 130.86, 130.81, 127.33 (arom. CH); 122.45 (*q*, *J*(C,F) = 271.7, 2 CF_3); 116.34 (2 CH=); 76.64 (CS); 70.84 (Me_2CH); 29.89 (2 CH_2C); 25.97, 21.21 (2 Me_2C=); 17.96 (Me_2CH). DIP-MS: 514 (0.6, M^+), 238 (13), 237 (100), 236 (82), 213 (20), 196 (19), 195 (86), 194 (86), 193 (82), 181 (16), 179 (59), 177 (29), 163 (10), 161 (19), 153 (12), 152 (12), 151 (62), 150 (18), 149 (87), 147 (13), 140 (24), 139 (39), 138 (46), 137 (35), 133 (21), 127 (39), 126 (28), 125 (27), 124 (12), 123 (35), 121 (19), 119 (13), 111 (33), 109 (53), 108 (15), 107 (62), 105 (21), 95 (37), 94 (16), 93 (83), 91 (30), 81 (29), 80 (13), 79 (47), 77 (28), 70 (14), 69 (22), 67 (22), 56 (12), 55 (12), 53 (18). HR-DIP-MS: 514.1650 ($C_{23}H_{28}F_6O_4S^+$; calc. 514.1613).

Benzyl 1-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}cyclopentanecarboxylate (**13h**). Yield 70 mg (73%). R_f 0.29 (hexane/AcOEt 3:1). IR: 1742, 1310, 1278, 1174, 1143. ^{1}H-NMR: 8.26 (*s*, 2 arom. H); 8.08 (*s*, 1 arom. H); 7.34–7.20 (*m*, 5 arom. H); 5.10 (*s*, CH_2O); 2.52–2.34 (*m*, 2 CH_2C); 1.98–1.86, 1.75–1.62 (2*m*,

2 CH_2CH$_2$C). ^{13}C-NMR: 168.23 (C=O); 140.26, 134.33 (arom. C); 132.42 (q, J(C,F) = 35.4, 2 CCF$_3$); 130.31, 130.26, 128.64, 127.84, 127.33, 127.29 (arom. CH); 122.34 (q, J(C,F) = 271.7, 2 CF$_3$); 79.68 (CS); 68.23 (CH$_2$O); 32.60 (2 CH$_2$C); 25.31 (2 CH$_2$CH$_2$C). DIP-MS: 480 (0.9, M^+), 349 (26), 261 (35), 213 (33), 204 (11), 203 (100), 202 (93), 157 (39), 113 (17), 108 (14), 107 (53), 97 (78), 95 (74), 92 (57), 91 (18), 90 (13), 89 (11), 79 (15), 77 (15), 69 (41), 68 (38), 67 (39), 65 (43), 50 (10). HR-DIP-MS: 480.0829 ($C_{21}H_{18}F_6O_4S^+$; calc. 480.0830).

Benzyl 1-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}cyclopent-3-ene-1-carboxylate (**13i**). Yield 88 mg (92%). R_f 0.38 (hexane/AcOEt 3:1). IR: 3093, 1732, 1626, 1362, 1281, 1182, 1143. ^{1}H-NMR: 8.31 (s, 2 arom. H); 8.02 (s, 1 arom. H); 7.34–7.10 (m, 5 arom. H); 5.58–5.41 (m, CH=CH); 5.07 (s, CH$_2$O); 2.39 (dd, J = 7.3, 5.50, 1 CH$_2$C); 2.13 (dd, J = 7.3, 6.1, 1 CH$_2$C). ^{13}C-NMR: 164.58 (C=O); 143.01, 133.94 (arom. C); 132.39 (q, J(C,F) = 34.1, 2 CCF$_3$); 130.05, 128.87, 128.76, 128.63, 128.18 (arom. CH); 122.31 (q, J(C,F) = 271.7, 2 CF$_3$); 121.43 (CH=CH); 79.04 (CS); 68.35 (CH$_2$O); 35.04 (2 CH$_2$C). DIP-MS: 478 (4, M^+), 395 (10), 391 (12), 382 (11), 355 (16), 277 (32), 272 (19), 261 (25), 228 (11), 227 (13), 224 (17), 214 (23), 213 (100), 194 (32), 176 (11), 159 (13), 149 (24), 148 (10), 145 (14), 143 (26), 141 (11), 138 (13), 132 (15), 131 (12), 123 (10), 119 (18), 111 (16), 102 (10), 99 (18), 98 (19), 97 (17), 96 (18), 92 (18), 91 (81), 90 (17), 89 (14), 85 (19), 83 (34), 81 (17), 77 (48), 75 (18), 71 (17), 70 (12), 69 (29), 65 (20), 57 (36). HR-DIP-MS: 387.0125 ($C_{14}H_9F_6O_4S^+$, [M – Bn]$^+$; calc. 387.0168).

*Benzyl 2-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-2,3-dihydro-1*H-*indene-2-carboxylate* (**13j**). Yield 60 mg (57%). R_f 0.35 (hexane/AcOEt 3:1). IR: 1732, 1353, 1281, 1180, 1140. ^{1}H-NMR: 8.20 (s, 2 arom. H); 8.02 (s, 1 arom. H); 7.38–7.07 (m, 9 arom. H); 5.16 (s, CH$_2$O); 3.83, 3.72 (2d, J = 17.1, 2 CH$_2$C). ^{13}C-NMR: 167.24 (C=O); 139.47, 137.92, 134.29 (arom. C); 132.43 (q, J(C,F) = 34.2, 2 CCF$_3$); 130.14, 130.09, 128.63, 127.81, 127.73, 124.18 (arom. CH); 122.89 (q, J(C,F) = 271.8, 2 CF$_3$); 79.49 (CS); 68.67 (CH$_2$O); 38.65 (2 CH$_2$C). DIP-MS: 528 (0.7, M^+), 261 (12), 250 (14), 213 (12), 149 (24), 143 (100), 139 (15), 116 (50), 105 (12), 104 (11), 97 (11), 91 (75), 83 (12), 71 (20), 70 (14), 69 (13), 57 (37). HR-DIP-MS: 251.1065 ($C_{17}H_{15}O_2^+$, [M – (CF$_3$)$_2$C$_6$H$_3$SO$_2$]$^+$; calc. 251.1072).

*Isopropyl 2-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-2,3-dihydro-1*H-*indene-2-carboxylate* (**13k**). Yield 58 mg (60%). R_f 0.43 (hexane/AcOEt 8:1). IR: 1732, 1359, 1284, 1182, 1144. ^{1}H-NMR: 8.27 (s, 2 arom. H); 8.08 (s, 1 arom. H); 7.14–7.07 (m, 4 arom. H); 5.04–4.98 (m, Me$_2$CH); 3.80, 3.70 (2d, J = 17.1, 2 CH$_2$C); 1.24 (d, J = 6.1, Me_2CH). ^{13}C-NMR: 166.72 (C=O); 139.63, 138.03 (arom. C); 132.92 (q, J(C,F) = 35.4, 2 CCF$_3$); 130.18, 130.13, 127.61, 124.08 (arom. CH); 122.39 (q, J(C,F) = 271.7, 2 CF$_3$); 79.44 (CS); 71.53 (CHO); 38.65 (2 CH$_2$C); 21.23 (Me_2CH). DIP-MS: 480 (0.2, M^+), 421 (34), 401 (23), 261 (29), 213 (16), 204 (23), 203 (88), 202 (81), 195 (10), 163 (18), 162 (86), 161 (75), 160 (45), 144 (50), 143 (47), 117 (100), 116 (35), 115 (83), 114 (13), 91 (12), 89 (20). HR-DIP-MS: 203.1080 ($C_{13}H_{15}O_2^+$, [M – (CF$_3$)$_2$C$_6$H$_3$SO$_2$]$^+$; calc. 203.1072).

*6-Isopropyl 1-Methyl (2*E*)-5-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}hex-2-enedioate* (**14a**). Yield 40 mg (42%). R_f 0.60. IR: 3100, 1731, 1660, 1357, 1282, 1191, 1147. ^{1}H-NMR: 8.35 (s, 2 arom. H); 8.21 (s, 1 arom. H); 6.79 (m, =CHCH$_2$); 5.96 (d, J = 15.3, =CHCO); 5.01–4.93 (m, Me$_2$CH); 4.10 (dd, J = 10.4, 4.3, CHS); 3.73 (s, MeO); 3.17–2.83 (m, CHCH_2); 1.18, 1.23 (2d, J = 6.1, Me_2CH). ^{13}C-NMR: 165.62, 165.59 (C=O); 141.91 (CH=CH$_2$); 138.63 (arom. C); 132.62 (q, J = 35.3, 2 CCF$_3$); 130.89, 128.13, 126.41 (arom. CH); 122.34 (q, J(C,F) = 271.3, 2 CF$_3$); 124.14 (COCH=); 72.16 (Me$_2$$C$H); 70.77 (CHS); 51.70 (MeO); 33.62 (CH$_2$CH); 21.26, 13.56 (Me_2CH). DIP-MS: 445 (2, [M – OMe]$^+$), 434 (41), 417 (11), 403 (11), 385 (13), 277 (10), 261 (13), 213 (73), 199 (10), 194 (15), 167 (17), 158 (18), 157 (99), 140 (12), 139 (100), 116 (15), 115 (91), 113 (21), 111 (87), 109 (19), 108 (24), 107 (42), 99 (11), 97 (95), 83 (13), 81 (62), 80 (15), 79 (10), 71 (11), 69 (17), 68 (11), 59 (34), 55 (35), 53 (53), 51 (10). HR-EI-MS: 476.0735 ($C_{18}H_{18}F_6O_6S^+$; calc. 476.0728).

1-Isopropyl 5-Methyl 2-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-4-methylenepentanedioate (**14b**). Yield 39 mg (41%). R_f 0.40 (hexane/AcOEt 8:1). IR: 3077, 1730, 1629, 1356, 1281, 1181, 1144. ^{1}H-NMR: 8.36 (s, 2 arom. H); 7.64 (s, 1 arom. H); 5.98, 5.24 (2s, =CH$_2$); 4.80–4.69 (m, Me$_2$CHO); 4.57 (dd, J = 11.0, 4.0, CHS); 3.17 (s, MeO); 3.14–3.13 (m, 1 H, CHCH_2); 2.88–2.80 (m, 1 H, CHCH_2); 0.81 (d, J = 6.1, Me_2CH). ^{13}C-NMR: 166.02, 164.10 (C=O); 140.21 (arom. C); 133.95 (C=CH$_2$); 133.01 (q, J(C,F) = 35.3, 2 CCF$_3$); 129.82, 127.90, 127.85, 127.82 (arom. CH); 122.28 (q, J(C,F) = 271.3, 2 CF$_3$); 124.10 (C=CH$_2$); 71.06 (CHO); 69.01 (CHS); 52.28 (MeO); 29.85 (CH$_2$C=); 21.45, 21.22 (Me$_2$CH). DIP-MS: 476 (1, M^+), 385 (24), 277 (11), 213 (27), 199 (11), 194 (18), 163 (16), 157 (72), 144 (14), 139 (18), 125 (100), 112 (16), 98 (21), 97 (84), 82 (17), 81 (24), 59 (23), 55 (23), 53 (88), 51 (16). HR-DIP-MS: 476.0733 ($C_{18}H_{18}F_6O_6S^+$; calc. 476.0728).

8. *Alkylation of* **9i** *with* Michael *Acceptors: General Procedure. Method A:* To a soln. of sulfonylacetate **9i** (76 mg, 0.2 mmol), DBU (6.1 µl, 0.04 mmol), and LiBr (11 mg, 0.12 mmol) in THF (3 ml), the corresponding electrophile (0.44 mmol) was added. The mixture was heated at 60° for 1 d. After quenching with sat. NH_4Cl soln., the mixture was extracted with AcOEt (2 × 5 ml) the combined org. phase dried (Na_2SO_4) and evaporated, and the crude products purified by FC (hexane, AcOEt).

Method B: Sulfonylacetate **9i** (76 mg, 0.2 mmol), $Si(OEt)_4$ (547 µl, 2.4 mmol), CsF (37 mg, 0.24 mmol), and the corresponding *Michael* acceptor (0.44 mmol) were stirred and heated at 60° for 1 d. AcOEt (5 ml) was then added, the mixture washed with H_2O (3 × 5 ml), the org. phase dried (Na_2SO_4) and evaporated, and the crude product purified by FC (hexane/AcOEt).

1,5-Diethyl 3-Isopropyl 3-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}pentane-1,3,5-tricarboxylate (**13l**). Yield, see *Table 3*. R_f 0.23. IR: 1739, 1359, 1281, 1191, 1140. ^{1}H-NMR: 8.35 (*s*, 2 arom. H); 8.18 (*s*, 1 arom. H); 5.07–4.97 (*m*, Me_2CH); 4.15 (*q*, *J* = 7.3, 2 $MeCH_2O$); 2.70–2.17 (*m*, 4 CH_2); 1.27 (*m*, Me_2CH, 2 $MeCH_2O$). ^{13}C-NMR: 171.67, 166.32 (C=O); 139.27 (arom. C); 132.56 (*q*, *J*(C,F) = 34.2, 2 CCF_3); 131.04, 127.64, 127.61 (arom. CH); 122.35 (*q*, *J*(C,F) = 271.4, 2 CF_3); 75.33 (CS); 71.63 (Me_2CH); 60.94 (2 CH_2O); 29.07, 26.49 (4 CH_2); 21.29 (Me_2CH); 14.08 (2 $MeCH_2O$). DIP-MS: 519 (25, $[M - O^iPr]^+$) 420 (11), 419 (45), 392 (19), 391 (81), 373 (100), 372 (15), 351 (23), 331 (62), 213 (18), 201 (51), 195 (28), 194 (14), 167 (26), 159 (21), 144 (18), 143 (15), 142 (22), 141 (25), 140 (10), 139 (33), 131 (64), 115 (15), 114 (54), 113 (66), 101 (16), 88 (30), 87 (14), 86 (29), 85 (27), 73 (15), 57 (13), 55 (33). HR-DIP-MS: 578.1416 ($C_{23}H_{28}F_6O_8S^+$; calc. 578.1409).

1,5-Di(tert-*butyl) 3-Isopropyl 3-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}pentane-1,3,5-tricarboxylate* (**13m**). Yield see *Table 3*. R_f 0.30. IR: 1730, 1364, 1281, 1150, 1103. ^{1}H-NMR: 8.34 (*s*, 2 arom. H); 8.18 (*s*, 1 arom. H); 5.07–4.98 (*m*, Me_2CH); 2.61–2.19 (*m*, 4 CH_2); 1.44 (*s*, 2 Me_3C); 1.26 (*d*, *J* = 6.1, Me_2CH). ^{13}C-NMR: 170.94, 166.42 (C=O); 139.37 (arom. C); 132.91 (*q*, *J*(C,F) = 35.1, 2 CCF_3); 131.09, 127.80, 127.76 (arom. CH); 122.30 (*q*, *J*(C,F) = 271.4, 2 CF_3); 81.38 (CS); 75.48 (2 Me_3C); 71.05 (Me_2CH); 30.14 (2 CH_2CO); 22.23 (2 CH_2C); 27.99 (2 Me_3C); 21.29 (Me_2CH). DIP-MS: 634 (0.3, $[M - O^iPr]^+$), 562 (18), 525 (23), 524 (100), 508 (14), 507 (43), 506 (67), 465 (50), 464 (92), 463 (31), 451 (13), 449 (14), 447 (72), 446 (64), 445 (55), 444 (79), 443 (70), 420 (14), 419 (68), 418 (46), 417 (19), 416 (12), 408 (32), 391 (12), 390 (73), 360 (12), 359 (88), 346 (16), 331 (19), 302 (20), 279 (24), 262 (12), 261 (79), 247 (14), 246 (78), 245 (39), 228 (40), 227 (66), 214 (25), 213 (70), 204 (22), 203 (88), 195 (20), 194 (30), 188 (10), 187 (78), 186 (94), 185 (50), 184 (10), 169 (30), 168 (70), 167 (31), 166 (16), 163 (10), 159 (10), 158 (20), 157 (89), 145 (26), 144 (14), 143 (27), 141 (54), 140 (69), 139 (71), 131 (10), 130 (38), 129 (38), 127 (73), 126 (10), 125 (69), 123 (13), 122 (14), 121 (11), 114 (11), 113 (73), 112 (54), 111 (53), 101 (14), 99 (40), 98 (14), 95 (45), 83 (15), 71 (26), 67 (17), 59 (23), 58 (55), 56 (46), 55 (45). HR-DIP-MS: 634.2037 ($C_{27}H_{36}F_6O_8S^+$; calc. 634.2035).

Isopropyl 2-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-5-oxo-2-(3-oxobutyl)hexanoate (**13n**). Yield 60 mg (58%). R_f 0.46. IR: 1739, 1713, 1352, 1280, 1141, 1130. ^{1}H-NMR: 8.27 (*s*, 2 arom. H); 8.19 (*s*, 1 arom. H); 5.12–5.06 (*m*, Me_2CH); 2.61–2.56 (*m*, 2 CH_2CO); 2.44–2.04 (*m* with *s* at 2.27, 2 CH_2C, 2 MeCO); 1.23 (*d*, *J* = 6.1, Me_2CH). ^{13}C-NMR: 213.19, 166.11 (C=O); 138.25 (arom. C); 132.56 (*q*, *J*(C,F) = 34.2, 2 CCF_3); 130.76, 127.84, 127.79 (arom. CH); 122.28 (*q*, *J*(C,F) = 271.4, 2 CF_3); 77.21 (CS); 73.57 (Me_2CH); 34.48 (2 CH_2CO); 28.23 (2 $MeCO$); 25.40 (2 CH_2C); 21.36 (Me_2CH). DIP-MS: 503 (2, $[M - Me]^+$), 241 (47), 240 (17), 182 (29), 181 (100), 180 (49), 165 (14), 163 (33), 153 (10), 139 (95), 138 (27), 137 (96), 123 (83), 121 (63), 113 (18), 111 (26), 109 (12), 96 (11), 95 (33), 93 (42), 85 (13), 77 (11), 71 (31), 58 (28). HR-DIP-MS: 518.1192 ($C_{21}H_{24}F_6O_6S^+$; calc. 518.1198).

Isopropyl 2-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-4-carbamoylbutanoate (**14c**).Yield 42 mg (47%). R_f 0.37. IR: 3393, 1730, 1729, 1667, 1366, 1278, 1134, 1100. ^{1}H-NMR: 8.36 (*s*, 2 arom. H); 8.19 (*s*, 1 arom. H); 5.62 (br. *s*, NH_2); 5.04–4.92 (*m*, Me_2CH); 4.31 (*dd*, *J* = 8.5, 4.3, CHS); 2.56–2.28 (*m*, 2 CH_2); 1.10 (*d*, *J* = 6.1, Me_2CH). ^{13}C-NMR: 172.76 ($CONH_2$); 164.46 (C=O); 140.45 (arom. C); 132.98 (*q*, *J* = 34.2, 2 CCF_3); 129.70, 127.87 (arom. CH); 122.21 (*q*, *J*(C,F) = 271.3, 2 CF_3); 71.11 (Me_2CH); 69.22 (CHS); 31.52 (CH_2CO); 22.05 (CH_2CH); 21.39, 21.15 (Me_2CH). DIP-MS: 449 (0.6, M^+), 391 (17), 390 (100), 373 (27), 368 (27), 350 (12), 336 (11), 331 (47), 318 (14), 271 (32), 261 (18), 213 (69), 194 (17), 172 (80), 130 (85), 113 (24), 112 (60), 86 (10), 85 (41), 84 (23), 73 (10), 72 (45), 69 (18), 59 (47), 55 (26). HR-DIP-MS: 172.0987 ($C_8H_{14}NO_3^+$, $[M - (CF_3)_2C_6H_3SO_2]^+$; calc. 172.0973).

9. *Synthesis of Aconitates* **18**. To a soln. of the corresponding sulfonylacetate **9** (0.2 mmol), K_2CO_3 (174 mg, 1.2 mmol), and Bu_4NBr (7 mg, 0.02 mmol) in MeCN (3 ml) was added ethyl bromoacetate (50 µl, 0.44 mmol). The mixture was stirred at r.t. for the time indicated in *Table 4*. The reaction was then quenched with sat. NH_4Cl soln., the mixture extracted with AcOEt (2 × 3 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the crude aconitate **18** purified by FC (hexane/AcOEt).

*2-Benzyl 1,3-Diethyl (1*E*)-Prop-1-ene-1,2,3-tricarboxylate* (**18a**). Yields, see *Table 4*. R_f 0.60. IR: 3074, 1732, 1656, 1362, 1280, 1142, 1134. ^{1}H-NMR (500 MHz): 7.37 (*s*, 5 arom. H); 6.97 (*s*, CH=C); 5.24 (*s*, $PhCH_2O$); 4.28–4.07 (*m*, 2 $MeCH_2O$); 3.97 (*s*, CH_2C=); 1.32–1.18 (*m*, 2 $MeCH_2O$). ^{13}C-NMR (125 MHz): 168.95, 165.38, 165.20 (C=O); 139.79 (*C*=CH); 132.14 (arom. C); 131.94, 128.95, 128.61, 128.56, 128.43, 128.24, 123.77 (C=*C*H, arom. CH); 68.86 ($PhCH_2O$); 61.39, 60.09 (2 $MeCH_2O$); 33.48 (CH_2C=); 19.72 (Me_2CH); 13.98, 13.64

(2 *Me*CH_2O). EI-MS: 276 (0.22, $[M-OEt]^+$), 214 (11), 185 (10), 139 (18), 90 (100). HR-EI-MS: 275.0906 ($C_{15}H_{15}O_5^+$, $[M-OEt]^+$; calc. 275.0919).

*1,3-Diethyl 2-Isopropyl (1*E*)-Prop-1-ene-1,2,3-tricarboxylate* (**18b**). Yields, see *Table 4*. R_f 0.57. IR: 3075, 1730, 1656, 1362, 1279, 1145, 1136. ^{1}H-NMR (500 MHz): 6.92 (*s*, CH=C); 5.15–5.07 (*m*, Me_2CH); 4.28–4.09 (*m*, 2 MeCH_2O); 3.95 (*s*, CH_2C=); 1.33–1.23 (*m*, 2 *Me*CH_2O). ^{13}C-NMR (125 MHz): 169.88, 165.41, 165.35 (C=O); 140.39 (*C*=CH); 128.74 (C=*C*H); 69.56 (Me_2CH); 60.92, 60.89 (Me*C*H_2O); 33.08 (CH_2C=); 21.58 (Me_2CH); 14.06, 14.02 (2 *Me*CH_2O). EI-MS: 272 (0.31, M^+), 211 (17), 184 (57), 183 (36), 166 (12), 156 (18), 155 (21), 139 (24), 138 (64), 137 (26), 111 (100), 110 (11), 83 (24). HR-EI-MS: 227.0906 ($C_{11}H_{15}O_5^+$, $[M-OEt]^+$; calc. 227.0919).

2-Benzyl 1,3-Diethyl 2-(Pyridin-2-ylsulfonyl)propane-1,2,3-tricarboxylate (**17**). Yield 46 mg (50%). R_f 0.18. IR: 1735, 1730, 1358, 1280, 1140, 1131. ^{1}H-NMR: 8.66 (*d*, *J* = 4.3, 1 arom. H); 7.90–7.84 (*m*, 2 arom. H); 7.36–7.23 (*m*, 6 arom. H); 5.09 (*m*, Me_2CH); 4.12 (*q*, *J* = 6.7, 2 MeCH_2O); 3.62–3.55 (*m*, 2 CH_2C); 1.25 (*t*, *J* = 6.7, 2 *Me*CH_2O). ^{13}C-NMR: 169.21, 165.88 (C=O); 153.86, 134.39 (arom. C); 150.09, 137.83, 128.37, 128.26, 127.95, 125.51 (arom. CH); 71.56 (CS); 68.39 (Me_2CH); 61.07 (2 Me*C*H_2O); 33.67 (*C*H_2C); 13.90 (*Me*CH_2). DIP-MS: 272 (0.69, M^+), 398 (18), 249 (10), 233 (62), 210 (10), 206 (14), 201 (14), 195 (13), 193 (31), 192 (39), 182 (21), 181 (17), 180 (11), 179 (21), 178 (52), 177 (12), 169 (94), 167 (82), 166 (10), 165 (16), 145 (12), 141 (82), 142 (23), 141 (100), 140 (42), 139 (27), 136 (15), 129 (13), 127 (24), 126 (23), 124 (13), 117 (18), 116 (13), 115 (25), 114 (25), 113 (82), 112 (29), 111 (14), 108 (20), 107 (31), 106 (18), 105 (14), 104 (10), 103 (12), 95 (31), 93 (12), 92 (91), 91 (55), 90 (18), 86 (19), 85 (39), 80 (56), 79 (79), 78 (82), 77 (33), 69 (15), 68 (27), 67 (18), 65 (93), 64 (14), 63 (23), 52 (60), 51 (79). HR-EI-MS: 463.1289 ($C_{22}H_{25}NO_8S^+$; calc. 463.1301).

10. *Cycloisomerization Reactions: General Procedure.* Dry HCl was bubbled through a soln. of the corresponding 1,6-diene (0.2 mmol) and palladium acetate (5 mol-%) in $CHCl_3$ (3 ml) for *ca.* 15 min. Then the mixture was stirred under reflux for 16 h. The resulting brown soln. was evaporated, the residue dissolved in AcOEt, the mixture filtered through *Celite* to remove the catalyst, the eluate evaporated, and the residue purified by FC (hexane/AcOEt): **15** or **16**.

rel-*(1*R*,4*S*)-Isopropyl 1-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-3,4-dimethylcyclopent-2-ene-1-carboxylate* (**15**). Yield 66 mg (72%). R_f 0.41 (hexane/AcOEt 8:1). IR: 3079, 1738, 1628, 1361, 1280, 1181, 1143. ^{1}H-NMR: 8.31 (*s*, 2 arom. H); 8.15 (*s*, 1 arom. H); 5.18–5.14 (*m*, CH=C); 5.06–4.94 (*m*, Me_2CH); 3.04–2.96, 2.39–2.33 (2*m*, CH_2C); 2.82–2.78 (*m*, MeC*H*); 1.78 (*s*, MeC=); 1.78–1.13 (*m*, *Me*CH, Me_2CH). ^{13}C-NMR (125 MHz): 166.78 (C=O); 156.66 (*C*=CH); 140.32 (arom. C); 132.51 (*q*, *J*(C,F) = 34.2, 2 *C*CF_3); 130.62, 127.23 (arom. CH); 122.40 (*q*, *J*(C,F) = 271.7, 2 CF_3); 119.23 (CH=); 85.77 (CS); 70.92 (Me_2CH); 42.81 (*C*HCH_2); 36.03 (CH_2); 21.32 (Me_2CH); 18.56 (Me*C*HC=); 14.93 (*Me*CHC=). DIP-MS: 458 (0.2, M^+), 394 (37), 393 (100), 392 (11), 352 (15), 351 (95), 350 (15), 333 (17), 332 (10), 331 (77), 311 (10), 307 (38), 306 (12), 305 (66), 292 (10), 291 (16), 241 (10), 227 (58), 208 (17), 107 (71), 79 (61), 78 (10), 77 (19), 59 (11). HR-DIP-MS: 371.05789 ($C_{15}H_{13}F_6O_2S^+$, $[M-CO_2{}^iPr]^+$; calc. 371.0540).

rel-*(1*R*,4*R*)-Isopropyl 1-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-3,4-diisopropylcyclopent-2-ene-1-carboxylate* (**16**). Yield 70 mg (68%). R_f 0.23 (hexane/AcOEt 8:1). IR: 3076, 1722, 1628, 1360, 1280, 1183, 1144. ^{1}H-NMR: 8.33 (*s*, 2 arom. H); 8.14 (*s*, 1 arom. H); 5.13–5.11 (*m*, CH=); 5.09–4.97 (*m*, Me_2CHO); 2.78–2.75 (*m*, CH_2, C*H*C=, CHC*H*Me); 1.70, 1.58 (2*s*, 2 Me_2CH); 1.24 (*d*, *J* = 6.1, 1 Me_2CH). ^{13}C-NMR (125 MHz): 167.06 (C=O); 140.21 (arom. C); 136.39 (*C*=CH); 132.53 (*q*, *J*(C,F) = 34.18, 2 *C*CF_3); 130.86, 130.81, 127.39, 127.34, 127.29 (arom. CH); 122.45 (*q*, *J*(C,F) = 271.7, 2 CF_3); 116.32 (CH=); 70.84 (CS); 70.84 (Me_2CHO); 39.38 (=C*C*HCH_2); 29.90 (CH_2); 25.97, 21.32, 17.97 (Me_2CHC=, Me_2CHCH, Me_2CHO). DIP-MS: 514 (2, M^+), 261 (10), 237 (54), 236 (91), 213 (36), 196 (14), 195 (100), 194 (97), 193 (92), 192 (16), 181 (12), 179 (49), 177 (39), 176 (15), 167 (13), 163 (13), 161 (26), 153 (27), 152 (20), 151 (57), 150 (15), 149 (72), 147 (18), 140 (19), 139 (97), 138 (34), 137 (36), 135 (15), 133 (60), 127 (29), 126 (28), 125 (39), 124 (16), 123 (43), 121 (38), 119 (17), 111 (40), 109 (63), 108 (19), 107 (80), 105 (30), 97 (15), 96 (11), 95 (70), 94 (20), 93 (85), 91 (49), 87 (12), 85 (13), 83 (15), 81 (42), 80 (17), 79 (66), 77 (38), 71 (45), 70 (20), 69 (56), 68 (11), 67 (43), 65 (11), 59 (78), 57 (22), 56 (22), 55 (57), 53 (27). HR-DIP-MS: 237.1829 ($C_{15}H_{25}O_2^+$, $[M-(CF_3)_2C_6H_3SO_2]^+$; calc. 237.1855).

11. Diels-Alder *Cycloadditions: Typical Procedure.* Paraformaldehyde (12 mg, 2 mmol), copper(II) acetate (2 mg, 0.01 mmol), AcOH (45 µl, 0.4 mmol), the corresponding 1,3-diene (0.4 mmol) and the (arylsulfonyl)-acetate (0.2 mmol) were placed in the sealed tube. The tube was shaken and then heated at 100° for the time indicated in *Scheme 6*. The solvent was then evaporated and the obtained crude mixture purified by FC (hexane/AcOEt): pure compounds **19–21**.

Benzyl 1-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}-3,4-dimethylcyclohex-3-ene-1-carboxylate (**19**). Yield 86 mg (83%). R_f 0.42 (hexane/AcOEt 8:1). IR: 3084, 1731, 1632, 1360, 1280, 1140, 1104. ^{1}H-NMR: 8.20 (*s*, 2 arom. H); 8.11 (*s*, 1 arom. H); 5.15, 5.06 (2*d*, *J* = 12.2, PhCH_2O); 2.75–2.58 (*m*, 1 CH_2C=); 2.33–2.29

(*m*, 1 CH_2C); 2.27–2.07 (*m*, CH_2CH_2C=); 1.60, 1.49 (2*s*, 2 MeC=). ^{13}C-NMR (125 MHz): 166.90 (C=O); 138.53, 134.53 (arom. C); 132.53 (*q*, *J*(C,F) = 34.2, 2 *C*CF_3); 130.53, 130.49, 128.54, 127.85, 127.56 (arom. CH); 125.23, 121.93 (*C*=*C*); 122.28 (*q*, *J*(C,F) = 271.4, 2 CF_3); 73.29 (CS); 67.99 (Ph*C*H_2O); 32.45, 28.62, 25.48 (CH_2); 19.35, 18.34 (*Me*C=). DIP-MS: 520 (0.7, M^+), 243 (69), 242 (78), 152 (39), 151 (47), 150 (41), 136 (10), 1035 (77), 133 (100), 121 (12), 108 (17), 107 (68), 92 (47), 91 (55), 83 (12), 69 (10), 65 (37), 55 (18). HR-DIP-MS: 385.0697 ($C_{16}H_{15}F_6O_2S^+$, [$M - CO_2Bn$]$^+$; calc. 385.0710).

(2-endo/*2*-exo*)-Isopropyl 2-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}bicyclo[2.2.1]hept-5-ene-2-carboxylate* (**20**). Yield 68 mg (73%). R_f 0.37 (hexane/AcOEt 8:1). IR: 1741, 1634, 1350, 1246, 1140, 1122. ^{1}H-NMR (500 MHz): 8.30 (*s*, 2 arom. H, *endo*); 8.28 (*s*, 2 arom. H, *exo*); 8.16 (*s*, 1 arom. H, *endo*); 8.14 (*s*, 1 arom. H, *exo*); 6.49 (*dd*, *J* = 5.5, 3.1, H–C(5), *exo*); 6.39 (*dd*, *J* = 5.5, 3.1, H–C(5), *endo*); 6.21 (*dd*, *J* = 5.2, 3.1, H–C(6) *exo*); 5.93 (*dd*, *J* = 5.2, 3.1, H–C(6), *endo*); 4.89–4.79 (*m*, 2 Me_2CH, *exo* + *endo*); 3.56 (br. *s*, H–C(1), *exo*); 3.37 (br. *s*, H–C(1), *endo*); 3.12 (br. *s*, 2 H–C(4), *exo* + *endo*); 2.81 (*dd*, *J* = 12.9, 4.0, H_{exo}–C(3), *exo*); 2.68 (*dd*, *J* = 12.9, 3.7, H_{exo}–C(3), *endo*); 2.29 (*m*, 2 H_{syn}–C(7), *endo* + *exo*); 2.18 (*dd*, *J* = 12.9, 2.8, H_{endo}–C(3), *endo*); 2.11 (*dd*, *J* = 12.9, 2.8, H_{endo}–C(3), *exo*); 1.61–1.54 (*m*, H_{anti}–C(7), *exo* + *endo*); 1.26–1.13 (*m*, 2 Me_2CH, *exo* + *endo*). ^{13}C-NMR (125 MHz): 167.90 (C=O, *exo*); 166.83 (C=O, *endo*); 141.60 (arom. C, *exo*); 140.83 (arom. C, *endo*); 142.30, 140.71, 133.86, 131.26, 130.10 (*m*), 129.75 (*m*), 127.46 (*m*), 127.36 (*m*) (2 *C*H=CH, arom. CH, *exo* + *endo*); 132.60 (*q*, *J*(C,F) = 35.4, 2 *C*CF_3, *exo* + *endo*); 122.40 (*q*, *J*(C,F) = 271.4, 2 CF_3, *exo* + *endo*); 81.40 (CS, *exo*); 80.98 (CS, *endo*); 71.22 (Me_2*C*H, *exo*); 70.81 (Me_2*C*H, *endo*); 51.59 (*C*HC, *exo*); 50.26 (*C*HC, *endo*); 49.29 (CH*C*H_2CH, *exo*); 47.14 (CH*C*H_2CH, *exo*); 43.00 (*C*HCH_2, *exo*); 42.42 (*C*HCH_2, *endo*); 33.94 (*C*H_2C, *exo*); 33.12 (*C*H_2C, *endo*); 21.28, 21.21, 21.15, 21.08 (2 *Me*$_2$CH, *exo* + *endo*). DIP-MS: 468 (0.4, M^+), 454 (24), 433 (17), 408 (21), 402 (18), 389 (13), 388 (64), 386 (13), 330 (22), 288 (10), 286 (14), 271 (13), 270 (100), 220 (45), 200 (18), 156 (17), 129 (41), 127 (24), 108 (13). HR-DIP-MS: 468.0848 ($C_{20}H_{28}F_6O_4S^+$; calc. 468.0830).

(2-endo/*2*-exo*)-Isopropyl 2-{[3,5-Bis(trifluoromethyl)phenyl]sulfonyl}bicyclo[2.2.2]oct-5-ene-2-carboxylate* (**21**). Yield 40 mg (42%). R_f 0.37 (hexane/AcOEt 8:1). IR: 3057, 1732, 1626, 1358, 1279, 1183, 1146. ^{1}H-NMR (500 MHz): 8.31–8.13 (*m*, 6 arom. H, *endo* + *exo*); 6.47 (*t*, *J* = 7.3, H–C(5), *exo*); 6.36 (*t*, *J* = 7.3, H–C(5), *endo*); 6.23 (*t*, *J* = 7.3, H–C(6), *exo*); 6.10 (*t*, *J* = 7.3, H–C(6), *endo*); 5.04–4.96 (*m*, Me_2CH, *exo*); 4.78–4.70 (*m*, Me_2CH, *endo*); 3.45 (br. *s*, H–C(1), *endo*); 3.10–2.65 (*m*, 4 H, *exo* + *endo*); 2.60–2.30 (*m*, 5 H, *exo* + *endo*); 1.90–1.75 (*m*, H_{anti}–C(8), *endo*); 1.50–1.01 (*m*, 18 H, *exo* + *endo*). ^{13}C-NMR (125 MHz): 167.65 (C=O, *exo*); 167.38 (C=O, *endo*); 140.85, 140.66 (arom. C, *exo* + *endo*); 142.45, 137.29, 136.13, 131.13, 130.57, 129.84, 128.68, 127.36 (2 *C*H=*C*H, arom. CH, *exo* + *endo*); 132.65 (*q*, *J*(C,F) = 34.8, 2 *C*CF_3, *exo* + *endo*); 122.28 (*q*, *J*(C,F) = 271.8, 2 CF_3, *exo* + *endo*); 78.57 (CS, *exo*); 78.17 (CS, *endo*); 71.31 (Me_2*C*H, *exo*); 71.01 (Me_2*C*H, *endo*); 35.25 (*C*HC, *exo*); 34.74 (*C*HC, *endo*); 30.83 (*C*H_2C, *endo*); 30.50 (*C*H_2C, *exo*); 29.68 (*C*HCH_2, *exo*); 29.62 (*C*HCH_2, *endo*); 24.24, 20.05 (CH*C*H_2*C*H_2CH, *endo*); 23.38, 22.21 (CH*C*H_2*C*H_2CH, *exo*); 21.55, 21.38, 21.30, 21.20 (2 *Me*$_2$CH, *exo* + *endo*). DIP-MS: 470 (3, M^+), 277 (12), 261 (23), 194 (10), 193 (100), 152 (48), 151 (12), 135 (14), 133 (52), 124 (12), 123 (17), 115 (15), 107 (10), 106 (28), 105 (19), 91 (25), 80 (41), 79 (65), 77 (28), 73 (33). HR-DIP-MS: 470.0975 ($C_{20}H_{20}F_6O_4S^+$; calc. 470.0986).

12. *Reduction of the Sulfonyl Group with Zinc: Typical Procedure.* To a soln. of sulfonylpropanoate **12i** (0.2 mmol, 137 mg) in THF (1 ml), was added activated Zn (78 mg, 1.2 mmol) and sat. aq. NH_4Cl soln. (3 ml). The mixture was stirred vigorously and heated at 80° for 2 d. The mixture was diluted with AcOEt and filtered through *Celite*. The filtrate was washed with a $NaHCO_3$ soln. and then with brine. The org. phase was dried (Na_2SO_4) and evaporated and the crude product purified by FC (hexane/AcOEt): 39 mg (70%) of *isopropyl 2-benzyl-3-phenylpropanoate* (**22**). R_f 0.55 (hexane/AcOEt 8:1). IR: 1727, 1355, 1279, 1175, 1142. ^{1}H-NMR: 7.28–7.16 (*m*, 10 arom. H); 6.97 (*s*, CH=C); 4.86–4.78 (*m*, Me_2CH); 2.97–2.94 (*m*, 2 PhCH_2); 2.88–2.79 (*m*, CHCO); 0.95 (*d*, *J* = 6.1, *Me*$_2$CH). ^{13}C-NMR: 174.39 (C=O); 139.11 (arom. C); 128.92, 128.29, 126.30 (arom. CH); 67.39 (CHO); 49.71 (*C*HCO); 38.39 (2 Ph*C*H_2); 21.52 (*Me*$_2$CH). DIP-MS: 282 (2, M^+), 190 (31), 148 (72), 147 (11), 130 (37), 116 (13), 91 (22), 90 (100), 64 (10). HR-DIP-MS: 282.1638 ($C_{19}H_{22}O_2^+$; calc. 282.1620).

REFERENCES

[1] 'The Chemistry of Sulphones and Sulphoxides', Eds. S. Patai, Z. Rappoport, C. Stirling, John Wiley & Sons, Chichester, 1988; N. S. Simpkins, 'Sulphones in Organic Synthesis', Pergamon Press, Oxford, 1993; J.-E. Bäckvall, R. Chinchilla, C. Nájera, M. Yus, *Chem. Rev.* **1998**, *98*, 2291; Z. Jin, P. C. Vandort, P. L. Fuchs,

Phosphorus, Sulfur Silicon Relat. Elem. **1999**, *95-96*, 1; E. N. Prilezhaeva, *Russian Chem. Rev.* **2000**, *69*, 367; T. G. Back, *Tetrahedron* **2001**, *57*, 5263; F. Chemla, *J. Chem. Soc., Perkin Trans. 1* **2002**, 275.
[2] C. Nájera, J. M. Sansano, *Recent Res. Devel. Org. Chem.* **1998**, *2*, 637.
[3] L. A. Paquette, *Synlett* **2001**, 1.
[4] R. Chinchilla, C. Nájera, *Recent. Res. Devel. Org. Chem.* **1997**, *1*, 437.
[5] C. Nájera, M. Yus, *Tetrahedron* **1999**, *55*, 10547.
[6] O. Menke, E. Steinhuber, A. García Martínez, L. R. Subramanian, M. Hanack, *Synthesis* **1994**, 1291 and ref. cit. therein.
[7] F. Terrier, E. Kizilian, R. Goumont, N. Faucher, C. Wakselman, *J. Am. Chem. Soc.* **1998**, *120*, 9496.
[8] R. Goumont, K. Magder, M. Tordeux, J. Marrot, F. Terrier, C. Wakselman, *Eur. J. Org. Chem.* **1999**, 2969.
[9] M. Tordeux, B. Langlois, C. Wakselman, *J. Org. Chem.* **1989**, *54*, 2452.
[10] G. Theodoridis, *Tetrahedron* **2000**, *56*, 2339.
[11] L. A. Carpino, G. M. Han, *J. Org. Chem.* **1972**, *37*, 3404.
[12] R. Ramaje, L. Jiang, Y.-D. Kim, K. Shaw, J.-L. Park, H.-J. Kim, *J. Pept. Sci.* **1999**, *5*, 195; C. Carreño, M. E. Méndez, Y.-D. Kim, H.-J. Kim, S. A. Kates, D. Andreu, F. Albericio, *J. Pept. Res.* **2000**, *56*, 63.
[13] C. G. J. Verhart, G. I. Tesser, *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 621.
[14] G. I. Tesser, 'Proceedings of the 13th Eur. Peptide Symposium', in 'Peptides 1974', Ed. Y. Wolman, J. Wiley & Sons, New York, 1975, p. 53; G. I. Tesser, I. C. Balvert-Geers, *Int. J. Pept. Protein Res.* **1975**, *7*, 295.
[15] J. Gurnani, C. K. Narang, M. R. K. Sherwani, *Hung. J. Ind. Chem.* **1999**, *27*, 1.
[16] D. L. J. Clive, V. S. C. Yeh, *Synth. Commun.* **2000**, *30*, 3267.
[17] S. F. Wnuk, M. J. Robins, *J. Am. Chem. Soc.* **1996**, *118*, 2519; S. F. Wnuk, J. M. Rios, J. Khan, Y.-L. Hsu, *J. Org. Chem.* **2000**, *65*, 4169; S. F. Wnuk, L. A. Bergolla, P. I. Garcia Jr., *J. Org. Chem.* **2002**, *67*, 3065.
[18] T. Skrydstrup, J.-M. Beau, *Angew. Chem., Int. Ed.* **1995**, *34*, 909; O. Jarreton, T. Skrydstrup, J.-M. Beau, *Tetrahedron Lett.* **1997**, *36*, 303; T. Skrydstrup, O. Jarreton, D. Mazéas, D. Urban, J.-M. Beau, *Chem.-Eur. J.* **1998**, *4*, 655; L. Andersen, L. Munch Mikkelsen, J.-M. Beau, T. Skrydstrup, *Synlett* **1998**, 1393; G. X. Chang, T. L. Lowary, *Org. Lett.* **2000**, *2*, 1505.
[19] R. Ballini, G. Bosica, S. Cossu, O. D. Lucchi, P. Pelusa, *Tetrahedron* **2001**, *57*, 4461.
[20] D. R. Williams, K. M. Werner, B. Feng, *Tetrahedron Lett.* **1997**, *38*, 6825.
[21] D. A. Alonso, C. Nájera, M. Varea, *Tetrahedron Lett.* **2001**, *42*, 8845.
[22] K. A. H. Chehade, H. P. Spielmann, *J. Org. Chem.* **2000**, *65*, 4949, and refs. cit. therein.
[23] R. T. Amel, P. J. Marek, *J. Org. Chem.* **1973**, *38*, 3513.
[24] A. Bright, J. F. Malone, J. K. Nicholson, J. Powell, B. L. Shaw, *J. Chem. Soc., Chem. Commun.* **1971**, 712; E. Schmitz, R. Urban, U. Heuck, G. Zimmermann, E. Gründemann, *J. Prakt. Chem.* **1976**, *318*, 185; E. Schmitz, U. Heuck, D. Habisch, *J. Prakt. Chem.* **1976**, *318*, 471; B. Bodoganovic, *Adv. Organomet. Chem.* **1979**, *17*, 105; R. Grigg, T. R. B. Mitchell, A. Ramasubbu, *J. Chem. Soc., Chem. Commun.* **1979**, 669; R. Grigg, T. R. B. Mitchell, A. Ramasubbu, *J. Chem. Soc., Chem. Commun.* **1980**, 27; R. Grigg, J. F. Malone, T. R. B. Mitchell, A. Ramasubbu, R. M. Scott, *J. Chem. Soc., Perkin Trans. 1* **1984**, 1745; A. Behr, U. Freudenberg, W. Keim, *J. Mol. Catal.* **1986**, *35*, 9; B. Radetich, T. V. RajanBabu, *J. Am. Chem. Soc.***1998**, *120*, 8007; A. Heumann, M. Moukhliss, *Synlett* **1998**, 1211; R. A. Widenhoefer, N. S. Perch, *Org. Lett.* **1999**, *1*, 1103; P. Kisanga, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2000**, *122*, 10017; Y. Yamamoto, Y. Nakagai, N. Ohkoshi, K. Itoh, *J. Am. Chem. Soc.* **2001**, *123*, 6372.
[25] M. H. Nantz, P. L. Fuchs, *J. Org. Chem.* **1987**, *52*, 5298.
[26] R. J. P. Corriu, R. Perz, *Tetrahedron Lett.* **1985**, *26*, 1311.
[27] D. Witthaut, R. Fröhlich, H. J. Schäfer, *Angew. Chem., Int. Ed.* **2001**, *40*, 4212.
[28] F. Eugene, B. Langlois, E. Laurent, *J. Fluorine Chem.* **1994**, *66*, 301.
[29] O. De Lucchi, V. Lucchini, L. Pasquato, M. Zamai, G. Modena, *Gazz. Chim. Ital.* **1984**, *114*, 293; H. M. R. Hoffman, A. Weichert, *J. Org. Chem.* **1991**, *56*, 4098; J. C. Carretero, J. L. García Ruano, L. M. Martín Cabrejas, *Tetrahedron: Asymmetry* **1997**, *8*, 2215; P. Hayes, G. Dujardin, C. Maignan, *Tetrahedron Lett.* **1996**, *37*, 3687; J. C. Westfahl, T. L. Gresham, *J. Am. Chem. Soc.* **1954**, *76*, 1076; A. E. Ardis, S. J. Averill, H. Gilbert, F. F. Miller, R. F. Schmidt, F. D. Stewart, H. L. Trumbull, *J. Am. Chem. Soc.* **1950**, 1305.
[30] V. G. Nenajdenko, A. V. Statsuk, E. S. Balenkova, *Tetrahedron* **2000**, *56*, 6549.

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