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Preparation of (*E*)-4-Aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones as Fluorinated Building Blocks and Their Application in Ready and Highly Stereoselective Routes to *trans*-2,3-Dihydrofurans Substituted with Trifluoromethyl and Sulfonyl Groups

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(*E*)-4-Aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-one fluorinated building blocks were prepared through a two-step process. Treatment of these (*E*)-4-aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones with arsonium bromides in the presence of Cs_2CO_3 in CH_2Cl_2 at reflux resulted in highly stereoselective ring closure to provide 4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofurans in good to excellent yields.

Introduction

Substituted 2,3-dihydrofurans occur frequently as subunits of many medicinally important compounds, as well as in biologically important natural products such as clerodin, aflatoxin B_1, rocaglamide and austocystin A.[1,2] In addition, substituted 2,3-dihydrofurans are potentially useful intermediates in the synthesis of a variety of substances, including γ-hydroxy aldehydes, γ-hydroxy ketones, γ-lactones, furans, cyclopropyl aldehydes and ketones, and hydroxy amino acids.[3] Polyfunctional 2,3-dihydrofurans are also of interest for the synthesis of natural compounds and potentially physiologically active compounds.[4] The development of efficient synthetic approaches to polysubstituted 2,3-dihydrofurans has thus been the focus of intense research for decades, and continues to be an active area of research today.[2d,5,6]

Sulfones are a core functional group in both organic and medicinal chemistry thanks to their versatile synthetic utilities and inhibition activities of various types of enzymatic processes.[7,8] The trifluoromethyl group, on the other hand, is an important structural motif in many biologically active compounds, because this substituent can often change their chemical and metabolic stabilities, lipophilicities and binding selectivities.[9]

In medicinal chemistry, molecular modifications involving the introduction of a sulfonyl group or a trifluoromethyl functionality have become a powerful and widely employed tactic in the process of drug design, and so it is of great synthetic interest to develop efficient methods for incorporation of trifluoromethyl or sulfonyl groups into diverse organic structures.[8,10]

In contrast with the significant number of preparations of trifluoromethyl- or sulfonyl-substituted 2,3-dihydrofurans,[5c,11,12] however, there was no article to be found in the literature for the preparation of 2,3-dihydrofurans that were both trifluoromethyl- and sulfonyl-substituted. During our research into the development of new fluorinated building blocks and our ongoing programs involving their application in the synthesis of potentially bioactive compounds,[12c,13] we were attracted by vinyl sulfones. The electron-withdrawing sulfonyl group in a vinyl sulfone results in electron deficiency in the double bond. This effect is even more pronounced in a vinyl sulfone containing a perfluoroalkyl group. The highly activated carbon–carbon double bond is suitable for nucleophilic attack and dipolar cycloaddition.[14] Having considered the fact that arsonium ylides show their high reactivities and high diastereoselectivities in heterocycle and carbocycle synthesis through reactions with electron-deficient alkenes,[15] we developed (*E*)-4-aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones as fluorinated building blocks and investigated their application in the synthesis of 2,3-dihydrofurans containing both trifluoromethyl and sulf-

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onyl substituents through the reactions of arsonium ylides with building blocks of this type. As a consequence, we found a convenient and highly stereoselective methodology for the synthesis of 4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofurans in good to excellent yields.

Results and Discussion

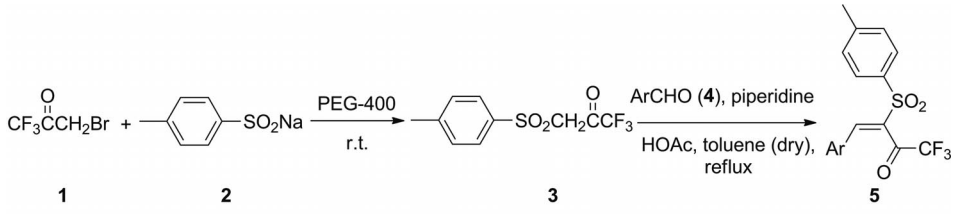
Synthesis of (*E*)-4-Aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones

(*E*)-4-Aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones **5** were prepared in a two-step fashion, as illustrated in Scheme 1. As in the reported procedure,[16] we found that the nucleophilic reaction between 1-bromo-3,3,3-trifluoropropan-2-one (**1**) and sodium *p*-toluenesulfinate (**2**) was promoted by polyethylene glycol (PEG-400) as an efficient reaction medium to afford 1,1,1-trifluoro-3-tosylpropan-2-one (**3**) in good yield (93%). For the preparation of compounds **5**, we modified the previous literature protocols by changing the solvent and the reaction temperature.[17] Knoevenagel condensations between compound **3** and aromatic aldehydes **4** occurred smoothly in toluene at reflux, giving **5A**–**G** as major products in moderate to good yields (Table 1). The ^{1}H NMR spectra of **5A**–**G** were similar, so the (*E*) configuration of **5** could be confirmed by X-ray diffraction analysis of **5E**.[18] The repulsion between aryl and sulfonyl groups in transition states **TS-I** (Scheme 2) and the intermediates **I** resulted in the (*Z*) isomers being minor products.[19] Furthermore, it was found that aromatic aldehydes with electron-donating substituents, such as OMe or NMe_2, gave higher yields than those with electron-withdrawing groups (Table 1, Entries 4 and 5 vs. 3 and 6–8), due to the fact that an electron-rich aryl group was beneficial for stabilization of the imine cation in the transition state.

Synthetic Application of (*E*)-4-Aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones in the Preparation of 4-Tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofurans

The optimization of the reaction conditions was carried out with (*E*)-1,1,1-trifluoro-4-*p*-tolyl-3-tosylbut-3-en-2-one (**5A**) and arsonium bromide **6a** as model substrates with different solvents and bases at various temperatures (Table 2). Solvents such as $CHCl_3$, DME (dimethoxyethane), DMSO and THF were found to be less effective than CH_2Cl_2 for this transformation (Table 2, Entries 1–4 vs. 5). Of the bases examined, Cs_2CO_3 showed the highest activity (Table 2, Entry 5). Moreover, reductions either in the number of equivalents of base or in the reaction temperature led to longer reaction times and lower yields (Table 2, Entries 10 and 11). The best result was obtained when the reaction was carried out in the presence of Cs_2CO_3 (2.0 equiv.) in CH_2Cl_2 at reflux, affording the desired (phenyl)(3-*p*-tolyl-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-yl)methanone (**7Aa**) in 91% yield after 3 h.

We explored the scope of the reaction under the optimized conditions; the results are summarized in Table 3. Every reaction proceeded smoothly to give only one major product and had gone to completion after a few hours. Treatment of arsonium bromide **6a** with various (*E*)-4-aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones **5** in the presence of Cs_2CO_3 furnished the corresponding 4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofurans **7** in good to excellent isolated yields (Table 3, Entries 1–7). As shown in Table 3, (*E*)-4-aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones **5** either with electron-withdrawing groups or with electron-donating groups on the benzene ring of the Ar group were all suitable for this protocol. In addition, the reaction appeared quite tolerant of the positions of the substituents: the cyclizations of **6a** with *p*-chlorophenyl-substituted **5C** or with *m*-

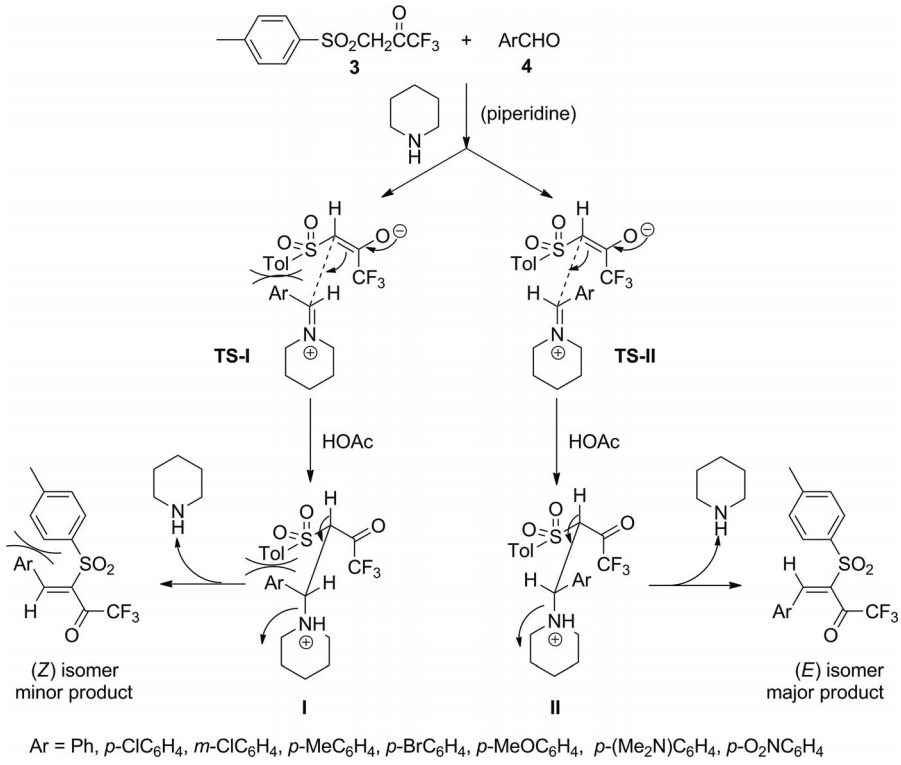


Scheme 1. Preparation of (*E*)-4-aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones **5**.

Table 1. Knoevenagel condensations between **3** and aromatic aldehydes **4**.[a]

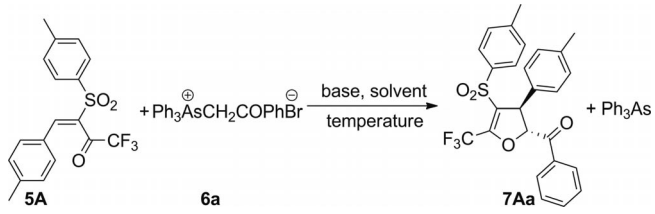
Entry	Aromatic aldehyde **4**	Ar	(*E*)-4-Aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-one **5**	Yield [%][b]
1	**4a**	*p*-MeC_6H_4	**5A**	68
2	**4b**	Ph	**5B**	59
3	**4c**	*p*-ClC_6H_4	**5C**	47
4	**4d**	*p*-$MeOC_6H_4$	**5D**	75
5	**4e**	*p*-$(Me_2N)C_6H_4$	**5E**	65
6	**4f**	*m*-ClC_6H_4	**5F**	50
7	**4g**	*p*-BrC_6H_4	**5G**	47
8	**4h**	*p*-$O_2NC_6H_4$	**5H**	trace

[a] Conditions: 1,1,1-trifluoro-3-tosylpropan-2-one (**3**) (1.0 mmol), aromatic aldehyde **4** (1.2 mmol), piperidine (0.3 mmol), glacial acetic acid (0.3 mmol), anhydrous toluene (10 mL), reflux, 24 h. [b] Isolated yields.



Scheme 2. The mechanism of the Knoevenagel condensations.

Table 2. Optimization of the reaction conditions.



Entry	Solvent	Base (equiv.)	Temperature [°C]	Time [h]	Yield [%][a]
1	$CHCl_3$	Cs_2CO_3 (2.0 equiv.)	60[b]	3	78
2	DME	Cs_2CO_3 (2.0 equiv.)	85[b]	3	76
3	DMSO	Cs_2CO_3 (2.0 equiv.)	80	3	76
4	THF	Cs_2CO_3 (2.0 equiv.)	65[b]	3	72
5	CH_2Cl_2	Cs_2CO_3 (2.0 equiv.)	***40***[b]	3	91
6	CH_2Cl_2	K_2CO_3 (2.0 equiv.)	40	3	78
7	CH_2Cl_2	$NaHCO_3$ (2.0 equiv.)	40	24	0
8	CH_2Cl_2	KF (2.0 equiv.)	40	3	77
9	CH_2Cl_2	Et_3N (2.0 equiv.)	40	24	0
10	CH_2Cl_2	Cs_2CO_3 (2.0 equiv.)	20	24	80
11	CH_2Cl_2	Cs_2CO_3 (1.0 equiv.)	20	24	60

[a] Isolated yields. [b] The reflux temperature of the corresponding solvent.

chlorophenyl-substituted **5F**, for example, led to 2,3-dihydrofurans in similarly good yields (Table 3, Entries 3 and 6).

The scope of the process with respect to other arsonium bromides was further pursued. The reactions of arsonium bromide **6** bearing –COPh, –CN and $–CO_2Me$ substituents proceeded smoothly in 83–93% yields.

The structures of the prepared 2,3-dihydrofurans **7** were fully characterized by ^1H NMR, ^{13}C NMR and IR spectroscopy, LR and HR mass spectrometry, and elemental analysis. In the ^1H NMR spectra of **7Aa**, the two protons in the 2- and 3-positions in the dihydrofuran ring appeared as two doublets at δ = 5.79 and 4.74 ppm with a vicinal coupling constant J = 5.0 Hz, whereas in **7Bb** the two protons in the 2- and 3-positions manifested as two doublets at δ = 5.19 and 4.89 ppm with J = 5.0 Hz. The similar peak patterns and coupling constants of < 6.0 Hz were also seen in the ^1H NMR spectra of the other prepared 2,3-dihy-

Table 3. Synthesis of 4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofurans **7**.[a]

Entry	5	Ar	6	R	7	Time [h]	Yield [%][b]
1	**5A**	*p*-MeC_6H_4	**6a**	COPh	**7Aa**	3.0	91
2	**5B**	Ph	**6a**	COPh	**7Ba**	3.0	91
3	**5C**	*p*-ClC_6H_4	**6a**	COPh	**7Ca**	4.5	87
4	**5D**	*p*-$MeOC_6H_4$	**6a**	COPh	**7Da**	5.0	88
5	**5E**	*p*-$(Me_2N)C_6H_4$	**6a**	COPh	**7Ea**	5.0	86
6	**5F**	*m*-ClC_6H_4	**6a**	COPh	**7Fa**	7.0	86
7	**5G**	*p*-BrC_6H_4	**6a**	COPh	**7Ga**	6.0	81
8	**5A**	*p*-MeC_6H_4	**6b**	CN	**7Ab**	3.0	87
9	**5A**	*p*-MeC_6H_4	**6c**	CO_2Me	**7Ac**	3.0	84
10	**5B**	Ph	**6b**	CN	**7Bb**	3.0	93
11	**5B**	Ph	**6c**	CO_2Me	**7Bc**	3.0	90
12	**5C**	*p*-ClC_6H_4	**6b**	CN	**7Cb**	5.0	84
13	**5C**	*p*-ClC_6H_4	**6c**	CO_2Me	**7Cc**	4.5	85
14	**5D**	*p*-$MeOC_6H_4$	**6b**	CN	**7Db**	5.0	86
15	**5D**	*p*-$MeOC_6H_4$	**6c**	CO_2Me	**7Dc**	4.0	83
16	**5E**	*p*-$(Me_2N)C_6H_4$	**6b**	CN	**7Eb**	5.5	84
17	**5E**	*p*-$(Me_2N)C_6H_4$	**6c**	CO_2Me	**7Ec**	6.0	84
18	**5F**	*m*-ClC_6H_4	**6c**	CO_2Me	**7Fc**	8.0	84

[a] Conditions: (*E*)-4-aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-one **5** (1.0 mmol), arsonium bromide **6** (1.2 mmol), Cs_2CO_3 (2.0 mmol), CH_2Cl_2 (10 mL), reflux. [b] Isolated yields.

drofuran derivatives. It has been established that in *cis*-2,3-dihydrofurans the vicinal coupling constants (*J*) of the two methine protons are ca. 7.0–10.0 Hz, whereas in *trans*-2,3-dihydrofurans the vicinal coupling constants are in the 4.0–7.0 Hz range.[5c,11c,20] From careful analysis of ^{1}H NMR spectroscopic data and comparison with previously reported results, we could tentatively conclude that 2,3-dihydrofuran derivatives **7** were the thermodynamically stable *trans* isomers. Single-crystal X-ray diffraction analysis of **7Ba** further confirmed this conclusion.[18] The interesting results revealed the arsonium-ylide-assisted reactions to be highly diastereoselective.[15]

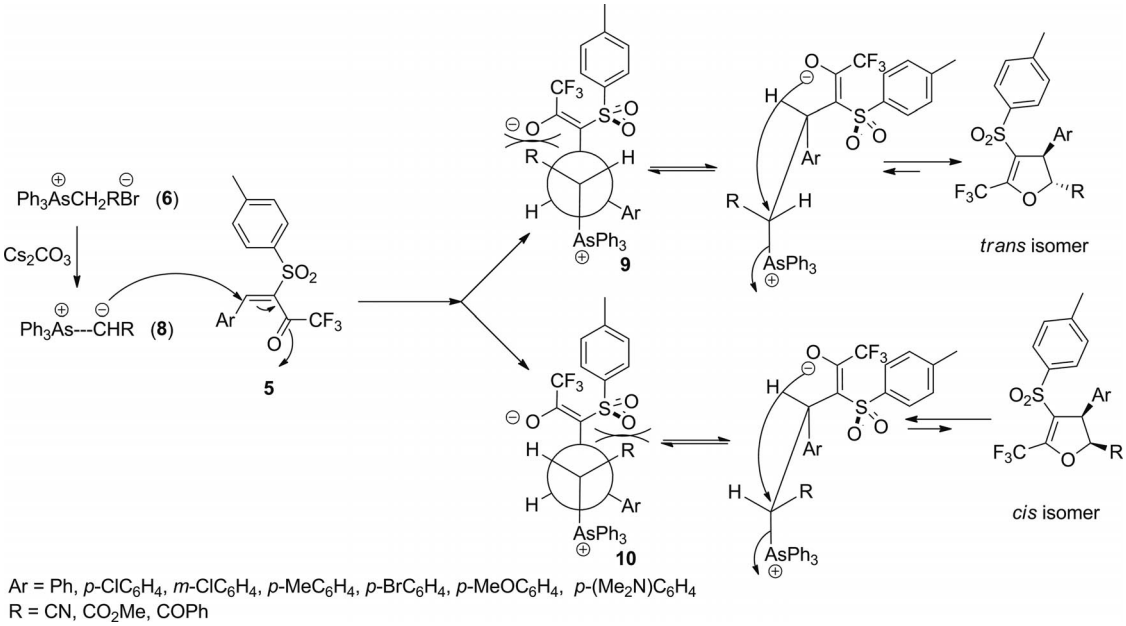
A plausible mechanism based on these results is shown in Scheme 3. Nucleophilic attack by the carbanions **8** derived from arsonium bromides **6** at the C-4 positions of the double bonds in (*E*)-4-aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones **5** would take place to yield the pairs of possible intermediates **9** and **10**. Intermediates **9** would be more stable than **10**, because the steric repulsion between enol anion and Ar groups in **9** would be less intense than that between the bulkier tosyl and Ar groups in **10**. Intermediates **9** would then undergo direct cyclization through intramolecular nucleophilic substitution reactions to afford the *trans* isomers as the major products.

Conclusions

We have demonstrated a convenient synthesis of (*E*)-4-aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones **5** as promising trifluoromethylated building blocks. In addition, a new and efficient approach leading in a stereoselective and high-yielding manner to *trans*-2,3-dihydrofuran derivatives substituted with both trifluoromethyl and sulfonyl groups from such fluorinated blocks has been developed. The reactions proceeded through Michael additions and intramolecular cyclizations of arsonium ylides formed in situ under very convenient conditions. A proposed mechanism for this diastereoselective formation of *trans*-2,3-dihydrofuran derivatives, based on steric hindrance in the cyclization step, is suggested. Further synthetic applications of (*E*)-4-aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones are in progress in our laboratory.

Experimental Section

General Information: All reagents were purchased from commercial sources and used without further purification, except that arsonium



Scheme 3. Plausible mechanism for the formation of products **7**.

bromides **1** were prepared by a known literature method.[13c] Solvents were distilled before use. Anhydrous toluene was dried with sodium and distilled. Melting points were recorded with a WRS-1 instrument and are uncorrected. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded with a Bruker DRX 500 MHz spectrometer. All chemical shifts are reported in ppm downfield (positive) of the standard: C_6F_6 for ^{19}F and TMS for ^{1}H and ^{13}C NMR spectra. IR spectra were obtained with an AVATAR370 FT-IR spectrometer. Elemental analysis was performed with an Elementar Vario EL-III instrument. LR and HRMS data were obtained with an Agilent LC/MSD SL and a Waters Miromass GCT instrument, respectively. X-ray analysis was performed with a Bruker Smart Apex2 CCD spectrometer. All yields reported in this publication refer to isolated compounds, and their purities were determined by ^{1}H NMR spectroscopy.

General Procedure for the Preparation of (*E*)-4-Aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones (5): A solution of 1-bromo-3,3,3-trifluoropropan-2-one (**1**) (1.0 mmol) and sodium *p*-toluenesulfinate (**2**) (1.1 mmol) in PEG-400 (polyethylene glycol; 10 mL) was stirred at room temperature for 18 h. The mixture was diluted with ethyl acetate (30 mL) and washed with water (10 mL) and saturated NaCl (40 mL). The organic layer was dried with Na_2SO_4 and filtered. The solvent was removed in vacuo to give the crude product, which was purified by silica gel chromatography to give pure 1,1,1-trifluoro-3-tosylpropan-2-one (**3**). A mixture of compound **3** (1.0 mmol) and an aromatic aldehyde **4** (1.2 mmol) was dissolved in anhydrous toluene (10 mL) and heated at reflux in the presence of piperidine (0.3 mmol) and glacial acetic acid (0.3 mmol) for 24 h. After that, the reaction mixture was concentrated under vacuum, and the residue was purified by column chromatography on silica gel [eluent: petroleum ether (60–90 °C)/ethyl acetate] to give pure **5**.

(*E*)-1,1,1-Trifluoro-4-*p*-tolyl-3-tosylbut-3-en-2-one (5A): Light yellow solid. Yield 250 mg, 68%. M.p. 44.4–45.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 7.17–7.23 (m, 4 H, Ar-H), 7.36 (d, J = 8.0 Hz, 2 H, Ar-H), 7.77 (d, J = 8.0 Hz, 2 H, Ar-H), 8.18 (s, 1 H, C=C–H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 21.7, 114.7 (q, $^1J_{C,F}$ = 290.0 Hz), 128.3, 128.6, 130.0, 130.1, 130.2, 134.7, 136.5, 143.7, 145.5, 146.6, 184.8 (q, $^2J_{C,F}$ = 38.8 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –74.55 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2925, 2860, 1721, 1598, 1328, 1213, 1159, 1085, 812 cm^{-1}. MS (EI): *m*/*z* (%) = 368 (2) [M]$^+$, 91 (100). HRMS (EI): calcd. for $C_{18}H_{15}F_3O_3S$ [M]$^+$ 368.0694; found 368.0697.

(*E*)-1,1,1-Trifluoro-4-phenyl-3-tosylbut-3-en-2-one (5B): Light yellow solid. Yield 209 mg, 59%. M.p. 111.5–112.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 3 H, CH_3), 7.28–7.38 (m, 4 H, Ar-H), 7.41–7.44 (m, 2 H, Ar-H), 7.48–7.52 (m, 1 H, Ar-H), 7.78 (d, J = 8.5 Hz, 2 H, Ar-H), 8.21 (s, 1 H, C=C–H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.8, 114.8 (q, $^1J_{C,F}$ = 290.0 Hz), 128.8, 129.5, 129.9, 130.3, 131.1, 132.5, 136.2, 136.3, 145.8, 146.4, 184.7 (q, $^2J_{C,F}$ = 40.0 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –74.65 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2928, 1726, 1598, 1328, 1214, 1162, 1086, 812, 692 cm^{-1}. MS (EI): *m*/*z* (%) = 354 (1) [M]$^+$, 91 (100). $C_{17}H_{13}F_3O_3S$ (354.34): calcd. C 57.62, H 3.70; found C 57.56, H 3.78.

(*E*)-4-(4-Chlorophenyl)-1,1,1-trifluoro-3-tosylbut-3-en-2-one (5C): Yellow oil. Yield 183 mg, 47%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 3 H, CH_3), 7.21 (d, J = 8.5 Hz, 2 H, Ar-H), 7.37–7.41 (m, 4 H, Ar-H), 7.75–7.77 (m, 2 H, Ar-H), 8.13 (s, 1 H, C=C–H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 114.6 (q, $^1J_{C,F}$ = 290.0 Hz), 128.7, 129.4, 129.8, 130.2, 130.9, 136.0, 136.6, 138.8, 144.6, 144.6, 145.8, 184.4 (q, $^2J_{C,F}$ = 40.0 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –74.63 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2927, 1732, 1595, 1333, 1213, 1150, 1085, 813 cm^{-1}. MS (EI): *m*/*z* (%) = 388 (1) [M]$^+$, 91(100). $C_{17}H_{12}ClF_3O_3S$ (388.79): calcd. C 52.52, H 3.11; found C 52.60, H 3.20.

(*E*)-1,1,1-Trifluoro-4-(4-methoxyphenyl)-3-tosylbut-3-en-2-one (5D): Yellow solid. Yield 288 mg, 75%. M.p. 79.6–79.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 6.92 (d, J = 9.0 Hz, 2 H, Ar-H), 7.35–7.37 (m, 2 H, Ar-H), 7.36 (d, J = 8.0 Hz, 2 H, Ar-H), 7.76–7.78 (m, 2 H, Ar-H), 8.14 (s, 1 H, C=C–H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 55.6, 114.8 (q, $^1J_{C,F}$ = 290.0 Hz), 115.0, 123.5, 128.5, 130.1, 132.3, 132.8, 136.8, 145.3, 146.3, 163.3, 184.9 (q, $^2J_{C,F}$ = 38.8 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –74.53 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2972, 2939, 1720, 1596, 1512, 1322, 1208, 1178, 1151, 1085, 813 cm^{-1}. MS (EI): *m*/*z* (%) = 384 (7) [M]$^+$, 93 (100). $C_{18}H_{15}F_3O_4S$ (384.37): calcd. C 56.25, H 3.93; found C 56.15, H 3.83.

(*E*)-4-[4-(Dimethylamino)phenyl]-1,1,1-trifluoro-3-tosylbut-3-en-2-one (5E): Brown solid. Yield 258 mg, 65%. M.p. 109.1–109.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 3.05 [s, 6 H, $N(CH_3)_2$], 6.62 (d, J = 8.5 Hz, 2 H, Ar-H), 7.18 (d, J = 8.5 Hz, 2 H, Ar-H),7.32 (d, J = 8.5 Hz, 2 H, Ar-H), 7.77 (d, J = 8.5 Hz, 2 H, Ar-H), 8.12 (s, 1 H, C=C–H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 40.0, 111.7, 115.1 (q, $^1J_{C,F}$ = 290.0 Hz), 118.6, 127.6, 128.3, 129.8, 133.1, 137.9, 144.6, 148.1, 153.4, 184.9 (q, $^2J_{C,F}$ = 38.8 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –74.24 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2919, 1700, 1609, 1565, 1525, 1380, 1319, 1210, 1189, 1148, 1085, 816 cm^{-1}. MS (EI): *m*/*z* (%) = 397 (37) [M]$^+$, 172 (100). $C_{19}H_{18}F_3NO_3S$ (397.41): calcd. C 57.42, H 4.57, N 3.52; found C 57.35, H 4.50, N 3.49.

(*E*)-4-(3-Chlorophenyl)-1,1,1-trifluoro-3-tosylbut-3-en-2-one (5F): Yellow oil. Yield 194 mg, 50%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.47 (s, 3 H, CH_3), 7.13–7.14 (m, 1 H, Ar-H), 7.28–7.29 (m, 1 H, Ar-H), 7.33–7.39 (m, 3 H, Ar-H), 7.45–7.47 (m, 1 H, Ar-H), 7.76 (d, J = 8.5 Hz, 2 H, Ar-H), 8.12 (s, 1 H, C=C–H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 114.6 (q, $^1J_{C,F}$ = 290.0 Hz), 128.7, 129.4, 129.8, 129.9, 130.0, 130.3, 130.9, 136.1, 136.6, 138.8, 144.6, 145.9, 184.4 (q, $^2J_{C,F}$ = 40.0 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –74.65 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2928, 1733, 1598, 1329, 1268, 1201, 1149, 1083, 876, 811 cm^{-1}. MS (EI): *m*/*z* (%) = 388 (1) [M]$^+$, 91 (100). $C_{17}H_{12}ClF_3O_3S$ (388.79): calcd. C 52.52, H 3.11; found C 52.50, H 3.08.

(*E*)-4-(4-Bromophenyl)-1,1,1-trifluoro-3-tosylbut-3-en-2-one (5G): Light yellow solid. Yield 204 mg, 47%. M.p. 155.0–155.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 3 H, CH_3), 7.13 (d, J = 8.5 Hz, 2 H, Ar-H), 7.38 (d, J = 8.5 Hz, 2 H, Ar-H), 7.56 (d, J = 8.5 Hz, 2 H, Ar-H), 7.76 (d, J = 8.5 Hz, 2 H, Ar-H), 8.11 (s, 1 H, C=C–H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.8, 114.7 (q, $^1J_{C,F}$ = 290.0 Hz), 127.4, 128.9, 129.9, 130.3, 131.1, 132.9, 136.0, 136.8, 144.8, 146.0, 184.5 (q, $^2J_{C,F}$ = 38.8 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –74.62 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 1698, 1643, 1596, 1330, 1207, 1168 1147, 1073, 811 cm^{-1}. MS (EI): *m*/*z* (%) = 434 (3) [M + H]$^+$, 433 (1) [M]$^+$, 91 (100). $C_{17}H_{12}BrF_3O_3S$ (433.24): calcd. C 47.13, H 2.79; found C 47.13, H 2.79.

General Procedure for the Preparation of 4-Tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofurans (7): Cs_2CO_3 (2.0 mmol) was added to a solution of a compound **5** (1.0 mmol) and an arsonium bromide **6** (1.2 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at reflux. On completion of the reaction (monitored by TLC), the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel [eluent: petroleum ether (60–90 °C)/ethyl acetate] to give a pure compound **7**.

(Phenyl)[3-*p*-tolyl-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-yl]methanone (7Aa): Light yellow solid. Yield 443 mg, 91%. M.p. 169.9–170.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 4.74 (d, J = 5.0 Hz, 1 H, furan-H), 5.79 (d, J = 5.0 Hz, 1 H, furan-H), 7.01–7.09 (m, 6 H, Ar-H), 7.21 (d, J = 8.5 Hz, 2 H, Ar-H), 7.45–7.48 (m, 2 H, Ar-H), 7.62–7.65 (m, 1 H, Ar-H), 7.80 (d, J = 7.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.1, 21.5, 30.9, 53.4, 89.9, 117.4 (q, $^1J_{C,F}$ = 272.5 Hz), 127.8, 128.0, 129.0, 129.0, 129.2, 129.9, 132.5, 134.5, 137.7, 138.6, 144.4, 150.1 (q, $^2J_{C,F}$ = 40.0 Hz), 190.6 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.20 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2949, 2922, 1698, 1647, 1597, 1374, 1330, 1203, 1148, 1106, 1077, 810, 694 cm^{-1}. MS (EI): m/z (%) = 486 (1) $[M]^+$, 105 (100). $C_{26}H_{21}F_3O_4S$ (486.50): calcd. C 64.19, H 4.35; found C 64.02, H 4.44.

3-*p*-Tolyl-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-carbonitrile (7Ab): Light yellow solid. Yield 354 mg, 87%. M.p. 110.9–111.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 4.83 (d, J = 5.0 Hz, 1 H, furan-H), 5.15 (d, J = 5.0 Hz, 1 H, furan-H), 6.94 (d, J = 8.0 Hz, 2 H, Ar-H), 7.05–7.08 (m, 4 H, Ar-H), 7.24 (d, J = 8.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.1, 21.6, 30.9, 56.4, 75.6, 114.8, 117.4 (q, $^1J_{C,F}$ = 272.5 Hz), 127.6, 128.0, 129.5, 130.1, 132.4, 136.9, 139.5, 145.1, 148.4 (q, $^2J_{C,F}$ = 42.5 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.08 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2969, 2924, 2244, 1652, 1596, 1516, 1334, 1198, 1158, 1135, 1105, 1078, 810 cm^{-1}. MS (EI): m/z (%) = 407 (12) $[M]^+$, 182 (100). $C_{20}H_{16}F_3NO_3S$ (407.41): calcd. C 58.96, H 3.96, N 3.44; found C 58.90, H 3.90, N 3.40.

Methyl 3-*p*-Tolyl-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-carboxylate (7Ac): Light yellow solid. Yield 370 mg, 84%. M.p. 77.0–77.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.33 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 3.84 (s, 3 H, CO_2CH_3), 4.69 (d, J = 5.0 Hz, 1 H, furan-H), 4.97 (d, J = 5.0 Hz, 1 H, furan-H), 6.96 (d, J = 8.0 Hz, 2 H, Ar-H), 7.00–7.03 (m, 4 H, Ar-H), 7.20 (d, J = 8.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.0, 21.5, 30.8, 53.2, 54.6, 86.4, 117.4 (q, $^1J_{C,F}$ = 272.5 Hz), 127.7, 127.8, 129.2, 129.7, 134.6, 137.5, 138.5, 144.5, 149.7 (q, $^2J_{C,F}$ = 40.0 Hz), 168.2 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.39 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2959, 2926, 1766, 1644, 1596, 1515, 1333, 1197, 1176, 1160, 1140, 1108, 1077, 811 cm^{-1}. MS (EI): m/z (%) = 440 (1) $[M]^+$, 91 (100). HRMS (EI): calcd. for $C_{21}H_{19}F_3O_5S$ $[M]^+$ 440.0905; found 440.0907.

(Phenyl)(3-phenyl-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-yl)methanone (7Ba): Light yellow solid. Yield 430 mg, 91%. M.p. 108.9–109.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.34 (s, 3 H, CH_3), 4.82 (d, J = 5.0 Hz, 1 H, furan-H), 5.81 (d, J = 5.0 Hz, 1 H, furan-H), 7.01–7.02 (m, 2 H, Ar-H), 7.14–7.20 (m, 4 H, Ar-H), 7.27–7.35 (m, 3 H, Ar-H), 7.46–7.49 (m, 2 H, Ar-H), 7.62–7.65 (m, 1 H, Ar-H), 7.81 (d, J = 7.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5, 30.9, 53.7, 89.8, 117.4 (q, $^1J_{C,F}$ = 272.5 Hz), 127.8, 128.2, 128.6, 129.0, 129.0, 129.3, 129.4, 132.5, 134.6, 137.6, 137.7, 144.5, 150.0 (q, $^2J_{C,F}$ = 40.0 Hz), 190.6 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.28 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2926, 1697, 1646, 1597, 1332, 1209, 1164, 1140, 1105, 1078, 814, 693 cm^{-1}. MS (EI): m/z (%) = 472 (1) $[M]^+$, 105 (100). $C_{25}H_{19}F_3O_4S$ (472.48): calcd. C 63.55, H 4.05; found C 63.48, H 4.00.

3-Phenyl-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-carbonitrile (7Bb): Yellow oil. Yield 366 mg, 93%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 4.89 (d, J = 5.0 Hz, 1 H, furan-H), 5.19 (d, J = 5.0 Hz, 1 H, furan-H), 7.04–7.08 (m, 4 H, Ar-H), 7.21–7.30 (m, 4 H, Ar-H), 7.41–7.44 (m, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 30.9, 56.7, 75.5, 114.8, 116.0 (q, $^1J_{C,F}$ = 272.5 Hz), 127.7, 128.0, 128.7, 129.3, 129.6, 130.4, 135.4, 136.8, 145.2, 148.6 (q, $^2J_{C,F}$ = 40.0 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.08 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2927, 2247, 1650, 1597, 1332, 1200, 1163, 1081, 815, 704 cm^{-1}. MS (EI): m/z (%) = 393 (1) $[M]^+$, 91 (100). $C_{19}H_{14}F_3NO_3S$ (393.38): calcd. C 58.01, H 3.59, N 3.56; found C 58.05, H 3.61, N 3.51.

Methyl 3-Phenyl-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-carboxylate (7Bc): Light yellow oil. Yield 383 mg, 90%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.34 (s, 3 H, CH_3), 3.86 (s, 3 H, CO_2CH_3), 4.72 (d, J = 5.0 Hz, 1 H, furan-H), 4.96 (d, J = 5.0 Hz, 1 H, furan-H), 7.01 (d, J = 8.0 Hz, 2 H, Ar-H), 7.09–7.11 (m, 2 H, Ar-H), 7.19 (d, J = 8.0 Hz, 2 H, Ar-H), 7.22–7.29 (m, 3 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5, 30.9, 55.0, 62.6, 86.4, 117.40 (q, $^1J_{C,F}$ = 273.5 Hz), 127.8, 127.9, 128.5, 129.2, 129.3, 137.5, 137.8, 144.5, 150.0 (q, $^2J_{C,F}$ = 41.3 Hz), 167.7 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.57 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2945, 2916, 1757, 1646, 1596, 1495, 1333, 1203, 1162, 1143, 1109, 1052, 813, 703 cm^{-1}. MS (EI): m/z (%) = 426 (1) $[M]^+$, 285 (100). $C_{20}H_{17}F_3O_5S$ (426.41): calcd. C 56.33, H 4.02; found C 56.43, H 4.05.

[3-(4-Chlorophenyl)-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-yl](phenyl)methanone (7Ca): Light yellow solid. Yield 441 mg, 87%. M.p. 149.7–150.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 4.81 (d, J = 5.0 Hz, 1 H, furan-H), 5.75 (d, J = 5.0 Hz, 1 H, furan-H), 7.04–7.08 (m, 4 H, Ar-H), 7.21–7.26 (m, 4 H, Ar-H), 7.46–7.49 (m, 2 H, Ar-H), 7.63–7.64 (m, 1 H, Ar-H), 7.78–7.79 (m, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 30.9, 52.8, 89.5, 117.3 (q, $^1J_{C,F}$ = 272.5 Hz), 127.7, 129.0, 129.1, 129.4, 129.5, 129.5, 132.5, 134.7, 134.7, 136.2, 137.5, 144.9, 150.2 (q, $^2J_{C,F}$ = 41.3 Hz), 190.3 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.03 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2929, 1698, 1645, 1596, 1330, 1205, 1169, 1149, 1107, 1059, 810, 694 cm^{-1}. MS (EI): m/z (%) = 506 (1) $[M]^+$, 105 (100). $C_{25}H_{18}ClF_3O_4S$ (506.92): calcd. C 59.23, H 3.58; found C 59.09, H 3.65.

3-(4-Chlorophenyl)-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-carbonitrile (7Cb): Light yellow oil. Yield 359 mg, 84%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 4.85 (d, J = 5.0 Hz, 1 H, furan-H), 5.13 (d, J = 5.0 Hz, 1 H, furan-H), 6.99 (d, J = 8.0 Hz, 2 H, Ar-H), 7.11 (d, J = 8.0 Hz, 2 H, Ar-H), 7.23–7.29 (m, 4 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 30.9, 53.1, 74.5, 114.9, 117.0 (q, $^1J_{C,F}$ = 272.5 Hz), 128.0, 129.4, 129.4, 129.4, 135.3, 135.7, 136.4, 145.6, 149.0 (q, $^2J_{C,F}$ = 40.0 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.97 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2926, 2245, 1698, 1645, 1596, 1330, 1206, 1149, 1107, 1089, 809, 694 cm^{-1}. MS (EI): m/z (%) = 427 (2) $[M]^+$, 91 (100). $C_{19}H_{13}ClF_3NO_3S$ (427.82): calcd. C 53.34, H 3.06, N 3.27; found C 53.41, H 3.10, N 3.33.

Methyl 3-(4-Chlorophenyl)-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-carboxylate (7Cc): Light yellow oil. Yield 392 mg, 85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3 H, CH_3), 3.85 (s, 3 H, CO_2CH_3), 4.71 (d, J = 5.0 Hz, 1 H, furan-H), 4.93 (d, J = 5.0 Hz, 1 H, furan-H), 6.99 (d, J = 8.0 Hz, 2 H, Ar-H), 7.06 (d, J = 8.5 Hz, 2 H, Ar-H), 7.17 (d, J = 8.0 Hz, 2 H, Ar-H), 7.24 (d, J = 8.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 31.0, 53.5, 54.7, 86.2, 117.4 (q, $^1J_{C,F}$ = 272.5 Hz), 128.0, 129.3, 129.4, 129.6, 134.7, 136.2, 137.5, 145.1, 150.3 (q, $^2J_{C,F}$ = 40.0 Hz), 168.0 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.27 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2927, 1760, 1647, 1597, 1338, 1199, 1167, 1144, 1080, 808 cm^{-1}. MS (EI): m/z (%) = 460 (1) $[M]^+$, 91 (100). HRMS (EI): calcd. for $C_{20}H_{16}ClF_3O_5S$ $[M]^+$ 460.0359; found 460.0363.

[3-(4-Methoxyphenyl)-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-yl](phenyl)methanone (7Da): Light yellow solid. Yield 442 mg, 88%. M.p. 157.9–158.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 4.74 (d, J = 5.0 Hz, 1 H, furan-H), 5.77 (d, J = 5.0 Hz, 1 H, furan-H), 6.79 (d, J = 8.0 Hz, 2 H, Ar-H), 7.04–7.05 (m, 4 H, Ar-H), 7.21–7.23 (m, 2 H, Ar-H), 7.46–7.48 (m, 2 H, Ar-H), 7.62–7.65 (m, 1 H, Ar-H), 7.80 (d, J = 7.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5, 30.9, 53.1, 55.4, 89.90 114.6,117.4 (q, $^1J_{C,F}$ = 272.5 Hz), 120.7, 127.8, 129.0, 129.2, 129.3, 129.3, 132.6, 133.9, 134.5, 137.8, 144.3, 149.8 (q, $^2J_{C,F}$ = 40.0 Hz), 159.9, 190.6 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.25 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2975, 2941, 1696, 1649, 1596, 1331, 1251, 1210, 1181, 1163, 1145, 1106, 1074, 812, 694 cm^{-1}. MS (EI): *m*/*z* (%) = 502 (1) [M]$^+$, 105 (100). $C_{26}H_{21}F_3O_5S$ (502.50): calcd. C 62.14, H 4.21; found C 62.24, H 4.30.

3-(4-Methoxyphenyl)-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-carbonitrile (7Db): Light yellow solid. Yield 364 mg, 86%. M.p. 83.1–84.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3 H, CH_3), 3.81 (s, 3 H, OCH_3), 4.83 (d, J = 5.0 Hz, 1 H, furan-H), 5.14 (d, J = 5.0 Hz, 1 H, furan-H), 6.78 (d, J = 8.5 Hz, 2 H, Ar-H), 6.97 (d, J = 8.5 Hz, 2 H, Ar-H), 7.08 (d, J = 8.0 Hz, 2 H, Ar-H), 7.22 (d, J = 8.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 31.0, 53.3, 55.5, 90.0, 114.8, 117.6 (q, $^1J_{C,F}$ = 272.5 Hz), 120.8, 127.9, 129.2, 129.5, 134.6, 137.9, 144.5, 149.9 (q, $^2J_{C,F}$ = 41.25 Hz), 160.0 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.15 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2961, 2925, 2249, 1652, 1598, 1515, 1334, 1259, 1198, 1162, 1140, 1079, 1033, 809 cm^{-1}. MS (EI): *m*/*z* (%) = 423 (12) [M]$^+$, 91 (100). $C_{20}H_{16}F_3NO_4S$ (423.40): calcd. C 56.73, H 3.81, N 3.31; found C 56.80, H 3.88, N 3.36.

Methyl 3-(4-Methoxyphenyl)-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-carboxylate (7Dc): Light yellow oil. Yield 379 mg, 83%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.32 (s, 3 H, CH_3), 3.77 (s, 3 H, CO_2CH_3), 3.81 (s, 3 H, OCH_3), 4.73 (d, J = 5.0 Hz, 1 H, furan-H), 4.93 (d, J = 5.0 Hz, 1 H, furan-H), 6.71 (d, J = 8.5 Hz, 2 H, Ar-H), 6.96 (d, J = 8.5 Hz, 2 H, Ar-H), 7.01 (d, J = 8.0 Hz, 2 H, Ar-H), 7.19 (d, J = 8.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5, 30.9, 53.2, 54.3, 55.4, 86.4, 114.5, 117.4 (q, $^1J_{C,F}$ = 272.5 Hz), 127.8, 129.0, 129.3, 129.6, 133.7, 137.6, 144.5, 149.5 (q, $^2J_{C,F}$ = 40.0 Hz), 159.8, 168.2 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.41 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2957, 1762, 1646, 1597, 1513, 1331, 1254, 1198, 1160, 1077, 1032, 813 cm^{-1}. MS (EI): *m*/*z* (%) = 456 (19) [M]$^+$, 301 (100). HRMS (EI): calcd. for $C_{21}H_{19}F_3O_6S$ [M]$^+$ 456.0854; found 456.0851.

{3-[4-(Dimethylamino)phenyl]-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-yl}(phenyl)methanone (7Ea): Brown solid. Yield 443 mg, 86%. M.p. 129.8–130.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.33 (s, 3 H, CH_3), 2.98 [s, 6 H, $N(CH_3)_2$], 4.66 (d, J = 5.0 Hz, 1 H, furan-H), 5.79 (d, J = 5.0 Hz, 1 H, furan-H), 6.58 (d, J = 8.5 Hz, 2 H, Ar-H), 6.98 (d, J = 8.5 Hz, 2 H, Ar-H), 7.00 (d, J = 8.0 Hz, 2 H, Ar-H), 7.21 (d, J = 8.0 Hz, 2 H, Ar-H), 7.45–7.48 (m, 2 H, Ar-H), 7.61–7.64 (m, 1 H, Ar-H), 7.80–7.82 (m, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5, 30.9, 40.4, 53.4, 90.0, 112.8, 117.5 (q, $^1J_{C,F}$ = 272.5 Hz), 124.7, 127.8, 128.9, 129.0, 129.2, 131.5, 132.5, 134.4, 138.0, 143.8, 149.4 (q, $^2J_{C,F}$ = 40.0 Hz), 150.7, 190.8 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.26 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2896, 1698, 1647, 1611, 1524, 1329, 1199, 1150, 1109, 1076, 809, 693 cm^{-1}. MS (EI): *m*/*z* (%) = 516 (8) [M + H]$^+$, 515 (28) [M]$^+$, 105 (100). HRMS (EI): calcd. for $C_{27}H_{24}F_3NO_4S$ [M]$^+$ 515.1378; found 515.1380.

3-[4-(Dimethylamino)phenyl]-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-carbonitrile (7Eb): Brown solid. Yield 367 mg, 84%. M.p. 143.4–143.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.15 (s, 3 H, CH_3), 2.94 [s, 6 H, $N(CH_3)_2$], 4.76 (d, J = 5.0 Hz, 1 H, furan-H), 5.11 (d, J = 5.0 Hz, 1 H, furan-H), 6.51 (d, J = 8.5 Hz, 2 H, Ar-H), 6.84 (d, J = 8.5 Hz, 2 H, Ar-H), 7.03 (d, J = 7.0 Hz, 2 H, Ar-H), 7.23 (d, J = 7.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 30.9, 40.3, 56.2, 75.6, 112.6, 115.2, 117.2 (q, $^1J_{C,F}$ = 273.5 Hz), 120.4, 124.8, 128.0, 128.5, 129.4, 137.1, 144.6, 147.7 (q, $^2J_{C,F}$ = 41.3 Hz), 151.1 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.11 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2922, 2814, 2245, 1649, 1597, 1527, 1349, 1329, 1203, 1163, 1133, 1076, 1013, 810 cm^{-1}. MS (EI): *m*/*z* (%) = 437 (2) [M + H]$^+$, 436 (9) [M]$^+$, 183 (100). $C_{21}H_{19}F_3N_2O_3S$ (436.45): calcd. C 57.79, H 4.39, N 6.42; found C 57.80, H 4.46, N 6.45.

Methyl 3-[4-(Dimethylamino)phenyl]-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-carboxylate (7Ec): Brown solid. Yield 394 mg, 84%. M.p. 124.5–125.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.32 (s, 3 H, CH_3), 2.93 [s, 6 H, $N(CH_3)_2$], 3.82 (s, 3 H, CO_2CH_3), 4.63 (d, J = 5.0 Hz, 1 H, furan-H), 4.94 (d, J = 5.0 Hz, 1 H, furan-H), 6.51 (d, J = 9.0 Hz, 2 H, Ar-H), 6.89 (d, J = 9.0 Hz, 2 H, Ar-H), 7.00 (d, J = 8.0 Hz, 2 H, Ar-H), 7.20 (d, J = 8.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5, 30.9, 40.5, 53.1, 54.4, 86.5, 112.7, 117.4 (q, $^1J_{C,F}$ = 272.5 Hz), 120.7, 124.8, 127.9, 128.5, 129.2, 137.8, 144.0, 149.1 (q, $^2J_{C,F}$ = 41.3 Hz), 150.6, 168.4 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.41 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2965, 2895, 1761, 1641, 1524, 1337, 1323, 1206, 1180, 1160, 1141, 1109, 1048, 812 cm^{-1}. MS (EI): *m*/*z* (%) = 470 (28) [M + H]$^+$, 469 (100) [M]$^+$. $C_{22}H_{22}F_3NO_5S$ (469.47): calcd. C 56.28, H 4.72, N 2.98; found C 56.38, H 4.79, N 3.02.

[3-(3-Chlorophenyl)-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-yl](phenyl)methanone (7Fa): Light yellow solid. Yield 436 mg, 86%. M.p. 99.5–100.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 4.79 (d, J = 5.0 Hz, 1 H, furan-H), 5.74 (d, J = 5.0 Hz, 1 H, furan-H), 6.97 (d, J = 8.0 Hz, 2 H, Ar-H), 7.07 (d, J = 8.0 Hz, 2 H, Ar-H), 7.24–7.26 (m, 2 H, Ar-H), 7.36–7.37 (m, 2 H, Ar-H), 7.46–7.49 (m, 2 H, Ar-H), 7.63–7.66 (m, 1 H, Ar-H), 7.79–7.81 (m, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 31.1, 53.0, 89.6, 117.4 (q, $^1J_{C,F}$ = 272.5 Hz), 127.8, 128.7, 128.7, 128.8, 129.2, 129.2, 129.6, 129.9, 132.5, 132.6, 134.8, 136.8, 137.6, 145.0, 150.3 (q, $^2J_{C,F}$ = 41.3 Hz), 190.4 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.00 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2925, 1699, 1597, 1645, 1597, 1334, 1199, 1161, 1109, 1079, 693 cm^{-1}. MS (EI): *m*/*z* (%) = 506 (1) [M]$^+$, 105 (100). HRMS (EI): calcd. for $C_{25}H_{18}ClF_3O_4S$ [M]$^+$ 506.0566; found 506.0564.

Methyl 3-(3-Chlorophenyl)-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-carboxylate (7Fc): Light yellow oil. Yield 387 mg, 84%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 3.86 (s, 3 H, CO_2CH_3), 4.72 (d, J = 5.0 Hz, 1 H, furan-H), 4.92 (d, J = 5.0 Hz, 1 H, furan-H), 6.87–6.88 (m, 1 H, Ar-H), 7.01–7.06 (m, 3 H, Ar-H), 7.16–7.28 (m, 4 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5, 30.9, 53.4, 54.5, 86.0, 117.2 (q, $^1J_{C,F}$ = 272.5 Hz), 126.2, 127.7, 127.8, 128.6, 129.5, 130.4, 135.1, 137.1, 139.3, 145.0, 150.4 (q, $^2J_{C,F}$ = 41.3 Hz), 167.8 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.17 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2954, 2928, 1759, 1645, 1596, 1336, 1198, 1168, 1143, 1080, 811, 797 cm^{-1}. MS (EI): *m*/*z* (%) = 461 (1) [M + H]$^+$, 460 (5) [M]$^+$, 305 (100). $C_{20}H_{16}ClF_3O_5S$ (460.85): calcd. C 52.12, H 3.50; found C 52.22, H 3.58.

[3-(4-Bromophenyl)-4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran-2-yl](phenyl)methanone (7Ga): Light yellow solid. Yield 447 mg, 81%. M.p. 166.3–167.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 4.80 (d, J = 5.0 Hz, 1 H, furan-H), 5.74 (d, J = 5.0 Hz, 1 H, furan-H), 6.98 (d, J = 8.0 Hz, 2 H, Ar-H), 7.08 (d, J = 8.0 Hz, 2 H, Ar-H), 7.25–7.27 (m, 2 H, Ar-H), 7.37 (d, J = 8.0 Hz, 2 H, Ar-H), 7.47–7.50 (m, 2 H, Ar-H), 7.63–7.66 (m, 1 H,

Ar-H), 7.80 (d, J = 8.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 30.9, 52.9, 89.5, 117.3 (q, $^1J_{C,F}$ = 272.5 Hz), 122.8, 127.7, 129.1, 129.1, 129.5, 129.8, 132.4, 132.5, 134.7, 136.8, 137.5, 144.8, 150.2 (q, $^2J_{C,F}$ = 41.3 Hz), 190.3 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.97 (s, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 1699, 1597, 1335, 1198, 1160, 1080, 814 cm^{-1}. MS (EI): m/z (%) = 550 (4) $[M]^+$, 105 (100). HRMS (EI): calcd. for $C_{25}H_{18}BrF_3O_4S$ $[M]^+$ 550.0061; found 550.0060.

Supporting Information (see footnote on the first page of this article): NMR spectra and X-ray crystal structures.

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[18] CCDC-832039 (**5E**) and CCDC -817608 (**7Ba**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Unit cell parameters (**5E**): a = 8.709(15) Å; b = 11.056(19) Å; c = 11.40(3) Å; α = 109.96(3)°; β = 96.57(3)°; γ = 110.65(2)°; space group: $P\bar{1}$. Unit cell parameters (**7Ba**): a = 7.507(3) Å; b = 9.928(4) Å; c = 15.803(7) Å; α = 94.793(6); β = 98.333(5)°; γ = 99.126(5)°; space group: $P\bar{1}$.

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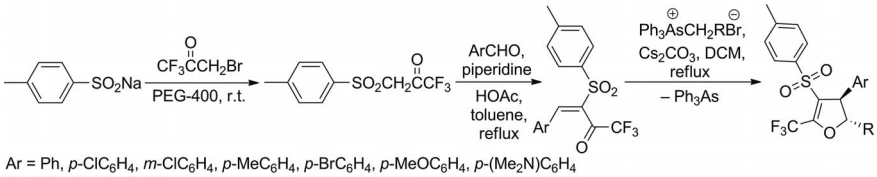
Substituted 2,3-Dihydrofurans



Ar = Ph, *p*-ClC_6H_4, *m*-ClC_6H_4, *p*-MeC_6H_4, *p*-BrC_6H_4, *p*-$MeOC_6H_4$, *p*-$(Me_2N)C_6H_4$
R = CN, CO_2Me, COPh

(*E*)-4-Aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones were prepared through a two-step process and used as fluorinated building blocks in the stereoselective preparation of a series of 4-tosyl-5-trifluoromethyl-*trans*-2,3-dihydrofuran derivatives with the assistance of arsonium ylides.

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Preparation of (*E*)-4-Aryl-1,1,1-trifluoro-3-tosylbut-3-en-2-ones as Fluorinated Building Blocks and Their Application in Ready and Highly Stereoselective Routes to *trans*-2,3-Dihydrofurans Substituted with Trifluoromethyl and Sulfonyl Groups

Keywords: 2,3-Dihydrofurans / Arsonium salts / Ylides / Sulfones / Trifluoromethyl substituent / Stereoselective synthesis / Oxygen heterocycles / Fluorine

