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Short communication

Divergent preparation of allenyl tosylates and α-tosyloxy ketones by facile and efficient isomerization of CF_3-containing propargylic tosylates

Yohsuke Watanabe, Takashi Yamazaki *

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei 184-8588, Japan

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ABSTRACT

Treatment of trifluoromethylated propargylic tosylates with hydroxides in a water-organic biphasic solvent system efficiently led to isomerization to allenyl tosylates or hydration to α-tosyloxy ketones at room temperature, just by selection of appropriate reaction conditions.

1. Introduction

Trifluoromethyl-containing molecules are very attractive because of their inherent properties applicable to pharmaceutical, agrochemical and advanced material fields [1]. However, commercially available sources of fluorinated molecules are structurally limited so that even simple compounds have to be prepared by ourselves and thus endeavors have still been required to develop novel synthetic routes, allowing ready access to a wide variety of organofluorine compounds. In continuing our application of trifluoromethylated propargylic alcohols as CF_3-containing building blocks [2], we have focused our attention for isomerization of propargylic tosylates **2** to the corresponding allenyl tosylates **3**, which was inspired by facile conversion of electron-deficient propargylic alcohols to (*E*)-enones through allenyl intermediates under basic conditions (Scheme 1) [3]. Moreover, hydration of **2** is also demonstrated in this communication for direct transformation to hitherto unknown α-tosyloxy-α′-trifluoromethyl ketones **4**. Because the corresponding non-fluorinated counterparts are recognized as significantly important building blocks for the construction of lactones and heteroaromatics such as pyrazoles, imidazoles, oxazoles, thiazoles, selenazoles and pyridines [4–6], these ketones **4** would have importance and value as long as they can tolerate under reaction conditions employed.

2. Results and discussion

Toluenesulfonates **2** employed in this study were obtained from these alcohols **1** whose condensation with *p*-toluenesulfonyl chloride (TsCl) was successfully mediated by Et_3N and a catalytic amount of 4-(dimethylamino)pyridine. However, **2a** was the exception which was prepared from the alcohol **1a** and TsCl in the presence of Ag_2O and KI [7] because of decomposition of **2a** under the former reaction condition. A solution of **2** (1.0 equiv) in THF was treated with 1 M aq NaOH (3.0 equiv) at room temperature and the reaction mixture was quenched with 1 M aq HCl. Table 1 summarized the results of the present facile isomerization with various tosylates. It is understood that tosylates **2b**–**2g** (Table 1, entries 2–7) with an aliphatic substituent at the propargylic position afforded the desired allenyl tosylates **3b**–**3g** in excellent yields but only a complex mixture was formed from **2a** (Table 1, entry 1) with a phenyl moiety at the same site. This was presumably due to instability of **2a** under this basic condition by "triple activation" of the benzyl proton which, at the same time, is α to the electronically inductive OTs and the propargylic position whose triple bond possesses a CF_3 group as the terminal substituent [8]. It is interesting to note that transformation of non-fluorinated propargylic tosylate **2h** did not proceed at all (Table 1, entry 8), which was nicely compared with the case shown in entry 2 and unambiguously proved the pivotal role of the strongly electron-withdrawing CF_3 group in this process for efficient increase of acidity of this proton.

During the course of optimization of reaction conditions, we discovered that addition of DMF to the mixture containing **3**

* Corresponding author. Tel.: +81 42 388 7038; fax: +81 42 388 7038.
E-mail address: tyamazak@cc.tuat.ac.jp (T. Yamazaki).

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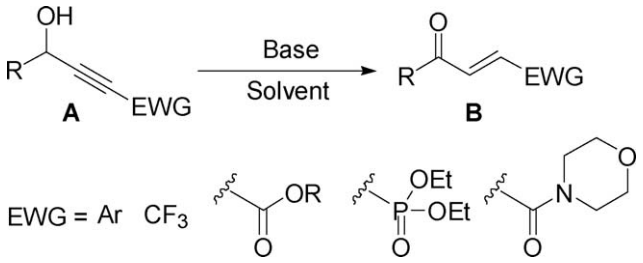
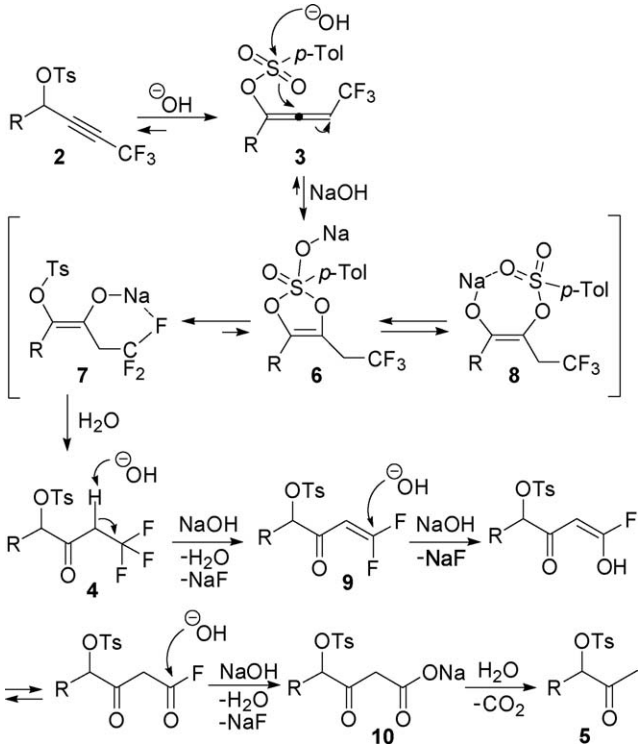


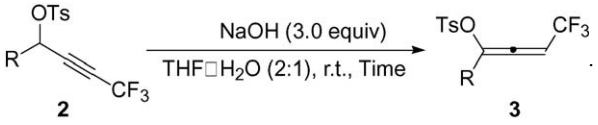
Scheme 1. Isomerization of propargylic alcohols **A** to *E*-enones **B**.



Scheme 2. Proposed mechanism for the hydration.

further promoted the hydration reaction to yield the corresponding ketone products **4** in good yields (Table 2). When substituents R were equivalent to primary alkyl groups, the desired tosyloxy ketones **4** were obtained in good to high yields (Table 2, entries 1–3). Meanwhile, low-yield formation of **4** was noticed for the secondary alkylated tosylates **2e** and **f**, with the product of the latter **4f** being unable to be purified by silica gel column chromatography due to its instability (Table 2, entries 4 and 5). Additionally, the tertiary alkylated tosylate **2g** could not afford the corresponding ketone **4g** at all.

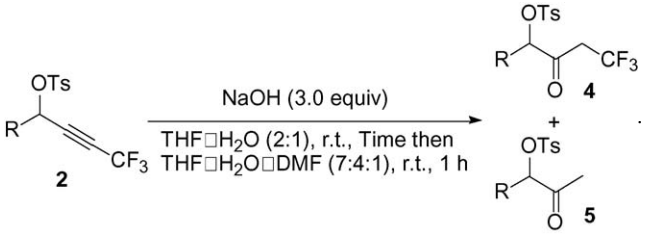
Table 1
Isomerization of **2**–**3**



Entry	R	2	Time (h)	3	Yield (%)[a]
1	Ph	**2a**	1	**3a**	–[b]
2	$Ph(CH_2)_2$	**2b**	5	**3b**	≥99
3	C_9H_{19}	**2c**	24	**3c**	90
4	$BnO(CH_2)_2$	**2d**	24	**3d**	80
5	*c*-Hex	**2e**	48	**3e**	≥99
6	Ph(MOMO)CH	**2f**	48	**3f**	78
7	*t*-Bu	**2g**	48	**3g**	97
8[c]	$Ph(CH_2)_2$	**2h**	24	**3h**	0[d]

[a] Isolated yield.
[b] A complex mixture.
[c] **2h** possessed a Bu group at the terminal position instead of a CF_3 group.
[d] 77% recovery of **2h**.

Table 2
Hydration of propargylic tosylates **2**



Entry	Time (h)	4	Yield[a] (%)	5	Yield[a] (%)
1	5	**4b**	76	**5b**	17
2	24	**4c**	61	**5c**	12
3	24	**4d**	58	**5d**	14
4[b]	24	**4e**	26	**5e**	16
5[c]	24	**4f**	41	**5f**	–
6[b,d]	48	**4g**	0	**5g**	0

[a] Isolated yield.
[b] This reaction was carried out in THF–H_2O–DMF (2:1:1).
[c] ^{19}F NMR yield using $PhCF_3$ as an internal standard.
[d] The second step was carried out at 90 °C.

These results can be explained by the mechanism shown in Scheme 2. After base-mediated isomerization of propargylic tosylates **2** to allenyl tosylates **3**, hydroxide ion would cause the transformation to **4** by possible initiation by nucleophilic attack at the electropositive sulfonyl sulfur atom to furnish the cyclic intermediate **6**. Selective cleavage of the S–O bond would proceed so as to afford energetically more favorable intermediate **7** stabilized by intramolecular Na...F interaction rather than **8**, which led to the formation of the desired α-tosyloxy ketones **4**. Further reaction of **4** with an excess amount of hydroxide ion affected defluorinative decarboxylation to **5** by way of repeated elimination of fluoride ion [9]. This mechanism consistently explains the fact that the conversion of **2h** to **3h** did not occur: thus, **2h** with an electron-donating butyl group should destabilize the anionic intermediate between **3h** and **6h** which resulted in suppression of this process.

3. Conclusion

In summary, we have developed facile and efficient synthetic routes which allowed the selective syntheses of both allenyl tosylates **3** and α-tosyloxy-α′-trifluoromethyl ketones **4** from CF_3-containing propargylic tosylates **2** as the single substrates. Advantage of the present method is that both allenes **3** and ketones **4** can be easily prepared only by selection of the condition whether DMF is added to the reaction mixture after transformation of **2**–**3** or not. Further synthetic study on the scope and limitation of this hydration and application of allenyl tosylates are underway in our laboratory.

4. Experimental

4.1. General

^1H, ^{13}C and ^{19}F NMR spectra were recorded (^1H: 300 MHz; ^{13}C: 75.5 MHz; ^{19}F: 283 MHz) at rt. (JEOL AL 300 spectrometer) with Me_4Si and $CFCl_3$ as the internal standards in $CDCl_3$. ^{13}C NMR spectra were obtained with complete proton decoupling. Infrared

(IR) spectra were obtained with a JASCO A-302 spectrometer. HRMS data were obtained with a JEOL JMS-700 spectrometer and FAB mass spectra were measured in a positive ion mode. Elemental analysis was run on a Perkin-Elmer Series II CHNS/O Analyzer.

Anhydrous THF (Cat. No. 41001-85) and CH_2Cl_2 (Cat. No. 11338-85) were obtained from Kanto Chemical Co., Inc. and used as received. DMF was freshly distilled from CaH_2. All other reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon in dried glassware with magnetic stirring.

Analytical thin layer chromatography (TLC) was routinely used for monitoring reactions by generally using a mixture of *n*-hexane and ethyl acetate (v/v). Spherical neutral silica gel (63–210 μm or 40–50 μm) was employed for column chromatography and flush chromatography, respectively.

4.2. Experimental procedure

4.2.1. Procedure for preparation of 5,5,5-trifluoro-2-[(methoxy)methoxy]pent-3-yn-2-ol (1f)

To a solution of diisopropylamine (12.1 mL, 86 mmol) in THF (80 mL) at 0 °C was added dropwise a 1.6 M solution of *n*-BuLi in hexane (53.8 mL, 86 mmol) and the mixture was stirred for 30 min at that temperature. The resultant LDA mixture was cooled to −80 °C, and 2-bromo-3,3,3-trifluoropropene (4.5 mL, 43 mmol) in THF (5 mL) was slowly added at −80 °C. After the solution was stirred for 5 min, 2-(methoxymethoxy)-2-phenylethanal (7.7 g, 43 mmol) was added and the whole was stirred for 1.5 h at that temperature. The reaction mixture was quenched with 1 M HCl aq. and extracted with EtOAc three times. Concentration after drying over $MgSO_4$ furnished a crude mixture that was purified by distillation under reduced pressure to afford **1f** (8.8 g, 75%, DR 76:24). Other fluorinated propargylic alcohols were synthesized by using Ref. [10] procedure.

4.2.2. Typical procedure for preparation of allenyl tosylates (3)

To a solution of **2a** (0.153 g, 0.40 mmol) in THF (2.4 mL) was added a 1 M NaOH aq. solution (1.2 mL) at r.t. and the solution was stirred at that temperature for 5 h. The reaction mixture was quenched with a 1 M HCl aq. solution (3 mL) and extracted with EtOAc (3 × 15 mL). Concentration by rotary evaporator after dried over Na_2SO_4 furnished **3b** in an almost pure state. If necessary, the residue was purified by short column chromatography (hexane–EtOAc, 8:1) to give pure allenyl tosylate **3b** (0.153 g, quant).

4.2.3. Typical procedure for preparation of α-tosyloxyketones (4)

To a solution of **2a** (0.153 g, 0.40 mmol) in THF (2.1 mL) was added a 1 M NaOH aq. solution (1.2 mL) at r.t. The solution was stirred at that temperature for 4 h before addition of DMF (0.3 mL). After the resulting solution was stirred for additional 1 h, the reaction mixture was quenched with a 1 M HCl aq. solution (3 mL) and extracted with hexane–EtOAc (1:1, 3× 15 mL). Concentration by rotary evaporator after dried over Na_2SO_4 furnished a crude mixture that was purified by silica gel chromatography (hexane–EtOAc, 18:1) to afford **4b** (0.121 g, 76%).

4.3. Experimental data

4.3.1. 5,5,5-Trifluoro-2-[(methoxy)methoxy]pent-3-yn-2-ol (1f)

IR (neat): 650, 701, 731, 758, 849, 921, 986, 1036, 1078, 1106, 1146, 1214, 1278, 1401, 1455, 1496, 2276, 2369, 2786, 2829, 2848, 2897, 2954, 3000, 3034, 3067, 3091, 3405 cm^{-1}. Anal. calcd for $C_{13}H_{13}O_3F_3$: C, 56.94; H, 4.78; found: C, 56.71; H, 4.61. DR 76:24. Yield: 75%. Colorless oil. bp: 150 °C (2.3 mmHg). R_f = 0.23 (*n*-hexane/EtOAc, 3:1, v/v). Major isomer; ^{1}H NMR δ 3.43 (s, 3H), 4.58 (quint, *J* = 3.0 Hz, 1H), 4.64 (d, *J* = 6.6 Hz, 1H), 4.68 (d, *J* = 6.9 Hz, 1H), 4.76 (d, *J* = 6.0 Hz, 1H), 7.26–7.39 (m, 5H); ^{13}C NMR δ 55.6, 65.7, 72.8 (q, *J* = 52.7 Hz, *C*–CF_3), 79.7, 85.6 (q, *J* = 6.2 Hz, *C*–CCF_3), 94.4, 113.7 (q, *J* = 257.4 Hz, CF_3), 127.6, 128.3, 128.7, 136.0; ^{19}F NMR δ −52.14 (s). Minor isomer; ^{1}H NMR δ 3.51 (s, 3H), 4.53 (br, 1H), 4.72 (d, *J* = 6.9 Hz, 1H), 4.77 (d, *J* = 6.9 Hz, 1H), 4.80 (d, *J* = 3.9 Hz, 1H), 7.26–7.39 (m, 5H); ^{13}C NMR δ 55.7, 66.0, 73.0 (q, *J* = 52.7 Hz, *C*–CF_3), 81.3, 85.6 (q, *J* = 6.2 Hz, *C*–CCF_3), 95.1, 113.8 (q, *J* = 257.4 Hz, CF_3), 127.2, 128.3, 128.6, 136.2; ^{19}F NMR δ −51.93 (s). IR (neat): 650, 701, 731, 758, 849, 921, 986, 1036, 1078, 1106, 1146, 1214, 1278, 1401, 1455, 1496, 2276, 2369, 2786, 2829, 2848, 2897, 2954, 3000, 3034, 3067, 3091, 3405 cm^{-1}. Anal. calcd for $C_{13}H_{13}O_3F_3$: C, 56.94; H, 4.78; found: C, 56.71; H, 4.61.

4.3.2. 1,1,1-Trifluoro-6-phenyl-4-(p-toluenesulfonyloxy)hex-2-yne (2b)

Yield: 94%. White solid. mp: 48 °C. R_f = 0.46 (*n*-hexane/EtOAc, 4:1, v/v). ^{1}H NMR δ 2.45 (s, 3H), 2.71–2.84 (m, 2H), 2.71–2.84 (m, 2H), 7.13–7.36 (m, 7H), 7.80 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR δ 21.6, 30.5, 36.4, 68.3, 74.3 (q, *J* = 52.9 Hz, *C*–CF_3), 81.9 (q, *J* = 6.4 Hz, *C*–CCF_3), 113.2 (q, *J* = 257.9 Hz, CF_3), 126.6, 128.1, 128.4, 128.7, 129.7, 133.0, 139.2, 145.7; ^{19}F NMR δ −52.53 (s). NMR spectra are in agreement with the published data [8h].

4.3.3. 1,1,1-Trifluoro-4-(p-toluenesulfonyloxy)tridec-2-yne (2c)

Yield: 98%. Colorless oil. R_f = 0.64 (*n*-hexane/EtOAc, 4:1, v/v). ^{1}H NMR δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.20–1.47 (m, 14H), 1.76–1.95 (m, 2H), 2.45 (s, 3H), 5.09 (tq, *J* = 6.6, 3.0 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR δ 14.0, 21.5, 22.6, 24.3, 28.6, 29.21, 29.22, 29.3, 31.8, 34.7, 69.2, 74.1 (q, *J* = 53.3 Hz, *C*–CF_3), 82.2 (q, *J* = 6.2 Hz, *C*–CCF_3), 113.4 (q, *J* = 258.2 Hz, CF_3), 128.1, 129.8, 133.1, 145.6; ^{19}F NMR δ −52.38 (s). IR (neat): 2954, 2928, 2857, 1711, 1599, 1467, 1378, 1280, 1212, 1192, 1179, 1151, 1096, 957, 918, 887, 814, 669, cm^{-1}. HRMS (FAB): *m*/*z* calcd for $C_{20}H_{28}O_3F_3S$ $[M+H]^+$: 405.1711; found: 405.1741.

4.3.4. 6-(Benzyloxy)-1,1,1-trifluoro-4-(p-toluenesulfonyloxy)hex-2-yne (2d)

Yield: 59%. Colorless oil. R_f = 0.53 (*n*-hexane/EtOAc, 4:1, v/v). ^{1}H NMR δ 2.03–2.23 (m, 2H), 2.42 (s, 3H), 3.55 (t, *J* = 5.7 Hz, 2H), 4.41 (d, *J* = 11.7 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 5.39 (ddq, *J* = 8.1, 5.4, 2.7 Hz, 1H), 7.27–7.38 (m, 7H), 7.81 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR δ 21.5, 35.3, 64.2, 66.4 (q, *J* = 1.3 Hz, *C*H–OTs), 73.2, 74.1 (q, *J* = 52.1 Hz, *C*–CF_3), 82.1 (q, *J* = 6.2 Hz, *C*–CCF_3), 113.3 (q, *J* = 257.9 Hz, CF_3), 127.7, 127.8, 128.1, 128.4, 129.9, 132.9, 137.7, 145.6; ^{19}F NMR δ −52.57 (s). IR (neat): 2963, 2933, 2871, 2275, 1722, 1598, 1496, 1455, 1376, 1277, 1211, 1192, 1148, 1098, 1070, 1030, 1020, 957, 940, 853, 816, 788, 749, 699, 669 cm^{-1}. HRMS (FAB): *m*/*z* calcd for $C_{20}H_{20}O_4F_3S$ $[M+H]^+$: 413.1034; found: 413.1045.

4.3.5. 4-Cyclohexyl-1,1,1-trifluoro-4-(p-toluenesulfonyloxy)but-2-yne (2e)

Yield: 88%. White solid. mp: 66 °C. R_f = 0.62 (*n*-hexane/EtOAc, 4:1, v/v). ^{1}H NMR δ 0.99–1.32 (m, 5H), 1.61–1.85 (m, 6H), 2.44 (s, 3H), 4.91 (dq, *J* = 5.4, 2.7 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR δ 21.5, 25.2, 25.3, 25.7, 27.7, 27.8, 41.9, 73.4 (q, *J* = 1.2 Hz, *C*H–OTs), 74.7 (q, *J* = 53.3 Hz, *C*–CF_3), 81.4 (q, *J* = 6.8 Hz, *C*–CCF_3), 113.3 (q, *J* = 257.4 Hz, CF_3), 128.0, 129.8, 133.0, 145.5; ^{19}F NMR δ −52.18 (s). IR (CH_2Cl_2): 2935, 2858, 1599, 1452, 1373, 1339, 1280, 1212, 1190, 1178, 1154, 1096, 965, 935, 916, 897, 887, 844, 829, 813, 787, 745, 670 cm^{-1}. HRMS (FAB): *m*/*z* calcd for $C_{17}H_{19}O_3F_3SNa$ $[M+Na]^+$: 383.0905; found: 383.0876.

4.3.6. 1,1,1-Trifluoro-5-[(methoxy)methoxy]-5-phenyl-4-(p-toluenesulfonyloxy)pent-2-yne (2f)

IR (neat): 3066, 3035, 2999, 2955, 2895, 2847, 2828, 2274, 1598, 1495, 1455, 1377, 1279, 1214, 1190, 1153, 1104, 1037, 1020,

959, 922, 903, 870, 810, 783, 758, 701, 667 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{20}H_{20}O_5F_3S$ $[M+H]^+$: 429.0984; found: 429.1029. DR 74:26. Yield: 89%. Colorless oil. R_f = 0.57 (*n*-hexane/EtOAc, 4:1, v/v). Major; ^1H NMR δ 2.43 (s, 3H), 3.34 (s, 3H), 4.55 (d, *J* = 6.6 Hz, 1H), 4.61 (d, *J* = 6.6 Hz, 1H), 4.85 (d, *J* = 6.9 Hz, 1H), 5.27 (dq, *J* = 6.9, 2.7 Hz, 1H), 7.26–7.37 (m, 7H), 7.76 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR δ 21.5, 55.8, 71.6 (q, *J* = 1.2 Hz, *C*H–OTs), 75.5 (q, *J* = 53.3 Hz, *C*–CF_3), 77.4, 80.0 (q, *J* = 6.8 Hz, *C*–CCF_3), 94.5, 113.1, (q, *J* = 258.0 Hz, CF_3), 127.8, 128.0, 128.5, 129.2, 129.7, 132.8, 134.5, 145.7; ^{19}F NMR δ −52.97 (d, *J* = 4.5 Hz). Minor; ^1H NMR 2.43 (s, 3H), 3.37 (s, 3H), 4.56 (d, *J* = 6.9 Hz, 1H), 4.61 (d, *J* = 6.6 Hz, 1H), 4.92 (d, *J* = 5.4 Hz, 1H), 5.16 (dq, *J* = 3.0, 3.0 Hz, 1H), 7.26–7.37 (m, 7H), 7.66 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR 21.5, 55.8, 71.5 (q, *J* = 1.2 Hz, *C*H–OTs), 74.9 (q, *J* = 52.7 Hz, *C*–CF_3), 77.1, 80.4 (q, *J* = 6.2 Hz, *C*–CCF_3), 94.2, 113.3, (q, *J* = 258.0 Hz, CF_3), 127.6, 128.0, 128.5, 129.1, 129.8, 132.5, 134.7, 145.7; ^{19}F NMR −52.67 (d, *J* = 4.5 Hz).

4.3.7. 1,1,1-Trifluoro-5,5-dimethyl-4-(p-toluenesulfonyloxy)hex-2-yne (2g)

Yield: 95%. White solid. mp: 64–67 °C. R_f = 0.63 (*n*-hexane/EtOAc, 4:1, v/v). ^1H NMR δ 1.03 (s, 9H), 2.45 (s, 3H), 4.77 (q, *J* = 2.7 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR δ 21.4, 25.0, 36.0, 74.7 (q, *J* = 53.3 Hz, *C*–CF_3), 77.2, 81.4 (q, *J* = 6.8 Hz, *C*–CCF_3), 113.3 (q, *J* = 258.0 Hz, CF_3), 128.1, 129.8, 133.0, 145.6; ^{19}F NMR δ −52.35 (s); IR (CH_2Cl_2): 2974, 1370, 1279, 1246, 1213, 1191, 1178, 1153, 956, 936, 897, 840, 814, 771, 704, 672 cm^{-1}. Anal. calcd for $C_{15}H_{17}O_3F_3S$: C, 53.88; H, 5.12; found: C, 53.43; H, 5.51.

4.3.8. 1-Phenyl-3-(p-toluenesulfonyloxy)non-4-yne (2h)

Yield: 40%. Colorless oil. R_f = 0.50 (*n*-hexane/EtOAc, 4:1, v/v). ^1H NMR δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.23–1.33 (m, 4H), 1.98–2.14 (m, 4H), 2.44 (s, 3H), 2.65–2.82 (m, 2H), 5.08 (tt, *J* = 6.3, 1.8 Hz, 1H), 7.13 − 7.33 (m, 7H), 7.79–7.83 (m, 2H); ^{13}C NMR δ 13.4, 18.2, 21.6, 21.7, 30.1, 30.8, 37.7, 72.0, 75.2, 89.8, 126.1, 128.0, 128.36, 128.42, 129.4, 134.3, 140.3, 144.4. IR (neat): 2957, 2932, 2871, 1600, 1496, 1455, 1366, 1189, 1175, 1097, 895, 814, 749, 700, 667 cm^{-1}. HRMS (FAB): calcd for $C_{22}H_{28}O_3S$ $[M+2H]^+$: 372.1759; found: 372.1798.

4.3.9. 1,1,1-Trifluoro-6-phenyl-4-(p-toluenesulfonyloxy)hexa-2,3-diene (3b)

Yield: quant. Colorless oil. R_f = 0.70 (*n*-hexane/EtOAc, 4:1, v/v). ^1H NMR δ 2.45 (s, 3H), 2.56–2.63 (m, 2H), 2.70–2.76 (m, 2H), 5.66 (qt, *J* = 5.7, 3.0 Hz, 1H), 7.09–7.35 (m, 7H), 7.75–7.79 (m, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.3, 31.6, 33.2, 96.2 (q, *J* = 39.1 Hz, *C*–CF_3), 120.5 (q, *J* = 271.6 Hz, CF_3), 126.2, 128.1, 128.2, 128.3, 129.8, 130.3, 132.1, 139.3, 145.7, 199.3 (q, *J* = 5.6 Hz, *C*–CCF_3). ^{19}F NMR (283 MHz, $CDCl_3$): δ −63.38 (t, *J* = 6.9 Hz). IR (neat): 3030, 2928, 1737, 1598, 1496, 1454, 1437, 1418, 1376, 1271, 1214, 1195, 1181, 1145, 1128, 1087, 1071, 1033, 940, 865, 846, 819, 745, 700, 680, 650 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{19}H_{18}O_3F_3S$ $[M+H]^+$: 383.0929; found: 383.0950.

4.3.10. 1,1,1-Trifluoro-4-(p-toluenesulfonyloxy)trideca-2,3-diene (3c)

Yield: 98%. Colorless oil. R_f = 0.74 (*n*-hexane/EtOAc, 4:1, v/v). ^1H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.18–1.41 (m, 14H), 2.27 (td, *J* = 7.5, 3.0 Hz, 2H), 2.46 (s, 3H), 5.73 (qt, *J* = 5.7, 3.0 Hz, 1H), 7.33–7.37 (m, 2H), 7.76–7.81 (m, 2H). ^{13}C NMR δ 14.1, 21.6, 22.6, 25.3, 28.4, 29.1, 29.2, 29.3 31.786, 31.794, 96.1 (q, *J* = 39.8 Hz, *C*–CF_3), 120.7 (q, *J* = 271.7 Hz, CF_3), 128.4, 129.8, 131.4, 132.4, 145.7 (q, *J* = 0.6 Hz, *C*–C═CCF_3), 199.3 (q, *J* = 6.0 Hz, *C*–CCF_3). ^{19}F NMR δ −63.38 (d, *J* = 6.8 Hz). IR (neat): 2957, 2927, 2857, 1599, 1466, 1418, 1379, 1306, 1283, 1213, 1193, 1179, 1129, 1088, 1020, 900, 841, 815, 785, 717, 687, 665 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{20}H_{27}O_3F_3S$ $[M]^+$: 404.1633; found: 404.1590.

4.3.11. 6-(Benzyloxy)-1,1,1-trifluoro-4-(p-toluenesulfonyloxy)hexa-2,3-diene (3d)

Yield: 80%. Colorless oil. R_f = 0.46 (*n*-hexane/EtOAc, 4:1, v/v). ^1H NMR δ 2.45 (s, 3H), 2.57–2.62 (m, 2H), 3.52 (dt, *J* = 9.9, 6.0 Hz, 1H), 3.57 (dt, *J* = 9.9, 6.0 Hz, 1H), 4.41 (d, *J* = 15.6 Hz, 1H), 4.46 (d, *J* = 15.6 Hz, 1H), 5.74 (qt, *J* = 5.7, 3.0 Hz, 1H), 7.24–7.36 (m, 7H), 7.75–7.79 (m, 2H); ^{13}C NMR δ 21.6, 32.6, 65.4, 73.0, 96.3 (q, *J* = 39.7 Hz, *C*–CF_3), 120.6 (q, *J* = 271.7 Hz, CF_3), 127.5, 127.6, 128.30, 128.34, 128.7, 129.8, 132.2, 137.8, 145.7 (q, *J* = 0.7 Hz, *C*–C═CCF_3), 199.6 (q, *J* = 5.6 Hz, *C*–CCF_3); ^{19}F NMR δ −63.40 (d, *J* = 6.8 Hz). IR (neat): 2867, 1598, 1454, 1436, 1415, 1380, 1308, 1273, 1195, 1181, 1133, 1091, 1060, 972, 851, 815, 740, 699, 680, 659 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{20}H_{20}O_4F_3S$ $[M+H]^+$: 413.1034; found: 413.1051.

4.3.12. 4-Cyclohexyl-1,1,1-trifluoro-4-(p-toluenesulfonyloxy)buta-2,3-diene (3e)

Yield: quant. Colorless oil. R_f = 0.63 (*n*-hexane/EtOAc, 4:1, v/v). ^1H NMR δ 0.95–1.32 (m, 5H), 1.61–1.85 (m, 5H), 2.20 (tq, *J* = 11.1, 3.3 Hz, 1H), 2.45 (s, 3H), 5.78 (qd, *J* = 5.7, 3.0 Hz, 1H), 7.32–7.37 (m, 2H), 7.75–7.79 (m, 2H); ^{13}C NMR δ 21.6, 25.35, 25.37, 25.7, 29.48, 29.52, 96.2 (q, *J* = 39.0 Hz, *C*–CF_3), 120.8 (q, *J* = 271.7 Hz, CF_3), 128.3, 129.8, 132.5, 135.3, 146.6, 198.4 (q, *J* = 5.6 Hz, *C*–CCF_3); ^{19}F NMR δ −63.61 (d, *J* = 4.5 Hz). IR (neat): 2934, 1404, 1373, 1292, 1218, 1192, 1179, 1152, 1134, 1086, 1004, 829, 815, 739, 665 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{17}H_{19}O_3F_3S$ $[M]^+$: 360.1007; found: 360.1034.

4.3.13. 1,1,1-Trifluoro-5-[(methoxy)methoxy]-5-phenyl-4-(p-toluenesulfonyloxy)penta-2,3-diene (3f)

DR: 50:50. Yield: 78%. Colorless oil. R_f = 0.47 (*n*-hexane/EtOAc, 4:1, v/v). ^1H NMR δ 2.44 (s, 6H), 3.32 (s, 6H), 4.53 (d, *J* = 6.9 Hz, 1H), 4.55 (d, *J* = 7.2 Hz, 1H), 4.63 (d, *J* = 6.6 Hz, 1H), 4.66 (d, *J* = 6.6 Hz, 1H), 5.27 (t, *J* = 2.1 Hz, 2H), 5.87 (qd, *J* = 5.7, 2.1 Hz, 1H), 5.89 (qd, *J* = 5.7, 2.1 Hz, 1H), 7.23–7.35 (m, 14H), 7.61–7.67 (m, 4H); ^{13}C NMR δ 21.6, 55.65, 55.68, 75.1, 75.2, 94.2, 98.0 (q, *J* = 39.8 Hz, *C*–CF_3), 98.1 (q, *J* = 39.1 Hz, *C*–CF_3), 120.6, (q, *J* = 271.7 Hz, CF_3), 120.7, (q, *J* = 271.7 Hz, CF_3), 127.27, 127.32, 128.25, 128.29, 128.4, 128.7, 129.4, 129.5, 129.7, 131.91, 131.93, 135.9, 136.0, 145.7, 198.7, (q, *J* = 5.6 Hz, *C*–CCF_3), 198.8, (q, *J* = 6.2 Hz, *C*–CCF_3); ^{19}F NMR δ −63.18 (d, *J* = 4.5 Hz), −63.11 (d, *J* = 4.5 Hz). IR (neat): 2928, 1721, 1674, 1598, 1450, 1365, 1307, 1271, 1191, 1178, 1139, 1097, 1020, 994, 816, 768, 699, 661 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{20}H_{21}O_5F_3S$ $[M+2H]^+$: 430.1063; found: 430.1082.

4.3.14. 1,1,1-Trifluoro-5,5-dimethyl-4-(p-toluenesulfonyloxy)hexan-2-one (3g)

Yield: 97%. Colorless oil. R_f = 0.63 (*n*-hexane/EtOAc, 4:1, v/v). ^1H NMR δ 1.07 (s, 9H), 2.45 (s, 3H), 5.85 (q, *J* = 5.7 Hz, 1H), 7.32–7.36 (m, 2H), 7.76–7.80 (m, 2H); ^{13}C NMR δ 21.6, 27.1, 34.9, 97.7 (q, *J* = 39.1 Hz, *C*–CF_3), 120.9 (q, *J* = 271.0 Hz, CF_3), 128.3, 129.8, 132.7, 138.0, 145.6, 196.6 (q, *J* = 6.2 Hz, *C*–CCF_3); ^{19}F NMR δ −63.52 (d, *J* = 6.8 Hz). IR (neat): 2360, 1419, 1381, 1269, 1195, 1180, 1128, 1048, 861, 776, 741, 661 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{15}H_{18}O_3F_3S$ $[M+H]^+$: 335.0929; found: 335.0969.

4.3.15. 1,1,1-Trifluoro-6-phenyl-4-(p-toluenesulfonyloxy)hexan-3-one (4b)

Yield: 76%. Colorless oil. R_f = 0.43 (*n*-hexane/EtOAc, 4:1, v/v). ^1H NMR δ 1.91–2.10 (m, 2H), 2.39–2.49 (m, 1H), 2.47 (s, 3H), 2.58 (ddd, *J* = 14.7, 9.3, 6.0 Hz, 1H), 3.40 (dq, *J* = 18.0, 9.9 Hz, 1H), 3.50 (dq, *J* = 18.0, 9.9 Hz, 1H), 4.65 (dd, *J* = 7.8, 5.1 Hz, 1H), 6.96–6.98 (m, 2H), 7.17–7.25 (m, 3H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.7, 30.4, 32.7, 41.7 (q, *J* = 29.1 Hz, *C*–CF_3), 82.8 (q, *J* = 1.8 Hz, *C*H–OTs), 123.4 (q, *J* = 276.7 Hz, CF_3), 126.5, 128.1, 128.3, 128.6, 130.2, 132.1, 139.2,

146.0, 197.2 (q, J = 2.5 Hz, C–CCF_3). ^{19}F NMR (283 MHz, $CDCl_3$): δ −63.66 (t, J = 6.9 Hz). IR (neat): 3030, 2931, 1742, 1598, 1496, 1455, 1410, 1374, 1275, 1192, 1177, 1109, 1051, 1017, 982, 930, 834, 816, 750, 700, 667 cm^{-1}. HRMS (FAB): m/z calcd for $C_{19}H_{20}O_4F_3S$ $[M+H]^+$: 401.1034; found: 401.1028.

*4.3.16. 1,1,1-Trifluoro-4-(p-toluenesulfonyloxy)tridecan-3-one (**4c**)*

Yield: 61%. Colorless oil. R_f = 0.57 (*n*-hexane/EtOAc, 4:1, v/v). ^{1}H NMR δ 0.88 (t, J = 6.6 Hz, 3H), 1.04–1.31 (m, 14H), 1.58–1.78 (m, 2H), 2.47 (s, 3H), 3.43 (dq, J = 18.0, 9.9 Hz, 1H), 3.53 (dq, J = 18.0, 9.9 Hz, 1H), 4.60 (dd, J = 8.1, 4.5 Hz, 1H), 7.37–7.41 (m, 2H), 7.79–7.82 (m, 2H); ^{13}C NMR δ 14.0, 21.6, 22.6, 24.2, 28.6, 29.1, 29.2, 29.3, 31.1, 31.8, 41.6 (q, J = 29.1 Hz, C–CF_3), 83.7 (q, J = 1.2 Hz, C–CCF_3), 123.4 (q, J = 276.0 Hz, CF_3), 128.1, 130.1, 132.1, 145.9, 197.6 (br); ^{19}F NMR δ −63.67 (t, J = 9.0 Hz). IR (neat): 2953, 2927, 2856, 1743, 1598, 1466, 1411, 1374, 1277, 1191, 1178, 1125, 1105, 1040, 1020, 982, 943, 912, 887, 842, 815, 771, 723, 707, 688, 667 cm^{-1}. HRMS (FAB): m/z calcd for $C_{20}H_{29}O_4F_3S$ $[M]^+$: 422.1739; found: 422.1710.

*4.3.17. 6-(Benzyloxy)-1,1,1-trifluoro-4-(p-toluenesulfonyloxy)hexan-3-one (**4d**)*

Yield: 58%. Colorless oil. R_f = 0.43 (*n*-hexane/EtOAc, 4:1, v/v). ^{1}H NMR δ 1.93–2.03 (m, 1H), 2.09–2.21 (m, 1H), 2.42 (s, 3H), 3.29–3.57 (m, 4H), 4.28 (s, 2H), 4.90 (t, J = 5.4 Hz, 1H), 7.17–7.21 (m, 2H), 7.28–7.37 (m, 5H), 7.77–7.81 (m, 2H); ^{13}C NMR δ 21.5, 31.8, 41.8 (q, J = 29.2 Hz, C–CF_3), 63.7, 72.8, 80.7 (q, J = 1.2 Hz, CH–OTs), 123.5 (q, J = 276.1 Hz, CF_3), 127.5, 127.7, 127.9, 128.3, 130.1, 132.3, 137.4, 145.8, 196.9 (q, J = 2.5 Hz, C–CCF_3); ^{19}F NMR δ −63.92 (t, J = 10.3 Hz). IR (neat): 1030, 1043, 1101, 1191, 2930, 2871, 1743, 1598, 1496, 1455, 1412, 1372, 1272, 1212, 962, 843, 816, 769, 740, 699, 668, 640 cm^{-1}; HRMS (FAB): m/z calcd for $C_{20}H_{22}O_5F_3S$ $[M+H]^+$: 431.1140; found: 431.1168.

*4.3.18. 4-Cyclohexyl-1,1,1-trifluoro-4-(p-toluenesulfonyloxy)butan-3-one (**4e**)*

Yield: 27%. Colorless oil. R_f = 0.56 (*n*-hexane/EtOAc, 4:1, v/v). ^{1}H NMR δ 0.86–1.35 (m, 6H), 1.56–1.70 (m, 4H), 1.73–1.85 (m, 1H), 2.47 (s, 3H), 3.43 (q, J = 9.9 Hz, 2H), 4.39 (d, J = 6.0 Hz, 1H), 7.37–7.41 (m, 2H), 7.77–7.81 (m, 2H); ^{13}C NMR δ 21.7, 25.4, 25.5, 27.2, 28.2, 39.9, 42.5 (q, J = 28.5 Hz, C–CF_3), 87.5 (q, J = 1.8 Hz, CH–OTs), 123.5 (q, J = 276.6 Hz, CF_3), 128.1, 130.1, 132.0, 145.9, 197.7 (q, J = 1.8 Hz, C–CCF_3); ^{19}F NMR δ −63.73 (t, J = 9.0 Hz). IR (neat): 2934, 2858, 1742, 1598, 1452, 1410, 1373, 1282, 1271, 1191, 1177, 1145, 1107, 1083, 1047, 976, 896, 852, 840, 830, 815, 784, 680, 669 cm^{-1}. HRMS (FAB): m/z calcd for $C_{17}H_{22}O_4F_3S$ $[M+H]^+$: 379.1191; found: 379.1178.

*4.3.19. 5-Phenyl-3-(p-toluenesulfonyloxy)pentan-2-one (**5b**)*

Yield: 17%. Colorless oil. R_f = 0.36 (*n*-hexane/EtOAc, 4:1, v/v). ^{1}H NMR δ 1.89–2.09 (m, 2H), 2.20 (s, 3H), 2.42–2.64 (m, 2H), 2.46 (s, 3H), 4.65 (dd, J = 7.8, 5.1 Hz, 1H), 6.99–7.02 (m, 2H), 7.17–7.25 (m, 3H), 7.36 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 21.7, 25.9, 30.6, 33.1, 83.7, 126.3, 128.0, 128.3, 128.5, 130.0, 132.8, 139.7, 145.4, 205.1. IR (neat): 2927, 1723, 1598, 1496, 1455, 1418, 1402, 1368, 1279, 1233, 1212, 1191, 1176, 1097, 1019, 928, 815, 749, 701, 668 cm^{-1}. HRMS (FAB): m/z calcd for $C_{18}H_{21}O_4S$ $[M+H]^+$: 333.1161; found: 333.1152.

*4.3.20. 3-(p-Toluenesulfonyloxy)dodecan-2-one (**5c**)*

Yield: 12%. Colorless oil. R_f = 0.50 (*n*-hexane/EtOAc, 4:1, v/v). ^{1}H NMR δ 0.88 (t, J = 6.6 Hz, 3H), 1.12–1.31 (m, 14H), 1.56–1.77 (m, 2H), 2.21 (s, 3H), 2.46 (s, 3H), 4.58 (dd, J = 8.4, 4.8 Hz, 1H), 7.34–7.38 (m, 2H), 7.79–7.83 (m, 2H); ^{13}C NMR δ 14.1, 21.7, 22.6, 24.4, 25.9, 28.8, 29.188, 29.189, 29.3, 31.4, 31.8, 84.5, 128.0, 129.9, 133.0, 145.3, 205.6. IR (neat): 2926, 2855, 1724, 1465, 1371, 1190, 1178, 1097, 969, 944, 888, 841, 814, 667 cm^{-1}. HRMS (FAB): m/z calcd for $C_{20}H_{30}O_4F_3S$ $[M+2H]^+$: 356.2021; found: 356.2027.

*4.3.21. 5-(Benzyloxy)-3-(p-toluenesulfonyloxy)pentan-2-one (**5d**)*

Yield: 14%. Colorless oil. R_f = 0.39 (*n*-hexane/EtOAc, 4:1, v/v). ^{1}H NMR δ 2.19 (s, 3H), 2.40 (s, 3H), 1.97–2.07 (m, 2H), 3.32–3.39 (m, 1H), 3.47–3.54 (m, 1H), 4.28 (s, 2H), 4.88 (dd, J = 6.6, 5.1 Hz, 1H), 7.26–7.38 (m, 5H), 7.77–7.82 (m, 2H); ^{13}C NMR δ 21.6, 26.1, 31.9, 64.4, 72.8, 81.4, 127.4, 127.6, 127.9, 128.3, 130.1, 132.9, 137.8, 145.3, 205.0. IR (neat): 2927, 1724, 1599, 1454, 1368, 1271, 1190, 1177, 1119, 1029, 1010, 956, 847, 816, 744, 714, 699, 668 cm^{-1}. HRMS (FAB): m/z calcd for $C_{19}H_{23}O_5S$ $[M+H]^+$: 363.1266; found: 363.1255.

*4.3.22. 3-Cyclohexyl-3-(p-toluenesulfonyloxy)propan-2-one (**5e**)*

Yield: 16%. Colorless oil. R_f = 0.47 (*n*-hexane/EtOAc, 4:1, v/v). ^{1}H NMR δ 0.85–1.40 (m, 6H), 1.56–1.83 (m, 5H), 2.16 (s, 3H), 2.46 (s, 3H), 4.38 (d, J = 5.7 Hz, 1H), 7.34–7.37 (m, 2H), 7.76–7.82 (m, 2H); ^{13}C NMR δ 21.7, 25.5, 25.6, 25.7, 26.9, 27.3, 28.5, 39.9, 88.4, 128.1, 129.9, 132.8, 145.3, 205.7. IR (neat): 2931, 2856, 1716, 1598, 1451, 1370, 1191, 1177, 1096, 954, 897, 885, 836, 816, 786, 684, 668 cm^{-1}. HRMS (FAB): m/z calcd for $C_{16}H_{23}O_4S$ $[M+H]^+$: 311.1317; found: 311.1349.

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