Advanced Synthesis & Catalysis

Accepted Article

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Authors: Perumal Saravanan and Pazhamalai Anbarasan

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201800366

Link to VoR: http://dx.doi.org/10.1002/adsc.201800366

10.1002/adsc.201800366

FULL PAPER

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

An Electrophilic Trifluoromethylthiolation of Silylenol Ethers and *β*-Naphthols with Diethylaminosulfur Trifluoride and (Trifluoromethyl)trimethylsilane

Perumal Saravanan and Pazhamalai Anbarasan*

Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600036. Email: anbarasansp@iitm.ac.in

Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.

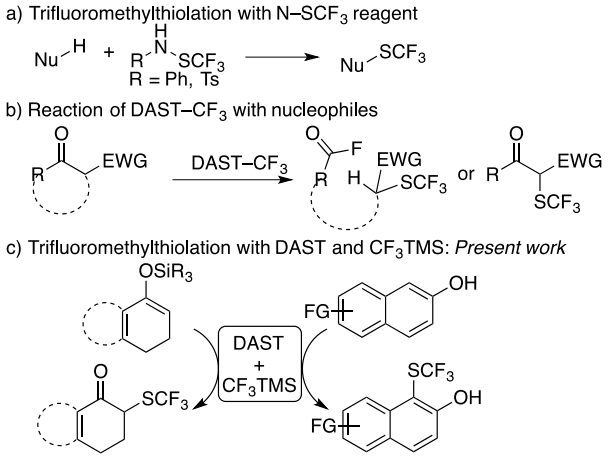
Abstract. An efficient and general trifluoromethylthiolation of silylenol ethers and *β*-naphthols have been accomplished employing the combination of diethylaminosulfur trifluoride (DAST) and (trifluoromethyl)trimethylsilane (CF_3TMS) as source of electrophilic trifluoromethylthio moiety for the synthesis of *α*-trifluoromethyl-thiolated carbonyl compounds and *β*-naphthols in good yields. Important features of this method include wide functional group tolerance and use of readily available DAST/CF_3TMS. Potential of the methodology was demonstrated *via* the synthesis of *α*-trifluoromethylthiolated (+)-4-cholesten-3-one and naphthoquinone.

Keywords: trifluoromethylthiolation; Diethylaminosulfur Trifluoride; (Trifluoromethyl)trimethylsilane; enol ether; naphthol

Introduction

Over the decades, significant attention has been devoted to the development of efficient methods for the selective introduction of fluoro and fluorinated moieties in the molecules of high importance. Because, the presence of fluorinated moieties in target molecules dramatically alters the physiochemical properties, such as solubility, lipophilicity, metabolic stability, and bioavailability.[1] Among the various established fluoroalkyl groups, trifluoromethylthio group (SCF_3) is of current interest in agrochemicals and pharmaceuticals due to its remarkable properties. Particularly, 'SCF_3' group has highest lipophilicity value (π_x = 1.44) that helps permeation across biological membranes, high stability, and electronegativity.[2] In addition, properties of the molecules could be altered through simple oxidation of 'SCF_3', which is highly useful in the rational design of drug candidates.

Recently, various methodologies have been developed for the trifluoromethylthiolation of organic molecules through nucleophilic,[3] electrophilic or radical strategies.[4] Among them, electrophilic strategy gained significant attention, especially in the development of new electrophilic trifluoromethylthiolating reagent. The known reagents include Munavalli,[5] Billard,[6] Shen,[7] Shibata[8] and other.[9] Most of these reagents were synthesized from $AgSCF_3$ and corresponding electrophilic partner. But the Billard's reagent is unique in this respect and are achieved from aniline, diethylaminosulfur trifluoride (DAST) and (trifluoromethyl)trimethylsilane (CF_3TMS), where DAST and CF_3TMS offer sulfur and trifluoromethyl moiety of 'SCF_3'.[6d]



Scheme 1. DAST & CF_3TMS as electrophilic trifluoromethylthiolating reagent with 'C'-nucleophile.

Interestingly, employing trifluoromethyl analog of DAST (DAST-CF_3) as an electrophilic reagent, very recently Shibata and co-workers demonstrated the successive C–C bond cleavage followed by fluorination and trifluoromethylthiolation of *β*-ketoesters.[10] Employing the same reagent, they have also established the electrophilic trifluoromethylthiolation of *β*-ketoesters.[11] Inspired

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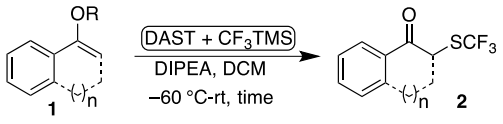
by these studies and our interest in the development of a method for the introduction of the fluorinated moiety,[12] we herein disclose a general and direct electrophilic trifluoromethylthiolation of carbon-based nucleophiles employing the combination of DAST and CF_3TMS, avoiding the synthesis of trifluoromethylthiolating reagent.

Results and Discussion

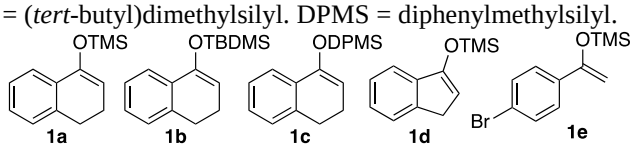
To begin with, trifluoromethylthiolation of various carbon-based nucleophiles have been tested using DAST and CF_3TMS in the presence of diisopropylethylamine (DIPEA) in dichloromethane (DCM) at –60 °C. Among them, tetralone derived trimethylsilylenol ether (TMSEE) **1a** showed the promising result with the formation of α-trifluoromethylthiolated tetralone **2a** in 35% yield, based on ^{19}F NMR (see supporting information and Table 1). Subsequently, various structurally different silylenol ether (**1b-1e**) were synthesized and treated with DAST and CF_3TMS. Unfortunately, all of them failed to provide the expected product, which suggested that the stability, reactivity, and conformation of silylenol ether is highly important for the successful trifluoromethylthiolation (Table 1, entry 2). Next, increasing the equivalents of **1a** afforded only the comparable yield (Table 1, entry 3). On the other hand, increasing the equivalents of either DAST, CF_3TMS or DIPEA decreased the yield of **2a** (Table 1, entries 4-6).

Table 1. Trifluoromethylthiolation of silylenol ethers with DAST and CF_3TMS: Optimization.[a)]

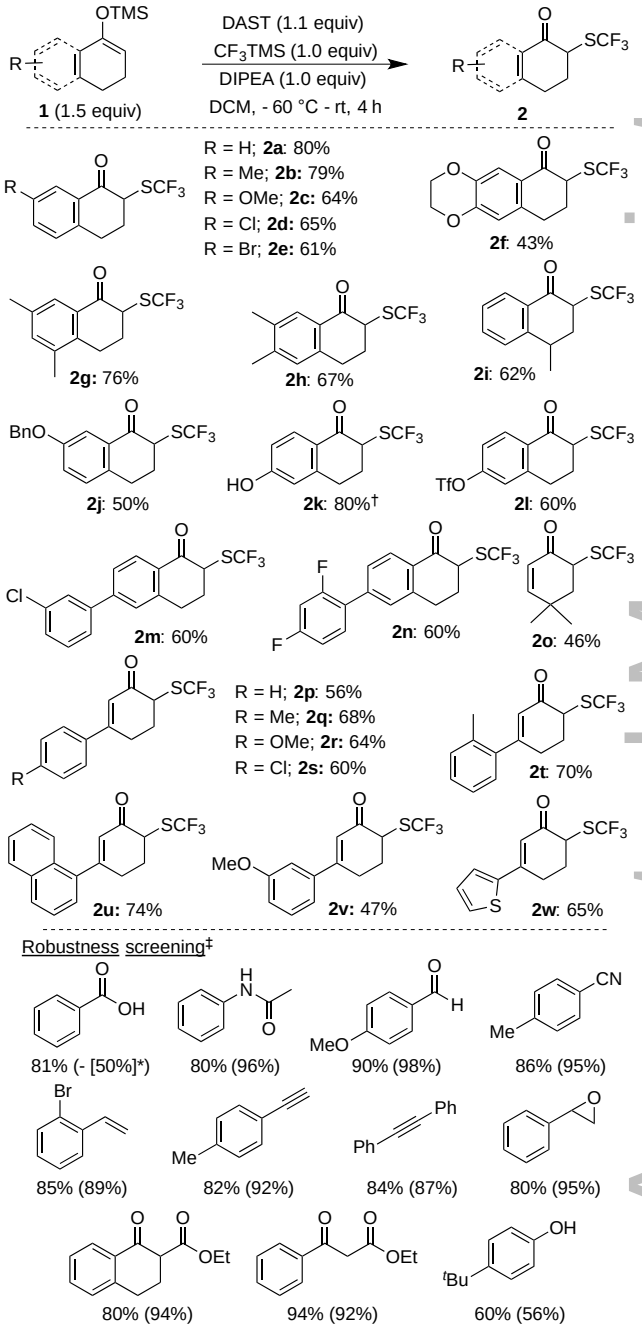


Entry	Conditions	Yield(%)[b)]
1	Standard conditions with **1a**	35
2	**1b-e** instead of **1a**	-
3	With 2 equiv. of **1a**	40
4	With 2.2 equiv. of DAST	20
5	With 2 equiv. of CF_3TMS	28
6	With 2 equiv. of DIPEA	28
7	Addition of 0.5 equiv. of aniline	50
8	Rapid addition of 1.5 equiv. of **1a**	84 (80)[c)]

[a)] Reaction conditions: **1** (0.69 mmol, 1 equiv.), DAST (0.76 mmol, 1.1 equiv.), CF_3TMS (0.69 mmol, 1 equiv.) DIPEA (0.69 mmol, 1 equiv.), DCM (0.23 M), –60 °C to rt. [b)] Yield based on ^{19}F NMR (hexafluorobenzene used as reference). [c)] Isolated yield. TMS = trimethylsilyl. TBDMS = (*tert*-butyl)dimethylsilyl. DPMS = diphenylmethylsilyl.



Similar results were observed when the initial reaction temperature was raised above –60 °C. When the reaction was performed in the presence of aniline, expecting an in-situ generation of Billard's reagent and subsequent trapping, afforded the product **1a** in 54% yield (Table 1, entry 7). Finally, it was realized that the concentration of DCM solution of **1a**, as well as the mode of addition, have an important role in the present reaction. Thus, the faster addition of 1.0 M solution of **1a** in DCM furnished the product **2a** in 86% ^{19}F NMR yield and 80% isolated yield (Table 1, entry 8).



Scheme 2. Trifluoromethylthiolation of silylenol ethers **1** with DAST and CF_3TMS: Scope and limitations. All are isolated yields. †Corresponding TMS ether was used as starting material. ‡ Reactions were performed with **1a** under the optimized conditions with the equimolar amount of additives. All are yield of **2a** and yield in parenthesis are

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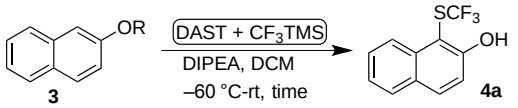
the recovered functionalized compounds. * Yield of *N*,*N*-diethylbenzamide.

With the best-optimized conditions in hand, the generality of the trifluoromethylthiolation of TMSEE was investigated. As can be seen in Scheme 2, structurally and functionally different TMSEE derived from tetralone were tested under the optimized conditions. For instance, alkyl substitution at the various position of tetralone TMSEE gave the product **2b**, **2g,** and **2h** in good yield. The racemic 4-methyl tetralone TMSEE provided the α-trifluoromethylthiolated product **2i** in 62% as a mixture of diastereomer in 1:1 ratio. Similarly, electron-donating alkoxy substituted α-trifluoromethylthiolated tetralone **2c**, **2f** and **2j** were achieved in good yield. Interestingly, electron withdrawing trifluoromethylsulfonyloxy and functionalizable halo substituted tetralone TMSEE also furnished the corresponding products **2l** and **2d**, **2e**, **2m**, **2n**, respectively. Subsequently, to extent the present scope, simple cyclohexenone derived TMSEE were subjected under the present optimized conditions. Gratifyingly, TMSEE derived from 4,4-dimethylcyclohexenone afforded the product **2o** in 46% yield. Having seen the promising result, various 3-aryl substituted cyclohexeone derived TMSEE were examined. All of them furnished the corresponding α-trifluoromethylthiolated product **2p**-**2v** in 56-74% yield. Furthermore, 3-thiophen-2-yl substituted cyclohexeone also gave the product **2w** in 65% yield.

After successful demonstration of generality and scope, we directed our attention to validate the robustness of the present trifluoromethylthiolation with respect to various reactive functional groups employing the ingenious method developed by Glorius and co-workers.[13] Thus, the trifluoromethylthiolation of **1a** with DAST and CF_3TMS was carried out in the presence of an equimolar amount of a number of potentially competing nucleophiles as additives under the optimized conditions (Scheme 2). Interestingly, no competing side reaction was observed with any of these nucleophiles, most importantly, the reactive β-keto esters showed high compatibility under the reaction conditions. In all the cases, expected product **2a** was also observed in comparable yield and most of the additives were recovered in high yield, except the carboxylic acid that reactivity with byproduct and converted to the corresponding amide. However, the presence of *tert*-butylphenol significantly affected the reaction and let to the trifluoromethylthiolation of **1a** in 60% yield and a detectable amount of trifluoromethylthiolation of phenol was observed. These studies demonstrated the robustness of the developed trifluoromethylthiolation towards various functional groups and possible application to complex silylenolether.

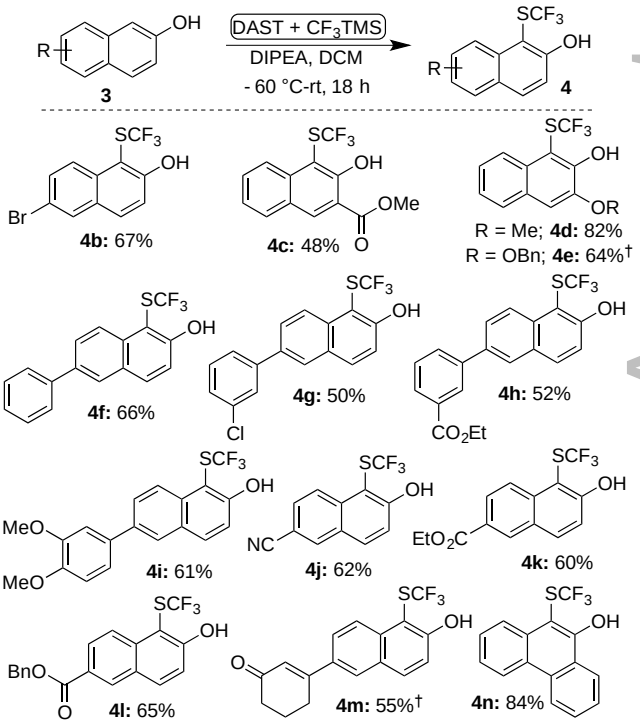
The involvement of phenol in robustness screening and our initial studies with different nucleophiles directed us to investigate the trifluoromethylthiolation of reactive phenol, such as β-naphthol, with DAST and CF_3TMS. Thus, the treatment of β-naphthol **3a** under the optimized conditions afforded the α-trifluoromethylthiolated β-naphthol **4a** in 20% yield (Table 2). Mimicking the TMSEE substrate, trimethylsilyl-protected β-naphthol **3b** was subjected under the optimized conditions, which also gave **4a** in 22%, even at prolonged reaction time (18 h). Subsequently, increasing the amount of **3b** to 5 equivalents afforded the corresponding product **4a** in 70% yield in 4 h. Interestingly, use of 5 equivalents of β-naphthol **3a** also furnished the product **4a** in 67% yield, but after 18 h. On the other hand, β-naphthol methyl ether did not afford the expected product. Since trifluoromethylthiolation of trimethylsilyl-protected β-naphthol derivative requires an addition step for its synthesis, the scope and generality of the method were investigated with unprotected β-naphthol derivatives.

Table 2. Trifluoromethylthiolation of β-naphthols with DAST and CF_3TMS: Optimization.[a)]



R (**3**, equiv.)	Time (h)	Yield (%)[b)]	R (**3**, equiv.)	Time (h)	Yield (%)[b)]
H (**3a**, 1)	4	20	TMS (**3b**, 5)	4	70
TMS (**3b**, 1)	18	22	H (**3a**, 5)	18	67 (30)[c)]

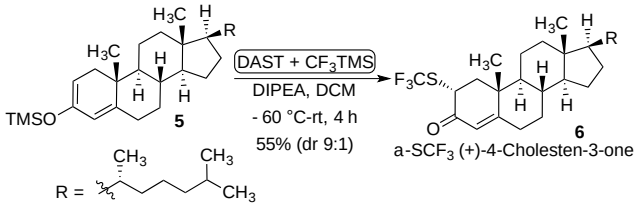
[a)] Reaction conditions: **3** (equiv.), DAST (0.76 mmol, 1.1 equiv.), CF_3TMS (0.69 mmol, 1 equiv.) DIPEA (0.69 mmol, 1 equiv.), DCM (0.23 M), –60 °C to rt. [b)] Yield based on ^{19}F NMR (hexafluorobenzene used as reference). [c)] 4 h.



Scheme 3. Trifluoromethylthiolation of *β*-naphthols **3** with DAST and CF_3TMS: Scope and limitations. All are isolated yields. † Yield based on ^1H NMR.

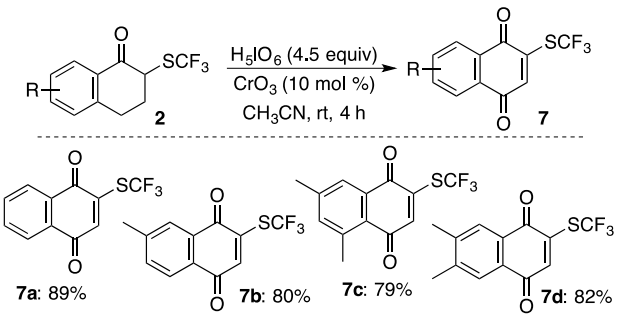
Simple bromo and phenyl at the 6th position of *β*-naphthol gave the products **4b** and **4f** in 67 and 66% yield (Scheme 3). Similarly, 3-chloro, 3-ethoxycarbonyl, 3,4-dimethoxy substituted phenyl containing *β*-naphthol also furnished the product **4g-4i** in good yield. Both electron-withdrawing methoxycarbonyl and electron donating alkoxy substitution at 3rd position of *β*-naphthols were well tolerated and afforded the corresponding product **4c**, **4d** and **4e** in 48, 82 and 64% yield. Electron-deficient, 6-cyano, 6-ethoxycarbonyl, and 6-benzyloxycarbonyl substituted *β*-naphthols also underwent smooth reaction to furnish the corresponding product **4j-4l** in good yield. Interestingly, active methylene containing cyclohexenyl-substituted *β*-naphthols gave the product **4m** in 55% yield. In addition to *β*-naphthols, polycyclic phenol like phenanthren-9-ol also afforded 10-(trifluoromethylthio)-phenanthren-9-ol **4n** in 84% yield.

Having successfully demonstrated the trifluoromethyl-thiolation of TMSEE and *β*-naphthol, the potential of the methodology was studied employing biologically important molecule like (+)-4-cholesten-3-one. Thus, the reaction of trimethylsilylenol ether of (+)-4-cholesten-3-one **5** with DAST and CF_3TMS in the presence of DIPEA in DCM at –60 °C afforded the corresponding product **6** in 55% yield as a diastereomeric mixture in 9:1 ratio, demonstrating the potency of the developed transformation (Scheme 4).



Scheme 4. Trifluoromethylthiolation of **5**.

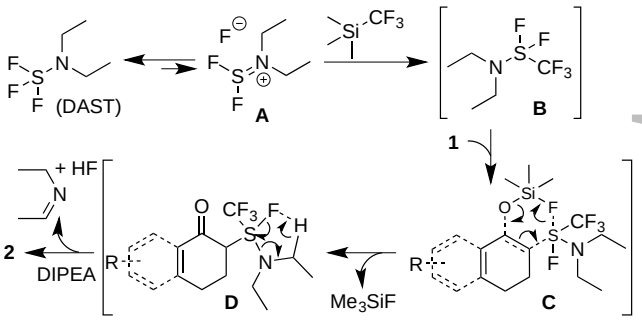
Subsequently, conversion of *α*-trifluoromethylthiolated tetralones **2** to *α*-trifluoromethylthiolated naphthoquinones **7** was envisioned, since quinones play a major role in various biological processes, as well as in drug discovery.[14] For instance, 2-trifluoromethyl-1,4-naphthoquinones have exhibited an antimalarial activity.[15]



Scheme 5. Synthesis of *α*-trifluoromethylthiolated naphthoquinone **7**.

Thus, oxidation of **2a** with periodic acid (H_5IO_6) in the presence of catalytic amount of CrO_3 in acetonitrile at room temperature gave the naphthoquinone derivative **7a** in 89% yield and no oxidation of sulfur was observed.[16] This selective oxidation was subsequently applied for the synthesis of substituted *α*-trifluoromethylthiolated naphthoquinones **7b-7d** in excellent yield.

Based on the above observation and literature precedent, we postulate the following mechanism for the trifluoromethylation of nucleophiles with DAST and CF_3TMS. DAST is known to exist in equilibrium with the isomeric form **A**, which on reaction with CF_3TMS would afford the intermediate **B** (Scheme 6). Reaction of formed **B** with reactive TMSEE **1** might furnish the intermediate **D** *via* the possible transition state **C**. Finally, base promoted reductive fragmentation of **D** would give the expected product **2**. Similar pathway could be anticipated for trifluoromethylthiolation of *β*-naphthols **3**.



Scheme 6. Plausible mechanism.

Conclusion

In conclusion, we have successfully developed an efficient and general trifluoromethylthiolation of silylenol ethers derived from tetralones and cyclohexenone as well as *β*-naphthols employing a combination of DAST and CF_3TMS as a source of the electrophilic trifluoromethylthio group. These reactions work well with various highly functionalized molecules and allow the synthesis of *α*-trifluoromethylthiolated carbonyls and naphthols in good yields. Additionally, robustness screening also

demonstrated excellent tolerance of the present reaction to various nucleophiles. Potential of the developed methodology was further demonstrated through the synthesis of biologically important *α*-trifluoromethylthoilated (+)-4-cholesten-3-one and naphthoquinone.

Experimental Section

General procedure for the synthesis of trimethylsilylenol ether 1: To the solution of carbonyl compound (3 mmol, 1 equiv.) in dry DCM (0.25 M) at 0 °C, triethylamine (6 mmol, 2 equiv.) was added dropwise over few minutes. Subsequently, trimethylsilyl trifluoromethanesulfonate (TMSOTf, 3.6 mmol, 1.2 equiv.) was introduced and the reaction mixture was stirred for 45 min at the temperature range of 0 to 10 °C. Next, the reaction mixture was concentrated under reduced pressure at 40 °C and the obtained crude product was purified by flash column chromatography using ethylacetate/hexane as an eluent to afford the corresponding silylenol ether **1**. All the characterization data (^{1}H &^{13}C NMR) were in good agreement with literature report.[17]

General procedure for the trifluoromethylthiolation of 1 to 2: A flame-dried Schlenk tube was successively charged with DIPEA (0.69 mmol) and anhydrous dichloromethane (2 mL) under the nitrogen atmosphere. The resulting mixture was cooled to –60 °C and DAST (0.76 mmol) was added followed by CF_3TMS (0.69 mmol) was introduced in 10 min intervals. After 1 hour at –60 °C, the solution of **1** (0.69 mmol) in DCM (1 M) was added in one shot at –60 °C. The reaction mixture was then warmed to room temperature over 4 h and diluted with 50 mL of DCM, followed by washing with 6% aq. $NaHCO_3$ and water. The combined organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. The crude mixture was purified by column chromatography over Silica gel using ethylacetate/hexane mixture as eluent to afford the corresponding *α*-trifluoromethylthiolated product **2**.

General procedure for the trifluoromethylthiolation of 3 to 4: A flame-dried Schlenk tube was successively charged with DIPEA (0.69 mmol) and anhydrous dichloromethane (2 mL) under nitrogen atmosphere. The resulting mixture was cooled to –60 °C and DAST (0.76 mmol) was added followed by CF_3TMS (0.69 mmol) was introduced in 10 min intervals. After 1 hour at –60 °C, the solution of *β*-naphthols **3** (3.45 mmol) in DCM (3.4 M) was added in one shot at –60 °C. The reaction mixture was then warmed to room temperature over 18 h and diluted with 50 mL of DCM, washed with 6% aq. $NaHCO_3$ followed by water. The combined organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography over Silica gel using ethylacetate /hexane mixture as eluent to afford the corresponding *α*-trifluoromethylthiolated *β*-naphthol **4**.

General procedure for the synthesis of 7: To the mixture of compound **2** (3.0 mmol) and H_5IO_6 (13.5 mmol), the solution of CrO_3 (0.3 mmol, 10 mol%) in acetonitrile was added under argon atmosphere over 20 min. The resultant reaction mixture was stirred for 4 h at room temperature. The mixture was diluted with water followed by extracted with diethyl ether. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by column chromatography over Silica gel using ethylacetate/hexane as eluent to furnish the compound **7**.

Acknowledgments

We acknowledge Indian Institute of Technology Madras (Project No. CHY/16-17/840/RFIR/ANBA) for financial support. P.S. thanks CSIR, New Delhi for a fellowship.

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10.1002/adsc.201800366

FULL PAPER

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