Synthetic Communications®, 37: 1747–1756, 2007
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ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910701266182

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Regioselective Synthesis of *2H*-Benzothiopyrano[3,2-*c*]quinolin-7(8*H*)-ones by Tri-*n*-butyltinhydride–Mediated Radical Cyclization

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Abstract: A number of hitherto unreported *2H*-benzothiopyrano[3,2-*c*]quinolin-7(8*H*)-ones have been regioselectively synthesized in 90–96% yield by tri-*n*-butyltinhydride–AIBN–mediated radical cyclization from 4-(2′-bromothioarylmethyl)-1-methylquinolin-2(1*H*)-ones and their corresponding sulfones. 4-(2′-Bromothioarylmethyl)quinolin-2(1*H*)-ones were in turn prepared from 4-bromomethylquinolin-2(1*H*)-one and *o*-bromothiophenols by refluxing in acetone in the presence of anhydrous K_2CO_3. These were converted to the corresponding sulfones by oxidation with two equivalents of *m*-CPBA in refluxing dichloromethane for 1 h.

Keywords: 4-bromomethyl-1-methylquinolin-2(1*H*)-one, 6-*endo-trig*, organotin reagent, radical cyclization, sulfur heterocycles

INTRODUCTION

Organic synthesis has benefitted enormously from reactions involving internal addition of a radical center to a double bond. In particular, cyclization of 5-hexenyl radicals represents a process that, over the years, has provided access to a large number of complex substances.[1] Contrary to predictions based on thermodynamic criteria, cyclization of 5-hexenyl systems generally gives cyclopentyl methyl radical via a prominent 5-*exo* mode of closure[1c,2] and not the more stable cyclohexyl radical via 6-*endo* cyclization,

Received October 16, 2006
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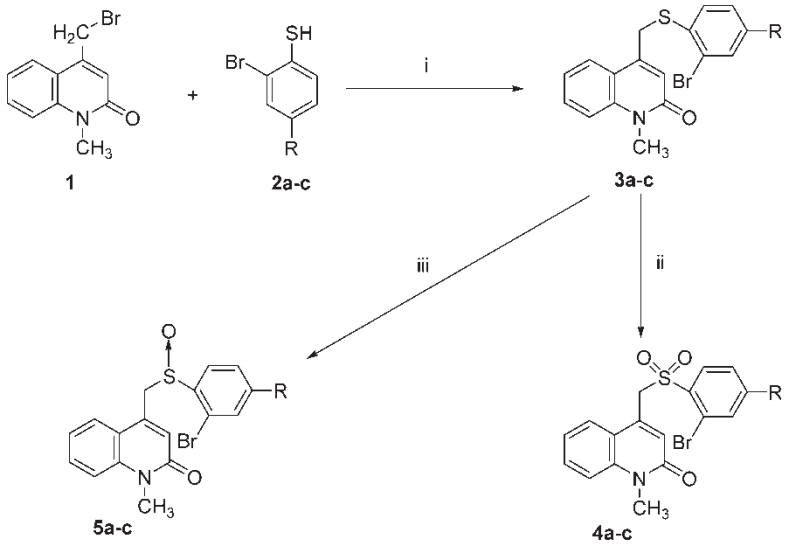
a feature that has been rationalized[3] in terms of stereoelectronic control of the reaction. Nevertheless, for stabilized radicals, the regiochemistry of ring closure of 5-hexenyl radicals is reversed.[4]

Ring closure of hexenyl systems containing first-row atoms such as oxygen and nitrogen have been studied intensively. However, a literature search revealed only a few examples of the synthesis of sulfur-based heterocycles via radical methods.[5] We recently reported the cyclization of 4-(2′-bromoaryloxymethyl)-1-methylquinolin-2(1*H*)-ones by $^{n}Bu_3SnH-AIBN$, where a 5-*exo* ring closure took place to give the *spiro* heterocyclic compound.[6] We thus directed our attention to an analogous study of sulfur-based heterocycle. Our objective was to examine, first, the effect of longer C-S bonds for the cyclization of sulfides, sulfones, and sulfoxides, and second, how the presence of these groups might influence the regiochemistry of ring closure. Ultimately, we were keen to determine whether this study may lead to a viable procedure for the efficient synthesis of heterocyclic compounds.

RESULTS AND DISCUSSION

The starting materials, 4-(2′-bromothioarylmethyl)-1-methylquinolin-2(1*H*)-ones **3** (X = S), were prepared in 92–95% yield from 4-bromomethyl-1-methylquinolin-2(1*H*)-one **1** and *o*-bromothiols **2a–c** in refluxing acetone for 8 h in the presence of anhydrous potassium carbonate and sodium iodide. The corresponding sulfones **4** ($X = SO_2$) were synthesized from the sulphides **3** by oxidizing with 2 equivalents of *m*-chloroperoxybenzoic acid (*m*-CPBA) in refluxing dichloromethane for 1 h (Scheme 1). Compounds **3** and **4** were characterized from their elemental analysis and spectroscopic data. The two-proton singlet due to -SC$\mathbf{H_2}$ protons of **3a** at δ 4.21 was shifted by 0.67 ppm downfield in **4a**. The substrate **3a** was refluxed in dry degassed toluene at 80°C under a nitrogen atmosphere with $^{n}Bu_3SnH$ in the presence of AIBN for 1 h to give the cyclic product **6a** (X = S) in 90% yield. Exposure of the sulfone **4a** to $^{n}Bu_3SnH$ under the same reaction condition as described previously afforded the cyclized sulfone **6d** ($X = SO_2$) in 95% yield (Scheme 2).

The structures of the compounds **6** (X = S, SO_2) were readily elucidated from ^{1}H NMR spectroscopy. Compound **6a** (X = S) exhibited a one-proton multiplet at δ 3.42–3.46 and another one-proton doublet at δ 3.89 ($J = 4.5$ Hz) due to ring junction protons H_c and H_d respectively, whereas the corresponding two protons in **6d** ($X = SO_2$) exhibited a multiplet at δ 4.15–4.19 and a doublet at δ 4.03 ($J = 5$ Hz). The stereochemistry of the ring fusion of the cyclic product can be surmised from the molecular model (Dreiding model), which showed a strain-free *cis* rearrangement and also from the small coupling constant values of the ring juncture protons of **6a** (X = S, $J = 4.5$ Hz) and **6d** ($X = SO_2$, $J = 5$ Hz). The ^{13}C NMR spectrum

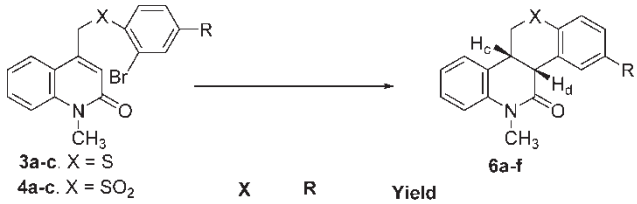


	R	Yield (Compound 3)	Yield (Compound 4)
a	Me	94%	95%
b	Et	92%	94%
c	H	95%	95%

Scheme 1. Reagents and conditions: i) acetone, K_2CO_3, NaI, reflux, 8 h; ii) *m*-CPBA (2 equiv.), CH_2Cl_2, reflux, 1 h; iii) *m*-CPBA (1 equiv.), CH_2Cl_2, stirring, 1 h, 0–5°C.

of **6a**,**d** (X = S, SO_2) also supported the proposed structure. The ^{13}C NMR chemical shifts as well as the multiplicity of compound **6a**,**d** were established by DEPT experiment. There are twelve protonated carbons, two CH_3, one CH_2, and nine CH moieties. The mass spectra of compounds **6a** and **6d** showed molecular ion peaks at m/z 295 and 327 (M^+) respectively. All these experiments clearly indicate that a 6-*endo* cyclization has taken place. To test the generality of the reaction, substrates **3b**,**c** and **4b**,**c** were also treated similarly with $^nBu_3SnH$ and AIBN to give exclusively the 6-*endo* cyclized product in 90–96% yield (Scheme 2).

We have also attempted to extend the radical cyclization reaction to the sulphoxides **5a**–**c** as well. Sulfoxides were prepared from the corresponding sulfides by slow addition of *m*-CPBA at 0–5°C in dichloromethane over 1 h. The formation of the sulfoxide was indicated by the disappearance of starting material and appearance of a highly polar spot on thin-layer chromatography (TLC). The sulphoxides were found to be unstable during workup.



3a-c. X = S
4a-c. X = SO_2

6a-f

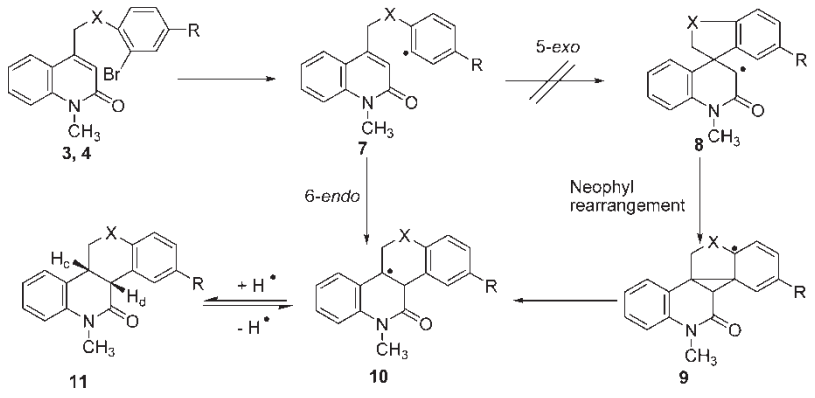
	X	R	Yield
6a	S	Me	90%
b	S	Et	92%
c	S	H	91%
d	SO_2	Me	95%
e	SO_2	Et	96%
f	SO_2	H	95%

Scheme 2. Reagents and conditions: $^{n}Bu_3SnH$, toluene, 80°C, N_2 atm, 1 h.

Therefore, no effort was made to characterize them. Dichloromethane was removed under reduced pressure, and radical reaction under conditions described previously was attempted. The starting materials, however, decomposed, and no cyclized product was obtained.

The formation of a six-membered sulfur heterocyclic ring can be explained by the addition of a hydrogen radical to the intermediate radical **10**, which in turn is formed from the aryl radical **7** by a 6-*endo* ring closure. An alternative route, via 5-*exo* ring closure to generate the *spiro* heterocyclic radical[7] **8** with a subsequent neophyl rearrangement,[8] has also been considered (Scheme 3).

However, the 5-*exo* cyclization to form the *spiro* heterocyclic radical **8** followed by a neophyl rearrangement is highly unlikely with the systems studied at present. It is known that β-fragmentation of alkyl thiyl radicals are very fast[9] ($>10^8\ s^{-1}$) compared to neophyl-type rearrangements, which are much slower[10] (about $10^3\ s^{-1}$–$10^4\ s^{-1}$). Therefore, neophyl rearrangement of radical **8** cannot compete with the β-fragmentation reaction, which would lead to another product. The other reason is that the intermediate tertiary radical **10** is more stable than the *spiro* heterocyclic secondary radical **8**. The stabilized conformational intermediate radical **10** gave preferably *cis*, the usual reduced product, and the dihydro heterocyclic ring is isolated in good yield. All the starting materials regioselectively gave the reduced six-membered heterocyclic ring by $^{n}Bu_3SnH$–mediated cyclization. The methodology described here is mild and interesting for its simplicity.



Scheme 3.

EXPERIMENTAL

Melting points were determined in an open capillary and are uncorrected. IR spectra were recorded on a Perkin-Elmer L 120-000A spectrometer (ν_{max} in cm^{-1}) using samples as neat liquids, and solid samples were recorded on KBr disks. UV absorption spectra were recorded in EtOH on a Shimadzu UV-2401PC spectrophotometer (λ_{max} in nm). ^1H NMR (400 MHz, 500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker DPX-400 and Bruker DPX-500 spectrometer in $CDCl_3$ (chemical shift in δ) with TMS as internal standard. Elemental analyses and mass spectra were recorded on a Leco 932 CHNS anlyser and on a Jeol JMS-600 instrument respectively. Silica gel [(60–120 mesh), Spectrochem, India] was used for chromatographic separation. Silica gel G [E-Merck (India)] was used for TLC. Petroleum ether refers to the fraction boiling between 60 and 80°C.

General Procedure for the Preparation of 3a–c

A mixture of 4-bromomethyl-*N*-methylquinolone (**1**, 5 mmol), 2-bromothiols (**2a–f**, 5 mmol), anhydrous potassium carbonate (5 g), and sodium iodide (20 mg) was heated under reflux in dry acetone (125 mL) for 8 h. The reaction mixture was cooled, filtered, and concentrated. The residual mass was extracted with CH_2Cl_2 (3 × 50 mL), washed with 10% Na_2CO_3 solution (2 × 25 mL) and brine (3 × 50 mL), and dried (Na_2SO_4). The residual mass after removal of solvent was subjected to column chromatography on silica gel using petroleum ether–EtOAc (7:3) as eluant to give compounds **3a–c**, which were recrystallized from $CHCl_3$–petroleum ether.

Data

Compound **(3a)**

Yield 94%, white solid, mp 108–110°C; IR (KBr) υ_{max}: 2921, 2850, 1654, 746 cm^{-1}; UV (EtOH) λ_{max}: 208, 333 nm; ^1H NMR (400 MHz, $CDCl_3$): δ_H 2.28 (s, 3H, ArC**H**$_3$), 3.71 (s, 3H, NC**H**$_3$), 4.21 (s, 2H, SC**H**$_2$), 6.59 (s, 1H, =C**H**), 6.97–7.90 (m, 7H, Ar**H**); MS (m/z): 373, 375 (M^+). Anal. calcd. for $C_{18}H_{16}BrNOS$: C, 57.76; H, 4.31; N, 3.74%. Found: C, 57.48; H, 4.35; N, 3.82%.

Compound **(3b)**

Yield 92%, white solid, mp 99–101°C; IR (KBr) υ_{max}: 2925, 1651, 747 cm^{-1}; UV (EtOH) λ_{max}: 214, 229, 334 nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.21 (t, $J = 7.5$ Hz, 3H, $ArCH_2C\mathbf{H}_3$), 2.59 (q, $J = 7.5$ Hz, 2H, $ArC\mathbf{H}_2CH_3$), 3.72 (s, 3H, NC**H**$_3$), 4.24 (s, 2H, SC**H**$_2$), 6.57 (s, 1H, =C**H**), 7.03–7.97 (m, 7H, Ar**H**); MS (m/z): 387, 389 (M^+). Anal. calcd. for $C_{19}H_{18}BrNOS$: C, 58.77; H, 4.67; N, 3.61%. Found: C, 59.06; H, 4.69; N, 3.27%.

Compound **(3c)**

Yield 95%, white solid, mp 98–100°C; IR (KBr) υ_{max}: 2922, 2851, 1639, 743 cm^{-1}; UV (EtOH) λ_{max}: 214, 333 nm; ^1H NMR (400 MHz, $CDCl_3$): δ_H 3.74 (s, 3H, NC**H**$_3$), 4.29 (s, 2H, SC**H**$_2$), 6.73 (s, 1H, =C**H**), 7.10–7.91 (m, 8H, Ar**H**); MS (m/z): 359, 361 (M^+). Anal. calcd. for $C_{17}H_{14}BrNOS$: C, 56.68; H, 3.92; N, 3.89%. Found: C, 56.99; H, 3.87; N, 4.03%.

General Procedure for the Preparation of 4a–c

The sulfide (**3a–c**, 5 mmol) and *m*-CPBA (10 mmol) were refluxed in CH_2Cl_2 (125 mL) for 1 h. The reaction mixture was cooled and washed with saturated sodium bicarbonate solution, water, and finally brine. The CH_2Cl_2 extract was then dried over anhydrous Na_2SO_4. The residual mass after removal of solvent was subjected to column chromatography over silica gel using petroleum ether–EtOAc (1:1) as eluant to give compounds **4a–c**, which were recrystallized from $CHCl_3$–petroleum ether.

Data

Compound **(4a)**

Yield 95%, white solid, mp 147–149°C; IR (KBr) υ_{max}: 2920, 1650, 1587, 752 cm^{-1}; UV (EtOH) λ_{max}: 212, 228, 279, 336 nm; ^1H NMR (500 MHz,

$CDCl_3$): δ_H 2.41 (s, 3H, ArC**H**$_3$), 3.68 (s, 3H, NC**H**$_3$), 4.88 (s, 2H, SO_2C**H**$_2$), 6.43 (s, 1H, =C**H**), 7.18–7.97 (m, 7H, Ar**H**); MS (m/z): 405, 407 (M^+). Anal. calcd. for $C_{18}H_{16}BrNO_3S$: C, 53.21; H, 3.97; N, 3.45%. Found: C, 53.49; H, 3.86; N, 3.51%.

Compound **(4b)**

Yield 94%, white solid, mp 148–150°C; IR (KBr) υ_{max}: 2928, 1646, 1588, 1319, 1154, 750 cm^{-1}; UV (EtOH) λ_{max}: 231, 279, 340 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.23 (t, $J = 7.5$ Hz, 3H, ArCH$_2$C**H**$_3$), 2.66 (q, $J = 7.5$ Hz, 2H, ArC**H**$_2$CH$_3$), 3.68 (s, 3H, NC**H**$_3$), 4.88 (s, 2H, SO_2C**H**$_2$), 6.46 (s, 1H, =C**H**), 7.20–7.95 (m, 7H, Ar**H**); MS (m/z): 419, 421 (M^+). Anal. calcd. for $C_{19}H_{18}BrNO_3S$: C, 54.29; H, 4.32; N, 3.33%. Found: C, 54.60; H, 4.20; N, 3.30%.

Compound **(4c)**

Yield 95%, white solid, mp 194–196°C; IR (KBr) υ_{max}: 2922, 1642, 1584, 743 cm^{-1}; UV (EtOH) λ_{max}: 206, 347, 343, 278 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.68 (s, 3H, NC**H**$_3$), 4.91 (s, 2H, SO_2C**H**$_2$), 6.46 (s, 1H, =C**H**), 7.30–7.95 (m, 8H, Ar**H**); MS (m/z): 391, 393 (M^+). Anal. calcd. for $C_{17}H_{14}BrNO_3S$: C, 52.05; H, 3.60; N, 3.57%. Found: C, 52.30; H, 3.47; N, 3.61%.

General Procedure for the Preparation of 6a–f

Tributyltin hydride (1.1 mmol) was added to a stirred solution of **3a–c** and **4a–c** (1 mmol) and azobisisobutyronitrile (0.5 mmol) in dry degassed toluene at 80°C (5 mL) under nitrogen. The mixture was heated under reflux for 1 h and concentrated. The residue was dissolved in ether (10 mL) and stirred with a 10% aq. potassium fluoride solution (10 mL) for 45 min. The white precipitate was filtered, and the aqueous phase extracted with ether (10 mL). The combined ether extract was washed with brine and dried over anhydrous Na_2SO_4. The residual mass after the removal of solvent was subjected to column chromatography using petroleum ether–ethyl acetate (9:1) and (7:3) as eluant to give cyclized product **6a–c** and **6d–f** respectively.

Data

Compound **(6a)**

Yield: 90%, viscous liquid; IR (neat) υ_{max}: 2922, 2851, 1666, 758 cm^{-1}; UV (EtOH) λ_{max}: 211, 248 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 2.29 (s, 3H,

ArC**H**$_3$), 2.83 (dd, $J = 12.8$, 3.4 Hz, 1H, SC**H**$_2$), 3.14 (t, $J = 12.3$ Hz, 1H, SC**H**$_2$), 3.40 (s, 3H, NC**H**$_3$), 3.42–3.46 (m, 1H, C**H**$_c$), 3.89 (d, $J = 4.5$ Hz, 1H, C**H**$_d$), 6.96–7.36 (m, 7H, Ar**H**); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 20.84 (Ar**C**H$_3$), 27.76 (**C**HCH$_2$), 30.07 (N**C**H$_3$), 36.35 (S**C**H$_2$), 45.55 (**C**HCO), 115.13 (Ar**C**H), 123.43 (Ar**C**H), 125.91 (Ar**C**H), 127.80 (Ar**C**H), 127.87 (Ar**C**H), 127.92 (Ar**C**H), 128.16 (Ar**C**H), 128.52 (Ar**C**), 128.94 (Ar**C**), 133.33 (Ar**C**), 133.80 (Ar**C**), 139.23 (Ar**C**), 169.10 (**C**O); MS (m/z): 295 (M^+). Anal. calcd. for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74%. Found: C, 72.90; H, 5.86; N, 4.61%.

Compound **(6b)**

Yield 92%, viscous liquid; IR (neat) υ_{max}: 2925, 2870, 1674, 754 cm^{-1}; UV (EtOH) λ_{max}: 217, 249 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.22 (t, $J = 7.5$ Hz, 3H, ArCH$_2$C**H**$_3$), 2.60 (q, $J = 7.5$ Hz, 2H, ArC**H**$_2$CH$_3$), 2.86 (dd, $J = 12.8$, 3.4 Hz, 1H, SC**H**$_2$), 3.17 (t, $J = 12.3$ Hz, 1H, SC**H**$_2$), 3.42 (s, 3H, NC**H**$_3$), 3.46–3.49 (m, 1H, C**H**$_c$), 3.94 (d, $J = 4.5$ Hz, 1H, C**H**$_d$), 7.00–7.37 (m, 7H, Ar**H**); MS (m/z): 309 (M^+). Anal. calcd. for $C_{19}H_{19}NOS$: C, 73.75; H, 6.19; N, 4.53%. Found: C, 73.56; H, 6.21; N, 4.69%.

Compound **(6c)**

Yield 91%, viscous liquid; IR (neat) υ_{max}: 2922, 2851, 1666, 758 cm^{-1}; UV (EtOH) λ_{max}: 211, 245 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 2.85 (dd, $J = 12.8$, 3.4 Hz, 1H, SC**H**$_2$), 3.16 (t, $J = 12.3$ Hz, 1H, SC**H**$_2$), 3.40 (s, 3H, NC**H**$_3$), 3.46–3.48 (m, 1H, C**H**$_c$), 3.94 (d, $J = 4.5$ Hz, 1H, C**H**$_d$), 7.03–7.35 (m, 8H, Ar**H**); MS (m/z) 281 (M^+). Anal. calcd. for $C_{17}H_{15}NOS$: C, 72.57; H, 5.37; N, 4.98%. Found: C, 72.82; H, 5.45; N, 4.95%.

Compound **(6d)**

Yield 95%, white solid, mp 214–216°C; IR (KBr) υ_{max}: 2921, 1671, 1601, 1274, 772 cm^{-1}; UV (EtOH) λ_{max}: 206, 254 nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 2.44 (s, 3H, ArC**H**$_3$), 3.29 (dd, $J = 13.8$, 2.4 Hz, 1H, SO$_2$C**H**$_2$), 3.42 (s, 3H, NC**H**$_3$), 3.51 (t, $J = 13.5$ Hz, 1H, SO$_2$C**H**$_2$), 4.03 (d, $J = 5$ Hz, 1H, C**H**$_d$), 4.15–4.19 (m, 1H, C**H**$_c$), 7.07–7.86 (m, 7H, Ar**H**); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.61 (Ar**C**H$_3$), 30.46 (N**C**H$_3$), 36.06 (**C**HCH$_2$), 45.29 (**C**HCO), 52.16 (SO$_2$**C**H$_2$), 115.54 (Ar**C**H), 123.39 (Ar**C**H), 124.20 (Ar**C**H), 124.81 (Ar**C**H), 127.89 (Ar**C**H), 129.52 (Ar**C**H), 130.26 (Ar**C**H), 131.17 (Ar**C**), 133.41 (Ar**C**), 135.51 (Ar**C**), 139.40 (Ar**C**), 142.66 (Ar**C**), 166.69 (Ar**C**O); MS (m/z): 327 (M^+). Anal. calcd. for $C_{18}H_{17}NO_3S$: C, 66.03; H, 5.23; N, 4.28%. Found: C, 66.27; H, 5.29; N, 4.31%.

Compound **(6e)**

Yield: 96%, white solid, mp 210–212°C; IR (KBr) υ_{max}: 2927, 1676, 1602, 1276, 758 cm^{-1}; UV (EtOH) λ_{max}: 207, 254 nm; ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.24 (t, $J = 7.5$ Hz, 3H, $ArCH_2C\mathbf{H}_3$), 2.70 (q, $J = 7.5$ Hz, 2H, $ArC\mathbf{H}_2CH_3$), 3.28 (dd, $J = 13.8$, 2.4 Hz, 1H, $SO_2C\mathbf{H}_2$), 3.41 (s, 3H, $NC\mathbf{H}_3$), 3.50 (t, $J = 13.5$ Hz, 1H, $SO_2C\mathbf{H}_2$), 4.04 (d, $J = 5$ Hz, 1H, $C\mathbf{H}_d$), 4.15–4.19 (m, 1H, $C\mathbf{H}_c$), 7.06–7.88 (m, 7H, Ar**H**); MS (m/z): 341 (M^+). Anal. calcd. for $C_{19}H_{19}NO_3S$: C, 66.84; H, 5.61; N, 4.10%. Found: C, 67.12; H, 5.24; N, 4.22%.

Compound **(6f)**

Yield 95%, white solid, mp 220–222°C; IR (KBr) υ_{max}: 2921, 1667, 1601, 1274, 763 cm^{-1}; UV (EtOH) λ_{max}: 209, 250 nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H 3.32 (dd, $J = 13.8$, 2.4 Hz, 1H, $SO_2C\mathbf{H}_2$), 3.42 (s, 3H, $NC\mathbf{H}_3$), 3.54 (t, $J = 13.5$ Hz, 1H, $SO_2C\mathbf{H}_2$), 4.09 (d, $J = 5$ Hz, 1H, $C\mathbf{H}_d$), 4.18–4.22 (m, 1H, $C\mathbf{H}_c$), 7.08–7.98 (m, 8H, Ar**H**); MS (m/z): 313 (M^+); Anal. calcd. for $C_{17}H_{15}NO_3S$: C, 65.16; H, 4.82; N, 4.47%. Found: C, 65.37; H, 4.86; N, 4.38%.

ACKNOWLEDGMENTS

N. Kundu is thankful to Council of Scientific and Industrial Research (CSIR) (New Delhi) for a senior research fellowship. We also thank Department of Science and Technology (DST) (New Delhi) for providing a UV-Vis spectrophotometer and FT-IR spectrometer under the Department of Science and Technology-Financial assistance for Infrastructural Development of Science and Technology (DST-FIST) program.

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