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Tandem cyclization: one pot regioselective synthesis of thieno[3,2-*c*]quinolin-4(5*H*)-one derivatives

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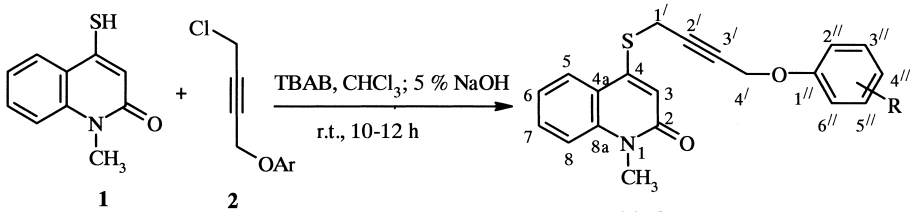
Abstract—A number of hitherto unreported 3-(aryloxyacetyl)-2,3-dihydro-5-alkylthieno[3,2-*c*]quinolin-4(5*H*)-ones are regioselectively synthesized in 80–90% yield from 4-(4′-aryloxybut-2′-ynyl)thioquinolin-2(1*H*)-ones by the oxidation with 1 equiv. of *m*-CPBA at 0–5°C for 1 h followed by heating under reflux in chloroform and subsequent treatment with 20% aqueous KOH. The substrate, sulfides were prepared by PTC alkylation of 4-mercaptoquinolin-2(1*H*)-one with 1-aryloxy-4-chlorobut-2-ynes.

The Claisen rearrangement[1] provides an excellent method for the formation of carbon–carbon bonds.[2–7] The present importance of the Claisen rearrangement is partly due to its application in the synthesis of oxygen,[8] nitrogen[9] and sulfur[10] heterocycles and partly because of the development of several variants[11–21] of its aliphatic counter part. We had earlier developed a new *ortho*-Claisen rearrangement of aryl propynyl sulfoxides[22–25] and aryl propynyl amine oxides,[26–28] a variant of the aromatic Claisen rearrangement for the construction of the five-membered heterocyclic ring in benzo(*b*)thiophenes and indoles. This protocol was found to be an excellent high yield one step process. Our initial success in the application[29–37] of this protocol and also in the synthesis of quinolone-annulated heterocycles[38,39] inspired us to investigate whether a five-membered thiophene ring in the hitherto unreported thieno[3,2-*c*]-quinolin-4(5*H*)-one system could be constructed via the aforesaid sulfoxide rearrangement. Herein we report the results.

1. Results and discussion

The starting materials for this study **3a–f** were easily



1 **2** **3(a-f)**

	R	Yield (%)
3a)	4″-Cl	80
b)	2″-Cl	75
c)	H	75
d)	2″-Me	85
e)	4″-Me	80
f)	2″,5″-Me_2	70

Scheme 1.

Keywords: thieno[3,2-*c*]quinolin-4(5*H*)-one; sulfoxide rearrangement; modified Claisen rearrangement; Michael addition; regioselective synthesis.

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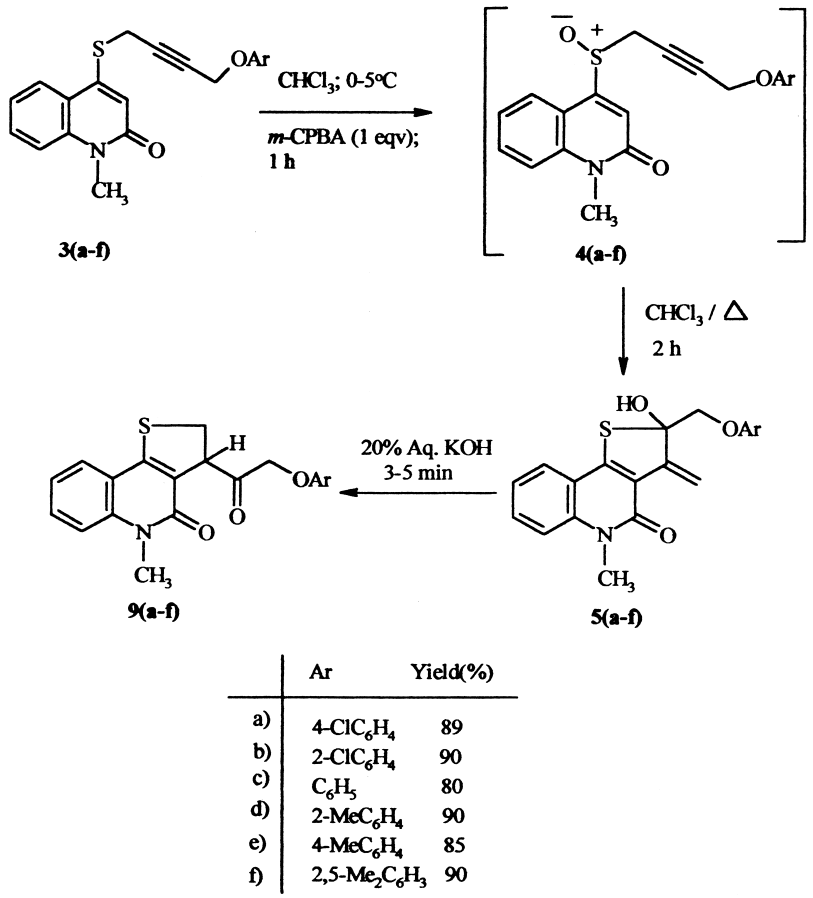


	Ar	Yield(%)
a)	4-ClC$_6$H$_4$	89
b)	2-ClC$_6$H$_4$	90
c)	C$_6$H$_5$	80
d)	2-MeC$_6$H$_4$	90
e)	4-MeC$_6$H$_4$	85
f)	2,5-Me$_2$C$_6$H$_3$	90

Scheme 2.

obtained in 70–85% yield by the phase transfer-catalysed alkylation of 4-mercaptoquinolin-2(1*H*)-one with 1-aryloxy-4-chlorobut-2-ynes in chloroform in the presence of tetrabutyl ammonium bromide (TBAB) and 5% aqueous NaOH for 10–12 h (Scheme 1).

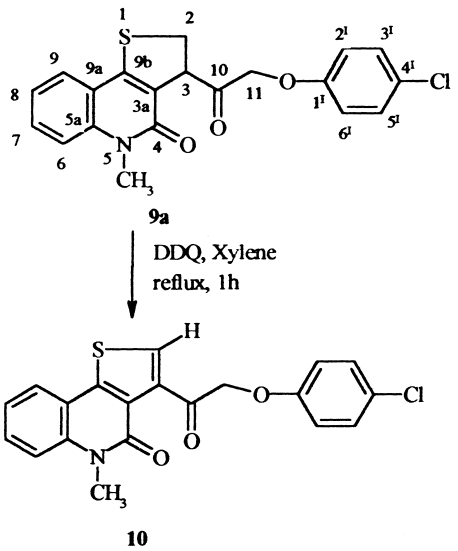
This alkylation when attempted under classical condition by refluxing in acetone in the presence of anhydrous potassium carbonate did not afford any tractable product.

The sulfides **3a–f** were characterized from their elemental analyses and spectroscopic data. The IR spectra of the sulfides **3a–f** exhibited ν_{max} at 1640–1650 cm^{-1} for the amide carbonyl function which establishes the alkylation preference for sulfur over oxygen. Compound **3a** showed a three-proton singlet at δ 3.71 due to NCH_3 group, a two proton-triplet at δ 3.79 due to SCH_2 group and a two-proton triplet at δ 4.66 due to OCH_2 group. It also showed a signal at δ 6.61 (s, 1H, C$_3$*H*). The sulfides **3a–f** were oxidised to the corresponding sulfoxides by slow addition of 1 equiv. of *m*-chloroperbenzoic acid in $CHCl_3$ at 0–5°C over a period of 1 h. A highly polar single spot on TLC indicated the formation of the sulfoxides. The sulfoxides were found to be unstable and showed a tendency to undergo reorganization even during work up. Therefore, no attempt was made to characterize these sulfoxides. The thermally labile crude sulfoxides **4a–f** were refluxed in chloroform for 2 h leading to the quantitative formation of new compounds **5a–f** in 93–96% yields, which were found to be somewhat unstable. We could only isolate compound **5c** in the pure state. Elemental analyses and mass spectroscopic data confirmed that the product was isomeric with the starting sulfoxide **4c**.

The ^{1}H NMR and IR spectra of **5c** indicated the presence of a terminal olefin and a hydroxyl function with signals at δ 5.92 (s, 1H); δ 5.98 (s, 1H) and at δ 3.9 (s, 1H), but showed no evidence for the presence of sulfoxide or acetylenic linkage. The monothiohemiacetal structure **5c** for this product was assigned on the basis of spectral data. As compounds **5a–f** showed tendency of decomposition and we failed to isolate compounds **5a**,**b** and **5d–f** in the pure state, the products **5a–f** were treated with 20% aqueous potassium hydroxide to give stable products **9a–f** (Scheme 2). The products **9a–f** were characterized from their elemental analyses and spectroscopic data.

Compound **9a** exhibited ν_{max} at 1640 cm^{-1} for the amide carbonyl function. ^{1}H NMR of **9a** showed a double doublet at δ 3.62–3.67 (J=9.5, 11 Hz, 1H) for (–SC*H*–), and another double doublet at δ 3.75–3.78 (J=6.5, 11 Hz, 1H) for (–SC*H*–). It also showed a double doublet at δ 4.82–4.85 (J=6.5, 9.5 Hz, 1H) for the (C$_3$*H*), a doublet at δ 4.96–4.99 (J=17 Hz, 1H) for (–CO–C*H*–OAr) and another doublet at δ 5.04–5.07 (J=17 Hz, 1H) for (CO–C*H*–OAr). ^{13}C NMR and DEPT experiment also supports the formation of **9a**. DEPT experiment showed the presence of one methyl group, two CH_2 group and nine CH groups which confirmed the proposed structure of **9a**.

Final confirmation of structure **9** was arrived at by



Scheme 3.

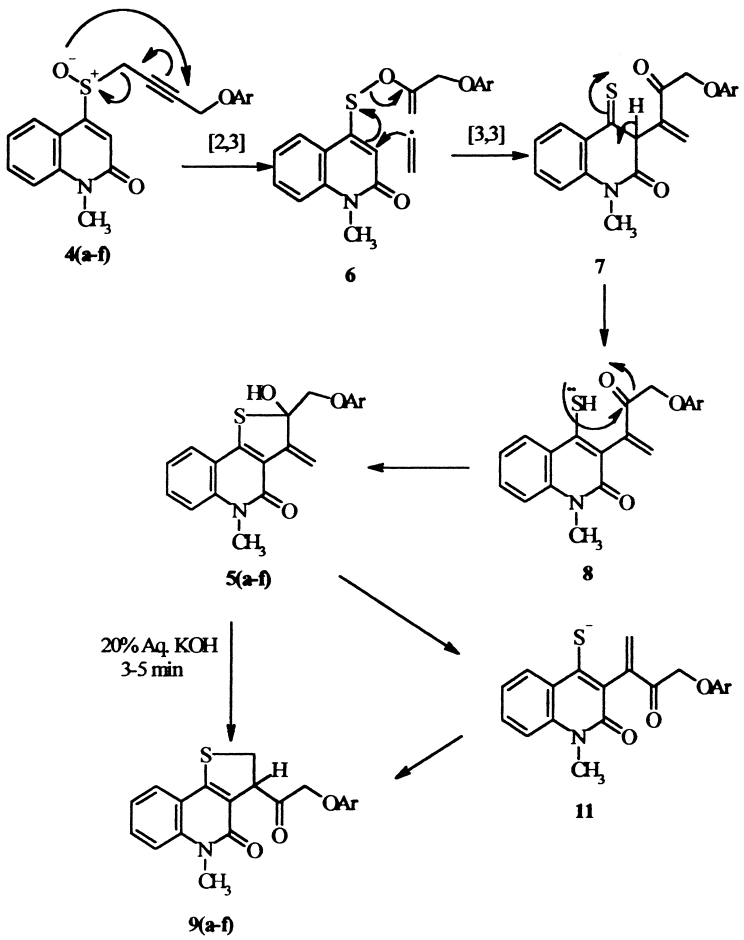
dehydrogenation of compound **9a** with DDQ in boiling xylene to afford product **10** (Scheme 3).

The formation of **5a–f** from the sulfoxides **4a–f** is easily explained by the occurrence of a [2,3] sigmatropic rearrangement in the sulfoxide **4** to give intermediate allenyl sulfenate **6**, which then may undergo a [3,3]sigmatropic rearrangement followed by enolisation leading to intermediate thiol **8**, containing an enone moiety favourably juxtaposed for the formation of the product monothiohemiacetal **5**. The compounds **5a–f** in the presence of a base may suffer ring opening and then via an intramolecular Michael addition of the thiophenolate to the enone moiety may afford the products **9a–f** (Scheme 4).

The whole operation if desired can be conducted in a single pot. The methodology described here is a general one for the synthesis of thieno[3,2-*c*]quinolin-4(5*H*)ones. This is an exceedingly mild and simple synthesis for this type of fused thieno heterocycles. This is also an example of the application of sulfoxide rearrangement in heterocyclic system.

2. Experimental

The melting points were recorded on sulfuric acid bath and are uncorrected. UV absorption spectra were recorded in ethanol on a Hitachi 200-20 spectrometer. IR spectra were run for KBr disks on a Perkin–Elmer-FT IR spectrometer. ^{1}H NMR, ^{13}C NMR and DEPT experiments were determined for solutions in deuteriochloroform with $SiMe_4$ as internal standard on a BRUKER 500 MHz Spectrometer at the Bose Institute (Calcutta). Elemental analyses and mass spectra were recorded at CDRI (LUCKNOW) on a (JEOL D-300 (El)) instrument. Silica



Scheme 4.

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.

2.1. Preparation of sulfides, (3a–f) from 4-mercaptoquinolin-2(1*H*)-ones

A mixture of 1-alkyl-4-mercaptoquinolin-2(1*H*)-one (0.57 g, 3 mmol) and 1-aryloxy-4-chloro-2-butyne (3.5 mmol) was taken up in $CHCl_3$ (50 mL). Tetrabutyl ammonium bromide (TBAB) (250 mg) in 5% aqueous NaOH (50 mL) was added and the mixture was stirred at room temperature for 10–12 h. TLC confirmed complete conversion of the starting material. It was then diluted with water (50 mL) and the aqueous layer was extracted with $CHCl_3$ (50 mL×2). The combined organic layer was washed with water (50 mL×2) followed by brine solution (50 mL) and dried (Na_2SO_4). Removal of solvent gave the crude gummy mass which was purified by column chromatography over silica gel (Spectrochem, 60–120 mesh). The pure products were obtained when the column was eluted with ethyl acetate: benzene (1:9). R_f: 0.3 (ethyl acetate/benzene (1:9)).

2.1.1. 4-(4′-*p*-Chlorophenoxybut-2′-ynylthio)-1-methylquinolin-2(1*H*)-one (3a). Yield 80%; solid (white); mp 134°C; UV (EtOH): λ_{max}: 231, 290, 332 nm; IR (KBr) ν_{max}: 2976, 2941, 1646, 1580, 1494 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 3.71 (s, 3H, NCH_3), 3.79 (t, J=1.9 Hz, 2H, SCH_2), 4.66 (t, J=1.9 Hz, 2H, OCH_2), 6.61 (s, 1H, C_3H), 6.86–6.83 (m, 2H, Ar*H*), 7.17–7.14 (m, 2H, Ar*H*), 7.26–7.25 (m, 1H, Ar*H*), 7.39–7.38 (d, J=8.5 Hz, 1H, Ar*H*), 7.62–7.58 (m, 1H, Ar*H*), 7.82–7.8 (dd, J=1, 8 Hz, 1H, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 23 (NCH_3), 32 (C_1'), 59 (C_4'), 82 (C_3'), 84 (C_2'), 115 (C_8), 117 (C_6'', C_2''), 122 (C_5), 125 (C_6), 127 (C_{4a}), 128 (C_3'', C_5''), 129 (C_4''), 131 (C_7), 132 (C_3), 142 (C_4), 144 (C_{8a}), 157 (C_1''), 159 (C_2). MS m/z 369, 371 (M^+); (Found: C, 65.27, H, 4.11, N, 4.0. $C_{20}H_{16}ClNO_2S$ requires C, 65.04, H, 4.33, N, 3.79%).

2.1.2. 4-(4′-*o*-Chlorophenoxybut-2′-ynylthio)-1-methylquinolin-2(1*H*)-one (3b). Yield 75%; viscous liquid; UV (EtOH): λ_{max}: 230, 290, 331 nm; IR (neat) ν_{max}: 2972, 2940, 1640, 1580, 1480 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 3.71 (s, 3H, NCH_3), 3.8 (t, J=1.95 Hz, 2H, SCH_2), 4.68 (t, J=1.95 Hz, 2H, OCH_2), 6.61 (s, 1H, C_3H), 6.86–6.83 (m, 2H, Ar*H*), 7.17–7.14 (m, 2H, ArH), 7.25–7.23 (m, 1H, Ar*H*), 7.39–7.38 (d, J=8.5 Hz, 1H, Ar*H*), 7.63–7.57 (m, 1H, Ar*H*), 7.82–7.8 (dd, J=1.0, 8 Hz, 1H, Ar*H*); MS m/z 369, 371 (M^+); (Found: C, 64.84, H, 4.1, N, 3.93. $C_{20}H_{16}ClNO_2S$ requires C, 65.04, H, 4.33, N, 3.79%).

2.1.3. 4-(4′-Phenoxybut-2′-ynylthio)-1-methylquinolin-2(1*H*)-one (3c). Yield 75%; Viscous liquid; UV (EtOH): λ_{max}: 230, 296, 333 nm; IR (neat) ν_{max}: 2975, 2940, 1645, 1580, 1490 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 3.7 (s, 3H, NCH_3), 3.80 (t, J=1.9 Hz, 2H, SCH_2), 4.68 (t, J=1.9 Hz, 2H, OCH_2), 6.62 (s, 1H, C_3H), 6.95–6.92 (m, 3H, Ar*H*), 7.27–7.22 (m, 3H, ArH), 7.38–7.36 (d, J=8.5 Hz, 1H, Ar*H*), 7.61–7.58 (m, 1H, Ar*H*), 7.83–7.81 (dd, J=1.0, 8 Hz, 1H, Ar*H*); MS m/z 335 (M^+); (Found: C, 71.42, H, 5.27, N, 4.4. $C_{20}H_{17}NO_2S$ requires C, 71.64, H, 5.07, N, 4.17%).

2.1.4. 4-(4′-*o*-Methylphenoxybut-2′-ynylthio)-1-methylquinolin-2(1*H*)-one (3d). Yield 85%; Viscous liquid; UV (EtOH): λ_{max}: 230, 331, 290 nm; IR (neat) ν_{max}: 2976, 2940, 1650, 1580, 1488 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 2.21 (s, 3H, CH_3), 3.7 (s, 3H, NCH_3), 3.8 (t, J=1.9 Hz, 2H, SCH_2), 4.7 (t, J=1.9 Hz, 2H, OCH_2), 6.63 (s, 1H, C_3H), 6.88–6.82 (m, 2H, Ar*H*), 7.11–7.08 (m, 2H, Ar*H*), 7.25–7.24 (m, 1H, Ar*H*), 7.38–7.36 (d, J=8.5 Hz, 1H, Ar*H*), 7.61–7.58 (m, 1H, Ar*H*), 7.83–7.81 (dd, J=1.0, 8 Hz, 1H, Ar*H*); MS m/z 349 (M^+); (Found: C, 72.48, H, 5.61, N, 3.74. $C_{21}H_{19}NO_2S$ requires C, 72.2, H, 5.44, N, 4.01%).

2.1.5. 4-(4′-*p*-Methylphenoxybut-2′-ynylthio)-1-methylquinolin-2(1*H*)-one (3e). Yield 80%; viscous liquid; UV (EtOH): λ_{max}: 229, 292, 330 nm; IR (neat) ν_{max}: 2970, 2938, 1640, 1582, 1490 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 2.25 (s, 3H, CH_3), 3.7 (s, 3H, NCH_3), 3.79 (t, J=2 Hz, 2H, SCH_2), 4.65 (t, J=2 Hz, 2H, OCH_2), 6.62 (s, 1H, C_3H), 6.83–6.80 (m, 2H, Ar*H*), 7.05–7.03 (m, 2H, Ar*H*), 7.25–7.22 (m, 1H, Ar*H*), 7.38–7.36 (d, J=8.5 Hz, 1H, Ar*H*), 7.61–7.58 (m, 1H, Ar*H*), 7.83–7.81 (dd, J=1.0, 8 Hz, 1H, Ar*H*); MS m/z 349 (M^+); (Found: C, 72.46, H, 5.15, N, 4.3. $C_{21}H_{19}NO_2S$ requires C, 72.2, H, 5.44, N, 4.01%).

2.1.6. 4-(4′-Dimethylphenoxybut-2′-ynylthio)-1-methylquinolin-2(1*H*)-one (3f). Yield 70%; viscous liquid; UV (EtOH): λ_{max}: 230, 333 nm; IR (neat) ν_{max}: 2974, 2940, 1640, 1580, 1490 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 2.21 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.69 (s, 3H, NCH_3), 3.8 (t, J=2 Hz, 2H, SCH_2), 4.68 (t, J=2 Hz, 2H, OCH_2), 6.61 (s, 1H, C_3H), 6.68–6.63 (m, 2H, Ar*H*), 6.98–6.96 (m, 1H, Ar*H*), 7.25–7.22 (m, 1H, Ar*H*), 7.37–7.36 (d, J=8.5 Hz, 1H, Ar*H*), 7.61–7.57 (m, 1H, Ar*H*), 7.83–7.81 (dd, J=1.0, 8 Hz, 1H, Ar*H*); MS m/z 363 (M^+); (Found: C, 72.47, H, 5.56, N, 4.1. $C_{22}H_{21}NO_2S$ requires C, 72.72, H, 5.78, N, 3.85%).

2.2. General procedure for the oxidation and rearrangement of 4-(4′-aryloxybut-2′ynylthio)-1-methylquinolin-2(1*H*)-one

*m*CPBA (0.345 g, 50%, 1 mmol) in $CHCl_3$ (50 mL) was slowly added to a well-stirred solution of 4-(4′-aryloxybut-2′-ynylthio)-1-methylquinolin-2(1*H*)-one (1 mmol) in $CHCl_3$ (30 mL) at 0–5°C over a period of 30 min. The mixture was stirred for half an hour more. Some *m*-chloroperbenzoic acid separated as insoluble solid at this low temperature. After completion of reaction (TLC monitoring), the reaction mass was washed successively with 5% Na_2CO_3 solution (50 mL×2) to remove the organic acid, water (50 mL×2) and dried (Na_2SO_4). Sodium sulfate was filtered off and the filtrate was refluxed for 2 h. Chloroform was evaporated under reduced pressure to give a yellow crystalline solid **5c** in almost quantitative yield. Products **5a**,**b** and **5d**–**f** could not be obtained in pure state due to their tendency of decomposition. These were therefore used for the next step without characterization.

2.2.1. Compound (5c). Yield 90%; solid; mp 112°C; UV (EtOH): λ_{max}: 350, 240, 367 nm; IR (KBr) ν_{max}: 3200,

2910,1620 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 3.7 (s, 3H, NCH_3), 3.9 (brs, 1H, OH), 4.26 (d, J=10 Hz, 1H), 4.38 (d, J=10 Hz, 1H), 5.92 (s, 1H), 5.98 (s, 1H), 6.78 (d, J=9 Hz, 1H, ArH), 6.87–7.05 (m, 3H, ArH), 7.19–7.4 (m, 4H, ArH), 8.2 (d, J=9 Hz, 1H, ArH); MS m/z 351 (M^+); (Found: C, 68.12; H, 4.6, N, 4.21. $C_{20}H_{17}NO_3S$ requires C, 68.37; H, 4.84, N, 3.98%).

2.3. General procedure for the intramolecular Michael addition, preparation of compounds 9a–f

The compounds **5a–f** were treated with aqueous 20% KOH solution (2 mL). Within 3–5 min, a white solid separated out in excellent yield. These were filtered off, dried and recrystallized from chloroform–hexane to give white crystalline solids **9a–f**.

2.3.1. 3-(4′-Chlorophenoxyacetyl)-2,3-dihydro-5-methylthieno[3,2-*c*]quinolin-4(5*H*)-one (9a). Yield 89%; solid; mp 116°C; UV (EtOH): λ_{max}: 319, 229, 202 nm; IR (KBr) ν_{max}: 2990, 2942, 1730, 1640, 1480 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 3.69 (s, 3H, NCH_3), 3.67–3.62 (dd, J=9.5, 11 Hz, 1H, SCH_2), 3.78–3.75 (dd, J=6.5, 11 Hz, 1H, SCH_2), 4.85–4.82 (dd, J=6.5, 9.5 Hz, 1H, C_3H), 4.99–4.96 (d, J=17 Hz, 1H, OCH_2), 5.07–5.04 (d, J=17 Hz, 1H, OCH_2), 6.89–6.87 (d, J=9 Hz, 2H, ArH), 7.22–7.21 (d, J=9 Hz, 2H, ArH), 7.28–7.26 (d, J=8 Hz, 1H, ArH), 7.38–7.36 (d, J=8.5 Hz, 1H, ArH), 7.49–7.48 (d, J=8 Hz, 1H, ArH), 7.62–7.59 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 29 (NCH_3), 34 (C_2), 54 (C_3), 72 (C_{11}), 114 (C_6), 116 (C_6', C_2'), 122 (C_9), 125 (C_8), 126 (C_{9a}), 127 (C_4'), 128 (C_3', C_5'), 129 (C_{3a}), 131 (C_7), 139 (C_{9b}), 153 (C_{5a}), 156 (C_1'), 158 (C4), 204 (C10); MS m/z 385,387 (M^+); (Found: C, 62.05, H, 3.9, N, 3.87. $C_{20}H_{16}ClNO_3S$ requires C, 62.33, H, 4.15, N, 3.63%).

2.3.2. 3-(2′-Chlorophenoxyacetyl)-2,3-dihydro-5-methylthieno[3,2-*c*]quinolin-4(5*H*)-one (9b). Yield 90%; solid; mp 148°C; UV (EtOH): λ_{max}: 319, 230, 202 nm; IR (KBr) ν_{max}: 2980, 2940, 1730, 1642, 1481 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 3.69 (s, 3H, NCH_3), 3.67–3.62 (dd, J=9.5, 11 Hz, 1H, SCH_2), 3.78–3.75 (dd, J=6.5, 11 Hz, 1H, SCH_2), 4.85–4.82 (dd, J=6.5, 9.5 Hz, 1H, C_3H), 4.99–4.96 (d, J=17 Hz, 1H, OCH_2), 5.07–5.04 (d, J=17 Hz, 1H, OCH_2), 6.88–6.86 (d, J=9 Hz, 2H, ArH), 7.21–7.2 (d, J=9 Hz, 2H, ArH), 7.28–7.25 (d, J=8 Hz, 1H, ArH), 7.38–7.36 (d, J=8.5 Hz, 1H, ArH), 7.49–7.48 (d, J=8 Hz, 1H, ArH), 7.62–7.59 (m, 1H, ArH); MS m/z 385,387 (M^+); (Found: C, 62.09, H, 4.38, N, 3.89. $C_{20}H_{16}ClNO_3S$ requires C, 62.33, H, 4.15, N, 3.63%).

2.3.3. 3-(Phenoxyacetyl)-2,3-dihydro-5-methylthieno-[3,2-*c*]quinolin-4(5*H*)-one (9c). Yield 80%; solid; mp 140°C; UV (EtOH): λ_{max}: 319, 229, 202 nm; IR (KBr) ν_{max}: 2981, 2943, 1728, 1645, 1490 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 3.69 (s, 3H, NCH_3), 3.66–3.63 (dd, J=9.5, 11 Hz, 1H, SCH_2), 3.77–3.75 (dd, J=6.6, 11 Hz, 1H, SCH_2), 4.85–4.83 (dd, J=6.6, 9.5 Hz, 1H, C_3H), 5.03–4.99 (d, J=17 Hz, 1H, OCH_2); 5.08–5.05 (d, J=17 Hz, 1H, OCH_2), 6.91–6.78 (m, 2H, ArH), 7.17–7.14 (m, 2H, ArH), 7.27–7.24 (m, 2H, ArH), 7.38–7.36 (d, J=8.5 Hz, 1H, ArH), 7.51–7.49 (m, 1H, ArH), 7.62–7.59 (m, 1H, ArH); MS m/z 351 (M^+); (Found: C, 68.6, H, 4.61, N, 3.76. $C_{20}H_{17}NO_3S$ requires C, 68.37, H, 4.84, N, 3.98%).

2.3.4. 3-(2′-Methylphenoxyacetyl)-2,3-dihydro-5-methylthieno[3,2-*c*]quinolin-4(5*H*)-one (9d). Yield 90%; solid; mp 174°C; UV (EtOH): λ_{max}: 320, 220, 201 nm; IR (KBr) ν_{max}: 2990, 2945, 1730, 1640, 1485 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 2.28 (s, 3H, CCH_3), 3.69 (s, 3H, NCH_3), 3.66–3.62 (dd, J=9.5, 11 Hz, 1H, SCH_2), 3.76–3.72 (dd, J=6.5, J=11 Hz, 1H, SCH_2), 4.85–4.83 (dd, J=6.5, 9.5 Hz, 1H, C_3H), 4.96–4.93 (d, J=17 Hz, 1H, OCH_2), 5.03–4.97 (d, J=17 Hz, 1H, OCH_2), 6.78–6.77 (d, J=8 Hz, 1H, ArH), 6.9–6.89 (d, J=7.5 Hz, 1H, ArH), 7.15–7.13 (d, J=7.5 Hz, 2H, ArH), 7.27–7.24 (m, 1H, ArH), 7.38–7.36 (d, J=8.5 Hz, 1H, ArH), 7.49–7.48 (d, J=8 Hz, 1H, ArH), 7.62–7.59 (m, 1H, ArH); MS m/z 365 (M^+); (Found: C, 68.79, H, 5.45, N, 3.57. $C_{21}H_{19}NO_3S$ requires C, 69.04, H, 5.2, N, 3.83%).

2.3.5. 3-(4′-Methylphenoxyacetyl)-2,3-dihydro-5-methylthieno[3,2-*c*]quinolin-4(5*H*)-one (9e). Yield 85%; solid; mp 132°C; UV (EtOH): λ_{max}: 319, 219, 202 nm; IR (KBr) ν_{max}: 2990, 2940, 1730, 1642, 1490 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 2.28 (s, 3H, CCH_3), 3.69 (s, 3H, NCH_3), 3.67–3.64 (dd, J=11, 9.5 Hz, 1H, SCH_2), 3.74–3.72 (dd, J=6.5, 11 Hz, 1H, SCH_2), 4.86–4.84 (dd, J=6.5, 9.5 Hz, 1H, C_3H), 4.95–4.93 (d, J=17 Hz, 1H, OCH_2), 5.03–4.97 (d, J=17 Hz, 1H, OCH_2), 6.78–6.77 (d, J=8 Hz, 1H, ArH), 6.9–6.89 (d, J=7.5 Hz, 1H, ArH), 7.15–7.13 (d, J=7.5 Hz, 2H, ArH), 7.27–7.25 (m, 1H, ArH), 7.38–7.36 (d, J=8.5 Hz, 1H, ArH), 7.5–7.48 (d, J=8 Hz, 1H, ArH), 7.62–7.59 (m, 1H, ArH); MS m/z 365 (M^+); (Found: C, 69.29, H, 5.43, N, 4.08. $C_{21}H_{19}NO_3S$ requires C, 69.04, H, 5.2, N, 3.83%).

2.3.6. 3-(2′,5′-Dimethylphenoxyacetyl)-2,3-dihydro-5-methylthieno[3,2-*c*]quinolin-4(5*H*)-one (9f). Yield 90%; solid; mp 156°C; UV (EtOH): λ_{max}: 320, 219, 202 nm; IR (KBr) ν_{max}: 2988, 2942, 1733, 1641, 1484 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 2.23 (s, 3H, CCH_3), 2.28 (s, 3H, CCH_3), 3.68 (s, 3H, NCH_3), 3.66–3.64 (dd, J=11, 9.5 Hz, 1H, OCH_2), 3.73–3.71 (dd, J=6.6, 11 Hz, 1H, SCH_2), 4.85–4.83 (dd, J=6.6, 9.5 Hz, 1H, C_3H), 4.97–4.95 (d, J=17 Hz, 1H, OCH_2), 5.04–4.98 (d, J=17 Hz, 1H, OCH_2), 6.66–6.64 (d, J=8 Hz, 1H, ArH), 6.7–6.69 (d, J=7.5 Hz, 1H, ArH), 7.02–7.0 (d, J=7.5 Hz, 1H, ArH), 7.25–7.23 (m, 1H, ArH), 7.37–7.35 (d, J=8.5 Hz, 1H, ArH), 7.49–7.47 (d, J=8 Hz, 1H, ArH), 7.61–7.58 (m, 1H, ArH); MS m/z 379 (M^+); (Found: C, 69.41, H, 5.79, N, 3.45. $C_{22}H_{21}NO_3S$ requires C, 69.65, H, 5.54, N, 3.69%).

2.4. General procedure for the dehydrogenation of compound 9a, preparation of compound 10

The compound **9a** (200 mg, 0.51 mmol) was refluxed with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.56 mmol) in dry xylene (15 mL) for 2 h. The reaction mixture was cooled, filtered and the residue was washed with $CHCl_3$ (100 mL). The filtrate was washed successively with 10% KOH solution, water (three times) and finally dried over anhydrous sodium sulfate. The $CHCl_3$ solution was then filtered through a silica gel column and the column was washed with $CHCl_3$ (300 mL). From the elutes, $CHCl_3$ and

xylene were removed under vacuum. The solid obtained was purified by recrystallization from chloroform–pet ether (60–80) mixture.

2.4.1. Compound (10). Yield 90%; solid; mp 131°C; UV (EtOH): λ_{max}: 348, 333, 283, 229 nm; IR (KBr) ν_{max}: 3083, 1700, 1640, 1491 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 3.78 (s, 3H, NCH_3), 5.35 (brs, 2H, OCH_2), 7.26–6.89 (m, 4H, Ar*H*), 7.64–7.3 (m, 3H, Ar*H*), 7.67 (s, 1H, C_2H), 7.85–7.88 (m, 1H, ArH); MS *m/z* 383, 385 (M^+); (Found: C, 62.41, H, 3.91, N, 3.41. $C_{20}H_{14}ClNO_3S$ requires C, 62.66, H, 3.65, N, 3.65%).

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