Carbanion induced synthesis of annulated unsymmetrical biaryls through ring transformation of 2*H*-pyran-2-one †

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Received (in Cambridge, UK) 10th April 2002, Accepted 19th April 2002
First published as an Advance Article on the web 23rd May 2002

An innovative and convenient one-pot synthesis of unsymmetrical macrocyclic biaryls (**3**, **5** and **8**), dibenzo[*a*,*c*]cycloheptenes (**10**), 3,4-dihydro-2(1*H*)-naphthones (**15**), tetrahydroisoquinolines (**18**), dihydro-1*H*-isothiochromenes (**20**), benzo[*c*]thiochromenes (**22**) and 2,3-dihydro-1-benzothiophenes (**24**) is described. These compounds are obtained through base-catalyzed ring transformation reactions of suitably functionalized 2*H*-pyran-2-ones (**1**,**6**) by a carbanion, generated from cycloalkanone (**2**,**4**,**7**), benzosuberone (**9**), cyclohexanedione monoketal (**12**), 4-piperidone (**17**), tetrahydrothiopyran-4-one (**19**), thiochroman-4-one (**21**) or tetrahydrothiophene-3-one (**23**).

Introduction

The need for an efficient and convenient synthesis for unsymmetrical biaryls has always been both a fascinating and a challenging undertaking in natural product chemistry. Arenes and annulated arenes with electron donor and acceptor substituents are recognized as molecular subunits for the expression of non-linear optical properties due to their high polarisability.[1] These compounds besides exhibiting optical properties, also display diverse pharmacological activities[2–6] and are useful as chiral reagents,[7] as chiral host molecules for inclusion compounds[8] and as chiral phases for chromatography.[9]

Despite the numerous procedures known for the synthesis of macrocyclic biaryls, dibenzo[*a*,*c*]cycloheptenes, tetrahydronaphthalene-2-one 2,2-dimethyltrimethylene ketals, 8-aryl-2(1*H*)-naphthones, 8-aryltetrahydroisoquinolines, 8-arylisochromenes, benzo[*c*]thiochromenes and 7-aryl-2,3-dihydrobenzo[*b*]thiophenes, many of them are of limited use due to the harshness or functional group intolerance of the conditions required.

We report here a methodology which permits direct access to diversely substituted biaryls, based upon carbocyclic, heterocyclic (tetrahydroisoquinolines, isothiochromenes) and macrocyclic ring systems.

Results and discussion

Our approach to the one-pot synthesis of biaryl systems of the type aryl–aryl, and aryl–heteroaryl is entirely different to those described in the Introduction and is based on the ring transformation reactions of 6-aryl-3-methoxycarbonyl-4-methylsulfanyl-2*H*-pyran-2-one (**1**), and 6-aryl-4-*sec*-amino-3-cyano-2*H*-pyran-2-one[10] (**6**), by carbanions generated from cycloalkanone (**2**, **4** or **7**), benzosuberone§ (**9**), cyclohexanedione monoketal (**12**), 4-piperidone (**17**), tetrahydrothiopyran-4-one (**19**), thiochroman-4-one (**21**) and tetrahydrothiophen-3-one (**23**).

The 6-aryl-3-methoxycarbonyl-4-methylsulfanyl-2*H*-pyran-2-one (**1**), and 6-aryl-4-*sec*-amino-3-cyano-2*H*-pyran-2-one (**6**) may be considered as cyclic pyran derivatives (**1**) and cyclic enone derivatives (**2**) respectively, with three electrophilic centres C-2, C-4, and C-6 in their molecular make-up, in which the latter is highly susceptible to nucleophilic attack due to extended conjugation and the presence of electron withdrawing substituents at the 3 positions.

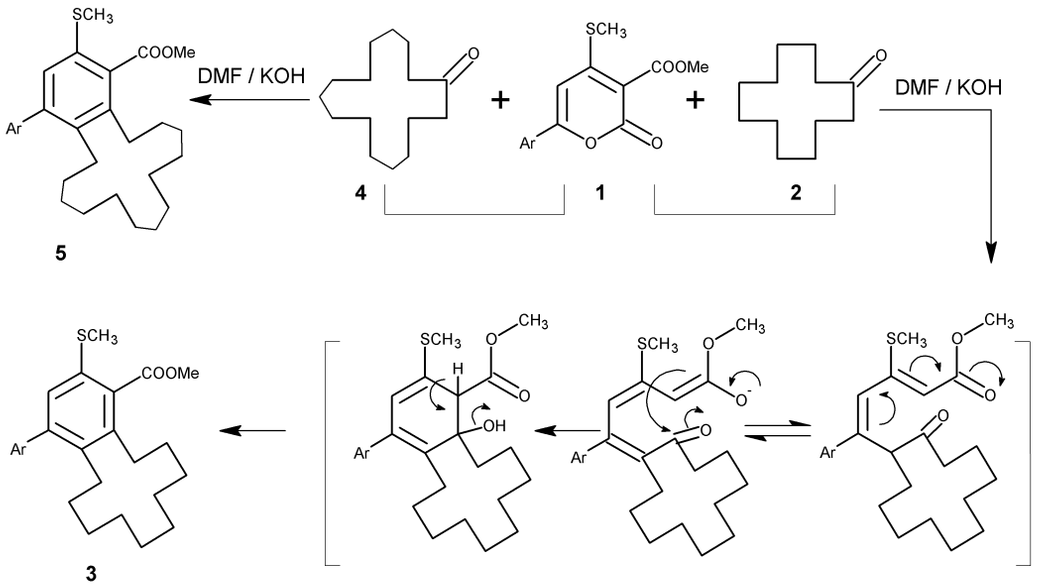
[*n*]Orthocyclophanes can be considered as annulated macrocycles and have been previously synthesized,[11] either by condensation of α-hydroxymethylenecyclohexanone with acetone dicarboxylic acid ester, by a Diels–Alder reaction[12] of 2*H*-cycloalka[*b*]pyran-2-one with an acetylene derivative or by heating with enamine above 200 °C. Base-catalyzed isomerization[13] of cycloalkadiyne at 160 °C and thermal isomerization of [*n*]paracyclophanes also led to[14,15] [*n*]orthocyclophanes but in poor yields. Previously, compounds containing the dibenzo[*a*,*c*]cycloheptene ring system have been prepared starting from phenanthrene,[16] by pyrolysis of 1,2:3,4 dibenzotropilidine§[17] or from biphenyl-5-propionic acid[18] albeit in poor yields. Recently, derivatives of the dibenzo[*a*,*c*]-cycloheptene ring system such as 6-methyl- and 6-phenyl-5*H*-dibenzo[*a*,*c*]cycloheptenes have been obtained[19] from reaction of either MeLi or PhLi with dibenzotropolone§.

We report herein a novel synthesis for the annulated macrocycles (**3** and **5**) and dibenzo[*a*,*c*]cycloheptene (**10**) from the reaction of **1** with macrocyclic ketones (**2** and **4**) and benzosuberone (**9**), respectively. Moderate yields were obtained. Analogously, a reaction of cyclic enone derivatives (**6**) with alicyclic ketone (**7**) also yielded benzocycloalkenes (**8**) (see Schemes 1–3).

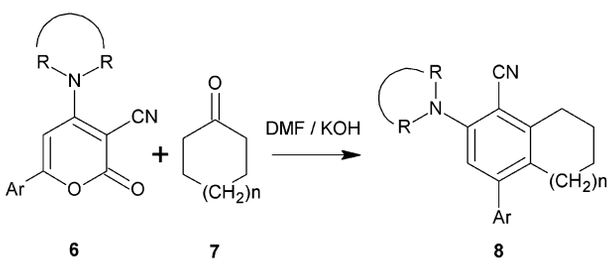
Among the various approaches known for the synthesis[20] of 3,4-dihydro-2(1*H*)-naphthone (**15**), reductive transformation of suitably functionalized 2-methoxynaphthalene derivatives is the most common. The 1-alkyl and 1-aryl derivatives of 2(1*H*)-naphthone have been obtained[21] by hydroboration of 1-alkyl- or 1-aryl-3,4-dihydronaphthalene followed by chromic acid oxidation. These compounds have also been obtained[22] either by acid hydrolysis of epoxy amides derived

† Central Drug Research Institute communication no. 6207
‡ For crystallographic queries.
§ The IUPAC name for benzosuberone is 6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one. The IUPAC name for 1,2:3,4-dibenzotropilidine is 5*H*-dibenzo[*a*,*c*]cycloheptene. The IUPAC name for dibenzotropolone is 5-hydroxydibenzo[*a*,*c*]cyclohepten-6-one and the IUPAC name for 1-tetralone is 3,4-dihydro-1-(2*H*)-naphthone.

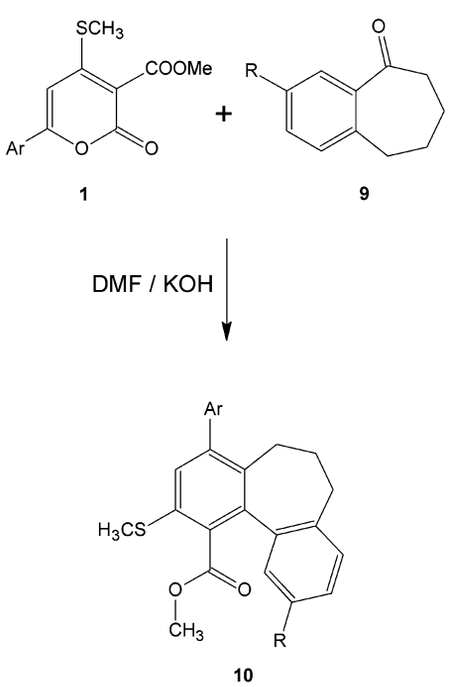
 DOI: 10.1039/b203544h



Scheme 1



Scheme 2



Scheme 3

from 1-tetralone§ or by reductive cyclization of 5-(4-methoxyphenyl)hexan-2-one[23] followed by dehydrogenation and subsequent reduction. Recently, derivatives of this ring system have been synthesized[24] either through carbo-palladation of aryl nitriles or $InCl_3$ promoted rearrangement[25] of epoxide derived from 3,4-dihydronaphthalene. The latest concise synthesis of 1-substituted-2(1*H*)-naphthone has been reported[26] and is achieved by selective dehydration of 1,2-dihydroxy-1,2,3,4-tetrahydronaphthalene.

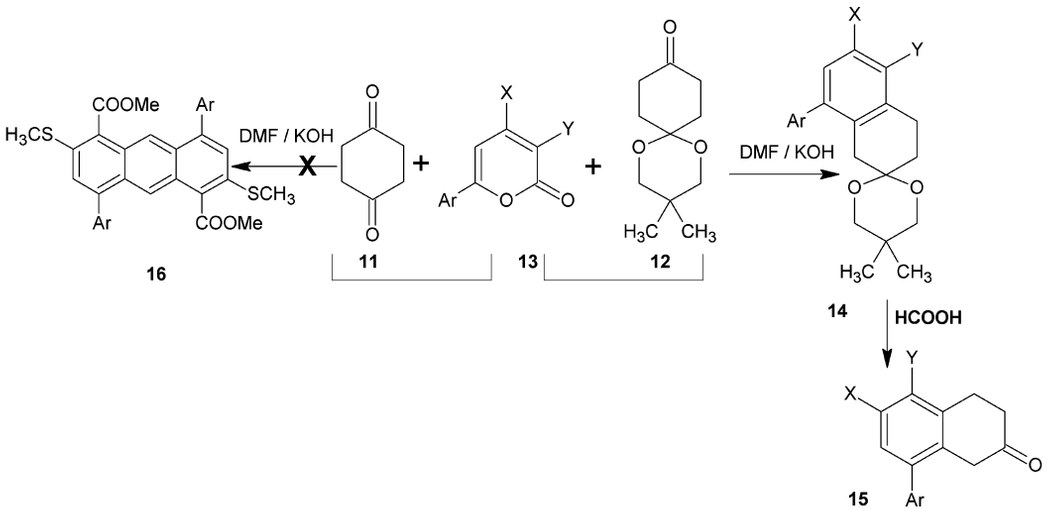
Our strategy to prepare derivatives of this ring system was based on the reaction of pyran-2-ones (**1**, **6**) with cyclohexane-1,4-dione mono-2,2-dimethyltrimethylene ketal (**12**) separately. The isolated tetrahydronaphthalen-2-one 2,2-dimethyltrimethylene ketals (**14**) on hydrolysis with formic acid produced 3,4-dihydro-2-(1*H*)-naphthones (**15**) (see Scheme 4).

The Pictet–Spengler reaction[27] is commonly used for the synthesis of tetrahydroisoquinoline but the disadvantage of not having regiochemical control has led to modifications of this approach[28,29] in order to obtain regioselectivity. We report herein the synthesis of the highly functionalized tetrahydroisoquinoline (**18**) through ring transformation of 2*H*-pyran-2-one (**6**) from *N*-substituted-4-piperidone (**17**) (see Scheme 5).

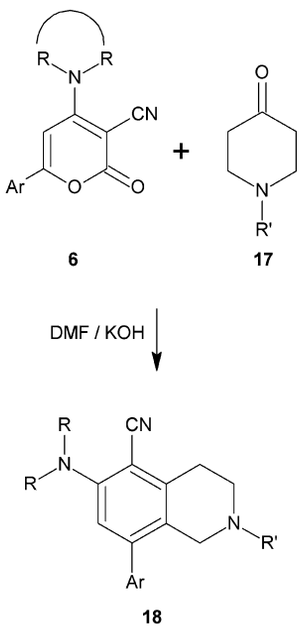
1*H*-Isothiochromenes have previously been prepared either from reaction of benzylmercaptans and haloacetic acid followed by Friedel–Crafts cyclization[30,31] or by treating homoxylene dibromide with potassium sulfide.[32] These compounds have also been prepared[33] photochemically from reaction of thiobenzophenone and propiolic acid. The synthesis of the 6*H*-benzo[*c*]thiochromene ring system has previously been reported to occur *via* Pschorr cyclization[34] and Pummerer rearrangement. Alternatively these compounds have been obtained[35] either photochemically from a range of benzyl alcohols or from reaction[36] of 4-substituted-bis(3-alkoxybenzoyl) peroxide and phenol. 2,3-Dihydro-1-benzothiophenes have been synthesized[37] either by ring contraction of *cis*-3-bromo-7-chloro-3,4-dihydro-2*H*-benzothiopyran-4-ol or reductive ring opening of 6a,11a-dihydrobenzothieno[3,2-*c*]-benzopyrans[38] with $LiAlH_4$.

We have prepared 3,4-dihydroisothiochromene (**20**), benzo[*c*]-thiochromenes (**22**) and 2,3-dihydrobenzothiophenes (**24**) through ring transformation of 2*H*-pyran-2-one (**13**) from heterocyclic ketones (**19**, **21**, **23**) which were used as the source of carbanions (see Scheme 6).

In all the ring transformation reactions an equimolar mixture of 2*H*-pyran-2-one (**1**,**6**), an alicyclic or heterocyclic ketone and powdered KOH in DMF was stirred at ambient temperature for 30–40 h. After pouring the reaction mixture into ice–water,



Scheme 4



Scheme 5

the solution was neutralized with 10% HCl and the product obtained was purified by chromatography using silica. The initial step in the ring transformation reactions is possibly the attack of the carbanion at position 6 of the pyran ring (**1**,**6**), followed by condensation between the keto group and activated methylene to form annulated biaryls. Our approach to the construction of unsymmetrical biaryls is superior in respect to (a) versatility and compatibility, (b) mild reaction conditions, (c) use of inexpensive reagents and (d) easy work-up. This procedure opens a new avenue for a convenient one pot synthesis of unsymmetrical biaryls (see Schemes 1–6), using economical reagents.

All the synthesized compounds were characterized by spectroscopic techniques and satisfactory elemental analyses for C, H and N (± 0.4%) were obtained. The structures of **8f** and **14k** were further confirmed by single crystal X-ray diffraction.[39] The molecular structure of **8f** (Fig. 1) shows that the equatorially

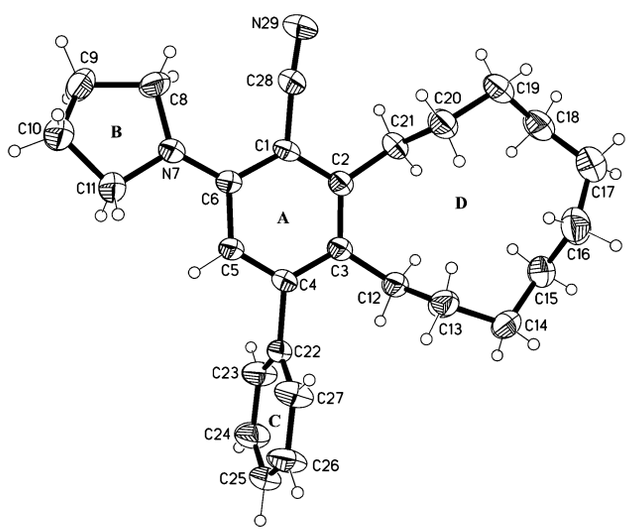
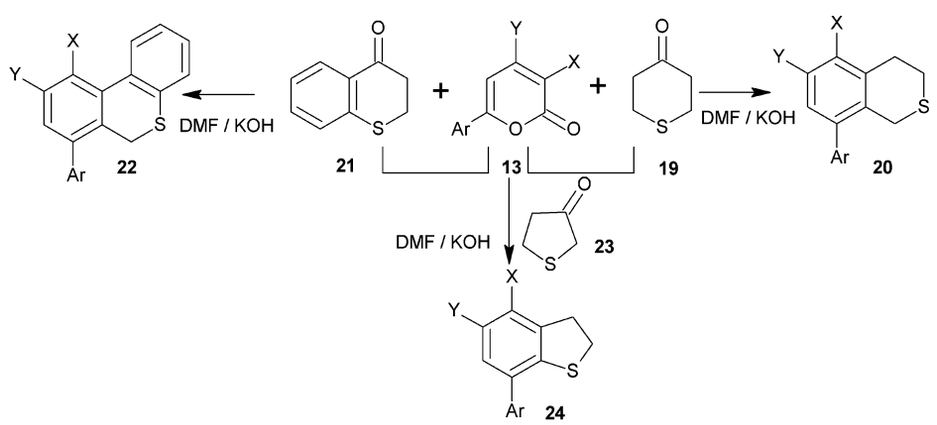


Fig. 1 ORTEP diagram showing the structure of **8f** with numbering scheme.



Scheme 6

substituted planar phenyl ring (C) is twisted with respect to the central planar A ring by 89.5(2)°. The pyrrolidine ring (B) adopts a distorted envelope conformation. The macrocyclic ring (D) is fused to the central ring (A) at the C2–C3 junction and is puckered to adopt a long chair-type conformation (atoms C16, C17 are above and C3, C12, C21, C2 are below the least-squares planes through atoms C13, C14, C15, C18, C19 and C20).

The ORTEP diagram of **14k** (Fig. 2) shows the conformation and molecular structure along with the atom-numbering

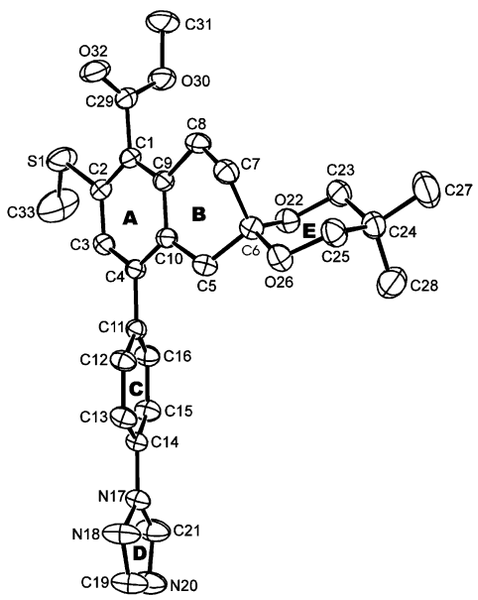


Fig. 2 ORTEP diagram showing the molecular structure of **14k** with atomic numbering scheme.

scheme. The phenyl rings (A and B) and the triazole ring (D) are planar. The cyclic ketal ring (E) adopts a chair conformation. The phenyl ring (C) is twisted by 54.7(1)° while the triazole ring (E) is further twisted by 6.7(2)°.

Experimental

Mps were determined on a Büchi-530 instrument in open capillary tubes and are uncorrected. The reagent grade reaction solvents such as DMF were further purified and dried following literature procedures.[40] Malononitrile and various cyclic ketones were purchased from Aldrich. TLC was performed on precoated silica gel plastic plates and visualized by UV irradiation, exposure to iodine vapors or by spraying with $KMnO_4$ solution. The IR spectra of concentrated liquid samples were run while the solid samples were analyzed as KBr pellets on a Perkin-Elmer Ac-1. ^{1}H NMR spectra were recorded at 200 MHz (Bruker WM-200) in $CDCl_3$ with tetramethylsilane as internal reference. Chemical shifts and coupling constants (J) were reported in δ (ppm) and Hz respectively. Mass spectra were collected at 70 eV using a JEOL JMS-300 spectrometer. Elemental analyses (C, H, and N) were determined on a Carlo Erba EA-1108 at RSIC, Central Drug Research Institute, Lucknow 226001, India.

Synthesis of 4-aryl-1-methoxycarbonyl-2-methylsulfanylbenzocycloalkenes (3a–f, 5a–j)

General procedure. A mixture of 6-aryl-3-methoxycarbonyl-4-methylsulfanyl-2*H*-pyran-2-one (**1**, 1 mmol), alicyclic ketone (**2** and **4**, 1 mmol) and potassium hydroxide (1.5 mmol) was stirred at ambient temperature in dry DMF for 35 hours. After completion the reaction mixture was poured into ice–water and the solution was neutralized with 10% HCl. The precipitate obtained was filtered and purified by column chromatography using $CHCl_3$: hexane (1 : 2) as eluent.

All the synthesized compounds were characterized spectroscopically and are listed in Table 1.

Synthesis of 4-aryl-2-*sec*-aminobenzocycloalkenecarbonitrile (8a–h)

General Procedure. A solution of 6-aryl-4-*sec*-amino-3-cyano-2*H*-pyran-2-one (**6**) (1 mmol) and cycloalkanone (**7**) (1 mmol) in dry DMF (12 mL) was stirred in the presence of powdered KOH (1 mmol) at room temperature for 28 h. After this time the reaction mixture was poured into ice–water and neutralized with 10% HCl. The solid obtained was filtered and purified by column chromatography eluting with $CHCl_3$: hexane (1 : 3).

The spectroscopic data and physical constants of all the synthesized compounds are listed in Table 2.

Synthesis of methyl 4-aryl-2-methylsulfanyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptene-1-carboxylate (10a–n)

General procedure. An equimolar mixture of pyran-2-one (**1**), benzosuberones (**9**) and powdered KOH in dry DMF was stirred at ambient temperature for 38 hours under an inert atmosphere. The reaction mixture was poured into ice–water and the solution was neutralized to pH 7 by 10% HCl. The precipitate obtained (**10**) was filtered and purified by column chromatography.

All the compounds were characterized by spectroscopic analyses and are listed in Table 3.

Synthesis of 8-aryl-5,6-disubstituted-1,2,3,4-tetrahydronaphthalene-2-one 2,2-dimethyltrimethylene ketal (14a–p)

General procedure. A mixture of 6-aryl-3,4-disubstituted-2*H*-pyran-2-one (**13**) (1 mmol), cyclohexane-1,4-dione mono-2,2-dimethyltrimethylene ketal (**12**, 1 mmol) and potassium hydroxide (1.5 mmol) was stirred at room temperature in dry DMF (15 mL) for 25 h. After completion, the reaction mixture was poured into ice–water and the solution was neutralized with 10% HCl. The solid obtained was filtered and purified on a silica gel column by eluting with $CHCl_3$: hexane (1 : 1).

All the synthesized compounds are listed in Table 4 with their physical constants and spectroscopic data.

Synthesis of 8-aryl-5,6-disubstituted-3,4-dihydro-2(1*H*)-naphthone (15a–l)

General procedure. A solution of **14** in formic acid (99%) was stirred at room temperature for 28 hours. After completion, excess formic acid was removed under reduced pressure and the product was extracted with $CHCl_3$, washed with water, dried over calcium sulfate and purified by column chromatography using $CHCl_3$: hexane (2 : 1) as eluent.

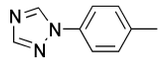
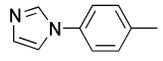
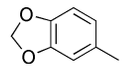
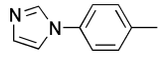
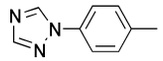
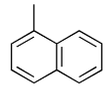
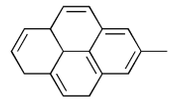
All the synthesized compounds are listed in Table 4 with their characterization data.

Synthesis of 8-aryl-6-*sec*-amino-1,2,3,4-tetrahydroisoquinoline-5-carbonitrile (18a–h)

General procedure. A mixture of 6-aryl-4-*sec*-amino-3-cyano-2*H*-pyran-2-one (**6**) (1 mmol), 4-piperidone **17** (1 mmol) and KOH (1 mmol) in dry DMF (12 mL) was stirred at room temperature for 30 h. After completion, the reaction mixture was poured into ice–water and neutralized with 10% HCl. The solid obtained was filtered and purified by column chromatography eluting with $CHCl_3$: hexane (1 : 2).

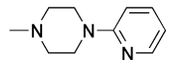
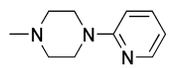
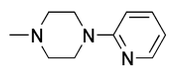
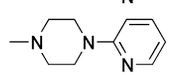
All the compounds synthesized are listed in Table 5 with their spectroscopic analyses.

Table 1 Physical and spectral data for compounds **3a**–**f** and **5a**–**i**

Compd	Ar	Yield (%)	Mp/°C [a]	ν_{max} [b]/cm^{-1}	δ_H, J/Hz [c]	*m*/*z* (%)
3a	4-ClC_6H_4	59	140	1728	1.25–1.31 (m, 4H, $2CH_2$), 1.45–1.50 (m, 4H, $2CH_2$), 1.67–1.74 (m, 8H, $4CH_2$), 2.41 (s, 3H, SCH_3), 2.56 (t, *J* 6.2, 2H, CH_2), 2.70 (t, *J* 6.4, 2H, CH_2), 3.95 (s, 3H, OMe), 6.98 (s, 1H, CH), 7.18 (d, *J* 8.1, 2H, ArH), 7.38 (d, *J* 8.1, 2H, ArH).	431 (63.5)
3b	4-BrC_6H_4	52	86	1726	1.26–1.32 (m, 4H, $2CH_2$), 1.44–1.50 (m, 4H, $2CH_2$), 1.67–1.75 (m, 8H, $4CH_2$), 2.42 (s, 3H, SCH_3), 2.58 (t, *J* 6.0, 2H, CH_2), 2.70 (t, *J* 6.2, 2H, CH_2), 3.94 (s, 3H, OMe), 6.98 (s, 1H, CH), 7.14 (d, *J* 8.0, 2H, ArH), 7.53 (d, *J* 8.0, 2H, ArH).	475 (100)
3c	2-Thienyl	44	98	1726	1.25–1.31 (m, 4H, $2CH_2$), 1.40–1.48 (m, 4H, $2CH_2$), 1.52–1.65 (m, 8H, $4CH_2$), 2.42 (s, 3H, SCH_3), 2.66 (t, *J* 6.4, 2H, CH_2), 2.73 (t, *J* 6.2, 2H, CH_2), 3.94 (s, 3H, OMe), 7.00 (s, 1H, CH), 7.04–7.16 (m, 2H, thienyl), 7.34 (d, *J* 7.9, 1H, thienyl).	402 (100)
3d	2-Pyridyl	38	160	1722	1.25–1.32 (m, 4H, $2CH_2$), 1.41–1.47 (m, 4H, $2CH_2$), 1.58–1.66 (m, 8H, $4CH_2$), 2.41 (s, 3H, SCH_3), 2.67 (t, *J* 6.4, 2H, CH_2), 2.75 (t, *J* 6.3, 2H, CH_2), 3.94 (s, 3H, OMe), 7.14 (s, 1H, CH), 7.30–7.39 (m, 2H, pyridyl), 7.71 (d, *J* 8.0, 1H, pyridyl), 8.66 (d, *J* 8.0, 1H, pyridyl).	397 (68)
3e		42	190	1724	1.26–1.32 (m, 4H, $2CH_2$), 1.45–1.50 (m, 4H, $2CH_2$), 1.68–1.75 (m, 8H, $4CH_2$), 2.41 (s, 3H, SCH_3), 2.58 (t, *J* 6.3, 2H, CH_2), 2.70 (t, *J* 6.0, 2H, CH_2), 3.95 (s, 3H, OMe), 6.98 (s, 1H, CH), 7.18 (d, *J* 8.1, 2H, ArH), 7.33 (d, *J* 7.9, 2H, ArH), 7.53 (d, *J* 7.9, 2H, imidazolyl), 8.10 (s, 1H, imidazolyl).	462 (52.3)
3f		41	170	1728	1.25–1.30 (m, 4H, $2CH_2$), 1.42–1.48 (m, 4H, $2CH_2$), 1.62–1.70 (m, 8H, $4CH_2$), 2.42 (s, 3H, SCH_3), 2.60 (t, *J* 6.2, 2H, CH_2), 2.76 (t, *J* 6.0, 2H, CH_2), 3.96 (s, 3H, OMe), 7.02 (s, 1H, CH), 7.38 (d, *J* 8.2, 2H, ArH), 7.73 (d, *J* 8.2, 2H, ArH), 7.92 (s, 1H, triazolyl), 8.51 (s, 1H, triazolyl).	463 (56.3)
5a	4-FC_6H_4	48	62	1737	1.29–1.45 (m, 22H, $11CH_2$), 2.40 (s, 3H, SCH_3), 2.44–2.62 (m, 4H, $2CH_2$), 3.94 (s, 3H, OMe), 7.04 (s, 1H, CH), 7.11 (d, *J* 8.0, 2H, ArH), 7.33 (d, *J* 8.0, 2H, ArH).	456 (100)
5b	4-ClC_6H_4	52	43	1717	1.24–1.48 (m, 22H, $11CH_2$), 2.41 (s, 3H, SCH_3), 2.44–2.56 (m, 4H, $2CH_2$), 3.83 (s, 3H, OMe), 7.02 (s, 1H, CH), 7.07 (d, *J* 8.2, 2H, ArH), 7.35 (d, *J* 8.2, 1H, ArH).	472 (34.9)
5c	4-BrC_6H_4	48	78	1724	1.25–1.47 (m, 22H, $11CH_2$), 2.40 (s, 3H, SCH_3), 2.46–2.58 (m, 4H, $2CH_2$), 3.94 (s, 3H, OMe), 6.99 (s, 1H, CH), 7.12 (d, *J* 7.8, 2H, ArH), 7.53 (d, *J* 7.8, 1H, ArH).	517 (32)
5d		45	Oil	1727	1.19–1.45 (m, 22H, $11CH_2$), 2.37 (s, 3H, SCH_3), 2.41–2.52 (m, 4H, $2CH_2$), 3.87 (s, 3H, OMe), 5.94 (s, 2H, CH_2O_2), 6.89 (s, 1H, CH), 6.70–7.82 (m, 3H, ArH).	482 (100)
5e	2-Pyridyl	41	58	1728	1.21–1.48 (m, 22H, $11CH_2$), 2.41 (s, 3H, SCH_3), 2.45–2.59 (m, 4H, $2CH_2$), 3.94 (s, 3H, OMe), 7.16 (s, 1H, CH), 7.30–7.35 (m, 2H, pyridyl), 7.71 (d, *J* 8.0, 1H, pyridyl), 8.66 (d, *J* 8.0, 1H, pyridyl).	439 (100)
5f		48	132	1718	1.26–1.66 (m, 22H, $11CH_2$), 2.52 (s, 3H, SCH_3), 2.59–274 (m, 4H, $2CH_2$), 3.96 (s, 3H, OMe), 7.04 (s, 1H, CH), 7.35 (d, *J* 7.8, 2H, ArH), 7.47 (d, *J* 8.0, 2H, ArH), 7.81 (d, *J* 8.0, 2H, imidazolyl), 7.99 (s, 1H, imidazolyl).	504 (31.3)
5g		42	153	1718	1.25–1.56 (m, 22H, $11CH_2$), 2.52 (s, 3H, SCH_3), 2.47–2.60 (m, 4H, $2CH_2$), 3.96 (s, 3H, OMe), 7.04 (s, 1H, CH), 7.39 (d, *J* 7.9, 2H, ArH), 7.73 (d, *J* 7.9, 2H, ArH), 8.14 (s, 1H, triazolyl), 8.61 (s, 1H, triazolyl).	505 (48.3)
5h		36	Oil	1728	1.22–1.53 (m, 22H, $11CH_2$), 2.5 (s, 3H, SCH_3), 2.42–2.62 (m, 4H, $2CH_2$), 3.96 (s, 3H, OMe), 7.06 (s, 1H, CH), 7.30–7.47 (m, 4H, ArH), 7.82–7.88 (m, 3H, ArH).	488 (75)
5i		38	Oil	1718	1.24–1.53 (m, 22H, $11CH_2$), 2.51 (s, 3H, SCH_3), 2.54–2.78 (m, 4H, $2CH_2$), 3.94 (s, 3H, OMe), 7.08 (s, 1H, CH), 7.58 (d, *J* 8.0, 2H, ArH), 7.81–7.89 (m, 5H, ArH), 7.99–8.04 (m, 2H, ArH).	562 (58)

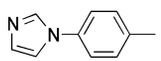
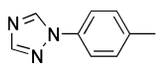
[a] Uncorrected. [b] From KBr discs/concentrated liquid. [c] From $CHCl_3$.

Table 2 Physical and spectral data for compounds **8a**–**h**

8	*n*		Ar	Yield (%)	Mp/ °C[a]	ν_{max}[b]/ cm^{-1}	δ_H, *J*/Hz[c]	*m*/*z* (%)
a	1		4-ClC_6H_4	44	144	2214	1.54–1.59 (m, 2H, CH_2), 1.71–1.74 (m, 2H, CH_2), 1.86 (t, *J* 6.0, CH_2), 1.94 (t, *J* 5.9, 2H, CH_2), 2.68 (t, *J* 6.1, 4H, $2CH_2$), 2.89 (t, *J* 6.0, 4H, $2CH_2$), 6.28 (s, 1H, CH), 7.14 (d, *J* 9.0, 2H, ArH), 7.28 (d, *J* 9.0, 2H, ArH).	336 (100)
b	1		4-$CH_3C_6H_4$	45	110	2215	1.64–1.71 (m, 2H, CH_2), 1.78–1.84 (m, 2H, CH_2), 2.30 (s, 3H, CH_3), 2.47 (t, *J* 6.0, 2H, CH_2), 2.83 (t, *J* 5.9, 2H, CH_2), 3.18 (t, *J* 6.0, 4H, $2CH_2$), 6.28 (s, 1H, CH), 7.11–7.26 (m, 4H, ArH), 8.30–8.38 (m, 3H, pyridyl).	409 (100)
c	1		2-Benzofuryl	42	105	2215	1.67–1.84 (m, 4H, $2CH_2$), 2.63 (s, 3H, CH_3), 2.91 (t, *J* 6.0, 2H, CH_2), 3.27 (t, *J* 5.8, 4H, $2CH_2$), 4.07 (t, *J* 5.9, 4H, $2CH_2$), 6.98 (s, 1H, CH), 7.31–7.40 (m, 4H, ArH), 8.32–8.41 (m, 3H, pyridyl).	435 (40)
d	2		4-$CH_3C_6H_4$	44	Oil	2216	1.48–1.66 (m, 6H, $3CH_2$), 2.33 (s, 3H, CH_3), 2.58 (t, *J* 6.0, 2H, CH_2), 2.64 (t, *J* 5.8, 2H, CH_2), 2.80 (t, *J* 6.0, 4H, $2CH_2$), 3.18 (t, *J* 6.0, 4H, $2CH_2$), 6.63 (s, 1H, CH), 7.07 (d, *J* 9.0, 2H, ArH), 7.14 (d, *J* 9.0, 2H, ArH).	330 (100)
e	3		C_6H_5	48	Oil	2216	1.44–1.73 (m, 4H, $2CH_2$), 1.78–1.86 (m, 4H, CH_2), 2.30 (t, *J* 6.0, 2H, CH_2), 2.38 (t, *J* 6.0, 2H, CH_2), 2.94 (t, *J* 5.8, 4H, 2 CH_2), 3.45 (t, *J* 6.0, 4H, CH_2), 6.30 (s, 1H, CH), 7.18–7.36 (m, 5H, ArH).	330 (100)
f	7		C_6H_5	40	145	2212	1.26–1.50 (m, 16H, $8CH_2$), 1.89–1.97 (m, 4H, $2CH_2$), 2.81 (t, *J* 6.0, 4H, $2CH_2$), 3.44 (t, 4H, $2CH_2$), 6.29 (s, 1H, CH), 7.16–7.29 (m, 5H, ArH).	386 (100)
g	10		4-FC_6H_4	38	Oil	2218	1.25–1.35 (m, 4H, $2CH_2$), 2.17–2.46 (m, 22H, $11CH_2$), 3.23 (t, *J* 6.0, 4H, $2CH_2$), 3.74 (t, *J* 6.0, 4H, $2CH_2$), 6.64 (s, 1H, CH), 7.14–7.21 (m, 4H, ArH), 7.26–7.50 (m, 3H, pyridyl).	538 (50)
h	10		2-Benzofuryl	39	164	2217	1.25–1.47 (m, 4H, $2CH_2$), 2.17–2.50 (m, 22H, $11CH_2$), 3.23 (t, *J* 5.8, 4H, $2CH_2$), 4.06 (t, *J* 5.8, 4H, $2CH_2$), 6.32 (s, 1H, furyl), 6.49 (s, 1H, CH), 7.23–7.37 (m, 4H, ArH), 8.32–8.39 (m, 3H, pyridyl).	561 (60)

[a] Uncorrected. [b] From KBr discs/concentrated liquid. [c] From $CHCl_3$.

Table 3 Physical and spectral data for compounds **10a**–**n**

10	R	Ar	Yield (%)	Mp/°C[a]	ν_{max}[b]/cm^{-1}	δ_H, *J*/Hz[c]	*m*/*z* (%)
a	H	4-FC_6H_4	38	Oil	1723	1.18–1.56 (m, 2H, CH_2), 1.98 (t, *J* 6.2, 2H, CH_2), 2.51 (s, 3H, SCH_3), 2.62 (t, *J* 6.2, 2H, CH_2), 3.97 (s, 3H, OCH_3), 6.88 (s, 1H, CH), 7.11–7.24 (m, 4H, ArH), 7.29–7.41 (m, 4H, ArH).	392 (60)
b	H	4-ClC_6H_4	35	173	1723	1.25–1.58 (m, 2H, CH_2), 2.05 (t, *J* 6.2, 2H, CH_2), 2.53 (s, 3H, SCH_3), 2.60 (t, *J* 6.2, 2H, CH_2), 3.96 (s, 3H, OCH_3), 6.91 (s, 1H, CH), 7.21 (d, *J* 8.0, 2H, ArH), 7.27–7.39 (m, 4H, ArH).	408 (100)
c	H	4-BrC_6H_4	33	189	1706	1.18–1.50 (m, 2H, CH_2), 2.03 (t, *J* 6.2, 2H, CH_2), 2.53 (s, 3H, SCH_3), 2.65 (t, *J* 6.2. 2H, CH_2), 3.94 (s, 3H, OCH_3), 6.92 (s, 1H, CH), 7.01–7.18 (m, 4H, ArH), 7.21–7.39 (m, 4H, ArH).	453 (100)
d	H	4-$CH_3C_6H_4$	37	Oil	1722	1.15–1.46 (m, 2H, CH_2), 2.03 (t, *J* 6.2, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.51 (s, 3H, SCH_3), 2.55 (t, *J* 6.2, 2H, CH_2), 3.93 (s, 3H, OCH_3), 6.92 (s, 1H, CH), 7.01–7.18 (m, 4H, ArH), 7.21–7.34 (m, 4H, ArH).	392 (80)
e	H	3-ClC_6H_4	31	130	1718	1.18–1.49 (m, 2H, CH_2), 1.97 (t, *J* 6.2, 2H, CH_2), 2.50 (s, 3H, SCH_3), 2.58 (t, *J* 6.2, 2H, CH_2), 3.96 (s, 3H, OCH_3), 6.98 (s, 1H, CH), 7.02–7.20 (m, 4H, ArH), 7.29–7.38 (m, 4H, ArH).	408 (100)
f	H	2-Pyridyl	33	Oil	1724	1.28–1.60 (m, 2H, CH_2), 2.09 (t, *J* 6.0, 2H, CH_2), 2.51 (s, 3H, SCH_3), 2.59 (t, *J* 6.0, 2H, CH_2), 3.93 (s, 3H, OCH_3), 6.90 (s, 1H, CH), 7.01–7.15 (m, 4H, ArH), 7.20–7.31 (m, 4H, pyridyl).	375 (100)
g	H	2-Thienyl	32	163	1710	1.25–1.56 (m, 2H, CH_2), 2.06 (t, *J* 6.4, 2H, CH_2), 2.50 (s, 3H, SCH_3), 2.62 (t, *J* 6.4, 2H, CH_2), 3.96 (s, 3H, OCH_3), 7.01 (s, 1H, CH), 7.08–7.13 (m, 3H, thienyl), 7.20–7.31 (m, 4H, ArH)	380 (50)
h	F	4-FC_6H_4	35	Oil	1723	1.25–1.52 (m, 2H, CH_2), 1.97 (t, *J* 6.2, 2H, CH_2), 2.50 (s, 3H, SCH_3), 2.58 (t, *J* 6.2, 2H, CH_2), 3.92 (s, 3H, OCH_3), 6.96 (s, 1H, CH), 7.05–7.16 (m, 4H, ArH), 7.22–7.36 (m, 3H, ArH).	410 (100)
i	F	4-ClC_6H_4	39	170	1728	1.26–1.58 (m, 2H, CH_2), 2.17 (t, *J* 6.2, 2H, CH_2), 2.56 (s, 3H, SCH_3), 2.68 (t, *J* 6.2, 2H, CH_2), 3.77 (s, 3H, OCH_3), 6.96 (s, 1H, CH), 7.16 (d, *J* 8.0, 2H, ArH), 7.28 (d, *J* 8.0, 2H, ArH), 7.35–7.54 (m, 3H, ArH).	426 (100)
j	F	4-BrC_6H_4	41	185	1718	1.25–1.48 (m, 2H, CH_2), 2.06 (t, *J* 6.0, 2H, CH_2), 2.50 (s, 3H, SCH_3), 2.59 (t, *J* 6.1, 2H, CH_2), 3.92 (s, 3H, OCH_3), 6.85 (s, 1H, CH), 7.13–7.22 (m, 4H, ArH), 7.26–7.39 (m, 3H, ArH).	471 (100)
k	F	3-ClC_6H_4	33	Oil	1728	1.23–1.49 (m, 2H, CH_2), 2.10 (t, *J* 6.2, 2H, CH_2), 2.51 (s, 3H, SCH_3), 2.59 (t, *J* 6.2, 2H, CH_2), 3.91 (s, 3H, OCH_3), 6.98 (s, 1H, CH), 7.09–7.27 (m, 4H, ArH), 7.32–7.44 (m, 3H, ArH).	426 (100)
l	F	2-Thienyl	33	Oil	1724	1.18–1.39 (m, 2H, CH_2), 2.01 (t, *J* 6.2, 2H, CH_2), 2.51 (s, 3H, SCH_3), 2.57 (t, *J* 6.2, 2H, CH_2), 3.90 (s, 3H, OCH_3), 6.95 (s, 1H, CH), 7.04–7.11 (m, 3H, thienyl), 7.19–7.47 (m, 3H, ArH).	398 (100)
m	F		31	Oil	1710	1.15–1.36 (m, 2H, CH_2), 2.08 (t, *J* 6.2, 2H, CH_2), 2.48 (s, 3H, SCH_3), 2.55 (t, *J* 6.2, 2H, CH_2), 3.68 (s, 3H, OCH_3), 6.96 (s, 1H, CH), 7.14–7.25 (m, 4H, ArH), 7.35–7.49 (m, 3H, ArH), 7.53–7.63 (m, 2H, imidazolyl), 7.91 (s, 1H, imidazolyl).	458 (100)
n	F		30	Oil	1724	1.25–1.49 (m, 2H, CH_2), 2.07 (t, *J* 6.2, 2H, CH_2), 2.45 (s, 3H, SCH_3), 2.53 (t, *J* 6.2, 2H, CH_2), 3.92 (s, 3H, OCH_3), 6.95 (s, 1H, CH), 7.16–7.28 (m, 3H, ArH), 7.42–7.56 (m, 3H, ArH), 7.99 (s, 1H, triazolyl).	459 (100)

[a] Uncorrected. [b] From KBr discs/concentrated liquid. [c] From $CHCl_3$.

Table 4 Physical and spectral data for compounds **14a**–**p** and **15a**–**l**

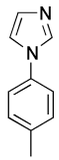
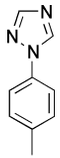
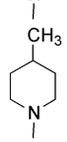
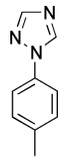
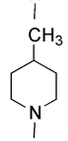
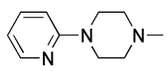
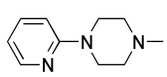
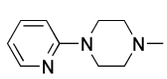
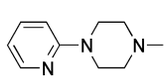
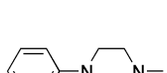
Compd	Ar	X	Y	Yield (%)	Mp/ °C[a]	ν_{max}[b]/ cm^{-1}	δ_H, *J*/Hz[c]	*m*/*z* (%)
14a	4-FC_6H_4	SMe	COOMe	42	125	1724	0.86 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 2.13 (s, 2H, CH_2), 2.51 (s, 3H, SCH_3), 2.80 (s, 4H, $2CH_2$), 3.31 (t, *J* 6.2, 2H, CH_2), 3.49 (t, *J* 6.2, 2H, CH_2), 3.86 (s, 3H, OMe), 6.93 (s, 1H, CH), 7.15–7.28 (m, 4H, ArH).	430 (63.5)
14b	4-ClC_6H_4	SMe	COOMe	49	145	1730	0.85 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 2.12 (s, 2H, CH_2), 2.53 (s, 3H, SCH_3), 2.81 (s, 4H, $2CH_2$), 3.31 (t, *J* 6.0, 2H, CH_2), 3.48 (t, *J* 6.0, 2H, CH_2), 3.94 (s, 3H, OMe), 7.06 (s, 1H, CH), 7.22 (d, *J* 8.0, 2H, ArH), 7.37 (d, *J* 8.0, 2H, ArH).	446 (100)
14c	4-$CH_3C_6H_4$	SMe	COOMe	52	140	1724	0.86 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 2.12 (s, 2H, CH_2), 2.41 (s, 3H, CH_3), 2.52 (s, 3H, SCH_3), 2.85 (s, 4H, $2CH_2$), 3.32 (t, *J* 6.4, 2H, CH_2), 3.53 (t, *J* 6.3, 2H, CH_2), 3.94 (s, 3H, OMe), 6.91 (s, 1H, CH), 7.17 (d, *J* 8.0, 2H, ArH), 7.26 (d, *J* 8.0, 2H, ArH).	426 (100)
14d	4-$CH_3OC_6H_4$	SMe	COOMe	54	121	1724	0.86 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 2.12 (s, 2H, CH_2), 2.49 (s, 3H, CH_3), 2.85 (s, 4H, $2CH_2$), 3.32 (t, *J* 6.2, 2H, CH_2), 3.52 (t, *J* 6.2, 2H, CH_2), 3.85 (s, 3H, OMe), 3.95 (s, 3H, OMe), 6.92 (s, 1H, CH), 7.17 (d, *J* 8.0, 2H, ArH), 7.26 (d, *J* 8.0, 2H, ArH).	442 (68)
14e	3-Cl, 4-FC_6H_3	SMe	COOMe	48	Oil	1726	0.85 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 2.13 (s, 2H, CH_2), 2.52 (s, 3H, CH_3), 2.85 (s, 4H, $2CH_2$), 3.33 (t, *J* 6.1, 2H, CH_2), 3.55 (t, *J* 6.2, 2H, CH_2), 3.94 (s, 3H, OMe), 6.69 (s, 1H, CH), 7.13–7.26 (m, 3H, ArH).	464 (52.3)
14f	3,4-$Cl_2C_6H_3$	SMe	COOMe	44	Oil	1726	0.84 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 2.17 (s, 2H, CH_2), 2.51 (s, 3H, SCH_3), 2.89 (s, 4H, $2CH_2$), 3.32 (t, 2H, *J* 6.0, CH_2), 3.49 (t, 2H, *J* 6.0, CH_2), 3.49 (t, *J* 6.0, 2H, CH_2), 3.94 (s, 3H, OMe), 7.04 (s, 1H, CH), 7.18–7.30 (m, 3H, ArH).	480 (56.3)
14g	2-Furyl	SMe	COOMe	48	Oil	1728	0.87 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 2.16 (s, 2H, CH_2), 2.52 (s, 3H, SCH_3), 2.88 (s, 4H, $2CH_2$), 3.13 (t, 2H, *J* 6.0, CH_2), 3.47 (t, 2H, *J* 6.0, CH_2), 3.94 (s, 3H, OMe), 7.04 (s, 1H, CH), 6.53–6.57 (m, 2H, furyl), 7.15 (s, 1H, furyl), 7.27 (s, 1H, furyl).	401 (100)
14h	4-Pyridyl	SMe	COOMe	51	133	1718	0.85 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 2.14 (s, 2H, CH_2), 2.52 (s, 3H, SCH_3), 2.88 (s, 4H, $2CH_2$), 3.31 (t, *J* 6.2, 2H, CH_2), 3.49 (t, *J* 6.2, 2H, CH_2), 3.98 (s, 3H, OMe), 7.06 (s, 1H, CH), 7.23 (d, *J* 7.9, 2H, pyridyl), 8.62 (d, 2H, *J* 7.9, pyridyl)	413 (34.9)
14i	2-Thienyl	SMe	COOMe	54	99	1724	0.88 (s, 3H, CH_3), 2.13 (s, 2H, CH_2), 2.51 (s, 3H, SCH_3), 2.89 (s, 4H, $2CH_2$), 3.37 (t, *J* 6.2, 2H, CH_2), 3.54 (t, *J* 6.2, 2H, CH_2), 3.93 (s, 3H, OMe), 7.02 (s, 1H, CH), 7.07–7.15 (m, 2H, thienyl), 7.36 (s, 1H, thienyl).	417 (32)
14j		SMe	COOMe	58	206	1724	0.84 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 2.19 (s, 2H, CH_2), 2.43 (s, 3H, SCH_3), 2.89 (s, 4H, $2CH_2$), 3.32 (t, *J* 6.2, 2H, CH_2), 3.48 (t, *J* 6.2, 2H, CH_2), 3.96 (s, 3H, OMe), 6.82 (s, 1H, CH), 7.28 (d, *J* 8.2, 2H, ArH), 7.44 (d, *J* 8.2, 2H, ArH), 7.76–8.11 (m, 2H, imidazolyl), 8.54 (s, 1H, imidazolyl).	478 (100)
14k		SMe	COOMe	56	222	1720	0.85 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 2.12 (s, 2H, CH_2), 2.52 (s, 3H, SCH_3), 2.90 (s, 4H, $2CH_2$), 3.31 (t, *J* 6.2, 2H, CH_2), 3.50 (t, *J* 6.2, 2H, CH_2), 3.96 (s, 3H, OMe), 7.11 (s, 1H, CH), 7.26 (d, *J* 8.2, 2H, ArH), 7.40 (d, *J* 8.2, 2H, ArH), 8.14 (s, 1H, triazolyl), 8.61 (s, 1H, triazolyl).	479 (100)
14l	1-Naphthyl	$N(CH_3)_2$	CN	52	162	2212	0.83 (d, *J* 2.56, 6H, $2CH_3$), 2.01–2.41 (m, 2H, CH_2), 2.50 (s, 2H, CH_2), 2.97 (s, 6H, $2NCH_3$), 3.11–3.27 (m, 2H, CH_2), 3.76 (d, *J* 2.38, 2H, OCH_2), 3.53 (d, *J* 2.34, 2H, OCH_2), 6.73 (s, 1H, ArH), 7.25–7.52 (m, 5H, ArH), 7.86–7.92 (m, 2H, ArH).	426 (100)
14m	1-Naphthyl		CN	47	166	2204	0.83 (d, *J* 4.0, 6H, $2CH_3$), 1.92–2.06 (m, 4H, $2CH_2$, pyrrolidinyl), 2.06–2.24 (m, 2H, CH_2), 2.45 (s, 2H, CH_2), 3.08–3.14 (m, 2H, CH_2), 3.46–3.48 (m, 4H, $2OCH_2$), 3.53–3.57 (m, 4H, $2NCH_2$, pyrrolidinyl), 6.49 (s, 2H, ArH), 7.36–7.55 (m, 5H, ArH), 7.85–7.91 (m, 2H, ArH).	452 (100)
14n	1-Naphthyl		CN	52	182	2215	0.83 (d, *J* 3.5 6H, $2CH_3$), 1.65–1.67 (m, 6H, $3CH_2$, piperidinyl), 2.05–2.26 (m, 2H, CH_2), 2.52 (s, 2H, CH2), 3.03–3.11 (m, 4H, $2NCH_2$, piperidinyl), 3.19–3.27 (m, 2H, CH_2), 3.47 (s, 2H, OCH_2), 3.53 (s, 2H, OCH_2), 6.78 (s, 1H, ArH), 7.30–7.56 (m, 5H, ArH), 7.86–7.92 (m, 2H, ArH).	466 (100)
14o	1-Naphthyl		CN	46	156	2216	0.83 (d, *J* 2.9, 6H, $2CH_2$), 0.95 (d, *J* 4.8, 3H, CH_3), 1.45–1.47 (m, 1H, piperidinyl), 2.08–2.24 (m, 2H, CH_2), 2.52 (s, 2H, CH_2), 2.70–2.90 (m, 4H, $2NCH_2$, piperidinyl), 3.11–3.27 (m, 2H, CH_2), 3.47 (s, 2H, OCH_2), 3.55 (s, 2H, OCH_2), 6.78 (s, 1H, ArH), 7.30–7.56 (m, 5H, ArH), 7.86–7.92 (m, 2H, ArH).	478 (100)

Table 4 (*Contd.*)

Compd	Ar	X	Y	Yield (%)	Mp/ °C[a]	ν_{max}[b]/ cm^{-1}	δ_H, *J*/Hz[c]	*m*/*z* (%)
14p	2-Naphthyl		CN	50	194	2195	0.85 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 1.94–2.0 (m, 4H, $2CH_2$, pyrrolidinyl), 2.20 (t, *J* 6.8, 2H, CH_2), 2.72 (s, 2H, CH_2), 3.07 (t, *J* 6.8, 2H, CH_2), 3.33 (d, *J* 11.4, 2H, CH_2), 3.30–3.60 (m, 6H, $3CH_2$), 6.51 (s, 1H, ArH), 7.37–7.56 (m, 3H, ArH), 7.73 (s, 1H, ArH), 7.82–7.89 (m, 3H, ArH).	452 (100)
15a	4-ClC_6H_4	SMe	COOMe	80	Oil	1726	2.56 (s, 3H, SCH_3), 2.62–2.73 (m, 2H, CH_2), 3.19 (s, 2H, CH_2), 3.92 (s, 3H, OCH_3), 3.95–4.01 (m, 2H, CH_2), 7.19 (s, 1H, CH), 7.34 (d, *J* 8.2, 2H, ArH), 7.94 (d, *J* 8.0, 2H, ArH).	340 (100)
15b	4-$CH_3C_6H_4$	SMe	COOMe	82	Oil	1722	2.43 (s, 3H, CH_3), 2.51 (s, 3H, SCH_3), 2.63–2.86 (m, 2H, CH_2), 3.63 (s, 2H, CH_2), 3.96 (s, 3H, OCH_3), 3.99–4.06 (m, 2H, CH_2), 7.14 (s, 1H, CH), 7.26 (d, *J* 8.2, 2H, ArH), 7.48 (d, *J* 8.2, 2H, ArH).	340 (48.3)
15c	4-$CH_3OC_6H_4$	SMe	COOMe	75	Oil	1726	2.51 (s, 3H, SCH_3), 2.62–2.78 (m, 2H, CH_2), 3.49 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 4.01–4.11 (m, 2H, CH_2), 7.02 (s, 1H, CH), 7.28 (d, *J* 8.2, 2H, ArH), 7.42 (d, *J* 8.2, 2H, ArH).	356 (75)
15d	3-Cl-, 4-FC_6H_3	SMe	COOMe	70	Oil	1724	2.53 (s, 3H, SCH_3), 2.63–2.79 (m, 2H, CH_2), 3.24 (s, 2H, CH_2), 3.96 (s, 3H, OCH_3), 3.98–4.04 (m, 2H, CH_2), 7.08 (s, 1H, CH), 7.21–7.36 (m, 3H, ArH).	378 (58)
15e	3,4-$Cl_2C_6H_3$	SMe	COOMe	68	Oil	1722	2.54 (s, 3H, SCH_3), 2.61–2.75 (m, 2H, CH_2), 3.21 (s, 2H, CH_2), 3.96 (s, 3H, OCH_3), 3.99–4.07 (m, 2H, CH_2), 6.99 (s, 1H, CH), 7.20–7.39 (m, 3H, ArH).	394 (75)
15f	2-Thienyl	SMe	COOMe	85	Oil	1724	2.50 (s, 3H, SCH_3), 2.60–2.73 (m, 2H, CH_2), 3.49 (s, 2H, CH_2), 3.94 (s, 3H, OCH_3), 3.99–4.08 (m, 2H, CH_2), 7.05 (s, 1H, CH), 7.18–7.28 (m, 2H, thienyl), 7.44 (s, 1H, thienyl).	332 (60)
15g		SMe	COOMe	68	Oil	1724	2.52 (s, 3H, SCH_3), 2.60–2.73 (m, 2H, CH_2), 3.48 (s, 2H, CH_2), 3.96 (s, 3H, $COOCH_3$), 3.99–4.08 (m, 2H, CH_2), 7.13 (s, 1H, CH), 7.28 (d, *J* 8.0, 2H, ArH), 7.59 (d, *J* 8.0, 2H, ArH), 8.31 (s, 1H, triazolyl), 8.56 (s, 1H, triazolyl).	393 (100)
15h	1-Naphthyl	$N(CH_2)_2$	CN	82	193	2213 1721	258–2.60 (m, 2H, CH_2), 3.04 (s, 6H, $2NCH_3$), 3.39 (t, *J* 6.68, 2H, CH_2), 3.80 (s, 2H, CH_2), 6.82 (s, 1H, ArH), 7.28–7.56 (m, 5H, ArH), 7.88–8.0 (m, 2H, ArH).	340 (100)
15i	1-Naphthyl		CN	84	210	2215 1716	1.89–1.96 (m, 4H, $2CH_2$, pyrrolidinyl), 2.46–2.53 (m, 2H, CH_2), 2.95 (s, 2H, CH_2), 3.33 (t, *J* 6.4, 2H, CH_2), 3.54–3.63 (m, 4H, $2NCH_2$, pyrrolidinyl), 6.50 (s, 1H, ArH), 7.31–7.48 (m, 5H, ArH), 7.79–7.85 (m, 2H, ArH).	366 (100)
15j	1-Naphthyl		CN	84	188	2216 1721	1.76–1.78 (m, 6H, $3CH_2$, piperidinyl), 2.42–2.52 (m, 2H, CH_2), 3.10 (s, 2H, CH_2), 3.16–3.17 (m, 4H, $2NCH_2$, piperidinyl), 6.89 (s, 1H, ArH), 7.30–7.48 (m, 5H, ArH), 7.79–7.85 (m, 2H, ArH).	380 (63)
15k	1-Naphthyl		CN	85	170	2214 1709	0.99 (d, *J* 5.4, 3H, CH_3), 1.55–1.70 (m, 1H, piperidinyl), 1.78–1.80 (m, 4H, $2CH_2$, piperidinyl), 2.54–2.63 (m, 2H, CH_2), 2.77–2.90 (m, 4H, $2NCH_2$, piperidinyl), 3.10 (s, 2H, CH_2), 3.39 (t, *J* 6.7, 2H, CH_2), 6.89 (s, 1H, ArH), 7.34–7.55 (m, 5H, ArH), 7.88–7.93 (m, 2H, ArH).	394 (100)
15l	2-Naphthyl		CN	86	206	2202 1715	1.98–205 (m, 4H, $2CH_2$, pyrrolidinyl), 2.54–2.60 (m, 2H, CH_2), 3.29–3.49 (m, 4H, $2CH_2$), 3.60–3.67 (m, 2H, $2CH_2$), 6.59 (s, 1H, ArH), 7.30–7.35 (m, 2H, ArH), 7.50–7.56 (m, 2H, ArH), 7.69 (s, 1H, ArH), 7.82–7.96 (m, 2H, ArH).	366 (100)

[a] Uncorrected. [b] From KBr discs/concentrated liquid. [c] From $CHCl_3$.

Table 5 Physical and spectral data for compounds **18a**–**h**

18	R′	—N(R)(R)	Ar	Yield (%)	Mp/ °C[a]	ν_{max}[b]/ cm^{-1}	δ_H, *J*/Hz[c]	*m*/*z* (%)
a	H		4-FC_6H_4	38	Oil	22173443	2.17 (t, *J* 6.0, 2H, CH_2), 2.53 (t, *J* 6.0, 2H, CH_2), 2.99 (t, *J* 6.1 4H, $2CH_2$), 3.45 (s, 2H, CH_2), 3.56 (t, 4H, $2CH_2$), 6.64 (s, 1H, CH), 7.09–7.20 (m, 4H, ArH), 7.26–7.50 (m, 3H, pyridyl), 8.02 (s, 1H, pyridyl), 8.22 (s, 1H, NH).	413 (100)
b	H		4-$CH_3C_6H_4$	35	152	22153437	2.09 (t, *J* 6.0, 2H, CH_2), 2.31 (s, 3H, CH_3), 2.74 (t, *J* 6.0, 2H, CH_2), 2.90 (t, *J* 6.0, 4H, $2CH_2$), 3.50 (s, 2H, CH_2), 3.62 (t, *J* 6.0 4H, $2CH_2$), 6.31 (s, 1H, CH), 7.04–7.18 (m, 4H, ArH), 8.24 (s, 1H, NH).	317 (100)
c	H		4-$CH_3C_6H_4$	38	168	22173347	2.17 (t, *J* 6.1, 2H, CH_2), 2.32 (s, 3H, CH_3), 2.78 (t, *J* 6.1, 2H, CH_2), 3.16 (t, *J* 6.1, 4H, $2CH_2$), 3.78 (s, 2H, CH_2), 4.03 (t, *J* 6.1, 4H, $2CH_2$), 6.48 (s, 1H, CH), 7.10–7.25 (m, 4H, ArH), 7.66–8.01 (m, 3H, pyridyl), 8.33 (s, 1H, NH).	410 (100)
d	H		3-Pyridyl	35	145	22193376	2.09 (t, *J* 6.1, 2H, CH_2), 2.95 (t, *J* 6.2, 2H, CH_2), 3.08 (t, *J* 6.2, 4H, $2CH_2$), 3.67 (s, 2H, CH_2), 3.97 (t, *J* 6.2, 4H, $2CH_2$), 6.64 (s, 1H, CH), 7.49–7.54 (m, 4H, pyridyl), 7.98–8.26 (m, 3H, pyridyl), 8.45 (s, 1H, NH).	397 (100)
e	*n*-C_3H_7		C_6H_5	34	148	2217	0.78 (t, *J* 6.0, 2H, CH_2), 2.09 (t, *J* 6.2, 2H, CH_2), 2.31–2.40 (m, 3H, CH_3), 2.47 (s, 2H, CH_2), 2.68 (t, *J* 6.0, 2H, CH_2), 3.08 (t, *J* 6.1, 4H, $2CH_2$), 3.48 (s, 2H, CH_2), 4.04 (t, *J* 6.1, 4H, $2CH_2$), 6.45 (s, 1H, CH), 7.05–7.27 (m, 5H, ArH), 7.89–8.25 (m, 3H, pyridyl).	438 (100)
f	*n*-C_3H_7		2-Benzofuryl	31	172	2219	0.94 (t, *J* 6.1, 2H, CH_2), 2.17 (t, *J* 6.1, 2H, CH_2), 2.47 (s, 2H, CH_2), 2.51–2.59 (m, 3H, CH_3), 2.85 (t, *J* 6.2, 2H, CH_2), 3.28 (t, *J* 6.2, 4H, $2CH_2$), 3.78 (s, 2H, CH_2), 4.07 (t, *J* 6.2, 4H, $2CH_2$), 6.49 (s, 1H, furyl), 6.54 (s, 1H, CH), 7.27–7.39 (m, 4H, ArH), 7.82–8.20 (m, 3H, pyridyl).	478 (100)
g	$(CH_2)_2C_6H_5$		4-$CH_3C_6H_4$	30	184	2205	2.10 (t, *J* 6.1, 2H, CH_2), 2.32 (s, 3H, CH_3), 2.59–2.74 (m, 6H, $3CH_2$), 2.99 (t, *J* 6.1, 4H, $2CH_2$), 3.47 (s, 2H, CH_2), 3.54 (t, *J* 6.1, 4H, $2CH_2$), 6.30 (s, 1H, CH), 7.15–7.48 (m, 9H, ArH).	331 (100)
h	$(CH_2)_2C_6H_5$		C_6H_5	32	134	2208	2.17 (t, *J* 6.1, 2H, CH_2), 2.80–2.95 (m, 2H, CH_2), 3.10–3.22 (m, 6H, $3CH_2$), 3.29 (t, *J* 6.1, 4H, $2CH_2$), 4.86 (s, 2H, CH_2), 6.45 (s, 1H, CH), 7.17–7.46 (m, 10H, ArH).	422 (100)

[a] Uncorrected. [b] From KBr discs/concentrated liquid. [c] From $CHCl_3$.

Synthesis of 8-aryl-5,6-disubstituted-3,4-dihydro-1*H*-isothiochromene (20a–e)

General procedure. A solution of 6-aryl-3,4-disubstituted-2*H*-pyran-2-one (**13**) (1 mmol), and tetrahydrothiopyran-4-one (**19**) (1 mmol) in dry DMF (12 mL) was stirred in the presence of powdered KOH (1 mmol) at room temperature for 25 h. After completion of the reaction, the mixture was poured into ice–water and neutralized with 10% HCl. The solid obtained was filtered and purified by column chromatography eluting with $CHCl_3$: hexane (1 : 1).

All the synthesized compounds are listed in Table 6 with their relevant data.

Synthesis of 7-aryl-9,10-disubstituted-6*H*-benzo[*c*]thiochromene (22a–c)

General procedure. The reaction mixture of 6-aryl-3,4-disubstituted-2*H*-pyran-2-one (**13**) (1 mmol), thiochroman-4-one (**21**) (1 mmol) and powdered KOH (1 mmol) in dry DMF (15 mL) was stirred at room temperature for 30 h. After completion of the reaction, the mixture was poured into ice–water and neutralized with 10% HCl. The solid obtained was filtered and purified by column chromatography eluting with $CHCl_3$: hexane (1 : 1).

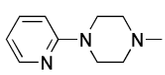
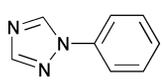
All the synthesized compounds are listed in Table 6 with their spectroscopic data.

Synthesis of 7-aryl-4,5-disubstituted-2,3-dihydro-1-benzothiophene (24a–d)

General procedure. A solution of 6-aryl-3,4-disubstituted-2*H*-pyran-2-one (**13**) (1 mmol), tetrahydrothiophen-3-one (**23**) (1 mmol) in dry DMF (12 mL) was stirred at room temperature in the presence of powdered KOH (1 mmol) for 25 h. After this time the reaction mixture was poured into ice–water and neutralized with 10% HCl. The solid was filtered and purified on a silica gel column eluting with $CHCl_3$: hexane (1 : 2).

The compounds synthesized are listed in Table 6 with their physical constants and spectroscopic data.

Table 6 Physical and spectral data for compounds **20a**–**e**, **22a**–**c** and **24a**–**e**

Compd	X	Y	Ar	Yield (%)	Mp/ °C[a]	ν_{max}[b]/ cm^{-1}	δ_H, *J*/Hz[c]	*m*/*z* (%)
20a	CN		4-Cl·C_6H_4	35	125	2218	1.96–2.02 (m, 4H, CH_2), 2.92 (t, *J* 6.0, 4H, $2CH_2$), 3.45 (s, 2H, CH_2), 3.60 (t, *J* 6.0, 4H, $2CH_2$), 6.46 (s, 1H, CH), 7.22 (d, *J* 8.8, 2H, ArH), 7.41 (d, *J* 8.8, 2H, ArH).	354 (100)
20b	CN		4-CH_3·C_6H_4	40	115	2215	1.94–2.05 (m, 4H, $2CH_2$), 2.40 (s, 3H, CH_3), 2.91 (t, *J* 6.1, 4H, $2CH_2$), 3.26 (s, 2H, CH_2), 3.51 (t, *J* 6.1, 4H, $2CH_2$), 6.47 (s, 1H, CH), 7.09 (d, *J* 8.8, 2H, ArH), 7.26 (d, *J* 8.8, 2H, ArH).	334 (100)
20c	CN		3-Pyridyl	38	135	2212	1.97–2.03 (m, 4H, $2CH_2$), 2.92 (t, *J* 6.0, 4H, $2CH_2$), 3.25 (s, 2H, CH_2), 3.35 (t, *J* 6.0, 4H, $2CH_2$), 6.43 (s, 1H, CH), 7.36–7.60 (m, 2H, pyridyl), 8.58 (s, 1H, pyridyl), 8.65 (s, 1H, pyridyl).	321 (100)
20d	CN		2-Benzofuryl	41	110	2218	1.99–2.07 (m, 4H, $2CH_2$), 3.20 (t, *J* 6.1, 4H, CH_2), 3.59 (s, 2H, CH_2), 4.09 (t, *J* 6.1, 4H, $2CH_2$), 6.54 (s, 1H, furyl), 6.77 (s, 1H, CH), 7.26–7.32 (m, 4H, ArH), 8.33–8.37 (m, 3H, pyridyl).	454 (100)
20e	COOMe	SMe		30		1710	2.47 (s, 3H, SCH_3), 2.88–2.99 (m, 4H, $2CH_2$), 3.58 (s, 2H, CH_2), 3.98 (s, 3H, OMe), 7.1 (s, 1H, CH), 7.46 (d, *J* 8.26, 2H, ArH), 7.78 (d, *J* 8.26, 2H, ArH), 8.15 (s, 1H, triazolyl), 8.55 (s, 1H, triazolyl).	397 (100)
22a	CN		4-BrC_6H_4	40	230	2203	2.03 (t, *J* 6.1, 4H, $2CH_2$), 3.53 (s, 2H, CH_2), 3.63 (t, *J* 6.1, 4H, $2CH_2$), 6.62 (s, 1H, CH), 7.26–7.42 (m, 4H, ArH), 7.51–7.64 (m, 4H, ArH).	447 (100)
22b	CN		3,4-$Cl_2C_6H_3$	53	245	2205	2.04 (t, *J* 6.1, 4H, $2CH_2$), 3.52 (s, 2H, CH_2), 3.62 (t, *J* 6.1, 4H, $2CH_2$), 6.59 (s, 1H, CH), 7.18–7.32 (m, 4H, ArH), 7.49–7.60 (m, 3H, ArH).	437 (100)
22c	COOEt	OH	4-ClC_6H_4	20		1607	1.26 (t, *J* 6.2, 3H, CH_3), 3.55 (s, 2H, CH_2), 4.16 (q, *J* 6.1, 2H, CH_2), 7.1 (s, 1H, ArH), 7.26–7.31 (m, 4H, ArH), 7.39–7.44 (m, 2H, ArH), 7.74 (m, 2H, ArH).	396 (48.7)
24a	CN		C_6H_5	38	130	2201	1.88–2.06 (m, 4H, $2CH_2$), 3.31 (t, *J* 6.2, 4H, $2CH_2$), 3.62 (t, *J* 6.1, 4H, $2CH_2$), 6.51 (s, 1H, CH), 7.22–7.45 (m, 5H, ArH).	306 (100)
24b	CN		4-ClC_6H_4	36	170	2201	1.76–2.00 (m, 4H, $2CH_2$), 3.32 (t, *J* 6.1, 4H, $2CH_2$), 3.58 (t, *J* 6.1, 4H, $2CH_2$), 6.46 (s, 1H, CH), 7.22 (d, *J* 9.0, 2H, ArH), 7.45 (d, *J* 9.0, 2H, ArH).	340 (100)
24c	CN		4-BrC_6H_4	35	150	2203	1.72–1.99 (m, 4H, $2CH_2$), 3.33 (t, *J* 6.2, 4H, $2CH_2$), 3.57 (t, *J* 6.2, 4H, $2CH_2$), 6.45 (s, 1H, CH), 7.38 (d, *J* 8.8, 2H, ArH), 7.56 (d, *J* 8.8, 2H, ArH).	385 (100)
24d	COOEt	SCH_3	4-ClC_6H_4	30	Oil	1717	1.41 (t, *J* 7.17, 3H, CH_3), 2.44 (s, 3H, SCH_3), 3.31–3.43 (m, 4H, $2CH_2$), 4.43 (q, *J* 7.18, 2H, CH_2), 7.1 (s, 1H, ArH), 7.46 (m, 4H, ArH).	364 (64)

[a] Uncorrected. [b] From KBr discs/concentrated liquid. [c] From $CHCl_3$.

Acknowledgements

We thank ICMR and CSIR for their financial support.

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39 Crystal data for **8f**: $C_{29}H_{22}ClF_2N_3O_4$, M = 386, triclinic, $P\bar{1}$, a = 9.372(1) Å, b = 11.433(1) Å, c = 11.527(1) Å, α = 66.83(1)°, β = 79.60(1)°, γ = 89.35(1)°, V = 1114.41(18) Å^3, Z = 2, D_c = 1.152 g cm^{-3}, μ(Mo-Kα) = 0.067 mm^{-1}, F(000) = 420.0, colorless rectangular crystal, size 0.30 × 0.20 × 0.075 mm, 4557 reflections measured (R_{int} = 0.03), 3794 unique, R_w = 0.192 for all data, conventional R = 0.08 [$(\Delta/\sigma)_{max}$ = 0.000] on F values of 1583 reflections with $I > 2\sigma(I)$, S = 1.039 for all data.
Crystal data for **14k**: $C_{26}H_{29}O_4N_3S$, monoclinic, space group $P2_1/n$, a = 8.622(1) Å, b = 14.255(1) Å, c = 20.537(2) Å, β = 95.83(1)°, V = 2511.1(4) Å^3, Z = 4, μ(Mo-Kα) = 0.17 mm^{-1}, D_c = 1.269 g cm^{-3}, F(000) = 1016, 6078 reflections measured, 4412 unique data (R_{int} = 0.0173). R = 0.0511 for 3205 reflections with $I > 2\sigma(I)$ [wR_2 = 0.1492, $(\Delta/\sigma)_{max}$ = 0.000, S = 1.054, 312 parameters].
Unit cell determination and intensity data collection (2θ = 50°) for both **8f** and **14k** were performed on a Bruker P4 diffractometer at 293(2) K. The structure was solved by direct methods with refinement by full-matrix least-square methods on F^2. Programs: XSCANS [Siemens Analytical X-ray Instruments Inc.; Madision, Wisconsin, USA 1996], SHELXTL-NT [Bruker AXS Inc.; Madision, Wisconsin, USA 1997]. Further details of the crystal structure investigation can be obtained form the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, UK CB2 1EZ. CCDC reference numbers 175565 and 182396.
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