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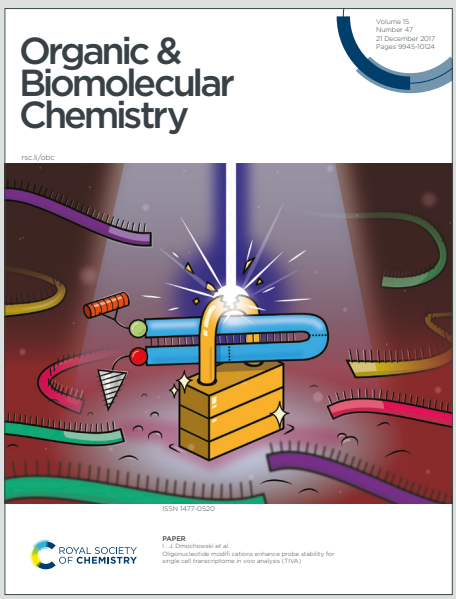

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ARTICLE

Transition metal free synthesis of sterically hindered allylarenes from 5-hexene-2-one

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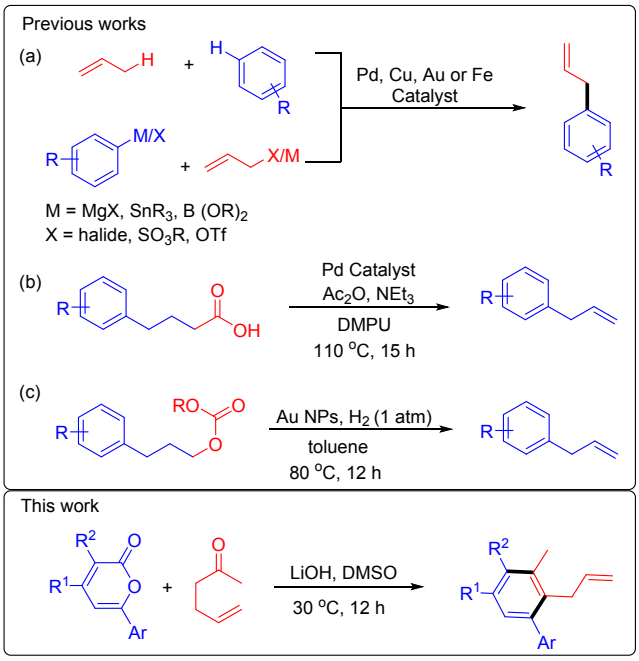
A simple, efficient and transition metal-free strategy was established for the synthesis of highly functionalized, sterically hindered allylarenes (**6,7 & 8**) by base mediated ring transformation of 2-oxo-6-aryl-4-(methylthio/sec.amino)-2*H*-pyran-3-carbonitriles (**3/4**) with 5-hexene-2-one (**5**). This provides a method for the synthesis of allylarenes functionalized with different electron donating and withdrawing groups in one pot. The structures of isolated products **6c** and **7a** were ascertained by spectroscopic and single crystal X-ray diffraction analyses. In addition, we have performed a molecular docking study to predict the biological activity of synthesized molecules as estrogen receptor alpha (ERα)and estrogen receptor beta (ERβ).

Introduction

Allylarenes are present as core or sub-structure in various naturally abundant compounds throughout the plant kingdom and serve to all aspects of plant responses toward abiotic and biotic stimuli and defend against herbivores and pathogens.[1] *Ortho* and *meta* substituted allylarenes are significantly used in flavour and perfume industry, pharmacological, cosmetic, material chemistry and also used as synthetic precursors or intermediates or catalysts for the synthesis of complex products.[1,2] Allylarenes are also used as chain-transfer agents in radical polymerization reactions due to presence of labile C-H bond at the α-position relative to the allylic double bond.[3] Regioselective allylation of multifunctional arenes by Friedel-Craft reaction could not be a good choice due to poor selectivity between ortho- and para- position.[4] In addition, over allylation and good reactivity of double bond also cannot be ignored.[5] Recently, various metal catalyzed cross coupling strategy for allyl-aryl bond formation have used to afford various substituted allylbenzene. Palladium and iron catalyzed synthesis of allylarenes by using Grignard reagents are well studied among them,[6] but very high nucleophilicity of Grignard reagents limits the utility of this method. Kaufman's group synthesized allylarenes via Stille coupling of allyltributylstannane and aryl halide.[7] Varma et al. and Gerbino et al. separately reported the Suzuki–Miyaura aryl-allyl coupling to afford allylarenes.[8]

Scheme 1. Earlier approaches versus our approach for the synthesis of allylarenes.



Recently, rhodium catalyzed C-H bond activation strategy was used for the synthesis of alkenylarenes.[9] Noujima et al. prepared allylarenes by Au/HT catalyzed hydrogenolysis of 3-arylallylic carbonates in toluene at 60 °C under 1 atm. pressure of H_2.[10] Chatterjee et al. reported the synthesis of allylarenes by palladium catalyzed decarbonylative dehydration of 4-

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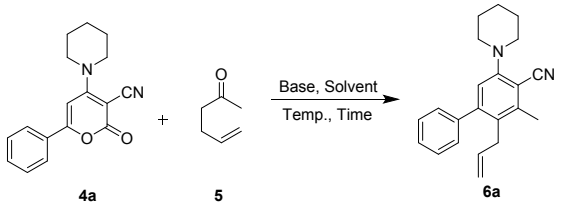
arylbutanoic acid.[11] Although excellent yield was observed, the requirement of transition metal catalyst and specific allyl carbonate substrates limits the scope of this method. In addition, most of the reported metal catalyzed protocols till date require special reaction conditions and expensive and toxic reagents to afford less hindered allylarenes. Herein, we wish to report a transition metal free, base mediate ring transformation strategy for the synthesis of highly hindered allylarenes from easily accessible suitably functionalized 2*H*-pyran-2-ones and 5-hexene-2-one.

Result and discussion

Suitably functionalized 2*H*-pyran-2-ones and ketene dithioacetals have been widely explored for the assembly of several important moieties.[12] Therefore, based on our past research experience, we planned to synthesize 3-allyl-4-aryl-2-methyl-6-(*sec.*amine)-benzonitriles (**6**) via 1,6-conjugate addition of thermally stable enolate of 5-hexene-2-one (**5**) on

Table 1. Optimization of the reaction conditions 4[a]



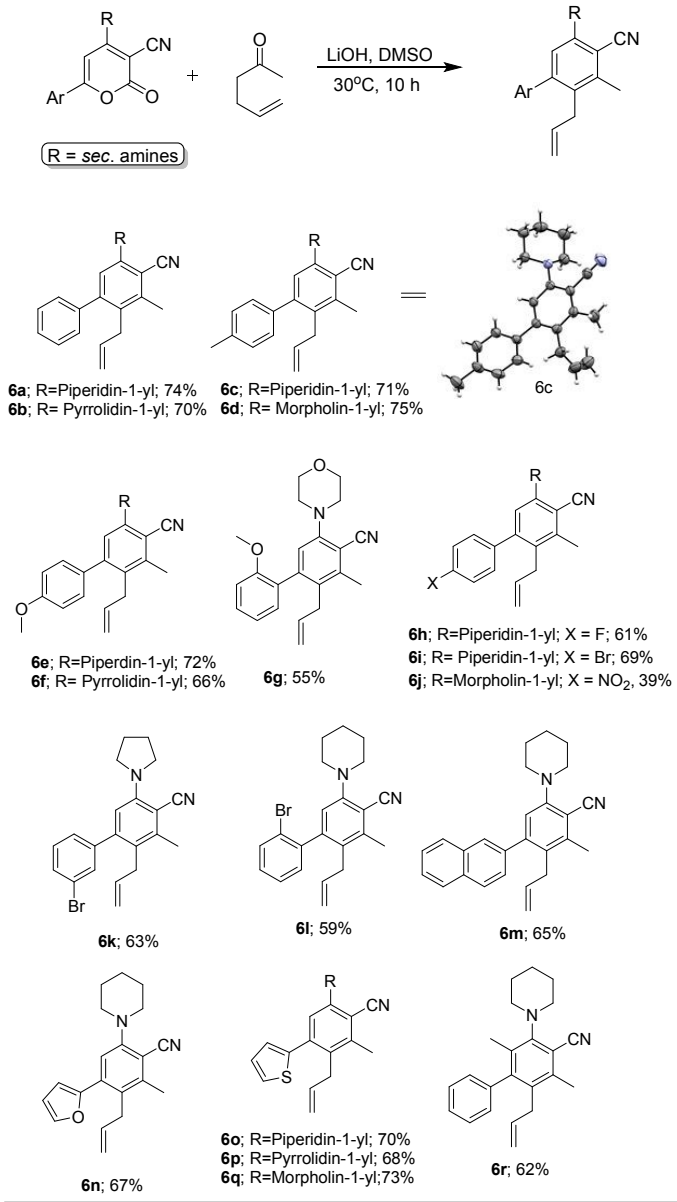
Entry	Base	Solvent	Temp.(°C)	Time (h)	Yield (%)[b]
1	KOH	DMF	30	12	58
2	NaH	DMF	30	12	54
3	$NaNH_2$	DMF	30	12	51
4	Cs_2CO_3	DMF	30	15	32[c]
5	LiOH	DMF	30	12	67
6	NaOH	DMF	30	12	61
7	*t*-BuOK	DMF	30	12	59
8	LiOH	DMSO	30	12	74
9	NaOH	DMSO	30	12	65
10	LiOH	MeCN	30	12	43
11	LiOH	THF	30	12	34c
12	LiOH	EtOH	70	12	Mix.[d]
13	LiOH	EG[e]	70	12	Mix.[d]
14	LiOH	DMSO	60	8	67
15	LiOH	DMSO	0	12	52[c]

(a) All reactions were carried out by stirring **4a** (0.5 mmol) and 5-hexen-1-one (**5**, 0.75 mmol, 1.5 equiv.); (b) Isolated yield after purification by column chromatography; (c) Incomplete reaction; (d) Mix. stands for inseparable mixture of several products and starting materials; (e) EG stands for Ethylene Glycol.

2-oxo-6-aryl-4-(*sec.*amino)-2*H*-pyran-3-carbonitriles (**4**) followed by intramolecular decarboxylative cyclization. The required precursor **4** was synthesized by reaction of methyl 2-cyano/carbomethoxy-3,3-bis(methylthio)acrylates (**1**) and aryl methyl ketones (**2**) in DMSO under basic condition followed by reflux of obtained 2*H*-pyranone (**3**) with different secondary amines in ethanol (see SI).

2-Oxo-4-(piperidin-1-yl)-6-(phenyl)-2*H*-pyran-3-carbonitrile (**4a**) and 5-hexene-2-one (**5**) was chosen as model substrates for optimization of reaction condition to afford functionalized allylarenes. We commenced the optimization by using KOH in DMF at 30 °C and 58% of product **6a** was obtained after 12 hours (Table 1, entry 1).

Scheme 2.Synthesis of various functionalized allylarenes **6**.



Further, several other bases were screened for the optimization of reaction condition. Stronger bases NaH and $NaNH_2$ provided lower yield of desired product, while weaker base like Cs_2CO_3 was not able to complete the reaction even in 15 hours (Table 1, entries 2-4). The reaction was further carried out in DMF using NaOH, LiOH and *t*-BuOK as a base and the combination of LiOH/DMF was found to be the best (Table 1, entries 5-7). Different solvents were also screened using

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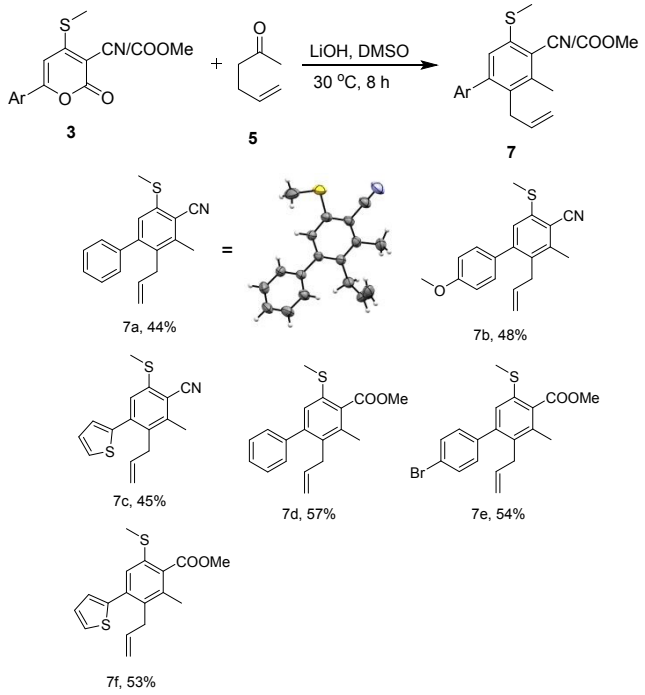
LiOH as a base and DMSO was found as the best solvent amongst them (Table 1, entry 8). Use of acetonitrile and THF gives lower yield of the product (Table 1, entries 10-11). Other solvents like ethanol and ethylene glycol were inefficient for this reaction and inseparable mixture of several products formed (Table 1, entries 12-13). The structures of the compounds were confirmed by ^{1}H and ^{13}C NMR and mass spectrometry data. Structure of compound **6c** is also confirmed by single crystal X-ray.[13]

The substrate scope was explored and presented in scheme 2, where various 2*H*-pyran-2-ones **4** were efficiently converted into desired products **6a-r** in good yield. Synthesis of halide bearing allylarenes via regioselective cross coupling reaction is always an issue for synthetic chemists. However, we have successfully afforded halogen bearing allylarenes **6h**, **6i**, **6k** and **6l** in good yield without any difficulties. The halide group was well tolerated under optimized reaction condition and complex allylarene can be afforded.

Scheme 3. Synthesis of –SMe bearing allylarenes **7**.



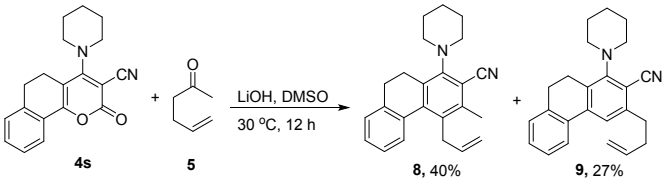
The electronic nature of aryl or heteroaryls group present at C-6 of 2*H*-pyran-2-ones did not affect the yield of the product significantly, while strong electron withdrawing group like $-NO_2$ (**6j**) significantly lower the yield. In addition, presence of sterically hindered aryl group slightly lower the yield (entry **6g** and **6l**), whereas different *sec.*amine substituents at C-4 position of the pyran ring had negligible effect on the yield. This synthetic methodology shows great functional group tolerance like amine, aryl, haloaryl and heteroaryl etc.

In the continuation, we also explored this method for the synthesis of -SMe bearing allylarenes (**7a-f**) by using 4-(methylthio)-2*H*-pyran-2-ones **3**. Structure of compound **7a** was confirmed by single crystal X-ray.[13] In addition, the feasibility of the reaction was also examined with 3-carbomethoxy-6-aryl-4-methylsulfanyl-2*H*-pyran-2-ones, which resulted up to 44-57% yield of allylarenes (**7e-f**).

To explore the efficacy of present protocol, 3,4-disubstituted 5,6-dihydro-2*H*-benzo[*h*]chromen-2-one (**4s**) were treated with 5-hexene-2-one. Surprisingly, two inseparable isomeric products **8** (40%) and **9** (27%) were obtained. We proposed that C-10b position of **4s** is relatively more hindered due to restricted rotation of bridge phenyl group, which reduce the possibility of nucleophilic attack of larger nucleophile at C-10b position. Compound **5** can provides two enolates from either side of carbon of carbonyl group and two different products may be isolated with different chemoselectivity based on the size of nucleophiles (1^{o} versus 2^{o} carbanion) and reaction condition. The polarity difference between products are not enough to separate them, however their structure and yield were assigned by proton NMR of mixture (see ESI). Mechanistically, base could generate two carbanion **5a** and **5b** as kinetic and thermodynamic controlled enolates. If the reaction is initiated by attack of thermodynamically stable enolate (**5b**) at C-6/C-10b position of 2-pyranones/2H-chromene-2-one (**3** and **4**), it forms new C-C bond though Michael addition. This leads decarboxylative ring opening followed by protonation to afford intermediate **C**. Further, in presence of excess of base, intermediate **C** undergoes intramolecular cyclization to afford **D**. At last, a base promoted elimination of water provides aromatization to generate the product **6**.

In case of 5,6-dihydro-2*H*-benzo[*h*]chromone **4s**, the reaction involves both kinetic as well as thermodynamic controlled enolates (**5a** & **5b**). When reaction is initiated from kinetically controlled carbanion **5a,** it provides intermediate **A** by Michael addition followed by decarboxylation. Intermediate **A** undergoes cyclization by involving C-3 of chromene-2-ones and carbonyl carbon of ketone to afford intermediate **B**, which produces the compound **9** after aromatization. The reaction of **4s** and **5b** results the product **8** by following the similar reaction pathway as for **6a**.

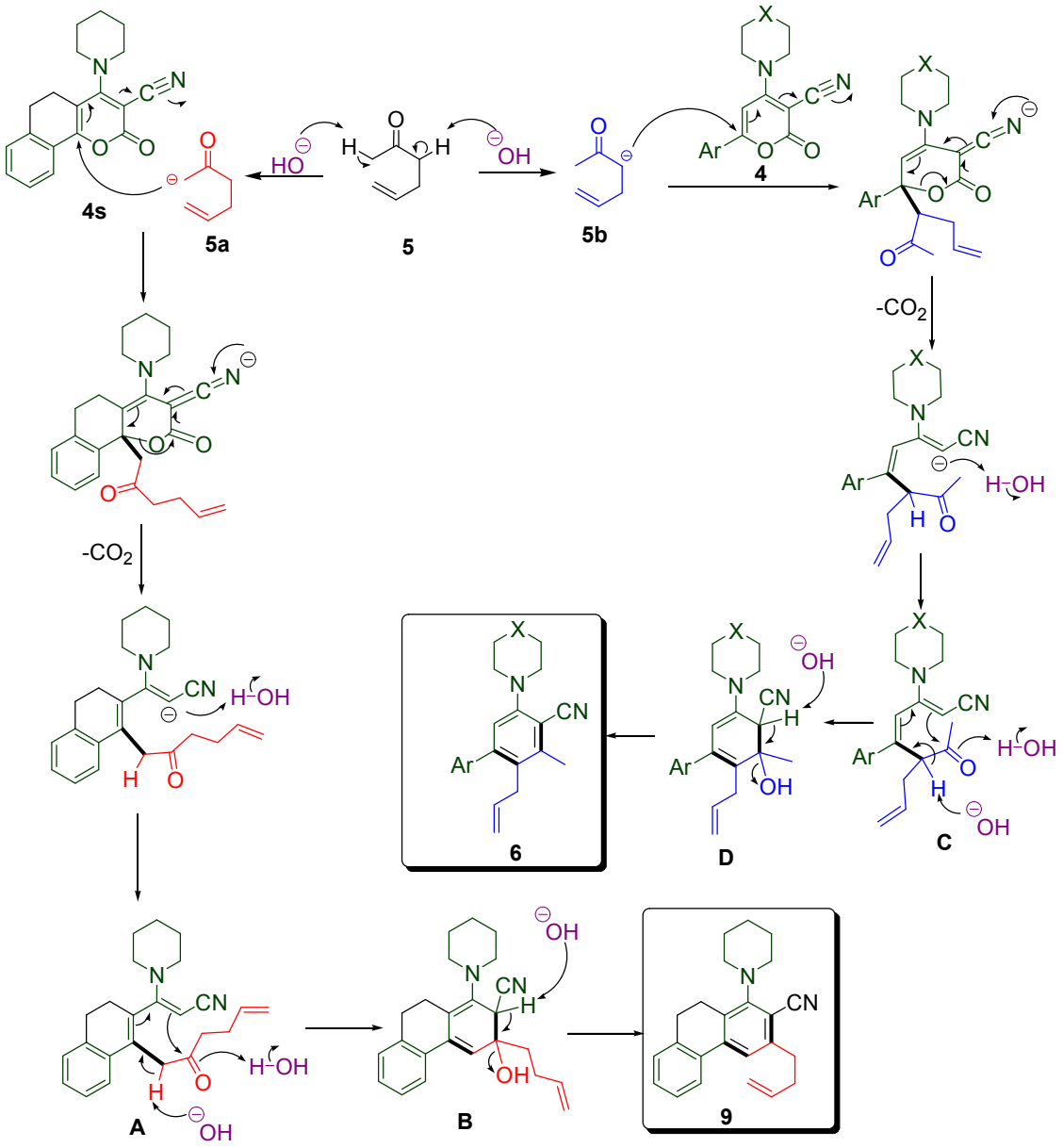
Scheme 4. Reaction of 2-oxo-4-(piperidin-1-yl)-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitrile (**4s**) with 5-hexene-2-one.



These synthesized allylarenes contain different synthetically important functional groups such as nitrile, ester, aromatic halides and thiomethyl groups. These groups can be further modified to attain other important products which are demonstrated in scheme **7**. An intramolecular Heck reaction of **6l** provided 84% of 1,9-dimethyl-3-(piperidin-1-yl)-phenanthrene-2-carbonitrile (**10**) in presence of $Pd(OAc)_2$ and Cs_2CO_3 in toluene. In order to, synthesize phenanthrene by dehydrogenative coupling, compound **6d** was treated with

$Pd(OAc)_2$, $PhI(AcO)_2$ and K_3PO_4 in toluene at 60 °C for 12 hours but this reaction provides isomerized product 3,4'-dimethyl-5-morpholino-2-(prop-1-en-1-yl)-[1,1'-biphenyl]-4-carbonitrile (**11**) in excellent yield. Isomerization of allylarenes to styrenes was also reported by heating with alcoholic solution of *t*-BuOK.[14] As reported, treatment of allylarene **6d** with 1.5 equivalent of *t*-BuOK in *t*-BuOH for 12 hours at 90 °C provides

Scheme 5. Plausible mechanism for the synthesis of **6** and **9**.



isomerized analogous **11** in 78% yields. However, 4 equivalent of *t*-BuOK in *t*-BuOH at 110 °C concurrently attack on nitrile group to convert them into corresponding amide (**12a-b)** in good yield. The oxidation of thioethers and alkene to corresponding sulfoxides and epoxides are well known with *m*-CPBA. H_2O_2 was often used for selective oxidation of thioethers in presence of C-C double bond.[15] However, the chemoselectivity of *m*-CPBA in presence of both functional group thioether and alkene were unmapped. Herein, we observed selective oxidation of thioether to corresponding sulfoxide to afford 2-allyl-5-methanesulfinyl-3-methyl-biaryls **13a-c** in excellent yield.

Scheme 6. Synthetic utility of multi-substituted allylarenes

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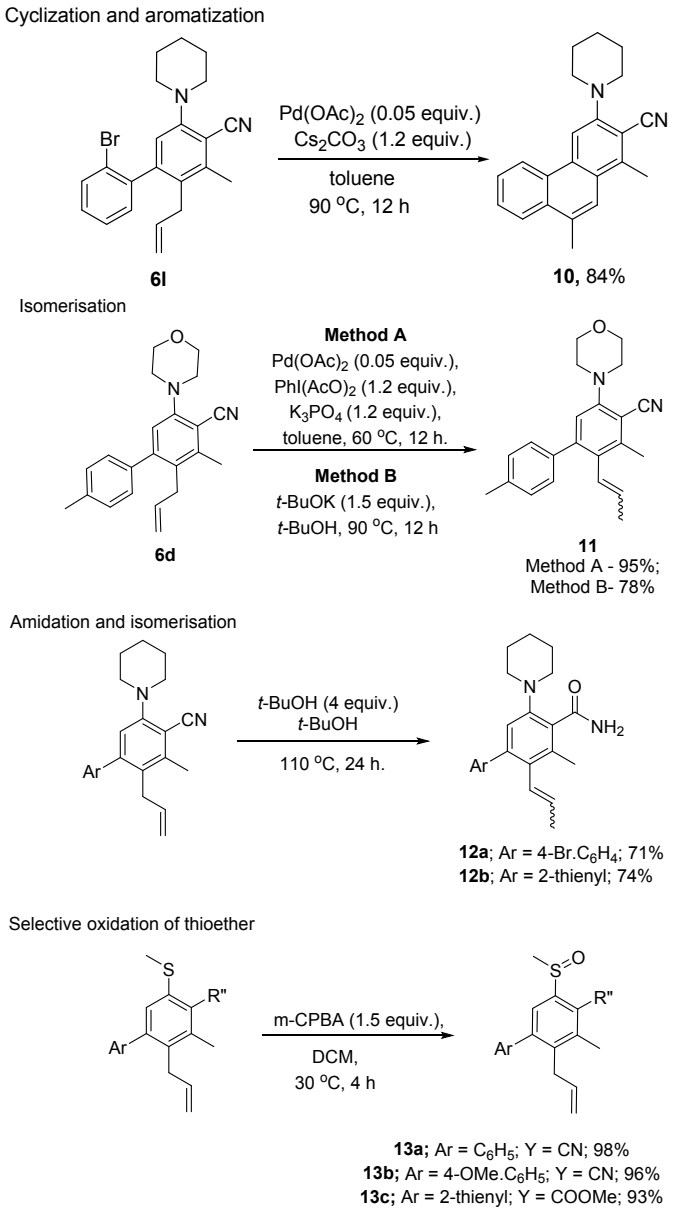

These class of compounds known to exhibit the estrogen receptor alpha (ERα) and estrogen receptor beta (ERβ) binding affinity depending on the substitution pattern.[16,17]

Molecular docking methods are mainly applied to predict the binding affinity between the ligand and target protein through the identification of precise conformation of ligands in the binding pocket of any protein.[18]

To elucidate the binding mechanism of newly synthesized compounds with ERα (PDB ID: 2I0J) and ERβ (PDB ID: 2I0G), a molecular docking simulation was performed using GLIDE module. The binding interaction of most active compound **7f** and **7d** showed that both fits well in the binding pockets of crystal structures of ER subtypes. The results clearly indicate that the compounds **7f** and **7d** exhibited significant binding affinities towards ERα (Glide energy -55.11 kcal mol^{-1} and -52.21 kcal mol^{-1}) and ERβ (Glide energy -58.95 kcal mol^{-1} and -57.14 kcal mol^{-1}) respectively (see SI; Table S2)**.** The best binding mode of **7f** in the binding site is stabilized with two H-bond interactions with His524, and Leu525 and **7d** is stabilized with three H-bond interactions with His475, Leu476, and Thr299. Along with these interactions, the Phe404 and Phe356 established π-π interaction with thienyl ring of **7f** at the 3.2 Å and 2.9 Å distance, while Phe404 and Phe356 stacked against

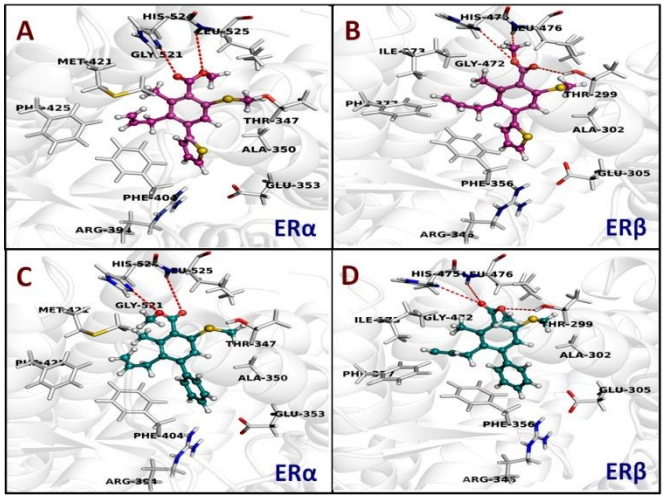

Figure 1. Docking analysis into ERα and ERβ: (A) docking of **7f** (pink) into ERα; (B) docking of **7f** (pink) into ERβ; (C) docking of **7d** (green) into ERα; (D) docking of **7d** (green) into ERβ. The residues are shown with sticks and compound **7f** and **7d** is shown in ball and stick model. Hydrogen bonds are shown as broken lines (red).

phenyl ring of **7d** showing favourable π-π interaction at 3.1 Å and 2.7Å in ERα and ERβ respectively (**Figure. 1**). Binding site residues Thr347, Ala350, Glu353, Arg394, Phe404, Met421, Phe425, Gly521, His524 and Leu525 are involved in hydrophobic interactions with active compounds in ERα and Thr299, Ala302, Glu305, Arg346, Phe356, Met294, Phe377, Gly472, His475 and Leu476 are involve in ERβ respectively. The in silico study confirm that compound **7f** and **7d** are strongly interacting and shows the same interactions in the binding sites with significant binding affinities for both ERs subtypes. These results suggest that these molecules may be further studied as estrogen receptor alpha (ERα) and estrogen receptor beta (ERβ). These molecules are under investigation for further results.

Conclusions

A simple, base mediate strategy was developed for the synthesis of highly functionalized sterically hindered allylarenes by ring transformation of 2-oxo-6-aryl-4-(methylthio/sec.amino)-2*H*-pyran-3-carbonitriles with 5-hexene-2-one. Interestingly, ring transformation of 2-oxo-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitrile with 5-hexene-2-one provides mixture of allylated 9,10-dihydrophenanthrene and (but-3-en-1-yl)-9,10-dihydrophenanthrene under the similar reaction conditions. These reactions suggest that reactivity of 5-hexene-2-one is also dependent on the nature of substrates used. This reaction had very good functional group tolerance, which is limitation for metal catalyzed approaches. In addition, this method is superior over other

methods as sterically hindered allylarenes are afforded under mild reaction conditions. The synthesized compounds have further synthetic potential and explored to achieve other important molecules. We have successfully achieved the functionalized phenanthrenes by intramolecular Heck cyclization. Other functional group modification was also carried out successfully, which enhances the importance of synthesized molecules.

We also performed the molecular docking study of synthesized molecules and found that they exhibit good estrogen receptor alpha (ERα) and estrogen receptor beta (ERβ) binding affinity.

Experimental

General

We used commercially available reagents and solvents from Alfa Aesar, Spectrochem, Sigma Aldrich, Fischer Scientific and TCI without any further purification. ^{1}H and ^{13}C NMR spectra were recorded by using a 400 MHz and 100 MHz NMR spectrometer respectively, and $CDCl_3$ (from Eurisotop) was used as solvent. Chemical shifts for all the compounds are reported in parts per million (ppm). One singlet at δ 7.26 ppm of ^{1}H and a triplet at 77.00 ppm of ^{13}C NMR for $CDCl_3$ were taken as an internal standard. Signal patterns are mentioned as s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet; bs, broad singlet and bm, broad multiplet. Coupling constant (J) for protons are reported in hertz (Hz). Infrared (IR) spectra was recorded on a Perkine Elmer AX-1 spectrophotometer and reported in wave number (cm^{-1}). HRMS of compounds are reported as $(M+H)^+$ using Agilent G6530AA (LC-HRMS-Q-TOF) spectrometer. The yields of the products are reported after chromatographic purification.

General protocol for the synthesis of allylarenes (6a-r)

To a vacuum dried screw capped vial, a mixture of 6-aryl-3-cyano-4-sec.amino-2*H*-pyran-2-ones (**4**; 0.5 mmol) and 5-hexen-2-one (**5**; 0.6 mmol) was stirred at 30 °C in presence of powdered LiOH (1.0 mmol) in DMSO (4 mL). TLC was used to monitor the completion of reaction. After completion of reaction, mixture was poured onto crushed ice water with constant stirring followed by neutralization with 10% solution of HCl. The crude solid obtained was filtered, dried and purified by silica gel column chromatography using ethylacetate/hexane (1:19) as an eluent.

6a. 2-Allyl-3-methyl-5-(piperidin-1-yl)-[1,1'-biphenyl]-4-carbonitrile: Yield: 74%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 96-98 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 3H, Ar-H), 7.27 (d, *J* = 5.3 Hz, 2H, Ar-H), 6.73 (s, 1H, Ar-H), 5.82 (dq, *J* = 10.9, 5.5 Hz, 1H, -C=C-H), 5.03 (d, *J* = 9.9 Hz, 1H, -C=C-H), 4.75 (d, *J* = 17.5 Hz, 1H, -C=C-H), 3.23 (d, *J* = 3.8 Hz, 2H, $-CH_2$), 3.11 (t, *J* = 5.0 Hz, 4H, $-CH_2$), 2.52 (s, 3H, $-CH_3$), 1.78 (t, *J* = 5.0 Hz, 4H, $-CH_2$), 1.58 (s, 2H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.4, 147.7, 142.9, 141.4, 136.2, 129.0, 128.5, 128.0, 127.5, 118.2, 118.1, 115.6, 107.2, 53.5, 34.0, 26.2, 24.1, 18.4; IR (cm^{-1}): 2932, 2856, 2807, 2217 (CN), 1642, 1588, 1454, 997, 916; Calculated Mass $(M+H)^+$: 317.2012, Observed Mass for $(C_{22}H_{25}N_2)^+$: 317.2001.

6b. 2-Allyl-3-methyl-5-(pyrrolidin-1-yl)-[1,1'-biphenyl]-4-carbonitrile: Yield: 70%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 100-102 °C;^{1}H-NMR (400 MHz, CDCl3) δ 7.39 (dd, *J* = 11.9, 5.2 Hz, 3H, Ar-H), 7.29 (dd, *J* = 5.4, 2.1 Hz, 2H, Ar-H), 6.45 (s, 1H, Ar-H), 5.83 (dq, *J* = 22.3, 5.2 Hz, 1H, -C=C-H), 5.03 (dd, *J* = 10.2, 1.2 Hz, 1H, -C=C-H), 4.78 (dd, *J* = 17.2, 1.5 Hz, 1H, -C=C-H), 3.60 (t, *J* = 6.4 Hz, 4H, $-CH_2$), 3.20 (t, *J* = 2.5 Hz, 2H, $-CH_2$), 2.51 (s, 3H, $-CH_3$), 2.00-1.97 (m, 4H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.5, 147.8, 142.9, 141.7, 136.6, 128.7, 128.4, 127.9, 127.2, 123.7, 120.3, 115.1, 113.5, 96.6, 50.2, 33.7, 25.7, 18.4; IR (cm^{-1}): 2925, 2857, 2211 (CN), 1718, 1594, 1462, 1027, 915; Calculated Mass $(M+H)^+$: 303.1856, Observed Mass for $(C_{21}H_{23}N_2)^+$: 303.1876.

6c. 2-Allyl-3,4'-dimethyl-5-(piperidin-1-yl)-[1,1'-biphenyl]-4-carbonitrile: Yield: 71%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 90-92 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.16 (d, *J* = 8.2 Hz, 2H, Ar-H), 6.72 (s, 1H, Ar-H), 5.88-5.78 (m, 1H, -C=C-H), 5.04 (dd, *J* = 10.1, 1.8 Hz, 1H, -C=C-H), 4.76 (dd, *J* = 17.2, 1.6 Hz, 1H, -C=C-H), 3.24 (d, *J* = 5.0 Hz, 2H, $-CH_2$), 3.10 (t, *J* = 5.3 Hz, 4H, $-CH_2$), 2.51 (s, 3H, $-CH_3$), 2.40 (s, 3H, $-CH_3$), 1.80-1.74 (m, 4H, $-CH_2$), 1.57 (t, *J* = 5.5 Hz, 2H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.4, 147.8, 142.8, 138.5, 137.3, 136.3, 129.1, 128.7, 128.4, 118.3, 118.1, 115.6, 107.1, 53.5, 34.0, 26.2, 24.1, 21.2, 18.4; IR (cm^{-1}): 2931, 2858, 2216 (CN), 1638, 1590, 1456, 1003, 915; Calculated Mass $(M+H)^+$: 331.2169, Observed Mass for $(C_{23}H_{27}N_2)^+$: 331.2167.

6d. 2-Allyl-3,4'-dimethyl-5-morpholino-[1,1'-biphenyl]-4-carbonitrile: Yield: 75%; 0.25 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 108-110 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.16 (d, *J* = 8.2 Hz, 2H, Ar-H), 6.73 (s, 1H, Ar-H), 5.88-5.78 (m, 1H, -C=C-H), 5.05 (dd, *J* = 10.1, 1.8 Hz, 1H, -C=C-H), 4.76 (dd, *J* = 16.9, 1.8 Hz, 1H, -C=C-H), 3.90 (t, *J* = 4.6 Hz, 4H, $-CH_2$), 3.26 (td, *J* = 3.7, 1.5 Hz, 2H, $-CH_2$), 3.16 (t, *J* = 4.6 Hz, 4H, $-CH_2$), 2.53 (s, 3H, $-CH_3$), 2.41 (s, 3H, $-CH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.8, 148.1, 143.2, 138.2, 137.5, 136.0, 130.2, 128.8, 128.3, 127.1, 118.2, 115.7, 107.1, 67.0, 52.2, 34.0, 21.2, 18.5; IR (cm^{-1}): 2921, 2857, 2217 (CN), 1636, 1590, 1449, 1008, 921; Calculated Mass $(M+H)^+$: 333.1961, Observed Mass for $(C_{22}H_{25}N_2O)^+$: 333.1959.

6e. 2-Allyl-4'-methoxy-3-methyl-5-(piperidin-1-yl)-[1,1'-biphenyl]-4-carbonitrile: Yield: 72%; 0.30 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 108-110 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.2 Hz, 2H, Ar-H), 6.92 (d, *J* = 8.2 Hz, 2H, Ar-H), 6.72 (s, 1H, Ar-H), 5.89-5.78 (m, 1H, -C=C-H), 5.04 (dd, *J* = 10.3, 1.6 Hz, 1H, -C=C-H), 4.76 (dd, *J* = 16.9, 1.8 Hz, 1H, -C=C-H), 3.85 (s, 3H, $-CH_3$), 3.25 (t, *J* = 2.5 Hz, 2H, $-CH_2$), 3.10 (t, *J* = 5.3 Hz, 4H, $-CH_2$), 2.51 (s, 3H, $-CH_3$), 1.80-1.75 (m, 4H, $-CH_2$), 1.60-1.55 (m, 2H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.1, 155.4, 147.5, 142.8, 136.3, 133.8, 131.2, 130.2, 129.7, 129.2, 118.4, 118.1, 115.6, 113.5, 107.0, 55.3, 53.5, 34.0, 26.2,

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24.1, 18.5; IR (cm^{-1}): 2926, 2856, 2210 (CN), 1741, 1602, 1464, 1034, 926; Calculated Mass $(M+H)^+$: 347.2118, Observed Mass for $(C_{23}H_{27}N_2O)^+$: 347.2117.

6f. 2-Allyl-4'-methoxy-3-methyl-5-(pyrrolidin-1-yl)-[1,1'-biphenyl]-4-carbonitrile: Yield: 66%; 0.30 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 110-112 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.91 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.41 (s, 1H, Ar-H), 5.88-5.79 (m, 1H, -C=C-H), 5.02 (dd, *J* = 10.2, 1.8 Hz, 1H, -C=C-H), 4.77 (dd, *J* = 17.2, 1.9 Hz, 1H, -C=C-H), 3.85 (s, 3H, $-CH_3$), 3.57 (t, *J* = 6.6 Hz, 4H, $-CH_2$), 3.20 (dd, *J* = 3.2, 2.1 Hz, 2H, $-CH_2$), 2.48 (s, 3H, $-CH_3$), 1.99-1.96 (m, 4H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.9, 149.7, 147.5, 143.0, 136.8, 134.2, 129.6, 124.1, 120.4, 115.2, 113.8, 113.3, 96.5, 55.3, 50.2, 33.8, 25.8, 18.5; IR (cm^{-1}): 2931, 2856, 2217 (CN), 1713, 1598, 1459, 1021, 918; Calculated Mass $(M+H)^+$: 333.1961, Observed Mass for $(C_{22}H_{25}N_2O)^+$: 333.1949.

6g. 2-Allyl-2'-methoxy-3-methyl-5-morpholino-[1,1'-biphenyl]-4-carbonitrile: Yield: 55%; 0.30 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 122-124 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 1H, Ar-H), 7.08 (dd, *J* = 7.4, 1.8 Hz, 1H, Ar-H), 7.02-6.96 (m, 2H, Ar-H), 6.71 (s, 1H, Ar-H), 5.72-5.62 (m, 1H, -C=C-H), 4.93 (dd, *J* = 10.2, 1.6 Hz, 1H, -C=C-H), 4.73 (dd, *J* = 17.2, 1.8 Hz, 1H, -C=C-H), 3.89 (t, *J* = 4.5 Hz, 4H, $-CH_2$), 3.74 (s, 3H, $-CH_3$), 3.25-3.09 (m, 6H, $-CH_2$), 2.54 (s, 3H, $-CH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.9, 153.7, 144.6, 142.6, 135.5, 131.4, 130.4, 129.6, 129.3, 120.3, 118.4, 117.9, 115.3, 110.7, 107.3, 67.3, 55.3, 52.1, 34.3, 18.4; IR (cm^{-1}) : 2926, 2857, 2216 (CN), 1735, 1591, 1459, 1018, 921; Calculated Mass $(M+H)^+$: 349.1911, Observed Mass for $(C_{22}H_{25}N_2O_2)^+$: 349.1913.

6h. 2-Allyl-4'-fluoro-3-methyl-5-(piperidin-1-yl)-[1,1'-biphenyl]-4-carbonitrile: Yield: 61%; 0.30 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 158-160 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 8.2, 5.5 Hz, 2H, Ar-H), 7.08 (t, *J* = 8.7 Hz, 2H, Ar-H), 6.69 (s, 1H, Ar-H), 5.82 (dq, *J* = 22.4, 5.2 Hz, 1H, -C=C-H), 5.04 (d, *J* = 9.2 Hz, 1H, -C=C-H), 4.74 (d, *J* = 17.4 Hz, 1H, -C=C-H), 3.21 (t, *J* = 2.5 Hz, 2H, $-CH_2$), 3.11 (t, *J* = 5.3 Hz, 4H, $-CH_2$), 2.51 (s, 3H, $-CH_3$), 1.81-1.75 (m, 4H, $-CH_2$), 1.61-1.55 (m, 2H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 163.4 & 160.9 (*J* = 245.3 Hz), 155.3, 146.6, 142.9, 137.2 & 137.2 (*J* = 2.8 Hz), 136.0, 130.1 & 130.0 (*J* = 8.6 Hz), 128.9, 118.2, 117.9, 115.6 &115.0 (*J* = 65.1 Hz), 114.8, 107.3, 53.4, 33.8, 26.1, 24.0, 18.3; IR (cm^{-1}) : 2933, 2856, 2218 (CN), 1738, 1595, 1455, 1228, 1001, 918; Calculated Mass $(M+H)^+$: 335.1918, Observed Mass for $(C_{22}H_{24}FN_2)^+$: 335.1948.

6i. 2-Allyl-4'-bromo-3-methyl-5-(piperidin-1-yl)-[1,1'-biphenyl]-4-carbonitrile: Yield: 69%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 136-138 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.14 (d, *J* = 8.2 Hz, 2H, Ar-H), 6.67 (s, 1H, Ar-H), 5.86-5.77 (m, 1H, -C=C-H), 5.04 (dd, *J* = 10.1, 1.8 Hz, 1H, -C=C-H), 4.73 (dd, *J* = 17.2, 1.6 Hz, 1H, -C=C-H), 3.21-3.19 (m, 2H, $-CH_2$), 3.10 (t, *J* = 5.5 Hz, 4H, $-CH_2$), 2.51 (s, 3H, $-CH_3$), 1.80-1.75 (m, 4H, $-CH_2$), 1.61-1.55 (m, 2H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.5, 146.4, 143.1, 140.3, 136.0, 131.2, 130.2, 128.7, 121.8, 118.0, 117.9, 115.8, 107.6, 53.5, 33.9, 26.2, 24.1, 18.4; IR (cm^{-1}): 2934, 2856, 2217 (CN), 1730, 1641, 1594, 1455, 1008, 918; Calculated Mass $(M+H)^+$: 395.1117, Observed Mass for $(C_{22}H_{24}BrN_2)^+$: 395. 1119.

6j. 2-Allyl-3-methyl-5-morpholino-4'-nitro-[1,1'-biphenyl]-4-carbonitrile: Yield: 39%; 0.30 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 162-164 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.82 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.05 (s, 1H, Ar-H), 6.23-6.14 (m, 1H, -C=C-H), 5.45 (dd, *J* = 10.2, 1.5 Hz, 1H, -C=C-H), 5.08 (dd, *J* = 17.2, 1.5 Hz, 1H, -C=C-H), 4.26 (t, *J* = 4.6 Hz, 4H, $-CH_2$), 3.56-3.53 (m, 6H, $-CH_2$), 2.90 (s, 3H, $-CH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.0, 147.7, 147.4, 145.6, 143.8, 135.4, 129.5, 123.4, 117.4, 116.3, 108.2, 66.9, 52.0, 33.9, 18.4; IR (cm^{-1}): 2927, 2858, 2221 (CN), 1744, 1593, 1457, 991, 922; Calculated Mass $(M+H)^+$: 364.1656, Observed Mass for $(C_{21}H_{22}N_3O_3)^+$: 364.1667.

6k. 2-Allyl-3'-bromo-3-methyl-5-(pyrrolidin-1-yl)-[1,1'-biphenyl]-4-carbonitrile: Yield: 63%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 126-128 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.50-7.47 (m, 1H, Ar-H), 7.42 (t, *J* = 1.6 Hz, 1H, Ar-H), 7.26-7.22 (m, 1H, Ar-H), 7.20 (dt, *J* = 7.6, 1.4 Hz, 1H, Ar-H), 6.36 (s, 1H, Ar-H), 5.85-5.76 (m, 1H, -C=C-H), 5.03 (dd, *J* = 10.2, 1.7 Hz, 1H, -C=C-H), 4.74 (dd, *J* = 17.2, 1.8 Hz, 1H, -C=C-H), 3.57 (t, *J* = 6.5 Hz, 4H, $-CH_2$), 3.15 (dd, *J* = 3.0, 2.1 Hz, 2H, $-CH_2$), 2.47 (s, 3H, $-CH_3$), 1.99-1.96 (m, 4H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.6, 146.2, 143.8, 143.3, 136.4, 131.5, 130.4, 129.5, 127.1, 123.5, 122.0, 120.2, 115.4, 113.4, 97.0, 50.3, 33.7, 25.8, 18.5; IR (cm^{-1}): 2927, 2857, 2212 (CN), 1726, 1594, 1465, 995, 919; Calculated Mass $(M+H)^+$: 381.0961, Observed Mass for $(C_{21}H_{22}BrN_2)^+$: 381.0960.

6l. 2-Allyl-2'-bromo-3-methyl-5-(piperidin-1-yl)-[1,1'-biphenyl]-4-carbonitrile: Yield: 59%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 114-116 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.33 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.24 (t, *J* = 6.9 Hz, 1H, Ar-H), 7.18 (d, *J* = 7.3 Hz, 1H, Ar-H), 6.64 (s, 1H, Ar-H), 5.67 (d, *J* = 6.0 Hz, 1H, -C=C-H), 4.94 (d, *J* = 10.1 Hz, 1H, -C=C-H), 4.70 (d, *J* = 16.9 Hz, 1H, -C=C-H), 3.24 (dd, *J* = 16.3, 5.7 Hz, 1H, $-CH_2$), 3.10 (q, J = 5.5 Hz, 4H, $-CH_2$), 3.01 (dd, *J* = 16.5, 5.5 Hz, 1H, $-CH_2$), 2.53 (s, 3H, $-CH_3$), 1.77 (q, *J* = 5.6 Hz, 4H, $-CH_2$), 1.60-1.56 (m, 2H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.4, 146.1, 142.8, 141.7, 135.2, 132.6, 130.5, 129.3, 129.2, 127.0, 123.0, 118.1, 117.9, 115.6, 107.8, 53.5, 34.1, 26.2, 24.1, 18.4; IR (cm^{-1}): 2932, 2856, 2219 (CN), 1738, 1590, 1452, 1034, 916; Calculated Mass $(M+H)^+$: 395.1117, Observed Mass for $(C_{22}H_{24}BrN_2)^+$: 395.1115.

6m. 3-Allyl-2-methyl-4-(naphthalen-2-yl)-6-(piperidin-1-yl)benzonitrile: Yield: 65%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 154-156 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.91-7.84 (m, 3H, Ar-H), 7.76 (s, 1H, Ar-H), 7.54-7.52 (m, 2H, Ar-H), 7.42 (dd, *J* = 8.4, 1.6 Hz, 1H, Ar-H), 6.83 (s, 1H, Ar-H), 5.90-5.80 (m, 1H, -C=C-H), 5.08 (dd, *J* = 10.2, 1.7 Hz, 1H, -C=C-H), 4.81 (dd, *J* = 17.2, 1.6 Hz, 1H, -C=C-H), 3.28 (dd, *J* = 3.3, 2.1 Hz, 2H, $-CH_2$), 3.14 (t, *J* = 5.4 Hz, 4H, $-CH_2$), 2.56 (s, 3H, -

CH_3), 1.83-1.77 (m, 4H, -CH_2), 1.62-1.56 (m, 2H, -CH_2); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.4, 147.6, 142.9, 138.9, 136.1, 132.9, 132.5, 129.1, 128.0, 127.7, 127.6, 127.2, 126.8, 126.4, 126.2, 118.4, 118.1, 115.7, 107.3, 53.5, 34.1, 26.2, 24.0, 18.4; IR (cm^{-1}) : 2925, 2854, 2215 (CN), 1741, 1587, 1453, 997, 913; Calculated Mass $(M+H)^+$: 367.2169, Observed Mass for $(C_{26}H_{27}N_2)^+$: 367.2169.

6n. 3-Allyl-4-(furan-2-yl)-2-methyl-6-(piperidin-1-yl)benzonitrile: Yield: 67%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 96-98 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 1.8 Hz, 1H, Ar-H), 7.15 (s, 1H, Ar-H), 6.62 (d, *J* = 3.4 Hz, 1H, Ar-H), 6.48 (q, *J* = 1.7 Hz, 1H, Ar-H), 6.04-5.94 (m, 1H, -C=C-H), 5.09 (dd, *J* = 10.3, 1.8 Hz, 1H, -C=C-H), 4.83 (dd, *J* = 17.2, 1.7 Hz, 1H, -C=C-H), 3.51-3.49 (m, 2H, -CH_2), 3.13 (t, *J* = 5.4 Hz, 4H, -CH_2), 2.51 (s, 3H, -CH_3), 1.81-1.76 (m, 4H, -CH_2), 1.60 (td, *J* = 11.9, 5.9 Hz, 2H, -CH_2); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.5, 152.0, 143.3, 142.7, 135.4, 128.0, 117.9, 117.2, 116.0, 115.8, 111.5, 110.2, 107.5, 53.4, 34.0, 26.1, 24.0, 18.3; IR (cm^{-1}): 2931, 2857, 2217 (CN), 1733, 1595, 1456, 998, 919; Calculated Mass $(M+H)^+$: 307.1805, Observed Mass for $(C_{20}H_{23}N_2O)^+$: 307.1820.

6o. 3-Allyl-2-methyl-6-(piperidin-1-yl)-4-(thiophen-2-yl)benzonitrile: Yield: 70%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 92-94 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 4.6 Hz, 1H, Ar-H), 7.06 (t, *J* = 4.1 Hz, 2H, Ar-H), 6.89 (s, 1H, Ar-H), 5.93 (dq, *J* = 22.1, 5.1 Hz, 1H, -C=C-H), 5.09 (d, *J* = 10.1 Hz, 1H, -C=C-H), 4.79 (d, *J* = 17.4 Hz, 1H, -C=C-H), 3.39 (t, *J* = 2.5 Hz, 2H, -CH_2), 3.12 (t, *J* = 5.3 Hz, 4H, -CH_2), 2.51 (s, 3H, -CH_3), 1.81-1.75 (m, 4H, -CH_2), 1.62-1.56 (m, 2H, -CH_2); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.3, 143.2, 142.0, 139.9, 136.2, 129.7, 127.1, 126.9, 125.9, 119.2, 117.9, 115.8, 107.8, 53.4, 34.1, 26.2, 24.1, 18.5; IR (cm^{-1}): 2932, 2854, 2216 (CN), 1639, 1587, 1447, 996, 918; Calculated Mass $(M+H)^+$: 323.1576, Observed Mass for $(C_{20}H_{23}N_2S)^+$: 323.1584.

6p. 3-Allyl-2-methyl-6-(pyrrolidin-1-yl)-4-(thiophen-2-yl)benzonitrile: Yield: 68%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 92-94 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 5.0 Hz, 1H, Ar-H), 6.99-6.95 (m, 2H, Ar-H), 6.52 (s, 1H, Ar-H), 5.83 (dq, *J* = 22.3, 5.1 Hz, 1H, -C=C-H), 4.98 (dd, *J* = 10.3, 1.6 Hz, 1H, -C=C-H), 4.72 (dd, *J* = 17.2, 1.6 Hz, 1H, -C=C-H), 3.50 (t, *J* = 6.6 Hz, 4H, -CH_2), 3.25 (t, *J* = 2.5 Hz, 2H, -CH_2), 2.41 (s, 3H, -CH_3), 1.92-1.87 (m, 4H, -CH_2); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.5, 143.4, 142.4, 139.9, 136.8, 127.0, 126.7, 125.6, 124.4, 120.2, 115.4, 114.6, 97.2, 50.3, 33.9, 25.8, 18.6; IR (cm^{-1}): 2924, 2854, 2206 (CN), 1739, 1590, 1446, 996, 916; Calculated Mass $(M+H)^+$: 309.1420, Observed Mass for $(C_{19}H_{21}N_2S)^+$: 309.1420.

6q. 3-Allyl-2-methyl-6-morpholino-4-(thiophen-2-yl)benzonitrile: Yield: 73%; 0.25 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 104-106 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 4.7 Hz, 1H, Ar-H), 7.08 (dd, *J* = 9.1, 3.9 Hz, 2H, Ar-H), 6.90 (s, 1H, Ar-H), 5.98-5.88 (m, 1H, -C=C-H), 5.10 (dd, *J* = 10.2, 1.5 Hz, 1H, -C=C-H), 4.78 (dd, *J* = 17.2, 1.6 Hz, 1H, -C=C-H), 3.90 (t, *J* = 4.5 Hz, 4H, -CH_2), 3.40 (t, *J* = 2.5 Hz, 2H, -CH_2), 3.17 (t, *J* = 4.5 Hz, 4H, -CH_2), 2.53 (s, 3H, -CH_3)); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.6, 143.6, 141.5, 140.2, 136.0, 130.8, 127.2, 127.0, 126.1, 119.0, 117.6, 115.9, 107.7, 66.9, 52.0, 34.1, 18.5; IR (cm^{-1}): 2926, 2857, 2216 (CN), 1630, 1590, 1470, 1009, 920; Calculated Mass $(M+H)^+$: 325.1369, Observed Mass for $(C_{19}H_{21}N_2OS)^+$: 325.1383.

6r. 2-Allyl-3,6-dimethyl-5-(piperidin-1-yl)-[1,1'-biphenyl]-4-carbonitrile: Yield: 62%; 0.40 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 118-120 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 3H, Ar-H), 7.06-7.04 (m, 2H, Ar-H), 5.72-5.62 (m, 1H, -C=C-H), 4.94 (dd, *J* = 10.2, 1.7 Hz, 1H, -C=C-H), 4.67 (dd, *J* = 17.2, 1.8 Hz, 1H, -C=C-H), 3.35 (s, 2H, -CH_2), 3.06 (td, *J* = 3.6, 1.7 Hz, 4H, -CH_2), 2.47 (s, 3H, -CH_3), 1.90 (s, 3H, -CH_3), 1.73-1.59 (m, 6H, -CH_2); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.9, 148.1, 140.6, 139.4, 135.6, 133.3, 132.5, 128.4, 128.3, 127.1, 118.7, 115.4, 110.7, 51.7, 35.0, 26.9, 24.2, 17.8, 16.5; IR (cm^{-1}): 2928, 2855, 2219 (CN), 1563, 1445, 1025, 916; Calculated Mass $(M+H)^+$: 331.2169, Observed Mass for $(C_{23}H_{27}N_2)^+$: 331.2181.

General protocol for the synthesis of methylthio substituted allylarenes (7a-f): A mixture of 6-aryl-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile (**3**; 0.5 mmol) and 5-hexen-2-ones (**5**; 0.75 mmol) was stirred at 30 °C in presence of powdered LiOH (1.0 mmol) In DMSO (4 mL). TLC was used to monitor the completion of reaction. After completion of reaction, mixture was poured onto crushed ice with constant stirring and neutralized with 10% solution of HCl. Obtained solid precipitate was filtered, dried and purified by silica gel column chromatography using ethyl acetate/hexane (1:19) as an eluent.

7a. 2-Allyl-3-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carbonitrile: Yield: 44%; 0.40 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 84-86 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 3H, Ar-H), 7.27-7.24 (m, 2H, Ar-H), 6.99 (s, 1H, Ar-H), 5.86-5.76 (m, 1H, -C=C-H), 5.05 (dd, *J* = 10.3, 1.6 Hz, 1H, -C=C-H), 4.73 (dd, *J* = 17.3, 1.6 Hz, 1H, -C=C-H), 3.26-3.24 (m, 2H, -CH_2), 2.53 (s, 3H, - CH_3), 2.50 (s, 3H, -CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.4, 142.8, 140.8, 140.6, 135.5, 133.0, 128.4, 128.2, 127.8, 125.3, 116.6, 116.0, 111.8, 34.1, 18.4, 15.8; IR (cm^{-1}): 2926, 2858, 2219 (CN), 1736, 1645, 1588, 1451, 1035, 919; Calculated Mass $(M+H)^+$: 280.1154, Observed Mass for $(C_{18}H_{18}NS)^+$: 280.1155.

7b. 2-Allyl-4'-methoxy-3-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carbonitrile: Yield: 48%; 0.40 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 94-96 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.00 (s, 1H, Ar-H), 6.94 (d, *J* = 8.8 Hz, 2H, Ar-H), 5.90-5.80 (m, 1H, -C=C-H), 5.07 (dd, *J* = 10.3, 1.6 Hz, 1H, -C=C-H), 4.75 (dd, *J* = 17.2, 1.6 Hz, 1H, -C=C-H), 3.85 (s, 3H, - CH_3), 3.28 (dd, *J* = 2.9, 2.2 Hz, 2H, -CH_2), 2.52 (d, *J* = 7.0 Hz, 6H, -CH_2); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.2, 147.1, 142.7, 140.6, 135.6, 133.1, 132.8, 129.6, 125.4, 116.6, 115.9, 113.5, 111.4, 55.2, 34.0, 18.3, 15.7; IR (cm^{-1}):

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2927, 2845, 2219 (CN), 1609, 1577, 1442, 1034, 920; Calculated Mass $(M+H)^+$: 310.1260, Observed Mass for $(C_{19}H_{20}NOS)^+$: 310.1265.

7c. 3-Allyl-2-methyl-6-(methylthio)-4-(thiophen-2-yl)benzonitrile: Yield: 45%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 78-80 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 4.9, 1.4 Hz, 1H, Ar-H), 7.16 (s, 1H, Ar-H), 7.11-7.07 (m, 2H, Ar-H), 5.98-5.89 (m, 1H, -C=C-H), 5.11 (dd, *J* = 10.3, 1.6 Hz, 1H, -C=C-H), 4.77 (dd, *J* = 17.2, 1.6 Hz, 1H, -C=C-H), 3.44-3.41 (m, 2H, $-CH_2$), 2.54 (s, 6H, $-CH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.1, 141.0, 140.9, 139.7, 135.6, 133.8, 127.3, 126.4, 126.1, 116.5, 116.2, 116.1, 112.2, 77.3, 77.0, 76.7, 34.2, 18.4, 15.8; IR (cm^{-1}): 2923, 2855, 2218 (CN), 1733, 1577, 1434, 1026, 918; Calculated Mass $(M+H)^+$: 286.0719, Observed Mass for $(C_{16}H_{16}NS_2)^+$: 286.0724.

7d. Methyl 2-allyl-3-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carboxylate: Yield: 57%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 98-100 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.37 (m, 3H, Ar-H), 7.30-7.28 (m, 2H, Ar-H), 7.12 (s, 1H, Ar-H), 5.88-5.79 (m, 1H, -C=C-H), 5.04 (d, *J* = 10.3 Hz, 1H, -C=C-H), 4.80 (dd, *J* = 17.2, 1.7 Hz, 1H, -C=C-H), 3.98 (s, 3H, $-CH_3$), 3.29-3.27 (m, 2H, $-CH_2$), 2.45 (s, 3H, $-CH_3$), 2.29 (s, 3H, $-CH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.6, 144.5, 141.3, 135.9, 134.6, 133.7, 132.3, 128.7, 127.9, 127.8, 127.2, 127.1, 115.7, 52.1, 34.1, 17.6, 16.8; IR (cm^{-1}): 2924, 2854, 1731(s, C=O, ester), 1638, 1582, 1436, 997, 918; Calculated Mass $(M+H)^+$: 313.1257, Observed Mass for $(C_{19}H_{21}O_2S)^+$: 313.1276.

7e. Methyl 2-allyl-4'-bromo-3-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carboxylate: Yield: 54%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 116-118 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 6.6, 1.8 Hz, 2H, Ar-H), 7.15 (dd, *J* = 6.5, 1.9 Hz, 2H, Ar-H), 7.05 (s, 1H, Ar-H), 5.86-5.77 (m, 1H, -C=C-H), 5.04 (dd, *J* = 10.3, 1.6 Hz, 1H, -C=C-H), 4.76 (dd, *J* = 17.2, 1.7 Hz, 1H, -C=C-H), 3.96 (s, 3H, $-CH_3$), 3.24 (dt, *J* = 4.8, 2.0 Hz, 2H, $-CH_2$), 2.44 (s, 3H, $-CH_3$), 2.26 (s, 3H, $-CH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.5, 143.3, 140.2, 135.8, 135.4, 134.9, 133.7, 132.6, 131.2, 130.5, 127.6, 121.6, 115.9, 52.3, 34.1, 17.7, 16.8; IR (cm^{-1}): 2928, 2855, 1732 (s, C=O, ester), 1588, 1436, 1018, 920; Calculated Mass $(M+H)^+$: 391.0362, Observed Mass for $(C_{19}H_{20}BrO_2S)^+$: 391.0368.

7f. Methyl 3-allyl-2-methyl-6-(methylthio)-4-(thiophen-2-yl)benzoate: Yield: 53%; 0.35 R_f (5% ethylacetate in hexane), Cream coloured solid; mp. 90-92 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.30 (m, 1H, Ar-H), 7.24 (d, *J* = 3.6 Hz, 1H, Ar-H), 7.04-7.03 (m, 2H, Ar-H), 5.94-5.85 (m, 1H, -C=C-H), 5.05 (dd, *J* = 10.2, 1.7 Hz, 1H, -C=C-H), 4.79 (dd, *J* = 17.3, 1.6 Hz, 1H, -C=C-H), 3.93 (s, 3H, $-CH_3$), 3.39-3.38 (m, 2H, $-CH_2$), 2.43 (s, 3H, $-CH_3$), 2.24 (s, 3H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.4, 141.9, 136.7, 136.0, 134.9, 132.5, 129.0, 127.0, 125.6, 124.6, 124.0, 115.9, 115.3, 52.2, 34.3, 17.7, 16.9; IR (cm^{-1}): 2923, 2853, 1729 (s, C=O, ester), 1640, 1593, 1433, 998, 916; Calculated Mass $(M+H)^+$: 319.0821, Observed Mass for $(C_{17}H_{19}O_2S_2)^+$: 319.0849.

General protocol for the synthesis of 4-allyl-3-methyl-1-(piperidin-1-yl)-9,10-dihydrophenanthrene-2-carbonitrile (8) and 3-(but-3-en-1-yl)-1-(piperidin-1-yl)-9,10-dihydrophenanthrene-2-carbonitrile (9): To a dried vial, mixture of 4-sec.amino-2-oxo-5,6-dihydro-2*H*-benzo[*h*]-chromene-3-carbonitriles (**4b**; 0.5 mmol) and 5-hexen-2-ones (**5**; 0.75 mmol) in DMSO (4.0 mL) was added followed by addition of powdered LiOH (1.0 mmol). The reaction mixture was stirred at 30 °C till completion of reaction. After completion, reaction mixture was poured onto crushed ice with constant stirring and neutralized with 10% solution of HCl. Obtained solid precipitate was filtered and purified by silica gel column chromatography using ethyl acetate/hexane (1:19) as an eluent.

Yield: 67% (8a: 40% & 9a: 27%) ; 0.40 R_f (5% ethylacetate in hexane), Cream coloured solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.66 (m, 2H, Ar-H), 7.40 (s, 1H, Ar-H), 7.32-7.23 (m, 6H, Ar-H), 6.22-6.13 (m, 1H, -C=C-H), 5.96-5.86 (m, 1H, -C=C-H), 5.29 (dd, *J* = 10.3, 1.9 Hz, 1H, -C=C-H), 5.10 (dd, *J* = 17.5, 1.5 Hz, 1H, -C=C-H), 5.04 (d, *J* = 9.9 Hz, 1H, -C=C-H), 4.98 (dd, *J* = 17.2, 1.9 Hz, 1H, -C=C-H), 3.55 (t, *J* = 2.3 Hz, 2H, $-CH_2$), 3.23 (bs, 7H, $-CH_2$), 2.95 (t, *J* = 8.0 Hz, 2H, $-CH_2$), 2.86 (t, *J* = 3.8 Hz, 2H, $-CH_2$), 2.81 (t, *J* = 3.8 Hz, 2H, $-CH_2$), 2.79-2.75 (m, 2H, $-CH_2$), 2.66 (t, *J* = 6.5 Hz, 2H, $-CH_2$), 2.51 (s, 3H, $-CH_3$), 2.47 (t, *J* = 7.6 Hz, 2H, $-CH_2$), 1.73 (s, 7H, $-CH_2$), 1.65 (s, 3H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.1, 151.5, 144.9, 141.6, 141.4, 140.0, 139.6, 137.9, 137.2, 136.8, 135.6, 134.2, 133.9, 133.2, 130.0, 128.4, 128.0, 127.9, 127.8, 127.1, 127.0, 125.8, 124.5, 120.7, 118.9, 118.2, 116.6, 115.6, 109.2, 107.8, 52.2, 52.0, 35.8, 34.7, 34.1, 29.6, 28.6, 26.8, 25.4, 24.2, 24.2, 23.2, 18.2; IR (cm^{-1}): 2935, 2851, 2221 (CN), 1646, 1594, 1431, 994, 916;Calculated Mass $(M+H)^+$: 343.1856, Observed Mass for $(C_{24}H_{27}N_2)^+$: 343.1857.

Synthesis of 1,9-dimethyl-3-(piperidin-1-yl)phenanthrene-2 carbonitrile (10): A mixture of 2-allyl-2'-bromo-3-methyl-5-(piperidin-1-yl)-[1,1'-biphenyl]-4-carbonitrile (**6l,** 0.2 mmol) was added to a nitrogen flushed air tight vial. Palladium (II) acetate (0.01 mmol, 5 mol %), Cs_2CO_3 (0.25 mmol) and of dry toluene (1.5 mL) was added to it and again purged with nitrogen gas. Then, the reaction mixture was stirred at 90 °C 12-15 hours. After completion, excess of solvent was removed under vacuum and purified by column chromatography using DCM/hexane (1: 9) mixture.

Yield: 84%; 0.45 R_f (5% ethylacetate in hexane), White crystalline solid; mp. 86-88 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.7 Hz, 1H, Ar-H), 8.05 (d, *J* = 6.9 Hz, 2H, Ar-H), 7.72 (s, 1H, Ar-H), 7.70-7.65 (m, 2H, Ar-H), 3.25 (t, *J* = 5.0 Hz, 4H, $-CH_2$), 2.95 (s, 3H, $-CH_3$), 2.75 (s, 3H, $-CH_3$), 1.91-1.85 (m, 4H, $-CH_2$), 1.69-1.63 (m, 2H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.9, 141.6, 132.9, 132.7, 131.7, 129.6, 127.7, 126.4, 125.6, 124.8, 123.7, 122.2, 118.1, 109.5, 108.5, 54.0, 26.3, 24.2, 20.3, 18.4; IR (cm^{-1}): 2935, 2855, 2218 (CN), 1592, 1453, 999, 756; Calculated Mass $(M+H)^+$: 315.1856, Observed Mass for $(C_{19}H_{20}NOS)^+$: 315.1856.

General protocol for the synthesis of 3,4'-dimethyl-5-morpholino-2-(prop-1-en-1-yl)-[1,1'-biphenyl]-4-carbonitrile(11):

Method A: A mixture of of 2-methyl-6-morpholino-3-(allyl)-4-(p-tolyl)benzonitriles (**6d**, 0.3 mmol) was taken in air tight vial followed by addition of $PhI(AcO)_2$ (0.36 mmol), $Pd(OAc)_2$ (0.015 mmol) and K_3PO_4 (0.36 mmol). To the vial, toluene (1.5 mL) was added and reaction mixture was flushed with nitrogen and sealed. Then reaction mixture was heated at 60 °C for 12 hours. After complete conversion, the excess of solvent as removed followed by addition of water (15 mL). The reaction mixture was neutralized with 10% of HCl and extracted with ethyl acetate (10 mLx2). The organic layer was separated and dried over anhydrous sodium sulphate. The product was purified by column chromatography using DCM/hexane (1:9) mixture as an eluent.

Method B: To a vacuum dried vial 2-methyl-6-morpholino-3-(allyl)-4-(*p*-tolyl)benzonitriles (**6d**, 0.2 mmol) was taken. To the vial further *t*-BuOK (0.3 mmol) and *t*-BuOH (3.0 mL) was added and stirred for 12 hours at 90 °C. After complete conversion, the excess of solvent was removed followed by addition of water (15 mL). The reaction mixture was neutralized with 10% of HCl and extracted with ethyl acetate (10mLx2). The organic layer was separated and dried over anhydrous sodium sulphate. The product was purified by column chromatography using DCM/hexane (1:9) mixture as an eluent.

Yield: 95% in method **A** and 78% in method **B**; 0.25 R_f (5% ethylacetate in hexane), White solid; mp. 126-128 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 10.8, 8.5 Hz, 4H, Ar-H), 6.75 (s, 1H, Ar-H), 6.09 (dd, *J* = 16.0, 1.4 Hz, 1H, -C=C-H), 5.48-5.39 (m, 1H, -C=C-H), 3.90 (t, *J* = 4.6 Hz, 4H, $-CH_2$), 3.17 (t, *J* = 4.4 Hz, 4H, $-CH_2$), 2.56 (s, 3H, $-CH_3$), 2.39 (s, 3H, $-CH_3$), 1.70 (dd, *J* = 6.6, 1.6 Hz, 3H, $-CH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.0, 146.3, 142.0, 138.3, 137.1, 132.7, 131.7, 129.4, 128.7, 127.2, 118.0, 117.9, 106.8, 67.0, 52.1, 21.2, 19.9, 18.7; IR (cm^{-1}): 2928, 2855, 2217(CN), 1636, 1558, 1491, 1443, 994, 907; Calculated Mass $(M+H)^+$: 333.1961, Observed Mass for $(C_{22}H_{25}N_2O)^+$: 333.1956.

General protocol for the synthesis of compound 12a and 12b: To a vacuum dried vial 2-methyl-6-(sec.amino)-3-(allyl)-4-(aryl)benzonitriles (**6i** or **6o,** 0.2 mmol) was heated with *t*-BuOK (0.8 mmol) in *t*-BuOH (3 mL) for 24 hours at 110 °C. After complete conversion, the excess of solvent was removed followed by addition of water (15 mL). The reaction mixture was neutralized with 10% of HCl and extracted with ethyl acetate (10mLx2). The organic layer was separated and dried over anhydrous sodium sulphate. The product was purified by column chromatography using ethyl acetate/hexane (1:9) as an eluent.

12a. 4'-Bromo-3-methyl-5-(piperidin-1-yl)-2-(prop-1-en-1-yl)-[1,1'-biphenyl]-4-carboxamide:

Yield: 71%; 0.25 R_f (15% ethylacetate in hexane), Cream coloured solid; mp. 180-182 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.15 (d, *J* = 8.2 Hz, 2H, Ar-H), 6.77 (s, 1H, Ar-H), 6.41 (s, 1H, $-NH_2$), 6.12 (d, *J* = 16.0 Hz, 1H, -C=C-H), 5.94 (s, 1H, $-NH_2$), 5.38-5.29 (m, 1H, -C=C-H), 2.96 (t, *J* = 4.8 Hz, 4H, $-CH_2$), 2.38 (s, 3H, $-CH_3$), 1.68 (q, *J* = 6.3 Hz, 7H, $-CH_2$ & $-CH_3$), 1.57-1.52 (m, 2H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 144.2, 141.3, 135.7, 132.4, 131.5, 131.0, 129.7, 129.3, 127.8, 125.9, 118.4, 112.1, 54.1, 29.7, 26.7, 24.1, 22.7, 18.7; IR (cm^{-1}): 3357 (NH), 2941, 2850, 1662 (C=O, amide), 1638, 1563, 1471, 1440, 989, 911; Calculated Mass $(M+H)^+$: 413.1223, Observed Mass for $(C_{22}H_{26}BrN_2O)^+$: 413.1226.

12b. 2-Methyl-6-(piperidin-1-yl)-3-(prop-1-en-1-yl)-4-(thiophen-2-yl)benzamide: Yield: 74%; 0.25 R_f (15% ethylacetate in hexane), Cream coloured solid; mp. 158-160 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 5.1, 1.2 Hz, 1H, Ar-H), 7.09 (dd, *J* = 3.6, 1.1 Hz, 1H, Ar-H), 7.04 (dd, *J* = 5.1, 3.6 Hz, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 6.40 (s, 1H, $-NH_2$), 6.25 (dd, *J* = 16.1, 1.6 Hz, 1H, -C=C-H), 5.91 (s, 1H, $-NH_2$), 5.62-5.53 (m, 1H, -C=C-H), 2.98 (t, *J* = 5.1 Hz, 4H, $-CH_2$), 2.39 (s, 3H, $-CH_3$), 1.80 (dd, *J* = 6.5, 1.7 Hz, 3H, $-CH_3$), 1.71-1.65 (m, 4H, $-CH_2$), 1.56-1.50 (m, 2H, $-CH_2$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 149.2, 143.6, 135.8, 135.0, 132.6, 132.1, 131.3, 128.3, 127.2, 126.7, 125.6, 118.6, 54.1, 26.7, 24.1, 18.7; IR (cm^{-1}): 3361 (NH), 2936, 2853, 1659 (C=O, amide), 1633, 1561, 1456, 1426, 994, 913; Calculated Mass $(M+H)^+$: 341.1682, Observed Mass for $(C_{20}H_{25}N_2OS)^+$: 341.1694.

General protocol for the synthesis of compound 13a-c: To a vacuum dried vial, 2-methyl-6-(methylthio)-3-(allyl)-4-(aryl)benzonitriles (**7,** 0.2 mmol) and *m*-CPBA (55-75% assay) (1.8 mmol) was added followed by addition of DCM (2 mL) and stirred for 5 hours at 30 °C. After completion, the reaction mixture was diluted with DCM (10 mL) and extracted with 10% aqueous solution of Na_2CO_3 (15 mLx3). Then, organic layer was separated and dried over sodium sulphate and purified by column chromatography using ethyl acetate/hexane (1:9) mixture as an eluent.

13a. 2-Allyl-3-methyl-5-(methylsulfinyl)-[1,1'-biphenyl]-4-carbonitrile: Yield: 98%; 0.35 R_f (10% ethylacetate in hexane), White crystalline solid; mp 98-100 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H, Ar-H), 7.43-7.40 (m, 3H, Ar-H), 7.30-7.26 (m, 2H, Ar-H), 5.90-5.80 (m, 1H, -C=C-H), 5.11 (dd, *J* = 10.3, 1.5 Hz, 1H, -C=C-H), 4.76 (dd, *J* = 17.2, 1.4 Hz, 1H, -C=C-H), 3.41-3.39 (m, 2H, $-CH_2$), 2.91 (s, 3H, $-CH_3$), 2.61 (s, 3H, $-CH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.8, 146.7, 143.4, 139.6, 139.5, 134.8, 128.4, 128.3, 128.2, 123.7, 116.6, 114.8, 107.8, 42.8, 34.5, 18.2; IR (cm^{-1}): 2933, 2855, 2216 (CN), 1592, 1501, 1451, 1064 (s, S=O, sulfoxide), 1021, 918; Calculated Mass $(M+H)^+$: 296.1104, Observed Mass for $(C_{18}H_{18}NOS)^+$: 296.1115.

13b. 2-Allyl-4'-methoxy-3-methyl-5-(methylsulfinyl)-[1,1'-biphenyl]-4-carbonitrile: Yield: 96%; 0.35 R_f (10% ethylacetate in hexane), White crystalline solid; mp. 110-112 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H, Ar-H), 7.24 (d, J = 8.7 Hz, 2H, Ar-H), 6.94 (d, *J* = 8.7 Hz, 2H, Ar-H), 5.88 (dq, *J* = 22.4, 5.2 Hz, 1H, -C=C-H), 5.12 (dd, J = 10.2, 1.2 Hz, 1H, -C=C-H), 4.77 (dd, *J* = 17.2, 1.3 Hz, 1H, -C=C-H), 3.85 (s, 3H, $-CH_3$), 3.41 (dd, J = 4.9, 1.8 Hz, 2H, $-CH_2$), 2.89 (s, 3H, $-CH_3$), 2.60 (s, 3H, $-CH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.6, 148.5, 146.7, 143.4, 139.5, 135.0, 131.9, 129.7, 123.8, 116.5, 114.9, 113.7, 107.4, 55.3, 42.8,

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34.6, 18.2; IR (cm^{-1}): 2922, 2853, 2220 (CN), 1606, 1513, 1458, 1066 (s, S=O, sulfoxide), 1030, 915; Calculated Mass $(M+H)^+$: 326.1209, Observed Mass for $(C_{19}H_{20}NO_2S)^+$: 326.1194.

13c. Methyl 3-allyl-2-methyl-6-(methylsulfinyl)-4-(thiophen-2-yl)benzoate: Yield: 93%; 0.35 R_f (10% ethylacetate in hexane), White crystalline solid; mp. 104-106 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H, Ar-H), 7.37 (d, *J* = 5.1 Hz, 1H, Ar-H), 7.11 (dd, *J* = 3.4, 1.1 Hz, 1H, Ar-H), 7.06 (dd, *J* = 5.0, 3.5 Hz, 1H, Ar-H), 5.99-5.90 (m, 1H, -C=C-H), 5.12 (dd, *J* = 10.3, 1.5 Hz, 1H, -C=C-H), 4.80 (dd, J = 17.3, 1.5 Hz, 1H, -C=C-H), 3.94 (s, 3H, -CH_3), 3.53 (t, *J* = 2.5 Hz, 2H, -CH_2), 2.84 (s, 3H, -CH_3), 2.38 (s, 3H, -CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.6, 143.1, 140.9, 140.4, 138.8, 137.0, 135.5, 129.7, 127.4, 127.1, 126.4, 123.7, 116.4, 52.5, 44.3, 34.8, 17.1; IR (cm^{-1}): 2929, 2851, 1728 (CO, Ester), 1598, 1513, 1448, 1058 (S=O, sulfoxide), 999, 910; Calculated Mass $(M+H)^+$: 302.0668, Observed Mass for $(C_{16}H_{16}NOS_2)^+$: 302.0659.

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Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

Transition metal free synthesis of sterically hindered allylarenes from 5-hexene-2-one

Ranjay Shaw, Ismail Althagafi, Amr Elagamy, Reeta Rai, Chandan Shah, Vishal Nemaysh, Harpreet Singh and Ramendra Pratap*

Sterically hindered allylarenes have been synthesized by ring transformation of 2-pyranones with 5-hexene-2-one.