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ARTICLE TYPE

Efficient synthesis of functionalized dihydroquinolines, quinolines and dihydrobenzo[*b*]azepine *via* an iron(III) chloride-catalyzed intramolecular alkyne-carbonyl metathesis of alkyne tethered 2-amino benzaldehyde/acetophenone derivatives

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In this study we have developed an efficient synthesis of 1,2-dihydroquinolines and dihydrobenzo[*b*]azepines derivatives involving iron(III) chloride intramolecular alkyne-carbonyl metathesis reaction for the first time. Various functionalized 1,2-dihydroquinolines and dihydrobenzo[*b*]azepines were prepared from easily accessible substrates in the presence of environmentally friendly and inexpensive iron(III) chloride (10 mol%) under mild conditions. The method is applicable to a wide range of substrates containing different functional groups and furnishing products in good to excellent yields. This methodology was further extended to the one–pot synthesis of 3-acyl quinolines via alkyne-carbonyl metathesis/detosylation/aromatization of *N*-propargyl-2-aminobenzaldehyde/acetophenone derivatives by the addition of NaOH/EtOH. While many Lewis acids and Brønsted acid catalysts were investigated but anhydrous iron (III) chloride turned out to be the best catalyst for this transformation.

Keywords: Nitrogen Heterocycles • Iron • Alkyne-Carbonyl Metathesis • One-Pot • Atom-Efficient

Introduction

Nitrogen-containing heterocycles are ubiquitous structural motifs in many natural products and small molecules of biomedical relevance.[1] In this regard, quinolines and their fully or partially hydrogenated derivatives are widely found in many biologically active natural or synthetic products.[2] In particular, 1,2-dihydroquinolines have received special attention because of their numerous applications as pharmaceuticals and agrochemicals, as well as their use as intermediates in the synthesis of other heterocycles of biological significance.[3] For example, 1,2-dihydroquinoline moieties are potential therapeutics such as antibacterial,[4a] anti-inflammatory,[4b] antimalarial,[4c] psychotropic,[4d] anti-allergic,[4e] lipid per oxidation inhibitors,[4f] HMG-CoA reductase,[4g] progesterone agonists[4h] and antagonists.[4i] In addition they can be easily transformed to corresponding 1,2,3,4-tetrahydroquinoline and quinoline derivatives.[5]

Considering the importance of 1,2-dihydroquinoline derivatives numerous synthetic strategies have been developed. In general, traditional procedures are laborious, low yielding, and require special synthetic precursors.[6] Recently, many new strategies towards the synthesis of 1,2-dihydroquinolines have been reported. For example, Brønsted and Lewis acid catalyzed tandem reaction of aniline with α-ketoesters,[7] Michael-aldol reactions,[8] tandem reaction of aromatic amines with alkynes,[9] olefin metathesis reactions,[10] intramolecular allylic amination[11] and many others are reported.[12] Despite these advances to obtain 1,2-dihydroquinolines, there still remain some limitations such as low yields, expensive and toxic metal catalysts, poor atom economy, and harsh reaction condition.

Similarly, nitrogen-containing medium ring heterocycles such as 1*H*-benzo[*b*]azepine ring constitutes the core structure of numerous pharmacologically important compounds.[13] Compounds having this skeleton have exhibited biological activity towards various targets such as enzymes, ion channels, and G-protein-coupled receptors (GPCRs).[14] Despite their interesting biological activities, the synthesis of 1-benzazepine derivatives has received little synthetic attention.[15] Typical synthetic routes are ring expansion,[15c,i,k] Dieckmann condensations,[15j] inter- and intramolecular metal-catalysed coupling[15a,c,e] and metathesis reactions.[15b] Thus, general, efficient and flexible synthetic strategies to prepare diverse 1,2-dihydroquinolines and 1*H*-benzo[*b*]azepine derivatives with specific substitution patterns is still a highly desirable and yet challenging task in organic synthesis.

In this regard, alkyne-carbonyl metathesis reaction i.e. the cycloaddition of C–O double bond to C–C triple bonds followed by cycloreversion has been recognized as an atom-economical alternative to the Wittig reaction for the

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construction of α,β-unsaturated carbonyl compounds.[16] The intramolecular version of this reaction is very attractive as it allows the formation of complex functionalized carbo- and heterocyclic compounds from easily available starting materials.[17] This reaction is considered to be proceeding *via* a formal [2+2] cycloaddition and cycloreversion process. Generally, Lewis or strong Brønsted acids or transition-metal such as TfOH, HBF_4, $BF_3.OEt_2$, $In(OTf)_3$, $AgSbF_6$, $AuCl_3$, and combination of $AuCl_3/AgSbF_6$ acted as catalyst for this process.

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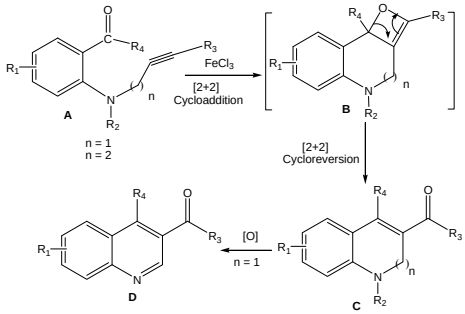
In recent years, iron-catalyzed organic transformations have attracted considerable attention because iron is one of the most inexpensive, sustainable and environmentally benign metals on earth. As part of our investigation on iron catalysis,[18a,b,c,19] we recently reported $FeCl_3$ can efficiently perform alkyne-carbonyl metathesis reaction.[18a,b,c] In continuation of our interest in this area, we thought that alkyne-carbonyl metathesis of *N*-propargyl-2-aminobenzaldehyde/acetophenone or *N*-homopropargyl-2-aminobenzaldehyde/acetophenone derivatives would be a new and an efficient synthetic route to access the libraries of 3-acyl 1,2-dihydroquinolines and 4-acyl benzo[*b*]azepine derivatives. (Scheme 1). Herein, we wish to report iron(III)-chloride catalyzed an intramolecular alkyne-carbonyl metathesis strategy for the synthesis of 3-acyl 1,2-dihydroquinolines and 4-acyl benzo[*b*]azepine derivatives under mild conditions in good to excellent yields. Moreover, this strategy also worked efficiently for the one-pot synthesis of 3-acyl quinolines in high yield.

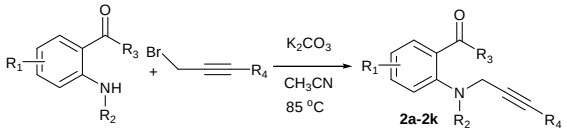


Scheme 1. Strategy for the synthesis of 1,2-dihydroquinolines, quinolines and benzo[*b*]azepine derivatives.

Results and Discussion

First we attempted the synthesis of 3-acyl 1,2-dihydroquinolines from 2-(*N*-(prop-2-ynyl)-*N*-tosylamino)benzaldehydes/acetophenone derivatives. The required substrates were easily prepared in high yields from 2-aminobenzaldehydes or acetophenone derivatives by simple alkylation using aryl or alkyl propargyl bromide in the presence of K_2CO_3, outlined in Scheme 2.

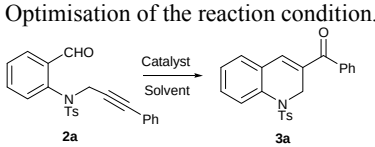
After having synthesised a series of substrates **2a**–**2k**, we next investigated the alkyne-carbonyl metathesis reaction for the synthesis of 1,2-dihydroquinolines. Our initial investigation began by examining the intramolecular alkyne-carbonyl metathesis of 2-(*N*-(3-phenylprop-2-ynyl)-*N*-tosylamino)benzaldehyde **2a** utilizing a variety of Lewis and Brønsted acid to develop the optimum reaction conditions.



Scheme 2. Preparation of 2-(*N*-(prop-2-ynyl)-*N*-tosylamino)benzaldehydes/acetophenone derivatives.

These results are summarized in Table 1. In view of the high catalytic activity of iron(III) chloride, we first examined the intramolecular alkyne-carbonyl metathesis of **2a** in the presence of anhydrous $FeCl_3$ in different solvents such as toluene, dichloromethane, 1,2-dichloroethane, acetonitrile and nitromethane (Table 1, entries 1 to 6). Gratifyingly, the desired 3-benzoyl-1-tosyl-1,2-dihydroquinoline **3a** was furnished in 95% yield as a sole product in the presence of anhydrous $FeCl_3$ (10 mol%) in CH_3CN at 85 °C in 4 h (Table 1 Entry 4). The other above mentioned solvents gave a lower yield of the desired product **3a**. Moreover, reduced the yield of **3a** to 60% was observed when the $FeCl_3$ was reduced to 5 mol%. In contrast, the same reaction with $FeBr_3$ (10 mol%) was found to result in 35% yield of the desired product **3a** (Table 1, entry 7). It also appeared that the reaction proceeded with other Lewis and Brønsted acids such as AgOTf, $InCl_3$, $BF_3.OEt_2$ and TfOH, albeit in lower yield. AgOTf was totally inactive (Table 1, entry 8), whereas $InCl_3$, $BF_3.OEt_2$ and TfOH gave moderate to good yields, 70%, 80% and 65%, respectively (Table 1, entries 9–11). Thus the best reaction condition for this coupling process was found to be heating the substrate **2a** in acetonitrile at 85 °C in the presence of anhydrous $FeCl_3$ (10 mol%).

Table 1. Optimisation of the reaction condition.[a]



Entry	Catalyst (mol%)	Solvent	Temperature	Time (h)	Yield (%)
1	$FeCl_3$ (10)	Toluene	85 °C	24	38
2	$FeCl_3$ (10)	DCE	reflux	4	55
3	$FeCl_3$ (10)	DCM	reflux	4	55
4	$FeCl_3$ (10)	CH_3CN	85 °C	4	95
5	$FeCl_3$ (5)	CH_3CN	85 °C	24	55
6	$FeCl_3$ (10)	CH_3NO_2	85 °C	8	75
7	$FeBr_3$ (10)	CH_3CN	85 °C	13	35
8	AgOTf (10)	CH_3CN	85 °C	24	n.r.
9	$InCl_3$ (10)	CH_3CN	85 °C	12	70
10	$BF_3.Et_2O$ (10)	CH_3CN	85 °C	6	80
11	TfOH (10)	CH_3CN	85 °C	19	65

[a]Reaction conditions: Substrates **2a** (0.5 mmol) and solvent (2 mL).

With these optimum conditions in hand, we next turned to explore the scope of the reaction for a series of 2-(*N*-(prop-2-

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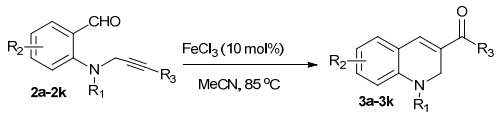
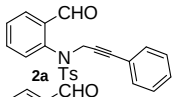
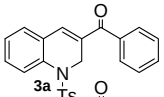
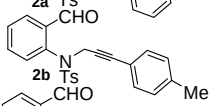
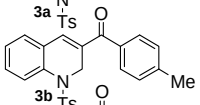
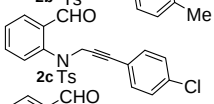
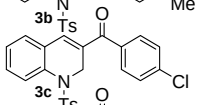
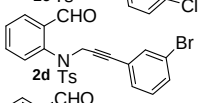
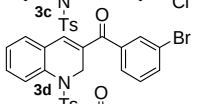
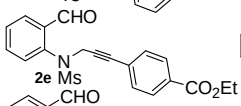
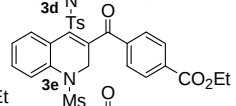
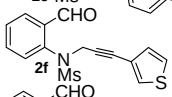
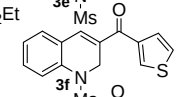
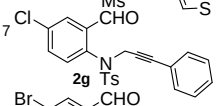
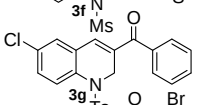
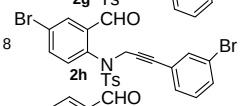
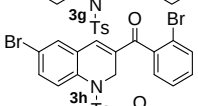
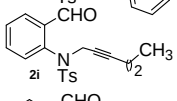
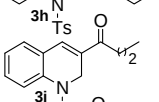
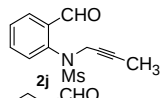
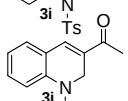
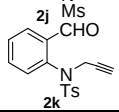
ynyl)-*N*-tosylamino)benzaldehydes **2a–2k** to synthesis a variety of functionalised dihydroquinoline derivatives. The results are summarized in Table 2. As shown in Table 2, a series of functional groups such as –Cl, –Br and –CO_2Et groups in the alkyne terminus were well tolerated and corresponding dihydroquinoline derivatives were obtained in good to excellent yields (Table 2, entries 1–8). The presence of electron-donating group such as *para*-Me at the aryl ring of alkyne terminus (Table 2, entry 2) also gave high yield 80%. Notably, thiophene substituted alkyne also worked efficiently and gave the desired hybrid heterocyclic product **3f** in a good yield of 70% (Table 2, entry 6). Both tosyl and mesyl protected 2-amino benzaldehyde survived under the reaction conditions and gave high yield of the desired products. Free amine did not work as it reduced the reactivity of carbonyl group.

Table 2. Fe-catalyzed intramolecular alkyne–aldehyde metathesis for the synthesis of varieties of polyfunctional 1,2-dihydroquinoline[a].



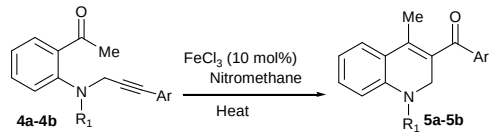
Entry	Substrates	Products	Time(h)	Yield (%)
1			4	95
2			7	80
3			9	89
4			12	84
5			14	75
6			8	70
7			21	88
8			5	93
9			3	74[b]
10			3	75[b]
11		–	12	NR

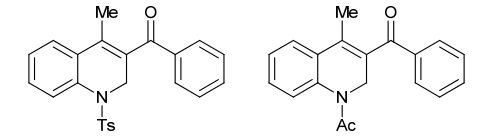
[a]Reaction conditions: Substrates (0.5 mmol), acetonitrile (2 mL), 85 °C.
[b]Reaction was carried out in 1,2-dichloroethane (2 mL), at 65 °C

Importantly, *para*-bromo group on benzene ring of alkyne unit and *para*-bromo with respect to aromatic amino group containing substrate **2h** afforded high yield of desired product **3h** (93%). It is noteworthy to mention that halogen containing functional groups on the dihydroquinoline derivatives could be utilized for further synthetic transformation using transition-metal catalyzed cross-coupling reactions to obtain library of complex dihydroquinoline derivatives that could be useful for their potential applications in medicinal chemistry.

Next, we studied a few alkyl groups at the alkyne terminus to show the versatility of this strategy (Table 2, entries 9 and 10). It appears that this strategy was also applicable to the internal alkynes bearing an aliphatic alkyls group such as **2i** and **2j** gave the desired dihydroquinoline derivatives **3i** and **3j** in good yields, 74% and 75%, respectively. Unfortunately, terminal alkyne containing substrate did not work (Table 3, entry 11), and only starting material was left even after 12 h heating in acetonitrile.

Table 3. Fe-catalyzed intramolecular alkyne-ketone meathesis for the synthesis of 3,4-substituted 1,2-dihydroquinolines.[a]





[a]Reaction condition: Substrates (0.5 mmol), Nitromethane (2 mL), heated at 85 °C

In addition, we also tested 2-aminoacetophenone derivative instead of an 2-aminobenzaldehyde derivative to show the potentiality of this reaction for the preparation of a variety of 3,4-disubstituted dihydroquinoline derivatives such as **5a** and **5b** (Table 3). To our delight, the coupling of internal alkyne with methylketone such as **4a** and **4b** also worked efficiently within short period of time in very good yields, 80% and 78%, respectively. However, in these cases the reaction in acetonitrile medium gave slightly lower yields compared to nitromethane. Possibly, for less reactive substrate in more polar solvent had beneficial effect. Notably, *N*-acyl protected 2-aminoacetophenone (Table 3, entry **5b**) was also survived under the reaction condition and furnish good yield of the desired product.

Having successfully established the suitable reaction condition for the synthesis of diverse range of *N*-tosyldihydroquinolines derivatives, next we aimed to develop a one-pot synthesis of 3-acyl substituted quinolines via alkyne-carbonyl metathesis/detosylation and oxidation of the intermediate products. *N*-propargyl-2-aminobenzaldehyde/acetophenone **2a**, **2c** and **4a** were first subjected to synthesise of 3-acyl dihydroquinoline derivatives via alkyne–carbonyl metathesis in the presence of iron, then after completion of the reaction

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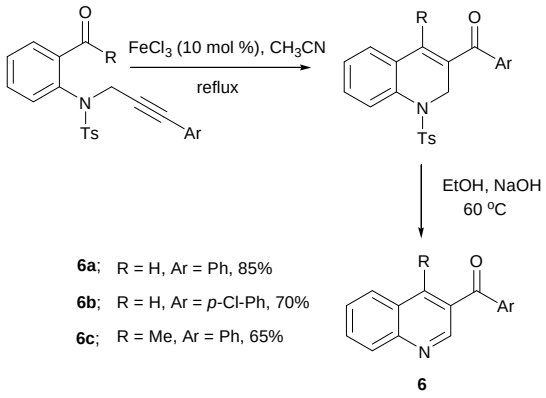
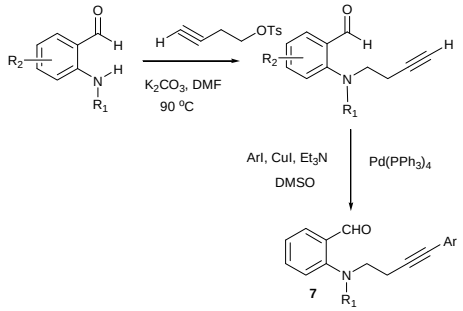
NaOH/EtOH was added to the reaction mixture, and the mixture was heated to 60 °C to obtain quinoline derivatives (Scheme 3). To our delight, this one pot strategy also worked efficiently for the synthesis of 3-acyl quinoline derivatives such as **6a**, **6b** and **6c** in high yields (85%, 70% and 65%). Therefore, this strategy of quinoline synthesis would be an important alternative of recently developed strategies[20] as present route is highly efficient and environmentally friendly. Moreover, specific substituent also could be introduced in this method.



Scheme 3. One-pot synthesis of 3-acyl quinoline *via* alkyne-carbonyl metathesis/detosylation/aromatization.

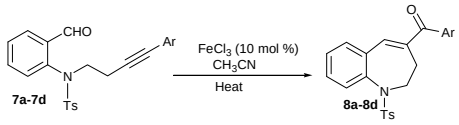
Finally, to expand the scope of this methodology we also decided to explore the possibility of synthesising of seven-membered nitrogen containing heterocycles such as benzo[*b*]azepine, **8a–8d**. The required substrates **7a–7d** can easily and efficiently be prepared by a two-step transformation in good yield from *N*-tosyl-2-aminobenzaldehyde. That involves *N*-alkylation with tosyl derivative of homopropargyl alcohol in presence of K_2CO_3 in DMF followed by palladium catalyzed Sonogashira coupling with aryl iodide (Scheme 4).

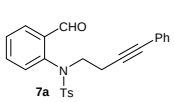
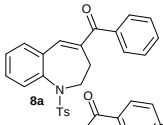
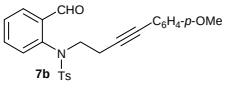
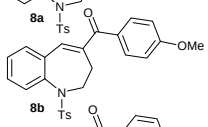
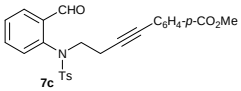
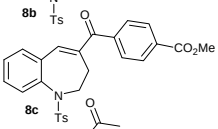
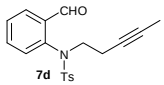
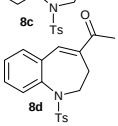


Scheme 4. Preparation of substrates for benzo[*b*]azepines synthesis.

After having synthesised the substrates **7a–7c**, these compounds were subjected to the alkyne-carbonyl metathesis reaction. The desired benzo[*b*]azepines were successfully synthesised achieved using the same optimized reaction conditions in good yield. The electronic effects of alkyne terminus groups have little influence on this reaction. Substrates with electron-rich and electron-deficient aryl rings at the alkyne terminus were reacted smoothly and gave **8a, 8b, 8c** and **8d** in 72%, 70% and 78%, respectively (Table 4). To our pleasant surprise, alkyne bearing an alkyl group (Table 4, Entry 4) such as substrate **7d** also reacted smoothly and gave the high yield of the desired benzo[*b*]azepine **8d**.

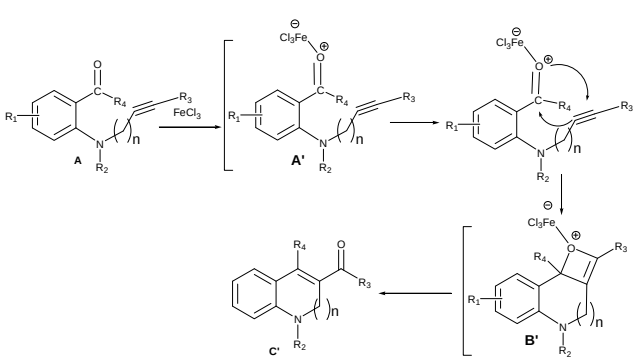
Table 4. Fe-catalyzed alkyne-carbonyl metathesis for the synthesis of benzo[*b*]azepine.[a]



Entry	Substrates	Products	Time [h]	Yield[%]
1			8	72
2			3	70
3			10	68
4			3	80[b]

[a]Reaction condition: Substrates (0.5 mmol), $FeCl_3$ (10 mol%), and acetonitrile (2 mL) at 85 °C. [b]Reaction was carried out in 1,2-dichloroethane (2 mL), at 65 °C

A plausible mechanism for the iron(III) chloride alkyne-carbonyl metathesis reaction is delineated in Scheme 5. This is very similar to our earlier work and reported by others.[17a,b,j, 18b,c] It is believed that the reaction may proceed through a formal [2+2] cycloaddition via an initial activation of the carbonyl group by the iron(III) which lowers the LUMO energy of carbonyl



Scheme 5. Possible mechanism for iron-catalyzed synthesis 1,2-dihydroquinolines and benzo[*b*]azepine derivatives.

group and hence accelerates the cycloaddition process producing an oxetene intermediate **B'** and which upon ring opening leading to the desired cyclic *α,β*-carbonyl derivative **C'** and regenerating the catalyst for next catalytic cycle. All structures of 1,2-dihydroquinolines, quinolines and benzo[*b*]azepine derivatives were confirmed by ^{1}H NMR, ^{13}C NMR and HRMS. The product **3b** (CCDC no-961970) was

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further proved by X-ray structure.

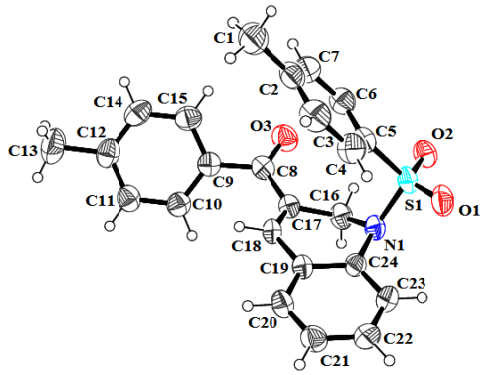


Figure 1. Representations of **3b** showing 40% probability of thermal ellipsoid.

Conclusion:

In summary, we have developed a general and flexible approach for the synthesis of six- and seven-membered nitrogen containing heterocycles such as 1, 2-dihydroquinolines, quinolines and benzo[*b*]azepine derivatives. The strategy involved iron (III)-catalyzed alkyne-carbonyl metathesis reactions of alkyne tethered 2-aminobenzaldehyde/acetophenone derivatives. The reactions are highly regioselective and worked under mild conditions in good to excellent yield. Among various Lewis and Brønsted acid catalysts, iron was found to be the most efficient. The advantages of this new method are the ease of the substrates preparation, operational simplicity, high atom-economy, and use of inexpensive and environmentally friendly $FeCl_3$ (10 mol%) as catalyst. Thus this method may find application toward the synthesis of libraries of nitrogen containing biologically active molecules to identify potential drug candidates.

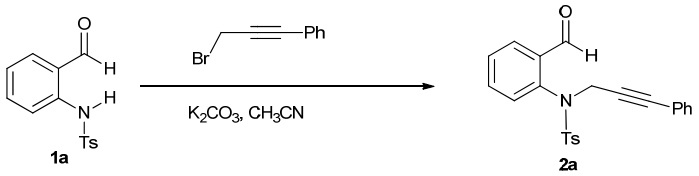
Acknowledgements: S. J., K. B., S. S. and K. P. are thankful to the CSIR, New Delhi, India, for their fellowships.

Experimental Section:

General Methods:

^{1}H NMR spectra were recorded in $CDCl_3$ solvents. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CHCl_3$ (δ = 7.26 ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hertz. Signal description: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, brs = broad singlet. ^{13}C NMR spectra were recorded in $CDCl_3$ solution with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ = 77.0 ppm) as an internal standard. High-resolution mass spectra (HRMS) were performed in dichloromethane solvent. The molecular fragments are quoted as the relation between mass and charge (m/z) ratio. The routine monitoring of reactions were performed with silica gel coated glass slides and pre-coated Al plates, which were analyzed with iodine, UV light, and alkaline $KMnO_4$, respectively. All reactions involving moisture-sensitive reactants were executed with oven-dried glassware.

Representative Experimental Procedure for the preparation of *N*-(2-formylphenyl)-4-methyl-*N*-(3-phenylprop-2-ynyl)benzenesulfonamide 2a:



Aldehyde **1a** (500 mg, 1.81 mmol) was dissolved in dry acetonitrile (10 mL) in a 50 mL round-bottom flask. To this solution were added anhydrous K_2CO_3 (751.5 mg, 5.34 mmol) and phenyl propargyl bromide (276 mg, 2.34 mmol). The reaction mixture was refluxed under argon atmosphere for 4 h. Then the mixture was cooled to room temperature and filtered through the sintered glass crucible. The filtrate was concentrated under reduced pressure, and the residue was purified by (silica gel, mess 60–120) column chromatography to obtain the product **2a**[21] (605 mg, 3.71 mmol, 86%) as an orange semisolid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.4 (s, 3H), 4.71 (s, 2H), 7.06 (d, J = 7.41 Hz, 1H), 7.15 (d, J = 7.32 Hz, 2H), 7.22–7.27 (m, 5H), 7.50–7.52 (m, 2H), 7.58 (d, J = 8.0 Hz, 2H), 8.03 (q, J = 2.2 Hz, 2H), 10.44 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 42.7, 82.3, 86.5, 121.8, 128.1, 128.3, 128.5, 128.7, 129.2, 129.7, 131.4, 134.3, 135.0, 136.0, 141.4, 144.4, 190.2 ppm. HRMS calcd. for $C_{23}H_{20}NO_3S$ [M+H] 390.1164, found 390.1160.

Compounds **2b, 2c**, **2d, 2e**, **2g, 2h, 2i, 2j, 2k** and **4a** were also synthesized by similar procedure.

***N*-(2-formylphenyl)-4-methyl-*N*-(3-*p*-tolylprop-2-ynyl)benzenesulfonamide 2b**:

Light yellow solid, m.p. 84 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.3 (s, 3H), 2.4 (s, 3H), 4.7 (s, 2H), 7.05 (s, 5H), 7.26 (d, J = 8 Hz, 2H), 7.48–7.51 (m, 2H), 7.58 (d, J = 8.8 Hz, 2H), 8.0–8.03 (m, 1H), 10.46 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 21.5, 42.8, 81.6, 86.7, 118.7, 128.1, 128.4, 128.7, 128.9, 129.1, 129.6, 131.3, 134.2, 135.9, 138.8, 141.4, 144.3, 190.1 ppm. HRMS calcd. for $C_{23}H_{18}ClNNaO_3S$ [M+Na] 446.0594, found 446.0594.

***N*-(3-(4-chlorophenyl)prop-2-ynyl)-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide 2c:**

Light yellow solid, m.p. 94 °C, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.4 (s, 3H), 4.69 (s, 2H), 7.02 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 8.4 Hz, 2H), 7.20–7.32 (m, 4H), 7.46–7.53 (m, 2H), 7.57 (d, J = 8.1 Hz, 2H), 8.0–8.03 (m, 1H), 10.43 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 42.8, 83.4, 85.4, 120.3, 127.7, 128.0, 128.1, 128.4, 128.6, 128.7, 128.8, 129.2, 129.3, 129.7, 129.8, 132.7, 134.3, 134.8, 136.0, 141.3, 144.4, 190.1 ppm. HRMS calcd. for $C_{23}H_{18}ClNNaO_3S$ [M+Na] 446.0594, found 446.0594.

***N*-(3-(3-bromophenyl)prop-2-ynyl)-*N*-(2-formylphenyl)-4-**

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methylbenzenesulfonamide 2d:
Yellow solid, m.p. 101 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.4 (s, 3H), 4.7 (s, 2H), 7.06–7.14 (m, 3H), 7.26–7.28 (m, 3H), 7.43 (d, J = 4.5 Hz, 1H), 7.5–7.6 (m, 4H), 8.03 (d, J = 0.6 Hz, 1H), 10.4 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 24.6, 83.8, 84.9, 122.1, 123.8, 128.2, 128.7, 129.3, 129.7, 129.8, 130.1, 131.9, 134.2, 134.3, 135.1, 135.9, 141.4, 144.5, 190.0 ppm. HRMS calcd. for $C_{23}H_{18}BrNNaO_3S$ [M+Na] 490.0088, found 490.0086.

Ethyl [4-(3-(N-(2-formylphenyl)methylsulfonamido)prop-1-yn-1-yl)]benzoate 2e:
Orange solid, m.p. 100 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.33 (t, J = 7.14 Hz, 3H), 3.1 (s, 3H), 4.32 (q, J = 7.8, Hz, 2H), 4.7 (brs, 2H), 7.37 (d, J = 7.9 Hz, 2H), 7.49–7.54 (m, 1H), 7.92 (s, 1H), 7.95–8.0 (m, 2H), 10.40 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.2, 39.1, 42.4, 61.2, 85.7, 85.9, 126.1, 128.8, 129.5, 129.5, 130.6, 131.4, 134.9, 135.4, 141.0, 165.7, 190.0 ppm. HRMS calcd. for $C_{20}H_{19}NNaO_5S$ [M+Na] 408.0882, found 408.0882.

***N*-(2-formylphenyl)-*N*-(3-(thiophen-3-yl)prop-2-ynyl)methanesulfonamide 2f:**
Black sticky solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.1 (s, 3H), 4.70 (brs, 2H), 7.04 (d, J = 3.8 Hz, 1H), 7.27 (q, J = 2.9 Hz, 4.9 Hz, 1H), 7.43 (d, J = 1.8 Hz, 1H), 7.54 (t, J = 7.0 Hz, 1H), 7.66–7.75 (m, 2H), 8.01 (d, J = 6 Hz, 1H), 10.42 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 39.1, 42.7, 82.1, 82.7, 120.7, 125.9, 128.6, 129.4, 129.6, 129.8, 134.9, 135.4, 141.4, 190.1 ppm. HRMS calcd. for $C_{15}H_{13}NNaO_3S_2$ [M+Na] 342.0235, found 342.0236.

***N*-(4-chloro-2-formylphenyl)-4-methyl-*N*-(3-phenylprop-2-ynyl)benzenesulfonamide 2g:**
Brown semisolid, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.42 (s, 3H), 4.69 (brs, 2H), 6.99 (d, J = 8.5 Hz, 1H), 7.14–7.17 (m, 2H), 7.19–7.37 (m, 5H), 7.47 (dd, J = 2.7, 8.6 Hz, 1H), 7.57 (d, J = 8.3 Hz, 2H), 7.98 (d, J = 2.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.7, 42.8, 82.1, 87.0, 121.8, 127.9, 128.3, 128.4, 128.7, 128.8, 129.0, 129.9, 130.1, 130.4, 131.6, 134.2, 135.0, 135.9, 137.4, 139.8, 144.8, 188.9 ppm. HRMS calcd. for $C_{23}H_{18}ClNNaO_3S$ [M+Na] 446.0594, found 446.0594.

***N*-(4-bromo-2-formylphenyl)-*N*-(3-(2-bromophenyl)prop-2-ynyl)4-methylbenzenesulfonamide 2h:**
Yellow solid, m.p. 134 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.39 (s, 3H), 4.72 (s, 2H), 7.01 (d, J = 8.5 Hz, 1H), 7.12–7.16 (m, 1H), 7.19–7.26 (m, 4H), 7.5 (d, J = 7.7 Hz, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.61 (q, J = 2.4, 8.5 Hz, 1H), 8.13 (d, J = 2.4 Hz, 1H), 10.37 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 42.4, 85.1, 86.3, 123.5, 123.9, 125.2, 127.0, 128.1, 129.7, 129.9, 130.3, 131.6, 132.4, 133.4, 134.3, 136.9, 137.3, 140.1, 144.7, 188.6 ppm. HRMS calcd. for $C_{23}H_{17}Br_2NNaO_3S$ [M+Na] 567.9194, found 567.9198.

***N*-(2-formylphenyl)-*N*-(hex-2-ynyl)-4-methylbenzenesulfonamide 2i:**
White solid, m.p. 48 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.75 (t, J = 7.3 Hz, 3H), 1.28 (q, J = 7.3, Hz, 2H), 1.91–1.96 (m, 2H), 2.4 (s, 3H), 4.43 (brs, 2H), 6.90–6.93 (m, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.43–7.53 (m, 4H), 7.97–8.0 (m, 1H), 10.3 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.2, 20.4, 21.5, 42.3, 73.1, 87.3, 128.0, 128.1, 128.4, 129.0, 129.5, 134.1, 134.8, 136.0, 141.4, 144.2, 190.3 ppm. HRMS calcd. for $C_{20}H_{21}NNaO_3S$ [M+Na] 378.1140, found 378.1145.

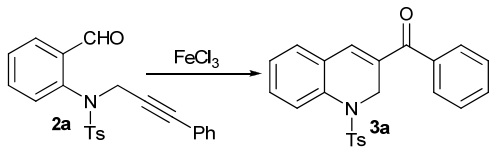
***N*-(but-2-ynyl)-*N*-(2-formylphenyl)methanesulfonamide 2j:**
Colorless semisolid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.82 (s, 3H), 4.43 (brs, 2H), 7.52–7.57 (m, 1H), 7.67–7.70 (m, 2H), 8.0 (t, J = 1.2 Hz, 1H), 10.34 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.7, 39.0, 42.3, 73.2, 83.2, 128.3, 129.1, 129.3, 134.8, 135.4, 141.6, 190.1 ppm. HRMS calcd. for $C_{12}H_{13}NNaO_3S$ [M+Na] 274.0514, found 274.0517.

***N*-(2-acetylphenyl)-4-methyl-*N*-(3-phenylprop-2-ynyl)benzenesulfonamide 4a:**
Yellow solid, m.p. 132 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.34 (s, 3H), 2.68 (s, 3H), 4.77 (brs, 2H), 7.03 (d, J = 7.8 Hz, 1H), 7.16–7.45 (m, 9 H), 7.58 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 16.3 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 30.1, 42.4, 83.4, 86.0, 122.3, 128.2, 128.3, 128.8, 128.9, 129.4, 129.5, 131.2, 131.5, 135.8, 136.6, 141.9, 143.9, 200.1 ppm. HRMS calcd. for $C_{24}H_{21}NNaO_3S$ [M+Na] 426.1140, found 426.1138.

***N*-(2-acetylphenyl)-*N*-(3-*p*-tolylprop-2-ynyl)acetamide 4b:**
Dark brown semisolid, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.85 (s, 3H), 2.32 (s, 3H), 2.6 (s, 1H), 4.42 (d, J = 10.5 Hz, 1H), 4.97 (d, J = 10.5 Hz, 1H), 7.07 (d, J = 4.5 H, 2H), 7.17 (d, J = 4.5 Hz, 2H), 7.42 (d, J = 4.5 Hz, 1H), 7.52 (t, J = 4.5 Hz, 1H), 7.61 (t, J = 4.5 Hz, 1H), 7.80–7.82 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.5, 22.7, 29.9, 38.8, 85.2, 119.7, 129.0, 129.1, 129.2, 130.0, 131.3, 131.5, 131.6, 132.9, 137.2, 139.5, 139.8, 170.1, 199.0 ppm. HRMS calcd. for $C_{20}H_{19}NNaO_2$ [M+Na] 328.1313, found 328.1313.

General Procedure for $FeCl_3$-Catalyzed Synthesis of 1,2-dihydroquinoline:

Representative Experimental Procedure for the Synthesis of phenyl(*N*-tosyl-1,2-dihydroquinolin-3-yl)methanone 3a:



Compound **2a** (195mg, 0.5 mmol) was taken in a dry 5 mL round-bottom flask containing 2 mL of dry acetonitrile solvent. Anhydrous $FeCl_3$ (8.11 mg, 0.05 mmol) was added, and the reaction mixture was heated to reflux for 4 h under argon atmosphere. After complete conversion of the starting material (monitoring by TLC), acetonitrile was removed under reduced pressure and the residue was purified by silica gel (mess 60–120) column chromatography to afford **3a** (179 mg, 0.46 mmol, 95%) as a white solid, m.p. 131 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.34 (s, 3H), 4.82 (s, 2H), 6.65 (s, 1H), 7.08 (d, J = 8.2 Hz, 3H), 7.22 (d, J = 7.2 Hz, 2H), 7.27–7.48 (m, 6H), 7.53 (t, J = 7.4 Hz, 1H), 7.81 (d, J = 8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 44.7, 127.0, 127.1, 127.5, 127.9,

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128.0, 128.4, 128.9, 129.0, 129.4, 129.8, 131.1, 132.0, 132.3, 136.5, 137.0, 143.7, 193.4 ppm. HRMS calcd. for $C_{23}H_{19}NNaO_3S$ [M+Na] 412.0983, found 412.0980.

***p*-tolyl(1-tosyl-1,2-dihydroquinolin-3-yl)methanone 3b:**

The general procedure was followed using **2b** (202 mg, 0.5 mmol), heating at reflux for 7 hr. The product was purified by silica gel (mess 60–120) column chromatography to afford **3b** as yellow solid, (161 mg, 0.4 mmol, 80%), m.p. 116 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.34 (s, 3H), 2.40 (s, 1H), 4.80 (s, 2H), 6.63 (s, 1H), 7.07 (d, J = 7.7 Hz, 3H), 7.12–7.16 (m, 4H), 7.19–7.28 (m, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.44 (t, J = 7.6 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 44.8, 126.9, 127.0, 127.4, 127.9, 128.8, 129.0, 129.4, 130.8, 132.4, 134.2, 136.3, 136.4, 142.7, 143.6, 193.1 ppm. HRMS calcd. for $C_{24}H_{21}NNaO_3S$ [M+Na] 426.1141, found 426.1141.

(4-chlorophenyl)(1-tosyl-1,2-dihydroquinolin-3-yl)methanone 3c:

The general procedure was followed using **2c** (212 mg, 0.5 mmol), heating at reflux for 9 hr. The product was purified by silica gel (mess 60–120) column chromatography to afford **3c** as light yellow solid (188 mg, 0.45 mmol, 89%), m.p. 170 °C. 1H NMR ($CDCl_3$, 300 MHz) δ 2.35 (s, 3H), 4.80 (s, 2H), 6.61 (s, 1H), 7.06–7.09 (m, 3H), 7.17 (dd, J = 1.8, 6.6 Hz, 2H), 7.25–7.27 (m, 1H), 7.30–7.37 (m, 4H), 7.44–7.5 (m, 1H), 7.81 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 44.5, 127.0, 127.4, 127.7, 128.5, 129.0, 129.3, 130.2, 131.2, 132.0, 135.2, 136.3, 136.5, 136.9, 138.4, 143.7, 192.1 ppm. HRMS calcd. for C23H18ClNNaO3S [M+Na] 446.0594, found 446.0594.

(3-bromophenyl)(1-tosyl-1,2-dihydroquinolin-3-yl)methanone 3d:

The general procedure was followed using **2d** (233 mg, 0.5 mmol), heating at reflux for 12 hr. The product was purified by silica gel (mess 60–120) column chromatography to afford afford **3d** as yellow solid (196 mg, 0.42 mmol, yield 84%), m.p. 152 °C, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.37 (s, 3H), 4.7 (s, 2H), 6.64 (s, 1H), 7.01 (d, J = 4.8 Hz, 3H), 7.19 (d, J = 4.8 Hz, 2H), 7.25–7.29 (m, 3H), 7.32 (d, J = 4.8 Hz, 1H), 7.46–7.49 (m, 1H), 7.65 (d, J = 4.5 Hz, 1H), 7.82 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 44.8, 126.9, 127.0, 127.4, 127.9, 128.8, 129.0, 129.4, 130.9, 132.4, 134.2, 136.3, 136.4, 142.8, 143.6, 193.1 ppm. HRMS calcd. for $C_{23}H_{18}BrNNaO_3S$ [M+Na] 490.0088, found 490.0074.

Ethyl-4-(1-(methylsulfonyl)-1,2-dihydroquinoline-3-carbonyl)benzoate 3e:

The general procedure was followed using **2e** (193 mg, 0.5 mmol), heating at reflux for 14 hr. The product was purified by silica gel (mess 60–120) column chromatography to afford afford **3e** as orange semi-solid, (144 mg, 0.375 mmol,75%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.42 (t, J = 7.11 Hz, 3H), 2.76 (s, 3H), 4.42 (q, J = 7.11 Hz, 2H), 4.82 (s, 2H), 7.18 (s, 1H), 7.27 (d, J = 4.5 Hz, 2H),7.40–7.45 (m, 1H), 7.69(d, J = 8.1 Hz, 1H), 7.78 (d, J = 8.3 Hz, 2H), 8.16 (d, J = 8.3 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.3, 29.7, 38.2, 44.4, 61.5, 126.1, 126.8, 127.0, 129.0, 129.6, 129.7, 131.6, 133.2, 133.8, 136.6, 137.3, 140.5, 165.7, 193.2 ppm. HRMS calcd. for $C_{20}H_{19}NNaO_5S$ [M+Na] 408.0882, found 408.0882.

(1-(methylsulfonyl)-1,2-dihydroquinolin-3-yl)(thiophen-3-yl)methanone 3f:

The general procedure was followed using **2f** (159 mg, 0.5 mmol), heating at reflux for 8 hr. The product was purified by silica gel (mess 60–120) column chromatography to afford afford **3f** as dark brown semi-solid, (112 mg, 0.35 mmol, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.75 (s, 1H), 4.79 (s, 2H), 7.28–7.34 (m, 2H), 7.36 (s, 1H), 7.40–7.43 (m, 2H), 7.53 (d, J = 3 Hz, 1H), 7.69 (d, J = 4.8 Hz, 1H), 7.97 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.0, 44.6, 126.3, 126.8, 126.9, 127.3, 128.0, 129.2, 129.7, 131.1, 132.5, 134.4, 134.8, 136.4, 140.2, 187.1 ppm. HRMS calcd. for $C_{15}H_{13}NNaO_3S_2$ [M+Na] 342.0235, found 342.0235.

(6-chloro-1-tosyl-1,2-dihydroquinolin-3-yl)(phenyl)methanone 3g:

The general procedure was followed using **2g** (211 mg, 0.5 mmol), heating at reflux for 21 hr. The product was purified by silica gel (mess 60–120) column chromatography to afford afford **3g** as yellow semi-solid (186.66 mg, 0.44 mmol, 88%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.4 (s, 3H), 4.81 (s, 2H), 6.21 (s, 1H), 7.07–7.12 (m, 3H), 7.19–7.23 (m, 2H), 7.33–7.42 (m, 5H), 7.54 (t, J = 7.4 Hz, 1H), 7.76 (d, J = 8.61 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 44.6, 127.0, 127.7, 128.2, 128.3, 128.7, 128.8, 129.2, 129.6, 129.8, 130.1, 132.2, 132.5, 133.3, 134.8, 135.4, 136.0, 136.6, 143.9, 193.1 ppm. HRMS calcd. for $C_{23}H_{18}ClNNaO_3S$ [M+Na] 446.0594, found 446.0593.

(6-bromo-1-(*p*-tolyl)-1,2-dihydroquinolin-3-yl)(2-bromophenyl)methanone 3h:

The general procedure was followed using **2h** (272 mg, 0.5 mmol), heating at reflux for 5 hr. The product was purified by silica gel (mess 60–120) column chromatography to afford **3h** as yellow solid, (253 mg, 0.35 mmol, 93%), m.p. 120 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.37 (s, 3H), 4.84 (s, 2H), 6.37 (s, 1H), 6.75–6.77 (m, 1H) 7.14 (d, J = 7.9 Hz, 1H), 7.21 (d, J = 1.9 Hz, 2H), 7.28–7.31 (m, 2H), 7.36 (d, J = 8.12 Hz, 1H), 7.54–7.59 (m, 3H), 7.72 (d, J = 8.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 43.3, 119.6, 120.2, 127.0, 127.1, 128.1, 128.6, 128.8, 129.4, 129.7, 131.6, 133.4, 133.8, 134.1, 135.7, 136.0, 136.9, 139.1, 144.1, 139.1 ppm. HRMS calcd. for $C_{23}H_{17}Br_2NNaO_3S$ [M+Na] 567.9194, found 567.9191.

1-(1-tosyl-1,2-dihydroquinolin-3-yl)butan-1-one 3i:

The general procedure was followed using **2d** (233 mg, 0.5 mmol), was heated to 65 °C for 3 h. The product was purified by silica gel (mess 60–120) column chromatography to afford **3i** as colourless oil (132 mg, 0.37 mmol, 74%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, J = 7.2 Hz, 3H), 1.55 (q, J = 7.3 Hz, 2H), 2.31–2.36 (m, 5H), 6.82 (s, 1H), 7.03 (d, J = 8 Hz, 2H), 7.15 (d, J = 7.5 Hz, 1H), 7.21 (s, 1H), 7.24–7.29 (m, 2H), 7.40–7.45 (m, 1H), 7.76 (d, J = 8.1 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.0, 18.0, 21.6, 39.0, 43.6, 127.1, 127.2,

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127.6, 128.8, 129.3, 130.9, 132.8, 133.2, 136.2, 136.8, 134.7, 197.9 ppm. HRMS calcd. for $C_{20}H_{21}NNaO_3S$ [M+Na] 378.1140, found 378.1142.

1-(1-(methylsulfonyl)-1,2-dihydroquinolin-3-yl)ethanone 3j:

The general procedure was followed using **2j** (126 mg, 0.5 mmol), heated at 65 °C for 3 hr. The product was purified by silica gel (mess 60–120) column chromatography to afford **3j** as colorless solid (94 mg, 0.37 mmol, 75%), m.p. 145 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.46 (s, 3H), 2.67 (s, 3H), 4.67 (s, 2H), 7.3 (d, J = 7.28 Hz, 1H), 7.3–7.45 (m, 3H), 7.67 (d, J = 8.1 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.3, 38.1, 43.5, 125.9, 126.8, 127.3, 129.4, 131.3, 134.4, 134.5, 136.6, 195.6 ppm. HRMS calcd. for $C_{12}H_{13}NNaO_3S$ [M+Na] 274.0514, found 274.0514.

(4-methyl-1-tosyl-1,2-dihydroquinolin-3-yl)(phenyl)methanone 5a:

Compound **4a** (202 mg, 0.5 mmol) was taken in an oven dry 5 mL round–bottom flask containing 2 mL of dry nitromethane solvent. Anhydrous $FeCl_3$ (8.11 mg, 0.05 mmol) was added, and the reaction mixture was heated to 85 °C for 6 h under inert atmosphere. After complete conversion of the starting material (monitoring by TLC), acetonitrile was removed under reduced pressure and the residue was purified by silica gel (mess 60–120) column chromatography to afford **5a** as light yellow solid (161 mg, 0.40 mmol, 80%), m.p. 144 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.47 (s, 3H), 2.32 (s, 3H), 4.61 (s, 2H), 7.07 (d, J = 8.1 Hz, 2H), 7.28–7.44 (m, 6H), 7.55 (d, J = 7.31 Hz, 2H), 7.62–7.65 (m, 2H), 7.8 (d, J = 7.78 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.0, 21.5, 47.0, 124.5, 126.9, 127.2, 127.6, 128.8, 128.9, 129.0, 129.3, 130.1, 131.5, 133.3, 133.8, 135.4, 135.8, 137.7, 143.4, 196.1 ppm. HRMS calcd. for $C_{24}H_{21}NNaO_3S$ [M+Na] 426.1140, found 426.1144.

1-(4-methyl-3-(4-methylbenzoyl)quinolin-1(2H)-yl)ethanone 5b:

The procedure of **4a** was followed using **4b** (153 mg, 0.5 mmol), heated at 85 °C for 4 h. The product was purified by silica gel (mess 60–120) column chromatography to afford **5b** as yellow semi-solid**,** (119 mg, 0.39 mmol, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.03 (s, 3H), 2.30 (s, 3H), 2.43 (s, 3H), 4.60 (s, 2H), 7.26–7.35 (m, 5H), 7.46 (d, J = 6 Hz, 1H), 7.77 (d, J = 6.3 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 22.5, 29.8, 124.7, 124.9, 125.7, 128.5, 129.6, 129.7, 129.9, 130.5, 136.5, 144.7, 169.4, 196.6 ppm. HRMS calcd. for $C_{20}H_{19}NNaO_2$ [M+Na] 328.1313, found 328.1313.

Experimental Procedure for the Synthesis of Phenyl(quinolin-3-yl)methanone 6a:[22]

Compound **2a** (195 mg, 0.5 mmol) was taken in an oven dry 5 mL round-bottom flask containing 2 mL of dry acetonitrile solvent. Anhydrous $FeCl_3$ (8.11 mg, 0.05 mmol) was added, and the reaction mixture was heated to reflux for 4 h under argon atmosphere. After complete conversion of the starting material (monitoring by TLC), acetonitrile was removed under reduced pressure. Then 1 mL EtOH and NaOH (2.5 mmol, 100 mg) were added to the reaction mixture and heated to 60 °C for 2 hr. The residue was purified by silica gel (mess 60–120) column chromatography to afford **6a** as a yellow semi-solid (99.1 mg, 0.43 mmol, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54 (t, J = 8.03 Hz, 2H), 7.64–7.69 (m, 2H), 7.83–7.89 (m, 3H), 7.93 (d, J = 8.2 Hz, 1H), 8.19 (d, J = 8.5 Hz, 1H), 8.56 (s, 1H), 9.3 (s, 1H) ppm. HRMS calcd. for $C_{16}H_{11}NNaO$ [M+Na] 256.0738, found 256.0738.

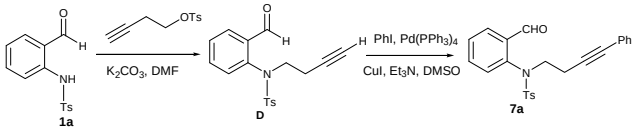
(4-chlorophenyl)(quinolin-3-yl)methanone 6b:[22]

Compound **6b** was prepared using **2c** (212 mg, 0.5 mmol) following similar method as described for **6a**. The product was purified by silica gel (mess 60–120) column chromatography to afford **6b** as a yellow semisolid (93 mg, 0.35 mmol,70%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 7.5 Hz, 1H), 7.81 (s, 1H), 7.85 (d, J = 2.6 Hz, 1H), 7.88–7.95 (m, 2H), 8.2 (d, J = 8.6 Hz, 1H), 8.55 (s, 1H), 9.3 (s, 1H) ppm. HRMS calcd. for $C_{16}H_{10}ClNNaO$ [M+Na] 290.0349, found 290.0344.

(4-methylquinolin-3-yl)(phenyl)methanone 6c:[22]

Compound **6c** was prepared using **4a** (202 mg, 0.5 mmol) following similar method as described for **6a.** The residue was purified by silica gel (mess 60–120) column chromatography to afford **6c** as a brown semi-solid (89 mg, 0.32 mmol, 65%), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.67 (s, 1H), 7.44–7.52 (m, 2H), 7.61–7.70 (m, 2H), 7.75–7.86 (m, 3H), 8.12–8.19 (m, 2H), 8.81 (s, 1H) ppm. HRMS calcd. for $C_{17}H_{13}NNaO$ [M+Na] 270.0895, found 270.0895.

Preparation of *N*-(2-formylphenyl)-4-methyl-*N*-(4-phenylbut-3-ynyl)benzenesulfonamide 7a:



Aldehyde **1a** (500 mg, 1.81 mmol) was dissolved in dry DMF (10 mL) in a 50 mL round-bottom flask. 5 mg KI was added, to this solution were added anhydrous K_2CO_3 (1.25 g, 9 mmol) followed by but-3-ynyl 4-methylbenzenesulfonate (812. mg, 3.62 mmol) and the reaction mixture was heated at 90 °C under inert atmosphere for 18 h. The mixture was cooled to room temperature and filtered through the sintered glass crucible. After that, the solvent DMF was removed under reduced pressure, and the residue was purified by column chromatography using silica gel (mess 60–120) to obtain the product **D** (325 mg, 0.99 mmol, 55%) as a white solid.

To a mixture of compound **D** (327 mg, 1.0 mmol), 4-iodoanisole (281 mg, 1.2 mmol), and triethylamine (303 mg, 3.0 mmol) in dry DMSO (5 mL) under inert atmosphere at room temperature were added $Pd(PPh_3)_4$ (11.55 mg, 0.01 mmol) and CuI (5.75 mg, 0.03 mmol) successively. The reaction mixture was stirred at room temperature for 8 h. Then the mixture was diluted with saturated brine solution and extracted with EtOAc. The compound was purified using silica gel (mess 60–120) column chromatography to afford the compound 7**a** as a brown semi solid (320 mg, 74%). ^{1}H NMR

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($CDCl_3$, 300 MHz) δ 2.42 (s, 3H), 2.62–2.68 (m, 2H), 3.53 (brs, 1H), 4.16 (brs, 1H), 6.77 (d, J = 7.2 Hz, 1H), 7.27 (brs, 7H), 7.42–7.51 (m, 4H), 8.0–8.03 (m, 1H), 10.5 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.3, 21.7, 42.0, 50.7, 83.1, 85.8, 123.1, 127.9, 128.0, 121.3, 128.7, 128.9, 129.8, 131.6, 132.1, 134.2, 134.4, 136.4, 141.6, 144.4, 190.1 ppm. HRMS calcd. for $C_{25}H_{23}NNaO_4S$ [M+Na] 426.1140, found 426.1143. Compound **7b**, **7c** and **7d** were also synthesized by similar procedure.

***N*-(2-formylphenyl)-*N*-(4-(4-methoxyphenyl)but-3-ynyl)-4-methylbenzenesulfonamide 7b:**
Brown semi–solid, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.43 (s, 3H), 2.63 (d, J = 5.8 Hz, 2H), 3.5 (s, 1H), 3.78 (s, 3H), 4.12 (s, 1H), 6.77–6.80 (m, 3H), 7.21 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 6.32 Hz, 3H), 7.42–7.50 (m, 4H), 8.0–8.03 (m, 1H), 10.53 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.4, 21.7, 50.8, 55.4, 83.0, 84.3, 114.0, 115.2, 127.9, 128.1, 128.8, 128.9, 129.9, 133.1, 134.3, 134.4, 136.4, 141.7, 144.4, 159.6, 190.2 ppm. HRMS calcd. for $C_{25}H_{23}NNaO_4S$ [M+Na] 456.1245, found 456.1245.

Methyl[4-(4-(N-(2-formylphenyl)-4-methylphenylsulfonamido)but-1-ynyl)]benzoate 7c:
Brown solid, m. p.156 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.43 (s, 3H), 2.64–2.72 (m, 2H), 3.55 (d, J = 6.1 Hz, 1H), 3.9 (s, 3H), 4.16 (d, J = 6.6 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 7.28–7.34 (m, 3H), 7.43–7.51 (m, 4H), 7.93 (d, J = 8.3 Hz, 2H), 8.01 (dd, J = 1.9, 7 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.4, 21.6, 50.4, 52.2, 82.4, 89.1, 127.7, 127.9, 128.6, 128.8, 129.4, 129.7, 131.5, 134.1, 134.2, 136.2, 141.5, 144.4, 166.5, 189.9 ppm. HRMS calcd. for $C_{26}H_{23}NNaO_5S$ [M+Na] 484.1195, found 484.1190.

N-(2-formylphenyl)-4-methyl-N-(pent-3-yn-1-yl)benzenesulfonamide 7d: Light yellow semi–solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H), 2.42 (s, 3H), 3.49 (brs, 1H), 4.17 (brs, 1H), 6.66 (d, J = 7.2 Hz, 1H), 7.26 (d, J = 8 Hz, 2H), 7.43–7.5 (M, 4H), 8.01 (d, J = 9.2 Hz, 1H), 10.5 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.5, 21.6, 21.7, 50.7, 75.3, 78.6, 127.3, 128.0, 128.4, 128.7, 129.8, 134.1, 134.2, 135.9, 136.3, 141.7, 144.3, 190.2 ppm. HRMS calcd. for $C_{19}H_{19}NNaO_3S$ [M+Na] 364.0983, found 364.0980.

Experimental Procedure for the Synthesis of Phenyl(1-tosyl-2,3-dihydro-1H-benzo[b]azepin-4-yl)methanone 8a: Compound **7a** (202 mg, 0.5 mmol) was taken in a 5 mL round-bottom flask containing 2 mL of dry acetonitrile solvent. Anhydrous $FeCl_3$ (8.11 mg, 0.05 mmol) was added, and the reaction mixture was heated to reflux for 8 h under inert atmosphere. After complete conversion of the starting material (monitoring by TLC), acetonitrile was remove under reduced pressure and the residue was purified by silica gel (mess 60–120) column chromatography to afford **8a** as light yellow semisolid (145 mg, 0.36 mmol, 72%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.3 (s, 3H), 3.03 (t, J =3.6 Hz, 2H), 3.99 (t, J = 3.3 Hz, 2H), 6.75 (s, 1H), 7.11 (d, J = 4.8 Hz, 1H), 7.60 (d, J = 4.8 Hz, 2H), 7.26 (t, J = 4.3 Hz, 1H), 7.32 (d, J = 4.8 Hz, 2H), 7.36–7.43 (m, 5H), 7.50–7.53 (m, 1H), 7.73 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 30.6, 48.9, 127.2, 127.5, 128.3, 129.4, 129.6, 129.7, 130.1, 131.3, 132.0, 133.9, 137.9, 138.3, 139.9, 140.0, 140.3, 143.4, 198.1 ppm. HRMS calcd. for $C_{25}H_{23}NNaO_4S$ [M+Na] 426.1140, found 426.1140.

(4-methoxyphenyl)(1-tosyl-2,3-dihydro-1H-benzo[b]azepin-4-yl)methanone 8b:
Compound **8b** was prepared using **7b** (217 mg, 0.5 mmol) following similar proceduer as described for **8a**. The residue was purified by silica gel (mess 60–120) column chromatography to afford **8b** as white solid (151.6 mg, 0.35 mmol, 70%), m. p. 197 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3H), 3.05 (t, J =3.4 Hz, 2H), 3.90 (s, 3H), 4.0 (s, 2H), 6.71 (s, 1H), 6.88 (d, J = 5.1 Hz, 2H), 7.14–7.17 (m, 3H), 7.28 (t, J = 4.8 Hz, 1H), 7.37–7.41 (m, 3H), 7.46 (d, J = 4.8 Hz, 2H), 7.75 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 29.8, 48.9, 55.6, 113.6, 127.2, 127.5, 129.5, 129.6, 129.7, 130.1, 131.4, 131.9, 133.7, 137.8, 138.3, 140.1, 140.3, 143.3, 163.1, 196.9 ppm. HRMS calcd. for $C_{25}H_{23}NNaO_4S$ [M+Na] 456.1245, found 456.1245.

Methyl [4-(1-tosyl-2,3-dihydro-1H-benzo[b]azepine-4-carbonyl)]benzoate 8c:
Compound **8c** was prepared using **7c** (231 mg, 0.5 mmol) following similar procedure as described for **8a**. The product was purified by silica gel (mess 60–120) column chromatography to afford **8c** as white solid (157 mg, 0.34 mmol, 68%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.38 (s, 1H), 3.04 (t, J = 5.8 Hz, 2H), 3.39 (s, 3H), 3.96–4.01 (m, 2H), 6.72 (s, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.17 (d, J = 8 Hz, 2H), 7.25 (d, J = 5.9 Hz, 1H), 7.33 (q, J = 8.3 Hz, 2H), 7.42 (d, J = 8.1 Hz, 3H), 7.73 (d, J = 8.1 Hz, 1H), 8.03 (d, J = 8 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 30.2, 48.7, 52.5, 127.0, 127.5, 129.0, 129.3, 129.5, 129.6, 130.3, 130.9, 132.8, 134.0, 138.1, 139.5, 140.0, 141.1, 141.8, 143.4, 166.2, 197.3 ppm. HRMS calcd. for $C_{26}H_{23}NNaO_5S$ [M+Na] 484.1195, found 484.1194.

1-(1-tosyl-2,3-dihydro-1H-benzo[b]azepin-4-yl)ethanone 8d:
Compound **8d** was prepared using **7d** (170.5 mg, 0.5 mmol) following similar procedure as described for **8a**. The product was purified by silica gel (mess 60–120) column chromatography to afford **8d** as white semisolid (136 mg, 0.40 mmol, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.18 (s, 3H), 2.34 (s, 3H), 2.87 (t, J = 5.7 Hz, 2H), 3.91 (t, J = 6 Hz, 2H), 7.02 (s, 1H), 7.1 (d, J = 8.4 Hz, 2H), 7.28–7.39 (m, 5H), 7.64 (d, J = 7.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 25.6, 29.0, 49.7, 127.2, 127.7, 129.4, 129.8, 130.2, 131.7, 133.8, 137.9, 140.4, 140.5, 143.4, 198.9 ppm. HRMS calcd. for $C_{19}H_{19}NaO_3S$ [M+Na] 364.0983, found 364.0983.

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References:

1. (a) H. Fan, J. Peng, M. T. Hamann, J. F. Hu, *Chem. Rev.*, 2008, **108**, 264; (b) S. Fustero, M. Sánchez-Roselló, P. Barrio, A. Simón-

Organic & Biomolecular Chemistry Accepted Manuscript

Fuentes, *Chem. Rev.*, 2011, **111**, 6984; (c) N. T. Patil, Y.Yamamoto, *Chem. Rev.*, 2008, **108**, 3395; (d) A. R. Katritzky, *Chem. Rev.*, 2004, **104**, 2125.

2. (a) V. R. Solomon, H. Lee, *Curr. Med. Chem.*, 2011, **18**, 1488; (b) V. Sridharan, P. A. Suryavanshi, C. Menendez, *Chem. Rev.*, 2011, **111**, 7157; (c) K. Kaur, M. Jain, R. P. Reddy, R. Jain, *Eur. J. Med. Chem.*, 2010, **45**, 3245; (d) J. P. Michael, *Nat. Prod. Rep.*, 2008, **25**, 166; (e) G. Jones, In: *Comprehensive Heterocyclic Chemistry II*; A. R. Katritzky, C. W. Rees, E. F. V. Scriven, Eds.; *Pergamon Press*: Oxford, 1996, **5**, 167; (f) S. Madapa, Z. T. S. Batra, *Curr. Org. Chem.*, 2008, **12**, 1116–1183; d) J. A. Joule, K. Mills, *In Heterocyclic Chemistry*., 5th Ed., Wiley, UK, 2010.
3. (a) H. Takahash, Y. Bekkali, A. J. Capolino, T. Gilmore, S. E. Goldrick, P. V. Kaplita, L. Liu, R. M. Nelson, D. Terenzio, J. Wang, L. Zuvela-Jelaska, J. Proudfoot, G. Nabozny, D. Thomson, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 5091; (b) L. Zhi, C. M. Tegley, B. Pio, S. J. West, K. B. Marschke, D. E. Mais, T. K. Jones, *Bioorg. Med. Chem. Lett.*, 2000, **10**, 415.
4. (a) J. V. Johnson, *J. Med. Chem.*, 1989, **32**, 1942; (b) I. V. Ukrainets, L. V. Sidorenko, O. V. Gorokhova, N. A. Jaradat, *Chemistry of Heterocyclic Compounds*., 2006, **42**, 475; (c) J. C. Craig, P. E. Person, *J. Med. Chem*., 1971, **14**, 1221; (d) N. Yamada, S. Kadowaki, K. Takahashi, K. Umezu, *Biochem. Pharmacol.*, 1992, **44**, 1211; (e) B. Lockhart, N. Bonhomme, A. Roger, G. Dorey, P. Casara, P. Lestage, *Eur. J. Pharmacol*., 2001, **416**, 59; (f) I. N. Nesterova, L. M. Alekseeva, S. M. Golovira, V. G. Granik, *Khim.-Farm. Zh.*, 1995, **29**, 31; (g) T. K. Jones, D. T. Winn, L. Zhi, L. G. Hamann, C. M. Tegley, C. L. F. Pooley, U.S. Patent 5688808, 1997; (h) L. Zhi, Tegley, M. Christopher, K. B. Marschke, D. E. Mais, Jones, K. Todd, *J. Med. Chem*., 1999, **42**, 1466; (i) M. J. Coughlan, S. W. Elmore, M. E. Kort, P. R. Kym, J. L. Moore, J. K. Pratt, A. X. Wang, J. P. Edwards, T. K. Jones, Patent WO 9941256, 1999(a) J. V. Johnson, *J. Med. Chem.*, 1989, **32**, 1942; (b) I. V. Ukrainets, L. V. Sidorenko, O. V. Gorokhova, N. A. Jaradat, *Chemistry of Heterocyclic Compounds*., 2006, **42**, 475; (c) J. C. Craig, P. E. Person, *J. Med. Chem*., 1971, **14**, 1221; (d) N. Yamada, S. Kadowaki, K. Takahashi, K. Umezu, *Biochem. Pharmacol.*, 1992, **44**, 1211; (e) B. Lockhart, N. Bonhomme, A. Roger, G. Dorey, P. Casara, P. Lestage, *Eur. J. Pharmacol*., 2001, **416**, 59; (f) I. N. Nesterova, L. M. Alekseeva, S. M. Golovira, V. G. Granik, *Khim.-Farm. Zh.*, 1995, **29**, 31; (g) T. K. Jones, D. T. Winn, L. Zhi, L. G. Hamann, C. M. Tegley, C. L. F. Pooley, U.S. Patent 5688808, 1997; (h) L. Zhi, Tegley, M. Christopher, K. B. Marschke, D. E. Mais, Jones, K. Todd, *J. Med. Chem*., 1999, **42**, 1466; (i) M. J. Coughlan, S. W. Elmore, M. E. Kort, P. R. Kym, J. L. Moore, J. K. Pratt, A. X. Wang, J. P. Edwards, T. K. Jones, Patent WO 9941256, 1999.
5. (a) P. Evans, A. O'Byrne, *Tetrahedron*., 2008, **64**, 8067–8072; (b) R. D. Dillard, D. E. Pravey, D. N. Benslay, *J. Med. Chem*., 1973, **16**, 251–253; (c) Gurunathan, S. Perumal, P.T. *Tetrahedron Lett*., 2011, **52**, 1783–1787; (d) J. A. Damavandi, M. A. Zolfigol, B. Karami, *Synth Commun*., 2001, **31**, 3183–3187; (e) K. Nikham, B. Karami, M. A. Zolfigol, *Catal. Commun.*, 2007, **8**, 1427–1430.
6. (a) Z. H. Skraup, *Monatsh. Chem.*, 1880, **1**, 316; (b) Z. H. Skraup, *Monatsh. Chem*., 1881, **2**, 587; (c) H. Skraup, *Chem. Ber*., 1880, **13**, 2086; (d) O. Doebner, W. V. Miller, *Ber. Dtsh. Chem. Ges.*, 1881, **14**, 2812; (e) R. H. F. Mansake, M. Kulka, *Org. React*., 1953, **7**, 5912.
7. (a) X.-Y. Hu, J.-C. Zhang, W. Wie, J.-X. Ji, *Tetrahedron Lett.*, 2011, **52**, 2903–2905 and references cited therein; (b) H. Waldmann, G. V. Karunakar, K. Kumar, *Org. Lett*., 2008, **10**, 2159-2162; (c) J.-C. Zhang, J.-X. Ji, *Catalysis*., 2011, 1360–1363. (d) J.-C. Zhang, J.-X. Ji, *ACS Catal.*, 2011, **1**, 1360–1363; (e) Y.-W. Zhu, J.-L. Qian, W.-B. Yi, C. Cai, *Tetrahedron Lett.*, 2013, **54**, 638–641.
8. (a) K. Makino, O. Hara, Y. Takiguchi, T. Katano, Y. Asakawa, K. Hatano, Y. Hamada, *Tetrahedron Lett.*, 2003, **44**, 8925–8929; (b) A. M. Wagner, C. E. Knezevic, J. L. Wall, V. L. Sun, J. A. Buss, L. A. T. Allen, A. G. Wenzel, *Tetrahedron Letts.*, 2012, **53**, 833–836.
9. (a) Y. M. Luo, Z. G. Li, C. J. Li, *Org. Lett.*, 2005, **7**, 2675; (b) X. Y. Liu, P. Ding, J. S. Huang, C. M. Che, *Org. Le*t., 2007, **9**, 2645; (c) Y. Zhou, E. Feng, G. Liu, D. Ye, J. Li, H. Jiang, H. Liu, *J. Org. Chem.*, 2009, **74**, 7344–7348.
10. (a) P. Evans, R. Grigg, M. Monteith, *Tetrahedron Lett.*, 1999, **40**, 5247; (b) M. Arisawa, C. Theeraladanon, A. Nishida, M. Nakagawa, *Tetrahedron Lett.*, 2001, **42**, 8029–8033.
11. (a) Z. Wang, S. Li, B. Yu, H. Wu, Y. Wang, X. Sun, *J. Org. Chem.*, 2012, **77**, 8615–8620; (b) P. Kothandraman, S. J. Foo, P. W. H. Chan, *J. Org. Chem.*, 2009, **74**, 5947–5952.
12. (a) Microreview: T. Kitamura, *Eur. J. Org. Chem.*, 2009, 1111–1125; (b) X. Y. Liu, C. M. Che, *Angew. Chem. Int. Ed.*, 2008, **47**, 3805; (c) M. Arisawa, C. Theeraladanon, A. Nishida, M. Nakagawa, *Tetrahedron Lett.*, 2001, **42**, 8029; (d) K. A. Parker, T. L. Mindt, *Org. Lett.*, 2002, **4**, 4265; (e) C. S. Yi, S. Y. Yun, I. A. Guzei, *J. Am. Chem. Soc.*, 2005, **127**, 5782; (f) R. Kamakshi, B. S. R. Reddy, *Catal. Commun.*, 2007, **8**, 825; (g) M. E. Theoclitou, L. A. Robinson, *Tetrahedron Lett.*, 2002, **43**, 3907; (h) B. C. Ranu, A. Hajra, S. S. Dey, U. Jana, *Tetrahedron*., 2003, **59**, 813–819; (i) K. Makino, O. Hara, Y. Takiguchi, T. Katano, Y. Asakawa, K. Hatano, Y. Hamada, *Tetrahedron Lett.*, 2003, **44**, 8925–8929; (j) R. H. F. Mansake, M. Kulka, *Org. React.*, 1953, **7**, 59–70; (k) C. S. Yi, S. Y. Yun, *J. Am. Chem. Soc.*, **2005**, *127*, 17000–17006; (l) X. Zhang, B. Liu, X. Shu, Y. Gao, H. Lv, J. Zhu, *J. Org. Chem.*, 2012, **77**, 501; (m) M. M. Lorion, D. Gasperini, J. Oble, G. Poli, *Org. Lett.,* 2013, **15**, 3050–3053.
13. Few selected examples; (a) T. Kametani, K. Fukumoto, *Heterocycles*., 1975, **3**, 931; (b) V. Kouznetsov, A. Palma, C. Ewert, *Curr. Org. Chem.*, 2001, **5**, 519; (c) J.-P. K. Meigh, *Sci. Synth.*, 2004, **17**, 825. (d) W. M. Kazmierski, J. P.Peckham, M. Duan, T. P. Kenakin, S. Jenkinson, K. S. Gudmundsson, S. C. Piscitelli, P. L. Feldman, *Curr. Med. Chem.*: *Anti-Infect. Agents*., 2005, **4**, 133; (e) M. Thibonnier, P. Coles, A. Thibonnier, M. Shoham, *Annu. Rev. Pharmacol. Toxicol.*, 2001, **41**, 175; (f) M. A. Xiang, P. J. Rybczynski, M. Patel, R. H. Chen, D. F. McComsey, H.-C. Zhang, J. W. Gunnet, R. Look, Y. Wang, L. K. Minor, H. M. Zhong, F. J. Villani, Demarest, K. T.; Damianob, B. P.; Maryanoff, B. E. *Bioorg. Med. Chem. Lett.*, 2007, **17**, 6623; (g) C. M. Yea, C. E. Allan, D. M. Ashworth, J. Barnett, A. J. Baxter, J. D. Broadbridge, R. J. Franklin, S. L. Hampton, P. Hudson, J. A. Horton, P. D. Jenkins, A. M. Penson, G. R. W. Pitt, P. Riviére, P. A. Robson, D. P. Rooker, G. Semple, A. Sheppard, R. M. Haigh, M. B. Roe, *J. Med. Chem.*, 2008, **51**, 8124; (h) Y. Yamamura, S. Nakamura, S. Ito, T. Hirano, T. Onogawa, T. Yamashita, Y. Yamada, K. Tsujimae, M. Aoyama, K. Kotosai, H. Ogawa, H. Yamashita, K. Kondo, M. Tominaga, G.Tsujimoto, T. Mori, J. Pharmacol. *Exp. Ther.*, 1998, **287**, 860.
14. (a) J. D. Albright, M. F. Reich, E. G. Delos Santos, J. P. Dusza, F.-W. Sum, A. M. Venkatesan, J. Coupet, P. S. Chan, X. Ru, H. Mazandarani, T. Bailey, *J. Med. Chem.*, 1998, **41**, 2442; (b) K. Kondo, H. Ogawa, T. Shinohara, M. Kurimura, Y. Tanada, K. Kan, H. Yamashita, S. Nakamura, T. Hirano, Y. Yamamura, T. Mori, M. Tominaga, A. Itai, *J. Med. Chem.*, 2000, **43**, 4388; (c) K. Kondo, K. Kan, Y. Tanada, M. Bando, T. Shinohara, M. Kurimura, H. Ogawa, S. Nakamura, T. Hirano, Y. Yamamura, M. Kido, T. Mori, M. Tominaga, *J. Med. Chem.*, 2002, **45**, 3805; (d) A. A. Failli, J. S. Shumsky, R. J. Steffan, T. J. Caggiano, D. K. Williams, E. J. Trybulski, X. Ning, Y. Lock, T. Tanikella, D. Hartmann, P. S. Chan, C. H. Park, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 954; (e) A. Martinez-Castelao, *Curr. Opin. Invest. Drugs*., 2001, **2**, 525–530; (f) T. J. Caggiano, *Drugs Future*,. 2002, **27**, 248; (g) M. Seto, N. Miyamoto, K. Aikawa, Y. Aramaki, N. Kanzaki, Y. Iizawa, M. Baba, M. Shiraishi, *Bioorg. Med. Chem.*, 2005, **13**, 363.
15. Selected examples: (a) E. M. L. Sze, M. J. Koh, Y. M. Tjia, W. Rao, P. W. H. Chan, *Tetrahedron*., 2013, **69**, 5558–5565 and references cited therein; (b) T. A. Moss, *Tetrahedron Lett.*, 2013, **54**, 993–997; (c) C. Kothandaraman, D. Huang, W. Susanti, P. Rao, W. H. Chan, *Chem. Eur. J.*, 2011, **17**, 10081–10088; (d) H. He, W.-B. Liu, L.-X. Dai, S.-L. You, *Angew. Chem. Int. Ed.*, 2010, **49**, 1496–1499; (e) Á. González-Gómez, G. Domínguez, J. Pérez-Castells, *Eur. J. Org. Chem.*, 2009, 5057–5062; (f) S. Kotha, V. R. Shah, *Eur. J. Org. Chem.*, 2008, 1054; (g) R. Abonia, P. Cuervo, B. Insuasty, J. Quiroga, M. Nogueras, J. Cobo, *Eur. J. Org. Chem.*, 2008, 4684; (h) D. Boeglin, D. Bonnet, M. Hibert, *J. Comb. Chem.*, 2007, **9**, 487; (i) V. Singh, S. Batra, *Eur. J. Org. Chem.*, 2007, 2970; (j) H. Stukenbrock, R. Mussmann, M. Geese, Y. Ferandin, O. Lozach, T.

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Lemcke, S. Kegel, A. Lomow, U. Burk, C. Dohrmann, L. Meijer, M. Austen, C. Kunick, *J. Med. Chem.*, 2008, **51**, 2196; (k) G. L. Grunewald, V. H. Dahanukar, P. Ching, K. R. Criscione, *J. Med. Chem.*, 1996, **39**, 3539

16. For intermolecular alkyne-carbonyl metathesis, see: (a) A. Hayashi, M. Yamaguchi, M. Hirama, *Synlett.*, 1995, **195**; (b) L.-W. Xu, L. Li, C.-Z. Xia, P.-Q. Zhao, *Helvitica Chimica Acta.*, 2004, **87**, 3080; (c) M. Curini, F. Epifano, F. Maltese, O. Rosati, *Synlett*., 2003, **552**; (d) K. C. M. Kurtz, R. P. Hsung, Y. Zhang, *Org. Lett.*, 2006, **8**, 231–234. (e) A. Saito, M. Umakoshi, N. Yagyu, Y. Hanazawa, *Org. Lett.*, 2008, **10**, 1783; (f) G. S. Viswanathan, C. -J. Lee, *Tetrahedron Lett.*, 2002, **43**, 1613.
17. Few selected literature for intramolecular alkyne–carbonyl metathesis: (a) HBF_4-catalyzed reaction, see: L. Escalante, C. González-Rodíguez, Jesús, A. Varela, and C. Saa, *Angew. Chem. Int. Ed.* 2012, **51**, 12316–12320; (b) Review on Au-catalysis, see: L. Liu, B. Xu, and G. B. Hammond, *Beilstein J. Org. Chem.* 2011, **7**, 606–614 and references cited therein; (c) SbF_5-MeOH catalyzed reaction, See: A. Saito, J. Kasai, Y. Odaira, H. Fukaya, and Y. Hanzawa, *J. Org. Chem.*, 2009, **74**, 5644–5647; (d) TfOH-catalyzed reaction, see: T. Jin, F. Yang, C. Liu, and Y. Yamamoto, *Chem. Comm*., 2009, 3533–3535; (e) TFA-catalyzed reaction, see: C. González-Rodríguez, L. Escalante, J. A. Varela, L. Castedo, and C. Saá, *Org. Lett.*, 2009, **11**, 1531; (f) T. Jin, Y. Yamamoto, *Org. Lett.*, 2008, **10**, 3137–3139; (j) Ag-catalyzed reaction: J. U. Rhee and M. J. Krische, *Org. Lett.*, 2005, **7**, 2493–2495.
18. Iron-catalyzed alkyne-carbonyl metathesis reaction, see: (a) K. Bera, S. Jalal, S. Sarkar, and U. Jana, *Org. Biomol. Chem.* 2014, **12**, 57;(b) K. Bera, S. Sarkar, S. Jalal, and U. Jana*, J. Org. Chem*., 2012, **77**, 8780–8786; (c) K. Bera, S. Sarkar, S. Biswas, S. Maiti, and U. Jana, *J. Org. Chem.*, 2011, **76**, 3539–3544; (d) Iron-catalyzed intramolecular Prins cyclization of alkynyl-dimethylacetals, see: D. Zheng, W. Gong; Z. Ma, B. Ma, X. Zhao, Z. Xie, and Y. Li, *Tetrahedron Letters*., 2011, **52**, 314–317.
19. (a) S. Sarkar, S. Maiti, K. Bera, S. Jalal, and U. Jana, *Tetrahedron Lett*., 2012, **53**, 5544–5547; (b) S. Maiti, S. Biswas, and U. Jana, *J. Org. Chem*., 2010, **75**, 1674–1683; (c) U. Jana, S. Biswas, and S. Maiti, *Eur. J. Org. Chem*., 2008, 5798–5800; (d) S. Biswas, S. Maiti, and U. Jana, *Eur. J. Org. Chem*., 2009, 2354–2359; (e) S. Jalal, S. Sarkar, K. Bera, S. Maiti, and U. Jana, *Eur. J. Org. Chem*., 2013, 4823–4828; (f) S. Sarkar, K. Bera, S. Jalal, and U. Jana, *Eur. J. Org. Chem*., 2013, 6055–6061.
20. Few selected recent articles on synthesis of quinolines: (a) K. K. Toh, S. Sanjaya, S. Sahnoun, S. Y. Chong, and S. Chiba, *Org. Lett.,* 2012, **14**, 2290–2292; (b) C. Chowdhury, B. Das, S. Mukherjee, and B. Achari, *J. Org. Chem.*, 2012, **77**, 5108−5119; (c) S. Cai, J. Zeng, Y. Bai, and X.-W. Liu, *J. Org. Chem.*, 2012, **77**, 801−807; (d) Y. Zhang, M. Wang, P. Li, and L. Wang, *Org. Lett.*, 2012, **14**, 2206–2209; (e) S. Khong, and O. Kwon, *J. Org. Chem.*, 2012, **77**, 8257−8267; (f) V. K. Tiwari, G. G. Pawar, R. Das, A. Adhikary, M. Kapur, *Org. Lett.*, 2013, **15**, 3310–3313; (g) Z. Huo, I. D. Gridnev, Y. Yamamoto, *J. Org. Chem.*, 2010, **75**, 1266–1270; (h) G.-L. Gao, Y.-N. Niu, Z.-Y. Yan, H.-L. Wang, G.-W. Wang, A. Shaukat, Y. -M.Liang, *J. Org. Chem.*, 2010, **75**, 1305–1308.
21. T. A. Biju, N. E. Wurz, F. Glorius,. *J. Am. Chem. Soc.* 2010, **132**, 5970.
22. H. Li, X. Xu, J. Yang, X. Xie, H. Huang, Y. Li, *Tetrahedron Letters.,* 2011, **52***,* 530–533.

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