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Studies towards iodine-catalyzed dehydrative- cycloisomerization of pent-4-yne-1,2-diols to di- and tri-substituted furans

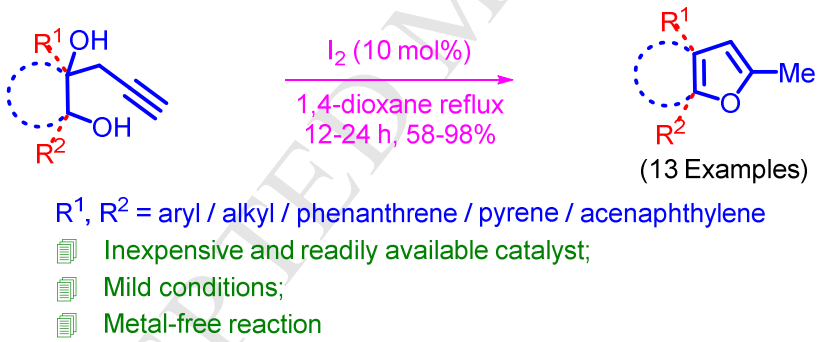
H. Surya Prakash Rao[a,b]*, Satish Vijjapu[a], Silambarasan Kanniyappan[a], Priyanka Kumari[a]

[a] Department of Chemistry, Pondicherry University, Pondicherry – 605 014. India.

[b] Department of Chemistry and Biochemistry, School of Basic Science and Research, Sharda University, Greater Noida – 201306. India

ABSTRACT

An efficient and single-step iodine catalyzed and metal-free synthesis of di and tri-substituted 2-methylfuran derivatives were achieved from 1-popargyl-1,2-diols. Stereospecific synthesis of starting 1,2-diols was achieved by indium mediated Barbier type propargylation on corresponding keto-alcohols or by sodium borohydride mediated reduction of 2-hydroxy-2-propargyl ketones. The furan synthesis proceeded through iodine mediated 5-exo-trig cyclization, dehydration and reductive deiodination. The method was applied to the synthesis of 2-methylfuran fused to phenanthrene, pyrene and acenaphthylene rings.



Keywords:

1. Furan synthesis

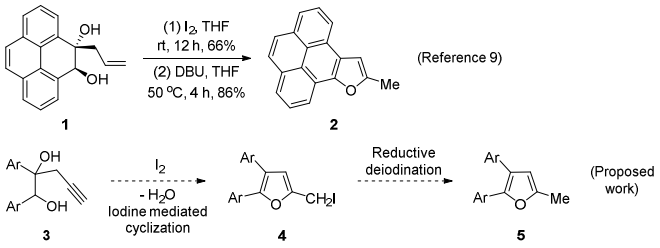
2. Iodine

3. Propargylated 1,2-diol

4. Reductive deiodination

1. Introduction

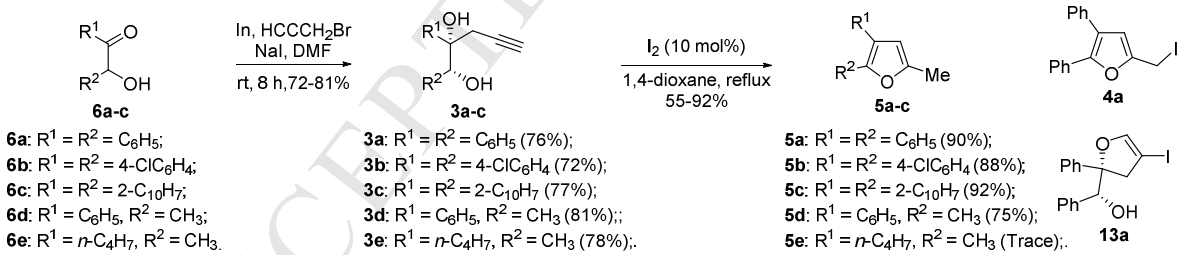
Furan is an oxygen containing five-membered hetero-aromatic compound of fundamental importance.[1] Its motif is present in a large number of natural products and medicinal drugs.[2] Moreover, several furan derivatives serve as useful intermediates in synthetic chemistry.[3] In view of its importance, development of new methods for synthesis of various furan derivatives has attracted considerable attention of chemists from the beginning of the field of Heterocyclic Chemistry.[4] Even after over one hundred twenty five years of the first synthesis of furan,[5] there is still room and indeed need for efficient and operationally simpler methods to hitherto unknown furans.[6] Acid catalyzed dehydrative transformation of acyclic 1,4-dicarbonyl compounds into the furan derivatives is a classical method.[7] In recent years, several new syntheses have been reported, in which acyclic precursors with an acetylenic group were converted into furan derivatives.[8] We have been interested in the synthesis of furans fused to polycyclic aromatic hydrocarbons (PAHs) to study their photochromic properties. Recently we have described a two-step synthesis of 2-methylfuran fused to pyrene ring **2** from corresponding allyl substituted vicinal diol **1** (Scheme **1**).[9] The iodine induced cyclization of **1** followed by dehydration lead to intermediate dihydrofuran, which on base mediated elimination of HI furnished furan-pyrene fused compound **2**. In continuation of this work, we planned a two-step one-pot synthesis of 2,3,5-trisubstituted furans like **5** from 1,2-diols having propargyl substitution e.g. **3** by using iodine as the reagent to induce coveted cyclization.[10] We reasoned that in the first-step **3** could undergo iodine mediated 5-exo-dig cyclization[11] to form corresponding iodomethylfurans **4**, which on reductive deiodination could furnish 2,3-disubstituted 5-methyl furans **5** (Scheme **1**). However, when we conducted the reaction on **3a** (Ar = Ph), serendipitously, discovered that 2,3-diphenyl 5-methylfuran **5a** (Ar = Ph) has formed in the reaction. The reaction apparently went through *in-situ* unprecedented reductive deiodination of the intermediate **4a** (Ar = Ph). Herein, we describe the scope of this facile iodine catalyzed and metal-free transformation of pent-4-yne-1,2-diols for a practical and scalable synthesis of 2-aryl-5-methylfurans, 3-aryl-5-methylfurans and 2,3-diaryl-5-methylfurans. Iodine is an inexpensive, non-toxic and readily available weak and soft Lewis acid useful for various organic transformations.[12] Generally, iodine mediated organic transformations provide excellent yield of the products with high regio, chemo and stereo-selectivity.



Scheme 1. Two-step transformation of vicinal diol **1** into furan fused pyrene **2** and proposed scheme for the synthesis of 2,3-diaryl-5-methyl furans **5** from corresponding pent-4-yne-1,2-diols **3**.

2. Results and discussion

Hitherto unknown propargylic 1,2-diols **3** are the starting compounds for the present work. They can be prepared either by propargylation of α-hydroxyketones **6** (eg. benzoins) or by propargylation followed by reduction of 1,2-carbonyl compounds **7** (e.g. benzils). We have explored both the methods. The Barbier type reaction of α-hydroxyketones **6a-e** with propargyl bromide in the presence of indium metal provided (1*RS*,2*SR*)-1,2diarylpent-4-yne-1,2-diols **3a-e** in good yield as single diastereomers (Scheme **2**). The high diastereoselectivity (>99%) is in agreement with the Cram's chelation model[13] and literature precedence of the indium mediated Barbier type allylation on benzoin **5a**.[14]



6a: $R^1 = R^2 = C_6H_5$;
6b: $R^1 = R^2 = 4\text{-}ClC_6H_4$;
6c: $R^1 = R^2 = 2\text{-}C_{10}H_7$;
6d: $R^1 = C_6H_5$, $R^2 = CH_3$;
6e: $R^1 = n\text{-}C_4H_7$, $R^2 = CH_3$.
$2\text{-}C_{10}H_7$ = 2- naphthyl

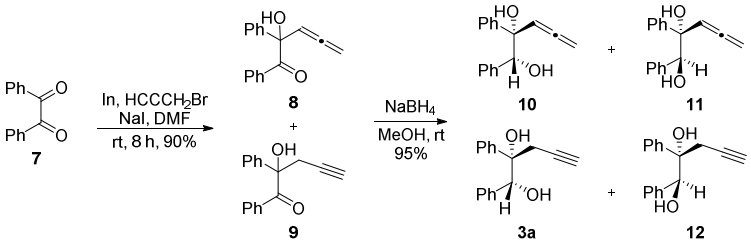
3a: $R^1 = R^2 = C_6H_5$ (76%);
3b: $R^1 = R^2 = 4\text{-}ClC_6H_4$ (72%);
3c: $R^1 = R^2 = 2\text{-}C_{10}H_7$ (77%);
3d: $R^1 = C_6H_5$, $R^2 = CH_3$ (81%);;
3e: $R^1 = n\text{-}C_4H_7$, $R^2 = CH_3$ (78%);.

5a: $R^1 = R^2 = C_6H_5$ (90%);
5b: $R^1 = R^2 = 4\text{-}ClC_6H_4$ (88%);
5c: $R^1 = R^2 = 2\text{-}C_{10}H_7$ (92%);
5d: $R^1 = C_6H_5$, $R^2 = CH_3$ (75%);
5e: $R^1 = n\text{-}C_4H_7$, $R^2 = CH_3$ (Trace);.

Scheme 2. Two-step synthesis of 2,3-disubstiutted 5-methylfurans from α-hydroxyketones.

In contrast to the propargylation of α-hydroxyketones **6**, which provided stereoselective propargylated products **3**, the reaction on the 1,2-diketone **7** (benzil) under above reaction conditions provided an inseparable mixture of α-hydroxy α-allenyl ketone **8** and α-hydroxy α-propargyl ketone **9** in 3:2 ratio (Scheme **3**). Reduction of the mixture with sodium borohydride furnished diastereomeric mixture of *syn*-vicinal diols **10** and **3a** along with anti-vicinal diols

11and **12**. Incisive analysis of the ^{1}H and ^{13}C NMR spectra indicated that *syn*-vicinal diol **3a** was the major product (70%) and anti-vicinal diol **12** (30%) was the minor product. The result is in agreement with the outcome of the reduction predicted by applying Felkin-Anh model[15] and by considering that phenyl group is bulkier than the propargyl group.[16]



Scheme 3. Indium mediated Barbier type propargylation of benzyl **7** followed by reduction to form vicinal diols **10-12** and **3a**.

Next, we subjected the syn-1,2-diphenyl pent-4-yne-1,2-diol **3a** to iodine mediated cyclization to generate furan **5a** and to work out optimal reaction conditions (Scheme **2**). The reaction of **3a** with one equivalent of iodine in dry THF at rt surprisingly provided known[17] 2,3-diphenyl-5-methylfuran **5a** as the only product in 90% yield. There was no trace of iodine incorporated product **4a** (formed via 5-exo-dig cyclization, followed by dehydration and double bond rearrangement) or **13a** (formed via 5-endo-dig cyclization). Since the product **5a** did not have iodine, we hypothesized that the reductive removal of iodide from the intermediate **4a** to form **5a** and regeneration of iodine was the final-step in the reaction sequence. Therefore, the reaction could work with a catalytic amount of iodine. Indeed, the transformation took place with 10 mol% of iodine, although yield was lower (65%). Switch over from refluxing THF to refluxing 1,4-dioxane resulted in an increase of the yield up to 90% (Scheme **2**). With optimized conditions in hand, we expanded the substrate scope of the reaction by converting four pent-4-yne-1,2-diols **3b-e** into hitherto unknown 2,3-diaryl-5-methylfurans **5b-e** (Scheme **2)**. It is noteworthy that the transformation worked well with bis-aromatic **3a-c**, aromatic and aliphatic **3d** propargylic 1,2-diols to provide corresponding furans **5a-d**. However, when both R^1 and R^2 were alkyl groups, e.g. **3e**, the product **5e** (IR, NMR, ESI-MS) formation was observed, but possibly due to its low stability column chromatographic purification was not possible. Of the five products, **5c** is interesting as the two naphthalene rings in it could align one above the other

like in a cleft (see Figure **1**; DFT/B3LYP/6-311G(d,p) energy minimized structure; using Gaussian 09) and act as a host for suitable aromatic guest molecules.

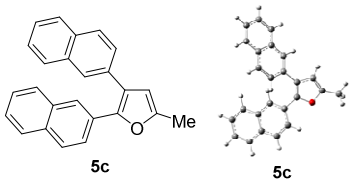


Figure 1. The energy minimized structure of **5c**.

After establishing a reliable procedure for the synthesis of 2,3-disubstituted-5-methylfurans e.g. **5a** we explored the possibilities of synthesis of 5-methylfuran fused to phenanthrene **14**, pyrene **2** and acenaphthylene **15** rings (Figure **2**) to extend the scope of the procedure and for the synthesis of furan fused polycyclic aromatic hydrocarbons (PAHs).

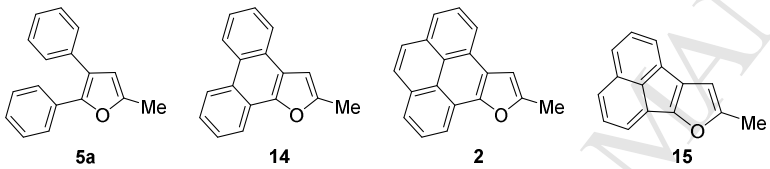
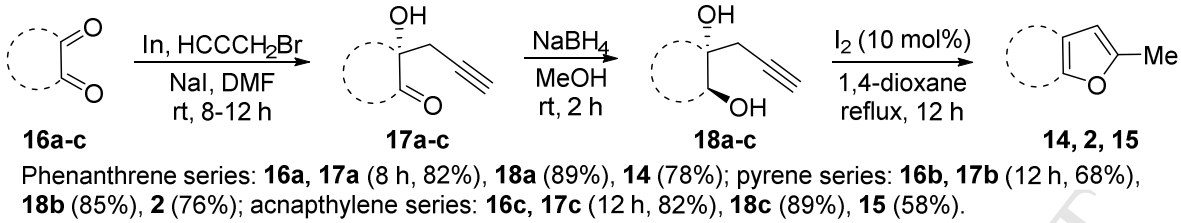


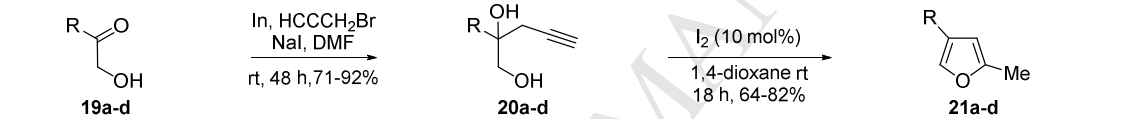
Figure 2. Structures of 5-methylfuran fused stilbene **5a**, phenanthrene **14**, pyrene **2** and acenaphthylene **15**.

Syntheses of 5-methylfuran fused PAHs **14**, **2** and **15** were achieved through three-step protocol from corresponding 1,2-diketones **16a-c** as given in Scheme 4. The indium metal mediated Barbier type reaction with propargyl bromide on one of the carbonyl groups in **16a-c** furnished keto alcohols **17a-c** in excellent yield (Scheme **5**).[18] Interestingly there were no allenyl products like **8** in the reaction mixture. The neighboring hydroxy group assisted the stereoselective reduction of the carbonyl group in **17a-c** with sodium borohydride furnished *trans*-diols **18a-c**. Stereochemistry of the vicinal hydroxyl group in **18a-c** as *trans* was finalized on the basis of spectral (IR, ^{1}H NMR, ^{13}C NMR, DEPT-135, 2D NMR HSQC, HMBC, COSY and NOESY) data and X-ray crystal structure analysis of (9*RS*, 10*RS*)-9-allyl-9,10-dihydrophenanthrene-9,10-diol.[19] The iodine mediated cyclization of **18a-c** delivered 5-methylfuran fused phenanthrene **14**, pyrene **2** and acenaphthylene **15** respectively in good yields. Each of them displayed furyl methyl group as a doublet at δ 2.6 (J = 1.0 Hz) ppm.



Scheme 4. Three-step synthesis of 5-methylfuran appended PAHs **14**, **2** and **15** from corresponding 1,2-diones **16a-c**.

After demonstrating the iodine mediated synthesis of 2,3-diaryl-5-methylfurans, we extended the study to the synthesis of C(4) substituted 2-methylfurans. Thus, propargylated 1,2-diols **20a-d** were subjected iodine mediated dehydrative cyclization to realize C(4) aryl 2-methylfurans **21a-d** [20] in good yield (Scheme **5**). The propargylated 1,2-diols **20a-d** were prepared from 2-hydroxyethanones **19a-c** by indium mediated propargylation.



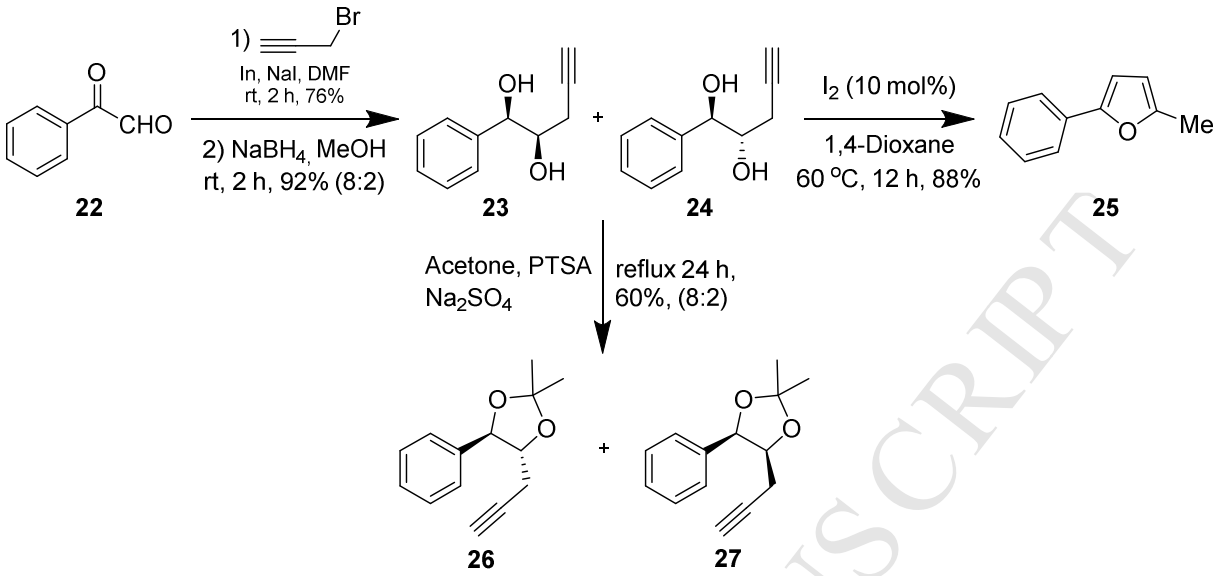
19a: R = C_6H_5;
19b: R = 4-ClC_6H_4;
19c: R = 4-$CH_3C_6H_4$;
19d: R = 4-$OCH_3C_6H_4$.

20a: R = C_6H_5 (92%);
20b: R = 4-ClC_6H_4 (76%);
20c: R = 4-$CH_3C_6H_4$(73%);
20d: R = 4-$OCH_3C_6H_4$(71%);.

21a: R = C_6H_5 (82%);
21b: R = 4-ClC_6H_4(64%);
21c: R = 4-$CH_3C_6H_4$ (71%);
21d: R = 4-$OCH_3C_6H_4$ (76%);.

Scheme 5. Two-step synthesis of C(4)aryl 2-methylfurans from corresponding 2-hydroxy-1-aryl ethanones **19a-d**.

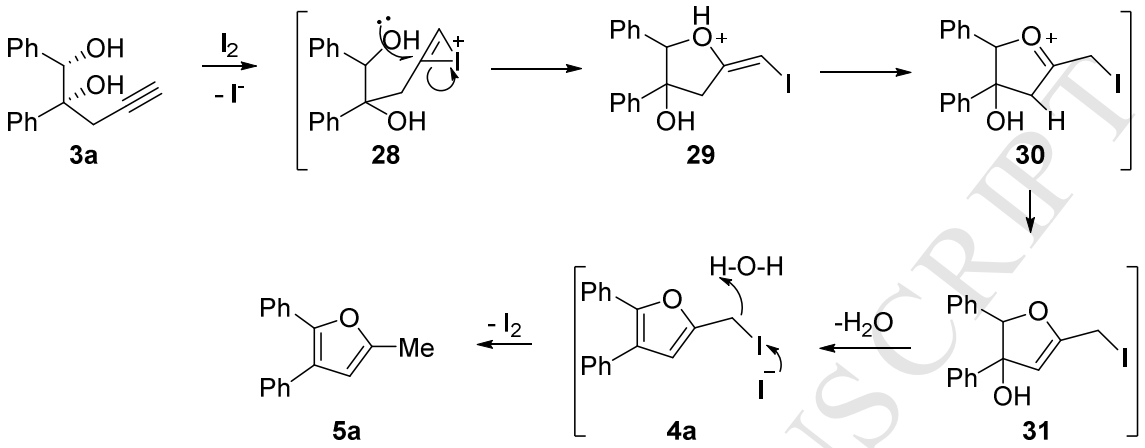
After demonstrating the use of iodine in the synthesis of 3- and 2,3-substituted 5-methylfurans we explored the scope of the transformation for the synthesis of 2-methyl-5-phenylfuran **25** from corresponding propargylated 1,2-diols **23** and **24** (Scheme **6**). Indium mediated propargylation of phenyl glyoxal **22** provided 2-hydroxy-1-phenylpent-4-yn-1-one in 76% yield. Further reduction with sodium borohydride provided an inseparable mixture of diastereomers **23** (C(1): *RS*; C(2): RS) and **24** (C(1): *RS*; C(2): SR) in 8:2 ratio in 92% yield. The stereochemistry of diols was confirmed by comparing the NOESY spectral data of the parent mixture and the corresponding acetonides **26** and **27**. The acetonides were separated and characterized independently.[21] Reaction of the mixture of diols **23** and **24** with catalytic amount of iodine provided known[22] 2-methyl-5-phenylfuran **25** in 88% yield.



Scheme 6. Synthesis of 2-methyl-5-phenylfuran **25** from phenyl glyoxal **22**.

Possible mechanism for the transformation of propargylated 1,2-diols e.g. **3a** into 2-methylfurans e.g. **5a** is given in Scheme **7**. The first-step is the electrophilic addition of iodine to the triple bond in **3a** to generate iodonium ion intermediate **28**. Subsequent 5-exo-trig-cyclization lead to vinyl iodide **29**. Step-wise 1,3-prototopic shifts in **29** via **30** lead to the intermediate **31**. Dehydration to trisubstituted 2-iodomethylfuran **4a** followed by reductive deiodinationyielded stable 2,3-diphenyl-5-methylfuran **5a**.To rule out the possibilities that iodine assisted dehydration precedes cyclization, we exposed **3a** to catalytic (10mol%) of *p*-tolunesulfornicacid intoluene at 70 ^{o}C, conc. H_2SO_4 in dichloromethane at rt and $F_3B{:}OEt_2$ in dichloromethane at rt. In all the cases furan did not form but there was extensive decomposition of the 1,2-diol. To rule out radical intermediates, we conducted the reaction of **3a** with catalytic amount of iodine in dark in 1,4-dioxane reflux. The transformation was efficient to provide **5a** in 90% yield. The reaction conducted at rt and in dark, as anticipated, took longer time (16 h) to provide the product **5a** but in lower yield (55%) and starting diol **3a** was still remained (35%). These results indicate that radical intermediates may not have formed enroute to furan **5a**. To further rule out involvement of radical intermediates we conducted the reaction in presence of one equivalent of Edaravone (3-methyl-1-phenyl-2-pyrazolin-5-one) a radical quencher.[23] Even in this reaction, product **5a** formed efficiently (71%). Based on above experiments, we conclude

that the cyclization involving iodinium ion and reductive deiodination were the crucial steps in the formation of the furan ring.



Scheme 7. Proposed mechanism for the iodine catalyzed dehydrative cyclization of 4-yne-1,2-diols, e.g. **3a** to furnish 2,3-diaryl-5-methyl furans e.g. **5a**.

3. Conclusion

In summary, we have developed a new single-step iodine mediated metal-free synthesis of 2-aryl, 3-aryl, and 2,3-diaryl 5-methylfurans from propargylated 1,2-diols. Key finding of this study is the reductive deiodination of the plausible 5-iodomethylfuran intermediate. Starting propargylated 1,2-diols were prepared by indium mediated Barbier type alkylation of corresponding α-hydroxyketones. To best of our knowledge, reductive deiodination for the conversion of **3** to **5** is unprecedented.

Experimental section

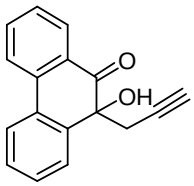
4.1 General Remarks

All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with silica gel GF-254 was used for TLC. Column chromatography was carried on silica gel (100-200 mesh, AVRA synthesis private limited) using increasing percentage of ethyl acetate in hexanes. Melting points were uncorrected and were determined using open-ended capillary tubes on VEEGO VMP-DS instrument. IR spectra were recorded as KBr pellets on a Nicolet-6700 spectrometer. ^{1}H NMR spectra (400 MHz), ^{13}C NMR (100MHz) and DEPT-135 spectra were recorded for ($CDCl_3$ or $CDCl_3$ + CCl_4, 1:1) solutions on

Bruker-Avance 400 MHz spectrometer with TMS as internal standard. ^{1}H-NMR data are reported as follows: chemical shift (multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of the doublet, dt = doublet of the triplet, td = triplet of the doublet and brs = broad singlet), coupling constant (*J*) and integrations. Coupling constant *J* values are given in Hz. The ^{13}C NMR spectra were recorded with broadband ^{1}H decoupling. The DEPT-135 NMR spectra were recorded for each sample to support assigned structure. High resolution mass spectra were recorded on a Water Q-TOF micro mass spectrometer using electron spray ionization mode. The X- ray diffraction measurements were carried out at 298 K on Oxford CrysAlis CCDCarea detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å).

4.2 General procedure for reduction of α-hydroxy ketones: To the solution of α-hydroxy ketones (1 mmol) dissolved in dry methanol (MeOH; 3 mL) and cooled to 0 ^{o}C sodium borohydride (74 mg, 2 equiv) was added under nitrogen atm at 0 ^{o}C and stirred for 10 min and then allowed to stir at for 2 h. After the completion of the reaction (TLC) MeOH was evaporated under reduced pressure and then diluted with DCM (30 mL). The DCM layer was washed with water (2 × 30 mL), brine (2 × 30 mL) and dried over anhydrous sodium sulfate. Removal of DCM under reduced pressure resulted in crude product which was purified by column chromatography using silica gel (100-200 mesh) and increasing amounts of (5 to 10%) EtOAc in hexanes to afford 1,2-diols.

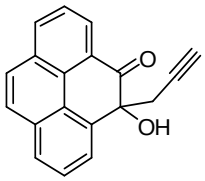
4.2a. *10-Hydroxy-10-(prop-2-yn-1-yl)phenanthren-9(10H)-one* (**17a**):



White solid;yield 82%; mp. 131-132 ºC (Reported mp. 130-133 ºC); IR (KBr) ν_{max} 3467, 3261, 3069, 1691, 1599, 1447, 1415, 1374, 1316, 1290, 1241, 1217, 1136, 1100, 1031, 987, 937, 783, 754, 729, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4) δ 7.87 (d, *J* = 7.4 Hz, 1H), 7.81 (d, *J*= 8.0 Hz, 1H), 7.75-7.67 (m, 2H), 7.58 (s, 1H), 7.36-7.27 (m, 3H), 4.25 (s, 1H), 2.63-2.47 (m, 2H), 1.92 (t, *J* = 2.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4) δ 200.9 (C=O), 139.2 (C),

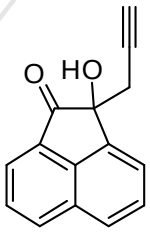
137.6 (C), 135.2 (CH), 129.5 (CH), 129.3 (C), 128.8 (CH), 128.7 (CH), 128.3 (C), 127.8 (CH), 126.5 (CH), 124.2 (CH), 123.3 (CH), 78.0 (acetylinic C), 73.0 (acetylinic C), 35.6 (CH_2).ppm; HRMS (ESI) calcd for $C_{17}H_{13}O_2$ $[M + H]^+$ 249.0910, found 249.0928.

4.2b. *5-Hydroxy-5-(prop-2-ynyl)pyren-4(5H)-one* (**17b**):



Light yellow solid; yield 68%; mp. 115-116 ºC; IR (KBr) ν_{max} 3478, 3295, 3054, 2923, 1690, 1620, 1587, 1423, 1337, 1294, 1227, 1171, 1146, 1035, 838, 721, 659 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ + CCl_4) δ 8.32 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.17 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.02 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.89-7.69 (m, 5H), 4.52 (s, 1H), 2.78-2.63 (q, 2H), 2.04 (t, *J* = 2.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4) δ 201.1 (C=O), 139.0 (C), 134.7 (CH), 132.0 (C), 131.2 (C), 129.8 (C), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.2 (CH), 127.0 (C), 126.6 (CH), 126.4 (CH), 124.4 (CH), 123.6 (C), 78.8 (C), 77.9 (acetylinic C), 73.1 (acetylinic C), 35.9 (CH_2) ppm; HRMS (ESI) calcd for $C_{19}H_{12}O_2Na$ $[M + Na]^+$ 295.0735, found 295.0738.

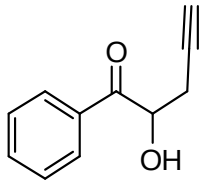
4.2c. *2-Hydroxy-2-(prop-2-yn-1-yl)acenaphthylen-1(2H)-one* (**17c**):



Light yellow semi solid; yield 82%; mp. 128-130 ºC; IR (KBr) ν_{max} 3423, 3297, 3060, 2926, 2118, 1953, 1773, 1725, 1604, 1493, 1465, 1428, 1343, 1305, 1262, 1217, 1183, 1137, 1183, 1072, 1016, 954, 837, 868, 782, 705, 657 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 7.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.76-7.67 (m, 2H), 3.32 (s, 1H), 2.99 (dd, J = 16.6, 2.6 Hz, 1H), 2.78 (dd, *J* = 16.6, 2.6 Hz, 1H), 1.95 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6 (C=O), 141.7 (C), 138.5 (C), 132.4 (CH), 130.7 (C), 130.4 (C), 128.9 (CH), 128.5 (CH), 126.0 (C), 122.6 (CH), 121.0 (CH), 78.3

(acetylinic C), 71.9 (acetylinic C), 28.5 (CH_2) ppm; HRMS (ESI) calcd for $C_{15}H_{10}O_2Na$ [M + Na]$^+$245.0573, found 245.0595.

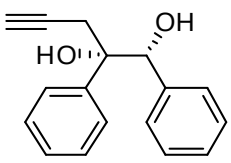
4.2d. *2-Hydroxy-1-phenylpent-4-yn-1-one* (**20**):



Light yellow semi solid; yield 76%; IR (KBr) ν_{max} 3404, 3354, 2974, 2951, 1697, 1597, 1450, 1222, 1111, 961, 844, 715, 684 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4) δ 7.91 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 5.20 (t, *J* = 5.1 Hz, 1H), 2.82-2.76 (m, 1H), 2.61-2.54 (m, 1H), 2.00 (t, *J* = 2.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3 (C=O), 134.1 (CH), 133.6 (C), 128.9 (CH), 128.7 (CH), 78.6 (C), 72.1 (CH), 71.0 (CH), 26.1 (CH_2) ppm; HRMS (ESI) calcd for $C_{11}H_{10}O_2Na$ [M + Na]$^+$ 197.0573, found 197.0578.

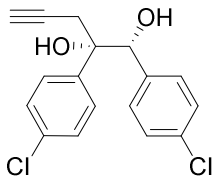
4. 3 General procedure for indium metal mediated Barbier type reaction on α-hydroxy ketones and 1,2-diones: To the solution of α-hydroxy ketones or 1,2-diones (1 mmol) in dry dimethylformamide (DMF; 3 mL) indium metal (119 mg, 1.05 equiv), propargyl bromide (80% propargyl bromide in toluene; (228 mg, 1.55 equiv); CAUTION: Lachrymatory) in DMF (1 mL) and sodium iodide (230 mg, 1.55 equiv) were added sequentially and stirred at rt for 8-48 h. After completion of the reaction (by TLC), 1*N* HCl solution (1 mL) was added to the reaction mixture and stirred for 15 min. Then the reaction mixture was diluted with dichloromethane (20 mL). The DCM solution was washed with water (2 × 20 mL), brine (2 × 20 mL) and dried with anhydrous sodium sulfate. Removal of the solvent resulted in the crude product which was subjected to column chromatography using silica gel (100-200 mesh) and increasing amounts of (2 to 5%) ethyl acetate (EtOAc) in hexanes to afford 1,2-diols or α-hydroxy ketones.

4.3a.(*1RS,2SR*)-*1,2-Diphenylpent-4-yne-1,2-diol* (**3a**):



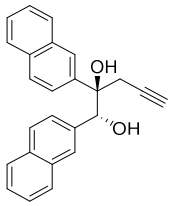
Light yellow semi solid; yield 76%; IR (KBr) ν_{max} 3458, 3067, 2965, 2925, 2857, 1676, 1595, 1450, 1148, 973, 898, 761, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ + CCl_4) δ 7.18-7.10 (m, 8H), 6.99-6.94 (m, 2H), 4.85 (s, 1H), 3.12 (s, 2H), 2.89-2.85 (m, 2H), 1.93 (t, *J* = 2.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4) δ 141.1 (C) , 139.0 (C), 127.9 (CH) , 127.8 (CH), 127.6 (CH), 127.5 (CH), 127.4 (C), 126.6 (CH), 80.5 (acetylenic C), 79.3 (CH), 78.1 (acetylenic CH), 72.4 (C), 29.1 (CH_2) ppm; HRMS (ESI) calcd for $C_{17}H_{16}O_2Na$ $[M + Na]^+$ 275.1048, found 275.1048.

4.3b.*(1RS,2SR)-1,2-Bis(4-chlorophenyl)pent-4-yne-1,2-diol* (**3b**):



Light yellow solid: yield 72%; mp. 68-70 ºC; IR (KBr) ν_{max} 3424, 3283, 2927, 1608, 1492, 1407, 1329, 1283, 1091, 1048, 654 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$+ CCl_4) δ 7.18 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.80 (s, 1H), 3.07 (br s, 2H), 2.84 (t, *J*= 2.3 Hz, 2H), 2.00 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4) δ 139.3 (C), 137.2 (C), 134.0 (C), 133.7 (C), 129.2 (CH), 128.0 (CH), 128.0 (CH), 127.9 (CH), 79.8 (acetylenic CH), 78.5 (CH), 77.7 (C), 73.0 (acetylenic CH), 29.2 (CH_3); HRMS (ESI) calcd for $C_{17}H_{14}Cl_2O_2Na$ $[M + Na]^+$ 343.0263, found 343.0271.

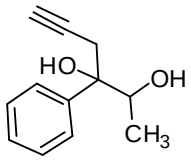
4.3c.*1RS,2SR)-1,2-Di(naphthalen-2-yl)pent-4-yne-1,2-diol* (**3c**):



Light yellow semi solid; yield 77%; IR (KBr) ν_{max} 3420, 3255, 2930, 1956, 1622, 1603, 1596, 1499, 1342, 1248, 1016, 849, 719, 664 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ + CCl_4) δ 7.82-7.77 (m, 2H), 7.77-7.72 (m, 2H), 7.72-7.67 (m, 2H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.49-7.40 (m, 4H), 7.29 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.12 (dd, *J* = 8.5, 1.7 Hz, 1H), 5.22 (s, 1H), 3.18 (s, 2H), 3.09-3.07 (m, 2H), 2.95 (br s, 1H), 2.02 (t, *J* = 2.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4) δ 138.5 (C), 136.4 (C), 133.1 (C), 132.8 (C), 132.8 (C), 132.7 (C), 128.5 (CH), 128.2 (CH), 127.7 (CH),

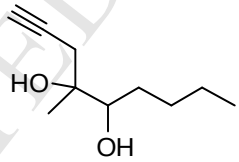
127.6 (CH), 127.3 (CH), 127.2 (CH), 127.0 (CH), 126.2 (CH), 126.1 (CH), 126.1 (CH), 126.07 (CH), 126.0 (CH), 125.8 (CH), 124.6 (CH), 80.2 (acetylenic C), 79.5 (CH), 78.5 (C), 72.6 (acetylenic CH), 29.2 (CH_2) ppm; HRMS (ESI) calcd for $C_{25}H_{21}O_2$ $[M + H]^+$ 353.1536, found 353.1539.

4.3d.*3-Phenylhex-5-yne-2,3-diol* (**3d**):



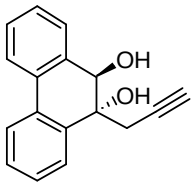
Yellow semi solid; yield 81%; IR (KBr) ν_{max}3400, 2929, 1629, 1492, 1446, 1389, 1186, 856, 765, 700, 645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 (dd, *J* = 8.3, 6.1 Hz, 1H),4.17-3.89 (m, 1H), 3.01 (dd, *J* = 16.9, 2.6 Hz, 1H), 2.93 – 2.74 (m, 2H), 2.37 (s, 1H), 1.94 (t, *J* = 2.5 Hz, 1H), 0.94 (d, *J*= 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6 (C), 128.6 (CH), 127.8 (CH), 125.6 (CH), 80.1 (C), 75.9 (C), 72.2 (acetylenic CH), 69.3 (CH), 29.3 (CH2), 17.8 (CH_3) ppm.

4.3e.*4-Methylnon-1-yne-4,5-diol* (**3e**):



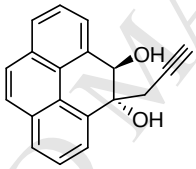
Light yellow semi solid; yield 78%; IR (KBr) ν_{max} 3423, 3307, 2947, 2118, 1664, 1457, 1069, 852, 784, 637 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.89 (dd, *J* = 6.6, 1.3 Hz, 1H), 3.68 – 3.37 (m, 1H), 2.45 (dd, *J*= 18.2, 3.6 Hz, 3H), 2.07 (dd, *J* = 2.6, 2.2 Hz, 1H), 1.41 – 1.28 (m, 5H), 1.22 (d, *J*= 10.7 Hz, 4H), 0.90 (dd, *J*= 8.2, 5.6 Hz, 4H);.^{13}C NMR (100 MHz, $CDCl_3$) δ 97.1 (C), 80.5 (CH), 76.0 (CH), 74.0 (CH), 71.5 (CH), 30.8 (CH_2), 29.9 (CH_2), 28.7 (CH_2), 22.7 (CH_2), 21.6 (CH_3), 14.1 (CH_3) ppm.

4.3f.*(9RS,10RS)-9-(Prop-2-yn-1-yl)-9,10-dihydrophenanthrene-9,10-diol* (**18a**):



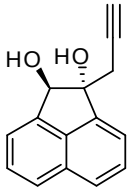
White semi solid; yield 89%; IR (KBr) ν_{max} 3507, 3475, 3283, 3061, 2923, 2856, 1600, 1481, 1448, 1388, 1349, 1322, 1283, 1261, 1239, 1225, 1193, 1110, 1073, 1059, 984, 878, 842, 760, 735, 675, 658, 635 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72-7.63 (m, 4H), 7.42-7.32 (m, 4H), 5.03 (s, 1H), 3.17 (s, 1H), 2.96 (s, 1H), 2.78 (dd, *J* = 17.0, 2.7 Hz, 1H), 2.20 (dd, *J* = 17.0, 1.4 Hz, 1H), 2.03-1.99 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9 (C), 135.7 (C), 132.3 (C),132.0 (C), 128.7 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 125.2 (CH), 124.7 (CH), 124.0 (CH), 123.8 (CH), 80.0 (C), 75.5 (acetylinic C), 75.0 (CH), 72.8 (acetylinic C), 24.6 (CH_2) ppm; HRMS (ESI) calcd for $C_{17}H_{14}O_2Na$ $[M + Na]^+$ 273.0891, found 273.0899.

4.3g.*(4RS,5RS)-4-(Prop-2-ynyl)-4,5-dihydropyrene-4,5-diol* (**18b**):



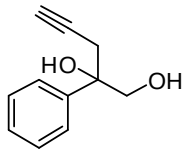
White solid; yield 85%; mp.146-147 ºC; IR (KBr) ν_{max}: 3421, 3300, 3040, 1685, 1587, 1431, 1221, 1168, 1124, 1067, 834, 757, 728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ + CCl_4) δ 7.92 (d, *J*= 7.2 Hz, 1H), 7.86 (d, *J*= 7.2 Hz, 1H), 7.78 (t, *J* = 7.4 Hz, 2H), 7.71 (s, 2H), 7.57 (t, *J*= 7.6 Hz, 2H), 5.49 (s, 1H), 3.99 (s, 1H), 3.12 (dd, *J*= 17.1, 2.5 Hz, 1H), 2.34 (dd, *J* = 17.1, 2.5 Hz, 1H), 2.40 (t, *J*= 2.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4) δ 137.8 (C), 135.1 (C), 131.1 (C), 130.9 (C), 127.6 (CH), 127.1 (CH), 127.0 (CH), 126.8 (CH), 126.6 (CH), 126.5 (CH), 125.6 (C), 125.4 (C), 123.3 (CH), 122.7 (CH), 80.2 (C), 76.8 (acetylinic C), 75.8 (CH), 72.9 (acetylinic C), 25.5 (CH_2). ppm; HRMS (ESI) calcd for $C_{19}H_{14}O_2Na$ $[M + Na]^+$ 297.0891, found 297.0894.

4.3h.*(1RS,2RS)-1-(Prop-2-yn-1-yl)-1,2-dihydroacenaphthylene-1,2-diol* (**18c**):



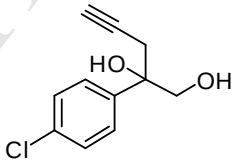
White semi solid; yield 89%; IR (KBr) ν_{max} 3293, 3270, 1489, 1410, 1363, 1332, 1280, 1248, 1157, 1089, 1071, 1027, 933, 912, 871, 776, 724, 641, 550 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81-7.77 (m, 2H), 7.61-7.53 (m, 4H), 5.54 (d, *J* = 6.8 Hz, 1H), 3.02 (dd, *J* = 16.8, 2.6 Hz, 1H), 2.99 (dd, *J* = 16.6, 2.6 Hz, 1H), 2.79 (s, 1H), 2.77 (s, 1H), 1.95 (t, *J*= 2.6 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8 (C), 141.2 (C), 135.6 (C), 131.0 (C), 128.7 (CH), 128.5 (CH), 125.6 (CH), 125.2 (CH), 120.8 (CH), 119.5 (CH), 84.9 (CH), 84.0 (C), 80.8 (acetylinic C), 72.1 (acetylinic C), 27.5 (CH_2) ppm; HRMS (ESI) calcd for $C_{15}H_{12}O_2Na$ $[M + Na]^+$ 247.0735, found 247.0734.

4.3i.*2-Phenylpent-4-yne-1,2-diol* (**20a**):



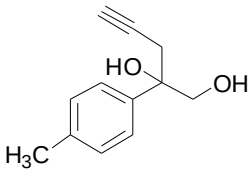
Light yellow semi solid; yield 92%; IR (KBr) ν_{max} 3400, 2929, 1629, 1492, 1446, 1389, 1186, 856, 765, 700, 645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.26 (m, 5H), 3.79-3.72 (m, 2H), 2.89-2.82 (m, 2H), 1.97 (t, *J* = 2.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6 (C), 128.6 (CH), 127.8 (CH), 125.6 (CH), 80.1 (C), 75.9 (C), 72.2 (acetylenic CH), 69.3 (CH_2), 29.3 (CH_2) ppm.

4.3j.*2-(4-Chlorophenyl)pent-4-yne-1,2-diol* (**20b**):



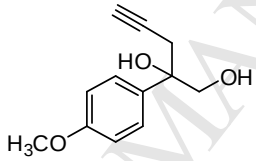
Brown liquid; yield; 76%; IR (KBr) ν_{max} 3424, 3297, 2930, 2119, 1598, 1492, 1268, 1091, 827, 722, 646 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J*= 8.6 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.18 (s, 2H), 4.90 (dd, *J* = 6.7, 2.7 Hz, 1H), 3.66 (d, *J* = 1.1 Hz, 2H), 2.71 (ddd, *J*= 50.1, 16.9, 2.6 Hz, 2H), 2.09 – 1.81 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6 (C), 128.6 (CH), 127.8 (CH), 125.6 (CH), 80.1 (C), 75.9 (C), 72.2 (acetylenic CH), 69.3 (CH), 30.3 (CH_2), 21.8 (CH_3), 21.2 (CH_3) ppm.

4.3k.*2-(p-Tolyl)pent-4-yne-1,2-diol* (**20c**):



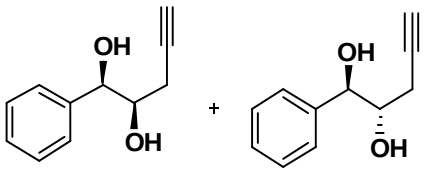
Yellow liquid; yield 73%; IR (KBr) ν_{max} 3530, 3296, 2922, 2118, 1684, 1609, 1514, 1282, 1051, 854, 644 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 1.7 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 5.56 (s, 1H), 4.88 (s, 1H), 3.99 (dd, *J* = 9.7, 3.0 Hz, 2H), 2.84 (dtd, *J* = 30.1, 16.8, 2.7 Hz, 2H), 2.36 (s, 3H), 2.31 – 2.24 (m, 3H), 2.05 – 1.82 (m, 1H). ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 144.4 (C), 138.6 (C), 137.2 (C), 130.4 (CH), 129.3 (CH), 129.1 (CH), 125.8 (CH), 125.9 (CH), 96.3 (C), 81.6 (C), 80.3 (C), 74.3 (CH), 71.9 (CH), 70.9 (CH), 30.9 (CH_2), 22.1 (CH_2), 21.2 (CH_3) ppm.

4.3l.*2-(4-Methoxyphenyl)pent-4-yne-1,2-diol* (**20d**):



Yellow liquid; yield 71%; IR (KBr) ν_{max} 3530, 3296, 2922, 2119, 1684, 1609, 1514, 1282, 1051, 854, 644 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J*= 7.9 Hz, 1H), 6.84 (dd, *J* = 24.3, 8.5 Hz, 3H), 4.72 (s, 1H), 3.92 – 3.80 (m, 1H), 3.74 (d, *J* = 12.7 Hz, 3H), 2.30 (dd, *J* = 7.7 Hz, 1H), 2.19 – 1.89 (m, 2H), 1.25 (d, *J*= 4.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3 (C), 132.3 (C), 131.9 (CH), 128.0 (CH), 113.9 (CH), 81.3 (C), 75.1 (CH), 73.4 (CH), 70.8 (CH), 55.2 (OCH_3), 21.9 (CH_2), 29.2 (CH_2) ppm.

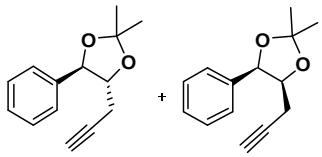
4.3m.*(1RS,2SR)-1-Phenylpent-4-yne-1,2-diol* (**23**) *and* (**24**):



Semi solid; The NMR data of the major isomer **24** was culled from the reaction mixture NMR; IR (KBr) ν_{max} 3398, 3294, 3063, 2922, 2854, 1602, 1452, 1417, 1217, 1070, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ + CCl_4) δ 7.33-7.30 (m, 4H), 7.30-7.26 (m, 1H), 4.80 (d, *J* = 4.5 Hz, 1H), 3.93 (dt, *J*= 8.1, 4.6 Hz, 1H), 3.10 (s, 1H), 2.81 (s, 1H), 2.45-2.37 (m, 1H), 2.20-2.13 (m, 1H), 2.00 (t,

J = 2.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+ CCl_4) δ 139.8 (CH), 128.6 (CH), 128.1 (CH), 126.7 (CH), 81.2 (CH), 75.5 (C), 73.4 (CH), 71.0 (CH), 21.8 (CH_2) ppm; HRMS (ESI) calcd for $C_{11}H_{12}O_2Na$ $[M + Na]^+$ 199.0735, found 199.0733.

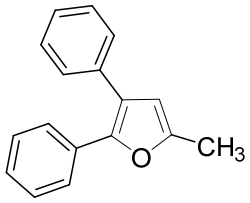
4.3n.*(4RS,5SR)-2,2-Dimethyl-4-phenyl-5-(prop-2-yn-1-yl)-1,3-dioxolane* **26** and **27**:



8:2 ratio as a semi solid; The NMR data of the major isomer **26** was culled from the reaction mixture NMR. IR (KBr) ν_{max}: 3275, 3039, 2994, 2942, 1452, 1269, 1219, 1161, 1107, 1022, 897, 852, 652 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4) δ 7.35-7.25 (m, 5H), 5.27 (t, *J*= 6.5 Hz, 1H), 4.55-4.47 (m, 1H), 1.84 (t, *J* = 2.7 Hz, 2H), 1.64 (s, 3H), 1.48 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9 (C), 128.5 (CH), 128.2 (CH), 126.9 (CH), 108.9 (CH), 81.0 (C), 79.6 (CH), 77.6 (CH), 69.9 (CH), 27.8 (CH_3), 25.3 (CH), 22.3 (CH_2) ppm. HRMS (ESI) calcd for $C_{14}H_{16}O_2Na$ $[M + Na]^+$ 239.1048, found 239.1048.

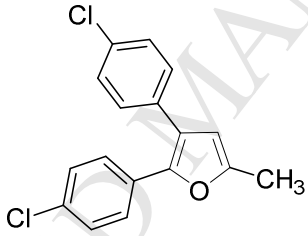
4.4 General procedure for iodine mediated reaction to form furans from 1,2-acetylenicdiols: To the solution of 1,2-acetylenicdiol (0.1 mmol) in 1,4-dioxane (1 mL), iodine 10 mol% (3 mg) was added and the resulting light violet colored solution was rt to reflux. After completion of the reaction (12-24 h, TLC) 1,4-dioxane was evaporated in a rotovap and the resulting crude product was diluted with dichloromethane (DCM, 20 mL). In some cases, the reaction worked at rt or at 60 ^{o}C (see supplementary information for experimental details and spectra of all the starting 1,2-acetylenicdiols and furan products). The DCM solution was washed sequentially with hypo (0.1 mol in water, 2 × 20 mL), brine (2 × 20 mL) and then dried over anhydrous sodium sulfate. Removal of DCM resulted in the crude product, which was purified by column chromatography using silica (100-200 mesh) and hexane as eluent to afford substituted furan derivatives.

4.4a.*5-Methyl-2,3-diphenylfuran* (**5a**):



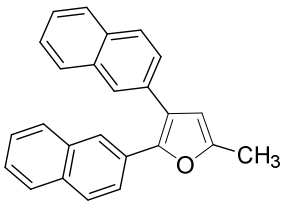
Colorless liquid; yield 90%; IR (KBr) ν_{max} 3057, 3029, 2920, 2852, 1601, 1559, 1502, 1444, 1274, 1242, 1128, 1070, 1026, 998, 952, 912, 808, 762, 695, 672 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.41-7.39 (m, 2H), 7.36-7.32 (m, 2H), 7.29-7.26 (m, 2H), 7.25-7.18 (m, 2H), 6.16 (d, *J* = 1.0 Hz, 1H), 2.39 (d, *J* = 1.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4 (C), 146.9 (C), 134.9 (C), 131.6 (C), 128.7 (CH), 128.6 (CH), 128.4 (CH), 127.2 (CH), 127.1 (CH), 126.1 (CH), 123.3(C), 110.3 (CH), 13.7 (CH_3) ppm; HRMS (ESI) calcd for $C_{17}H_{15}O$ $[M + H]^+$ 235.1117, found 235.1108.

4.4b.*2,3-Bis(4-chlorophenyl)-5-methylfuran* (**5b**):



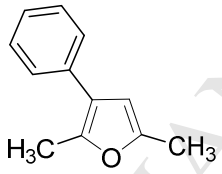
Colorless liquid; yield 88%; IR (KBr) ν_{max} 3032, 2916, 2858, 1650, 1607, 1548, 1494, 1285, 1092, 831, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4) δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.30-7.27 (m, 4H), 7.22 (d, *J* = 8.8 Hz, 2H), 6.09 (d, *J* = 1.0 Hz, 1H), 2.37 (d, *J* = 0.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+ CCl_4) δ 151.9 (C), 146.1 (C), 133.3 (C), 133.2 (C), 133.1 (C), 130.0 (CH), 129.8 (C), 129.1 (CH), 128.9 (CH), 127.3 (CH), 122.7 (C), 110.3 (CH), 13.8 (CH_3) ppm; HRMS (ESI) calcd for $C_{17}H_{14}Cl_2O_2Na$ $[M + Na]^+$ 325.0157, found 325.0159.

4.4c.*5-Methyl-2,3-di(naphthalen-2-yl)furan* (**5c**):



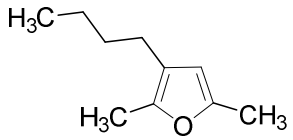
Colorless liquid; yield 92%; IR (KBr) ν_{max} 3053, 2916, 1669, 1627, 1597, 1573, 1506, 1434, 1355, 1271, 1230, 1174, 1017, 962, 894, 858, 818, 747, 707, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.95 (s, 1H), 7.89-7.86 (m, 1H), 7.83-7.72 (m, 4H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.60 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.52-7.48 (m, 2H), 7.46-7.42 (m, 2H), 6.34 (d, *J* = 1.0 Hz, 1H), 2.48 (d, *J* = 1.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9 (C), 147.3 (C), 133.8 (C), 133.6 (C), 132.7 (C), 132.6 (C), 132.3 (C), 129.0 (C), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 127.3 (CH), 127.2 (CH), 126.3 (CH), 126.0 (CH), 125.8 (CH), 124.7 (CH), 124.5 (CH), 123.8 (C), 110.6 (CH), 13.8 (CH_3) ppm; HRMS (ESI) calcd for $C_{25}H_{19}O$ $[M + H]^+$ 335.1430, found 335.1415.

4.4d.*2,5-dimethyl-3-phenylfuran* (**5d**):[24]



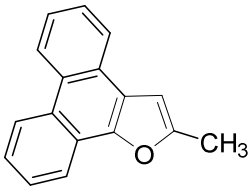
Light yellow liquid; yield 65%; IR (KBr) ν_{max} 3039, 2922, 2863, 1730, 1592, 1492, 1444, 1380, 1275, 1130, 1007, 926, 806, 762, 697, 615,526, 422 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 8.3, 2.5 Hz, 4H), 7.15 – 7.01 (m, 1H),5.97 (d, *J* = 6.3 Hz, 1H), 2.29 (d, *J* = 6.4 Hz, 3H), 2.17 (d, *J* = 5.7 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5 (C), 145.6 (C), 134.6 (C), 128.5 (CH), 127.4 (CH), 126.0 (CH), 121.5 (CH), 107.0(CH), 96.2 (CH), 13.4 (CH_3), 13.0 (CH_3) ppm.

4.4e.*3-Butyl-2,5-dimethylfuran* (**5e**):[25]



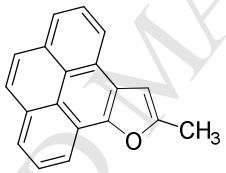
Dark brown liquid; yield 55%; IR (KBr) ν_{max} 2929, 2864, 1601, 1456, 1265, 1069, 1015, 807, 748, 633 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.04 (dd, *J* = 57.9, 11.7 Hz, 1H), 1.77 (s, 3H), 1.40 – 1.30 (m, 3H), 1.26 (d, *J* = 13.7 Hz, 3H), 0.99 – 0.76 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8 (C), 142.0 (C), 129.9 (C), 128.2 (C), 102.9 (CH), 31.0, (CH_2), 29.8 (CH_2), 28.7 (CH_2), 27.9 (CH_3), 22.7 (d, J = 15.7 Hz), 14.2 (CH_3) ppm. HRMS (ESI) calcd for $C_{10}H_{16}O$ $[M + H]^+$152.1201, found 152.1181.

4.4f.*2-Methylphenanthro[9,10-b]furan* (**14**):



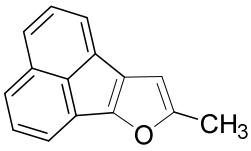
White solid;yield 78%; mp. 125-126 ºC (Reported mp. 125-126 ºC); IR (KBr) ν_{max} 3058, 2923, 2852, 1610, 1579, 1517, 1449, 1349, 1328, 1260, 1235, 1158, 1101, 1033, 943, 802, 755, 722 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.2 Hz, 2H), 8.29-8.24 (m, 1H), 8.02 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.65-7.52 (m, 4H), 6.79 (d, *J* = 0.8 Hz, 1H), 2.55 (d, *J* = 0.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4 (C), 148.3 (C), 128.5 (C), 128.1 (C), 127.6 (C), 127.0 (CH), 126.9 (CH), 125.3 (CH), 125.0 (CH), 124.0 (CH), 123.7 (CH), 123.6 (CH), 122.5 (CH), 121.5 (C), 120.3 (CH), 102.6 (CH), 14.3 (CH_3).ppm; HRMS (ESI) calcd for $C_{17}H_{13}O$ $[M + H]^+$ 233.0961, found 233.0950.

4.4g.*10-Methylpyreno[4,5-b]furan* (**2**):



White solid; yield 76%; mp. 170-171 ºC; IR (KBr) ν_{max} 1595, 1577, 1423, 1063, 1020, 937, 824, 800, 759, 711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.31 (dd, *J* = 7.6, 1.0 Hz, 1H), 8.12-8.10 (m, 2H), 8.05-7.99 (m, 4H), 6.99 (s, 1H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6 (C), 148.9 (C), 132.1 (C), 131.9 (C), 128.0 (CH), 127.7 (CH), 126.9 (C), 126.1 (CH), 126.0 (CH), 124.2 (2 x CH), 123.1 (C), 122.7 (C), 122.2 (C), 121.8 (C), 121.0 (CH), 117.1 (CH), 103.0 (CH), 14.0 (CH_3) ppm; HRMS (ESI) calcd for $C_{19}H_{13}O$ $[M + H]^+$ 257.0961, found 257.0953.

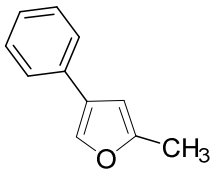
4.4h.*8-Methylacenaphtho[1,2-b]furan* (**15**):



Yellow liquid; yield 58%; IR (KBr) ν_{max} 3047, 2916, 2850, 1715, 1614, 1565, 1476, 1440, 1329, 1216, 1186, 1140, 1076, 1032, 923, 815, 766, 709, 658, 619 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ

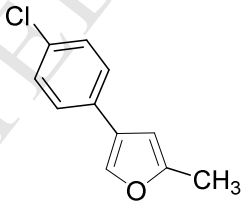
7.66 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.48-7.44 (m, 2H), 6.38 (s, 1H), 2.66 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5 (C), 157.2 (C), 131.2 (C), 130.9 (C), 129.3 (C), 128.0 (C), 127.5 (CH), 127.4 (CH), 126.5 (CH), 126.4 (CH), 121.7 (CH), 118.4 (CH), 103.2 (C), 14.7 (CH_3) ppm; HRMS (ESI) calcd for $C_{15}H_{10}OK$ $[M + K]^+$ 245.0639, found 245.0645.

4.4i.*2-Methyl-4-phenylfuran* (**21a**):



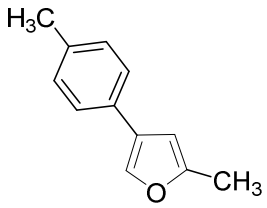
Solid;yield 82%; mp. 62-64 ºC (Reported mp. 64-68 ºC); IR (KBr) ν_{max} 2921, 1606, 1549, 1445, 1125, 1076, 1029, 918, 807, 748, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26-7.21 (m, 1H), 6.29 (d, *J* = 1.0 Hz, 1H), 2.34 (d, *J* = 1.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3 (C), 136.8 (CH), 133.1 (C), 128.9 (CH), 127.4 (C), 126.9 (CH), 125.9 (CH), 105.1 (CH), 13.7 (CH_3) ppm.

4.4j.*4-(4-Chlorophenyl)-2-methylfuran* (**21b**):



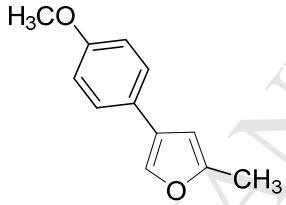
Yellow liquid; yield 64%; IR (KBr) ν_{max} 2924, 2857, 1579, 1513, 1454, 1285, 1177, 1042, 807, 644 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.24 (d, *J* = 11.8 Hz, 2H), 7.18-7.16 (d, *J*= 11.8 Hz, 2H), 6.07 (s, 1H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9 (C), 142.5 (CH), 136.3 (C), 130.9 (CH), 129.5 (C), 122.9 (CH), 107.6 (CH), 13.7 (CH_3) ppm.

4.4k.*2-Methyl-4-(p-tolyl)furan* (**21c**):



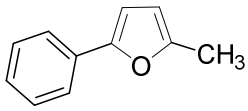
Yellow liquid; yield 71%; IR (KBr) ν_{max} 2924, 2857, 1579, 1513, 1454, 1285, 1177, 1042, 807, 644 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.24 (d, *J* = 11.8 Hz, 2H), 7.18-7.16 (d, *J* = 11.8 Hz, 2H), 6.07 (s, 1H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9 (C), 142.5 (CH), 136.3 (C), 130.9 (CH), 129.5 (C), 122.9 (CH), 107.6 (CH), , 21.4 (CH_3) 13.7 (CH_3) ppm.

4.4l.*4-(4-Methoxyphenyl)-2-methylfuran* (**21d**):



Yellow liquid; yield 76%; IR (KBr) ν_{max} 2926, 2848, 1672, 1579, 1513, 1454, 1285, 1177, 1028, 1005, 833, 644 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.24 (d, *J* = 11.8 Hz, 2H), 7.18-7.16 (d, *J* = 11.8 Hz, 2H), 6.07 (s, 1H), 3.81 (s, 3H), 1.26 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5 (C), 150.9 (C), 124.9 (C), 124.6 (CH), 114.5 (C), 107.6 (CH), 104.3 (CH), 55.3 (OCH_3) 13.9 (CH_3) ppm.

4.4m.*2-Methyl-5-phenylfuran* (**25**):



Colorless liquid; yield 88%; IR (KBr) ν_{max} 3012, 2924, 1597, 1548, 1489, 1448, 1022, 739, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4) δ 7.55-7.49 (m, 2H), 7.24 (t, *J* = 7.8 Hz, 2H), 7.12-7.08 (m, 1H), 6.42 (d, *J* = 3.2 Hz, 1H), 5.95-5.92 (m, 1H), 2.28 (d, *J* = 0.6 Hz, 3H)ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5 (C), 151.9 (C), 131.4 (C), 128.7 (CH), 126.9 (CH), 123.5 (CH), 107.9 (CH), 106.0 (CH), 14.0 (CH_3) ppm. HRMS (ESI) calcd for $C_{11}H_{10}ONa$ $[M + Na]^+$ 181.0629, found 181.0610.

5. Acknowledgement

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