Article

Visible Light Mediated [2+2] Cycloaddition Reactions of 1,4-Quinones and Terminal Alkynes

Shaista Sultan, Muneer-Ul-Shafi Bhat, Masood Ahmad Rizvi, and Bhahwal Ali Shah

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b00855 • Publication Date (Web): 17 Jun 2019

Visible Light Mediated [2+2] Cycloaddition Reactions of 1,4-Quinones and Terminal Alkynes

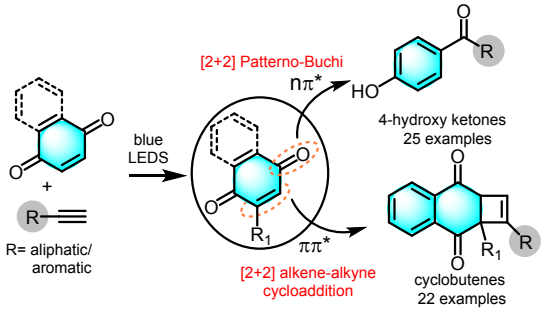
Shaista Sultan,[a,†] Muneer-ul-Shafi Bhat, [a,†] Masood Ahmad Rizvi,*[,‡] and Bhahwal Ali Shah*[,†]

[†]AcSIR and Natural Product Microbes, CSIR-Indian Institute of Integrative Medicine, Jammu-180001,

[‡]Department of Chemistry, University of Kashmir, Srinagar, 190006

[a] Both authors contributed equally

Supporting Information Placeholder



ABSTRACT: A single-step synthesis of 4-hydroxy functionalized bi-aryl and aryl-alkyl ketones *via* oxidative coupling of terminal alkynes with benzoquinones is reported. Furthermore, with naphthoquinones, owing to cross-resonance of carbonyl with aromatic ring, alkene-alkyne cycloaddition is more favoured to give 4-membered carbocyclic adducts, thereby precluding the requirement of preactivated alkynes.

INTRODUCTION

Ketones are valuable intermediates and core structural components in a diverse array of pharmaceuticals, natural products, organic materials, agrochemicals and photosensitizers.[1,2] The synthesis of ketones particularly aryl ketones is one of the most addressed problems in the synthetic organic chemistry (Fig. 1). They are generally accessed *via* Friedel-Craft's acylation reaction,[3] which notably requires creation of high energy acylating reagents. Other approaches to access ketones include: (a) addition of organometallic reagents over activated carboxylic acid derivatives like Weinreb amides, anhydrides, acid chlorides and acyl silanes;[4] (b) transition metal catalyzed cross-coupling acylation reactions such as Kumada-arylation and Suzuki-Miyaura reactions employing use of activated arenes like boronic acids, organoborates, organotriflates and halides; [5,6] (c) decarboxylative addition of benzoic acids and α-oxocarboxylates;[7] (d) carbonylation of arene C-H bonds; [8] (e) photoredox catalysis involving the C-H arylation/alkylation of aldehydes with aryl/alkyl bromides and cross-coupling of alkenes or halides with silyl enol ethers, aryl boronic acids and salicylate esters and carboxylic acids.[9] In this regard, synthesis of 4-hydroxy functionalized aryl/alkyl ketones, precursor to pharmaceutically important molecules like pitofenone, tamoxifen, ospemifene, clomefine, finofibrate, antibiotics, anticholesteremic agents, acetylcholinesterase inhibitors and leukotriene A4 hydrolase inhibitors represents an interesting challenge.[10] Conventionally, 4-hydroxy functional group is introduced indirectly *via* hydroxylation of halo-aryl ketones and deprotection of alkoxy substituted aryl ketones.[11] The only direct method for their synthesis was recently reported by Hwang and co-workers[12] using visible light mediated coupling of phenols and terminal alkynes.

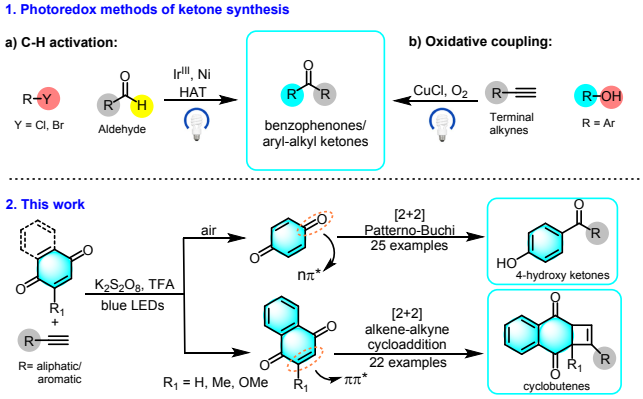


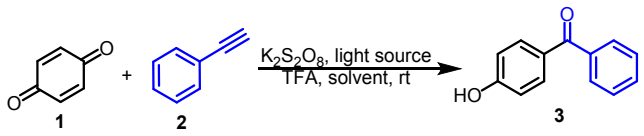
Figure 1. Synthesis of aryl ketones and cyclobutenes.

Thus, in continuation of our interests[13] and inspired by recent advancements in radical reactions,[14] particularly photoredox catalysis,[15] we envisaged the use of 1,4-benzoquinones as they have an innate capability of producing

4-hydroxy functionality post-aromatization. Herein, we report a photoredox catalyzed approach for oxidative coupling of acetylenes with 1,4-benzoquinones to synthesize various 4-hydroxy functionalized aryl/alkyl ketones. However, with naphthoquinone the formation of 4-membered carbocycles was more favourable owing to participation of ππ* excited state of C-C double bond rather than nπ* of carbonyl group,[16] which may be attributed to the cross-resonance of carbonyl with aromatic ring. To the best of our knowledge synthesis of this class of cylcobutenes is hitherto unreported. Also, this observation is significant as such reactions are difficult to achieve using unactivated terminal alkynes given the fact that two coupling partners should either be electrophilic or nucleophilic, so as to match their frontier molecular orbitals.[17]

RESULTS AND DISCUSSION

Table 1. Optimization of Reaction Conditions[a]



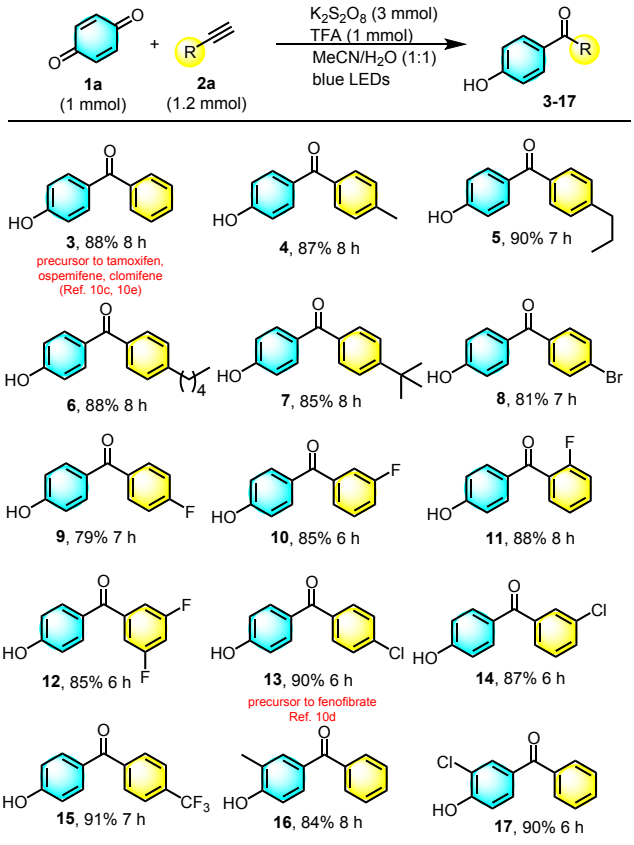
entry	oxidant	light source	solvent	acid source	yield (%)
1	$K_2S_2O_8$	CFL	MeCN/H_2O	TFA	71
2	$K_2S_2O_8$	blue LEDs	MeCN/H_2O	TFA	88
3	$K_2S_2O_8$	blue LEDs	MeOH/H_2O	TFA	-
4	$K_2S_2O_8$	blue LEDs	DCE	TFA	-
5	$K_2S_2O_8$	blue LEDs	DMSO	TFA	-
6	$K_2S_2O_8$	blue LEDs	CH_2Cl_2/H_2O	TFA	traces
7	$K_2S_2O_8$	blue LEDs	MeCN/H_2O	-	traces
8	-	blue LEDs	MeCN/H_2O	TFA	-
9	$K_2S_2O_8$	no light	MeCN/H_2O	TFA	traces
10	$Na_2S_2O_8$	blue LEDs	MeCN/H_2O	TFA	84
11	$(NH_4)_2S_2O_8$	blue LEDs	MeCN/H_2O	TFA	75
12[b]	$K_2S_2O_8$	blue LEDs	MeCN/H_2O	TFA	traces

[a]**1** (1 mmol), **2** (1.2 mmol), oxidant (3 mmol), trifluoroacetic acid (TFA, 1 mmol), solvent (4 mL), rt = 25 °C. [b]The reactions was carried out under argon atmosphere with degassed solvent system (freeze-thaw process). Note: The reactions were monitored upto 10 h reaction time.

Preliminary studies using benzoquinone **1** and phenylacetylene **2** as model substrates in the presence of various oxidants and acid sources showed that the combination of potassium persulfate, trifluoroacetic acid (TFA) and visible light was required for synthesis of benzophenones (Table 1). The irradiation of the reaction mixture with CFL in presence of MeCN:H_2O as solvent afforded the 4-hydroxy benzophenone **3** in 71% yields (Table 1, entry 1), albeit with side product formation possibly because of the heat generated by CFL. Nevertheless, the use of blue light not only improved the reaction yields to 88%, but also showed no side product formation (Table 1, entry 2). Furthermore, screening of different solvents like MeOH/H_2O, DCE, DMSO and CH_2Cl_2/H_2O resulted in no product formation (Table 1, entries 3-6). Moreover, the ketone could not be isolated in absence of acid source (TFA), oxidant (persulfate) or light source (Table 1, entries 7-9). Reaction in presence of sodium and ammonium persulfate also gave the product **3** in 84 and 75% yields respectively (Table 1, entries 10-11). Furthermore, there was no product formation in absence of atmospheric oxygen, under argon atmosphere with degassed solvent system (Table 1, entries 10-11).

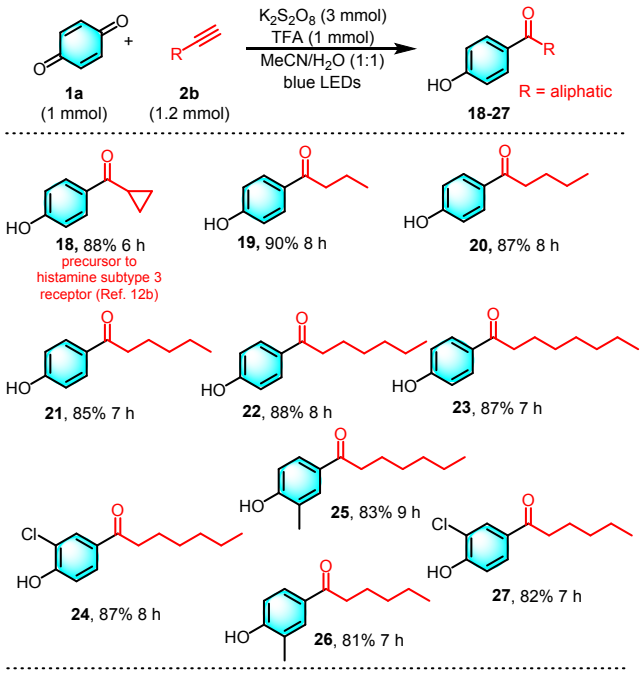
The reaction conditions thus optimized were applied to a series of phenylacetylenes using benzoquinone **1** for the synthesis of diverse benzophenones (Scheme 1). The products (**4-7**) with 4-methyl, propyl, pentyl and *tert*-butyl phenylacetylenes were synthesized in 85-90% yields. The reaction with various halo-substituted phenylacetylenes ranging from 4-bromo, 4-fluoro, 3-fluoro, 2-fluoro, 3,5-difluoro, 4-chloro and 3-chloro phenylacetylene gave corresponding products (**8-14**) in 79-90% yields. The electron deficient 4-trifluoromethylphenylacetylene produced **15** in 91% yields. The reaction of phenylacetylene was also feasible with substituted benzoquinones *viz*., 2-methyl and 2-chloro benzoquinone giving benzophenones (**16-17**) in 84 and 90% yields respectively.

Scheme 1. Synthesis of benzophenones



We further examined the scope of this reaction with aliphatic acetylenes for the synthesis of aryl-alkyl ketones (Scheme 2). Aliphatic alkynes like cyclopropylacetylene, 1-pentyne, 1-hexyne and 1-heptyne also underwent coupling with benzoquinone to generate corresponding products (**18-21**) in 85-90% yields. Similarly, long chain alkynes like 1-octyne and 1-nonyne also produced ketones (**22-23**) in 88 and 87% yields respectively. Also, 2-methyl and 2-chloro benzoquinone with 1-heptyne and 1-octyne produced substituted aryl-alkyl ketones (**24-27**) in 81-87% yields.

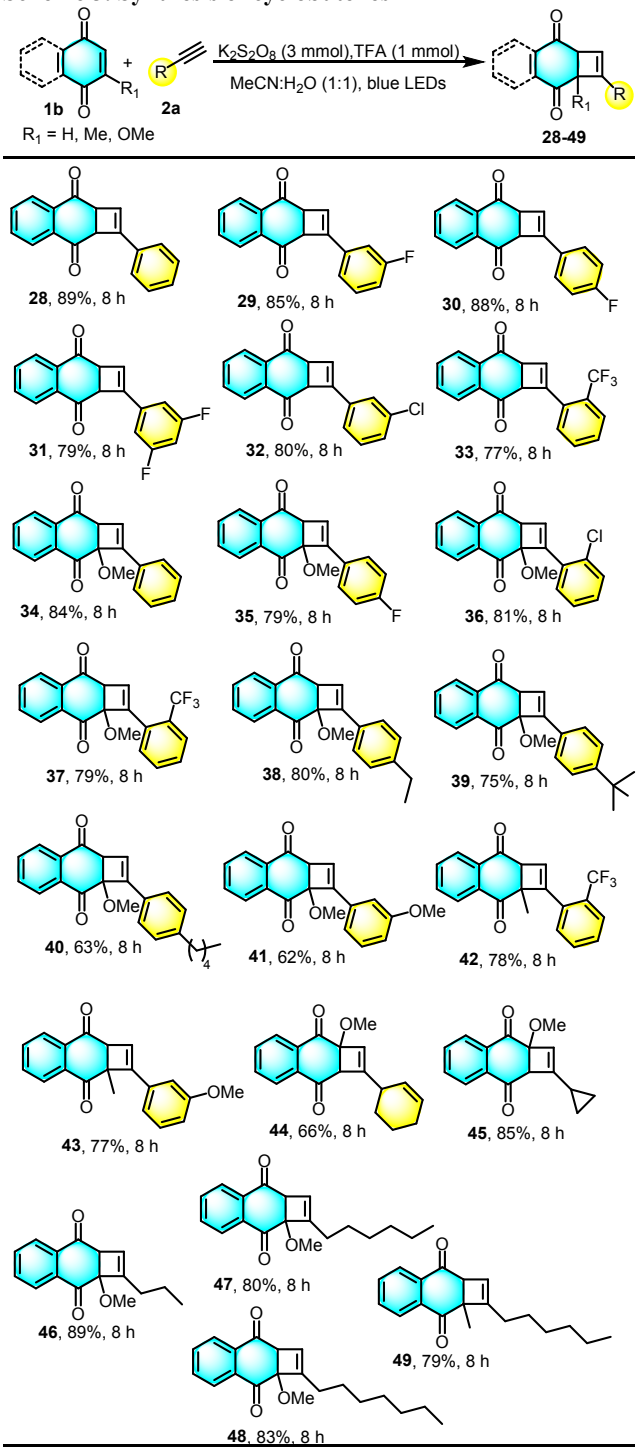
Scheme 2. Synthesis of aryl-alkyl ketones



To expand the utility of this methodology, we directed our efforts towards probing the reaction scope with 1,4-naphthoquinones. However, under standard conditions, instead of 4-hydroxy ketones, it produced alkene-alkyne cycloaddition product **28** in 89% yields. Notably, 4-membered ring of cyclobutanes and cyclobutenes are important precursor for the synthesis of natural products and pharmaceuticals and also utilized as important intermediate during ring expansion reactions.[18] The 4-membered carbocycles are mostly accessed *via* thermal and photochemical [2+2] cycloaddition reactions.[19] The reaction of 1,4-naphthoquinone proceeded efficiently with halo-substituted (3-fluoro, 4- fluoro, 3,5-difluoro, and 3-chloro) and electron deficient 4-trifluoromethyl phenylacetylene to generate cyclobutenes (**29-33**) in excellent yields (Scheme 3). Also, 2-methoxy naphthoquinone appeared to be a suitable coupling partner with a range of phenylacetylenes *viz.*, phenylacetylene, halo-substituted (4- fluoro and 2-chloro), electron deficient (2-trifluoromethyl), alkyl substituted (4-ethyl, 4-*tert*-butyl, 4-pentyl) and electron rich 3-methoxy phenylacetylene to afford carbocycles (**34-41**) in 62-84% yields. Similarly, 2-methyl naphthoquinone (menadione) participated in [2+2] cycloaddition reaction with 2-trifluoromethyl and 3-methoxy phenylacetylene generating (**42-43**) in 77-78% yields. As demonstrated, the reaction of 2-methoxy naphthoquinone also proceeded efficiently with aliphatic acetylenes like 1-ethynylcyclohexene, cyclopropylacetylene, 1-pentyne, 1-octyne and 1-nonyne to produce (**44-48**) in excellent yields. Also, reaction of menadione with 1-octyne gave **49** in 79% yields.

To get an insight about the plausible mechanism of the reaction, physico-chemical investigations like cyclic voltammetry (CV) and spectrophotometric dye-degradation studies were conducted as parallel experiments for mechanistic support. The dye-degradation study of eosin, malachite green and Rose Bengal was conducted to confirm the visible light mediated cleavage of SO_4^{2-} to sulfate radical anion ($SO_4^{\bullet-}$). These dyes are known to degrade under oxidative conditions,[20] and in our observation these dyes displayed a sequential decrease in the absorbance at their corresponding λ_{max} with the increasing irradiation time in presence of $K_2S_2O_8$ (See supporting information for details).

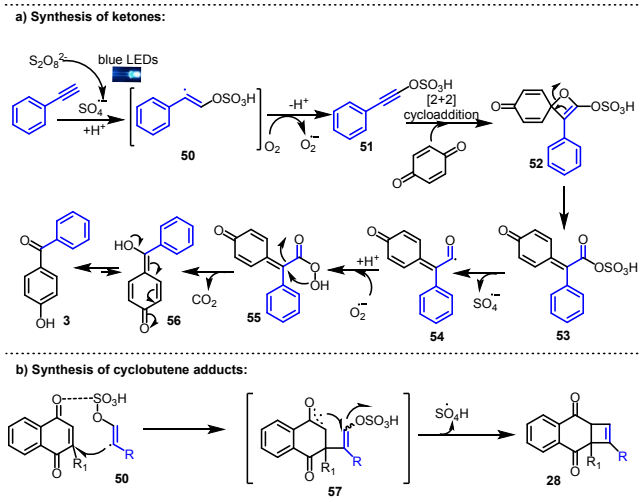
Scheme 3. Synthesis of cyclobutenes



A recent work by Xia and co-workers[21] also presented a visible light mediated cleavage of SO_4^{2-} to $SO_4^{\bullet-}$. The CV studies were also performed to ascertain the thermodynamic feasibility of the proposed reaction between the photochemically generated $SO4^{\bullet-}$ and phenylacetylene. The observed CV plot for phenylacetylene depicts an irreversible redox behavior with only single oxidation peak current starting at a potential close to 1.9 V (vs. SCE) and no

reduction peak. The onset of oxidation peak is close to 1.9 V and it maximizes around 2.4 V (vs. SCE). The results suggest a single redox system of irreversible nature which in turn implies a single electron transfer (SET) reaction. The calculated formal potentials of phenylacetylene (1.9-2.4 vs. SCE) show that it can be oxidized by the photochemically generated $SO_4^{\bullet-}$ having a higher reduction potential (2.6 V vs. SCE).[22] Moreover, inhibition of the reaction in presence of radical-quencher TEMPO also indicates its radical nature which goes inconformity with the CV studies (See supporting information for details).

Scheme 4. Plausible mechanism



Based on control experiments and literature precedence a plausible reaction mechanism is proposed (Scheme 4a). The reaction possibly initiates by the homolysis of persulfate to $SO_4^{\bullet-}$.[21] As suggested by the redox potentials of phenylacetylene and sulfate radical anion, and based on earlier reports,[23] the $SO_4^{\bullet-}$ adds to the C-C triple bond of terminal alkyne, thereby generating transitory vinyl radical adduct **50** which after SET with molecular oxygen produces comparatively stable intermediate **51**. A [2+2] Patterno-Buchi reaction between intermediate **51** and carbonyl group of benzoquinone generates a 4-membered oxetene derivative **52** which rearranges *via* cycloreversion reaction to yield intermediate **53**. Rapid fragmentation of this intermediate to release $SO_4^{\bullet-}$ gives an acyl radical intermediate **54**. Subsequent reaction with oxygen radical anion and protonation assisted by TFA leads to the formation of peracid intermediate **55**. Thereafter, decarboxylation followed by Keto-enol tautomerism of quinone methide **56** affords the final product. However with naphthoquinones, the free-radical of intermediate **50** possibly attacks the C-C double bond of naphthoquinone leading to the formation of **57**, which on loss of sulfate radical anion gives the cyclobutene **28** (Scheme 4b). Mechanistically, we believe the predominant formation of *syn*-isomers in case of 2-substituted naphthoquinones is possibly because sulfate part of **50** interacts with the carbonyl oxygen of naphthoquinone from the less hindered side. The structure of these cyclobutene adducts were found to be in accordance with the reported NMR data,[24] wherein the coupling constants (*J* value) between 1-2 Hz are characteristics of *syn*-isomer. However, in case of compound **44** and **45**, no coupling was observed between the H atoms, indicating that these two products are *anti*-isomers. This may be because of nature of axial-axial interaction between methoxy of naphthoquinone and axial hydrogens of cyclopropyl and cyclohexene, which unlike other interactions is not of stabilizing nature owing to lower electronegativity of sp^3 carbon bonded hydrogen atom, due to which steric interactions predominate and invert the regioselectivity. Notably, the reaction in absence of persulfate salt didn't yield desired product.

CONCLUSION

In conclusion, we have developed a visible-light mediated synthesis of 4-hydroxy functionalized ketones using 1,4-benzoquinones and terminal alkynes. Moreover the 1,4-naphthoquinones undergo [2+2] alkene-alkyne cycloaddition with acetylenes to afford 4-membered carbocycles in high yields. The protocol presents a mild and efficient system which offers a viable method for generation of 4-hydroxy benzophenones, aryl-alkyl ketones and carbocycles. Further applicability of this method is under investigation in our laboratory.

EXPERIMENTAL SECTION

General Information. All reactions were conducted in oven-dried glassware. The reactions were irradiated using regular blue light-emitting diode (LED) array (30 lamps, power density: 40mW/cm^2 at 460 nm). Irradiation occurred along the sides at a uniform distance of 5 cm. ^{1}H and ^{13}C NMR spectra were recorded on FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$, 7.26 ppm). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 125 MHz or 100 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent. Mass spectra were obtained by using Q-TOF-LC-MS Spectrometer using electron spray ionization.

General Procedure for the Synthesis of Ketones. To a 30 mL glass vial was added benzoquinone (1.0 equiv.) in 4 mL MeCN:H_2O (1:1), followed by addition of terminal alkyne (1.2 equiv.), potassium persulfate $K_2S_2O_8$ (3 equiv.) and trifluoroacetic acid TFA (1 equiv.). The reaction mixture was then irradiated with continuous stirring under blue LEDs for a period of 8 h. The progress of reaction was monitored by TLC. After completion of reaction, the crude reaction mixture was extracted with ethyl acetate (10 mL×3) and water (10 mL). The aqueous layers were then washed with saturated sodium bicarbonate ($NaHCO_3$) (5 mL) and again extracted with ethyl acetate (10 mL). The combined organic layers were dried over sodium sulfate (Na_2SO_4) and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography using ethyl acetate/hexane as solvent system.

(4-hydroxyphenyl)(phenyl)methanone (3). The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), phenylacetylene (110 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 80:20) as yellow solid (161 mg, 88%), mp 132-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.76 (dd, *J* = 11.6, 4.9 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 6.96 (d , *J* = 8.7 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.2, 161.1, 138.0, 133.3(2C), 132.3, 129.9(2C), 129.4, 128.3(2C), 115.5(2C). HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{13}H_{11}O_2$, 199.0754; found, 199.0754. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[12]

(4-hydroxyphenyl)(p-tolyl)methanone ***(4)***. The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 4-ethynyltoluene (137 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 80:20) as white solid (171 mg, 87%), mp 174-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.30 (s, 1H), 2.38 (s, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 196.6, 161.3, 142.9, 135.4, 132.9(2C), 130.1(2C), 129.3, 128.9(2C), 115.2(2C), 21.6. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{13}O_2$, 213.0910; found, 213.0913. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[11j]

(4-hydroxyphenyl)(4-propylphenyl)methanone ***(5)***. The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-ethyl-4-propylbenzene (155 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 82:18) as white solid (199 mg, 90%), mp 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.69 (t, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 2.69 – 2.63 (m, 2H), 1.68 (dd, *J* = 15.1, 7.5 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.1, 161.1, 147.9, 135.5, 133.1(2C), 130.2(2C), 129.5, 128.4(2C), 115.5(2C), 38.1, 24.9, 13.8. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{17}O_2$, 241.1223; found, 241.1226.

(4-hydroxyphenyl)(4-pentylphenyl)methanone ***(6)***. The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-ethyl-4-pentylbenzene (185 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 80:20) as white solid (218 mg, 88%), mp 128-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 2.70 – 2.65 (m, 2H), 1.65 (dd, *J* = 15.0, 7.4 Hz, 2H), 1.37 – 1.31 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.0, 160.9, 148.1, 135.4, 133.1(2C), 130.2(2C), 129.7, 128.4(2C), 115.4(2C), 36.0, 31.5, 30.9, 22.5, 14.0. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{21}O_2$, 269.1536; found, 269.1541.

(4-(tert-butyl)phenyl)(4-hydroxyphenyl)methanone ***(7)***. The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 4-*tert*-butylphenylacetylene (170 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 82:18) as white solid (199 mg, 85%), mp 103-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 1.36 (s, 9H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 196.3, 160.3, 155.9, 135.3, 133.0(2C), 130.1, 130.0(2C), 125.2(2C), 115.3(2C), 35.1, 31.2(3C). HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{17}H_{19}O_2$, 255.1380; found, 255.1375. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[12]

(4-bromophenyl)(4-hydroxyphenyl)methanone ***(8)***.

The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-ethynyl-4-bromobenzene (195 µl, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µl, 0.9 mmol) and purified by column chromatography (hexane:EA = 75:25) as white solid (208 mg, 81%), mp 190-193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.63 (s, 4H), 6.94-6.89 (m, 2H); ^{13}C {^{1}H}NMR (125 MHz, $CDCl_3$) δ 194.7, 160.0, 136.9, 132.9(2C), 131.6(2C), 131.3(2C), 129.6, 127.0, 115.3(2C); HRMS (ESI) m/z: $[M-H]^-$ calculated for $C_{13}H_8BrO_2$, 274.9713; found, 274.9717. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[12]

(4-fluorophenyl)(4-hydroxyphenyl)methanone ***(9)***. The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-ethynyl-4-fluorobenzene (129 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 78:22) (158 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$ and MeOD) δ 194.8, 165.1 (d, *J* = 253.26 Hz), 161.5, 134.5 (d, *J* = 2.52 Hz), 132.8, 132.3 (d, *J* = 8.82 Hz), 128.9, 115.4, 115.2. HRMS (ESI) (m/z): $[M-H]^-$ calculated for $C_{13}H_8FO_2$, 215.0508; found, 215.0529. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[11j]

(3-fluorophenyl)(4-hydroxyphenyl)methanone ***(10)***. The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-ethynyl-3-fluorobenzene (129 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 78:22) (170 mg, 85%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 7.95 (brs, 1H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.29 – 7.23 (m, 1H), 6.97 (d, *J* = 8.7 Hz, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.7, 162.4 (d, *J* = 247.5 Hz), 161.5, 140.1 (d, *J* = 6.25 Hz), 133.3(2C), 130.1 (d, *J* = 10.0 Hz), 128.7, 125.6 (d, *J* = 2.5 Hz), 119.3 (d, *J* = 21.25 Hz), 116.6 (d, *J* = 22.5 Hz), 115.7(2C). HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{13}H_{10}FO_2$, 217.0659; found, 217.0639. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[11g]

(2-fluorophenyl)(4-hydroxyphenyl)methanone ***(11)***. The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-ethynyl-2-fluorobenzene (129 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 78:22) (176 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 12.2 Hz, 2H), 7.57 – 7.42 (m, 2H), 7.26 (m, 1H), 7.17 (t, *J* = 9.2 Hz, 1H), 6.99 – 6.89 (m, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 193.5, 161.9, 159.8 (d, *J* = 250 Hz), 133.0(2C), 132.9 (d, *J* = 5.0 Hz), 130.4 (d, *J* = 3.75 Hz), 129.4, 127.1 (d, *J* = 15 Hz), 124.3 (d, *J* = 3.75 Hz), 116.3 (d, *J* = 22.5 Hz), 115.7(2C). HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{13}H_{10}FO_2$, 217.0659; found, 217.0640.

(3,5-difluorophenyl)(4-hydroxyphenyl)methanone ***(12)***:

The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-ethynyl-3,5-difluorobenzene (128 µl, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µl, 0.9 mmol) and purified by column chromatography (hexane:EA = 75:25) as white solid (184 mg, 85%), mp 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.18 (m, 2H), 6.98 (m, 1H), 6.88 (d, *J* = 8.7 Hz, 2H); ^{13}C {^{1}H}NMR (125 MHz, $CDCl_3$) δ 193.4, 162.5 (dd, *J* = 250, 11.3 Hz, 2C), 162.1, 141.3 (t, *J* = 7.7 Hz), 133.0, 127.9, 115.5, 112.6 (dd, *J* = 19.9, 6.5 Hz), 107.1 (t, *J* = 25.3 Hz). HRMS (ESI) (m/z): $[M-H]^-$ calculated for $C_{13}H_7F_2O_2$, 233.0420; found, 233.0417.

(4-chlorophenyl)(4-hydroxyphenyl)methanone ***(13)***. The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-chloro-4-ethynylbenzene (128 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 78:22) as white solid (193 mg, 90%), mp 179-181 °C. ^{1}H NMR (400 MHz, $CDCl_3$ and MeOD) δ 7.54 (dd, *J* = 13.1, 8.6 Hz, 5H), 7.30 (d, *J* = 8.4 Hz, 1H), 6.74 (s, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$ and MeOD)

δ 195.4, 162.1, 138.3, 136.6, 132.9(2C), 131.1(2C), 128.5(2C), 128.3, 115.3(2C). HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{13}H_{10}ClO_2$, 233.0364; found, 233.0353. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[12]

(3-chlorophenyl)(4-hydroxyphenyl)methanone (14). The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-chloro-3-ethynylbenzene (128 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 78:22) as white solid (187 mg, 87%), mp 168-170 °C. ^1H NMR (400 MHz, $CDCl_3$ and MeOD) δ 7.69 (dd, *J* = 14.1, 5.1 Hz, 3H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.50 (m, 1H), 6.89 (d, *J* = 8.7 Hz, 3H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$ and MeOD) δ 195.0, 162.3, 140.0, 134.3, 133.0(2C), 131.8, 129.6, 129.4, 128.1, 127.7, 115.3(2C). HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{13}H_{10}ClO_2$, 233.0364; found, 233.0362. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[11h]

(4-hydroxyphenyl)(4-(trifluoromethyl)phenyl)methanone (15). The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 4-trifluoromethylphenylacetylene (183 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 70:30) (224 mg, 91%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.72 – 7.66 (m, 4H), 6.87 (d, *J* = 8.5 Hz, 2H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 195.4, 162.3, 141.5, 133.1(2C), 129.7(2C), 128.1, 125.2 (q, *J* = 11.25 Hz, 2C), 123.7 (q, *J* = 271.25 Hz), 115.5(2C). HRMS (ESI) (m/z): $[M-H]^-$ calculated for $C_{14}H_8F_3O_2$, 265.0476; found, 265.0496. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[11j]

(4-hydroxy-3-methylphenyl)(phenyl)methanone (16). The title compound was prepared according to the general procedure described above using methyl-*p*-benzoquinone (100 mg, 0.8 mmol), phenylacetylene (98 µL, 0.96 mmol), $K_2S_2O_8$ (649 mg, 2.4 mmol) and TFA (61 µL, 0.8 mmol) and purified by column chromatography as white solid (hexane:EA = 80:20) (146 mg, 84%), mp 163-165 °C. ^1H NMR (400 MHz, $CDCl_3$ and MeOD) δ 7.78 – 7.70 (m, 2H), 7.65 (s, 1H), 7.60 – 7.53 (m, 2H), 7.49 – 7.44 (m, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 2.26 (s, 3H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$ and MeOD) δ 196.8, 159.9, 138.5, 133.8, 131.8, 130.6, 130.0, 129.7, 128.8, 128.3, 128.1, 124.7, 114.2, 15.9; HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{14}H_{13}O_2$, 213.0910; found, 213.0908. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[12]

(3-chloro-4-hydroxyphenyl)(phenyl)methanone (17). The title compound was prepared according to the general procedure described above using 2-chloro-1,4-benzoquinone (100 mg, 0.7 mmol), phenylacetylene (86 µL, 0.84 mmol), $K_2S_2O_8$ (568 mg, 2.1 mmol) and TFA (53 µL, 0.7 mmol) and purified by column chromatography (hexane:EA = 78:22) as white solid (147 mg, 90%), mp 180-181 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 1H), 7.73 (ddd, *J* = 6.2, 4.3, 2.0 Hz, 2H), 7.67 – 7.56 (m, 2H), 7.53 – 7.46 (m, 2H), 7.02 (dd, *J* = 8.4, 3.6 Hz, 1H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$ and MeOD) δ 195.4, 157.3, 137.6, 132.6, 132.3, 130.8, 129.7, 129.6(2C), 128.3(2C), 120.8, 116.0. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{13}H_{10}ClO_2$, 233.0364; found, 233.0353. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature .[11a]

cyclopropyl(4-hydroxyphenyl)methanone (18). The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), cyclopropylacetylene (71 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 90:10) as yellow solid (132 mg, 88%), mp 105-107 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 18.3 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 2.66 (m, 1H), 1.25 (m, 2H), 1.04 (m, 2H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 201.0, 161.2, 140.0, 130.8(2C), 130.3, 115.5, 17.0, 11.8(2C). HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{10}H_{11}O_2$, 163.0754; found, 163.0754. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[11b]

1-(4-hydroxyphenyl)butan-1-one (19). The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-pentyne (61 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 88:12) (137 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 1.85 – 1.72 (m, 2H), 1.11 – 0.97 (m, 3H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 201.0, 161.2, 130.9(2C), 129.5, 115.6(2C), 40.3, 18.3, 13.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{10}H_{13}O_2$, 165.0910; found, 165.0895. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[12]

1-(4-hydroxyphenyl)pentan-1-one (20). The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-hexyne (88 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 88:12) as yellow solid (143 mg, 87%), mp 62-63 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 2.99 – 2.88 (m, 2H), 1.71 (dt, *J* = 15.2, 7.5 Hz, 2H), 1.41 (dt, *J* = 14.9, 7.4 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 201.5, 161.4, 140.7, 131.0, 129.3, 122.4, 115.6, 38.1, 27.1, 22.5, 13.9; HRMS (ESI) m/z: $[M+H]^+$calculated for $C_{11}H_{15}O_2$, 179.1067; found, 179.1067. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[12]

1-(4-hydroxyphenyl)hexan-1-one (21). The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-heptyne (104 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 88:12) as yellow solid (151 mg, 85%), mp 61-63 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2H), 6.93 (t, *J* = 9.0 Hz, 2H), 2.96 – 2.88 (m, 2H), 1.72 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.37 – 1.31 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 201.5, 161.4, 131.0(2C), 129.4, 115.6(2C), 38.4, 31.6, 24.7, 22.5, 13.9. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{12}H_{17}O_2$, 193.1223; found, 193.1207. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[11e]

1-(4-hydroxyphenyl)heptan-1-one (22). The title compound was prepared according to the general procedure described above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-octyne (119 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 90:10) as yellow solid (168 mg, 88%), mp 92-93 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 2.93 (t, *J* = 7.5 Hz, 2H), 1.71 (dd, *J* = 14.9, 7.6 Hz, 2H), 1.36 (dd, *J* = 13.3, 5.2 Hz, 2H), 1.32 – 1.27 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 201.5, 161.3, 131.0(2C), 129.3, 115.6(2C), 38.4, 31.6, 29.1, 25.0, 22.5, 14.0. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{13}H_{19}O_2$, 207.1380; found, 207.1360. The observed characterization data (^1H & ^{13}C) was consistent with that previously reported in the literature.[12]

1-(4-hydroxyphenyl)octan-1-one (23). The title compound was prepared according to the general procedure described

above using 1,4-benzoquinone (100 mg, 0.9 mmol), 1-nonyne (134 µL, 1.08 mmol), $K_2S_2O_8$ (730 mg, 2.7 mmol) and TFA (70 µL, 0.9 mmol) and purified by column chromatography (hexane:EA = 90:10) as yellow solid (177 mg, 87%), mp 60-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 1.78 – 1.66 (m, 2H), 1.34 – 1.23 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 201.3, 161.3, 140.7, 131.0, 129.4, 116.1, 115.6, 38.4, 31.7, 29.4, 29.1, 25.0, 22.6, 14.1. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{14}H_{21}O_2$, 221.1536; found, 221.1532. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[11d]

1-(3-chloro-4-hydroxyphenyl)heptan-1-one (24). The title compound was prepared according to the general procedure described above using 2-chloro-1,4-benzoquinone (100 mg, 0.7 mmol), 1-octyne (92 µL, 0.84 mmol), $K_2S_2O_8$ (568 mg, 2.1 mmol) and TFA (53 µL, 0.7 mmol) and purified by column chromatography (hexane:EA = 86:14) (147 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.1 Hz, 1H), 7.84 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.11 – 7.07 (m, 1H), 2.93 – 2.89 (m, 2H), 1.73 (dd, *J* = 14.1, 6.7 Hz, 2H), 1.39 – 1.30 (m, 6H), 0.91 (dd, *J* = 9.0, 4.8 Hz, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.4, 155.4, 131.0, 129.7, 129.0, 120.5, 116.1, 38.3, 31.6, 29.0, 24.4, 22.5, 14.0. HRMS (ESI) (m/z): $[M-H]^-$ calculated for $C_{13}H_{16}ClO_2$, 239.0839; found, 239.0864.

1-(4-hydroxy-3-methylphenyl)heptan-1-one (25). The title compound was prepared according to the general procedure described above using methyl-*p*-benzoquinone (100 mg, 0.8 mmol), 1-octyne (106 µL, 0.96 mmol), $K_2S_2O_8$ (649 mg, 2.4 mmol) and TFA (61 µL, 0.8 mmol) and purified by column chromatography (hexane:EA = 90:10) (150 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 1.5 Hz, 1H), 7.76 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 2.95 – 2.91 (m, 2H), 2.32 (s, 3H), 1.77 – 1.71 (m, 2H), 1.38 – 1.29 (m, 6H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 200.4, 158.7, 131.7, 129.9, 128.3, 124.2, 114.7, 38.3, 31.7, 29.1, 24.8, 22.5, 15.8, 14.0. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{21}O_2$, 221.1536; found, 221.1505. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[11e]

1-(4-hydroxy-3-methylphenyl)hexan-1-one (26). The title compound was prepared according to the general procedure described above using methyl-*p*-benzoquinone (100 mg, 0.8 mmol), 1-heptyne (92 µL, 0.96 mmol), $K_2S_2O_8$ (649 mg, 2.4 mmol) and TFA (61 µL, 0.8 mmol) and purified by column chromatography (hexane:EA = 88:12) (137 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 1.5 Hz, 1H), 7.75 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 2.96 – 2.91 (m, 2H), 2.32 (s, 3H), 1.79 – 1.71 (m, 2H), 1.38 (td, *J* = 7.1, 3.6 Hz, 4H), 0.92 (t, *J* = 7.0 Hz, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 200.8, 159.0, 131.7, 129.7, 128.3, 124.3, 114.8, 38.3, 31.6, 24.6, 22.5, 15.9, 13.9. HRMS (ESI) (m/z): $[M-H]^-$ calculated for $C_{13}H_{17}O_2$, 205.1229; found, 205.1252. The observed characterization data (^{1}H & ^{13}C) was consistent with that previously reported in the literature.[11e]

1-(3-chloro-4-hydroxyphenyl)hexan-1-one (27). The title compound was prepared according to the general procedure described above using 2-chloro-1,4-benzoquinone (100 mg, 0.7 mmol), 1-heptyne (81 µL, 0.84 mmol), $K_2S_2O_8$ (568 mg, 2.1 mmol) and TFA (53 µL, 0.7 mmol) and purified by column chromatography (hexane:EA = 86:14) (130 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.1 Hz, 1H), 7.84 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.11 – 7.07 (m, 1H), 2.93 – 2.89 (m, 2H), 1.78 – 1.70 (m, 2H), 1.40 – 1.35 (m, 4H), 0.93 (dd, *J* = 9.4, 4.6 Hz, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.4, 155.5, 131.0, 129.7, 129.0, 120.5, 116.1, 38.3, 31.5, 24.2, 22.5, 13.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{12}H_{16}ClO_2$, 227.0833; found, 227.0816.

General Procedure for the Synthesis of Cyclobutenes. To a 30 mL glass vial was added 1,4-naphthoquinone (1.0 equiv.) in 4 mL MeCN:H_2O (1:1), followed by addition of terminal alkyne (2 equiv.), potassium persulfate $K_2S_2O_8$ (3 equiv.) and trifluoroacetic acid TFA (1 equiv.). The reaction mixture was then irradiated with continuous stirring under blue LEDs for a period of 8 h. The progress of reaction was monitored by TLC. After completion of reaction, the crude reaction mixture was extracted with ethyl acetate (10 mL×3) and water (10 mL). The aqueous layers were washed with saturated sodium bicarbonate ($NaHCO_3$) (5 mL) and again extracted with ethyl acetate (10 mL). The combined organic layers were dried over sodium sulfate (Na_2SO_4) and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography using EtOAc/Hexane as solvent system

1-phenyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (28). The title compound was prepared according to the general procedure described above using 1,4-naphthoquinone (100 mg, 0.6 mmol), phenylacetylene (122 µL, 1.2 mmol), $K_2S_2O_8$ (486 mg, 1.8 mmol) and TFA (46 µL, 0.6 mmol) and purified by column chromatography (hexane:EA = 95:05) (147 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 1H), 8.03 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.58 – 7.53 (m, 2H), 7.39 – 7.28 (m, 3H), 6.57 (d, *J* = 0.9 Hz, 1H), 4.53 (d, *J* = 3.8 Hz, 1H), 4.14 (dd, *J* = 3.7, 1.6 Hz, 1H).; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.7, 195.7, 149.2, 134.6, 134.6, 133.9, 133.7, 132.0, 129.2, 128.6, 128.6(2C), 127.8, 127.6, 125.5(2C), 52.2, 49.1. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{13}O_2$, 261.0910; found, 261.0896.

1-(3-fluorophenyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (29). The title compound was prepared according to the general procedure described above using 1,4-naphthoquinone (100 mg, 0.6 mmol), 1-ethynyl-3-fluorobenzene (144 µL, 1.2 mmol), $K_2S_2O_8$ (486 mg, 1.8 mmol) and TFA (46 µL, 0.6 mmol) and purified by column chromatography (hexane:EA = 94:06) as brown semi-solid (149 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 1H), 8.08 – 8.04 (m, 1H), 7.80 – 7.72 (m, 2H), 7.40 – 7.26 (m, 3H), 7.00 (m, 1H), 6.61 (d, *J* = 1.1 Hz, 1H), 4.51 (d, *J* = 3.8 Hz, 1H), 4.16 (m, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.3, 195.3, 162.8 (d, *J* = 246.25 Hz), 147.9 (d, *J* = 2.5 Hz), 134.7 (d, *J* = 6.25 Hz, 2C), 133.9 (d, *J* = 8.75 Hz), 133.9 (d, *J* = 27.5 Hz), 130.2 (d, *J* = 8.75 Hz, 2C), 130.1(2C), 127.5 (d, *J* = 28.75 Hz, 2C), 121.4 (d, *J* = 2.5 Hz), 116.2 (d, *J* = 21.25 Hz), 112.4 (d, *J* = 22.5 Hz), 52.1, 49.1. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{12}FO_2$, 279.0816; found, 279.0800.

1-(4-fluorophenyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (30). The title compound was prepared according to the general procedure described above using 1,4-naphthoquinone (100 mg, 0.6 mmol), 1-ethynyl-4-fluorobenzene (144 µL, 1.2 mmol), $K_2S_2O_8$ (486 mg, 1.8 mmol) and TFA (46 µL, 0.6 mmol) and purified by column chromatography (hexane:EA = 94:06) as dark red semi-solid (154 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.0 Hz, 1H), 8.04 (d, *J* = 7.0 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.54 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 6.50 (s, 1H), 4.50 (d, *J* = 3.6 Hz, 1H), 4.13 (s, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.5(2C), 163.1 (d, *J* = 248.75 Hz), 148.0, 134.7 (d, *J* = 12.5 Hz, 2C), 133.8 (d, *J* = 20.0 Hz), 128.3 (d, *J* = 3.75 Hz), 127.9 (d, *J* = 2.5 Hz), 127.8(2C), 127.6 (d, *J* = 3.75 Hz, 2C), 127.5, 115.7 (d, *J* = 21.25, 2C), 52.1, 48.9. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{12}FO_2$, 279.0816; found, 279.0794.

1-(3,5-difluorophenyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (31). The title

compound was prepared according to the general procedure described above using 1,4-naphthoquinone (100 mg, 0.6 mmol), 1-ethynyl-3,5-difluorobenzene (165 µL, 1.2 mmol), $K_2S_2O_8$ (486 mg, 1.8 mmol) and TFA (46 µL, 0.6 mmol) and purified by column chromatography (hexane:EA = 94:06) as pale yellow semi-solid (148 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.05 (m, 2H), 7.76 (m, 2H), 7.13 – 7.06 (m, 2H), 6.75 (m, 1H), 6.64 (d, *J* = 1.2 Hz, 1H), 4.48 (d, *J* = 3.7 Hz, 1H), 4.16 (dd, *J* = 3.8, 1.7 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 194.8, 194.8, 163.1 (dd, *J* = 250.1, 12.1 Hz, 2C), 146.9, 134.8 (d, *J* = 10.0 Hz, 2C), 133.7 (d, *J* = 20.2 Hz, 2C) , 131.4 (2C), 127.8 (d, *J* = 27.3 Hz, 2C), 108.6 (dd, *J* = 19.9, 6.3 Hz, 2C), 104.6 (t, *J* = 25.4 Hz), 52.0, 49.0; HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{11}F_2O_2$, 297.0722; found, 297.0725.

1-(3-chlorophenyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (32). The title compound was prepared according to the general procedure described above using 1,4-naphthoquinone (100 mg, 0.6 mmol), 1-chloro-3-ethynylbenzene (163 µL, 1.2 mmol), $K_2S_2O_8$ (486 mg, 1.8 mmol) and TFA (46 µL, 0.6 mmol) and purified by column chromatography (hexane:EA = 95:05) as dark red semi-solid (148 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 1H), 8.07 – 8.02 (m, 1H), 7.78 – 7.71 (m, 2H), 7.52 (s, 1H), 7.47 – 7.42 (m, 1H), 7.31 – 7.25 (m, 2H), 6.60 (d, *J* = 1.1 Hz, 1H), 4.50 (d, *J* = 3.7 Hz, 1H), 4.14 (dd, *J* = 3.7, 1.6 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.2, 195.1, 147.7, 134.7(2C), 134.6, 133.9, 133.7, 133.6, 130.2, 129.9, 129.2, 127.8, 127.6, 125.5, 123.8, 52.1, 49.1. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{12}ClO_2$, 295.0520; found, 295.0498.

1-(2-(trifluoromethyl)phenyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (33). The title compound was prepared according to the general procedure described above using 1,4-naphthoquinone (100 mg, 0.6 mmol), 2-trifluoromethylphenylacetylene (204 µL, 1.2 mmol), $K_2S_2O_8$ (486 mg, 1.8 mmol) and TFA (46 µL, 0.6 mmol) and purified by column chromatography (hexane:EA = 91:09) as whitish yellow semi-solid (159 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.6, 1.0 Hz, 1H), 8.02 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.78 (m, 3H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 6.71 (s, 1H), 4.63 (d, *J* = 3.7 Hz, 1H), 4.18 (dd, *J* = 3.7, 1.5 Hz, 1H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.2, 195.1, 145.2, 136.0 (q, *J* = 5.0 Hz), 134.7(2C), 134.6(2C), 133.8 (d. *J* = 27.5 Hz), 132.0, 130.0(2C), 128.8, 127.7, 127.6, 126.4 (q, *J* = 6.25 Hz), 126.2 (q, *J* = 256.25 Hz), 53.3, 49.1. HRMS (ESI) m/z: [M+H] calculated for $C_{19}H_{12}F_3O_2$, 329.0784; found, 329.0771.

8a-methoxy-1-phenyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (34). The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol), phenylacetylene (102 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column chromatography (hexane:EA = 93:07) as pale yellow semi-solid (126 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.00 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.58 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.37 – 7.30 (m, 3H), 6.75 (d, *J* = 1.6 Hz, 1H), 4.15 (d, *J* = 1.5 Hz, 1H), 3.48 (s, 3H).; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.7, 194.7, 150.4, 134.7, 134.4, 133.4, 131.5, 130.6, 129.6, 128.7, 128.3, 127.1, 126.1, 85.9, 55.4, 53.3, 29.7. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{15}O_3$, 291.1016; found, 291.1005.

1-(4-fluorophenyl)-8a-methoxy-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (35). The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol), 1-ethynyl-4-fluorobenzene (120 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column chromatography (hexane:EA = 92:08) (198 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.10 (m, 1H), 8.06 – 8.01 (m, 1H), 7.82 – 7.74 (m, 2H), 7.64 – 7.57 (m, 2H), 7.09 – 7.02 (m, 2H), 6.71 (d, *J* = 1.5 Hz, 1H), 4.16 (s, 1H), 3.50 (s, 3H).; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.6, 194.7, 163.3 (d, *J* = 250 Hz), 149.2, 134.7 (d, *J* = 46.6 Hz), 133.2 (d, *J* = 17.6 Hz), 130.8 (d, *J* = 1.3 Hz), 128.2 (d, *J* = 16.4 Hz), 128.2, 127.2, 126.8 (d, *J* = 2.52 Hz), 115.8 (d, *J* = 22.7), 85.7, 55.3, 53.4. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{19}H_{14}FO_3$, 309.0921; found, 309.0900.

1-(2-chlorophenyl)-8a-methoxy-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (36). The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol), 1-chloro-2-ethynylbenzene (136 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column chromatography (hexane:EA = 94:06) as yellow semi-solid (139 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 7.83 (m, 3H), 7.77 (m, 2H), 7.40 – 7.31 (m, 2H), 7.25 (m, 1H), 7.18 (d, *J* = 1.7 Hz, 1H), 4.22 (d, *J* = 3.3 Hz, 1H), 3.50 (s, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.2, 194.6, 146.9, 138.6, 134.9, 134.5, 133.4, 133.3, 133.3, 130.4, 130.4, 129.9, 128.3, 128.3, 127.1, 127.1, 86.5, 56.4, 53.2. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{14}ClO_3$, 325.0626; found, 325.0619.

8a-methoxy-1-(2-(trifluoromethyl)phenyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (37). The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol), 2-trifluoromethylphenylacetylene (170 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column chromatography (hexane:EA = 91:09) as yellow semi-solid (150 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 7.98 (m, 3H), 7.78 (m, 2H), 7.65 (dd, *J* = 14.1, 7.7 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 1.9 Hz, 1H), 4.17 (d, *J* = 1.6 Hz, 1H), 3.51 (s, 3H).; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.0, 194.7, 145.7, 139.0 (q, *J* = 5.0 Hz), 134.9(2C), 134.6(2C), 133.3, 133.3, 132.2, 130.6, 129.0, 128.2, 127.1, 126.3 (q, *J* = 6.25 Hz), 125.5 (q, *J* = 228.75 Hz), 86.7, 55.7, 53.4. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{14}F_3O_3$, 359.0890; found, 359.0903.

1-(4-ethylphenyl)-8a-methoxy-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (38). The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol), 1-ethyl-4-ethynylbenzene (130 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column chromatography (hexane:EA = 92:08) as brown semi-solid (135 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.02 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.80 – 7.71 (m, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 1.6 Hz, 1H), 4.17 (d, *J* = 1.3 Hz, 1H), 3.51 (s, 3H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.9, 194.8, 150.3, 146.1, 134.7, 134.4, 133.3, 133.3, 130.3, 128.3, 128.2(2C), 128.1, 127.0, 126.1, 85.9, 55.3, 53.2, 30.9, 28.8, 15.3. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{19}O_3$, 319.1329; found, 319.1322.

1-(4-(tert-butyl)phenyl)-8a-methoxy-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (39). The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol), 4-*tert*-butylphenylacetylene (158 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column chromatography (hexane:EA = 92:08) as brown semi-solid (138 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.02 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.38 (m, 2H), 6.72 (d, *J* = 1.7 Hz, 1H), 4.17 (d, *J* = 1.6 Hz, 1H), 3.51 (s, 3H), 1.32 (s, 9H).; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.9, 194.8, 152.9, 150.3, 134.7, 134.4, 133.3, 133.3, 130.5, 128.3, 128.1,

127.9, 127.7, 127.0, 125.8, 125.6, 85.9, 55.3, 53.3, 34.8, 31.1(3C). HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{23}O_3$, 347.1642; found, 347.1628.

8a-methoxy-1-(4-pentylphenyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione ***(40).*** The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol), 1-ethyl-4-pentylbenzene (172 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column chromatography (hexane:EA = 93:07) as brown semi-solid (120 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.03 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.76 (m, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.71 (d, *J* = 1.6 Hz, 1H), 4.16 (d, *J* = 1.4 Hz, 1H), 3.51 (s, 3H), 2.65 – 2.55 (m, 2H), 1.61 (s, 2H), 1.37 – 1.29 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.9, 194.8, 150.4, 144.9, 134.7, 134.4, 133.3, 130.3(2C), 128.7(2C), 128.3, 128.1, 127.0, 125.9(2C), 85.9, 55.3, 53.3, 35.9, 31.4, 30.9, 22.5, 14.0. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{25}O_3$, 361.1798; found, 361.1782.

8a-methoxy-1-(3-methoxyphenyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione ***(41).*** The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol), 3-methoxyphenylacetylene (132 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column chromatography (hexane:EA = 90:10) as yellowish semi-solid (105 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.03 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.83 – 7.72 (m, 2H), 7.27 (s, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 2.2 Hz, 1H), 6.89 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.77 (d, *J* = 1.7 Hz, 1H), 4.17 (d, *J* = 1.5 Hz, 1H), 3.85 (s, 3H), 3.51 (s, 3H).; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.7, 194.6, 159.7, 150.3, 134.8, 134.5, 133.3, 131.9, 131.7, 129.8, 128.3, 127.1, 118.5, 115.8, 110.9, 85.8, 55.3, 53.3. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{17}O_4$, 321.1121; found, 321.1117.

8a-methyl-1-(2-(trifluoromethyl)phenyl)-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione ***(42).*** The title compound was prepared according to the general procedure described above using menadione (100 mg, 0.6 mmol), 2-trifluoromethylphenylacetylene (204 µL, 1.2 mmol), $K_2S_2O_8$ (486 mg, 1.8 mmol) and TFA (46 µL, 0.6 mmol) and purified by column chromatography (hexane:EA = 92:08) (156 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (m, 2H), 7.78 (m, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.42 (m, 1H), 6.66 (d, *J* = 1.8 Hz, 1H), 3.84 (d, *J* = 1.7 Hz, 1H), 1.82 (s, 3H).; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.5, 196.1, 149.3, 135.5 (q, *J* = 5.0 Hz), 134.6, 134.5, 133.8, 133.8, 131.8, 130.9 (q, *J*=76.9 Hz), 129.0, 128.6, 127.9, 127.1, 126.6 (q, *J* = 6.25 Hz), 125.7 (q, *J* = 272.5 Hz), 58.9, 57.6, 19.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{20}H_{14}F_3O_2$, 343.0940; found, 343.0919.

1-(3-methoxyphenyl)-8a-methyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione ***(43).*** The title compound was prepared according to the general procedure described above using menadione (100 mg, 0.6 mmol), 3-methoxyphenylacetylene (158 µL, 1.2 mmol), $K_2S_2O_8$ (486 mg, 1.8 mmol) and TFA (46 µL, 0.6 mmol) and purified by column chromatography (hexane:EA = 92:08) (136 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.03 (m, 2H), 7.77 – 7.73 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 6.87 (m, 1H), 6.58 (d, *J* = 1.7 Hz, 1H), 3.84 (s, 3H), 3.81 (d, *J* = 1.6 Hz, 1H), 1.86 (s, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.4, 196.7, 159.7, 153.3, 134.5, 134.4, 133.7, 133.6, 132.8, 129.7, 128.0, 127.9, 127.0, 118.0, 115.1, 110.6, 57.4, 57.1, 55.3, 19.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{20}H_{17}O_3$, 305.1172; found, 305.1143.

1-(cyclohex-1-en-1-yl)-2a-methoxy-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione ***(44).*** The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol),1-ethynylcyclohexene (106 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column chromatography (hexane:EA = 93:07) (103 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.13 (m, 1H), 8.04 – 7.97 (m, 1H), 7.81 – 7.75 (m, 2H), 6.37 (s, 1H), 6.22 (s, 1H), 4.01 (s, 1H), 3.45 (s, 3H), 2.18 (s, 2H), 1.66 – 1.54 (m, 6H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 196.2, 194.9, 151.9, 134.6, 134.3, 133.5, 133.3, 132.3, 129.5, 128.6, 128.2, 127.1, 85.9, 55.2, 53.3, 25.5, 23.6, 21.8(2C). HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{19}O_3$, 295.1329; found, 295.1308.

1-cyclopropyl-2a-methoxy-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione ***(45).*** The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol), cyclopropylacetylene (66 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column chromatography (hexane:EA = 93:07) (115 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.12 (m, 1H), 8.04 – 7.97 (m, 1H), 7.82 – 7.76 (m, 2H), 6.14 (s, 1H), 3.90 (s, 1H), 3.46 (s, 3H), 1.46 – 1.38 (m, 1H), 0.81 – 0.74 (m, 2H), 0.68 – 0.61 (m, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 196.5, 195.4, 156.8, 134.7, 134.4, 133.5, 133.2, 131.0, 127.9, 127.2, 85.9, 54.7, 53.6, 9.0, 6.9, 6.8. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{15}O_3$, 255.1016; found, 255.1014.

8a-methoxy-1-propyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione ***(46).*** The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol),1-pentyne (68 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column chromatography (hexane:EA = 94:06) (121 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.10 (m, 1H), 8.07 – 7.98 (m, 1H), 7.83 – 7.76 (m, 2H), 6.32 (d, *J* = 1.5 Hz, 1H), 3.94 (d, *J* = 1.2 Hz, 1H), 3.42 (s, 3H), 2.17 – 2.09 (m, 1H), 2.05 – 1.97 (m, 1H), 1.51 – 1.42 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 196.5, 195.3, 155.5, 134.8, 134.4, 134.3, 133.3, 133.2, 127.8, 127.3, 85.9, 55.2, 53.8, 29.1, 18.9, 13.8. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{17}O_3$, 257.1172; found, 257.1160.

1-hexyl-8a-methoxy-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione ***(47).*** The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol), 1-octyne (110 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column chromatography (hexane:EA = 94:06) (128 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 1H), 8.05 – 8.01 (m, 1H), 7.82 – 7.76 (m, 2H), 6.31 (d, *J* = 1.4 Hz, 1H), 3.94 (d, *J* = 1.2 Hz, 1H), 3.42 (s, 3H), 2.19 – 2.09 (m, 1H), 2.07 – 1.97 (m, 1H), 1.47 – 1.38 (m, 2H), 1.27 – 1.18 (m, 6H), 0.84 (t, *J* = 6.8 Hz, 3H).; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 196.5, 195.3, 155.7, 134.8, 134.4, 134.2, 133.4, 133.2, 127.8, 127.3, 85.9, 55.2, 53.8, 31.4, 28.9, 27.0, 25.3, 22.5, 13.9. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{23}O_3$, 299.1642; found, 299.1619.

1-heptyl-8a-methoxy-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione ***(48).*** The title compound was prepared according to the general procedure described above using 2-methoxy-1,4-naphthoquinone (100 mg, 0.5 mmol), 1-nonyne (124 µL, 1 mmol), $K_2S_2O_8$ (405 mg, 1.5 mmol) and TFA (38 µL, 0.5 mmol) and purified by column

chromatography (hexane:EA = 94:06) (141 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.12 (m, 1H), 8.06 – 7.98 (m, 1H), 7.82 – 7.75 (m, 2H), 6.30 (d, *J* = 1.4 Hz, 1H), 3.93 (d, *J* = 1.2 Hz, 1H), 3.42 (s, 3H), 2.18 – 2.10 (m, 1H), 2.06 – 1.97 (m, 1H), 1.48 – 1.34 (m, 2H), 1.30 – 1.15 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 196.5, 195.3, 155.7, 134.8, 134.4, 134.2, 133.4, 133.2, 127.8, 127.3, 85.9, 55.2, 53.8, 31.7, 29.2, 28.9, 27.0, 25.4, 22.6, 14.1. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{20}H_{25}O_3$, 313.1798; found, 313.1778.

*1-hexyl-8a-methyl-2a,8a-dihydrocyclobuta[b]naphthalene-3,8-dione (**49**).* The title compound was prepared according to the general procedure described above using menadione (100 mg, 0.6 mmol), 1-octyne (132 µL, 1.2 mmol), $K_2S_2O_8$ (486 mg, 1.8 mmol) and TFA (46 µL, 0.6 mmol) and purified by column chromatography (hexane:EA = 94:06) (129 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.09 (m, 1H), 8.10 – 8.02 (m, 1H), 7.81 – 7.73 (m, 2H), 6.04 (d, *J* = 1.5 Hz, 1H), 3.64 (d, *J* = 1.3 Hz, 1H), 2.11 – 2.03 (m, 1H), 2.01 – 1.92 (m, 1H), 1.61 (s, 3H), 1.45 – 1.35 (m, 2H), 1.29 – 1.19 (m, 6H), 0.85 (t, *J* = 5.2 Hz, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.1, 197.7, 159.2, 134.4, 134.3, 133.7, 133.4, 128.8, 127.6, 127.1, 57.9, 57.0, 31.5, 28.9, 27.3, 25.3, 22.5, 18.9, 14.0. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{19}H_{23}O_2$, 283.1693; found, 283.1676.

ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of all compounds, dye-degradation experiment and cyclic voltammetry. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

E-mail: bashah@iiim.ac.in, masoodku2@gmail.com
Orcid ID: 0000-0003-0041-5049 (SS); 0000-0003-0470-6329 (MAR); 0000-0001-6629-0002 (BAS)

ACKNOWLEDGMENT

BAS thank CSIR for Young Scientist Award Grant (P-81-113) and DBT (1151/2016), New Delhi for financial assistance. SS thanks CSIR for Senior Research Fellowship. IIIM communication No. 2299/2019

REFERENCES

( ) Application of ketones: (a) Kamat, P. V. Photochemistry on nonreactive and reactive (semiconductor) surfaces. *Chem. Rev.* **1993**, *93*, 267. (b) McDaniel, R.; Thamchaipenet, A.; Gustafsson, C.; Fu, H.; Betlach, M.; Betlach, M.; Ashley, G. Multiple genetic modifications of the erythromycin polyketide synthase to produce a library of novel "unnatural" natural products. *Proc. Natl. Acad. Sci. U. S. A.***1999**, 96, 1846. (c) Walter, M. W. Structure-based design of agrochemicals. *Nat. Prod. Rep.* **2002**, *19*, 278. (d) Romines, K. R.; Freeman, G. A.; Schaller, L. T.; Cowan, J. R.; Gonzales, S. S.; Tidwell, J. H.; Andrews, C. W.; Stammers, D. K.; Hazen, R. J.; Ferris, R. G. S.; Short, A.; Chan, J. H.; Boone, L. R. Structure−Activity Relationship Studies of Novel Benzophenones Leading to the Discovery of a Potent, Next Generation HIV Nonnucleoside Reverse Transcriptase Inhibitor. *J. Med. Chem.* **2006**, *49*, 727. (e) Maeyama, K.; Yamashita, K.; Saito, H.; Aikawa, S.; Yoshida, Y. Synthesis of aromatic poly(ether ketone)s bearing optically active macrocycles through Suzuki coupling polymerization. *Polym. J.* **2012**, *44*, 315. (f) Cuquerella, M. C.; Lhiaubet-Vallet, V.; Cadet, J.; Miranda, M. A. Benzophenone Photosensitized DNA Damage. *Acc. Chem. Res.* **2012**, *45*, 1558. (g) Toh, Q. Y.; McNally, A.; Vera, S.; Erdmann, N.; Gaunt, M. J. Organocatalytic C–H Bond Arylation of Aldehydes to Bis-heteroaryl Ketones. *J. Am. Chem. Soc.* **2013**, *135*, 3772. and references cited therein.

(2) (a) Dugas, H.; *Bioorganic Chemistry*, 3rd ed.; Ed.; Springer Verlag: New York, **1996**. (b) Smith, M. B.; March, J. *Advanced Organic Chemistry*. Wiley: New York, **2007**.

(3) Friedel-Craft's acylation for synthesis of ketones: (a) Nahm, S.; Weinreb, S. M. N-methoxy-n-methylamides as effective acylating agents. *Tetrahedron Lett.* **1981**, *22*, 3815. (b) Sartori, G.; Maggi, R. Use of Solid Catalysts in Friedel−Crafts Acylation Reactions. Use of Solid Catalysts in Friedel−Crafts Acylation Reactions. *Chem. Rev.* **2006**, *106*, 1077. and references cited therein.

(4) Organomettalic addition reactions: (a) Brunet, J. J.; Chauvin, R. Synthesis of diarylketones through carbonylative coupling. *Chem. Soc. Rev.* **1995**, *24*, 89. (b) Dieter, R. K. Reaction of Acyl Chlorides with Organometallic Reagents: A Banquet Table of Metals for Ketone Synthesis. *Tetrahedron* **1999**, *55*, 4177. (c) Bechara, W. S.; Pelletier, G.; Charette, A. B. Chemoselective synthesis of ketones and ketimines by addition of organometallic reagents to secondary amides. *Nat. Chem.* **2012**, *4*, 228. (d) Senatore, R.; Castoldi, L.; Ielo, L.; Holzer, W.; Pace, V. Expeditious and Chemoselective Synthesis of α-Aryl and α-Alkyl Selenomethylketones *via* Homologation Chemistry.
Org. Lett. **2018**, *20*, 2685. and references cited therein.

(5) Selected reviews on transition metal catalyzed acylation reactions, see (a) Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds**.** *Chem. Rev.* **1995**, *95*, 2457. (b) Willis, M. C. Transition Metal Catalyzed Alkene and Alkyne Hydroacylation. *Chem. Rev.* **2010**, *110*, 725. (c) Wu, X. F.; Neumann, H.; Beller, M. Palladium-catalyzed carbonylative coupling reactions between Ar-X and carbon nucleophiles. *Chem. Soc. Rev.* **2011**, *40*, 4986. (d) Moragas, T.; Correa, A.; Martin, R. Metal-Catalyzed Reductive Coupling Reactions of Organic Halides with Carbonyl-Type Compounds. *Chem. Eur. J.* **2014**, *20*, 8242.

(6) For selected examples on transition metal catalyzed acylation reactions, see: (a) Takemiya, A.; Hartwig, J. F. Palladium-Catalyzed Synthesis of Aryl Ketones by Coupling of Aryl Bromides with an Acyl Anion Equivalent. *J. Am. Chem. Soc.* **2006**, *128*, 14800. (b) Goossen, L. J.; Rudolphi, F.; Oppel, C.; Rodríguez, N. Synthesis of ketones from alpha-oxocarboxylates and aryl bromides by Cu/Pd-catalyzed decarboxylative cross-coupling. *Angew. Chem. Int. Ed.* **2008**, *47*, 3043. (c) Weires, N. A.; Baker, E. L.; Garg, N. K. Nickel-catalysed Suzuki-Miyaura coupling of amides. *Nat. Chem.* **2016**, 8, 75. (d) Amani, J.; Molander, G. A. Synergistic Photoredox/Nickel Coupling of Acyl Chlorides with Secondary Alkyltrifluoroborates: Dialkyl Ketone Synthesis. *J. Org. Chem.* **2017**, *82*, 1856. (e) Wakaki, T.; Togo, T.; Yoshidome, D.; Kuninobu, Y.; Kanai, M. Palladium-Catalyzed Synthesis of Diaryl Ketones from Aldehydes and (Hetero)Aryl Halides via C–H Bond Activation. *ACS Catal.* **2018**, *8*, 3123. and references cited therein.

(7) For selected examples on decarboxylative additions reactions, see: (a) Goossen, L. J.; Rudolphi, F.; Oppel, C.; Rodríguez, N. Synthesis of ketones from alpha-oxocarboxylates and aryl bromides by Cu/Pd-catalyzed decarboxylative cross-coupling. *Angew. Chem. Int. Ed.* **2008**, *47*, 3043. (b) Lindh, J.; Sjoberg, P. J. R.; Larhed, M. Synthesis of aryl ketones by palladium(II)-catalyzed decarboxylative addition of benzoic acids to nitriles. *Angew. Chem. Int. Ed.* **2010**, *49*, 7733.

(8) For selected examples on carbonylation of arene C-H for synthesis of ketones, see: (a) Brunet, J. J.; Chauvin, R.. Synthesis of diarylketones through carbonylative coupling. *Chem. Soc. Rev.* **1995**, *24*, 89. (b) Brennfuhrer, A.; Neumann, H.; Beller, M. Palladium-Catalyzed Carbonylation Reactions of Aryl Halides and Related Compounds. *Angew. Chem. Int. Ed.* **2009**, *48*, 4114. (c) Wu, X. F.; Neumann, H.; Beller, M. Palladium-catalyzed carbonylative coupling reactions between Ar–X and carbon nucleophiles. *Chem. Soc. Rev.* **2011**, *40*, 4986. (d) Magano, J.; Dunetz, J. R. Large-Scale Applications of Transition Metal-Catalyzed Couplings for the Synthesis of Pharmaceuticals. *Chem. Rev.* **2011**, *111*, 2177. (e) Wu, X. F.; Neumann, H.; Beller, M. Synthesis of Heterocycles via Palladium-Catalyzed Carbonylations. *Chem. Rev.* **2013**, *113*, 1. (f) Kinney, R. G.; Tjutrins, J.; Torres, G. M.; Liu, N. J.; Kulkarni, O.; Arndtsen, B. A. A general approach to intermolecular carbonylation

of arene C–H bonds to ketones through catalytic aroyl triflate formation. *Nat. Chem.* **2018**, *10*, 193 and the references cited therein.

(9) For selected examples on visible light mediated synthesis of ketones, see: (a) Pham, P. V.; Nagib, D. A.; MacMillan, D. W. C. Photoredox catalysis: a mild, operationally simple approach to the synthesis of α-trifluoromethyl carbonyl compounds. *Angew. Chem. Int. Ed.* **2011**, *50*, 6119. (b) Serratore, N. A.; Anderson, C. B.; Frost, G. B.; Hoang, T. G.; Underwood, S. J.; Gemmel, P. M.; Hardy, M. A.; Douglas C. J. Integrating Metal-Catalyzed C–H and C–O Functionalization To Achieve Sterically Controlled Regioselectivity in Arene Acylation. *J. Am. Chem. Soc.* **2018**, *140*, 10025. (c) Zhang, M.; Xie, J.; Zhu, C. A general deoxygenation approach for synthesis of ketones from aromatic carboxylic acids and alkenes. *Nat. Commun.* **2018**, *9*, 3517. (d) Capaldo, L.; Riccardi, R.; Ravelli, D.; Fagnoni, M. Acyl Radicals from Acylsilanes: Photoredox-Catalyzed Synthesis of Unsymmetrical Ketones. *ACS Catal.* **2018**, *8*, 304 and references cited therein.

(10) For selected examples on applications of 4-hydroxy ketones, see: (a) Vasudevan, A.; Conner, S. E.; Gentles, R. G.; Faghih, R.; Liu, H.; Dwight, W.; Ireland, L.; Kang, C. H.; Esbenshade, T. A.; Bennani,Y. L.; Hancock, A. A. Synthesis and evaluation of potent pyrrolidine H_3 antagonists. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 3055. (b) Perrone, R.; Berardi, F.; Colabufo, N. A.; Lacivita, E.; Leopoldo, M.; Tortorella, V. Synthesis and Structure−Affinity Relationships of 1-[ω-(4-Aryl-1-piperazinyl)alkyl]-1-aryl Ketones as 5-HT_7 Receptor Ligands. *J. Med. Chem.* **2003**, *46*, 646. (c) Wyss, D. F.; Arasappan, A.; Senior, M. M.; Wang, Y. S.; Beyer, B. M.; Njoroge, F. G.; McCoy, M. A. Non-Peptidic Small-Molecule Inhibitors of the Single-Chain Hepatitis C Virus NS3 Protease/NS4A Cofactor Complex Discovered by Structure-Based NMR Screening. *J. Med. Chem.* **2004**, *47*, 2486. (d) Guazzi, G. Process for the preparation of fibrates. *U.S. pat., US2004073058(A1)*, **2004**. (e) Shao, L. X.; Shi, M. Facile synthesis of multisubstituted buta-1,3-dienes via Suzuki– Miyaura and Kumada cross-coupling strategy of 2,4-diiodobuta-1-enes with arylboronic acids and Grignard reagents. *Org. Biomol. Chem.* **2005**, *3*, 1828. (f) Sandanayaka, V.; Singh, J.; Gurney, M.; Mamat, B.; Yu, P.; Bedel, L.; ZhaO, L. Biaryl substituted heterocycle inhibitors of lta4h for treating inflammation. *US20070066820(A1),* **2007**. (g) Reux, B.; Nevalainen, T.; Raitio, K. H.; Koskinen, A. M. P. Synthesis and agonist properties of novel quinoline and isoquinoline derivatives toward the cannabinoid receptor CB2. *Bioorg. Med. Chem.* **2009**, *17*, 4441. (h) Davies, D. R.; Mamat, B.; Magnusson, O.T.; Christensen, J.; Haraldsson, M. H.; Mishra, R.; Pease, B.; Hansen, E.; Singh, J.; Zembower, D.; Kim, H.; Kiselyov, A. S.; Burgin, A. B.; Gurney, M. E.; Stewart, L. J. Discovery of Leukotriene A4 Hydrolase Inhibitors Using Metabolomics Biased Fragment Crystallography. *J. Med. Chem.* **2009**, *52*, 4694. (i) Liang, J.; Ortwine, D. F; Wang, X. Govek, S. P.; Kahraman, M.; Nagasawa, J. Y.; Smith, N. D.; Goodacre, S. C.; Ray, N. C. *U.S. pat. US2016304450 (A1),* **2016**.

(11) (a) Schulz, T.; Torborg, C.; Schaffner, B.; Huang, J.; Zapf, A.; Kadyrov, R.; Borner, A.; Beller. M. Practical imidazole-based phosphine ligands for selective palladium-catalyzed hydroxylation of aryl halides. *Angew. Chem. Int. Ed.* **2009**, *48*, 918. (b) Cheung, C. W.; Buchwald, S. L. Palladium-Catalyzed Hydroxylation of Aryl and Heteroaryl Halides Enabled by the Use of a Palladacycle Precatalyst. *J. Org. Chem.* **2014**, *79*, 5351. (c) Yu, Z.; Veldhoven, J.P.D.V.; Hart, I.M.E.; Kopf, A.H.; Heitman, L. H.; IJzerman, A. P. Synthesis and biological evaluation of negative allosteric modulators of the Kv11.1(hERG) channel. *Eur. J. Med. Chem.* **2015***,106,* 50. (d) Kinney, R. G.; Tjutrins, J.; Torres, G. M.; Liu, N. J.; Kulkarni, O.; Arndtsen, B. A. A general approach to intermolecular carbonylation of arene C–H bonds to ketones through catalytic aroyl triflate formation. *Nat. Chem.* **2018***, 10*, 193.

(12) Sagadevan, A.; Charpe, V. P.; Ragupathi, A.; Hwang, K. C. Visible Light Copper Photoredox-Catalyzed Aerobic Oxidative Coupling of Phenols and Terminal Alkynes: Regioselective Synthesis of Functionalized Ketones via C≡C Triple Bond Cleavage. *J. Am. Chem. Soc.* **2017**, *139*, 2896.

(13) (a) Kumar, A.; Shah, B. A. Synthesis of Biaryls via Benzylic C–C Bond Cleavage of Styrenes and Benzyl Alcohols**.** *Org. Lett*. **2015**, *17*, 5232. (b) Devari, S.; Shah, B. A. Visible light-promoted C–H functionalization of ethers and electron-deficient arenes**.** *Chem. Commun.* **2016**, *52***,** 1490. (c) Sultan, S.; Gupta, V.; Shah, B. A. Photoredox-catalyzed isatin reactions: access to dibenzo-1,7-naphthyridine carboxylate and tryptanthrin.*ChemPhotoChem*, **2017**, *1*, 120. (d) Sultan, S.; Rizvi, M. A.; Kumar, J.; Shah, B. A. acyl radicals from terminal alkynes: photoredox-catalyzed acylation of heteroarenes. *Chem. Eur. J.* **2018**, *24*,10617. (e) Chalotra, N.; Ahmed, A.; Rizvi, M. A.; Hussain, Z.; Ahmed, Q. N.; Shah, B. A. Photoredox Generated Vinyl Radicals: synthesis of bisindoles and β-carbolines. *J. Org. Chem.* **2018**, *83* (23), 14443. (f) Sultan, S.; Shah, B. A. Carbon-carbon and carbon-heteroatom bond formation reactions using unsaturated carbon compounds. *Chem. Rec.* **2019**, *19*, 644. (g) Chalotra, N.; Rizvi, M. A.; Shah, B. A. Photoredox-mediated generation of gem-difunctionalized ketones: synthesis of α, α-aminothioketones. *Org. Lett*. DOI: 10.1021/acs.orglett.9b01677.

(14) For selected reviews on synthetic radical chemistry, see: (a) Yi, H.; Zhang, G.; Wang, H.; Huang, Z.; Wang, J.; Singh, A. K.; Lei, A. Recent Advances in Radical C–H Activation/Radical Cross-Coupling. *Chem. Rev.* **2017**, *117*, 9016. (b) Xuan, J.; Studer, A. Radical cascade cyclization of 1,*n*-enynes and diynes for the synthesis of carbocycles and heterocycles**.** *Chem. Soc. Rev.* **2017**, *46*, 4329. (c) Chatgilialoglu, C.; Ferreri, C.; Landais, Y.; Timokhin, V. I. Thirty Years of $(TMS)_3SiH$: A Milestone in Radical-Based Synthetic Chemistry. *Chem. Rev.* **2018**, *118*, 6516. and references cited therein.

(15) For selected reviews on photoredox catalysis, see: (a) Xie, J.; Jinb, H.; Hashmi, A. S. K. The recent achievements of redox-neutral radical C–C cross-coupling enabled by visible-light**.** *Chem. Soc. Rev.* **2017**, *46*, 5193. (b) Wang, C. S.; Dixneuf, P. H.; Soule, J. F. Photoredox Catalysis for Building C-C Bonds from $C(sp^2)$-H Bonds. *Chem. Rev.* **2018**, *118*, 7532 and references cited therein.

(16) Kumarasamy, E.; Raghunathan, R.; Kandappa, S. K.; Sreenithya, A.; Jockusch, S.; Sunoj, R. B.; Sivaguru, J. Transposed Paternò–Büchi Reaction. *J. Am. Chem. Soc.* **2017**, *139*, 655.

(17) (a) Bach, T.; Spiegel, A. Stereoselective Photochemical Synthesis and Structure Elucidation of 1-Methyl-Substituted Tricyclo[$6.2.0.0^{2,6}$]decanes and Tricyclo[$7.2.0.0^{2,7}$]undecanes. *Eur. J. Org. Chem.* **2002**, *2002*, 645. (b) Schultz, D. M.; Yoon, T. P. Solar Synthesis: Prospects in Visible Light Photocatalysis. *Science*, **2014**, *343*, 1239176. (c) Hu, L.; Chen, H. Substrate-Dependent Two-State Reactivity in Iron-Catalyzed Alkene [2+2] Cycloaddition Reactions. *J. Am. Chem. Soc.* **2017**, *139*, 15564.

(18) (a) Namyslo, J. C.; Kaufmann, D. E. The Application of Cyclobutane Derivatives in Organic Synthesis. *Chem. Rev.* **2003**, *103*, 1485. (b) Lee-Ruff, E.; Mladenova, G. Enantiomerically Pure Cyclobutane Derivatives and Their Use in Organic Synthesis. *Chem. Rev.* **2003***, 103*, 1449. (c) Xu, Y.; Conner, M. L.; Brown, M. K. Cyclobutane and Cyclobutene Synthesis: Catalytic Enantioselective [2+2] Cycloadditions. *Angew. Chem. Int. Ed.* **2015**, *54*, 11918 and references cited therein.

(19) For selected examples and reviews on [2+2] cycloaddition reactions see: (a) Ischay, M. A.; Lu, Z.; Yoon, T. P. [2+2] Cycloadditions by Oxidative Visible Light Photocatalysis. *J. Am. Chem. Soc.* **2010**, *132*, 8572. (b) Lu, Z.; Yoon, T. P. Visible Light Photocatalysis of [2+2] Styrene Cycloadditions via Energy Transfer. *Angew. Chem. Int. Ed.* **2012**, *51*, 10329. (c) Nishimura, A.; Ohashi, M.; Ogoshi, S. Nickel-Catalyzed Intermolecular [2 + 2] Cycloaddition of Conjugated Enynes with Alkenes. *J. Am. Chem. Soc.* **2012**, *134*, 15692. (d) Du, J.; Skubi, K. L.; Schultz, D. M.; Yoon, T. P. A dual-catalysis approach to enantioselective [2 + 2] photocycloadditions using visible light. *Science* **2014**, *344*, 392. (e) Bai, Y.; Luo, Z.; Wang, Y.; Gao, J.; Zhang, L. Au-Catalyzed Intermolecular [2+2] Cycloadditions between Chloroalkynes and Unactivated Alkenes. *J. Am. Chem. Soc.* **2018**, *140*, 5860. (f) Michinobu, T.; Diederich, F. The [2+2] Cycloaddition-Retroelectrocyclization (CA-RE) Click Reaction: Facile Access to Molecular and Polymeric Push-Pull Chromophores**.** *Angew. Chem. Int. Ed.* **2018**, *57*, 3552 and references cited therein.

(20) (a) Li, X. Z.; Liu, H. L.; Yue, P. T. Photoelectrocatalytic Oxidation of Rose Bengal in Aqueous Solution Using a Ti/TiO_2 Mesh Electrode. *Environ. Sci. Technol.* **2000**, *34*, 4401. (b) Chen, F.; Ma, W.; He, J.; Zhao, J. Fenton Degradation of Malachite Green Catalyzed by Aromatic Additives. *J. Phys. Chem. A* **2002**,*106*, 9485.

(21) Zhao, Y.; Huang, B.; Yang, C.; Xia, W.; Visible-Light-Promoted Direct Amination of Phenols via Oxidative Cross-Dehydrogenative Coupling Reaction. *Org. Lett.* **2016**, *18*, 3326.

(22) (a) Gau, B. C.; Chen, H.; Zhang, Y.; Gross, M. L. Sulfate Radical Anion as a New Reagent for Fast Photochemical Oxidation of Proteins. *Anal. Chem.* **2010**, *82*, 7821. (b) More, N. Y.; Jeganmohan, M. Oxidative Cross-Coupling of Two Different Phenols: An Efficient Route to Unsymmetrical Biphenols. *Org. Lett.* **2015**, *17*, 3042.

(23) Wille, U. Sulfate radical anions ($SO_4^{\bullet-}$) as donor of atomic oxygen in anionic transannular, self-terminating, oxidative radical cyclizations. *Org. Lett.* **2000**, *2*, 3485.

(24) Farid, S.; Kothe W.; Pfundt, G. *Tet. Letts.* **1968**, *39*, 4151-4154.