Note

Rh(II)-Catalyzed Denitrogenative Transannulation of N-Sulfonyl-1,2,3-triazolyl Cyclohexadienones for the Synthesis of Benzofurans and Cyclopropa[cd]indole-carbaldehydes

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Rh(II)-Catalyzed Denitrogenative Transannulation of *N*-Sulfonyl-1,2,3-triazolyl Cyclohexadienones for the Synthesis of Benzofurans and Cyclopropa[*cd*]indole-carbaldehydes

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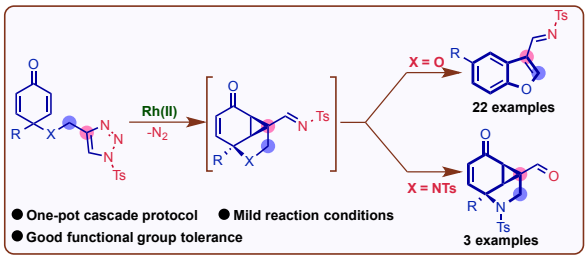


Abstract: A rhodium-catalyzed intramolecular denitrogenative transannulation of *N*-sulfonyl-1,2,3-triazole tethered cyclohexadienones has been achieved for the synthesis of benzofurans and cyclopropa[*cd*]indole-carbaldehydes in an operationally simple procedure. Remarkably, the reaction pathway is fully dependent on the linker heteroatom (O or N) present between the cyclohexadienone unit and triazole moiety. In the case of *O*-linked triazoles, a cascade sequence consisting of intramolecular cyclopropanation and rearrangement takes place leading to the formation of benzofurans, while in case of *N*-linked triazoles, cyclopropa[*cd*]indole-carbaldehydes were isolated exclusively.

Benzofurans are one of the most common oxygen-containing structural motifs found in many natural products, drugs and display potent biological activities such as antibacterial, antifungal, anti-inflammatory and antidiabetic.[1] A number of benzofuran derived drugs such as dronedarone, amiodarone and benzbromarone are clinically approved for treating various diseases (Figure 1).[2] Also, certain benzofuran derivatives are studied as imaging agents for detecting aggregates of beta-amyloid (Aβ) peptides, useful for treating Alzheimer's disease.[3] The extraordinary biological and pharmacological activities of benzofurans have drawn significant attention from the synthetic community to develop effective and concise approaches for accessing these skeletons.[4] Though, various transition-metal catalyzed as well as acid and base mediated strategies are available to synthesize benzofurans, they often suffer from various disadvantages like complex reaction conditions, low substrate scope and limited functional-group tolerance. Therefore, development of an operationally simple and step-economical method to access these heterocycles is highly desirable.

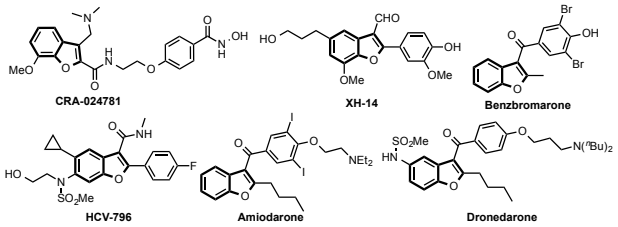
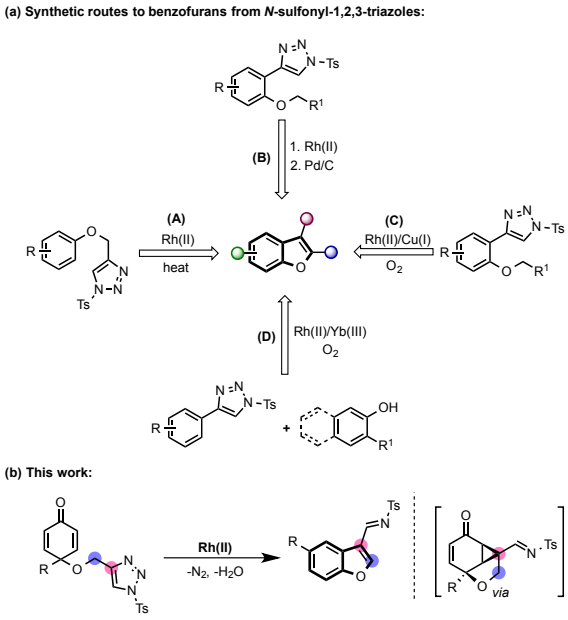


Figure 1. Some benzofuran based bioactive compounds.

Recently, Rh(II)-catalyzed ring-opening of *N*-sulfonyl-1,2,3-triazoles have gained a lot of attention and emerged as a powerful tool for accessing various oxygen- and nitrogen-containing heterocycles.[5] The highly reactive rhodium azavinyl carbenes derived *via* Rh(II)-catalyzed denitrogenative ring-opening of *N*-sulfonyl-1,2,3-triazoles readily undergo a variety of transformations including transannulations,[6] cycloadditions,[7] X–H bond insertion[8] (X = carbon or heteroatoms), and other reactions.[9] The versatility of Rh azavinyl carbenes and importance of benzofurans prompted various groups to study ring-opening of triazoles as an efficient strategy for the construction of these building blocks (Scheme 1).

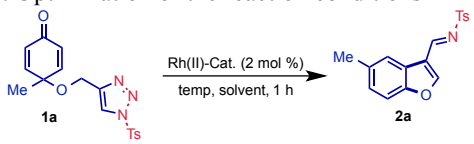
Scheme 1. Overview of the work.



In 2015, Shi and co-workers established a simple methodology for the synthesis of 2-aminobenzofurans from *N*-propargyl phenol-derived triazoles by a tandem sequence consisting of Friedel–Crafts type intramolecular nucleophilic addition to carbenoids followed by a temperature assisted ring rearrangement (Scheme 1a, Path A).[10] Chen and co-workers disclosed intramolecular sp^3 C–H insertion with α-imino rhodium carbenes for the construction of benzofuran derivatives (Path B).[11] A similar but step-economic approach to access benzofurans was reported by Kang and co-workers through Rh(II) and Cu(I) catalyzed sequential sp^3 C–H insertion and aerobic oxidation (Path C).[12] A Rh(II)-catalyzed O-H insertion followed by Yb(III)-catalyzed cyclization and oxidation sequence of triazoles and phenols was reported by Anbarasan and co-workers for the synthesis of benzo/naphthofurans.[13] Despite these efficient methods, development of novel synthetic methods for the construction of benzofurans are still desirable[14] and herein, we report a new protocol to prepare benzofurans *via* a Rh(II)-catalyzed denitrogenative cascade process.

In the past few years, transition-metal or organo-catalyzed cascade cyclizations of alkyne tethered-cyclohexadienones *via* C-H bond activations and/or carbocyclizations have appeared as a useful route for the synthesis of functionalized hydrobenzofurans.[15] In 2017, Chegondi's group developed a copper-catalyzed three component coupling reaction for the construction of *cis*-hydrobenzofurans by reacting alkynyl-cyclohexadienones with tosyl azide and alcohols.[16] At the same time, Sun and co-workers described a one-pot protocol to access fused tricyclic compounds by using diazoesters and cyclohexadienone-tethered terminal alkynes as starting materials.[17] These reactions proceeded through the *in situ* formation of tetrasubstituted allenoates followed by an anion prompted annulation, and oxidative aromatization. These reports on the cascade cyclizations with cyclohexadienones and our continuous efforts[18] on Rh(II)-catalyzed transannulation reactions, encouraged us to synthesize cyclohexadienone-linked *N*-sulfonyl-1,2,3-triazoles and explore their reactivity in the intramolecular Rh-catalyzed denitrogenative process.

Table 1. Optimization of the reaction conditions[a]

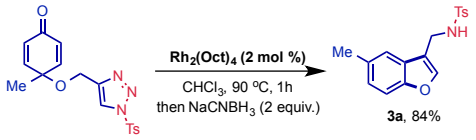


entry	Rh(II)-cat.	temp (°C)	solvent	yield (%)[b]
1	$Rh_2(Oct)_4$	100	DCE	74 (71)[c]
2	$Rh_2(OAc)_4$	100	DCE	72
3	$Rh_2(esp)_2$	100	DCE	63
4	$Rh_2(TFA)_4$	100	DCE	<5
5	-	100	DCE	0
6	$Rh_2(Oct)_4$	90	DCE	81
7	$Rh_2(Oct)_4$	90	Toluene	76
8	$Rh_2(Oct)_4$	80	DCM	79
9	**$Rh_2(Oct)_4$**	**90**	**$CHCl_3$**	**86 (80)[c]**
10	$Rh_2(Oct)_4$	70	$CHCl_3$	56

Reaction conditions: [a] 0.1 mmol of triazole **1a**, 2 mol % Rh-catalyst in 1 mL solvent. [b] NMR yield was taken by using 0.1 mmol of 1,3,5-trimethoxybenzene as an internal standard. [c] Yield of the product in parenthesis for 0.2 mmol triazole **1a**.

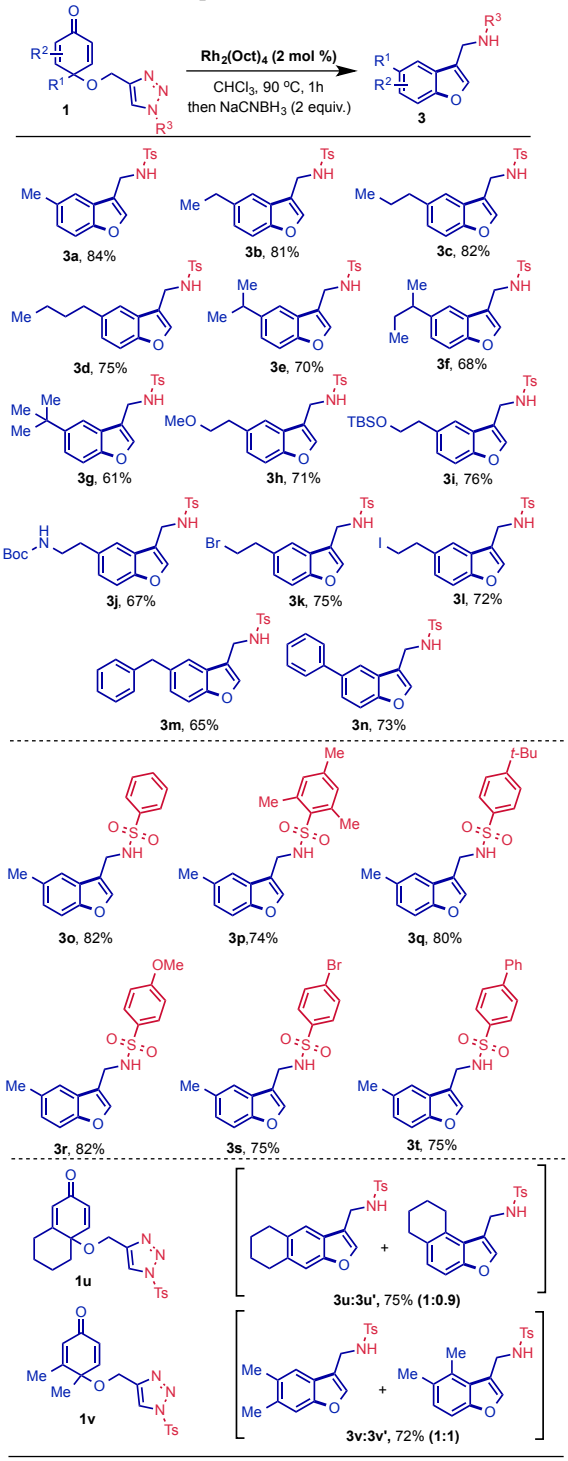
We initiated our studies using cyclohexa-2,5-dien-1-one **1a** as a model substrate and treated with 2 mol% of Rh(II)-catalyst in 1,2-DCE at 100 °C. We were pleased to observe the clean formation of 3-imino benzofuran **2a** in 74% NMR yield using catalytic amount of $Rh_2(Oct)_4$ after 1 h. Intrigued by this result, different rhodium catalysts were tested to improve the yield of the transannulated product **2a**. While $Rh_2(OAc)_4$ displayed similar reactivity (72 % NMR yield), $Rh_2(esp)_2$ was found to be less efficient for this transformation (entries 2-3). Only traces of **2a** was detected when $Rh_2(TFA)_4$ was used as a catalyst (Table 1, entry 4). As expected, the reaction was not proceeding in the absence of catalyst, indicating that rhodium salt was crucial for the sequence (Table 1, entry 5). Interestingly, by lowering the temperature to 90 °C (entry 6), the yield of **2a** was increased to 81% and other solvents like toluene, dichloromethane and chloroform were screened (Table 1, entries 7−9). Satisfyingly, the yield was further improved to 86% when chloroform was used as a solvent and the benzofuran **2a** was isolated in 80%. The yield of **2a** was decreased to 56% when the reaction was carried out at 70 °C (entry 10). As imines were unstable for long time at room temperature, we intended to reduce the imine *in situ* for evaluating the scope of this current protocol. Using optimized conditions in entry 9, 2 equiv. of $NaCNBH_3$ was added at the end of the reaction to isolate **3a** in 84% yield (Scheme 2). Thereafter, all the imines were reduced in one-pot by following the same procedure.

Scheme 2. *In situ* reduction of the imine.



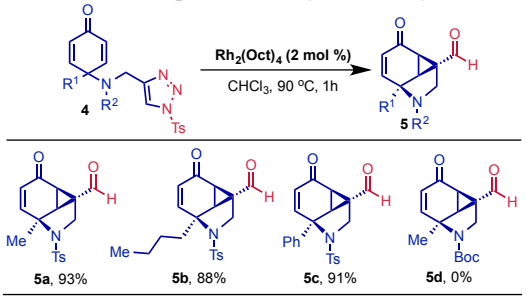
With the optimized one-pot reaction conditions for the preparation of **3a** in hand, we investigated the substrate scope for a range of triazolyl-cyclohexadienones **1** (Table 2). Similar to methyl group, other primary alkyls like ethyl, *n*-propyl and *n*-butyl substituents on the cyclohexadienone moiety were well tolerated and delivered the corresponding 5-substituted benzofurans **3b**−**3d** in good yields (75−82%). Notably, by increasing the bulkiness of R^1 substituent (^{i}Pr, ^{s}Bu and ^{t}Bu) at the quaternary carbon center, the yields of the corresponding products **3e-3g** gradually decreased from 70% to 61% indicating the steric hindrance for the intramolecular cyclization. We were delighted to observe that sensitive functional groups like ether (**3h**), silyloxy ether (**3i**), protected amine (**3j**) on R^1 were well tolerated in the reaction (67−76%). In addition, halogens such as Br and I on R^1 furnished the related products **3k** and **3l** in 75% and 72% yields respectively. Furthermore, benzyl and phenyl substituted cyclohexadienone-tethered triazoles were found to be suitable substrates for this process. To our delight, triazoles with various sulfonyl protected groups proceeded equally well to deliver the benzofurans **3o-3t** in similar yields (74-82%). Interestingly, when tetrahydronapthalenone derivative **1u** was used, a mixture of 1:0.9 **3u** and **3u'** was isolated in 75% yield. Similarly, 3-methyl substituted triazole **1v** led to a 1:1 mixture of **3v** and **3v'** in 72% yield.

Table 2. Substrate scope of the benzofurans.



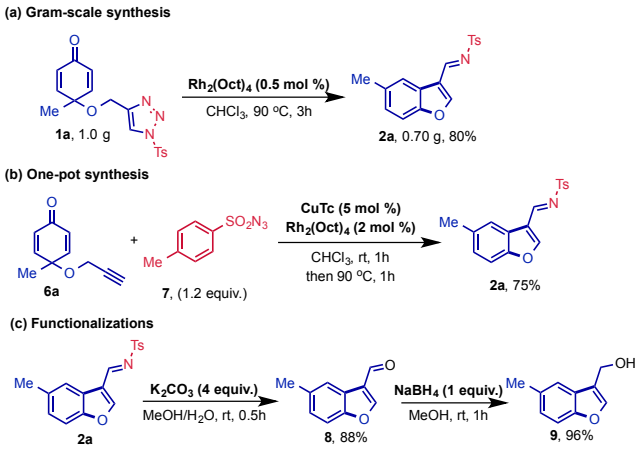
Next, we sought to investigate the scope of *N*-tethered triazolyl-cyclohexadienones **4** in the denitrogenative transannulation reactions (Table 3). Interestingly, while using *N*-tethered triazole **4a**, fused tricyclic aldehyde **5a** was obtained exclusively in 93% yield upon treating with 2 mol% $Rh_2(Oct)_4$ in $CHCl_3$ at 90 °C. An intramolecular cyclopropanation of *in situ* generated α-imino rhodium carbene with cyclohexadienone followed by imine hydrolysis led to the formation of tricyclic cyclopropa[*cd*]indole-carbaldehyde **5a**. To generalize this finding, *n*-Bu and Ph-substituted triazoles were tested and the corresponding tricyclic aldehydes **5b** and **5c** were isolated in 88% and 91% respectively. Protecting group on nitrogen was found to be crucial as *N*-Boc linked triazole was inefficient for this transformation and failed to deliver the aldehyde **5d**.

Table 3. Substrate scope of the tricyclic aldehydes.



In order to improve the efficacy of the transformation, a gram-scale reaction was performed with 1.0 g of **1a** using only 0.5 mol% of $Rh_2(Oct)_4$ and after 3h at 90 °C, 0.70 g of benzofuran **2a** was isolated in 80% (Scheme 3a). Furthermore, a one-pot reaction of alkyne **6a** and tosyl azide **7** was carried out to synthesize the benzofuran derivative **2a** by combining the Cu(I)-catalyzed azide−alkyne cycloaddition and Rh(II)-catalyzed denitrogenative transannulation reaction together in a single step (Scheme 3b). Pleasingly, the yield of one-pot process was comparable with the stepwise pathway. The synthetic utility of this protocol was illustrated by hydrolyzing the imine **2a** to 5-methylbenzofuran-3-carbaldehyde **8** (88% yield) followed by reduction to isolate synthetically useful (5-methylbenzofuran-3-yl)methanol **9** in 96% yield (Scheme 3c).

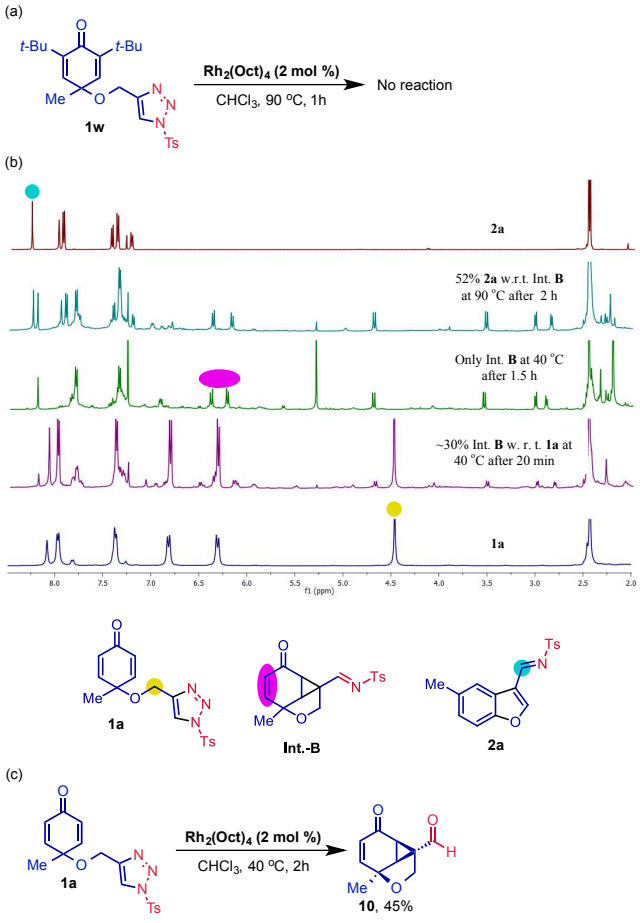
Scheme 3: Gram-scale synthesis, one-pot protocol and functionalizations.



In order to gain some insights on the reaction mechanism, the reactivity of 2,6-di-*tert*-butyl-substituted-cyclohexadienone **1w** was tested under the standard conditions and as expected, no product formation was observed in ^{1}H-NMR of the crude reaction mixture, indicating the importance of the proton at the 2nd position of cyclohexadienone (Scheme 4a). The formation of tricyclic aldehyde **5** in the case of *N*-tethered triazoles **4** (Table 3)

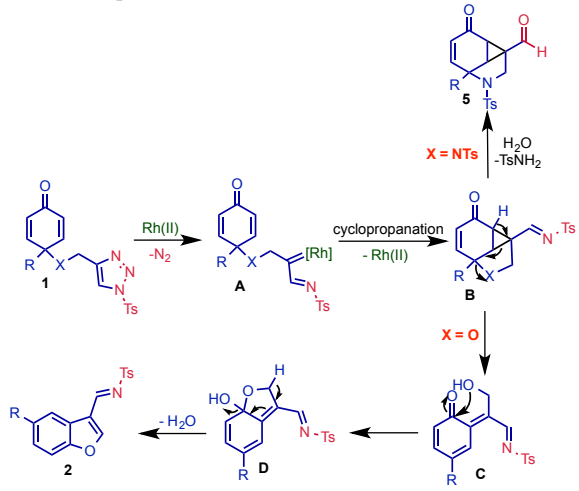
conveyed substantial synthetic importance to the developed methodology and also provided basic information about the intermediate of reaction mechanism. This inspired us to conduct a ^{1}H NMR study with *O*-tethered triazole **1** to find more details about the reaction mechanism (Scheme 4b). When **1a** was heated to 40 °C under the standard conditions, around 30% of fused tricyclic imine **Int. B** (*vide infra*: Scheme 5) was observed after 20 mins and no **2a** was detected at this temperature. Continuing the reaction to 90 mins led to the full conversion of **1a** into **Int. B**. At this point, temperature was raised from 40 °C to 90 °C and ^{1}H NMR indicated the conversion of **Int. B** into imine **2a** at this temperature. Around 52% of **2a** was detected after 30 mins. The imine intermediate (Int. **B**) was sensitive and attempted isolation led to its hydrolysis to afford cyclopropa[*cd*]benzofuran-carbaldehyde **10** in 45% (Scheme 4c). The NMR study clearly indicates that tricyclic imine intermediate **Int. B** forms at low temperature (40 °C) and on heating undergoes rearrangement to deliver the benzofurans **2**.

Scheme 4: Mechanistic studies.



Based on these control studies and previous literature reports, the proposed mechanism of this reaction is illustrated in Scheme 5. Intramolecular cyclopropanation of Rh-azavinyl carbene intermediate **A** with the olefin leads to the formation of fused tricyclic imine **Int. B**. In case of *O*-linker, the intermediate **B** undergoes cyclopropane ring-opening and proton transfer to form the alcohol intermediate **C**. Subsequent intramolecular nucleophilic addition to the carbonyl group followed by water elimination generates the 3-imino benzofuran **2**. If the linker was nitrogen, the imine intermediate (**Int. B)** undergoes hydrolysis to afford cyclopropanecarbaldehyde **5**. In the case of *N*-linker, hydrolysis of imines seems to be faster leading to carbaldehydes **5**. In the case of *O*-linker, ring-opening and intramolecular nucleophilic addition might be favored because of the more nucleophiilc nature of oxygen.

Scheme 5: Proposed mechanism.



In summary, we have successfully established a Rh(II)-catalyzed highly efficient and step-economical methodology for the synthesis of functionalized benzofurans and fused tricyclic aldehydes from easily preparable *N*-sulfonyl-1,2,3-triazole tethered cyclohexadienones. Remarkably, the reactivity pattern of the substrates fully depends on the connecter atom (O or N atom) present at the quaternary carbon center of cyclohexa-2,5- dienone moiety. 5-Substituted benzofurans were formed when the connecter atom was oxygen, while cyclopropa[*cd*]indole-carbaldehydes were observed in case of nitrogen. A diverse range of benzofurans were isolated in good to excellent yields. Furthermore, the successive transformations can be easily carried out in a one pot Cu(I)/Rh(II) process starting from the alkynyl-cyclohexadienones and tosyl azide. A gram-scale synthesis of **2a** also amplified the impact of this protocol.

EXPERIMENTAL SECTION

Materials and methods:

All reactions were carried out under nitrogen atmosphere in screw cap reaction tubes and the workups were performed under air. All the solvents used for the reactions were dried by following the reported procedures. Reactions were monitored using thin-layer chromatography (SiO_2). A gradient elution using petroleum ether and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel $60F_{254}$). TLC plates were visualized with UV light (254 nm) or $KMnO_4$ stain or Vanillin stain or 2,4-DNP stain. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. NMR studies were performed on Bruker Advance DPX at 400 MHz (^{1}H) or 500 MHz (^{1}H) and at 100 MHz (^{13}C) or 125 MHz (^{13}C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (δH = 7.26 and δC = 77.16) ppm as internal standards, and coupling constants (*J*) are given in Hz. HRMS were recorded on Bruker MaXis impact mass spectrometer using ESI-TOF techniques.

Alkynyl-cyclohexadienone **6a** was prepared following the reported procedure.[19]

(a) General procedure for the synthesis of *N*-sulfonyl-1,2,3-triazolyl *O*-tethered cyclohexa-2,5-dienones (1).

In a 50 mL round bottom flask equipped with a magnetic stirrer bar, *O*-tethered alkynyl-cyclohexa-2,5-dienone (0.5 mmol, 1.0 equiv.), TsN_3 (99 mg, 0.5 mmol, 1.0 equiv.) and CuTc (4.8 mg, 0.025 mmol, 5 mol %) in toluene (10 mL) were placed. The resulting mixture was stirred for 1-2 h at room temperature. After completion, the reaction was quenched with saturated aq. NH_4Cl solution, and extracted with EtOAc, the combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by recrystallization (Hexane/DCM 19:1) to give the desired product.

***4-methyl-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)Cyclohexa-2,5-dienone* (1a):** White solid, 0.30 Rf in EtOAc:Hexane (1:4), 174 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.97 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 7.5 Hz, 2H), 6.81 (d, J = 9.5 Hz, 2H), 6.30 (d, J = 9.5 Hz, 2H), 4.46 (s, 2H), 2.43 (s, 3H), 1.46 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 184.9, 150.8, 147.6, 132.9, 130.7, 130.6, 128.8, 127.6, 122.4, 73.2, 59.1, 26.3, 21.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}N_3O_4S$ 360.1012; Found 360.1009.

***4-ethyl-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)Cyclohexa-2,5-dienone* (1b)**: White semi-solid, 0.31 Rf in EtOAc:Hexane (1:4), 173 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.96 (d, J = 6.6 Hz, 2H), 7.36 (d, J = 6.3 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 6.36 (d, J = 8.8 Hz, 2H), 4.48 (s, 2H), 2.42 (s, 3H), 1.79 (q, J = 6.3 Hz, 2H), 0.81 (t, J = 6.3 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.2, 150.1, 147.6, 145.0, 132.9, 131.9, 130.5, 128.8, 122.3, 76.9, 59.0, 32.3, 21.9, 7.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}N_3NaO_4S$ 396.0988; Found 396.0990.

***4-propyl-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy) cyclohexa-2,5-dienone* (1c)**: Yellow semi-solid, 0.35 Rf in EtOAc:Hexane (1:4), 182 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.93 (d, J = 6.8 Hz, 2H), 7.34 (d, J = 6.7 Hz, 2H), 6.76 (d, J = 9.1 Hz, 2H), 6.31 (d, J = 8.9 Hz, 2H), 4.45 (s, 2H), 2.39 (s, 3H), 1.70 (t, J = 9.2 Hz, 2H), 1.24 – 1.19 (m, 2H), 0.83 (t, J = 6.8 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.2, 150.3, 147.5, 145.0, 132.8, 131.5, 130.5, 128.7, 122.2, 76.3, 58.7, 41.4, 21.8, 16.8, 14.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}N_3NaO_4S$ 410.1144; Found 410.1139.

***4-butyl-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy) cyclohexa2,5-dienone* (1d)**: Yellow semi-solid, 0.33 Rf in EtOAc:Hexane (1:4), 181 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.97 (d, J = 7.2 Hz, 2H), 7.36 (d, J = 7.2 Hz, 2H), 6.77 (d, J = 9.6 Hz, 2H), 6.34 (d, J = 9.4 Hz, 2H), 4.48 (s, 2H), 2.42 (s, 3H), 1.76 (t, J = 7.5 Hz, 2H), 1.28 – 1.19 (m, 4H), 0.84 (t, J = 5.7 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.2, 150.3, 147.5, 145.1, 133.1, 131.7, 130.5, 128.8, 122.2, 76.4, 58.9, 39.2, 25.6, 22.9, 21.9, 13.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}N_3O_4S$ 402.1482; Found 402.1485.

***4-isopropyl-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)cyclohexa-2,5-dienone* (1e)**: White solid, 0.32 Rf in EtOAc:Hexane (1:4), 180 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.97 (d, J = 7.8 Hz, 2H), 7.37 (d, J = 7.7 Hz, 2H), 6.76 (d, J = 9.8 Hz, 2H), 6.40 (d, J = 9.8 Hz, 2H), 4.47 (s, 2H), 2.43 (s, 3H), 2.06 – 1.97 (m, 1H), 0.93 (s, 3H), 0.91 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.3, 149.2, 147.5, 132.9, 132.5, 130.5, 128.8, 78.9, 59.0, 36.6, 21.9, 17.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}N_3NaO_4S$ 410.1144; Found 410.1146.

***4-(sec-butyl)-4-((1-tosyl-1H-1,2,3-triazol-4-yl) methoxy)cyclohexa-2,5-dienone* (1f)**: White semi-solid, 0.30 Rf in EtOAc:Hexane (1:4), 181 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.97 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 7.5 Hz, 2H), 6.74 (d, J = 10.1 Hz, 2H), 6.38 (t, J = 8.7 Hz, 2H), 4.47 (s, 2H), 2.42 (s, 3H), 1.80 – 1.66 (m, 2H), 1.30 – 1.19 (m, 1H), 0.89 (s, 3H), 0.87 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.4, 149.5, 149.1, 147.5, 132.6, 132.2, 130.5, 128.8, 122.1, 79.0, 58.8, 43.5, 23.8, 21.9, 13.4, 12.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}N_3NaO_4S$ 424.1301; Found 424.1299.

***4-(tert-butyl)-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)cyclohexa-2,5-dienone* (1g)**: White semi-solid 0.29 Rf in EtOAc:Hexane (1:4), 158 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 8.00 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 6.92 (d, J = 10.3 Hz, 2H), 6.41 (d, J = 10.3 Hz, 2H), 4.48 (s, 2H), 2.45 (s, 3H), 1.02 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 184.8, 149.5, 147.6, 145.7, 133.0, 132.7, 130.6, 128.9, 121.8, 80.3, 59.3, 39.7, 25.8, 22.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}N_3NaO_4S$ 424.1301; Found 424.1307.

***4-(2-methoxyethyl)-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy) cyclohexa-2,5-dienone* (1h)**: White semi-solid, 0.22 Rf in EtOAc:Hexane (1:4), 181 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.95 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 6.82 (d, J = 10.2 Hz, 2H), 6.31 (d, J = 12.1 Hz, 2H), 4.46 (s, 2H), 3.39 (t, J = 6.2 Hz, 2H), 3.20 (s, 3H), 2.41 (s, 3H), 2.00 (t, J = 6.2 Hz, 2H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 185.1, 149.9, 147.5, 132.9, 131.1, 130.5, 128.7, 127.5, 122.3, 74.8, 67.2, 58.7, 58.5, 39.5, 21.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}N_3NaO_5S$ 426.1094; Found 426.1094.

***4-(2-((tert-butyldimethylsilyl)oxy)ethyl)-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy) cyclohexa-2,5-dienone* (1i)**: Yellow semi-solid, 0.28 Rf in EtOAc:Hexane (1:4), 231 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.97 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 7.6 Hz, 2H), 6.85 (d, J = 9.8 Hz, 2H), 6.32 (d, J = 15.3 Hz, 2H), 4.47 (s, 2H), 3.67 (t, J = 5.7 Hz, 3H), 2.43 (s, 3H), 1.98 (t, J = 5.7 Hz, 2H), 0.83 (s, 9H), -0.02 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.3, 150.2, 147.6, 145.0, 133.0, 131.0, 130.6, 128.8, 127.6, 122.2, 75.0, 58.7, 57.9, 42.9, 25.9, 21.9, 18.2, -5.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{33}N_3NaO_5SSi$ 526.1802; Found 526.1797.

***tert-butyl (2-(4-oxo-1-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy) cyclohexa-2,5-dien-1-yl)ethyl)carbamate* (1j)**: Yellow semi-solid, 0.17 Rf in EtOAc:Hexane (1:4), 212 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 10.1 Hz, 2H), 6.27 (d, J = 10.0 Hz, 2H), 4.95 (t, J = 8.0 Hz, 1H), 4.40 (s, 2H), 2.35 (s, 3H), 1.90 (q, J = 7.2 Hz, 2H), 1.31 (s, 9H), 1.14 (t, J = 7.2 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 184.6, 155.6, 149.2, 147.4, 144.7, 132.6, 131.4, 130.4, 128.5, 122.3, 79.1, 74.9, 58.6, 39.4, 35.6, 28.2, 21.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{23}H_{28}N_4NaO_6S$ 511.1621; found 511.1615.

***4-(2-bromoethyl)-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy) cyclohexa-2,5-dienone* (1k)**: White semi-solid, 0.30 Rf in EtOAc:Hexane (1:4), 206 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.99 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 7.9 Hz, 2H), 6.83 (d, J = 9.9 Hz, 2H), 6.41 (d, J = 10.0 Hz, 2H), 4.48 (s, 2H), 3.33 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H), 2.35 (t, J = 8.0 Hz, 2H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 184.6, 148.6, 147.7, 132.9, 132.2, 130.6, 128.9, 122.40, 122.37, 75.5, 58.9, 42.9, 25.4, 22.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{18}BrN_3NaO_4S$ 474.0093; found 474.0090.

4-(2-iodoethyl)-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)

cyclohexa-2,5-dienone **(1l)**: White solid, 0.31 Rf in EtOAc:Hexane (1:4), 239 mg, 96% yield ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 6.79 (t, J = 11.2 Hz, 2H), 6.41 (d, J = 10.2 Hz, 2H), 4.47 (s, 2H), 3.06 (t, J = 8.0 Hz, 2H), 2.44 (s, 3H), 2.37 (t, J = 8.0 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 184.6, 148.6, 147.7, 144.5, 132.8, 132.3, 130.6, 128.8, 122.4, 76.6, 58.9, 44.1, 22.0, -4.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{18}IN_3NaO_4S$ 521.9954; Found 521.9956.

4-benzyl-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)cyclohexa-2,5-dienone **(1m):** White semi-solid, 0.35 Rf in EtOAc:Hexane (1:4), 197 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.26 – 7.22 (m, 3H), 7.16 – 7.11 (m, 2H), 6.76 (d, J = 10.2 Hz, 2H), 6.28 (d, J = 10.2 Hz, 2H), 4.48 (s, 2H), 3.04 (s, 2H), 2.44 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 184.8, 149.5, 147.5, 145.3, 134.4, 133.0, 131.6, 130.8, 130.5, 128.8, 128.1, 127.3, 122.2, 76.0, 59.2, 46.2, 21.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd $C_{23}H_{22}N_3O_4S$ 436.1325; Found 436.1325.

1-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)-[1,1'-biphenyl]-4(1H)-one **(1n)**: White solid, 0.31 Rf in EtOAc:Hexane (1:4), 200 mg, 95% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 7.4 Hz, 2H), 7.41 – 7.33 (m, 5H), 6.87 (d, J = 9.8 Hz, 2H), 6.42 (d, J = 9.8 Hz, 2H), 4.74 (s, 2H), 2.46 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.3, 149.5, 147.6, 137.7, 132.9, 130.6, 130.3, 129.0, 128.8, 128.7, 127.6, 125.8, 122.4, 76.8, 58.8, 21.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}N_3O_4S$ 422.1169; Found 422.1169.

4-methyl-4-((1-(phenylsulfonyl)-1H-1,2,3-triazol-4-yl)methoxy)cyclohexa-2,5-dienone **(1o)**: White solid, 0.35 Rf in EtOAc:Hexane (1:4), 150 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 – 8.05 (m, 3H), 7.72 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.7 Hz, 2H), 6.82 (d, J = 10.0 Hz, 2H), 6.31 (d, J = 10.0 Hz, 2H), 4.47 (s, 2H), 1.43 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 185.0, 150.9, 145.0, 136.0, 135.9, 130.7, 130.0, 128.8, 122.5, 73.2, 59.0, 26.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}N_3O_4S$ 346.0856; Found 346.0861.

4-((1-(mesitylsulfonyl)-1H-1,2,3-triazol-4-yl)methoxy)-4-methylcyclohexa-2,5-dienone **(1p)**: White solid, 0.35 Rf in EtOAc:Hexane (1:4), 174 mg, 90% yield.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.02 (s, 2H), 6.84 (d, J = 10.1 Hz, 2H), 6.33 (d, J = 10.0 Hz, 2H), 4.50 (s, 2H), 2.66 (s, 6H), 2.32 (s, 3H), 1.48 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 184.9, 150.9, 146.4, 142.1, 132.8, 130.8, 73.3, 59.2, 26.4, 23.3, 21.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}N_3NaO_4S$ 410.1144; Found 410.1148.

4-((1-((4-(tert-butyl)phenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)methoxy)-4-methylcyclohexa-2,5-dienone **(1q)**: White semi-solid, 0.31 Rf in EtOAc:Hexane (1:4), 170 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 8.02 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 10.2 Hz, 2H), 6.32 (d, J = 9.9 Hz, 2H), 4.48 (s, 2H), 1.47 (s, 3H), 1.32 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 184.9, 160.4, 150.8, 144.9, 132.9, 130.8, 128.8, 127.1, 122.4, 73.3, 59.1, 35.7, 31.0, 26.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}N_3O_4S$ 402.1482; Found 402.1479.

4-((1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)methoxy)-4-methylcyclohexa-2,5-dienone **(1r)**: White solid, 0.25 Rf in EtOAc:Hexane (1:4), 173 mg, 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (s, 1H), 8.05 (d, J = 6.9 Hz, 2H), 7.04 (d, J = 7.9 Hz, 2H), 6.85 (d, J = 9.7 Hz, 2H), 6.34 (d, J = 8.8 Hz, 2H), 4.49 (s, 2H), 3.90 (s, 3H), 1.49 (s, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 185.0, 165.6, 150.9, 144.8, 131.4, 130.8, 126.8, 122.2, 115.2, 73.2, 59.1, 56.1, 26.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}N_3O_5S$ 376.0961; Found 376.0961.

4-((1-((4-bromophenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)methoxy)-4-methylcyclohexa-2,5-dienone **(1s)**: White solid, 0.32 Rf in EtOAc:Hexane (1:4), 193 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.97 (d, J = 8.7 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 10.1 Hz, 2H), 6.33 (d, J = 10.1 Hz, 2H), 4.48 (s, 2H), 1.48 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 184.9, 150.7, 145.2, 135.0, 133.4, 131.8, 130.9, 130.2, 122.4, 73.3, 59.1, 26.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{14}BrN_3NaO_4S$ 445.9780; Found 445.9778.

4-((1-([1,1'-biphenyl]-4-ylsulfonyl)-1H-1,2,3-triazol-4-yl)methoxy)-4-methylcyclohexa-2,5-dienone **(1t)**: White solid, 0.31 Rf in EtOAc:Hexane (1:4), 179 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.6 Hz, 2H), 8.13 (s, 1H), 7.77 (d, J = 8.6 Hz, 2H), 7.57 (dd, J = 8.0, 1.3 Hz, 2H), 7.52 – 7.42 (m, 3H), 6.83 (d, J = 10.2 Hz, 2H), 6.34 (d, J = 10.2 Hz, 2H), 4.49 (s, 2H), 1.47 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 184.9, 150.8, 149.0, 145.0, 138.5, 134.3, 130.8, 129.4, 129.3, 128.5, 127.5, 122.4, 73.3, 59.1, 26.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}N_3O_4S$ 422.1169; Found 422.1165.

4a-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)-5,6,7,8-tetrahydronaphthalen-2(4aH)-one **(1u)**: White solid, 0.21 Rf in EtOAc:Hexane (1:4), 170 mg, 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.99 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 10.0 Hz, 1H), 6.32 (d, J = 9.9 Hz, 1H), 6.23 (s, 1H), 4.35 (d, J = 11.9 Hz, 1H), 4.23 (d, J = 12.0 Hz, 1H), 2.48 – 2.42 (m, 4H), 2.35 (d, J = 12.3 Hz, 1H), 2.17 (d, J = 13.6 Hz, 1H), 2.00 (d, J = 11.8 Hz, 1H), 1.89 (d, J = 13.4 Hz, 1H), 1.60 (d, J = 12.9 Hz, 1H), 1.24 (s, 1H), 0.86 (t, J = 6.9 Hz, 1H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 185.9, 162.3, 150.4, 147.6, 133.0, 131.2, 130.6, 128.9, 126.9, 122.2, 74.3, 57.9, 39.3, 32.6, 28.1, 21.9, 20.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{21}N_3NaO_4S$ 422.1145; Found 422.1147.

3,4-dimethyl-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy) cyclohexa-2,5-dienone **(1v)**: White solid, 0.31 Rf in EtOAc:Hexane (1:4), 168 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.97 (d, J = 7.2 Hz, 2H), 7.37 (d, J = 6.9 Hz, 2H), 6.81 (d, J = 9.7 Hz, 1H), 6.29 (d, J = 9.6 Hz, 1H), 6.20 (s, 1H), 4.37 (d, J = 11.7 Hz, 1H), 4.21 (d, J = 11.7 Hz, 1H), 2.43 (s, 3H), 2.01 (s, 3H), 1.39 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.3, 159.7, 151.2, 147.6, 144.5, 132.9, 130.5, 130.4, 129.4, 128.8, 122.3, 75.1, 58.6, 25.6, 21.9, 18.0. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{18}H_{19}KN_3O_4S$ 412.0728; Found 412.0725.

2,6-di-tert-butyl-4-methyl-4-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)cyclohexa-2,5-dienone **(1w)**: White solid, 0.35 Rf in EtOAc:Hexane (1:4), 211 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.97 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 6.44 (s, 2H), 4.39 (s, 2H), 2.43 (s, 3H), 1.39 (s, 3H), 1.19 (s, 18H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 185.8, 149.2, 147.5, 141.7, 133.0, 130.5, 130.4, 128.8, 122.0, 73.1, 58.4, 35.0, 29.6, 27.3, 21.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{33}N_3NaO_4S$ 494.2083; Found 494.2091.

(b) General procedure for the synthesis of *N*-sulfonyl-1,2,3-triazolyl *N*-tethered cyclohexa-2,5-dienones (4).

In a 50 mL round bottom flask equipped with a magnetic stirrer bar, *N*-tethered alkynyl-cyclohexa-2,5-dienone (0.5 mmol, 1.0 equiv.), TsN_3 (99 mg, 0.5 mmol, 1.0 equiv.) and CuTc (4.8 mg, 0.025 mmol, 5 mol %) in toluene (10 mL) were placed. The resulting mixture was stirred for 1-2 h at room temperature. After completion, the reaction was quenched with saturated aq. NH_4Cl solution, and extracted with EtOAc, the combined organic phases

were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by recrystallization (Hexane/DCM 19:1) to give the desired product.

4-methyl-N-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide **(4a)**: White solid, 0.32 Rf in EtOAc:Hexane (1:4), 244 mg, 95% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (s, 1H), 8.00 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 10.0 Hz, 2H), 6.09 (d, J = 10.0 Hz, 2H), 4.59 (s, 2H), 2.46 (s, 3H), 2.40 (s, 3H), 1.51 (s, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 184.3, 150.8, 147.6, 144.3, 138.8, 133.1, 130.7, 130.6, 130.0, 128.9, 128.4, 127.4, 123.9, 60.6, 42.1, 26.2, 22.0, 21.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}N_4O_5S_2$ 513.1260; Found 513.1253.

N-(1-butyl-4-oxocyclohexa-2,5-dien-1-yl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide **(4b)**: White solid, 0.33 Rf in EtOAc:Hexane (1:4), 250 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (s, 1H), 8.00 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 6.80 (d, J = 10.0 Hz, 2H), 6.14 (d, J = 9.9 Hz, 2H), 4.62 (s, 2H), 2.46 (s, 3H), 2.40 (s, 3H), 1.90 – 1.83 (m, 2H), 1.10 – 1.03 (m, 2H), 0.93 – 0.88 (m, 2H), 0.67 (t, J = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 184.8, 148.9, 147.6, 144.3, 138.7, 133.1, 130.6, 129.84, 129.82, 128.9, 127.5, 124.0, 64.5, 41.8, 36.7, 26.1, 22.5, 22.0, 21.7, 13.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{30}N_4NaO_5S_2$ 577.1549; Found 577.1551.

4-methyl-N-(4-oxo-1,4-dihydro-[1,1'-biphenyl]-1-yl)-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide **(4c)**: White solid, 0.31 Rf in EtOAc:Hexane (1:4), 267 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.01 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 10.2 Hz, 2H), 7.27 – 7.21 (m, 5H), 7.13 (t, J = 7.6 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H), 6.08 (d, J = 10.1 Hz, 2H), 4.54 (s, 2H), 2.46 (s, 3H), 2.37 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 184.5, 147.6, 147.4, 144.4, 137.5, 137.1, 133.3, 130.7, 129.6, 129.3, 129.2, 129.1, 128.9, 128.4, 128.1, 127.9, 127.2, 65.3, 42.7, 22.0, 21.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{26}N_4NaO_5S_2$ 597.1236; Found 597.1239.

(c) General procedure for the synthesis of benzofurans:

The substituted *N*-sulfonyl 1,2,3-triazolyl *O*-tethered cyclohexa-2,5-dienone **1**, (0.2 mmol, 1.0 equiv.) and $Rh_2(Oct)_4$ (3.1 mg, 0.004 mmol, 2 mol %) were taken into an oven-dried screw cap reaction tube equipped with a stir bar. The tube was evacuated and refilled with nitrogen three times. Then, chloroform (2 mL) was added via syringe. The reaction mixture was heated to 90 ^{o}C for 1 h using an oil bath. After that $NaCNBH_3$ (0.4 mmol, 2.0 equiv., 25.13 mg) was added to the reaction mixture and further stirred at room temperature for 1-2h. The resulting mixture was cooled, evaporated under reduced pressure and the residue was purified by column chromatography (EtOAc/Hex 1:4) to afford the respective product.

(E)-4-methyl-N-((5-methylbenzofuran-3-yl)methylene)benzenesulfonamide **(2a):** White solid, 0.65 Rf in EtOAc:Hexane (1:4), 50 mg, 80% yield, mp = 157-159 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.17 (s, 1H), 8.24 (s, 1H), 7.96 (s, 1H), 7.91 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.5 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.4 Hz, 1H), 2.45 (s, 3H), 2.43 (s, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 162.3, 156.3, 154.9, 144.6, 135.6, 135.0, 130.0, 128.1, 128.0, 123.2, 123.1, 118.7, 111.3, 21.8, 21.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{16}NO_3S$ 314.0845; Found 314.0849.

4-methyl-N-((5-methylbenzofuran-3-yl)methyl)benzenesulfonamide **(3a)**: White solid, 0.45 Rf in EtOAc:Hexane (1:4), 53 mg, 84% yield, mp = 140-142 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2H), 7.37 (s, 1H), 7.31 – 7.26 (m, 3H), 7.14 (s, 1H), 7.08 (dd, J = 8.4, 1.6 Hz, 1H), 4.80 (t, J = 5.6 Hz, 1H), 4.22 (d, J = 5.9 Hz, 2H), 2.42 (s, 3H), 2.39 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.0, 143.8, 143.1, 136.7, 132.5, 129.8, 127.4, 126.4, 126.2, 119.5, 115.7, 111.2, 37.5, 21.7, 21.4. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{17}H_{17}KNO_3S$ 354.0561; Found 354.0563.

N-((5-ethylbenzofuran-3-yl)methyl)-4-methylbenzenesulfonamide **(3b)**: Off-white solid, 0.51 Rf in EtOAc:Hexane (1:4), 53 mg, 81% yield, mp = 120-122 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2H), 7.40 (s, 1H), 7.35 – 7.26 (m, 3H), 7.15 (s, 1H), 7.12 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 4.73 (t, J = 5.5 Hz, 1H), 4.24 (d, J = 5.8 Hz, 2H), 2.67 (q, J = 7.6 Hz, 2H), 2.43 (s, 3H), 1.24 (t, J = 7.6 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ154.2, 143.8, 143.2, 139.2, 136.8, 129.9, 127.4, 126.4, 125.2, 118.3, 115.8, 111.4, 37.6, 28.9, 21.7, 16.5. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{18}H_{19}KNO_3S$ 368.0717; Found 368.0710.

4-methyl-N-((5-propylbenzofuran-3-yl)methyl)benzenesulfonamide **(3c)**. Off-white solid, 0.50 Rf in EtOAc:Hexane (1:4), 56 mg, 82% yield, mp = 107-109 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.2 Hz, 2H), 7.41 (s, 1H), 7.31 (t, J = 8.9 Hz, 3H), 7.13 (s, 1H), 7.10 (dd, J = 8.4, 1.5 Hz, 1H), 4.62 (s, 1H), 4.25 (d, J = 5.6 Hz, 2H), 2.61 (t, J = 8.0 Hz, 2H), 2.43 (s, 3H), 1.65 – 1.62 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.2, 143.8, 143.2, 137.6, 136.8, 129.9, 127.4, 126.3, 125.7, 118.9, 115.7, 111.3, 38.1, 37.6, 25.3, 21.7, 14.0. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{19}H_{21}KNO_3S$ 382.0873; Found 382.0871.

N-((5-butylbenzofuran-3-yl)methyl)-4-methylbenzenesulfonamide **(3d)**: Off-white solid, 0.55 Rf in EtOAc:Hexane (1:4), 54 mg, 75% yield, mp = 93-95 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2H), 7.40 (s, 1H), 7.34 – 7.26 (m, 3H), 7.15 (s, 1H), 7.10 (dd, J = 8.4, 1.2 Hz, 1H), 4.72 (s, 1H), 4.24 (d, J = 5.8 Hz, 2H), 2.64 (t, J = 8.0 Hz, 2H), 2.43 (s, 3H), 1.62 – 1.57 (m, 2H), 1.41 – 1.31 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.2, 143.8, 143.1, 137.8, 136.8, 129.9, 127.4, 126.4, 125.7, 118.9, 115.8, 111.2, 37.6, 35.7, 34.5, 22.5, 21.7, 14.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}NNaO_3S$ 380.1290; Found 380.1295.

N-((5-isopropylbenzofuran-3-yl)methyl)-4-methylbenzenesulfonamide **(3e)**: Off-white solid, 0.52 Rf in EtOAc:Hexane (1:4), 48 mg, 70% yield, mp = 123-125 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2H), 7.40 (s, 1H), 7.33 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 8.1 Hz, 2H), 7.20 (s, 1H), 7.16 (dd, J = 8.5, 1.5 Hz, 1H), 4.80 (t, J = 5.7 Hz, 1H), 4.25 (d, J = 5.6 Hz, 2H), 2.99 – 2.90 (m, 1H), 2.42 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.2, 143.9, 143.7, 143.2, 136.8, 129.8, 127.3, 126.3, 123.8, 116.8, 115.9, 111.4, 37.6, 34.3, 24.6, 21.6. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{19}H_{21}KNO_3S$ 382.0873; Found 382.0877.

N-((5-(sec-butyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide **(3f)**: White solid, 0.51 Rf in EtOAc:Hexane (1:4), 48 mg, 68% yield, mp = 87-89 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 2H), 7.40 (s, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.26 (d, J = 7.8 Hz, 1H), 7.16 (s, 1H), 7.11 (dd, J = 8.5, 2.0 Hz, 1H), 4.93 (s, 1H), 4.25 (d, J = 5.5 Hz, 2H), 2.67 – 2.59 (m, 1H), 2.41 (s, 3H), 1.62 – 1.56 (m, 2H), 1.24 (d, J = 6.9 Hz, 3H), 0.81

(t, J = 7.3 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.2, 143.7, 143.1, 142.7, 136.8, 129.8, 127.3, 126.3, 124.1, 117.5, 115.8, 111.3, 41.8, 37.5, 31.6, 22.5, 21.6, 12.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}NNaO_3S$ 380.1290; Found 380.1293.

***N-((5-(tert-butyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide* (3g)**: White semi-solid, 0.45 Rf in EtOAc:Hexane (1:4), 44 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 3.9 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.25 (dd, J = 6.5, 2.4 Hz, 2H), 4.91 (bs, 1H), 4.26 (d, J = 5.9 Hz, 2H), 2.41 (s, 3H), 1.34 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.8, 146.1, 143.7, 143.2, 136.8, 129.8, 127.3, 126.0, 122.9, 116.0, 115.7, 111.0, 37.5, 34.9, 31.9, 21.6. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{20}H_{23}KNO_3S$ 396.1030; Found 396.1036.

***N-((5-(2-methoxyethyl)benzofuran-3-yl)methyl)-4-methylbenZenesulfonamide* (3h)**: White solid, 0.42 Rf in EtOAc:Hexane (1:4), 51 mg, 71% yield, mp = 93-95 ^{o}C ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.2 Hz, 2H), 7.40 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 8.6 Hz, 2H), 7.22 (s, 1H), 7.14 (dd, J = 8.4, 1.4 Hz, 1H), 4.88 (t, J = 5.8 Hz, 1H), 4.23 (d, J = 5.9 Hz, 2H), 3.59 (t, J = 7.0 Hz, 2H), 3.35 (s, 3H), 2.91 (t, J = 7.0 Hz, 2H), 2.42 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 143.8, 143.2, 136.8, 133.8, 129.8, 127.3, 126.5, 126.0, 119.6, 115.9, 111.4, 74.1, 58.8, 37.5, 36.1, 21.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}NNaO_4S$ 382.1083; Found 382.1082.

***N-((5-(2-((tert-butyldimethylsilyl)oxy)ethyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide* (3i)**: White solid, 0.50 Rf in EtOAc:Hexane (1:4), 70 mg, 76% yield, mp = 92-94 ^{o}C ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2H), 7.41 (s, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.28 (d, J = 8.1 Hz 2H), 7.16 (s, 1H), 7.13 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 4.77 (t, J = 5.7 Hz, 1H), 4.23 (d, J = 5.8 Hz, 2H), 3.78 (t, J = 7.0 Hz, 2H), 2.84 (t, J = 7.0 Hz, 2H), 2.43 (s, 3H), 0.87 (s, 9H), -0.02 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 143.8, 143.2, 136.8, 134.0, 129.9, 127.4, 126.4, 126.3, 119.8, 115.8, 111.2, 65.0, 39.5, 37.5, 26.1, 21.7, 18.4, -5.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{33}NNaO_4SSi$ 482.1792; Found 482.1812.

***tert-butyl (2-(3-((4-methylphenylsulfonamido)methyl)benzofuran-5-yl)ethyl)carbamate* (3j)**: White solid, 0.45 Rf in EtOAc:Hexane (1:4), 60 mg, 67% yield**,** mp = 111-113 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 8.3 Hz, 2H), 7.42 (s, 1H), 7.32 (d, J = 7.2 Hz, 1H), 7.26 (d, J = 8.0 Hz ,2H), 7.21 (s, 1H), 7.09 (dd, J = 8.4 1.7 Hz, 1H), 5.13 (t, J = 7.0 Hz, 1H), 4.60 (s, 1H), 4.21 (d, J = 7.9 Hz, 2H), 3.39 – 3.29 (m, 2H), 2.81 (t, J = 7.0 Hz, 2H), 2.41 (s, 3H), 1.41 (s, 9H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 156.1, 154.5, 143.7, 143.4, 136.8, 133.7, 129.8, 127.3, 126.7, 125.8, 119.6, 115.9, 111.6, 79.5, 42.3, 37.5, 36.2, 28.5, 21.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{28}N_2NaO_5S$ 467.1611; Found 467.1618.

***N-((5-(2-bromoethyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide* (3k)**: Off-white solid, 0.43 Rf in EtOAc:Hexane (1:4), 61 mg, 75% yield, mp = 118-120 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 8.2 Hz, 2H), 7.41 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.25 (d, J = 5.5 Hz, 2H), 7.19 (s, 1H), 7.10 (dd, J = 8.4, 1.6 Hz, 1H), 5.18 (t, J = 5.9 Hz, 1H), 4.22 (d, J = 5.9 Hz, 2H), 3.53 (t, J = 7.6 Hz, 2H), 3.16 (t, J = 7.6 Hz, 2H), 2.41 (s, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 154.6, 143.8, 143.5, 136.7, 133.7, 129.8, 127.2, 126.7, 125.6, 119.6, 115.9, 111.6, 39.3, 37.4, 33.5, 21.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{18}BrNNaO_3S$ 430.0082; Found 430.0086.

***N-((5-(2-iodoethyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide* (3l)**: Off-white solid, 0.42 Rf in EtOAc:Hexane (1:4), 65 mg, 72% yield, mp = 117-119 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2H), 7.44 (s, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.17 (d, J = 1.0 Hz, 1H), 7.10 (dd, J = 8.4, 1.6 Hz, 1H), 4.88 (t, J = 5.8 Hz, 1H), 4.24 (d, J = 6.0 Hz, 2H), 3.33 (t, J = 7.8 Hz, 2H), 3.18 (t, J = 7.7 Hz, 2H), 2.44 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.7, 143.9, 143.6, 136.7, 135.6, 129.9, 127.4, 126.7, 125.4, 119.3, 115.9, 111.7, 40.3, 37.5, 21.7, 6.3. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{18}H_{18}IKNO_3S$ 493.9683; Found 493.9696.

***N-((5-benzylbenzofuran-3-yl)methyl)-4-methylbenzenesulfonamide* (3m)**: White solid, 0.41 Rf in EtOAc:Hexane (1:4), 51 mg, 65% yield, mp = 125-127 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.41 (s, 1H), 7.33 – 7.27 (m, 3H), 7.24 – 7.17 (m, 6H), 7.10 (dd, J = 8.5, 1.6 Hz, 1H), 4.75 (t, J = 6.4 Hz, 1H), 4.23 (d, J = 4.9 Hz, 2H), 4.01 (s, 2H), 2.37 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 143.8, 143.4, 141.6, 136.7, 136.0, 129.8, 128.9, 128.6, 127.4, 126.6, 126.3, 126.2, 119.6, 115.9, 111.6, 41.9, 37.5, 21.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{21}NNaO_3S$ 414.1134; Found 414.1112**.**

***4-methyl-N-((5-phenylbenzofuran-3-yl)methyl)benzenesulfonamide* (3n)**: Off-white solid, 0.45 Rf in EtOAc:Hexane (1:4), 55 mg, 73% yield, mp = 137-139 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 1.4 Hz, 1H), 7.56 (dd, J = 8.1, 1.0 Hz, 2H), 7.50 (dd, J = 8.6, 1.8 Hz, 1H), 7.48 – 7.43 (m, 4H), 7.37 – 7.34 (m, 1H), 7.21 (d, J = 8.0 Hz, 2H), 5.02 (t, J = 5.9 Hz, 1H), 4.28 (dd, J = 5.9, 0.5 Hz, 2H), 2.36 (s, 3H). ^{13}C {^{1}H} NMR (125 MHz, CDCl3): δ 155.1, 143.74, 143.70, 141.4, 136.72, 136.65, 129.8, 128.9, 127.6, 127.3, 127.2, 126.9, 124.6, 118.2, 116.3, 111.8, 37.5, 21.6. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{22}H_{19}KNO_3S$ 416.0717; Found = 416.0724.

***N-((5-methylbenzofuran-3-yl)methyl)benzenesulfonamide* (3o)**: White semi-solid, 0.50 Rf in EtOAc:Hexane (1:4), 49 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, J = 7.3 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.39 (s, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.15 (s, 1H), 7.10 (dd, J = 8.4, 1.5 Hz, 1H), 4.64 (t, J = 5.4 Hz, 1H), 4.26 (d, J = 5.8 Hz, 2H), 2.39 (s, 2H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 154.1, 143.2, 139.8, 133.0, 132.6, 129.3, 127.3, 126.4, 126.3, 119.4, 115.6, 111.3, 37.6, 21.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{15}NNaO_3S$ 324.0664; Found 324.0657.

***2,4,6-trimethyl-N-((5-methylbenzofuran-3-yl)methyl)benzenesulfonamide* (3p)**: White solid, 0.45 Rf in EtOAc:Hexane (1:4), 51 mg, 74% yield, mp = 121-123 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (s, 1H), 7.28 (d, J = 8.1 Hz, 1H), 7.08 (d, J = 6.1 Hz, 2H), 6.94 (s, 2H), 4.80 (t, J = 5.0 Hz, 1H), 4.18 (d, J = 5.6 Hz, 2H), 2.63 (s, 6H), 2.38 (s, 3H), 2.30 (s, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 154.0, 143.1, 142.5, 139.3, 133.4, 132.4, 132.1, 126.5, 126.1, 119.3, 115.8, 111.1, 36.9, 23.1, 21.3, 21.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}NNaO_3S$ 366.1134; Found 366.1126.

***4-(tert-butyl)-N-((5-methylbenzofuran-3-yl)methyl)benzenesulfonamide* (3q)**: White solid, 0.47 Rf in EtOAc:Hexane (1:4), 57 mg, 80% yield, mp = 88-90 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.37 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.07 (dd, J = 8.4, 1.6 Hz, 1H), 5.16 (t, J = 5.9 Hz, 1H), 4.23 (d, J = 5.5 Hz, 2H), 2.38 (s, 3H), 1.33 (s, 9H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 156.6, 153.9, 143.1, 136.6, 132.4, 127.1, 126.5, 126.10, 126.08, 119.6, 115.7, 111.1, 37.5, 35.2, 31.2, 21.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}NNaO_3S$ 380.1290; Found 380.1301.

***4-methoxy-N-((5-methylbenzofuran-3-yl)methyl)benzenesulfonamide* (3r)**: White solid, 0.40 Rf in EtOAc:Hexane (1:4), 54 mg, 82% yield, mp = 177-179 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.6 Hz, 2H), 7.40 (s, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.14 (s, 1H), 7.09 (d, J = 8.2 Hz, 1H), 6.96 (d, J = 8.5 Hz, 2H), 4.63 (t, J = 4.0 Hz, 1H), 4.22 (d, J = 5.7 Hz, 2H), 3.87 (s, 3H), 2.39 (s, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 163.2, 154.1, 143.2, 132.6, 131.3, 129.5, 126.5, 126.2, 119.5, 115.7, 114.4, 111.2, 55.8, 37.6, 21.4. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{17}H_{17}KNO_4S$ 370.0509; Found 370.0516.

***4-bromo-N-((5-methylbenzofuran-3-yl)methyl)benzenesulfonamide* (3s)**: White semi-solid, 0.45 Rf in EtOAc:Hexane (1:4), 57 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 7.43 (s, 1H), 7.31 (d, J = 9.0 Hz, 1H), 7.11 (d, J = 7.1 Hz, 2H), 4.70 (t, J = 5.2 Hz, 1H), 4.27 (d, J = 5.7 Hz, 2H), 2.40 (s, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 154.1, 143.3, 139.0, 132.7, 132.5, 128.8, 128.0, 126.4, 126.3, 119.4, 115.4, 111.4, 37.7, 21.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{14}BrNNaO_3S$ 401.9769; Found 401.9780

***N-((5-methylbenzofuran-3-yl)methyl)-[1,1'-biphenyl]-4-sulfonamide* (3t)**: White solid, 0.46 Rf in EtOAc:Hexane (1:4), 57 mg, 75% yield, mp = 140-142 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 7.1 Hz, 2H), 7.50 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 7.3 Hz, 2H), 7.29 (d, J = 8.4 Hz, 1H), 7.20 (s, 1H), 7.08 (dd, J = 8.4, 1.5 Hz, 1H), 4.72 (t, J = 5.8 Hz, 1H), 4.30 (d, J = 5.2 Hz, 2H), 2.38 (s, 3H). .^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 154.1, 146.0, 143.2, 139.4, 138.3, 132.6, 129.2, 128.7, 127.8, 127.5, 126.4, 126.3, 119.5, 115.6, 111.3, 37.7, 21.4. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd $C_{22}H_{19}KNO_3S$ 416.0717; Found 416.0721.

***4-methyl-N-((5,6,7,8-tetrahydronaphtho[2,3-b]furan-3-yl)methyl)benzenesulfonamide: 4-methyl-N-((6,7,8,9-tetrahydronaphtho[2,1-b]furan-1-yl)methyl)benzenesulfonamide (Regioisomers (1:0.9 ratio))* (3u)**: White solid, 0.41 Rf in EtOAc:Hexane (1:4), 53 mg, 75% yield, mp = 127-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.72 (m, 4H), 7.33 (d, J = 10.5 Hz, 2H), 7.31 – 7.26 (m, 4H), 7.15 (d, J = 8.4 Hz, 1H), 7.11 (s, 1H), 7.00 (s, 1H), 6.97 (d, J = 8.5 Hz, 1H), 4.71 (t, J = 5.8 Hz, 1H), 4.65 (t, J = 5.6 Hz, 1H), 4.28 (dd, J = 5.7, 0.6 Hz, 2H), 4.20 (dd, J = 5.9, 0.7 Hz, 2H), 2.93 (t, J = 5.8 Hz, 2H), 2.86 (t, J = 8.0 Hz, 2H), 2.82 – 2.76 (m, 4H), 2.43 (s, 3H), 2.42 (s, 3H), 1.83 – 1.74 (m, 8H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.32, 154.27, 143.8, 143.74, 143.71, 142.5, 136.7, 136.6, 134.8, 132.3, 131.5, 130.3, 129.84, 129.82, 127.4, 127.3, 126.7, 124.6, 124.3, 119.1, 116.4, 115.4, 111.1, 109.1, 38.9, 37.6, 30.2, 29.7, 26.5, 23.5, 23.3, 23.1, 23.0, 21.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{21}NNaO_3S$ 378.1134; Found 378.1149.

***N-((5,6-dimethylbenzofuran-3-yl)methyl)-4-methylbenzenesulfonamide: N-((4,5-dimethylbenzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (Regioisomers (1:1 ratio))* (3v)**: White semi-solid, 0.45 Rf in EtOAc:Hexane (1:4), 47 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (t, J = 7.4 Hz, 3H), 7.33 (d, J = 6.4 Hz, 2H), 7.26 (t, J = 6.7 Hz, 3H), 7.19 (s, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.10 (s, 1H), 7.05 (d, J = 8.4 Hz, 1H), 4.86 (t, J = 5.7 Hz, 1H), 4.81 (t, J = 5.6 Hz, 1H), 4.29 (d, J = 5.7 Hz, 2H), 4.19 (d, J = 5.9 Hz, 2H), 2.41 (d, J = 5.0 Hz, 9H), 2.31 (d, J = 6.6 Hz, 6H), 2.27 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.7, 154.6, 143.9, 143.74, 143.68, 142.3, 136.8, 136.6, 134.1, 131.6, 130.9, 129.80, 129.78, 129.3, 127.33, 127.29, 127.1, 125.2, 124.2, 119.7, 116.2, 115.6, 112.0, 108.8, 39.0, 37.6, 21.6, 20.5, 20.0, 19.6, 15.7. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{18}H_{19}KNO_3S$ 368.0717; Found 368.0724.

(d) General procedure for the synthesis of Cyclopropa[*cd*]indole-carbaldehyde:

The substituted *N*-sulfonyl 1,2,3-triazolyl *N*-tethered cyclohexa-2,5-dienone **4** (0.2 mmol, 1.0 equiv.) and $Rh_2(Oct)_4$ (3.1 mg, 0.004 mmol, 2 mol%) in $CHCl_3$ (2 mL) under nitrogen atmosphere were charged to a reaction tube and the resulting reaction mixture was heated at 90 °C for 1h using an oil bath. After completion of the reaction, the mixture was cooled and evaporated under reduced pressure. The residue was purified by column chromatography (EtOAc/Hex 1:4) to afford the respective product.

***5a-methyl-3-oxo-1-tosyl-2,2a,2a1,2b,3,5a-hexahydro-1H-cyclopropa[cd]indole-2a-carbaldehyde* (5a)**: White solid, 0.55 Rf in EtOAc:Hexane (1:4), 62 mg, 93% yield, mp = 109-111 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.97 (s, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.73 (dd, J = 10.1, 0.7 Hz, 1H), 6.02 (dd, J = 10.2, 1.0 Hz, 1H), 4.35 (d, J = 11.7 Hz, 1H), 3.11 (d, J = 11.7 Hz, 1H), 2.79 (dd, J = 7.8, 0.7 Hz, 1H), 2.67 (dd, J = 7.8, 0.9 Hz, 1H), 2.43 (s, 3H), 1.94 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.8, 189.3, 147.4, 144.4, 136.9, 130.0, 128.3, 127.5, 62.4, 46.1, 45.4, 43.7, 36.2, 25.3, 21.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{17}NNaO_4S$ 354.0770; Found 354.0775.

***5a-butyl-3-oxo-1-tosyl-2,2a,2a1,2b,3,5a-hexahydro-1H-cyclopropa[cd]indole-2a-carbaldehyde* (5b)**: White solid, 0.61 Rf in EtOAc:Hexane (1:4), 66 mg, 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.99 (s, 1H), 7.67 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 10.2 Hz, 1H), 6.03 (d, J = 10.1 Hz, 1H), 4.33 (d, J = 11.6 Hz, 1H), 3.11 (d, J = 11.6 Hz, 1H), 2.85 (d, J = 7.8 Hz, 1H), 2.67 (d, J = 7.8 Hz, 1H), 2.42 (s, 4H), 2.15 – 2.08 (m, 1H), 1.47 – 1.35 (m, 4H), 0.93 (t, J = 6.9 Hz, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 194.0, 189.6, 147.6, 144.4, 136.8, 129.9, 129.0, 127.6, 66.2, 45.9, 45.6, 41.8, 36.8, 36.2, 27.1, 23.0, 21.7, 14.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{23}NNaO_4S$ 396.1240; Found 396.1240.

***3-oxo-5a-phenyl-1-tosyl-2,2a,2a1,2b,3,5a-hexahydro-1H-cyclopropa[cd]indole-2a-carbaldehyde* (5c)**: White solid, 0.32 Rf in EtOAc:Hexane (1:4), 71 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 7.52 (d, J = 8.1 Hz, 2H), 7.46 – 7.33 (m, 6H), 7.27 (d, J = 8.0 Hz, 2H), 6.35 (d, J = 10.3 Hz, 1H), 4.44 (d, J = 11.4 Hz, 1H), 3.31 (d, J = 11.4 Hz, 1H), 2.86 (d, J = 7.8 Hz, 1H), 2.65 (d, J = 7.8 Hz, 1H), 2.42 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.4, 189.2, 145.2, 144.5, 140.9, 135.9, 129.8, 129.7, 129.0, 128.7, 127.8, 125.7, 67.5, 47.1, 45.5, 45.0, 35.7, 21.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{19}NNaO_4S$ 416.0927; Found 416.0924.

(e) Gram-scale synthesis:

In a 50 mL round bottom flask equipped with magnetic stirring bar, was added **1a** (1.0 g, 2.78 mmol, 1.0 equiv.), $Rh_2(Oct)_4$ (10.8 mg, 0.014 mmol, 0.5 mol%), followed by $CHCl_3$ (20 mL). The reaction mixture was heated at 90 °C for 3h (In oil bath). After completion of the reaction, the resulting mixture was cooled, evaporated under reduced pressure and the residue was purified by column chromatography (EtOAc/Hex 1:4) to afford the respective product **2a** with 80% yield (0.7 g).

(f) One-pot synthesis:

6a (32.4 mg, 0.2 mmol, 1.0 equiv.), **7** (47.3 mg, 0.24 mmol, 1.2 equiv.), CuTc (2 mg, 0.01 mmol, 5 mol%), $Rh_2(Oct)_4$ (3.1 mg, 0.004 mmol, 2 mol%) and 5 mL $CHCl_3$ were charged to an oven-dried reaction tube equipped with a stir bar. The reaction mixture was stirred at room temperature for 1h and then heated at 90 °C

for another 1h using an oil bath. The resulting mixture was cooled, evaporated under reduced pressure and the residue was purified by column chromatography (EtOAc/Hex 1:4) to afford the respective product **2a** (47 mg, 75% yield).

(g) Functionalizations:

Synthesis of 8: To a solution of **2a** (126 mg, 0.4 mmol. 1.0 equiv.) in MeOH (10 mL) was added K_2CO_3 (220 mg, 1.6 mmol, 4.0 equiv.) and H_2O (288 mg, 16.0 mmol, 40.0 equiv.), the resulting reaction mixture was allowed to stir at room temperature till the complete consumption of starting material (appox. 30 mins.). Filter the reaction mixture to get the crude product **8** as white solid (56 mg, 88% yield).

***5-methylbenzofuran-3-carbaldehyde* (8):** White solid, 0.85 Rf in EtOAc:Heaxane (1:4), 28 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.14 (s, 1H), 8.22 (s, 1H), 7.98 (s, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 2.47 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.0, 155.7, 154.6, 134.8, 127.6, 123.6, 123.0, 122.4, 111.2, 21.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{10}H_8NaO_2$ 183.0416; Found 183.0420.

Synthesis of 9: The solution of **8** (32 mg, 0.2 mmol, 1.0 equiv.) in MeOH (5 mL) was allowed to cool at 0 ^{o}C with constant swirling then $NaBH_4$ (8 mg, 0.2 mmol, 1.0 equiv.) was added portion wise and stirred for 1h at the same temperature. After the completion of the reaction, the reaction mixture was quenched with saturated aq. NH_4Cl solution, extracted with EtOAc, dried over Na_2SO_4 and the combined organic phases were evaporated under vaccuo. The crude product was purified by column chromatography (EtOAc/Hex 1:4) to give **9** as white solid (31 mg, 96% yield).

***(5-methylbenzofuran-3-yl)methanol* (9):** White solid, 0.35 Rf in EtOAc:Heaxane (1:4), 31 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.46 (s, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 4.81 (d, J = 0.6 Hz, 2H), 2.46 (s, 3H), 1.80 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.2, 142.6, 132.4, 126.9, 126.0, 120.2, 119.8, 111.2, 56.1, 21.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{10}NaO_2$ 185.0573; Found 185.0577.

(h) Control experiment:

Reaction of 4-methyl-4-((1-tosyl-1*H*-1,2,3-triazol-4-yl)metho xy) Cyclohexa-2,5-dienone at 40 ^{o}C

1a (72 mg, 0.2 mmol, 1.0 equiv.) and $Rh_2(Oct)_4$ (3.1 mg, 0.004 mmol, 2 mol%) in $CHCl_3$ (2 mL) were added to a reaction tube under nitrogen. The resulting reaction mixture was heated at 40 ^{o}C for 2h using an oil bath. The resulting mixture was cooled, the solvent was evaporated under reduced pressure and purified by column chromatography (EtOAc/Hex 1:4) to afford the respective product **10** as white solid (16 mg, 45% yield).

***5a-methyl-3-oxo-2,2a,2a1,2b,3,5a-hexahydrocyclopropa[cd] benzofuran-2a-carbaldehyde* (10):** White solid, 0.30 Rf in EtOAc:Hexane (1:4), 16 mg, 45% yield, mp = 85-87 ^{o}C ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.11 (s, 1H), 6.34 (d, J = 10.1 Hz, 1H), 6.14 (d, J = 10.1 Hz, 1H), 4.68 (d, J = 10.9 Hz, 1H), 3.50 (d, J = 10.9 Hz, 1H), 2.92 (d, J = 7.7 Hz, 1H), 2.86 (d, J = 7.6 Hz, 1H), 1.64 (s, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 194.2, 190.7, 145.3, 128.8, 76.9, 62.8, 55.6, 43.2, 38.9, 25.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{11}O_3$ 179.0702; Found 179.0699.

SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website at DOI: Copies of ^{1}H and ^{13}C NMR spectra of all the compounds.

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