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PII: S0040-4020(17)30003-0

DOI: 10.1016/j.tet.2017.01.003

Reference: TET 28373

To appear in: *Tetrahedron*

Received Date: 12 November 2016

Revised Date: 2 January 2017

Accepted Date: 3 January 2017

Please cite this article as: Lal S, Namboothiri INN, Synthesis of annulated oxa-triquinanes and oxa-diquinanes via cascade Michael addition-intramolecular alkylation involving α-halodicyclopentadienones, *Tetrahedron* (2017), doi: 10.1016/j.tet.2017.01.003.

Graphical Abstract

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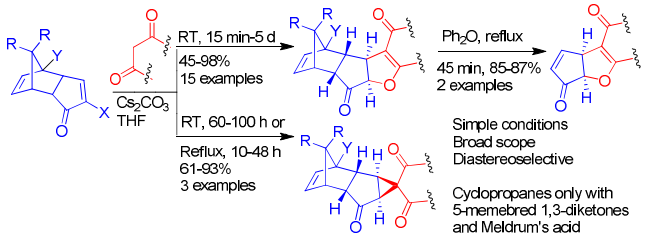

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Halodicyclopentadienone
1,3-Dicarbonyl compounds
Michael addition
Dihydrofurans
Oxa-triquinanes

ABSTRACT

Base Mediated Michael addition of 1,3-dicarbonyl compounds to α-halodicyclopentadienones followed by cyclization of the intermediate Michael adducts leads to novel annulated dihydrofurans as single diastereomers. Such fused dihydrofurans, which are also oxa-triquinanes and oxa-diquinanes, undergo retro-Diels-Alder reaction to give cyclopentadiene-eliminated products in excellent yield. Certain 1,3-dicarbonyl compounds exhibited a different reactivity profile with α-halodicyclopentadienones leading to spiro-cyclopropanes fused to dicyclopentadiene skeleton.

1. Introduction

Functionalized and fused furans are remarkable structural entities that are abundant in numerous natural products and designed molecules of biological significance.[1] The dihydrofuran moiety, in particular, is an extremely useful synthetic intermediate and is present in many plants and marine organisms.[2] Dihydrofurans are key substrates in the preparation of functionalized tetrahydrofurans with high stereoselectivity.[3] Annulated 2,3-dihydrofurans have been reported to function as flavoring agents and exhibit insecticidal and fish antifeedant properties.[4]

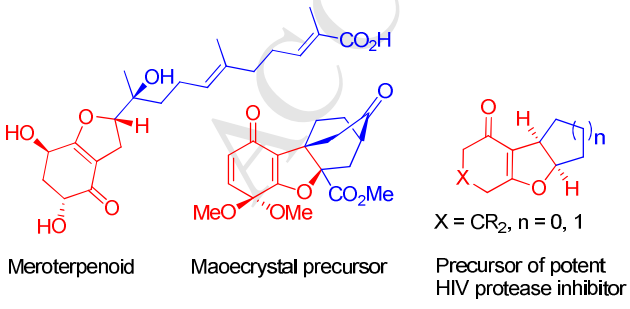


Figure 1. Selected dihydrofuran fused enone containing bioactive compounds

The 2,3-dihydrofuran moiety is an integral part of bioactive molecules such as histamine H_4R antagonist,[5] α-chymotrypsin inhibitor[6] and aflatoxins,[7] to name a few. A 2,3-dihydrofuran fused enone moiety is part of meroterpenoids[8] and advanced intermediates in the synthesis of Maoecrystal[9] and HIV protease inhibitors (Figure 1).[10]

Due to the presence of dihydrofuran moiety in bioactive molecules, including natural products, considerable efforts have been made towards the development of various approaches to its construction from readily available reactants and reagents. These approaches include intramolecular cyclization of intermediates arising from Michael addition,[11] interrupted Feist-Benary reaction,[12] nucleophilic ring opening,[13] aldol condensation,[5,14] radical mediated coupling[15] and other miscellaneous methods.[16]

From another perspective, *endo*-dicyclopentadiene is an excellent substrate for the synthesis of triquinane terpenoids such as hirsutene, coriolin etc possessing a cis-anti-cis fused cyclopentane framework.[17] The corresponding dicyclopentadienone[18] has also been employed in the synthesis of sesquiterpenoids,[19] pyranone based natural product sibrinone,[20] optically pure cross-conjugated cyclopentadienones,[21] and polycarbocyclic cage compounds.[22] Although the dienophilic reactivity of α-halodicyclopentadienone has been investigated,[23] the possibility of its other annulation pathways remained unexplored.[24] In particular, a cascade Michael addition-intramolecular alkylation, involving α-halodicyclopentadienone with various 1,3-dicarbonyl compounds leading to fused dihydrofurans, remains unreported, to our knowledge, despite its tremendous

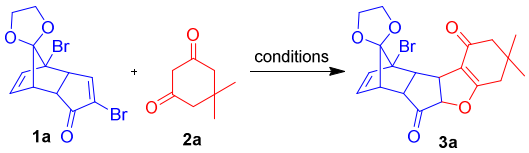
potential in the stereoselective synthesis of complex polycycles.

In the above scenario, we intended to investigate the application of α-halodicyclopentadienones as key substrates in the cascade Michael-alkylation with 1,3-dicarbonyl compounds for the stereoselective synthesis of novel annulated 2,3-dihydrofurans. Such 2,3-dihydrofurans, extending to an oxa-polyquinane skeleton, due to extensive ring fusion, are attractive intermediates for the synthesis of complex molecules including natural products.

2. Results and discussion

We started the synthesis of dihydrofuran containing polycycles *via* Michael addition of 1,3-dicarbonyl compounds to halodicyclopentadienones under mild conditions. *α*-Bromoenone **1a**[25] and dimedone **2a** were chosen as the model substrates (Table 1).

Table 1. Optimization of reaction conditions[a]



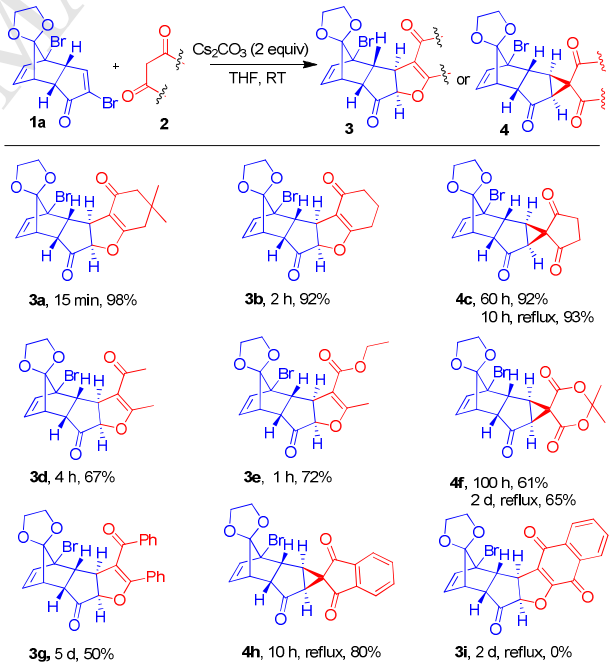
entry	base (equiv)	solvent	time	% Yield[b]
1	K_2CO_3 (2)	THF	5 h	93
2	**Cs_2CO_3 (2)**	**THF**	**15 min**	**98**
3	DABCO (2)	THF	22 h	88
4	DMAP (2)	THF	24 h	86
5	DBU (2)	THF	50 min	91
6	NEt_3 (2)	THF	48 h	90
7	Cs_2CO_3 (1)	THF	48 h	98[c]
8	Cs_2CO_3 (2)	CH_3CN	50 h	94
9	Cs_2CO_3 (2)	DCM	48 h	65
10	Cs_2CO_3 (2)	Toluene	50 h	72

[a]The reactions were carried out with 0.3 mmol of α-bromoenone **1a** and 0.36 mmol of 1,3-dicarbonyl compound **2a**. [b]Yield after purification by trituration with 5% EtOAc-petroleum ether. [c]α-Bromoenone **1a** was consumed within 30 min and the Michael adduct obtained was further converted to final product **3a** by adding an additional equiv of base.

To our delight, the reaction proceeded smoothly in THF at room temperature with 2 equiv of K_2CO_3 as base affording **3a** in 93% yield in 5 h (entry 1). The effect of base on the rate of reaction and product yield was evaluated by screening Cs_2CO_3 and amine bases such as DABCO, DMAP, DBU and Et_3N (entries 2-6). With 2 equiv of Cs_2CO_3 as base the reaction was complete within 15 min to furnish the product in 98% yield (entry 2). Among organic bases DBU was superior both in terms of reaction time (50 min) and product yield (91%, entry 5) while others required longer time (22-48 h) and the yield remained ≤90% (entries 3-4 and 6). Having confirmed Cs_2CO_3 to be the best base, we proceeded to investigate the quantity of base required and the effect of solvent (entries 7-10). With one equiv of Cs_2CO_3, the reaction stopped at the Michael addition stage and an additional equivalent was required to complete the cyclization (entry 7). Longer reaction time (48-50 h) and/or lower yields (65-72%) were encountered with solvents such as CH_3CN and less polar solvents such as DCM and toluene (entries 8-10). Finally, the optimization studies confirmed that 2 equiv of Cs_2CO_3 as base in THF as solvent constitute the best conditions for our reaction.

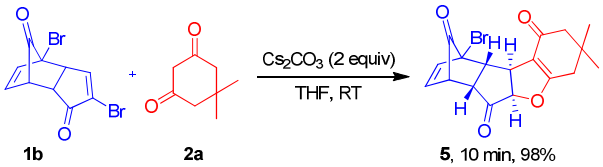
The scope of the above reaction was investigated first with enone **1a** as the representative acceptor and various cyclic and open chain 1,3-dicarbonyls **2** as the donors (Table 2). Besides dimedone **2a** which delivered the highly functionalized polycycle **3a** in 98% yield, cyclohexanedione **2b** reacted with **1a** to afford the product **3b** in 92% yield in 2 h. Acetylacetone **2d** and ethylacetoacetate **2e** also reacted with **1a** over 1-4 h and furnished the products **3d** and **3e** respectively in good (67-72%) yield. Although benzoylacetophenone **2g** required long reaction time (5 d), it too provided the corresponding fused polycycle **3g** in satisfactory (50%) yield. On the other hand, hydroxynaphthaquinone **2i** did not react with **1a** under our experimental conditions and also upon reflux for 2 days. Surprisingly, treatment of **1a** with cyclopentan-1,3-dione **2c**, Meldrum's acid **2f** and indan-1,3-dione **2h** did not lead to the expected fused product **3**. Instead, the spiro compounds **4c**, **4f** and **4h** were formed in good to excellent yield (61-93%).

Table 2. Scope of 1,3-dicarbonyls



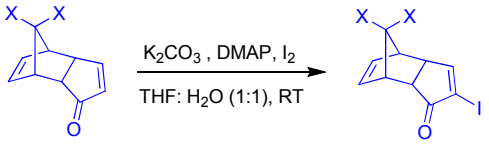
[a]The reactions were carried out with 0.3 mmol of α-bromoenone **1a** and 0.36 mmol of 1,3-dicarbonyl compound **2**. [b]Yield after purification by trituration with 5-10% EtOAc-petroleum ether or silica gel column chromatography.

The diketone **1b**,[25-26] derived from enone **1a**, also reacted exceptionally well with dimedone **2a** and afforded the fused polycycle **5** in 98% yield in just 10 min (Scheme 1).



Scheme 1

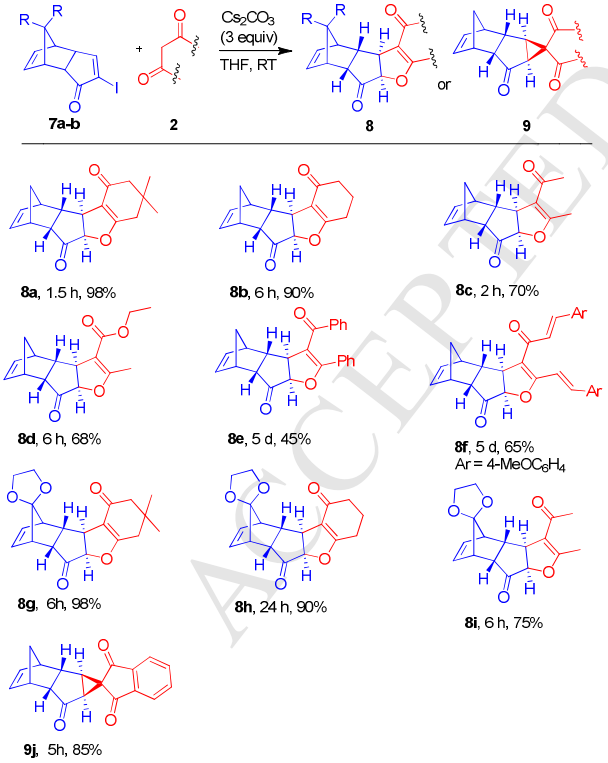
Subsequently, iododicyclopentadienones **7a-b** were readily prepared from known dicyclopentadienones **6a-b**[18,25] (Scheme 2).



Scheme 2. Preparation of iodoenones

The reactivity of **7a-b** with various 1,3-dicarbonyl compounds **2** was then investigated (Table 3). Thus iodoenone **7a** reacted smoothly with dimedone **2a** and cyclohexanedione **2b** and afforded the corresponding fused polycycles **8a** and **8b** in excellent yield (98% and 90% respectively).

Table 3. Scope of enone and 1, 3-dicarbonyls

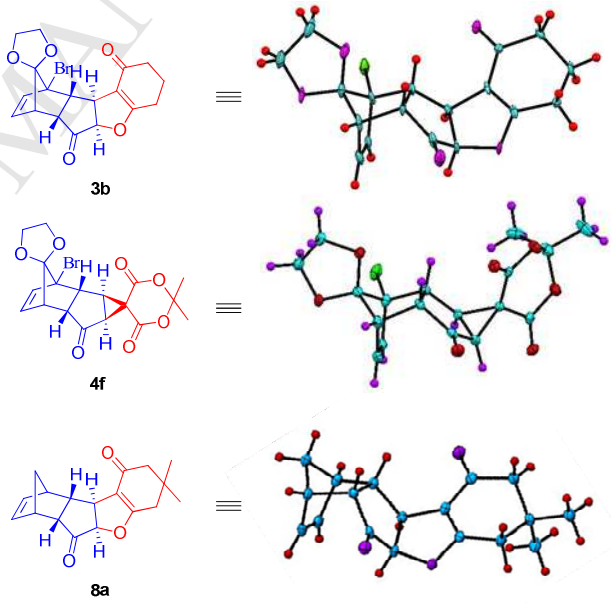


[a]The reactions were carried out with 0.3 mmol of *α*-bromoenone **7a** or **7b** and 0.36 mmol of 1,3-dicarbonyl compound **2**. [b]Yield after purification by trituration with 2-5% EtOAc-petroleum ether or silica gel column chromatography.

The yields of polycycles **8c**, **8d** and **8f**, derived from iodoenone **7a** and 1,3-dicarbonyl compounds **2d**, **2e** and curcumin analog **2j** were also good (70%, 68% and 65% respectively) although the reaction times were short (2 h and 6 h) for the formation of **8c** and **8d** and long (5 d) for the formation of **8f**. The reaction of **7a** with benzoylacetophenone **2g** was also sluggish (5 d) delivering the desired product **8e** in moderate yield (45%). Further, the reaction of iodoenone **7b** with representative 1,3-dicarbonyl compounds, viz dimedone **2a**, cyclohexanedione **2b** and acetylacetone **2d** was investigated. This led to the formation of polycycles **8g**, **8h** and **8i** in 98%, 90% and 75% yields respectively. That the reaction pathway (fused dihydrofuran vs spirocyclopropane) is sensitive to the nature of 1,3-dicarbonyl compounds as observed in the case of enone **1a** is reflected in the case of enone **7** as well. Thus the reaction of **7a** with indan-1,3-dione **2h** afforded the spirocyclopropane **9j** in 85% yield.

The structure and stereochemistry of the fused products and spiro products were unambiguously established by single crystal X-ray analysis of representative compounds **3b**, **4f** and **8a** (Table 4).

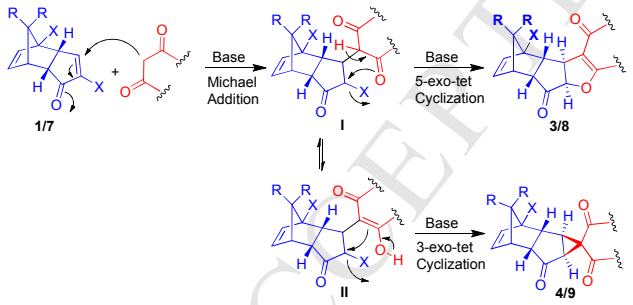
Table 4. Single crystal X-ray structures and selected data for **3b**, **4f** and **8a**



	3b	4f	8a
CCDC No	1513035	1513047	1513046
Empirical formula	$C_{18}H_{17}BrO_5$	$C_{18}H_{17}BrO_7$	$C_{18}H_{20}O_3$
Formula weight	393.23	425.22	284.34
T [K]	100(2) K	150(2) K	100(2) K
λ [Å]	0.71073	0.71073	0.71070
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P 1 2_1/n 1	P 2_1/c	P 1 2_1/c 1
a [Å]	10.1122(3)	13.2374(5)	9.126(2)
b [Å]	22.0892(5)	11.7385(5)	6.5778(15)
c [Å]	21.5138(5)	11.2250(4)	23.812(5)
α [°]	90	90	90
β [°]	97.673	104.070(4)	92.039(4)

γ [°]	90	90	90
V [Å^3]	4747(2)	1691.89(12)	1428.5(5)
Z	12	4	4
ρ_{calcd} [mg/m^3]	1.645	1.669	1.322
μ [mm^{-1}]	2.615	2.469	0.089
F(000)	2400	864	608
θ [°]	3.02 to 29.18	3.236 to 24.996	4.47 to 25.00
Index ranges	-12<=h<=12, -26<=k<=26, -25<=l<=25	-5<=h<=14, -13<=k<=13, -13<=l<=13	-10<=h<=10, -7<=k<=7, -28<=l<=28
Reflections collected	74458	7873	16705
Independent reflections	8360 [R(int) = 0.0852]	2960 [R(int) = 0.0294]	2493 [R(int) = 0.0432]
Completeness to theta	99.7 % θ = 29.18°	99.6 % θ = 24.996°	99.2 % θ = 25.00°
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8360 / 0 / 649	2960 / 0 / 243	2493 / 0 / 190
Goodness-of-fit on F^2	1.061	0.917	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.1002	R1 = 0.0249 wR2 = 0.0604	R1 = 0.0383, wR2 = 0.0977
R indices (all data)	R1 = 0.0487, wR2 = 0.1060	R1 = 0.0272 wR2 = 0.0621	R1 = 0.0430, wR2 = 0.1014
Largest diff. peak and hole ([e Å^{-3}])	10.835 and -5.520	0.346 and -0.269	0.284 and -0.187

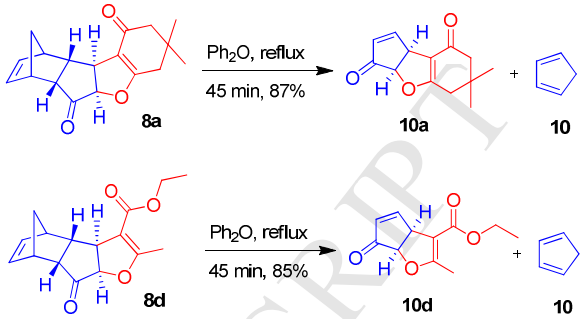
A mechanism for the formation of fused dihydrofurans **3/8** and spiro-cyclopropanes **4/9** is proposed in Scheme 3. Thus, base mediated 1,4-addition of β-dicarbonyl compound **2** to enone **1/7** generates the intermediate Michael adduct whose keto and enol forms **I** and **II**, respectively, are in tautomeric equilibrium. While intramolecular O-alkylation of **I** in a 5-exo-tet fashion delivers the fused product **3/8** through an overall [3+2] annulation, intramolecular C-alkylation of **II** in a 3-exo-tet fashion leads to cyclopropanes **4/9** in an overall [2+1] annulation.



Scheme 3. Proposed mechanism

Although **2a** and majority of other β-dicarbonyl compounds exhibited 1,3-binucleophilic character and afforded fused dihydrofurans **3/8**, cyclopentanedione **2c**, Meldrum's acid **2f** and indanedione **2h** displayed a different reactivity profile, 1,1-binucleophilic character, and delivered spiro compounds **4c**, **4f**, **4h** and **9j**. This is attributable to the geometric constraints associated with the intermediate Michael adducts to undergo oxa-Michael addition.

Finally, synthesis of fused and functionalized oxadiquinanes was successfully carried out via retro-Diels-Alder reaction of representative dihydrofurans **8a** and **8d** (Scheme 4). Thus refluxing pentacycle **8a** in diphenyl ether for 45 min led to the formation of fused tricycle **10a** in excellent yield. Under the same conditions, tetracycle **8d** afforded fused bicycle **10d** in 85% yield.



Scheme 4. Retro-Diels-Alder reaction

3. Conclusions

In conclusion, α-halodicyclopentadienones reacted with various open chain and cyclic 1,3-dicarbonyl compounds under basic conditions to afford dihydrofuran containing linear tetracycles and pentacycles as single diastereomers in good to excellent yields in most cases. The reaction sequence involved Michael addition of the 1,3-dicarbonyl compound to α-halodicyclopentadienone followed by enolization and intramolecular nucleophilic substitution of the halogen (O-alkylation). However, the reaction of α-halodicyclopentadienones with 1,3-dicarbonyls such as cyclopentan-1,3-dione, indan-1,3-dione and Meldrum's acid led to the formation of spirocyclopropanes. Selected polycycles have been successfully transformed to fused and functionalized oxadiquinanes through retro-Diels-Alder reaction under thermal conditions.

4. Experimental section

4.1. General experimental details.

The melting points recorded are uncorrected. NMR spectra (^{1}H, ^{1}H decoupled ^{13}C, APT and ^{1}H- ^{1}H NOESY, COSY, ^{1}H-^{13}C HSQC) were recorded with TMS as the internal standard. The coupling constants (J values are given in Hz). High resolution mass spectra were recorded under ESI Q-TOF conditions. X-ray data were collected on a diffractometer equipped with graphite monochromated Mo Kα radiation. The structure was solved by direct methods shelxs97 and refined by full-matrix least squares against F^2 using shelxl97 software. *α*-Bromoenone **1a** was synthesized from readily available cyclopentanone in four steps as reported by Chapman and co-workers.[25] Diketone **1b** was synthesized in five steps from cyclopentanones as reported in the literature.[25,26] Enones **6a**[18] and **6b**[25,27] were also prepared by literature procedures.

4.2. General procedure for the synthesis of α-iodoenones (7a-b).[28]

To a solution of enone **6** (3.5 mmol, 1 equiv, 511 mg of **6a** or 714 mg of **6b**) in THF: H_2O (1:1, 20 mL) was added K_2CO_3 (731 mg, 5.3 mmol, 1.5 equiv) and DMAP (128 mg, 1.05 mmol, 0.3 equiv) followed by molecular iodine (1.058 g, 4.2 mmol, 1.2 equiv). After completion of reaction (8 h for **7a** and 12 h for **7b**), monitored by TLC), saturated aqueous sodium sulfite (10 mL) was added and the aqueous layer was extracted with ethyl acetate (5 × 50 mL). The combined organic layer was washed with brine (2 × 10 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography by eluting with 2-10% EtOAc-petroleum ether.

4.2.1. *2-Iodo-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one* (**7a**). Yellow solid; 818 mg, 86%; mp 51-52 °C; IR (neat, cm^{-1}) 3059 (w), 2980 (s), 2937 (m), 2869 (w), 1712 (vs), 1566 (w), 1298 (m), 1285 (m), 1276 (m), 1123 (w), 1019 (w), 961 (w), 743 (s), 726 (s), 691 (s); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.59 (d, *J* = 8.6 Hz, 1H), 1.72 (d, *J* = 8.6 Hz, 1H), 2.85 (t, *J* = 5.1 Hz, 1H), 2.99-3.01 (unresolved m, 1H), 3.23-3.25 (unresolved m, 1H), 3.41-3.43 (m, 1H), 5.81 (dd, *J* = 5.5, 2.9 Hz, 1H), 5.89 (dd, *J* = 5.5, 2.9 Hz, 1H), 7.70 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 44.5, 45.3, 47.3, 50.2, 52.0, 104.6, 132.9, 132.9, 170.2, 204.1; HRMS calcd for $C_{10}H_9INaO$ (MNa^+) 294.9590, found 294.9591.

4.2.2. *2-Iodo-3a,4,7,7a-tetrahydro-1H-spiro[4,7-methanoindene-8,2'-[1,3]dioxolan]-1-one* (**7b**). Yellow solid; 820 mg, 71%; mp 97-98 °C; IR (neat, cm^{-1}) 2983 (w), 2887 (w), 1709 (vs), 1565 (w), 1297 (vs), 1266 (m), 1100 (s), 1072 (s), 1006 (m), 728 (m), 693 (s); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.82-2.85 (m, 1H), 3.02 (t, *J* = 5.0 Hz, 1H), 3.04-3.06 (m, 1H), 3.59 (td, *J* = 4.7, 2.9 Hz, 1H), 3.81-3.84 (m, 2H), 3.92-3.94 (m, 2H), 5.92, 5.98 (ABqd, *J* = 6.4, 3.3 Hz, 2H), 7.69 (d, *J* = 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 44.5, 47.2, 48.8, 49.8, 64.7, 65.2, 106.4, 127.2, 131.1, 131.1, 168.7, 203.2; HRMS calcd for $C_{12}H_{11}INaO_3$ (MNa^+) 352.9645, found 352.9644.

4.3. General procedure for the synthesis of polycycles 3, 4, 5, 8 and 9.

To a solution of 1,3-diketone **2** (0.36 mmol, 1.2 equiv) and Cs_2CO_3 (196 mg, 0.6 mmol, 2 equiv for **1** and 294 mg, 0.9 mmol, 3 equiv for **7**) in THF (4 mL) was added to *α*- haloenone **1a, 1b, 7a** or **7b** (0.3 mmol, 1 equiv, 108 mg of **1a**, 95 mg of **1b,** 82 mg of **7a** or 99 mg of **7b**) at room temperature. Then the reaction mixture was stirred at ambient temperature (see Tables 2 and 3). After completion of the reaction (monitored by TLC), the solvent was evaporated in vacuo. The reaction mixture was then extracted with ethyl acetate (3 × 20 mL), the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The residue was purified by trituration with 2-10% EtOAc in petroleum ether or silica gel column chromatography by eluting with 5-30% EtOAc in petroleum ether (gradient elution).

4.3.1. *10-Bromo-3,3-dimethyl-3,4,5a,6a,7,10,10a,10b-octahydro-1H-spiro[7,10-methanoindeno[2,1-b]benzofuran-11,2'-[1,3] dioxolane]-1,6(2H)-dione* (**3a**). White solid; 123 mg, 98%; mp 155-156 °C; IR (neat, cm^{-1}) 2959 (s), 2895 (s), 1750 (vs), 1654 (vs), 1635 (vs), 1396 (s), 1267 (s), 1218 (s), 1155 (m), 1141 (s), 1028 (m), 982 (w), 904 (w), 735 (s); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.03 (s, 3H), 1.05 (s, 3H), 2.15-2.34 (m, 4H), 2.92-2.94 (m, 1H), 3.09-3.12 (m, 1H), 3.58 (d, *J* = 8.4 Hz, 1H), 3.73 (d, *J* = 9.5 Hz, 1H), 3.86-3.95 (m, 1H), 3.96-3.99 (m, 1H), 4.16-4.24 (m, 2H), 4.46 (d, *J* = 9.5 Hz, 1H), 6.17 (dd, *J* = 6.5, 3.6 Hz, 1H), 6.30 (d, *J* = 6.5 Hz, 1H), Confirmed by ^{1}H-^{1}H COSY experiment; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.1, 29.2, 34.3, 37.8, 41.9, 48.6, 50.6, 51.5, 52.3, 65.9, 66.6, 68.5, 87.8, 112.0, 126.2, 133.6, 138.1, 176.0, 194.2, 216.0; HRMS calcd for $C_{20}H_{22}BrO_5$ (MH^+) 421.0645, found 421.0644.

4.3.2. *10-Bromo-3,4,5a,6a,7,10,10a,10b-octahydro-1H-spiro [7,10-methanoindeno[2,1-b]benzofuran-11,2'-[1,3]dioxolane]-1,6(2H)-dione* (**3b**). White solid; 108 mg, 92%; mp 248-249 °C; IR (neat, cm^{-1}) 2964 (m), 2947 (m), 2894 (m), 1749 (vs), 1650 (vs), 1630 (vs), 1392 (s), 1270 (s), 1148 (m), 1022 (w), 743 (w); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.01 (m, 2H), 2.34-2.47 (m, 4H), 2.95-2.97 (m, 1H), 3.14 (m, 1H), 3.62 (d, *J* = 8.4 Hz, 1H), 3.72 (d, *J* = 9.5 Hz, 1H), 3.88-3.93 (m, 1H), 3.94-4.00 (m, 1H), 4.18-4.25 (m, 2H), 4.44 (d, *J* = 9.5 Hz, 1H), 6.20 (dd, *J* = 6.5, 3.7 Hz, 1H), 6.32 (d, *J* = 6.5, 1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.7, 24.0, 37.0, 42.0, 48.6, 50.6, 52.4, 65.9, 66.6, 68.5, 87.5, 113.4, 126.2, 133.6, 138.1, 177.0, 194.9, 215.2; HRMS calcd for $C_{18}H_{17}BrNaO_5$ (MNa^+) 415.0152, found 415.0151; Selected X-ray data: $C_{18}H_{17}BrO_5$, M = 393.23, Monoclinic, space group P 1 2_1/n 1, a = 10.1122(3) Å, b = 22.0892(5) Å, c = 21.5138(5) Å, α =90°, β = 97.673 (4)°, γ = 90°, V = 4747(2) $Å^3$, Z = 12, ρcald = 1.645 mg/m^3, F(000) = 2400, λ = 0.71073 Å, μ = 2.615 mm^{-1}, total/unique reflections = 74458/8360. Final R indices [I>2sigma(I)]: R1 = 0.0403, wR2 = 0.1002. R (all data): R1 = 0.0487, wR2 = 0.1060.

4.3.3. *2'-Bromo-1a',1b',2',5',5a',6a'-hexahydro-6'H-dispiro[cyclopentane-1,1'-[2,5]methanocyclo-propa[a]indene-7',2''-[1,3]dioxolane]-2,5,6'-trione* (**4c**). White solid; 105 mg, 93%; mp 269-270 °C; IR (neat, cm^{-1}) 2913 (w), 1735 (s), 1714 (vs), 1359 (m), 1269 (s), 1148 (m), 1089 (m), 1021 (w), 899 (w), 738 (w), 710 (w); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.65 (d, *J* = 5.6 Hz, 1H), 2.77 (d, *J* = 5.6 Hz, 1H), 2.79-2.96 (m, 4H), 2.97-2.99 (m, 1H), 3.18 (d, *J* = 6.6 Hz, 1H), 3.56 (t, *J* = 6.0 Hz, 1H), 3.90-3.95 (m, 1H), 3.99-4.02 (m, 1H), 4.14-4.21 (m, 2H), 6.08 (dd, *J* = 6.5 Hz, 3.6 Hz, 1H), 6.23 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 35.4, 36.4, 46.2, 46.3, 47.2, 48.0, 50.3, 54.0, 65.8, 66.6, 68.0, 126.3, 131.5, 135.4, 207.7, 209.1, 210.0; HRMS calcd for $C_{17}H_{15}BrNaO_5$ (MNa^+) 400.9995, found 400.9983.

4.3.4. *3-Acetyl-4-bromo-2-methyl-3b,4,7,7a-tetrahydro-3aH-spiro[4,7-methanoindeno[2,1-b]furan-9,2'-[1,3]dioxolan]-8 (8aH)-one* (**3d**). White solid; 76 mg, 67%; mp 130-131 °C; IR (neat, cm^{-1}) 2984 (m), 2964 (m), 2899 (m), 1748 (vs), 1668 (s), 1615 (vs), 1597 (vs), 1383 (m), 1267 (s), 1221 (s), 1140 (m), 1023 (s), 930 (m), 733 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.16 (s, 3H), 2.37 (s, 3H), 2.95-2.98 (m, 1H), 3.11-3.15 (m, 1H), 3.40 (d, *J* = 8.4 Hz, 1H), 3.85 (d, *J* = 10.0 Hz, 1H), 3.88-4.02 (m, 2H), 4.15-4.24 (m, 2H), 4.32 (d, *J* = 10.0, 1H), 6.18 (dd, *J* = 6.2, 3.7 Hz, 1H), 6.31 (d, *J* = 6.2, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.3, 30.1, 45.4, 48.3, 51.7, 52.1, 65.9, 66.7, 69.2, 85.3, 114.2, 126.1, 134.1, 137.6, 168.4, 194.5, 216.2; HRMS calcd for $C_{17}H_{18}BrO_5$ (MH^+) 381.0332, found 381.0332.

4.3.5. *Ethyl-4-bromo-2-methyl-8-oxo-3b,4,7,7a,8,8a-hexahydro-3aH-spiro[4,7-methanoindeno[2,1-b]furan-9,2'-[1,3]dioxolane]-3-carboxylate* (**3e**). White solid; 88 mg, 72%; mp 151-152°C; IR (neat, cm^{-1}) IR (neat, cm^{-1}) 2979 (m), 2920 (m), 2905 (m), 1751 (s), 1698 (vs), 1638 (s), 1380 (w), 1324 (w), 1266 (s), 1222 (m), 1136 (s), 1079 (s), 1025 (m), 953 (w), 772 (m), 737 (m), 714 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, *J* = 7.1 Hz, 3H), 2.16 (s, 3H), 2.94-2.96 (m, 1H), 3.10-3.14 (m, 1H), 3.51 (d, *J* = 8.5 Hz, 1H), 3.76 (d, *J* = 10.0 Hz, 1H), 3.88-3.97 (m, 1H), 3.98-4.01 (m, 1H), 4.15-4.28 (m, 4H), 4.31 (d, *J* = 10.0 Hz, 1H), 6.18 (dd, *J* = 6.5 Hz, 3.6 Hz, 1H), 6.30 (dd, *J* = 6.5, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.4, 14.8, 44.9, 48.4, 51.5, 52.0, 60.1, 65.9, 66.7, 69.0, 85.4, 103.9, 126.0, 133.8, 137.9, 165.1, 169.2, 216.7; HRMS calcd for $C_{18}H_{19}BrNaO_6$ (MNa^+) 433.0257, found 433.0256.

4.3.6. *2'-Bromo-2,2-dimethyl-1a',1b',2',5',5a',6a'-hexahydro-6'H-dispiro[[1,3]dioxane-5,1'-[2,5]-methanocyclopropa[a]indene-7', 2''-[1,3] dioxolane]-4,6,6'-trione* (**4f**). White solid; 82 mg, 65%;

mp 223-225 °C; IR (neat, cm^{-1}) 2920 (m), 2900 (m), 1774 (m), 1741 (vs), 1358 (w), 1269 (s), 1246 (m), 1159 (w), 1014 (w), 902 (w), 731 (m), 714 (s); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.80 (s, 3H), 1.88 (s, 3H), 2.80 (d, *J* = 6.1 Hz, 1H), 2.97-2.99 (m, 1H), 3.00 (d, *J* = 6.1 Hz, 1H), 3.22 (d, *J* = 6.8 Hz, 1H), 3.51 (t, *J* = 6.0 Hz, 1H), 3.91-3.95 (m, 1H), 3.96-4.03 (m, 1H), 4.14-4.21 (m, 2H), 6.18 (dd, *J* = 6.5, 3.6 Hz, 1H), 6.24 (d, *J* = 6.5 Hz, 1H), ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.6, 27.8, 36.3, 45.1, 45.7, 48.0, 48.4, 55.2, 65.9, 66.6, 67.9, 105.9, 126.3, 133.4, 135.7, 164.2, 165.1, 207.7; HRMS calcd for $C_{18}H_{17}BrNaO_7$ (MNa^+) 447.0050, found 447.0054; Selected X-ray data: $C_{18}H_{17}BrO_7$, M = 425.22, Monoclinic, space group P $2_1/c$, a = 13.2374(5) Å, b = 11.7385(5) Å, c = 11.2250(4) Å, α = 90°, β =104.070(4)°, γ = 90°, V =1691.89(12) $Å^3$, Z = 4, ρcald =1.669 mg/m^3, F(000) = 864, λ = .71073 Å, μ = 2.469 mm^{-1}, total/unique reflections = 7873/2960, Final R indices [I>2sigma(I)]: R1 = 0.0249, wR2 = 0.0604. R (all data): R1 = 0.0272, wR2 = 0.0621.

4.3.7. *3-Benzoyl-4-bromo-2-phenyl-3b,4,7,7a-tetrahydro-3aH-spiro[4,7-methanoindeno[2,1-b]furan-9,2'-[1,3]dioxolan]-8 (8aH)-one* (**3g**). White solid; 75 mg, 50%; mp 207-208 °C; IR (neat, cm^{-1}) 3058 (m), 2985 (m), 2960 (m), 2897 (m), 1749 (vs), 1623 (vs), 1594 (s), 1575 (m), 1358 (s), 1266 (s), 1225 (m), 1145 (m), 1099 (s), 1024 (s), 890 (m), 736 (vs), 698 (vs); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.00-3.03 (m, 1H), 3.23-3.26 (m, 1H), 3.42 (d, *J* = 8.4 Hz, 1H), 3.88-3.94 (m, 1H), 3.88-3.99 (m, 1H), 4.16-4.27 (m, 2H), 4.34 (d, *J* = 9.8 Hz, 1H), 4.55 (dd, *J* = 9.8, 1.2 Hz, 1H), 6.26 (dd, *J* = 6.5, 3.7 Hz, 1H), 6.40 (dd, *J* = 6.5, 1.2 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 2H), 7.16-7.22 (m, 3H), 7.25-7.29 (m, 1H), 7.48 (dd, *J* = 8.3, 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 48.5, 48.6, 50.8, 52.2, 65.9, 66.6, 68.4, 84.9, 112.3, 126.2, 127.9, 128.0, 128.9, 129.2, 129.5, 130.7, 132.2, 133.7, 138.1, 138.5, 165.1, 192.6, 216.8; HRMS calcd for $C_{27}H_{21}BrNaO_5$ (MNa^+) 527.0465, found 527.0463.

4.3.8. *2'-Bromo-1a',1b',2',5',5a',6a'-hexahydro-6'H-dispiro [indene-2,1'-[2,5]methanocyclopropa[a]-indene-7',2''-[1,3] dioxolane]-1,3,6'-trione* (**4h**). White solid; 102 mg, 80%; mp 232-233 °C; IR (neat, cm^{-1}) 3055 (w), 2985 (w), 1732 (vs), 1656 (m), 1638 (m), 1265 (vs), 1245 (vs), 1046 (s), 737 (s); ^1H NMR ($CDCl_3$, 500 MHz) δ 2.70, 2.85 (ABq, *J* = 5.5 Hz, 2H), 2.86-3.03 (m, 1H), 3.30 (d, *J* = 6.5 Hz, 1H), 3.72 (t, *J* = 6.5 Hz, 1H), 3.90-3.98 (m, 1H), 4.00-4.03 (m, 1H), 4.13-4.21 (m, 2H), 6.11 (dd, *J* = 6.5, 3.8 Hz, 1H), 6.28 (d, *J* = 6.5 Hz, 1H), 7.81-7.84 (m, 2H), 7.92-7.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 40.7, 43.6, 46.7, 47.2, 48.0, 53.9, 65.8, 66.5, 68.3, 123.0, 123.3, 126.3, 131.5, 135.5, 135.6, 135.7, 140.7, 142.9, 194.7, 195.4, 210.5; Confirmed by ^1H-^1H COSY and ^1H-^{13}C HSQC experiments; HRMS calcd for $C_{21}H_{15}BrO_5Na$ (MNa^+) 448.9995, found 448.9995.

4.3.9. *10-Bromo-3,3-dimethyl-3,4,6a,7,10,10a-hexahydro-1H-7,10-methanoindeno[2,1-b]benzofuran-1,6,11(2H,5aH,10bH)-trione* (**5**). White solid; 110 mg, 98%; mp 171-172 °C; IR (neat, cm^{-1}) 2986 (m), 1729 (vs), 1710 (vs), 1372 (m), 1255 (m), 1044 (m), 1025 (m); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.06 (s, 3H), 1.07 (s, 3H), 2.20, 2.21 (ABq, *J* = 16.2 Hz, 2H), 2.26, 2.34 (ABq, *J* = 17.1 Hz, 2H), 3.12 (dd, *J* = 9.0, 3.9 Hz, 1H), 3.46-3.51 (m, 2H), 3.92 (d, *J* = 9.6 Hz, 1H), 4.51 (d, *J* = 9.6 Hz, 1H), 6.53 (dd, *J* = 6.8, 3.9 Hz, 1H), 6.61 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.1, 29.2, 34.4, 37.8, 43.1, 47.1, 47.3, 49.4, 51.4, 62.6, 87.2, 110.7, 132.7, 137.1, 176.5, 192.2, 194.3, 213.8; HRMS calcd for $C_{18}H_{18}BrO_4$ (MH^+) 377.0383, found 377.0384.

4.3.10. *3,3-Dimethyl-3,4,5a,6a,7,10,10a,10b-octahydro-1H-7,10-methan oindeno[2,1-b]benzofuran-1,6(2H)-dione* (**8a**). White solid; 84 mg, 98%; mp 158-159 °C; IR (neat, cm^{-1}) 2957 (s), 2870 (m), 1743 (vs), 1634 (vs), 1396 (s), 1343 (m), 1208 (w), 1160 (m), 1143 (m), 1031 (m), 974 (m), 744 (m), 708 (m); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.02 (s, 3H), 1.04 (s, 3H), 1.43, 1.54 (ABq, *J* = 8.5 Hz, 2H), 2.13-2.27 (m, 4H), 2.85 (dd, *J* = 8.5, 4.8 Hz, 1H), 3.22-3.30 (m, 3H), 3.46 (d, *J* = 9.6 Hz, 1H), 4.44 (d, *J* = 9.6 Hz, 1H), 6.12, 6.26 (ABqd, *J* = 5.6, 2.8 Hz, 2H); Confirmed by ^1H-^1H COSY experiment; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.1, 29.1, 34.4, 37.8, 43.2, 46.2, 47.2, 48.2, 51.4, 51.8, 53.3, 88.4, 113.6, 136.5 (×2), 176.2, 195.0, 217.4; HRMS calcd for $C_{18}H_{20}NaO_3$ (MNa^+) 307.1305, found 307.1302; Selected X-ray data: $C_{18}H_{20}O_3$, M = 284.34, Monoclinic, space group P $1\ 2_1/c\ 1$ a = 9.126(2) Å, b = 6.5778(15) Å, c = 23.812(5) Å, α =90°, β = 92.039(4)°, γ = 90°, V = 1428.5(5) $Å^3$, Z = 4, ρcald = 1.322 mg/m^3, F(000) = 608, λ = 0.71070 Å, μ = 0.089 mm^{-1}, total/unique reflections = 16705/2493, Final R indices [I>2sigma(I)]: R1 = 0.0383, wR2 = 0.0977. R (all data): R1 = 0.0430, wR2 = 0.1014.

4.3.11. *10b-Octahydro-1H-7,10-methanoindeno[2,1-b]benzo furan-1,6 (2H) -dione* (**8b**). White solid; 70 mg, 90%; mp 151-152 °C; IR (neat, cm^{-1}) 2945 (m), 2870 (m), 1744 (s), 1633 (vs), 1396 (s), 1171 (m), 1005 (m), 981 (m), 737 (m), 708 (m); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.43 (d, *J* = 7.5 Hz, 1H), 1.56 (d, *J* = 7.5 Hz, 1H), 1.95-2.00 (m, 2H), 2.27-2.46 (m, 4H), 2.87 (dd, *J* = 8.3, 4.5 Hz, 1H), 3.23-3.27 (m, 2H), 3.31-3.32 (m, 1H), 3.43 (d, *J* = 9.5 Hz, 1H), 4.45 (d, *J* = 9.5 Hz, 1H), 6.13 (dd, *J* = 5.3, 2.9 Hz, 1H), 6.31 (dd, *J* = 5.3, 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.8, 24.1, 37.0, 43.4, 46.4, 47.3, 48.3, 51.9, 53.6, 88.2, 115.2, 136.5, 136.6, 177.2, 195.8, 217.5, Confirmed by ^1H-^{13}C HSQC experiment; HRMS calcd for $C_{16}H_{16}O_3$ (MH^+) 257.1172, found 257.1178.

4.3.12. *3-Acetyl-2-methyl-3b,4,7,7a-tetrahydro-3aH-4,7-methano indeno[2,1-b]furan-8(8aH)-one* (**8c**). White solid; 51 mg, 70%; mp 116-117 °C; IR (neat, cm^{-1}) 2977 (m), 2968 (m), 1741 (s), 1614 (vs), 1387 (m), 1366 (m), 1225 (m), 1207 (m), 1172 (m), 1011 (m); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.45 (d, *J* = 8.3 Hz, 1H), 1.56 (d, *J* = 8.3 Hz, 1H), 2.16 (s, 3H), 2.29 (s, 3H), 2.89 (dd, *J* = 8.3, 4.8 Hz 1H), 3.03 (dd, *J* = 8.3, 3.8 Hz, 1H), 3.26 (d, *J* = 14.1 Hz, 2H), 3.49 (d, *J* = 10.0 Hz, 1H), 4.29 (d, *J* = 10.0 Hz, 1H); 6.13 (dd, *J* = 5.6, 2.9 Hz, 1H), 6.29 (dd, *J* = 5.6, 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.3, 29.6, 47.0, 47.4, 48.2, 48.5, 51.9, 53.4, 86.0, 116.6, 136.3, 136.4, 167.4, 193.9, 217.5; HRMS calcd for $C_{15}H_{16}NaO_3$ (MNa^+) 267.0992, found 267.0995.

4.3.13. *Ethyl-2-methyl-8-oxo-3b,4,7,7a,8,8a-hexahydro-3aH-4,7-metha noindeno[2,1-b]furan-3-carboxylate* (**8d**). White solid; 56 mg, 68%; mp 71-72 °C; IR (neat, cm^{-1}) 2977 (s), 2942 (m), 1746 (vs), 1700 (vs), 1645 (s), 1381 (m), 1339 (m), 1175 (m), 1132 (m), 1081 (s), 1016 (m), 770 (m), 738 (m), 707 (m); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.27 (t, *J* = 7.1 Hz, 3H), 1.41, 1.51 (ABq, *J* = 8.5 Hz, 2H), 2.08 (s, 3H), 2.85 (dd, *J* = 8.5, 4.7 Hz, 1H), 3.11 (dd, *J* = 8.5, 4.1 Hz, 1H), 3.18 (d, *J* = 11.4 Hz, 2H), 3.40 (d, *J* = 10.0 Hz, 1H), 4.11- 4.21 (m, 2H), 4.25 (d, *J* = 10.0 Hz, 1H), 6.08 (dd, *J* = 5.6, 2.9 Hz, 1H), 6.25 (dd, *J* = 5.6, 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3, 14.5, 46.3, 47.2, 48.1, 48.1, 51.8, 53.1, 59.8, 86.0, 105.4, 136.2, 136.3, 165.4, 168.0, 217.8; HRMS calcd for $C_{16}H_{18}NaO_4$ (MNa^+) 297.1097, found 297.1096.

4.3.14. *3-Benzoyl-2-phenyl-3b,4,7,7a-tetrahydro-3aH-4,7-metha noindeno[2,1-b]furan-8(8aH)-one* (**8e**). White solid; 50 mg, 45%; mp 162-163; IR (neat, cm^{-1}) 3059 (m), 2967 (s), 2937 (s), 2868 (m), 1746 (vs), 1614 (vs), 1595 (vs), 1576 (s), 1447 (m), 1360 (s), 1341 (m), 1265 (m), 1175 (m), 1100 (m), 1073 (m), 1002 (m), 890 (m), 769 (m), 732 (vs), 709 (vs), 696 (vs); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.46 (d, *J* = 8.5 Hz, 1H), 1.59 (d, *J* = 8.5 Hz, 1H), 2.99 (dd, *J* = 8.5, 4.6 Hz, 1H) 3.13 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.31-3.32 (m, 2H), 4.05 (d, *J* = 9.6 Hz, 1H), 4.53 (d, *J* = 9.6 Hz, 1H), 6.20 (dd, *J* = 5.6, 3.0 Hz, 1H), 6.39 (dd, *J* = 5.6, 3.0 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 7.7 Hz, 2H), 7.14-7.18 (m, 2H), 7.23-7.27 (m, 2H), 7.41-7.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 46.9, 47.5, 48.4, 49.9, 52.1, 53.5, 85.5, 114.4, 127.8, 128.0, 128.2, 129.1, 129.2, 129.7, 130.6, 132.0, 136.6, 138.8, 165.3, 193.5, 218.2; HRMS calcd for $C_{25}H_{20}NaO_3$ (MNa^+) 391.1305, found 391.1307.

4.3.15. *3-(4-Methoxyphenyl)acryloyl)-2-((E)-4-methoxystyryl)-3b,4,7,7a-tetrahydro-3aH-4,7-methanoindeno[2,1-b]furan-8 (8aH)-one* (**8f**). Yellow solid; 94 mg, 65%; mp 196-198 °C; IR

(neat, cm^{-1}) 2956 (m), 2936 (m), 1746 (s), 1715 (m), 1601 (vs), 1575 (m) 1512 (s), 1306 (m), 1254 (vs), 1172 (s), 1030 (m), 969 (w), 829 (s), 735 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.49 (d, *J* = 7.8 Hz, 1H), 1.62 (d, *J* = 7.8 Hz, 1H), 2.90-3.01 (m, 1H), 3.11-3.13 (m, 1H), 3.31 (d, *J* = 9.5 Hz, 2H), 3.81 (s, 6H), 3.85 (s, 1H); 4.45 (d, *J* = 9.5 Hz, 1H), 6.21-6.23 (unresolved m, 1H), 6.39-6.41 (unresolved m, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.98-7.01 (m, 1H), 7.33 (d, *J* = 15.5 Hz, 1H), 7.46-7.50 (m, 3H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 47.1, 47.5, 48.0, 49.4, 52.0, 53.4, 55.5, 55.6, 85.8, 113.8, 114.4, 114.7, 116.0, 122.7, 127.9, 128.7, 129.6, 130.2, 136.0, 137.0, 139.4, 142.3, 161.1, 161.7, 164.4, 186.0, 217.1; HRMS calcd for $C_{31}H_{29}O_5$ (MH^+) 481.2010, found 481.2023.

4.3.16. *3,3-Dimethyl-3,4,5a,6a,7,10,10a,10b-octahydro-1H-spiro[7,10-methanoindeno[2,1-b]benzofuran-11,2'-[1,3] dioxolane]-1,6(2H)-dione* (**8g**). White solid; 100 mg, 98%; mp 97-98 °C; IR (neat, cm^{-1}) 2990 (m), 2955 (s), 2900 (m), 1746 (vs), 1640 (vs), 1395 (m), 1074 (m), 1029 (m), 974 (m), 753 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.02 (s, 3H), 1.04 (s, 3H), 2.13-2.33 (m, 4H), 2.95-3.11 (m, 3H), 3.36-3.88 (unresolved m, 1H), 3.48 (d, *J* = 9.6 Hz, 1H), 3.77-4.92 (m, 4H), 4.43 (d, *J* = 9.6 Hz, 1H), 6.19-6.21 (unresolved m, 1H), 6.37-6.39 (unresolved m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.2, 29.1, 29.8, 34.4, 37.8, 42.8, 43.4, 50.9, 51.0, 51.4, 64.9, 65.3, 88.7, 113.3, 126.6, 134.2, 135.0, 176.0, 194.8, 217.0; HRMS calcd for $C_{20}H_{23}O_5$ (MH^+) 343.1540, found 343.1542.

4.3.17. *10b-Octahydro-1H-spiro[7,10-methanoindeno[2,1-b]benzofuran-11,2'-[1,3]dioxolane]-1,6(2H)-dione* (**8h**). White solid; 85 mg, 90%; mp 163-164 °C; IR (neat, cm^{-1}) 2958 (m), 2892 (m), 1745 (s), 1631 (vs), 1396 (s), 1296 (s), 1273 (m), 1227 (m), 1170 (m), 1101 (m), 1074 (m), 988 (m), 735 (s), 711 (m); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.00 (quint, *J* = 6.4 Hz, 2H), 2.33 (q, *J* = 6.4 Hz, 2H), 2.37-2.47 (m, 2H), 2.96-2.98 (m, 1H), 3.05-3.07 (m, 1H), 3.12-3.14 (m, 1H), 3.39 (dq, *J* = 4.4, 1.3 Hz, 1H), 3.46 (d, *J* = 9.8 Hz, 1H), 3.78-3.94 (m, 4H), 4.43 (dd, *J* = 9.8, 1.2 Hz, 1H), 6.22, 6.40 (ABqd, *J* = 3.2, 1.0 Hz, 2H); NMR ($CDCl_3$, 125 MHz) δ 21.7, 23.9, 36.9, 42.9, 43.4, 50.9, 51.0, 51.1, 64.9, 65.3, 88.3, 114.7, 126.5, 134.1, 135.0, 176.9, 195.4, 216.9; HRMS calcd for $C_{18}H_{18}NaO_5$ (MNa^+) 337.1046, found 337.1047.

4.3.18. *3-Acetyl-2-methyl-3b,4,7,7a-tetrahydro-3aH-spiro[4,7-methanoindeno[2,1-b]furan-9,2'-[1,3]dioxolan]-8(8aH)-one* (**8i**). Colourless liquid; 68 mg, 75%; IR (neat, cm^{-1}) 2983 (m), 2893 (m), 1745 (vs), 1669 (m), 1617 (vs), 1426 (w), 1387 (m), 1297 (m), 1102 (m), 1076 (m), 925 (m), 736 (vs), 709 (s); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.18 (s, 3H), 2.29 (s, 3H), 2.96-2.98 (m, 1H), 3.06-3.08 (m, 2H), 3.19 (dq, *J* = 4.4, 1.8 Hz, 1H), 3.53 (d, *J* = 10.0 Hz, 1H), 3.80-3.94 (m, 4H), 4.26 (dd, *J* = 10.3, 1.2 Hz, 1H), 6.21, 6.39 (ABdq, *J* = 3.2, 1.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.3, 29.5, 45.4, 46.4, 50.8, 50.9, 51.0, 64.8, 65.3, 86.1, 116.3, 126.5, 134.1, 134.8, 167.3, 193.8, 217.2; HRMS calcd for $C_{17}H_{19}O_5$ (MH^+) 303.1227, found 303.1230.

4.3.19. *1a',1b',2',5',5a',6a'-Hexahydro-6'H-spiro[indene-2,1'-[2,5]methan ocyclopropa[a]indene]-1,3,6'-trione* (**9j**). White solid; 75 mg, 85%; mp 237-238 °C; IR (neat, cm^{-1}) 3043 (w), 2991 (w), 2963 (w), 1723 (vs), 1713 (vs), 1359 (m), 1336 (m), 1254 (m), 1094 (m), 987 (m), 767 (m), 742 (m); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.46 (d, *J* = 8.3 Hz, 1H), 1.61 (d, *J* = 8.3 Hz, 1H), 2.67, 2.70 (ABq, *J* = 5.6 Hz, 2H), 2.95 (dd, *J* = 6.5, 4.2 Hz, 1H), 3.10-3.13 (unresolved m, 1H), 3.31-3.34 (unresolved m, 1H), 3.41-3.44 (m, 1H), 6.07 (dd, *J* = 5.6, 2.8 Hz, 1H), 6.26 (dd, *J* = 5.6, 2.8 Hz, 1H), 7.79-7.84 (m, 2H), 7.90-7.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 41.2, 44.6, 45.0, 46.3, 46.7, 47.1, 51.1, 55.2, 122.9, 123.1, 133.7, 134.4, 135.5, 135.6, 140.7, 143.0, 195.5, 196.0, 212.5; HRMS calcd for $C_{19}H_{14}NaO_3$ (MNa^+) 313.0835, found 313.0837.

4.4. General procedure for the retro-Diels-Alder reaction of polycycles (8a and 8d)

A solution of polycycle **8a** (568 mg, 2 mmol) or **8d** (548 mg, 2 mmol) in diphenylether (5 mL) was refluxed for 45 min (the progress of the reaction was monitored by TLC). After completion of reaction, the reaction mixture was cooled to room temperature and directly purified by silica gel column chromatography by eluting with 5-20% EtOAc-petroleum ether.

4.4.1. *6,6-Dimethyl-5,6,7,8b-tetrahydro-3H-cyclopenta[b] benzo furan-3,8(3aH)-dione* (**10a**). Yellow liquid; 380 mg, 87%; IR (neat, cm^{-1}) 2960 (m), 2874 (m), 1722 (vs), 1635 (vs), 1579 (m), 1397 (s), 1213 (s), 1038 (m), 1003 (m), 889 (w), 825 (w), 791 (w), 640 (w); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.00 (s, 3H), 1.06 (s, 3H), 2.16, 2.20 (ABq, *J* = 8.2 Hz, 2H), 2.26, 2.30 (ABq, *J* = 9.9 Hz, 2H), 4.29 (dd, *J* = 7.2, 1.8 Hz, 1H), 4.94 (d, *J* = 7.2 Hz, 1H), 6.20 (dt, *J* = 5.8, 1.8 Hz, 1H), 7.97-7.99 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.6, 28.7, 34.5, 37.8, 46.4, 51.0, 83.3, 113.8, 132.7, 166.1, 176.9, 194.2, 202.9; HRMS calcd for $C_{13}H_{14}NaO_3$ (MNa^+) 241.0835, found 241.0832.

4.4.2. *Ethyl-2-methyl-6-oxo-6,6a-dihydro-3aH-cyclopenta [b]furan-3-carboxylate* (**10d**). Yellow liquid; 354 mg, 85%; IR (neat, cm^{-1}) 2980 (m), 1723 (vs), 1704 (vs), 1643 (s), 1380 (m), 1341 (m), 1212 (s), 1082 (s), 1022 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (t, *J* = 7.1 Hz, 3H), 2.16 (s, 3H), 4.15-4.24 (m, 2H), 4.28 (dd, *J* = 7.5, 1.4 Hz, 1H), 4.78 (d, *J* = 7.5 Hz, 1H), 6.25 (dd, *J* = 5.8, 1.4 Hz, 1H), 7.99 (dd, *J* = 5.8, 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) 14.5 (×2), 49.5, 60.1, 80.8, 104.7, 132.9, 165.0, 167.0, 169.2, 203.9; HRMS calcd for $C_{11}H_{11}O_4$ ([MH-2H]$^+$) 207.0652, found 207.0652.

Acknowledgements

INNN thanks SERB, DST India (EMR/2014/000395) for financial assistance. SL thanks ISRO, DRDO and CSIR for research fellowship. The authors also thank Prof. Arindrajit Chowdhury, Department of Mechanical Engineering, IIT Bombay, for his support and Ms. Deepa Nair, Mr. Gulzar Ahmad Bhat and Mr. R. Saravanan, Department of Chemistry, IIT Bombay, for the X-Ray data.

Supplementary Material

Copies of NMR spectra for all the new compounds. Supplementary data associated with this article can be found in the online version, at

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