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Synthesis of cyclopropyl silyl ethers and their facile ring opening by photoinduced electron transfer as key step in radical/radical cationic cascade reactions

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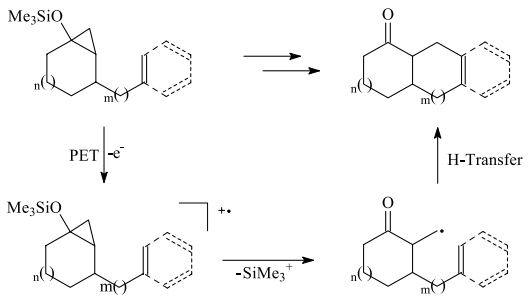
Abstract—Various ring-fused cyclopropyl silyl ethers with an benzylic, olefinic or acetylenic side chain have been synthesized. Upon oxidative photoinduced electron transfer (PET) the cyclopropane ring opens and forms a reactive β-keto radical, which undergoes intramolecular cyclization. In some cases we observed only formation of ring opened non-cyclized products. With olefinic side chain 5-*exo-trig* mode of cyclization rather than 6-*endo-trig* mode of cyclization takes place whereas in case of acetylenic side chain we observed 6-*endo* cyclization.

1. Introduction

Since almost three decades radical cascade reactions (also called domino reactions) have often been used for synthesizing polycyclic compounds.[1–5] Still the tin hydride method introduced by Giese et al. is one of the mostly applied method to perform radical chain processes despite some disadvantages. In order to circumvent toxic tin reagents and to facilitate the working-up procedures, for example, electron transfer activation has been introduced to generate radical or radical ions.[5b,6] In these reactions metal salts are generally used as oxidizing and reducing agents, respectively. Another way to generate radical ions is possible by the photoinduced electron transfer (PET).[7] This procedure has several advantages: metal reagents and other toxic compounds are avoided, the working-up procedures are often very easy, and in general, photochemistry certainly provides powerful methods for a new and sustainable chemistry.[8]

Upon oxidative photoinduced electron transfer (PET) the cyclopropane ring opens and forms a reactive β-keto radical, which undergoes intramolecular cyclization. The oxidative ring-opening reactions of cyclopropanone acetals with carbonyl compounds via PET have been already studied by Akira Oku and co-workers.[8d–g] Recently, we have reported on radical/radical ionic cascade reactions initiated by photoinduced electron transfer (PET).[9–11] All these reactions have in common that the redox properties of molecules are changed upon excitation, that is, both the electron donating as well as electron accepting behavior of the excited species are drastically enhanced. This leads either to oxidative PET or to reductive PET processes. For details of PET and for special synthetic procedures such as sensitization and co-sensitization processes see, for example, Refs. 9–11.

Here, we will report on some further examples of PET initiated radical/radical cationic cascade reactions of bicyclic cyclopropyl silyl ethers functionalized by unsaturated side chains leading to polycyclic compounds. We were especially interested in checking the suitability of alkyne and arene groups in comparison of simple alkenes (Scheme 1).



Scheme 1.

Keywords: Siloxy cyclopropanes; Domino reactions; Electron transfer; Polycycles; Radical ions; Radical reactions.
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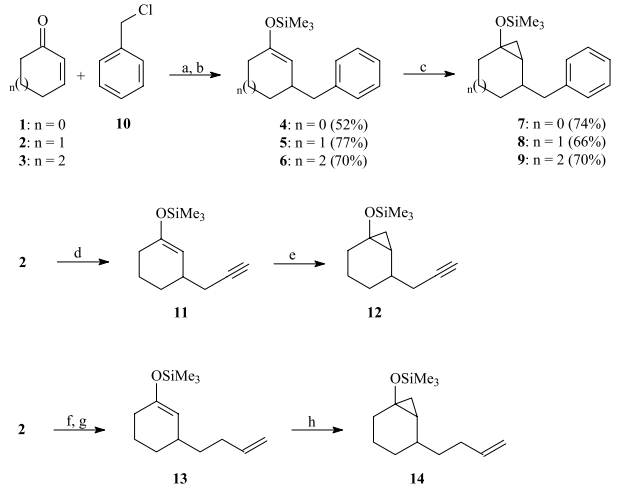
2. Results and discussion

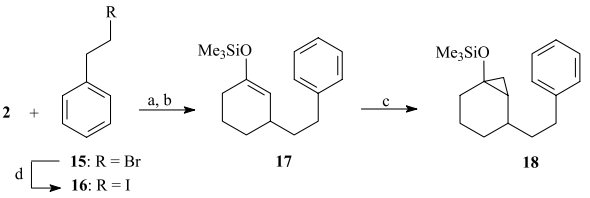
2.1. Preparation of cyclopropyl silyl ethers

The silyl enol ethers were prepared by the copper catalyzed conjugate addition of various Grignard Reagent (GR) to the enones followed by trapping of the enolates with trimethylsilyl chloride (Scheme 2). The addition of propargyl magnesium bromide catalyzed by CuI to 2-cyclohexenone did not afford the expected product, however, use of the procedure developed by Lee[12] afforded the propargylated silyl enol ether in good yield. In general the corresponding bromides were used for the preparation of GR. In case of benzyl bromide we observed only the formation of 1,2-diphenyl ethane. This problem was circumvented by using benzyl chloride. The 1:1 mixture of diethyl ether/THF proved to be the best solvent for the preparation of GR and conjugate addition reactions. The selective cyclopropanation of respective silyl enol ethers in presence of alkenes or alkyne were successfully carried out using diethylzinc, methylene iodide and methylene chloride as the solvent of choice. Unfortunately, these conditions were not successful for related cyclopropanation of *tert*-butyl dimethyl silyl enol ethers, but we found that the corresponding trimethyl silyl enol ether **11** could be cyclopropanated in 75% yield.



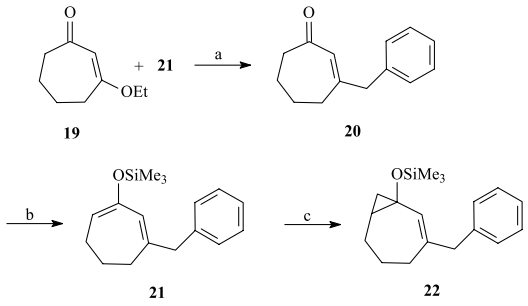
Scheme 2. (a) Mg metal, dry THF/diethyl ether 0 °C; (b) CuI, TMS-Cl, −78 °C, Et_3N, rt; (c) Et_2Zn, CH_2I_2, CH_2Cl_2, rt, 12 h; (d) in metal, propargyl bromide, dry THF, rt, 1 h, Me_2S, TMSOTf, 3 h, (65%); (e) Et_2Zn, CH_2I_2, CH_2Cl_2, 2 days, (75%); (f) Mg metal, 4-bromobut-1-ene, dry THF/diethyl ether, 0 °C; (g) CuI, TMS-Cl, −78 °C, 3 h, Et_3N, rt, (54%); (h) Et_2Zn, CH_2I_2, CH_2Cl_2, 2 h, (84%).

In case of 2-phenyl-1-bromo ethane, we did not observe any formation of GR. To overcome this problem we converted the less reactive bromide to the iodide by refluxing it with NaI in acetone (Scheme 3). The primary alkyllithium was readily prepared at −78 °C (dry ice–acetone bath) under an atmosphere of dry, deoxygenated argon by addition of 2.2 mol equiv of commercial *tert*-butyllithium (*t*-BuLi) in pentane to an approximately 0.1 M solution of **16** in dry *n*-pentane–diethyl ether (3/2 by volume).[13] The CuI catalyzed conjugate addition of this organolithium compound to 2-cyclohexenone in presence of TMS-Cl afforded silyl enol ether **17**.



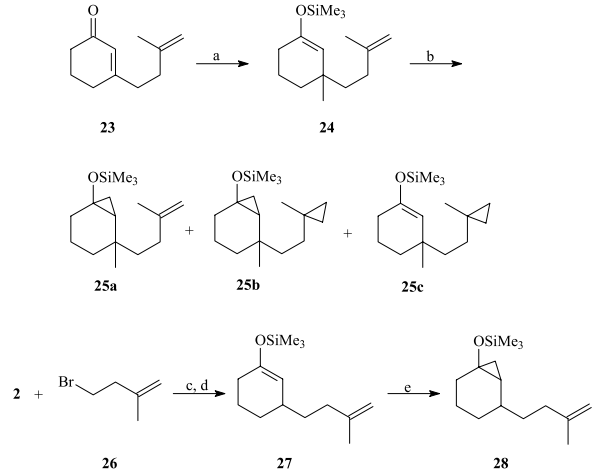
Scheme 3. (a) *t*-BuLi, THF, −78 °C to rt; (b) CuI, TMS-Cl, −78 °C, Et_3N, rt, (62%); (c) Et_2Zn, CH_2I_2, CH_2Cl_2, 12 h, (36%); (d) NaI, acetone, reflux 2 h, (72%).

The 3-substituted enones were prepared from the reaction of vinylogous ester **19** with GR prepared from corresponding bromides or chlorides (Scheme 4). The enone **20** is a very important intermediate in pharmaceutical industry, besides of several filed patents and to the best of our knowledge no one has reported its actual synthesis. We prepared enone **20** by the reaction of 3-ethoxy-2-cycloheptenone **19**[9] and benzyl magnesium chloride in 91% yield. Treatment of enone **20** with lithiumdiisopropylamine (LDA) in presence of TMS-Cl afforded its silyl enol ether **21**, which was cyclopropanated to **22** in 81% yield, using Et_2Zn, CH_2I_2 in CH_2Cl_2.



Scheme 4. (a) Mg metal, dry THF/diethyl ether, 0 °C, 3 h, (91%); (b) LDA, TMS-Cl, dry THF, −78 °C to rt, 2 h, (90%); (c) Et_2Zn, CH_2I_2, CH_2Cl_2, 12 h, (81%).

The cyclohexenone **23** was synthesized by treatment of 3-ethoxy-2-cyclohexenone and GR prepared from 4-bromo-2-methyl-1-butene and subsequent acid hydrolysis (Scheme 5).[14] Treatment of **23** with methyl lithium under



Scheme 5. (a) CuI, MeLi, 0 °C, 10 min, −78 °C, TMS-Cl, 3 h, Et_3N, rt, (75%); (b) Et_2Zn, CH_2I_2, CH_2Cl_2; (c) Mg metal, THF/diethyl ether, 0 °C; (d) CuI, TMS-Cl, −78 °C, Et_3N, rt, (83%); (e) Et_2Zn, CH_2I_2, CH_2Cl_2, 12 h, (65%).

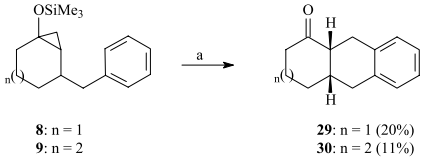
our previously developed conditions gave enol ether **24** in 75% yield. The cyclopropanation of **24** with Et_2Zn, CH_2I_2 in various solvents resulted in the mixture of products **25a–c** in poor yields.

However, the enol ether **27** was prepared in good yield by copper catalyzed conjugate addition of GR as shown in Scheme 5. The silyl enol ether **27** could be cyclopropanated in 65% yield by using our standard conditions.

2.2. Photoinduced electron transfer (PET) cyclizations

The deoxygenated solutions of respective cyclopropyl silyl ethers in dry acetonitrile containing the PET sensitizer dicyanoanthracene (DCA) were irradiated in a Rayonet photochemical reactor using 420 nm lamps. All the reactions were monitored by GC or GC–MS.

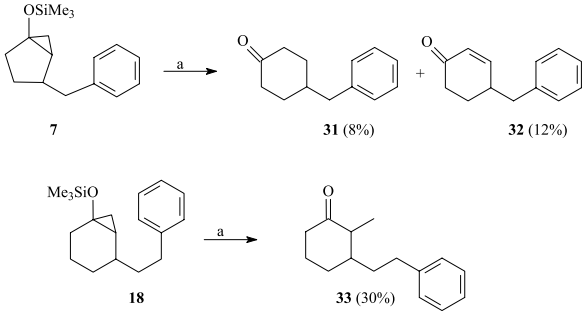
The irradiation of **8** and **9** in dry acetonitrile resulted in the formation of tricyclic products **29** and **30** with high stereoselectivity (Scheme 6). The formation of these products can be explained as follows—for details of the mechanism see Ref. 9 (cf. Scheme 2): the sensitizer DCA gets electronically excited at 420 nm and thus is enabled to oxidize the substrate to its radical cation. Exocyclic cyclopropane ring opening leads to the formation of a β-keto radical, which further cyclizes to the tricyclic products. The last step is the elimination of a hydrogen atom to retain the aromatic ring. Surprisingly we observed only formation of cis isomers. The structure and stereochemistry were assigned using modern NMR techniques such as ^{1}H COSY, HMBC, HMQC and NOESY. The cyclopropane **7** under PET condition leads to the formation of non-cyclized ring enlarged products (scheme 7). In this case cyclopropyl ring opening takes place via endocyclic cleavage, indicating the formation of the thermodynamically favored more stable secondary radical. Obviously the formation of a new strained polycyclic product is energically disfavored.



8: n = 1
9: n = 2

29: n = 1 (20%)
30: n = 2 (11%)

Scheme 6. (a) DCA, acetonitrile, irradiated for 12 h at 420 nm.

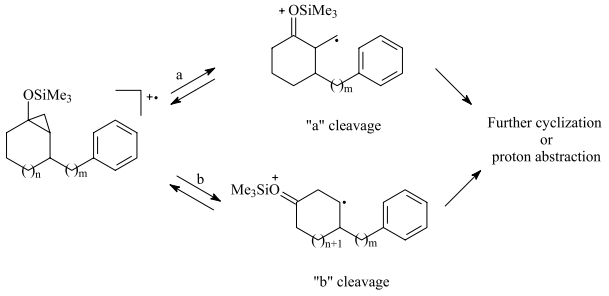


7 **31** (8%) **32** (12%)

18 **33** (30%)

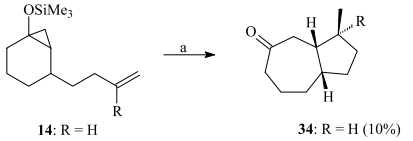
Scheme 7. (a) DCA, acetonitrile, irradiated for 12 h at 420 nm.

Irradiation of **18** leads to the exocyclic ring opened noncyclized product **33** as well. In this case intra-molecular cyclization was not observed due to the large distance between exocyclic radical and phenyl ring. To explain the two contrasting ring opening results from very similar structures, we propose that both processes involve the endocyclic ring opening (cleavage of bond 'b', see Scheme 8) as first step[9] followed by a reversible ring-closure process. If $n=1$ or 2 and $m=1$ or 2 (as in case of **8**, **9** and **18**), reclosure could became more facile leading to a cyclohexylmethyl radical, which attack the phenyl ring depending on the chain lengths of its tether. If $n=0$ (as in case of **7**) the formation of ring enlarged product is favored leading to **31** and the α-β unsaturated ketone **32**, respectively. The structure of cyclopropane radical cations and their reactivity has been already discussed by Roth and co-workers.[15] Further, mechanistic investigations are underway using flash laser photolysis and quantum chemical calculations and will be published separately.[9b,9c]



Scheme 8. cleavage of exocyclic (a) and endocyclic (b) C–C bond.

In accordance with this rationalization treatment of **14** and **28** under PET conditions leads to the cleavage of bond 'b', the formed cyclic radical undergoes 5-*exo-trig* cyclization affording products **34** and **35** due to the higher reactivity of alkenes rather than arenes in radical additions (Scheme 9). In these cases the final step is saturation of the radical, which takes places either by direct abstraction of hydrogen from solvent molecule or by reduction to the corresponding anion by the sensitizer radical anion followed up by protonation (e.g., by traces of water in the highly hygroscopic acetonitrile).[9] The stereochemistry at ring junction is cis, and was confirmed by NOESY analysis.

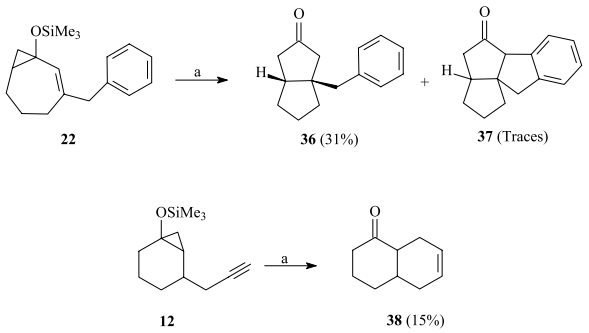


14: R = H
28: R = Me

34: R = H (10%)
35: R = Me (14%)

Scheme 9. (a) DCA, acetonitrile, irradiated for 12 h at 420 nm.

In case of **22** we observed formation of the bicyclic product **36** as only one isomer (31%) in which both substituents are cis to each other (Scheme 10). This is not surprising for products, which contain a bicyclooctenone substructure because of the high ring strain of the corresponding trans products. In addition, we observed some traces of product **37**, which indicates that the second cyclization step is energetically disfavored. The propargyl substituted



Scheme 10. (a) DCA, acetonitrile, irradiated for 12 h at 420 nm.

compound **12** was irradiated under PET conditions afforded the bicyclic product **38** via 6-*endo* cyclization. If the cyclopropane ring would have opened in a endocyclic way, the formed secondary radical must cyclize in a 5-*endo* mode, which is known to be disfavored according to the Baldwin–Beckwith rules.[16,17]

3. Conclusion

Various new ring-fused cyclopropyl silyl ethers with an benzylic, olefinic or acetylenic side chain have been synthesized in good yields. We have also been able to demonstrate that the PET induced ring opening of cyclopropyl silyl ethers is quite suitable for the production of polycylic compounds with high stereoselectivity. PET oxidative initiated reactions of these cyclopropyl silyl ethers lead to β-carbonyl radical cationic species and β-keto-radicals, respectively, which can be used for the construction of polycyclic compounds.[9] The termination step is supposed to be either a hydrogen radical transfer from the solvent (acetonitrile) or a stepwise electron transfer/protonation by traces of water in the solvent.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR were recorded using Bruker DRX 500 or Bruker Avance 600 spectrometer. Spectra were recorded in $CDCl_3$; chemical shifts were calibrated to the residual $CHCl_3$ (δH = 7.24 ppm, δC = 77.00 ppm). IR spectra were recorded on a Perkin-Elmer 841 spectrometer. HRMS were recorded on AutospecX (Vacuum Generators, Manchester). GC/MS were recorded on a Shimadzu GC 17A/QP 5050A equipped with a 5MS capillary column (Hewlett Packard). GC analysis were carried out using Shimadzu GC-2010, equipped with HP-5MS (Hewlett Packard) capillary column (column length 25.0 m, inner diameter 0.20 mm). Analytical thin-layer chromatography was performed on a aluminum sheets coated with 0.20 mm silica gel with fluorescent indicator UV_{254} (Macherey-Nagel GmbH). Column chromatography was performed on silica gel MN60 (70–230 mesh; Macherey-Nagel GmbH). Photochemical reactions were performed using an RPR-100 Rayonet photochemical chamber reactor (Southern New England Ultraviolet Company) with RPR 4190 Å lamps that show an emission maximum at 419 ± 15 nm at half bandwidth. All reactions were carried out under an atmosphere of argon. All solvents were distilled prior to use; dry solvents were prepared using standard procedures, dry acetonitrile was stored over activated molecular sieves (size 4 Å). DCA was prepared using literature known method and recrystallized from toluene. All commercially available compounds were used as received unless stated otherwise.

4.2. General procedure A

Synthesis of silyl enol ethers. To a stirred suspension of magnesium metal (Mg), catalytic amount of iodine crystals and dry THF–diethyl ether (1/1 by volume) were added corresponding bromide or chloride (1.2 equiv) in such that the solution was slightly boiling, after addition the solution was heated under reflux for 1 h. This GR was added to the previously cooled suspension of CuI (1 equiv) in THF. The reaction temperature was maintained 0 °C for 10 min and then cooled to −78 °C by using dry ice–acetone bath. The solution of corresponding enones and TMS-Cl in dry THF were added dropwise and stirred for 3 h. Triethyl amine was added and reaction mixture was brought to room temperature (rt), reaction was monitored by GC–MS. Solvents were removed under high vacuum; *n*-pentane was added and the mixture was quickly filtered. The solvent was evaporated under reduced pressure and the crude product was used immediately for the next reaction.

4.3. General procedure B

Synthesis of silyl enol ether by LDA. The solution of diisopropyl amine in dry THF was placed in a oven dried apparatus under argon atmosphere and cooled to 0 °C. *n*-BuLi (1.6 M in hexane) were added dropwise, the stirring was continued for next 25 min and the reaction mixture was cooled to −78 °C using dry ice–acetone bath, followed by addition of respective enones in dry THF. The solution was stirred for 1 h and neat TMS-Cl was added. The solution was brought to rt and stirred for an additional hour at this temperature (monitored by GC–MS). After removal of solvent under reduced pressure, the residue was diluted with *n*-pentane. The precipitate of lithium chloride was removed by filtration; the solvent was removed under vacuum. The product was used immediately for next reaction.

4.4. General procedure C

Cyclopropanation of silyl enol ethers. The respective silyl enol ether was placed in dry apparatus under argon atmosphere, dry dichloromethane was added. The solution was cooled to 0 °C using ice bath, diethyl zinc (1.0 M in hexane) was added. After stirring for 10 min, the solution of diiodomethane in dry THF was added dropwise, the reaction mixture was warmed to rt and stirred for 2–24 h. The conversion was monitored by Gas Chromatography (GC), after complete consumption of starting material; the solution was carefully hydrolyzed by saturated aqueous solution of ammonium chloride until complete dissolution of zinc salt. The aqueous phase was separated and extracted two times with diethyl ether; collective organic layers were washed with water and dried over sodium sulphate. The

solvent was evaporated and the residue was purified with kugelrohr distillation.

4.5. General procedure D

PET oxidative reaction. The solution of cyclopropyl silyl ether and PET sensitizer DCA in dry acetonitrile was placed into a dry Pyrex tubes (diameter 12 mm, length 20 cm, capacity 12 mL). Flushed with argon for 25 min and irradiated for 12–24 h using 420 nm lamps. After complete consumption of starting material (monitored by GC and GC–MS), solvent removed under vacuum and the residue was purified by silica gel column chromatography (EtOAc/Cyclohexane).

4.5.1. Synthesis of 3-benzyl-1-trimethylsilyloxylcyclopent-1-ene (4).[20] Following general procedure A; cyclopentenone **1** (820 mg, 10 mmol) was treated with GR prepared from benzyl chloride (2.9 mL, 25 mmol) and Mg metal (610 mg, 25 mmol) in presence of CuI (1.90 g, 10 mmol) and TMS-Cl (1.5 mL, 12 mmol), gave silyl enol ether **4** (1.254 g, 70%). GC–MS (EI, 70 eV): *m/z* (%)=246 (M^+, 1), 155 (100), 139 (4), 115 (1), 91 (6) 75 (10).

4.5.2. Synthesis of 3-benzyl-1-trimethylsilyloxylcyclohex-1-ene (5). Following General procedure A; cyclohexenone **2** (1.705 g, 17.77 mmol) was treated with GR prepared from benzyl chloride (5.1 mL, 44.7 mmol) and Mg metal (911 mg, 37.3 mmol) in presence of CuI (3.376 g, 17.7 mmol) and TMS-Cl (2.2 mL, 17.7 mmol), gave **5** (3.755 g, 77%). GC–MS (EI, 70 eV): *m/z* (%)=260 (M^+, 1), 245 (6), 169 (100), 153 (4), 139 (1), 128 (2), 115 (4), 91 (31), 75 (32), 65 (14).

4.5.3. Synthesis of 3-benzyl-1-trimethylsilyloxylcyclohept-1-ene (6). Following General procedure A; cycloheptenone **3** (550 mg, 5 mmol) was treated with GR prepared form benzyl chloride (1.4 mL, 12.5 mmol) and Mg metal (305 mg, 12.5 mmol) in presence of CuI (950 mg, 5 mmol) and TMS-Cl (0.8 mL, 6 mmol), gave **6** (150 mg, 70%). GC–MS (EI, 70 eV): *m/z* (%)=274 (M^+, 1), 184 (100), 167 (2), 141 (1), 115 (1), 103 (1), 91 (9), 73 (56).

4.5.4. Synthesis of 2-propargyl-1-trimethylsililoxylcyclohex-1-ene (11).[12] To a stirred solution of **2** (145 mg, 1.5 mmol) in dry THF (3 mL) were added successfully dimethyl sulfide (0.1 mL, 1.95 mmol) and TMSOTf (366 mg, 1.65 mmol) at −78 °C under a argon atmosphere. After 10 min, organoindium reagent generated in situ from indium metal (344 mg, 1.65 mmol) and propargyl bromide (0.55 mL, 4.7 mmol) in THF at rt was added and mixture was stirred at −78 °C for 30 min. The reaction mixture was quenched with saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with ether (3×25 mL) and combined organic layers were washed with water, brine and dried with sodium sulphate, filtered and concentrated under reduced pressure, gave **11** (204 mg, 65%). GC–MS (EI, 70 eV): *m/z* (%)=208 (M^+, 1), 168 (41), 150 (2), 110 (1), 96 (1), 78 (3), 72 (100), 61 (3), 44 (22).

4.5.5. Synthesis of 3-(but-3-enyl)-1-trimethylsilyloxylcyclohex-1-ene (13).[19] Following general procedure A; compound **2** (960 mg, 10 mmol) was treated with GR prepared from 1-bromo-3-butene (2.970 g, 22 mmol) and Mg metal (536 mg, 22 mmol) in presence of CuI (1.90 g, 10 mmol) and TMS-Cl (2.8 mL, 22 mmol), gave silyl enol ether **13** (1.20 g, 54%). GC–MS (EI, 70 eV): *m/z* (%)=223 (M^+, 2), 170 (26), 152 (12), 136 (2), 114 (4), 100 (19).

4.5.6. Synthesis of 3-(2-phenylethyl)-1-trimethylsilyloxylcyclohex-1-ene (17). Solution of 2-phenyl-1-iodo ethane **16** (1.919 g, 8.27 mmol) was placed in a dry apparatus equipped with argon balloon, magnetic needle and septum 15 mL dry *n*-pentane–diethyl ether (3/2 by volume) was added. The solution was cooled to −78 °C by using dry ice-acetone bath, the stirrer was started and solution of *t*-BuLi (1.160 g, 18.2 mmol) in *n*-pentane was then added dropwise via argon flushed syringe. Stirring was then continued at −78 °C for additional 5 min, the cooling bath was then removed and mixture was allowed to warm and stand at rt for 1 h to consume the unreacted *t*-BuLi. The mixture was then added dropwise to a solution of CuI (826 mg, 4.35 mmol) in dry diethyl ether at 0 °C, stirring was continued for 10 min and then solution was cooled to −78 °C. The solution of cyclohexenone **2** (391 mg, 4.35 mmol) and TMS-Cl (0.8 mL, 6.525 mmol) were added via syringe. Reaction was monitored by GC and workedup as reported in general procedure A, gave silyl enol ether **17** (692 mg, 62%). GC–MS (EI, 70 eV): *m/z* (%)=274 (M^+, 1), 183 (100), 156 (2), 144 (5), 129 (6), 117 (2), 105 (3), 91 (13), 85 (2), 73 (59).

4.5.7. Synthesis of 6-benzyl-1-trimethylsilyloxyl-1,6-cycloheptadiene (21). Following general procedure B; enone **20** (70 mg, 0.35 mmol) was treated with LDA prepared from diisopropyl amine and (42 mg, 0.42 mmol) and *n*-Butyllithium (0.3 mL, 0.38 mmol) in presence of TMS-Cl (0.06 mL, 0.52 mmol). Gave enol ether **21** (85 mg, 90%). GC–MS (EI, 70 eV): *m/z* (%)=272 (M^+, 52), 257 (17), 181 (9), 165 (13), 153 (9), 141 (3), 128 (3), 115 (4), 91 (35), 73 (100).

4.5.8. Synthesis of 3-methyl-3-(3-methylbut-3-enyl)-1-trimethylsilyloxylcyclohex-1-ene (24). CuI (695 mg, 3.698 mmol) was taken in a dry 25 mL round bottom flask; 10 mL of dry diethyl ether was added and solution was cooled to 0 °C using ice bath and MeLi (168 mg, 7.681 mol) was added. The stirring was continued for additional 10 min and then solution was cooled to −78 °C using dry ice acetone bath. The solution of **2** (500 mg, 3.048 mmol) and TMS-Cl (0.6 mL, 6.096 mmol) in 5 mL dry diethyl ether was added via syringe. The reaction was monitored by GC and reaction mixture was worked up using general procedure A, gave silyl enol ether **24** (570 mg, 75%). GC–MS (EI, 70 eV): *m/z* (%)=252 (M^+, 1), 237 (4), 183 (100), 170 (6), 162 (2), 118 (2), 105 (3), 91 (5), 73 (80).

4.5.9. Synthesis of 3-(3-methylbut-3-enyl)-1-trimethylsilyloxylcyclohex-1-ene (27). Following general procedure A; compound **2** was treated with GR prepared form 4-bromo-2-methyl-1-butene (5.02 g, 33.7 mmol) and Mg metal (720 mg, 30 mmol) in presence of CuI (2.850 g, 15 mmol) and TMS-Cl (2.3 mL, 18 mmol), gave enol ether **27** (2.80 g, 83%). GC–MS (EI, 70 eV): *m/z* (%)=238 (M^+, 1), 182 (52), 170 (8), 147 (8), 105 (4), 73 (100), 52 (2).

4.5.10. Synthesis of 4-benzyl-1-trimethylsilyloxylbicyclo[3.1.0]hexane (7).[20] Following general procedure C; to a stirred solution of silyl enol ether **4** (2.429 g, 9.87 mmol) in 10 mL dichloromethane, was added diethyl zinc (30.2 mL, 23.6 mmol). Solution was cooled to 0 °C using ice bath and neat CH_2I_2 (3.277 g, 12.2 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to rt and stirred for 12 h. Reaction was monitored by GC and usual workup gave **7** (1.90 g, 74%) as colorless oil. GC–MS (EI, 70 eV): *m/z* (%)=260 (M^+, 2), 245 (4), 231 (6), 169 (98), 142 (10), 127 (11), 103 (91), 79 (17), 73 (100).

4.5.11. Synthesis of 4-benzyl-1-trimethylsilyloxylbicyclo[4.1.0]hepane (8). Following general procedure C; to a stirred solution of silyl enol ether **5** (1.49 g, 5.38 mmol) in 5 mL dichloromethane, was added diethyl zinc (14.4 mL, 11.3 mmol). Solution was cooled to 0 °C using ice bath and neat CH_2I_2 (2.821 g, 10.56 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to rt and stirred for 12 h and usual workup gave **8** (980 mg, 66%) as colorless oil. IR (neat): υ=2928, 2862, 1704, 1453 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=0.15 (s, 9H), 0.30 (dd, 1H, J=5.6, 5.6 Hz), 0.83–0.89 (m, 1H), 0.90–0.99 (m, 3H), 1.55–1.64 (m, 1H), 1.65–1.75 (m, 2H), 1.84 (ddd, 1H, J=5.0, 13.8, 5.6 Hz), 2.18 (dd, 1H, J=3.7, 13.2 Hz), 2.70 (dd, 1H, J=7.8, 8.0 Hz), 2.81 (dd, 1H, J=7.5, 7.5 Hz), 7.19 (dd, 3H, J=7.5, 7.5 Hz), 7.27 (dd, 2H, J=8.1, 6.9 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=1.40 (CH_3), 19.00 (CH_2), 21.00 (CH_2), 24.29 (CH), 26.88 (CH_2), 31.98 (CH_2), 39.64 (CH), 44.35 (CH_2), 57.41 (C), 125.72 (CH), 128.14 (C), 128.96 (CH), 140.00 (CH) ppm. GC–MS (EI, 70 eV): *m/z* (%)=274 (M^+, 1), 259 (3), 246 (5), 245 (2), 231 (9), 185 (10), 184 (60), 183 (100), 169 (11), 156 (15), 155 (26), 142 (13), 130 (17), 129 (9), 93 (13), 91 (25).

4.5.12. Synthesis of 4-benzyl-1-trimethylsilyloxylbicyclo[5.1.0]octane (9). Following general procedure C; to a stirred solution of silyl enol ether **6** (1.37 g, 5 mmol) in 5 mL dichloromethane, was added diethyl zinc (14.4 mL, 11.3 mmol). Solution was cooled to 0 °C using ice bath and neat CH_2I_2 (1.53 g, 5.629 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to rt and stirred for 12 h, usual workup gave **9** (1.0 g, 70%) as a colorless oil. IR (neat): υ=2932, 2368, 2344, 1702, 1456 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=0.05 (s, 9H), 0.25 (m, 1H), 0.50–0.70 (m, 1H), 0.94 (dd, 2H, J=4.3, 2.5 Hz), 1.03 (dd, 2H, J=10.6, 10.6 Hz), 1.49–1.60 (m, 2H), 1.63–1.77 (m, 1H), 1.88 (d, 1H, J=13.8 Hz), 2.10–2.25 (dm, 2H, J=14.4 Hz), 2.40 (dd, 1H, J=8.1, 8.1 Hz), 2.56 (dd, 1H, J=6.9, 6.9 Hz), 7.15 (ddd, 3H, J=1.2, 4.3, 6.2 Hz), 7.25 (dd, 2H, J=7.5, 8.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=1.20 (CH_3), 24.97 (CH), 28.09 (CH_2), 31.78 (CH_2), 38.34 (CH), 38.86 (CH_2), 43.12 (CH_2), 44.48 (CH_2), 69.65 (C), 125.64 (CH), 128.14 (CH), 129.32 (CH), 141.32 (C) ppm. GC–MS (EI, 70 eV): *m/z* (%)=288 (M^+, 3), 273 (3), 259 (6), 231 (5), 197 (71), 184 (12), 170 (39), 157 (26), 144 (29), 130 (11), 114 (5), 91 (23), 73 (100). HRMS: Calcd for $C_{18}H_{28}OSi$ (M^+) 288.190944, found 288.190933.

4.5.13. Synthesis of 4-(prop-2-ynyl)-1-trimethylsilyloxylbicyclo[4.1.0]heptane (12). Following general procedure C; to a stirred solution of silyl enol ether **11** (150 mg, 0.433 mmol) in 2 mL dichloromethane, was added diethyl zinc (2.2 mL, 1.03 mmol). Solution was cooled to 0 °C using ice bath and neat CH_2I_2 (211 mg, 0.793 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to rt and stirred for 2 days, usual workup gave **12** (120 mg, 75%) as colorless oil. IR (neat): υ=2929, 2866, 1715, 1686 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=0.13 (s, 3H), 0.18 (s, 6H), 0.82–0.93 (m, 1H), 1.15–1.35 (m, 2H), 1.68–1.78 (m, 3H), 1.90–1.99 (m, 3H), 2.12 (tt, 2H), 2.20–2.30 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=0.90 (Si–(CH_3)$_3$), 22.08 (CH_2), 22.58 (CH_2), 25.00 (CH_2), 35.18 (CH_2), 33.41 (CH), 33.99 (CH), 38.04 (CH), 69.21 (C), 84.10 (C) ppm. GC–MS (EI, 70 eV): *m/z* (%)=222 (M^+, 1), 206 (7), 154 (2), 131 (3), 116 (2), 93 (5), 77 (2), 72 (100).

4.5.14. Synthesis of 5-(but-3-enyl)-1-trimethylsilyloxylbicyclo[4.1.0]heptane (14).[19] Following general procedure C; to a stirred solution of silyl enol ether **13** (223 mg, 1 mmol) in 2 mL dichloromethane, was added diethyl zinc (2.9 mL, 2.32 mmol). Solution was cooled to 0 °C using ice bath and neat CH_2I_2 (264 mg, 0.9 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to rt and stirred for 2 days, usual workup gave **14** (200 mg, 84%) as a colorless oil. GC–MS (EI, 70 eV): *m/z* (%)=238 (M^+, 2), 194 (8), 183 (9), 166 (3), 155 (3), 142 (3), 132 (2), 126 (4), 114 (3), 104 (2), 90 (5), 74 (30), 72 (100), 67 (6), 59 (5), 44 (14).

4.5.15. Synthesis of 4-(2-phenylethyl)-1-trimethylsilyloxylcyclohex-1-ene (18). Following general procedure C; to a stirred solution of silyl enol ether **17** (652 mg, 2.525 mmol) in 2.5 mL dichloromethane, was added diethyl zinc (7.6 mL, 6.04 mmol). Solution was cooled to 0 °C using ice bath and neat CH_2I_2 (1.362 g, 5.10 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to rt and stirred for 2 days, usual workup gave **18** (545 mg, 36%) as a colorless oil. IR (neat): υ=2920, 28,235, 1704, 1453 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=0.14 (s, 9H), 0.85–0.86 (m, 1H), 1.10–1.40 (m, 2H), 1.50–1.65 (m, 6H), 1.80–1.90 (m, 1H), 1.96–2.10 (m, 2H), 2.40–2.55 (m, 1H), 2.60–2.70 (m, 1H), 7.16 (dd, 2H, J=6.2, 7.0 Hz), 7.27 (dd, 2H, J=7.0, 8.0 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=20.48 (CH_2), 27.14 (CH_2), 29.13 (CH_2), 30.48 (CH_2), 33.55 (CH_2), 34.55 (CH), 34.97 (CH_2), 51.00 (C), 125.57 (CH), 125.63 (C), 128.27 (CH), 128.32 (CH) ppm. GC–MS (EI, 70 eV): *m/z* (%)=288 (M^+, 6), 184 (17), 183 (100), 144 (4), 127 (3), 91 (14), 75 (18).

4.5.16. Synthesis of 3-benzyl-1-trimethylsilyloxylbicyclo[5.1.0]oct-2-ene (22). Following general procedure C; to a stirred solution of silyl enol ether **21** (118 mg, 0.433 mmol) in 2 mL dichloromethane, was added diethyl zinc (1.3 mL, 1.03 mmol). Solution was cooled to 0 °C using ice bath and neat CH_2I_2 (117 mg, 0.438 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to rt and stirred for 12 h, usual workup gave **22** (100 mg, 81%) as a colorless oil. IR (neat): υ=2929, 2863, 1706, 1662, 1455, 1376 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=0.19 (dd, 1H, J=1.8, 5.0 Hz), 0.70–0.77 (m, 1H), 0.78–0.83 (m, 1H), 0.85–0.97 (m, 2H), 1.50–1.68 (m, 1H), 1.74–1.86 (m, 2H), 2.18–2.28 (m, 1H), 3.15 (d, 2H,

J=3.8 Hz), 5.55 (s, 1H), 7.03 (dd, 2H, J=2.0, 7.0 Hz), 7.13 (dd, 2H, J=5.0, 7.0 Hz), 7.18 (dd, 1H, J=7.5, 6.9 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=1.32 (CH_3), 21.24 (CH_2), 22.55 (CH_2), 25.42 (CH), 28.33 (CH_2), 31.07 (CH_2), 45.76 (CH_2), 57.60 (C), 126.04 (CH), 127.37 (CH), 128.19 (CH), 128.98 (C), 129.11 (CH), 139.59 (C) ppm. GC–MS (EI, 70 eV): m/z (%)=286 (M^+, 20), 271 (14), 257 (15), 244 (8), 196 (20), 195 (100), 179 (7), 167 (12), 91 (35), 73 (83). HRMS: Calcd for $C_{18}H_{26}OSi$ (M^+) 286.175294, found 286.175284.

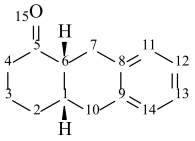
4.5.17. Synthesis of 4-(3-methylbut-3-enyl)-1-trimethylsilyloxylbicyclo[4.1.0]heptane (28). Following general procedure C; to a stirred solution of silyl enol ether **27** (133 mg, 0.561 mmol) in 2 mL dichloromethane, was added diethyl zinc (0.6 mL, 0.49 mmol). Solution was cooled to 0 °C using ice bath and neat CH_2I_2 (135 mg, 0.505 mmol) was added dropwise over a period of 15 min, reaction mixture was brought to rt and stirred for 12 h, usual workup gave **28** (91 mg, 65%) as a colorless oil. IR (neat): υ=2917, 2873, 1558 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.12 (s, 9H), 0.30 (t, 1H, J=3.5 Hz), 0.80–0.98 (m, 3H), 1.30 (td, 2H, J=7.3, 7.0 Hz), 1.41–1.68 (m, 4H), 1.70 (ddd, 4H, J=6.2, 5.4, 4.2 Hz), 2.00 (ddd, 3H, J=6.8, 7.2, 7.7 Hz), 4.68 (s, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=1.43 (CH_3), 18.95 (CH_2), 21.20 (CH_2), 22.50 (CH_2), 24.80 (CH), 31.20 (CH_2), 35.60 (CH_2), 36.30 (CH_2), 37.80 (CH), 57.23 (C), 109.00 (CH_2), 146.00 (C) ppm. GC–MS (EI, 70 eV): m/z (%)=252 (M^+, 2), 195 (17), 183 (14), 196 (4), 162 (4), 155 (2), 143 (5), 107 (26), 93 (7), 79 (7), 75 (26), 73 (100), 55 (10). HRMS: Calcd for $C_{15}H_{28}OSi$ (M^+) 252.19094, found 252.18994.

4.6. General procedure E

Synthesis of 3-substituted enones by reaction of vinylogous ester with GR: The GR was prepared analogously to the general procedure A, under argon atmosphere, the vinylogous ester in dry THF was added dropwise to the solution of GR at 0 °C, after addition reaction mixture was brought to rt and stirred for additional hour, water was added and reaction mixture was acidified with dilute HCl, solution was stirred for next 1 h, ether phase was separated and aqueous phase was extracted with ether, collective ether phases were washed with $NaHCO_3$ (aqueous, Saturated), water, brine and dried over sodium sulphate, concentrated under reduced pressure and residue was purified by silica gel column chromatography (EtOAc/cyclohexane).

4.6.1. Synthesis of 3-benzyl-2-cycloheptene-1-one (20). Follwing general procedure E; under argon atmosphere 3-ethoxy-2-cycloheptene-1-one **19** (500 mg, 3.246 mmol) was treated with GR prepared from benzyl chloride (449 mg, 3.57 mmol) and Mg metal (85 mg, 3.5 mmol) in THF–ether (1/1 by volume). The crude product was purified using silica gel column chromatography (25% EtOAc in cyclohexane) afforded enone **20** (590 mg, 91%). IR (neat): υ=2939, 2865, 1658, 1492, 1454, 1265 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.64–1.70 (m, 2H), 1.71–1.78 (m, 2H), 2.34 (t, 2H, J=6.2 Hz), 2.56 (t, 2H, J=6.4 Hz), 3.46 (s, 2H), 5.94 (s, 1H), 7.15 (d, 2H, J=7.0 Hz), 7.28 (ddd, 1H, J=4.0, 7.0, 8.0 Hz), 7.29 (dd, 2H, J=2.0, 8.0 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=21.28 (CH_2), 25.17 (CH_2), 32.31 (CH_2), 42.25 (CH_2), 47.09 (CH_2), 126.77 (CH), 128.58 (CH), 129.09 (CH), 130.61 (CH), 137.58 (C), 160.09 (C), 204.07 (C=O) ppm. GC–MS (EI, 70 eV): m/z (%)=158 (M^+, 7), 129 (13), 115 (11), 109 (100), 92 (1), 91 (21), 81 (46), 79 (22), 81 (46), 79 (22), 67 (14), 65 (36).

4.6.2. *cis*-3,4,4a,9,9a,10-Hexahydro-1(2*H*)-antracenone (29).[22] Following general procedure D; the solution of cyclopropane **8** (200 mg, 0.72 mmol) and DCA (55 mg, 0.24 mmol) in 120 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 12 h using 420 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford **29** (29 mg, 20%). IR (KBr): υ=2377, 2320, 1718, 1689, 1519 cm^{-1}. NMR (^{1}H, ^{13}C, ^{13}C-DEPT); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.54 (dddd, 1H, J=3.7, 3.7, 3.7, 3.1 Hz), 1.74 (tttt, 1H, J=4.0, 3.7, 4.0, 4.0 Hz), 1.82–1.93 (m, 1H), 2.04 (dq, 1H, J=1.2, 1.2 Hz), 2.11 (qq, 1H, J=2.8, 2.9 Hz), 2.40 (dddd, 2H, J=5.6, 6.9, 6.2, 6.2 Hz), 2.46–2.53 (1H, m), 2.69 (dd, 1H, J=11.9, 11.9 Hz), 2.92 (d, 1H, J=10.0 Hz), 2.96 (t, 2H, J=2.8 Hz), 7.04 (dd, 1H, J=2.5, 6.2 Hz), 7.10 (ddd, 2H, J=7.2, 5.4, 1.8 Hz), 7.16 (dd, 1H, J=2.5, 3.1 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=26.05 (CH_2), 28.63 (CH_2), 32.69 (CH_2), 37.79 (CH_2), 40.74 (CH_2), 41.91 (CH_2), 50.82 (CH), 125.72 (CH), 125.91 (CH), 128.42 (CH), 129.30 (CH), 135.04 (CH), 135.04 (C), 135.36 (C), 211.80 (C=O) ppm. NMR (^{1}H COSY, HMBC, HMQC and NOESY):

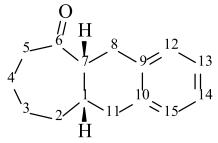


HMBC correlations of C-6 (50.82) to H-6 (δ 2.40), C-4 (41.91) to H-4 (2.50), C-1 (40.74) to H-1 (1.82–1.93), C-10 (37.79) to H-7 and H-10 (2.69 and 2.96), C-2 (32.69), to H-2 (1.54 and 2.04), C-7 (28.63) H-7 (2.96), C-3 (26.05), H-3 (1.54; 1.74; 2.04; 2.11). NOESY correlation of H-6 and H-1 leads to the assignment of cis ring fusion. GC–MS (EI, 70 eV): m/z (%)=200 (M^+, 100), 185 (27), 167 (24), 154 (47), 142 (21), 129 (59), 115 (17), 91 (13), 77 (18).

4.6.3. (5a*R*,10a*S*)-5,5a,7,8,9,10,10a,11-Octahydro-6*H*-cyclohepta[*b*]naphthalene-6-one (30). Following general procedure D; the solution of cyclopropane **9** (200 mg, 0.69 mmol) and DCA (30 mg, 0.131 mmol) in 120 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 12 h using 420 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford **30** (23 mg, 16%). IR (KBr): υ=2925, 2857, 1690, 1454 cm^{-1}. NMR (^{1}H, ^{13}C, ^{13}C-DEPT, ^{1}H COSY, HMBC, HMQC and NOESY); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.37 (ddd, 2H, J=12.5, 10.0, 9.8 Hz), 1.46–1.70 (m, 3H), 1.71–1.80 (m, 2H), 1.81–2.10 (m, 1H), 2.41 (ddt, 2H, J=6.3, 6.3, 2.0 Hz), 2.51–2.60 (2H, m), 2.65 (dt, 2H, J=11.0, 8.0 Hz), 2.84 (ddd, 2H, J=16.0, 16.2, 11.5 Hz), 7.09 (ddd, 3H, J=8.0, 3.0, 4.0 Hz), 7.26 (dd, 1H, J=6.9, 3.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=25.79 (CH_2), 32.74 (CH_2), 35.79 (CH_2), 35.52 (CH), 37.75 (CH_2), 41.19 (CH_2), 44.22 (CH_2),

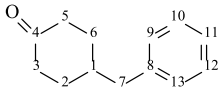
54.92 (CH), 125.92 (CH), 128.25 (CH), 128.47 (CH), 128.58 (CH), 135.16 (C), 136.31 (C), 215.64 (C=O) ppm.

NMR (^{1}H COSY, HMBC, HMQC and NOESY):

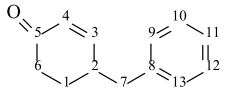


HSQC correlation of C-7 (54.92) to H-7 (2.51–2.60), C-5 (41.19) to H-5 (2.54), C-2 (41.19) to H-2 (2.50–2.65), C-11 (35.75) to (1.81–2.10 and 2.40–2.70 and 2.84), C-8 (32.74) to H-8 (2.84), C-3 (25.79) to H-3 (1.54 and 2.10). NOESY correlation between H-1 and H-7 lead to the assignment of cis ring fusion. GC–MS (EI, 70 eV): *m/z* (%)=214 (M^+, 90), 210 (6), 199 (20), 181 (26), 172 (11), 167 (3), 157 (15), 155 (17), 142 (28), 129 (100), 115 (35), 91 (15), 80 (10), 77 (16). HRMS: Calcd for $C_{15}H_{18}O$ (M^+) 214.1359, found 214.1347.

4.6.4. Benzylcyclohexanone (31)[23a] and 4-benzyl-2-cyclohexen-1-one (32).[23b] Following general procedure D; the solution of cyclopropane **7** (100 mg, 0.384 mmol) and DCA (25 mg, 0.109 mmol) in 60 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 12 h using 420 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford products **31** (6 mg, 8%) and **32** (9 mg, 12%). *Ketone* (**31**): IR (KBr): υ=1718, 1654 cm^{-1}. NMR (^{1}H, ^{13}C, ^{13}C-DEPT); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.20–1.37 (m, 1H), 1.42 (dq, 2H, *J*=4.3, 3.7 Hz), 1.99 (td, 3H, *J*=3.1, 4.3 Hz), 2.20–2.40 (m, 4H), 2.60 (d, 2H, *J*=6.9 Hz), 7.15 (d, 2H, *J*=6.9 Hz), 7.20 (t, 1H, *J*=7.2 Hz), 7.28 (t, 2H, *J*=7.2 Hz) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ=26.91 (CH_2), 38.14 (CH), 40.76 (CH_2), 42.19 (CH_2), 126.11 (CH), 128.35 (CH), 129.01 (CH), 140.36 (C), 211.20 (C=O) ppm. NMR (^{1}H COSY, HMBC, HMQC):



HMBC correlation of C-8 (140.36) to H-7 (2.60), C-7 (42.19) to H-1 (1.99), C-1 (38.14) to H-6 and H-2 (1.42) and H-5; H-2 (2.20–2.40) and H-7 (2.60), C-4 (211.20), to H-5; H-3; (2.20–2.40) and H-7 (2.60); H-6. COSEY correlation of H-2 to H-1; H-13; H-9 and H-1 to H-6; H-7 and H-2. GC–MS (EI, 70 eV): *m/z* (%)=188 (M^+, 1), 187 (7), 186 (50), 168 (60), 129 (8), 127 (2), 115 (4), 91 (100), 77 (6), 74 (1.2), 65 (54), 63 (13). *Enone* (**32**): IR (KBr): υ=1716, 1673 cm^{-1}. NMR (^{1}H, ^{13}C, ^{13}C-DEPT); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.66 (tdd, 1H, *J*=4.7, 4.3, 5.0 Hz), 1.99 (dtd, 1H, *J*=4.3, 5.0, 4.7 Hz), 2.27 (dtd, 1H, *J*=5.0, 4.5, 5.0 Hz), 2.42 (tt, 1H, *J*=4.8, 4.8 Hz), 2.65 (dd, 2H, *J*=8.5, 5.4 Hz), 2.72 (ddd, 1H, *J*=10.3, 5.3, 1.5 Hz), 5.92 (dd, 1H, *J*=1.8, 10.2 Hz), 6.77 (dt, 1H, *J*=2.0, 10.0 Hz), 7.13 (d, 2H, *J*=6.9 Hz), 7.18 (dd, 1H, *J*=1.8, 7.4 Hz), 7.26 (dd, 2H, *J*=1.8, 7.3 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=28.62 (CH_2), 36.79 (CH_2), 37.95 (CH), 40.90 (CH_2), 128.60 (CH), 128.56 (CH), 129.05 (CH), 129.31 (CH), 138.80 (C), 153.80 (CH), 199.70 (C=O) ppm. NMR (^{1}H COSY, HMBC, HMQC):

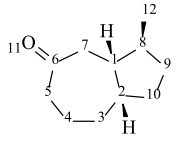


HMBC correlation of C-8 (138.80), to H-7 (2.65), H-9; H-13 (7.13), C-2 to (37.95) H-1a (1.66); H-1b (1.99), H-6a and H-6b (2.42); H-7 (2.65); H-3 (5.92) and H-4 (6.77), C-5 (199.70) to H-1; H-6; H-4. GC–MS (EI, 70 eV): *m/z* (%)=187 (M^+, 4), 186 (33), 168 (4), 158 (1), 129 (5), 127 (2), 115 (3), 91 (100), 79 (2), 77 (4), 65 (37), 51 (11).

4.6.5. 1-Methyl-3-(2-phenylethyl)-cyclohexanone (33). Following general procedure D; the solution of cyclopropane **18** (100 mg, 0.347 mmol) and DCA (45 mg, 0.19 mmol) in 50 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 12 h using 420 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford **33** (23 mg, 30%). IR: (KBr): υ=3391, 2961, 2932, 2866, 1710, 1452, 1070, 1452, 1070, 1070 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.99 (d, 3H, *J*=6.2 Hz), 1.31 (dd, 1H, *J*=12.8, 3.4 Hz), 1.36 (dd, 1H, *J*=12.5, 3.1 Hz), 1.40 (dd, 1H, *J*=5.0, 1.8 Hz), 1.43 (dd, 1H, *J*=13.1, 3.1 Hz), 1.58–1.72 (m, 2H), 1.94 (dt, 1H, *J*=13.0, 3.0 Hz), 2.05–2.15 (m, 1H), 2.33 (sep, 1H, *J*=6.2 Hz), 2.46 (dddd, 1H, *J*=1.8, 1.8, 1.8, 2.5 Hz), 2.60 (t, 2H, *J*=7.8 Hz), 7.15 (dd, 3H, *J*=6.0, 6.9 Hz), 7.26 (ddd, 2H, *J*=4.0, 7.0, 5.0 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=14.35 (CH_3), 31.98 (CH_2), 32.98 (CH_2), 34.87 (CH_2), 39.86 (CH), 44.87 (CH_2), 48.23 (CH_2), 125.83 (CH), 128.25 (CH), 128.38 (CH), 142 (C), 212.80 (C=O) ppm. GC–MS (EI, 70 eV): *m/z* (%)=216 (M^+, 20), 131 (10), 115 (11), 111 (65), 104 (14), 92 (23), 91 (100), 79 (7), 77 (10), 65 (13), 56 (8), 55 (30).

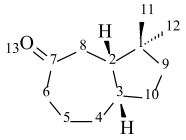
4.6.6. (3*S*,3a*R*,8a*S*)-3-Methyloctahydroazulen-5(1*H*)-one (34).[21] Following general procedure D; the solution of cyclopropyl silyl ether **14** (150 mg, 0.63 mmol) and DCA (48 mg, 0.21 mmol) in 60 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min. and irradiated for 12 h using 420 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford 35 (10 mg, 10%).

IR (KBr): υ=1653, 1507 cm^{-1}. NMR (^{1}H, ^{13}C, ^{13}C-DEPT); ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.80 (d, 3H), 1.15–1.35 m, 4H), 1.50–1.55 and 1.85–1.95 (m, 2H), 1.60–1.70 and 2.45–2.58 (m, 2H), 1.75–1.88 (m, 2H), 1.09–1.95 (m, 1H), 2.02–2.10 (m, 1H), 2.10–2.20 (m, 1H), 2.35–2.45 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=16.07 (CH_3), 24.86 (CH_2), 32.12 (CH_2), 32.53 (CH_2), 36.14 (CH_2), 37.64 (CH), 44.04 (CH_2), 44.28 (CH), 45.26 (CH_2), 45.88 (CH), 215.20 (C=O) ppm. NMR (^{1}H COSY, HMBC, HMQC and NOESY):



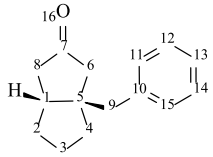
HMBC correlation of C-6 (215.20) to H-4 (1.50–1.55) and H-5; H-7 (1.75–1.95), and H-7 (2.30–2.50), C-12 (16.07) to H-9 and H-10 (1.15–1.35), H-1 and H-2 (1.75–1.85), H-8 (2.10–2.20). NOESY correlation between H-12 to H-1 and H-2 lead to the assignment of cis ring fusion. GC–MS (EI, 70 eV): *m/z* (%)=166 (M^+, 1), 165 (14), 123 (15), 121 (46), 110 (11), 107 (24), 94 (60), 80 (55), 78 (40), 67 (82), 55 (94), 41 (100).

4.6.7. (3a*S*,8a*S*)-3,3-Dimethyloctahydroazulen-5(1*H*)-one (35). Following general procedure D; the solution of cyclopropyl silyl ether **28** (120 mg, 0.476 mmol) and DCA (48 mg, 0.21 mmol) in 60 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 12 h using 420 nm lamps. The residue was purified by silica column chromatography (9% EtOAc in cyclohexane) to afford **35** (12 mg, 14%). IR (KBr): υ=1690, 1540 cm^{-1}. NMR (^1H, ^{13}C, ^{13}C-DEPT); ^1H NMR (500 MHz, $CDCl_3$): δ=0.75 (s, 3H), 0.96 (s, 3H), 1.26–1.32 (m, 2H), 1.38–1.46 (m, 1H), 1.45–1.50 (2H, m), 1.57 and 2.50 (m, 2H), 1.60 and 2.40 (m, 1H), 1.68–1.78 (2H, m), 1.87–1.95 (m, 2H), 1.98–2.10 (m, 1H), 2.24 (dd, 1H, *J*=16.4, 12.0 Hz), 2.48–2.52 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=22.31 (CH_3), 27.84 (CH_2), 27.93 (CH_3), 30.5 (CH_2), 37.02 (CH_2), 40.30 (CH_2), 43.65 (CH_2), 44.70 (C), 44.17 (CH_2), 46.69 (CH), 51.28 (CH), 215.18 (C=O) ppm. NMR (^1H COSY, HMBC, HMQC and NOESY):



HMBC correlation of C-1 (217.18) to H-8 and H-6 (2.20–2.52), C-2 (51.28) to H-11 and H-12 (0.75, 0.96), H-3a (2.49); H-8 (2.20–2.48), C-3 (46.69) to H-11 and H-12; H-4 (1.42–1.50), H-10 (2.00), H-8. NOESY correlation between H-3 and H-2 and H-11 lead to the assignment of cis stereochemistry of the molecule. GC–MS (EI, 70 eV): *m/z* (%)=180 (M^+, 10), 165 (8), 152 (3), 147 (11), 136 (13), 124 (20), 120 (11), 109 (23), 94 (24), 90 (8), 79 (20), 70 (30), 66 (60), 40 (100), 38 (32). HRMS: Calcd for $C_{12}H_{20}O$ (M^+) 180.15142, found 180.15086.

4.6.8. 3a-Benzyl-hexahydropentalen-2-one (36).[24] Following general procedure D; the solution of cyclopropyl silyl ether **22** (160 mg, 0.56 mmol) and DCA (52 mg, 0.228 mmol) in 96 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 17 h using 420 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford **36** (36 mg, 31%). IR (KBr): υ= 2947, 2868, 1737, 1660, 1450, 1405, 1166 cm^{-1}. NMR (^1H, ^{13}C, ^{13}C-DEPT); ^1H NMR (500 MHz, $CDCl_3$): δ=1.38 (ddd, 1H, *J*=5.0, 11.7, 6.4 Hz), 1.50 (ddd, 1H, *J*=7.5, 12.5, 6.5 Hz), 1.65–1.80 (m, 4H), 1.90–2.10 (m, 2H), 2.25–2.45 (m, 3H), 2.65 (d, 1H, *J*=13.1 Hz), 2.69 (d, 1H, *J*= 13.1 Hz), 6.79 (dd, 2H, *J*=1.5, 6.9 Hz), 7.16 (dd, 1H, *J*= 7.2, 4.7 Hz), 7.22 (dd, 2H, *J*=1.9, 6.5 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ=23.86 (CH_2), 32.52 (CH_2), 37.82 (CH_2), 44.44 (CH_2), 45.46 (CH_2), 48.95 (CH_2), 51.79 (C), 126.37 (CH), 128.20 (CH), 130.02 (CH), 138.62 (C), 219.87 (C=O) ppm. NMR (^1H COSY, HMBC, HMQC and NOESY):



HMBC correlation of C-7 (219.87) to H-6 and H-8 (1.90–2.10; 2.25; 2.45), C-10 (138.62) to H-9 (2.65), C-1 (44.44) to H-3 and H-2 (1.70) and H-8 (1.90–2.09) and to H-9. NOESY correlation between H-9 and H-1a leads to the assignment of cis ring fusion. GC–MS (EI, 70 eV): *m/z* (%)=214 (M^+, 16), 149 (11), 123 (34), 117 (5), 95 (100), 81 (81), 67 (23), 65 (30).

4.6.9. 3,4,4a,5,8,8a-Hexahydro-1-(2*H*)-naphthalenone (38).[18] Following general procedure D; the solution of cyclopropyl silyl ether **12** (100 mg, 0.45 mmol) and DCA (25 mg, 0.109 mmol) in 60 mL dry acetonitrile was filled into Pyrex irradiation tubes, flushed with argon for 20 min and irradiated for 17 h using 420 nm lamps. The residue was purified by silica gel column chromatography (9% EtOAc in cyclohexane) to afford **38** (10 mg, 15%). IR (KBr): υ= 1720, 1666 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=1.40–2.45 (m, 10H), 2.55 (dd, 1H, *J*=6.9, 7.5 Hz), 2.75 (dd, 1H, *J*=4.3, 7.5 Hz), 4.87 (t, 2H, *J*=1.2 Hz) ppm. GC–MS (EI, 70 eV): *m/z* (%)=150 (M^+, 13), 134 (11.4), 121 (19.5), 106 (24), 91 (35), 79 (100), 77 (76), 52 (43), 40 (32).

5. Supplementary data

Supplementary data associated with 2D NMR experiments are available from the authors on request.

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