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Studies on photochemical rearrangement of non-oxygenated bicyclo[2.2.2]octenones and mono-oxygenated bicyclo[2.2.2]octenones from masked *o*-benzoquinones: Access to protoilludane and marasmane skeletons

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Abstract

In this work, we described flexible approaches to protoilludane-like (5,6,4-tricyclic ring) and marasmane-like (5,6,3-tricyclic ring) skeletons with naturally occurring *cis*/*anti*/*cis* stereochemistry using photochemical rearrangement of bicyclo[2.2.2] octenones and Diels-Alder reaction of masked *o*-benzoquinones as the key steps.

KEYWORDS

bicyclo[2.2.2]octenones, marasmane, masked *o*-benzoquinones, photoreaction, protoilludane

1 | INTRODUCTION

Bicyclo[2.2.2]octenone housing β,γ-unsaturated carbonyl chromophore has shown significant reactivity in photochemistry,[1] and therefore the photochemical rearrangement of bicyclo[2.2.2]octenone has proven to be an useful tool for forging of carbon skeleton in total synthesis of natural products or complex molecular frameworks.[2] For instance, the use of oxa-di-π-methane rearrangement in total synthesis of (±)-magellanine[3] and the formal synthesis of (±)-pentalenolactone A methyl ester.[4] Additionally, utilization of photoinduced 1,3-migration could also be found in the enantiomeric synthesis of (+)-armillarivin[5] and formal synthesis of (±)-coriolin.[6] Another type of photochemically mediate reaction, which involved 1,3-acyl migration and additional decarbonylation, we called it photoinduced decarbonylative 1,3-migration (PIDM), can be used in construction of some natural occurring skeletons, like protoilludane.[7]8c In addition, some cases were reported that products of PIDM resulted from 1,3-acyl migration via prolonged irradiation with ultraviolet (UV) light.[8]

Recently, we have enticed to the unique tricyclic 5,6,3-framework (marasmane skeleton),[7] which consists in a number of bioactive sesquiterpenoids such as isovelleral[9] and its derivitives[10] (Figure 1). Although many of promising synthetic strategies for the angularly tricyclic structure and approaches to isovelleral have been demonstrated;[9] an efficient route toward the marasmane core still has presented many synthetic challenges.

Previous synthetic efforts in our laboratory were targeted at the tricyclic 5,6,3-framework, and we have reported a rapid approach to which via PIDM.[11] On the basis of our recent experiences, the efficient decarbonylative rearrangement of **6a** results from the formation of relatively stable dimethyl ketal radical species **biradical II** (Scheme 1) to yield the PIDM product. Based on this knowledge, we became interested in how the existence of oxygen

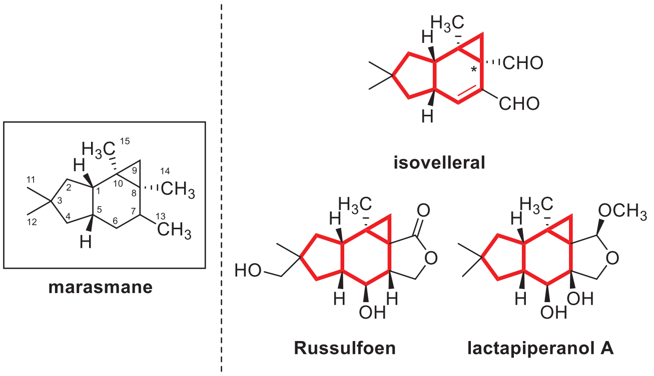
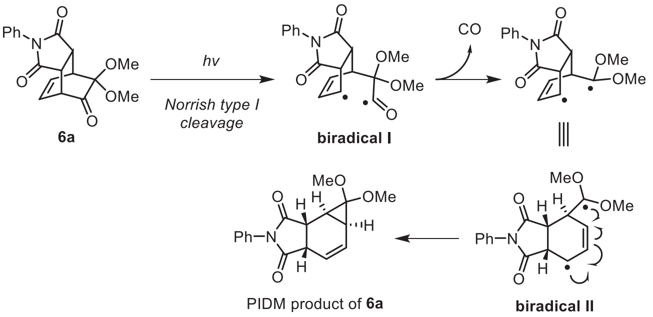


FIGURE 1 Bioactive sesquiterpenoids containing marasmane skeleton



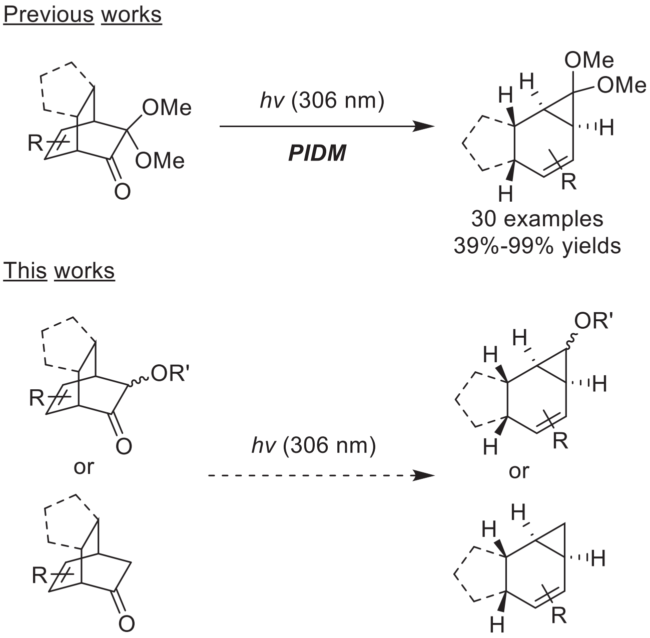
SCHEME 1 Proposed reaction pathway for photoinduced decarbonylative 1,3-migration of **6a**

adjacent to carbonyl group on bicycle ring affects reaction pathway during irradiation of UV light. Herein, we report the photoreaction of nonoxygenated bicyclo[2.2.2]octenones and mono-oxygenated bicyclo[2.2.2]octenones (Scheme 2).

2 | RESULTS AND DISCUSSION

2.1 | Synthesis of various bicyclo[2.2.2] octenones for the photoinduced reaction

To prepare bicyclo[2.2.2]octenones as the starting material for photoinduced reactions, we applied the Diels-Alder reaction of masked *o*-benzoquinone (MOB), which were developed by Liao and Quideau.[12] The preparation of bicyclo [2.2.2]octenones were depicted in Table 1. MOBs **2** were rapidly generated in situ from 2-methoxyphenols **1** in the presence of (diacetoxy)iodobenzene (PhI(OAc)$_2$), and directly underwent efficient self-Diels-Alder reaction to afford dimer **3** in refluxing methanol.[13,14] Subsequent reaction of the resulting dimer with the selected dienophile **4** (for its high reactivity) and **5** (for its structure that resemble the five-member ring on marasmane skeleton) provided the corresponding cycloaddition products **6** and **7** in 66–92% yield, respectively via a retro Diel-Alder/Diels-Alder process.



SCHEME 2 Photoreactions of bicyclo[2.2.2]octenones

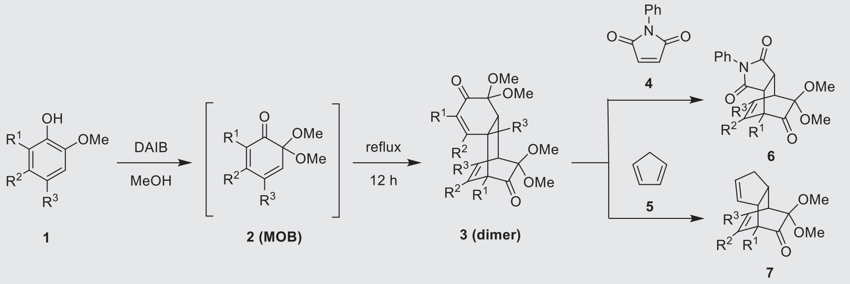
2.2 | Photoinduced reaction of demethoxylated bicyclo[2.2.2]octenones

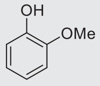
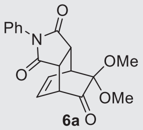
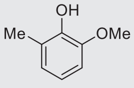
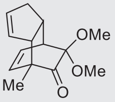
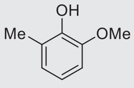
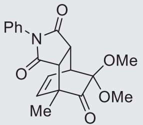
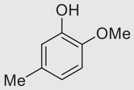
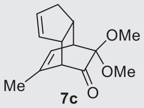
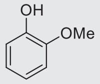
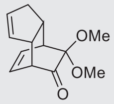
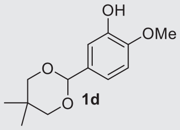
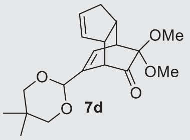
Having the various bicyclo[2.2.2]octenones in hand, we then carried out the photoinduced reaction of demethoxylated bicyclo[2.2.2]octenones. As shown in Table 2, the selected D-A adducts **6a**, **6b**, and **7a** underwent reductive deketalization with SmI$_2$ at room temperature to give **8a**, **8b**, and **9a** in 24–88% yield, which were subsequently examined the photoinduced rearrangement. Unfortunately, after 1.5 hr irradiation with a broad band UV light centered at 306 nm, deketal product **8a** was transformed to the 1,3-acyl migration product **10a** in 42% isolated yield instead of the desired PIDM product **12a** (Table 2, entry 1). The same results were obtained in the examples of **8b** and **9a**, which gave the corresponding 1,3-acyl migration product **10b**, **11a** in 53 and 16% yield, respectively (Table 2, entries 2–3). The structures of photoreaction were established by ^{1}H, ^{13}C, DEPT NMR, and HRMS. It is not surprising to afford the protoilludane-like results, which probably proved that bicyclo[2.2.2] octenones bore dimethyl ketal adjacent to carbonyl group, which was required to stabilize the radical intermediate and promote 1,3-acyl migration instead of PIDM.8c

2.3 | Photoinduced reaction of α-hydroxybicyclo[2.2.2]octenones

Our next object was to examine the photoreaction of α-hydroxybicyclo[2.2.2]octenones, which could be synthesized

TABLE 1 Preparation of bicyclo[2.2.2]octenones **6** and **7** from 2-methoxyphenols **1**



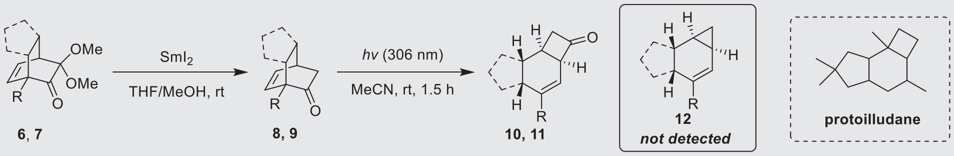
Entry	2-Methoxyphenol	Diel-Alder adduct	Yield[a] (%)	Entry	2-Methoxyphenol	Diel-Alder adduct	Yield[a] (%)
1	 **1a**	 **6a**	92	4	 **1b**	 **7b**	85
2	 **1b**	 **6b**	87	5	 **1c**	 **7c**	83
3	 **1a**	 **7a**	73	6	 **1d**	 **7d**	66

[a] The yields of two steps were determined after column chromatography.

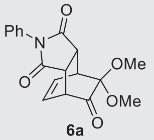
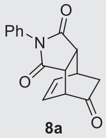
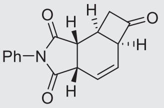
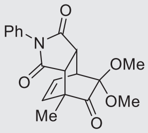
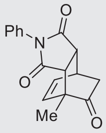
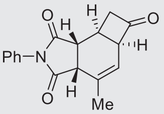
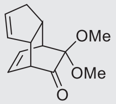
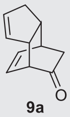
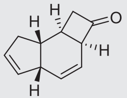
from D-A products **7**. In the two-step sequence, D-A products **7** were first treated with $NaBH_4$ for carbonyl group reduction to deliver the *exo* isomer and the *endo* isomer, and then the obtained epimeric ketal alcohols were hydrolyzed under acidic conditions to afford **13** in 19–34% yields and **14** in 21–68% yields (Table 3). To expand the tolerance of functional groups, **7d** (for its ketal group that resemble aldehyde moiety on natural product, isovelleral; Figure 1) was elaborated to α-hydroxybicyclo[2.2.2]octenone isomers **13d** and **14d** in four-step sequence (Scheme 3). Exposure of **7d** to HCl in ethyl acetate and water at room temperature, followed by Wittig olefination of the resulting aldehyde **15**, delivered vinylated product **16** in 62% isolated yield. Subsequently, a two-step reduction/hydrolysis protocol was used to give a pair of isomers, **13d** and **14d**, in 36 and 31% isolated yields, respectively. The stereochemistry of **13a**, **14a** was diagnosed with nuclear overhauser effect (NOE) experiments. In addition, **14a** provided single crystals, which allowed to be further confirmed by X-ray analysis (Figure 2).

With the synthesized α-hydroxybicyclo[2.2.2]octenones **13** and **14** in hand, we then examined photoinduced reactions of selected **13a** and **14a**. Under photolysis conditions, both **13a** and **14a** unfortunately gave complex mixture with no desired product detected in ^{1}H NMR of the crude product mixture. Despite the reaction, solvent was switched from acetonitrile to benzene, none of which were successful. Considering that the free hydroxyl group on **13** or **14** would frustrate the photoreaction, we planned to apply tert-butyldimethylsilyl (TBS) protection of **13** and **14** before irradiation of UV light. The results of cases of PIDM products **17** and **18** were successfully obtained and are shown in Table 4. The *exo* isomer **13a** proceeded silyl protection/photolysis sequence to provide the *anti*product **18a** (the relative orientation between -OTBS and bridgehead hydrogen atom on cyclopropane ring) in 57% yield, and *syn* product **17a** was isolated from *endo* isomer **14a** in 52% yield (Table 4, entries 1–2). Of note, apart from non-substituent cases, substituents at C-8 or C-10 led to unexpected epimerization at C-9 during photolysis. The *exo* isomers **13b-d** were found to form the *syn* products **18b-d** (29–65% yield) as the major products along with minor *anti*products **17b-d** (7–11% yield) (Table 4, entries 3, 5 and 7), in contrast, the *endo* isomers **14b-d** underwent PIDM reaction to give the major *anti*product **17b-d** (32–58% yield), accompanied by minor *syn* product **18b-d** (10–28% yield) (Table 4, entries 4, 6 and 8).

TABLE 2 Photoinduced reaction of demethoxylated bicyclo[2.2.2]octenones

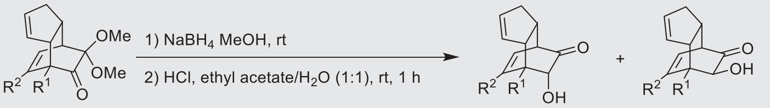


6, 7 — 8, 9 — 10, 11 — 12 *not detected*

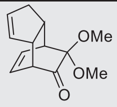
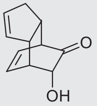
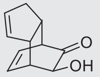
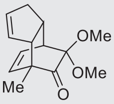
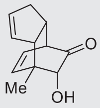
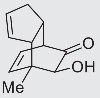
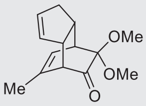
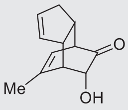
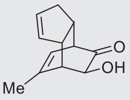
Entry	Diel-Alder adduct	Deketal product	Yield[a] (%)	Product **10, 11**	Yield[a] (%)
1	 **6a**	 **8a**	62[b]	 **10a**	42
2	 **6b**	 **8b**	88[b]	 **10b**	53
3	 **7a**	 **9a**	24[c]	 **11a**	16

[a] Isolated yield. [b] Reaction time: 0.5 h. [c] Reaction time: 6 h.

TABLE 3 Preparation of α-hydroxybicyclo[2.2.2]octenones from Diels-Alder products of MOBs

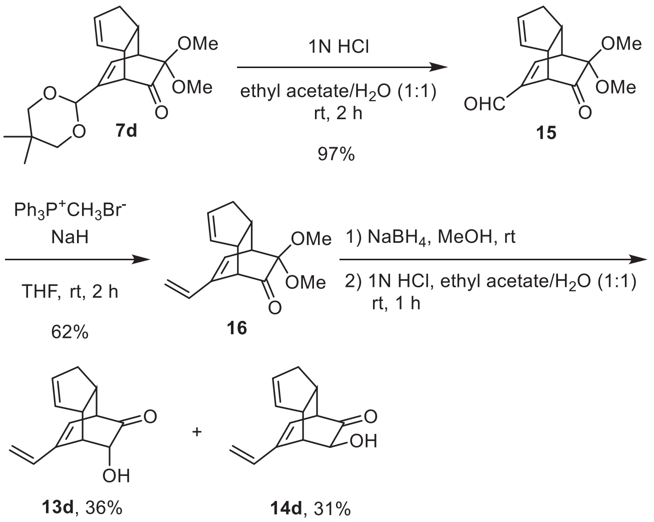


7 — **13** (*exo* isomer) — **14** (*endo* isomer)

Entry	Diel-Alder adduct	Product **13**+**14**	Yield[a] (%)
1	 **7a**	 **13a** +  **14a**	**13a** (19)+**14a** (68)
2	 **7b**	 **13b** +  **14b**	**13b** (34)+**14b** (21)
3	 **7c**	 **13c** +  **14c**	**13c** (34)+**14c** (32)

[a] The yields of two steps were determined after column chromatography.

The unexpected epimerization during the photolysis of **13b** was proposed in two plausible pathways. Path A involves that **biradical III** was generated from **19b** through Norrish type I cleavage, immediately releasing CO to form **biradical IV**. Finally, PIDM products **17b** and **18b** were given by recombination of **biradical IV**



SCHEME 3 Synthesis of α-hydroxybicyclo[2.2.2]octenones **13d** and **14d**

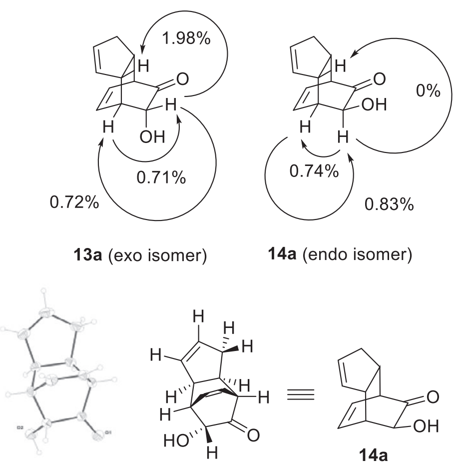


FIGURE 2 NOE experiments of **13a**, **14a** and ORTEP diagram of **14a**

(Scheme 4, path A). Alternative pathway involves the combination of **biradical III** afforded 5,6,4-tricyclic compound **11b**, followed by the second time Norrish type I cleavage and sequential extrusion of CO to provide PIDM products **17b** and **18b** (Scheme 4, path B).

3 | CONCLUSIONS

In summary, we present versatile methods to achieve functionalized protoilludane-like skeleton via 1,3-acyl migration of nonoxygenated bicyclo[2.2.2]octenones, and marasmane-like skeleton by PIDM of mono-oxygenated bicyclo[2.2.2]octenones, which could be easily obtained by the Diels-Alder reaction of mask *o*-benzoquinones. We anticipate these successful transformations will be a useful tool for building strained and complex molecular frameworks.

4 | EXPERIMENTAL

4.1 | General information

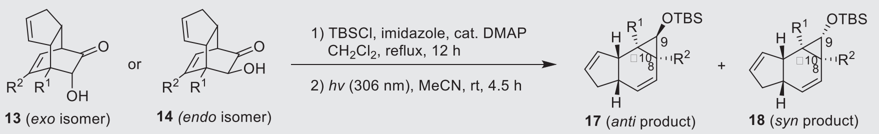
Reactions were carried out under ambient atmosphere unless otherwise specified. Methanol and dichloromethane were dried by distillation from CaH_2. tetrahydrofuran (THF) was dried by distillation from Na/benzophenone. Commercially obtained reagents were used as received unless otherwise specified. Tributyltin hydride was purchased from Merck, Acros, and Alfa Aesar. Photoreaction was carried out using PANCHUM Photochemical Reactor PR-2000. Yields refer to purified and spectroscopically pure compounds. Thin-layer chromatography (TLC) was performed using Merck TLC Aluminum sheets silica gel 60 F_{254} plates and visualized by fluorescence quenching under UV light and $KMnO_4$ stain. Flash chromatography was performed using silica gel (Chromatorex, MB 70-40/75, 40–75 μm) purchased by Fuji Silysia Chemicals. NMR spectra were recorded on a Bruker AVANCE spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C, Bruker AVANCE II operating at 400 MHz for ^1H and 100 MHz for ^{13}C acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard: $CDCl_3$ = 7.26 (^1H), 77.0 (^{13}C). Data are reported as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. High-resolution mass spectra were obtained on JMS-700 at the Academia Sinica.

The analytical data for compounds **6a-b**, **7a-d** are identical with those already reported in the literature.[11]

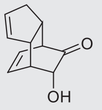
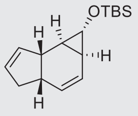
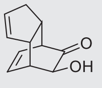
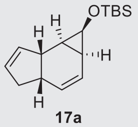
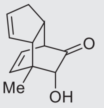
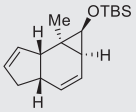
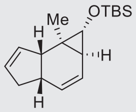
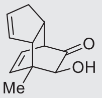
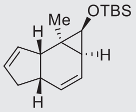
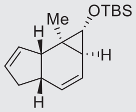
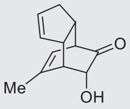
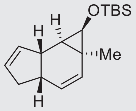
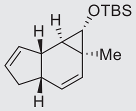
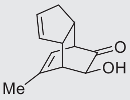
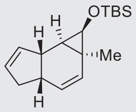
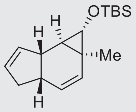
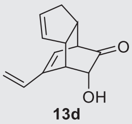
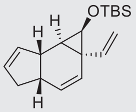
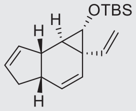
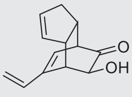
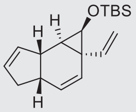
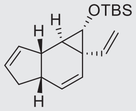
4.2 | General procedure for deketalization of bicyclo[2.2.2]octenones (synthesis of 8a as example)

Preparation of SmI_2/THF solution (Kagan's method): An oven-dried 100 ml round-bottomed flask equipped with a Teflon-coated magnetic stir bar and a septum was placed under a positive pressure of argon. In air, samarium metal (11.48 g, 76.4 mmol) and 1,2-diiodoethane (10.77 g, 38.2 mmol) were weighed out and added to the reaction flask. The flask was sealed with a septum, and stirring was started at medium speed. Freshly dried THF (220 ml) was added at 0°C and the septum was sealed with Parafilm. After being stirred for 30 min, the ice bath was removed and the mixture was stirred at room temperature overnight. The deep blue solution was allowed to use for the deketalizaiton.

TABLE 4 TBS protection/photoinduced decarbonylative 1,3-acyl migration of **13** and **14**



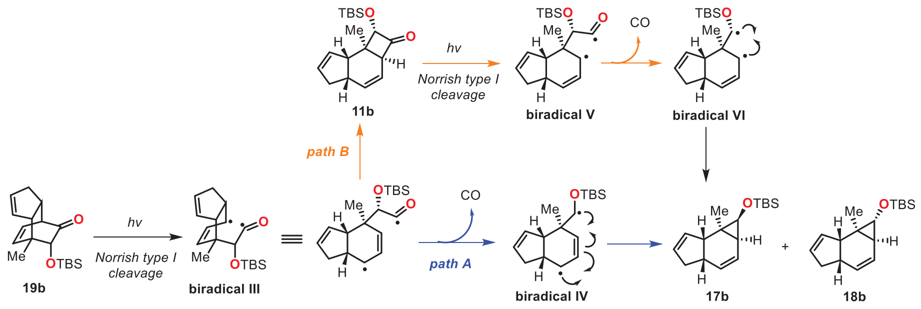
13 (*exo* isomer) **14** (*endo* isomer) **17** (*anti* product) **18** (*syn* product)

Entry	Precursor **13** or **14**	PIDM product **17**+**18**	Yield[a] (%)
1[b]	 **13a**	 **18a**	**18a** (57)
2[b]	 **14a**	 **17a**	**17a** (52)
3	 **13b**	 **17b** +  **18b**	**17b** (7)+**18b** (55)
4	 **14b**	 **17b** +  **18b**	**17b** (37)+**18b** (10)
5	 **13c**	 **17c** +  **18c**	**17c** (7)+**18c** (65)
6	 **14c**	 **17c** +  **18c**	**17c** (32)+**18c** (19)
7	 **13d**	 **17d** +  **18d**	**17d** (11)+**18d** (29)
8	 **14d**	 **17d** +  **18d**	**17d** (58)+**18d** (28)

[a] The yields of two steps were determined after column chromatography.

[b] Irradiation of UV light for 17 h.

To a stirred solution of **6a** (0.327 g, 1.00 mmol) in the mix solvent of dry THF (1 ml) and dry MeOH (0.4 ml, d = 0.791 g/ml) was added to the freshly prepared SmI_2/THF solution in a dropwise manner at room temperature (Caution: SmI_2 solution was extremely air sensitive, make sure to run this reaction under inert gas). After being stirred for a period of time (Table 2 for the duration of reaction time), the reaction mixture was opened to air until the blue color was faded. The reaction mixture was filtered through a pad of Celite® then concentrated under reduced pressure to remove THF. The residue was diluted with CH_2Cl_2, and the organic layer was washed sequentially with 1 N HCl, saturated aqueous $Na_2S_2O_3$, and brine. The organic solution was dried over $MgSO_4$,



SCHEME 4 Proposed mechanism for the generation of **17b** and **18b** from **19b**

filtered, and concentrated. The residue was purified by flash chromatography on silica gel (EtOAc: *n*-Hexane = 1:10 → 1:3) to afford **8a** (0.166 g, 62% yield) as a white solid.

4.3 | (3a*R**,4*S**,7*R**,7a*S**)-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoisoindole-1,3,8(2*H*)-trione (8a)

White solid, 166 mg, 62% yield; R_f = 0.25 (silica gel, EtOAc: *n*-Hexane = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 7.51–7.37 (m, 3H), 7.23–7.16 (m, 2H), 6.56 (ddd, J = 7.8, 6.2, 1.3 Hz, 1H), 6.32 (ddd, J = 8.1, 6.2, 1.8 Hz, 1H), 3.79 (ddd, J = 6.4, 3.1, 1.3 Hz, 1H), 3.71–3.66 (m, 1H), 3.40–3.26 (m, 2H), 2.23 (ddd, J = 2.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 206.9 (C), 176.1 (CH), 175.1 (CH), 135.3 (CH), 131.5 (CH), 129.2 (2xCH), 128.9 (CH), 127.6 (CH), 126.3 (2xCH), 49.5 (CH), 44.0 (CH), 41.0 (CH), 38.1 (CH_2), 34.5 (CH); IR (neat, cm^{-1}) 1,732, 1,700, 1,592, 1,496, 1,455, 1,382, 1,224, 1,185, 1,096, 1,059, 955, 876, 830, 797, 763, 744, 721, 692, 621, 502; HRMS (EI) *m/z* calcd for $C_{16}H_{13}NO_3$ $[M]^+$ 267.0895, found 267.0893.

4.4 | (3a*R**,4*S**,7*R**,7a*R**)-7-methyl-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoisoindole-1,3,8(2*H*)-trione (8b)

White solid, 221 mg, 88% yield; R_f = 0.28 (silica gel, EtOAc: *n*-Hexane = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 7.44 (ddd, J = 12.5, 7.9, 6.1 Hz, 3H), 7.23–7.17 (m, 2H), 6.56 (ddd, J = 7.8, 6.2, 1.3 Hz, 1H), 6.32 (ddd, J = 8.1, 6.2, 1.8 Hz, 1H), 3.79 (ddd, J = 6.4, 3.1, 1.3 Hz, 1H), 3.71–3.65 (m, 1H), 3.37 (dd, J = 8.5, 3.0 Hz, 1H), 3.29 (dd, J = 8.4, 3.2 Hz, 1H), 2.23 (t, J = 2.9 Hz, 3H), 1.67 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 208.5 (C), 176.1 (C), 174.6 (C), 162.3 (C), 134.6 (CH), 131.4 (C), 133.3 (CH), 129.2 (2xCH), 128.9 (CH), 126.4 (2xCH), 74.0 (CH_3), 45.7 (CH), 45.0 (CH), 38.1 (CH_2), 33.9 (CH); IR (neat, cm^{-1}) 1,701, 1,593, 1,492, 1,455, 1,382, 1,305, 1,229, 1,188, 1,093, 988, 847, 805, 781, 738, 692, 644, 622, 575, 539, 513; HRMS (APCI) *m/z* calcd for $C_{17}H_{15}NO_3$ $[M + H]^+$ 282.1130, found 282.1132.

4.5 | (3a*R**,4*R**,7*S**,7a*R**)-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-9-one (9a)

White solid, 40 mg, 25% yield, R_f = 0.35 (silica gel, EtOAc: *n*-Hexane = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 6.38–6.27 (m, 1H), 6.03–6.01 (m, 1H), 5.64 (dd, J = 6.3, 2.3 Hz, 1H), 5.42 (dd, J = 4.8, 2.3 Hz, 1H), 3.23–3.09 (m, 2H), 3.02–2.96 (m, 1H), 2.73–2.62 (m, 1H), 2.59–2.48 (m, 1H), 2.05 (d, J = 2.8 Hz, 2H), 2.02–1.85 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 212.8 (C), 134.4 (CH), 132.7 (CH), 130.2 (CH), 128.3 (CH), 52.7 (CH), 49.5 (CH), 40.3 (CH_2), 39.9 (CH), 38.9 (CH_2), 37.6 (CH); IR (neat, cm^{-1}) 1,718, 1,442, 987, 936, 894, 869, 744, 675, 540; HRMS (ESI) *m/z* calcd for $C_{11}H_{12}O$ $[M]^+$ 160.0888, found 160.0885.

4.6 | General procedure of the photoreaction of demethoxylated compound 8 or 9 (synthesis of 10a as example)

To a solution of 8a (70 mg, 0.262 mmol) in acetonitrile (70 ml) was transferred into the quartz tube and degassed by purging with N_2 for 45 min. The reaction mixture was irradiated with a broad band centered at 306 nm in a Rayonet-type photoreactor and stirred for 90 min. The reaction mixture was then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc: *n*-Hexane = 1:50 → 1:20) to afford 10a (30 mg, 42% yield, 57% brsm) as a white solid.

4.7 | (3a*S**,5a*S**,7a*S**,7b*R**)-2-phenyl-3a,7,7a,7b-tetrahydro-1*H*-cyclobuta[*e*]isoindole-1,3,6(2*H*,5a*H*)-trione (10a)

White solid, 30 mg, 42% yield; R_f = 0.34 (silica gel, EtOAc: *n*-Hexane = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 7.53–7.37 (m, 2H), 7.31–7.24 (m, 2H), 6.08 (ddd, J = 10.1, 3.0, 2.0 Hz, 1H), 5.95 (ddd, J = 10.1, 4.6, 2.4 Hz, 1H), 3.87–3.79 (m, 1H), 3.75–3.70 (m, 1H), 3.56–3.43 (m, 2H), 3.35 (ddd, J = 17.3, 9.0, 4.8 Hz, 1H), 3.17 (ddd, J = 17.4, 8.9, 2.8 Hz, 1H), 1.27 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 202.1 (C), 176.4 (C), 174.9 (C), 131.5 (CH), 129.2 (2xCH), 128.7 (CH), 126.2 (2xCH), 123.2 (CH), 122.7 (CH), 57.5 (CH), 50.4 (CH_2), 39.9 (CH), 39.1 (CH), 19.7 (CH); IR (neat, cm^{-1}) 2,914, 2,361, 1,776, 1,706, 1,495, 1,374, 1,175, 1,107, 815, 779, 754, 724, 691, 666. HRMS (EI) m/z calcd for $C_{16}H_{13}NO_3$ $[M]^+$ 267.0895, found 267.0900.

4.8 | (3a*S**,5a*S**,7a*S**,7b*S**)-7a-methyl-2-phenyl-3a,7,7a,7b-tetrahydro-1*H*-cyclobuta[*e*]isoindole-1,3,6(2*H*,5a*H*)-trione (10b)

White solid, 37 mg, 53% yield; R_f = 0.30 (silica gel, EtOAc: *n*-Hexane = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 7.52–7.37 (m, 3H), 7.30–7.25 (m, 2H), 5.64 (dd, J = 4.1, 2.1 Hz, 1H), 3.81–3.72 (m, 1H), 3.68–3.40 (m, 3H), 3.36–3.08 (m, 2H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 202.8 (C), 176.4 (CH), 173.8 (CH), 131.6 (CH), 129.5 (CH), 129.1 (2xCH), 128.6 (CH), 126.2 (2xCH), 118.4 (CH), 58.0 (CH), 50.1 (CH_2), 42.7 (CH), 41.7 (CH), 22.1 (CH_3), 19.5 (CH); IR (neat, cm^{-1}) 2,917, 2,360, 2,360, 1,776, 1,708, 1,595, 1,497, 1,455, 1,403, 1,383, 1,319, 1,289, 1,218, 1,175, 1,085, 911, 844, 748, 730, 694, 568, 519, 498, 445; HRMS (ESI) m/z calcd for $C_{17}H_{15}NO_3$ $[M + H]^+$ 282.1130, found 282.1123.

4.9 | (2a*S**,4a*S**,7a*R**,7b*R**)-1,2a,4a,7,7a,7b-hexahydro-2*H*-cyclobuta[*e*]inden-2-one (11a)

White solid, 8 mg, 16% yield; R_f = 0.45 (silica gel, EtOAc: *n*-Hexane = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 5.84–5.80 (m, 1H), 5.76–5.68 (m, 1H), 5.68–5.62 (m, 1H), 5.57 (ddd, J = 10.2, 4.7, 2.2 Hz, 1H), 5.64 (m, 1H), 3.22–3.13 (m, 1H), 3.13–3.01 (m, 2H), 2.77–2.56 (m, 2H), 2.41 (dddd, J = 16.0, 8.3, 2.8, 1.4 Hz, 1H), 2.10–2.05 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 205.9 (C), 132.7 (CH_2), 130.3 (CH_2), 128.7 (CH_2), 117.4 (CH_2), 56.9 (CH), 50.3 (CH_2), 40.4 (CH), 36.9 (CH), 36.8 (CH_2), 24.3 (CH). IR (neat, cm^{-1}) 2,905, 2,354, 1,718, 1,457, 987, 936, 921, 894, 867, 747, 679, 544; HRMS (ESI) m/z calcd for $C_{11}H_{12}O$ $[M]^+$ 160.0888, found 160.0890.

4.10 | General procedure for $NaBH_4$ reduction/hydrolysis of bicyclo[2.2.2] octenones 7 (synthesis of 13a and 14a as example)

To a stirred solution of **7a** (0.220 g, 1.00 mmol) in MeOH (10 ml) was added $NaBH_4$ (0.038 g, 1.0 mmol) at 0°C. The reaction mixture was warmed to room temperature. After the consumption of **7**, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with CH_2Cl_2 several times. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (EtOAc: *n*-Hexane = 1:10 → 1:4) to afford unseparated alcohols **S1a** and **S2a** (0.222 g, 99% yield) as a sticky colorless oil. To a stirred solution of the above oil (0.222 g, 1.00 mmol) in ethyl acetate (5 ml) was sequentially added deionic water (5 ml) and 1 N HCl solution (3 ml) at room temperature. After being stirred for 3 hr, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2 several times. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (EtOAc: *n*-Hexane = 1:10 → 1:2) to afford two white solid **13a** (34 mg, 19% yield) and **14a** (122 mg, 69% yield), respectively.

4.11 | (3a*R**,4*R**,7*S**,7a*S**,9*R**)-9-hydroxy-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (13a)

White solid, 34 mg, 19% yield; R_f = 0.13 (silica gel, EtOAc: *n*-Hexane = 1:2); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 6.32–6.26 (m, 1H), 6.13–6.08 (m, 1H), 5.72–5.66 (m, 1H), 5.53–5.48 (m, 1H), 3.77 (s, 1H), 3.27–3.19 (m, 2H), 3.15–3.09 (m, 1H), 2.82–2.74 (m, 1H), 2.68–2.63 (m, 1H), 2.63–2.56 (m, 1H), 2.07–1.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 24°C, δ) 211.4 (C), 135.6 (CH), 132.5 (CH), 131.1 (CH), 124.3 (CH), 71.2 (CH), 52.8 (CH), 49.8 (CH), 42.7 (CH), 38.4 (CH_2), 34.4 (CH); IR (neat, cm^{-1}) 3,458, 3,049, 2,944, 2,847, 2,847, 2,360, 1,717, 1,441, 1,353, 1,239, 1,191, 1,136, 1,090, 1,036, 979, 954, 835, 768, 727, 695, 593, 502; HRMS (EI) m/z calcd for $C_{11}H_{12}O_2$ $[M]^+$ 176.0837, found 176.0839.

4.12 | (3a*R**,4*R**,7*S**,7a*S**,9*S**)-9-hydroxy-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (14a)

White solid, 122 mg, 69% yield; R_f = 0.2 (silica gel, EtOAc: *n*-Hexane = 1:2); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 6.36–6.31 (m, 1H), 6.12–6.05 (m, 1H), 5.63–5.58 (m, 1H), 5.56–5.52 (m, 1H), 3.66 (d, J = 3.3 Hz, 1H), 3.44–3.36 (m, 1H), 3.30–3.20 (m, 1H), 3.14–3.09 (m, 1H), 2.79–2.70 (m, 1H), 2.61–2.50 (m, 2H), 2.09–2.00 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 212.5 (C), 134.9 (CH), 132.0 (CH), 131.8 (CH), 126.1 (CH), 70.7 (CH), 51.9 (CH), 44.7 (CH), 43.3 (CH), 39.2 (CH), 38.2(CH_2); IR (neat, cm^{-1}) 3,448, 3,046, 2,964, 2,905, 2,842, 2,360, 1,722, 1,437, 1,401, 1,358, 1,330, 1,271, 1,213, 1,192, 1,147, 1,088, 980, 961, 924, 854, 824, 798, 754, 730, 702, 687, 559, 789; HRMS (EI) *m/z* calcd for $C_{11}H_{12}O_2$ [M]$^+$ 176.0837, found 176.0838.

4.13 | (3aR*,4R*,7S*,7aS*,9R*)-8,8-dimethoxy-4-methyl-3a,4,7,7a-tetrahydro-1H-4,7-ethanoinden-9-ol (S1b)

White solid, 533 mg, 35% yield; R_f = 0.30 (silica gel, EtOAc: *n*-Hexane = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 5.95–5.90 (m, 1H), 5.67–5.64 (m, 1H), 5.55–5.52 (m, 1H), 5.49–5.46 (m, 1H), 3.25 (d, J = 6.8 Hz, 1H), 3.20 (d, J = 1.1 Hz, 3H), 3.17 (d, J = 1.1 Hz, 3H), 2.85 (dd, J = 7.0, 1.0 Hz, 1H), 2.79 (dd, J = 6.6, 2.9 Hz, 1H), 2.77–2.69 (m, 1H), 2.54–2.47 (m, 1H), 2.44–2.32 (m, 1H), 1.84–1.73 (m, 1H), 1.18 (d, J = 1.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 137.2 (CH), 132.6 (CH), 130.0 (CH), 127.2 (CH), 103.1 (C), 77.8 (CH), 55.5 (CH), 49.7 (CH_3), 49.1 (CH_3), 44.5 (CH), 42.5 (C), 38.6 (CH_2), 34.6 (CH), 18.9 (CH_3); IR (neat, cm^{-1}) 3,671, 3,515, 2,950, 2,845, 2,351, 1,718, 1,371, 1,295, 1,185, 1,121, 1,074, 951, 852, 820, 755, 681, 653, 610; HRMS (HR-ESI) *m/z* calcd for $C_{14}H_{20}O_3$ [M + Na]$^+$ 259.1310, found 259.1315.

4.14 | (3aR*,4R*,7S*,7aS*,9S*)-8,8-dimethoxy-4-methyl-3a,4,7,7a-tetrahydro-1H-4,7-ethanoinden-9-ol (S2b)

White solid, 343 mg, 23% yield; R_f = 0.28 (silica gel, EtOAc: *n*-Hexane = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 5.93–5.89 (m, 1H), 5.73–5.69 (m, 1H), 5.50 (d, J = 1.7 Hz, 2H), 3.29 (d, J = 1.7 Hz, 3H), 3.12 (d, J = 14.3 Hz, 1H), 3.06 (d, J = 1.9 Hz, 3H), 2.81–2.74 (m, 3H), 2.58–2.46 (m, 1H), 2.37–2.28 (m, 1H), 1.84–1.76 (m, 1H), 1.14 (d, J = 1.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 138.0 (CH), 131.9 (CH), 131.2 (CH), 128.4 (CH), 100.5 (C), 75.5 (CH), 48.8 (CH), 48.4 (CH_3), 48.3 (CH_3), 43.8 (CH), 41.7 (C), 37.8 (CH_2), 35.8 (CH), 19.3 (CH_3); IR (neat, cm^{-1}) 3,675, 3,511, 2,951, 2,840, 2,350, 1,720, 1,378, 1,290, 1,190, 1,128, 1,078, 955, 859, 821, 752, 689, 651, 610; HRMS (HR-ESI) *m/z* calcd for $C_{14}H_{20}O_3$ [M + Na]$^+$ 259.1310; found 259.1313.

4.15 | (3aR*,4R*,7S*,7aS*,9R*)-9-hydroxy-4-methyl-3a,4,7,7a-tetrahydro-1H-4,7-ethanoinden-8-one (13b)

White solid, 172 mg, 96% yield; R_f = 0.43 (silica gel, EtOAc: *n*-Hexane = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 6.05 (t, J = 7.3 Hz, 1H), 5.94 (d, J = 7.9 Hz, 1H), 5.77–5.73 (m, 1H), 5.62 (dd, J = 5.9, 2.6 Hz, 1H), 3.47 (d, J = 2.7 Hz, 1H), 3.22 (d, J = 6.8 Hz, 1H), 2.93–2.77 (m, 2H), 2.66–2.56 (m, 1H), 2.09–1.99 (m, 1H), 1.38 (s, 3H), 1.26 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 140.3 (CH), 133.9 (CH), 129.0 (CH), 124.2 (CH), 74.8 (CH), 56.4 (CH), 52.5 (CH), 45.1 (C), 38.7 (CH_2), 35.3 (CH), 18.3 (CH_3); IR (neat, cm^{-1}) 3,437, 304, 2,962, 2,927, 2,359, 1,715, 1,437, 1,375, 1,308, 1,241, 1,206, 1,139, 1,103, 1,079, 1,004, 984, 940, 926, 912, 845, 787, 773, 741, 689, 640, 552, 511, 501; HRMS (ESI) *m/z* calcd for $C_{12}H_{14}O_2$ [M + Na]$^+$ 213.0891, found 213.0888.

4.16 | (3aR*,4R*,7S*,7aS*,9S*)-9-hydroxy-4-methyl-3a,4,7,7a-tetrahydro-1H-4,7-ethanoinden-8-one (14b)

White solid, 301 mg, 92% yield; R_f = 0.45 (silica gel, EtOAc: *n*-Hexane = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 6.12–6.03 (m, 2H), 5.71–5.62 (m, 2H), 3.40 (s, 1H), 3.25 (dd, J = 5.2, 2.6 Hz, 1H), 3.20–3.13 (m, 1H), 2.84–2.73 (m, 1H), 2.57 (dd, J = 17.3, 1.7 Hz, 1H), 2.12–2.00 (m, 1H), 1.37 (s, 3H), 1.32–1.22 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 212.9 (C), 140.6 (CH), 132.9 (CH), 130.3 (CH), 125.2 (CH), 75.2 (CH), 51.7 (CH), 49.8 (CH), 45.7 (C), 41.5 (CH), 38.2 (CH), 18.7 (CH_3); IR (neat, cm^{-1}) 3,674, 3,504, 2,959, 2,898, 2,840, 2,359, 1,718, 1,457, 1,378, 1,298, 1,245, 1,230, 1,195, 1,164, 1,128, 1,078, 1,045, 955, 926, 859, 823, 758, 729, 689, 657, 618, 518; HRMS (EI) *m/z* calcd for $C_{12}H_{14}O_2$ [M]$^+$ 190.0994, found 190.0997.

4.17 | (3aS*,4S*,7R*,7aS*,9R*)-8,8-dimethoxy-5-methyl-3a,4,7,7a-tetrahydro-1H-4,7-ethanoinden-9-ol (S1c)

White solid, 210 mg, 45% yield; R_f = 0.33 (silica gel, EtOAc: *n*-Hexane = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 5.63 (d, J = 6.4 Hz, 1H), 5.58–5.54 (m, 1H), 5.40 (dt, J = 5.7, 2.4 Hz, 1H), 3.72 (dd, J = 6.6, 2.7 Hz, 1H), 3.28 (s, 3H), 3.25 (s, 3H), 3.06 (d, J = 6.6 Hz, 1H), 2.93 (ddd, J = 8.7, 4.1, 2.0 Hz, 1H), 2.74 (dd, J = 6.6, 2.8 Hz, 1H), 2.72–2.67 (m, 1H), 2.55 (dd, J = 2.4 Hz, 1H), 2.47–2.42 (m, 1H), 1.89 (dddd, J = 16.9, 6.6, 4.3, 2.4 Hz, 1H), 1.73 (d, J = 1.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 141.3 (C), 131.9 (CH), 131.3 (CH), 118.5 (CH), 102.9 (C), 74.4 (CH), 49.7 (CH_3), 49.3 (CH_3), 49.1 (2xCH), 42.4 (CH), 38.5 (CH_2), 33.5 (CH), 23.1 (CH_3); IR (neat, cm^{-1}) 3,648, 2,956, 1,653, 1,443, 1,394, 1,234, 1,125, 1,069, 1,049, 991, 970, 946, 918, 894, 827, 797, 754, 727, 697, 612, 586, 529; HRMS (EI) *m/z* calcd for $C_{14}H_{20}O_3$ [M + Na]$^+$ 259.1310, found 259.1311.

4.18 | (3a*R**,4*S**,7*R**,7a*S**,9*S**)-8,8-dimethoxy-5-methyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-9-ol (S2c)

White solid, 224 mg, 47% yield; R_f = 0.35 (silica gel, EtOAc: *n*-Hexane = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 5.71–5.63 (m, 1H), 5.64–5.60 (m, 1H), 5.53–5.50 (m, 1H), 3.67 (d, *J* = 3.4 Hz, 1H), 3.43–3.36 (m, 1H), 3.11 (dd, *J* = 6.0, 3.1 Hz, 1H), 2.89–2.87 (m, 1H), 2.78–2.66 (m, 2H), 2.61–2.48 (m, 1H), 2.1–2.05 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 213.6 (C), 143.9 (C), 132.1 (CH), 131.3 (CH), 117.8 (CH), 71.3 (CH), 51.3 (CH), 48.5 (CH), 44.6 (CH), 39.9 (CH), 38.3 (CH_2), 22.0 (CH_3); IR (neat, cm^{-1}) 3,399, 2,902, 2,361, 1,715, 1,442, 1,262, 1,216, 1,168, 1,110, 1,075, 1,042, 978, 946, 890, 789, 705, 669, 646, 593; HRMS (EI) *m/z* calcd for $C_{12}H_{14}O_2$ [M]$^+$ 190.0994, found 190.0995.

4.19 | (3a*R**,4*S**,7*R**,7a*S**,9*R**)-9-hydroxy-5-methyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (13c)

White solid, 83 mg, 67% yield; R_f = 0.35 (silica gel, EtOAc: *n*-Hexane = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 5.69 (dd, *J* = 5.7, 2.2 Hz, 1H), 5.50–5.46 (m, 1H), 3.76 (d, *J* = 2.2 Hz, 1H), 3.25–3.19 (m, 1H), 3.09 (dd, *J* = 6.7, 2.6 Hz, 1H), 2.89 (q, *J* = 2.5 Hz, 1H), 2.77–2.70 (m, 1H), 2.64 (d, *J* = 2.3 Hz, 1H), 2.59 (ddd, *J* = 17.2, 9.9, 2.1 Hz, 1H), 1.80 (d, *J* = 1.7 Hz, 4H), 1.73 (ddd, *J* = 10.6, 6.0, 1.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 211.7 (C), 145.5 (C), 132.8 (CH), 130.2 (CH), 115.6 (CH), 71.8 (CH), 52.1 (CH), 49.7 (CH), 48.1 (CH), 38.4 (CH_2), 34.0 (CH), 22.8 (CH_3); IR (neat, cm^{-1}) 3,469, 3,043, 2,899, 1,716, 1,437, 1,177, 1,081, 953, 764, 770, 718, 693, 518; HRMS (EI) *m/z* calcd for $C_{12}H_{14}O_2$ [M]$^+$ 190.0994, found 190.0992.

4.20 | (3a*R**,4*S**,7*R**,7a*S**,9*S**)-9-hydroxy-5-methyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (14c)

White solid, 130 mg, 76% yield; R_f = 0.35 (silica gel, EtOAc: *n*-Hexane = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 5.71–5.63 (m, 1H), 5.64–5.60 (m, 1H), 5.53–5.50 (m, 1H), 3.67 (d, *J* = 3.4 Hz, 1H), 3.43–3.36 (m, 1H), 3.11 (dd, *J* = 6.0, 3.1 Hz, 1H), 2.89–2.87 (m, 1H), 2.78–2.66 (m, 2H), 2.61–2.48 (m, 1H), 2.10–2.05 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 213.6 (C), 143.9 (C), 132.1 (CH), 131.3 (CH), 117.8 (CH), 71.3 (CH), 51.3 (CH), 48.5 (CH), 44.6 (CH), 39.9 (CH), 38.3 (CH_2), 22.0 (CH_3); IR (neat, cm^{-1}) 3,399, 2,902, 2,361, 1,715, 1,442, 1,262, 1,216, 1,168, 1,110, 1,075, 1,042, 978, 946, 890, 789, 705, 669, 646, 593; HRMS (EI) *m/z* calcd for $C_{12}H_{14}O_2$ [M]$^+$ 190.0994, found 190.0995.

4.21 | (3a*R**,4*S**,7*R**,7a*S**,9*R**)-9-hydroxy-5-vinyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (13d)

Colorless liquid, 130 mg, 43% yield; R_f = 0.40 (silica gel, EtOAc: *n*-Hexane = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ)6.43 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.96–5.90 (m, 1H), 5.65 (dd, *J* = 5.8, 2.3 Hz, 1H), 5.45–5.42 (m, 1H), 5.37 (d, *J* = 17.4 Hz, 1H), 5.10 (d, *J* = 10.7 Hz, 1H), 3.87 (d, *J* = 2.5 Hz, 1H), 3.49 (dd, *J* = 2.6 Hz, 1H), 3.41–3.27 (m, 1H), 3.23 (dd, *J* = 6.8, 2.7 Hz, 1H), 2.83–2.76 (m, 1H), 2.72–2.55 (m, 3H), 2.11–2.04 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 210.2 (C), 145.0 (C), 135.7 (CH), 132.7 (CH), 130.2 (CH), 121.1 (CH), 114.2 (CH_2), 71.5 (CH), 52.9 (CH), 49.5 (CH), 41.6 (CH), 38.6 (CH_2), 34.3 (CH); IR (neat, cm^{-1}) 3,423, 2,900, 2,360, 2,341, 1,731, 1,395, 1,258, 1,054, 700, 517, 508; HRMS (HR-APCI) *m/z* calcd for $C_{13}H_{15}O_2$ [M + H]$^+$ 203.1072, found 203.1072.

4.22 | (3a*R**,4*S**,7*R**,7a*S**,9*S**)-9-hydroxy-5-vinyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (14d)

Colorless liquid, 110 mg, 37% yield; R_f = 0.40 (silica gel, EtOAc: *n*-Hexane = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 6.43–6.32 (m, 1H), 5.93 (d, *J* = 6.1 Hz, 1H), 5.60–5.55 (m, 1H), 5.49–5.44 (m, 1H), 5.33 (d, *J* = 17.4 Hz, 1H), 5.10 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.64 (d, *J* = 3.0 Hz, 1H), 3.51–3.46 (m, 2H), 3.26 (dd, *J* = 6.3, 3.0 Hz, 1H), 2.96 (s, 1H), 2.85–2.75 (m, 1H), 2.62–2.51 (m, 1H), 2.16–2.07 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 212.7 (C), 144.3 (C), 134.8 (CH), 131.9 (CH), 131.3 (CH), 122.8 (CH), 113.7 (CH_2), 71.6 (CH), 52.1 (CH), 44.4 (CH), 42.0 (CH), 40.2 (CH), 38.4 (CH_2); IR (neat, cm^{-1}) 3,395, 3,645, 2,938, 2,359, 2,341, 1,709, 1,626, 1,445, 1,411, 1,255, 1,185, 1,134, 1,082, 997, 986, 973, 903, 864, 819, 773, 700, 643, 532, 510; HRMS (HR-APCI) *m/z* calcd for $C_{13}H_{15}O_2$ [M + H]$^+$ 203.1072, found 203.1079.

4.23 | (3a*R**,4*S**,7*R**,7a*S**)-8,8-dimethoxy-9-oxo-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoindene-5-carbaldehyde (15)

To a stirred solution of **7d** (0.193 g, 0.578 mmol) in ethyl acetate (19 ml) was sequentially added 1 N HCl solution (19 ml) at room temperature. After being stirred for 2 hr, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2 several times. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (EtOAc: *n*-Hexane = 1:5 → 1:3) to afford **15** (140 mg, 97% yield) as a white solid.

R_f = 0.40 (silica gel, EtOAc: *n*-Hexane = 1:3); ^1H NMR (400 MHz, $CDCl_3$, 24°C, δ) 9.42 (s, 1H), 7.13 (dd, *J* = 6.8, 1.7 Hz, 1H), 5.54 (dd, *J* = 5.6, 2.3 Hz, 1H), 5.31–5.21 (m, 1H), 3.72 (t, *J* = 2.2 Hz, 1H), 3.44 (dd, *J* = 6.9, 3.0 Hz, 2H), 3.32 (s, 3H), 3.20 (d, *J* = 3.8 Hz, 3H), 2.94–2.88 (m, 1H), 2.58–2.50 (m, 1H), 1.99–1.94 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 201.6 (C), 188.6 (CH), 149.5 (CH), 140.5 (C), 133.1 (CH), 129.5 (CH), 94.6 (C), 50.7 (CH_3), 49.6 (CH_3), 49.5 (CH), 48.3 (CH), 45.5 (CH), 38.4 (CH_2), 33.7 (CH); IR (neat, cm^{-1}) 3,398, 3,046, 2,938, 2,360, 2,341, 1,717, 1,674, 1,626, 1,445, 1,411, 1,254, 1,185, 1,132, 1,084, 1,018, 986, 903, 864, 819, 789, 776, 736, 719, 663, 638, 594; HRMS (APCI) *m/z* calcd for $C_{14}H_{16}O_4$ $[M + H]^+$ 249.1127, found 249.1124.

4.24 | (3a*R**,4*S**,7*R**,7a*S**)-8,8-dimethoxy-5-vinyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-9-one (16)

Methyltriphenyl phosphonium bromide (0.313 g, 0.877 mmol) and sodium hydride (54 mg, 2.34 mmol) in anhydrous THF (6 ml) was stirred at 0°C. After stirring for 30 min, the suspension was added a solution of **15** (0.145 g, 0.584 mmol) in anhydrous THF (2 ml) and then stirred at room temperature for 2 hr. The mixture was quenched by saturated aqueous NH_4Cl solution, extracted with ether. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The residue was was purified by flash chromatography on silica gel (EtOAc: *n*-Hexane = 1:10 → 1:3) to afford **16** (89 mg, 62% yield) as a white solid.

R_f = 0.30 (silica gel, EtOAc: *n*-Hexane = 1:3); ^1H NMR (400 MHz, $CDCl_3$, 24°C, δ) 6.35 (dd, *J* = 17.5, 10.8 Hz, 1H), 6.12–6.05 (m, 1H), 5.66–5.59 (m, 1H), 5.34 (dd, *J* = 5.6, 2.4 Hz, 1H), 5.19 (d, *J* = 17.4 Hz, 1H), 5.01 (dd, *J* = 10.8, 0.8 Hz, 1H), 3.51 (s, 1H), 3.37 (d, *J* = 0.7 Hz, 3H), 3.30 (d, *J* = 0.7 Hz, 4H), 3.16 (dd, *J* = 6.8, 3.0 Hz, 1H), 2.97–2.85 (m, 1H), 2.61–2.48 (m, 1H), 2.11–1.99 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 203.5 (C), 137.7 (C), 134.7 (CH), 132.9 (CH), 129.5 (CH), 128.3 (CH), 113.2 (CH_2), 95.0 (C), 51.2 (CH), 50.5 (CH_3), 49.7 (CH_3), 49.2 (CH), 44.0 (CH), 38.4 (CH_2), 33.8 (CH); IR (neat, cm^{-1}) 3,674, 3,395, 2,938, 2,359, 2,341, 1,709, 1,626, 1,445, 1,411, 1,215, 1,181, 1,130, 1,081, 995, 901, 865, 810, 771, 643, 532, 510; HRMS (APCI) *m/z* calcd for $C_{15}H_{18}O_3$ $[M + H]^+$ 247.1329, found 247.1333.

4.25 | General procedure of the photoreaction: Method A for the synthesis of 17a and 18a (synthesis of 18a as example)

To a solution of **13a** (176 mg, 1.00 mmol), imidazole (204 mg, 3.00 mmol) and a catalytic amount of 4-Dimethylaminopyridine (DMAP) in dry CH_2Cl_2 (5 ml) were slowly added TBSCl (226 mg, 1.50 mmol) at 0°C. The reaction mixture was then heated at reflux temperature for 12 hr. The reaction mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc: *n*-Hexane = 1:39) to afford **S3a** (288 mg, 98% yield) as a colorless oil. To a solution of **S3a** (102 mg, 0.305 mmol) in acetonitrile (70 ml) was transferred into the quartz tube and degassed by purging with N_2 for 45 min. The reaction mixture was irradiated with a broad band centered at 306 nm in a Rayonet-type photoreactor and stirred for 17 hr. The reaction mixture was then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (*n*-Hexane) to afford **18a** (52 mg, 57% yield) as a sticky colorless oil.

4.26 | General procedure of the photoreaction: Method B for the synthesis of 17b-d and 18b-d (synthesis of 17b and 18b as example)

To a solution of **13b** (195 mg, 1.00 mmol), imidazole (204 mg, 3.00 mmol) and a catalytic amount of DMAP in dry CH_2Cl_2 (5 ml) were slowly added TBSCl (226 mg, 1.50 mmol) at 0°C. The reaction mixture was then heated at reflux temperature for 12 hr. The reaction mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc: *n*-Hexane = 1:20 → 1:10) to afford **S3b** (257 mg, 84% yield) as a white solid. To a solution of **S3b** (160 mg, 0.525 mmol) in acetonitrile (160 ml) was transferred into the quartz tube and degassed by purging with N_2 for 45 min. The reaction mixture was irradiated with a broad band centered at 306 nm in a Rayonet-type photoreactor and stirred for 4.5 hr. The reaction mixture was then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (*n*-Hexane) to afford two colorless oil **17b** (12 mg, 8% yield) and **18b** (95 mg, 65% yield).

4.27 | (3a*R**,4*R**,7*S**,7a*S**,9*R**)-9-((*tert*-Butyldimethylsilyl)oxy)-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (S3a)

Colorless oil, 288 mg, 98% yield; R_f = 0.33 (silica gel, EtOAc: *n*-Hexane = 1:39); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ): δ 6.26 (t, *J* = 7.1 Hz, 1H), 6.06 (t, *J* = 7.2 Hz, 1H), 5.66 (dd, *J* = 5.6, 2.2 Hz, 1H), 5.48 (dd, *J* = 5.4, 2.3 Hz, 1H), 3.69 (s, 1H), 3.11 (dd, *J* = 14.7, 7.7 Hz, 2H), 2.90 (d, *J* = 6.1 Hz, 1H), 2.72 (t, *J* = 9.6 Hz, 1H), 2.57 (dd, *J* = 16.1, 9.3 Hz, 1H), 2.10–1.90 (m, 1H), 1.25 (s, 3H), 0.88 (s, 6H), 0.12 (s, 2H), 0.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 24°C, δ) 209.1 (C), 135.1 (CH), 132.7 (CH), 131.0 (CH), 124.2 (CH), 72.1 (CH), 53.1 (CH), 49.5 (CH), 44.3 (CH), 38.6 (CH_2), 35.2 (CH), 25.8 (CH_3)x3, 18.3 (C), −4.5 (CH_3), −5.2 (CH_3); IR (neat, cm^{-1}) 3,736, 3,455, 3,054, 2,928, 2,855, 2,361, 1,736, 1,624, 1,472, 1,463, 1,443, 1,388, 1,359, 1,312, 1,252, 1,224, 1,189, 1,129, 1,096, 1,068, 1,039, 1,006, 991, 972, 939, 926, 888, 837, 779, 696, 681, 648; HRMS (APCI) *m/z* calcd for $C_{17}H_{27}O_2Si$ $[M + H]^+$ 291.1780, found 219.1772.

4.28 | *tert*-butyl (((1*R**,1a*S**,3a*S**,6a*S**,6b*R**)-1,1a,3a,4,6a,6b-hexahydrocyclopropa[*e*]inden-1-yl)oxy) dimethylsilane (18a)

Sticky colorless oil, 52 mg, 57% yield; R_f = 0.13 (silica gel, *n*-Hexane); ^{1}H NMR (300 MHz, $CDCl_3$, 24°C, δ) 5.97 (ddd, *J* = 9.9, 4.8, 1.9 Hz, 1H), 5.71–5.52 (m, 2H), 5.08 (dd, *J* = 10.1, 2.2 Hz, 1H), 3.29 (d, *J* = 6.3 Hz, 1H), 3.06–2.97 (m, 1H), 2.77–2.51 (m, 2H), 2.01 (d, *J* = 15.0 Hz, 1H), 1.48–1.32 (m, 2H), 0.90 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 135.2, 128.2, 127.9, 124.5, 61.0, 41.2, 39.7, 34.8, 25.8, 23.5, 19.6, 18.0, −4.9; IR (neat, cm^{-1}) 3,371, 3,021, 2,928, 2,856, 1,725, 1,471, 1,424, 1,389, 1,361, 1,348, 1,308, 1,254, 1,219, 1,146, 1,046, 1,006, 962, 940, 900, 838, 778, 723, 695, 664; HRMS (APCI) *m/z* calcd for $C_{16}H_{27}OSi$ $[M + H]^+$ 263.1831 found 263.1828.

4.29 | (3a*R**,4*R**,7*S**,7a*S**,9*S**)-9-((*tert*-butyldimethylsilyl)oxy)-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (S4a)

Colorless oil, 288 mg, 98% yield; R_f = 0.33 (silica gel, EtOAc: *n*-Hexane = 1:39); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 6.25 (s, 1H), 6.08 (d, *J* = 7.6 Hz, 1H), 5.63 (dd, *J* = 5.7, 2.2 Hz, 1H), 5.55 (d, *J* = 2.2 Hz, 1H), 3.64 (d, *J* = 3.6 Hz, 1H), 3.61–3.43 (m, 1H), 3.12 (dd, *J* = 5.7, 2.1 Hz, 1H), 2.99–2.71 (m, 1H), 2.56 (ddd, *J* = 17.2, 10.1, 1.6 Hz, 2H), 2.07–1.93 (m, 1H), 0.90 (s, 9H), 0.12 (d, *J* = 8.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 24°C, δ) 208.8 (C), 134.8 (CH), 132.2 (CH), 132.0 (CH), 126.9 (CH), 70.9 (CH), 52.7 (CH), 45.0 (CH), 44.7 (CH), 38.4 (CH2), 38.1 (CH), 25.8 (CH_3)x3, 18.2 (C), −4.5 (CH_3), −5.2 (CH_3); IR (neat, cm^{-1}) 3,053, 2,929, 2,855, 1,739, 1,471, 1,443, 1,389, 1,360, 1,295, 1,254, 1,216, 1,120, 1,007, 983, 939, 924, 887, 839, 780, 754, 681; HRMS (APCI) *m/z* calcd for $C_{17}H_{27}O_2Si$ $[M + H]^+$ 291.1780, found 219.1771.

4.30 | *tert*-butyl (((1*S**,1a*S**,3a*S**,6a*S**,6b*R**)-1,1a,3a,4,6a,6b-hexahydrocyclopropa[*e*]inden-1-yl)oxy) dimethylsilane (17a)

Sticky colorless oil, 48 mg, 52% yield; R_f = 0.23 (silica gel, *n*-Hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 5.75–5.62 (m, 2H), 5.32 (dd, *J* = 10.1, 2.3 Hz, 1H), 3.52 (t, *J* = 6.6 Hz, 1H), 3.14–3.09 (m, 1H), 2.77–2.60 (m, 2H), 2.08 (dt, *J* = 13.8, 2.0 Hz, 1H), 1.29–1.17 (m, 3H), 0.89 (s, 9H), 0.06 (d, *J* = 22.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 24°C, δ) 135.3 (CH), 130.6 (CH), 128.2 (CH), 119.6 (CH), 55.8 (CH), 41.5 (CH_2), 37.9 (CH), 36.7 (CH), 25.9 (CH_3)x3, 18.1 (C), 17.7 (CH), 14.5 (CH), −5.1 (CH_3), −5.4 (CH_3); IR (neat, cm^{-1}) 3,049, 3,016, 2,955, 2,928, 2,855, 1,653, 1,471, 1,444, 1,404, 1,351, 1,284, 1,251, 1,224, 1,211, 1,134, 1,105, 1,053, 1,006, 961, 875, 839, 777, 734, 672; HRMS (APCI) *m/z* calcd for $C_{16}H_{27}OSi$ $[M + H]^+$ 263.1831, found 263.1828.

4.31 | (3a*R**,4*R**,7*S**,7a*S**,9*R**)-9-((*tert*-butyldimethylsilyl)oxy)-4-methyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (S3b)

White solid, 257 mg, 84% yield; R_f = 0.45 (silica gel, EtOAc: *n*-Hexane = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$, 24°C, δ) 6.01–5.97 (m, 1H), 5.91–5.86 (m, 1H), 5.72–5.70

(m, 1H), 5.62–5.57 (m, 1H), 3.36 (s, 1H), 3.14–3.06 (m, 1H), 2.77–2.75 (m, 2H), 2.64–2.50 (m, 1H), 2.06–1.99(m, 1H), 1.27 (s, 3H), 0.87 (d, J = 0.8 Hz, 9H), 0.11 (d, J = 0.7 Hz, 6H); ^{13}C NMR (75 MHz, CDCl$_3$, 24°C, δ) 209.7(C), 139.8 (CH), 133.6 (CH), 129.4 (CH), 123.4 (CH), 75.5 (CH), 55.6 (CH), 52.8 (CH), 45.6 (C), 38.7 (CH$_2$), 36.4 (CH), 25.9 (3xCH$_3$), 19.2 (CH), 18.4 (C), −4.1 (CH$_3$), −5.2 (CH$_3$); IR (neat, cm^{-1}) 2,953, 2,926, 2,854, 2,359, 1,720, 1,462, 1,359, 1,252, 1,218, 1,107, 1,051, 1,007, 990, 956, 937, 923, 853, 830, 768, 746, 707, 686, 635, 551, 519, 509; HRMS (HR-APCI) *m/z* calcd for C$_{18}$H$_{29}$O$_2$ [M + H]$^+$ 305.1937, found 305.1940.

4.32 | (3a*R**,4*R**,7*S**,7a*S**,9*S**)-9-((*tert*-butyldimethylsilyl)oxy)-4-methyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (S4b)

White solid, 364 mg, 73% yield; R$_f$ = 0.45 (silica gel, EtOAc: *n*-Hexane = 1:10); ^{1}H NMR (400 MHz, CDCl$_3$, 24°C, δ) 6.05–6.00 (m, 1H), 5.95–5.90 (m, 1H), 5.64–5.62 (m, 1H), 5.59–5.56 (m, 1H), 3.31 (d, J = 1.2 Hz, 1H), 3.27–3.19 (m, 1H), 3.07–3.05 (m, 1H), 2.83–2.72 (m, 1H), 2.51 (dd, J = 17.2, 10.1, 1.8 Hz, 1H), 2.05–1.94 (m, 1H), 1.25 (d, J = 1.2 Hz, 3H), 0.88 (d, J = 1.3 Hz, 9H), 0.12 (d, J = 1.2 Hz, 3H), 0.07 (d, J = 1.1 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 24°C, δ) 140.3 (CH), 132.7 (CH), 130.5 (CH), 125.9 (CH), 75.1 (CH), 52.8 (CH), 50.3 (CH), 46.1 (C), 39.3 (CH), 38.4 (CH$_2$), 25.9 (3xCH$_3$), 19.6 (CH), 18.4 (C), −4.0 (CH$_3$), −5.2 (CH$_3$); IR (neat, cm^{-1}) 2,956, 2,928, 2,856, 2,360, 1,738, 1,460, 1,362, 1,251, 1,105, 1,090, 1,051, 939, 883, 836, 778, 754, 739, 682, 662, 603; HRMS (HR-APCI) *m/z* calcd for C$_{18}$H$_{29}$O$_2$ [M + H]$^+$ 305.1937, found 305.1932.

4.33 | *tert*-butyldimethyl(((1*S**,1a*S**,3a*S**,6a*S**,6b*R**)-6b-methyl-1,1a,3a,4,6a,6b-hexahydrocyclopropa[*e*]inden-1-yl)oxy)silane (17b)

Colorless liquid, 73 mg, 50% yield; R$_f$ = 0.45 (silica gel, *n*-Hexane); ^{1}H NMR (400 MHz, CDCl$_3$, 24°C, δ) 5.85–5.82 (m, 1H), 5.73–5.61 (m, 2H), 5.23 (dd, J = 10.0, 2.3 Hz, 1H), 3.19 (d, J = 6.5 Hz, 1H), 3.02–2.94 (m, 1H), 2.86–2.81 (m, 1H), 2.72–2.58 (m, 1H), 2.16–2.06 (m, 1H), 1.14 (s, 3H), 1.09 (s, 1H), 0.89 (s, 9H), 0.08 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 24°C, δ) 132.4 (CH), 130.4 (CH), 128.9 (CH), 120.6 (CH), 64.0 (CH), 43.5 (CH), 40.8 (CH$_2$), 38.1 (CH), 25.9 (3xCH$_3$), 23.6 (CH$_3$), 23.0 (CH), 20.7 (C), 18.2 (C), −5.1 (CH$_3$), −5.4 (CH$_3$); IR (neat, cm^{-1}) 2,928, 2,856, 1,722, 1,253, 1,086, 836, 778, 411; HRMS (HR-APCI) *m/z* calcd for C$_{18}$H$_{29}$O$_2$Si [M + H]$^+$ 305.1937, found 305.1940.

4.34 | *tert*-Butyldimethyl(((1*R**,1a*S**,3a*S**,6a*S**,6b*R**)-6b-methyl-1,1a,3a,4,6a,6b-hexahydrocyclopropa[*e*]inden-1-yl)oxy)silane (18b)

Colorless liquid, 19 mg, 13% yield; R$_f$ = 0.45 (silica gel, *n*-Hexane); ^{1}H NMR (400 MHz, CDCl$_3$, 24°C, δ) 6.00 (ddd, J = 10.1, 5.7, 2.6 Hz, 1H), 5.96–5.89 (m, 1H), 5.69–5.65 (m, 1H), 4.95 (dd, J = 10.0, 2.1 Hz, 1H), 3.16 (dd, J = 2.2, 0.7 Hz, 1H), 2.78–2.68 (m, 1H), 2.68–2.56 (m, 1H), 2.10–2.01 (m, 1H), 1.35–1.22 (m, 4H), 1.00 (dd, J = 5.7, 2.2 Hz, 1H), 0.95–0.86 (m, 9H), 0.13–0.06 (m, 6H); ^{13}C NMR (75 MHz, CDCl$_3$, 24°C, δ) 133.1 (CH), 129.0 (CH), 126.9 (CH), 126.6 (CH), 77.1 (CH), 64.1 (CH), 46.3 (CH$_2$), 36.7 (CH), 26.5 (3xCH$_3$), 25.9 (CH$_3$), 25.9 (CH), 23.9 (C), 18.1 (C), 16.3 (CH$_3$), −4.9 (CH$_3$), −5.0 (CH$_3$); IR (neat, cm^{-1}) 2,930, 2,851, 1,720, 1,255, 1,081, 832, 775, 419.

4.35 | (3a*R**,4*S**,7*R**,7a*S**,9*R**)-9-((*tert*-butyldimethylsilyl)oxy)-5-methyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (S3c)

White solid, 221 mg, 98% yield; R$_f$ = 0.38 (silica gel, EtOAc: *n*-Hexane = 1:10); ^{1}H NMR (400 MHz, CDCl$_3$, 24°C, δ) 5.67–5.64 (m, 2H), 5.48–5.44 (m, 1H), 3.68 (d, J = 2.6 Hz, 1H), 3.16–3.06 (m, 1H), 2.97 (dd, J = 6.6, 2.8 Hz, 1H), 2.73–2.62 (m, 2H), 2.60–2.49 (m, 1H), 2.12–1.99 (m, 1H), 1.79 (d, J = 1.8 Hz, 3H), 0.88 (d, J = 2.3 Hz, 9H), 0.12 (d, J = 3.2 Hz, 5H); ^{13}C NMR (75 MHz, CDCl$_3$, 24°C, δ) 209.8 (C), 144.7 (C), 132.7 (CH), 130.4 (CH), 115.1 (CH), 72.3 (CH), 52.4 (CH), 49.8 (CH), 49.1 (CH), 38.5 (CH$_2$), 34.9 (CH), 25.7 (2xCH$_3$), 23.1 (CH$_3$), 18.3 (C), −4.6 (CH$_3$), −5.3 (CH$_3$); IR (neat, cm^{-1}) 2,928, 2,854, 2,359, 1,732, 1,472, 1,441, 1,360, 1,250, 1,176, 1,138, 1,114, 1,065, 1,005, 980, 835, 777, 740, 696; HRMS (EI) *m/z* calcd for C$_{18}$H$_{28}$O$_2$Si [M]$^+$ 327.1756, found 327.1747.

4.36 | (3a*R**,4*S**,7*R**,7a*S**,9*S**)-9-((*tert*-butyldimethylsilyl)oxy)-5-methyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (S4c)

White solid, 150 mg, 98% yield; R$_f$ = 0.35 (silica gel, EtOAc: *n*-Hexane = 1:10); ^{1}H NMR (400 MHz, CDCl$_3$, 24°C, δ) 5.69–5.60 (m, 3H), 5.55–5.48 (m, 1H), 3.65 (d, J = 3.7 Hz, 1H), 3.50 (d, J = 9.1 Hz, 1H), 2.98 (dd, J = 6.4, 2.9 Hz, 1H), 2.83–2.66 (m, 2H), 2.55 (dd, J = 17.1, 10.0 Hz, 1H), 1.77 (d, J = 1.6 Hz, 3H), 0.91 (d, J = 1.3 Hz, 9H), 0.14 (d, J = 4.1 Hz, 6H); ^{13}C NMR (75 MHz, CDCl$_3$, 24°C, δ) 209.4 (C), 143.8 (C), 132.0 (CH), 131.5 (CH), 118.3 (CH), 70.6 (CH$_2$), 52.4 (CH), 50.2 (CH), 44.8 (CH), 38.3 (CH_2), 37.6 (CH), 25.7 ($3xCH_3$), 22.1 (CH_3), 18.2 (C), −4.5 (CH_3), −5.2 (CH_3); IR (neat, cm^{-1}) 2,927, 2,855, 2,358, 1,737, 1,471, 1,441, 1,359, 1,251, 1,166, 1,099, 1,005, 906, 835, 777, 702, 688, 645, 582, 518, 510, 502; HRMS (EI) *m/z* calcd for $C_{18}H_{28}O_2Si$ $[M]^+$ 327.1756, found 327.1750.

4.37 | *tert*-butyldimethyl(((1R*,1aS*,3aS*,6aS*,6bR*)-1a-methyl-1,1a,3a,4,6a,6b-hexahydrocyclopropa[e]inden-1-yl)oxy)silane (17c)

Colorless liquid, 10 mg, 7% yield; $R_f = 0.43$ (silica gel, *n*-Hexane); ^1H NMR (400 MHz, $CDCl_3$, 24°C, δ) 5.63–5.59 (m, 2H), 5.47 (dd, *J* = 10.1, 2.3 Hz, 1H), 5.34–5.29 (m, 1H), 3.16 (d, *J* = 6.7 Hz, 1H), 3.07 (d, *J* = 7.4 Hz, 1H), 2.73–2.68 (m, 1H), 2.68–2.63 (m, 2H), 2.08 (dd, *J* = 14.9, 2.7 Hz, 1H), 1.10 (s, 3H), 0.89 (s, 8H), 0.07 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 135.7 (CH), 130.1 (CH), 127.8 (CH), 125.1 (CH), 62.8 (CH), 41.3 (CH_2), 38.5 (CH), 36.6 (CH), 25.9 ($3xCH_3$), 25.8 (CH), 23.4 (CH_3), 18.5 (C), 18.1 (C), −5.0 (CH_3), −5.5 (CH_3); IR (neat, cm^{-1}) 2,930, 2,815, 2,358, 1,720, 1,465, 1,351, 1,254, 1,106, 837, 789, 670; HRMS (EI) *m/z* calcd for $C_{17}H_{28}OSi$ $[M]^+$ 276.1909, found 276.1911.

4.38 | *tert*-butyldimethyl(((1S*,1aS*,3aS*,6aS*,6bR*)-1a-methyl-1,1a,3a,4,6a,6b-hexahydrocyclopropa[e]inden-1-yl)oxy)silane (18c)

Colorless liquid, 66% yield; $R_f = 0.43$ (silica gel, *n*-Hexane); ^1H NMR (400 MHz, $CDCl_3$, 24°C, δ) 5.77 (dd, *J* = 10.1, 2.3 Hz, 1H), 5.61–5.58 (m, 2H), 5.11–5.07 (m, 1H), 3.26 (d, *J* = 7.1 Hz, 1H), 2.96 (d, *J* = 3.3 Hz, 1H), 2.71–2.56 (m, 3H), 2.02 (d, *J* = 15.0 Hz, 1H), 1.19 (s, 3H), 0.91 (s, 9H), 0.10 (s, 4H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 135.6 (CH), 131.4 (CH), 128.0 (CH), 127.4 (CH), 63.6 (CH), 41.0 (CH_2), 40.3 (CH), 34.6 (CH), 29.8 ($3xCH_3$), 25.9 (CH), 20.6 (CH_3), 18.1 (C), 17.0 (C), −4.9 (CH_3), −5.0 (CH_3); IR (neat, cm^{-1}) 2,929, 2,827, 2,360, 1,720, 1,462, 1,361, 1,254, 1,106, 837, 779, 679, 417; HRMS (EI) *m/z* calcd for $C_{17}H_{28}OSi$ $[M]^+$ 276.1909, found 276.1906.

4.39 | (3aR*,4S*,7R*,7aS*,9R*)-9-((*tert*-butyldimethylsilyl)oxy)-5-vinyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (S3d)

White solid, 650 mg, 42% yield; $R_f = 0.35$ (silica gel, EtOAc: *n*-Hexane = 1:15); ^1H NMR (400 MHz, $CDCl_3$, 24°C, δ) 6.42 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.88 (dd, *J* = 6.6, 1.9 Hz, 1H), 5.62 (dd, *J* = 5.7, 2.2, 1.0 Hz, 1H), 5.41 (dd, *J* = 5.6, 2.5 Hz, 1H), 5.29–5.22 (m, 1H), 5.02 (dd, *J* = 10.7, 0.9 Hz, 1H), 3.77 (d, *J* = 2.7 Hz, 1H), 3.27 (q, *J* = 2.6 Hz, 1H), 3.23–3.15 (m, 1H), 3.11 (dd, *J* = 6.6, 2.8 Hz, 1H), 2.72 (dd, *J* = 2.5, 1.4 Hz, 1H), 2.61–2.52 (m, 1H), 2.11–2.02 (m, 1H), 0.84 (d, *J* = 0.8 Hz, 9H), 0.12–0.08 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 208.7 (C), 144.5 (C), 136.2 (CH), 132.4 (CH), 130.4 (CH), 120.7 (CH), 112.9 (CH_2), 71.8 (CH), 53.2 (CH), 48.9 (CH), 43.3 (CH), 38.6 (CH_2), 35.2 (CH), 25.7 ($3xCH_3$), 18.4 (C), −4.5 (CH_3), −5.3 (CH_3); IR (neat, cm^{-1}) 2,925, 2,360, 2,341, 1,734, 1,459, 1,248, 1,114, 1,066, 995, 982, 900, 836, 774, 735, 696; HRMS (HR-APCI) *m/z* calcd for $C_{19}H_{29}O_2Si$ $[M + H]^+$ 317.1937, found 317.1942.

4.40 | (3aR*,4S*,7R*,7aS*,9S*)-9-((*tert*-butyldimethylsilyl)oxy)-5-vinyl-3a,4,7,7a-tetrahydro-1*H*-4,7-ethanoinden-8-one (S4d)

White solid, 188 mg, 92% yield; $R_f = 0.35$ (silica gel, EtOAc: *n*-Hexane = 1:15); ^1H NMR (400 MHz, $CDCl_3$, 24°C, δ) 6.36 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.92 (dd, *J* = 6.4, 2.0 Hz, 1H), 5.61–5.58 (m, 1H), 5.48–5.44 (m, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 5.08 (d, *J* = 10.7 Hz, 1H), 3.59 (dd, *J* = 14.4, 6.4 Hz, 2H), 3.25 (q, *J* = 2.9 Hz, 1H), 3.14 (dd, *J* = 6.3, 3.0 Hz, 1H), 2.86–2.79 (m, 1H), 2.63–2.50 (m, 1H), 2.11–2.03 (m, 1H), 0.92 (s, 9H), 0.14 (d, *J* = 4.4 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 208.4 (C), 144.2 (C), 135.2 (CH), 131.8 (CH), 131.5 (CH), 123.6 (CH), 113.0 (CH_2), 71.1 (CH), 53.2 (CH), 44.5 (CH), 43.6 (CH), 38.4 (CH_2), 38.2 (CH), 25.8 ($3xCH_3$), 18.3 (C), −4.5 (CH_3), −5.1 (CH_3); IR (neat, cm^{-1}) 2,930, 2,356, 2,341, 1,732, 1,459, 1,248, 1,114, 1,066, 995, 982, 900, 836, 774, 735, 696; HRMS (HR-APCI) *m/z* calcd for $C_{19}H_{29}O_2Si$ $[M + H]^+$ 317.1937, found 317.1936.

4.41 | *tert*-butyldimethyl(((1R*,1aS*,3aS*,6aS*,6bR*)-1a-vinyl-1,1a,3a,4,6a,6b-hexahydrocyclopropa[e]inden-1-yl)oxy)silane (17d)

Colorless liquid, 50 mg, 27% yield; $R_f = 0.35$ (silica gel, *n*-Hexane); ^1H NMR (400 MHz, $CDCl_3$, 24°C, δ) 5.77 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.69 (dd, *J* = 10.3, 1.9 Hz, 1H), 5.63–5.59 (m, 2H), 5.38 (dd, *J* = 10.2, 2.2 Hz, 1H), 4.91–4.81 (m, 2H), 3.34 (d, *J* = 6.8 Hz, 1H), 3.16 (t, *J* = 5.6 Hz, 1H), 2.78–2.63 (m, 2H), 2.12–2.08 (m, 1H), 1.49 (d, *J* = 6.9, Hz, 1H), 0.89 (s, 9H), 0.06 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 24°C, δ) 142.7 (CH), 135.0 (CH), 130.4 (CH), 128.2 (CH), 121.4 (CH), 109.4 (CH_2), 65.4 (CH), 41.2 (CH_2), 38.3 (CH), 36.8 (CH), 27.2

(CH), 26.3 (C), 25.9 (3xCH$_3$), 18.1 (C), −5.1 (CH$_3$), −5.6 (CH$_3$); IR (neat, cm^{-1}) 3,081, 3,051, 3,015, 2,950, 2,921, 2,894, 2,856, 1,625, 1,475, 1,412, 1,360, 1,340, 1,328, 1,289, 1,250, 1,185, 1,070, 1,031, 997, 971, 951, 939, 891, 859, 778, 723, 700, 616; HRMS (HR-APCI) *m/z* calcd for $C_{18}H_{29}OSi$ $[M + H]^+$ 289.1988, found 289.1990.

4.42 | *tert*-butyldimethyl(((1_S_*,1a_S_*,3a_S_*,6a_S_*,6b_R_*)-1a-vinyl-1,1a,3a,4,6a,6b-hexahydrocyclopropa[*e*]inden-1-yl)oxy)silane (18d)

Colorless liquid, 107 mg, 70% yield; ^{1}H NMR (400 MHz, CDCl$_3$, 24°C, δ):6.14–6.03 (m, 1H), 5.86 (dd, J = 17.6, 10.8 Hz, 1H), 5.61 (s, 2H), 5.25 (dd, J = 10.4, 2.3 Hz, 1H), 5.18–5.01 (m, 2H), 3.41–3.30 (m, 1H), 3.22 (d, J = 3.8 Hz, 1H), 2.74–2.63 (m, 2H), 2.14–2.01 (m, 1H), 1.50 (d, J = 2.7 Hz, 1H), 0.93 (s, 9H), 0.11 (d, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, CDCl$_3$, 24°C, δ) 138.4 (CH), 134.8 (CH), 128.2 (2xCH), 126.1 (CH), 111.4 (CH$_2$), 66.1 (CH), 40.8 (CH$_2$), 40.3 (CH), 34.8 (CH), 32.1 (CH), 28.2 (C), 25.8 (3xCH$_3$), 18.1 (C), −4.9 (CH$_3$), −5.1 (CH$_3$); IR (neat, cm^{-1}) 3,084, 3,052, 3,019, 2,955, 2,928, 2,899, 2,856, 1,627, 1,471, 1,413, 1,361, 1,348, 1,329, 1,289, 1,256, 1,186, 1,071, 1,032, 997, 970, 959, 939, 893, 859, 837, 778, 723, 700, 666; HRMS (HR-APCI) *m/z* calcd for $C_{18}H_{29}OSi$ $[M + H]^+$ 289.1988, found 289.1993.

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